STUDIES ON PHOSPHAAMIDINES, PHOSPHINODIIMINES, AND DIPHOSPHANES

LEILA MOKHTABAD AMREI
B.Sc. in Chemistry, University of Mazandaran, 2000
M.Sc. in Chemistry, University of North Tehran Azad, 2004

A thesis
Submitted to the School of Graduate Studies
of the University of Lethbridge
in partial Fulfilment of the
Requirements for the Degree

DOCTOR OF PHILOSOPHY

Department of Chemistry and Biochemistry
University of Lethbridge
LETHBRIDGE, ALBERTA, CANADA

STUDIES ON PHOSPHAAMIDINES, PHOSPHINODIIMINES, AND DIPHOSPHANES

LEILA MOKHTABAD AMREI

Date of Defence: November 30, 2015

Dr. René T. Boeré Supervisor	Professor	Ph.D
Dr. Peter W. Dibble Thesis Examination Committee Member	Professor	Ph.D
Dr. Michael. Gerken Thesis Examination Committee Member	Professor	Ph.D
Dr. Locke Spencer Internal External Examiner	Associate Professor	Ph.D
Dr. Derek P. Gates External Examiner University of British Columbia Vancouver, British Columbia	Professor	Ph.D
Dr. Marc R. Roussel Chair, Thesis Examination Committee	Professor	Ph.D

To my dear husband Mohammad, and my sweet daughter Shayla,

for their absolute love and patience.

Abstract

The synthesis of a new neutral phosphaamidine (Dipp)N=C(CH_3)P(Dipp) and new protonated phosphaamidines ((Dipp)HN$^+$=C(R)PH(Dipp), R = ^{t}Bu, CH_3, *p*CH_3O-Ph and Dipp = 2,6-diisopropylphenylphosphane are described. The protonated phosphaamidines have *Z-anti*(N=C) geometry in the solid state. A new phosphinodiimine (Dipp)P((^{t}Bu)C=N(Dipp))$_2$ and a new amidinophosphaalkene (Dipp)P=C(CH_3)-N(Dipp)-C(CH_3)=N(Dipp) are described which were synthesized by using the related phosphaamidines as starting materials. The substitution at the carbon backbone plays a significant role in isomerisation and for the geometric preference of these compounds in solution and in the solid state. A new diphosphane (Dipp)HP-PH(Dipp), which was first observed as a side product while making phosphaamidines, was crystallographically characterized. All of these compounds, including phosphaamidines, phosphinodiimines, and diphosphanes, display isomerism in solution which has been studied through 1D and 2D (^{1}H, ^{13}C, ^{31}P) nuclear magnetic resonance and solid-state NMR spectroscopies, X-ray crystallography, IR and Raman in the case of (Dipp)HP-PH(Dipp), spectroscopies and Hybridge Density Functional Theory calculations.

Acknowledgements

First and foremost I would like to deeply from my heart thank my supervisor Prof. René T. Boeré, for his encouragement, knowledge and support. His time, patience and guidance will never be forgotten for my entire life.

I thank Dr. Peter Dibble for his helpful advice and taking the time to guide me through the area of synthesis and mechanism of reactions. I thank Dr. Michael Gerken for his helpful advice regarding solution and solid state NMR spectroscopy. I also thank Dr. Locke Spencer for his smart questions and his kind advice in our meeting.

To all of the members of the Boeré, Dibble and Gerken labs, I thank all of you for the assistance and fun in the lab. Most importantly, I would like to thank Tracey Roemmele for her training instruments in the lab. Many thanks go to Tony Montina who was a tremendous asset in NMR spectroscopy training. Thanks also to Susan Hill for helping me with the administrative paperwork.

Finally, I would like to thank my family and friend that have been important throughout my degree: Thank you to my dear husband Mohammad for his love, patience, and support in all aspect of life. Thank you to my sweet daughter Shayla for making my life colorful and fun. Thank you to my dad Ebrahim, my mom Roghiyeh and my sisters, Maryam, Sara and Masy for their emotionally support, energy and encouragements in all these years. Thank you to my close friend Kristina for her encouragement and helpful comments and being like an older sister.

Table of Contents

List of Tables

List of Figures

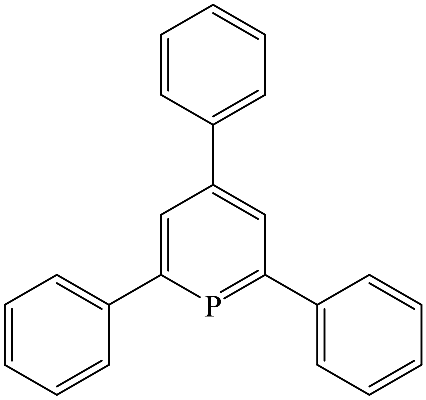
List of Schemes

List of Abbreviations

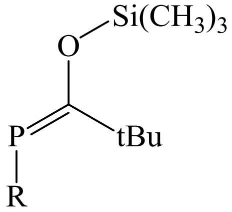
A	area
Å	angstrom
B3LYP	Becke's Three Parameter Hybrid Functional Using the Lee, Yang, and Parr Correlation Functional
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
COZY	homonulclear correlated spectroscopy
DFT	density functional theory
Dipp	2,6-diisopropylphenyl group
Et	ethanol
g	gram
Hz	Hertz
HMBC	Heteronuclear Multiple Bond Correlation
HOMO	highest occupied molecular orbital
HSQC	Heteronuclear Single Quantum Correlation
I	spin
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
kJ	Kilojoule
LUMO	lowest unoccupied molecular orbital
Me	methyl
MeOH	methanol
Mes	2,4,6-tri-methylphenyl
Mes*	2,4,6-tri-tertbutylphenyl
mL	milliliters
mmol	millimole
MO	molecular orbital
MS	mass spectrum
NMR	nuclear magnetic resonance
ORTEP	Oakridge thermal ellipsoid plot
Ph	phenyl
^{i}Pr	isopropyl
RT	room temperature
THF	tetrahydrofuran
Trip	2,4,6-triisopropylphenyl
p-tolyl	4-$CH_3C_6H_4$
VT	variable temperature
°C	degrees Celsius

Compound Numbering Scheme

1-8

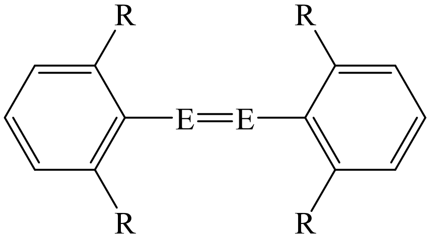


1



R = CH_3, ^{t}Bu, Cy, Ph

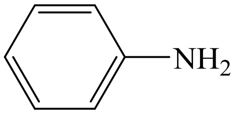
2



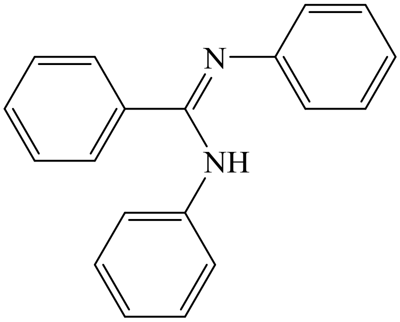
3

R = Mes (C_6H_2-2,4,6-CH_3),
Trip (C_6H_2-2,4,6-iPr_3)

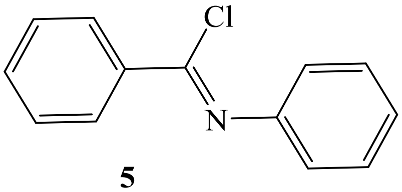
E = P, As, Sb, Bi



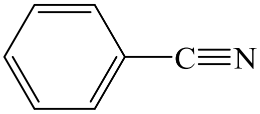
4



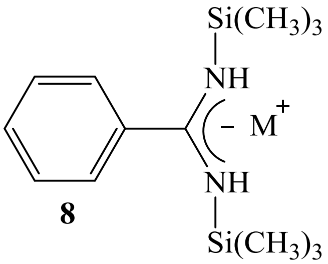
6



5



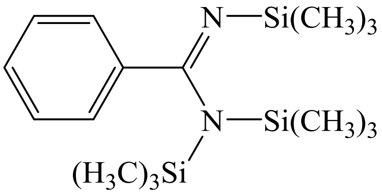
7



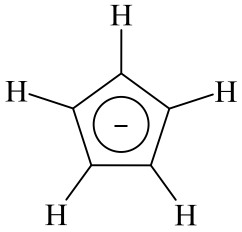
8

Compound Numbering Scheme

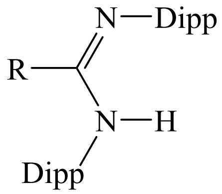
9-17

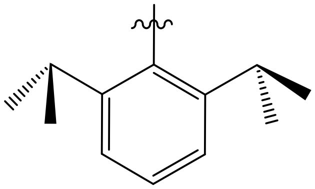


9



10



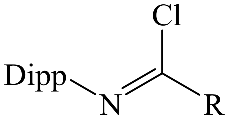


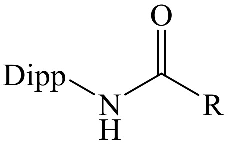
Dipp = 2,6 diisopropyl phenyl

Dipp—NH_2

12

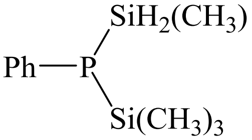
11a. R = p-$CH_3C_6H_5$; **11b.** R = p-$CH_3OC_6H_5$
11c. R = CH_3; **11d.** R = CF_3



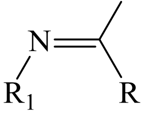


14a. R = p-$CH_3C_6H_4$
14b. R = p-$CH_3OC_6H_4$
14c. R = CH_3

13a. R = p-$CH_3C_6H_4$
13b. R=p-$CH_3OC_6H_4$
13c. R = CH_3



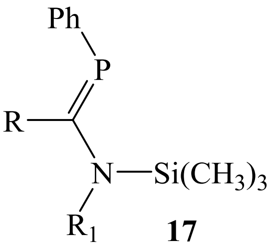
15



16

R= Ph **16a.** R_1= Ph
16b. R_1= CH_3
16c. R_1= 2,6-Et_2Ph
16d. R_1= Cy
R_1=Ph **16e.** R = ^{t}Bu
16f. R = Mes

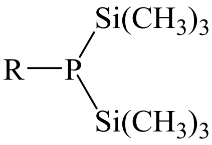
R= Ph **17a.** R_1= Ph
17b. R_1= CH_3
17c. R_1= 2,6-Et_2Ph
17d. R_1= Cy
R_1=Ph **17e.** R = ^{t}Bu
17f. R = Mes



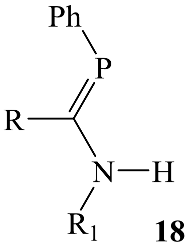
17

Compound Numbering Scheme

18-28



19



18

R= Ph **18a.** R_1= Ph

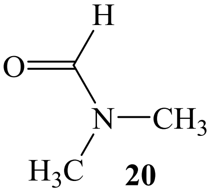
18b. R_1= CH_3

18c. R_1= 2,6-Et_2Ph

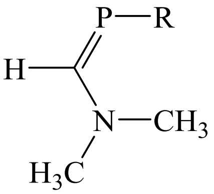
18d. R_1= Cy

R_1=Ph **18e.** R = ^{t}Bu

18f. R = Mes

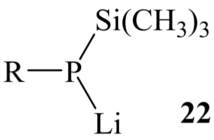


20

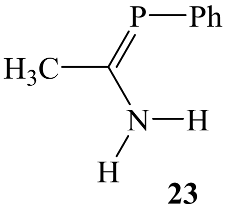


21a. R = ^{t}Bu

21b. R = Ph

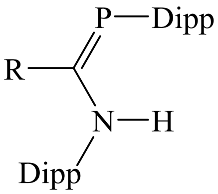


22



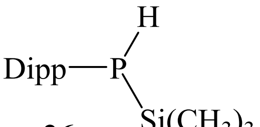
23

$DippPH_2$ **24**

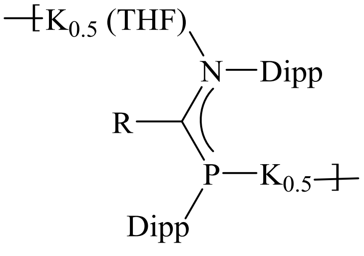


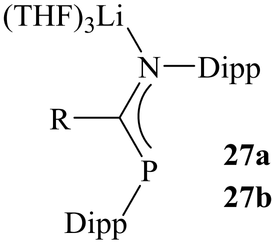
25a. R = $p$$CH_3$-$C_6H_4$

25b. R = $p$$CH_3O$-$C_6H_4$



26





27a. R = $p$$CH_3$-$C_6H_4$

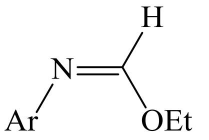
27b. R = $p$$CH_3O$-$C_6H_4$

28a. R = $p$$CH_3$-$C_6H_4$

28b. R = $p$$CH_3O$-$C_6H_4$

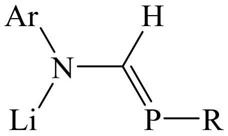
Compound Numbering Scheme

29-38

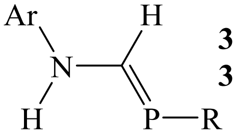


29a. Ar = Dipp
29b. Ar = Mes

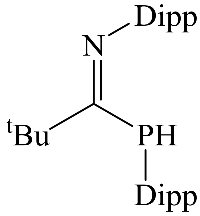
R = Mes, Mes*



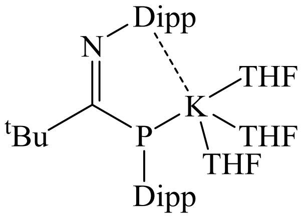
30a. Ar = Dipp
30b. Ar = Mes



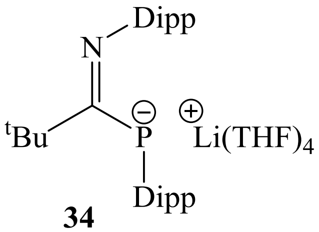
31a. Ar = Dipp
31b. Ar = Mes



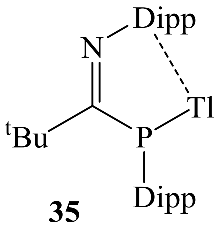
32



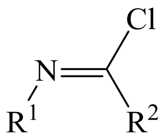
33



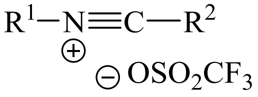
34



35



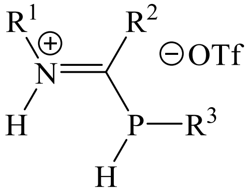
R^2 = ^{t}Bu	R^2 = Ph
36a. R^1=Ph	**36e.** R^1=Ph
36b. R^1=Mes	**36f.** R^1=Mes
36c. R^1= *i*Pr	**36g.** R^1= *i*Pr
36d. R^1= Cy	**36h.** R^1= Cy



$R^1{-}\overset{\oplus}{N}{\equiv}C{-}R^2 \quad \ominus OSO_2CF_3$

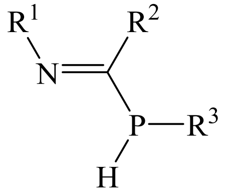
R^2 = ^{t}Bu	R^2 = Ph
37a. R^1=Ph	**37e.** R^1=Ph
37b. R^1=Mes	**37f.** R^1=Mes
37c. R^1= *i*Pr	**37g.** R^1= *i*Pr
37d. R^1= Cy	**37h.** R^1= Cy

38a. R^3 = Ph
38b. R^3 = Cy

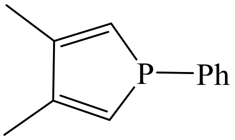


Compound Numbering Scheme

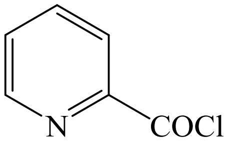
39-49



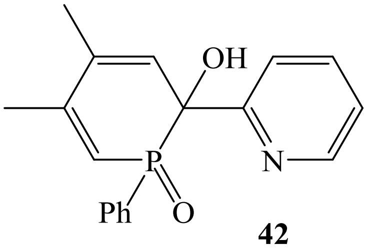
39a. R^3 = Ph **39b.** R^3 = Cy



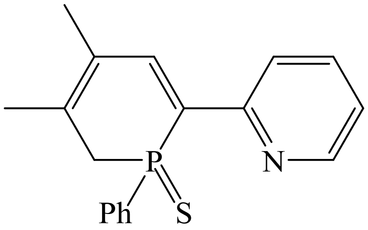
40



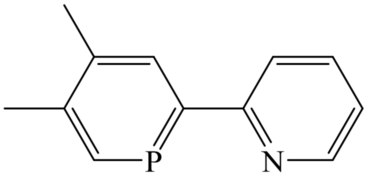
41



42

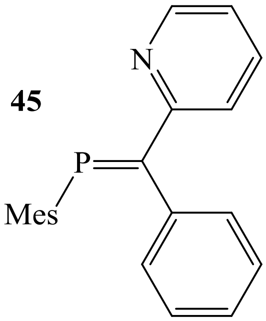


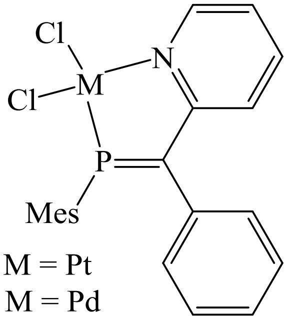
43



44

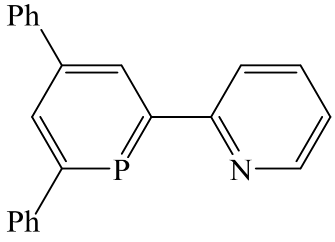
45

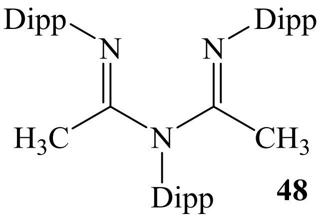




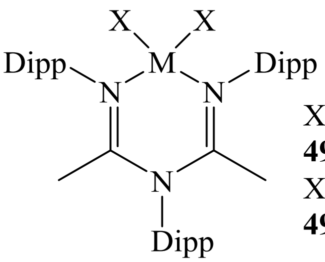
46a. M = Pt
46b. M = Pd

47





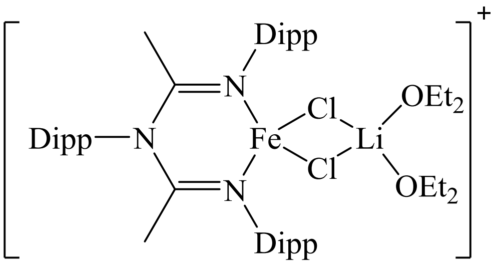
48



X=Cl;
49a-c. M=Fe, Co, Ni
X=Br;
49d-e. M=Cu, Zn

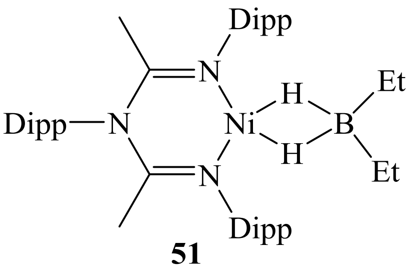
Compound Numbering Scheme

50-57

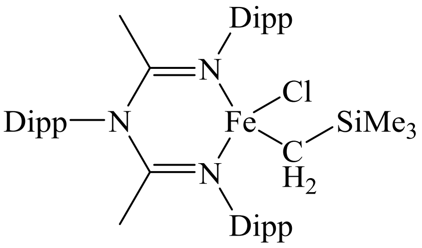


$[B(C_6F_5)_4^-]$

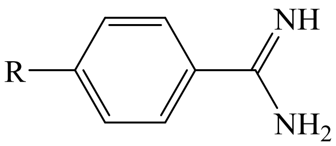
50



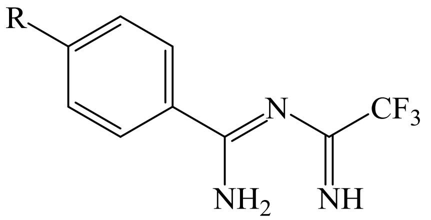
51



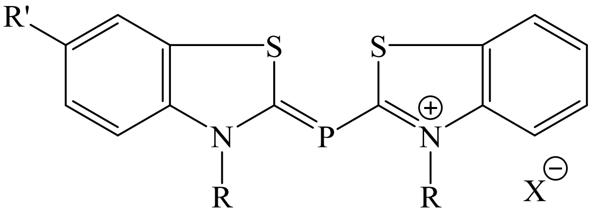
52



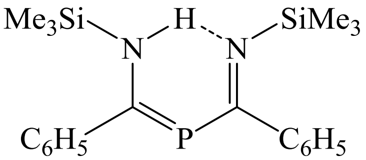
53a. R = OCH_3, **53b.** R = CH_3
53c. R = H, **53d.** R = Cl
53e. R = CF_3



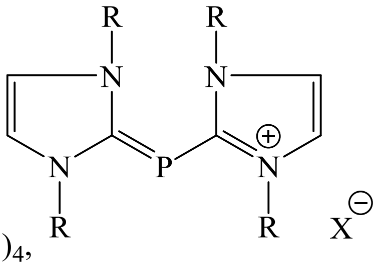
54a. R = OCH_3, **54b.** R = CH_3
54c. R = H, **54d.** R = Cl
54e. R = CF_3



R = Me **55a-c.** R' = H, OMe, Me
R = Et **55d-f.** R' = H, OMe, Me
X = BF_4



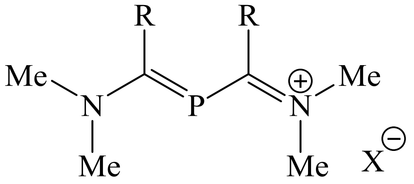
56



X=$B(C_6H_5)_4$,
57a. R = Me; **57b.**R = Et

Compound Numbering Scheme

58-69

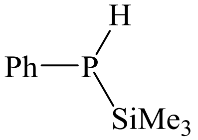


X = Cl, ClO$_4$

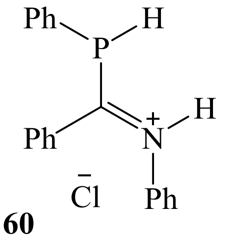
58a. R = H; **58b.** R = NMe$_2$

58c. R = C$_6$H$_5$; **58d.** R = SMe;

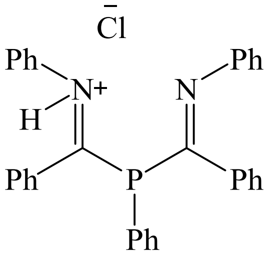
58e. R = ^{t}Bu



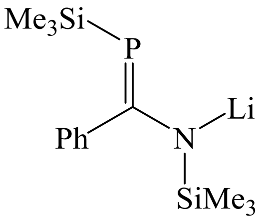
59



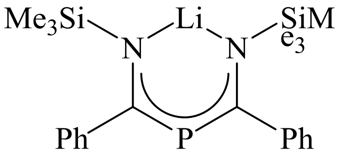
60



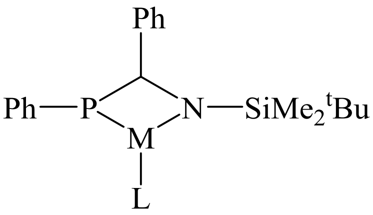
61



62

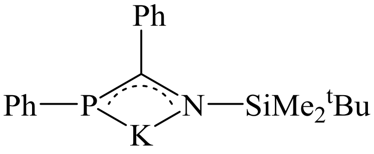


63

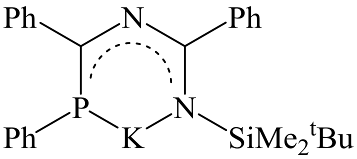


64a. M = Li, L = THF

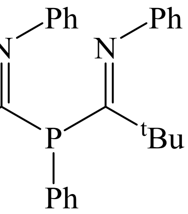
64b. M = K, L = Et$_2$O



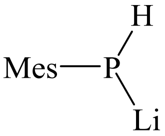
65



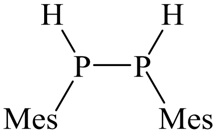
66



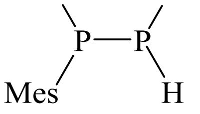
67



68



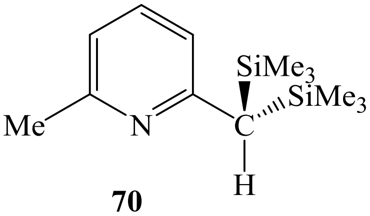
69a



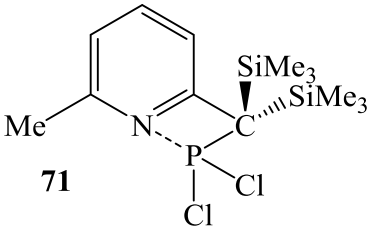
69b

Compound Numbering Scheme

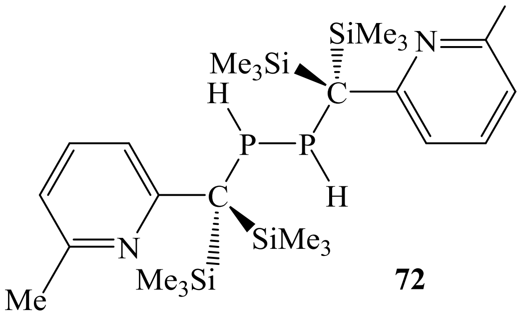
70-80



70



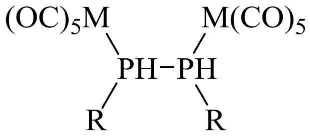
71



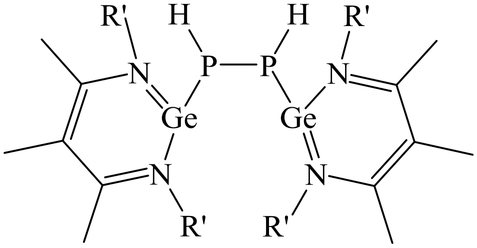
72

RP(H)-P(H)R

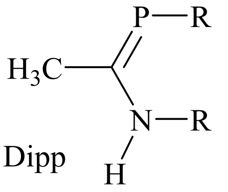
73



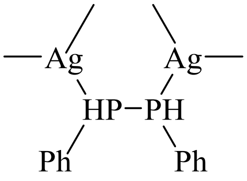
75a. R = Me, M = W
75b. R = Ph, M = W
75c. R = 2-thienyl, M = W
75d. R = Mes, M = Cr



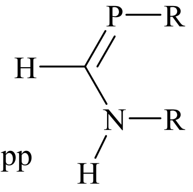
74. R' = Dipp



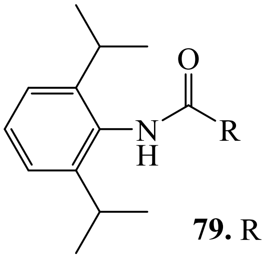
77. R = Dipp



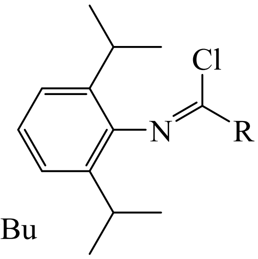
76



78. R = Dipp



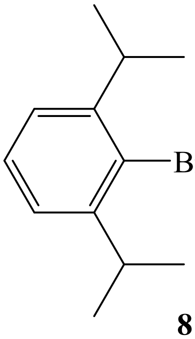
79. R = ^{t}Bu



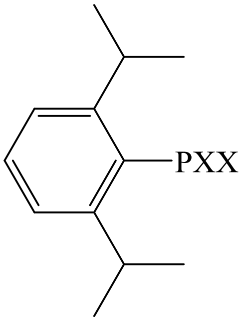
80. R = ^{t}Bu

Compound Numbering Scheme

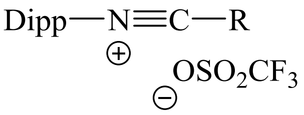
81-99



81



82. XX= Cl_2, ClBr, Br_2

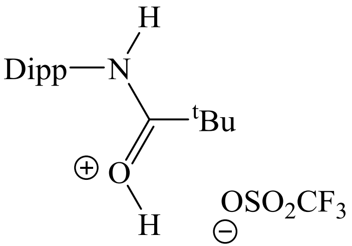


$\text{Dipp—N}^{\oplus}\equiv\text{C—R}\quad {}^{\ominus}OSO_2CF_3$

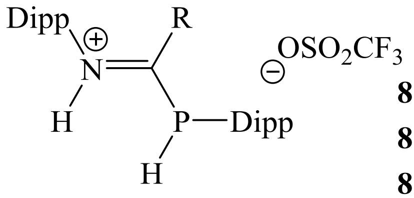
83. R =^{t}Bu

84. R = CH_3

85. R = *p*CH_3O-Ph



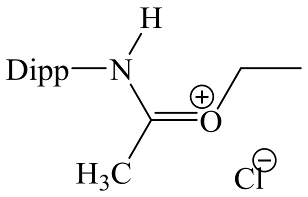
86



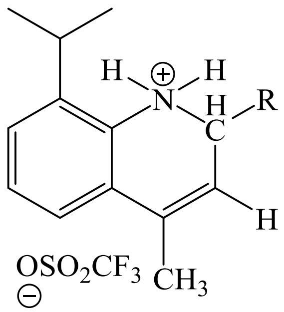
87. R =^{t}Bu

88. R = CH_3

89. R = *p*CH_3O-Ph



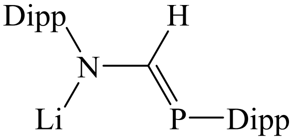
90



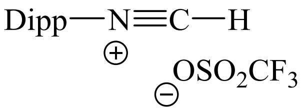
91. R = ^{t}Bu

92. R = CH_3

93. R = *p*CH_3O-Ph

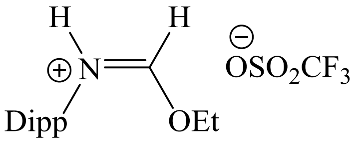


94

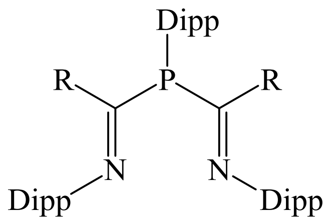


$\text{Dipp—N}^{\oplus}\equiv\text{C—H}\quad {}^{\ominus}OSO_2CF_3$

96

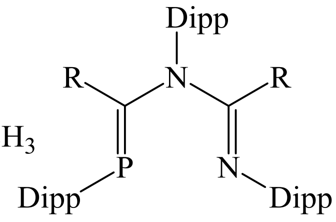


97



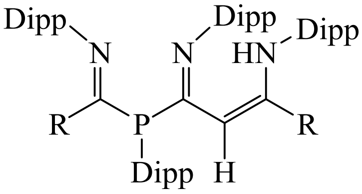
98. R = ^{t}Bu

99. **R =** CH_3

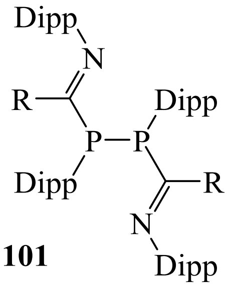


Compound Numbering Scheme

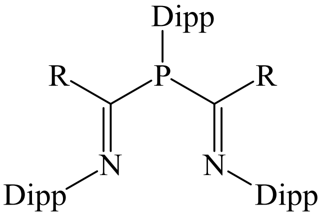
100-114



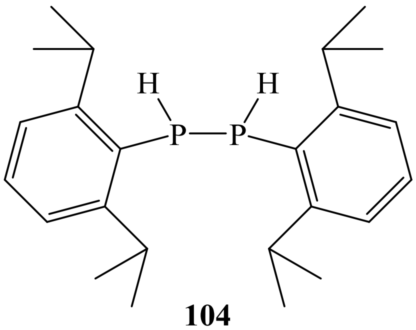
100



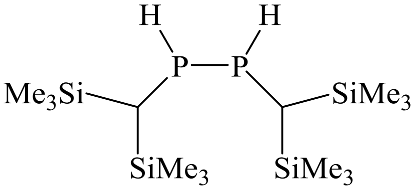
101



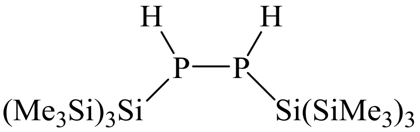
102. *p*CH_3Ph **103.** *p*OCH_3Ph



104



105



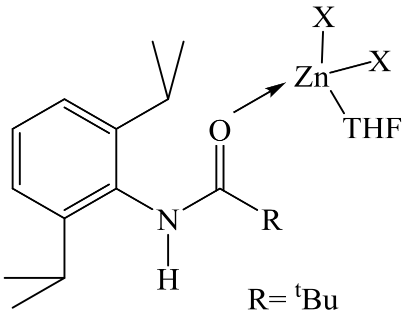
106

$(2,4,6\text{-}^tBu_3C_6H_2)(H)P\text{-}P(H)(2,4,6\text{-}^tBu_3C_6H_2)$
108

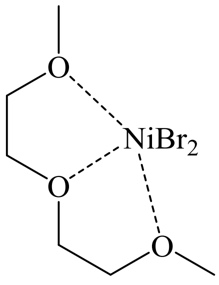
Me(H)P-P(H)Me **109**

Ph(H)P-P(H)Ph **110**

$^tBu(H)P\text{-}P(H)^tBu$ **111**



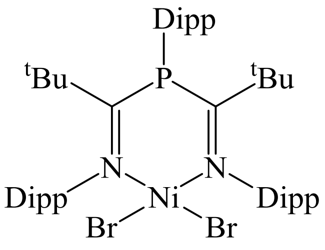
R= ^tBu
112: X = Cl
113a-c: X = Br



114

Compound Numbering Scheme

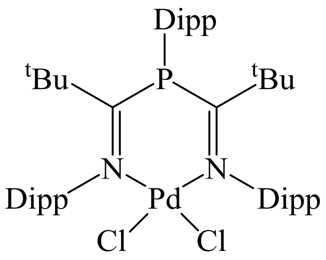
115-125



115

$(PhCN)_2PdCl_2$

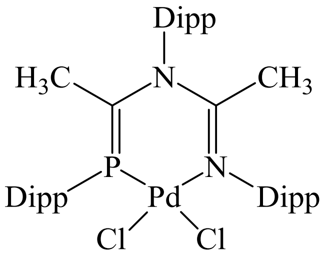
116



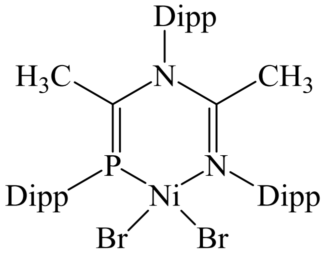
117

$(COD)PdCl2$ **118**

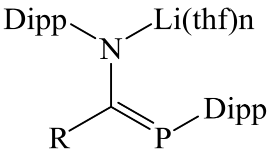
$[RhCl(COD)]_2$ **121**



119

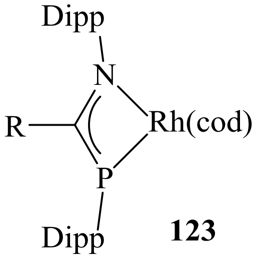


120



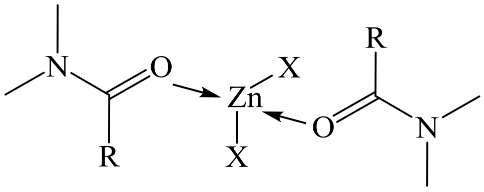
122

R = ^tBu, CH_3, $p CH_3O\text{-}C_6H_4$



123

R = ^tBu, CH_3, $p CH_3O\text{-}C_6H_4$



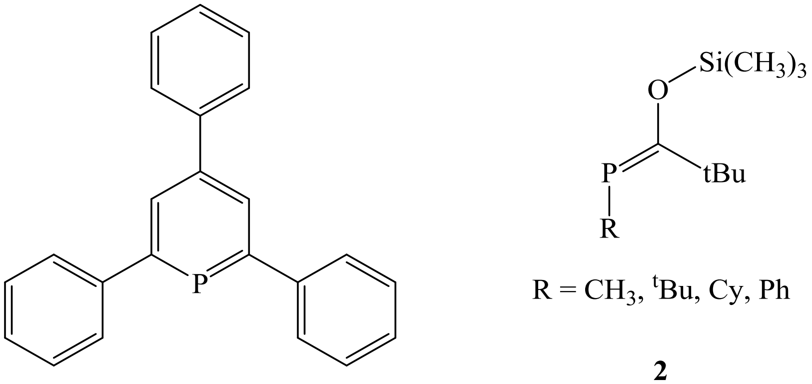
124: X = Br
125: X = Cl

Chapter 1

Literature review

1.1 Introduction

Compounds of nitrogen do not usually need bulky substituents for kinetic and thermodynamic stabilization, but this is not the case for heavier elements of Group 15. For example, using sterically bulky substitution is necessary for low coordinate phosphorus systems to be stabilized kinetically.[1,2] Isolation of low-coordinate π-bonded phosphorus was thought to be impossible until 1966, when the first neutral cyclic two-coordinate P(III) system **1** was synthesized[3] and the first stable acyclic phosphaalkenes **2** were isolated by Becker, using the silyloxy group to electronically stabilize the P=C double bond (Scheme 1.1).[4]



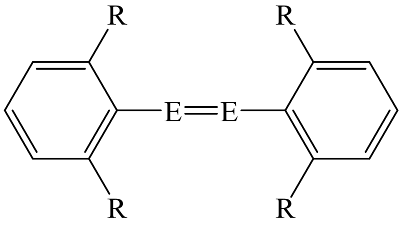
R = CH_3, ^tBu, Cy, Ph

1

2

Scheme 1.1 First isolated low-coordinate π-bonded phosphorus cyclic and acyclic.

In 1981 Yoshifuji isolated the first diphosphene (Mes*-P=P-Mes*) by using bulky 2,4,6-tritert-butylphenyl (Mes*) substituents.[1,2] Such sterically bulky substituents can sometimes kinetically and thermodynamically stabilize compounds that otherwise would not be isolable. Several other studies have been done on the heavier pnictogens: As, Sb and Bi, resulting in a series of compounds containing those elements by using bulky substituents (Scheme 1.2).[5]

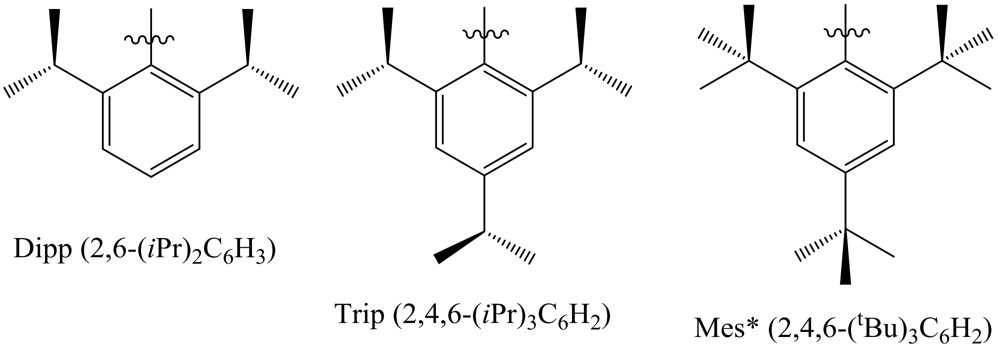


R = Mes (C_6H_2-2,4,6-CH_3), Trip (C_6H_2-2,4,6-$^iPr_3$)

3a: E = P, **3b**: E = As, **3c**: E = Sb, **3d**: E = Bi

Scheme 1.2 One low-coordinate system stabilized through the use of bulky substituents.

To study the effect of bulky substitution on amidines, our group deliberately used sterically bulky 2,6-diisopropylphenyl substituents to isolate a series of amidines (bulky substituents are not necessary for nitrogen compounds).[6] In addition to bulky Mes*, 2,4,6-(*i*-Pr)$_3C_6H_2$ (Tripp) and 2,6-(*i*-Pr)$_2C_6H_3$ (Dipp) groups can be used to stabilize low-coordinate main-group elements of the 3rd period and beyond (Scheme 1.3).[7]

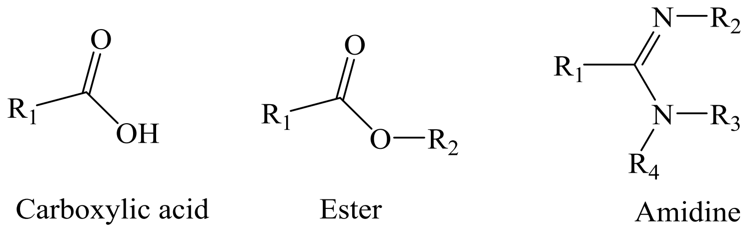


Scheme 1.3 Sterically bulky Dipp, Tripp, and Mes* groups.

One of the properties of Dipp-containing compounds is their high solubility in non-polar solvents and/or insolubility in water; the former is likely a consequence of the two isopropyl groups attached to the phenyl ring. To compare the bulky Dipp group with bulky substituent Mes*, the *ortho* diisopropyl groups (for Dipp) are significantly less bulky than *ortho* ^{t}Bu groups. However, the use of *ortho* diisopropyl groups has the advantage of providing stereochemical information from the ^{1}H NMR signals.[8] In case of the Tripp group, the sterically unnecessary *para i*-Pr substituent will obscure the ^{1}H NMR signals of the sterically essential *ortho i*-Pr substituents. Based on the experience of our group, Mes* was too bulky and prevents the synthesis of amidines. Our group demonstrated that the bulky substituent Dipp neither prevents the synthesis of the amidines nor subsequent reaction with transition elements. Because of the considerable advantage of Dipp, this substituent has been used extensively in our research.[8] Thereafter, our group decided to deliberately produce the mono-phosphorus derivatives of these amidines (Scheme 1.12) which contain bulky Dipp substituents to stabilize the reactive low-coordinate phosphorus atom. We decided to complete this study and synthesize the mono-substituted phosphorus analogue of amidines (with the Dipp group on nitrogen and phosphorus) and study the influence of different carbon backbone substitution on the reactivity and structure of such compounds.

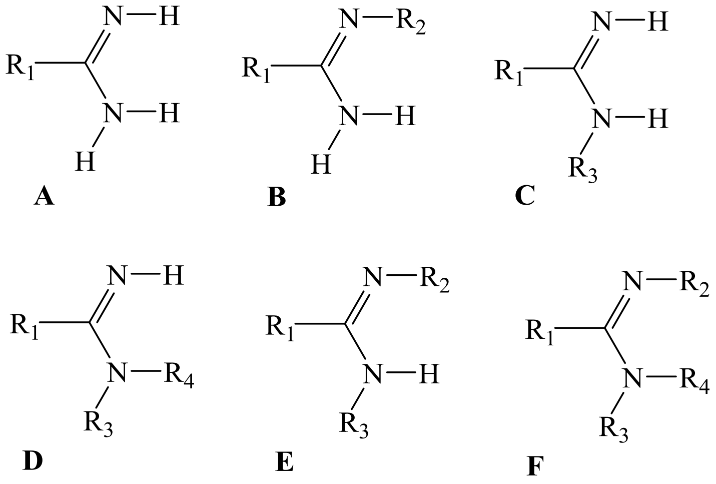
1.2 Amidines

Amidines are the nitrogen analogues of carboxylic acids and esters. Due to the resonance stabilization of positive charge over two nitrogen atoms in their conjugate acid, they are classified as relatively strong bases (Scheme 1.4).[9]



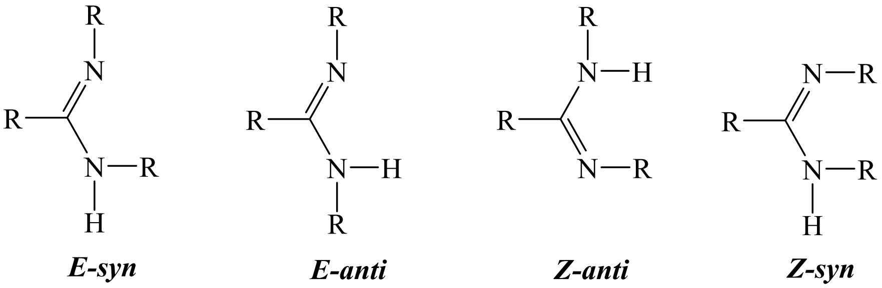
Scheme 1.4 The carboxylic acid, ester and amidine functional groups.

Based on the number and placement of the substituents, there are six kinds of amidines: unsubstituted ($R_1 \neq H$, $R_2 = R_3 = R_4 = H$) **A**, imino ($R_1 = R_2 \neq H$, $R_3 = R_4 = H$) **B**, amino-monosubstituted ($R_1 = R_3 \neq H$, $R_2 = R_4 = H$) **C**, *N,N*-disubstituted ($R_1 = R_3 = R_4 \neq H$, $R_2 = H$) **D**, *N,N'*-disubstituted ($R_1 = R_2 = R_3 \neq H$, $R_4 = H$) **E**, and trisubstituted amidines ($R_1 = R_2 = R_3 = R_4 \neq H$) **F** (Scheme 1.5).[9,10]

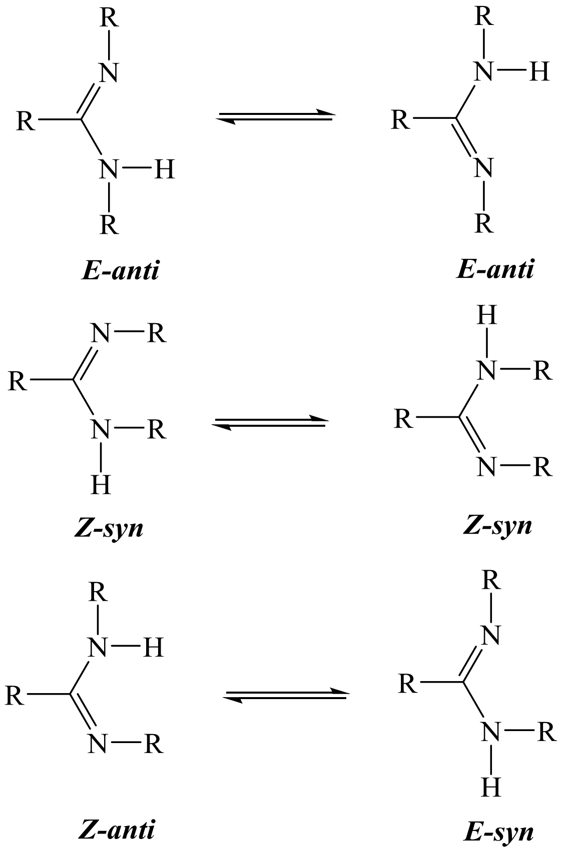


Scheme 1.5 The six classified types of amidines.

For each type of amidine, there is *cis-trans* isomerism with respect to C=N.[8] Scheme 1.6 shows four different stereochemical designations expected for *N,N'*-disubstituted amidines. The *E-anti* and *Z-syn* isomers and also the *Z-anti* and *E-syn* isomers are related by tautomerism.[8] For monosubstituted and disubstituted amidines, tautomerism also can be exhibited (Scheme 1.7).[10]

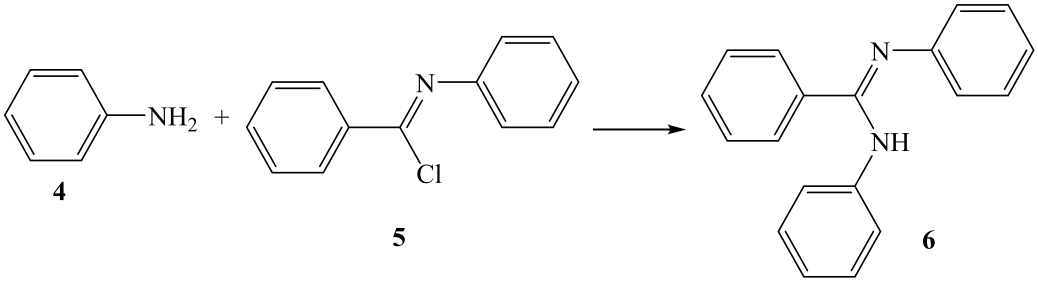


Scheme 1.6 The four different stereochemical designations for *N,N'*-disubstituted amidines.



Scheme 1.7 Tautomerism exhibited by *N,N'*-disubstituted amidines.

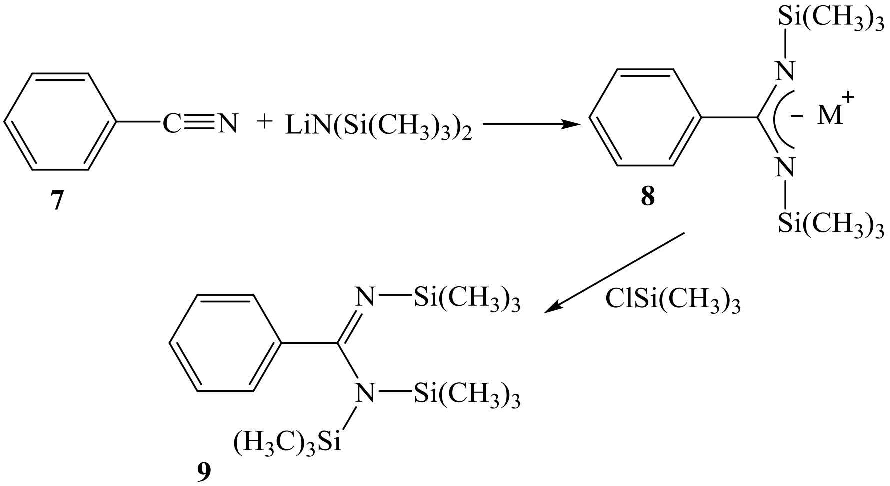
The first amidine, bis-*N*,*N*'-diphenylbenzamidine **6**, was synthesized by Gerhardt in 1858 by reacting aniline **4** with *N*-phenylbenzimidoyl chloride **5** (Scheme 1.8).[11]



4 **5** **6**

Scheme 1.8 Synthesis of the first amidine, bis-*N*,*N*'-diphenylbenzamidine.

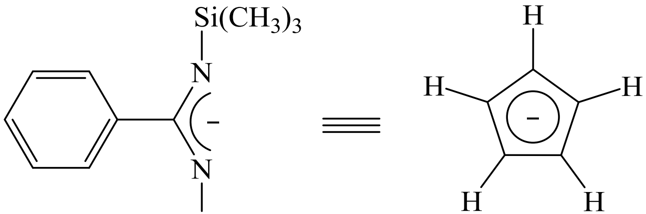
In the 1980's it was found that silylated benzamidines react with metal halides and silylated benzamidinate **8** can be isolated as the Li, Na, K salts[12]. Alternately, **8** can be reacted with one equivalent of $ClSi(CH_3)$ to give *tris*-substituted amidines **9** (Scheme 1.9)[13].



7 **8** **9**

Scheme 1.9 Synthesis of silylated lithium benzamidinate and tris-substituted silylated benzamidines.

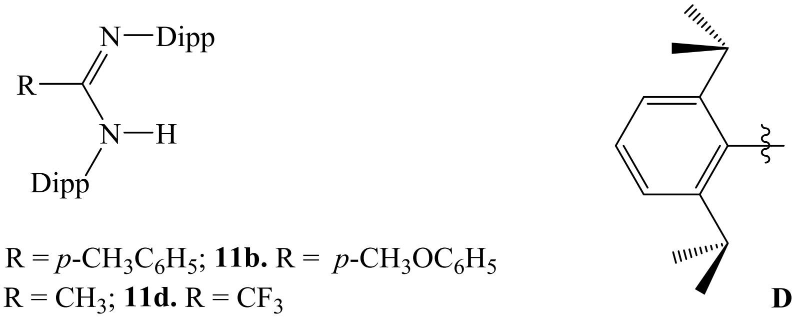
Due to the utility of the benzamidinate derivatives as a ligand, lots of metals in the periodic table were used to isolate the silylated amidinate **8**. The silylated benzamidinate ligand **8** is steric and charge equivalent to an η^5-cyclopentadienyl (Cp) ligand **10**; thus a lot of interest has been devoted to producing new homogeneous polymerization catalysts by using silylated amidinates instead of commonly used Cp ligands (Scheme 1.10).[12] There was also a lot of interest to use amidinate-metal complexes as catalysts in olefin[14,15,16,17,18] and isocyanate[19] polymerization.



8 **10**

Scheme 1.10 Silylated benzamidinate ligand and η^5-cyclopentadienyl (Cp).

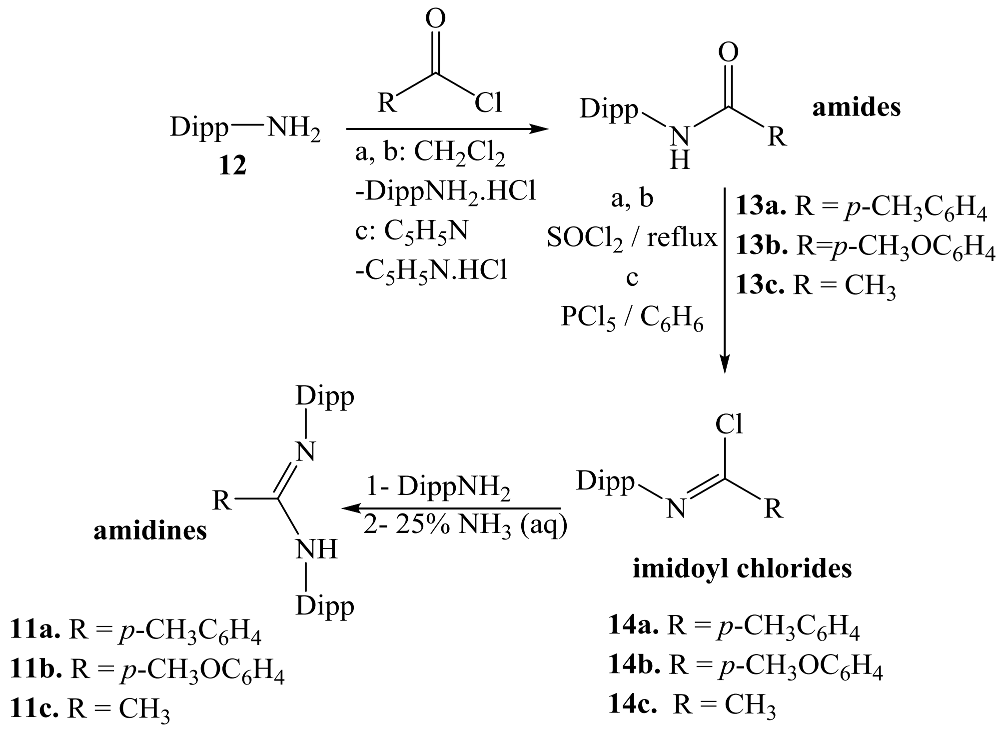
Four sterically bulky amidines **11a-d** that contain the Dipp groups on both amino and imino nitrogen were reported by Boeré in 1998 (Scheme 1.11).[10,6,20] *N,N'*-disubstituted amidines **11a-d** (Scheme 1.12) were synthesized from 2,6-diisopropylaniline **12** and the acid chlorides *via* the corresponding imidoyl chlorides **14a-c**.



11a. R = p-$CH_3C_6H_5$; **11b.** R = p-$CH_3OC_6H_5$
11c. R = CH_3; **11d.** R = CF_3

Dipp

Scheme 1.11 Amidines with sterically bulky Dipp group.

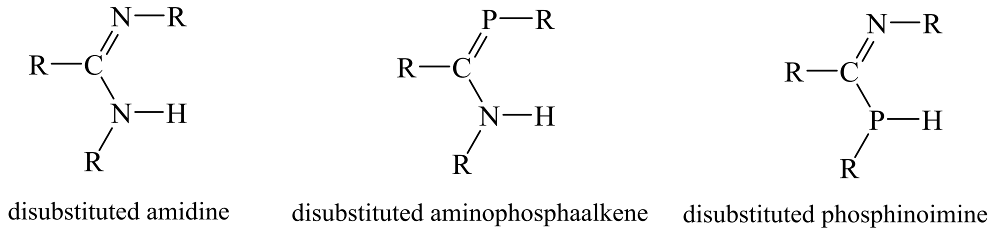


Scheme 1.12 Synthetic route for sterically bulky Dipp amidines.

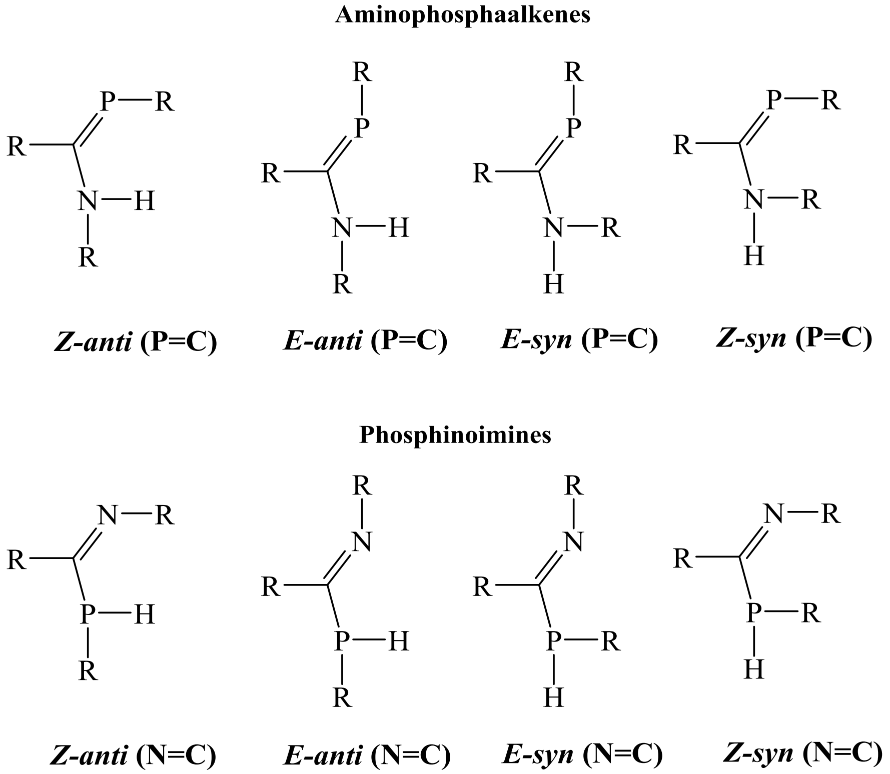
These amidines exhibit isomerism in solution and amongst the set of backbone substituents shown in Scheme 1.6 have been found to adopt three of four possible isomers in the solid state.[10]

1.3 Literature background of research on phosphaamidines

Amino and imino phosphaamidines are two possible phosphorus analogues to disubstituted amidines (Scheme 1.13).[11] Based on the MSc thesis of Dr. Jason Masuda, there are eight possible structures for disubstituted phosphaamidines as shown in Scheme 1.14.[8]



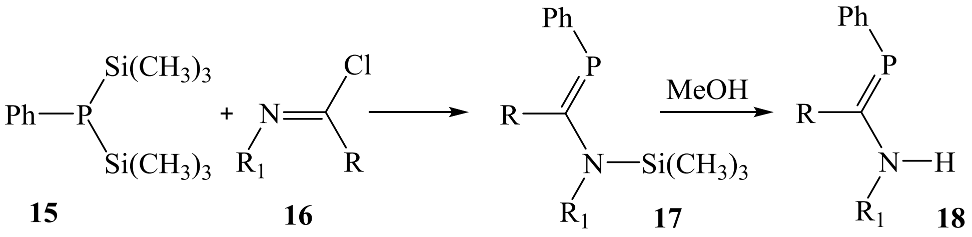
Scheme 1.13 Disubstituted amidine, aminophosphaalkene and phosphinoimine.



Scheme 1.14 Eight isomers of *N,P*-disubstituted phosphaamidines.

For each phosphaamidine, a *cis-trans* isomerism exists with respect to the C=P or C=N double bond as well as rotational conformers around the C-N or C-P single bond. If the double bond is between P and C, a *C-amino-*(σ^2,λ^3)*-phosphaalkene* is formed; if between N and C, a *C-*(σ^3,λ^3)*-phosphinoimine*. For *N,P*-disubstituted-*C*-aminophosphaalkenes, there are four possible isomers or conformers, which we designate as *E-anti*(P=C), *E-syn*(P=C), *Z-anti*(P=C) and *Z-syn*(P=C). For *N,P*-disubstituted-*C*-phosphinoimine, there are also four possible isomers or conformers (*E-anti*(N=C), *E-syn*(N=C), *Z-anti*(N=C) and *Z-syn*(N=C)) (Scheme 1.14). In addition to the isomerism, tautomerism can be exhibited in the monosubstituted and disubstituted forms. [Note that the tautomer of *Z-anti*(P=C) is *E-syn*(N=C) and that of *E-syn*(P=C) is *Z-anti*(N=C)].

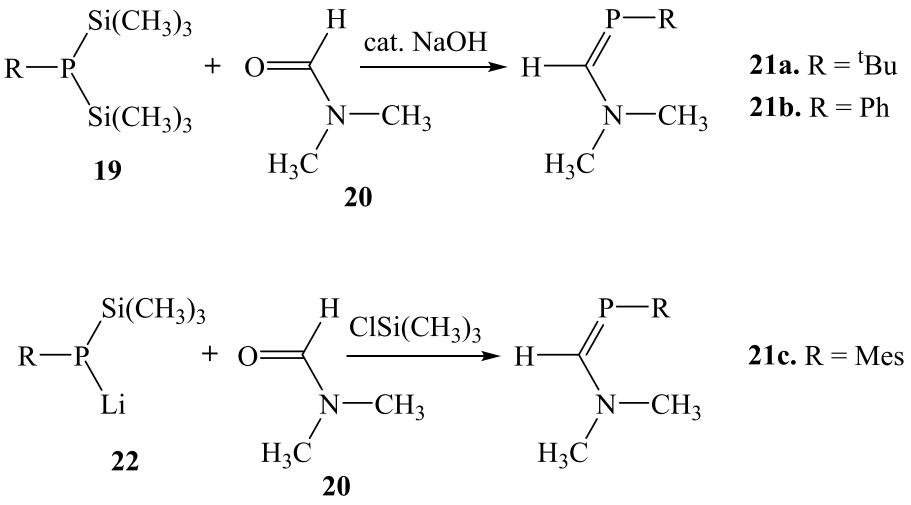
One of the first groups who synthesized disubstituted phosphaamidines, was that of Prof. Kurt Issleib of the University of Jena (in East Germany) in 1978.[21] They used an imidoyl chloride **16a-f** with a disilylated primary phosphane **15** to make amino phosphaamidines **17a-f**. Amino phosphaamidines with proton substitution on nitrogen **18a-f** were isolated after treatment with MeOH (Scheme 1.15).



R= Ph **16a.** R_1= Ph	R= Ph **17a.** R_1= Ph	R= Ph **18a.** R_1= Ph
16b. R_1= CH_3	**17b.** R_1= CH_3	**18b.** R_1= CH_3
16c. R_1= 2,6-Et_2Ph	**17c.** R_1= 2,6-Et_2Ph	**18c.** R_1= 2,6-Et_2Ph
16d. R_1= Cy	**17d.** R_1= Cy	**18d.** R_1= Cy
R_1=Ph **16e.** R = ^{t}Bu	R_1=Ph **17e.** R = ^{t}Bu	R_1=Ph **18e.** R = ^{t}Bu
16f. R = Mes	**17f.** R = Mes	**18f.** R = Mes

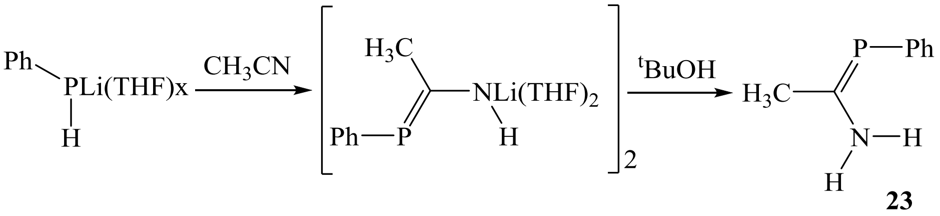
Scheme 1.15 Synthesis of N,P-disubstituted monophosphaamidines.

Another route, by Prof. Dr. Gerd Becker's group at the University of Stuttgart, Germany in 1980, involves using NaOH as a catalyst, to react the R-P[$Si(CH_3)_3$]$_2$ **19** with *N,N*-dimethylformamide **20**. With elimination of bis-trimethylsiloxane, dimethylamino phosphaamidines (R = ^{t}Bu, Ph) **21a-b** were synthesized.[22] They also reacted the *N,N*-dimethylformamide **20** with $MesPSi(CH_3)_3$ **22** to form the phosphaamidine (R = Mes) **21c** (Scheme 1.16).[23]



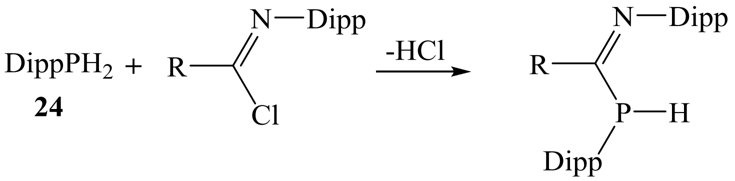
Scheme 1.16 Synthesis of dimethylaminophosphaamidines.

The first monophosphaamidines **23** containing an NH_2 group was isolated in 1995 by Prof. Dr. Edgar Niecke and his group at the University of Bonn, Germany (Scheme 1.17).[24] The NH_2 substituted phosphaamidine was prepared *via* the Li^+ salts but nothing further has been reported about these interesting examples.



Scheme 1.17 Synthesis of the first monophosphaamidines containing an NH_2 group.

Later in 2004 our group reported two new phosphaamidines **25a-b** which were made for the first time from the thermal reaction of a new bulky primary phosphine (DippPH$_2$) **24** with imidoylchloride **14a-b** (Scheme 1.18). This reaction was very slow and needed refluxing for up to ten days.[25] To decrease the reaction time and impurities, they used silylated phosphine, DippPHSi(CH$_3$)$_3$ **26**. In this case there was no HCl formation, so there were no side products. Using this procedure the products were obtained with greater purity in less than five days (Scheme 1.19).

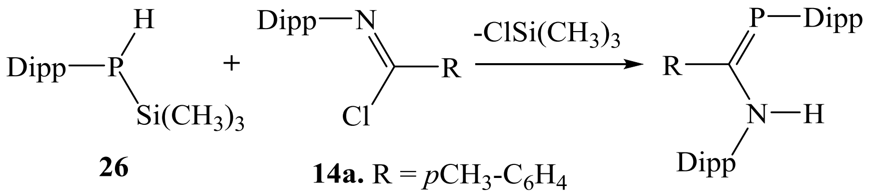


24

14a. R = pCH$_3$-C$_6$H$_4$
14b. R = pCH$_3$O-C$_6$H$_4$

25a. R = pCH$_3$-C$_6$H$_4$
25b. R = pCH$_3$O-C$_6$H$_4$

Scheme 1.18 Synthesis of the two new phosphaamidines using primary phosphine.



26

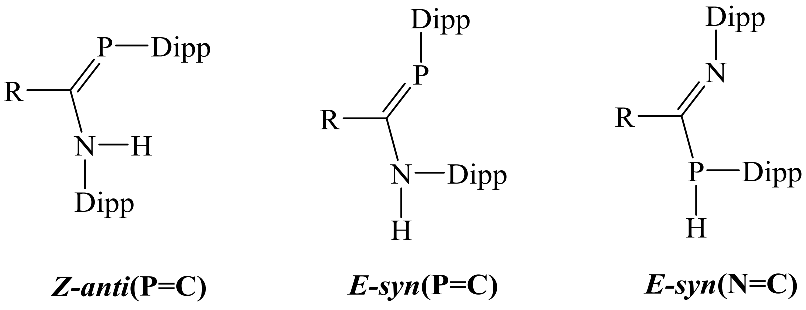
14a. R = pCH$_3$-C$_6$H$_4$
14b. R = pCH$_3$O-C$_6$H$_4$

25a. R = pCH$_3$-C$_6$H$_4$
25b. R = pCH$_3$O-C$_6$H$_4$

Scheme 1.19 Synthesis of the two new phosphaamidines using silylated phosphine.

Crystallization of the crude material with hot ethanol produced a yellow amorphous solid which contained traces of impurity. Recrystallization from hot methanol produced block-like yellow crystals that were pure by ^{1}H NMR spectroscopy. ^{1}H and ^{31}P

NMR data for both phosphaamidines are similar to each other and for reason of brevity, only the NMR data for 4-$CH_3C_6H_4$ (abbreviated to *p*CH_3Ph-phosphaamidine **25a**) will be discussed in this section.[8] Our group found out that there are multiple isomers and tautomers present in solutions of phosphaamidines. The proton-coupled ^{31}P NMR spectrum shows one large singlet located at 53.4 ppm, a medium doublet at 79.0 ppm (small coupling constant $^3J_{P\text{-}H}$ = 10 Hz), a small doublet at -80.1 ppm ($^1J_{PH}$ = 243 Hz, H directly bonded to phosphorous indicated by large coupling constant), and a very small doublet at -52.5 ppm ($^1J_{PH}$ = 243 Hz). The proton-decoupled spectrum was run and loss of the coupling confirmed the presence of two P-H isomers. NMR spectroscopy data for the major isomers of both phosphaamidines (*p*CH_3Ph and *p*CH_3OPh phosphaamidine) is presented in Appendix II Table A136. Based on this data, the structure was presumed to be *Z-anti*(P=C).[8] DFT calculations have shown that the *Z-anti* (P=C) structure is the most stable isomer. Crystal structures of both phosphaamidines and their metal complexes which were determined by our group are in the *Z-anti*(P=C) form.[26] This evidence proved the major isomer is *Z-anti*(P=C) 87% (Scheme 1.20). [8]

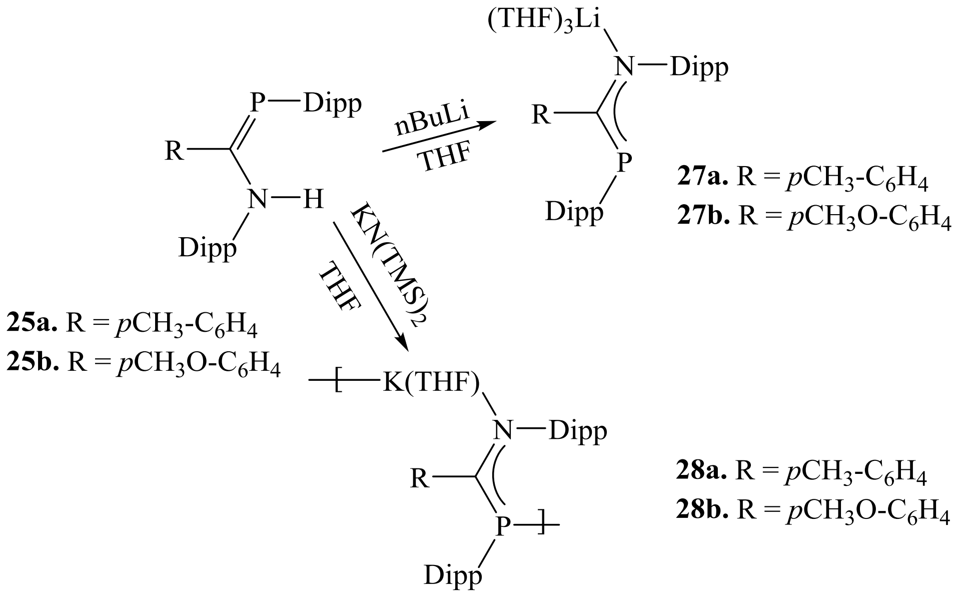


Scheme 1.20 The major isomers *Z-anti*(P=C), the second most common isomer *E-syn*(P=C), larger of possible P-H isomer *E-syn*(N=C) present in solution.

Analysis of the NMR data for the second most intense peak in the ^{31}P NMR spectrum indicates that it is likely the *E*-*syn*(P=C), at 10% of the major N-H peak. *Z*-*anti*(P=C) has the N-H proton *cis* to the phosphorus center with small coupling. The coupling constant for the second most intense peak is larger than *Z*-*anti*(P=C) which confirmed the second isomer has N-H *trans* to the phosphorus center. There are only two possible structures with the N-H proton *trans* to the phosphorus, *E*-*syn*(P=C) and *Z*-*syn*(P=C). Because of steric interactions in the *Z*-*syn*(P=C) our group assigned the second N-H isomer as *E*-*syn*(P=C). The doublet integrating to 3% at 4.92 ppm ($^{3}J_{(P\text{-}H)}$ = 242 Hz) in the ^{1}H NMR spectrum correlated to the larger P-H isomer at -80.3 ppm ($^{3}J_{(P\text{-}H)}$ = 243 Hz) that is 3% of the major isomer and possibly is *E*-*syn*(N=C) (Scheme 1.20). The fourth isomer which is P-H isomer didn't show up in ^{1}H NMR spectrum, maybe because it has a very similar chemical shift and coupling constant and overlaps in the ^{1}H NMR spectrum.

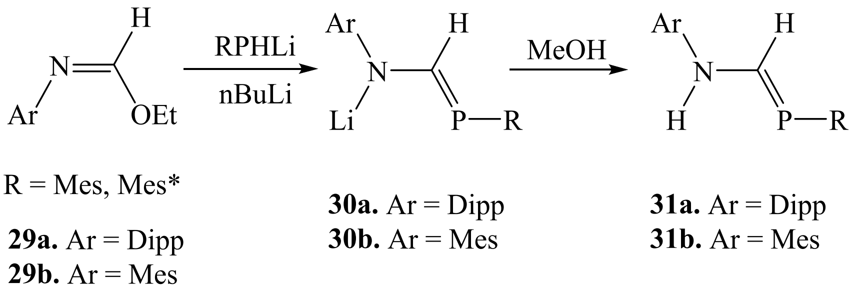
In order to further examine this complex isomerism in solution, extensive NMR spectroscopic investigations were undertaken in CD_3CN and $(CD_3)_2C{=}O$ and C_6D_6. In C_6D_6 which is a non-polar solvent the intensity of the minor isomers is lower. In the case of more polar solvents, such as CD_3CN, $(CD_3)_2C{=}O$, *Z*-*anti*(P=C) and *E*-*syn*(P=C) isomers present almost the same intensity and no significant change is observed in the intensity of the P-H isomers. This shows that there is fast exchange between the *Z*-*anti*(P=C) and *E*-*syn*(N=C) isomers that indicates tautomerism. Our group also showed that there is slow exchange due to the rotation around either the P-C or N-C bond in the *E*-*syn*(P=C) isomer. There is a protonated intermediate for this slow exchange and this intermediate can be a candidate for *E*-*Z* isomerism. The evidence of two isomers (*E* and *Z*) for different protonated phosphaamidines that I synthesized is explained in details in Sections 2.2.2.4, 2.3.2 and 2.4.2.

Our group also deprotonated the phosphaamidines and produced lithium (**27a-b**) and potassium (**28a-b**) complexes of phosphaamidines (Scheme 1.21).[25] These are the first *N,P*-disubstituted aminophosphaalkenes and their Li and K complexes have been structurally characterized.



Scheme 1.21 Lithium and potassium complexes of *N,P*-disubstituted phosphaamidines. Compound **28** is polymerized.

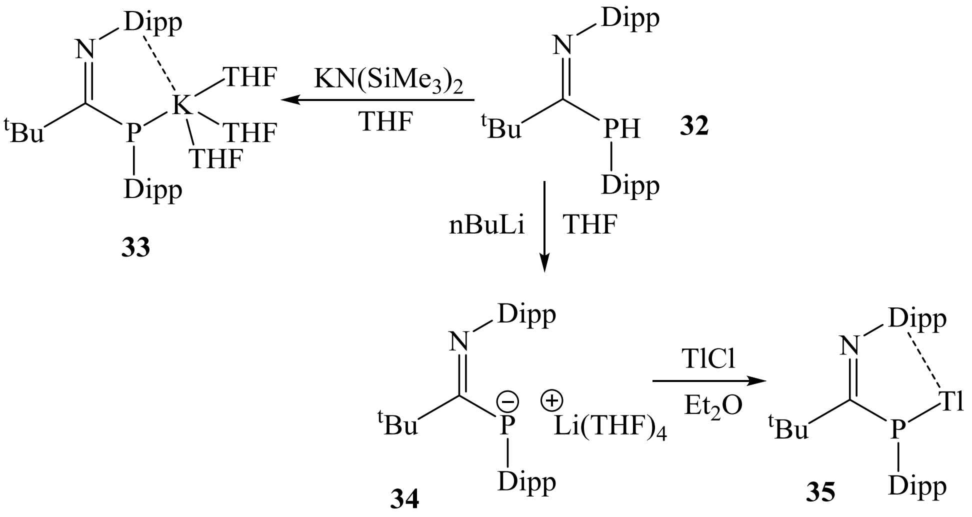
In 2007 Song reported the synthesis of new phosphaamidines with R' = H (substitution on carbon backbone). They reacted ethyl N-arylformimidates (ArN=CH(OEt)) **29a-b** with lithium dialkyl- and diarylphosphanides to afford the corresponding *N*-aryl phosphaformamidines. Reaction of primary lithium arylphosphanides with ethyl *N*-arylformimidates and *n*BuLi produced phosphaformamidinates **30a-b**. Subsequent reaction with methanol gave the *N*-aryl-*N*-hydrogenophosphaformamidines (Scheme 1.22).[27]



29a. Ar = Dipp
29b. Ar = Mes
30a. Ar = Dipp
30b. Ar = Mes
31a. Ar = Dipp
31b. Ar = Mes

Scheme 1.22 Synthesis of phosphaformamidines and phosphaformamidinates.

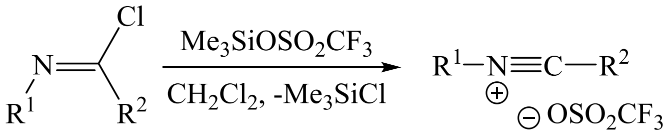
In 2009, Li's group also used the Dipp group, the only others than ourselves to used this substituent on phosphorus. They prepared phosphaamidine **32**, with a ^{t}Bu substituent on the carbon backbone, and its lithium, potassium and thallium complexes **33-35**. The structure of the lithium complex consists of separated non-interacting cations and anions, and the potassium and thallium complexes display η^1-coordination mode to the phosphorus atom (Scheme 1.23).[28]



32
33
34
35

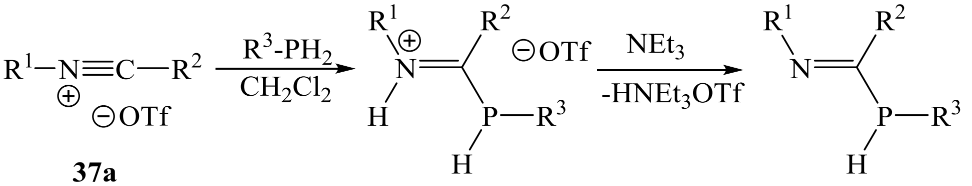
Scheme 1.23 Synthesis of new bulky phosphaamidine and its metal complexes.

Recently, in 2014, Lammertsma reported a new route to make phosphaamidines through the reaction of nitrilium triflate with primary phosphane. In the first step, an imidoyl chloride **36a-h** reacts with trimethylsilyl triflate in CH_2Cl_2 to afford the nitrilium triflate **37a-h** (Scheme 1.24). The reaction of nitrilium triflate with primary phosphane in the next step, and subsequent addition of triethylamine affords the secondary iminophosphanes **39a-b** (Scheme 1.25).[29]



$R^2 = {}^tBu$	$R^2 = Ph$	$R^2 = {}^tBu$	$R^2 = Ph$
36a. R^1=Ph	**36e.** R^1=Ph	**37a.** R^1=Ph	**37e.** R^1=Ph
36b. R^1=Mes	**36f.** R^1=Mes	**37b.** R^1=Mes	**37f.** R^1=Mes
36c. R^1= *i*Pr	**36g.** R^1= *i*Pr	**37c.** R^1= *i*Pr	**37g.** R^1= *i*Pr
36d. R^1= Cy	**36h.** R^1= Cy	**37d.** R^1= Cy	**37h.** R^1= Cy

Scheme 1.24 Synthesis of the nitrilium triflate.



37a

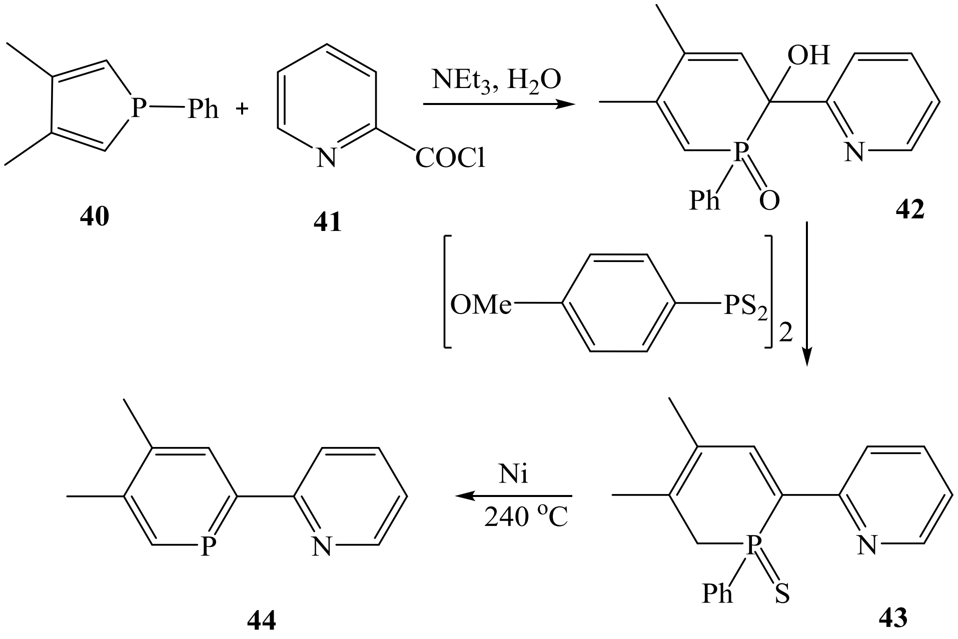
R^1 = Ph, R^2 = ${}^tBu$ **38a.** R^3 = Ph **38b.** R^3 = Cy **39a.** R^3 = Ph **39b.** R^3 = Cy

Scheme 1.25 Synthesis of the phosphaamidine salts and phosphaamidines.

1.3.1 *P,N*-chelating ligands

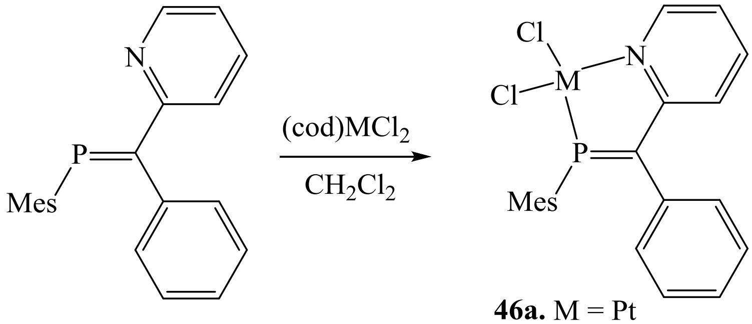
P,N-chelating ligands have attracted increasing attention due to the presence of a “soft”

(P) and a “hard” (N) reaction center.[30] Low-coordinate phosphorus ligands are attractive because their unique σ-donor and *π*-acceptor properties impart desirable characteristics to electron-rich transition metal centers.[31] These ligands can stabilize metal ions in a variety of oxidation states, geometries and different coordination modes compared with P,P and N,N ligands. Such chelates are bidentate hybrid ligands, which have first been described by Prof. François Mathey and co-workers in 1982 (then at the University of Paris-East) with the synthesis of 2-(2'-pyridyl)-4,5-dimethylphosphinine **44** (Scheme 1.26).[32]



Scheme 1.26 Synthesis of first 2-(2'-pyridyl)phosphinine.

In 2007 Prof. Derek Gates’s group at the University of British Columbia reported two new chelating phosphaalkene-based complexes of palladium(II), MesPC(Ph)(Py)PtCl$_2$ **46a** and platinum(II),MesPC(Ph)(Py)PdCl$_2$ **46b** (Scheme 1.27).[33]

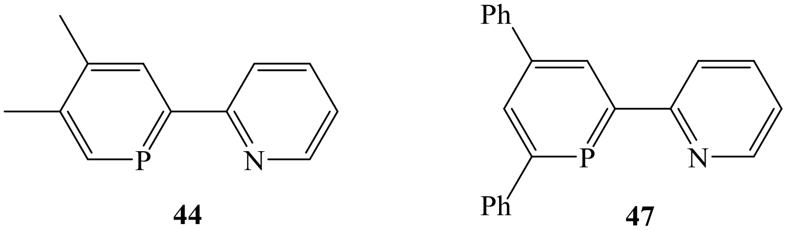


45

46a. M = Pt
46b. M = Pd

Scheme 1.27 Synthesis of chelating phosphaalkene-based complexes of platinum(II) and palladium(II).

Another example is the replacement of a pyridine unit by a π-accepting phosphinine which leads to 2-(2'-pyridyl)phosphinine **44** and **47** (Scheme 1.28)[34], approximate analogues to bipyridyl containing a low-coordinated ‘‘soft’’ phosphorus and a ‘‘hard’’ nitrogen heteroatom.



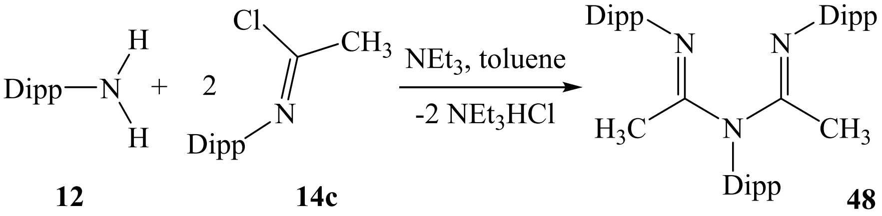
44 **47**

Scheme 1.28 2-(2'-pyridyl)-4,5-dimethylphosphinine and 2-(2'-pyridyl)-4,6-diphenylphosphinine.

Due to the presence of electronically and sterically different phosphorus and nitrogen centers within the same structure, significant differences in the coordination behaviour of the P,N ligand towards metals, compared to the structurally related P,P' ligand, was also observed by others such as Muller’s group.[35]

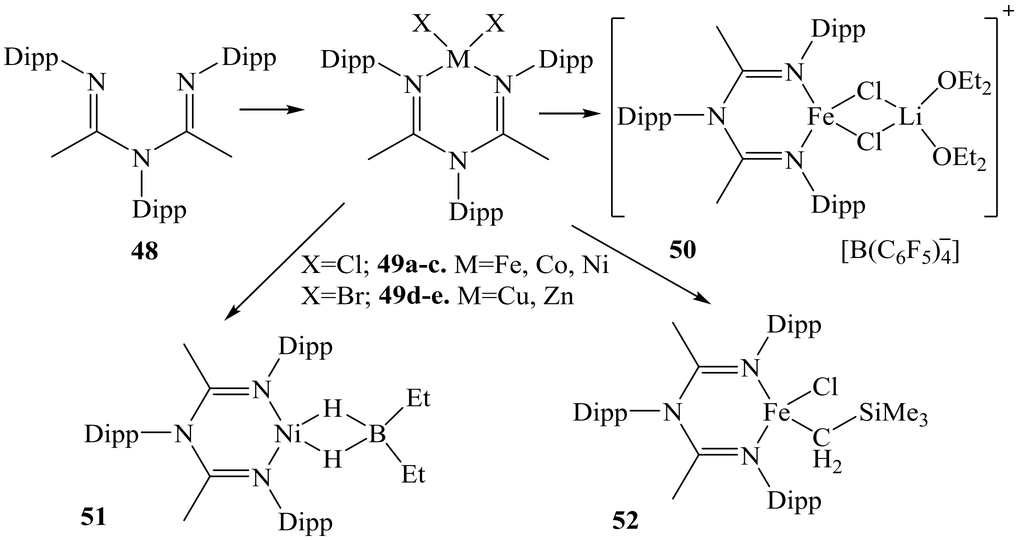
1.4 Sterically bulky *N*-imidoylamidines

The *N*-imidoylamidine ligand **48** can be synthesized by using Prof. Doug Stephan's procedure. They have reacted two equivalents of imidoyl chloride **14c** with aniline **12** by using Et_3N and refluxing in toluene (Scheme 1.29). Based on their evidence, reaction proceeds via an amidine intermediate.[36] Stephan's group have also reacted the *N*-imidoylamidine with AlI_3 and $AlMe_3$ to make metal complexes.



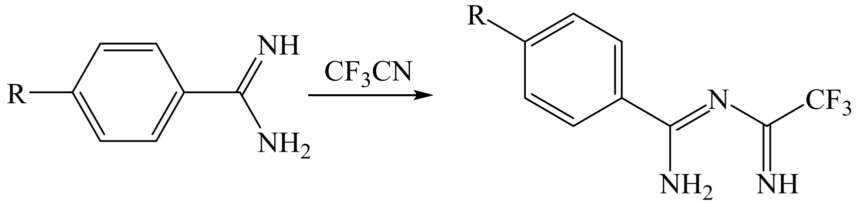
Scheme 1.29 Synthesis of the sterically demanding *N*-imidoylamidine.

They also reported the synthesis of a series of transition metal complexes of *N*-imidoylamidine ligands **49a-e** and **50-52** (Scheme 1.30).[37]



Scheme 1.30 Synthesis of neutral and cationic complexes of diimine ligand.

Sterically demanding chelating ligands have proved to be effective in developing late transition-metal olefin polymerization catalysts.[38,39] There are several examples of metal complexes involving the *N*-imidoylamidines ($HN(C(R)NH)_2$) [40,41,42,43,44,45] and a few examples of *N*-arylimidoylamidine ligand complexes.[46,47,48] Our group synthesized a series of *N*-imidoylamidine **54a-e** system ($HN(C(R)NH)_2$) by direct reaction of trifluoroacetonitrile with amidines **53a-e** and X-ray structures were determined. X-ray structures of imidoylamidines are rare (Scheme 1.31). Then they converted the *N*-imidoylamidine to *N*-imidoylamidine hydrochlorides to synthesize thiatriazines in a few steps.[49]

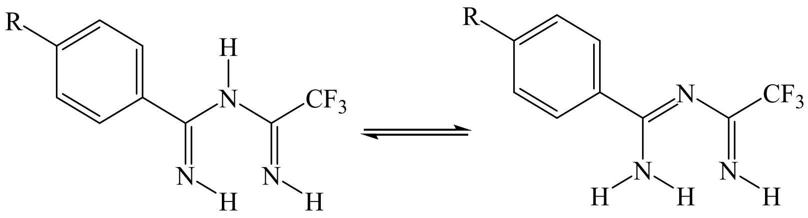


53a. R = OCH_3, **53b.** R = CH_3
53c. R = H, **53d.** R = Cl
53e. R = CF_3

54a. R = OCH_3, **54b.** R = CH_3
54c. R = H, **54d.** R = Cl
54e. R = CF_3

Scheme 1.31 Synthesis of new *N*-imidoylamidine.

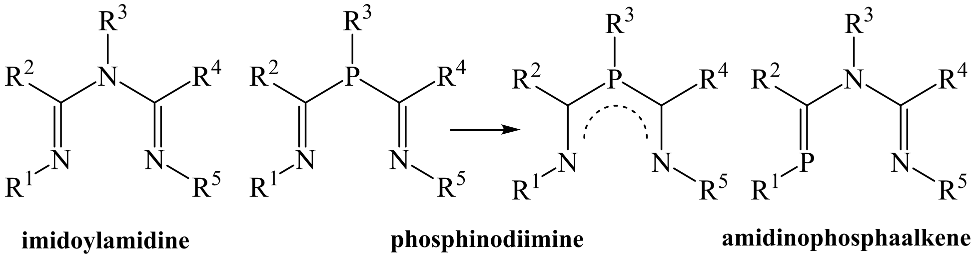
Based on their report three different NH peaks were observed in ^1H NMR spectra which indicated the three nonequivalent hydrogen atom environments. Two of these peaks are broadened compared to the third one, indicating an exchange due to tautomerism (Scheme 1.32).



Scheme 1.32 Tautomers of *N*-imidoylamidine.

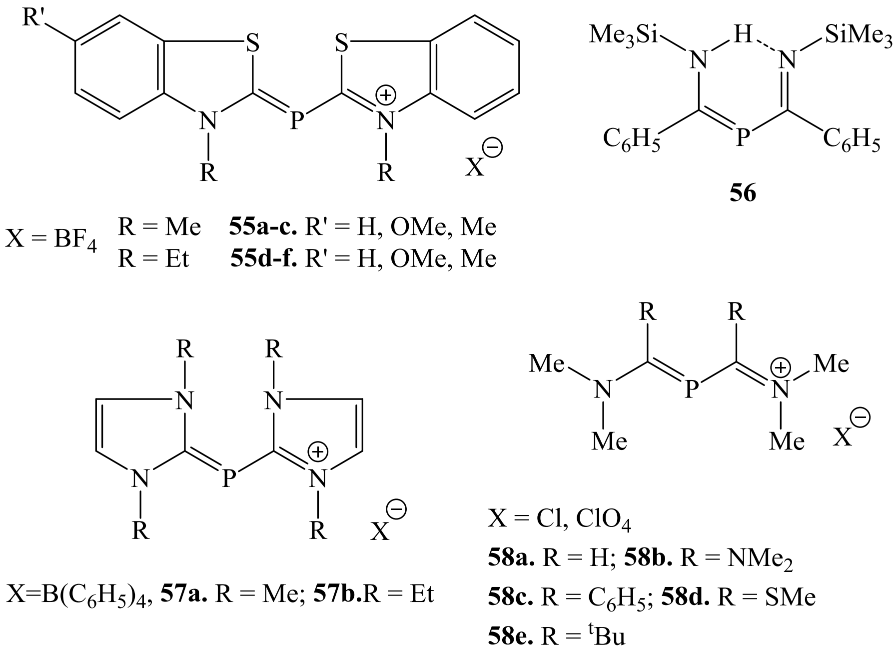
1.5 Sterically bulky phosphinodiimines

Replacement of one of the nitrogen atoms of an imidoylamidine conceptually leads to two different isomeric possibilities: if the phosphorus atom is at a chain end, a *C*-amidinophosphaalkene is formed; if instead phosphorus is at the middle site, a phosphinodiimine is formed (Scheme 1.33).



Scheme 1.33 Two phosphorus analogues of imidoylamidine.

There are two kinds of substituents which may have different influences on selection of the final product, the ones on the N or P atoms which can be the same or different and the ones on the backbone (central) C atoms. R^1 and R^5 are the “fronting or “sterically controlling” substituents. The substituents on the carbon backbone, R^2 and R^4, can be hydrogen, aromatic or aliphatic groups. There are several examples for phosphinodiimine salts which have been synthesized since 1964 (Scheme 1.34)[50,51,52,53] and based on my literature survey only one example of a neutral phosphinodiimine has been reported which was $PhP((^tBu)C{=}N(Ph))_2$.[54,29]



$X = BF_4$ R = Me **55a-c.** R' = H, OMe, Me
R = Et **55d-f.** R' = H, OMe, Me

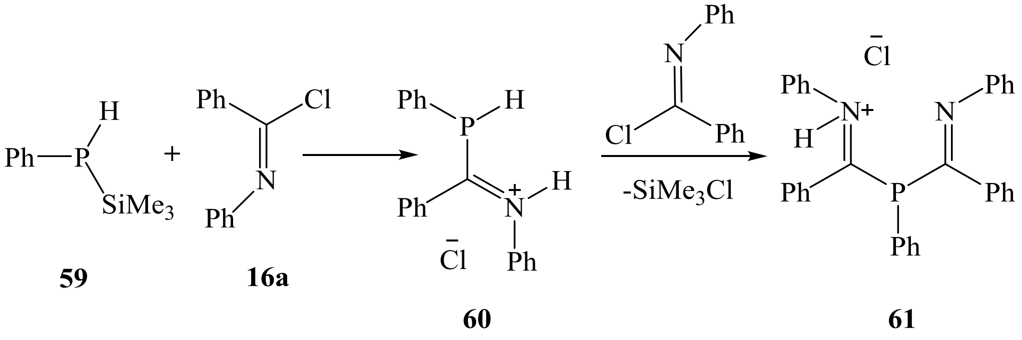
56

$X=B(C_6H_5)_4$, **57a.** R = Me; **57b.**R = Et

$X = Cl, ClO_4$
58a. R = H; **58b.** $R = NMe_2$
58c. $R = C_6H_5$; **58d.** R = SMe
58e. $R = {}^tBu$

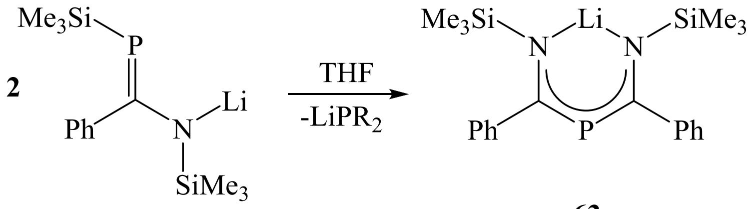
Scheme 1.34 Examples of phosphinodiimine salts.

In 1991, a Russian group synthesized a phosphinodiimine salt **61** by reaction of phenyl(trimethylsilyl)phosphine **59** with N-phenyl benzimidoyl chloride **16a** in refluxing THF (Scheme 1.35). Reaction progress was monitored by ^{31}P NMR and two compounds with chemical shift δ = -3 ppm, and δ = -48 ppm were formed. By continuing heating, the signal at δ = -48 ppm disappeared (belong to phosphaamidine salt **60**) and the signal at δ = -3 ppm became stronger. The product that was isolated with δ = -3 ppm was phenyl-*bis*(N-phenyl-benzimidoyl)phosphine hydrochloride.[55]



Scheme 1.35 Synthesis of a phosphinodiimine salt.

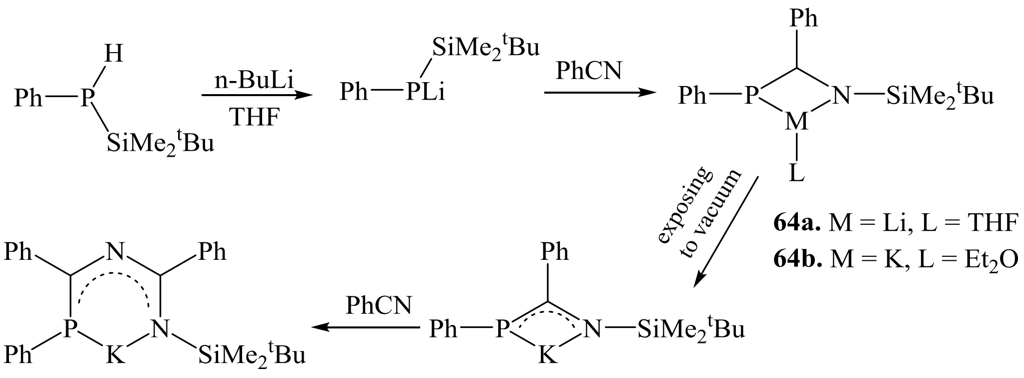
Becker’s group showed that reacting two equivalents of 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphaallyl lithium **62** at -50°C with loss of lithium bis-(trimethylsilyl) phosphanide afforded lithium bis((trimethylsilylimino)benzoyl)- phosphanide **63** (Scheme 1.36).[56]



62 **63**

Scheme 1.36 Synthesis of the phosphinodiimine lithium complex.

Another phosphinodiimine metal complex **66** was synthesized in 2003 by reacting phosphaamidine lithium complex **64a-b** with PhCN to produce the phosphaamidine potassium complex, K[(P(Ph)C(Ph)NC(Ph)NSiMe$_2$^{t}Bu)] **66**. They reported addition of the nitrogen atom to PhCN followed by a 1,3-N→N' migration of the SiMe$_2$^{t}Bu group (Scheme 1.37).[57]

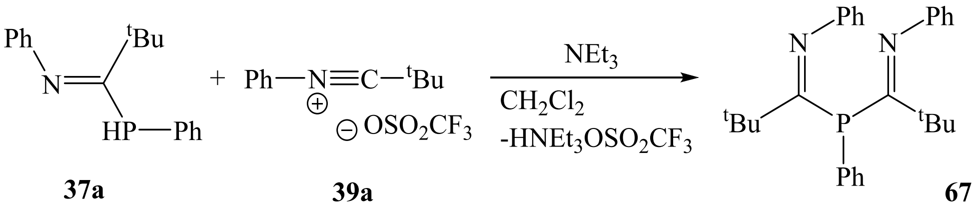


64a. M = Li, L = THF
64b. M = K, L = Et$_2$O

66 **65**

Scheme 1.37 Synthesis of the phosphaamidine metal complex.

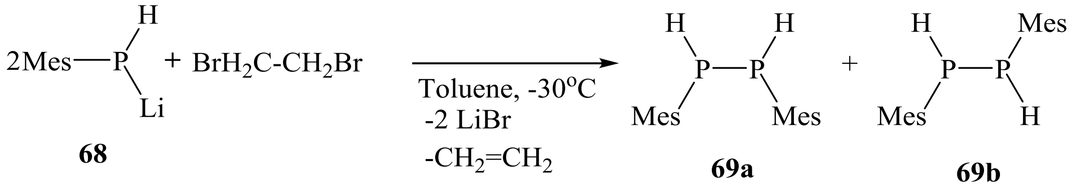
There are several examples of phosphinodiimine salts and metal complexes, but neutral phosphinodiimine compounds are rare. The most recent work on neutral phosphinodiimine compounds was developed by Lammertsma's group in 2014. They synthesized the bis(imino)phosphane **67**, a neutral phosphinodiimine, by reacting phosphaamidine **37a** with nitrilium triflate **39a** and NEt_3 to give the product as yellow solid (Scheme 1.38). A ^{31}P NMR spectrum measured for the product and shows a peak at $\delta = 17$ ppm, but no further investigation to determine isomers has been done. An X-ray crystal structure has been determined, which is the first reported crystal structure for neutral phosphinodiimine with *ZE* geometry.[29]



Scheme 1.38 Synthesis of the bis (imino) phosphane.

1.6 Sterically bulky diphosphane

As previously explained in Sections 1.2 and 1.4, phenyl phosphane, $PhPH_2$ is one of the starting materials to make the phosphaamidines and phosphinodiimines. Phenylphosphane are extremely toxic, malodorous and also very reactive and reactions are hard to control. For those reasons, our group developed a less malodorous and more bulky phosphane which is 2,6-diisopropylphenylphosphane, $DippPH_2$. Although $DippPH_2$ is less reactive and more bulky than phenylphosphane, it is still very reactive and can undergo further reaction to make dihydro diphosphane, Dipp(H)P-P(H)Dipp, which will be discussed in Chapter 4. Dihydrodiphosphanes R(H)P-P(H)R are interesting products of dehydrocoupling reactions,[58] especially those leading to the stoichiometric [59,60,61,62] and catalytic [63,64,65] formation of this compound. Diphosphanes are very reactive compounds that can only be handled under inert atmosphere. The two phosphorus atoms in diphosphanes are linked by σ-bonds and a lone pair of electrons remains on each atom. The thermal stability of diphosphanes is very low and substitution like alkyl, perfluoroalkyl, or aryl groups can increase the thermal stability.[66] There are only three reported crystal structures for secondary diphosphanes R(H)P–P(H)R. The first one reported by Hey-Hawkins in 1996 is the only reported aryl derivative (R = Mes) **69a-b** of a secondary diphosphane. This diphosphane was synthesized by reaction of LiPHMes **68** with 1,2-dibromoethane (Scheme 1.39) and the crystal grew in toluene.[67]



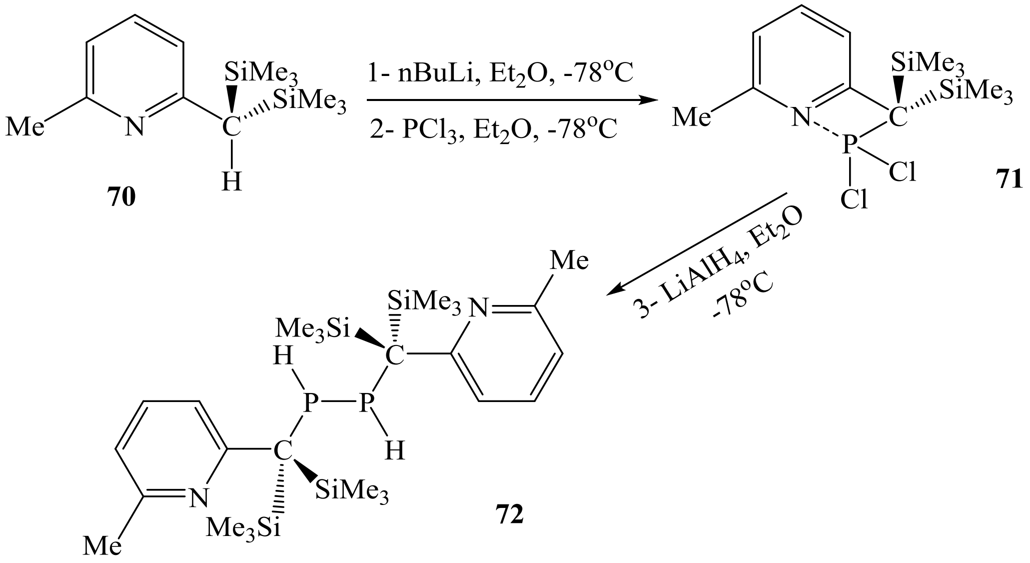
68 **69a** **69b**

Scheme 1.39 Synthesis of aryl diphosphanes.

Based on their report, the ^{31}P NMR spectrum of Mes(H)P-P(H)Mes showed both diastereomers in solution, 60% *rac* : 40% *meso*, for which the ratio of isomers were not dependent on temperature. They have determined the molecular structure of *meso* Mes(H)P-P(H)Mes and any of their attempts to pick the *d,l* isomer was unsuccessful.

The second crystal structure was reported by Andrews's group in 1998 which was the first non-complexed *N*-functionalised disecondary diphosphane.[68] When they were attempting to synthesize the phosphorus dihydride derivative of the bulky alkyl ligand (6-

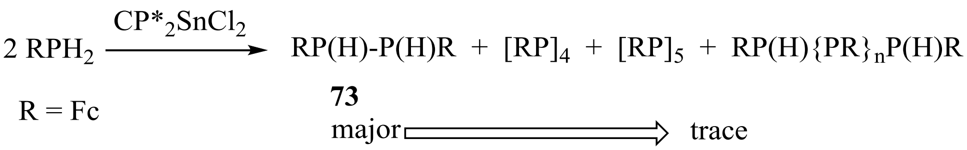
Me-2-pyridyl)$(SiMe_3)_2C$ = R, via the reduction of $RPCl_2$ with $LiAlH_4$. They observed an unexpected product which was the diphosphane, [(6-Me-2-pyridyl)$(SiMe_3)_2CPH]_2$ **72** (Scheme 1.40). The colorless needle-shaped crystals were characterized by X-ray techniques and proved to be the *meso* isomer.



Scheme 1.40 Synthesis of N-functionalised disecondary diphosphane.

The third example is reduction of dichlorophosphane $RPCl_2$ [R= $(Me_3Si)_2CH$] with $LiAlH_4$ in ether under reflux. Product of this reaction is diphosphane R(H)P-P(H)R, along with the primary phosphane RPH_2.[69] The colorless crystals of diphosphane were isolated from hexamethyldisiloxane solvent as mixtures of *rac* and *meso* diastereomers.

Reactions of Cp^*_2Sn with primary phosphine (RPH_2, R=Fc) at room temperature produced diphosphanes R(H)P-P(H)R **73** as a major product (Scheme 1.41) along with four membered and five membered phosphorus rings as minor products.[64]



$$2\,RPH_2 \xrightarrow{CP^*{}_2SnCl_2} RP(H)\text{-}P(H)R + [RP]_4 + [RP]_5 + RP(H)\{PR\}_nP(H)R$$

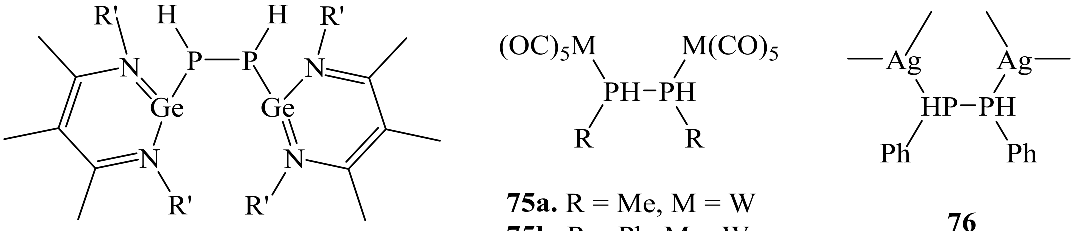
R = Fc

73

major ⟹ trace

Scheme 1.41 Synthesis diphosphane as a major product.

There are several dihydrodiphosphanes which have been structurally characterized as coordination compounds with main group and transition metals (Scheme 1.42).[59,60,70]



74. R' = Dipp

75a. R = Me, M = W
75b. R = Ph, M = W
75c. R = 2-thienyl, M = W
75d. R = Mes, M = Cr

76

Scheme 1.42 Example of dihydrophosphane metal complexes.

1.7 Contents of this thesis

This thesis deals with the synthesis and characterization of the *N*,*P*-disubstituted phosphaamidines, phosphinodiimines and a dihydrodiphosphane. Chapter 2 describes the *N*,*P*-disubstituted phosphaamidines; ^{t}Bu-phosphaamidine, CH_3-phosphaamidine, *p*CH_3OPh-phosphaamidine and phosphaformamidine. As mentioned in Section 1.1, *p*CH_3OPh-phosphaamidine was previously synthesized in five days at reflux and four isomers were detected and studied by advanced NMR spectroscopy, XRD, and DFT calculations. Because the reaction process was long, a new procedure was followed this compound was prepared in only one day. With knowledge of possible isomers and tautomers for the phosphaamidine, I expected to detect isomers for other phosphaamidines. I realized that ^{t}Bu-phosphaamidine was reported but only one isomer was determined with no NMR study, no crystal structure nor calculations. This was the first point of this thesis. I synthesized ^{t}Bu-phosphaamidine and looked for isomerisation and tautomerization with advanced solution NMR studies, solid-state NMR, XRD and DFT calculations. Thereafter, I synthesized the less bulky phosphaamidine, CH_3-phosphaamidine, which is novel, to study the effect of substitution on the carbon backbone on isomerisation. Finally, I attempted to use the smallest backbone substituent, R = H, to complete my study.

Chapter 3 describes the synthesis of a new *N*,*P*,*N*-phosphinodiimine and a *P*,*N*,*N*-aminophosphaalkene. As mentioned in Section 1.2 there are only a few examples of neutral phosphinodiimines, with few crystal structures reported and I didn't find any evidence of a study of isomerisation. I synthesized ^{t}Bu-phosphinodiimine and CH_3-amidinophosphaalkene, studied the effect of substitution on the carbon backbone, studied the isomerisation with advanced solution and solid state NMR spectroscopy, XRD and DFT calculations.

Chapter 4 describes the synthesis of a new dihydrodiphosphane. The crystal structure of this compound was determined, the fourth structure of a dihydro diphosphane that has ever been reported. The conformations of the dihydro diphosphane were studied by advanced solution NMR, XRD, NMR simulations and DFT calculations.

Chapter 5 presents some initially unsuccessful attempts to prepare metal complexes. The *N*,*P*,*N*-phosphinodiimine appears to have been cleaved under zinc catalysis and only complexes of amide (from hydrolysis of the ligand) was found to coordinate the metal halides. In addition, some ideas are suggested for how successful metal complexes may be prepared in the future.

Chapter 6 provides the experimental details for all the preparative chemistry described in this thesis. A comprehensive reference list follows at the very end.

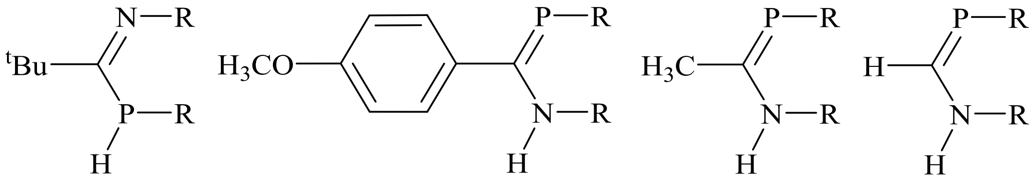
Chapter 2

Phosphaamidines

2.1 Introduction

The goal of this chapter is to describe the synthesis of novel phosphaamidines, study the isomerism and tautomerism by using solution and solid state NMR spectroscopy, and compare data with crystal structures and computational results to find the most stable geometry for the isomer. Different routes were attempted to make *N*,*P*-phosphaamidines in the past[25,27,28] and several disubstituted phosphaamidines have been produced and reported with no further study about isomerization and tautomerization (Section 1.2). Our group previously demonstrated that slow isomerization between several such isomers can be detected in solution on the NMR timescale for disubstituted phosphaamidines. Eight possible isomers and conformers of phosphaamidines are shown in Scheme 1.14.[8]

Due to the advantages of using Dipp rather than Mes, Mes* and Tripp (Section 1.1.1) our group prefers to use Dipp as substituent on nitrogen and phosphorus. I have attempted to synthesize disubstituted phosphaamidines with different substitutions (R = *p*CH_3OPh, ^tBu, CH_3, H) (Scheme 2.1) to understand the effect of substitution at the carbon backbone on isomerisation. These studies are explained in detail in this chapter.



32 **25b** **77** **78**

Scheme 2.1 Four *N*,*P*-disubstituted phosphaamidines discussed in Chapter 2.

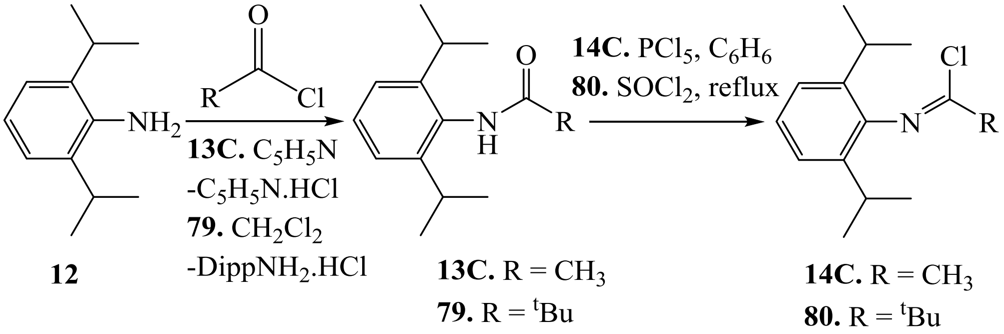
The first disubstituted phosphaamidine to be discussed in this chapter is *N*-(2,2-dimethyl-1-(2,6-diisopropylphenylphosphino)propylidene)aniline, which I am abbreviating to: ^{t}Bu-phosphaamidine **32**. This compound was originally synthesized by Li *et al*. [28] and in their ^{31}P NMR data, they observed only one peak at δ = -84.3 ppm. After we studied their paper, the question which came to mind was why ^{t}Bu-phosphaamidine doesn't show any other isomers as do *p*CH_3Ph and *p*CH_3OPh phosphaamidine **25a-b** which were previously reported by our group? Is it possible that Li's group only reported the major isomer? Is it possible that changing the substitution on the carbon backbone to the bulkier group (^{t}Bu is bulkier than *p*CH_3Ph and *p*CH_3OPh) changes the isomerization? Li's group didn't do any advanced NMR study or obtain any computational results and they also didn't report the crystal structure of **32**. To answer these questions, we decided to synthesize ^{t}Bu-phosphaamidine via two different synthesis routes and determine the crystal structure. We performed advanced solution NMR spectroscopy and a solid-state NMR studies and also computational investigations, and compared these data with my crystallographic data to study the isomerisation. We also synthesized *p*CH_3OPh-phosphaamidine **25b** following a more efficient synthetic route (Scheme 1.21-1.22).[29] This compound previously was synthesized by our group over five days reflux and several purification steps which was very time consuming (Scheme 1.14-1.15).[8, 25]

Thereafter, I attempted to synthesize the *N*-(1-(2,6-diisopropylphenylphosphino)-ethylidene) aniline (which I will abbreviate to: CH_3-phosphaamidine **77**) which is a phosphaamidine. Because of its small group, CH_3-phosphaamidine is much more reactive than ^{t}Bu-phosphaamidine, *p*CH_3Ph and *p*CH_3OPh phosphaamidine and it is hard to control the reaction. I attempted several synthetic routes to make this compound but

Lammertsma's procedure (Scheme 1.25) worked better than the others (Scheme 1.22).[29,28,27] An advanced NMR spectroscopy was used to study the isomerization.

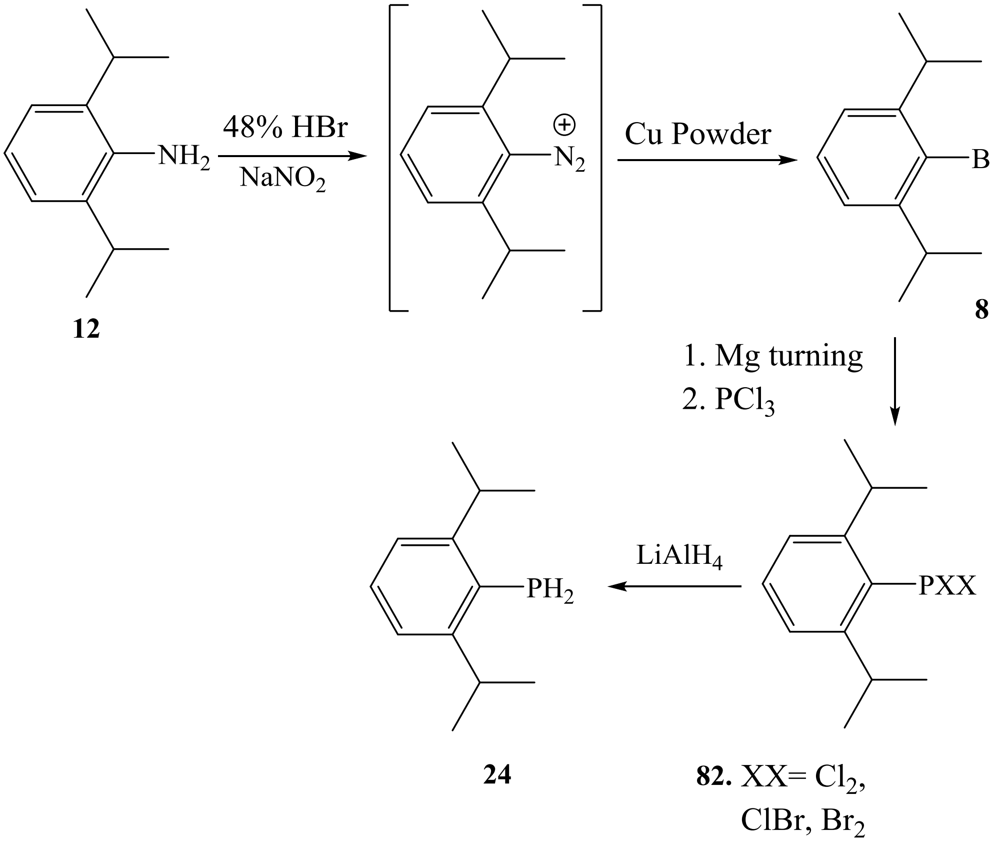
The last phosphaamidine which I attempted to synthesize is *N*-(1-hydrogen-1-(2,6-diisopropylphenylphosphino)methylidene)aniline[27] which I will abbreviate as phosphaformamidine **78**. In this case the substituent on the carbon backbone is hydrogen, which is a small group and could cause phosphaformamidine to be more reactive than other phosphaamidines. I attempted to synthesize this compound following Song's[27] and Lammertsma's[29] procedures.

To synthesize ^{t}Bu-phosphaamidine, CH_3-phosphaamidine and *p*CH_3OPh-phosphaamidine, starting materials are imidoyl chlorides which were prepared in two steps following Scheme 2.2.[10] Amides were reacted with PCl_5 (R = ^{t}Bu, CH_3) or $SOCl_2$ (R = *p*CH_3OPh) to make imidoyl chlorides, which are sensitive to moisture. ^{t}Bu-imidoyl chloride **79** is a yellow liquid and CH_3-imidoyl chloride **14c** is a colorless liquid which needed to be purified by vacuum distillation (*p*CH_3OPh-imidoyl chloride **14b** is a yellow solid).



Scheme 2.2 Synthesis route to make imidoyl chlorides.

DippPH$_2$ **24** is the other starting material used to synthesize our phosphaamidines and was prepared in several steps (Scheme 2.3).[8] Crude DippPH$_2$ needs to be purified by vacuum distillation. This compound is a malodorous colorless liquid and very sensitive to the air and moisture and needs extra care in handling. Pure DippPH$_2$ **24** was stored in a Schlenk tube under nitrogen.



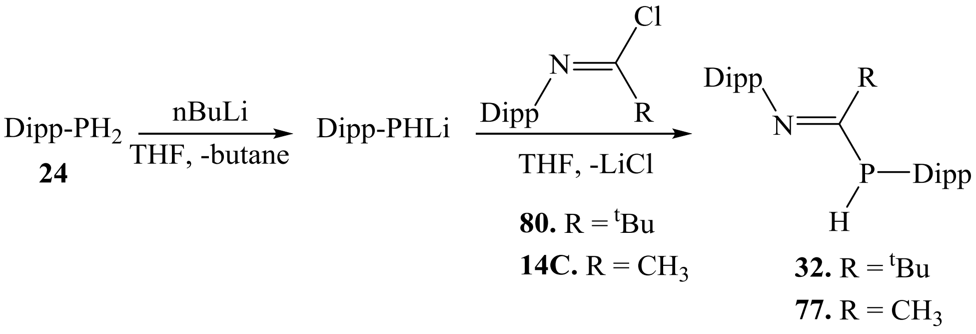
Scheme 2.3 Synthesis of DippPH$_2$ **24** in several steps.

2.2 ^{t}Bu-phosphaamidine

I synthesized ^{t}Bu-phosphaamidine following two different procedures to understand the chemistry of the phosphorus or nitrogen atom bearing an H atom, isomerisation and tautomerization. The first synthesis route followed Li's procedure[28] by using *n*BuLi and the second synthesis route followed Lammertsma's[29] procedures by using a phosphaamidine salt.

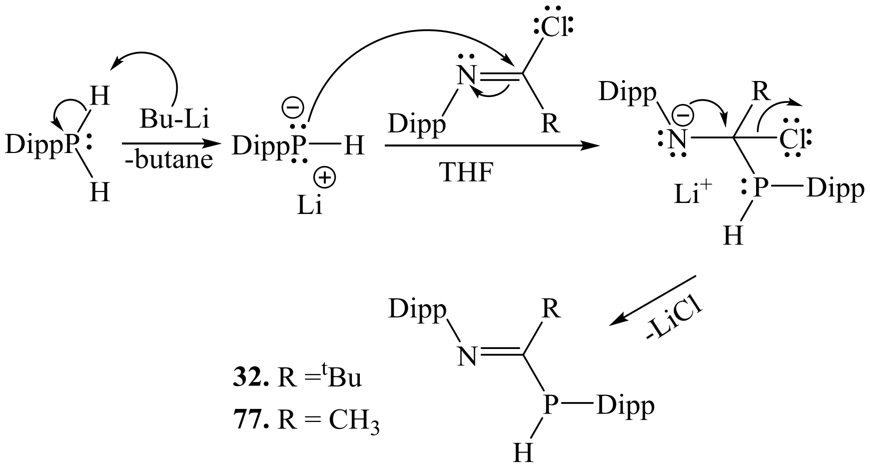
2.2.1 Synthesis of ^{t}Bu-phosphaamidine using *n*BuLi[28]

In the first step, DippPH$_2$ (^{31}P NMR: δ = -161.39 ppm, triplet in THF) was reacted with *n*BuLi at -60°C under N$_2$ to produce DippPHLi. Reaction progress was followed by ^{31}P NMR spectroscopy and after 30 min stirring at RT, a doublet at δ = -164.35 ppm (J = 165 Hz) was observed for DippPHLi in THF. In the second step, ^{t}Bu-imidoyl chloride was added to the solution of DippPHLi at -30°C under N$_2$ to produce ^{t}Bu-phosphaamidine (Scheme 2.4). After two hours stirring at room temperature, the reaction was complete and proton-coupled ^{31}P NMR showed a doublet at δ = -86.68 ppm (J= 251 Hz) in THF.



Scheme 2.4 Synthesis of ^{t}Bu-phosphaamidine under N$_2$.

Workup consisted of removal of tetrahydrofuran from the reaction mixture and removal of LiCl by precipitation with hexane and filtration. Crystallization from a minimum quantity of hot methanol produced colorless crystals which were pure by ^{31}P and ^{1}H NMR spectroscopy and suitable for X-ray crystallographic work. The proposed mechanism to form ^{t}Bu-phosphaamidine is outlined in Scheme 2.5. First, *n*BuLi as a strong base removes a proton from $DippPH_2$ and produced $DippPH^{-}Li^{+}$ as the first intermediate. In the next step, the phosphorus of $DippPH^{-}Li^{+}$ as a nucleophile adds to the carbon backbone (which is electrophilic) to produce the second intermediate. This intermediate undergoes elimination of Cl^{-} to make phosphaamidine.



32. R =^{t}Bu
77. R = CH_3

Scheme 2.5 Proposed mechanisms to the formation of ^{t}Bu-phosphaamidine.

2.2.1.1 Crystal structure of 32

Pure colorless crystals grew from methanol at -25°C under N_2 and crystallographic data was determined at -100°C (Figure 2.1). Based on the crystal structure, there is a proton bonded to P and the geometry is Z-*anti*. The P-C bond length is 1.865(3) Å, which is longer than the P=C double bond that was observed for **25a** (1.709(2) Å) and **25b** (1.716(2) Å) (the range of P=C is 1.70-1.76 Å for C-amino substituted phosphaalkenes[71] and the range of P-C is (1.840-1.870 Å) for C-P-Csp^3)[72]. The N=C bond length is 1.273(3) Å, which is shorter than the N-C bond in **25a** (1.368(2) Å) and **25b** (1.366(3) Å) (the range of Csp^3-Nsp^2 is (1.446-1.461 Å) and the range of Csp^2=N is (1.275-1.285 Å).[72]

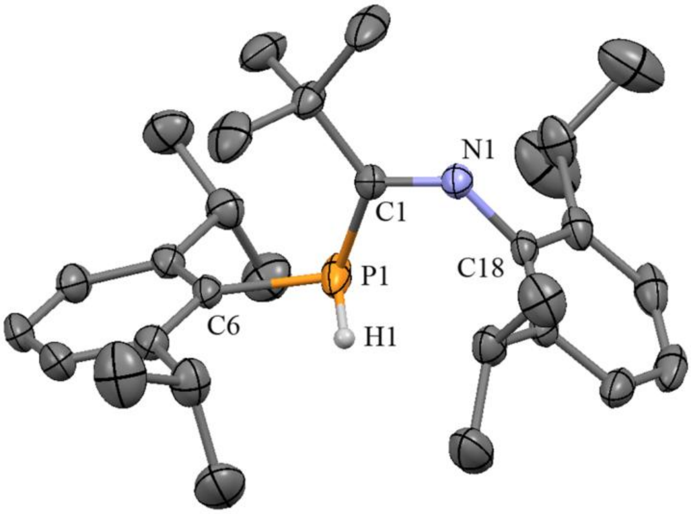


Figure 2.1 40% probability displacement ellipsoids diagram of ^{t}Bu-phosphaamidine as the *Z-anti*(N=C) isomer as found in the crystal. Hydrogen atoms on carbon are omitted for clarity.

Table 2.1 Crystal data and structure refinement for ^{t}Bu-phosphaamidine **32**, ^{t}Bu-Oxonium triflate **86** and ^{t}Bu-phosphaamidinium triflate **87**.

	32	**86**	**87**
Space group	$P2_1/c$	$P2_12_12_1$	C2/c
a/ Å	11.649(3)	14.9178(12)	20.211(2)
b/ Å	25.508(6)	17.0084(13)	17.2366(19)
c/ Å	9.885(2)	17.1879(14)	18.350(2)
α	90°	90°	90°
β	111.027(3)°	90°	97.711(3)°
γ	90°	90°	90°
Z	4	8	8
Goodness-of-fit on F2	1.029	1.035	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.1400	R1 = 0.0579, wR2 = 0.1578	R1 = 0.0389, wR2 = 0.0993
R indices (all data)	R1 = 0.1336, wR2 = 0.1669	R1 = 0.0640, wR2 = 0.1645	R1 = 0.0507, wR2 = 0.1069

Table 2.2 Selected bond lengths (Å) and angles (°) for ^{t}Bu-phosphaamidine **32**, *p*CH_3Ph-phosphaamidine **25a** and *p*CH_3OPh-phosphaamidine **25b**.

	32	**25a**	**25b**
P-C	1.865(3)	-	-
P=C	-	1.709(2)	1.716(2)
P-C_{aryl}	1.843(2)	1.847(2)	1.849(2)
C=N	1.272(3)	-	-
C-N	-	1.368(2)	1.366(3)
N-C_{aryl}	1.421(3)	1.429(3)	1.435(3)
C-P-C	113.77(12)	101.87(10)	103.56(11)
P-C=N	116.11(19)	-	-
P=C-N	-	123.38(17)	123.03(18)
C-N=C	123.3(2)	-	-
C-N-C	-	131.6(2)	130.9(2)

All these crystallographic data confirmed that the geometry of ^{t}Bu-phosphaamidine in the solid state is *Z-anti*(N=C). Selected bond lengths and angles and crystallographic data can be found in Tables 2.1 and 2.2. In Table 2.2 bond lengths and angles of **32** were compared with previously made **25a** and **25b**.[73] The sum of the angles around phosphorus is only 298.07(2)°, indicative of a relatively pyramidal structure at phosphorus. The detailed crystallographic data can be found in Appendix III Table A1-A6.

2.2.1.2 Solution NMR Spectroscopy

Pure colorless crystals of ^{t}Bu-phosphaamidine **32** were dissolved in $CDCl_3$ under N_2 to make NMR samples. The ^{31}P NMR spectrum shows a doublet at $\delta = -84.73$ ppm ($J = 251$ Hz) due to the coupling to hydrogen (Figure 2.2), while the proton-decoupled ^{31}P NMR shows a singlet which confirms there is a hydrogen atom bonded directly to phosphorus.

The doublet pattern for P-H coupling also occurs in the ^{1}H NMR spectrum in $CDCl_3$ (δ = 4.74 ppm, J = 250 Hz) which again confirms the presence of a P-H bond in solution (Figure 2.3). The same pattern was observed by our group previously for the minor isomer of **25a** (− 80.3 ppm, J_{PH} = 243 Hz) and **25b** (−80.1 ppm, J_{PH} = 241 Hz) which are both thought to be (N=C) isomers.[25]

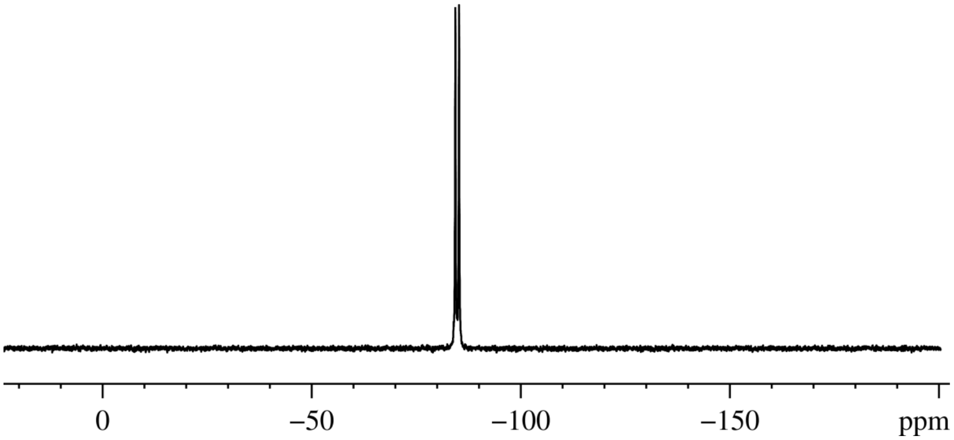
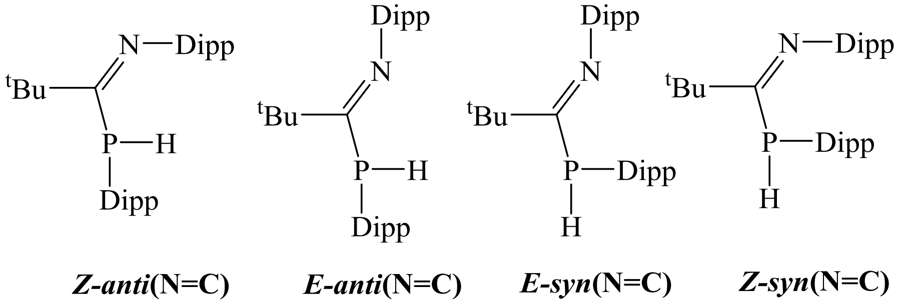


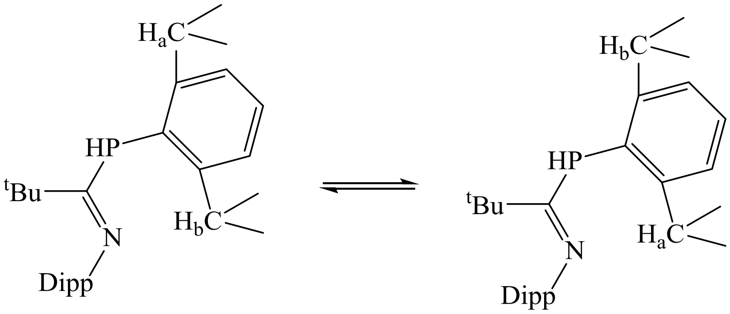
Figure 2.2 ^{31}P NMR spectrum of ^{t}Bu-phosphaamidine **32** in $CDCl_3$ at RT.

At this point, based on the solution NMR and crystal structure data, we are confident that **32** is an (N=C) isomer. Based on Scheme 1.14, there are four (P=C) and four (N=C) isomers and conformers for phosphaamidines, so for **32** there are four possible (N=C) isomers which are shown in Scheme 2.6.



Scheme 2.6 Four possible isomers and conformers for ^{t}Bu-phosphaamidines **32**.

To find out if we can observe any other isomer and understand the effect of solvent on isomerisation, I attempted to run NMR in different solvents. I changed the solvent to toluene as a non-polar solvent, and to more polar ones such as CD_3CN and $CD_3(CO)CD_3$ because this has previously altered isomer ratios for phosphaamdines with aryl backbone substituents.[8] Based on the NMR evidence, no signs of any other tautomer or isomer was observed in any of those solvents which is another indication that only one isomer exists for **32**.



Scheme 2.7 Exchange of CH_a, CH_b.

The ^1H NMR spectrum of ^tBu-phosphaamidine **32** in $CDCl_3$ at RT is shown in Figure 2.3. ^{13}C NMR and 2D NMR experiments such as COSY, HSQC and HMBC were run at RT in $CDCl_3$ and data are listed in Table 2.3. The coupling constant reported in all the Tables in this thesis (unless otherwise mentioned) is based on the precision of 700 MHz NMR spectrometer for ^{31}P (±1) Hz, ^{13}C (±1) Hz and ^1H (±0.1) Hz, experiments. Our NMR data are similar to the data previously reported for this compound (but without structural assignments) by Li et al.[28] The *i*pr-CH_3 groups form 6 doublets, integrating to 24 hydrogens. The *i*pr-CH protons form three sets of peaks, one broad peak corresponding to the phosphino Dipp group, and two sets of septets corresponding to the amino Dipp group. The aromatic signals for CH_{meta} forms four doublets and for CH_{para}

forms two triplets for the amino and phosphino Dipp groups. Most noticeable in the ^{1}H NMR spectrum is the difference between signals from the DippN and DippP rings. For example, in the *i*pr-CH signals, there is a single featureless broad peak for DippP (implying equivalence for both groups which appear to be coalesced). But there are two different, resolved, septets for the DippN, implying that the two groups are inequivalent. Moreover, the upfield signal is somewhat line broadened compared to the more downfield multiplet. Due to rapid exchange for two isopropyl groups CH, a broad singlet is observed (marked with a star in Figure 2.3). As is shown in Scheme 2.7, the two CH groups (as shown by CH_a, CH_b), can exchange by rotation about the $C_{backbone}$-P bond.

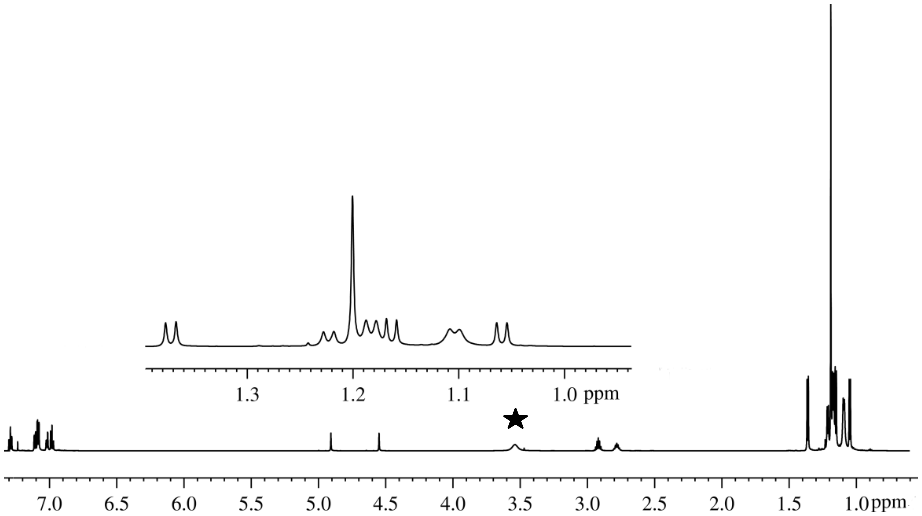
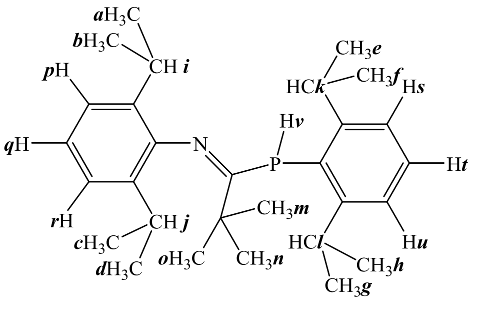


Figure 2.3 ^{1}H NMR spectrum of ^{t}Bu-phosphaamidine **32** in $CDCl_3$ at RT.



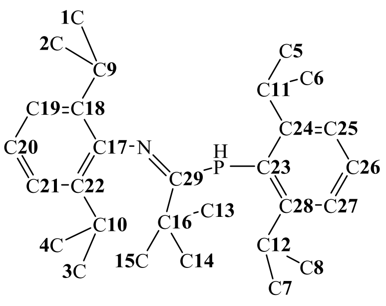


Table 2.3 ^{1}H, ^{31}P, ^{13}C data for ^{t}Bu-phosphaamidine **32**.

Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult	J, Hz
^{31}P				^{13}C [^{1}H]			
P	-84.73	d	251	C ***2***	21.65	s	
^{1}H				C ***4***	21.70	s	
H ***a***	1.06	d	7.0	C ***3***	23.49	s	
H ***e,f***	1.10	d	6.3	C ***1,5,6,7,8***	27.03	s	
H ***c***	1.16	d	6.3	C ***9***	28.32	d	7
H ***g,h***	1.18	d	7.0	C ***10***	28.77	s	
H ***m,n,o***	1.20	s		C ***13,14,15***	29.30	s	
H ***b***	1.22	d	7.0	C ***11,12***	33.63	d	12
H ***d***	1.37	d	7.0	C ***16***	45.32	d	12
H ***i***	2.79	sep	7.0	C ***21***	122.70	s	
H ***j***	2.93	sep	7.0	C ***19***	123.03	s	
H ***k,l***	3.55	br-s[2]		C ***20***	123.33	s	
H ***v***	4.74	d	250	C ***25,27***	123.36	d	4
H ***q***	6.99	t	7.7	C ***23***	128.62	d	19
H ***r***	7.01	d	7.7	C ***26***	130.78	s	
H ***p***	7.03	d	7.0	C ***22***	134.53	s	
H ***s,u***	7.09	d	7.7	C ***18***	134.89	s	
H ***t***	7.30	t	7.7	C ***17***	146.64	d	8
				C ***24,28***	154.59	s	
				C ***29***	182.21	d	60

[1] multiplicity; [2] broad singlet

The chemical shift of the C=N carbon atom for **32** is δ = 182.21 ppm (J_{CP} = 60 Hz) which is very close to the chemical shift of the C=P carbon atom for *p*CH_3Ph-phosphaamidine (δ = 186.2 ppm, $J_{C\text{-}P}$ = 61 Hz). Phosphaamidines synthesized by Song's group showed different chemical shifts but close coupling constants for the C=P carbon atom (δ = 171.7 ppm, J_{CP} = 66 Hz; δ = 166.9 ppm, J_{CP} = 65 Hz and δ = 173.1 ppm, J_{CP} = 67 Hz). These data show that the coupling constant of these carbon atoms are not diagnostic for C=P versus C=N phosphaamidine isomers.

2.2.1.3 Solid State NMR Spectroscopy

In solution NMR, molecules are rapidly tumbling, leading to the observation of sharp peaks. This sharp peak for the isotropic chemical shift relates to the *average* orientation of the molecules with respect to the magnetic field B_0.[74,75,76] In the solid state molecules (powdered crystalline material) are oriented randomly in an infinite number of possible *fixed* orientations with respect to the external magnetic field. *Anisotropic* chemical shifts can be observed, resulting in broad powder patterns whose lineshapes are dependent on the anisotropic shielding, quadrupolar and dipolar interactions. To narrow these broad powder patterns, the magic-angle spinning (MAS) technique is used.[77] Magic-angle spinning means rotating the sample very fast about an axis oriented at 54.74° with respect to the external magnetic field. For successful MAS results, spinning has to be of equal rate or greater than the dipolar linewidth (many kHz wide).[77] It is possible to get the same type of information from high-resolution MAS solid-state NMR spectrum that is available from the corresponding solution NMR spectra. To increase signal to noise and reduce waiting time between experiments, polarization from abundant nuclei like ^{1}H or ^{31}P can be transferred to rare nuclei such as ^{13}C or ^{15}N, which is called cross polarization (CP) and is done in combination with MAS. The isotropic centre band can easily be identified because it remains in the same position at different spinning rates and the spinning sidebands vary in position with changes in spinning speed, and are separated by a distance equal to the spinning speed in Hz.[78]

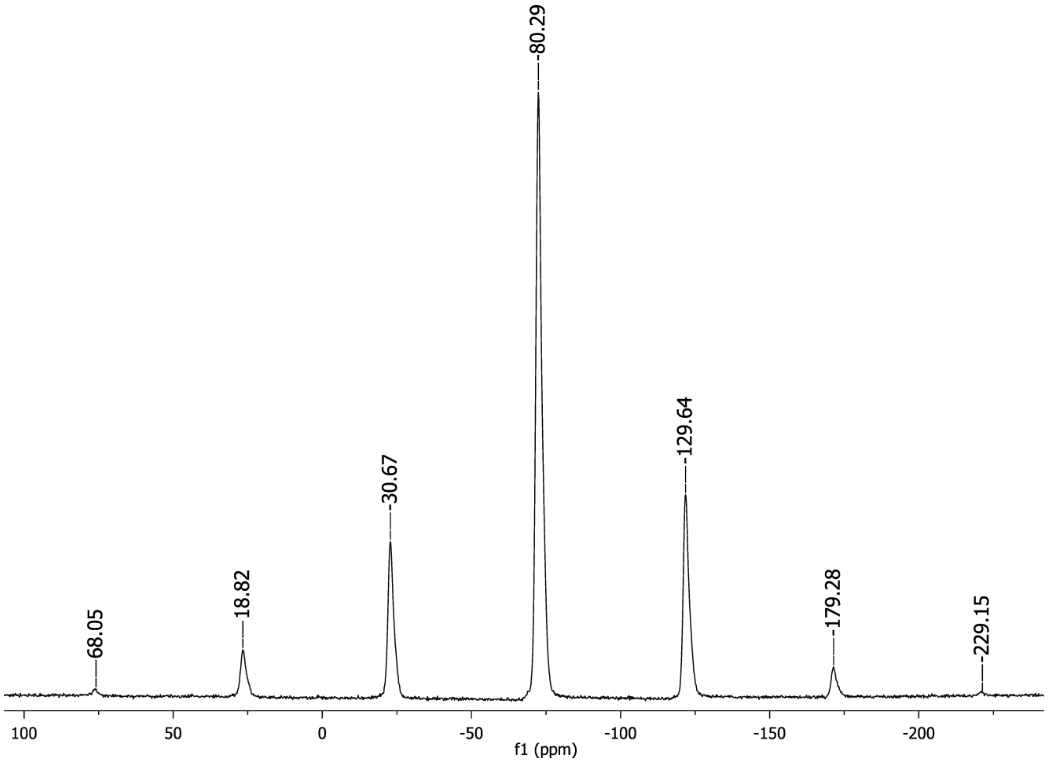


Figure 2.4 CP-MAS ^{31}P-{^{1}H} solid-state NMR spectrum (10 kHz) of ^{t}Bu-phosphaamidine.

To study the possible isomers of ^{t}Bu-phosphaamidine **32**, we have done ^{31}P CP solid-state NMR experiment at different MAS spinning rates. There was only one center band for ^{t}Bu-phosphaamidine at δ_{iso} = -80.29 ppm (Figure 2.4). This centre band was present at spinning rates of 4, 6, 10 and 15 kHz. This evidence confirmed the presence of only one isomer in the solid state, for which the averaged chemical shift is very close to the solution ^{31}P NMR data for **32** that shows one isomer at δ = -84.7 ppm and is also very close to the solution ^{31}P NMR data for the minor isomers of **25a** (δ = -80.3 ppm) and **25b** (δ = -80.1 ppm). Crystallographic data showed that the geometry of **32** is *Z-anti*(N=C) and solid-state NMR spectrum proved that these crystals have very close chemical shifts to what was observed for the only isomer in solution. Based on this evidence, it is very clear that the isomer we observed in solution is *Z-anti*(N=C).

2.2.1.4 Computational Results

As already presented in Scheme 1.14, there are eight possible isomers or conformers for ^{t}Bu-phosphaamidine **32**. Solution NMR evidence including a doublet pattern in the ^{31}P NMR spectrum (δ = -84.73 ppm) and ^{1}H NMR (δ = 4.74 ppm) due to the coupling of proton (directly bonded to phosphorus) to phosphorus confirmed there is only one isomer in solution and it is a (N=C) isomer. In the solid state, NMR evidence (only one isotropic signal was observed at δ_{iso} = -80.28 ppm) is in agreement with solution NMR data. There are two possible (N=C) isomers, *E* and *Z*, each of which have two limiting conformers *anti* and *syn*. The next step would be finding out which isomer and/or conformer is the most stable. In order to confirm the most stable conformation we have done DFT calculation and optimized the geometries. The computed energy differences and geometries of the four possible (N=C) isomers is shown in Table 2.4 and Figure 2.5. The absolute accuracy of DFT calculation of total energies at the B3LYP/6-31G* level is 22-26 kJ/mol and the precision on total energies is ±5 kJ/mol.[79] Small differences in calculated isomer energies cannot be taken as proof for the existence of a given isomer or conformer. However, trends in such energies are very useful for probing which species are in solution. This thesis makes extensive use of such DFT energy calculations to guide the interpretation of solution-phase NMR structures in comparison to the many reported crystallographic structures.

Table 2.4 Calculated relative energy (kJ/mol)[1] for four possible isomers of **32**.

	Z-anti(N=C)	*Z-syn*(N=C)	*E-anti*(N=C)	*E-syn*(N=C)
32	0	9	23	23

[1] B3LYP/6-31G(2d,2P); the estimated precision is ±5 kJ/mol.

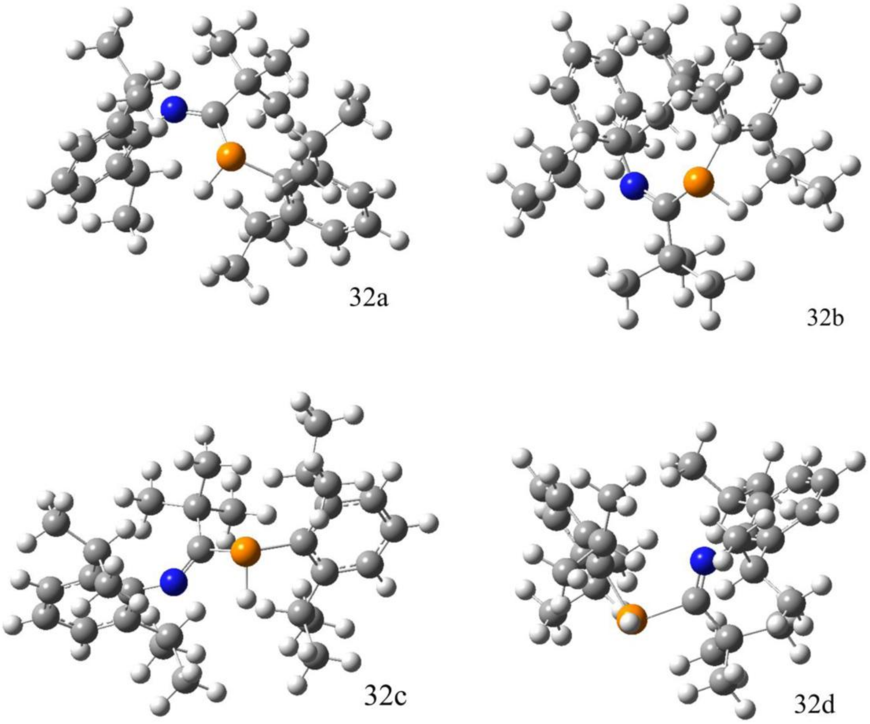


Figure 2.5 Optimized geometries at the B3LYP/6-31G(2d,2P) level for four possible conformers of **32**; *Z-anti* (N=C) **32a**; *Z-syn* (N=C) **32b**; *E-anti* (N=C) **32c**; *E-syn* (N=C) **32d**.

These calculations show that the experimentally-observed isomer from the crystal structure which is *Z-anti*(N=C) with relative energy of 0 kJ/mol corresponds to the most stable calculated isomer in the gas phase (*Z-anti*(N=C)). The second lowest energy conformation (9 kJ/mol) for **32** is *Z-syn*(N=C) and can be formed due to twisting at the P–C single bond which may have a lower energy barrier. *E-anti*(N=C) and *E-syn*(N=C) are two conformers of the *E* isomer that have a higher energy (Table 2.4) than the two limiting conformers of the *Z* isomer (*Z-anti*(N=C) and *Z-syn*(N=C)). The energy difference between *Z* and *E* isomers is 23 kJ/mol (it is in the range of the absolute error (22-26 kJ/mol)) and is not a large energy difference. We can conclude that if the energy difference between species is small, but there is no evidence of them in the NMR, the barrier to interconversion may be very high. Alternatively, all are in fast exchange but the chemical shift is dominated by the *Z* configurations.

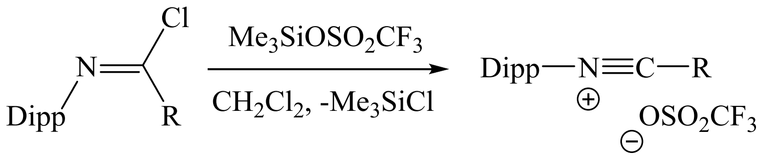
Finally we compared the NMR data with the most stable geometry in the gas phase, *Z-anti*(N=C), which is the same geometry we found in the crystal structure. As we see in Dipp-P ring CH_3*iso* and CH*iso* can easily exchange and have similar environment due to rotation around P-C bond, so we observed two doublets for CH_3*iso* and one septet for CH*iso*. In case of Dipp-N ring, we see four different doublets for CH_3*iso* and two different septets for CH*iso* (Table 2.3). Our group previously reported that the major isomer of *p*CH_3Ph-phosphaamidine **25a** is *E-syn*(P=C). They observed two doublets for CH_3*iso* and one septet for CH*iso* for each Dipp-N and Dipp-P[26] due to the planar geometry of P in P=C bond and having a mirror plane. Here, a different pattern was observed for ^{t}Bu-phosphaamidine due to the pyramidal geometry of P in P-C bond which results in no mirror plane. Based on this evidence, we are positive that the isomer we observed in solution is the *Z* isomer not *E* due to difference in the NMR pattern compared to **25a**.

2.2.2 Synthesis of ^{t}Bu-phosphaamidine 32 using triethylamine[29]

We decided also synthesize ^{t}Bu-phosphaamidine following a recently reported paper[29] in order to complete the investigation and study its isomerisation. The new synthesis route follows three steps: first synthesizing carbonitrilium triflate; second making phosphaamidinium triflate; and the third step synthesizing phosphaamidine. The products of each step are novel compounds and were isolated in order to understand the properties of related phosphaamidines. I also attempted to grow good quality crystals and determined the structures for further investigation of possible isomers.

2.2.2.1 Synthesis of (*N*-2,6-disopropylphenyl)(*tert*-butyl)carbonitriliumtriflate 83

The first step to synthesize ^{t}Bu-phosphaamidine **32** by this method was making (*N*-2,6-diisopropylphenyl)(*tert*-butyl)carbonitriliumtriflate which I am abbreviating to: ^{t}Bu-nitrilium triflate. Reacting ^{t}Bu-imidoylchloride **80** with trimethylsilyl trifluoromethane sulfonate at -70°C under N_2 produced **83** (Scheme 2.8). Trimethylsilyl trifluoromethane sulfonate ($Me_3SiCF_3SO_3$) is very reactive and will vigorously react with moisture, so it needs to be handled very carefully, for example by using it only in the glove box.

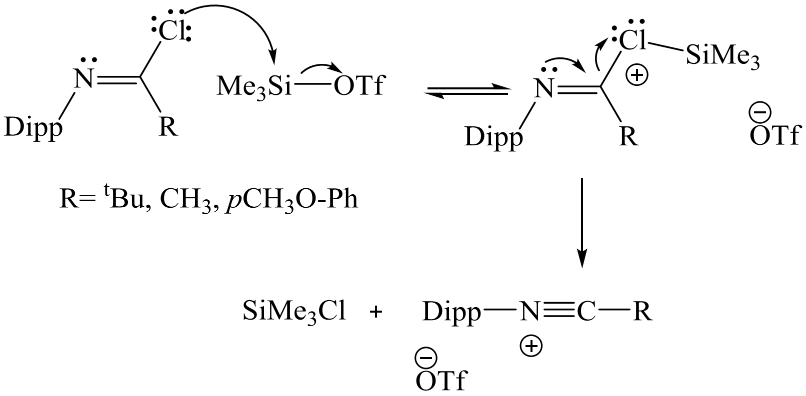


80. R = ^{t}Bu
14c. R = CH_3
14b. R = *p*CH_3O-Ph

83. R = ^{t}Bu
84. R = CH_3
85. R = *p*CH_3O-Ph

Scheme 2.8 Synthesis of nitrilium triflate.

Work-up consisted of removal of dichloromethane on a vacuum line and washing the crude material with pentane to obtain ^{t}Bu-nitrilium triflate as a white solid. The product is sensitive to the air and moisture and needs to be stored under N_2 in a fridge otherwise it might undergo decomposition or hydrolysis. Conversion to the product follows the proposed mechanism outlined in Scheme 2.9. In the first step, chlorine (from imidoyl chloride) as nucleophile was added to Si (of $SiMe_3OTf$) as electrophile, followed by elimination of OTf^-. The next step would be addition of the lone pair of N to C=N bond and elimination of $SiMe_3Cl$ to produce ^{t}Bu-nitrilium triflate.



Scheme 2.9 Proposed mechanisms to the formation of nitrilium triflate.

2.2.2.2 Crystal Structure

^{t}Bu-nitrilium triflate **83** was dissolved in a minimum quantity of hot CH_3CN. After cooling to RT, the colorless solution was left in a freezer at -25°C to grow crystals. The color of the solution changed from colorless to yellow, orange and red after three days in the freezer and no crystals grew. CH_3CN was removed on the vacuum line and ^{1}H NMR spectroscopy was recorded on the red residue in $CDCl_3$.^{1}H NMR evidence exhibited the sign of ^{t}Bu-nitrilium triflate, ^{t}Bu-quinolium triflate (see Section 2.4.3 for more information) and ^{t}Bu-amide. In a second attempt to grow crystals, ^{t}Bu-nitrilium triflate was dissolved in a minimum quantity of CH_2Cl_2 at RT and the colorless solution was left at -25°C to grow crystals. After two days, colorless block-shaped crystals grew in a colorless solution. The crystal structure was determined at -100°C and I thereby found out that the colorless crystal is (1-(2,6-diisopropylphenylamino)-2,2-dimethylpropylidene) oxonium trifluoromethane-sulfonate **86** compound instead of the expected ^{t}Bu-nitrilium triflate. Crystal structure and crystallographic data can be found in Figures 2.6 and Table 2.2.

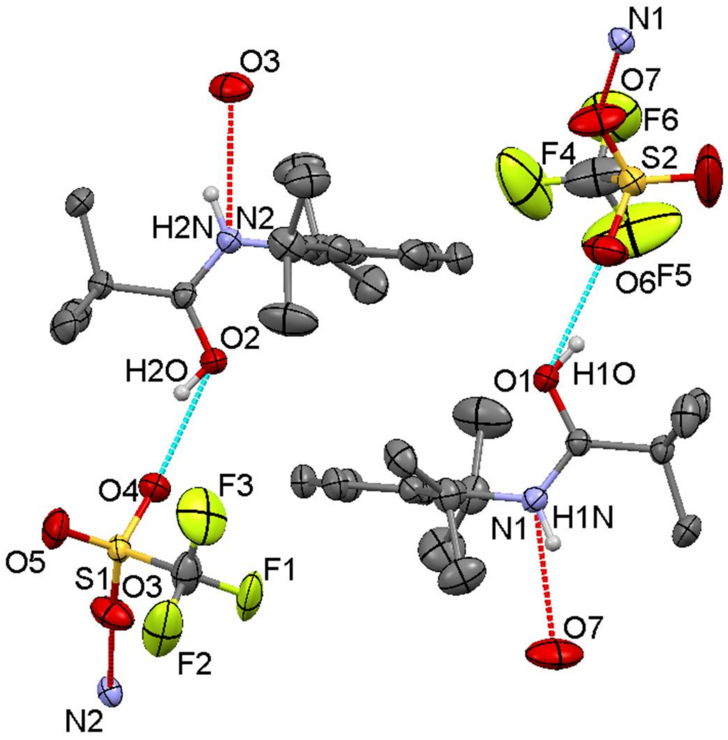
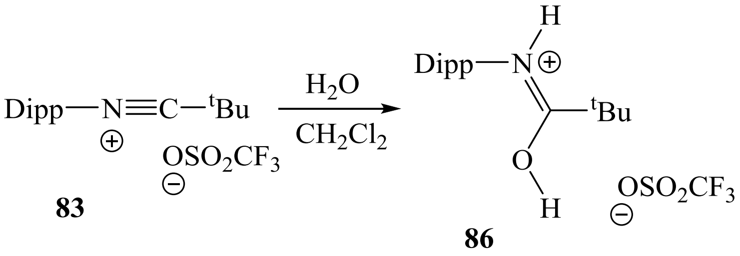


Figure 2.6 Displacement ellipsoids plot (40% probability) showing the molecular structure of two protonated amides and two triflate anions linked through H-bonding into chains. H atoms other than those involved in these bonds are omitted to enhance visibility. Red dashed lines indicated H-bonding contacts to adjacent asymmetric units.

The N-C_{aryl} bond length is 1.454(4) Å, which is a single bond (the range of Csp^2-Nsp^2 in acyclic amides is (1.446-1.461 Å).[72] The N-C bond length in **86** is 1.294(2) Å, which is shorter than the C-N single bond in ^{t}Bu amide **79** (1.341(17) Å) (selected bond length and angles for **79** can be found in Table 5.2). The C=O bond length is 1.297(4) Å, which is longer than the C=O double bond in ^{t}Bu amide **79** (1.228(16) Å) (range of C=O for amide is 1.225-1.243 Å)[72]. The C-N-C angle is 123.2(2)° and the sum of angles around nitrogen is 359.2(5)°, which shows that nitrogen is planar. The detailed crystallographic data can be found in Appendix III Table A7-A13. This crystal structure is a rare example of a protonated amide; only a limited number of structures of this class have been reported previously.[80,81] This compound was most likely made through the reaction of **83** with a trace of water (hydrolysis reaction) (Scheme 2.10).



Scheme 2.10 Possible synthesis route for **86**.

2.2.2.3 Solution NMR Spectroscopy

Pure ^{t}Bu-nitrilium triflate **83** was dissolved in $CDCl_3$ in a glove box to make an NMR sample. ^{1}H NMR, ^{13}C NMR and HSQC spectra were run at RT to completely assign the peaks (Table 2.5). Figure 2.7 shows the ^{13}C NMR spectra for ^{t}Bu-nitrilium triflate. The carbon of $CF_3SO_3^-$ has a chemical shift of $\delta = 120.3$ ppm and shows a quartet pattern and large coupling (J = 320 Hz) due to the coupling to F (black star shape in Figure 2.7). The C_{ipso} of Dipp ring (C_{ipso}-N) with chemical shift of $\delta = 118.51$ ppm (J = 12 Hz) with small coupling shows a triplet pattern due to the coupling of nitrogen to C_{ipso} (red star shape in Figure 2.7). The natural abundance of the ^{13}C is 1.1% which is low and is the cause of the absence of spin-spin coupling in ^{13}C NMR spectra. The natural abundance of the ^{14}N is 99.7% but it is unusual to see coupling of carbon to this quadrupolar nucleus. The coupling of ^{13}C to ^{14}N for C≡N also showed up as a triplet due to the coupling of carbon to the nitrogen with a chemical shift of $\delta = 125.74$ ppm (J = 42 Hz).[82,83,84] In both cases, C≡N and C_{ipso}-N, we see a triplet pattern ($2NI+1$, $N = 1$, $I = 1$) with intensity ratio of

1:1:1. The presence of resolved ^{14}N splitting is evidence of a very low electric field gradient, whereas the distortion in the relative intensities implies that the gradient is non-zero. The low gradient is likely due to the effective cylindrical symmetry of the molecule in solution and probably due to accidental equivalence of the gradient along the symmetry axis for this set of substituents.

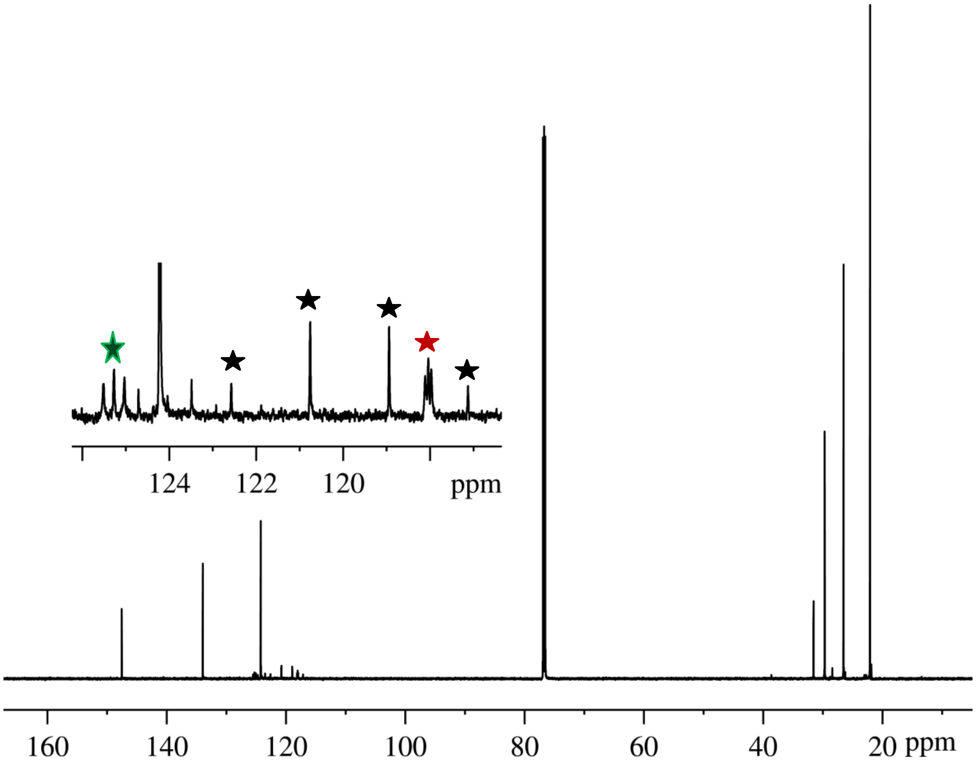
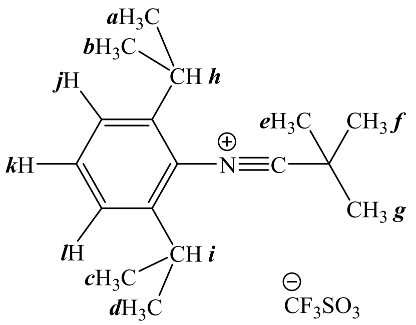


Figure 2.7 ^{13}C NMR of ^{t}Bu-nitrilium triflate in $CDCl_3$ at RT.



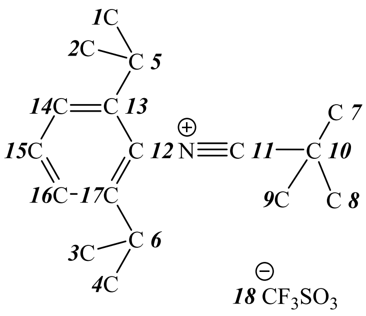


Table 2.5 ^{1}H NMR and ^{13}C NMR data of ^{t}Bu-nitrilium triflate.

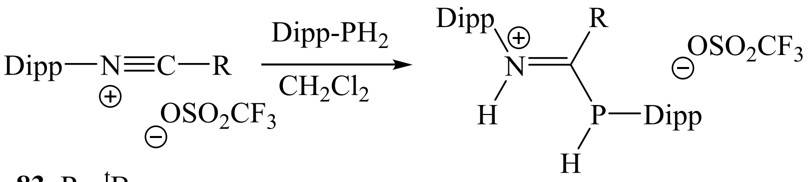
Nucleus	δ, ppm	mult[2]	J, Hz	**Nucleus**	δ, ppm	mult[2]	J, Hz
^{1}H				^{13}C [^{1}H]			
H ***a,b,c,d***	1.33	d	7.0	C ***1,2,3,4***	22.59	s	
H ***e,f,g***	1.87	s		C ***7,8,9***	27.03	s	
H ***h,i***	3.21	sep		C ***5,6***	30.19	s	
H ***j,l***	7.32	d	7.7	C ***10***	32.06	s	
H ***k***	7.61	s		C ***12***	118.51	t	12
				C ***18***	120.3	q	320[1]
				C ***14,16***	124.69	s	
				C ***11***	125.74	t	42
				C ***15***	134.41	s	
				C ***13,17***	148.00	s	

[1] J_{CF}; [2] multiplicity

2.2.2.4 Synthesis of N-(2,2-dimethyl-1-(2,6-iisopropylphenylphosphino)propylidene) 2,6-diisopropylphenylaminium triflate 87

The second step to make ^{t}Bu-phosphaamidine is synthesizing *N*-(2,2-dimethyl-1-(2,6-diisopropylphenylphosphino)propylidene)2,6-diisopropylphenylaminiumtriflate **87** (I will abbreviate this to: ^{t}Bu-phosphaamidinium triflate) from ^{t}Bu-nitrilium triflate which was made in the first step (Section 2.2.2.1). Reacting ^{t}Bu-nitrilium triflate with $DippPH_2$ at -70°C under N_2 produced ^{t}Bu-phosphaamidinium triflate (Scheme 2.11). Reaction progress was followed by ^{31}P NMR spectroscopy and after one hour stirring at room temperature, the ^{31}P NMR spectrum shows a broad peak at δ = -63.69 ppm in CH_2Cl_2.

There was no sign of starting material (DippPH_2, δ = -156.92 ppm) which confirmed that the reaction had completed.

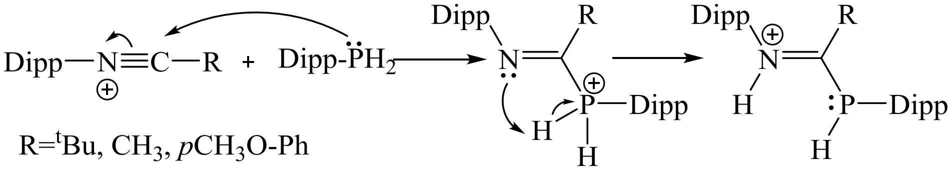


83. R =^{t}Bu
84. R = CH_3
85. R = *p*CH_3O-Ph

87. R =^{t}Bu
88. R = CH_3
89. R = *p*CH_3O-Ph

Scheme 2.11 Synthesis of phosphaamidinium triflate.

Work-up consisted of removal of dichloromethane from the reaction mixture on a vacuum line and washing the crude material with pentane. Conversion to the product follows the proposed mechanism outlined in Scheme 2.12. Adding phosphorus of DippPH_2 as a nucleophile to the carbon of C≡N as the electrophile in a first step will produce the intermediate. The intermediate salt tautomerises to produce ^{t}Bu-phosphaamidinium triflate **87**.



R=^{t}Bu, CH_3, *p*CH_3O-Ph

Scheme 2.12 Proposed mechanisms to formation of ^{t}Bu-phosphaamidinium triflate.

2.2.2.5 Crystal structure

^{t}Bu-phosphaamidinium triflate **87** (a white solid) was dissolved in a minimum quantity of hot dichloromethane and after cooling to RT, was layered gently with heptanes under $N_{2,}$ then left at -25°C to grow X-ray quality crystals. After two days, colorless crystals grew and crystallographic data was collected at -100°C. The crystal structure is shown in Figure 2.8 and crystallographic data and selected bond length and angles can be found in Tables 2.2 and 2.6. When we compare the bond lengths and angles of neutral ^{t}Bu-phosphaamidine **32** (Table 2.1) with ^{t}Bu-phosphaamidinium triflate **87**, we see that the bond length of N=C in **87** (1.296(15) Å) is longer than in **32** (1.272(3) Å) due to protonation of nitrogen. The C-P bond length in **87** (1.846(2) Å) is slightly shorter than **32** (1.865(3) Å). The C-N=C angle for ^{t}Bu-phosphaamidine triflate is 124.38(10)° and the sum of angles around **N** is 359.88(17)° that shows nitrogen is planar. The sum of angles around **P** is 308.08(15)°, which shows that **P** is pyramidal. The detailed crystallographic data for **87** can be found in Appendix III Table A14-A20.

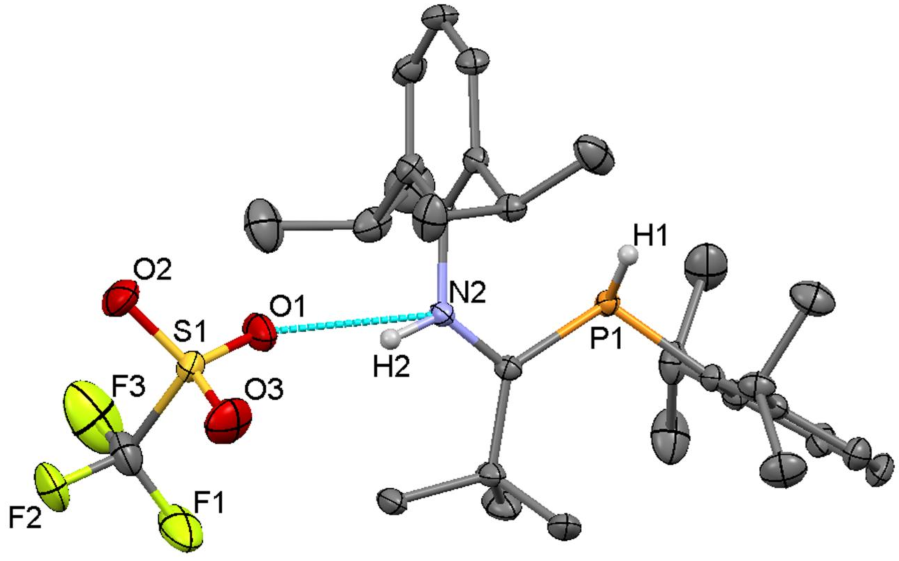


Figure 2.8 Displacement ellipsoids plot (40% probability) showing the molecular structure of ^{t}Bu-phosphaamidinium and triflate anions linked through H-bonding into

chains. H atoms other than those involved in these bonds and P-H are omitted to enhance visibility.

Table 2.6 Selected bond lengths (Å) and angles (°) for ^{t}Bu-phosphaamidinium triflate **87**, CH_3-phosphaamidinium triflate **88** and *p*CH_3OPh-phosphaamidinium triflate **89**.

	87	**88**	**89**
P-C	1.846(2)	1.825(3)	1.836(17)
P-C_{aryl}	1.835(2)	1.842(2)	1.825(2)
C=N	1.296(15)	1.295(3)	1.302(2)
N-C_{aryl}	1.459(15)	1.450(3)	1.455(2)
C-P-C	112.18(10)	102.15(11)	106.93(8)
P-C=N	114.14(10)	123.33(19)	116.96(12)
C-N=C	124.38(10)	126.2(2)	125.12(15)

2.2.2.6 Solution NMR Spectroscopy

The pure colorless crystals of ^{t}Bu-phosphaamidinium triflate **87** were dissolved in $CDCl_3$ for an NMR study. The ^{31}P NMR spectrum of **87** at RT exhibits a broad peak at δ = -65.54 ppm and the ^{1}H NMR spectrum was also broad at RT due to dynamic effects. In the next step, low temperature ^{31}P NMR and ^{1}H NMR spectroscopy was attempted to slow down the exchange in solution. Different temperature such as T = 0 °C, -10 °C, -20 °C and -30 °C were tried. By lowering the temperature, the ratio of major isomer to minor isomer in the ^{31}P NMR spectra changed from 0 °C to -30 °C (0 ° C: 78:22; -10 °C: 73:27; -20 °C: 68:32; -30 °C: 67:33), which showed that the ratio of the minor isomer increased by lowering the temperature (Figure 2.9). The ^{31}P NMR spectrum at -30°C represents two doublets at δ = -65.04 ppm (J = 287 Hz) and δ = -82.15 ppm (J = 277 Hz). This temperature (-30°C) was used for further NMR study such as ^{1}H NMR, ^{13}C NMR, COSY, HSQC and HMBC spectroscopy to assign the isomers (Table 2.7). The doublet pattern for P-H was also observed for both isomers in ^{1}H NMR spectra.

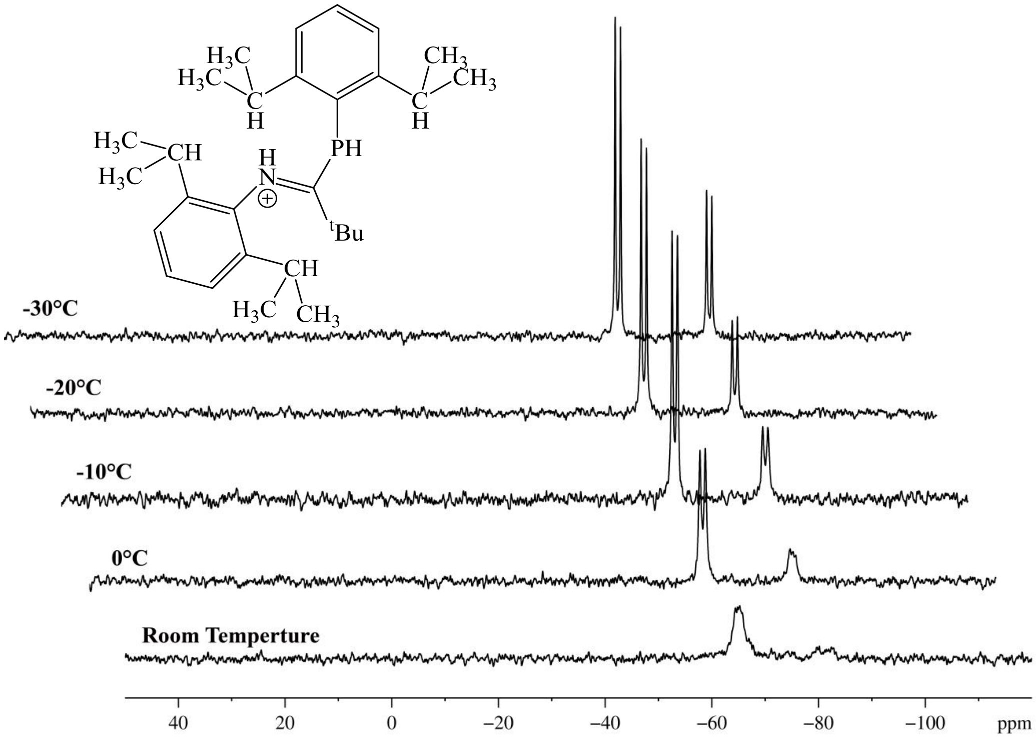


Figure 2.9 ^{31}P NMR spectrum of **87** in $CDCl_3$ at RT, 0°C, -10°C, -20°C, -30°C.

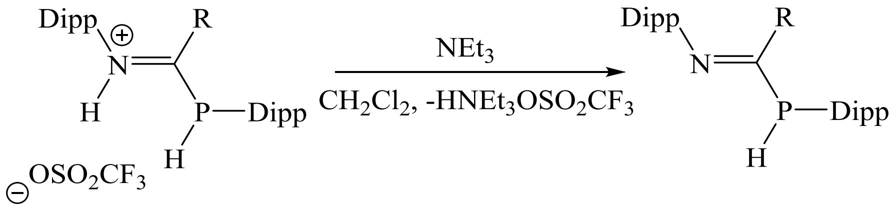
Table 2.7 ^{1}H NMR and ^{31}P NMR data of **87** at RT in $CDCl_3$.

Major				**Minor**			
Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult[1]	J, Hz
^{31}P NMR				**^{31}P NMR**			
P-H	-65.04	d	287	P-H	-82.15	d	277
^{1}H NMR				**^{1}H NMR**			
P-H	5.01	d	287	P-H	5.39	d	277
N-H	12.45	s		N-H	12.59	s	

[1] multiplicity

2.2.2.7 Synthesis of ^{t}Bu-phosphaamidine 32

The third step is synthesizing ^{t}Bu-phosphaamidine **32** from ^{t}Bu-phosphaamidinium triflate **87**. Reacting **87** with triethylamine in dichloromethane at -70°C under N_2 produced ^{t}Bu-phosphaamidine. Reaction progress was followed by ^{31}P NMR spectroscopy and after half an hour reaction was completed (Scheme 2.13).

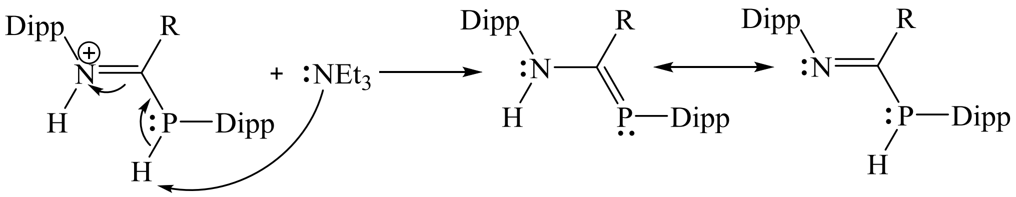


87. R =^{t}Bu
88. R = CH_3
89. R = *p*CH_3O-Ph

32. R =^{t}Bu
77. R = CH_3
25b. R = *p*CH_3O-Ph

Scheme 2.13 Synthesis of ^{t}Bu-phosphaamidine.

Work up consists of removal of dichloromethane from the reaction mixture and extracting the product with diethyl ether by removal of $HNEt_3OSO_2CF_3$ as a white precipitate. After filtration of $HNEt_3OSO_2CF_3$, diethyl ether was removed with vacuum and ^{t}Bu-phosphaamidine was isolated as a white solid. The proposed mechanism to produce ^{t}Bu-phosphaamidine from **87** is outlined in Scheme 2.14. First, the proton of P-H was removed with base (NEt_3) from **87**, and then electron pair was transferred from phosphorus to nitrogen through tautomerism. ^{31}P NMR and ^{1}H NMR evidence of pure ^{t}Bu-phosphaamidine **32** in $CDCl_3$ at RT showed only one isomer which was completely in agreement with the data that we achieved for synthesizing **32** from the *n*BuLi reaction (Section 2.2.1).



87. R =^{t}Bu
88. R = CH_3
89. R = *p*CH_3O-Ph

32. R =^{t}Bu
77. R = CH_3
25b. R = *p*CH_3O-Ph

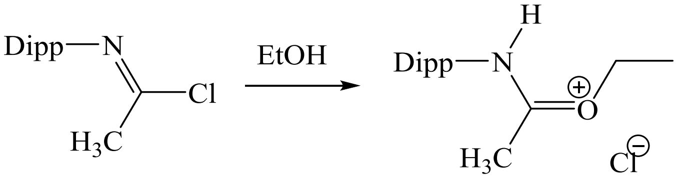
Scheme 2.14 Proposed mechanisms to the formation of phosphaamidine **32**, **77**, and **25b**.

2.3 CH_3-phosphaamidine 77

I attempted several synthesis routes to make CH_3-phosphaamidine **77** which is explained in this section. The first attempt was a thermal reaction of DippPH$_2$ **24** with CH_3-imidoyl chloride **14c** in xylenes. This route was previously used to synthesize the *p*CH_3OPh and *p*CH_3Ph phosphaamidines **25a**, **25b** by our group.[25] ^{31}P NMR spectroscopy was run on the crude material and evidence showed presence of CH_3-aminophosphaalkene **99** (δ = 5.98 ppm in xylene) as a major product (for more information look at Section 3.3.2) and four other phosphorus peaks that have not been identified. Any attempts to isolate the phosphorus containing compounds by column chromatography, crystallization and sublimation were unsuccessful.

The second synthesis route followed the same procedure used to synthesize ^{t}Bu-phosphaamidine **32** with *n*BuLi (Scheme 2.5). In this case, ^{31}P NMR evidence showed a peak for **99** (δ = 6.10 ppm in THF) as a major product and five other phosphorus peaks that have not been identified. *n*BuLi was a useful base to synthesize bulky ^{t}Bu-phosphaamidine **32** and that reaction worked well, but it wasn't the case for CH_3-phosphaamidine **77**, so I decided to choose a weaker base like pyridine.

In the third attempt, the starting materials (DippPH$_2$ **24** and CH$_3$-imidoylcholoride **14c**) were dissolved in pyridine and stirred at RT. Reaction progress was followed by ^{31}P NMR spectroscopy and after one hour stirring at RT, indications of a protonated CH$_3$-phosphaamidine salt were observed as a doublet at δ = -64.95 ppm (J = 216 Hz) in pyridine. After removing pyridine on a vacuum line, the product was extracted with pentane. A ^{31}P NMR spectrum in CDCl$_3$ at RT was recorded and several peaks were observed including δ = -62.82 ppm (**77**) and δ = 7.17 ppm (**99**). Any attempt to purify and grow crystals was unsuccessful. Crystallization of the crude material with ethanol gave small colorless crystals of N-(1-ethoxyethylidene)-2,6-diisopropylanilinium chloride or dippimidic ethoxy ester hydrochloride **90** (Figure 2.10 and Table 2.8). This particular crystal formed from reaction of unreacted imidoyl chloride (Scheme 2.15) and ethanol solvent molecules. The detailed crystallographic data for **90** can be found in Appendix III Table A21-A27.



14c **90**

Scheme 2.15 Synthesis of Dippimidic ethoxy ester hydrochloride **90**.

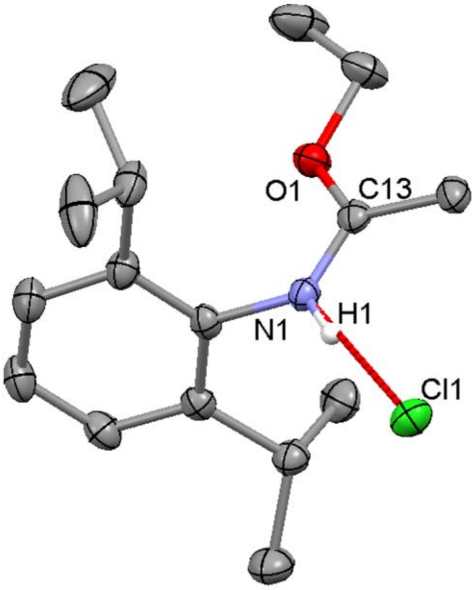


Figure 2.10 Displacement ellipsoids plot (40% probability) showing the molecular structure of dippimidic ethoxy ester hydrochloride **90** linked through H-bonding to Cl. H atoms other than those involved in these bonds are omitted for clarity.

Table 2.8 Crystal data and structure refinement for **90** and **88**.

	90	**88**
Space group	P-1	P-1
a/ Å	11.2193(7)	11.1652(16)
b/ Å	12.9719(8)	12.1824(18)
c/ Å	12.9832(8)	12.5097(18)
α	82.6370(10)°	95.960(2)°
β	69.8310(10)°	112.048(2)°
γ	82.9760(10)°	109.637(2)°
Z	2	2
Goodness-of-fit on F2	1.035	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.0988	R1 = 0.0555, wR2 = 0.1282
R indices (all data)	R1 = 0.0612, wR2 = 0.1100	R1 = 0.0758, wR2 = 0.1369

The last attempt was synthesizing **77** using Lammertsma's procedure.[29] We produced CH_3-nitrilium triflate **84** in the first step, CH_3-phosphaamidinium triflate **88** in the second step and CH_3-phosphaamidine **77** in the last step.

2.3.1 Synthesis of CH_3-nitrilium triflate 84

Reacting CH_3-imidoyl chloride **14c** with trimethylsilyl trifluoromethanesulfonate ($Me_3SiCF_3SO_3$) at -70°C under N_2 produced CH_3-nitrilium triflate **84** after 30 min stirring at RT. Work-up consisted of removal of dichloromethane on the vacuum line and washing of the crude material with pentane. The reaction scheme and mechanism can be found in Schemes 2.10 and 2.11. CH_3-nitrilium triflate **84** as a white solid was dissolved in a minimum quantity of hot CH_3CN under N_2. After cooling to RT, the colorless solution was left in a freezer at -25°C to grow crystals. The colorless solution changed to yellow, orange, then red after three days in the freezer and no crystals grew. CH_3CN was removed on a vacuum line and ^1H NMR spectroscopy was run on the red residue. ^1H NMR evidence exhibited signals of **84** and quinolium triflate (see Section 2.4.3 for more information).

2.3.1.1 Solution NMR Spectroscopy

CH_3-nitrilium triflate **84** was dissolved in $CDCl_3$ in a glove box to make an NMR sample. ^1H NMR (Figure 2.11), ^{13}C NMR and HSQC for **84** were run at RT to completely assign the peaks (Table 2.9). We see only one septet for both CH*iso* of the Dipp ring which means both CH*iso* are equivalent. This is also the case for 4 CH_3*iso* which shows only a doublet and that means all CH_3*iso* are equivalent.

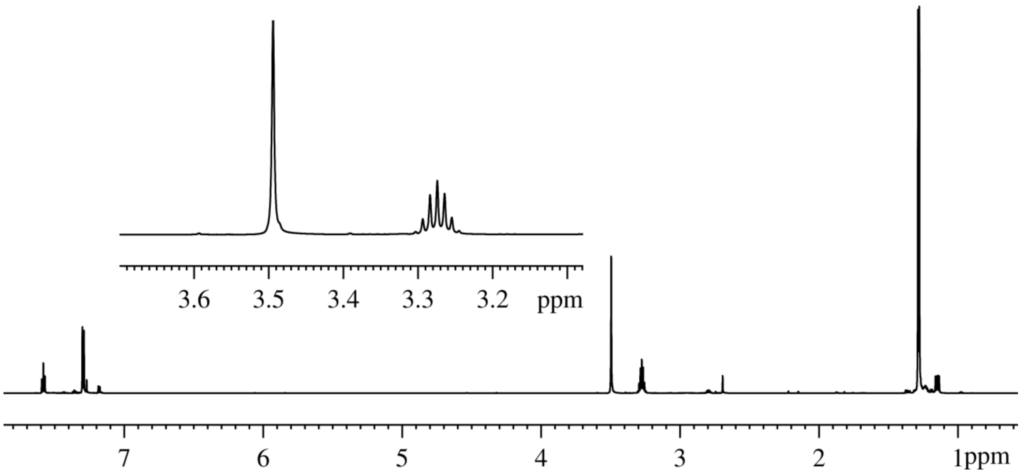


Figure 2.11 ^{1}H NMR spectrum of **84** in $CDCl_3$ at RT.

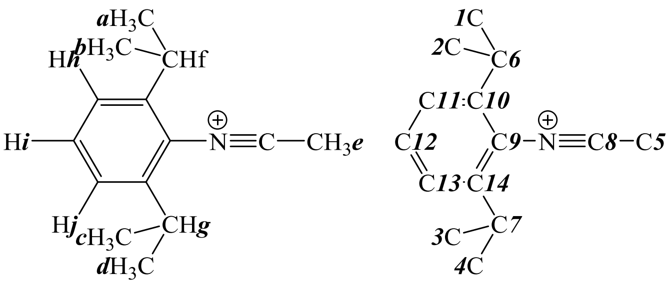


Table 2.9 ^{1}H NMR and ^{13}C NMR data for **84** at RT in $CDCl_3$.

Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult[1]	J, Hz
^{1}H				^{13}C [^{1}H]			
H ***a,b,c,d***	1.28	d	7.0	C ***5***	5.93		
H ***f,g***	3.27	sep	7.0	C ***1,2,3,4***	22.95		
H ***e***	3.49	s		C ***6,7***	30.00		
H ***h,j***	7.30	d	8.4	C ***9***	118.79	t	12
H ***i***	7.58	t	7.7	C ***8***	121.52	t	21
				C ***11,13***	124.74		
				C ***12***	134.17		
				C ***10,14***	148.44		

[1] multiplicity

^{13}C NMR spectra for C$_{ipso}$ of Dipp ring (C$_{ipso}$-N) with a chemical shift of δ = 118 ppm (J = 12 Hz) shows a triplet pattern due to the coupling of nitrogen to C$_{ipso}$ (the same pattern was observed for **83** and shown in Figure 2.7). The coupling of ^{13}C to ^{14}N for C≡N also showed up as a distorted 1:1:1 triplet. This is due to the coupling of carbon to the nitrogen with chemical shift of δ = 121.52 ppm ($^1J_{CN}$ =21 Hz).[82]

2.3.2 Synthesis of CH$_3$-phosphaamidinium triflate 88

The same procedure used to prepare ^{t}Bu-phosphaamidinium triflate **87** (Section 2.2.2.4) was used to make CH$_3$-phosphaamidinium triflate **88**.[29] Reacting CH$_3$-nitrilium triflate **84** with DippPH$_2$ **24** at -70°C under N$_2$ produced **88** and reaction progress was followed by ^{31}P NMR spectroscopy. After 30 min stirring at RT, ^{31}P NMR spectroscopy on an aliquot of the reaction mixture showed two doublets at δ = -71.14 ppm (J = 266 Hz) and δ = -60.68 ppm (J = 280 Hz) and there was no sign of DippPH$_2$, which confirmed that reaction was complete. Work-up consisted of removal of dichloromethane from the reaction mixture with a vacuum line and the crude material was washed with pentane. The reaction scheme is presented in Scheme 2.11 and conversion to the product follows the proposed mechanism outlined in Scheme 2.12. Adding DippPH$_2$ **24** (as nucleophile) to carbon of C≡N (as electrophile), followed by a [1,3]-hydrogen shift, produced CH$_3$-phosphaamidinium triflate **88** as a white solid.

2.3.2.1 Crystal Structure

CH$_3$-phosphaamidinium triflate **88** was dissolved in a minimum quantity of hot dichloromethane under N$_2$ and after cooling to RT, the solution was gently layered with heptanes. The colorless solution was left in freezer at -25°C to grow crystals. Good quality colorless crystals grew after two days at -25°C and the crystal structure was determined at -100°C (Figure 2.12).

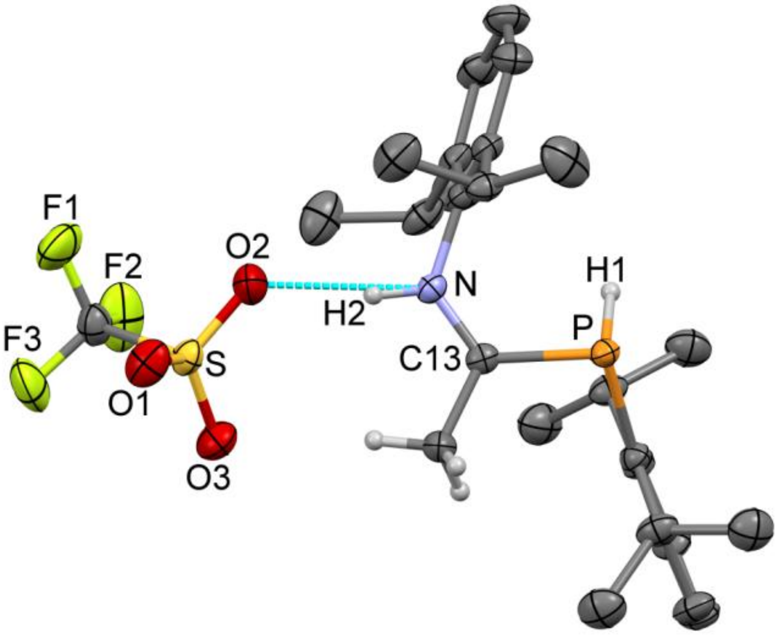


Figure 2.12 Displacement ellipsoids plot (40% probability) showing the molecular structure of **88** linked through H-bonding to O. H atoms on the Dipp rings are omitted for clarity.

The crystal structure shows the *Z-anti*(N=C*)* conformation which is the same as we saw for ^{t}Bu-phosphaamidine triflate **87**. Selected bond lengths and angles are presented in Table 2.6 and crystallographic data in Table 2.8. I compared the bond lengths and angles of CH_3-phosphaamidinium triflate **88** with ^{t}Bu-phosphaamidinium triflate **87** and found that the N=C bond length in **88** (1.295(3)) Å is the same as that in **87** (1.296(15)) Å and the C-P bond length in **88** (1.825(3)) Å is slightly shorter than in **87** (1.846(2)) Å. The C-N=C angle for **88** is 126.2(2)° and the sum of angles around **N** is 360.5(3)°, which shows that nitrogen is planar. The C-P-C angle for **88** is 102.15(11) ° and the sum of angles around **P** is 301.1(2)°. The detailed crystallographic data for **88** can be found in Appendix III Table A28-A34.

2.3.2.2 Solution NMR Spectroscopy

Pure crystalline CH_3-phosphaamidinium triflate **87** was dissolved in $CDCl_3$ under N_2 to make an NMR sample. The ^{31}P NMR spectrum at RT shows two isomers in solution at δ = -60.68 ppm (J = 280 Hz) for the minor isomer and δ = -71.14 ppm (J = 266 Hz) for the major isomer. The ratio of major to minor isomers is 75:25 as shown in Figure 2.13, with the major isomer at higher frequency. This result is different compared with ^tBu-phosphaamidinium triflate data where the signal of major isomer is at lower frequency (Section 2.2.2.6).

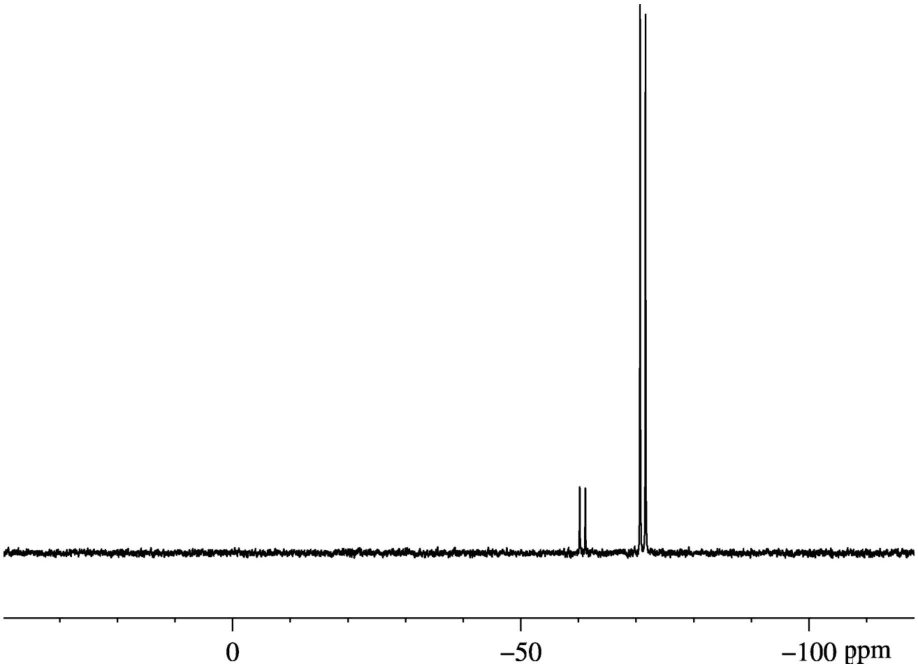


Figure 2.13 ^{31}P NMR spectrum of CH_3-phosphaamidinium triflate **88** at RT in $CDCl_3$.

The ^1H NMR of CH_3-phosphaamidinium triflate **88** also shows both isomers at RT (Figure 2.14 and 2.15). The P-H coupling for the major isomer at δ = 5.13 ppm is J = 266 Hz and for the minor isomer at δ = 6.73 ppm is J = 278 Hz. The N-H signal for the major isomer show at δ = 14.04 ppm and minor at δ = 14.23 ppm as shown in Figure 2.14. ^1H

NMR, ^{31}P NMR, ^{13}C NMR, COSY, HSQC and HMBC spectra were run at RT to better understand the properties of **87** and data are listed in Table 2.10.

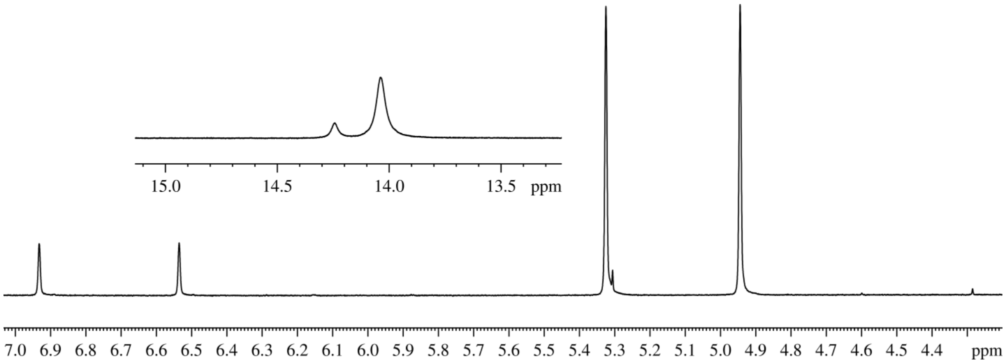


Figure 2.14 ^{1}H NMR spectrum of **88** in the P-H and N-H region at RT in CDCl$_3$.

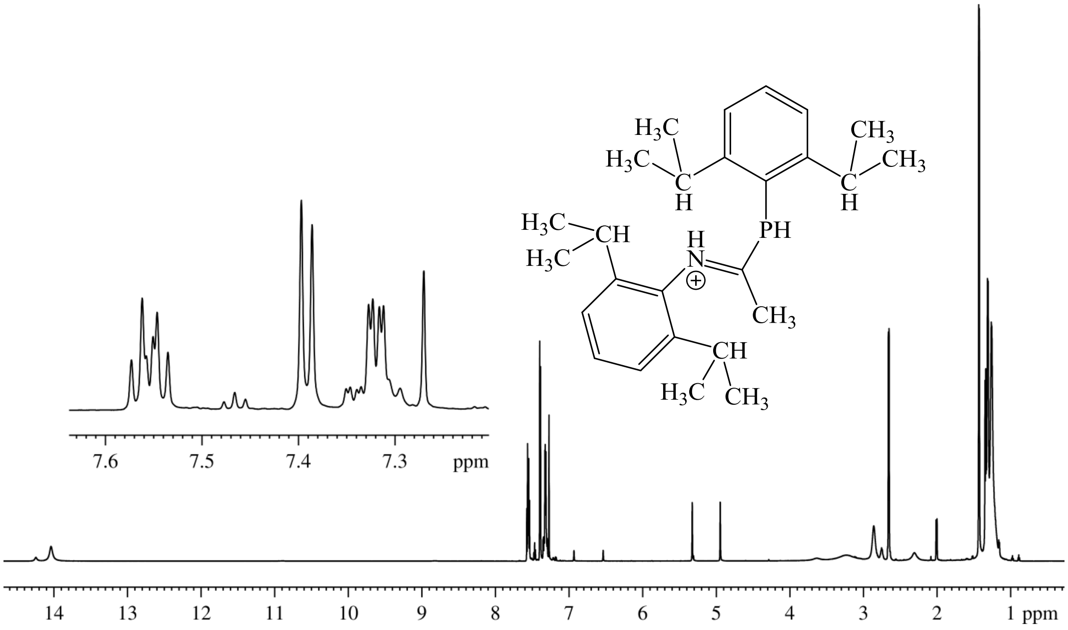


Figure 2.15 ^{1}H NMR spectrum of CH$_3$-phosphaamidine triflate **88** at RT in CDCl$_3$.

One septet at δ = 2.86 ppm (Dipp-P) and the other at δ = 3.25 ppm (Dipp-N) was observed for both CH*iso* of each ring. For CH$_{3}$*-iso*, two doublets were observed for each ring which means that there are two different environments for each isopropyl group, above and below the rings. A doublet for C-H_{meta} at δ = 7.32 ppm is due to coupling to phosphorus for both the major and minor isomers. The backbone CH_3 shows a doublet pattern due to coupling of H to P at δ = 2.65 ppm for the major isomer and at δ = 2.00 ppm for the minor isomer.

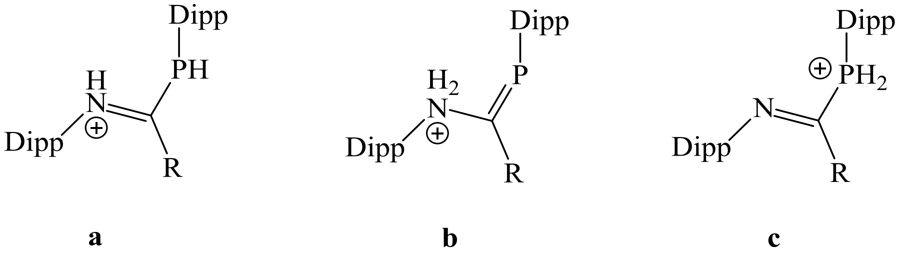
Table 2.10 ^{1}H NMR and ^{13}C NMR of CH_3-phosphaamidinium triflate **88** at RT.

Major				**Minor**			
Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult[1]	J, Hz
^{31}P NMR				**^{31}P NMR**			
P-H	-71.14	d	266	P-H	-60.68	d	281
^{1}H NMR				**^{1}H NMR**			
P-H	5.13	d	266	P-H	6.73	d	278
N-H	14.04	s		N-H	14.24	s	
Dipp-P				*Dipp-P*			
CH_3-*iso*	1.31	d	6.3	CH_3-*iso*	1.33	d	7.0
CH_3-*iso*	1.43	d	7.0	CH_3-*iso*	1.34	d	7.0
CH-*iso*	2.86	br s*		CH-*iso*	2.74	br s[2]	
CH_{meta}	7.32	d	7.7	CH_{meta}	7.34	d	8.4
CH_{para}	7.56	t	7.7	CH_{para}	7.56	t	4.9
Dipp-N				*Dipp-N*			
CH_3-*iso*	1.26	br		CH_3-*iso*	1.26	br s*	
CH-*iso*	3.25	br s*		CH-*iso*	3.65	br s*	
CH_{meta}	7.40	d	7.7	CH_{meta}	7.30	br s*	
CH_{para}	7.55	t	7.7	CH_{para}	7.47	t	7.7
Backbone				*Backbone*			
CH_3	2.65	d	16.8	CH_3	2.0	d	9.1
^{13}C NMR				**^{13}C NMR**			
C=N	211.69	d	41	C=N	208.00	d	48

[1] multiplicity; [2] Broad singlet

2.3.2.3 Computational Results

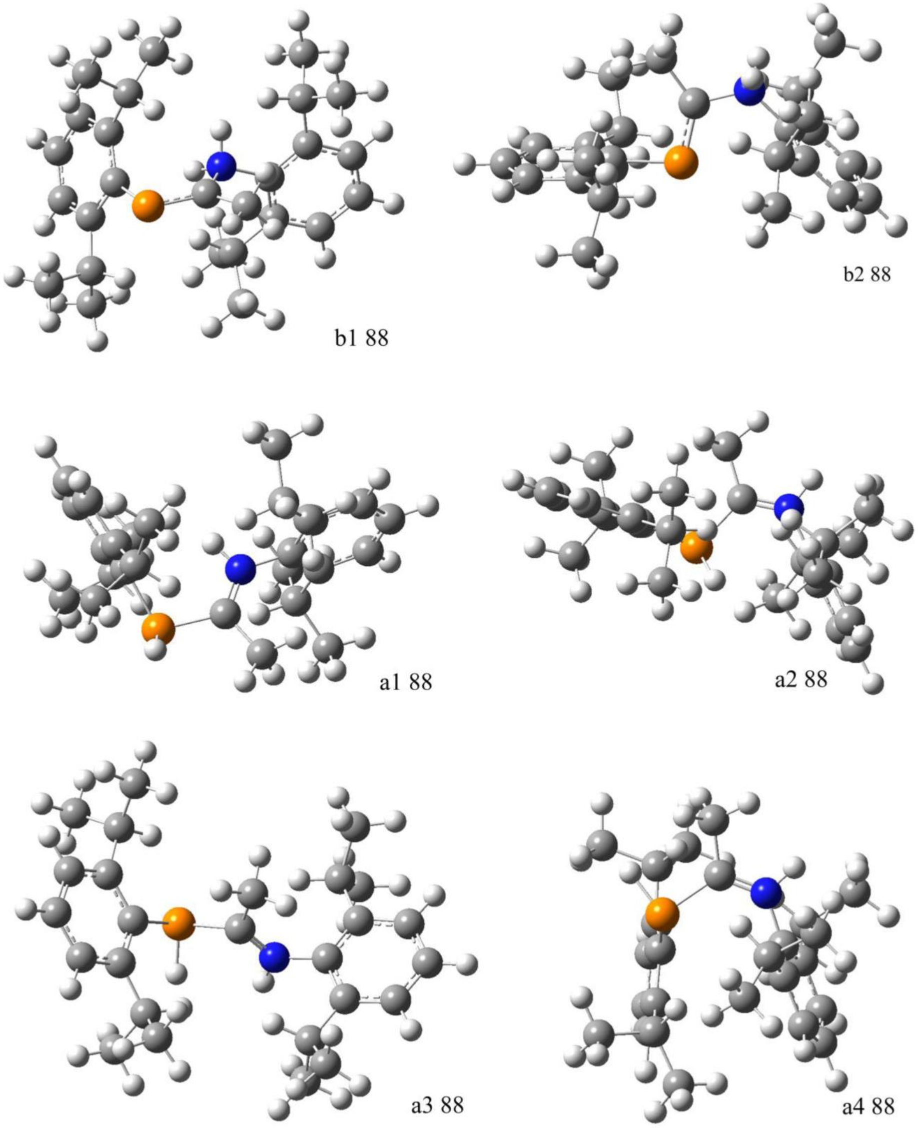
The CH_3-phosphaamidinium triflate **88** or protonated phosphaamidine contains an additional H^+ other than the P-H or N-H of phosphaamidine. The question comes to mind as to whether both protons bond to phosphorus or both to nitrogen or one proton bonds to phosphorus and the other one to nitrogen (Scheme 2.16).



R = CH_3, ^tBu, $p CH_3O-C_6H_4$

Scheme 2.16 Three possible isomers for protonated phosphaamidines.

Solution NMR evidence includes two doublets in ^{31}P NMR spectrum (δ = -71.14 ppm and δ = -60 ppm) and also two doublets in ^1H NMR (δ = 5.13 ppm and δ = 6.73 ppm) due to the coupling of one proton to phosphorus (this proton is directly bonded to phosphorus). At this point, we understand that there should be only one proton attached to phosphorus like isomer **a** in Scheme 2.18. ^1H NMR spectroscopy also shows evidence of N-H as two broad singlets (δ = 14.04 ppm and δ = 14.24 ppm) for two isomers of **88**. Based on this NMR evidence, isomer **c** (Scheme 2.18) cannot be the expected isomer because ^{31}P NMR spectroscopy for **c** should show a triplet pattern and there shouldn't be any broad singlet for N-H in the ^1H NMR spectrum (there is no NH in **c**). Isomer **b** also cannot be the expected isomer because ^{31}P NMR spectroscopy for **b** should show a singlet pattern for phosphorus. All of this evidence confirm that the expected isomers in solution (both the major and minor species) should be **a**, which means one proton bonds to phosphorus and the other one to nitrogen. Crystallographic data also shows that the expected isomer is **a** and the geometry of the crystal structure is *Z-anti*(N=C). To better understand these results, we have done DFT calculations on two possible isomers of **b** (*Z-anti*(P=C) and *E-syn*(P=C)) and also four possible isomers of **a** (*Z-anti*(N=C), *E-syn*(N=C), *E-anti*(N=C) and *Z-syn*(N=C)) and we are also interested to find the most stable isomers in the gas phase. The computed relative energy and geometries of these possible isomers is shown in Table 2.11 and Figure 2.16. As we see in Table 2.11, the relative energy for two isomers of **b** ($E_{Z\text{-}anti(\mathrm{P=C})}$ = 82 kJ/mol and $E_{E\text{-}syn(\mathrm{P=C})}$ = 85 kJ/mol) is high and that means more energy needs to be provided to form these structures. In the case of the four possible conformers of **a,** $E_{E\text{-}syn(\mathrm{N=C})}$ = 0 kJ/mol with lowest energy is the most stable, which is different from the crystal structure, which is *Z-anti*(N=C). This result is similar to the cation of $p\mathrm{CH_3}$Ph-phosphaamidinium triflate **89a**, which has the calculated *E* isomer (*E* = 0 kJ/mol) as the most stable isomer in the gas phase. This result is different compared with ^{t}Bu-phosphaamidinium triflate **87** where the *Z* isomer (*Z* = 0 kJ/mol) is the most stable calculated isomer. ^{t}Bu-phosphaamidinium triflate also shows different patterns in solution NMR data since its major isomer shows up at higher field, but in the case of $p\mathrm{CH_3}$Ph-phosphaamidinium triflate **89a** and $\mathrm{CH_3}$-phosphaamidinium triflate **88**, the major isomer shows up at lower field. The conformation that has highest energy for $\mathrm{CH_3}$-phosphaamidinium triflate **88** is *Z-syn*(N=C) = 24 kJ/mol (the absolute accuracy of DFT calculation for energy of isomerization at the B3LYP/6-31G* level is 17 kJ/mol).[79] The other two conformers have small relative energies (Table 2.11) and it seems that it may be easy to convert *Z-anti*(N=C) to *Z-syn*(N=C) or *E-syn*(N=C) to *E-anti*(N=C) (by rotation around P-C bond with an expected low barrier). Based on these data, it is obvious now that in solution there are actually two isomers for $\mathrm{CH_3}$-phosphaamidinium triflate **88** (an average *E* as major isomer and an average *Z* as minor isomer) and the conformers of each isomer are in equilibrium.



b1 88

b2 88

a1 88

a2 88

a3 88

a4 88

Figure 2.16 Six calculated possible isomers and conformers at the B3LYP/6-31G(2d,p) level for **88**; *Z-anti*(P=C) **b1 88**; *E-syn*(P=C) **b2 88**; *E-syn*(N=C) **a1 88**; *Z-anti*(N=C) **a2 88**; *E-anti*(N=C) **a3 88**; *Z-syn*(N=C) **a4 88**.

Table 2.11 Calculated relative energy (kJ/mol)[1] for four possible isomers of **88**.

E-syn(N=C)	*Z-anti*(N=C)	*E-anti*(N=C)	*Z-syn*(N=C)	*Z-anti*(P=C)	*E-syn*(P=C)
0	10	12	24	82	85

[1] B3LYP/6-31G(2d,p); the estimate precision is ±5 kJ/mol.

2.3.3 Synthesis of CH_3-phosphaamidine 77

Methyl phosphaamidine **77** was synthesized by reacting methyl phosphaamidinium triflate **84** with triethylamine at -70°C under N_2. Reaction progress was followed by ^{31}P NMR spectroscopy and the reaction was completed in 30 min. The ^{31}P NMR spectrum in CH_2Cl_2 shows four different peaks at δ = - 81.35 ppm (J = 238 Hz, doublet), δ = - 68.94 ppm (J = 235 Hz, doublet), δ = 37.36 ppm and δ = 71.22 ppm which are assumed to be four isomers of CH_3-phosphaamidine **77**. This pattern was observed previously for *p*CH_3Ph-phosphaamidine **25a** and *p*CH_3OPh-phosphaamidine **25b** by our group. Work-up consisted of removal of dichloromethane from the reaction mixture and extracting the product with diethyl ether by removing $HNEt_3OSO_2CF_3$ as a white precipitate (Scheme 2.15). The proposed mechanism to produce CH_3-phosphaamidine **77** from CH_3-phosphaamidinium triflate **84** is outlined in Scheme 2.16.

2.3.3.1 Solution NMR Spectroscopy

CH_3-phosphaamidine **77**, a pale yellow solid, was dissolved in $CDCl_3$ under N_2 to make an NMR sample and ^1H NMR, ^{31}P NMR, ^{13}C NMR, COSY and HSQC spectra were run at RT to study the isomers in solution. Four isomers were detected of which two are P-H phosphaamidine (δ = - 80.52 ppm (J = 238 Hz, doublet) and δ = - 66.68 ppm (J = 238 Hz, doublet)) and the other two are N-H phosphaamidine (δ = 74.61 ppm and δ = 34.43 ppm as major isomer). The backbone CH_3 shows the same doublet pattern as we observed for **88** due to the coupling of CH_3 protons to phosphorus at δ = 1.91 ppm for the major isomer. The ratio of isomers are very similar to that of the previously made **25a**.[8] The major isomer for **25a** is also an NH isomer (δ = 53.4 ppm) and the other three isomers have ^{31}P chemical shifts similar to **77** (NH isomer (δ = -79.2 ppm), PH isomer (δ = -80.3 ppm, J = 243 Hz) and PH isomer (δ = -66.4 ppm, J = 243 Hz).

Table 2.12 ^{1}H NMR and ^{13}C NMR data for major isomer of **77** at RT in $CDCl_3$.

Nucleus	δ, ppm	mult[1]	J, Hz
^{31}P NMR			
P-H	-80.52	d	238
P-H	-66.68	d	238
N-H (Major isomer)	34.43	d	17
N-H	74.61	s	
Major isomer			
^{1}H NMR			
N-H	6.08	s	
Dipp-P			
CH_3-*iso*	1.26,1.36	d	7.0
CH-*iso*	3.82	sep	7.0
CH_{meta}	7.22	d	7.7
CH_{para}	7.32	t	7.7
Dipp-N			
CH_3-*iso*	1.02,1.24	d	7.0
CH-*iso*	3.06	sep	7.0
CH_{meta}	7.11	d	7.7
CH_{para}	7.25	t	9.1
backbone			
CH_3	1.91	d	18.9
^{13}C NMR			
C=P	185.09	d	62

[1] multiplicity

In *p*CH_3Ph-phosphaamidine **25a**, the geometry of the phosphorus atom is planar (C=P), so the whole molecule has a mirror plane. This is the reason only two doublets and one septet was observed for CH_3*iso* and CH*iso* of Dipp-N and Dipp-P ring. The same coupling pattern was also observed for CH_3-phosphaamidine **77** based on the solution NMR data (Table 2.12), so there should be a mirror plane as well for the major isomer of **77**. This result can be the reason to say that the major isomer of CH_3-phosphaamidine **77** has the same *Z-anti*(P=C) geometry as *p*CH_3Ph-phosphaamidine **25a**.

2.4 *p*CH$_3$OPh-phosphaamidine 25b

After synthesis of the ^{t}Bu-phosphaamidinium triflate **87** which has bulky substitution on the backbone carbon and CH_3-phosphaamidinium triflate **88** with small substitution on the backbone carbon, I decided to synthesize *p*CH_3OPh-phosphaamidinium triflate **89** which sterically in between (not too bulky and not small) in order to complete my study on phosphaamidine salts.

2.4.1 Synthesis of *p*CH$_3$OPh-nitrilium triflate 85

The first step, to synthesize *p*CH_3OPh-phosphaamidine **25b**, would be making *p*CH_3OPh-nitrilium triflate **85**. Reacting *p*CH_3OPh-imidoyl chloride **14b** with trimethylsilyl trifluoromethanesulfonate at -70°C under N_2 produced **85**. Work-up consisted of removal of dichloromethane on a vacuum line and washing the crude material with pentane. The reaction scheme and mechanism can be found in Scheme 2.10 and 2.11.

2.4.1.1 Solution NMR Spectroscopy

pCH_3OPh-nitrilium triflate **85** is a yellow solid which was dissolved in $CDCl_3$ under N_2 to make an NMR sample. ^{1}H NMR, ^{13}C NMR and HSQC spectra were run at RT to characterize the compound and all the peaks were assigned. The ^{1}H NMR spectrum is shown in Figure 2.17 and NMR data are listed in Table 2.14.

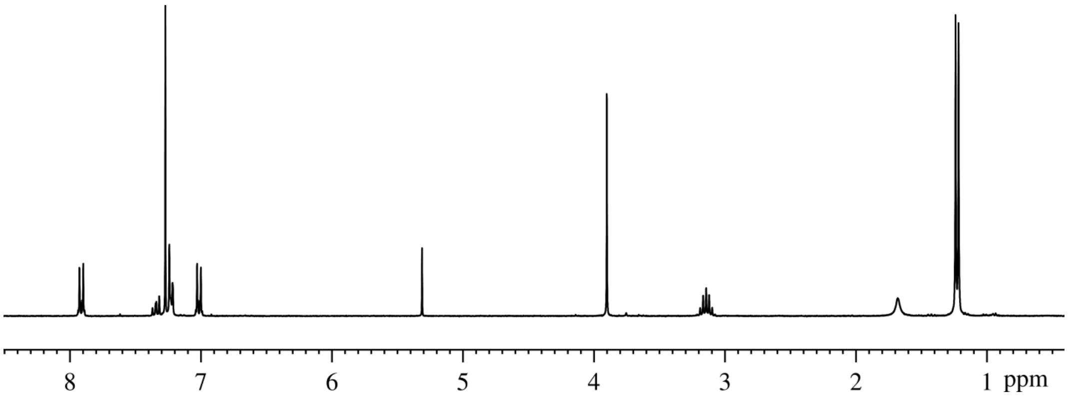
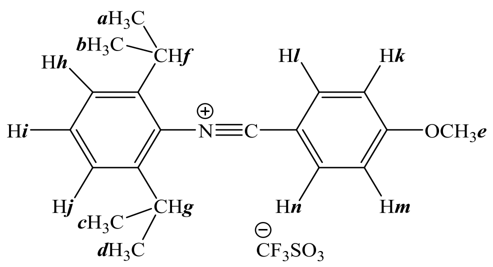


Figure 2.17 ^{1}H NMR spectrum of *p*CH_3OPh-nitrilium triflate **85** in $CDCl_3$ at RT.

The same pattern as **83** and **84** was observed for *p*CH_3OPh-nitrilium triflate **85**. One septet at $\delta = 3.30$ ppm for both CH*iso* and for four CH_3-*iso* only one doublet at $\delta = 1.33$ ppm was observed, which means these protons are equivalent. As we expected, a singlet was observed for methoxy group protons at $\delta = 4.01$ ppm which is far downfield due to the bonding to oxygen as an electronegative atom. A singlet peak at $\delta = 5.30$ ppm is the residue of CH_2Cl_2 (solvent of reaction) in $CDCl_3$.



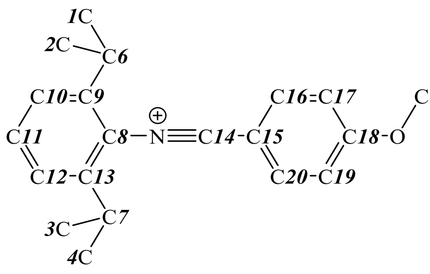


Table 2.13 ^{1}H NMR and ^{13}C NMR data for *p*CH_3OPh-nitrilium triflate **85** at RT.

Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult[1]
^{1}H				^{13}C [^{1}H]		
H ***a,b,c,d***	1.33	d	7.0	C ***1,2,3,4***	22.78	s
H ***f,g***	3.30	sep	7.0	C ***6,7***	30.44	s
H ***e***	4.01	s		C ***5***	56.87	s
H ***k,m***	7.27	d	8.4	C ***17,19***	117.23	s
H ***h,j***	7.36	d	8.4	C ***8***	119.51	t
H***i***	7.53	t	7.7	C ***14***	121.32	t
H***l,n***	8.40	d	9.1	C ***10,12***	124.86	s
				C ***15***	131.21	s
				C ***11***	134.35	s
				C ***16,20***	139.37	s
				C ***9,13***	148.33	s
				C ***18***	169.08	s

[1] multiplicity

2.4.1.2 Crystal Structure

pCH_3OPh-nitrilium triflate **85** was dissolved in a minimum quantity of hot acetonitrile under N_2 to grow crystals. After cooling to RT, a yellow solution was left in a freezer at -25°C and after four days yellow crystals grew from the now red solution. X-ray diffraction at -100°C found that the structure is dihydroquinolium triflate **93** instead of *p*CH_3OPh-nitrilium triflate **85** (Figure 2.18). Crystallographic data for dihydroquinolium triflate **93** is listed in Table 2.14 and bond lengths and angles can be found in Appendix III Table A35-A41. The crystal system for **93** is monoclinic with $P2_1/n$ space group and there are four molecules in the unit cell. The N-C_{aryl} bond length is 1.4682(14) Å (the range of bond lengths for C*ar*-N^+-$(C,H)_3$ is 1.461-1.470 Å)[72] and N-C1 is 1.5205(14) Å (the range of bond lengths for $(Csp^3)_2\text{-}NH_2^+$ is 1.484-1.503 Å and overall bond lengths for $Csp^3\text{-}N^+$ are 1.488-1.510 Å)[72]. The nitrogen has approximately tetrahedral geometry.

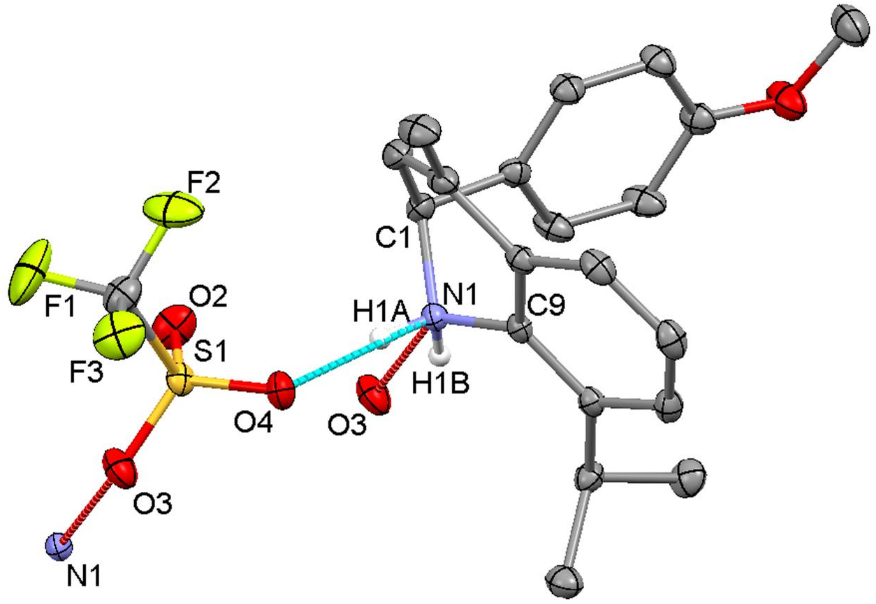
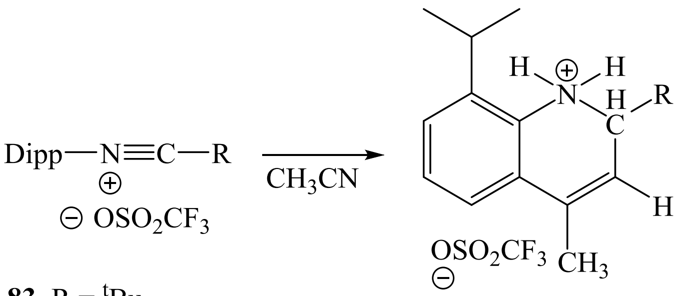


Figure 2.18 Displacement ellipsoids plot (40% probability) showing the molecular structure of **93** linked through H-bonding to O. H atoms other than those involved in these bonds are omitted for clarity.



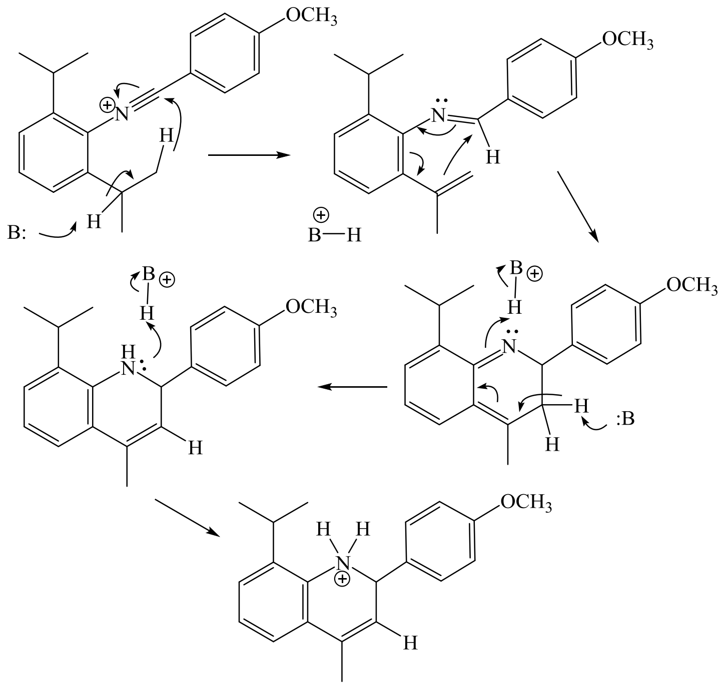
83. R = ^{t}Bu
84. R = CH_3
85. R = $p$$CH_3O$-Ph

91. R = ^{t}Bu
92. R = CH_3
93. R = $p$$CH_3O$-Ph

Scheme 2.17 Synthesis of dihydro quinolinium triflate.

Table 2.14 Crystal data and structure refinement for **93** and **89**.

	93	**89**
Space group	P 2_1/n	P-1
a/ Å	13.3830(15)	11.3706(7) Å
b/ Å	10.8157(12)	12.1824(18)
c/ Å	14.6913(16)	12.5097(18)
α	90°	95.960(2)°
β	99.9821(12)°	112.048(2)°
γ	90°	109.637(2)°
Z	4	2
Goodness-of-fit on F2	1.024	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0911	R1 = 0.0555, wR2 = 0.1282
R indices (all data)	R1 = 0.0405, wR2 = 0.0955	R1 = 0.0758, wR2 = 0.1369



Scheme 2.18 Proposed mechanisms to the formation of dihydro quinolium triflate.

Conversion of *p*CH_3OPh-nitrilium triflate **85** to the dihydroquinolium triflate **93** is presented in Scheme 2.17. A proposed mechanism of the conversion that occurred during recrystallization is outlined in Scheme 2.18. CH_3CN as a base removed a hydrogen from a CH_3 of a Dipp isopropyl group, followed by electrocyclic ring closure.

2.4.1.3 Solution NMR Spectroscopy

Pure yellow crystals of dihydro quinolium triflate were dissolved in $CDCl_3$ under N_2 to make an NMR sample. ^1H NMR, ^{13}C NMR, COSY and HSQC spectra were run to characterize the compound **93** and assign the spectra completely (Figure 2.19 and Table 2.15). A singlet for the methoxy group occurs at $\delta = 3.73$ ppm. Both hydrogens of NH_2^+ in **93** show singlets at $\delta = 8.80$ ppm and $\delta = 10.30$ ppm, which are very downfield due to the positive charge on nitrogen.

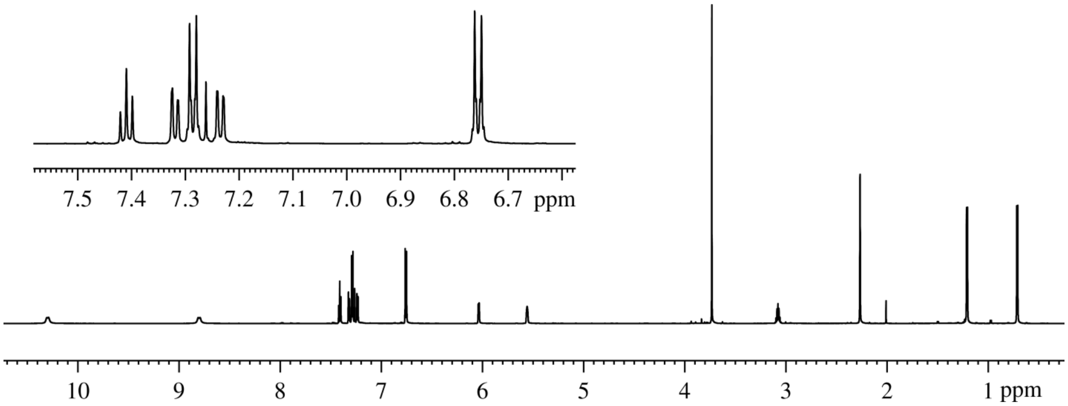
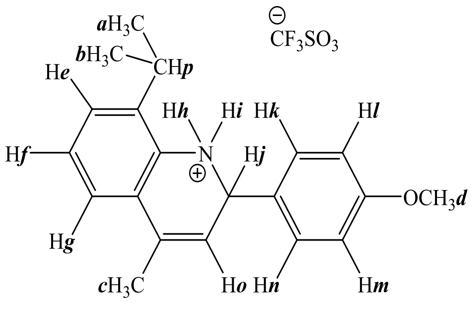


Figure 2.19 ^1H NMR spectrum of dihydro quinolium triflate **93** in $CDCl_3$ at RT.

2.4.2 Synthesis of *p*CH_3OPh-phosphaamidinium triflate 89

Reacting *p*CH_3OPh-nitrilium triflate **85** with $DippPH_2$ **24** at -70°C under N_2 produced *p*CH_3OPh-phosphaamidinium triflate **89**. Work-up consisted of removal of dichloromethane on the vacuum line from the reaction mixture. The reaction scheme can be found in Scheme 2.13 and the mechanism is the same as we proposed for **87** and **88** (Scheme 2.14).



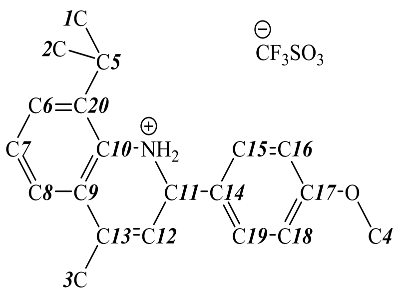


Table 2.15 ^{1}H NMR and ^{13}C NMR of dihydro quinolium triflate **93**.

Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult
^{1}H				^{13}C [^{1}H]		
H ***a***	0.71	d	7.0	C ***3***	18.46	s
H ***b***	1.21	d	6.3	C ***2***	22.23	s
H ***c***	2.27	s		C ***1***	23.32	s
H ***p***	3.08	sep	7.0	C ***5***	27.06	s
H ***d***	3.73	s		C ***4***	55.24	s
H ***o***	5.56	br s[2]		C ***11,12***	55.78	s
H ***j***	6.04	d	4.9	C ***16,18***	114.18	s
H ***l,m***	6.76	d	8.4	C ***6,10***	122.10	d
H ***g***	7.24	d	7.7	C ***14***	123.75	s
H ***k,n***	7.27	d	8.4	C ***8***	126.52	s
H ***e***	7.32	d	7.7	C ***7***	129.94	s
H ***f***	7.41	t	7.7	C ***15,19***	130.49	s
H ***i***	8.80	d	10.5	C ***9***	131.11	s
H ***h***	10.30	d	11.2	C ***13***	133.19	s
				C ***20***	142.43	s
				C ***17***	160.83	s

[1] multiplicity; [2] Broad singlet

2.4.2.1 Crystal Structure

Crude *p*CH_3OPh-phosphaamidinium triflate **89** was dissolved in a minimum quantity of hot dichloromethane and after cooling to RT, was layered gently with heptanes under N_2. A pale yellow solution was left at -25°C and after three days yellow crystals grew. Crystallographic data was collected at -100°C and the crystal structure is shown in Figure 2.20. Selected crystallographic data is shown in Table 2.14 and selected bond lengths and angles in Table 2.6.

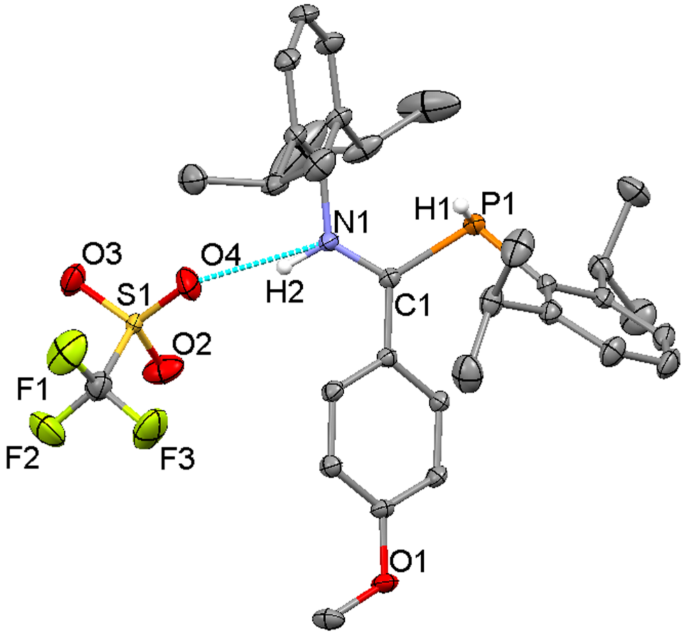


Figure 2.20 Displacement ellipsoids plot (40% probability) showing the molecular structure of **89** linked through H-bonding to O. H atoms other than those involved in these bonds and P-H are omitted for clarity.

The crystal structure shows the *Z-anti*(N=C) conformation which is the same as we saw for ^{t}Bu-phosphaamidinium triflate **87** and CH_3-phosphaamidinium triflate **88**. If we compare the bond lengths and angles of neutral *p*CH_3OPh-phosphaamidine **25b**[8] with *p*CH_3OPh-phosphaamidinium triflate **89** we found that the N=C bond length in **25b**

(1.366(3)) Å is longer than in **89** (1.302(2)) Å and the C-P bond length in **25b** (1.716(2)) Å is shorter than in **89** (1.836(17)) Å. The C-N=C angle for **89** is 125.12(15)° and the sum of the angles around nitrogen is 360.02(2)°, which shows that nitrogen is planar. The C-P-C angle for **89** is 106.93(12)° and sum of the angles around phosphorus is 288.23(2)°, which confirms that phosphorus has a pyramidal geometry. Details of crystallographic data for **89** can be found in Appendix III Table A42-A48.

2.4.2.2 Solution NMR Spectroscopy

Pure crystals of *p*CH_3OPh-phosphaamidinium triflate **89** were dissolved in $CDCl_3$ to make an NMR sample. The ^{31}P NMR spectrum shows two doublets, the major isomer at δ = −70.02 ppm (J = 269 Hz, 71%) and the minor isomer at δ = -58.10 ppm (J = 277 Hz, 29%, Figure 2.21). This result is similar to CH_3-phosphaamidinium triflate (which shows the major isomer at higher frequency) and different from ^{t}Bu-phosphaamidinium triflate (the major isomer shows at lower frequency).

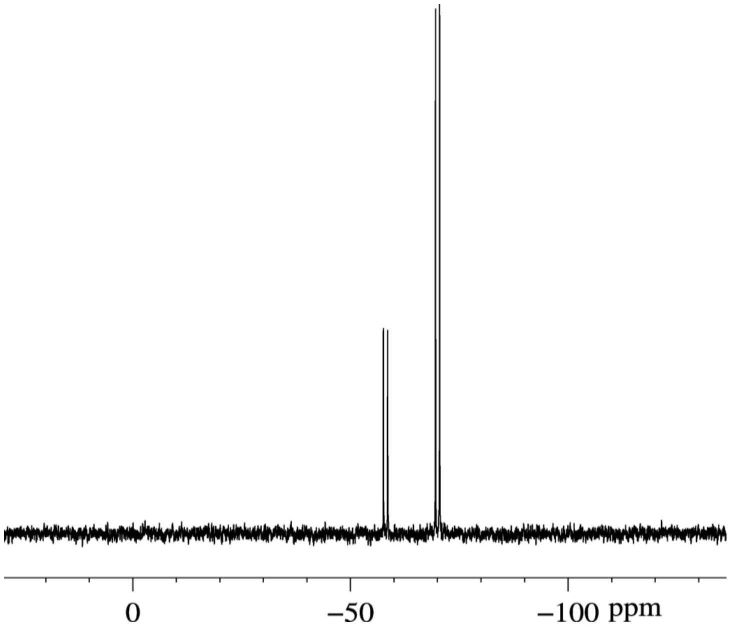


Figure 2.21 ^{31}P NMR spectrum of *p*CH_3OPh-phosphaamidine triflate **89** in $CDCl_3$ at RT.

The ^1H NMR spectrum of *p*CH_3OPh-phosphaamidinium triflate **89** also shows both isomers at RT (Figure 2.22). P-H coupling for the major isomer shows as a doublet at δ = 5.25 ppm (J = 266 Hz) and for the minor isomer at δ = 6.73 ppm (J = 277 Hz). The N-H coupling for the major isomer shows as a broad singlet at δ = 13.24 and the minor isomer at δ = 13.62 ppm. ^1H NMR, ^{13}C NMR, COSY, HSQC and HMBC spectra were run at RT to assign the spectra and data is listed in Table 2.16.

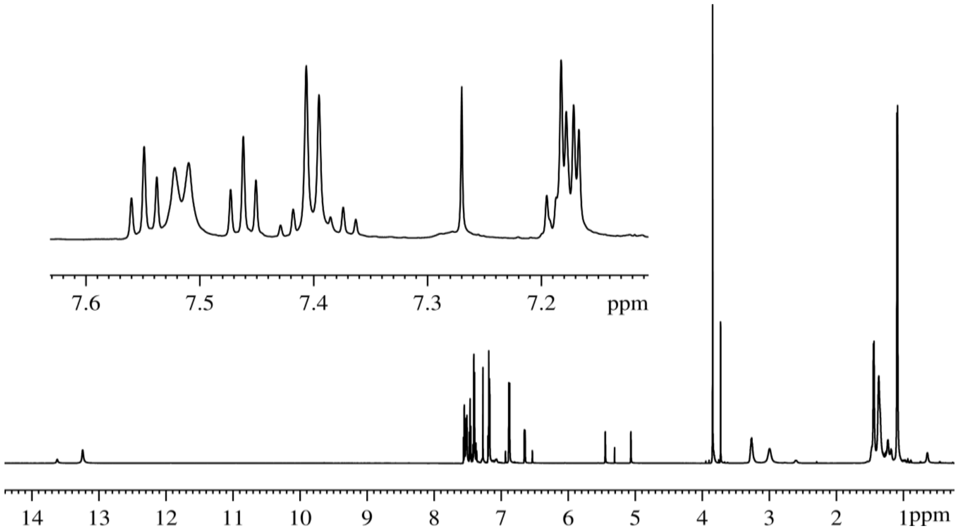


Figure 2.22 ^1H NMR spectrum of *p*CH_3OPh-phosphaamidinium triflate **89** in $CDCl_3$ at RT.

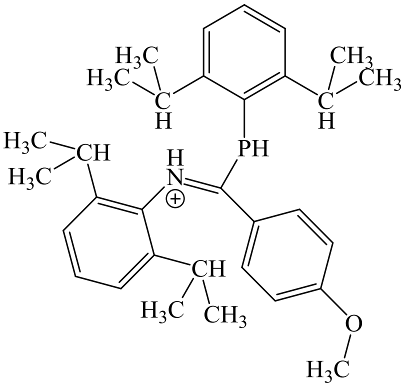


Table 2.16 ^{1}H NMR and ^{13}C NMR data for **89** in CDCl$_3$ at RT.

Major				**Minor**			
Nucleus	δ, ppm	mult[1]	J, Hz	**Nucleus**	δ, ppm	mult	J, Hz
^{31}P NMR				**^{31}P NMR**			
P-H	-70.02	d	269	P-H	-58.10	d	277
^{1}H NMR				**^{1}H NMR**			
P-H	5.25	d	266	P-H	6.73	d	280
N-H	13.24	s		N-H	13.62	s	
Dipp-P				*Dipp-P*			
CH$_3$-*iso*	1.09	d	6.3	CH$_3$-*iso*	0.64,1.23,1.82	br s*	
CH-*iso*	3.26	br s[2]		CH-*iso*	3.82	br s*	
CH$_{\mathrm{meta}}$	7.18	d	7.7	CH$_{\mathrm{meta}}$	7.28	d	7.7
CH$_{\mathrm{para}}$	7.46	t	7.7	CH$_{\mathrm{para}}$	7.37	t	7.7
Dipp-N				*Dipp-N*			
CH$_3$-*iso*	1.44,1.36	d	6.3	CH$_3$-*iso*	1.33,1.47	d	
CH-*iso*	2.99	br s*		CH-*iso*	2.61,3.24	br s*	
CH$_{\mathrm{meta}}$	7.40	d	7.7	CH$_{\mathrm{meta}}$	7.51	d	8.4
CH$_{\mathrm{para}}$	7.55	t	7.7	CH$_{\mathrm{para}}$	7.42	t	7.7
Methoxy				*Methoxy*			
OCH$_3$	3.84	s		OCH$_3$	3.72	s	
CH$_{\mathrm{meta}}$	6.88	d	8.4	CH$_{\mathrm{meta}}$	6.65	d	5.6
CH$_{\mathrm{ortho}}$	7.51	d	8.4	CH$_{\mathrm{ortho}}$	7.2	d	5.6
^{13}C NMR				**^{13}C NMR**			
Dipp-P				*Dipp-P*			
CH$_3$-*iso*	24.25	s		CH$_3$-*iso*	24.25,25.03	s	
CH-*iso*	34.55	d	16	CH-*iso*	34.55	d	14
CH$_{\mathrm{meta}}$	124.76		5	CH$_{\mathrm{meta}}$	124.72		7
CH$_{\mathrm{para}}$	133.36	s		CH$_{\mathrm{para}}$	133.25	s	
Dipp-N				*Dipp-N*			

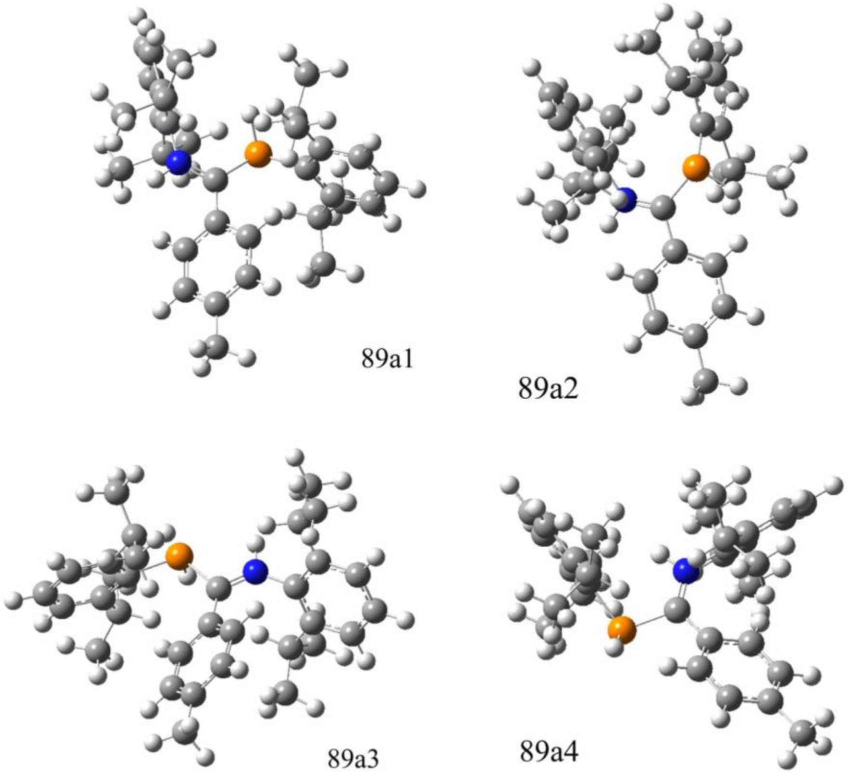
CH_3-*iso*	25.39,23.06	s		CH_3-*iso*			
CH-*iso*	29.70			CH-*iso*			
CH$_{meta}$	125.5			CH$_{meta}$	131.82		9
CH$_{para}$	113.79			CH$_{para}$	130.94		
Methoxy				*Methoxy*			
OCH_3	56.13	s		OCH_3	55.92	s	
CH$_{meta}$	115.16	s		CH$_{meta}$	114.63	s	
CH$_{oertho}$	132.14			CH$_{oertho}$	132.49		
C=N	200.94	d	42	Others	121.37,121.17		

[1]multiplicity; [2]Broad singlet

2.4.2.3 Computational Results

Solution NMR evidence includes two doublets in the ^{31}P NMR spectrum (δ = -70.02 ppm and δ = -58.10 ppm) and also two doublets in ^{1}H NMR spectrum (δ = 5.25 ppm and δ = 6.73 ppm) which confirms there is only one proton attached to phosphorus. Similar to CH_3-phosphaamidinium triflate **88**, the expected isomers should have conformation **a** (Scheme 2.18). Crystallographic data also shows the presence of a proton bonded to phosphorus with the *Z-anti*(N=C) geometry in the crystal structure. In order to find the most stable conformation and compare it with the crystal structure geometry, we have done DFT calculations on four possible conformers of *p*CH_3Ph-phosphaamidinium triflate **89a** (*Z-anti*(N=C), *E-syn*(N=C), *E-anti*(N=C) and *Z-syn*(N=C)) which we expect to have the same computational features as *p*CH_3OPh-phosphaamidinium triflate **89** but is a computationally simpler model. The computed energy differences and geometries of these four possible isomers are shown in Table 2.17 and Figure 2.23.

Calculations show that the most stable conformation in the gas phase is *E-syn*(N=C) which is different from the crystal structure (*Z-anti*(N=C)). This result is similar to CH_3-phosphaamidinium triflate **88** and different from ^{t}Bu-phosphaamidinium triflate **87**. All the conformers listed in Table 2.17 have a low relative energy and can easily convert to each other if the energy barrier is low for free rotation at the P–C bond. Based on the evidence observed for **87** and **88**, the two isomers that we see in solution NMR spectroscopy for **89** are actually *Z* (average of all *Z* conformers) and *E* isomers (average of all *E* conformers). These isomers could already exist in the solid or be formed in solution through conversion of *E* to *Z*. Although rotation of the C=N double bond is likely to be unfavorable, a pathway mediated through tautomerism is conceivable. Based on the NMR data, four equal CH_3*iso* are observed as one doublet for Dipp-P ring. In case of Dipp-N ring, two doublets are observed for two CH_3*iso* of Dipp-N ring. This evidence is probably a match with the *E-syn*(N=C) conformer in solution.



89a1

89a2

89a3

89a4

Figure 2.23 Optimized geometries at the B3LYP/6-31G(2d,2p) level for possible isomers of **89a**; *Z-anti*(N=C) **89a1**; *Z-syn*(N=C) **89a2**; *E-anti*(N=C) **89a3**; *E-syn*(N=C) **89a4**.

Table 2.17 Calculated relative energy (kJ/mol) for four possible isomers of **89a**[1].

	E-syn(N=C)	*Z-anti(N=C)*	*Z-syn(N=C)*	*E-anti(N=C)*
89a	0	2	10	18

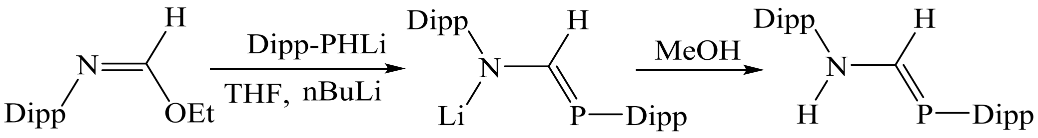
[1] B3LYP/6-31G(2d,2p); the estimate precision is ±5 kJ/mol.

2.4.3 Synthesis of *p*CH_3OPh-phosphaamidine 25b

pCH_3OPh-phosphaamidine **25b** can be synthesized from *p*CH_3OPh-phosphaamidinium triflate **89**. One equivalent of triethylamine was added to the solution of *p*CH_3OPh-phosphaamidinium triflate **89** in CH_2Cl_2 under N_2 at -70°C. Reaction progress was monitored with ^{31}P NMR spectroscopy and completed after 30 min stirring at RT. Dichloromethane was removed on a vacuum line and the product was extracted with diethyl ether by precipitating $HNEt_3CF_3SO_3$ as a white solid. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra of *p*CH_3OPh-phosphaamidine were run at RT in $CDCl_3$. These new results show that there are four isomers in solution and the major isomer is N-H which is in agreement with previously reported data from thermal reactions. A reaction scheme and mechanism can be found in Schemes 2.13 and 2.14.

2.5 Attempt at synthesis of phosphaformamidine 78

I attempted to synthesize novel phosphaformamidine **78** by two different procedures. In the first synthesis route, DippPH_2 was reacted with formimidate **29a** at -70°C under N_2 to produce lithium salt of phosphaformamidine **94** as intermediate. By adding methanol to the intermediate, phosphaformamidine **78** can be produced in the second step (Scheme 2.19).



29a **94** **78**

Scheme 2.19 Synthesis of phosphaformamidine **78**.

The ^{31}P NMR spectrum of crude material showed several peaks, so I attempted to purify the mixture. The product (phosphaphormamidine) is expected to be sensitive to the air and column chromatography couldn't be done in this case, so I attempted to isolate compound **78** from the mixture and grow good quality crystals. Several solvents such as heptanes, pentane, toluene and methanol were used to crystallize the crude material but the only crystals I could grow was a lithium ion coordination cluster that likely formed from air-oxidation and hydrolysis of the phosphaformamidine **78** through recrystallization from methanol (Figure 2.24 and Table 2.18). Details of the crystallographic data for **95** can be found in Appendix III Table A49-A54.

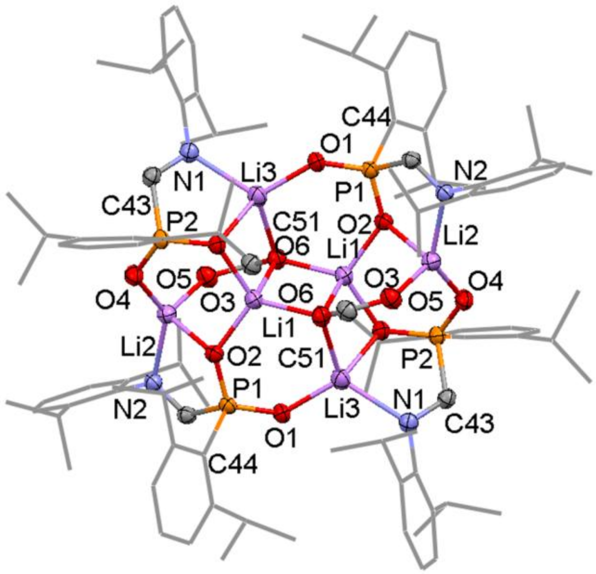
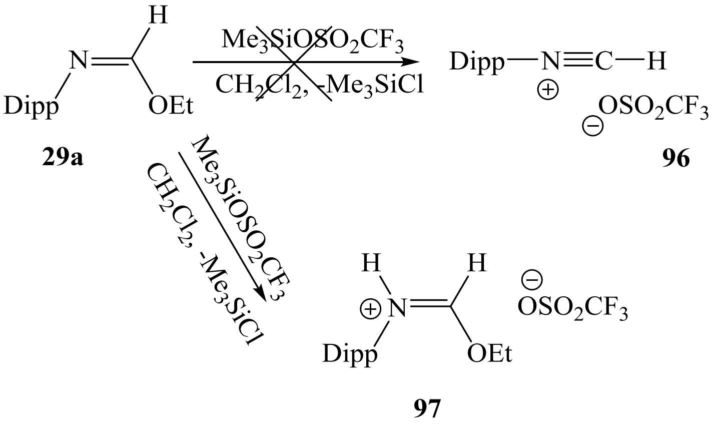


Figure 2.24 The central core of the cluster **95** as displacement ellipsoids (40% probability) and the Dipp group C atoms as line structures; all H atoms are omitted for clarity.

Table 2.18 Crystal data and structure refinement for cluster **95** and **97**

	95	**97**
Space group	P-1	Pccn
a/ Å	13.434(2)	13.7928(15)
b/ Å	15.249(3)	20.388(2)
c/ Å	16.906(5)	13.7109(15)
α	99.961(3)°	90°
β	102.179(3)°	90°
γ	113.131(2)°	90°
Z	1	8
Goodness-of-fit on F2	1.047	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1413	R1 = 0.0418, wR2 = 0.1058
R indices (all data)	R1 = 0.0952, wR2 = 0.1614	R1 = 0.0475, wR2 = 0.1113

After several unsuccessful attempts to make phosphaformamidine **78**, I decided to synthesize compound **78** by following Lammertsma's procedure[29] (Scheme 2.21). As already explained for **32**, **25b** and **77**, the first step to synthesize phosphaformamidine **78** is making formiminium triflate **96**.



Scheme 2.20 Attempted synthesis of **96** which ended up to compound **97**.

$Me_3SiOSO_2CF_3$ was added to the solution of formimidate **29a** in dichloromethane at -70°C under N_2 and stirred for 30 min at RT. The solution was concentrated by removing some of the solvent and then left at -25°C to grow crystals. The difference of this reaction with those mentioned in Sections 1-3 is the leaving group. In all other cases, one of the starting materials was imidoyl chloride (compound **80**, **14c**, **14b**) which contains chloride as a good leaving group, but to synthesize phosphaformamidine **78**, the available starting material is formimidate **29a** and $^-$OEt is a leaving group. Because $^-$OEt is a poorer leaving group compared with $^-$Cl from imidoyl chloride, it was not easy to remove it and instead of H-nitrilium triflate, the product formed is ethyl-formimidaminium triflate **97** which is merely the protonation of the formimidate starting material).

2.5.1 Crystal Structure

The crystal structure of ethyl-formimidaminium triflate **97** or protonated formimidate was determined at -100°C and crystallographic data for **97** can be found in Table 2.18 and Appendix III Table A55-A61. The C=N bond length in **97** is 1.287(2) Å which is shorter than C=N in protonated ^{t}Bu-amide **86** (1.294(2) Å) and C-N bond in ^{t}Bu amide **79** (1.341(17) Å). The C-O bond length in **97** is 1.2881(18) Å, which is not significantly different than C-O in **86** 1.297(4) Å and longer than the C=O double bond in ^{t}Bu amide **79** (1.228(16) Å) (the range of C=O for amides is 1.225-1.243 Å)[72]. The C-N-C angle is 123.2(2) and the sum of angles around nitrogen is 359.87(2)°, which shows that nitrogen is planar. The sum of angles around the backbone carbon is 359.93(2)°, which shows that carbon is planar.

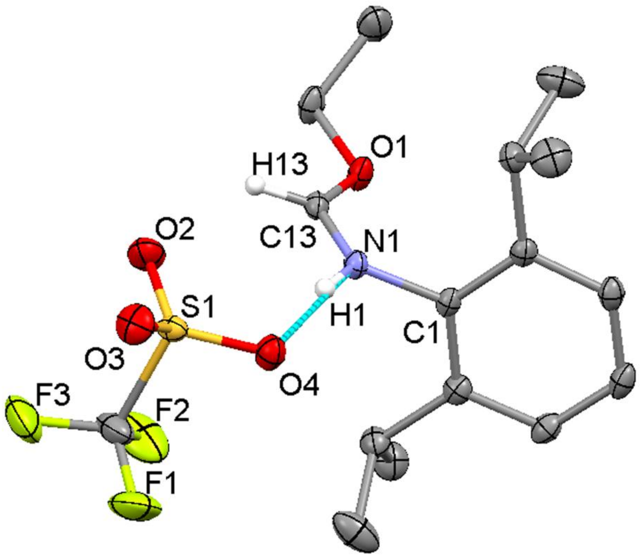


Figure 2.25 Displacement ellipsoids plot (40% probability) showing the molecular structure of **97** linked through H-bonding to O. H atoms other than those involved in these bonds are omitted for clarity.

2.5.2 NMR Spectroscopy

Pure crystals of ethyl-formimidaminium triflate **97** were used to make an NMR sample in $CDCl_3$ under N_2. ^1H NMR, ^{13}C NMR and HSQC spectra were run to assign all the peaks (Table 2.19). The ^1H NMR spectrum of ethyl-formimidaminium triflate **97** for CH of ^+NH-CH showed a singlet at $\delta = 9.21$ ppm and the NH of ^+NH-CH showed a broad singlet at $\delta = 12.51$ ppm. The ^{13}C NMR of ethyl-formimidaminium triflate **97** (Figure 2.26) shows a singlet for CH_2 of the EtO group with a very downfield chemical shift at $\delta = 76.95$ ppm due to a neighbouring oxygen atom (the high intensity triplet pattern peak at $\delta = 77.23$ ppm is from the $CDCl_3$ solvent).

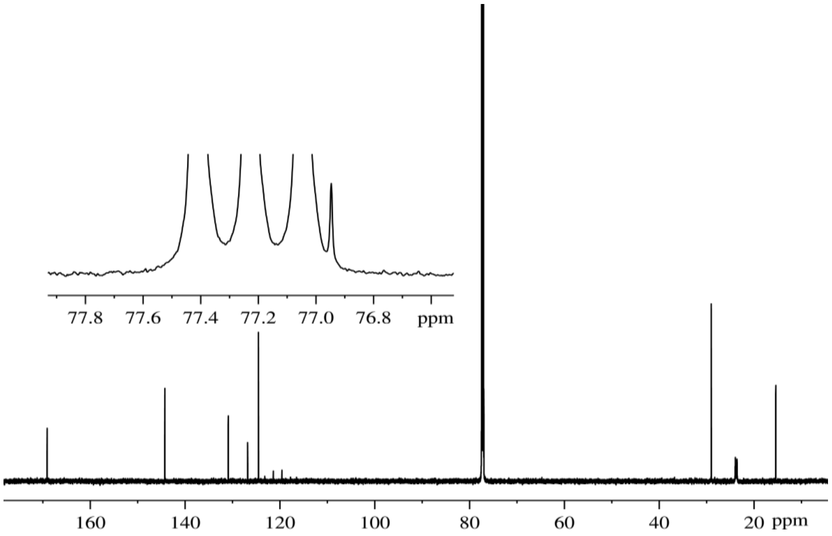


Figure 2.26 ^{13}C NMR spectrum of ethyl-formimidaminium triflate **97** in CDCl$_3$ at RT.

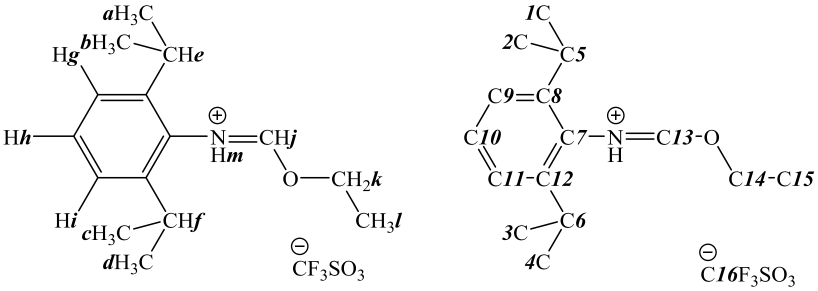


Table 2.19 ^{1}H NMR and ^{13}C NMR data for **97** at RT in CDCl$_3$.

Nucleus	δ, ppm	mult	J, Hz	**Nucleus**	δ, ppm	mult
^{1}H				^{13}C [^{1}H]		
H ***a,b,c,d***	1.21	d	6.3	C ***15***	15.37	s
H ***l***	1.47	t	7.7	C ***1,2,3,4***	23.74	s
H ***e,f***	2.91	sep	7.0	C ***5,6***	28.98	s
H ***k***	4.82	q	7.0	C ***14***	76.95	s
H ***g,i***	7.26	d	7.8	C ***16***	120.47	q
H ***h***	7.44	t	7.7	C ***9,11***	124.50	s
H ***j***	9.21	s		C ***7***	126.78	s
H ***m***	12.51	br s		C ***10***	130.88	s
				C ***8,12***	144.26	s
				C ***13***	169.09	s

Because of producing the unexpected compound **97** in the first step, I would not continue with the next steps to make phosphaformamidine triflate and phosphaformamidine.

2.6 Conclusions

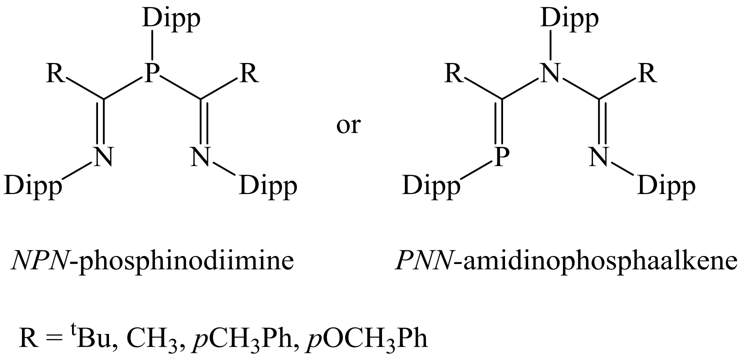
Three different protonated phosphaamidines (pCH$_3$OPh-phosphaaminium triflate **89**, CH$_3$-phosphaaminium triflate **88** and ^{t}Bu-phosphaaminium triflate **87** were synthesized and fully characterized. We found out that for both **88** and **89**, *E* is the major isomer and this result is different with **87** where *Z* is the major isomer. These results are confirmed by solution NMR spectroscopy, crystal structures and DFT calculations. In the case of **88** and **89**, the major isomers show up at higher frequency in the ^{31}P NMR spectra. This is different with the case of ^{t}Bu-phosphaamidinium triflate which shows the major isomer at lower frequency. We also realized that neutral ^{t}Bu-phosphaamidine **32** also shows different results compared with pCH$_3$OPh-phosphaamidine **25b** and CH$_3$-phosphaamidine **77**. Both **77** and **25b** show four isomers with similar ratios for each isomer in solution and the major isomer has the *E* geometry, but **32** shows only one isomer with *Z* geometry. If we compare these three different backbone substitutions with respect to the electron donating ability, then both CH$_3$ and ^{t}Bu are electron donors and pCH$_3$Ph is weakly electron withdrawing, so **32** and **77** should show the same result. If we consider the resonance properties, then we expect again that **32** and **77** should show the same result, because only pCH$_3$Ph can have resonance. The last property is size, where CH$_3$ and pCH$_3$Ph are both smaller than a ^{t}Bu group, so we propose that the size of the substituent at the backbone carbon is the major reason that we see only one isomer for **32** and similar distribution of isomeric species for **77** and **25b**.

Chapter 3

Phosphinodiimines

3.1 Introduction

This chapter discuses the synthesis of novel neutral phosphinodiimines, the study of their possible isomers using solution and solid-state NMR spectroscopy, and comparing data with crystal structures and computational results to find the most stable geometries for the compounds. There are several examples of phosphinodiimine salts and metal complexes but neutral phosphinodiimines are rare (Section 1.4) and we are the first group that studied the isomerization of these compounds. Because of several advantages in using the Dipp group (Chapter 1), we decided to use it as the bulky substituent on nitrogen and phosphorus to synthesize phosphinodiimines. To understand the effect of substitution on the backbone carbon in isomerisation, I attempted to synthesize trisubstituted phosphinodiimines with different substitution (R = ^{t}Bu, CH_3, *p*OCH_3Ph, *p*CH_3Ph) (Scheme 3.1) which will be explained in detail in this chapter.



Scheme 3.1 *N,P,N*-trisubstituted phosphinodiimines or *P,N,N*-trisubstituted amidinophosphaalkenes.

The first trisubstituted phosphinodiimine studied in this chapter is 2,6-diisopropylphenyl-*bis*(*N*-(2,2-dimethylpropylidene-2,6-diisopropylphenylimidoyl) phosphane which I will abbreviate to: ^{t}Bu-phosphinodiimine **98** or just ‘NPN’. After I synthesized this novel compound, I performed an advanced NMR study and also determined the crystal structure along with a computational study to determine the possible isomers for **98**. Thereafter, I synthesized 2,6-diisopropylphenyl-*bis*(*N*-(ethylidine-2,6-diisopropylphenylimidoyl)phosphane which I will abbreviate to: CH_3-phosphinodiimine **99** or just ‘PNN’ as a novel compound by two different procedures. CH_3-phosphinodiimine **99** has CH_3 groups on the backbone carbon atoms which are less bulky than ^{t}Bu and is a very good example to study the effect of substitution on isomerism. CH_3-phosphinodiimine **99** is much more reactive than ^{t}Bu-phosphinodiimine **98**, perhaps because of the small size of CH_3 groups, and it is hard to control its reaction. An advanced NMR study along with computation has been done to understand the isomerisation and find the most stable geometry. For CH_3-phosphinodiimine **99**, the result was different compared with ^{t}Bu-phosphinodiimine **98** and the product is an amidinophosphaalkene (Scheme 3.1). We attempted to synthesize the *p*CH_3Ph **102** and *p*OCH_3Ph phosphinodiimines **103** which have *p*CH_3Ph and *p*OCH_3Ph groups on the backbone carbon to see if the result is in agreement with ^{t}Bu-phosphinodiimine **98** or CH_3-phosphinodiimine **99**.

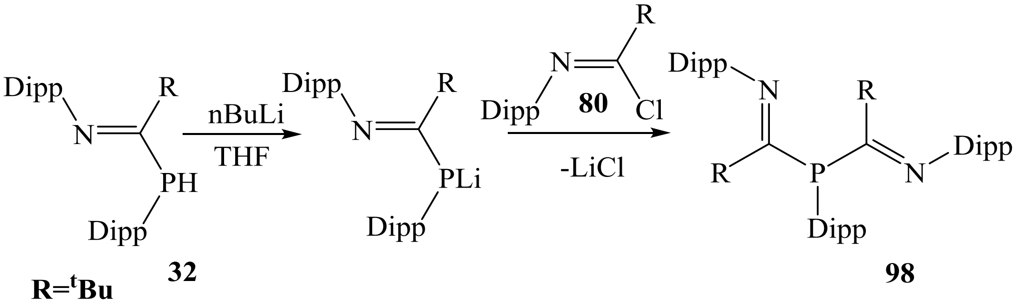
One of the major starting materials to synthesize all the phosphinodiimines in this chapter are imidoyl chlorides which were prepared as previously described following Scheme 2.3.[10] $DippPH_2$ **24** is the other major starting material to synthesize our phosphinodiimines (see Scheme 2.4).[8]

3.2 ^{t}Bu-phosphinodiimine (NPN)

^{t}Bu-phosphinodiimine formed when we were synthesizing the ^{t}Bu-phosphaamidine **32** for the first time. After filtration and isolation of ^{t}Bu-phosphaamidine as a white solid, the yellow filtrate was left in a freezer. The next morning bright yellow block shaped crystals formed in the Schlenk tube. We determined the crystal structure and found it to be ^{t}Bu-phosphinodiimine **98**. Based on our experience in synthesizing phosphaamidines we eager making phosphinodiimines on purpose.

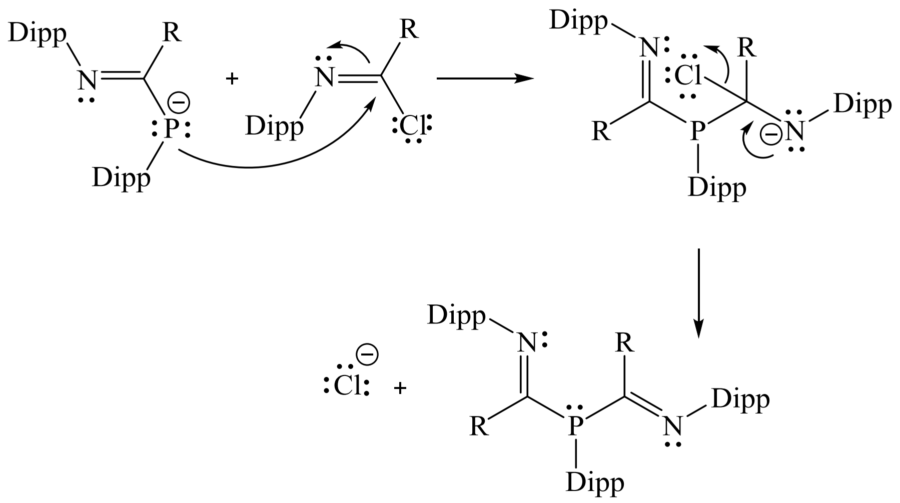
3.2.1 Synthesis of ^{t}Bu-phosphinodiimine 98 using *n*BuLi

After discovering **98** by accident, I decided to prepare it deliberately and if possible, quantitatively. In the first step, I synthesized ^{t}Bu-phosphaamidine **32** (Section 2.2.1 and Scheme 2.5), then one equivalent of *n*BuLi at -60°C under N_2 was added to the solution of ^{t}Bu-phosphaamidine in THF. Reaction progress was followed by ^{31}P NMR spectroscopy and after an hour stirring at RT, one equivalent of ^{t}Bu-imidoylchloride **80** was added to the solution at -30°C under N_2 to produce ^{t}Bu-phosphinodiimine **98** (Scheme 3.2). Workup consisted of removing THF on the vacuum and removal of LiCl as a white precipitate by extraction with hexane.



Scheme 3.2 Synthesis of ^{t}Bu-phosphinodiimine **98** using *n*BuLi.

Crystallization from a minimum volume of hot heptanes produced bright yellow crystals which were pure by ^{31}P and ^{1}H NMR spectroscopy and suitable for X-ray crystallographic work. The proposed mechanism to form ^{t}Bu-phosphaamidine **98** is outlined in Scheme 3.3. *n*BuLi as a strong base removes a proton from phosphaamidine **32** and produces the phosphaamidine anion or phosphaamidinate as an intermediate. In the next step, the phosphorus atom of phosphaamidinate acts as a nucleophile adding to the carbon of imidoyl chloride **80** which is an electrophile to produce a second intermediate. From this intermediate, reformation of a double bond from N induces the loss of Cl$^-$, resulting in phosphinodiimine **98**.



Scheme 3.3 Proposed mechanisms for the formation of ^{t}Bu-phosphinodiimine **98**.

3.2.2 Crystal structure

Pure yellow crystals grew from heptanes at -25°C under N_2 and crystallographic data was collected at -100°C (Figure 3.1). Based on the crystal structure, the P-C bond lengths are 1.8898(17) Å and 1.9039(17) Å, which are both longer than P-C in ^{t}Bu-phosphaamidine

32 (1.865(3) Å) (the range of P=C is (1.70-1.76 Å) for C-amino substituted phosphaalkenes[71] and the range of P-C is (1.840-1.870 Å) for C-P-Csp^3)[72]. The N=C bond lengths are 1.267(2) Å and 1.271(2) Å, which is close to N=C in **32** (1.273(3) Å) (the range of Csp^3-Nsp^2 is (1.446-1.461 Å) and the range of Csp^2=N is (1.275-1.285 Å).[72] For each derivative, whether phosphinodiimine or amidinophosphaalkene, a *cis-trans* isomerism could exist with respect to each C=P or N=C double bond as well as rotational conformations around the C-N or C-P single bonds. The crystallographic data confirmed that the geometry of ^{t}Bu-phosphinodiimine **98** in solid-state is *ZE*. The sum of angles around phosphorus is only 328.70(14)°, indicative of a strongly pyramidal structure at phosphorus. Crystallographic data and selected bond lengths and angles can be found in Tables 3.1 and 3.2. The detailed crystallographic data can be found in Appendix III Table A62-A68.

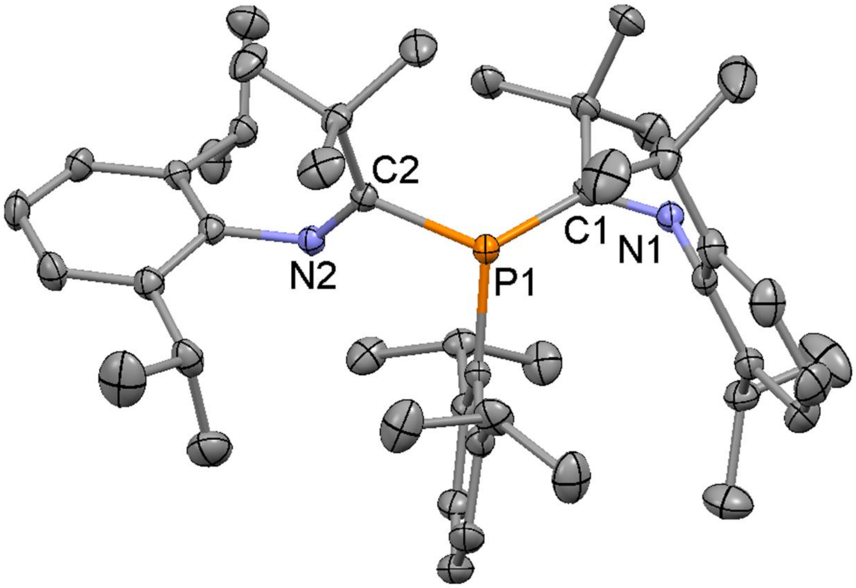


Figure 3.1 Displacement ellipsoids plot (40% probability) showing the molecular structure of ^{t}Bu-phosphinodiimine **98**. Hydrogen atoms on carbon are omitted for clarity.

Table 3.1 Crystal data and structure refinement for **98**, **100** and **101**.

	98	**100**	**101**
Space group	P2$_1$/c	P2$_1$/c	C2/c
a/ Å	17.7011(11)	17.0825(10)	22.2410(15)
b/ Å	11.0019(7)	14.1119(9)	12.8371(9)
c/ Å	25.0671(16)	20.0528(12)	19.073(2)
α	90°	90°	90°
β	103.698(1)°	92.0680°	117.5930(10)°
γ	90°	90°	90°
Z	4	4	4
Goodness-of-fit on F2	1.030	1.018	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1337	R1 = 0.0475, wR2 = 0.1188	R1 = 0.0660, wR2 = 0.1776
R indices (all data)	R1 = 0.0875, wR2 = 0.1519	R1 = 0.0663, wR2 = 0.1313	R1 = 0.1009, wR2 = 0.2031

Table 3.2 Selected Bond lengths and angles for **98**, **100** and **99**.

	98		**100**		**99**
P-C$_1$	1.8911(19)	P-C$_1$	1.8435(15)	P=C$_{13}$	1.696(9)
P-C$_2$	1.889(2)	P-C$_{28}$	1.8609(15)	P-C$_{\mathrm{aryl}}$	1.839(11)
P-C$_{\mathrm{aryl}}$	1.851(2)	P-C$_{\mathrm{aryl}}$	1.8548(16)	N$_1$-C$_{13}$	1.440(10)
C$_1$=N$_1$	1.270(2)	C$_1$=N$_1$	1.2788(19)	N$_1$-C$_{\mathrm{aryl}}$	1.464(11)
C$_2$=N$_2$	1.279(2)	C$_2$-N$_{28}$	1.3453(19)	N$_1$-C$_{15}$	1.387(11)
N$_1$-C$_{\mathrm{aryl}}$	1.417(3)	N$_1$-C$_{\mathrm{aryl}}$	1.4298(18)	N$_2$=C$_{15}$	1.358(11)
N$_2$-C$_{\mathrm{aryl}}$	1.425(2)	N$_2$-C$_{\mathrm{aryl}}$	1.4276(19)	N$_2$-C$_{\mathrm{aryl}}$	1.465(11)
C$_1$-P-C$_2$	115.75(8)	C$_1$-P-C$_{28}$	107.60(7)	C$_{\mathrm{aryl}}$-P=C$_{13}$	100.3(5)
C$_1$=N-C$_{\mathrm{aryl}}$	132.06(17)	C$_1$=N-C$_{\mathrm{aryl}}$	119.77(12)	C$_{15}$=N$_2$-C$_{\mathrm{aryl}}$	118.4(9)
C$_2$=N-C$_{\mathrm{aryl}}$	127.15(17)	C$_2$-N-C$_{\mathrm{aryl}}$	123.87(13)	C$_{13}$-N$_1$-C$_{15}$	122.0(8)

3.2.3 Solution NMR Spectroscopy

Pure yellow crystals of ^{t}Bu-phosphinodiimine **98** were dissolved in $CDCl_3$ under N_2 to make an NMR sample. The ^{31}P NMR (proton-coupled) spectrum at RT showed two broad singlets and the ^{1}H NMR spectrum also showed line broadening at RT, so low temperature NMR spectroscopy was tried (Figure 3.2). At -25°C better resolution of the coupling patterns was observed in ^{1}H NMR and ^{31}P NMR spectra.

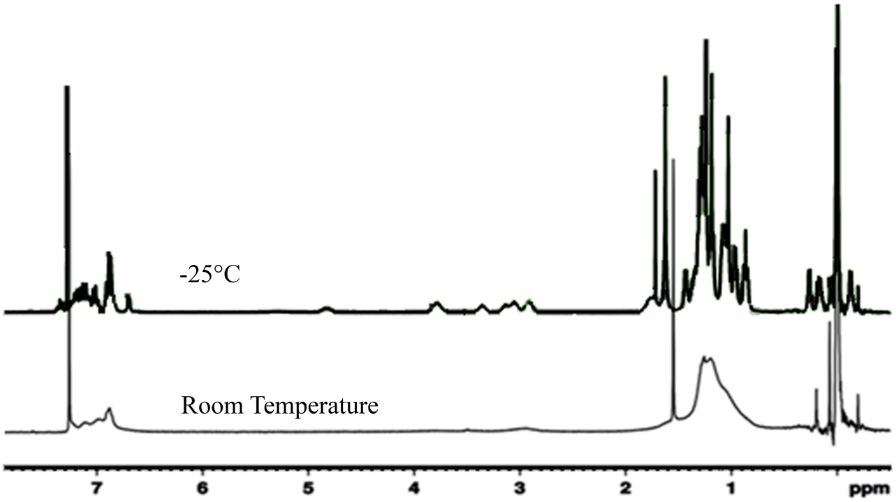


Figure 3.2 ^{1}H NMR spectrum of ^{t}Bu-phosphinodiimine **98** at RT and -25°C in $CDCl_3$.

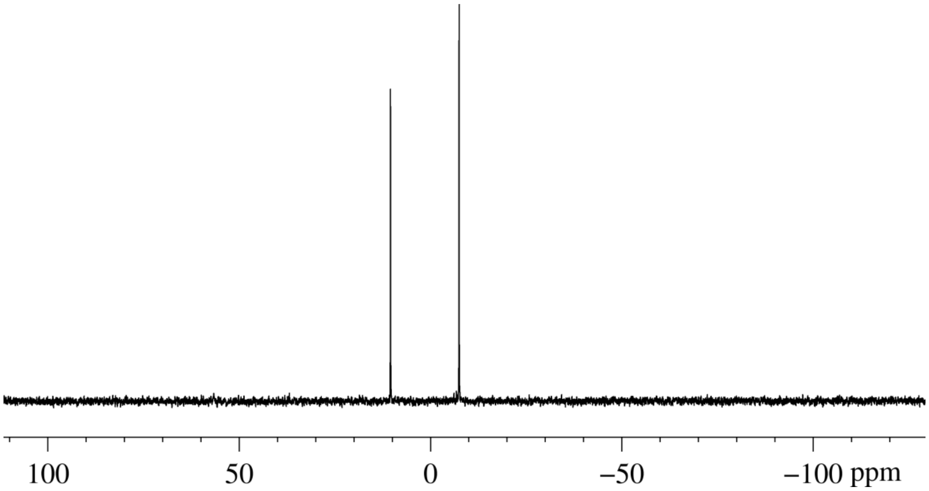


Figure 3.3 ^{31}P NMR spectrum of ^{t}Bu-phosphinodiimine **98** at -25°C in $CDCl_3$.

The ^{31}P NMR proton-coupled spectra at −25°C showed two sharp singlet at δ = -7.54 ppm and δ = 10.40 ppm in $CDCl_3$ which means there are two isomers in solution (Figure 3.3). Previously in 1990, a singlet with δ = –3 ppm was observed for phenyl bis(*N*-phenyl-benzimidoyl)phosphane hydrochloride by Romanov's group.[55]

The ^{1}H NMR spectrum of ^{t}Bu-phosphinodiimine **98** in $CDCl_3$ at −25°C is shown in Figure 3.4. Integration of the ^{1}H resonance also fits for two isomers at −25°C. One of the interesting points is some very high field chemical shifts for CH_3-*iso* groups due to the ring shielding effect. ^{13}C NMR, COSY, HSQC and HMBC spectra were run at -25°C in $CDCl_3$ to assign all the peaks. A list of ^{31}P NMR and ^{1}H NMR data can be found in Table 3.1. Based on these data, two singlets for ^{t}Bu groups are observed at δ = 1.23 ppm and δ = 1.61 ppm for the major isomer and at δ = 1.02 ppm and δ = 1.17 ppm for minor isomer indicating that there is no symmetry in this compound in both cases of major and minor isomers.

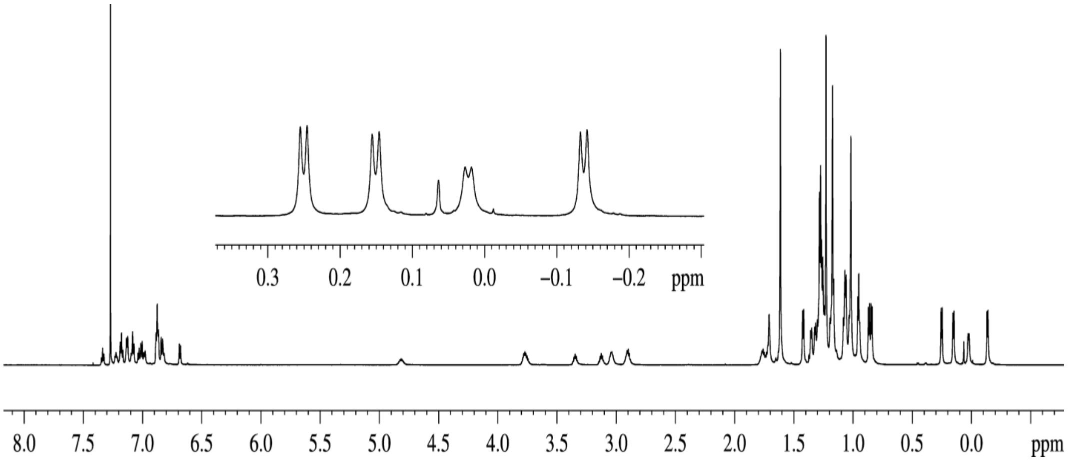


Figure 3.4 ^{1}H NMR spectrum of ^{t}Bu-phosphinodiimine **98** at -25°C in $CDCl_3$.

Table 3.3 ^{1}H NMR, ^{13}C NMR and ^{31}P NMR data for **98** at -25°C in $CDCl_3$.

	Major				**Minor**		
Nucleus	δ, ppm	mult	J, Hz	**Nucleus**	δ, ppm	mult	J, Hz
^{31}P NMR				**^{31}P NMR**			
P	-7.54	s		P-H	10.41	s	
^{1}H NMR				**^{1}H NMR**			
backbone				*backbone*			
^{t}Bu	1.61,1.23	s		^{t}Bu	1.17,1.02	s	
Dipp-P				*Dipp-P*			
CH_3-*iso*	0.25,0.95,1.28	d	6.3	CH_3-*iso*	1.27,1.29, 1.32,1.35	br d	
CH-*iso*	3.74,3.35	sep	6.3	CH-*iso*	4.82,3.77	sep	6.3
CH_{meta}	6.86-6.89	d	7.7	CH_{meta}	7.18,7.23	br d	
CH_{para}	7.18	t	7.7	CH_{para}	7.34	t	7.7
Dipp-N$_1$				*Dipp-N$_1$*			
CH_3-*iso*	1.42,1.07, 0.95,0.02	d	6.3	CH_3-*iso*	1.06,1.19, 1.29,1.32	br d	
CH-*iso*	3.13,1.78	sep	7.0	CH-*iso*	3.04,3.05	br s	
CH_{meta}	7.01,7.13	br d		CH_{meta}	7.03,7.22	br d	
CH_{para}	6.88	t	7.0	CH_{para}	7.08	t	7.7
Dipp-N$_2$				*Dipp-N$_2$*			
CH_3-*iso*	0.86,0.84, -0.15,0.14	d		CH_3-*iso*	1.03,1.08, 1.17,1.26	br s	
CH-*iso*	1.75,1.73	sep	7.0	CH-*iso*	2.88,2.91	br sep	
CH_{meta}	6.84,6.68	br d		CH_{meta}	6.89	br	
CH_{para}	6.88	br s		CH_{para}	7.08	t	7.7
^{13}C NMR				**^{13}C NMR**			
C=N	182.63	d	44	C=N	187.51	d	39

3.2.4 Solid state NMR spectroscopy

As already explained in Section 2.2.1.3, we can get the same type of information from high resolution MAS solid state NMR for comparison to solution NMR spectra. To study the presence of possible isomers for ^{t}Bu-phosphinodiimine **98**, we have done solid state ^{31}P CP NMR spectroscopy, at different MAS spinning rates. The isotropic centre band for **98** can easily be identified because it remains in the same position at different spinning rates. The spinning sidebands are separated by a distance equal to the spinning speed in Hz.[78]

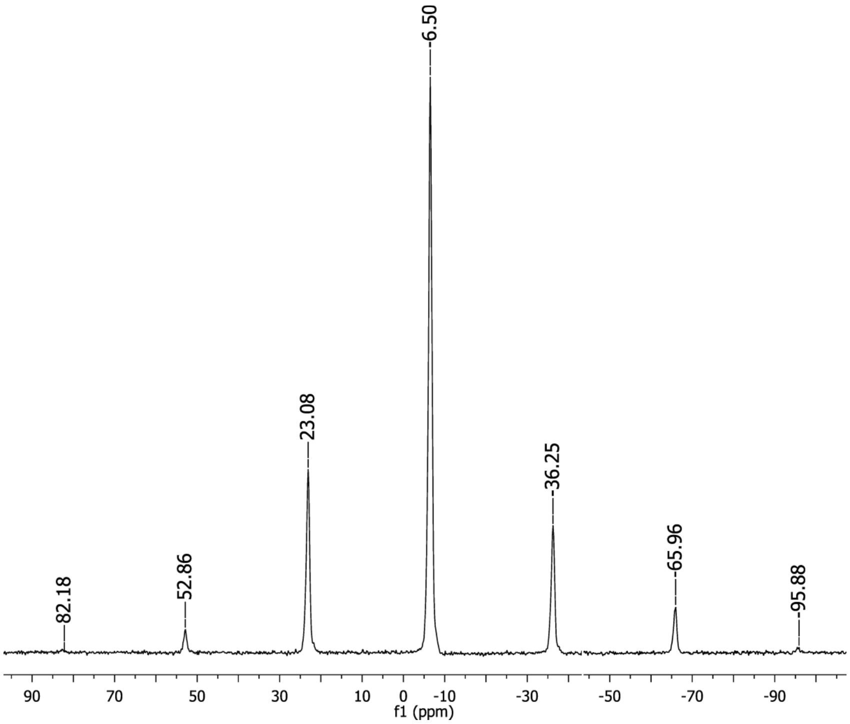


Figure 3.5 CP-MAS ^{31}P-{^{1}H} solid-state NMR spectrum (6 kHz) of ^{t}Bu-phosphinodiimine **98**.

The isotropic centre band for ^{t}Bu-phosphinodiimine **98** showed up at δ_{iso} = - 6.50 ppm as the only isotropic centre band present at MAS spinning rates of 4, 6, 10 and 15 kHz. This chemical shift is close to the chemical shift of the major isomer (δ = - 7.54 ppm). This evidence confirmed the presence of only one isomer in solid state which is in agreement with the crystal structure that we found as *ZE*. This result is different than the solution NMR observation where we found two isomers at RT and at -25°C (Figure 3.5).

3.2.5 Computational Results

Solution NMR evidence for ^{t}Bu-phosphinodiimine **98** includes two singlets in the ^{31}P NMR spectrum (δ = -7.54 ppm and δ = 10.41 ppm). At this point we understand that there should be two isomers in solution. Based on crystallographic data, the geometry in the crystal structure is *ZE*. To better understand this evidence, we have done hybrid DFT calculations (B3LYP/6-31G2d2p//B3LYP/6-31Gdp) on three possible isomers of **98** and we were also interested to find the most stable isomer in the gas phase. The computed energy differences and geometries of these possible isomers were shown in Table 3.4 and Figure 3.6. As we see in Table 3.4, the relative energy of the *ZE* isomer of **98** is set to 0 kJ/mol, which is the most stable isomer. The chemical shift in the solid state is -6.50 ppm which is very close to the chemical shift of the major isomer in solution (-7.54 ppm). We also know that the isomer in the solid state (based on crystal data) is *ZE*, so we can conclude that the major isomer in solution is also *ZE*. The second isomer which is *EE* has a calculated relative energy of 15 kJ/mol which is low enough to be observed in solution. The third isomer is *ZZ* with the relative energy of 39 kJ/mol and this energy is higher than the accuracy energy for isomerization at the B3LYP/6-31G* level (17 kJ/mol), so it is reasonable to assume that the minor solution isomer is *EE*.[79]

Table 3.4 Calculated relative energy (kJ/mol) for three possible isomers of **98**[1].

Compound	*ZE*	*EE*	*ZZ*
98	0	15	39

[1] B3LYP/6-31G(2d,2p); the estimate precision is ±5 kJ/mol.

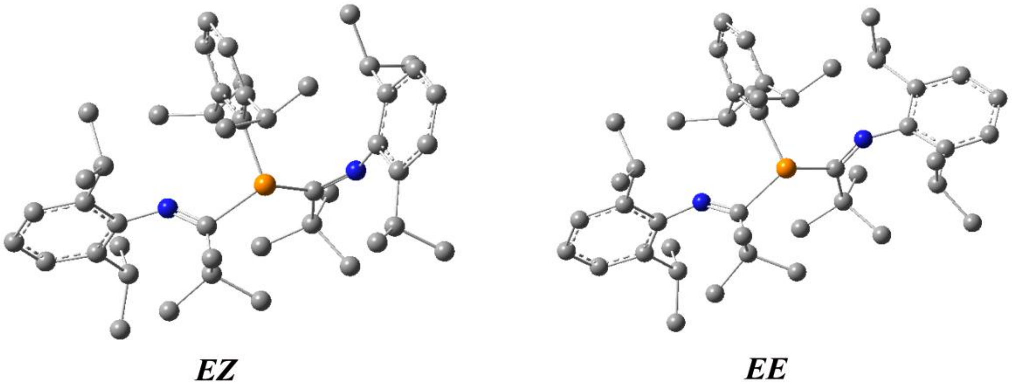


Figure 3.6 Optimized geometry at the level of B3LYP/6-31G(2d,2p) for *EZ*, *EE* and *ZZ* isomers of ^{t}Bu-phosphinodiimine **98**.

3.3 CH$_3$-phosphinodiimine (PNN) 99

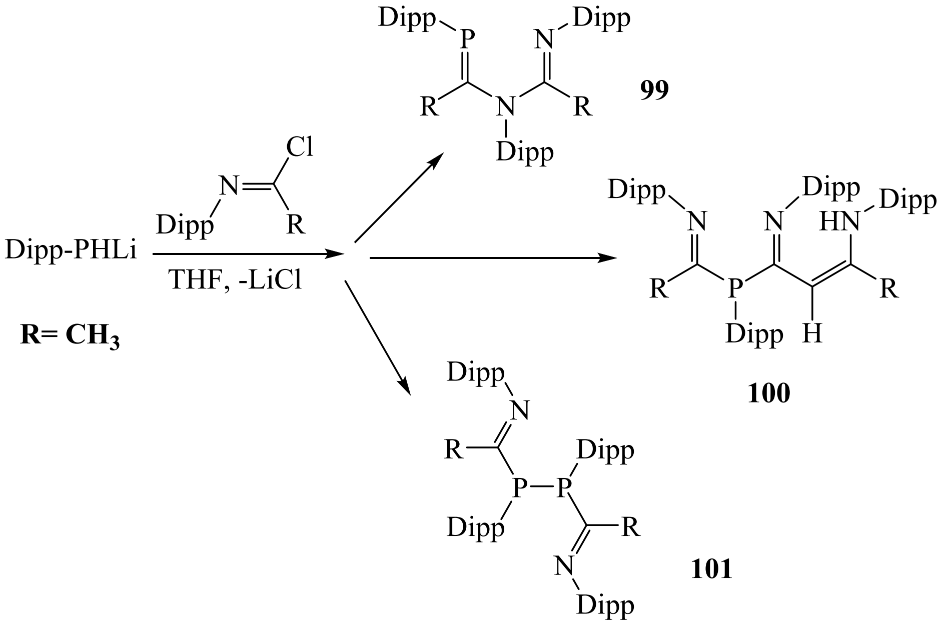
I attempted two different synthesis routes to make the CH$_3$-phosphinodiimine compound **99**. The first attempt followed the same procedure used to synthesize the ^{t}Bu-phosphinodiimine **98** with *n*BuLi. ^{31}P NMR evidence on crude material synthesized with this procedure showed several peaks which are explained in Section 3.3.2.2. Using *n*BuLi to synthesize the bulky ^{t}Bu-phosphinodiimine **98** or ^{t}Bu-NPN worked well, but in case of CH$_3$-phosphinodiimine **99** or CH$_3$-PNN, it was hard to control the reaction, purify the crude material or isolate different components, so I decided to attempt another procedure.

The second attempt used a direct thermal reaction of DippPH$_2$ **24** with CH$_3$-imidoyl chloride **14c** in xylenes which was previously used for the synthesis of the *p*CH$_3$Ph and *p*CH$_3$OPh phosphaamidines **25a-b** by our group.[25] ^{31}P NMR evidence of pure product which was synthesized following this second procedure showed CH$_3$-phosphinodiimine **99** as the only product.

3.3.1 Synthesis of CH$_3$-phosphinodiimine 99 using *n*BuLi

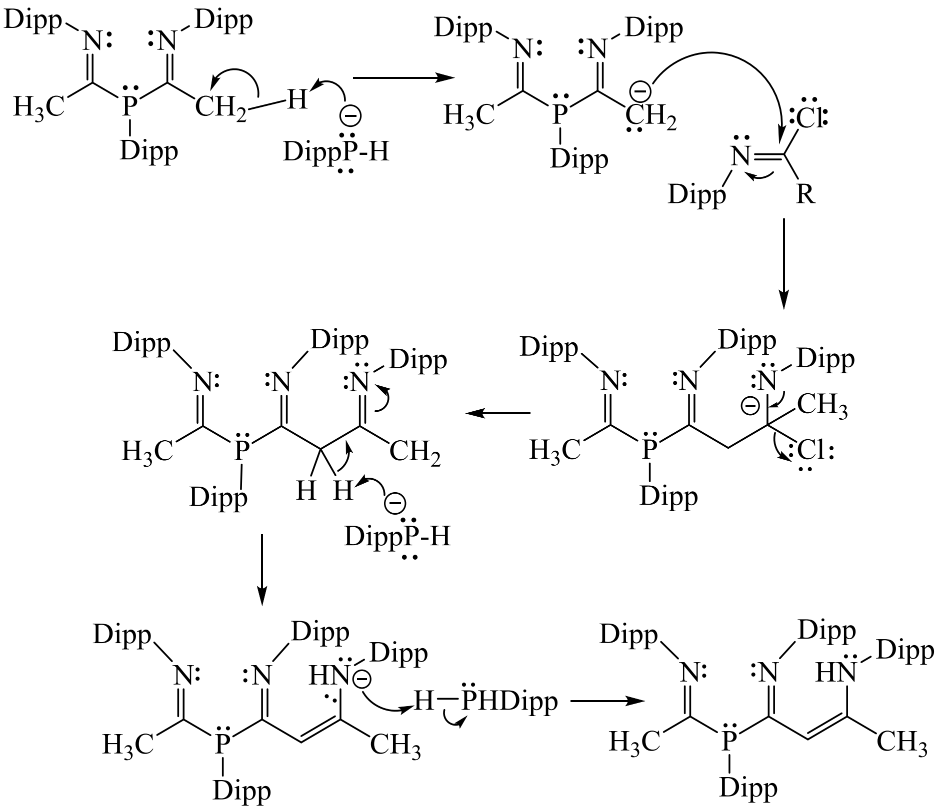
The first synthesis route followed the same procedure that I used for ^{t}Bu-phosphinodiimine **98** (Section 3.2.1) by reacting two equivalents of imidoyl chloride **14c** with DippPHLi in THF. The ^{31}P NMR spectrum showed signals of more than three components. Yellow crude material was recrystallized with EtOH and at RT pale yellow crystals formed (CH$_3$-phosphinodiimine **99**, 30%) which were isolated by filtration. The yellow filtrate was left in a freezer to see if another component would crystallize. Nothing came out after several days, so EtOH was removed on a vacuum line and the yellow residue was recrystallized from heptanes and hexane in two separate Schlenk tubes and left in a freezer to grow crystals and two other components were isolated (**100** in 25% and **101** in 21% yields). There were other phosphorus components that we could not isolate by recrystallization or sublimation. The entire components that we could isolate from the *n*BuLi reaction are shown in Scheme 3.4.

Compound **99** (PNN) was made through a similar mechanism to ^{t}Bu-phosphinodiimine **98** (for further details check Section 3.2.1). The only difference is which phosphaamidine isomer starts the reaction. These results can be rationalized if for **99**, the major isomer of CH$_3$-phosphaamidine, which is a C=P isomer, reacted with imidoyl chloride. However, in the case of **98** (NPN), the (C=N) isomer reacted with imidoyl chloride.



Scheme 3.4 Synthesis of CH_3-phosphinodiimine **99** and two others isolated components **100-101**.

The proposed mechanism to synthesize compound **100** is presented in Scheme 3.5. The important point in this mechanism is that the starting material is CH_3-NPN, not **99** (CH_3-PNN). To make CH_3-NPN, the minor isomer of CH_3-phosphaamidine (C=N isomer) should react with imidoyl chloride by exactly the same mechanism as explained in Scheme 3.3 for ^{t}Bu-phosphinodiimine. After making CH_3-NPN, in the next step $DippPH^-$ removes (as a base) the H from the backbone CH_3 group and makes CH_2^-, which as nucleophile will add to the carbon atom of imidoyl chloride and in a next step, Cl^- is eliminated.



Scheme 3.5 Proposed mechanism for the formation of compound **100**.

Compound **101** can be made through the radical reaction of two CH_3-phosphaamidines. In this case, both of the CH_3-phosphaamidines are the minor isomer ((C=N) isomer) where there is P-H in the compound.

3.3.1.1 Crystal structure of 100

Pure yellow crystals of **100** grew from heptanes at -25°C under N_2 after three days. Crystallographic data was determined at -100°C and a depiction of the crystal structure can be found in Figure 3.7. Based on this crystal structure, the P-C bond lengths are 1.8435(15) Å and 1.8609(15) Å, which are shorter than the P-C bond lengths in ^{t}Bu-phosphinodiimine **98** (1.8898(17) Å and 1.9039(17) Å) (the range of P=C is (1.70-1.76

Å) for C-amino substituted phosphaalkenes[71] and the range of P-C is (1.840-1.870 Å)[72]). The N_1=C_1 bond length is 1.2788(19) Å and N_2-C_{28} is 1.3453(19) Å, which are longer than the N=C bond length in **98** (1.267(2) Å and 1.271(2) Å). The sum of angles around phosphorus is 316.34(12)°, indicative of a strongly pyramidal structure at phosphorus similar to ^{t}Bu-phosphinodiimine **98**. Both compounds **98** and **100** have the $P2_1/c$ space group with four molecules in the unit cells in both cases. The sum of angles around N_2 is 357.27(3)° that shows N2 is planar. Crystallographic data and selected bond lengths and angles can be found in Tables 3.1 and 3.2. The detailed crystallographic data can be found in Appendix III Table A69-A75.

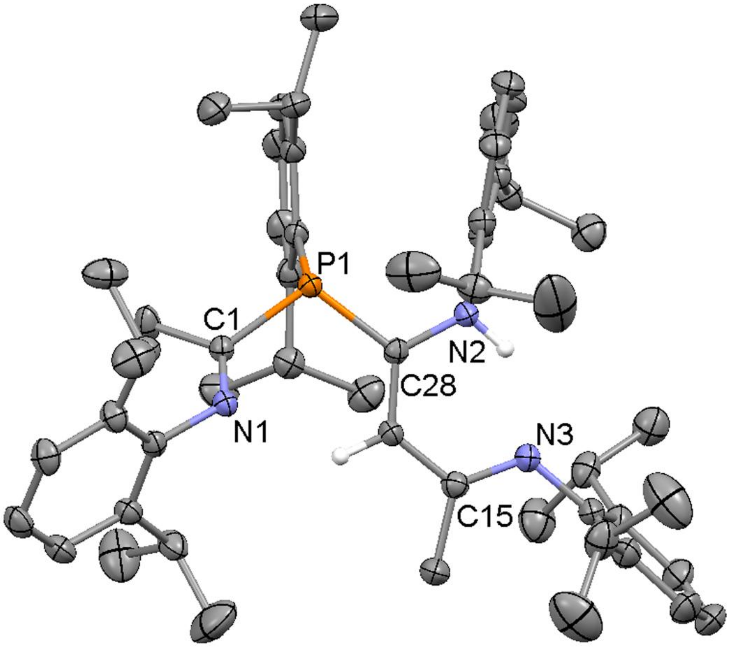


Figure 3.7 Displacement ellipsoids plot (40% probability) showing the molecular structure of **100**. Hydrogen atoms on carbon are omitted for clarity.

Pure yellow crystals of **101** grew from hexanes at -25°C under N_2 after four days. Crystallographic data was determined at -100°C and a representation of the crystal structure is found in Figure 3.8. The space group of **101** is C2/c with four molecules in the unit cell. The midpoint of the P–P bond is located at a 2-fold rotation axis. Based on the crystal structure, the P-P bond length is 2.2456(13) Å and is a single bond (the P-P single bond for Dipp(H)P-P(H)Dipp **104** is 2.2060(8) Å, Table 4.2). The N_1=C_1 bond length is 1.325(3) Å which is longer than the N=C bond length in **32** (1.273(3) Å) and shorter than the N-C bond in **25a** (1.368(2) Å) and **25b** (1.366(3) Å) (the range of Csp^3-Nsp^2 is (1.446-1.461 Å) and the range of Csp^2=N is (1.275-1.285 Å)).[72] The sum of angles around phosphorus in **101** is 314.40(16)°, indicative of a pyramidal structure at phosphorus, which is larger than those found for **104** (309.84(19)°) and ^{t}Bu-phosphaamidine **32** (298.1(2)°). Crystallographic data can be found in Table 3.1 and detailed crystallographic data in Appendix III Table A76-A81.

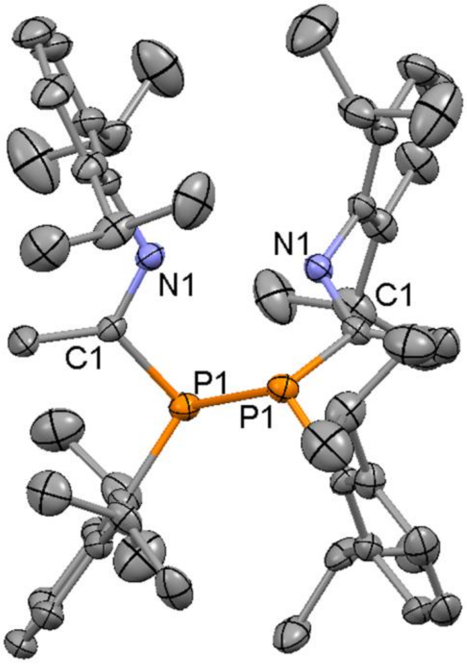
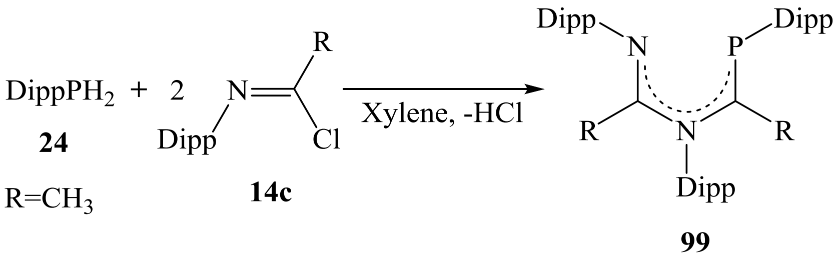


Figure 3.8 Displacement ellipsoids plot (40% probability) of the molecular structure of diphosphaamidine **101** with crystallographic 2-fold symmetry. Hydrogen atoms on methyl and Dipp groups are omitted.

3.3.2 Synthesis of CH_3-phosphinodiimine 99 using thermal reaction

I also attempted to make CH_3-phosphinodiimine **99** using a direct thermal reaction. One equivalent of $DippPH_2$ **24** and two equivalents of CH_3-imidoyl chloride **14c** were refluxed in xylenes overnight to produce the product.[25] The reaction was monitored by ^{31}P NMR spectroscopy and after one night reflux, NMR evidence showed the presence of CH_3-phosphinodiimine **99** (δ = 5.98 ppm in xylenes) as a major product. This reaction relied on high temperature by refluxing in xylenes to drive off the HCl that is expected to be formed in the reaction (Scheme 3.6). Workup consisted of removal of xylene from the reaction mixture and crystallization of the crude product from a minimum of hot ethanol to produce pale yellow crystals of CH_3-phosphinodiimine **99** in 55% yield, which is almost twice the yield as when *n*BuLi was used to synthesize **99**.



Scheme 3.6 Synthesis of CH_3-phosphinodiimine **99** following thermal reaction.

3.3.2.1 Crystal structure of 99

Pure pale yellow crystals grew from ethanol at -25°C under N_2 and crystallographic data was determined at -100°C. Crystallographic data and selected bond lengths and angles can be found in Tables 3.5-3.6 and a representation of the crystal structure is found in Figure 3.9. Based on the crystal structure, the P=C bond length is 1.696(9) Å which is shorter than the P-C bond lengths in **100** (1.8435(15) Å and 1.8609(15) Å) and shorter than P-C in ^{t}Bu-phosphinodiimine **98** (1.8898(17) Å and 1.9039(17) Å) (the range of P=C is (1.70-1.76 Å) for C-amino substituted phosphaalkenes[71] and the range of P-C is (1.840-1.870 Å)[72]). The N_2=C_{15} bond length is 1.358(11) Å, N_1-C_{13} is 1.440(10) Å and N_1-C_{15} is 1.387(11) Å, which are all longer than the N_1=C_1 (1.2788(19) Å) and N_2-C_{28} (1.3453(19) Å) bond lengths in **100** and longer than N=C in **98** (1.267(2) Å and 1.271(2) Å). For CH_3-phosphinodiimine **99**, *cis-trans* isomerism could exist with respect to each C=P and N=C double bond. Crystallographic data confirmed that the geometry of CH_3-phosphinodiimine **99** in the solid state is *EE*. The sum of angles around N_1 is 360.0(14)°, indicative of a planar structure at nitrogen. Detailed crystallographic data can be found in Appendix III Table A82-A87.

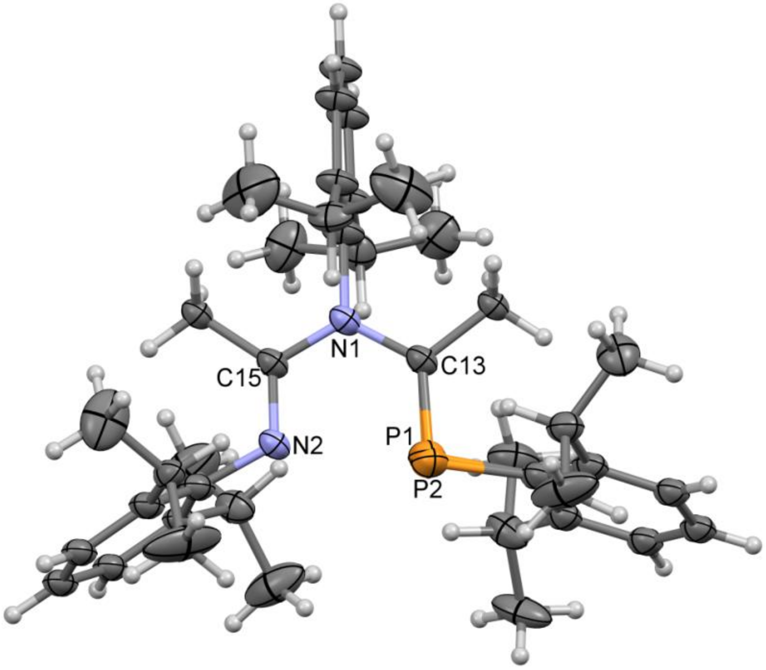


Figure 3.9 Displacement ellipsoids plot (40% probability) showing the molecular structure of CH_3-phosphinodiimine **99**. There is disorder in the positions of the P atoms, with refined occupancies 45% P1 and 55% P2.

Table 3.5 Crystal data and structure refinement for **99** and *p*CH_3-amide **13a**.

	99	**13a**
Space group	P 2_1/c	P 2_1/c
a/ Å	13.332(6)	21.882(3)
b/ Å	14.122(7)	9.9235(13)
c/ Å	19.596(7)	17.082(2)
α	90°	90°
β	92.028(10)°	107.0080(17)°
γ	90°	90°
Z	4	8
Goodness-of-fit on F2	1.021	1.025
Final R indices[I>2sigma(I)]	R1 = 0.0872	R1 = 0.0857
	wR2 = 0.1745	wR2 = 0.2045
R indices (all data)	R1 = 0.2164	R1 = 0.1909
	wR2 = 0.2265	wR2 = 0.2561

3.3.2.2 Solution NMR spectroscopy

Pure pale yellow crystals of CH_3-phosphinodiimine **99** (PNN) were dissolved in $CDCl_3$ under N_2 to make an NMR sample. ^{31}P NMR (proton-coupled) spectrum at RT shows a sharp singlet at $\delta = 7.22$ ppm (this chemical shift is unusual for C=P, even with a nitrogen substituent on carbon; for comparison, the chemical shifts **25a-b**, which are C=P phosphaamidines, are 53.4 ppm and 51.4 ppm.) unlike ^{t}Bu-phosphinodiimine **98**, which shows two broad peaks at RT. There was also a very small peak at $\delta = -18.53$ ppm that might be a second isomer (Figure 3.10). The ^{1}H NMR spectrum is shown in Figure 3.11 and three sets of septets were observed. Two CH_{isopr} of the Dipp-P ring showed one septet which is the most downfield septet ($\delta = 3.66$ ppm). Two septets that we see at $\delta = 3.02$

ppm and δ = 2.99 ppm belong to four CH $_{isopr}$ of the two Dipp-N rings which showed up at higher field. One of the backbone CH_3 groups is coupled with phosphorus (doublet at 1.79 ppm) and the other is a singlet at 1.28 ppm. Detailed NMR data are listed in Table 3.6.

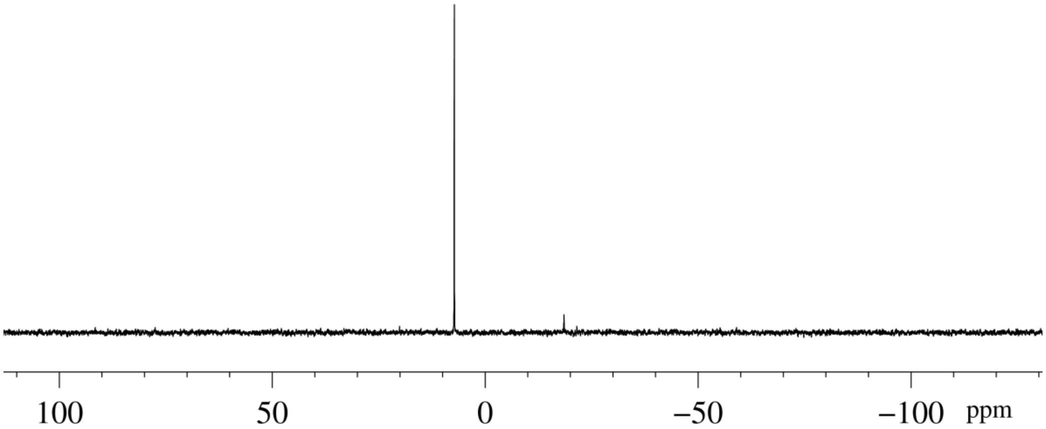


Figure 3.10 ^{31}P NMR spectrum of CH_3-phosphinodiimine **99** at RT in $CDCl_3$.

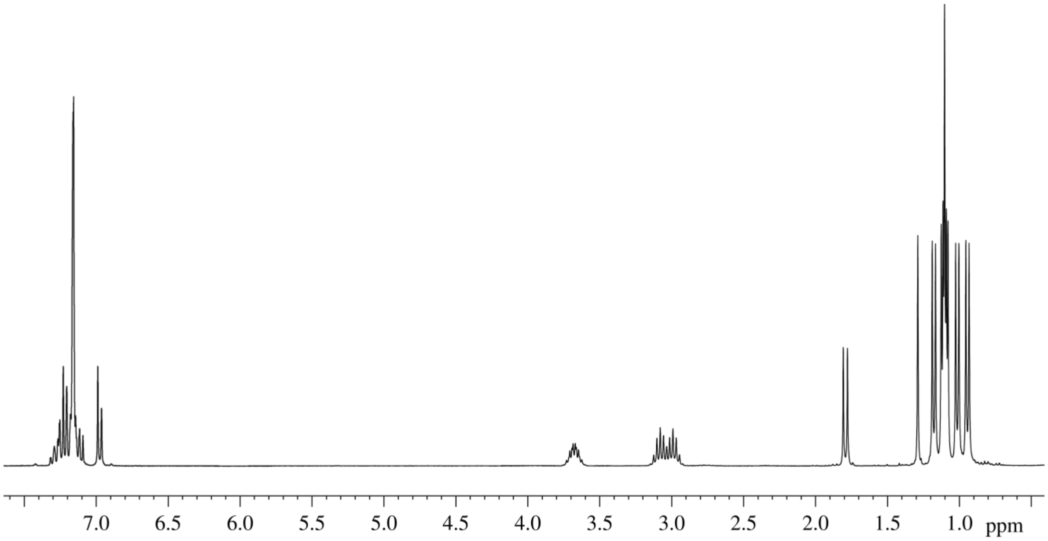


Figure 3.11 ^{1}H NMR spectrum of CH_3-phosphinodiimine **99** at RT in $CDCl_3$.

Table 3.6 ^{1}H NMR, ^{13}C NMR and ^{31}P NMR data for **99** at RT in $CDCl_3$.

Nucleus	δ, ppm	mult[1]	J, Hz
^{31}P NMR			
P	7.23	s	
^{1}H NMR			
backbone			
CH_3	1.79	d	8.7
CH_3	1.28	s	
Dipp-P			
CH_3-*iso*	1.09,1.11	d	6.3
CH-*iso*	3.66	br sep	14.0
CH_{meta}	7.02	d	7.5
CH_{para}	7.15	br t	22.4
Dipp-N_1			
CH_3-*iso*	1.14,1.19	d	6.0,7.5
CH-*iso*	2.99	br sep	16.1
CH_{meta}	7.06	d	7.80
CH_{para}	6.93	br t	24.5
Dipp-N_2			
CH_3-*iso*	1.17	d	6.6
CH-*iso*	3.02	br sep	16.8
CH_{meta}	7.17	d	8.1
CH_{para}	7.33	br t	16.8
^{13}C NMR			
C=P	176.16	d	5

[1] multiplicity

3.3.2.3 Solid State NMR spectroscopy

To study the presence of possible isomers for CH_3-phosphinodiimine, I have undertaken solid-state ^{31}P CP-MAS NMR spectroscopy at different spinning rates. The isotropic centre band for CH_3-phosphinodiimine **99** shows up at δ = 7.92 ppm with spinning rates of 4, 6, 10 and 15 Hz. This chemical shift is very close to the chemical shift of **99** in solution (δ = 7.23 ppm). Figure 3.12 shows the SS ^{31}P NMR spectrum; since it is proton decoupled, we don't expect to see any coupling to ^1H. The doubling of the signals in this solid state NMR spectrum can be due to disorder of the phosphorus atoms (the crystal structure shows evidence of disorder for the phosphorus atom, see Fig. 3.9). This doublet pattern is not observed in solution because it is due to a lattice effect. There is also a small peak at δ = -17.56 ppm that we think might be the second isomer. This small peak was also shows up at δ = -18.53 ppm in the solution NMR spectra.

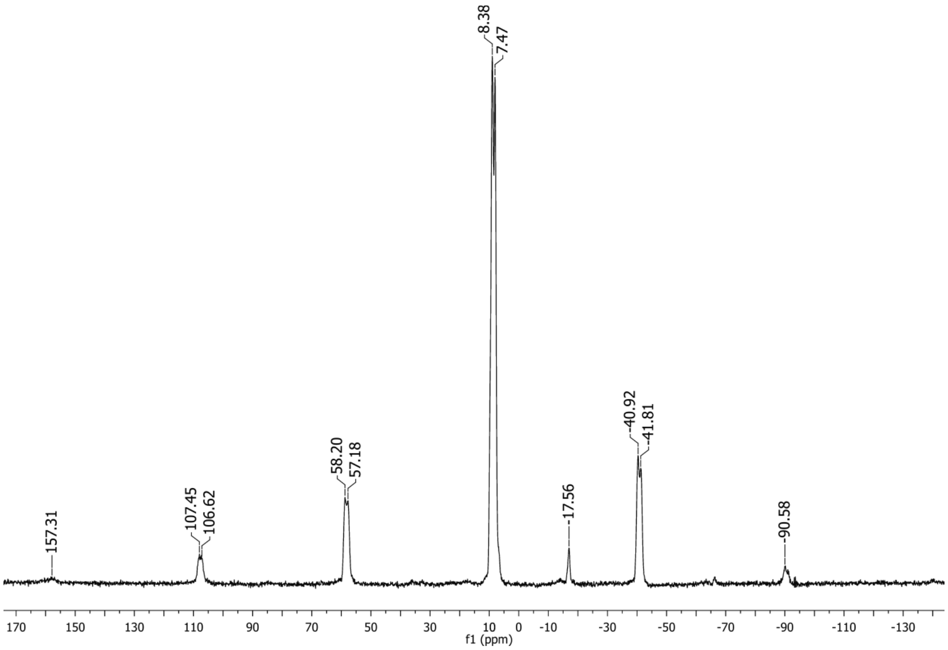
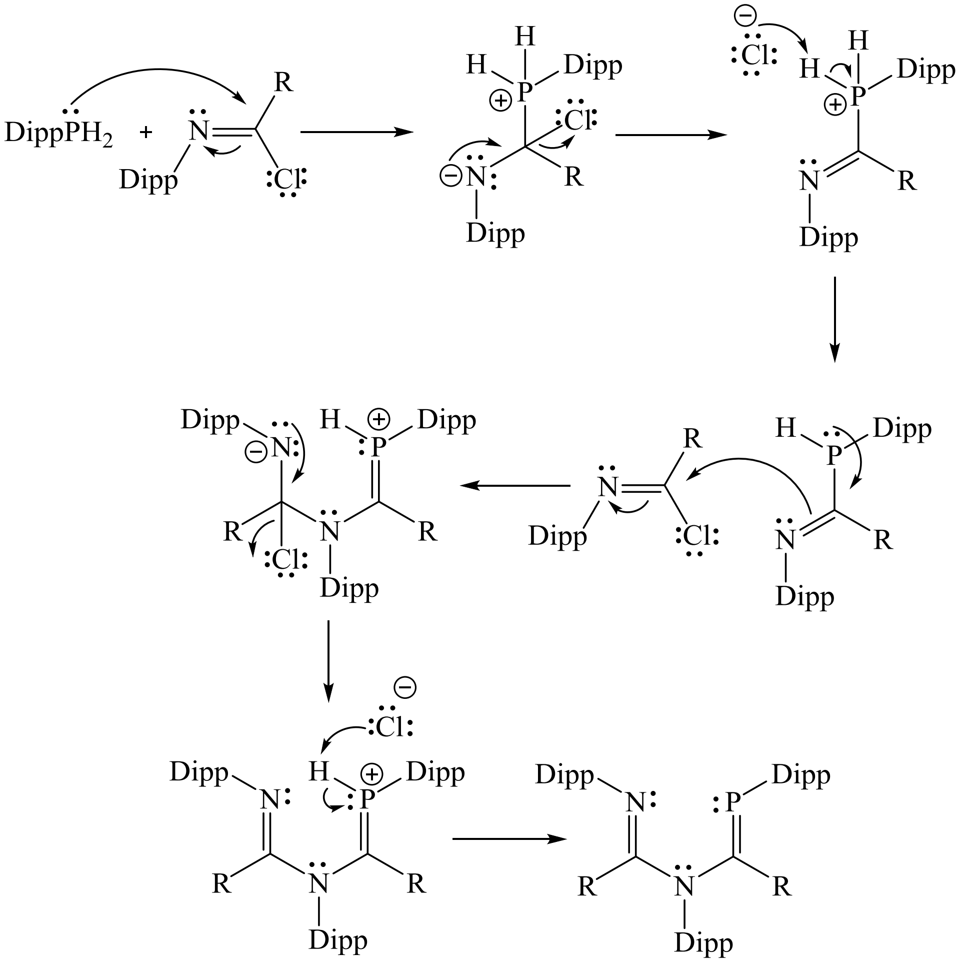


Figure 3.12 CP-MAS ^{31}P-{^1H} solid-state NMR spectrum (10 KHz) of **99** at RT.

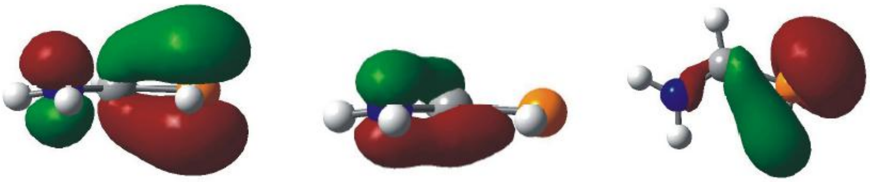
3.3.2.4 Reaction mechanism and computational chemistry

The proposed mechanism to synthesize the CH_3-phosphinodiimine **99** is outlined in Scheme 3.7. Addition of $DippPH_2$ as a nucleophile to the carbon backbone of imidoyl chloride **14c** as an electrophile, followed by elimination of Cl^-, makes CH_3-phosphaamidine **77** in the first step. Addition of this phosphaamidine **77** to the second equivalent of imidoyl chloride **14c**, followed by elimination of Cl^- makes CH_3-phosphinodiimine **99**.



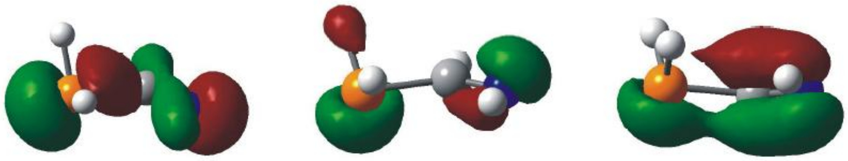
Scheme 3.7 Proposed mechanism for the formation of CH_3-phosphinodiimine **99**.

In such a thermal reaction, the ease of elimination of Cl^- or HCl from imidoyl chloride **14c** or from a transition state could play a critical role. The reaction is expected to work well when the HOMO of the nucleophile matches the energy of the LUMO of the electrophile. The imidoyl chloride **14c** is the electrophile and the aminophosphaalkene **77** is the nucleophile. The frontier MOs of the two forms of phosphaamidine (P=C and N=C isomers) (as explained in Chapter 2, CH$_3$-phosphaamidine shows two isomers, P=C and N=C, in solution) and imidoyl chloride are shown in Figures 3.13 - 3.15.



π(2) HOMO π(1) HOMO-4 n(P) HOMO-1

Figure 3.13 Selected individual Kohn–Sham orbital surface topologies for *Z*-(P=C) isomer.



n(P)/π' HOMO n(P)/n(N) HOMO-1 π' (1) HOMO-2

Figure 3.14 Selected individual Kohn–Sham orbital surface topologies for *Z*-(N=C) isomer.

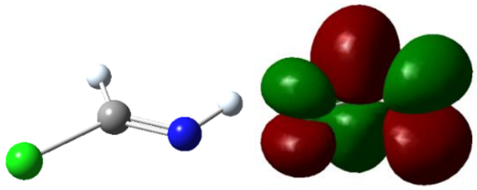


Figure 3.15 Orientation of model and Kohn–Sham orbital surface for the LUMO of **14c**.

When the reaction is thermally controlled, it is the P=C HOMO that is involved in the reaction. This is the most reactive orbital that can react with the imidoyl chloride

LUMO. The isomeric preferences of the phosphaamidines are extremely important and substitutions on the carbon backbone can control the preferred isomer in solution. As explained in Sections 1.2 and 2.2, changing the substitution on the carbon backbone from *p*CH_3OPh or CH_3 to ^tBu changed the tautomeric preference of phosphaamidines. Reactions with the imidoyl chloride **14c** (e.g. $R^4 = CH_3$) are concerted reactions that operate under thermal control. In this case, the nature of the nucleophile (e.g. phosphaamidine) may determine the isomeric type of product that is formed. Concerted reactions of delocalized π systems are often under "orbital control". The transition state for an orbital symmetry allowed thermal reaction must match the phase of the orbitals of nucleophile and electrophile. It may also be that the R^2 group that is the backbone of the phosphaamidine controls the preferred geometry of the phosphaamidine (Figure 3.16). For CH_3-phosphaamidine, as already explained, both kinds of phosphaamidine ((C=P) and (C=N)) exist in solution, and in the case of ^tBu-phosphaamidine the evidence confirmed the presence of only (C=N) phosphaamidine in solution. Based on Figure 3.13 the electron density is more on phosphorus of the π (2) HOMO, which results in the phosphorus as the nucleophile which reacts with the carbon of imidoyl chloride as electrophile. The product of this reaction would be NPN. In Figure 3.14 π' (1) HOMO-2 orbital shows the electron density more on nitrogen which results in the nitrogen as a nucleophile which reacts with the carbon of the electrophile. The product in this case would be PNN. The position of the Dipp groups is also important whether it is in the blocking side or in the non-blocking side, to choose the reaction paths **A** or **B** (Figure 3.16).

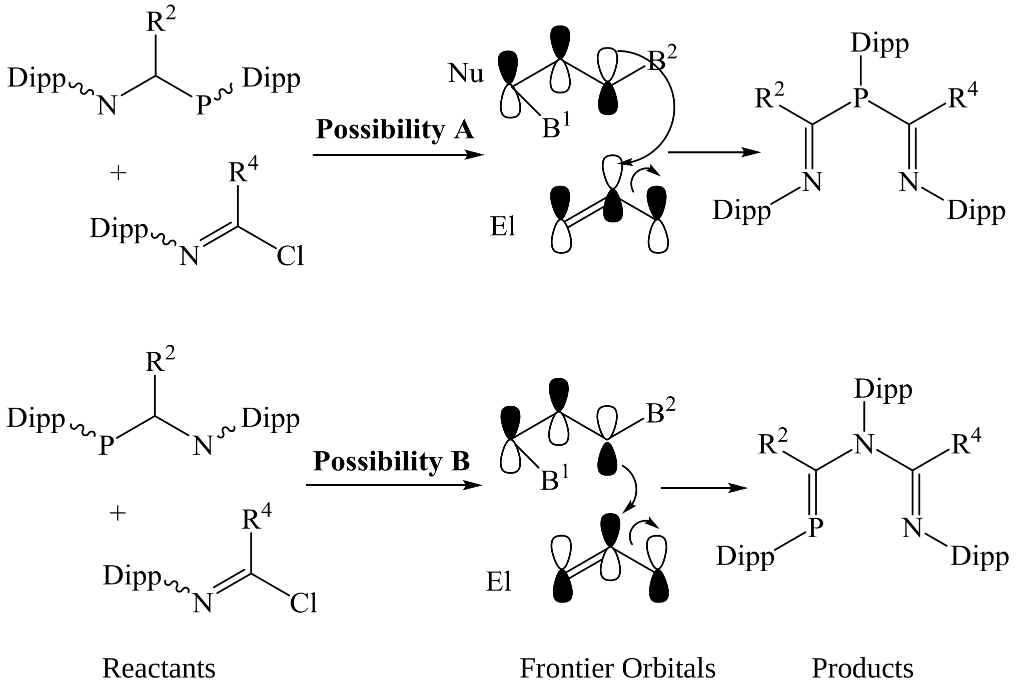


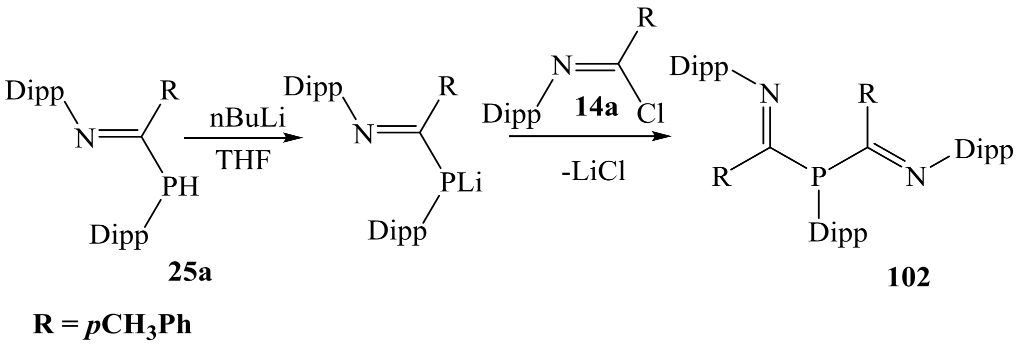
Figure 3.16 Transition states of orbitally allowed thermal reactions; B^1=Dipp group in blocking side, B^2=Dipp group in non-blocking side.

3.4 *p*CH_3Ph-phosphinodiimine 102

To understand the origin of isomerism and study the mechanism of these reactions, I attempted the synthesis of new bulky phosphorus-substituted diimine ligands with different "backbone" substituents, R^2= C_6H_4-X; X=OCH_3. It was an attempt to find the two most reliable routes to make on purpose either NPN or PNN with a variety of different substituents and also to see if in fact the methyl imidoyl chloride is "special" by allowing the thermal reaction to proceed as the easiest path to product.

3.4.1 Synthesis of *p*CH_3Ph-phosphinodiimine 102

pCH_3Ph-phosphinodiimine was synthesized following the same procedure that I used to synthesize the ^{t}Bu-phosphinodiimine **98** (Scheme 3.8). Any attempt to purify the crude material such as sublimation, column chromatography, and crystallization from heptanes, toluene, 1-propanol and acetonitrile was unsuccessful.



Scheme 3.8 Synthesis of pCH$_3$Ph-phosphinodiimine **102** using *n*BuLi.

3.4.2 Solution NMR spectroscopy

The spectra of crude material are shown in Figure 3.17. A singlet peak at δ = 18.27 ppm can be pCH$_3$Ph-phosphinodiimine **102**, but any attempt to isolate this component was unsuccessful and ended up with amide **13a**.

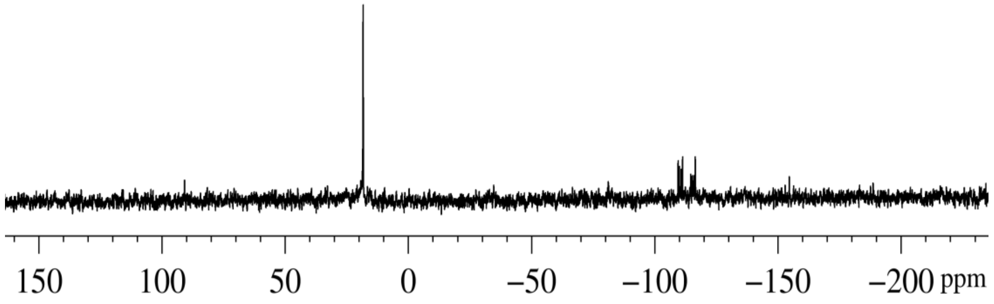


Figure 3.17 ^{31}PNMR spectrum signals of pCH$_3$Ph-phosphinodiimine at RT in CDCl$_3$.

3.4.3 Crystal structure

Recrystallization of crude *p*CH_3Ph-phosphinodiimine **102** with EtOH resulted only in *p*CH_3Ph-amide **13a** (Figure 3.18). This is most likely formed from the hydrolysis reaction of unreacted imidoyl chloride **14a** with traces of water that exist in EtOH.

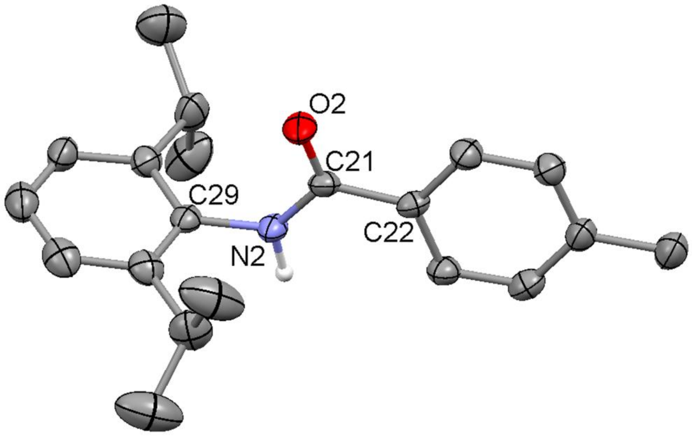


Figure 3.18 The 40% probability displacement ellipsoids of *p*CH_3Ph-amide **13a**. This compound has two molecules in the asymmetric unit, of which only one is shown. H atoms other than N-H are omitted for clarity.

The crystal structure was determined at -100°C and crystallographic data can be found in Table 3.5. Based on the crystal structure, the N-C bond length is 1.332(5) Å, which is slightly shorter than the C-N single bond in ^{t}Bu amide **79** (1.341(17) Å) and it is shorter than normal C-N single bonds (the range of Csp^2-Nsp^2 in acyclic amides is (1.446-1.461 Å)[72]. The C=O bond length is 1.234(4) Å, which is the same as C=O double bond in ^{t}Bu amide **79** (1.228(16) Å) (the range of C=O for amide is 1.225-1.243 Å)[72]. The sum of angles around N is 360.0(2)°, indicative of a planar structure at nitrogen. Nitrogen is also planar in ^{t}Bu amide **79** (the sum of angles around nitrogen is 359.2(11)°). The detailed crystallographic data can be found in Appendix III Tables A88-A94.

3.5 Conclusion

I have produced two new phosphinodiimines, CH_3-PNN **99** and ^{t}Bu-NPN **98**, the first well characterized examples of this system. Both CH_3 and ^{t}Bu are electron donating substituents and are only different in size (^{t}Bu is more bulky than CH_3). Both **98** and **99** were made by reacting phosphaamidine with imidoyl chloride and the reason we see two different products is different isomerisation properties of CH_3-phosphaamidine **77** and ^{t}Bu-phosphaamidine **32**. Because compound **32** has only one isomer, there is only one possible product as NPN. In case of **77** there are two isomers, C=N and C=P, that could make either NPN or PNN. Because the major isomer for **77** is P=C isomer, then there was more chance to get PNN as product. For ^{t}Bu-NPN **93**, the geometry in the crystal structure is the same as the solution geometry for the major isomer (*EZ*). This was proved by solid state NMR, advanced solution NMR spectroscopy and DFT calculations. For CH_3-PNN **99** the geometry in the crystal structure is *EE*. Evidence of solution NMR and solid-state NMR spectroscopy along with crystal data confirmed that the only isomer that we observed for **99** is *EE*. We propose that the steric bulk of the substituent on the carbon backbone is the major reason that we see two different kinds of diimines, PNN and NPN.

Chapter 4

1,2-Bis(2,6-diisopropylphenyl)diphosphane

4.1 Introduction

The first sign of Dipp(H)P-P(H)Dipp **104** was observed on attempting to synthesize the phosphaformamidine **78** (Figure 4.1). Since then, this compound showed up several times in other reactions such as preparation of CH_3-phosphaamidine **77**, CH_3-amidinophosphaalkene **99** and ^{t}Bu-phosphinodiimine **98**. The complex multiplets at δ = -110 and δ = -115 ppm were thought to be **104** based on a preliminary analysis of the spectral patterns and literature precedents.[64]

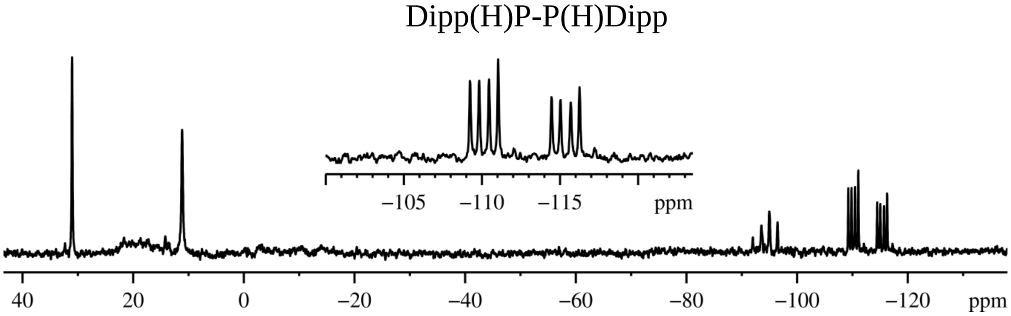
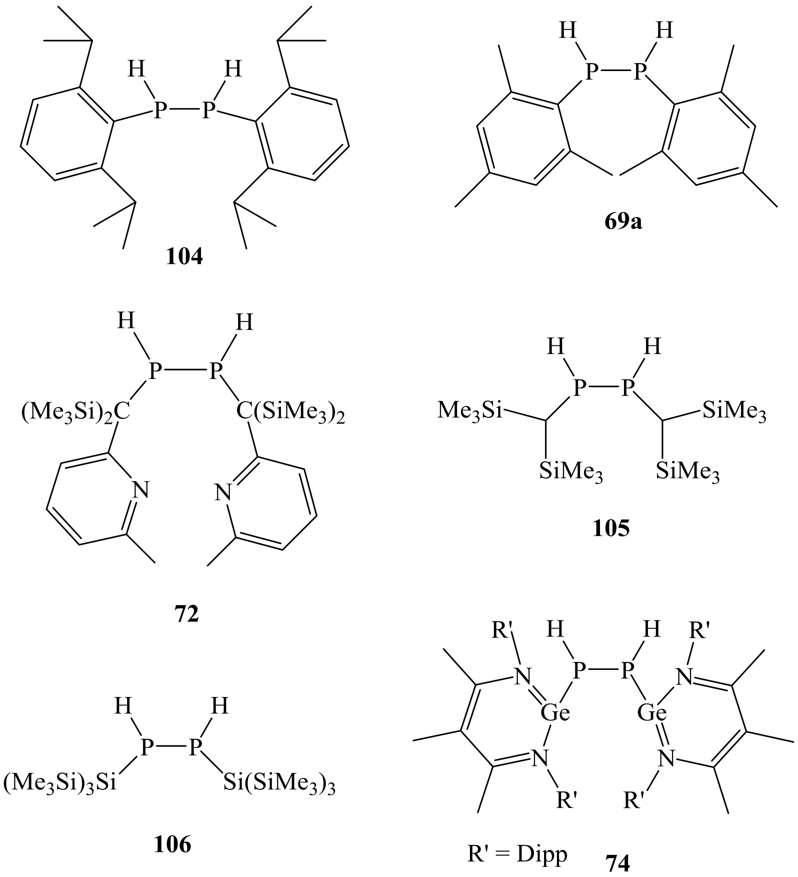


Figure 4.1 First sign of Dipp(H)P-P(H)Dipp **104** in synthesizing **78**.

We decided to synthesize this compound on purpose and fully characterize it because some dihydrodiphosphanes have recently been reported without full details of their properties.[64,73,68] As already mentioned there are only three previously reported crystal structures for secondary organodiphosphanes R(H)P–P(H)R: the aryl derivative (R = Mes) **69a,b** reported by Hey-Hawkins,[67] *bis*(trimethylsilyl)methyl structures R = $[Me_3Si]_2CH$ **105**,[73] and R = $[Me_3Si]_2C$(6-Me-2-pyridyl) **72**.[68] Our Dipp(H)P-P(H)Dipp compound **104** is the fourth reported crystal structure of diphosphane. There are also two structures with heavier Group 14 substituents, R = $(Me_3Si)_3Si$ **106**,[85] and NacNacGe **74** (Scheme 4.1).[86]



Scheme 4.1 Line structures of the six reported crystal structures of dihydrodiphosphanes.

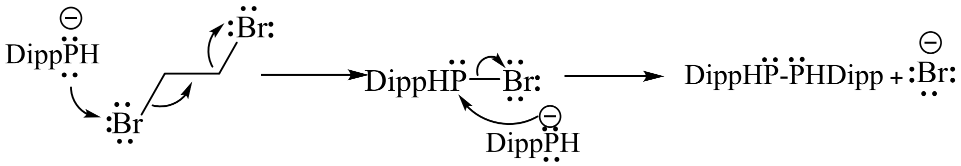
4.2 Synthesis of diphosphane, Dipp(H)P-P(H)Dipp 104

I attempted to make Dipp(H)P-P(H)Dipp **104** on purpose by modifying the Kurz *et al.* procedure (Scheme 4.2).[67] *n*-Butyl lithium was added to a solution of $DippPH_2$ **24** and tetrahydrofuran at -70°C and the mixture was stirred for 30 min at RT. Solvent was removed *in vacuo*, then dry toluene was added to the DippPHLi residue. The mixture was cooled to -30°C and 1,2-dibromoethane was added with stirring. The resulting mixture was allowed to warm to RT overnight. Solvent was removed *in vacuo* and the residue was extracted with pentane to leave a white precipitate of LiBr; after filtering, the pentane was removed *in vacuo*.

$$2\ \text{DippPHLi} + \text{CH}_2\text{Br-CH}_2\text{Br} \xrightarrow[\text{Toluene}]{} \underset{\mathbf{104}}{\text{DippPH-HPDipp}} + 2\ \text{LiBr} + \text{CH}_2\text{=CH}_2$$

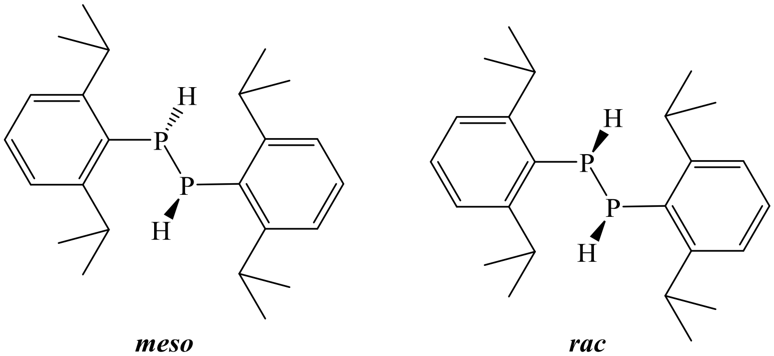
Scheme 4.2 Synthesis of 1,2-*bis*(2,6-diisopropyl phenyl)diphosphane **104**.

The ^{31}P NMR spectrum of crude product exhibits a mixture of DippPH$_2$ **24**, Dipp(H)P-P(H)Dipp **104** and DippPOH$_2$ **107**. Any attempt to purify the yellow semi-solid residue by recrystallization with different solvents such as methanol, heptane, ethanol, n-propanol, and toluene, on cooling to -30 °C, was unsuccessful. The colorless crystals obtained from sublimation were very poor quality crystals. The proposed mechanism to produce the product is outlined in Scheme 4.3.



Scheme 4.3 Proposed mechanisms to the formation of diphosphane **104**.

Pure colorless crystals were finally obtained in the liquid phosphane DippPH$_2$, **24**, which was stored for some time at -10 °C in a freezer; decanting and rinsing with a minimum of dichloromethane produced pure material which was used for further characterization. Like the diastereomeric mixture of (Mes*)(H)P-P(H)(Mes*) (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) **108** (m.p = 144-147°C for 5:1 mixture of *rac/meso*),[87] and Mes(H)P-P(H)Mes **69a,b** (majority melts in the range 77-85°C and remainder in the range 95-100°C for mixture of *rac/meso*),[67] Dipp(H)P-P(H)Dipp **104** exhibits a melting range 85-89°C for the majority and the remainder shows a melting range 102-105°C. Scheme 4.4 shows the structure for *meso* and *rac* stereoisomers of **104**.



meso ***rac***

Scheme 4.4 Two stereoisomer of Dipp(H)P-P(H)Dipp **104**.

4.3 Crystal structure of 104

Good quality crystals grew in a sample of liquid DippPH$_2$ **24** kept in a Schlenk tube in a freezer at -10°C. Figure 4.2 contains a depiction of the crystal structure which was determined at low-temperature (153±2 K). The detailed crystallographic data can be found in Appendix III Tables A95-A100. The molecule crystallizes in space group *P*-1 with $Z = 1$, which means there is a crystallographic inversion centre, so that half the molecular formula forms the asymmetric unit. At each phosphorus atom, electron density shows the presence of two H rather than the expected one H, as shown in Figure 4.2. The structure was refined using a two-position disorder model as the *meso* stereoisomer, with refined occupancies in 60:40 ratios for H1 and H1A. Note that at 50:50 occupancy the structure could be a result of co-crystallized *meso* and *rac* stereoisomers. Selected bond lengths and angles for diphosphane **104** and five other related structures are listed in Table 4.1. Our low-temperature crystal structure seems to be closer to the structure of

105. All of these compounds contain bulky substituents and crystallize with antiperiplanar geometry.

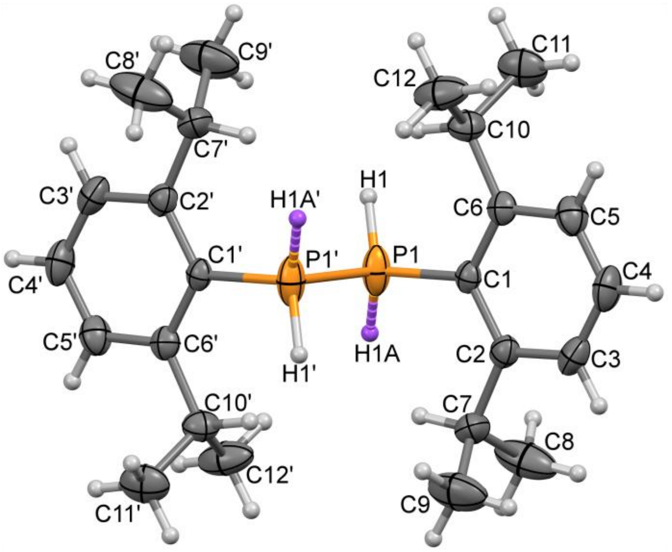


Figure 4.2 Displacement ellipsoids plot (50% probability) showing the molecular structure of **104** within the crystal lattice; the midpoint of the P1-P1’ bond is located at a centre of symmetry in space group *P*-1 with all symmetry-related atoms denoted by ‘. The refined model is based on positional disorder of two *meso* isomers in 60:40 ratio [*SR* (H1): *RS* (H1A)]; the minor component H atom positions are indicated with dashed bonds and rendered purple.

Table 4.1 Comparative distances (Å), angles (°) and torsions (°) in crystal structures of **104**, related compounds **69**, **72**, **74**, **105** and **106**.

Comp.	P–P'	P–E	E–P–P'	E–P–H	P'–P–H	E-P-P'-E'
104	2.2060(8)[a]	1.8414(13)	98.14(4)	107.8(13)	103.9(13)	180.00(6)
69[67]	2.2284(11)[a]	1.837(2)	98.33(6)	97.7(13)	95.(3)	180.0(1)
105[73]	2.2086(8)[a]	1.8679(15)	100.15(5)	---	---	180.00(7)
72[68]	2.222(3)[a]	1.872(4)	101.82(7) 102.50(7)	---	---	180.0(2)
106[85]	2.202(2)[b]	2.269(2)	101.82(7)	86(6)	89(6)	180.00(7)
	2.195(2)	2.269(2)	102.50(7)	95(5)	111(5)	180.00(6)
74[86]	2.221(2)[c]	2.408(2)	93.09(9)	89(3)	95(3)	180.00(7)

[a]E = C. [b]E = Si. [c] E= Gev.

We have done RHF and hybrid DFT calculations on both the *meso* and *rac*-isomers of **104** (for the *rac* form, all work was done on the *RR* isomer) to understand the possible stereoisomers and compare data with the crystal structure, solid-state Raman spectroscopy and solution NMR spectroscopy. DFT calculations predicted only 4% longer bonds for *meso* and 1% for *rac* compared to RHF. The calculations shows that the *meso* isomer is more stable than *rac* by only 0.25 kJ/mol at the RHF level, and 1.43 kJ/mol at the B3LYP/6-31G(d,p) level of theory. The calculation also shows that the *meso* geometry has a longer P–P bond length of 2.237 Å compared to 2.221 Å for *rac* and both of them are longer than the X-ray data 2.2060(8) Å (Appendix III Table A137).

4.4 Raman Spectroscopy

The Raman spectrum of solid **104** shows an intense, broad peak for P–H stretching at 2314 cm^{-1} and two peaks at 460 and 450 cm^{-1} for P–P stretching. These data were confirmed by RHF/63-1G+(3d,2p) frequency calculations on the *anti* conformers (Figure 4.3 and Table 4.2). The crystal structure was modelled as a disorder between *RS* and *SR* *meso* forms, with *anti* conformation. It seems that *meso* and *rac* isomers co-crystallize. To understand better if this is the case, the Raman spectrum of the crystals was measured.

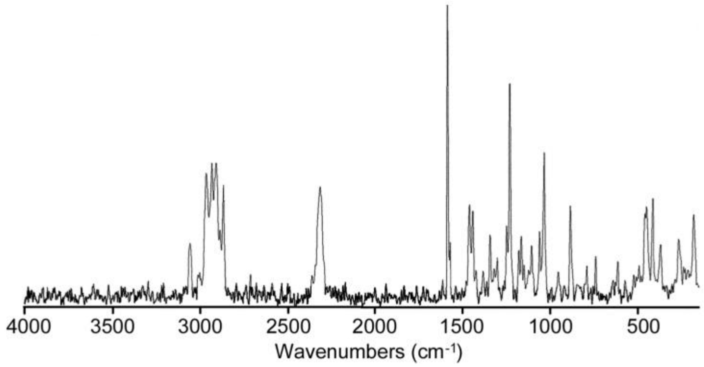


Figure 4.3 FT Raman spectrum of **104** at RT (1064 nm Nd:YAG laser; Ge detector).

Table 4.2 Measured and Computed Raman Spectroscopic Data (cm^{-1}, relative intensity) for **104**.

Band	Experiment [1]	*rac*-Isomer computed [2]	*meso*-Isomer computed [2]
ν(P—H), sym	2314, 0.38 (broad)	2325, 131	2309, 143
ν (P—H), asym		2293, 32	2317, 0
ν (P—P)	460, 0.28	—	448, 27
ν (P—P)	450, 0.30	442,33	—

[1] Measured on a Bruker Vector FTIR/Raman spectrometer (KBr optics, Ge detector, Nd:YAG laser.); [2] RHF/63-1G+(3d,2p) frequency calculations on the *anti* conformers only; the computed values have been scaled by 0.894.[88]

In solid Me(H)P–P(H)Me **109**, a broad band was reported at 2277 cm^{-1} for P–H stretching vibrations,[89] while in solutions of Ph(H)P–P(H)Ph, **110**, there are two sharp peaks at 2278 cm^{-1} and 2283 cm^{-1}.[90] For ^{t}Bu(H)P–P(H)^{t}Bu, **111**, there is a single band at 2290 cm^{-1} in solution.[91] The P–P stretching vibrations for Me(H)P–P(H)Me, **109**, were reported at 451 (*anti* conformer of *meso* isomer), 435 (*anti* conformer of *rac* isomer) and 427 cm^{-1} (*gauche* conformer of *meso* isomer),[89] while in Ph(H)P–P(H)Ph, **110**, a single band at 437 cm^{-1} is attributed to the gauche conformer.[90] Our computational vibrational spectra for the *meso* and *rac* isomers fit best for the *meso* isomer as is reported in Table 4.3. The ν(P-H) band is broad for the experimental data, and since it is between *meso* and *rac* isomers, we cannot ignore the possible presence of *rac* isomer. Thus we cannot confirm the origin of the observed disorder in the H atom positions by crystallography from the Raman spectra.

4.5 Solution NMR spectroscopy

1D (^{1}H, ^{13}C, ^{31}P) and 2D NMR (COSY, HSQC, HMBC) spectroscopy studies were done on Dipp(H)P-P(H)Dipp **104** in $CDCl_3$ under N_2. The ^{31}P NMR spectra (Figures 4.4-4.5) show two isomers in solution, each with AA'XX' spin coupling systems at chemical shifts of δ = -112.5 ppm and δ = -117.7 ppm, in a 58:42 ratio, respectively.

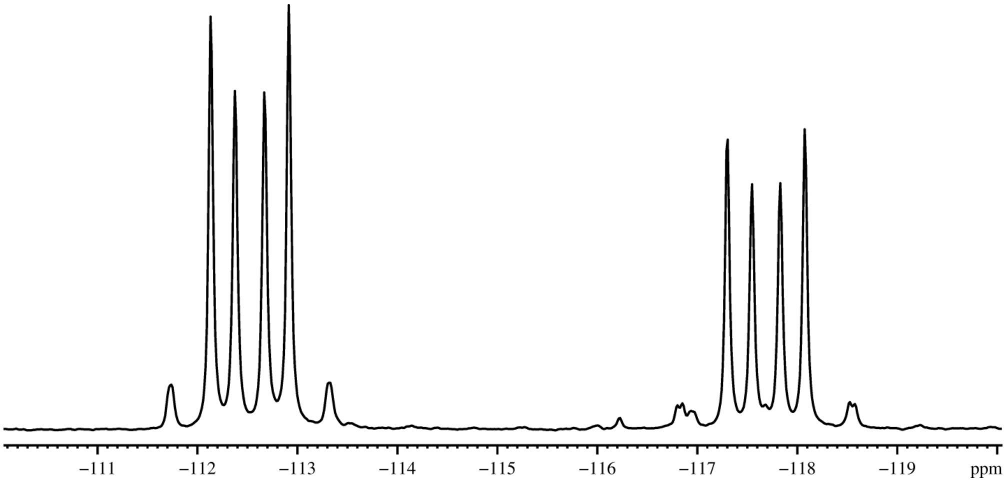


Figure 4.4 ^{31}P NMR spectrum of **104** in $CDCl_3$ solution at RT. Broadband ^{1}H decoupling simplifies this spectrum to two singlets at δ = -112.52 ppm and δ = -117.68 ppm in Figure 4.5.

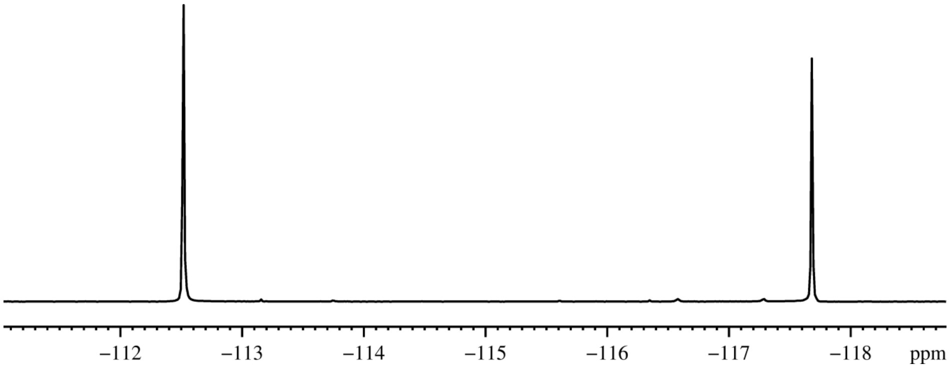


Figure 4.5 ^{31}P NMR spectrum with H decoupling for the two diastereomers of **104** in $CDCl_3$ at RT.

A similar pattern was observed in the ^{1}H NMR spectrum (peaks of these isomers show overlapping AA'XX' patterns) at $\delta = 4.45$ ppm and $\delta = 4.63$ ppm (Figure 4.6). Integration of the ^{1}H NMR spectra of dissolved crystalline materials shows that the ratio is 58:42 (red stars belong to major isomer and black stars to the minor isomer).

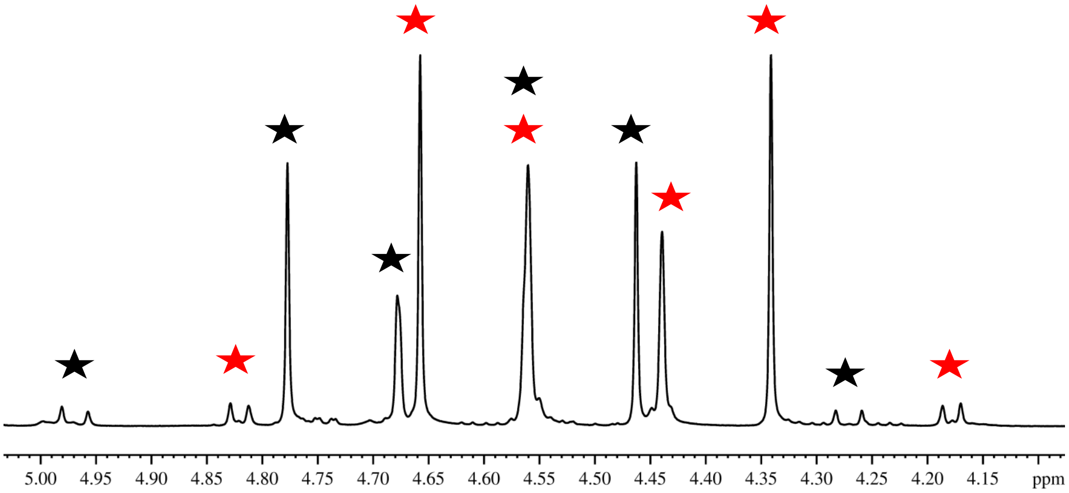


Figure 4.6 ^{1}H NMR signals of **104** due to the two diastereomers overlapping in $CDCl_3$ at RT.

In the ^{13}C NMR spectrum (Figure 4.7), ^{31}P-^{13}C coupling is resolved for the C_{ipso} carbons (red star) in both diastereomers (*meso* and *rac*) and each signal appears as a (*pseudo*) triplet due to coupling to the two phosphorus atoms. C_{ipso} can couple with adjacent phosphorus and split into a doublet with ^{1}J and this doublet will split to two other doublets due to the coupling to the second phosphorus with ^{2}J. Only in the case where $^1J = {^2J}$ we can see this (*pseudo*) triplet pattern with an intensity ratio of 1:2:1. The ^{31}P-^{13}C coupling for the C_{ortho} carbons (black star) also appears as a (*pseudo*)triplet for both diastereomers (*meso* and *rac*) due to coupling to the phosphorus atoms and CH_{ispr} (Figure 4.8).

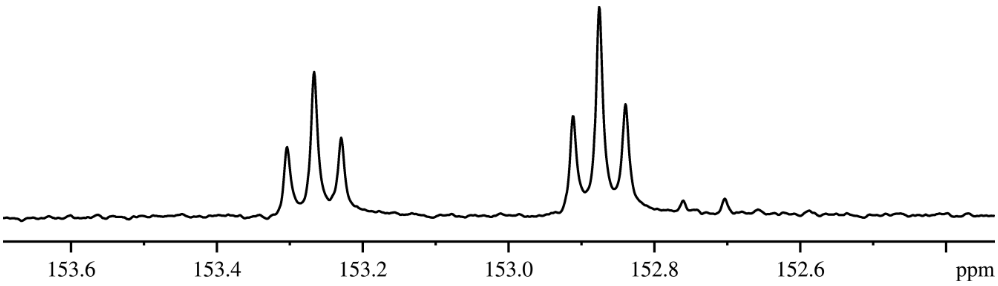


Figure 4.7 ^{13}C NMR spectrum for two diastereomers of **104** in $CDCl_3$ at RT.

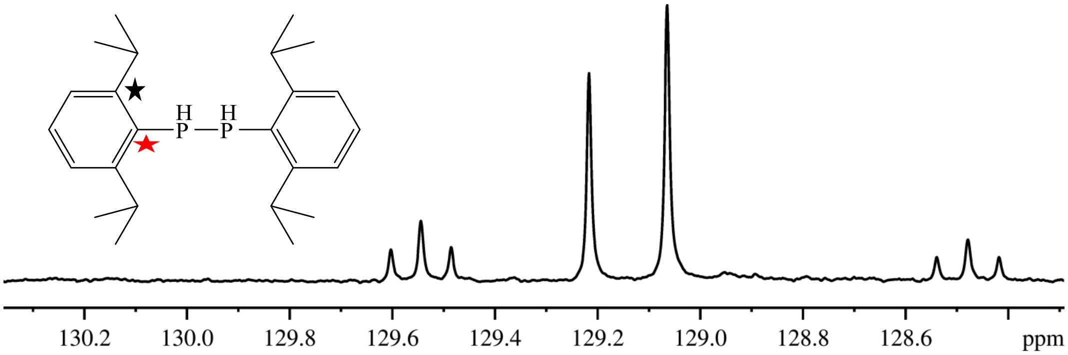


Figure 4.8 ^{13}C NMR spectrum for two diastereomers in $CDCl_3$ at RT.

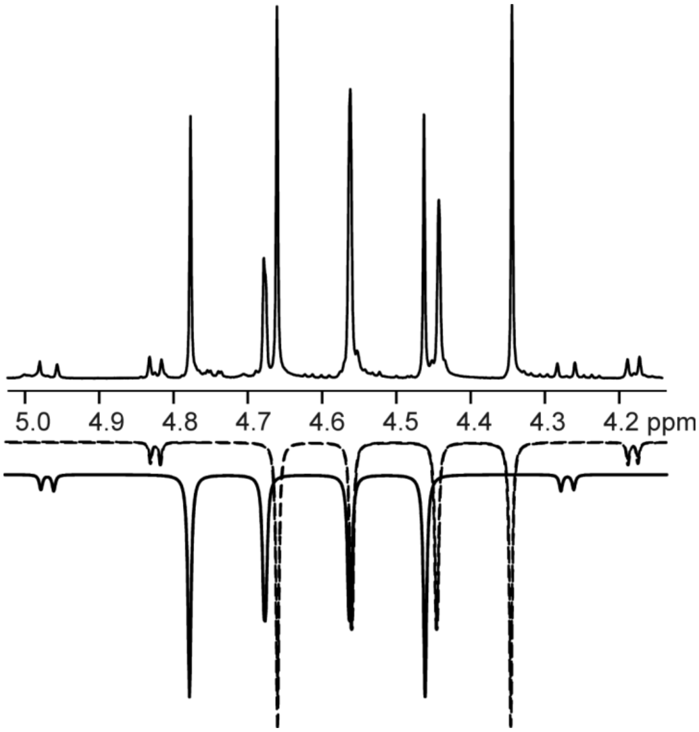


Figure 4.9 Upright: a portion of ^{1}H NMR spectrum of **104** in $CDCl_3$ solution at RT, showing the PH resonances. Inverted: simulations of the AA' sub-spectra for *meso* (—) and *rac* (---) isomers.

I simulated the AA'XX' spin systems for both ^{31}P and ^{1}H NMR spectra using MestReNova 10 program. Calculation of AA'XX' spin systems for **104** represent $^{1}J_{PP'}$ values of (−)189 and (−)205 Hz. I could assign the spectrum with the smaller coupling constant to *meso* (58% at RT) and the other to *rac* (42%). The inverted spectra in Figure 4.9 and 4.10 show the result of the simulations. To fully assign the spectra, I have also done 2D NMR (COSY, HMBC, and HSQC) spectroscopy and all the experimental and simulated NMR data are listed in Table 4.3.

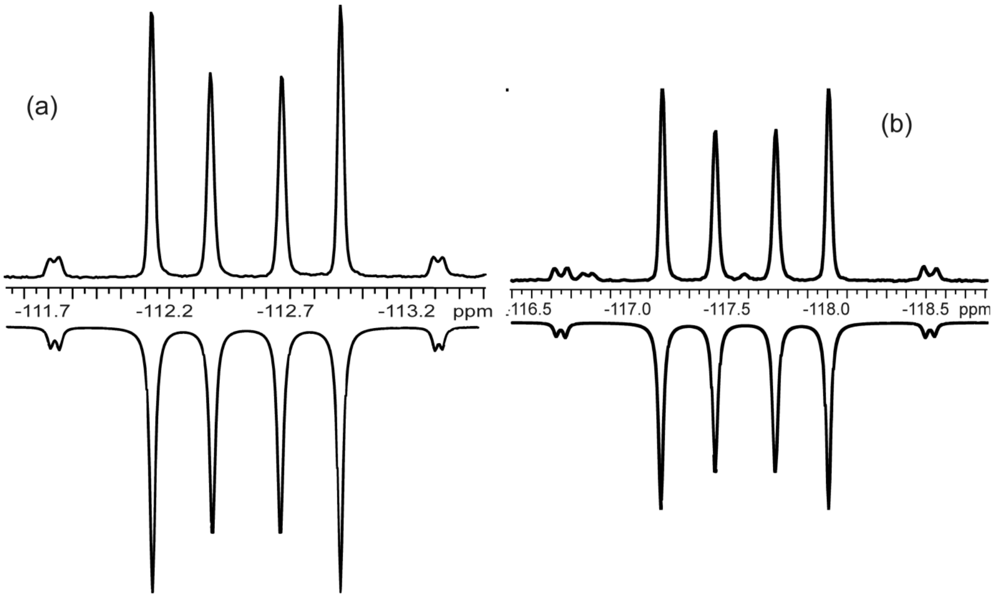


Figure 4.10 (a) Upright: ^{31}P NMR spectrum of the *meso* isomer of **104** in $CDCl_3$ solution at RT. Inverted: simulation of the XX' sub-spectrum. (b) Upright: ^{31}P NMR spectrum of the *rac* isomer of **104** in $CDCl_3$ solution at RT. Inverted: simulation of the XX' sub-spectrum.

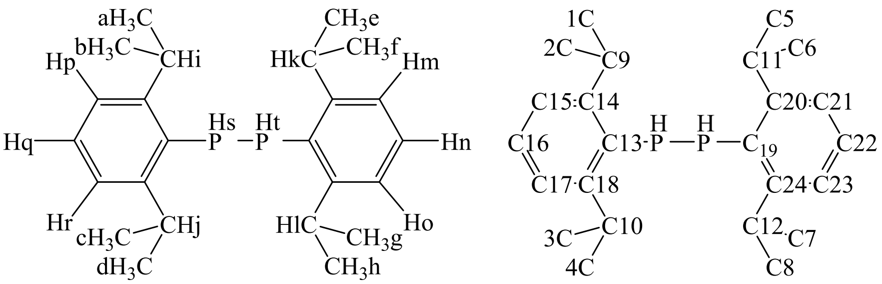


Table 4.3 Experimental and simulated NMR data for *meso* and *rac* isomers of **104**.

58% *meso*				**42% *rac***		
Nucleus	δ, ppm	mult	J, Hz	**Nucleus**	mult	J, Hz
^{31}P NMR				**^{31}P NMR**		
P1	−112.5	AA'XX'		−117.7	AA'XX'	
${}^{1}J_{PH}$			205			210
${}^{2}J_{PH'}$			15			12
${}^{1}J_{PP'}$			187			205
${}^{3}J_{HH'}$			6			7
^{1}H NMR				**^{1}H NMR**		
Ha,b,c,d	1.11	d	6.3	1.09	d	6.3
He,f,g,h	1.18	d	6.3	1.10	d	6.3
Hi,j,k,l	3.44	t of sep	1.4, 6.3	3.46	t of sep	1.6, 6.3
Hs,t	4.50	XX'AA'	see P1	4.62	XX'AA'	see P1
Hp,r,m,o	7.12	*ps*-d [a]	7.7	7.08	*ps*-d [a]	7.7
Hq,n	7.24	*ps*-t	7.7	7.22	*ps*-t	7.7
^{13}C NMR						
C1,2,3,4	24.23	s		24.15	s	
C3,4,5,6	24.57	s		24.31	s	
C9,10,11,12	33.27	*ps*-t	7	33.19	*ps*-t	7
C15,17,21,23	123.47	s		123.43	s	
C16,22	129.29	s		129.45	s	
C13,19	129.77	*ps*-t	11	128.71	*ps*-t	11
C14,18,20,24	153.10	*ps*-t	6	153.50	*ps*-t	6

[a] Broad lines, incipient *pseudo*-triplets with ${}^{4}J_{HP}$ ~ 1 Hz.

The coupling constants $^1J_{pp}$ for $^tBu(H)P\text{-}P(H)^tBu$, **111**, [206.6 Hz (*rac*) and 162.7 Hz (*meso*)][91] exhibit a large difference, but in the case of (2,4,6-$^tBu_3C_6H_2$)(H)P-P(H)(2,4,6-$^tBu_3C_6H_2$) **108** (191.8 Hz (*rac*) and 190.6 Hz (*meso*)), the difference between the coupling constants is small and one reason can be the steric effect. Table 4.4 shows the coupling constants for our compound and other dihydrodiphosphanes.

Table 4.4 Comparative AA'XX' NMR parameters for dihydrodiphosphanes R(H)P–P(H)R.

R		%	$\delta(^{31}P)$	$\delta(^1H\text{-}P)$	$^1J_{PH}$	$^2J_{PH'}$	$^1J_{PP'}$	$^3J_{HH'}$
Dipp	*meso*	58	-112.5	4.499	205	15	(−)189[a]	5.5
	rac	42	-117.0	4.620	210	12	(−)205[a]	7
^{t}Bu	*meso*		-60.8	2.99	190.7	14.2	-162.7	+9.4
	rac		-62.0	3.35	191.9	2.4	-206.6	+13
Mes*	*meso*		-63.9				(−)190.6[a]	
	rac		-63.1				(−)191.8[a]	
TMS_3Si	*meso*	~50	-202	2.0			-80.9	
	rac	~50	-212	2.9			-254.1	
TMS_3C	*meso*						(−)139.7	
	rac						(−)351.5	
CH_3	*meso*		-109.5		189.4	11.2	-167.1	+5.6
	rac		-117.0	6.5	191	8.5	-167.1	10.4
C_6H_{11}	*meso*		-86.3		192.5	12.2	-181.7	+2.9
	rac		-89.7		199.3	4.3	-182.2	+9.3

[a] The sign of $^1J_{PP'}$ is assumed to be negative by analogy with ^{t}Bu, but has not been independently determined.

4.6 Computational study

We used the *ab initio* method at the RHF/63-1G+(3d,2p) level of theory to optimize the geometry of the *meso* and *rac* isomers of **104** for the *anti* (most stable) conformations.

The computational analysis of the energy barrier for rotation about the P–P bond for the *meso* diastereomer (Figure 4.12, Table 4.5) is only ~5 kJ/mol^{-1} and thus low enough to convert *anti* to *gauche* and the reverse. This is even easier for the *rac* diastereomer with a barrier of ~1 kJ/mol^{-1}. Thus, the solution NMR is likely to be the result of a population-weighted average. The result of the average ϕ angles (torsions of the P lone pairs) are 110° for *meso* and 103° for *rac* which means the *rac* with smaller ϕ angle has the larger $^{1}J_{PP'}$ value (205 Hz).

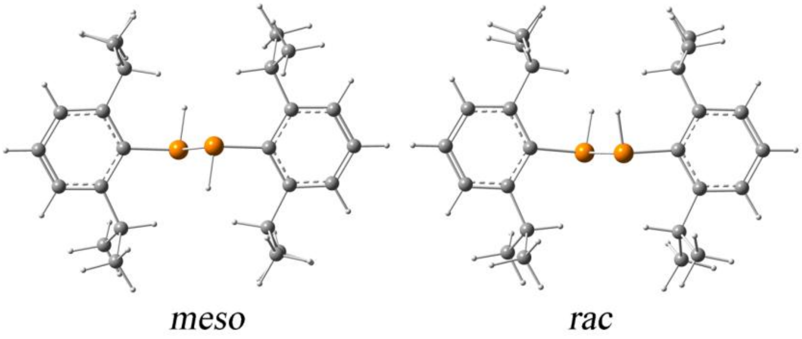


Figure 4.11 Computed geometries (RHF-631G+[3d,2p]) for the *meso* and *rac* isomers of **104**.

We calculated the energy barriers between different conformations of the *meso*-isomer, which is more symmetrical than the *rac*-isomer. We started from the *anti* conformation and calculated the relative energies for every 20° step from *anti* to eclipsed to gauche and back to the *anti* starting point (Figure 4.12a). These relative energies were also calculated for the *rac*-isomer in 10° degree steps to describe its more complex conformations (Figure 4.12b). The optimized geometries of the two *anti* and four *gauche* isomers are included in Figure 4.12 and a summary of the torsion angles and energies are listed in Table 4.5. The calculations show higher populations for the *anti* and the two *gauche* conformers. The data for angle ϕ (the dihedral angle relating the two P non-bonded electron pairs) is also listed in Table 4.6, which is usually used to correlate the size of $^1J_{PP'}$ in the literature.[92,93,94,95] The results showed that there is only a small difference in energy between the *anti* and *gauche* conformers for both *meso* and *rac* isomers.

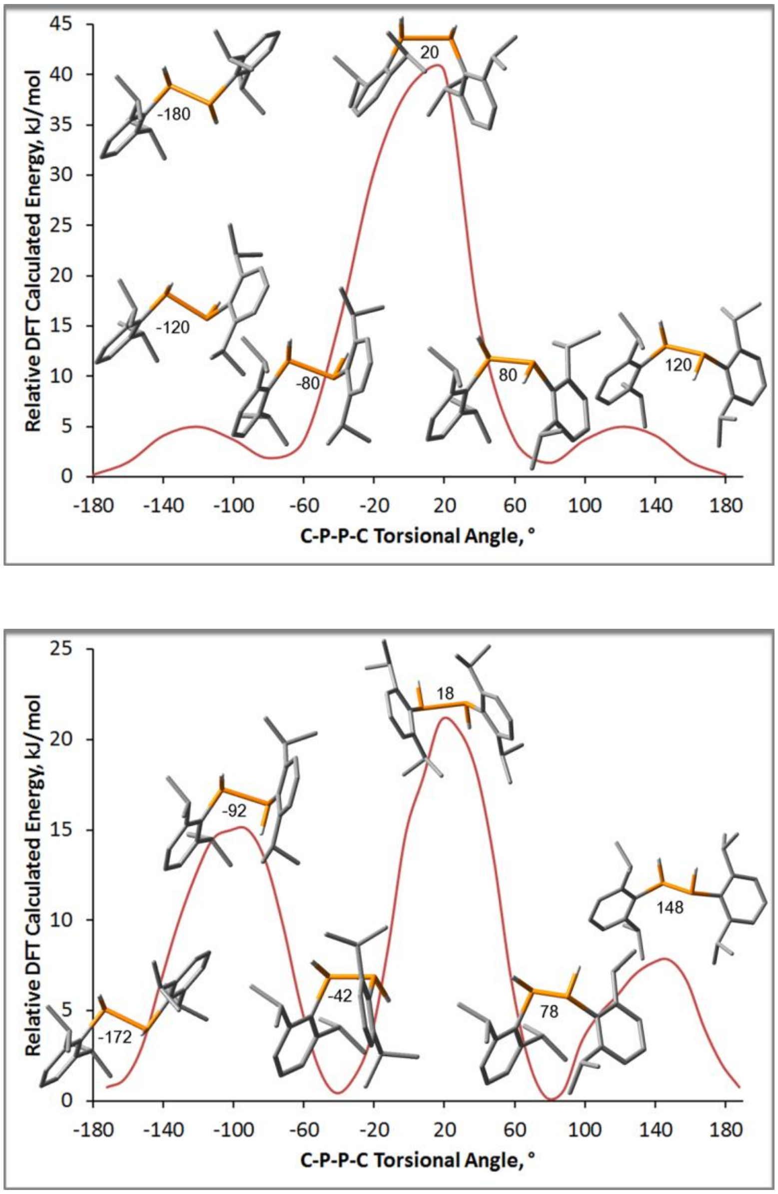


Figure 4.12 B3LYP/6-31G(d,p) computed energy profiles for rotations about the P—P bond of (up) the *meso*- isomer of **104** and (b) the *rac*-isomer of **104**. The structures at maxima and minima are shown with the corresponding torsion angles.

Table 4.5 Geometries and energies of optimized conformers using Hybrid DFT [a].

isomer	conformer	∠CPP'C',°	∠HPP'H',°	φ, °	Relative E, kJ mol^{-1}
meso	*Anti*	-180	180	180	0
	gauche 1	-75.3	75.3	74.8	+1.01
	gauche 2	75.8	-74.8	74.4	+1.04
	Average:			110	
rac	*Anti*	-169.4	33.4	68.1	0
	gauche 1	-82.5	78.2	178.7	+0.74
	gauche 2	+39.6	-165.7	62.9	+0.80
	Average:			103	

[a] Each of the minima in Figure 4.7 was fully optimized at the B3LYP/6-31G(d,p) level of theory; the estimate precision is ±5 kJ/mol.

The computed frontier orbitals show that the HOMO of *meso* isomer has P lone-pair character and is delocalized into the aromatic ring π orbitals. The LUMO is the corresponding out-of-phase combination (Figure 4.13). This is the reason that there are several structurally characterized dicoordinated metal complexes, including Mes(H)P–P(H)Mes **69** to $Cr(CO)_5$,[59] *d*(P–P') = 2.253(2) Å; Ph(H)P–P(H)Ph **110** to $W(CO)_5$,[60] *d*(P–P') = 2.235(1) Å, or to Ag^+,[96] *d*(P–P') = 2.259 Å; **109** to $W(CO)_5$.[60] The conformational preferences for dihydrodiphosphanes in structures of their metal coordination complexes are more diverse than those of the free ligands and worth further investigation.

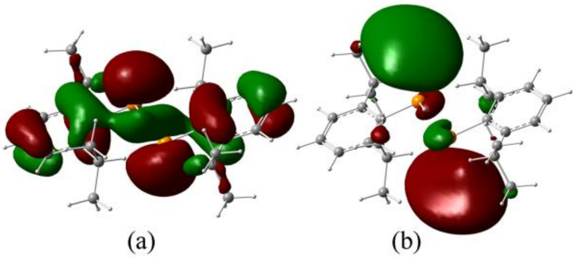

(a) (b)

Figure 4.13 RHF-631G+[3d,2p] frontier molecular orbitals (FMO) of the *meso* isomer for **104**(a) HOMO and (b) LUMO.

4.7 Conclusions

Dihydro diphosphanes are conformationally flexible molecules linked through a particularly elastic P–P bond.[97] NMR evidence indicates that only molecules with the very largest bulky groups such as supersilyl and hypersilyl (which also have spherical shapes) show the *anti* conformations predominant in solution. Our study has shown that it is very important to do a full analysis of the AA'XX' spin system, with spectral simulation which is a powerful check on the correctness of the extracted parameters. The $^{1}J_{P,P'}$ parameter is crucial for characterizing the conformational behaviour in solution for all members of this class of compounds, regardless of the nature of the R groups. Although we know that there are limitations to the use gas-phase calculations for comparison with solution behavior, these calculations provide valuable insights into the behaviour of dihydro diphosphanes in solution.

Chapter 5

Coordination chemistry and suggestions for future work

5.1 Introduction

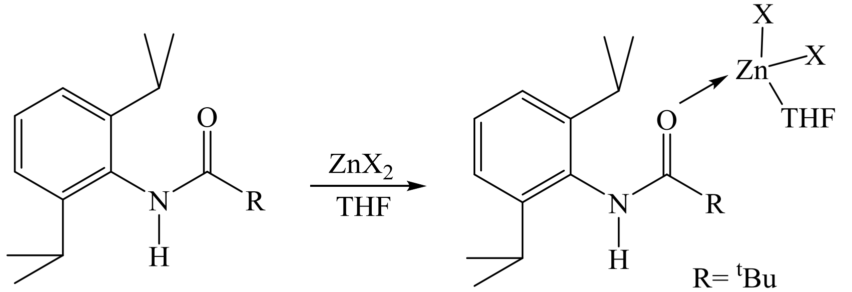
After synthesizing the phosphaamidines and phosphinodiimines, the next step would be exploring the synthesis and coordination chemistry of some metal complexes. Based on the general principle of HSAB (Hard and Soft Acid-Base) theory, hard bases like N prefer hard acids like Ca^{2+}, Sc^{3+} or other very ionic metals. Phosphorus is always a lot softer than nitrogen because it is lower down in the periodic table. Soft bases like phosphorus prefer soft acids, metals like Pd^{2+}, Pt^{2+} or Au^{+}.

5.2 Attempted synthesis of metal complexes for ^{t}Bu-phosphinodiimine 98

As already explained in Chapter 3, I synthesized two phosphinodiimine compounds (**98-99**) that can potentially be used as ligands to make metal complexes. I only attempted to make metal complexes of ^{t}Bu-phosphinodiimine **98** and because results were unexpected, I decided to include these results in this chapter to provide guidance for researchers who might follow my lead in this area of chemistry.

5.2.1 Attempted synthesis of ^{t}Bu-phosphinodiimine metal complexes using $ZnBr_2$ and $ZnCl_2$

I followed Stephan's procedure[37] by using $ZnBr_2$ and $ZnCl_2$ to make zinc complexes of ^{t}Bu-phosphinodiimine. $ZnBr_2$ or $ZnCl_2$ is added to the solution of ^{t}Bu-phosphinodiimine **98** in THF and stirred overnight. After filtration, the crude product was recrystallized from $CHCl_3$ and colorless crystals grew at -25°C. The ^{1}H NMR spectrum showed evidence of the ^{t}Bu-amide zinc complex **112** instead of a ^{t}Bu-phosphinodiimine zinc complex in both cases of $ZnBr_2$ or $ZnCl_2$. Amides can coordinate with zinc (II) either through O or N atom as monodentate ligands[98] or both as bidentate ligands.[99,100] We think that traces of water hydrolysized the phosphinodiimine **98** to amide **79** and zinc catalyzed this dissociation. I was then interested to synthesize the zinc amide complexes on purpose by reacting ^{t}Bu-amide **79** with $ZnBr_2$ in THF (yield 40%). The product was the same as the reaction of phosphinodiimine **98** with $ZnBr_2$ (yield 19%), but the yield was more than double (Scheme 5.1).



79

R= ^{t}Bu
112: X = Cl
113a-c: X = Br

Scheme5.1 Synthesis of zinc amide complexes **112** and **113a-c**.

Based on my literature survey, there are only a few examples for zinc complex of amides, and most of them are bidentate complexes.[98,92] Monodendate zinc complexes of amide are rare compounds and our monodentate zinc complex of ^{t}Bu-amide are novel structures. We previously synthesized and crystallized ^{t}Bu-amide **79** when we had planned to make phosphaamidine **32**. Pure colorless crystals of ^{t}Bu-amide **79** were recrystallized from toluene at RT, and its crystal structure was determined at -100°C (Figure 5.1). The N-C bond length in **79** is 1.3407(17) Å, which is shorter than a C-N single bond (the range of Csp^2-Nsp^2 in acyclic amides is (1.446-1.461 Å))[72] and the C=O bond length is 1.2277(16) Å, which is in the range of a double bond (range of C=O for amide is 1.225-1.243 Å)[72]. The sum of angles around N is 359.9(11)°, which shows that nitrogen is planar. The crystallographic data and selected bond lengths and angles can be found in Tables 5.1 and 5.2 and Appendix III Tables A101-A107.

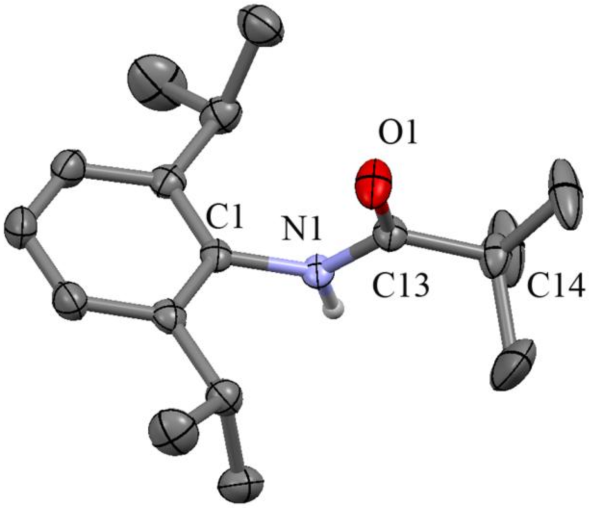


Figure 5.1 Displacement ellipsoids plot (40% probability) showing the molecular structure of ^{t}Bu-amide **79**. Hydrogen atoms on carbon are omitted for clarity.

Crude product of ^{t}Bu-amide zinc dibromide, **112**, and the zinc dichloride complex **113a** were recrystallized from $CHCl_3$ and their colorless crystals grew at -25°C. Crystal structures were determined at -100°C and representations of their structures are shown in Figures 5.2 and 5.3. As is shown in both figures, zinc is tetrahedrally coordinated with the amide and THF oxygen atoms as donor centers and two other coordination sites were filled with two bromides or two chlorides. Crystallographic data for compounds **112** and **113a-c** can be found in Table 5.1 and Appendix III Tables A108-A114. These complexes exhibit distorted tetrahedral geometry around the zinc(II) atom. The C=O bond distances in **112** (1.244(2) Å) and **113a** (1.248(4) Å) have higher single bond character than **79** (1.227(16) Å) due to donation of electron density as a result of coordination that affected the C-O bond. The C-N bond in **112** and **113a** corresponds to greater double bond character. The X-Zn-X angle in zinc dibromide complex **112** (122.864(16) Å) is similar to the zinc dichloride complex **113a** (122.44(7) Å) which is determined by the electronic structure of the complexes. Perhaps the steric factor increases the Br-Zn-Br angle with respect to the Cl-Zn-Cl angle (Table 5.2).

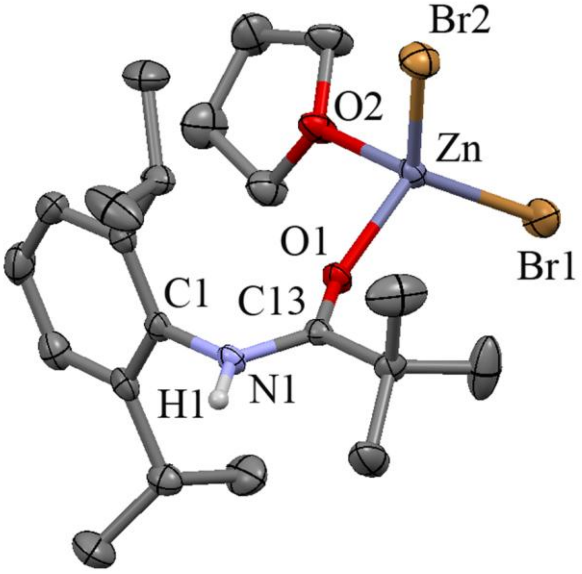


Figure 5.2 Displacement ellipsoids plot (40% probability) showing the molecular structure of ^{t}Bu-amide zinc dibromide complex **112**. Hydrogen atoms on carbon are omitted for clarity.

During the recrystallization of ^{t}Bu-amide zinc dichloride **113a** from $CHCl_3$, two other by-products **113b** and **113c** were formed and crystal structures were determined at -100°C (Fig 5.4 and 5.5). In compound **113b**, which is dimeric, each zinc has tetrahedral coordination through oxygen of the amide, a terminal chlorine atom and two bridging chlorine atoms. **113b** has the $P2_1/n$ space group with two molecules in each unit cell and crystallizes at an inversion center. The detailed crystallographic data can be found in Appendix III Tables A115-A121 for **113a**, Tables A122-A128 for **113b** and Tables A129-A135 for **113c**.

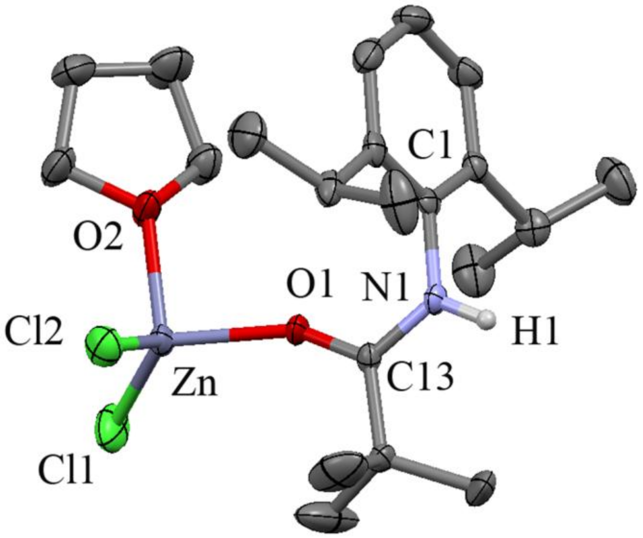


Figure 5.3 Displacement ellipsoids plot (40% probability) showing the molecular structure of ^{t}Bu-amide zinc dichloride complex **113a**. Hydrogen atoms on carbon are omitted for clarity.

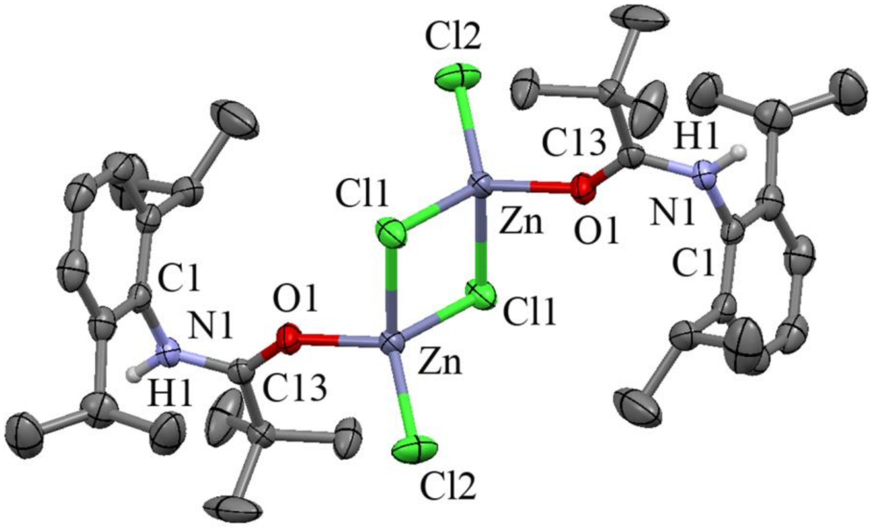


Figure 5.4 Displacement ellipsoids plot (40% probability) showing the molecular structure of **113b**. Hydrogen atoms on carbon are omitted for clarity. The middle of the dimer is located at an inversion centre.

Compound **113c** is similar to compound **113a** with one extra solvent molecule ($CHCl_3$) in the crystal lattice. All **112**, **113a**, and **113c** have one coordinated THF molecule (the solvent that was used for synthesis), but **113c** also has $CHCl_3$ in the crystal lattice ($CHCl_3$ is a solvent that was used for recrystallization). **113c** has the $P2_1/c$ space group and there are four molecules in the unit cell.

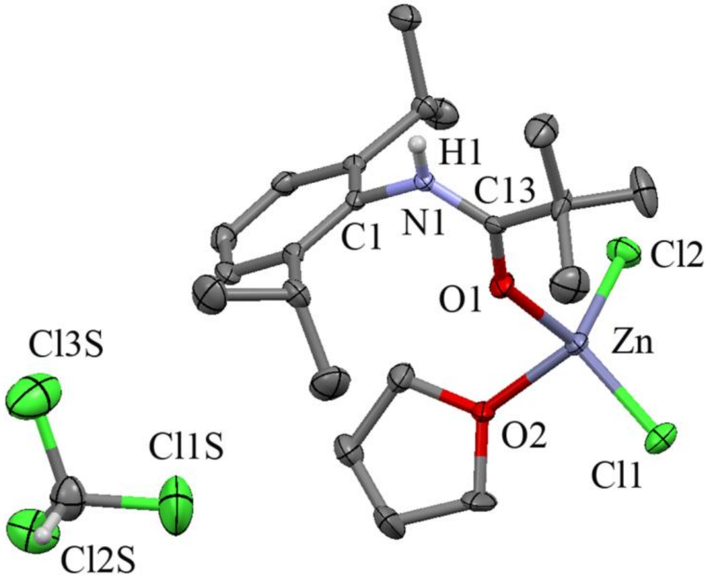


Figure 5.5 Displacement ellipsoids plot (40% probability) showing the molecular structure of **113c**. Hydrogen atoms on carbon are omitted for clarity.

$ZnBr_2$(dimethylacetamide)$_2$ **124** and $ZnCl_2$(dimethylacetamide)$_2$ **125** complexes were synthesized by Wilkins's group[98a] and selected bond length and angles are listed in Table 5.2. The C=O bond in bidendate $ZnBr_2$ complex **124** (1.250(4)°) and **125** (1.249(6)°) is the same as our monodentate $ZnBr_2$ complex **112** (1.244(2)°) and **113a** (1.248(4)°). The O-Zn-O angle of **124** and **125** is smaller than our complexes **112** and **113a**. That might be due to the greater bulk from two dimethylacetamide ligands compared with one amide and one THF in our complexes (Scheme 5.1).

Table 5.1 Crystal data and structure refinement results for ligand **79** and **112** and **113a-c**.

Compound	**79**	**112**	**113a**	**113b**
Space group	$P2_1/c$	Cc	Cc	$P2_1/n$
a/ Å	10.134(5)	14.1856(8)	13.9291(16)	8.6018(14)
b/ Å	18.359(9)	10.8746(6)	10.7019(13)	14.238(2)
c/ Å	9.873(5)	16.5621(9)	16.583(2)	16.507(3)
α	90	90	90	90
β	116.471(5)	106.4390(10)	106.417(2)	92.272(2)
γ	90	90	90	90
Z	4	4	4	2
Goodness-of-fit on F^2	1.041	1.038	0.961	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2= 0.1185	R1 = 0.0186, wR2= 0.0429	R1 = 0.0516, wR2= 0.0784	R1 = 0.0463, wR2= 0.0849
R indices (all data)	R1 = 0.0735, wR2 =0.1332	R1 = 0.0203, wR2= 0.0433	R1 = 0.1000, wR2= 0.0912	R1 = 0.0990, wR2= 0.1075

Table 5.2 Selected bond length (Å) and angles (°) for **79**, **112**, **113**a, **113b**, **124**, and **125**.

	79	**112**	**113a**	**113b**	**124**[98a]	**125**[98a]
O1-C13	1.2277(16)	1.244(2)	1.248(4)	1.253(4)	1.250(4)	1.249(6)
N1-C13	1.3407(17)	1.330(2)	1.323(5)	1.321(4)	---	---
C13-C14	1.536(2)	1.526(3)	1.511(5)	1.517(5)	---	---
Zn-O1	---	1.9713(13)	1.974(3)	1.936(2)	1.982(2)	1.979(3)
Zn-O2	---	2.0325(14)	2.030(3)	---	1.984(2)	1.979(3)
N1-C13-C14	116.83(11)	118.71(17)	118.8(4)	118.0(3)	---	---
O1-C13-C14	121.64(2)	122.42(17)	121.9(4)	123.9(3)		
O1-C13-N1	121.52(13)	118.85(17)	119.3(4)	118.1(3)		
O1-Zn-O2	---	93.55(6)	92.52(11)	---	89.22(10)	90.62(14)
Br2-Zn-Br1	---	122.864(16)	---	---	117.82(2)	---
Cl2-Zn-Cl1	---	---	122.44(7)	---	---	114.87(5)
C13-O1-Zn	---	145.87(13)	145.0(3)	145.7(2)	133.4(2)	131.5(3)

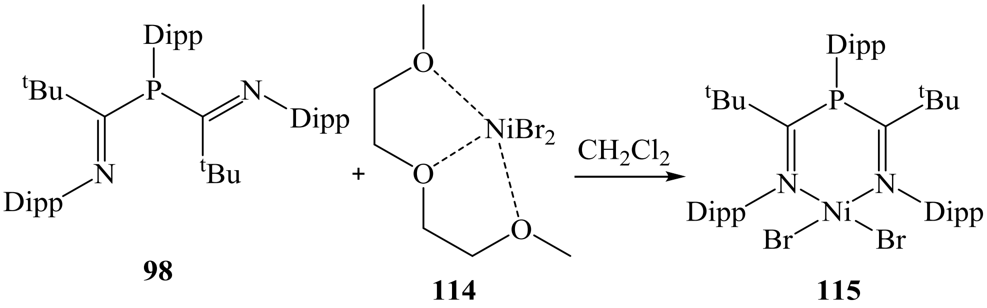
In the IR spectrum, the ν(N-H) band at 3315 cm^{-1} for ligand **79** and 3313 cm^{-1} for $[Zn(L)(THF)Br_2]$ **112** and $[Zn(L)(THF)Cl_2]$ **113a** confirmed that the nitrogen atom does not take apart in the coordination (Table 5.3). The frequency of ν(C=O) was observed at 1646 cm^{-1} in the IR spectra for ligand **79** and a strong band at 1580 and 1581 cm^{-1} was observed for the **112** and **113a**. These shifts in the carbonyl band to lower energy in the complexes are consistent with zinc bonding to ligand through the carbonyl oxygen.[99]

Table 5.3 Selected IR data for ligand **79** and zinc complexes **112** and **113a**.

	79	112	113a
ν(C=O)/ cm^{-1}	1646	1580	1581
ν(N-H)/ cm^{-1}	3315	3313	3313

5.2.2 Suggested synthesis of ^{t}Bu-phosphinodiimine metal complex using $NiBr_2$

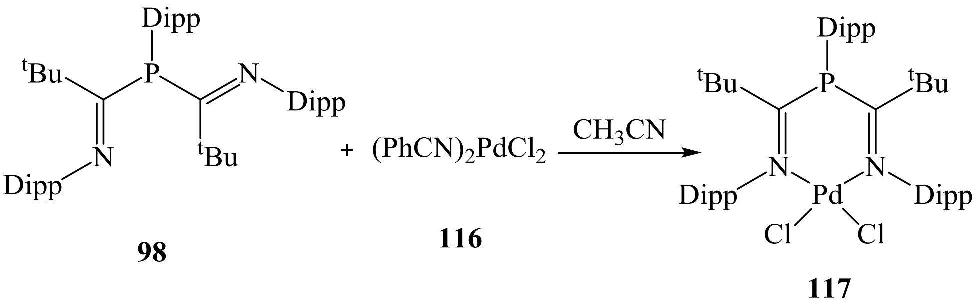
As explained in Section 5.2.1, results for reaction of ^{t}Bu-phosphinodiimine **98** with $ZnCl_2$ and $ZnBr_2$ to make metal complexes of diimine was different compared to what I expected. For further work with coordination of **98**, the following questions need to be answered. First we need to know if the result is the same if we use other metals like Ni? Second it is important to investigate if bulky substituents like ^{t}Bu prevent coordination to metals or not? In its crystal structure and in the solution structure we have deduced, **98** do not have a suitable chelating geometry and that makes it harder to make metal coordination. We believe the bulky ^{t}Bu groups prevent it from having a chelating geometry (Figure 3.1). By changing the ^{t}Bu to a smaller group like CH_3, we observed that CH_3-phosphinodiimine **99** has a chelating geometry (Figure 3.8). Reaction situation should provide the necessary energy to convert the *EZ* isomer of **98** to the chelating geometry. Using other metals may help to synthesize metal complexes of **98**. We suggest following Rojas procedure for making nickel complexes of phosphinodiimine.[101,102] One equivalent of nickel(II) dibromide 2-methoxyethyl ether **114** can be added to a solution of ^{t}Bu-phosphinodiimine **98** in DCM. After stirring at RT, the solution is filtered, solvent evaporated and solid extracted with ether. Because of paramagnetic properties of such a compound, NMR characterization will not be possible and IR spectroscopy needs to be done to characterize such complexes (Scheme 5.2).



Scheme 5.2 Synthesis route to make phosphinodiimine nickel complex **115**.

5.2.3 Suggested synthesis of ^{t}Bu-phosphinodiimine metal complex using (PhCN)$_2$PdCl$_2$

The other suggestion would be following Krämer's procedure for making palladium complexes of ^{t}Bu-phosphinodiimine **98**.[103,93] A solution of (PhCN)$_2$PdCl$_2$, **116**, in acetonitrile can be added to ^{t}Bu-phosphinodiimine **98**. After stirring at RT, the solution should be treated with diethylether and pentane to grow crystals. Product **117** could be characterized by ^{1}H NMR spectroscopy (Scheme 5.3).



98 **116** **117**

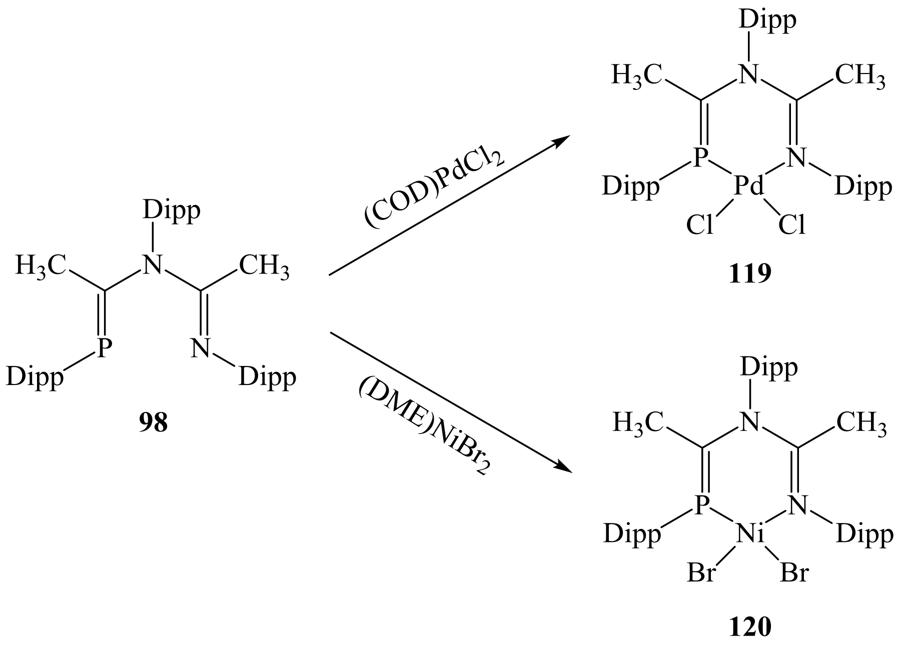
Scheme 5.3 Synthesis route to make phosphinodiimine palladium complex **117**.

5.3 Suggested synthesis of CH_3-phosphinodiimine metal complexes

To understand the effect of substitution on coordination chemistry, I suggest using CH_3-phosphinodiimine **99** which has a small group as a substituent on the backbone carbon instead of bulky ^{t}Bu substitution.

5.3.1 Suggested synthesis of CH_3-phosphinodiimine metal complex using (COD)$PdCl_2$ and (DME)$NiBr_2$

CH_3-phosphinodiimine **99** as PNN ligand could be used for coordination chemistry to make metal complexes by following Guan's procedure.[104,103] CH_3-phosphinodiimine **99** can be added to a suspension of dichloro(1,5-cyclooctadiene)-palladium ((COD)$PdCl_2$) **118** or dibromo(1,2-dimethoxyethane)-nickel ((DME)$NiBr_2$) **114** in dichloromethane. After stirring at RT, the insoluble impurity can be removed by passing through Celite. The complex could perhaps be precipitated with hexanes (Scheme 5.4).



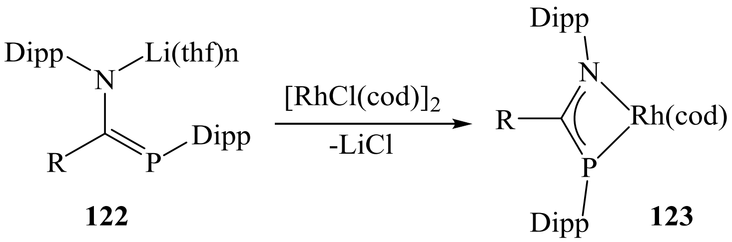
Scheme 5.4 Synthesis route to make phosphinodiimine palladium **119** and nickel **120** complexes.

5.4 Suggested synthesis of *N,P* phosphaamidine metal complex

As explained in Chapter 2, I synthesized different phosphaamidine compounds which potentially can be used as ligands to make metal complexes.

5.4.1 Suggested synthesis of a phosphaamidine metal complex using [RhCl(cod)]$_2$

There are several approaches that could be taken for the synthesis of metal complexes of our phosphaamidines. Lammertsma's route involves reacting *P,N*-chelating lithium adducts with the rhodium complex [RhCl(cod)]$_2$, **121**. In a first step, our phosphaamidine could react with *n*-butyl lithium at -78°C in THF to provide the *N*-coordinated lithium complexes **122** bearing two molecules of THF. The next step would be reacting rhodium complex [RhCl(cod)]$_2$ **121** with **122** to perhaps obtain rhodium complexes of phosphaamidines, **123** (Scheme 5.5).



122 **123**

R = ^{t}Bu, CH_3, $p$$CH_3O$-$C_6H_4$

Scheme 5.5 Synthesis of phosphaamidine rhodium complexes **123**.

Chapter 6

Experimental

6.1 General

All experimental procedures were carried out under a nitrogen atmosphere using modified Schlenk techniques or a glove box, unless otherwise noted. 2,6-diisopropylaniline (Aldrich) was distilled from KOH and stored under nitrogen. Dichloromethane was distilled from CaH_2. 1,2-dibromoethane, 1.6M and 2.5M *n*BuLi in hexanes (Aldrich) were used as received. Solvents for synthesis were collected from a Solvent Purification System (MBraun) (pentane, heptanes, ether) or distilled under an N_2 atmosphere and degassed by the freeze-pump-thaw method or distilled from sodium/benzophenone (tetrahydrofuran), over sodium (xylenes), NaOH (isopropanol) and I_2/Mg (methanol). Air-sensitive liquid reagents were weighed in the glove box under N_2 by using syringes. Melting points were determined on an electrothermal melting point apparatus (capillaries). Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. Raman data were collected at RT on a Bruker RamII-equipped Vertex79 spectrometer (1064 nm laser Nd: YAG laser; Ge detector) operating at 300 mW laser power. 512 scans were co-added; naphthalene was used as the wavenumber reference. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a 300 MHz Bruker Avance II spectrometer (^{1}H 300.138 MHz, ^{13}C 75.468 MHz, and ^{31}P 121.495 MHz) and on 700 MHz Bruker Avance III HD spectrometer (^{1}H 700.27 MHz, ^{13}C 176.12 MHz, ^{31}P 283.52 MHz). ^{1}H NMR signals were referenced to tetramethylsilane and deuterated chloroform, ^{13}C to $CDCl_3$ ($\delta = 77.23$ ppm), ^{31}P to an external H_3PO_4 sample. X-Ray Crystallography: Crystals were selected and mounted in Paratone oil on the ends of thin glass capillaries and cooled on the goniometer head to -100 °C with the Bruker low-temperature accessory attached to the APEX-II diffractometer. Mo K_α radiation (λ = 0.71073 Å) graphite monochromator, was used throughout.[105,106] Computational Details: DFT calculations employed geometry optimization at the B3LYP/6-31G(d,p) and B3LYP/6-31G2(d2,p) levels of theory. Harmonic vibrational frequencies and energy constants were calculated for all optimized geometries. All calculations were performed using Gaussian03W installed on an eight-coprocessor personal computer.[107]

6.2 Preparation of *N*-2,6diisopropylphenylpivalamide or ^{t}Bu-amide 79.

Trimethyl acetyl chloride (14.0 mL, 113.0 mmol) was carefully pipetted into a solution of 2,6-diisopropylaniline **12** (20.0 g, 113.0 mmol) in 200 mL of dry pyridine (CAUTION: vigorous reaction, use cooling), then the mixture was refluxed for 3 h. The solvent was removed, and the residues taken up in 200 mL CH_2Cl_2 and washed twice with 200 mL water. After drying and removal of solvent, the crude product was recrystallized from toluene to give colourless crystals. Yield: 24.58g, 83%. Melting Point: 254-255°C.

^{1}H NMR ($CDCl_3$): δ 1.20 (d, J(H-H) 6.9 Hz, 12H, $CH(CH_3)_2$), 1.36 (s, 9H, $C(CH_3)_3$), 3.01 (septet, 2H, $CH(CH_3)_2$), 6.83 (br, 1H, N-H), 7.16 (d, J(H-H) 7.50 Hz, 2H, m-Dipp), 7.28 (t, 1H, p-Dipp).

^{13}C NMR ($CDCl_3$): δ 23.7 (CH_3 of iso-pr), 27.9 (CH_3 of ^{t}Bu), 28.8 ($CH(CH_3)_2$), 39.4 ($C(CH_3)_3$), 123.5 (m-Dipp), 128.3 (p-Dipp), 131.6 (ipso-Dipp), 146.3 (o-Dipp), 177.4 (CO).

IR cm^{-1}: 3315 (s, N-H), 2960 (vs), 2868 (m), 1646 (vs, CO), 1501 (vs), 1469 (s), 1443 (m), 1361 (w), 1331 (w), 1257 (w),1209 (m), 1168 (m), 934 (s), 807 (m), 789 (s), 735 (vs), 655 (vs), 548 (s).

Elemental Analysis: Calc. for $C_{17}H_{27}NO$: C, 78.11; H, 10.41; N, 5.36. Found: C, 78.06; H, 10.13; N, 5.33.

6.3 Preparation of *N*-2,6diisopropylphenylpivalamide zinc tetrahydrofuran dibromide 112.

Zinc dibromide (0.86 g, 3.83 mmol) was added into a solution of ligand **79** (L= ^{t}BuC(O)NHDipp) (1.00 g, 3.83 mmol) in 30 mL of tetrahydrofuran, then the mixture was stirred overnight. Solvent was removed by rotovap and the crude product was recrystallized from chloroform to give colorless crystals at room temperature. Yield: 0.86 g, 40.0%. Melting Point: 264-267°C.

^{1}H NMR ($CDCl_3$): δ 1.21 (d, J(H-H) 6.9 Hz, 12H, $CH(CH_3)_2$), 1.45 (s, J(H-H) 9H, $C(CH_3)$), 1.74 (pentet, J(H-H) 4H, CH_2-THF), 2.96 (septet, 2H, $CH(CH_3)_2$), 3.59 (pentet, J(H-H) 4H, OCH_2-THF), 7.19 (d, J(H-H) 7.50 Hz, 2H, m-Dipp), 7.32 (t, J(H-H) 1H, p-Dipp), 7.36 (s, J(N-H) 1H).

^{13}C NMR ($CDCl_3$): δ 23.75 (CH_3 of iso-pr), 25.34 (CH_2-THF), 28.01 (CH_3 of ^{t}Bu), 28.91 ($CH(CH_3)_2$), 39.66 ($C(CH_3)_3$), 69.29 (CH_2O-THF), 123.73 (m-Dipp), 129.00 (p-Dipp), 130.70 (ipso-Dipp), 146.36 (o-Dipp), 180.63 (CO).

IR cm^{-1}: 3313 (s, N-H), 2962 (vs), 2932 (w), 2869 (w), 1599 (vs, CO), 1580 (s, CO), 1518 (vs), 1465 (w), 1442 (w), 1383 (m), 1214 (m), 1026 (s), 955 (m), 872 (s), 807 (s), 796 (m), 744 (s), 650 (m), 547 (w).

MS (*m/z*): 665.26 (L_2ZnBr^+, 1.1%); 476.11 ($THFLZnBrTHF^+$, 6.5); 404.05 ($LZnBr^+$, 6.5); 262.22 (LH^+, 100); 220.17 ($L – 3(CH_3)^+$, 12.5).

Elemental Analysis: Calc. for $C_{17}H_{27}NZnBr_2O$: C, 41.96; H, 5.59; N, 2.88. Found: C, 42.21; H, 6.42; N, 2.62.

6.4 Preparation of *N*-2,6diisopropylphenylpivalamide zinc tetrahydrofuran dichloride 113a.

$ZnCl_2$(THF) (0.54 g, 1.92 mmol) was added into a solution of ligand (L= ^{t}BuCONDipp) **79** (0.50 g, 1.92 mmol) in 30 mL of tetrahydrofuran, then the mixture was stirred overnight. Solvent was removed by rotovap and the crude product was recrystallized from chloroform to give colorless crystals at room temperature. Yield: 0.48 g, 41.0%.

^{1}H NMR ($CDCl_3$): δ 1.19 (d, J(H-H) 6.9 Hz, 12H, $CH(CH_3)_2$), 1.42 (s, J(H-H) 9H, $C(CH_3)$), 1.75 (pentet, J(H-H) 4H, CH_2-THF), 2.94 (septet, 2H, $CH(CH_3)_2$), 3.64 (pentet, J(H-H) 4H, OCH_2-THF), 7.17 (d, J(H-H), 7.50 (2H, m-Dipp), 7.30 (t, J(H-H) 1H, p-Dipp), 7.34 (s, J(N-H) 1H).

IR cm^{-1}: 3313 (s, N-H), 2962 (vs), 2870 (w), 1601 (vs, CO), 1581 (s, CO), 1521 (vs), 1467 (w), 1444 (w), 1362 (w), 1259 (s), 1026 (s), 956 (m), 875 (m), 807 (m), 796 (vs), 744 (s), 662 (m), 548 (w).

6.5 Preparation of *N*-(2,2-dimethyl-1-(2,6-diisopropylphenylphosphino)propylidene) aniline 32.

First route: *n*-butyl lithium (2.2 mL, 1.6 M) was added into a solution of DippPH$_2$ **24** (0.65 g, 3.33 mmol) and tetrahydrofuran (7.5 mL) in -60°C and was stirred for 30 min. The mixture was allowed to warm to RT. ^{t}BuCClNDipp **80** (0.93 g, 3.33 mmol) was added to the solution at -60°C and the mixture was allowed to warm to RT and stirred overnight. Solvent was removed with vacuum line and the residue was washed with hexane to precipitate LiCl. Crude product was recrystallized from 15 mL methanol to give colorless crystals. Yield: 1.05 g, 72%.

Second route: Triethylamine (0.14 mL, 1.03 mmol) was added at -70°C under N$_2$ to the solution of ^{t}Bu-phosphaamidine triflate **87** (0.60 g, 1.02 mmol) in dichloromethane. Reaction progress was followed by ^{31}P NMR and completed in 30 min. Work-up consisted of removal of dichloromethane from the reaction mixture and extract the product with diethyl ether by removing HNEt$_3$OSO$_2$CF$_3$ as white precipitate. Yield: 0.37g, 82%.

^{1}H NMR (CDCl$_3$): δ 1.06 (d, 3H, CH(CH$_3$)$_2$), 1.10 (d, 6 H, CH(CH$_3$)$_2$), 1.16 (d, 3H, CH(CH$_3$)$_2$), 1.20 (d, 6H, CH(CH$_3$)$_2$), 1.20 (s, 9H, C(CH$_3$)$_3$), 1.22 (d, 3H, CH(CH$_3$)$_2$), 1.37 (d, 3H,CH(CH$_3$)$_2$), 2.79 (sept, 1H, CH(CH$_3$)$_2$), 2.93 (sept, 1H, CH(CH$_3$)$_2$), 3.55 (sept, 2H, CH(CH$_3$)$_2$), 4.74 (d, 1H, PH), 6.99 (t, 1H, p-Dipp), 7.01 (d, 2H, m-Dipp), 7.03 (d, 2H, m-Dipp), 7.09 (d, 4H, m-Dipp), 7.30 (t, 1H, p-Dipp).

^{31}P NMR (CDCl$_3$): δ -84.73 (d, J(P-H) = 251.26).

^{13}C NMR (CDCl$_3$): δ 21.65 (CH$_3$ of iso-pr), 21.70 (CH$_3$ of iso-pr), 23.49 (CH$_3$ of iso-pr), 27.03 (CH$_3$ of iso-pr), 28.32 (CH(CH$_3$)$_2$), 28.77 (CH(CH$_3$)$_2$), 29.30 (CH$_3$ of ^{t}Bu), 33.63 (CH(CH$_3$)$_2$), 45.32 (C(CH$_3$)$_3$), 122.70 (m-Dipp-N), 123.03 (m-Dipp-N), 123.33 (p-Dipp-

N), 123.36 (m-Dipp-N), 128.62 (ipso-Dipp-P), 130.78 (p-Dipp-P), 134.53 (o-Dipp-N), 134.89 (o-Dipp-N), 146.64 (ipso-Dipp-N), 154.59 (o-Dipp-P), 182.21 (C=N).

Elemental Analysis: Calc. for $C_{29}H_{44}NP$: C, 79.59; H, 10.13; N, 3.20. Found: C, 79.30; H, 10.16; N, 3.65.

6.6 Preparation of 2,6-diisopropylphenylbis(*N*-2,6-diisopropylphenyl*tert*-butylimidoyl) phosphane or ^{t}Bu-phosphinodiimine 98.

n-Butyl lithium (2.0 mL, 1.6 M) was added into a solution of DippPH$_2$ **24** (0.55 g, 2.80 mmol) and tetrahydrofuran (15 mL) in -70°C and was stirred for 30 min. The mixture was allowed to warm to RT. ^{t}BuCClNDipp **80** (0.75 g, 2.80 mmol) was added to the solution in -70°C and the mixture was allowed to warm to RT and stirred overnight. In the morning another equivalent of n-butyl lithium (2.0 mL, 1.6 M) was added into a solution in -70°C and was stirred for 30 min. The mixture was allowed to warm to RT. Another equivalent of ^{t}BuCClNDipp **80** (0.75 g, 2.80 mmol) was added to the solution in -70°C and the mixture was allowed to warm to RT and stirred overnight. In the morning, solvent was removed with a vacuum line and the residue was washed with hexane to precipitate LiCl. LiCl was filtered off on a filter stick and hexane was removed with a vacuum line. Crude product was recrystallized from 20 mL heptanes to give yellow crystals. Yield: 1.25 g, 65%. NMR was run at -25°C and shows two isomers. Melting Point: 179.5-181.5°C.

^{1}H NMR (CDCl$_3$) major: δ 0.02 (d, 3H, CH(CH$_3$)$_2$), 0.14 (d, 3H, CH(CH$_3$)$_2$), 0.15 (d, 3H, CH(CH$_3$)$_2$), 0.25 (d, 6H, CH(CH$_3$)$_2$), 0.84 (d, 3H, CH(CH$_3$)$_2$), 0.86 (d, 3H, CH(CH$_3$)$_2$), 0.95 (d, 6H, CH(CH$_3$)$_2$), 1.07 (d, 3H, CH(CH$_3$)$_2$), 1.28 (d, 3H, CH(CH$_3$)$_2$), 1.42 (d, 3H, CH(CH$_3$)$_2$), 1.23 (s, 9H, C(CH$_3$)$_3$), 1.61 (s, 9H, C(CH$_3$)$_3$), 1.73 (sept, 1H, CH(CH$_3$)$_2$), 1.75 (sept, 1H, CH(CH$_3$)$_2$), 1.78 (sept, 1H, CH(CH$_3$)$_2$), 3.13 (sept, 1H, CH(CH$_3$)$_2$), 3.35 (sept, 1H, CH(CH$_3$)$_2$), 3.74 (sept, 1H, CH(CH$_3$)$_2$), 6.68 (d, 1H, m-Dipp-N), 6.84 (d, 1H, m-Dipp-N), 6.88 (t, 1H, p-Dipp-N), 6.86-6.89 (d, 2H, m-Dipp-P), 7.01 (d, 1H, m-Dipp-N), 7.13 (d, 1H, m-Dipp-N), 7.18 (t, 1H, p-Dipp-P).

^{1}H NMR (CDCl$_3$) minor: δ 1.03 (d, 3H, CH(CH$_3$)$_2$), 1.06 (d, 3H, CH(CH$_3$)$_2$), 1.08 (d, 3H,

$CH(CH_3)_2$), 1.17 (d, 3H, $CH(CH_3)_2$), 1.19 (d, 3H, $CH(CH_3)_2$), 1.26 (d, 3H, $CH(CH_3)_2$), 1.27 (d, 3H, $CH(CH_3)_2$), 1.29 (d, 6H, $CH(CH_3)_2$), 1.32 (d, 6H, $CH(CH_3)_2$), 1.35 (d, 3H, $CH(CH_3)_2$), 1.02 (s, 9H, $C(CH_3)_3$), 1.17 (s, 9H, $C(CH_3)_3$), 2.88 (sept, 1H, $CH(CH_3)_2$), 2.91 (sept, 1H, $CH(CH_3)_2$), 3.04 (sept, 1H, $CH(CH_3)_2$), 3.05 (sept, 1H, $CH(CH_3)_2$), 3.77 (sept, 1H, $CH(CH_3)_2$), 4.82 (sept, 1H, $CH(CH_3)_2$), 7.03(d, 1H, m-Dipp-N), 7.08 (t, 2H, p-Dipp-N), 7.18 (d, 1H, p-Dipp-P), 7.22 (d, 1H, m-Dipp-N), 7.23 (d, 1H, m-Dipp-P), 7.34 (t, 1H, p-Dipp-P), 7.86-7.89 (br, 1H, m-Dipp-N).

^{13}C NMR ($CDCl_3$): δ 20.20, 21.00, 21.31, 21.84, 22.45, 22.83, 23.02, 23.24, 23.77, 24.15, 24.62, 24.86, 25.41, 25.89, 26.07, 26.19, 26.45, 26.84, 27.30, 27.68, 27.90, 28.02, 28.08, 28.30, 28.41, 28.51, 29.13, 29.45, 29.80, 30.51, 31.33, 31.56, 32.02, 32.13, 32.36, 34.53, 35.32, 121.73, 122.09, 122.17, 122.39, 123.17, 123.30, 123.41, 123.66, 124.16, 124.45, 124.81, 125.00, 130.47, 130.67, 133.13, 133.65, 133.88, 134.17, 135.03, 145.92, 147.02, 148.12, 154.43, 155.67, 156.72, 156.94, 179.87, 180.11, 180.62,182.63 major (C=N), 187.51 major (C=N).

^{31}P NMR ($CDCl_3$): two isomers: δ -7.54 (s) and 10.41 (s).

IR cm^{-1}: 3053 (w), 2962 (vs), 2927 (s), 2866 (s), 1652 (s), 1580 (vs), 1460 (vs), 1429 (vs), 1382 (s), 1359 (s), 1255 (m), 1206 (w), 1177 (w), 1157 (m), 1124 (m), 1044 (m), 1033 (m), 928 (s), 900 (vs), 804 (s), 790 (vs), 746 (vs), 507 (w).

MS (*m/z*): 379.31 (Dipp(NH)CCH_3Dipp(NH)+, 100%); 202.16 (DippN≡CCH_3+, 15%).

Elemental Analysis: Calc. for $C_{46}H_{69}N_2P$: C, 81.13; H, 10.21; N, 4.11 and Found: C, 80.87; H, 10.06; N, 4.08.

6.7 Preparation of 2,6-diisopropylphenylbis(*N*-2,6-diisopropylphenylmethyl) phosphaalkene or CH_3-amidinophosphalkene 99.

30 mL xylene was freeze-thaw degassed five times in a side arm flask. DippPH$_2$ **24** (0.53 g, 2.70 mmol) and CH_3CClNDipp **14c** (1.30 g, 5.46 mmol) was added to the solvent. Solution was stirred and refluxed overnight. Monitoring the reaction with ^{31}P NMR spectroscopy showed that DippPH$_2$ was consumed and a singlet (around δ = 7.00 ppm) started to grow. There was no sign of phosphaamidine as intermediate in the ^{31}P NMR spectrum (for example, a singlet around δ = 50 ppm as a C=P phosphaamidine or a doublet around δ = 80 as a C=N phosphaamidine). In the morning, solvent was removed with a vacuum line and the residue was washed with hot ethanol to precipitate product. Product was collected on a filter stick and dried with a vacuum line to remove any ethanol to give pale yellow crystals. Yield: 0.90 g, 55%. MP: 125.5-127.0°C.

^{1}H NMR ($CDCl_3$): δ 1.09 (d, 6H, $CH(CH_3)_2$), 1.11 (d, 6H, $CH(CH_3)_2$), 1.14 (d, 6H, $CH(CH_3)_2$), 1.17 (d, 12H, $CH(CH_3)_2$), 1.19 (d, 6H, $CH(CH_3)_2$), 1.48 (s, 3H, CH_3), 1.79 (d, 3H, CH_3), 2.99 (sept, 2H, $CH(CH_3)_2$), 3.02 (sept, 2H, $CH(CH_3)_2$), 3.66 (sept, 2H, $CH(CH_3)_2$), 6.93 (t, 1H, p-Dipp-N), 7.02 (d, 2H, m-Dipp-P), 7.06 (d, 2H, m-Dipp-N), 7.15 (t, 1H, m-Dipp-P), 7.17 (d, 2H, m-Dipp-N), 7.33 (t, 1H, m-Dipp-N).

^{13}C NMR ($CDCl_3$): 22.97, 23.38, 23.86, 23.96, 24.27, 24.44, 24.51, 24.92, 26.62, 27.77, 28.39, 28.57, 34.04, 122.68, 122.72, 123.03, 123.62, 124.28, 124.86, 125.22, 131.72, 146.75 (C=P), 176.16 (C=N).

^{31}P NMR ($CDCl_3$): δ 7.23 (s).

IR cm^{-1}: 3059 (w), 2959 (vs), 2926 (s), 2865 (s), 1601 (s), 1584 (vs), 1461 (vs), 1433 (s), 1380 (s), 1359 (vs), 1322 (s), 1260 (s), 1244 (w), 1159 (vs), 1127 (s), 1097 (m), 1058 (m), 1042 (m),955 (w), 805 (vs), 797 (vs), 766 (vs), 743 (s), 689 (m).

MS (*m/z*): 798.58 (M+, 14%), 403.31 (DippHN=C(CH_3)C≡CNHDipp+, 91%), (DippHNC(CH_3)=NHDipp+, 100%).

Elemental Analysis: Calc. for $C_{40}H_{57}N_2P$: C, 80.49; H, 9.63; N, 4.96 and Found: C, 80.21; H, 9.33; N, 4.65.

6.8 Preparation of 2,6-diisopropylphenylbis(*N*-2,6-diisopropylphenylmethylimidoyl) phosphane methylimidoyl 100.

n-butyl lithium (2.3 mL, 1.6 M) was added into a solution of DippPH$_2$ **24** (0.70 g, 3.60 mmol) and tetrahydrofuran (20 mL) in -70°C and was stirred for 30 min. The mixture was allowed to warm to RT. CH$_3$CClNDipp **14c** (0.86 g, 3.60 mmol) was added to the solution in -70°C and the mixture was allowed to warm to RT and stirred overnight. In the morning, another equivalent of n-butyl lithium (2.3 mL, 1.6 M) was added into a solution at -70°C and was stirred for 30 min. The mixture was allowed to warm to RT. Another equivalent of CH$_3$CClNDipp **14c** (0.86 g, 3.60 mmol) was added to the solution in -70°C and the mixture was allowed to warm to RT and stirred overnight. In the morning solvent was removed with a vacuum line and the residue was washed with hexane to precipitate LiCl. LiCl was filtered off with a filter stick and hexane was removed with a vacuum line. The residue was washed with hot ethanol to precipitate product. Pale yellow solid from filtration with filter stick was **99**. The filtrate was transferred to another Schlenk tube and ethanol was removed with a vacuum line. The yellow residue was recrystallized with heptanes to give yellow crystals. Melting Point: 195.5-196.5°C.

^{1}H NMR (C$_6$D$_6$): δ 0.26 (d, 3H, CH(CH$_3$)$_2$), 0.78 (d, 3H, CH(CH$_3$)$_2$), 0.88 (d, 3H, CH(CH$_3$)$_2$), 0.929-0.974 (m, 6H, CH(CH$_3$)$_2$), 1.06 (d, 3H, CH(CH$_3$)$_2$), 1.11 (d, 3H, CH(CH$_3$)$_2$), 1.14-1.35 (m, 27H, CH(CH$_3$)$_2$, 3H, CH$_3$), 1.55 (d, 3H, CH(CH$_3$)$_2$), 1.69 (d, 3H, CH(CH$_3$)$_2$), 1.82 (s, 3H, CH$_3$), 2.46 (sept, 1H, CH(CH$_3$)$_2$), 2.58 (sept, 1H, CH(CH$_3$)$_2$), 2.95 (sept, 1H, CH(CH$_3$)$_2$), 3.04 (sept, 1H, CH(CH$_3$)$_2$), 3.13 (sept, 1H, CH(CH$_3$)$_2$), 3.23 (sept, 1H, CH(CH$_3$)$_2$), 3.53 (sept, 1H, CH(CH$_3$)$_2$), 3.99 (sept, 1H, CH(CH$_3$)$_2$), 6.24 (s, 1H, N-H), 6.85 (d, 1H, DippH), 7.0–7.36 (m, 11H, DippH), 12.09 (d, 1H, CH).

^{31}P NMR (C_6D_6): δ -14.68 (s).

IR cm^{-1}: 3056 (w), 2959 (vs), 2924 (s), 2865 (s), 1639 (s), 1584 (w), 1597 (vs), 1583 (vs), 1526 (s), 1499 (m), 1459 (s), 1441 (s), 1381 (s), 1360 (vs), 1338 (vs), 1257 (s), 1127 (vs), 1099 (vs), 1057 (m), 1041 (m), 933 (w), 870 (w), 796 (s), 770 (vs), 748 (vs), 710 (vs), 689 (w), 618 (w).

Elemental Analysis: Calc. for $C_{54}H_{76}N_3P$: C, 81.26; H, 9.60; N, 5.26 and Found: C, 80.96; H, 9.86; N, 5.13.

6.9 Preparation of 1,2-Bis(2,6-diisopropylphenyl)diphosphane 104.

n-butyl lithium (1.1 mL, 2.5 M) was added into a solution of DippPH$_2$ **24** (0.50 g, 2.57 mmol) and tetrahydrofuran (10 mL) in -70°C and was stirred for 30 min. The mixture was allowed to warm to RT and solvent was removed with a vacuum line. 10 mL dry toluene was added to the residue which is DippPHLi. The solution was cooled to -30 °C and 1,2-dibromoethane (0.48 g, 2.57 mmol) was added with stirring and the mixture was allowed to warm to RT overnight. Solvent was removed with a vacuum line and the residue was washed with pentane to precipitate LiBr. LiBr is isolated by filtration and pentane was removed by vacuum line. The crude product was a light yellow; recrystallization from hot methanol ended up with too small colorless crystals which did not diffract well. Pure colorless crystals were finally obtained in the liquid phosphane (DippPH$_2$) which was stored for some time at -10 °C in a freezer; decanting and rinsing with a minimum of cold pentane produced **104** which were used for further characterization. ^{31}P NMR shows two isomers.

^{1}H NMR (CDCl$_3$): *meso* isomer; δ 1.11 (d, 12H, CH(CH$_3$)$_2$), 1.18 (d, 12H, CH(CH$_3$)$_2$), 3.44 (t of sep, 4H, CH(CH$_3$)$_2$), 4.50 (AA'XX', 2H, PH), 7.12 (ps-d, 2H, m-Dipp), 7.24 (ps-t, 1H, p-Dipp).

^{1}H NMR (CDCl$_3$): *rac* isomer; δ 1.09 (d, 12H, CH(CH$_3$)$_2$), 1.10 (d, 12H, CH(CH$_3$)$_2$), 3.46 (t of sep, 4H, CH(CH$_3$)$_2$), 4.62 (AA'XX', 2H, PH), 7.08 (ps-d, 2H, m-Dipp), 7.22 (ps-t, 1H, p-Dipp).

^{13}C NMR (CDCl$_3$): *meso* isomer; δ 24.23 (CH$_3$ of iso-pr), 24.57 (CH$_3$ of iso-pr), 28.32 (CH(CH$_3$)$_2$), 33.27 (CH(CH$_3$)$_2$), 123.47 (m-Dipp), 129.29 (p-Dipp), 129.77 (ipso-Dipp), 153.10 (o-Dipp).

^{13}C NMR (CDCl$_3$): *rac* isomer; δ 24.15 (CH$_3$ of iso-pr), 24.31 (CH$_3$ of iso-pr), 33.19

$(CH(CH_3)_2)$, 123.43 (m-Dipp), 128.71 (p-Dipp), 129.45 (ipso-Dipp), 153.50 (o-Dipp).

^{31}P NMR ($CDCl_3$): δ -112.5 ppm (AA'XX', *meso* 58%) and -117.7 ppm (AA'XX', *rac* 42%).

MS (*m/z*): 386.22877 (M+, $C_{24}H_{36}P$+, 40%); 193.11289 (DippPH+, 100%).

Elemental Analysis: Calc. for $C_{24}H_{36}P$: C, 74.6; H, 9.4%. and Found: C, 72.8; H, 9.8 %.

6.10 Preparation of (*N*-2,6 diisopropylphenyl)(*tert*-butyl)carbonitrilium triflate 83.

^{t}Bu-imidoyl chloride **80** (2.00 g, 7.15 mmol) solution in dichloromethane reacted with trimethylsilyl trifluoromethanesulfonate (1.80 mL, 9.29 mmol) at -70°C under N_2 to produce ^{t}Bu-nitrilium triflate **83**. Trimethylsilyl trifluoromethanesulfonate ($Me_3SiCF_3SO_3$) is very reactive and will vigorously react with moisture, so it needs to be handling very carefully and using a glove box. Work-up consisted of removal of dichloromethane and washing of crude material with pentane to achieve **83** as a white solid. Yield: 1.25 g, 77%. Melting Point: 184-186°C.

^{1}H NMR ($CDCl_3$): δ 1.33 (d, 12H, $CH(CH_3)_2$), 1.87 (s, 9H, $C(CH_3)_3$), 3.21 (sept, 1H, $CH(CH_3)_2$), 7.32 (d, 2H, m-Dipp), 7.61 (t, 1H, p-Dipp).

^{13}C NMR ($CDCl_3$): δ 22.59 (CH_3 of iso-pr), 27.03 (CH_3 of ^{t}Bu), 30.19 ($CH(CH_3)_2$), 32.06 ($C(CH_3)_3$), 118.51 (ipso-Dipp), 120.3 (CF_3SO_3), 124.69 (m-Dipp), 125.74 (C=N), 134.41 (p-Dipp), 148.0 (o-Dipp).

IR cm^{-1}: 3314 (w), 3208 (w), 2960 (s), 2872 (w), 1645 (s), 1501 (s), 1469 (s), 1294 (vs), 1256 (s), 1168 (vs), 1107 (w), 1027 (vs), 921 (w), 859 (w), 802 (s), 738 (m), 636 (vs), 576 (w), 543 (w), 515 (m).

Elemental Analysis: Calc. for $C_{18}H_{26}NF_3SO_3$: C, 54.95; H, 6.66; N, 3.56 and Found: C, 54.11; H, 6.66; N, 3.37.

6.11 Preparation of N-(2,2-dimethyl-1-(2,6-iisopropylphenylphosphino)propylidene) 2,6-diisopropylphenylaminium triflate 87.

DippPH$_2$ **24** (0.74 g, 3.80 mmol) reacted with solution of ^{t}Bu-nitrilium triflate **83** (1.5 g, 3.8 mmol) in dichloromethane at -70°C under N$_2$ to produce ^{t}Bu-phosphaamidines triflate **87**. Reaction progress was followed by ^{31}P NMR and after one hour stirring at RT a broad peak at δ = -63.69 ppm in CH$_2$Cl$_2$ was observed and there was no sign of starting material (DippPH$_2$ **24**, δ = -156.92 ppm) which confirmed reaction was complete. Work-up consisted of removal of dichloromethane from the reaction mixture and washing the crude material with pentane. **87** as a white solid dissolved in a minimum quantity of hot dichloromethane and after cool to RT, layered gently with heptanes under N$_2$ and left at -25°C to grow X-ray quality crystals. After two days, colorless crystals grew at -25°C and crystallographic data was collected at -100°C. Yield: 2.02 g, 90%. Melting Point: 174-176°C.

^{1}H NMR (CDCl$_3$) major: δ 1.10 (d, 6H, CH(CH$_3$)$_2$), 1.13 (d, 6H, CH(CH$_3$)$_2$), 1.29 (s, 9H, C(CH$_3$)$_3$), 1.42 (d, 12H, CH(CH$_3$)$_2$), 2.77 (br s, 2H, CH(CH$_3$)$_2$) 3.27 (sept, 2H, CH(CH$_3$)$_2$), , 5.01 (d, 1H, PH, J = 288 Hz), 7.17 (d, 2H, m-Dipp-P), 7.33 (t, 1H, p-Dipp-P), 7.37 (d, 2H, m-Dipp-N), 7.52 (t, 1H, p-Dipp-P).

^{13}C NMR (CDCl$_3$): δ 22.76, 23.30, 23.61, 23.70, 28.73, 29.45, 30.58, 32.97, 34.95, 39.06, 46.34, 117.28, 119.09, 120.91, 122.82, 123.76, 126.40, 128.19, 129.38, 131.81, 133.98, 145.03, 151.36 major (C=N).

^{31}P NMR (CDCl$_3$): δ = -60.68 ppm (d, J_{PH} = 280 Hz, major) and -71.14 ppm (d, J_{PH} = 266, minor).

IR cm^{-1}: 3316 (w), 2967 (m), 2372 (w), 1646 (w), 1588 (w), 1557 (m), 1467 (m), 1366 (m), 1291 (vs), 1233 (vs), 1221 (vs), 1153 (vs), 1057 (w), 1029 (vs), 941 (m), 902 (w), 811 (m), 801 (s), 753 (m), 741 (m), 636 (vs), 600 (s), 571 (m), 514 (s), 432 (m).

Elemental Analysis: Calc. for $C_{30}H_{45}NF_3O_3PS$: C, 61.31; H, 7.72; N, 2.38 and Found: C, 61.50; H, 7.23; N, 2.75.

6.12 Preparation of (*N*-2,6 diisopropylphenyl)(methyl)carbonitrilium triflate 84.

Trimethylsilyl trifluoromethanesulfonate ($Me_3SiCF_3SO_3$) (1.7 mL, 8.73 mmol) was added to the solution of CH_3-imidoyl chloride **14c** (2.0 g, 6.7 mmol) in CH_2Cl_2 at -70°C under N_2 to produce CH_3-nitrilium triflate **84** after 30 min stir at RT. Work-up consisted of removal of dichloromethane with a vacuum line and washing of the crude material with pentane to achieve compound **84** as a white solid. Yield: 2.1 g, 93%. Melting Point: 76-77°C.

^{1}H NMR ($CDCl_3$): δ 1.28 (d, 12H, $CH(CH_3)_2$), 3.27 (sept, 2H, $CH(CH_3)_2$), 3.49 (s, 3H, CH_3), 7.30 (d, 2H, m-Dipp), 7.58 (t, 1H, p-Dipp-N), 6.88 (t, 1H, p-Dipp).

^{13}C NMR ($CDCl_3$): δ 5.93 (CH_3 of backbone), 22.95 (CH_3 of iso-pr), 30.00 ($CH(CH_3)_2$), 118.79 (ipso-Dipp), 121.52 (C=N), 124.74 (m-Dipp), 134.17 (p-Dipp), 148.44 (o-Dipp).

IR cm^{-1}: 3394 (w), 3170 (w), 3074 (w), 2969 (m), 2874 (w), 1832 (w), 1672 (m), 1550 (w), 1385 (w), 1365 (w), 1294 (s), 1216 (vs), 1173 (vs), 1101 (w), 1056 (w), 1025 (vs), 799 (s), 763 (w), 750 (w), 634 (s), 575 (m), 515 (s), 423 (m).

Elemental Analysis: Calc. for $C_{15}H_{20}NF_3O_3S$: C, 51.27; H, 5.74; N, 3.99 and Found: C, 49.24; H, 5.85; N, 3.76.

6.13 Preparation of N-(2,6-diisopropylphenylphosphino)methyl)2,6-diisopropylphenyl-aminium triflate 88.

CH_3-nitrilium triflate **84** (1.00 g, 2.98 mmol) was added to the solution of $DippPH_2$ **24** (0.58 g, 2.98 mmol) in dichloromethane at -70°C under N_2 to produce CH_3-phosphaamidines triflate **88** and reaction progress was followed by ^{31}P NMR. After 30 min stirring at RT, two doublets were observed at -71.14 ppm (J = 266.5 Hz) and -60.68 ppm (J = 280.7 Hz) and there was no sign of $DippPH_2$ **24** which confirmed reaction is complete. Work-up consisted of removal of dichloromethane from the reaction mixture with a vacuum line and washing crude material with pentane. CH_3-phosphaamidine triflate **88** dissolved in a minimum quantity of hot dichloromethane under N_2 and after cooling to RT, was gently layered with heptanes. The colorless solution was left in a freezer at -25°C to grow crystals. Good quality colorless crystals grew after two days at -25°C and the crystal structure was determined at -100. Yield: 1.46 g, 92%. Melting Point: 141-143°C.

^1H NMR ($CDCl_3$) major: δ 1.26 (d, 12H, $CH(CH_3)_2$), 1.31 (d, 6H, $CH(CH_3)_2$), 1.43 (d, 6H, $CH(CH_3)_2$), 2.65 (s, 3H, CH_3 backbone), 2.86 (sept, 2H, $CH(CH_3)_2$), 3.25 (sept, 2H, $CH(CH_3)_2$), 5.13 (d, 1H, PH), 7.32 (d, 2H, m-Dipp-P), 7.40 (d, 2H, m-Dipp-N), 7.55 (t, 1H, p-Dipp-N), 7.56 (t, 1H, p-Dipp-P), 14.04 (s, 1H, NH).

^1H NMR ($CDCl_3$) minor: δ 1.26 (br, 12H, $CH(CH_3)_2$), 1.33 (d, 6H, $CH(CH_3)_2$), 1.34 (d, 6H, $CH(CH_3)_2$), 2.00 (s, 3H, CH_3 backbone), 2.74 (sept, 2H, $CH(CH_3)_2$), 3.65 (sept, 2H, $CH(CH_3)_2$), 6.73 (d, 1H, PH), 7.30 (d, 2H, m-Dipp-N), 7.34 (d, 2H, m-Dipp-P), 7.47 (t, 1H, p-Dipp-N), 7.56 (t, 1H, p-Dipp-P), 14.24 (s, 1H, NH).

^{13}C NMR ($CDCl_3$): δ 22.43, 22.86, 23.33, 24.38, 25.50, 25.57, 29.50, 29.55, 34.37, 34.46, 119.50, 121.34, 123.15, 124.90, 124.95, 131.39, 131.68, 132.01, 132.16, 133.62, 133.74, 143.27, 143.47, 208.0 minor (C=N), 211.69 major (C=N).

^{31}P NMR ($CDCl_3$): two isomers: δ -71.14 (d) and -60.68 (d).

IR cm^{-1}: 2967 (m), 2929 (w), 2872 (w), 1671 (w), 1606 (m), 1464 (m), 1386 (w), 1365 (w), 1294 (s), 1235 (s), 1219 (s), 1156 (s), 1026 (vs), 939 (w), 857 (w), 801 (m), 754 (w), 635 (vs), 589 (m), 572 (m), 516 (s), 413 (m).

Elemental Analysis: Calc. for $C_{27}H_{39}NF_3O_3SP$: C, 59.43; H, 7.20; N, 2.57 and Found: C, 60.06; H, 6.90; N, 2.72.

6.14 Preparation of *N*-((2,6-diisopropylphenylphosphino)methyl)aniline or CH_3-phosphaamidine 77.

Triethylamine (0.2 mL, 1.45 mmol) was added at -70°C under N_2 to the solution of CH_3-phosphaamidine triflate **88** (0.77 g, 1.45 mmol) in dichloromethane. Reaction progress was followed by ^{31}P NMR and completed in 30 min. ^{31}P NMR in CH_2Cl_2 shows four different peaks at δ = - 81.35 ppm (J = 238.13 Hz), δ = - 68.94 ppm (J = 235.70 Hz), δ = 37.36 ppm and δ = 71.22 ppm which is assumed to be four isomers of CH_3-phosphaamidine **77**. Work-up consisted of removal of dichloromethane from the reaction mixture and extracting the product with diethyl ether and removing $HNEt_3OSO_2CF_3$ as a white precipitate. Yield: 0.45g, 82%.

^1H NMR ($CDCl_3$) major: δ 1.02 (d, 6H, $CH(CH_3)_2$), 1.24 (d, 6H, $CH(CH_3)_2$), 1.26 (d, 6H, $CH(CH_3)_2$), 1.36 (d, 6H, $CH(CH_3)_2$), 1.91 (s, 3H, CH_3 of backbone), 3.06 (sept, 2H, $CH(CH_3)_2$), 3.82 (sept, 2H, $CH(CH_3)_2$), 6.08 (s, 1H, NH), 7.11 (d, 2H, m-Dipp-N), 7.22 (d, 2H, m-Dipp-P), 7.25 (t, 1H, p-Dipp-N), 7.32 (t, 1H, p-Dipp-P).

^{13}C NMR ($CDCl_3$): δ 18.53, 18.66, 18.83, 20.29, 21.78, 22.03, 22.53, 22.82, 22.96, 23.04, 23.14, 23.25, 23.30, 23.46, 23.51, 23.65, 23.89, 24.29, 24.50, 24.62, 24.74, 24.77, 25.03, 25.20, 25.38, 26.19, 27.30, 28.11, 28.19, 28.27, 28.51, 28.64, 29.03, 29.20, 30.10, 30.79, 31.81, 33.23, 46.37, 123.04, 123.14, 123.33, 123.61, 123.72, 123.93, 124.14, 124.34, 124.40, 124.47, 124.81, 125.00, 125.12, 125.69, 128.41, 128.46, 128.71, 129.31, 129.50, 131.28, 132.10, 133.09, 134.82, 134.94, 135.19, 135.27, 145.00, 146.52, 147.00, 147.14, 149.01, 153.79, 153.97, 155.43, 169.85, 174.26, 174.92, 185.08 major (C=N).

^{31}P NMR ($CDCl_3$): four isomers: δ -80.52 (d, 238.12 Hz), -66.68 (d, 238.12 Hz), 34.43 (d, 17.0 Hz) and 74.61 (s).

6.15 Preparation of (N-2,6 diisopropylphenyl)(para-methoxyphenyl)carbonitrilium triflate 85.

*p*MeO-imidoyl chloride **14b** (1.0 g, 2.8 mmol) was added to the solution of trimethylsilyl trifluoromethanesulfonate (0.80 mL, 4.14 mmol) in CH_2Cl_2 at -70°C under N_2 to produce *p*MeO-nitrilium triflate **85**. The solution was stirred for 30 min at RT and solvent was removed by vacuum line and the crude material washed with pentane. Yield: 1.26 g, 93%. Melting Point: 123-126°C.

^{1}H NMR ($CDCl_3$): δ 1.33 (d, 12H, $CH(CH_3)_2$), 3.30 (sept, 2H, $CH(CH_3)_2$), 4.01 (s, 3H, CH_3 of MeO-C_6H_4), 7.27 (d, 2H, m-MeO-C_6H_4), 7.36 (d, 2H, m-Dipp), 7.63 (t, 1H, p-Dipp), 8.40 (d, 2H, o-MeO-C_6H_4).

^{13}C NMR ($CDCl_3$): δ 22.78 (CH_3 of iso-pr), 30.44 ($CH(CH_3)_2$), 56.87(CH_3 of MeO), 117.23 (m-MeOC_6H_4), 119.51 (ipso-Dipp), 121.32 (C≡N), 124.86 (m-Dipp), 131.21 (ipso-Dipp), 134.35 (t-Dipp), 139.37 (o-MeO-C_6H_4), 148.33 (o-Dipp), 169.08 (p-MeOC_6H_4).

IR cm^{-1}: 3328 (m), 2959 (m), 2931 (w), 2867 (w), 1639 (s), 1605 (s), 1575 (w), 1522 (m), 1486 (vs), 1461 (s), 1438 (m), 1306 (w), 1254 (vs), 1181 (s), 1101 (s), 1031 (vs), 916 (w), 844 (s), 800 (s), 766 (s), 737 (s), 612 (s), 555 (m).

6.16 Preparation of N,N-dihydro-1H-*para*-methoxyphenyl-1,2dihydro(2,6-diisopropyl) quinolium trifluoromethansulfonate 93.

*p*MeO-imidoyl chloride **14b** (1.0 g, 3.2 mmol) was added to the solution of trimethylsilyl trifluoromethanesulfonate (0.80 mL, 4.14 mmol) at -70°C under N_2 to produce *p*MeO-nitrilium triflate **85**. The solution was stirred for 30 min at RT and solvent removed by vacuum line and the crude material washed with pentane. CH_3O-nitrilium triflate **85** as a white solid was dissolved in a minimum quantity of hot CH_3CN under N_2. After cooling to RT, the colorless solution was left in a freezer at -25°C to grow crystals. The colorless solution changed to yellow, orange, then red after three days in the freezer and yellow crystals grew in the red solution. Crystals were isolated by filtration and X-ray was run. Yield: 0.99 g, 70%. Melting Point: 137-139°C.

^{1}H NMR ($CDCl_3$): δ 0.71 (d, 3H, $CH(CH_3)_2$), 1.21 (d, 3H, $CH(CH_3)_2$), 2.27 (s, 3H, CH_3), 3.08 (sep, 1H, $CH(CH_3)_2$), 3.73 (s, 3H, OCH_3), 5.56 (br, 1H, CH), 6.04 (d, 1H, CH), 6.76 (d, 2H, m-$MeOC_6H_4$), 7.24 (d, 1H, m-Dipp), 7.27 (d, 2H, o-Dipp), 7.32 (d, 1H, m-Dipp), 7.41 (t, 1H, p-Dipp), 8.80 (d, 1H, NH), 10.30 (d, 1H, NH).

^{13}C NMR ($CDCl_3$): δ 18.46 (CH_3), 22.23 (CH_3 of iso-pr), 23.32 (CH_3 of iso-pr), 27.06 ($CH(CH_3)_2$), 55.24 (OCH_3), 55.78 (CH-CH), 114.18 (m-$MeOC_6H_4$), 122.10 (m-Dipp, ipso-Dipp), 123.75 (ipso- $MeOC_6H_4$), 126.52 (m-Dipp), 129.94 (p-Dipp), 130.49 (o-Dipp), 131.11 (o-Dipp), 133.19 (C-CH_3), 142.43 (o-Dipp), 160.83 (p-Dipp).

IR cm^{-1}: 2972 (m), 2935 (w), 1663 (m), 1626 (m), 1603 (m), 1579 (w), 1510 (m), 1460 (m), 1286 (s), 1244 (vs), 1222 (vs), 1159 (vs), 1025 (vs), 812 (m), 629 (vs), 572 (m), 515 (s).

Elemental Analysis: Calc. for $C_{21}H_{24}NF_3SO_4$: C, 56.88; H, 5.46; N, 3.16 and Found: C, 58.10; H, 5.82; N, 3.57.

6.17 Preparation of N-(2,6-diisopropylphenylphosphino)(*para*-methoxyphenyl)2,6-diisopropylphenylaminium triflate 89.

Reacting *p*MeO-nitrilium triflate **85** (1.26 g, 2.95 mmol) with DippPH$_2$ **24** (0.57 g, 2.95 mmol) at -70°C under N$_2$ in dichloromethane produced *p*MeO-phosphaamidine triflate **89**. Work-up consisted of removal of dichloromethane from the reaction mixture. Crude *p*MeO-phosphaamidine triflate **89** as a yellow solid was dissolved in a minimum quantity of hot dichloromethane and after cooling to RT, was layered gently with heptanes under N$_2$. The pale yellow solution was left at -25°C and after three days yellow crystals grew for X-ray. Yield: 1.40 g, 77%. Melting Point: 194-197°C.

^{1}H NMR (CDCl$_3$) major: δ 1.09 (d, 12H, CH(CH$_3$)$_2$), 1.36 (d, 6H, CH(CH$_3$)$_2$), 1.44 (d, 6H, CH(CH$_3$)$_2$), 2.99 (sep, 2H, CH(CH$_3$)$_2$), 3.26 (sep, 4H, CH(CH$_3$)$_2$), 3.84 (s, 3H, OCH$_3$), 5.25 (d, 1H, PH), 7.18 (d, 2H, m-Dipp-P), 7.40 (d, 2H, m-Dipp-N), 7.46 (t, 1H, p-Dipp-P), 7.55 (t, 1H, p-Dipp-N), 13.24 (s, 1H, NH).

^{1}H NMR (CDCl$_3$) minor: δ 0.64 (d, 6H, CH(CH$_3$)$_2$), 1.23 (d, 3H, CH(CH$_3$)$_2$), 1.33 (d, 6H, CH(CH$_3$)$_2$), 1.47 (d, 6H, CH(CH$_3$)$_2$), 1.82 (d, 3H, CH(CH$_3$)$_2$), 3.72 (s, 3H, OCH$_3$), 3.82 (sep, 4H, CH(CH$_3$)$_2$), 6.73 (d, 1H, PH), 7.28 (d, 2H, m-Dipp-P), 7.37 (t, 1H, p-Dipp-P), 7.42 (t, 1H, p-Dipp-N), 7.51 (d, 2H, m-Dipp-N), 13.62 (s, 1H, NH).

^{13}C NMR (CDCl$_3$) Major: δ 23.06 (CH$_3$ of iso-pr), 24.25 (CH$_3$ of iso-pr), 25.39 (CH$_3$ of iso-pr), 29.70 (CH(CH$_3$)$_2$), 34.55 (CH(CH$_3$)$_2$), 56.13 (OCH$_3$), 113.79 (p-Dipp-N), 115.16 (m-MeOC$_6$H$_4$), 124.76 (m-Dipp-P), 125.5 (m-Dipp-N), 132.14 (o-MeOC$_6$H$_4$), 133.36 (p-Dipp-P), 200.94 (C=N).

^{31}P NMR (CDCl$_3$): two isomers: δ -70.02 (d) and -58.10 (d).

IR cm^{-1}: 2964 (m), 2927 (w), 2868 (w), 1601 (m), 1573 (m), 1554 (m), 1462 (m), 1365 (w), 1294 (s), 1271 (m), 1235 (s), 1158 (s), 1123 (vs), 1025 (vs), 937 (m), 838 (m), 803 (m), 758 (w), 711 (w), 634 (vs), 573 (m), 530 (m), 516 (s).

Elemental Analysis: Calc. for $C_{33}H_{43}NPSO_4F_3$: C, 62.15; H, 6.80; N, 2.20 and Found: C, 62.53; H, 6.42; N, 2.39.

6.18 Preparation of *N*,*P*-*bis*(2,6-diisopropylphenyl)-*p*-methoxy-benzphosphaamidine 25b.

One equivalent of triethylamine (0.15 g, 1.40 mmol) was added to the solution of *p*CH_3O-phosphaamidine triflate **89** (0.9 g, 1.4 mmol) in CH_2Cl_2 under N_2 at -70°C. Reaction progress was monitored with ^{31}P NMR and was complete after 30 min stirring at RT. Dichloromethane was removed a with vacuum line and the product was extracted with diethyl ether by precipitating $HNEt_3CF_3SO_3$ as a white solid. Yield: 0.53 g, 78%. Melting Point: 134-137°C.

^{1}H NMR ($CDCl_3$) major: δ 0.82 (d, 6H, $CH(CH_3)_2$), 0.93 (d, 6H, $CH(CH_3)_2$), 1.27 (d, 6H, $CH(CH_3)_2$), 1.35 (d, 6H, $CH(CH_3)_2$), 3.01 (sept, 2H, $CH(CH_3)_2$), 3.71 (s, 3H, CH_3 backbone), 3.86 (sept, 2H, $CH(CH_3)_2$), 6.25 (d, 2H, m-Dipp-N), 6.89 (t, 1H, p-Dipp-N), 7.13 (d, 2H, m-Dipp-N), 7.35 (t, 1H, p-Dipp-P).

^{13}C NMR ($CDCl_3$): δ 22.52, 23.32, 25.45, 26.20, 26.27, 28.55, 33.23, 33.34, 55.45, 113.42, 123.24, 123.72, 127.10, 128.92, 129.15, 129.75, 130.15, 130.58, 135.33, 135.47, 135.53, 136.12, 144.97, 144.94, 154.12, 154.20, 160.30, 160.35, 185.61, 186.66.

^{31}P NMR ($CDCl_3$): major 51.36 ppm(s).

6.19 Preparation of (N-(2,6-diisopropylphenyl)iminium)(ethoxy)methylene triflate 97.

$Me_3SiOSO_2CF_3$ (0.86 g, 5.98 mmol) was added to the solution of formimidate **29a** (1.0 g, 4.6 mmol) in dichloromethane at -70°C under N_2 and stirred for 30 min at RT. The colorless solution was concentrated by removing some of the solvent, then left at -25 °C to grow crystals. Colorless crystals grew in CH_2Cl_2 at -25 °C and the crystal structure determined at -100 °C and find out to be **97** instead of formnitrilium triflate **96**. Yield: 1.23 g, 83%. Melting Point: 135-137°C.

^{1}H NMR ($CDCl_3$): δ 1.21 (d, 12H, $CH(CH_3)_2$), 1.47 (t, 3H, CH_3CH_2O), 2.91 (sept, 2H, $CH(CH_3)_2$), 4.82 (q, 2H, CH_3CH_2O), 7.26 (d, 2H, m-Dipp), 7.44 (t, 1H, p-Dipp), 9.21 (d, 1H, CH), 12.51 (d, 1H, NH).

^{13}C NMR ($CDCl_3$): δ 15.37 (CH_3 of EtO), 23.74 (CH_3 of iso-pr), 28.98 ($CH(CH_3)_2$), 76.95 (CH_3 of EtO), 120.47 (CF_3), 124.50 (m-Dipp), 126.78 (ipso-Dipp), 130.88 (p-Dipp), 144.26 (o-Dipp), 169.09 (CH).

IR cm^{-1}: 2972 (m), 2933 (w), 2872 (w), 1663 (s), 1525 (w), 1461 (w), 1390 (w), 1289 (vs), 1246 (vs), 1162 (vs), 1094 (w), 1025 (vs), 1005 (vs), 932 (w), 863 (w), 813 (m), 766 (m), 698 (w), 631 (vs), 578 (m), 522 (s), 458 (w).

Elemental Analysis: Calc. for $C_{16}H_{24}NF_3O_3S$: C, 52.30; H, 6.58; N, 3.81 and Found: C, 49.93; H, 6.82; N, 3.98

Reference list

1. Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T., Synthesis and structure of bis(2,4,6-tri-tert-butylphenyl)diphosphene - Isolation of a true phosphobenzene. *J. Am. Chem. Soc*. **1981**, *103*, 4587-4589.

2. Yoshifuji, M., Correction. *J. Am. Chem. Soc*. **1982**, *104*, 6167-6167.

3. Markl, G., 2,4,6-Triphenylphosphabenzene. *Angew. Chem. Int. Ed*. **1966**, *5*, 846-847.

4. Becker, G. Z., *Anorg. Allg. Chem.* **1976**, *423*, 242-254.

5. Eshtiaghhosseini, H.; Kroto, H. W.; Nixon, J. F.; Maah, M. J.; Taylor, M. J., Synthesis of phospha-alkene transition-metal complexes. *J. Chem. Soc., Chem. Commun*. **1981**, 199-200.

6. Boeré, R. T.; Klassen, V.; Wolmershauser, G., Superamidines 2. Synthesis of the bulky ligand N,N'-bis-(2,6-diisopropylphenyl)-trifluoroacetamidine and its molybdenum carbonyl complex *Can. J. Chem.* **2000**, *78*, 583-589.

7. Yoshifuji, M.; Shima, I.; Shibayama, K.; Inamoto, N., Reaction of a diphosphene with various halogens. *Tetrahedron Lett*. **1984**, *25*, 411-414.

8. Masuda, J. D. Mono phosphaamidine functional group. Master Thesis, University of Lethbridge, 2002.

9. (a) Patai, S., The chemistry of amidines and imidates,. **1975**, *1*; (b) Patai, S., Amidines and imidates. **1991**, *2*.

10. Boere, R. T.; Klassen, V.; Wolmershauser, G., Synthesis of some very bulky N,N '-disubstituted amidines and initial studies of their coordination chemistry. *J. Chem. Soc., Dalton Trans*. **1998**, 4147-4154.

11. Barker, J.; Kilner, M., The coordination chemistry of the amidine ligand. *Coord. Chem. Rev*. **1994**, *133*, 219-300.

12. Edelmann, F. T., N-silylated benzamidines: versatile building blocks in main group and coordination chemistry. *Coord. Chem. Rev.* **1994**, *137*, 403-481.

13. Boeré, R. T.; Hicks, R. G.; Oakley, R. T., *N,N,N'*-tris(trimethylsilyl)amidines. *Inorg. Synth.* **1997**, *31*, 94-98.

14. Aubrecht, K. B.; Chang, K.; Hillmyer, M. A.; Tolman, W. B., Lactide polymerization activity of alkoxide, phenoxide, and amide derivatives of yttrium(III) arylamidinates. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 284-293.

15. Jordan, R. F.; Coles, M. P., Cationic aluminum alkyl complexes incorporating amidinate ligands. Transition-metal-free ethylene polymerization catalysts. *J. Am. Chem. Soc.* **1997**, *119*, 8125-8126.

16. Brussee, E. A. C.; Meetsma., A.; Hessen, B.; Teuben, J. H., Electron-deficient vanadium(III) alkyl and allyl complexes with amidinate ancillary ligands. *Organometallics*. **1998**, *17*, 4090-4095.

17. Sita, L. R.; Babcock, J. R., Method for the preparation of well-defined metal acetamidinate-based catalysts on solid supports. *Organometallics*. **1998**, *17*, 5228-5230.

18. Britovsek, G. J. P. Gibson, V. C.; Wass, D. F., The search for new-generation olefin polymerization catalysts: life beyond metallocenes. *Angew. Chem. Int. Ed.* **1999**, *38*, 428-447.

19. Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S., Synthesis of $M(II)[N(SiMe_3)_2][Me_3SiNC(^tBu)NSiMe_3]$ (M = Sn, Ge) From amidinate precursors: active catalysts for phenyl isocyanate cyclization. *Inorg. Chem.* **2000**, *39*, 924-929.

20. Boeré, R. E.; Boeré, R. T.; Masuda, J.; Wolmershauser, G., Preparation, x-ray structure, and dynamic solution behaviour of N,N',N"-tris(2,6-diisopropylphenyl)-guanidine, and its reaction with molybdenum carbonyl. *Can. J. Chem.* **2000**, *78*, 1613-1619.

21. Issleib, K.; Schmidt, H.; Meyer, H., Phospha-amidines. *J. Organomet. Chem*. **1978**, *160*, 47-57.

22. Becker, G.; Mundt, O., Syntheses and properties of acylphosphanes .9. Reaction of phenylbis(trimethylsilyl)phosphane with formaldehyde and dimethylformamide. *Z. Anorg. Allg. Chem.* **1980**, *462*, 130-142.

23. Becker, G.; Uhl, W.; Wessely, H. J., Acylidenephosphines and alkylidenephosphines .16. (dimethylaminomethylidene)phosphines and (diphenylmethylidene)phosphines. *Z. Anorg. Allg. Chem.* **1981**, *479*, 41-56.

24. Paasch, K.; Nieger, M.; Niecke, E., A simple route to the 1-aza-3-phosphaallyl system - structure of a dimeric lithium complex and protonation to give the first NH_2-substituted phosphaalkene. *Angew. Chem. Int. Ed*. **1995**, *34*, 2369-2371.

25. Boeré, R. T.; Cole, M. L.; Junk, P. C.; Masuda, J. D.; Wolmershauser, G., An N,P-disubstituted-2-aminophosphaalkene and lithium and potassium complexes of the deprotonated "phosphaamidinate" anion. *Chem. Commun*. **2004**, 2564-2565.

26. Masuda, D. J.; Boeré, R. T., Metal carbonyl complexes of phosphaamidines. Coordinative integrity detected in C-amino(λ3,σ2)-phosphaalkene isomers coordinated through n(P) HOMO-1 donor orbitals. *Dalton Trans.,* **2015**.

27. Song, M. Y.; Donnadieu, B.; Soleilhavoup, M.; Bertrand, G., Synthesis Of Phosphaformamidines And Phosphaformamidinates. *Chem-an Asian. J*. **2007**, *2*, 904-908.

28. Li, X. F.; Song, H. B.; Cui, C. M., Azaphosphaallyl anion lithium $ArNC(^tBu)PArLi^+(THF)_4$ and its monomeric potassium and thallium complexes ($Ar=2,6\text{-}i Pr_2C_6H_3$). *Dalton Trans*. **2009**, 9728-9730.

29. van Dijk, T.; Burck, S.; Rong, M. K.; Rosenthal, A. J.; Nieger, M.; Slootweg, J. C.; Lammertsma, K., Facile synthesis of phosphaamidines and phosphaamidinates using nitrilium ions as an imine synthon. *Angew. Chem. Int. Ed*. **2014**, *53*, 9068-9071.

30. Espinet, P.; Soulantica, K., Phosphine-pyridyl and related ligands in synthesis and catalysis. *Coord. Chem. Rev*. **1999**, *193*, 499-556.

31. Newkome, G. R., Pyridylphosphines. *Chem. Rev*. **1993**, *93*, 2067-2089.

32. Alcaraz, J. M.; Breque, A.; Mathey, F., Synthesis of 2-(2'-pyridyl)phosphorin. *Tetrahedron Lett*. **1982**, *23*, 1565-1568.

33. Dugal-Tessier, J.; Dake, G. R.; Gates, D. P., P,N-chelate complexes of Pd(II) and Pt(II) based on a phosphaalkene motif: a catalyst for the overman-claisen rearrangement. *Organometallics*. **2007**, *26*, 6481-6486.

34. Muller, C.; Vogt, D., Phosphinines as ligands in homogeneous catalysis: recent developments, concepts and perspectives. *Dalton Trans*. **2007**, 5505-5523.

35. Muller, C.; Vogt, D., Recent developments in the chemistry of donor-functionalized phosphinines. *Comptes Rendus Chimie*. **2010**, *13*, 1127-1143.

36. Masuda, J. D.; Stephan, D. W., Neutral and cationic aluminium complexes of a sterically demanding N-imidoylamidine ligand. *Dalton Trans*. **2006**, 2089-2097.

37. Masuda, J. D.; Stephan, D. W., Transition metal complexes of a sterically demanding diimine ligand. *Can. J. Chem*. **2005**, *83*, 477-484.

38. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F., The search for new generation olefin polymerization catalysts: life beyond metallocenes. *Angew. Chem., Int. Ed.* **1999**, *38*, 428–447.

39. Ittel, S. D.; Johnson, L. K., Late-metal catalysts for ethylene homo and copolymerization. *Chem. Rev*. **2000**, *100*, 1169–1203.

40. Kopylovich, M. N.; Pombeiro, A. J. L.; Fischer, A.; Kloo, L.; Kukushkin, V. Yu., Facile Ni(II)/ketoxime-Mediated conversion of organonitriles into imidoylamidine ligands. Synthesis of imidoylamidines and acetyl amides. *Inorg. Chem.* **2003**, *42*, 7239-7248.

41. Kryatov, S.V.; Nazarenko, A. Y.; Smith, M. B.;.Rybak-Akimova, E.V., Condensation of acetonitrile into *N*-acetimidoylacetamidine promoted by a dinuclear nickel(II) complex. *Chem. Commun.* **2001**, 1174-1175.

42. Brown, H. C.; Schuman, P. D., Reactions of perfluoroalkylnitriles .4. Preparation and characterization of some *N*-(perfluoroacylimidoyl)perfluoroalkylamidines and their metal chelates. *J. Org. Chem.* **1963**, *28*, 1122-1127.

43. Aris, D. R.; Barker, J.; Phillips, P. R.; Alcock N. W.; Wallbridge, M. G. H., Metallacycles of the imidoylamidinato compounds HNC(R)NC(R)NH and Group 13 elements. Crystal structure of the complex $[GaMe_2\{HNC(CF_3)NC(CF_3)NH\}]$. *J. Chem. Soc., Dalton Trans.* **1997**, 909-910.

44. Barker, J.; Kilner, M.; Mahmoud, M. M.; Wallwork, S. C., Tri-aza analog of an acetylacetonato-complex formed by nucleophilic attack of a co-ordinated nitrile by amidines. X-ray crystal-structure of $[Pt\{HNC(Ph)NC(Ph)NH\}_2]$.2/3 PhMe. *J. Chem. Soc., Dalton Trans.* **1989**, 837-841.

45. Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A., Complexes of the platinum metals .46. 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminato derivatives of ruthenium, osmium and iridium - Crystal-structure of $[Ru(NHC(CF_3)NC(CF_3)NH)H(CO)(PPh(3))(2)]$. *J. Chem.Soc., Dalton Trans.* **1994**, 3615-3620.

46. Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Wang, X. P.; Murillo, C. A., Metal-assisted unorthodox reactions of formamidines: coupling, cleavage and insertions. *Polyhedron* **1997**, *16*, 1177-1191.

47. Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B., Reactions of imido complexes of iridium, rhodium and ruthenium. *J. Chem.Soc., Dalton Trans.* **1996**, 3771-3778.

48. Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E., Synthesis and reactivity of Palladium complexes with *N,N'*-di-para-tolyl-formamidine, *N,N'*-di-para-tolyl-triazene or *N,N'*-di-para-tolyl-formamidinato ligands - Insertion of CNC_6H_4Me-P, Cs(II) or Co(II) into a Pd-N bond. *J. Organomet. Chem*. **1987**, *334*, 399-408.

49. Boere, R. T.; Roemmele, T. L.; Yu, X., Unsymmetrical 1 lambda(3)-1,2,4,6-thiatriazinyls with aryl and trifluoromethyl substituents: Synthesis, crystal structures, EPR spectroscopy, and voltammetry. *Inorg. Chem*. **2011**, *50*, 5123-5136.

50. Becker, G.; Heck, J. R.; Hubler, U.; Schwarz, W.; Wurthwein, E. U., Acyl- and alkylidenephosphanes. XXXV. Bis N-(trimethylsilyl)iminobenzoyl phosphanides of lithium and zinc-synthesis as well as NMR spectroscopic, structural, and quantumchemical studies. *Z. Anorg. Allg. Chem*. **1999**, *625*, 2008-2024.

51. Schmidpeter, A.; Lochschmidt, S.; Willhalm, A., 2-Phosphaallyl cations by formal insertion of P^+ into the C=C double-bond. *Angew. Chem., Int. Ed.* **1983**, *22*, 545-546.

52. Schmidpeter, A.; Wilhalm, A., 4-Membered and 5-membered phosphorus-heterocycles .64. 1H-1,2,4-diazaphospholes via 2-phosphaallyl chlorides. *Angew. Chem., Int. Ed.* **1984**, *23*, 903-904.

53. Day, R. O.; Willhalm, A.; Holmes, J. M.; Holmes, R. R.; Schmidpeter, A., How is phosphorus bound in 2-phosphaallyl and 2-phosphoniaallyl cations. *Angew. Chem., Int. Ed.* **1985**, *24*, 764-765.

54. Heinicke, J.; Tzschach, A., Organoarsenic compounds .36. Synthesis of aminoacylarsines. *Z. Anorg. Allg. Chem*. **1978**, *18*, 452-453.

55. Romanov, G. V.; Ryzhikova, T. Y.; Pudovik, A. N., Reactions of organic hydridophosphines with azomethines and *N*-phenylbenzimidoyl chloride. *Zh. Obshch. Khim*. **1990**, *60*, 1718-1722.

56. Becker, G. D., G.; Hu¨bler, K.; Hu¨bler, U.; Merz, K.; Niemeyer,; M.; Seidler, N. W., M.; Zheng, Z., In organosilicon chemistry II: from molecules to materials. *Auner, N., Weis, J., Ed.; Verlag Chemie, Weinheim, Germany*. **1996**, 161.

57. Wang, Z. X.; Wang, D. Q.; Dou, J. M., Synthesis and reactions of 1-^{t}Butyldimethylsilyl-2,3-diphenyl-1-aza-3-phosphaallyl lithium and potassium. Crystal structures of $[M(P(Ph)C(Ph)NSiMe_2{}^tBu)(L)]_2$ (M=Li, L=THF; M=K, L=Et_2O), $[Sn(P(Ph)C(Ph)NSiMe_2{}^tBu)_2]$ and $[P(Ph)C(Ph)NSiMe_2{}^tBu]_2$. *J. Organomet. Chem*. **2003**, 205-213.

58. Leitao, E. M.; Jurca, T.; Manners, I., Catalysis in service of main group chemistry offers a versatile approach to P-block molecules and materials. *Nat. Chem*. **2013**, *5*, 817-829.

59. Bartlett, R. A.; Dias, H. V. R.; Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P., Reaction of bulky monosubstituted phosphorus(III) halides with disodium pentacarbonylchromate - Steric and electronic factors in the synthesis of $Cr(Co)_5$ complexes of diphosphenes, phosphinidenes, phosphanes, diphosphanes, and cyclopolyphosphanes. *J. Am. Chem. Soc*. **1987**, *109*, 5693-5698.

60. Duffy, M. P.; Ting, L. Y.; Nicholls, L.; Li, Y. X.; Ganguly, R.; Mathey, F., Reaction of terminal phosphinidene complexes with dihydrogen. *Organometallics*. **2012**, *31*, 2936-2939.

61. Felsberg, R.; Blaurock, S.; Junk, P. C.; Kirmse, R.; Voigt, A.; Hey-Hawkins, E., Organometallic molybdenum(V) complexes with primary phosphine ligands. Syntheses, spectroscopic properties and molecular structures of $[Cp°MoCl_4(PH_2R)]$ (R = But, 1-Ad, Cy, Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-($i$$Pr_3C_6H_2$), Cp° = C_5EtMe_4). *Z. Anorg. Allg. Chem*. **2004**, *630*, 806-816.

62. Blaurock, S.; Hey-Hawkins, E., Unexpected reduction of $Cp^*TaCl_4(PH_2R)$ (R = ^{t}Bu, Cy, Ad, Ph, 2,4,6-$Me_3C_6H_2$; Cp* = C_5Me_5 by reaction with DBU - Molecular structure of [(DBU)H] Cp^*TaCl_4 (DBU=1,8-diazabicyclo [5.4.0] undec-7-en). *Z. Anorg. Allg. Chem*. **2002**, *628*, 37-40.

63. Han, L. B.; Tilley, T. D., Selective homo and heterodehydrocouplings of phosphines catalyzed by rhodium phosphido complexes. *J. Am. Chem. Soc*. **2006**, *128*, 13698-13699.

64. Naseri, V.; Less, R. J.; Mulvey, R. E.; McPartlin, M.; Wright, D. S., Stoichiometric and catalytic Sn-mediated dehydrocoupling of primary phosphines. *Chem. Commun*. **2010**, *46*, 5000-5002.

65. Yakhvarov, D. G.; Hey-Hawkins, E.; Kagirov, R. M.; Budnikova, Y. H.; Ganushevich, Y. S.; Sinyashina, O. G., Electrocatalytic reduction of aryldichlorophosphines with the (2,2'-bipyridine)nickel complexes. *Russ. Chem. Bull*. **2007**, *56*, 935-942.

66. Goldwhite, H.; Kaminski, J.; Millhauser, G.; Ortiz, J.; Vargas, M.; Vertal, L.; Lappert, M. F.; Smith, S. J., Phosphorus phosphorus single or double-bond formation from PCl_3-NRN (N = 1 or 2) and a bis-imidazolidine reducing agent. *J. Organomet. Chem*. **1986**, *310*, 21-25.

67. Kurz, S.; Oesen, H.; Sieler, J.; HeyHawkins, E., Synthesis and molecular structure of Mes(H)P-P(H)Mes (Mes equals2,4,6-$Me_3C_6H_2$). *Phosphorus Sulfur and Silicon and the Related Elements*. **1996**, *117*, 189-196.

68. Andrews, P. C.; King, S. J.; Raston, C. L.; Roberts, B. A., Structural authentication of an N-functionalised disecondary diphosphane. *Chem. Commun*. **1998**, 547-548.

69. Blair, S.; Izod, K.; Taylor, R.; Clegg, W., Isolation and structural characterisation of two sterically crowded diphosphanes. *J. Organomet. Chem*. **2002**, *656*, 43-48.

70. Tian, R. Q.; Mei, Y. B.; Duan, Z.; Mathey, F., Simple access to tungsten-Stabilized disecondary diphosphines. *Organometallics*. **2013**, *32*, 5615-5618.

71. Weber, L., Phosphaalkenes with inverse electron density. *Eur. J. Inorg. Chem*. **2000**, 2425-2441.

72. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R., Tables of bond lengths determined by X-ray and neutron-diffraction .1. bond lengths in organic-compounds. *J. Chem. Soc., Perkin Trans. 2*. **1987**, S1-S19.

73. Boere, R. T.; Masuda, J. D., 2,6-Diisopropylphenylphosphane: a new, bulky primary phosphane and its mono- and disilylated $Si(CH_3)(3)$ and $Si(CH_3)(2)$-^{t}Bu derivatives - A synthetic, crystallographic, and dynamic NMR investigation. *Can. J. Chem*. **2002**, *80*, 1607-1617.

74. Keeler, J., Understanding NMR spectroscopy. *John Wiley & Sons, Inc.,* **2005**, 476.

75. Pavia, D., Lampman, G., Kriz, G, Introduction to spectroscopy. *Saunders College Publishing* **1976**, 96.

76. Silverstein, R., Webster, F., Spectrometric identification of organic compounds *John Wiley & Sons Inc*., **1997**, 145.

77. Sanders, J., Hunter, B., Modern NMR spectroscopy. *Oxford University Press, Inc*., **1993**, 260.

78. Macomber, S., A complete introduction to modern NMR spectroscopy. *A Wiley-interscience publication*. **1997**, 283.

79. Lewars, E. G., *Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics, Second Edition*. **2011**; 1-664.

80. Herbstein, F. H.; Kapon, M.; Schwotzer, W., Crystal-structures of polyiodide salts and molecular-complexes .6. Crystal-structure of tetrakis(phenacetin) dihydrogentetraiodide dihydrate $\{[H_5C_2OC_6H_4N(H)C(CH_3)=O]_4\ H_2I_4.2H_2O\}$. *Helv. Chim. Acta*. **1983**, *66*, 35-43.

81. Calabrese, J. C.; Gardner, K. H., Structure of 4-1 sulfuric acid-N,N'-(para-phenylene)dibenzamide Complex, $C_{20}H_{16}N_2O_2.4H_2SO_4$. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 389-392.

82. Schulman, J. M.; Venanzi, T., Theory and calculation of carbon-nitrogen spin-spin coupling-constants. *J. Am. Chem. Soc*. **1976**, *98*, 4701-4705.

83. Taylor, M. J.; Calvert, D. J.; Hobbis, C. M., C-13 To N-14 Coupling-constants in some heterocyclic cations containing quaternary nitrogen-atoms. *Magn. Reson. Chem.* **1988**, *26*, 619-621.

84. Grehn, L.; Ragnarsson, U.; Welch, C. J., Carbon-carbon and carbon-nitrogen spin-spin coupling in NMR spectroscopy - Simple examples based on isotope-labeled glycines. *J. Chem. Educ*. **1997**, *74*, 1477-1479.

85. Cappello, V.; Baumgartner, J.; Dransfeld, A.; Hassler, K., Monophosphanes and disphosphanes with the hypersilyl substituent. *Eur. J. Inorg. Chem*. **2006**, 4589-4599.

86. Yao, S.; Brym, M.; Merz, K.; Driess, M., Facile access to a stable divalent germanium compound with a terminal PH_2 group and related PR_2 derivatives. *Organometallics*. **2008**, *27*, 3601-3607.

87. Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Watanabe, T., Reduction of diphosphene - formation of d1-diphosphanes and meso-diphosphanes. *Chem Lett*. **1983**, 585-588.

88. Halls, M. D. V., J.; Schlegel, H. B. , *Theor. Chim. Acta*. **2001**, *105, 413*.

89. Bard, J. R.; Sandoval, A. A.; Wurrey, C. J.; Durig, J. R., Infrared and Raman study of 1,2-dimethyldiphosphine. *Inorg. Chem*. **1978**, *17*, 286-291.

90. Baudler, M.; Carlsohn, B.; Koch, D.; Medda, P. K., Contributions to chemistry of phosphorus, 73: 1,2-diphenyldiphosphane. *Chem. Ber. Recl.* **1978**, *111*, 1210-1216.

91. Baudler, M.; Gruner, C.; Tschabunin, H.; Hahn, J., Contributions to the chemistry of phosphorus .110. 1,2-di-tert-butyldiphosphane and tert-butyldiphosphane. *Chem. Ber. Recl*. **1982**, *115*, 1739-1745.

92. Albrand, J. P.; Robert, J. B.; Goldwhite, H., Large difference between diastereomeric ^{1}J(PP) values of 1,2-bis trifluoromethyldiphosphine. *Tetrahedron Lett*. **1976**, 949-952.

93. Albrand, J. P.; Gagnaire, D.; Robert, J. B., P-31 Nuclear Magnetic-Resonance spectrum of pentamethylcyclopentaphosphine - Evidence for a large stereochemical dependence of ^{1}J(PP) spin-spin coupling. *J. Am. Chem. Soc*. **1973**, *95*, 6498-6500.

94. Albrand, J. P.; Robert, J. B., Stereochemical dependence and substituent effects on ^{1}J(PP) NMR spin-spin coupling in cyclopentaphosphines (PR)$_5$. *J. Chem. Soc., Chem.Commun*. **1974**, 644-645.

95. Albrand, J. P., Correction. *J. Am. Chem. Soc*. **1974**, *96*, 1643-1643.

96. Jones, P. G.; Roesky, H. W.; Grutzmacher, H.; Sheldrick, G. M., The oxidative formation of a phosphorus-phosphorus bond in the presence of Ag(I) and Cu(II) ions - Synthesis and structure of $(C_6H_5)PH_2Ag\{$^-$(C_6H_5pH)_2\}]_2$ $(AsF_6)_2$, containing a 6-membered silver-phosphorus ring. *Z Naturforsch., B: Chem. Sci*. **1985**, *40*, 590-593.

97. Katsyuba, S.; Schmutzler, R., Comparative studies of geometric and quasielastic characteristics of PP and SS bonds. *Dalton Trans*. **2008**, 1465-1470.

98. (a) Turnbull, M. M.; Wikaira, J. L.; Wilkins, C. J., A comparison of the molecular and crystal structures of the dimethylacetamide complexes from zinc Chloride, bromide, and Iodide. *Z. Kristallogr*. **2000**, *215*, 702-706; (b) Lemoine, P.; Viossat, B.; Brion, J. D.; Bekaert, A., dibromidobis(4-hydroxy-1,5-dimethyl-2-phenyl-3-pyrazolone)zinc(II). *Acta Crystallogr., Sect. E: Struct. Rep. Online*. **2008**, *64*, m891-m892.

99. Despaigne, A. A. R.; Da Silva, J. G.; Do Carmo, A. C. M.; Sives, F.; Piro, O. E.; Castellano, E. E.; Beraldo, H., Copper(II) and zinc(II) complexes with 2-formylpyridine-derived hydrazones. *Polyhedron*. **2009**, *28,* 3797-3803.

100. Despaigne, A. A. R.; Da Silva, J. G.; Do Carmo, A. C. M.; Piro, O. E.; Castellano, E. E.; Beraldo, H., Structural studies on zinc(II) complexes with 2-benzoylpyridine-derived hydrazones. *Inorg. Chim. Acta*. **2009**, *362*, 2117-2122.

101. Valdebenito, C.; Garland, M. T.; Quijada, R.; Rojas, R., Acetamidine complexes as catalysts for ethylene polymerization. *J. Organomet. Chem*. **2009**, *694*, 717-725.

102. Peoples, B. C.; De la Vega, G.; Valdebenito, C.; Quijada, R.; Ibanez, A.; Valderrama, M.; Rojas, R., Nickel pre-catalysts bearing (*N*)-imidoylamidine ligands; influence of the presence of pyridine and pentafluorophenyl groups in ligand backbone on the reactivity in ethylene polymerizations. *J. Organomet. Chem*. **2012**, *700*, 147-153.

103. Aust, N. C.; Beckmann, A.; Deters, R.; Kramer, R.; Terfloth, L.; Warzeska, S.; Wurthwein, E. U., Unsaturated hetero chains, VIII - First metal complexes of oligonitrile ligands: palladium(II) complexes of *N*-methoxycarbonyl- and *N*-thiobenzoyl-1,3,5,7-tetraazaoctatetraenes. *Eur. J. Inorg. Chem*. **1999**, 1189-1192.

104. Guan, Z. B.; Marshall, W. J., Synthesis of new phosphine imine ligands and their effects on the thermal stability of late-transition-metal olefin polymerization catalysts. *Organometallics*. **2002**, *21*, 3580-3586.

105. Bruker., *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison Wisconsin, USA, **2008**.

116. Sheldrick, G. M., *Acta Cryst.* **2008**. A64, 112–122.

107. Gaussian 03, R. C., Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.

Appendices

Appendix I:

Tables of crystallographic data for all the compounds of this thesis. These tables include the crystal data and structure refinement, bond lengths (Å) and angles (°), torsion angles (°), anisotropic displacement parameters, etc.

Appendix II:

Table of selected ^{1}H, ^{31}P and ^{15}N NMR data for *p*CH_3 and *p*CH_3O-phosphaamidines.

Appendix III:

Table of selected inter-atomic distances (Å) and angles (°) in the crystal and computed structures of Dipp(H)P-P(H)Dipp.

Appendix I

Table A1. Crystal data and structure refinement for **32**.

Empirical formula	C29 H44 N P	
Formula weight	437.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.649(3) Å	α= 90°.
b = 25.508(6) Å	β= 111.027(3)°.	
c = 9.885(2) Å	γ = 90°.	
Volume	2741.6(11) $Å^3$	
Z	4	
Density (calculated)	1.060 Mg/m^3	
Absorption coefficient	0.115 mm^{-1}	
F(000)	960	
Crystal size	0.33 x 0.14 x 0.07 mm^3	
Theta range for data collection	1.87 to 27.56°.	
Index ranges	-15<=h<=15, -33<=k<=33, -12<=l<=12	
Reflections collected	39414	
Independent reflections	6299 [R(int) = 0.0846]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.9925 and 0.9631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6299 / 1 / 294	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.1400	
R indices (all data)	R1 = 0.1336, wR2 = 0.1669	
Largest diff. peak and hole	1.134 and -1.006 e.$Å^{-3}$	

Table A2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **32**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	2506(1)	1346(1)	8119(1)	50(1)
N(1)	831(2)	904(1)	9040(2)	31(1)
C(1)	1922(2)	839(1)	9069(3)	29(1)
C(2)	2568(2)	326(1)	9713(3)	37(1)
C(3)	1689(3)	-32(1)	10114(5)	72(1)
C(4)	3689(3)	438(1)	11063(4)	62(1)
C(5)	2987(3)	47(1)	8603(4)	58(1)

C(6)	4183(2)	1320(1)	8558(3)	31(1)
C(7)	4562(2)	1145(1)	7433(3)	34(1)
C(8)	5801(3)	1186(1)	7615(3)	42(1)
C(9)	6650(3)	1387(1)	8863(4)	46(1)
C(10)	6278(3)	1554(1)	9963(3)	44(1)
C(11)	5051(2)	1528(1)	9842(3)	37(1)
C(12)	3675(3)	932(1)	6008(3)	42(1)
C(13)	4200(3)	477(1)	5411(4)	58(1)
C(14)	3243(3)	1364(1)	4871(4)	62(1)
C(15)	4703(3)	1754(1)	11070(3)	51(1)
C(16)	5633(4)	1625(2)	12572(4)	80(1)
C(17)	4534(4)	2351(1)	10883(4)	70(1)
C(18)	92(2)	1343(1)	8379(3)	30(1)
C(19)	-681(2)	1305(1)	6922(3)	39(1)
C(20)	-1503(3)	1713(1)	6336(4)	52(1)
C(21)	-1553(3)	2142(1)	7151(4)	55(1)
C(22)	-782(3)	2178(1)	8572(4)	46(1)
C(23)	51(2)	1778(1)	9221(3)	35(1)
C(24)	-645(3)	832(2)	6016(3)	54(1)
C(25)	-1749(4)	478(2)	5783(5)	88(1)
C(26)	-545(4)	977(2)	4569(4)	96(2)
C(27)	843(3)	1801(1)	10810(3)	42(1)
C(28)	127(3)	1572(2)	11702(4)	60(1)
C(29)	1315(3)	2349(1)	11350(4)	67(1)

Table A3. Bond lengths [Å] and angles [°] for **32**.

P(1)-C(6)	1.843(2)
P(1)-C(1)	1.865(3)
P(1)-H(1)	1.267(18)
N(1)-C(1)	1.272(3)
N(1)-C(18)	1.421(3)
C(1)-C(2)	1.530(4)
C(2)-C(4)	1.522(4)
C(2)-C(3)	1.526(4)
C(2)-C(5)	1.528(4)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.409(4)
C(6)-C(11)	1.413(4)
C(7)-C(8)	1.393(4)
C(7)-C(12)	1.517(4)
C(8)-C(9)	1.373(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.375(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.393(4)
C(10)-H(10)	0.9500
C(11)-C(15)	1.523(4)
C(12)-C(14)	1.525(4)
C(12)-C(13)	1.526(4)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.527(5)
C(15)-C(17)	1.538(5)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800

C(17)-H(17C)	0.9800
C(18)-C(23)	1.398(4)
C(18)-C(19)	1.401(4)
C(19)-C(20)	1.393(4)
C(19)-C(24)	1.511(4)
C(20)-C(21)	1.371(5)
C(20)-H(20)	0.9500
C(21)-C(22)	1.372(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.396(4)
C(22)-H(22)	0.9500
C(23)-C(27)	1.510(4)
C(24)-C(25)	1.520(5)
C(24)-C(26)	1.522(5)
C(24)-H(24)	1.0000
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-C(29)	1.527(4)
C(27)-C(28)	1.531(4)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(6)-P(1)-C(1)	113.77(12)
C(6)-P(1)-H(1)	93.9(15)
C(1)-P(1)-H(1)	90.4(15)
C(1)-N(1)-C(18)	123.3(2)
N(1)-C(1)-C(2)	117.3(2)
N(1)-C(1)-P(1)	116.11(19)
C(2)-C(1)-P(1)	126.15(18)
C(4)-C(2)-C(3)	109.3(3)
C(4)-C(2)-C(5)	108.8(3)
C(3)-C(2)-C(5)	109.0(3)
C(4)-C(2)-C(1)	110.0(2)
C(3)-C(2)-C(1)	110.1(2)
C(5)-C(2)-C(1)	109.6(2)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-C(11)	120.1(2)
C(7)-C(6)-P(1)	115.6(2)
C(11)-C(6)-P(1)	123.7(2)
C(8)-C(7)-C(6)	118.6(3)
C(8)-C(7)-C(12)	118.4(3)
C(6)-C(7)-C(12)	123.0(2)
C(9)-C(8)-C(7)	121.6(3)
C(9)-C(8)-H(8)	119.2
C(7)-C(8)-H(8)	119.2
C(8)-C(9)-C(10)	119.7(3)
C(8)-C(9)-H(9)	120.1
C(10)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	121.5(3)
C(9)-C(10)-H(10)	119.2
C(11)-C(10)-H(10)	119.2
C(10)-C(11)-C(6)	118.5(3)
C(10)-C(11)-C(15)	118.2(3)
C(6)-C(11)-C(15)	123.2(2)
C(7)-C(12)-C(14)	111.1(3)
C(7)-C(12)-C(13)	113.4(2)
C(14)-C(12)-C(13)	109.7(3)
C(7)-C(12)-H(12)	107.5
C(14)-C(12)-H(12)	107.5
C(13)-C(12)-H(12)	107.5
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(11)-C(15)-C(16)	113.2(3)
C(11)-C(15)-C(17)	109.7(3)
C(16)-C(15)-C(17)	110.2(3)
C(11)-C(15)-H(15)	107.8
C(16)-C(15)-H(15)	107.8

C(17)-C(15)-H(15)	107.8
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(23)-C(18)-C(19)	121.4(2)
C(23)-C(18)-N(1)	119.7(2)
C(19)-C(18)-N(1)	118.5(3)
C(20)-C(19)-C(18)	117.9(3)
C(20)-C(19)-C(24)	120.8(3)
C(18)-C(19)-C(24)	121.4(3)
C(21)-C(20)-C(19)	121.3(3)
C(21)-C(20)-H(20)	119.3
C(19)-C(20)-H(20)	119.3
C(20)-C(21)-C(22)	120.3(3)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	120.9(3)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(22)-C(23)-C(18)	118.2(3)
C(22)-C(23)-C(27)	121.0(3)
C(18)-C(23)-C(27)	120.7(2)
C(19)-C(24)-C(25)	111.2(3)
C(19)-C(24)-C(26)	113.1(3)
C(25)-C(24)-C(26)	110.3(3)
C(19)-C(24)-H(24)	107.3
C(25)-C(24)-H(24)	107.3
C(26)-C(24)-H(24)	107.3
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(23)-C(27)-C(29)	114.0(3)
C(23)-C(27)-C(28)	109.2(2)
C(29)-C(27)-C(28)	110.5(3)
C(23)-C(27)-H(27)	107.6
C(29)-C(27)-H(27)	107.6
C(28)-C(27)-H(27)	107.6
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

Table A4. Anisotropic displacement parameters (Å^{2}x 10^3)for **32**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	28(1)	49(1)	78(1)	29(1)	27(1)	9(1)
N(1)	26(1)	32(1)	37(1)	5(1)	12(1)	2(1)
C(1)	27(1)	31(1)	28(1)	1(1)	9(1)	1(1)
C(2)	35(2)	35(2)	48(2)	12(1)	23(1)	8(1)
C(3)	62(2)	46(2)	129(4)	43(2)	58(2)	19(2)
C(4)	60(2)	63(2)	57(2)	26(2)	15(2)	20(2)
C(5)	69(2)	38(2)	80(3)	7(2)	41(2)	16(2)
C(6)	24(1)	29(1)	42(2)	7(1)	15(1)	2(1)

C(7)	30(1)	32(1)	40(2)	7(1)	15(1)	0(1)
C(8)	38(2)	40(2)	58(2)	2(1)	30(2)	0(1)
C(9)	24(1)	42(2)	73(2)	3(2)	21(2)	-4(1)
C(10)	32(2)	41(2)	55(2)	-2(2)	11(1)	-5(1)
C(11)	33(1)	34(2)	45(2)	4(1)	15(1)	2(1)
C(12)	40(2)	45(2)	41(2)	2(1)	15(1)	-2(1)
C(13)	68(2)	54(2)	53(2)	-10(2)	20(2)	3(2)
C(14)	68(2)	63(2)	52(2)	9(2)	16(2)	8(2)
C(15)	45(2)	64(2)	46(2)	-6(2)	16(2)	1(2)
C(16)	71(3)	119(4)	48(2)	-5(2)	19(2)	-1(2)
C(17)	71(2)	59(2)	87(3)	-25(2)	34(2)	0(2)
C(18)	20(1)	36(1)	36(2)	7(1)	12(1)	0(1)
C(19)	26(1)	52(2)	40(2)	8(1)	12(1)	-3(1)
C(20)	29(2)	74(2)	48(2)	23(2)	8(1)	2(2)
C(21)	34(2)	55(2)	77(3)	33(2)	21(2)	14(2)
C(22)	37(2)	39(2)	71(2)	13(2)	29(2)	8(1)
C(23)	25(1)	37(2)	50(2)	5(1)	21(1)	1(1)
C(24)	39(2)	76(2)	38(2)	-6(2)	6(1)	-7(2)
C(25)	106(3)	92(3)	82(3)	-29(3)	54(3)	-44(3)
C(26)	105(3)	134(4)	67(3)	-21(3)	53(3)	-39(3)
C(27)	33(2)	47(2)	48(2)	-7(1)	19(1)	1(1)
C(28)	57(2)	80(3)	46(2)	-3(2)	22(2)	-8(2)
C(29)	52(2)	63(2)	86(3)	-27(2)	25(2)	-11(2)

Table A5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **32**.

	x	y	z	U(eq)
H(1)	2580(30)	1675(11)	9110(30)	75
H(3A)	2117	-356	10548	109
H(3B)	982	-117	9240	109
H(3C)	1402	147	10811	109
H(4A)	3435	632	11764	92
H(4B)	4281	648	10798	92
H(4C)	4073	107	11495	92
H(5A)	3361	-290	8997	88
H(5B)	3593	265	8387	88
H(5C)	2277	-12	7711	88
H(8)	6065	1073	6859	50
H(9)	7491	1410	8965	55
H(10)	6872	1689	10826	53
H(12)	2936	798	6188	50
H(13A)	4895	602	5161	88
H(13B)	3562	337	4543	88
H(13C)	4482	201	6146	88
H(14A)	2815	1636	5210	94
H(14B)	2681	1216	3959	94

H(14C)	3955	1519	4714	94
H(15)	3894	1599	10996	62
H(16A)	5764	1245	12660	119
H(16B)	5316	1745	13313	119
H(16C)	6414	1801	12707	119
H(17A)	5307	2511	10912	106
H(17B)	4301	2494	11668	106
H(17C)	3886	2428	9949	106
H(20)	-2040	1695	5353	62
H(21)	-2125	2415	6730	66
H(22)	-816	2479	9121	56
H(24)	107	626	6573	64
H(25A)	-1763	364	6724	132
H(25B)	-1688	170	5218	132
H(25C)	-2506	670	5256	132
H(26A)	-1313	1141	3947	143
H(26B)	-396	659	4097	143
H(26C)	138	1222	4730	143
H(27)	1575	1571	10961	50
H(28A)	-630	1774	11518	90
H(28B)	633	1590	12735	90
H(28C)	-82	1206	11424	90
H(29A)	1734	2497	10737	101
H(29B)	1893	2327	12353	101
H(29C)	621	2574	11306	101

Table A6. Torsion angles [°] for **32**.

C(18)-N(1)-C(1)-C(2)	-175.2(2)
C(18)-N(1)-C(1)-P(1)	-2.2(3)
C(6)-P(1)-C(1)-N(1)	166.3(2)
C(6)-P(1)-C(1)-C(2)	-21.4(3)
N(1)-C(1)-C(2)-C(4)	-116.6(3)
P(1)-C(1)-C(2)-C(4)	71.1(3)
N(1)-C(1)-C(2)-C(3)	3.9(4)
P(1)-C(1)-C(2)-C(3)	-168.3(2)
N(1)-C(1)-C(2)-C(5)	123.8(3)
P(1)-C(1)-C(2)-C(5)	-48.4(3)
C(1)-P(1)-C(6)-C(7)	109.7(2)
C(1)-P(1)-C(6)-C(11)	-79.3(2)
C(11)-C(6)-C(7)-C(8)	-0.5(4)
P(1)-C(6)-C(7)-C(8)	170.9(2)
C(11)-C(6)-C(7)-C(12)	-178.1(2)
P(1)-C(6)-C(7)-C(12)	-6.7(3)
C(6)-C(7)-C(8)-C(9)	0.7(4)
C(12)-C(7)-C(8)-C(9)	178.4(3)
C(7)-C(8)-C(9)-C(10)	-0.2(4)
C(8)-C(9)-C(10)-C(11)	-0.5(5)
C(9)-C(10)-C(11)-C(6)	0.7(4)
C(9)-C(10)-C(11)-C(15)	-176.1(3)
C(7)-C(6)-C(11)-C(10)	-0.2(4)
P(1)-C(6)-C(11)-C(10)	-170.9(2)
C(7)-C(6)-C(11)-C(15)	176.5(3)
P(1)-C(6)-C(11)-C(15)	5.8(4)
C(8)-C(7)-C(12)-C(14)	-84.5(3)
C(6)-C(7)-C(12)-C(14)	93.1(3)
C(8)-C(7)-C(12)-C(13)	39.6(4)
C(6)-C(7)-C(12)-C(13)	-142.8(3)
C(10)-C(11)-C(15)-C(16)	-41.3(4)
C(6)-C(11)-C(15)-C(16)	142.0(3)
C(10)-C(11)-C(15)-C(17)	82.3(3)
C(6)-C(11)-C(15)-C(17)	-94.4(3)
C(1)-N(1)-C(18)-C(23)	-95.2(3)
C(1)-N(1)-C(18)-C(19)	91.6(3)
C(23)-C(18)-C(19)-C(20)	-0.4(4)
N(1)-C(18)-C(19)-C(20)	172.6(2)
C(23)-C(18)-C(19)-C(24)	-179.4(2)
N(1)-C(18)-C(19)-C(24)	-6.3(4)
C(18)-C(19)-C(20)-C(21)	0.4(4)
C(24)-C(19)-C(20)-C(21)	179.4(3)

C(19)-C(20)-C(21)-C(22)	0.3(5)	C(20)-C(19)-C(24)-C(25)	-74.0(4)
C(20)-C(21)-C(22)-C(23)	-1.0(4)	C(18)-C(19)-C(24)-C(25)	105.0(3)
C(21)-C(22)-C(23)-C(18)	0.9(4)	C(20)-C(19)-C(24)-C(26)	50.8(4)
C(21)-C(22)-C(23)-C(27)	-176.0(3)	C(18)-C(19)-C(24)-C(26)	-130.2(3)
C(19)-C(18)-C(23)-C(22)	-0.2(4)	C(22)-C(23)-C(27)-C(29)	-38.3(4)
N(1)-C(18)-C(23)-C(22)	-173.2(2)	C(18)-C(23)-C(27)-C(29)	144.8(3)
C(19)-C(18)-C(23)-C(27)	176.8(2)	C(22)-C(23)-C(27)-C(28)	85.8(3)
N(1)-C(18)-C(23)-C(27)	3.8(3)	C(18)-C(23)-C(27)-C(28)	-91.1(3)

Table A7. Crystal data and structure refinement for **83**.

Empirical formula	C18 H28 F3 N O4 S	
Formula weight	411.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 14.9178(12) Å	α= 90°.
	b = 17.0084(13) Å	β= 90°.
	c = 17.1879(14) Å	γ = 90°.
Volume	4361.0(6) Å^3	
Z	8	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	1744	
Crystal size	0.520 x 0.342 x 0.174 mm^3	
Theta range for data collection	1.684 to 27.446°.	
Index ranges	-19<=h<=19, -21<=k<=22, -22<=l<=22	
Reflections collected	55303	
Independent reflections	9964 [R(int) = 0.0392]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7026	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9964 / 4 / 514	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1578	
R indices (all data)	R1 = 0.0640, wR2 = 0.1645	
Absolute structure parameter	0.48(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.421 and -0.505 e.Å^{-3}	

Table A8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **83**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5981(2)	5180(2)	6364(2)	31(1)
C(2)	5781(3)	4477(2)	6748(2)	38(1)
C(3)	4892(3)	4235(3)	6742(3)	47(1)
C(4)	4246(3)	4667(3)	6367(3)	47(1)
C(5)	4461(2)	5365(2)	5994(2)	42(1)
C(6)	5339(2)	5641(2)	5982(2)	35(1)
C(7)	6500(3)	3999(3)	7159(3)	49(1)
C(8)	6780(6)	3305(4)	6658(4)	98(2)

C(9)	6202(5)	3743(4)	7961(3)	76(2)
C(10)	5578(3)	6420(2)	5605(2)	41(1)
C(11)	4939(3)	6652(3)	4943(3)	52(1)
C(12)	5618(5)	7069(3)	6207(3)	69(2)
C(13)	7476(2)	5280(2)	5829(2)	31(1)
C(14)	8442(2)	5553(2)	5845(2)	34(1)
C(15)	8650(3)	6021(3)	6583(3)	55(1)
C(16)	8597(3)	6072(3)	5129(3)	55(1)
C(17)	9044(3)	4825(3)	5816(3)	49(1)
N(1)	6906(2)	5451(2)	6371(2)	31(1)
O(1)	7165(2)	4867(2)	5256(2)	42(1)
C(21)	4182(2)	4949(2)	3309(2)	36(1)
C(22)	4354(3)	5643(2)	2909(2)	44(1)
C(23)	5244(3)	5910(3)	2907(3)	57(1)
C(24)	5907(3)	5483(4)	3276(3)	61(1)
C(25)	5710(3)	4804(3)	3657(3)	54(1)
C(26)	4839(2)	4509(3)	3689(2)	41(1)
C(27)	3622(3)	6101(3)	2513(3)	54(1)
C(28)	3823(4)	6243(3)	1656(3)	67(1)
C(29)	3459(6)	6891(4)	2937(4)	93(2)
C(30)	4609(3)	3747(3)	4099(2)	49(1)
C(31)	4515(5)	3079(3)	3510(3)	73(2)
C(32)	5290(4)	3527(4)	4729(3)	67(1)
C(33)	2683(2)	4793(2)	3842(2)	33(1)
C(34)	1730(2)	4506(2)	3793(2)	38(1)
C(35)	1117(3)	5234(3)	3809(3)	56(1)
C(36)	1553(4)	3966(3)	4496(3)	60(1)
C(37)	1569(3)	4041(3)	3040(2)	49(1)
N(2)	3268(2)	4653(2)	3306(2)	32(1)
O(2)	2967(2)	5210(2)	4426(2)	42(1)
S(1)	1613(1)	6124(1)	6057(1)	30(1)
O(3)	1559(3)	6077(2)	6877(2)	63(1)
O(4)	2188(2)	5531(2)	5717(2)	45(1)
O(5)	794(2)	6252(2)	5648(2)	58(1)
C(18)	2230(3)	7025(3)	5871(3)	57(1)
F(1)	3017(2)	7009(2)	6237(3)	83(1)
F(2)	1789(2)	7642(2)	6133(3)	98(1)
F(3)	2374(3)	7116(3)	5127(3)	108(2)
S(2)	8424(1)	3889(1)	3541(1)	44(1)
O(6)	7983(3)	4443(2)	4022(2)	72(1)
O(7)	8008(4)	3774(2)	2816(2)	86(1)
O(8)	9351(3)	3965(5)	3520(6)	165(4)
C(19)	8227(8)	2962(4)	4036(4)	106(3)
F(4)	7359(5)	2836(3)	4108(5)	182(4)
F(5)	8658(7)	3003(4)	4724(4)	218(5)
F(6)	8529(4)	2362(2)	3685(3)	125(2)

Table A9. Bond lengths [Å] and angles [°] for **83**.

C(1)-C(2)	1.397(5)
C(1)-C(6)	1.402(5)
C(1)-N(1)	1.454(4)
C(2)-C(3)	1.389(6)
C(2)-C(7)	1.520(6)
C(3)-C(4)	1.373(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.392(5)
C(5)-H(5)	0.9500
C(6)-C(10)	1.517(5)
C(7)-C(9)	1.513(7)
C(7)-C(8)	1.521(8)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.514(7)
C(10)-C(11)	1.537(6)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-N(1)	1.294(4)
C(13)-O(1)	1.297(4)
C(13)-C(14)	1.513(5)
C(14)-C(15)	1.530(5)
C(14)-C(17)	1.530(5)
C(14)-C(16)	1.532(6)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
N(1)-H(1N)	0.86(2)
O(1)-H(1O)	0.83(3)
C(21)-C(22)	1.389(6)
C(21)-C(26)	1.396(5)
C(21)-N(2)	1.453(4)
C(22)-C(23)	1.403(6)
C(22)-C(27)	1.505(7)
C(23)-C(24)	1.381(8)
C(23)-H(23)	0.9500
C(24)-C(25)	1.360(8)
C(24)-H(24)	0.9500
C(25)-C(26)	1.394(6)
C(25)-H(25)	0.9500
C(26)-C(30)	1.515(7)
C(27)-C(28)	1.523(7)
C(27)-C(29)	1.547(7)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.529(7)
C(30)-C(32)	1.531(6)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-N(2)	1.290(5)
C(33)-O(2)	1.300(4)
C(33)-C(34)	1.507(5)
C(34)-C(37)	1.535(5)
C(34)-C(35)	1.540(6)
C(34)-C(36)	1.540(6)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
N(2)-H(2N)	0.89(2)
O(2)-H(2O)	0.81(3)
S(1)-O(3)	1.414(3)
S(1)-O(5)	1.427(3)

S(1)-O(4)	1.447(3)	C(12)-C(10)-H(10)	107.5
S(1)-C(18)	1.814(4)	C(6)-C(10)-H(10)	107.5
C(18)-F(3)	1.305(7)	C(11)-C(10)-H(10)	107.5
C(18)-F(2)	1.317(6)	C(10)-C(11)-H(11A)	109.5
C(18)-F(1)	1.333(6)	C(10)-C(11)-H(11B)	109.5
S(2)-O(8)	1.388(5)	H(11A)-C(11)-H(11B)	109.5
S(2)-O(7)	1.406(4)	C(10)-C(11)-H(11C)	109.5
S(2)-O(6)	1.416(4)	H(11A)-C(11)-H(11C)	109.5
S(2)-C(19)	1.816(8)	H(11B)-C(11)-H(11C)	109.5
C(19)-F(6)	1.267(8)	C(10)-C(12)-H(12A)	109.5
C(19)-F(4)	1.320(12)	C(10)-C(12)-H(12B)	109.5
C(19)-F(5)	1.348(9)	H(12A)-C(12)-H(12B)	109.5
C(2)-C(1)-C(6)	123.7(3)	C(10)-C(12)-H(12C)	109.5
C(2)-C(1)-N(1)	118.1(3)	H(12A)-C(12)-H(12C)	109.5
C(6)-C(1)-N(1)	118.3(3)	H(12B)-C(12)-H(12C)	109.5
C(3)-C(2)-C(1)	117.0(4)	N(1)-C(13)-O(1)	115.7(3)
C(3)-C(2)-C(7)	121.2(4)	N(1)-C(13)-C(14)	123.0(3)
C(1)-C(2)-C(7)	121.8(3)	O(1)-C(13)-C(14)	121.3(3)
C(4)-C(3)-C(2)	121.0(4)	C(13)-C(14)-C(15)	111.6(3)
C(4)-C(3)-H(3)	119.5	C(13)-C(14)-C(17)	108.1(3)
C(2)-C(3)-H(3)	119.5	C(15)-C(14)-C(17)	109.2(3)
C(3)-C(4)-C(5)	120.9(4)	C(13)-C(14)-C(16)	107.8(3)
C(3)-C(4)-H(4)	119.6	C(15)-C(14)-C(16)	109.6(4)
C(5)-C(4)-H(4)	119.6	C(17)-C(14)-C(16)	110.6(4)
C(4)-C(5)-C(6)	120.8(4)	C(14)-C(15)-H(15A)	109.5
C(4)-C(5)-H(5)	119.6	C(14)-C(15)-H(15B)	109.5
C(6)-C(5)-H(5)	119.6	H(15A)-C(15)-H(15B)	109.5
C(5)-C(6)-C(1)	116.6(3)	C(14)-C(15)-H(15C)	109.5
C(5)-C(6)-C(10)	121.4(3)	H(15A)-C(15)-H(15C)	109.5
C(1)-C(6)-C(10)	121.9(3)	H(15B)-C(15)-H(15C)	109.5
C(9)-C(7)-C(2)	111.7(4)	C(14)-C(16)-H(16A)	109.5
C(9)-C(7)-C(8)	111.9(5)	C(14)-C(16)-H(16B)	109.5
C(2)-C(7)-C(8)	110.2(4)	H(16A)-C(16)-H(16B)	109.5
C(9)-C(7)-H(7)	107.6	C(14)-C(16)-H(16C)	109.5
C(2)-C(7)-H(7)	107.6	H(16A)-C(16)-H(16C)	109.5
C(8)-C(7)-H(7)	107.6	H(16B)-C(16)-H(16C)	109.5
C(7)-C(8)-H(8A)	109.5	C(14)-C(17)-H(17A)	109.5
C(7)-C(8)-H(8B)	109.5	C(14)-C(17)-H(17B)	109.5
H(8A)-C(8)-H(8B)	109.5	H(17A)-C(17)-H(17B)	109.5
C(7)-C(8)-H(8C)	109.5	C(14)-C(17)-H(17C)	109.5
H(8A)-C(8)-H(8C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(8B)-C(8)-H(8C)	109.5	H(17B)-C(17)-H(17C)	109.5
C(7)-C(9)-H(9A)	109.5	C(13)-N(1)-C(1)	123.2(3)
C(7)-C(9)-H(9B)	109.5	C(13)-N(1)-H(1N)	119(3)
H(9A)-C(9)-H(9B)	109.5	C(1)-N(1)-H(1N)	117(3)
C(7)-C(9)-H(9C)	109.5	C(13)-O(1)-H(1O)	111(4)
H(9A)-C(9)-H(9C)	109.5	C(22)-C(21)-C(26)	123.9(4)
H(9B)-C(9)-H(9C)	109.5	C(22)-C(21)-N(2)	117.8(3)
C(12)-C(10)-C(6)	110.8(4)	C(26)-C(21)-N(2)	118.3(3)
C(12)-C(10)-C(11)	110.1(4)	C(21)-C(22)-C(23)	116.8(4)
C(6)-C(10)-C(11)	113.2(4)	C(21)-C(22)-C(27)	122.0(4)

C(23)-C(22)-C(27)	121.2(4)
C(24)-C(23)-C(22)	120.5(5)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(25)-C(24)-C(23)	120.8(4)
C(25)-C(24)-H(24)	119.6
C(23)-C(24)-H(24)	119.6
C(24)-C(25)-C(26)	121.7(4)
C(24)-C(25)-H(25)	119.1
C(26)-C(25)-H(25)	119.1
C(25)-C(26)-C(21)	116.3(4)
C(25)-C(26)-C(30)	122.5(4)
C(21)-C(26)-C(30)	121.2(4)
C(22)-C(27)-C(28)	112.1(4)
C(22)-C(27)-C(29)	110.6(5)
C(28)-C(27)-C(29)	110.5(4)
C(22)-C(27)-H(27)	107.8
C(28)-C(27)-H(27)	107.8
C(29)-C(27)-H(27)	107.8
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(26)-C(30)-C(31)	110.4(4)
C(26)-C(30)-C(32)	112.8(4)
C(31)-C(30)-C(32)	110.3(4)
C(26)-C(30)-H(30)	107.7
C(31)-C(30)-H(30)	107.7
C(32)-C(30)-H(30)	107.7
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
N(2)-C(33)-O(2)	115.6(3)
N(2)-C(33)-C(34)	122.6(3)
O(2)-C(33)-C(34)	121.8(3)
C(33)-C(34)-C(37)	111.2(3)
C(33)-C(34)-C(35)	107.4(3)
C(37)-C(34)-C(35)	109.7(3)
C(33)-C(34)-C(36)	108.2(3)
C(37)-C(34)-C(36)	109.2(3)
C(35)-C(34)-C(36)	111.3(4)
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(34)-C(37)-H(37A)	109.5
C(34)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(34)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(33)-N(2)-C(21)	124.7(3)
C(33)-N(2)-H(2N)	119(3)
C(21)-N(2)-H(2N)	117(3)
C(33)-O(2)-H(2O)	110(4)
O(3)-S(1)-O(5)	116.8(2)
O(3)-S(1)-O(4)	113.3(2)
O(5)-S(1)-O(4)	114.5(2)
O(3)-S(1)-C(18)	104.7(3)
O(5)-S(1)-C(18)	102.7(2)
O(4)-S(1)-C(18)	102.5(2)
F(3)-C(18)-F(2)	108.8(5)
F(3)-C(18)-F(1)	108.6(5)
F(2)-C(18)-F(1)	107.1(4)
F(3)-C(18)-S(1)	110.9(4)
F(2)-C(18)-S(1)	111.0(3)
F(1)-C(18)-S(1)	110.3(3)
O(8)-S(2)-O(7)	115.4(5)
O(8)-S(2)-O(6)	114.7(4)
O(7)-S(2)-O(6)	113.9(3)
O(8)-S(2)-C(19)	104.7(5)
O(7)-S(2)-C(19)	102.9(3)
O(6)-S(2)-C(19)	103.2(3)
F(6)-C(19)-F(4)	105.2(8)
F(6)-C(19)-F(5)	106.9(7)
F(4)-C(19)-F(5)	113.2(10)
F(6)-C(19)-S(2)	114.7(7)

F(4)-C(19)-S(2)	110.1(6)	F(5)-C(19)-S(2)	106.8(6)

Symmetry transformations used to generate equivalent atoms:

Table A10. Anisotropic displacement parameters (Å^{2}x 10^3) for **83**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	28(2)	33(2)	31(2)	-3(1)	1(1)	-2(1)
C(2)	45(2)	36(2)	33(2)	1(1)	-1(2)	-2(2)
C(3)	51(2)	43(2)	47(2)	2(2)	7(2)	-12(2)
C(4)	32(2)	58(2)	51(2)	-6(2)	5(2)	-9(2)
C(5)	30(2)	48(2)	47(2)	-2(2)	0(2)	2(2)
C(6)	32(2)	39(2)	34(2)	-2(1)	3(1)	2(1)
C(7)	50(2)	41(2)	56(2)	12(2)	-8(2)	1(2)
C(8)	127(6)	84(4)	83(4)	-3(3)	-14(4)	65(4)
C(9)	92(4)	80(4)	57(3)	28(3)	-11(3)	9(3)
C(10)	36(2)	39(2)	48(2)	8(2)	-1(2)	4(2)
C(11)	45(2)	62(3)	50(2)	13(2)	1(2)	16(2)
C(12)	101(4)	39(2)	66(3)	3(2)	-16(3)	-2(2)
C(13)	28(2)	33(2)	32(2)	-1(1)	-3(1)	2(1)
C(14)	25(2)	37(2)	39(2)	-3(1)	-4(1)	1(1)
C(15)	39(2)	66(3)	60(3)	-21(2)	-6(2)	-14(2)
C(16)	40(2)	60(3)	63(3)	22(2)	-6(2)	-7(2)
C(17)	30(2)	53(2)	62(3)	-1(2)	-10(2)	8(2)
N(1)	31(1)	31(1)	32(1)	-2(1)	-4(1)	0(1)
O(1)	28(1)	55(2)	42(1)	-16(1)	-2(1)	-3(1)
C(21)	27(2)	45(2)	36(2)	-12(2)	1(1)	2(1)
C(22)	44(2)	46(2)	41(2)	-9(2)	10(2)	-2(2)
C(23)	56(3)	63(3)	52(2)	-16(2)	16(2)	-18(2)
C(24)	37(2)	89(4)	57(3)	-25(3)	12(2)	-17(2)
C(25)	29(2)	86(3)	47(2)	-22(2)	-4(2)	10(2)
C(26)	33(2)	53(2)	36(2)	-13(2)	-2(1)	8(2)
C(27)	61(3)	45(2)	56(2)	5(2)	8(2)	5(2)
C(28)	93(4)	54(3)	54(3)	-2(2)	-1(3)	-3(3)
C(29)	138(6)	73(4)	68(3)	-14(3)	6(4)	47(4)
C(30)	45(2)	61(3)	42(2)	-7(2)	-11(2)	19(2)
C(31)	108(5)	48(3)	61(3)	-9(2)	-24(3)	18(3)
C(32)	58(3)	92(4)	51(3)	6(3)	-15(2)	21(3)
C(33)	28(2)	36(2)	34(2)	-4(1)	-8(1)	4(1)
C(34)	27(2)	48(2)	38(2)	-8(2)	-5(1)	1(1)
C(35)	32(2)	67(3)	70(3)	-21(2)	-12(2)	13(2)
C(36)	61(3)	74(3)	46(2)	0(2)	3(2)	-27(3)
C(37)	37(2)	63(2)	46(2)	-18(2)	-6(2)	-7(2)
N(2)	28(1)	35(1)	34(1)	-7(1)	-2(1)	3(1)
O(2)	30(1)	57(2)	40(1)	-18(1)	1(1)	-2(1)
S(1)	24(1)	35(1)	31(1)	2(1)	2(1)	-3(1)
O(3)	75(2)	77(2)	37(2)	9(2)	11(2)	19(2)

O(4)	42(1)	48(2)	46(2)	-10(1)	3(1)	2(1)
O(5)	32(1)	68(2)	74(2)	-2(2)	-15(1)	-3(1)
C(18)	43(2)	41(2)	88(4)	5(2)	-2(2)	-9(2)
F(1)	34(1)	65(2)	150(3)	-26(2)	-12(2)	-15(1)
F(2)	65(2)	40(1)	191(4)	-14(2)	-19(2)	8(1)
F(3)	124(3)	99(3)	100(3)	52(2)	27(3)	-30(3)
S(2)	34(1)	54(1)	45(1)	-11(1)	2(1)	1(1)
O(6)	83(3)	77(2)	56(2)	-21(2)	8(2)	14(2)
O(7)	150(4)	73(2)	33(2)	2(2)	-15(2)	-5(3)
O(8)	41(2)	181(7)	273(10)	-78(7)	23(4)	-34(3)
C(19)	184(9)	64(4)	68(4)	-1(3)	-33(5)	29(5)
F(4)	163(5)	100(4)	284(10)	13(5)	128(6)	-34(4)
F(5)	417(14)	126(4)	111(4)	20(3)	-129(6)	53(6)
F(6)	155(5)	62(2)	159(5)	-7(3)	-9(4)	37(3)

Table A11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **83**.

	x	y	z	U(eq)
H(3)	4729	3763	7002	56
H(4)	3644	4485	6363	56
H(5)	4003	5659	5743	50
H(7)	7036	4346	7225	59
H(8A)	7262	3015	6918	147
H(8B)	6993	3496	6153	147
H(8C)	6265	2956	6579	147
H(9A)	6003	4203	8258	115
H(9B)	6704	3491	8231	115
H(9C)	5705	3369	7913	115
H(10)	6191	6364	5377	49
H(11A)	4889	6215	4573	79
H(11B)	5174	7117	4675	79
H(11C)	4346	6771	5158	79
H(12A)	5031	7124	6457	104
H(12B)	5780	7565	5953	104
H(12C)	6070	6939	6601	104
H(15A)	8274	6493	6599	82
H(15B)	9283	6175	6582	82
H(15C)	8526	5695	7041	82
H(16A)	8449	5775	4658	82
H(16B)	9227	6234	5110	82
H(16C)	8214	6539	5162	82
H(17A)	8922	4491	6269	73
H(17B)	9674	4988	5823	73
H(17C)	8922	4529	5338	73
H(1N)	7060(30)	5770(20)	6730(20)	38
H(1O)	7550(30)	4790(30)	4920(20)	50

H(23)	5391	6387	2651	69
H(24)	6509	5667	3264	74
H(25)	6179	4523	3908	65
H(27)	3058	5786	2547	65
H(28A)	4384	6539	1606	101
H(28B)	3333	6543	1421	101
H(28C)	3883	5736	1388	101
H(29A)	3351	6792	3491	140
H(29B)	2935	7153	2710	140
H(29C)	3987	7229	2878	140
H(30)	4014	3819	4358	59
H(31A)	3991	3175	3180	109
H(31B)	4439	2580	3787	109
H(31C)	5054	3054	3186	109
H(32A)	5876	3435	4488	101
H(32B)	5092	3048	4996	101
H(32C)	5338	3957	5106	101
H(35A)	1235	5538	4283	85
H(35B)	488	5066	3804	85
H(35C)	1237	5561	3352	85
H(36A)	1945	3505	4466	90
H(36B)	925	3796	4491	90
H(36C)	1675	4255	4978	90
H(37A)	1701	4377	2590	73
H(37B)	942	3871	3018	73
H(37C)	1962	3579	3030	73
H(2N)	3110(30)	4360(20)	2898(19)	39
H(2O)	2560(30)	5290(30)	4730(20)	50

Table A12. Torsion angles [°] for **83**.

C(6)-C(1)-C(2)-C(3)	0.1(5)
N(1)-C(1)-C(2)-C(3)	179.2(3)
C(6)-C(1)-C(2)-C(7)	-179.6(4)
N(1)-C(1)-C(2)-C(7)	-0.4(5)
C(1)-C(2)-C(3)-C(4)	0.6(6)
C(7)-C(2)-C(3)-C(4)	-179.7(4)
C(2)-C(3)-C(4)-C(5)	-1.1(7)
C(3)-C(4)-C(5)-C(6)	0.8(6)
C(4)-C(5)-C(6)-C(1)	-0.1(6)
C(4)-C(5)-C(6)-C(10)	-177.5(4)
C(2)-C(1)-C(6)-C(5)	-0.3(5)
N(1)-C(1)-C(6)-C(5)	-179.5(3)
C(2)-C(1)-C(6)-C(10)	177.0(3)
N(1)-C(1)-C(6)-C(10)	-2.2(5)
C(3)-C(2)-C(7)-C(9)	-46.0(6)
C(1)-C(2)-C(7)-C(9)	133.7(5)
C(3)-C(2)-C(7)-C(8)	79.1(6)
C(1)-C(2)-C(7)-C(8)	-101.3(5)
C(5)-C(6)-C(10)-C(12)	96.3(5)
C(1)-C(6)-C(10)-C(12)	-80.9(5)
C(5)-C(6)-C(10)-C(11)	-27.9(5)
C(1)-C(6)-C(10)-C(11)	154.9(4)
N(1)-C(13)-C(14)-C(15)	1.9(5)
O(1)-C(13)-C(14)-C(15)	-179.4(4)
N(1)-C(13)-C(14)-C(17)	121.9(4)
O(1)-C(13)-C(14)-C(17)	-59.3(4)
N(1)-C(13)-C(14)-C(16)	-118.5(4)
O(1)-C(13)-C(14)-C(16)	60.3(5)
O(1)-C(13)-N(1)-C(1)	2.3(5)
C(14)-C(13)-N(1)-C(1)	-178.9(3)
C(2)-C(1)-N(1)-C(13)	92.4(4)
C(6)-C(1)-N(1)-C(13)	-88.4(4)
C(26)-C(21)-C(22)-C(23)	-1.0(6)
N(2)-C(21)-C(22)-C(23)	-178.9(3)
C(26)-C(21)-C(22)-C(27)	-179.4(4)
N(2)-C(21)-C(22)-C(27)	2.7(5)

C(21)-C(22)-C(23)-C(24)	1.3(6)
C(27)-C(22)-C(23)-C(24)	179.7(4)
C(22)-C(23)-C(24)-C(25)	-0.9(7)
C(23)-C(24)-C(25)-C(26)	0.2(7)
C(24)-C(25)-C(26)-C(21)	0.1(6)
C(24)-C(25)-C(26)-C(30)	179.0(4)
C(22)-C(21)-C(26)-C(25)	0.3(5)
N(2)-C(21)-C(26)-C(25)	178.2(3)
C(22)-C(21)-C(26)-C(30)	-178.6(4)
N(2)-C(21)-C(26)-C(30)	-0.7(5)
C(21)-C(22)-C(27)-C(28)	-124.9(4)
C(23)-C(22)-C(27)-C(28)	56.8(6)
C(21)-C(22)-C(27)-C(29)	111.4(5)
C(23)-C(22)-C(27)-C(29)	-67.0(6)
C(25)-C(26)-C(30)-C(31)	-100.1(5)
C(21)-C(26)-C(30)-C(31)	78.7(5)
C(25)-C(26)-C(30)-C(32)	23.8(6)
C(21)-C(26)-C(30)-C(32)	-157.4(4)
N(2)-C(33)-C(34)-C(37)	0.0(5)
O(2)-C(33)-C(34)-C(37)	179.0(4)
N(2)-C(33)-C(34)-C(35)	-120.0(4)
O(2)-C(33)-C(34)-C(35)	59.0(5)
N(2)-C(33)-C(34)-C(36)	119.8(4)
O(2)-C(33)-C(34)-C(36)	-61.1(5)
O(2)-C(33)-N(2)-C(21)	-2.2(5)
C(34)-C(33)-N(2)-C(21)	176.9(3)
C(22)-C(21)-N(2)-C(33)	-94.4(4)
C(26)-C(21)-N(2)-C(33)	87.6(4)
O(3)-S(1)-C(18)-F(3)	176.2(4)
O(5)-S(1)-C(18)-F(3)	-61.4(4)
O(4)-S(1)-C(18)-F(3)	57.7(4)
O(3)-S(1)-C(18)-F(2)	-62.7(4)
O(5)-S(1)-C(18)-F(2)	59.7(5)
O(4)-S(1)-C(18)-F(2)	178.8(4)
O(3)-S(1)-C(18)-F(1)	55.9(4)
O(5)-S(1)-C(18)-F(1)	178.3(4)
O(4)-S(1)-C(18)-F(1)	-62.6(4)
O(8)-S(2)-C(19)-F(6)	-63.0(8)
O(7)-S(2)-C(19)-F(6)	57.9(8)
O(6)-S(2)-C(19)-F(6)	176.7(7)
O(8)-S(2)-C(19)-F(4)	178.5(7)
O(7)-S(2)-C(19)-F(4)	-60.5(7)
O(6)-S(2)-C(19)-F(4)	58.2(7)
O(8)-S(2)-C(19)-F(5)	55.2(9)
O(7)-S(2)-C(19)-F(5)	176.1(7)
O(6)-S(2)-C(19)-F(5)	-65.1(8)

Symmetry transformations used to generate equivalent atoms:

Table A13. Hydrogen bonds for **83** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(6)	0.83(3)	1.77(3)	2.550(4)	156(5)
O(2)-H(2O)...O(4)	0.81(3)	1.83(3)	2.563(4)	150(5)
N(1)-H(1N)...O(7)#1	0.86(2)	2.01(3)	2.814(5)	154(4)
N(2)-H(2N)...O(3)#2	0.89(2)	1.97(3)	2.765(4)	147(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1,z+1/2 #2 -x+1/2,-y+1,z-1/2

Table A14. Crystal data and structure refinement for **87**.

Identification code	**87**	
Empirical formula	C30 H45 F3 N O3 P S	
Formula weight	587.70	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.211(2) Å	α= 90°.
	b = 17.2366(19) Å	β= 97.711(3)°.
	c = 18.350(2) Å	γ = 90°.
Volume	6334.4(13) Å^3	
Z	8	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	2512	
Crystal size	0.274 x 0.258 x 0.144 mm^3	
Theta range for data collection	1.559 to 29.201°.	
Index ranges	-27<=h<=27, -23<=k<=23, -25<=l<=25	
Reflections collected	48269	
Independent reflections	8144 [R(int) = 0.0275]	
Completeness to theta = 25.500°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7105	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8144 / 8 / 381	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0993	
R indices (all data)	R1 = 0.0507, wR2 = 0.1069	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.455 and -0.515 e.Å^{-3}	

Table A15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **87**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5284(1)	1821(1)	5067(1)	19(1)
P(1A)	5221(3)	1672(4)	4917(4)	54(2)
N(2)	4388(1)	2741(1)	4310(1)	19(1)
C(1)	5015(1)	2560(1)	4360(1)	18(1)
C(2)	6091(1)	1388(1)	4944(1)	21(1)
C(3)	6199(1)	843(1)	4396(1)	23(1)
C(4)	6828(1)	500(1)	4433(1)	28(1)
C(5)	7329(1)	671(1)	5000(1)	31(1)

C(6)	7218(1)	1186(1)	5542(1)	28(1)
C(7)	6605(1)	1565(1)	5524(1)	23(1)
C(8)	5660(1)	592(1)	3781(1)	28(1)
C(9)	5346(1)	-173(1)	3983(1)	41(1)
C(10)	5927(1)	505(1)	3043(1)	42(1)
C(11)	6517(1)	2124(1)	6144(1)	32(1)
C(12)	6317(1)	1684(1)	6804(1)	50(1)
C(13)	7139(1)	2622(1)	6369(1)	52(1)
C(14)	3920(1)	2401(1)	4759(1)	19(1)
C(15)	3520(1)	1780(1)	4480(1)	21(1)
C(16)	3068(1)	1493(1)	4924(1)	27(1)
C(17)	3026(1)	1805(1)	5611(1)	32(1)
C(18)	3435(1)	2412(1)	5872(1)	30(1)
C(19)	3891(1)	2733(1)	5452(1)	24(1)
C(20)	3556(1)	1436(1)	3724(1)	24(1)
C(21)	3462(1)	557(1)	3714(1)	45(1)
C(22)	3042(1)	1823(1)	3154(1)	41(1)
C(23)	4316(1)	3420(1)	5742(1)	34(1)
C(24)	4623(1)	3315(1)	6542(1)	54(1)
C(25)	3904(1)	4168(1)	5640(1)	58(1)
C(26)	5474(1)	3051(1)	3954(1)	24(1)
C(27)	5784(1)	2545(1)	3399(1)	33(1)
C(28)	6030(1)	3379(1)	4525(1)	36(1)
C(29)	5105(1)	3728(1)	3543(1)	29(1)
S(1)	3184(1)	4255(1)	2996(1)	27(1)
O(1)	3526(1)	3856(1)	3629(1)	46(1)
O(2)	2506(1)	4440(1)	3059(1)	46(1)
O(3)	3312(1)	3956(1)	2303(1)	57(1)
C(30)	3599(1)	5193(1)	3039(1)	44(1)
F(1)	4232(1)	5122(1)	2910(1)	78(1)
F(2)	3307(1)	5680(1)	2538(1)	64(1)
F(3)	3590(1)	5527(1)	3686(1)	97(1)

Table A16. Bond lengths [Å] and angles [°] for **87**.

P(1)-C(2)	1.835(2)
P(1)-C(1)	1.846(2)
P(1)-H(1)	1.341(15)
P(1A)-C(2)	1.819(7)
P(1A)-C(1)	1.857(7)
P(1A)-H(1A)	1.33(2)
N(2)-C(1)	1.2956(15)
N(2)-C(14)	1.4590(15)
N(2)-H(2)	0.874(17)
C(1)-C(26)	1.5229(16)
C(2)-C(3)	1.4140(18)
C(2)-C(7)	1.4178(17)
C(3)-C(4)	1.3959(18)
C(3)-C(8)	1.5220(18)
C(4)-C(5)	1.382(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.374(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.3967(18)
C(6)-H(6)	0.9300
C(7)-C(11)	1.5207(19)
C(8)-C(9)	1.530(2)
C(8)-C(10)	1.531(2)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600

C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-C(12)	1.528(2)
C(11)-C(13)	1.532(2)
C(11)-H(11)	0.9800
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(15)	1.3973(17)
C(14)-C(19)	1.4026(18)
C(15)-C(16)	1.3950(17)
C(15)-C(20)	1.5195(18)
C(16)-C(17)	1.382(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.378(2)
C(17)-H(17)	0.9300
C(18)-C(19)	1.3926(19)
C(18)-H(18)	0.9300
C(19)-C(23)	1.5171(19)
C(20)-C(22)	1.5251(19)
C(20)-C(21)	1.526(2)
C(20)-H(20)	0.9800
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-C(24)	1.527(2)
C(23)-C(25)	1.531(2)
C(23)-H(23)	0.9800
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(29)	1.5288(18)
C(26)-C(27)	1.5368(19)
C(26)-C(28)	1.5381(19)
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
S(1)-O(2)	1.4251(11)
S(1)-O(3)	1.4272(13)
S(1)-O(1)	1.4438(11)
S(1)-C(30)	1.8181(17)
C(30)-F(3)	1.323(2)
C(30)-F(2)	1.3233(19)
C(30)-F(1)	1.338(2)
C(2)-P(1)-C(1)	112.18(10)
C(2)-P(1)-H(1)	102.1(8)
C(1)-P(1)-H(1)	93.8(8)
C(2)-P(1A)-C(1)	112.5(4)
C(2)-P(1A)-H(1A)	111(5)
C(1)-P(1A)-H(1A)	104(5)
C(1)-N(2)-C(14)	124.38(10)
C(1)-N(2)-H(2)	120.1(10)
C(14)-N(2)-H(2)	115.4(10)
N(2)-C(1)-C(26)	119.00(11)
N(2)-C(1)-P(1)	114.14(10)
C(26)-C(1)-P(1)	125.89(10)
N(2)-C(1)-P(1A)	112.5(2)
C(26)-C(1)-P(1A)	128.4(2)
C(3)-C(2)-C(7)	120.62(11)
C(3)-C(2)-P(1A)	113.6(2)
C(7)-C(2)-P(1A)	124.8(2)
C(3)-C(2)-P(1)	125.59(10)
C(7)-C(2)-P(1)	113.25(10)
C(4)-C(3)-C(2)	118.24(12)
C(4)-C(3)-C(8)	118.17(12)
C(2)-C(3)-C(8)	123.57(11)
C(5)-C(4)-C(3)	121.08(13)
C(5)-C(4)-H(4)	119.5
C(3)-C(4)-H(4)	119.5
C(6)-C(5)-C(4)	120.63(12)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(5)-C(6)-C(7)	120.98(13)
C(5)-C(6)-H(6)	119.5
C(7)-C(6)-H(6)	119.5
C(6)-C(7)-C(2)	118.41(12)
C(6)-C(7)-C(11)	118.15(12)
C(2)-C(7)-C(11)	123.40(11)
C(3)-C(8)-C(9)	110.21(11)
C(3)-C(8)-C(10)	112.45(12)
C(9)-C(8)-C(10)	109.64(13)
C(3)-C(8)-H(8)	108.1
C(9)-C(8)-H(8)	108.1
C(10)-C(8)-H(8)	108.1
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5

C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(7)-C(11)-C(12)	110.36(13)
C(7)-C(11)-C(13)	112.41(13)
C(12)-C(11)-C(13)	111.11(14)
C(7)-C(11)-H(11)	107.6
C(12)-C(11)-H(11)	107.6
C(13)-C(11)-H(11)	107.6
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(19)	123.56(11)
C(15)-C(14)-N(2)	119.19(11)
C(19)-C(14)-N(2)	117.23(11)
C(16)-C(15)-C(14)	116.67(12)
C(16)-C(15)-C(20)	120.72(11)
C(14)-C(15)-C(20)	122.59(11)
C(17)-C(16)-C(15)	121.37(13)
C(17)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(18)-C(17)-C(16)	120.25(12)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	121.38(13)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(18)-C(19)-C(14)	116.75(12)
C(18)-C(19)-C(23)	120.17(12)
C(14)-C(19)-C(23)	123.06(12)
C(15)-C(20)-C(22)	110.11(11)
C(15)-C(20)-C(21)	112.17(11)
C(22)-C(20)-C(21)	110.79(13)
C(15)-C(20)-H(20)	107.9
C(22)-C(20)-H(20)	107.9
C(21)-C(20)-H(20)	107.9
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(19)-C(23)-C(24)	112.44(14)
C(19)-C(23)-C(25)	109.95(13)
C(24)-C(23)-C(25)	111.15(15)
C(19)-C(23)-H(23)	107.7
C(24)-C(23)-H(23)	107.7
C(25)-C(23)-H(23)	107.7
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(1)-C(26)-C(29)	112.12(10)
C(1)-C(26)-C(27)	109.77(11)
C(29)-C(26)-C(27)	108.85(11)
C(1)-C(26)-C(28)	107.94(11)
C(29)-C(26)-C(28)	108.62(11)
C(27)-C(26)-C(28)	109.51(12)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5

C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
O(2)-S(1)-O(3)	116.30(8)
O(2)-S(1)-O(1)	113.80(7)
O(3)-S(1)-O(1)	114.90(9)
O(2)-S(1)-C(30)	103.88(8)
O(3)-S(1)-C(30)	102.79(9)
O(1)-S(1)-C(30)	102.70(8)
F(3)-C(30)-F(2)	106.81(15)
F(3)-C(30)-F(1)	109.04(17)
F(2)-C(30)-F(1)	106.40(15)
F(3)-C(30)-S(1)	111.38(14)
F(2)-C(30)-S(1)	112.01(13)
F(1)-C(30)-S(1)	110.98(12)

Symmetry transformations used to generate equivalent atoms.

Table A17. Anisotropic displacement parameters (Å^{2}x 10^3) for **87**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2 a^{*2}U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	16(1)	23(1)	17(1)	4(1)	2(1)	3(1)
P(1A)	22(2)	59(4)	85(4)	50(3)	19(3)	16(2)
N(2)	17(1)	19(1)	21(1)	5(1)	2(1)	0(1)
C(1)	18(1)	19(1)	18(1)	0(1)	2(1)	-2(1)
C(2)	18(1)	22(1)	23(1)	5(1)	3(1)	2(1)
C(3)	24(1)	22(1)	22(1)	4(1)	4(1)	-2(1)
C(4)	29(1)	25(1)	33(1)	-2(1)	9(1)	3(1)
C(5)	20(1)	29(1)	46(1)	3(1)	6(1)	6(1)
C(6)	19(1)	29(1)	36(1)	2(1)	-2(1)	2(1)
C(7)	22(1)	21(1)	26(1)	3(1)	1(1)	2(1)
C(8)	28(1)	33(1)	22(1)	1(1)	3(1)	-6(1)
C(9)	47(1)	37(1)	38(1)	-1(1)	4(1)	-15(1)
C(10)	44(1)	57(1)	26(1)	-3(1)	8(1)	-6(1)
C(11)	33(1)	30(1)	31(1)	-6(1)	-5(1)	8(1)
C(12)	65(1)	56(1)	29(1)	-3(1)	6(1)	11(1)
C(13)	48(1)	36(1)	65(1)	-19(1)	-15(1)	0(1)
C(14)	14(1)	22(1)	22(1)	5(1)	4(1)	2(1)
C(15)	17(1)	21(1)	24(1)	4(1)	3(1)	2(1)
C(16)	22(1)	28(1)	34(1)	3(1)	7(1)	-4(1)
C(17)	27(1)	37(1)	34(1)	6(1)	15(1)	-1(1)
C(18)	28(1)	38(1)	26(1)	-1(1)	10(1)	4(1)
C(19)	20(1)	26(1)	26(1)	-1(1)	4(1)	2(1)
C(20)	22(1)	25(1)	24(1)	1(1)	4(1)	-2(1)
C(21)	74(1)	27(1)	36(1)	-3(1)	19(1)	-3(1)
C(22)	47(1)	47(1)	28(1)	-2(1)	-5(1)	14(1)
C(23)	32(1)	36(1)	34(1)	-11(1)	8(1)	-6(1)
C(24)	51(1)	62(1)	45(1)	-15(1)	-8(1)	-9(1)
C(25)	70(1)	31(1)	70(1)	-9(1)	1(1)	-1(1)
C(26)	18(1)	25(1)	28(1)	8(1)	4(1)	-2(1)
C(27)	33(1)	34(1)	36(1)	12(1)	18(1)	4(1)
C(28)	24(1)	35(1)	47(1)	9(1)	-3(1)	-10(1)
C(29)	24(1)	27(1)	37(1)	13(1)	7(1)	-1(1)
S(1)	23(1)	25(1)	35(1)	1(1)	6(1)	5(1)
O(1)	31(1)	42(1)	66(1)	26(1)	2(1)	6(1)

O(2)	26(1)	61(1)	53(1)	12(1)	10(1)	13(1)
O(3)	64(1)	54(1)	57(1)	-24(1)	24(1)	-1(1)
C(30)	50(1)	26(1)	53(1)	6(1)	-1(1)	3(1)
F(1)	40(1)	48(1)	143(1)	34(1)	3(1)	-11(1)
F(2)	72(1)	39(1)	80(1)	29(1)	12(1)	16(1)
F(3)	168(2)	49(1)	67(1)	-23(1)	-10(1)	-16(1)

Table A18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **87**.

	x	y	z	U(eq)
H(1)	4851(9)	1287(10)	4761(10)	22
H(1A)	5090(50)	1870(60)	5580(30)	65
H(2)	4228(8)	3116(10)	4018(9)	28
H(4)	6912	151	4070	34
H(5)	7744	434	5016	37
H(6)	7557	1285	5926	34
H(8)	5311	989	3726	33
H(9A)	5683	-570	4047	61
H(9B)	5002	-321	3596	61
H(9C)	5158	-109	4432	61
H(10A)	6158	970	2938	63
H(10B)	5561	417	2661	63
H(10C)	6229	73	3066	63
H(11)	6149	2476	5966	39
H(12A)	5907	1410	6658	75
H(12B)	6255	2045	7188	75
H(12C)	6662	1322	6981	75
H(13A)	7493	2301	6605	78
H(13B)	7038	3020	6703	78
H(13C)	7277	2857	5939	78
H(16)	2788	1085	4755	33
H(17)	2721	1604	5898	38
H(18)	3405	2611	6337	36
H(20)	4000	1547	3591	28
H(21A)	3755	329	4112	67
H(21B)	3566	352	3255	67
H(21C)	3008	435	3767	67
H(22A)	2601	1727	3275	62
H(22B)	3078	1615	2676	62
H(22C)	3122	2372	3153	62
H(23)	4683	3467	5445	41
H(24A)	4275	3313	6851	81
H(24B)	4926	3734	6684	81
H(24C)	4861	2832	6595	81
H(25A)	3728	4227	5131	87
H(25B)	4183	4603	5797	87

H(25C)	3543	4140	5930	87
H(27A)	6068	2160	3658	50
H(27B)	6043	2865	3115	50
H(27C)	5436	2294	3076	50
H(28A)	5834	3650	4900	54
H(28B)	6302	3730	4288	54
H(28C)	6301	2961	4743	54
H(29A)	4753	3532	3187	44
H(29B)	5411	4024	3297	44
H(29C)	4918	4055	3887	44

Table A19. Torsion angles [°] for **87**.

C(14)-N(2)-C(1)-C(26)	-169.77(11)
C(14)-N(2)-C(1)-P(1)	-0.37(16)
C(14)-N(2)-C(1)-P(1A)	12.5(3)
C(2)-P(1)-C(1)-N(2)	163.83(10)
C(2)-P(1)-C(1)-C(26)	-27.63(14)
C(2)-P(1A)-C(1)-N(2)	176.8(2)
C(2)-P(1A)-C(1)-C(26)	-0.7(5)
C(1)-P(1A)-C(2)-C(3)	-93.1(3)
C(1)-P(1A)-C(2)-C(7)	98.1(3)
C(1)-P(1)-C(2)-C(3)	-74.36(14)
C(1)-P(1)-C(2)-C(7)	114.06(10)
C(7)-C(2)-C(3)-C(4)	-1.38(18)
P(1A)-C(2)-C(3)-C(4)	-170.7(3)
P(1)-C(2)-C(3)-C(4)	-172.39(12)
C(7)-C(2)-C(3)-C(8)	176.54(12)
P(1A)-C(2)-C(3)-C(8)	7.2(3)
P(1)-C(2)-C(3)-C(8)	5.53(19)
C(2)-C(3)-C(4)-C(5)	1.7(2)
C(8)-C(3)-C(4)-C(5)	-176.38(13)
C(3)-C(4)-C(5)-C(6)	-0.2(2)
C(4)-C(5)-C(6)-C(7)	-1.6(2)
C(5)-C(6)-C(7)-C(2)	1.8(2)
C(5)-C(6)-C(7)-C(11)	179.67(13)
C(3)-C(2)-C(7)-C(6)	-0.30(18)
P(1A)-C(2)-C(7)-C(6)	167.8(3)
P(1)-C(2)-C(7)-C(6)	171.75(11)
C(3)-C(2)-C(7)-C(11)	-178.06(12)
P(1A)-C(2)-C(7)-C(11)	-10.0(3)
P(1)-C(2)-C(7)-C(11)	-6.02(17)
C(4)-C(3)-C(8)-C(9)	80.57(16)
C(2)-C(3)-C(8)-C(9)	-97.35(16)
C(4)-C(3)-C(8)-C(10)	-42.08(18)
C(2)-C(3)-C(8)-C(10)	140.00(14)
C(6)-C(7)-C(11)-C(12)	-84.02(16)
C(2)-C(7)-C(11)-C(12)	93.74(16)
C(6)-C(7)-C(11)-C(13)	40.63(18)
C(2)-C(7)-C(11)-C(13)	-141.60(14)
C(1)-N(2)-C(14)-C(15)	-96.13(14)
C(1)-N(2)-C(14)-C(19)	84.90(15)
C(19)-C(14)-C(15)-C(16)	0.81(18)
N(2)-C(14)-C(15)-C(16)	-178.09(11)
C(19)-C(14)-C(15)-C(20)	179.32(11)
N(2)-C(14)-C(15)-C(20)	0.42(17)
C(14)-C(15)-C(16)-C(17)	-0.90(19)
C(20)-C(15)-C(16)-C(17)	-179.44(12)
C(15)-C(16)-C(17)-C(18)	0.1(2)
C(16)-C(17)-C(18)-C(19)	0.8(2)
C(17)-C(18)-C(19)-C(14)	-0.9(2)
C(17)-C(18)-C(19)-C(23)	177.67(13)
C(15)-C(14)-C(19)-C(18)	0.07(18)
N(2)-C(14)-C(19)-C(18)	178.98(11)
C(15)-C(14)-C(19)-C(23)	-178.45(12)
N(2)-C(14)-C(19)-C(23)	0.46(18)
C(16)-C(15)-C(20)-C(22)	85.75(15)
C(14)-C(15)-C(20)-C(22)	-92.70(15)
C(16)-C(15)-C(20)-C(21)	-38.12(17)
C(14)-C(15)-C(20)-C(21)	143.42(13)
C(18)-C(19)-C(23)-C(24)	45.80(19)
C(14)-C(19)-C(23)-C(24)	-135.73(15)
C(18)-C(19)-C(23)-C(25)	-78.63(18)
C(14)-C(19)-C(23)-C(25)	99.84(17)
N(2)-C(1)-C(26)-C(29)	1.40(17)
P(1)-C(1)-C(26)-C(29)	-166.64(10)
P(1A)-C(1)-C(26)-C(29)	178.8(3)
N(2)-C(1)-C(26)-C(27)	-119.71(13)
P(1)-C(1)-C(26)-C(27)	72.25(14)
P(1A)-C(1)-C(26)-C(27)	57.6(3)
N(2)-C(1)-C(26)-C(28)	120.99(13)
P(1)-C(1)-C(26)-C(28)	-47.05(15)
P(1A)-C(1)-C(26)-C(28)	-61.7(3)
O(2)-S(1)-C(30)-F(3)	64.71(15)
O(3)-S(1)-C(30)-F(3)	-173.68(14)

O(1)-S(1)-C(30)-F(3)	-54.10(15)	O(2)-S(1)-C(30)-F(1)	-173.60(13)
O(2)-S(1)-C(30)-F(2)	-54.84(15)	O(3)-S(1)-C(30)-F(1)	-51.99(15)
O(3)-S(1)-C(30)-F(2)	66.76(15)	O(1)-S(1)-C(30)-F(1)	67.59(15)
O(1)-S(1)-C(30)-F(2)	-173.65(13)		

Symmetry transformations used to generate equivalent atoms:

Table A20. Hydrogen bonds for **87** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(1)	0.874(17)	1.968(17)	2.7756(15)	153.1(15)

Symmetry transformations used to generate equivalent atoms:

Table A21. Crystal data and structure refinement for **90**.

Identification code	**90**	
Empirical formula	C32 H54 Cl2 N2 O3	
Formula weight	585.67	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2193(7) Å	α= 82.6370(10)°.
	b = 12.9719(8) Å	β= 69.8310(10)°.
	c = 12.9832(8) Å	γ = 82.9760(10)°.
Volume	1752.83(19) Å^3	
Z	2	
Density (calculated)	1.110 Mg/m^3	
Absorption coefficient	0.216 mm^{-1}	
F(000)	636	
Crystal size	0.448 x 0.195 x 0.102 mm^3	
Theta range for data collection	1.59 to 27.53°.	
Index ranges	-14<=h<=14, -16<=k<=16, -16<=l<=16	
Reflections collected	25695	
Independent reflections	8002 [R(int) = 0.0252]	
Completeness to theta = 25.25°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7188	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8002 / 2 / 372	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.0988	
R indices (all data)	R1 = 0.0612, wR2 = 0.1100	
Largest diff. peak and hole	0.407 and -0.374 e.Å^{-3}	

Table A22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **90**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	10954(1)	2034(1)	9258(1)	38(1)
N(1)	9766(1)	732(1)	8104(1)	26(1)
O(1)	8168(1)	-208(1)	8304(1)	35(1)
C(1)	10394(1)	539(1)	6959(1)	27(1)
C(2)	11067(2)	-429(1)	6712(1)	32(1)
C(3)	11688(2)	-570(1)	5603(1)	38(1)
C(4)	11639(2)	210(1)	4792(1)	40(1)
C(5)	10986(2)	1165(1)	5061(1)	35(1)
C(6)	10350(1)	1357(1)	6155(1)	28(1)

C(7)	11165(2)	-1302(1)	7581(1)	43(1)
C(8)	10589(3)	-2270(2)	7463(2)	76(1)
C(9)	12546(2)	-1539(2)	7543(2)	71(1)
C(10)	9602(2)	2391(1)	6473(1)	33(1)
C(11)	8183(2)	2324(2)	6697(2)	44(1)
C(12)	10077(2)	3307(1)	5614(2)	48(1)
C(13)	8711(2)	364(1)	8744(1)	28(1)
C(14)	8168(2)	597(1)	9908(1)	34(1)
C(16)	6582(2)	-1249(2)	8260(2)	60(1)
C(15)	6972(2)	-655(2)	8990(2)	46(1)
Cl(2)	4077(1)	7350(1)	366(1)	56(1)
N(2)	5613(1)	6288(1)	1754(1)	30(1)
O(2)	7436(1)	5568(1)	1920(1)	31(1)
C(21)	4945(1)	6161(1)	2928(1)	28(1)
C(22)	5069(1)	6884(1)	3587(1)	31(1)
C(23)	4381(2)	6743(1)	4709(1)	36(1)
C(24)	3616(2)	5928(1)	5136(1)	37(1)
C(25)	3499(2)	5241(1)	4457(1)	34(1)
C(26)	4157(1)	5345(1)	3326(1)	30(1)
C(27)	5885(2)	7794(1)	3101(2)	39(1)
C(28)	5143(2)	8689(2)	2643(2)	66(1)
C(29)	6417(2)	8171(2)	3904(2)	74(1)
C(30)	4038(2)	4588(1)	2568(1)	35(1)
C(31)	4917(3)	3620(2)	2577(3)	94(1)
C(32)	2695(2)	4340(2)	2807(2)	80(1)
C(33)	6799(1)	5986(1)	1276(1)	28(1)
C(34)	7366(2)	6107(1)	59(1)	34(1)
C(35)	8799(1)	5240(1)	1449(1)	33(1)
C(36)	9330(2)	5176(2)	2366(2)	44(1)
O(1S)	1665(2)	6410(1)	165(2)	70(1)

Table A23. Bond lengths [Å] and angles [°] for **90**.

N(1)-C(13)	1.2953(19)
N(1)-C(1)	1.4485(18)
N(1)-H(1)	0.8800
O(1)-C(13)	1.3074(18)
O(1)-C(15)	1.4709(19)
C(1)-C(2)	1.398(2)
C(1)-C(6)	1.399(2)
C(2)-C(3)	1.392(2)
C(2)-C(7)	1.515(2)
C(3)-C(4)	1.375(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.380(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(2)
C(5)-H(5)	0.9500
C(6)-C(10)	1.517(2)
C(7)-C(9)	1.527(3)
C(7)-C(8)	1.528(3)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.528(2)
C(10)-C(12)	1.531(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800

C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.478(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(16)-C(15)	1.496(3)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
N(2)-C(33)	1.2940(19)
N(2)-C(21)	1.4456(18)
N(2)-H(2)	0.8800
O(2)-C(33)	1.3059(18)
O(2)-C(35)	1.4686(18)
C(21)-C(26)	1.394(2)
C(21)-C(22)	1.397(2)
C(22)-C(23)	1.394(2)
C(22)-C(27)	1.518(2)
C(23)-C(24)	1.380(2)
C(23)-H(23)	0.9500
C(24)-C(25)	1.379(2)
C(24)-H(24)	0.9500
C(25)-C(26)	1.395(2)
C(25)-H(25)	0.9500
C(26)-C(30)	1.523(2)
C(27)-C(29)	1.520(3)
C(27)-C(28)	1.524(3)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(32)	1.498(3)
C(30)-C(31)	1.500(3)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-C(34)	1.481(2)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-C(36)	1.493(2)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
O(1S)-H(1S)	0.860(17)
O(1S)-H(2S)	0.837(16)
C(13)-N(1)-C(1)	125.20(13)
C(13)-N(1)-H(1)	117.4
C(1)-N(1)-H(1)	117.4
C(13)-O(1)-C(15)	119.19(13)
C(2)-C(1)-C(6)	123.22(14)
C(2)-C(1)-N(1)	118.81(13)
C(6)-C(1)-N(1)	117.88(13)
C(3)-C(2)-C(1)	116.97(14)
C(3)-C(2)-C(7)	119.55(15)
C(1)-C(2)-C(7)	123.47(14)
C(4)-C(3)-C(2)	121.18(16)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	120.60(15)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.99(15)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	117.01(14)
C(5)-C(6)-C(10)	122.12(14)
C(1)-C(6)-C(10)	120.84(13)
C(2)-C(7)-C(9)	110.46(16)
C(2)-C(7)-C(8)	111.08(15)
C(9)-C(7)-C(8)	112.10(19)
C(2)-C(7)-H(7)	107.7
C(9)-C(7)-H(7)	107.7
C(8)-C(7)-H(7)	107.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(11)	110.71(13)
C(6)-C(10)-C(12)	113.36(14)
C(11)-C(10)-C(12)	109.76(15)
C(6)-C(10)-H(10)	107.6

C(11)-C(10)-H(10)	107.6
C(12)-C(10)-H(10)	107.6
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(1)-C(13)-O(1)	116.59(13)
N(1)-C(13)-C(14)	120.55(14)
O(1)-C(13)-C(14)	122.86(14)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(1)-C(15)-C(16)	106.68(15)
O(1)-C(15)-H(15A)	110.4
C(16)-C(15)-H(15A)	110.4
O(1)-C(15)-H(15B)	110.4
C(16)-C(15)-H(15B)	110.4
H(15A)-C(15)-H(15B)	108.6
C(33)-N(2)-C(21)	125.00(13)
C(33)-N(2)-H(2)	117.5
C(21)-N(2)-H(2)	117.5
C(33)-O(2)-C(35)	120.02(12)
C(26)-C(21)-C(22)	123.80(14)
C(26)-C(21)-N(2)	117.26(13)
C(22)-C(21)-N(2)	118.85(14)
C(23)-C(22)-C(21)	116.67(15)
C(23)-C(22)-C(27)	121.63(15)
C(21)-C(22)-C(27)	121.69(14)
C(24)-C(23)-C(22)	121.09(15)
C(24)-C(23)-H(23)	119.5
C(22)-C(23)-H(23)	119.5
C(25)-C(24)-C(23)	120.60(15)
C(25)-C(24)-H(24)	119.7
C(23)-C(24)-H(24)	119.7
C(24)-C(25)-C(26)	120.99(15)
C(24)-C(25)-H(25)	119.5
C(26)-C(25)-H(25)	119.5
C(21)-C(26)-C(25)	116.81(14)
C(21)-C(26)-C(30)	121.76(14)
C(25)-C(26)-C(30)	121.43(14)
C(22)-C(27)-C(29)	113.62(16)
C(22)-C(27)-C(28)	110.24(15)
C(29)-C(27)-C(28)	110.70(18)
C(22)-C(27)-H(27)	107.3
C(29)-C(27)-H(27)	107.3
C(28)-C(27)-H(27)	107.3
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(32)-C(30)-C(31)	111.9(2)
C(32)-C(30)-C(26)	113.13(15)
C(31)-C(30)-C(26)	110.86(15)
C(32)-C(30)-H(30)	106.8
C(31)-C(30)-H(30)	106.8
C(26)-C(30)-H(30)	106.8
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
N(2)-C(33)-O(2)	116.50(13)
N(2)-C(33)-C(34)	120.25(14)
O(2)-C(33)-C(34)	123.24(14)
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5

O(2)-C(35)-C(36)	106.28(13)	C(35)-C(36)-H(36B)	109.5
O(2)-C(35)-H(35A)	110.5	H(36A)-C(36)-H(36B)	109.5
C(36)-C(35)-H(35A)	110.5	C(35)-C(36)-H(36C)	109.5
O(2)-C(35)-H(35B)	110.5	H(36A)-C(36)-H(36C)	109.5
C(36)-C(35)-H(35B)	110.5	H(36B)-C(36)-H(36C)	109.5
H(35A)-C(35)-H(35B)	108.7	H(1S)-O(1S)-H(2S)	107(3)
C(35)-C(36)-H(36A)	109.5		

Symmetry transformations used to generate equivalent atoms.

Table A24. Anisotropic displacement parameters ($Å^2$x 10^3) for **90**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	42(1)	33(1)	44(1)	-6(1)	-18(1)	-5(1)
N(1)	31(1)	25(1)	24(1)	-5(1)	-9(1)	-2(1)
O(1)	38(1)	35(1)	30(1)	-1(1)	-8(1)	-11(1)
C(1)	26(1)	31(1)	23(1)	-5(1)	-7(1)	-3(1)
C(2)	35(1)	33(1)	29(1)	-7(1)	-12(1)	2(1)
C(3)	40(1)	39(1)	33(1)	-12(1)	-11(1)	8(1)
C(4)	39(1)	51(1)	25(1)	-9(1)	-5(1)	2(1)
C(5)	35(1)	42(1)	26(1)	2(1)	-9(1)	-4(1)
C(6)	26(1)	31(1)	28(1)	-3(1)	-10(1)	-4(1)
C(7)	60(1)	34(1)	31(1)	-8(1)	-16(1)	14(1)
C(8)	145(3)	29(1)	56(1)	0(1)	-37(2)	-4(1)
C(9)	72(2)	92(2)	38(1)	-14(1)	-20(1)	48(1)
C(10)	39(1)	29(1)	30(1)	-2(1)	-12(1)	-1(1)
C(11)	38(1)	38(1)	51(1)	-4(1)	-13(1)	8(1)
C(12)	62(1)	33(1)	44(1)	4(1)	-16(1)	-6(1)
C(13)	33(1)	22(1)	26(1)	0(1)	-10(1)	3(1)
C(14)	41(1)	31(1)	26(1)	-2(1)	-6(1)	2(1)
C(16)	66(1)	61(1)	59(1)	9(1)	-21(1)	-37(1)
C(15)	42(1)	51(1)	41(1)	7(1)	-7(1)	-20(1)
Cl(2)	39(1)	78(1)	49(1)	16(1)	-22(1)	0(1)
N(2)	28(1)	36(1)	25(1)	0(1)	-9(1)	2(1)
O(2)	25(1)	35(1)	29(1)	-2(1)	-7(1)	2(1)
C(21)	22(1)	35(1)	24(1)	-3(1)	-7(1)	5(1)
C(22)	23(1)	35(1)	34(1)	-5(1)	-9(1)	2(1)
C(23)	31(1)	44(1)	33(1)	-12(1)	-10(1)	2(1)
C(24)	32(1)	49(1)	26(1)	-6(1)	-4(1)	0(1)
C(25)	31(1)	38(1)	32(1)	-1(1)	-7(1)	-3(1)
C(26)	26(1)	33(1)	29(1)	-4(1)	-10(1)	4(1)
C(27)	31(1)	42(1)	44(1)	-10(1)	-7(1)	-6(1)
C(28)	59(1)	44(1)	94(2)	10(1)	-27(1)	-14(1)
C(29)	74(2)	85(2)	79(2)	0(1)	-36(1)	-41(1)
C(30)	37(1)	38(1)	32(1)	-5(1)	-12(1)	-3(1)
C(31)	113(2)	71(2)	137(3)	-68(2)	-90(2)	48(2)
C(32)	46(1)	119(2)	86(2)	-60(2)	-17(1)	-13(1)

C(33)	29(1)	26(1)	28(1)	-2(1)	-9(1)	-3(1)
C(34)	35(1)	38(1)	27(1)	-4(1)	-6(1)	-2(1)
C(35)	23(1)	33(1)	40(1)	-4(1)	-6(1)	3(1)
C(36)	33(1)	52(1)	49(1)	-4(1)	-17(1)	-2(1)
O(1S)	51(1)	43(1)	118(2)	-28(1)	-25(1)	-2(1)

Table A25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **90**.

	x	y	z	U(eq)
H(1)	10131	1130	8387	32
H(3)	12155	-1218	5403	45
H(4)	12057	91	4040	47
H(5)	10972	1699	4491	42
H(7)	10658	-1055	8318	51
H(8A)	9712	-2081	7474	114
H(8B)	10589	-2797	8075	114
H(8C)	11096	-2553	6764	114
H(9A)	13062	-1801	6835	106
H(9B)	12585	-2069	8144	106
H(9C)	12876	-901	7627	106
H(10)	9703	2540	7175	39
H(11A)	8047	2229	6010	66
H(11B)	7706	2969	6986	66
H(11C)	7887	1730	7239	66
H(12A)	10993	3333	5455	72
H(12B)	9624	3960	5902	72
H(12C)	9918	3215	4937	72
H(14A)	8739	1016	10073	52
H(14B)	8072	-57	10388	52
H(14C)	7333	988	10035	52
H(16A)	6403	-767	7676	91
H(16B)	5816	-1599	8697	91
H(16C)	7274	-1771	7930	91
H(15A)	6305	-93	9292	56
H(15B)	7103	-1125	9612	56
H(2)	5180	6594	1332	36
H(23)	4440	7216	5188	43
H(24)	3166	5840	5906	44
H(25)	2963	4688	4764	41
H(27)	6627	7550	2468	47
H(28A)	4827	8435	2114	99
H(28B)	5703	9245	2273	99
H(28C)	4421	8962	3248	99
H(29A)	5716	8468	4508	111
H(29B)	7004	8705	3519	111
H(29C)	6874	7582	4202	111
H(30)	4329	4940	1802	42

H(31A)	4599	3204	3287	141
H(31B)	5772	3815	2470	141
H(31C)	4955	3210	1981	141
H(32A)	2665	3910	2250	120
H(32B)	2152	4989	2790	120
H(32C)	2388	3958	3538	120
H(34A)	8028	6597	-160	51
H(34B)	6702	6375	-260	51
H(34C)	7744	5428	-209	51
H(35A)	9228	5754	842	40
H(35B)	8920	4552	1156	40
H(36A)	9191	5859	2653	66
H(36B)	10246	4966	2089	66
H(36C)	8902	4659	2956	66
H(1S)	1040(20)	6885(18)	350(20)	94(10)
H(2S)	2290(20)	6630(19)	250(20)	80(9)

Table A26. Torsion angles [°] for **90**.

C(13)-N(1)-C(1)-C(2)	-76.05(19)
C(13)-N(1)-C(1)-C(6)	107.29(17)
C(6)-C(1)-C(2)-C(3)	-1.6(2)
N(1)-C(1)-C(2)-C(3)	-178.06(14)
C(6)-C(1)-C(2)-C(7)	177.26(15)
N(1)-C(1)-C(2)-C(7)	0.8(2)
C(1)-C(2)-C(3)-C(4)	0.0(2)
C(7)-C(2)-C(3)-C(4)	-178.86(17)
C(2)-C(3)-C(4)-C(5)	1.2(3)
C(3)-C(4)-C(5)-C(6)	-0.9(3)
C(4)-C(5)-C(6)-C(1)	-0.6(2)
C(4)-C(5)-C(6)-C(10)	-178.69(15)
C(2)-C(1)-C(6)-C(5)	1.9(2)
N(1)-C(1)-C(6)-C(5)	178.36(13)
C(2)-C(1)-C(6)-C(10)	179.99(14)
N(1)-C(1)-C(6)-C(10)	-3.5(2)
C(3)-C(2)-C(7)-C(9)	62.8(2)
C(1)-C(2)-C(7)-C(9)	-115.98(18)
C(3)-C(2)-C(7)-C(8)	-62.2(2)
C(1)-C(2)-C(7)-C(8)	118.97(19)
C(5)-C(6)-C(10)-C(11)	97.84(18)
C(1)-C(6)-C(10)-C(11)	-80.20(18)
C(5)-C(6)-C(10)-C(12)	-26.0(2)
C(1)-C(6)-C(10)-C(12)	155.95(15)
C(1)-N(1)-C(13)-O(1)	-1.5(2)
C(1)-N(1)-C(13)-C(14)	178.91(13)
C(15)-O(1)-C(13)-N(1)	179.58(14)
C(15)-O(1)-C(13)-C(14)	-0.8(2)
C(13)-O(1)-C(15)-C(16)	179.31(15)
C(33)-N(2)-C(21)-C(26)	-101.11(18)
C(33)-N(2)-C(21)-C(22)	82.10(19)
C(26)-C(21)-C(22)-C(23)	1.9(2)
N(2)-C(21)-C(22)-C(23)	178.46(13)
C(26)-C(21)-C(22)-C(27)	-176.60(15)
N(2)-C(21)-C(22)-C(27)	0.0(2)
C(21)-C(22)-C(23)-C(24)	-0.2(2)
C(27)-C(22)-C(23)-C(24)	178.32(16)
C(22)-C(23)-C(24)-C(25)	-1.0(3)
C(23)-C(24)-C(25)-C(26)	0.6(3)
C(22)-C(21)-C(26)-C(25)	-2.3(2)
N(2)-C(21)-C(26)-C(25)	-178.93(13)
C(22)-C(21)-C(26)-C(30)	178.94(14)
N(2)-C(21)-C(26)-C(30)	2.3(2)
C(24)-C(25)-C(26)-C(21)	1.0(2)
C(24)-C(25)-C(26)-C(30)	179.78(15)
C(23)-C(22)-C(27)-C(29)	29.1(2)
C(21)-C(22)-C(27)-C(29)	-152.44(18)
C(23)-C(22)-C(27)-C(28)	-95.8(2)
C(21)-C(22)-C(27)-C(28)	82.6(2)
C(21)-C(26)-C(30)-C(32)	-137.61(19)
C(25)-C(26)-C(30)-C(32)	43.7(2)
C(21)-C(26)-C(30)-C(31)	95.8(2)
C(25)-C(26)-C(30)-C(31)	-82.9(2)
C(21)-N(2)-C(33)-O(2)	-2.4(2)
C(21)-N(2)-C(33)-C(34)	176.78(14)
C(35)-O(2)-C(33)-N(2)	-177.70(13)
C(35)-O(2)-C(33)-C(34)	3.1(2)
C(33)-O(2)-C(35)-C(36)	159.70(14)

Symmetry transformations used to generate equivalent atoms.

Table A27. Hydrogen bonds for **90** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(1)	0.88	2.20	3.0745(13)	174.1
N(2)-H(2)...Cl(2)	0.88	2.13	3.0060(13)	177.8
O(1S)-H(2S)...Cl(2)	0.837(16)	2.367(17)	3.2022(18)	176(2)
O(1S)-H(1S)...Cl(1)#1	0.860(17)	2.424(18)	3.2693(18)	168(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table A28. Crystal data and structure refinement for **88**.

Identification code	**88**	
Empirical formula	C27 H39 F3 N O3 P S	
Formula weight	545.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.139(6) Å	α= 95.710(7)°.
	b = 12.197(8) Å	β= 112.133(7)°.
	c = 12.487(7) Å	γ = 109.880(8)°.
Volume	1426.4(15) $Å^3$	
Z	2	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	580	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.824 to 27.693°.	
Index ranges	-14<=h<=13, -15<=k<=15, 0<=l<=16	
Reflections collected	6528	
Independent reflections	6528 [R(int) = ?]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745552 and 0.425956	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6528 / 0 / 340	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0821, wR2 = 0.1901	
R indices (all data)	R1 = 0.1223, wR2 = 0.2194	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.571 and -0.883 e.$Å^{-3}$	

Table A29. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **88**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P	3089(1)	9734(1)	3790(1)	23(1)
N	675(3)	8183(3)	1817(3)	23(1)
C(1)	2977(4)	10518(3)	5070(3)	24(1)
C(2)	2523(4)	9932(3)	5841(3)	25(1)
C(3)	2630(5)	10634(4)	6854(4)	33(1)
C(4)	3141(5)	11868(4)	7094(4)	35(1)
C(5)	3555(5)	12443(4)	6326(4)	36(1)
C(6)	3492(4)	11804(4)	5305(3)	28(1)

C(7)	1910(4)	8571(4)	5651(4)	28(1)
C(8)	2938(5)	8192(4)	6585(4)	41(1)
C(9)	479(5)	8101(4)	5656(5)	44(1)
C(10)	3955(5)	12492(4)	4491(4)	30(1)
C(11)	5544(5)	13244(4)	5094(5)	45(1)
C(12)	3162(5)	13286(4)	4079(5)	42(1)
C(13)	1281(4)	9193(3)	2617(3)	21(1)
C(14)	1235(4)	7288(3)	1728(3)	23(1)
C(15)	784(4)	6269(4)	2140(4)	29(1)
C(16)	1281(5)	5400(4)	1961(4)	40(1)
C(17)	2184(6)	5531(4)	1437(4)	44(1)
C(18)	2622(5)	6559(4)	1053(4)	36(1)
C(19)	2130(4)	7457(4)	1162(4)	26(1)
C(20)	-235(5)	6109(4)	2692(4)	36(1)
C(21)	-60(7)	5345(5)	3581(5)	60(2)
C(22)	-1752(5)	5606(5)	1744(5)	50(1)
C(23)	2492(4)	8514(4)	628(4)	28(1)
C(24)	4037(5)	9066(5)	873(6)	56(2)
C(25)	1519(6)	8114(5)	-714(4)	55(2)
C(26)	545(5)	10016(4)	2508(4)	32(1)
S(1)	2832(1)	1974(1)	586(1)	28(1)
O(1)	2797(3)	1242(3)	-407(3)	39(1)
O(2)	2978(3)	1484(3)	1602(3)	42(1)
O(3)	1800(3)	2492(3)	266(3)	41(1)
C(27)	4495(5)	3277(4)	1117(4)	36(1)
F(1)	4557(3)	3839(3)	273(3)	66(1)
F(2)	5581(3)	2973(3)	1459(3)	60(1)
F(3)	4716(3)	4089(3)	2035(3)	62(1)

Table A30. Bond lengths [Å] and angles [°] for **88**.

P-C(13)	1.821(4)
P-C(1)	1.847(4)
P-H(1)	0.87(5)
N-C(13)	1.285(5)
N-C(14)	1.443(5)
N-H(2)	0.67(5)
C(1)-C(2)	1.397(6)
C(1)-C(6)	1.429(6)
C(2)-C(3)	1.396(6)
C(2)-C(7)	1.518(6)
C(3)-C(4)	1.371(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.369(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(6)
C(5)-H(5)	0.9500
C(6)-C(10)	1.508(6)
C(7)-C(9)	1.503(6)
C(7)-C(8)	1.532(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.515(7)
C(10)-C(12)	1.523(6)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(26)	1.483(5)

C(14)-C(19)	1.399(6)	C(4)-C(3)-C(2)	121.9(4)
C(14)-C(15)	1.400(6)	C(4)-C(3)-H(3)	119.1
C(15)-C(16)	1.387(6)	C(2)-C(3)-H(3)	119.1
C(15)-C(20)	1.506(7)	C(5)-C(4)-C(3)	119.9(4)
C(16)-C(17)	1.368(8)	C(5)-C(4)-H(4)	120.1
C(16)-H(16)	0.9500	C(3)-C(4)-H(4)	120.1
C(17)-C(18)	1.386(7)	C(4)-C(5)-C(6)	121.4(4)
C(17)-H(17)	0.9500	C(4)-C(5)-H(5)	119.3
C(18)-C(19)	1.397(6)	C(6)-C(5)-H(5)	119.3
C(18)-H(18)	0.9500	C(5)-C(6)-C(1)	118.3(4)
C(19)-C(23)	1.514(6)	C(5)-C(6)-C(10)	118.7(4)
C(20)-C(22)	1.509(7)	C(1)-C(6)-C(10)	122.9(4)
C(20)-C(21)	1.518(7)	C(9)-C(7)-C(2)	112.0(3)
C(20)-H(20)	1.0000	C(9)-C(7)-C(8)	110.7(4)
C(21)-H(21A)	0.9800	C(2)-C(7)-C(8)	111.0(3)
C(21)-H(21B)	0.9800	C(9)-C(7)-H(7)	107.7
C(21)-H(21C)	0.9800	C(2)-C(7)-H(7)	107.7
C(22)-H(22A)	0.9800	C(8)-C(7)-H(7)	107.7
C(22)-H(22B)	0.9800	C(7)-C(8)-H(8A)	109.5
C(22)-H(22C)	0.9800	C(7)-C(8)-H(8B)	109.5
C(23)-C(24)	1.511(6)	H(8A)-C(8)-H(8B)	109.5
C(23)-C(25)	1.526(6)	C(7)-C(8)-H(8C)	109.5
C(23)-H(23)	1.0000	H(8A)-C(8)-H(8C)	109.5
C(24)-H(24A)	0.9800	H(8B)-C(8)-H(8C)	109.5
C(24)-H(24B)	0.9800	C(7)-C(9)-H(9A)	109.5
C(24)-H(24C)	0.9800	C(7)-C(9)-H(9B)	109.5
C(25)-H(25A)	0.9800	H(9A)-C(9)-H(9B)	109.5
C(25)-H(25B)	0.9800	C(7)-C(9)-H(9C)	109.5
C(25)-H(25C)	0.9800	H(9A)-C(9)-H(9C)	109.5
C(26)-H(26A)	0.9800	H(9B)-C(9)-H(9C)	109.5
C(26)-H(26B)	0.9800	C(6)-C(10)-C(11)	110.8(4)
C(26)-H(26C)	0.9800	C(6)-C(10)-C(12)	112.1(4)
S(1)-O(2)	1.433(3)	C(11)-C(10)-C(12)	110.4(4)
S(1)-O(1)	1.434(3)	C(6)-C(10)-H(10)	107.8
S(1)-O(3)	1.443(3)	C(11)-C(10)-H(10)	107.8
S(1)-C(27)	1.805(5)	C(12)-C(10)-H(10)	107.8
C(27)-F(2)	1.315(5)	C(10)-C(11)-H(11A)	109.5
C(27)-F(1)	1.324(6)	C(10)-C(11)-H(11B)	109.5
C(27)-F(3)	1.324(5)	H(11A)-C(11)-H(11B)	109.5
C(13)-P-C(1)	102.12(18)	C(10)-C(11)-H(11C)	109.5
C(13)-P-H(1)	122(3)	H(11A)-C(11)-H(11C)	109.5
C(1)-P-H(1)	135(3)	H(11B)-C(11)-H(11C)	109.5
C(13)-N-C(14)	127.5(3)	C(10)-C(12)-H(12A)	109.5
C(13)-N-H(2)	115(4)	C(10)-C(12)-H(12B)	109.5
C(14)-N-H(2)	118(4)	H(12A)-C(12)-H(12B)	109.5
C(2)-C(1)-C(6)	120.1(3)	C(10)-C(12)-H(12C)	109.5
C(2)-C(1)-P	123.5(3)	H(12A)-C(12)-H(12C)	109.5
C(6)-C(1)-P	116.3(3)	H(12B)-C(12)-H(12C)	109.5
C(3)-C(2)-C(1)	118.4(4)	N-C(13)-C(26)	118.9(3)
C(3)-C(2)-C(7)	117.3(4)	N-C(13)-P	122.7(3)
C(1)-C(2)-C(7)	124.3(3)	C(26)-C(13)-P	118.1(3)

C(19)-C(14)-C(15)	123.7(4)
C(19)-C(14)-N	117.6(4)
C(15)-C(14)-N	118.6(4)
C(16)-C(15)-C(14)	116.2(4)
C(16)-C(15)-C(20)	122.4(4)
C(14)-C(15)-C(20)	121.4(4)
C(17)-C(16)-C(15)	122.5(5)
C(17)-C(16)-H(16)	118.7
C(15)-C(16)-H(16)	118.7
C(16)-C(17)-C(18)	119.8(4)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(19)	121.2(5)
C(17)-C(18)-H(18)	119.4
C(19)-C(18)-H(18)	119.4
C(18)-C(19)-C(14)	116.6(4)
C(18)-C(19)-C(23)	120.9(4)
C(14)-C(19)-C(23)	122.4(4)
C(15)-C(20)-C(22)	111.3(4)
C(15)-C(20)-C(21)	112.8(4)
C(22)-C(20)-C(21)	110.9(4)
C(15)-C(20)-H(20)	107.2
C(22)-C(20)-H(20)	107.2
C(21)-C(20)-H(20)	107.2
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-C(19)	113.2(4)
C(24)-C(23)-C(25)	111.2(4)
C(19)-C(23)-C(25)	109.2(4)
C(24)-C(23)-H(23)	107.7
C(19)-C(23)-H(23)	107.7
C(25)-C(23)-H(23)	107.7
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(13)-C(26)-H(26A)	109.5
C(13)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(13)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
O(2)-S(1)-O(1)	115.1(2)
O(2)-S(1)-O(3)	114.8(2)
O(1)-S(1)-O(3)	114.73(19)
O(2)-S(1)-C(27)	103.5(2)
O(1)-S(1)-C(27)	103.4(2)
O(3)-S(1)-C(27)	102.8(2)
F(2)-C(27)-F(1)	106.4(4)
F(2)-C(27)-F(3)	107.3(4)
F(1)-C(27)-F(3)	106.6(4)
F(2)-C(27)-S(1)	111.5(3)
F(1)-C(27)-S(1)	111.9(3)
F(3)-C(27)-S(1)	112.8(3)

Symmetry transformations used to generate equivalent atoms:

Table A31. Anisotropic displacement parameters ($Å^2$x 10^3) for **88**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P	26(1)	28(1)	14(1)	5(1)	5(1)	13(1)
N	24(2)	30(2)	12(2)	5(1)	4(1)	12(2)
C(1)	26(2)	26(2)	13(2)	4(2)	3(2)	10(2)
C(2)	28(2)	27(2)	15(2)	6(2)	5(2)	11(2)
C(3)	40(2)	35(2)	20(2)	5(2)	12(2)	15(2)

C(4)	51(3)	37(2)	14(2)	0(2)	10(2)	23(2)
C(5)	50(3)	24(2)	22(2)	1(2)	9(2)	12(2)
C(6)	36(2)	29(2)	11(2)	5(2)	1(2)	15(2)
C(7)	33(2)	31(2)	17(2)	7(2)	9(2)	12(2)
C(8)	54(3)	38(3)	38(3)	19(2)	19(2)	24(2)
C(9)	42(3)	33(2)	52(3)	9(2)	22(2)	10(2)
C(10)	44(2)	23(2)	19(2)	6(2)	12(2)	12(2)
C(11)	49(3)	39(3)	43(3)	18(2)	18(2)	15(2)
C(12)	53(3)	36(2)	37(3)	18(2)	16(2)	19(2)
C(13)	26(2)	22(2)	16(2)	9(2)	11(2)	10(2)
C(14)	25(2)	23(2)	12(2)	2(1)	0(2)	8(2)
C(15)	37(2)	23(2)	13(2)	2(2)	2(2)	7(2)
C(16)	57(3)	28(2)	25(2)	10(2)	6(2)	18(2)
C(17)	57(3)	38(3)	34(3)	6(2)	8(2)	31(2)
C(18)	41(3)	33(2)	30(3)	2(2)	12(2)	17(2)
C(19)	23(2)	25(2)	18(2)	2(2)	0(2)	7(2)
C(20)	49(3)	25(2)	18(2)	6(2)	9(2)	3(2)
C(21)	96(5)	45(3)	34(3)	21(2)	30(3)	19(3)
C(22)	43(3)	52(3)	36(3)	10(2)	14(2)	2(2)
C(23)	35(2)	27(2)	21(2)	6(2)	13(2)	11(2)
C(24)	38(3)	58(3)	73(4)	28(3)	27(3)	16(2)
C(25)	72(4)	44(3)	26(3)	14(2)	7(2)	13(3)
C(26)	36(2)	36(2)	22(2)	5(2)	6(2)	19(2)
S(1)	30(1)	31(1)	15(1)	9(1)	4(1)	11(1)
O(1)	46(2)	41(2)	24(2)	4(1)	12(1)	15(2)
O(2)	58(2)	41(2)	16(2)	15(1)	12(1)	13(2)
O(3)	31(2)	45(2)	36(2)	6(2)	3(1)	17(1)
C(27)	33(2)	41(2)	28(3)	11(2)	4(2)	18(2)
F(1)	51(2)	70(2)	56(2)	43(2)	12(2)	4(2)
F(2)	32(2)	68(2)	72(2)	28(2)	10(2)	24(1)
F(3)	54(2)	43(2)	58(2)	-11(2)	13(2)	4(1)

Table A32. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **88**.

	x	y	z	U(eq)
H(1)	3770(50)	9670(40)	3650(40)	35
H(2)	60(50)	8100(50)	1370(50)	35
H(3)	2341	10246	7392	39
H(4)	3208	12324	7793	42
H(5)	3893	13298	6493	43
H(7)	1783	8196	4845	33
H(8A)	3080	8545	7386	62
H(8B)	3852	8478	6545	62
H(8C)	2540	7309	6421	62
H(9A)	79	7216	5453	66
H(9B)	-157	8366	5065	66

H(9C)	580	8412	6454	66
H(10)	3732	11890	3764	35
H(11A)	5832	13635	4530	67
H(11B)	6040	12720	5346	67
H(11C)	5788	13861	5797	67
H(12A)	3388	13904	4774	63
H(12B)	2137	12788	3684	63
H(12C)	3451	13678	3516	63
H(16)	983	4686	2212	48
H(17)	2510	4920	1337	52
H(18)	3268	6655	708	43
H(20)	-19	6930	3145	43
H(21A)	-685	5330	3965	90
H(21B)	930	5692	4192	90
H(21C)	-310	4520	3160	90
H(22A)	-1828	6079	1150	75
H(22B)	-2373	5650	2117	75
H(22C)	-2042	4762	1349	75
H(23)	2287	9152	999	33
H(24A)	4636	9292	1738	83
H(24B)	4225	9787	571	83
H(24C)	4251	8478	470	83
H(25A)	1652	7450	-1094	82
H(25B)	1753	8795	-1065	82
H(25C)	528	7840	-844	82
H(26A)	1070	10743	2331	49
H(26B)	500	10244	3263	49
H(26C)	-420	9605	1859	49

Table A33. Torsion angles [°] for **88**.

C(13)-P-C(1)-C(2)	84.9(4)
C(13)-P-C(1)-C(6)	-99.8(3)
C(6)-C(1)-C(2)-C(3)	-2.1(6)
P-C(1)-C(2)-C(3)	173.0(3)
C(6)-C(1)-C(2)-C(7)	177.8(3)
P-C(1)-C(2)-C(7)	-7.2(6)
C(1)-C(2)-C(3)-C(4)	1.2(6)
C(7)-C(2)-C(3)-C(4)	-178.6(4)
C(2)-C(3)-C(4)-C(5)	0.4(7)
C(3)-C(4)-C(5)-C(6)	-1.0(7)
C(4)-C(5)-C(6)-C(1)	0.1(7)
C(4)-C(5)-C(6)-C(10)	179.6(4)
C(2)-C(1)-C(6)-C(5)	1.4(6)
P-C(1)-C(6)-C(5)	-174.0(3)
C(2)-C(1)-C(6)-C(10)	-178.0(4)
P-C(1)-C(6)-C(10)	6.6(5)
C(3)-C(2)-C(7)-C(9)	54.5(5)
C(1)-C(2)-C(7)-C(9)	-125.3(4)
C(3)-C(2)-C(7)-C(8)	-69.8(5)
C(1)-C(2)-C(7)-C(8)	110.4(5)
C(5)-C(6)-C(10)-C(11)	68.9(5)
C(1)-C(6)-C(10)-C(11)	-111.7(4)
C(5)-C(6)-C(10)-C(12)	-55.0(5)
C(1)-C(6)-C(10)-C(12)	124.4(4)
C(14)-N-C(13)-C(26)	176.9(4)
C(14)-N-C(13)-P	3.9(6)
C(1)-P-C(13)-N	-145.2(3)
C(1)-P-C(13)-C(26)	41.7(3)
C(13)-N-C(14)-C(19)	-84.0(5)
C(13)-N-C(14)-C(15)	100.0(5)
C(19)-C(14)-C(15)-C(16)	0.2(6)
N-C(14)-C(15)-C(16)	175.9(3)
C(19)-C(14)-C(15)-C(20)	-177.1(4)
N-C(14)-C(15)-C(20)	-1.4(6)
C(14)-C(15)-C(16)-C(17)	1.3(6)
C(20)-C(15)-C(16)-C(17)	178.6(5)
C(15)-C(16)-C(17)-C(18)	-0.6(7)
C(16)-C(17)-C(18)-C(19)	-1.6(7)
C(17)-C(18)-C(19)-C(14)	2.9(6)
C(17)-C(18)-C(19)-C(23)	-173.7(4)
C(15)-C(14)-C(19)-C(18)	-2.3(6)
N-C(14)-C(19)-C(18)	-178.0(3)
C(15)-C(14)-C(19)-C(23)	174.4(4)
N-C(14)-C(19)-C(23)	-1.4(5)
C(16)-C(15)-C(20)-C(22)	-94.9(5)
C(14)-C(15)-C(20)-C(22)	82.2(5)
C(16)-C(15)-C(20)-C(21)	30.4(6)
C(14)-C(15)-C(20)-C(21)	-152.4(4)
C(18)-C(19)-C(23)-C(24)	-45.1(5)
C(14)-C(19)-C(23)-C(24)	138.4(4)
C(18)-C(19)-C(23)-C(25)	79.4(5)
C(14)-C(19)-C(23)-C(25)	-97.1(5)
O(2)-S(1)-C(27)-F(2)	59.9(4)
O(1)-S(1)-C(27)-F(2)	-60.5(4)
O(3)-S(1)-C(27)-F(2)	179.8(3)
O(2)-S(1)-C(27)-F(1)	179.0(3)
O(1)-S(1)-C(27)-F(1)	58.5(4)
O(3)-S(1)-C(27)-F(1)	-61.2(4)
O(2)-S(1)-C(27)-F(3)	-60.9(4)
O(1)-S(1)-C(27)-F(3)	178.7(3)
O(3)-S(1)-C(27)-F(3)	59.0(4)

Symmetry transformations used to generate equivalent atoms:

Table A34. Hydrogen bonds for **88** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(2)...O(3)#1	0.67(5)	2.12(5)	2.769(4)	166(6)
C(26)-H(26A)...O(2)#2	0.98	2.55	3.353(6)	139.7
C(26)-H(26C)...O(1)#1	0.98	2.35	3.324(5)	174.0

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z   #2 x,y+1,z

Table A35. Crystal data and structure refinement for **93**.

Identification code	**93**	
Empirical formula	C21 H24 F3 N O4 S	
Formula weight	443.47	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.3830(15) Å	α= 90°.
	b = 10.8157(12) Å	β= 99.9821(12)°.
	c = 14.6913(16) Å	γ = 90°.
Volume	2094.3(4) Å^{3}	
Z	4	
Density (calculated)	1.406 Mg/m^{3}	
Absorption coefficient	0.209 mm^{-1}	
F(000)	928	
Crystal size	0.414 x 0.203 x 0.136 mm^{3}	
Theta range for data collection	1.901 to 29.160°.	
Index ranges	-18<=h<=18, -14<=k<=14, -19<=l<=19	
Reflections collected	31350	
Independent reflections	5377 [R(int) = 0.0236]	
Completeness to theta = 25.500°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7138	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	5377 / 0 / 281	
Goodness-of-fit on F^{2}	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0911	
R indices (all data)	R1 = 0.0405, wR2 = 0.0955	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.431 and -0.363 e.Å^{-3}	

Table A36. Atomic coordinates (x 10^{4}) and equivalent isotropic displacement parameters (Å^{2}x 10^{3}) for **93**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3574(1)	10321(1)	4086(1)	38(1)
N(1)	5012(1)	5857(1)	1953(1)	20(1)
C(1)	3935(1)	5836(1)	2153(1)	23(1)
C(2)	3753(1)	7028(1)	2652(1)	22(1)
C(3)	3960(1)	8180(1)	2293(1)	29(1)
C(4)	3898(1)	9253(1)	2789(1)	32(1)
C(5)	3603(1)	9210(1)	3654(1)	27(1)
C(6)	3346(1)	8087(1)	4002(1)	28(1)

C(7)	3429(1)	7011(1)	3500(1)	26(1)
C(8)	3407(1)	10315(1)	5022(1)	42(1)
C(9)	5752(1)	5916(1)	2815(1)	18(1)
C(10)	5574(1)	5068(1)	3493(1)	21(1)
C(11)	6259(1)	5052(1)	4320(1)	26(1)
C(12)	7073(1)	5868(1)	4461(1)	27(1)
C(13)	7220(1)	6697(1)	3781(1)	24(1)
C(14)	6558(1)	6740(1)	2928(1)	19(1)
C(15)	4654(1)	4281(1)	3314(1)	25(1)
C(16)	3866(1)	4666(1)	2694(1)	27(1)
C(17)	4629(1)	3097(1)	3847(1)	35(1)
C(18)	6760(1)	7639(1)	2187(1)	23(1)
C(19)	6870(1)	8966(1)	2550(1)	32(1)
C(20)	7701(1)	7247(1)	1796(1)	32(1)
S(1)	4940(1)	3165(1)	421(1)	21(1)
O(2)	4049(1)	3895(1)	124(1)	38(1)
O(3)	5467(1)	2766(1)	-306(1)	34(1)
O(4)	5597(1)	3623(1)	1237(1)	27(1)
C(21)	4462(1)	1722(1)	823(1)	34(1)
F(1)	3799(1)	1197(1)	164(1)	69(1)
F(2)	3993(1)	1926(1)	1538(1)	57(1)
F(3)	5204(1)	920(1)	1092(1)	48(1)

Table A37. Bond lengths [Å] and angles [°] for **93**.

O(1)-C(5)	1.3631(16)
O(1)-C(8)	1.4307(17)
N(1)-C(9)	1.4682(14)
N(1)-C(1)	1.5205(14)
N(1)-H(1A)	0.891(16)
N(1)-H(1B)	0.931(16)
C(1)-C(16)	1.5053(17)
C(1)-C(2)	1.5235(16)
C(1)-H(1)	1.0000
C(2)-C(7)	1.3874(16)
C(2)-C(3)	1.3995(17)
C(3)-C(4)	1.3804(19)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3953(17)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3844(17)
C(6)-C(7)	1.3921(18)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(14)	1.3873(15)
C(9)-C(10)	1.4034(15)
C(10)-C(11)	1.3906(16)
C(10)-C(15)	1.4824(16)
C(11)-C(12)	1.3887(19)
C(11)-H(11)	0.9500
C(12)-C(13)	1.3810(17)
C(12)-H(12)	0.9500
C(13)-C(14)	1.4056(15)
C(13)-H(13)	0.9500
C(14)-C(18)	1.5180(15)
C(15)-C(16)	1.3356(18)
C(15)-C(17)	1.5049(17)
C(16)-H(16)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.5302(17)
C(18)-C(20)	1.5325(17)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

S(1)-O(2)	1.4341(10)
S(1)-O(3)	1.4438(9)
S(1)-O(4)	1.4453(8)
S(1)-C(21)	1.8234(14)
C(21)-F(1)	1.3229(17)
C(21)-F(3)	1.3253(16)
C(21)-F(2)	1.3314(18)
C(5)-O(1)-C(8)	117.68(11)
C(9)-N(1)-C(1)	110.71(8)
C(9)-N(1)-H(1A)	107.4(9)
C(1)-N(1)-H(1A)	109.4(10)
C(9)-N(1)-H(1B)	113.9(9)
C(1)-N(1)-H(1B)	109.1(9)
H(1A)-N(1)-H(1B)	106.1(13)
C(16)-C(1)-N(1)	105.15(9)
C(16)-C(1)-C(2)	115.29(9)
N(1)-C(1)-C(2)	108.46(9)
C(16)-C(1)-H(1)	109.2
N(1)-C(1)-H(1)	109.2
C(2)-C(1)-H(1)	109.2
C(7)-C(2)-C(3)	117.55(11)
C(7)-C(2)-C(1)	121.49(10)
C(3)-C(2)-C(1)	120.87(10)
C(4)-C(3)-C(2)	121.06(11)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.32(12)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
O(1)-C(5)-C(6)	124.97(11)
O(1)-C(5)-C(4)	115.47(11)
C(6)-C(5)-C(4)	119.55(12)
C(5)-C(6)-C(7)	119.31(11)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(2)-C(7)-C(6)	122.08(11)
C(2)-C(7)-H(7)	119.0
C(6)-C(7)-H(7)	119.0
O(1)-C(8)-H(8A)	109.5
O(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	124.01(10)
C(14)-C(9)-N(1)	121.66(9)
C(10)-C(9)-N(1)	114.33(9)
C(11)-C(10)-C(9)	117.47(11)
C(11)-C(10)-C(15)	123.30(10)
C(9)-C(10)-C(15)	119.17(10)
C(12)-C(11)-C(10)	120.20(11)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(13)-C(12)-C(11)	120.76(11)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(12)-C(13)-C(14)	121.33(11)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(9)-C(14)-C(13)	116.21(10)
C(9)-C(14)-C(18)	123.88(10)
C(13)-C(14)-C(18)	119.91(10)
C(16)-C(15)-C(10)	118.37(10)
C(16)-C(15)-C(17)	122.31(12)
C(10)-C(15)-C(17)	119.31(11)
C(15)-C(16)-C(1)	120.59(10)
C(15)-C(16)-H(16)	119.7
C(1)-C(16)-H(16)	119.7
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-C(19)	111.63(10)
C(14)-C(18)-C(20)	110.58(10)
C(19)-C(18)-C(20)	110.74(10)
C(14)-C(18)-H(18)	107.9
C(19)-C(18)-H(18)	107.9
C(20)-C(18)-H(18)	107.9
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(2)-S(1)-O(3)	115.23(6)
O(2)-S(1)-O(4)	114.71(6)
O(3)-S(1)-O(4)	114.25(6)
O(2)-S(1)-C(21)	104.48(6)
O(3)-S(1)-C(21)	103.14(7)
O(4)-S(1)-C(21)	102.85(6)
F(1)-C(21)-F(3)	108.11(13)
F(1)-C(21)-F(2)	107.49(13)
F(3)-C(21)-F(2)	107.73(12)
F(1)-C(21)-S(1)	111.00(10)

F(3)-C(21)-S(1)	111.68(10)	F(2)-C(21)-S(1)	110.65(10)

Symmetry transformations used to generate equivalent atoms:

Table A38. Anisotropic displacement parameters (Å^{2}x 10^3) for **93**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	57(1)	23(1)	40(1)	-1(1)	24(1)	0(1)
N(1)	21(1)	21(1)	17(1)	-2(1)	3(1)	-2(1)
C(1)	19(1)	28(1)	22(1)	-2(1)	3(1)	-3(1)
C(2)	19(1)	25(1)	22(1)	2(1)	4(1)	1(1)
C(3)	36(1)	29(1)	26(1)	7(1)	15(1)	7(1)
C(4)	41(1)	25(1)	36(1)	9(1)	19(1)	5(1)
C(5)	29(1)	24(1)	29(1)	2(1)	9(1)	4(1)
C(6)	35(1)	28(1)	23(1)	4(1)	10(1)	1(1)
C(7)	30(1)	24(1)	24(1)	4(1)	8(1)	-2(1)
C(8)	61(1)	33(1)	36(1)	-7(1)	19(1)	-2(1)
C(9)	21(1)	17(1)	16(1)	-2(1)	3(1)	2(1)
C(10)	26(1)	17(1)	21(1)	0(1)	8(1)	2(1)
C(11)	36(1)	24(1)	20(1)	5(1)	7(1)	7(1)
C(12)	31(1)	29(1)	20(1)	-1(1)	-2(1)	8(1)
C(13)	22(1)	24(1)	24(1)	-4(1)	-1(1)	1(1)
C(14)	21(1)	17(1)	19(1)	-1(1)	4(1)	2(1)
C(15)	32(1)	19(1)	28(1)	-1(1)	14(1)	-2(1)
C(16)	27(1)	24(1)	31(1)	-4(1)	10(1)	-7(1)
C(17)	44(1)	22(1)	43(1)	6(1)	21(1)	-1(1)
C(18)	23(1)	21(1)	23(1)	2(1)	2(1)	-4(1)
C(19)	36(1)	20(1)	39(1)	1(1)	7(1)	-1(1)
C(20)	36(1)	30(1)	31(1)	1(1)	15(1)	-2(1)
S(1)	26(1)	20(1)	17(1)	2(1)	1(1)	0(1)
O(2)	32(1)	32(1)	45(1)	11(1)	-4(1)	5(1)
O(3)	49(1)	34(1)	20(1)	-1(1)	10(1)	2(1)
O(4)	32(1)	27(1)	21(1)	-4(1)	0(1)	0(1)
C(21)	34(1)	27(1)	38(1)	7(1)	2(1)	-4(1)
F(1)	74(1)	45(1)	76(1)	6(1)	-23(1)	-33(1)
F(2)	62(1)	48(1)	70(1)	20(1)	38(1)	0(1)
F(3)	54(1)	27(1)	64(1)	17(1)	9(1)	9(1)

Table A39. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **93**.

	x	y	z	U(eq)
H(1A)	5130(11)	5161(15)	1664(10)	24

H(1B)	5072(11)	6497(14)	1543(10)	24
H(1)	3446	5790	1556	28
H(3)	4146	8224	1699	35
H(4)	4057	10025	2540	39
H(6)	3116	8050	4578	34
H(7)	3258	6242	3745	31
H(8A)	2729	9985	5044	63
H(8B)	3458	11160	5265	63
H(8C)	3919	9793	5397	63
H(11)	6171	4481	4791	32
H(12)	7533	5855	5031	33
H(13)	7780	7249	3893	29
H(16)	3256	4197	2592	32
H(17A)	3975	2684	3650	53
H(17B)	4717	3281	4509	53
H(17C)	5179	2554	3729	53
H(18)	6164	7612	1671	27
H(19A)	6259	9201	2792	47
H(19B)	6960	9526	2047	47
H(19C)	7462	9021	3046	47
H(20A)	8297	7266	2289	47
H(20B)	7804	7818	1302	47
H(20C)	7605	6407	1546	47

Table A40. Torsion angles [°] for **93**.

C(9)-N(1)-C(1)-C(16)	-62.46(11)
C(9)-N(1)-C(1)-C(2)	61.40(11)
C(16)-C(1)-C(2)-C(7)	-7.32(15)
N(1)-C(1)-C(2)-C(7)	-124.88(11)
C(16)-C(1)-C(2)-C(3)	169.24(11)
N(1)-C(1)-C(2)-C(3)	51.68(14)
C(7)-C(2)-C(3)-C(4)	3.54(19)
C(1)-C(2)-C(3)-C(4)	-173.15(12)
C(2)-C(3)-C(4)-C(5)	-1.5(2)
C(8)-O(1)-C(5)-C(6)	9.4(2)
C(8)-O(1)-C(5)-C(4)	-171.95(13)
C(3)-C(4)-C(5)-O(1)	179.59(13)
C(3)-C(4)-C(5)-C(6)	-1.7(2)
O(1)-C(5)-C(6)-C(7)	-178.67(12)
C(4)-C(5)-C(6)-C(7)	2.7(2)
C(3)-C(2)-C(7)-C(6)	-2.47(18)
C(1)-C(2)-C(7)-C(6)	174.19(11)
C(5)-C(6)-C(7)-C(2)	-0.6(2)
C(1)-N(1)-C(9)-C(14)	-133.20(10)
C(1)-N(1)-C(9)-C(10)	47.55(12)
C(14)-C(9)-C(10)-C(11)	-0.74(16)
N(1)-C(9)-C(10)-C(11)	178.49(10)
C(14)-C(9)-C(10)-C(15)	176.57(10)
N(1)-C(9)-C(10)-C(15)	-4.20(14)
C(9)-C(10)-C(11)-C(12)	1.08(17)
C(15)-C(10)-C(11)-C(12)	-176.11(11)
C(10)-C(11)-C(12)-C(13)	-0.61(18)
C(11)-C(12)-C(13)-C(14)	-0.29(18)
C(10)-C(9)-C(14)-C(13)	-0.11(16)
N(1)-C(9)-C(14)-C(13)	-179.28(10)
C(10)-C(9)-C(14)-C(18)	178.77(10)
N(1)-C(9)-C(14)-C(18)	-0.40(16)
C(12)-C(13)-C(14)-C(9)	0.63(16)
C(12)-C(13)-C(14)-C(18)	-178.30(11)
C(11)-C(10)-C(15)-C(16)	154.42(12)
C(9)-C(10)-C(15)-C(16)	-22.72(16)
C(11)-C(10)-C(15)-C(17)	-24.41(17)
C(9)-C(10)-C(15)-C(17)	158.45(11)
C(10)-C(15)-C(16)-C(1)	3.26(17)
C(17)-C(15)-C(16)-C(1)	-177.95(11)
N(1)-C(1)-C(16)-C(15)	37.50(14)
C(2)-C(1)-C(16)-C(15)	-81.89(14)
C(9)-C(14)-C(18)-C(19)	127.04(12)
C(13)-C(14)-C(18)-C(19)	-54.12(14)
C(9)-C(14)-C(18)-C(20)	-109.20(12)
C(13)-C(14)-C(18)-C(20)	69.65(13)
O(2)-S(1)-C(21)-F(1)	56.89(13)
O(3)-S(1)-C(21)-F(1)	-63.93(12)
O(4)-S(1)-C(21)-F(1)	177.01(11)
O(2)-S(1)-C(21)-F(3)	177.62(10)
O(3)-S(1)-C(21)-F(3)	56.81(11)
O(4)-S(1)-C(21)-F(3)	-62.26(11)
O(2)-S(1)-C(21)-F(2)	-62.37(11)
O(3)-S(1)-C(21)-F(2)	176.82(10)
O(4)-S(1)-C(21)-F(2)	57.75(11)

Symmetry transformations used to generate equivalent atoms:

Table A41. Hydrogen bonds for **93** [Å and °]. The highlighted rows are the "important" H-bonds. The connection to S is probably a consequence of the O being attached to S, and not a real H-bond. The fluorine contacts are "non-classical" H bonds and probably accentuated by the negative charge on the triflate anion.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...S(1)	0.891(16)	2.811(16)	3.6703(10)	162.6(12)
N(1)-H(1A)...O(4)	0.891(16)	1.921(16)	2.8003(13)	169.0(14)
N(1)-H(1B)...S(1)#1	0.931(16)	2.906(15)	3.6559(10)	138.6(12)
N(1)-H(1B)...O(3)#1	0.931(16)	2.001(15)	2.8190(14)	145.7(13)
C(4)-H(4)...F(2)#2	0.95	2.52	3.4404(16)	162.5
C(8)-H(8A)...O(2)#3	0.98	2.63	3.599(2)	171.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 x,y+1,z #3 -x+1/2,y+1/2,-z+1/2

Table A42. Crystal data and structure refinement for **89**.

Identification code	MeOPAmH2-CF3SO3	
Empirical formula	C33 H43 F3 N O4 P S	
Formula weight	637.71	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.3706(7) Å	α= 68.5470(10)°.
	b = 12.0449(8) Å	β= 75.3630(10)°.
	c = 13.8213(9) Å	γ = 73.5590(10)°.
Volume	1665.99(19) $Å^3$	
Z	2	
Density (calculated)	1.271 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	676	
Crystal size	0.220 x 0.215 x 0.210 mm^3	
Theta range for data collection	1.606 to 27.508°.	
Index ranges	-14<=h<=14, -15<=k<=15, -17<=l<=17	
Reflections collected	24646	
Independent reflections	7594 [R(int) = 0.0200]	
Completeness to theta = 25.500°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.7088	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7594 / 14 / 471	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1253	
R indices (all data)	R1 = 0.0615, wR2 = 0.1334	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.256 and -0.798 e.$Å^{-3}$	

Table A43. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **89**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	997(1)	8040(1)	6436(1)	30(1)
O(1)	3941(1)	2079(1)	7927(1)	29(1)
N(1)	1385(1)	7306(1)	8437(1)	21(1)
C(1)	1552(2)	6923(2)	7635(1)	19(1)
C(2)	2143(2)	5646(2)	7742(1)	19(1)
C(3)	1780(2)	4977(2)	7264(1)	22(1)
C(4)	2395(2)	3791(2)	7351(1)	24(1)
C(5)	3398(2)	3254(2)	7892(1)	22(1)

C(6)	3780(2)	3908(2)	8358(1)	23(1)
C(7)	3142(2)	5089(2)	8292(1)	22(1)
C(8)	4935(2)	1471(2)	8515(2)	33(1)
C(9)	1739(2)	7406(2)	5361(1)	23(1)
C(10)	902(2)	7189(2)	4876(1)	26(1)
C(11)	1379(2)	6820(2)	3987(2)	33(1)
C(12)	2634(2)	6653(2)	3592(2)	39(1)
C(13)	3448(2)	6852(2)	4072(2)	36(1)
C(14)	3021(2)	7226(2)	4968(1)	27(1)
C(15)	-496(2)	7379(2)	5280(2)	33(1)
C(16)	-1125(2)	6513(3)	5123(2)	53(1)
C(17)	-1121(2)	8702(2)	4770(2)	50(1)
C(18)	3977(2)	7423(2)	5453(2)	34(1)
C(19)	5039(2)	6306(3)	5681(2)	52(1)
C(20)	4461(3)	8568(3)	4743(2)	53(1)
C(21)	974(2)	8575(2)	8408(1)	22(1)
C(22)	1875(2)	9170(2)	8391(1)	25(1)
C(23)	1478(2)	10379(2)	8389(2)	31(1)
C(24)	241(2)	10957(2)	8409(2)	34(1)
C(25)	-626(2)	10340(2)	8432(2)	33(1)
C(26)	-286(2)	9132(2)	8437(2)	27(1)
C(27)	3239(2)	8550(2)	8389(2)	32(1)
C(28)	3633(2)	8431(2)	9411(2)	44(1)
C(29)	4055(2)	9230(2)	7419(2)	44(1)
C(30)	-1269(2)	8452(2)	8529(2)	44(1)
C(31)	-1879(5)	8025(5)	9661(3)	134(2)
C(32)	-2187(3)	9229(3)	7751(4)	101(2)
S(1)	1595(1)	5221(1)	1408(1)	19(1)
C(33)	3139(5)	4345(5)	1608(5)	41(1)
F(1)	3843(2)	4989(3)	1707(3)	72(1)
F(2)	3109(3)	3396(2)	2492(2)	76(1)
F(3)	3715(5)	3906(6)	826(4)	79(2)
O(2)	974(2)	4378(2)	1356(3)	53(1)
O(3)	1118(3)	5664(3)	2293(2)	44(1)
O(4)	1849(2)	6171(2)	418(2)	48(1)
S(1A)	1723(13)	5344(13)	1386(11)	146(5)
C(33A)	3340(17)	4590(17)	1342(14)	51(8)
F(1A)	3981(10)	5410(11)	713(14)	108(6)
F(2A)	3680(13)	4096(13)	2291(9)	88(4)
F(3A)	3717(13)	3722(19)	904(17)	54(5)
O(2A)	1166(10)	4125(9)	2057(10)	58(3)
O(3A)	1450(15)	6111(15)	1888(15)	74(5)
O(4A)	1545(10)	5579(11)	327(6)	47(3)

Table A44. Bond lengths [Å] and angles [°] for **89**.

P(1)-C(9)	1.8250(18)	O(1)-C(5)	1.363(2)
P(1)-C(1)	1.8361(17)	O(1)-C(8)	1.426(2)
P(1)-H(1)	1.107(16)	N(1)-C(1)	1.302(2)

N(1)-C(21)	1.455(2)
N(1)-H(2)	0.950(15)
C(1)-C(2)	1.463(2)
C(2)-C(7)	1.397(2)
C(2)-C(3)	1.404(2)
C(3)-C(4)	1.376(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.392(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.389(2)
C(6)-C(7)	1.383(2)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(14)	1.405(3)
C(9)-C(10)	1.420(3)
C(10)-C(11)	1.387(3)
C(10)-C(15)	1.526(3)
C(11)-C(12)	1.379(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.380(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.397(3)
C(13)-H(13)	0.9500
C(14)-C(18)	1.523(3)
C(15)-C(16)	1.522(3)
C(15)-C(17)	1.527(3)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.526(3)
C(18)-C(20)	1.528(3)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(26)	1.397(3)
C(21)-C(22)	1.399(3)
C(22)-C(23)	1.396(3)
C(22)-C(27)	1.518(3)
C(23)-C(24)	1.380(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.381(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.394(3)
C(25)-H(25)	0.9500
C(26)-C(30)	1.518(3)
C(27)-C(29)	1.525(3)
C(27)-C(28)	1.535(3)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-C(31)	1.504(4)
C(30)-C(32)	1.549(5)
C(30)-H(30)	1.0000
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
S(1)-O(2)	1.422(2)
S(1)-O(3)	1.433(3)
S(1)-O(4)	1.451(2)
S(1)-C(33)	1.804(5)
C(33)-F(3)	1.319(5)
C(33)-F(1)	1.322(6)
C(33)-F(2)	1.335(6)
S(1A)-O(3A)	1.277(18)
S(1A)-O(4A)	1.442(16)
S(1A)-O(2A)	1.628(17)
S(1A)-C(33A)	1.80(2)
C(33A)-F(3A)	1.311(16)
C(33A)-F(1A)	1.312(16)
C(33A)-F(2A)	1.335(17)
C(9)-P(1)-C(1)	106.93(8)
C(9)-P(1)-H(1)	92.8(13)
C(1)-P(1)-H(1)	88.5(13)
C(5)-O(1)-C(8)	117.62(14)
C(1)-N(1)-C(21)	125.12(15)
C(1)-N(1)-H(2)	119.9(14)
C(21)-N(1)-H(2)	115.0(14)
N(1)-C(1)-C(2)	118.89(15)
N(1)-C(1)-P(1)	116.96(12)
C(2)-C(1)-P(1)	124.15(12)
C(7)-C(2)-C(3)	118.74(15)
C(7)-C(2)-C(1)	119.09(15)
C(3)-C(2)-C(1)	122.09(15)
C(4)-C(3)-C(2)	120.14(16)

C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	120.40(16)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
O(1)-C(5)-C(6)	124.22(16)
O(1)-C(5)-C(4)	115.56(15)
C(6)-C(5)-C(4)	120.22(15)
C(7)-C(6)-C(5)	119.33(16)
C(7)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(6)-C(7)-C(2)	121.13(16)
C(6)-C(7)-H(7)	119.4
C(2)-C(7)-H(7)	119.4
O(1)-C(8)-H(8A)	109.5
O(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	120.96(16)
C(14)-C(9)-P(1)	124.21(14)
C(10)-C(9)-P(1)	114.65(14)
C(11)-C(10)-C(9)	118.30(18)
C(11)-C(10)-C(15)	119.40(18)
C(9)-C(10)-C(15)	122.28(17)
C(12)-C(11)-C(10)	120.99(19)
C(12)-C(11)-H(11)	119.5
C(10)-C(11)-H(11)	119.5
C(11)-C(12)-C(13)	120.60(19)
C(11)-C(12)-H(12)	119.7
C(13)-C(12)-H(12)	119.7
C(12)-C(13)-C(14)	121.0(2)
C(12)-C(13)-H(13)	119.5
C(14)-C(13)-H(13)	119.5
C(13)-C(14)-C(9)	118.17(18)
C(13)-C(14)-C(18)	117.78(18)
C(9)-C(14)-C(18)	124.05(17)
C(16)-C(15)-C(10)	114.25(19)
C(16)-C(15)-C(17)	110.2(2)
C(10)-C(15)-C(17)	109.77(18)
C(16)-C(15)-H(15)	107.4
C(10)-C(15)-H(15)	107.4
C(17)-C(15)-H(15)	107.4
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-C(19)	111.74(19)
C(14)-C(18)-C(20)	110.28(19)
C(19)-C(18)-C(20)	111.4(2)
C(14)-C(18)-H(18)	107.7
C(19)-C(18)-H(18)	107.7
C(20)-C(18)-H(18)	107.7
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	122.93(16)
C(26)-C(21)-N(1)	119.71(16)
C(22)-C(21)-N(1)	117.32(15)
C(23)-C(22)-C(21)	117.42(17)
C(23)-C(22)-C(27)	119.87(17)
C(21)-C(22)-C(27)	122.71(16)
C(24)-C(23)-C(22)	121.04(18)
C(24)-C(23)-H(23)	119.5
C(22)-C(23)-H(23)	119.5
C(23)-C(24)-C(25)	120.02(17)
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(24)-C(25)-C(26)	121.57(18)
C(24)-C(25)-H(25)	119.2
C(26)-C(25)-H(25)	119.2
C(25)-C(26)-C(21)	117.01(17)
C(25)-C(26)-C(30)	120.43(18)
C(21)-C(26)-C(30)	122.48(17)
C(22)-C(27)-C(29)	111.08(18)
C(22)-C(27)-C(28)	110.29(17)
C(29)-C(27)-C(28)	111.43(18)
C(22)-C(27)-H(27)	108.0
C(29)-C(27)-H(27)	108.0
C(28)-C(27)-H(27)	108.0
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5

H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(31)-C(30)-C(26)	109.5(2)
C(31)-C(30)-C(32)	114.3(3)
C(26)-C(30)-C(32)	111.1(2)
C(31)-C(30)-H(30)	107.2
C(26)-C(30)-H(30)	107.2
C(32)-C(30)-H(30)	107.2
C(30)-C(31)-H(31A)	109.5
C(30)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(30)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(30)-C(32)-H(32A)	109.5
C(30)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(30)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
O(2)-S(1)-O(3)	115.44(17)
O(2)-S(1)-O(4)	114.71(17)
O(3)-S(1)-O(4)	113.51(16)
O(2)-S(1)-C(33)	104.4(2)
O(3)-S(1)-C(33)	104.9(2)
O(4)-S(1)-C(33)	101.9(2)
F(3)-C(33)-F(1)	108.0(5)
F(3)-C(33)-F(2)	107.1(5)
F(1)-C(33)-F(2)	105.7(4)
F(3)-C(33)-S(1)	111.7(4)
F(1)-C(33)-S(1)	112.5(4)
F(2)-C(33)-S(1)	111.4(4)
O(3A)-S(1A)-O(4A)	127.2(14)
O(3A)-S(1A)-O(2A)	112.5(13)
O(4A)-S(1A)-O(2A)	103.4(11)
O(3A)-S(1A)-C(33A)	110.8(13)
O(4A)-S(1A)-C(33A)	101.9(11)
O(2A)-S(1A)-C(33A)	96.3(9)
F(3A)-C(33A)-F(1A)	102.8(16)
F(3A)-C(33A)-F(2A)	105.9(17)
F(1A)-C(33A)-F(2A)	111.5(16)
F(3A)-C(33A)-S(1A)	116.6(14)
F(1A)-C(33A)-S(1A)	106.6(13)
F(2A)-C(33A)-S(1A)	113.1(14)

Symmetry transformations used to generate equivalent atoms:

Table A45. Anisotropic displacement parameters (Å^{2}x 10^3) for **89**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	40(1)	23(1)	23(1)	-10(1)	-10(1)	4(1)
O(1)	30(1)	20(1)	38(1)	-14(1)	-10(1)	2(1)
N(1)	27(1)	17(1)	18(1)	-7(1)	-2(1)	-4(1)
C(1)	17(1)	19(1)	21(1)	-7(1)	-2(1)	-5(1)
C(2)	21(1)	18(1)	18(1)	-7(1)	-1(1)	-4(1)
C(3)	24(1)	21(1)	22(1)	-7(1)	-7(1)	-4(1)
C(4)	29(1)	22(1)	26(1)	-12(1)	-7(1)	-6(1)
C(5)	23(1)	18(1)	25(1)	-10(1)	-1(1)	-3(1)
C(6)	21(1)	23(1)	28(1)	-10(1)	-7(1)	-3(1)
C(7)	25(1)	22(1)	25(1)	-11(1)	-5(1)	-6(1)
C(8)	26(1)	22(1)	47(1)	-12(1)	-9(1)	3(1)
C(9)	33(1)	18(1)	17(1)	-5(1)	-5(1)	-4(1)
C(10)	35(1)	20(1)	22(1)	-3(1)	-8(1)	-6(1)
C(11)	47(1)	33(1)	25(1)	-11(1)	-9(1)	-13(1)
C(12)	53(1)	44(1)	26(1)	-20(1)	0(1)	-12(1)
C(13)	37(1)	44(1)	29(1)	-17(1)	3(1)	-11(1)

C(14)	34(1)	26(1)	22(1)	-8(1)	-3(1)	-9(1)
C(15)	34(1)	32(1)	31(1)	-6(1)	-12(1)	-5(1)
C(16)	44(1)	60(2)	64(2)	-24(1)	-7(1)	-21(1)
C(17)	47(1)	39(1)	54(2)	-5(1)	-22(1)	5(1)
C(18)	32(1)	46(1)	28(1)	-14(1)	0(1)	-15(1)
C(19)	39(1)	69(2)	49(1)	-20(1)	-12(1)	-6(1)
C(20)	64(2)	62(2)	45(1)	-19(1)	3(1)	-40(1)
C(21)	30(1)	17(1)	18(1)	-8(1)	-2(1)	-4(1)
C(22)	31(1)	22(1)	25(1)	-10(1)	-7(1)	-4(1)
C(23)	39(1)	24(1)	37(1)	-13(1)	-11(1)	-7(1)
C(24)	44(1)	19(1)	41(1)	-15(1)	-9(1)	0(1)
C(25)	29(1)	28(1)	41(1)	-18(1)	-4(1)	1(1)
C(26)	27(1)	26(1)	30(1)	-16(1)	1(1)	-5(1)
C(27)	32(1)	27(1)	46(1)	-20(1)	-13(1)	-3(1)
C(28)	44(1)	43(1)	52(1)	-16(1)	-24(1)	-2(1)
C(29)	35(1)	55(1)	52(1)	-30(1)	-1(1)	-12(1)
C(30)	27(1)	48(1)	70(2)	-41(1)	14(1)	-15(1)
C(31)	161(4)	195(5)	111(3)	-118(4)	104(3)	-154(4)
C(32)	39(2)	72(2)	227(5)	-82(3)	-58(2)	14(2)
S(1)	27(1)	19(1)	15(1)	-7(1)	-6(1)	-4(1)
C(33)	41(2)	47(2)	41(2)	-22(2)	-15(2)	0(2)
F(1)	39(1)	105(2)	100(2)	-62(2)	-19(1)	-15(1)
F(2)	87(2)	56(2)	62(1)	-3(1)	-34(1)	16(1)
F(3)	66(3)	105(4)	72(3)	-64(3)	-16(2)	24(2)
O(2)	45(1)	46(1)	84(2)	-35(2)	-11(1)	-14(1)
O(3)	48(2)	55(2)	32(1)	-25(1)	-6(1)	-4(1)
O(4)	72(2)	43(1)	24(1)	2(1)	-13(1)	-16(1)
C(33A)	38(10)	57(13)	66(16)	-24(11)	-18(10)	-10(8)
F(1A)	61(7)	107(10)	153(15)	-13(9)	-13(7)	-53(7)
F(2A)	104(9)	86(10)	80(8)	-8(7)	-55(7)	-19(8)
F(3A)	11(5)	49(6)	111(14)	-47(7)	-3(6)	0(4)
O(2A)	49(6)	54(6)	50(7)	6(5)	2(5)	-16(5)
O(3A)	73(10)	74(10)	111(14)	-87(11)	-25(9)	16(7)
O(4A)	66(6)	51(6)	12(4)	2(4)	-14(4)	-2(5)

Table A46. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **89**.

	x	y	z	U(eq)
H(1)	1768(19)	8490(20)	6310(20)	44
H(2)	1540(20)	6738(18)	9105(14)	31
H(3)	1109	5343	6880	26
H(4)	2133	3337	7040	29
H(6)	4471	3547	8719	28
H(7)	3389	5530	8627	27
H(8A)	5618	1907	8210	49
H(8B)	5231	633	8489	49

H(8C)	4640	1454	9249	49
H(11)	832	6681	3646	39
H(12)	2943	6399	2983	47
H(13)	4310	6733	3790	43
H(15)	-620	7236	6055	39
H(16A)	-1999	6637	5461	79
H(16B)	-704	5668	5439	79
H(16C)	-1078	6676	4367	79
H(17A)	-979	8884	4003	75
H(17B)	-768	9248	4941	75
H(17C)	-2016	8822	5038	75
H(18)	3549	7559	6140	41
H(19A)	4697	5579	6098	78
H(19B)	5574	6421	6077	78
H(19C)	5528	6201	5015	78
H(20A)	4901	8453	4068	80
H(20B)	5033	8716	5086	80
H(20C)	3761	9270	4621	80
H(23)	2068	10809	8374	38
H(24)	-15	11780	8408	41
H(25)	-1475	10749	8444	39
H(27)	3343	7709	8361	39
H(28A)	3519	9245	9465	66
H(28B)	4510	8018	9405	66
H(28C)	3121	7954	10017	66
H(29A)	3781	9289	6781	66
H(29B)	4923	8785	7415	66
H(29C)	3985	10051	7439	66
H(30)	-830	7708	8320	53
H(31A)	-1249	7490	10095	201
H(31B)	-2505	7576	9722	201
H(31C)	-2281	8733	9906	201
H(32A)	-2762	8743	7778	152
H(32B)	-1722	9483	7035	152
H(32C)	-2659	9953	7950	152

Table A47. Torsion angles [°] for **89**.

C(21)-N(1)-C(1)-C(2)	170.98(15)
C(21)-N(1)-C(1)-P(1)	-9.9(2)
C(9)-P(1)-C(1)-N(1)	163.75(13)
C(9)-P(1)-C(1)-C(2)	-17.18(16)
N(1)-C(1)-C(2)-C(7)	-39.9(2)
P(1)-C(1)-C(2)-C(7)	141.10(14)
N(1)-C(1)-C(2)-C(3)	143.44(17)
P(1)-C(1)-C(2)-C(3)	-35.6(2)
C(7)-C(2)-C(3)-C(4)	0.7(3)
C(1)-C(2)-C(3)-C(4)	177.44(16)
C(2)-C(3)-C(4)-C(5)	-1.4(3)
C(8)-O(1)-C(5)-C(6)	2.4(3)
C(8)-O(1)-C(5)-C(4)	-177.14(16)
C(3)-C(4)-C(5)-O(1)	-179.78(16)
C(3)-C(4)-C(5)-C(6)	0.6(3)
O(1)-C(5)-C(6)-C(7)	-178.63(16)
C(4)-C(5)-C(6)-C(7)	0.9(3)
C(5)-C(6)-C(7)-C(2)	-1.7(3)
C(3)-C(2)-C(7)-C(6)	0.8(3)
C(1)-C(2)-C(7)-C(6)	-175.98(16)
C(1)-P(1)-C(9)-C(14)	-66.94(17)
C(1)-P(1)-C(9)-C(10)	117.97(13)

C(14)-C(9)-C(10)-C(11)	-1.4(3)	C(24)-C(25)-C(26)-C(21)	-0.6(3)
P(1)-C(9)-C(10)-C(11)	173.82(14)	C(24)-C(25)-C(26)-C(30)	176.3(2)
C(14)-C(9)-C(10)-C(15)	-179.77(17)	C(22)-C(21)-C(26)-C(25)	1.0(3)
P(1)-C(9)-C(10)-C(15)	-4.5(2)	N(1)-C(21)-C(26)-C(25)	178.53(17)
C(9)-C(10)-C(11)-C(12)	0.8(3)	C(22)-C(21)-C(26)-C(30)	-175.83(19)
C(15)-C(10)-C(11)-C(12)	179.19(19)	N(1)-C(21)-C(26)-C(30)	1.7(3)
C(10)-C(11)-C(12)-C(13)	-0.1(3)	C(23)-C(22)-C(27)-C(29)	-59.6(2)
C(11)-C(12)-C(13)-C(14)	0.0(3)	C(21)-C(22)-C(27)-C(29)	121.3(2)
C(12)-C(13)-C(14)-C(9)	-0.6(3)	C(23)-C(22)-C(27)-C(28)	64.5(2)
C(12)-C(13)-C(14)-C(18)	179.9(2)	C(21)-C(22)-C(27)-C(28)	-114.6(2)
C(10)-C(9)-C(14)-C(13)	1.3(3)	C(25)-C(26)-C(30)-C(31)	-79.3(4)
P(1)-C(9)-C(14)-C(13)	-173.46(15)	C(21)-C(26)-C(30)-C(31)	97.4(3)
C(10)-C(9)-C(14)-C(18)	-179.17(17)	C(25)-C(26)-C(30)-C(32)	47.8(3)
P(1)-C(9)-C(14)-C(18)	6.0(3)	C(21)-C(26)-C(30)-C(32)	-135.5(2)
C(11)-C(10)-C(15)-C(16)	33.8(3)	O(2)-S(1)-C(33)-F(3)	60.2(5)
C(9)-C(10)-C(15)-C(16)	-147.9(2)	O(3)-S(1)-C(33)-F(3)	-178.0(5)
C(11)-C(10)-C(15)-C(17)	-90.6(2)	O(4)-S(1)-C(33)-F(3)	-59.5(5)
C(9)-C(10)-C(15)-C(17)	87.7(2)	O(2)-S(1)-C(33)-F(1)	-178.1(4)
C(13)-C(14)-C(18)-C(19)	-53.2(3)	O(3)-S(1)-C(33)-F(1)	-56.3(5)
C(9)-C(14)-C(18)-C(19)	127.3(2)	O(4)-S(1)-C(33)-F(1)	62.3(4)
C(13)-C(14)-C(18)-C(20)	71.3(2)	O(2)-S(1)-C(33)-F(2)	-59.6(4)
C(9)-C(14)-C(18)-C(20)	-108.2(2)	O(3)-S(1)-C(33)-F(2)	62.2(4)
C(1)-N(1)-C(21)-C(26)	79.2(2)	O(4)-S(1)-C(33)-F(2)	-179.3(3)
C(1)-N(1)-C(21)-C(22)	-103.1(2)	O(3A)-S(1A)-C(33A)-F(3A)	175.8(17)
C(26)-C(21)-C(22)-C(23)	-0.8(3)	O(4A)-S(1A)-C(33A)-F(3A)	-46.4(19)
N(1)-C(21)-C(22)-C(23)	-178.45(16)	O(2A)-S(1A)-C(33A)-F(3A)	58.8(17)
C(26)-C(21)-C(22)-C(27)	178.31(18)	O(3A)-S(1A)-C(33A)-F(1A)	-70.2(19)
N(1)-C(21)-C(22)-C(27)	0.7(3)	O(4A)-S(1A)-C(33A)-F(1A)	67.7(17)
C(21)-C(22)-C(23)-C(24)	0.3(3)	O(2A)-S(1A)-C(33A)-F(1A)	172.8(14)
C(27)-C(22)-C(23)-C(24)	-178.86(19)	O(3A)-S(1A)-C(33A)-F(2A)	52.7(19)
C(22)-C(23)-C(24)-C(25)	0.0(3)	O(4A)-S(1A)-C(33A)-F(2A)	-169.5(15)
C(23)-C(24)-C(25)-C(26)	0.1(3)	O(2A)-S(1A)-C(33A)-F(2A)	-64.4(15)

Symmetry transformations used to generate equivalent atoms:

Table A48. Hydrogen bonds for **89** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(2)...O(4)#1	0.950(15)	1.780(17)	2.689(3)	159(2)
N(1)-H(2)...O(4A)#1	0.950(15)	1.754(18)	2.689(8)	168(2)

Symmetry transformations used to generate equivalent atoms: #1 x,y,z+1

Table A49. Crystal data and structure refinement for **95**.

Identification code	**95**	
Empirical formula	C102 H142 Li6 N4 O12 P4	
Formula weight	1781.71	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.434(2) Å	α= 99.961(3)°.
	b = 15.249(3) Å	β= 102.179(3)°.
	c = 16.906(5) Å	γ = 113.131(2)°.
Volume	2984.4(12) Å^3	
Z	1	
Density (calculated)	0.991 Mg/m^3	
Absorption coefficient	0.113 mm^{-1}	
F(000)	956	
Crystal size	0.461 x 0.301 x 0.172 mm^3	
Theta range for data collection	1.719 to 27.624°.	
Index ranges	-17<=h<=17, -19<=k<=19, -22<=l<=21	
Reflections collected	43804	
Independent reflections	13711 [R(int) = 0.0439]	
Completeness to theta = 25.250°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13711 / 1 / 597	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.1413	
R indices (all data)	R1 = 0.0952, wR2 = 0.1614	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.650 and -0.572 e.Å^{-3}	

Table A50. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **95**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	107(1)	6896(1)	3877(1)	32(1)
P(2)	1405(1)	6791(1)	7448(1)	34(1)
N(1)	2606(1)	8151(1)	6773(1)	37(1)
N(2)	-2054(1)	6272(1)	2966(1)	34(1)
O(1)	631(1)	7371(1)	4807(1)	38(1)
O(2)	-296(1)	5791(1)	3588(1)	33(1)
O(3)	629(1)	6403(1)	6552(1)	35(1)
O(4)	1908(1)	6146(1)	7743(1)	41(1)
C(1)	-3048(2)	6363(2)	2552(1)	39(1)

C(2)	-3227(2)	6338(2)	1704(1)	50(1)
C(3)	-4212(2)	6381(2)	1281(2)	65(1)
C(4)	-4981(2)	6421(2)	1689(2)	70(1)
C(5)	-4803(2)	6422(2)	2525(2)	61(1)
C(6)	-3825(2)	6392(2)	2980(2)	45(1)
C(7)	-2353(2)	6302(2)	1267(1)	56(1)
C(8)	-1447(3)	7342(2)	1377(2)	72(1)
C(9)	-2873(3)	5706(2)	340(2)	84(1)
C(10)	-3630(2)	6397(2)	3896(2)	51(1)
C(11)	-3260(3)	7439(2)	4464(2)	73(1)
C(12)	-4662(3)	5640(2)	4049(2)	88(1)
C(13)	744(2)	7165(2)	8194(1)	43(1)
C(14)	1330(3)	7428(2)	9063(2)	58(1)
C(15)	770(3)	7599(3)	9649(2)	88(1)
C(16)	-294(4)	7532(3)	9383(2)	107(1)
C(17)	-844(3)	7311(3)	8547(2)	88(1)
C(18)	-358(2)	7136(2)	7931(2)	57(1)
C(19)	-1021(2)	6957(2)	7020(2)	63(1)
C(20)	-540(3)	7870(2)	6741(2)	86(1)
C(21)	-2306(3)	6556(3)	6835(3)	114(1)
C(22)	2522(2)	7545(2)	9415(1)	61(1)
C(23)	3303(3)	8570(3)	10065(2)	108(1)
C(24)	2523(3)	6709(3)	9805(2)	86(1)
C(25)	974(2)	7567(1)	3282(1)	36(1)
C(26)	1339(2)	8611(2)	3478(1)	42(1)
C(27)	1902(2)	9135(2)	2980(2)	60(1)
C(28)	2112(2)	8665(2)	2318(2)	70(1)
C(29)	1778(2)	7664(2)	2130(2)	60(1)
C(30)	1206(2)	7086(2)	2591(1)	43(1)
C(31)	1202(2)	9226(2)	4224(1)	43(1)
C(32)	914(2)	5986(2)	2340(2)	56(1)
C(33)	3498(2)	9073(2)	6787(1)	40(1)
C(34)	3577(2)	9984(2)	7204(1)	45(1)
C(35)	4421(2)	10846(2)	7149(2)	58(1)
C(36)	5146(2)	10810(2)	6704(2)	68(1)
C(37)	5049(2)	9909(2)	6286(2)	66(1)
C(38)	4227(2)	9013(2)	6316(2)	50(1)
C(39)	2778(2)	10094(2)	7685(2)	54(1)
C(40)	4137(2)	8026(2)	5864(2)	61(1)
C(41)	3913(3)	7874(3)	4929(2)	96(1)
C(42)	5175(3)	7882(3)	6224(2)	104(1)
C(43)	2566(2)	7948(2)	7468(1)	37(1)
C(44)	-1181(2)	7039(1)	3459(1)	34(1)
C(45)	2337(2)	9783(2)	4927(2)	58(1)
C(46)	754(3)	9950(2)	3980(2)	72(1)
C(47)	3389(3)	10611(2)	8620(2)	85(1)
C(48)	589(4)	5525(2)	1403(2)	119(2)
C(49)	2155(3)	10645(3)	7313(2)	88(1)
C(50)	1810(4)	5793(3)	2832(3)	149(2)
C(51)	2116(2)	5429(2)	5396(1)	42(1)
O(6)	1212(1)	5533(1)	5165(1)	40(1)

O(5)	2575(1)	5421(1)	6104(1)	45(1)
Li(1)	-73(3)	4916(2)	4162(2)	39(1)
Li(2)	1920(3)	5083(2)	6989(2)	38(1)
Li(3)	1216(3)	6994(3)	5716(2)	43(1)

Table A51. Bond lengths [Å] and angles [°] for **95**.

P(1)-O(1)	1.4940(14)
P(1)-O(2)	1.5023(14)
P(1)-C(25)	1.825(2)
P(1)-C(44)	1.837(2)
P(1)-Li(2)#1	3.000(3)
P(1)-Li(1)	3.064(3)
P(1)-Li(3)	3.101(4)
P(2)-O(4)	1.4904(14)
P(2)-O(3)	1.5080(14)
P(2)-C(13)	1.823(2)
P(2)-C(43)	1.829(2)
P(2)-Li(3)	2.967(3)
P(2)-Li(2)	2.968(3)
P(2)-Li(1)#1	3.037(3)
N(1)-C(43)	1.272(2)
N(1)-C(33)	1.438(3)
N(1)-Li(3)	2.170(4)
N(2)-C(44)	1.270(2)
N(2)-C(1)	1.441(3)
N(2)-Li(2)#1	2.155(4)
O(1)-Li(3)	1.860(4)
O(2)-Li(1)	1.860(4)
O(2)-Li(2)#1	1.964(4)
O(3)-Li(1)#1	1.912(4)
O(3)-Li(3)	1.945(4)
O(4)-Li(2)	1.889(4)
C(1)-C(2)	1.395(3)
C(1)-C(6)	1.400(3)
C(2)-C(3)	1.397(3)
C(2)-C(7)	1.526(3)
C(3)-C(4)	1.371(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.397(3)
C(5)-H(5)	0.9500
C(6)-C(10)	1.514(3)
C(7)-C(9)	1.522(3)
C(7)-C(8)	1.522(4)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.523(3)
C(10)-C(11)	1.530(3)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.414(3)
C(13)-C(18)	1.434(3)
C(14)-C(15)	1.412(4)
C(14)-C(22)	1.512(4)
C(15)-C(16)	1.361(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.363(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.383(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.525(4)
C(19)-C(20)	1.492(4)
C(19)-C(21)	1.527(4)
C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(24)	1.534(4)
C(22)-C(23)	1.543(4)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800

C(25)-C(26)	1.421(3)
C(25)-C(30)	1.427(3)
C(26)-C(27)	1.394(3)
C(26)-C(31)	1.527(3)
C(27)-C(28)	1.365(4)
C(27)-H(27)	0.9500
C(28)-C(29)	1.367(4)
C(28)-H(28)	0.9500
C(29)-C(30)	1.390(3)
C(29)-H(29)	0.9500
C(30)-C(32)	1.522(3)
C(31)-C(46)	1.524(3)
C(31)-C(45)	1.526(3)
C(31)-H(31)	1.0000
C(32)-C(50)	1.472(4)
C(32)-C(48)	1.508(4)
C(32)-H(32)	1.0000
C(33)-C(34)	1.396(3)
C(33)-C(38)	1.406(3)
C(34)-C(35)	1.391(3)
C(34)-C(39)	1.519(3)
C(35)-C(36)	1.362(4)
C(35)-H(35)	0.9500
C(36)-C(37)	1.375(4)
C(36)-H(36)	0.9500
C(37)-C(38)	1.397(3)
C(37)-H(37)	0.9500
C(38)-C(40)	1.511(3)
C(39)-C(47)	1.518(4)
C(39)-C(49)	1.522(4)
C(39)-H(39)	1.0000
C(40)-C(41)	1.504(4)
C(40)-C(42)	1.513(4)
C(40)-H(40)	1.0000
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43)	0.9500
C(44)-H(44)	0.9500
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-O(5)	1.230(2)
C(51)-O(6)	1.275(2)
C(51)-H(51)	1.119(14)
O(6)-Li(1)	1.917(4)
O(6)-Li(1)#1	2.069(4)
O(6)-Li(3)	2.258(4)
O(5)-Li(2)	1.936(4)
Li(1)-O(3)#1	1.912(4)
Li(1)-O(6)#1	2.069(4)
Li(1)-Li(1)#1	2.756(6)
Li(1)-Li(3)#1	2.776(5)
Li(1)-Li(2)#1	2.814(5)
Li(1)-P(2)#1	3.037(3)
Li(1)-Li(3)	3.291(5)
Li(2)-O(2)#1	1.964(4)
Li(2)-N(2)#1	2.155(4)
Li(2)-Li(1)#1	2.814(5)
Li(2)-P(1)#1	3.000(3)
Li(3)-Li(1)#1	2.776(5)
O(1)-P(1)-O(2)	115.86(8)
O(1)-P(1)-C(25)	112.13(9)
O(2)-P(1)-C(25)	113.05(8)
O(1)-P(1)-C(44)	112.06(8)
O(2)-P(1)-C(44)	103.20(8)
C(25)-P(1)-C(44)	98.85(9)
O(1)-P(1)-Li(2)#1	126.57(9)
O(2)-P(1)-Li(2)#1	34.82(8)
C(25)-P(1)-Li(2)#1	120.67(9)
C(44)-P(1)-Li(2)#1	68.53(9)
O(1)-P(1)-Li(1)	89.05(8)
O(2)-P(1)-Li(1)	27.20(8)
C(25)-P(1)-Li(1)	124.39(9)
C(44)-P(1)-Li(1)	120.53(9)
Li(2)#1-P(1)-Li(1)	55.28(9)
O(1)-P(1)-Li(3)	25.12(9)
O(2)-P(1)-Li(3)	91.66(9)
C(25)-P(1)-Li(3)	120.60(9)
C(44)-P(1)-Li(3)	128.04(9)
Li(2)#1-P(1)-Li(3)	110.31(9)
Li(1)-P(1)-Li(3)	64.51(9)
O(4)-P(2)-O(3)	116.59(8)
O(4)-P(2)-C(13)	110.39(9)

O(3)-P(2)-C(13)	111.84(10)
O(4)-P(2)-C(43)	108.11(9)
O(3)-P(2)-C(43)	103.92(9)
C(13)-P(2)-C(43)	105.06(10)
O(4)-P(2)-Li(3)	119.81(9)
O(3)-P(2)-Li(3)	35.41(9)
C(13)-P(2)-Li(3)	128.74(10)
C(43)-P(2)-Li(3)	69.54(9)
O(4)-P(2)-Li(2)	32.51(8)
O(3)-P(2)-Li(2)	85.16(8)
C(13)-P(2)-Li(2)	135.00(10)
C(43)-P(2)-Li(2)	110.79(9)
Li(3)-P(2)-Li(2)	89.64(10)
O(4)-P(2)-Li(1)#1	85.84(9)
O(3)-P(2)-Li(1)#1	31.14(8)
C(13)-P(2)-Li(1)#1	123.20(10)
C(43)-P(2)-Li(1)#1	121.30(9)
Li(3)-P(2)-Li(1)#1	55.06(9)
Li(2)-P(2)-Li(1)#1	55.87(9)
C(43)-N(1)-C(33)	118.68(17)
C(43)-N(1)-Li(3)	111.55(17)
C(33)-N(1)-Li(3)	129.76(15)
C(44)-N(2)-C(1)	119.73(17)
C(44)-N(2)-Li(2)#1	112.38(16)
C(1)-N(2)-Li(2)#1	127.19(15)
P(1)-O(1)-Li(3)	134.95(14)
P(1)-O(2)-Li(1)	131.13(13)
P(1)-O(2)-Li(2)#1	119.28(12)
Li(1)-O(2)-Li(2)#1	94.72(15)
P(2)-O(3)-Li(1)#1	124.80(13)
P(2)-O(3)-Li(3)	117.90(14)
Li(1)#1-O(3)-Li(3)	92.04(15)
P(2)-O(4)-Li(2)	122.40(13)
C(2)-C(1)-C(6)	123.0(2)
C(2)-C(1)-N(2)	116.73(19)
C(6)-C(1)-N(2)	120.12(19)
C(1)-C(2)-C(3)	117.6(2)
C(1)-C(2)-C(7)	120.8(2)
C(3)-C(2)-C(7)	121.6(2)
C(4)-C(3)-C(2)	120.6(3)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	121.1(2)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	120.6(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	117.1(2)
C(5)-C(6)-C(10)	120.5(2)
C(1)-C(6)-C(10)	122.33(19)
C(9)-C(7)-C(8)	110.8(2)
C(9)-C(7)-C(2)	113.8(2)
C(8)-C(7)-C(2)	111.4(2)
C(9)-C(7)-H(7)	106.8
C(8)-C(7)-H(7)	106.8
C(2)-C(7)-H(7)	106.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(12)	112.9(2)
C(6)-C(10)-C(11)	110.7(2)
C(12)-C(10)-C(11)	110.4(2)
C(6)-C(10)-H(10)	107.5
C(12)-C(10)-H(10)	107.5
C(11)-C(10)-H(10)	107.5
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(14)-C(13)-C(18)	120.0(2)
C(14)-C(13)-P(2)	117.22(18)
C(18)-C(13)-P(2)	122.65(17)
C(15)-C(14)-C(13)	118.1(3)
C(15)-C(14)-C(22)	117.2(2)
C(13)-C(14)-C(22)	124.7(2)
C(16)-C(15)-C(14)	120.8(3)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	121.2(3)
C(15)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(16)-C(17)-C(18)	121.8(3)
C(16)-C(17)-H(17)	119.1
C(18)-C(17)-H(17)	119.1

C(17)-C(18)-C(13)	118.0(3)
C(17)-C(18)-C(19)	117.4(3)
C(13)-C(18)-C(19)	124.6(2)
C(20)-C(19)-C(18)	110.5(2)
C(20)-C(19)-C(21)	111.2(3)
C(18)-C(19)-C(21)	115.1(2)
C(20)-C(19)-H(19)	106.5
C(18)-C(19)-H(19)	106.5
C(21)-C(19)-H(19)	106.5
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(14)-C(22)-C(24)	111.7(2)
C(14)-C(22)-C(23)	111.6(2)
C(24)-C(22)-C(23)	110.4(2)
C(14)-C(22)-H(22)	107.6
C(24)-C(22)-H(22)	107.6
C(23)-C(22)-H(22)	107.6
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-C(30)	119.27(18)
C(26)-C(25)-P(1)	117.12(15)
C(30)-C(25)-P(1)	123.35(15)
C(27)-C(26)-C(25)	118.9(2)
C(27)-C(26)-C(31)	116.3(2)
C(25)-C(26)-C(31)	124.72(18)
C(28)-C(27)-C(26)	121.3(2)
C(28)-C(27)-H(27)	119.4
C(26)-C(27)-H(27)	119.4
C(27)-C(28)-C(29)	120.4(2)
C(27)-C(28)-H(28)	119.8
C(29)-C(28)-H(28)	119.8
C(28)-C(29)-C(30)	122.0(2)
C(28)-C(29)-H(29)	119.0
C(30)-C(29)-H(29)	119.0
C(29)-C(30)-C(25)	118.2(2)
C(29)-C(30)-C(32)	117.1(2)
C(25)-C(30)-C(32)	124.68(19)
C(46)-C(31)-C(45)	110.5(2)
C(46)-C(31)-C(26)	112.64(19)
C(45)-C(31)-C(26)	109.46(19)
C(46)-C(31)-H(31)	108.0
C(45)-C(31)-H(31)	108.0
C(26)-C(31)-H(31)	108.0
C(50)-C(32)-C(48)	112.7(3)
C(50)-C(32)-C(30)	111.3(2)
C(48)-C(32)-C(30)	114.3(2)
C(50)-C(32)-H(32)	105.9
C(48)-C(32)-H(32)	105.9
C(30)-C(32)-H(32)	105.9
C(34)-C(33)-C(38)	122.0(2)
C(34)-C(33)-N(1)	120.81(19)
C(38)-C(33)-N(1)	117.06(19)
C(35)-C(34)-C(33)	117.8(2)
C(35)-C(34)-C(39)	117.9(2)
C(33)-C(34)-C(39)	124.3(2)
C(36)-C(35)-C(34)	121.5(2)
C(36)-C(35)-H(35)	119.2
C(34)-C(35)-H(35)	119.2
C(35)-C(36)-C(37)	120.2(2)
C(35)-C(36)-H(36)	119.9
C(37)-C(36)-H(36)	119.9
C(36)-C(37)-C(38)	121.4(2)
C(36)-C(37)-H(37)	119.3
C(38)-C(37)-H(37)	119.3
C(37)-C(38)-C(33)	117.1(2)
C(37)-C(38)-C(40)	121.1(2)
C(33)-C(38)-C(40)	121.8(2)
C(47)-C(39)-C(34)	112.3(2)
C(47)-C(39)-C(49)	109.9(2)
C(34)-C(39)-C(49)	111.2(2)
C(47)-C(39)-H(39)	107.7
C(34)-C(39)-H(39)	107.7
C(49)-C(39)-H(39)	107.7
C(41)-C(40)-C(38)	112.5(2)
C(41)-C(40)-C(42)	109.5(2)
C(38)-C(40)-C(42)	112.6(2)
C(41)-C(40)-H(40)	107.3
C(38)-C(40)-H(40)	107.3
C(42)-C(40)-H(40)	107.3
C(40)-C(41)-H(41A)	109.5
C(40)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5

C(40)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
N(1)-C(43)-P(2)	118.39(15)
N(1)-C(43)-H(43)	120.8
P(2)-C(43)-H(43)	120.8
N(2)-C(44)-P(1)	117.52(15)
N(2)-C(44)-H(44)	121.2
P(1)-C(44)-H(44)	121.2
C(31)-C(45)-H(45A)	109.5
C(31)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(31)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(31)-C(46)-H(46A)	109.5
C(31)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(31)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(39)-C(47)-H(47A)	109.5
C(39)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(39)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(32)-C(48)-H(48A)	109.5
C(32)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(32)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(39)-C(49)-H(49A)	109.5
C(39)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(39)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(32)-C(50)-H(50A)	109.5
C(32)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(32)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
O(5)-C(51)-O(6)	126.8(2)
O(5)-C(51)-H(51)	117.0(9)
O(6)-C(51)-H(51)	116.0(9)
C(51)-O(6)-Li(1)	133.24(17)
C(51)-O(6)-Li(1)#1	116.16(16)
Li(1)-O(6)-Li(1)#1	87.41(15)
C(51)-O(6)-Li(3)	119.27(16)
Li(1)-O(6)-Li(3)	103.71(15)
Li(1)#1-O(6)-Li(3)	79.67(14)
C(51)-O(5)-Li(2)	129.48(18)
O(2)-Li(1)-O(3)#1	113.56(18)
O(2)-Li(1)-O(6)	114.43(18)
O(3)#1-Li(1)-O(6)	124.85(19)
O(2)-Li(1)-O(6)#1	112.26(18)
O(3)#1-Li(1)-O(6)#1	93.22(15)
O(6)-Li(1)-O(6)#1	92.59(15)
O(2)-Li(1)-Li(1)#1	124.9(2)
O(3)#1-Li(1)-Li(1)#1	116.1(2)
O(6)-Li(1)-Li(1)#1	48.58(11)
O(6)#1-Li(1)-Li(1)#1	44.01(11)
O(2)-Li(1)-Li(3)#1	140.87(19)
O(3)#1-Li(1)-Li(3)#1	44.44(11)
O(6)-Li(1)-Li(3)#1	103.09(15)
O(6)#1-Li(1)-Li(3)#1	53.17(11)
Li(1)#1-Li(1)-Li(3)#1	72.99(15)
O(2)-Li(1)-Li(2)#1	44.08(11)
O(3)#1-Li(1)-Li(2)#1	83.34(14)
O(6)-Li(1)-Li(2)#1	151.78(18)
O(6)#1-Li(1)-Li(2)#1	83.57(14)
Li(1)#1-Li(1)-Li(2)#1	121.9(2)
Li(3)#1-Li(1)-Li(2)#1	96.89(15)
O(2)-Li(1)-P(2)#1	90.07(13)
O(3)#1-Li(1)-P(2)#1	24.07(6)
O(6)-Li(1)-P(2)#1	147.13(17)
O(6)#1-Li(1)-P(2)#1	98.09(13)
Li(1)#1-Li(1)-P(2)#1	133.61(19)
Li(3)#1-Li(1)-P(2)#1	61.18(10)
Li(2)#1-Li(1)-P(2)#1	60.82(10)
O(2)-Li(1)-P(1)	21.67(6)
O(3)#1-Li(1)-P(1)	135.01(15)
O(6)-Li(1)-P(1)	94.03(13)
O(6)#1-Li(1)-P(1)	108.08(14)
Li(1)#1-Li(1)-P(1)	106.37(17)
Li(3)#1-Li(1)-P(1)	154.57(16)
Li(2)#1-Li(1)-P(1)	61.20(9)
P(2)#1-Li(1)-P(1)	111.73(10)
O(2)-Li(1)-Li(3)	79.91(13)
O(3)#1-Li(1)-Li(3)	166.04(17)
O(6)-Li(1)-Li(3)	41.82(10)
O(6)#1-Li(1)-Li(3)	84.45(13)
Li(1)#1-Li(1)-Li(3)	53.77(13)

Li(3)#1-Li(1)-Li(3)	126.77(13)
Li(2)#1-Li(1)-Li(3)	109.98(14)
P(2)#1-Li(1)-Li(3)	169.86(14)
P(1)-Li(1)-Li(3)	58.28(9)
O(4)-Li(2)-O(5)	115.62(18)
O(4)-Li(2)-O(2)#1	103.02(17)
O(5)-Li(2)-O(2)#1	105.41(17)
O(4)-Li(2)-N(2)#1	137.40(19)
O(5)-Li(2)-N(2)#1	101.62(16)
O(2)#1-Li(2)-N(2)#1	85.23(14)
O(4)-Li(2)-Li(1)#1	86.24(14)
O(5)-Li(2)-Li(1)#1	79.55(14)
O(2)#1-Li(2)-Li(1)#1	41.20(10)
N(2)#1-Li(2)-Li(1)#1	121.78(16)
O(4)-Li(2)-P(2)	25.09(6)
O(5)-Li(2)-P(2)	99.48(13)
O(2)#1-Li(2)-P(2)	90.15(12)
N(2)#1-Li(2)-P(2)	158.87(16)
Li(1)#1-Li(2)-P(2)	63.31(10)
O(4)-Li(2)-P(1)#1	124.33(16)
O(5)-Li(2)-P(1)#1	103.96(14)
O(2)#1-Li(2)-P(1)#1	25.90(6)
N(2)#1-Li(2)-P(1)#1	59.81(9)
Li(1)#1-Li(2)-P(1)#1	63.53(10)
P(2)-Li(2)-P(1)#1	115.61(11)
O(1)-Li(3)-O(3)	135.2(2)
O(1)-Li(3)-N(1)	117.81(19)
O(3)-Li(3)-N(1)	86.47(14)
O(1)-Li(3)-O(6)	106.45(17)
O(3)-Li(3)-O(6)	86.74(14)
N(1)-Li(3)-O(6)	122.43(17)
O(1)-Li(3)-Li(1)#1	120.14(18)
O(3)-Li(3)-Li(1)#1	43.52(11)
N(1)-Li(3)-Li(1)#1	121.00(16)
O(6)-Li(3)-Li(1)#1	47.16(10)
O(1)-Li(3)-P(2)	151.18(18)
O(3)-Li(3)-P(2)	26.70(7)
N(1)-Li(3)-P(2)	60.52(9)
O(6)-Li(3)-P(2)	95.87(12)
Li(1)#1-Li(3)-P(2)	63.76(10)
O(1)-Li(3)-P(1)	19.94(7)
O(3)-Li(3)-P(1)	133.84(16)
N(1)-Li(3)-P(1)	134.05(15)
O(6)-Li(3)-P(1)	86.63(11)
Li(1)#1-Li(3)-P(1)	104.91(13)
P(2)-Li(3)-P(1)	159.32(13)
O(1)-Li(3)-Li(1)	76.71(13)
O(3)-Li(3)-Li(1)	95.74(15)
N(1)-Li(3)-Li(1)	156.09(18)
O(6)-Li(3)-Li(1)	34.47(9)
Li(1)#1-Li(3)-Li(1)	53.23(13)
P(2)-Li(3)-Li(1)	116.59(13)
P(1)-Li(3)-Li(1)	57.21(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table A52. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **95**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	33(1)	33(1)	29(1)	12(1)	10(1)	12(1)
P(2)	41(1)	35(1)	26(1)	8(1)	13(1)	16(1)
N(1)	33(1)	42(1)	34(1)	11(1)	12(1)	14(1)
N(2)	36(1)	36(1)	33(1)	13(1)	11(1)	16(1)
O(1)	45(1)	39(1)	28(1)	12(1)	10(1)	15(1)
O(2)	35(1)	33(1)	33(1)	13(1)	12(1)	14(1)
O(3)	39(1)	35(1)	28(1)	9(1)	10(1)	13(1)
O(4)	50(1)	40(1)	31(1)	9(1)	10(1)	23(1)
C(1)	34(1)	34(1)	44(1)	10(1)	5(1)	14(1)
C(2)	53(1)	44(1)	47(1)	11(1)	3(1)	22(1)
C(3)	64(2)	66(2)	56(2)	16(1)	-4(1)	31(1)
C(4)	49(2)	71(2)	80(2)	18(2)	-7(2)	32(1)
C(5)	41(1)	57(2)	84(2)	18(1)	14(1)	24(1)
C(6)	38(1)	36(1)	59(1)	14(1)	10(1)	16(1)

C(7)	72(2)	62(2)	37(1)	18(1)	10(1)	34(1)
C(8)	84(2)	83(2)	57(2)	29(2)	31(2)	36(2)
C(9)	112(3)	90(2)	44(2)	14(2)	13(2)	49(2)
C(10)	48(1)	54(1)	64(2)	23(1)	28(1)	25(1)
C(11)	78(2)	68(2)	71(2)	11(2)	27(2)	33(2)
C(12)	75(2)	84(2)	106(3)	44(2)	48(2)	18(2)
C(13)	61(2)	42(1)	38(1)	18(1)	27(1)	26(1)
C(14)	97(2)	56(2)	39(1)	18(1)	32(1)	45(2)
C(15)	140(3)	126(3)	43(2)	35(2)	47(2)	90(3)
C(16)	153(4)	172(4)	76(2)	58(2)	76(3)	122(3)
C(17)	106(3)	132(3)	84(2)	55(2)	64(2)	84(2)
C(18)	71(2)	59(2)	66(2)	30(1)	42(1)	39(1)
C(19)	56(2)	78(2)	71(2)	28(2)	26(1)	39(2)
C(20)	89(2)	88(2)	83(2)	39(2)	17(2)	40(2)
C(21)	65(2)	136(3)	142(4)	44(3)	33(2)	45(2)
C(22)	89(2)	60(2)	27(1)	8(1)	10(1)	32(2)
C(23)	142(3)	88(2)	53(2)	-12(2)	-7(2)	41(2)
C(24)	130(3)	110(3)	57(2)	48(2)	40(2)	76(2)
C(25)	32(1)	38(1)	33(1)	14(1)	8(1)	10(1)
C(26)	39(1)	41(1)	35(1)	14(1)	7(1)	9(1)
C(27)	69(2)	40(1)	53(2)	18(1)	21(1)	4(1)
C(28)	82(2)	56(2)	53(2)	20(1)	37(2)	4(1)
C(29)	65(2)	60(2)	44(1)	15(1)	30(1)	12(1)
C(30)	42(1)	49(1)	36(1)	14(1)	16(1)	14(1)
C(31)	45(1)	36(1)	44(1)	14(1)	12(1)	14(1)
C(32)	76(2)	54(2)	51(2)	16(1)	39(1)	31(1)
C(33)	30(1)	44(1)	40(1)	16(1)	8(1)	11(1)
C(34)	37(1)	46(1)	42(1)	10(1)	4(1)	15(1)
C(35)	52(2)	44(1)	66(2)	14(1)	9(1)	14(1)
C(36)	53(2)	50(2)	86(2)	24(2)	22(2)	7(1)
C(37)	50(2)	62(2)	84(2)	27(2)	36(1)	15(1)
C(38)	38(1)	49(1)	58(2)	18(1)	17(1)	13(1)
C(39)	53(1)	47(1)	55(2)	4(1)	13(1)	21(1)
C(40)	57(2)	54(2)	76(2)	16(1)	39(1)	21(1)
C(41)	113(3)	103(3)	73(2)	5(2)	15(2)	65(2)
C(42)	132(3)	107(3)	88(3)	20(2)	15(2)	83(3)
C(43)	37(1)	38(1)	32(1)	6(1)	10(1)	15(1)
C(44)	38(1)	32(1)	35(1)	11(1)	15(1)	15(1)
C(45)	60(2)	52(2)	46(1)	4(1)	3(1)	20(1)
C(46)	76(2)	68(2)	78(2)	28(2)	13(2)	42(2)
C(47)	102(3)	84(2)	57(2)	7(2)	20(2)	39(2)
C(48)	186(4)	59(2)	75(2)	4(2)	48(3)	22(2)
C(49)	88(2)	116(3)	87(2)	28(2)	30(2)	71(2)
C(50)	125(3)	86(3)	209(5)	5(3)	-14(3)	70(3)
C(51)	45(1)	46(1)	39(1)	15(1)	19(1)	22(1)
O(6)	38(1)	46(1)	34(1)	13(1)	11(1)	18(1)
O(5)	40(1)	54(1)	47(1)	23(1)	14(1)	22(1)
Li(1)	45(2)	36(2)	31(2)	12(1)	11(2)	15(2)
Li(2)	39(2)	34(2)	39(2)	10(2)	9(2)	15(2)
Li(3)	41(2)	48(2)	36(2)	16(2)	13(2)	13(2)

Table A53. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **95**.

	x	y	z	U(eq)
H(3)	-4351	6382	707	78
H(4)	-5647	6448	1392	84
H(5)	-5352	6443	2793	73
H(7)	-1957	5958	1559	67
H(8A)	-841	7294	1164	109
H(8B)	-1128	7713	1977	109
H(8C)	-1790	7688	1061	109
H(9A)	-3471	5049	282	125
H(9B)	-2282	5630	123	125
H(9C)	-3201	6057	19	125
H(10)	-2991	6216	4060	62
H(11A)	-2557	7908	4395	110
H(11B)	-3126	7429	5054	110
H(11C)	-3859	7647	4305	110
H(12A)	-5310	5788	3881	132
H(12B)	-4489	5673	4649	132
H(12C)	-4853	4970	3714	132
H(15)	1141	7763	10236	106
H(16)	-659	7640	9788	128
H(17)	-1583	7277	8383	105
H(19)	-893	6438	6665	76
H(20A)	-671	8395	7057	129
H(20B)	-912	7719	6136	129
H(20C)	280	8096	6846	129
H(21A)	-2483	7092	7066	170
H(21B)	-2583	6019	7097	170
H(21C)	-2678	6298	6223	170
H(22)	2843	7502	8935	73
H(23A)	3255	9095	9819	163
H(23B)	4090	8662	10216	163
H(23C)	3059	8605	10572	163
H(24A)	2167	6705	10255	129
H(24B)	3309	6819	10041	129
H(24C)	2096	6067	9369	129
H(27)	2143	9832	3105	72
H(28)	2494	9037	1985	83
H(29)	1941	7353	1670	71
H(31)	642	8758	4444	52
H(32)	223	5640	2507	68
H(35)	4492	11474	7429	70
H(36)	5720	11410	6682	82
H(37)	5552	9895	5970	79
H(39)	2195	9411	7629	65
H(40)	3472	7492	5947	73
H(41A)	3230	7951	4694	144

H(41B)	3799	7204	4659	144
H(41C)	4566	8368	4824	144
H(42A)	5836	8368	6122	155
H(42B)	5043	7208	5951	155
H(42C)	5318	7978	6833	155
H(43)	3126	8388	7985	44
H(44)	-1194	7664	3607	41
H(45A)	2613	9308	5076	87
H(45B)	2235	10133	5424	87
H(45C)	2893	10264	4733	87
H(46A)	1336	10472	3837	108
H(46B)	571	10251	4455	108
H(46C)	67	9591	3490	108
H(47A)	3805	10263	8852	127
H(47B)	2832	10604	8914	127
H(47C)	3926	11301	8696	127
H(48A)	1273	5740	1222	178
H(48B)	57	5737	1101	178
H(48C)	226	4799	1276	178
H(49A)	2706	11323	7370	132
H(49B)	1615	10672	7614	132
H(49C)	1743	10295	6714	132
H(50A)	2492	6066	2655	223
H(50B)	1541	5074	2735	223
H(50C)	1994	6111	3433	223
H(51)	2486(15)	5270(13)	4887(10)	33(5)

Table A54. Torsion angles [°] for **95**.

O(2)-P(1)-O(1)-Li(3)	16.5(2)	O(4)-P(2)-O(3)-Li(3)	-104.80(16)
C(25)-P(1)-O(1)-Li(3)	-115.3(2)	C(13)-P(2)-O(3)-Li(3)	126.85(16)
C(44)-P(1)-O(1)-Li(3)	134.6(2)	C(43)-P(2)-O(3)-Li(3)	14.03(16)
Li(2)#1-P(1)-O(1)-Li(3)	55.6(2)	Li(2)-P(2)-O(3)-Li(3)	-96.21(16)
Li(1)-P(1)-O(1)-Li(3)	11.8(2)	Li(1)#1-P(2)-O(3)-Li(3)	-114.6(2)
O(1)-P(1)-O(2)-Li(1)	-10.4(2)	O(3)-P(2)-O(4)-Li(2)	16.08(18)
C(25)-P(1)-O(2)-Li(1)	121.00(18)	C(13)-P(2)-O(4)-Li(2)	145.13(16)
C(44)-P(1)-O(2)-Li(1)	-133.24(18)	C(43)-P(2)-O(4)-Li(2)	-100.46(17)
Li(2)#1-P(1)-O(2)-Li(1)	-128.0(2)	Li(3)-P(2)-O(4)-Li(2)	-24.14(19)
Li(3)-P(1)-O(2)-Li(1)	-3.45(19)	Li(1)#1-P(2)-O(4)-Li(2)	21.16(16)
O(1)-P(1)-O(2)-Li(2)#1	117.56(14)	C(44)-N(2)-C(1)-C(2)	102.9(2)
C(25)-P(1)-O(2)-Li(2)#1	-111.05(15)	Li(2)#1-N(2)-C(1)-C(2)	-87.4(2)
C(44)-P(1)-O(2)-Li(2)#1	-5.29(15)	C(44)-N(2)-C(1)-C(6)	-82.0(2)
Li(1)-P(1)-O(2)-Li(2)#1	128.0(2)	Li(2)#1-N(2)-C(1)-C(6)	87.6(2)
Li(3)-P(1)-O(2)-Li(2)#1	124.50(15)	C(6)-C(1)-C(2)-C(3)	2.3(3)
O(4)-P(2)-O(3)-Li(1)#1	9.84(18)	N(2)-C(1)-C(2)-C(3)	177.22(19)
C(13)-P(2)-O(3)-Li(1)#1	-118.51(16)	C(6)-C(1)-C(2)-C(7)	-179.7(2)
C(43)-P(2)-O(3)-Li(1)#1	128.67(16)	N(2)-C(1)-C(2)-C(7)	-4.8(3)
Li(3)-P(2)-O(3)-Li(1)#1	114.6(2)	C(1)-C(2)-C(3)-C(4)	-1.6(4)
Li(2)-P(2)-O(3)-Li(1)#1	18.43(16)	C(7)-C(2)-C(3)-C(4)	-179.5(2)

C(2)-C(3)-C(4)-C(5)	0.1(4)
C(3)-C(4)-C(5)-C(6)	0.7(4)
C(4)-C(5)-C(6)-C(1)	0.1(3)
C(4)-C(5)-C(6)-C(10)	179.8(2)
C(2)-C(1)-C(6)-C(5)	-1.6(3)
N(2)-C(1)-C(6)-C(5)	-176.31(19)
C(2)-C(1)-C(6)-C(10)	178.7(2)
N(2)-C(1)-C(6)-C(10)	4.0(3)
C(1)-C(2)-C(7)-C(9)	146.4(2)
C(3)-C(2)-C(7)-C(9)	-35.8(3)
C(1)-C(2)-C(7)-C(8)	-87.5(3)
C(3)-C(2)-C(7)-C(8)	90.4(3)
C(5)-C(6)-C(10)-C(12)	48.8(3)
C(1)-C(6)-C(10)-C(12)	-131.5(2)
C(5)-C(6)-C(10)-C(11)	-75.6(3)
C(1)-C(6)-C(10)-C(11)	104.1(2)
O(4)-P(2)-C(13)-C(14)	41.0(2)
O(3)-P(2)-C(13)-C(14)	172.54(16)
C(43)-P(2)-C(13)-C(14)	-75.36(19)
Li(3)-P(2)-C(13)-C(14)	-150.99(17)
Li(2)-P(2)-C(13)-C(14)	66.7(2)
Li(1)#1-P(2)-C(13)-C(14)	139.65(17)
O(4)-P(2)-C(13)-C(18)	-134.90(18)
O(3)-P(2)-C(13)-C(18)	-3.3(2)
C(43)-P(2)-C(13)-C(18)	108.77(19)
Li(3)-P(2)-C(13)-C(18)	33.1(2)
Li(2)-P(2)-C(13)-C(18)	-109.1(2)
Li(1)#1-P(2)-C(13)-C(18)	-36.2(2)
C(18)-C(13)-C(14)-C(15)	3.8(4)
P(2)-C(13)-C(14)-C(15)	-172.2(2)
C(18)-C(13)-C(14)-C(22)	-176.0(2)
P(2)-C(13)-C(14)-C(22)	8.0(3)
C(13)-C(14)-C(15)-C(16)	-1.3(5)
C(22)-C(14)-C(15)-C(16)	178.4(3)
C(14)-C(15)-C(16)-C(17)	-0.9(6)
C(15)-C(16)-C(17)-C(18)	0.7(6)
C(16)-C(17)-C(18)-C(13)	1.8(5)
C(16)-C(17)-C(18)-C(19)	-176.5(3)
C(14)-C(13)-C(18)-C(17)	-4.0(4)
P(2)-C(13)-C(18)-C(17)	171.8(2)
C(14)-C(13)-C(18)-C(19)	174.1(2)
P(2)-C(13)-C(18)-C(19)	-10.1(3)
C(17)-C(18)-C(19)-C(20)	102.0(3)
C(13)-C(18)-C(19)-C(20)	-76.2(3)
C(17)-C(18)-C(19)-C(21)	-25.0(4)
C(13)-C(18)-C(19)-C(21)	156.8(3)
C(15)-C(14)-C(22)-C(24)	70.4(3)
C(13)-C(14)-C(22)-C(24)	-109.9(3)
C(15)-C(14)-C(22)-C(23)	-53.8(3)
C(13)-C(14)-C(22)-C(23)	126.0(3)
O(1)-P(1)-C(25)-C(26)	-50.35(18)
O(2)-P(1)-C(25)-C(26)	176.43(14)
C(44)-P(1)-C(25)-C(26)	67.92(17)
Li(2)#1-P(1)-C(25)-C(26)	138.14(15)
Li(1)-P(1)-C(25)-C(26)	-155.23(15)
Li(3)-P(1)-C(25)-C(26)	-76.83(18)
O(1)-P(1)-C(25)-C(30)	135.53(17)
O(2)-P(1)-C(25)-C(30)	2.3(2)
C(44)-P(1)-C(25)-C(30)	-106.20(18)
Li(2)#1-P(1)-C(25)-C(30)	-36.0(2)
Li(1)-P(1)-C(25)-C(30)	30.7(2)
Li(3)-P(1)-C(25)-C(30)	109.05(18)
C(30)-C(25)-C(26)-C(27)	0.9(3)
P(1)-C(25)-C(26)-C(27)	-173.48(18)
C(30)-C(25)-C(26)-C(31)	-176.68(19)
P(1)-C(25)-C(26)-C(31)	9.0(3)
C(25)-C(26)-C(27)-C(28)	-0.5(4)
C(31)-C(26)-C(27)-C(28)	177.3(2)
C(26)-C(27)-C(28)-C(29)	-0.3(4)
C(27)-C(28)-C(29)-C(30)	0.7(4)
C(28)-C(29)-C(30)-C(25)	-0.3(4)
C(28)-C(29)-C(30)-C(32)	-177.9(3)
C(26)-C(25)-C(30)-C(29)	-0.5(3)
P(1)-C(25)-C(30)-C(29)	173.48(17)
C(26)-C(25)-C(30)-C(32)	176.9(2)
P(1)-C(25)-C(30)-C(32)	-9.1(3)
C(27)-C(26)-C(31)-C(46)	48.1(3)
C(25)-C(26)-C(31)-C(46)	-134.3(2)
C(27)-C(26)-C(31)-C(45)	-75.3(3)
C(25)-C(26)-C(31)-C(45)	102.3(2)
C(29)-C(30)-C(32)-C(50)	92.6(3)
C(25)-C(30)-C(32)-C(50)	-84.9(4)
C(29)-C(30)-C(32)-C(48)	-36.5(4)
C(25)-C(30)-C(32)-C(48)	146.1(3)
C(43)-N(1)-C(33)-C(34)	-63.0(3)
Li(3)-N(1)-C(33)-C(34)	115.5(2)
C(43)-N(1)-C(33)-C(38)	121.4(2)
Li(3)-N(1)-C(33)-C(38)	-60.1(3)
C(38)-C(33)-C(34)-C(35)	-0.8(3)
N(1)-C(33)-C(34)-C(35)	-176.25(19)
C(38)-C(33)-C(34)-C(39)	176.8(2)
N(1)-C(33)-C(34)-C(39)	1.4(3)
C(33)-C(34)-C(35)-C(36)	0.2(4)
C(39)-C(34)-C(35)-C(36)	-177.7(2)
C(34)-C(35)-C(36)-C(37)	0.8(4)
C(35)-C(36)-C(37)-C(38)	-1.1(4)
C(36)-C(37)-C(38)-C(33)	0.4(4)
C(36)-C(37)-C(38)-C(40)	-179.1(3)
C(34)-C(33)-C(38)-C(37)	0.5(3)
N(1)-C(33)-C(38)-C(37)	176.1(2)
C(34)-C(33)-C(38)-C(40)	-179.9(2)
N(1)-C(33)-C(38)-C(40)	-4.3(3)

C(35)-C(34)-C(39)-C(47)	-65.6(3)
C(33)-C(34)-C(39)-C(47)	116.7(3)
C(35)-C(34)-C(39)-C(49)	58.1(3)
C(33)-C(34)-C(39)-C(49)	-119.6(3)
C(37)-C(38)-C(40)-C(41)	-59.4(3)
C(33)-C(38)-C(40)-C(41)	121.1(3)
C(37)-C(38)-C(40)-C(42)	65.1(3)
C(33)-C(38)-C(40)-C(42)	-114.5(3)
C(33)-N(1)-C(43)-P(2)	178.30(14)
Li(3)-N(1)-C(43)-P(2)	-0.5(2)
O(4)-P(2)-C(43)-N(1)	116.21(16)
O(3)-P(2)-C(43)-N(1)	-8.27(18)
C(13)-P(2)-C(43)-N(1)	-125.90(16)
Li(3)-P(2)-C(43)-N(1)	0.35(16)
Li(2)-P(2)-C(43)-N(1)	81.79(18)
Li(1)#1-P(2)-C(43)-N(1)	19.9(2)
C(1)-N(2)-C(44)-P(1)	-173.60(14)
Li(2)#1-N(2)-C(44)-P(1)	15.3(2)
O(1)-P(1)-C(44)-N(2)	-132.96(15)
O(2)-P(1)-C(44)-N(2)	-7.61(17)
C(25)-P(1)-C(44)-N(2)	108.71(16)
Li(2)#1-P(1)-C(44)-N(2)	-10.86(15)
Li(1)-P(1)-C(44)-N(2)	-30.35(19)
Li(3)-P(1)-C(44)-N(2)	-110.39(17)
O(5)-C(51)-O(6)-Li(1)	-139.5(2)
O(5)-C(51)-O(6)-Li(1)#1	-26.4(3)
O(5)-C(51)-O(6)-Li(3)	66.3(3)
O(6)-C(51)-O(5)-Li(2)	24.6(4)
P(1)-O(2)-Li(1)-O(3)#1	-172.85(12)
Li(2)#1-O(2)-Li(1)-O(3)#1	50.8(2)
P(1)-O(2)-Li(1)-O(6)	-20.9(3)
Li(2)#1-O(2)-Li(1)-O(6)	-157.23(19)
P(1)-O(2)-Li(1)-O(6)#1	83.0(2)
Li(2)#1-O(2)-Li(1)-O(6)#1	-53.37(19)
P(1)-O(2)-Li(1)-Li(1)#1	34.4(4)
Li(2)#1-O(2)-Li(1)-Li(1)#1	-101.9(3)
P(1)-O(2)-Li(1)-Li(3)#1	141.4(2)
Li(2)#1-O(2)-Li(1)-Li(3)#1	5.1(3)
P(1)-O(2)-Li(1)-Li(2)#1	136.36(19)
P(1)-O(2)-Li(1)-P(2)#1	-178.25(11)
Li(2)#1-O(2)-Li(1)-P(2)#1	45.40(13)
Li(2)#1-O(2)-Li(1)-P(1)	-136.36(19)
P(1)-O(2)-Li(1)-Li(3)	3.30(18)
Li(2)#1-O(2)-Li(1)-Li(3)	-133.06(13)
P(2)-O(4)-Li(2)-O(5)	53.6(2)
P(2)-O(4)-Li(2)-O(2)#1	-60.8(2)
P(2)-O(4)-Li(2)-N(2)#1	-158.0(2)
P(2)-O(4)-Li(2)-Li(1)#1	-22.92(17)
P(2)-O(4)-Li(2)-P(1)#1	-77.1(2)
P(1)-O(1)-Li(3)-O(3)	-96.0(3)
P(1)-O(1)-Li(3)-N(1)	148.33(15)
P(1)-O(1)-Li(3)-O(6)	6.3(3)
P(1)-O(1)-Li(3)-Li(1)#1	-43.3(3)
P(1)-O(1)-Li(3)-P(2)	-132.9(3)
P(1)-O(1)-Li(3)-Li(1)	-11.30(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table A55. Crystal data and structure refinement for **97**.

Identification code	**97**	
Empirical formula	C16 H24 F3 N O4 S	
Formula weight	383.42	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 13.7928(15) Å	α= 90°.
	b = 20.388(2) Å	β= 90°.
	c = 13.7109(15) Å	γ = 90°.
Volume	3855.6(7) Å^3	
Z	8	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	1616	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.783 to 27.518°.	
Index ranges	-17<=h<=17, -26<=k<=26, -17<=l<=17	
Reflections collected	53117	
Independent reflections	4425 [R(int) = 0.0229]	
Completeness to theta = 25.500°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4425 / 0 / 235	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1058	
R indices (all data)	R1 = 0.0475, wR2 = 0.1113	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.718 and -0.627 e.Å^{-3}	

Table A56. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **97**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	314(1)	5053(1)	2240(1)	20(1)
O(1)	-837(1)	4422(1)	2904(1)	25(1)
C(1)	998(1)	4987(1)	3038(1)	19(1)
C(2)	1036(1)	5494(1)	3726(1)	22(1)
C(3)	1753(1)	5450(1)	4440(1)	26(1)
C(4)	2380(1)	4922(1)	4476(1)	26(1)
C(5)	2310(1)	4423(1)	3795(1)	24(1)
C(6)	1620(1)	4444(1)	3049(1)	21(1)
C(7)	340(1)	6073(1)	3715(1)	26(1)
C(8)	-230(1)	6107(1)	4668(1)	33(1)

C(9)	866(2)	6715(1)	3510(2)	48(1)
C(10)	1572(1)	3900(1)	2294(1)	26(1)
C(11)	1254(2)	3254(1)	2760(2)	43(1)
C(12)	2543(2)	3815(1)	1772(1)	39(1)
C(13)	-532(1)	4787(1)	2201(1)	20(1)
C(14)	-1808(1)	4127(1)	2805(1)	29(1)
C(15)	-1726(1)	3411(1)	3012(2)	40(1)
S(1)	334(1)	6092(1)	161(1)	22(1)
O(2)	-519(1)	5689(1)	201(1)	38(1)
O(3)	717(1)	6215(1)	-792(1)	38(1)
O(4)	1051(1)	5928(1)	894(1)	31(1)
C(16)	-122(2)	6886(1)	561(1)	41(1)
F(1)	570(1)	7324(1)	627(1)	70(1)
F(2)	-544(1)	6828(1)	1435(1)	68(1)
F(3)	-782(1)	7120(1)	-49(1)	64(1)

Table A57. Bond lengths [Å] and angles [°] for **97**.

N(1)-C(13)	1.287(2)
N(1)-C(1)	1.4512(18)
N(1)-H(1)	0.87(2)
O(1)-C(13)	1.2881(18)
O(1)-C(14)	1.4750(18)
C(1)-C(6)	1.399(2)
C(1)-C(2)	1.400(2)
C(2)-C(3)	1.395(2)
C(2)-C(7)	1.522(2)
C(3)-C(4)	1.381(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.398(2)
C(5)-H(5)	0.9500
C(6)-C(10)	1.519(2)
C(7)-C(9)	1.523(3)
C(7)-C(8)	1.526(2)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.528(2)
C(10)-C(12)	1.529(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13)	0.9500
C(14)-C(15)	1.492(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
S(1)-O(3)	1.4304(13)
S(1)-O(2)	1.4370(13)
S(1)-O(4)	1.4495(12)
S(1)-C(16)	1.8203(19)
C(16)-F(1)	1.310(3)
C(16)-F(3)	1.325(2)
C(16)-F(2)	1.337(2)
C(13)-N(1)-C(1)	125.57(13)
C(13)-N(1)-H(1)	120.3(14)
C(1)-N(1)-H(1)	114.0(14)
C(13)-O(1)-C(14)	117.59(12)
C(6)-C(1)-C(2)	123.58(13)
C(6)-C(1)-N(1)	118.67(13)
C(2)-C(1)-N(1)	117.63(13)
C(3)-C(2)-C(1)	116.87(14)
C(3)-C(2)-C(7)	120.26(14)
C(1)-C(2)-C(7)	122.87(13)
C(4)-C(3)-C(2)	121.28(15)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	120.29(14)

C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	121.20(14)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	116.75(14)
C(5)-C(6)-C(10)	120.34(14)
C(1)-C(6)-C(10)	122.91(13)
C(2)-C(7)-C(9)	111.64(14)
C(2)-C(7)-C(8)	110.60(13)
C(9)-C(7)-C(8)	111.36(15)
C(2)-C(7)-H(7)	107.7
C(9)-C(7)-H(7)	107.7
C(8)-C(7)-H(7)	107.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(11)	110.95(14)
C(6)-C(10)-C(12)	111.38(14)
C(11)-C(10)-C(12)	110.42(15)
C(6)-C(10)-H(10)	108.0
C(11)-C(10)-H(10)	108.0
C(12)-C(10)-H(10)	108.0
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(1)-C(13)-O(1)	120.53(13)
N(1)-C(13)-H(13)	119.7
O(1)-C(13)-H(13)	119.7
O(1)-C(14)-C(15)	108.19(13)
O(1)-C(14)-H(14A)	110.1
C(15)-C(14)-H(14A)	110.1
O(1)-C(14)-H(14B)	110.1
C(15)-C(14)-H(14B)	110.1
H(14A)-C(14)-H(14B)	108.4
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(3)-S(1)-O(2)	115.96(9)
O(3)-S(1)-O(4)	114.99(8)
O(2)-S(1)-O(4)	113.53(8)
O(3)-S(1)-C(16)	104.31(9)
O(2)-S(1)-C(16)	102.34(9)
O(4)-S(1)-C(16)	103.43(9)
F(1)-C(16)-F(3)	107.35(16)
F(1)-C(16)-F(2)	108.32(17)
F(3)-C(16)-F(2)	107.38(19)
F(1)-C(16)-S(1)	112.03(16)
F(3)-C(16)-S(1)	111.55(14)
F(2)-C(16)-S(1)	110.03(13)

Symmetry transformations used to generate equivalent atoms:

Table A58. Anisotropic displacement parameters (Å^{2}x 10^3) for **97**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	20(1)	22(1)	17(1)	3(1)	-2(1)	0(1)
O(1)	19(1)	34(1)	22(1)	7(1)	-4(1)	-4(1)
C(1)	16(1)	24(1)	17(1)	4(1)	-1(1)	-3(1)
C(2)	21(1)	26(1)	18(1)	2(1)	2(1)	-2(1)
C(3)	24(1)	34(1)	19(1)	-2(1)	0(1)	-4(1)

C(4)	18(1)	38(1)	21(1)	6(1)	-3(1)	-5(1)
C(5)	17(1)	29(1)	26(1)	7(1)	-1(1)	0(1)
C(6)	17(1)	24(1)	22(1)	4(1)	1(1)	-3(1)
C(7)	29(1)	27(1)	23(1)	-2(1)	-1(1)	4(1)
C(8)	27(1)	40(1)	33(1)	0(1)	7(1)	3(1)
C(9)	50(1)	31(1)	62(1)	9(1)	24(1)	4(1)
C(10)	23(1)	25(1)	29(1)	-1(1)	-2(1)	3(1)
C(11)	50(1)	26(1)	53(1)	-4(1)	12(1)	-8(1)
C(12)	37(1)	45(1)	34(1)	-4(1)	10(1)	1(1)
C(13)	21(1)	22(1)	17(1)	0(1)	-2(1)	4(1)
C(14)	16(1)	40(1)	30(1)	9(1)	-4(1)	-4(1)
C(15)	32(1)	37(1)	49(1)	9(1)	-9(1)	-8(1)
S(1)	26(1)	19(1)	20(1)	0(1)	2(1)	-2(1)
O(2)	30(1)	30(1)	53(1)	4(1)	-2(1)	-7(1)
O(3)	46(1)	46(1)	21(1)	2(1)	7(1)	-1(1)
O(4)	30(1)	34(1)	27(1)	6(1)	-3(1)	-3(1)
C(16)	66(1)	22(1)	35(1)	-1(1)	-2(1)	5(1)
F(1)	106(1)	27(1)	78(1)	-6(1)	-18(1)	-19(1)
F(2)	106(1)	55(1)	44(1)	-8(1)	25(1)	28(1)
F(3)	84(1)	41(1)	68(1)	6(1)	-13(1)	28(1)

Table A59. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **97**.

	x	y	z	U(eq)
H(1)	503(15)	5317(11)	1783(17)	37(6)
H(3)	1812	5789	4911	31
H(4)	2862	4902	4970	31
H(5)	2738	4059	3836	29
H(7)	-134	5999	3175	32
H(8A)	-559	5688	4780	50
H(8B)	-711	6459	4627	50
H(8C)	216	6196	5209	50
H(9A)	1360	6789	4012	71
H(9B)	399	7078	3517	71
H(9C)	1177	6692	2868	71
H(10)	1075	4025	1796	31
H(11A)	1742	3113	3235	65
H(11B)	1186	2918	2253	65
H(11C)	631	3316	3090	65
H(12A)	2747	4236	1495	58
H(12B)	2472	3492	1247	58
H(12C)	3032	3662	2238	58
H(13)	-935	4861	1650	24
H(14A)	-2058	4197	2136	35
H(14B)	-2264	4334	3271	35
H(15A)	-1339	3201	2500	59

H(15B)	-2374	3215	3027	59
H(15C)	-1410	3347	3645	59

Table A60. Torsion angles [°] for **97**.

C(13)-N(1)-C(1)-C(6)	85.55(18)	C(3)-C(2)-C(7)-C(8)	-59.52(19)
C(13)-N(1)-C(1)-C(2)	-98.21(18)	C(1)-C(2)-C(7)-C(8)	120.55(16)
C(6)-C(1)-C(2)-C(3)	1.3(2)	C(5)-C(6)-C(10)-C(11)	66.74(19)
N(1)-C(1)-C(2)-C(3)	-174.69(13)	C(1)-C(6)-C(10)-C(11)	-113.71(17)
C(6)-C(1)-C(2)-C(7)	-178.72(14)	C(5)-C(6)-C(10)-C(12)	-56.71(19)
N(1)-C(1)-C(2)-C(7)	5.2(2)	C(1)-C(6)-C(10)-C(12)	122.85(16)
C(1)-C(2)-C(3)-C(4)	-1.4(2)	C(1)-N(1)-C(13)-O(1)	-0.6(2)
C(7)-C(2)-C(3)-C(4)	178.70(14)	C(14)-O(1)-C(13)-N(1)	-179.24(14)
C(2)-C(3)-C(4)-C(5)	0.2(2)	C(13)-O(1)-C(14)-C(15)	129.72(16)
C(3)-C(4)-C(5)-C(6)	1.2(2)	O(3)-S(1)-C(16)-F(1)	-62.30(16)
C(4)-C(5)-C(6)-C(1)	-1.2(2)	O(2)-S(1)-C(16)-F(1)	176.49(14)
C(4)-C(5)-C(6)-C(10)	178.41(14)	O(4)-S(1)-C(16)-F(1)	58.31(16)
C(2)-C(1)-C(6)-C(5)	-0.1(2)	O(3)-S(1)-C(16)-F(3)	58.07(18)
N(1)-C(1)-C(6)-C(5)	175.90(13)	O(2)-S(1)-C(16)-F(3)	-63.14(17)
C(2)-C(1)-C(6)-C(10)	-179.67(14)	O(4)-S(1)-C(16)-F(3)	178.68(15)
N(1)-C(1)-C(6)-C(10)	-3.7(2)	O(3)-S(1)-C(16)-F(2)	177.14(15)
C(3)-C(2)-C(7)-C(9)	65.1(2)	O(2)-S(1)-C(16)-F(2)	55.93(17)
C(1)-C(2)-C(7)-C(9)	-114.86(18)	O(4)-S(1)-C(16)-F(2)	-62.26(17)

Symmetry transformations used to generate equivalent atoms:

Table A61. Hydrogen bonds for **97** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...S(1)	0.87(2)	2.74(2)	3.5533(13)	156.9(18)
N(1)-H(1)...O(4)	0.87(2)	1.90(2)	2.7616(18)	173(2)
C(14)-H(14B)...O(4)#1	0.99	2.65	3.451(2)	138.6
C(15)-H(15C)...F(1)#2	0.98	2.59	3.307(2)	130.5

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y+1,-z+1/2   #2 -x,y-1/2,-z+1/2

Table A62. Crystal data and structure refinement for **98**.

Identification code	**98**	
Empirical formula	C46 H69 N2 P	
Formula weight	681.00	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.9856(9) Å	α= 90°.
	b = 18.7821(14) Å	β= 104.3440(10)°.
	c = 18.3606(13) Å	γ = 90°.
Volume	4338.5(5) Å^3	
Z	4	
Density (calculated)	1.043 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	1496	
Crystal size	0.33 x 0.29 x 0.15 mm^3	
Theta range for data collection	1.58 to 27.54°.	
Index ranges	-16<=h<=16, -24<=k<=24, -23<=l<=23	
Reflections collected	62578	
Independent reflections	10004 [R(int) = 0.0363]	
Completeness to theta = 27.54°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9858 and 0.9700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10004 / 0 / 460	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1543	
R indices (all data)	R1 = 0.0867, wR2 = 0.1755	
Largest diff. peak and hole	0.614 and -0.686 e.Å^{-3}	

Table A63. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **98**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	1985(1)	3565(1)	2522(1)	39(1)
N(1)	4087(1)	3281(1)	3107(1)	52(1)
N(2)	141(1)	3507(1)	2965(1)	45(1)
C(1)	2417(1)	4476(1)	2850(1)	49(1)
C(2)	2302(2)	4987(1)	2262(1)	62(1)
C(3)	2684(2)	5680(1)	2449(2)	88(1)
C(4)	3138(2)	5870(2)	3175(2)	102(1)
C(5)	3216(2)	5392(2)	3734(2)	87(1)
C(6)	2873(2)	4691(1)	3598(1)	63(1)

C(7)	1785(2)	4843(1)	1441(2)	75(1)
C(8)	2592(3)	4849(2)	958(2)	126(1)
C(9)	899(2)	5369(2)	1113(2)	108(1)
C(10)	3018(2)	4206(2)	4276(1)	75(1)
C(11)	4182(2)	4097(2)	4690(2)	103(1)
C(12)	2451(3)	4489(2)	4859(2)	111(1)
C(13)	3278(1)	3051(1)	2627(1)	44(1)
C(14)	3217(2)	2493(1)	1994(1)	57(1)
C(15)	3187(3)	2893(2)	1268(2)	112(1)
C(16)	2204(2)	2061(2)	1855(2)	89(1)
C(17)	4164(3)	1987(2)	2130(2)	152(2)
C(18)	5185(2)	3113(1)	3178(1)	65(1)
C(19)	5759(2)	3552(2)	2800(2)	81(1)
C(20)	6843(2)	3412(2)	2911(2)	118(1)
C(21)	7339(2)	2884(3)	3385(3)	136(2)
C(22)	6782(2)	2490(2)	3784(2)	116(1)
C(23)	5690(2)	2597(2)	3701(2)	81(1)
C(24)	5264(2)	4181(2)	2336(2)	85(1)
C(25)	5603(3)	4256(2)	1599(2)	131(1)
C(26)	5498(3)	4860(2)	2800(3)	130(1)
C(27)	5131(2)	2183(2)	4184(2)	102(1)
C(28)	5264(5)	1385(3)	4147(3)	179(2)
C(29)	5513(4)	2392(3)	5010(2)	176(2)
C(30)	1067(1)	3236(1)	3103(1)	42(1)
C(31)	1208(2)	2602(1)	3665(1)	59(1)
C(32)	433(2)	2017(1)	3288(2)	88(1)
C(33)	899(2)	2850(2)	4379(2)	93(1)
C(34)	2329(2)	2289(1)	3891(1)	73(1)
C(35)	-356(1)	4009(1)	2417(1)	45(1)
C(36)	-563(1)	4693(1)	2658(1)	52(1)
C(37)	-1232(2)	5139(1)	2148(1)	66(1)
C(38)	-1682(2)	4931(1)	1424(2)	74(1)
C(39)	-1474(2)	4261(1)	1194(1)	68(1)
C(40)	-821(1)	3782(1)	1678(1)	53(1)
C(41)	-126(2)	4912(1)	3463(1)	64(1)
C(42)	272(2)	5675(2)	3560(2)	95(1)
C(43)	-942(3)	4769(2)	3911(2)	119(1)
C(44)	-703(2)	3028(1)	1426(1)	63(1)
C(45)	-505(3)	2986(2)	646(2)	108(1)
C(46)	-1667(2)	2584(2)	1477(2)	99(1)

Table A64. Bond lengths [Å] and angles [°] for **98**.

P(1)-C(1)	1.8555(19)
P(1)-C(30)	1.8898(17)
P(1)-C(13)	1.9039(17)
N(1)-C(13)	1.267(2)
N(1)-C(18)	1.435(2)
N(2)-C(30)	1.271(2)
N(2)-C(35)	1.413(2)
C(1)-C(6)	1.412(3)
C(1)-C(2)	1.423(3)
C(2)-C(3)	1.404(3)
C(2)-C(7)	1.516(4)
C(3)-C(4)	1.365(4)

C(3)-H(3)	0.9300
C(4)-C(5)	1.349(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.391(3)
C(5)-H(5)	0.9300
C(6)-C(10)	1.518(4)
C(7)-C(9)	1.521(4)
C(7)-C(8)	1.532(4)
C(7)-H(7)	0.9800
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.528(3)
C(10)-C(12)	1.535(4)
C(10)-H(10)	0.9800
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-C(14)	1.553(3)
C(13)-H(13)	0.9800
C(14)-C(16)	1.512(3)
C(14)-C(15)	1.523(4)
C(14)-C(17)	1.524(3)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-C(19)	1.404(4)
C(18)-C(23)	1.406(4)
C(19)-C(20)	1.396(3)
C(19)-C(24)	1.505(4)
C(20)-C(21)	1.370(6)
C(20)-H(20)	0.9300
C(21)-C(22)	1.367(6)
C(21)-H(21)	0.9300
C(22)-C(23)	1.403(3)
C(22)-H(22)	0.9300
C(23)-C(27)	1.497(4)
C(24)-C(26)	1.523(4)
C(24)-C(25)	1.528(4)
C(24)-H(24)	0.9800
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-C(28)	1.512(5)
C(27)-C(29)	1.527(5)
C(27)-H(27)	0.9800
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-C(31)	1.557(3)
C(31)-C(34)	1.528(3)
C(31)-C(32)	1.534(3)
C(31)-C(33)	1.536(3)
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(35)-C(36)	1.404(3)
C(35)-C(40)	1.409(3)
C(36)-C(37)	1.390(3)
C(36)-C(41)	1.505(3)
C(37)-C(38)	1.370(3)
C(37)-H(37)	0.9300
C(38)-C(39)	1.375(4)
C(38)-H(38)	0.9300
C(39)-C(40)	1.395(3)
C(39)-H(39)	0.9300
C(40)-C(44)	1.509(3)
C(41)-C(43)	1.517(4)
C(41)-C(42)	1.519(4)
C(41)-H(41)	0.9800
C(42)-H(42A)	0.9600
C(42)-H(42B)	0.9600
C(42)-H(42C)	0.9600
C(43)-H(43A)	0.9600
C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600
C(44)-C(45)	1.518(4)
C(44)-C(46)	1.527(3)

C(44)-H(44)	0.9800
C(45)-H(45A)	0.9600
C(45)-H(45B)	0.9600
C(45)-H(45C)	0.9600
C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600
C(46)-H(46C)	0.9600
C(1)-P(1)-C(30)	107.48(8)
C(1)-P(1)-C(13)	104.26(8)
C(30)-P(1)-C(13)	116.21(8)
C(13)-N(1)-C(18)	128.45(17)
C(30)-N(2)-C(35)	130.62(15)
C(6)-C(1)-C(2)	118.94(19)
C(6)-C(1)-P(1)	126.84(16)
C(2)-C(1)-P(1)	114.17(15)
C(3)-C(2)-C(1)	118.4(2)
C(3)-C(2)-C(7)	116.8(2)
C(1)-C(2)-C(7)	124.87(19)
C(4)-C(3)-C(2)	121.5(3)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	120.0(3)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	122.2(3)
C(4)-C(5)-H(5)	118.9
C(6)-C(5)-H(5)	118.9
C(5)-C(6)-C(1)	118.9(2)
C(5)-C(6)-C(10)	116.8(2)
C(1)-C(6)-C(10)	124.28(19)
C(2)-C(7)-C(9)	112.6(2)
C(2)-C(7)-C(8)	112.1(2)
C(9)-C(7)-C(8)	109.0(2)
C(2)-C(7)-H(7)	107.7
C(9)-C(7)-H(7)	107.7
C(8)-C(7)-H(7)	107.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(11)	113.2(2)
C(6)-C(10)-C(12)	112.4(2)
C(11)-C(10)-C(12)	106.7(2)
C(6)-C(10)-H(10)	108.1
C(11)-C(10)-H(10)	108.1
C(12)-C(10)-H(10)	108.1
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(1)-C(13)-C(14)	129.08(16)
N(1)-C(13)-P(1)	117.13(13)
C(14)-C(13)-P(1)	112.68(12)
N(1)-C(13)-H(13)	93.5
C(14)-C(13)-H(13)	93.5
P(1)-C(13)-H(13)	93.5
C(16)-C(14)-C(15)	106.4(2)
C(16)-C(14)-C(17)	109.1(3)
C(15)-C(14)-C(17)	107.1(3)
C(16)-C(14)-C(13)	111.77(17)
C(15)-C(14)-C(13)	107.90(19)
C(17)-C(14)-C(13)	114.14(18)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(23)	121.8(2)
C(19)-C(18)-N(1)	117.6(2)
C(23)-C(18)-N(1)	119.9(2)
C(20)-C(19)-C(18)	117.2(3)
C(20)-C(19)-C(24)	120.3(3)
C(18)-C(19)-C(24)	122.45(19)

C(21)-C(20)-C(19)	121.8(4)	C(34)-C(31)-C(32)	108.73(19)
C(21)-C(20)-H(20)	119.1	C(34)-C(31)-C(33)	108.6(2)
C(19)-C(20)-H(20)	119.1	C(32)-C(31)-C(33)	108.7(2)
C(22)-C(21)-C(20)	120.2(3)	C(34)-C(31)-C(30)	114.99(16)
C(22)-C(21)-H(21)	119.9	C(32)-C(31)-C(30)	106.96(18)
C(20)-C(21)-H(21)	119.9	C(33)-C(31)-C(30)	108.70(18)
C(21)-C(22)-C(23)	121.3(3)	C(31)-C(32)-H(32A)	109.5
C(21)-C(22)-H(22)	119.4	C(31)-C(32)-H(32B)	109.5
C(23)-C(22)-H(22)	119.4	H(32A)-C(32)-H(32B)	109.5
C(22)-C(23)-C(18)	117.4(3)	C(31)-C(32)-H(32C)	109.5
C(22)-C(23)-C(27)	119.1(3)	H(32A)-C(32)-H(32C)	109.5
C(18)-C(23)-C(27)	123.4(2)	H(32B)-C(32)-H(32C)	109.5
C(19)-C(24)-C(26)	110.0(3)	C(31)-C(33)-H(33A)	109.5
C(19)-C(24)-C(25)	113.4(3)	C(31)-C(33)-H(33B)	109.5
C(26)-C(24)-C(25)	110.9(3)	H(33A)-C(33)-H(33B)	109.5
C(19)-C(24)-H(24)	107.4	C(31)-C(33)-H(33C)	109.5
C(26)-C(24)-H(24)	107.4	H(33A)-C(33)-H(33C)	109.5
C(25)-C(24)-H(24)	107.4	H(33B)-C(33)-H(33C)	109.5
C(24)-C(25)-H(25A)	109.5	C(31)-C(34)-H(34A)	109.5
C(24)-C(25)-H(25B)	109.5	C(31)-C(34)-H(34B)	109.5
H(25A)-C(25)-H(25B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(24)-C(25)-H(25C)	109.5	C(31)-C(34)-H(34C)	109.5
H(25A)-C(25)-H(25C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(25B)-C(25)-H(25C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(24)-C(26)-H(26A)	109.5	C(36)-C(35)-C(40)	120.71(17)
C(24)-C(26)-H(26B)	109.5	C(36)-C(35)-N(2)	118.37(17)
H(26A)-C(26)-H(26B)	109.5	C(40)-C(35)-N(2)	119.64(17)
C(24)-C(26)-H(26C)	109.5	C(37)-C(36)-C(35)	118.42(19)
H(26A)-C(26)-H(26C)	109.5	C(37)-C(36)-C(41)	121.14(19)
H(26B)-C(26)-H(26C)	109.5	C(35)-C(36)-C(41)	120.31(18)
C(23)-C(27)-C(28)	114.3(3)	C(38)-C(37)-C(36)	121.7(2)
C(23)-C(27)-C(29)	111.7(4)	C(38)-C(37)-H(37)	119.1
C(28)-C(27)-C(29)	106.7(3)	C(36)-C(37)-H(37)	119.1
C(23)-C(27)-H(27)	108.0	C(37)-C(38)-C(39)	119.4(2)
C(28)-C(27)-H(27)	108.0	C(37)-C(38)-H(38)	120.3
C(29)-C(27)-H(27)	108.0	C(39)-C(38)-H(38)	120.3
C(27)-C(28)-H(28A)	109.5	C(38)-C(39)-C(40)	122.0(2)
C(27)-C(28)-H(28B)	109.5	C(38)-C(39)-H(39)	119.0
H(28A)-C(28)-H(28B)	109.5	C(40)-C(39)-H(39)	119.0
C(27)-C(28)-H(28C)	109.5	C(39)-C(40)-C(35)	117.76(19)
H(28A)-C(28)-H(28C)	109.5	C(39)-C(40)-C(44)	120.12(19)
H(28B)-C(28)-H(28C)	109.5	C(35)-C(40)-C(44)	121.93(18)
C(27)-C(29)-H(29A)	109.5	C(36)-C(41)-C(43)	109.9(2)
C(27)-C(29)-H(29B)	109.5	C(36)-C(41)-C(42)	114.1(2)
H(29A)-C(29)-H(29B)	109.5	C(43)-C(41)-C(42)	111.5(2)
C(27)-C(29)-H(29C)	109.5	C(36)-C(41)-H(41)	107.0
H(29A)-C(29)-H(29C)	109.5	C(43)-C(41)-H(41)	107.0
H(29B)-C(29)-H(29C)	109.5	C(42)-C(41)-H(41)	107.0
N(2)-C(30)-C(31)	112.87(15)	C(41)-C(42)-H(42A)	109.5
N(2)-C(30)-P(1)	117.07(13)	C(41)-C(42)-H(42B)	109.5
C(31)-C(30)-P(1)	129.52(12)	H(42A)-C(42)-H(42B)	109.5

C(41)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(40)-C(44)-C(45)	113.1(2)
C(40)-C(44)-C(46)	110.27(19)
C(45)-C(44)-C(46)	111.3(2)
C(40)-C(44)-H(44)	107.3
C(45)-C(44)-H(44)	107.3
C(46)-C(44)-H(44)	107.3
C(44)-C(45)-H(45A)	109.5
C(44)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(44)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(44)-C(46)-H(46A)	109.5
C(44)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(44)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A65. Anisotropic displacement parameters ($Å^2 x 10^3$) for **98**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	29(1)	45(1)	44(1)	1(1)	10(1)	-1(1)
N(1)	31(1)	60(1)	62(1)	-10(1)	9(1)	3(1)
N(2)	37(1)	51(1)	49(1)	1(1)	16(1)	1(1)
C(1)	33(1)	47(1)	68(1)	-4(1)	14(1)	-1(1)
C(2)	51(1)	50(1)	90(2)	9(1)	27(1)	1(1)
C(3)	77(2)	53(1)	141(3)	14(2)	39(2)	-3(1)
C(4)	80(2)	53(2)	170(3)	-27(2)	26(2)	-11(1)
C(5)	67(2)	69(2)	119(2)	-33(2)	9(2)	-5(1)
C(6)	41(1)	62(1)	82(2)	-20(1)	9(1)	0(1)
C(7)	80(2)	69(1)	81(2)	26(1)	29(1)	3(1)
C(8)	116(3)	170(4)	105(2)	38(2)	55(2)	45(3)
C(9)	82(2)	123(3)	119(3)	44(2)	27(2)	21(2)
C(10)	66(1)	89(2)	62(1)	-18(1)	-2(1)	3(1)
C(11)	78(2)	120(2)	91(2)	-28(2)	-15(2)	21(2)
C(12)	93(2)	167(3)	64(2)	-21(2)	7(2)	25(2)
C(13)	38(1)	46(1)	51(1)	1(1)	15(1)	0(1)
C(14)	46(1)	62(1)	64(1)	-18(1)	13(1)	2(1)
C(15)	160(3)	120(3)	77(2)	-36(2)	66(2)	-49(2)
C(16)	88(2)	83(2)	104(2)	-41(2)	42(2)	-36(1)
C(17)	108(2)	141(3)	171(4)	-104(3)	-35(2)	68(2)
C(18)	32(1)	79(2)	80(2)	-26(1)	8(1)	6(1)
C(19)	38(1)	90(2)	120(2)	-32(2)	27(1)	-7(1)
C(20)	42(1)	137(3)	182(4)	-32(3)	41(2)	0(2)
C(21)	40(1)	173(4)	190(4)	-39(3)	21(2)	25(2)
C(22)	49(2)	152(3)	133(3)	-27(2)	-2(2)	42(2)
C(23)	44(1)	103(2)	88(2)	-19(2)	-2(1)	24(1)
C(24)	51(1)	86(2)	128(2)	-12(2)	41(1)	-15(1)

C(25)	104(2)	146(3)	170(4)	8(3)	83(3)	-20(2)
C(26)	104(3)	93(2)	196(4)	-34(3)	44(3)	-9(2)
C(27)	67(2)	131(3)	96(2)	23(2)	0(2)	41(2)
C(28)	251(6)	132(4)	146(4)	30(3)	34(4)	22(4)
C(29)	207(5)	214(5)	104(3)	13(3)	33(3)	88(4)
C(30)	37(1)	46(1)	43(1)	-1(1)	13(1)	-2(1)
C(31)	53(1)	63(1)	67(1)	21(1)	24(1)	8(1)
C(32)	70(2)	58(1)	139(3)	27(2)	33(2)	-6(1)
C(33)	97(2)	122(2)	73(2)	41(2)	48(2)	32(2)
C(34)	63(1)	76(2)	81(2)	32(1)	22(1)	21(1)
C(35)	31(1)	55(1)	50(1)	5(1)	14(1)	2(1)
C(36)	39(1)	58(1)	60(1)	1(1)	14(1)	4(1)
C(37)	55(1)	61(1)	81(2)	8(1)	14(1)	14(1)
C(38)	56(1)	83(2)	75(2)	19(1)	3(1)	15(1)
C(39)	49(1)	95(2)	54(1)	5(1)	3(1)	3(1)
C(40)	36(1)	70(1)	53(1)	-2(1)	12(1)	-1(1)
C(41)	59(1)	62(1)	69(1)	-9(1)	10(1)	10(1)
C(42)	86(2)	72(2)	112(2)	-24(2)	-1(2)	11(1)
C(43)	111(2)	183(4)	73(2)	-34(2)	40(2)	-28(2)
C(44)	46(1)	79(2)	62(1)	-15(1)	8(1)	1(1)
C(45)	119(3)	132(3)	77(2)	-32(2)	33(2)	11(2)
C(46)	68(2)	88(2)	139(3)	-26(2)	23(2)	-18(1)

Table A66. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **98**.

	x	y	z	U(eq)
H(3)	2627	6016	2069	106
H(4)	3394	6331	3285	122
H(5)	3509	5534	4227	105
H(7)	1469	4367	1406	90
H(8A)	2905	5314	974	189
H(8B)	2240	4733	448	189
H(8C)	3138	4504	1149	189
H(9A)	385	5363	1409	161
H(9B)	562	5235	605	161
H(9C)	1192	5838	1118	161
H(10)	2713	3741	4103	90
H(11A)	4589	3988	4333	154
H(11B)	4236	3710	5039	154
H(11C)	4452	4524	4957	154
H(12A)	2714	4955	5019	166
H(12B)	2583	4174	5284	166
H(12C)	1700	4514	4637	166
H(13)	3102	2704	2975	53
H(15A)	3808	3186	1335	169
H(15B)	2563	3186	1141	169

H(15C)	3170	2557	870	169
H(16A)	2136	1779	1409	133
H(16B)	1606	2377	1789	133
H(16C)	2226	1754	2276	133
H(17A)	4221	1736	2593	228
H(17B)	4802	2255	2158	228
H(17C)	4064	1653	1723	228
H(20)	7239	3684	2656	141
H(21)	8058	2794	3437	163
H(22)	7134	2145	4116	139
H(24)	4492	4110	2206	102
H(25A)	5189	4623	1298	197
H(25B)	5489	3813	1331	197
H(25C)	6343	4379	1707	197
H(26A)	5262	4805	3253	195
H(26B)	5130	5252	2515	195
H(26C)	6249	4951	2926	195
H(27)	4370	2291	4019	122
H(28A)	4951	1222	3645	269
H(28B)	4918	1158	4491	269
H(28C)	6007	1268	4281	269
H(29A)	6197	2183	5220	264
H(29B)	5015	2224	5280	264
H(29C)	5567	2901	5051	264
H(32A)	600	1872	2829	132
H(32B)	-280	2197	3179	132
H(32C)	495	1616	3620	132
H(33A)	926	2454	4713	139
H(33B)	191	3041	4246	139
H(33C)	1385	3212	4624	139
H(34A)	2342	1898	4229	109
H(34B)	2819	2649	4135	109
H(34C)	2528	2124	3450	109
H(37)	-1379	5591	2302	79
H(38)	-2124	5239	1091	88
H(39)	-1778	4123	701	81
H(41)	486	4604	3671	77
H(42A)	764	5754	3254	142
H(42B)	623	5758	4078	142
H(42C)	-318	5996	3409	142
H(43A)	-1574	5039	3702	179
H(43B)	-657	4907	4425	179
H(43C)	-1111	4271	3889	179
H(44)	-81	2822	1778	76
H(45A)	-1114	3164	283	162
H(45B)	-380	2500	531	162
H(45C)	106	3268	631	162
H(46A)	-1734	2584	1986	148
H(46B)	-1576	2104	1324	148
H(46C)	-2296	2784	1153	148

Table A67. Torsion angles [°] for **98**.

C(30)-P(1)-C(1)-C(6)	52.59(18)
C(13)-P(1)-C(1)-C(6)	-71.32(17)
C(30)-P(1)-C(1)-C(2)	-130.26(14)
C(13)-P(1)-C(1)-C(2)	105.83(14)
C(6)-C(1)-C(2)-C(3)	2.3(3)
P(1)-C(1)-C(2)-C(3)	-175.12(17)
C(6)-C(1)-C(2)-C(7)	-177.13(19)
P(1)-C(1)-C(2)-C(7)	5.5(3)
C(1)-C(2)-C(3)-C(4)	-1.2(4)
C(7)-C(2)-C(3)-C(4)	178.2(2)
C(2)-C(3)-C(4)-C(5)	-0.8(4)
C(3)-C(4)-C(5)-C(6)	1.8(4)
C(4)-C(5)-C(6)-C(1)	-0.7(4)
C(4)-C(5)-C(6)-C(10)	179.4(3)
C(2)-C(1)-C(6)-C(5)	-1.4(3)
P(1)-C(1)-C(6)-C(5)	175.68(17)
C(2)-C(1)-C(6)-C(10)	178.52(19)
P(1)-C(1)-C(6)-C(10)	-4.5(3)
C(3)-C(2)-C(7)-C(9)	-53.5(3)
C(1)-C(2)-C(7)-C(9)	125.9(2)
C(3)-C(2)-C(7)-C(8)	69.8(3)
C(1)-C(2)-C(7)-C(8)	-110.8(3)
C(5)-C(6)-C(10)-C(11)	-62.9(3)
C(1)-C(6)-C(10)-C(11)	117.2(2)
C(5)-C(6)-C(10)-C(12)	58.0(3)
C(1)-C(6)-C(10)-C(12)	-121.8(2)
C(18)-N(1)-C(13)-C(14)	3.3(4)
C(18)-N(1)-C(13)-P(1)	-163.70(18)
C(1)-P(1)-C(13)-N(1)	24.65(17)
C(30)-P(1)-C(13)-N(1)	-93.43(16)
C(1)-P(1)-C(13)-C(14)	-144.40(14)
C(30)-P(1)-C(13)-C(14)	97.52(15)
N(1)-C(13)-C(14)-C(16)	146.8(2)
P(1)-C(13)-C(14)-C(16)	-45.8(2)
N(1)-C(13)-C(14)-C(15)	-96.5(3)
P(1)-C(13)-C(14)-C(15)	70.9(2)
N(1)-C(13)-C(14)-C(17)	22.4(4)
P(1)-C(13)-C(14)-C(17)	-170.2(3)
C(13)-N(1)-C(18)-C(19)	91.5(3)
C(13)-N(1)-C(18)-C(23)	-98.1(3)
C(23)-C(18)-C(19)-C(20)	5.9(4)
N(1)-C(18)-C(19)-C(20)	176.0(2)
C(23)-C(18)-C(19)-C(24)	-170.0(2)
N(1)-C(18)-C(19)-C(24)	0.2(3)
C(18)-C(19)-C(20)-C(21)	-2.0(5)
C(24)-C(19)-C(20)-C(21)	173.9(3)
C(19)-C(20)-C(21)-C(22)	-1.9(6)
C(20)-C(21)-C(22)-C(23)	2.1(6)
C(21)-C(22)-C(23)-C(18)	1.6(5)
C(21)-C(22)-C(23)-C(27)	-176.3(3)
C(19)-C(18)-C(23)-C(22)	-5.7(4)
N(1)-C(18)-C(23)-C(22)	-175.6(2)
C(19)-C(18)-C(23)-C(27)	172.2(3)
N(1)-C(18)-C(23)-C(27)	2.2(4)
C(20)-C(19)-C(24)-C(26)	-79.3(3)
C(18)-C(19)-C(24)-C(26)	96.4(3)
C(20)-C(19)-C(24)-C(25)	45.6(4)
C(18)-C(19)-C(24)-C(25)	-138.7(3)
C(22)-C(23)-C(27)-C(28)	-54.6(4)
C(18)-C(23)-C(27)-C(28)	127.6(3)
C(22)-C(23)-C(27)-C(29)	66.7(4)
C(18)-C(23)-C(27)-C(29)	-111.1(3)
C(35)-N(2)-C(30)-C(31)	-169.60(18)
C(35)-N(2)-C(30)-P(1)	2.8(3)
C(1)-P(1)-C(30)-N(2)	73.09(16)
C(13)-P(1)-C(30)-N(2)	-170.61(13)
C(1)-P(1)-C(30)-C(31)	-116.04(18)
C(13)-P(1)-C(30)-C(31)	0.3(2)
N(2)-C(30)-C(31)-C(34)	-176.05(19)
P(1)-C(30)-C(31)-C(34)	12.8(3)
N(2)-C(30)-C(31)-C(32)	63.1(2)
P(1)-C(30)-C(31)-C(32)	-108.06(19)
N(2)-C(30)-C(31)-C(33)	-54.1(2)
P(1)-C(30)-C(31)-C(33)	134.69(19)
C(30)-N(2)-C(35)-C(36)	-111.0(2)
C(30)-N(2)-C(35)-C(40)	81.8(2)
C(40)-C(35)-C(36)-C(37)	-0.3(3)
N(2)-C(35)-C(36)-C(37)	-167.40(17)
C(40)-C(35)-C(36)-C(41)	175.59(17)
N(2)-C(35)-C(36)-C(41)	8.5(3)
C(35)-C(36)-C(37)-C(38)	-0.5(3)
C(41)-C(36)-C(37)-C(38)	-176.4(2)
C(36)-C(37)-C(38)-C(39)	0.5(4)
C(37)-C(38)-C(39)-C(40)	0.4(4)
C(38)-C(39)-C(40)-C(35)	-1.2(3)
C(38)-C(39)-C(40)-C(44)	173.9(2)
C(36)-C(35)-C(40)-C(39)	1.1(3)
N(2)-C(35)-C(40)-C(39)	168.02(17)
C(36)-C(35)-C(40)-C(44)	-173.80(17)
N(2)-C(35)-C(40)-C(44)	-6.9(2)
C(37)-C(36)-C(41)-C(43)	82.3(3)
C(35)-C(36)-C(41)-C(43)	-93.6(3)
C(37)-C(36)-C(41)-C(42)	-43.8(3)
C(35)-C(36)-C(41)-C(42)	140.3(2)
C(39)-C(40)-C(44)-C(45)	46.7(3)
C(35)-C(40)-C(44)-C(45)	-138.5(2)
C(39)-C(40)-C(44)-C(46)	-78.6(3)
C(35)-C(40)-C(44)-C(46)	96.2(2)

Symmetry transformations used to generate equivalent atoms:

Table A68. Hydrogen bonds for **98** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Table A69. Crystal data and structure refinement for **100**.

Identification code	**100**	
Empirical formula	C54 H76 N3 P	
Formula weight	798.14	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.0825(10) Å	α= 90°.
	b = 14.1119(9) Å	β= 92.0680(10)°.
	c = 20.0528(12) Å	γ = 90°.
Volume	4830.9(5) $Å^3$	
Z	4	
Density (calculated)	1.097 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	1744	
Crystal size	0.326 x 0.325 x 0.168 mm^3	
Theta range for data collection	1.765 to 27.238°.	
Index ranges	-21<=h<=22, -18<=k<=18, -25<=l<=25	
Reflections collected	67815	
Independent reflections	10777 [R(int) = 0.0362]	
Completeness to theta = 25.250°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.7112	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10777 / 1 / 571	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1188	
R indices (all data)	R1 = 0.0663, wR2 = 0.1313	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.389 and -0.262 e.$Å^{-3}$	

Table A70. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **100**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	3310(1)	2770(1)	4834(1)	25(1)
N(1)	3725(1)	1450(1)	3954(1)	26(1)
N(2)	1862(1)	3544(1)	4645(1)	28(1)
N(3)	644(1)	2656(1)	4046(1)	29(1)
C(1)	3767(1)	1652(1)	4575(1)	26(1)
C(2)	4280(1)	1138(1)	5084(1)	39(1)
C(3)	4198(1)	705(1)	3701(1)	26(1)
C(4)	3932(1)	-234(1)	3686(1)	31(1)

C(5)	4412(1)	-923(1)	3419(1)	38(1)
C(6)	5128(1)	-700(1)	3168(1)	40(1)
C(7)	5373(1)	228(1)	3168(1)	39(1)
C(8)	4919(1)	949(1)	3426(1)	33(1)
C(9)	3139(1)	-516(1)	3941(1)	41(1)
C(10)	3204(2)	-1311(2)	4452(2)	75(1)
C(11)	2580(1)	-768(3)	3368(2)	86(1)
C(12)	5171(4)	1954(5)	3371(2)	34(1)
C(13)	5705(2)	2190(2)	3976(2)	56(1)
C(14)	5603(2)	2201(2)	2746(1)	54(1)
C(12A)	5284(8)	2007(11)	3584(5)	23(2)
C(13A)	6153(4)	2083(5)	3533(4)	50(2)
C(14A)	4878(5)	2612(5)	3049(4)	52(2)
C(15)	1131(1)	1949(1)	3952(1)	29(1)
C(16)	870(1)	1034(1)	3626(1)	42(1)
C(17)	-155(1)	2593(1)	3806(1)	31(1)
C(18)	-735(1)	2375(1)	4260(1)	36(1)
C(19)	-1502(1)	2267(1)	4009(1)	45(1)
C(20)	-1692(1)	2396(2)	3340(1)	52(1)
C(21)	-1122(1)	2666(2)	2913(1)	50(1)
C(22)	-546(1)	2251(1)	4998(1)	42(1)
C(23)	-626(1)	1219(2)	5206(1)	62(1)
C(24)	-1052(1)	2887(2)	5422(1)	53(1)
C(25)	268(1)	3094(2)	2653(1)	51(1)
C(26)	300(2)	2440(2)	2057(1)	92(1)
C(27)	124(2)	4114(2)	2430(2)	91(1)
C(28)	2274(1)	2757(1)	4516(1)	25(1)
C(29)	1931(1)	2002(1)	4175(1)	27(1)
C(30)	2210(1)	4438(1)	4808(1)	27(1)
C(31)	2611(1)	4934(1)	4318(1)	31(1)
C(32)	2957(1)	5795(1)	4495(1)	38(1)
C(33)	2897(1)	6161(1)	5127(1)	41(1)
C(34)	2464(1)	5692(1)	5591(1)	37(1)
C(35)	2103(1)	4828(1)	5443(1)	30(1)
C(36)	2633(1)	4593(1)	3601(1)	41(1)
C(37)	3449(2)	4572(2)	3342(1)	76(1)
C(38)	2099(2)	5213(3)	3166(1)	119(2)
C(39)	1579(1)	4347(1)	5934(1)	36(1)
C(40)	1739(1)	4652(2)	6656(1)	51(1)
C(41)	719(1)	4537(2)	5735(1)	49(1)
C(42)	-344(1)	2778(1)	3134(1)	40(1)
C(43)	3230(1)	2670(1)	5751(1)	28(1)
C(44)	3641(1)	3369(1)	6138(1)	34(1)
C(45)	3586(1)	3345(1)	6828(1)	45(1)
C(46)	3137(1)	2683(2)	7139(1)	51(1)
C(47)	2745(1)	1998(1)	6764(1)	45(1)
C(48)	2793(1)	1966(1)	6072(1)	33(1)
C(49)	4155(1)	4116(1)	5824(1)	39(1)
C(50)	4943(1)	3692(2)	5633(1)	51(1)
C(51)	4307(1)	4989(2)	6265(1)	54(1)
C(52)	2373(1)	1159(1)	5706(1)	35(1)

C(53)	2583(1)	188(1)	6007(1)	51(1)
C(54)	1485(1)	1295(2)	5689(1)	50(1)

Table A71. Bond lengths [Å] and angles [°] for **100**.

P(1)-C(1)	1.8435(15)
P(1)-C(43)	1.8548(16)
P(1)-C(28)	1.8609(15)
N(1)-C(1)	1.2788(19)
N(1)-C(3)	1.4298(18)
N(2)-C(28)	1.3453(19)
N(2)-C(30)	1.4276(19)
N(2)-H(1)	0.90(3)
N(3)-C(15)	1.317(2)
N(3)-C(17)	1.4342(19)
C(1)-C(2)	1.507(2)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.400(2)
C(3)-C(8)	1.409(2)
C(4)-C(5)	1.392(2)
C(4)-C(9)	1.518(2)
C(5)-C(6)	1.376(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.375(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.391(2)
C(7)-H(7)	0.9500
C(8)-C(12)	1.488(7)
C(8)-C(12A)	1.645(14)
C(9)-C(11)	1.510(3)
C(9)-C(10)	1.521(3)
C(9)-H(9)	1.0000
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(14)	1.519(6)
C(12)-C(13)	1.527(4)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(12A)-C(13A)	1.496(16)
C(12A)-C(14A)	1.518(14)
C(12A)-H(12A)	1.0000
C(13A)-H(13D)	0.9800
C(13A)-H(13E)	0.9800
C(13A)-H(13F)	0.9800
C(14A)-H(14D)	0.9800
C(14A)-H(14E)	0.9800
C(14A)-H(14F)	0.9800
C(15)-C(29)	1.424(2)
C(15)-C(16)	1.507(2)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(42)	1.398(2)
C(17)-C(18)	1.403(2)
C(18)-C(19)	1.394(2)
C(18)-C(22)	1.515(3)
C(19)-C(20)	1.380(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.373(3)
C(20)-H(20)	0.9500
C(21)-C(42)	1.393(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.522(3)
C(22)-C(24)	1.525(3)
C(22)-H(22)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(26)	1.513(3)
C(25)-C(42)	1.516(3)
C(25)-C(27)	1.524(3)
C(25)-H(25)	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-C(29)	1.385(2)

C(29)-H(29)	0.9500
C(30)-C(35)	1.404(2)
C(30)-C(31)	1.405(2)
C(31)-C(32)	1.392(2)
C(31)-C(36)	1.517(2)
C(32)-C(33)	1.375(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.378(3)
C(33)-H(33)	0.9500
C(34)-C(35)	1.394(2)
C(34)-H(34)	0.9500
C(35)-C(39)	1.515(2)
C(36)-C(37)	1.506(3)
C(36)-C(38)	1.517(3)
C(36)-H(36)	1.0000
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-C(40)	1.525(2)
C(39)-C(41)	1.533(3)
C(39)-H(39)	1.0000
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(43)-C(48)	1.412(2)
C(43)-C(44)	1.425(2)
C(44)-C(45)	1.390(2)
C(44)-C(49)	1.522(3)
C(45)-C(46)	1.373(3)
C(45)-H(45)	0.9500
C(46)-C(47)	1.383(3)
C(46)-H(46)	0.9500
C(47)-C(48)	1.394(2)
C(47)-H(47)	0.9500
C(48)-C(52)	1.521(2)
C(49)-C(51)	1.533(2)
C(49)-C(50)	1.535(3)
C(49)-H(49)	1.0000
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-C(54)	1.527(3)
C(52)-C(53)	1.534(2)
C(52)-H(52)	1.0000
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(1)-P(1)-C(43)	105.11(7)
C(1)-P(1)-C(28)	107.60(7)
C(43)-P(1)-C(28)	103.63(7)
C(1)-N(1)-C(3)	119.77(12)
C(28)-N(2)-C(30)	123.87(13)
C(28)-N(2)-H(1)	111.0(18)
C(30)-N(2)-H(1)	122.4(18)
C(15)-N(3)-C(17)	120.23(13)
N(1)-C(1)-C(2)	124.34(14)
N(1)-C(1)-P(1)	117.12(11)
C(2)-C(1)-P(1)	117.61(11)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(8)	120.69(14)
C(4)-C(3)-N(1)	121.03(13)
C(8)-C(3)-N(1)	118.14(14)
C(5)-C(4)-C(3)	118.30(15)
C(5)-C(4)-C(9)	119.43(15)
C(3)-C(4)-C(9)	122.27(14)
C(6)-C(5)-C(4)	121.65(16)
C(6)-C(5)-H(5)	119.2
C(4)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	119.48(15)
C(7)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(6)-C(7)-C(8)	121.55(16)
C(6)-C(7)-H(7)	119.2
C(8)-C(7)-H(7)	119.2
C(7)-C(8)-C(3)	118.27(15)
C(7)-C(8)-C(12)	120.2(3)
C(3)-C(8)-C(12)	121.4(3)
C(7)-C(8)-C(12A)	121.5(6)
C(3)-C(8)-C(12A)	118.5(5)
C(11)-C(9)-C(4)	110.69(18)
C(11)-C(9)-C(10)	111.5(2)
C(4)-C(9)-C(10)	112.10(16)
C(11)-C(9)-H(9)	107.4
C(4)-C(9)-H(9)	107.4
C(10)-C(9)-H(9)	107.4

C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-C(14)	115.5(4)
C(8)-C(12)-C(13)	108.3(4)
C(14)-C(12)-C(13)	108.2(4)
C(8)-C(12)-H(12)	108.2
C(14)-C(12)-H(12)	108.2
C(13)-C(12)-H(12)	108.2
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13A)-C(12A)-C(14A)	110.0(10)
C(13A)-C(12A)-C(8)	115.0(10)
C(14A)-C(12A)-C(8)	102.4(6)
C(13A)-C(12A)-H(12A)	109.7
C(14A)-C(12A)-H(12A)	109.7
C(8)-C(12A)-H(12A)	109.7
C(12A)-C(13A)-H(13D)	109.5
C(12A)-C(13A)-H(13E)	109.5
H(13D)-C(13A)-H(13E)	109.5
C(12A)-C(13A)-H(13F)	109.5
H(13D)-C(13A)-H(13F)	109.5
H(13E)-C(13A)-H(13F)	109.5
C(12A)-C(14A)-H(14D)	109.5
C(12A)-C(14A)-H(14E)	109.5
H(14D)-C(14A)-H(14E)	109.5
C(12A)-C(14A)-H(14F)	109.5
H(14D)-C(14A)-H(14F)	109.5
H(14E)-C(14A)-H(14F)	109.5
N(3)-C(15)-C(29)	121.28(14)
N(3)-C(15)-C(16)	122.20(14)
C(29)-C(15)-C(16)	116.49(14)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(42)-C(17)-C(18)	121.45(15)
C(42)-C(17)-N(3)	119.75(15)
C(18)-C(17)-N(3)	118.77(14)
C(19)-C(18)-C(17)	117.79(17)
C(19)-C(18)-C(22)	120.32(16)
C(17)-C(18)-C(22)	121.89(15)
C(20)-C(19)-C(18)	121.33(18)
C(20)-C(19)-H(19)	119.3
C(18)-C(19)-H(19)	119.3
C(21)-C(20)-C(19)	119.72(17)
C(21)-C(20)-H(20)	120.1
C(19)-C(20)-H(20)	120.1
C(20)-C(21)-C(42)	121.48(19)
C(20)-C(21)-H(21)	119.3
C(42)-C(21)-H(21)	119.3
C(18)-C(22)-C(23)	111.08(17)
C(18)-C(22)-C(24)	111.82(15)
C(23)-C(22)-C(24)	110.59(17)
C(18)-C(22)-H(22)	107.7
C(23)-C(22)-H(22)	107.7
C(24)-C(22)-H(22)	107.7
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-C(42)	111.6(2)
C(26)-C(25)-C(27)	110.7(2)
C(42)-C(25)-C(27)	110.94(18)
C(26)-C(25)-H(25)	107.8
C(42)-C(25)-H(25)	107.8
C(27)-C(25)-H(25)	107.8
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

C(25)-C(27)-H(27A)	109.5	C(35)-C(39)-H(39)	107.9
C(25)-C(27)-H(27B)	109.5	C(40)-C(39)-H(39)	107.9
H(27A)-C(27)-H(27B)	109.5	C(41)-C(39)-H(39)	107.9
C(25)-C(27)-H(27C)	109.5	C(39)-C(40)-H(40A)	109.5
H(27A)-C(27)-H(27C)	109.5	C(39)-C(40)-H(40B)	109.5
H(27B)-C(27)-H(27C)	109.5	H(40A)-C(40)-H(40B)	109.5
N(2)-C(28)-C(29)	121.04(13)	C(39)-C(40)-H(40C)	109.5
N(2)-C(28)-P(1)	115.07(11)	H(40A)-C(40)-H(40C)	109.5
C(29)-C(28)-P(1)	123.89(11)	H(40B)-C(40)-H(40C)	109.5
C(28)-C(29)-C(15)	125.41(13)	C(39)-C(41)-H(41A)	109.5
C(28)-C(29)-H(29)	117.3	C(39)-C(41)-H(41B)	109.5
C(15)-C(29)-H(29)	117.3	H(41A)-C(41)-H(41B)	109.5
C(35)-C(30)-C(31)	121.47(14)	C(39)-C(41)-H(41C)	109.5
C(35)-C(30)-N(2)	119.18(14)	H(41A)-C(41)-H(41C)	109.5
C(31)-C(30)-N(2)	119.24(14)	H(41B)-C(41)-H(41C)	109.5
C(32)-C(31)-C(30)	117.99(15)	C(21)-C(42)-C(17)	117.99(17)
C(32)-C(31)-C(36)	119.57(15)	C(21)-C(42)-C(25)	120.19(17)
C(30)-C(31)-C(36)	122.32(15)	C(17)-C(42)-C(25)	121.82(16)
C(33)-C(32)-C(31)	121.16(16)	C(48)-C(43)-C(44)	119.82(14)
C(33)-C(32)-H(32)	119.4	C(48)-C(43)-P(1)	124.38(12)
C(31)-C(32)-H(32)	119.4	C(44)-C(43)-P(1)	115.79(12)
C(32)-C(33)-C(34)	120.13(16)	C(45)-C(44)-C(43)	118.42(17)
C(32)-C(33)-H(33)	119.9	C(45)-C(44)-C(49)	119.29(15)
C(34)-C(33)-H(33)	119.9	C(43)-C(44)-C(49)	122.26(15)
C(33)-C(34)-C(35)	121.35(16)	C(46)-C(45)-C(44)	121.78(17)
C(33)-C(34)-H(34)	119.3	C(46)-C(45)-H(45)	119.1
C(35)-C(34)-H(34)	119.3	C(44)-C(45)-H(45)	119.1
C(34)-C(35)-C(30)	117.67(15)	C(45)-C(46)-C(47)	119.82(17)
C(34)-C(35)-C(39)	121.40(15)	C(45)-C(46)-H(46)	120.1
C(30)-C(35)-C(39)	120.86(14)	C(47)-C(46)-H(46)	120.1
C(37)-C(36)-C(38)	111.0(2)	C(46)-C(47)-C(48)	121.24(18)
C(37)-C(36)-C(31)	112.81(16)	C(46)-C(47)-H(47)	119.4
C(38)-C(36)-C(31)	109.12(17)	C(48)-C(47)-H(47)	119.4
C(37)-C(36)-H(36)	107.9	C(47)-C(48)-C(43)	118.84(16)
C(38)-C(36)-H(36)	107.9	C(47)-C(48)-C(52)	117.41(16)
C(31)-C(36)-H(36)	107.9	C(43)-C(48)-C(52)	123.74(14)
C(36)-C(37)-H(37A)	109.5	C(44)-C(49)-C(51)	114.00(16)
C(36)-C(37)-H(37B)	109.5	C(44)-C(49)-C(50)	110.96(15)
H(37A)-C(37)-H(37B)	109.5	C(51)-C(49)-C(50)	108.96(15)
C(36)-C(37)-H(37C)	109.5	C(44)-C(49)-H(49)	107.6
H(37A)-C(37)-H(37C)	109.5	C(51)-C(49)-H(49)	107.6
H(37B)-C(37)-H(37C)	109.5	C(50)-C(49)-H(49)	107.6
C(36)-C(38)-H(38A)	109.5	C(49)-C(50)-H(50A)	109.5
C(36)-C(38)-H(38B)	109.5	C(49)-C(50)-H(50B)	109.5
H(38A)-C(38)-H(38B)	109.5	H(50A)-C(50)-H(50B)	109.5
C(36)-C(38)-H(38C)	109.5	C(49)-C(50)-H(50C)	109.5
H(38A)-C(38)-H(38C)	109.5	H(50A)-C(50)-H(50C)	109.5
H(38B)-C(38)-H(38C)	109.5	H(50B)-C(50)-H(50C)	109.5
C(35)-C(39)-C(40)	113.64(15)	C(49)-C(51)-H(51A)	109.5
C(35)-C(39)-C(41)	109.65(14)	C(49)-C(51)-H(51B)	109.5
C(40)-C(39)-C(41)	109.60(15)	H(51A)-C(51)-H(51B)	109.5

C(49)-C(51)-H(51C)	109.5	H(53A)-C(53)-H(53B)	109.5
H(51A)-C(51)-H(51C)	109.5	C(52)-C(53)-H(53C)	109.5
H(51B)-C(51)-H(51C)	109.5	H(53A)-C(53)-H(53C)	109.5
C(48)-C(52)-C(54)	111.56(15)	H(53B)-C(53)-H(53C)	109.5
C(48)-C(52)-C(53)	112.27(15)	C(52)-C(54)-H(54A)	109.5
C(54)-C(52)-C(53)	109.84(16)	C(52)-C(54)-H(54B)	109.5
C(48)-C(52)-H(52)	107.7	H(54A)-C(54)-H(54B)	109.5
C(54)-C(52)-H(52)	107.7	C(52)-C(54)-H(54C)	109.5
C(53)-C(52)-H(52)	107.7	H(54A)-C(54)-H(54C)	109.5
C(52)-C(53)-H(53A)	109.5	H(54B)-C(54)-H(54C)	109.5
C(52)-C(53)-H(53B)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table A72. Anisotropic displacement parameters (Å^{2}x 10^3) for **100**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	24(1)	25(1)	25(1)	-3(1)	-1(1)	3(1)
N(1)	25(1)	25(1)	27(1)	-1(1)	2(1)	3(1)
N(2)	24(1)	25(1)	36(1)	-6(1)	-1(1)	2(1)
N(3)	26(1)	30(1)	32(1)	-2(1)	0(1)	2(1)
C(1)	24(1)	25(1)	28(1)	0(1)	0(1)	2(1)
C(2)	43(1)	45(1)	28(1)	1(1)	-2(1)	18(1)
C(3)	29(1)	28(1)	22(1)	-1(1)	-1(1)	5(1)
C(4)	32(1)	31(1)	30(1)	-4(1)	0(1)	3(1)
C(5)	44(1)	28(1)	41(1)	-9(1)	2(1)	3(1)
C(6)	45(1)	38(1)	38(1)	-10(1)	7(1)	11(1)
C(7)	36(1)	44(1)	38(1)	2(1)	13(1)	7(1)
C(8)	34(1)	32(1)	33(1)	2(1)	6(1)	3(1)
C(9)	35(1)	29(1)	59(1)	-6(1)	6(1)	-2(1)
C(10)	61(2)	64(2)	100(2)	30(1)	28(1)	-1(1)
C(11)	40(1)	131(3)	87(2)	-20(2)	-11(1)	-10(1)
C(12)	32(2)	34(2)	35(3)	-1(2)	-1(2)	-2(1)
C(13)	76(2)	45(2)	47(2)	0(1)	-5(2)	-20(2)
C(14)	62(2)	57(2)	45(2)	16(1)	5(1)	-15(1)
C(12A)	26(5)	25(3)	17(5)	-6(4)	-3(4)	-7(3)
C(13A)	32(3)	45(4)	72(5)	-10(4)	8(3)	-9(3)
C(14A)	62(5)	33(4)	60(5)	10(3)	-12(4)	-12(3)
C(15)	31(1)	28(1)	28(1)	-2(1)	0(1)	0(1)
C(16)	39(1)	31(1)	53(1)	-11(1)	-10(1)	3(1)
C(17)	28(1)	27(1)	39(1)	-5(1)	-4(1)	3(1)
C(18)	30(1)	31(1)	47(1)	-1(1)	-2(1)	1(1)
C(19)	31(1)	44(1)	61(1)	-3(1)	-1(1)	-1(1)
C(20)	33(1)	56(1)	65(1)	-15(1)	-15(1)	4(1)
C(21)	45(1)	60(1)	44(1)	-11(1)	-15(1)	11(1)
C(22)	31(1)	47(1)	47(1)	9(1)	0(1)	0(1)
C(23)	62(1)	52(1)	72(2)	19(1)	3(1)	3(1)

C(24)	49(1)	65(1)	46(1)	1(1)	2(1)	4(1)
C(25)	48(1)	69(1)	35(1)	3(1)	1(1)	12(1)
C(26)	130(3)	87(2)	60(2)	-10(2)	33(2)	13(2)
C(27)	112(2)	65(2)	99(2)	9(2)	52(2)	9(2)
C(28)	25(1)	28(1)	22(1)	0(1)	1(1)	3(1)
C(29)	27(1)	25(1)	29(1)	-3(1)	0(1)	4(1)
C(30)	25(1)	24(1)	32(1)	-3(1)	-2(1)	2(1)
C(31)	29(1)	32(1)	33(1)	-1(1)	1(1)	2(1)
C(32)	36(1)	33(1)	45(1)	2(1)	3(1)	-5(1)
C(33)	42(1)	28(1)	52(1)	-7(1)	-3(1)	-4(1)
C(34)	42(1)	32(1)	36(1)	-10(1)	-2(1)	3(1)
C(35)	30(1)	27(1)	31(1)	-2(1)	-2(1)	6(1)
C(36)	48(1)	41(1)	34(1)	-3(1)	6(1)	-4(1)
C(37)	74(2)	101(2)	56(1)	-23(1)	32(1)	-25(2)
C(38)	159(3)	150(3)	45(2)	-23(2)	-33(2)	82(3)
C(39)	42(1)	34(1)	33(1)	-1(1)	7(1)	5(1)
C(40)	60(1)	59(1)	35(1)	-2(1)	9(1)	5(1)
C(41)	40(1)	58(1)	49(1)	-1(1)	9(1)	-1(1)
C(42)	38(1)	44(1)	37(1)	-8(1)	-4(1)	8(1)
C(43)	28(1)	32(1)	25(1)	-3(1)	-3(1)	7(1)
C(44)	34(1)	35(1)	32(1)	-7(1)	-7(1)	9(1)
C(45)	58(1)	44(1)	32(1)	-11(1)	-12(1)	7(1)
C(46)	74(1)	55(1)	24(1)	-5(1)	-2(1)	10(1)
C(47)	57(1)	50(1)	30(1)	4(1)	5(1)	5(1)
C(48)	36(1)	35(1)	28(1)	0(1)	0(1)	7(1)
C(49)	36(1)	36(1)	43(1)	-8(1)	-10(1)	-1(1)
C(50)	37(1)	54(1)	63(1)	-11(1)	-5(1)	-3(1)
C(51)	57(1)	44(1)	59(1)	-16(1)	-17(1)	-3(1)
C(52)	39(1)	36(1)	32(1)	3(1)	3(1)	-1(1)
C(53)	70(1)	39(1)	45(1)	8(1)	0(1)	-4(1)
C(54)	41(1)	62(1)	47(1)	2(1)	7(1)	-6(1)

Table A73. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{3}) for **100**.

	x	y	z	U(eq)
H(1)	1366(16)	3491(19)	4489(13)	83(8)
H(2A)	3973	646	5301	59
H(2B)	4480	1588	5421	59
H(2C)	4720	844	4863	59
H(5)	4241	-1564	3410	45
H(6)	5451	-1184	2995	48
H(7)	5864	381	2987	47
H(9)	2919	49	4170	49
H(10A)	2693	-1413	4648	112
H(10B)	3590	-1139	4804	112
H(10C)	3371	-1895	4233	112

H(11A)	2526	-228	3064	130
H(11B)	2067	-926	3542	130
H(11C)	2783	-1315	3128	130
H(12)	4695	2365	3386	41
H(13A)	5877	2851	3947	85
H(13B)	5417	2099	4385	85
H(13C)	6162	1771	3982	85
H(14A)	5744	2875	2755	82
H(14B)	6080	1817	2727	82
H(14C)	5265	2072	2351	82
H(12A)	5127	2223	4035	27
H(13D)	6411	1691	3879	75
H(13E)	6305	1863	3093	75
H(13F)	6313	2745	3594	75
H(14D)	4309	2558	3086	78
H(14E)	5035	3275	3110	78
H(14F)	5026	2393	2608	78
H(16A)	303	1052	3534	62
H(16B)	1000	503	3924	62
H(16C)	1139	953	3206	62
H(19)	-1903	2102	4304	55
H(20)	-2214	2298	3176	62
H(21)	-1261	2780	2457	60
H(22)	13	2441	5083	50
H(23A)	-1174	1021	5146	93
H(23B)	-459	1149	5676	93
H(23C)	-297	822	4930	93
H(24A)	-986	3548	5286	80
H(24B)	-891	2816	5894	80
H(24C)	-1603	2703	5359	80
H(25)	790	3071	2895	61
H(26A)	312	1781	2210	138
H(26B)	774	2574	1812	138
H(26C)	-163	2542	1764	138
H(27A)	543	4314	2140	136
H(27B)	117	4528	2822	136
H(27C)	-381	4155	2184	136
H(29)	2256	1476	4081	32
H(32)	3239	6136	4174	46
H(33)	3154	6737	5243	49
H(34)	2410	5965	6020	44
H(36)	2421	3932	3584	49
H(37A)	3648	5221	3309	114
H(37B)	3438	4275	2900	114
H(37C)	3792	4206	3648	114
H(38A)	1560	5162	3316	178
H(38B)	2118	5003	2701	178
H(38C)	2272	5873	3201	178
H(39)	1670	3649	5906	44
H(40A)	2299	4579	6771	76
H(40B)	1434	4254	6952	76

H(40C)	1588	5316	6709	76
H(41A)	614	5219	5759	73
H(41B)	381	4201	6041	73
H(41C)	611	4313	5279	73
H(45)	3867	3800	7092	54
H(46)	3097	2694	7610	61
H(47)	2437	1540	6982	54
H(49)	3878	4335	5404	46
H(50A)	5206	3415	6029	77
H(50B)	5273	4191	5452	77
H(50C)	4853	3198	5295	77
H(51A)	3809	5229	6424	81
H(51B)	4561	5483	6004	81
H(51C)	4650	4815	6648	81
H(52)	2545	1162	5234	42
H(53A)	2369	139	6453	77
H(53B)	3154	120	6041	77
H(53C)	2360	-313	5720	77
H(54A)	1293	1229	6141	74
H(54B)	1238	815	5398	74
H(54C)	1356	1928	5516	74

Table A74. Torsion angles [°] for **100**.

C(3)-N(1)-C(1)-C(2)	-1.5(2)
C(3)-N(1)-C(1)-P(1)	167.15(11)
C(43)-P(1)-C(1)-N(1)	164.36(12)
C(28)-P(1)-C(1)-N(1)	54.38(13)
C(43)-P(1)-C(1)-C(2)	-26.22(14)
C(28)-P(1)-C(1)-C(2)	-136.21(12)
C(1)-N(1)-C(3)-C(4)	88.71(18)
C(1)-N(1)-C(3)-C(8)	-95.44(17)
C(8)-C(3)-C(4)-C(5)	2.7(2)
N(1)-C(3)-C(4)-C(5)	178.41(14)
C(8)-C(3)-C(4)-C(9)	-176.50(15)
N(1)-C(3)-C(4)-C(9)	-0.8(2)
C(3)-C(4)-C(5)-C(6)	-0.6(3)
C(9)-C(4)-C(5)-C(6)	178.55(17)
C(4)-C(5)-C(6)-C(7)	-1.2(3)
C(5)-C(6)-C(7)-C(8)	1.0(3)
C(6)-C(7)-C(8)-C(3)	0.9(3)
C(6)-C(7)-C(8)-C(12)	-175.2(2)
C(6)-C(7)-C(8)-C(12A)	166.0(4)
C(4)-C(3)-C(8)-C(7)	-2.8(2)
N(1)-C(3)-C(8)-C(7)	-178.68(14)
C(4)-C(3)-C(8)-C(12)	173.3(2)
N(1)-C(3)-C(8)-C(12)	-2.6(3)
C(4)-C(3)-C(8)-C(12A)	-168.3(4)
N(1)-C(3)-C(8)-C(12A)	15.8(5)
C(5)-C(4)-C(9)-C(11)	-71.0(2)
C(3)-C(4)-C(9)-C(11)	108.2(2)
C(5)-C(4)-C(9)-C(10)	54.2(2)
C(3)-C(4)-C(9)-C(10)	-126.6(2)
C(7)-C(8)-C(12)-C(14)	33.4(5)
C(3)-C(8)-C(12)-C(14)	-142.6(3)
C(7)-C(8)-C(12)-C(13)	-88.1(4)
C(3)-C(8)-C(12)-C(13)	95.9(4)
C(7)-C(8)-C(12A)-C(13A)	-9.4(9)
C(3)-C(8)-C(12A)-C(13A)	155.6(6)
C(7)-C(8)-C(12A)-C(14A)	109.8(8)
C(3)-C(8)-C(12A)-C(14A)	-85.1(8)
C(17)-N(3)-C(15)-C(29)	178.74(14)
C(17)-N(3)-C(15)-C(16)	-3.2(2)
C(15)-N(3)-C(17)-C(42)	-80.7(2)
C(15)-N(3)-C(17)-C(18)	101.29(18)
C(42)-C(17)-C(18)-C(19)	5.4(2)
N(3)-C(17)-C(18)-C(19)	-176.67(15)
C(42)-C(17)-C(18)-C(22)	-174.98(16)
N(3)-C(17)-C(18)-C(22)	3.0(2)
C(17)-C(18)-C(19)-C(20)	-1.7(3)
C(22)-C(18)-C(19)-C(20)	178.62(18)
C(18)-C(19)-C(20)-C(21)	-2.2(3)
C(19)-C(20)-C(21)-C(42)	2.7(3)
C(19)-C(18)-C(22)-C(23)	69.7(2)

C(17)-C(18)-C(22)-C(23)	-109.94(19)
C(19)-C(18)-C(22)-C(24)	-54.4(2)
C(17)-C(18)-C(22)-C(24)	125.98(18)
C(30)-N(2)-C(28)-C(29)	-160.65(15)
C(30)-N(2)-C(28)-P(1)	19.84(19)
C(1)-P(1)-C(28)-N(2)	-177.92(11)
C(43)-P(1)-C(28)-N(2)	71.08(12)
C(1)-P(1)-C(28)-C(29)	2.59(15)
C(43)-P(1)-C(28)-C(29)	-108.41(13)
N(2)-C(28)-C(29)-C(15)	-2.6(2)
P(1)-C(28)-C(29)-C(15)	176.83(12)
N(3)-C(15)-C(29)-C(28)	1.7(2)
C(16)-C(15)-C(29)-C(28)	-176.49(16)
C(28)-N(2)-C(30)-C(35)	-115.47(17)
C(28)-N(2)-C(30)-C(31)	68.3(2)
C(35)-C(30)-C(31)-C(32)	5.0(2)
N(2)-C(30)-C(31)-C(32)	-178.86(14)
C(35)-C(30)-C(31)-C(36)	-170.98(15)
N(2)-C(30)-C(31)-C(36)	5.1(2)
C(30)-C(31)-C(32)-C(33)	-1.2(2)
C(36)-C(31)-C(32)-C(33)	174.95(16)
C(31)-C(32)-C(33)-C(34)	-2.5(3)
C(32)-C(33)-C(34)-C(35)	2.4(3)
C(33)-C(34)-C(35)-C(30)	1.3(2)
C(33)-C(34)-C(35)-C(39)	-175.50(16)
C(31)-C(30)-C(35)-C(34)	-5.1(2)
N(2)-C(30)-C(35)-C(34)	178.80(14)
C(31)-C(30)-C(35)-C(39)	171.76(14)
N(2)-C(30)-C(35)-C(39)	-4.4(2)
C(32)-C(31)-C(36)-C(37)	53.6(2)
C(30)-C(31)-C(36)-C(37)	-130.5(2)
C(32)-C(31)-C(36)-C(38)	-70.3(3)
C(30)-C(31)-C(36)-C(38)	105.7(3)
C(34)-C(35)-C(39)-C(40)	-23.0(2)
C(30)-C(35)-C(39)-C(40)	160.24(15)
C(34)-C(35)-C(39)-C(41)	99.98(18)
C(30)-C(35)-C(39)-C(41)	-76.73(19)
C(20)-C(21)-C(42)-C(17)	0.9(3)
C(20)-C(21)-C(42)-C(25)	-178.88(19)
C(18)-C(17)-C(42)-C(21)	-5.0(3)
N(3)-C(17)-C(42)-C(21)	177.09(16)
C(18)-C(17)-C(42)-C(25)	174.78(17)
N(3)-C(17)-C(42)-C(25)	-3.2(2)
C(26)-C(25)-C(42)-C(21)	-56.5(3)
C(27)-C(25)-C(42)-C(21)	67.5(3)
C(26)-C(25)-C(42)-C(17)	123.8(2)
C(27)-C(25)-C(42)-C(17)	-112.2(2)
C(1)-P(1)-C(43)-C(48)	-61.06(14)
C(28)-P(1)-C(43)-C(48)	51.76(14)
C(1)-P(1)-C(43)-C(44)	119.45(12)
C(28)-P(1)-C(43)-C(44)	-127.73(12)
C(48)-C(43)-C(44)-C(45)	-1.1(2)
P(1)-C(43)-C(44)-C(45)	178.38(13)
C(48)-C(43)-C(44)-C(49)	176.86(14)
P(1)-C(43)-C(44)-C(49)	-3.6(2)
C(43)-C(44)-C(45)-C(46)	-1.4(3)
C(49)-C(44)-C(45)-C(46)	-179.43(17)
C(44)-C(45)-C(46)-C(47)	2.1(3)
C(45)-C(46)-C(47)-C(48)	-0.2(3)
C(46)-C(47)-C(48)-C(43)	-2.3(3)
C(46)-C(47)-C(48)-C(52)	177.13(17)
C(44)-C(43)-C(48)-C(47)	2.9(2)
P(1)-C(43)-C(48)-C(47)	-176.58(13)
C(44)-C(43)-C(48)-C(52)	-176.45(14)
P(1)-C(43)-C(48)-C(52)	4.1(2)
C(45)-C(44)-C(49)-C(51)	-22.5(2)
C(43)-C(44)-C(49)-C(51)	159.54(15)
C(45)-C(44)-C(49)-C(50)	100.99(19)
C(43)-C(44)-C(49)-C(50)	-77.0(2)
C(47)-C(48)-C(52)-C(54)	72.7(2)
C(43)-C(48)-C(52)-C(54)	-107.89(18)
C(47)-C(48)-C(52)-C(53)	-51.0(2)
C(43)-C(48)-C(52)-C(53)	128.32(17)

Symmetry transformations used to generate equivalent atoms:

Table A75. Hydrogen bonds for **100** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(1)...N(3)	0.90(3)	1.90(3)	2.6757(18)	144(2)
C(29)-H(29)...N(1)	0.95	2.53	3.2088(19)	128.4

Symmetry transformations used to generate equivalent atoms:

Table A76. Crystal data and structure refinement for **101**.

Identification code	**101**	
Empirical formula	C52 H74 N2 P2	
Formula weight	789.07	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.2410(15) Å	α= 90°.
	b = 12.8371(9) Å	β= 117.5930(10)°.
	c = 19.073(2) Å	γ = 90°.
Volume	4826.1(7) Å^3	
Z	4	
Density (calculated)	1.086 Mg/m^3	
Absorption coefficient	0.125 mm^{-1}	
F(000)	1720	
Crystal size	0.274 x 0.211 x 0.072 mm^3	
Theta range for data collection	1.893 to 27.438°.	
Index ranges	-28<=h<=28, -16<=k<=16, -24<=l<=24	
Reflections collected	34286	
Independent reflections	5497 [R(int) = 0.0584]	
Completeness to theta = 25.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6955	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5497 / 210 / 262	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0660, wR2 = 0.1776	
R indices (all data)	R1 = 0.1009, wR2 = 0.2031	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.758 and -0.560 e.Å^{-3}	

Table A77. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **101**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	10402(1)	9718(1)	3134(1)	30(1)
N(1)	9740(1)	8008(2)	3063(1)	30(1)
C(1)	9956(1)	8859(2)	3503(1)	27(1)
C(2)	9918(2)	9032(2)	4220(2)	45(1)
C(3)	10480(1)	10914(2)	3697(1)	30(1)
C(4)	9954(1)	11598(2)	3605(2)	31(1)
C(5)	10115(2)	12446(2)	4121(2)	40(1)
C(6)	10757(2)	12624(2)	4700(2)	45(1)

C(7)	11272(2)	11966(2)	4781(2)	44(1)
C(8)	11156(1)	11110(2)	4285(2)	36(1)
C(9)	11755(2)	10418(3)	4413(2)	49(1)
C(10)	12408(2)	11031(4)	4624(3)	76(1)
C(11)	11867(2)	9588(3)	5015(3)	74(1)
C(12)	9224(1)	11477(2)	2984(2)	40(1)
C(13)	8990(2)	12427(3)	2434(2)	54(1)
C(14)	8751(2)	11296(3)	3352(2)	59(1)
C(15)	9440(1)	7152(2)	3260(1)	32(1)
C(16)	9838(2)	6282(2)	3632(2)	40(1)
C(17)	9518(2)	5429(2)	3771(2)	55(1)
C(18)	8834(2)	5437(2)	3537(2)	59(1)
C(19)	8450(2)	6296(3)	3168(2)	55(1)
C(20)	8741(1)	7172(2)	3016(2)	41(1)
C(21)	10589(2)	6269(2)	3871(2)	53(1)
C(22)	10822(2)	5311(4)	3604(3)	93(2)
C(23)	11010(2)	6431(5)	4748(3)	100(2)
C(24)	8310(1)	8095(3)	2568(2)	49(1)
C(25)	7910(2)	7836(4)	1683(2)	77(1)
C(26)	7837(2)	8462(3)	2887(3)	73(1)

Table A78. Bond lengths [Å] and angles [°] for **101**.

P(1)-C(1)	1.827(2)
P(1)-C(3)	1.835(2)
P(1)-P(1)#1	2.2456(13)
N(1)-C(1)	1.325(3)
N(1)-C(15)	1.424(3)
C(1)-C(2)	1.424(4)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.408(3)
C(3)-C(8)	1.420(4)
C(4)-C(5)	1.398(3)
C(4)-C(12)	1.510(4)
C(5)-C(6)	1.360(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.373(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.394(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.525(4)
C(9)-C(11)	1.500(5)
C(9)-C(10)	1.532(5)
C(9)-H(9)	1.0000
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(14)	1.529(4)
C(12)-C(13)	1.533(4)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.398(4)
C(15)-C(20)	1.400(4)
C(16)-C(17)	1.397(4)
C(16)-C(21)	1.515(4)
C(17)-C(18)	1.372(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.373(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.393(4)
C(19)-H(19)	0.9500
C(20)-C(24)	1.515(4)
C(21)-C(23)	1.505(5)
C(21)-C(22)	1.512(5)
C(21)-H(21)	1.0000

C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(26)	1.514(5)
C(24)-C(25)	1.535(5)
C(24)-H(24)	1.0000
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(1)-P(1)-C(3)	101.65(11)
C(1)-P(1)-P(1)#1	96.45(8)
C(3)-P(1)-P(1)#1	116.30(8)
C(1)-N(1)-C(15)	123.0(2)
N(1)-C(1)-C(2)	124.9(2)
N(1)-C(1)-P(1)	110.76(17)
C(2)-C(1)-P(1)	123.96(19)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(8)	120.1(2)
C(4)-C(3)-P(1)	126.91(19)
C(8)-C(3)-P(1)	112.94(18)
C(5)-C(4)-C(3)	118.1(2)
C(5)-C(4)-C(12)	117.7(2)
C(3)-C(4)-C(12)	124.3(2)
C(6)-C(5)-C(4)	122.2(3)
C(6)-C(5)-H(5)	118.9
C(4)-C(5)-H(5)	118.9
C(5)-C(6)-C(7)	119.8(3)
C(5)-C(6)-H(6)	120.1
C(7)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	121.6(3)
C(6)-C(7)-H(7)	119.2
C(8)-C(7)-H(7)	119.2
C(7)-C(8)-C(3)	118.2(2)
C(7)-C(8)-C(9)	118.5(2)
C(3)-C(8)-C(9)	123.3(2)
C(11)-C(9)-C(8)	111.1(3)
C(11)-C(9)-C(10)	111.3(3)
C(8)-C(9)-C(10)	113.2(3)
C(11)-C(9)-H(9)	107.0
C(8)-C(9)-H(9)	107.0
C(10)-C(9)-H(9)	107.0
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(4)-C(12)-C(14)	112.0(2)
C(4)-C(12)-C(13)	110.8(2)
C(14)-C(12)-C(13)	110.3(2)
C(4)-C(12)-H(12)	107.9
C(14)-C(12)-H(12)	107.9
C(13)-C(12)-H(12)	107.9
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(20)	121.8(2)
C(16)-C(15)-N(1)	119.1(2)
C(20)-C(15)-N(1)	118.9(2)
C(17)-C(16)-C(15)	117.7(3)
C(17)-C(16)-C(21)	121.5(3)
C(15)-C(16)-C(21)	120.8(2)
C(18)-C(17)-C(16)	121.2(3)
C(18)-C(17)-H(17)	119.4
C(16)-C(17)-H(17)	119.4
C(17)-C(18)-C(19)	120.3(3)
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-H(18)	119.8
C(18)-C(19)-C(20)	121.1(3)
C(18)-C(19)-H(19)	119.4
C(20)-C(19)-H(19)	119.4
C(19)-C(20)-C(15)	117.9(3)
C(19)-C(20)-C(24)	121.0(3)
C(15)-C(20)-C(24)	121.1(2)
C(23)-C(21)-C(22)	110.7(3)
C(23)-C(21)-C(16)	111.4(3)

C(22)-C(21)-C(16)	114.2(3)	C(26)-C(24)-C(25)	110.6(3)
C(23)-C(21)-H(21)	106.7	C(20)-C(24)-C(25)	110.1(3)
C(22)-C(21)-H(21)	106.7	C(26)-C(24)-H(24)	107.6
C(16)-C(21)-H(21)	106.7	C(20)-C(24)-H(24)	107.6
C(21)-C(22)-H(22A)	109.5	C(25)-C(24)-H(24)	107.6
C(21)-C(22)-H(22B)	109.5	C(24)-C(25)-H(25A)	109.5
H(22A)-C(22)-H(22B)	109.5	C(24)-C(25)-H(25B)	109.5
C(21)-C(22)-H(22C)	109.5	H(25A)-C(25)-H(25B)	109.5
H(22A)-C(22)-H(22C)	109.5	C(24)-C(25)-H(25C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(25A)-C(25)-H(25C)	109.5
C(21)-C(23)-H(23A)	109.5	H(25B)-C(25)-H(25C)	109.5
C(21)-C(23)-H(23B)	109.5	C(24)-C(26)-H(26A)	109.5
H(23A)-C(23)-H(23B)	109.5	C(24)-C(26)-H(26B)	109.5
C(21)-C(23)-H(23C)	109.5	H(26A)-C(26)-H(26B)	109.5
H(23A)-C(23)-H(23C)	109.5	C(24)-C(26)-H(26C)	109.5
H(23B)-C(23)-H(23C)	109.5	H(26A)-C(26)-H(26C)	109.5
C(26)-C(24)-C(20)	113.1(3)	H(26B)-C(26)-H(26C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table A79. Anisotropic displacement parameters (Å^{2}x 10^3) for **101**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	29(1)	28(1)	32(1)	0(1)	12(1)	-2(1)
N(1)	32(1)	27(1)	30(1)	3(1)	14(1)	-1(1)
C(1)	24(1)	26(1)	27(1)	5(1)	10(1)	-1(1)
C(2)	60(2)	41(2)	46(2)	-8(1)	34(2)	-16(1)
C(3)	35(1)	28(1)	29(1)	-5(1)	16(1)	-3(1)
C(4)	38(1)	26(1)	33(1)	0(1)	20(1)	-1(1)
C(5)	58(2)	27(1)	43(2)	-4(1)	30(1)	0(1)
C(6)	68(2)	33(1)	39(2)	-11(1)	28(1)	-14(1)
C(7)	46(2)	47(2)	35(1)	-9(1)	14(1)	-19(1)
C(8)	33(1)	41(1)	32(1)	-5(1)	14(1)	-7(1)
C(9)	31(1)	59(2)	43(2)	-9(1)	5(1)	0(1)
C(10)	43(2)	93(3)	87(3)	14(2)	26(2)	1(2)
C(11)	62(2)	62(2)	95(3)	11(2)	34(2)	10(2)
C(12)	37(1)	40(1)	46(2)	-9(1)	20(1)	7(1)
C(13)	57(2)	56(2)	45(2)	0(1)	21(2)	24(2)
C(14)	38(2)	68(2)	77(2)	-3(2)	32(2)	3(2)
C(15)	40(1)	28(1)	26(1)	0(1)	13(1)	-6(1)
C(16)	51(2)	29(1)	39(2)	1(1)	19(1)	-1(1)
C(17)	75(2)	30(1)	54(2)	6(1)	25(2)	-6(1)
C(18)	70(2)	42(2)	56(2)	3(1)	22(2)	-24(2)
C(19)	46(2)	56(2)	49(2)	2(1)	11(2)	-25(1)
C(20)	39(2)	40(1)	35(1)	2(1)	10(1)	-11(1)
C(21)	57(2)	40(2)	62(2)	17(1)	29(2)	13(1)

C(22)	79(3)	104(3)	86(3)	-17(3)	30(3)	34(3)
C(23)	53(2)	150(5)	78(3)	-40(3)	14(2)	5(3)
C(24)	28(1)	55(2)	55(2)	15(1)	10(1)	-6(1)
C(25)	56(2)	108(3)	50(2)	25(2)	11(2)	10(2)
C(26)	62(2)	74(2)	82(3)	11(2)	33(2)	10(2)

Table A80. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for **101**.

	x	y	z	U(eq)
H(2A)	10290	9490	4566	68
H(2B)	9956	8364	4486	68
H(2C)	9483	9359	4100	68
H(5)	9764	12913	4066	48
H(6)	10849	13201	5046	54
H(7)	11720	12098	5186	53
H(9)	11632	10056	3900	59
H(10A)	12599	11274	5172	114
H(10B)	12305	11631	4269	114
H(10C)	12737	10580	4565	114
H(11A)	12000	9911	5531	110
H(11B)	12228	9117	5052	110
H(11C)	11447	9192	4854	110
H(12)	9196	10853	2656	49
H(13A)	8981	13041	2734	81
H(13B)	8535	12299	2001	81
H(13C)	9306	12547	2216	81
H(14A)	8905	10688	3701	89
H(14B)	8289	11175	2931	89
H(14C)	8755	11911	3658	89
H(17)	9779	4833	4033	66
H(18)	8626	4845	3632	70
H(19)	7978	6293	3013	66
H(21)	10678	6879	3606	63
H(22A)	10799	4704	3902	139
H(22B)	11291	5410	3699	139
H(22C)	10528	5199	3038	139
H(23A)	10866	7073	4905	150
H(23B)	11490	6486	4877	150
H(23C)	10948	5839	5032	150
H(24)	8624	8684	2624	59
H(25A)	8227	7726	1465	115
H(25B)	7605	8416	1406	115
H(25C)	7643	7202	1615	115
H(26A)	7501	7919	2804	110
H(26B)	7604	9098	2609	110
H(26C)	8099	8607	3454	110

Table A81. Torsion angles [°] for **101**.

C(15)-N(1)-C(1)-C(2)	0.1(4)
C(15)-N(1)-C(1)-P(1)	173.21(19)
C(3)-P(1)-C(1)-N(1)	168.64(17)
P(1)#1-P(1)-C(1)-N(1)	50.04(17)
C(3)-P(1)-C(1)-C(2)	-18.2(3)
P(1)#1-P(1)-C(1)-C(2)	-136.8(2)
C(1)-P(1)-C(3)-C(4)	-70.2(2)
P(1)#1-P(1)-C(3)-C(4)	33.1(3)
C(1)-P(1)-C(3)-C(8)	108.62(19)
P(1)#1-P(1)-C(3)-C(8)	-148.08(16)
C(8)-C(3)-C(4)-C(5)	-1.9(4)
P(1)-C(3)-C(4)-C(5)	176.92(19)
C(8)-C(3)-C(4)-C(12)	178.2(2)
P(1)-C(3)-C(4)-C(12)	-3.0(4)
C(3)-C(4)-C(5)-C(6)	0.1(4)
C(12)-C(4)-C(5)-C(6)	-179.9(3)
C(4)-C(5)-C(6)-C(7)	0.9(4)
C(5)-C(6)-C(7)-C(8)	-0.2(4)
C(6)-C(7)-C(8)-C(3)	-1.5(4)
C(6)-C(7)-C(8)-C(9)	179.9(3)
C(4)-C(3)-C(8)-C(7)	2.5(4)
P(1)-C(3)-C(8)-C(7)	-176.4(2)
C(4)-C(3)-C(8)-C(9)	-178.9(3)
P(1)-C(3)-C(8)-C(9)	2.1(3)
C(7)-C(8)-C(9)-C(11)	87.0(3)
C(3)-C(8)-C(9)-C(11)	-91.5(3)
C(7)-C(8)-C(9)-C(10)	-39.0(4)
C(3)-C(8)-C(9)-C(10)	142.4(3)
C(5)-C(4)-C(12)-C(14)	-63.0(3)
C(3)-C(4)-C(12)-C(14)	116.9(3)
C(5)-C(4)-C(12)-C(13)	60.6(3)
C(3)-C(4)-C(12)-C(13)	-119.5(3)
C(1)-N(1)-C(15)-C(16)	-98.9(3)
C(1)-N(1)-C(15)-C(20)	86.2(3)
C(20)-C(15)-C(16)-C(17)	-1.3(4)
N(1)-C(15)-C(16)-C(17)	-176.0(2)
C(20)-C(15)-C(16)-C(21)	178.5(3)
N(1)-C(15)-C(16)-C(21)	3.8(4)
C(15)-C(16)-C(17)-C(18)	1.2(5)
C(21)-C(16)-C(17)-C(18)	-178.5(3)
C(16)-C(17)-C(18)-C(19)	-0.8(5)
C(17)-C(18)-C(19)-C(20)	0.5(5)
C(18)-C(19)-C(20)-C(15)	-0.5(5)
C(18)-C(19)-C(20)-C(24)	176.6(3)
C(16)-C(15)-C(20)-C(19)	1.0(4)
N(1)-C(15)-C(20)-C(19)	175.7(2)
C(16)-C(15)-C(20)-C(24)	-176.1(3)
N(1)-C(15)-C(20)-C(24)	-1.4(4)
C(17)-C(16)-C(21)-C(23)	-76.6(4)
C(15)-C(16)-C(21)-C(23)	103.7(4)
C(17)-C(16)-C(21)-C(22)	49.7(4)
C(15)-C(16)-C(21)-C(22)	-130.1(3)
C(19)-C(20)-C(24)-C(26)	49.7(4)
C(15)-C(20)-C(24)-C(26)	-133.3(3)
C(19)-C(20)-C(24)-C(25)	-74.7(4)
C(15)-C(20)-C(24)-C(25)	102.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+1/2

Table A82. Crystal data and structure refinement for **99**.

Identification code	**99**	
Empirical formula	C40 H57 N2 P	
Formula weight	596.85	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.332(6) Å	α= 90°.
	b = 14.122(7) Å	β= 92.028(5)°.
	c = 19.596(9) Å	γ = 90°.
Volume	3687(3) $Å^3$	
Z	4	
Density (calculated)	1.075 Mg/m^3	
Absorption coefficient	0.102 mm^{-1}	
F(000)	1304	
Crystal size	0.252 x 0.063 x 0.047 mm^3	
Theta range for data collection	1.53 to 18.83°.	
Index ranges	-11<=h<=12, -11<=k<=12, -17<=l<=16	
Reflections collected	18530	
Independent reflections	2880 [R(int) = 0.2086]	
Completeness to theta = 18.83°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9534 and 0.7822	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2880 / 0 / 282	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0872, wR2 = 0.1745	
R indices (all data)	R1 = 0.2164, wR2 = 0.2265	
Largest diff. peak and hole	0.402 and -0.245 e.$Å^{-3}$	

Table A83. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **99**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P	7217(2)	6811(2)	1066(2)	70(1)
C(12)	4671(9)	8253(8)	1958(6)	103(5)
C(11)	4801(9)	8120(8)	681(6)	88(4)
C(37)	10850(13)	7155(9)	2035(7)	161(8)
C(35)	10595(8)	7636(8)	1352(5)	52(3)
C(30)	10168(8)	8613(8)	1454(5)	51(1)
C(29)	9188(8)	8825(8)	1187(5)	51(1)
N(2)	8560(5)	8083(5)	870(4)	46(1)
C(15)	8557(7)	8051(7)	178(5)	46(1)

N(1)	7906(5)	7426(5)	-158(4)	46(1)
C(13)	7190(7)	6870(7)	201(5)	46(1)
C(3)	5148(7)	4729(8)	1460(4)	56(2)
C(4)	4325(8)	5254(8)	1634(4)	56(2)
C(5)	4366(8)	6224(8)	1612(4)	56(2)
C(6)	5220(8)	6706(9)	1403(5)	56(2)
C(17)	7920(8)	7358(8)	-904(5)	59(2)
C(22)	8548(8)	6666(8)	-1184(5)	59(2)
C(21)	8555(7)	6599(7)	-1893(5)	59(2)
C(20)	7976(7)	7193(7)	-2275(5)	59(2)
C(19)	7352(7)	7856(7)	-2016(5)	59(2)
C(18)	7303(8)	7928(8)	-1307(5)	59(2)
C(23)	6617(8)	8656(8)	-1013(5)	63(3)
C(24)	5504(8)	8506(8)	-1237(6)	98(4)
C(25)	6923(8)	9674(8)	-1181(6)	96(4)
C(26)	9202(9)	6026(9)	-750(5)	66(4)
C(28)	10302(10)	6178(11)	-897(7)	141(6)
C(16)	9216(6)	8637(6)	-270(4)	46(1)
C(31)	10692(8)	9300(7)	1805(5)	51(1)
C(32)	10288(8)	10178(7)	1915(5)	51(1)
C(33)	9326(7)	10376(7)	1675(4)	51(1)
C(34)	8750(8)	9715(8)	1312(5)	51(1)
C(38)	7689(8)	9941(8)	1080(6)	61(3)
C(39)	7633(9)	10809(10)	629(6)	117(5)
C(40)	7029(9)	10058(10)	1680(6)	120(5)
C(36)	11541(9)	7666(8)	962(7)	114(5)
C(14)	6466(6)	6338(6)	-258(4)	46(1)
C(7)	6899(8)	4561(8)	1069(6)	62(3)
C(9)	7335(9)	4095(11)	1710(6)	132(6)
C(8)	6630(8)	3815(8)	528(6)	82(4)
C(1)	6052(8)	6149(8)	1200(5)	56(2)
C(10)	5224(8)	7778(8)	1379(6)	74(4)
C(2)	6026(9)	5180(9)	1248(5)	56(2)
C(27)	8922(11)	5000(10)	-871(7)	137(6)

Table A84. Bond lengths [Å] and angles [°] for **99**.

P-C(13)	1.696(9)
P-C(1)	1.839(11)
C(12)-C(10)	1.531(13)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(11)-C(10)	1.539(13)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(37)-C(35)	1.529(14)
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(35)-C(36)	1.499(12)
C(35)-C(30)	1.508(13)
C(35)-H(35)	1.0000
C(30)-C(31)	1.367(12)
C(30)-C(29)	1.421(13)
C(29)-C(34)	1.411(12)
C(29)-N(2)	1.465(11)
N(2)-C(15)	1.358(11)
C(15)-N(1)	1.387(11)
C(15)-C(16)	1.511(11)

N(1)-C(13)	1.440(10)
N(1)-C(17)	1.464(11)
C(13)-C(14)	1.497(11)
C(3)-C(4)	1.376(12)
C(3)-C(2)	1.409(12)
C(3)-H(3)	0.9500
C(4)-C(5)	1.371(12)
C(4)-H(4)	0.9500
C(5)-C(6)	1.400(12)
C(5)-H(5)	0.9500
C(6)-C(1)	1.429(13)
C(6)-C(10)	1.514(13)
C(17)-C(18)	1.380(13)
C(17)-C(22)	1.411(13)
C(22)-C(21)	1.393(12)
C(22)-C(26)	1.499(13)
C(21)-C(20)	1.348(12)
C(21)-H(21)	0.9500
C(20)-C(19)	1.362(12)
C(20)-H(20)	0.9500
C(19)-C(18)	1.396(12)
C(19)-H(19)	0.9500
C(18)-C(23)	1.505(13)
C(23)-C(25)	1.533(13)
C(23)-C(24)	1.547(13)
C(23)-H(23)	1.0000
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.513(14)
C(26)-C(28)	1.519(14)
C(26)-H(26)	1.0000
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(31)-C(32)	1.373(12)
C(31)-H(31)	0.9500
C(32)-C(33)	1.379(12)
C(32)-H(32)	0.9500
C(33)-C(34)	1.389(12)
C(33)-H(33)	0.9500
C(34)-C(38)	1.506(13)
C(38)-C(40)	1.503(13)
C(38)-C(39)	1.511(13)
C(38)-H(38)	1.0000
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(7)-C(2)	1.507(13)
C(7)-C(9)	1.517(13)
C(7)-C(8)	1.529(12)
C(7)-H(7)	1.0000
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(1)-C(2)	1.372(13)
C(10)-H(10)	1.0000
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(13)-P-C(1)	100.3(5)
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(35)-C(37)-H(37A)	109.5
C(35)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(35)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(35)-C(30)	111.7(9)
C(36)-C(35)-C(37)	107.1(10)
C(30)-C(35)-C(37)	111.4(9)
C(36)-C(35)-H(35)	108.9
C(30)-C(35)-H(35)	108.9

C(37)-C(35)-H(35)	108.9
C(31)-C(30)-C(29)	118.9(11)
C(31)-C(30)-C(35)	121.8(10)
C(29)-C(30)-C(35)	119.4(10)
C(34)-C(29)-C(30)	120.3(11)
C(34)-C(29)-N(2)	118.5(9)
C(30)-C(29)-N(2)	120.6(10)
C(15)-N(2)-C(29)	115.4(8)
N(2)-C(15)-N(1)	118.4(9)
N(2)-C(15)-C(16)	125.5(9)
N(1)-C(15)-C(16)	116.1(8)
C(15)-N(1)-C(13)	122.0(8)
C(15)-N(1)-C(17)	119.0(8)
C(13)-N(1)-C(17)	119.0(8)
N(1)-C(13)-C(14)	113.8(8)
N(1)-C(13)-P	121.6(7)
C(14)-C(13)-P	124.5(7)
C(4)-C(3)-C(2)	120.5(11)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	119.8(11)
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	121.9(12)
C(4)-C(5)-H(5)	119.0
C(6)-C(5)-H(5)	119.0
C(5)-C(6)-C(1)	117.4(11)
C(5)-C(6)-C(10)	120.0(11)
C(1)-C(6)-C(10)	122.5(11)
C(18)-C(17)-C(22)	122.1(10)
C(18)-C(17)-N(1)	120.3(10)
C(22)-C(17)-N(1)	117.5(9)
C(21)-C(22)-C(17)	117.3(10)
C(21)-C(22)-C(26)	120.1(10)
C(17)-C(22)-C(26)	122.6(10)
C(20)-C(21)-C(22)	119.3(11)
C(20)-C(21)-H(21)	120.4
C(22)-C(21)-H(21)	120.4
C(21)-C(20)-C(19)	124.5(10)
C(21)-C(20)-H(20)	117.8
C(19)-C(20)-H(20)	117.8
C(20)-C(19)-C(18)	118.1(10)
C(20)-C(19)-H(19)	121.0
C(18)-C(19)-H(19)	121.0
C(17)-C(18)-C(19)	118.7(11)
C(17)-C(18)-C(23)	122.5(10)
C(19)-C(18)-C(23)	118.8(10)
C(18)-C(23)-C(25)	112.8(9)
C(18)-C(23)-C(24)	112.8(9)
C(25)-C(23)-C(24)	109.1(9)
C(18)-C(23)-H(23)	107.3
C(25)-C(23)-H(23)	107.3
C(24)-C(23)-H(23)	107.3
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(22)-C(26)-C(27)	110.7(10)
C(22)-C(26)-C(28)	110.7(10)
C(27)-C(26)-C(28)	109.8(11)
C(22)-C(26)-H(26)	108.5
C(27)-C(26)-H(26)	108.5
C(28)-C(26)-H(26)	108.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(30)-C(31)-C(32)	121.6(11)
C(30)-C(31)-H(31)	119.2
C(32)-C(31)-H(31)	119.2
C(31)-C(32)-C(33)	119.6(11)
C(31)-C(32)-H(32)	120.2
C(33)-C(32)-H(32)	120.2
C(32)-C(33)-C(34)	122.0(11)
C(32)-C(33)-H(33)	119.0
C(34)-C(33)-H(33)	119.0
C(33)-C(34)-C(29)	117.6(10)
C(33)-C(34)-C(38)	120.6(10)
C(29)-C(34)-C(38)	121.8(10)
C(40)-C(38)-C(34)	110.9(9)
C(40)-C(38)-C(39)	110.5(9)
C(34)-C(38)-C(39)	112.0(10)
C(40)-C(38)-H(38)	107.7
C(34)-C(38)-H(38)	107.7
C(39)-C(38)-H(38)	107.7
C(38)-C(39)-H(39A)	109.5

C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(2)-C(7)-C(9)	109.6(9)
C(2)-C(7)-C(8)	113.4(9)
C(9)-C(7)-C(8)	110.4(10)
C(2)-C(7)-H(7)	107.8
C(9)-C(7)-H(7)	107.8
C(8)-C(7)-H(7)	107.8
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(2)-C(1)-C(6)	120.6(11)
C(2)-C(1)-P	122.7(9)
C(6)-C(1)-P	115.3(9)
C(6)-C(10)-C(12)	114.4(11)
C(6)-C(10)-C(11)	109.9(9)
C(12)-C(10)-C(11)	110.5(9)
C(6)-C(10)-H(10)	107.3
C(12)-C(10)-H(10)	107.3
C(11)-C(10)-H(10)	107.3
C(1)-C(2)-C(3)	119.6(12)
C(1)-C(2)-C(7)	122.7(11)
C(3)-C(2)-C(7)	117.7(11)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A85. Anisotropic displacement parameters (Å^{2}x 10^3) for **99**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P	68(2)	95(3)	46(2)	1(2)	2(2)	-13(2)
C(12)	114(11)	128(12)	66(9)	-50(9)	-22(8)	51(10)
C(11)	115(11)	94(10)	55(9)	-2(8)	-9(8)	17(9)
C(37)	340(20)	86(11)	68(11)	38(9)	67(13)	54(13)
C(35)	39(7)	79(10)	39(8)	4(7)	0(6)	-4(7)
C(30)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
C(29)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
N(2)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)
C(15)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)
N(1)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)
C(13)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)

C(3)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(4)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(5)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(6)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(17)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(22)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(21)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(20)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(19)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(18)	72(4)	71(4)	33(3)	-2(3)	-11(3)	11(3)
C(23)	57(9)	69(10)	61(8)	18(8)	-13(7)	-6(8)
C(24)	76(10)	115(12)	102(11)	18(9)	-16(8)	18(9)
C(25)	85(10)	78(11)	125(12)	26(9)	14(8)	10(9)
C(26)	67(10)	84(11)	49(8)	-9(8)	9(7)	25(8)
C(28)	69(11)	225(18)	130(13)	27(12)	0(9)	38(11)
C(16)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)
C(31)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
C(32)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
C(33)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
C(34)	68(4)	53(4)	31(3)	-1(3)	0(3)	-4(3)
C(38)	60(9)	66(9)	57(8)	-7(8)	-5(7)	10(7)
C(39)	94(11)	153(14)	106(12)	69(11)	10(9)	46(10)
C(40)	78(10)	198(16)	86(11)	49(10)	28(9)	53(10)
C(36)	98(11)	64(10)	181(15)	20(10)	27(11)	30(9)
C(14)	48(3)	51(3)	40(3)	-3(2)	-9(2)	-1(2)
C(7)	61(9)	82(10)	44(8)	-2(8)	2(7)	-1(8)
C(9)	99(11)	242(18)	55(10)	34(11)	5(8)	69(12)
C(8)	74(9)	74(9)	98(11)	-17(9)	12(8)	13(8)
C(1)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(10)	64(8)	82(11)	75(10)	-25(9)	-15(8)	14(8)
C(2)	52(3)	81(4)	35(3)	-4(3)	-5(2)	0(4)
C(27)	208(18)	75(12)	126(13)	-10(10)	-32(12)	30(12)

Table A86. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **99**.

	x	y	z	U(eq)
H(12A)	3951	8115	1908	154
H(12B)	4775	8940	1939	154
H(12C)	4931	8010	2398	154
H(11A)	5198	7850	317	133
H(11B)	4833	8813	661	133
H(11C)	4101	7915	620	133
H(37A)	11344	7537	2294	242
H(37B)	11129	6525	1952	242
H(37C)	10240	7094	2296	242
H(35)	10087	7243	1093	63

H(3)	5123	4058	1484	67
H(4)	3731	4945	1769	67
H(5)	3798	6579	1741	67
H(21)	8962	6141	-2105	71
H(20)	8005	7146	-2757	71
H(19)	6961	8257	-2309	71
H(23)	6665	8588	-505	75
H(24A)	5417	8631	-1728	147
H(24B)	5081	8940	-984	147
H(24C)	5310	7851	-1143	147
H(25A)	7622	9779	-1028	144
H(25B)	6486	10119	-949	144
H(25C)	6857	9774	-1676	144
H(26)	9099	6180	-259	80
H(28A)	10407	6061	-1382	212
H(28B)	10715	5739	-620	212
H(28C)	10492	6831	-783	212
H(16A)	9703	8991	16	70
H(16B)	8800	9081	-540	70
H(16C)	9574	8219	-578	70
H(31)	11352	9165	1977	61
H(32)	10669	10648	2156	61
H(33)	9049	10982	1761	61
H(38)	7427	9392	804	73
H(39A)	7858	11364	893	176
H(39B)	6938	10905	463	176
H(39C)	8065	10722	240	176
H(40A)	7057	9482	1959	180
H(40B)	6336	10170	1516	180
H(40C)	7263	10598	1956	180
H(36A)	11404	7961	515	171
H(36B)	11789	7020	897	171
H(36C)	12049	8037	1218	171
H(14A)	6126	6781	-574	70
H(14B)	5968	6020	18	70
H(14C)	6831	5865	-518	70
H(7)	7429	4979	882	75
H(9A)	7592	4583	2026	198
H(9B)	7884	3672	1590	198
H(9C)	6811	3729	1929	198
H(8A)	6138	3373	708	123
H(8B)	7236	3467	410	123
H(8C)	6342	4126	119	123
H(10)	5941	7986	1419	89
H(27A)	8232	4963	-1059	206
H(27B)	8972	4654	-438	206
H(27C)	9381	4719	-1195	206

Table A87. Torsion angles [°] for **99**.

C(36)-C(35)-C(30)-C(31)	-61.0(13)
C(37)-C(35)-C(30)-C(31)	58.7(14)
C(36)-C(35)-C(30)-C(29)	120.0(11)
C(37)-C(35)-C(30)-C(29)	-120.3(11)
C(31)-C(30)-C(29)-C(34)	-2.9(14)
C(35)-C(30)-C(29)-C(34)	176.2(8)
C(31)-C(30)-C(29)-N(2)	-173.6(8)
C(35)-C(30)-C(29)-N(2)	5.5(13)
C(34)-C(29)-N(2)-C(15)	90.8(10)
C(30)-C(29)-N(2)-C(15)	-98.3(10)
C(29)-N(2)-C(15)-N(1)	-173.9(8)
C(29)-N(2)-C(15)-C(16)	6.7(13)
N(2)-C(15)-N(1)-C(13)	4.7(12)
C(16)-C(15)-N(1)-C(13)	-175.9(8)
N(2)-C(15)-N(1)-C(17)	-177.8(8)
C(16)-C(15)-N(1)-C(17)	1.7(12)
C(15)-N(1)-C(13)-C(14)	172.3(8)
C(17)-N(1)-C(13)-C(14)	-5.3(12)
C(15)-N(1)-C(13)-P	-9.8(12)
C(17)-N(1)-C(13)-P	172.7(7)
C(1)-P-C(13)-N(1)	172.8(8)
C(1)-P-C(13)-C(14)	-9.4(9)
C(2)-C(3)-C(4)-C(5)	-1.1(14)
C(3)-C(4)-C(5)-C(6)	1.2(15)
C(4)-C(5)-C(6)-C(1)	1.1(14)
C(4)-C(5)-C(6)-C(10)	179.3(9)
C(15)-N(1)-C(17)-C(18)	-90.4(11)
C(13)-N(1)-C(17)-C(18)	87.1(12)
C(15)-N(1)-C(17)-C(22)	92.3(11)
C(13)-N(1)-C(17)-C(22)	-90.1(11)
C(18)-C(17)-C(22)-C(21)	2.4(15)
N(1)-C(17)-C(22)-C(21)	179.6(9)
C(18)-C(17)-C(22)-C(26)	-178.4(10)
N(1)-C(17)-C(22)-C(26)	-1.2(15)
C(17)-C(22)-C(21)-C(20)	0.4(15)
C(26)-C(22)-C(21)-C(20)	-178.7(10)
C(22)-C(21)-C(20)-C(19)	-1.6(16)
C(21)-C(20)-C(19)-C(18)	-0.1(15)
C(22)-C(17)-C(18)-C(19)	-4.1(16)
N(1)-C(17)-C(18)-C(19)	178.8(9)
C(22)-C(17)-C(18)-C(23)	178.8(10)
N(1)-C(17)-C(18)-C(23)	1.7(15)
C(20)-C(19)-C(18)-C(17)	2.9(15)
C(20)-C(19)-C(18)-C(23)	-179.9(9)
C(17)-C(18)-C(23)-C(25)	113.1(12)
C(19)-C(18)-C(23)-C(25)	-64.0(13)
C(17)-C(18)-C(23)-C(24)	-122.8(11)
C(19)-C(18)-C(23)-C(24)	60.2(13)
C(21)-C(22)-C(26)-C(27)	-61.3(14)
C(17)-C(22)-C(26)-C(27)	119.5(12)
C(21)-C(22)-C(26)-C(28)	60.6(14)
C(17)-C(22)-C(26)-C(28)	-118.5(12)
C(29)-C(30)-C(31)-C(32)	1.2(14)
C(35)-C(30)-C(31)-C(32)	-177.9(8)
C(30)-C(31)-C(32)-C(33)	0.8(14)
C(31)-C(32)-C(33)-C(34)	-1.1(14)
C(32)-C(33)-C(34)-C(29)	-0.6(13)
C(32)-C(33)-C(34)-C(38)	177.7(9)
C(30)-C(29)-C(34)-C(33)	2.6(13)
N(2)-C(29)-C(34)-C(33)	173.5(8)
C(30)-C(29)-C(34)-C(38)	-175.7(9)
N(2)-C(29)-C(34)-C(38)	-4.8(13)
C(33)-C(34)-C(38)-C(40)	-65.8(13)
C(29)-C(34)-C(38)-C(40)	112.4(11)
C(33)-C(34)-C(38)-C(39)	58.1(13)
C(29)-C(34)-C(38)-C(39)	-123.7(11)
C(5)-C(6)-C(1)-C(2)	-3.7(14)
C(10)-C(6)-C(1)-C(2)	178.2(10)
C(5)-C(6)-C(1)-P	-170.5(7)
C(10)-C(6)-C(1)-P	11.4(12)
C(13)-P-C(1)-C(2)	91.5(9)
C(13)-P-C(1)-C(6)	-102.1(8)
C(5)-C(6)-C(10)-C(12)	37.3(14)
C(1)-C(6)-C(10)-C(12)	-144.6(10)
C(5)-C(6)-C(10)-C(11)	-87.6(12)
C(1)-C(6)-C(10)-C(11)	90.5(12)
C(6)-C(1)-C(2)-C(3)	3.9(15)
P-C(1)-C(2)-C(3)	169.7(7)
C(6)-C(1)-C(2)-C(7)	-177.3(9)
P-C(1)-C(2)-C(7)	-11.6(14)
C(4)-C(3)-C(2)-C(1)	-1.5(15)
C(4)-C(3)-C(2)-C(7)	179.7(8)
C(9)-C(7)-C(2)-C(1)	112.2(12)
C(8)-C(7)-C(2)-C(1)	-124.0(11)
C(9)-C(7)-C(2)-C(3)	-69.0(13)
C(8)-C(7)-C(2)-C(3)	54.8(12)

Symmetry transformations used to generate equivalent atoms:

Table A88. Crystal data and structure refinement for **13a**.

Identification code	**13a**	
Empirical formula	C20 H25 N O	
Formula weight	294.90	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 21.882(3) Å	α= 90°.
	b = 9.9235(13) Å	β= 107.0080(17)°.
	c = 17.082(2) Å	γ = 90°.
Volume	3547.0(8) Å^3	
Z	8	
Density (calculated)	1.104 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	1276	
Crystal size	0.232 x 0.159 x 0.104 mm^3	
Theta range for data collection	1.946 to 25.681°.	
Index ranges	-26<=h<=26, -12<=k<=12, -20<=l<=20	
Reflections collected	42767	
Independent reflections	6702 [R(int) = 0.1279]	
Completeness to theta = 25.500°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6775	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6702 / 110 / 413	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0857, wR2 = 0.2045	
R indices (all data)	R1 = 0.1909, wR2 = 0.2561	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.289 and -0.246 e.Å^{-3}	

Table A89. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **13a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	245(2)	7188(4)	2290(3)	40(1)
C(2)	812(2)	7559(4)	2022(2)	37(1)
C(3)	1003(2)	8872(4)	1948(3)	46(1)
C(4)	1527(2)	9138(4)	1691(3)	50(1)
C(5)	1883(2)	8128(4)	1486(2)	42(1)
C(6)	1699(2)	6802(4)	1566(3)	45(1)
C(7)	1168(2)	6528(4)	1819(3)	44(1)
C(8)	2458(2)	8434(5)	1197(3)	56(1)

C(9)	-596(2)	7962(4)	2848(3)	47(1)
C(10)	-1208(2)	7918(4)	2319(3)	51(1)
C(11)	-1717(2)	7822(5)	2654(3)	59(1)
C(12)	-1614(3)	7787(5)	3479(4)	64(1)
C(13)	-1003(3)	7802(5)	3994(4)	67(1)
C(14)	-472(2)	7878(4)	3700(3)	58(1)
C(15)	-1336(2)	8002(5)	1394(3)	67(1)
C(16)	-1633(3)	9349(7)	1075(4)	114(2)
C(17)	-1743(3)	6852(7)	959(4)	98(2)
C(18)	191(3)	7841(6)	4305(4)	91(2)
C(19)	542(4)	9063(7)	4446(5)	157(4)
C(20)	415(4)	6586(8)	4574(5)	168(4)
N(1)	-64(2)	8184(3)	2536(3)	50(1)
O(1)	78(1)	6005(3)	2312(2)	55(1)
C(21)	4642(2)	9105(4)	2651(2)	33(1)
C(22)	4078(2)	8787(4)	2951(2)	33(1)
C(23)	3728(2)	9859(4)	3098(2)	42(1)
C(24)	3200(2)	9638(4)	3378(2)	42(1)
C(25)	3009(2)	8354(4)	3511(2)	41(1)
C(26)	3362(2)	7297(4)	3351(3)	43(1)
C(27)	3889(2)	7491(4)	3075(2)	39(1)
C(28)	2442(2)	8116(5)	3820(3)	54(1)
C(29)	5522(2)	8273(4)	2202(2)	35(1)
C(30)	6124(2)	8640(4)	2699(3)	40(1)
C(31)	6605(2)	8808(4)	2325(3)	48(1)
C(32)	6477(2)	8625(4)	1494(3)	55(1)
C(33)	5886(2)	8270(4)	1020(3)	51(1)
C(34)	5385(2)	8077(4)	1366(3)	43(1)
C(35)	6266(2)	8769(5)	3622(3)	56(1)
C(36)	6506(3)	7428(6)	4024(3)	80(2)
C(37)	6731(3)	9891(6)	3998(3)	80(2)
C(38)	4728(2)	7663(5)	849(3)	58(1)
C(39)	4333(3)	8858(6)	436(4)	99(2)
C(40)	4728(3)	6563(6)	240(4)	98(2)
N(2)	5017(2)	8082(3)	2574(2)	35(1)
O(2)	4761(1)	10264(3)	2493(2)	50(1)

Table A90. Bond lengths [Å] and angles [°] for **13a**.

C(1)-O(1)	1.234(4)
C(1)-N(1)	1.332(5)
C(1)-C(2)	1.490(6)
C(2)-C(3)	1.385(5)
C(2)-C(7)	1.389(5)
C(3)-C(4)	1.368(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.376(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.395(6)
C(5)-C(8)	1.511(6)
C(6)-C(7)	1.380(6)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.379(6)
C(9)-C(14)	1.403(7)
C(9)-N(1)	1.434(5)

C(10)-C(11)	1.395(6)
C(10)-C(15)	1.525(7)
C(11)-C(12)	1.361(7)
C(11)-H(11)	0.9500
C(12)-C(13)	1.370(7)
C(12)-H(12)	0.9500
C(13)-C(14)	1.395(7)
C(13)-H(13)	0.9500
C(14)-C(18)	1.517(7)
C(15)-C(17)	1.503(7)
C(15)-C(16)	1.517(7)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(20)	1.368(8)
C(18)-C(19)	1.417(8)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
N(1)-H(1)	0.92(5)
C(21)-O(2)	1.226(4)
C(21)-N(2)	1.337(5)
C(21)-C(22)	1.501(5)
C(22)-C(23)	1.378(5)
C(22)-C(27)	1.386(5)
C(23)-C(24)	1.390(5)
C(23)-H(23)	0.9500
C(24)-C(25)	1.379(5)
C(24)-H(24)	0.9500
C(25)-C(26)	1.377(5)
C(25)-C(28)	1.503(6)
C(26)-C(27)	1.379(6)
C(26)-H(26)	0.9500
C(27)-H(27)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(34)	1.384(6)
C(29)-C(30)	1.392(5)
C(29)-N(2)	1.438(5)
C(30)-C(31)	1.392(5)
C(30)-C(35)	1.520(6)
C(31)-C(32)	1.376(6)
C(31)-H(31)	0.9500
C(32)-C(33)	1.357(6)
C(32)-H(32)	0.9500
C(33)-C(34)	1.401(6)
C(33)-H(33)	0.9500
C(34)-C(38)	1.508(6)
C(35)-C(36)	1.519(7)
C(35)-C(37)	1.519(6)
C(35)-H(35)	1.0000
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-C(40)	1.508(7)
C(38)-C(39)	1.515(7)
C(38)-H(38)	1.0000
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
N(2)-H(2)	0.95(4)
O(1)-C(1)-N(1)	121.0(4)
O(1)-C(1)-C(2)	121.7(4)
N(1)-C(1)-C(2)	117.3(3)
C(3)-C(2)-C(7)	117.6(4)
C(3)-C(2)-C(1)	124.1(4)
C(7)-C(2)-C(1)	118.2(4)
C(4)-C(3)-C(2)	121.0(4)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	122.0(4)
C(3)-C(4)-H(4)	119.0
C(5)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	117.5(4)
C(4)-C(5)-C(8)	121.6(4)
C(6)-C(5)-C(8)	120.9(4)
C(7)-C(6)-C(5)	120.7(4)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(2)	121.2(4)
C(6)-C(7)-H(7)	119.4
C(2)-C(7)-H(7)	119.4
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

C(10)-C(9)-C(14)	122.3(4)
C(10)-C(9)-N(1)	120.0(4)
C(14)-C(9)-N(1)	117.6(4)
C(9)-C(10)-C(11)	118.1(5)
C(9)-C(10)-C(15)	121.8(4)
C(11)-C(10)-C(15)	120.1(4)
C(12)-C(11)-C(10)	121.1(5)
C(12)-C(11)-H(11)	119.5
C(10)-C(11)-H(11)	119.5
C(11)-C(12)-C(13)	120.0(5)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	121.9(5)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(13)-C(14)-C(9)	116.6(5)
C(13)-C(14)-C(18)	119.0(5)
C(9)-C(14)-C(18)	124.4(5)
C(17)-C(15)-C(16)	111.2(5)
C(17)-C(15)-C(10)	112.0(5)
C(16)-C(15)-C(10)	110.5(5)
C(17)-C(15)-H(15)	107.6
C(16)-C(15)-H(15)	107.6
C(10)-C(15)-H(15)	107.6
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(20)-C(18)-C(19)	126.8(6)
C(20)-C(18)-C(14)	115.3(5)
C(19)-C(18)-C(14)	117.3(5)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(1)-N(1)-C(9)	123.0(4)
C(1)-N(1)-H(1)	116(3)
C(9)-N(1)-H(1)	121(3)
O(2)-C(21)-N(2)	121.0(4)
O(2)-C(21)-C(22)	121.4(3)
N(2)-C(21)-C(22)	117.6(3)
C(23)-C(22)-C(27)	118.8(4)
C(23)-C(22)-C(21)	117.2(3)
C(27)-C(22)-C(21)	124.1(3)
C(22)-C(23)-C(24)	120.2(4)
C(22)-C(23)-H(23)	119.9
C(24)-C(23)-H(23)	119.9
C(25)-C(24)-C(23)	121.6(4)
C(25)-C(24)-H(24)	119.2
C(23)-C(24)-H(24)	119.2
C(26)-C(25)-C(24)	117.2(4)
C(26)-C(25)-C(28)	121.2(4)
C(24)-C(25)-C(28)	121.6(4)
C(25)-C(26)-C(27)	122.3(4)
C(25)-C(26)-H(26)	118.9
C(27)-C(26)-H(26)	118.9
C(26)-C(27)-C(22)	119.9(4)
C(26)-C(27)-H(27)	120.0
C(22)-C(27)-H(27)	120.0
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(34)-C(29)-C(30)	123.2(4)
C(34)-C(29)-N(2)	118.4(4)
C(30)-C(29)-N(2)	118.5(4)
C(31)-C(30)-C(29)	117.3(4)
C(31)-C(30)-C(35)	121.0(4)
C(29)-C(30)-C(35)	121.6(4)
C(32)-C(31)-C(30)	120.3(4)
C(32)-C(31)-H(31)	119.8
C(30)-C(31)-H(31)	119.8
C(33)-C(32)-C(31)	121.3(4)
C(33)-C(32)-H(32)	119.3
C(31)-C(32)-H(32)	119.3
C(32)-C(33)-C(34)	120.8(4)
C(32)-C(33)-H(33)	119.6
C(34)-C(33)-H(33)	119.6
C(29)-C(34)-C(33)	117.1(4)
C(29)-C(34)-C(38)	121.6(4)
C(33)-C(34)-C(38)	121.3(4)
C(36)-C(35)-C(37)	110.5(4)
C(36)-C(35)-C(30)	109.5(4)
C(37)-C(35)-C(30)	114.0(4)

C(36)-C(35)-H(35)	107.5
C(37)-C(35)-H(35)	107.5
C(30)-C(35)-H(35)	107.5
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(35)-C(37)-H(37A)	109.5
C(35)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(35)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(40)-C(38)-C(34)	114.1(4)
C(40)-C(38)-C(39)	111.2(4)
C(34)-C(38)-C(39)	112.1(4)
C(40)-C(38)-H(38)	106.3
C(34)-C(38)-H(38)	106.3
C(39)-C(38)-H(38)	106.3
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-H(40A)	109.5
C(38)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(38)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(21)-N(2)-C(29)	121.1(3)
C(21)-N(2)-H(2)	129(3)
C(29)-N(2)-H(2)	110(2)

Symmetry transformations used to generate equivalent atoms:

Table A91. Anisotropic displacement parameters (Å^{2}x 10^3) for **13a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	32(2)	28(2)	56(3)	-2(2)	5(2)	4(2)
C(2)	31(2)	32(2)	45(3)	-2(2)	7(2)	2(2)
C(3)	45(3)	34(2)	63(3)	2(2)	21(2)	4(2)
C(4)	55(3)	33(2)	62(3)	2(2)	21(2)	-4(2)
C(5)	38(2)	45(3)	38(2)	1(2)	6(2)	-2(2)
C(6)	40(2)	42(2)	51(3)	-2(2)	11(2)	11(2)
C(7)	42(3)	31(2)	58(3)	-5(2)	12(2)	0(2)
C(8)	50(3)	65(3)	57(3)	3(2)	20(2)	-4(2)
C(9)	43(3)	24(2)	80(3)	0(2)	28(2)	-1(2)
C(10)	40(3)	40(3)	81(3)	1(2)	29(2)	5(2)
C(11)	39(3)	54(3)	89(4)	-4(3)	26(3)	-2(2)
C(12)	62(3)	48(3)	96(4)	-4(3)	47(3)	-2(3)
C(13)	79(4)	52(3)	78(4)	2(3)	37(3)	-1(3)
C(14)	53(3)	39(3)	83(3)	0(2)	23(3)	-2(2)
C(15)	41(3)	82(4)	80(3)	1(3)	22(3)	-4(3)
C(16)	128(6)	100(5)	109(5)	40(4)	27(5)	9(4)
C(17)	92(5)	115(5)	91(5)	-23(4)	31(4)	-33(4)
C(18)	61(3)	69(4)	124(5)	18(4)	-3(3)	-10(3)
C(19)	179(8)	106(5)	118(6)	14(5)	-64(6)	-64(5)
C(20)	158(8)	104(5)	156(8)	23(5)	-88(6)	-1(5)
N(1)	34(2)	26(2)	96(3)	-3(2)	28(2)	0(2)
O(1)	61(2)	24(2)	88(2)	-5(2)	37(2)	-2(1)
C(21)	33(2)	25(2)	39(2)	-6(2)	7(2)	-2(2)

C(22)	33(2)	25(2)	37(2)	0(2)	5(2)	-3(2)
C(23)	39(2)	32(2)	58(3)	-1(2)	16(2)	2(2)
C(24)	38(2)	39(2)	50(3)	-3(2)	14(2)	1(2)
C(25)	34(2)	47(3)	44(3)	-3(2)	13(2)	-6(2)
C(26)	43(3)	37(2)	47(3)	2(2)	11(2)	-9(2)
C(27)	40(2)	28(2)	50(3)	-4(2)	13(2)	-1(2)
C(28)	47(3)	62(3)	55(3)	-4(2)	21(2)	-13(2)
C(29)	33(2)	23(2)	49(2)	0(2)	14(2)	1(2)
C(30)	34(2)	35(2)	52(3)	-3(2)	13(2)	2(2)
C(31)	38(2)	43(3)	66(3)	-3(2)	23(2)	-4(2)
C(32)	59(3)	45(3)	72(3)	6(2)	37(3)	5(2)
C(33)	64(3)	43(3)	51(3)	11(2)	23(2)	12(2)
C(34)	44(2)	35(2)	49(3)	4(2)	13(2)	10(2)
C(35)	36(3)	75(3)	57(3)	-10(3)	14(2)	-8(2)
C(36)	82(4)	97(4)	53(3)	19(3)	11(3)	-27(3)
C(37)	77(4)	85(4)	70(4)	-18(3)	10(3)	-17(3)
C(38)	55(3)	72(3)	40(3)	-4(2)	2(2)	-1(3)
C(39)	84(4)	80(4)	101(5)	-29(3)	-25(4)	40(3)
C(40)	112(5)	66(4)	86(4)	-22(3)	-18(4)	25(3)
N(2)	32(2)	23(2)	52(2)	0(2)	16(2)	0(2)
O(2)	58(2)	23(2)	81(2)	-1(1)	38(2)	-2(1)

Table A92. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{3}) for **13a**.

	x	y	z	U(eq)
H(3)	767	9598	2078	56
H(4)	1649	10049	1653	59
H(6)	1942	6079	1446	54
H(7)	1044	5619	1855	53
H(8A)	2429	9360	989	84
H(8B)	2471	7806	759	84
H(8C)	2849	8335	1655	84
H(11)	-2142	7781	2300	71
H(12)	-1966	7752	3697	76
H(13)	-938	7760	4568	80
H(15)	-915	7942	1277	80
H(16A)	-2025	9479	1233	171
H(16B)	-1736	9366	476	171
H(16C)	-1330	10074	1308	171
H(17A)	-1533	5996	1163	148
H(17B)	-1801	6922	369	148
H(17C)	-2161	6888	1060	148
H(19A)	605	9354	5013	236
H(19B)	305	9757	4071	236
H(19C)	958	8922	4353	236
H(20A)	373	5992	4103	252

H(20B)	166	6219	4918	252
H(20C)	866	6648	4895	252
H(1)	100(20)	9030(50)	2520(30)	75
H(23)	3847	10753	3009	51
H(24)	2965	10388	3481	51
H(26)	3239	6403	3434	52
H(27)	4121	6738	2971	47
H(28A)	2068	7896	3359	80
H(28B)	2355	8931	4093	80
H(28C)	2533	7365	4210	80
H(31)	7024	9050	2645	57
H(32)	6810	8749	1247	66
H(33)	5810	8151	448	62
H(35)	5853	8972	3738	67
H(36A)	6204	6714	3769	119
H(36B)	6545	7476	4609	119
H(36C)	6926	7230	3953	119
H(37A)	6751	10001	4575	120
H(37B)	6586	10734	3703	120
H(37C)	7156	9662	3957	120
H(38)	4506	7284	1235	70
H(39A)	4347	9563	843	149
H(39B)	3889	8574	188	149
H(39C)	4507	9212	10	149
H(40A)	4896	6918	-191	147
H(40B)	4290	6239	-4	147
H(40C)	4998	5816	520	147
H(2)	4972(19)	7150(40)	2670(20)	53

Table A93. Torsion angles [°] for **13a**.

O(1)-C(1)-C(2)-C(3)	176.8(4)
N(1)-C(1)-C(2)-C(3)	-5.7(6)
O(1)-C(1)-C(2)-C(7)	-2.1(6)
N(1)-C(1)-C(2)-C(7)	175.4(4)
C(7)-C(2)-C(3)-C(4)	-0.5(6)
C(1)-C(2)-C(3)-C(4)	-179.4(4)
C(2)-C(3)-C(4)-C(5)	0.7(7)
C(3)-C(4)-C(5)-C(6)	-1.4(6)
C(3)-C(4)-C(5)-C(8)	179.6(4)
C(4)-C(5)-C(6)-C(7)	1.9(6)
C(8)-C(5)-C(6)-C(7)	-179.1(4)
C(5)-C(6)-C(7)-C(2)	-1.8(6)
C(3)-C(2)-C(7)-C(6)	1.0(6)
C(1)-C(2)-C(7)-C(6)	-180.0(4)
C(14)-C(9)-C(10)-C(11)	1.6(6)
N(1)-C(9)-C(10)-C(11)	-174.3(4)
C(14)-C(9)-C(10)-C(15)	-179.6(4)
N(1)-C(9)-C(10)-C(15)	4.5(6)
C(9)-C(10)-C(11)-C(12)	0.7(7)
C(15)-C(10)-C(11)-C(12)	-178.0(4)
C(10)-C(11)-C(12)-C(13)	-2.1(7)
C(11)-C(12)-C(13)-C(14)	1.2(7)
C(12)-C(13)-C(14)-C(9)	1.0(7)
C(12)-C(13)-C(14)-C(18)	-177.9(5)
C(10)-C(9)-C(14)-C(13)	-2.5(6)
N(1)-C(9)-C(14)-C(13)	173.5(4)
C(10)-C(9)-C(14)-C(18)	176.4(4)
N(1)-C(9)-C(14)-C(18)	-7.6(7)
C(9)-C(10)-C(15)-C(17)	126.7(5)
C(11)-C(10)-C(15)-C(17)	-54.6(6)
C(9)-C(10)-C(15)-C(16)	-108.7(5)
C(11)-C(10)-C(15)-C(16)	70.0(6)
C(13)-C(14)-C(18)-C(20)	80.9(8)
C(9)-C(14)-C(18)-C(20)	-97.9(8)
C(13)-C(14)-C(18)-C(19)	-107.1(7)
C(9)-C(14)-C(18)-C(19)	74.1(8)

O(1)-C(1)-N(1)-C(9)	0.8(7)	C(29)-C(30)-C(31)-C(32)	0.6(6)
C(2)-C(1)-N(1)-C(9)	-176.8(4)	C(35)-C(30)-C(31)-C(32)	176.9(4)
C(10)-C(9)-N(1)-C(1)	-88.5(5)	C(30)-C(31)-C(32)-C(33)	-0.4(7)
C(14)-C(9)-N(1)-C(1)	95.4(5)	C(31)-C(32)-C(33)-C(34)	-0.1(7)
O(2)-C(21)-C(22)-C(23)	-4.6(6)	C(30)-C(29)-C(34)-C(33)	-0.3(6)
N(2)-C(21)-C(22)-C(23)	174.3(4)	N(2)-C(29)-C(34)-C(33)	-180.0(3)
O(2)-C(21)-C(22)-C(27)	174.6(4)	C(30)-C(29)-C(34)-C(38)	179.2(4)
N(2)-C(21)-C(22)-C(27)	-6.6(6)	N(2)-C(29)-C(34)-C(38)	-0.5(6)
C(27)-C(22)-C(23)-C(24)	0.9(6)	C(32)-C(33)-C(34)-C(29)	0.4(6)
C(21)-C(22)-C(23)-C(24)	-179.9(4)	C(32)-C(33)-C(34)-C(38)	-179.1(4)
C(22)-C(23)-C(24)-C(25)	-0.5(6)	C(31)-C(30)-C(35)-C(36)	-85.2(5)
C(23)-C(24)-C(25)-C(26)	-0.2(6)	C(29)-C(30)-C(35)-C(36)	91.0(5)
C(23)-C(24)-C(25)-C(28)	179.5(4)	C(31)-C(30)-C(35)-C(37)	39.2(6)
C(24)-C(25)-C(26)-C(27)	0.4(6)	C(29)-C(30)-C(35)-C(37)	-144.7(4)
C(28)-C(25)-C(26)-C(27)	-179.3(4)	C(29)-C(34)-C(38)-C(40)	-135.6(5)
C(25)-C(26)-C(27)-C(22)	0.1(6)	C(33)-C(34)-C(38)-C(40)	44.0(6)
C(23)-C(22)-C(27)-C(26)	-0.7(6)	C(29)-C(34)-C(38)-C(39)	96.9(5)
C(21)-C(22)-C(27)-C(26)	-179.9(4)	C(33)-C(34)-C(38)-C(39)	-83.6(5)
C(34)-C(29)-C(30)-C(31)	-0.2(6)	O(2)-C(21)-N(2)-C(29)	-8.5(6)
N(2)-C(29)-C(30)-C(31)	179.5(3)	C(22)-C(21)-N(2)-C(29)	172.7(3)
C(34)-C(29)-C(30)-C(35)	-176.5(4)	C(34)-C(29)-N(2)-C(21)	-90.7(4)
N(2)-C(29)-C(30)-C(35)	3.2(5)	C(30)-C(29)-N(2)-C(21)	89.6(5)

Symmetry transformations used to generate equivalent atoms:

Table A94. Hydrogen bonds for **13a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.92(5)	2.03(5)	2.812(4)	143(4)
N(2)-H(2)...O(2)#2	0.95(4)	2.00(4)	2.846(4)	147(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y+1/2,-z+1/2   #2 -x+1,y-1/2,-z+1/2

Table A95. Crystal data and structure refinement for **104**.

Identification code	**104**	
Empirical formula	C24 H36 P2	
Formula weight	386.47	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.0164(10) Å	α= 111.468(2)°.
	b = 9.5689(16) Å	β= 91.930(2)°.
	c = 11.0336(18) Å	γ = 97.865(2)°.
Volume	583.16(17) Å^3	
Z	1	
Density (calculated)	1.100 Mg/m^3	
Absorption coefficient	0.192 mm^{-1}	
F(000)	210	
Crystal size	0.187 x 0.164 x 0.115 mm^3	
Theta range for data collection	1.992 to 29.051°.	
Index ranges	-8<=h<=7, -12<=k<=12, -14<=l<=15	
Reflections collected	8865	
Independent reflections	2891 [R(int) = 0.0310]	
Completeness to theta = 25.500°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6994	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2891 / 2 / 128	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1068	
R indices (all data)	R1 = 0.0565, wR2 = 0.1140	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.327 and -0.481 e.Å^{-3}	

Table A96. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **104**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	6172(1)	4166(1)	4772(1)	42(1)
C(1)	5346(2)	3216(2)	3004(1)	25(1)
C(2)	3684(2)	1900(2)	2549(1)	31(1)
C(3)	3066(3)	1195(2)	1208(2)	39(1)
C(4)	4054(3)	1756(2)	334(2)	43(1)
C(5)	5671(3)	3037(2)	776(1)	38(1)
C(6)	6350(2)	3793(2)	2108(1)	28(1)
C(7)	2538(3)	1193(2)	3450(2)	42(1)

C(8)	3254(3)	-327(3)	3262(3)	72(1)
C(9)	0(3)	1028(3)	3293(3)	75(1)
C(10)	8121(3)	5219(2)	2509(2)	36(1)
C(11)	10330(3)	4883(2)	1912(2)	52(1)
C(12)	7264(3)	6463(2)	2156(2)	60(1)

Table A97. Bond lengths [Å] and angles [°] for **104**.

P(1)-C(1)	1.8414(13)
P(1)-P(1)#1	2.2060(8)
P(1)-H(1)	1.319(17)
P(1)-H(1A)	1.351(19)
C(1)-C(6)	1.4129(19)
C(1)-C(2)	1.4134(19)
C(2)-C(3)	1.395(2)
C(2)-C(7)	1.527(2)
C(3)-C(4)	1.379(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.375(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.396(2)
C(5)-H(5)	0.9500
C(6)-C(10)	1.523(2)
C(7)-C(9)	1.511(3)
C(7)-C(8)	1.517(3)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.524(2)
C(10)-C(12)	1.527(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(1)-P(1)-P(1)#1	98.14(4)
C(1)-P(1)-H(1)	107.8(13)
P(1)#1-P(1)-H(1)	103.9(13)
C(1)-P(1)-H(1A)	111.0(19)
P(1)#1-P(1)-H(1A)	110.6(19)
H(1)-P(1)-H(1A)	122(2)
C(6)-C(1)-C(2)	120.05(12)
C(6)-C(1)-P(1)	120.70(10)
C(2)-C(1)-P(1)	119.25(10)
C(3)-C(2)-C(1)	118.70(14)
C(3)-C(2)-C(7)	117.99(13)
C(1)-C(2)-C(7)	123.31(13)
C(4)-C(3)-C(2)	121.16(15)
C(4)-C(3)-H(3)	119.4
C(2)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	120.18(14)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	121.17(14)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	118.74(13)
C(5)-C(6)-C(10)	117.48(13)
C(1)-C(6)-C(10)	123.77(12)
C(9)-C(7)-C(8)	110.39(16)
C(9)-C(7)-C(2)	112.75(15)
C(8)-C(7)-C(2)	111.31(14)
C(9)-C(7)-H(7)	107.4
C(8)-C(7)-H(7)	107.4
C(2)-C(7)-H(7)	107.4
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(11)	111.99(14)
C(6)-C(10)-C(12)	111.41(13)
C(11)-C(10)-C(12)	110.21(14)
C(6)-C(10)-H(10)	107.7
C(11)-C(10)-H(10)	107.7
C(12)-C(10)-H(10)	107.7
C(10)-C(11)-H(11A)	109.5

C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table A98. Anisotropic displacement parameters (Å^{2}x 10^3) for **104**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 a*^{2}U^{11} + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	44(1)	50(1)	26(1)	0(1)	-7(1)	24(1)
C(1)	24(1)	24(1)	25(1)	6(1)	2(1)	9(1)
C(2)	29(1)	27(1)	32(1)	5(1)	3(1)	6(1)
C(3)	42(1)	27(1)	38(1)	2(1)	-6(1)	2(1)
C(4)	58(1)	40(1)	25(1)	2(1)	-6(1)	12(1)
C(5)	49(1)	40(1)	29(1)	14(1)	5(1)	13(1)
C(6)	30(1)	27(1)	30(1)	11(1)	3(1)	10(1)
C(7)	39(1)	38(1)	40(1)	9(1)	6(1)	-7(1)
C(8)	51(1)	95(2)	113(2)	81(2)	31(1)	28(1)
C(9)	44(1)	79(2)	127(2)	61(2)	36(1)	24(1)
C(10)	36(1)	37(1)	38(1)	19(1)	3(1)	2(1)
C(11)	32(1)	63(1)	71(1)	34(1)	3(1)	11(1)
C(12)	40(1)	42(1)	111(2)	41(1)	9(1)	7(1)

Table A99. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **104**.

	x	y	z	U(eq)
H(1)	8170(30)	5000(30)	4930(30)	51
H(1A)	5700(70)	3190(40)	5390(40)	51
H(3)	1945	312	891	47
H(4)	3616	1256	-576	52
H(5)	6337	3414	165	46
H(7)	3051	1894	4371	50
H(8A)	2756	-1048	2370	108
H(8B)	2569	-721	3890	108
H(8C)	4899	-194	3404	108
H(9A)	-565	310	2411	112
H(9B)	-437	2020	3429	112
H(9C)	-643	647	3939	112

H(10)	8436	5613	3481	43
H(11A)	10909	4127	2188	78
H(11B)	11432	5821	2209	78
H(11C)	10068	4484	957	78
H(12A)	6962	6113	1204	91
H(12B)	8407	7381	2467	91
H(12C)	5873	6695	2570	91

Table A100. Torsion angles [°] for **104**.

P(1)#1-P(1)-C(1)-C(6)	86.77(11)
P(1)#1-P(1)-C(1)-C(2)	-93.03(11)
C(6)-C(1)-C(2)-C(3)	-0.1(2)
P(1)-C(1)-C(2)-C(3)	179.74(10)
C(6)-C(1)-C(2)-C(7)	179.22(13)
P(1)-C(1)-C(2)-C(7)	-0.98(19)
C(1)-C(2)-C(3)-C(4)	0.3(2)
C(7)-C(2)-C(3)-C(4)	-179.02(15)
C(2)-C(3)-C(4)-C(5)	-0.3(2)
C(3)-C(4)-C(5)-C(6)	0.1(2)
C(4)-C(5)-C(6)-C(1)	0.1(2)
C(4)-C(5)-C(6)-C(10)	-178.93(14)
C(2)-C(1)-C(6)-C(5)	-0.14(19)
P(1)-C(1)-C(6)-C(5)	-179.94(10)
C(2)-C(1)-C(6)-C(10)	178.83(12)
P(1)-C(1)-C(6)-C(10)	-0.96(18)
C(3)-C(2)-C(7)-C(9)	-56.1(2)
C(1)-C(2)-C(7)-C(9)	124.61(17)
C(3)-C(2)-C(7)-C(8)	68.6(2)
C(1)-C(2)-C(7)-C(8)	-110.71(18)
C(5)-C(6)-C(10)-C(11)	-61.07(18)
C(1)-C(6)-C(10)-C(11)	119.94(15)
C(5)-C(6)-C(10)-C(12)	62.88(19)
C(1)-C(6)-C(10)-C(12)	-116.10(16)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table A101. Crystal data and structure refinement for **79**.

Identification code	**79**	
Empirical formula	C17 H27 N O	
Formula weight	261.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.134(5) Å	α= 90°.
	b = 18.359(9) Å	β= 116.471(5)°.
	c = 9.873(5) Å	γ = 90°.
Volume	1644.3(13) $Å^3$	
Z	4	
Density (calculated)	1.056 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	576	
Crystal size	0.305 x 0.143 x 0.114 mm^3	
Theta range for data collection	2.22 to 27.46°.	
Index ranges	-13<=h<=13, -23<=k<=23, -12<=l<=12	
Reflections collected	23450	
Independent reflections	3761 [R(int) = 0.0392]	
Completeness to theta = 25.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9927 and 0.9806	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3761 / 0 / 210	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1185	
R indices (all data)	R1 = 0.0735, wR2 = 0.1332	
Largest diff. peak and hole	0.219 and -0.189 e.$Å^{-3}$	

Table A102. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **79**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2502(1)	2742(1)	6492(1)	46(1)
N(1)	2502(1)	2382(1)	4323(1)	27(1)
C(1)	2430(1)	1616(1)	4584(1)	26(1)
C(2)	1054(2)	1273(1)	3919(2)	31(1)
C(3)	1011(2)	527(1)	4153(2)	40(1)
C(4)	2281(2)	143(1)	4993(2)	45(1)
C(5)	3631(2)	490(1)	5637(2)	40(1)
C(6)	3737(2)	1235(1)	5450(2)	30(1)
C(7)	-352(2)	1699(1)	3011(2)	39(1)

C(8)	-1002(2)	1971(1)	4043(2)	55(1)
C(9)	-1510(2)	1261(1)	1707(2)	74(1)
C(10)	5216(2)	1627(1)	6129(2)	36(1)
C(11)	6415(2)	1211(1)	7447(2)	54(1)
C(12)	5736(2)	1780(1)	4923(2)	48(1)
C(13)	2512(2)	2898(1)	5288(1)	29(1)
C(14)	2559(2)	3693(1)	4824(2)	38(1)
C(15)	2274(6)	4196(2)	5832(5)	80(2)
C(16)	1554(6)	3821(2)	3187(3)	74(2)
C(17)	4188(5)	3816(2)	5086(8)	95(2)
C(15A)	3300(30)	4136(7)	6196(16)	208(14)
C(16A)	839(12)	3935(6)	4110(20)	168(10)
C(17A)	3080(20)	3828(4)	3726(16)	126(9)

Table A103. Bond lengths [Å] and angles [°] for **79**.

O(1)-C(13)	1.2277(16)
N(1)-C(13)	1.3407(17)
N(1)-C(1)	1.4378(18)
N(1)-H(1)	0.8800
C(1)-C(2)	1.3989(19)
C(1)-C(6)	1.4010(19)
C(2)-C(3)	1.392(2)
C(2)-C(7)	1.518(2)
C(3)-C(4)	1.375(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.381(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(2)
C(5)-H(5)	0.9500
C(6)-C(10)	1.521(2)
C(7)-C(8)	1.523(2)
C(7)-C(9)	1.527(2)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.528(2)
C(10)-C(11)	1.530(2)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.536(2)
C(14)-C(17A)	1.421(8)
C(14)-C(15A)	1.467(14)
C(14)-C(15)	1.477(4)
C(14)-C(16)	1.496(3)
C(14)-C(17)	1.569(4)
C(14)-C(16A)	1.624(11)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(15A)-H(15D)	0.9800
C(15A)-H(15E)	0.9800
C(15A)-H(15F)	0.9800
C(16A)-H(16D)	0.9800
C(16A)-H(16E)	0.9800
C(16A)-H(16F)	0.9800
C(17A)-H(17D)	0.9800
C(17A)-H(17E)	0.9800
C(17A)-H(17F)	0.9800
C(13)-N(1)-C(1)	123.30(11)
C(13)-N(1)-H(1)	118.3
C(1)-N(1)-H(1)	118.3
C(2)-C(1)-C(6)	122.41(12)
C(2)-C(1)-N(1)	118.39(12)
C(6)-C(1)-N(1)	119.16(12)
C(3)-C(2)-C(1)	117.55(13)
C(3)-C(2)-C(7)	120.91(13)

C(1)-C(2)-C(7)	121.52(13)
C(4)-C(3)-C(2)	121.00(14)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	120.63(14)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.82(14)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	117.58(13)
C(5)-C(6)-C(10)	121.66(13)
C(1)-C(6)-C(10)	120.74(12)
C(2)-C(7)-C(8)	110.21(12)
C(2)-C(7)-C(9)	113.20(14)
C(8)-C(7)-C(9)	109.74(15)
C(2)-C(7)-H(7)	107.8
C(8)-C(7)-H(7)	107.8
C(9)-C(7)-H(7)	107.8
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(12)	110.92(12)
C(6)-C(10)-C(11)	113.12(13)
C(12)-C(10)-C(11)	109.58(14)
C(6)-C(10)-H(10)	107.7
C(12)-C(10)-H(10)	107.7
C(11)-C(10)-H(10)	107.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-N(1)	121.52(13)
O(1)-C(13)-C(14)	121.64(12)
N(1)-C(13)-C(14)	116.83(11)
C(17A)-C(14)-C(15A)	113.4(10)
C(17A)-C(14)-C(15)	130.8(4)
C(15)-C(14)-C(16)	112.7(2)
C(15A)-C(14)-C(13)	108.8(5)
C(15)-C(14)-C(13)	110.6(2)
C(16)-C(14)-C(13)	112.04(17)
C(17A)-C(14)-C(17)	51.8(7)
C(15A)-C(14)-C(17)	72.6(10)
C(15)-C(14)-C(17)	107.8(3)
C(16)-C(14)-C(17)	108.3(3)
C(13)-C(14)-C(17)	104.93(17)
C(17A)-C(14)-C(16A)	108.2(9)
C(15A)-C(14)-C(16A)	104.8(10)
C(15)-C(14)-C(16A)	68.0(8)
C(16)-C(14)-C(16A)	53.6(7)
C(13)-C(14)-C(16A)	102.7(3)
C(17)-C(14)-C(16A)	151.5(4)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
C(14)-C(15A)-H(15D)	109.5
C(14)-C(15A)-H(15E)	109.5
H(15D)-C(15A)-H(15E)	109.5
C(14)-C(15A)-H(15F)	109.5
H(15D)-C(15A)-H(15F)	109.5
H(15E)-C(15A)-H(15F)	109.5
C(14)-C(16A)-H(16D)	109.5
C(14)-C(16A)-H(16E)	109.5
H(16D)-C(16A)-H(16E)	109.5
C(14)-C(16A)-H(16F)	109.5
H(16D)-C(16A)-H(16F)	109.5
H(16E)-C(16A)-H(16F)	109.5
C(14)-C(17A)-H(17D)	109.5
C(14)-C(17A)-H(17E)	109.5
H(17D)-C(17A)-H(17E)	109.5
C(14)-C(17A)-H(17F)	109.5
H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5

Symmetry transformations used to generate equivalent atoms:

Table A104. Anisotropic displacement parameters (Å^{2}x 10^3) for **79**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[$h^2 a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	87(1)	33(1)	32(1)	-2(1)	39(1)	-6(1)
N(1)	38(1)	26(1)	22(1)	1(1)	18(1)	0(1)
C(1)	37(1)	26(1)	22(1)	-1(1)	18(1)	0(1)
C(2)	37(1)	34(1)	28(1)	-3(1)	19(1)	-2(1)
C(3)	44(1)	35(1)	48(1)	-7(1)	25(1)	-10(1)
C(4)	57(1)	25(1)	62(1)	0(1)	35(1)	-1(1)
C(5)	45(1)	32(1)	48(1)	4(1)	25(1)	9(1)
C(6)	37(1)	30(1)	28(1)	-2(1)	19(1)	2(1)
C(7)	34(1)	44(1)	37(1)	2(1)	14(1)	-2(1)
C(8)	51(1)	55(1)	65(1)	6(1)	31(1)	16(1)
C(9)	50(1)	89(2)	58(1)	-18(1)	2(1)	5(1)
C(10)	35(1)	36(1)	37(1)	-2(1)	15(1)	1(1)
C(11)	42(1)	61(1)	46(1)	3(1)	9(1)	5(1)
C(12)	40(1)	54(1)	57(1)	1(1)	28(1)	-2(1)
C(13)	38(1)	29(1)	24(1)	-1(1)	17(1)	-1(1)
C(14)	62(1)	27(1)	32(1)	1(1)	26(1)	-2(1)
C(15)	179(5)	29(2)	64(3)	2(2)	85(4)	14(2)
C(16)	129(4)	34(2)	38(2)	11(1)	19(2)	18(2)
C(17)	85(3)	52(2)	166(5)	25(3)	72(3)	-15(2)
C(15A)	430(40)	25(5)	69(6)	-7(4)	26(15)	-43(13)
C(16A)	97(8)	69(7)	310(30)	102(11)	64(11)	35(6)
C(17A)	290(30)	32(4)	151(14)	-8(6)	182(18)	-27(8)

Table A105. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **79**.

	x	y	z	U(eq)
H(1)	2541	2519	3487	32
H(3)	91	280	3725	48
H(4)	2229	-366	5132	54
H(5)	4498	217	6214	48
H(7)	-90	2133	2570	47
H(8A)	-1204	1556	4546	83
H(8B)	-1922	2234	3440	83
H(8C)	-299	2299	4806	83
H(9A)	-1073	1067	1074	111
H(9B)	-2342	1579	1096	111
H(9C)	-1859	858	2113	111
H(10)	5074	2106	6526	43
H(11A)	6068	1101	8206	80
H(11B)	7307	1511	7907	80

H(11C)	6637	756	7073	80
H(12A)	5874	1318	4504	72
H(12B)	6673	2045	5379	72
H(12C)	4996	2074	4112	72
H(15A)	2376	4700	5564	119
H(15B)	2985	4104	6884	119
H(15C)	1272	4119	5715	119
H(16A)	550	3673	2969	111
H(16B)	1893	3535	2564	111
H(16C)	1561	4340	2955	111
H(17A)	4312	4323	4856	143
H(17B)	4402	3492	4421	143
H(17C)	4866	3710	6143	143
H(15D)	4300	3951	6798	312
H(15E)	2745	4108	6794	312
H(15F)	3344	4643	5913	312
H(16D)	776	4461	4234	252
H(16E)	355	3678	4639	252
H(16F)	349	3811	3034	252
H(17D)	2984	4349	3480	189
H(17E)	2488	3547	2809	189
H(17F)	4113	3683	4132	189

Table A106. Torsion angles [°] for **79**.

C(13)-N(1)-C(1)-C(2)	96.30(15)
C(13)-N(1)-C(1)-C(6)	-85.75(15)
C(6)-C(1)-C(2)-C(3)	0.47(19)
N(1)-C(1)-C(2)-C(3)	178.36(11)
C(6)-C(1)-C(2)-C(7)	178.83(12)
N(1)-C(1)-C(2)-C(7)	-3.29(18)
C(1)-C(2)-C(3)-C(4)	-0.7(2)
C(7)-C(2)-C(3)-C(4)	-179.08(14)
C(2)-C(3)-C(4)-C(5)	0.5(2)
C(3)-C(4)-C(5)-C(6)	0.0(2)
C(4)-C(5)-C(6)-C(1)	-0.2(2)
C(4)-C(5)-C(6)-C(10)	-179.08(13)
C(2)-C(1)-C(6)-C(5)	-0.02(18)
N(1)-C(1)-C(6)-C(5)	-177.89(12)
C(2)-C(1)-C(6)-C(10)	178.86(12)
N(1)-C(1)-C(6)-C(10)	0.99(17)
C(3)-C(2)-C(7)-C(8)	88.61(17)
C(1)-C(2)-C(7)-C(8)	-89.69(16)
C(3)-C(2)-C(7)-C(9)	-34.7(2)
C(1)-C(2)-C(7)-C(9)	146.99(15)
C(5)-C(6)-C(10)-C(12)	102.40(16)
C(1)-C(6)-C(10)-C(12)	-76.43(16)
C(5)-C(6)-C(10)-C(11)	-21.20(19)
C(1)-C(6)-C(10)-C(11)	159.97(13)
C(1)-N(1)-C(13)-O(1)	2.1(2)
C(1)-N(1)-C(13)-C(14)	-178.72(12)
O(1)-C(13)-C(14)-C(17A)	158.5(9)
N(1)-C(13)-C(14)-C(17A)	-20.7(9)
O(1)-C(13)-C(14)-C(15A)	27.9(12)
N(1)-C(13)-C(14)-C(15A)	-151.4(12)
O(1)-C(13)-C(14)-C(15)	-11.8(3)
N(1)-C(13)-C(14)-C(15)	169.0(3)
O(1)-C(13)-C(14)-C(16)	-138.5(3)
N(1)-C(13)-C(14)-C(16)	42.3(3)
O(1)-C(13)-C(14)-C(17)	104.2(3)
N(1)-C(13)-C(14)-C(17)	-75.0(3)
O(1)-C(13)-C(14)-C(16A)	-82.9(9)
N(1)-C(13)-C(14)-C(16A)	97.9(9)

Symmetry transformations used to generate equivalent atoms:

Table A107. Hydrogen bonds for **79** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.88	2.01	2.8039(19)	149.4

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z-1/2

Table A108. Crystal data and structure refinement for **112**.

Identification code	**112**	
Empirical formula	C21 H35 Br2 N O2 Zn	
Formula weight	558.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 14.1856(8) Å	α= 90°.
	b = 10.8746(6) Å	β= 106.4390(10)°.
	c = 16.5621(9) Å	γ = 90°.
Volume	2450.5(2) $Å^3$	
Z	4	
Density (calculated)	1.514 Mg/m^3	
Absorption coefficient	4.278 mm^{-1}	
F(000)	1136	
Crystal size	0.323 x 0.153 x 0.133 mm^3	
Theta range for data collection	2.40 to 27.37°.	
Index ranges	-18<=h<=18, -13<=k<=14, -21<=l<=21	
Reflections collected	16993	
Independent reflections	5475 [R(int) = 0.0170]	
Completeness to theta = 25.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5554	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5475 / 2 / 251	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0186, wR2 = 0.0429	
R indices (all data)	R1 = 0.0203, wR2 = 0.0433	
Absolute structure parameter	0.006(5)	
Largest diff. peak and hole	0.363 and -0.385 e.$Å^{-3}$	

Table A109. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **112**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2685(1)	5113(1)	-946(1)	48(1)
Br(2)	5103(1)	5916(1)	1013(1)	43(1)
Zn	4075(1)	4518(1)	128(1)	26(1)
O(1)	4832(1)	3219(1)	-238(1)	27(1)
N(1)	6054(1)	1951(1)	-242(1)	23(1)
C(1)	5809(1)	1122(2)	348(1)	24(1)
C(2)	5305(2)	39(2)	38(1)	29(1)
C(3)	5064(2)	-739(2)	614(2)	38(1)

C(4)	5324(2)	-449(2)	1458(2)	44(1)
C(5)	5840(2)	618(2)	1755(1)	39(1)
C(6)	6094(2)	1436(2)	1204(1)	30(1)
C(7)	5016(2)	-265(2)	-896(1)	32(1)
C(8)	5039(2)	-1644(2)	-1072(2)	57(1)
C(9)	4010(2)	269(3)	-1334(2)	54(1)
C(10)	6683(2)	2594(2)	1513(1)	35(1)
C(11)	7761(2)	2400(3)	1592(2)	69(1)
C(12)	6536(2)	3087(3)	2339(2)	57(1)
C(13)	5555(1)	2982(2)	-496(1)	22(1)
C(14)	5902(2)	3843(2)	-1081(1)	28(1)
C(15)	6605(3)	4776(3)	-523(2)	66(1)
C(16)	5029(2)	4572(3)	-1614(2)	68(1)
C(17)	6425(2)	3197(2)	-1632(2)	53(1)
O(2)	3586(1)	3369(1)	890(1)	35(1)
C(18)	3252(2)	2130(2)	661(2)	43(1)
C(19)	2998(2)	1638(3)	1418(2)	57(1)
C(20)	2739(2)	2742(3)	1850(2)	54(1)
C(21)	3065(2)	3851(2)	1452(2)	49(1)

Table A110. Bond lengths [Å] and angles [°] for **112**.

Br(1)-Zn	2.3416(3)
Br(2)-Zn	2.3186(3)
Zn-O(1)	1.9713(13)
Zn-O(2)	2.0325(14)
O(1)-C(13)	1.244(2)
N(1)-C(13)	1.330(2)
N(1)-C(1)	1.442(2)
N(1)-H(1)	0.8800
C(1)-C(2)	1.398(3)
C(1)-C(6)	1.402(3)
C(2)-C(3)	1.389(3)
C(2)-C(7)	1.521(3)
C(3)-C(4)	1.376(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.386(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.393(3)
C(5)-H(5)	0.9500
C(6)-C(10)	1.518(3)
C(7)-C(9)	1.520(3)
C(7)-C(8)	1.530(3)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.512(3)
C(10)-C(12)	1.538(3)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.526(3)
C(14)-C(17)	1.503(3)
C(14)-C(16)	1.524(3)
C(14)-C(15)	1.536(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
O(2)-C(21)	1.441(3)
O(2)-C(18)	1.443(3)
C(18)-C(19)	1.498(3)
C(18)-H(18A)	0.9900

C(18)-H(18B)	0.9900
C(19)-C(20)	1.495(4)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.509(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
O(1)-Zn-O(2)	93.55(6)
O(1)-Zn-Br(2)	111.37(4)
O(2)-Zn-Br(2)	105.95(4)
O(1)-Zn-Br(1)	112.30(4)
O(2)-Zn-Br(1)	106.21(4)
Br(2)-Zn-Br(1)	122.864(16)
C(13)-O(1)-Zn	145.87(13)
C(13)-N(1)-C(1)	122.22(16)
C(13)-N(1)-H(1)	118.9
C(1)-N(1)-H(1)	118.9
C(2)-C(1)-C(6)	123.22(19)
C(2)-C(1)-N(1)	118.28(17)
C(6)-C(1)-N(1)	118.49(17)
C(3)-C(2)-C(1)	117.4(2)
C(3)-C(2)-C(7)	121.25(19)
C(1)-C(2)-C(7)	121.32(18)
C(4)-C(3)-C(2)	120.7(2)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	121.0(2)
C(3)-C(4)-H(4)	119.5
C(5)-C(4)-H(4)	119.5
C(4)-C(5)-C(6)	120.7(2)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	116.9(2)
C(5)-C(6)-C(10)	121.94(18)
C(1)-C(6)-C(10)	121.11(18)
C(9)-C(7)-C(2)	110.38(18)
C(9)-C(7)-C(8)	110.6(2)
C(2)-C(7)-C(8)	113.13(19)
C(9)-C(7)-H(7)	107.5
C(2)-C(7)-H(7)	107.5
C(8)-C(7)-H(7)	107.5
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(6)	111.10(18)
C(11)-C(10)-C(12)	111.1(2)
C(6)-C(10)-C(12)	112.9(2)
C(11)-C(10)-H(10)	107.1
C(6)-C(10)-H(10)	107.1
C(12)-C(10)-H(10)	107.1
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-N(1)	118.85(17)
O(1)-C(13)-C(14)	122.42(17)
N(1)-C(13)-C(14)	118.71(17)
C(17)-C(14)-C(16)	110.6(2)
C(17)-C(14)-C(13)	113.72(17)
C(16)-C(14)-C(13)	109.39(18)
C(17)-C(14)-C(15)	109.0(2)
C(16)-C(14)-C(15)	106.7(2)
C(13)-C(14)-C(15)	107.09(18)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(21)-O(2)-C(18)	108.62(17)
C(21)-O(2)-Zn	120.32(14)

C(18)-O(2)-Zn	123.74(12)	C(19)-C(20)-C(21)	106.6(2)
O(2)-C(18)-C(19)	104.61(19)	C(19)-C(20)-H(20A)	110.4
O(2)-C(18)-H(18A)	110.8	C(21)-C(20)-H(20A)	110.4
C(19)-C(18)-H(18A)	110.8	C(19)-C(20)-H(20B)	110.4
O(2)-C(18)-H(18B)	110.8	C(21)-C(20)-H(20B)	110.4
C(19)-C(18)-H(18B)	110.8	H(20A)-C(20)-H(20B)	108.6
H(18A)-C(18)-H(18B)	108.9	O(2)-C(21)-C(20)	105.54(19)
C(20)-C(19)-C(18)	105.3(2)	O(2)-C(21)-H(21A)	110.6
C(20)-C(19)-H(19A)	110.7	C(20)-C(21)-H(21A)	110.6
C(18)-C(19)-H(19A)	110.7	O(2)-C(21)-H(21B)	110.6
C(20)-C(19)-H(19B)	110.7	C(20)-C(21)-H(21B)	110.6
C(18)-C(19)-H(19B)	110.7	H(21A)-C(21)-H(21B)	108.8
H(19A)-C(19)-H(19B)	108.8		

Symmetry transformations used to generate equivalent atoms:

Table A111. Anisotropic displacement parameters ($Å^2$x 10^3) for **112**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	35(1)	64(1)	43(1)	0(1)	7(1)	25(1)
Br(2)	51(1)	34(1)	45(1)	-7(1)	14(1)	-9(1)
Zn	27(1)	22(1)	31(1)	2(1)	13(1)	5(1)
O(1)	29(1)	25(1)	32(1)	4(1)	17(1)	7(1)
N(1)	22(1)	22(1)	29(1)	0(1)	11(1)	4(1)
C(1)	22(1)	24(1)	28(1)	3(1)	10(1)	8(1)
C(2)	27(1)	23(1)	36(1)	2(1)	8(1)	7(1)
C(3)	41(1)	28(1)	48(1)	5(1)	14(1)	3(1)
C(4)	55(2)	38(1)	44(1)	17(1)	20(1)	10(1)
C(5)	51(2)	40(1)	28(1)	5(1)	13(1)	13(1)
C(6)	31(1)	29(1)	28(1)	1(1)	7(1)	11(1)
C(7)	31(1)	32(1)	34(1)	-5(1)	8(1)	-1(1)
C(8)	80(2)	34(1)	55(2)	-11(1)	17(1)	3(1)
C(9)	44(2)	63(2)	44(1)	-8(1)	-5(1)	9(1)
C(10)	37(1)	35(1)	29(1)	-7(1)	4(1)	8(1)
C(11)	36(1)	61(2)	99(2)	-38(2)	4(1)	-1(1)
C(12)	84(2)	49(2)	39(1)	-16(1)	17(1)	1(1)
C(13)	21(1)	24(1)	21(1)	-4(1)	4(1)	1(1)
C(14)	30(1)	30(1)	29(1)	2(1)	15(1)	1(1)
C(15)	81(2)	68(2)	63(2)	-18(2)	42(2)	-44(2)
C(16)	49(2)	84(2)	80(2)	52(2)	31(2)	20(2)
C(17)	86(2)	38(1)	52(1)	5(1)	45(1)	9(1)
O(2)	44(1)	27(1)	44(1)	-4(1)	28(1)	-3(1)
C(18)	57(2)	30(1)	47(1)	-4(1)	26(1)	-9(1)
C(19)	70(2)	48(2)	61(2)	5(1)	34(1)	-18(1)
C(20)	65(2)	56(2)	54(2)	12(1)	37(1)	8(1)
C(21)	62(2)	45(2)	54(1)	-9(1)	42(1)	-4(1)

Table A112. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **112**.

	x	y	z	U(eq)
H(1)	6551	1768	-440	28
H(3)	4716	-1480	425	46
H(4)	5146	-988	1842	53
H(5)	6022	793	2341	47
H(7)	5503	141	-1143	39
H(8A)	5667	-1989	-739	86
H(8B)	4966	-1774	-1672	86
H(8C)	4499	-2052	-917	86
H(9A)	3517	-102	-1098	81
H(9B)	3845	92	-1938	81
H(9C)	4022	1161	-1247	81
H(10)	6439	3242	1075	42
H(11A)	8038	1812	2045	103
H(11B)	8110	3185	1721	103
H(11C)	7833	2078	1060	103
H(12A)	5834	3088	2301	86
H(12B)	6793	3927	2437	86
H(12C)	6888	2559	2808	86
H(15A)	6264	5214	-171	100
H(15B)	6824	5367	-878	100
H(15C)	7176	4343	-162	100
H(16A)	4527	4003	-1937	103
H(16B)	5247	5109	-2002	103
H(16C)	4751	5074	-1246	103
H(17A)	7007	2776	-1279	80
H(17B)	6626	3801	-1990	80
H(17C)	5982	2594	-1986	80
H(18A)	3777	1632	535	51
H(18B)	2669	2128	162	51
H(19A)	2434	1065	1248	68
H(19B)	3565	1198	1794	68
H(20A)	3081	2714	2460	65
H(20B)	2022	2772	1774	65
H(21A)	2490	4341	1137	58
H(21B)	3500	4381	1886	58

Table A113. Torsion angles [°] for **112**.

O(2)-Zn-O(1)-C(13)	-151.9(2)
Br(2)-Zn-O(1)-C(13)	-43.2(2)
Br(1)-Zn-O(1)-C(13)	99.0(2)
C(13)-N(1)-C(1)-C(2)	103.2(2)
C(13)-N(1)-C(1)-C(6)	-77.3(2)
C(6)-C(1)-C(2)-C(3)	1.3(3)
N(1)-C(1)-C(2)-C(3)	-179.16(18)
C(6)-C(1)-C(2)-C(7)	-179.68(18)

N(1)-C(1)-C(2)-C(7)	-0.1(3)
C(1)-C(2)-C(3)-C(4)	-0.5(3)
C(7)-C(2)-C(3)-C(4)	-179.5(2)
C(2)-C(3)-C(4)-C(5)	-0.7(4)
C(3)-C(4)-C(5)-C(6)	1.2(4)
C(4)-C(5)-C(6)-C(1)	-0.4(3)
C(4)-C(5)-C(6)-C(10)	-178.3(2)
C(2)-C(1)-C(6)-C(5)	-0.9(3)
N(1)-C(1)-C(6)-C(5)	179.61(17)
C(2)-C(1)-C(6)-C(10)	177.07(18)
N(1)-C(1)-C(6)-C(10)	-2.5(3)
C(3)-C(2)-C(7)-C(9)	90.0(2)
C(1)-C(2)-C(7)-C(9)	-89.0(2)
C(3)-C(2)-C(7)-C(8)	-34.5(3)
C(1)-C(2)-C(7)-C(8)	146.5(2)
C(5)-C(6)-C(10)-C(11)	97.8(3)
C(1)-C(6)-C(10)-C(11)	-80.1(3)
C(5)-C(6)-C(10)-C(12)	-27.8(3)
C(1)-C(6)-C(10)-C(12)	154.4(2)
Zn-O(1)-C(13)-N(1)	143.54(17)
Zn-O(1)-C(13)-C(14)	-35.3(3)
C(1)-N(1)-C(13)-O(1)	-2.4(3)
C(1)-N(1)-C(13)-C(14)	176.46(16)
O(1)-C(13)-C(14)-C(17)	-152.6(2)
N(1)-C(13)-C(14)-C(17)	28.6(3)
O(1)-C(13)-C(14)-C(16)	-28.4(3)
N(1)-C(13)-C(14)-C(16)	152.8(2)
O(1)-C(13)-C(14)-C(15)	86.9(3)
N(1)-C(13)-C(14)-C(15)	-91.9(2)
O(1)-Zn-O(2)-C(21)	171.42(17)
Br(2)-Zn-O(2)-C(21)	58.00(17)
Br(1)-Zn-O(2)-C(21)	-74.13(17)
O(1)-Zn-O(2)-C(18)	-41.92(17)
Br(2)-Zn-O(2)-C(18)	-155.34(16)
Br(1)-Zn-O(2)-C(18)	72.53(17)
C(21)-O(2)-C(18)-C(19)	-31.7(3)
Zn-O(2)-C(18)-C(19)	178.34(17)
O(2)-C(18)-C(19)-C(20)	26.5(3)
C(18)-C(19)-C(20)-C(21)	-12.4(3)
C(18)-O(2)-C(21)-C(20)	23.8(3)
Zn-O(2)-C(21)-C(20)	174.93(17)
C(19)-C(20)-C(21)-O(2)	-6.3(3)

Symmetry transformations used to generate equivalent atoms:

Table A114. Hydrogen bonds for **112** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Br(1)#1	0.88	2.70	3.4981(15)	151.2

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,y-1/2,z

Table A115. Crystal data and structure refinement for **113a**.

Identification code	**113a**	
Empirical formula	C21 H35 Cl2 N O2 Zn	
Formula weight	469.77	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 13.9291(16) Å	α= 90°.
	b = 10.7019(13) Å	β= 106.417(2)°.
	c = 16.583(2) Å	γ = 90°.
Volume	2371.2(5) $Å^3$	
Z	4	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	1.276 mm^{-1}	
F(000)	992	
Crystal size	0.173 x 0.102 x 0.064 mm^3	
Theta range for data collection	2.44 to 27.47°.	
Index ranges	-18<=h<=17, -13<=k<=13, -21<=l<=21	
Reflections collected	16969	
Independent reflections	5364 [R(int) = 0.0818]	
Completeness to theta = 27.47°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9217 and 0.8085	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5364 / 3 / 254	
Goodness-of-fit on F^2	0.961	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.0784	
R indices (all data)	R1 = 0.1000, wR2 = 0.0912	
Absolute structure parameter	0.045(13)	
Largest diff. peak and hole	0.341 and -0.383 e.$Å^{-3}$	

Table A116. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **113a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn	3(1)	425(1)	2500(1)	28(1)
Cl(1)	-1320(1)	-230(1)	1514(1)	57(1)
Cl(2)	1026(1)	-855(1)	3351(1)	46(1)
O(1)	741(2)	1767(3)	2115(2)	28(1)
N(1)	1998(3)	3044(3)	2119(2)	24(1)
C(1)	1764(3)	3893(4)	2719(3)	24(1)
C(2)	1284(3)	5003(4)	2418(3)	27(1)
C(3)	1045(4)	5789(4)	2998(3)	36(1)

C(4)	1306(4)	5473(5)	3834(4)	44(1)
C(5)	1811(4)	4376(5)	4125(3)	40(1)
C(6)	2054(3)	3545(4)	3567(3)	29(1)
C(7)	1001(3)	5336(4)	1494(3)	34(1)
C(8)	1045(5)	6710(4)	1321(4)	61(2)
C(9)	-20(4)	4786(5)	1035(4)	58(2)
C(10)	2625(3)	2368(4)	3872(3)	32(1)
C(11)	3734(4)	2525(5)	3919(5)	66(2)
C(12)	2525(5)	1878(5)	4700(3)	58(2)
C(13)	1479(3)	2013(4)	1857(3)	21(1)
C(14)	1804(4)	1162(4)	1256(3)	26(1)
C(15)	2494(5)	170(5)	1792(4)	73(2)
C(16)	914(4)	459(6)	726(4)	87(3)
C(17)	2346(5)	1823(5)	714(4)	69(2)
O(2)	-507(3)	1612(3)	3241(2)	41(1)
C(18)	-990(5)	1146(5)	3829(4)	52(2)
C(19)	-1280(5)	2281(5)	4243(4)	61(2)
C(20)	-1107(5)	3375(5)	3762(4)	65(2)
C(21)	-837(4)	2845(4)	3024(3)	45(1)

Table A117. Bond lengths [Å] and angles [°] for **113a**.

Zn-O(1)	1.974(3)
Zn-O(2)	2.030(3)
Zn-Cl(2)	2.1821(15)
Zn-Cl(1)	2.2044(15)
O(1)-C(13)	1.248(4)
N(1)-C(13)	1.323(5)
N(1)-C(1)	1.451(5)
N(1)-H(1)	0.856(18)
C(1)-C(2)	1.385(6)
C(1)-C(6)	1.400(6)
C(2)-C(3)	1.387(6)
C(2)-C(7)	1.513(6)
C(3)-C(4)	1.372(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(7)
C(4)-H(4)	0.9500
C(5)-C(6)	1.393(6)
C(5)-H(5)	0.9500
C(6)-C(10)	1.499(6)
C(7)-C(8)	1.502(6)
C(7)-C(9)	1.528(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.514(6)
C(10)-C(11)	1.533(6)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.511(5)
C(14)-C(16)	1.503(7)
C(14)-C(17)	1.505(6)
C(14)-C(15)	1.536(7)
C(15)-H(13A)	0.9800
C(15)-H(13B)	0.9800
C(15)-H(13C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
O(2)-C(21)	1.411(5)
O(2)-C(18)	1.422(5)
C(18)-C(19)	1.506(7)
C(18)-H(18A)	0.9900

C(18)-H(18B)	0.9900
C(19)-C(20)	1.474(7)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.490(6)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
O(1)-Zn-O(2)	92.52(11)
O(1)-Zn-Cl(2)	111.19(10)
O(2)-Zn-Cl(2)	106.07(11)
O(1)-Zn-Cl(1)	113.24(10)
O(2)-Zn-Cl(1)	106.59(11)
Cl(2)-Zn-Cl(1)	122.44(7)
C(13)-O(1)-Zn	145.0(3)
C(13)-N(1)-C(1)	122.6(3)
C(13)-N(1)-H(1)	119(3)
C(1)-N(1)-H(1)	118(3)
C(2)-C(1)-C(6)	124.2(4)
C(2)-C(1)-N(1)	118.0(4)
C(6)-C(1)-N(1)	117.8(4)
C(1)-C(2)-C(3)	117.2(4)
C(1)-C(2)-C(7)	121.8(4)
C(3)-C(2)-C(7)	120.9(4)
C(4)-C(3)-C(2)	120.2(5)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(3)-C(4)-C(5)	121.7(5)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	120.4(4)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	116.2(4)
C(5)-C(6)-C(10)	121.3(4)
C(1)-C(6)-C(10)	122.5(4)
C(8)-C(7)-C(2)	114.3(4)
C(8)-C(7)-C(9)	111.4(4)
C(2)-C(7)-C(9)	110.6(4)
C(8)-C(7)-H(7)	106.7
C(2)-C(7)-H(7)	106.7
C(9)-C(7)-H(7)	106.7
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(6)-C(10)-C(12)	114.9(4)
C(6)-C(10)-C(11)	110.9(4)
C(12)-C(10)-C(11)	110.0(4)
C(6)-C(10)-H(10)	106.9
C(12)-C(10)-H(10)	106.9
C(11)-C(10)-H(10)	106.9
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-N(1)	119.3(4)
O(1)-C(13)-C(14)	121.9(4)
N(1)-C(13)-C(14)	118.8(4)
C(16)-C(14)-C(17)	110.8(5)
C(16)-C(14)-C(13)	109.6(4)
C(17)-C(14)-C(13)	113.9(4)
C(16)-C(14)-C(15)	105.7(5)
C(17)-C(14)-C(15)	109.5(5)
C(13)-C(14)-C(15)	106.9(4)
C(14)-C(15)-H(13A)	109.5
C(14)-C(15)-H(13B)	109.5
H(13A)-C(15)-H(13B)	109.5
C(14)-C(15)-H(13C)	109.5
H(13A)-C(15)-H(13C)	109.5
H(13B)-C(15)-H(13C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(21)-O(2)-C(18)	108.6(4)
C(21)-O(2)-Zn	125.2(3)

C(18)-O(2)-Zn	120.7(3)	C(19)-C(20)-C(21)	105.1(4)
O(2)-C(18)-C(19)	105.7(4)	C(19)-C(20)-H(20A)	110.7
O(2)-C(18)-H(18A)	110.6	C(21)-C(20)-H(20A)	110.7
C(19)-C(18)-H(18A)	110.6	C(19)-C(20)-H(20B)	110.7
O(2)-C(18)-H(18B)	110.6	C(21)-C(20)-H(20B)	110.7
C(19)-C(18)-H(18B)	110.6	H(20A)-C(20)-H(20B)	108.8
H(18A)-C(18)-H(18B)	108.7	O(2)-C(21)-C(20)	106.7(4)
C(20)-C(19)-C(18)	106.7(4)	O(2)-C(21)-H(21A)	110.4
C(20)-C(19)-H(19A)	110.4	C(20)-C(21)-H(21A)	110.4
C(18)-C(19)-H(19A)	110.4	O(2)-C(21)-H(21B)	110.4
C(20)-C(19)-H(19B)	110.4	C(20)-C(21)-H(21B)	110.4
C(18)-C(19)-H(19B)	110.4	H(21A)-C(21)-H(21B)	108.6
H(19A)-C(19)-H(19B)	108.6		

Symmetry transformations used to generate equivalent atoms:

Table A118. Anisotropic displacement parameters (Å^{2}x 10^3) for **113a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn	29(1)	23(1)	38(1)	-2(1)	19(1)	-6(1)
Cl(1)	42(1)	74(1)	55(1)	-5(1)	16(1)	-32(1)
Cl(2)	54(1)	32(1)	55(1)	8(1)	22(1)	8(1)
O(1)	32(2)	23(2)	36(2)	-2(2)	22(2)	-6(1)
N(1)	20(2)	24(2)	30(2)	-1(2)	13(2)	-5(2)
C(1)	19(2)	23(2)	30(3)	-7(2)	9(2)	-10(2)
C(2)	27(3)	21(2)	35(3)	-1(2)	11(2)	-7(2)
C(3)	41(3)	23(3)	50(4)	-4(2)	19(3)	2(2)
C(4)	49(3)	40(3)	52(4)	-22(3)	26(3)	-7(3)
C(5)	43(3)	51(4)	30(3)	-3(3)	16(3)	-14(3)
C(6)	23(3)	28(3)	36(3)	2(2)	9(2)	-11(2)
C(7)	29(3)	34(3)	37(3)	4(2)	7(2)	2(2)
C(8)	77(5)	31(3)	71(4)	9(3)	17(4)	-6(3)
C(9)	46(4)	61(4)	55(4)	14(3)	-2(3)	-7(3)
C(10)	34(3)	37(3)	24(3)	6(2)	6(2)	-10(2)
C(11)	37(3)	52(4)	100(5)	33(4)	6(3)	1(3)
C(12)	83(5)	51(4)	45(4)	15(3)	23(4)	0(3)
C(13)	20(2)	18(2)	28(3)	5(2)	10(2)	1(2)
C(14)	29(3)	25(3)	31(3)	-2(2)	18(2)	-2(2)
C(15)	104(5)	62(4)	67(4)	6(3)	45(4)	47(4)
C(16)	53(4)	110(6)	112(6)	-85(5)	44(4)	-32(4)
C(17)	132(6)	41(3)	66(4)	-4(3)	78(4)	-16(4)
O(2)	56(2)	28(2)	54(2)	7(2)	40(2)	5(2)
C(18)	70(4)	47(3)	57(4)	6(3)	47(4)	4(3)
C(19)	77(4)	64(4)	56(4)	-22(3)	42(4)	-12(3)
C(20)	87(5)	52(4)	75(5)	4(3)	53(4)	23(3)
C(21)	57(4)	38(3)	50(4)	11(3)	29(3)	11(3)

Table A119. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **113a**.

	x	y	z	U(eq)
H(1)	2490(20)	3230(40)	1920(20)	28
H(3)	699	6549	2815	44
H(4)	1135	6021	4222	53
H(5)	1992	4189	4709	48
H(7)	1503	4922	1254	40
H(8A)	511	7143	1489	91
H(8B)	956	6841	720	91
H(8C)	1696	7043	1643	91
H(9A)	-28	3893	1166	87
H(9B)	-142	4895	428	87
H(9C)	-543	5216	1218	87
H(10)	2350	1710	3440	38
H(11A)	3793	2833	3379	99
H(11B)	4074	1717	4047	99
H(11C)	4043	3125	4363	99
H(12A)	2879	2435	5156	88
H(12B)	2815	1038	4801	88
H(12C)	1815	1842	4680	88
H(13A)	3085	577	2164	110
H(13B)	2704	-421	1423	110
H(13C)	2134	-280	2132	110
H(16A)	645	-82	1087	131
H(16B)	1118	-51	313	131
H(16C)	398	1054	433	131
H(17A)	1916	2482	391	104
H(17B)	2510	1223	326	104
H(17C)	2963	2195	1070	104
H(18A)	-530	606	4251	63
H(18B)	-1590	654	3539	63
H(19A)	-1993	2234	4233	74
H(19B)	-867	2340	4836	74
H(20A)	-555	3896	4107	78
H(20B)	-1719	3893	3577	78
H(21A)	-1426	2846	2522	54
H(21B)	-299	3346	2899	54

Table A120. Torsion angles [°] for **113a**.

O(2)-Zn-O(1)-C(13)	151.3(5)	C(6)-C(1)-C(2)-C(3)	-2.7(6)
Cl(2)-Zn-O(1)-C(13)	43.0(5)	N(1)-C(1)-C(2)-C(3)	178.5(4)
Cl(1)-Zn-O(1)-C(13)	-99.4(5)	C(6)-C(1)-C(2)-C(7)	179.1(4)
C(13)-N(1)-C(1)-C(2)	-104.0(5)	N(1)-C(1)-C(2)-C(7)	0.3(6)
C(13)-N(1)-C(1)-C(6)	77.1(5)	C(1)-C(2)-C(3)-C(4)	1.7(7)

C(7)-C(2)-C(3)-C(4)	179.9(4)
C(2)-C(3)-C(4)-C(5)	0.1(8)
C(3)-C(4)-C(5)-C(6)	-1.1(8)
C(4)-C(5)-C(6)-C(1)	0.3(7)
C(4)-C(5)-C(6)-C(10)	178.3(4)
C(2)-C(1)-C(6)-C(5)	1.7(6)
N(1)-C(1)-C(6)-C(5)	-179.5(4)
C(2)-C(1)-C(6)-C(10)	-176.4(4)
N(1)-C(1)-C(6)-C(10)	2.5(6)
C(1)-C(2)-C(7)-C(8)	-147.0(4)
C(3)-C(2)-C(7)-C(8)	34.8(6)
C(1)-C(2)-C(7)-C(9)	86.3(5)
C(3)-C(2)-C(7)-C(9)	-91.8(5)
C(5)-C(6)-C(10)-C(12)	25.1(6)
C(1)-C(6)-C(10)-C(12)	-156.9(4)
C(5)-C(6)-C(10)-C(11)	-100.2(5)
C(1)-C(6)-C(10)-C(11)	77.7(6)
Zn-O(1)-C(13)-N(1)	-140.4(4)
Zn-O(1)-C(13)-C(14)	39.1(8)
C(1)-N(1)-C(13)-O(1)	1.8(6)
C(1)-N(1)-C(13)-C(14)	-177.6(4)
O(1)-C(13)-C(14)-C(16)	28.2(6)
N(1)-C(13)-C(14)-C(16)	-152.3(5)
O(1)-C(13)-C(14)-C(17)	153.0(5)
N(1)-C(13)-C(14)-C(17)	-27.5(6)
O(1)-C(13)-C(14)-C(15)	-86.0(6)
N(1)-C(13)-C(14)-C(15)	93.5(5)
O(1)-Zn-O(2)-C(21)	40.0(4)
Cl(2)-Zn-O(2)-C(21)	152.9(4)
Cl(1)-Zn-O(2)-C(21)	-75.2(4)
O(1)-Zn-O(2)-C(18)	-169.4(4)
Cl(2)-Zn-O(2)-C(18)	-56.5(4)
Cl(1)-Zn-O(2)-C(18)	75.4(4)
C(21)-O(2)-C(18)-C(19)	-23.8(6)
Zn-O(2)-C(18)-C(19)	-178.8(4)
O(2)-C(18)-C(19)-C(20)	10.0(7)
C(18)-C(19)-C(20)-C(21)	6.5(7)
C(18)-O(2)-C(21)-C(20)	28.3(6)
Zn-O(2)-C(21)-C(20)	-178.1(3)
C(19)-C(20)-C(21)-O(2)	-20.9(6)

Symmetry transformations used to generate equivalent atoms:

Table A121. Hydrogen bonds for **113a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(1)#1	0.856(18)	2.56(2)	3.352(3)	153(4)

Symmetry transformations used to generate equivalent atoms:
#1 x+1/2,y+1/2,z

Table A122. Crystal data and structure refinement for **113b**.

Identification code	**113b**	
Empirical formula	C34 H54 Cl4 N2 O2 Zn2	
Formula weight	795.33	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.6018(14) Å	α= 90°.
	b = 14.238(2) Å	β= 92.272(2)°.
	c = 16.507(3) Å	γ = 90°.
Volume	2020.1(6) $Å^3$	
Z	2	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	1.481 mm^{-1}	
F(000)	832	
Crystal size	0.361 x 0.357 x 0.224 mm^3	
Theta range for data collection	1.89 to 27.55°.	
Index ranges	-11<=h<=11, -18<=k<=18, -21<=l<=21	
Reflections collected	25540	
Independent reflections	4624 [R(int) = 0.0671]	
Completeness to theta = 25.50°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5522	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4624 / 0 / 209	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0849	
R indices (all data)	R1 = 0.0990, wR2 = 0.1075	
Largest diff. peak and hole	0.595 and -0.709 e.$Å^{-3}$	

Table A123. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **113b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn	709(1)	5076(1)	895(1)	34(1)
Cl(1)	-1711(1)	4625(1)	350(1)	45(1)
Cl(2)	661(1)	6188(1)	1804(1)	58(1)
O(1)	1465(3)	3895(2)	1339(2)	41(1)
N(1)	2260(4)	2665(2)	2058(2)	35(1)
C(1)	757(4)	2211(2)	2021(2)	36(1)
C(2)	-132(5)	2235(3)	2714(2)	44(1)
C(3)	-1544(5)	1767(3)	2678(3)	52(1)
C(4)	-2039(5)	1302(3)	1982(3)	53(1)

C(5)	-1146(5)	1297(3)	1308(3)	51(1)
C(6)	277(5)	1750(2)	1312(2)	41(1)
C(7)	400(6)	2802(3)	3449(3)	56(1)
C(8)	-9(7)	2352(4)	4256(3)	80(2)
C(9)	-267(7)	3793(3)	3393(3)	78(2)
C(10)	1291(5)	1718(3)	582(2)	50(1)
C(11)	2339(8)	869(4)	628(3)	92(2)
C(12)	363(8)	1768(5)	-217(3)	108(2)
C(13)	2551(4)	3489(2)	1728(2)	33(1)
C(14)	4170(4)	3897(3)	1859(2)	38(1)
C(15)	5389(6)	3171(3)	1672(4)	86(2)
C(16)	4327(8)	4202(5)	2738(3)	113(3)
C(17)	4399(5)	4736(3)	1315(3)	56(1)

Table A124. Bond lengths [Å] and angles [°] for **113b**.

Zn-O(1)	1.936(2)
Zn-Cl(2)	2.1830(11)
Zn-Cl(1)#1	2.2989(11)
Zn-Cl(1)	2.3251(10)
Zn-Zn#1	3.1584(9)
Cl(1)-Zn#1	2.2990(11)
O(1)-C(13)	1.253(4)
N(1)-C(13)	1.321(4)
N(1)-C(1)	1.445(5)
N(1)-H(1)	0.85(4)
C(1)-C(6)	1.390(5)
C(1)-C(2)	1.402(5)
C(2)-C(3)	1.385(6)
C(2)-C(7)	1.513(6)
C(3)-C(4)	1.377(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.378(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.383(5)
C(5)-H(5)	0.9500
C(6)-C(10)	1.516(6)
C(7)-C(9)	1.524(6)
C(7)-C(8)	1.531(6)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.508(7)
C(10)-C(12)	1.516(6)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.517(5)
C(14)-C(17)	1.511(5)
C(14)-C(15)	1.514(6)
C(14)-C(16)	1.515(6)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
O(1)-Zn-Cl(2)	112.61(8)
O(1)-Zn-Cl(1)#1	111.56(9)
Cl(2)-Zn-Cl(1)#1	119.84(5)
O(1)-Zn-Cl(1)	100.90(8)
Cl(2)-Zn-Cl(1)	115.17(4)
Cl(1)#1-Zn-Cl(1)	93.84(4)
O(1)-Zn-Zn#1	114.00(8)
Cl(2)-Zn-Zn#1	132.48(4)
Cl(1)#1-Zn-Zn#1	47.27(3)
Cl(1)-Zn-Zn#1	46.57(3)
Zn#1-Cl(1)-Zn	86.16(4)
C(13)-O(1)-Zn	145.7(2)
C(13)-N(1)-C(1)	124.3(3)
C(13)-N(1)-H(1)	120(3)

C(1)-N(1)-H(1)	116(3)
C(6)-C(1)-C(2)	123.1(4)
C(6)-C(1)-N(1)	118.8(3)
C(2)-C(1)-N(1)	118.1(3)
C(3)-C(2)-C(1)	117.3(4)
C(3)-C(2)-C(7)	122.0(4)
C(1)-C(2)-C(7)	120.7(4)
C(4)-C(3)-C(2)	120.6(4)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	120.8(4)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	121.0(4)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	117.3(4)
C(5)-C(6)-C(10)	121.3(4)
C(1)-C(6)-C(10)	121.5(3)
C(2)-C(7)-C(9)	110.1(4)
C(2)-C(7)-C(8)	113.6(4)
C(9)-C(7)-C(8)	109.9(4)
C(2)-C(7)-H(7)	107.6
C(9)-C(7)-H(7)	107.6
C(8)-C(7)-H(7)	107.6
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(6)	110.3(4)
C(11)-C(10)-C(12)	112.0(5)
C(6)-C(10)-C(12)	113.0(4)
C(11)-C(10)-H(10)	107.1
C(6)-C(10)-H(10)	107.1
C(12)-C(10)-H(10)	107.1
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-N(1)	118.1(3)
O(1)-C(13)-C(14)	123.9(3)
N(1)-C(13)-C(14)	118.0(3)
C(17)-C(14)-C(15)	108.1(4)
C(17)-C(14)-C(16)	109.5(4)
C(15)-C(14)-C(16)	110.8(5)
C(17)-C(14)-C(13)	111.0(3)
C(15)-C(14)-C(13)	110.4(3)
C(16)-C(14)-C(13)	107.1(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table A125. Anisotropic displacement parameters ($Å^2$x 10^3) for **113b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

Zn	42(1)	30(1)	29(1)	0(1)	-5(1)	1(1)
Cl(1)	40(1)	59(1)	35(1)	8(1)	-4(1)	-8(1)
Cl(2)	57(1)	55(1)	61(1)	-29(1)	-5(1)	0(1)
O(1)	43(2)	32(1)	47(2)	12(1)	-12(1)	-2(1)
N(1)	42(2)	30(2)	33(2)	6(1)	-6(1)	2(1)
C(1)	39(2)	24(2)	45(2)	9(2)	-4(2)	1(2)
C(2)	47(2)	35(2)	49(2)	8(2)	0(2)	7(2)
C(3)	48(3)	45(2)	65(3)	11(2)	10(2)	7(2)
C(4)	43(3)	37(2)	79(3)	11(2)	-1(2)	-1(2)
C(5)	55(3)	39(2)	58(3)	3(2)	-11(2)	-5(2)
C(6)	50(2)	27(2)	46(2)	8(2)	-8(2)	-5(2)
C(7)	60(3)	58(3)	50(3)	-5(2)	11(2)	3(2)
C(8)	122(5)	65(3)	53(3)	1(2)	14(3)	18(3)
C(9)	126(5)	47(3)	63(3)	-4(2)	22(3)	-3(3)
C(10)	68(3)	43(2)	38(2)	-2(2)	-1(2)	-14(2)
C(11)	135(6)	70(3)	76(4)	7(3)	54(4)	17(4)
C(12)	119(5)	156(6)	48(3)	19(4)	-20(3)	-55(5)
C(13)	43(2)	28(2)	28(2)	-3(1)	-1(2)	3(2)
C(14)	45(2)	37(2)	32(2)	2(2)	-5(2)	-5(2)
C(15)	49(3)	48(3)	160(6)	25(3)	16(3)	9(2)
C(16)	125(5)	165(6)	48(3)	-21(4)	-10(3)	-95(5)
C(17)	41(2)	45(2)	80(3)	23(2)	-3(2)	-6(2)

Table A126. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **113b**.

	x	y	z	U(eq)
H(1)	2970(50)	2380(30)	2340(30)	53
H(3)	-2178	1766	3136	63
H(4)	-3008	982	1968	64
H(5)	-1513	977	832	62
H(7)	1559	2855	3444	67
H(8A)	-1142	2340	4298	120
H(8B)	457	2720	4705	120
H(8C)	396	1709	4280	120
H(9A)	9	4079	2879	118
H(9B)	163	4172	3845	118
H(9C)	-1402	3765	3421	118
H(10)	1977	2285	612	60
H(11A)	2946	875	1143	138
H(11B)	3046	883	177	138
H(11C)	1705	298	594	138
H(12A)	-197	1176	-309	162
H(12B)	1071	1875	-658	162
H(12C)	-385	2287	-199	162
H(15A)	5291	2632	2035	128

H(15B)	6427	3447	1751	128
H(15C)	5238	2963	1108	128
H(16A)	3534	4676	2845	169
H(16B)	5364	4470	2847	169
H(16C)	4185	3658	3091	169
H(17A)	4229	4548	748	83
H(17B)	5461	4976	1400	83
H(17C)	3654	5229	1446	83

Table A127. Torsion angles [°] for **113b**.

O(1)-Zn-Cl(1)-Zn#1	-112.83(9)
Cl(2)-Zn-Cl(1)-Zn#1	125.63(5)
Cl(1)#1-Zn-Cl(1)-Zn#1	0.0
Cl(2)-Zn-O(1)-C(13)	-54.6(5)
Cl(1)#1-Zn-O(1)-C(13)	83.5(5)
Cl(1)-Zn-O(1)-C(13)	-177.9(4)
Zn#1-Zn-O(1)-C(13)	135.0(4)
C(13)-N(1)-C(1)-C(6)	78.5(4)
C(13)-N(1)-C(1)-C(2)	-103.3(4)
C(6)-C(1)-C(2)-C(3)	0.5(5)
N(1)-C(1)-C(2)-C(3)	-177.7(3)
C(6)-C(1)-C(2)-C(7)	-175.9(3)
N(1)-C(1)-C(2)-C(7)	5.9(5)
C(1)-C(2)-C(3)-C(4)	-0.2(6)
C(7)-C(2)-C(3)-C(4)	176.1(4)
C(2)-C(3)-C(4)-C(5)	-0.3(6)
C(3)-C(4)-C(5)-C(6)	0.6(6)
C(4)-C(5)-C(6)-C(1)	-0.3(6)
C(4)-C(5)-C(6)-C(10)	177.8(4)
C(2)-C(1)-C(6)-C(5)	-0.3(5)
N(1)-C(1)-C(6)-C(5)	177.9(3)
C(2)-C(1)-C(6)-C(10)	-178.3(3)
N(1)-C(1)-C(6)-C(10)	-0.2(5)
C(3)-C(2)-C(7)-C(9)	-85.2(5)
C(1)-C(2)-C(7)-C(9)	91.0(5)
C(3)-C(2)-C(7)-C(8)	38.6(6)
C(1)-C(2)-C(7)-C(8)	-145.2(4)
C(5)-C(6)-C(10)-C(11)	-88.1(5)
C(1)-C(6)-C(10)-C(11)	89.9(5)
C(5)-C(6)-C(10)-C(12)	38.0(6)
C(1)-C(6)-C(10)-C(12)	-144.0(4)
Zn-O(1)-C(13)-N(1)	161.7(3)
Zn-O(1)-C(13)-C(14)	-16.8(7)
C(1)-N(1)-C(13)-O(1)	-1.9(5)
C(1)-N(1)-C(13)-C(14)	176.7(3)
O(1)-C(13)-C(14)-C(17)	-12.5(5)
N(1)-C(13)-C(14)-C(17)	169.0(3)
O(1)-C(13)-C(14)-C(15)	-132.4(4)
N(1)-C(13)-C(14)-C(15)	49.1(5)
O(1)-C(13)-C(14)-C(16)	106.9(5)
N(1)-C(13)-C(14)-C(16)	-71.6(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table A128. Hydrogen bonds for **113b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(2)#2	0.85(4)	2.48(4)	3.300(3)	161(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z   #2 -x+1/2,y-1/2,-z+1/2

Table A129. Crystal data and structure refinement for **113c**.

Identification code	**113c**	
Empirical formula	C22 H36 Cl5 N O2 Zn	
Formula weight	589.14	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.302(8) Å	α= 90°.
	b = 8.929(3) Å	β= 114.751(3)°.
	c = 17.068(5) Å	γ = 90°.
Volume	2809.9(16) Å^3	
Z	4	
Density (calculated)	1.388 Mg/m^3	
Absorption coefficient	1.368 mm^{-1}	
F(000)	1224	
Crystal size	0.378 x 0.285 x 0.21 mm^3	
Theta range for data collection	2.04 to 26.50°.	
Index ranges	-25<=h<=25, -11<=k<=11, -21<=l<=21	
Reflections collected	37053	
Independent reflections	5751 [R(int) = 0.0512]	
Completeness to theta = 26.50°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.5201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5751 / 1 / 289	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0751, wR2 = 0.2058	
R indices (all data)	R1 = 0.0884, wR2 = 0.2168	
Largest diff. peak and hole	2.218 and -1.065 e.Å^{-3}	

Table A130. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **113c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

U(eq)	x	y	z	
Zn	2856(1)	1208(1)	1299(1)	22(1)
Cl(1)	2029(1)	-603(2)	852(1)	33(1)
Cl(2)	3585(1)	1472(2)	2662(1)	37(1)
O(1)	2494(2)	3219(4)	814(2)	27(1)
O(2)	3423(2)	937(4)	579(3)	30(1)
N(1)	2450(2)	5698(5)	776(2)	16(1)
C(1)	3061(3)	5812(5)	554(3)	19(1)
C(2)	2918(3)	5866(6)	-322(3)	22(1)
C(3)	3515(3)	5953(6)	-527(4)	29(1)

C(4)	4209(3)	6018(6)	107(4)	33(1)
C(5)	4342(3)	5997(6)	971(4)	26(1)
C(6)	3756(3)	5854(5)	1210(3)	20(1)
C(7)	2155(3)	5776(7)	-1037(4)	31(1)
C(8)	2038(4)	6887(9)	-1782(4)	51(2)
C(9)	1988(5)	4183(9)	-1397(5)	55(2)
C(10)	3888(3)	5767(6)	2158(3)	25(1)
C(11)	3853(4)	7342(7)	2490(4)	38(1)
C(12)	4599(3)	4994(8)	2719(4)	38(1)
C(13)	2196(3)	4396(5)	892(3)	19(1)
C(14)	1520(3)	4357(6)	1060(4)	27(1)
C(15)	1696(4)	3442(10)	1881(5)	54(2)
C(16)	939(4)	3498(9)	284(5)	51(2)
C(17)	1227(4)	5890(7)	1128(5)	43(2)
C(18)	3856(3)	2111(7)	437(4)	34(1)
C(19)	4125(4)	1475(8)	-191(5)	44(2)
C(20)	3594(7)	311(11)	-639(6)	80(3)
C(21)	3313(3)	-247(6)	-24(4)	86(4)
C(1S)	9563(3)	320(6)	1062(4)	53(2)
Cl(1S)	9173(2)	-801(4)	1579(2)	106(1)
Cl(2S)	10408(1)	-335(3)	1178(1)	68(1)
Cl(3S)	9633(2)	2179(3)	1415(2)	91(1)

Table A131. Bond lengths [Å] and angles [°] for **113c**.

Zn-O(1)	1.984(4)
Zn-O(2)	2.019(4)
Zn-Cl(2)	2.1855(16)
Zn-Cl(1)	2.2241(15)
O(1)-C(13)	1.248(6)
O(2)-C(21)	1.425(6)
O(2)-C(18)	1.452(7)
N(1)-C(13)	1.320(6)
N(1)-C(1)	1.446(6)
N(1)-H(1)	0.84(2)
C(1)-C(6)	1.386(7)
C(1)-C(2)	1.399(7)
C(2)-C(3)	1.399(7)
C(2)-C(7)	1.520(8)
C(3)-C(4)	1.372(9)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(8)
C(4)-H(4)	0.9500
C(5)-C(6)	1.415(7)
C(5)-H(5)	0.9500
C(6)-C(10)	1.529(7)
C(7)-C(9)	1.530(9)
C(7)-C(8)	1.551(9)
C(7)-H(7)	1.0000
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(12)	1.522(8)
C(10)-C(11)	1.529(8)
C(10)-H(10)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.515(7)
C(14)-C(17)	1.516(8)
C(14)-C(15)	1.529(8)
C(14)-C(16)	1.558(9)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800

C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.502(8)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.461(11)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.476(9)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(1S)-Cl(1S)	1.730(6)
C(1S)-Cl(2S)	1.744(6)
C(1S)-Cl(3S)	1.751(6)
C(1S)-H(1S)	1.0000
O(1)-Zn-O(2)	93.49(16)
O(1)-Zn-Cl(2)	108.29(12)
O(2)-Zn-Cl(2)	110.86(14)
O(1)-Zn-Cl(1)	114.86(13)
O(2)-Zn-Cl(1)	104.18(12)
Cl(2)-Zn-Cl(1)	121.41(6)
C(13)-O(1)-Zn	146.0(3)
C(21)-O(2)-C(18)	109.8(4)
C(21)-O(2)-Zn	124.8(3)
C(18)-O(2)-Zn	123.7(3)
C(13)-N(1)-C(1)	122.3(4)
C(13)-N(1)-H(1)	119(5)
C(1)-N(1)-H(1)	118(5)
C(6)-C(1)-C(2)	123.3(4)
C(6)-C(1)-N(1)	119.0(4)
C(2)-C(1)-N(1)	117.7(4)
C(1)-C(2)-C(3)	117.1(5)
C(1)-C(2)-C(7)	122.9(5)
C(3)-C(2)-C(7)	120.0(5)
C(4)-C(3)-C(2)	121.1(5)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	121.2(5)
C(3)-C(4)-H(4)	119.4
C(5)-C(4)-H(4)	119.4
C(4)-C(5)-C(6)	119.7(5)
C(4)-C(5)-H(5)	120.1
C(6)-C(5)-H(5)	120.1
C(1)-C(6)-C(5)	117.6(5)
C(1)-C(6)-C(10)	121.4(4)
C(5)-C(6)-C(10)	121.0(5)
C(2)-C(7)-C(9)	110.6(5)
C(2)-C(7)-C(8)	112.4(5)
C(9)-C(7)-C(8)	109.5(5)
C(2)-C(7)-H(7)	108.1
C(9)-C(7)-H(7)	108.1
C(8)-C(7)-H(7)	108.1
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-C(10)-C(11)	111.3(5)
C(12)-C(10)-C(6)	112.8(5)
C(11)-C(10)-C(6)	109.3(4)
C(12)-C(10)-H(10)	107.7
C(11)-C(10)-H(10)	107.7
C(6)-C(10)-H(10)	107.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(12)-H(12A)	109.5
C(10)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(10)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-N(1)	119.2(4)
O(1)-C(13)-C(14)	121.3(4)
N(1)-C(13)-C(14)	119.4(4)
C(13)-C(14)-C(17)	114.1(4)
C(13)-C(14)-C(15)	107.6(5)
C(17)-C(14)-C(15)	111.2(6)
C(13)-C(14)-C(16)	105.9(5)
C(17)-C(14)-C(16)	109.2(5)
C(15)-C(14)-C(16)	108.6(6)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.5

C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(2)-C(18)-C(19)	105.8(5)
O(2)-C(18)-H(18A)	110.6
C(19)-C(18)-H(18A)	110.6
O(2)-C(18)-H(18B)	110.6
C(19)-C(18)-H(18B)	110.6
H(18A)-C(18)-H(18B)	108.7
C(20)-C(19)-C(18)	103.5(6)
C(20)-C(19)-H(19A)	111.1
C(18)-C(19)-H(19A)	111.1
C(20)-C(19)-H(19B)	111.1
C(18)-C(19)-H(19B)	111.1
H(19A)-C(19)-H(19B)	109.0
C(19)-C(20)-C(21)	106.7(6)
C(19)-C(20)-H(20A)	110.4
C(21)-C(20)-H(20A)	110.4
C(19)-C(20)-H(20B)	110.4
C(21)-C(20)-H(20B)	110.4
H(20A)-C(20)-H(20B)	108.6
O(2)-C(21)-C(20)	105.8(5)
O(2)-C(21)-H(21A)	110.6
C(20)-C(21)-H(21A)	110.6
O(2)-C(21)-H(21B)	110.6
C(20)-C(21)-H(21B)	110.6
H(21A)-C(21)-H(21B)	108.7
Cl(1S)-C(1S)-Cl(2S)	112.7(4)
Cl(1S)-C(1S)-Cl(3S)	111.2(3)
Cl(2S)-C(1S)-Cl(3S)	110.1(3)
Cl(1S)-C(1S)-H(1S)	107.5
Cl(2S)-C(1S)-H(1S)	107.5
Cl(3S)-C(1S)-H(1S)	107.5

Symmetry transformations used to generate equivalent atoms:

Table A132. Anisotropic displacement parameters (Å^{2}x 10^3) for **113c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn	32(1)	14(1)	23(1)	0(1)	15(1)	0(1)
Cl(1)	34(1)	20(1)	43(1)	1(1)	14(1)	-3(1)
Cl(2)	41(1)	41(1)	24(1)	-2(1)	9(1)	1(1)
O(1)	40(2)	16(2)	34(2)	5(2)	23(2)	5(2)
O(2)	53(2)	17(2)	36(2)	-7(2)	34(2)	-5(2)
N(1)	21(2)	16(2)	16(2)	0(2)	10(2)	0(2)
C(1)	25(2)	13(2)	24(2)	-1(2)	17(2)	-1(2)
C(2)	34(3)	15(2)	22(2)	1(2)	16(2)	0(2)
C(3)	44(3)	23(3)	33(3)	-4(2)	29(3)	0(2)
C(4)	40(3)	26(3)	49(4)	-2(2)	32(3)	-3(2)
C(5)	23(2)	22(3)	34(3)	-6(2)	14(2)	-6(2)
C(6)	28(2)	14(2)	23(2)	-2(2)	16(2)	0(2)
C(7)	39(3)	36(3)	21(2)	0(2)	15(2)	-1(2)
C(8)	60(4)	57(5)	28(3)	7(3)	9(3)	-6(4)
C(9)	65(5)	47(4)	39(4)	-9(3)	9(3)	-19(4)
C(10)	26(2)	26(3)	21(2)	-1(2)	10(2)	-2(2)
C(11)	57(4)	29(3)	33(3)	-5(2)	24(3)	1(3)
C(12)	34(3)	43(4)	30(3)	-3(3)	7(2)	3(3)
C(13)	28(2)	16(2)	13(2)	-3(2)	10(2)	2(2)
C(14)	31(3)	16(2)	42(3)	8(2)	22(2)	-1(2)

C(15)	50(4)	78(6)	50(4)	25(4)	37(3)	13(4)
C(16)	33(3)	60(5)	58(4)	-13(4)	18(3)	-13(3)
C(17)	43(3)	31(3)	71(5)	-2(3)	39(4)	3(3)
C(18)	45(3)	23(3)	44(3)	1(2)	27(3)	-3(2)
C(19)	58(4)	44(4)	45(4)	-4(3)	38(3)	-5(3)
C(20)	142(9)	75(6)	63(5)	-32(5)	82(6)	-48(6)
C(21)	164(10)	48(5)	109(8)	-54(5)	119(8)	-52(6)
C(1S)	47(4)	61(5)	46(4)	11(4)	15(3)	-2(4)
Cl(1S)	144(3)	104(2)	96(2)	20(2)	74(2)	-32(2)
Cl(2S)	58(1)	75(2)	59(1)	-1(1)	13(1)	20(1)
Cl(3S)	76(2)	68(2)	147(3)	-24(2)	64(2)	-6(1)

Table A133. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).for **113c**.

	x	y	z	U(eq)
H(1)	2220(30)	6480(40)	770(40)	31(17)
H(3)	3439	5967	-1116	35
H(4)	4605	6079	-50	40
H(5)	4824	6078	1402	31
H(7)	1805	6037	-785	37
H(8A)	2215	7881	-1543	77
H(8B)	1519	6946	-2164	77
H(8C)	2304	6537	-2111	77
H(9A)	2375	3838	-1554	82
H(9B)	1525	4176	-1909	82
H(9C)	1957	3516	-958	82
H(10)	3485	5167	2193	29
H(11A)	3923	7285	3094	57
H(11B)	3378	7786	2141	57
H(11C)	4235	7963	2449	57
H(12A)	4588	3959	2523	57
H(12B)	4663	4996	3321	57
H(12C)	5002	5530	2673	57
H(15A)	1945	2517	1853	81
H(15B)	1246	3194	1932	81
H(15C)	2011	4029	2384	81
H(16A)	886	3973	-257	76
H(16B)	473	3526	328	76
H(16C)	1091	2455	292	76
H(17A)	1110	6445	591	65
H(17B)	1594	6441	1610	65
H(17C)	788	5776	1228	65
H(18A)	4269	2384	985	41
H(18B)	3558	3015	195	41
H(19A)	4136	2251	-599	52
H(19B)	4617	1044	114	52

H(20A)	3826	-512	-820	96
H(20B)	3195	730	-1158	96
H(21A)	2791	-492	-327	104
H(21B)	3579	-1157	274	104
H(1S)	9234	309	432	63

Table A134. Torsion angles [°] for **113c**.

O(2)-Zn-O(1)-C(13)	-166.1(7)
Cl(2)-Zn-O(1)-C(13)	-52.7(7)
Cl(1)-Zn-O(1)-C(13)	86.6(7)
O(1)-Zn-O(2)-C(21)	-120.5(5)
Cl(2)-Zn-O(2)-C(21)	128.4(4)
Cl(1)-Zn-O(2)-C(21)	-3.8(5)
O(1)-Zn-O(2)-C(18)	42.6(5)
Cl(2)-Zn-O(2)-C(18)	-68.5(4)
Cl(1)-Zn-O(2)-C(18)	159.3(4)
C(13)-N(1)-C(1)-C(6)	-87.9(6)
C(13)-N(1)-C(1)-C(2)	91.7(6)
C(6)-C(1)-C(2)-C(3)	0.5(7)
N(1)-C(1)-C(2)-C(3)	-179.0(4)
C(6)-C(1)-C(2)-C(7)	178.2(5)
N(1)-C(1)-C(2)-C(7)	-1.3(7)
C(1)-C(2)-C(3)-C(4)	-1.5(8)
C(7)-C(2)-C(3)-C(4)	-179.3(5)
C(2)-C(3)-C(4)-C(5)	0.1(9)
C(3)-C(4)-C(5)-C(6)	2.2(8)
C(2)-C(1)-C(6)-C(5)	1.7(7)
N(1)-C(1)-C(6)-C(5)	-178.7(4)
C(2)-C(1)-C(6)-C(10)	-179.0(5)
N(1)-C(1)-C(6)-C(10)	0.6(7)
C(4)-C(5)-C(6)-C(1)	-3.1(7)
C(4)-C(5)-C(6)-C(10)	177.6(5)
C(1)-C(2)-C(7)-C(9)	-98.6(6)
C(3)-C(2)-C(7)-C(9)	79.0(7)
C(1)-C(2)-C(7)-C(8)	138.7(6)
C(3)-C(2)-C(7)-C(8)	-43.7(7)
C(1)-C(6)-C(10)-C(12)	148.4(5)
C(5)-C(6)-C(10)-C(12)	-32.4(7)
C(1)-C(6)-C(10)-C(11)	-87.3(6)
C(5)-C(6)-C(10)-C(11)	92.0(6)
Zn-O(1)-C(13)-N(1)	136.7(5)
Zn-O(1)-C(13)-C(14)	-47.3(9)
C(1)-N(1)-C(13)-O(1)	0.5(7)
C(1)-N(1)-C(13)-C(14)	-175.6(4)
O(1)-C(13)-C(14)-C(17)	-179.4(5)
N(1)-C(13)-C(14)-C(17)	-3.4(7)
O(1)-C(13)-C(14)-C(15)	56.7(7)
N(1)-C(13)-C(14)-C(15)	-127.3(6)
O(1)-C(13)-C(14)-C(16)	-59.4(7)
N(1)-C(13)-C(14)-C(16)	116.7(5)
C(21)-O(2)-C(18)-C(19)	-9.8(7)
Zn-O(2)-C(18)-C(19)	-175.1(4)
O(2)-C(18)-C(19)-C(20)	24.0(8)
C(18)-C(19)-C(20)-C(21)	-29.4(10)
C(18)-O(2)-C(21)-C(20)	-8.4(8)
Zn-O(2)-C(21)-C(20)	156.7(6)
C(19)-C(20)-C(21)-O(2)	24.0(10)

Table A135. Hydrogen bonds for **113c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...Cl(1)#1	0.84(2)	2.64(3)	3.427(4)	157(6)

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z

Table A136. Selected ^{1}H, ^{31}P and ^{15}N NMR data for *p*CH$_3$ and *p*CH$_3$O-phosphaamidines. **25a-b**

1H NMR		***p*CH$_3$-phosphaamidine**	***p*CH$_3$O-phosphaamidine**
^{i}Pr-CH$_3$ (amino)	δ (^{1}H)	0.81	0.83
	^{3}J$_{HH}$, Hz	6.7	6.9
^{i}Pr-CH$_3$ (amino)	δ (^{1}H)	0.89	0.92
	^{3}J$_{HH}$, Hz	6.7	6.9
^{i}Pr-CH$_3$ (phosphino)	δ (^{1}H)	1.27	1.27
	^{3}J$_{HH}$, Hz	6.7	6.7
^{i}Pr-CH$_3$ (phosphino)	δ (^{1}H)	1.35	1.36
	^{3}J$_{HH}$, Hz	6.9	6.9
R= *p*-CH$_3$, *p*-CH$_3$O	δ (^{1}H)	2.22	3.70
^{i}Pr - H (amino)	δ (^{1}H)	3.00	3.00
	^{3}J$_{HH}$, Hz	6.7	6.7
^{i}Pr - H (phosphino)	δ (^{1}H)	3.84	3.85
	^{3}J$_{HH}$, Hz	6.8	6.7
	^{4}J$_{HH}$, Hz	3.4	3.4
Aromatic signals			
p- R- C$_6$H$_4$	δ (^{1}H)	7.12	7.18
	^{3}J$_{HH}$, Hz	8.1	8.7
	^{4}J$_{HH}$, Hz	1.7	2.1
p- R- C$_6$H$_4$	δ (^{1}H)	6.92	6.62
	^{3}J$_{HH}$, Hz	6.6	8.9
Dipp-N	δ (^{1}H)	6.94	6.95
	^{3}J$_{HH}$, Hz	6.9	7.6
Dipp-N	δ (^{1}H)	7.08	7.09
	^{3}J$_{HH}$, Hz	7.0	7.0
Dipp-P	δ (^{1}H)	7.23	7.23
	^{3}J$_{HH}$, Hz	7.3	7.5
Dipp-P	δ (^{1}H)	7.33	7.33
	^{3}J$_{HH}$, Hz	7.6	7.6
	^{5}J$_{HH}$, Hz	2.4	2.4
Major isomer			
N-H	δ (^{1}H)	6.23	6.24
	^{3}J$_{HH}$, Hz	2.4	2.4
Minor isomers			
N-H	δ (^{1}H)	5.90	5.91
	^{3}J$_{HH}$, Hz	11.0	12.8
P-H	δ (^{1}H)	4.92	4.91
	^{3}J$_{HH}$, Hz	242.2	241.4
^{31}P NMR			
Major isomers			
N-H	δ (^{31}P)	53.4	51.4
	^{3}J$_{PH}$, Hz	< linewidth	< linewidth
Minor isomers			
N-H	δ (^{31}P)	79.2 (medium)	79.0 (medium)
	^{3}J$_{PH}$, Hz	9.9	
P-H	δ (^{31}P)	-80.3 (small)	-80.1 (small)

	$^1J_{PH}$, Hz	243	241
P-H	δ (^{31}P)	-66.4 (very small)	-52.5 (very small)
	$^1J_{PH}$, Hz	243	241
^{13}C NMR			
C=P	δ (^{13}C)	186.2	186.1
	$^3J_{PH}$, Hz	61.4	62.0

Table A137. Selected inter-atomic distances (Å) and angles (°) in the crystal and computed structures of **104**.

Parameter	X-ray str.	HF *meso* [a]	HF *rac* [a]	DFT *meso* [b]	DFT *rac* [b]
P1–P1'	2.2060(8)	2.221	2.237	2.279	2.263
P1–C1	1.8414(13)	1.856	1.856	1.868	1.866
P1–H1	1.319(17)	1.396	1.397	1.418	1.417
P1–H1A	1.351(19)				
C1–P1–P1	98.14(4)	102.0	101.5	100.6	100.7
C1–P1–H1	107.8(13)	101.0	100.5	98.8	99.4
C1–P1–H1A	111.0(19)				
P1'–P1–H1	103.9(13)	100.9	95.6	94.0	99.02
P1'–P1–H1A	110.6(19)				
C2–C1–C6	120.05(12)	119.6	119.6	119.7	119.6
C1–C2–C7	123.31(13)	123.4	123.5	123.2	123.1
C1–C6–C10	123.77(12)	123.6	123.5	123.4	123.4
C1-P1-P1'-C1'	180.0	180.0	180.0	180.0	-169.4

[a] RHF-631G+(3d,2p) optimized structures in Gaussian W03. [b] B3LYP/6-31G(d,p) optimized structures.