Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Expanding the chemistry of 1,4-diphosphinines by stable mono anion formation

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A new sulfur-enriched tricyclic 1,4-diphosphinine (2) was synthesized and novel reactivity studies on the phosphorus heterocycle was performed: A weak anionic nucleophile (KHMDS) adds selectively thus forming a stable anionic 1,4-diphosphinine derivative (3b) which was fully characterized. The substitution potential of 3b was demonstrated using Ph_2PCl to give 4b, while oxidation of 3b using elemental iodine furnished cleanly the P-P coupling product 5.

Heteroatom-substituted benzene derivatives **I** (Fig. 1) have had a great impact on the chemistry of arenes.[1] By contrast, the properties and reactivity of phosphinines **II**[2] are largely dominated by the presence of aryl substituents,[3] and heteroatom persubstitution is completely unknown; 2-hydroxy derivatives have been described recently.[4] Phosphinine, the heavy homologue of pyridine, possesses about 90 % of the aromaticity of benzene.[5] These alluring species (**II**) have initiated intense research for more than five decades,[6] and, nowadays, the spectrum of applications range from lumi-nescent materials, to polymer precursors and ligands in catalysis.[7] A broad spectrum of studies have revealed com-plexation,[8] P-alkylation,[9] P-oxidation,[10] P-reduction[11] and cycloaddition reactions.[12] Interestingly, most of the chemical disparities of pyridines and phosphinines can be attributed to the lower lying LUMO energies and, consequently, increased electron affinity of the latter.[13]

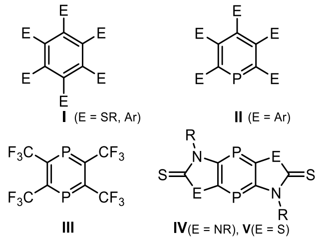

Figure 1. Benzenes (**I**) and phosphinines (**II**) having a complete set of substituents as well as electron-poor (**III**) and -rich (**IV,V**) 1,4-diphosphinines.

In particular, phosphinines have interesting π-ligand accepting properties, and a decidedly electrophilic phosphorus center. Therefore, they readily react with Grignard and lithio compounds to furnish dihydrophosphinine anions; the latter offer access to regiochemically different substitution products, *i.e.,* 1,1- or 1,2- or 1,4-regioisomers, depending on the nature of the electrophile used in the next step.[14]

In contrast, the chemistry of 1,4-diphosphinines is almost unexplored and, until recently, only a single derivative (**III**) of a 1,4-diphosphinine had been reported.[15] Synthesis of **III** is very laborious, the compound is not isolable and, hence, only a few physical properties and reactions are known, including formal [4+1] and [4+2] cycloaddition, and one example of a photoisomerization.[16] The easy access to imidazole-2-thione-based tricyclic 1,4-diphosphinines **IV**[17] has now reopened this area of research. This compound possess a high degree of aromaticity: NICS(1) value of the central ring = −9.5. Another very remarkable feature was revealed by voltammetry which showed a double reduction with an unresolved cathodic peak at −1.87 V to form the dianion.[17] Initial reactivity studies demonstrated that **IV** undergo [4+2] cycloaddition reactions to give 1,4-diphosphabarrelenes in high yield, but also react with dichalcogenides PhCh-ChPh (Ch = S, Se) in (rare) [$4\pi+2\sigma$] cycloaddition reactions, followed by inversion at the phosphorus center.[18] To investigate if the new 1,4-diphosphinine syn-thetic protocol could be transferred to other five-membered unsaturated heterocycles, we have started to examine the accessibility of tricyclic 1,4-diphosphinines **V** (Fig. 1), having a sulfur atom instead of an NR unit in the ring, and explore their chemistry. The required starting material, the 1,3-thiazole-2-thiones, have been previously used in coordination chemistry[19] and, sparingly, in N-heterocyclic carbene chemistry.[20] Herein, synthesis and characterization of a new sulfur-containing tricyclic 1,4-diphosphinine is described, including first ex-

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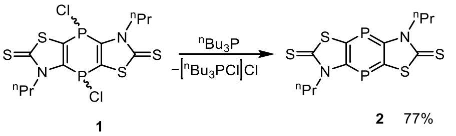
† Electronic Supplementary Information (ESI) available: [experimental protocols, X-ray structures, CV measurements and calculations]. See DOI: 10.1039/x0xx00000x

amples of nucleophilic reactions, thus revealing the huge synthetic potential to access novel multi-topic hetero-cyclic ligand arrays.

Using the recently published ring closing protocol with subsequent facile conversion of the *P*-NEt_2 into the *P*-Cl group (see ESI),[17] the dichloro derivative **1** was obtained in high yield as *cis/trans* mixture (53:47); the identity of the *trans* isomer has been confirmed by a single crystal X-ray structure determination (see S1 in the ESI). Interestingly, our DFT calculations reveal only a marginal energy difference (0.3 kcal/mol at M06-2X-6-311+G**) in favor of the *trans* isomer. The 1,4-dihydro-1,4-diphosphinine **1** was then used to obtain 1,4-diphosphinine **2** which, upon treatment of **1** with $^nBu_3P$, was cleanly formed (Scheme 1) and isolated in good yields (77 %) (see ESI). The $^{31}P\{^1H\}$ NMR spectrum of an aliquot shows resonances for **2** (134.7 ppm) and the (known) chlorophosphonium salt (105 ppm).



Scheme 1. Reduction of 1,4-dichloro-1,4-diphosphinine **1** with $^nBu_3P$ to yield 1,4-diphosphinine **2**.

Single crystal X-ray diffraction analysis of **2** reveals an all-planar tricycle having the ^{n}propyl groups *trans*. Two molecules of **2** in the unit cell are oriented so that each independent 1,4-diphosphinine unit is facing the thiazole-2-thione unit of the neighbouring molecule. The interplanar distance of 3.595 Å indicates effective π–π interactions. The P-C bond length (P-C1 1.7390(15) Å, P-C3 1.7494(15) Å) in the six-membered ring is in good agreement with the literature values for phosphinines.[6e, 6f, 21] The C-C bond lengths (1.406(2) Å) in the six-membered ring are comparable with the C-C bond lengths of benzene (1.397 Å)[22] which suggests a high degree of aromaticity in **2**.

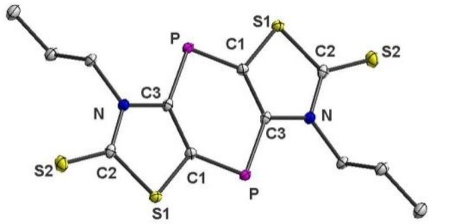


Figure 2. Displacement ellipsoids plot (50% probability) of molecular structure of **2** in the solid state. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P-C1 1.7390(15), P-C3 1.7494(15), C1-C3 1.406(2), C1-P-C3 100.02(7).

According to the calculated NICS(1) values (M06-2X/6-311+G**) all three rings of **2'** (the notation ' stands for using Me substituents instead of ^nPr) are aromatic, but the central 1,4-diphosphinine moiety (NICS(1) = −8.8) is more aromatic than the outer rings (NICS(1) = -4.9) (cf. benzene −12.8).[23] Strong absorption in the UV/Vis spectrum of **2** is observed in dichloromethane solution (λ_{max} = 497 nm). This value is found to be in a very good agreement with the TD DFT calculated 502 nm (B3LYP/6-311+G**//M06-2X/6-311+G** for **2'**), which is basically the HOMO(π)–LUMO(π^*) transition (Figure S4 in the ESI), with high transition probability (Table S4 in ESI).

Solution voltammetry on **2** in THF/$[nBu_4N][PF_6]$ at Pt (Fig. 3) and Au working electrodes identifies two central reduction processes that are very closely spaced ($E_p^c(2)$ = -1.28 V and $E_p^c(3)$ = -1.45 V vs. the ferrocene/ferrocenium redox couple,[24] hereafter $Fc^{+/0}$) and are not electrochemically reversible. Nevertheless, return peaks $E_p^a(3)$ and $E_p^a(2)$ are observed and the general appearance of the solid trace (—) in Fig. 3, including off-set re-oxidation $E_p^a(')$, is constant over multiple cycles and variation in scan rates from 0.1–1.0 V·s⁻¹, except that the re-oxidation peak $E_p^a('')$ increases in intensity with slower scanning but loses intensity with multiple cycles that do not go negative of the starting potential.

Oxidation process $E_p^a(1)$ is irreversible at +0.70 V vs. $Fc^{+/0}$ and no further processes can be observed before the solvent limit is reached (compound reactivity limits solvent selection.) There are also further reduction processes observable at much more negative potentials. (A detailed description of this complex behaviour is provided in the ESI).

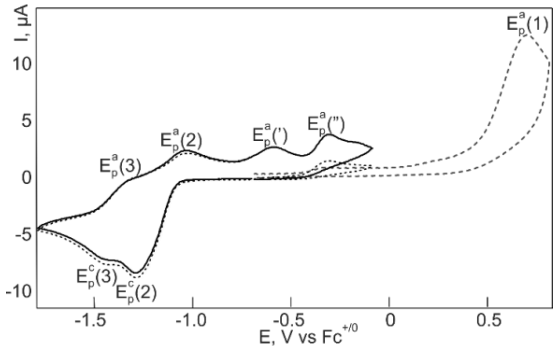
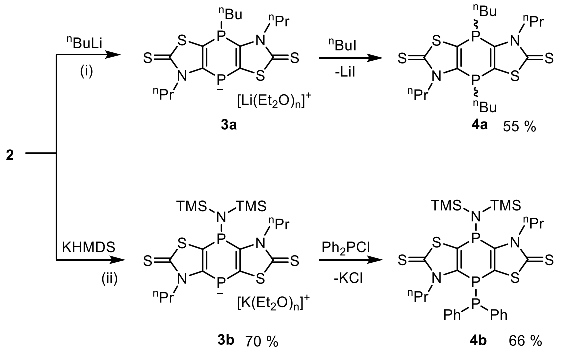


Figure 3. Composite CVs obtained on **2** 2.0 mM in THF (0.2 M $[nBu_4N][PF_6]$, v = 0.2 V·s⁻¹; scans start from o.c.p. = −0.69 V). (−−−) Anodic scan through E(1). (—) Cycle in cathodic direction through E(2,3); (·····) same but starting anodic.

The most important feature of the voltammetry is that $E_p^c(2)$ and $E_p^c(3)$ are at significantly *lower* potential than in **IV** (by 0.52 and 0.50 V). This is in full agreement with the calculated LUMO energies of the two compounds, which are −3.20 eV and −2.93 eV at B3LYP/6-311+G**(PCM:THF) – see Fig. S3 in the ESI. Also the M06-2X/6-311+G** (PCM:THF) anion and dianion is more stable for **2'** than for **IV'** by 0.30 and 0.44 eV, respectively (see Table S2 in the ESI).

To examine the scope of nucleophilic additions, we decided to test the well-known strong nucleophile (^nBuLi) and, by contrast, a rather weak nucleophile (KHMDS) (Scheme 2). Upon treatment of an ether suspension of **2** with ^nBuLi at −78 °C, a dark red solution was formed, and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed two signals at δ = −59.1 and −21.1, assigned to the anionic (−59.1) and neutral (-21.1) phosphorus centers of product **3a**. Quenching of freshly prepared **3a** with ^nBuI at −78 °C led to an immediate color change from red to yellow. $^{31}P\{^1H\}$ NMR spectroscopic reaction monitoring indicated fast and clean conversion to **4a** (Scheme 2). The two signals in the $^{31}P\{^1H\}$ NMR spectrum of **4a** (δ = −44.1 and −38.3) are assigned to two isomers of **4a** which are isolated in good yields in a 2:1 ratio (see ESI). This outcome represents a noteworthy contrast to a similar reaction sequence of 2,4,6-tri-^{t}Bu-1,3,5-triphosphabenzene (step 1, ^{n}BuLi; step 2, MeI) that resulted in dialkylation of the *same* phosphorus atom yielding the corresponding 1λ^5,3λ^3,5λ^3-triphosphabenzene derivative.[25] Noteworthy here is that the calculated energy difference between the (methyl analogue) of **4a’** and its mixed valence isomer (1λ^5,4λ^3-diphosphinine) reveals that the latter is less stable by 14.7 kcal/mol (M06-2X/6-311+G**).



Scheme 2. Sequential addition of nucleophiles and electrophiles to 1,4-diphosphinine **2**.

In the second case, treatment of **2** with KHMDS in diethyl ether at ambient temperature resulted in a sequence of colour changes from red to green and, after a few minutes, to bright red. The appearance and subsequent fast disappearance of the green colour is likely to be attributed to the formation of an intermediate radical anion **2**$^{\bullet-}$, which could form easily due to the low lying LUMO of **2**. In agreement with this assumption, the calculated TD-DFT spectra of the radical **2’**$^{\bullet-}$ suggests a green colour (Table S4 B3LYP/6-311+G**//M06-2X/6-311+G**). Finally, the bright red color can be attributed to the anion **3b** (for the TD DFT B3LYP/6-311+G**//M06-2X/6-311+G** excitation energies of **3b’** see Table S5). The ^{31}P{^{1}H} NMR spectrum of the reaction mixture shows two rather broad singlets at −28.6 and 6.7 ppm, which can be assigned to the anionic and neutral phosphorus nuclei of product **3b**, respectively. Compound **3b** was isolated as a red powder in good yields (70%) if the solvent was removed rapidly. The negative ESI-MS experiment shows a peak at *m/z* 538.0453 (calc. 538.0451) which confirms the composition of the product as **3b**. A single crystal X-ray structure determination confirms the geometry but also the presence of three solvent molecules per unit cell. Within a 1D-coordination polymer, each potassium cation is coordinated to the thione sulfur centers of two neighbouring molecules and three solvent molecules (Fig. 3). Having the isolated ionic compound **3b** in hand, its reactivity was investigated starting with the reaction of Ph$_2$PCl, representing a rather common main group element electrophile (Scheme 2). Upon addition of Ph$_2$PCl to a freshly prepared, precooled Et$_2$O solution of **3b** immediate colour change from red to yellow was observed. The ^{31}P{^{1}H} NMR spectrum showed three signals of an ABM spin habitus with three different $J_{P,P}$ couplings, *i.e.,* -50.8 ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^4J_{P,P}$ = 15.9 Hz), 9.5 ppm (dd, $^1J_{P,P}$ = 294.2 Hz, $^3J_{P,P}$ = 18.4 Hz), 15.0 ppm (t, $^JJ_{P,P}$ = 17.1 Hz)}, thus also revealing that the $^3J_{P,P}$ and $^4J_{P,P}$ coupling constant magnitudes are very similar.

Compound **4b** was isolated in good yield (65%) after filtration.Crystals were grown for **4b** and characterized via single crystal X-ray analysis, will be discussed later. (for details see ESI, S2).

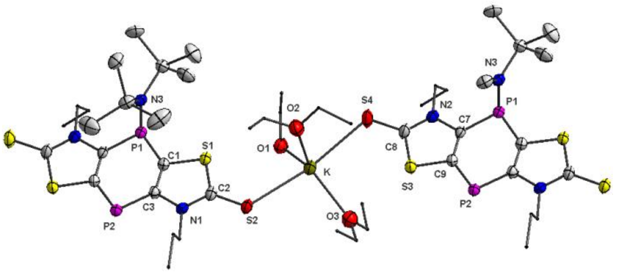
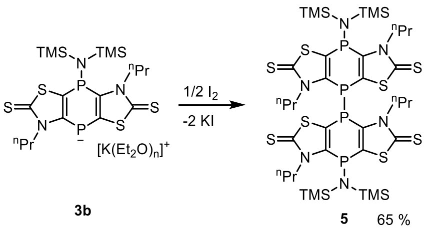


Figure 3. Displacement ellipsoids plot (50%) of the polymeric structure of **3b** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.807(4), P1-C7 1.805(4), P2-C3 1.776(4), P2-C9 1.777(4), C1-C3, 1.376(6), C7-C9 1.373(6), P1-N3 1.744(4). C1-P1-C7 95.24(19), C3-P2-C9 96.6(9).

An ethereal solution of **3b** was then treated with half an equivalent of elemental iodine at low temperature (−70 °C) resulting in an immediate color change from red to green and finally to yellow, suggesting a short-lived radical. Unfortunately, first attempts to achieve EPR characterization were not successful, but the calculated spin density distribution showed that the radical is localized mainly at the phosphorus atom (Figure S5). As in case of **4b** the *trans* isomer forms overwhelmingly, which suggests a rather strong directional effect of the N(SiMe$_3$)$_2$ moiety onto the incoming group. The final product **5** is isolated by dissolving the reaction mixture in toluene and filtering it via canula to remove the KI byproduct (for more details, see the SI). The ^{31}P{^{1}H} NMR spectrum of **5** shows two sets of signals for a major (98 %) and a minor (2 %) isomer, which have been assigned to **5** {−42.1 ppm (t, $^{3/4}J_{P,P}$ = 20.1 Hz) −40.4 ppm (t, $^{3/4}J_{P,P}$ = 20.4 Hz), 17.9 ppm (t, $^{3/4}J_{P,P}$ = 20.2) 19.9 ppm (t, $^{3/4}J_{P,P}$ = 20.8)}.



Scheme 3. Oxidation of mono anion **3b** with I$_2$ to generate **5**.

Single crystal X-ray diffraction studies of **4b** and **5** show very similar P-C bond lengths in the central 1,4-dihydro-1,4-diphosphinine rings. However, a slightly longer P1-P3 bond distance of 2.2893(7) Å is found in **5** (Fig. 5), compared to 2.246(6) Å in **4b**. Furthermore, one of the phenyl groups in **4b** is observed to have π–π interactions with the central 1,4-dihydro-1,4-diphosphinine ring on the same molecule. The molecular structure of **5** shows a dispersion forces inducated (see ESI) orientation of the two tricyclic units with a torsion angle of 60.5° between the P1-P3-C1 and P1-P3-C19 planes. It seems that dispersive forces are responsible for the observed arrangement of substituents in **5’** (which is similar to that in **5**) since there was no sign of secondary orbital interactions in a second-order perturbation theory analysis made on the NBO basis.

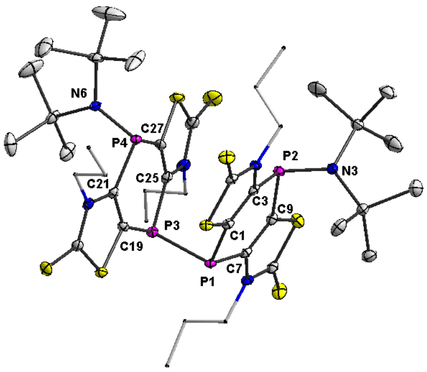


Figure 5. Displacement ellipsoids plot (50%) of the molecular structure of **5** in the crystal lattice. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.793(2), P1-C7 1.811(2), P1-P3 2.2893(7), P2-N3 1.7048(18), P2-C3 1.831(2), P2-C9 1824(2), C1-C3, 1.364(3). C1-P1-C7 99.43(9), C3-P2-C9 97.55(9), C1-P1-P3 101.64(7), P1-P3-C25 105.88(7).

In conclusion, a multigram scale synthesis of a new, sulfur-enriched tricyclic 1,4-diphosphinine was described. The key property of the 1,4-diphosphinine is its high electrophilicity as revealed by cyclic voltammetry and DFT calculations. Accordingly, reactivity studies with nucleophiles show interesting differences to phosphinines and the first stable anionic 1,4-diphosphinine derivative was obtained via reaction with the weak anionic nucleophile KHMDS. It was illustrated that the latter represents an interesting starting material for selective 1,4-disubstitution or for oxidation to give a P-P coupling pro-duct.

Acknowledgements

Financial support from the University of Bonn, the Alexander von Humboldt Stiftung (re-invitation of L.N. and R.T.B.), NKFIH OTKA NN 113772 and BME-Nanotechnology FIKP grant of EMMI (BME FIKP-NAT) (L.N.), the EU COST network CM10302 “Smart Inorganic Polymers” (SIPs; to R.S., L.N.) and NSERC-Canada (R.T.B.) is gratefully acknowledged. We also appreciate the X-ray determination support of Prof. A.C. Filippou and Prof. K. Menche. This contribution is dedicated to Prof. A. J. Arduengo III.

Conflicts of interest

There are no conflicts to declare.

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Electronic Supplementary Material (ESI) for ChemComm.

Electronic supporting information

Expanding the chemistry of ring-fused 1,4-diphosphinines by stable mono anion formation

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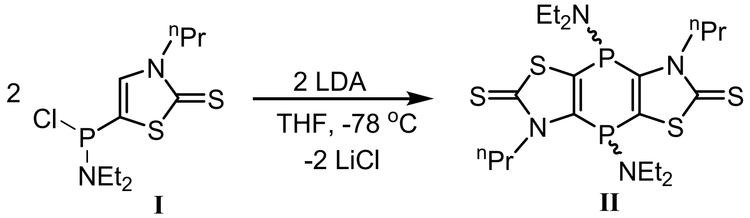
1 Experimental Procedures

General information

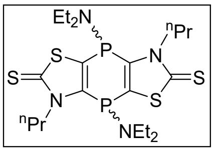
All operations were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Diethyl ether, tetrahydrofuran, and *n*-pentane were dried over sodium wire/benzophenone and further purified by subsequent distillation. The NMR spectra for compound 7a and 7b were recorded on a Bruker AX-300 spectrometer (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P). While the NMR spectra for the rest of the compounds were recorded on a Bruker Avance III HD Ascend 500 MHz spectrometer (500.1 MHz for ^{1}H, 125.7 MHz for ^{13}C, and 202.4 MHz for ^{31}P). The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standard, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S or a Carl Roth Type MPM-2 apparatus, they are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Kratos MS 50 spectrometer using EI, 70 eV. IR spectra of all compounds were recorded on a Thermo IR spectrometer with an attenuated total reflection (ATR) attachment. The X-ray analyses were performed on a Bruker APEX-II CCD or a Bruker X8-KappaApexII type diffractometer at 100(2) K. The structures were solved by direct methods refined by full-matrix least-squares technique in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97[1] program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1866473 (**1**), CCDC-1866472 (**2**), CCDC-1866474 (**3b**), CCDC-1866475 (**4b**) and CCDC-1866476 (**5**) which can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

1.1 Synthesis of tricyclic compounds II



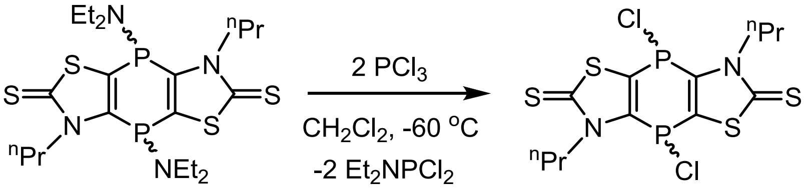
1.1.1 Procedure for synthesis of II

To a solution of 3-^{n}propyl-5-diethylamino(chloro)thiazole-2-thione (2.60 g, 8.75 mmol) in a Schlenk flask, in 85 mL of dry THF, solution (THF 65 mL) of LDA (1.03 g, 9.63 mmol) was added at −78 °C and the reaction mixture was warmed up to ambient temperature. It was stirred for two h at this temperature. The solvent was removed in vacuo ($8•10^{-3}$ mbar) and the residue was taken in dichloromethane and filtered over frit having silica gel. The filtrate was collected and solvent was removed *in vacuo* ($8•10^{-3}$ mbar). The obtained solid was washed twice with *n*-pentane (20 mL, 15 mL) and dried in vacuo ($8•10^{-3}$ mbar).



Yield 2.22 g (4.26 mmol), 97 %, white solid, m.p. 181°C. ^{1}H NMR (500.1 MHz, CDCl$_3$): δ = 0.95-1.02 (m, 24H, $\text{N–CH}_2\text{C}\mathit{H}_3$), 1.03-1.12 (br, 12H, $\text{N–CH}_2\text{CH}_2\text{C}\mathit{H}_3$), 1.80-2.04 (m, 8H, $\text{N–CH}_2\text{C}\mathit{H_2}\text{CH}_3$), 2.74-2.99 (br, 8H, $\text{N–C}\mathit{H_2}\text{CH}_3$), 2.99-3.16 (br, 8H, $\text{N–C}\mathit{H_2}\text{CH}_3$ *2nd isomer*) 3.87-4.03 (m, 4H $\text{N–C}\mathit{H_2}\text{-CH}_2\text{-CH}_3$), 4.48-4.59 (m, 4H, , $\text{N–C}\mathit{H_2}\text{-CH}_2\text{-CH}_3$ *2nd isomer*), ^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): δ = 11.2 (s, $\text{N-CH}_2\text{CH}_2\mathit{C}\text{H}_3$), 11.3 (, $\text{N-CH}_2\text{CH}_2\mathit{C}\text{H}_3$ *2nd isomer*), 14.4 (br, $\text{N-CH}_2\mathit{C}\text{H}_3$), 14.6 (br, $\text{N-CH}_2\mathit{C}\text{H}_3$ *2nd isomer*), 20.7 (t $^{4/5}J_{\text{P,C}}$ = 2.2 Hz, $\text{N-CH}_2\mathit{C}\text{H}_2\text{CH}_3$), 20.8 (t, $^{4/5}J_{\text{P,C}}$ = 2.6 Hz, $\text{N-CH}_2\mathit{C}\text{H}_2\text{CH}_3$ *2nd isomer*) 44.7 (br, $\text{N-}\mathit{C}\text{H}_2\text{CH}_3$), 44.8 (br, $\text{N-}\mathit{C}\text{H}_2\text{CH}_3$ *2nd isomer*), 49.4 (t, $^{3/4}J_{\text{P,C}}$ = 3.4 Hz $\text{N-}\mathit{C}\text{H}_2\text{CH}_2\text{CH}_3$), 51.3 (t, $^{3/4}J_{\text{P,C}}$ = 4.8 Hz $\text{N-}\mathit{C}\text{H}_2\text{CH}_2\text{CH}_3$ *2nd isomer*), 126.4 (dd, $^{1}J_{\text{P,C}}$ = 21.0 Hz, $^{2}J_{\text{P,C}}$ = 10.5 Hz, $\text{C}^{4/5}$), 129.1 (dd, $^{1}J_{\text{P,C}}$ = 12.4 Hz, $^{2}J_{\text{P,C}}$ = 10.4 Hz, $\text{C}^{4/5}$ *2nd isomer*), 137.4 (dd, $^{1}J_{\text{P,C}}$ = 24.3 Hz, $^{2}J_{\text{P,C}}$ = 9.3 Hz, $\text{C}^{4/5}$), 143.7 (dd, $^{1}J_{\text{P,C}}$ = 9.0 Hz, $^{2}J_{\text{P,C}}$ = 7.8 Hz, $\text{C}^{4/5}$ *2nd isomer*) 190.3 (t, $^{3}J_{\text{P,C}}$ = 2.8 Hz, *C*=S), 190.5 (t, $^{3}J_{\text{P,C}}$ = 3.6 Hz, *C*=S *2nd isomer*), ^{31}P{^{1}H} NMR (202.5 MHz, CDCl$_3$): δ= 16.5 (s), δ= 19.3 (s); MS (EI,70 eV): m/z (%) = 520.1 (100) $[\text{M}]^+$, 449.0 (10) $[\text{M−Et}_2\text{N}]^+$, 376.0 (70) $[\text{M-2Et}_2\text{N}]^+$, 434.0 (10) $[\text{M-2}^{n}\text{Pr}]^+$, 72.1 (85) $[\text{Et}_2\text{N}]^+$; HR-MS: found = 520.1141, calc. = 520.1142; IR (ATR, ṽ {cm^{-1}}): ṽ = 2961 (m), 2926 (w), 2867 (w), 1458 (m), 1377 (m), 1348 (s), 1294 (m), 1212 (s), 1177 (s), 1139 (vs) 1039 (vs), 1019 (vs), 1001 (vs), 928 (vs) 817 (s), 817 (vs), 661 (vs)...

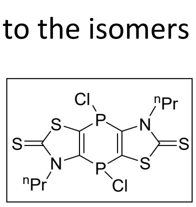
1.2 Synthesis of tricyclic 1,4-dichloro compound 1



II **1**

1.2.1 Procedure for synthesis of 1

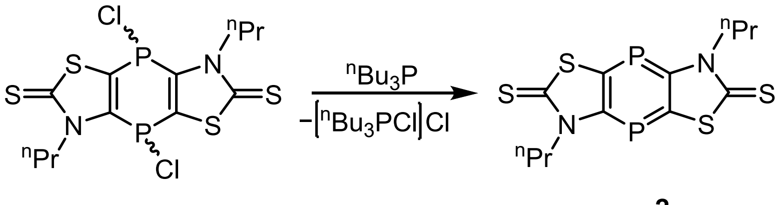
To a solution of **II** (1.71 g, 3.28 mmol) in dichloromethane (65 mL), PCl$_3$ (0.62 mL, 7.18 mmol) was added (dropwise with a syringe) at 0 °C in a Schlenk flask. The reaction mixture was warmed to ambient temperature and stirred for two days. The solvent was removed *in vacuo* ($8\bullet10^{-3}$ mbar) and the remaining yellow colored precipitate was dried *in vacuo* ($8\bullet10^{-3}$ mbar). The obtained solid was washed twice with *n*-pentane ($2\bullet5$ mL) and dried in vacuo ($8\bullet10^{-3}$ mbar). Compound **1** was obtained as 1:1.1 mixture of *cis* and *trans* isomers. This mixture was used for the following characterization and measurements; further assignments to the isomers was not achieved.



Yield 1.24 g (2.77 mmol), 85 %, Yellow solid, m.p. 235°C. ^{1}H NMR (500.1 MHz, CDCl$_3$): δ = 1.05 (t, 6H, $^{3}J_{\text{H,H}}$ = 7.4 Hz, $\text{CH}_2\text{CH}_2\text{C}\mathit{H}_3$), 1.85-2.10 (m, 4H, $\text{CH}_2\text{C}\mathit{H_2}\text{CH}_3$), 4.20 (m, 2H, $\text{C}\mathit{H_2}\text{-CH}_2\text{-CH}_3$), 4.55 (m, 2H, $\text{C}\mathit{H_2}\text{-CH}_2\text{-CH}_3$), ^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$): δ = 11.2 (s, $\text{CH}_2\text{CH}_2\mathit{C}\text{H}_3$), 21.s (s, $\text{CH}_2\mathit{C}\text{H}_2\text{CH}_3$), 21.5 (s, $\text{CH}_2\mathit{C}\text{H}_2\text{CH}_3$ *2nd isomer*), 50.8 (s, $\mathit{C}\text{H}_2\text{CH}_2\text{CH}_3$), 52.2 (s, $\mathit{C}\text{H}_2\text{CH}_2\text{CH}_3$ *2nd isomer*), 124.6 (d, $J_{\text{P,C}}$ = 42.0 Hz, $\text{C}^{4/5}$), 141.5 (d, $J_{\text{P,C}}$ = 37.4 Hz, $\text{C}^{4/5}$), 189.8 (s, br *C*=S), ^{31}P{^{1}H} NMR (121.5MHz, CDCl$_3$): δ= 12.7 (s), δ= 21.3 (s); MS (EI,70 eV): m/z (%) = 445.9

(28) $[M]^+$, 412.9 (15) $[M{-}Cl]^+$, 375.9 (85) $[M\text{-}2Cl]^+$, 345.0 (6) $[M\text{-}S]^+$, 291.8 (100) $[M\text{-}2^nPr,\text{-}2Cl]^+$; HR-MS: found = 445.8896, calc. = 445.8892; IR (ATR, ũ {cm^{-1}}): ũ = 2927 (w), 2867 (w), 1480 (m), 1352 (s), 1280 (s), 1214 (s), 1136 (s), 1011 (s) 924 (m), 833 (vs), 669 (vs), 583 (s) 546 (s), 437 (vs).

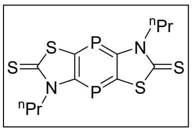
1.3 Synthesis of tricyclic 1,4-diphosphinine 2



1 **2**

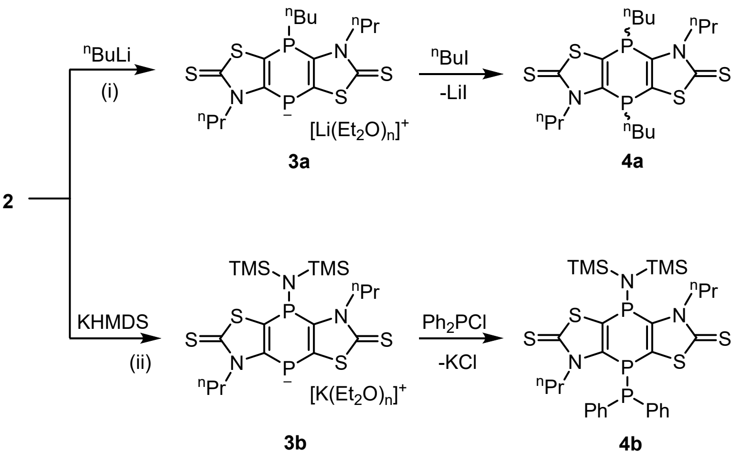
1.3.1 Procedure for synthesis of 2

In a Schlenk flask, ^{n}Bu$_3$P (0.41 mL, 1.66 mmol) was added to a suspension of the 1:1.1 mixture of **1** (0.62 g, 1.38 mmol) in 15 mL of dichloromethane at 0 °C. The reaction mixture was warmed to ambient temperature and stirred overnight. The reaction mixture was filtered via a cannula and the obtained red residue was washed with dichloromethane (1.5 mL) and then with *n*-pentane (2•5 mL). The obtained bright red color solid was dried *in vacuo* (8•10^{-3} mbar).



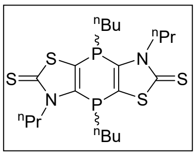
Yield 0.40 g (1.06 mmol), 77 %, red solid, m.p. 249°C. ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 1.07 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, $CH_2CH_2CH_3$), 4.57 (m, 4H, $CH_2CH_2CH_3$), 4.57 (m, 4H, $CH_2CH_2CH_3$), ^{13}C{^{1}H} NMR (125.75 MHz, CD_2Cl_2): δ = δ = 11.3 (s, $CH_2CH_2CH_3$), 19.6 (t, $^{4/5}J_{P,C}$ = 2.3 Hz, $CH_2CH_2CH_3$), 50.7 (t, $^{3/4}J_{P,C}$ = 7.8 Hz, $CH_2CH_2CH_3$), 154.2 (dd, $^1J_{P,C}$ = 36.0 Hz, $^2J_{P,C}$ = 32.1 Hz, $C^{4/5}$), 164.0 (dd, $^1J_{P,C}$ = 33.4 Hz, $^2J_{P,C}$ = 30.1 Hz, $C^{4/5}$), 190.0 (t, $^3J_{P,C}$ = 3.5 Hz, C=S), ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ = 134.3 (s); MS (EI,70 eV): m/z (%) = 376.0 (75) $[M]^+$, 333.9 (37) $[M{-}^nPr]^+$, 301.0 (8) $[M\text{-}^nPr\text{-}S]^+$, 291.9 (100) $[M\text{-}2^nPr]^+$, HR-MS: found = 375.9516, calc. = 375.9515; IR (ATR, ũ {cm^{-1}}): ũ = 1455 (w), 1348 (m), 1307 (s), 1287 (s), 1158 (s), 1105 (vs), 1017 (vs), 932 (s), 888 (s), 848 (s) 746 (s), 678 (s); UV/Vis (CH_2Cl_2): λ_{max}, nm (ε, L.M^{-1} cm^{-1}) 313 (18855), 341 (27904), 369 (5055), 497 (10767); Elemental analysis for $C_{12}H_{14}N_2P_2S_4$: found: C 38.20, H 3.77, N 7.34, S 33.94 Calc.: C 38.29, H 3.75, N 7.44, S 34.07.

1.4 Synthesis of the mono anions 3a and 3b and tricyclic compounds 4a and 4b.



1.4.1 Procedure for synthesis of 4a

To a suspension of 1,4-diphosphinine **2** (0.13 g, 0.34 mmol) in a Schlenk tube, in 10 mL of dry diethylether, ^{n}Buli (0.21 mL, 0.35 mmol) was added at −78 °C. Very dark red solution was formed which was stirred for 30 min at this temperature and then. *n*-butyl iodide (0.04 mL, 0.35 mmol) was added dropwise and the reaction mixture was stirred for two h and warmed up to ambient temperature. The solvent was removed in-vacuo ($8{\bullet}10^{-3}$ mbar) and the residue was taken in dicholoromethane and filtered to reove the formed salt (over frit having silica gel). The filtrate was collected; solvent was removed *in vacuo* ($8{\bullet}10^{-3}$ mbar). The obtained solid was washed twice with *n*-pentane (3 mL) and dried *in vacuo* ($8{\bullet}10^{-3}$ mbar).

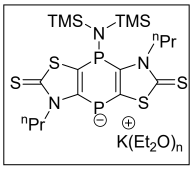

Yield 0.09 g (0.18 mmol), 55 %, white solid, m.p. 165 °C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.82 (t, 6H, $^3J_{H,H}$ = 7.12 Hz, N–$CH_2CH_2C\mathit{H_3}$), 0.91 (t, 6H, $^3J_{H,H}$ = 7.23 Hz, N–$CH_2CH_2C\mathit{H_3}$ *2nd isomer*), 1.00 (t, 12H, $^3J_{H,H}$ = 7.40 Hz, P–$CH_2CH_2CH_2C\mathit{H_3}$), 1.05-1.19 (m, 4H, N–$CH_2C\mathit{H}_2CH_3$) 1.21-1.31 (m, 4H, N-$CH_2C\mathit{H}_2CH_3$ *2nd isomer*), 1.31-1.50 (m, 4H, P-$CH_2CH_2C\mathit{H}_2CH_3$), 1.51-1.66 (m, 4H, P-$CH_2CH_2C\mathit{H}_2CH_3$ *2nd isomer*), 1.67-1.74 (m, 4H, P-$CH_2C\mathit{H}_2CH_2CH_3$), 1.74-1.82 (m, 4H, P-$CH_2C\mathit{H}_2CH_2CH_3$ *2nd isomer*), 1.83-1.89 (m 4H, P-$C\mathit{H}_2CH_2CH_2CH_3$), 1.91-214 (m, 4H, P-$C\mathit{H}_2CH_2CH_2CH_3$ *2nd isomer*), 3.79-3.93 (m, 4H, N-$C\mathit{H}_2CH_2CH_3$), 4.42-4.60 (m. 4H, N-$C\mathit{H}_2CH_2CH_3$ *2nd isomer*), ^{13}C{^{1}H} NMR (75 5 MHz, $CDCl_3$): δ = 11.1 (s, br, P-$CH_2CH_2CH_2\mathit{C}H_3$), 11.2 (s, br, P-$CH_2CH_2CH_2\mathit{C}H_3$ *2nd isomer*), 13.6 (s, br, N-$CH_2CH_2\mathit{C}H_3$), 13.7 (s, br, N-$CH_2CH_2\mathit{C}H_3$ *2nd isomer*), 20.8 (s, br, P-$CH_2CH_2\mathit{C}H_2CH_3$), 21.3 (s, br, P-$CH_2CH_2\mathit{C}H_2CH_3$ *2nd isomer*), 23.7 (t, $^{4/5}J_{P,H}$ = 5.0 Hz, N-$CH_2\mathit{C}H_2CH_3$), 24.03 (t, $^{4/5}J_{P,H}$ = 6.1 Hz, N-$CH_2\mathit{C}H_2CH_3$ *2nd isomer*), 26.7 (s, br, P-$CH_2\mathit{C}H_2CH_2CH_3$), 28.5 (t, $^{2/5}J_{P,H}$ = 6.3 Hz, P-$CH_2\mathit{C}H_2CH_2CH_3$ *2nd isomer*), 31.0 (dd, $^1J_{P,C}$ = 19.9 Hz, $^4J_{P,C}$ = 5.6 Hz, P-$\mathit{C}H_2CH_2CH_2CH_3$), 33.4 (dd, $^1J_{P,C}$ = 25.0, Hz, $^4J_{P,C}$ = 11.0 Hz, P-$\mathit{C}H_2CH_2CH_2CH_3$ *2nd isomer*), 50.7 (t, $^{3/5}J_{P,C}$ = 7,0, Hz, N-$\mathit{C}H_2CHCH_2CH_3$), 51.8 (dd, $^3J_{P,C}$ = 13.7 Hz, $^5J_{P,C}$ = 6,9 Hz, N-$\mathit{C}H_2CHCH_2CH_3$ *2nd isomer*), 122.5 (dd, $^1J_{P,C}$ = 13.6 Hz, $^2J_{P,C}$ = 8.0 Hz, $C^{4/5}$), 123.4 (dd, $^1J_{P,C}$ = 12.1 Hz, $^2J_{P,C}$ = 10.2 Hz, $C^{4/5}$ *2nd isomer*),139.2 (dd, $^1J_{P,C}$ = 13.5 Hz, $^2J_{P,C}$ = 6.8 Hz, $C^{4/5}$), 141.5 (dd, $^1J_{P,C}$ = 7.9 Hz, $^2J_{P,C}$ = 6.8 Hz, $C^{4/5}$ *2nd isomer*), 189.9 (br, *C*=S), 190.1 (br, *C*=S *2nd isomer*), ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −44.1 (s), −38.3 (s); MS (EI,70 eV): m/z (%) = 549.0 (90) $[M]^+$, 433.0 (10) $[M{-}^nBu]^+$, 390.9 (65) $[M\text{-}^nBu\text{-}^nPr]^+$, 376.9 (50) $[M\text{-}2^nBu]^+$, 348.9 (25) $[M\text{-}^nBu\text{-}2^nPr]^+$, 291.8 (80) $[M\text{-}2^nBu\text{-}2^nPr]^+$, 57.1

(60) [^{n}Bu]$^+$,; HR-MS: found = 490.0921, calc. = 490.0924; IR (ATR, ῦ {cm^{-1}}): ῦ = 2961 (m), 2926 (w), 2867 (w), 1458 (w), 1348 (s), 11294 (m), 1212 (m), 1177 (m), 1139 (vs), 1097 (s), 1001 (s), 928 (s) 817(s), 795 (m), 780 (m), 661 (s); Elemental analysis for $C_{20}H_{32}N_2P_2S_4$: found: C 48.37, H 6.68, N 5.62, 23.79 Calc.: C 48.96, H 6.57, N 5.71, S 26.14.

1.4.2 Procedure for synthesis of 3b

To a suspension of 1,4-diphosphinine **2** (0.15 g, 0.39 mmol) in a Schlenk tube, in 10 mL of dry diethylether, ether (7 mL) solution of KHMDS (0.09 mg, 0.44 mmol) was added at ambient temperature. Red solution was formed which was stirred for 10 min at ambient temperature. Solvent was removed under reduced pressure. The residue was taken washed with *n*-pentane (2•3 mL) and dried in vacuo (8•10^{-3} mbar).

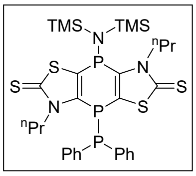
Note: The exact number of solvent ligands (in solution) could not be determined due to in situ preparation and characterization in THF-d8 because of stability issues so the yield is calculated without the solvent ligands.



Yield 0.23 g (0.28 mmol), 70 %, red solid. ^{1}H NMR (500.1 MHz, THFd$_8$): δ = −0.11 (s, br, 9H, $-\mathrm{Si}(\mathrm{C}\mathit{H_3})_3$), 0.30 (s, br, 9H, = $-\mathrm{Si}(\mathrm{C}\mathit{H_3})_3$), 0.90 (t, 3H, $^3J_{H,H}$ = 7.43 Hz, $CH_2CH_2C\mathit{H_3}$), 0.97 (t, 3H, $^3J_{H,H}$ = 7.43 Hz, $CH_2CH_2C\mathit{H_3}$), 1.74-193 (m, 4H, $CH_2C\mathit{H_2}CH_3$), 3.78-3.96 (br, 2H, $C\mathit{H_2}$-CH_2-CH_3), 4.23 (br, 1H $C\mathit{H_2}CH_2CH_3$), 4.58 (td, 1H $^2J_{H,H}$ = 5.3 Hz, $^3J_{H,H}$ = 12.2 Hz, $C\mathit{H_2}CH_2CH_3$), ^{13}C{^{1}H} NMR (125.75 MHz, THF-*d$_8$*): δ = 2.7 (s, br, -Si($\mathit{CH_3}$)$_3$), 4.9 (d, $^3J_{P,C}$ = 17.4 Hz, Si($\mathit{CH_3}$)$_3$), 11.5 (s, $CH_2CH_2\mathit{C}H_3$), 20.6 (d, $^4J_{P,C}$ = 4.4 Hz, $CH_2\mathit{C}H_2CH_3$), 21.8 (d, $^4J_{P,C}$ = 8.4 Hz, $CH_2\mathit{C}H_2CH_3$) 49.3 (d, $^3J_{P,C}$ = 21.3 Hz, $\mathit{C}H_2CH_2CH_3$), 49.6 (d, $^3J_{P,C}$ = 13.9 Hz, $\mathit{C}H_2CH_2CH_3$), 106.7 (dd, $^1J_{P,C}$ = 17.3 Hz, $^2J_{P,C}$ = 8.2 Hz, $C^{4/5}$), 126.5 (dd, $^1J_{P,C}$ = 12.0 Hz, $^2J_{P,C}$ = 8.9 Hz, $C^{4/5}$), 148.5 (dd, $^1J_{P,C}$ = 54.0 Hz, $^2J_{P,C}$ = 8.2 Hz, $C^{4/5}$), 161.2 (dd, $^1J_{P,C}$ = 51.1, $^2J_{P,C}$ = 5.9 Hz, $C^{4/5}$), 184.3 (d, $^3J_{P,C}$ = 5.83 Hz *C*=S), 188.7 (d, $^3J_{P,C}$ = 11.1 Hz *C*=S), ^{31}P{^{1}H} NMR (202.45MHz, THF-*d$_8$*): δ = −28.8 (s, P), 6.7 (s, N-P); MS (neg. ESI-MS): $C_{18}H_{31}N_3P_2S_4Si_2^-$ = found = 538.0499, calc. = 538.0499; IR (ATR, ῦ {cm^{-1}}): ῦ = 2959 (m), 1436 (w), 1397 (m), 1254 (s), 1251 (s), 1207(s), 1133 (vs), 1102 (s), 998 (vs), 856 (vs) 819 (s), 761 (s), 676 (vs), 430 (vs).

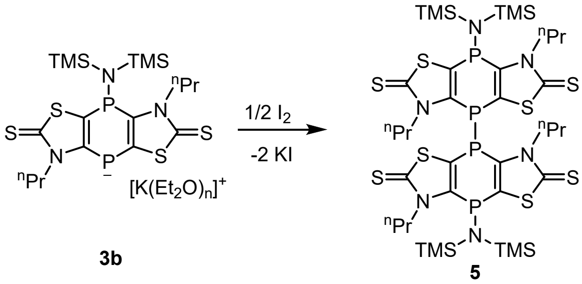
1.4.3 Procedure for synthesis of 4b

To a suspension of 1,4-diphosphinine **2** (0.15 g, 0.39 mmol) in a Schlenk tube, in 10 mL of dry diethylether, ether (7 mL) solution of KHMDS (0.09 mg, 0.44 mmol) was added at ambient temperature. Red solution was formed which was stirred for 10 min at ambient temperature and then cooled down to −70°C. Chloro(diphenyl)phosphane (0.08 mL, 0.49 mmol) was added dropwise and the reaction mixture turned orange. The reaction solution was stirred for half an h and then solvent was removed under reduced pressure. The residue was taken in toluene and filtered via canula to remove the formed potassium chloride. Solvent was removed again *in vacuo* (8•10^{-3} mbar) and the obtained yellow solid was washed with *n*-pentane (2•3 mL) and dried in vacuo (mbar).



Yield 0.19 g (0.26 mmol), 66 %, yellow solid, m.p. 147°C. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = −0.10 (s, br, 9H, $-Si(CH_3)_3$), 0.33 (d, 9H, $^{4}J_{P,H}$ = 2.7 Hz, $-Si(CH_3)_3$), 1.01 (m, 6H, $CH_2CH_2CH_3$), 1.41-2.10 (m, 4H, $CH_2CH_2CH_3$), 3.75-3.9 (m, 2H, $CH_2CH_2CH_3$), 4.36-4.68 (m, 2H $CH_2CH_2CH_3$), 7.05 (t, 2H, $^{3/4}J_{P,H}$ = 7.56 Hz, *o*-C_6H_5), 7.26 (t, 2H, $^{3/4}J_{P,H}$ = 7.64 Hz, *o*-C_6H_5), 7.38-7.51 (m, 6H, *m,p*-C_6H_5), $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 3.5 (s, $-Si(CH_3)_3$), 4.1 (d, $^{3}J_{P,C}$ = 15.2 Hz, $-Si(CH_3)_3$), 11.2 (s, $CH_2CH_2CH_3$), 11.3 (s, $CH_2CH_2CH_3$), 21.2 (dd, $^{4}J_{P,C}$ = 4.5, Hz, $^{5}J_{P,C}$ = 1.6 Hz, $CH_2CH_2CH_3$), 21.5 (d, $^{4}J_{P,C}$ = 4.6 Hz, $CH_2CH_2CH_3$), 50.9 (d, $^{3}J_{P,C}$ = 6.2 Hz $CH_2CH_2CH_3$), 51.6 (dd, $^{3}J_{P,C}$ = 10.5, Hz, $^{4}J_{P,C}$ = 7.0 Hz, $CH_2CH_2CH_3$), 116.5 (dd, $^{1}J_{P,C}$ = 9.3 Hz, $^{2}J_{P,C}$ = 1.4 $C^{4/5}$), 117.0 (dd, $^{1}J_{P,C}$ = 9.0 Hz, $^{2}J_{P,C}$ = 1.3 $C^{4/5}$),129.0 (d, $^{3}J_{P,C}$ =7.5 Hz, *m*-C_6H_5), 129.3 (d, $^{3}J_{P,C}$ = 5.0 Hz, *m*-C_6H_5), 129.6 (d, $^{4}J_{P,C}$ = 2.0 Hz, *p*-C_6H_5), 130.4 (s, br, *p*-C_6H_5), 130.4 (dd, $^{1}J_{P,C}$ = 28.2 Hz, $^{2}J_{P,C}$ = 12.6 Hz, *ipso*-C_6H_5), 131.4 (dd, $^{1}J_{P,C}$ = 20.1 Hz, $^{2}J_{P,C}$ = 4.6 Hz *ipso*-C_6H_5), 132.7 (dd, $^{2}J_{P,C}$ = 15.3 Hz, $^{3}J_{P,C}$ = 11.5 Hz, *o*-C_6H_5), 133.4 (dd, $^{2}J_{P,C}$ = 20.6 Hz, $^{3}J_{P,C}$ = 3.7 Hz, *o*-C_6H_5), 147.5 (dd, $^{1}J_{P,C}$ = 5.1 Hz, $^{2}J_{P,C}$ = 4.4 Hz, $C^{4/5}$), 148.1 (dd, $^{1}J_{P,C}$ = 5.2 Hz, $^{2}J_{P,C}$ = 4.3 Hz, $C^{4/5}$), 189.3 (dd, $^{3}J_{P,C}$ = 6.6 Hz, $^{4}J_{P,C}$ = 1.2 Hz, *C*=S), 189.6 (d, $^{3}J_{P,C}$ = 5.2 Hz), $^{31}P\{^{1}H\}$ NMR (121.5MHz, $CDCl_3$): δ = −50.8 ppm (dd, $^{1}J_{P,P}$ = 294.2 Hz, $^{4}J_{P,P}$ = 15.9 Hz, PPh_2), 9.5 ppm (dd, $^{1}J_{P,P}$ = 294.2 Hz, $^{3}J_{P,P}$ = 18.4 Hz, $PPPh_2$), 15.0 ppm (t, $J_{P,P}$ = 17.1 Hz, -$PNSi(CH_3)_3$); MS (APCI): HR-MS: found for $[C_{30}H_{42}N_3P_3S_4Si_2]H$ = 723.1136, calc. = 723.1112; IR (ATR, ῦ {cm^{-1}}): ῦ = 2959 (m), 1436 (w), 1397 (m), 1354 (s), 1251 (s), 1207 (s), 1133 (vs), 1102 (s), 998 (s), 856 (vs) 761 (m), 734 (m), 676 (s), 620 (w); Elemental analysis for $C_{30}H_{42}N_3P_3S_4Si_2$: found: C 50.17, H 5.95, N 5.75, S 17.34 Calc.: C 49.91, H 5.86, N 5.82, S 17.76.

1.5 Oxidation reaction of the mono anion 3b

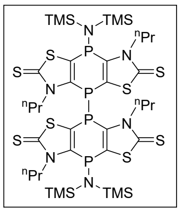


3b

5

1.5.1 Procedure for synthesis of 5

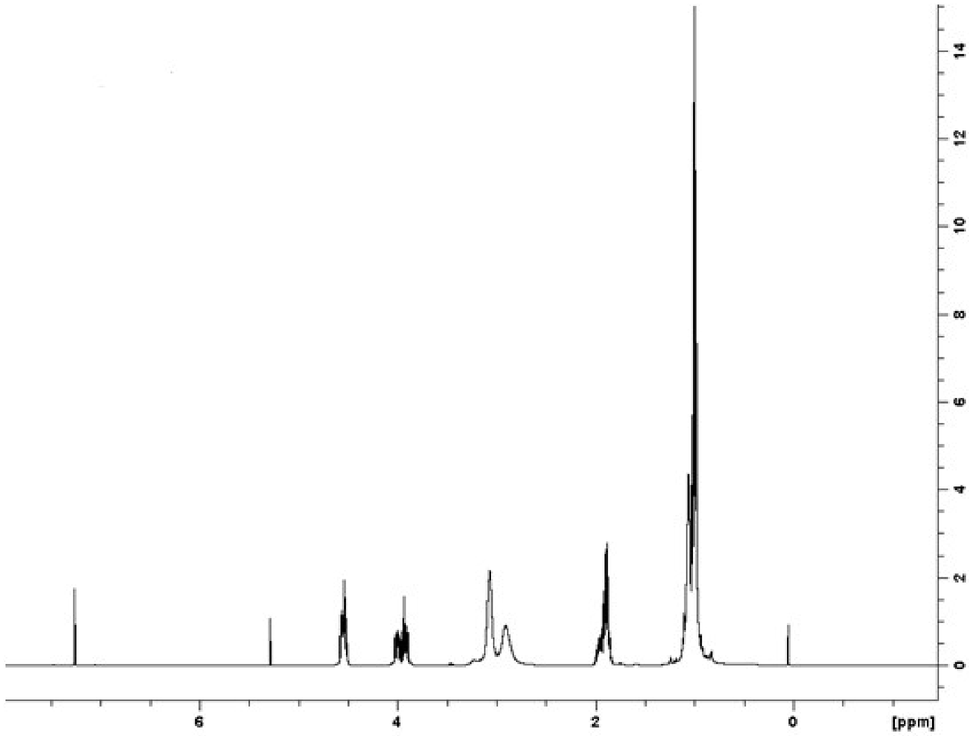
In a Schlenk flask a suspension **2** (0.31 g, 0.85 mmol) was prepared using 20 mL of dry diethylether. To this suspension, ether (15 mL) solution of KHMDS (0.18 mg, 0.90 mmol) was added at ambient temperature. Red solution (**3b**) was formed which was stirred for 10 min at ambient temperature and then cooled down to −70°C. Ether (10 mL) solution of iodine (0.06 g, 0.44 mmol) was added dropwise and the reaction mixture turned greenish. The reaction solution was stirred for half an hour and then solvent was removed under reduced pressure (8•10−3 mbar). The residue was taken in dry toluene and filtered via cannula to remove the formed potassium chloride. Solvent was removed again in-vacuo (8•10−3 mbar) and the obtained greenish yellow solid was washed with *n*-pentane (2x5 mL) and dried *in vacuo* (8•10−3 mbar).



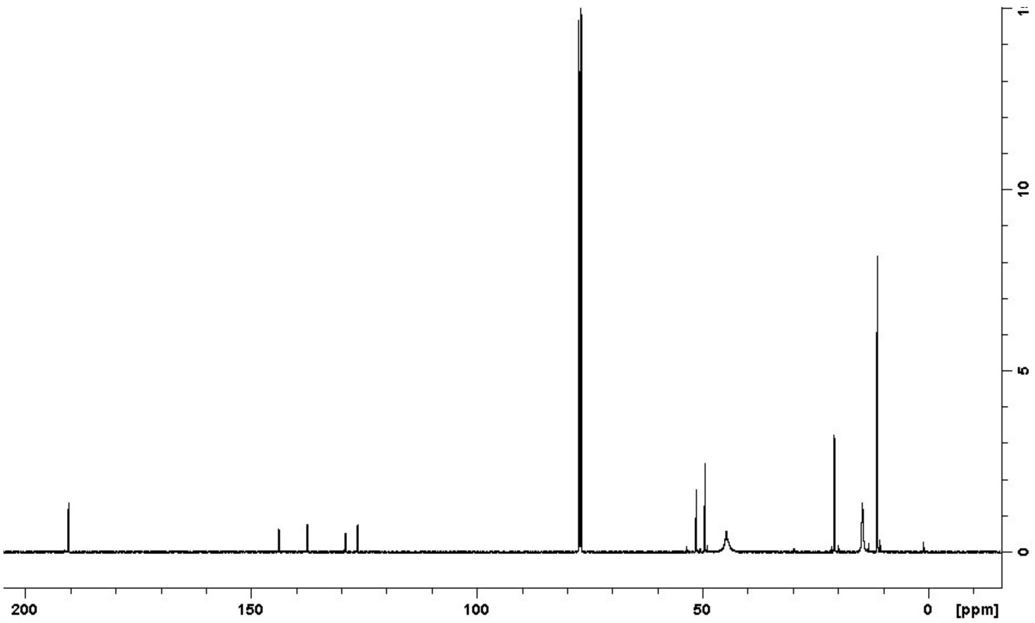
Yield 0.60 g (0.55 mmol), 65 %, Greenish yellow solid, m.p. 260°C. $\delta = -0.10$ (s, br, 18H, $-\mathrm{Si}(\mathrm{C}H_3)_3$), 0.41 (d, 18H, $^4J_{\mathrm{P,H}} = 2.0$ Hz, $-\mathrm{Si}(\mathrm{C}H_3)_3$), 0.97 (t, 6H, $^3J_{\mathrm{H,H}} = 7.4$ Hz, $\mathrm{CH_2CH_2C}H_3$), 1.10 (t, 6H, $^3J_{\mathrm{H,H}} = 7.4$ Hz, $\mathrm{CH_2CH_2C}H_3$), 1.62-1.75 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.78-1.88 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 1.88-1.98 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 2.10-2.23 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_3}$), 3.23-3.35 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.96-4.05 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.45-4.60 (m, 4H, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), $\delta = 3.6$ (s, $-\mathrm{Si}(C\mathrm{H_3})_3$), 4.1 (d, $^3J_{\mathrm{P,C}} = 13.6$ Hz, $-\mathrm{Si}(C\mathrm{H_3})_3$), 11.2 (s, N-$\mathrm{CH_2CH_2}C\mathrm{H_3}$), 11.4 (s, N-$\mathrm{CH_2CH_2}C\mathrm{H_3}$), 21.2 (s, br, N-$\mathrm{CH_2}C\mathrm{H_2CH_3}$), 22.0 (s, br, N-$\mathrm{CH_2}C\mathrm{H_2CH_3}$), 50.9 (t, $^{3/4}J_{\mathrm{P,C}} = 7.3$ Hz, N-$C\mathrm{H_2CH_2CH_3}$), 51.4 (d, $^3J_{\mathrm{P,C}} = 4.6$, Hz, -N $C\mathrm{H_2CH_2CH_3}$), 110.2 (m, C^4), 128.6 (m, C^4), 139.0 (d, $^1J_{\mathrm{P,C}} = 39.5$ Hz, C^5), 151.3 (d, $^1J_{\mathrm{P,C}} = 44.7$ Hz, C^5), 189.2 (d, $^3J_{\mathrm{P,C}} = 3.5$ Hz, C=S), 190.2 (d, $^3J_{\mathrm{P,C}} = 3.5$ Hz, C=S), $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (202.4 MHz, $\mathrm{CDCl_3}$): $\delta = -42.1$ (t, $^{3/4}J_{\mathrm{P,P}} = 20.1$ Hz, P-P), -40.4 (t, $^{3/4}J_{\mathrm{P,P}} = 20.4$ Hz, P-P *2nd isomer*), 17.9 (t, $^{3/4}J_{\mathrm{P,P}} = 20.2$ Hz, -$P\mathrm{NSi_2(CH_3)_3}$) 19.9 (t, $^{3/4}J_{\mathrm{P,P}} = 20.8$ Hz, -$P\mathrm{NSi_2(CH_3)_3}$ *2nd isomer*); MS (APCI): HR-MS: found for $[\mathrm{C_{36}H_{64}N_6P_4S_8Si_4}]\mathrm{H} = 1073.1057$, calc. = 1073.1058; IR (ATR, ũ {cm⁻¹}): ũ = 2963 (m), 1460 (w), 1432 (w), 1352 (vs), 1345 (s), 1213 (vs), 1141 (vs), 1001 (s), 898 (s), 844 (s) 824 (s), 764 (m), 681 (w), 664 (w), 548 (s), 433 (s); Elemental analysis for $\mathrm{C_{36}H_{64}N_6P_4S_8Si_4}$: found: C 40.17, H 5.88, N 7.48, S 23.22 Calc.: C 40.27, H 6.01, N 7.53, S 23.89.

2 NMR spectra of all compounds

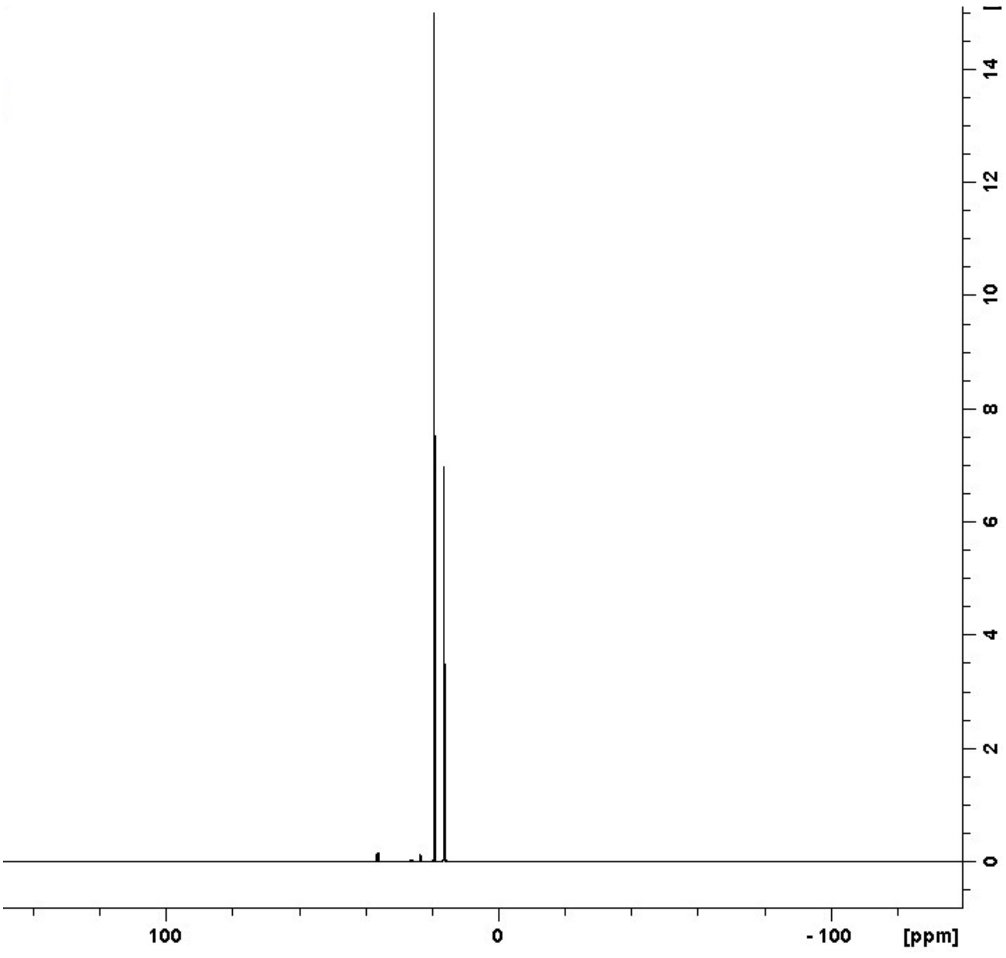
2.1 ^{1}H NMR (500.1 MHz, $\mathrm{CDCl_3}$) of II.



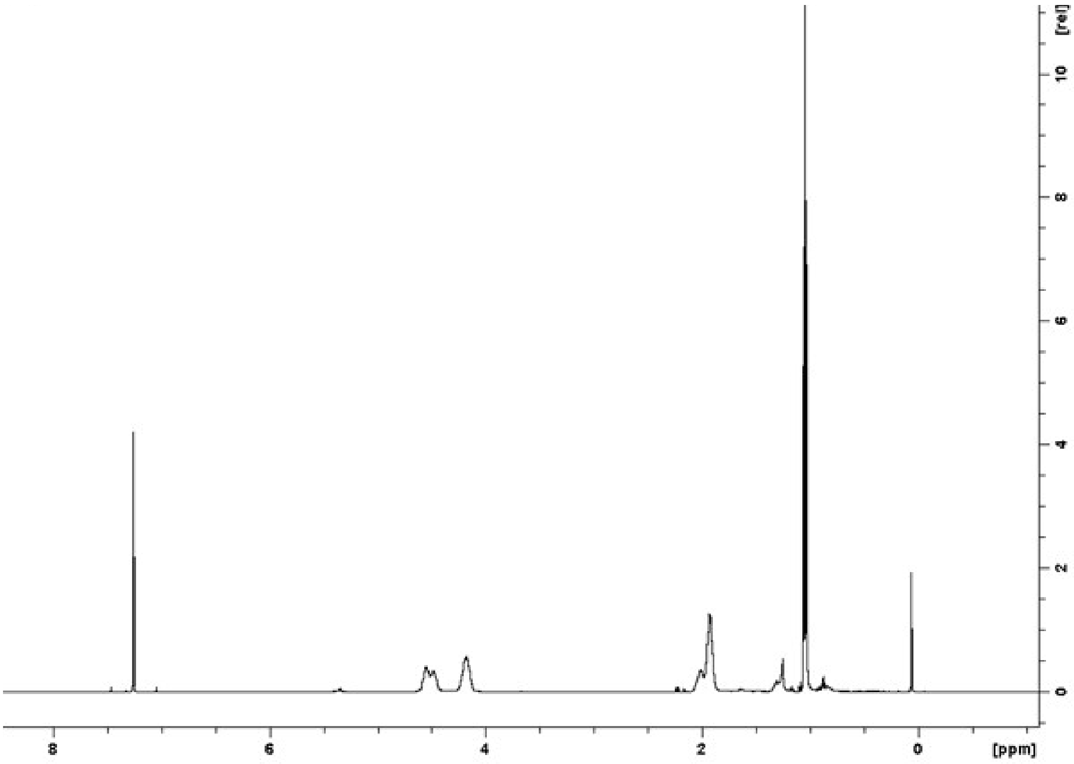
2.2 $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$) of II



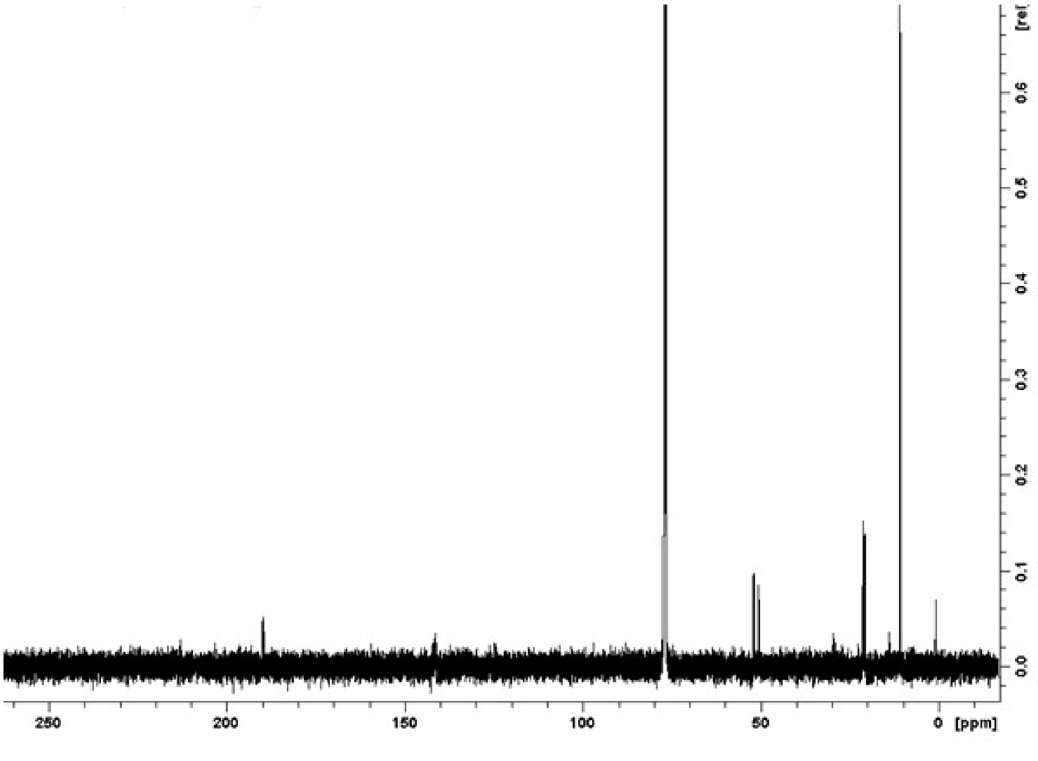
2.3 $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) of II



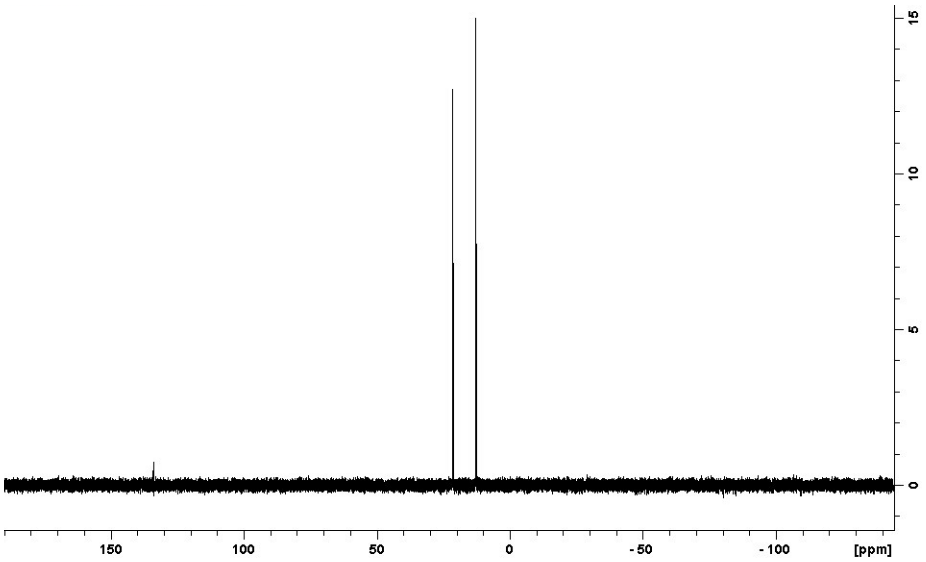
2.4 ^{1}H NMR (500.1 MHz, $CDCl_3$) of 1



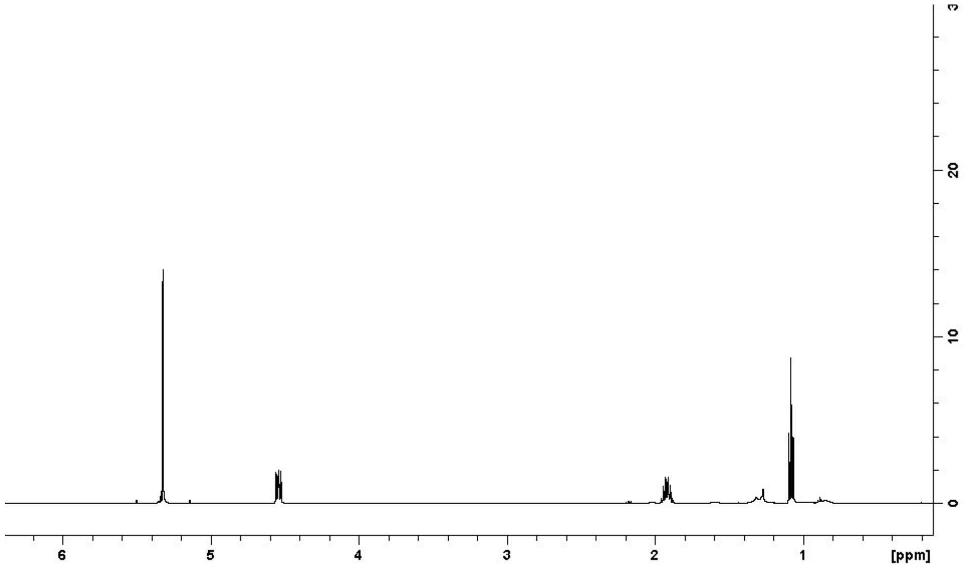
2.5 $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$) of 1



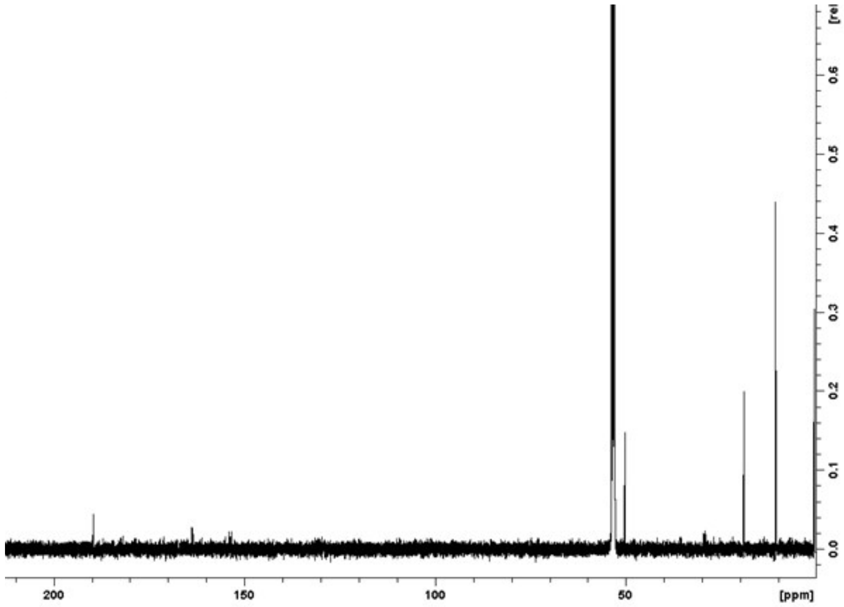
2.6 $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) of 1



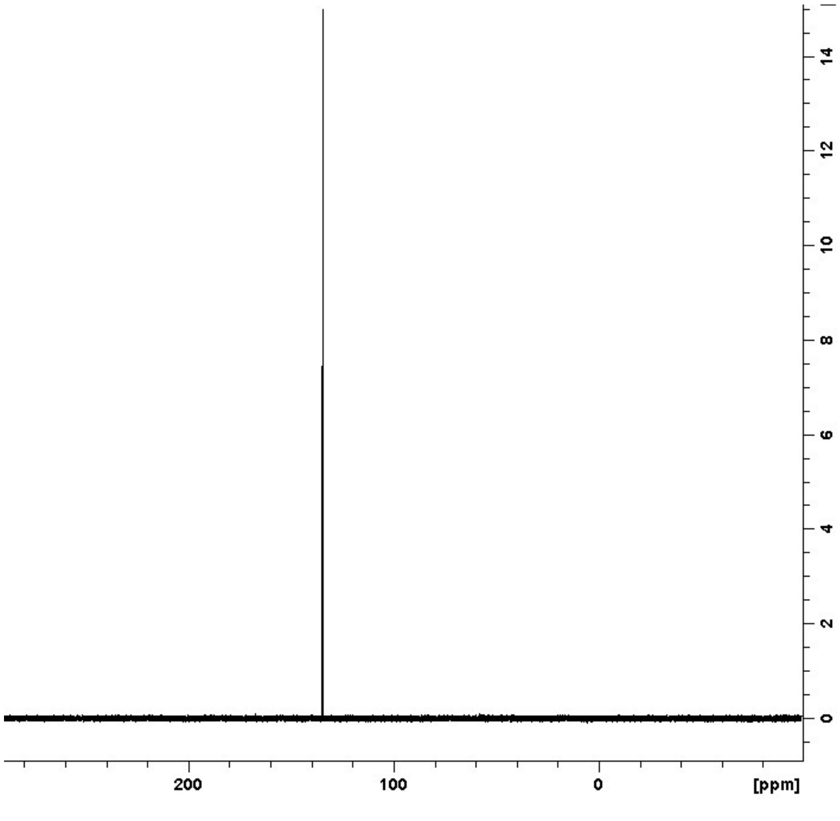
2.7 ^1H NMR (500.1 MHz, CD_2Cl_2) of 2



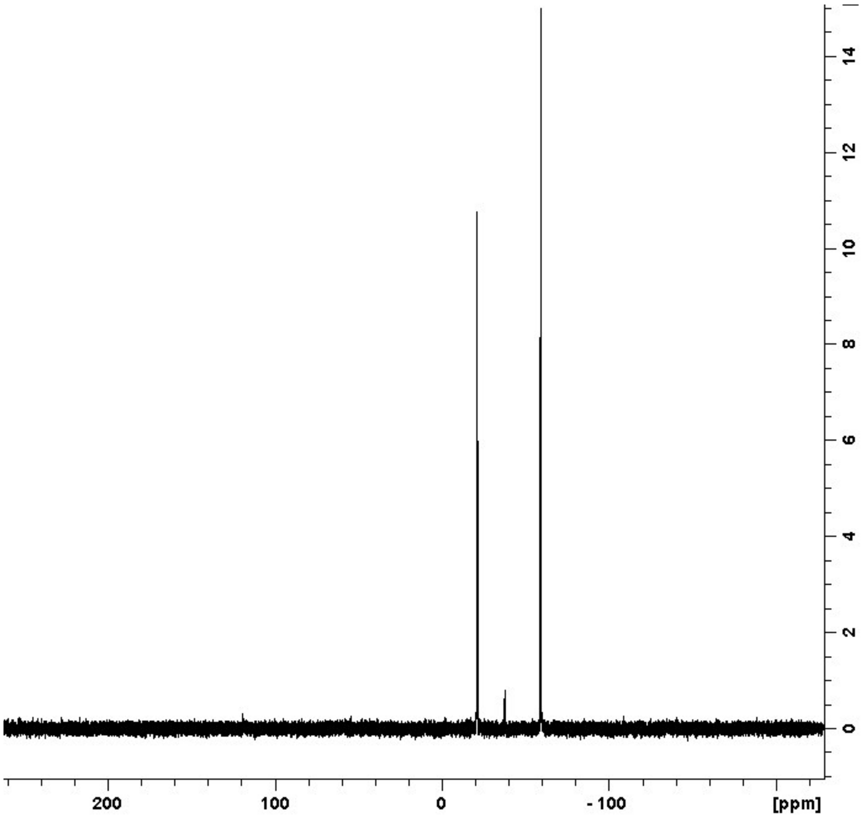
2.8 $^{13}C\{^{1}H\}$ NMR (125.75 MHz, CD_2Cl_2) of 2



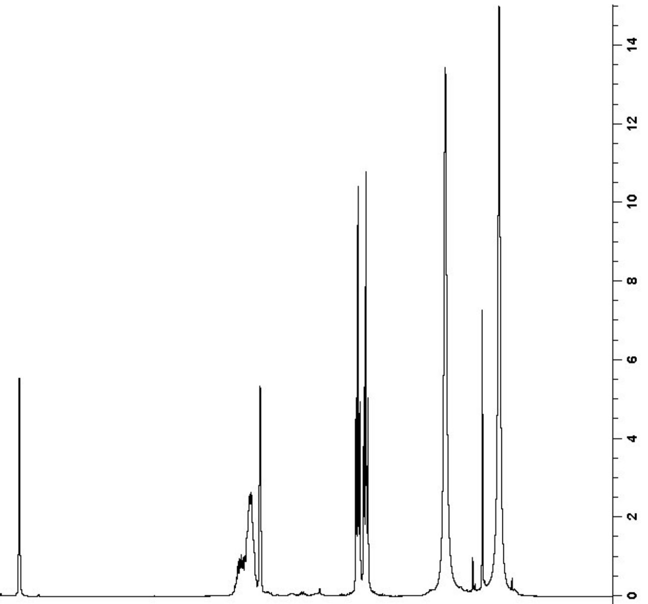
2.9 $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2) of 2



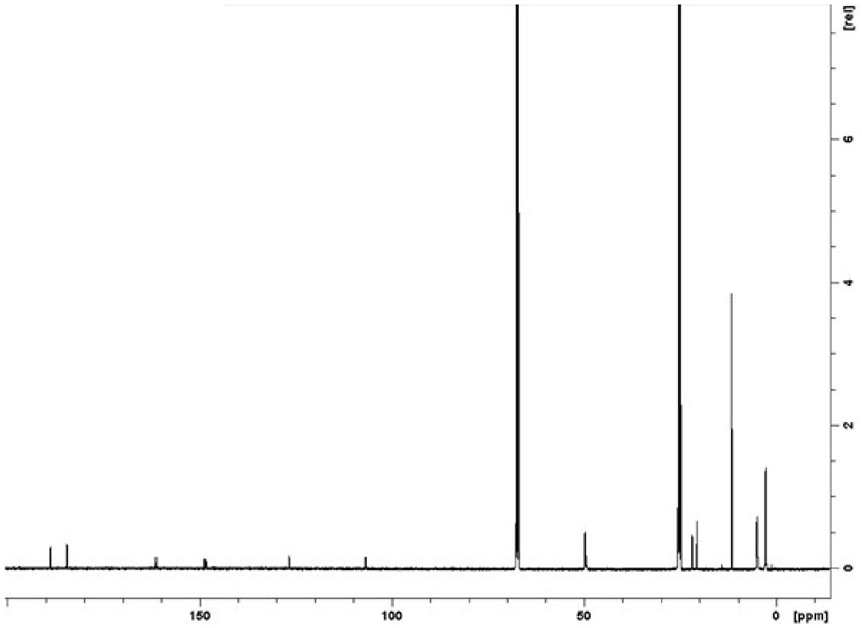
2.10 $^{31}P\{^1H\}$ NMR (202.4 MHz, Et_2O) of 3a



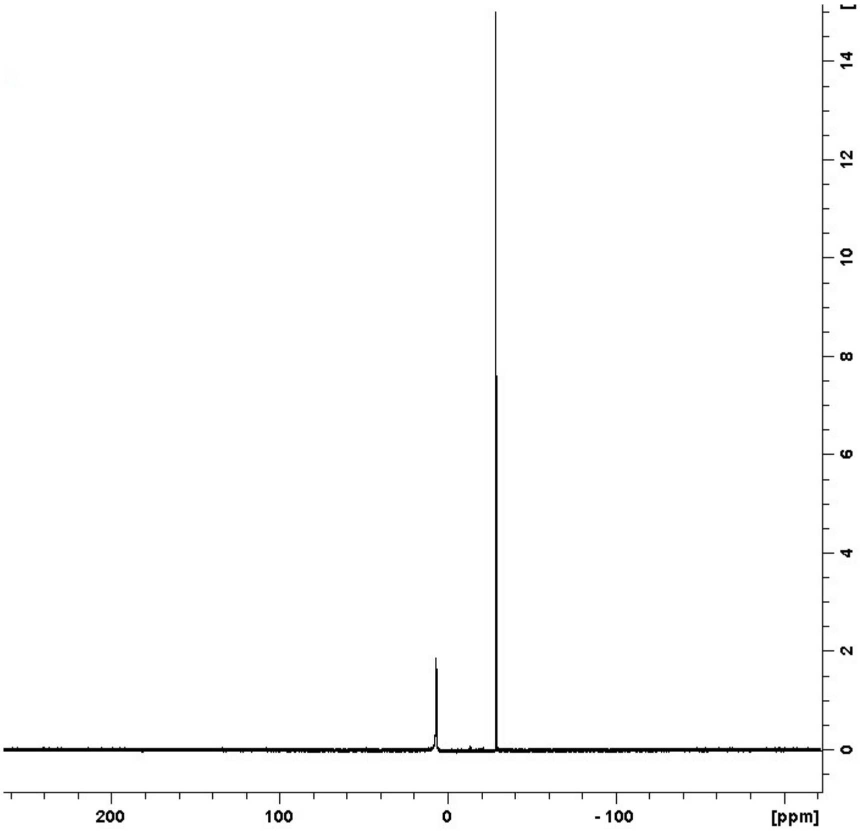
2.11 ^1H NMR (500.1 MHz, THF-d_8, -30 °C) of 3b



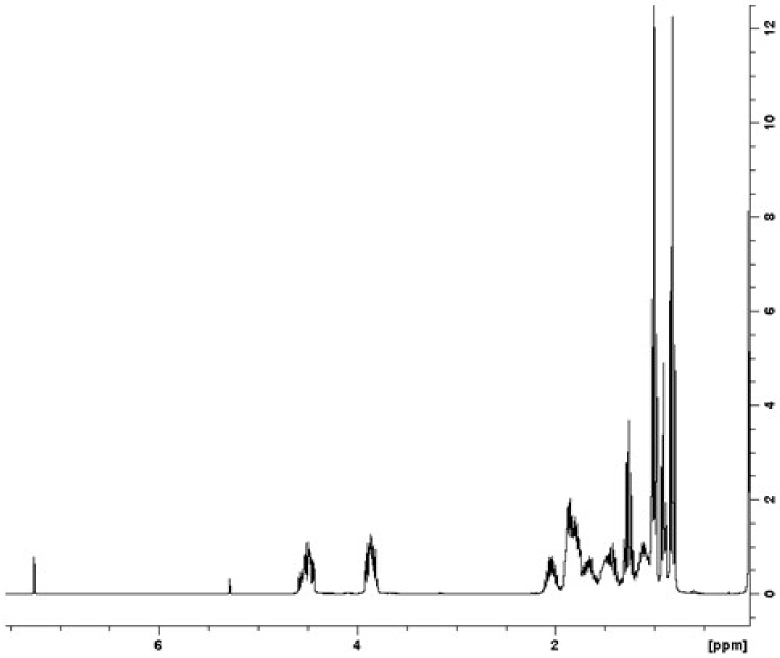
2.12 $^{13}C\{^{1}H\}$ NMR (125.75 MHz, THFd$_8$, -30 °C) of 3b



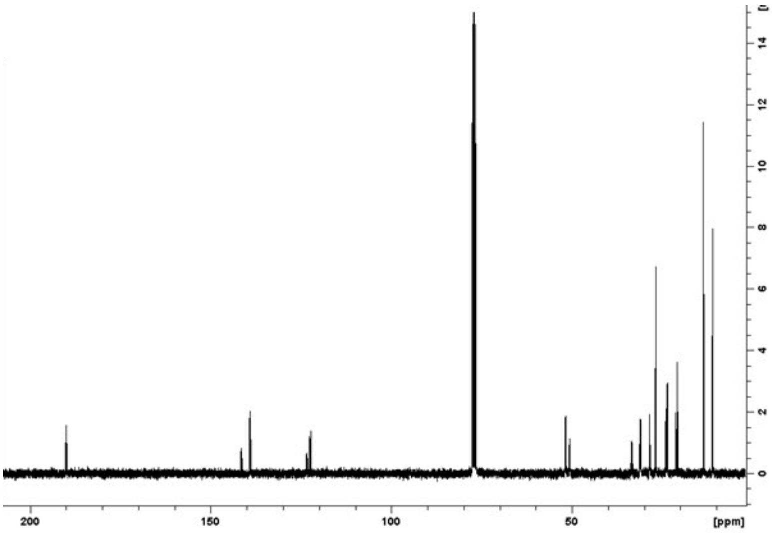
2.13 $^{31}P\{^{1}H\}$ NMR (202.4 MHz, THF-*d$_8$*, -30 °C) of 3b



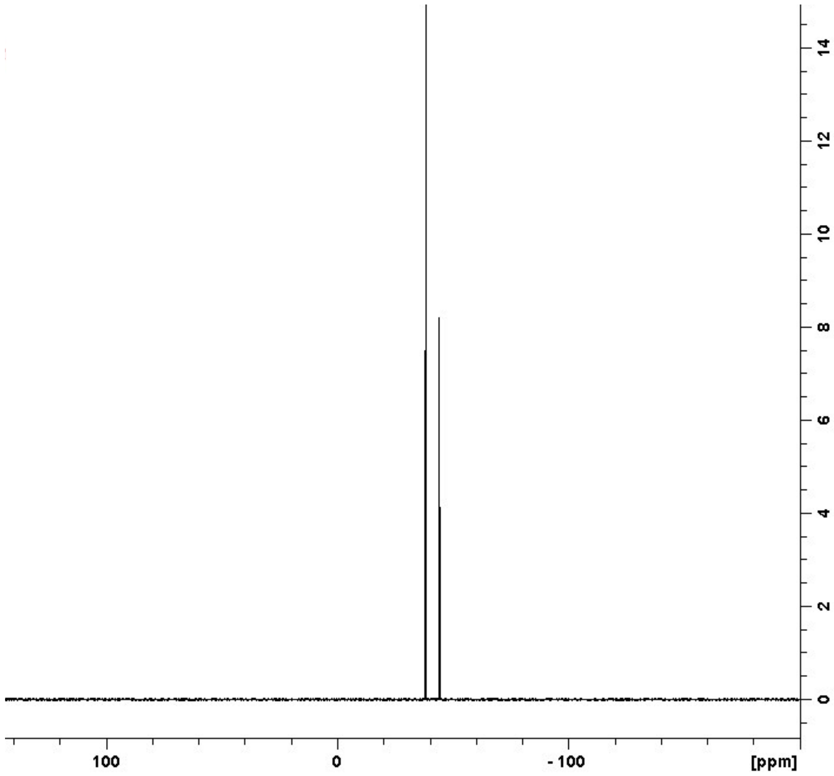
2.14 ^{1}H NMR (300.1 MHz, CDCl$_3$) of 4a



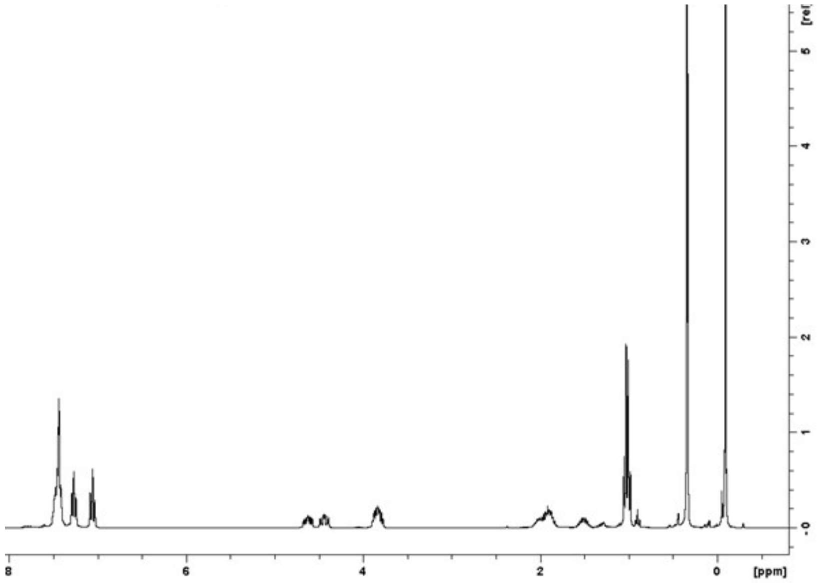
2.15 ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$) of 4a



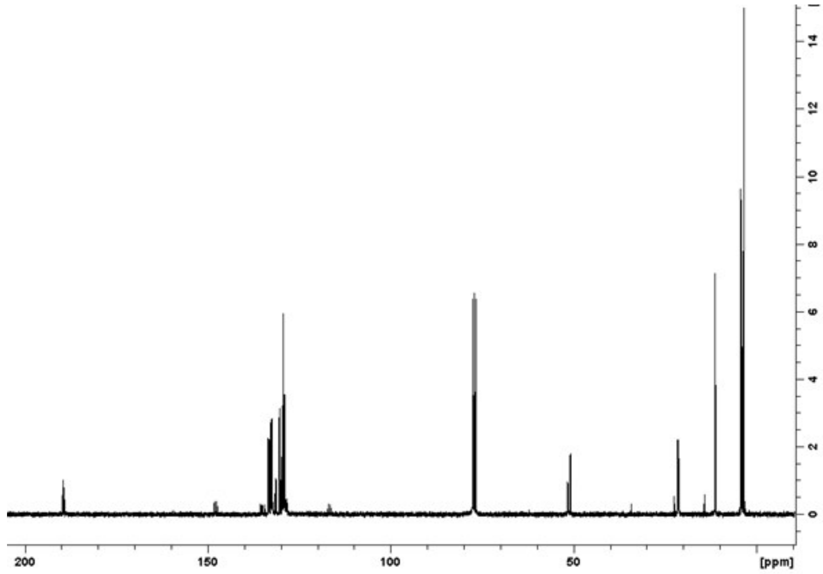
2.16 $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) of 4a



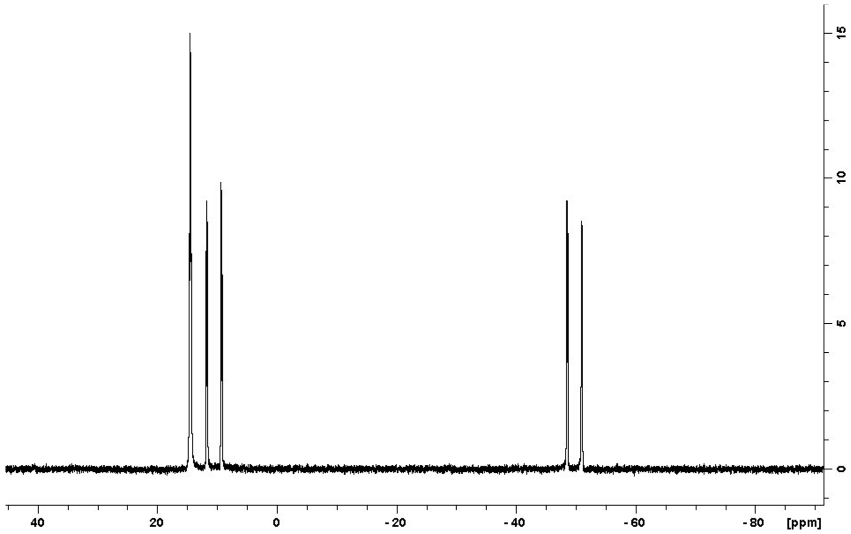
2.17 ^1H NMR (300.1 MHz, $CDCl_3$) of 4b



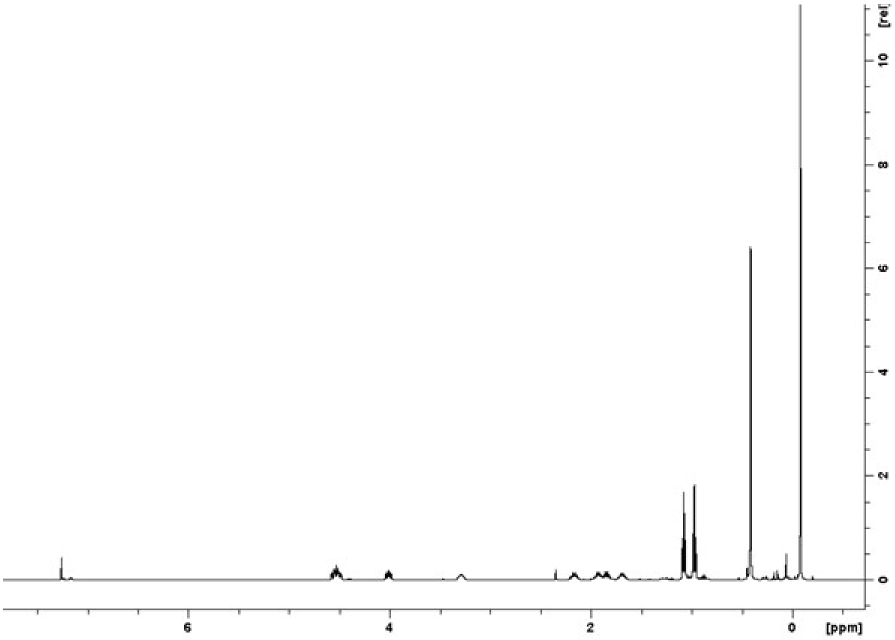
2.18 $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) of 4b



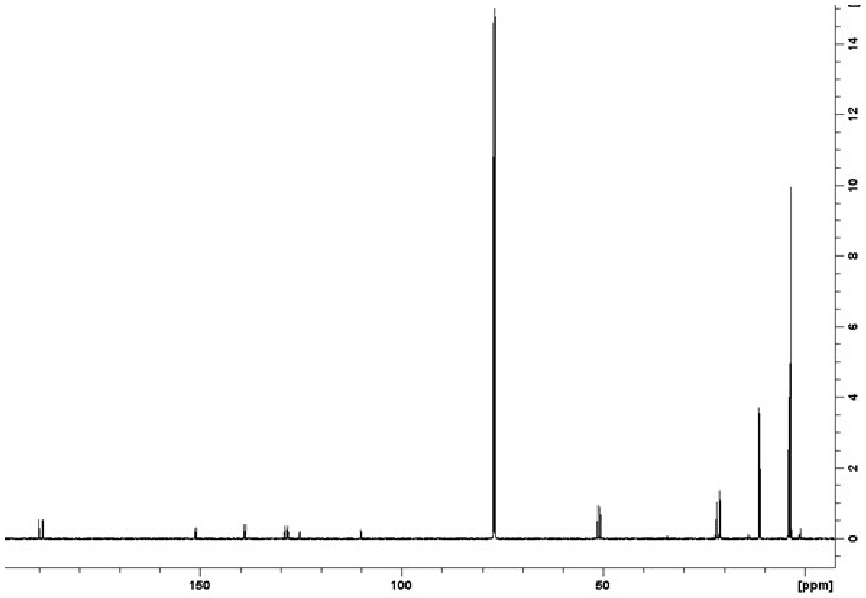
2.19 $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) of 4a



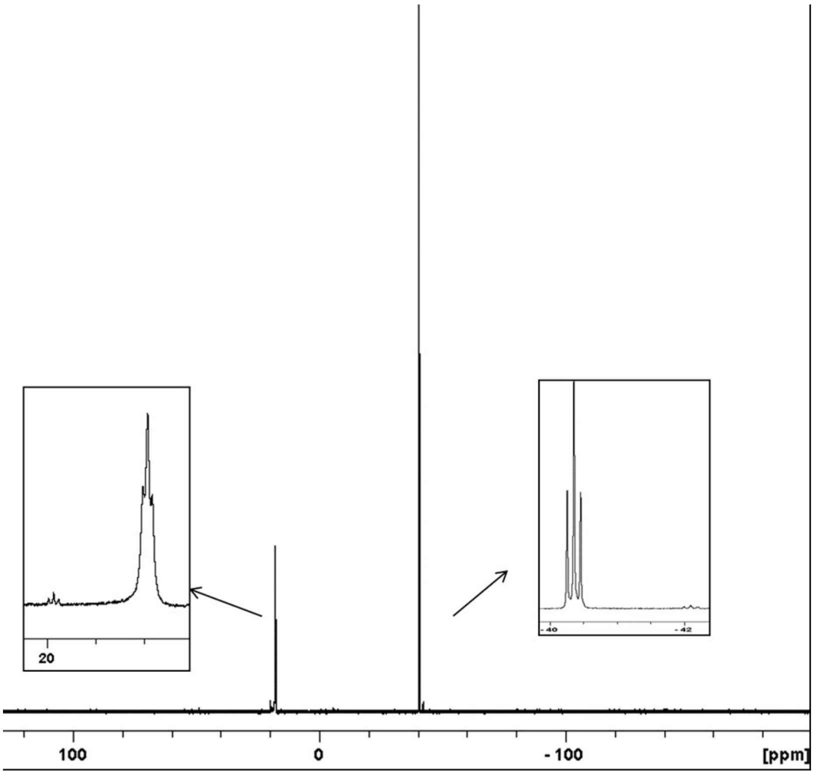
2.20 ^{1}H NMR (500.1 MHz, CDCl$_3$) of 5



2.21 ^{13}C{^{1}H} NMR (125.75 MHz, CDCl$_3$) of 5



2.22 $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$) of 5



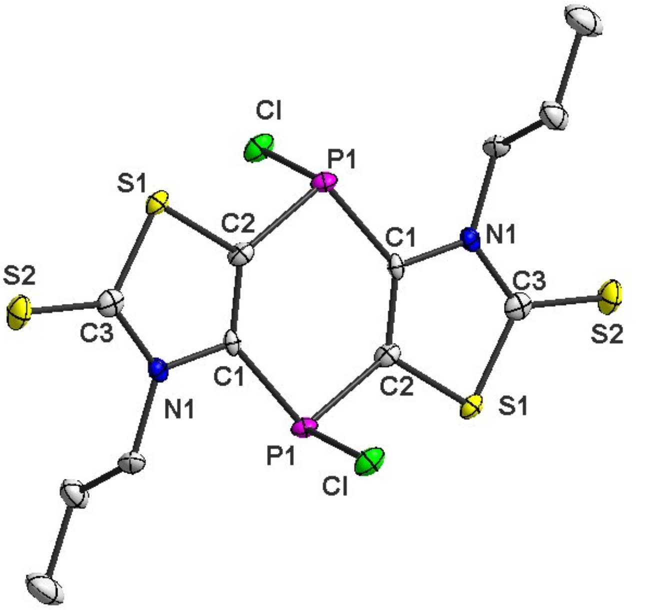


Figure S1. Diamond plot of the molecular structure of **1** in the solid state. Thermal ellipsoids are drawn at a 50 % probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.828(4), P1-C2 1.817(4), C1-C2 1.350(5), P1-Cl 2.0973(13),C1-P-C2 98.32(17).

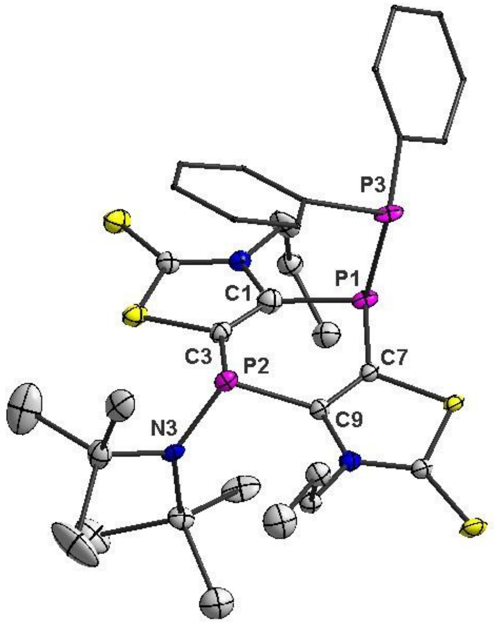


Figure S2. Displacement ellipsoids plot (50%) of molecular structure of **4b** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) P1-C1 1.81(2), P1-C7 1.813(19), P1-P3 2.246(6), P2-N3 1.691(16), P2-C3 1.856(19), P2-C9 1.845(19), C1-C3, 1.28(3). C1-P1-C7 96.6(8), C3-P2-C9 96.1(9), C1-P1-P3 106.6(7), P1-P3-C25 101.9(6).

3 Electrochemistry experiments and results

3.1 Experimental details

The solvent tetrahydrofuran (THF) was first distilled and further purified by recondensation over potassium mirror, and subsequently stored under argon (Ar) in a controlled-atmosphere glove box. All solution and sample preparations were undertaken within the same glove box. Solutions for voltammetry were 0.2 M in $^{n}Bu_4NPF_6$ (purchased from Aldrich and dried for several hours under vacuum before use). After background scans were taken on the solvent/electrolyte solutions, the analyte **2** was added to make a 2.0 mM solution. After all measurements were completed, ferrocene ($C_{10}H_{10}Fe$, hereafter designated as Fc) was added to a concentration of 2.0 mM and served as an internal reference using the ferrocene/ferrocenium ($Fc^{+/0}$) redox couple, set to 0 V according to IUPAC recommendations.[2] Voltammograms were obtained using a Pine Instruments, Inc., WaveNano potentiostat/galvanostat connected to platinum (Pt) or gold (Au) screen-printed electrodes on rugged ceramic substrates. The patterned electrodes formed an inner working disk and outer auxiliary ring separated by a Ag/AgCl spot (for further information, consult the website at https://www.pineresearch.com/shop/products/electrodes/screen-printed-electrodes/ceramic/).

Background scans established an electrochemical window 3.2 V wide and identified the anodic and cathodic limits with respect to the nominal voltage of the solid silver 'dot' reference. Next, open circuit potential measurements were taken to establish the starting point of CV experiments. Careful CV scans were then taken in the anodic and cathodic directions to encounter the most accessible processes, and only after these were investigated thoroughly were scans taken to higher positive and negative potentials. Only at the end of the investigation is the Fc reference compound added to the mixture, and then scans are carefully repeated at the standard scan rate of 0.2 $V \cdot s^{-1}$ so as to include the $Fc^{+/0}$ signal within the scan windows. Considerable caution is required to protect the integrity of the electrode surfaces which cannot be polished between scans and are cleaned after use by immersion in an ultrasonic bath containing suitable detergents.

3.2 Cyclic voltammetry results

Cyclic voltammograms (CVs) were measured under rigorous exclusion of the atmosphere by working in an argon-filled glove box. THF was employed as solvent due to the instability of **2** in other typical solvents suitable for voltammetry. CVs measured at Au and Pt electrodes "screen printed" onto patterned ceramic plates were very similar and the analysis is here reported in detail only for results at the Pt-surfaced electrodes. The starting potential of -0.690 V (versus $Fc^{+/0}$; hereafter all potentials are quoted on this scale) was determined from an open circuit potential (o.c.p.) experiment.

In typical scans from the central region of the voltammetric window (Fig. S1), a closely-spaced two-step reduction is observed, each step corresponding to a 1*e* reduction as indicated by comparable currents with that of the internal ferrocene reference. The molecular volumes and polarity of Fc and **2** are sufficiently close that similar diffusion coefficients can be expected. Scan rates were varied from 0.1 to 1.0 $V \cdot s^{-1}$ with very little change in the observed scan behaviours. The behaviour of **2** at the electrode interface is complex and was investigated repeatedly using different parameters and the traces shown in Figure 1 are representative of the observed behaviour. On scans starting in the anodic direction (purple line in Fig. S3), the small peak identified as $E_p^a('')$ is always observed, whereas process $E_p^a(')$ is absent. This $E_p^a('')$ peak is considerably more intense in scans that start in the cathodic direction and pass through reductions E(2) and E(3). Furthermore, this peak is relatively more intense in scans with slower scan rates, but the current falls in repeated cycling between -0.69 V and -0.09 V. Together, these results are consistent with a surface-confined irreversible oxidation process from a species generated during the E(2,3) reductions. Similarly, the peak labelled as $E_p^a(')$ fits for an irreversible off-set re-oxidation of some species generated at E(2,3) that remains in solution and is not surface-confined.

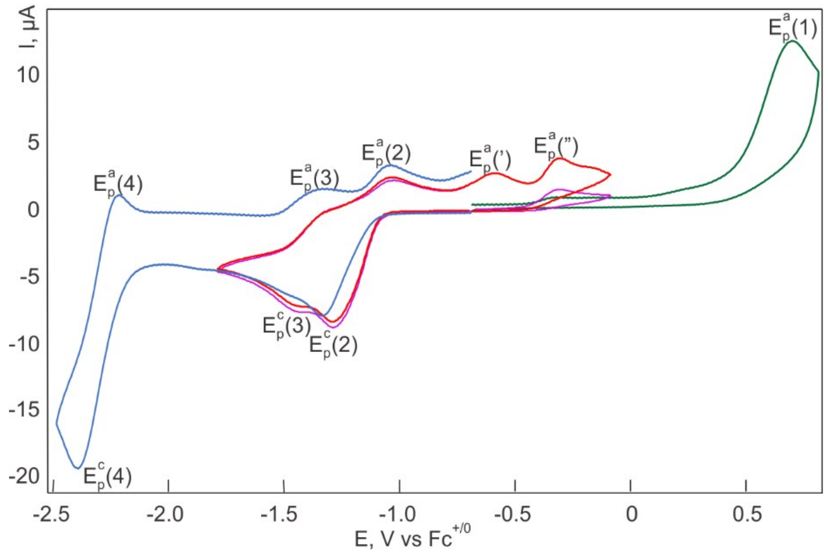


Figure S3. Composite CVs from solutions 0.2 mM in **2** (purple line) scanning first in the anodic direction and (red line) first in the cathodic direction from the OCP. Anodic scans to more positive (green line) and more negative (blue line) are also shown. Scan rate: 0.2 V·s^{-1}; 0.2 M ^{n}Bu$_4$NPF$_6$ in THF.

Justification for treating the radical anion and the dianion as *chemically* stable species (although quite reactive towards Pt and Au electrode materials) is provided by the recent NMR observation of a related imidazole-2-thione-based dianion[3] (i), computational results (for details see below) showing that the dianion is more stable than the neutral species at M06-2X/6-311+G** (PCM: THF) as shown in Table S2 (ii), observation of further well-behaved reduction waves (see S.I.) (iii) and the great similarity to the CV behavior of analogue compound **IV** [4](iv).

Consistent with the existence of the E_p^a(') and E_p^a(") processes, reductions E(2) and E(3) are only partly chemically reversible with $I_p^a(1)/I_p^c(2) = 0.4$ and $I_p^a(2)/I_p^c(3) = 0.4$ ratios, as well as considerably lower overall current for E(3) compared to E(2). Nevertheless, return peaks $E_p^a(3)$ and $E_p^a(2)$ are observed, with rather large peak separations indicative of slowed electron transfer (electrochemically quasi- and irreversible, respectively) – see Table S1. The peak potentials are quite insensitive to scan rate changes, whereas as mentioned above, the intensity of E_p^a("), alone, seems to increase with decreased scan rates.

Table S1. Potential data from cyclic voltammetry on **2** and the closely analogous **IV** ^{a}

Process	Bis(thiazole)diphosphinine **2** ^{b}	Bis(thiourea)diphosphinine **IV** ^{c}
$E_p^a(1)$	+0.698 V (IRR)	*not investigated*
E_p^a(")	-0.322 V (IRR)	-0.34 V (IRR)
E_p^a(')	-0.592 V (IRR)	-0.61 V (IRR)
$E_p^c(2)$	-1.283 V	-1.87 V (*estimate ~-1.80 V*) QR
$E_p^a(2)$	-1.042 V	-1.60 v
$E_m(2)$	-1.16 V	-1.70 V
$\Delta E^{c\text{-}a}$	241 mV	~200 mV
$E_p^c(3)$	-1.453 V	-1.87 (*estimate ~-1.95 V*) QR
$E_p^a(3)$	-1.343 V	-1.75
$E_m(3)$	-1.40	-1.85 V
$\Delta E^{c\text{-}a}$	110 mV	~200 mV
$E_p^c(4)$	-2.393 V	-2.69 V
$E_p^a(4)$	-2.223 V	-2.49 V
$E_m(4)$	-2.31	-2.59 V
$\Delta E^{c\text{-}a}$	170 mV	200 mV

^{a} Ref.[3]. ^{b} Scan rate: 0.2 V·s^{-1}; 0.2 M in ^{n}Bu$_4$NPF$_6$ in THF. ^{c} Scan rate: 0.1 V·s^{-1}; 0.1 M in ^{n}Bu$_4$NPF$_6$ in THF at Pt wire electrodes.

In addition to the two central reduction processes and associated re-oxidations, additional processes occur at more positive and negative potentials (Fig. S3). An irreversible oxidation peak, $E_p^a(1)$ of comparable current magnitude to $E_p^c(2)$, is observed at +0.698 V. No further oxidation processed occur before the anodic limit. The green trace also shows the small peak from E_p^a(") at -0.322 V; the low intensity indicates this is not a process due to bulk analyte. Remarkably, a reasonably well-behaved third reduction is observed with $E_p^c(4)$ = -2.393 V and re-oxidation at $E_p^a(4)$ = -2.223 V (ΔE_{pp} = 170 mV) and with an $I_p^a(4)/I_p^c(4)$ that is close to unity as best as can be determined so close to the cathodic limit. Finally, it should be noted that there is rather large current flowing over the intermediate region from E(3) to E(4).

Bis(thiazole)diphosphinine **2**

Bis(thiourea)diphosphinine **IV**

Figure. Chemical structures of tricyclic fused diphosphinines

3.3 Interpretation of the CV results

There are several considerations that provide insight into the rather complex behaviour of **2** in CV at Pt and Au screen-printed electrode interfaces. First there is the close structural and electronic analogy (Fig. S3) with previously reported bis(thiourea)diphosphinine **IV**.[4] Supporting Information.) Importantly, the latter shows remarkably similar voltammetric behaviour, although the double reduction is even more closely spaced than in **2** so that the $E_p^c(2)$ and $E_p^c(3)$ peaks (but not those of the return waves) overlap. Interestingly, at Pt wire electrodes, irreversible oxidation processes E_p^a(') and E_p^a(") are observed at the *same* potentials as those in **2** (see Table 1) and with similar relative intensities to the E(2,3) peaks. There is strong evidence for the intrinsic stability of the double-reduction product **2**$^{2-}$ and helps to understand why a third reduction process E(4) can be observed in the CVs of **2** and **IV**, following on the messy earlier reduction events.

We consider the two heterocycles to be intrinsically stable to one and two electron reductions. However, we suggest that these electron rich, heteroatom-centred reduction products are not fully stable to the Au and Pt electrode surfaces, and that some decomposition and/or adhesion to the electrode surfaces competes with solution-phase reduction. This accounts for the low current ratios for E(2) and E(3) as well as for the repeatable occurrence of the E_p^a(') and E_p^a(") processes that appear indistinguishable between **2** and **IV** under the experimental conditions. From the perspective of the chemical redox processes of these diphosphinenes, this surface-related behaviour may be ignored.

The close parallels in the voltammetry of the two fused-ring diphosphinines allows the comparison of the potentials for $E_p^c(2)$ and $E_p^c(3)$ (or the related $E_m(2)$ and $E_m(3)$, which more closely resemble the Differential Pulse Voltammetry data also reported for **IV**). For both processes, the reduction of **2** occurs at lower potentials than **IV** ($\Delta E_m(2)$ = 0.54 V, and $\Delta E_m(3)$ = 0.45 V). The bis(thiazole)-diphosphinine is thus considerably easier to reduce than the closely related bis(thiourea)diphosphinine. This means that the LUMO of **2** should be of lower energy than those of **IV**. This is substantiated by computational results (see Figure S4, for details see below) which calculate the LUMO energy of **2'** to be 0.27 eV lower than that of **IV'** in the PCM:THF model that should most closely reflect the solution voltammetry conditions. Also the calculated anionic and dianionic state (Table S2) is more stable for **2'** than for **IV'**, by 0.34 and 0.64 eV (0.30 and 0.44 in PCM: THF), respectively. Importantly, the calculations indicate that even upon addition of the second electron, the dianion is more stable than the neutral **2'**, showing the stability of the dianion. While according to the gas phase calculations the radical anion exhibits higher stability than the dianion both for **2‘** and **IV‘**, using PCM:THF model the dianion is stabilized significantly, which was in good agreement with the observed close spacing of the two reduction processes.

The origins of the very close spacings of $E_p^c(2)$ and $E_p^c(3)$, in both **2** and **IV**, which approach but do not reach potential inversion,[5-8] might be sought in the structural changes that accompany the *second* reduction: the geometry of $\mathbf{2}^{-\bullet}$ remains planar, whilst $\mathbf{2}^{2-}$ bends appreciably.[5] Indeed, according to our DFT calculations (for the details see below), at M06-2X/6-311+G** (PCM:THF) $\mathbf{2'}^{2-}$ and $\mathbf{IV'}^{2-}$ exhibit pyramidalized phosphorus atoms (although, the barrier to planarization is only 4 and 2.3 kcal/mol, respectively). The calculated stability of the anion is larger than that of the dianion in the gas phase calculation, however, using the PCM:THF model the dianionic state is significantly stabilized (see Table S2) in reasonable agreement with the observed CV behavior. In this regard, diphosphinines **2** and **IV** appear to be less structurally robust towards reduction than the comparably-sized PAH anthracene, which remains robustly planar also in the dianion at B3LYP/6-311+G**. It is noteworthy that all structures in Table S2 are planar, with the exception of the dianion derived from **2‘** and **IV‘**, which exhibits pyramidalized phosphorus atoms. The planar structure of **the dianon** is a first order saddle point (+4.0 kcal/mol for $\mathbf{2'}^{2-}$ and +2.3 kcal/mol for $\mathbf{IV'}^{2-}$ at M06-2X/6-311+G** PCM:THF level of theory) of the pyramidalization motion of the phosphorus atoms.

Correspondingly, the separation of E(2) and E(3) in anthracene is 0.83 V in DMF and 0.60 V in (more strongly solvating) $HNMe_2$ solutions.[6,9] In further comparisons to the PAH analogue, the electrochemical stability window for **2**, defined as $\Delta E_{SW} = E_p^a(1) - E_p^a(2)$, is 1.74 V. In anthracene, $\Delta E_{SW} \approx 3.2$ V with an uncertainty caused by measurements of reduction and oxidation in separate experiments using DME and ACN, respectively.[8,10] Consistent with this, the HOMO-LUMO gap in anthracene is correspondingly larger at 3.55 eV than in **2’** (2.99 eV; gas phase computations).

Table S2 M062x/6-311+G** (PCM: THF) relative energies (with respect to the neutral molecule in eV) of the calculated cationic (dicationic) and anionic (dianionic) states for **2‘** and **IV‘**.

M062x/6-311+G**					
	Dication	monocation	neutral	monoanion	dianion
2’	19.53	7.80	**0.0**	-2.27	-0.60
IV’	18.47	7.24	**0.0**	-1.93	+0.04
M062x/6-311+G** (PCM: THF)					
2’	14.10	6.49	**0.0**	-3.50	-5.67
IV’	13.49	6.11	**0.0**	-3.20	-5.23

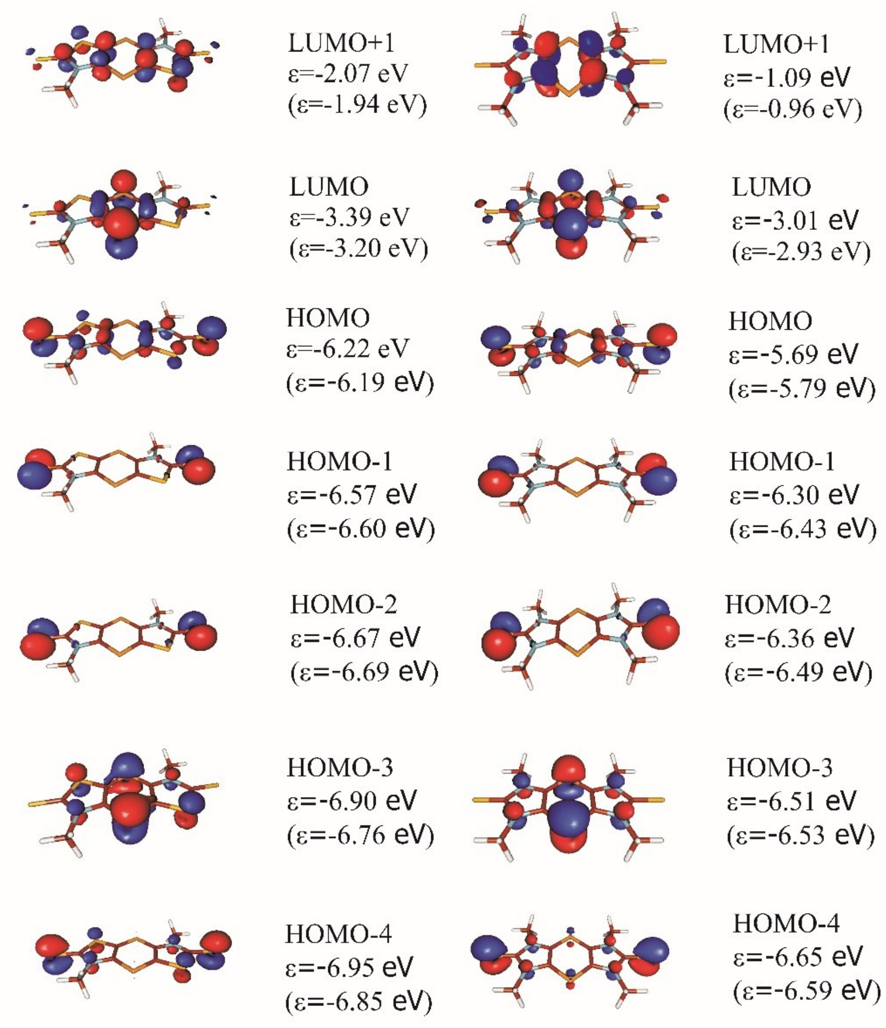


Figure S4. Comparative orbital energy manifolds for (left) **2'** and (right) **IV'** from B3LYP/6-311+G** and (in brackets) B3LYP/6-311+G**(PCM:THF) calculations.

In addition to this confirmation of the lower LUMO in **2'**, the voltammetric results for oxidation, $E_p^a(1)$ = +0.698 V, establishes a redox-stability window for **2'** that is about 1.7 V wide. Such a substantial range between the oxidation and reduction potentials corroborates the calculated high aromaticity of **2'** and also fits with the calculated HOMO-LUMO gap of 3.0 eV (PCM:THF). At the same time, compared to comparable aromatic hydrocarbons – e.g. anthracene – it is noteworthy that both the oxidation and reduction potentials of **2** are smaller: E^{red} = −1.16 V for **2** vs. −2.29 V anthracene; E^{ox} = +0.70 V for **2** vs. +0.92 V for anthracene on the $Fc^{+/0}$ scale.[11] This results in a smaller *electrochemical stability window* ΔE_{SW} = 1.86 V for **2** compared to 3.21 V in anthracene. Gas phase DFT calculations at the B3LYP/6-311+G** level of theory report a HOMO-LUMO gap of 3.55 eV for neutral anthracene which is indeed considerably larger than 2.99 eV calculated for **2** and 2.68 eV for **IV** (see Fig. S4).

4 Computational details

All calculations were carried out with the Gaussian 09 program package.[12] Full geometry optimization calculations were performed, followed by calculation of the second derivatives at the optimized structures to establish the nature of the stationary points obtained, as characterized by only positive eigenvalues of the Hessian for minima. The Gibbs free energies were calculated based on the harmonic vibrational frequencies (atmospheric pressure, 298.15 K). The dispersion corrected M06-2X funcitonal (ultrafine integration grid was apllied for the M06-2X frequency calculations) was used to estimate the energy differences between the different species, while B3LYP functional was used for the TD-DFT calculations (using the M06-2X optimized structure) and to calculate the energy level of the molecular orbitals, since it gives much better results for the excitation. **2**, **IV** and their derivatives were calculated with methyl substituents at the nitrogen atoms (instead of the *n*-propyl) to reduce the computational time and they were labeled by the special character **‘**. The 6-311+G** basis has been used throughout, while in case of the PP bonded **5** and **4b** the smaller 6-31G* basis was selected for optimization, and further single point calculations were carried out with larger 6-311+G** basis set. In case of the anionic structures the wavefunction was carefully investigated, whether or not the electrons reside on diffuse orbitals, indicating spontaneous electron loss. All anions and dianions proved to be stable. For the visualization of the molecular structures and the molecular orbitals the MOLDEN program was used.[13]

TD DFT calculations to obtain vertical excitation energies

Table S3 B3LYP/6-311+G**//M06-2X/6-311+G** TD DFT vertical excitation energies of **2‘** Calculated electronic transitions with oscillator strentgth smaller than 0.001 are not shown. S0 is the (singlet) ground state, Sx is the xth excited (singlet) state.

λ_{abs} (nm) Experimental data on **2**	λ_{abs} (nm) Calculated data on **2’**	Oscillator strength	Transition	Coefficient
497	502 (S0→S1)	0.2550	HOMO→LUMO	0.69
			HOMO-4→LUMO	0.11
368	368 (S0→S5)	0.0489	HOMO-4→LUMO	0.64

			HOMO→LUMO+1	-0.26
341	330 (S0→S8)	0.2524	HOMO-4→LUMO	0.26
			HOMO→LUMO+1	0.64
313	286 (S0→S14)	0.3328	HOMO-7→LUMO+1	-0.21
			HOMO-4→LUMO+1	0.65

Table S4 B3LYP/6-311+G**//M06-2X/6-311+G** TD DFT vertical excitation energies of **2’**$^{\cdot -}$ Calculated electronic transitions with oscillator strentgth smaller than 0.001 are not shown. D0 is the (doublet) ground state, Dx is the xth excited (doublet) state.

λ_{abs} (nm) Calculated	Oscillator strength	Transition	Coefficient
657 (D0→D2)	0.0468	α-SOMO→ α-LUMO+1	0.97
493 (D0→D5)	0.0426	β-SOMO→ β-LUMO	0.94
491 (D0→D6)	0.0122	β-SOMO→ β-LUMO+3	0.98
455 (D0→D8)	0.1450	β-SOMO→ β-LUMO+2	0.15

Table S5 B3LYP/6-311+G**//M06-2X/6-311+G** TD DFT vertical excitation energies of **3b’**$^{-}$ Calculated electronic transitions with oscillator strentgth smaller than 0.001 are not shown. S0 is the (doublet) ground state, Sx is the xth excited (doublet) state.

λ_{abs} (nm) Calculated	Oscillator strength	Transition	Coefficient
425 (S0→S1)	0.0439	HOMO→ LUMO	0.62
		HOMO→ LUMO+1	-0.29
		HOMO→ LUMO+2	0.10
415 (S0→S1)	0.0933	HOMO→ LUMO	0.30
		HOMO→ LUMO+1	0.52
		HOMO→ LUMO+2	-0.33

DFT calculations on the assumed transient radical formed in the (**3b** -> **5 reaction**;with Me substituents at the N of the thiazole ring)

Table S6 B3LYP/6-311+G**//M06-2X/6-311+G** TD DFT vertical excitation energies of the assumed transient radical intermediate (**3b** -> **5**;with Me substituents at the N of the thiazole ring). Calculated electronic transitions with oscillator strentgth smaller than 0.001 are not shown. D0 is the (doublet) ground state, Dx is the xth excited (doublet) state.

λ_{abs} (nm) Calculated	Oscillator strength	Transition	Coefficient
750 (D0→D5)	0.0078	β-SOMO-4→ β-LUMO	0.91
432 (D0→D7)	0.0086	β-SOMO-7→ β-LUMO	-0.43
		β-SOMO-1→ β-LUMO	0.47
		α-SOMO-1→ α-LUMO	0.36

		α-SOMO-1→ α-LUMO	0.29
		α-SOMO→ α-LUMO	0.28
		β-SOMO-2→ β-LUMO	0.29
419 (D0→D8)	0.0080	β-SOMO-7→ β-LUMO	0.78
		β-SOMO-6→ β-LUMO	-0.31
		β-SOMO→ β-LUMO+1	0.24
		α–SOMO-1→ α -LUMO	0.23

The S^2 values of the D7 and D8 excited state are 2.07 and 1.33, which are significanty higher than the theoretical value 0.75, indicating the admixture of the triplet state.

Calculation of the TD-DFT spectrum of the assumed radical (Table S6) also results in excitation energies corresponding to absorption in the blue and red regions, which rationalizes the observed greenish color. The Gibbs free energy of for the dimerization is -63.5 kcal/mol. In accordance with this large thermodynamic stabilization of the P-P bonded dimer it is fully understandable that the radicals, which used to dimerize without a substantial reaction barrier, can not be observed of the assumed radical to afford the P-P bond lend further support to a rapid reaction.

Calculations to understand the stabilizing effects on the observed conformation of 5.

It seems that dispersive forces are responsible for the observed arrangement of substituents in **5’** (which is similar to that in **5**). First we considered the effect of secondary orbital interactions, and have carried out a second-order perturbation theory analysis on the NBO basis using the B3LYP/6-311+G** structure and wavefunction, but could not find stabilizing interactions larger than 2 kcal/mol between the two parts of the molecule. Nevertheless, optimization of a structure with the two tricycles bound via PP bond (**5’**) in a *trans* arrangement results in a geometry which is ~12 kcal/mol higher in energy when using functionals that account for dispersion interactions (12.6 kcal/mol for M06-2X and 12.2 kcal/mol for ωB97XD), whereas with the B3LYP functional (no dispersion correction), the energy of this trans oriented structure structures is nearly identical (ΔE = 0.2 kcal/mol; basis set used is 6-311+G**) with those related to the X-ray structure. For calculations of the rotation of the propeller shaped diphenylphosphino unit about the P–P bond in the case of **4b’**, the energy difference between the two possible rotated structures is only 2.5 kcal/mol using the M06-2X functional, whereas with B3LYP it is just slightly less: 0.8 kcal/mol). Altogether, the dispersive forces operating between the planes of the two tricycles has a sizeable contribution to the energy of the adopted structure.

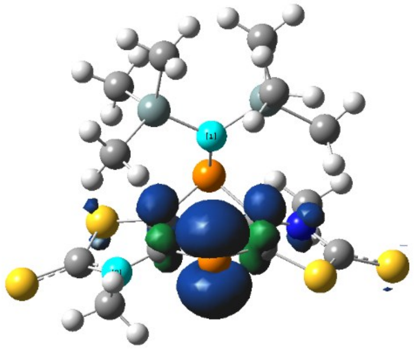


Figure S5. Spin density distribution of the assumed radical intermediate (**3b** -> **5**;with Me substituents at the N of the thiazole ring) at the M06-2X/6-311+G** level of theory

XYZ coordinates and total energies of the investigated systems

cis isomer of **1’**

G(M06-2X/6-31G*)= -3613.682069
E(M06-2X/6-31G*)= -3613.768355

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.400698
N	1.291016	0.000000	1.929235
C	2.323376	0.000000	1.030551
S	1.653280	0.000000	-0.590082
P	-1.375516	0.000000	2.486781
C	-2.680229	0.000000	1.340684
S	-4.333510	0.000000	1.930757
C	-5.003610	0.000000	0.310112
N	-3.971235	0.000000	-0.588552
C	-2.680224	0.000000	-0.059991
P	-1.304719	0.000000	-1.146097
C	-4.198210	0.000000	-2.027629
S	-6.620032	0.000000	0.004657
C	1.518016	0.000000	3.368309
S	3.939801	0.000000	1.336007
H	-5.270916	0.000000	-2.199410
H	-3.750177	0.891816	-2.470726
H	-3.750176	-0.891817	-2.470726
H	2.590727	0.000000	3.540053
H	1.069990	0.891816	3.811413
H	1.069990	-0.891816	3.811413
Cl	-1.197417	-1.643871	-2.315102
Cl	-0.711031	-1.040323	4.085714

trans isomer of **1’**

G(M06-2X/6-31G*)= -3613.682035
E(M06-2X/6-31G*)= -3613.768894

C	0.021872	0.039379	0.042885
C	0.018640	-0.083973	1.393689

N	1.283718	-0.010187	1.958617
C	2.315372	0.218177	1.079284
S	1.653255	0.280536	-0.540114
P	-1.413955	-0.408792	2.480162
C	-2.748054	-0.138206	1.296088
S	-4.390728	-0.107823	1.893762
C	-5.052613	0.001873	0.273514
N	-4.009735	-0.024379	-0.618308
C	-2.738653	-0.085464	-0.057968
P	-1.302756	0.017033	-1.179353
C	-4.247346	0.070663	-2.058533
S	-6.661284	0.127870	-0.049305
C	1.564116	-0.089540	3.391896
S	3.907476	0.413141	1.443607
H	-5.277849	-0.222235	-2.242962
H	-4.097238	1.096531	-2.399265
H	-3.578294	-0.607155	-2.586790
H	2.495242	-0.637211	3.522630
H	1.674402	0.912514	3.808249
H	0.755150	-0.615802	3.895027
Cl	-1.226408	-2.010480	-1.769751
Cl	-1.456574	1.443829	3.482530

2’

G(M06-2X/6-311+G**)= -2693.252056
E(M06-2X/6-311+G**)= -2693.340554

S	0.000083	0.000000	0.000210
C	-0.000317	0.000000	1.755637
C	1.318753	0.000000	2.226788
N	2.250750	0.000000	1.188777
C	1.751694	0.000000	-0.085718
P	-1.518492	0.000000	2.598821
C	-0.958361	0.000000	4.259506
N	-1.890348	0.000000	5.297520
C	-1.391282	0.000000	6.572013
S	0.360317	0.000000	6.486088
C	0.360722	0.000000	4.730648
C	-3.321928	0.000000	5.027255
P	1.878889	0.000000	3.887477
S	-2.222647	0.000000	7.991508
C	3.682327	0.000000	1.459052
S	2.583054	0.000000	-1.505213
H	4.204891	0.000000	0.506617
H	3.948911	0.891813	2.030023
H	3.948911	-0.891814	2.030023
H	-3.844484	0.000000	5.979694
H	-3.588514	0.891814	4.456287
H	-3.588515	-0.891813	4.456287

PCM:THF
G(M06-2X/6-311+G**)= -2693.261422

E(M06-2X/6-311+G**)=-2693.350532

S	0.000450	0.000000	0.004549
C	-0.001059	0.000000	1.760437
C	1.318434	-0.000000	2.229275
N	2.250471	-0.000000	1.187169
C	1.745880	-0.000000	-0.074219
P	-1.522376	0.000000	2.598688
C	-0.958033	0.000000	4.257026
N	-1.890070	0.000000	5.299131
C	-1.385479	0.000000	6.560520
S	0.359951	-0.000000	6.481751
C	0.361460	-0.000000	4.725863
C	-3.324778	0.000000	5.025609
P	1.882777	-0.000000	3.887612
S	-2.215525	0.000000	7.998239
C	3.685179	-0.000000	1.460691
S	2.575926	-0.000000	-1.511939
H	4.213194	-0.000000	0.512118
H	3.946772	0.892867	2.030812
H	3.946772	-0.892867	2.030812
H	-3.852792	0.000000	5.974182
H	-3.586371	0.892867	4.455488
H	-3.586371	-0.892866	4.455488

3b’

G(M06-2X/6-311+G**)= -3566.392853
E(M06-2X/6-311+G**)= -3566.697110

C	-0.046061	-0.022876	0.053540
C	0.006611	-0.140972	1.416342
S	1.692879	-0.158363	1.925565
C	2.285544	-0.079583	0.282774
N	1.233844	-0.041237	-0.554658
P	-1.281244	-0.421757	2.627553
C	-2.486585	-1.058046	1.465572
C	-2.539807	-0.903204	0.099056
S	-3.824255	-1.895062	-0.576880
C	-4.343245	-2.429762	0.992296
N	-3.530187	-1.880376	1.931161
P	-1.575749	0.249395	-0.883676
N	-2.149075	1.822058	-0.260899
Si	-3.905037	2.020635	-0.158626
C	-4.734785	1.153547	1.287637
C	-3.708251	-2.122795	3.353944
S	-5.640605	-3.461727	1.234518
S	3.907238	-0.064849	-0.139377
C	1.457518	-0.032928	-1.992343
Si	-1.126090	3.254572	-0.237090
C	-1.374741	4.258157	-1.822536
C	-1.496487	4.294090	1.295792
C	0.724103	2.948659	-0.195653
C	-4.403560	3.829328	0.092575

C	-4.679939	1.496095	-1.792937
H	2.134084	0.783577	-2.249824
H	1.933638	-0.969069	-2.290148
H	0.502099	0.081163	-2.498140
H	-4.573551	-2.766640	3.484528
H	-2.808998	-2.594737	3.754097
H	-3.864588	-1.168780	3.863005
H	-5.769683	1.578308	-1.738805
H	-4.323989	2.150520	-2.594704
H	-4.441321	0.467521	-2.068401
H	-5.638779	1.709720	1.556057
H	-5.031007	0.127192	1.066607
H	-4.065738	1.145429	2.153147
H	-5.478480	3.866641	-0.116095
H	-4.264635	4.138938	1.130172
H	-3.917840	4.559923	-0.554065
H	-0.854063	5.219263	-1.763191
H	-0.945188	3.700367	-2.661007
H	-2.421117	4.451504	-2.063762
H	-0.562754	4.720384	1.673026
H	-2.189292	5.115169	1.106645
H	-1.912476	3.661286	2.084920
H	1.185144	3.942811	-0.177483
H	1.058483	2.411874	0.694024
H	1.107972	2.437457	-1.079155

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G(M06-2X/6-31G*)= -3565.838502
E(M06-2X/6-31G*)=-3566.146086

N	-0.001679	-0.010204	-0.009043
C	-0.003669	-0.003813	1.385874
C	1.253153	0.012294	1.917674
S	2.448758	-0.045479	0.655617
C	1.229825	-0.036155	-0.609539
P	-1.577125	-0.016280	2.283998
C	-0.987579	-0.799540	3.770932
C	0.289571	-0.862553	4.262384
N	0.425280	-1.746780	5.317560
C	-0.732299	-2.343450	5.755314
S	-2.055301	-1.795633	4.745954
P	1.673293	0.232752	3.685501
N	0.996729	1.820630	3.972875
Si	0.601539	2.330100	5.639961
C	0.075644	0.920097	6.765741
S	-0.873440	-3.401825	7.013155
C	1.684693	-2.088769	5.971806
S	1.584857	-0.058534	-2.224277
C	-1.236859	0.020390	-0.784227
Si	1.493518	3.116385	2.836412
C	3.353900	3.011050	2.573841

C	0.560834	3.097531	1.200049
C	1.122755	4.833616	3.518561
C	2.132965	3.051005	6.470943
C	-0.858382	3.522113	5.597117
H	1.596832	-1.903694	7.044367
H	1.882554	-3.152979	5.824762
H	2.484003	-1.489792	5.538851
H	-0.971688	-0.040501	-1.838428
H	-1.867394	-0.827646	-0.506313
H	-1.770639	0.955259	-0.589991
H	3.674029	3.766450	1.847762
H	3.873706	3.208766	3.518235
H	3.697819	2.040767	2.203746
H	0.623852	4.102761	0.767281
H	0.957196	2.401097	0.457472
H	-0.500545	2.875026	1.361602
H	1.631679	5.530048	2.840310
H	0.054951	5.065863	3.475732
H	1.482148	5.045110	4.527252
H	1.889436	3.423437	7.472409
H	2.883539	2.260178	6.588677
H	2.604038	3.866541	5.915952
H	-1.527326	3.293545	6.433589
H	-0.566746	4.571468	5.681367
H	-1.434164	3.400234	4.673267
H	-0.160293	1.390376	7.728589
H	-0.826566	0.396621	6.434245
H	0.862874	0.188034	6.963196

G(M06-2X/6-311+G**)= -3566.273355
E(M06-2X/6-311+G**)= -3566.577169

C	-0.029983	0.012147	0.106687
C	-0.015958	-0.058151	1.471842
S	1.641637	-0.073398	2.052531
C	2.281775	-0.073964	0.423603
N	1.231433	-0.044730	-0.459178
P	-1.372242	-0.303958	2.596287
C	-2.521647	-1.062032	1.422650
C	-2.551460	-0.889476	0.071484
S	-3.806993	-1.862532	-0.637451
C	-4.330444	-2.465624	0.925604
N	-3.517328	-1.924164	1.883813
P	-1.567508	0.318509	-0.888921
N	-2.138043	1.814878	-0.186972
Si	-3.913197	2.052860	-0.107442
C	-4.758568	1.134426	1.297120
C	-3.700826	-2.206961	3.303655
S	-5.597430	-3.507241	1.123473
S	3.885182	-0.106248	0.040834
C	1.509306	-0.090504	-1.892066
Si	-1.134934	3.289053	-0.291858

C	-1.513612	4.204149	-1.892567
C	-1.409196	4.328340	1.252311
C	0.708537	2.956730	-0.370676
C	-4.359142	3.848960	0.232377
C	-4.651208	1.586202	-1.768993
H	2.200042	0.712124	-2.150824
H	1.988495	-1.040950	-2.130152
H	0.576021	0.010139	-2.439502
H	-4.483195	-2.955357	3.397574
H	-2.769170	-2.585245	3.725964
H	-3.999662	-1.295079	3.825302
H	-5.740045	1.684190	-1.737721
H	-4.272306	2.256924	-2.545734
H	-4.427207	0.562785	-2.076055
H	-5.703797	1.647319	1.500594
H	-4.999343	0.093782	1.080439
H	-4.157981	1.180073	2.210270
H	-5.439445	3.910043	0.061769
H	-4.183728	4.116285	1.276035
H	-3.889605	4.599695	-0.401234
H	-0.989958	5.164384	-1.918916
H	-1.149580	3.609828	-2.736695
H	-2.573695	4.395088	-2.062814
H	-0.448209	4.726333	1.588557
H	-2.082485	5.171350	1.094991
H	-1.812486	3.714118	2.061988
H	1.170985	3.947662	-0.437309
H	1.114508	2.472046	0.519511
H	1.023650	2.408012	-1.259092

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G(M06-2X/6-31G*)= -7131.776061
E(M06-2X/6-31G*)=-7132.420203
E(M06-2X/6-311+G**//M06-2X/6-31G*)= -7133,2857957
E(ωB97XD/6-311+G**//M06-2X/6-31G*)= -7133,6550298
E(B3LYP/6-311+G**//M06-2X/6-31G*)= -7134,3341941

C	2.805841	0.954867	0.092430
C	2.316603	2.143260	-0.340752
N	3.088422	3.240488	0.056912
C	4.192674	2.949827	0.812622
S	4.268094	1.206665	1.019356
P	0.813478	2.431160	-1.336842
C	0.453807	0.726791	-1.799367
C	0.913459	-0.460808	-1.316398
N	0.334100	-1.559653	-1.939352
C	-0.561306	-1.284015	-2.940206
S	-0.663980	0.448766	-3.121910
P	2.087270	-0.721470	0.083530
N	3.350087	-1.688850	-0.537191
Si	3.897489	-3.000519	0.561711
C	3.207450	-2.720466	2.282214

C	0.592030	-2.933814	-1.521041
S	-1.431268	-2.362489	-3.853189
C	2.743325	4.609299	-0.314969
S	5.301100	3.996866	1.452208
P	-0.642129	2.772248	0.434766
C	-0.379245	1.292903	1.457989
C	-1.054397	0.116833	1.376750
S	-0.570406	-0.958346	2.661819
C	0.596882	0.195654	3.285801
N	0.527194	1.328810	2.528865
P	-2.221045	-0.555112	0.147411
N	-3.536090	-1.061906	1.116560
Si	-4.519035	0.053975	2.118112
C	-3.522574	1.468529	2.850413
S	1.578936	-0.067373	4.589289
C	1.352771	2.474676	2.899730
C	-2.127750	2.260963	-0.461441
C	-2.731130	1.050384	-0.598242
N	-3.736107	1.047526	-1.562958
C	-3.972558	2.240648	-2.195561
S	-2.859289	3.428889	-1.542251
S	-5.092057	2.581460	-3.361364
C	-4.407771	-0.181149	-1.982990
Si	-3.987320	-2.791698	0.998280
C	-5.803380	-2.950105	0.531874
C	-2.945135	-3.626754	-0.320727
C	-3.653076	-3.689219	2.616289
Si	4.245859	-1.382949	-2.061207
C	3.227490	-0.448532	-3.333365
C	5.809103	-0.381368	-1.771238
C	4.683363	-3.043216	-2.834697
C	3.321182	-4.689104	-0.036772
C	5.772691	-2.958392	0.684346
C	-5.909704	0.775460	1.077760
C	-5.245839	-0.886762	3.574604
H	-5.189072	0.092798	-2.690223
H	-3.683467	-0.844875	-2.471094
H	-4.846137	-0.670933	-1.112146
H	1.052922	2.831181	3.888233
H	2.399047	2.164938	2.949195
H	1.227566	3.271128	2.166514

G(M06-2X/6-311+G**)= -7132.647919
E(M06-2X/6-311+G**)= -7133.2874941

C	2.795934	0.956417	0.059875
C	2.308009	2.126172	-0.414136
N	3.075182	3.239901	-0.052510
C	4.174985	2.976669	0.716086
S	4.250840	1.244326	0.990212
P	0.813974	2.371532	-1.434993
C	0.455436	0.650988	-1.825408

C	0.912726	-0.515619	-1.298961
N	0.335835	-1.639043	-1.877276
C	-0.558234	-1.402287	-2.886670
S	-0.662422	0.320344	-3.137402
P	2.086022	-0.721406	0.109049
N	3.355027	-1.701296	-0.482174
Si	3.917919	-2.971301	0.655287
C	3.230398	-2.640815	2.363290
C	0.599113	-2.996674	-1.408118
S	-1.427586	-2.514762	-3.755749
C	2.725544	4.594860	-0.471093
S	5.280976	4.044778	1.320863
P	-0.651564	2.780932	0.323788
C	-0.375981	1.345606	1.402657
C	-1.043096	0.166071	1.367741
S	-0.547891	-0.856197	2.691862
C	0.611517	0.329560	3.266178
N	0.531438	1.432339	2.470082
P	-2.203702	-0.564099	0.168171
N	-3.530210	-1.018298	1.149324
Si	-4.499720	0.147617	2.104251
C	-3.493193	1.571334	2.793489
S	1.598253	0.118876	4.574414
C	1.344094	2.602192	2.796513
C	-2.128964	2.220865	-0.553575
C	-2.717159	1.002435	-0.649662
N	-3.729088	0.953367	-1.605662
C	-3.995427	2.126329	-2.259906
S	-2.886395	3.345692	-1.662899
S	-5.146349	2.425646	-3.404545
C	-4.404417	-0.292767	-1.966179
Si	-3.989485	-2.748679	1.110963
C	-5.795094	-2.918999	0.624860
C	-2.928050	-3.653752	-0.138941
C	-3.689627	-3.559921	2.777214
Si	4.237248	-1.435669	-2.019397
C	3.211986	-0.557034	-3.319171
C	5.784617	-0.408935	-1.762364
C	4.691346	-3.111186	-2.740255
C	3.355122	-4.676593	0.106663
C	5.789481	-2.908829	0.768463
C	-5.879209	0.851075	1.044509
C	-5.247400	-0.732376	3.583490
H	-5.025288	-0.091909	-2.835358
H	-3.654882	-1.048129	-2.218769
H	-5.025002	-0.630858	-1.136519
H	1.047087	2.984194	3.774340
H	2.393296	2.310890	2.846880
H	1.201360	3.371956	2.041611
H	0.662032	-2.987083	-0.318096
H	-0.228673	-3.625331	-1.728522
H	1.535938	-3.370579	-1.824660

H	2.811537	4.685773	-1.554688
H	1.703145	4.826536	-0.163179
H	3.416492	5.280276	0.013295
H	6.412249	-0.481154	-2.656143
H	5.536954	0.645128	-1.616606
H	6.378401	-0.732878	-0.906674
H	3.840399	-0.505770	-4.214794
H	2.294631	-1.081852	-3.596653
H	2.960567	0.466828	-3.037571
H	5.236812	-2.939322	-3.673265
H	5.326998	-3.724944	-2.100224
H	3.797962	-3.690186	-2.989874
H	6.123358	-3.684432	1.464174
H	6.308831	-3.070633	-0.177515
H	6.110897	-1.944663	1.172255
H	3.670604	-3.365857	3.055523
H	3.477170	-1.641471	2.733683
H	2.144200	-2.744377	2.418012
H	3.626299	-4.911834	-0.923627
H	3.819417	-5.428974	0.751552
H	2.272769	-4.788874	0.209801
H	-4.170190	2.147860	3.432660
H	-2.656786	1.238005	3.411543
H	-3.120671	2.244271	2.020611
H	-6.521189	1.482489	1.666379
H	-5.505982	1.474077	0.227255
H	-6.508629	0.067365	0.615054
H	-5.818057	0.008775	4.151686
H	-5.931274	-1.544504	3.331900
H	-4.469628	-1.126548	4.242034
H	-3.598567	-4.640737	2.633220
H	-2.755738	-3.205530	3.222118
H	-4.491765	-3.388989	3.495456
H	-3.292796	-4.683944	-0.204674
H	-2.946567	-3.224478	-1.143631
H	-1.884971	-3.693323	0.187101
H	-6.095974	-3.966118	0.726236
H	-6.467226	-2.325385	1.247994
H	-5.958830	-2.632475	-0.417140

Isomer of 5b'

E(M06-2X/6-31G*)= -7132.401979
E(M06-2X/6-311+G**//M06-2X/6-31G*)= -7133,2656459
E(ωB97XD/6-311+G**//M06-2X/6-31G*)= -7133,6355851
E(B3LYP/6-311+G**//M06-2X/6-31G*)= -7134,333927

C	2.785327	1.309703	-0.042468
C	1.661054	1.228218	-0.800870
S	1.290817	2.776796	-1.530463
C	2.665254	3.541460	-0.756674
N	3.311381	2.598038	0.004639
P	0.480313	-0.131489	-1.021867
C	1.575439	-1.533242	-0.595374

C	2.742122	-1.450470	0.088387
S	3.506715	-3.017909	0.186860
C	2.203699	-3.786072	-0.711003
N	1.277684	-2.831309	-1.026422
P	3.559485	-0.054627	0.934895
N	5.155777	-0.145244	0.326572
Si	6.457942	-0.298814	1.546460
C	7.822486	0.936020	1.157724
S	2.150056	-5.388327	-1.102439
C	0.080944	-3.225577	-1.764432
S	3.084450	5.129370	-0.918751
C	4.435169	3.014605	0.838849
P	-0.489345	0.030141	1.025006
C	-1.666667	-1.322163	0.771446
C	-2.825066	-1.375292	0.065182
N	-3.380943	-2.650517	0.032072
C	-2.716979	-3.618075	0.747567
S	-1.293173	-2.887142	1.460491
P	-3.615122	-0.005592	-0.881661
N	-5.202593	0.116945	-0.252218
Si	-5.627181	0.190939	1.491099
C	-4.409592	-0.717817	2.596017
C	-4.608592	-2.972116	-0.688431
S	-3.140764	-5.203993	0.933592
C	-1.581064	1.442321	0.618733
N	-1.202392	2.747351	0.951228
C	-2.055601	3.735671	0.540531
S	-3.389864	2.988775	-0.324083
C	-2.750716	1.381920	-0.066667
C	-0.015081	3.118958	1.715886
S	-1.898495	5.355056	0.813689
Si	-6.489976	0.391792	-1.468625
C	-5.727426	0.862646	-3.119089
C	-7.535860	-1.148967	-1.734727
C	-7.564906	1.835747	-0.927035
Si	5.585292	-0.091526	-1.417798
C	4.215815	-0.661572	-2.572692
C	6.035021	1.664181	-1.923096
C	7.040585	-1.240703	-1.728030
C	5.796289	0.091428	3.262841
C	7.129550	-2.050685	1.611728
C	-5.717930	1.958076	2.122923
C	-7.289675	-0.662145	1.730646
H	4.153378	3.933220	1.356730
H	4.660622	2.230192	1.558478
H	5.311262	3.218409	0.218479
H	0.358562	-3.529909	-2.776744
H	-0.379724	-4.077510	-1.258053
H	-0.615321	-2.387310	-1.803101
H	-4.638228	-2.398514	-1.617219
H	-4.596992	-4.039437	-0.906609
H	-5.486477	-2.729137	-0.082524

H	-0.317764	3.517440	2.687730
H	0.620258	2.243569	1.852696
H	0.522582	3.901471	1.174261
H	-6.230183	1.964481	3.092363
H	-4.716572	2.373293	2.275583
H	-6.256974	2.632161	1.452438
H	-4.816487	-0.659241	3.613120

4b’

E(M06-2X/6-31G*)= -4370.627655
E(M06-2X/6-311+G**//M06-2X/6-31G*)= -4371.2042577
E(ωB97XD/6-311+G**//M06-2X/6-31G*)= -4371.4367523
E(B3LYP/6-311+G**//M06-2X/6-31G*)= -4371.9591962

C	-1.010369	1.774133	2.717365
C	-1.854568	1.003955	1.903029
C	-1.952514	-0.374411	2.149892
C	-1.243474	-0.957289	3.195396
C	-0.413475	-0.177004	3.999718
C	-0.293816	1.188286	3.757702
P	-2.660909	1.914911	0.533507
C	-4.276799	1.085470	0.231460
C	-4.932883	0.269434	1.158268
C	-6.184093	-0.270851	0.862379
C	-6.801685	0.005659	-0.353158
C	-6.174100	0.851681	-1.266823
C	-4.929056	1.393740	-0.972420
P	-1.562398	1.119798	-1.287311
C	0.048938	1.861591	-0.897090
S	0.281430	3.536584	-1.354947
C	1.844254	3.607632	-0.573814
N	2.111198	2.377949	-0.036184
C	1.128546	1.400327	-0.211865
C	3.337168	2.199696	0.734937
H	3.256813	2.744618	1.679754
S	2.812676	4.947833	-0.507228
P	1.269554	-0.225099	0.648287
C	-0.091201	-1.069290	-0.217447
S	-0.163363	-2.805057	-0.034717
C	-1.737262	-2.892021	-0.806666
N	-2.094036	-1.633244	-1.196049
C	-1.192074	-0.612188	-0.861007
C	-3.360390	-1.434635	-1.896278
H	-3.467215	-2.223794	-2.641835
S	-2.600190	-4.288293	-1.020833
N	2.649869	-0.998138	-0.023939
Si	3.742834	-1.792430	1.144436
C	5.506133	-1.190046	0.871195
C	3.658834	-3.663567	1.007265
C	3.237751	-1.333174	2.897026
Si	3.065022	-0.964764	-1.764439
C	4.145498	0.534181	-2.119479
C	3.983680	-2.542415	-2.219047

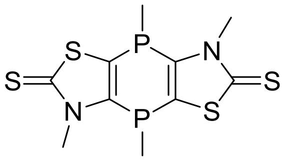
C	1.567080	-0.888600	-2.894879
H	-3.352744	-0.458066	-2.378668
H	-4.195699	-1.494764	-1.191319
H	3.497524	1.139236	0.912866
H	4.173287	2.610769	0.165966
H	3.346829	-3.418168	-2.054935
H	4.924687	-2.697470	-1.684342
H	4.219459	-2.502131	-3.288900
H	0.981854	0.026774	-2.774172
H	0.902304	-1.748980	-2.770889
H	1.946441	-0.905846	-3.924119
H	5.003475	0.594899	-1.441800
H	3.578924	1.468884	-2.036441
H	4.533105	0.478680	-3.143039
H	4.126041	-4.053737	0.100090
H	2.618974	-4.007392	1.024977
H	4.171139	-4.112973	1.865865

Isomer of 4b’

E(M06-2X/6-31G*)= -4370.624335
E(M06-2X/6-311+G**//M06-2X/6-31G*)= -4371.2001984
E(ωB97XD/6-311+G**//M06-2X/6-31G*)= -4371.4367523
E(B3LYP/6-311+G**//M06-2X/6-31G*)= -4371.957879

C	-0.673372	-1.062146	-0.778318
C	0.399846	-1.211592	0.033699
S	0.877164	-2.890844	0.114840
C	-0.432364	-3.382464	-0.947339
N	-1.112444	-2.266458	-1.335944
P	1.326576	-0.001784	1.043847
N	2.947099	-0.324659	0.581930
Si	3.562447	-0.371872	-1.106518
C	2.229528	-0.511099	-2.425090
S	-0.758139	-4.946886	-1.380418
C	-2.264082	-2.411459	-2.220114
H	-1.957394	-2.971357	-3.105658
P	-1.565209	0.513090	-1.091179
C	-0.159805	1.633799	-0.792466
S	-0.054172	3.157606	-1.649636
C	1.422912	3.605698	-0.822252
N	1.741262	2.602653	0.056825
C	0.902915	1.490351	0.038720
S	2.263210	5.007723	-1.076840
C	2.813039	2.801742	1.029947
H	2.824349	3.858226	1.300156
P	-2.491602	0.500306	0.975931
C	-3.789772	1.794147	0.818191
C	-4.949980	1.692797	1.598368
C	-5.896713	2.711289	1.593284
C	-5.695972	3.851627	0.817785
C	-4.541249	3.968063	0.050738

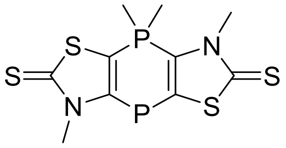
C	-3.593468	2.947552	0.053390
C	-3.459105	-1.052953	0.731909
C	-2.897102	-2.234150	1.234161
C	-3.529423	-3.459987	1.041585
C	-4.748799	-3.513354	0.368975
C	-5.320443	-2.343122	-0.128651
C	-4.673915	-1.121192	0.037681
Si	4.047686	-0.772592	1.918610
C	3.412449	-0.127665	3.567026
C	5.739089	0.000822	1.634516
C	4.174694	-2.639832	2.077783
C	4.544419	1.182259	-1.512521
C	4.653304	-1.891344	-1.316578
H	-2.625888	-1.424094	-2.502265
H	-3.047319	-2.970512	-1.701575
H	2.605554	2.192145	1.908971
H	3.782170	2.529135	0.607430
H	4.065935	-2.802995	-1.161311
H	5.523424	-1.928806	-0.655512
H	5.024592	-1.910114	-2.347853
H	1.503229	0.305672	-2.412243
H	1.691960	-1.463303	-2.393488
H	2.758284	-0.463443	-3.385545
H	5.329435	1.408658	-0.785165
H	3.896824	2.062445	-1.605285
H	5.031048	1.039462	-2.484771
H	4.546063	-3.126778	1.172664
H	3.192441	-3.068333	2.307873
H	4.847919	-2.900598	2.902548



E(M06-2X/6-311+G**)= -2773.146401

C	0.109638	0.219881	0.053835
C	0.127426	-0.020686	1.384948
N	1.416926	-0.001182	1.927623
C	2.430981	0.273663	1.053215
S	1.736536	0.502297	-0.535338
P	-1.290148	-0.351049	2.499781
C	-2.640762	-0.220006	1.290501
S	-4.267693	-0.501879	1.879777
C	-4.962177	-0.272832	0.291290
N	-3.948084	0.001657	-0.583175
C	-2.658520	0.020612	-0.040612
P	-1.240922	0.350625	-1.155496
C	-4.265484	0.231854	-1.989336
S	-6.572241	-0.386248	-0.058222
C	1.734131	-0.231696	3.333779
S	4.040982	0.387907	1.402799

H	-5.113940	0.912386	-2.045946
H	-3.406861	0.676029	-2.488928
H	-4.547028	-0.707946	-2.468280
H	2.584315	-0.910056	3.390188
H	2.012949	0.708389	3.813795
H	0.876343	-0.678507	3.832475
C	-1.111472	-1.325525	-1.948167
H	-1.943083	-1.462197	-2.641842
H	-0.182584	-1.366421	-2.519617
H	-1.118637	-2.119317	-1.201168
C	-1.419391	1.324789	3.293072
H	-2.348093	1.365498	3.864834
H	-0.587556	1.461040	3.986568
H	-1.412363	2.118919	2.546434



E(M06-2X/6-311+G**)= -2773.123007

C	0.076592	-0.038738	-0.012768
C	0.033623	0.031223	1.368732
N	1.323757	-0.008516	1.906103
C	2.370637	-0.091843	1.029485
S	1.736087	-0.136520	-0.602063
P	-1.347772	0.144656	2.483303
C	-2.636054	0.070025	1.260546
S	-4.286132	0.063930	1.866065
C	-4.996301	-0.037470	0.268193
N	-3.995234	-0.032824	-0.650535
C	-2.684975	0.003396	-0.116489
P	-1.245711	0.095827	-1.125080
C	-4.282989	-0.215059	-2.064048
S	-6.626706	-0.135432	-0.001481
C	1.535455	0.033274	3.349514
S	3.985350	-0.155317	1.360273
H	-5.322660	0.058229	-2.230026
H	-3.646225	0.434214	-2.664848
H	-4.141231	-1.259273	-2.355526
H	2.604486	-0.012778	3.535750
H	1.123660	0.960892	3.750496
H	1.034331	-0.817441	3.813956
C	-1.126342	-1.216619	-2.383940
H	-1.829120	-1.054274	-3.200496
H	-0.109964	-1.207861	-2.785516
H	-1.312807	-2.179065	-1.907885
C	-1.122936	1.642116	-2.090894
H	-1.875590	1.694032	-2.878387
H	-1.241568	2.481885	-1.406154
H	-0.129443	1.685532	-2.544202

2$^{2+\prime}$

G(M06-2X/6-311+G**)= -2692.534272
E(M06-2X/6-311+G**)= -2692.619918

C	-0.002332	0.000000	0.000309
C	-0.000931	0.000000	1.465097
N	1.222645	0.000000	1.975325
C	2.294914	0.000000	1.031478
S	1.621571	0.000000	-0.589024
P	-1.396251	0.000000	2.623261
C	-2.685961	0.000000	1.492483
S	-4.309863	0.000000	2.081816
C	-4.983207	0.000000	0.461313
N	-3.910938	0.000000	-0.482533
C	-2.687362	0.000000	0.027695
P	-1.292042	0.000000	-1.130469
C	-4.185777	0.000000	-1.937040
S	-6.555353	0.000000	0.132110
C	1.497482	0.000000	3.429832
S	3.867061	0.000000	1.360681
H	-5.261800	0.000000	-2.080471
H	-3.754206	0.898424	-2.379398
H	-3.754206	-0.898424	-2.379398
H	2.573506	0.000000	3.573264
H	1.065911	0.898424	3.872189
H	1.065911	-0.898424	3.872189

PCM:THF
G(M06-2X/6-311+G**)= -2692.743413
E(M06-2X/6-311+G**)= -2692.831011

S	-0.057532	0.000000	-0.010593
C	-0.068523	0.000000	1.724118
C	1.301487	-0.000000	2.224696
N	2.201273	-0.000000	1.260069
C	1.684750	-0.000000	-0.074639
P	-1.560049	0.000000	2.543510
C	-0.941086	0.000000	4.261604
N	-1.840872	0.000000	5.226231
C	-1.324349	0.000000	6.560939
S	0.417934	-0.000000	6.496892
C	0.428924	-0.000000	4.762182
C	-3.298320	0.000000	4.981122
P	1.920450	-0.000000	3.942790
S	-2.195476	0.000000	7.912904
C	3.658721	-0.000000	1.505178
S	2.555877	-0.000000	-1.426604
H	4.161594	-0.000000	0.544728
H	3.919806	0.898807	2.062120
H	3.919806	-0.898807	2.062120
H	-3.801192	0.000000	5.941573
H	-3.559405	0.898807	4.424181
H	-3.559405	-0.898807	4.424181

2$^{\cdot+\prime}$

G(M06-2X/6-311+G**)= -2692.965298
E(M06-2X/6-311+G**)= -2693.0531926

S	2.749530	-1.695793	-0.000154
C	1.220851	-0.878258	0.000007
C	1.427644	0.534279	0.000224
N	2.756304	0.861346	0.000247
C	3.646467	-0.195001	-0.000068
P	-0.229096	-1.831572	0.000115
C	-1.427635	-0.534282	0.000219
N	-2.756295	-0.861350	0.000238
C	-3.646457	0.194997	-0.000069
S	-2.749537	1.695791	-0.000142
C	-1.220858	0.878256	-0.000006
C	-3.208500	-2.257337	0.000367
P	0.229078	1.831585	0.000102
S	-5.280983	0.130056	-0.000332
C	3.208509	2.257334	0.000369
S	5.280992	-0.130061	-0.000330
H	4.294128	2.264974	0.000796
H	2.833611	2.756520	-0.894256
H	2.832906	2.756513	0.894691
H	-4.294119	-2.264977	0.000790
H	-2.833598	-2.756529	-0.894253
H	-2.832885	-2.756516	0.894686

PCM:THF
G(M06-2X/6-311+G**)= -2693.023009
E(M06-2X/6-311+G**)= -2693.111969

S	-0.021815	0.000000	0.018590
C	-0.023989	0.000000	1.754445
C	1.319656	-0.000000	2.236505
N	2.233757	-0.000000	1.219465
C	1.719300	-0.000000	-0.057727
P	-1.544802	0.000000	2.581795
C	-0.959255	0.000000	4.249795
N	-1.873356	0.000000	5.266835
C	-1.358899	0.000000	6.544027
S	0.382217	-0.000000	6.467711
C	0.384391	-0.000000	4.731855
C	-3.318299	0.000000	5.007549
P	1.905203	-0.000000	3.904506
S	-2.190771	0.000000	7.959776
C	3.678701	-0.000000	1.478751
S	2.551172	-0.000000	-1.473476
H	4.196519	-0.000000	0.525500
H	3.940424	0.895093	2.043405
H	3.940424	-0.895093	2.043405
H	-3.836118	0.000000	5.960800
H	-3.580023	0.895093	4.442895

H	-3.580023	-0.895093	4.442895

2$^{\cdot-}$’

G(M06-2X/6-311+G**)= -2693.335063
E(M06-2X/6-311+G**)= -2693.0531926

N	2.810726	-0.837907	-0.000134
C	1.436989	-0.510745	-0.000264
C	1.229952	0.850825	-0.000263
S	2.782722	1.678971	0.000105
C	3.686213	0.193724	0.000111
P	0.246871	-1.850506	-0.000465
C	-1.229952	-0.850825	-0.000259
C	-1.436990	0.510745	-0.000266
N	-2.810725	0.837907	-0.000131
C	-3.686213	-0.193724	0.000133
S	-2.782722	-1.678971	0.000091
P	-0.246871	1.850506	-0.000469
S	-5.362079	-0.129287	0.000489
C	-3.247678	2.225329	0.000091
S	5.362078	0.129287	0.000484
C	3.247678	-2.225329	0.000100
H	-4.334138	2.237485	-0.000309
H	-2.861030	2.727542	0.889190
H	-2.860380	2.727994	-0.888469
H	4.334138	-2.237484	-0.000302
H	2.861032	-2.727534	0.889203
H	2.860379	-2.728001	-0.888456

PCM:THF
G(M06-2X/6-311+G**) = -2693.390109
E(M06-2X/6-311+G**)= -2693.476565

S	0.025410	0.000000	0.000370
C	0.018096	0.000000	1.757971
C	1.316042	-0.000000	2.220952
N	2.256568	-0.000000	1.168795
C	1.758810	-0.000000	-0.084532
P	-1.565338	0.000000	2.579868
C	-0.955641	0.000000	4.265348
N	-1.896167	0.000000	5.317505
C	-1.398409	0.000000	6.570832
S	0.334991	-0.000000	6.485930
C	0.342306	-0.000000	4.728329
C	-3.328809	0.000000	5.041486
P	1.925740	-0.000000	3.906432
S	-2.243355	0.000000	8.027241
C	3.689210	-0.000000	1.444814
S	2.603756	-0.000000	-1.540941
H	4.220840	-0.000000	0.498273
H	3.947833	0.890735	2.019368
H	3.947833	-0.890735	2.019368
H	-3.860439	0.000000	5.988027

H	-3.587432	0.890735	4.466932
H	-3.587432	-0.890735	4.466932

2$^{2-\prime}$

G(M06-2X/6-311+G**)= -2693.273998
E(M06-2X/6-311+G**)=-2693.361133

C	-0.047765	-0.332381	0.003430
C	-0.064412	-0.363831	1.369420
S	1.540786	0.032695	1.977686
C	2.233683	0.126675	0.393873
N	1.244495	-0.034742	-0.504853
P	-1.447099	-0.736092	2.495992
C	-2.712746	0.066209	1.437426
C	-2.694378	0.108082	0.071737
S	-4.081354	1.032894	-0.498264
C	-4.722041	1.255097	1.094705
N	-3.845553	0.734093	1.973668
P	-1.494164	-0.624564	-1.086832
C	-4.100215	0.784017	3.402069
S	-6.216704	1.991021	1.458628
S	3.888859	0.362658	0.058095
C	1.514973	0.011102	-1.930480
H	2.258825	0.782740	-2.123364
H	1.914647	-0.948718	-2.269892
H	0.573485	0.225890	-2.436631
H	-4.558498	1.741563	3.645026
H	-4.790196	-0.014034	3.690577
H	-3.144383	0.656083	3.910735

PCM:THF
G(M06-2X/6-311+G**)= -2693.476203
E(M06-2X/6-311+G**)= -2693.563746

N	-0.013026	0.001001	0.004816
C	-0.008880	-0.023212	1.422073
C	1.256703	-0.019477	1.934055
S	2.419155	0.065741	0.617357
C	1.188361	-0.006618	-0.597737
P	-1.540989	-0.031981	2.431177
C	-0.840593	0.986546	3.771587
C	0.422697	0.975405	4.289097
N	0.572846	1.898198	5.354521
C	-0.521991	2.596926	5.700312
S	-1.803037	2.198644	4.606313
P	1.790289	-0.082930	3.676442
S	-0.666425	3.684498	6.999812
C	1.813530	2.035548	6.106558
S	1.487396	-0.091399	-2.269791
C	-1.240645	-0.051596	-0.778708
H	1.996788	3.090232	6.303743
H	1.734493	1.507933	7.059329

H	2.618633	1.614034	5.508334
H	-1.155929	0.631853	-1.621646
H	-1.398819	-1.062588	-1.159854
H	-2.065689	0.240573	-0.132430

planar structure of **2**$^{2-\prime}$

G(M06-2X/6-311+G**)= -2693.252122
E(M06-2X/6-311+G**)= -2693.341052

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.400860
N	1.291111	0.000000	1.929841
C	2.323538	0.000000	1.031107
S	1.654266	-0.000000	-0.589993
P	-1.376033	0.000000	2.485729
C	-2.680326	0.000000	1.339627
S	-4.334507	0.000000	1.929720
C	-5.003886	0.000000	0.308679
N	-3.971649	0.000000	-0.590217
C	-2.680542	0.000000	-0.061313
P	-1.304385	0.000000	-1.146187
C	-4.199567	0.000000	-2.029577
S	-6.620729	0.000000	0.005286
C	1.518867	0.000000	3.369243
S	3.940308	0.000000	1.334863
H	-5.272418	0.000000	-2.200782
H	-3.752082	0.891652	-2.473268
H	-3.752082	-0.891652	-2.473268
H	2.591690	0.000000	3.540605
H	1.071332	0.891646	3.812899
H	1.071332	-0.891646	3.812899

PCM:THF
G(M06-2X/6-311+G**)= -2693.469896
E(M06-2X/6-311+G**)= -2693.557210

S	0.047173	0.000000	-0.006679
C	0.034494	0.000000	1.746941
C	1.319884	-0.000000	2.205737
N	2.263012	-0.000000	1.148835
C	1.772644	-0.000000	-0.102269
P	-1.604686	0.000000	2.562022
C	-0.959483	0.000000	4.280563
N	-1.902611	0.000000	5.337466
C	-1.412243	0.000000	6.588569
S	0.313228	-0.000000	6.492980
C	0.325907	-0.000000	4.739359
C	-3.332851	0.000000	5.056696
P	1.965088	-0.000000	3.924278
S	-2.271675	0.000000	8.059580
C	3.693253	-0.000000	1.429604
S	2.632076	-0.000000	-1.573280

H	4.231834	-0.000000	0.486863
H	3.945560	0.888723	2.010089
H	3.945560	-0.888723	2.010089
H	-3.871433	0.000000	5.999437
H	-3.585159	0.888723	4.476211
H	-3.585159	-0.888723	4.476211

IV$^{2+\prime}$

G(M06-2X/6-311+G**)= -2085.454192
E(M06-2X/6-311+G**)= -2085.627522

N	-0.007041	0.000522	0.046517
C	-0.012775	0.001147	1.381984
C	1.407106	0.001171	1.802149
N	2.129031	0.000616	0.678633
C	1.305569	0.000448	-0.463946
P	-1.516908	0.001505	2.294985
C	-0.751808	0.001971	3.879505
N	-1.473733	0.002275	5.003022
C	-0.650271	0.002506	6.145601
N	0.662339	0.002026	5.635137
C	0.668073	0.001865	4.299670
C	-2.941403	0.002214	5.048987
P	2.172206	0.001432	3.386669
C	1.868656	0.001856	6.472372
S	-1.106611	0.002598	7.687656
C	3.596701	0.000144	0.632667
S	1.761909	-0.000552	-2.006002
C	-1.213358	0.000044	-0.790717
H	1.563610	0.001832	7.515114
H	2.451267	0.898835	6.257034
H	2.451088	-0.895218	6.256947
H	3.967947	-0.897117	1.130141
H	3.908211	0.000312	-0.408161
H	3.968478	0.896937	1.130582
H	-0.908312	-0.000383	-1.833459
H	-1.795812	-0.896935	-0.574949
H	-1.795948	0.897119	-0.575721
H	-3.252913	0.003284	6.089816
H	-3.312951	0.898709	4.550367
H	-3.312878	-0.895344	4.552220

PCM:THF
G(M06-2X/6-311+G**) = -2085.651589
E(M06-2X/6-311+G**)= -2085.828919

N	-0.040438	0.002892	0.061462
C	-0.041079	0.001155	1.395864
C	1.380676	-0.001287	1.808722
N	2.094852	-0.000818	0.681521
C	1.265863	0.001930	-0.450365
P	-1.540301	0.001915	2.309278
C	-0.763503	-0.001111	3.883626

C	0.658251	-0.003263	4.296489
N	0.657600	-0.004688	5.630894
C	-0.648703	-0.003772	6.142713
N	-1.477685	-0.001597	5.010822
P	2.157473	-0.004266	3.383074
C	-2.941173	0.000267	5.060099
S	-1.097662	-0.004897	7.688756
C	1.867057	-0.007194	6.456383
C	3.558338	-0.002817	0.632220
S	1.714818	0.003326	-1.996409
C	-1.249908	0.005445	-0.764008
H	-3.311329	-0.894594	4.559575
H	-3.248722	-0.000443	6.100949
H	-3.308965	0.897169	4.561496
H	1.569261	-0.008186	7.500065
H	2.445137	-0.903483	6.230998
H	2.447301	0.888280	6.233318
H	-1.829838	-0.890367	-0.541471
H	-0.952130	0.007190	-1.807695
H	-1.828294	0.901395	-0.538073
H	3.926065	-0.899638	1.131013
H	3.928583	0.892128	1.132529
H	3.865866	-0.002390	-0.408637

IV$^{+\prime}$

G(M06-2X/6-311+G**)= -2085.866813
E(M06-2X/6-311+G**)= -2086.040924

N	-0.001460	-0.000105	0.037757
C	-0.005419	-0.000280	1.400054
C	1.372470	-0.000282	1.805112
N	2.106379	-0.000071	0.657398
C	1.289610	-0.000069	-0.459139
P	-1.491307	-0.000324	2.327282
C	-0.743594	-0.000508	3.911119
C	0.634294	-0.000571	4.316176
N	0.630336	-0.000637	5.678474
C	-0.660734	-0.000752	6.175370
N	-1.477503	-0.000518	5.058833
P	2.120183	-0.000425	3.388949
C	-2.936126	-0.000351	5.096077
S	-1.124087	-0.000703	7.751566
C	1.836754	-0.000556	6.499159
C	3.565002	0.000056	0.620154
S	1.752963	0.000247	-2.035336
C	-1.207878	0.000108	-0.782928
H	3.879044	0.000350	-0.419941
H	3.939785	-0.893812	1.120923
H	3.939647	0.893721	1.121388
H	2.422756	0.893431	6.280930
H	1.537966	-0.000964	7.543737

H	2.423212	-0.894101	6.280360
H	-3.250168	-0.000426	6.136172
H	-3.310747	0.893506	4.595167
H	-3.310934	-0.894027	4.594983
H	-0.909089	-0.000246	-1.827507
H	-1.794389	-0.893417	-0.564192
H	-1.793826	0.894115	-0.564638

PCM:THF
G(M06-2X/6-311+G**) = -2085.922822
E(M06-2X/6-311+G**)= -2086.097185

N	-0.017115	0.002759	0.030898
C	-0.017603	0.001137	1.392643
C	1.362558	-0.001110	1.793425
N	2.091517	-0.000655	0.643222
C	1.270226	0.001725	-0.465395
P	-1.501174	0.001760	2.320641
C	-0.745399	-0.001029	3.898918
C	0.634763	-0.003135	4.299700
N	0.634277	-0.004654	5.661446
C	-0.653064	-0.003786	6.157739
N	-1.474356	-0.001621	5.049124
P	2.118333	-0.003852	3.371702
C	-2.932439	0.000277	5.086434
S	-1.112591	-0.005112	7.740200
C	1.845591	-0.007288	6.473919
C	3.549599	-0.002629	0.605921
S	1.729752	0.002998	-2.047857
C	-1.228430	0.005368	-0.781574
H	-3.305545	-0.892056	4.582881
H	-3.247739	-0.001129	6.125311
H	-3.303168	0.895351	4.585992
H	1.555413	-0.007739	7.520091
H	2.427139	-0.901710	6.248417
H	2.429940	0.885699	6.249992
H	-1.812382	-0.888036	-0.558267
H	-0.938250	0.006681	-1.827746
H	-1.810373	0.899373	-0.555453
H	3.920274	-0.897453	1.106845
H	3.922751	0.889956	1.108996
H	3.864905	-0.001805	-0.432955

IV’

G(M06-2X/6-311+G**)= -2086.132988
E(M06-2X/6-311+G**)= -2086.307531

N	-0.000054	0.002402	0.000188
C	-0.000336	0.000982	1.385584
C	1.351765	-0.000851	1.778217
N	2.093562	-0.000198	0.608150
C	1.279724	0.001734	-0.498092

P	-1.466198	0.001281	2.330799
C	-0.734606	-0.001154	3.914132
C	0.617498	-0.002920	4.306767
N	0.617213	-0.004415	5.692163
C	-0.662563	-0.003800	6.190441
N	-1.476401	-0.001795	5.084201
P	2.083359	-0.003254	3.361554
C	-2.925648	0.000627	5.122817
S	-1.126120	-0.005189	7.786778
C	1.820366	-0.007753	6.501006
C	3.542811	-0.002449	0.569532
S	1.743278	0.002961	-2.094431
C	-1.203208	0.005256	-0.808654
H	-3.310728	-0.889653	4.621100
H	-3.231883	-0.000365	6.166131
H	-3.307685	0.893625	4.623617
H	1.520154	-0.008656	7.546070
H	2.410699	-0.900156	6.282548
H	2.413942	0.883121	6.285103
H	-1.796389	-0.885904	-0.592839
H	-0.902997	0.006381	-1.853719
H	-1.793927	0.897383	-0.590127
H	3.924949	-0.895298	1.068917
H	3.927794	0.887990	1.071039
H	3.849039	-0.001649	-0.473786

PCM:THF
G(M06-2X/6-311+G**) = -2086.147203
E(M06-2X/6-311+G**)= -2086.319841

N	0.000218	-0.000095	0.002400
C	-0.001201	-0.000178	1.388765
C	1.350766	0.000008	1.781362
N	2.092125	0.002155	0.609878
C	1.276280	0.001815	-0.486267
P	-1.469080	0.001457	2.329938
C	-0.733606	-0.002436	3.910940
C	0.618369	-0.002021	4.303533
N	0.616954	-0.001918	5.689899
C	-0.659105	-0.003997	6.178571
N	-1.474960	-0.004711	5.082434
P	2.086249	-0.003751	3.362349
C	-2.927291	-0.002324	5.115227
S	-1.126899	-0.005351	7.789502
C	1.825832	-0.004784	6.495477
C	3.544454	-0.000154	0.577169
S	1.744083	0.003442	-2.097194
C	-1.208681	0.003165	-0.803139
H	-3.306165	-0.871961	4.576092
H	-3.243076	-0.046206	6.153533
H	-3.305222	0.910665	4.652018
H	1.536359	0.037798	7.541478
H	2.393435	-0.917341	6.305710

H	2.434209	0.865373	6.244108
H	-1.816234	-0.868100	-0.553598
H	-0.919188	-0.036922	-1.849232
H	-1.777145	0.914768	-0.611393
H	3.922297	-0.911484	1.043692
H	3.923343	0.871390	1.113231
H	3.860290	0.039981	-0.461273

IV^{-}’

G(M06-2X/6-311+G**)= -2085.922822
E(M06-2X/6-311+G**)= -2086.376252

C	0.000069	0.008804	0.001063
C	0.000080	0.008776	1.386127
N	1.343667	0.000033	1.773790
C	2.171433	-0.005480	0.693577
N	1.343648	-0.000107	-0.386622
P	-1.317948	0.017579	2.590659
C	-2.635999	0.026180	1.386149
C	-2.636011	0.026167	0.001086
N	-3.979597	0.035122	-0.386577
C	-4.807363	0.040544	0.693636
N	-3.979579	0.034993	1.773835
P	-1.317981	0.017593	-1.203446
C	-4.415255	0.037634	3.152391
S	-6.502757	0.051744	0.693649
C	-4.415295	0.037939	-1.765126
C	1.779364	-0.002872	3.152339
S	3.866827	-0.016626	0.693562
C	1.779322	-0.003205	-1.765178
H	1.390252	-0.888766	3.659715
H	2.866983	-0.010547	3.161171
H	1.402854	0.888551	3.659552
H	2.866941	-0.010931	-1.774025
H	1.390164	-0.889141	-2.272445
H	1.402842	0.888175	-2.272487
H	-4.037819	-0.853363	3.659654
H	-5.502881	0.044258	3.161240
H	-4.027047	0.923966	3.659705
H	-5.502921	0.044600	-1.773956
H	-4.037894	-0.853013	-2.272492
H	-4.027069	0.924315	-2.272350

PCM:THF
G(M06-2X/6-311+G**) = -2086.264944
E(M06-2X/6-311+G**)= -2086.436583

N	0.011828	0.002413	-0.011170
C	0.010953	0.000945	1.385438
C	1.342306	-0.000905	1.772048
N	2.089609	-0.000225	0.592196

C	1.279732	0.001716	-0.498124
P	-1.512986	0.001420	2.317211
C	-0.725145	-0.001226	3.920298
C	0.606208	-0.002997	4.306908
N	0.605333	-0.004393	5.703516
C	-0.662571	-0.003869	6.190471
N	-1.472449	-0.001934	5.100151
P	2.130147	-0.003460	3.375136
C	-2.922503	0.000422	5.129933
S	-1.137304	-0.005201	7.825279
C	1.813899	-0.007481	6.505331
C	3.539663	-0.002506	0.562415
S	1.754464	0.003030	-2.132933
C	-1.196738	0.005325	-0.812984
H	-3.302353	-0.888669	4.623179
H	-3.242438	0.000236	6.168383
H	-3.299340	0.891462	4.624357
H	1.527866	-0.009182	7.553624
H	2.403345	-0.897860	6.278737
H	2.405667	0.882269	6.282339
H	-1.788121	-0.884789	-0.590413
H	-0.910705	0.007647	-1.861276
H	-1.786570	0.895339	-0.585970
H	3.916532	-0.893368	1.068280
H	3.919481	0.886764	1.068882
H	3.859599	-0.002641	-0.476034

Planar **IV**$^{2-\prime}$

G(M06-2X/6-311+G**)= -2086.131613
E(M06-2X/6-311+G**)= -2086.300528

N	0.000496	-0.000018	0.000568
C	0.001181	0.000003	1.402187
C	1.322744	-0.000003	1.779862
N	2.063955	-0.000024	0.590268
C	1.260242	-0.000023	-0.502456
P	-1.571300	-0.000002	2.332333
C	-0.727777	0.000118	3.952931
C	0.593784	0.000115	4.330610
N	0.594472	0.000248	5.732227
C	-0.665276	0.000318	6.235252
N	-1.468987	0.000259	5.142527
P	2.166265	0.000003	3.400463
C	-2.911109	0.000305	5.171572
S	-1.138878	0.000435	7.892471
C	1.803471	0.000145	6.518918
C	3.506076	-0.000010	0.561218
S	1.733847	-0.000034	-2.159678
C	-1.208505	-0.000110	-0.786117
H	1.526139	0.000611	7.571284
H	2.395960	-0.886077	6.275549
H	2.396494	0.885821	6.274875

H	-0.931176	-0.000313	-1.838484
H	-1.801289	-0.885994	-0.542241
H	-1.801230	0.885905	-0.542579
H	-3.285537	0.886064	4.651102
H	-3.285619	-0.885838	4.651812
H	-3.231736	0.000718	6.211566
H	3.880555	0.886126	1.081012
H	3.880539	-0.885774	1.081656
H	3.826701	-0.000376	-0.478777

PCM:THF
G(M06-2X/6-311+G**)= -2086.335911
E(M06-2X/6-311+G**)= -2086.509557

C	0.005648	-0.003171	0.000754
C	0.005647	0.003154	1.373398
N	1.350651	0.006694	1.763191
C	2.173702	-0.000024	0.687079
N	1.350653	-0.006731	-0.389035
P	-1.326579	-0.000954	2.626847
C	-2.658802	-0.003817	1.373392
C	-2.658800	0.003861	0.000754
N	-4.003804	0.007815	-0.389034
C	-4.826855	0.000055	0.687070
N	-4.003806	-0.007730	1.763177
P	-1.326574	0.000956	-1.252697
C	-4.430452	-0.018671	3.147173
S	-6.548129	0.000078	0.687069
C	-4.430447	0.018765	-1.773031
C	1.777293	0.016276	3.147198
S	3.894976	-0.000036	0.687082
C	1.777300	-0.016320	-1.773041
H	-5.516150	0.061636	-1.799498
H	-4.078416	-0.884769	-2.275185
H	-4.007373	0.889778	-2.277523
H	1.425257	0.887701	-2.274310
H	2.863004	-0.059149	-1.799547
H	1.354239	-0.886843	-2.278387
H	2.862998	0.059086	3.173708
H	1.354246	0.886807	3.652543
H	1.425233	-0.887739	3.648467
H	-5.516158	-0.061485	3.173638
H	-4.007425	-0.889710	3.651659
H	-4.078374	0.884840	3.649335

Bended **IV**$^{2-\prime}$

G(M06-2X/6-311+G**)= -2086.131635
E(M06-2X/6-311+G**)= -2086.3002762

C	1.327913	-0.686624	0.237092
C	1.327935	0.686669	0.237094
N	2.650208	1.074683	-0.034856

C	3.463934	-0.000006	-0.175862
N	2.650176	-1.074672	-0.034875
P	-0.000008	1.909203	0.524804
C	-1.327933	0.686652	0.237098
C	-1.327932	-0.686642	0.237094
N	-2.650201	-1.074676	-0.034847
C	-3.463941	0.000000	-0.175864
N	-2.650183	1.074664	-0.034867
P	0.000014	-1.909170	0.524803
C	-3.087781	2.447560	-0.105863
S	-5.164155	-0.000004	-0.448321
C	-3.087770	-2.447578	-0.105899
C	3.087818	2.447570	-0.105931
S	5.164152	-0.000030	-0.448305
C	3.087745	-2.447577	-0.105868
H	-4.018963	-2.486358	-0.668707
H	-3.254424	-2.851008	0.897866
H	-2.303136	-3.029284	-0.594332
H	2.303178	-3.029276	-0.594419
H	4.019020	-2.486361	-0.668540
H	3.254249	-2.851012	0.897918
H	4.019010	2.486313	-0.668743
H	2.303200	3.029291	-0.594371
H	3.254488	2.851011	0.897827
H	-4.019057	2.486323	-0.668535
H	-3.254294	2.850993	0.897923
H	-2.303226	3.029273	-0.594415

PCM:THF
G(M06-2X/6-311+G**)= -2086.339540
E(M06-2X/6-311+G**)= -2086.510222

N	-0.017096	0.010583	0.038120
C	0.000692	-0.040701	1.440224
C	1.322264	-0.041438	1.807931
N	2.061694	0.009421	0.616475
C	1.241685	0.005213	-0.461242
P	-1.514833	-0.105547	2.461060
C	-0.695032	0.585392	3.942156
C	0.626538	0.584633	4.309868
N	0.690577	1.243252	5.547189
C	-0.544492	1.612576	5.962068
N	-1.388208	1.244470	4.968817
P	2.092737	-0.107604	3.464768
C	-2.825341	1.425660	4.999844
S	-0.959918	2.356188	7.456714
C	1.905417	1.423073	6.315927
C	3.508722	-0.019896	0.550191
S	1.702624	-0.039796	-2.118049
C	-1.222020	-0.017026	-0.765949
H	3.828929	0.421126	-0.390729
H	3.876541	-1.047326	0.609617
H	3.902843	0.550605	1.391173

H	2.725898	1.610123	5.623191
H	1.776837	2.267656	6.988587
H	2.127185	0.527266	6.901432
H	-3.061771	2.270486	5.642288
H	-3.170080	1.613044	3.982939
H	-3.318438	0.530336	5.386732
H	-1.009693	0.423808	-1.736983
H	-1.569062	-1.043991	-0.905136
H	-1.993082	0.554445	-0.249281

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