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Electronic Supporting Information

Elimination reactions in 1,4-diphosphinine chemistry: The quest for mixed-valence intermediates

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Content

1 Experimental methods

If not specified, all reactions were performed in a dried and deoxygenated argon atmosphere using Schlenk or glovebox techniques. The used argon (>99.998%) was purified by a system of three columns (deoxygenation by a BTS copper catalyst (BASF PuriStar® R3-155) at ca. 100 °C, drying with silica gel, phosphorus pentoxide desiccant with indicator (Sicapent®) and calcium chloride). Glassware, spatulas, cannulas and filter papers were dried in a compartment drier at 110 °C for at least 1 h. Additionally, glassware was heated with a heat gun (up to 550 °C) under active vacuum (10^{-2} mbar) and kept under vacuum for 5–10 min. Sterile syringes were purged with argon three times before use. The used solvents were dried using standard procedures[1] by refluxing over proper desiccants (*n*-pentane, petroleum ether 40/65 and toluene over sodium wire (Ø = 2 mm); diethyl ether stabilized with 3,5-di-tert-butyl-4-hydroxytoluene (BHT) and tetrahydrofuran over benzophenone and sodium wire; dichloromethane over calcium hydride) in an argon atmosphere for several days and distilled before use. Alternatively, diethyl ether and toluene were dried using a Mbraun SPS-800 solvent purification system. For filtration Schlenk frits or stainless steel cannulas (Ø = 1–2 mm) with Whatman® glass microfiber filters (grade GF/B) were used. After use, stainless steel cannulas were cleaned with diluted hydrochloric acid, water and acetone, while glassware was stored in a concentrated solution of potassium hydroxide in *i*-propanol for at least 2 d (only overnight for glass frits) and in diluted hydrochloric acid for at least several hours. Afterwards, the glassware was washed with demineralised water and acetone. All glass joints were greased with either OKS 1112 grease of PTFE paste (Carl Roth).

NMR spectra were recorded on a Bruker Avance I 300 MHz, Bruker Avance I 400 MHz, Bruker Avance I 500 Mhz, Bruker Avance III HD Ascend 500 MHz or a Bruker Avance III HD Ascend 700 MHz spectrometer at the NMR department of the University of Bonn and subsequently analysed using the program Mestrenova 14.2 by *Mestrelab Research S.L*. Obtained ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated using the residual proton/carbon signal of the used deuterated solvents relative to tetramethylsilane[2] (residual peaks given in ppm, C_6D_6: $\delta(^{1}H) = 7.160$, $\delta(^{13}C) = 128.060$, $CDCl_3$: $\delta(^{1}H) = 7.260$, $\delta(^{13}C) = 77.160$, CD_2Cl_2: $\delta(^{1}H) = 5.320$, $\delta(^{13}C) = 53.840$, THF-d8: $\delta(^{1}H) = 1.730/3.580$, $\delta(^{13}C) = 25.370/67.570$, toluene-d8: $\delta(^{1}H) = 2.090$, $\delta(^{13}C) = 20.400$). For heteronuclear NMR spectra the IUPAC recommended method was used, which specifies the chemical shift δ of a compound as

$$\delta = 10^{6} \cdot \frac{\Xi_{\text{sample}} - \Xi_{\text{reference}}}{\Xi_{\text{reference}}}$$

in which Ξ_{sample} denotes the frequency of the respective nucleus relative to the frequency of ^{1}H. Deuterated solvents were stored over 10w% molecular sieve (3 Å) for at least 2 d before use. All chemical shifts δ are given in parts per million (ppm) and scalar coupling constants $^{n}J_{X,Y}$ in Hertz (Hz), with n being the number of covalent bonds between the nuclei X and Y. The multiplicity of a given signal is described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, m = multiplet and combinations of these. Broad signals were denotet with “br.”. In ^{1}H NMR data, the number of nuclei in a respective signal is given according to integration. Complex NMR spectra were analysed by a combination of 1D and 2D NMR experiments (*i.e.*, COSY, HSQC, HMBC). All NMR measurements were carried out at 298 K if not stated otherwise.

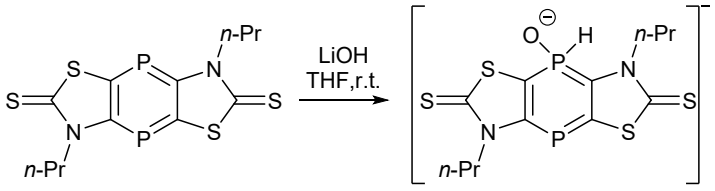
All samples were measured by the analytical department of the University of Bonn. Electron impact ionisation (EI) experiments were performed on a Thermo Finnigan MAT 95 XL sector field instrument using an ionisation energy of 70 eV, calibration and referencing were done using perfluorokerosene (PKF). Electrospray injection (ESI) and atomospheric pressure chemical ionisation (APCI) measurements were done on a Thermo Fisher Scientific Orbitrap XL spectrometer using acetonitrile

or dichloromethane as solvents. Air sensitive samples were submitted in sealed glass vials after preparation in a glovebox and only opened shortly before measuring. For all samples, selected data is given, reducing isotopic patterns to the mass-to-charge ratio (m/z) of the isotopomer with the highest relative abundance, which is given in parentheses. As high-resolution mass spectra (HRMS) using ESI or APCI were recorded in a single measurement, no standard deviations were obtained.

ATR-IR spectra of solids were recorded inside a glovebox at ambient temperature in a spectral range from 400–4000 cm^{-1} using a Bruker Alpha FTIR spectrometer with a single-reflection ATR unit (Platinum-ATR Diamond) or a Shimadzu IRSpirit FTIR spectrometer with a single-reflection ATR unit (QATR-S). Apodisation was done using the Happ-Genzel function. The data sets were analysed with the software *EZ Omnic 7.3* from *Fisher Scientific* and *LabSolutions IR 2.26* from *Shimadzu*. Peak intensities are given as very strong (vs), strong (s), medium (m) or weak (w). Only selected peaks at wave numbers >1500 cm^{-1} are given.

2 Experimental procedures and characterisation

2.1 1,1-addition product 3



1 **3** $[Li(THF)_4]^+$

In a 10 mL Schlenk tube, 2 mL of THF were added to a mixture of 42.0 mg (0.112 mmol, 1.00 eq.) of **1** and 3.0 mg (0.125 mmol, 1.12 eq.) of LiOH at ambient temperature. The mixture was stirred for 21 h before removing solvent *in vacuo* (10^{-2} mbar). The residue was extracted twice with 0.5 mL of toluene each, before washing with 2 mL of *n*-pentane.

Molecular formula: $LiC_{12}H_{15}N_2OP_2S_4$

Molecular weight: 400.39 g/mol

Yield: —

MS (neg. ESI, selected data): m/z (%): 424.945 (100) $[M+2O]^{-\bullet}$.

IR (ATR Diamond, selected data): $\tilde{\nu}$ / cm^{-1} = 2439 (w, PH), 2871 (m, CH), 2961 (m, CH).

^{1}H NMR (500.1 MHz, 298.0 K, THF-d8): δ / ppm = 0.97 (t, 3H, $^3J_{H,H}$ = 7.47 Hz, $CH_2CH_2\mathit{CH_3}$), 1.00 (t, 3H, $^3J_{H,H}$ = 7.55 Hz, $CH_2CH_2\mathit{CH_3}$), 1.80–1.88 (m, 2H, $CH_2\mathit{CH_2}CH_3$), 1.93–2.02 (m, 2H, $CH_2\mathit{CH_2}CH_3$), 4.01–4.09 (m, 1H, $\mathit{CH_2}CH_2CH_3$), 4.10–4.17 (m ,1H, $\mathit{CH_2}CH_2CH_3$), 4.18–4.26 (m, 1H, $\mathit{CH_2}CH_2CH_3$), 4.60–4.68 (m, 1H, $\mathit{CH_2}CH_2CH_3$), 9.06 (dd, 1H, $^4J_{P,H}$ = 1.50 Hz, $^1J_{P,H}$ = 544.8 Hz, P*H*).

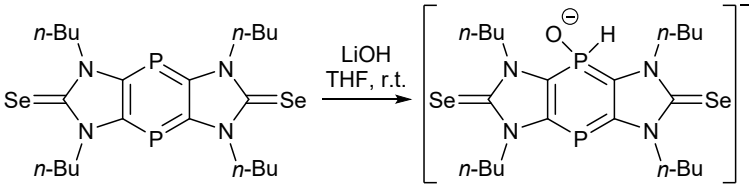
^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, THF-d8): δ / ppm = 11.6 (s, $CH_2CH_2\mathit{CH_3}$), 11.6 (s, $CH_2CH_2\mathit{CH_3}$), 20.5 (d, $^4J_{P,C}$ = 4.66 Hz, $CH_2\mathit{CH_2}CH_3$), 22.5 (s, $CH_2\mathit{CH_2}CH_3$), 50.3 (d, $^3J_{P,C}$ = 2.04 Hz, $\mathit{CH_2}CH_2CH_3$), 50.4 (d, $^3J_{P,C}$ = 21.0 Hz, $\mathit{CH_2}CH_2CH_3$), 95.8 (dd, $^1J_{P,C}$ = 140.3 Hz, $^2J_{P,C}$ = 11.0 Hz, S*C*PH-O$^-$), 122.5 (dd, $^1J_{P,C}$ = 134.3 Hz, $^2J_{P,C}$ = 11.2 Hz, N*C*PH-O$^-$), 153.8 ($^1J_{P,C}$ = 61.9 Hz, $^2J_{P,C}$ = 17.3 Hz, S*C*P), 168.7 ($^1J_{P,C}$ = 58.5 Hz, $^2J_{P,C}$ = 13.4 Hz, N*C*P), 187.3 (dd, $^3J_{P,C}$ = 9.37 Hz, $^3J_{P,C}$ = 5.39 Hz, *C*=S), 190.8 (d, $^3J_{P,C}$ = 7.33 Hz, *C*=S).

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, 298.0 K, THF-d8): δ / ppm = −18.9 (s, PH-O$^-$), −16.0 (s, PR_2).

^{31}P NMR (202.5 MHz, 298.0 K, THF-d8): δ / ppm = −18.9 (d, $^{1}J_{P,H}$ = 544.9 Hz, PH-O$^-$), −16.0 (s, PR_2).

2.2 1,1-Addition product 5

*2.2.1 Without 12-crown-4 (**5a**)*



4 **5a**

In a 20 mL Schlenk tube 84.2 mg (0.146 mmol, 1.0 eq.) of **4** and 3.5 mg (0.146 mmol, 1.0 eq.) anhydrous LiOH were dissolved in 2 mL THF and stirred for 2 days at ambient temperature. Afterwards the solvent was removed *in vacuo* (≤ 0.05 mbar) and the oily, slightly pink residue was washed with four times 2–4 mL *n*-pentane yielding a beige solid that was dried for 2.5 hours *in vacuo* (≤ 0.02 mbar).

Molecular formula: $LiC_{22}H_{37}N_4OP_2Se_2$, 4 C_4H_8O

Molecular weight: 888.82 g/mol, 600.39 g/mol (without THF molecules)

Yield: 54 mg (0.608 mmol, 42 %)

Melting point: 97 °C (decomposition)

MS (neg. ESI, selected data): m/z (%): 627.068 (100) $[M-Li-4(C_4H_8O)+2O]^{-\bullet}$.

HRMS (neg ESI): m/z calculated $[C_{22}H_{37}N_4OP_2Se_2O_2]^-$: 627.0681; found: 627.0682.

IR (ATR Diamond, selected data): ṽ / cm^{-1} = 2334 (w, PH), 2868 (m, CH), 2928 (w, CH), 2955 (w, CH).

^{1}H NMR (500.1 MHz, 298.0 K, THF-d8): δ / ppm = 0.99 (m, 12H, CH_3), 1.45 (m, 8H, CH_2CH$_3$), 1.77 (m, THF), 1.75–1.80 (m, 2H, NCH$_2$CH_2), 1.81–1.89 (m, 4H, NCH$_2$CH_2), 1.90–1.99 (m, 2H, NCH$_2$CH_2), 3.62 (m, THF), 4.07–4.14 (m, 2H, NCH_2), 4.14–4.22 (m, 2H, NCH_2), 4.26–4.35 (m, 2H, NCH_2), 4.66–4.73 (m, 2H, NCH_2), 9.42 (d, 1H, $^{1}J_{P,H}$ = 540.3 Hz, P*H*).

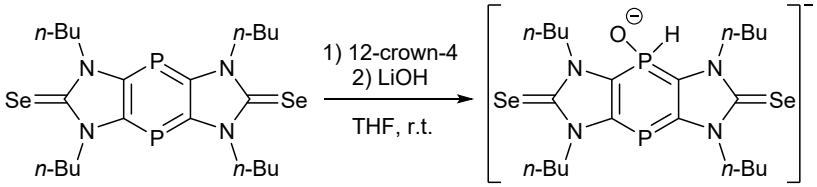
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, 298.0 K, THF-d8): δ / ppm = 14.4 (s, *C*H$_3$), 21.1 (s, *C*H$_2$CH$_3$), 21.1 (s, *C*H$_2$CH$_3$), 26.6 (s, THF), 30.2 (d, $^{4}J_{P,C}$ = 4.1 Hz, NCH$_2$*C*H$_2$), 48.5 (d, $^{3}J_{P,C}$ = 13.8 Hz, N*C*H$_2$), 48.6 (s, N*C*H$_2$), 68.4 (s, THF), 113.5 (dd, $^{1}J_{P,C}$ = 149.2 Hz, $^{2}J_{P,C}$ = 11.1 Hz, *C*PH-O$^-$), 156.2 ($^{1}J_{P,C}$ = 47.0 Hz, $^{2}J_{P,C}$ = 19.4 Hz, *C*P), 162.5 (d_{sat}, $^{3}J_{P,C}$ = 5.9 Hz, $^{1}J_{Se,C}$ = 234 Hz, *C*=Se).

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, 298.0 K, THF-d8): δ / ppm = −26.6 (s, *P*H-O$^-$), −69.0 (s, *P*R$_2$).

^{31}P NMR (202.5 MHz, 298.0 K, THF-d8): δ / ppm = −26.6 (d, $^{1}J_{P,H}$ = 540.3 Hz, *P*H-O$^-$), −69.0 (s, *P*R$_2$).

$^{7}Li\{^{1}H\}$ NMR (116.6 MHz, 297.9 K, THF): *δ* / ppm = −0.16.

*2.2.2 With 12-crown-4 (**5b**)*



4 **5b**

In a 20 mL Schlenk tube 149.8 mg (0.260 mmol, 1.0 eq.) of **4** and 0.084 mL (91.6 mg, 0.520 mmol, 2.0 eq.) 12-crown-4 were dissolved in 5 mL THF and 6.2 mg (0.260 mmol, 1.0 eq.) anhydrous LiOH were added and the suspension was stirred for 7 days at ambient temperature. in 2 mL THF and stirred for 2 days at ambient temperature. After removal of the solvent *in vacuo* (≤ 0.05 mbar) and extraction with three times 2–5 mL toluene, the solvent was removed *in vacuo* (≤ 0.05 mbar) yielding a in an oily, slightly pink residue. After washing with four times 2–5 mL *n*-pentane an orange solid was obtained and dried for 2 hours *in vacuo* (≤ 0.02 mbar).

Molecular formula: $LiC_{38}H_{69}N_4O_9P_2Se_2$

Molecular weight: 952.80 g/mol

Yield: 173.8 mg (0.182 mmol, 70 %)

Melting point: 92 °C (decomposition)

IR (ATR Diamond, selected data): $\tilde{\nu}$ / cm^{-1} = 2278 (w, PH), 2867 (m, CH), 2926 (w, CH), 2957 (w, CH).

^{1}H NMR (500.1 MHz, 298.0 K, C_6D_6): δ / ppm = 0.91 (t, 6H, $^3J_{H,H}$ = 7.37 Hz, CH_3), 0.95 (t, 6H, $^3J_{H,H}$ = 7.39 Hz, CH_3), 1.39–1.47 (m, 4H, CH_2CH$_3$), 1.47–1.56 (m, 4H, CH_2CH$_3$), 1.77–1.87 (m, 2H, NCH$_2$CH_2), 2.07–2.16 (m, 2H, NCH$_2$CH_2), 2.18–2.28 (m, 4H, NCH$_2$CH_2), 3.16 (s, 12-crown-4), 4.35–4.45 (m, 2H, NCH_2), 4.61–4.76 (m, 4H, NCH_2), 4.86–4.96 (m, 2H, NCH_2), 9.46 (d, 1H, $^1J_{P,H}$ = 538.5 Hz, P*H*).

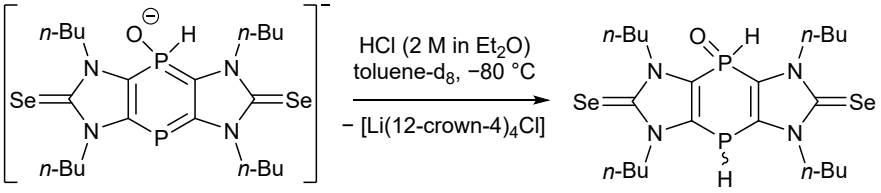
^{13}C{^{1}H} NMR (125.8 MHz, 298.0 K, C_6D_6): δ / ppm = 14.1 (s, *C*H$_3$), 20.5 (s, *C*H$_2$CH$_3$), 20.7 (s, *C*H$_2$CH$_3$), 29.9 (d, $^4J_{P,C}$ = 4.1 Hz, NCH$_2$*C*H$_2$), 48.5 (s, N*C*H$_2$), 48.6 (d, $^3J_{P,C}$ = 13.6 Hz, N*C*H$_2$), 68.5 (s, 12-crown-4), 112.9 (dd, $^1J_{P,C}$ = 149.2 Hz, $^2J_{P,C}$ = 10.9 Hz, *C*PH-O$^-$), 155.8 ($^1J_{P,C}$ = 46.8 Hz, $^2J_{P,C}$ = 19.9 Hz, *C*P), 161.7 (d, $^3J_{P,C}$ = 5.0 Hz, *C*=Se).

^{31}P{^{1}H} NMR (202.5 MHz, 298.0 K, C_6D_6): δ / ppm = −23.8 (s, *P*H-O$^-$), −69.0 (s, *P*R$_2$).

^{31}P NMR (202.5 MHz, 298.0 K, C_6D_6): δ / ppm = −23.8 (d, $^1J_{P,H}$ = 538.5 Hz, *P*H-O$^-$), −69.0 (s, *P*R$_2$).

^{7}Li{^{1}H} NMR (116.6 MHz, 297.9 K, THF): *δ* / ppm = −0.29.

2.3 Generation of 6



5b **6**

7.2 mg (0.008 mmol, 1.0 eq.) of **5b** were dissolved in 0.5 mL toluene-d_8 in a *J Young®* NMR tube and cooled to −80 °C. After addition of one drop of HCl (2 M in Et_2O) the suspension changed colour from orange to yellow and was investigated via ^{31}P NMR spectroscopy.

Molecular formula: $C_{22}H_{38}N_4OP_2Se_2$

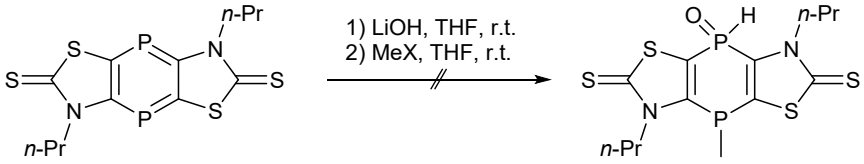
Molecular weight: 594.46 g/mol

Content in mixture: 85 % (^{31}P NMR integration of reaction mixture)

^{31}P NMR (121.5 MHz, 298.0 K, THF-d8): δ / ppm = −26.8 (d, $^1J_{P,H}$ = 536 Hz, *P*H=O, 1st isomer), −27.9 (d, $^1J_{P,H}$ = 537 Hz, *P*H=O, 2nd isomer), −114.5 (d, $^1J_{P,H}$ = 206 Hz, *P*H, 2nd isomer), −116.3 (d, $^1J_{P,H}$ = 213 Hz, *P*H, 1st isomer).

2.4 Methylation of 3 targeting 7a

2.4.1 Methyl iodide/methyl triflate



1 **7a**

In a 10 mL Schlenk vessel, 5 mL THF were added to a mixture of 46.5 mg (0.124 mmol, 1.00 eq.) of **1** and 3.0 mg (0.125 mmol, 1.01 eq.) of LiOH at ambient temperature. The mixture was stirred for 28 h before the addition of 1.56 mL (0.125 mmol, 1.01 eq.) of a 0.0803 M solution of MeI in THF at ambient temperature. The reaction mixture was stirred further for 1 h.

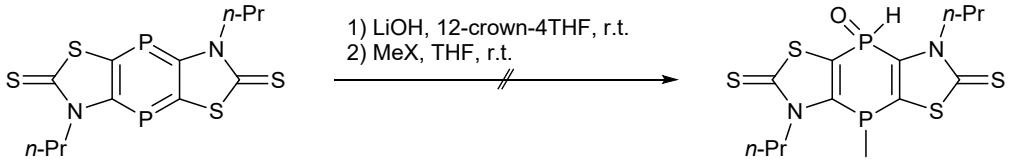
$^{31}P\{^1H\}$ NMR (162.0 MHz, 298.0 K, THF): δ / ppm = −18.7 (s, PH-O^-), −15.7 (s, PR_2).

^{31}P NMR (162.5 MHz, 298.0 K, THF): δ / ppm = −18.7 (d, $^1J_{P,H}$ = 544.8 Hz, PH-O^-), −15.7 (s, PR_2).

In a 10 mL Schlenk vessel, 3 mL THF were added to a mixture of 33.5 mg (0.089 mmol, 1.00 eq.) of **1** and 2.1 mg (0.088 mmol, 0.99 eq.) of LiOH at ambient temperature. The mixture was stirred for 4 h before the addition of 0.39 mL (0.089 mmol, 1.00 eq.) of a 0.2285 M solution of MeOTf in THF at ambient temperature. The reaction mixture was stirred further for 30 min.

$^{31}P\{^1H\}$ NMR (162.0 MHz, 298.0 K, THF): δ / ppm = −18.7 (s, PH-O^-), −15.7 (s, PR_2).

2.4.2 Methyl iodide/methyl triflate, 12-crown-4

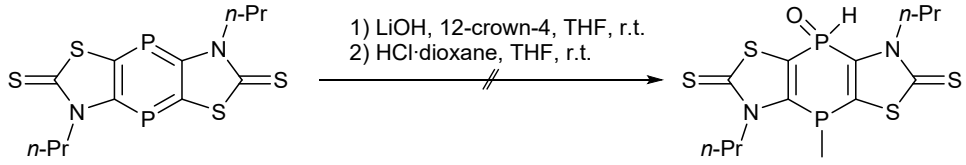


1 **7a**

In a 10 mL Schlenk vessel, a solution of 14 µL (0.087 mmol, 1.00 eq.) of 12-crown-4 in 3 mL THF were added to a mixture of 32.8 mg (0.087 mmol, 1.00 eq.) of **1** and 2.1 mg (0.088 mmol, 1.01 eq.) of LiOH at ambient temperature. The mixture was stirred for 2 h before the addition of 0.11 mL (0.088 mmol, 1.01 eq.) of a 0.803 M solution of MeI in THF at −80 °C. The reaction mixture was stirred further for 1 h while slowly warming up.

In a 10 mL Schlenk vessel, a solution of 19 µL (0.118 mmol, 0.99 eq.) of 12-crown-4 in 3 mL THF were added to a mixture of 44.7 mg (0.119 mmol, 1.00 eq.) of **1** and 2.8 mg (0.117 mmol, 0.99 eq.) of LiOH at ambient temperature. The mixture was stirred for 4 h before the addition of 0.52 mL (0.119 mmol, 1.00 eq.) of a 0.229 M solution of MeOTf in THF at −80 °C. The reaction mixture was stirred further for 30 min while slowly warming up.

2.5 Protonation of 3 using HCl targeting 7b



1 **7b**

In a 10 mL Schlenk tube, a solution of 12 µL (0.074 mmol, 1.00 eq.) of 12-crown-4 in 4 mL THF is added to a mixture of 27.8 mg (0.074 mmol, 1.00 eq.) **1** and 1.7 mg (0.071 mmol, 0.96 eq.) LiOH at ambient temperature. The mixture was stirred 28 h before the addition of 0.02 mL (0.080 mmol, 1.08 eq. of a 4 M solution of HCl in dioxane. The orange suspension was stirred for another 10 min.

$^{31}P\{^{1}H\}$ NMR (121.5 MHz, 298.0 K, THF): δ / ppm = 53.3 (s), 133.0 (s).

3 NMR spectra

3.1 3

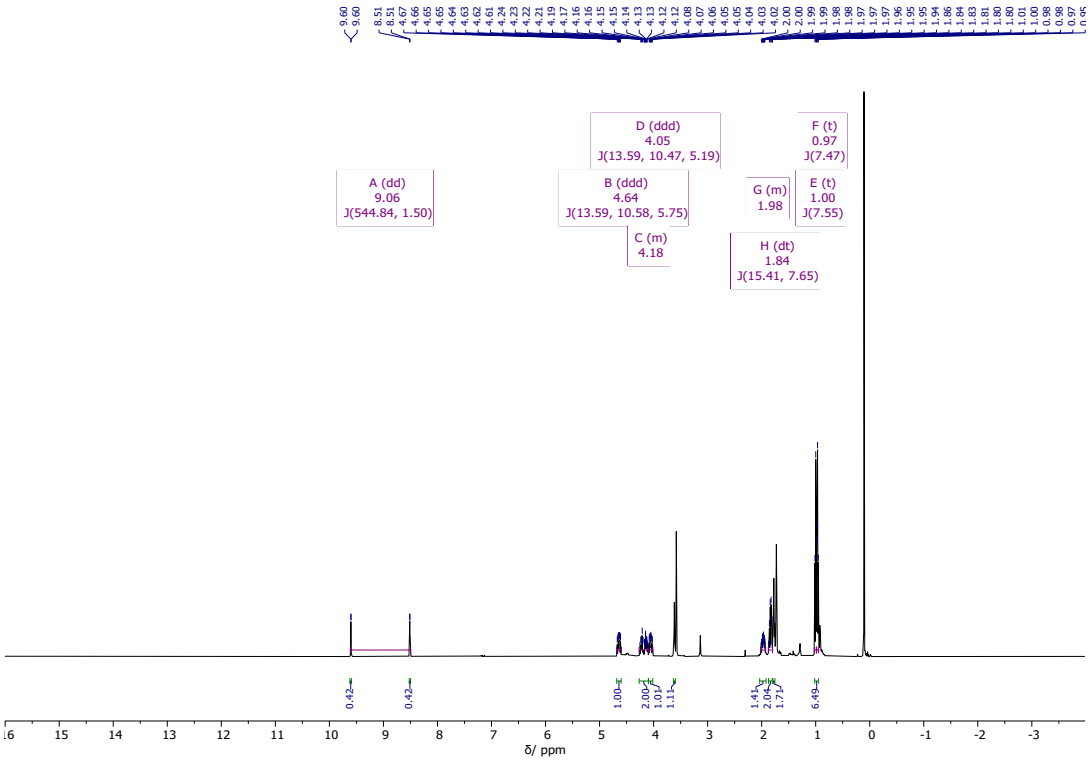


Fig. S1 ^{1}H NMR spectrum **3** in THF-d8.

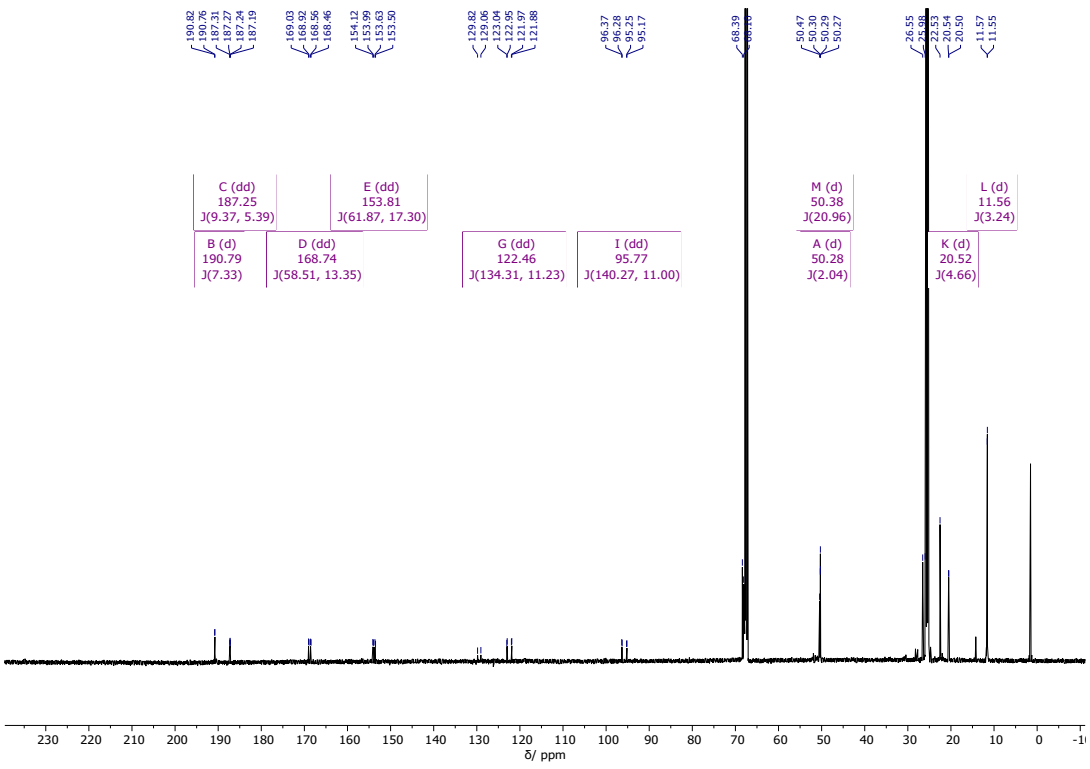


Fig. S2 ^{13}C NMR spectrum **3** in THF-d8.

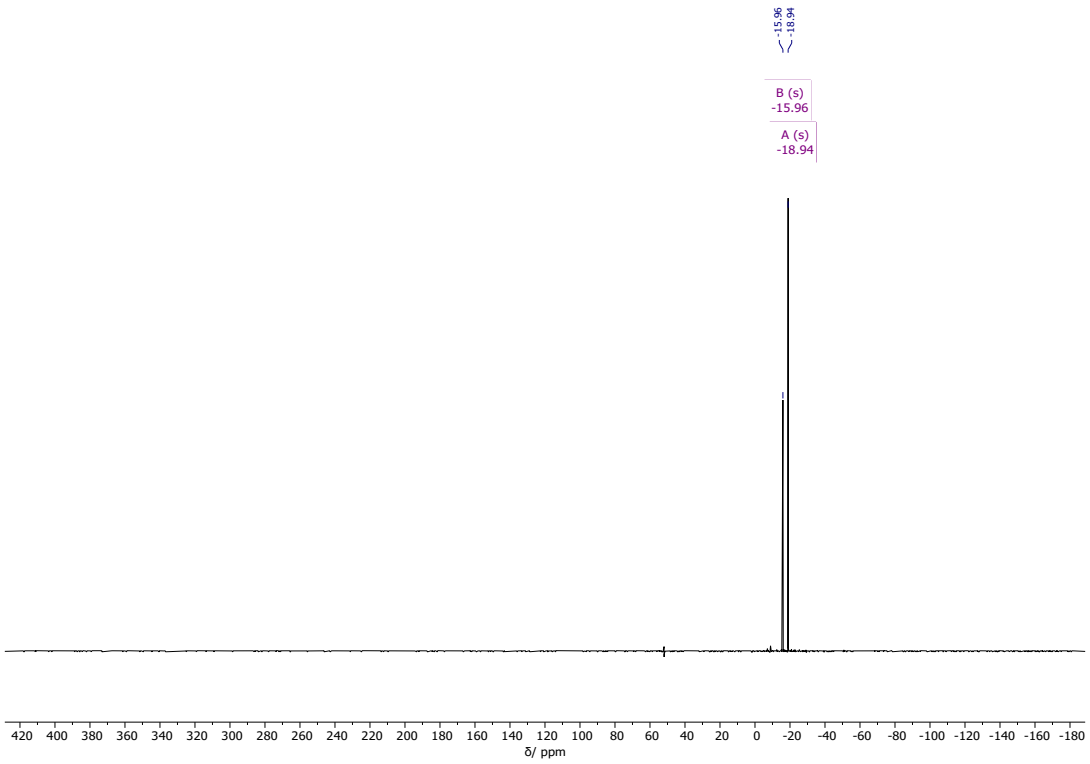


Fig. S3 $^{31}P\{^{1}H\}$ NMR spectrum **3** in THF-d8.

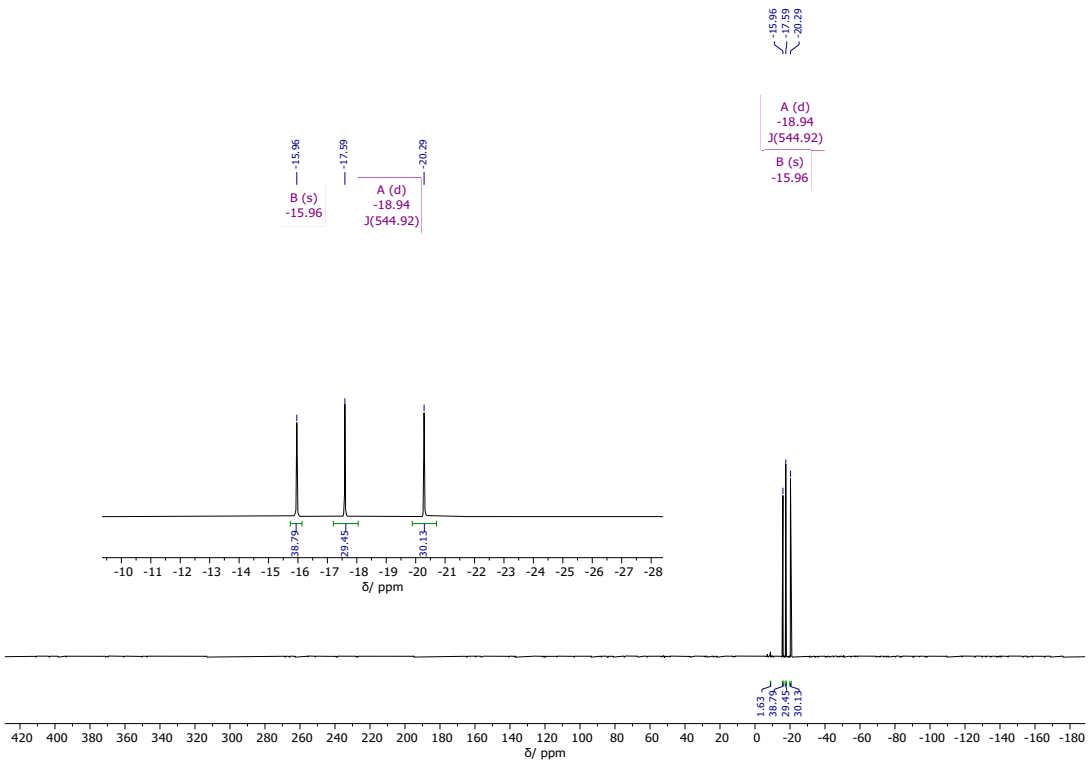


Fig. S4 ^{31}P NMR spectrum **3** in THF-d8.

3.2 5a

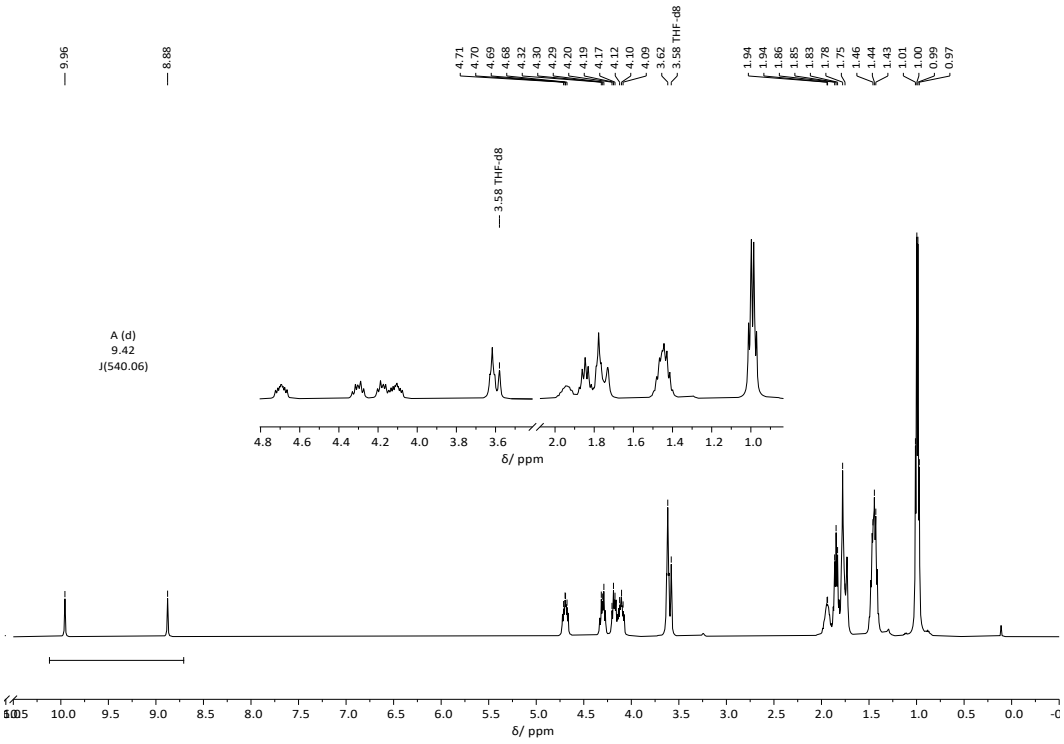


Fig. S5. ^{1}H NMR spectrum of **5a** in THF-d8.

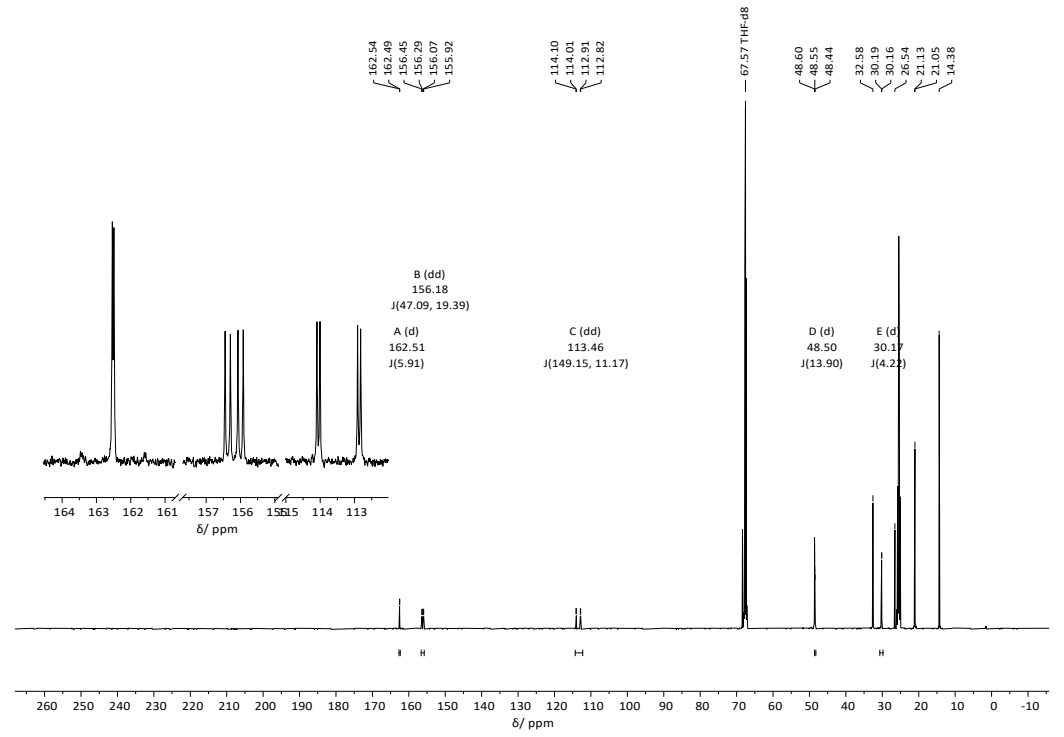


Fig. S6. ^{13}C{^{1}H} NMR spectrum of **5a** in THF-d8.

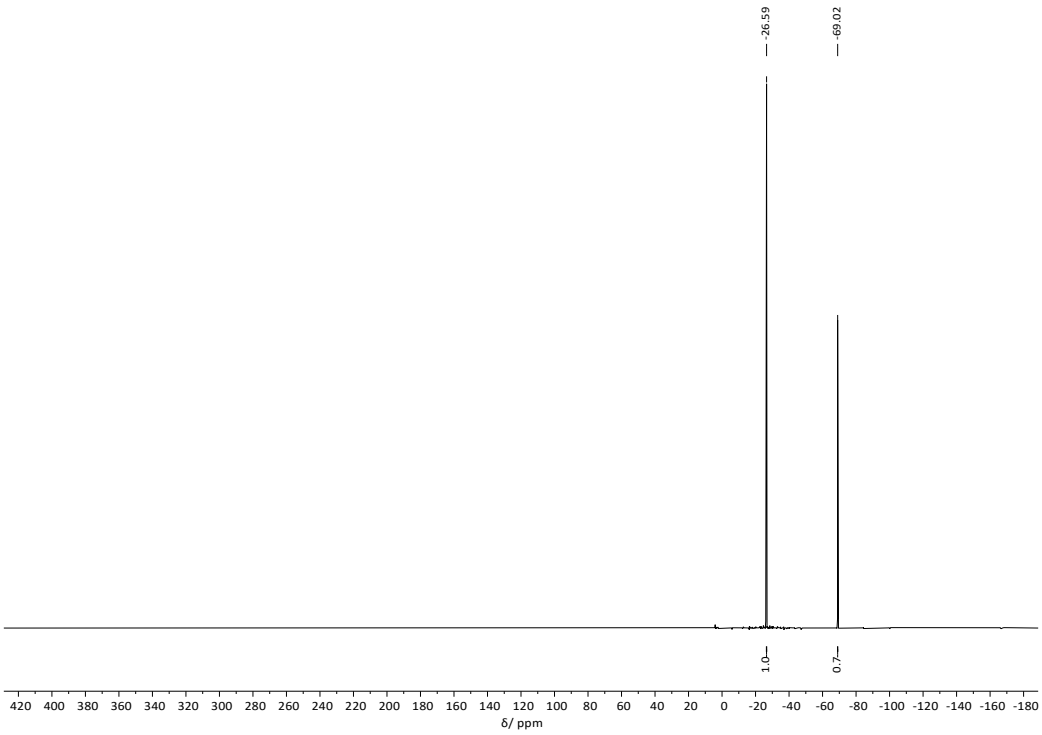


Fig. S7. $^{31}P\{^{1}H\}$ NMR spectrum of **5a** in THF-d8.

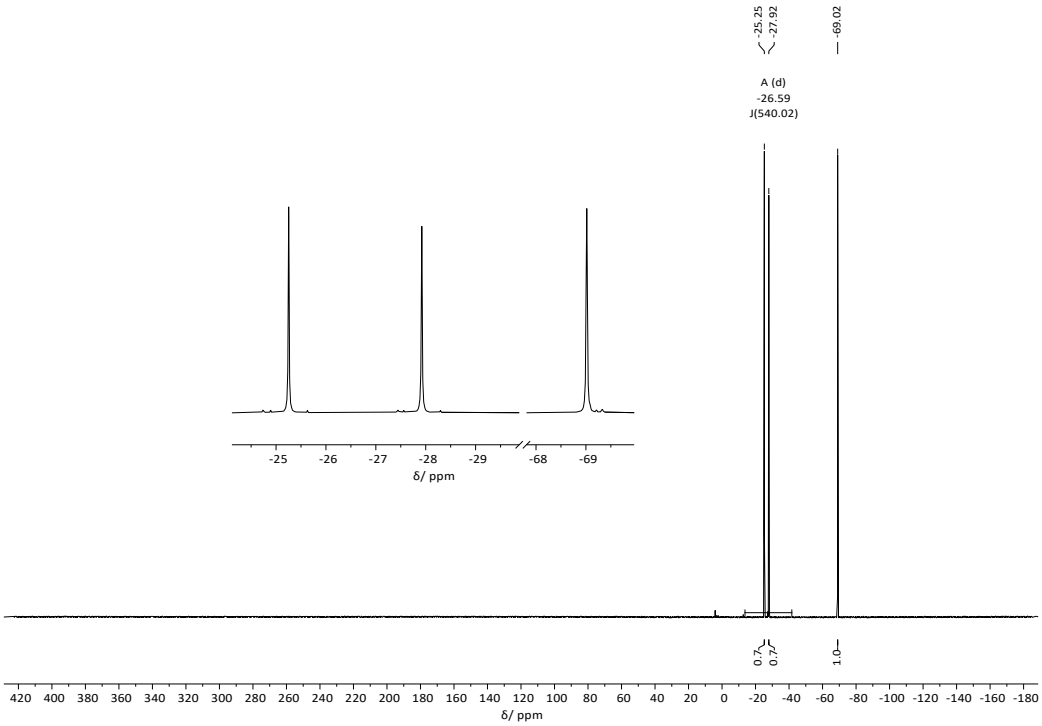


Fig. S8. ^{31}P NMR spectrum of **5a** in THF-d8.

3.3 5b

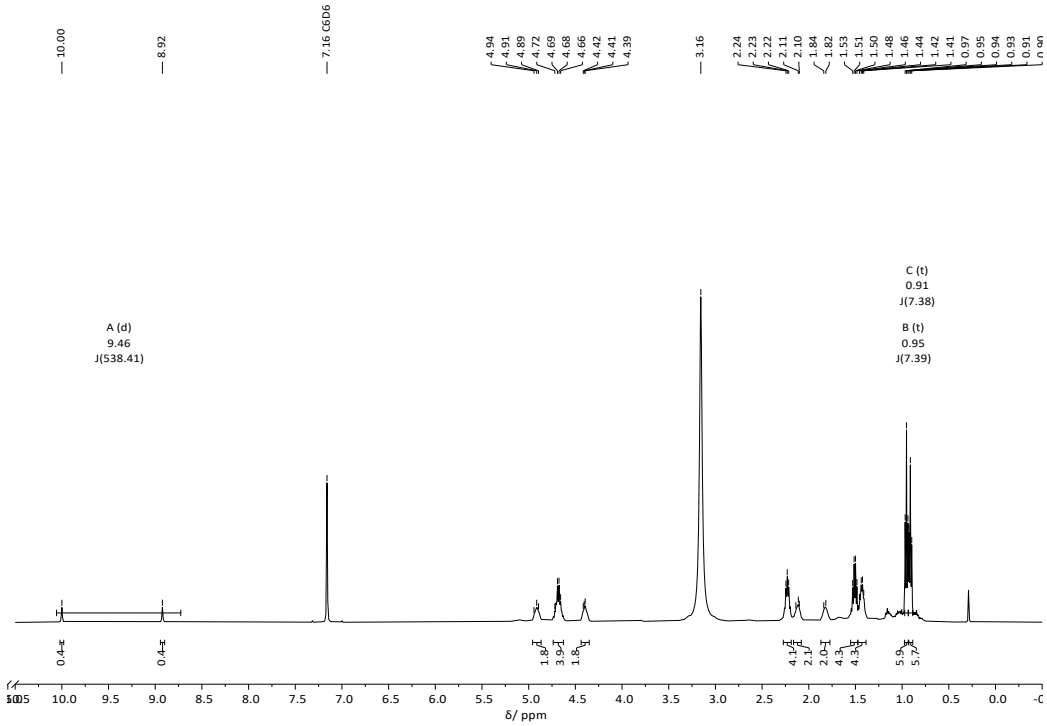


Fig. S9. ^{1}H NMR spectrum of **5b** in C_6D_6.

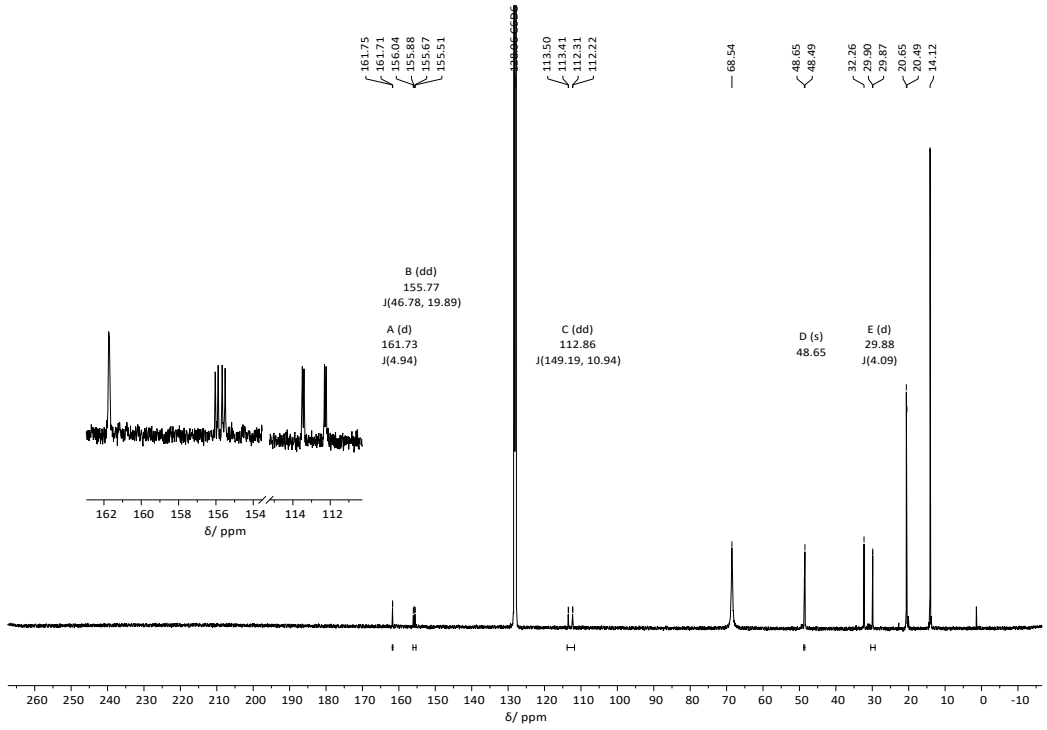


Fig. S10. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in C_6D_6.

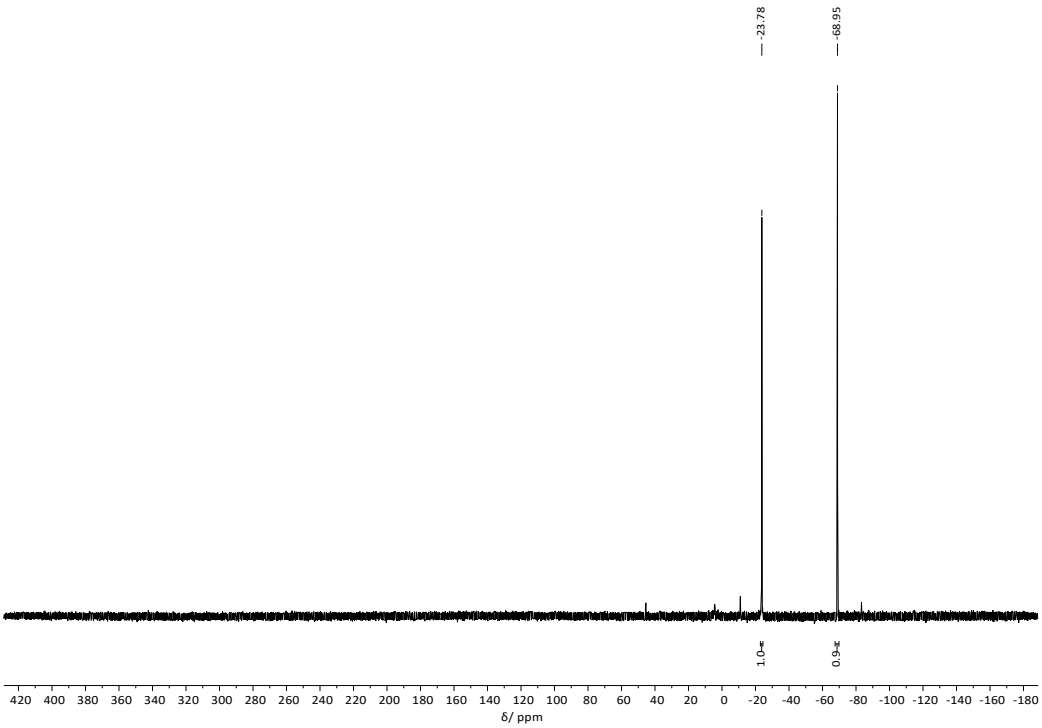


Fig. S11. $^{31}P\{^{1}H\}$ NMR spectrum of **5b** in C_6D_6.

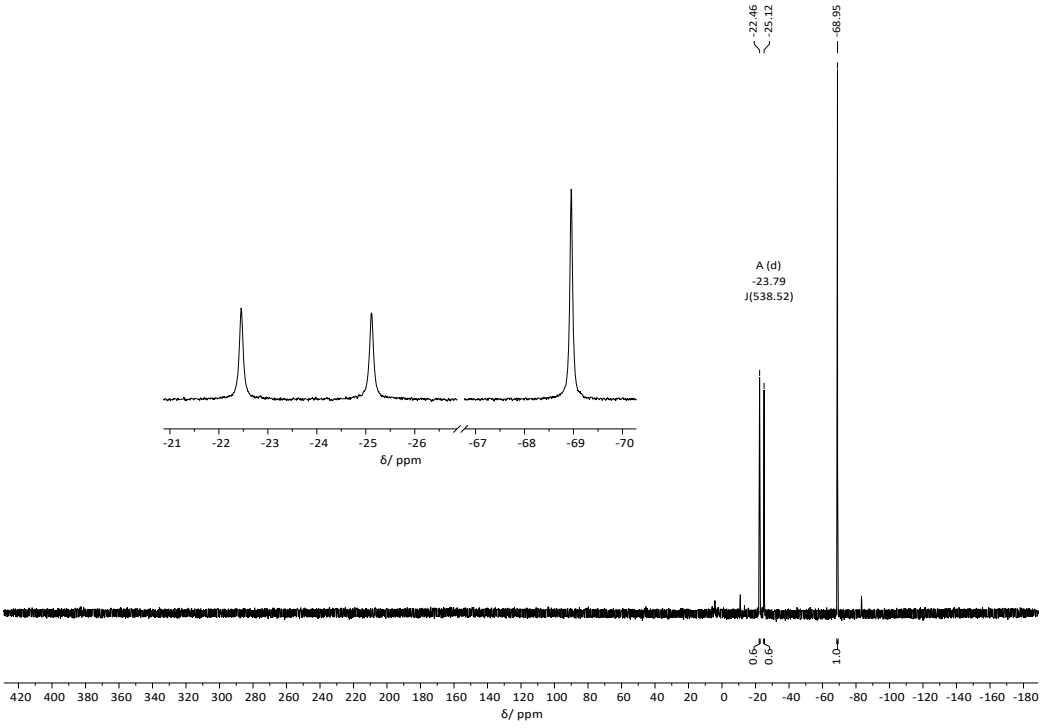


Fig. S12. ^{31}P NMR spectrum of **5b** in C_6D_6.

3.4 Generation of 6

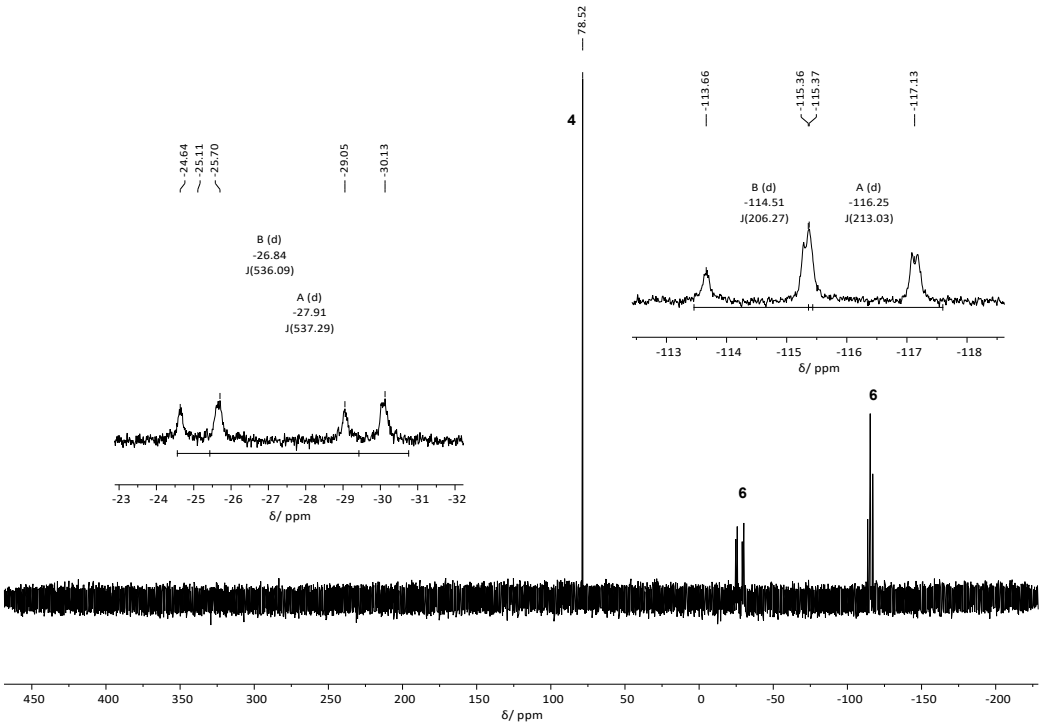


Fig. S13. ^{31}P NMR spectrum of **6** and **4** in toluene-d_8.

3.5 Targeted methylation of 3 using methyl iodide

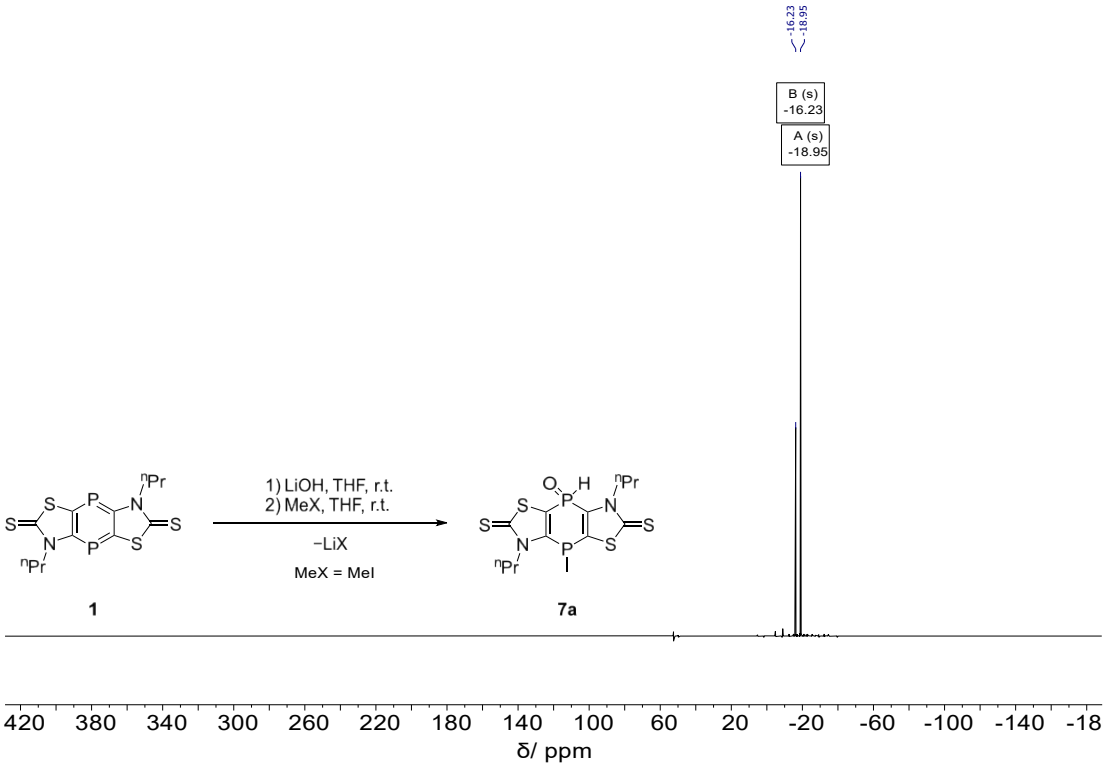


Fig. S14 ^{31}P{^{1}H} NMR spectrum of the targeted methylation of **3** using methyl iodide.

3.6 Targeted methylation of 3 using methyl triflate

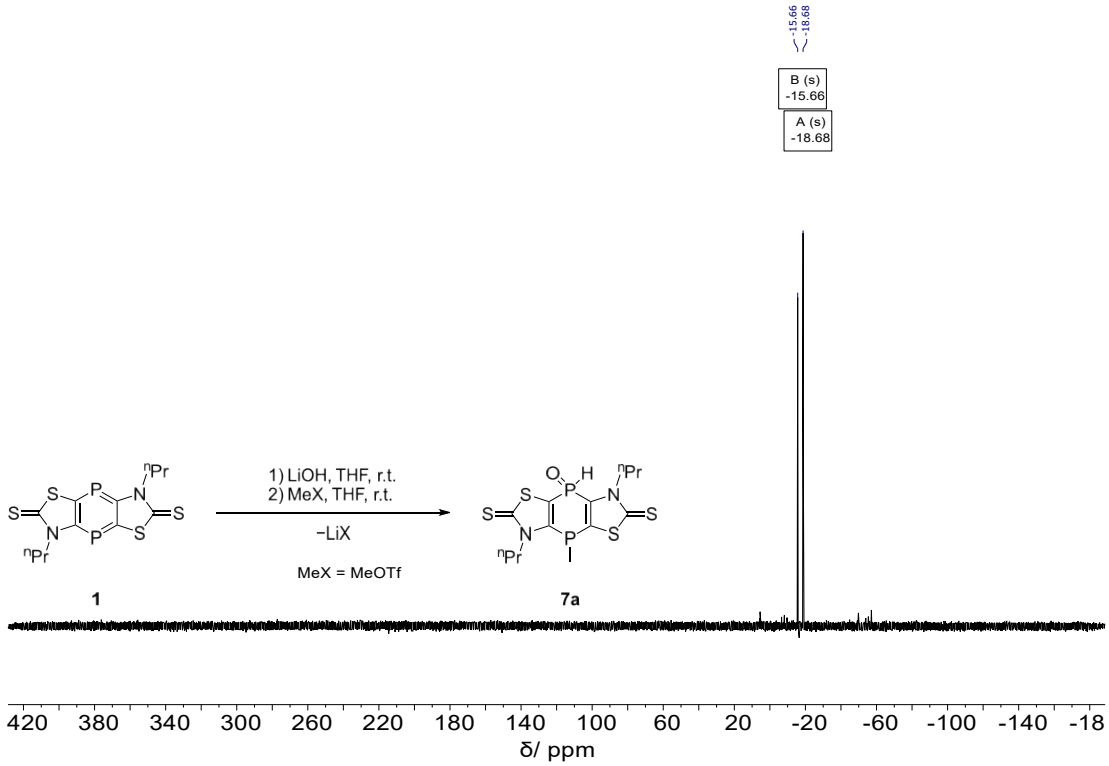


Fig. S15 $^{31}P\{^{1}H\}$ NMR spectrum of the targeted methylation of **3** using methyl triflate.

3.7 Targeted methylation of 3 using methyl iodide, 12-crown-4

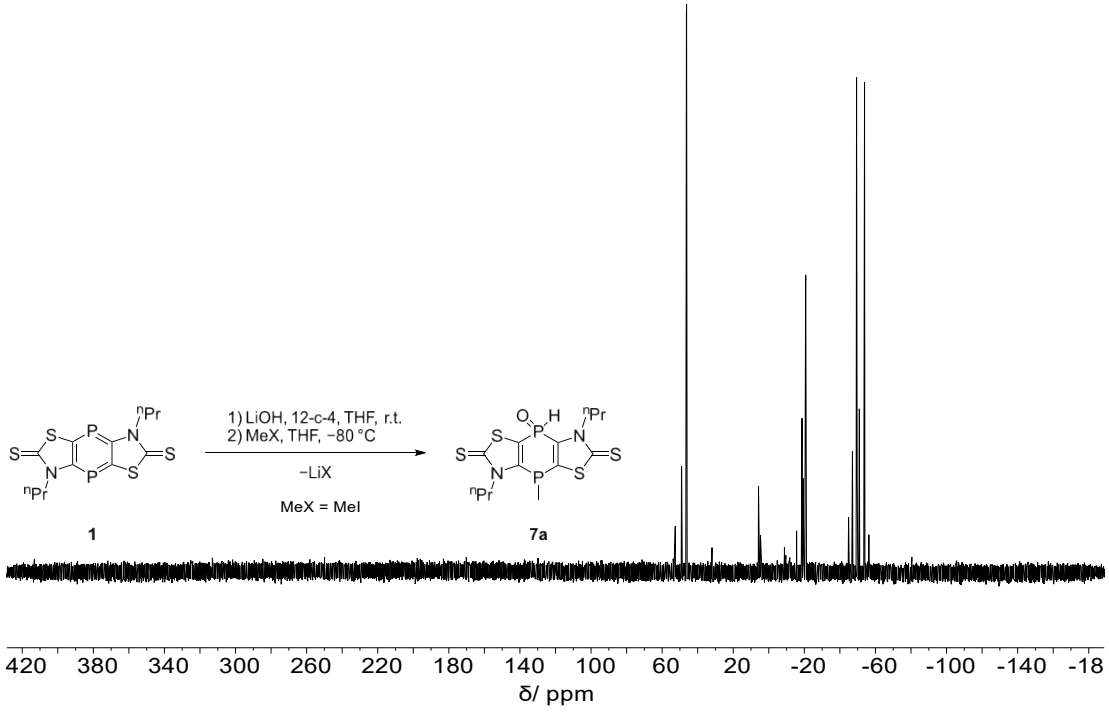


Fig. S16 $^{31}P\{^{1}H\}$ NMR spectrum of the targeted methylation of **3** using methyl iodide and 12-crown-4.

3.8 Targeted methylation of 3 using methyl triflate, 12-crown-4

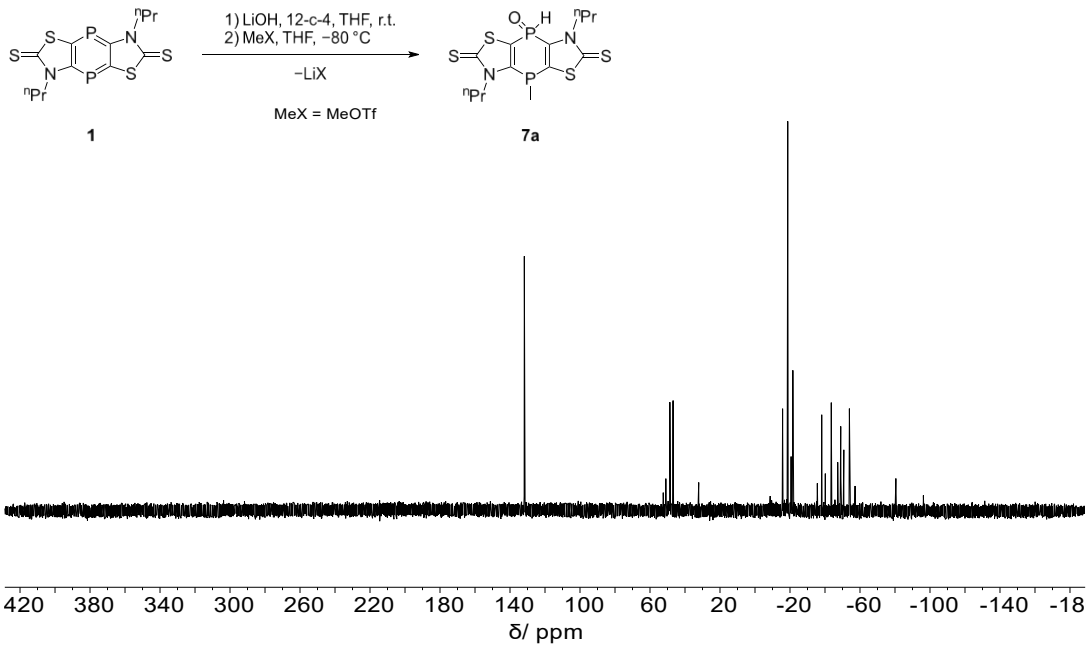


Fig. S17 $^{31}P\{^{1}H\}$ NMR spectrum of the targeted methylation of **3** using methyl triflate and 12-crown-4.

3.9 Targeted protonation of 3 using HCl

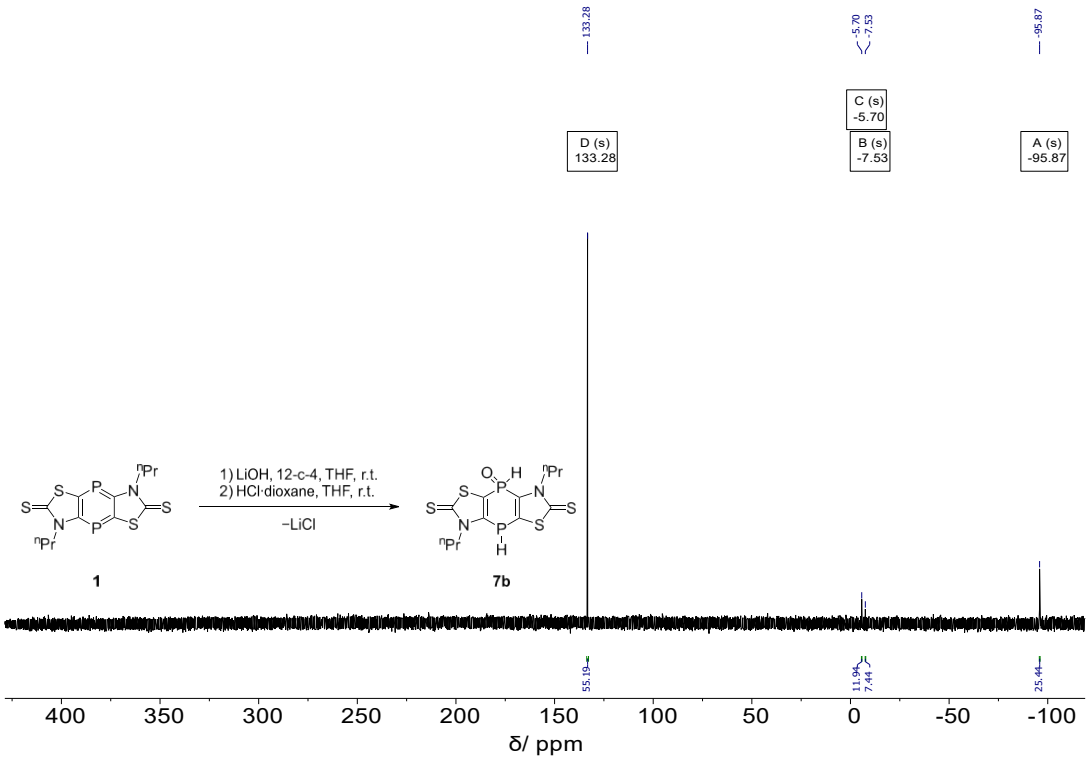


Fig. S18 $^{31}P\{^{1}H\}$ NMR spectrum of the targeted protonation of **3** using HCl in dioxane.

4 Computational details

4.1 Theoretical methods

All structures were built with the open-source software *Avogadro 1.2.0*.[3] Structures were optimised using the *ORCA*[4] 4.0.1.2 program package at the TPSS-D3BJ/def2-TZVP(CPCM$_{THF}$) level of theory, a combination of the mega-GGA density functional TPSS[5] with BJ-damped DFT-D3[6] dispersion correction and the def2-TZVP[7] basis set, including the conductor-like polarisable continuum model (CPCM)[8] as a solvent model for THF. In order to accelerate the optimisations and following harmonic frequency calculations, the density-fitting RI-J (def2/J) approach was used.[9] The DFT grid was set to 4, with the grid for the final energy being set to 5. Optimised structures were characterised by frequency analyses in order to identify the nature of the respective located stationary point (no imaginary frequency below −30 cm^{-1} for minima and only one imaginary frequency for transition states) and to get access to thermal corrections (for 298.15 K and 1 atm) according to the modified ideal gas-rigid rotor-harmonic oscillator model. Transition states were obtained via relaxed potential energy surface scans along the important bond in *ORCA* 4.0.1.2 or by nudged elastic band calculations[10] using *ORCA* 5.0.4. The transition state vibration was taken from the respective highest energy structure and the structure was optimised, keeping the imaginary frequency. Final single point energies were calculated with *ORCA* 4.0.1.2 on the RI-PW6B95-D3BJ/def2-QZVP(CPCM$_{THF}$)[7,11] level of theory using the density-fitting RI-JK (def2/JK)[12] approach. Theoretical calculations on **5** were performed with *ORCA* 5.0.4. The structure was optimised at the TPSS-D4/def2-TZVP/CPCM$_{THF}$ level of theory which combines the aforementioned functional with the charge dependent atom-pairwise DFT-D4 dispersion correction which uses the D4(EEQ)-ATM dispersion model[13] and the def2-TZVP basis set using the CPCM for THF. Single point energy calculations were performed at the PW6B95-D4/def2-QZVP/CPCM$_{THF}$ level of theory which combines the above-described functional with the DFT-D4 dispersion correction and the larger def2-QZVP basis set. The density-fitting RI-JCOSX (def2/J) approach was used to accelerate the calculations for **5**.

The final Gibbs free energies G were obtained from the sum of the electronic single point energies and the thermal corrections accessed from the frequency analyses. Calculated structures were visualised using the software *UCSF Chimera 1.17.2*.[14]

4.2 Additional tables/figures

Table S1 Out-of-plane angles φ and average P-C/C-C bond lengths for **1^{Me}** and isomers of **3**.

	1^{Me}	**3^{Me}**	**3^{Me}-PLi**	**3^{Me}-OLi**
φ	0.0°	10.9°	8.8°	11.7°
Ø d(P-C) / Å	1.751	1.773	1.781	1.765
Ø d(C-C) / Å	1.410	1.391	1.383	1.393

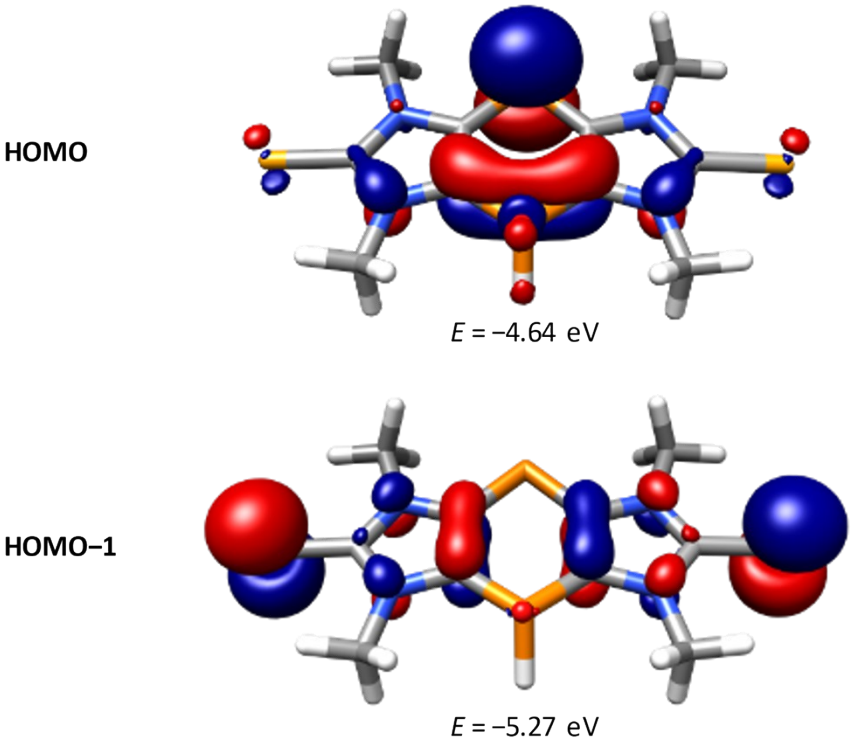


Fig. S19. HOMO and HOMO−1 of the anion in **5** at the PW6B95-D4/CPCM$_{THF}$/def2-QZVP//TPSS-D4/CPCM$_{THF}$/def2-TZVP level of theory.

4.3 Coordinates

4.3.1 ***1^{Me}***

E = −2696.235653675209

C	3.972083	6.503908	1.249647
C	2.565938	6.575210	1.320480
P	1.400545	6.515237	0.003816
C	2.475970	6.346970	-1.358836
C	3.882109	6.275521	-1.429660
P	5.047562	6.336801	-0.113112
N	4.338315	6.139387	-2.739973
C	3.379465	6.098055	-3.733366
S	1.802903	6.237618	-2.975836
N	2.109660	6.709924	2.630916
C	3.068453	6.750151	3.624406
S	4.645097	6.612363	2.866722
S	2.837375	6.901697	5.248675
S	3.610511	5.945923	-5.357583
C	5.764815	6.045985	-3.050295
H	5.851238	5.936474	-4.132268
H	6.193954	5.178335	-2.539860
H	6.273266	6.954979	-2.714371
C	0.683148	6.803147	2.941237
H	0.596569	6.909467	4.023515
H	0.174366	5.895420	2.602417
H	0.254488	7.672558	2.433390

4.3.2 2^{Me} solvent separated ion pair

E = −2772.338810351457

C	3.94718325383053	6.33626481237622	1.23142627719235
C	2.56645735206907	6.44892511206197	1.29510027257402
P	1.36794688308154	6.13291863345987	-0.00625393007023
C	2.50898382458415	6.28329939505400	-1.36220491031714
C	3.89320196774021	6.15432193295606	-1.42926042630259
P	5.08068663660300	6.05524993884920	-0.10786228260844
N	4.35483250480137	6.17170336493613	-2.75958512166800
C	3.40963453801652	6.32962619862542	-3.73594378214431
S	1.85240168061191	6.45387811394798	-2.98695801409917
N	2.10078807178752	6.74385541906124	2.60019394041236
C	3.04404568774350	6.84957646873649	3.56857809638451
S	4.61118948851971	6.58665715422693	2.84740987711689
S	2.82965788921021	7.17855632747862	5.20616977296543
S	3.66206360793161	6.40856434870075	-5.39691934250225
C	5.78051377171773	6.05334809970144	-3.06754427011261
H	5.89056925591194	6.11575623112479	-4.15026544223947
H	6.15139411026636	5.09282480786511	-2.69879024118942
H	6.32240255457498	6.86705743241215	-2.57656940756049
C	0.67466429458163	6.91503001135843	2.88879611994912
H	0.58284623764285	7.11666909972171	3.95646607675280
H	0.13687139455640	5.99946387070185	2.62799209475090
H	0.28200811623306	7.75116217243715	2.30558807357595
O	1.18577555023767	4.44597154260057	0.17934604261296
H	0.23959132774652	4.23335951160588	0.09739052652683

4.3.3 3^{Me} solvent separated ion pair

E = −2772.352054979830

C	3.954245	6.427315	1.222653
C	2.573810	6.543932	1.304050
P	1.429553	6.218495	-0.016094
C	2.505057	6.327662	-1.401232
C	3.891565	6.201098	-1.443135
P	5.085991	6.171014	-0.123228
N	4.355833	6.130462	-2.769276
C	3.413032	6.199602	-3.758397
S	1.844363	6.345357	-3.030254
N	2.105733	6.772458	2.616596
C	3.055138	6.857535	3.582589
S	4.620715	6.617317	2.843440
S	2.835734	7.147697	5.221689
S	3.665815	6.163426	-5.416245
C	5.784308	6.008591	-3.065891
H	5.893387	5.985274	-4.150246
H	6.167595	5.086074	-2.621165
H	6.313644	6.867717	-2.644091
C	0.679994	6.943255	2.915963
H	0.541776	6.758966	3.981491
H	0.109781	6.222260	2.325198
H	0.367114	7.962897	2.674402

O	0.570052	4.987780	0.117050
H	0.599874	7.356516	-0.095538

4.3.4 3^{Me}-PLi

E = −2779.835234385106

C	3.939521	6.193161	1.247316
C	2.585932	6.453006	1.317449
P	1.432684	6.301652	-0.034685
C	2.530844	6.367350	-1.413192
C	3.886871	6.085804	-1.454703
P	5.035735	5.808533	-0.109897
N	4.365831	6.033536	-2.769315
C	3.454602	6.284277	-3.765410
S	1.900310	6.563595	-3.040200
N	2.127754	6.702299	2.625934
C	3.072833	6.672233	3.603966
S	4.612445	6.274211	2.868469
S	2.873777	6.957345	5.240144
S	3.743138	6.335510	-5.410859
C	5.772672	5.756541	-3.064185
H	5.849606	5.535787	-4.128942
H	6.097030	4.900202	-2.467635
H	6.384474	6.631720	-2.824264
C	0.720574	7.003209	2.917165
H	0.559386	6.826009	3.980462
H	0.090306	6.340755	2.319206
H	0.505624	8.048692	2.680381
O	0.476318	5.144521	0.035435
H	0.730360	7.522366	-0.067961
Li	6.441172	7.895946	-0.094250

4.3.5 3^{Me}-OLi

E = −2779.855339789607

C	3.878578	6.433663	1.363813
C	2.534065	6.784977	1.397189
P	1.430641	6.658744	0.026272
C	2.545108	6.652665	-1.314912
C	3.896022	6.301146	-1.308115
P	5.004814	6.026821	0.054161
N	4.397811	6.196940	-2.615637
C	3.520438	6.444470	-3.638202
S	1.963184	6.827045	-2.965580
N	2.051566	7.056869	2.695379
C	2.957448	6.941667	3.702031
S	4.491893	6.456056	3.014881
S	2.720215	7.208986	5.338281
S	3.829721	6.411999	-5.281379
C	5.801376	5.858372	-2.864180
H	5.951883	5.855075	-3.943663
H	6.014569	4.871528	-2.444383
H	6.440883	6.607405	-2.389065

C	0.670811	7.487875	2.936229
H	0.481005	7.397637	4.005795
H	-0.007987	6.842131	2.373078
H	0.546704	8.528535	2.624414
O	0.416418	5.522412	0.094383
H	0.692367	7.850395	-0.049662
Li	0.409865	3.707086	0.024210

*4.3.6 **2**^{Me} tight ion pair*

E = −2779.823996405636

C	3.90924016376426	6.34950149962899	1.22689860562173
C	2.53557808962240	6.45632658951523	1.28605839576233
P	1.33714713807094	6.11871304023554	-0.02080291729325
C	2.48070012462953	6.25970913850161	-1.38672377601276
C	3.85750844328263	6.13392450879781	-1.45740478597734
P	5.02945695381247	5.98750602503827	-0.11493210011647
N	4.32547092119522	6.14992264003028	-2.77830604621239
C	3.38062378783887	6.31939106895515	-3.75946612443315
S	1.82146306871480	6.43275469890766	-3.00781860393928
N	2.06743260869211	6.79292404061986	2.57700826677815
C	3.01313025812457	6.94717266538015	3.54053303373776
S	4.58195951463529	6.65997954987411	2.82230612151811
S	2.80506305693330	7.34443446894270	5.15704290381739
S	3.64805183041194	6.41979431314221	-5.41083917569679
C	5.74985797883075	6.03130548865688	-3.09031805327023
H	5.83969388522676	5.81893208256125	-4.15585456307132
H	6.17556109992820	5.21811353156641	-2.49699559571341
H	6.26317860675408	6.97024006162793	-2.85901108811962
C	0.63842825061040	6.95488669045837	2.86445390935481
H	0.54588982084760	7.17459325623408	3.92831378381994
H	0.11173413383486	6.02828595526929	2.62190480118897
H	0.23587344310381	7.77680914029441	2.26828284889628
O	1.18954957235290	4.44337347292938	0.17753230580825
H	0.24971009889847	4.20325612639823	0.09768370379783
Li	6.43479514988383	8.05998994643419	-0.14467985024554

*4.3.7 **5**^{Me} solvent separated ion pair*

E = −6 173.07666289906

C	-6.61451172040847	-6.75520073896150	-0.64814708796058
C	-7.00917904377866	-5.47837861620269	-1.04480911275677
C	-4.55805043988437	-4.59097916130392	-0.51573325163997
C	-4.19498653998730	-5.87953363459511	-0.12637992191075
P	-5.06911113518103	-7.42752420669778	-0.08031233002446
N	-7.76190133306642	-7.54664331333186	-0.74350282050550
N	-8.37503584101261	-5.55557187639442	-1.37260109112612
N	-3.43597783784177	-3.76859396440946	-0.30644580705229
N	-2.87259063346878	-5.77741107034320	0.31269273671789
C	-9.18295915285083	-4.42380806763074	-1.81027729960298
H	-9.47245243491134	-3.80873252963529	-0.95277930151408
H	-8.59878801231446	-3.82523107199304	-2.51415876500651
H	-10.07673892423302	-4.81737103620983	-2.29603771030871

C	-7.78982906205911	-8.96315404378589	-0.41106923534873
H	-7.12402439032870	-9.51263837410532	-1.08339588791289
H	-7.45553109838950	-9.10040954442808	0.62193409013529
H	-8.81663280980484	-9.31204672601682	-0.52844652477557
C	-2.10570454356296	-6.90529545038917	0.81971036314758
H	-1.95942112943984	-7.64172135204472	0.02361824488809
H	-1.14236354201763	-6.52533967224109	1.16282097148752
H	-2.65006330723455	-7.36996685297759	1.64755222619658
C	-3.40641819553259	-2.33435683212047	-0.56516859107092
H	-2.36181932354624	-2.02427692685576	-0.61526897926835
H	-3.90889128918878	-2.13706039699311	-1.51575275311893
H	-3.91190802095123	-1.79247636970522	0.23994621637808
Se	-0.73471648724291	-3.86292848211062	0.69784143649707
C	-2.41232696817072	-4.49035228774481	0.21087956743971
C	-8.83692230390798	-6.81427518679926	-1.17575225268865
Se	-10.57407437331583	-7.41936546594514	-1.42376090552098
P	-6.00898245559199	-4.06471063057118	-1.36284754106120
H	-6.55696573438096	-3.01613793198051	-0.59234837719946
O	-5.87172191639456	-3.59390818547639	-2.78860030551340

4.3.8 $7a^{Me}$

E = −2812.201600387441

C	3.95354160233059	5.96421677466263	1.24887814546939
C	2.64271721610621	6.34761268588317	1.31529050736226
P	1.53676421528413	6.57416433756641	-0.08466136269598
C	2.64701447354306	6.45592719784766	-1.46714783270171
C	3.94492121124423	6.02073152471790	-1.52057829588312
P	5.00918558787746	5.48869977600703	-0.14105106294064
N	4.42211530369254	5.91628834085495	-2.82113137270747
C	3.54640803701558	6.29202834984621	-3.81720315822582
S	2.03246014531839	6.74393729627491	-3.07899154114953
N	2.17883621610596	6.53524952552381	2.61887079706934
C	3.10322881164514	6.33650329566505	3.61017027455811
S	4.60857894932764	5.84184131638185	2.86275605924500
S	2.88384482600019	6.52313047241543	5.24826293110739
S	3.85471338169865	6.31587758585206	-5.44997495783948
C	5.76646172673439	5.43294400598487	-3.15972012045770
H	5.68935668111511	4.82946736511312	-4.06465906013611
H	6.13335816010241	4.82165348214134	-2.33195473633198
H	6.43523575895677	6.27738316664717	-3.34059315995549
C	0.80788897326503	6.96303224566229	2.93672422398956
H	0.53099903843713	6.51117736738938	3.88947342158510
H	0.14191035988904	6.61489204131273	2.14584158931203
H	0.77114529217870	8.05183494467283	3.02424970424372
O	0.35058865956487	5.66309519435030	-0.14153059990166
H	1.17954048743534	7.93331278868994	-0.01823107384986
C	6.24751385989028	6.87075315442837	-0.08428711921081
H	6.93066522165970	6.77100761662323	-0.93071266655491
H	6.82325367032582	6.75109352236009	0.83802103368386
H	5.75987613325563	7.84725162512524	-0.10009656708350

4.3.9 ***7b^{Me}***

E = −2772.807480535621

C	3.89478144130727	5.88401767852581	1.22928782548124
C	2.57991198836118	6.25432400613721	1.28927347257586
P	1.44245092557859	6.35048495953133	-0.10261260342983
C	2.55559392949040	6.32554510038428	-1.48816314869934
C	3.86321954728172	5.92222187469769	-1.53577666237396
P	4.86889502352281	5.27127353022636	-0.16558219299190
N	4.38729456314608	5.91997034498716	-2.81821774219709
C	3.53418833522673	6.34206980209576	-3.81679507501542
S	1.98691050087232	6.70911295105236	-3.09686219408241
N	2.13364984341108	6.51547196376733	2.58562625231568
C	3.07499583786050	6.38613066853907	3.57302399951910
S	4.57698242782632	5.86534255830481	2.83329395979624
S	2.88050257753895	6.66935882424945	5.19986935061725
S	3.88727272094843	6.49271860581936	-5.43296722573575
C	5.77638256370072	5.54485999398444	-3.10814363721237
H	5.81262771945371	5.15823764735012	-4.12656148891407
H	6.08298330735001	4.76948219710100	-2.40115829402645
H	6.42552972049122	6.41954702956741	-3.02047149652656
C	0.76001545794175	6.94077171849494	2.89318496362294
H	0.51755339731684	6.58080054250333	3.89313659913586
H	0.08442086632807	6.49687534787056	2.15995086314141
H	0.69470487015630	8.03140548772179	2.87004898438283
O	0.34564514569748	5.33299734222552	-0.11680744686718
H	0.96747786836958	7.67364889062266	-0.06177314700433
H	5.85938242082190	6.28503393424023	-0.17311591551174

4.3.10 ***8a^{Me}***

E = −2812.161170880679

C	3.87059536956213	6.44409211883145	1.36381604728448
C	2.53055183547329	6.83559987006231	1.40490149469227
P	1.48106294933357	6.83956891397398	0.01777578679127
C	2.54895962966625	6.73362724766186	-1.32240313981238
C	3.89732449828078	6.34614879081552	-1.30757491825040
P	4.98736488268960	6.04378533063199	0.05478533674342
N	4.39417203104526	6.22476735849993	-2.60897834604159
C	3.52385851755026	6.49055472569747	-3.63689697767088
S	1.96882579722753	6.91440882475712	-2.97423000707990
N	2.04547158391533	7.08423448163321	2.70512478815684
C	2.94718431332104	6.91307196858942	3.71121383375545
S	4.47132616065919	6.39953260697504	3.01497644660193
S	2.71635694693987	7.14149490349908	5.34745411425902
S	3.83217325981126	6.44419527068288	-5.27271322366375
C	5.78881990933091	5.84462574213402	-2.85512731366912
H	5.93388876236820	5.81532039174753	-3.93481072417656
H	5.97577820947102	4.86101817542781	-2.41624112475649
H	6.44936625655284	6.58732224714540	-2.39965952998005
C	0.68049245026941	7.56227117321213	2.95111173784441
H	0.50528026283336	7.50361129011570	4.02523274846053
H	-0.02903562099832	6.92332058390090	2.41912034908916

H	0.58557306834255	8.59843852601932	2.61543131287971
O	0.30841626149202	5.73410037203320	0.06109899723171
H	0.63622518558712	7.94872745917408	-0.04609247838998
C	0.70536251554538	4.32227759573606	0.11451639113528
H	-0.22655833331493	3.76117498205397	0.13513092512012
H	1.28759189661304	4.13821093309165	1.02038837483170
H	1.28810892983205	4.07279791869696	-0.77501003508621

*4.3.11 **8b**^{Me}*

E = −2772.797389647108

C	3.88317991489447	6.42302397494451	1.35961090357144
C	2.52941266933640	6.76454017592705	1.40224427631797
P	1.47673416030784	6.71100328474407	0.01984234712899
C	2.54039427054787	6.62866409374501	-1.32507905199793
C	3.90303253629515	6.29469049869383	-1.31027997388522
P	5.00925245842070	6.05229092185778	0.05045354875677
N	4.40166830201093	6.18303070069545	-2.61215747360181
C	3.52044881463403	6.40990280168836	-3.63978230451849
S	1.95189928584973	6.77958754431092	-2.97673232895718
N	2.04279527973768	7.01769887568943	2.70074688663261
C	2.95511993363251	6.89409633447408	3.70411657372293
S	4.49293297712603	6.42520654555826	3.00779577145761
S	2.72537624648544	7.13931294364533	5.33852256679835
S	3.82721796267320	6.36638038179184	-5.27615499532082
C	5.81012919871531	5.85811403819470	-2.85881029728920
H	5.95307642340235	5.82323371038377	-3.93862349768813
H	6.03896255834201	4.88795915940462	-2.41004544872001
H	6.44085774472967	6.63240174970045	-2.41368221792924
C	0.66386647789408	7.45326988948220	2.94747344306885
H	0.50306184760025	7.42279833769605	4.02499409040996
H	-0.02724672669549	6.77204679089596	2.44474586924980
H	0.52789990322371	8.47414191731021	2.58057828335227
O	0.31001958153397	5.59183025095571	0.07759986615027
H	0.60946209762617	7.80149074874957	-0.05347567998918
H	0.65840608167599	4.67994432946082	0.12824884327939

4.3.12 Li^{+}

E = −7.464875636692

4.3.13 OH^{-}

E = −76.031917082615

O	4.16593378121175	6.39804000000000	-6.89902000000000
H	5.13764621878824	6.39804000000000	-6.89902000000000

4.3.14 MeI

E = −337.877041050312

C	1.46212843491492	6.62801912582051	-0.92393140603205
I	0.01712812783369	5.01468452046864	-0.92394305728956
H	1.36869091430749	7.12746732704284	0.03688788763011

H 1.19884331227551 7.27958600432134 -1.75307012470709
H 2.43861360616838 6.16931834404667 -1.05565542560140

4.3.15 LiI

E = −305.563586048127
Li 2.49971615045000 5.62859234654984 -1.92590944401208
I 1.76895278575000 4.04171702035016 0.02975669701208

4.3.16 HCl

E = −461.191770195815
H -7.67865977832925 0.85802488644623 0.00000000000000
Cl -6.40024022167075 0.70233511355377 0.00000000000000

4.3.17 LiCl

E = −468.254403301347
Li -4.86629402849971 1.06762000000000 0.00000000000000
Cl -2.67762597150029 1.06762000000000 0.00000000000000

4.3.18 H_2O

E = −76.559004013456
O -3.29451847967782 2.87385625217368 -0.00108558972035
H -2.32492607238138 2.92145125185510 0.00137204261148
H -3.57277544794080 3.80264249597122 0.04687354710887

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