Electronic Supplementary Material (ESI) for ChemComm.

Triple dehydrofluorination as a route to amidine-functionalized, aromatic phosphorus heterocycles

Nathan T. Coles, Lucie J. Groth, Lea Dettling, Daniel S. Frost, Massimo Rigo, Samuel E. Neale and Christian Müller

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1 NMR spectra from initial reactions of 3a with H_2N^nPr

3a with 2 eq. of H_2N^nPr in protic DCM

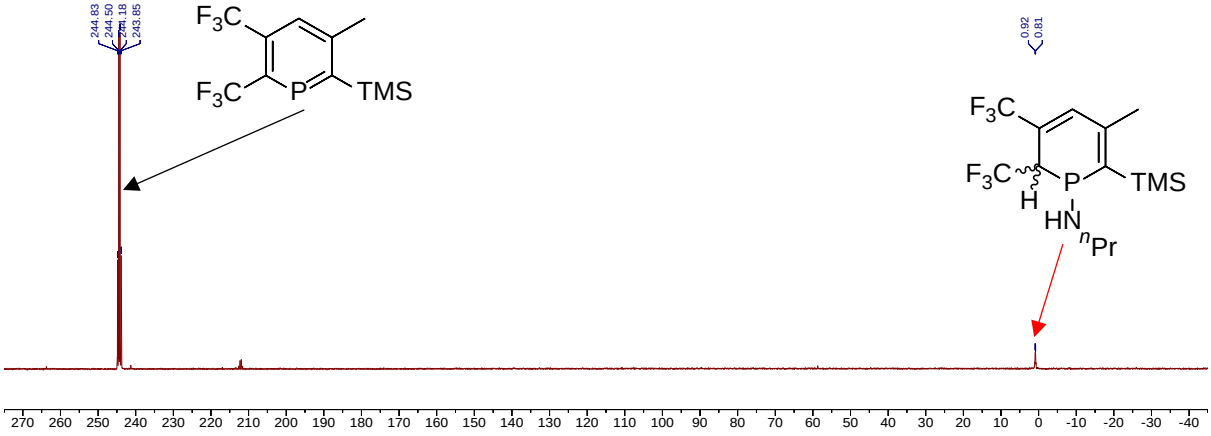


Figure S1 – Crude $^{31}P\{^1H\}$ NMR spectrum of the reaction between **3a** and 2 equivalents of $^nPrNH_2$ in protic DCM. **3a** and **4a** observed.

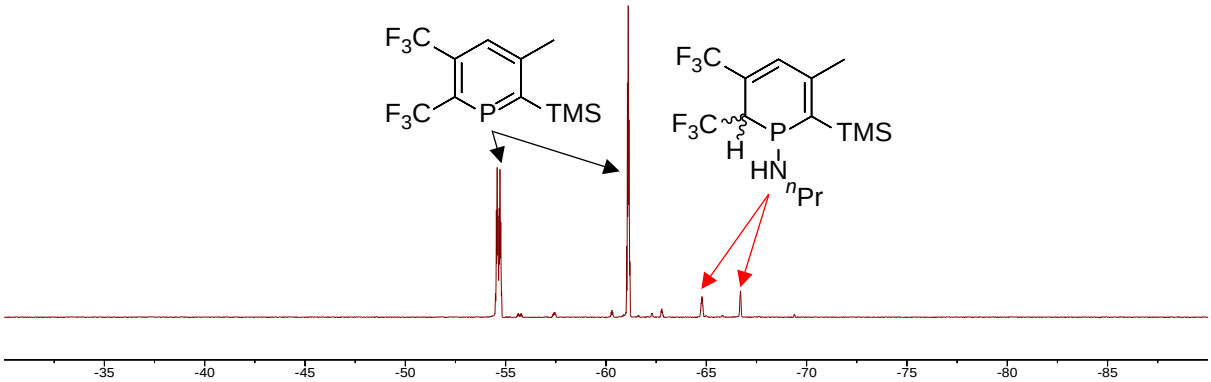


Figure S2 – Crude ^{19}F NMR spectrum of the reaction between **3a** and 2 equivalents of $^nPrNH_2$ in DCM. **3a** and **4a** observed.

3a with an additional 2 eq. of H_2N^nPr in protic THF after previously reacting in DCM (see above)

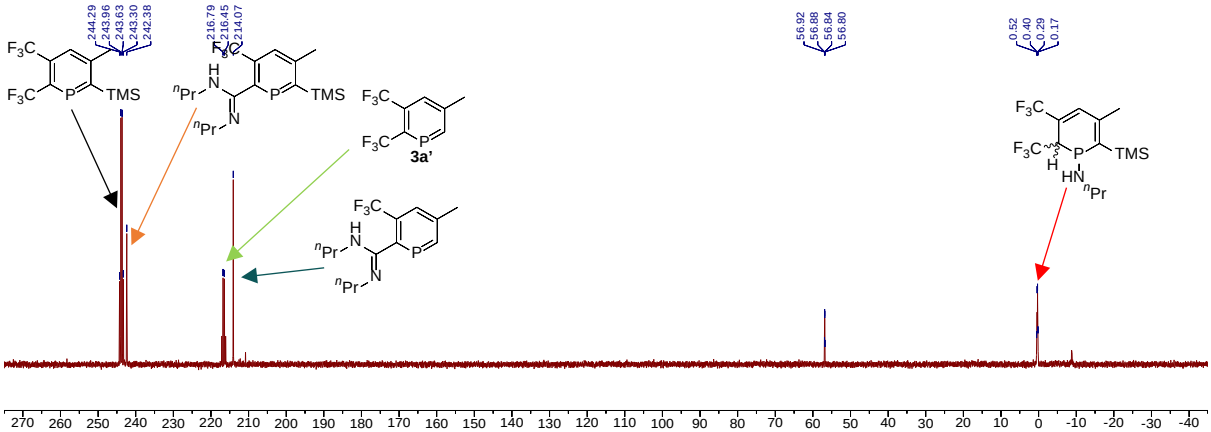


Figure S3 – Crude $^{31}P\{^1H\}$ NMR spectrum of the reaction between **3a** and 2 equivalents of $^nPrNH_2$ in protic THF, after previously being reacted in DCM (see above spectra). **3a**, **4a**, **5a**, **5a'** and desilylated **3a** observed. Peak at 56.9 ppm is a water decomposition product.

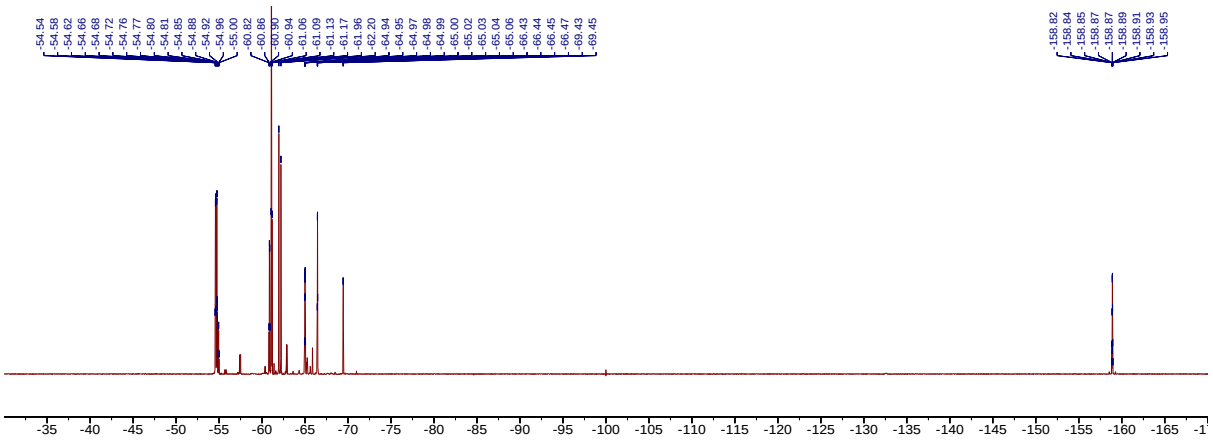


Figure S4 – Crude ^{19}F NMR spectrum of the reaction between **3a** and 2 equivalents of $^{n}PrNH_2$ in protic THF, after previously being reacted in DCM (see above spectra). **3a**, **4a**, **5a**, **5a'**, desilylated **3a** and TMS-F observed. Peak at -69.4 ppm is a water decomposition product.

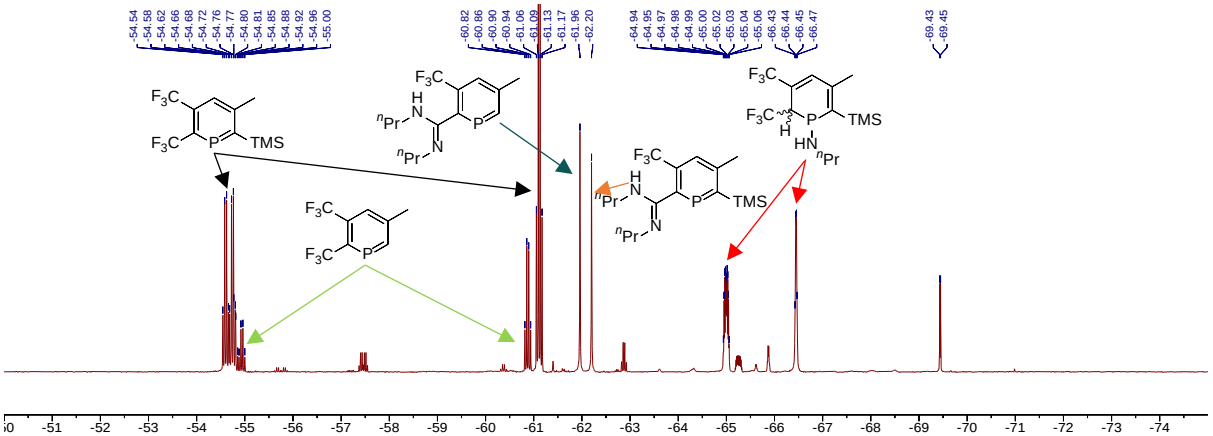


Figure S5 – Close up of the crude ^{19}F NMR spectrum of the reaction between **3a** and 2 equivalents of $^{n}PrNH_2$ in protic THF, after previously being reacted in DCM (see above spectra). **3a**, **4a**, **5a**, **5a'** and desilylated **3a** observed in the shown region. Peak at -69.4 ppm is a water decomposition product.

3a with 10 eq. of $H_2N^{n}Pr$ in protic THF

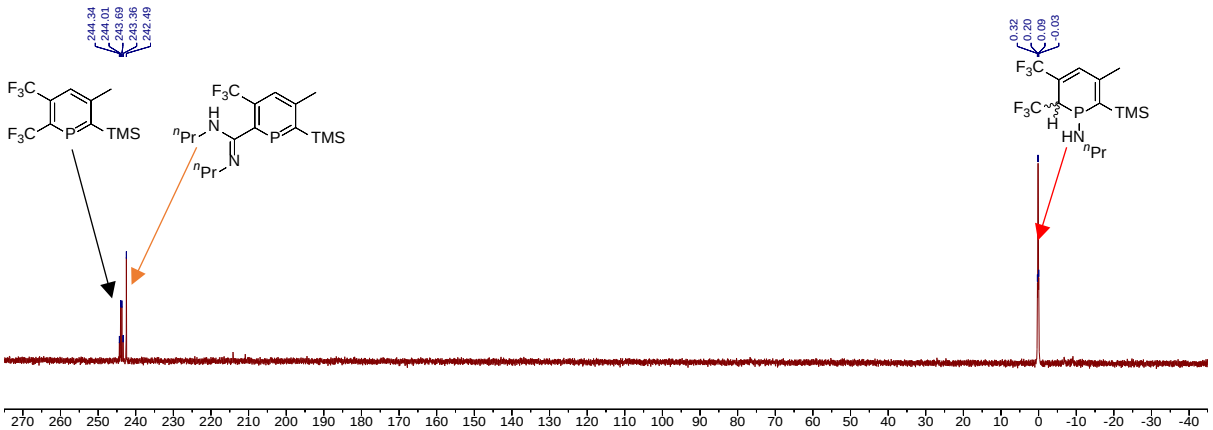


Figure S6 – Crude $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between **3a** and 10 equivalents of $^{n}PrNH_2$ in protic THF after 30 minutes. **3a**, **4a** and **5a**, **5a'** and desilylated **3a** observed.

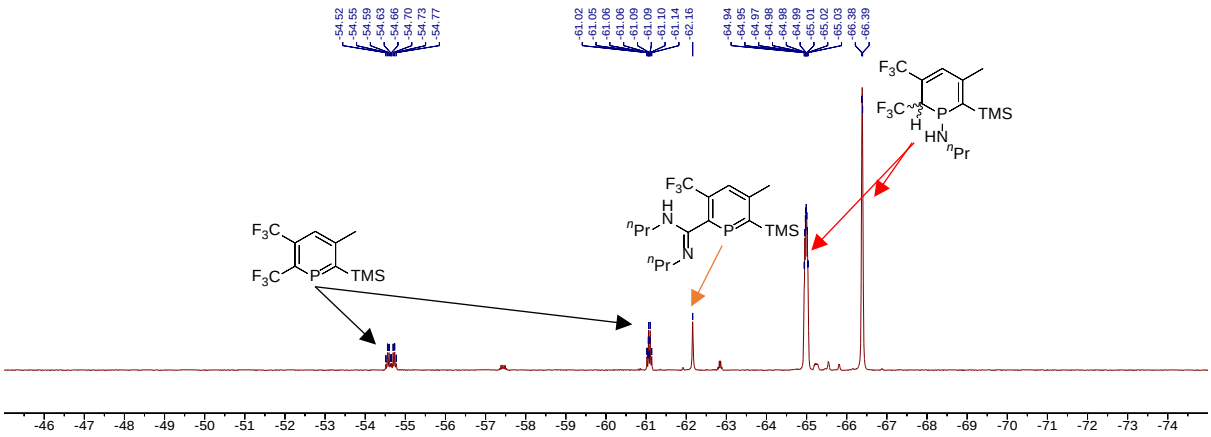


Figure S7 – Crude ^{19}F NMR spectrum of the reaction between **3a** and 10 equivalents of $^{n}PrNH_2$ in protic THF after 30 minutes. **3a**, **4a** and **5a**, **5a'** and desilylated **3a** observed.

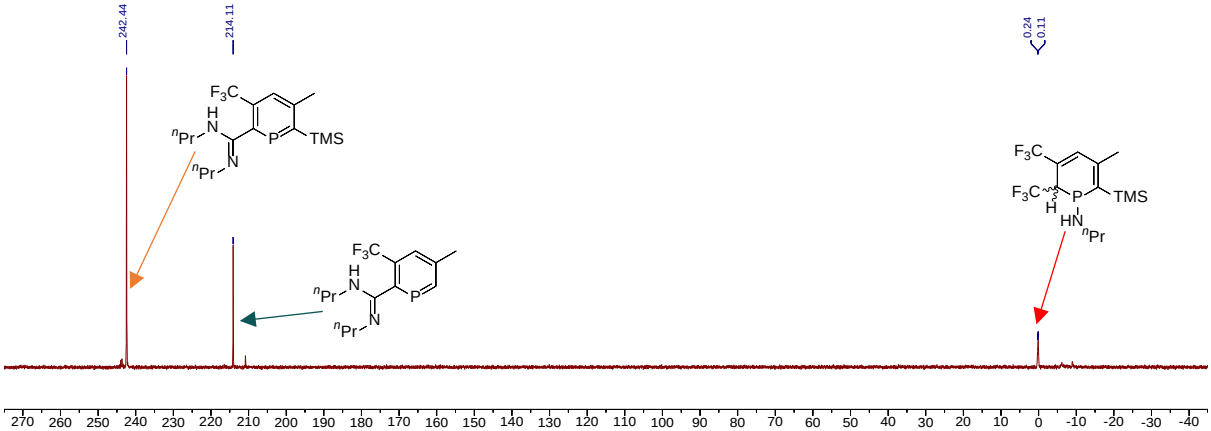


Figure S8 – Crude $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between **3a** and 10 equivalents of $^{n}PrNH_2$ in protic THF after 20 hours. **4a, 5a**, and **5a'** observed.

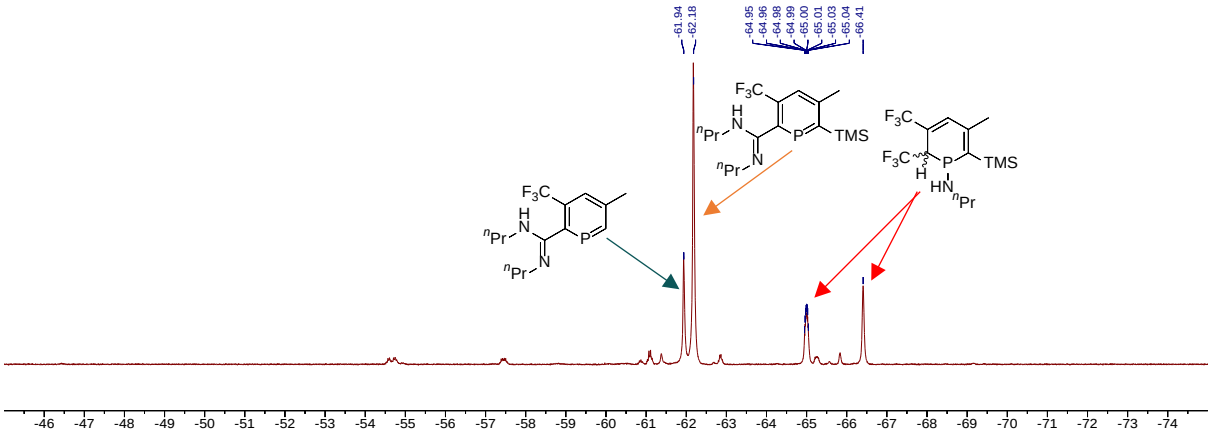


Figure S9 – Crude $^{31}P\{^{1}H\}$ NMR spectrum of the reaction between **3a** and 10 equivalents of $^{n}PrNH_2$ in protic THF after 20 hours. **4a, 5a**, and **5a'** observed.

3a with 10 eq. of H_2N^nPr in protic THF at 60 °C

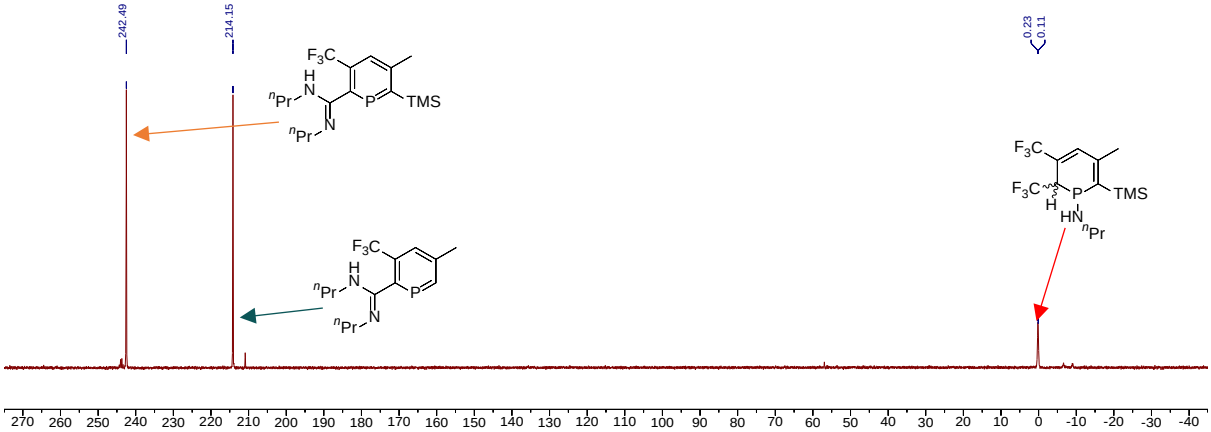


Figure S10 – Crude $^{31}P\{^1H\}$ NMR spectrum of the reaction between **3a** and 10 equivalents of $^nPrNH_2$ in protic THF after 1 hour at 60 °C. **4a, 5a**, and **5a'** observed.

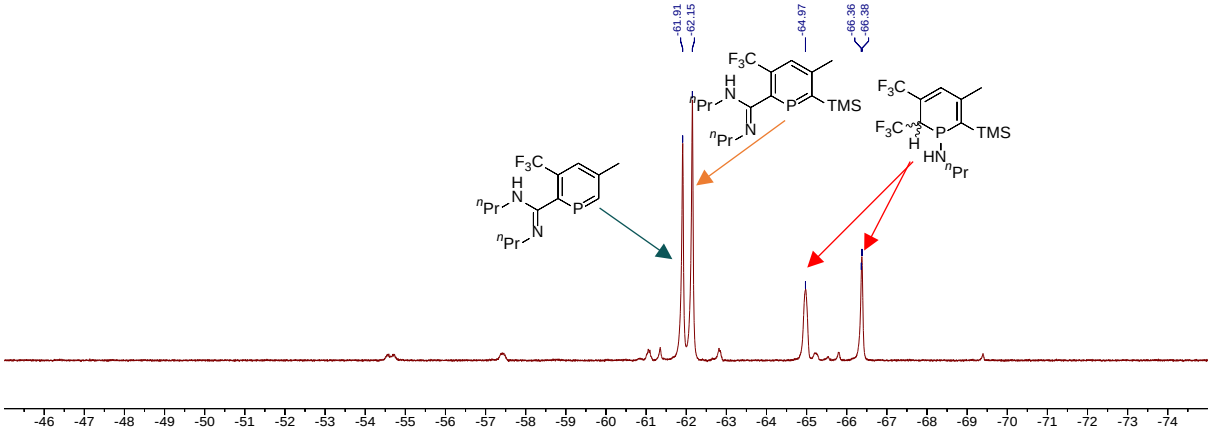


Figure S11 – Crude ^{19}F NMR spectrum of the reaction between **3a** and 10 equivalents of $^nPrNH_2$ in protic THF after 1 hour at 60 °C. **4a, 5a**, and **5a'** observed.

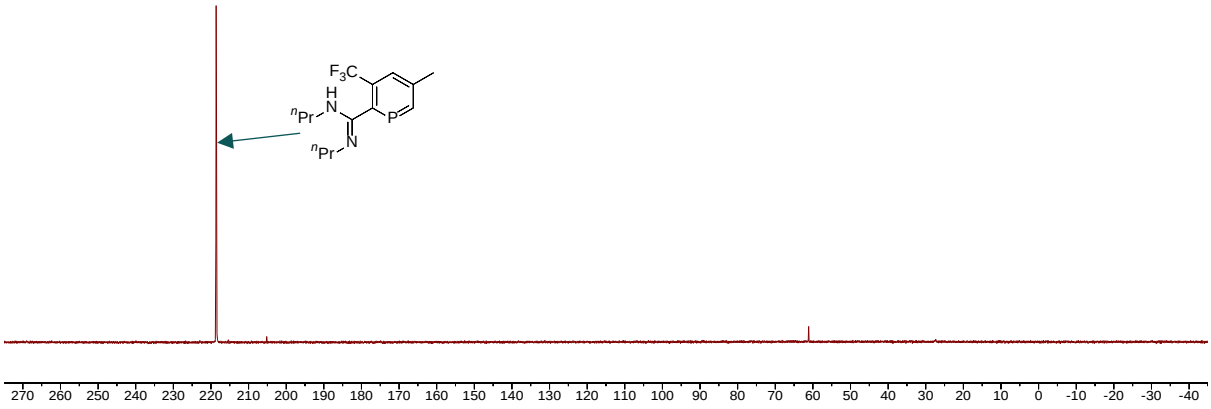


Figure S12 – Crude $^{31}P\{^1H\}$ NMR spectrum of the reaction between **3a** and 10 equivalents of $^nPrNH_2$ in protic THF after 1 hour at 60 °C and 2 months at room temperature. **5a'** observed.

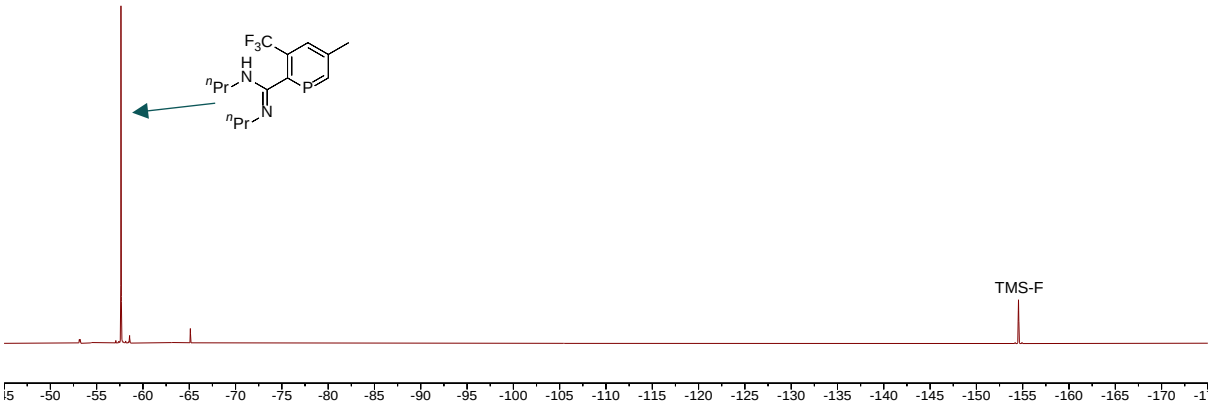


Figure S13 – Crude ^{19}F NMR spectrum of the reaction between **3a** and 10 equivalents of $^{n}PrNH_2$ in protic THF after 1 hour at 60 °C and then 2 months at room temperature. **5a'** and TMS-F observed.

2 Experimental procedures

General remarks

All reactions were performed under an argon atmosphere in oven-dried glassware using modified Schlenk techniques or in an MBraun glovebox unless otherwise stated. Solvents were dried using standard techniques or collected from the MBraun SPS and further dried over 3 Å molecular sieves prior to use. Amines (H_2N^nPr, H_2N^iPr, H_2NCy and H_2N^tBu) were dried over CaH_2 and distilled prior to use. H_2NMe was dried over Li/Na and condensed directly into the reaction flask. The ^1H, $^{13}C\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL ECA400/ECX400/ECZ600 spectrometer and all chemical shifts are reported relative to the residual resonance in the deuterated solvents. The HRMS EI mass spectra were measured on a Waters Autospec Premier. The HRMS ESI mass spectra were measured on an Agilent 6210 ESI-TOF. Low-temperature x-ray diffractometry was performed on a Bruker-AXS X8 Kappa Duo diffractometer with *IμS* micro-sources, performing ϕ-and ω-scans. Data was collected using a Photon 2 CPAD detector with Mo K_α radiation (λ = 0.71073 Å). The structures were solved by dual-space methods using SHELXT[1] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[2] following established refinement strategies[3]. The program Olex2[4] was also used to aid in the refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U*-value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in **Table S1** below. Tables **S2**, **S4**, **S6** and **S8** give all bond lengths for the structures and **S3**, **S5**, **S7** and **S9** give all angles for the structures.

Phosphinine synthesis

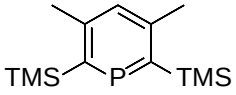
Adapted work-up for 2,6-TMS-3,5-methylphosphinine (1a) and 2,6-TMS-3,5-methylphosphinine (1b)

The synthesis procedure was carried out using the procedure first detailed by Le Floch *et al*[5] which was later adapted by Doux[6]. Once the reaction was complete, an alternative workup procedure was used. The reaction solvent was removed and the crude product was extracted with dry pentane and filtered through celite to remove all the insoluble solids. The pentane was removed and the crude product was purified by sublimation ($2x10^{-2}$ mbar, 60 °C). If the solid obtained after sublimation was orange then a second sublimation was carried out. If a pale yellow solid is obtained it can then be purified by crystallisation from a MeCN solution at -20 °C. The product is obtained as a colourless, crystalline solid.

For 2,6-TMS-3,5-phenylphosphinine a similar procedure can also be used. However, sublimation is usually unnecessary and pure product can be obtained through multiple crystallisations from MeCN at -20 °C.

Important note: Dry solvents must be used. The procedure by Cataldo *et al*[7] states that related phosphinines could be purified by column chromatography, however, we found that protodesilylation occurred if the silica was not thoroughly dried beforehand and so the decision to avoid column chromatography was taken.

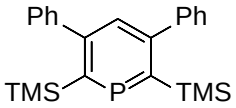
2,6-bis(trimethylsilyl)-3,5-dimethylphosphinine (**1a**)



Single crystals suitable for X-ray diffraction were grown from a saturated MeCN solution at -21 °C.

The data obtained is consistent with the literature.[7]
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10 (s, 1H, *p*-pinin*H*), 2.57 (d, $^{4}J_{P\text{-}H}$ = 1.5 Hz, 6H, Me), 0.43 (d, $^{4}J_{P\text{-}H}$ = 1.7 Hz, 18H, $SiMe_3$).
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 163.6 (d, $^{1}J_{P\text{-}C}$ = 85 Hz, *o*-pinin), 149.9 (d, $^{2}J_{P\text{-}C}$ = 12 Hz, *m*-pinin), 133.4 (d, $^{3}J_{P\text{-}C}$ = 23 Hz, *p*-pinin), 26.2 (d $^{3}J_{P\text{-}C}$ = 2 Hz, *C*H_3), 1.4 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, $SiMe_3$).
^{31}P ($CDCl_3$, 162 MHz): δ 265.5.

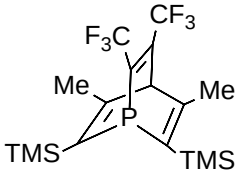
2,6-bis(trimethylsilyl)-3,5-diphenylphosphinine (**1b**)



The data obtained is consistent with the literature.[5]
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.36 (m, 6H, *m*/*p*-Ph*H*), 7.33-7.31 (m, 4H, *o*-Ph*H*), 7.24 (s, 1H, *p*-pinin*H*), 0.14 (d, $^{4}J_{P\text{-}H}$ = 1.4 Hz, 18H, $SiMe_3$).
^{13}C {^{1}H} NMR ($CDCl_3$, 101 MHz): δ 165.8 (d, $^{1}J_{P\text{-}C}$ = 90 Hz, *o*-pinin), 153.7 (d, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 145.8 (d, $^{2}J_{P\text{-}C}$ = 3 Hz, *i*-Ph), 132.4 (d, $^{3}J_{P\text{-}C}$ = 21 Hz, *p*-pinin), 129.1 (s, *o*-Ph), 127.9 (s, *m*-Ph), 127.5 (s, *p*-Ph), 2.2 (d, $^{3}J_{P\text{-}C}$ = 10 Hz, Si*Me*$_3$).
^{31}P ($CDCl_3$, 162 MHz): δ 270.6.

Synthesis of CF_3-substituted phosphabarrelenes

2a

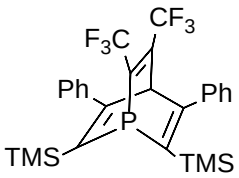


A solution of 2,6-bis(trimethylsilyl)-3,5-bis(methyl)-phosphinine (**1a,** 4 mmol, 1.07 g) in toluene (25 mL) was degassed and hexafluorobut-2-yne (6 mmol) was condensed into the flask and sealed under vacuum. The reaction was stirred at 60 °C for 16 hours and once finished, the

solvent was removed. The crude phosphabarrelene was purified by sublimation (45 °C, 2x10^{-2} mbar) yielding **2a** as an off-white microcrystalline solid, 1.58 g (3.7 mmol, 92 %).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.11 (d, $^{4}J_{P-H}$ = 1.4 Hz, 1H, *p*-C*H),* 2.20 (d, $^{4}J_{P-H}$ = 1.1 Hz, 6H, *m*-C*H$_3$*), 0.19 (d, $^{4}J_{P-H}$ = 1.2 Hz, 18H, SiMe$_3$).
^{13}C {^{1}H,^{19}F} NMR (CDCl$_3$, 101 MHz): δ 167.7 (d, $^{2}J_{P-C}$ = 2 Hz, *m*-*C*Me), 148.4 (d, $^{2}J_{P-C}$ = 4 Hz, *m*-*C*-CF$_3$), 146.1 (d, $^{1}J_{P-C}$ = 46 Hz, *o*-*C*-CF$_3$), 136.0 (d, $^{1}J_{P-C}$ = 52 Hz, *o*-*C*-TMS), 123.3 (d, $^{2}J_{P-C}$ = 27 Hz, *o*-*C*F$_3$), 121.9 (s, *m*-*C*F$_3$), 69.6 (d, $^{3}J_{P-C}$ = 7 Hz, *p*-*C*H), 24.1 (d, $^{3}J_{P-C}$ = 3 Hz, *m*-*Me*), 0.1 (d, $^{3}J_{P-C}$ = 7 Hz, *o*-Si*Me$_3$*).
^{19}F (CDCl$_3$, 377 MHz): δ -56.2 (dq, $^{3}J_{P-F}$ = 30 Hz, $^{5}J_{F-F}$ = 12 Hz, *o*-C*F$_3$*), -61.5 (dq, $^{5}J_{F-F}$ = 12 Hz, $^{4}J_{P-F}$ = 1 Hz, *m*-C*F$_3$*).
^{31}P{^{1}H} (CDCl$_3$, 162 MHz): δ -51.3 (q, $^{3}J_{P-F}$ = 30 Hz).
HRMS (EI): Calculated $[M]^{+\cdot}$: 430.1131, Observed: 430.1133.

2b

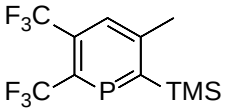


A solution of 2,6-bis(trimethylsilyl)-3,5-bis(phenyl)-phosphinine (7.6 mmol, 3.0 g) in toluene (50 mL) was degassed, hexafluorobut-2-yne (11.5 mmol) was condensed into the flask and sealed under vacuum. The reaction was stirred at 60 °C for 17 hours and once finished, the volatiles were removed. The crude phosphabarrelene was purified by crystallization from MeCN (45 mL) to obtain the product as a colourless solid 3.6 g (6.5 mmol, 86 %).

The data obtained was consistent with the previous literature.[8]
^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.32-7.28 (m, 6H, *m*/*p*-Ph*H)*, 7.02-6.96 (m, 4H, *o*-Ph*H)*, 5.75 (s, 1H, *p*-C*H),* -0.03 (d, $^{4}J_{P-H}$ = 1.0 Hz, 18H, SiMe$_3$).
^{19}F (CDCl$_3$, 377 MHz): δ -56.1 (dq, $^{3}J_{P-F}$ = 30 Hz, $^{5}J_{F-F}$ = 12 Hz, *o*-C*F$_3$*), -60.9(dq, $^{5}J_{F-F}$ = 12 Hz, $^{4}J_{P-F}$ = 1 Hz, *m*-C*F$_3$*).
^{31}P{^{1}H} (CDCl$_3$, 162 MHz): δ -50.7 (q, $^{3}J_{P-F}$ = 30 Hz).

Synthesis of CF$_3$-substituted phosphinines

2-(trimethylsilyl)-3-methyl-5,6-bis(trifluoromethyl)phosphinine (**3a**)

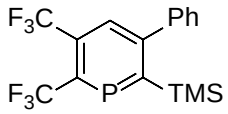


Phosphabarrelene **2a** (2 g, 4.6 mmol) was dissolved in toluene (20 mL) and heated in a thick glass walled reaction flask to 200 °C. The reaction was heated for 2 h before cooling and removing the solvent and excess acetylene. The progress of the reaction was monitored by ^{19}F NMR. If the reaction did not reach completion additional toluene was added (20 mL) and the reaction heated for a further 2h. This was continued until a conversion of at least 94% was achieved. The crude product was then purified by sublimation (cold finger temperature – 5 °C,

heating bath 35 °C, vacuum 2 x 10^{-1} mbar) and isolated as colourless needles. 1.3 g (4 mmol, 87 %).

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.75 (br. s, 1H, *p*-pinin*H*), 2.73 (s, 3H, Me), 0.49 (d, $^{4}J_{P\text{-}H}$ = 1.6 Hz, 9H, $SiMe_3$).
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 173.2 (d, $^{1}J_{P\text{-}C}$ = 82 Hz, *o*-*C*$SiMe_3$), 154.0 (d, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 153.0 (dq, $^{1}J_{P\text{-}C}$ = 72, $^{2}J_{F\text{-}C}$ = 30 Hz, *o*-*C*CF_3), 143.5 (d, $^{3}J_{P\text{-}C}$ = 19 Hz, *i*-Ph), 134.7 (dq, $^{2}J_{F\text{-}C}$ = 32, $^{2}J_{P\text{-}C}$ = 13 Hz, *m*-*C*CF_3), 131.0 (dq, $^{3}J_{P\text{-}C}$ = 15 Hz, $^{3}J_{F\text{-}C}$ = 5.9, *p*-*C*H), 125.8 (qd, $^{1}J_{F\text{-}C}$ = 275, $^{2}J_{P\text{-}C}$ = 25 Hz, *o*-*C*F_3), 122.8 (q, $^{1}J_{F\text{-}C}$ = 277 Hz, *m*-*C*F_3), 26.4 (d, $^{3}J_{P\text{-}C}$ = 4 Hz, Me), 0.7 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, *o*-Si*Me*$_3$).
^{19}F (CD_2Cl_2, 565 MHz): δ -53.6 (dq, $^{3}J_{P\text{-}F}$ = 53 Hz, $^{5}J_{F\text{-}F}$ = 15 Hz, *o*-C*F*$_3$), -60.1 (q, $^{5}J_{F\text{-}F}$ = 15 Hz, *m*-C*F*$_3$).
^{31}P{^{1}H} ($CDCl_3$, 243 MHz): δ 245.6 (q, $^{3}J_{P\text{-}F}$ = 53 Hz).
HRMS (EI): Calculated $[M]^{+\cdot}$: 303.0188, Observed: 303.0180.

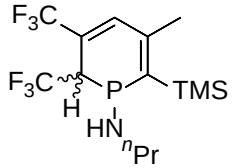
2-(trimethylsilyl)-3-phenyl-5,6-bis(trifluoromethyl)phosphinine (**3b**)



A solution of phosphabarrelene **2b** (1.4 g, 2.5 mmol) in toluene (10 mL) was heated in a microwave reactor to 200 °C for 110 min. The reaction was monitored by ^{31}P {^{1}H} NMR, which showed no evidence of residual barrelene. The crude product was purified by trap-to-trap distillation (100 °C, 1x10^{-3} mbar) yielding a colourless oil which crystallised upon cooling to −20 °C, yielding crystals suitable for single crystal X-ray diffraction. 695 mg (1.8 mmol, 73 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (br. s, 1H, *p*-pinin*H*), 7.49-7.43 (m, 3H, *o*/*p*-Ph*H*), 7.30-7.26 (m, 2H, *m*-Ph*H*), 0.14 (d, $^{4}J_{P\text{-}H}$ = 1.8 Hz, 9H, $SiMe_3$).
^{13}C {^{1}H,^{19}F} NMR ($CDCl_3$, 101 MHz): δ 173.5 (d, $^{1}J_{P\text{-}C}$ = 85 Hz, *o*-*C*$SiMe_3$), 157.1 (d, $^{2}J_{P\text{-}C}$ = 10 Hz, *m*-pinin), 153.0 (d, $^{1}J_{P\text{-}C}$ = 74 Hz, *o*-*C*CF_3), 143.5 (d, $^{3}J_{P\text{-}C}$ = 19 Hz, *i*-Ph), 134.2 (d, $^{2}J_{P\text{-}C}$ = 13 Hz, *m*-*C*CF_3), 130.7 (d, $^{3}J_{P\text{-}C}$ = 15 Hz, *p*-pinin), 128.8 (br., *m*/*p*-Ph), 128.4 (*o*-Ph), 125.2 (d, $^{2}J_{P\text{-}C}$ = 25 Hz, *o*-*C*F_3), 122.8 (s, *m*-*C*F_3), 1.7 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, *o*-Si*Me*$_3$).
^{19}F ($CDCl_3$, 377 MHz): δ -53.4 (dq, $^{3}J_{P\text{-}F}$ = 53 Hz, $^{5}J_{F\text{-}F}$ = 15 Hz, *o*-C*F*$_3$), -59.7 (q, $^{5}J_{F\text{-}F}$ = 15 Hz, *m*-C*F*$_3$).
^{31}P{^{1}H} ($CDCl_3$, 162 MHz): δ 249.4 (q, $^{3}J_{P\text{-}F}$ = 53 Hz).
HRMS (EI): Calculated $[M\text{-}CH_3]^{+}$: 365.0345, Observed: 365.0310.

Characterisation of intermediate species 4a

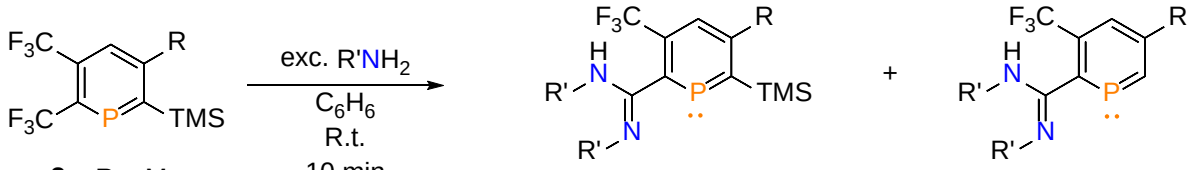


3a (29 mg, 0.1 mmol) was placed into a Schlenk flask followed by toluene (0.5 mL). To this was added $H_2N^{n}Pr$ (74 µL, 1 mmol, 10 eq.) and the reaction left to react for 2 hours. After this time, all of the volatiles were removed from the reaction and the residue was dissolved in C_6D_6.

The compound was characterised without further purification. A conversion of ~77% from **3a** to **4a** was achieved based on the relative integrals of **3a**/**4a** (Figure S34).

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 6.60 (br. s, 1H, *p*-pinin), 3.52 (qd, $^{3}J_{F\text{-}H}$ = 10.6 Hz, $^{2}J_{P\text{-}H}$ = 2.5 Hz, 1H, *o*-pinin), 2.23-2.16 (m, 1H, NCH_2), 2.15-2.08 (m, 1H, NCH_2), 1.70 (d, $J_{P\text{-}H}$ = 3.9 Hz, 2H, Me), 0.98 (app. h, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2H, $NCH_2CH_2CH_3$), 0.58 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 3H, CH_2CH_3), 0.25 (br. s, 9H, $SiMe_3$) ppm.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 146.6 (s, *C*Me), 136.0 (m, pinin-*C*H), 131.9 (d, $^{1}J_{P\text{-}C}$ = 43 Hz, P*C*SiMe$_3$), 124.0 (qd, $^{1}J_{F\text{-}C}$ = 273 Hz, $^{2}J_{P\text{-}C}$ = 3 Hz, *C*F$_3$),123.5 (q, $^{1}J_{F\text{-}C}$ = 277 Hz, *C*F$_3$), 117.1 (qd, $^{1}J_{F\text{-}C}$ = 32 Hz, $^{1}J_{F\text{-}C}$ = 5 Hz F$_3$C*C*), 47.1 (d, $^{2}J_{P\text{-}C}$ = 6 Hz, N*C*H$_2$), 41.4 (dq, $^{2}J_{P\text{-}C}$ = 47 Hz, $^{2}J_{F\text{-}C}$ = 26 Hz, P*C*HCF$_3$), 25.8 (d, $^{3}J_{P\text{-}C}$ = 4 Hz, $NCH_2CH_2CH_3$), 24.6 (d, $^{3}J_{P\text{-}C}$ = 4 Hz, pinin-*C*H$_3$), 11.2 (s, $NCH_2CH_2CH_3$), 0.3 (d, $^{3}J_{C\text{-}P}$ = 7 Hz, Si*Me*$_3$) ppm.
^{19}F (CD_2Cl_2, 565 MHz): δ -63.1 (m, *o*-C*F*$_3$), -64.9 (br. s, *m*-C*F*$_3$) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 1.6 (q, $^{3}J_{P\text{-}F}$ = 18 Hz) ppm.

Synthesis of amidine functionalised phosphinines



3a, R = Me
3b, R = Ph

5a, R = Me, R' = ^{n}Pr
5b, R = Ph, R' = ^{n}Pr

6a, R = Me, R' = Me
6b, R = Ph, R' = Me

7a, R = Me, R' = ^{i}Pr
7b, R = Ph, R' = ^{i}Pr

8a, R = Me, R' = Cy
8b, R = Ph, R' = Cy

9a, R = Me, R' = ^{t}Bu

5a', R = Me, R' = ^{n}Pr
5b', R = Ph, R' = ^{n}Pr

6a', R = Me, R' = Me
6b', R = Ph, R' = Me

7a', R = Me, R' = ^{i}Pr
7b', R = Ph, R' = ^{i}Pr

8a', R = Me, R' = Cy
8b', R = Ph, R' = Cy

9a', R = Me, R' = ^{t}Bu

Scheme S1- Overview of synthesized compounds.

Additional notes:

1. These species are highly water sensitive and readily decompose. They are particularly sensitive during the reaction. Secondly, if the reactions are performed in a Schlenk tube with stirring more protodesilylated product is obtained.

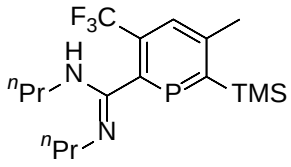
2. The masses given below for **3a/b** for the spectroscopic yield were the masses used when calculating the spectroscopic yield due to **3a/b** readily melting at room temperature it was difficult to reliably measure out set amounts.

3. Yields were not calculated for the desilyl species as these were minor species, with the exception of the reactions with $MeNH_2$.

Synthesis of 5, 7-9

CF_3-substituted phosphinine (**3a/b**, 30-40 mg) was placed into a J-Young NMR tube. To this, for the at room temperature liquid amines dry benzene (0.1 mL) was added to dissolve the phosphinine. Amine (0.5 mL) was added to the tube, yielding a viscous solution and a large quantity of precipitate. Once complete, the reactions were filtered using a canula fitted with glass filter paper. The solid was washed with dry benzene (3 x 0.5 mL) and the solvent was removed from the filtrate *in vacuo*. Removing the solvent yielded extremely sticky, viscous oils. Therefore, the yields were calculated *in situ* against a PPh_3 standard.

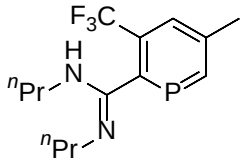
5a



3a (40.0 mg, 0.126 mmol). Spectroscopic yield (0.059 mmol, 47%)

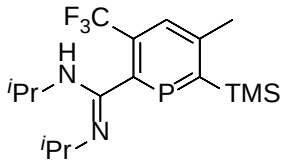
^{1}H NMR (C_6D_6, 600 MHz): δ 7.40 (s, 1H, *p*-pinin), 3.54 (br. s, 1H, N*H*), 3.30 (br. s, 4H, NCH_2), 2.16 (s, 3H, Me), 1.66 (br. s, 4H, CH_2), 0.91 (br. s, 6H, CH_3), 0.31 (d, $^3J_{H,P}$ = 1.5 Hz, 9H, $SiMe_3$) ppm.
^{13}C {^{1}H} NMR (C_6D_6, 151 MHz): δ 174.4 (d, $^1J_{P-C}$ = 85 Hz, *o*-pininTMS), 160.0 (d, $^1J_{P-C}$ = 70 Hz, *o*-pinin), 154.6 (d, $^2J_{P-C}$ = 18 Hz, amidine-*C*), 149.8 (d, $^2J_{P-C}$ = 13 Hz, *m*-pinin), 133.3 (qd, $^2J_{F-C}$ = 29, $^2J_{P-C}$ = 11 Hz, *m*-pinin), 128.8 (dq, $^3J_{P-C}$ = 17, $^3J_{F-C}$ = 4 Hz, *p*-pinin), 124.0 (q, $^1J_{F-C}$ = 278 Hz, *C*F_3), 25.8 (d, $^3J_{P-C}$ = 2 Hz, Me), 12.1 (br. s, CH_3), 0.69 (d, $^3J_{P-C}$ = 11 Hz, TMS) ppm. Neither propyl CH_2 moieties could be located.
^{19}F (C_6D_6, 565 MHz): δ – 60.5 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 243 MHz): δ 244.6 (s) ppm.
HRMS (ESI): Calculated $[M+H]^+$: 377.1785, Observed: 377.1797; Calculated $[M+H_3O]^+$: 395.1890, Observed: 395.1906.

5a'



^{1}H NMR (C_6D_6, 600 MHz): δ 8.18 (d, $^2J_{H,P}$ = 39.4 Hz, 1H, *o*-pinin), 7.36 (s, 1H, *p*-pinin), 1.90 (s, 3H, Me) ppm. The propyl groups overlap with compound **6a**.
^{19}F (C_6D_6, 565 MHz): δ -60.3 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 243 MHz): δ 216.3 (s) ppm.
HRMS (ESI): Calculated $[M+H]^+$: 305.1389, Observed: 305.1388; Calculated $[M+H_3O]^+$: 323.1495, Observed: 323.1494.

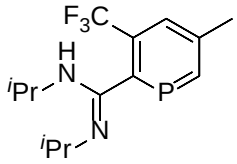
7a



3a (41.4 mg, 0.130 mmol). Spectroscopic yield (0.065 mmol, 49%).

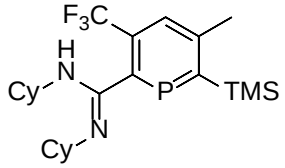
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.56 (s, 1H, *p*-pinin), 3.63 (br. s, 1H, N*H*), 2.67 (s, 3H, Me), 1.17-0.95 (br., 12H, ^{i}Pr-CH_3), 0.46 (d, $^{3}J_{H,P}$ = 1.7 Hz, 9H, $SiMe_3$) ppm. ^{i}Pr-CH cannot be located due to fluxionality of this compound.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 174.4 (d, $^{1}J_{P\text{-}C}$ = 85 Hz, *o*-pininTMS), 159.1 (d, $^{1}J_{P\text{-}C}$ = 69 Hz, *o*-pinin), 152.8 (d, $^{2}J_{P\text{-}C}$ = 19 Hz, amidine-*C*), 150.2 (d, $^{2}J_{P\text{-}C}$ = 13 Hz, *m*-pinin), 133.0 (qd, $^{2}J_{F\text{-}C}$ = 29, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 128.8 (dq, $^{3}J_{P\text{-}C}$ = 18, $^{3}J_{F\text{-}C}$ = 5 Hz, *p*-pinin), 124.0 (q, $^{1}J_{F\text{-}C}$ = 277 Hz, CF_3), 26.3 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, Me), 23.8 (br. s, ^{i}Pr-CH_3), 0.82 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, TMS) ppm. ^{i}Pr-*C*H signals could not be located.
^{19}F (CD_2Cl_2, 565 MHz): δ -60.5 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 243.1 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 377.1785, Observed: 377.1786; Calculated $[M+H_3O]^+$: 395.1890, Observed: 395.1892.

7a'



^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.77 (d, $^{2}J_{H,P}$ = 39.6 Hz, 1H, *o*-pinin), 7.65 (s, 1H, *p*-pinin), 2.56 (s, 3H, Me) ppm. ^{i}Pr-CH_3 overlaps with compound **7a** and ^{i}Pr-CH can not be located.
^{19}F (CD_2Cl_2, 565 MHz): δ -60.2 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 215.0 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 305.1389, Observed: 305.1386; Calculated $[M+H_3O]^+$: 323.1495, Observed: 323.1495.

8a

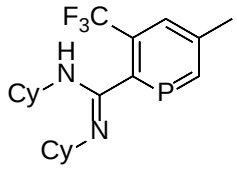


3a (41.4 mg, 0.130 mmol). Spectroscopic yield (0.066 mmol, 50%).

^{1}H NMR (C_6D_6, 600 MHz): δ 7.40 (s, 1H, *p*-pinin), 3.51 (br. s, 1H, N*H*), 2.40 (m, 1H, Cy), 2.14 (s, 3H, Me), 2.01 (br., 2H Cy), 1.66-0.87 (m, 19H, Cy), 0.31 (d, $^{3}J_{H,P}$ = 1.3 Hz, 9H, $SiMe_3$) ppm.

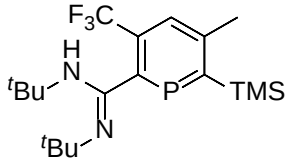
^{13}C {^{1}H} NMR (C_6D_6, 151 MHz): δ 174.1 (d, $^{1}J_{P\text{-}C}$ = 85 Hz, *o*-pininTMS), 160.0 (d, $^{1}J_{P\text{-}C}$ = 70 Hz, *o*-pinin), 151.8 (d, $^{2}J_{P\text{-}C}$ = 19 Hz, amidine-*C*), 149.8 (d, $^{2}J_{P\text{-}C}$ = 13 Hz, *m*-pinin), 133.3 (m, *m*-pinin), 128.9 (dq, $^{3}J_{P\text{-}C}$ = 18, $^{3}J_{F\text{-}C}$ = 4 Hz, *p*-pinin), 124.4 (q, $^{1}J_{F\text{-}C}$ = 278 Hz, *C*F_3), 50.7 (s, Cy), 37.3 (s, Cy), 26.5 (s, Cy), 25.8 (s, Me), 25.5 (s, Cy), 25.4-25.1 (br. , Cy), 0.73 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, TMS) ppm.
^{19}F (C_6D_6, 565 MHz): δ -59.7 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 243 MHz): δ 244.5 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 457.2410, Observed: 457.2462.

8a'



^{1}H NMR (C_6D_6, 600 MHz): δ 8.17 (d, $^{2}J_{H,P}$ = 39.2 Hz, 1H, *o*-pinin), 7.36 (s, 1H, *p*-pinin) ppm. Cy signals overlap with **8a**.
^{19}F (CD_2Cl_2, 565 MHz): δ -59.5 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 216.2 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 385.2015, Observed: 385.2057.

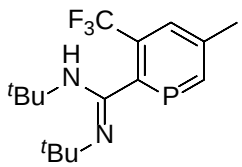
9a



3a (39.8 mg, 0.125 mmol). Spectroscopic yield (0.054 mmol, 43%).

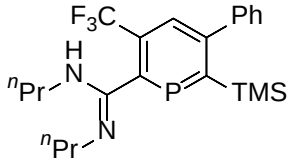
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.46 (s, 1H, *p*-pinin), 3.36 (br. s, 1H, N*H*), 2.64 (s, 3H, Me), 1.50-0.87 (br., 18H, ^{t}Bu-CH_3), 0.45 (d, $^{3}J_{H,P}$ = 1.7 Hz, 9H, $SiMe_3$) ppm.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 173.1 (d, $^{1}J_{P\text{-}C}$ = 84 Hz, *o*-pininTMS), 161.9 (d, $^{1}J_{P\text{-}C}$ = 69 Hz, *o*-pinin), 149.3 (d, $^{2}J_{P\text{-}C}$ = 13 Hz, *m*-pinin), 146.6 (d, $^{2}J_{P\text{-}C}$ = 21 Hz, amidine-*C*), 132.7 (qd, $^{2}J_{F\text{-}C}$ = 29, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 128.4 (dq, $^{3}J_{P\text{-}C}$ = 18, $^{3}J_{F\text{-}C}$ = 4 Hz, *p*-pinin), 123.9 (q, $^{1}J_{F\text{-}C}$ = 278 Hz, *C*F_3), 25.8 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, Me), 0.48 (d, $^{3}J_{P\text{-}C}$ = 11 Hz, TMS) ppm. ^{t}Bu-*C*H_3 signals could not be located.
^{19}F (CD_2Cl_2, 565 MHz): δ -59.1 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 244.1 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 405.2097, Observed: 405.2107; Calculated $[M+H_3O]^+$: 423.2203, Observed: 423.2226.

9a'



^{19}F (CD_2Cl_2, 565 MHz): δ -58.9 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 215.8 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 333.1702, Observed: 331.1702; Calculated $[M+H_3O]^+$: 351.1808, Observed: 351.1825.

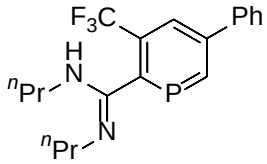
5b



3b (30.0 mg, 0.079 mmol). Spectroscopic yield (0.017 mmol, 22%).

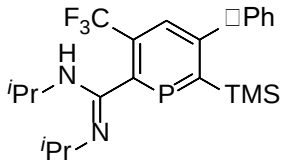
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.62 (s, 1H, *p*-pinin), 7.47-7.41 (m, 3H, *o*/*p*-Ph*H*), 7.33-7.25 (m, 2H, *m*-Ph*H*), 4.19 (br. s, 1H, N*H*), 3.08 (br. s, 4H, ^{n}Pr-CH_2), 1.56 (br. s, 4H, ^{n}Pr-CH_2), 0.91 (br. s, 6H, ^{n}Pr-CH_3), 0.11 (s, 9H, $SiMe_3$) ppm.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 175.4 (d, $^1J_{P\text{-}C}$ = 88 Hz, *o*-pinin), 160.8 (d, $^1J_{P\text{-}C}$ = 70 Hz, *o*-pinin), 155.5 (d, $^2J_{C\text{-}P}$ = 18 Hz, amidine-*C*), 154.7 (d, $^2J_{C\text{-}P}$ = 12 Hz, *m*-pinin), 144.6 (s, *i*-Ph), 132.4 (dq, $^2J_{F\text{-}C}$ = 29, $^2J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 129.3 (s, *o*/*p*-Ph), 128.8 (m, *p*-pinin), 128.5 (s, *m*-Ph), 123.8 (q, $^1J_{F\text{-}C}$ = 278 Hz, *C*F_3), 24.5 (br. s, ^{n}Pr-*C*H_2), 12.0 (s, ^{n}Pr-*C*H_3), 1.8 (d, $^3J_{C\text{-}P}$ = 9 Hz, $SiMe_3$) ppm.
^{19}F (CD_2Cl_2, 565 MHz): δ -61.1 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 247.3 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 439.1941, Observed: 439.1780.

5b'



Observed alongside **5b**.
^{19}F (CD_2Cl_2, 565 MHz): δ -60.9 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 216.7ppm.

7b

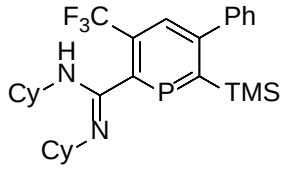


3b (30.0 mg, 0.079 mmol). Spectroscopic yield (0.036 mmol, 46%).

^{1}H NMR (C_6D_6, 600 MHz): δ 7.61 (s, 1H, *p*-pinin), 7.49-7.41 (m, 3H, *o*/*p*-Ph*H*), 7.33-7.25 (m, 2H, *m*-Ph*H*), 4.11 (br. s, 1H, ^{i}Pr-C*H*), 3.73 (br. s, 1H, N*H*), 3.05 (br. s, 1H, ^{i}Pr-C*H*), 1.12 (br. s, 12H, ^{i}Pr-CH_3), 0.10 (s, 9H, $SiMe_3$) ppm.

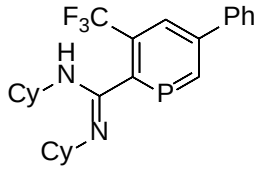
^{13}C {^{1}H} NMR (C_6D_6, 151 MHz): δ 174.9 (d, $^{1}J_{P\text{-}C}$ = 88 Hz, *o*-pinin), 160.8 (d, $^{1}J_{P\text{-}C}$ = 70 Hz, *o*-pinin), 154.6 (d, $^{2}J_{C\text{-}P}$ = 14 Hz, *m*-pinin), 152.6 (d, $^{2}J_{C\text{-}P}$ = 18 Hz, amidine-*C*), 144.6 (s, *i*-Ph), 132.3 (dq, $^{2}J_{F\text{-}C}$ = 29, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 129.3 (s, *o*/*p*-Ph), 128.7 (s, *p*-pinin), 128.5 (s, *m*-Ph), 123.9 (q, $^{1}J_{F\text{-}C}$ = 278 Hz, *C*F_3), 50.6 (br. s, ^{i}Pr-*C*H), 43.9 (br. s, ^{i}Pr-*C*H), 23.8 (br. s, ^{i}Pr-*C*H_3), 1.8 (d, $^{3}J_{C\text{-}P}$ = 10 Hz, $SiMe_3$) ppm.
^{19}F (C_6D_6, 565 MHz): δ -60.4 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 243 MHz): δ 246.5 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 439.1941, Observed: 439.1885.

8b



^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.60 (s, 1H, *p*-pinin), 7.46-7.42 (m, 3H, *o*/*p*-Ph*H*), 7.33-7.28 (m, 2H, *m*-Ph*H*), 2.56 (tt, $J_{H\text{-}H}$ = 3.9 Hz, $J_{H\text{-}H}$ = 10.6 Hz, 2H, NC$H_{ax}(CH_2)_2$), 1.76 (app. d, $J_{H\text{-}H}$ = 13.3 Hz, 4H, NCH(CH$H_{eq})_2$), 1.68 (app. dt, $J_{H\text{-}H}$ = 13.5 Hz, $J_{H\text{-}H}$ = 3.9 Hz, 4H, NCH(CH_2CH$H_{eq})_2$), 1.57 (dt, $J_{H\text{-}H}$ = 12.8 Hz, $J_{H\text{-}H}$ = 3.8 Hz, 2H, (CH_2CH_2)CHH_{eq}), 1.25 (app. qt, $J_{H\text{-}H}$ = 12.6 Hz, $J_{H\text{-}H}$ = 3.4 Hz, 4H, NCH(CH_2CH$H_{ax})_2$), 1.11 (app. qt, $J_{H\text{-}H}$ = 12.8 Hz, $J_{H\text{-}H}$ = 3.8 Hz, 2H, (CH_2CH_2)CHH_{ax}), 0.99 (app. qd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}H}$ = 4.4 Hz, 4H, NCH(CH$H_{ax})_2$), 0.1 (s, 9H, $SiMe_3$) ppm.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 174.9 (d, $^{1}J_{P\text{-}C}$ = 88 Hz, *o*-pinin), 161.0 (d, $^{1}J_{P\text{-}C}$ = 71 Hz, *o*-pinin), 154.5 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, *m*-pinin), 152.3 (d, $^{2}J_{C\text{-}P}$ = 18 Hz, amidine-*C*), 144.6 (s, *i*-Ph), 132.3 (dq, $^{2}J_{F\text{-}C}$ = 30, $^{2}J_{P\text{-}C}$ = 10 Hz, *m*-pinin), 129.3 (s, *o*/*p*-Ph), 128.7 (d, $^{3}J_{C\text{-}P}$ = 13 Hz, *p*-pinin), 128.5 (s, *m*-Ph), 123.9 (q, $^{1}J_{F\text{-}C}$ = 278 Hz, *C*F_3), 51.0 (s, N*C*H($CH_2)_2$), 37.5 (s, NCH(*C*$H_2)_2$), 26.2 (s, (CH_2CH_2)*C*H_2), 25.6 (s, NCH(CH_2*C*$H_2)_2$, 1.8 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, $SiMe_3$) ppm.
^{19}F (CD_2Cl_2, 565 MHz): δ -60.3 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 246.5 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 519.267, Observed: 519.2472.

8b'



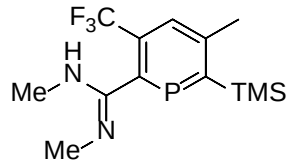
^{19}F (CD_2Cl_2, 565 MHz): δ -60.1 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 216.8 ppm.
HRMS (ESI): Calculated $[M+H]^+$: 447.2172, Observed: 447.2099.

Synthesis of 6

3a/**b** was dissolved in toluene (0.1 mL) and $MeNH_2$ (0.5 mL) was condensed in. The reaction was performed at −60 °C. The reactions were not agitated during the course of the reaction

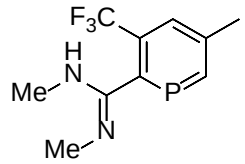
and monitored by ^{19}F. Once complete, the reactions were filtered using a canula fitted with glass filter paper. The solid was washed with dry benzene (3 x 0.5 mL) and the solvent was removed from the filtrate *in vacuo*. Removing the solvent yielded a viscous oil. Therefore, the yield were calculated *in situ* against a PPh_3 standard.

6a



^{1}H NMR (C_6D_6, 400 MHz): δ 7.38 (s, 1H, *p*-pinin), 3.98 (br. s, 1H, N*H*), 2.93 (br. s, 6H, NMe), 2.17 (s, 3H, Me), 0.32 (s, 9H, TMS) ppm.
^{19}F (C_6D_6, 376 MHz): δ -61.0 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 162 MHz): δ 244.3 (s) ppm.

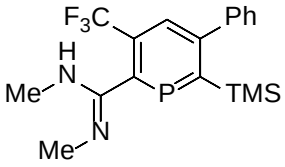
6a'



3a (22.3 mg, 0.070 mmol). Spectroscopic yield (0.044 mmol, 63%).

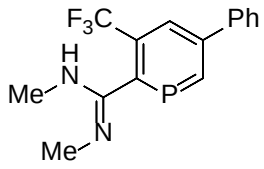
^{1}H NMR (CD_2Cl_2, 600 MHz): δ 8.81 (d, $^{2}J_{H,P}$ = 39.9 Hz, 1H, *o*-pinin), 7.68 (s, 1H, *p*-pinin), 4.54 (br. s, 1H, N*H*), 2.79 (br. s, 6H, NMe), 2.57 (s, 3H, Me) ppm. It is not possible to distinguish the two amidine methyl groups due to rapid tautomerisation.
^{13}C {^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 159.1 (d, $^{1}J_{P-C}$ = 60 Hz, *o*-pinin), 158.9 (d, $^{1}J_{P-C}$ = 57 Hz, *o*-pininH), 158.4 (d, $^{2}J_{P-C}$ = 18 Hz, amidine-*C*), 145.5 (d, $^{2}J_{P-C}$ = 14 Hz, *m*-pinin), 133.2 (qd, $^{2}J_{F-C}$ = 30, $^{2}J_{P-C}$ = 13 Hz, *m*-pinin), 129.3 (dq, $^{3}J_{P-C}$ = 16, $^{3}J_{F-C}$ = 5 Hz, *p*-pinin), 123.7 (q, $^{1}J_{F-C}$ = 277 Hz, *C*F_3), 24.9 (d, $^{3}J_{P-C}$ = 3 Hz, Me) ppm. Amidine methyl signals could not be located.
^{19}F (CD_2Cl_2, 565 MHz): δ -61.2 (s) ppm.
^{31}P {^{1}H} (CD_2Cl_2, 243 MHz): δ 214.9 (s) ppm.

6b



^{19}F (C_6D_6, 377 MHz): δ -61.1 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 162 MHz): δ 247.5 ppm.
HRMS (ESI): Calculated $[M+OH_3]^+$: 401.1420, Observed: 401.1411.

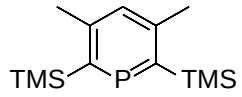
6b'



3b (18.0 mg, 0.074 mmol). Spectroscopic yield (0.041 mmol, 55%).

^{1}H NMR (C_6D_6, 600 MHz): δ 8.70 (d, $^{2}J_{H\text{-}P}$ = 38.5 Hz, 1H, *o*-pinin), 7.93 (s, 1H, *p*-pinin), 7.24-7.14 (m, 5H, Ph*H*), 3.47 (br. s, 1H, N*H*), 2.98 (br. s, 6H, NMe) ppm.
^{13}C {^{1}H} NMR (C_6D_6, 151 MHz): δ 161.3 (d, $^{1}J_{P\text{-}C}$ = 62 Hz, *o*-pinin), 156.9 (d, $^{1}J_{P\text{-}C}$ = 59 Hz, *o*-pinin), 156.8 (d, $^{2}J_{C\text{-}P}$ = 18 Hz, amidine-*C*), 147.2 (d, $^{2}J_{C\text{-}P}$ = 14 Hz, *m*-pinin), 140.9 (s, *i*-Ph), 133.9 (dq, $^{2}J_{F\text{-}C}$ = 29 Hz, $^{2}J_{P\text{-}C}$ = 11 Hz, *m*-pinin), 128.9 (s, *m*/*p*-Ph), 129.4 (s, *o*-Ph), 123.8 (q, $^{1}J_{F\text{-}C}$ = 277 Hz, *C*F_3), 38.3 (br. s, NMe), 29.3 (br. s, NMe) ppm. The signal for *p*-pinin is under the signal for C_6D_6.
^{19}F (C_6D_6, 565 MHz): δ -60.9 (s) ppm.
^{31}P {^{1}H} (C_6D_6, 243 MHz): δ 218.1 ppm.
HRMS (ESI): Calculated $[M+OH_3]^+$: 329.1025, Observed: 329.1010.

3 NMR spectra



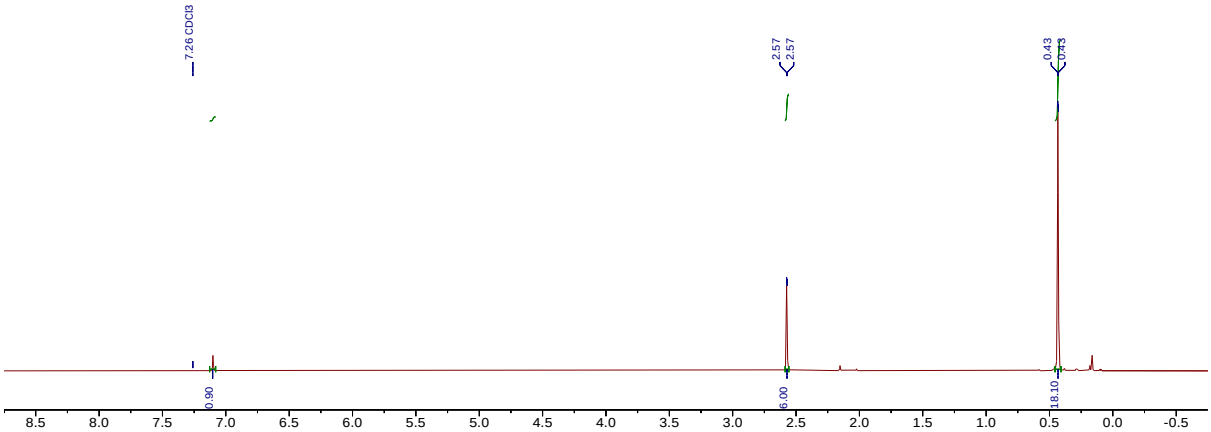


Figure S14- ^{1}H NMR spectra of **1a** in $CDCl_3$.

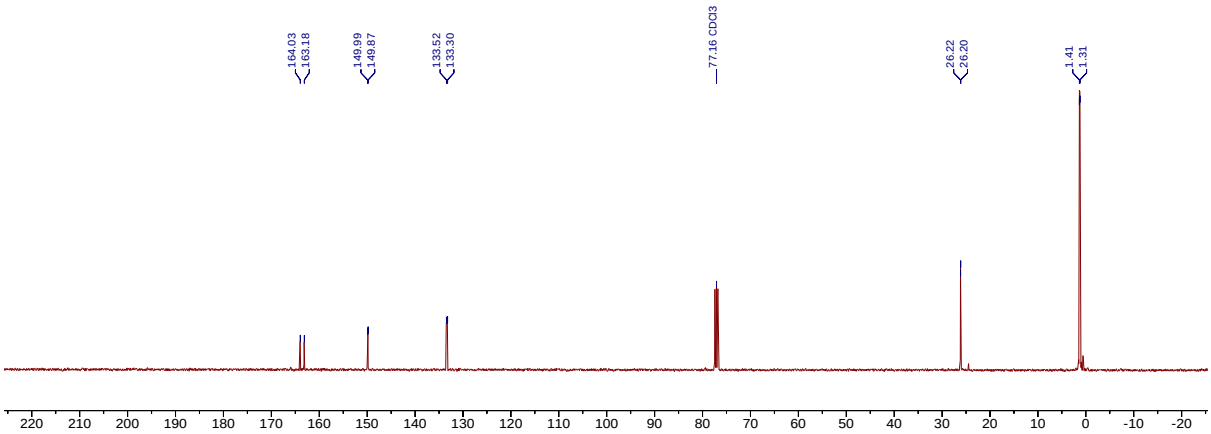


Figure S15- ^{13}C $\{^{1}H\}$ NMR spectra of **1a** in $CDCl_3$.

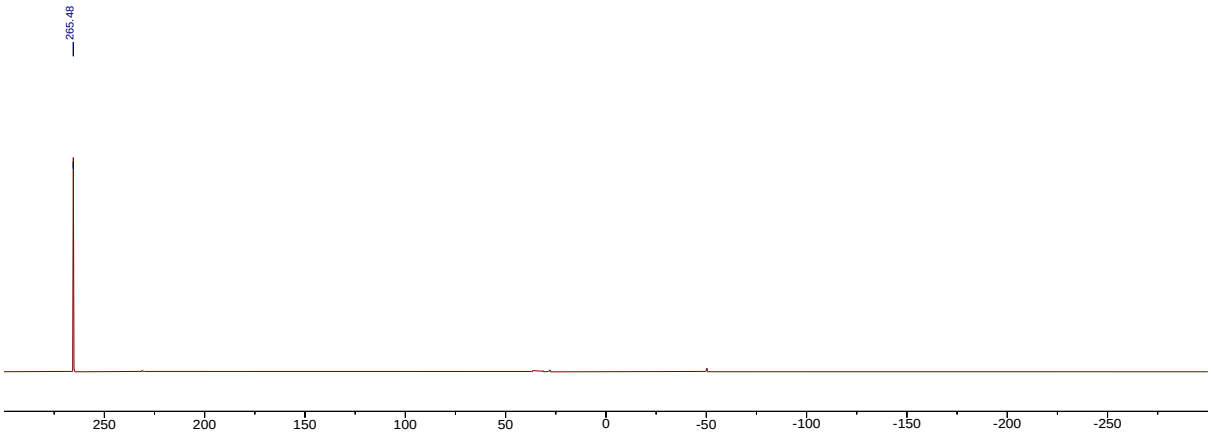
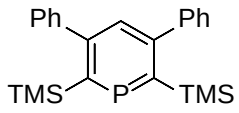


Figure S16- ^{31}P $\{^{1}H\}$ NMR spectra of 1**a** in $CDCl_3$.



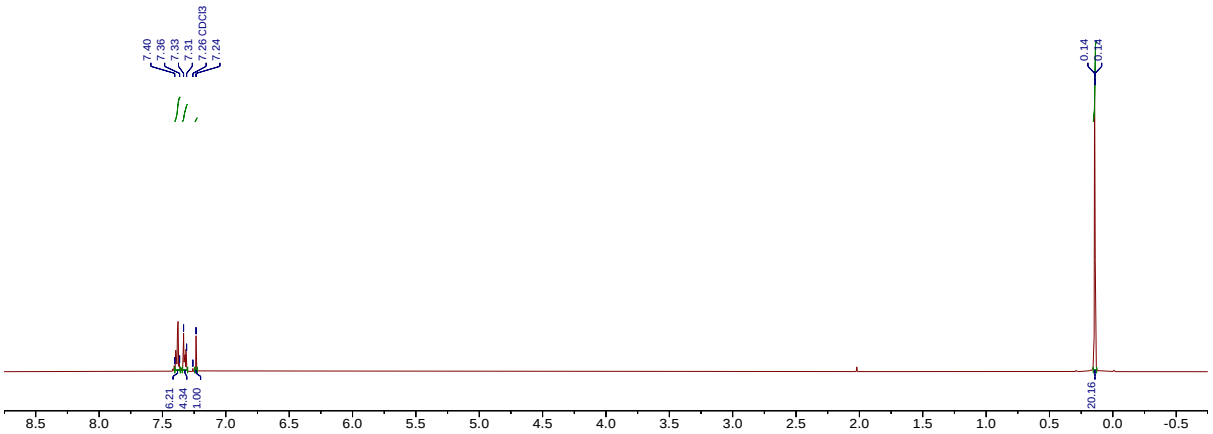


Figure S17- ^{1}H NMR spectra of **1b** in $CDCl_3$.

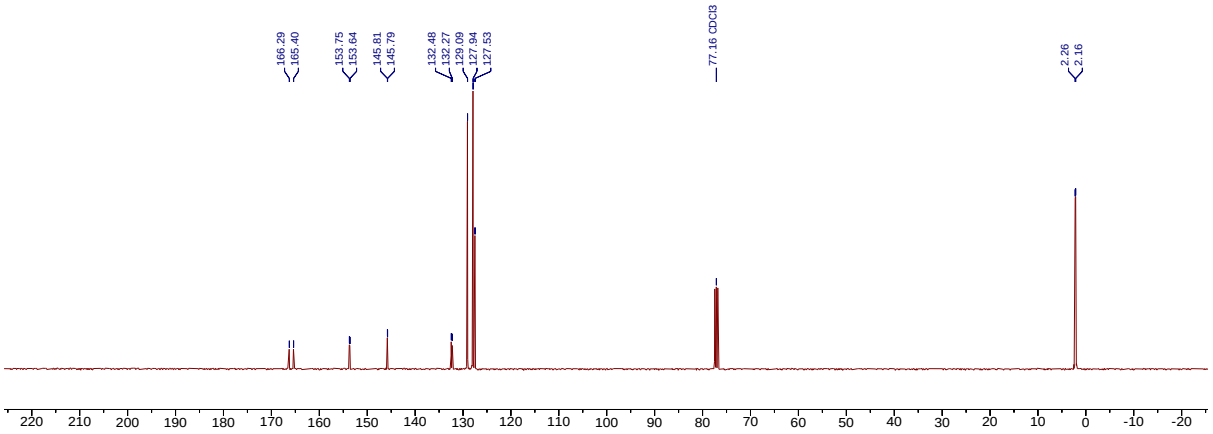


Figure S18- ^{13}C $\{^{1}H\}$ NMR spectra of **1b** in $CDCl_3$.

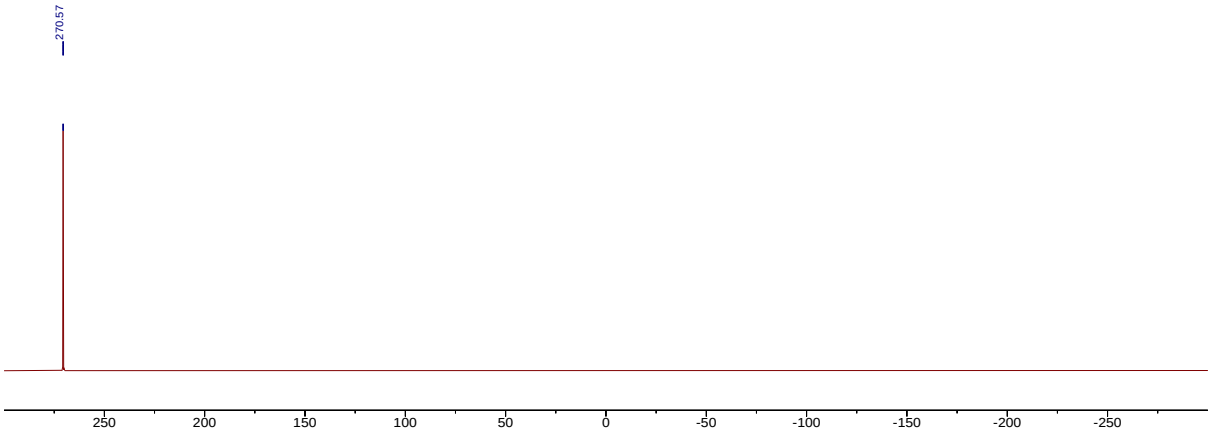
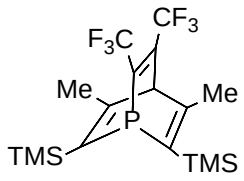


Figure S19- ^{31}P $\{^{1}H\}$ NMR spectra of **1b** in $CDCl_3$.



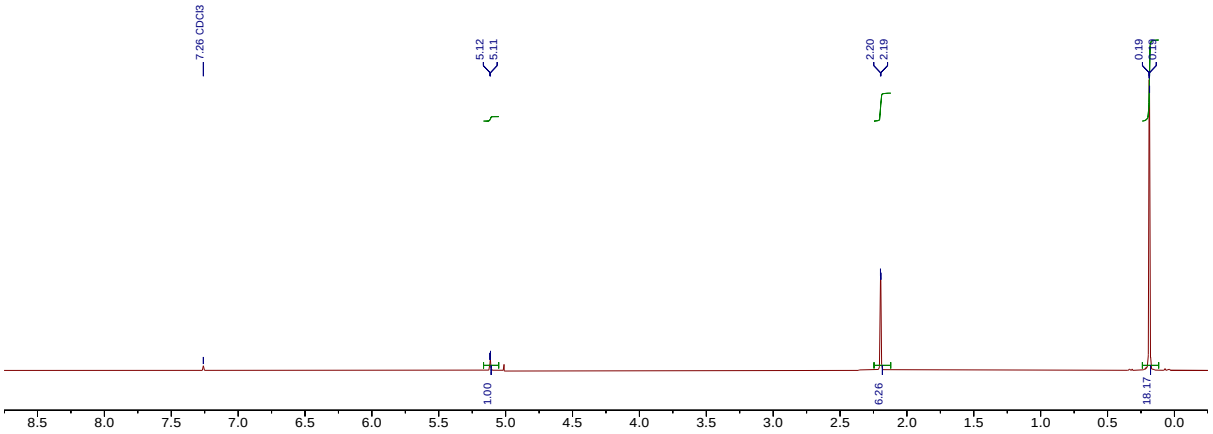


Figure S20- ^{1}H NMR spectra of **2a** in $CDCl_3$.

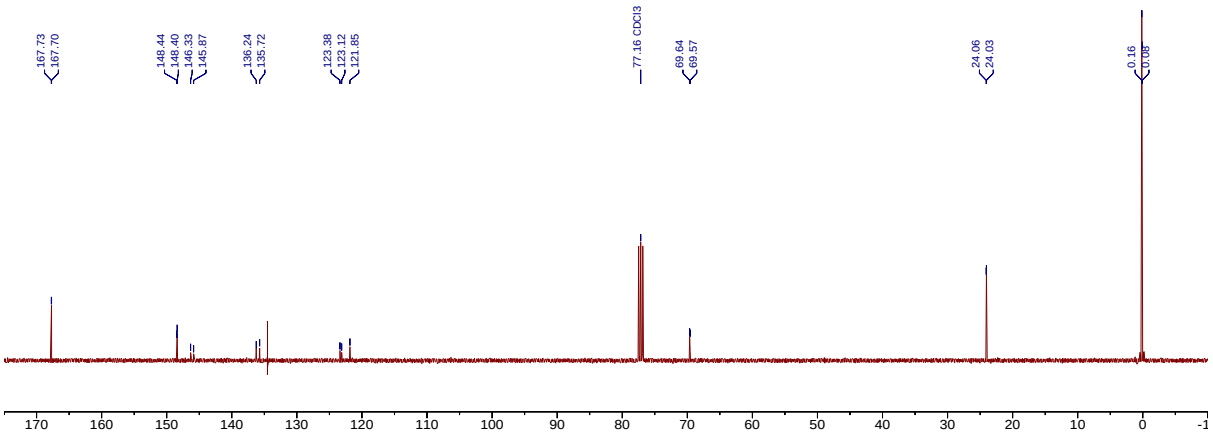


Figure S21- ^{13}C {^{1}H,^{19}F} NMR spectra of **2a** in $CDCl_3$.

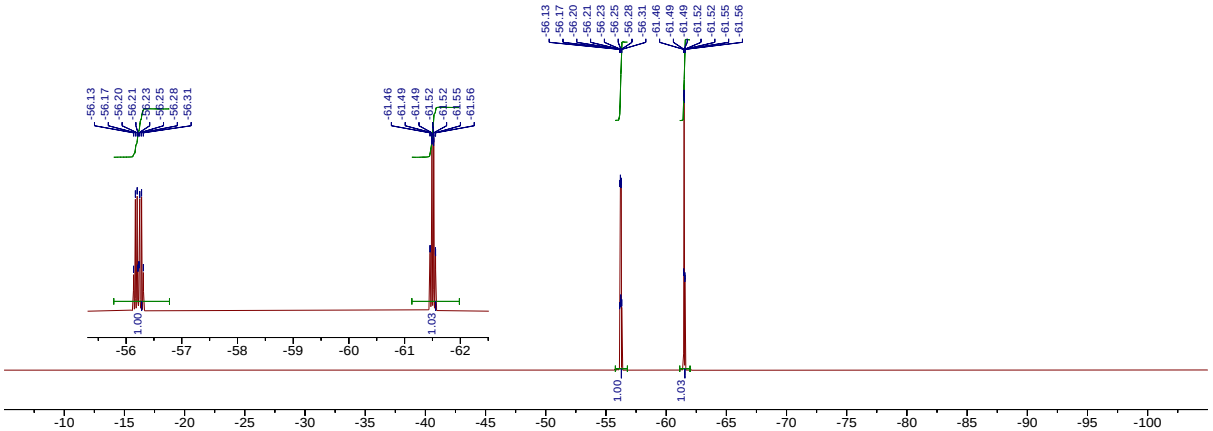


Figure S22- ^{19}F NMR spectra of **2a** in $CDCl_3$.

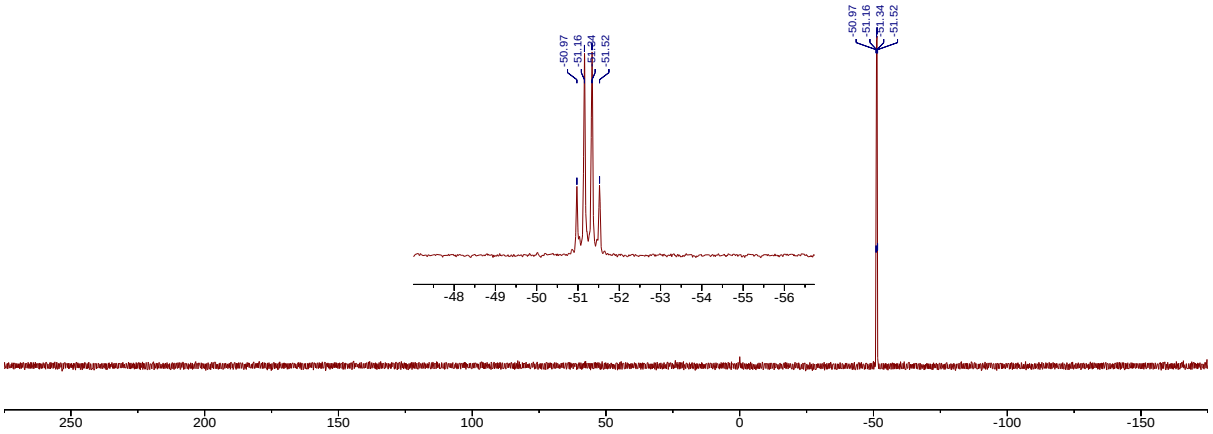
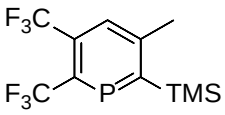


Figure S23- ^{31}P {^{1}H} NMR spectra of **2a** in $CDCl_3$.



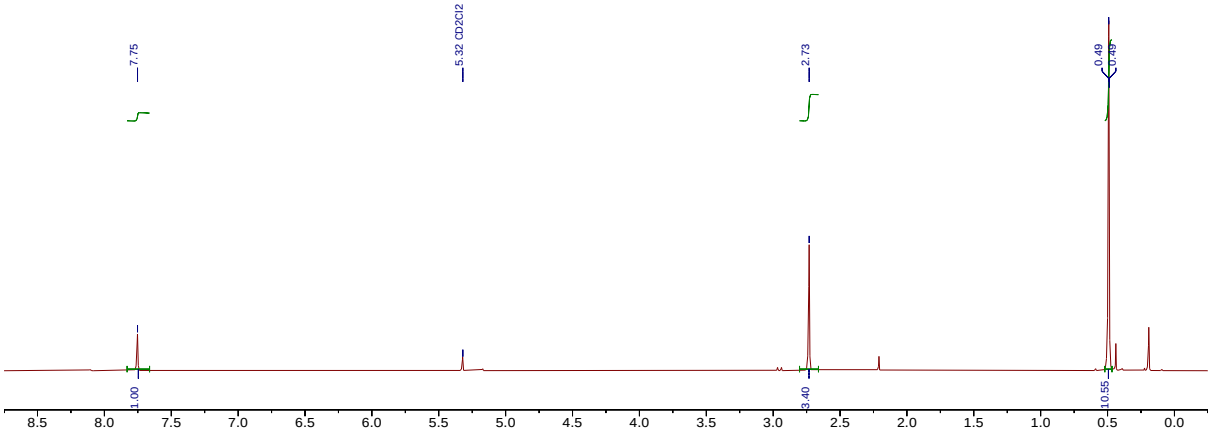


Figure S24- ^{1}H NMR spectra of **3a** in CD_2Cl_2.

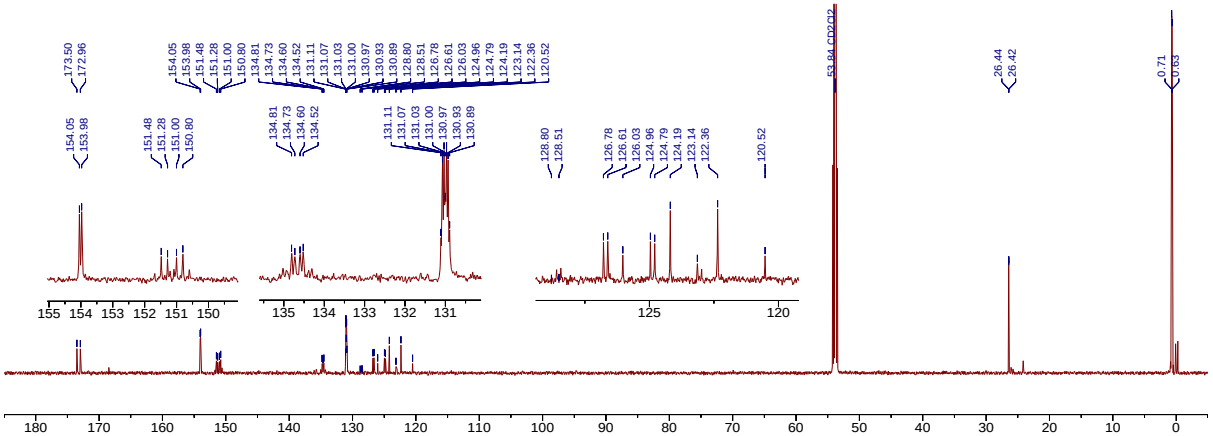


Figure S25- ^{13}C {^{1}H} NMR spectra of **3a** in CD_2Cl_2.

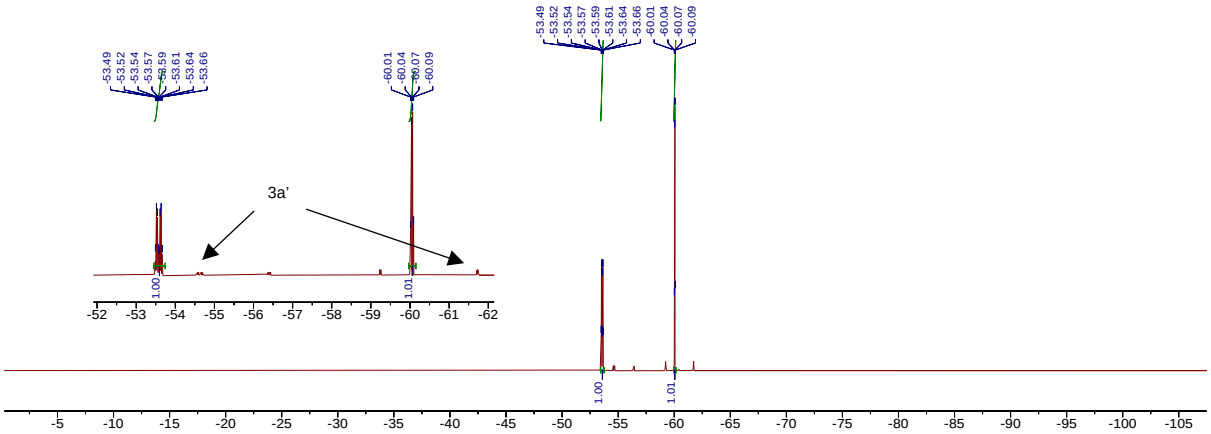


Figure S26- ^{19}F NMR spectra of **3a** in CD_2Cl_2.

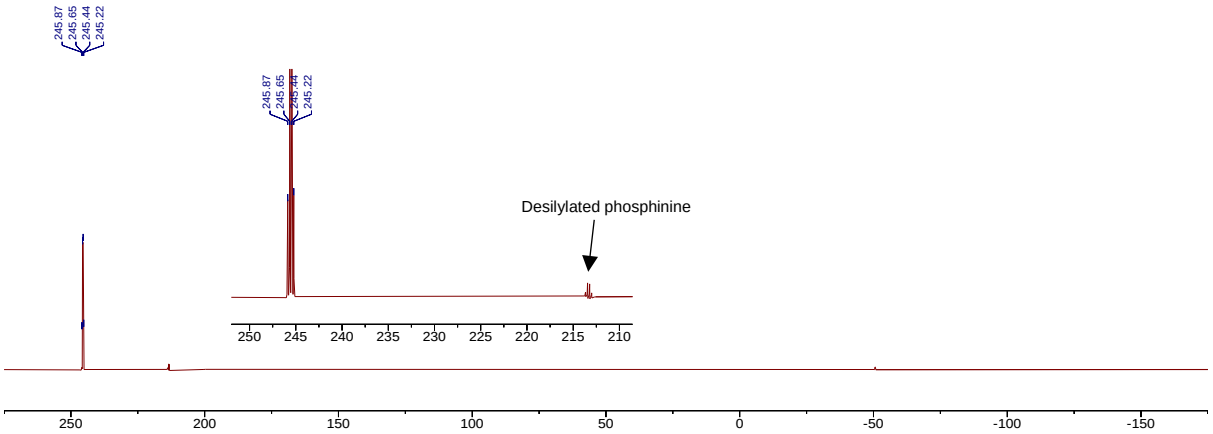


Figure S27- ^{31}P $\{^1H\}$ NMR spectra of **3a** in CD_2Cl_2.

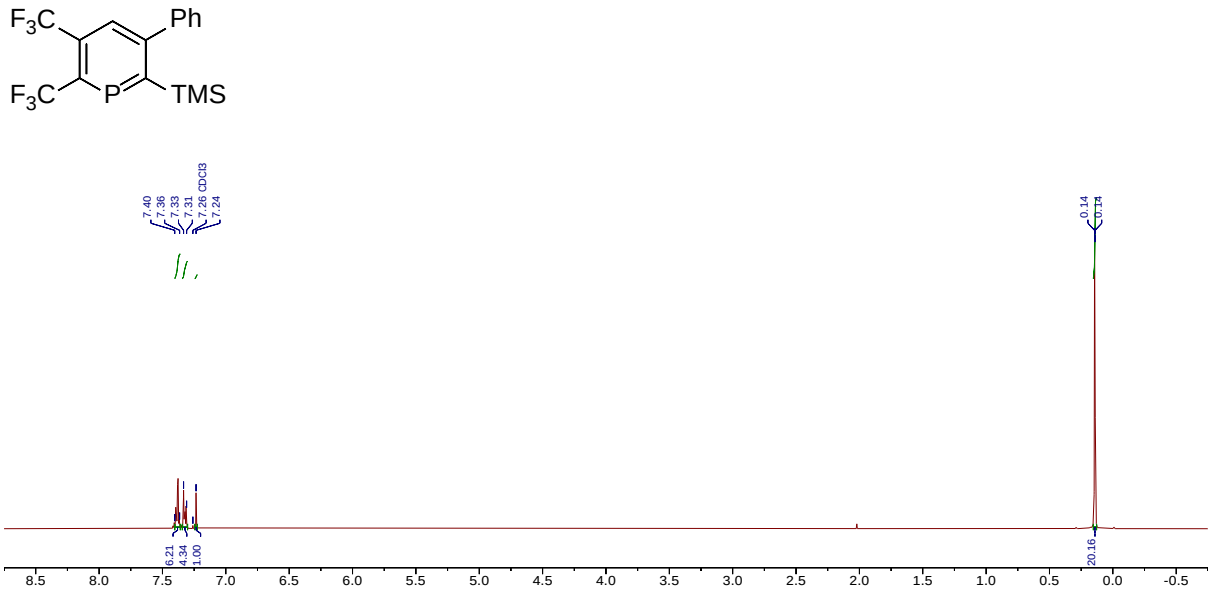


Figure S28- ^1H NMR spectra of **3b** in $CDCl_3$.

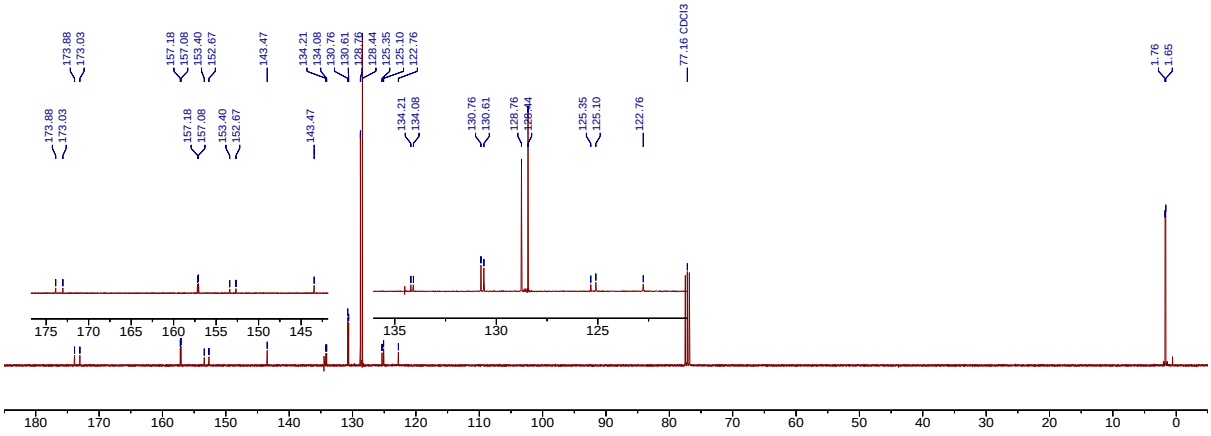


Figure S29- ^{13}C {^{1}H,^{19}F} NMR spectra of **3b** in $CDCl_3$.

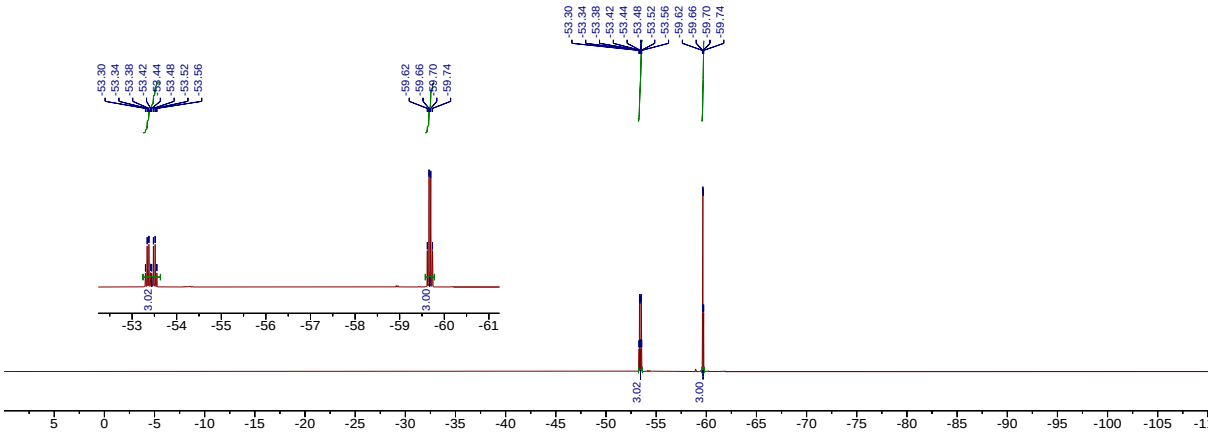


Figure S30- ^{19}F NMR spectra of **3b** in $CDCl_3$.

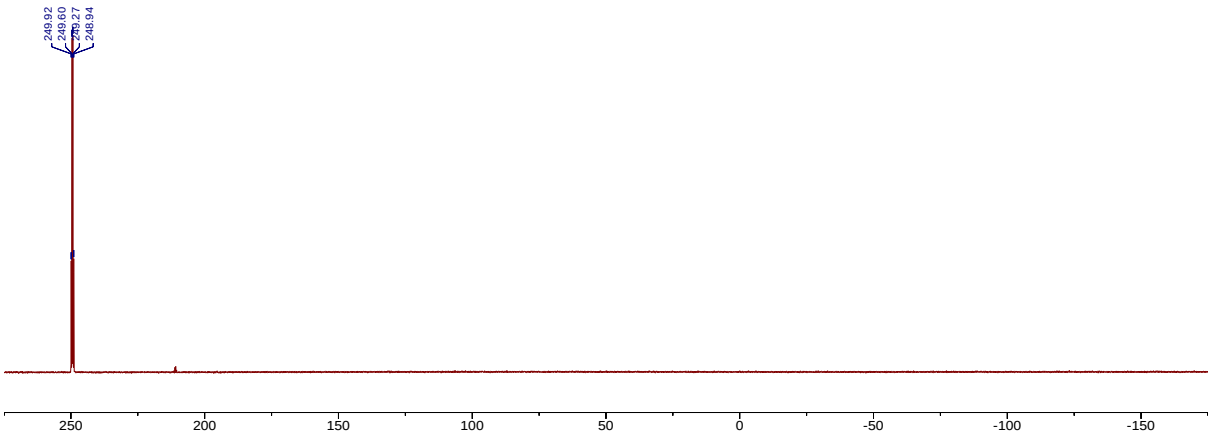


Figure S31- ^{31}P {^{1}H} NMR spectra of **3b** in $CDCl_3$.

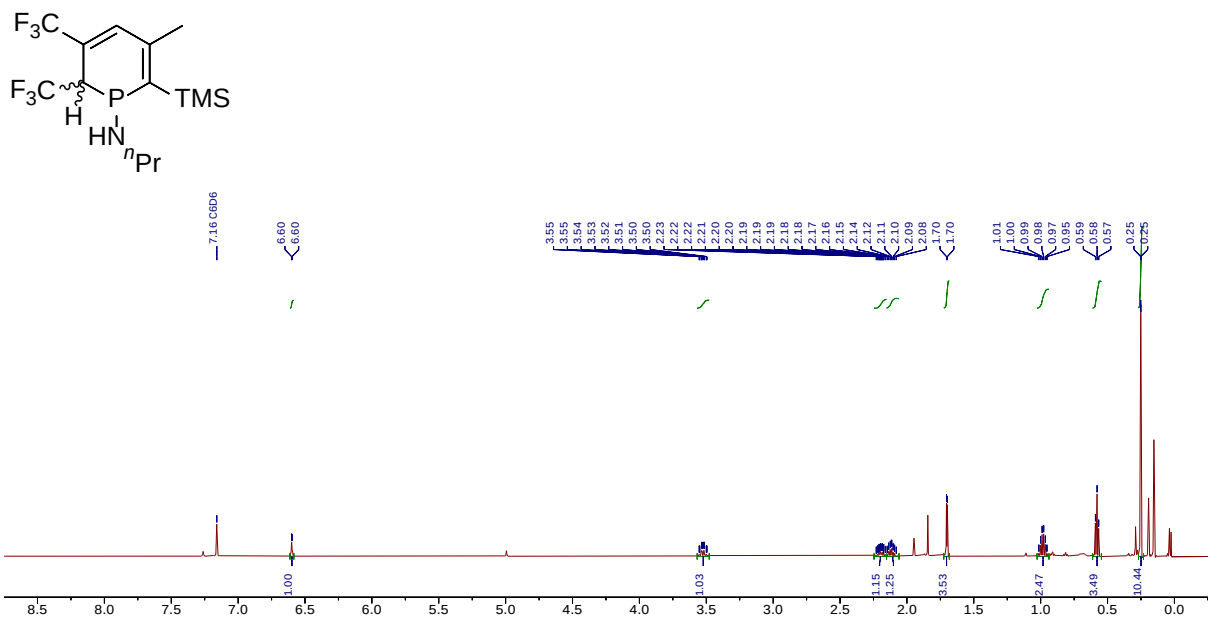


Figure S32- ^{1}H NMR spectra of **4a** in C_6D_6.

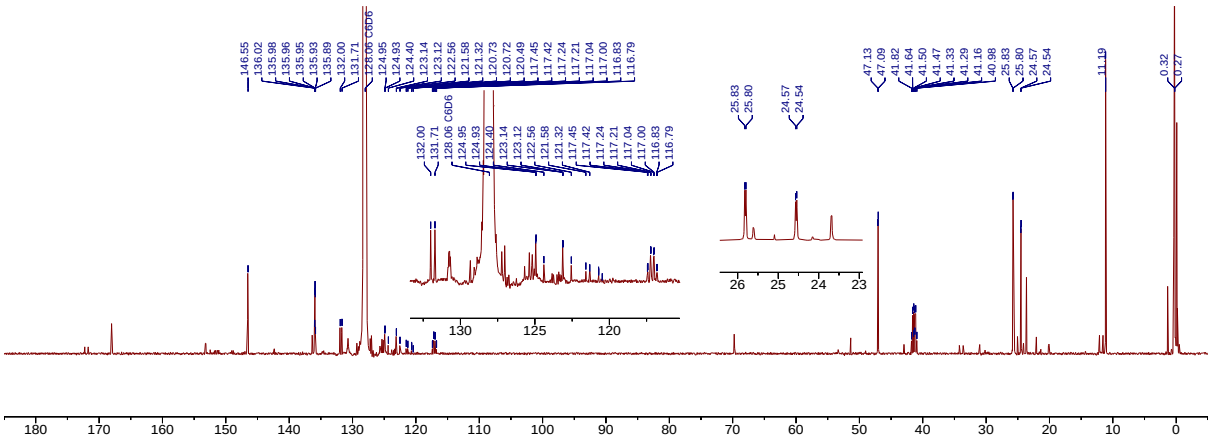


Figure S33- ^{13}C {^{1}H} NMR spectra of **4a** in C_6D_6.

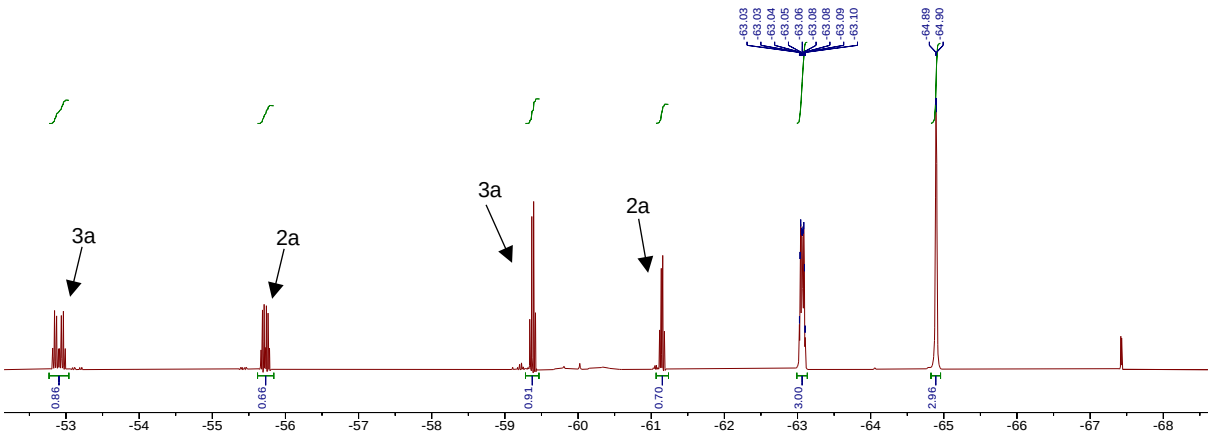


Figure S34- ^{19}F NMR spectra of **4a** in $CDCl_3$.

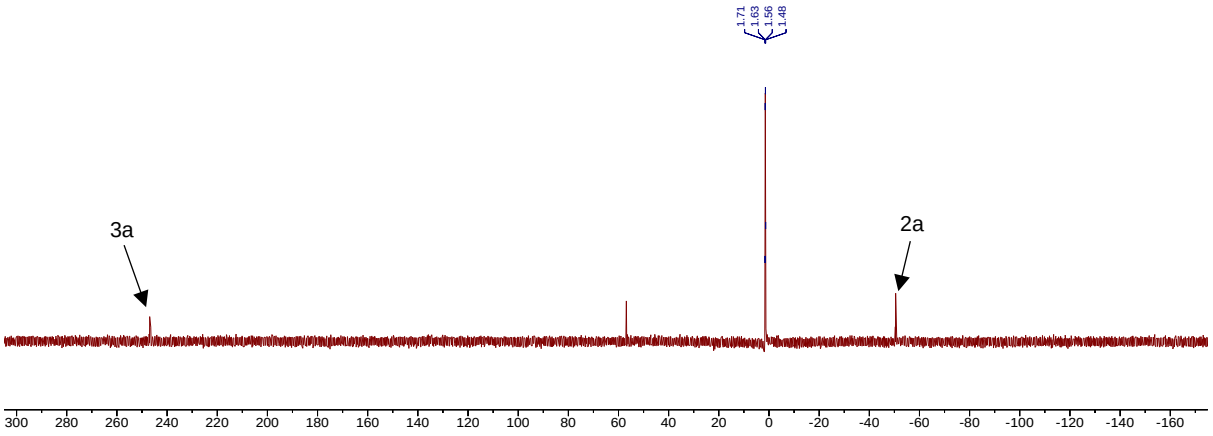


Figure S35- ^{31}P {^{1}H} NMR spectra of **4a** in $CDCl_3$.

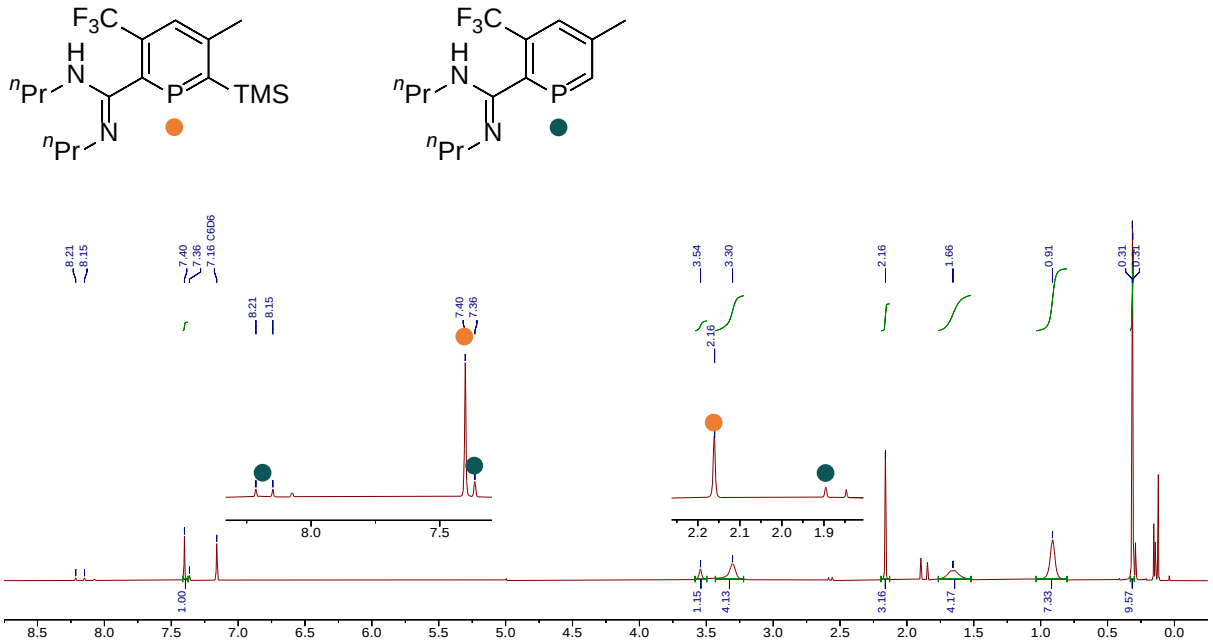


Figure S36- ^{1}H NMR spectra of **5a** (orange) containing traces of **5a'** (teal) in C_6D_6.

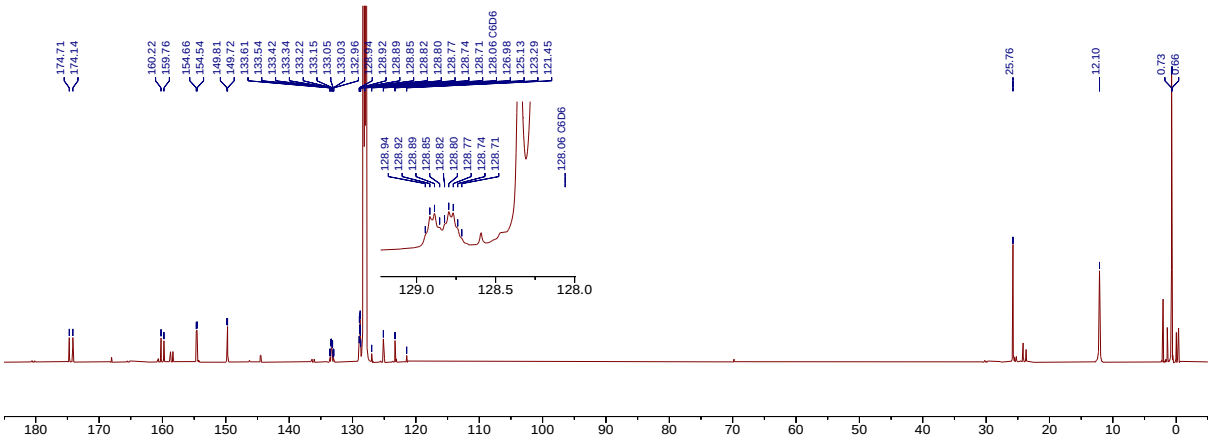


Figure S37- ^{13}C {^{1}H} NMR spectra of **5a** in C_6D_6.

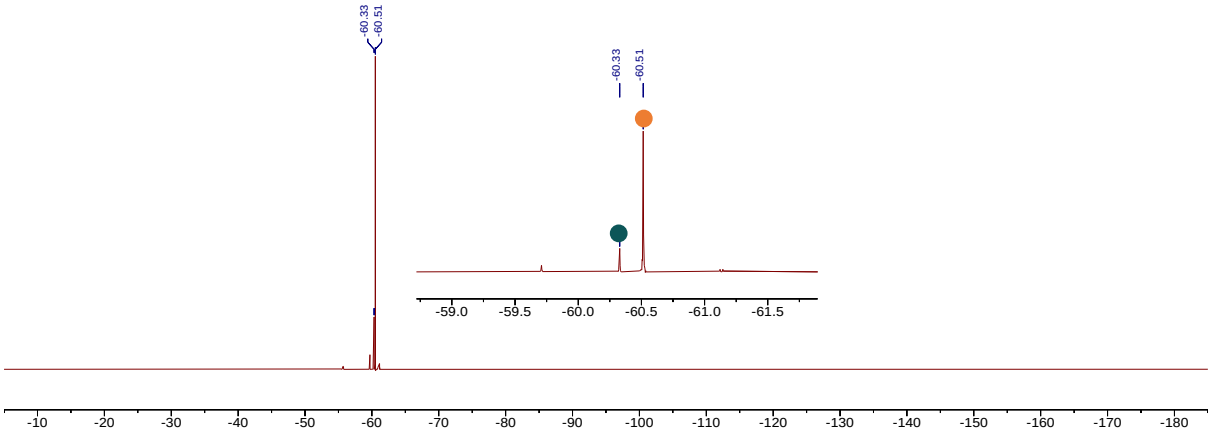


Figure S38- ^{19}F NMR spectra of **5a** (orange) containing traces of **5a'** (teal) in C_6D_6.

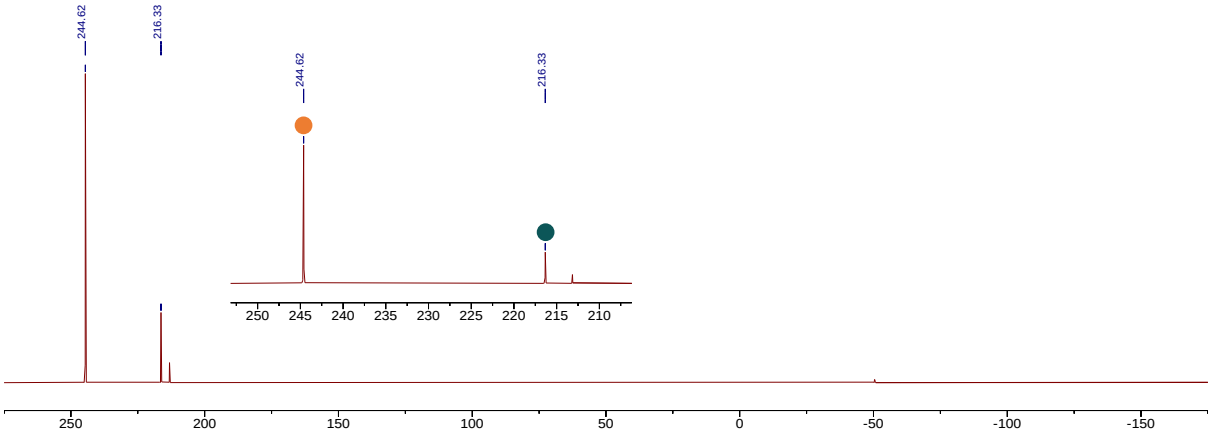


Figure S39- ^{31}P $\{^1H\}$ NMR spectra of **5a** (orange) containing traces of **5a'** (teal) in C_6D_6.

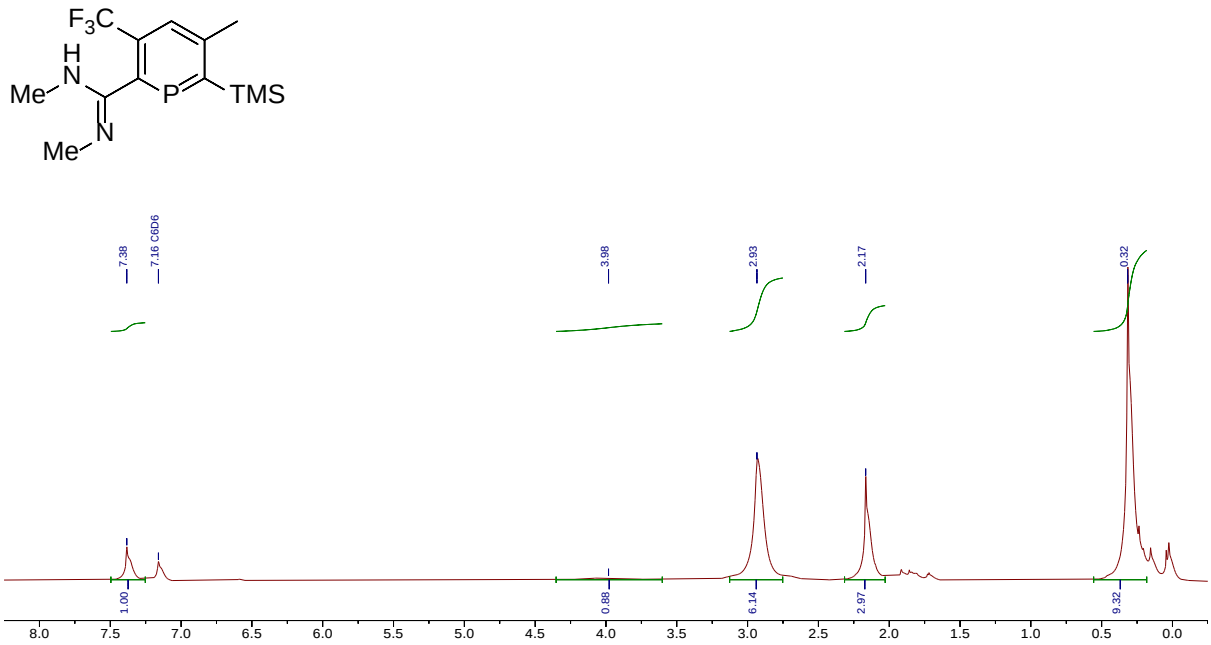


Figure S40- ^1H NMR spectra of **6a** in C_6D_6.

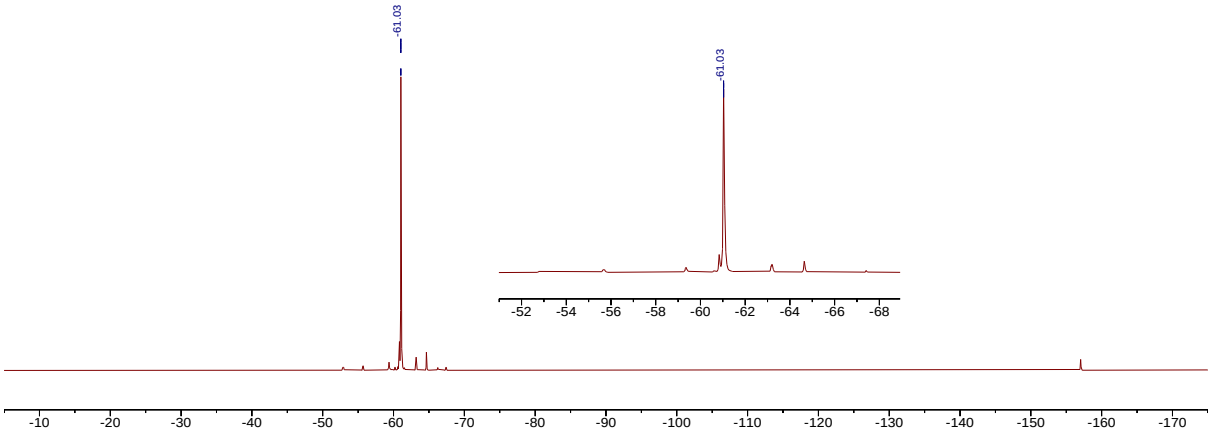


Figure S41- ^{19}F NMR spectra of **6a** in C_6D_6.

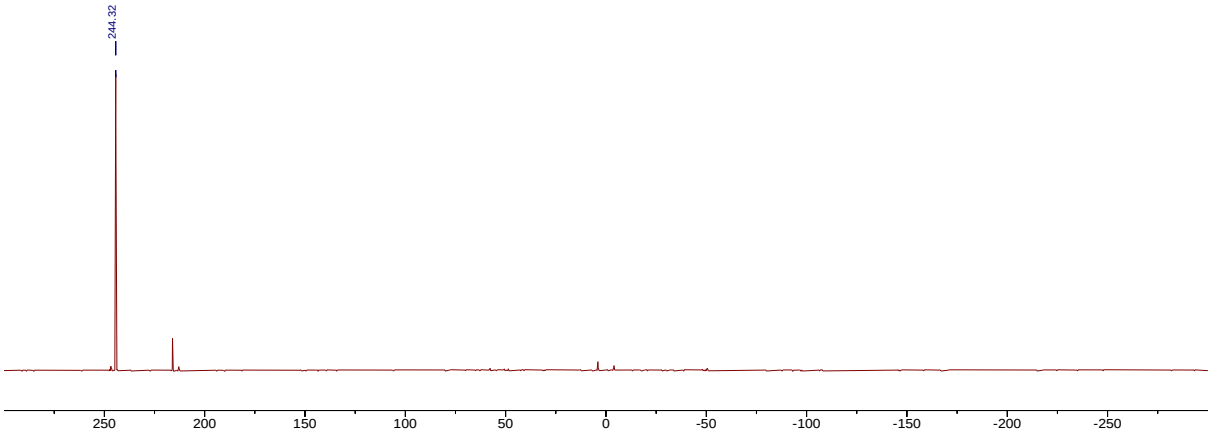


Figure S42- ^{31}P {^{1}H} NMR spectra of **6a** in C_6D_6.

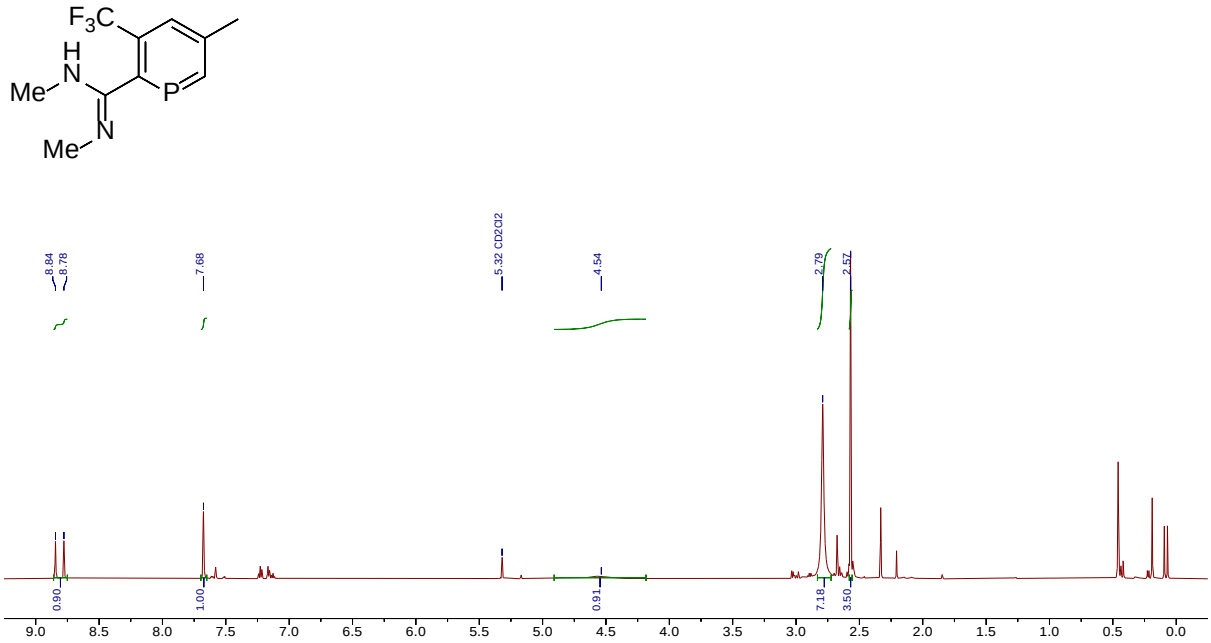


Figure S43- ^{1}H NMR spectra of **6a'** in CD_2Cl_2.

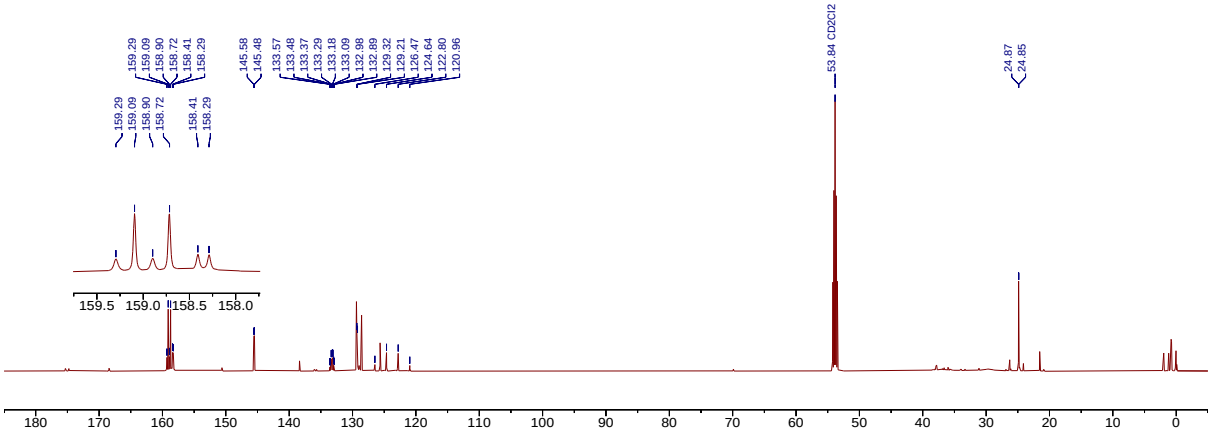


Figure S44- ^{13}C {^{1}H} NMR spectra of **6a'** in CD_2Cl_2.

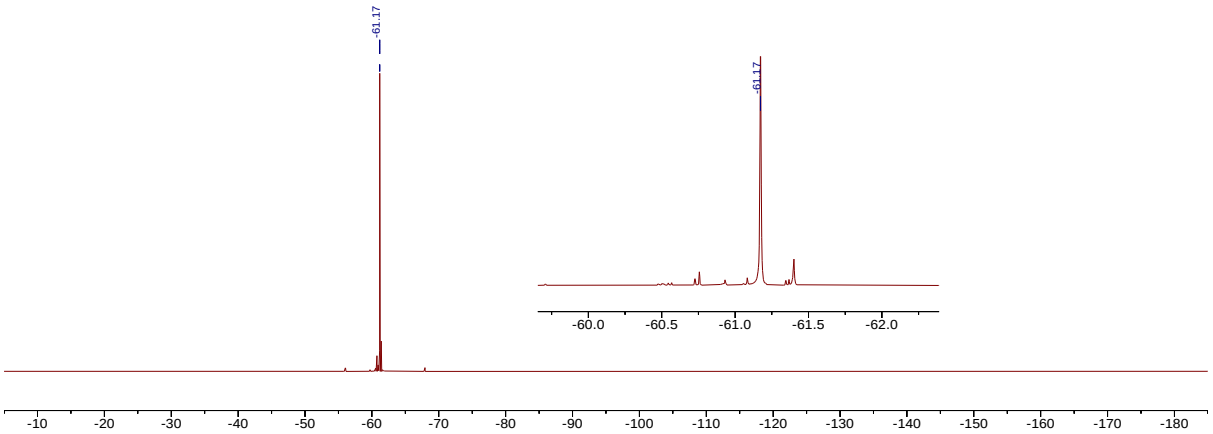


Figure S45- ^{19}F NMR spectra of **6a'** in CD_2Cl_2.

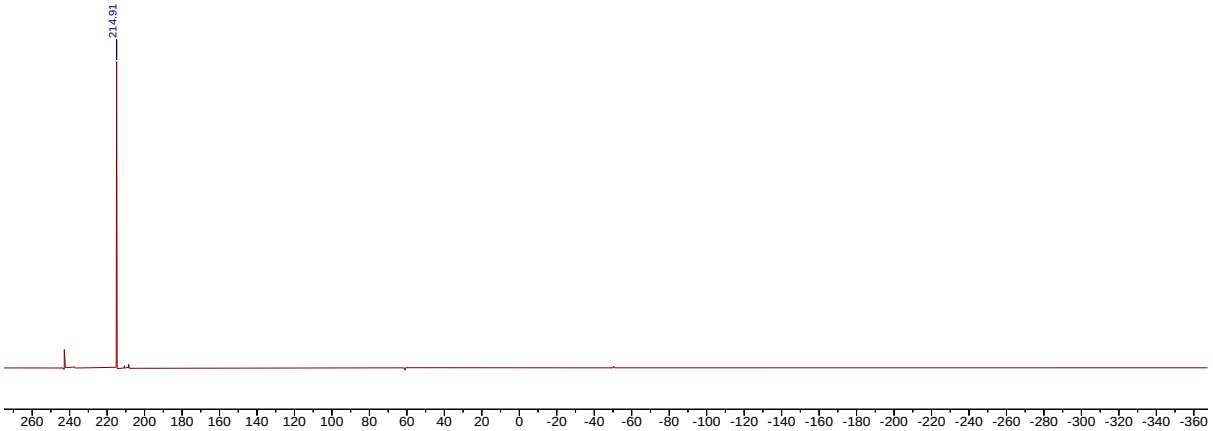


Figure S46- ^{31}P {^{1}H} NMR spectra of **6a'** in CD_2Cl_2.

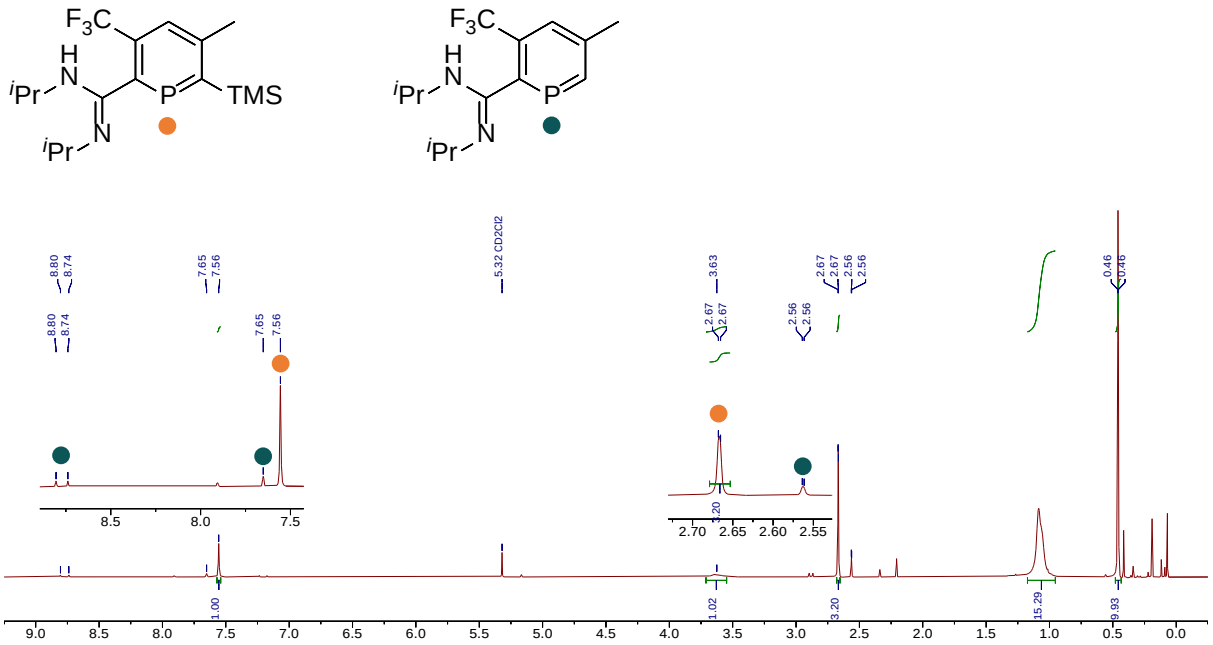


Figure S47- ^{1}H NMR spectra of **7a** (orange) containing traces of **7a'** (teal) in CD_2Cl_2.

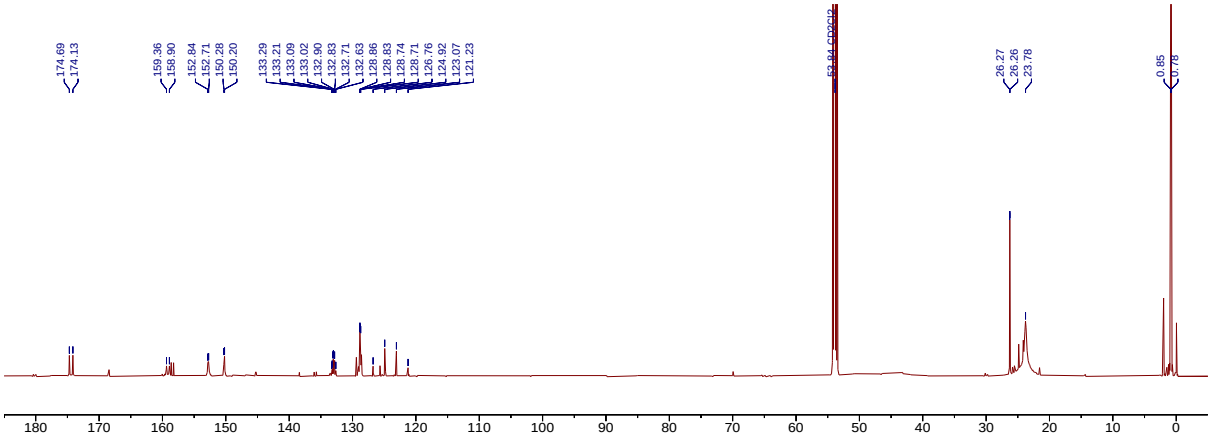


Figure S48- ^{13}C $\{^{1}H\}$ NMR spectra of **7a** in CD_2Cl_2.

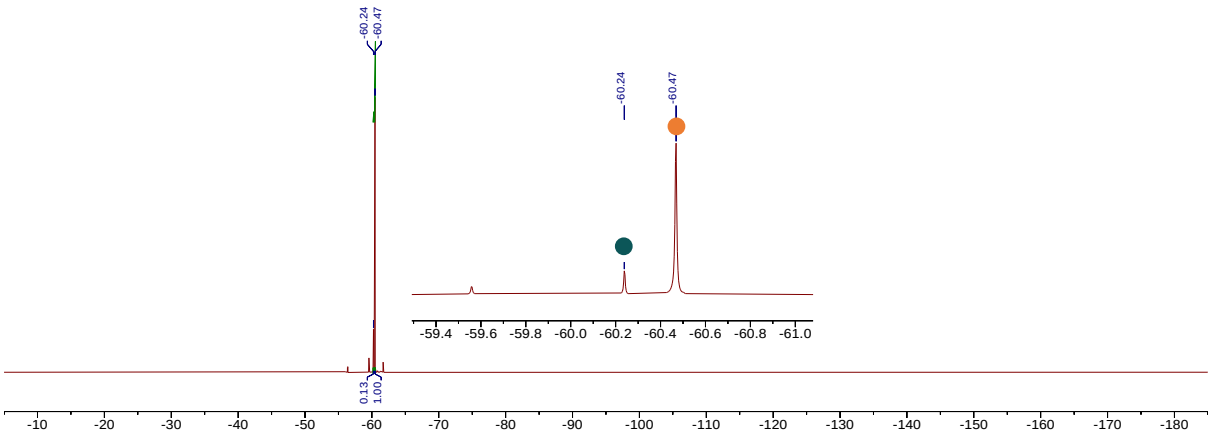


Figure S49- ^{19}F NMR spectra of **7a** (orange) containing traces of **7a'** (teal) in CD_2Cl_2.

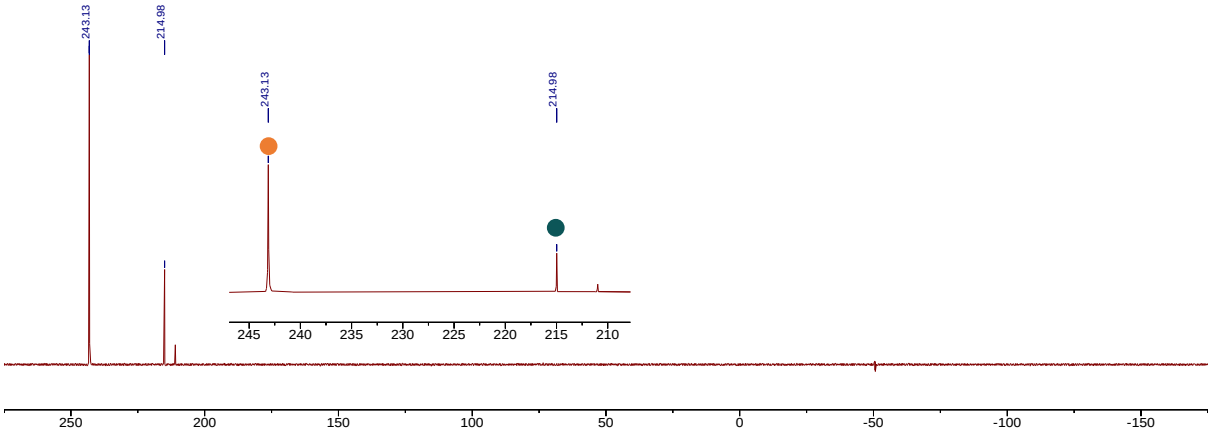


Figure S50- ^{31}P {^{1}H} NMR spectra of **7a** (orange) containing traces of **7a'** (teal) in CD_2Cl_2.

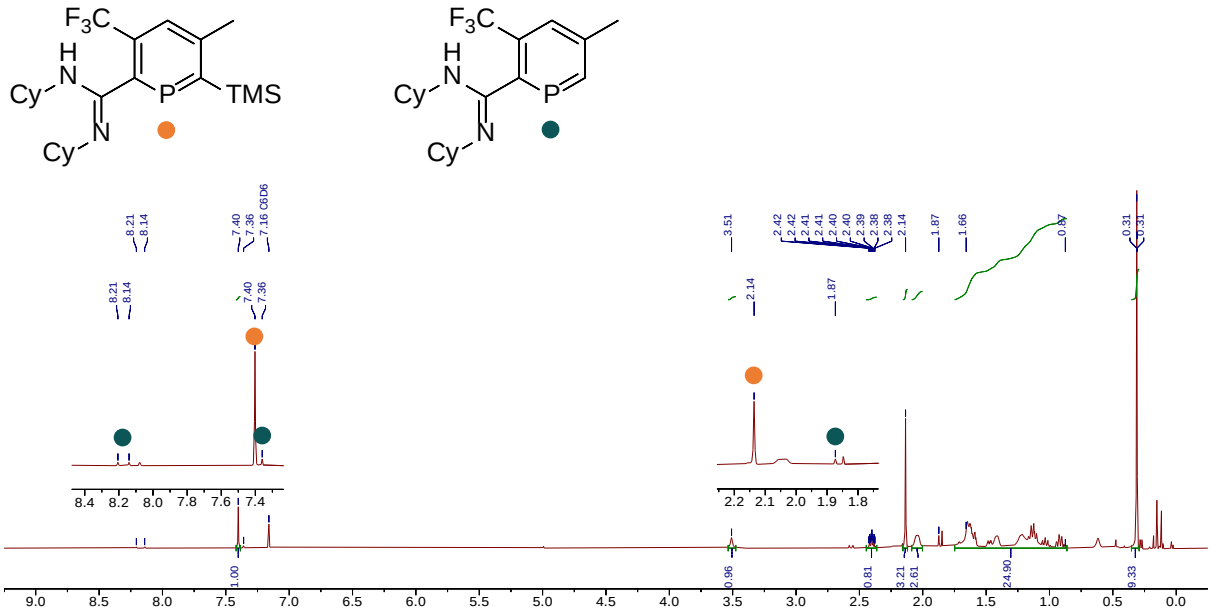


Figure S51- ^{1}H NMR spectra of **8a** (orange) containing traces of **8a'** (teal) in C_6D_6.

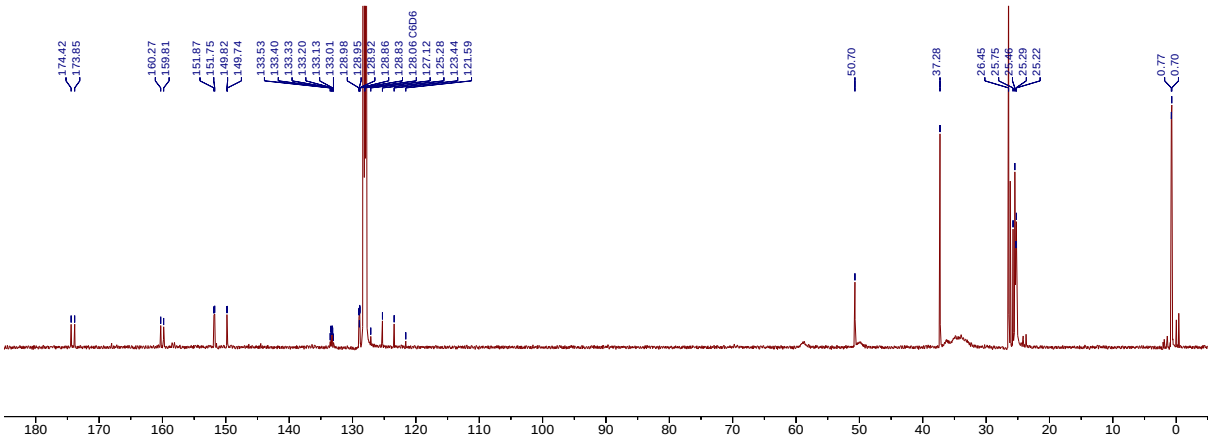


Figure S52- ^{13}C {^{1}H} NMR spectra of **8a** in C_6D_6.

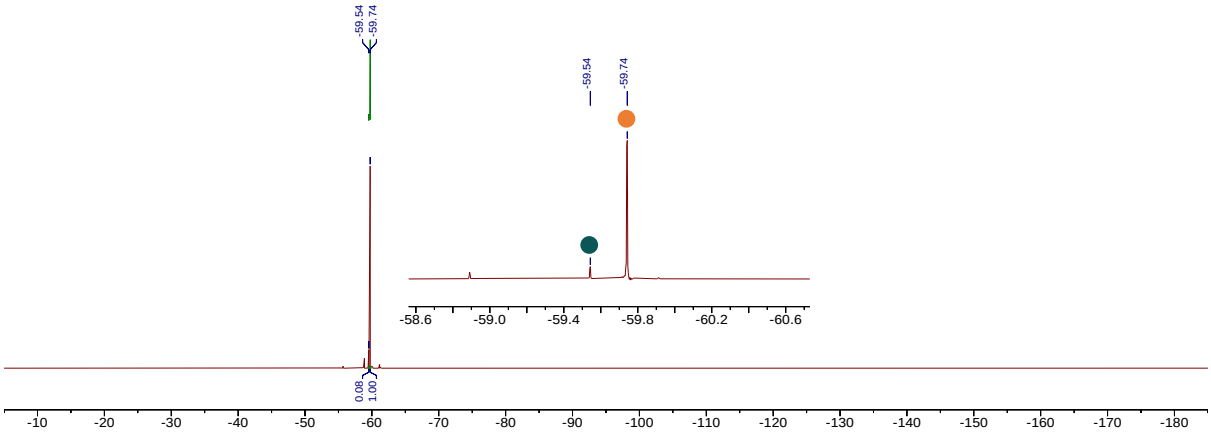


Figure S53- ^{19}F NMR spectra of **8a** (orange) containing traces of **8a'** (teal) in C_6D_6.

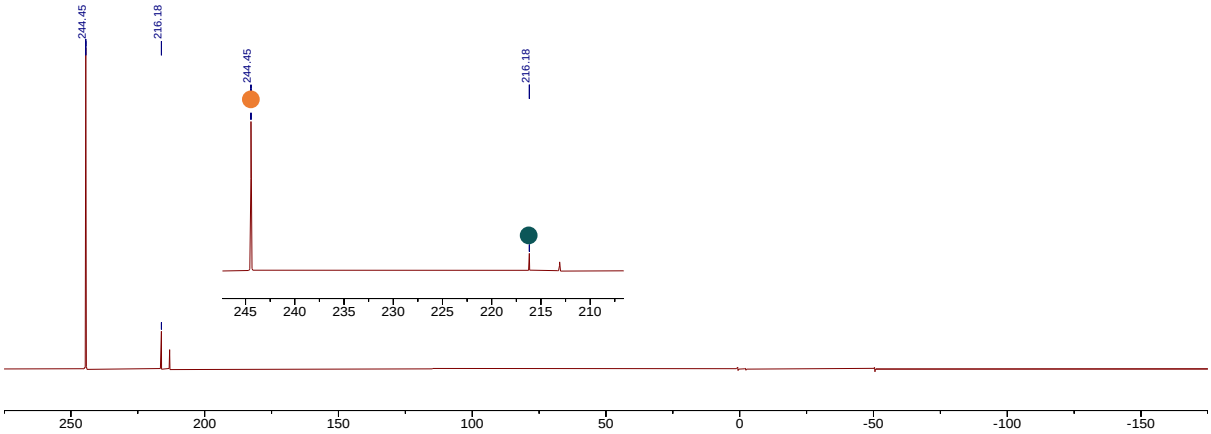


Figure S54- ^{31}P $\{^1H\}$ NMR spectra of **8a** (orange) containing traces of **8a'** (teal) in C_6D_6.

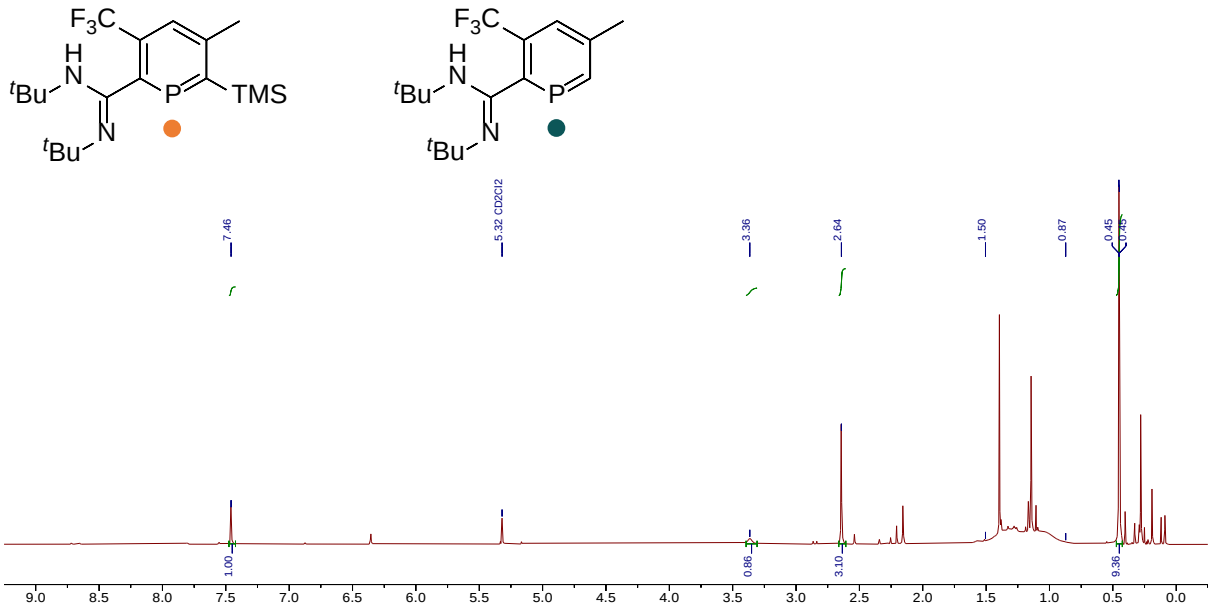


Figure S55- ^1H NMR spectra of **9a** in CD_2Cl_2. Spectra contains an unknown impurity.

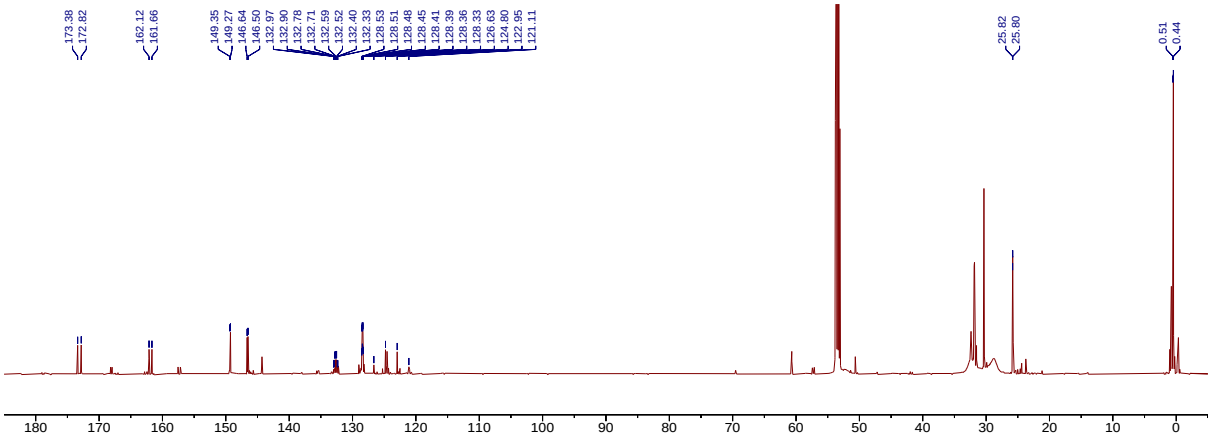


Figure S56- ^{13}C {^{1}H} NMR spectra of **9a** in CD_2Cl_2. Spectra contains an unknown impurity.

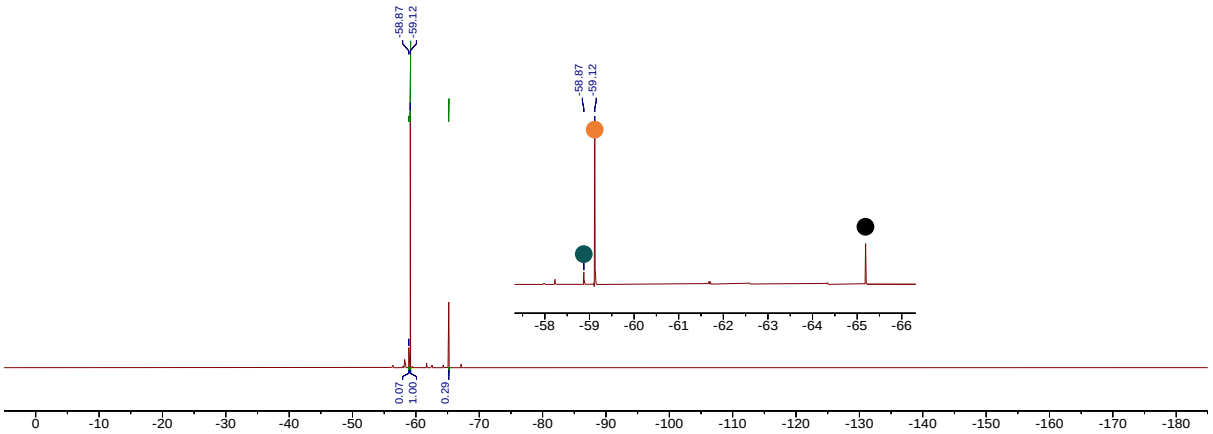


Figure S57- ^{19}F NMR spectra of **9a** (orange) containing traces of **9a'** (teal) in CD_2Cl_2. Unknown impurity marked in black.

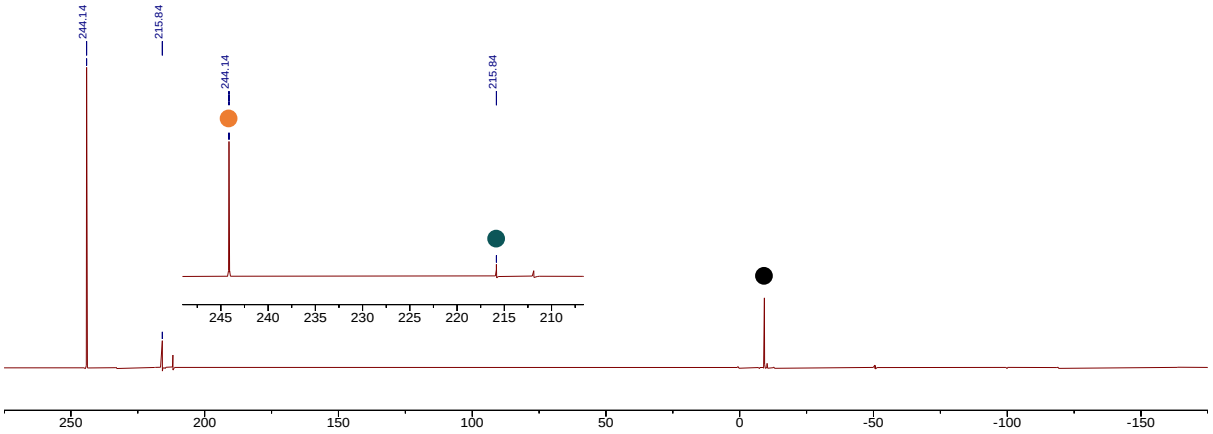
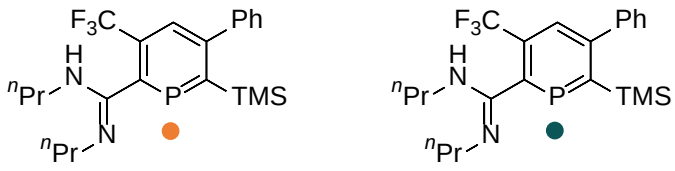


Figure S58 - ^{31}P {^{1}H} NMR spectra of **9a** (orange) containing traces of **9a'** (teal) in CD_2Cl_2. Unknown impurity marked in black.



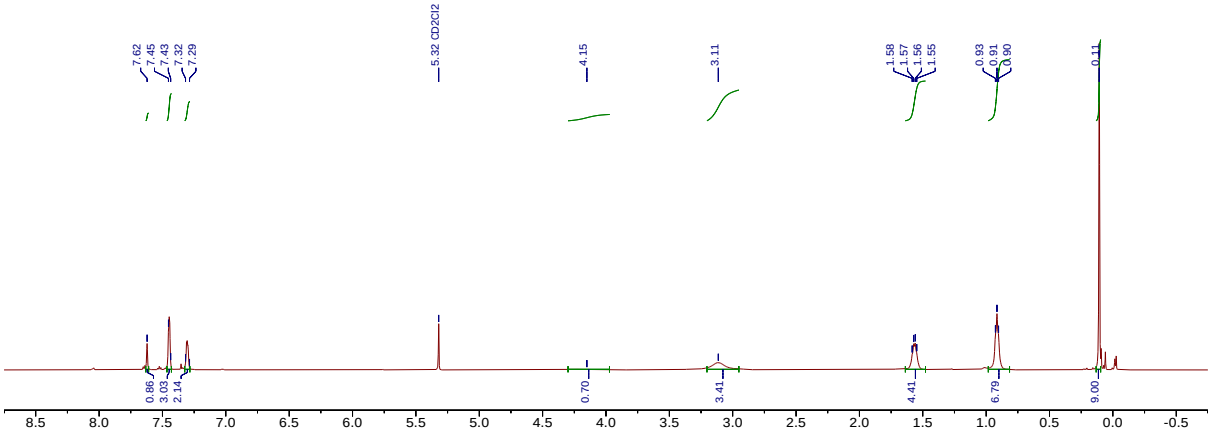


Figure S59- ^{1}H NMR spectra of **5b** in CD_2Cl_2.

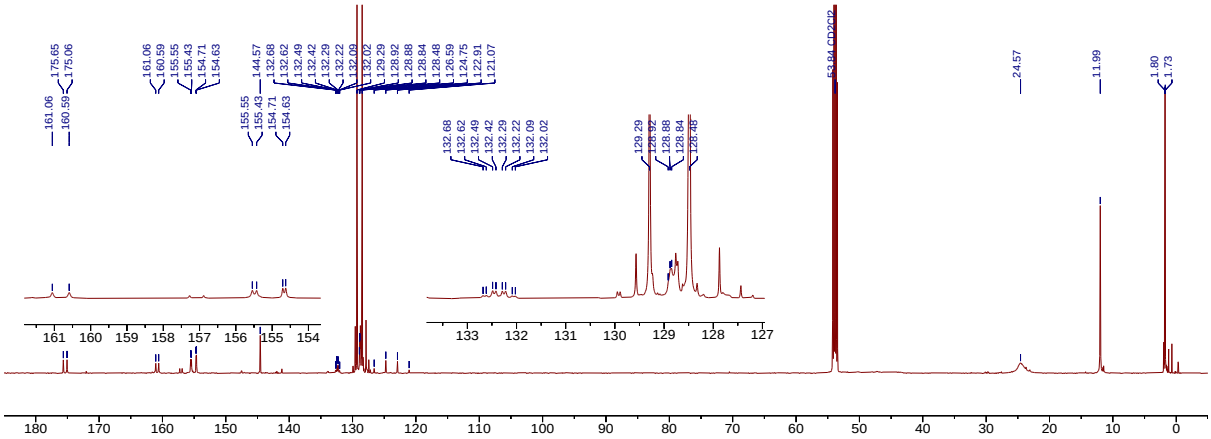


Figure S60- ^{13}C $\{^{1}H\}$ NMR spectra of **5b** in CD_2Cl_2.

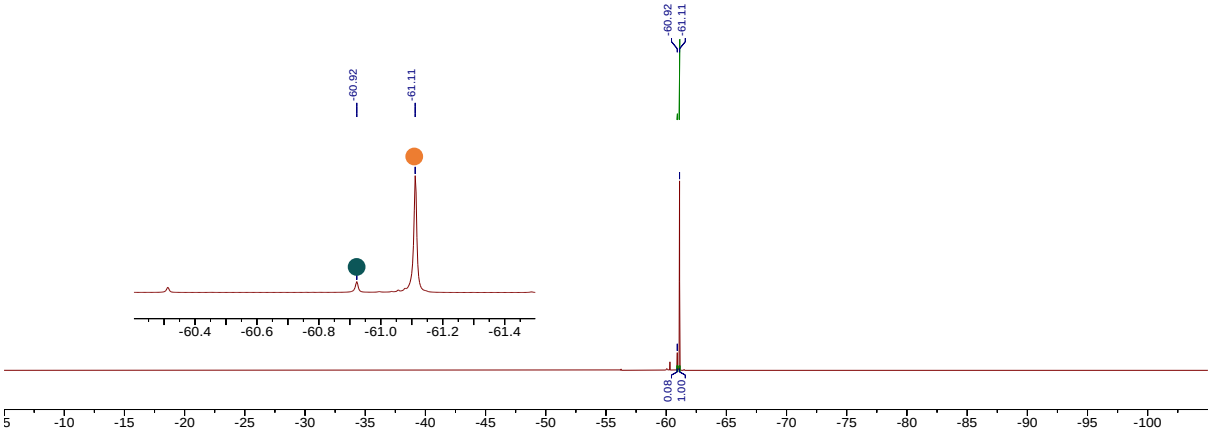


Figure S61- ^{19}F NMR spectra of **5b** (orange) containing traces of **5b'** (teal) in CD_2Cl_2.

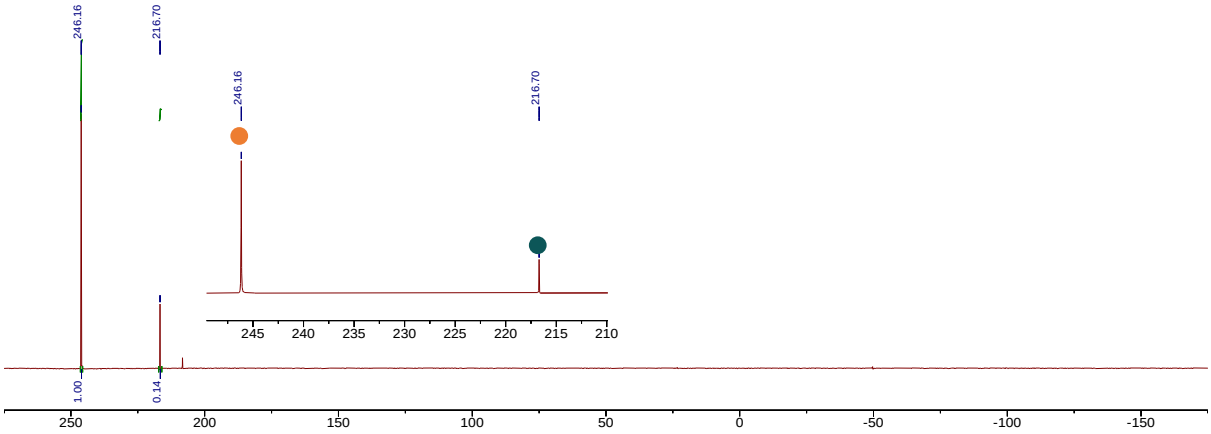
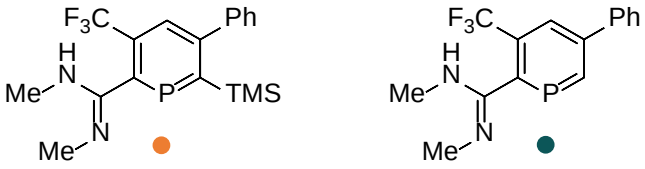


Figure S62 - ^{31}P $\{^{1}H\}$ NMR spectra of **5b** (orange) containing traces of **5b'** (teal) in CD_2Cl_2.



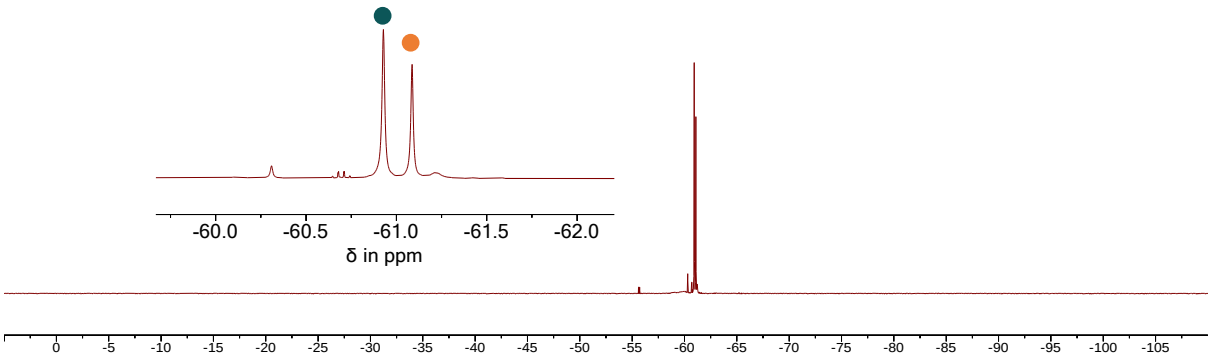


Figure S63- ^{19}F NMR spectra of **6b** and **6b'** in C_6D_6.

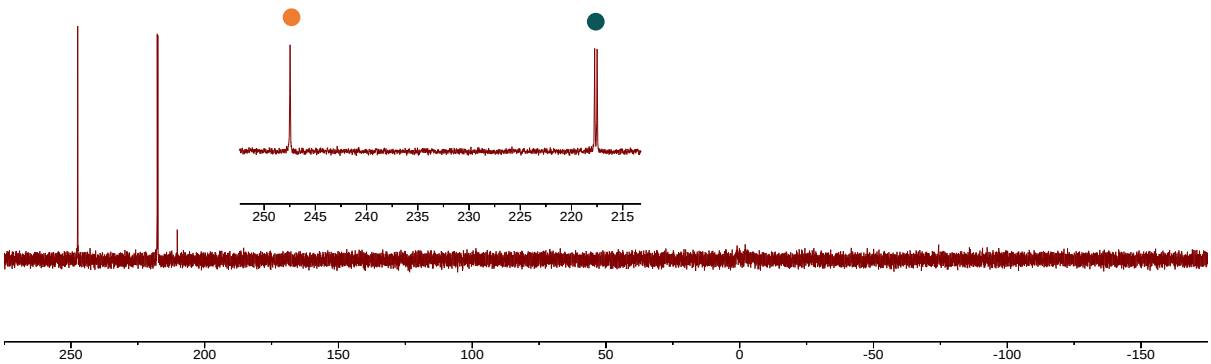


Figure S64- ^{31}P NMR spectra of **6b** and **6b'** in C_6D_6.

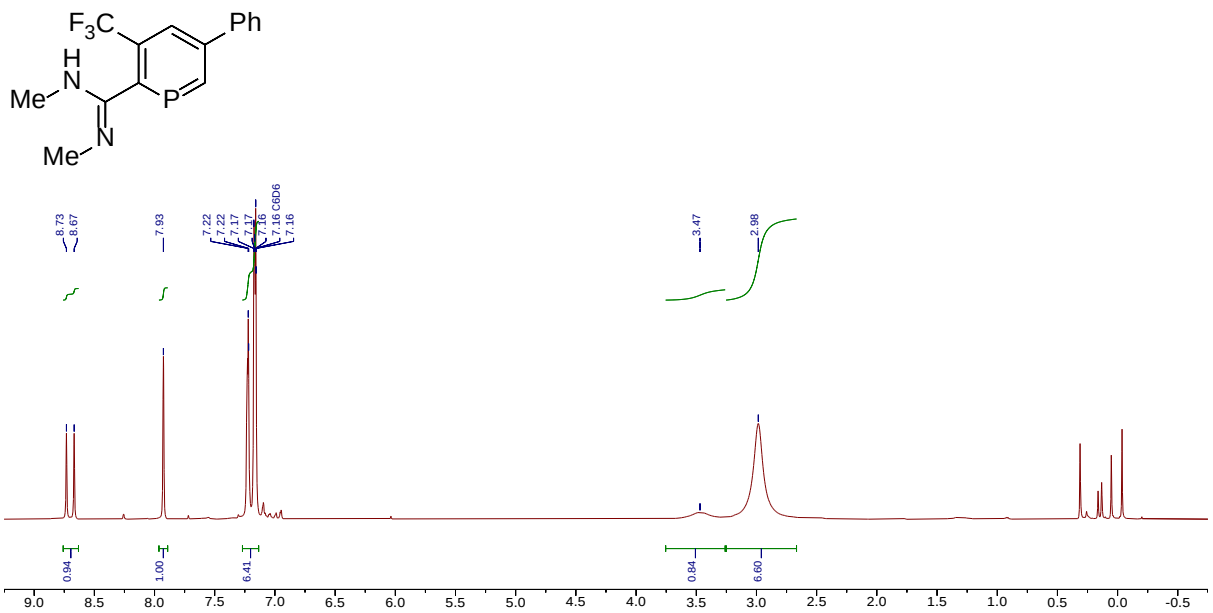


Figure S65- ^{1}H NMR spectra of **6b'** in C_6D_6.

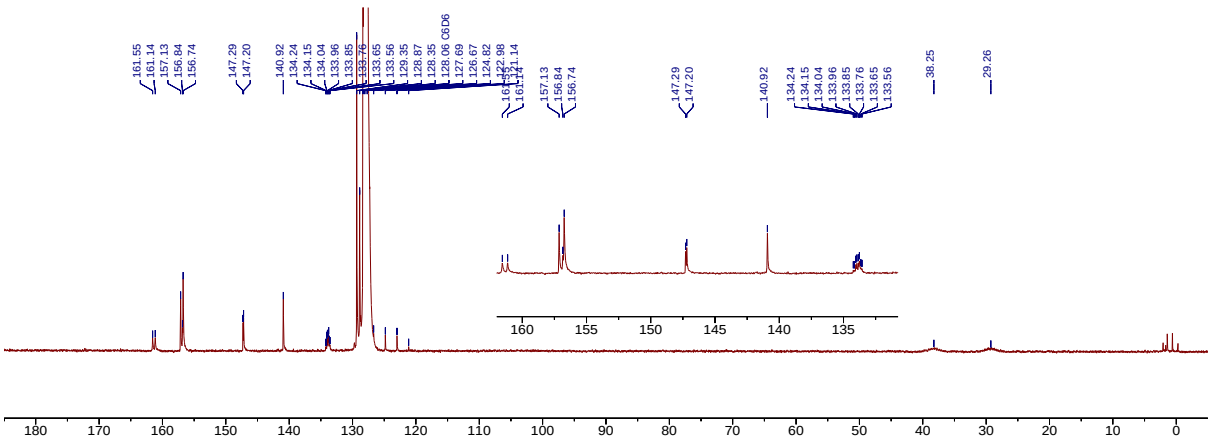


Figure S66- ^{13}C $\{^{1}H\}$ NMR spectra of **6b'** in C_6D_6.

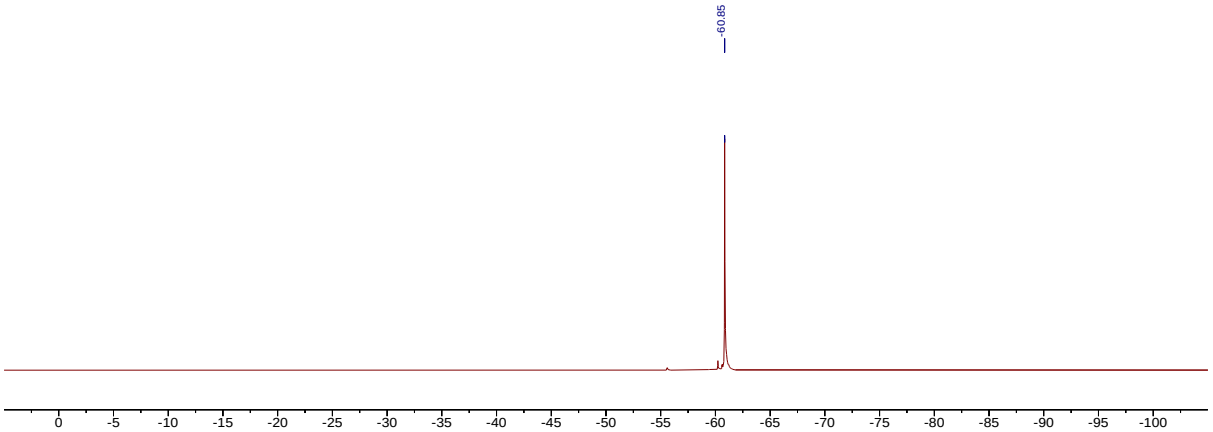


Figure S67- ^{19}F NMR spectra of **6b'** in C_6D_6.

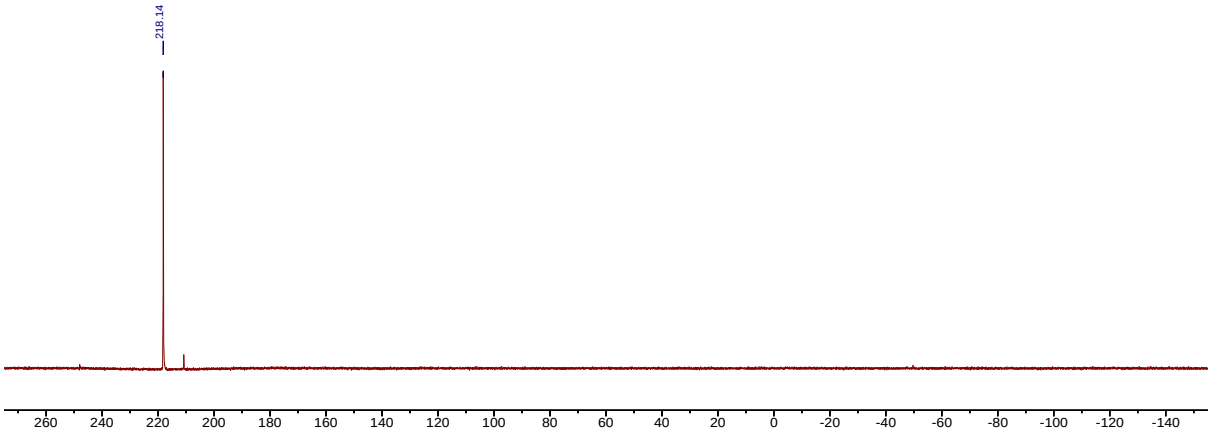


Figure S68- ^{31}P {^{1}H} NMR spectra of **6b'** in C_6D_6.

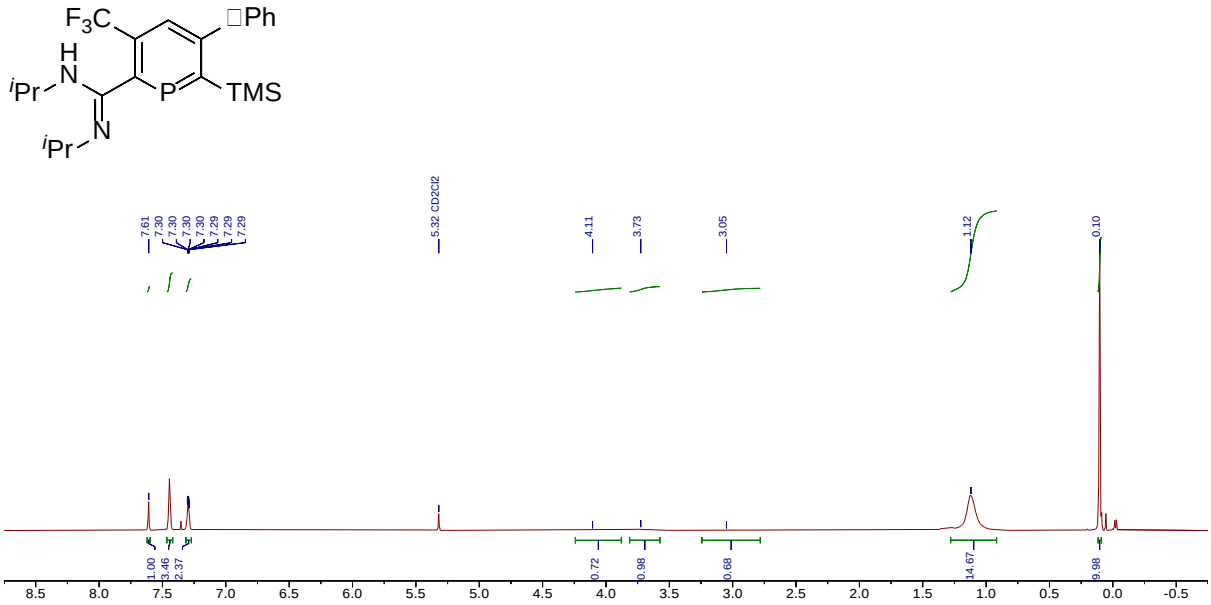


Figure S69- ^{1}H NMR spectra of **7b** in CD_2Cl_2.

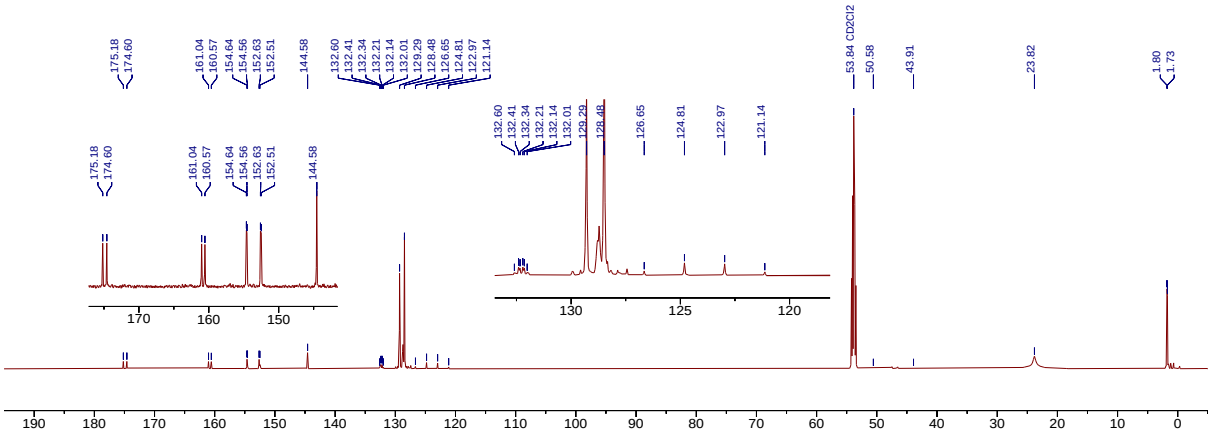


Figure S70- ^{13}C {^{1}H} NMR spectra of **7b** in CD_2Cl_2.

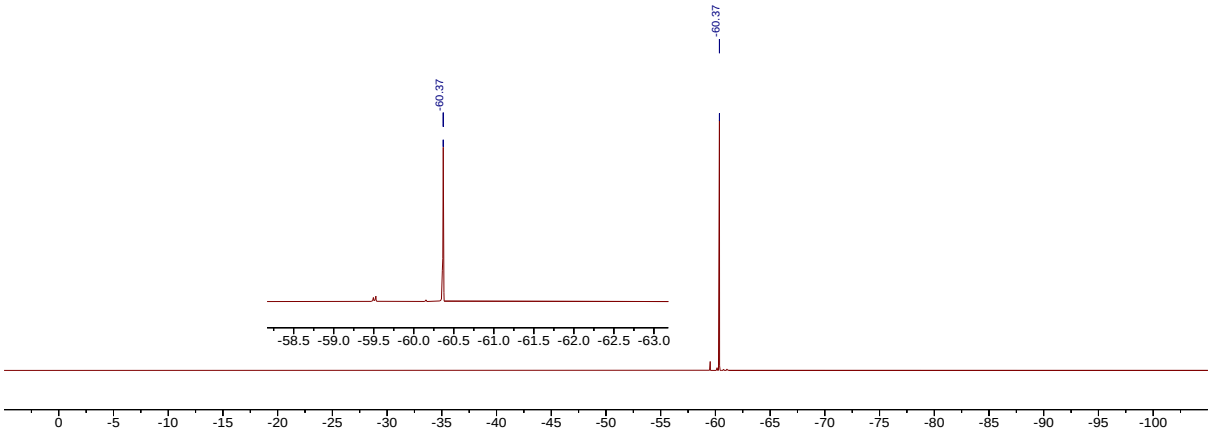


Figure S71- ^{19}F NMR spectra of **7b** in CD_2Cl_2.

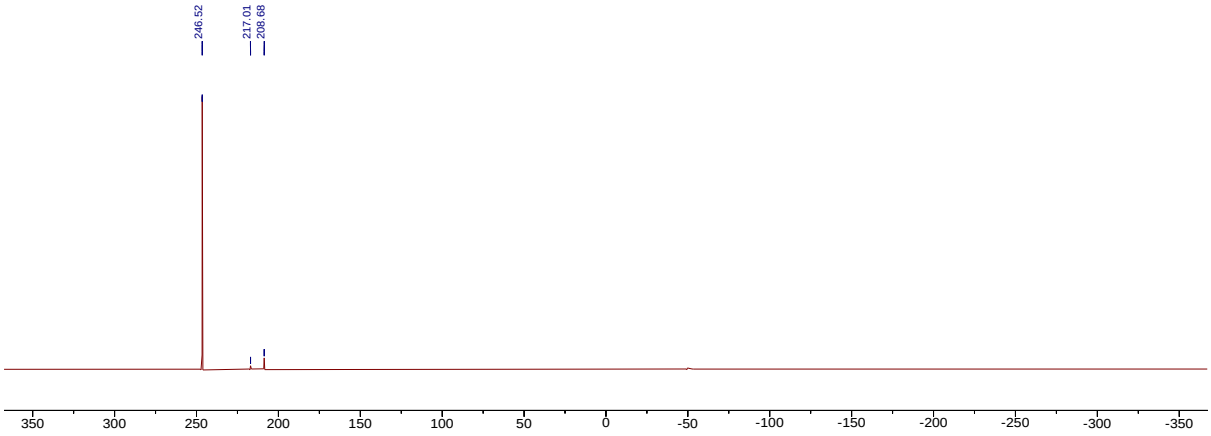


Figure S72- ^{31}P $\{^1H\}$ NMR spectra of **7b** in CD_2Cl_2.

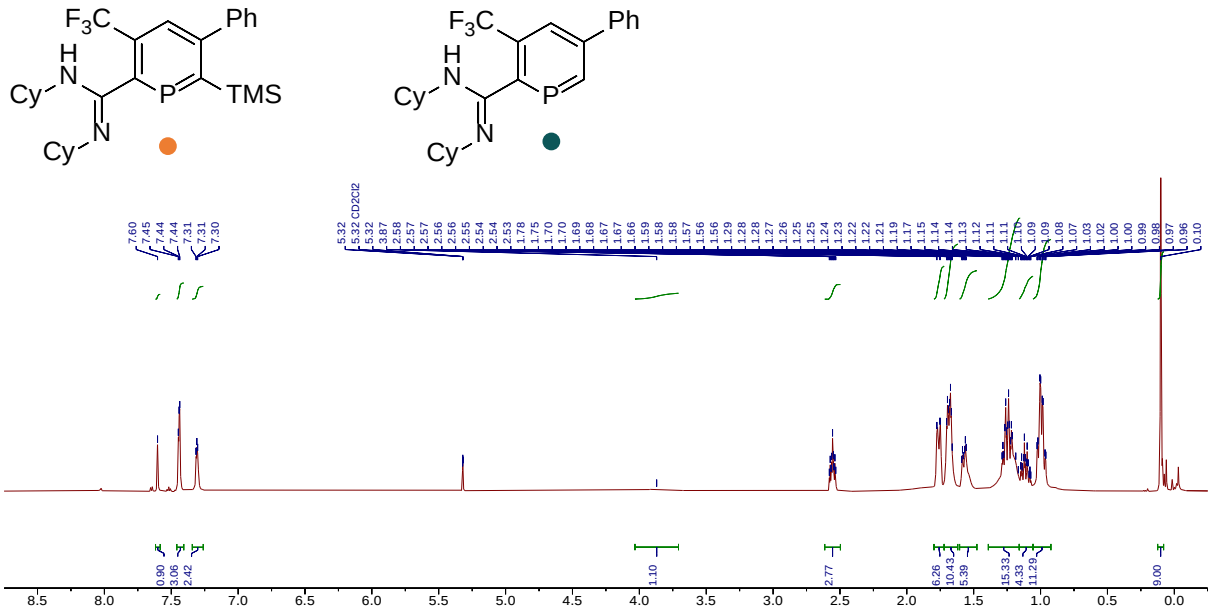


Figure S73- ^1H NMR spectra of **8b** in CD_2Cl_2.

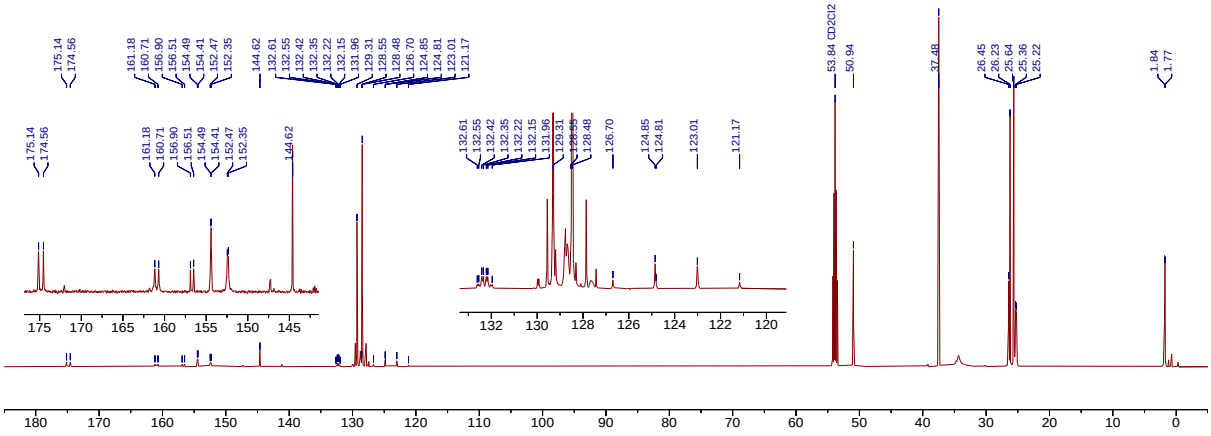


Figure S74- ^{13}C {^{1}H} NMR spectra of **8b** in CD_2Cl_2.

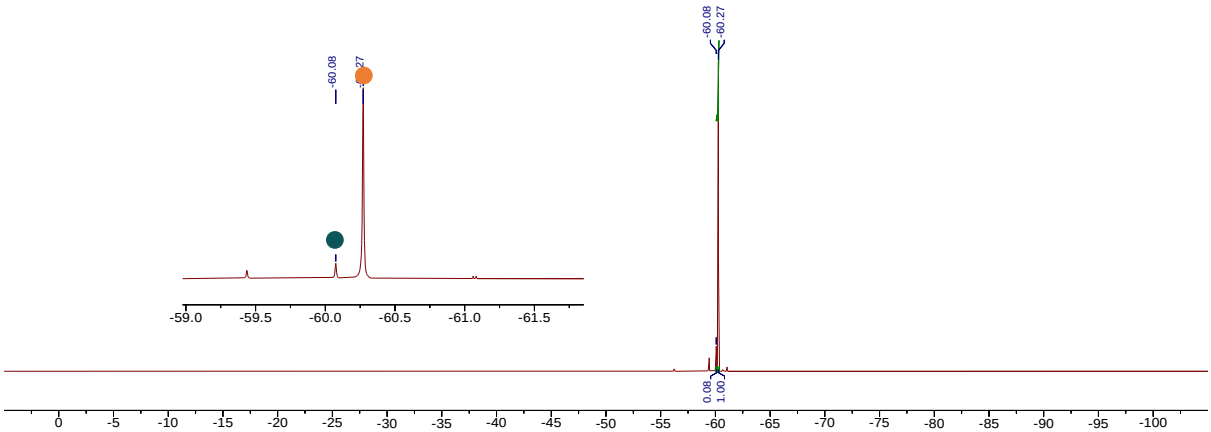


Figure S75- ^{19}F NMR spectra of **8b** (orange) containing traces of **8b'** (teal) in CD_2Cl_2.

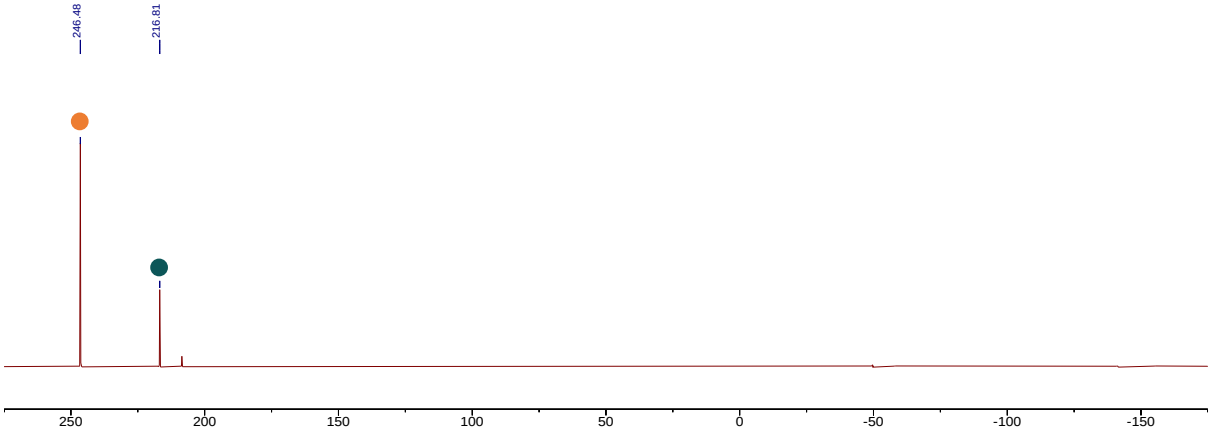


Figure S76 - ^{31}P {^{1}H} NMR spectra of **8b** (orange) containing traces of **8b'** (teal) in CD_2Cl_2.

4 Mass spectra

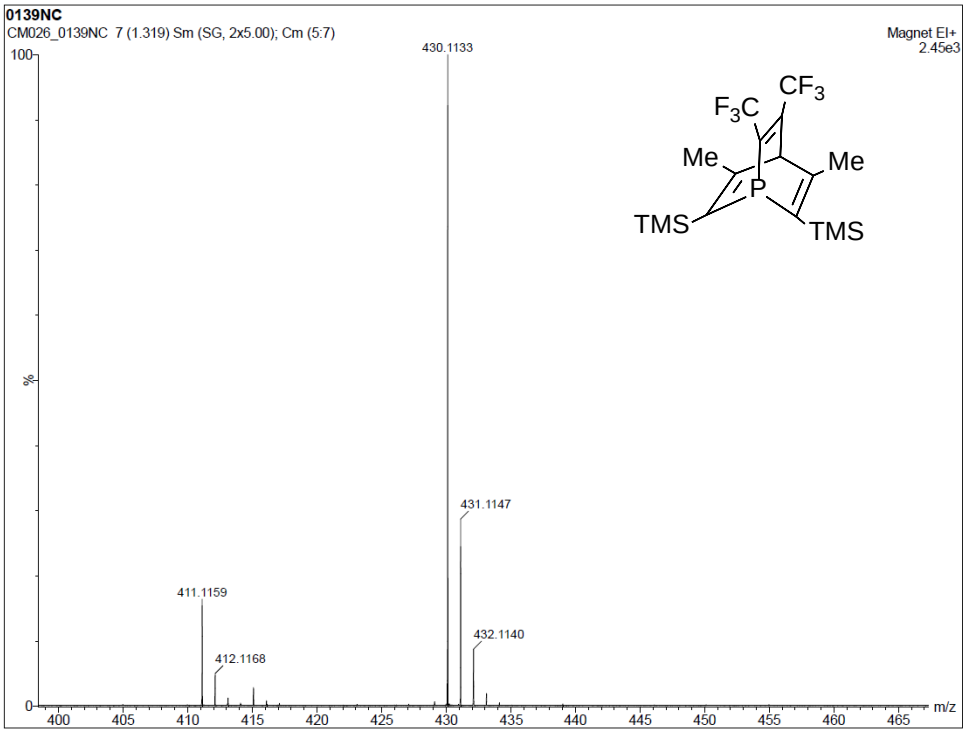


Figure S77 - Mass spectrum (EI) of **2a**.

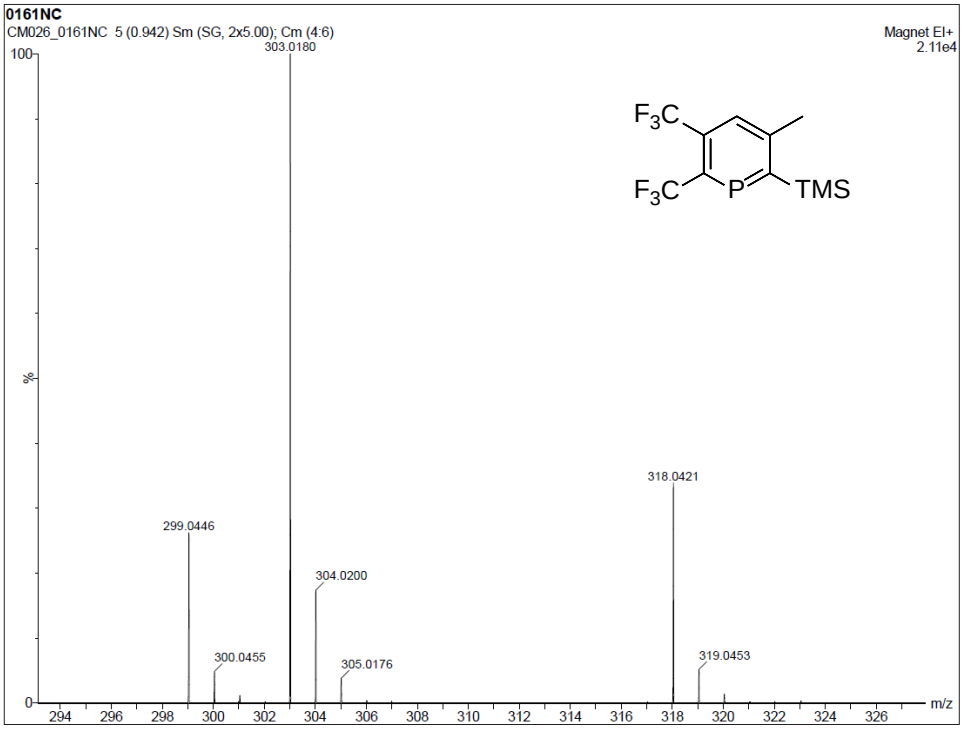


Figure S78 – Mass spectrum (EI) of **3a**.

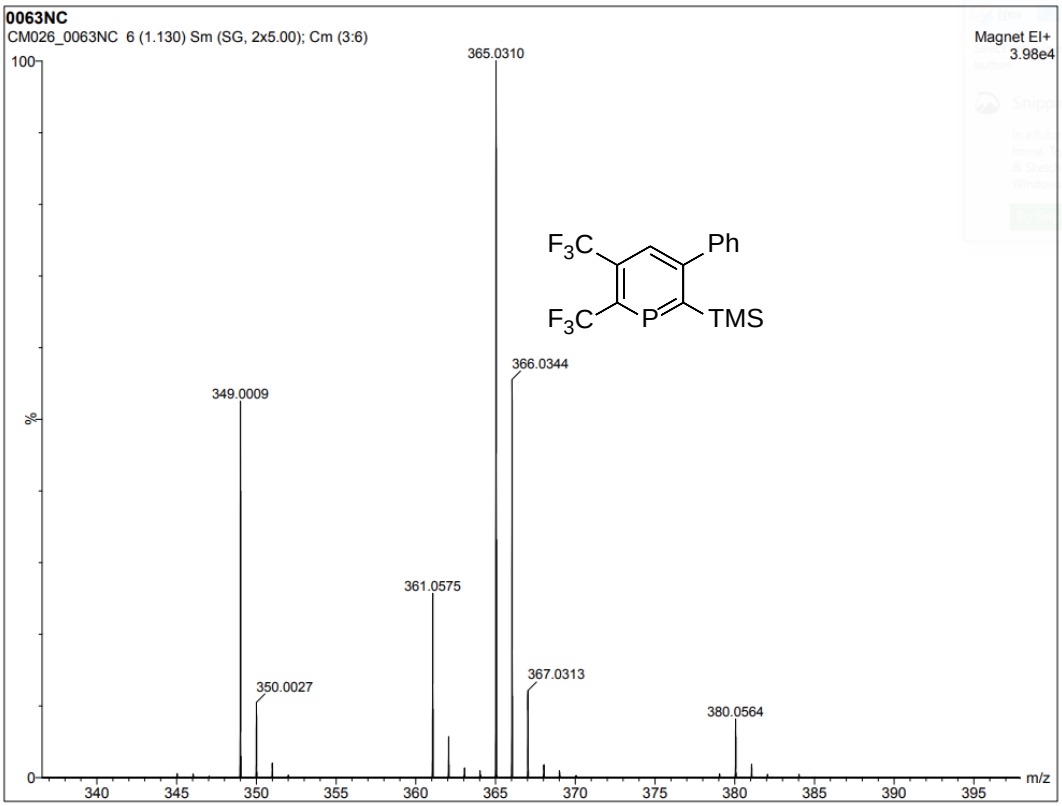


Figure S79 – Mass spectrum (EI) of **3b**.

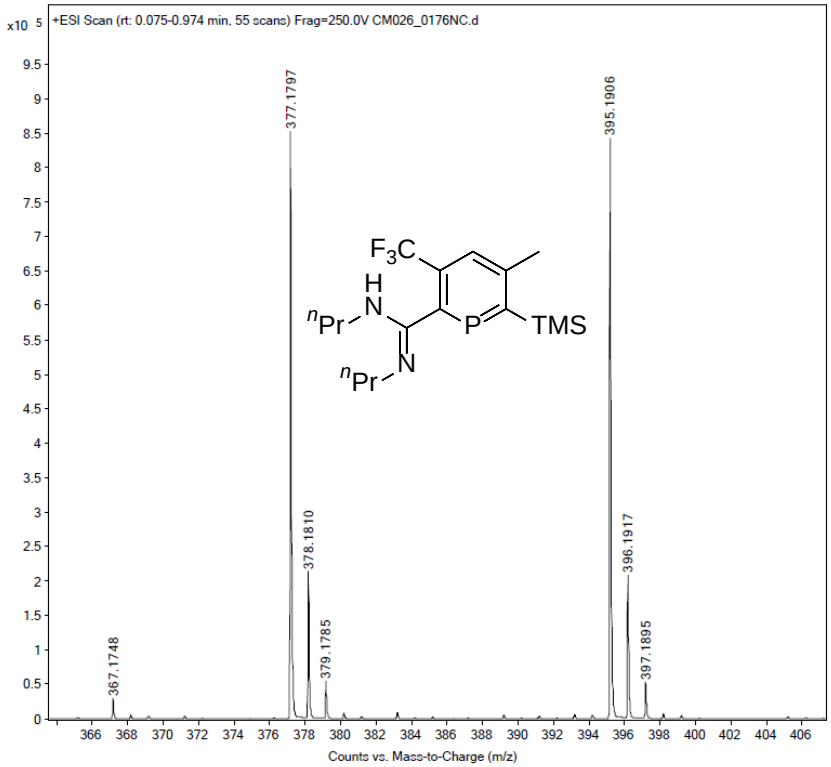


Figure S80 – Mass spectrum (ESI) of **5a**.

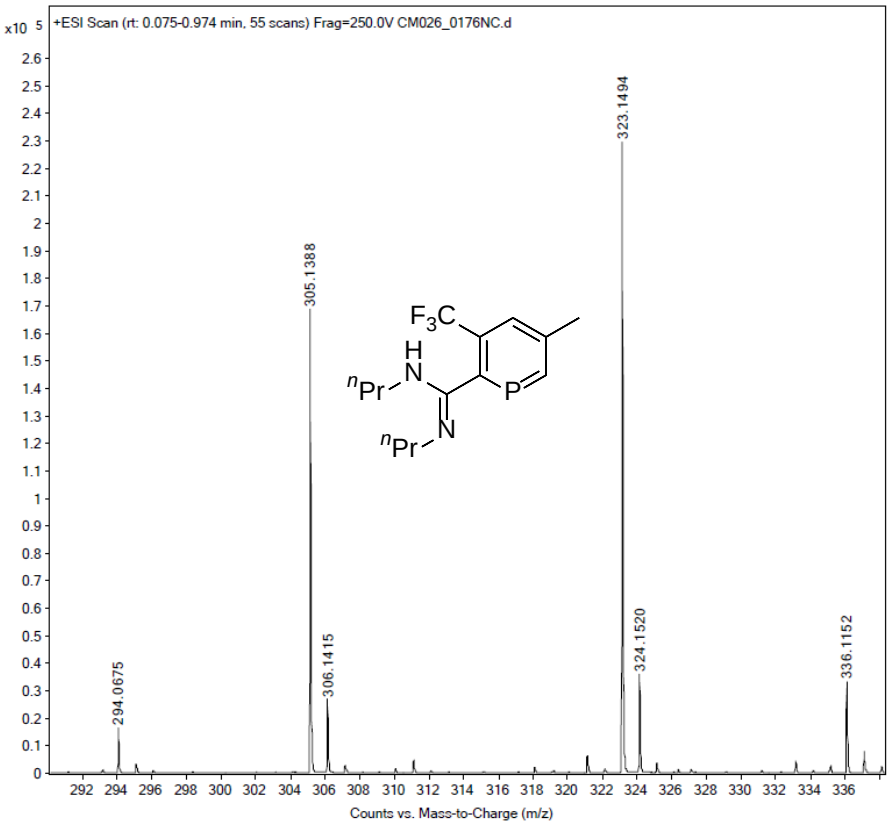


Figure S81 – Mass spectrum (ESI) of **5a'**.

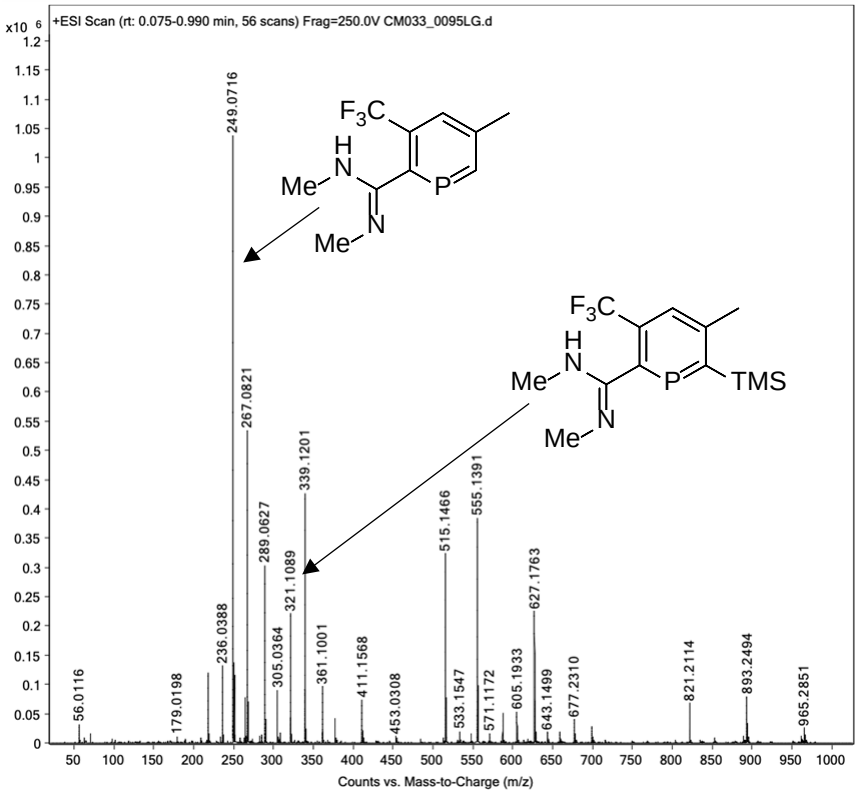


Figure S82 - Mass spectrum (ESI) of **6a**/**6a'**.

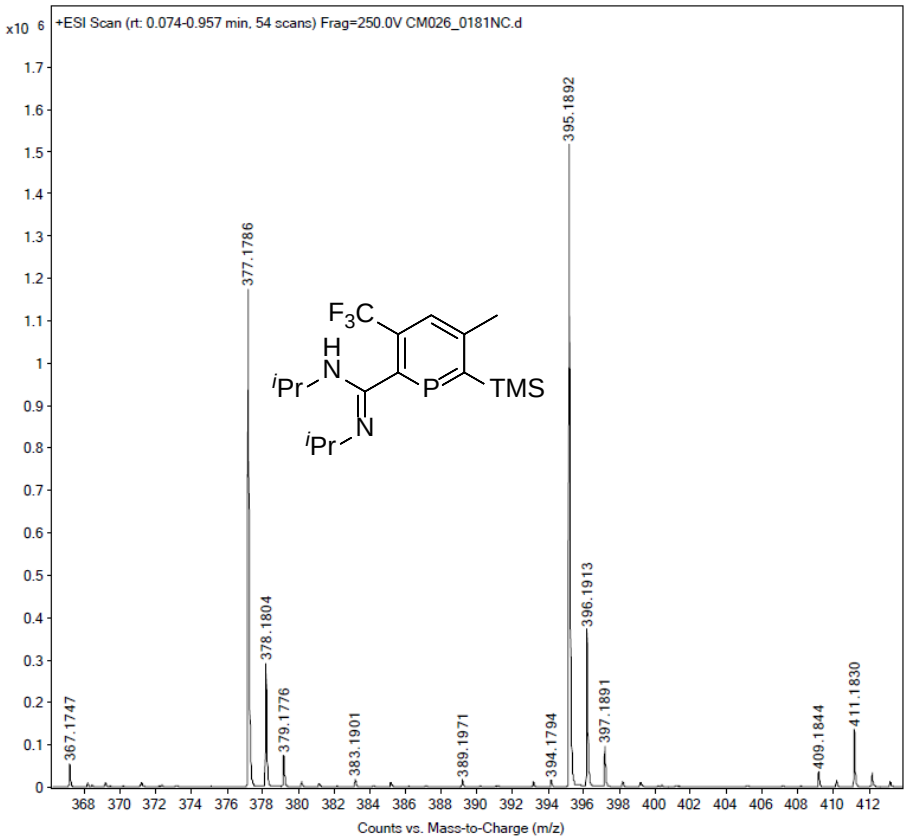


Figure S83 – Mass spectrum (ESI) of **7a**.

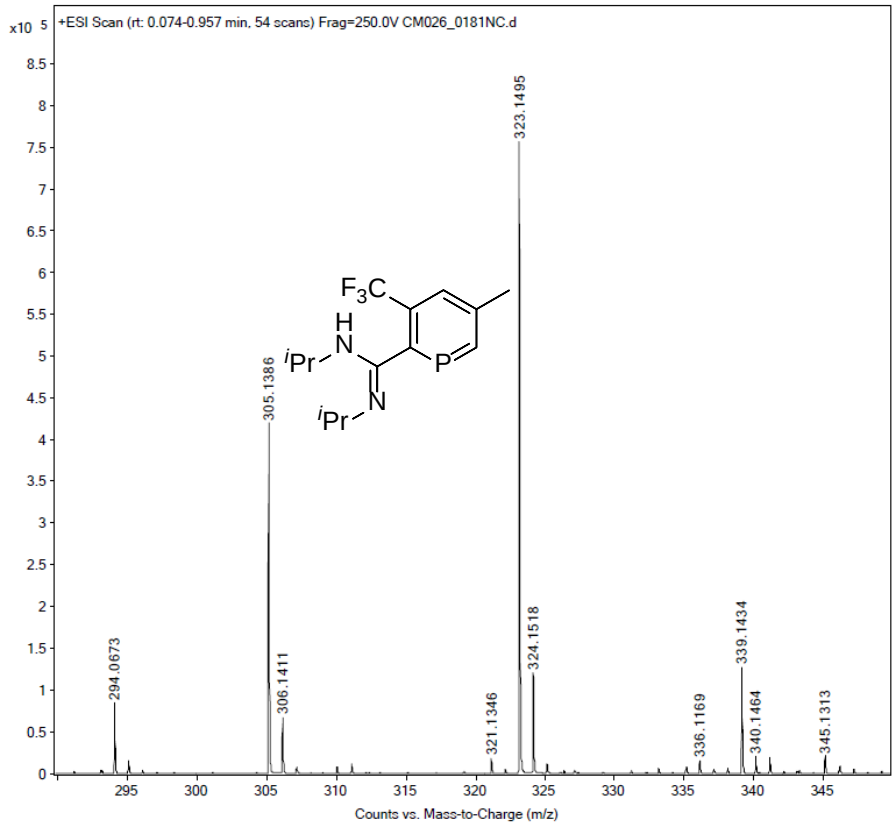


Figure S84 – Mass spectrum (ESI) of **7a'**.

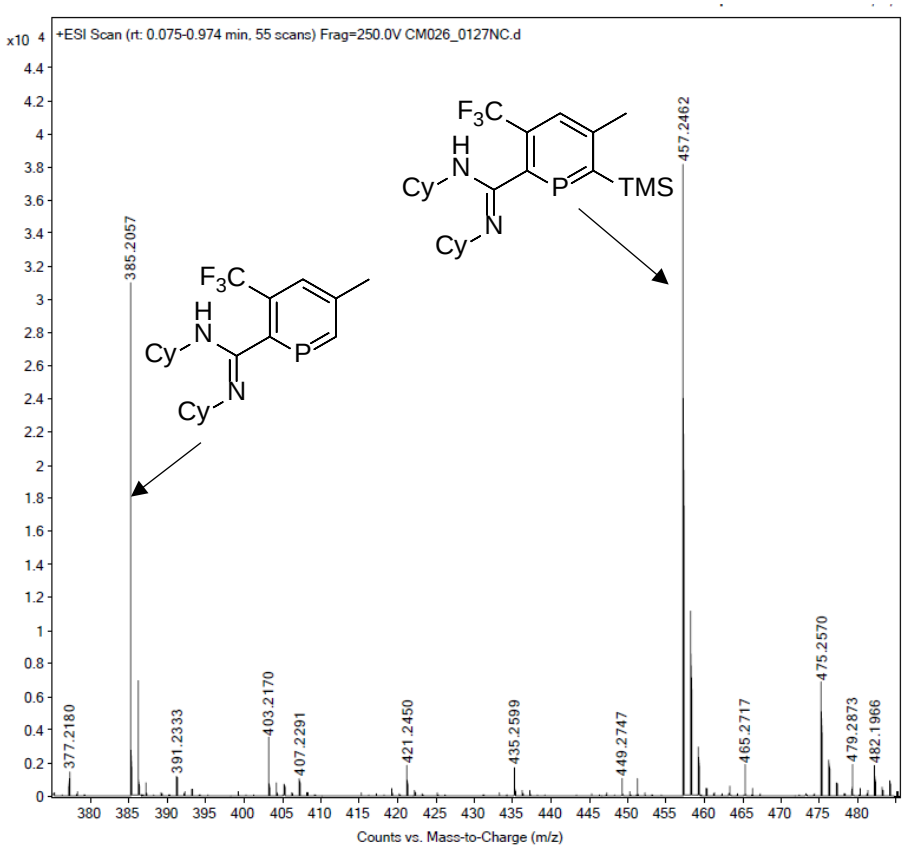


Figure S85 – Mass spectrum (ESI) of **8a** and **8a'**.

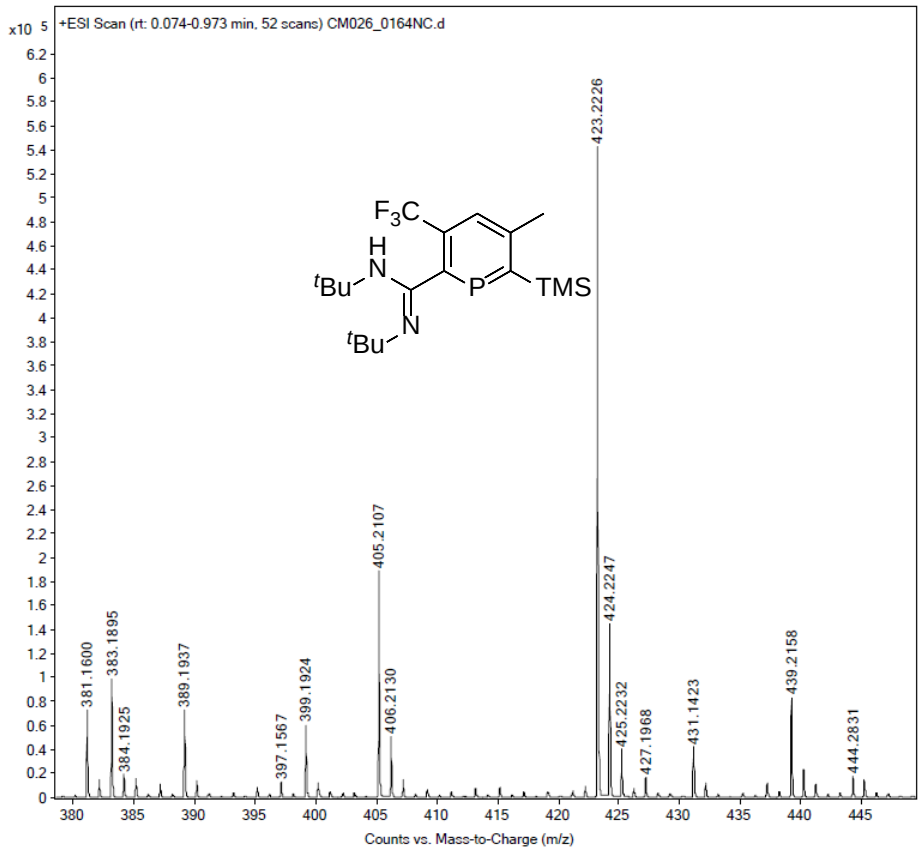


Figure S86 – Mass spectrum (ESI) of **9a**.

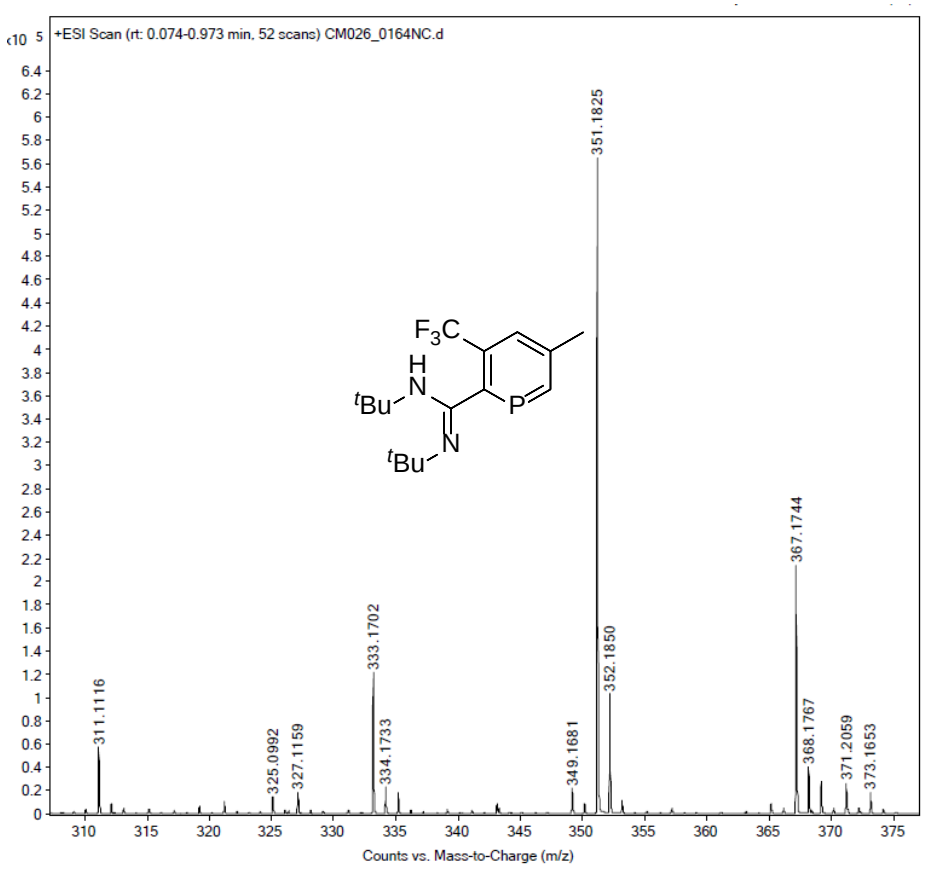


Figure S87 – Mass spectrum (ESI) of **9a'**.

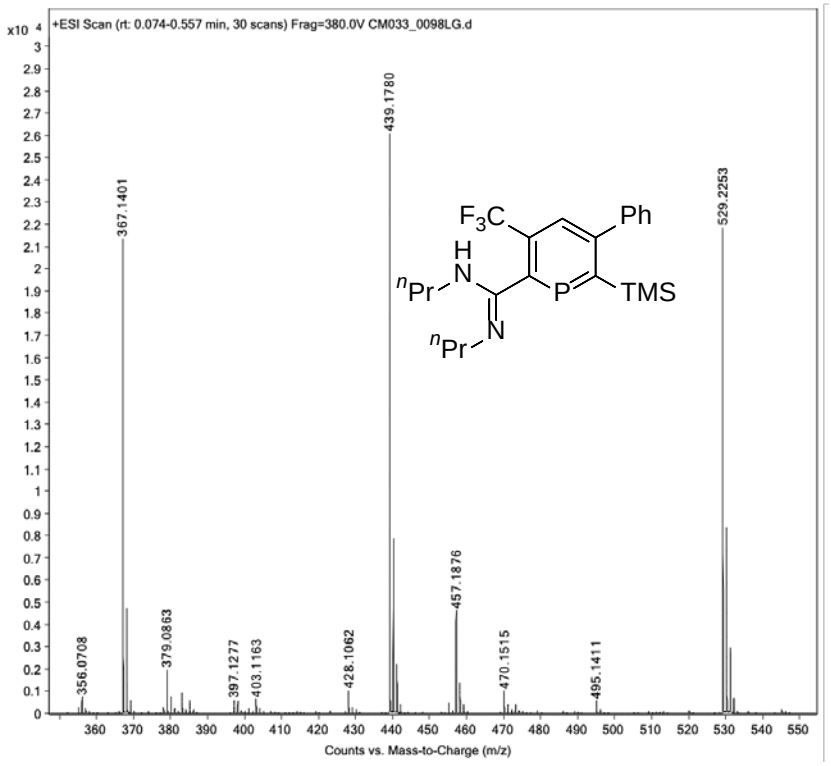


Figure S88 – Mass spectrum (ESI) of **5b**.

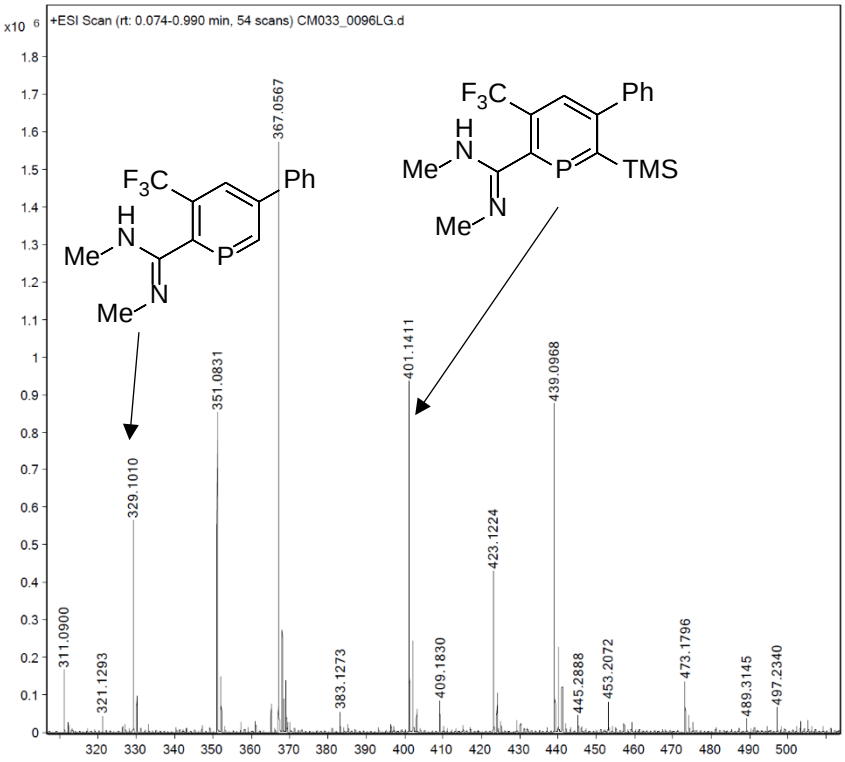


Figure S89 – Mass spectrum (ESI) of **6b** and **6b'**.

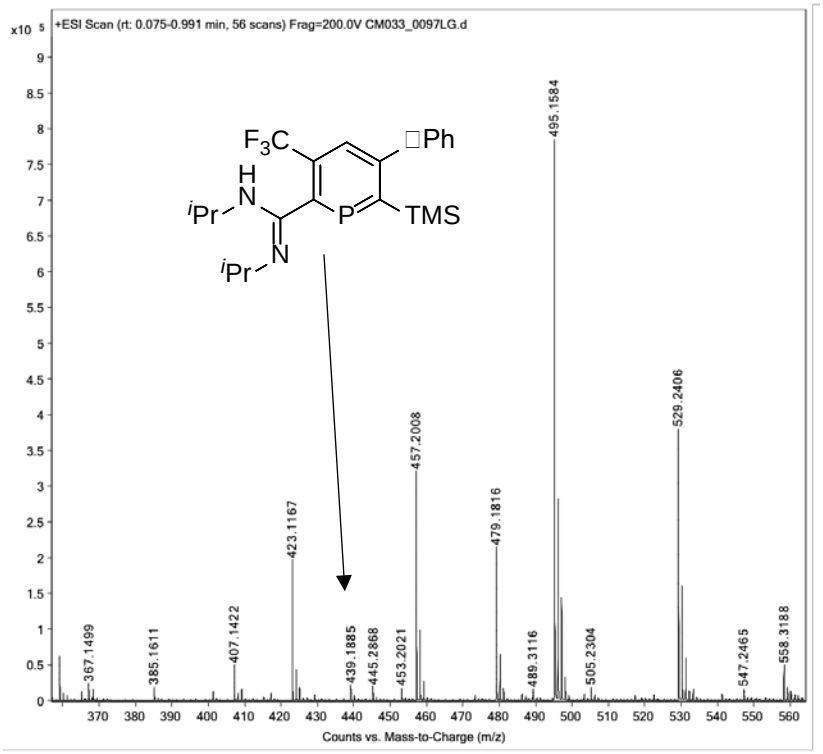


Figure S90 – Mass spectrum (ESI) of **7b**.

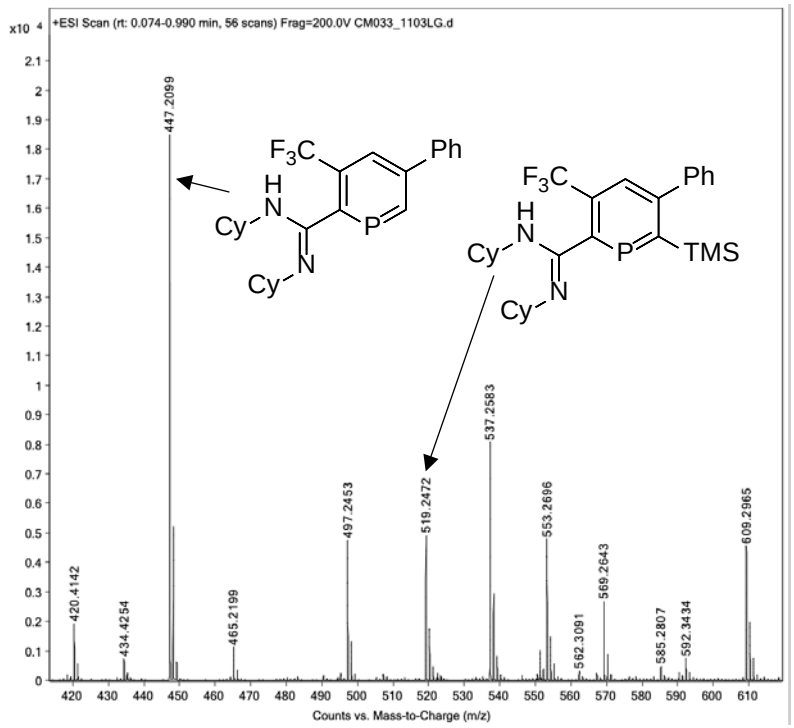


Figure S91 – Mass spectrum (ESI) of **8b** and **8b'**.

5 Crystallographic details

The supplementary crystallographic data for **1a**, **2a**, **3b** and **6a'** can be found in the CCDC with the following deposit numbers CCDC 2176809 (**2a**), 2176810 (**3b**), 2176811 (**1a**) and 2176812 (**6a'**). These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Table S1 – Selected crystallographic data for **1a**, **2a**, **3b** and **6a'**.

	1a	**2a**	**3b**	**6a'**
Sample Name	NTC043_1	NTC_046_1	NTC-013	NTC-155
CCDC number	2176811	2176809	2176810	2176812
Empirical formula	$C_{13}H_{25}PSi_2$	$C_{17}H_{25}F_6PSi_2$	$C_{16}H_{15}F_6PSi$	$C_{10}H_{12}F_3N_2P$
Formula Weight	268.48	430.52	380.34	248.19
Temperature/K	100.0	100.0	100.0	100.0
Crystal system	Triclinic	Monoclinic	Tetragonal	Monoclinic
Space group	*P*-1	$P2_1/c$	$P4_32_12$	C_c
a/Å	10.5114(3)	13.9601(6)	10.4652(2)	12.2387(8)
b/Å	13.5050(3)	7.9856(3)	10.4652(2)	11.0061(7)
c/Å	14.7354(3)	19.8245(9)	31.2709(11)	8.6295(5)
α/°	85.5620(10)	90	90	90
β/°	79.3630(10)	103.593(2)	90	95.664(2)
γ/°	86.7690(10)	90	90	90
Volume/Å^3	2047.79(9)	2148.13(16)	3424.87(18)	1156.72(13)
Z	5	4	8	4

Reflections collected	54129	73161	63344	19732
Independent reflections (R_{int})	13897 (0.0554)	6576 (0.0438)	5224 (0.0630)	3536 (0.0500)
R_1 [I>2σ (I)]	0.0453	0.0452	0.0349	0.0452
wR_2 (all data)	0.1166	0.1073	0.0863	0.1170

Additional refinement details for 1a (NTC043_1)

The crystal shows 2.5 molecules of the compound per ASU, with one molecule being disordered about a special position. The molecule that is disordered consists of atoms P3, Si5/6 and C27-39. To give an acceptable model RIGU restraints were used for atoms P3 and C27-C31 and DFIX restraints for P3-C27 and P3-C31 of 1.74 angstrom and for C27-Si5 and C31-Si6 of 1.9 angstrom. The DFIX distances used were taken as an average of the distances observed in the two molecules that did not show disorder.

1a

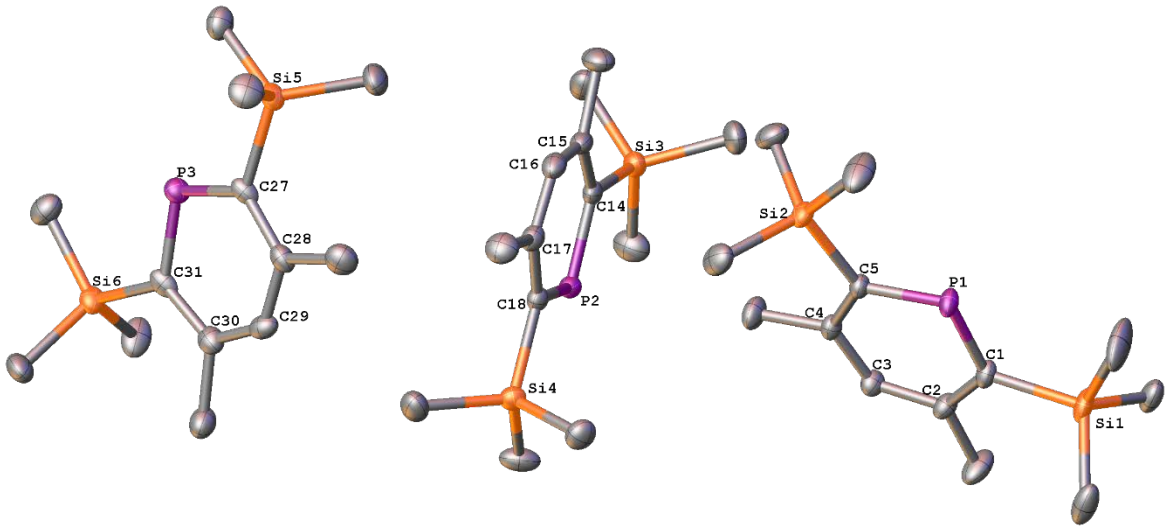


Figure S92 – Asymmetric unit of the crystal of **1a**. Hydrogens omitted for clarity. Thermal ellipsoids shown at the 50% level.

Table S2- List of bond lengths for **1a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.7410(15)	Si4	C25	1.8766(18)
P1	C5	1.7397(14)	Si4	C26	1.8697(18)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C1	1.8961(15)	C14	C15	1.412(2)
Si1	C8	1.8731(18)	C15	C16	1.388(2)
Si1	C9	1.869(2)	C15	C19	1.520(2)
Si1	C10	1.864(2)	C16	C17	1.398(2)
Si2	C5	1.8904(15)	C17	C18	1.411(2)
Si2	C11	1.864(2)	C17	C20	1.512(2)
Si2	C12	1.8766(18)	P3	C27	1.733(11)
Si2	C13	1.8703(19)	P3	C31	1.741(12)
C1	C2	1.406(2)	Si5	C27	1.895(11)
C2	C3	1.398(2)	Si5	C34	1.876(14)
C2	C6	1.511(2)	Si5	C35	1.880(4)
C3	C4	1.395(2)	Si5	C36	1.843(8)
C4	C5	1.408(2)	Si6	C31	1.893(11)
C4	C7	1.512(2)	Si6	C37	1.889(14)
P2	C14	1.7405(15)	Si6	C38	1.880(4)
P2	C18	1.7380(16)	Si6	C39	1.856(19)
Si3	C14	1.8919(16)	C27	C28	1.420(13)
Si3	C21	1.8711(18)	C28	C29	1.405(4)
Si3	C22	1.8707(19)	C28	C32	1.551(14)
Si3	C23	1.8680(18)	C29	C30	1.370(5)
Si4	C18	1.8921(15)	C30	C31	1.409(13)
Si4	C24	1.8695(18)	C30	C33	1.541(7)

Table S3 – List of angles for **1a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	P1	C1	105.81(7)	P2	C14	Si3	115.25(8)
C8	Si1	C1	112.25(8)	C15	C14	P2	120.77(12)
C9	Si1	C1	111.98(8)	C15	C14	Si3	123.94(12)
C9	Si1	C8	108.92(8)	C14	C15	C19	120.65(15)
C10	Si1	C1	109.24(8)	C16	C15	C14	122.81(14)
C10	Si1	C8	106.66(11)	C16	C15	C19	116.53(14)
C10	Si1	C9	107.54(12)	C15	C16	C17	126.73(14)
C11	Si2	C5	110.10(8)	C16	C17	C18	122.32(15)
C11	Si2	C12	107.81(11)	C16	C17	C20	116.53(14)
C11	Si2	C13	107.11(11)	C18	C17	C20	121.13(14)
C12	Si2	C5	110.30(8)	P2	C18	Si4	115.28(8)
C13	Si2	C5	112.00(8)	C17	C18	P2	121.16(12)
C13	Si2	C12	109.40(9)	C17	C18	Si4	123.53(12)
P1	C1	Si1	115.34(8)	C27	P3	C31	106.2(6)
C2	C1	P1	121.31(11)	C34	Si5	C27	111.5(8)
C2	C1	Si1	123.35(11)	C34	Si5	C35	110.1(6)
C1	C2	C6	121.54(14)	C35	Si5	C27	109.3(7)
C3	C2	C1	122.47(13)	C36	Si5	C27	109.1(4)
C3	C2	C6	115.99(14)	C36	Si5	C34	109.4(5)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C3	C2	126.69(14)	C36	Si5	C35	107.4(3)
C3	C4	C5	122.26(13)	C37	Si6	C31	108.4(8)
C3	C4	C7	116.04(13)	C38	Si6	C31	111.9(8)
C5	C4	C7	121.70(13)	C38	Si6	C37	110.3(5)
P1	C5	Si2	115.66(8)	C39	Si6	C31	108.1(6)
C4	C5	P1	121.47(11)	C39	Si6	C37	109.2(6)
C4	C5	Si2	122.81(10)	C39	Si6	C38	108.9(5)
C18	P2	C14	106.20(7)	P3	C27	Si5	115.9(6)
C21	Si3	C14	110.05(8)	C28	C27	P3	121.1(7)
C22	Si3	C14	109.23(8)	C28	C27	Si5	122.6(7)
C22	Si3	C21	107.78(9)	C27	C28	C32	121.0(9)
C23	Si3	C14	112.60(8)	C29	C28	C27	121.1(5)
C23	Si3	C21	109.04(9)	C29	C28	C32	117.8(8)
C23	Si3	C22	108.00(10)	C30	C29	C28	128.2(3)
C24	Si4	C18	109.41(7)	C29	C30	C31	122.1(5)
C24	Si4	C25	107.92(9)	C29	C30	C33	115.2(4)
C24	Si4	C26	106.74(9)	C31	C30	C33	122.5(6)
C25	Si4	C18	109.90(7)	P3	C31	Si6	115.7(6)
C26	Si4	C18	112.08(7)	C30	C31	P3	120.8(8)
C26	Si4	C25	110.65(9)	C30	C31	Si6	122.8(8)

2a

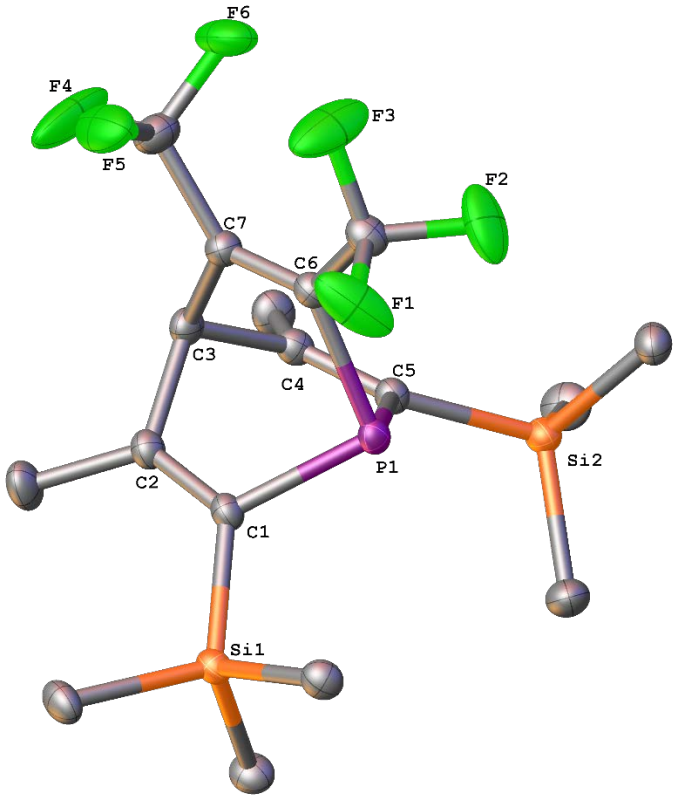


Figure S93 – Molecular structure of **2a** in the crystal Hydrogens omitted for clarity. Thermal ellipsoids shown at the 50% level.

Table S4- List of bond lengths for **2a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.8613(16)	F4	C11	1.327(2)
P1	C5	1.8673(17)	F5	C11	1.337(2)
P1	C6	1.8554(17)	F6	C11	1.333(2)
Si1	C1	1.8791(17)	C1	C2	1.342(2)
Si1	C12	1.8684(18)	C2	C3	1.543(2)
Si1	C13	1.8611(19)	C2	C8	1.499(2)
Si1	C14	1.8707(18)	C3	C4	1.544(2)
Si2	C5	1.8755(17)	C3	C7	1.519(2)
Si2	C15	1.8698(19)	C4	C5	1.338(2)
Si2	C16	1.864(2)	C4	C9	1.502(2)
Si2	C17	1.8751(19)	C6	C7	1.336(2)
F1	C10	1.324(2)	C6	C10	1.499(2)
F2	C10	1.338(2)	C7	C11	1.511(2)
F3	C10	1.317(2)			

Table S5 – List of angles for **2a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C5	96.80(7)	C5	C4	C3	117.40(15)
C6	P1	C1	95.44(8)	C5	C4	C9	128.49(16)
C6	P1	C5	95.26(7)	C9	C4	C3	114.03(15)
C12	Si1	C1	113.75(8)	P1	C5	Si2	112.51(9)
C12	Si1	C14	109.12(8)	C4	C5	P1	113.80(12)
C13	Si1	C1	107.60(8)	C4	C5	Si2	133.68(13)
C13	Si1	C12	108.17(9)	C7	C6	P1	115.62(13)
C13	Si1	C14	110.69(9)	C7	C6	C10	128.70(16)
C14	Si1	C1	107.51(8)	C10	C6	P1	115.67(12)
C15	Si2	C5	106.57(8)	C6	C7	C3	116.11(15)
C15	Si2	C17	110.43(9)	C6	C7	C11	125.82(16)
C16	Si2	C5	115.42(9)	C11	C7	C3	118.07(15)
C16	Si2	C15	108.17(9)	F1	C10	F2	104.47(17)
C16	Si2	C17	108.78(10)	F1	C10	C6	111.57(15)
C17	Si2	C5	107.43(8)	F2	C10	C6	110.98(15)
P1	C1	Si1	117.23(9)	F3	C10	F1	107.57(18)
C2	C1	P1	113.57(12)	F3	C10	F2	105.31(17)
C2	C1	Si1	128.95(13)	F3	C10	C6	116.13(16)
C1	C2	C3	117.64(15)	F4	C11	F5	106.01(19)
C1	C2	C8	128.09(16)	F4	C11	F6	106.68(19)
C8	C2	C3	114.23(15)	F4	C11	C7	112.18(16)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C3	C4	107.10(13)	F5	C11	C7	112.47(16)
C7	C3	C2	108.94(14)	F6	C11	F5	106.18(16)
C7	C3	C4	109.61(14)	F6	C11	C7	112.81(17)

3b

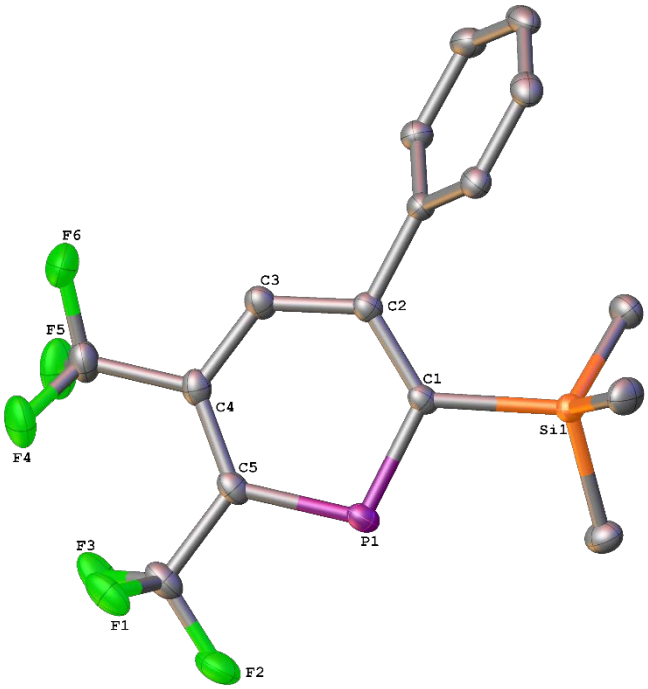


Figure S94 – Molecular structure of **3b** in the crystal. Hydrogens omitted for clarity. Thermal ellipsoids shown at the 50% level.

Table S6- List of bond lengths for **3b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P(1)	C(1)	1.739(2)	C(2)	C(3)	1.411(3)
P(1)	C(5)	1.743(2)	C(2)	C(6)	1.492(3)
Si(1)	C(1)	1.918(2)	C(3)	C(4)	1.393(3)
Si(1)	C(14)	1.869(3)	C(4)	C(5)	1.396(3)
Si(1)	C(15)	1.872(2)	C(4)	C(12)	1.524(3)
Si(1)	C(16)	1.866(3)	C(5)	C(13)	1.521(3)
F(1)	C(13)	1.342(3)	C(6)	C(7)	1.398(3)
F(2)	C(13)	1.339(3)	C(6)	C(11)	1.395(3)
F(3)	C(13)	1.338(3)	C(7)	C(8)	1.390(3)
F(4)	C(12)	1.331(3)	C(8)	C(9)	1.387(4)
F(5)	C(12)	1.345(3)	C(9)	C(10)	1.388(4)
F(6)	C(12)	1.335(3)	C(10)	C(11)	1.390(3)
C(1)	C(2)	1.403(3)			

Table S7 – List of angles for **3b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1)	P(1)	C(5)	103.89(11)	C(7)	C(6)	C(2)	120.4(2)
C(14)	Si(1)	C(1)	111.96(11)	C(11)	C(6)	C(2)	120.4(2)
C(14)	Si(1)	C(15)	111.30(12)	C(11)	C(6)	C(7)	119.2(2)
C(15)	Si(1)	C(1)	110.92(11)	C(8)	C(7)	C(6)	120.3(2)
C(16)	Si(1)	C(1)	107.19(11)	C(9)	C(8)	C(7)	120.1(2)
C(16)	Si(1)	C(14)	108.25(12)	C(8)	C(9)	C(10)	120.1(2)
C(16)	Si(1)	C(15)	106.95(12)	C(9)	C(10)	C(11)	120.0(2)
P(1)	C(1)	Si(1)	113.34(12)	C(10)	C(11)	C(6)	120.4(2)
C(2)	C(1)	P(1)	122.09(17)	F(4)	C(12)	F(5)	106.8(2)
C(2)	C(1)	Si(1)	124.41(17)	F(4)	C(12)	F(6)	106.6(2)
C(1)	C(2)	C(3)	123.3(2)	F(4)	C(12)	C(4)	113.4(2)
C(1)	C(2)	C(6)	121.1(2)	F(5)	C(12)	C(4)	111.2(2)
C(3)	C(2)	C(6)	115.6(2)	F(6)	C(12)	F(5)	106.2(2)
C(4)	C(3)	C(2)	124.7(2)	F(6)	C(12)	C(4)	112.3(2)
C(3)	C(4)	C(5)	122.5(2)	F(1)	C(13)	C(5)	112.9(2)
C(3)	C(4)	C(12)	114.1(2)	F(2)	C(13)	F(1)	106.0(2)
C(5)	C(4)	C(12)	123.4(2)	F(2)	C(13)	C(5)	111.4(2)
C(4)	C(5)	P(1)	123.42(18)	F(3)	C(13)	F(1)	107.5(2)
C(4)	C(5)	C(13)	122.8(2)	F(3)	C(13)	F(2)	106.0(2)
C(13)	C(5)	P(1)	113.74(18)	F(3)	C(13)	C(5)	112.7(2)

6a'

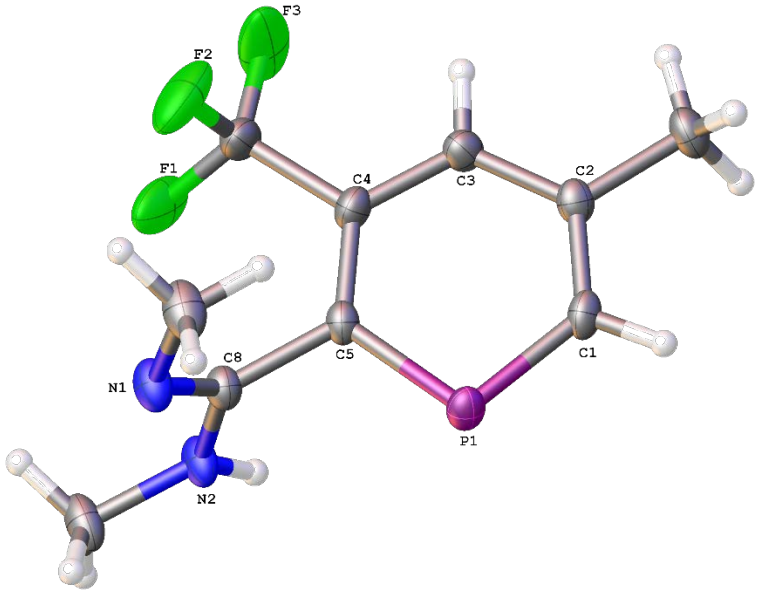


Figure S95 – Molecular **s**tructure of **6a'** in the crystal. Thermal ellipsoids shown at the 50% level.

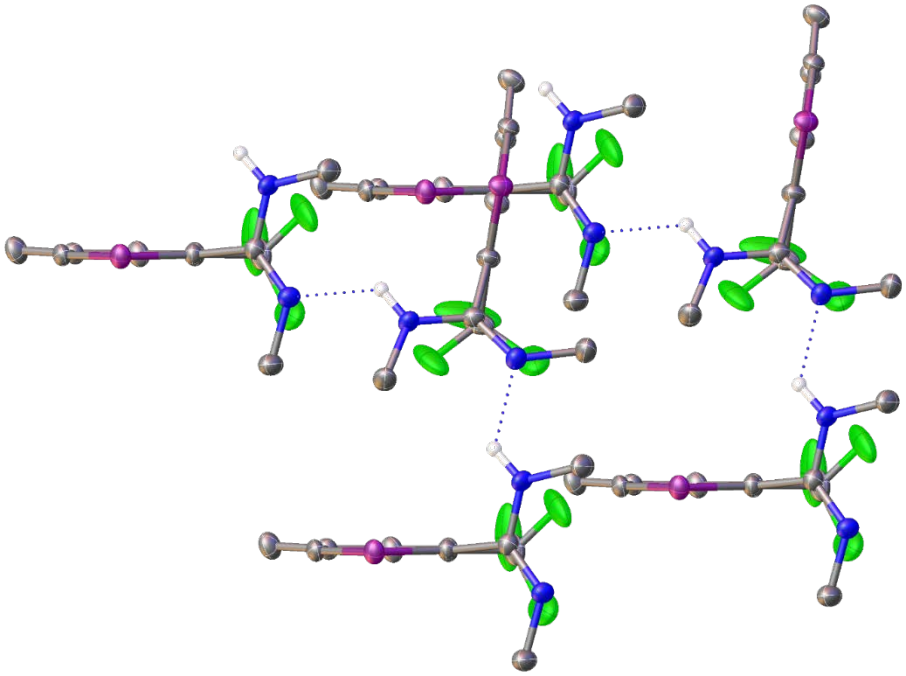


Figure S96 – Image depicting intermolecular hydrogen bonding in **6a'**.

Table S8- List of bond lengths for **6a'**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.728(3)	N2	C9	1.450(4)
P1	C5	1.740(3)	C1	C2	1.390(4)
F1	C7	1.319(4)	C2	C3	1.395(4)
F2	C7	1.335(5)	C2	C6	1.516(4)
F3	C7	1.312(5)	C3	C4	1.395(4)
N1	C8	1.288(4)	C4	C5	1.392(4)
N1	C10	1.452(4)	C4	C7	1.515(4)
N2	C8	1.358(4)	C5	C8	1.508(4)

Table S9 – List of angles for **6a'**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C5	101.26(14)	C4	C5	C8	122.9(3)
C8	N1	C10	119.6(3)	C8	C5	P1	113.5(2)
C8	N2	C9	119.8(3)	F1	C7	F2	105.0(3)
C2	C1	P1	126.3(2)	F1	C7	C4	113.7(3)
C1	C2	C3	121.2(3)	F2	C7	C4	111.2(3)
C1	C2	C6	119.5(3)	F3	C7	F1	107.9(4)
C3	C2	C6	119.4(3)	F3	C7	F2	105.5(4)
C2	C3	C4	124.1(3)	F3	C7	C4	112.9(3)
C3	C4	C7	116.5(3)	N1	C8	N2	121.0(3)
C5	C4	C3	123.7(3)	N1	C8	C5	125.9(3)
C5	C4	C7	119.8(3)	N2	C8	C5	112.9(2)
C4	C5	P1	123.5(2)				

6 Computational details

Energy levels of the frontier molecular orbitals
General information

DFT Calculations were carried out with the ORCA 4.2.0 program suite.[9,10] Initial molecular structures were created in the program Avogadro[11] or were based on crystal structures, if available. Geometry optimizations were then performed with the PBEh-3c method developed by Grimme and co-workers.[12,13] Numerical Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimizations. The absence of imaginary vibrational frequencies indicated that the optimized structure was a local minimum. Final single point calculations on the optimized structures were conducted with the B3LYP functional.[14,15] Additionally, for all calculations the empirical Van der Waals Correction (D3) was used. [16–19] Standardized convergence criteria were used for the geometry optimization (OPT) and the addition "tight" for SCF-calculations ("TIGHTSCF"). A Triple-ζ-valence-basis set (def2-TZVPP) was applied for all atoms (single point calculation).[20] Singe point calculations with the B3LYP-functional were done with the RIJCOSX-approximation[21–27] and solvent effects were taken into account with the Conductor-like-Polarizable-Continuum-Modell (CPCM)[28–31] for THF. Molecular orbitals were visualized via the freely available program IBOView v20150427.[32,33] The computational data for C_5H_5P at the same level of theory as mentioned above have been previously reported by us.[34]

Computed Cartesian coordinates (Å) for 1b and 3b (PBEh-3c).

1b

```
C   -0.90123311487248     -1.38091952520793     -0.08881300043503
C   -0.60400579138643     -0.36307264720712      0.82205300399243
C   0.44248615734408      0.53808530602156      0.63885374163852
C   1.33670158208173      0.53223835397748     -0.42890453004931
C   1.29870240374404     -0.42247689546010     -1.44961303980066
P   0.07115830068463     -1.64672252592082     -1.50009747283314
H   0.57335923657600      1.30717755395085      1.39191065654068
```

C	-1.35250670127292	-1.11226856700079	3.08518188764909
C	-2.11656416771874	-0.94649694862281	4.23042940570725
C	-2.94677846991021	0.15712508323794	4.35940054536128
C	-2.99848255154786	1.10083977643253	3.34367334314803
C	-2.23244454735578	0.93513538693601	2.20058974770950
C	2.36838168363664	1.60103688583333	-0.42688449827625
C	3.38071446167780	1.60090299990498	0.52822697153263
C	4.35888055751055	2.58260971136943	0.51704426061231
C	4.32921893085986	3.58433394463199	-0.44233695373714
Si	-2.37989297795135	-2.56933111520590	0.06435030636061
C	-3.93394587823154	-1.70889634980865	0.69369466530523
H	-3.90539603497463	-1.48889715370298	1.75995944154217
H	-4.80043137663118	-2.34861154015064	0.51177499633277
H	-4.10979821059839	-0.76907694393931	0.16861061097133
C	-2.76481979427874	-3.23879305937274	-1.65736703664292
H	-1.95034363387527	-3.82918672671670	-2.07662819835728
H	-2.98687628962014	-2.44105972071324	-2.36745448098356
H	-3.64414440162491	-3.88493561429894	-1.60673191346167
C	-1.93890595072609	-4.04401043795102	1.15801102103547
H	-1.86250555158630	-3.78026062322189	2.21205171862432
H	-0.98893428844203	-4.48575049310888	0.85369078781234
H	-2.70155992805628	-4.82080946537495	1.07345794535853
Si	2.56516433571936	-0.53856282879873	-2.86666506170963
C	2.51153045935463	-2.29917650748438	-3.54385821776127
C	4.32809607125772	-0.20939441743492	-2.28791753878238
C	2.10255569692655	0.62318760207718	-4.28119604286423
H	2.72684926327691	-3.04163643452933	-2.77424678529253
H	3.26608567198191	-2.41129921981721	-4.32574756062425
H	1.54753698792873	-2.55697890541688	-3.98223191025922
H	1.04946463051452	0.51926413709842	-4.54670452074125
H	2.68766358138230	0.38570714368874	-5.17198227013047
H	2.28601663761021	1.67043090839034	-4.04466290027210
H	4.56217547890000	-0.76860426072942	-1.38113211526108
H	4.52748310198826	0.84222148676067	-2.08688386567123
H	5.02798491444860	-0.53626676716812	-3.06020668874093
H	-2.05881581953196	-1.67806384408735	5.02580714342954
H	-3.54658255406475	0.28498737917979	5.25075401259121
H	-3.64110853991552	1.96617317799600	3.43957823112266
H	5.14937153282023	2.56223372639949	1.25569506774184
C	2.33294137325638	2.62127353477453	-1.37162188948459
C	-1.41437433855429	-0.18110066670927	2.05374814337780
H	-2.28147983469275	1.66641430426263	1.40339774425676
C	3.30929813543079	3.60586772654451	-1.38202889701959
H	5.09472216159894	4.34882753325146	-0.45335633024384
H	3.27032969659483	4.39360641601030	-2.12300712268635
H	3.41217492730239	0.81181016103016	1.26921420880062
H	-0.69220355344698	-1.96486021794096	2.99161654955893
H	1.52900632845893	2.64605018334167	-2.09609531599197

3b

C	-2.69674331979610	2.46878312196209	-0.45441596607118
C	-2.82363605704859	1.09183206186123	-0.26483450789121
C	-1.46115341531763	3.10041887840597	-0.37663626526262
C	-0.23967557278998	2.47363731572006	-0.14307662923136
P	-1.47705959353737	0.04023268669475	0.07029851581604
C	-0.11053123922530	1.10176870576424	0.07114131800420
C	-3.87994024238478	3.38938523944380	-0.72305874421864
F	-3.47821734119237	4.56389586891939	-1.22109983072056
F	-4.54598400759609	3.66107773364926	0.39970875185893
C	-4.14217910021606	0.35656441186535	-0.34880355193871
F	-4.03142683054438	-0.86359924260068	0.18914171360501
F	-4.53260179544772	0.18068759800416	-1.61288637716534
F	-5.12623891320278	0.97158493945502	0.30794421703965
H	-1.42078975967744	4.16926604523644	-0.52802380955687
C	0.95186745349800	3.36176799563623	-0.13646614903275
C	1.16765497863229	4.23680214582215	0.92349779370396
C	1.85329455118888	3.34059370472874	-1.19514209779824
C	2.28601330757117	5.05533135296452	0.93959732252173
C	3.19240020132587	5.01615908669693	-0.11008015570602
C	2.96968733261878	4.16337329973572	-1.18122863449763
H	2.45146749725336	5.72273966273265	1.77485824800710

```
H    4.06518270622790      5.65522214273903     -0.09728658868561
H    0.46644842897134      4.26082009524520      1.74844031226539
H    3.66301096957143      4.14218194194911     -2.01162473705044
H    1.67156380309371      2.68652282353234     -2.03840171371983
Si   1.55169189669344      0.22299591745456      0.43890825364761
C    1.15655833760855     -1.41726357248726      1.27935526594256
H    0.59107441742242     -1.28559655645924      2.20276695167954
H    2.09242341748204     -1.91601833147422      1.54169837401687
H    0.59329462638069     -2.10278670025775      0.64621139075799
C    2.64863884407596      1.21356660373442      1.60379520596135
H    2.09786603420654      1.57040552996957      2.47482776345014
H    3.11719282242993      2.07560910093929      1.13148641830523
H    3.44798701774255      0.56582223379655      1.97097060859259
C    2.45942791069823     -0.15962646166343     -1.16714487227519
H    1.80447805476633     -0.64376846234836     -1.89287164419045
H    3.28746910295769     -0.84356613685267     -0.97032108126016
H    2.88054569317523      0.72880809230029     -1.63566963477888
F   -4.73674221761576      2.88261912718448     -1.60556543412422
```

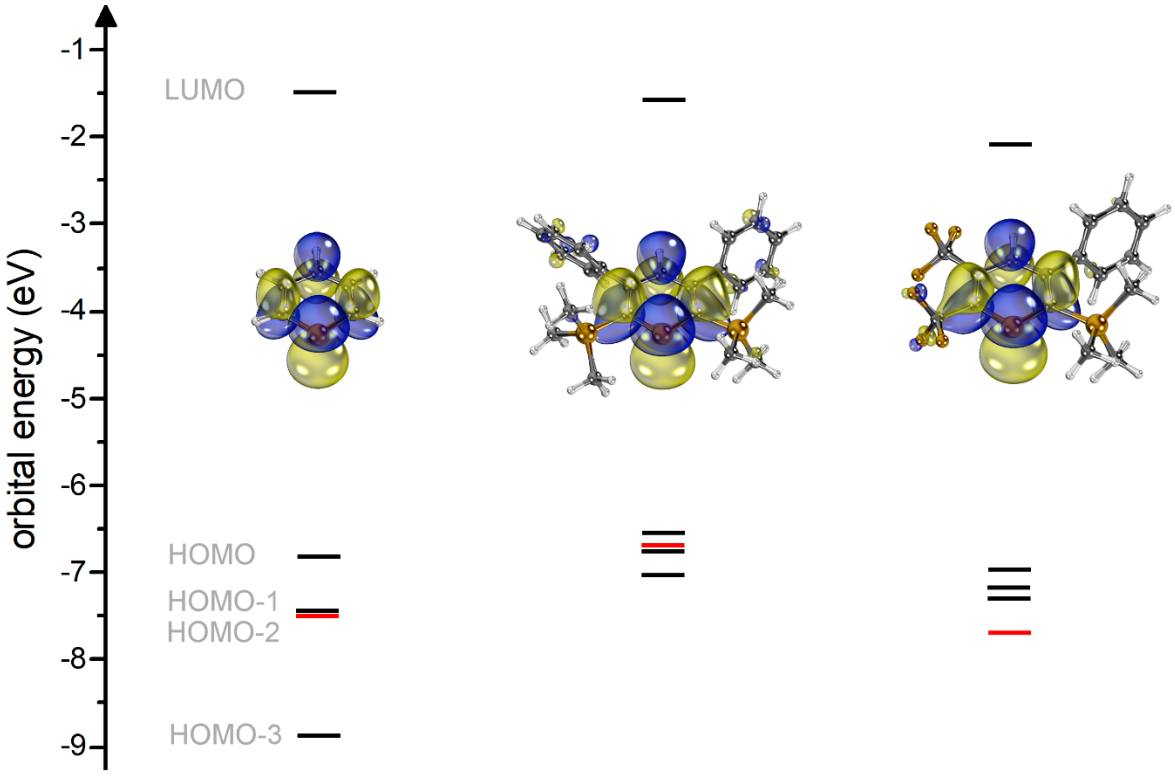


Figure S97 - Frontier orbital energies of C_5H_5P (left), 1b (middle) and 3b (right) and Kohn-Sham-orbitals of the corresponding LUMOs, calculated at the B3LYP-D3,THF/def2-TZVP//PBEh-3c level. Red: mainly P-lone pair.[35]

Free energy profiles
General information

Gaussian 16 (Revision C.01)[36] was used to perform the DFT calculations at the TPSS/def2-TZVPP level[20,37] with the ultrafine integral grid option invoked, and frequency calculations carried out at the same level of theory yielded free energy corrections and confirmed local minima, which were confirmed with no imaginary frequencies. Saddle points were also confirmed via the identification of a single negative eigenvalue upon frequency analysis which constituted the relevant bond forming or breaking process. Transition states were then perturbed along the forward and reverse directions of the imaginary frequency, and the

resulting structures subsequently optimized to confirm and yield the respective reactants and products. Single point energy corrections were calculated at the M052X-D3,THF/def2-QZVPP level,[20,38,39] which was identified as a reliable functional in a benchmarking evaluation of main group kinetics, thermodynamics and non-covalent interactions by Grimme and coworkers.[40] Solvation corrections were carried out using the IEFPCM approximation[41] with THF as the solvent (where ε = 7.4257), except for calculations on the energetics of formation of **2a** from **1a**, and **3a** from **2a**, where toluene (ε = 2.3741) was employed to reflect the solvent used in the reaction conditions of synthesis of **2a** and **3a**. Empirical corrections for dispersion interactions were obtained with Grimme's standalone D3 program,[17] with the zero-damping function.

Free energy profiles

Note: In reaction steps where HF forms (for instance, in **I** → **II** and **IV** → **V**), a lower energy adduct to the respective product whereby HF is coordinated *via* H-bonding, typically forms, and these can be found in Section 6.4 with a "**+HF**" suffix for each species. However, for the sake of clarity these are not illustrated in Figure 4 and S98.

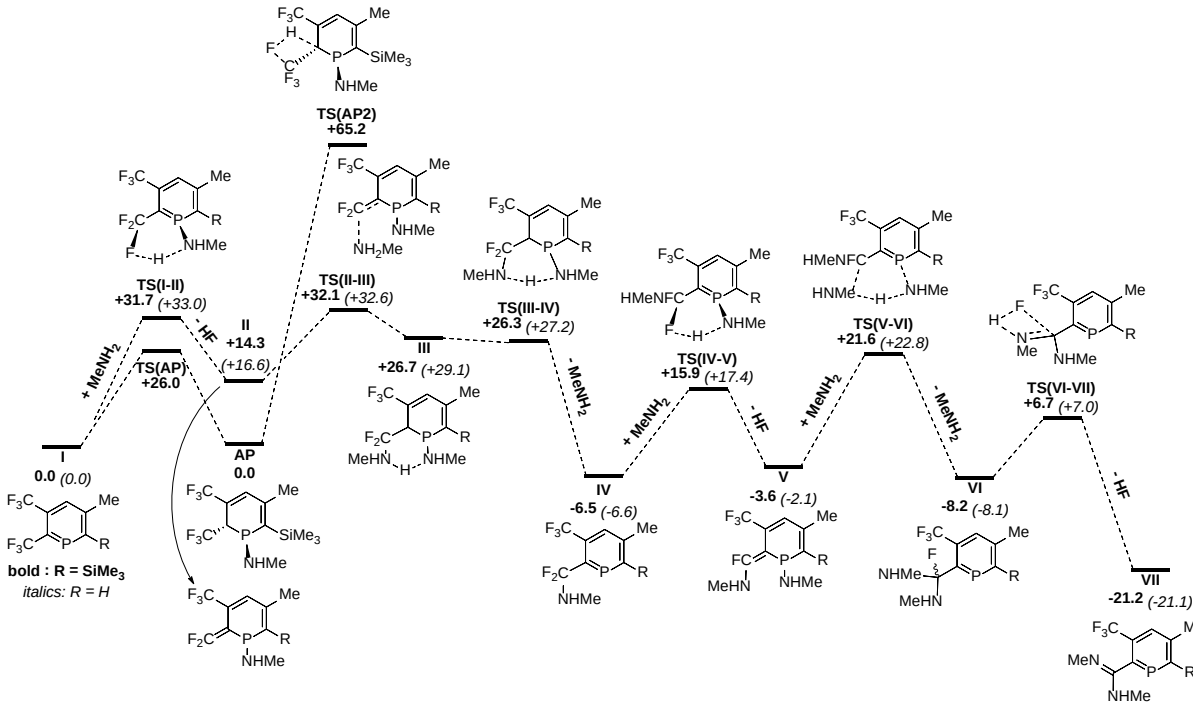


Figure S98 - Free energy profile of triple dehydrofluorination of phosphinine **3a**, either with the *ortho*-$SiMe_3$ group (I, bold numbers), or with a *ortho*-H group (IH, numbers in italics and parentheses). Free energies were calculated at the M052X-D3,THF/def2-QZVPP//TPSS/def2-TZVPP level.

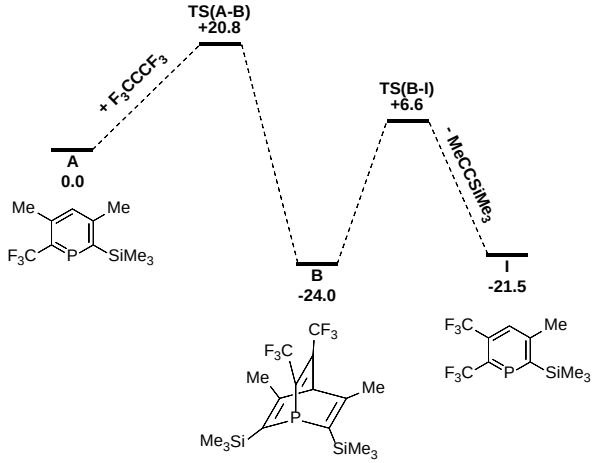


Figure S99 - Free energy profile of formation of **B** (**2a**) from **A** (**1a**), and formation of **I** (**3a**) from **B** (**2a**). Free energies were calculated at the M052X-D3,toluene/def2-QZVPP//TPSS/def2-TZVPP level.

Computed Cartesian coordinates (Å) and energies (au) for all species.

MeNH2

SCF (TPSS/def2-TZVPP) Energy = -95.9116746792
Enthalpy 298K = -95.844277
Free Energy 298K = -95.871611
Lowest Frequency = 300.9525 cm^{-1}
Second Frequency = 836.5308 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -95.8899852350

N	0.75450	-0.00000	-0.12543
H	1.14837	0.81313	0.34529
C	-0.71088	-0.00000	0.01775
H	-1.11547	0.88235	-0.48712
H	-1.08196	-0.00016	1.05547
H	-1.11552	-0.88216	-0.48741
H	1.14837	-0.81313	0.34529

HF

SCF (TPSS/def2-TZVPP) Energy = -100.493156054
Enthalpy 298K = -100.480758
Free Energy 298K = -100.500483
Lowest Frequency = 3991.3313 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -100.491030203

F	0.00000	0.00000	0.09288
H	0.00000	0.00000	-0.83595

F3CCCCF3

SCF (TPSS/def2-TZVP) Energy = -751.801587491
Enthalpy 298K = -751.754290
Free Energy 298K = -751.803183
Lowest Frequency = 2.5750 cm^{-1}
Second Frequency = 74.2335 cm^{-1}
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -751.719394343

F	2.55295	-0.57347	1.12446
F	2.55281	1.26071	-0.06576
F	-2.55286	1.26055	-0.06603
F	2.55246	-0.68720	-1.05895
F	-2.55287	-0.57326	1.12468
F	-2.55244	-0.68754	-1.05885
C	-0.60166	0.00020	0.00027
C	0.60161	0.00019	0.00034
C	2.06670	-0.00026	0.00005
C	-2.06672	0.00019	0.00002

MeCCSiMe3

SCF (TPSS/def2-TZVP) Energy = -525.517645947
Enthalpy 298K = -525.348891
Free Energy 298K = -525.399697
Lowest Frequency = 16.6284 cm^{-1}
Second Frequency = 78.3251 cm^{-1}
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -525.444498847

Si	0.86489	0.00008	-0.00003
C	-2.18953	0.00041	-0.00044
C	-0.97091	0.00087	-0.00056
C	1.46889	-1.46124	1.02639
H	2.56487	-1.49668	1.05184
H	1.11206	-2.41036	0.61144
H	1.11117	-1.39393	2.05972
C	1.47124	1.61879	0.75226
H	1.11480	1.73509	1.78166
H	1.11539	2.48059	0.17697
H	2.56733	1.65638	0.77010
C	1.47111	-0.15864	-1.77788
H	2.56713	-0.16117	-1.81983
H	1.11358	0.67385	-2.39384
H	1.11564	-1.08838	-2.23564
C	-3.64662	0.00028	-0.00010
H	-4.03823	-0.84756	0.57318

```
H  -4.03845  0.92047  0.44772
H  -4.03874 -0.07214 -1.02078
```

A

SCF (TPSS/def2-TZVP) Energy = -1431.23926124
Enthalpy 298K = -1430.877086
Free Energy 298K = -1430.955634
Lowest Frequency = 28.3494 cm^{-1}
Second Frequency = 32.3381 cm^{-1}
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -1431.09217613

```
P   0.00000 -0.81454  0.03706
Si  3.06396 -0.66853 -0.00256
C   1.25347  1.64601 -0.00428
C   0.00000  2.27182 -0.01922
H   0.00000  3.36137 -0.04715
C   1.39283  0.24204  0.01826
C   2.78146 -2.51829  0.23916
H   3.75082 -3.03324  0.23060
H   2.16355 -2.95391 -0.55256
H   2.29389 -2.73984  1.19459
C   4.20221 -0.08588  1.39314
H   3.69855 -0.14588  2.36487
H   4.55563  0.94142  1.26205
H   5.08622 -0.73420  1.44015
C   3.92418 -0.43665 -1.67367
H   4.85982 -1.00930 -1.69737
H   4.17320  0.60656 -1.89491
H   3.28939 -0.80429 -2.48794
C   2.46412  2.56039  0.01166
H   2.84296  2.67934  1.03385
H   3.28241  2.16439 -0.59531
H   2.20890  3.55550 -0.36447
Si -3.06396 -0.66853 -0.00255
C  -1.25347  1.64601 -0.00428
C  -1.39283  0.24204  0.01827
C  -2.78146 -2.51829  0.23913
H  -3.75082 -3.03324  0.23056
H  -2.29389 -2.73985  1.19456
H  -2.16355 -2.95390 -0.55260
C  -3.92419 -0.43662 -1.67366
H  -3.28941 -0.80425 -2.48794
H  -4.17320  0.60659 -1.89488
H  -4.85983 -1.00927 -1.69736
C  -4.20220 -0.08590  1.39316
H  -5.08621 -0.73423  1.44016
H  -4.55563  0.94140  1.26208
H  -3.69854 -0.14591  2.36488
C  -2.46412  2.56039  0.01165
H  -2.20890  3.55550 -0.36447
H  -3.28240  2.16439 -0.59532
H  -2.84297  2.67934  1.03384
```

TS(A-B)

SCF (TPSS/def2-TZVP) Energy = -2183.01904210
Enthalpy 298K = -2182.609323
Free Energy 298K = -2182.712665
Lowest Frequency = -202.5618 cm^{-1}
Second Frequency = 27.0020 cm^{-1}
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -2182.80273177

```
P  -0.00002 -1.28783  0.34412
Si -3.06158 -1.66906 -0.07911
F  -1.09515  0.36650  2.97545
F   0.00002  2.24797  3.09700
F   0.00007  4.21280  0.41400
F   1.09512  0.36646  2.97546
F  -1.09526  3.44464 -1.30967
F   1.09540  3.44460 -1.30965
C   0.00003  1.89953  0.07331
C  -1.26649 -0.02357 -1.71218
```

```
C   0.00001  0.55525 -2.01376
H   0.00002  1.32836 -2.78185
C  -1.41237 -0.90918 -0.65501
C   0.00001  1.12149  1.03826
C  -0.00000  1.02264  2.51126
C   0.00006  3.23320 -0.52761
C  -2.74078 -2.83836  1.36379
H  -3.69164 -3.27824  1.69072
H  -2.29828 -2.32503  2.22373
H  -2.07034 -3.65987  1.08935
C  -3.83782 -2.67343 -1.48167
H  -3.15135 -3.45447 -1.82811
H  -4.11219 -2.06414 -2.34869
H  -4.74918 -3.16875 -1.12414
C  -4.25582 -0.32870  0.51554
H  -5.18048 -0.79107  0.88291
H  -4.53414  0.38792 -0.26395
H  -3.81752  0.23775  1.34481
C  -2.41850  0.43173 -2.58433
H  -2.34609 -0.02226 -3.58029
H  -3.38743  0.16279 -2.16239
H  -2.39046  1.51805 -2.71962
Si  3.06154 -1.66913 -0.07909
C   1.26649 -0.02360 -1.71218
C   1.41234 -0.90921 -0.65501
C   2.74069 -2.83848  1.36375
H   3.69154 -3.27838  1.69069
H   2.07025 -3.65996  1.08927
H   2.29818 -2.32517  2.22371
C   4.25577 -0.32879  0.51563
H   3.81745  0.23763  1.34491
H   4.53412  0.38785 -0.26383
H   5.18042 -0.79118  0.88301
C   3.83780 -2.67344 -1.48168
H   4.74915 -3.16879 -1.12414
H   4.11221 -2.06412 -2.34865
H   3.15133 -3.45445 -1.82818
C   2.41852  0.43165 -2.58434
H   2.39034  1.51793 -2.71991
H   3.38744  0.16295 -2.16224
H   2.34626 -0.02261 -3.58019
```

B

SCF (TPSS/def2-TZVP) Energy = -2183.08444210
Enthalpy 298K = -2182.672356
Free Energy 298K = -2182.772644
Lowest Frequency = 17.4213 cm^{-1}
Second Frequency = 26.7467 cm^{-1}
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -2182.87964767

```
P   0.65181  0.10932 -0.84148
Si  1.84619  2.90578 -0.09350
F  -2.86889  1.06575 -2.12206
F  -2.68768 -1.11400 -2.29181
F  -4.06980 -0.27406 -0.07264
F  -1.15714  0.18329 -3.13050
F  -3.49112  0.79290  1.73923
F  -3.32542 -1.38636  1.64765
C  -1.72250 -0.11807  0.46866
C   0.07772  1.19873  1.58206
C  -0.72647 -0.12020  1.62261
H  -1.25371 -0.21041  2.57399
C   0.77298  1.45870  0.46516
C  -1.21622 -0.00714 -0.76768
C  -1.98748  0.03101 -2.06592
C  -3.15774 -0.24445  0.91066
C   3.56190  2.22785 -0.49708
H   4.20977  3.02472 -0.88226
H   3.51217  1.44419 -1.26112
H   4.04648  1.80408  0.39010
```

```
C   2.03504  4.28838  1.18091
H   2.51480  3.94981  2.10584
H   1.07965  4.75720  1.44057
H   2.67402  5.07113  0.75224
C   1.06417  3.62258 -1.65334
H   1.68801  4.42629 -2.06333
H   0.07256  4.04154 -1.44764
H   0.94957  2.86031 -2.43181
C  -0.04129  2.03452  2.82699
H   0.29357  1.46378  3.70326
H   0.54487  2.95009  2.76582
H  -1.09135  2.29894  3.00650
Si  2.19194 -2.67514 -0.23764
C   0.24232 -1.30124  1.43368
C   0.95959 -1.34079  0.29808
C   2.87345 -2.24813 -1.94074
H   3.57045 -3.02965 -2.26810
H   3.41676 -1.29697 -1.94069
H   2.08056 -2.17117 -2.69255
C   1.32673 -4.35212 -0.34259
H   0.49388 -4.31773 -1.05406
H   0.92434 -4.68423  0.62031
H   2.02870 -5.12043 -0.68968
C   3.63295 -2.76123  0.98391
H   4.36652 -3.50799  0.65573
H   3.31508 -3.03458  1.99587
H   4.14855 -1.79621  1.04896
C   0.26137 -2.29543  2.56236
H  -0.73620 -2.72990  2.70541
H   0.97069 -3.10524  2.38438
H   0.53060 -1.80173  3.50527
```

TS(B-I)

```
SCF (TPSS/def2-TZVP) Energy = -2183.03832265
Enthalpy 298K = -2182.628846
Free Energy 298K = -2182.730226
Lowest Frequency = -220.8260 cm-1
Second Frequency = 25.3568 cm-1
SCF (M052X-D3,toluene/def2-QZVPP) Energy = -2182.82714019

P   0.52565  0.08832 -0.90286
Si  0.95555  3.16222  0.26788
F  -2.69926  1.27574 -1.69470
F  -3.05760 -0.81749 -2.22560
F  -3.93796 -0.22529  0.28510
F  -1.35828  0.25115 -3.06791
F  -3.31245 -1.30876  2.05621
F  -3.55277 -2.37419  0.16883
C  -1.64215 -0.95231  0.38177
C  -0.13456  1.00911  1.89902
C  -0.72117 -1.35625  1.38456
H  -1.14822 -1.73609  2.30687
C   0.34663  1.48087  0.83986
C  -1.19921 -0.36237 -0.78543
C  -2.08077  0.07773 -1.92450
C  -3.11063 -1.20781  0.70619
C   2.78152  3.03180 -0.16995
H   3.16284  4.01153 -0.48310
H   2.94752  2.33276 -0.99578
H   3.37987  2.69906  0.68520
C   0.72586  4.37220  1.69561
H   1.29605  4.06772  2.58055
H  -0.32784  4.45840  1.98346
H   1.07229  5.37245  1.40805
C  -0.04846  3.71416 -1.22054
H   0.28118  4.71015 -1.54172
H  -1.11677  3.77225 -0.98803
H   0.07340  3.03175 -2.06770
C  -0.59953  0.96662  3.28674
H  -0.03468  0.23714  3.87641
H  -0.46375  1.95499  3.74580
```

```
H  -1.65960  0.70105  3.34580
Si  3.07242 -1.68806 -0.49742
C   0.62515 -1.73738  1.10259
C   1.31366 -1.20690  0.02874
C   3.48086 -0.87953 -2.15137
H   4.48585 -1.18579 -2.46832
H   3.46901  0.21407 -2.10217
H   2.77759 -1.17939 -2.93579
C   3.19675 -3.55994 -0.73470
H   2.45445 -3.91038 -1.46076
H   3.04881 -4.12478  0.19100
H   4.18933 -3.81919 -1.12390
C   4.35362 -1.11278  0.77247
H   5.36397 -1.37330  0.43328
H   4.21286 -1.56437  1.76036
H   4.31731 -0.02498  0.89919
C   1.22790 -2.74299  2.06436
H   0.85733 -3.75295  1.85135
H   2.31749 -2.76362  2.01177
H   0.93945 -2.50710  3.09491
```

I

```
SCF (TPSS/def2-TZVPP) Energy = -1657.55462522
Enthalpy 298K = -1657.313808
Free Energy 298K = -1657.388046
Lowest Frequency = 26.1266 cm-1
Second Frequency = 35.8057 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1657.40607616
SCF (M052X-D3,toluene/def2-QZVPP) Energy =  -1657.40382380

P   0.56684 -1.25115  0.00475
Si  3.44326 -0.21771 -0.00631
F  -3.15551 -1.44802 -0.85945
F  -2.69075 -1.86351  1.24054
F  -3.62595  0.66373  0.81021
F  -1.62185 -2.89823 -0.34591
F  -3.30096  1.30026 -1.25952
F  -2.80830  2.62773  0.39248
C  -1.35379  0.76108  0.01784
C   1.03686  1.48117  0.00845
C  -0.34177  1.72578  0.00968
H  -0.65609  2.76365  0.00731
C   1.56776  0.17549  0.01375
C  -1.06883 -0.61342  0.00178
C  -2.14238 -1.69070  0.00831
C  -2.77816  1.32518 -0.00621
C   3.68752 -2.07403  0.20664
H   4.76357 -2.29022  0.20752
H   3.23311 -2.65564 -0.60193
H   3.27468 -2.44369  1.15138
C   4.33375  0.65104  1.41518
H   3.85929  0.42565  2.37701
H   4.37070  1.73878  1.30504
H   5.36864  0.29080  1.46725
C   4.18667  0.28230 -1.67074
H   5.24588 -0.00174 -1.70132
H   4.13046  1.35661 -1.87336
H   3.68093 -0.23710 -2.49235
C   1.93260  2.70358  0.03204
H   2.22930  2.93810  1.06122
H   2.84631  2.54954 -0.54614
H   1.41347  3.57787 -0.36985
```

TS(AP)

```
SCF (TPSS/def2-TZVPP) Energy = -1849.35919537
Enthalpy 298K = -1848.984612
Free Energy 298K = -1849.077043
Lowest Frequency = -728.3067 cm-1
Second Frequency = 23.8231 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1849.17999758

P   0.55286  1.06306  0.00865
Si  3.51092 -0.04489  0.38941
F  -3.52105 -0.77881 -0.90499
F  -3.04450 -2.28246  0.61223
```

```
F  -2.62226 -2.67548 -1.48289
C  -1.20017 -1.09110 -0.36399
C   1.24303 -1.52291 -0.66625
C  -0.15847 -1.78940 -0.91101
H  -0.38724 -2.69467 -1.46488
C   1.72643 -0.33133 -0.18143
C  -1.04046  0.20373  0.29678
C  -2.57847 -1.70839 -0.52496
C   3.66258  1.67816  1.14504
H   4.69167  1.83575  1.49268
H   2.99313  1.80952  2.00151
H   3.42901  2.47174  0.42680
C   4.73375 -0.12969 -1.05913
H   4.48654  0.61127 -1.82853
H   4.76412 -1.10989 -1.54635
H   5.74797  0.09249 -0.70394
C   4.02095 -1.29022  1.72069
H   5.02918 -1.06089  2.08802
H   4.02694 -2.32497  1.36316
H   3.33675 -1.24076  2.57553
C   2.13290 -2.71921 -0.95019
H   1.98745 -3.05942 -1.98321
H   3.19091 -2.49367 -0.81393
H   1.87287 -3.56124 -0.29731
N   0.29955  1.54359 -1.69806
H   0.29976  0.71717 -2.30104
C   1.29834  2.51014 -2.20130
H   1.31286  3.37798 -1.53604
H   2.31758  2.10324 -2.25404
H   1.01328  2.84327 -3.20510
N  -2.46352  2.03676 -1.18797
H  -1.60722  2.21010 -1.75092
H  -1.96136  1.19846 -0.47136
C  -2.95486  3.23696 -0.46967
H  -3.27932  4.00903 -1.17151
H  -3.78599  2.94845  0.17479
H  -2.14229  3.61926  0.14917
C  -1.61190  0.38904  1.66937
F  -2.98481  0.27218  1.70564
F  -1.15644 -0.49384  2.61400
F  -1.34780  1.63694  2.16841
H  -3.18466  1.59636 -1.75797
```

AP

SCF (TPSS/def2-TZVPP) Energy = -1753.47535948
Enthalpy 298K = -1753.165650
Free Energy 298K = -1753.250092
Lowest Frequency = 23.5764 cm^{-1}
Second Frequency = 30.9080 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) -1753.31467700

```
P  -0.47794 -1.20409 -0.19876
Si -3.23610  0.23346  0.02404
F   3.09643  0.07007 -2.00577
F   4.05728  0.44879 -0.08695
F   3.26106  2.11754 -1.24474
C   1.67476  0.65509 -0.21290
C  -0.64133  1.55763  0.10304
C   0.78313  1.66785 -0.19960
H   1.12373  2.65332 -0.50909
C  -1.33657  0.38455 -0.03763
C   1.32047 -0.71393  0.27093
C   3.01756  0.83821 -0.86728
C  -3.74452 -1.54615 -0.33907
H  -4.84007 -1.61175 -0.33622
H  -3.36721 -2.24814  0.41150
H  -3.39310 -1.88192 -1.32012
C  -4.03379  1.33090 -1.29466
H  -3.67973  1.05150 -2.29370
H  -3.83291  2.39823 -1.15902
H  -5.12254  1.19647 -1.28128
C  -3.88479  0.67524  1.74463
H  -4.96830  0.50834  1.78956
H  -3.69837  1.71702  2.02434
H  -3.41888  0.04011  2.50649
C  -1.29619  2.87911  0.43833
```

```
H  -1.05397  3.63619 -0.31755
H  -2.38065  2.80137  0.51538
H  -0.91442  3.25216  1.39715
N  -0.50603 -1.40953 -1.87924
H  -0.29590 -0.60614 -2.46357
C  -0.21167 -2.70544 -2.49838
H  -0.51350 -3.49710 -1.80742
H  -0.78656 -2.81711 -3.42355
H   0.85375 -2.83584 -2.73174
H   1.96880 -1.47131 -0.18296
C   1.49148 -0.89584  1.78145
F   2.73931 -0.57828  2.21323
F   0.62673 -0.13349  2.50426
F   1.27532 -2.19008  2.13645
```

TS(AP2)

SCF (TPSS/def2-TZVPP) Energy = -1753.38055366
Enthalpy 298K = -1753.076898
Free Energy 298K = -1753.161353
Lowest Frequency = -1637.5939 cm^{-1}
Second Frequency = 28.2047 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1753.20470326

```
P   0.53046 -1.12830  0.22099
F  -3.18371  0.52607  1.70006
F  -3.87360  0.94981 -0.32622
F  -3.01614  2.54712  0.88246
C  -1.51109  0.87996  0.06014
C   0.87459  1.60254 -0.21533
C  -0.54053  1.82124  0.06429
H  -0.82073  2.83923  0.32364
C   1.49251  0.38774 -0.06779
C  -1.18961 -0.53178 -0.25907
C  -2.89129  1.23115  0.56698
C   1.61801  2.87256 -0.57432
H   1.47158  3.63597  0.19968
H   2.68849  2.70955 -0.69819
H   1.22681  3.29001 -1.51052
N   0.59558 -1.18483  1.91263
H   0.45974 -0.31352  2.41726
C   0.15070 -2.37770  2.64312
H   0.38507 -3.26059  2.04255
H   0.68882 -2.45184  3.59345
H  -0.92799 -2.37562  2.84768
H  -2.10503 -1.39546  0.19858
C  -1.69824 -1.10616 -1.46181
F  -2.48745 -0.48270 -2.29221
F  -1.13916 -2.13426 -2.04049
F  -2.97303 -2.12420 -0.38894
Si  3.37462  0.09901 -0.18500
C   4.28706  1.15235  1.09404
H   5.36168  0.93478  1.05568
H   4.16426  2.22964  0.94480
H   3.93867  0.91540  2.10584
C   4.00569  0.47280 -1.92920
H   3.48644 -0.14683 -2.66929
H   3.87619  1.51896 -2.22445
H   5.07582  0.23999 -1.99604
C   3.76018 -1.70850  0.18705
H   3.40569 -2.00735  1.17902
H   3.31618 -2.38933 -0.54623
H   4.84766 -1.85460  0.16296
```

AP2

SCF (TPSS/def2-TZVPP) Energy = -1652.94589190
Enthalpy 298K = -1652.651804
Free Energy 298K = -1652.732707
Lowest Frequency = 27.3364 cm^{-1}
Second Frequency = 34.6229 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1652.78146464

```
P  -0.48053  1.18355 -0.04498
F   3.67778 -0.03852  1.00108
F   3.82118 -1.42316 -0.68623
F   3.13829 -2.13859  1.25120
```

```
C   1.62796 -0.75665  0.01835
C  -0.73519 -1.59604 -0.08929
C   0.69298 -1.73215  0.15318
H   1.02923 -2.71326  0.47802
C  -1.38781 -0.39127 -0.11987
C   1.24174  0.57704 -0.41869
C   3.05889 -1.08540  0.39165
C  -1.44818 -2.92680 -0.21980
H  -1.23714 -3.56231  0.64902
H  -2.52865 -2.81557 -0.30890
H  -1.08767 -3.46639 -1.10453
N  -0.58839  1.45392  1.63520
H  -0.40138  0.66366  2.24645
C  -0.21773  2.75190  2.20827
H  -0.50067  3.53682  1.50152
H  -0.76451  2.91498  3.14279
H   0.85820  2.84277  2.41196
C   2.02771  1.40910 -1.12105
F   3.25038  1.15294 -1.56776
F   1.68379  2.63454 -1.49835
Si -3.27852 -0.18278 -0.24177
C  -4.14096 -1.01975  1.21988
H  -5.22303 -0.84783  1.16266
H  -3.98178 -2.10184  1.26347
H  -3.78854 -0.59398  2.16637
C  -3.92613 -0.87529 -1.87998
H  -3.43504 -0.38351 -2.72748
H  -3.77270 -1.95356 -1.98955
H  -5.00318 -0.68373 -1.96508
C  -3.72385  1.64892 -0.18930
H  -3.37838  2.12891  0.73212
H  -3.30247  2.20361 -1.03376
H  -4.81572  1.75294 -0.23163
```

TS(I-II)

SCF (TPSS/def2-TZVPP) Energy = -1753.43252184
Enthalpy 298K = -1753.125911
Free Energy 298K = -1753.207610
Lowest Frequency = -394.0218 cm^{-1}
Second Frequency = 26.1787 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1753.26374959

```
P   0.49813 -1.02381 -0.35547
Si  3.37163  0.22257 -0.37331
F  -1.72949 -2.35177 -1.57851
F  -3.38808 -1.15670 -0.90748
F  -3.68237  0.76043  0.94292
F  -2.12006 -2.42382  0.86467
F  -3.50023  1.50290 -1.11376
F  -2.96516  2.77381  0.56572
C  -1.47493  0.96669  0.03823
C   0.92403  1.61333  0.37578
C  -0.49452  1.82648  0.46918
H  -0.80812  2.79903  0.82988
C   1.51267  0.43091 -0.02719
C  -1.17401 -0.32546 -0.50536
C  -2.09110 -1.31417 -0.84331
C  -2.90492  1.49352  0.10836
C   3.68618 -1.48711 -1.10821
H   4.75606 -1.58745 -1.33153
H   3.13427 -1.64334 -2.04094
H   3.41497 -2.30323 -0.42982
C   4.39245  0.35326  1.21786
H   4.08729 -0.40504  1.94868
H   4.31361  1.32923  1.70785
H   5.45294  0.18306  0.99403
C   3.97855  1.49147 -1.63698
H   5.03068  1.29864 -1.88093
H   3.90601  2.52597 -1.28777
H   3.40427  1.41468 -2.56729
C   1.73834  2.84777  0.70874
H   1.43139  3.24581  1.68306
H   2.80975  2.65045  0.74227
H   1.55573  3.63763 -0.02986
N   0.16119 -1.68006  1.40854
H   0.13885 -0.89932  2.06816
```

```
H  -0.91669 -2.07511  1.26717
C   1.08163 -2.74262  1.88247
H   1.07609 -3.55055  1.14938
H   2.09953 -2.36032  1.99259
H   0.73262 -3.12665  2.84409
```

II+HF

```
SCF (TPSS/def2-TZVPP) Energy = -1753.45100742
Enthalpy 298K = -1753.142153
Free Energy 298K = -1753.228744
Lowest Frequency = 24.2827 cm-1
Second Frequency = 27.0124 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1753.28811570

P   0.48552 -1.05120 -0.30140
Si  3.36319  0.24970 -0.32140
F  -1.64996 -2.11445 -2.01795
F  -3.18308 -0.61705 -1.81871
F  -3.70050  0.27761  0.74646
F  -2.11752 -2.88340  1.43673
F  -3.55709  1.87992 -0.73820
F  -3.04921  2.26921  1.34212
C  -1.51018  0.94940  0.07951
C   0.89135  1.64413  0.30129
C  -0.54123  1.80262  0.50070
H  -0.85645  2.71283  1.00191
C   1.48887  0.45745 -0.03434
C  -1.16614 -0.29756 -0.59203
C  -1.97400 -0.97571 -1.43248
C  -2.95340  1.33548  0.35644
C   3.73068 -1.52005 -0.86127
H   4.81034 -1.62235 -1.03016
H   3.21994 -1.78088 -1.79371
H   3.44655 -2.26667 -0.11215
C   4.33761  0.57903  1.26770
H   4.02126 -0.09794  2.06994
H   4.23086  1.60238  1.64135
H   5.40602  0.40245  1.09211
C   3.95719  1.38544 -1.71212
H   5.01776  1.19382 -1.91769
H   3.85230  2.45055 -1.48427
H   3.40109  1.18767 -2.63556
C   1.66356  2.92666  0.53309
H   1.43313  3.33136  1.52628
H   2.74192  2.78718  0.46257
H   1.36728  3.68952 -0.19749
N   0.22485 -1.65832  1.33938
H   0.16488 -0.91018  2.03145
H  -1.27868 -2.39434  1.37916
C   1.13359 -2.73070  1.80772
H   1.19855 -3.49342  1.02890
H   2.14331 -2.36989  2.03706
H   0.70737 -3.18545  2.70596
```

II

```
SCF (TPSS/def2-TZVPP) Energy = -1652.94589187
Enthalpy 298K = -1652.651804
Free Energy 298K = -1652.732701
Lowest Frequency = 27.3516 cm-1
Second Frequency = 34.6397 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1652.78146295

P   0.48058 -1.18351 -0.04525
Si  3.27871  0.18264 -0.24180
F  -1.68389 -2.63483 -1.49751
F  -3.25103 -1.15381 -1.56641
F  -3.67760  0.03941  1.00159
F  -3.82113  1.42243 -0.68709
F  -3.13843  2.13984  1.24970
C  -1.62786  0.75685  0.01825
C   0.73543  1.59602 -0.08916
C  -0.69276  1.73224  0.15315
H  -1.02896  2.71341  0.47781
C   1.38798  0.39124 -0.11990
C  -1.24181 -0.57690 -0.41873
```

```
C  -2.02802 -1.40936 -1.12033
C  -3.05877  1.08582  0.39117
C   3.72382 -1.64910 -0.18931
H   4.81568 -1.75334 -0.23129
H   3.30262 -2.20361 -1.03399
H   3.37792 -2.12913  0.73193
C   4.14101  1.01963  1.21992
H   3.78709  0.59519  2.16645
H   3.98341  2.10200  1.26241
H   5.22287  0.84604  1.16383
C   3.92639  0.87501 -1.88003
H   5.00380  0.68504 -1.96426
H   3.77134  1.95294 -1.99057
H   3.43664  0.38177 -2.72746
C   1.44854  2.92677 -0.21927
H   1.23781  3.56188  0.64992
H   2.52897  2.81546 -0.30870
H   1.08786  3.46682 -1.10363
N   0.58839 -1.45393  1.63497
H   0.40114 -0.66356  2.24601
C   0.21713 -2.75174  2.20804
H   0.49894 -3.53670  1.50089
H   0.76446 -2.91551  3.14213
H  -0.85871 -2.84178  2.41247
```

TS(II-III)

SCF (TPSS/def2-TZVPP) Energy = -1748.84656083
Enthalpy 298K = -1748.484007
Free Energy 298K = -1748.570146
Lowest Frequency = -199.9862 cm^{-1}
Second Frequency = 27.9027 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1748.66626458

```
P  -0.52556 -0.99493  0.19326
Si -3.53409 -0.10925  0.37460
F   3.40360  1.15813 -0.83890
F   3.05099  2.27245  1.01886
F   2.44262  3.10624 -0.88832
C   1.13688  1.27250 -0.04486
C  -1.31930  1.62379 -0.33817
C   0.05455  2.01660 -0.46372
H   0.24309  3.01534 -0.84006
C  -1.73346  0.35539  0.01730
C   1.00023 -0.04411  0.49761
C   2.48681  1.95474 -0.17279
C  -3.62876 -1.88521  1.01165
H  -4.67170 -2.12557  1.25607
H  -3.02771 -2.02914  1.91539
H  -3.28447 -2.61738  0.27323
C  -4.61666 -0.02737 -1.18267
H  -4.22863 -0.69091 -1.96467
H  -4.68711  0.97737 -1.61248
H  -5.63683 -0.35714 -0.94839
C  -4.28427  0.99415  1.71950
H  -5.30289  0.66116  1.95565
H  -4.33972  2.04938  1.43402
H  -3.69336  0.93212  2.64068
C  -2.29719  2.75678 -0.59353
H  -2.06268  3.24941 -1.54485
H  -3.33261  2.41726 -0.63449
H  -2.21782  3.52025  0.19019
N  -0.12659 -1.50874 -1.47885
H  -0.10284 -0.71779 -2.12585
C  -0.93848 -2.60534 -2.04027
H  -0.99233 -3.40992 -1.30095
H  -1.96502 -2.30770 -2.29464
H  -0.46319 -2.99582 -2.94700
C   2.05752 -0.87515  0.92812
F   3.22259 -0.37424  1.38917
F   1.74701 -1.94349  1.69781
N   2.69257 -1.79466 -0.54278
H   1.78906 -1.92959 -1.04933
H   3.22612 -1.07600 -1.03298
C   3.47394 -3.02910 -0.33085
H   2.85686 -3.74310  0.21484
H   3.77865 -3.46830 -1.28670
```

```
H   4.36178 -2.79452  0.25888
```

III

```
SCF (TPSS/def2-TZVPP) Energy = -1748.84806584
Enthalpy 298K = -1748.485182
Free Energy 298K = -1748.570868
Lowest Frequency = 29.3625 cm-1
Second Frequency = 30.7674 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1748.67564724

P   0.54065 -0.97507 -0.25293
Si  3.52600 -0.07690 -0.36932
F  -3.40179  1.14821  0.84135
F  -3.07580  2.19894 -1.06153
F  -2.46742  3.11018  0.80720
C  -1.13958  1.25986  0.02677
C   1.29826  1.62870  0.38187
C  -0.06584  2.01971  0.47511
H  -0.26960  3.01933  0.83913
C   1.72398  0.36693 -0.01643
C  -0.99662 -0.04271 -0.51084
C  -2.49463  1.93694  0.13203
C   3.62979 -1.79747 -1.14471
H   4.67628 -2.01920 -1.39170
H   3.04288 -1.86696 -2.06657
H   3.27244 -2.58570 -0.47345
C   4.58026 -0.12700  1.21046
H   4.18455 -0.86091  1.92282
H   4.63124  0.83621  1.72951
H   5.60872 -0.42485  0.96931
C   4.32264  1.12251 -1.60123
H   5.33829  0.78815 -1.84831
H   4.39624  2.14678 -1.22262
H   3.74816  1.15507 -2.53425
C   2.28342  2.74235  0.69368
H   1.95836  3.29862  1.58013
H   3.29238  2.36972  0.87738
H   2.33149  3.45831 -0.13605
N   0.08193 -1.57640  1.43195
H   0.10137 -0.80275  2.10148
C   0.87664 -2.70910  1.94962
H   0.91688 -3.48415  1.17856
H   1.90719 -2.43052  2.20482
H   0.40501 -3.12909  2.84533
C  -2.09468 -0.95151 -0.81977
F  -3.26230 -0.45296 -1.32926
F  -1.74835 -1.99518 -1.63666
N  -2.54170 -1.68199  0.51922
H  -1.57692 -1.83448  1.01697
H  -3.02580 -0.94442  1.04127
C  -3.39304 -2.89865  0.38996
H  -2.82343 -3.66558 -0.13155
H  -3.66147 -3.24646  1.38959
H  -4.29240 -2.65168 -0.17472
```

TS(III-IV)

```
SCF (TPSS/def2-TZVPP) Energy = -1748.84785291
Enthalpy 298K = -1748.487679
Free Energy 298K = -1748.571845
Lowest Frequency = -334.8718 cm-1
Second Frequency = 32.2706 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1748.67505358

P   0.54718 -0.94780 -0.31877
Si  3.52587 -0.06165 -0.34819
F  -3.39717  1.16573  0.85615
F  -3.09485  2.18139 -1.06981
F  -2.47223  3.13011  0.77537
C  -1.14549  1.26918  0.01689
C   1.28809  1.64094  0.39035
C  -0.07198  2.03368  0.46772
H  -0.27894  3.03379  0.82794
C   1.71853  0.38195 -0.02418
C  -1.00318 -0.02892 -0.51935
C  -2.50365  1.94324  0.12338
```

```
C   3.63955 -1.76045 -1.16955
H   4.69057 -1.97799 -1.40058
H   3.07276 -1.80154 -2.10562
H   3.26658 -2.56725 -0.52962
C   4.54233 -0.16197  1.25387
H   4.12674 -0.91337  1.93612
H   4.58524  0.78617  1.80075
H   5.57503 -0.45797  1.02914
C   4.35989  1.16578 -1.52624
H   5.37383  0.82248 -1.76796
H   4.44468  2.17517 -1.11191
H   3.80189  1.23923 -2.46688
C   2.27583  2.74364  0.73129
H   1.91315  3.32949  1.58285
H   3.26528  2.35617  0.98054
H   2.38637  3.43521 -0.11297
N   0.06594 -1.63026  1.37803
H   0.13098 -0.88381  2.07509
C   0.82720 -2.81250  1.83188
H   0.83106 -3.55152  1.02553
H   1.86877 -2.57391  2.07893
H   0.35848 -3.25818  2.71672
C  -2.10728 -0.96368 -0.78582
F  -3.28693 -0.47436 -1.28196
F  -1.75747 -1.99381 -1.62439
N  -2.47767 -1.67964  0.54262
H  -1.42620 -1.81775  1.02661
H  -2.94920 -0.95281  1.08985
C  -3.32969 -2.89783  0.43975
H  -2.77513 -3.66597 -0.09634
H  -3.56101 -3.24302  1.44939
H  -4.25156 -2.66302 -0.09428
```

IV+MeNH$_2$

```
SCF (TPSS/def2-TZVPP) Energy = -1748.88744461
Enthalpy 298K = -1748.523008
Free Energy 298K = -1748.617836
Lowest Frequency = 12.1043 cm-1
Second Frequency = 21.2555 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1748.71289531

P  -0.62689  0.61666 -0.65885
Si -3.57458 -0.04279 -0.22734
F   3.36823 -1.19682  0.94709
F   3.02848 -2.55140 -0.74198
F   2.37736 -3.09905  1.25554
C   1.10607 -1.40720  0.12942
C  -1.33840 -1.88111  0.31242
C   0.01104 -2.22421  0.44078
H   0.23114 -3.21313  0.82715
C  -1.74941 -0.61278 -0.14703
C   0.94851 -0.11856 -0.40175
C   2.46867 -2.05513  0.38468
C  -3.66191  1.65032 -1.04992
H  -4.71131  1.96905 -1.09413
H  -3.27464  1.63824 -2.07434
H  -3.10507  2.41065 -0.49281
C  -4.25355  0.12918  1.52856
H  -3.64829  0.84049  2.10159
H  -4.27642 -0.81336  2.08519
H  -5.27990  0.51527  1.49457
C  -4.63285 -1.23594 -1.24257
H  -5.62729 -0.79799 -1.39434
H  -4.77327 -2.20867 -0.76188
H  -4.19641 -1.40942 -2.23284
C  -2.34416 -2.95424  0.67983
H  -1.88820 -3.72178  1.31103
H  -3.20411 -2.53866  1.21097
H  -2.72345 -3.44689 -0.22306
N  -0.06996  3.37557  1.76390
H   0.23325  3.60405  2.70940
C  -0.40573  4.60774  1.03287
H  -0.71158  4.34137  0.01701
H  -1.25670  5.09448  1.52001
H   0.41111  5.34425  0.95908
C   2.10081  0.81162 -0.77433
```

F   3.10724 0.09817 -1.44817
F   1.67042 1.70831 -1.74527
N   2.58348 1.56776 0.31747
H   0.71729 2.90772 1.31223
H   2.71693 0.96382 1.12234
C   3.76645 2.40977 0.05689
H   3.53465 3.10144 -0.75416
H   3.97102 2.98854 0.95999
H   4.65522 1.82676 -0.21121

IV

SCF (TPSS/def2-TZVPP) Energy = -1652.97241158
Enthalpy 298K = -1652.677454
Free Energy 298K = -1652.756309
Lowest Frequency = 24.9526 cm^{-1}
Second Frequency = 35.4311 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1652.81756943

P   0.62004 -1.16599 -0.12777
Si 3.58740 -0.46243 0.05913
F -3.33961 1.12110 0.79144
F -2.94722 1.94118 -1.20286
F -2.29593 3.00730 0.57350
C -1.06595 1.03771 -0.01517
C   1.38901 1.49470 0.02870
C   0.04766 1.88730 0.04376
H -0.15123 2.95114 0.11186
C   1.77136 0.13708 -0.01339
C -0.93833 -0.35326 -0.13247
C -2.41339 1.76346 0.02669
C   3.63958 -2.32852 -0.20015
H   4.68412 -2.66290 -0.15726
H   3.23546 -2.62439 -1.17409
H   3.08295 -2.87647 0.56698
C   4.31358 -0.09151 1.76567
H   3.72515 -0.57989 2.55053
H   4.35765 0.97674 2.00119
H   5.33663 -0.48302 1.82627
C   4.63432 0.33713 -1.29615
H   5.61929 -0.14529 -1.32456
H   4.79815 1.40793 -1.14322
H   4.17531 0.20395 -2.28237
C   2.41699 2.60887 0.04476
H   1.98355 3.53851 0.42341
H   3.28136 2.35576 0.66353
H   2.78523 2.80230 -0.96959
C -2.11077 -1.32579 -0.25317
F -3.08121 -0.80041 -1.13235
F -1.68730 -2.46205 -0.93675
N -2.62795 -1.73512 0.98537
H -2.72689 -0.94565 1.61350
C -3.82062 -2.59725 0.95995
H -3.60123 -3.48396 0.36346
H -4.02893 -2.91204 1.98460
H -4.70429 -2.09643 0.54600

TS(IV-V)

SCF (TPSS/def2-TZVPP) Energy = -1748.87166274
Enthalpy 298K = -1748.508731
Free Energy 298K = -1748.595982
Lowest Frequency = -222.1284 cm^{-1}
Second Frequency = 25.9496 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1748.69136554

P   0.49874 -0.94570 -0.06895
Si 3.44674 -0.08930 -0.51996
F -3.42624 -0.69411 -0.38411
F -3.39603 1.56487 1.01001
F -2.14762 -2.01957 1.16222
F -3.19262 1.80696 -1.16377
F -2.42396 3.31912 0.18870
C -1.21002 1.24607 0.06313
C   1.24536 1.67564 0.24603
C -0.11116 2.05358 0.36371
H -0.30765 3.09497 0.58695

```
C   1.67083  0.37900 -0.06888
C  -1.08508 -0.12340 -0.24509
C  -2.15389 -1.06966 -0.50746
C  -2.55465  1.97249  0.02522
C   3.48553 -1.86412 -1.16806
H   4.51173 -2.11680 -1.46389
H   2.84464 -1.99372 -2.04703
H   3.16659 -2.59771 -0.41995
C   4.61718 -0.01594  0.97171
H   4.30034 -0.70763  1.76122
H   4.68651  0.98129  1.41926
H   5.63016 -0.30914  0.66817
C   4.12819  1.02115 -1.89175
H   5.11298  0.65767 -2.21111
H   4.24850  2.06383 -1.58189
H   3.47002  1.00850 -2.76803
C   2.23638  2.81696  0.38824
H   1.90559  3.51586  1.16322
H   3.23820  2.46801  0.64576
H   2.30654  3.38257 -0.54883
N   0.18394 -1.28395  1.91775
H   0.18797 -0.38476  2.40090
H  -0.82336 -1.63107  1.81976
C   1.07817 -2.26010  2.57096
H   1.03204 -3.19616  2.01134
H   2.10650 -1.89074  2.56587
H   0.76723 -2.44390  3.60345
N  -1.99444 -2.06991 -1.39664
H  -1.01625 -2.30831 -1.54060
C  -2.94687 -3.18358 -1.45833
H  -3.95274 -2.79021 -1.60652
H  -2.68056 -3.80703 -2.31318
H  -2.91855 -3.76701 -0.53302
```

V+HF

SCF (TPSS/def2-TZVPP) Energy = -1748.89863868
Enthalpy 298K = -1748.537000
Free Energy 298K = -1748.625756
Lowest Frequency = 31.8772 cm^{-1}
Second Frequency = 40.5500 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1748.72304292

```
P   0.44448 -0.97210  0.01664
Si  3.39033 -0.01488 -0.58828
F  -3.08593 -0.24533 -1.59700
F  -3.55656  0.99678  0.81319
F  -1.40484 -3.11286  1.57297
F  -3.14768  2.41148 -0.80623
F  -2.61078  2.90969  1.24163
C  -1.26853  1.25828  0.14710
C   1.18281  1.71018  0.16311
C  -0.19264  2.06482  0.40686
H  -0.38616  3.07823  0.74319
C   1.61940  0.42141 -0.05324
C  -1.13220 -0.11910 -0.24845
C  -2.13469 -0.86659 -0.86155
C  -2.64057  1.88603  0.34295
C   3.51798 -1.86329 -0.95152
H   4.53833 -2.09228 -1.28511
H   2.82761 -2.17623 -1.74138
H   3.31248 -2.48559 -0.07408
C   4.66856  0.37734  0.75651
H   4.46132 -0.17842  1.67831
H   4.71792  1.43905  1.01884
H   5.66660  0.07742  0.41281
C   3.85352  0.89104 -2.18469
H   4.85017  0.57673 -2.51918
H   3.86957  1.98006 -2.07679
H   3.14399  0.64879 -2.98421
C   2.11401  2.90681  0.13623
H   2.00045  3.48855  1.05910
H   3.16228  2.62431  0.03961
H   1.85910  3.57529 -0.69508
N   0.28527 -1.31185  1.80310
H  -0.01960 -0.47253  2.30018
H  -0.71822 -2.32552  1.75875
```

```
C   1.48269 -1.88332  2.46158
H   1.76854 -2.79450  1.93069
H   2.32922 -1.18856  2.46288
H   1.23536 -2.14548  3.49376
N  -2.27147 -2.18461 -0.83215
H  -1.85091 -2.66960 -0.01922
C  -3.16717 -2.93773 -1.70672
H  -3.18928 -2.48748 -2.70003
H  -2.78860 -3.95847 -1.77940
H  -4.18542 -2.96179 -1.30399
```

V

SCF (TPSS/def2-TZVPP) Energy = -1648.38476323
Enthalpy 298K = -1648.036373
Free Energy 298K = -1648.121733
Lowest Frequency = 28.5146 cm^{-1}
Second Frequency = 35.0119 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1648.21145322

```
P  -0.47870  1.00013  0.36457
Si -3.37270  0.05582 -0.36136
F   3.22966  0.92595 -1.14353
F   3.55992 -0.80363  1.02841
F   3.51288 -1.82177 -0.90803
F   2.77381 -2.83089  0.87073
C   1.41908 -1.06296 -0.00398
C  -0.99725 -1.63253 -0.32483
C   0.39214 -1.96023 -0.08418
H   0.62969 -3.01592  0.00890
C  -1.53697 -0.37888 -0.15585
C   1.17435  0.35541 -0.10786
C   2.05812  1.29218 -0.58208
C   2.80801 -1.62073  0.24219
C  -3.62992  1.89315 -0.01237
H  -4.69869  2.13085 -0.08961
H  -3.09362  2.52881 -0.72460
H  -3.29844  2.16757  0.99476
C  -4.44396 -0.90365  0.87059
H  -4.13086 -0.68399  1.89776
H  -4.39930 -1.98925  0.73616
H  -5.49427 -0.60195  0.77156
C  -3.96873 -0.26663 -2.13033
H  -5.00942  0.06305 -2.24204
H  -3.92419 -1.32204 -2.41782
H  -3.36392  0.29681 -2.85033
C  -1.83148 -2.82637 -0.74868
H  -1.71080 -3.64883 -0.03322
H  -2.89356 -2.59135 -0.82220
H  -1.49674 -3.20009 -1.72433
N  -0.70056  0.85472  2.05574
H  -0.63763 -0.08719  2.43447
C  -0.21029  1.88938  2.96960
H  -0.39009  2.86872  2.51527
H  -0.76456  1.84512  3.91301
H   0.86309  1.80480  3.19221
N   1.91076  2.63862 -0.56076
H   0.97871  2.90959 -0.24169
C   2.57325  3.52114 -1.52385
H   2.17347  3.40519 -2.53954
H   2.42109  4.55016 -1.19453
H   3.64259  3.31062 -1.53689
```

VI

SCF (TPSS/def2-TZVPP) Energy = -1648.38355413
Enthalpy 298K = -1648.034522
Free Energy 298K = -1648.118285
Lowest Frequency = 23.0568 cm^{-1}
Second Frequency = 30.8304 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1648.22101159

```
P  -0.65573 -1.08829 -0.11276
Si -3.64824 -0.45626 -0.16813
F   3.13051 -0.60124  0.80508
F   3.16585  1.46694 -0.87962
F   2.87295  2.03818  1.22028
```

```
F   2.05405  3.25332 -0.37851
C   0.95398  1.16863  0.04768
C  -1.51657  1.53948  0.15355
C  -0.18944  1.97630  0.14794
H  -0.02749  3.04584  0.22303
C  -1.85343  0.18008 -0.01582
C   0.87714 -0.23148  0.00006
C   2.06891 -1.20352 -0.02778
C   2.26665  1.96049  0.01449
C  -3.64938 -2.34074 -0.23850
H  -4.68433 -2.69170 -0.34171
H  -3.23366 -2.79067  0.66930
H  -3.07854 -2.72909 -1.08814
C  -4.42001  0.17724 -1.77567
H  -3.83129 -0.14908 -2.64048
H  -4.50105  1.26803 -1.82373
H  -5.43148 -0.23222 -1.88944
C  -4.70235  0.05930  1.31516
H  -5.67395 -0.44798  1.26543
H  -4.89573  1.13537  1.35607
H  -4.22735 -0.23277  2.25876
C  -2.57683  2.60505  0.35413
H  -2.92263  2.60845  1.39458
H  -2.18196  3.60038  0.13253
H  -3.45095  2.43404 -0.27929
N   1.71157 -2.45279  0.56259
H   2.25289 -3.21158  0.16344
C   1.64195 -2.52454  2.02472
H   1.24915 -3.50729  2.29777
H   2.60909 -2.36479  2.51585
H   0.94187 -1.76657  2.38719
N   2.53020 -1.40322 -1.36009
H   2.52699 -0.51916 -1.85620
C   3.82064 -2.08787 -1.53548
H   3.74447 -3.13727 -1.23410
H   4.05977 -2.07513 -2.60121
H   4.63725 -1.61825 -0.97392
```

TS(VI-VII)

SCF (TPSS/def2-TZVPP) Energy = -1648.35095962
Enthalpy 298K = -1648.002861
Free Energy 298K = -1648.087033
Lowest Frequency = -253.3385 cm^{-1}
Second Frequency = 24.2109 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1648.19590809

```
P  -0.74137 -1.12823 -0.13397
Si -3.73810 -0.52240 -0.10339
F   4.03768 -0.65207  0.76107
F   3.04793  1.40972 -1.01762
F   2.82170  1.89359  1.11557
F   2.00481  3.20912 -0.40754
C   0.87547  1.13267 -0.04208
C  -1.59561  1.49354  0.09604
C  -0.26908  1.93491  0.06223
H  -0.10640  3.00549  0.11675
C  -1.93929  0.12894 -0.02300
C   0.79510 -0.26448 -0.08533
C   1.94353 -1.22328 -0.15656
C   2.20714  1.89320 -0.07520
C  -3.71322 -2.40717 -0.11028
H  -4.74641 -2.77375 -0.16175
H  -3.25935 -2.82221  0.79597
H  -3.17245 -2.81914 -0.96857
C  -4.55411  0.05460 -1.70800
H  -3.98681 -0.29441 -2.57812
H  -4.64670  1.14246 -1.78756
H  -5.56451 -0.36642 -1.78069
C  -4.73853  0.03936  1.39717
H  -5.71008 -0.47020  1.39599
H  -4.93276  1.11582  1.40987
H  -4.23170 -0.22253  2.33287
C  -2.65554  2.56151  0.27842
H  -2.96982  2.60953  1.32768
H  -2.27172  3.54701  0.00186
H  -3.54625  2.35810 -0.32087
```

```
N   2.09179 -2.14090  0.82297
H   3.07004 -2.44899  0.79598
C   1.77189 -1.78181  2.21697
H   1.83189 -2.69345  2.81443
H   2.50759 -1.04668  2.55710
H   0.75910 -1.38414  2.28470
N   2.48410 -1.42646 -1.36217
H   2.33222 -0.67516 -2.02059
C   3.69414 -2.23421 -1.55595
H   3.46750 -3.28982 -1.37425
H   4.01500 -2.11791 -2.59160
H   4.44393 -1.85510 -0.84774
```

VII+HF

SCF (TPSS/def2-TZVPP) Energy = -1648.40950191
Enthalpy 298K = -1648.061884
Free Energy 298K = -1648.150262
Lowest Frequency = 19.4386 cm^{-1}
Second Frequency = 25.6438 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1648.24628615

```
P  -0.68927 -1.09960 -0.14774
Si -3.73675 -0.83715 -0.00887
F   4.92088 -2.55546  0.96667
F   2.70902  1.83688 -1.15767
F   2.65254  2.03900  1.01721
F   1.64458  3.50106 -0.24227
C   0.64200  1.32843 -0.06725
C  -1.84043  1.41464  0.09631
C  -0.57325  2.00988  0.04926
H  -0.53007  3.09274  0.10144
C  -2.02337  0.01795 -0.00020
C   0.72586 -0.06697 -0.14319
C   2.03047 -0.82041 -0.23003
C   1.90877  2.17508 -0.11017
C  -3.49422 -2.70577  0.03181
H  -4.47920 -3.18985  0.02986
H  -2.96372 -3.03798  0.93059
H  -2.93974 -3.07939 -0.83517
C  -4.66114 -0.40480 -1.60072
H  -4.08248 -0.71022 -2.47973
H  -4.88321  0.66214 -1.70452
H  -5.61679 -0.94268 -1.63027
C  -4.75494 -0.35350  1.50739
H  -5.65508 -0.97904  1.55224
H  -5.08167  0.69045  1.49628
H  -4.19289 -0.52111  2.43314
C  -3.01620  2.35492  0.27620
H  -3.31915  2.38994  1.32922
H  -2.75501  3.37229 -0.02747
H  -3.88519  2.03577 -0.30402
N   2.74735 -1.18371  0.78177
H   4.09807 -2.02445  0.83242
C   2.34598 -0.88872  2.15299
H   2.26770 -1.83123  2.70574
H   3.12794 -0.29122  2.63232
H   1.39440 -0.35193  2.23110
N   2.35760 -1.20215 -1.50043
H   1.88696 -0.70462 -2.24208
C   3.61130 -1.87659 -1.82756
H   3.69563 -2.80490 -1.25979
H   3.60259 -2.10298 -2.89522
H   4.48157 -1.25479 -1.58952
```

VII

SCF (TPSS/def2-TZVPP) Energy = -1547.89188629
Enthalpy 298K = -1547.559075
Free Energy 298K = -1547.641141
Lowest Frequency = 24.6758 cm^{-1}
Second Frequency = 29.1963 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1547.72886986

```
P  -0.57577 -1.18180 -0.01163
Si -3.55653 -0.48251 -0.03830
F   3.24801  1.12291 -1.10137
```

```
F   3.12946  1.58201  1.03163
F   2.39315  3.01119 -0.43581
C   1.08351  1.03062 -0.08428
C  -1.36418  1.48049 -0.04630
C  -0.02421  1.88484 -0.08667
H   0.17228  2.95114 -0.13024
C  -1.74167  0.11990 -0.02610
C   0.97269 -0.36370 -0.03151
C   2.15988 -1.29433  0.04350
C   2.45854  1.68403 -0.14433
C  -3.59198 -2.35469  0.18115
H  -4.63614 -2.69285  0.17636
H  -3.14481 -2.67034  1.12982
H  -3.06752 -2.88325 -0.62148
C  -4.35995 -0.07977 -1.70286
H  -3.80377 -0.54709 -2.52331
H  -4.42037  0.99301 -1.91289
H  -5.38242 -0.47671 -1.72724
C  -4.54918  0.27998  1.37821
H  -5.53106 -0.20613  1.43582
H  -4.72141  1.35367  1.25836
H  -4.04914  0.12461  2.34099
C  -2.39837  2.58917 -0.00573
H  -2.73011  2.76601  1.02418
H  -1.98303  3.52683 -0.38537
H  -3.28366  2.34243 -0.59679
N   2.78201 -1.65105  1.10751
C   2.38279 -1.17488  2.42033
H   2.14573 -2.03939  3.05242
H   3.23055 -0.65934  2.88547
H   1.51945 -0.49437  2.42750
N   2.48301 -1.87702 -1.16656
H   2.22768 -1.34349 -1.98647
C   3.67082 -2.71701 -1.27401
H   3.58652 -3.54927 -0.57252
H   3.72662 -3.10304 -2.29434
H   4.58990 -2.16675 -1.03485
```

I_H

```
SCF (TPSS/def2-TZVPP) Energy = -1248.78237191
Enthalpy 298K = -1248.649483
Free Energy 298K = -1248.706936
Lowest Frequency = 26.7815 cm-1
Second Frequency = 48.9058 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1248.67077967

P  -0.82048 -2.15426  0.01955
F   2.41309 -0.30656  0.85627
F   2.23557 -0.90792 -1.24233
F   1.67721  1.71768 -0.81746
F   1.89502 -2.35362  0.34595
F   1.07033  2.08360  1.25425
F  -0.05853  2.94488 -0.39401
C  -0.29710  0.59109 -0.01724
C  -2.69217 -0.07364  0.00203
C  -1.66667  0.87792 -0.00819
H  -1.95423  1.92310 -0.01114
C  -2.39387 -1.43526  0.00867
C   0.20004 -0.72510  0.00396
C   1.68636 -1.05467 -0.00818
C   0.61077  1.82657  0.00268
C  -4.13037  0.39248 -0.01989
H  -4.50673  0.41331 -1.04995
H  -4.77199 -0.28399  0.55130
H  -4.22963  1.40089  0.39035
H  -3.22651 -2.13833  0.01922
```

$TS(I\text{-}II)_H$

```
SCF (TPSS/def2-TZVPP) Energy = -1344.66109878
Enthalpy 298K = -1344.462434
Free Energy 298K = -1344.526225
Lowest Frequency = -397.9638 cm-1
Second Frequency = 32.5265 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1344.52762711
```

```
P   1.76125  0.13453 -0.79090
F   0.71098 -2.42516 -1.43466
F  -1.21428 -2.39812 -0.47313
F  -2.36810 -0.79603  1.32567
F   0.80834 -2.35113  1.02516
F  -3.00081 -0.45115 -0.74712
F  -3.15926  1.13471  0.72902
C  -0.95665  0.57296 -0.04113
C   0.51214  2.57999 -0.23338
C  -0.71350  1.91453  0.11265
H  -1.52511  2.53891  0.46559
C   1.62952  1.90687 -0.63673
C   0.02152 -0.34221 -0.56963
C  -0.11218 -1.72370 -0.67051
C  -2.36543  0.10939  0.31654
C   0.50279  4.08958 -0.16762
H   0.23649  4.42757  0.84088
H   1.47687  4.50830 -0.43042
H  -0.24965  4.50042 -0.85096
N   2.27092 -0.37441  0.98678
H   1.94219  0.32954  1.65099
H   1.63387 -1.32983  1.11714
C   3.72141 -0.63243  1.16624
H   4.02383 -1.39476  0.44697
H   4.30452  0.27629  0.99467
H   3.90671 -0.99818  2.17898
H   2.50561  2.47669 -0.94069
```

II_H+HF

SCF (TPSS/def2-TZVPP) Energy = -1344.67784308
Enthalpy 298K = -1344.477876
Free Energy 298K = -1344.545396
Lowest Frequency = -154.6101 cm^{-1}
Second Frequency = 27.1858 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1344.54912051

```
P   1.75305  0.16144 -0.71617
F   0.63161 -2.32747 -1.70195
F  -1.46737 -2.11043 -1.28120
F  -2.13440 -1.18340  1.21445
F   1.36880 -2.62853  1.58032
F  -3.24240 -0.23592 -0.41963
F  -2.89701  0.84488  1.43578
C  -1.01308  0.53656 -0.00061
C   0.37500  2.59440 -0.31055
C  -0.81005  1.87641  0.11427
H  -1.59634  2.46833  0.57107
C   1.52657  1.94771 -0.62988
C  -0.01646 -0.34063 -0.60984
C  -0.28440 -1.54293 -1.16364
C  -2.31564 -0.01478  0.55529
C   0.30293  4.11028 -0.32345
H  -0.70035  4.46504 -0.07420
H   1.00477  4.54321  0.39768
H   0.56451  4.50123 -1.31159
N   2.32190 -0.25243  0.90642
H   1.96409  0.37863  1.62453
H   1.68352 -1.74578  1.32238
C   3.78862 -0.42765  1.04567
H   4.13218 -1.09667  0.25397
H   4.34189  0.51644  0.97574
H   3.99773 -0.89253  2.01259
H   2.40490  2.53913 -0.88815
```

II

SCF (TPSS/def2-TZVPP) Energy = -1244.17111733
Enthalpy 298K = -1243.985937
Free Energy 298K = -1244.047604
Lowest Frequency = -152.9329 cm^{-1}
Second Frequency = 29.9556 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1244.04183965

```
P   1.92253 -0.38052 -0.40186
F   0.37960 -2.72742 -1.32070
F  -1.65901 -2.04048 -1.17398
```

```
F  -2.19674 -0.85327  1.33153
F  -3.13544  0.15038 -0.37115
F  -2.58246  1.29339  1.39393
C  -0.79598  0.54065 -0.00399
C   0.94068  2.26896 -0.49799
C  -0.37123  1.83138 -0.06389
H  -1.05594  2.60760  0.26476
C   1.98704  1.40685 -0.59378
C   0.06080 -0.55632 -0.44068
C  -0.39455 -1.71574 -0.94615
C  -2.16945  0.28121  0.58171
C   1.13338  3.75547 -0.74146
H   0.18858  4.29955 -0.66069
H   1.83487  4.18596 -0.01832
H   1.54124  3.93399 -1.74113
N   2.46448 -0.50273  1.20386
H   2.08350  0.13873  1.89291
C   2.92679 -1.77998  1.75381
H   3.34964 -2.37449  0.93945
H   3.71194 -1.60506  2.49692
H   2.12213 -2.36147  2.22407
H   2.97637  1.80379 -0.81929
```

TS(II-III)$_H$

```
SCF (TPSS/def2-TZVPP) Energy = -1340.07537026
Enthalpy 298K = -1339.820792
Free Energy 298K = -1339.888879
Lowest Frequency = -199.2555 cm-1
Second Frequency = 33.4342 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1339.93136508

P   0.37850 -1.80160 -0.68551
F  -0.79116  2.23776  1.20042
F  -0.03875  3.11029 -0.66815
F   1.23260  3.02113  1.08473
C   0.80864  0.94166 -0.04385
C   2.83242 -0.49306 -0.21314
C   2.15504  0.72004  0.14319
H   2.75704  1.52632  0.54461
C   2.16440 -1.61764 -0.60396
C  -0.07707 -0.03673 -0.61255
C   0.31820  2.31635  0.37219
C   4.34441 -0.47150 -0.15190
H   4.68794 -0.19508  0.85251
H   4.76628 -1.44733 -0.40542
H   4.75256  0.27310 -0.84599
N  -0.12944 -2.26721  0.97831
H   0.47413 -1.84792  1.68867
C  -0.27662 -3.71625  1.22246
H  -0.85520 -4.14766  0.40039
H   0.68172 -4.25028  1.27924
H  -0.81874 -3.88629  2.15930
C  -1.46457  0.13916 -0.82761
F  -2.00677  1.35568 -1.04666
F  -2.08017 -0.73038 -1.66740
N  -2.34898 -0.31891  0.69959
H  -1.77062 -1.14457  0.98008
H  -2.11992  0.45611  1.32318
C  -3.80260 -0.57439  0.63214
H  -3.97992 -1.39643 -0.06135
H  -4.19734 -0.83848  1.61866
H  -4.30672  0.32218  0.26773
H   2.74504 -2.49313 -0.89241
```

III$_H$

```
SCF (TPSS/def2-TZVPP) Energy = -1340.07533607
Enthalpy 298K = -1339.821535
Free Energy 298K = -1339.887887
Lowest Frequency = -114.2825 cm-1
Second Frequency = 35.3917 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1339.93793302

P  -0.31139  1.80187 -0.73252
F   0.67538 -2.27979  1.19369
F  -0.05477 -3.08667 -0.71629
```

```
F  -1.36772 -2.99701  1.00315
C  -0.84916 -0.90259 -0.06179
C  -2.80535  0.61420 -0.17455
C  -2.19382 -0.62626  0.15152
H  -2.82673 -1.41570  0.53576
C  -2.08586  1.70277 -0.60703
C   0.06835  0.02829 -0.62208
C  -0.41943 -2.30539  0.32751
C  -4.31657  0.70703 -0.06619
H  -4.61311  1.47800  0.65391
H  -4.75739  0.97720 -1.03199
H  -4.75357 -0.24356  0.25194
N   0.31656  2.23984  0.96351
H  -0.33721  1.90136  1.67421
C   0.59804  3.67436  1.18062
H   1.20067  4.03808  0.34311
H  -0.31200  4.28601  1.23220
H   1.16192  3.82026  2.10907
C   1.51140 -0.17648 -0.72166
F   2.00059 -1.42444 -0.98701
F   2.13412  0.66312 -1.61099
N   2.18177  0.22251  0.65772
H   1.60825  1.12532  0.92229
H   1.87573 -0.51917  1.29567
C   3.66430  0.37713  0.68304
H   3.93766  1.19841  0.02311
H   3.97573  0.59951  1.70565
H   4.13035 -0.54776  0.34239
H  -2.62761  2.60238 -0.89718
```

TS(III-IV)$_H$

SCF (TPSS/def2-TZVPP) Energy = -1340.07617877
Enthalpy 298K = -1339.824068
Free Energy 298K = -1339.890855
Lowest Frequency = -354.2589 cm^{-1}
Second Frequency = 38.6628 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1339.93879785

```
P   0.05471 -1.81339 -0.76764
F  -0.29864  2.37179  1.18796
F   0.50388  3.03766 -0.74732
F   1.82155  2.78497  0.95202
C   0.98502  0.77203 -0.06925
C   2.68566 -1.02667 -0.14184
C   2.27152  0.29920  0.15683
H   3.01597  0.98953  0.53257
C   1.81389 -1.99666 -0.57598
C  -0.06123 -0.01043 -0.62658
C   0.76903  2.22868  0.30494
C   4.16059 -1.33897 -0.00122
H   4.50625 -1.12726  1.01775
H   4.36860 -2.38827 -0.22565
H   4.75663 -0.71568 -0.67834
N  -0.69957 -2.16500  0.94275
H   0.00423 -1.97807  1.66162
C  -1.25298 -3.52426  1.11716
H  -1.90617 -3.74298  0.26754
H  -0.47270 -4.29454  1.15030
H  -1.84056 -3.58960  2.04008
C  -1.47422  0.39287 -0.68883
F  -1.78312  1.69985 -0.95151
F  -2.20799 -0.34454 -1.59059
N  -2.15099  0.06493  0.67170
H  -1.67020 -0.96978  0.91590
H  -1.73512  0.73755  1.32315
C  -3.63882  0.13328  0.72157
H  -4.04420 -0.62781  0.05709
H  -3.95950 -0.06041  1.74712
H  -3.97660  1.12134  0.40579
H   2.21486 -2.97488 -0.83733
```

IV$_H$+MeNH$_2$

SCF (TPSS/def2-TZVPP) Energy = -1340.11498287
Enthalpy 298K = -1339.858522
Free Energy 298K = -1339.936653

Lowest Frequency = 14.5374 cm^{-1}
Second Frequency = 15.7779 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1339.97620351

P	0.62692	1.62214	-0.95184
F	-0.99645	-2.23758	1.15131
F	-2.34026	-2.17934	-0.57831
F	-2.95463	-1.32811	1.32181
C	-1.32282	-0.10166	0.06385
C	-1.94755	2.29833	-0.08541
C	-2.21647	0.96596	0.23547
H	-3.19127	0.73835	0.65083
C	-0.70762	2.66565	-0.60755
C	-0.03609	0.06192	-0.47887
C	-1.89395	-1.46066	0.47689
C	-3.02035	3.34376	0.12650
H	-3.84742	2.95362	0.72526
H	-2.61210	4.22593	0.62960
H	-3.42701	3.67584	-0.83603
N	2.93811	1.62437	1.47063
H	2.99152	1.65296	2.48743
C	4.19280	2.11193	0.87899
H	4.10429	2.07611	-0.21059
H	4.34287	3.15755	1.16556
H	5.09342	1.54642	1.16816
C	0.95896	-1.07835	-0.68926
F	0.31453	-2.19150	-1.25372
F	1.86117	-0.71831	-1.68440
N	1.71105	-1.39306	0.46636
H	2.77446	0.65106	1.20900
H	1.09141	-1.47087	1.26656
C	2.61575	-2.55398	0.35792
H	3.31772	-2.37880	-0.45842
H	3.17820	-2.62844	1.29094
H	2.08315	-3.49497	0.17790
H	-0.54236	3.72012	-0.82904

IV_H

SCF (TPSS/def2-TZVPP) Energy = -1244.20048461
Enthalpy 298K = -1244.013457
Free Energy 298K = -1244.075443
Lowest Frequency = 32.6301 cm^{-1}
Second Frequency = 46.5824 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1244.08239598

P	-0.67376	-2.21742	0.02352
F	1.14215	2.02128	-0.71479
F	0.30741	2.36219	1.28294
F	-0.81948	2.91197	-0.48963
C	-0.65350	0.57307	0.00123
C	-2.88720	-0.51069	-0.13438
C	-2.05349	0.60843	-0.09007
H	-2.52382	1.58400	-0.13609
C	-2.34546	-1.79675	-0.11073
C	0.07265	-0.62636	0.08868
C	0.00352	1.95672	0.02965
C	-4.38609	-0.31860	-0.20040
H	-4.64681	0.70530	-0.48041
H	-4.83742	-1.00409	-0.92416
H	-4.84102	-0.52723	0.77526
C	1.59369	-0.70868	0.22825
F	2.04502	0.25257	1.15451
F	1.92065	-1.90222	0.86783
N	2.26993	-0.67975	-1.00025
H	1.88690	0.03608	-1.60713
C	3.74113	-0.66313	-0.95425
H	4.08520	-1.52814	-0.38549
H	4.10958	-0.75306	-1.97816
H	4.14637	0.24917	-0.49994
H	-3.03532	-2.63881	-0.17051

$TS(IV\text{-}V)_H$

SCF (TPSS/def2-TZVPP) Energy = -1340.09920415
Enthalpy 298K = -1339.844291
Free Energy 298K = -1339.914077

Lowest Frequency = -229.9629 cm^{-1}
Second Frequency = 33.7003 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1339.95425711

P	0.04562	-1.71884	-0.72113
F	-2.02849	1.49722	0.17502
F	0.00114	2.45336	1.56187
F	-2.18734	-0.69759	1.15163
F	-0.02693	3.01883	-0.56108
F	1.83691	2.99689	0.54754
C	0.87746	0.86393	-0.01457
C	2.65808	-0.78857	-0.54721
C	2.20904	0.46097	-0.05531
H	2.96432	1.18783	0.21509
C	1.78698	-1.78656	-0.93521
C	-0.20137	0.01921	-0.38203
C	-1.61537	0.35228	-0.36514
C	0.66299	2.32433	0.38317
C	4.15152	-0.98378	-0.69610
H	4.64851	-0.91031	0.27852
H	4.38455	-1.96016	-1.12801
H	4.58449	-0.20727	-1.33667
N	-0.19067	-2.28249	1.24680
H	0.59549	-1.91783	1.78546
H	-1.05878	-1.68382	1.42669
C	-0.39963	-3.72326	1.48506
H	-1.24828	-4.05171	0.88205
H	0.48815	-4.28695	1.18582
H	-0.61236	-3.92109	2.53980
N	-2.44694	-0.09234	-1.32804
H	-2.09219	-0.91869	-1.80160
C	-3.90275	-0.01721	-1.16545
H	-4.18754	1.01130	-0.94324
H	-4.36268	-0.31684	-2.10841
H	-4.23310	-0.66858	-0.35074
H	2.18904	-2.69590	-1.37727

V_H+HF

SCF (TPSS/def2-TZVPP) Energy = -1340.12844201
Enthalpy 298K = -1339.874768
Free Energy 298K = -1339.945745
Lowest Frequency = 40.9388 cm^{-1}
Second Frequency = 47.9359 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1339.98790594

P	0.64670	1.52830	-0.66076
F	0.81826	-2.38727	-1.00452
F	-0.43467	-2.34403	1.43529
F	3.17994	0.88027	1.29101
F	-1.77477	-2.85377	-0.21929
F	-2.54497	-1.81913	1.52991
C	-1.17593	-0.53846	0.04278
C	-2.17097	1.61801	-0.68657
C	-2.24018	0.31116	-0.08440
H	-3.20942	-0.02211	0.27126
C	-0.98395	2.23475	-0.94500
C	0.17019	-0.19488	-0.36126
C	1.16257	-1.13339	-0.63069
C	-1.47449	-1.88413	0.68836
C	-3.48625	2.28845	-1.01212
H	-4.11626	2.35701	-0.11708
H	-3.33326	3.29533	-1.40796
H	-4.04629	1.70574	-1.75329
N	1.04768	2.11235	1.02558
H	0.31003	1.85638	1.68476
H	2.25982	1.41246	1.26912
C	1.32217	3.56782	1.10929
H	2.09702	3.81462	0.37890
H	0.43187	4.17116	0.90107
H	1.69288	3.81003	2.10865
N	2.47476	-0.94033	-0.59954
H	2.82462	-0.18325	0.01529
C	3.44886	-1.86531	-1.17579
H	3.07751	-2.26498	-2.12072
H	4.37160	-1.31154	-1.35432
H	3.65690	-2.69736	-0.49473

H -1.00069 3.21920 -1.41101

V_H

SCF (TPSS/def2-TZVPP) Energy = -1239.61182509
Enthalpy 298K = -1239.371398
Free Energy 298K = -1239.438850
Lowest Frequency = 35.4249 cm^{-1}
Second Frequency = 53.3297 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1239.47473181

P -0.03187 1.91689 -0.21876
F   2.09951 -1.43526 -0.70207
F   0.62484 -2.15459 1.53839
F -0.01560 -3.15295 -0.30101
F -1.46113 -2.72403 1.26463
C -0.66549 -0.85600 -0.00172
C -2.43996 0.65039 -0.89092
C -1.96846 -0.58836 -0.31373
H -2.71138 -1.35741 -0.12585
C -1.69490 1.79019 -0.88537
C   0.38043 0.12300 -0.21331
C   1.69552 -0.16723 -0.48019
C -0.37506 -2.21062 0.61753
C -3.84096 0.64013 -1.46145
H -4.56217 0.29023 -0.71298
H -4.14171 1.63672 -1.79384
H -3.90867 -0.04447 -2.31572
N -0.41321 2.45813 1.35518
H -1.16793 1.97700 1.83692
C   0.61859 2.99002 2.24689
H   1.34179 3.55006 1.64590
H   0.16920 3.68117 2.96796
H   1.16117 2.21163 2.80239
N   2.72869 0.70642 -0.55683
H   2.40848 1.67528 -0.51243
C   3.93065 0.43677 -1.34992
H   3.72708 0.43385 -2.42845
H   4.66081 1.21580 -1.12534
H   4.34771 -0.52888 -1.06437
H -2.12538 2.70558 -1.28760

$TS(V\text{-}VI)_H$

SCF (TPSS/def2-TZVPP) Energy = -1335.49162881
Enthalpy 298K = -1335.185769
Free Energy 298K = -1335.257443
Lowest Frequency = -827.2399 cm^{-1}
Second Frequency = 44.7442 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1335.34627772

P -0.42834 -1.84147 0.63131
F   2.18816 1.16153 0.45936
F   0.55873 2.22616 -1.34916
F   0.28816 2.97032 0.70394
F -1.33183 3.08943 -0.72617
C -0.80641 0.89604 0.11726
C -2.85159 -0.44910 0.50456
C -2.19672 0.74730 0.13901
H -2.80890 1.61187 -0.08364
C -2.17294 -1.62326 0.76861
C   0.10455 -0.12763 0.45930
C   1.60856 -0.09861 0.33540
C -0.32937 2.28442 -0.28738
C -4.35935 -0.40588 0.64704
H -4.82690 -0.05936 -0.28210
H -4.76486 -1.39146 0.89025
H -4.65634 0.29384 1.43707
N -0.02460 -2.33838 -1.19443
H   0.17644 -3.34015 -1.21680
C -1.01223 -1.98937 -2.23963
H -1.12094 -0.90196 -2.26924
H -0.67647 -2.33896 -3.22275
H -1.99808 -2.41823 -2.02803
N   2.37032 -0.96773 1.20593
H   1.93039 -1.89283 1.16326
C   2.34154 -0.52910 2.61788

```
H   1.32155 -0.42880  3.01365
H   2.88489 -1.27252  3.20506
H   2.85436  0.42927  2.70495
N   1.91186 -0.54813 -1.11202
H   1.14268 -1.47873 -1.27023
C   3.34052 -0.77944 -1.45932
H   3.93269  0.10418 -1.21578
H   3.71071 -1.62853 -0.88884
H   3.40171 -0.98695 -2.53028
H   1.53110  0.21207 -1.68305
H  -2.74033 -2.49027  1.10240
```

VI_H+NH2Me

SCF (TPSS/def2-TZVPP) Energy = -1335.52691867
Enthalpy 298K = -1335.217219
Free Energy 298K = -1335.297249
Lowest Frequency = -13.6588 cm^{-1}
Second Frequency = 8.9614 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1335.38021470

```
P   0.01405 -1.52326  1.35461
F   0.67029  2.24777  0.67734
F  -0.34893  1.92845 -1.76810
F  -1.79533  2.67263 -0.29413
F  -2.45762  1.49949 -1.99366
C  -1.31388  0.31370 -0.25120
C  -2.55041 -1.77916  0.29421
C  -2.43529 -0.52971 -0.31885
H  -3.27838 -0.18799 -0.90818
C  -1.49233 -2.30443  1.03637
C  -0.16469 -0.00181  0.49687
C   1.10486  0.88051  0.63758
C  -1.46625  1.60780 -1.05994
C  -3.83887 -2.55961  0.15276
H  -4.45389 -2.17150 -0.66335
H  -3.63693 -3.61843 -0.03581
H  -4.42756 -2.49789  1.07594
N   2.93132 -2.64531 -0.95929
H   3.77486 -2.89287 -0.44482
C   3.16258 -2.79505 -2.40341
H   2.24613 -2.52770 -2.93913
H   3.98523 -2.18596 -2.81443
H   3.37704 -3.84482 -2.62723
N   1.85331  0.72525  1.86296
H   2.25880 -0.20694  1.89373
C   1.18265  1.07933  3.11735
H   0.28127  0.48215  3.32939
H   1.89545  0.93113  3.93216
H   0.90426  2.13334  3.08511
N   1.98655  0.61468 -0.45527
H   2.72988 -1.66923 -0.73390
C   3.13937  1.52476 -0.60601
H   2.83627  2.55416 -0.83199
H   3.71516  1.52247  0.31910
H   3.76429  1.14555 -1.41839
H   1.45247  0.56286 -1.31768
H  -1.61555 -3.29484  1.47400
```

VI_H

SCF (TPSS/def2-TZVPP) Energy = -1239.61215150
Enthalpy 298K = -1239.371025
Free Energy 298K = -1239.437469
Lowest Frequency = 37.0528 cm^{-1}
Second Frequency = 42.7557 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1239.48605339

```
P  -0.53242 -2.15114 -0.42230
F   1.93818  0.56915  0.91537
F   0.69300  2.35383 -0.62235
F  -0.00472  2.33286  1.45928
F  -1.33678  2.92679 -0.14528
C  -0.83354  0.58949  0.01572
C  -2.93607 -0.73246 -0.15554
C  -2.23201  0.46117  0.01661
H  -2.81335  1.36575  0.15365
```

```
C  -2.25157 -1.92448 -0.39157
C   0.03156 -0.51243 -0.11401
C   1.56999 -0.46155 -0.07115
C  -0.35330  2.03630  0.18724
C  -4.44742 -0.71817 -0.08296
H  -4.78569 -1.04718  0.90723
H  -4.84761  0.28469 -0.25524
H  -4.88258 -1.39941 -0.82017
N   2.09608 -1.70843  0.38627
H   3.00375 -1.89437 -0.02533
C   2.06169 -1.98394  1.82523
H   2.38897 -3.01505  1.98094
H   2.68922 -1.30492  2.41435
H   1.03147 -1.89733  2.18184
N   2.10424 -0.14804 -1.35366
H   1.53094  0.55954 -1.79905
C   3.52635  0.22381 -1.42147
H   4.15962 -0.62807 -1.15562
H   3.75163  0.48456 -2.45799
H   3.78216  1.06754 -0.76935
H  -2.84566 -2.82338 -0.56081
```

$TS(VI\text{-}VII)_H$

```
SCF (TPSS/def2-TZVPP) Energy = -1239.57838259
Enthalpy 298K = -1239.338215
Free Energy 298K = -1239.405702
Lowest Frequency = -252.5369 cm-1
Second Frequency = 25.1801 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1239.46006937

P  -0.92873 -2.16328 -0.34147
F   2.83257  0.71501  0.86095
F   0.94229  2.06700 -0.86392
F   0.43515  2.17397  1.27329
F  -0.90730  2.99676 -0.22253
C  -0.78709  0.61307 -0.05791
C  -3.06783 -0.38590 -0.08666
C  -2.18677  0.69527 -0.00619
H  -2.61726  1.68452  0.09756
C  -2.58643 -1.68604 -0.25719
C  -0.10990 -0.61085 -0.16707
C   1.37722 -0.80219 -0.21047
C  -0.05302  1.95717  0.04450
C  -4.55653 -0.13913  0.01455
H  -4.93097 -0.46286  0.99294
H  -4.79497  0.92080 -0.10306
H  -5.10046 -0.70647 -0.74692
N   1.96184 -1.57229  0.73146
H   2.95776 -1.32747  0.74389
C   1.47073 -1.53046  2.12183
H   1.98244 -2.31931  2.67618
H   1.70969 -0.54633  2.53598
H   0.39757 -1.71962  2.15274
N   1.97368 -0.59852 -1.38856
H   1.45809 -0.00482 -2.02309
C   3.43268 -0.62324 -1.54883
H   3.79993 -1.64920 -1.44243
H   3.66741 -0.26927 -2.55308
H   3.84469  0.03654 -0.77245
H  -3.31437 -2.49253 -0.34599
```

VII_H+HF

```
SCF (TPSS/def2-TZVPP) Energy = -1239.63732248
Enthalpy 298K = -1239.397610
Free Energy 298K = -1239.469048
Lowest Frequency = 20.2675 cm-1
Second Frequency = 26.2495 cm-1
SCF (M052X-D3,THF/def2-QZVPP) Energy =  -1239.51098512

P  -0.86607 -2.20712 -0.16783
F   4.65964 -0.46041  0.96419
F   0.49041  2.08291 -1.14164
F   0.32632  2.21328  1.03332
F  -1.28698  2.94799 -0.22984
C  -1.02047  0.56982 -0.06785
```

```
C  -3.17675 -0.64273  0.07663
C  -2.41494  0.53080  0.04245
H  -2.94062  1.47798  0.09671
C  -2.56440 -1.89392 -0.02194
C  -0.21879 -0.57873 -0.15010
C   1.28876 -0.53142 -0.23428
C  -0.37384  1.95084 -0.09922
C  -4.67807 -0.54455  0.23522
H  -4.96310 -0.71824  1.27990
H  -5.04616  0.44424 -0.05082
H  -5.18805 -1.29714 -0.37297
N   2.08704 -0.46639  0.77910
H   3.68121 -0.45408  0.83070
C   1.58967 -0.43601  2.15035
H   2.01757 -1.28349  2.69679
H   1.94183  0.47926  2.63638
H   0.49794 -0.47897  2.22812
N   1.76902 -0.68205 -1.50438
H   1.10947 -0.50067 -2.24693
C   3.19112 -0.59883 -1.82868
H   3.74802 -1.34524 -1.25956
H   3.30445 -0.79640 -2.89603
H   3.60551  0.38686 -1.58958
H  -3.20763 -2.77387 -0.00805
```

VII$_H$

SCF (TPSS/def2-TZVPP) Energy = -1139.12002798
Enthalpy 298K = -1138.895143
Free Energy 298K = -1138.960121
Lowest Frequency = 29.7067 cm^{-1}
Second Frequency = 33.4451 cm^{-1}
SCF (M052X-D3,THF/def2-QZVPP) Energy = -1138.99370590

```
P  -0.68976 -2.19660 -0.09454
F   1.11010  1.92536 -1.04942
F   0.74218  2.16260  1.09147
F  -0.67128  2.96594 -0.35507
C  -0.62117  0.58203 -0.08478
C  -2.87574 -0.44513 -0.11130
C  -2.01889  0.66072 -0.10553
H  -2.46652  1.64856 -0.12778
C  -2.36325 -1.74435 -0.11689
C   0.08917 -0.62743 -0.05985
C   1.59656 -0.70329  0.02744
C   0.13816  1.90372 -0.09619
C  -4.37229 -0.22076 -0.09801
H  -4.76816 -0.34003  0.91785
H  -4.62823  0.78593 -0.43929
H  -4.88472 -0.94649 -0.73635
N   2.30002 -0.66485  1.09940
C   1.68790 -0.54227  2.41090
H   1.98022 -1.40696  3.01910
H   2.08624  0.34952  2.90751
H   0.59069 -0.47507  2.40978
N   2.20663 -0.96271 -1.18443
H   1.69933 -0.64944 -2.00100
C   3.66260 -0.96523 -1.27835
H   4.06501 -1.71187 -0.59107
H   3.93950 -1.22418 -2.30272
H   4.09605  0.00705 -1.01125
H  -3.07701 -2.56824 -0.13890
```

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