Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Materials for

Reactions of Lewis acidic methylene phosphonium dications with olefins

Linkun Miao, Amir Yeganeh-Salman, Jason Yeung, and Douglas W. Stephan*

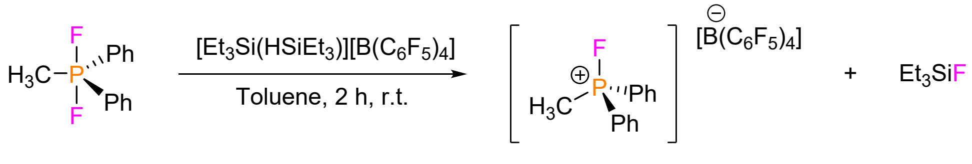
Correspondence to: dstephan@chem.utoronto.ca

Contents

Materials and Methods

General considerations: All manipulations were performed in a Glove box MB LABmaster produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2 unless otherwise mentioned. All glassware and Teflon-coated stir bars were oven-dried and cooled under vacuum before use. Dry, oxygen-free pentane, toluene and dichlormethane was prepared using an Innovative Technologies solvent purification system and stored over activated 4 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. $Ph_2PF_2CH_3$[1] and Ph_2FPCH_2[2] were synethesized according to literature procedures. $[Et_3Si(HSiEt_3)][B(C_6F_5)_4]$ was prepared according to the method reported by Heinekey *et al.*[3] NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer or an Agilent DD2 500 MHz spectrometer. ^1H NMR data are reported relative to protio-solvent signals as follows: chemical shift (δ/ppm), coupling constant (Hz), normalized integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ/ppm) are referenced relative to protio-solvent signals. $^{31}P\{^1H\}$, ^{19}F, and ^{11}B NMR chemical shifts (δ/ppm) are reported relative to H_3PO_4, $CFCl_3$, and $(Et_2O)\cdot BF_3$ external standards. For compounds 7, 10-12, $^{13}C\{^1H\}$ NMR resonance signals corresponding to OTf anions could not be explicitly identified due to low compound solubility. Repeated elemental analysis carried out on compounds 7-12 were found consistently low in carbon content,[4] thus not relied upon for characterization. X-ray data were collected on a Bruker Apex II diffractometer at 150(±2) K for all crystals.

Preparation of $[Ph_2PFCH_3][B(C_6F_5)_4]$ (2a)



2a

To a 20 mL scintillation vial containing a slurry of $[Et_3Si(HSiEt_3)][B(C_6F_5)_4]$ in 3 mL of toluene (0.302 g, 0.331 mmol, 1 equiv) was added a 3 mL toluene solution of $Ph_2PF_2CH_3$ (0.087 g, 0.37 mmol, 1.2 equiv). The resultant reaction mixture was stirred for 2 hours and allowed to settle. The clear colorless supernatant was decanted leaving an orange oil. With rapid stirring, 4 mL of pentane was added resulting in the precipitation of an off-white powder. After decantation of the supernatant, the residue was washed with 3x2 mL pentane and dried *in vacuo* affording $[Ph_2PFCH_3][B(C_6F_5)_4]$ (**2a**) as an off-while powder (0.249 g, 0.277 mmol, 84% yield).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 8.07 – 8.00 (m, 2H), 7.84 – 7.73 (m, 8H), 2.75 (dd, $^2J_{HP}$ = 12.7 Hz, $^3J_{HF}$ = 11.2 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ 148.2 (d, J = 243.9 Hz), 139.2 – 138.4 (m), 138.3 (d, J = 242.4 Hz), 136.2 (d, J = 242.9 Hz), 132.2 (dd, J = 13.3, 2.0 Hz), 131.2 (d, J = 14.4 Hz), 116.3 (dd, J = 106.2, 13.0 Hz), 11.4 (dd, J = 67.5, 12.2 Hz).

Resonance signal corresponding to i-C_6F_5 could not be explictily identified due to broadening and low compound solubility.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298K) δ 107.0 (d, $^1J_{PF}$ = 989 Hz, 1P).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ -129.7 (dq, $^1J_{PF}$ = 989 Hz, $^3J_{HF}$ = 11 Hz, 1F), -132.2 – -133.2 (m, 8F), -162.8 (t, $^3J_{FF}$ = 20.5 Hz, 4F), -165.2 – -171.6 (m, 8F).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ –16.7 (s).

Elemental analysis calcd (%) for $C_{37}H_{13}BF_{21}P$: C 49.47, H 1.46; found: C 49.60, H 1.29.

Figure S1. ^1H NMR spectrum of 2a ($CDCl_3$).

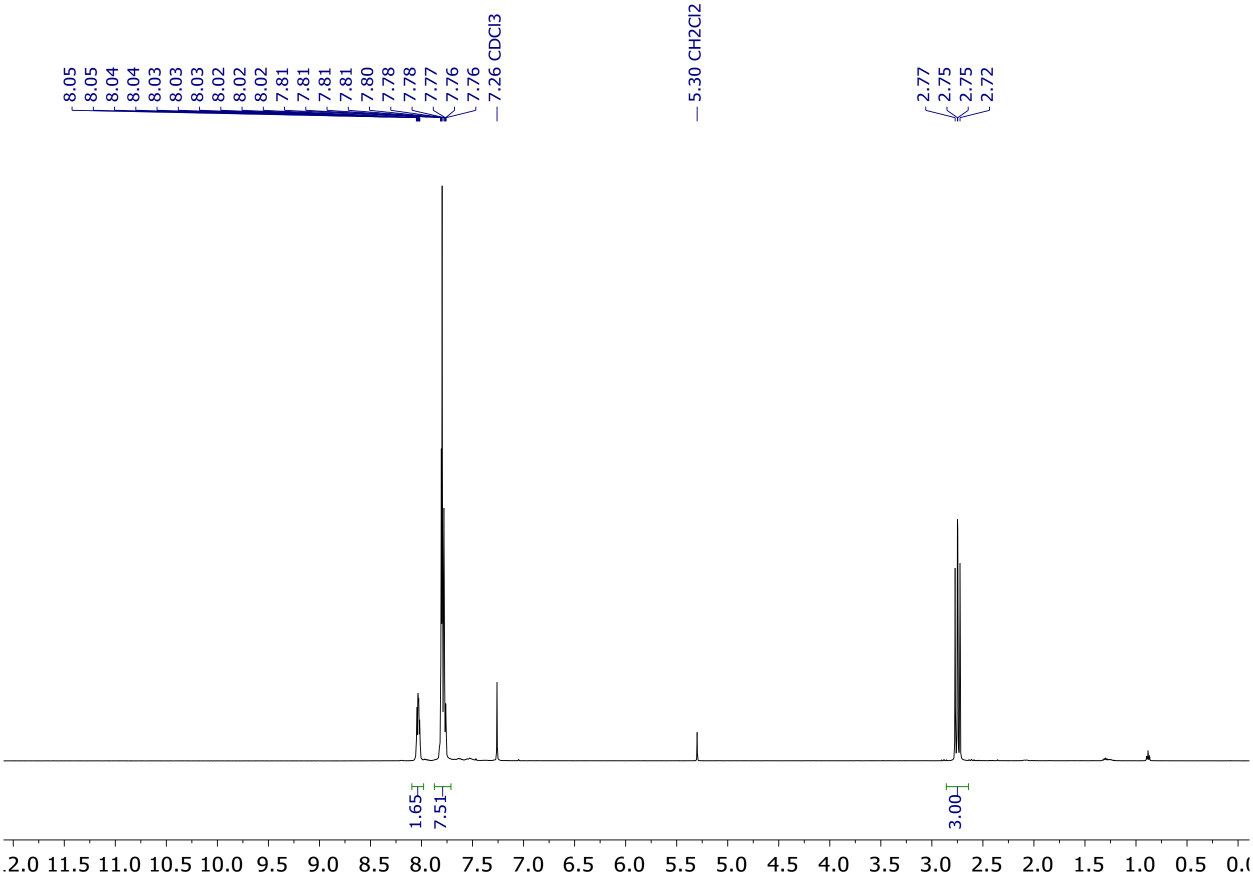


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 2a ($CDCl_3$).

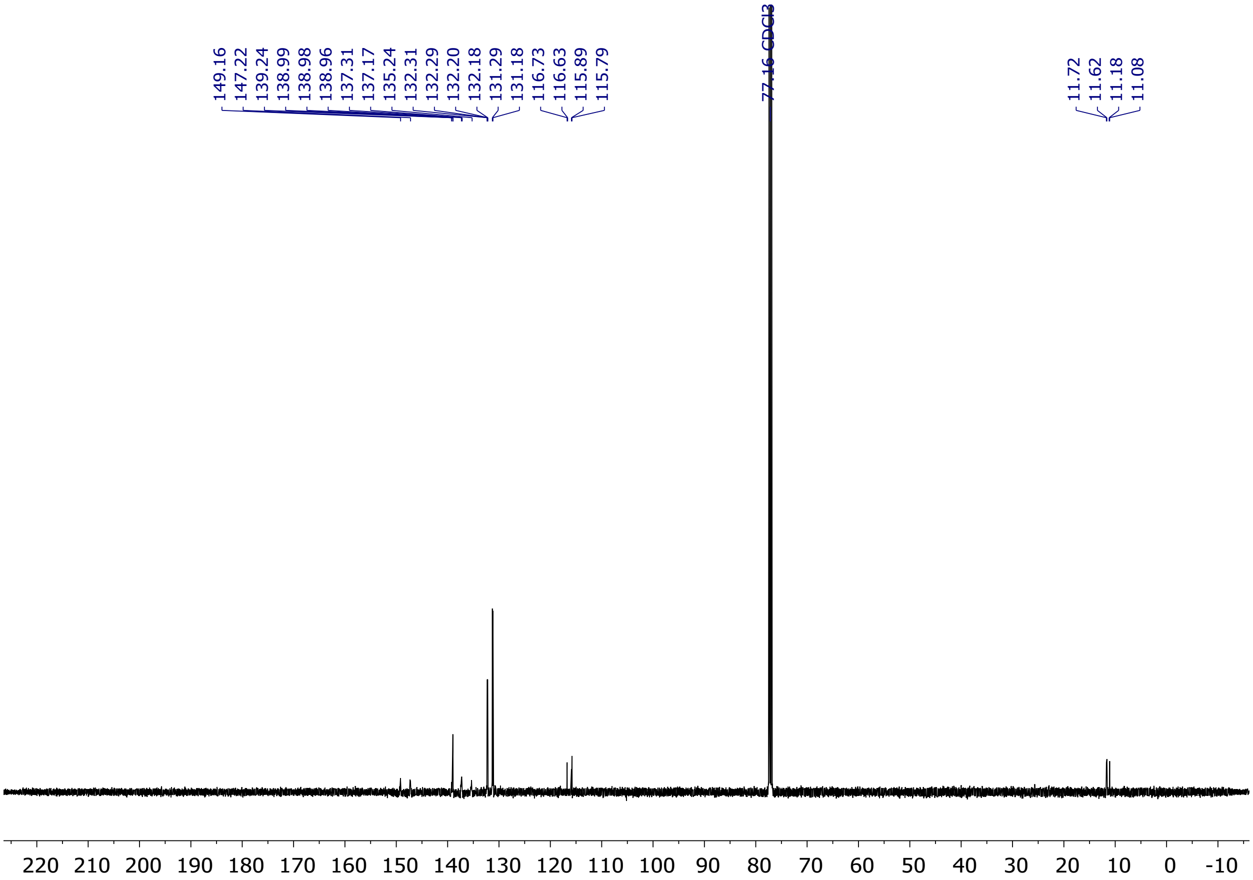


Figure S3. $^{31}P\{^1H\}$ **NMR spectrum of 2a** ($CDCl_3$).

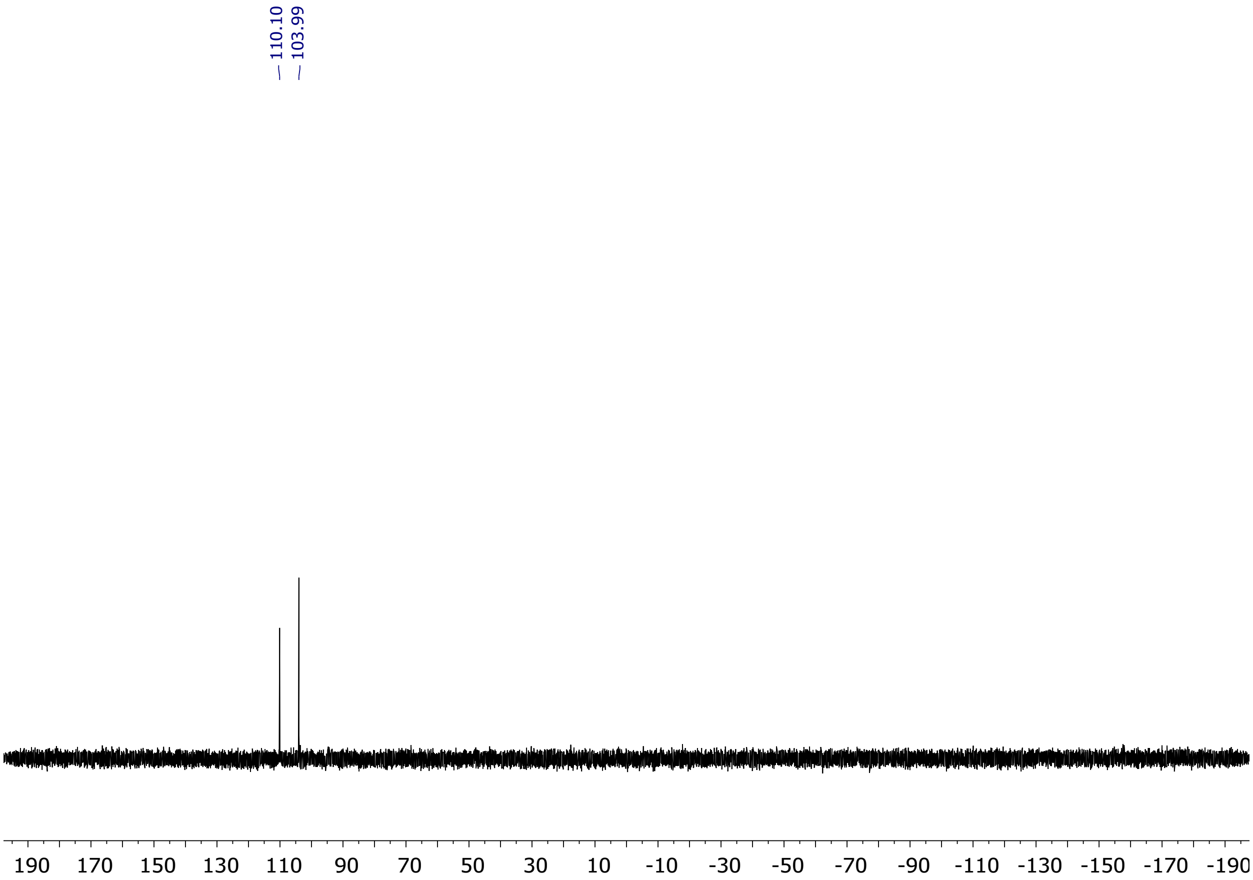


Figure S4. ^{19}F **NMR spectrum of 2a (CDCl$_3$).**

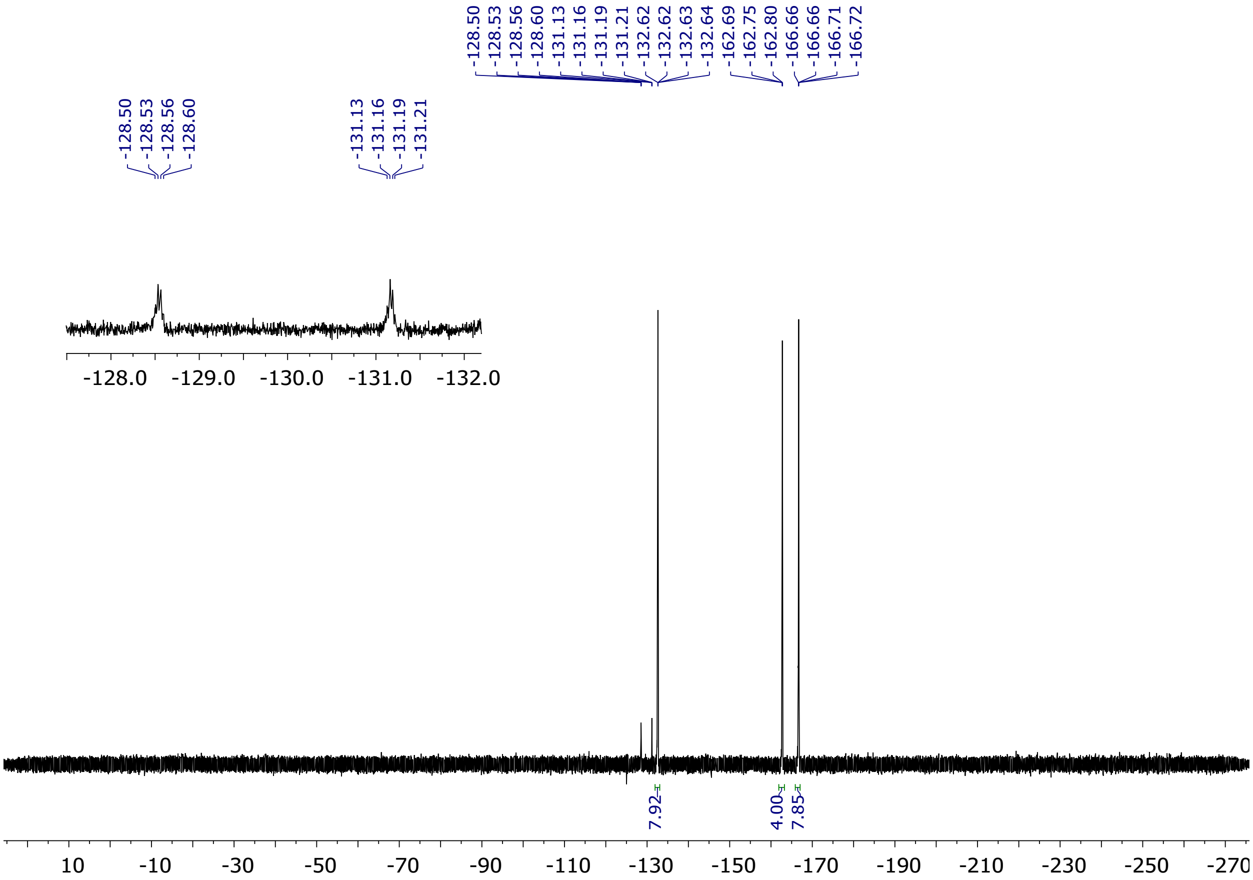
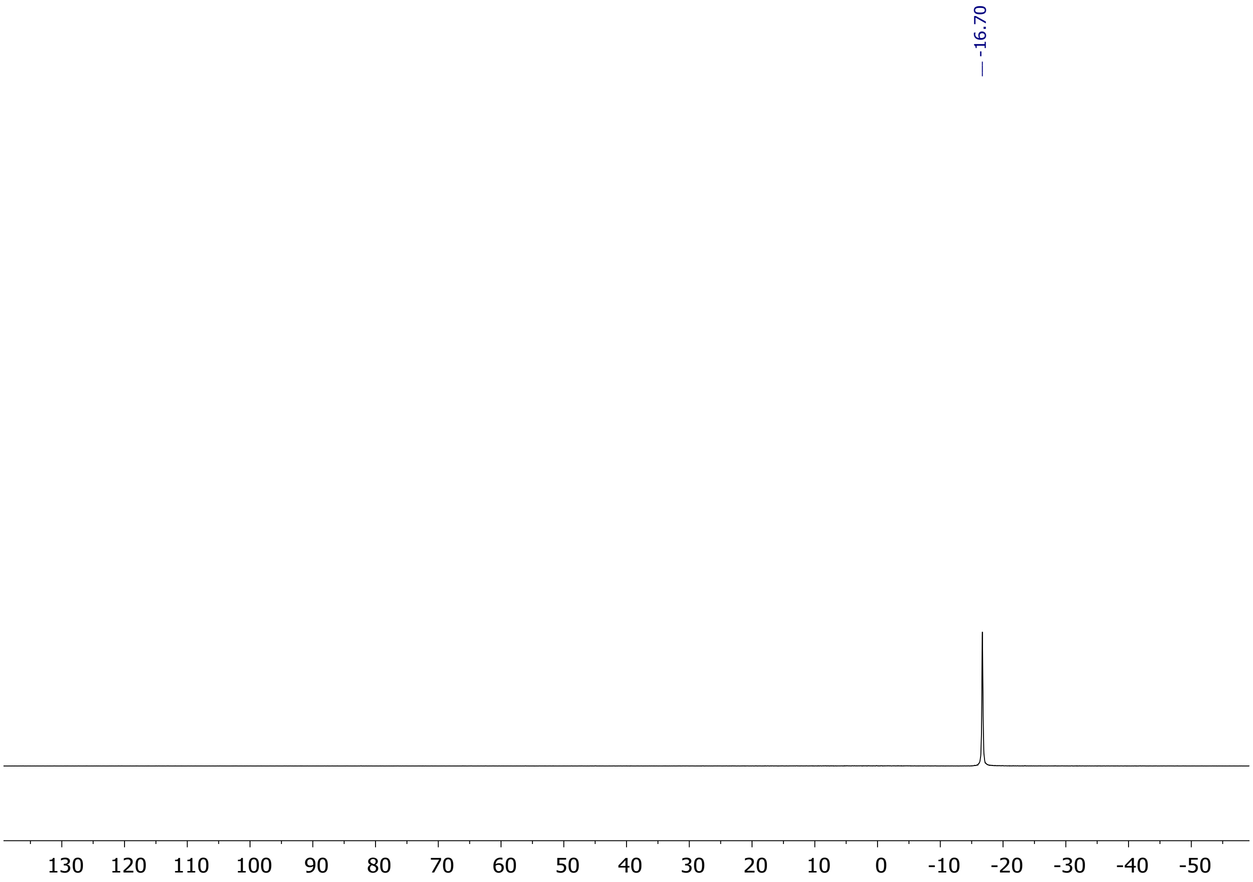
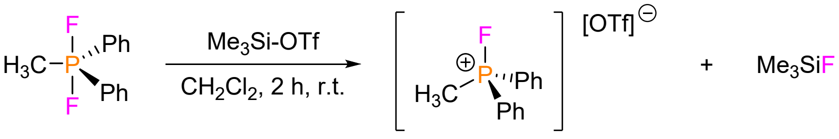


Figure S5. ^{11}**B NMR spectrum of 2a (CDCl$_3$).**



Preparation of [Ph$_2$PFCH$_3$][OTf] (2b)



2b

A 20 mL scintillation vial containing Ph$_2$PF$_2$CH$_3$ (0.118 g, 0.495 mmol, 1 equiv) was taken up in 2 ml DCM and added Me$_3$Si-OTf dropwise via syringe (0.090 mL, 0.50 mmol, 1 equiv). The resultant reaction mixture was stirred for 2 hours before the solvent was removed *in vacuo*. The resultant residue was washed with 3x2 mL pentane to afford [Ph$_2$PFCH$_3$][OTf] (**2b**) as a colorless oil (0.155 g, 0.421 mmol, 85% yield).

^{1}**H NMR** (400 MHz, CDCl$_3$, 298 K) δ 8.04 – 7.95 (m, 4H), 7.94 – 7.86 (m, 2H), 7.79 – 7.68 (m, 4H), 3.12 (dd, $^{2}J_{\mathrm{HP}}$ = 13.2 Hz, $^{3}J_{\mathrm{HF}}$ =12.1 Hz, 3H).

^{13}**C{**^{1}**H} NMR** (126 MHz, CDCl$_3$, 298 K) δ 137.6 (t, J = 2.2 Hz), 132.9 (dd, J = 13.5, 2.1 Hz), 130.5 (d, J = 14.3 Hz), 120.6 (q, J = 320.2 Hz), 117.9 (dd, J = 105.7, 13.0 Hz), 11.4 (dd, J = 64.2, 10.2 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298K) δ 109.6 (d, $^1J_{PF}$ = 976 Hz, 1P).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ -78.4 (s, 3F), -131.3 (dq, $^1J_{FP}$ = 976, $^3J_{FH}$ = 12 Hz, 1F).

Figure S6. ^1H NMR spectrum of 2b ($CDCl_3$).

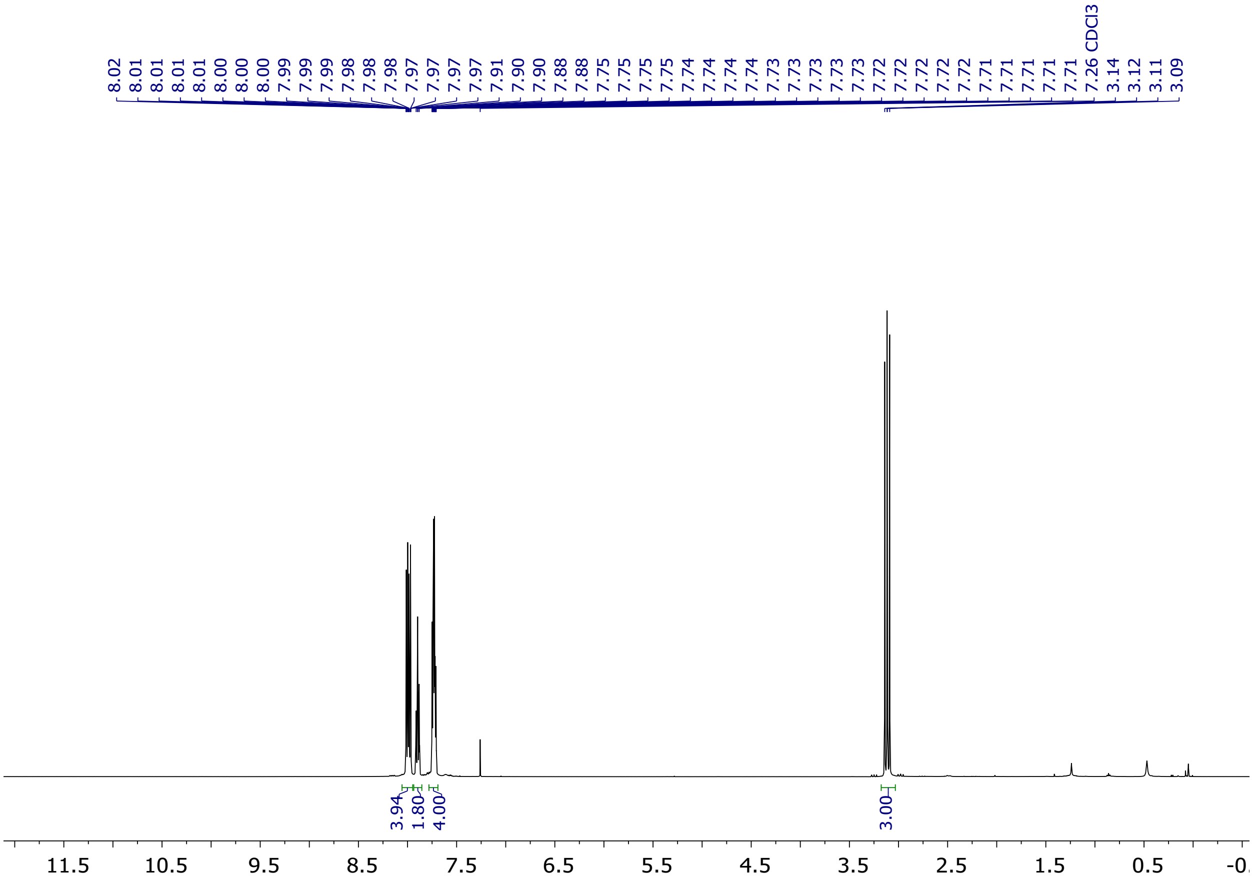


Figure S7. $^{13}C\{^1H\}$ NMR spectrum of 2b ($CDCl_3$).

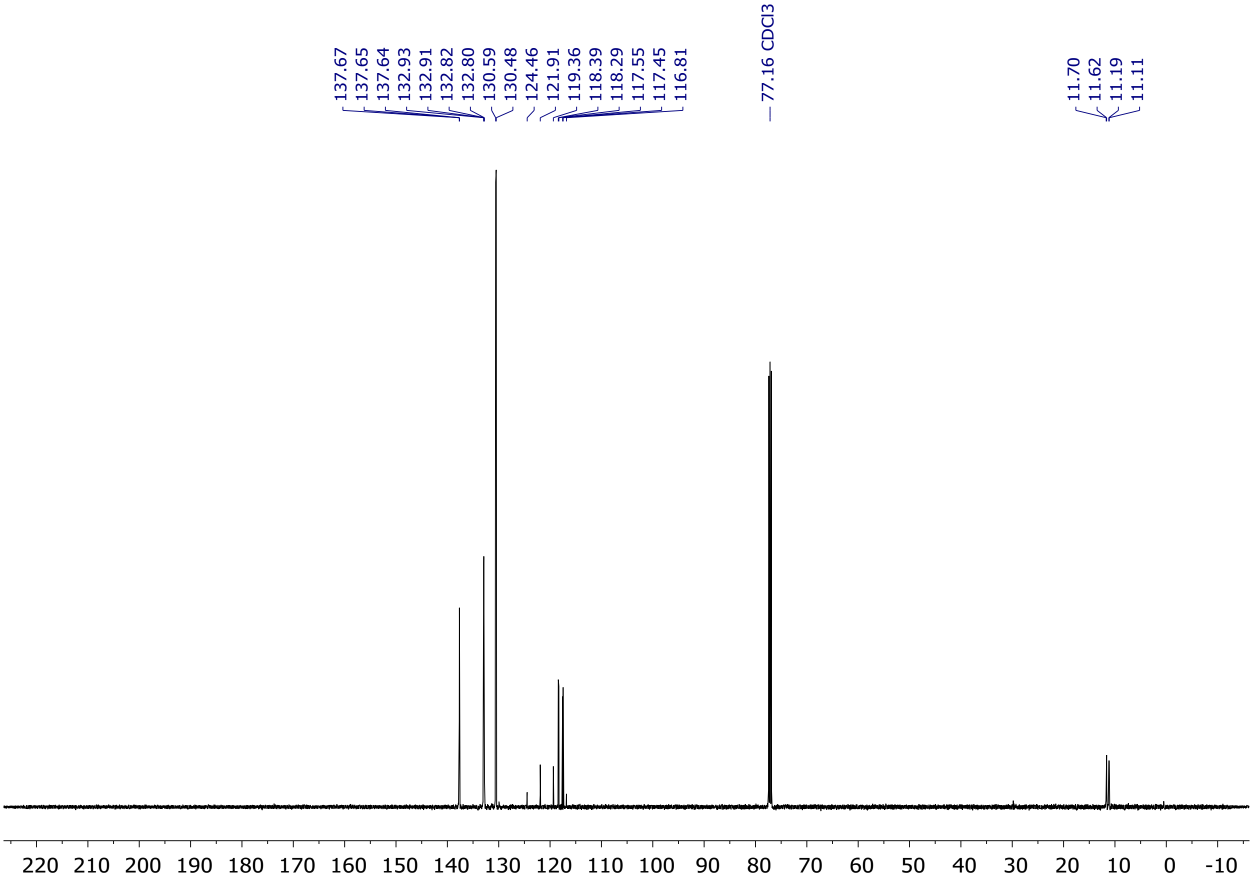


Figure S8. $^{31}P\{^1H\}$ **NMR spectrum of 2b** ($CDCl_3$).

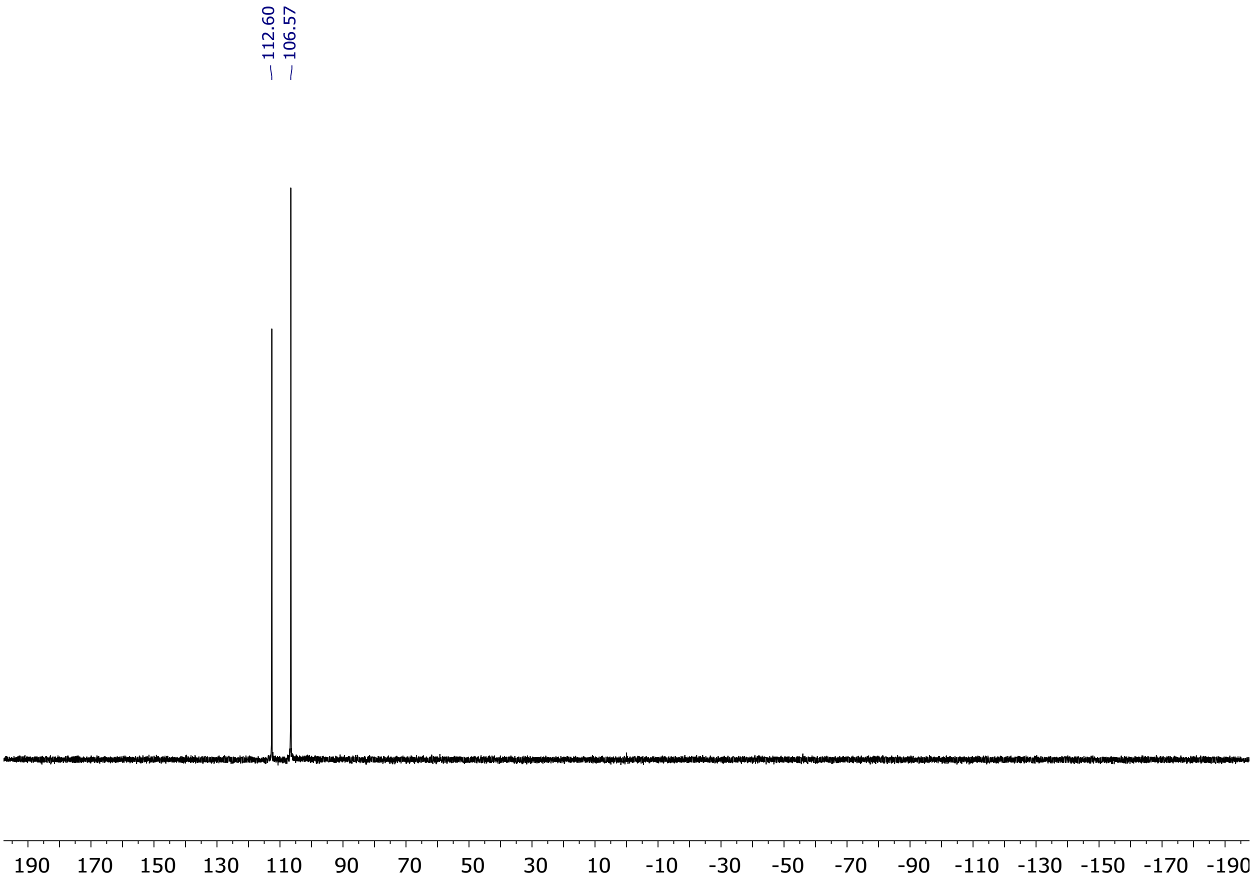
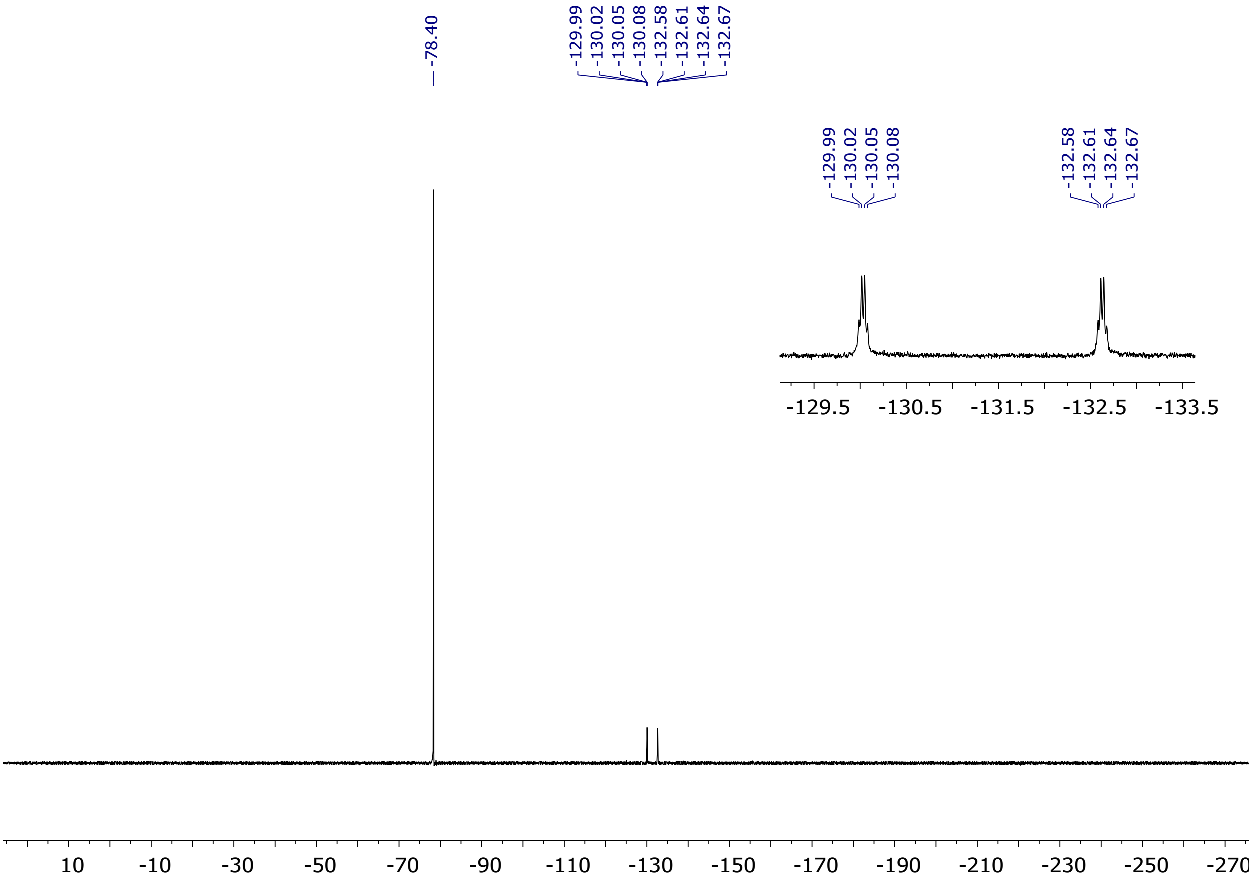
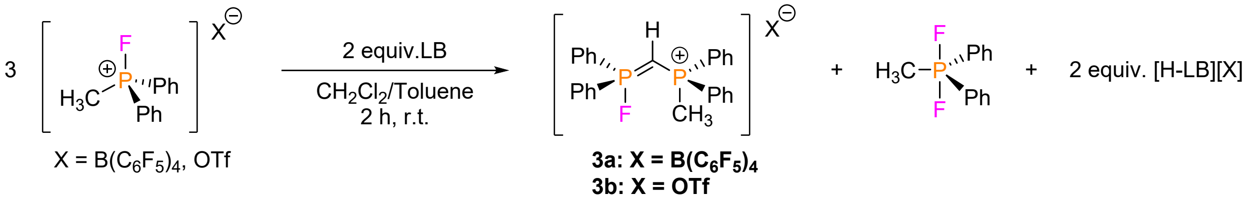


Figure S9. ^{19}F NMR spectrum of **2b** ($CDCl_3$).



Generation of $[Ph_2FPC(H)PPh_2CH_3][X]$ ($X = B(C_6F_5)_4$, OTf)



Method A: To a 20 mL scintillation vial containing a solution of **2a** in 3 mL of DCM (0.117 g, 0.130 mmol, 3 equiv) was added dropwise a 2 mL DCM solution of DMAP (0.0106 g, 0.0868 mmol, 2 equiv). The resultant homogeneous solution was stirred for 2 hours before the solvent was removed *in vacuo* affording an off-white oily residue. ^1H, $^{31}P\{^1H\}$, and ^{19}F NMR analysis indicated the presence of **3a**, $Ph_2PF_2CH_3$, and $[H\text{-}DMAP][B(C_6F_5)_4]$. While $Ph_2PF_2CH_3$ could be removed by washing with 3x2 mL pentane, **3a** and $[H\text{-}DMAP][B(C_6F_5)_4]$ could not be explicitly separated due to similar solubility properties. Note: the same products were observed using **2b**, with the corresponding OTf counter anion.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 16.46 (s, 1H, [*H*-DMAP]$^+$), 7.93 (br s, 2H, Ar-*H*), 6.65 (br s, 2H, Ar-*H*), 3.16 (s, 6H, N(C*H*$_3$)$_2$), 2.79 – 2.69 (m, 1H, [Ph$_2$FPC(*H*)PPh$_2$CH$_3$]$^+$), 2.64 – 2.58 (m, 3H, Ph$_2$PF$_2$C*H*$_3$), 2.02 (d, $^2J_{\mathrm{HP}}$ = 13.0 Hz, 3H, [Ph$_2$FPC(H)PPh$_2$C*H*$_3$]$^+$).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K) δ 75.1 (dd, $^1J_{\mathrm{PF}}$ = 1031 Hz, $^2J_{\mathrm{PP}}$ = 16 Hz, 1P, [Ph$_2$F*P*C(H)PPh$_2$CH$_3$]$^+$), 17.2 (dd, $^3J_{\mathrm{PF}}$ = 24 Hz, $^2J_{\mathrm{PP}}$ = 16 Hz, 1P, [Ph$_2$FPC(H)*P*Ph$_2$CH$_3$]$^+$), -40.1 (t, $^1J_{\mathrm{PF}}$ = 620 Hz, Ph$_2$*P*F$_2$CH$_3$).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ -27.8 (dq, $^1J_{\mathrm{FP}}$ = 620 Hz, $^3J_{\mathrm{FH}}$ = 13 Hz, 2F, Ph$_2$P*F*$_2$CH$_3$), -88.0 (ddd, $^1J_{\mathrm{FP}}$ = 1031 Hz, $^3J_{\mathrm{FP}}$ = 24 Hz, $^3J_{\mathrm{FH}}$ = 9 Hz, 1F, [Ph$_2$*F*PC(H)PPh$_2$CH$_3$]$^+$), -130.8 – -131.2 (br m, 8F, B(*o*-C$_6$*F*$_5$)), -161.9 (t, $^3J_{\mathrm{FF}}$ = 21 Hz, 4F, B(*p*-C$_6$*F*$_5$)), -165.6 – -166.0 (br m, 8F, B(*m*-C$_6$*F*$_5$)).

^{11}B NMR (128 MHz, CDCl$_3$, 298 K): δ –16.3 (s, *B*(C$_6$F$_5$)$_4$).

Figure S10. ^{1}H NMR spectrum of the reaction mixture generating 3a (CDCl$_3$).

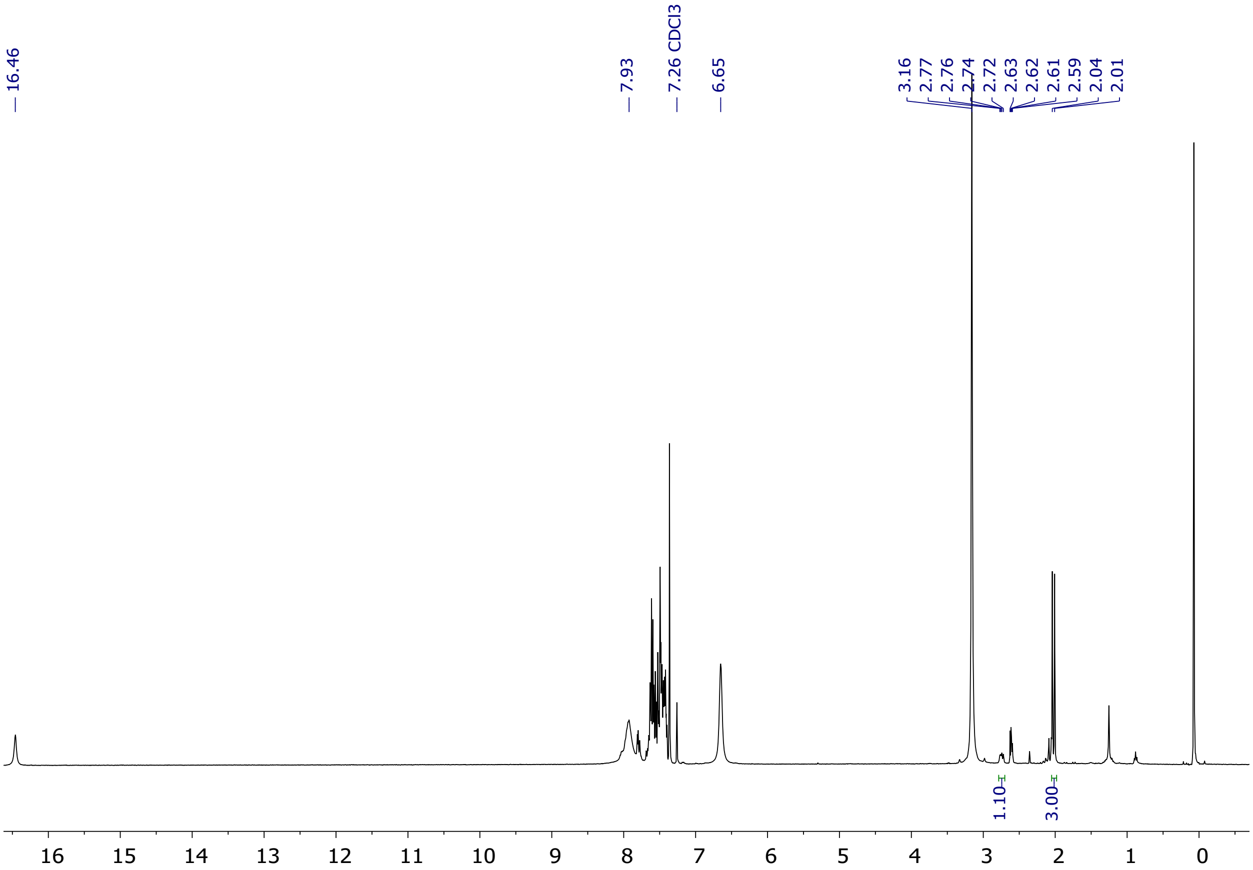


Figure S11. $^{31}P\{^{1}H\}$ **NMR spectrum of the reaction mixture generating 3a (CDCl$_3$).**

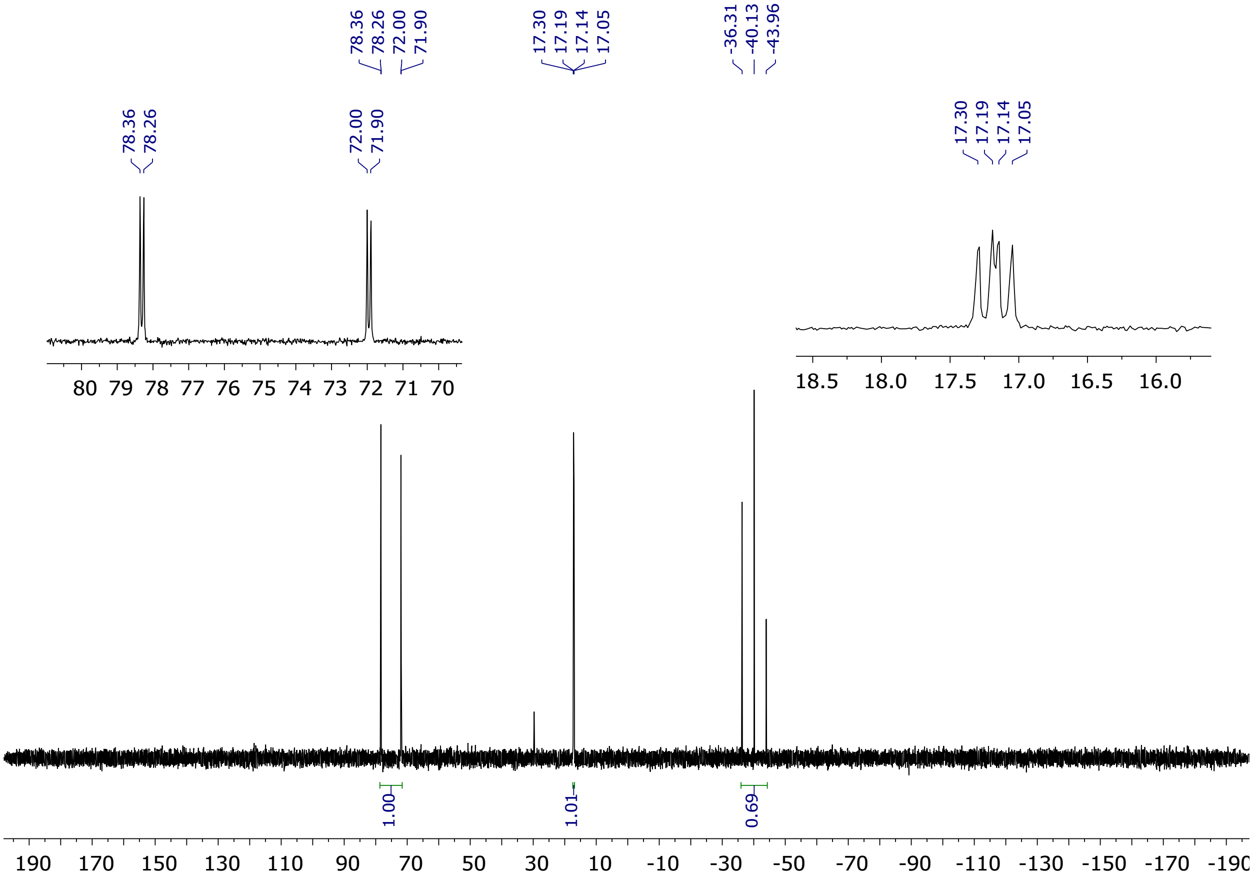


Figure S12. ^{19}F NMR spectrum of the reaction mixture generating 3a (CDCl$_3$).

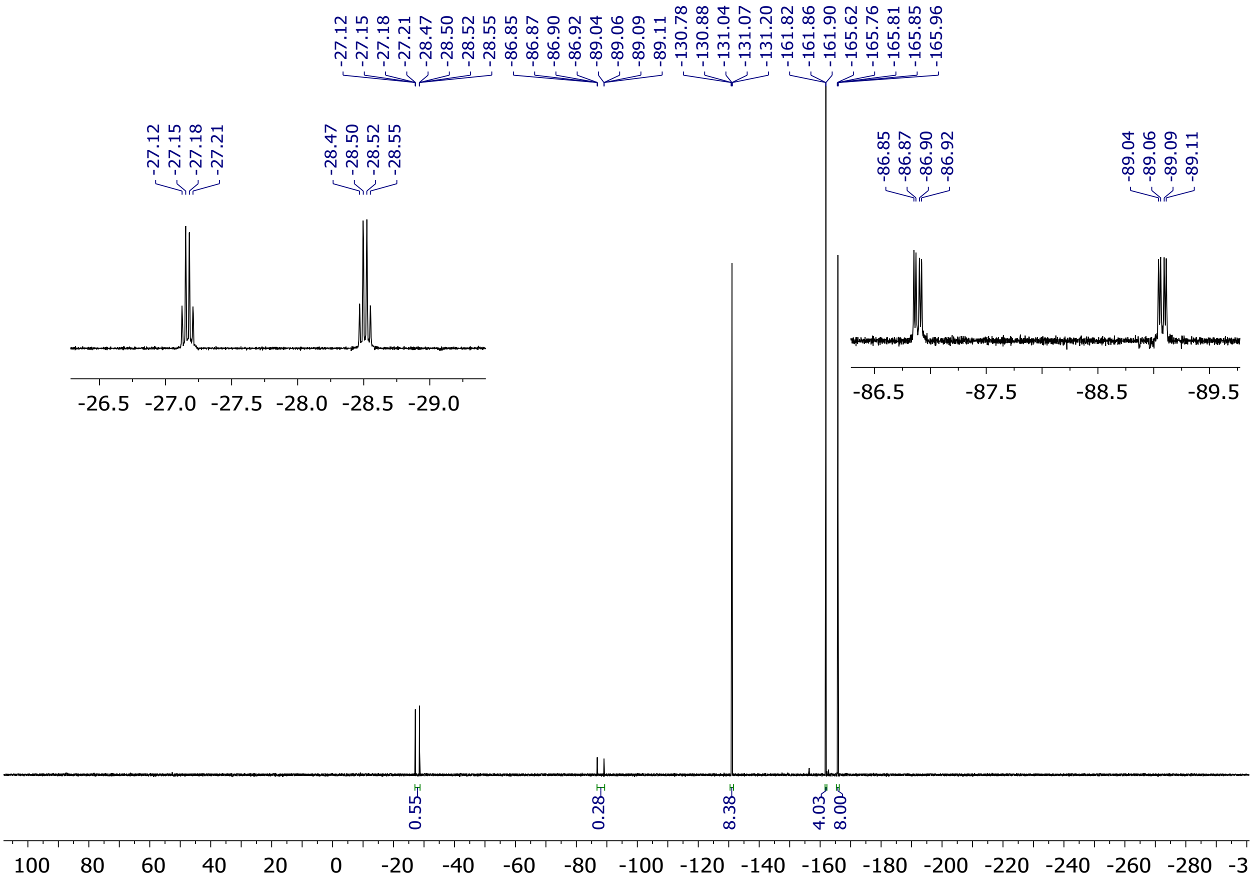
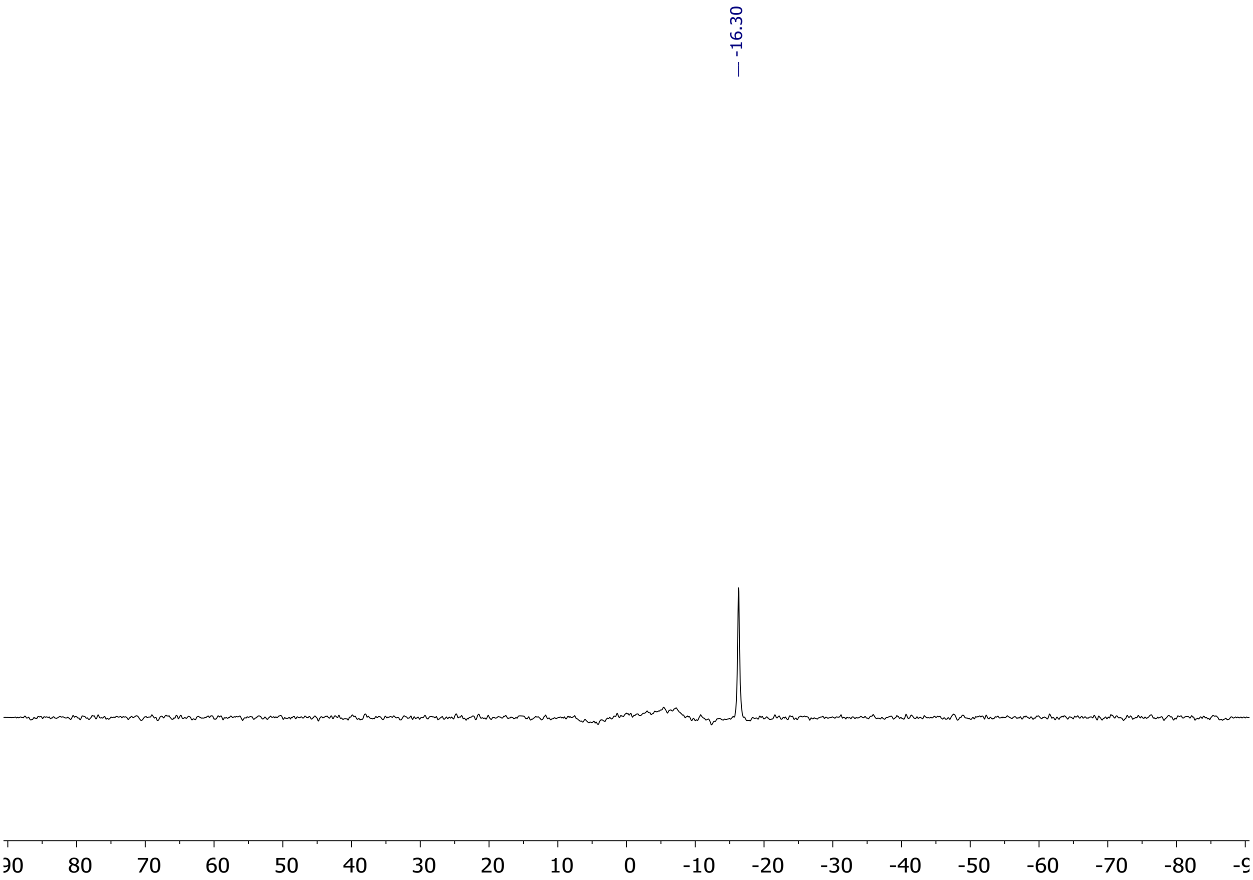


Figure S13. ^{11}B NMR spectrum of the reaction mixture generating 3a (CDCl$_3$).



Method B: To a 20 mL scintillation vial charged with **2b** (0.0270 g, 0.0733 mmol, 3 equiv) was added 3 mL of toluene. To the resultant slurry, a 2 mL toluene solution of IDipp (0.0190 g, 0.0489 mmol, 2 equiv) was added and the mixture stirred for 2 hours. The solvent was then removed *in vacuo* affording an off-white residue. ^{1}H, ^{31}P{^{1}H}, and ^{19}F NMR analysis indicated presence of **3b**, $Ph_2PF_2CH_3$ and [H-IDipp][OTf].

Note: the same products were observed using **2a**, with the corresponding $B[C_6F_5]_4$ counter anion; use of BAC and SIMes carbenes still led to the generation of the same three species as observed above, in addition to minor unidentified byproducts.

^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 9.16 (s, 1H, NC(*H*)N), 7.79 (s, 2H, NC*H*), 7.57 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-Ar*H*), 7.34 (d, $^3J_{HH}$ = 7.8 Hz, 4H, m-Ar*H*), 2.91 – 2.82 (m, 1H, [Ph$_2$FPC(*H*)PPh$_2$CH$_3$]$^+$), 2.61 (br d, $^2J_{HP}$ = 13.0 Hz, 3H, Ph$_2$PF$_2$C*H*$_3$), 2.39 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 1.99 (d, $^2J_{HP}$ = 13.2 Hz, 3H, [Ph$_2$FPC(H)PPh$_2$C*H*$_3$]$^+$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K) δ 74.4 (dd, $^1J_{PF}$ = 1030 Hz, $^2J_{PP}$ = 17 Hz, 1P, [Ph$_2$F*P*C(H)PPh$_2$CH$_3$]$^+$), 16.8 (dd, $^3J_{PF}$ = 24 Hz, $^2J_{PP}$ = 17 Hz, [Ph$_2$FPC(H)*P*Ph$_2$CH$_3$]$^+$), -42.4 (t, $^1J_{PF}$ = 620 Hz, Ph$_2$*P*F$_2$CH$_3$).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ -28.2 (dq, $^1J_{FP}$ = 620 Hz, $^3J_{FH}$ = 13 Hz, 1F, Ph$_2$PF_2CH$_3$), -79.0 (s, OSO$_2$CF_3), -88.4 (ddd, $^1J_{FP}$ = 1030 Hz, $^3J_{FP}$ = 24 Hz, $^3J_{FH}$ = 9 Hz, 1F, [Ph$_2$$F$PC(H)PPh$_2CH_3$]$^+$).

Figure S14. ^{1}H NMR spectrum of the reaction mixture generating 3b (CDCl$_3$).

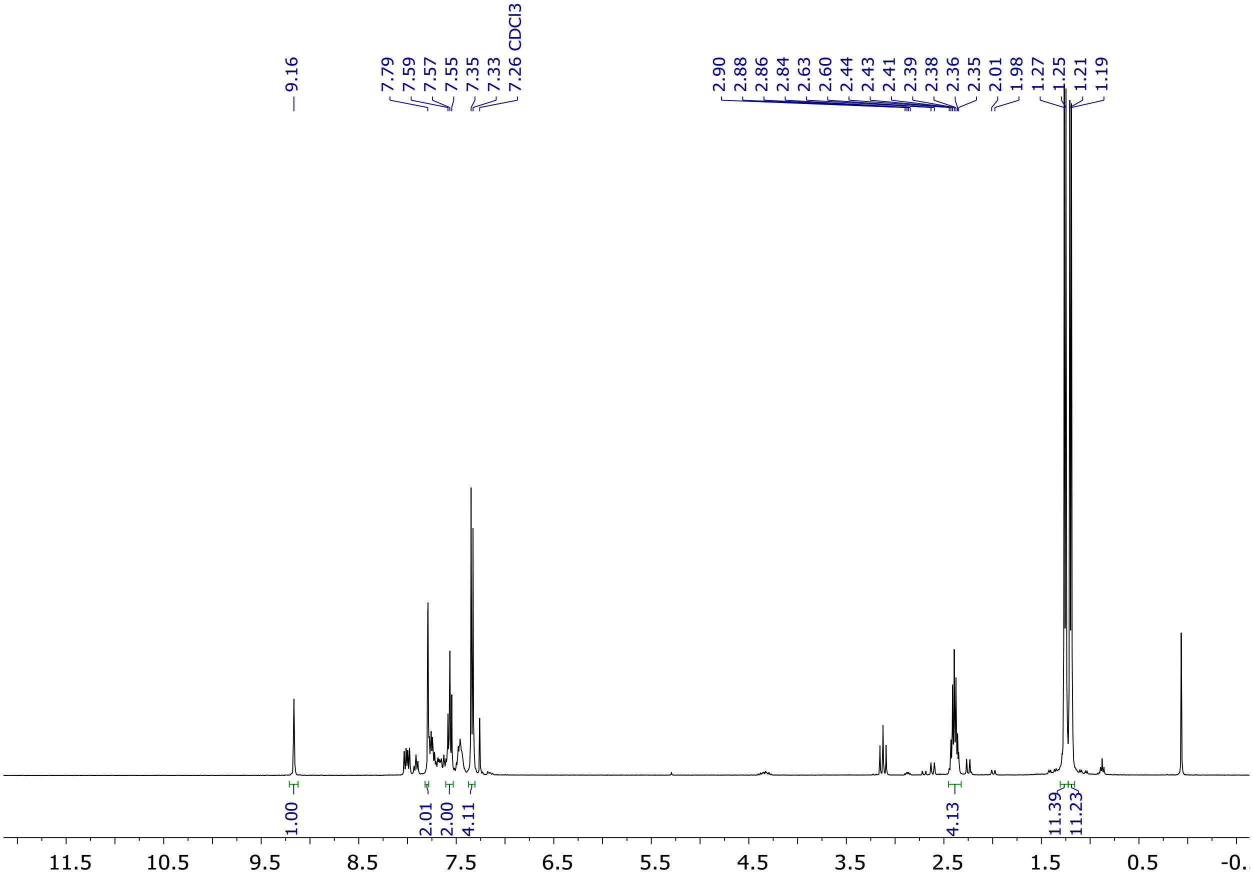


Figure S15. $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture generating 3b ($CDCl_3$).

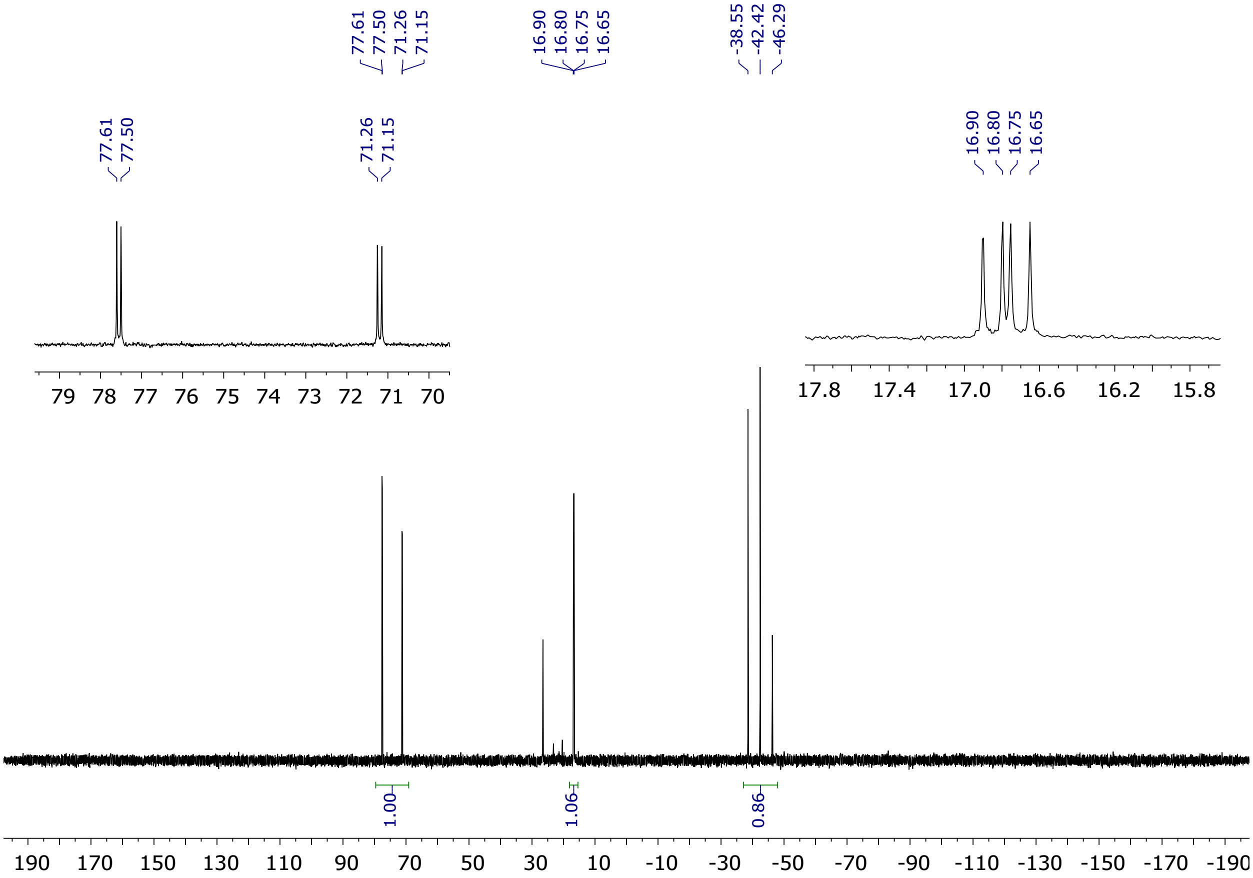
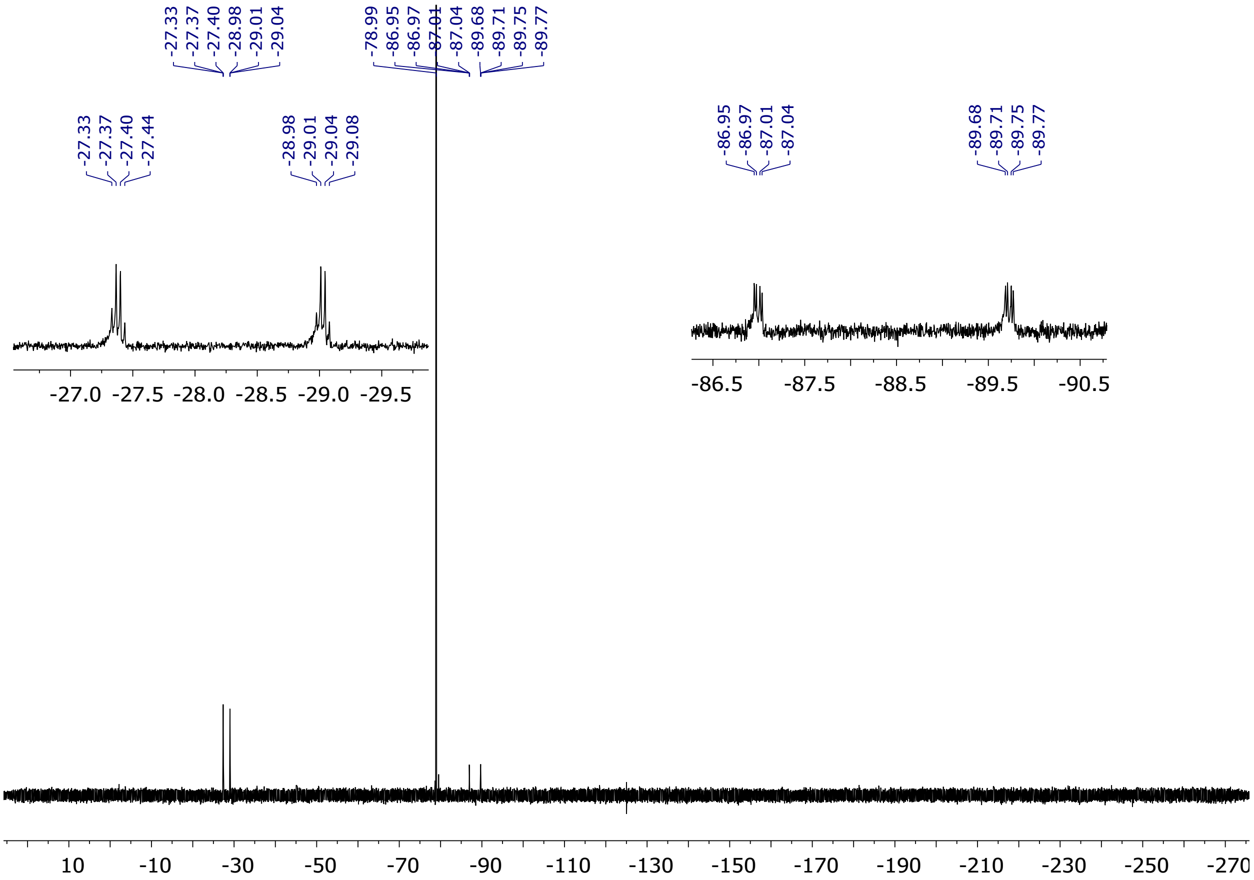
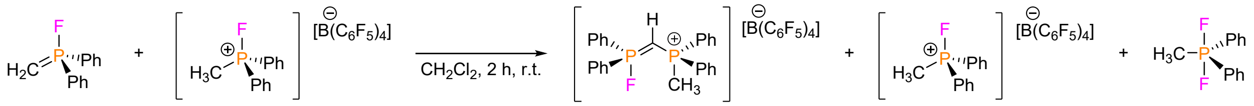


Figure S16. ^{19}F NMR spectrum of the reaction mixture generating **3b** ($CDCl_3$).



Reaction of Ph_2FPCH_2 with 2a



3a

To a 20 mL scintillation vial containing a solution of **2a** (49.3 mg, 0.0550 mmol, 1 equiv) in 2 mL of DCM was added a 2 mL DCM solution of Ph_2FPCH_2 (12.0 mg, 0.0550 mmol, 1 equiv) resulting in a clear colorless solution. The reaction was stirred for 2 hours before solvent was removed *in vacuo* affording a colorless residue. NMR analysis indicates the presence of three distinct chemical species identified as **3a**, **2a**, and $Ph_2PF_2CH_3$. The species $Ph_2PF_2CH_3$ could be removed via 2x2 mL pentane wash, but similar solubility properties of **3a** and **2a** precludes their explicit isolation.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.06 – 7.97 (m, Ar-*H*), 7.82 – 7.74 (m, Ar-*H*), 7.68 – 7.33 (m, Ar-*H*), 2.75 (dd, $^2J_{HP}$ = 12.7 Hz, $^3J_{HF}$ = 11.2 Hz, 3H, $[Ph_2PFCH_3]^+$), 2.67 – 2.56 (m, 1H, $[Ph_2FPC(H)PPh_2CH_3]^+$), 2.44 – 2.33 (m, 3H, $Ph_2PF_2CH_3$), 2.03 (d, $^2J_{HP}$ = 13.1 Hz, 3H, $[Ph_2FPC(H)PPh_2CH_3]^+$).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298K) δ 107.4 (d, $^{1}J_{PF}$ = 990 Hz, 1P, $[Ph_2\mathit{P}FCH_3]^+$), 75.4 (dd, $^{1}J_{PF}$ = 1031 Hz, $^{2}J_{PP}$ = 16 Hz, 1P, $[Ph_2F\mathit{P}C(H)PPh_2CH_3]^+$), 16.8 (dd, $^{3}J_{PF}$ = 23 Hz, $^{2}J_{PP}$ = 16 Hz, 1P, $[Ph_2FPC(H)\mathit{P}Ph_2CH_3]^+$), -40.1 (t, $^{1}J_{PF}$ = 616 Hz, $Ph_2\mathit{P}F_2CH_3$).

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ -26.4 (br d, $^{1}J_{FP}$ = 616 Hz, $Ph_2P\mathit{F}_2CH_3$), -87.0 (ddd, $^{1}J_{FP}$ = 1031 Hz, $^{3}J_{FP}$ = 23 Hz, $^{3}J_{FH}$ = 9 Hz, $[Ph_2\mathit{F}PC(H)PPh_2CH_3]^+$), -128.3 (br d, $^{1}J_{FP}$ = 990 Hz, $[Ph_2P\mathit{F}CH_3]^+$), -131.1 – -131.8 (br m, 8F, B(*o*-$C_6\mathit{F}_5$)), -161.9 (t, $^{3}J_{FF}$ = 20 Hz, 4F, B(*p*-$C_6\mathit{F}_5$)), -165.4 – -166.2 (br m, 8F, B(*m*-$C_6\mathit{F}_5$)).

Figure S17. ^{1}H NMR spectrum of reaction of Ph_2FPCH_2 with 2a ($CDCl_3$).

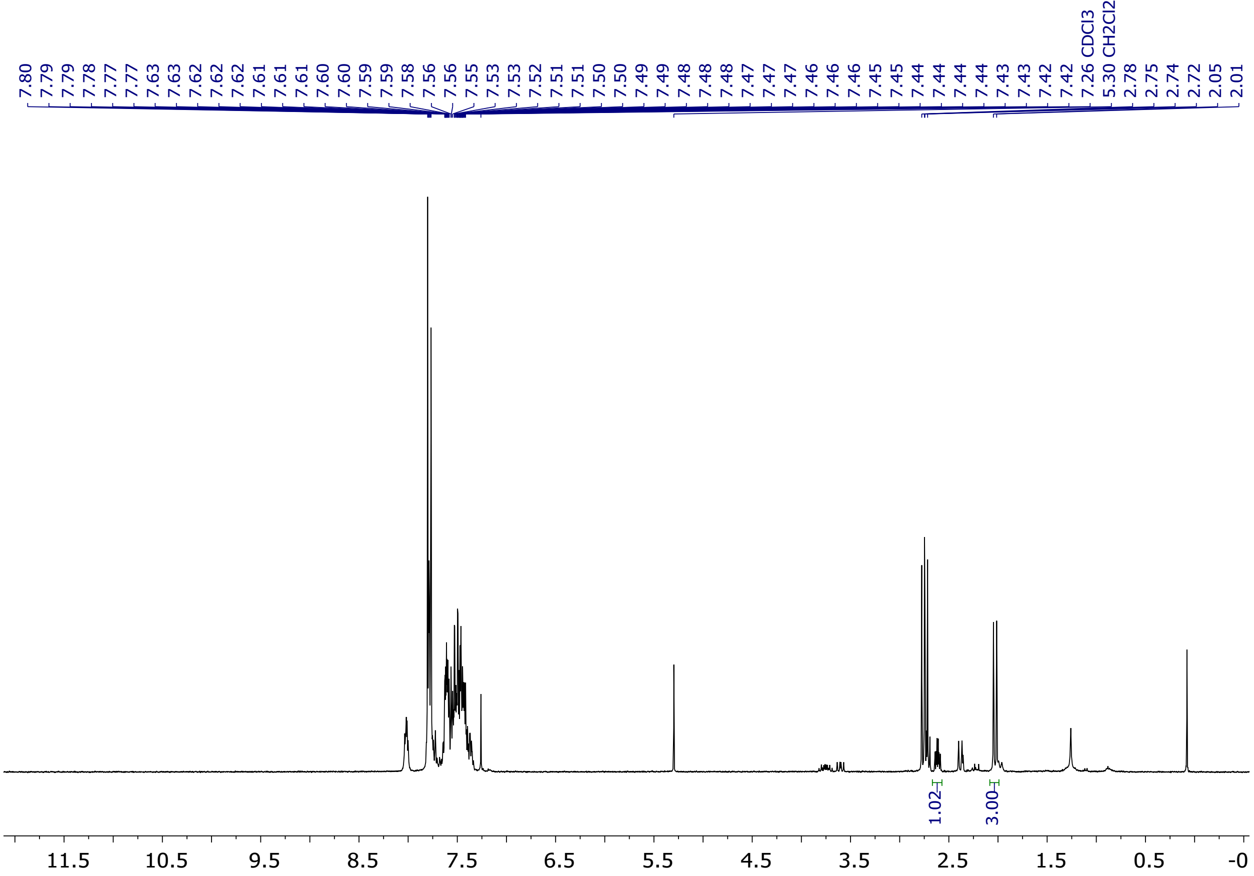


Figure S18. $^{31}P\{^1H\}$ NMR spectrum of reaction of Ph_2FPCH_2 with 2a ($CDCl_3$).

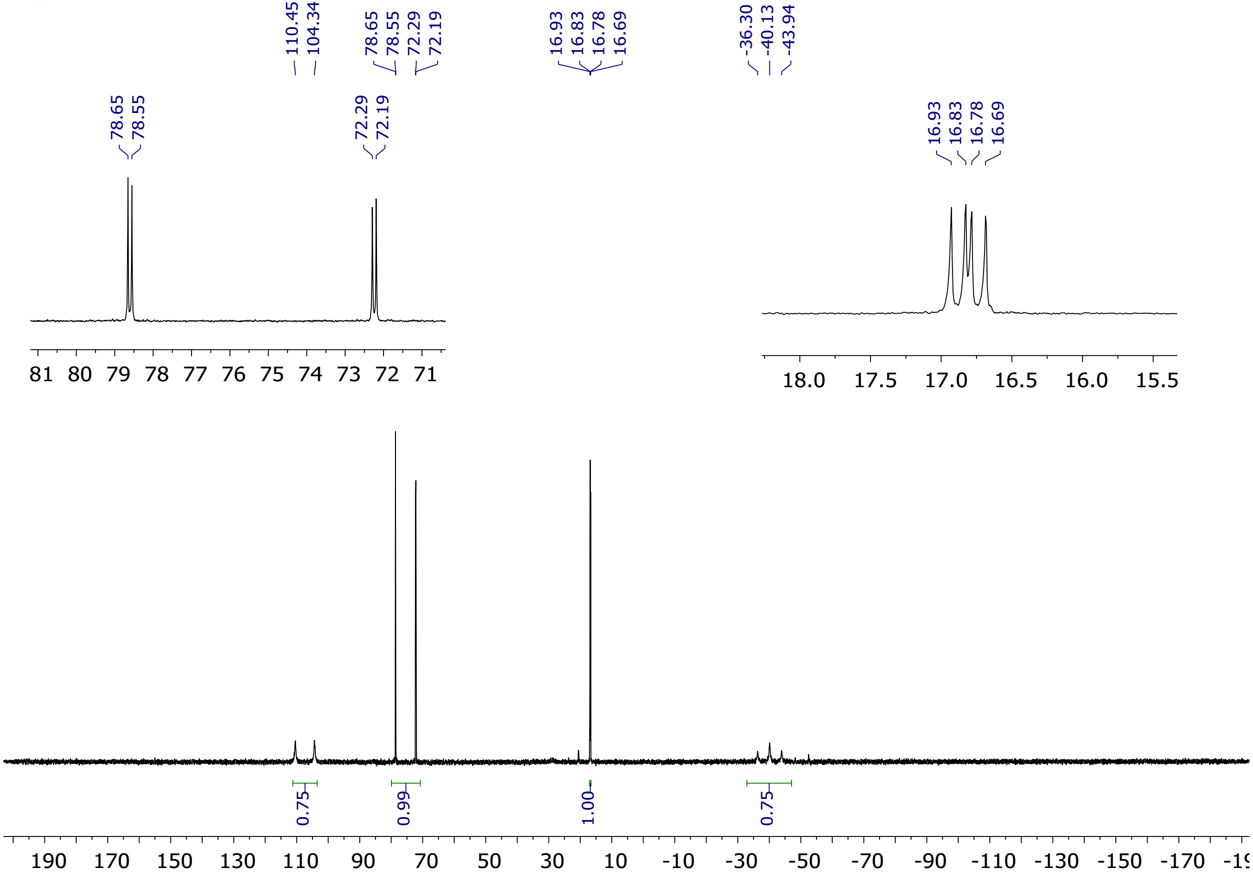
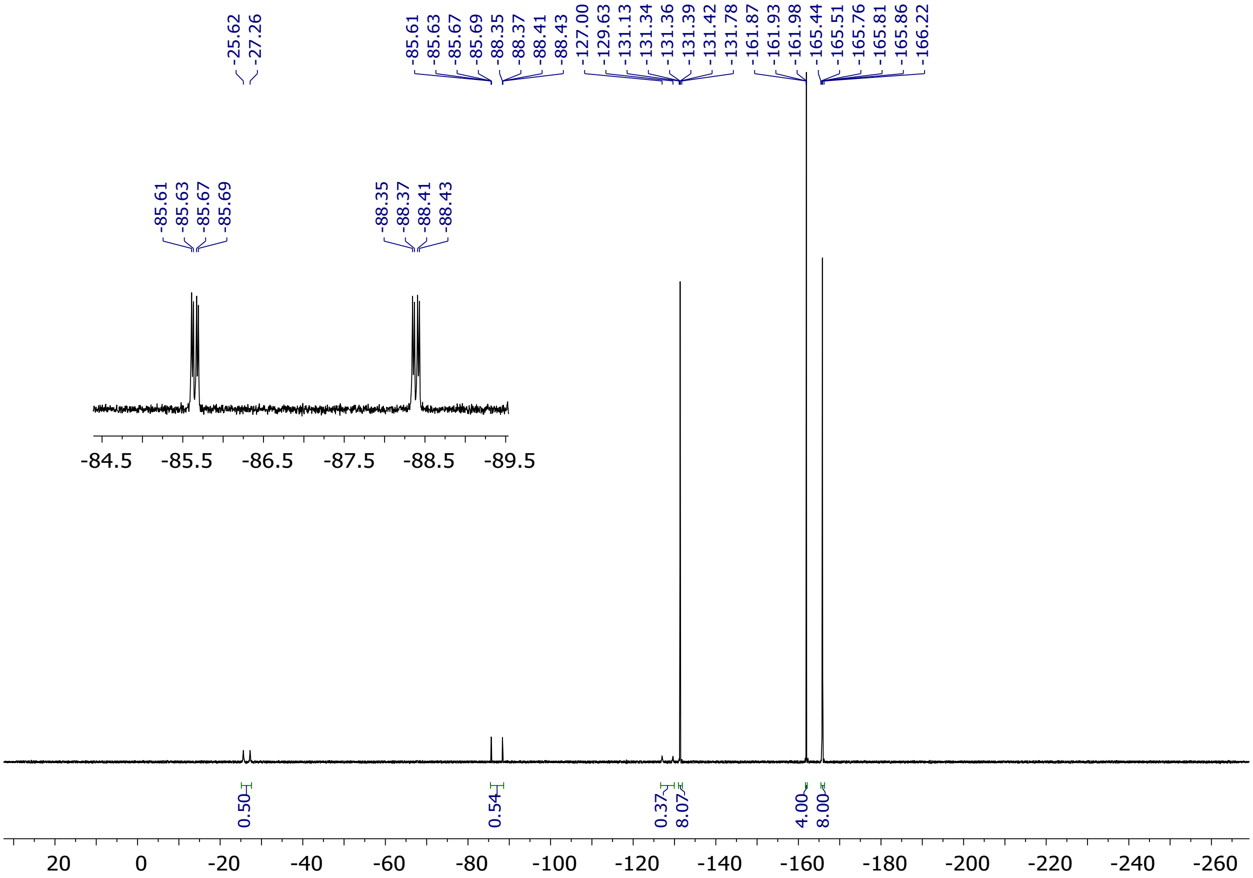
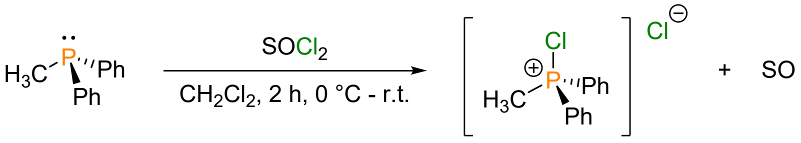


Figure S19. ^{19}F NMR spectrum of reaction of Ph_2FPCH_2 with 2a ($CDCl_3$).



Preparation of $[Ph_2PClCH_3][Cl]$ (5)



5

In a 50 mL Schlenk flask, Ph_2PCH_3 (1.59 g, 7.93 mmol, 1 equiv) was dissolved with 10 mL of DCM. After sealing the flask with a threaded Teflon stopper, it was attached to a N_2/vacuum manifold and placed under a positive pressure of dry N_2 gas. The homogeneous solution was cooled to 0 °C in an ice bath before the Teflon stopper was removed and replaced with a rubber septum. Using a gas-tight syringe, $SOCl_2$ (0.580 mL, 7.95 mmol, 1 equiv) was added dropwise. Once the rubber septum was replaced with the Teflon stopper, the solution was warmed to room temperature and stirred for 2 hours. The Schlenk tube containing the reaction mixture was brought back into the glovebox, where its contents were transferred to a scintillation vial (washing with 1 mL of DCM), and the volatiles were then removed *in vacuo*. The resulting yellow residue was triturated with 3x3 mL of pentane and dried under high vacuum to yield $[Ph_2PClCH_3][Cl]$ (**5**) as an off-white powder (1.82 g, 6.70 mmol, 85% yield). NMR spectroscopy data are in line with previously reported values.[5, 6]

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.29 – 8.09 (m, 4H), 7.83 – 7.72 (m, 2H), 7.73 – 7.62 (m, 4H), 3.80 (d, $^2J_{HP}$ = 12.9 Hz, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) δ 136.3 (d, *J* = 3.3 Hz), 132.6 (d, *J* = 13.8 Hz), 130.4 (d, *J* = 15.0 Hz), 121.1 (d, *J* = 91.5 Hz), 17.9 (d, *J* = 52.2 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298K) δ 70.5 (s, 1P).

Figure S20. ^{1}H NMR spectrum of 5 ($CDCl_3$).

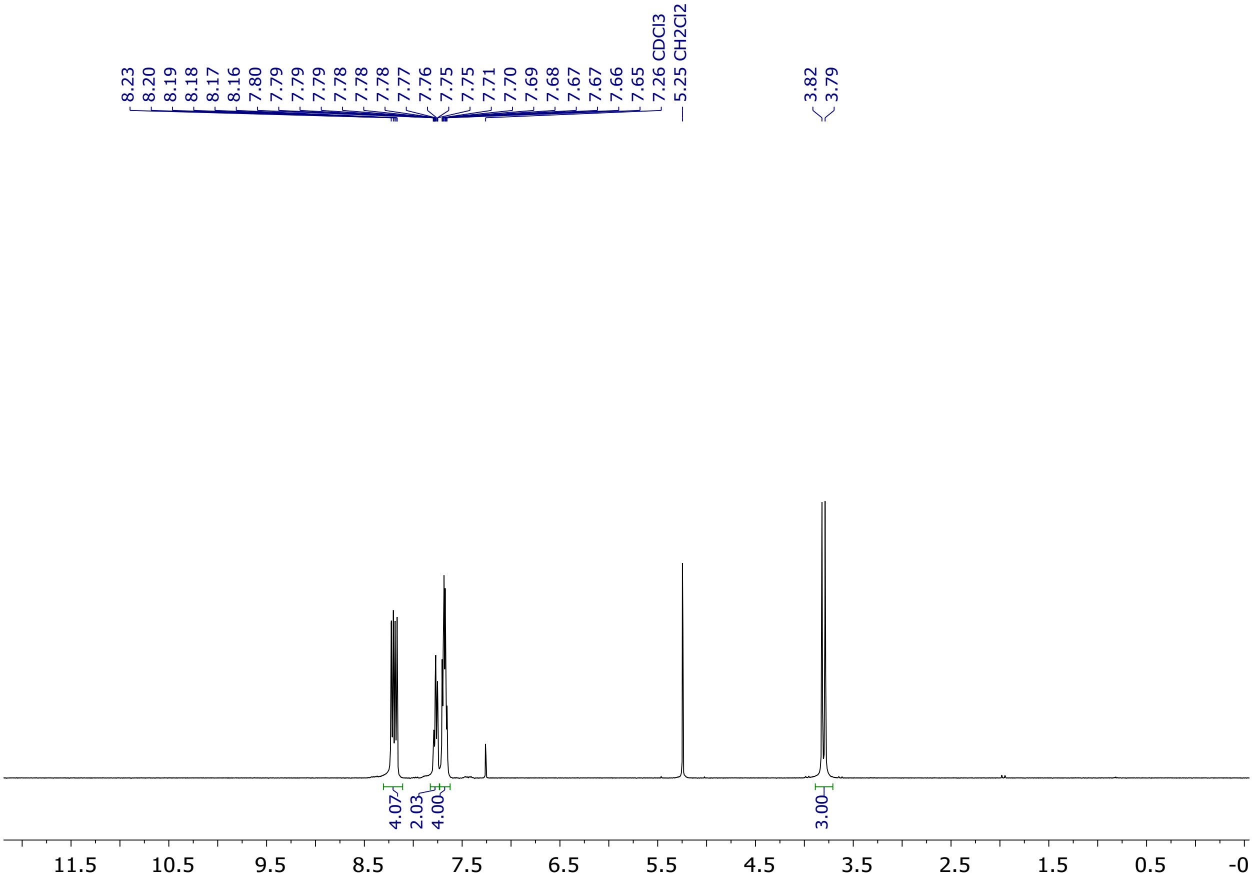


Figure S21. $^{13}C\{^1H\}$ **NMR spectrum of 5 ($CDCl_3$).**

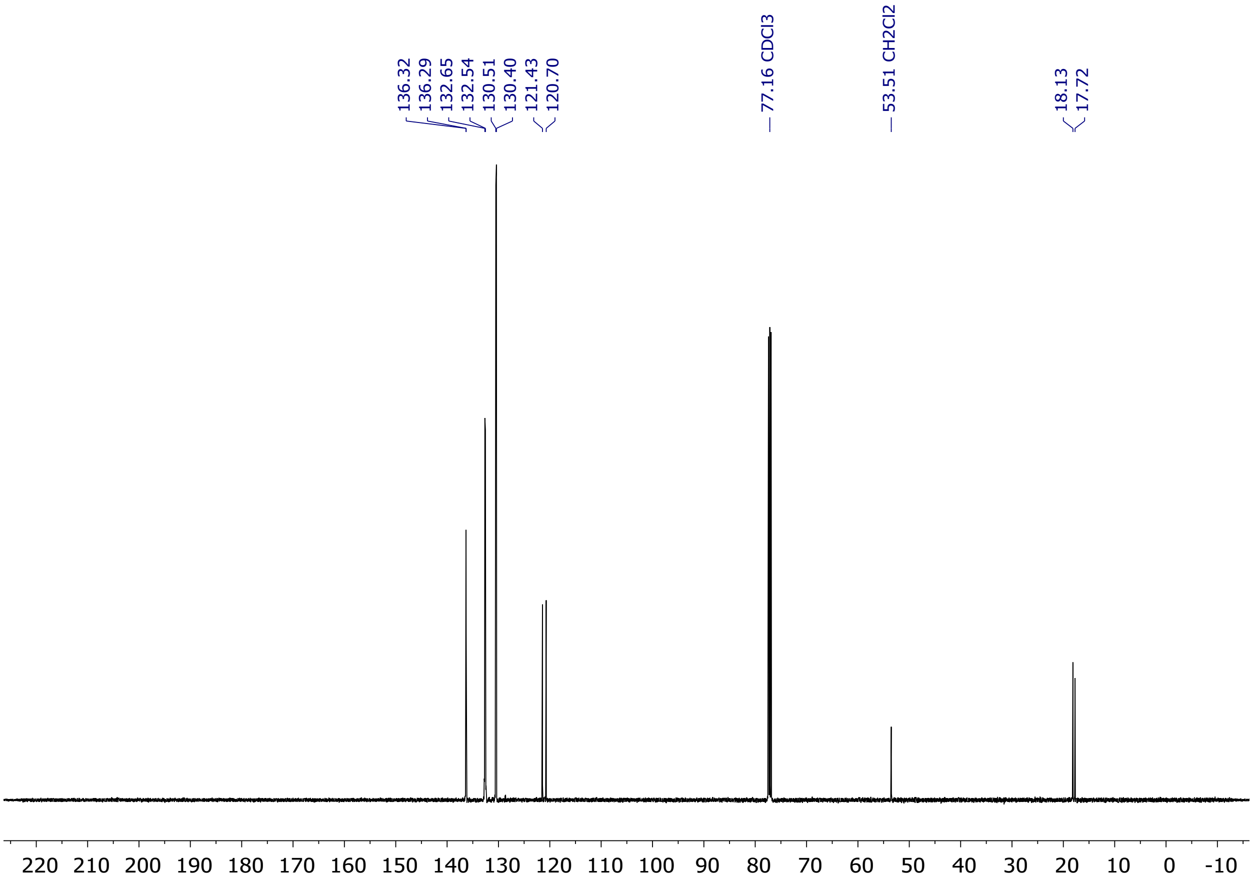
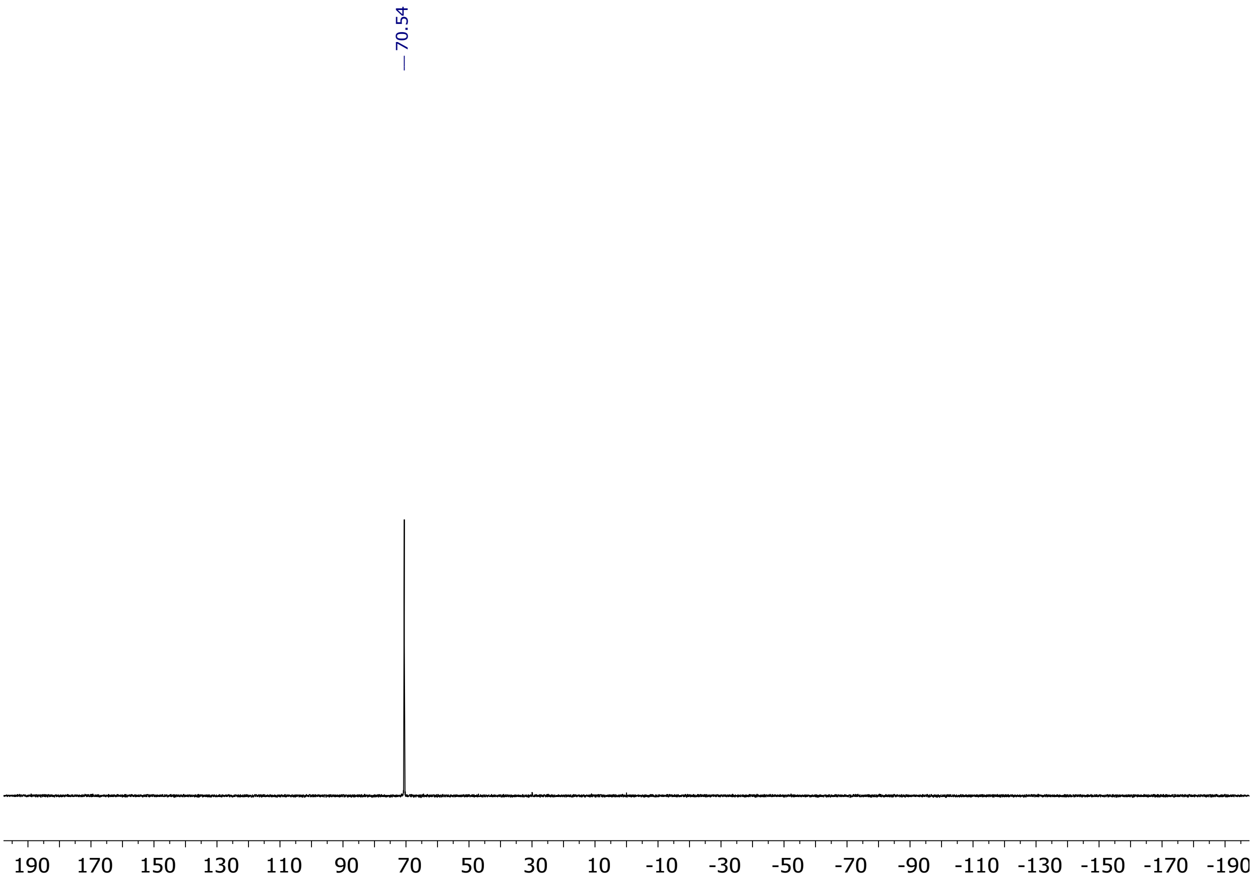
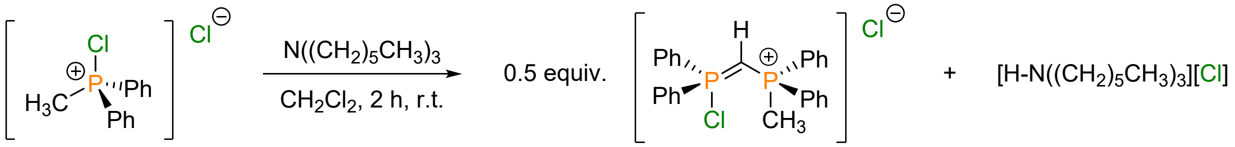


Figure S22. $^{31}P\{^1H\}$ **NMR spectrum of 5 ($CDCl_3$).**



Preparation of [$Ph_2ClPC(H)PPh_2CH_3$][Cl] (6)



6

This previously reported compound[7] was prepared in an alternative method as follows:
To a 20 mL scintillation vial containing a 3 mL DCM solution of **5** (0.240 g, 0.885 mmol, 1 equiv) was added a 2 mL DCM solution of $N((CH_2)_5CH_3)_3$ (0.241 g, 0.894 mmol, 1 equiv), leading to a homogeneous, pale-yellow solution which was stirred for 2 hours. After 2 hours, the solvent was removed *in vacuo* and the residue washed with 3x3 mL toluene and dried under high vacuum to afford **6** as a white powder (0.163 g, 0.347 mmol, 77% yield).
X-ray quality crystal was obtained by layering a DCM solution of **6** with pentane and storing at -35 °C.

^{1}**H NMR** (400 MHz, $CDCl_3$, 298 K) δ 7.90 – 7.80 (m, 4H), 7.77 – 7.69 (m, 4H), 7.62 – 7.52 (m, 4H), 7.52 – 7.41 (m, 8H), 2.87 – 2.80 (m, 1H), 2.55 (d, $^2J_{HP}$ = 13.3 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) δ 134.1 (d, *J* = 3.4 Hz), 133.6 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 11.0 Hz), 132.2 (d, *J* = 11.8 Hz), 129.7 (d, *J* = 14.8 Hz), 129.6 (d, *J* = 12.8 Hz), 127.6 (br d, *J* = 113.3 Hz), 124.8 (br d, *J* = 90.6 Hz), 18.7 – 16.1 (m), 14.9 (dd, *J* = 63.7, 4.9 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298K) δ 59.9 (d, $^{2}J_{PP}$ = 8 Hz, 1P), 17.4 (d, $^{2}J_{PP}$ = 8 Hz, 1P).

Figure S23. ^{1}H NMR spectrum of 6 ($CDCl_3$).

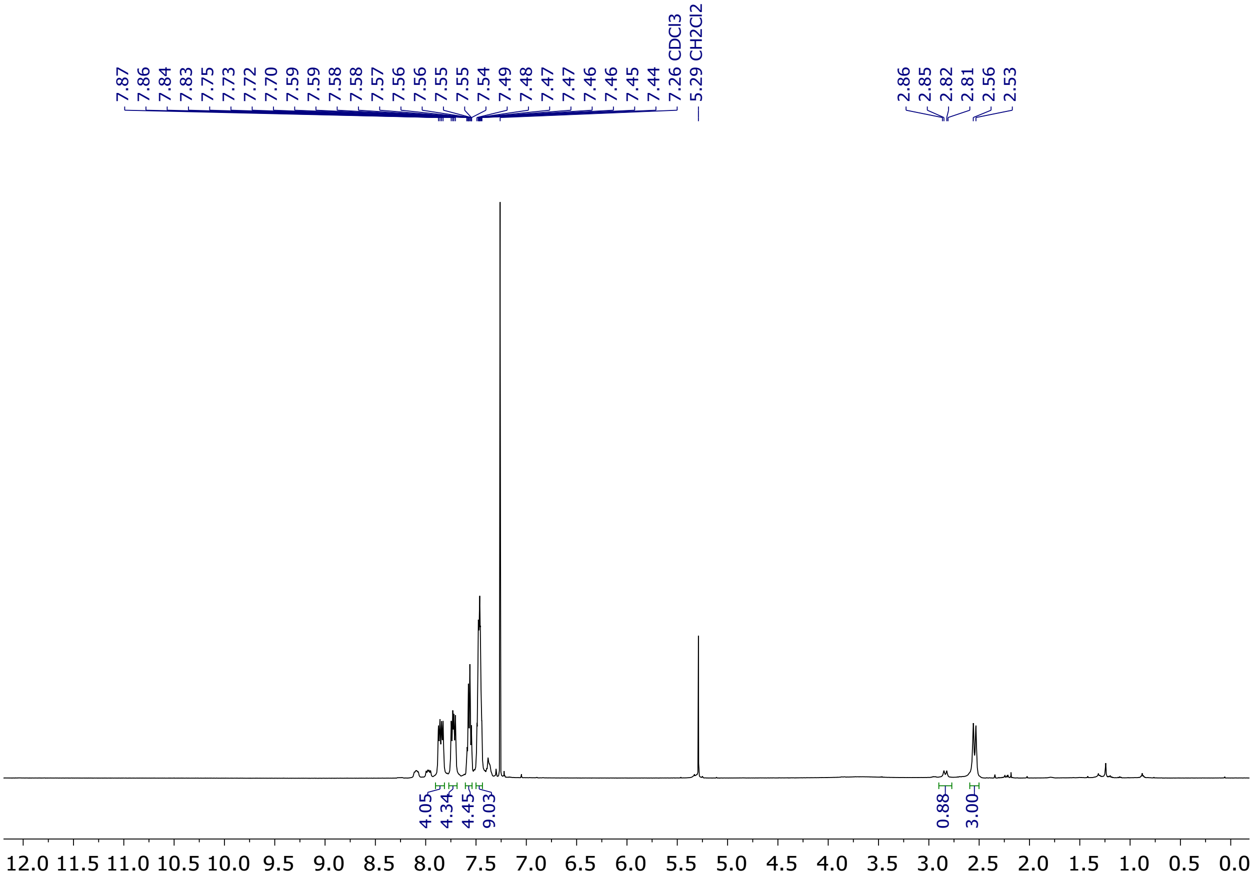


Figure S24. $^{13}C\{^{1}H\}$ **NMR spectrum of 6 ($CDCl_3$).**

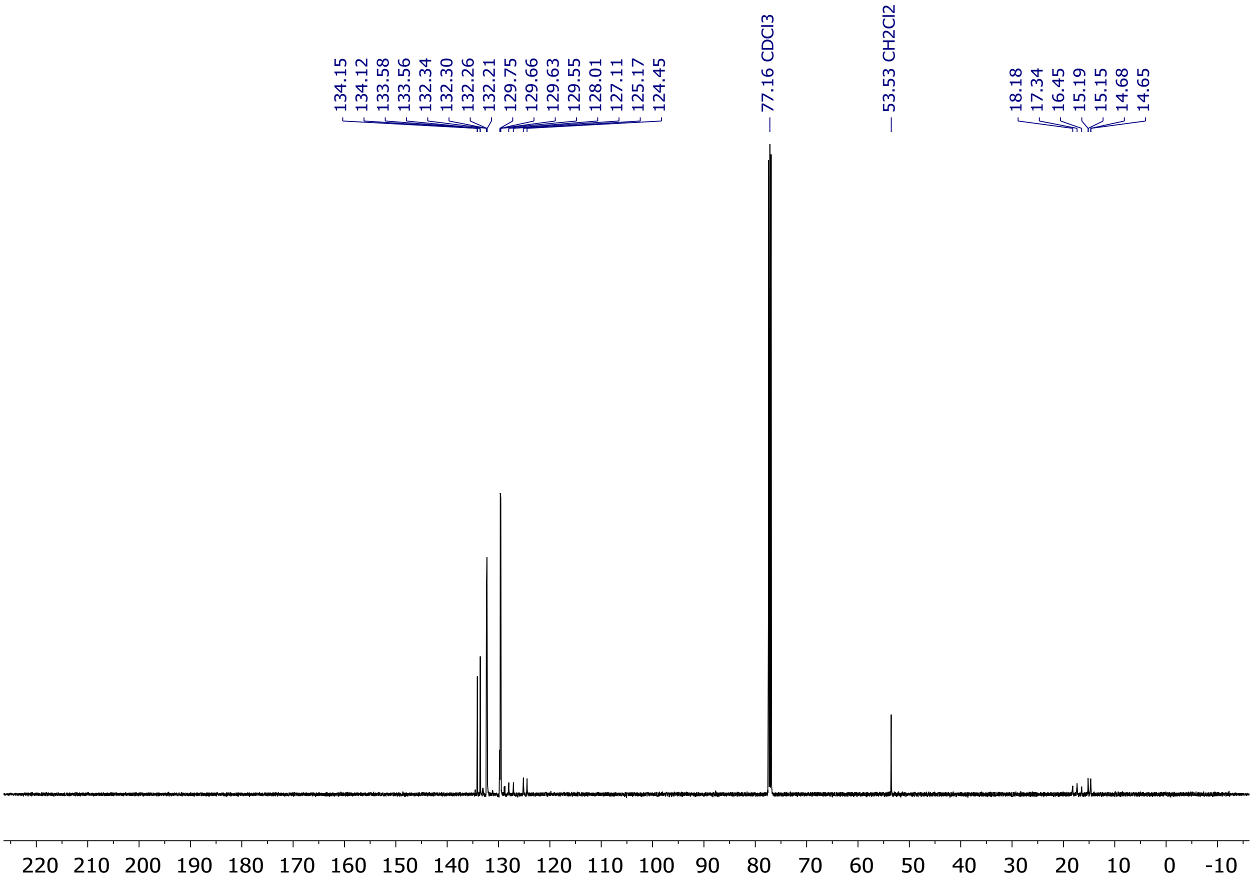
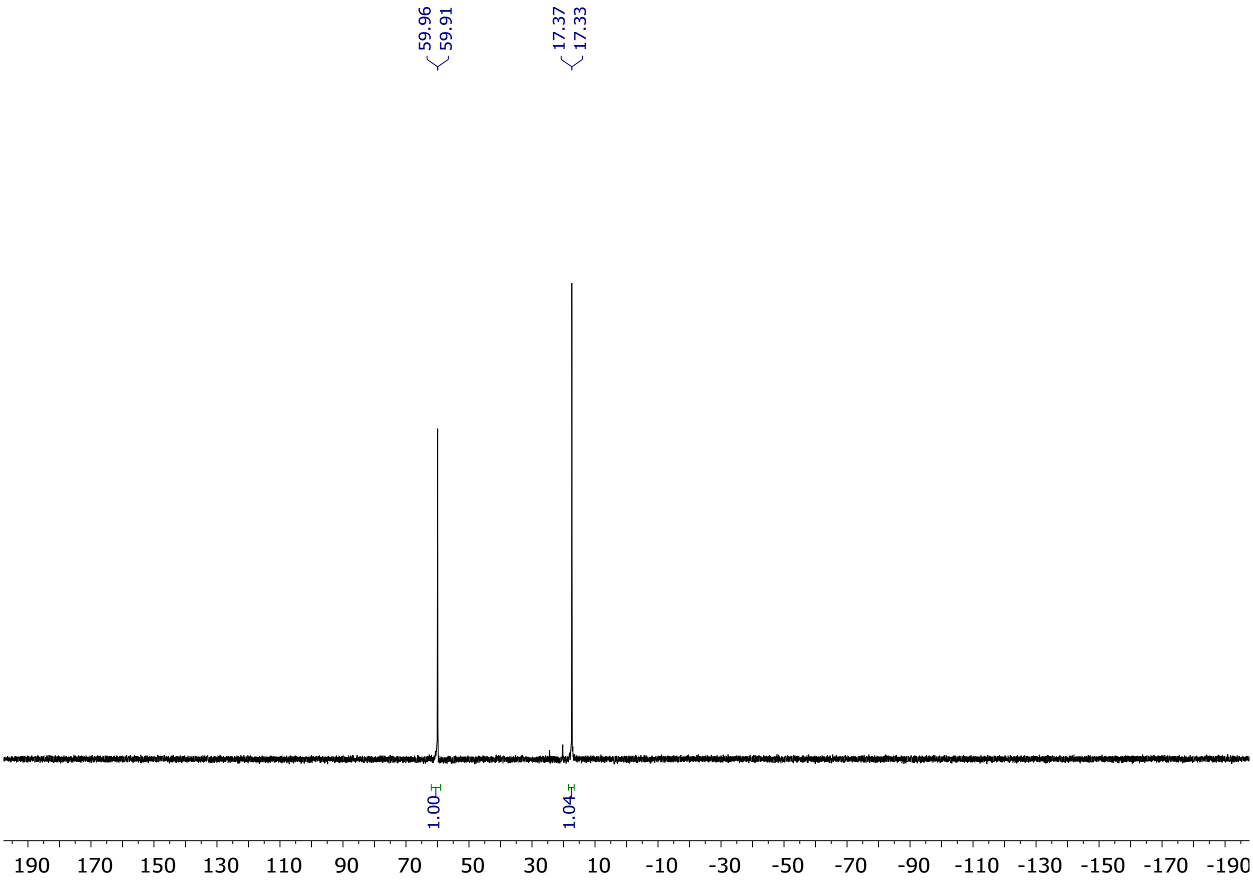
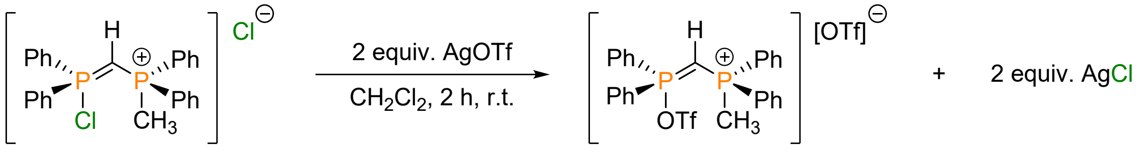


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of 6 ($CDCl_3$).



Preparation of $[Ph_2(OTf)PC(H)PPh_2CH_3][OTf]$ (7)



7

To a 20 mL scintillation vial containing a 2 mL DCM slurry of AgOTf (57.6 mg, 0.220 mmol, 2 equiv) was added a 2 mL DCM solution of **6** (56.5 mg, 0.110 mmol, 1 equiv). The white cloudy mixture was stirred in the dark for 2 hours, then filtered through Celite and the solvent removed *in vacuo* to yield **7** as a colorless residue (40.1 mg, 0.0580 mmol, 52% yield).

^{1}H NMR (500 MHz, C_6D_5Br, 298 K) δ 7.66 – 7.56 (m, 4H), 7.55 – 7.45 (m, 4H), 7.32 – 7.24 (m, 4H), 7.24 – 7.13 (m, 8H), 3.82 (dd, $^{2}J_{HP}$ = 9.0 Hz, $^{2}J_{HP}$ = 7.1 Hz, 1H), 2.19 (d, $^{2}J_{HP}$ = 13.5 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_5Br, 298 K) δ 134.7 (d, J = 3.3 Hz), 133.4 (d, J = 3.1 Hz), 132.1 (d, J = 11.8 Hz), 131.9 (d, J = 11.2 Hz), 129.8 (d, J = 15.0 Hz), 129.4 (d, J = 12.8 Hz), 123.7 (dd, J = 91.9, 4.3 Hz), 123.6 (dd, J = 100.8, 4.3 Hz), 19.6 (dd, J = 133.4, 108.2 Hz), 13.7 (dd, J = 63.2, 4.2 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_5Br, 298K) δ 70.2 (d, $^{2}J_{PP}$ = 14 Hz, 1P), 17.6 (d, $^{2}J_{PP}$ = 14 Hz, 1P).

^{19}F NMR (376 MHz, C_6D_5Br, 298 K) δ -75.4 (s), -77.0 (s).

Figure S26. ^{1}H NMR spectrum of 7 (C_6D_5Br).

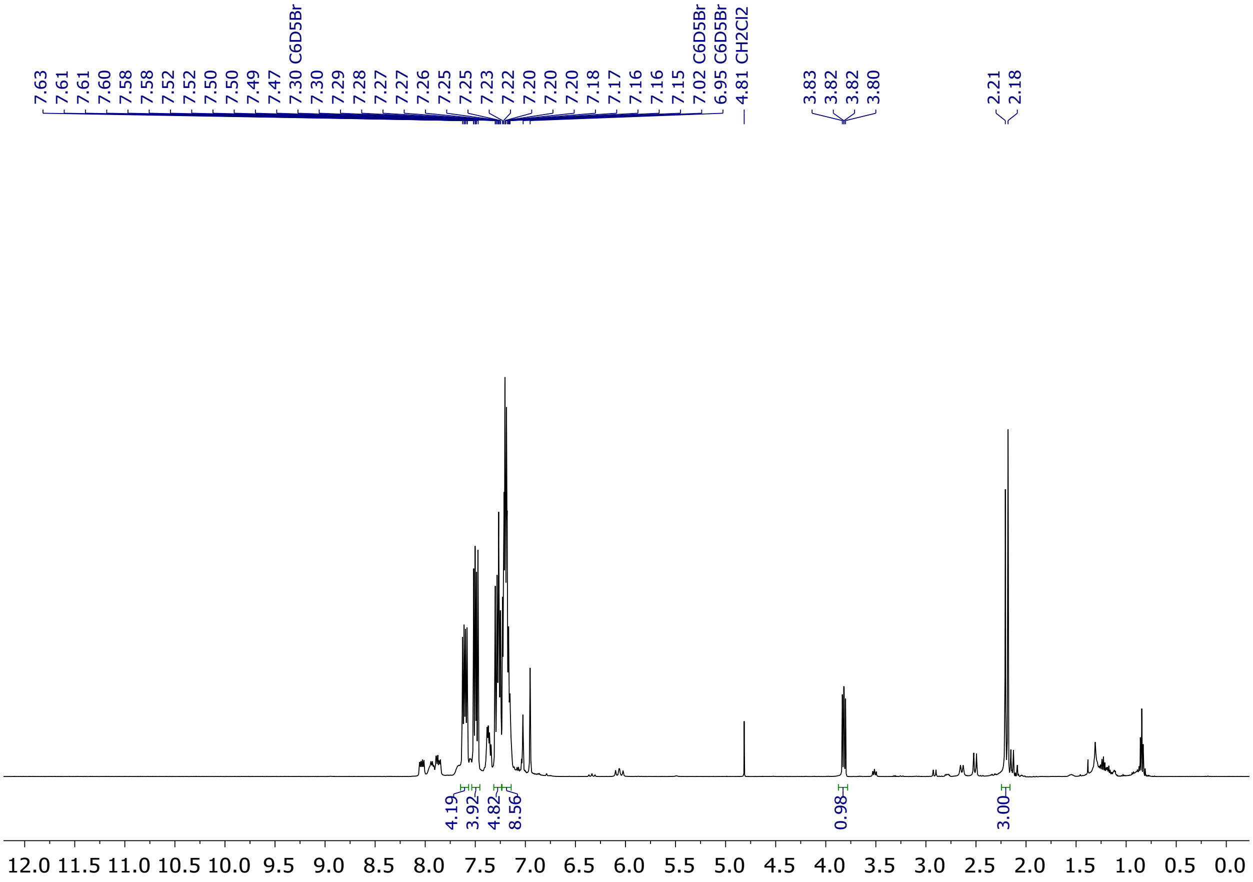


Figure S27. $^{13}C\{^1H\}$ **NMR spectrum of 7 (C_6D_5Br).**

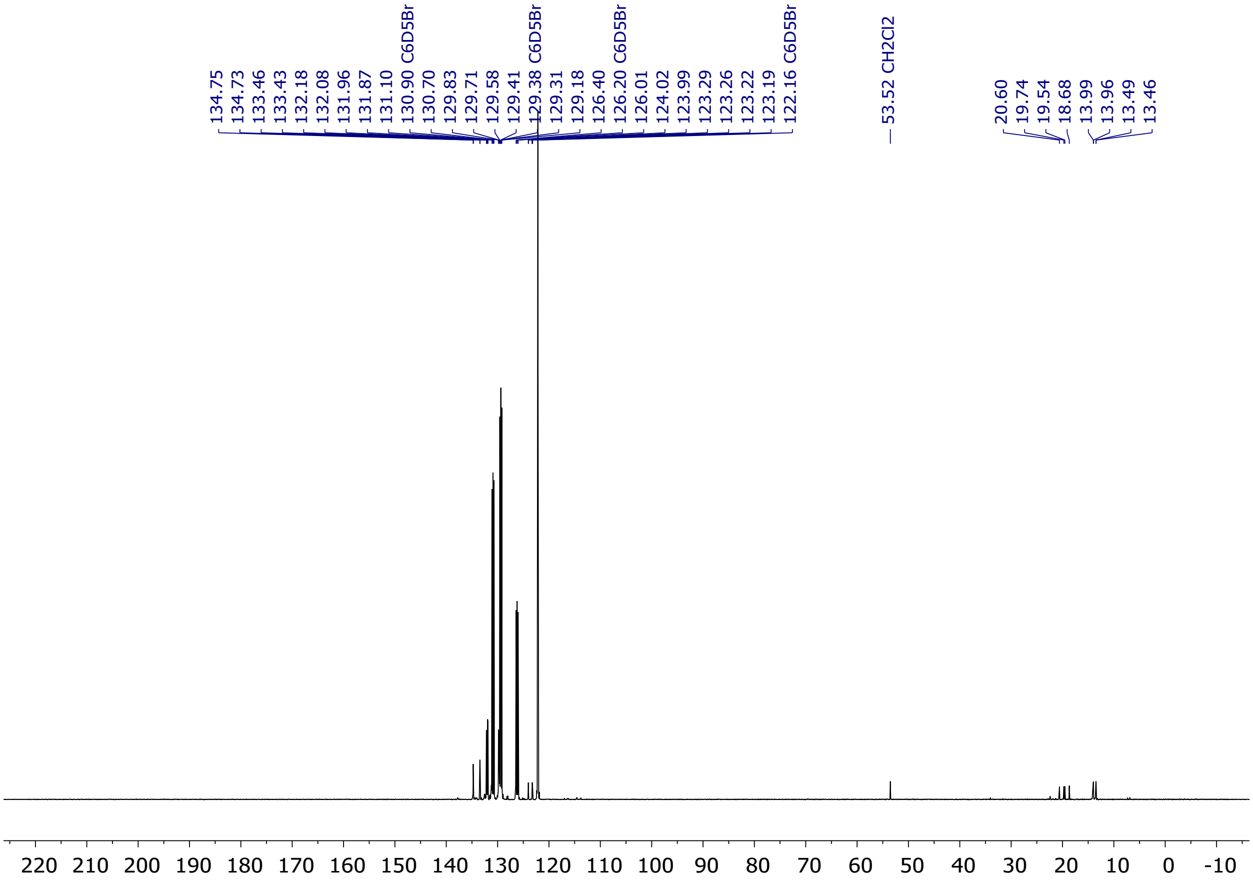


Figure S28. $^{31}P\{^{1}H\}$ **NMR spectrum of 7** (C_6D_5Br).

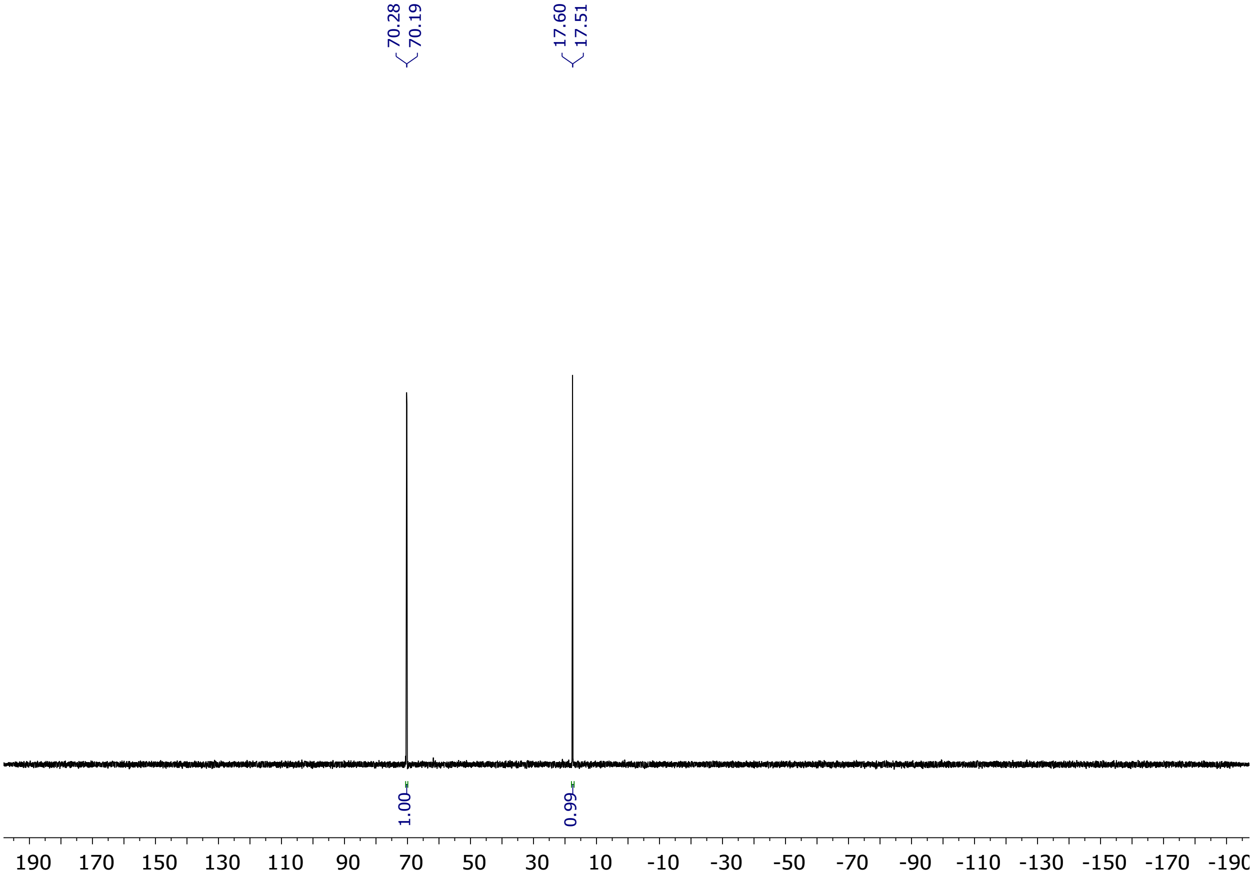
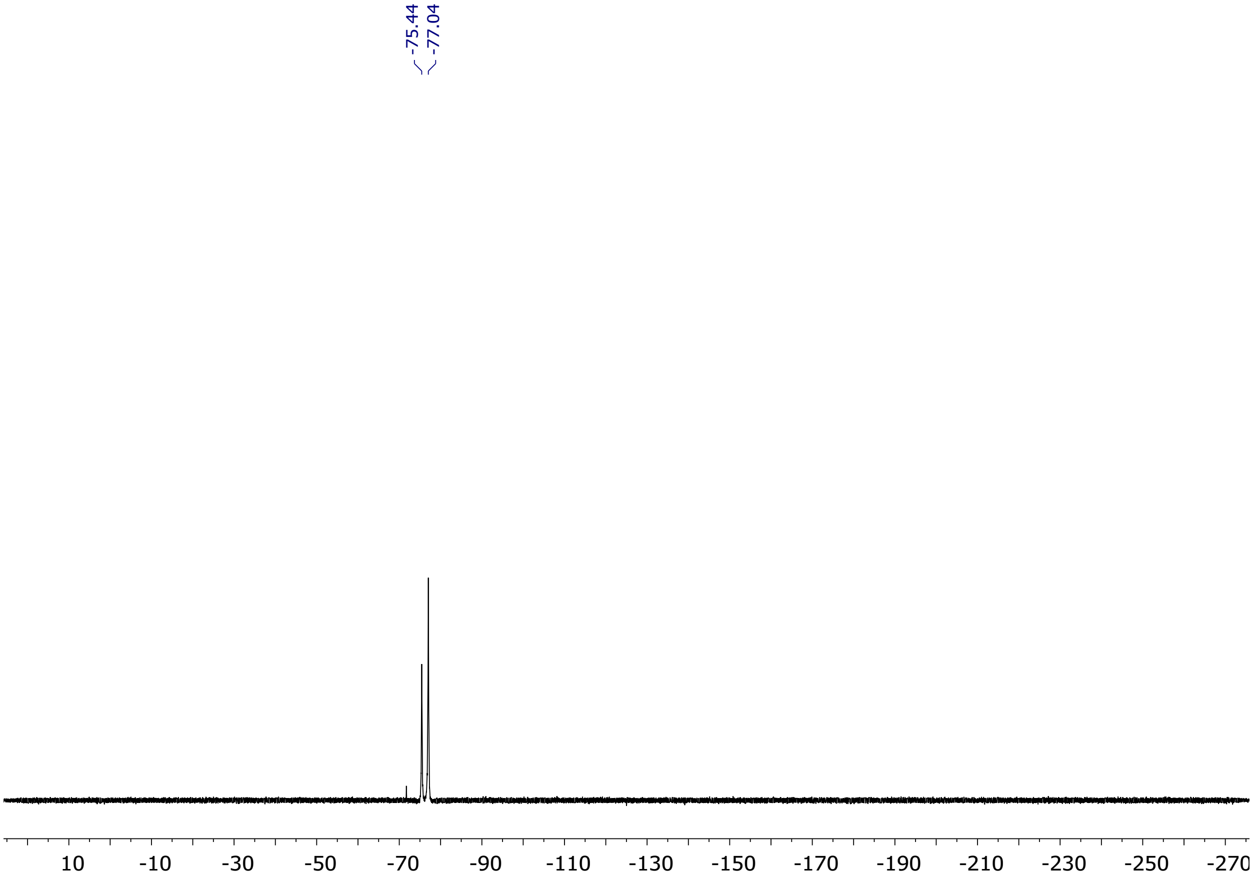
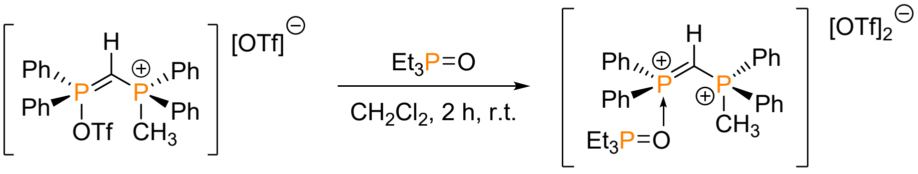


Figure S29. ^{19}F **NMR spectrum of 7 (C_6D_5Br).**





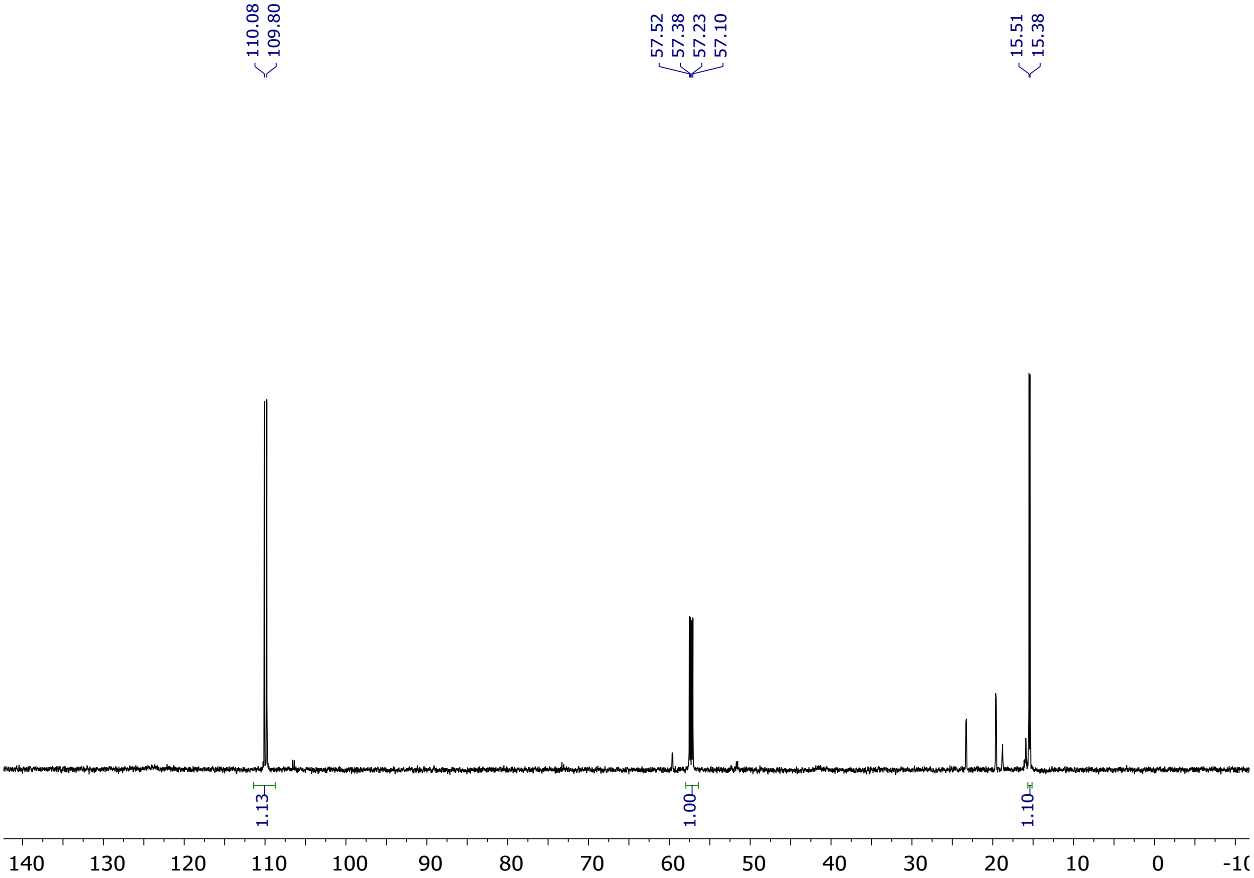
8

Reaction of Et_3PO with 7 (Gutmann-Beckett Lewis Acidity Test)

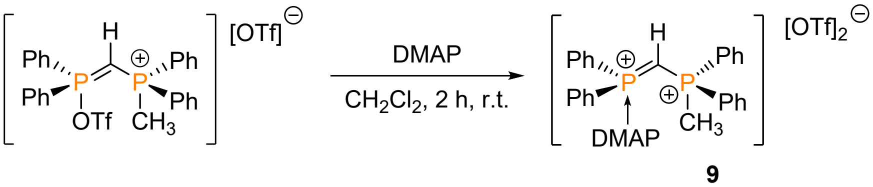
Compound **7** (33.0 mg, 0.0474 mmol, 1 equiv) was weighed into a 5 mL vial. In a separate 5 mL vial, Et_3PO (6.4 mg, 0.048 mmol, 1 equiv) was dissolved in 1 mL of DCM and added to **7**. The solution was stirred for 1 h and transferred to an NMR tube via pipette. $^{31}P\{^1H\}$ NMR analysis indicated the adduct formation of Et_3PO with **7** to form **8**.

$^{31}P\{^1H\}$ NMR (162 MHz, CH_2Cl_2, 298K) δ 109.9 (d, $^2J_{PP}$ = 46 Hz, 1P, Et_3*P*-O-P), 57.3 (dd, $^2J_{PP}$ = 46 Hz, $^2J_{PP}$ = 22 Hz, 1P, Et_3P-O-*P*), 15.4 (d, $^2J_{PP}$ = 22 Hz, 1P, *P*Ph_2CH_3).

Figure S30. $^{31}P\{^1H\}$ **NMR spectrum of reaction of** Et_3PO **with 7 (**CH_2Cl_2**).**



Preparation of $[Ph_2(DMAP)PC(H)PPh_2CH_3][OTf]_2$ (9)



9

To a 20 mL scintillation vial containing a 3 mL DCM solution of **7** (49.3 mg, 0.0708 mmol, 1 equiv) was added a 2 mL DCM solution of DMAP (8.7 mg, 0.071 mmol, 1 equiv). The resultant mixture was stirred for 2 hours before the solvent was removed *in vacuo*. The product residue was triturated with 3x3 mL of pentane and dried under high vacuum to yield **9** as a white powder (41.7 mg, 0.0509 mmol, 72% yield).

^{1}**H NMR** (400 MHz, $CDCl_3$, 298 K) δ 8.49 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HP}$ = 8.0 Hz, 2H), 7.69 – 7.40 (m, 20H), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 3.34 (s, 6H), 2.97 (dd, $^2J_{HP}$ = 9.5 Hz, $^2J_{HP}$ = 6.4 Hz, 1H), 2.35 (d, $^2J_{HP}$ = 13.1 Hz, 3H).

^{13}**C{**^{1}**H} NMR** (126 MHz, $CDCl_3$, 298 K) δ 157.9 (d, J = 1.2 Hz), 140.2 (d, J = 6.5 Hz), 135.5 (d, J = 3.2 Hz), 133.8 (d, J = 3.0 Hz), 132.7 (d, J = 11.4 Hz), 131.9 (d, J = 11.0 Hz), 130.6 (d, J = 14.2

Hz), 130.0 (d, J = 12.8 Hz), 124.7 (dd, J = 92.2, 3.9 Hz), 120.9 (q, J = 321.6 Hz), 120.5 (dd, J = 112.4, 3.6 Hz), 109.8 (d, J = 5.7 Hz), 41.0, 15.5 (d, J = 63.7, 2.8 Hz), 8.43 (dd, J = 138.4, 114.0 Hz).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K) δ 51.5 (d, $^{2}J_{PP}$ = 23 Hz, 1P), 18.0 (d, $^{2}J_{PP}$ = 23 Hz, 1P).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ -78.3 (s).

Figure S31. ^{1}H NMR spectrum of 9 (CDCl$_3$).

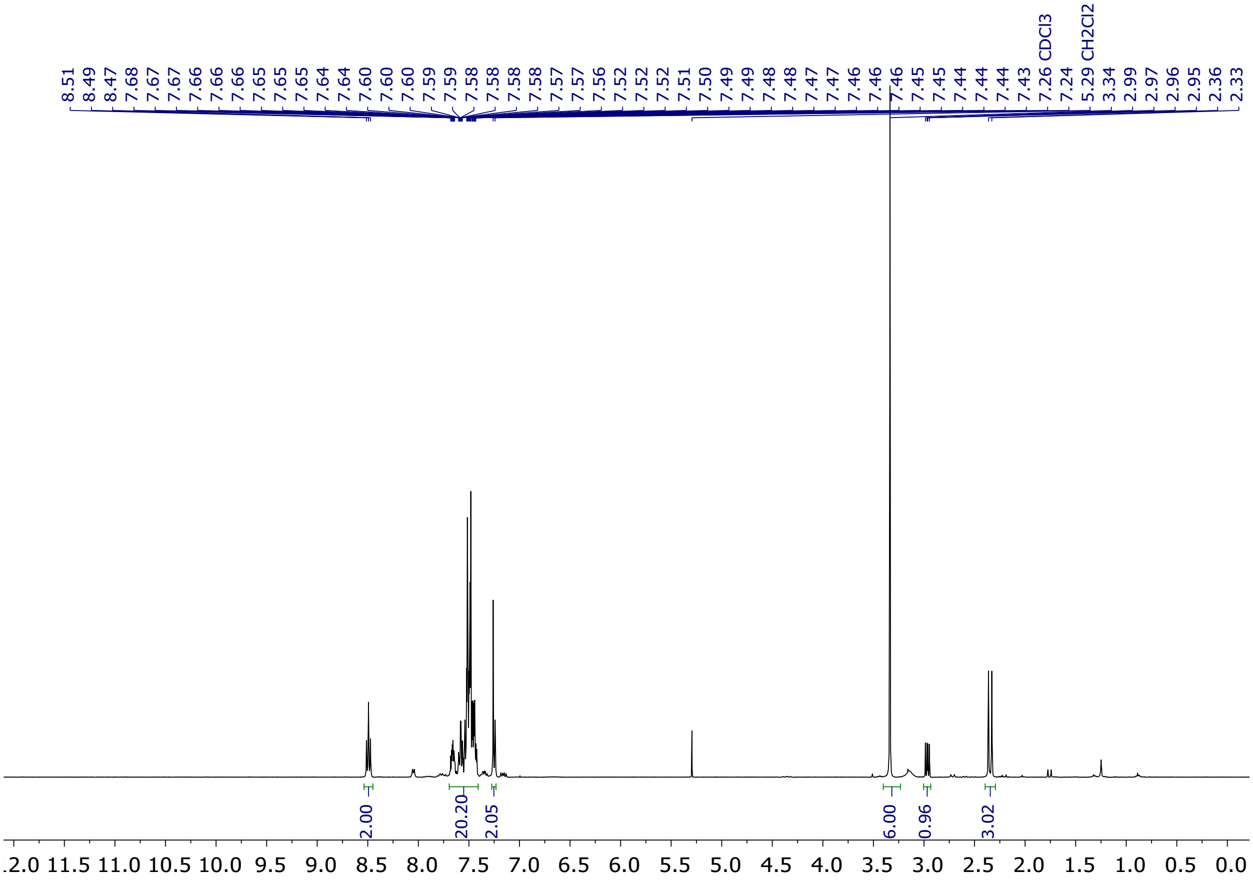


Figure S32. $^{13}C\{^1H\}$ **NMR spectrum of 9 ($CDCl_3$).**

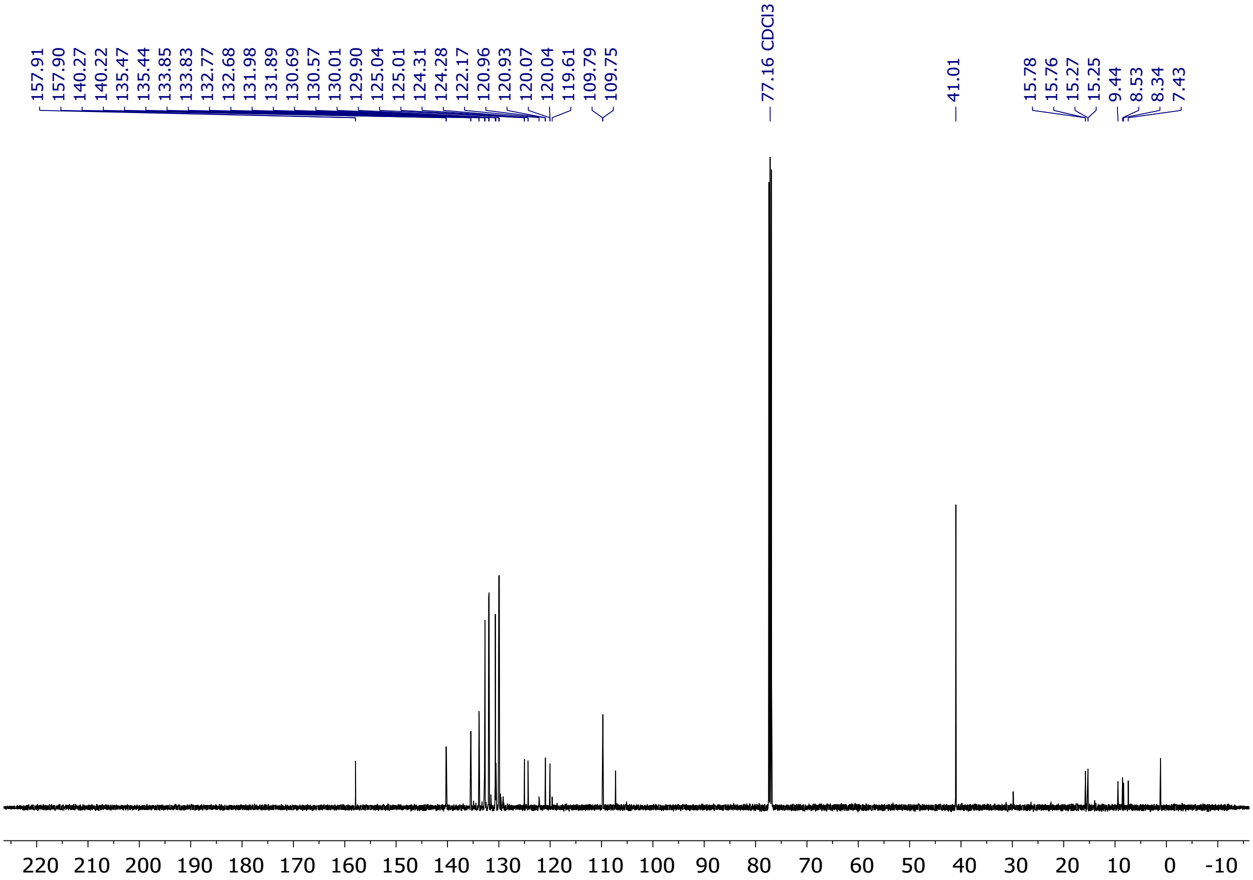


Figure S33. $^{31}P\{^1H\}$ **NMR spectrum of 9 ($CDCl_3$).**

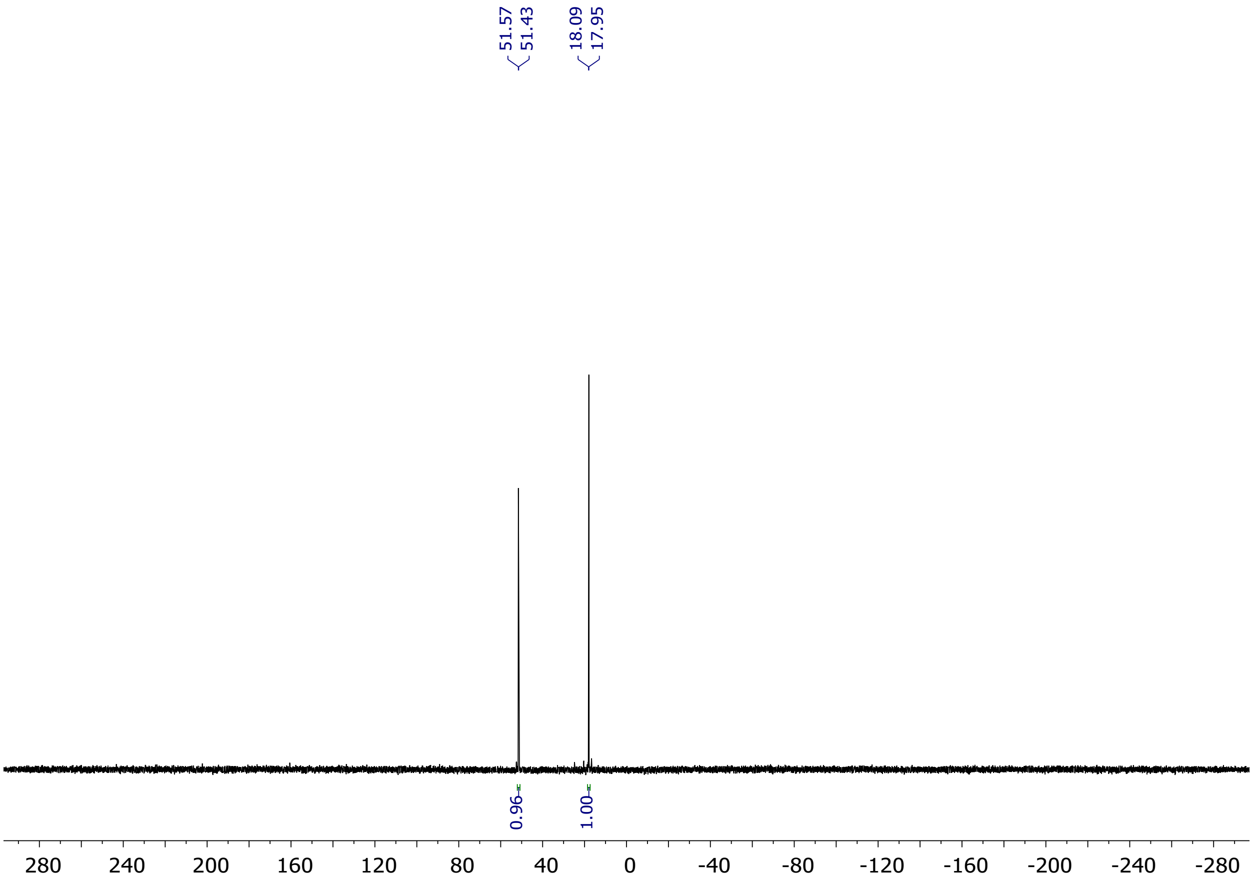
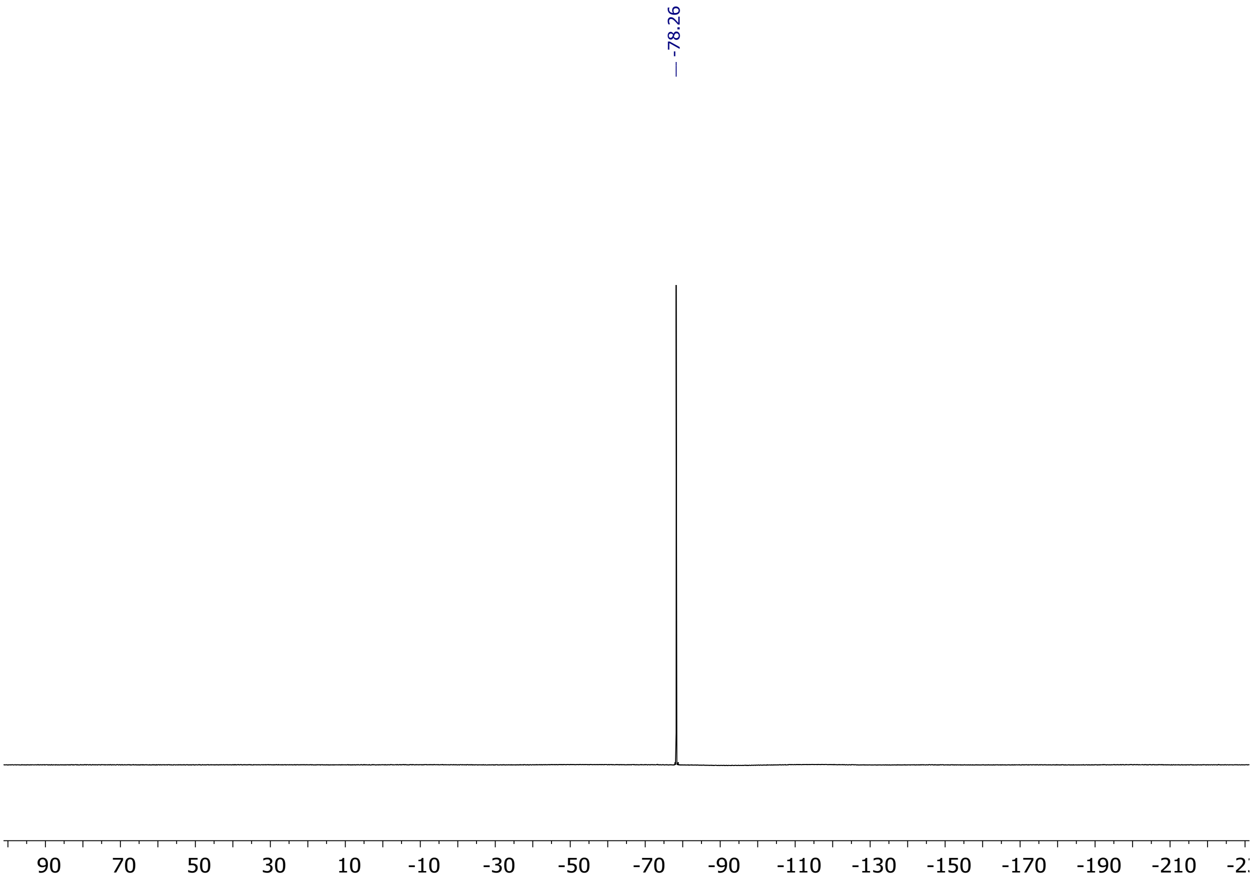
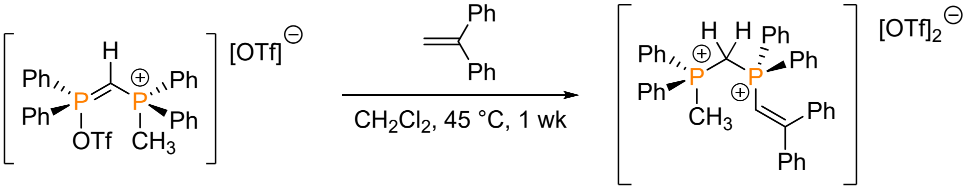


Figure S34. ^{19}F NMR spectrum of 9 ($CDCl_3$).





10

Reaction of 7 with 1,1-Diphenylethylene (10)

To a 3 mL DCM solution of **7** (40.0 mg, 0.0574 mmol, 1 equiv.) was added 10.1 µL of 1,1-diphenylethylene via syringe and the resultant mixture was transferred to a Schlenk tube. The reaction was heated at 45 °C for 1 week, then brought into the glovebox and filtered over Celite to yield a colorless residue. The product was triturated with 3x3ml pentane and dried under high vacuum to yield **10** as a white powder (38.2 mg, 0.0436 mmol, 76% yield).
X-ray quality crystal was obtained by layering a DCM solution of **10** with pentane and storing at -35 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) 7.92 – 7.62 (m, 12H), 7.61 – 7.42 (m, 8H), 7.40 – 7.30 (m, 4H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.88 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 6.66 – 6.46 (m, 3H), 5.23 (t, $^2J_{HP}$ = 16.0 Hz, 2H), 2.65 (d, $^2J_{HP}$ = 13.8 Hz, 1H), 2.15 (d, $^2J_{HP}$ = 13.5 Hz, 3H).
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) 172.0 (d, J = 3.8 Hz), 138.8 (d, J = 17.8 Hz), 136.2 (d, J = 7.6 Hz), 135.7 (d, J = 3.3 Hz), 135.5 (d, J = 3.1 Hz), 133.8 (d, J = 11.4 Hz), 132.9 (d, J = 11.2 Hz), 132.7 (d, J = 11.0 Hz), 132.3, 130.7 (d, J = 15.3 Hz), 130.6 (d, J = 15.5 Hz), 130.3 (d, J = 13.3 Hz), 129.9, 129.6 (d, J = 13.6 Hz), 129.4, 128.8 (d, J = 34.9 Hz), 128.7, 128.4 (d, J = 13.5 Hz), 127.8, 117.6 (dd, J = 88.0, 2.8 Hz), 117.1 (dd, J = 88.9, 2.3 Hz), 101.9 (d, J = 91.9 Hz), 21.6 – 20.2 (m), 8.33 (d, J = 55.7 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K) δ 19.7 (d, $^2J_{PP}$ = 17 Hz, 1P), 11.0 (d, $^2J_{PP}$ = 17 Hz, 1P)

^{19}F NMR (376 MHz, $CDCl_3$, 298 K) δ -78.3 (s).

Figure S35. ^{1}H NMR spectrum of **10** ($CDCl_3$).

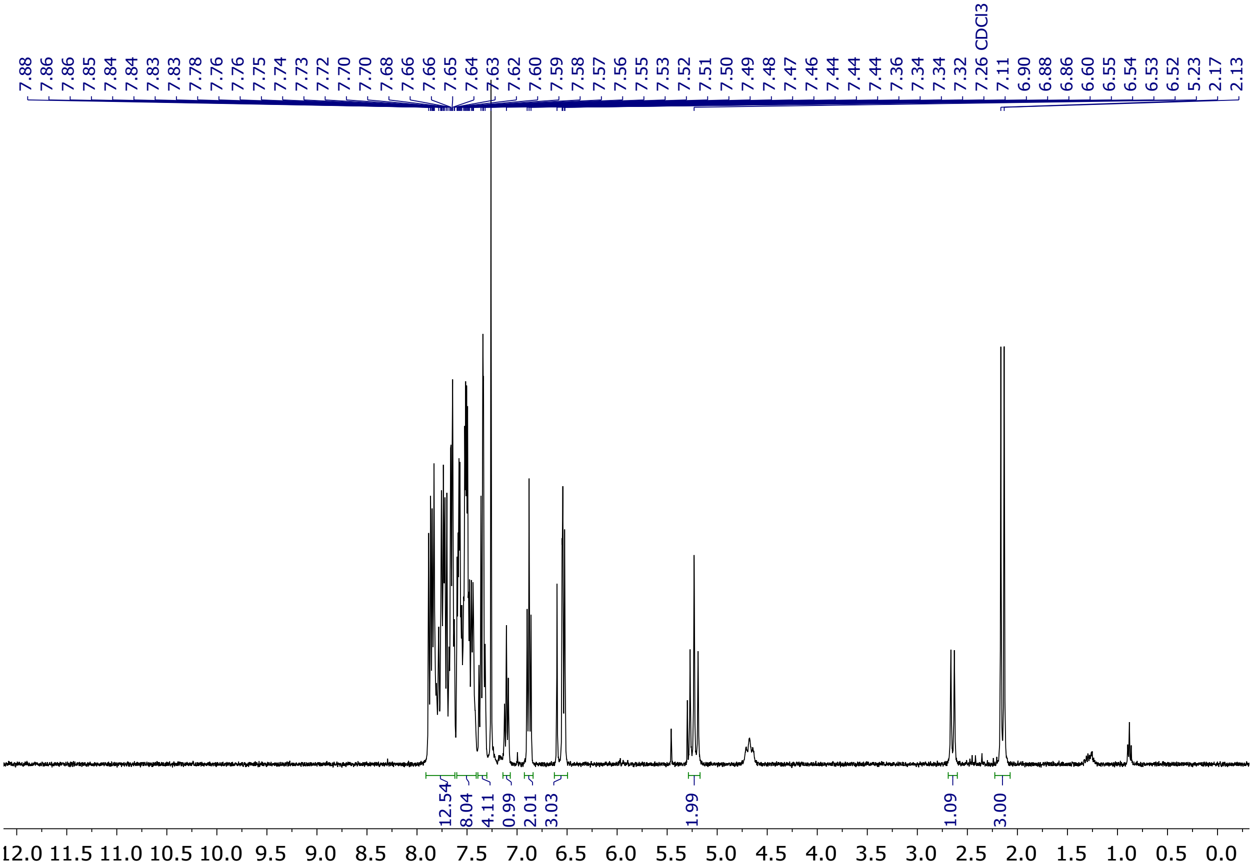


Figure S36. $^{13}C\{^1H\}$ **NMR spectrum of 10 (CDCl$_3$).**

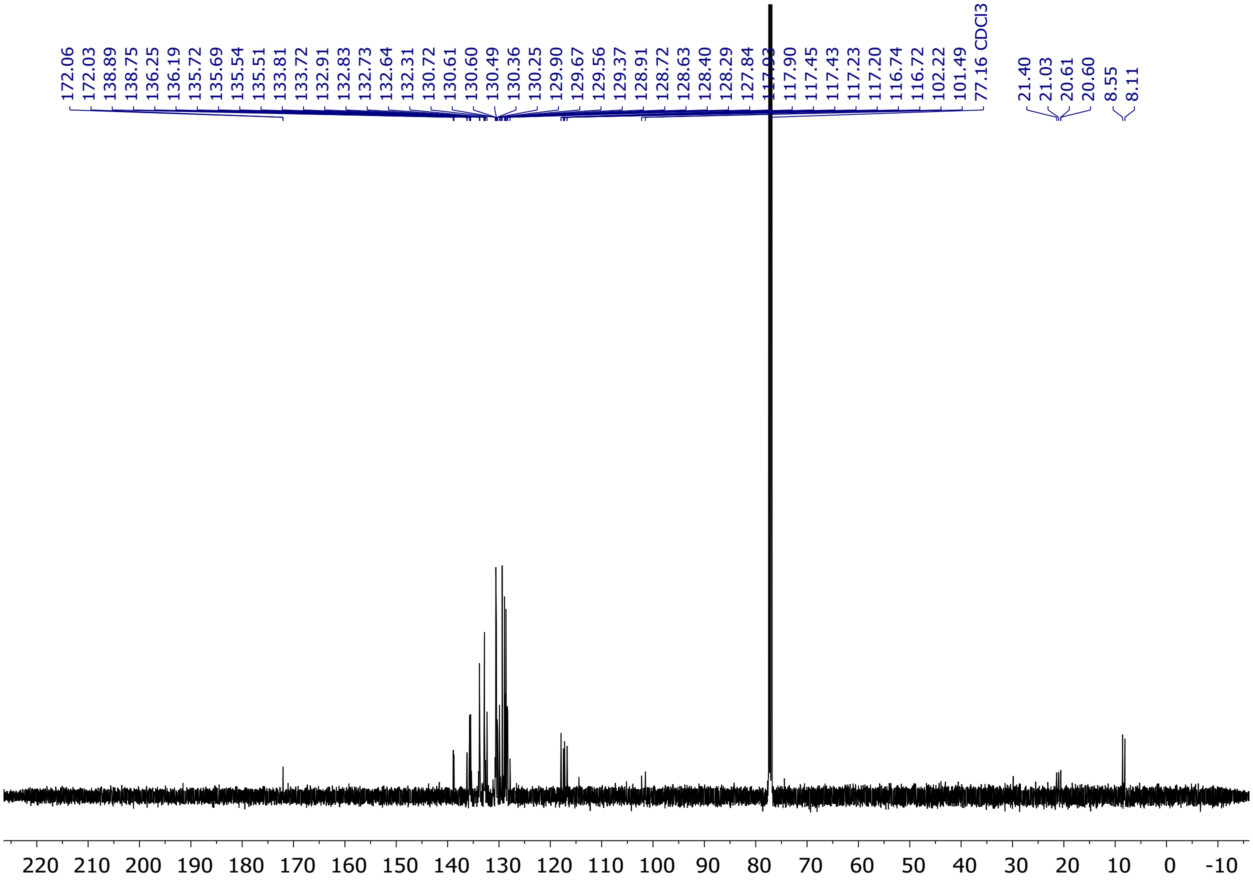


Figure S37. $^{31}P\{^{1}H\}$ **NMR spectrum of 10 ($CDCl_3$).**

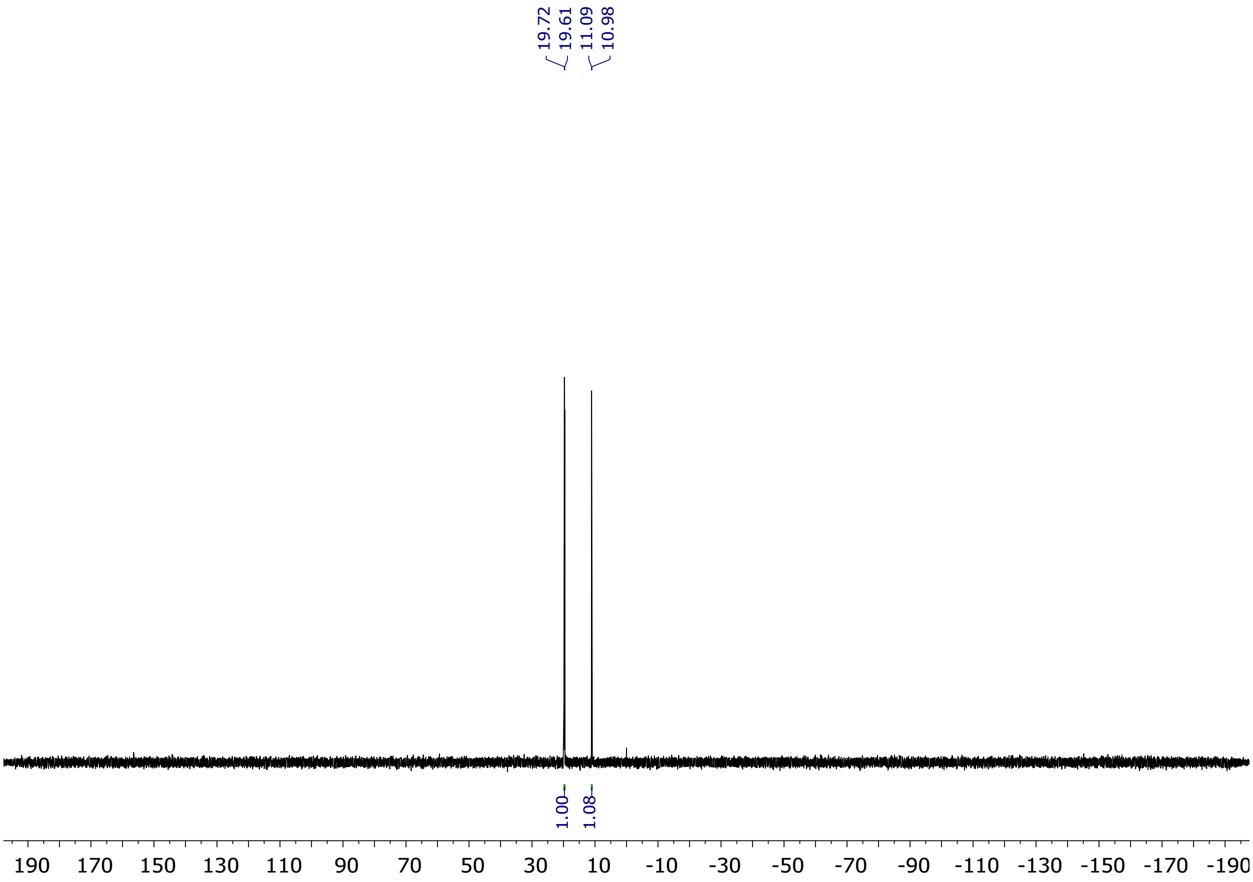
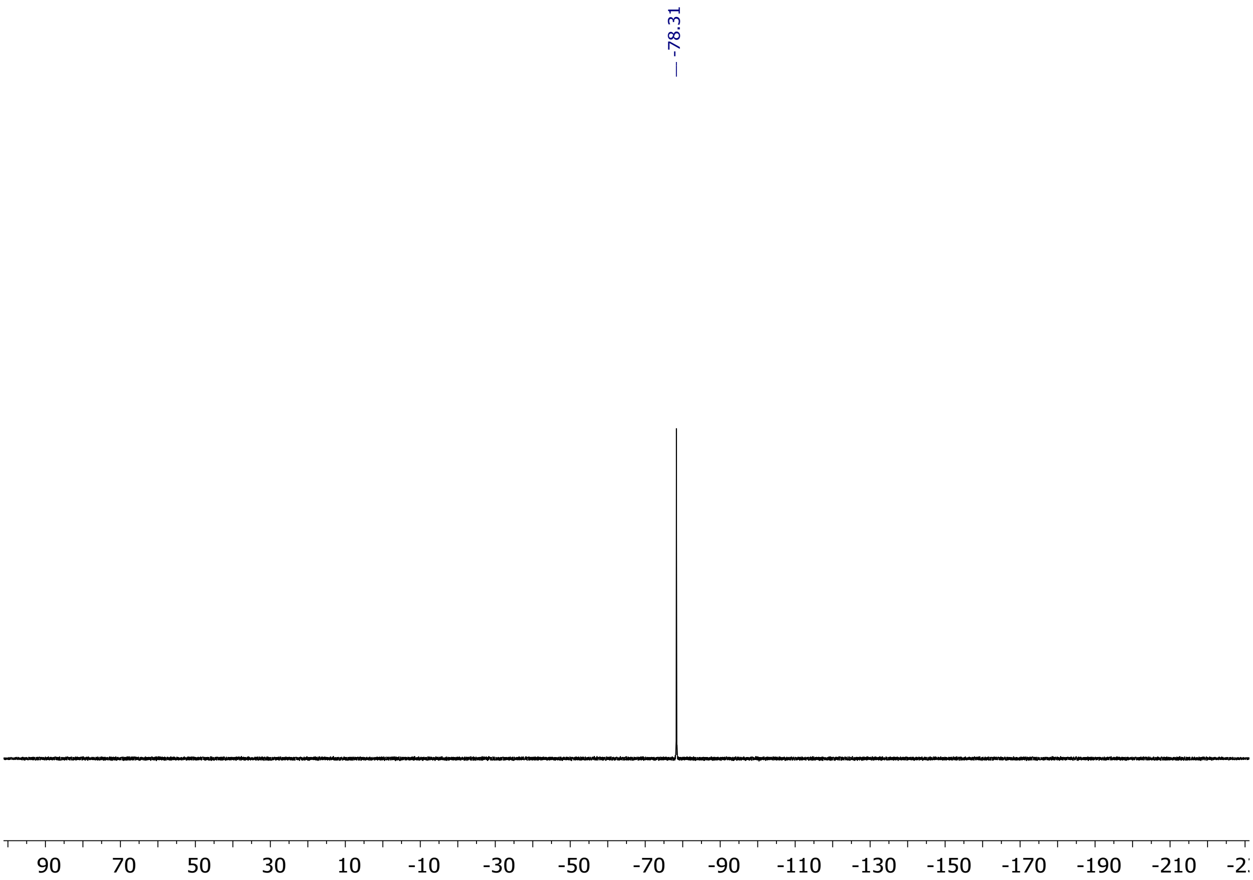
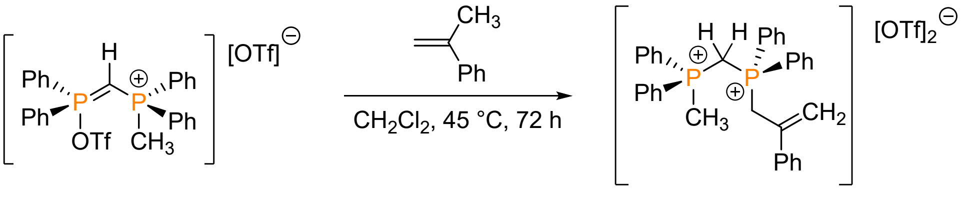


Figure S38. ^{19}**F NMR spectrum of 10 (CDCl$_3$).**



Reaction of 7 with α-Methylstyrene (11)



11

To a 0.7 mL DCM solution of **7** (36.3 mg, 0.0521 mmol, 1 equiv.) was added 6.7 μL of α-methylstyrene via syringe and the resultant mixture was transferred to a J-young tube. The reaction was heated at 45 °C for 72 hours, then brought into the glovebox and filtered over Celite to yield a colorless residue. NMR analysis indicated formation of **11**.

^{1}**H NMR** (400 MHz, CDCl$_3$, 298 K) δ 7.86 – 7.61 (m, 15H), 7.60 – 7.38 (m, 10H), 5.41 (br d, $^4J_{HP}$ = 6.1 Hz, 1H), 5.31 (t, $^2J_{HP}$ = 16.1 Hz, 2H), 5.17 (br d, $^4J_{HP}$ = 6.1 Hz, 1H), 4.36 (d, $^2J_{HP}$ = 15.2 Hz, 2H), 2.23 (d, $^2J_{HP}$ = 13.4 Hz, 3H).

^{13}**C{^{1}H} NMR** (126 MHz, CDCl$_3$, 298 K) δ 133.0 – 132.6 (m), 130.8 – 130.6 (m), 130.1 (d, J = 13.2 Hz), 129.2 (d, J = 13.0 Hz), 29.9.

Complete $^{13}C\{^1H\}$ NMR spectrum could not be obtained due to low compound solubility.

$^{31}P\{^1H\}$ NMR (162 MHz, CDCl$_3$, 298K) δ 21.7 (d, $^2J_{PP}$ = 19 Hz, 1P), 20.0 (d, $^2J_{PP}$ = 19 Hz, 1P)

^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ -78.0 (s).

Figure S39. ^1H NMR spectrum of the reaction of 7 with α-Methylstyrene (CDCl$_3$).

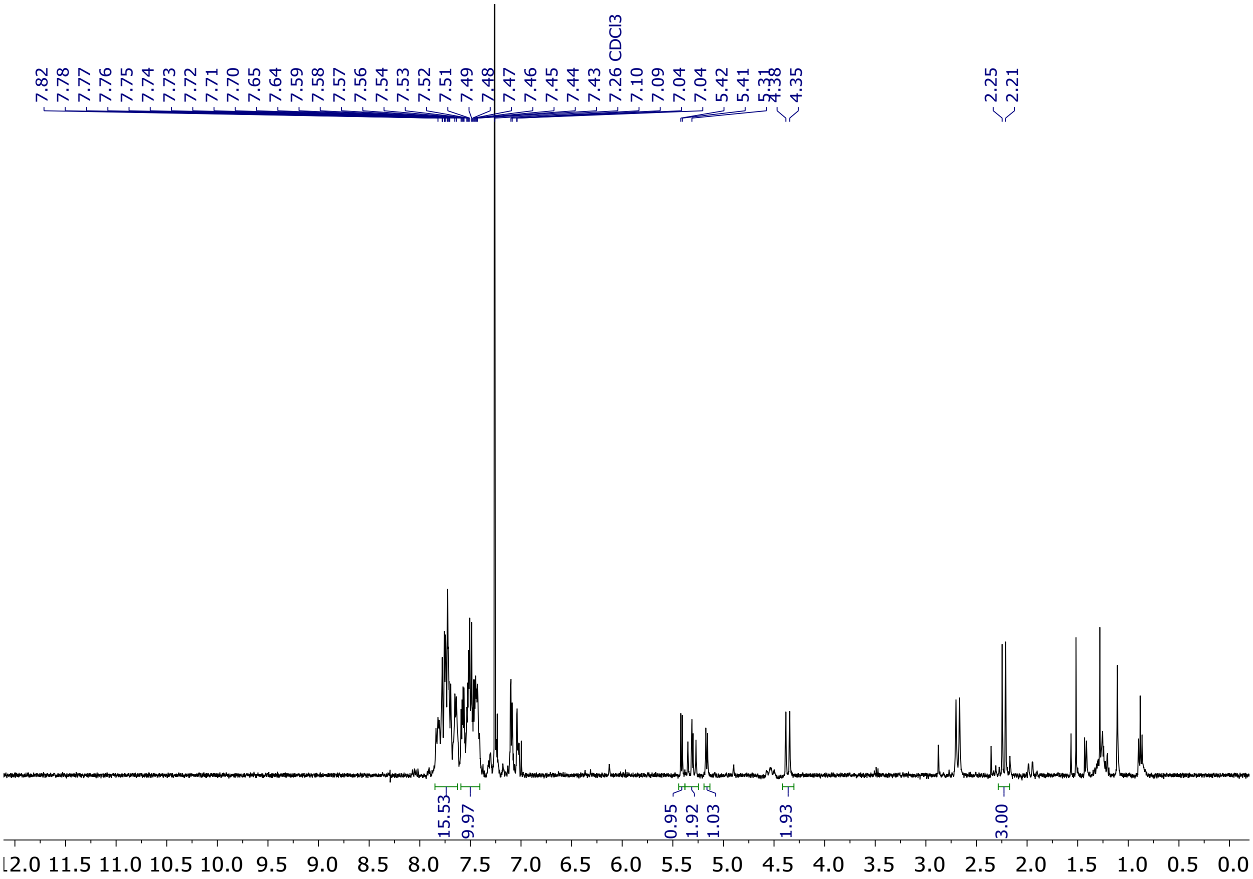


Figure S40. $^{13}C\{^{1}H\}$ **NMR spectrum of the reaction of 7 with α-Methylstyrene (CDCl$_3$).**

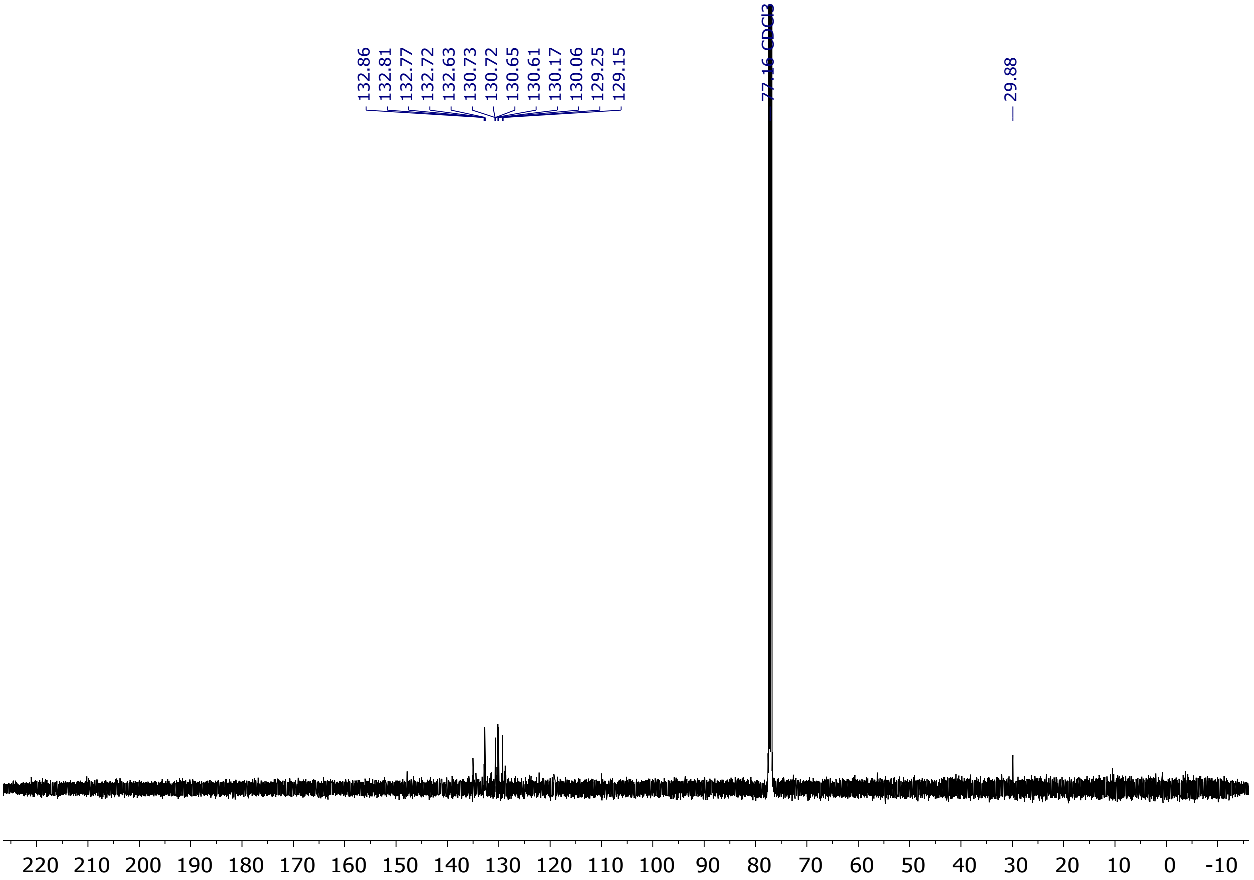


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of 7 with α-Methylstyrene ($CDCl_3$).

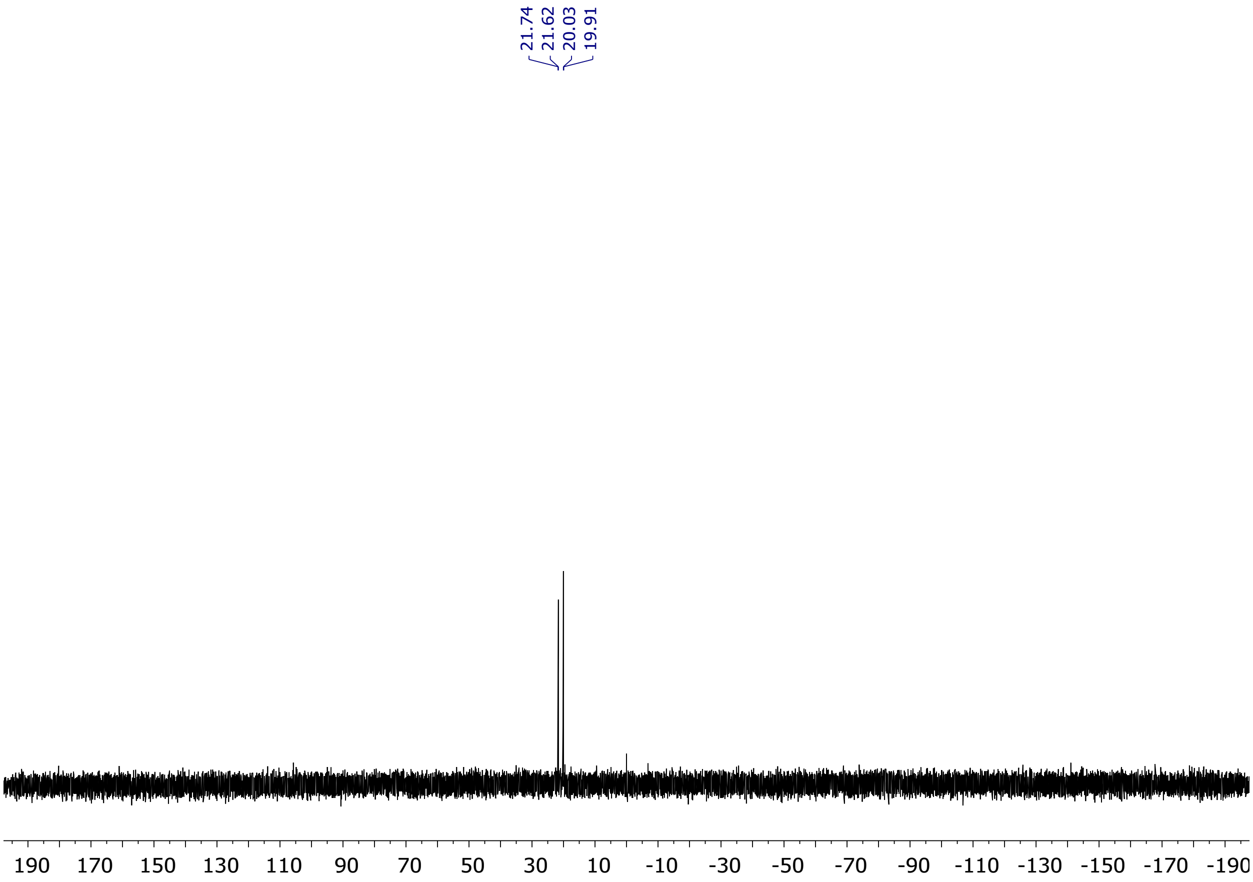
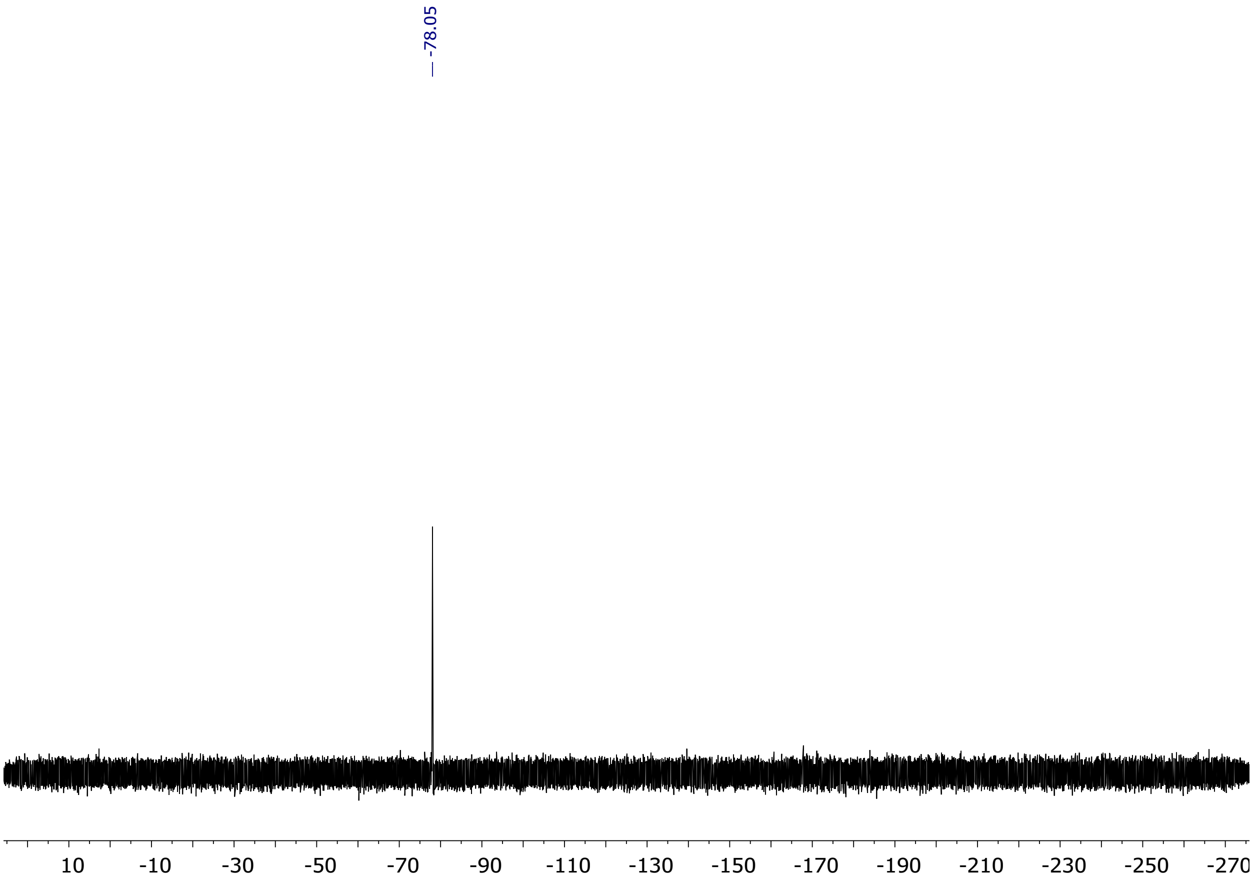
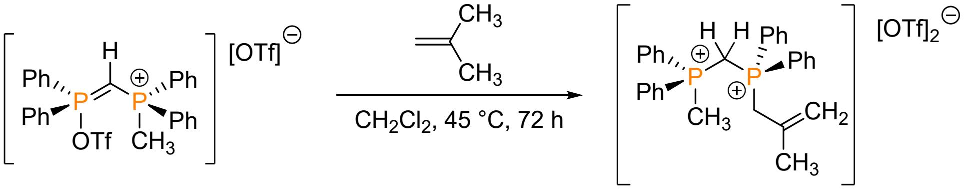


Figure S42. ^{19}F NMR spectrum of the reaction of 7 with α-Methylstyrene (CDCl$_3$).



Reaction of 7 with 2-Methylpropene (12)



12

7 (28.7 mg, 0.0412 mmol, 1 equiv.) was dissolved in 1 ml of DCM and transferred to a J-young tube. The solution was freeze-thaw degassed under vacuum; 2-methylpropene was then added at liquid N_2 temperature (-196 °C) and warmed up to room temperature (*ca*. 4 atm of 2-methylpropene). The reaction was heated at 45 °C for 72 hours, then brought into the glovebox and filtered over Celite. The solvent was removed *in vacuo* leading to a white residue which was triturated with 3x3 mL pentane and dried under high vacuum to yield **12** as a white powder (27.0 mg, 0.0359 mmol, 87% yield).

X-ray quality crystal was obtained by layering a DCM solution of **12** with pentane and storing at -35 ºC.

^{1}H NMR (500 MHz, CDCl$_3$, 298 K) δ 7.92 – 7.37 (m, 20H), 5.30 (t, $^{2}J_{HP}$ = 16.1 Hz, 2H), 4.90 (br d, $^{4}J_{HP}$ = 5.8 Hz, 1H), 4.77 (br d, $^{4}J_{HP}$ = 6.0 Hz, 1H), 3.94 (d, $^{2}J_{HP}$ = 15.4 Hz, 2H), 2.41 (d, $^{2}J_{HP}$ = 13.6 Hz, 3H), 1.27 (d, $^{4}J_{HP}$ = 3.0 Hz, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K) 136.2 (d, *J* = 3.0 Hz), 135.7 (d, *J* = 2.8 Hz), 134.3 (d, *J* = 10.3 Hz), 132.8 (d, *J* = 11.2 Hz), 131.8 (d, *J* = 10.5 Hz), 130.6 (d, *J* = 13.0 Hz), 130.5 (d, *J* = 13.5 Hz), 122.3 – 121.8 (m), 117.3 (dd, *J* = 88.3, 3.0 Hz), 114.2 (dd, *J* = 84.5, 2.1 Hz), 32.4 (d, *J* = 46.2 Hz), 24.0, 19.0 – 17.7 (m), 8.6 (d, *J* = 55.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298K) δ 21.4 (d, $^{2}J_{PP}$ = 18 Hz, 1P), 20.0 (d, $^{2}J_{PP}$ = 18 Hz, 1P).

^{19}F NMR (376 MHz, CDCl$_3$, 298 K) δ -78.4 (s).

Figure S43. ^{1}H NMR spectrum of 12 (CDCl$_3$).

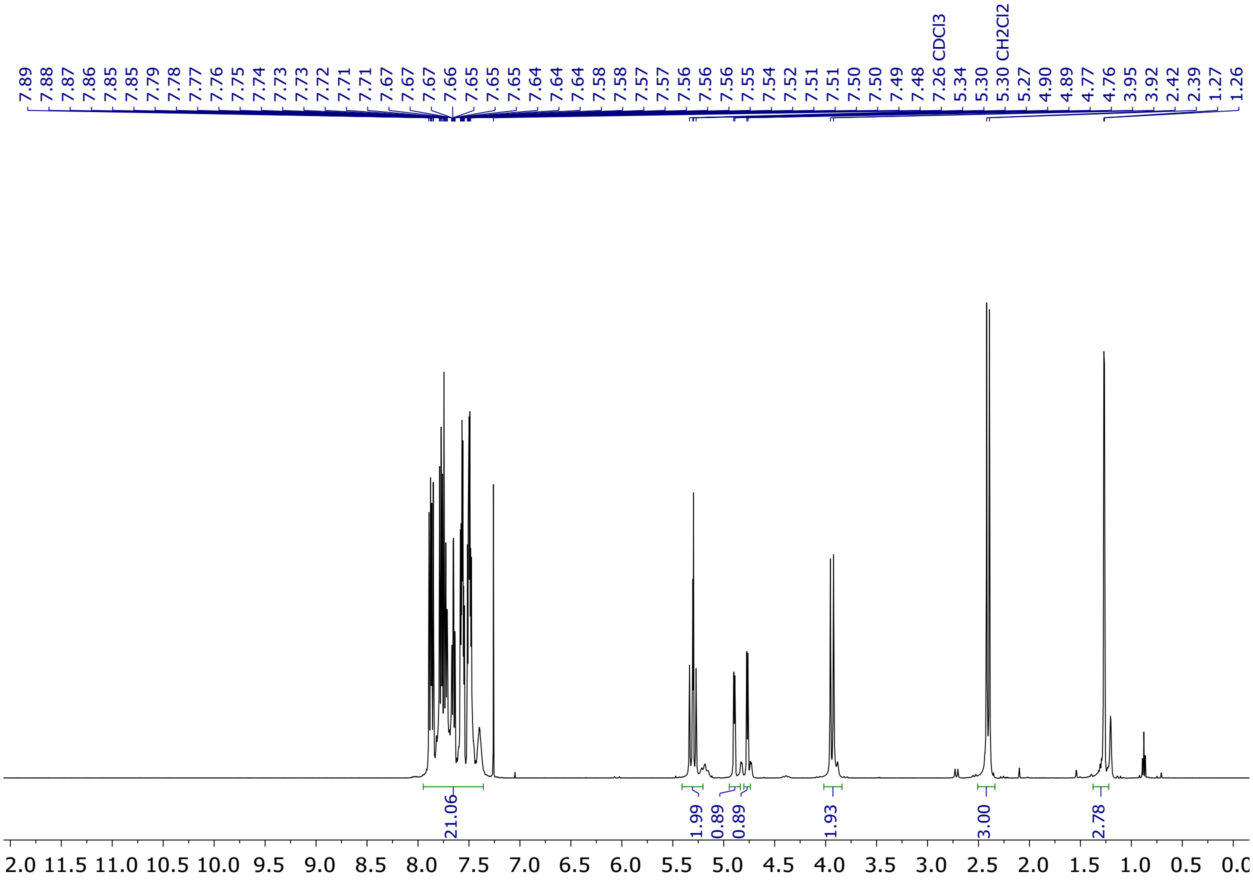


Figure S44. $^{13}C\{^{1}H\}$ **NMR spectrum of 12 ($CDCl_3$).**

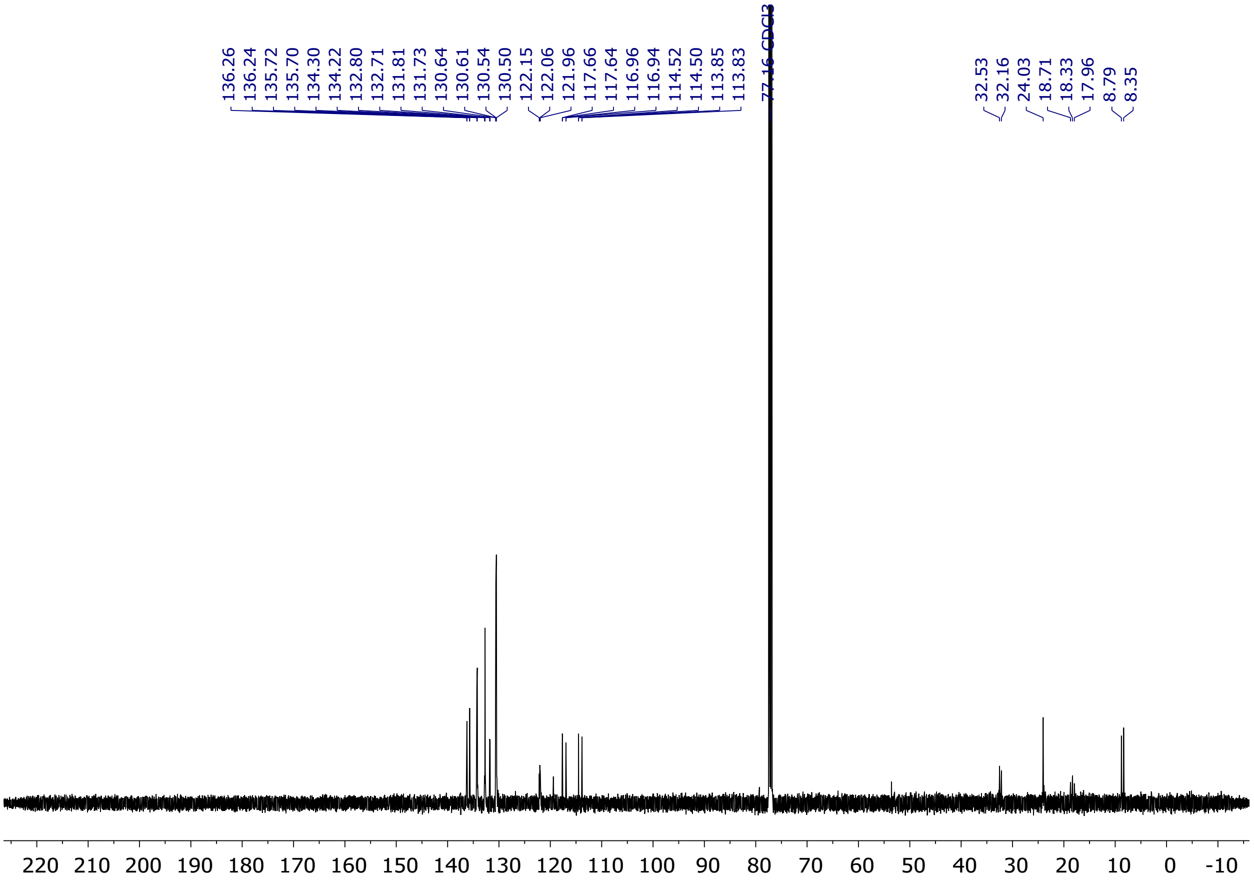


Figure S45. $^{31}P\{^1H\}$ **NMR spectrum of 12 (CDCl$_3$).**

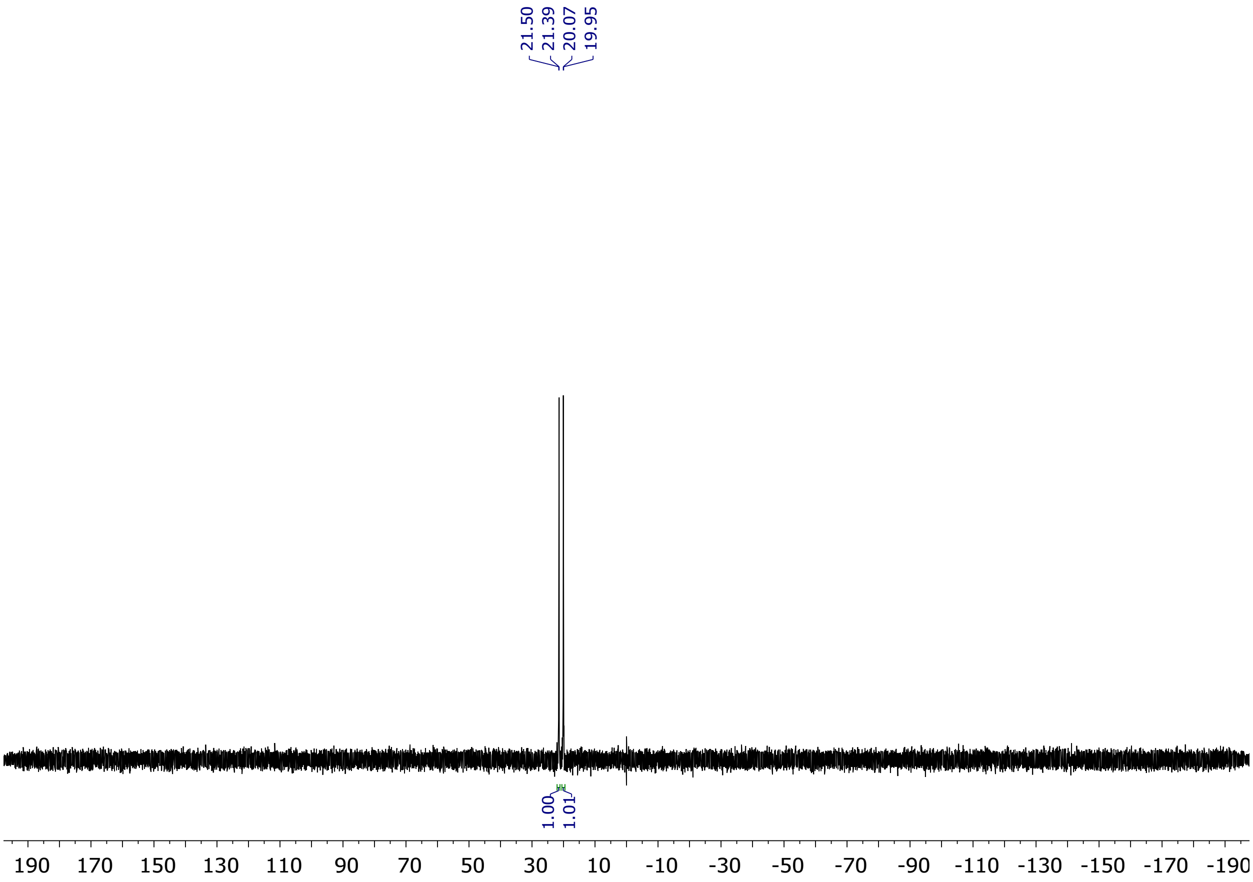
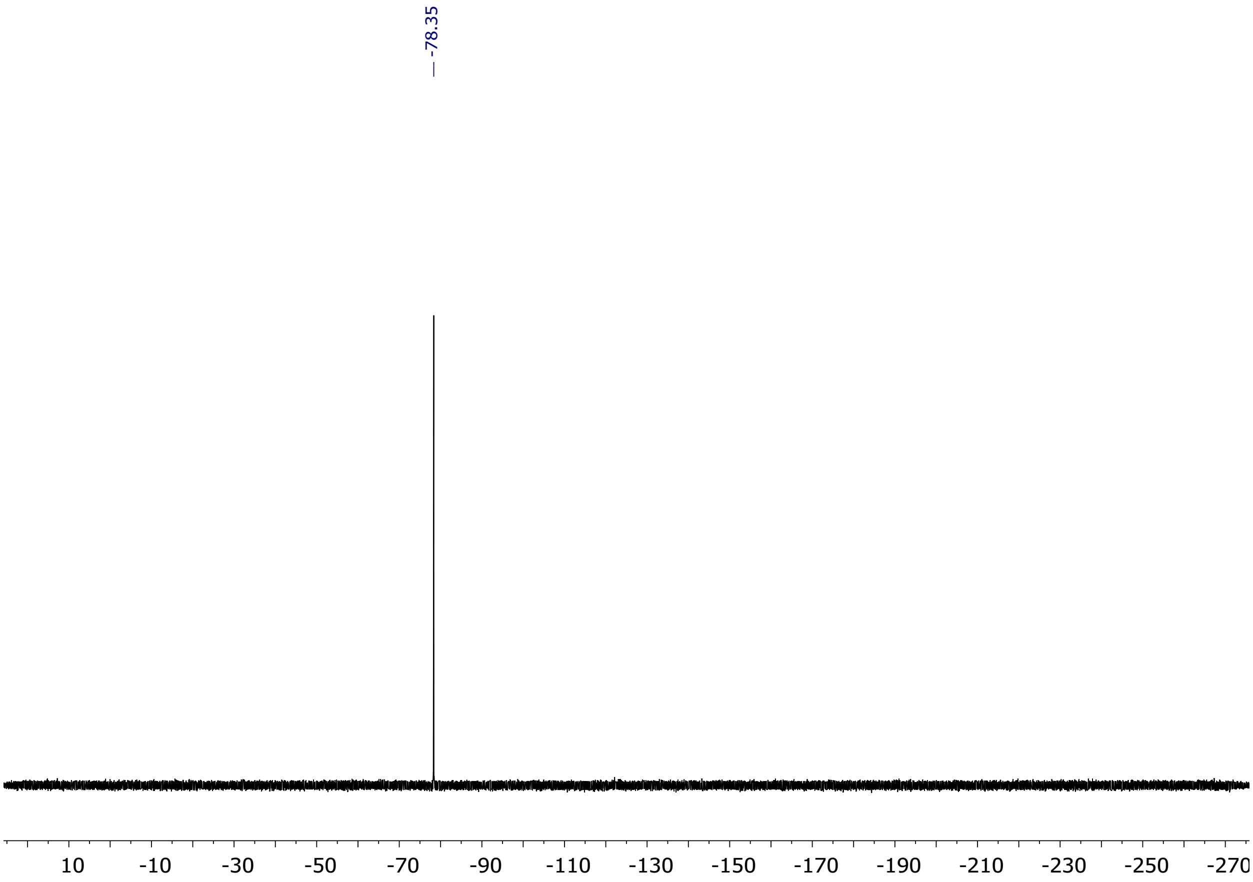


Figure S46. ^{19}F NMR spectrum of 12 ($CDCl_3$).



References

1. K. Alam and A. F. Janzen, *J. Fluorine Chem.*, 1987, **36**, 179-184.
2. E. Fluck and R. Braun, *Phosphorus and Sulfur and the Related Elements*, 1988, **40**, 83-90.
3. S. J. Connelly, W. Kaminsky and D. M. Heinekey, *Organometallics*, 2013, **32**, 7478-7481.
4. R. E. H. Kuveke, L. Barwise, Y. van Ingen, K. Vashisth, N. Roberts, S. S. Chitnis, J. L. Dutton, C. D. Martin and R. L. Melen, *ACS Cent. Sci.*, 2022, DOI: 10.1021/acscentsci.2c00325.
5. R. M. Denton, J. An, B. Adeniran, A. J. Blake, W. Lewis and A. M. Poulton, *J. Org. Chem.*, 2011, **76**, 6749-6767.
6. S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, J. M. Sheffield and G. M. Thompson, *J. Chem. Soc., Dalton Trans.*, 1997, 4823-4828.
7. R. Appel, H.-F. Schöler and H.-D. Wihler, *Chem. Ber.*, 1979, **112**, 462-467.