Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

# Interception of Intermediates in Phosphine Oxidation by Mesityl Nitrile-*N*-Oxide using Frustrated Lewis Pairs

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# 1. **Materials and Methods**

### *General Remarks*

All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free $N_2$ by means of standard Schlenk techniques or glovebox techniques (VAC glovebox equipped with a -25 °C freezer) unless otherwise specified. All glassware was oven-dried and cooled under vacuum before use. Dichloromethane (DCM) were distilled over $CaH_2$. Pentane and hexane were collected from a Grubbs-type column system manufactured by Innovative Technology and degassed. Solvents were stored over activated 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating under vacuum for 24 hours. $CDCl_3$ purchased from Cambridge Isotope Laboratories was vacuum distilled, further degassed, and stored over activated 4 Å molecular sieves in the glovebox for at least 8 hours prior to use. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. Mesityl nitrile *N*-oxide (MesCNO) was prepared using literature methods.[1] $B(C_6F_5)_3$ was purchased from Boulder Scientific and sublimed under vacuum at 85 °C prior to use. NMR spectra were recorded at room temperature (298 K) unless otherwise mentioned on a Bruker Avance III 400 MHz, an Agilent DD2 500, an Agilent DD2 600, and an Agilent DD2 700 Spectrometers. Spectra were referenced to the residual solvent signals ($CDCl_3$: $^1H$= 7.26 ppm and $^{13}C$ = 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are listed as absolute values in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), multiplet (m), overlapping (ov), and broad (br). High-resolution mass spectra (HRMS) were obtained on a JMS-T100LC JOEL DART mass spectrometer. Elemental analyses for C, H, and N were performed by ANALEST (University of Toronto) employing a Perkin Elmer 2400 Series II CHNS Analyser.

### *X-ray Diffraction Studies*

Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150(2) K for all crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an

absorption correction applied using multi-scan within the APEX-2 program. All structures were solved and refined by direct methods within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

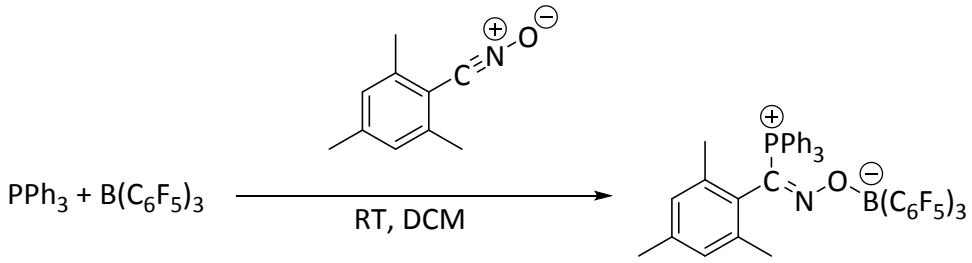
***Mass Spectrometry Studies***

All attempts to observe the products by high-resolution mass spectrometry failed due to the instability of these compounds under mass spectrometry conditions, by either ESI or DART methods. In positive mode ESI, the protonated phosphonium cation or protonated phosphine oxide were observed. By negative mode, [HO-B($C_6F_5$)$_3$] or [$H_2$NO-B($C_6F_5$)$_3$] were observed.

(1) M. V. Barybin, P. L. Diaconescu, C. C. Cummins, *Inorg. Chem.* **2001,** *40*, 2892-2897.

# 2. Synthesis and Characterization

### *2.1 [MesC(Ph$_3$P)NOB(C$_6$F$_5$)$_3$] (1)*




$PPh_3$ (65.3 mg, 0.25 mmol, 1 equiv.) and $B(C_6F_5)_3$ (127.9 mg, 0.25 mmol, 1 equiv.) were combined in 2mL $CH_2Cl_2$. To the resulting suspension, a solution of MesCNO (40.3 mg, 0.25 mmol, 1 equiv.) in 1 mL of $CH_2Cl_2$ was added dropwise, yielding a clear and homogenous solution. After 20 minutes, 5mL of cold pentane was added with vigorous stirring which led to the precipitation of a white precipitate. The solution was then decanted and dried in vacuo, yielding the desired product as a white powder. Yield: 206.5 mg (88% isolated yield). Diffraction quality single crystals were obtained through slow diffusion of pentane into benzene at room temperature.

**$^1$H NMR** (600 MHz, $CDCl_3$, 253 K): δ 7.80 (m, 4H, Ar), 7.67 (m, 2H, Ar), 7.48 (m, 5H, Ar), 7.18 (m, 2H, Ar), 6.71 (m, 2H, Ar), 6.64 (s, 2H, *m*-H, Mes), 2.16 (s, 3H, *p*-$CH_3$, Mes), 1.90 (s, 6H, *o*-$CH_3$, Mes).

**$^{19}$F{$^1$H} NMR** (377 MHz, $CDCl_3$): δ -132.3 (d, $^3J_{FF}$ = 22.6 Hz, 2F, *o*-$C_6F_5$), -160.0 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-$C_6F_5$), -165.5 (m, 2F, *m*-$C_6F_5$).

**$^{31}$P {$^1$H}** NMR (162 MHz, $CDCl_3$): δ 5.4 (s).

**$^{11}$B{$^1$H} NMR** (128 MHz, $CDCl_3$): δ 0.5 (s).

**$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$): δ 148.09 (dm, 239 Hz, $C_6F_5$), 140.28 (d, 3 Hz), 139.11 (dm, 252 Hz, $C_6F_5$), 139.08 (d, 4 Hz), 136.84 (dm, 232 Hz, $C_6F_5$), 134.49 (b), 133.92 (d, 11 Hz), 132.76, 132.48, 129.62 (b), 129.03, 128.74, 128.60, 21.14, 20.75.

**Elemental analysis**: Calc.: C 59.06%, H 2.80%, N 1.51%. Exp.: C 58.76%, H 2.46%, N 1.43%

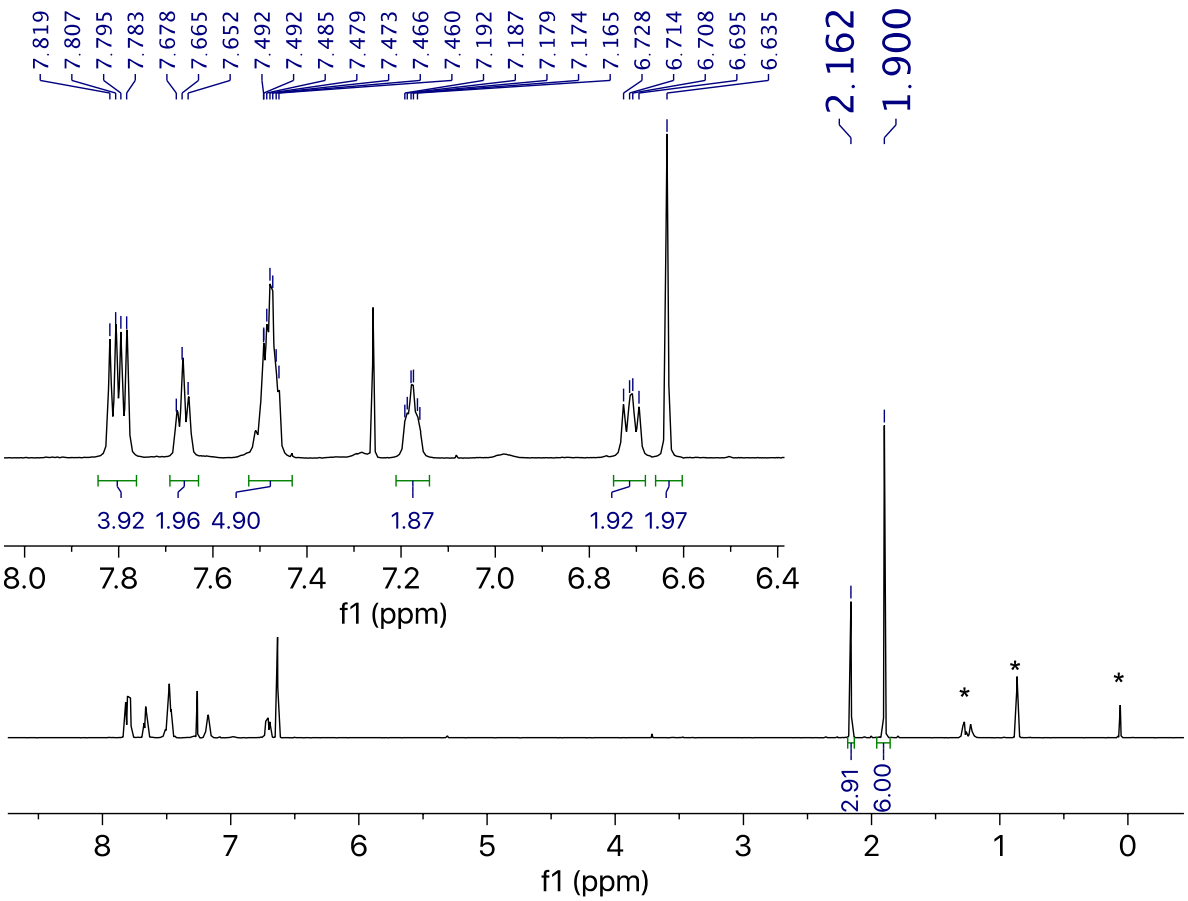



**Figure 1.** $^{1}$H NMR spectrum of **1** ($CDCl_3$, 253 K). Asterisks denote solvent impurities.

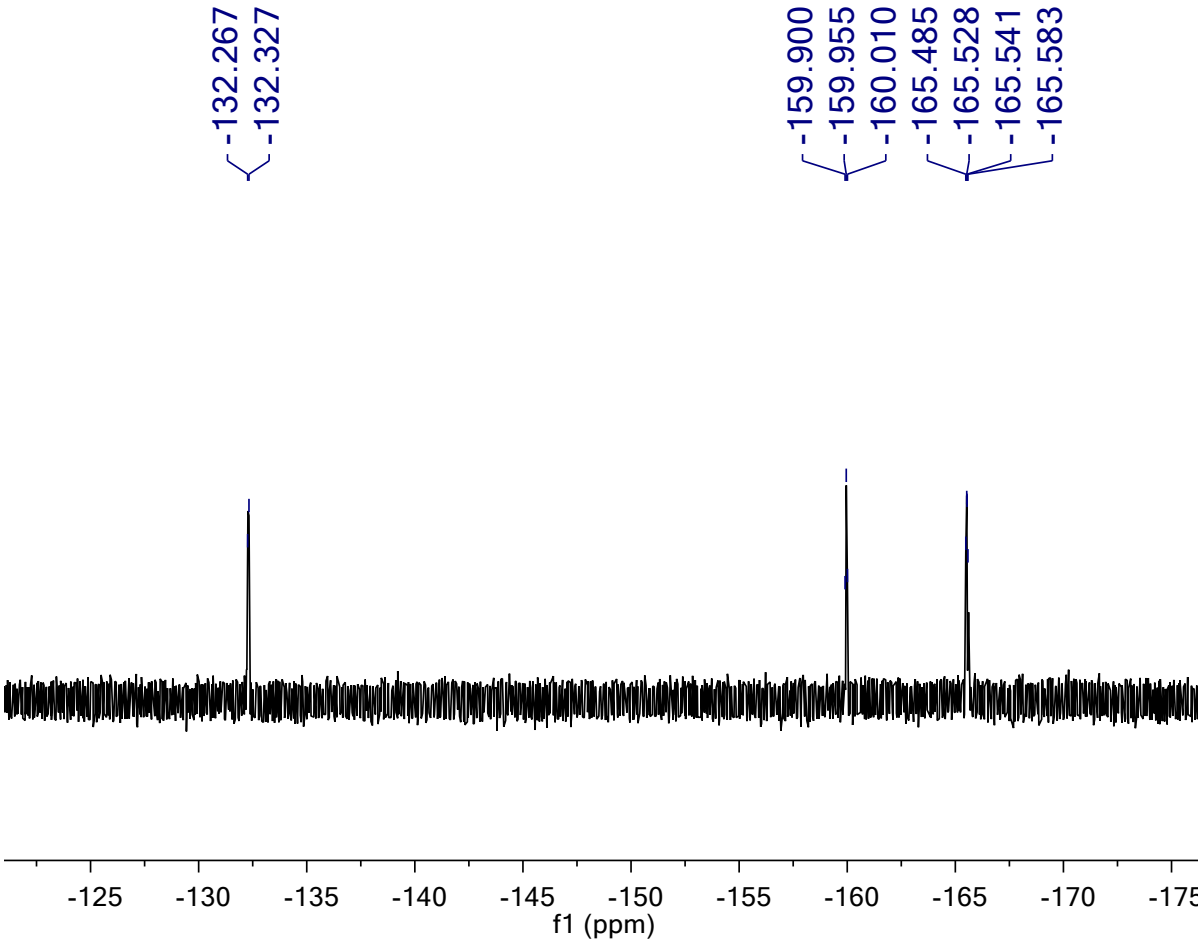



**Figure 2.** $^{19}F\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

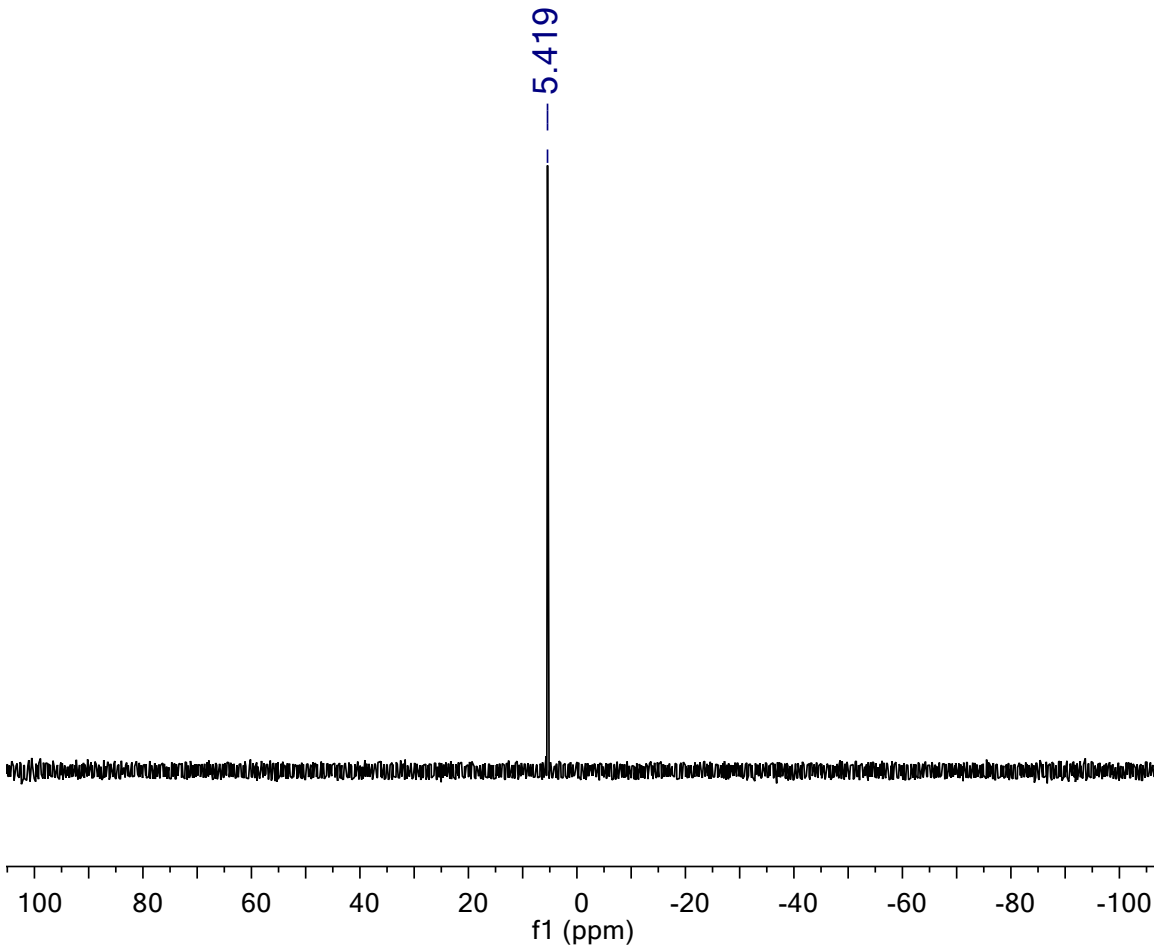



**Figure 3.** $^{13}P\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

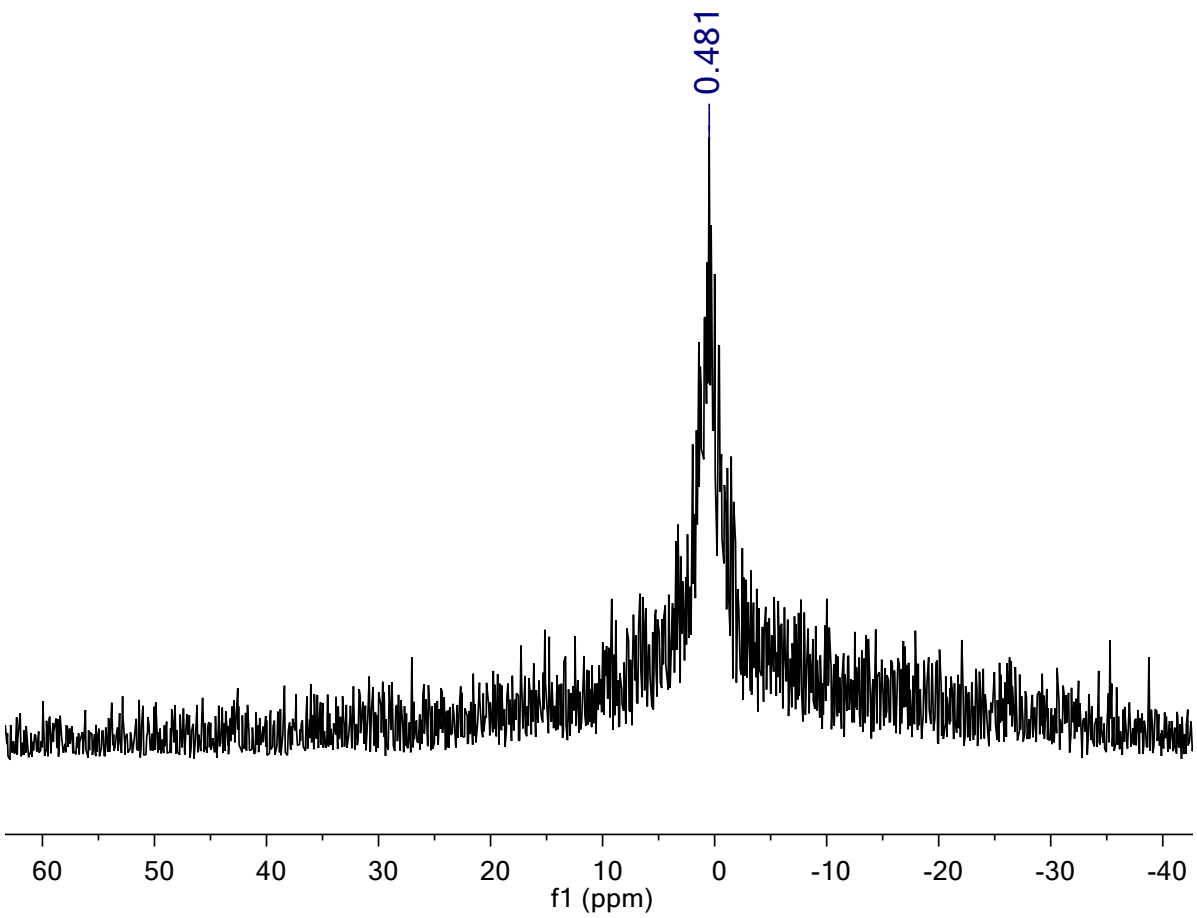



**Figure 4.** $^{11}B\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

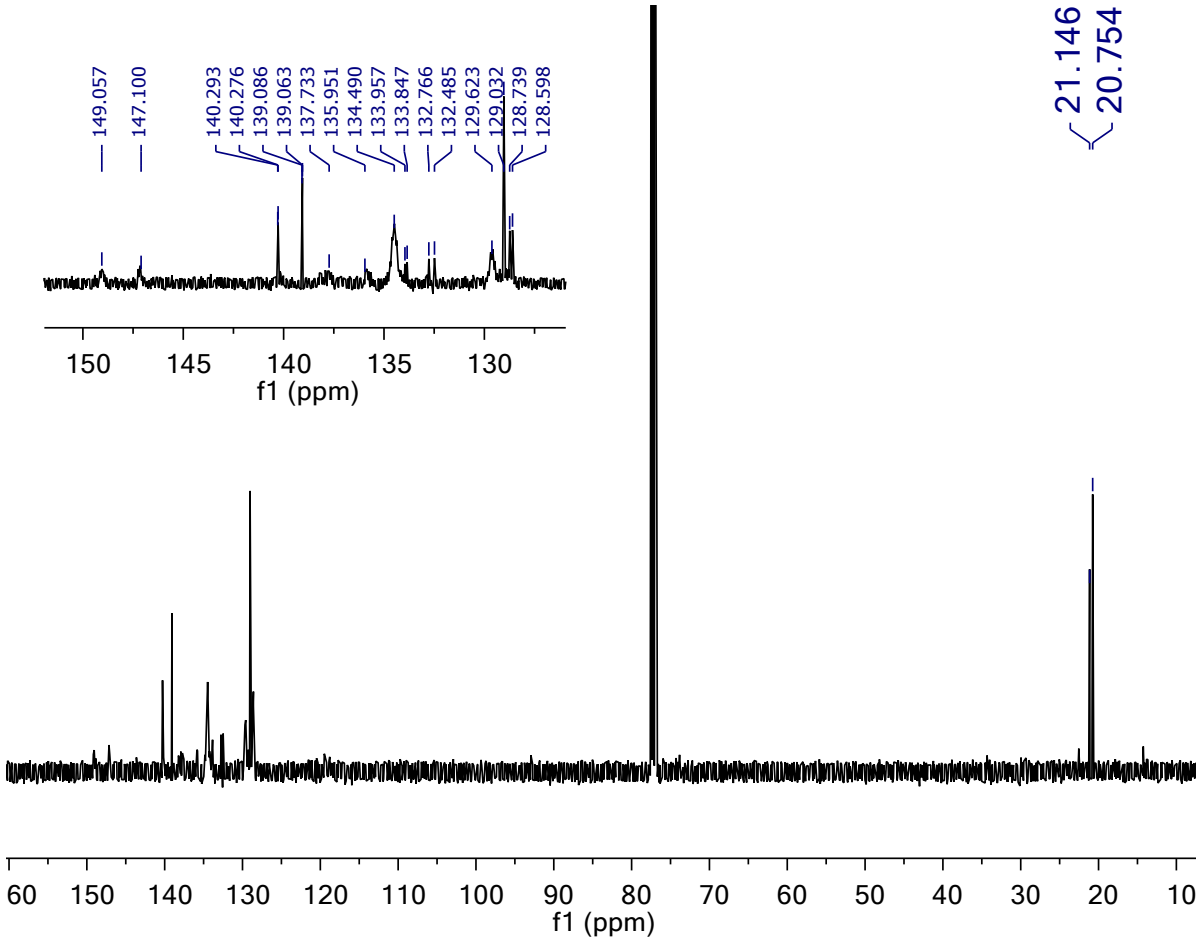
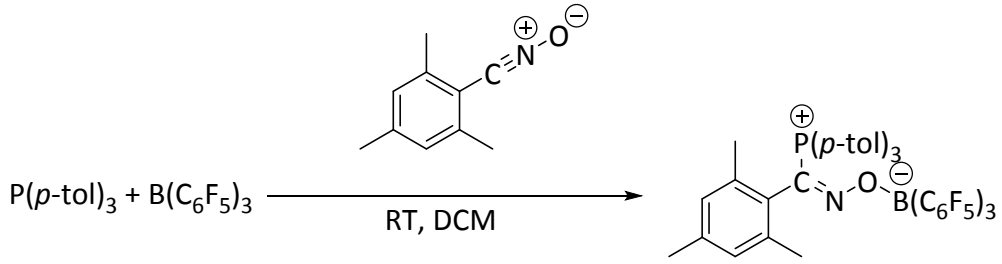



**Figure 5.** $^{13}C\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

### *2.2 [MesC((p-tol)$_3$P)NOB(C$_6$F$_5$)$_3$] (2)*




**Note**: Once precipitated from solution, compound **2** has very low solubility in common organic solvents, preventing full characterization by multinuclear NMR spectroscopy. $^{1}$H, $^{11}$B{$^{1}$H}, $^{19}$F{$^{1}$H} and $^{31}$P{$^{1}$H} NMR spectra are reported. Chemical connectivity and bulk purity are unambiguously confirmed by single-crystal X-ray diffraction studies and elemental analysis, respectively.

Solutions of P(*p*-tol)$_3$ (43.9mg, 0.14 mmol, 1 equiv.) and B(C$_6$F$_5$)$_3$ (73.8mg, 0.14 mmol, 1 equiv.) were combined in 4mL of $CH_2Cl_2$. The mixture remained homogeneous. To this solution, 2 mL of $CH_2Cl_2$ were carefully layered and the solution was left undisturbed for 5 minutes. A solution of MesCNO (23.2mg, 0.14 mmol, 1 equiv.) in 2mL $CH_2Cl_2$ was then carefully layered on top of the reaction vial. This final 3-layer mixture was left undisturbed for 48 hours at ambient temperature. After this time, clear and colourless diffraction-quality crystals precipitated from the yellow reaction mixture. The solvent was decanted and the crystalline product washed with pentane (3 x 5 mL), then dried in vacuo. Yield: 57.8 mg (41% isolated yield). Note: the yield can be improved by cooling the filtrate to -35 °C over one week, yielding additional product as an amorphous white precipitate.

**$^{1}$H NMR** (600 MHz, THF-d$_8$, 313 K): δ 7.72-7.26 (br, 12 H, Ar), 6.67 (s, 2H, *m*-H, Mes), 2.38 (br, 9H, *p*-$CH_3$, Ar), 2.15 (s, 3H, *p*-$CH_3$, Mes), 1.95 (s, 6H, *o*-$CH_3$, Mes).

**$^{19}$F{$^{1}$H} NMR** (377 MHz, THF-d$_8$): δ -134.6 (m, 2F, *o*-B(C$_6$*F*$_5$)$_3$), -164.4 (m, 1F, *p*-B(C$_6$*F*$_5$)$_3$), -169.5 (m, 2F, *m*-B(C$_6$*F*$_5$)$_3$).

**$^{31}$P{$^{1}$H} NMR** (162 MHz, THF-d$_8$): δ 4.0 (s).

**$^{11}$B{$^{1}$H} NMR** (128 MHz, THF-d$_8$): δ -2.4 (b).

**Elemental Analysis**: Calc.: C 60.20%, H 3.30%, N 1.43%. Exp.: C 59.45%, H 3.29%, N 1.45%

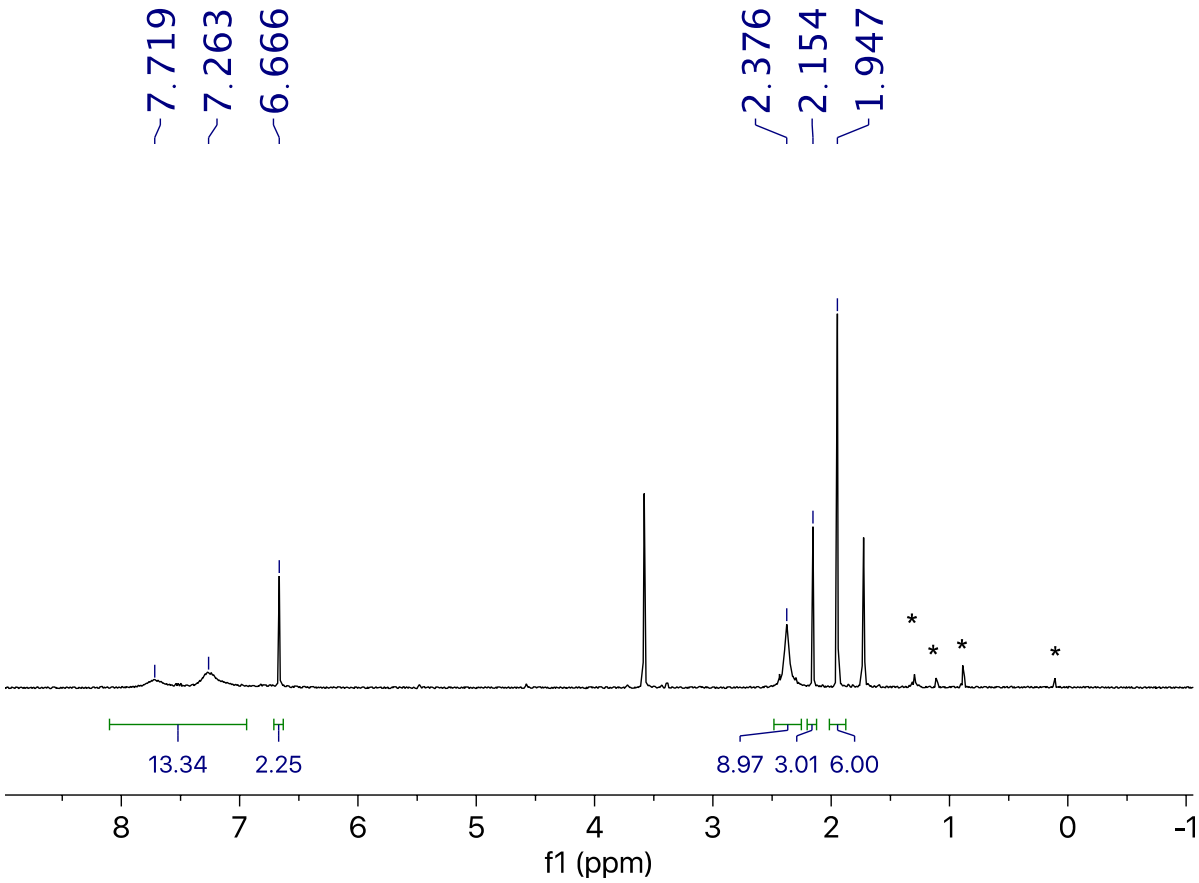



**Figure 6.** $^{1}$H NMR spectrum of **2** (THF-*d8*, 313 K). Asterisks denote solvent impurities.

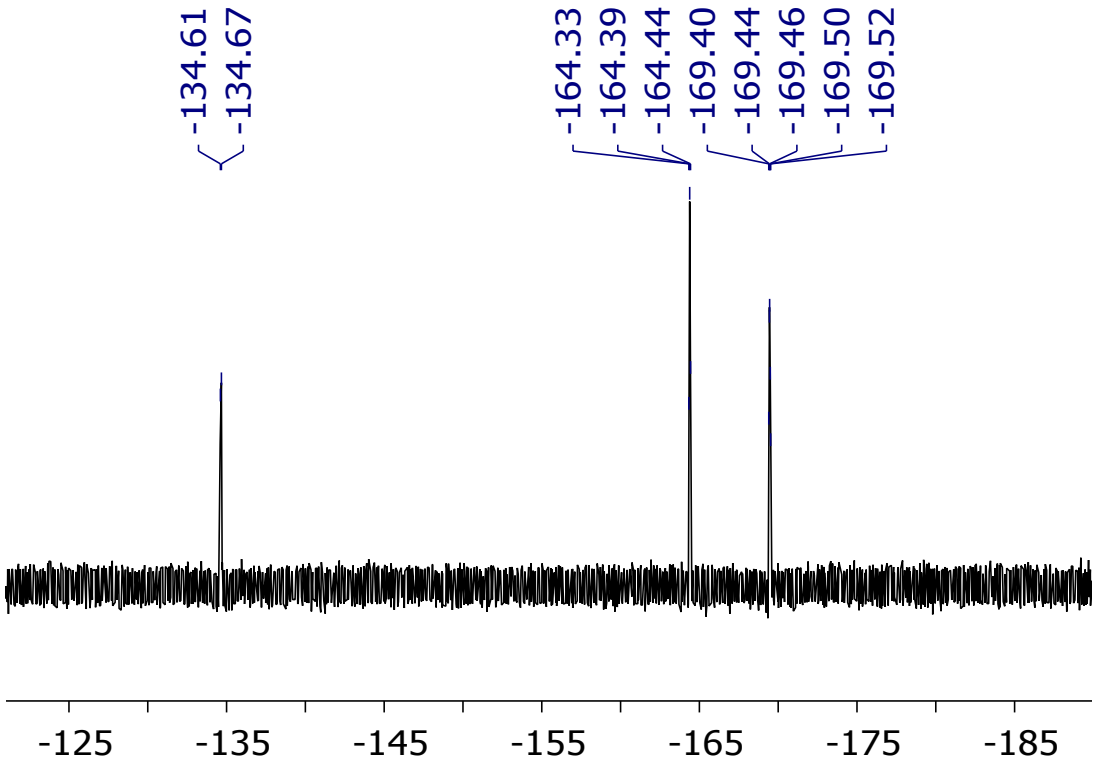



**Figure 7.** $^{19}F\{^{1}H\}$ NMR spectrum of **2** (THF-$d_8$)

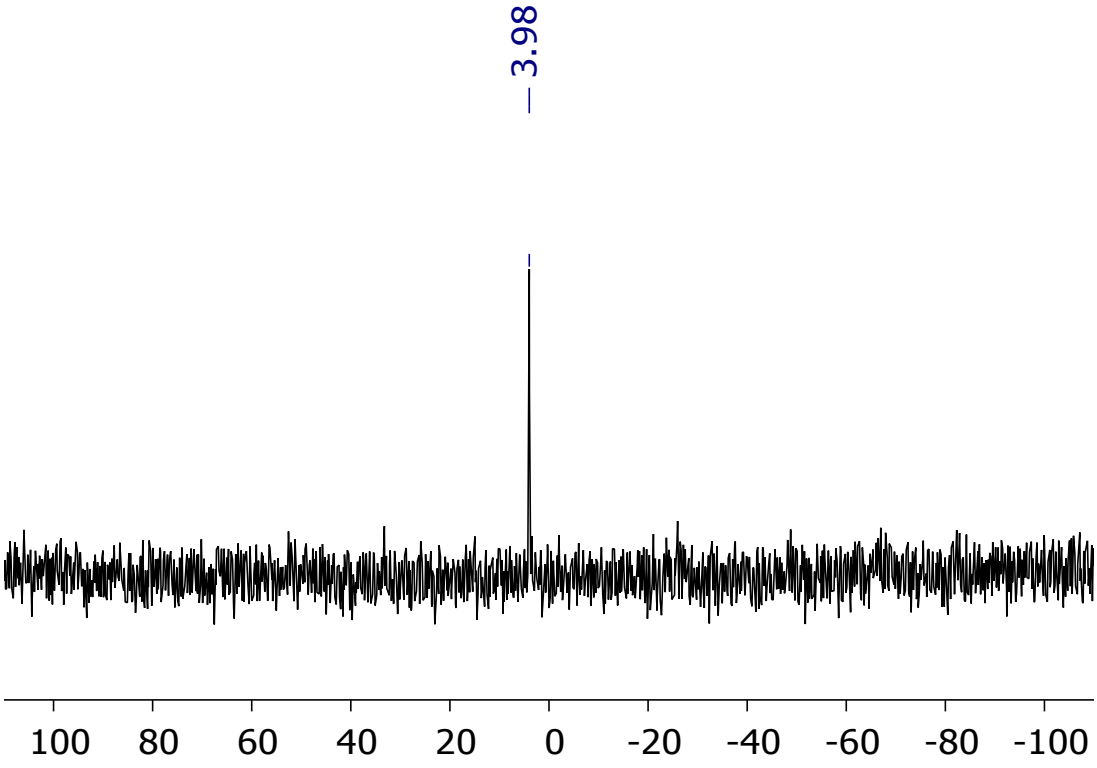


**Figure 8.** $^{31}P\{^{1}H\}$ NMR spectrum of **2** (THF-$d_8$)

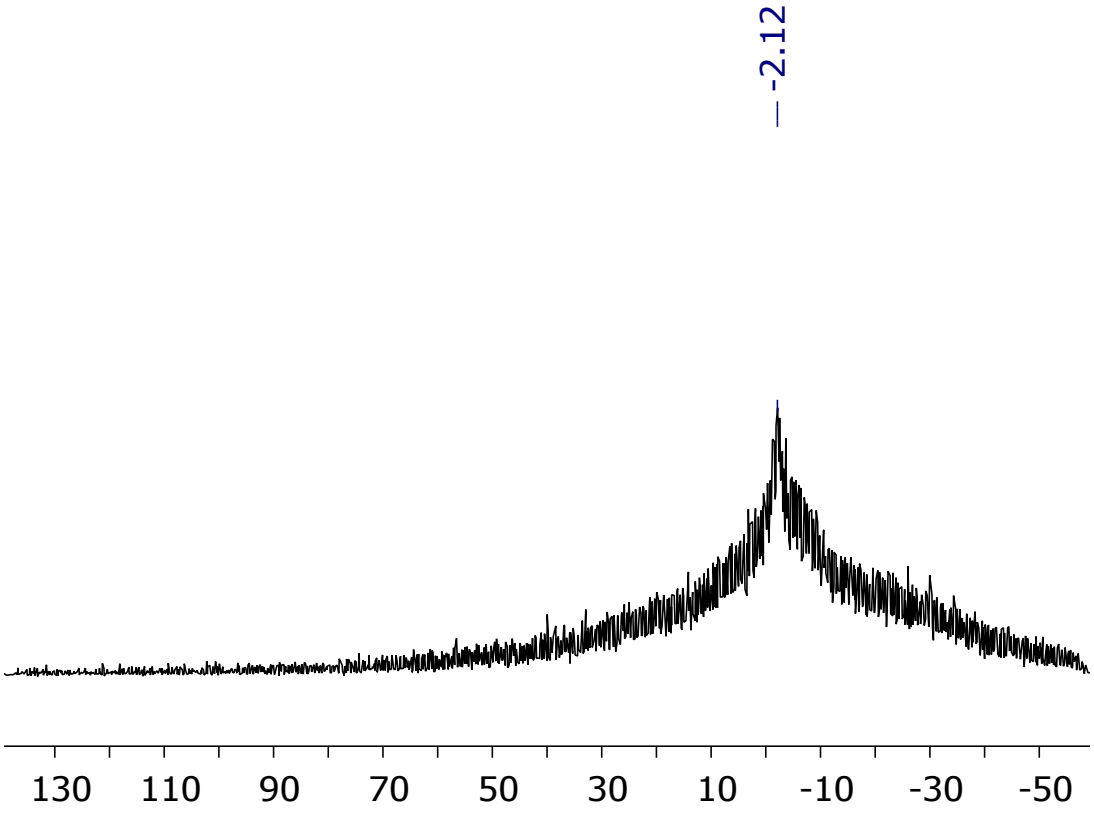
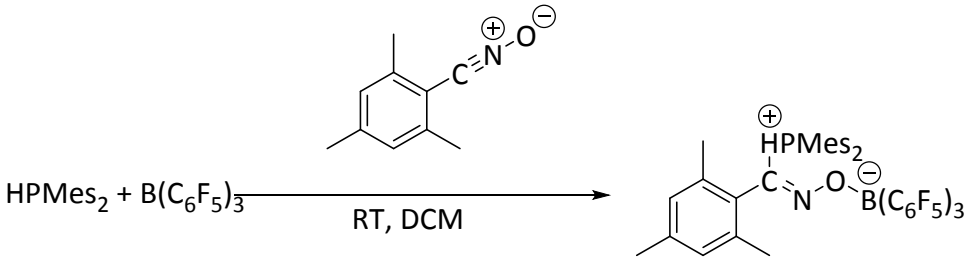



**Figure 9.** $^{11}B\{^{1}H\}$ NMR spectrum of **2** (THF-$d_8$)

### *2.3 [MesC(Mes$_2$PH)NOB(C$_6$F$_5$)$_3$] (3)*




$HPMes_2$ (31.8 mg, 0.12 mmol, 1 equiv.) and $B(C_6F_5)_3$ (60.2 mg, 0.12 mmol, 1 equiv.) were combined in 2mL $CH_2Cl_2$. To the resulting suspension, a solution of MesCNO (18.9 mg, 0.12 mmol, 1 equiv.) in 1 mL of $CH_2Cl_2$ was added dropwise to the light-yellow solution. After 20 minutes, the solvent was removed *in vacuo* to yield a faint yellow gel. Yield: 72.1 mg (65% isolated yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 9.10 (d, $^1J_{PH}$ = 510.8 Hz, 1H, P*H*), 7.46–7.45 (ov, 6H, $P(Mes)_2$), 2.89-2.84 (ov, 18H, Mes), 2.74-2.68 (ov, 9H, Mes).

**$^{19}$F{$^1$H} NMR** (377 MHz, $CDCl_3$): δ -133.7 (d, $^3J_{FF}$ = 23.4 Hz, 2F, *o*-$C_6F_5$), -161.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-$C_6F_5$), -166.4 (m, 2F, *m*-$C_6F_5$).

**$^{31}$P NMR** (162 MHz, $CDCl_3$): δ -39.1 (d, $^1J_{PH}$ = 518.4 Hz,).

**$^{11}$B{$^1$H} NMR** (128 MHz, $CDCl_3$): δ 0.1 (s).

**$^{13}$C{$^1$H} NMR** (126 MHz, $CDCl_3$): δ 148.02 (dm, 240 Hz, $C_6F_5$), 144.84 (d, 3 Hz), 143.40 (d, 10 Hz), 140.04, 139.12 (dm, 248 Hz, $C_6F_5$), 139.01 (d, 3 Hz), 138.19 (d, 13 Hz), 136.82 (dm, 247 Hz, $C_6F_5$), 131.33 (d,11 Hz), 129.28, 126.19(d, 13 Hz), 121.34 (b) 114.18 (d, 80 Hz), 22.59, 22.52, 21.89, 21.25, 21.24, 21.07. The resonance for the *ipso*-$B(C_6F_4H)_3$ carbon is likely not observed.

**Elemental analysis**: Calc.: C 58.56%, H 3.63%, N 1.48%. Exp.: C 58.09%, H 3.41% N 1.50%

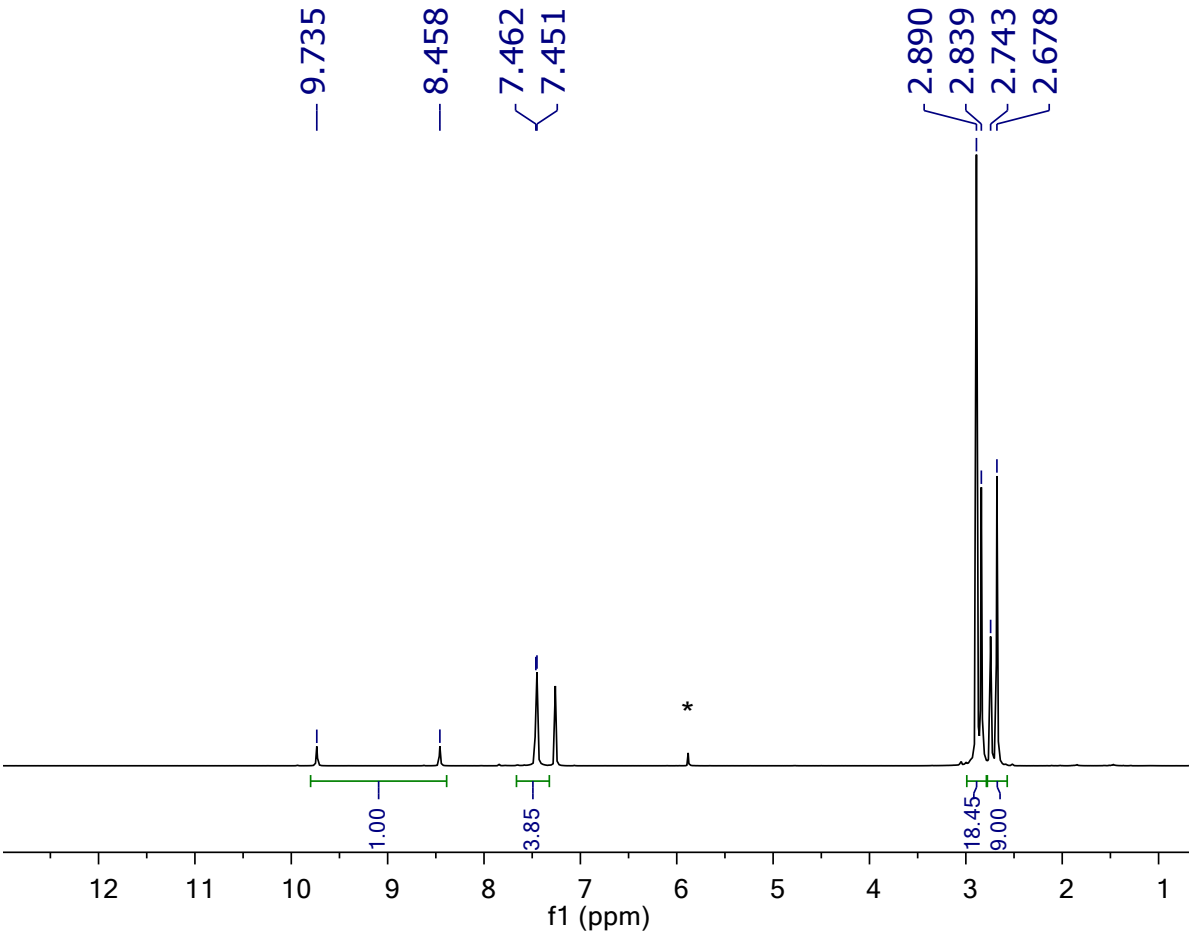



**Figure 10.** $^{1}$H NMR spectrum of **3** ($CDCl_3$). Asterisks denote solvent impurities.

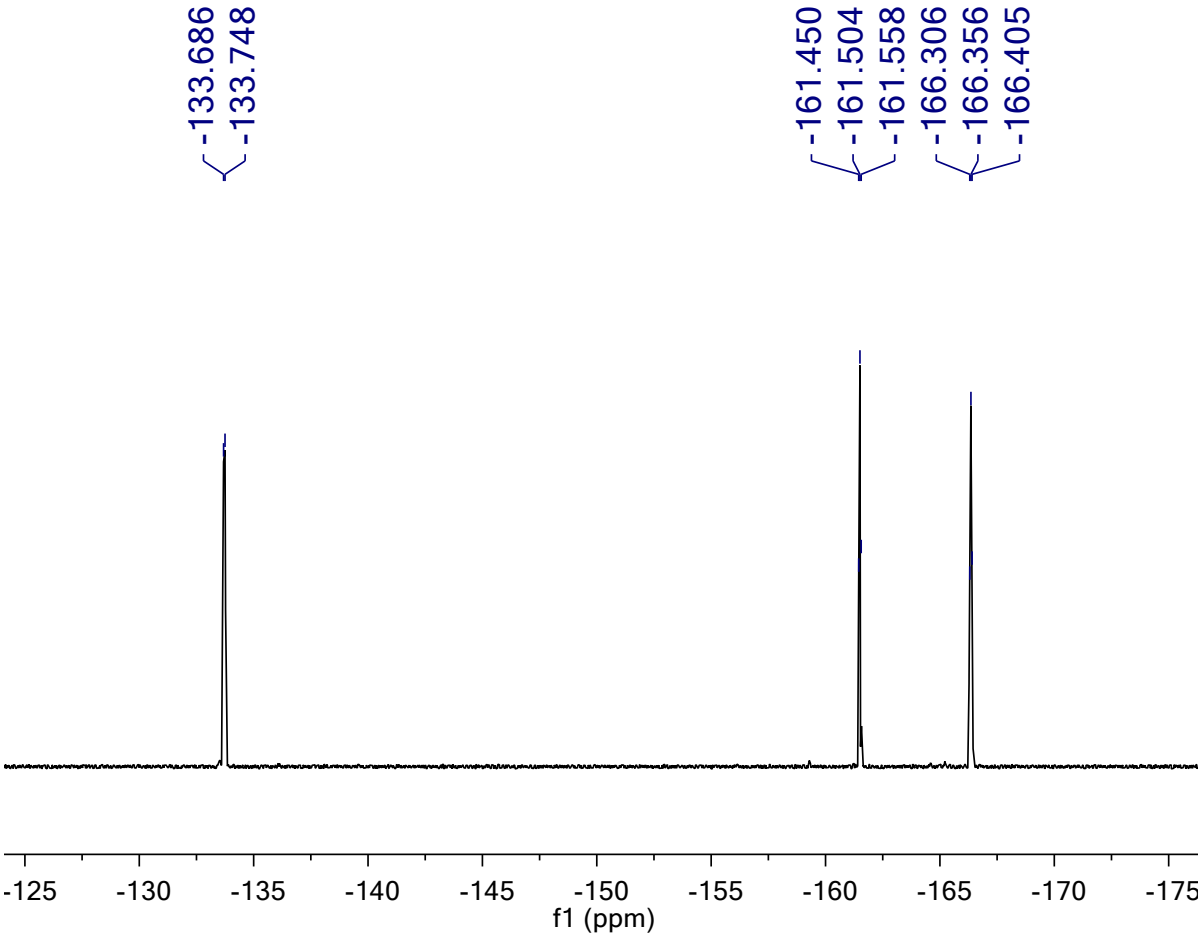



**Figure 11.** $^{19}F\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$).

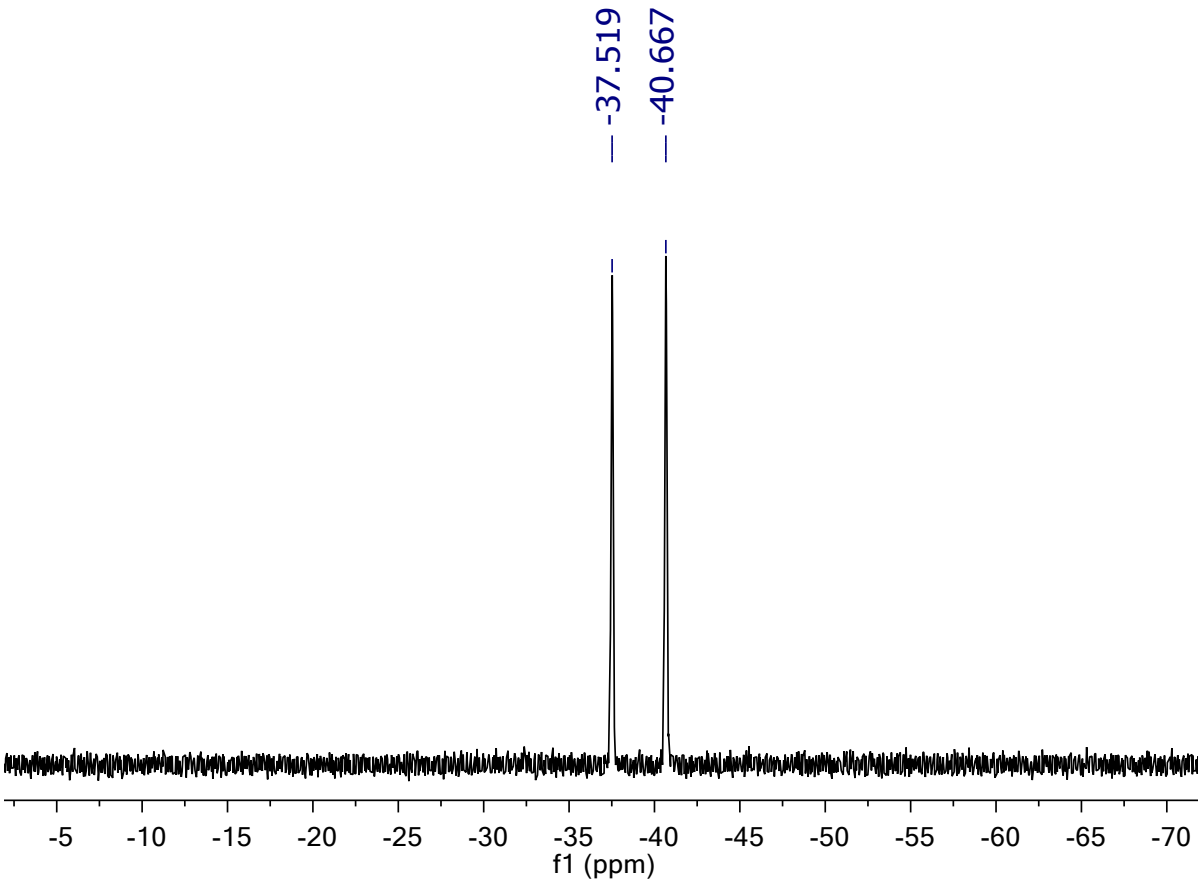



**Figure 12.** $^{31}P$ NMR spectrum of **3** ($CDCl_3$).

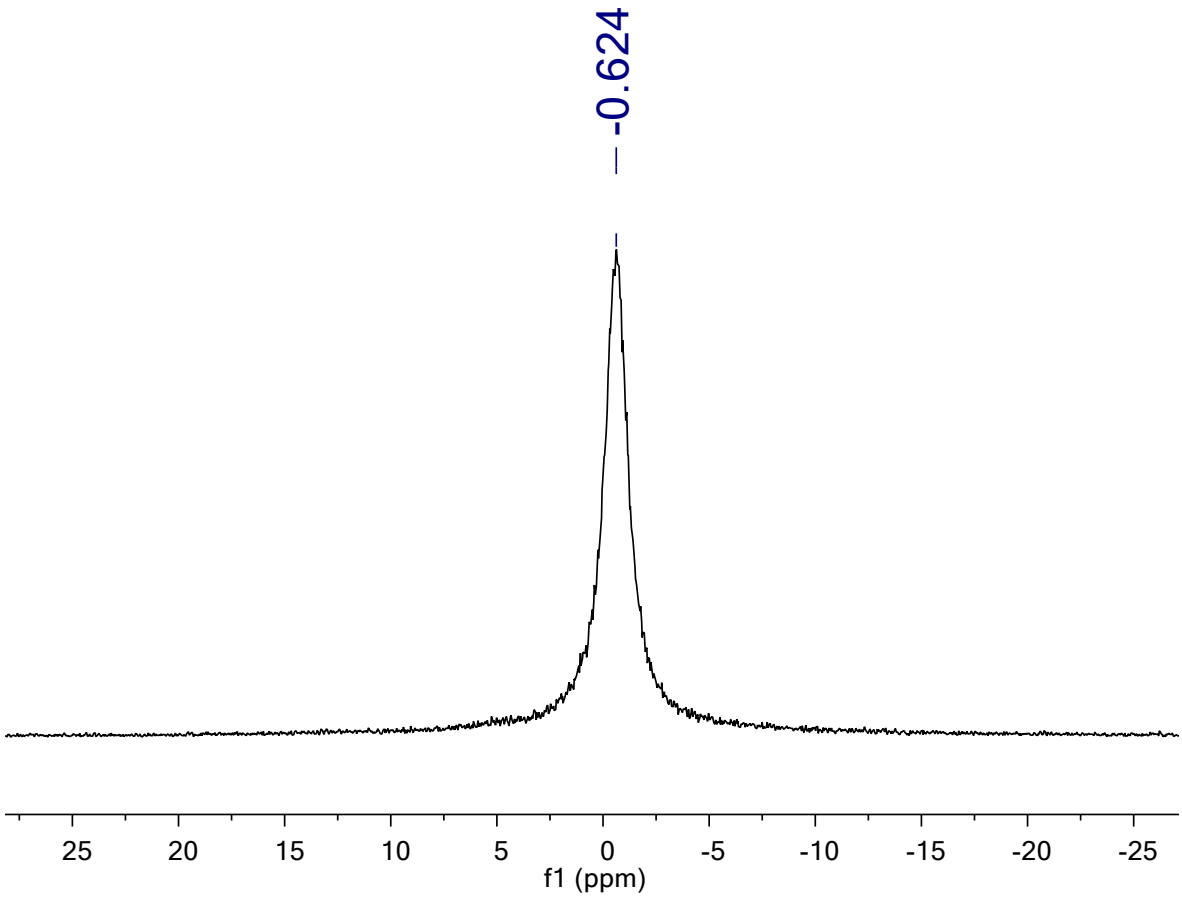



**Figure 13.** $^{11}B\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$).

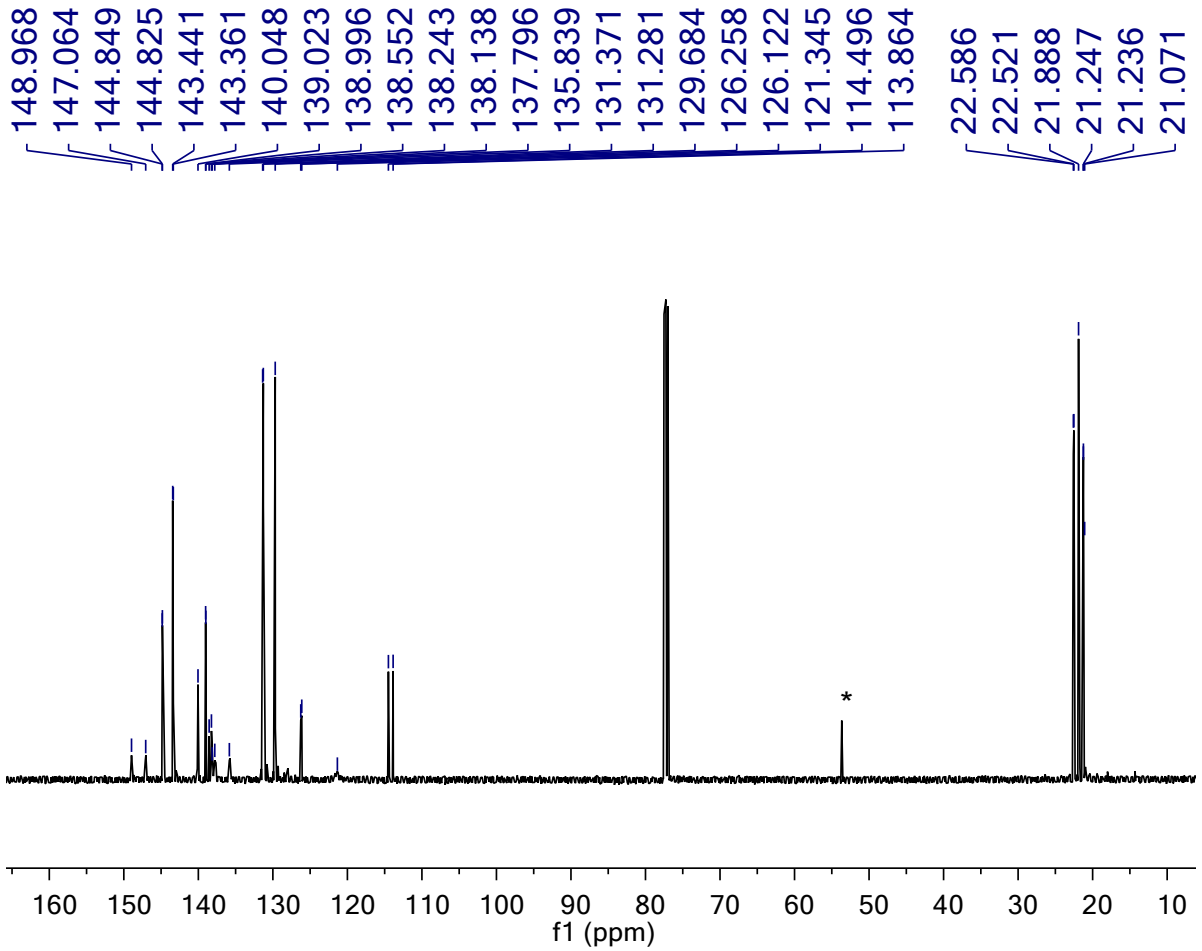
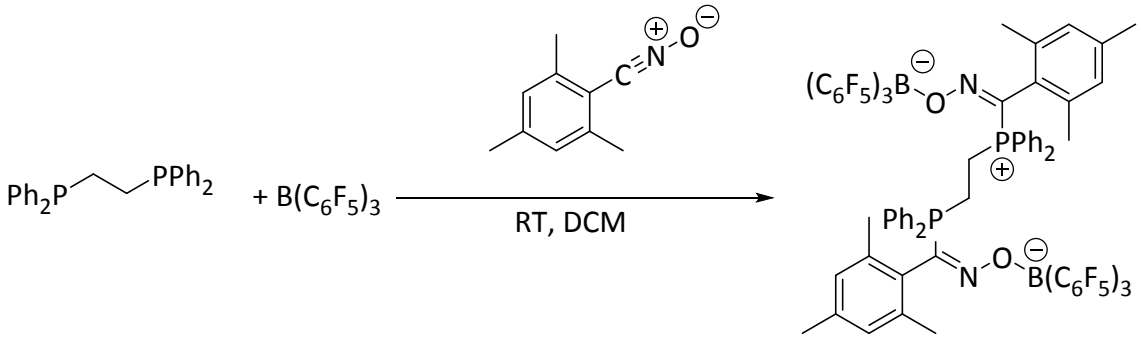



**Figure 14.** $^{13}C\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$). Asterisk denotes solvent impurities.

### *2.4 (MesC(NOB($C_6F_5$)$_3$)$Ph_2PCH_2$)$_2$ (4)*




A 1 mL $CH_2Cl_2$ solution of dppe (10.0 mg, 0.025 mmol) was combined with a 1 mL $CH_2Cl_2$ solution of $B(C_6F_5)_3$ (25.0 mg, 0.050 mmol). A white precipitate formed. To this suspension, a solution of MesCNO (8.0 mg, 0.050 mmol) in 1 mL of DCM was added dropwise. After 20 mins, 5 mL of cold pentane was added with vigorous stirring, yielding a white precipitate. The product was washed with 10 mL of pentane and collected by filtration. Yield: 38 mg (87% isolated yield). Diffraction quality single crystals were grown by vapour diffusion of hexane into a $CH_2Cl_2$ solution.

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.25 (m, 4H, Mes), 8.01-7.90 (ov, 20H, $P(C_6H_5)_3$), 4.01 (br, 4H, $CH_2$), 2.79 (s, 6H, *p*-$CH_3$, Mes), 2.55 (s, 12H, *o*-$CH_3$, Mes).

**$^{19}$F {$^1$H} NMR** (377 MHz, $CDCl_3$): δ -133.8 (d, $^3J_{FF}$ = 24.9 Hz, 2F, *o*-$C_6F_5$), -160.0 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-$C_6F_5$), -165.7 (m, 2F, *m*-$C_6F_5$).

**$^{31}$P {$^1$H}** NMR (162 MHz, $CDCl_3$): δ 12.6 (s).

**$^{11}$B {$^1$H} NMR** (128 MHz, $CDCl_3$): δ 0.1 (s).

**$^{13}$C {$^1$H} NMR** (126 MHz, $CDCl_3$): δ 148.07 (dm, 240 Hz, $C_6F_5$), 140.31, 139.23(dm, 248 Hz, $C_6F_5$), 137.62 (d, 3 Hz), 137. 03 (dm, 244 Hz, $C_6F_5$), 134.90 (d, 3 Hz), 133.77 (d, 10Hz), 129.69, 129.44 (d, 13 Hz), 128.94, 127.80 (d, 16 Hz), 121.49 (b), 117.13 (d, 82 Hz), 29.91, 21.07, 20.59. The resonance for the *ipso*-$B(C_6F_4H)_3$ carbon is likely not observed.

**Elemental analysis**: Calc.: C 56.45%, H 2.66%, N 1.61%. Exp.: C 55.64%, H 2.53%, N 1.60%

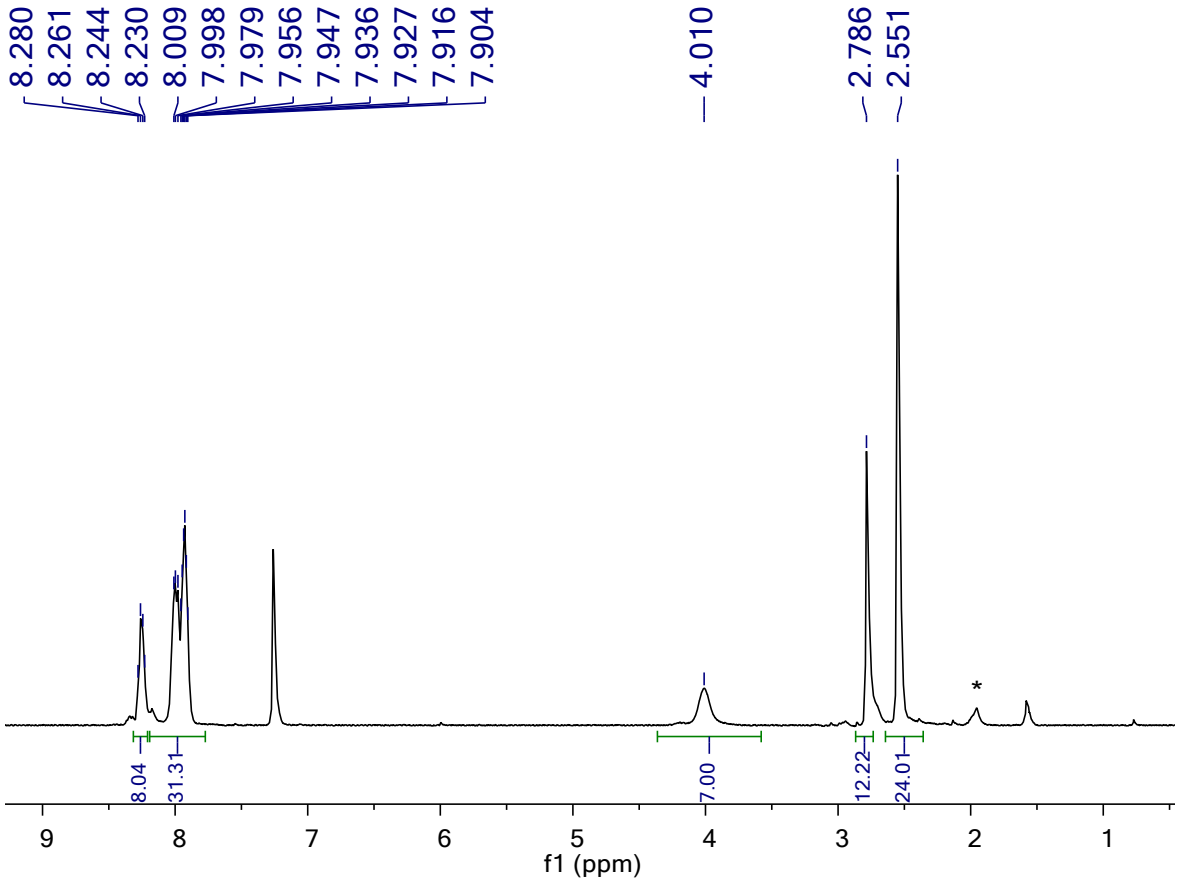



**Figure 15.** $^{1}$H NMR spectrum of **4** ($CDCl_3$). Asterisks denote solvent impurities.

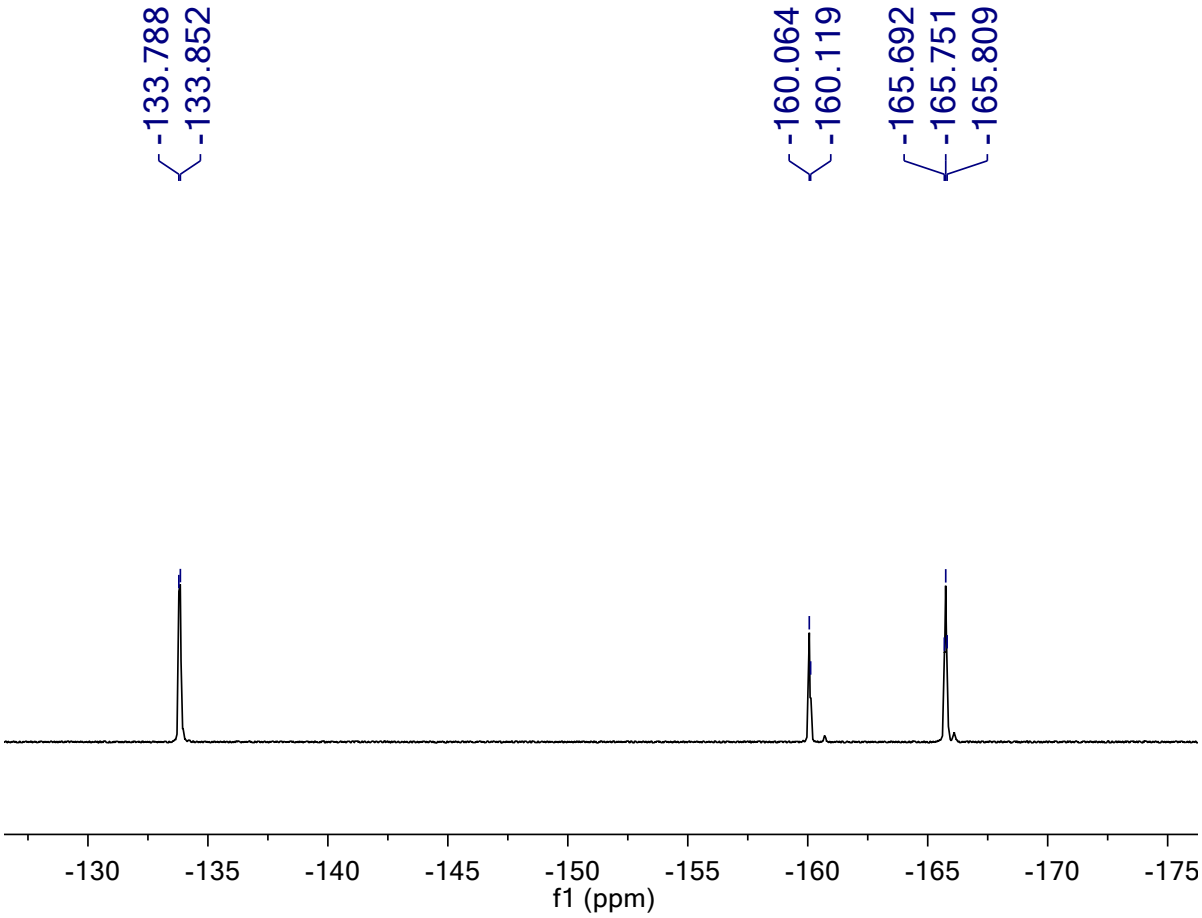



**Figure 16.** $^{19}F\{^{1}H\}$ NMR spectrum of **4** ($CDCl_3$).

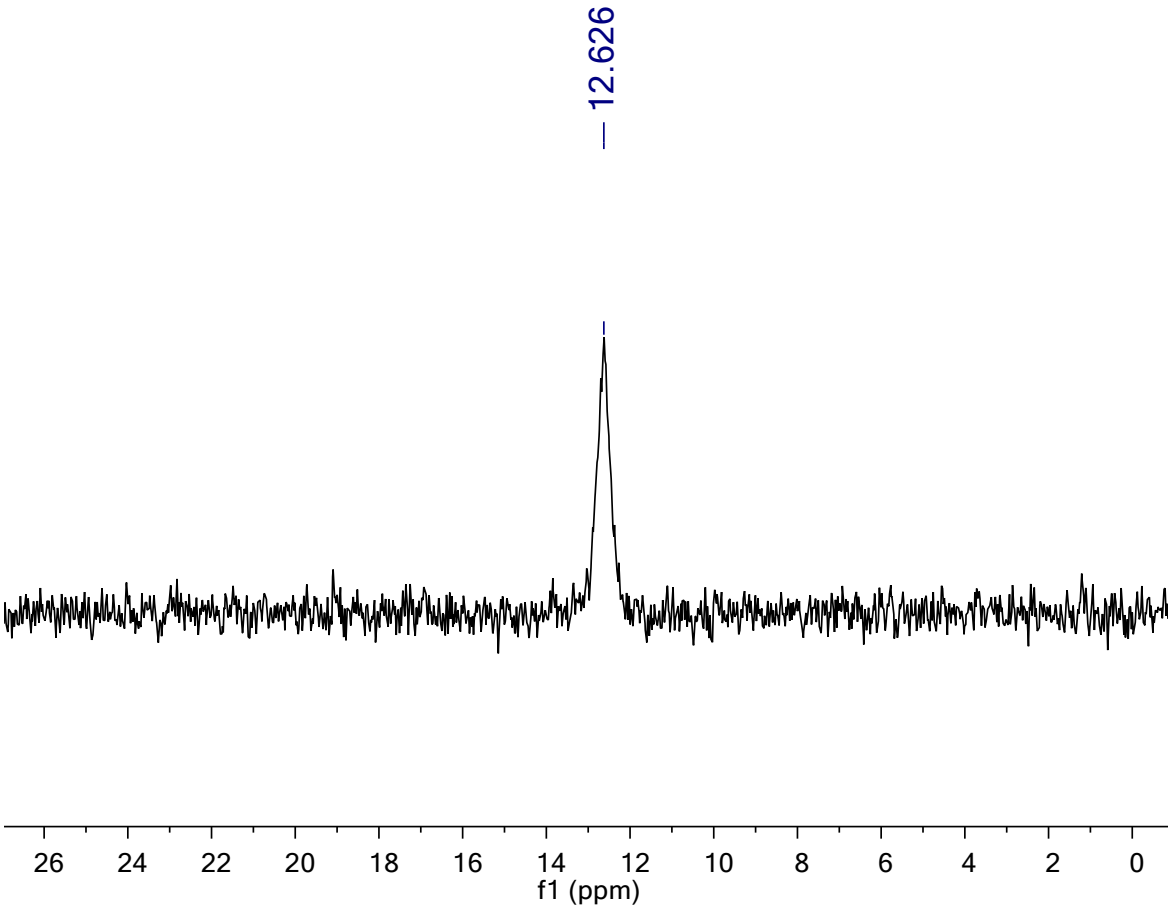



**Figure 17.** $^{31}P$ NMR spectrum of **4** ($CDCl_3$).

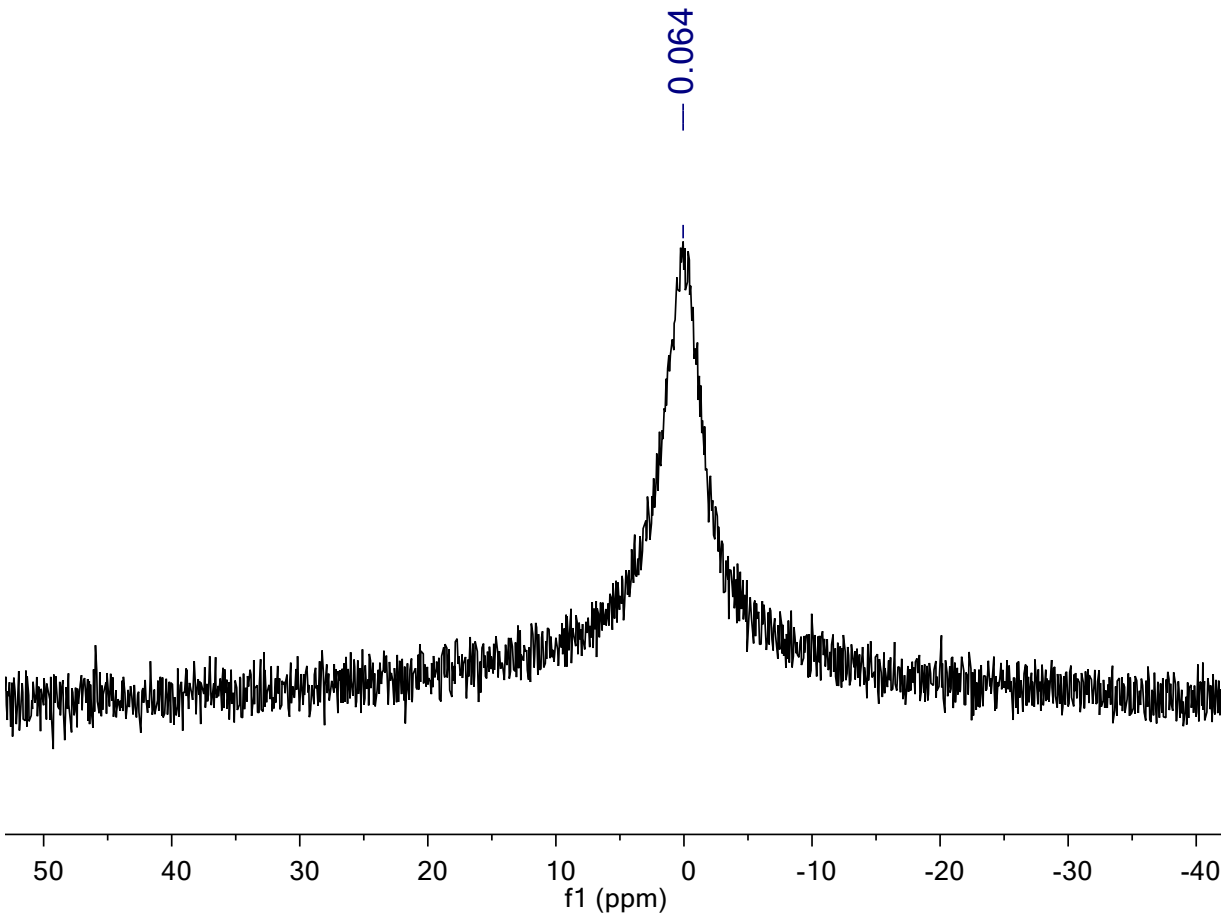



**Figure 18.** $^{11}B$ {$^{1}H$} NMR spectrum of **4** ($CDCl_3$).

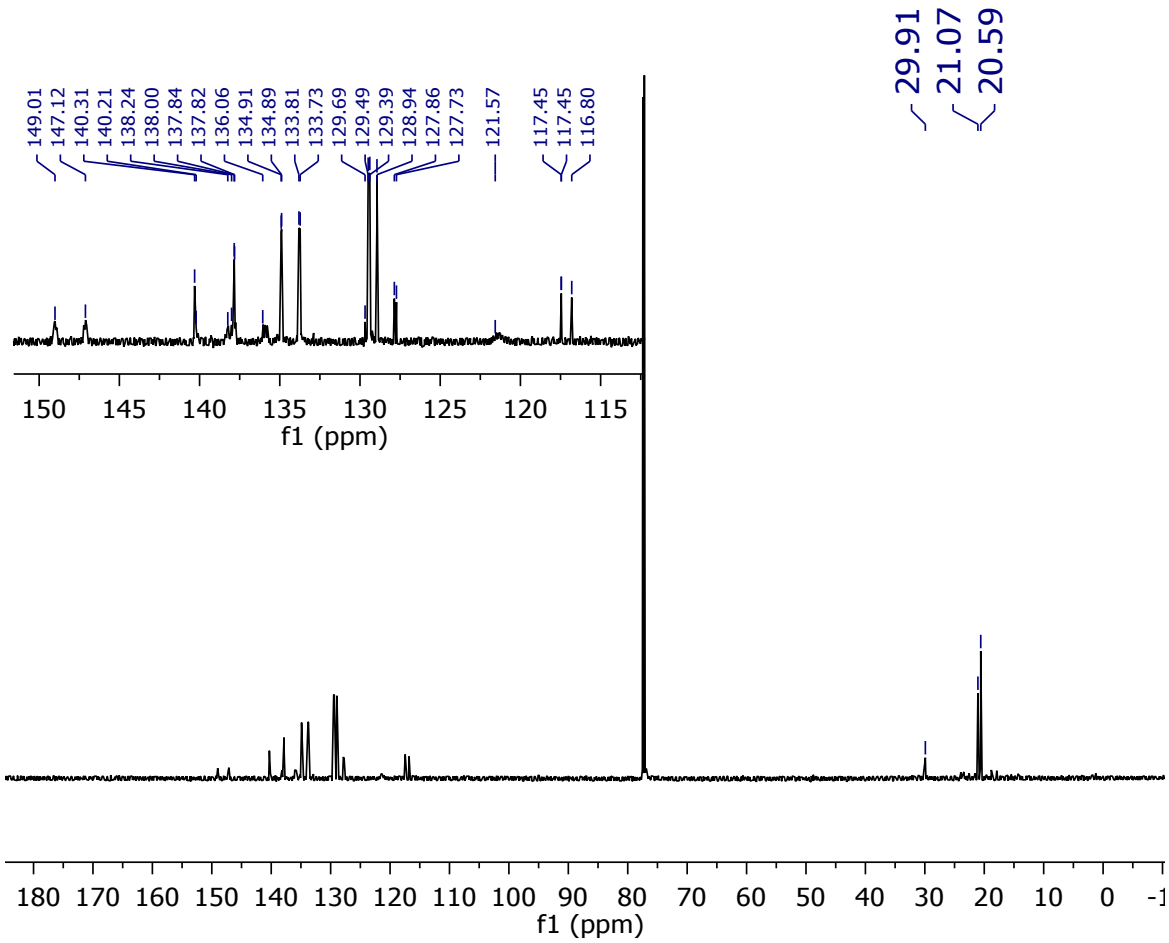
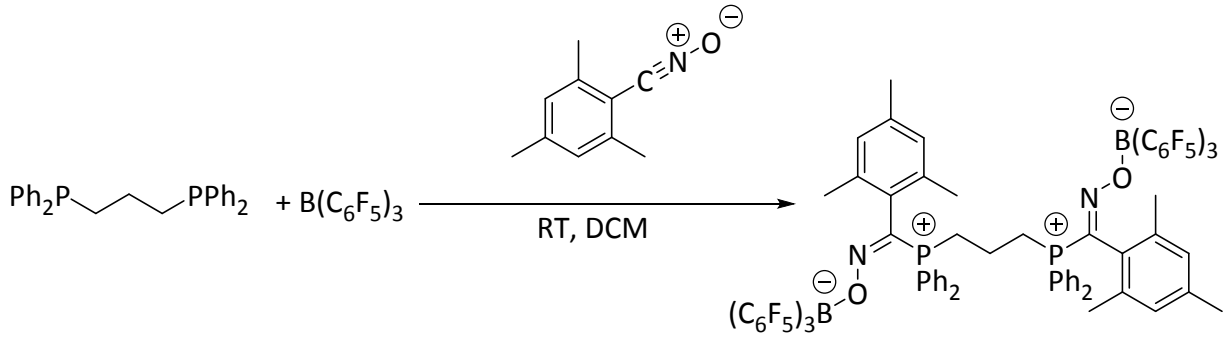



**Figure 19.** $^{13}C\{^{1}H\}$ NMR spectrum of **4** ($CDCl_3$).

### *2.4 (MesC(NOB($C_6F_5$)$_3$)$Ph_2PCH_2$)$_2CH_2$ (5)*




A 1 mL $CH_2Cl_2$ solution of dppp (16 mg, 0.039 mmol) was added to a 1 mL $CH_2Cl_2$ solution of $B(C_6F_5)_3$ (40 mg, 0.078 mmol). To the mixture, a solution of MesCNO (13 mg, 0.078 mmol) in 1 mL of $CH_2Cl_2$ was added dropwise. After 20 mins, 5 mL of cold pentane was added with vigorous stirring, yielding a white precipitate. The solution was then decanted, yielding the desired product as a white powder. Yield: 51.4 mg (88% isolated yield).

**$^1$H NMR** (400 MHz, $CDCl_3$): δ 8.28-8.24 (m, 4H, Mes), 8.03-7.90 (ov, 15H, $P(C_6H_5)_3$), 4.02 (br, 4H, $CH_2$), 2.79 (s, 6H, *p*-$CH_3$, Mes), 2.55 (s, 12H, *o*-$CH_3$, Mes), 1.95 (br, 2H, $CH_2$).

**$^{19}$F{$^1$H} NMR** (377 MHz, $CDCl_3$): δ -133.7 (d, $^3J_{FF}$ = 22.6 Hz, 2F, *o*-$C_6F_5$), -160.3 (t, $^3J_{FF}$ = 18.9 Hz, 1F, *p*-$C_6F_5$), -165.8 (m, 2F, *m*-$C_6F_5$).

**$^{31}$P{$^1$H}** NMR (162 MHz, $CDCl_3$): δ 9.8 (s).

**$^{11}$B{$^1$H} NMR** (128 MHz, $CDCl_3$): δ 0.3 (s).

**$^{13}$C{$^1$H}** NMR (176 MHz, $CDCl_3$) δ 147.84 (dm, 241 Hz, $C_6F_5$), 140.08, 139.00 (dm, 250 Hz, $C_6F_5$), 137.61 (d, 3 Hz), 136.73 (dm, 236 Hz, $C_6F_5$), 134.68 (d, 3 Hz), 133.57 (d, 11 Hz), 130.44 (d, 11 Hz), 129.22 (d, 12 Hz), 128.72, 127.57 (d, 16 Hz), 116.90 (d, 80 Hz), 34.14, 31.61, 20.89, 20.41, 14.10 (d, 10 Hz). The resonance for the *ipso*-$B(C_6F_4H)_3$ carbon is likely not observed.

**Elemental analysis**: Calc.: C 56.68%, H 2.75%, N 1.59%. Exp.: C 56.42%, H 2.65%, N 1.61%

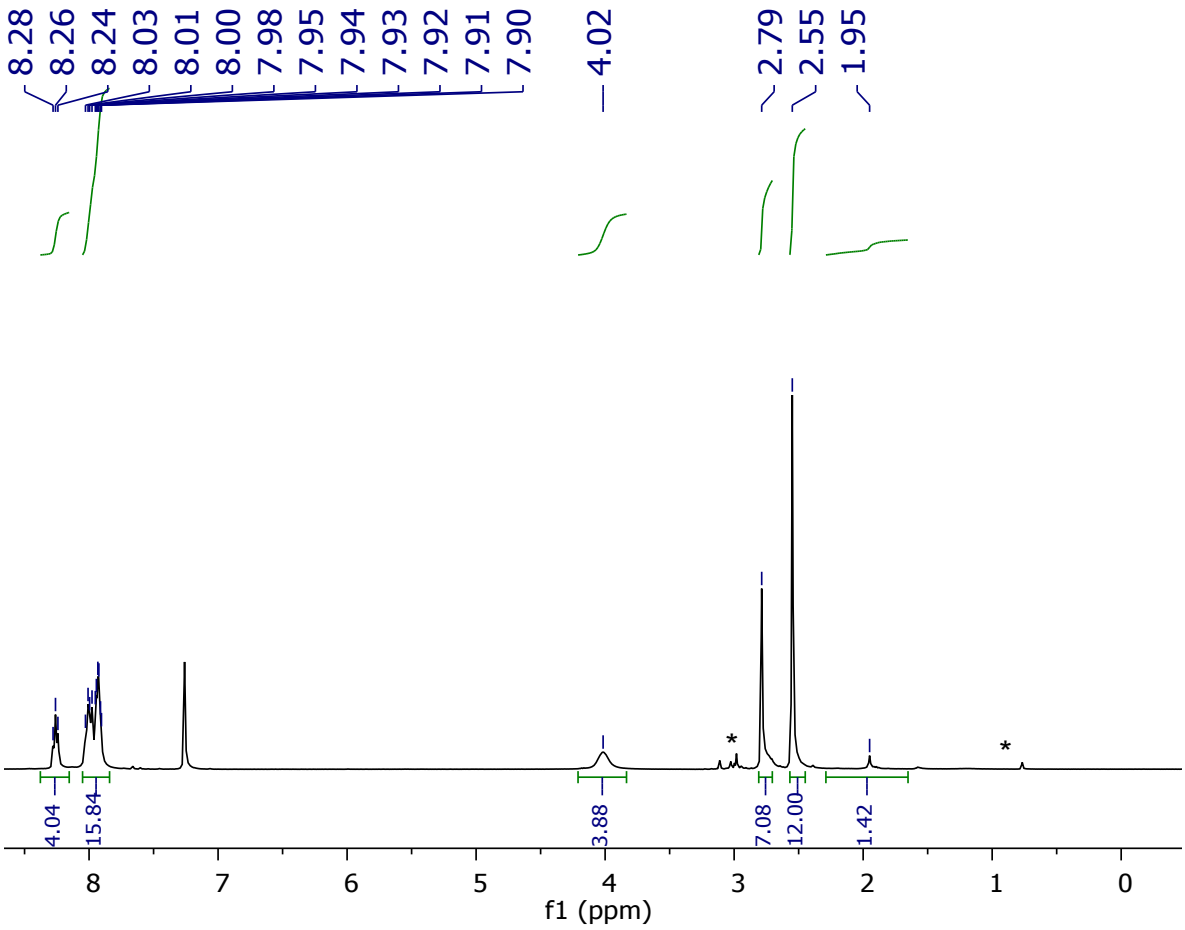



**Figure 20.** $^{1}$H NMR spectrum of **5** ($CDCl_3$). Asterisks denote solvent impurities.

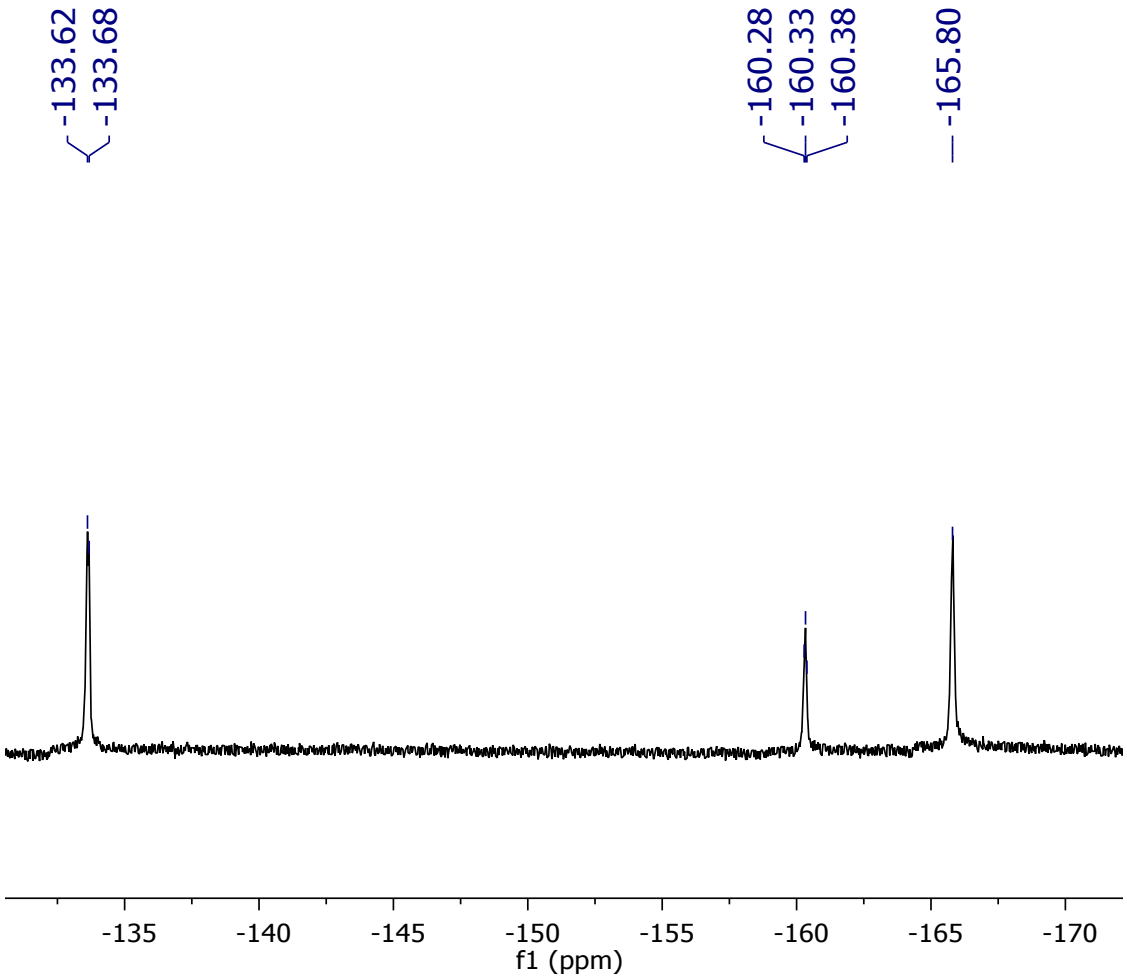



**Figure 21.** $^{19}F\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

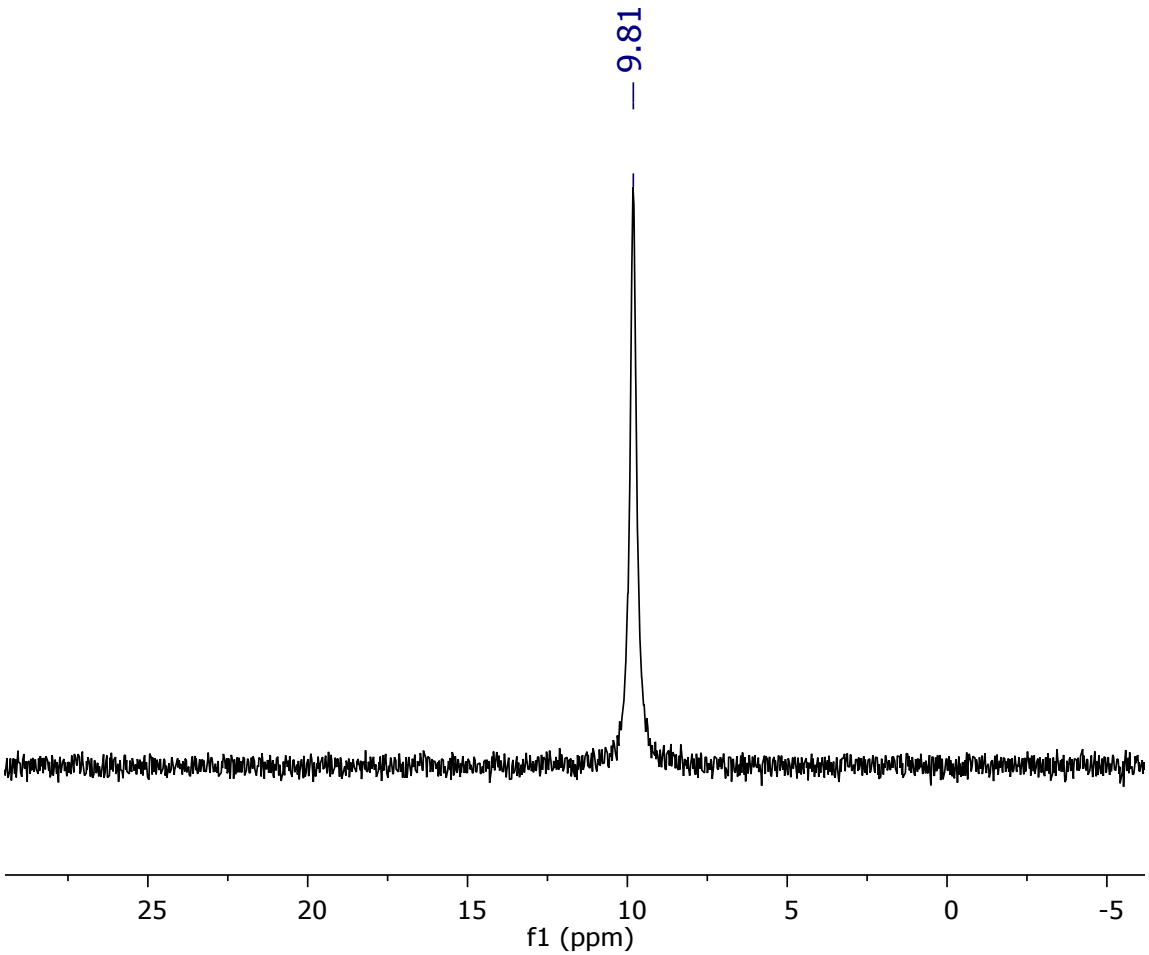



**Figure 22.** $^{31}P\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

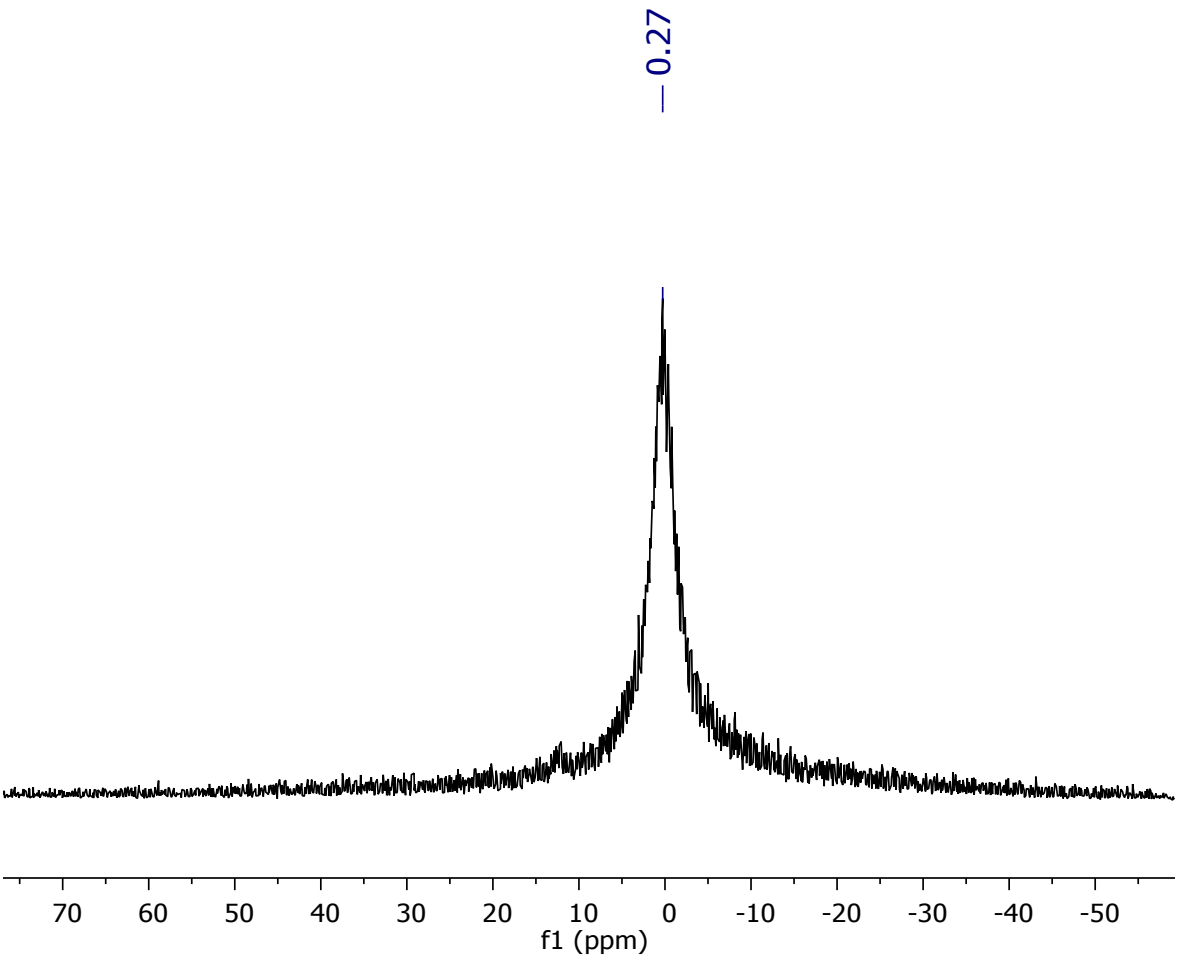



**Figure 23.** $^{11}B\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

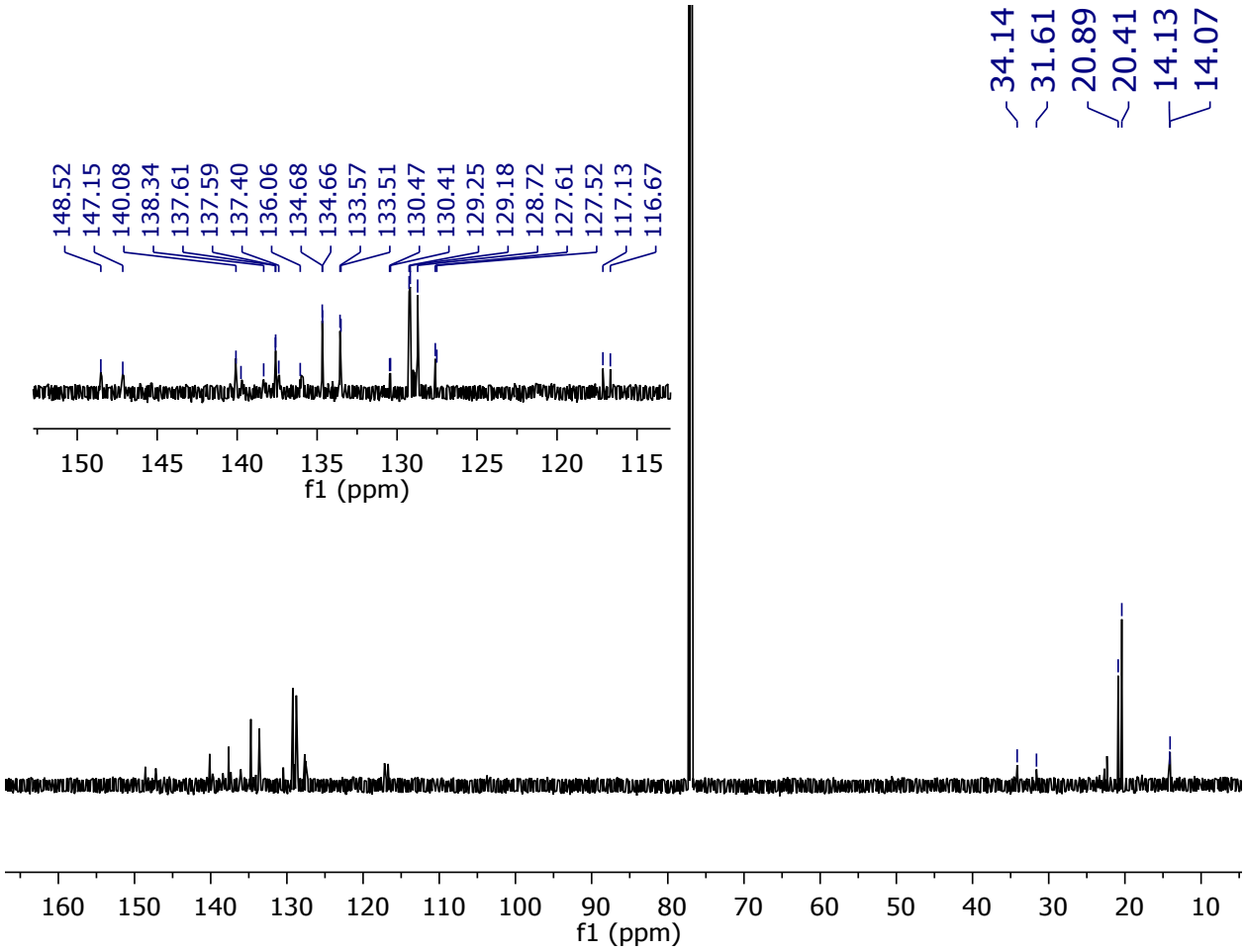
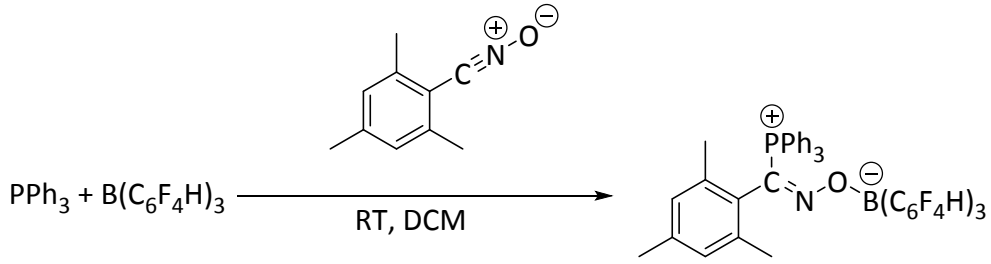



**Figure 24.** $^{13}C\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$).

### *2.6 [MesC(Ph$_3$P)NOB(C$_6$F$_4$H)$_3$] (6)*




Solutions of $PPh_3$ (22.0mg, 0.084 mmol, 1 equiv.) and $B(C_6F_4H)_3$ (38.5mg, 0.084 mmol, 1 equiv.) were combined in 3mL of $CH_2Cl_2$, yielding a white precipitate. To this heterogenous mixture, a solution of MesCNO (13.6mg, 0.084 mmol, 1 equiv.) in 1mL $CH_2Cl_2$ was added dropwise. After complete addition of MesCNO, the reaction mixture was clear and homogeneous. The solvent removed *in vacuo*, and the white solid was recrystallized from benzene/pentane at room temperature over 24 hours. Yield: 52.5 mg (71 % isolated yield).

**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K): δ 8.0-7.1 (b, 15H, P($C_6H_5$)$_3$), 6.7 (m, 3H, B($C_6F_4H$)$_3$), 6.6 (s, 2H, C*H*, Mes), 2.16 (s, 3H, *p*-C$H_3$, Mes), 1.93 ppm (s, 6H, *o*-C$H_3$, Mes).

**$^{19}$F{$^1$H} NMR** (376 MHz, $CDCl_3$, 298 K): δ -132.9 (m, *o*-B($C_6F_4$H)$_3$), -143.4 ppm (m, *m*-B($C_6F_4$H)$_3$).

**$^{31}$P{$^1$H} NMR** (162 MHz, $CDCl_3$, 298 K): δ 5.5 ppm (s)

**$^{11}$B{$^1$H} NMR** (128 MHz, $CDCl_3$, 298 K): δ 0.1 (b)

**$^{13}$C{$^1$H} NMR** (125 MHz, $CDCl_3$, 298 K): δ 148.21 (dm, 248 Hz, $C_6F_5$), 145.34 (dm, 255 Hz, $C_6F_5$), 139.95, 139.15, 134.50 (d, 164 Hz), 131.83 (d, 35 Hz), 130.29 (b), 129.62, 128.74 (b), 128.08, 119.17 (dt, 84 Hz, 8 Hz), 102.57 (dt, 166 Hz, 22 Hz), 21.40, 20.14. The resonance for the *ipso*-B($C_6F_4H$)$_3$ carbon is likely not observed.

**Elemental Analysis**: Calc.: C 62.75%, H 3.21%, N 1.59%. Exp.: C 62.52%, H 3.40%, N 1.62%

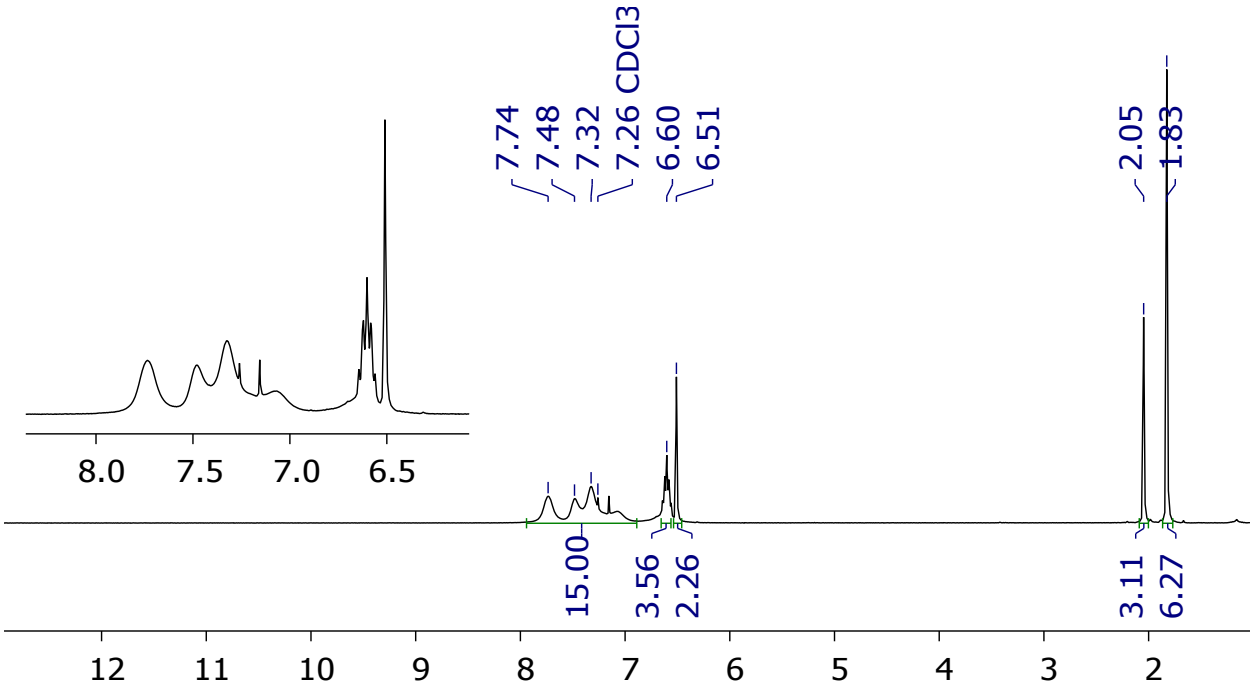



**Figure 25.** $^{1}H$ NMR spectrum of **6** ($CDCl_3$).

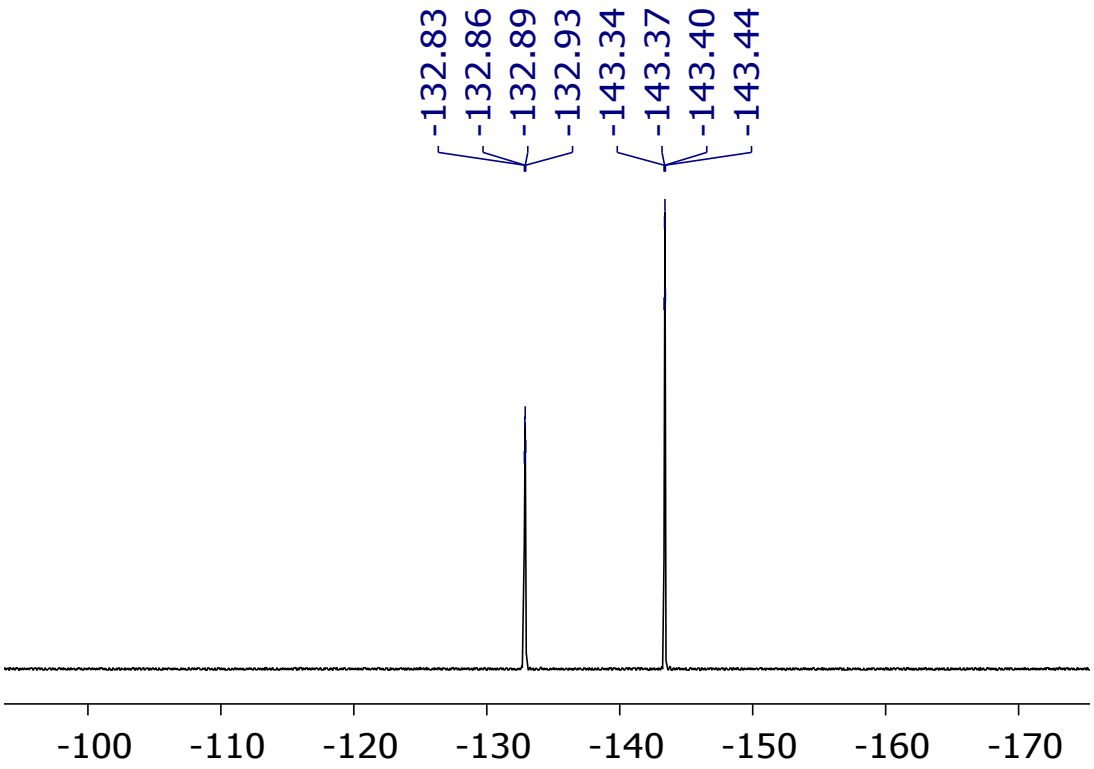



**Figure 26.** $^{19}F$ NMR spectrum of **6** ($CDCl_3$).

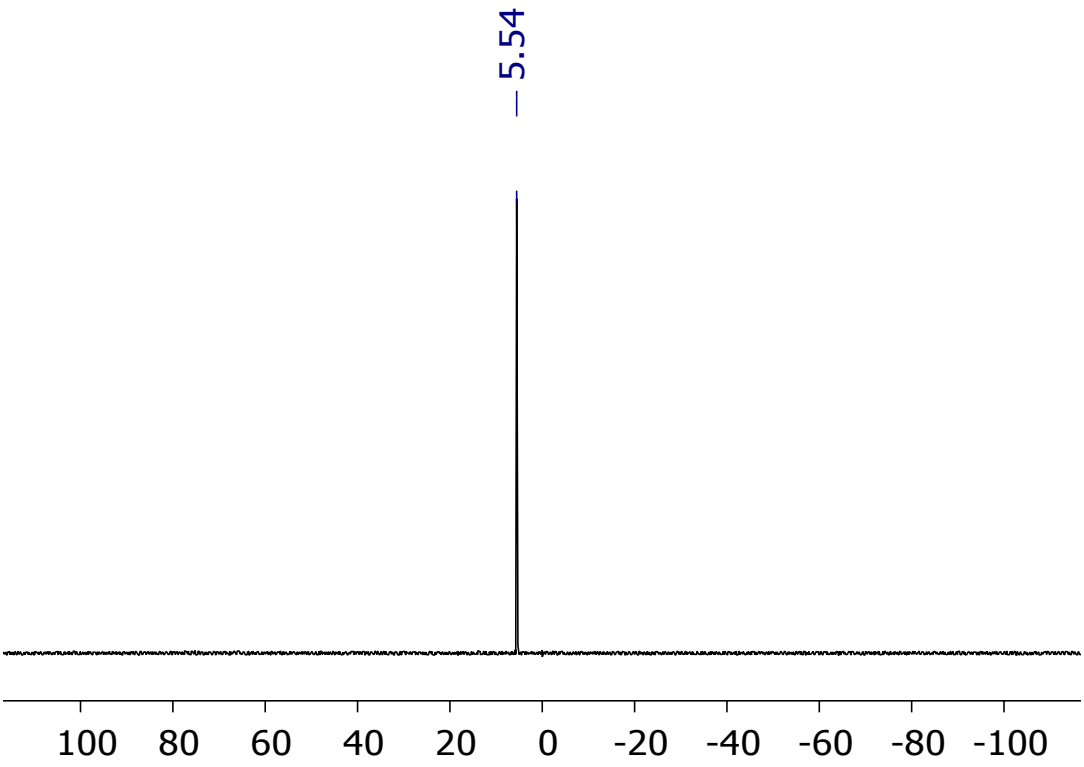



**Figure 27.** $^{31}P\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$).

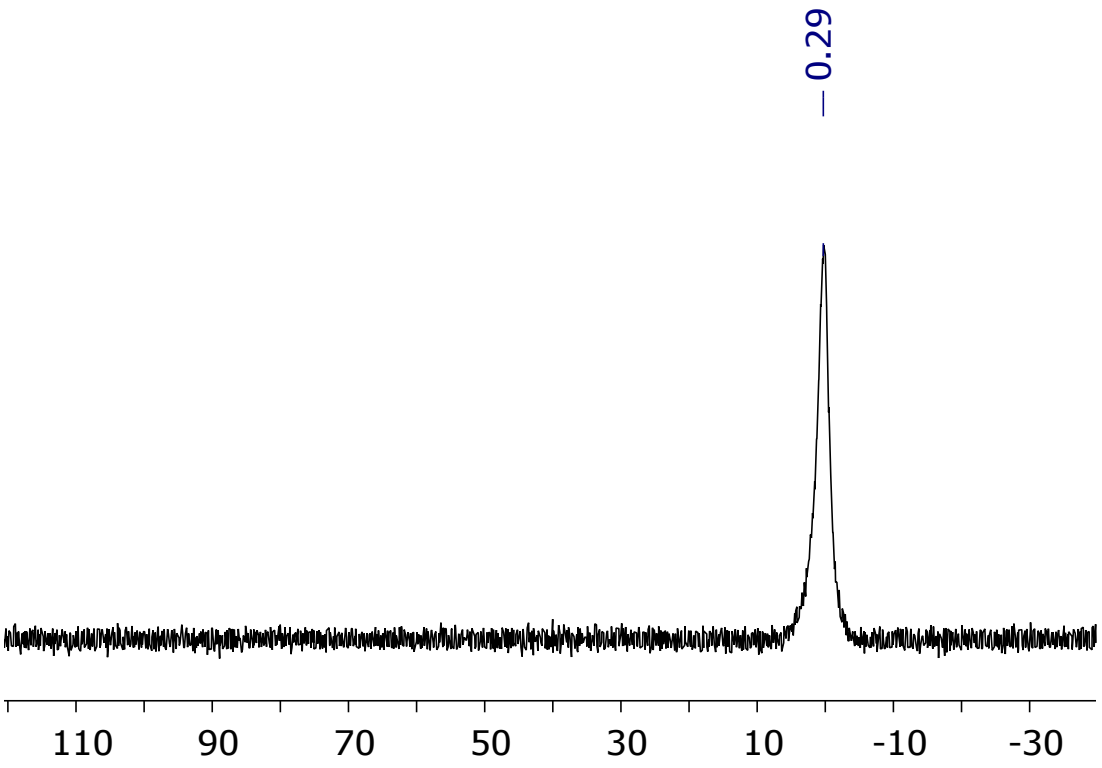



**Figure 28.** $^{11}B\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$).

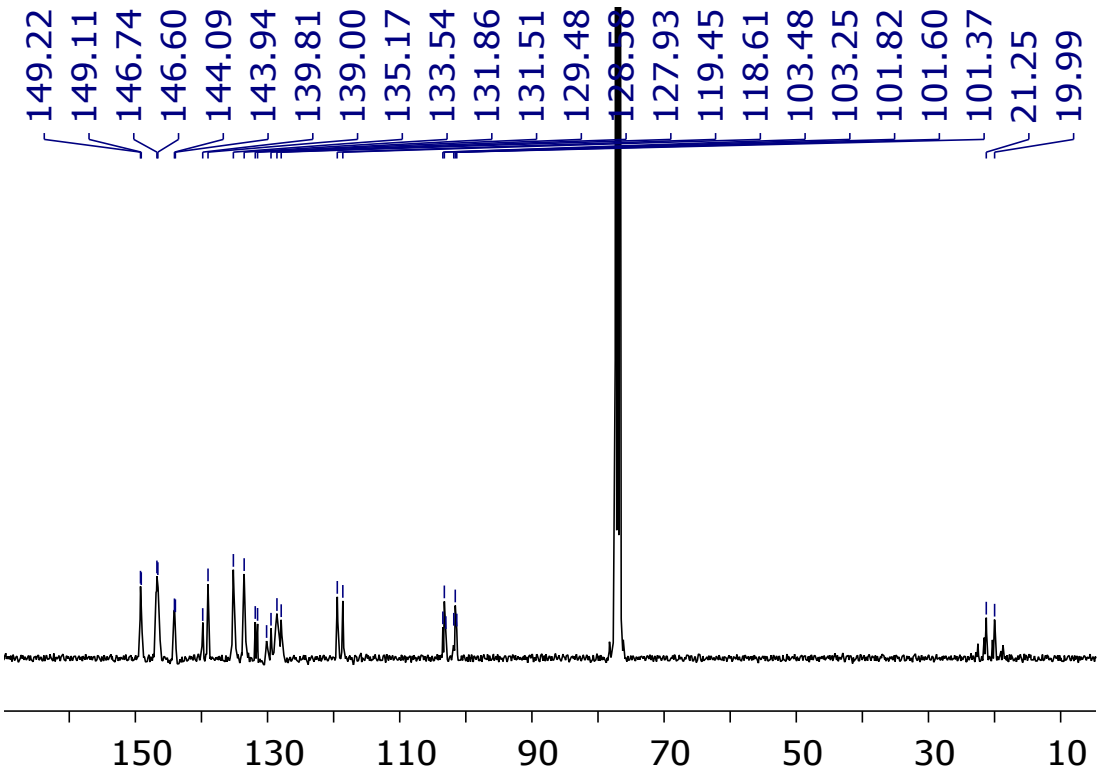
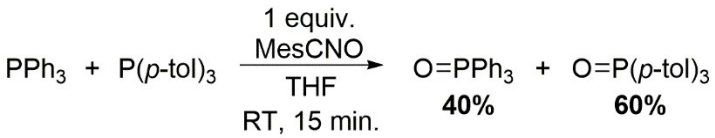



**Figure 29.** $^{13}C\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$).

## 3. Borane Abstraction from Compound 1




Solutions of $PPh_3$ (10.1mg, 3.9 x $10^{-2}$ mmol, 1 equiv.) and P(*p*-tol)$_3$ (11.7mg, 3.9 x $10^{-2}$ mmol, 1 equiv.) in THF were combined in a 4mL vial. A THF solution of MesCNO (6.2mg, 3.9 x $10^{-2}$ mmol, 1 equiv.) was slowly added to the phosphine mixture. This reaction mixture was transferred to an NMR tube. After 30 minutes, $^{31}P\{^1H\}$ NMR spectroscopy indicated phosphine oxidation in the following ratio: 40% $OPPh_3$ and 60% OP(*p*-tol)$_3$. Unreacted $PPh_3$ and P(*p*-tol)$_3$ were also observed. The reaction mixture is completely homogeneous.

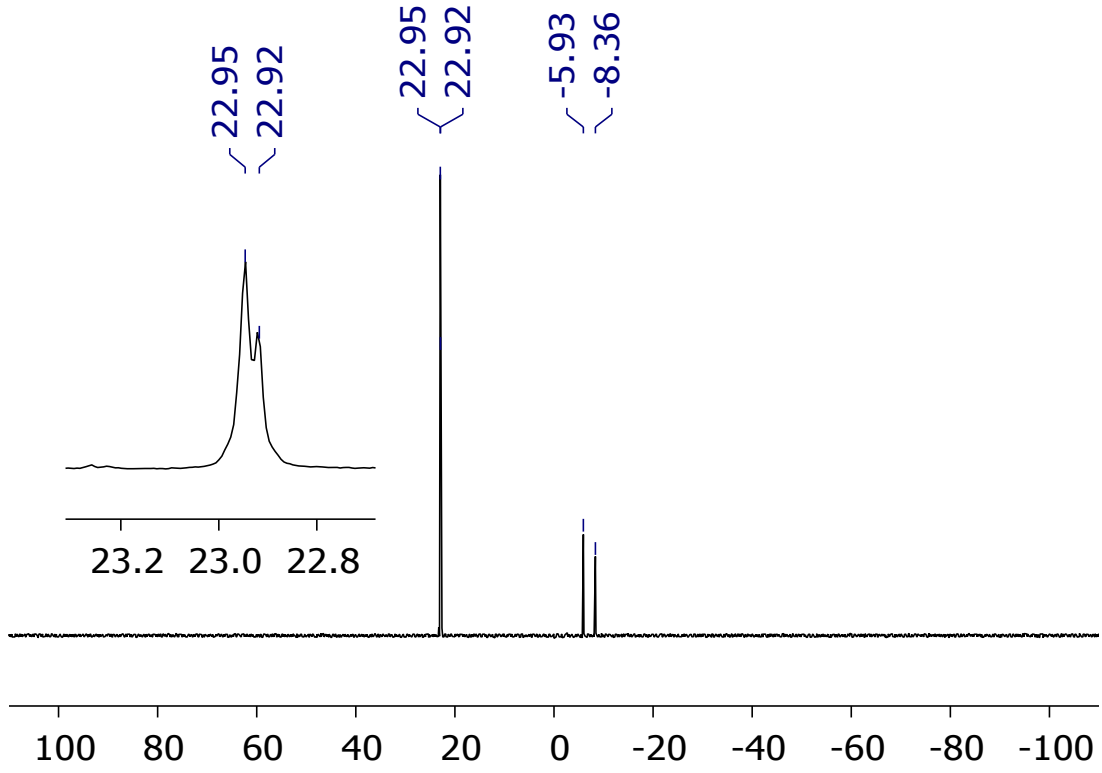
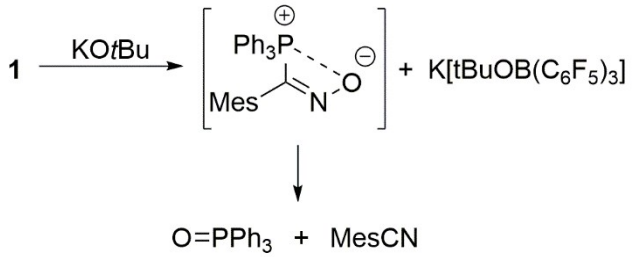



**Figure 30.** $^{31}P\{^1H\}$ NMR spectrum (THF) of reaction mixture of $PPh_3$, $OPPh_3$, P(*p*-tol)$_3$, OP(*p*-tol)$_3$




Compound **1** (7.8 mg, 8.3 x $10^{-3}$ mmol, 1 equiv.) was dissolved in $CH_3CN$, then transferred to an NMR tube charged with excess KO*t*Bu (~15 mg, 0.133 mmol, ~15 equiv). The heterogeneous solution because pale yellow, and a large amount of undissolved KO*t*Bu was observed in the NMR tube. $^{31}P\{^1H\}$ NMR spectroscopy after 30 minutes indicated complete consumption of **1** and quantitative formation of $OPPh_3$.

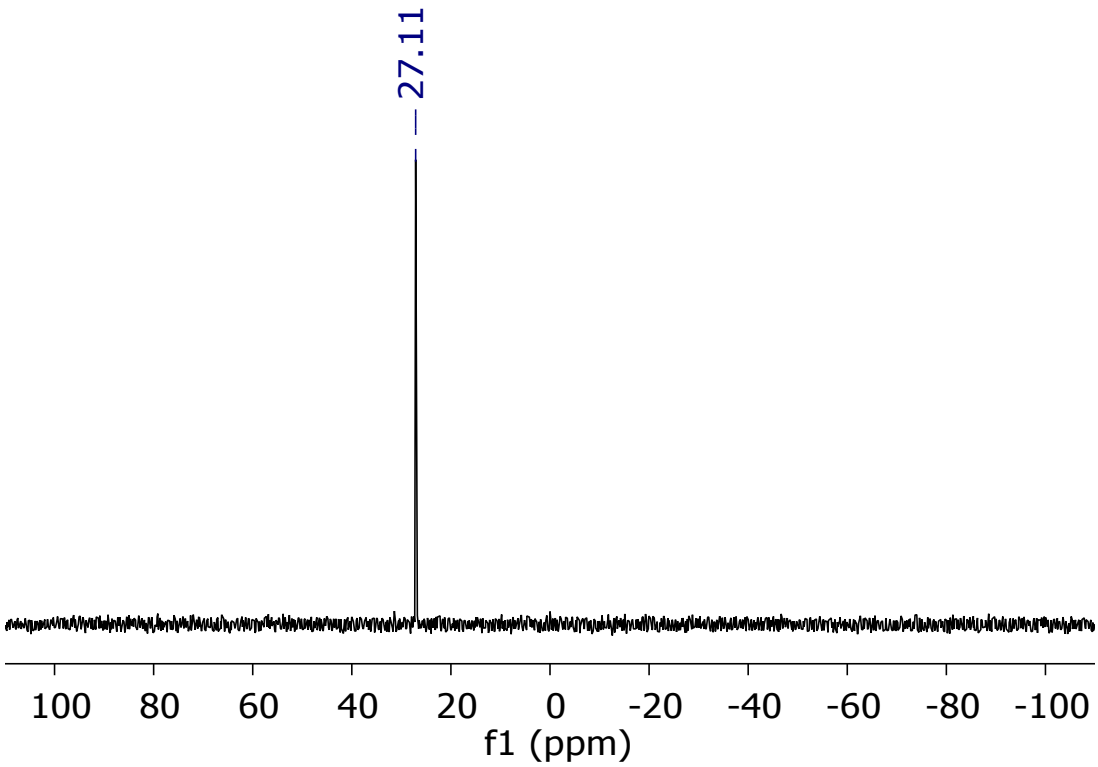
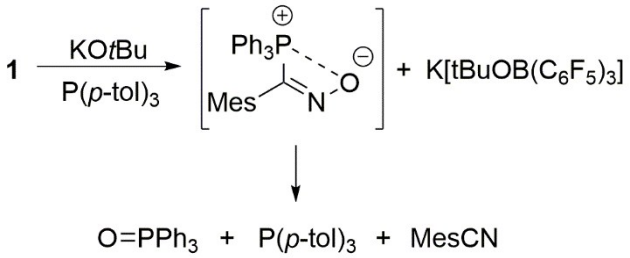



**Figure 31.** $^{31}P\{^1H\}$ NMR spectrum ($CH_3CN$) of reaction mixture of **1** and KO*t*Bu




Compound **1** (7.8 mg, 8.3 x $10^{-3}$ mmol, 1 equiv.) was dissolved in $CH_3CN$, then transferred to a vial charged with P(*p*-tol)$_3$ (2.5mg, 8.3 x $10^{-3}$ mmol, 1 equiv.). This homogeneous solution was agitated for 10 minutes, then transferred to an NMR tube charged with excess solid KO*t*Bu (~15 mg, 0.133 mmol, ~15 equiv). The heterogeneous solution because pale yellow, and a large amount of undissolved KO*t*Bu was observed in the NMR tube. $^{31}P\{^1H\}$ NMR spectroscopy after 30 minutes indicated complete consumption of **1** and quantitative formation of $OPPh_3$ and unreacted P(*p*-tol)$_3$.

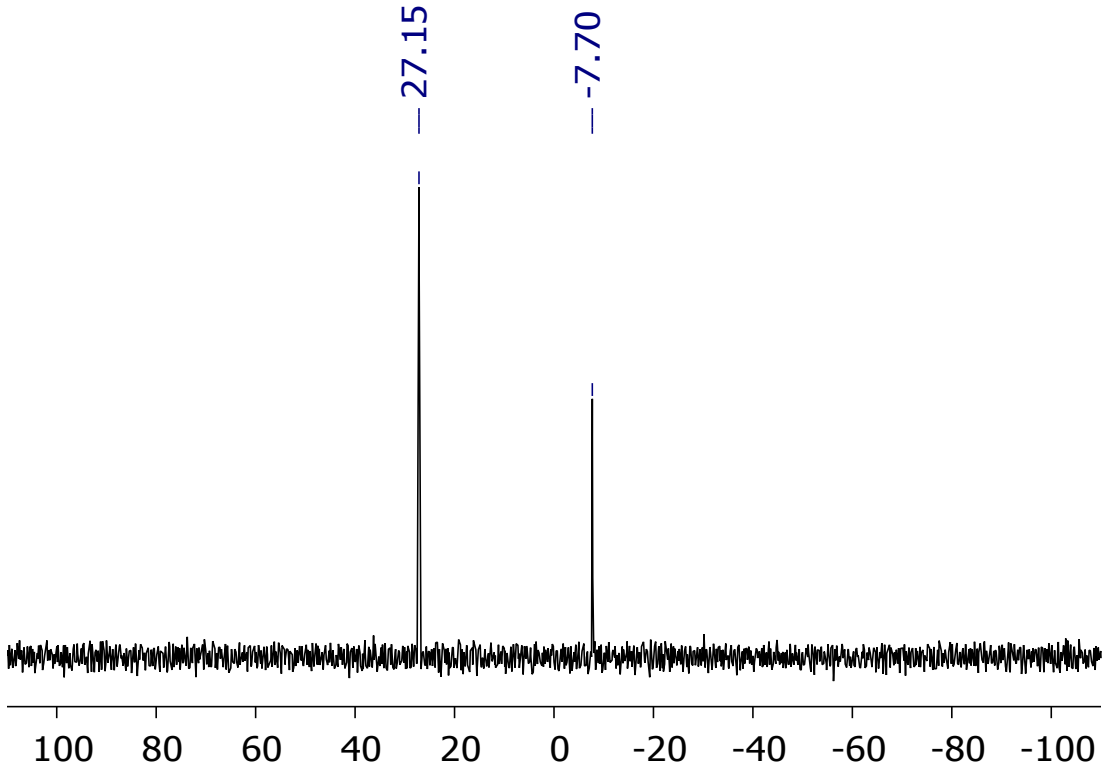
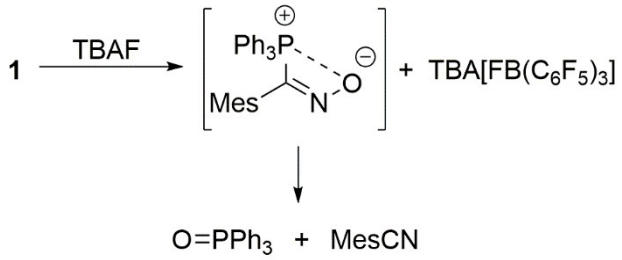



**Figure 32.** $^{31}P\{^1H\}$ NMR spectrum ($CH_3CN$) of reaction mixture of **1**, P(*p*-tol)$_3$, and KO*t*Bu




Compound **1** (5.7 mg, 6.1 x $10^{-3}$ mmol, 1 equiv.) was dissolved in THF, then transferred to an NMR tube. TBAF (1M solution in THF, 21 µL, 1.8 x $10^{-2}$ mmol, ~3 equiv) was added to the NMR tube. The solution remained homogeneous and colourless. $^{31}P\{^{1}H\}$ NMR spectroscopy after 30 minutes indicated complete consumption of **1** and quantitative formation of $OPPh_3$.

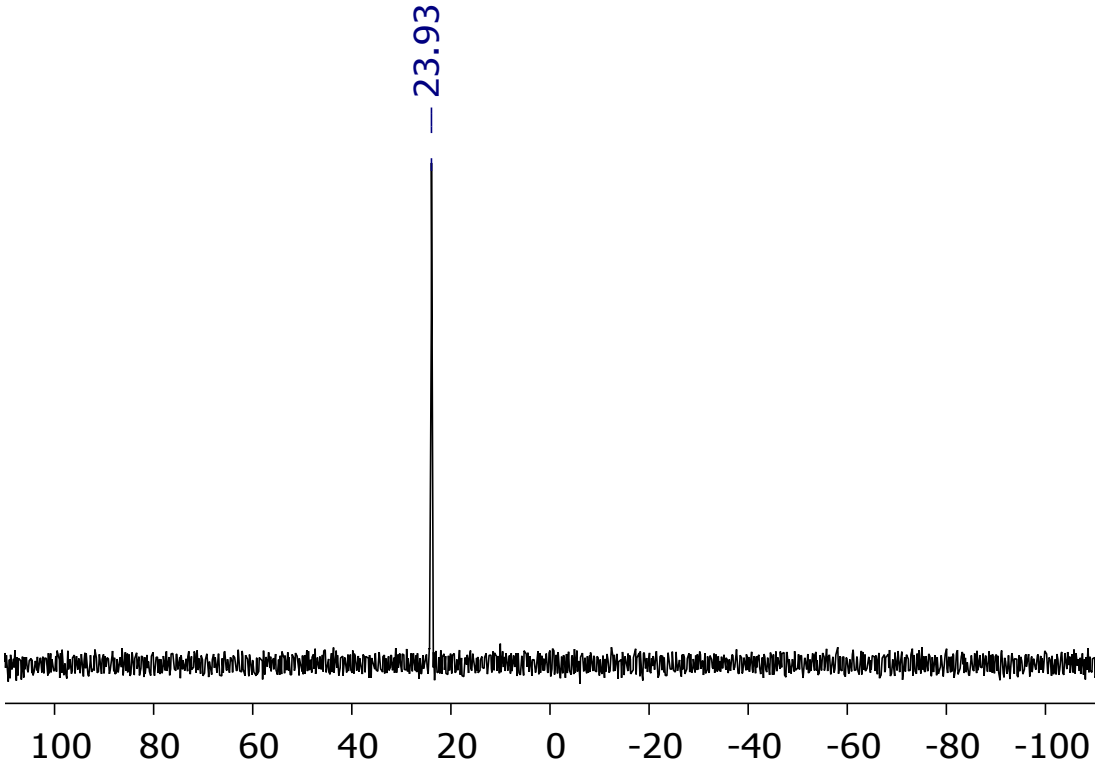
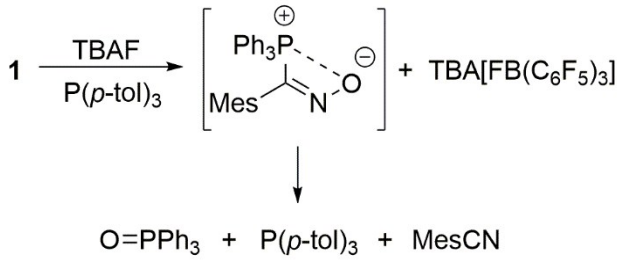



**Figure 33.** $^{31}P\{^{1}H\}$ NMR spectrum (THF) of reaction mixture of **1** and TBAF




Compound **1** (5.7 mg, 6.1 x $10^{-3}$ mmol, 1 equiv.) was dissolved in THF, then transferred to a vial charged with P(*p*-tol)$_3$ (2.2mg, 6.1 x $10^{-3}$ mmol, 1 equiv.). The clear and colourless solution was transferred to an NMR tube. TBAF (1M solution in THF, 22 µL, 1.8 x $10^{-2}$ mmol, ~3 equiv) was added to the NMR tube. The solution remained homogeneous and colourless. $^{31}P\{^{1}H\}$ NMR spectroscopy after 30 minutes indicated complete consumption of **1** and quantitative formation of $OPPh_3$ and unreacted P(*p*-tol)$_3$. The reaction mixture is completely homogeneous.

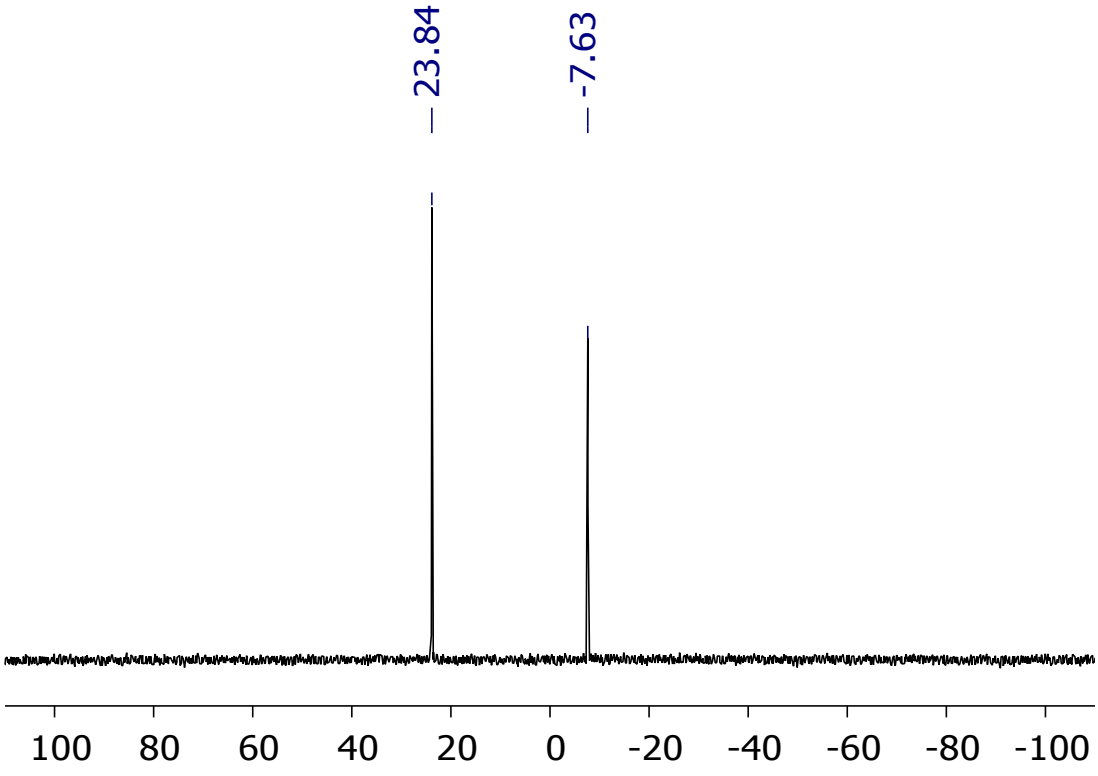



**Figure 34.** $^{31}P\{^{1}H\}$ NMR spectrum (THF) of reaction mixture of **1**, P(*p*-tol)$_3$, and TBAF

# 4. Lewis Acid Exchange reactions

**a)** Reaction of compound **1** and $B(C_6F_4H)_3$

Compound **1** (25.1mg, 1 equiv.) and $B(C_6F_4H)_3$ (12.3mg, 1 equiv.) were combined in 0.4 mL of bromobenzene. The homogeneous solution was transferred to an NMR tube, which was kept in the glove box for 16 hours at ambient temperature. After this time, the reaction mixture was analyzed by $^{19}F$ and $^{31}P\{^1H\}$ NMR spectroscopy, indicating ~30% conversion to compound **6** and ~70% of unreacted compound **1**.

**b)** Reaction of compound **6** and $B(C_6F_5)_3$

Compound **6** (14.6mg, 1 equiv.) and $B(C_6F_5)_3$ (8.5mg, 1 equiv.) were combined in 0.4 mL of bromobenzene. The homogeneous solution was transferred to an NMR tube, which was kept in the glove box for 16 hours at ambient temperature. After this time, the reaction mixture was analyzed by $^{19}F$ and $^{31}P\{^1H\}$ NMR spectroscopy, indicating ~70% conversion to compound **1** and ~30% of unreacted compound **6**.

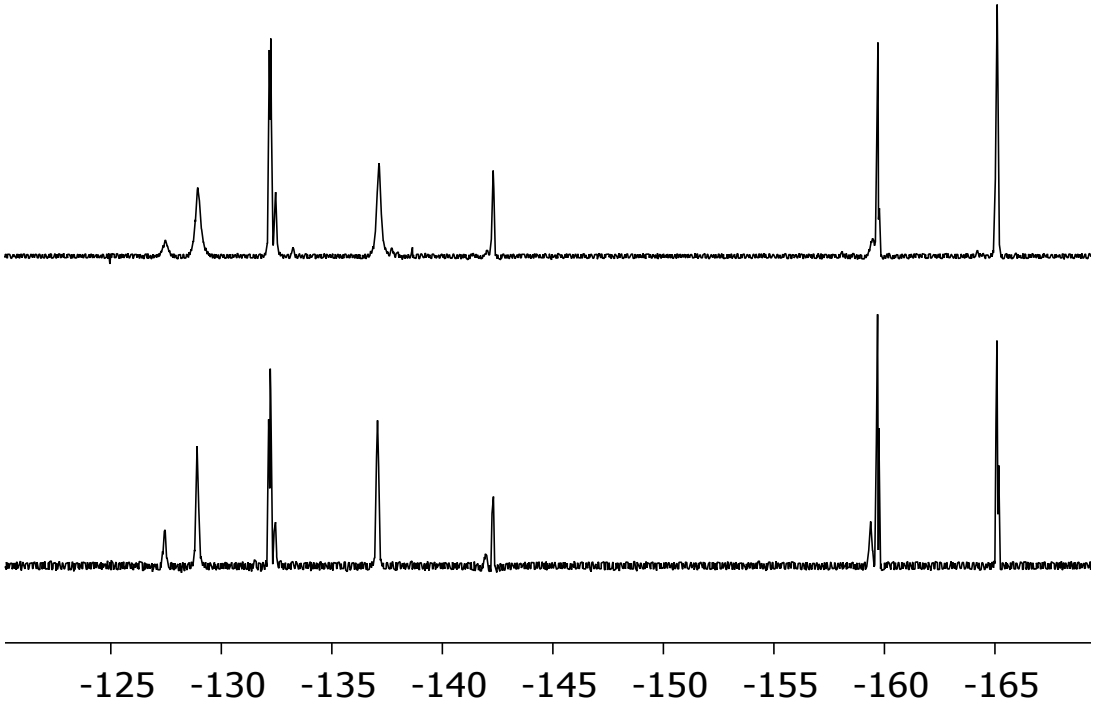



**Figure 35.** $^{19}F$ NMR spectra ($C_6H_5Br$) of reactions **(a)** (top) and **(b)** (bottom) after 16 hours.

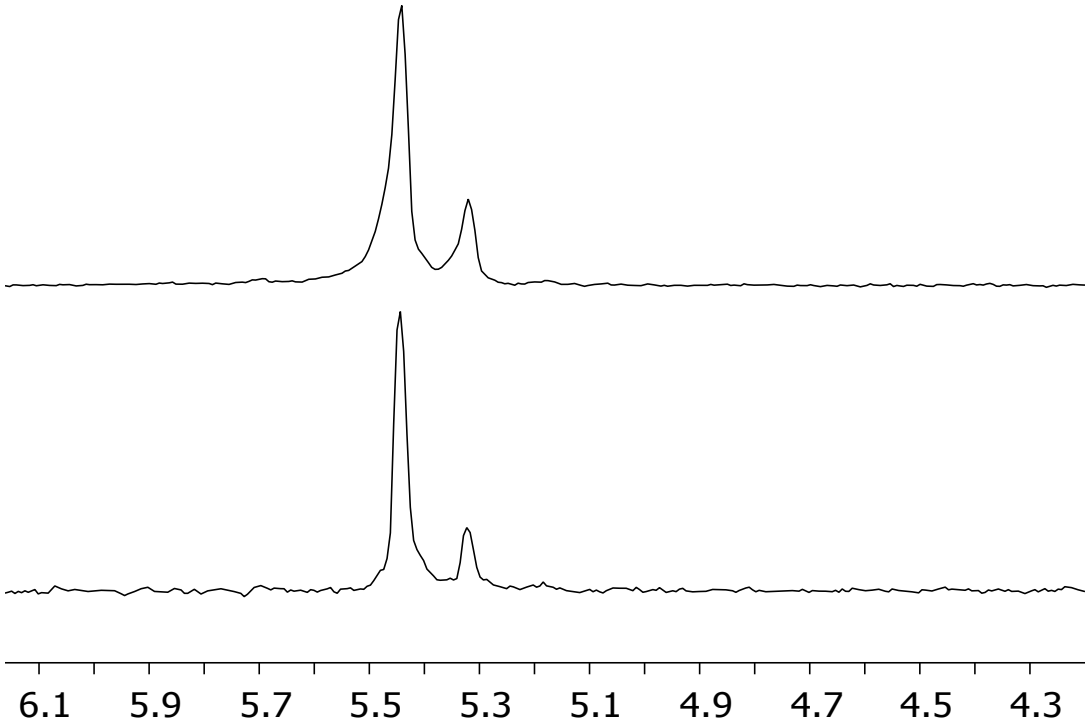



**Figure 36.** $^{31}P\{^{1}H\}$ NMR spectra ($C_6H_5Br$) of reactions **(a)** (top) and **(b)** (bottom) after 16 hours.