Supporting Information for: Coordination chemistry and FLP reactivity of 1,1- and 1,2-*bis*-boranes

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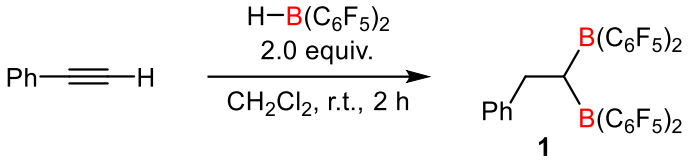
1.1 Spectra of $PhCH_2CH(B(C_6F_5)_2)_2$, 1



1

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.19 – 7.07 (m, 3H, H_{Ar}), 6.89 – 6.82 (m, 2H, H_{Ar}), 4.17 (t, $^3J_{HH}$ = 7 Hz, 1H, $HC(B(C_6F_5)_2)_2$), 3.36 (d, $^3J_{HH}$ = 7 Hz, 2H, $PhCH_2$).

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 6.91 (m, 3H, H_{Ar}), 6.72 (d, $^3J_{HH}$ = 6 Hz, 2H, H_{Ar}), 4.17 (t, $^3J_{HH}$ = 7 Hz, 1H, $HC(B(C_6F_5)_2)_2$), 3.24 (d, $^3J_{HH}$ = 7 Hz, 2H, $PhCH_2$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 72.4.

^{11}B NMR (128 MHz, C_6D_6, 298 K) δ: 72.5.

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) δ: 145.8 (dm, $^1J_{CF}$ = ~247 Hz), 143.4 (dm, $^1J_{CF}$ = ~260 Hz), 141.2 (i-C_{Ar}), 137.5 (dm, $^1J_{CF}$ = ~253 Hz), 128.9 (m-C_{Ar}), 127.6 (o-C_{Ar}), 126.8 (p-C_{Ar}), 58.5 ($CH(B(C_6F_5)_2)_2$), 34.9 ($PhCH_2$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -130.0 (d, $^3J_{FF}$ = 20 Hz, 2F, o-C_6F_5), -146.6 (t, $^3J_{FF}$ = 20 Hz, 1F, p-C_6F_5), -159.9 (m, 2F, m-C_6F_5).

^{19}F NMR (377 MHz, C_6D_6, 298 K) δ: -130.3 (m, 2F, o-C_6F_5), -147.7 (t, $^3J_{FF}$ = 20 Hz, 1F, p-C_6F_5), -161.9 (m, 2F, m-C_6F_5).

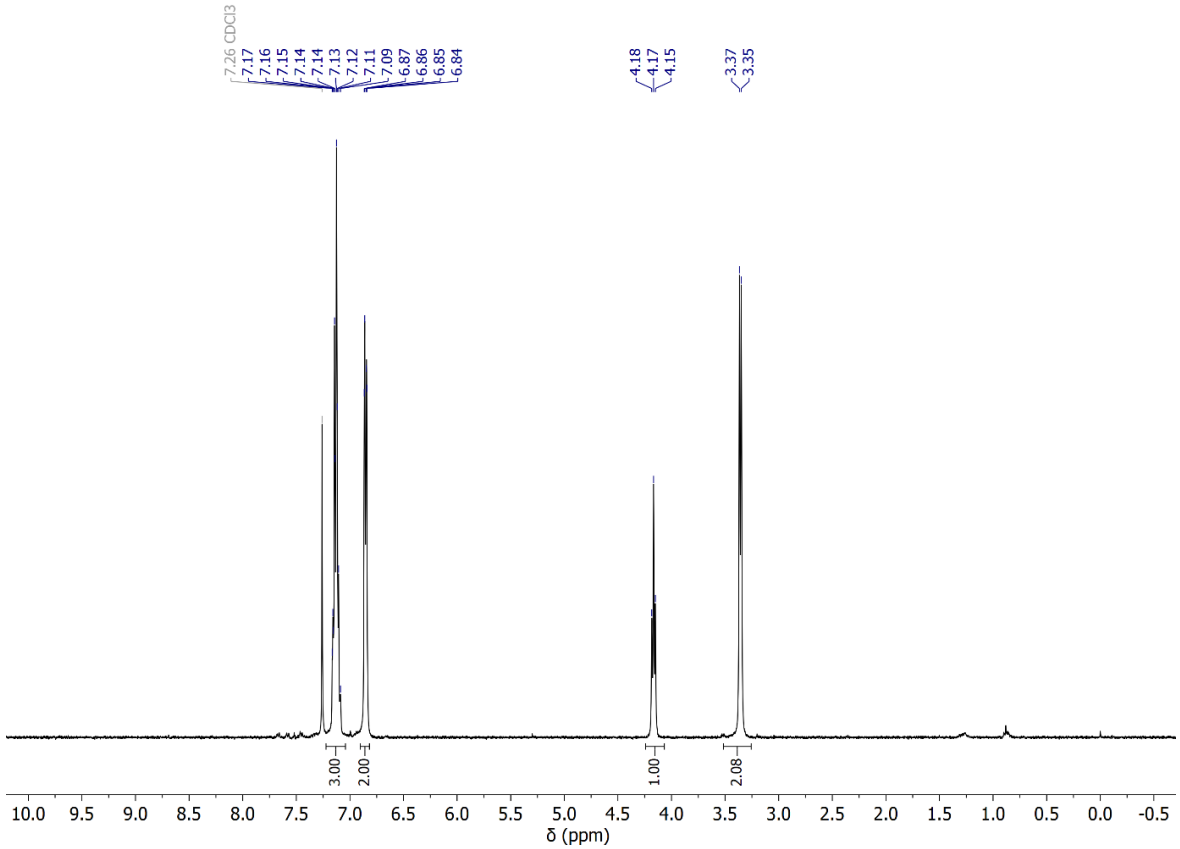


Figure S 1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of *bis*-borane **1**.

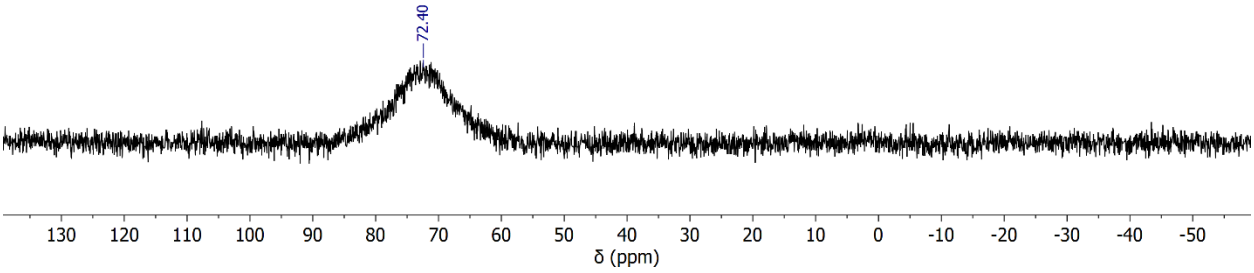


Figure S 2. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of *bis*-borane **1**.

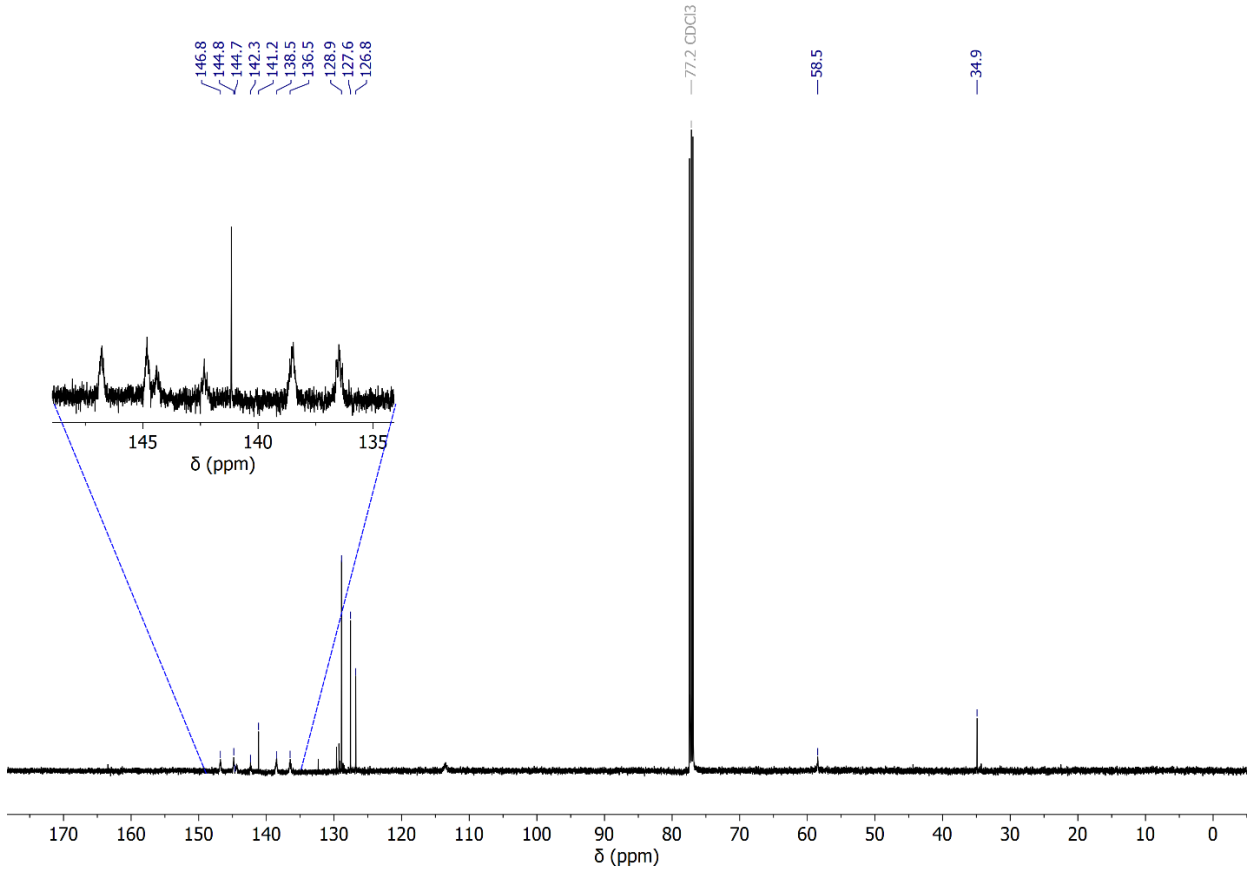


Figure S 3. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of *bis*-borane **1**.

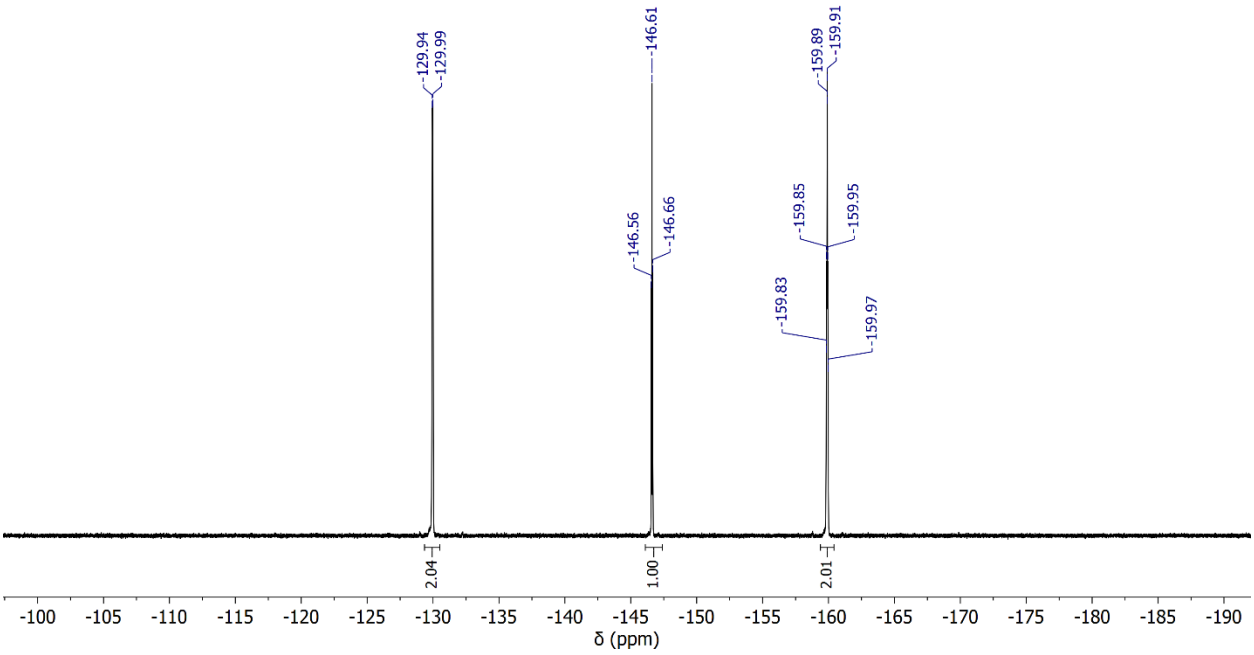
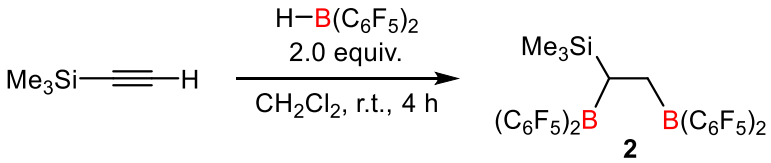


Figure S 4. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of *bis*-borane **1**.

1.2 Spectra of $Me_3SiCH(B(C_6F_5)_2)CH_2B(C_6F_5)_2$, 2



^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 3.09 (dd, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 4 Hz, 1H, C*H*), 2.78 (dd, $^2J_{HH}$ = 18 Hz, $^3J_{HH}$ = 9 Hz, 1H, CH_2), 2.22 (dd, $^2J_{HH}$ = 18 Hz, $^3J_{HH}$ = 4 Hz, 1H, CH_2), -0.04 (s, 9H, Si(CH_3)$_3$).

^{11}B NMR (128 MHz, C_6D_6, 298 K) δ: 71.9.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ: 146.9 (dm, $^1J_{CF}$ = 248 Hz, *o*-C_6F_5), 146.4 (dm, $^1J_{CF}$ = 246 Hz, *o*-C_6F_5), 143.8 (dm, $^1J_{CF}$ = 261 Hz, *m/p*-C_6F_5), 143.1 (dm, $^1J_{CF}$ = 259 Hz, *m/p*-C_6F_5), 138.0 (dm, $^1J_{CF}$ = 255 Hz, *m/p*-C_6F_5), 137.9 (dm, $^1J_{CF}$ = 249 Hz, *m/p*-C_6F_5), 114.6 (br m, *i*-C_6F_5), 113.2 (br m, *i*-C_6F_5), 40.5 (*C*H_2), 31.8 (*C*H), 0.0 (Si(*C*H_3)$_3$).

^{19}F NMR (377 MHz, C_6D_6, 298 K) δ: -130.5 (d, $^3J_{FF}$ = 20 Hz, 4F, *o*-C_6F_5), -130.9 (br, 4F, *o*-C_6F_5), -146.0 (t, $^3J_{FF}$ = 21 Hz, 2F, *p*-C_6F_5), -147.4 (br, 2F, *p*-C_6F_5), -160.2 (m, 8F, *m*-C_6F_5).

HRMS (ESI- Ionization, *m/z*): Calcd. for $C_{30}H_{15}B_2F_{20}OSi^-$ ([M+CH_3O]$^-$): 821.0775; Found: 821.0757.

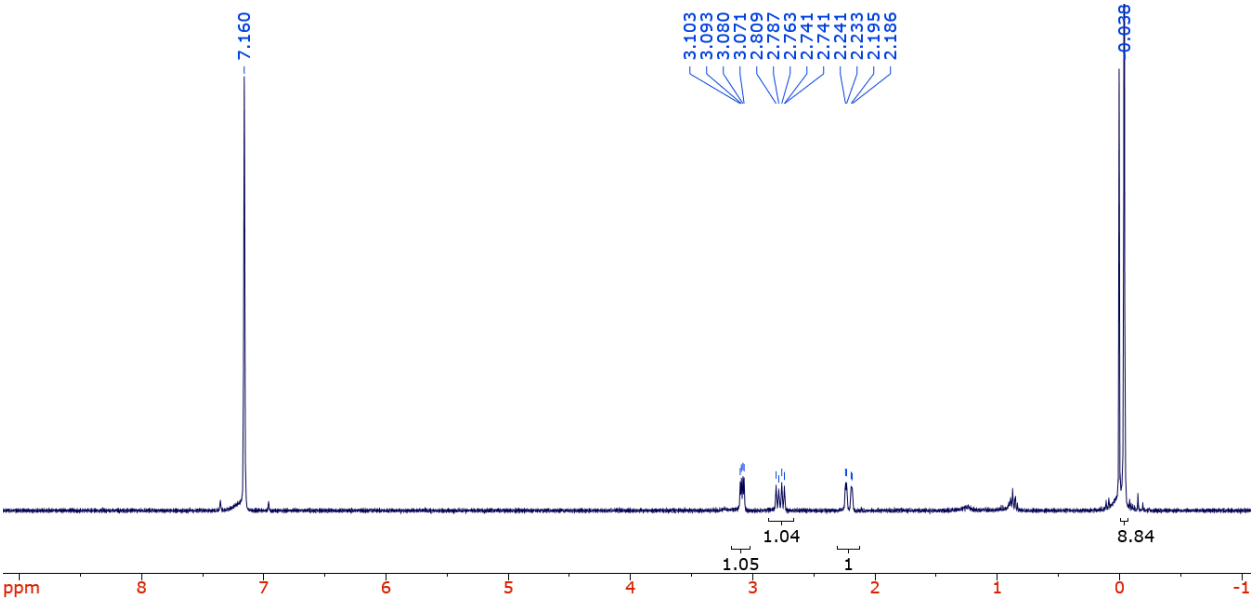


Figure S 5. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **2.**

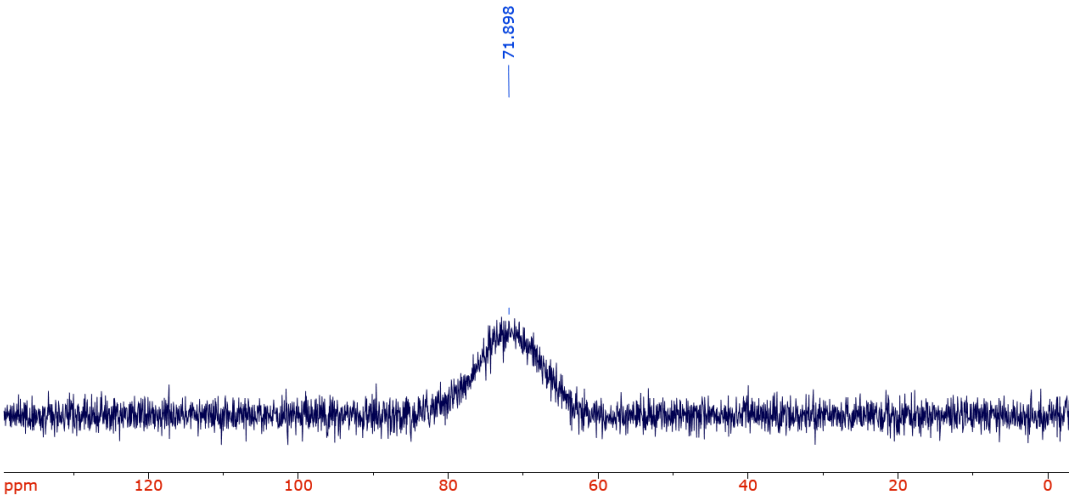


Figure S 6. ^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **2.**

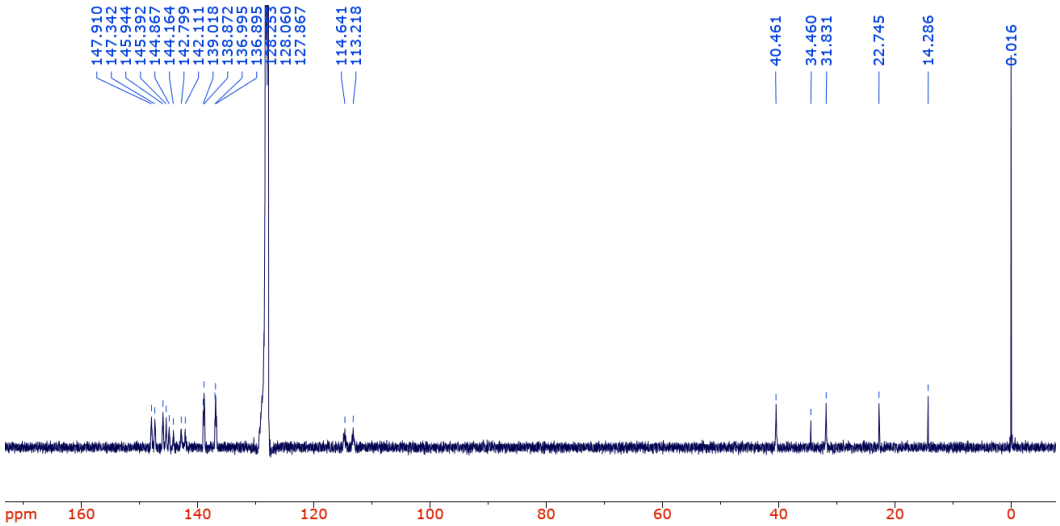


Figure S 7. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **2.**

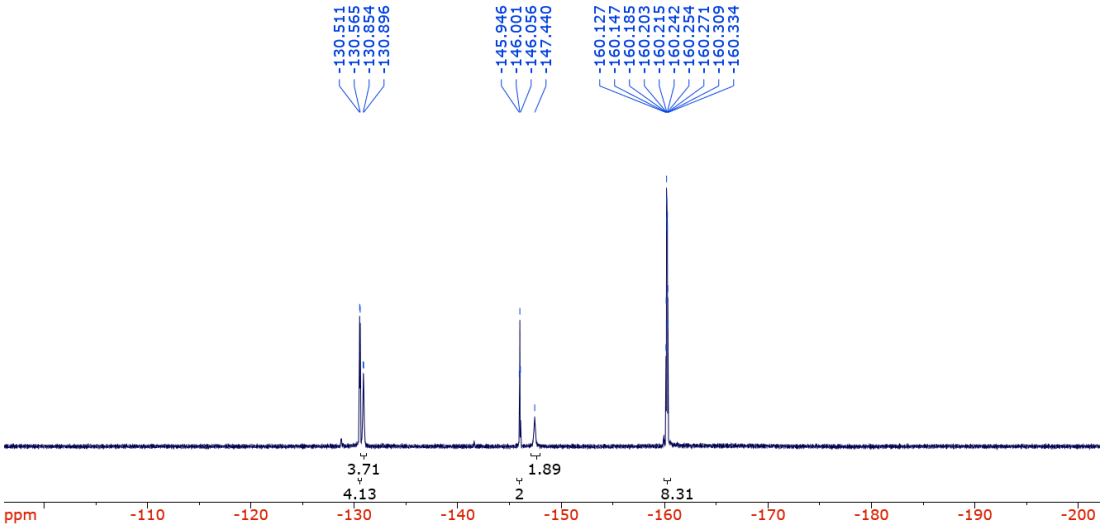
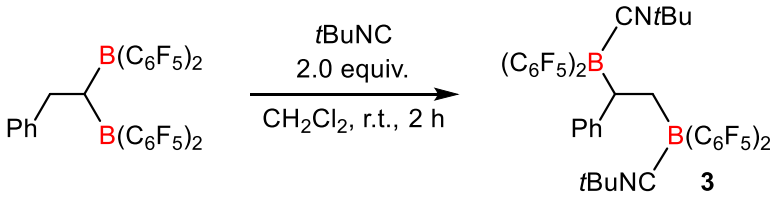


Figure S 8. ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **2.**

1.3 Spectra of PhCH(B(C$_6$F$_5$)$_2$CN*t*Bu)CH$_2$(B(C$_6$F$_5$)$_2$CN*t*Bu), 3



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 6.82 – 6.67 (m, 5H, H_{Ar}), 3.16 (d, $^3J_{HH}$ = 13 Hz, 1H, CH_2), 2.16 (br dd, 1H, PhC*H*), 1.77 (s, 9H, C(CH_3)$_3$), 1.72 (s, 9H, C(CH_3)$_3$), 1.51 (d, $^3J_{HH}$ = 14 Hz, 1H, CH_2).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -15.1, -18.2.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K, *partial*) δ: 148.4 (dm, *o*-C_6F_5), 146.5 (dm, *o*-C_6F_5), 147.2 (*i*-C_{Ar}), 139.9 (dm, *p*-C_6F_5), 139.7 (dm, *p*-C_6F_5), 138.8 (dm, *p*-C_6F_5), 138.4 (dm, *p*-C_6F_5), 137.3 (dm, *m*-C_6F_5), 137.2 (dm, *m*-C_6F_5), 136.7 (dm, *m*-C_6F_5), 136.5 (dm, *m*-C_6F_5), 127.3 (br, *t*BuN≡*C*), 127.1 (*m*-C_{Ar}), 126.6 (*o*-C_{Ar}), 124.4 (*p*-C_{Ar}), 119.4 (br, *i*-C_6F_5), 118.9 (br, *i*-C_6F_5), 117.5 (br, *i*-C_6F_5), 116.8 (br, *i*-C_6F_5), 60.3 (*C*(CH_3)$_3$), 60.1 (*C*(CH_3)$_3$), 37.8 (br s, Ph*C*HB(C_6F_5)$_2$), 29.2 (C(*C*H_3)$_3$), 29.1 (C(*C*H_3)$_3$), 21.7 (br, *C*H_2B(C_6F_5)$_2$).

^{13}C, ^{19}F GC2HSQC (126 MHz / 470 MHz, $CDCl_3$, 298 K) δ ^{13}C / δ ^{19}F: 148.4/ -132.2, 148.4/ -132.5, 146.5/ -133.7, 139.9/ -157.1, 139.7/ -158.1, 138.8/ -159.0, 138.4/ -160.4, 137.3/ -163.2, 137.2/ -163.9, 136.7/ -164.2, 136.5/ -165.2.

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -132.2 (d, $^3J_{FF}$ = 21 Hz, 2F, *o*-C_6F_5), -132.4 (d, $^3J_{FF}$ = 19 Hz, 2F, *o*-C_6F_5), -133.7 (d, $^3J_{FF}$ = 21, 4F, Hz, *o*-C_6F_5), -157.1 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -158.1 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -158.9 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -160.4 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -163.1 (m, 2F, *m*-C_6F_5), -163.9 (m, 2F, *m*-C_6F_5), -164.2 (m, 2F, *m*-C_6F_5), -165.2 (m, 2F, *m*-C_6F_5).

HRMS (ESI+ Ionization, *m/z*): Calcd. for $C_{42}H_{30}B_2F_{20}N_3^+$ ([M+NH_4]$^+$): 978.2315; Found: 978.2320.

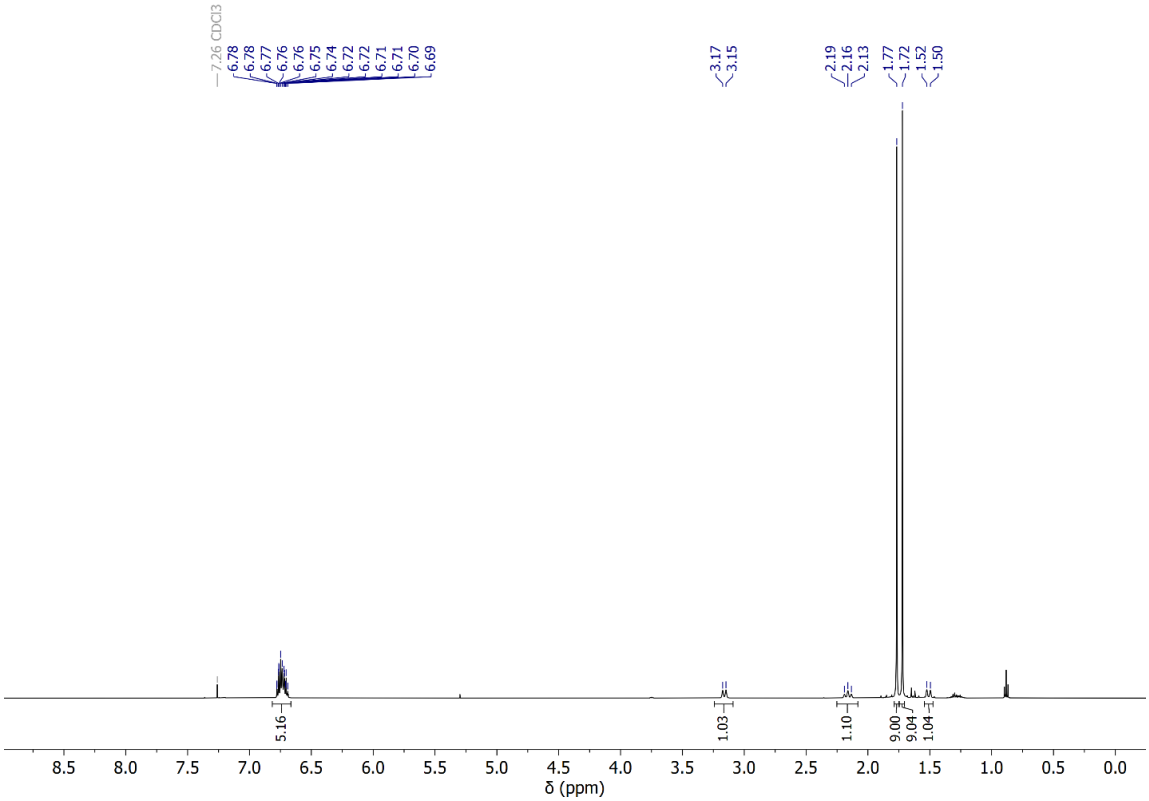


Figure S 9. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **3**.

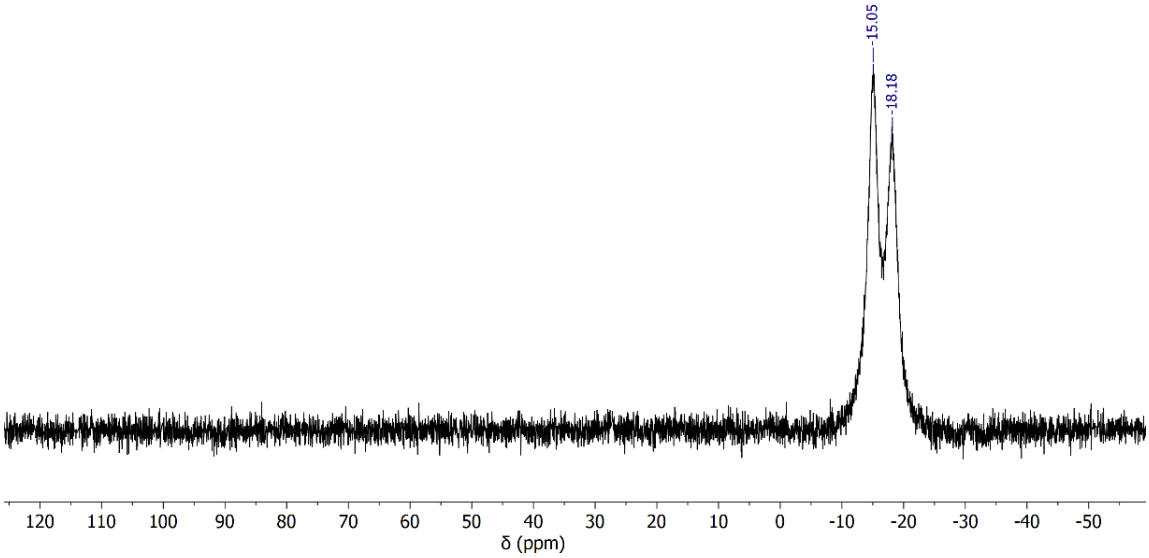


Figure S 10. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **3**.

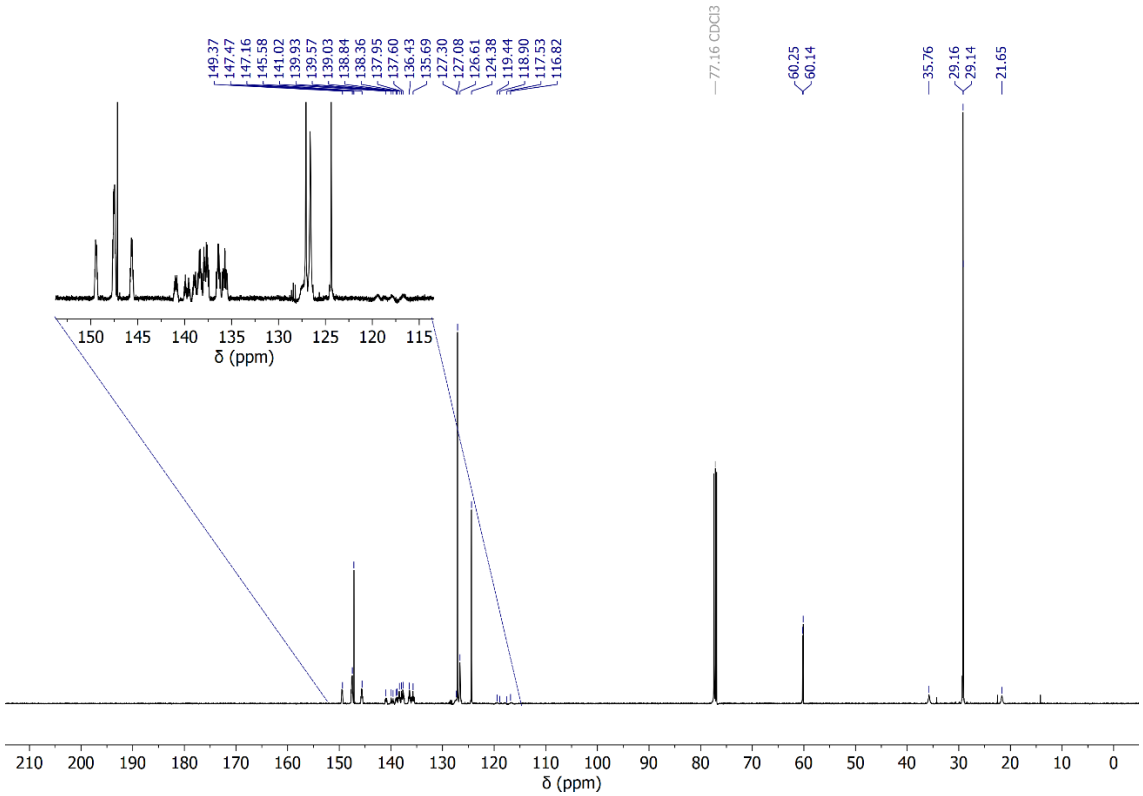


Figure S 11. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **3**.

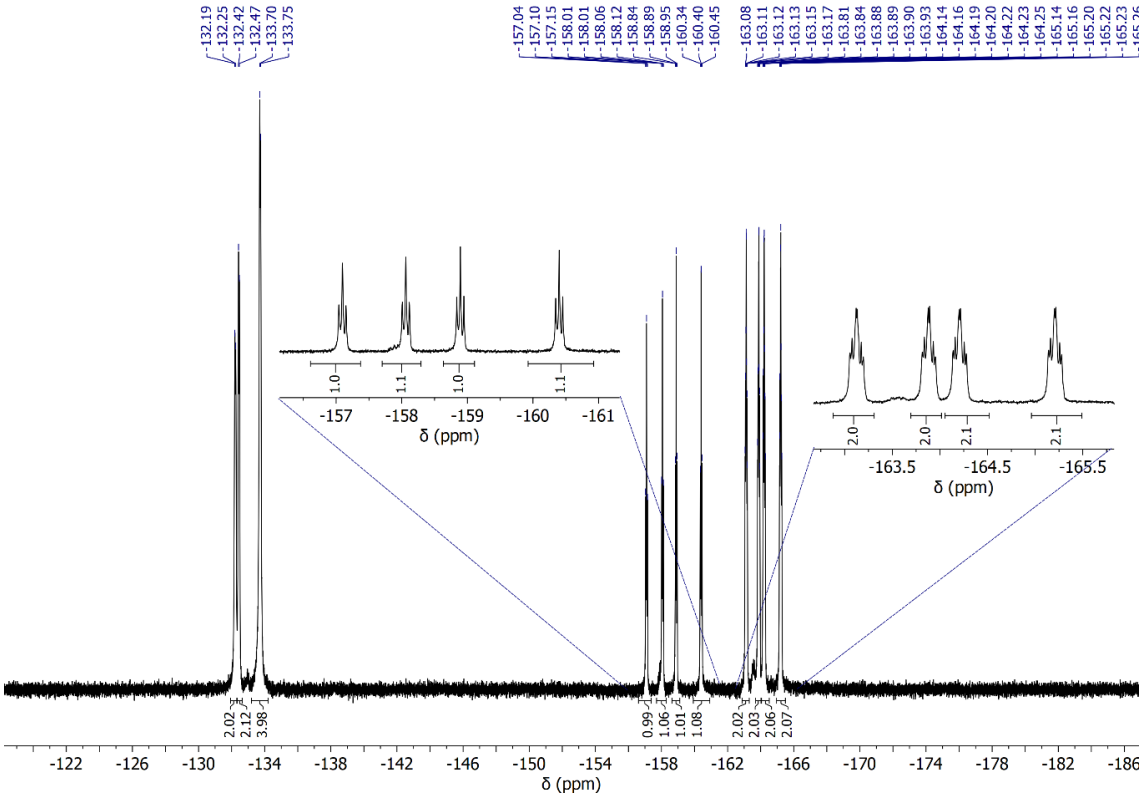


Figure S 12. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **3**.

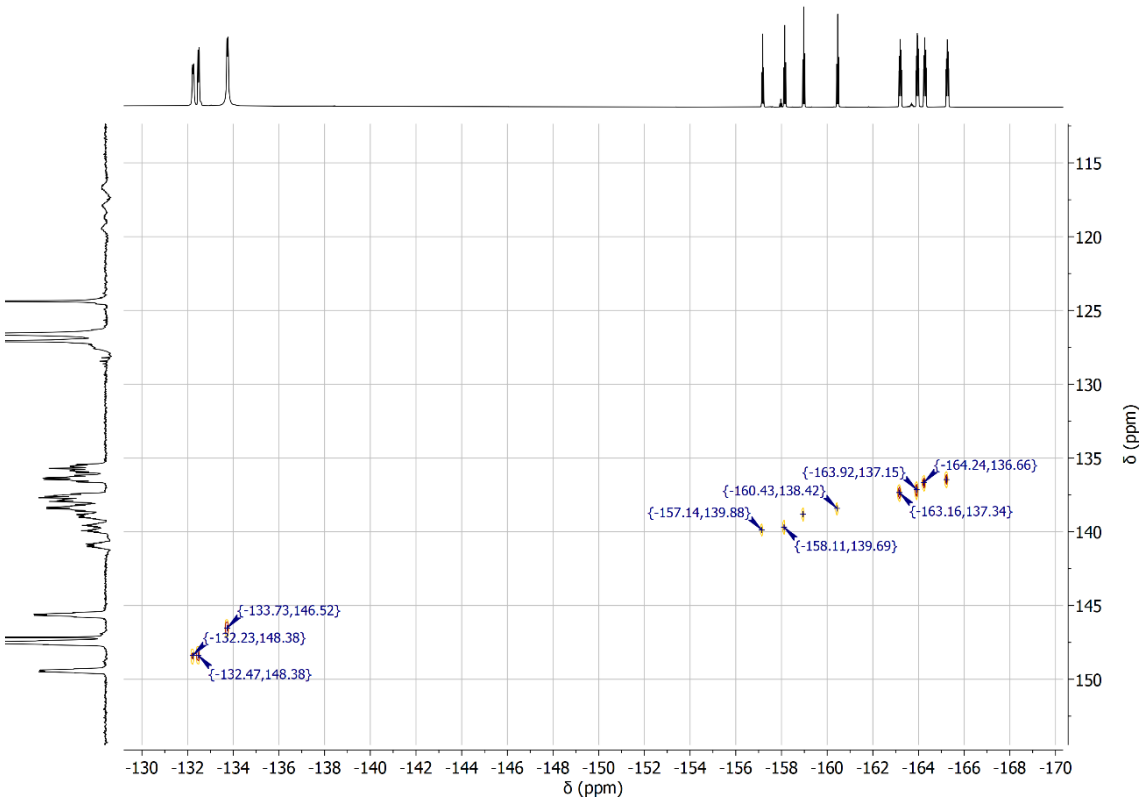
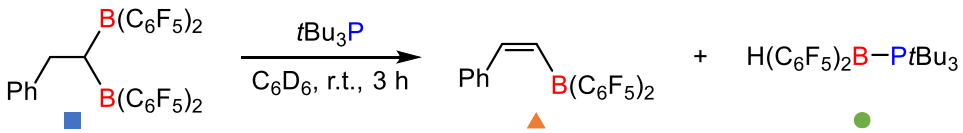


Figure S 13. ^{13}C, ^{19}F GC2HSQC (126 MHz / 470 MHz, $CDCl_3$, 298 k) spectrum of compound **3**.

1.4 Spectra of the control reactions of *bis*-borane 1 with donors

Reaction of *bis*-borane 1 and *t*Bu$_3$P



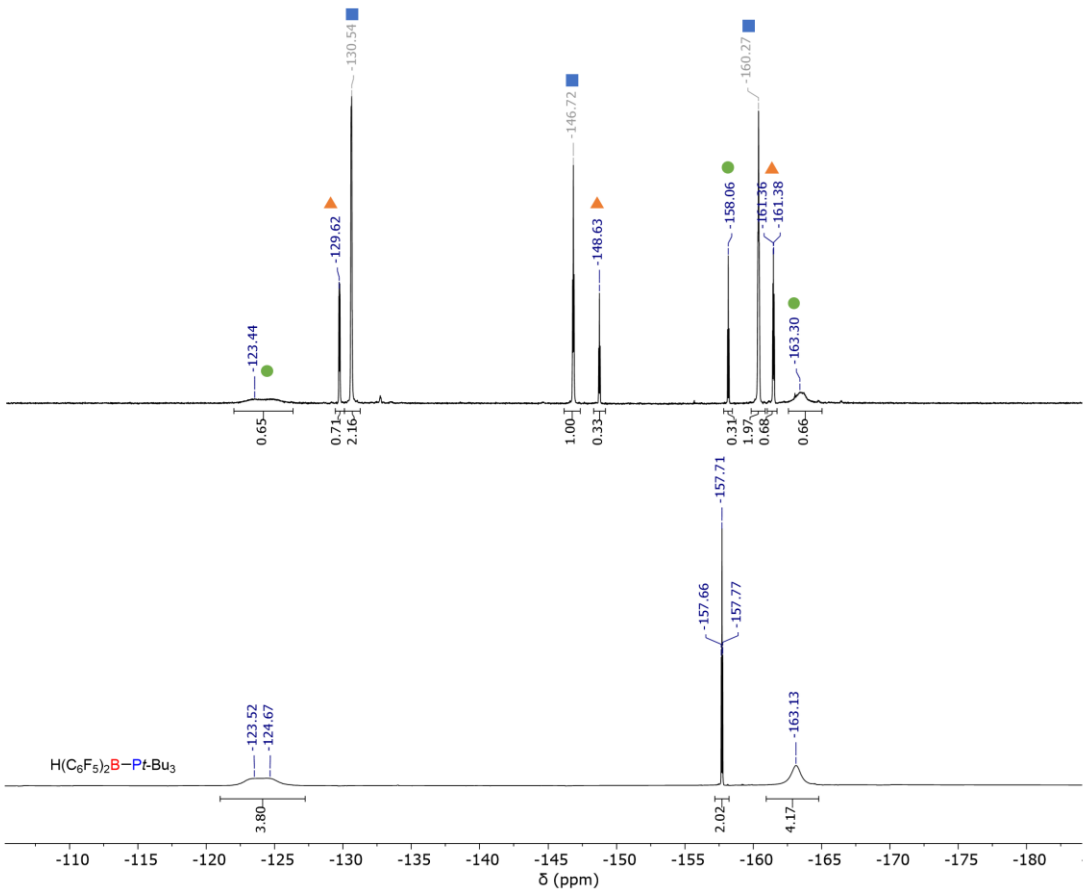


Figure S 14. ^{19}F NMR (377 MHz, C_6D_6/CH_2Cl_2, 298 K) spectrum of the reaction between the *bis*-borane **1** and *t*Bu$_3$P. The adduct of $HB(C_6F_5)_2$ with *t*Bu$_3$P was prepared separately and the corresponding ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of is provided as a reference.

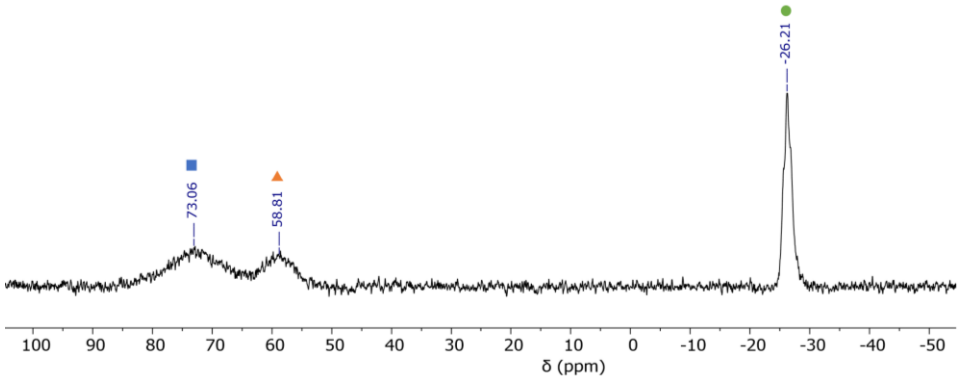


Figure S 15. ^{11}B NMR (128 MHz, C_6D_6/CH_2Cl_2, 298 K) spectrum of the reaction *bis*-borane **1** with *t*Bu$_3$P.

Reaction of *bis*-borane 1 and TMP

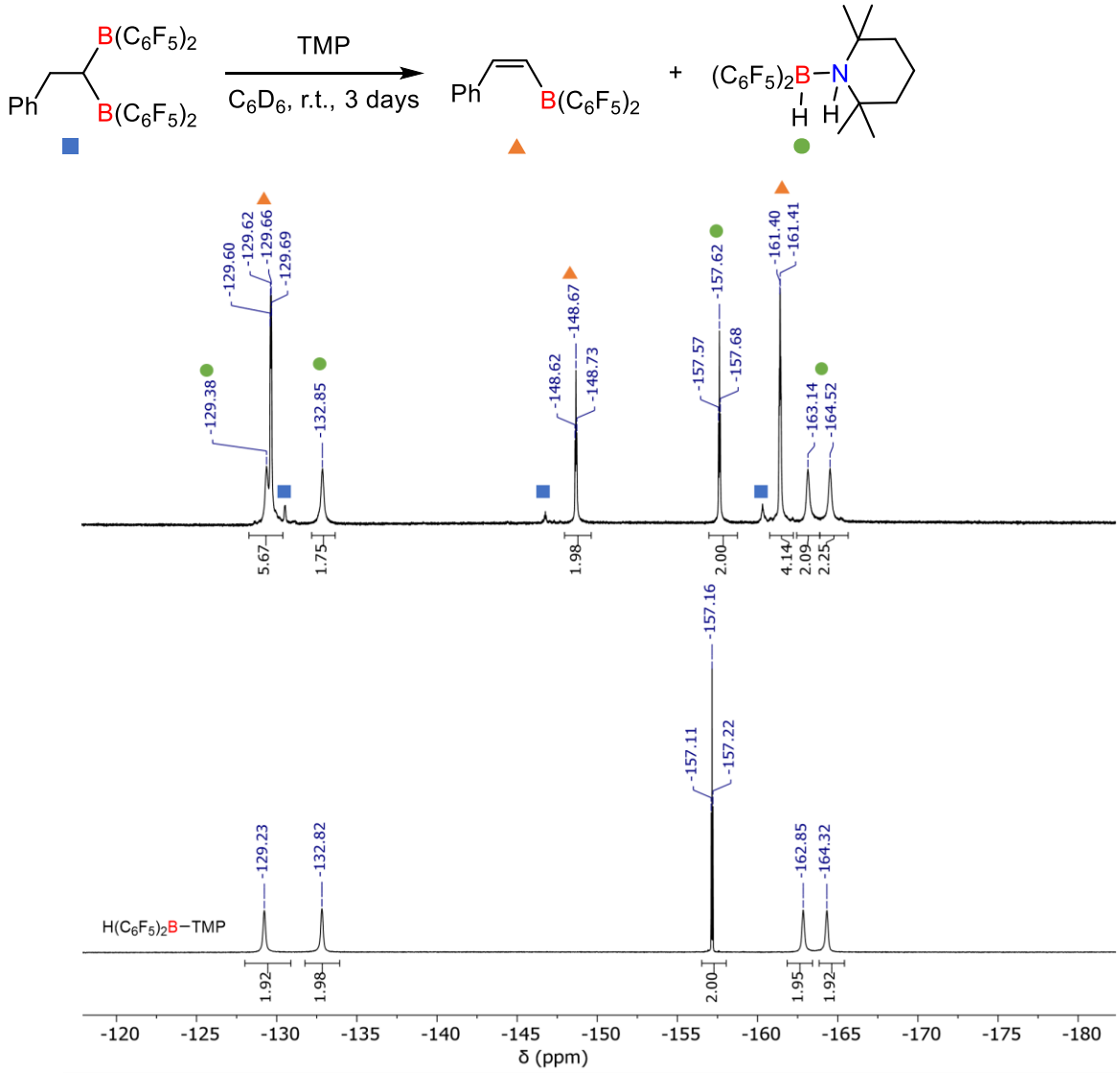


Figure S 16. ^{19}F NMR (377 MHz, C_6D_6/CH_2Cl_2, 298 K) spectrum of the reaction between the *bis*-borane **1** and TMP. The adduct of $HB(C_6F_5)_2$ with TMP was prepared separately and the corresponding ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of is provided as a reference.

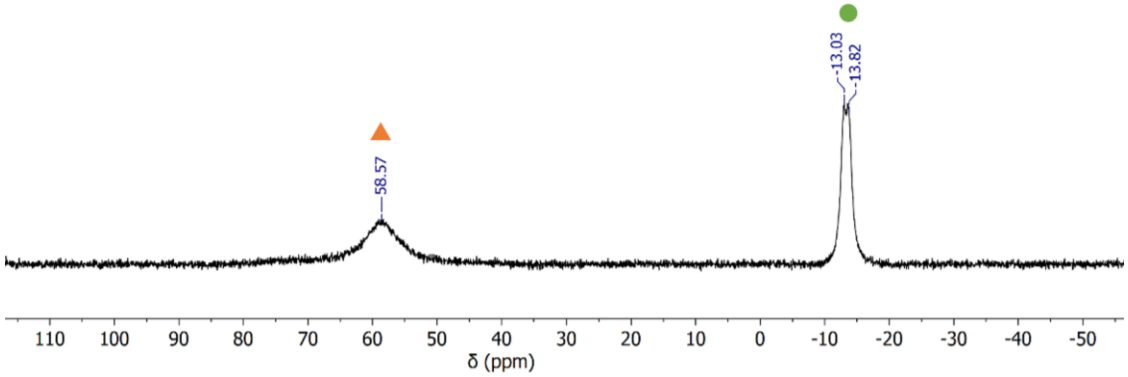


Figure S 17. ^{11}B NMR (128 MHz, C_6D_6/CH_2Cl_2, 298 K) spectrum of the reaction *bis*-borane **1** with TMP.

Reaction of *bis*-borane 1 and DMAP

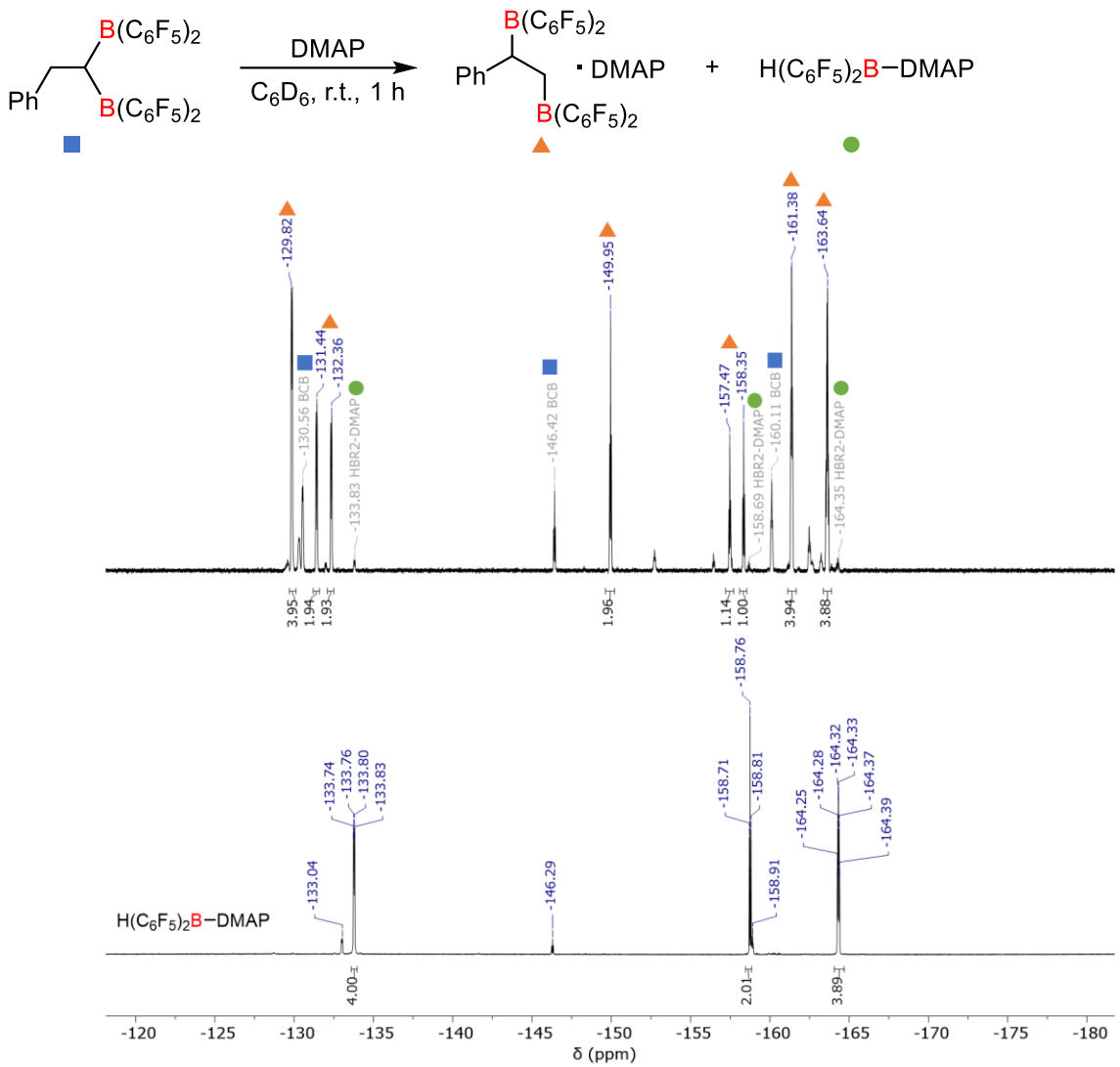


Figure S 18. ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of the reaction between the *bis*-borane **1** and DMAP. The adduct of $HB(C_6F_5)_2$ with DMAP was prepared separately and the corresponding ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of is provided as a reference.

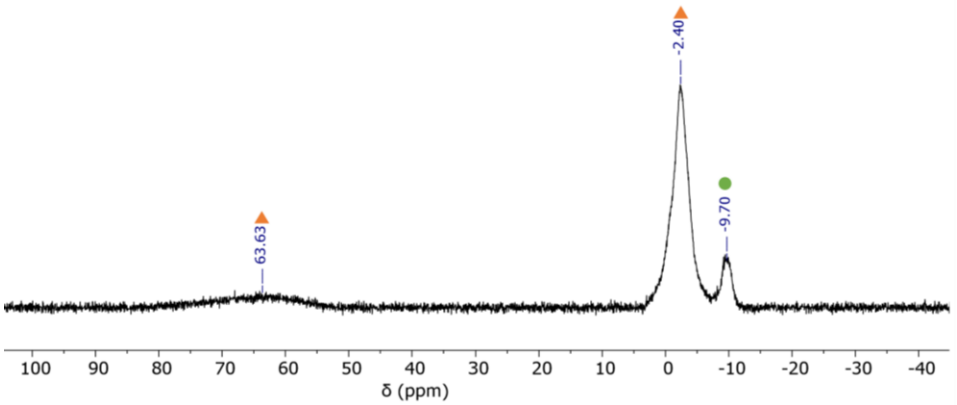
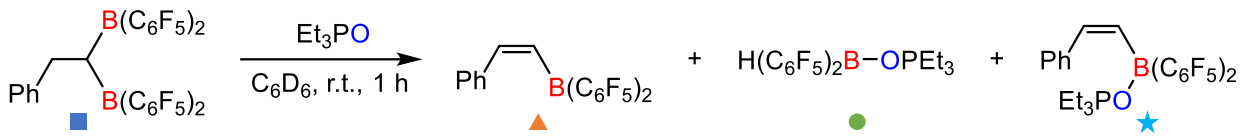


Figure S 19. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of the reaction of *bis*-borane **1** with DMAP.

Reaction of *bis*-borane 1 and Et_3PO



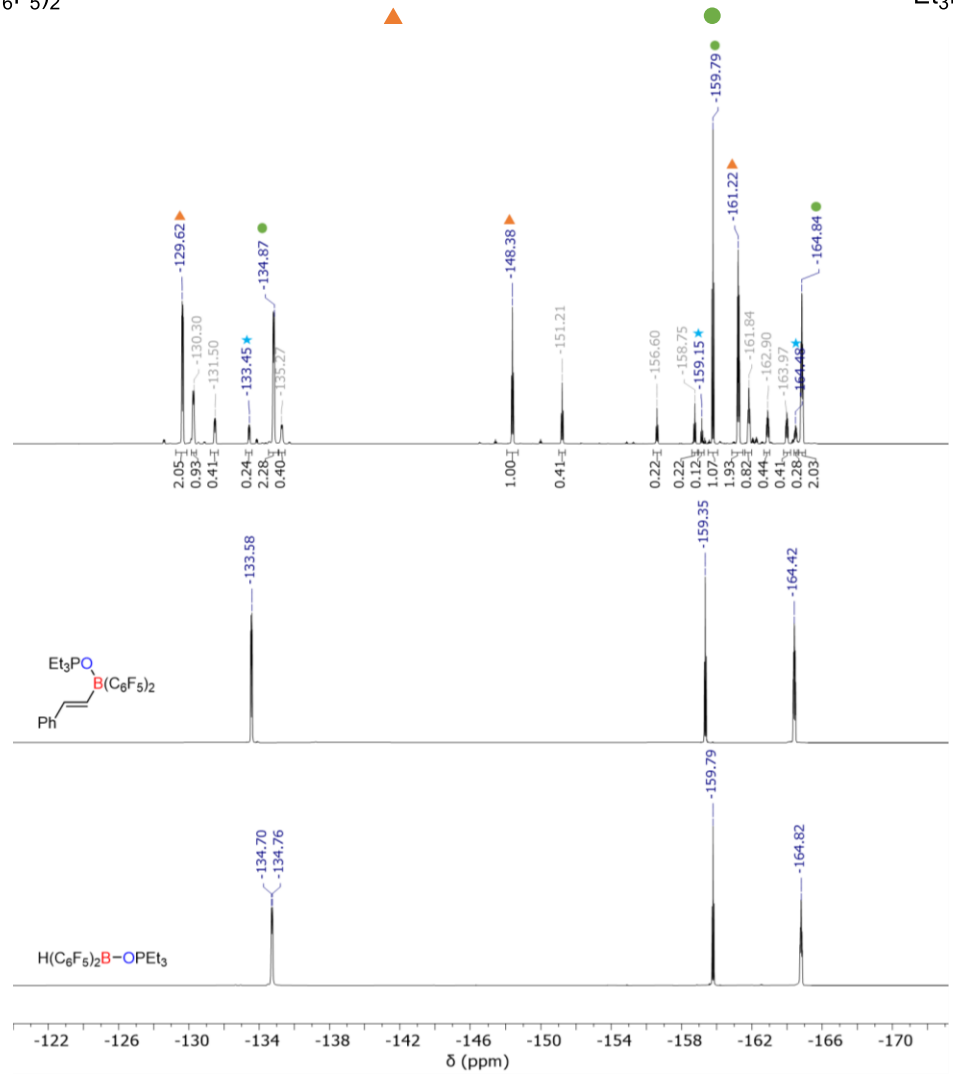


Figure S 20. ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of the reaction between the *bis*-borane **1** and Et_3PO. The adducts of Et_3PO with $HB(C_6F_5)_2$ and the vinylic borane were prepared separately and the corresponding ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectra are provided as a reference.

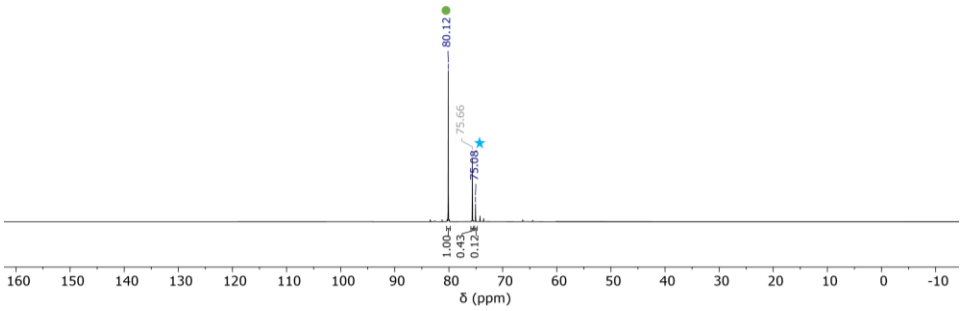
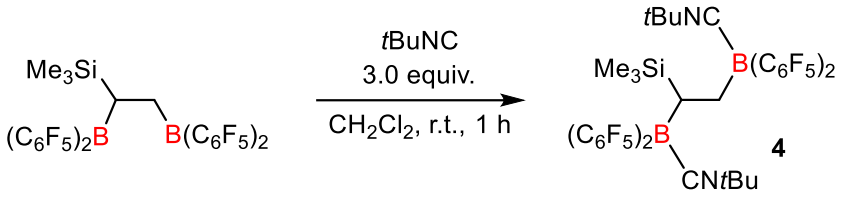


Figure S 21. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of the reaction of *bis*-borane **1** with Et_3PO.

1.5 Spectra of $Me_3SiCH(B(C_6F_5)_2CNtBu)CH_2(B(C_6F_5)_2CNtBu)$, 4



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 1.71 (s, 9H, C-CH_3), 1.70 (s, 9H, CH_3), 1.44 (m, 2H, CH_2), 1.16 (br, 1H, C*H*), -0.22 (s, 9H, Si(CH_3)$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -16.6, -17.9.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 147.6 (dm, $^1J_{CF}$ = 239 Hz, *o*-C_6F_5), 139.3 (dm, $^1J_{CF}$ = 252 Hz, *m/p*-C_6F_5), 137.2 (dm, $^1J_{CF}$ = 251 Hz, *m/p*-C_6F_5), 127.7 (br, *t*BuN≡*C*), 119.2 (br m, *i*-C_6F_5), 60.2 (*C*(CH_3)$_3$), 60.0 (*C*(CH_3)$_3$), 29.2 (C(*C*H_3)$_3$), 29.1 ((C(*C*H_3)$_3$), 17.6 (br, *C*H_2), 11.3 (br, *C*H), 0.4 (Si(*C*H_3)$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -131.6 (m, 2F, *o*-C_6F_5), -132.1 (m, 4F, *o*-C_6F_5), -132.5 (br, 2F, *o*-C_6F_5), -158.3 (m, 3F, *overlapping m*-C_6F_5 and *p*-C_6F_5), -158.7 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -163.4 (m, 4F, *m*-C_6F_5), -164.0 (m, 4F, *m*-C_6F_5).

HRMS (ESI- Ionization, *m/z*): fragmentation to compound **2**, Calcd. For $C_{30}H_{15}B_2F_{20}Osi^-$ ([M+CH_3O]$^-$) 821.0775; Found: 821.0789.

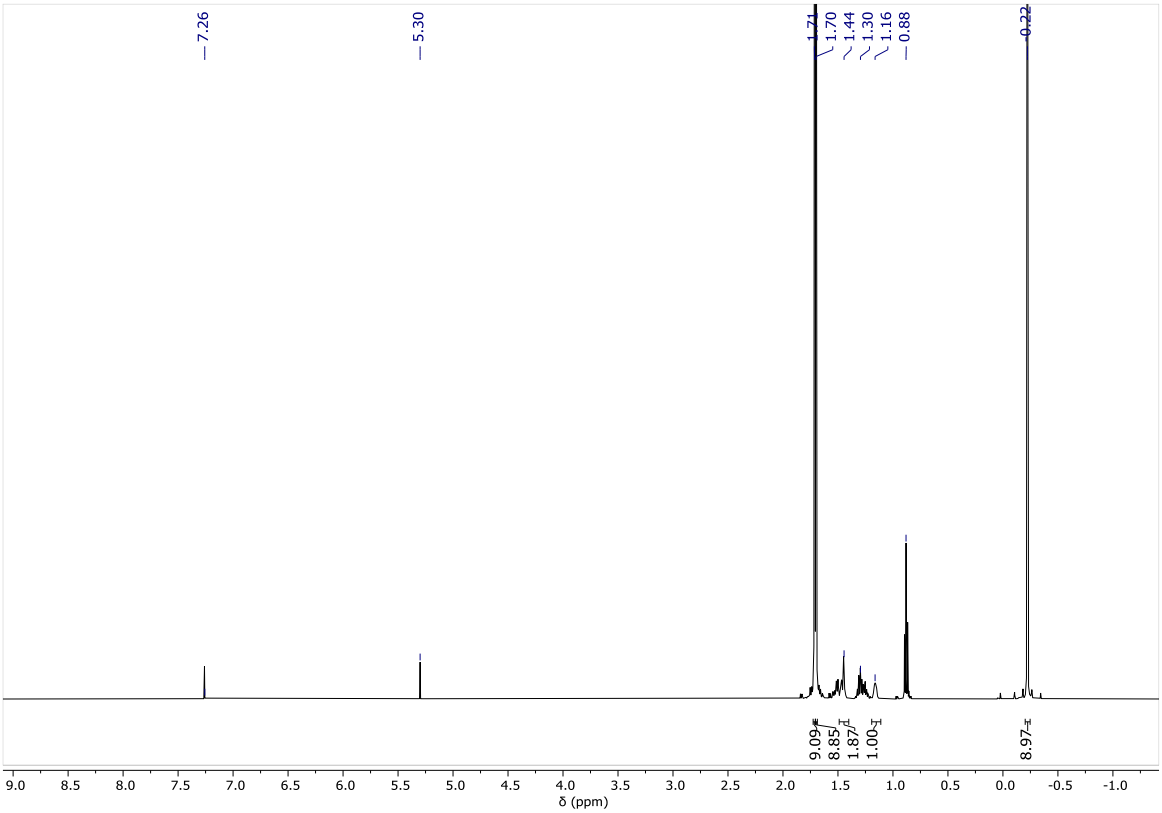


Figure S 22. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **4.**

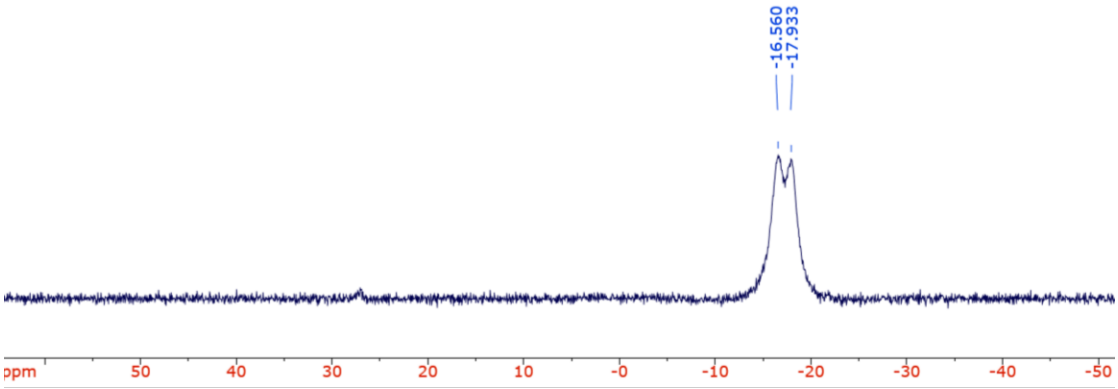


Figure S 23. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **4.**

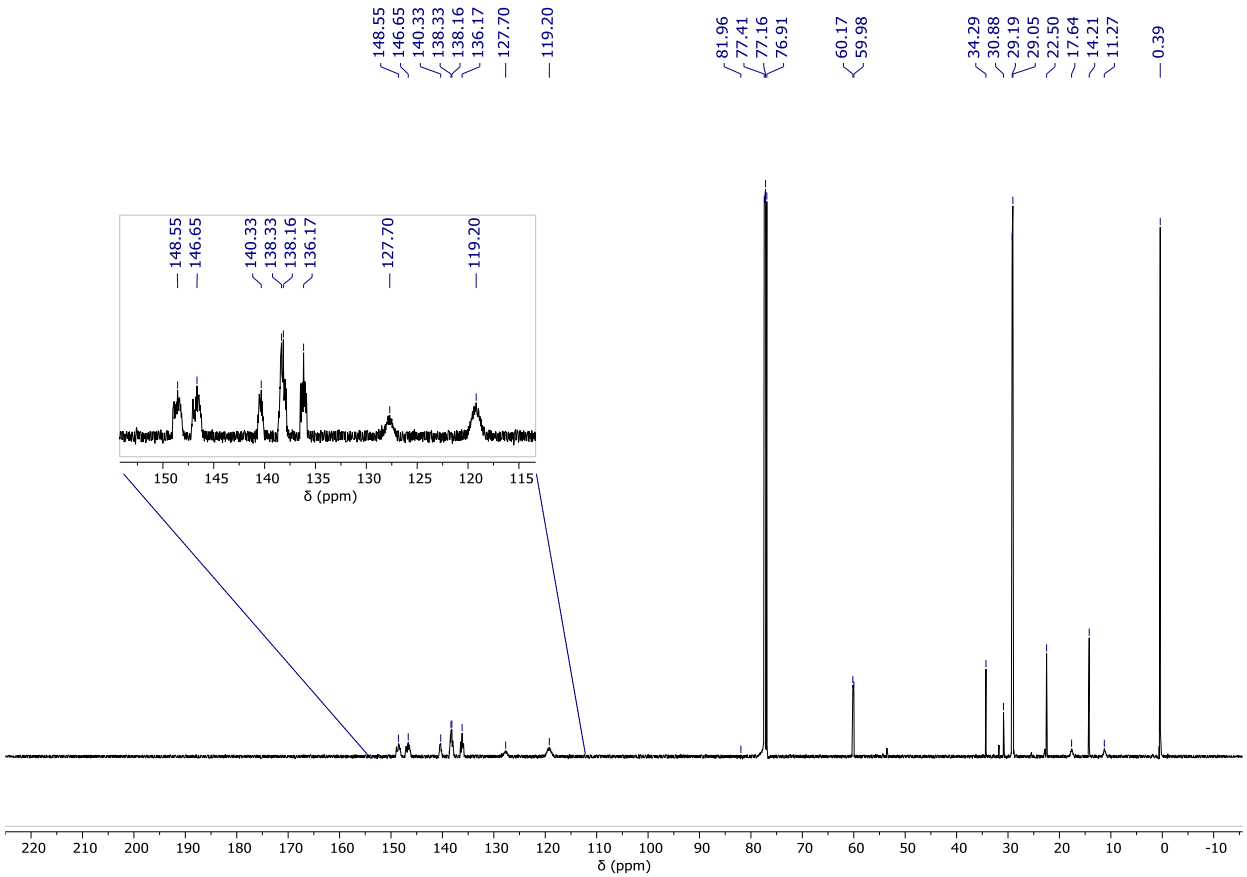


Figure S 24. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **4**.

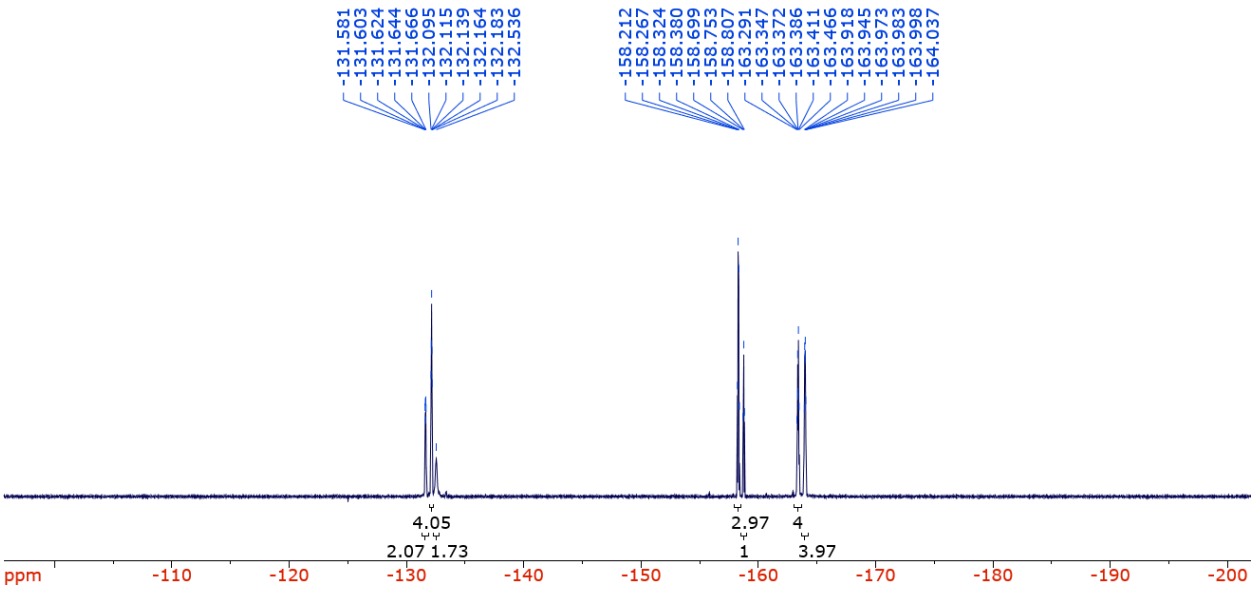


Figure S 25. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **4**.

1.6 Spectra of the Gutmann-Beckett Lewis acidity test for *bis*-borane 2

$\Delta\delta^{31}P$ is 73.5 ppm – 45.6 ppm = **<u>27.9 ppm</u>** in C_6D_6. (Et_3PO: $^{31}P\{^1H\}$ (C_6D_6) δ: 45.6 ppm).

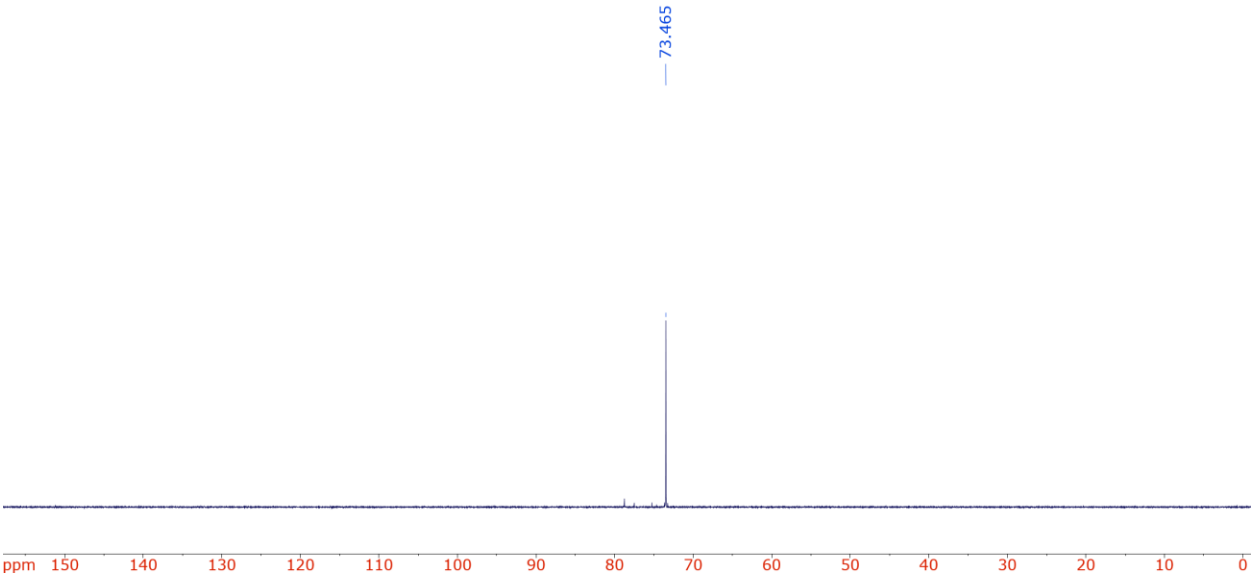
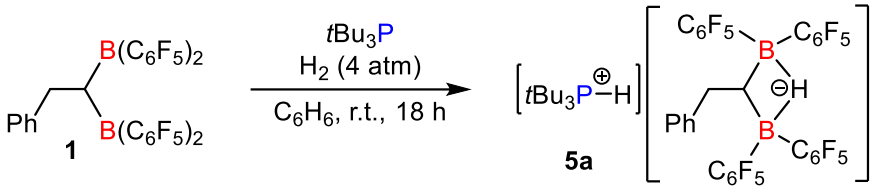


Figure S 26. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K) spectrum of Gutmann-Beckett Lewis acidity test on *bis*-borane **2.**

1.7 Spectra of [*t*Bu$_3$PH][PhCH$_2$CH(B(C$_6$F$_5$)$_2$)$_2$(μ-H)], 5a



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.09 – 6.92 (m, 5H, *H$_{Ar}$*), 5.02 (d, $^1J_{PH}$ = 431 Hz, 1H, *t*Bu$_3$P*H*), 2.70 (br, 1H, *H*(B(C$_6$F$_5$)$_2$)$_2$), 2.57 (d, $^3J_{HH}$ = 9 Hz, 2H, PhC*H*$_2$), 2.07 (dd, $^3J_{HH}$ = 8.9, 8.8 Hz, 1H, *H*C(B(C$_6$F$_5$)$_2$)$_2$), 1.65 (d, $^3J_{PH}$ = 16 Hz, 27H, (C*H*$_3$)$_3$CPH).

^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.16 – 6.84 (m, 5H, *H$_{Ar}$*), 5.02 (d, $^1J_{PH}$ = 431 Hz, 1H, *t*Bu$_3$P*H*), 2.71 (br, 1H, *H*(B(C$_6$F$_5$)$_2$)$_2$), 2.57 (d, $^3J_{HH}$ = 9 Hz, 2H, PhC*H*$_2$), 2.08 (dd, $^3J_{HH}$ = 9.3, 8.7 Hz, 1H, *H*C(B(C$_6$F$_5$)$_2$)$_2$), 1.65 (d, $^3J_{PH}$ = 16 Hz, 27H, (C*H*$_3$)$_3$CPH).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -19.1.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 149.0 (dm, $^1J_{CF}$ = ~241 Hz, C_6F_5), 147.1 (dm, $^1J_{CF}$ = ~240 Hz, C_6F_5), 146.3 (*i*-C$_{Ar}$), 138.8 (dm, $^1J_{CF}$ = ~252 Hz, C_6F_5), 128.1 (*m*-C$_{Ar}$), 127.3 (*o*-C$_{Ar}$), 124.3 (*p*-C$_{Ar}$), 37.8 (d, $^1J_{CP}$ = 27 Hz, *C*(CH$_3$)$_3$PH), 36.0 (PhCH$_2$), 30.1 (C(*C*H$_3$)$_3$PH), 9.8 (br, H*C*(B(C$_6$F$_5$)$_2$)$_2$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -129.0 (br, 4F, *o*-C_6F_5), -131.1 (br, 4F, *o*-C_6F_5), -159.8 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -160.8 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -165.5 (m, 8F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ: 60.2 (s).

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 60.2 (dm, $^1J_{PH}$ = 434 Hz).

HRMS (ESI+/- Ionization, *m/z*): Calcd. For $C_{12}H_{28}P^+$ ([M]$^+$): 203.1923; Found: 203.1924. Calcd. For $C_{32}H_9B_2F_{20}^-$ ([M]$^-$): 795.0587; Found: 795.0591.

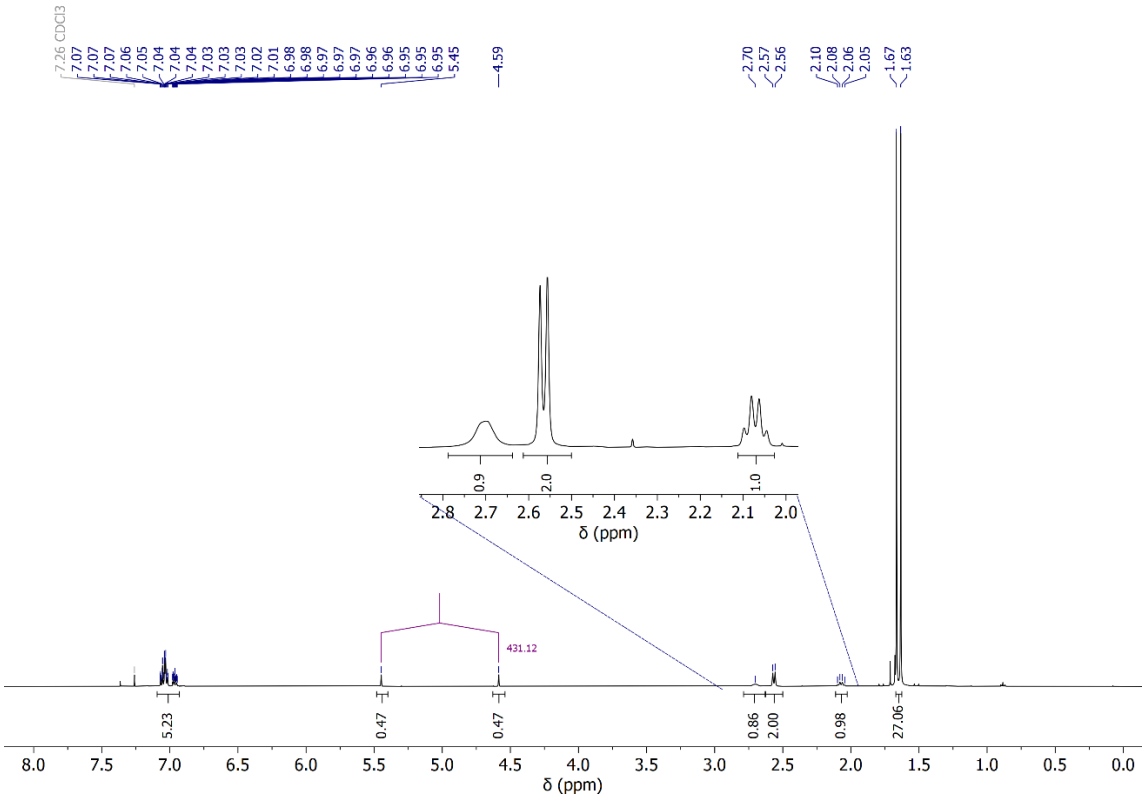


Figure S 27. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **5a**.

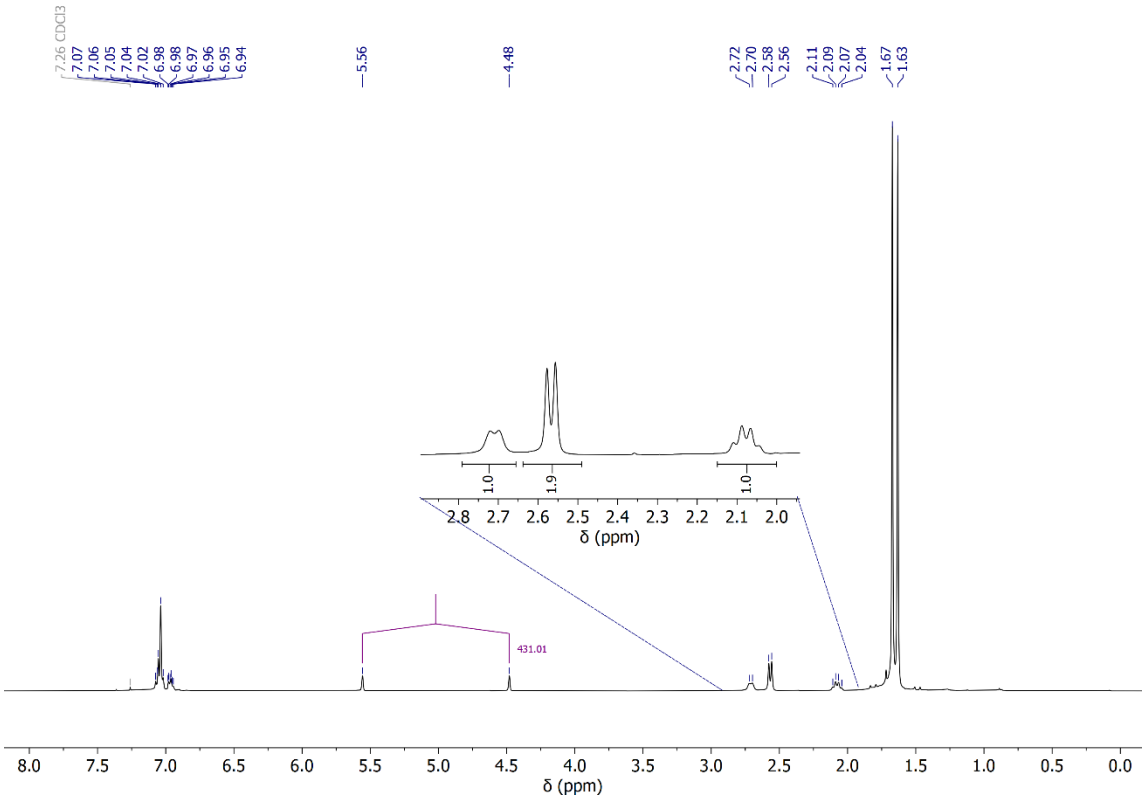


Figure S 28. ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **5a**.

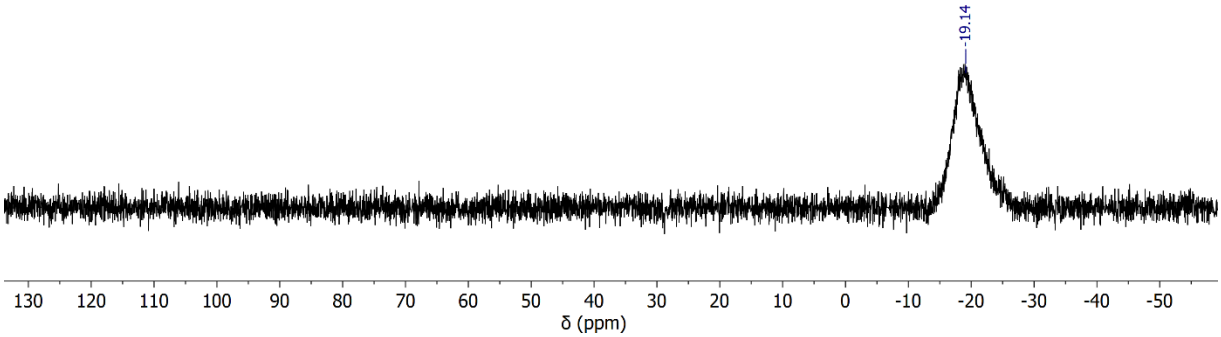


Figure S 29. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of bisborane H_2-activated product **5a**.

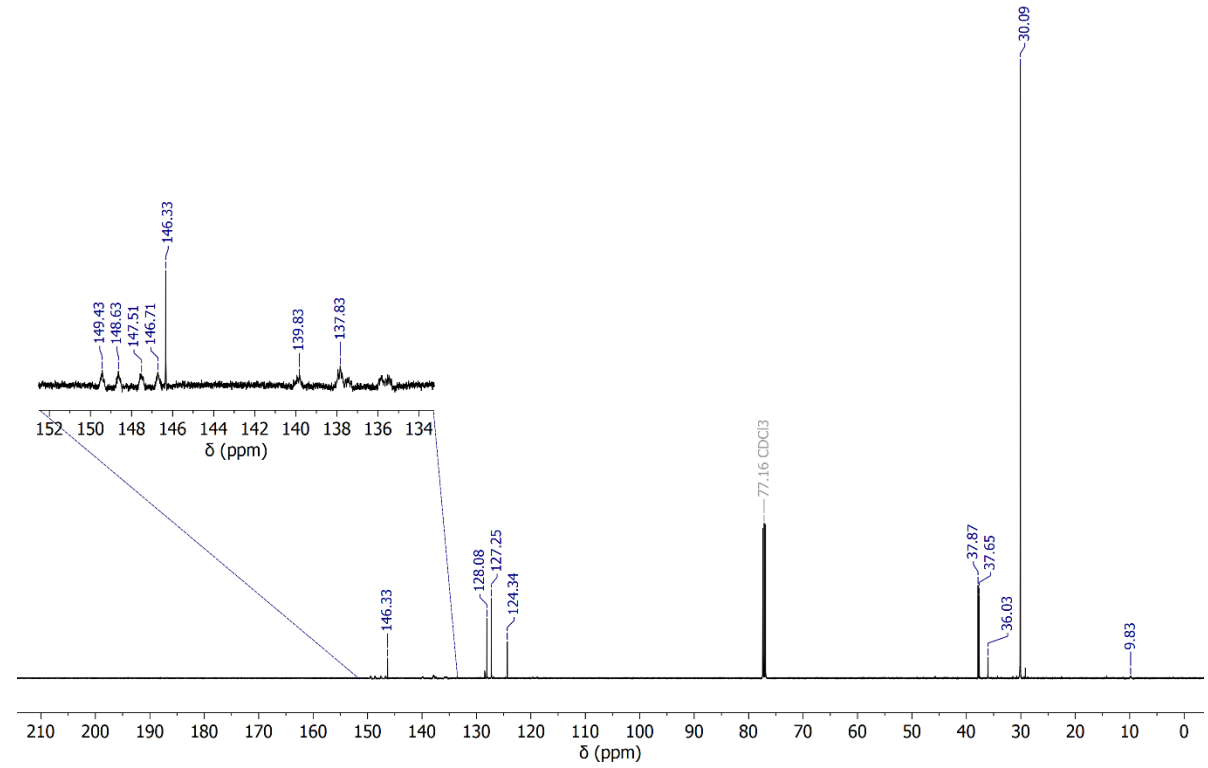


Figure S 30. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of bisborane H_2-activated product **5a**.

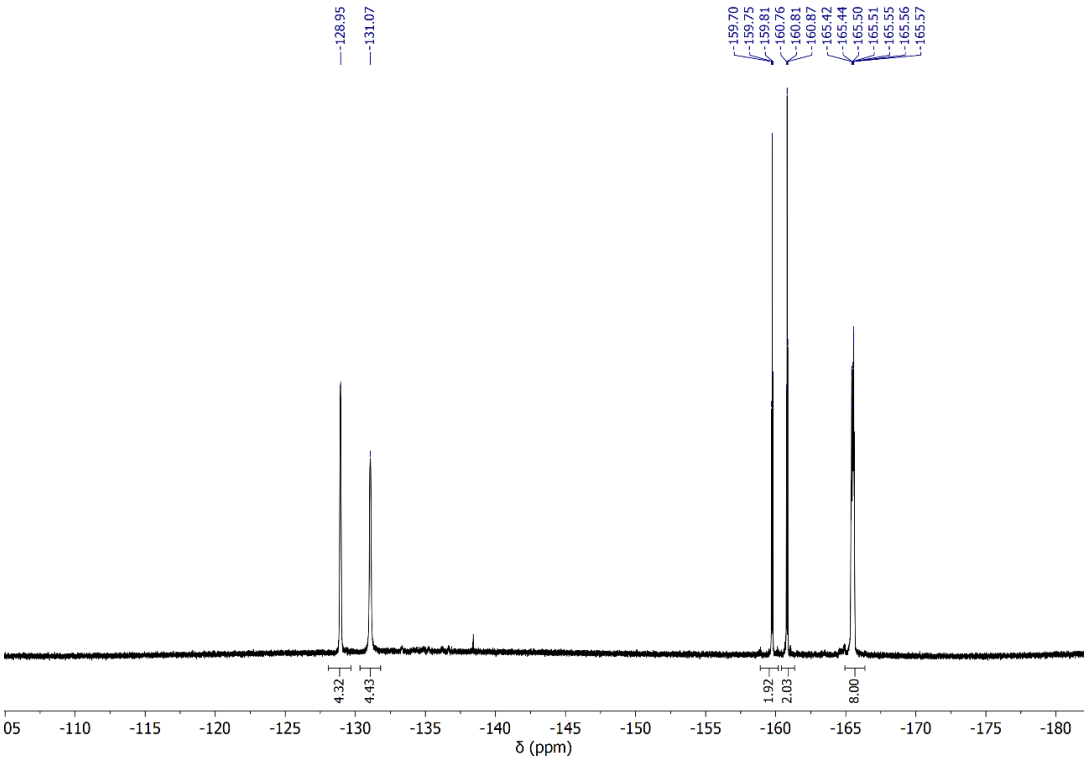


Figure S 31. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **5a**.

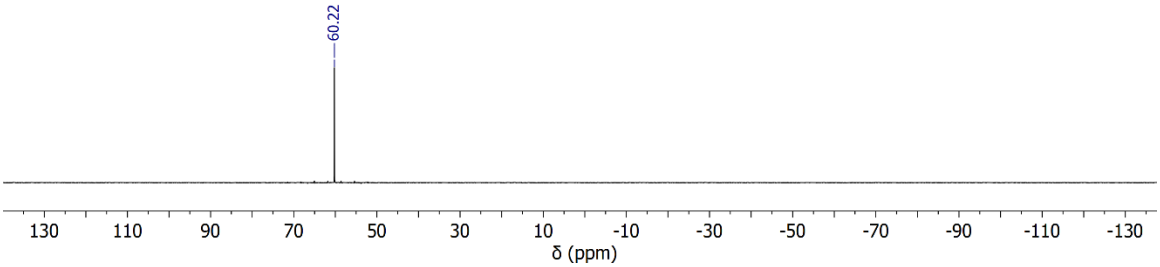


Figure S 32. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **5a**.

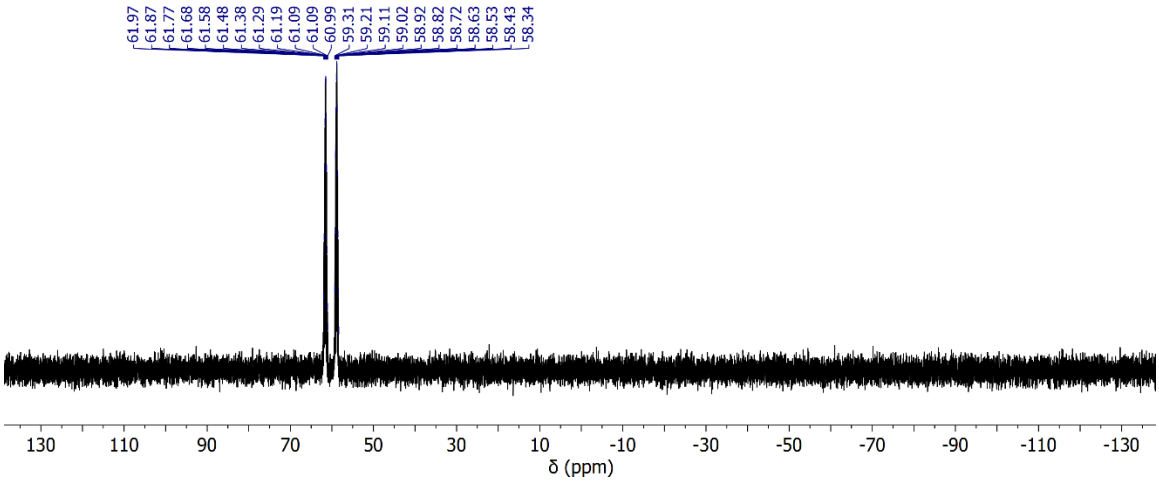
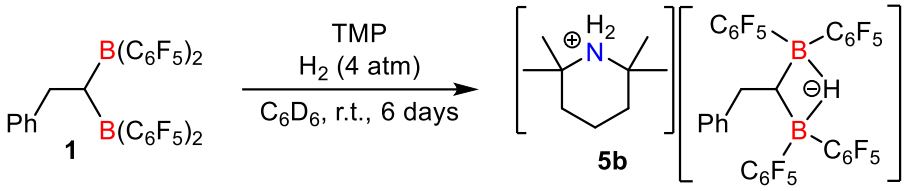


Figure S 33. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **5a**.

1.8 Spectra of $[C_5H_6Me_4NH_2][PhCH_2CH(B(C_6F_5)_2)_2(\mu\text{-}H)]$, 5b



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 7.17 – 6.95 (m, 5H, H_{Ar}), 4.86 (br, 2H, NH_2), 2.70 (br, 1H, H(B(C_6F_5)$_2$)$_2$), 2.56 (d, $^{3}J_{HH}$ = 8 Hz, 2H, PhCH_2), 2.02 (dd, $^{3}J_{HH}$ = 7.8, 8.0 Hz, 1H, HC(B(C_6F_5)$_2$)$_2$), 1.89 – 1.80 (m, 2H, 4-CH_2), 1.79 – 1.72 (m, 4H, 3-CH_2), 1.50 (s, 12H, CH_3).

^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ: -18.8.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) δ: 147.0 (*i*-C_{Ar}), 128.5 (*m*-C_{Ar}), 127.6 (*o*-C_{Ar}), 124.6 (*p*-C_{Ar}), 61.7 (C(CH_3)$_2$), 36.3 (PhCH_2), 35.6 (3,5-CH_2), 28.5 (CH_3), 16.0 (4-CH_2).

^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ: -129.5 (br, 4F, *o*-C_6F_5), -131.7 (br, 4F, *o*-C_6F_5), -160.4 (t, $^{3}J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -161.5 (t, $^{3}J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -165.6 to -166.1 (m, 4F, *m*-C_6F_5), -166.2 (t, $^{3}J_{FF}$ = 18 Hz, 4F, *m*-C_6F_5).

HRMS (ESI+/- Ionization, *m/z*): Calcd. For $C_9H_{20}N^+$ ([M]$^+$): 142.1590; Found: 142.1587. Calcd. For $C_{32}H_9B_2F_{20}^-$ ([M]$^-$): 795.0587; Found: 795.0572.

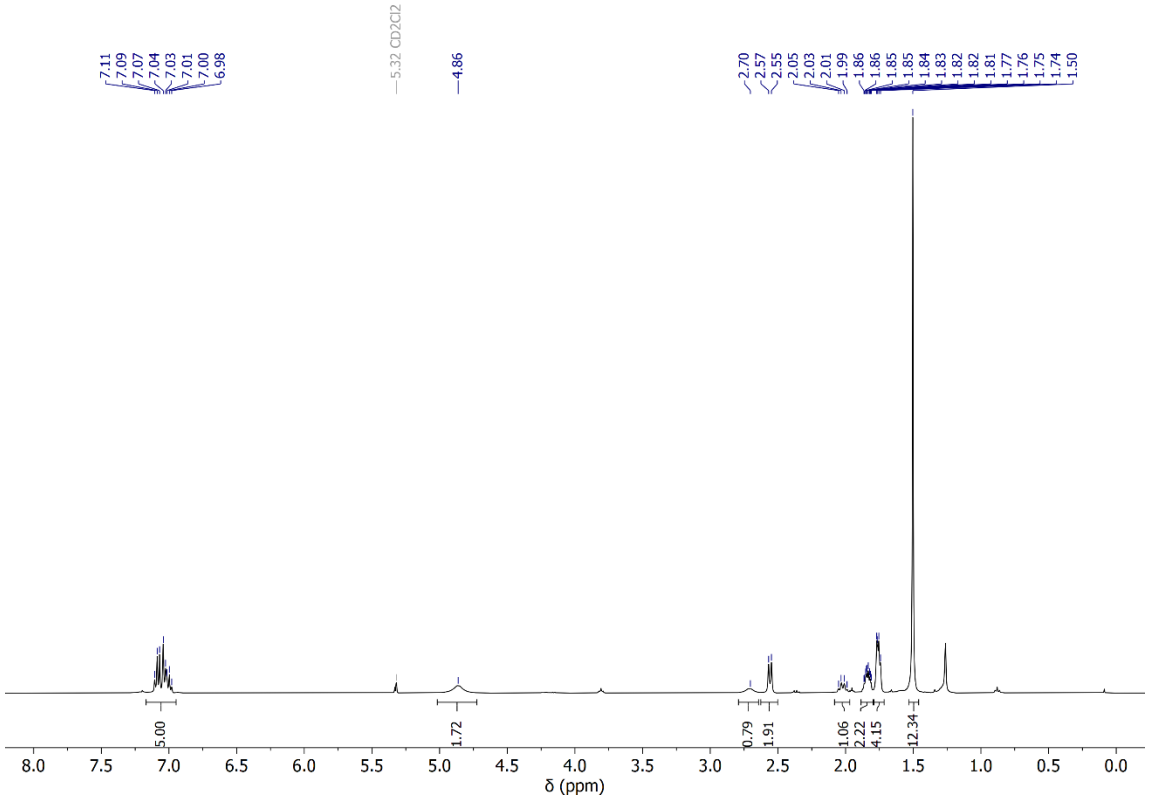


Figure S 34. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of H_2-activated product **5b**.

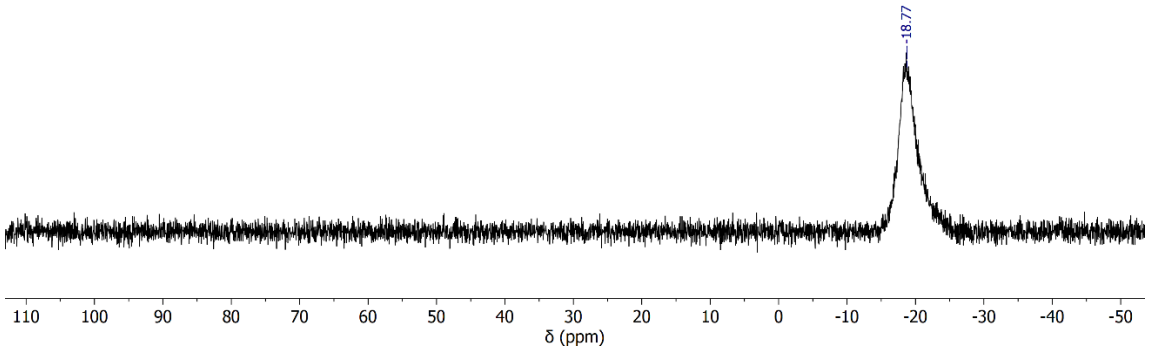


Figure S 35. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of bisborane H_2-activated product **5b**.

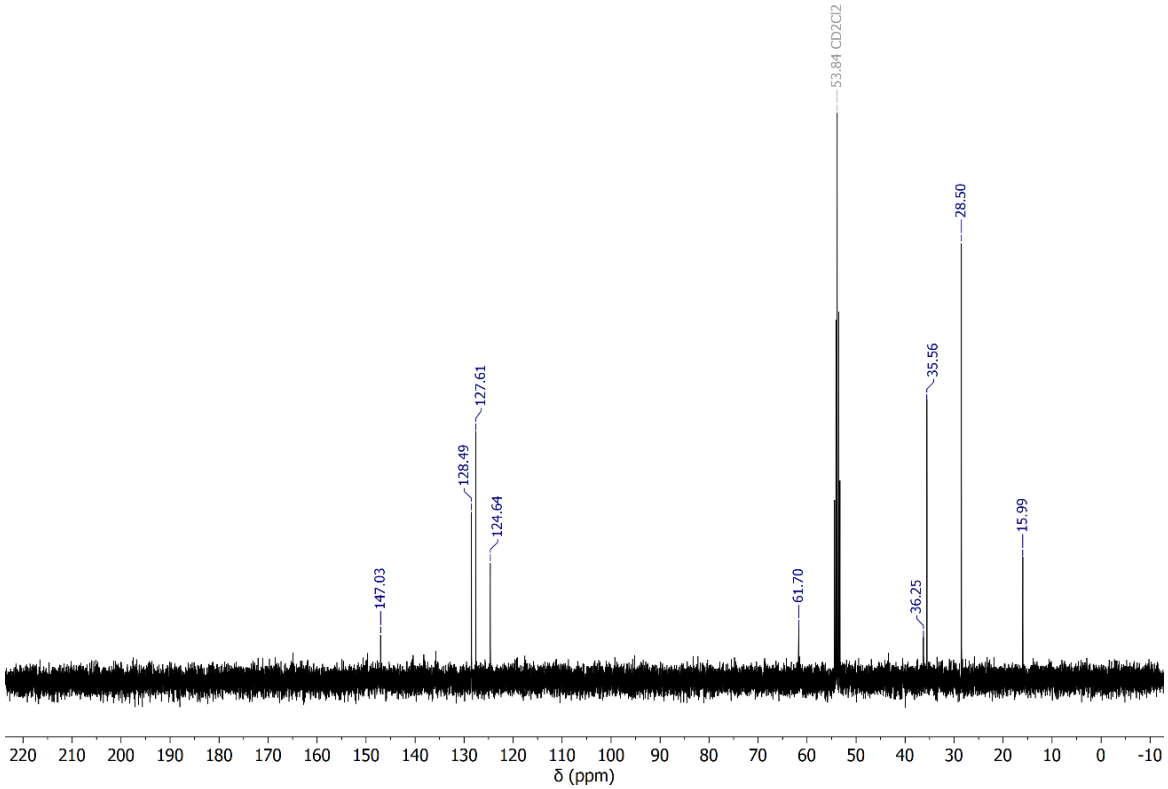


Figure S 36. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) spectrum of bisborane H_2-activated product **5b**.

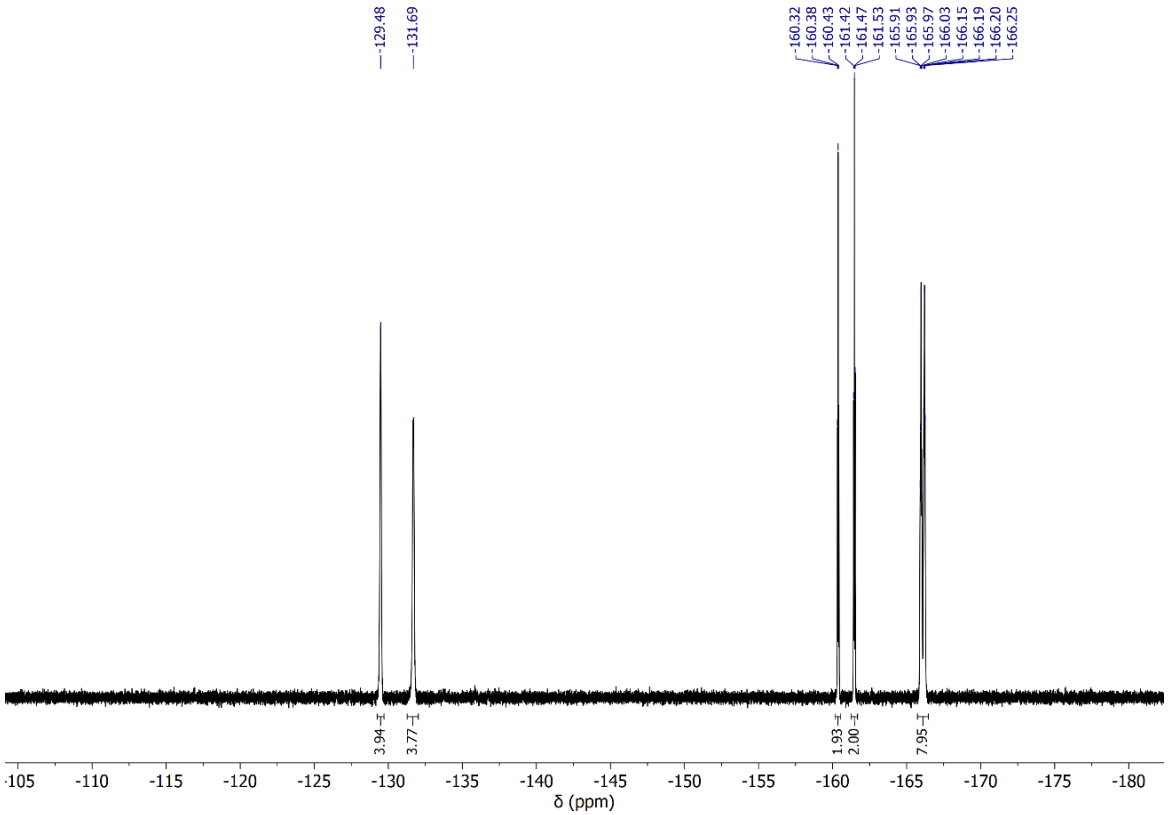
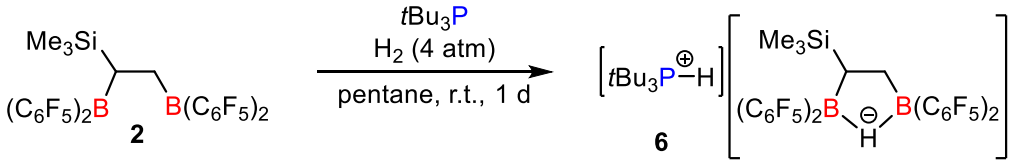


Figure S 37. ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of H_2-activated product **5b**.

1.9 Spectra of [*t*Bu$_3$PH][Me$_3$SiCH(B(C$_6$F$_5$)$_2$)CH$_2$(B(C$_6$F$_5$)$_2$(μ-H)], 6



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 5.15 (d, $^1J_{PH}$ = 430 Hz, 1H, *t*Bu$_3$P*H*), 2.72 (br, 1H, B*H*), 1.71 (d, $^3J_{PH}$ = 16 Hz, 27H, (C*H*$_3$)$_3$CPH), 1.47 (br, 1H, C*H*), 0.15 (d, $^3J_{HH}$ = 5 Hz, 2H, C*H*$_2$), 0.0 (s, Si(C*H*$_3$)$_3$).

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K) δ: 3.3, -17.7.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 148.5 (dm, $^1J_{CF}$ = 241 Hz, *o*-C$_6$F$_5$), 147.6 (dm, $^1J_{CF}$ = 246 Hz, *o*-C$_6$F$_5$), 138.8 (dm, $^1J_{CF}$ = 234 Hz, *m/p*-C$_6$F$_5$), 136.9 (dm, $^1J_{CF}$ = 243 Hz, *m/p*-C$_6$F$_5$), 136.5 (dm, $^1J_{CF}$ = 257 Hz, *m/p*-C$_6$F$_5$), 119.8 (br, *i*-C$_6$F$_5$), 37.9 (d, $^1J_{CP}$ = 28 Hz, (CH$_3$)$_3$*C*PH), 30.2 (s, (*C*H$_3$)$_3$CPH), 15.9 (s, *C*H$_2$), 2.8 (br, *C*H), -1.2 (Si(*C*H$_3$)$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -129.8 (br, 4F, *o*-C$_6$F$_5$), -133.2 (br, 4F, *o*-C$_6$F$_5$), -160.0 (br, 3F, *p*-C$_6$F$_5$), -162.1 (br, 1F, *p*-C$_6$F$_5$), -165.7 (br, 8F, *m*-C$_6$F$_5$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K) δ: 61.0 (s, *P*-H).

^{31}P NMR (162 MHz, $CDCl_3$, 298K) δ: 61.0 (dm, $^1J_{PH}$ = 426 Hz, *P*-H).

HRMS (ESI+ Ionization, *m/z*): Calcd. For $C_{12}H_{28}P^+$ ([M]$^+$): 203.1923; Found: 203.1935.

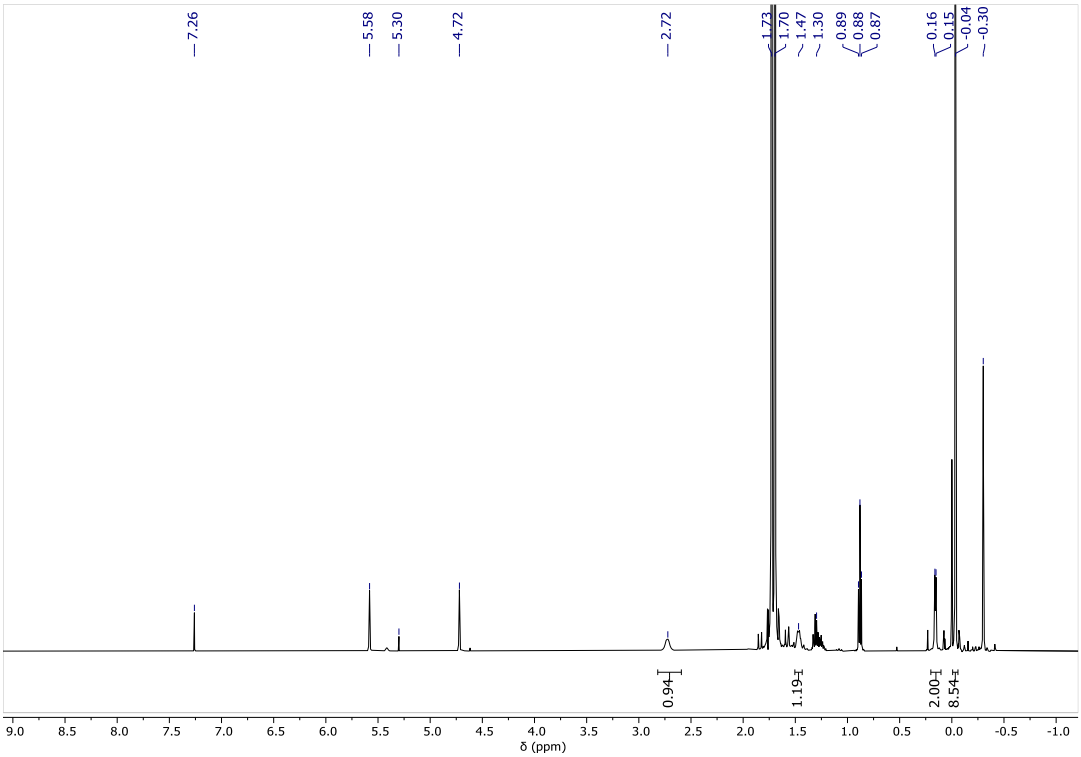


Figure S 38. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

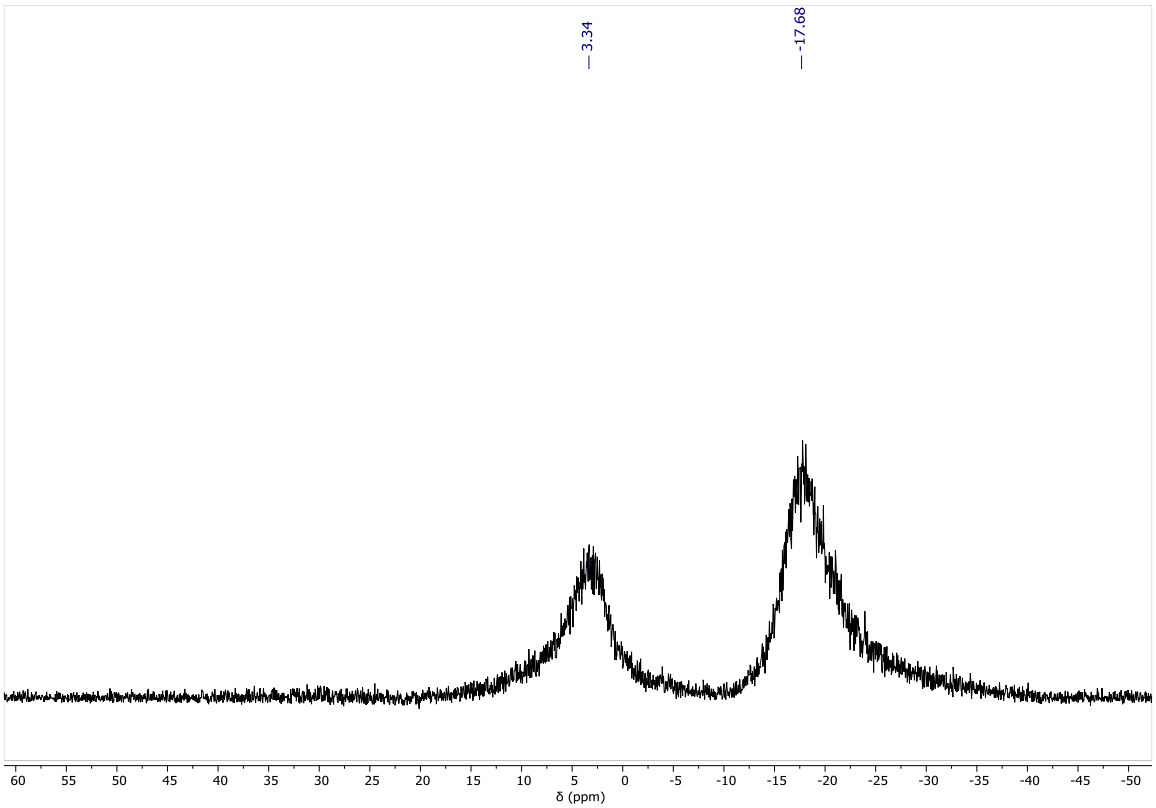


Figure S 39. $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

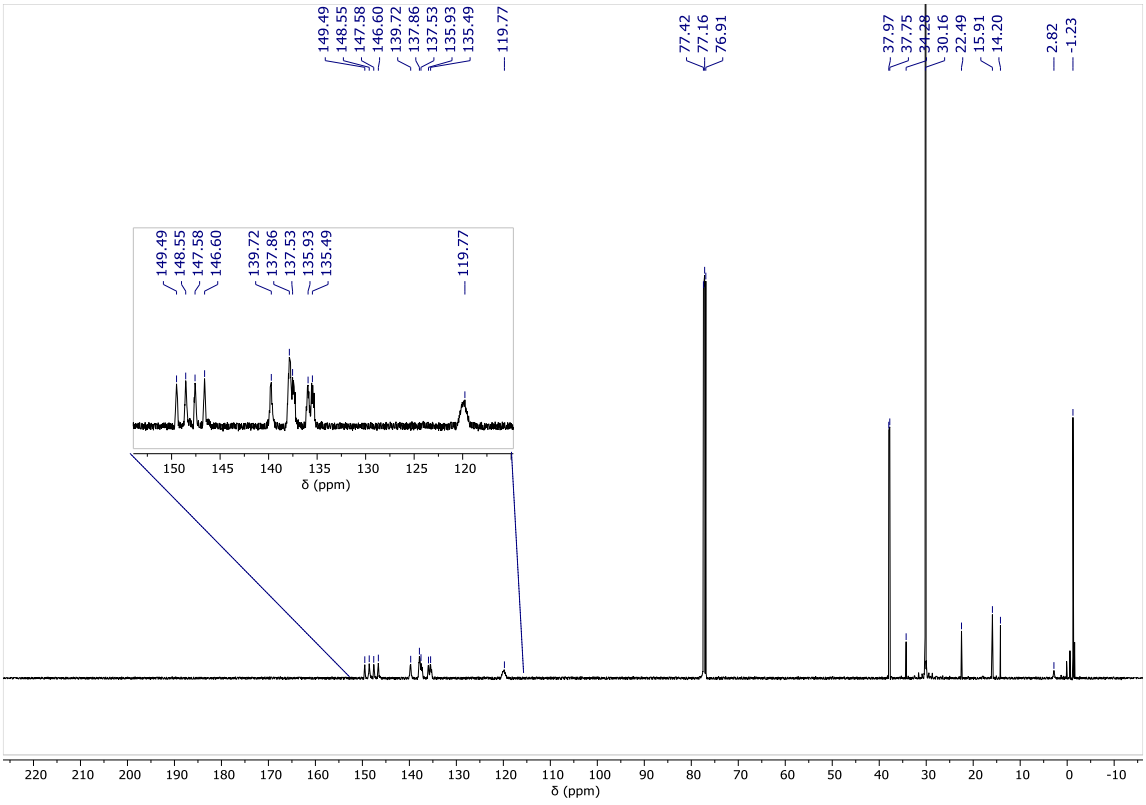


Figure S 40. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

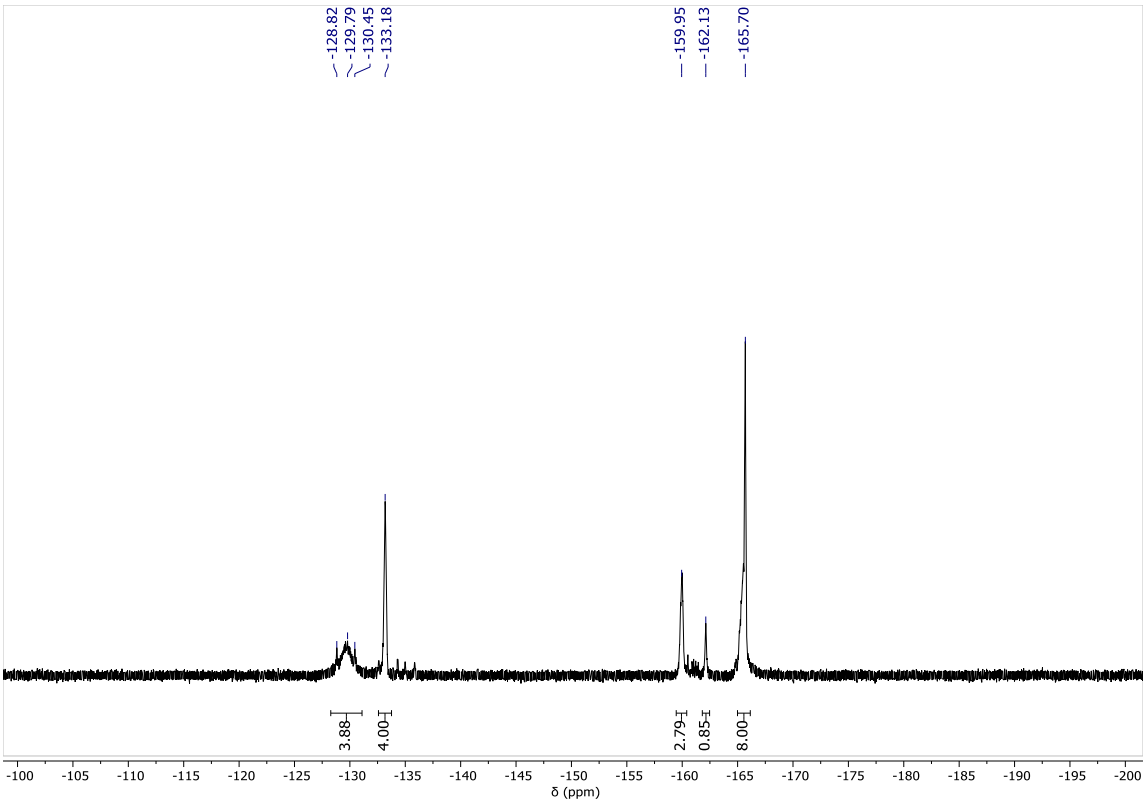


Figure S 41. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

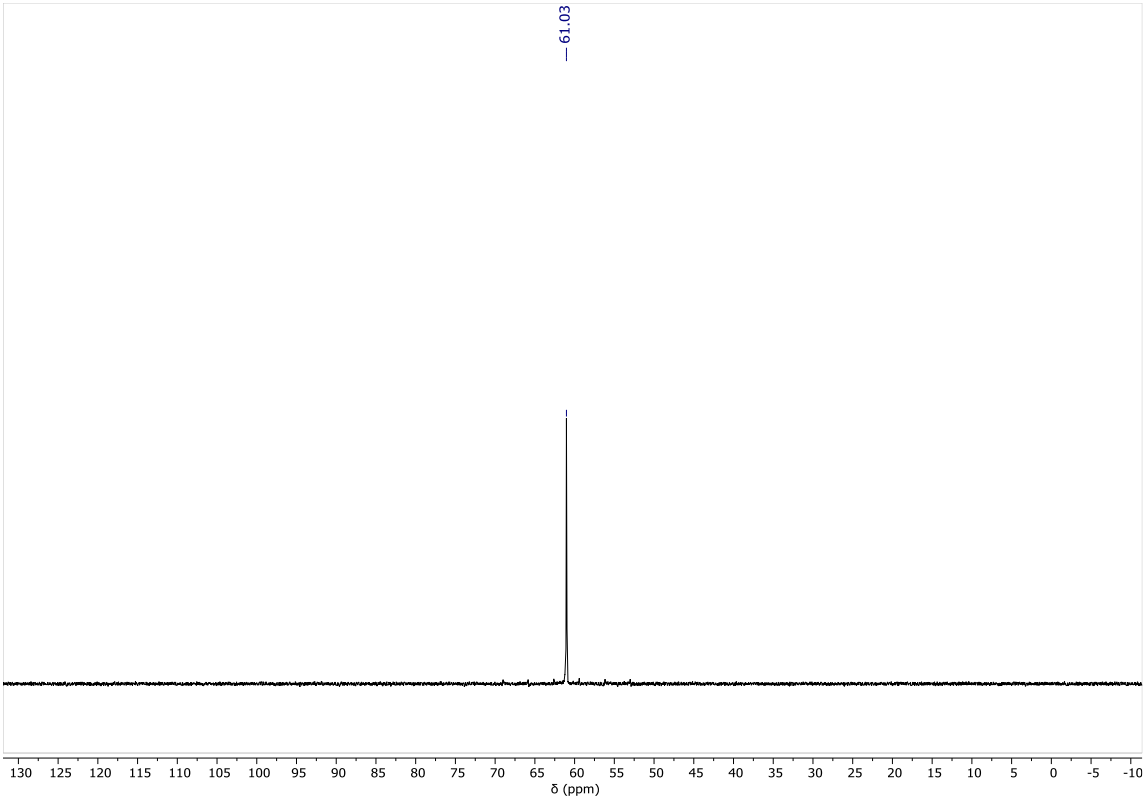


Figure S 42. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

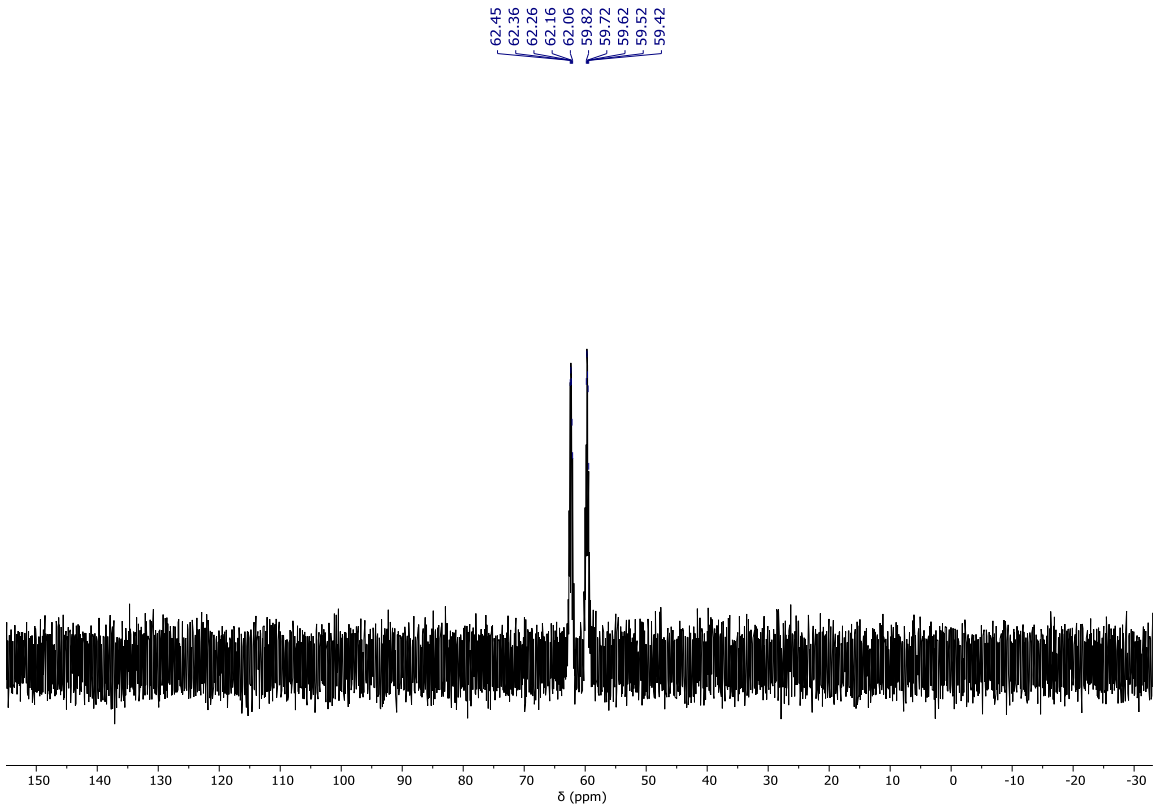
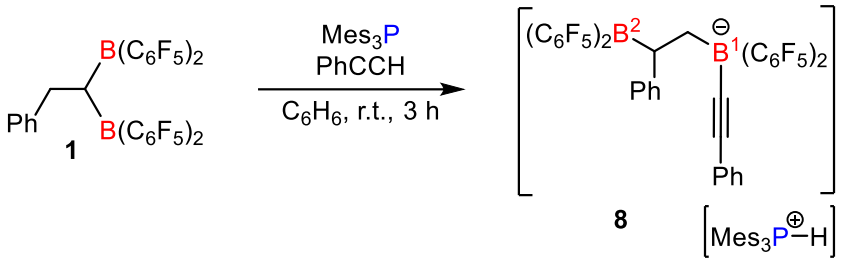


Figure S 43. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of H_2-activated product **6**.

1.10 Generation of [Mes$_3$PH][PhCH(B(C$_6$F$_5$)$_2$)CH$_2$B(C$_6$F$_5$)$_2$(CCPh)], 8



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.18 (d, $^{1}J_{PH}$ = 478 Hz, 1H, Mes$_3$P*H*), 7.10 – 7.00 (m, 10H, *H$_{Ar}$*), 6.98 – 6.84 (m, 5H, *H$_{Ar}$*), 6.79 – 6.70 (m, 5H, *H$_{Ar}$*), 5.32 (br dd, 1H, PhC*H*), 5.12* (s, *unknown impurity*) 3.15 (dd, $^{3}J_{HH}$ = 16, 8 Hz, 1H, C*H*$_2$), 2.72 (dd, $^{3}J_{HH}$ = 16, 6 Hz, 1H, C*H*$_2$), 2.36 (s, 9H, Mes-*p*-C*H*$_3$), 2.23 (s, 9H, Mes-*o*-C*H*$_3$), 1.98 (s, 9H, Mes-*o*-C*H*$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -7.8.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K, *partial*) δ: 149.8 (i-*C$_{Ar}$*), 147.4 (d, $^{4}J_{CP}$ = 3 Hz, *p*-Mes), 146.9 (i-*C$_{Ar}$*), 144.1 (d, $^{2}J_{CP}$ = 11 Hz, *o*-Mes), 142.7 (d, $^{2}J_{CP}$ = 11 Hz, *o*-Mes), 133.4 (d, $^{3}J_{CP}$ = 12 Hz, *m*-Mes), 132.0 (d, $^{3}J_{CP}$ = 10 Hz, *m*-Mes), 129.8, 128.7, 128.5, 127.6, 127.7, 127.4, 126.2, 126.0, 125.4, 124.7, 124.4, 111.4 (d, $^{1}J_{CP}$ = 83 Hz, *i*-Mes), 63.2 (Ph*C*H), 37.0 (*C*H$_2$), 22.1 (br, Mes-*o*-*C*H$_3$), 21.5 (br, Mes-*p*-*C*H$_3$), 21.2 (d, $^{3}J_{CP}$ = 12 Hz, Mes-*o*-*C*H$_3$).

^{13}C{^{1}H} DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K, *partial*) δ: 133.4 (d, $^{3}J_{CP}$ = 12 Hz, *m*-Mes), 132.0 (d, $^{3}J_{CP}$ = 10 Hz, *m*-Mes), 129.8, 128.7, 128.5, 127.6, 127.7, 127.4, 126.2, 126.0, 125.4, 124.7, 124.4, 63.2 (Ph*C*H), 37.0 (*C*H$_2$), 22.1 (br, Mes-*o*-*C*H$_3$), 21.5 (d, $^{5}J_{CP}$ = 1 Hz, Mes-*p*-*C*H$_3$), 21.2 (d, $^{3}J_{CP}$ = 12 Hz, Mes-*o*-*C*H$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -128.8 (d, $^{3}J_{FF}$ = 26 Hz, 2F, B^{1} *o*-C$_6$F$_5$), -129.7 (d, $^{3}J_{FF}$ = 26 Hz, 2F, B^{1} *o*-C$_6$F$_5$), -131.2 (br, 4F, B^{2} *o*-C$_6$F$_5$), -154.8 (t, $^{3}J_{FF}$ = 20 Hz, 2F, B^{2} *p*-C$_6$F$_5$), -164.0 (br, 4F, B^{2} *m*-C$_6$F$_5$), -164.9 (m, 2F, B^{1} *p*-C$_6$F$_5$), -166.2 (m, 2F, B^{1} *m*-C$_6$F$_5$), -167.2 (m, 2F, B^{1} *m*-C$_6$F$_5$).

^{19}F, ^{19}F COSY (377 MHz / 377 MHz, $CDCl_3$, 298 K) δ ^{19}F / δ ^{19}F: -128.9 / -166.3, -129.8 / -167.1, -154.8 / -163.9.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ: -27.5.

^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: -27.5 (d, $^{1}J_{PH}$ = 476 Hz).

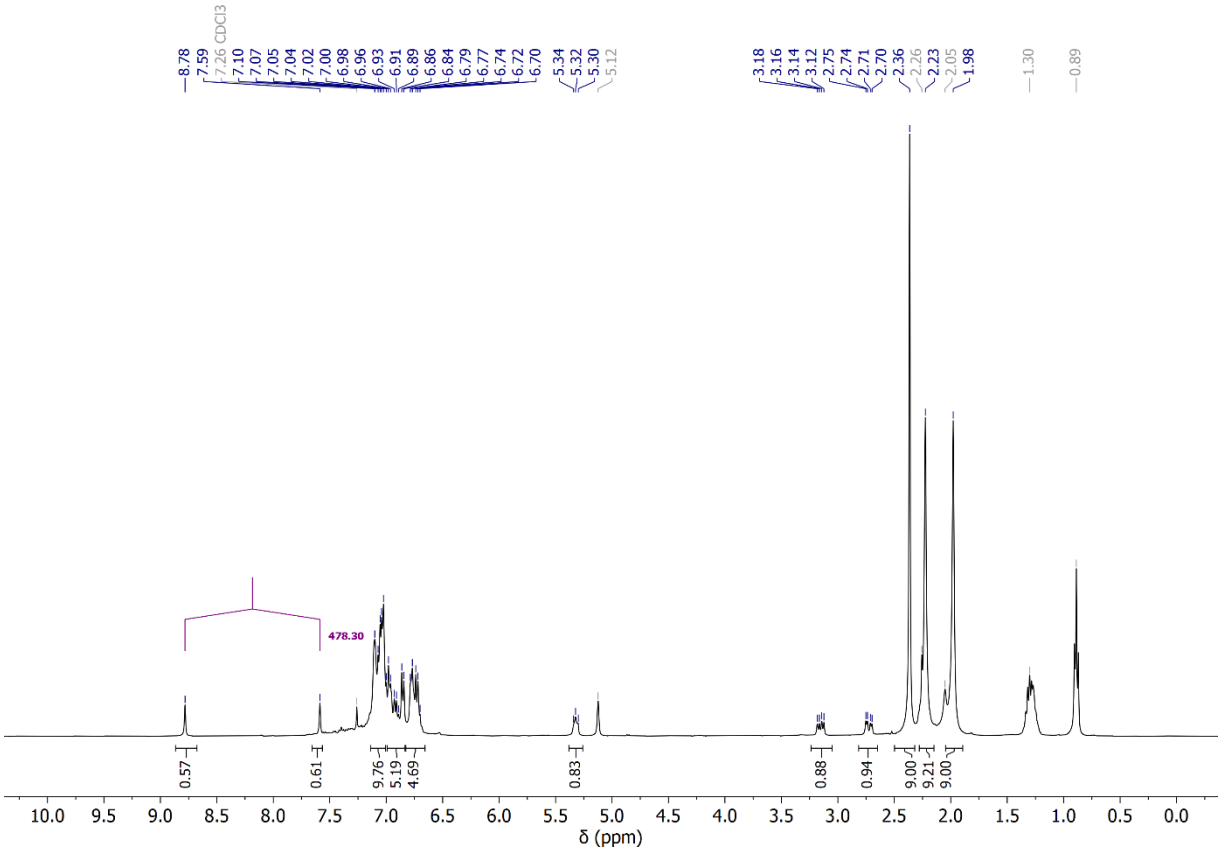


Figure S 44. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

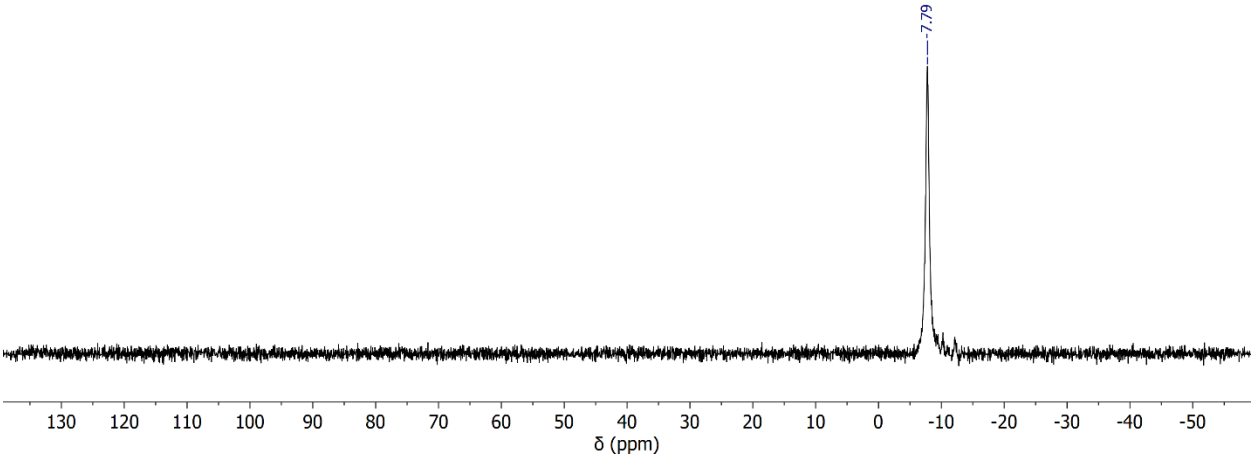


Figure S 45. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

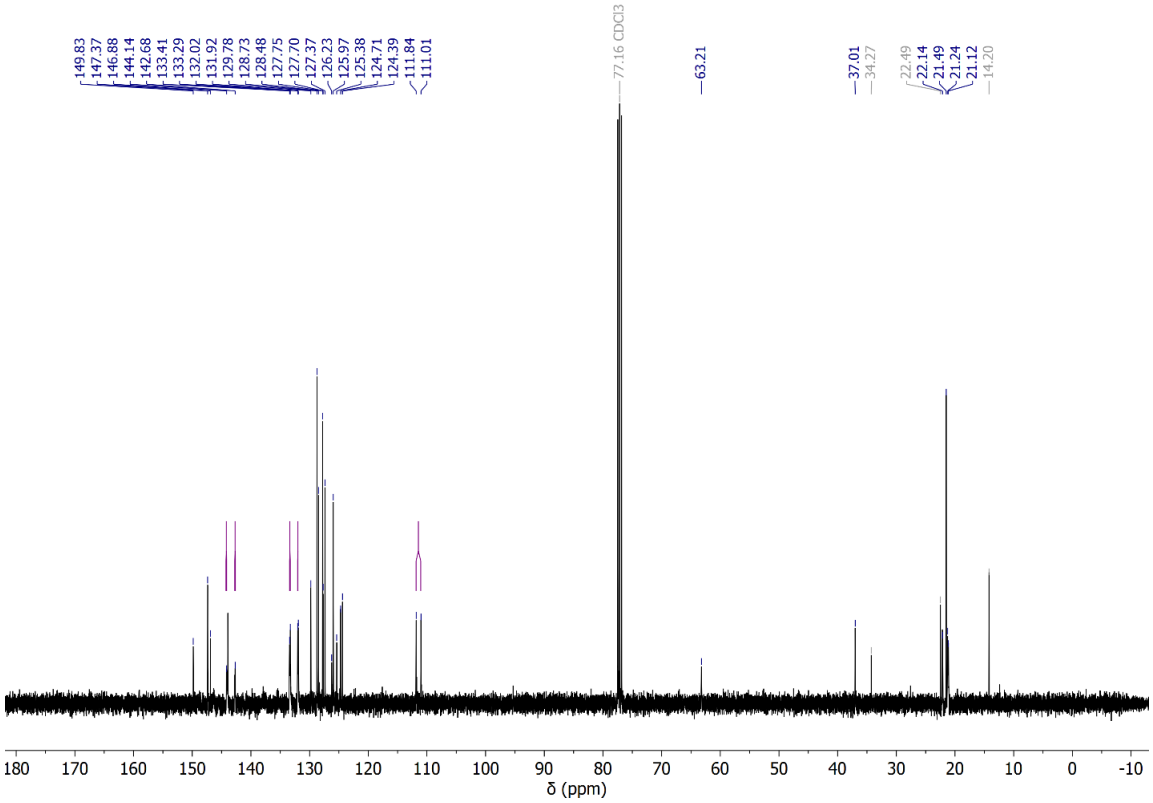


Figure S 46. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

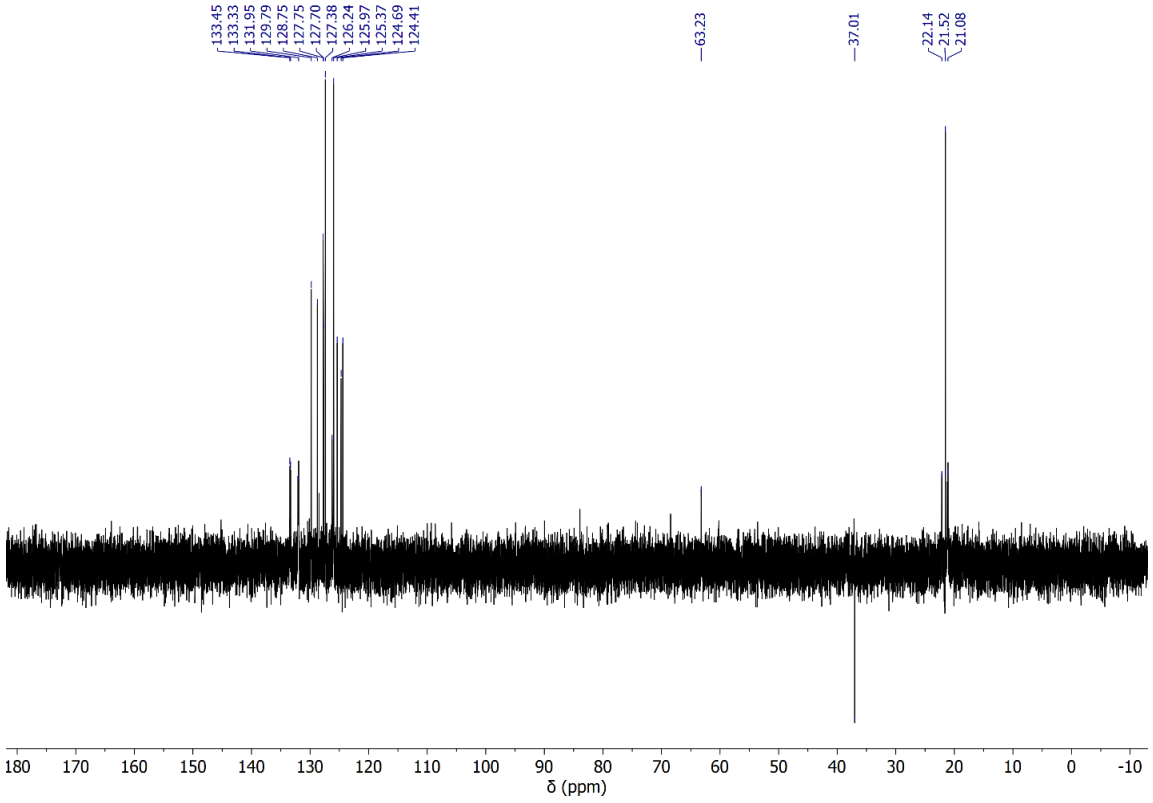


Figure S 47. $^{13}C\{^{1}H\}$ DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

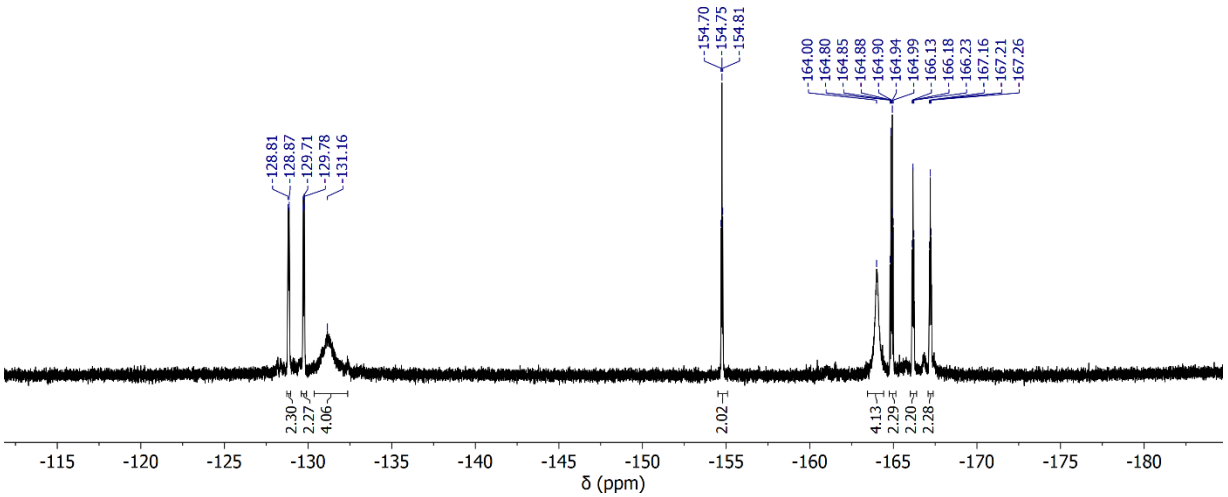


Figure S 48. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

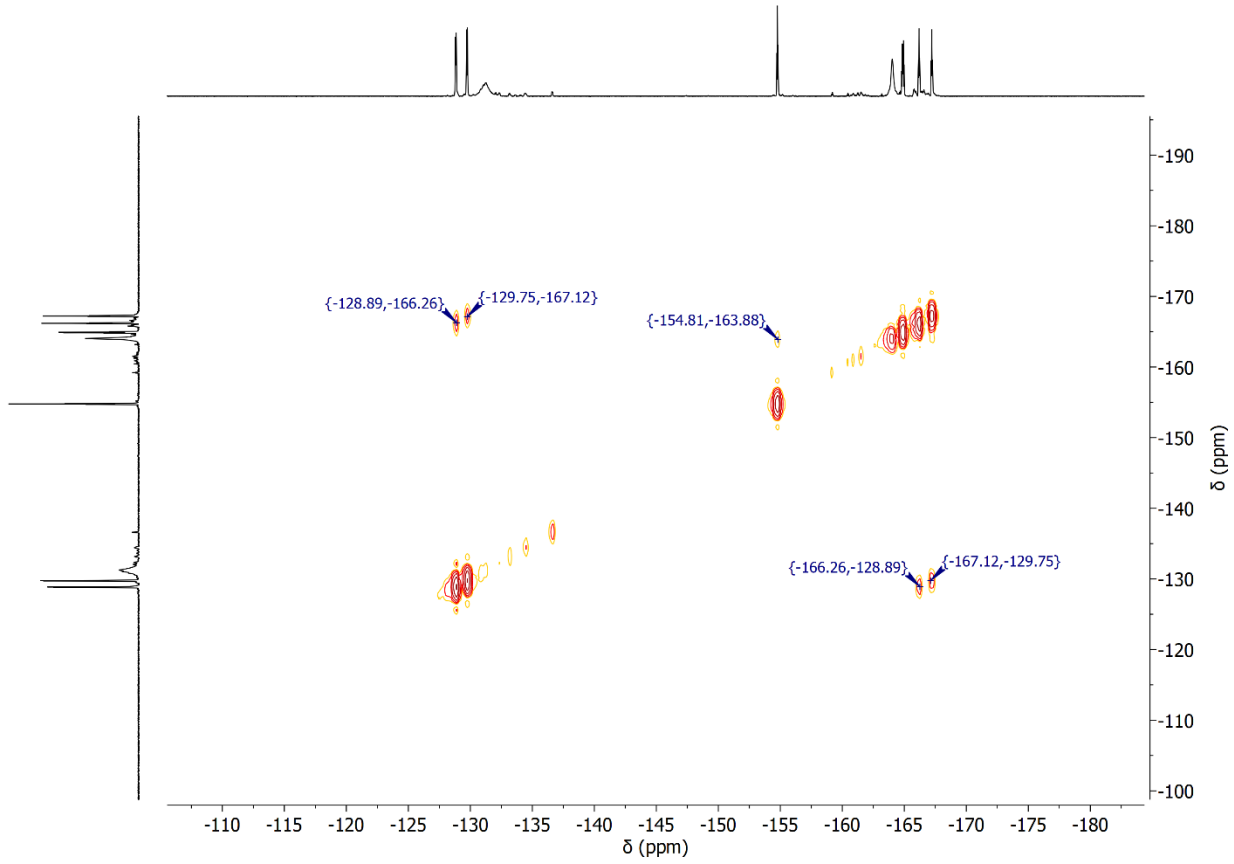


Figure S 49. ^{19}F, ^{19}F COSY (377 MHz / 377 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

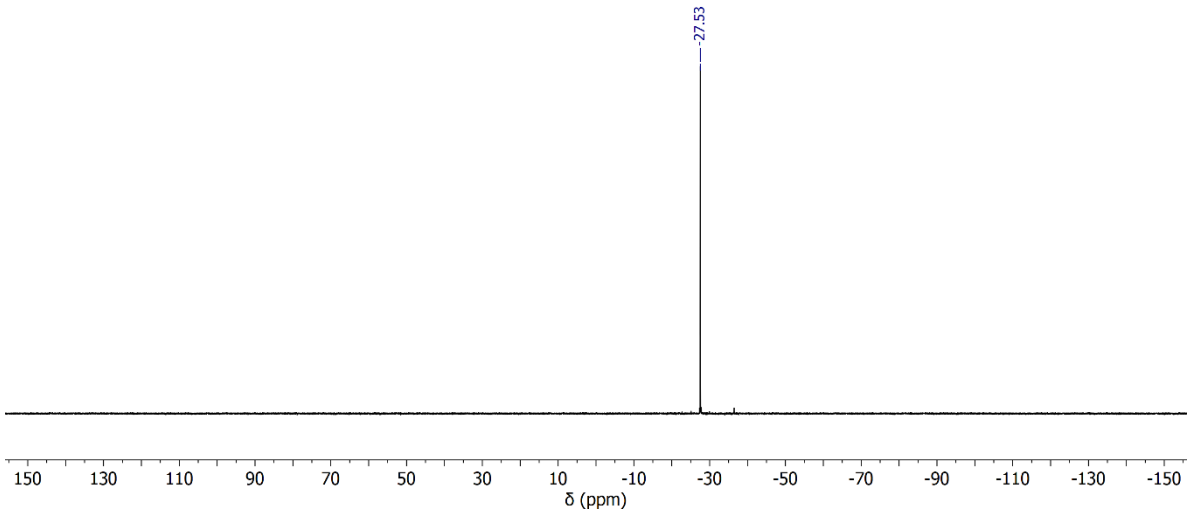


Figure S 50. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

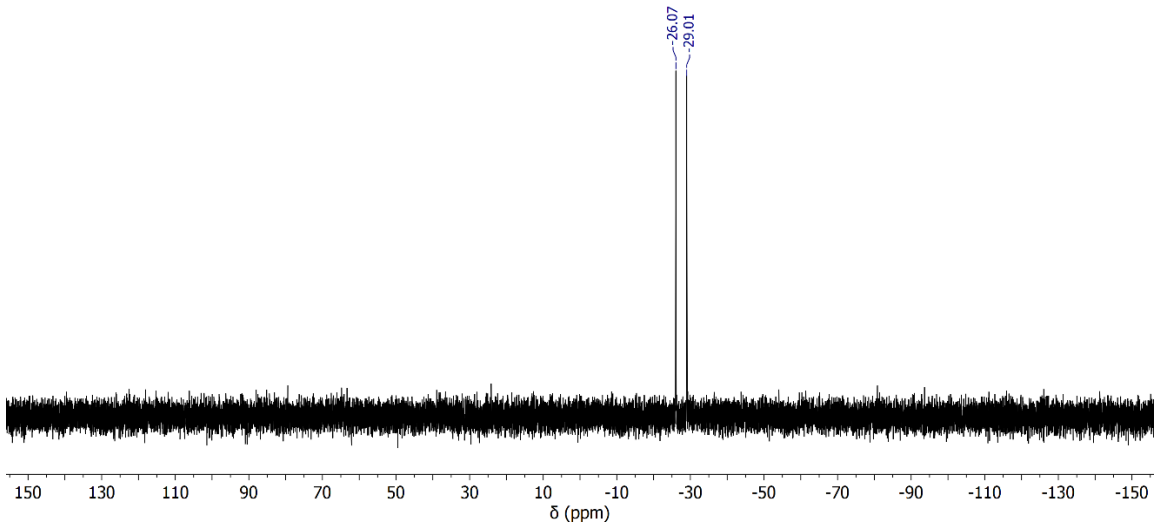
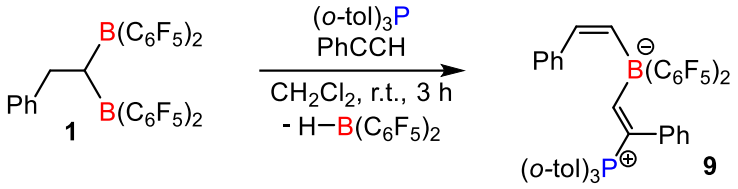


Figure S 51. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

1.11 Spectra of PhC(H)C(H)B(C$_6$F$_5$)$_2$C(H)C(Ph)(P(*o*-tol)$_3$), 9



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.10 (d, $^3J_{PH}$ = 34 Hz, 1H, PC=C*H*), 7.41 (d, $^3J_{HH}$ = 8 Hz, 2H, C(H)Ph-*H*$_{Ar}$), 7.30 – 7.36 (m and d, $^3J_{HH}$ = 18 Hz, 4H, *H*CPh-*H*$_{Ar}$ *overlapping*), 7.27 – 7.13 (m, 12H, *o*-tol-*H*$_{Ar}$), 7.03 (t, $^3J_{HH}$ = 7 Hz, 1H, *p*-*H*$_{Ar}$), 6.94 (br dd, 2H, *m*-*H*$_{Ar}$), 6.75 (d, $^3J_{HH}$ = 7 Hz, 2H, *o*-*H*$_{Ar}$), 6.00 (d, $^3J_{HH}$ = 18 Hz, 1H, BC*H*=C), 2.42 (s, 9H, PhC*H*$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -13.4.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ: 141.6 (*i*-PhCCB), 137.9 (Ph*C*CB), 135.4 (d, $^2J_{CP}$ = 15 Hz, *o*-Ph(CH$_3$)P), 134.4 (d, $^3J_{CP}$ = 10 Hz, *m*-PhP), 131.5 (br, *p*-PhP), 130.5 (d, $^3J_{CP}$ = 5 Hz, *o*-PhCP), 130.4 (d, $^2J_{CP}$ = 13 Hz, *o*-PhP), 128.4 (*m*-PhCCB), 127.6 (d, $^4J_{CP}$ = 2 Hz, *m*-PhCP), 127.5 (d, $^5J_{CP}$ = 3 Hz, *p*-PhCP), 125.8 (*o*-PhCCB), 125.6 (*p*-PhCCB), 117.5 (d, $^1J_{CP}$ = 88 Hz, P*C*=C), 115.5 (d, $^1J_{CP}$ = 70 Hz, *i*-PhP), 21.8 (d, $^3J_{CP}$ = 2 Hz, CH_3).

^{13}C{^{1}H} DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K) δ: 134.4 (d, $^3J_{CP}$ = 10 Hz, *m*-PhP), 131.5 (br, *p*-PhP), 130.5 (d, $^3J_{CP}$ = 5 Hz, *o*-PhCP), 130.4 (d, $^2J_{CP}$ = 13 Hz, *o*-PhP), 128.4 (*m*-PhCCB), 127.6 (d, $^4J_{CP}$ = 2 Hz, *m*-PhCP), 127.5 (d, $^5J_{CP}$ = 3 Hz, *p*-PhCP), 125.8 (*o*-PhCCB), 125.6 (*p*-PhCCB), 21.8 (d, $^3J_{CP}$ = 2 Hz, CH_3).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -131.4 (d, $^3J_{FF}$ = 24 Hz, 4F, *o*-C_6F_5), -163.0 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -166.3 (d, $^3J_{FF}$ = 21 Hz, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 3.3 ppm]

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K) δ: 22.1 (s).

HRMS (ESI+ Ionization, *m/z*): Calcd. For $C_{49}H_{34}BF_{10}NaP^+$ ([M+Na]$^+$): 877.2231; Found: 877.2221.

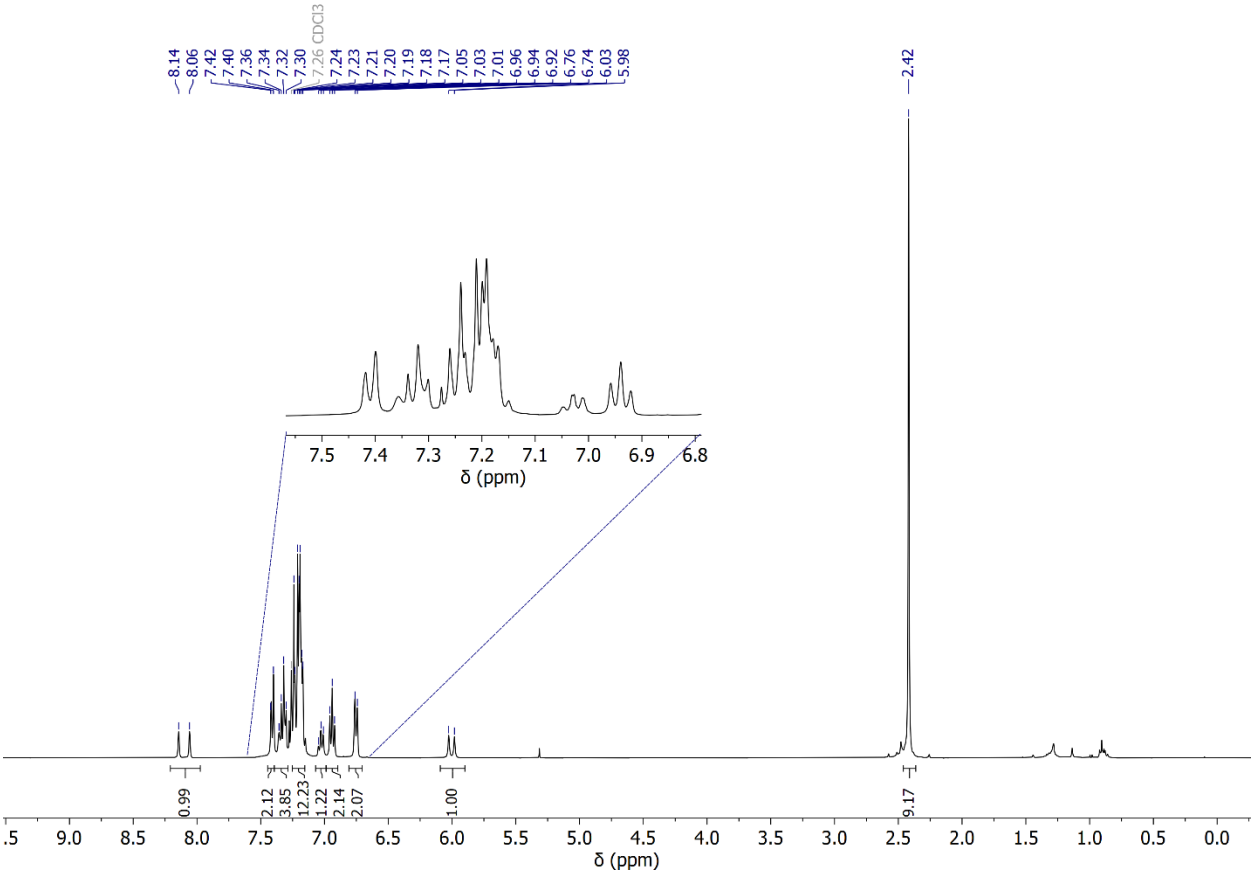


Figure S 52. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum compound **9**.

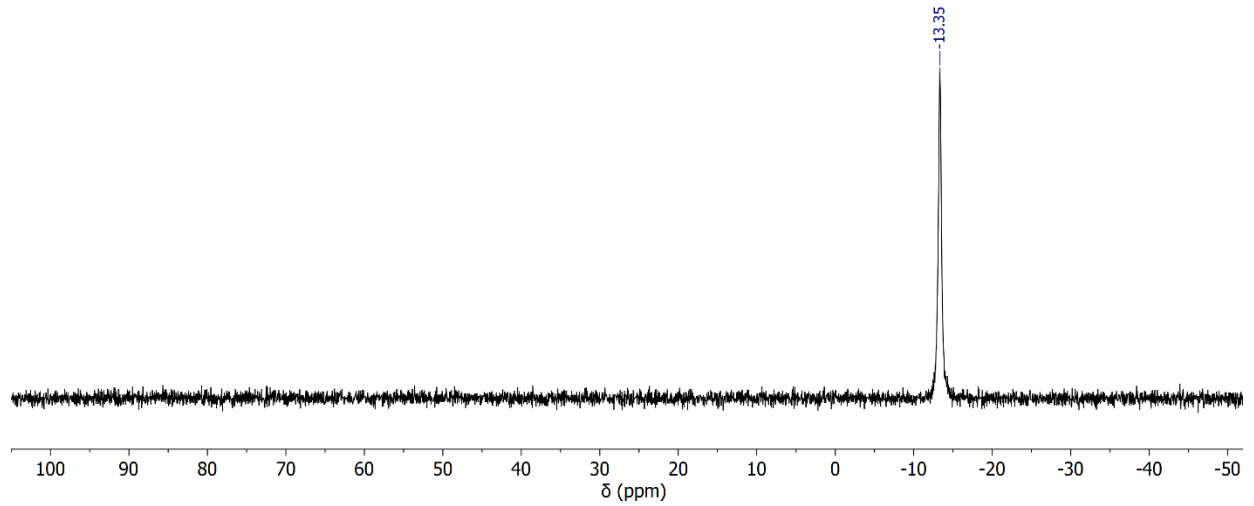


Figure S 53. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **9**.

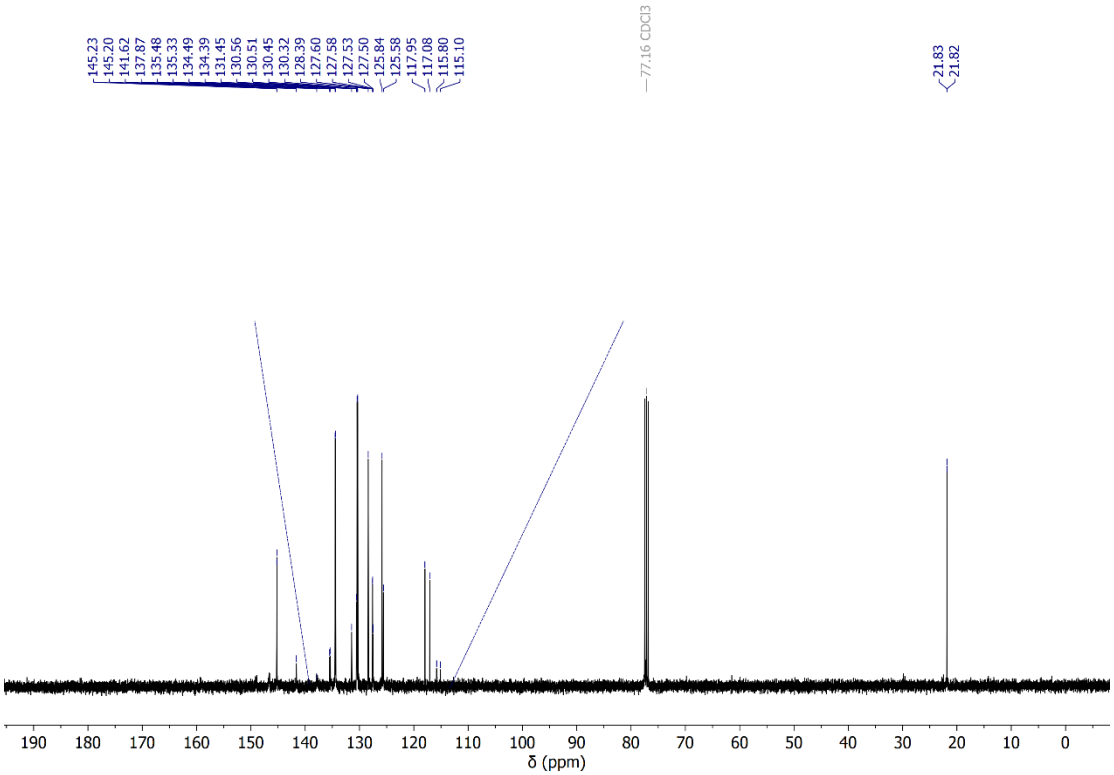


Figure S 54. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9**.

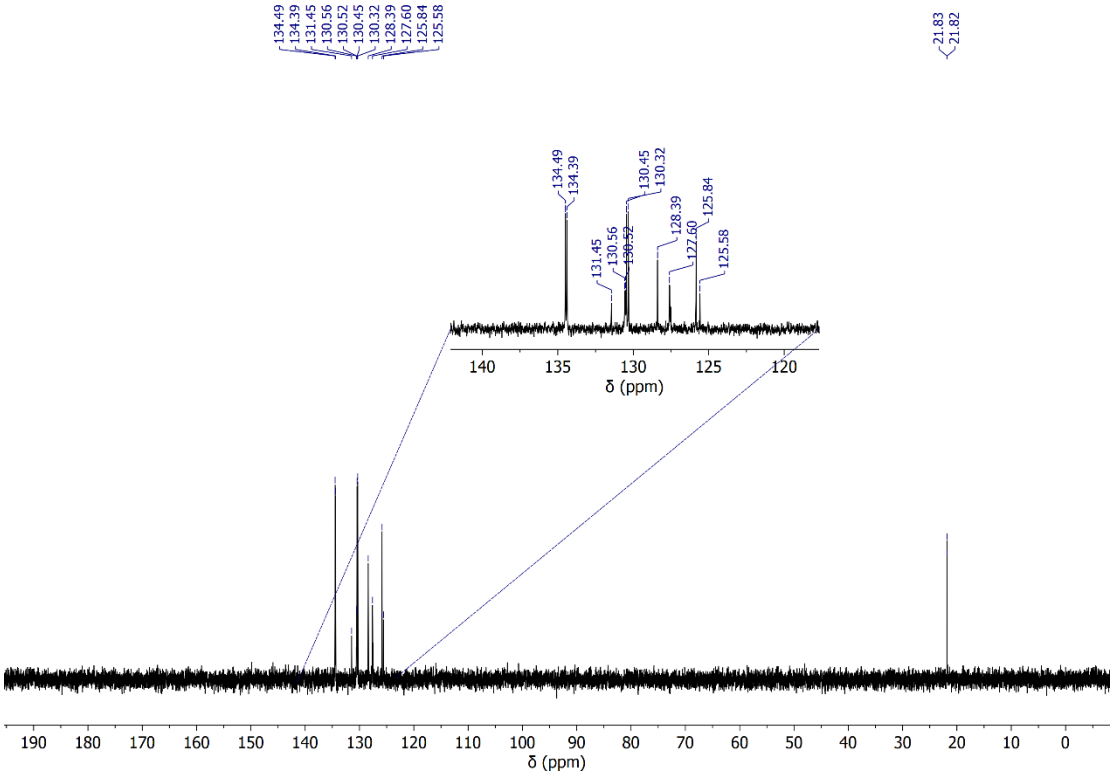


Figure S 55. $^{13}C\{^{1}H\}$ DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **9**.

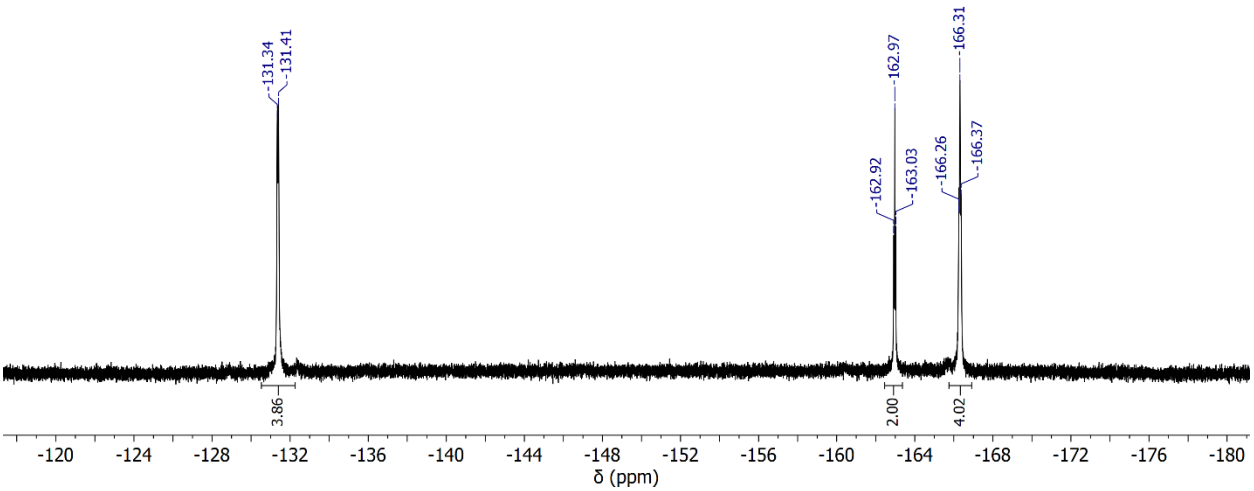


Figure S 56. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **9**.

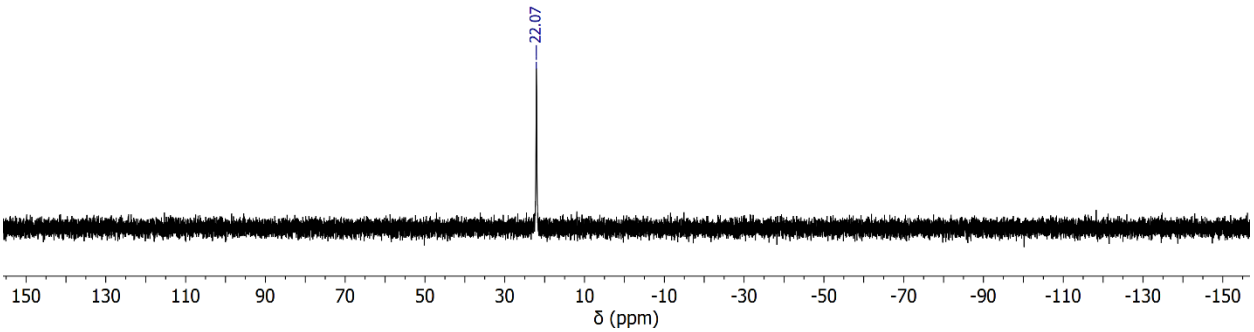
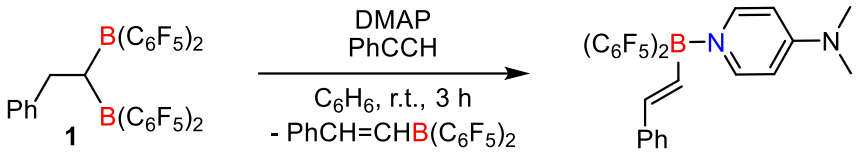


Figure S 57. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **9**.

1.12 Preparation of PhC(H)C(H)B(C$_6$F$_5$)$_2$(DMAP), 10



^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.09 (d, $^3J_{HH}$ = 8 Hz, 1H, NC*H*), 7.44 – 7.37 (m, 2H, Ph-*H*$_{Ar}$), 7.28 (d, $^3J_{HH}$ = 17 Hz, 1H, PhC*H*), 7.28 (br, 1H, Ph-*H*$_{Ar}$), 7.22 – 7.12 (m, 2H, Ph-*H*$_{Ar}$), 6.56 (d, $^3J_{HH}$ = 8 Hz, 1H, NCC*H*), 6.20 (d, $^3J_{HH}$ = 18 Hz, 1H, BC*H*), 3.15 (s, 3H, C*H*$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -3.6.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ: 155.7 (*p*-Py), 145.5 (*o*-Py), 139.9 (*i*-Ph), 137.2 (Ph*C*H=), 128.5 (*m*-Ph), 126.9 (*o*-Ph), 126.4 (*p*-Ph), 106.7 (*m*-Py), 39.7 (*C*H$_3$).

^{13}C{^{1}H} DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K) δ: 145.5 (*o*-Py), 137.2 (Ph*C*H=), 128.5 (*m*-Ph), 126.9 (*o*-Ph), 126.4 (*p*-Ph), 106.7 (*m*-Py), 39.7 (*C*H$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -132.0 (m, 2F, *o*-C$_6$F$_5$), -158.7 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C$_6$F$_5$), -164.1 (m, 4F, *m*-C$_6$F$_5$).

HRMS (ESI+ Ionization, *m/z*): Calcd. For $C_{27}H_{17}BF_{10}Nna^+$ ([M+Na]$^+$): 593.1222; Found: 593.1211.

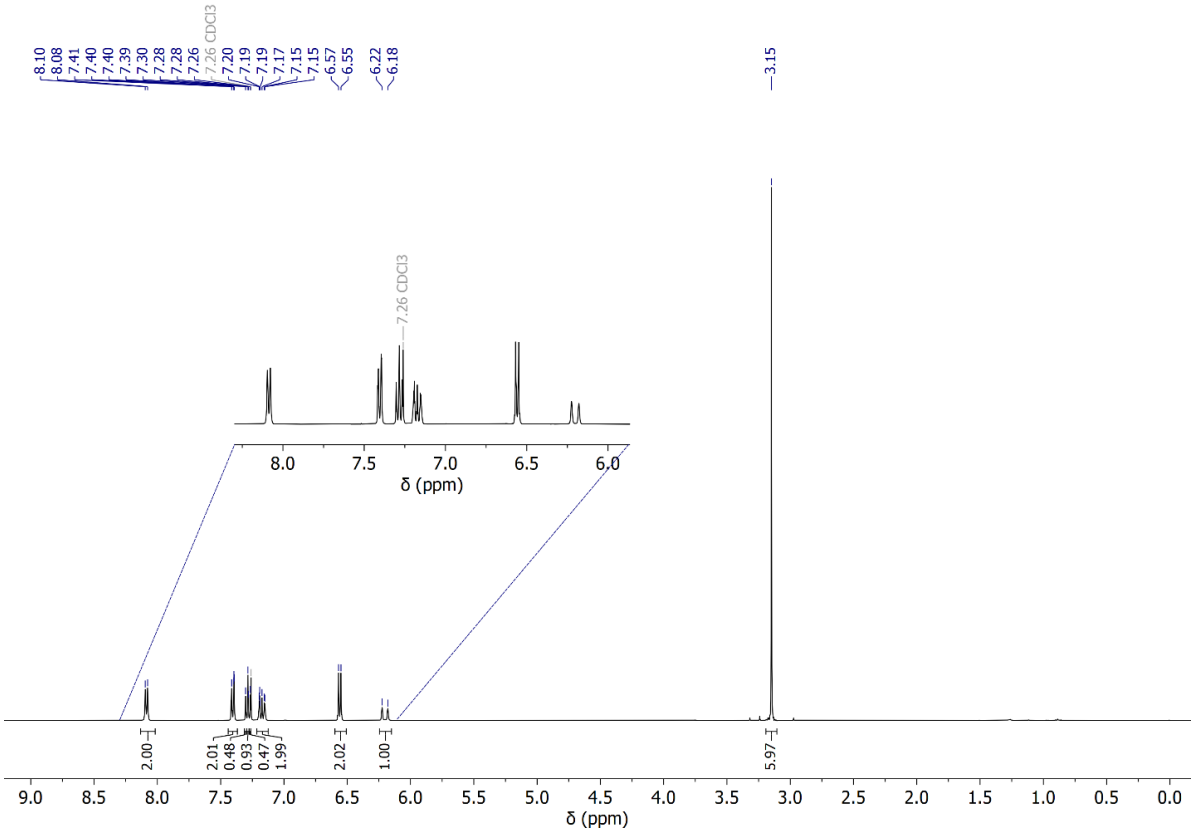


Figure S 58. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **10**.

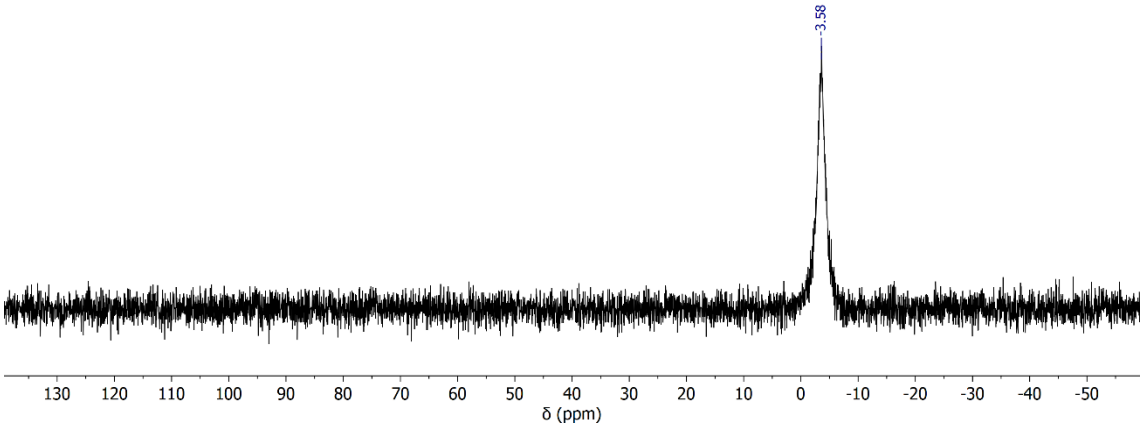


Figure S 59. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **10**.

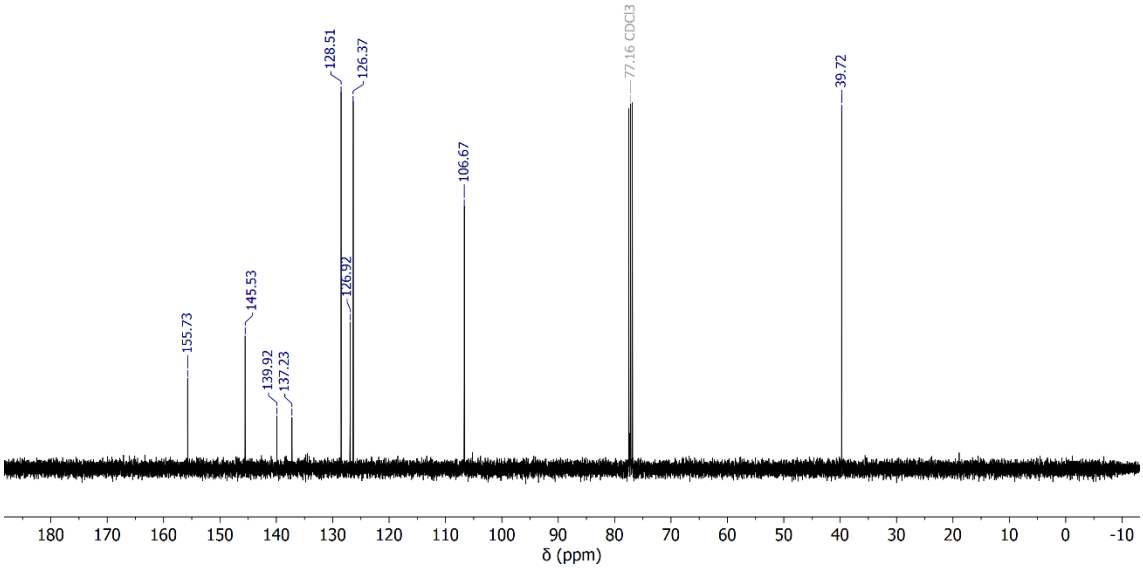


Figure S 60. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **10**.

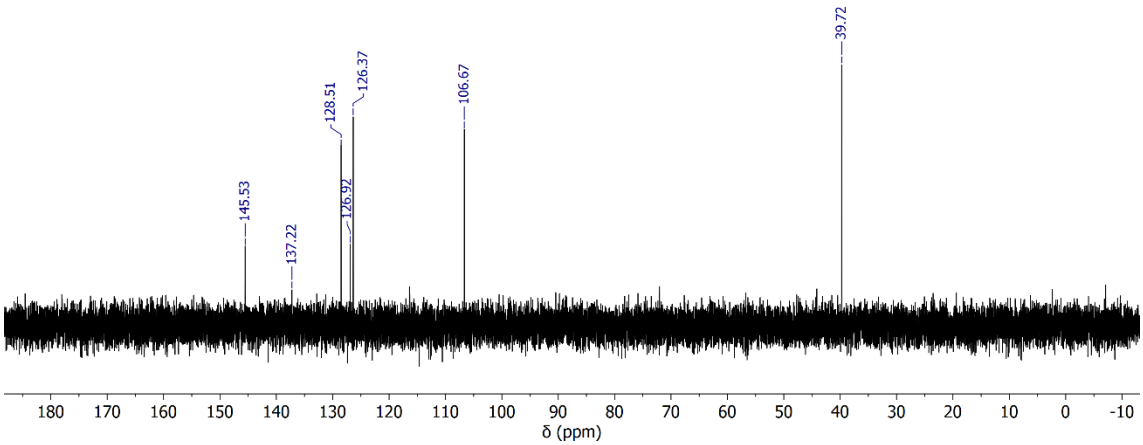


Figure S 61. $^{13}C\{^1H\}$ DEPT-135 NMR (101 MHz, $CDCl_3$, 298 K) spectrum of compound **10**.

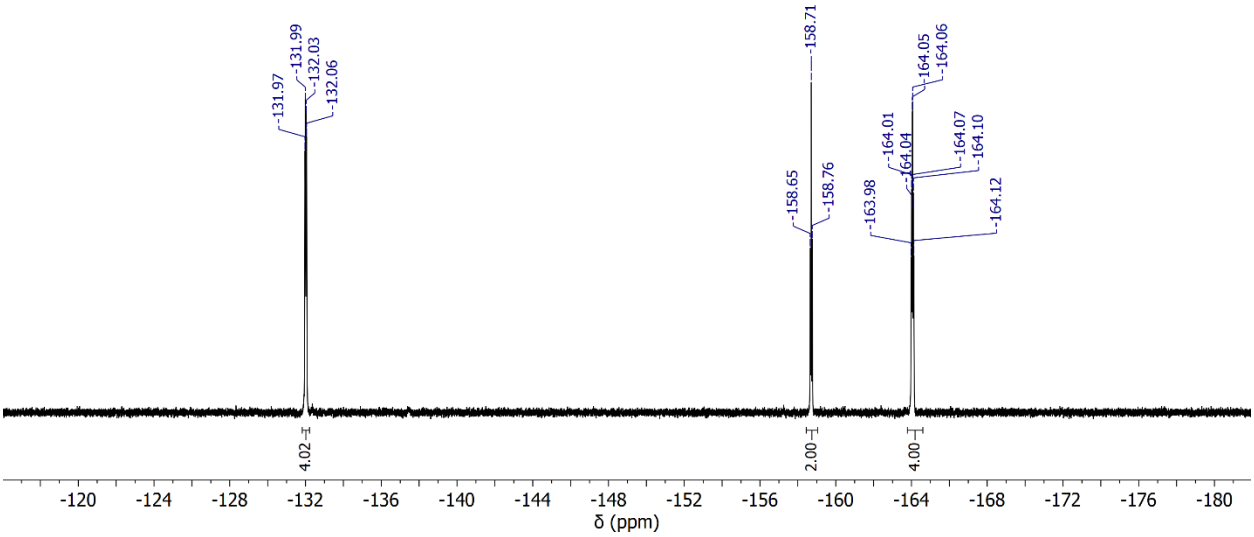
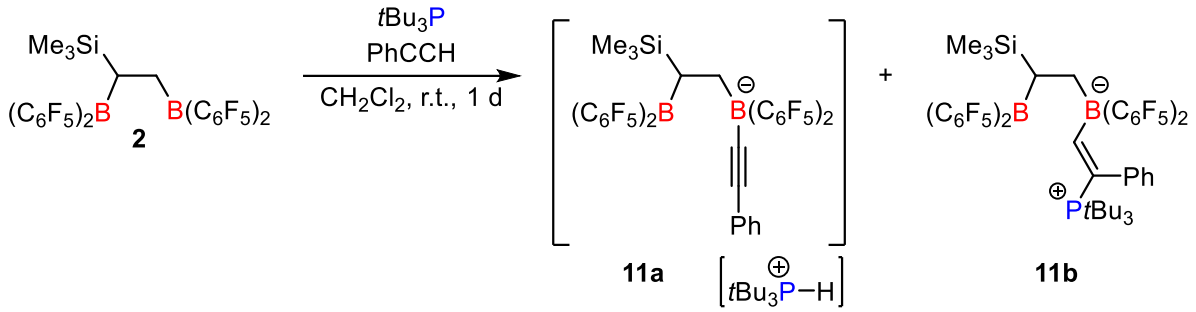


Figure S 62. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **10**.

1.13 Reaction of *bis*-borane 2 and *t*Bu$_3$P with phenylacetylene, 11



^{1}H NMR (400 MHz, $CDCl_3$, 298 K, *partial*) δ: 8.42 (d, $^3J_{PH}$ = 29 Hz, PCC*H*, **11b**), 7.15, 7.07, 6.88, 6.70, 6.51, 5.28 (d, $^1J_{PH}$ = 434 Hz, *t*Bu$_3$P*H*, **11a**), 2.95, 2.73, 1.68 – 1.50, 1.46 – 1.33, 0.97, -0.10 (s, Si(C*H*$_3$)$_3$, **11b**), -0.20 (s, Si(C*H*$_3$)$_3$, **11a**).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -6.0 (**11a**), -11.5 (**11b**).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K, *unassigned*) δ: -126.9, -127.7, -128.4, -129.1, -131.2, -150.0, -152.6, -162.3, -162.7, -163.4, -163.6, -164.4, -164.8, -165.8, -166.4, -166.8.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K) δ: 58.7 (s, **11a**), 42.0 (s, **11b**).

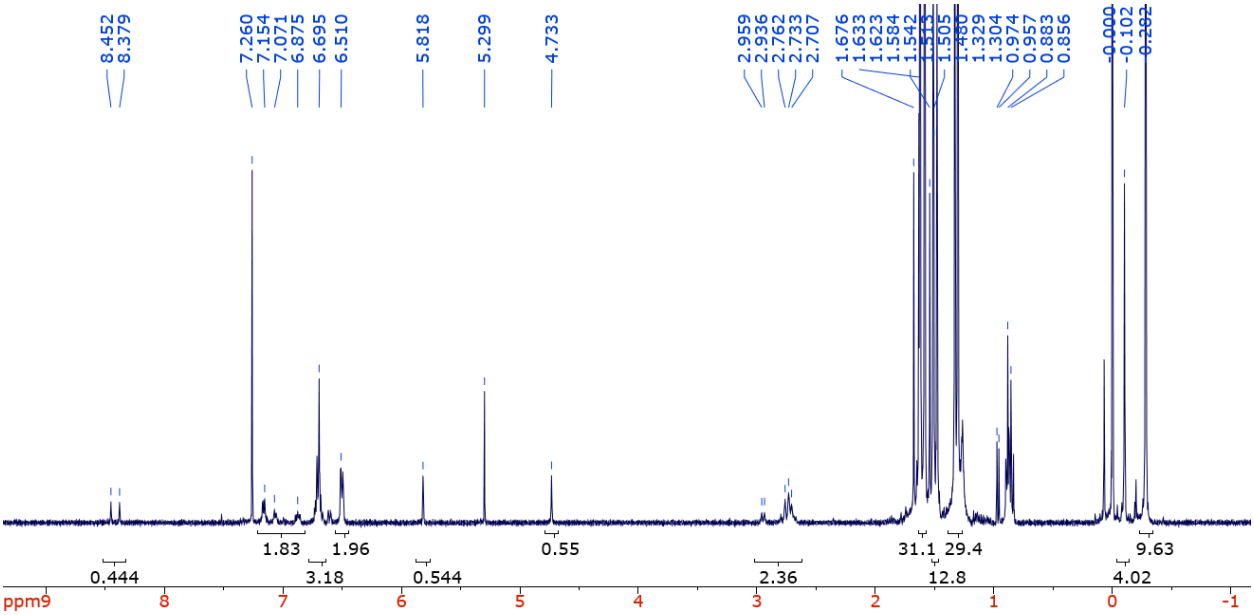


Figure S 63. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of FLP reaction of *bis*-borane **2** and *t*Bu$_3$P with phenylacetylene.

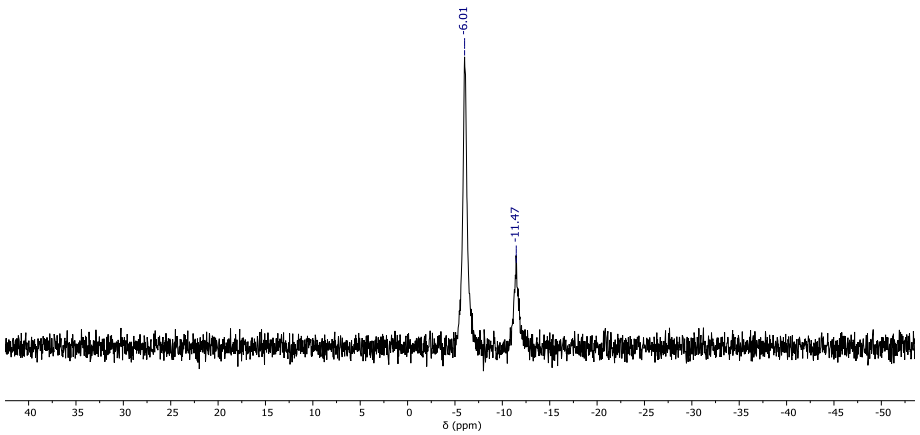


Figure S 64. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of FLP reaction of *bis*-borane **2** and *t*Bu_3P with phenylacetylene.

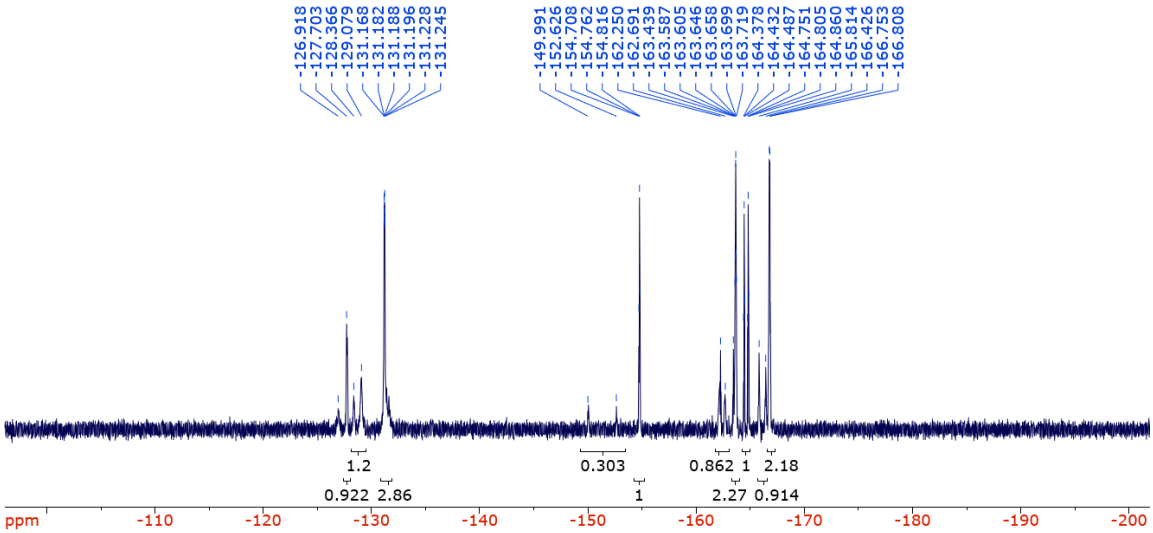


Figure S 65. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of FLP reaction of *bis*-borane **2** and *t*Bu_3P with phenylacetylene.

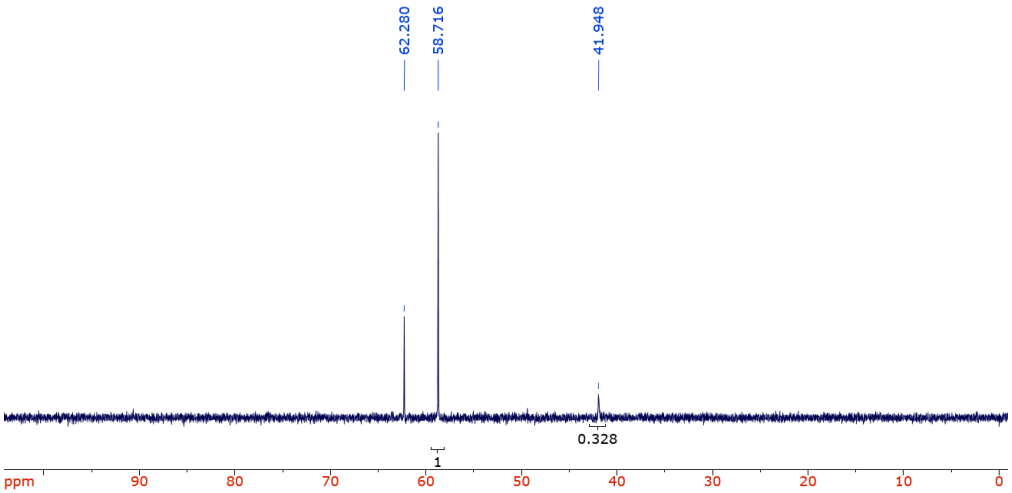
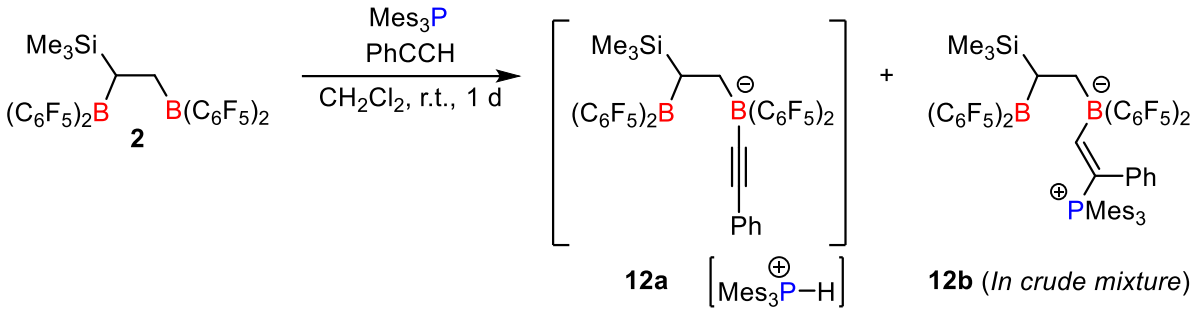


Figure S 66. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of FLP reaction of *bis*-borane **2** and *t*Bu_3P with phenylacetylene. The peak at 62.3 ppm represents excess *t*Bu_3P in the mixture of products.

1.14 Spectra of [Mes$_3$PH][Me$_3$SiCH(B(C$_6$F$_5$)$_2$)CH$_2$B(C$_6$F$_5$)$_2$(CCPh)], 12a



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 8.21 (d, $^1J_{PH}$ = 479 Hz, 1H, Mes$_3$P*H*), 7.14 (s, 3H, Mes-*H*), 7.05 (s, 3H, Mes-*H*), 6.67 – 6.50 (m, 5H, Ph-*H*), 2.74 (m, 2H, C*H*$_2$), 2.39 (s, 9H, Mes-*p*-C*H*$_3$), 2.26 (s, 9H, Mes-*o*-C*H*$_3$), 2.04 (s, 1H, *overlapping* C*H*), 2.00 (s, 9H, Mes-*o*-C*H*$_3$), -0.31 (s, 9H, Si(C*H*$_3$)$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -6.0 (**12a**), -10.6 (**12b** *in crude mixture*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 147.4 (d, $^4J_{CP}$ = 4 Hz, *p*-Mes), 147.2 (*i*-Ph), 144.1 (d, $^2J_{CP}$ = 10 Hz, *o*-Mes), 142.7 (d, $^2J_{CP}$ = 10 Hz, *o*-Mes), 133.4 (d, $^3J_{CP}$ = 13 Hz, *m*-Mes), 132.0 (d, $^3J_{CP}$ = 10 Hz, *m*-Mes), 126.5 (*m*-Ph), 125.5 (*o*-Ph), 124.6 (*p*-Ph), 111.4 (d, $^1J_{CP}$ = 83 Hz, *i*-Mes), 41.7 (*C*H$_2$), 31.8 (*C*H), 22.2 (d, $^3J_{CP}$ = 6 Hz, Mes-*o*-*C*H$_3$), 21.6 (d, $^5J_{CP}$ = 3 Hz, Mes-*p*-*C*H$_3$), 21.2 (d, $^3J_{CP}$ = 10 Hz, Mes-*o*-*C*H$_3$), -0.3 (Si(*C*H$_3$)$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -127.9 (d, $^3J_{FF}$ = 17 Hz, 2F, *o*-C$_6$F$_5$), -129.3 (br, 2F, *o*-C$_6$F$_5$), -131.1 (d, $^3J_{FF}$ = 15 Hz, 4F, *o*-C$_6$F$_5$), -155.2 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C$_6$F$_5$), -163.8 (m, 4F, *m*-C$_6$F$_5$), -164.9 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C$_6$F$_5$), -165.1 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C$_6$F$_5$), -167.1 (m, 4F, *m*-C$_6$F$_5$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K) δ: 18.5 (s, **12b** *in crude mixture*), -27.5 (s, **12a**).

^{31}P NMR (162 MHz, $CDCl_3$, 298K) δ: -27.5 (d, $^1J_{PH}$ = 481 Hz, Mes$_3$*P*H, **12a**).

HRMS (ESI+/- Ionization, *m/z*): Calcd. for $C_{27}H_{34}P^+$ ([M$^+$]): 389.2393; Found 389.2399. Calcd for $C_{37}H_{17}B_2F_{20}Si^-$ ([M$^-$]): 891.0984; Found 891.0986.

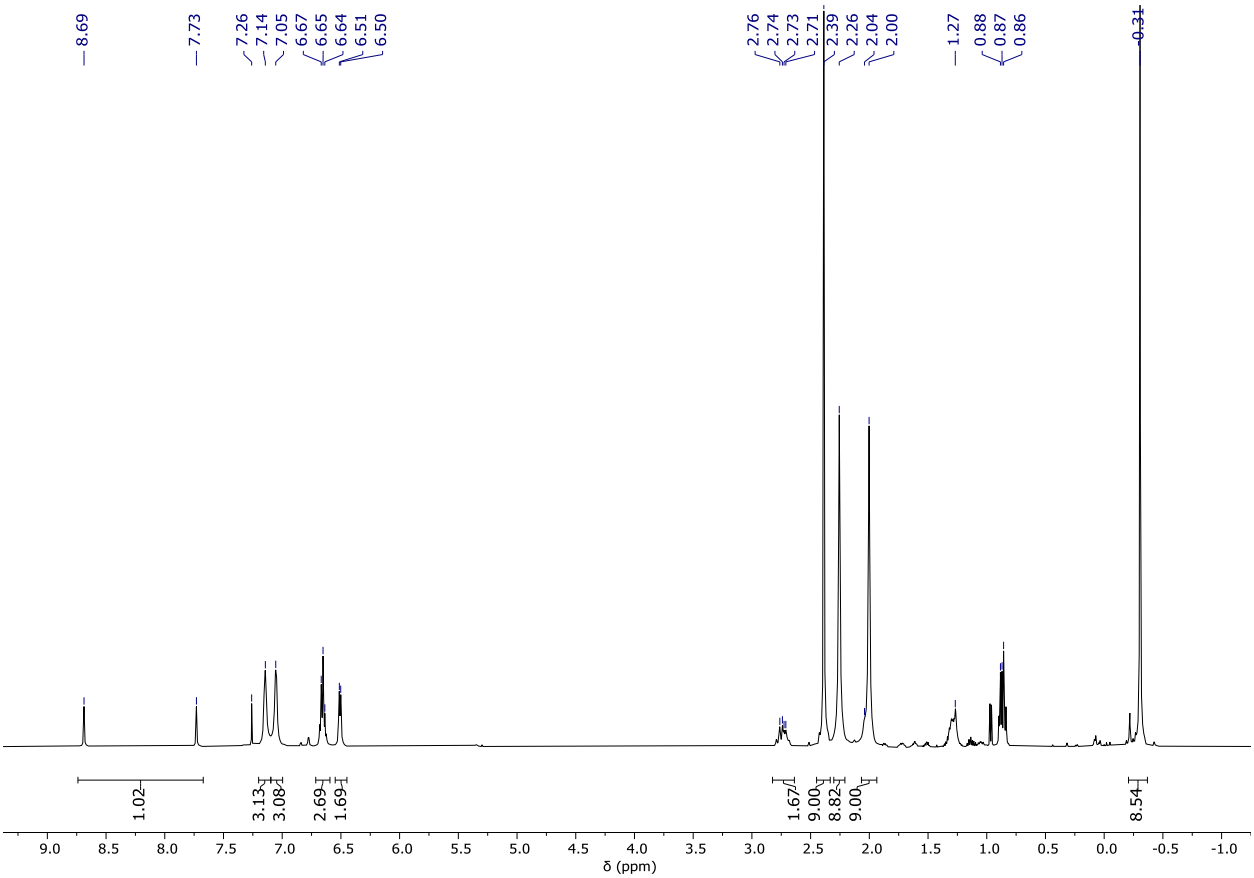


Figure S 67. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

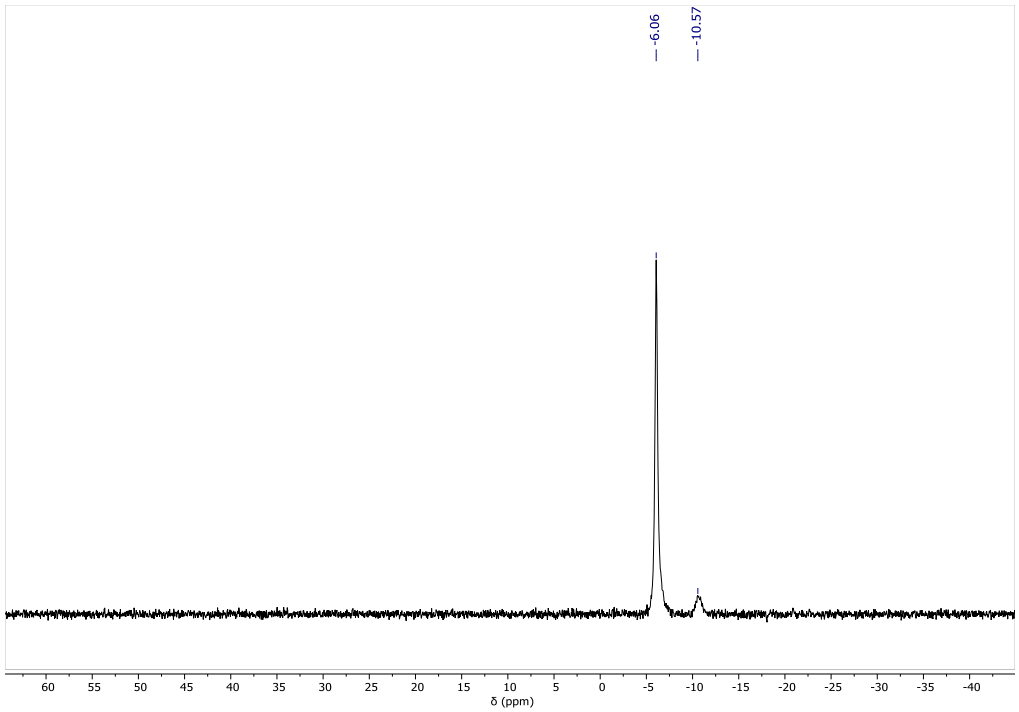


Figure S 68. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of the crude reaction mixture including **12a** and **12b**.

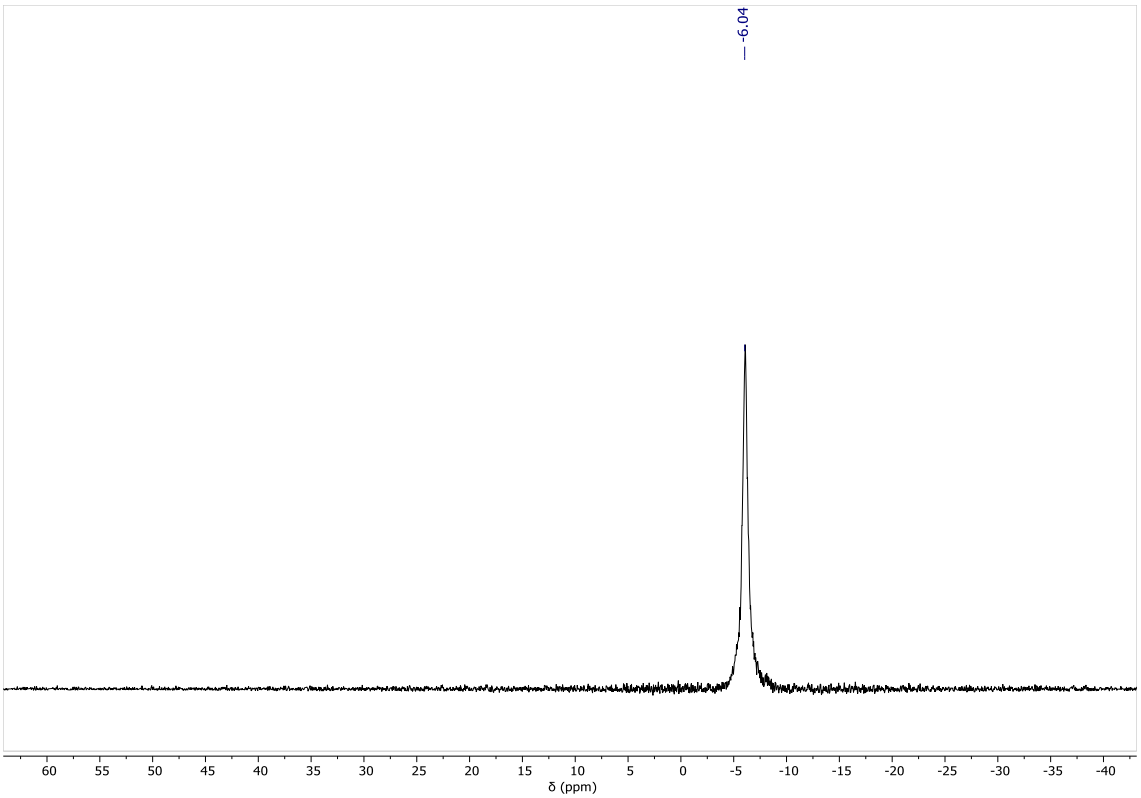


Figure S 69. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

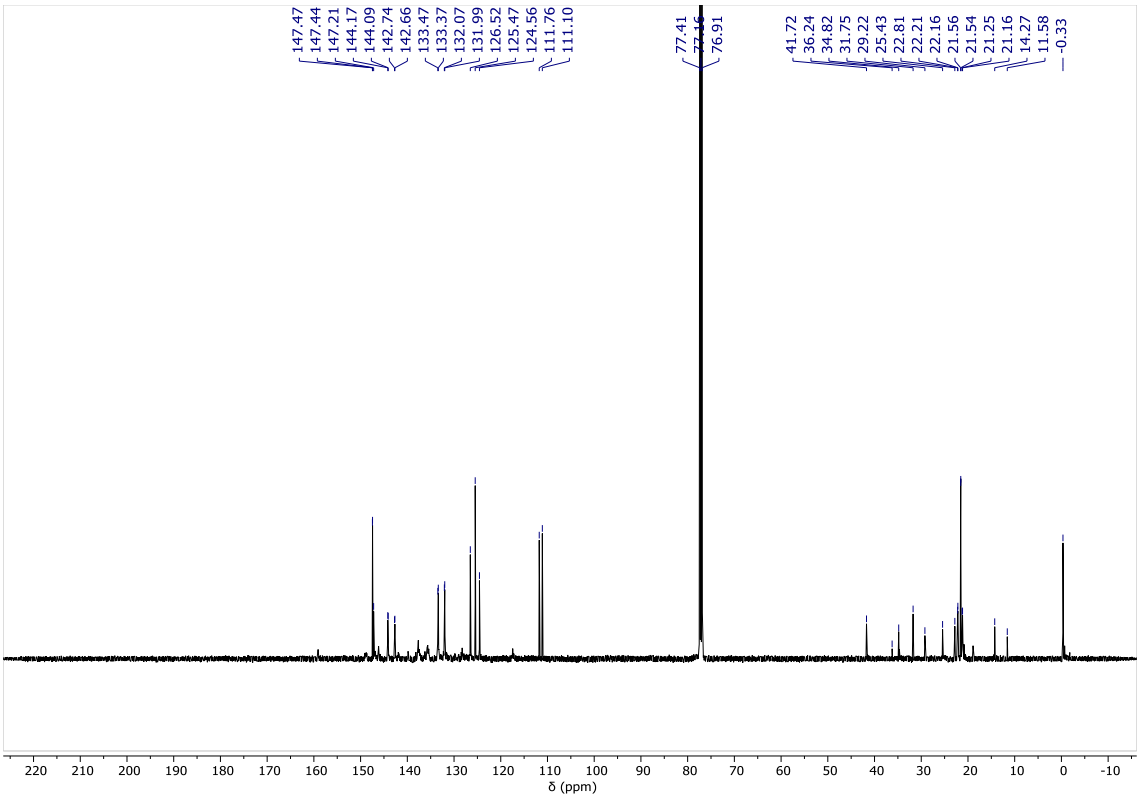


Figure S 70. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

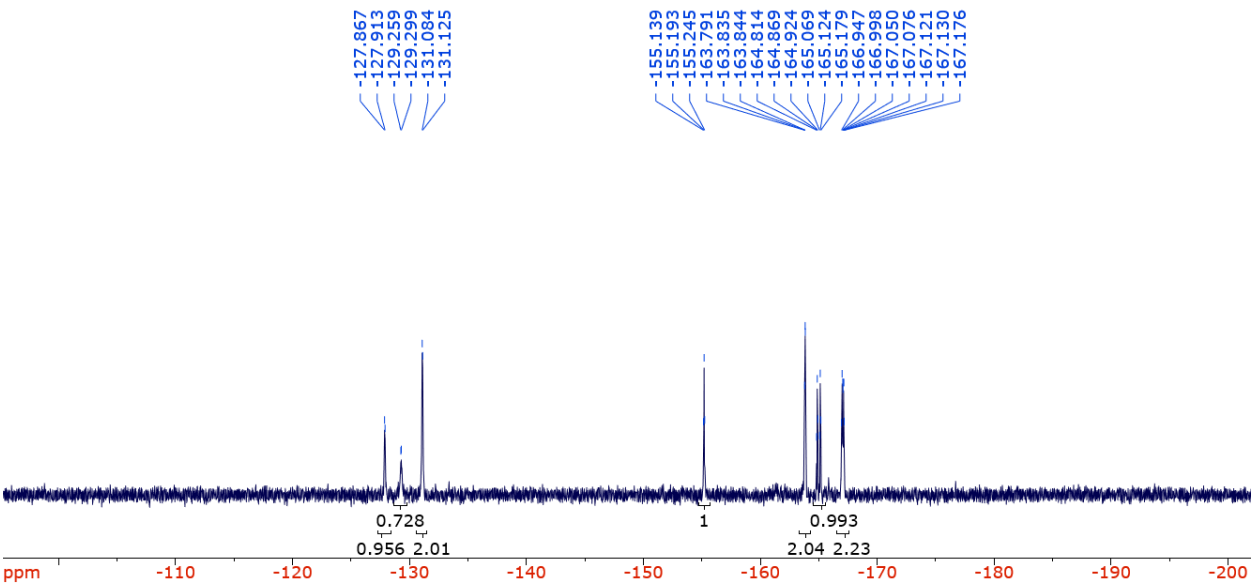


Figure S 71. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

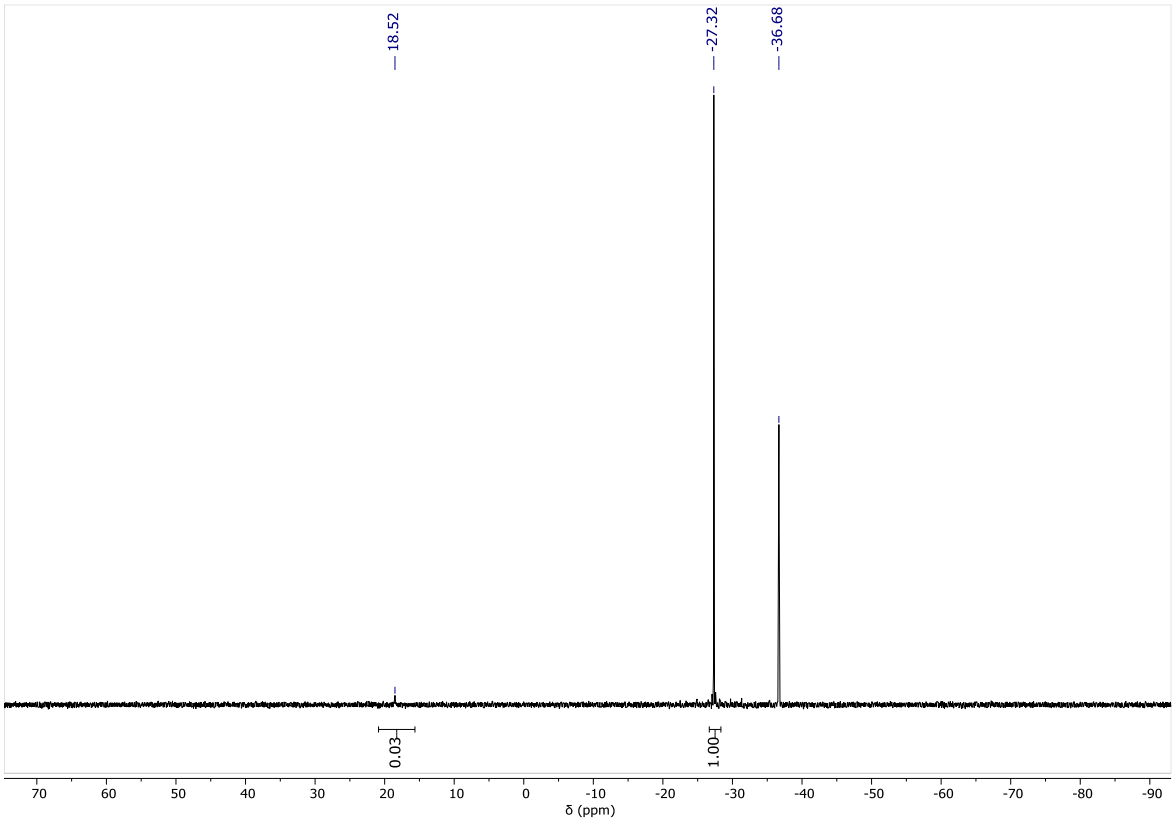


Figure S 72. $^{31}P\{H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of the crude reaction mixture including **12a** and **12b**. The peak at -36.7 ppm represents excess Mes_3P in the crude mixture.

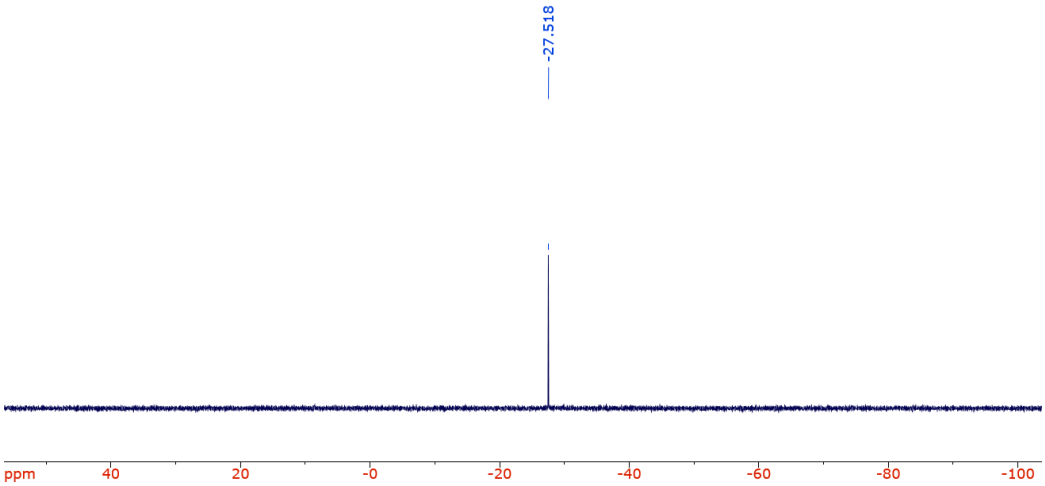


Figure S 73. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

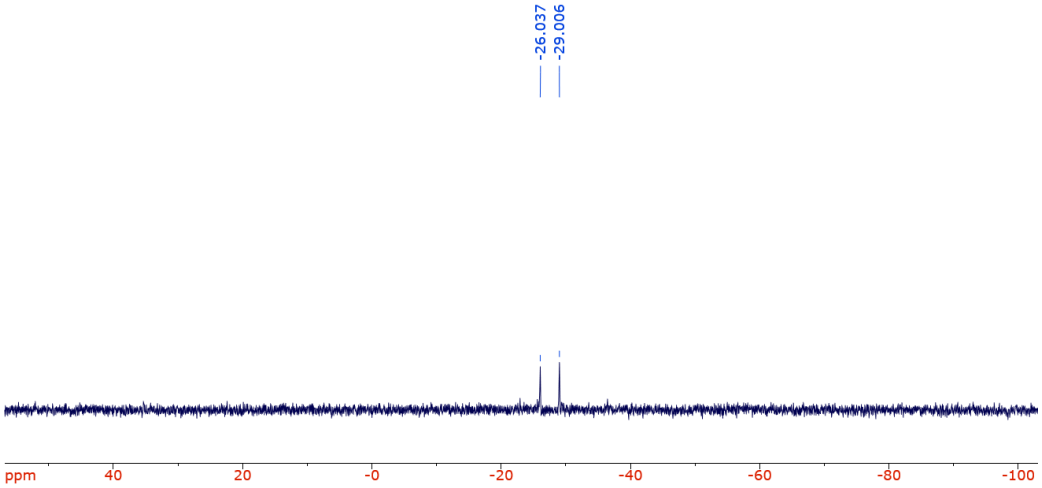
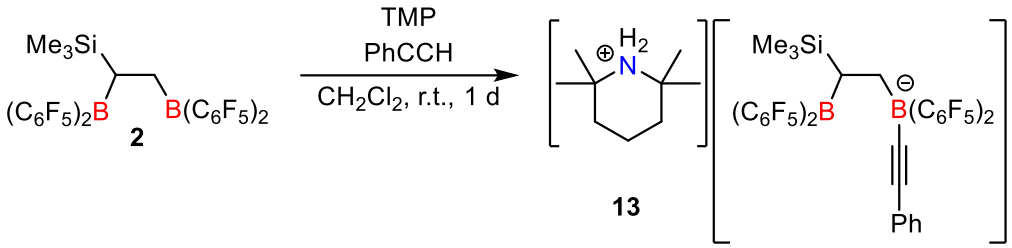


Figure S 74. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **12a**.

1.15 Preparation of [(TMP)H][Me$_3$SiCH(B(C$_6$F$_5$)$_2$)CH$_2$B(C$_6$F$_5$)$_2$(CCPh)], 13



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 6.76 – 6.54 (m, 5H, Ph-*H*), 4.45 (br, 2H, N*H*$_2$), 2.73 (m, 2H, BC*H*$_2$), 1.79 (m, 2H, 4-C*H*$_2$), 1.67 (m, 4H, 3-C*H*$_2$), 1.36 (s, 12H, C(C*H*$_3$)$_2$), -0.28 (s, 9H, Si(C*H*$_3$)$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -6.0.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 160.1 (PhCCB), 148.1 (dm, $^1J_{CF}$ = 238 Hz, *o*-C_6F_5), 148.0 (*i*-Ph), 145.3 (dm, $^1J_{CF}$ = 243 Hz, *o*-C_6F_5), 141.2 (dm, $^1J_{CF}$ = 255 Hz, *m/p*-C_6F_5), 137.2 (dm, $^1J_{CF}$ = 247 Hz, *m/p*-C_6F_5), 136.8 (dm, $^1J_{CF}$ = 249 Hz, *m/p*-C_6F_5), 127.0 (*m*-Ph), 125.9 (*o*-Ph), 124.9 (*p*-Ph), 117.0 (m, *i*-C_6F_5), 60.8 (NC(CH$_3$)$_2$), 42.0 (BCH$_2$), 35.2 (NC(CH$_3$)$_2$CH$_2$), 28.3 (NC(CH$_3$)$_2$), 25.3 (br, CH), 15.8 (NC(CH$_3$)$_2$CH$_2$CH$_2$), -0.3 (Si(CH$_3$)$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -127.6 (d, $^3J_{FF}$ = 26 Hz, 2F, *o*-C_6F_5), -129.1 (d, $^3J_{FF}$ = 22 Hz, 2F, *o*-C_6F_5), -131.4 (d, $^3J_{FF}$ = 19 Hz, 4F, *o*-C_6F_5), -153.7 (t, $^3J_{FF}$ = 20 Hz, 4F, *p*-C_6F_5), -163.1 (m, 3F, *overlapping m*-C_6F_5 and *p*-C_6F_5), -163.5 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -165.8 (m, 4F, *m*-C_6F_5).

HRMS (ESI+/- Ionization, m/z): Calcd. for $C_9H_{20}N^+$ ([M$^+$]): 142.1590; Found 142.1593. Calcd. for $C_{37}H_{17}B_2F_{20}Si^-$ ([M$^-$]): 891.0984; Found: 891.0982.

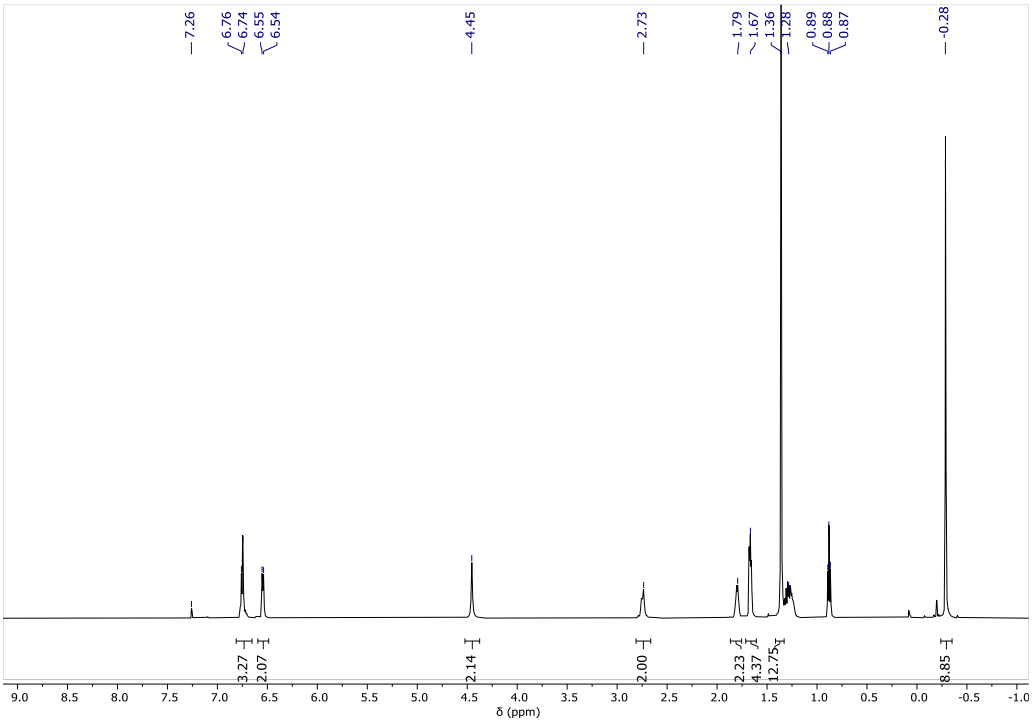


Figure S 75. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **13**.

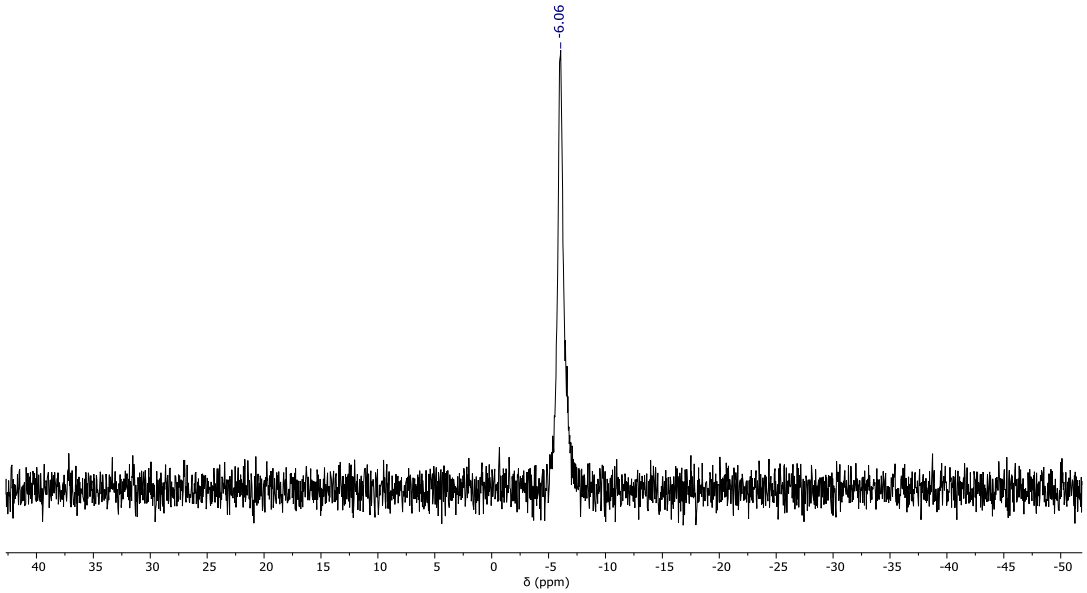


Figure S 76. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **13**.

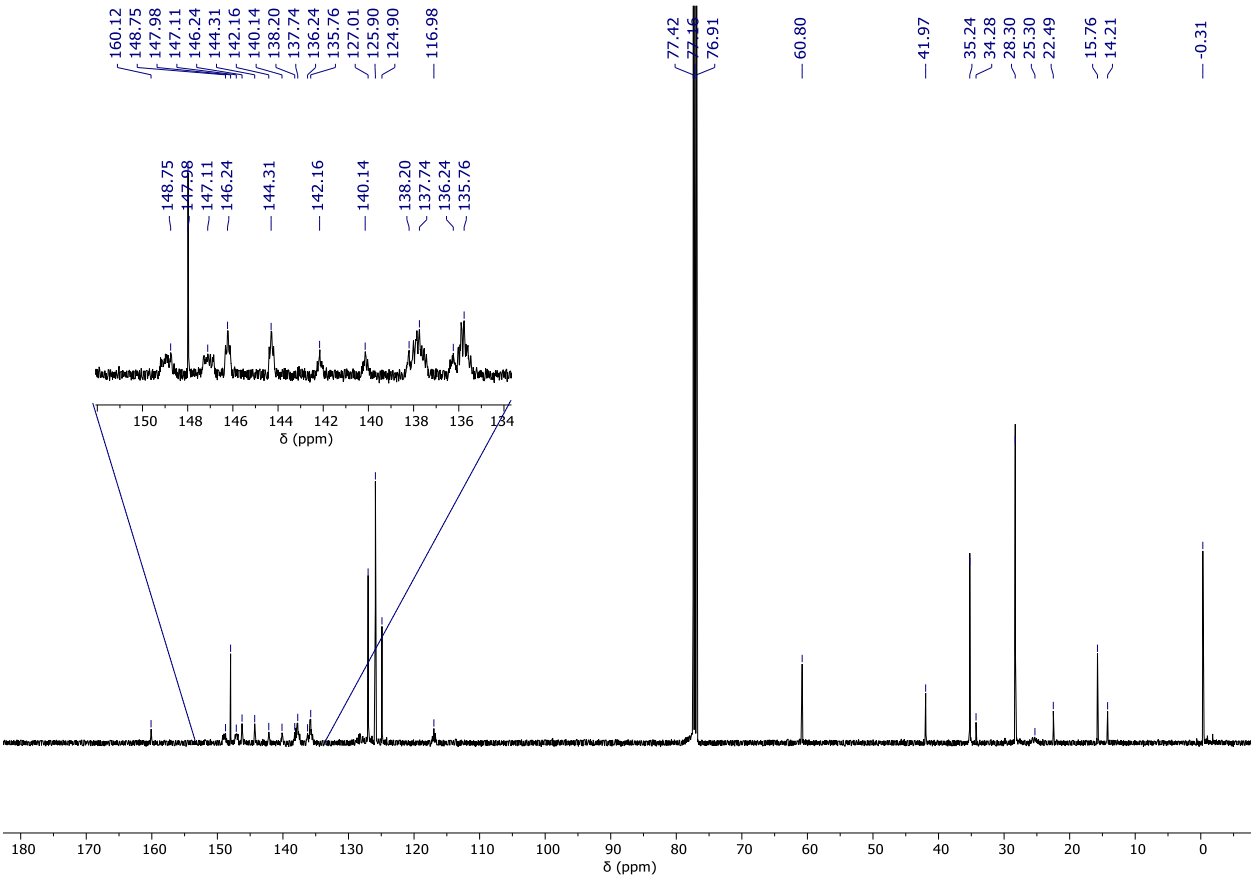


Figure S 77. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **13**.

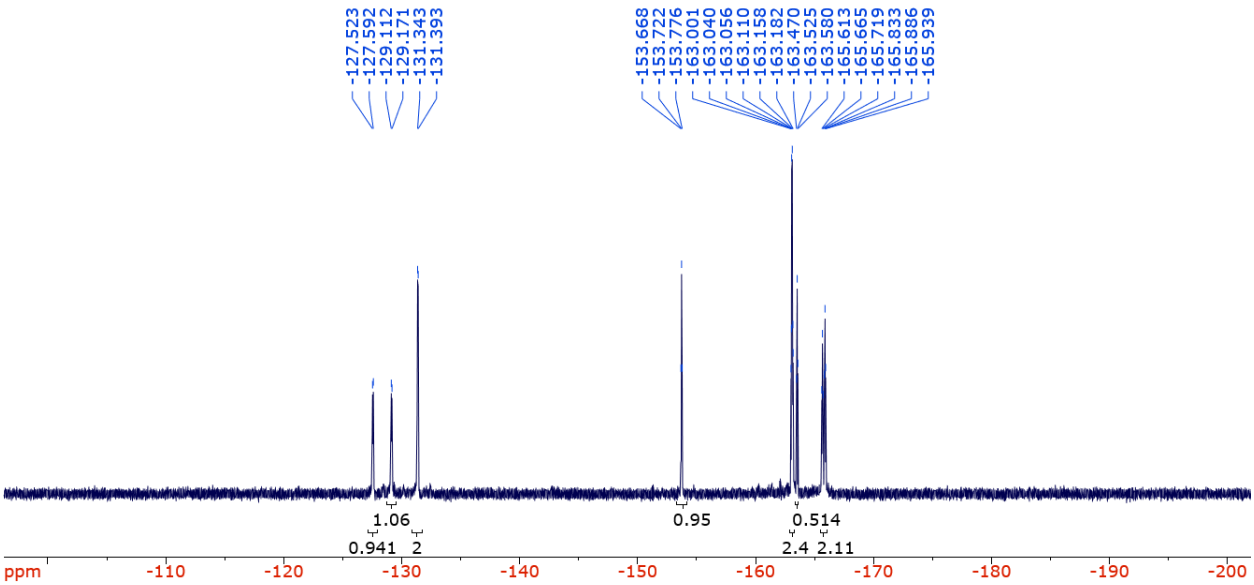
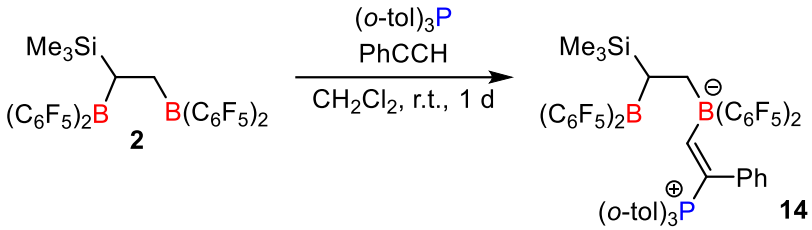


Figure S 78. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **13**.

1.16 Preparation of $Me_3SiCH(B(C_6F_5)_2)CH_2(B(C_6F_5)_2C(H)C(Ph)(P(o\text{-}tol)_3)$, 14



^{1}H NMR (500 MHz, $CDCl_3$, 298 K, *partial*) δ: 8.29 (br), 7.84 – 6.92 (br), 6.59 (br), 2.94 (br), 2.69 (br), 1.58 (br), -0.22 (s, 9H, Si(CH_3)$_3$).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: -11.1.

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -126.8 (br, 1F, *o*-C_6F_5), -127.5 (br, 1F, *o*-C_6F_5), -128.7 (br, 2F, *o*-C_6F_5), -131.2 (br m, 4F, *o*-C_6F_5), -150.4 (br, 1F, *p*-C_6F_5), -153.0 (br, 1F, *p*-C_6F_5), -162.6 (br m, 6F, *overlapping m*-C_6F_5 and *p*-C_6F_5), -165.9 (br m, 4F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298K) δ: 26.0 (s).

HRMS (ESI- Ionization, m/z): Calcd. for $C_{59}H_{40}B_2F_{20}O_2PSi^-$ ([M+HCOO]$^-$): 1241.2407; Found 1241.2399.

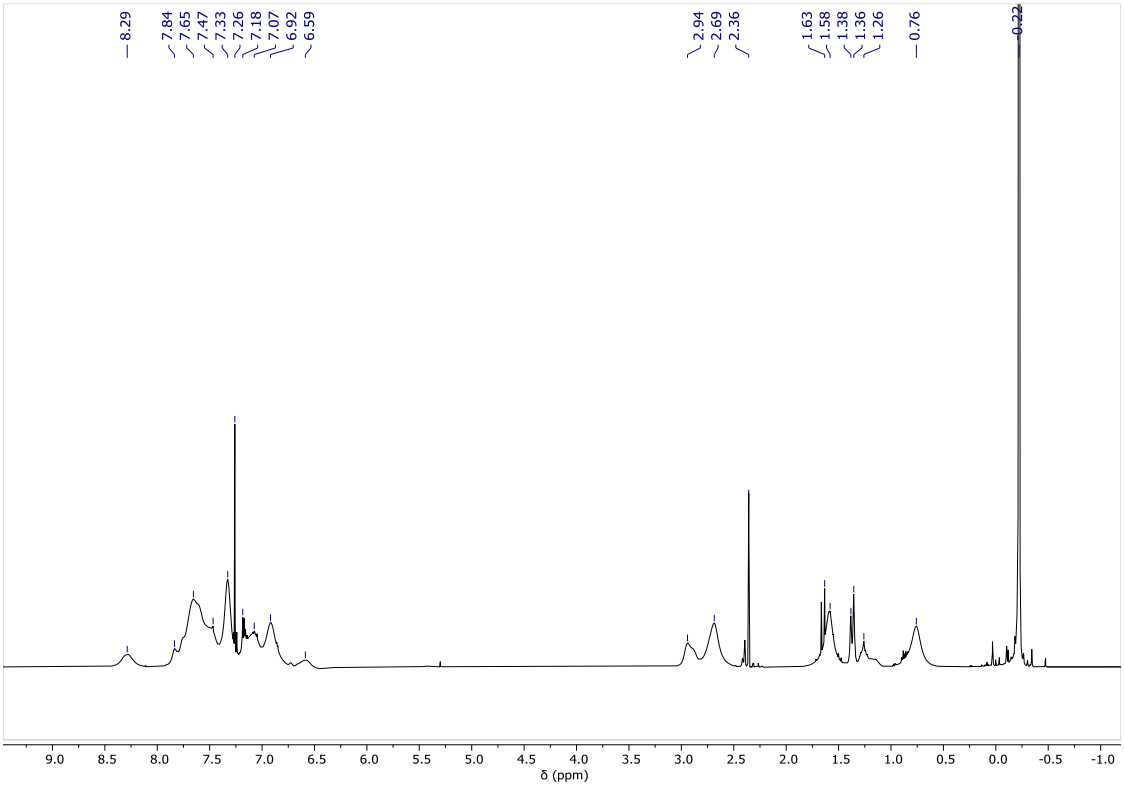


Figure S 79. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **14**.

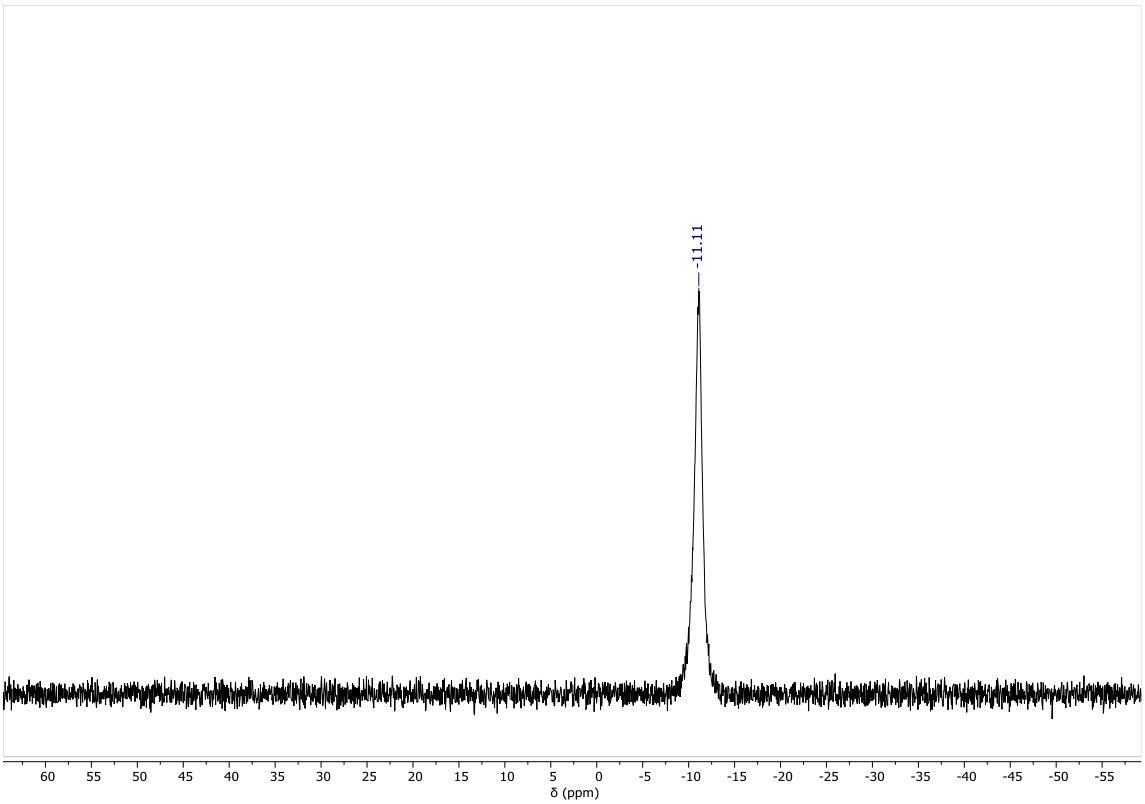


Figure S 80. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **14**.

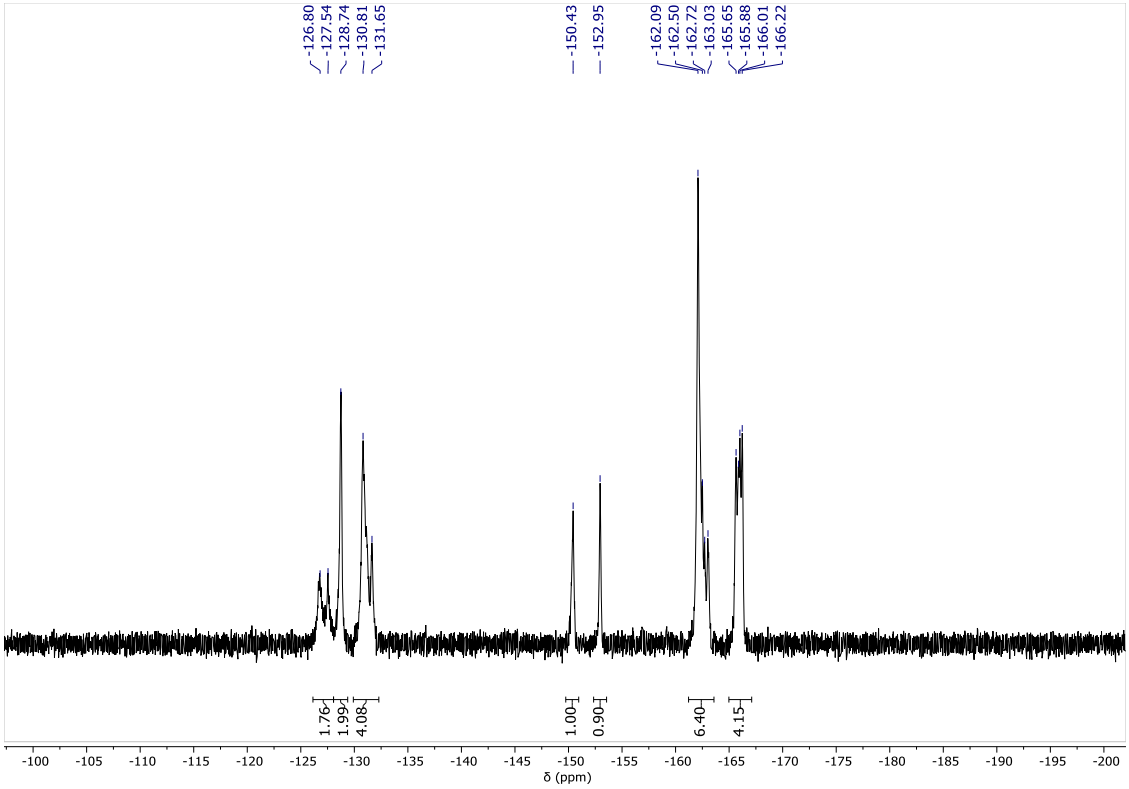


Figure S 81. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **13**.

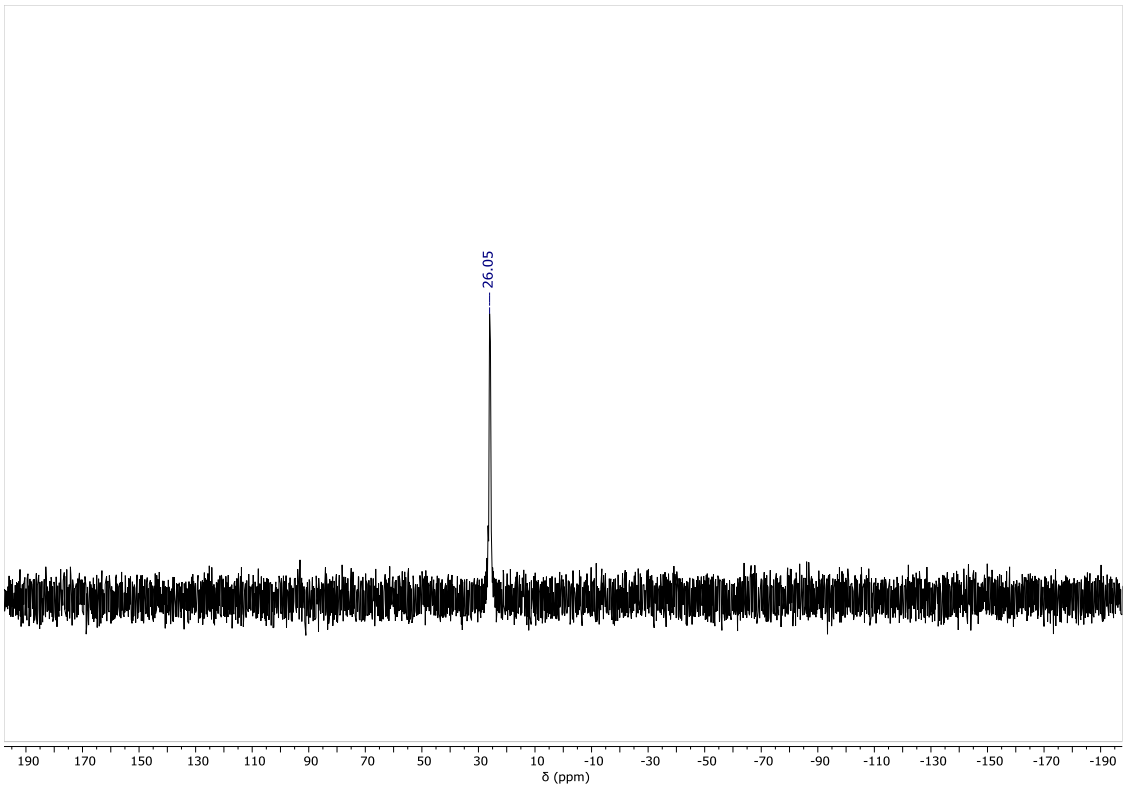


Figure S 82. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K) spectrum of compound **14**.