

Supporting Information for:

Examining the Reactivity of Tris(*ortho*-carboranyl)borane with Lewis Bases and Application in Frustrated Lewis Pair Si-H Bond Cleavage

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NMR and IR spectra:

Figure S-1: Stacked ^1H NMR (400 MHz) spectra of $\text{EtOAc}\cdot\text{BoCb}_3$ with varying concentration (5, 10, 20, 50, and 100 equivalents) of EtOAc in CDCl_3 (*corresponds to the diagnostic C-H resonance on the *ortho*-carbon).

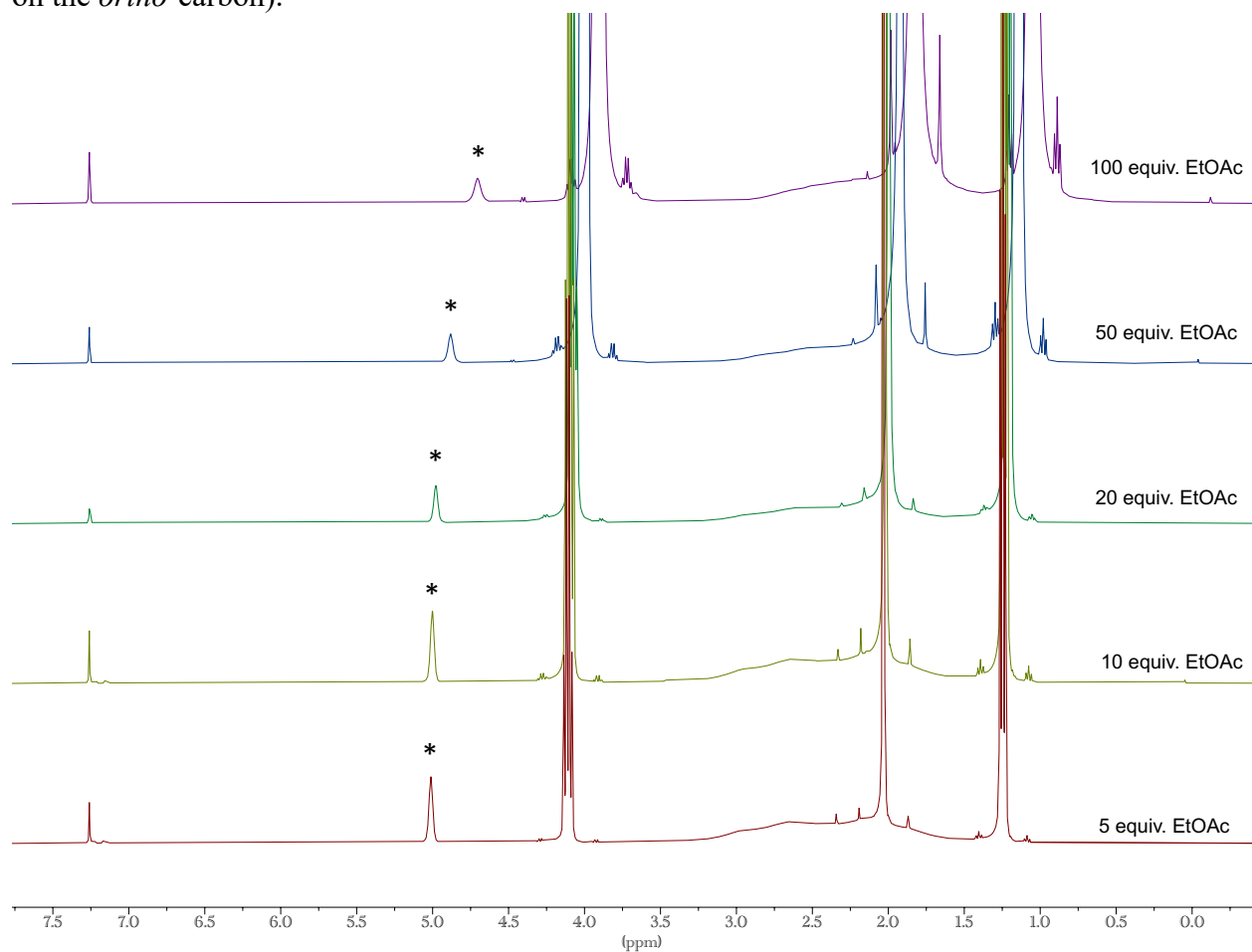


Figure S-2: Stacked ^{11}B NMR (128 MHz) spectra of $\text{EtOAc}\cdot\text{BoCb}_3$ with varying concentration (5, 10, 20, 50, and 100 equivalents) of EtOAc in CDCl_3 .

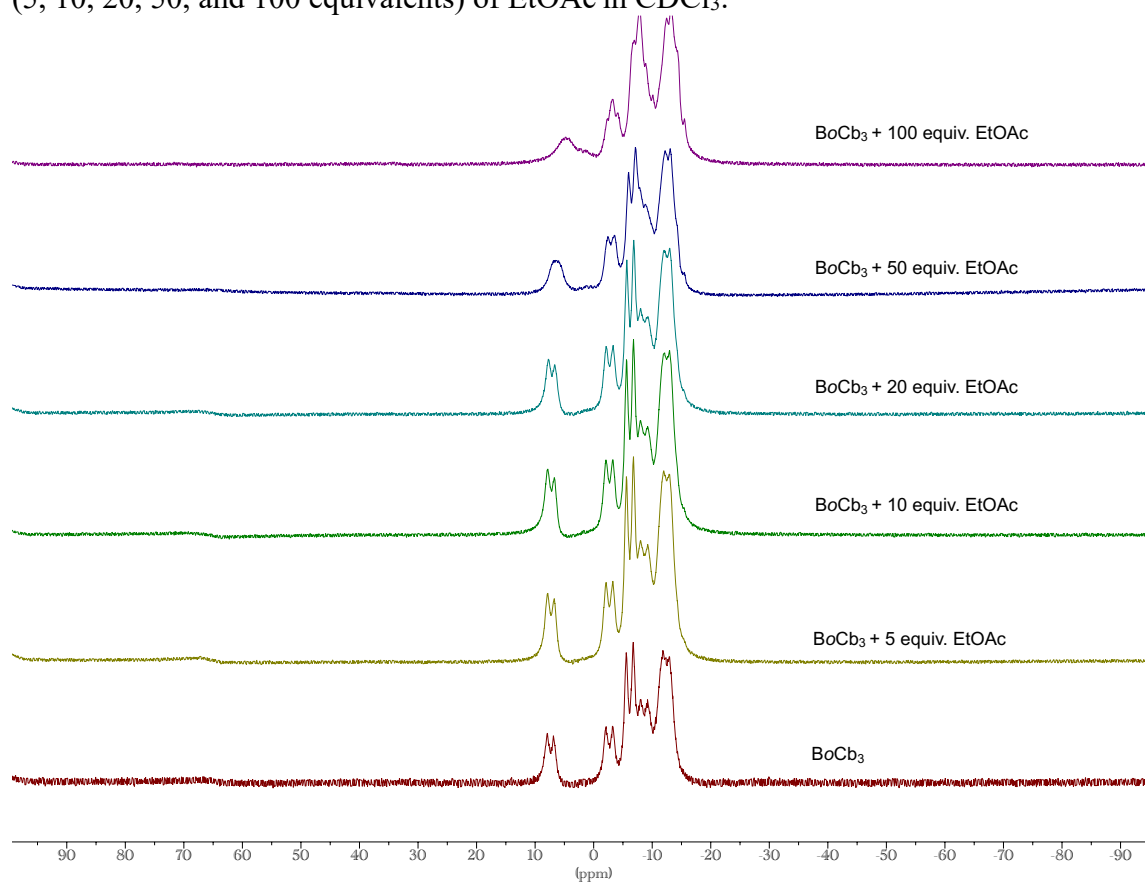


Figure S-3: ^1H NMR (400 MHz) spectrum of $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}\cdot\text{B}o\text{Cb}_3$ in CDCl_3 .

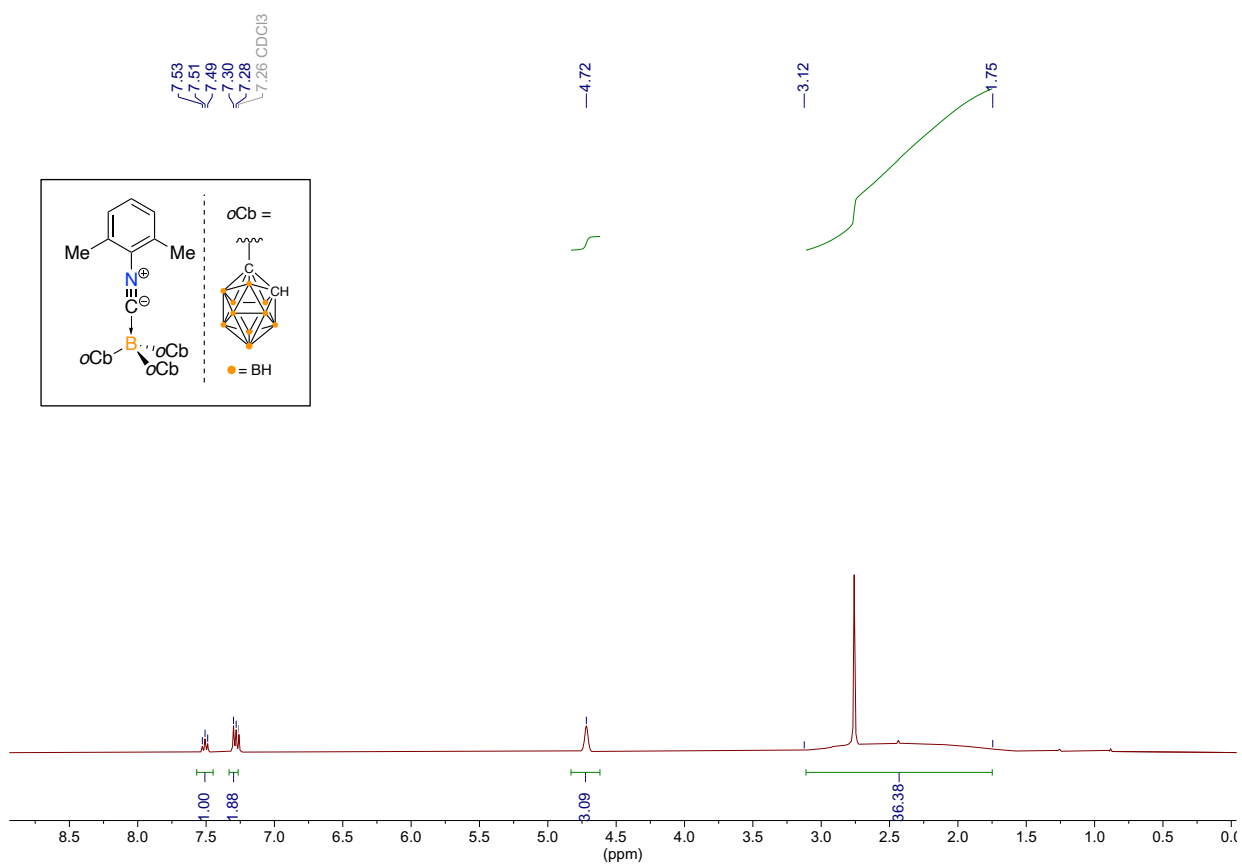


Figure S-4: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}\cdot\text{B}(\text{oCb})_3$ in CDCl_3 .

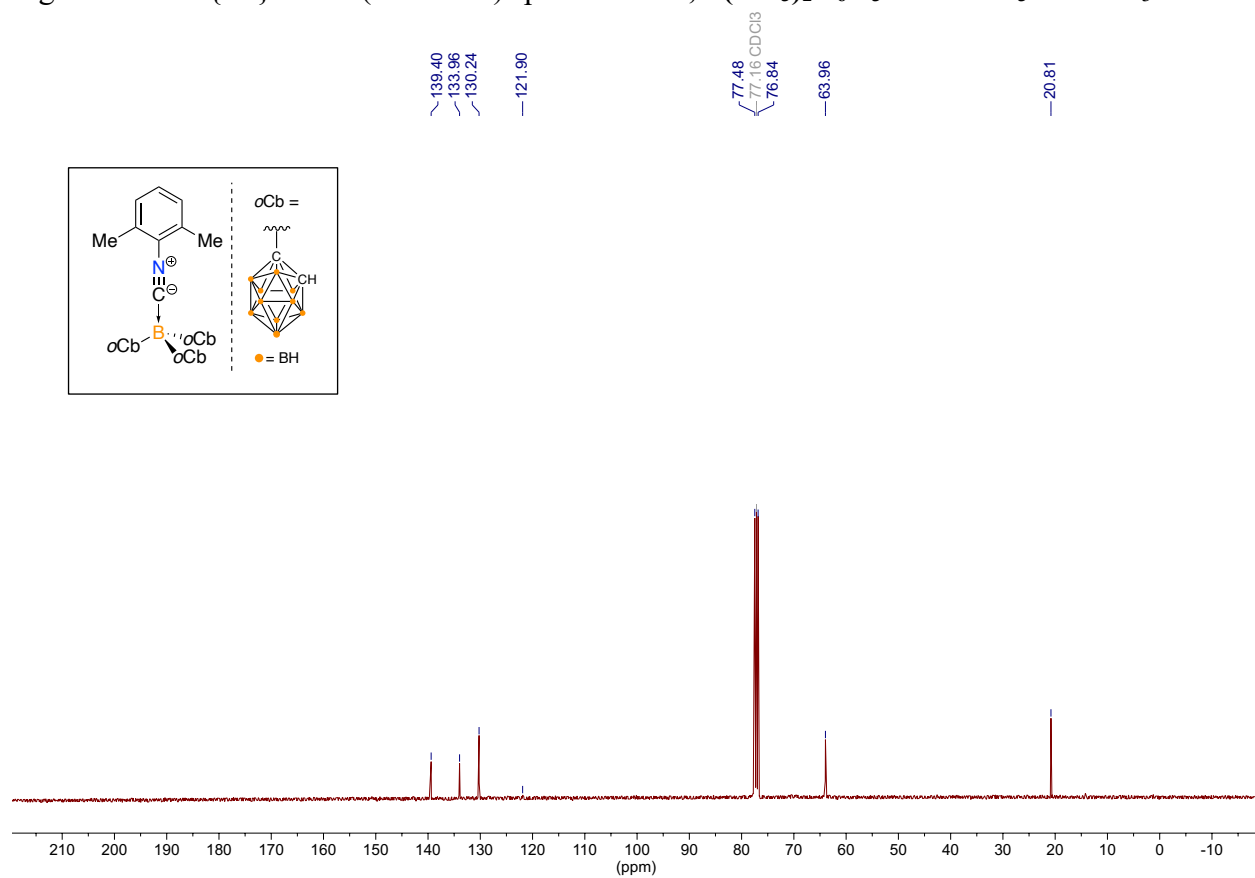


Figure S-5: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}\cdot\text{B}(\text{oCb})_3$ in CDCl_3 .

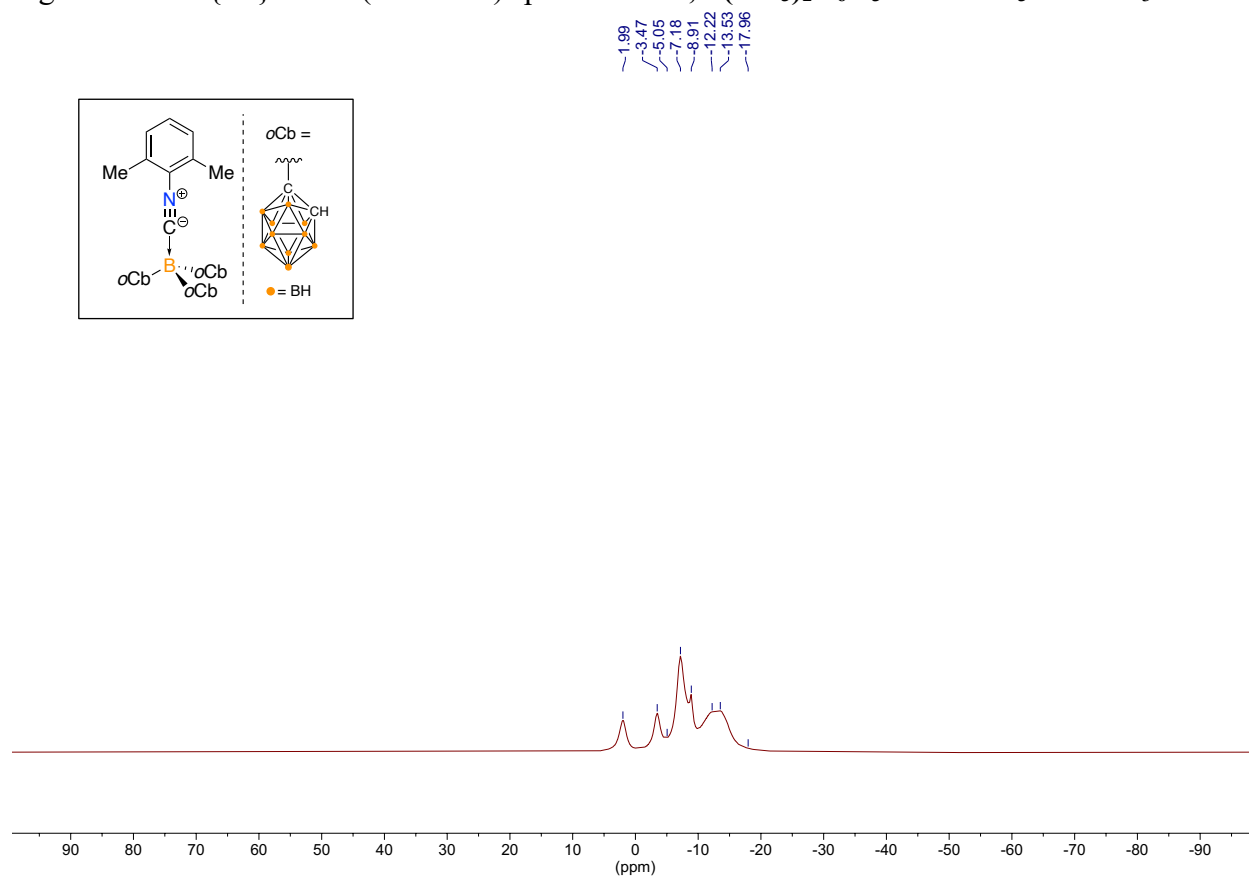


Figure S-6: ^{11}B NMR (128 MHz) spectrum of $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}\cdot\text{B}(\text{oCb})_3$ in CDCl_3 .

2.40
1.44
-2.98
-4.06
-5.05
-6.78
-7.66
-8.91
-12.78
-19.89

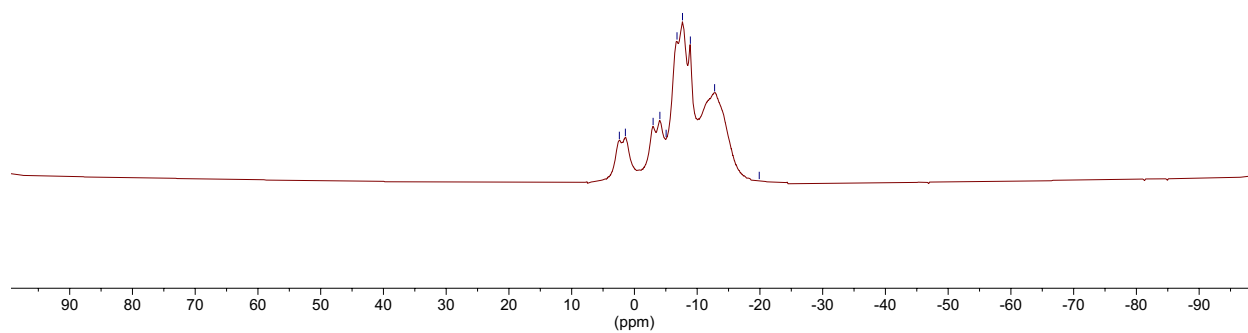
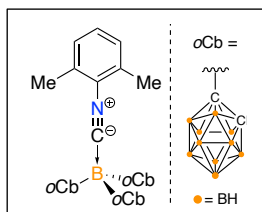


Figure S-7: FT-IR spectrum of **2,6-(CH₃)₂C₆H₃NC·B₁₀Cb₃**.

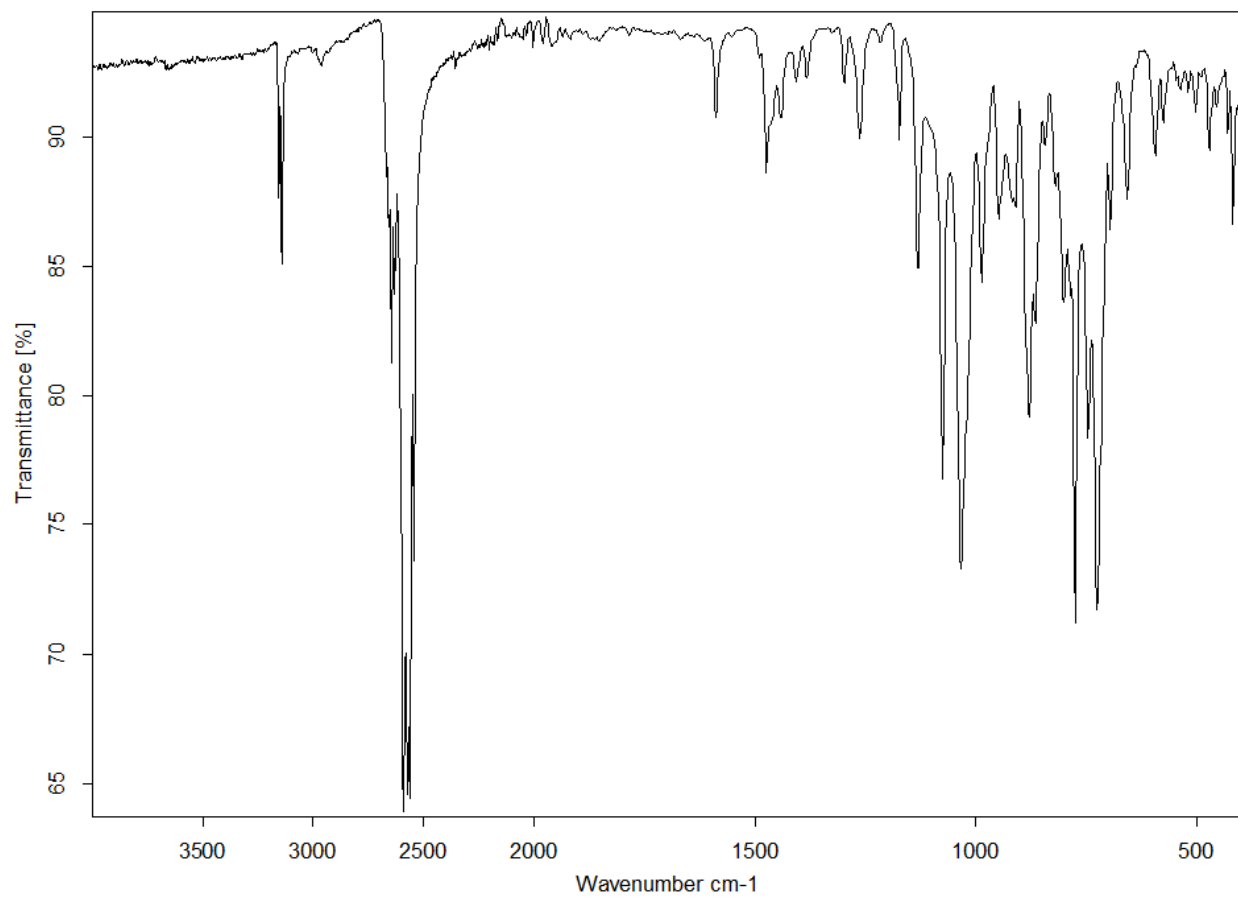


Figure S-8: ^1H NMR (400 MHz) spectrum of $[\text{Me}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 (* residual benzene).

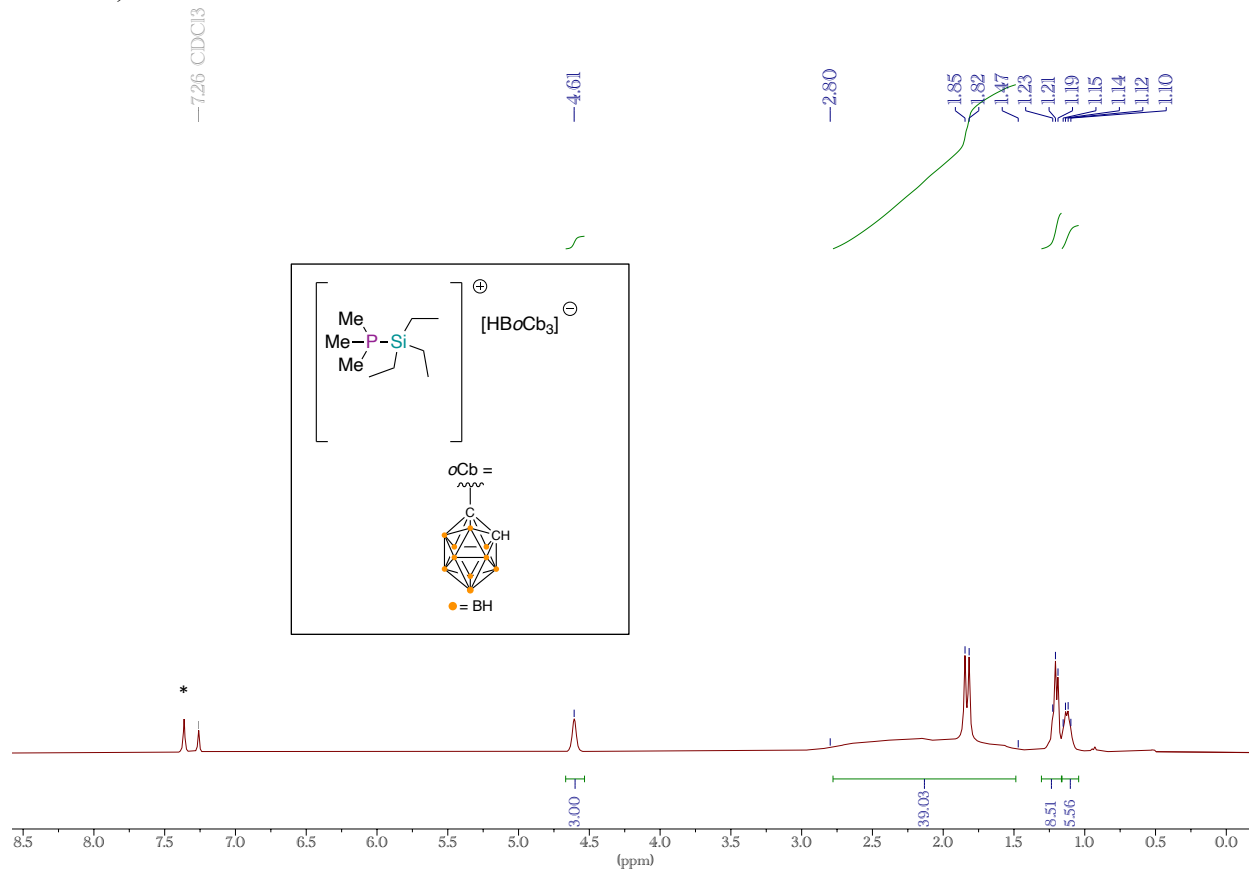


Figure S-9: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[\text{Me}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 (* residual benzene).

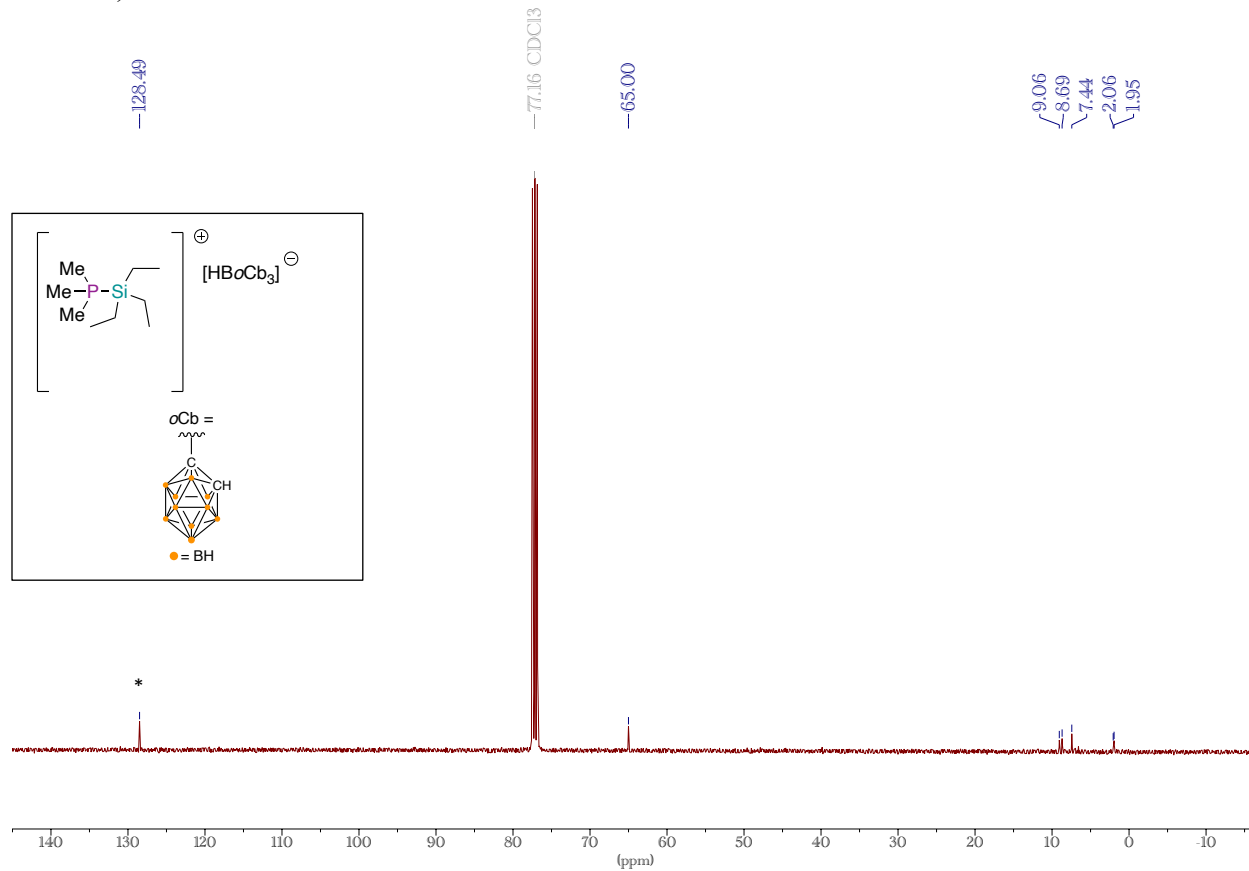


Figure S-10: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[\text{Me}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

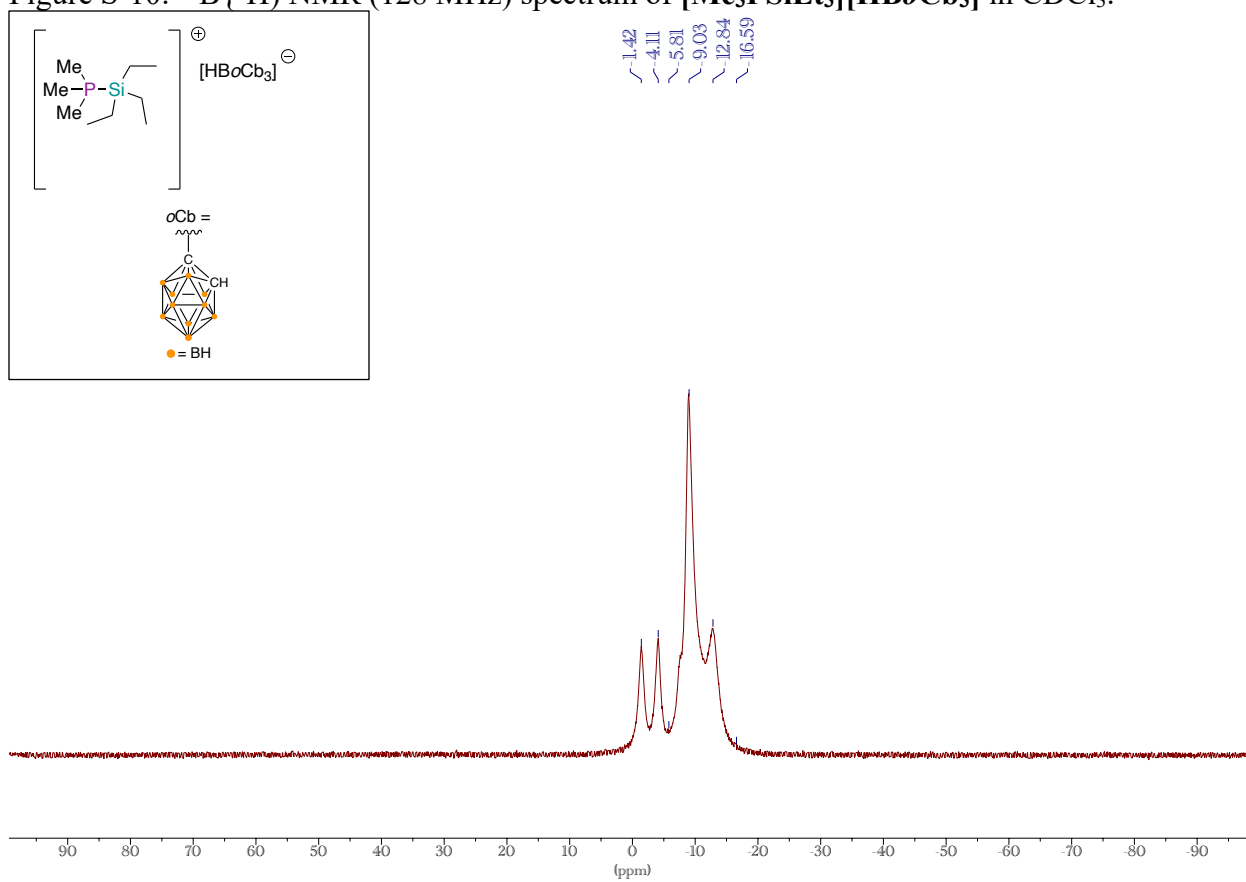


Figure S-11: ^{11}B NMR (128 MHz) spectrum of $[\text{Me}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 .

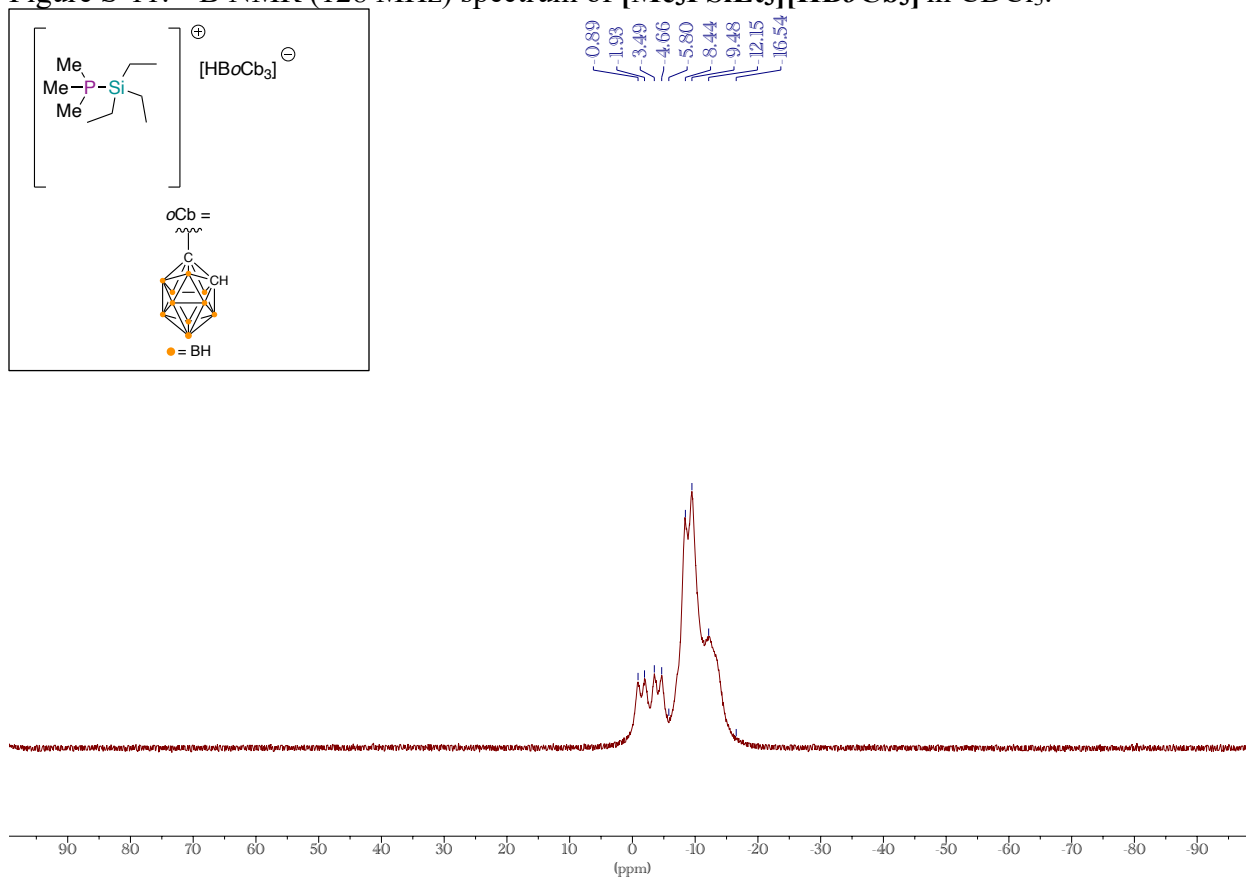


Figure S-12: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[\text{Me}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

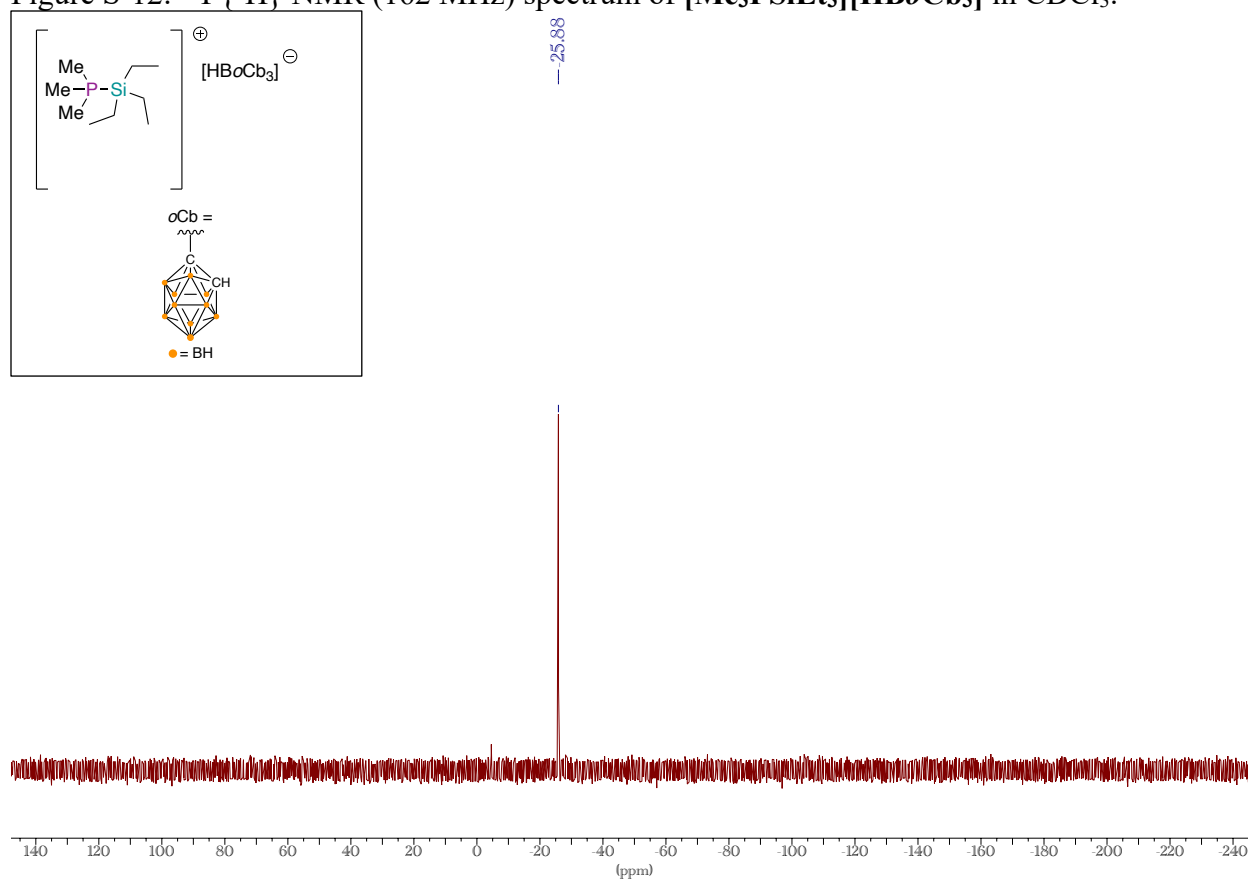


Figure S-13: ^1H NMR (400 MHz) spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 (* residual benzene).

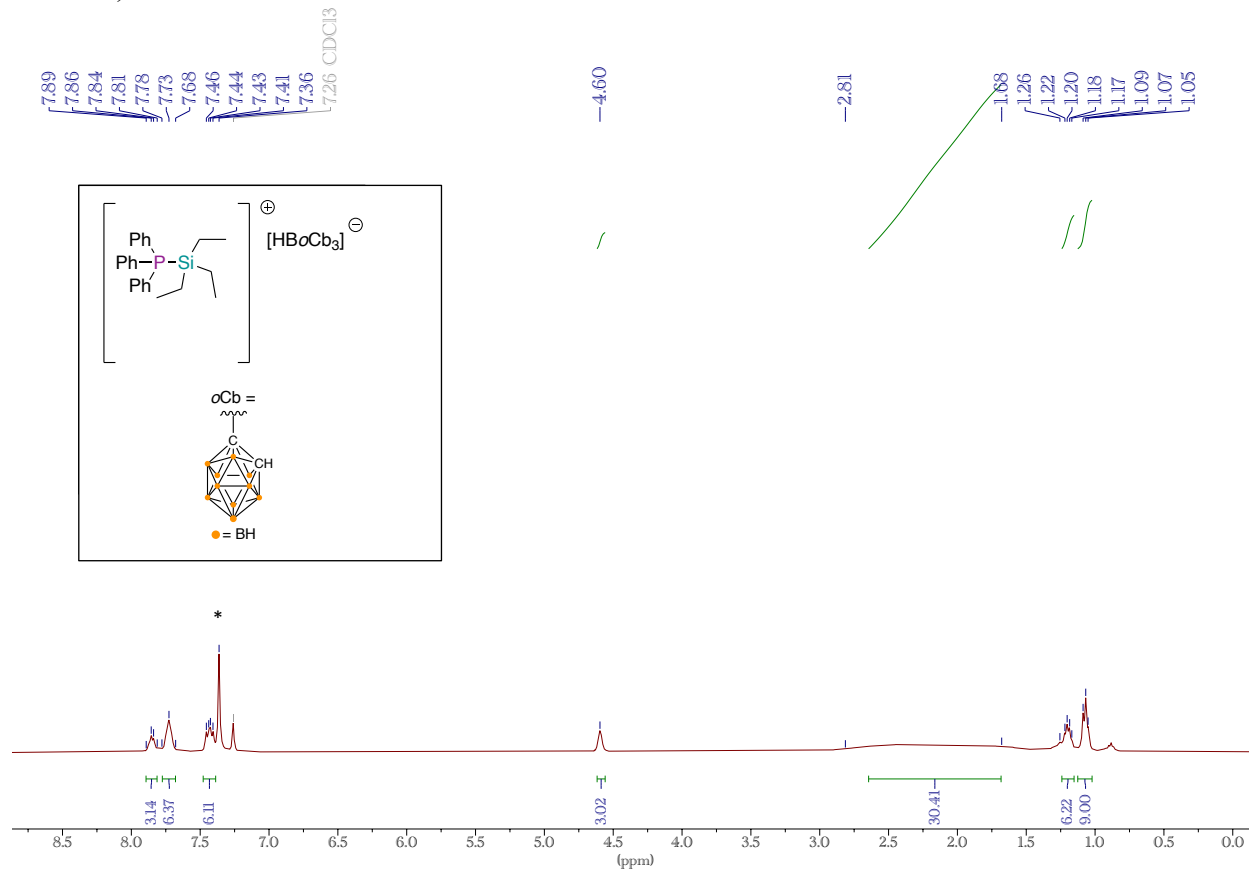


Figure S-14: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 (* residual benzene).

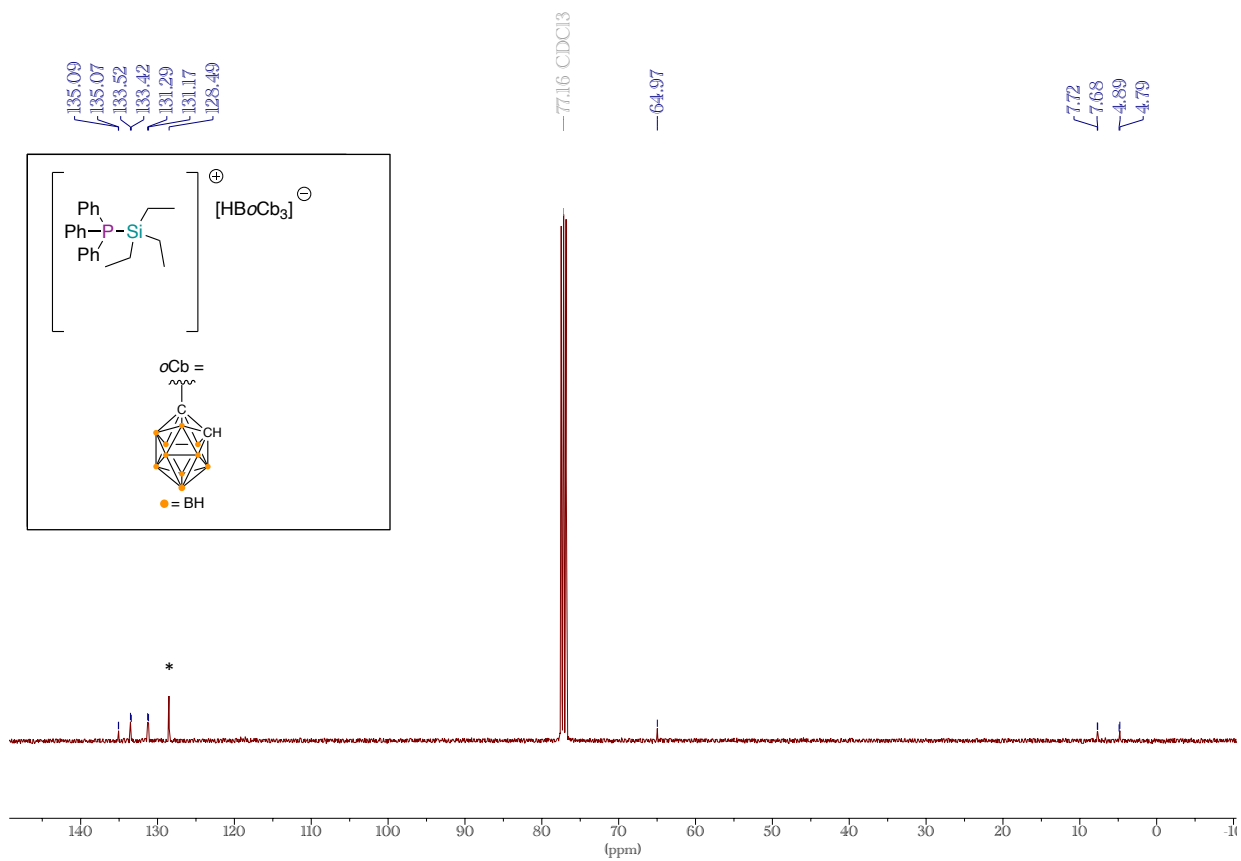


Figure S-15: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 .

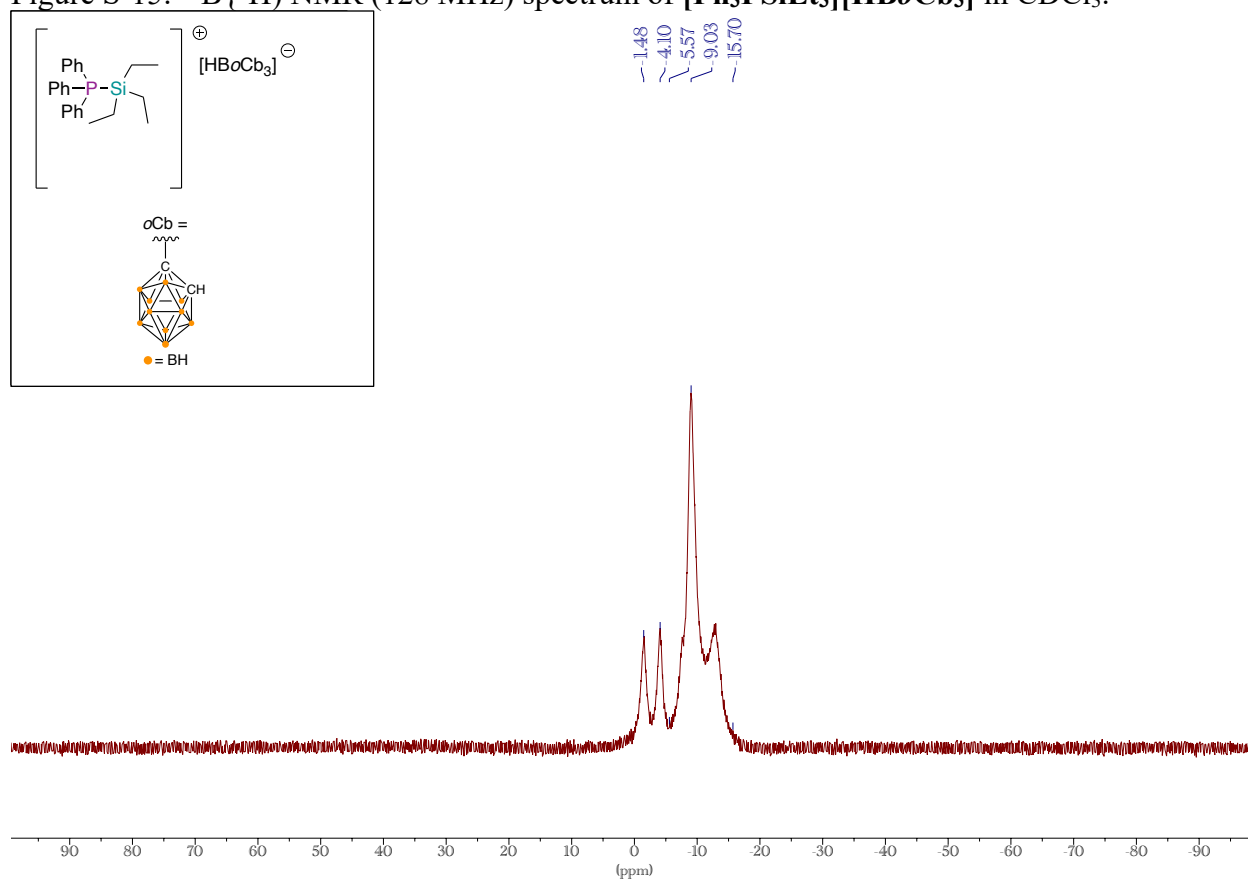


Figure S-16: ^{11}B NMR (128 MHz) spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}\alpha\text{Cb}_3]$ in CDCl_3 .

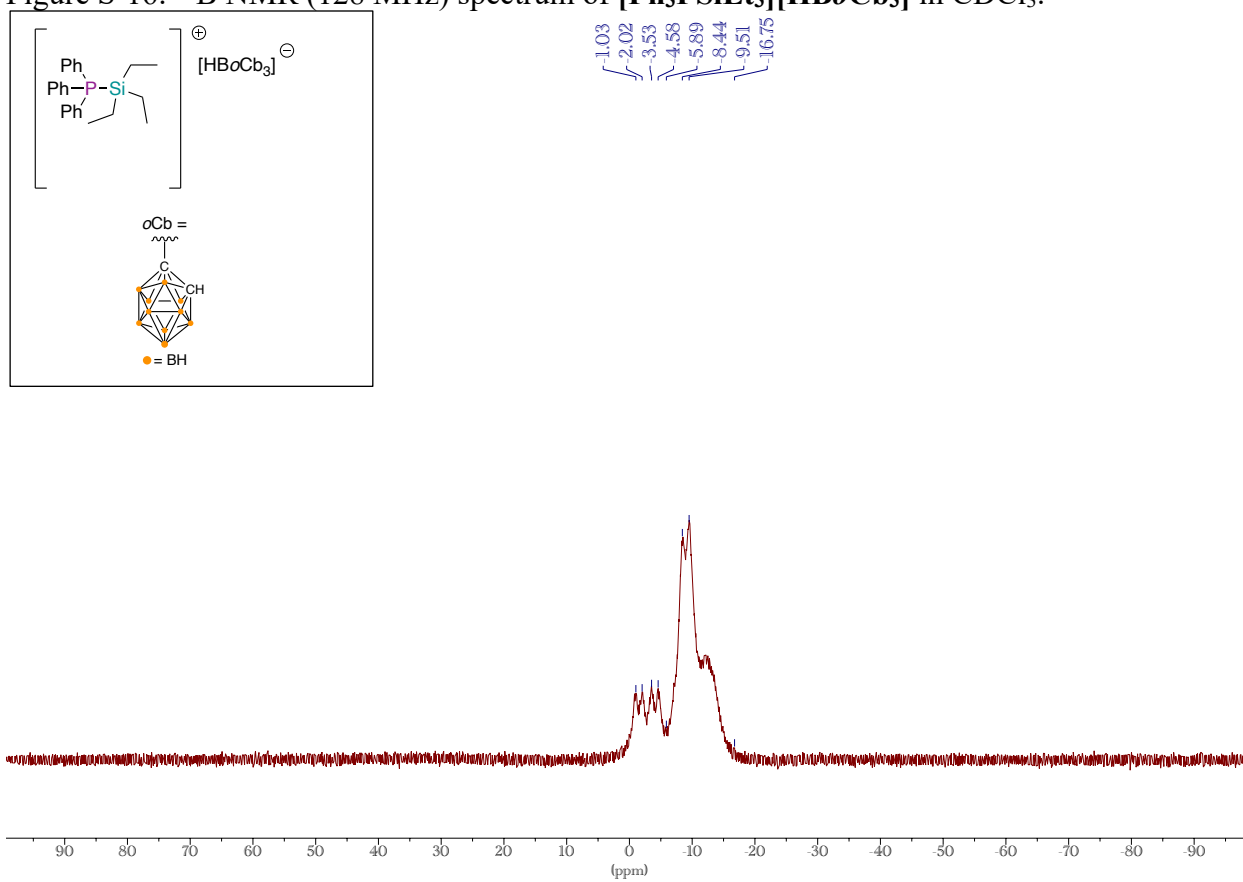


Figure S-17: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 .

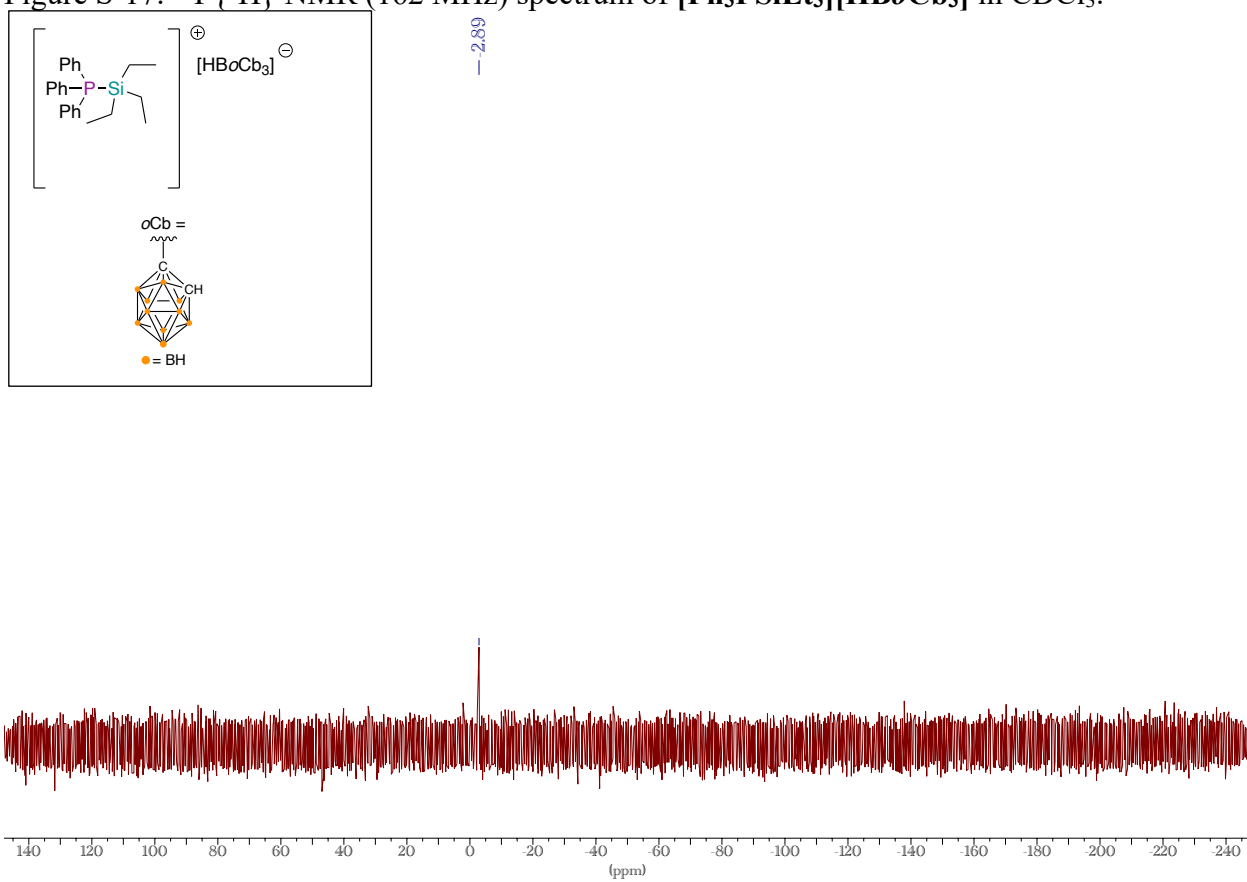


Figure S-18: FT-IR spectrum of $[\text{Ph}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$.

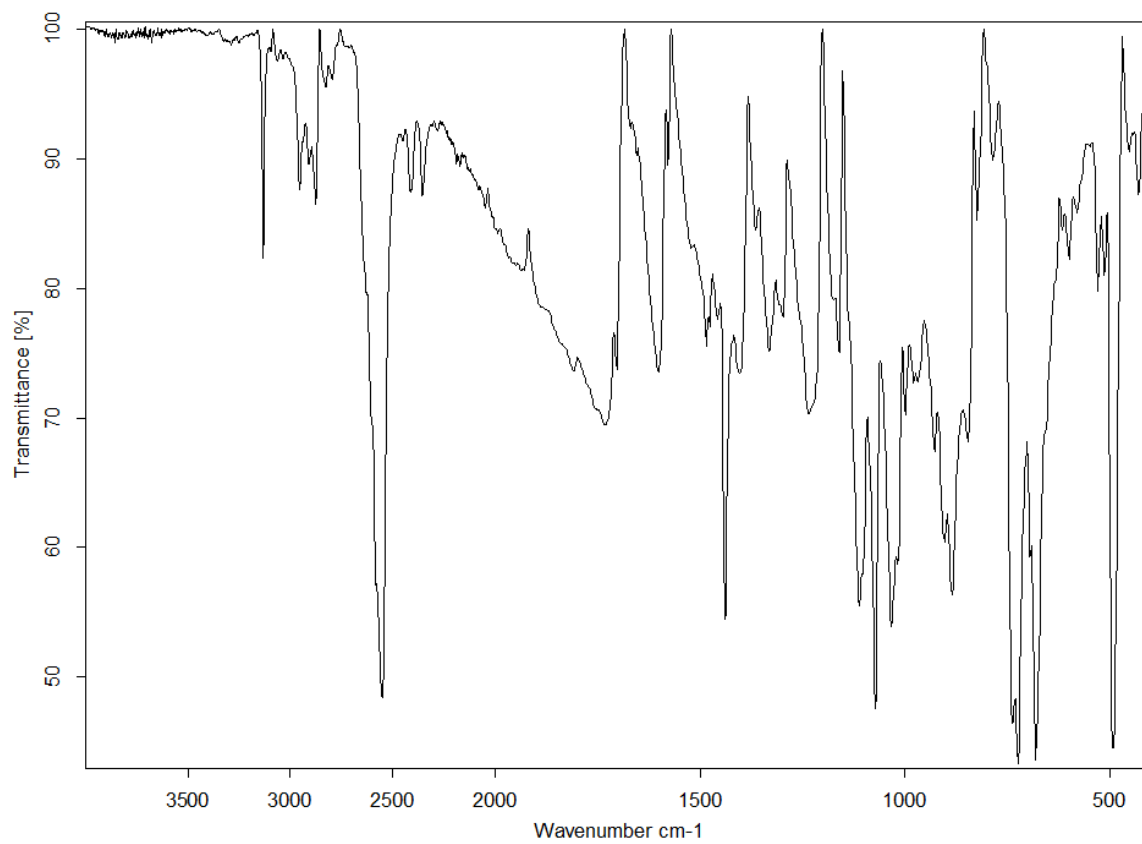


Figure S-19: ^1H NMR (400 MHz) spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HBoCb}_3]$ in CD_2Cl_2 (* residual benzene).

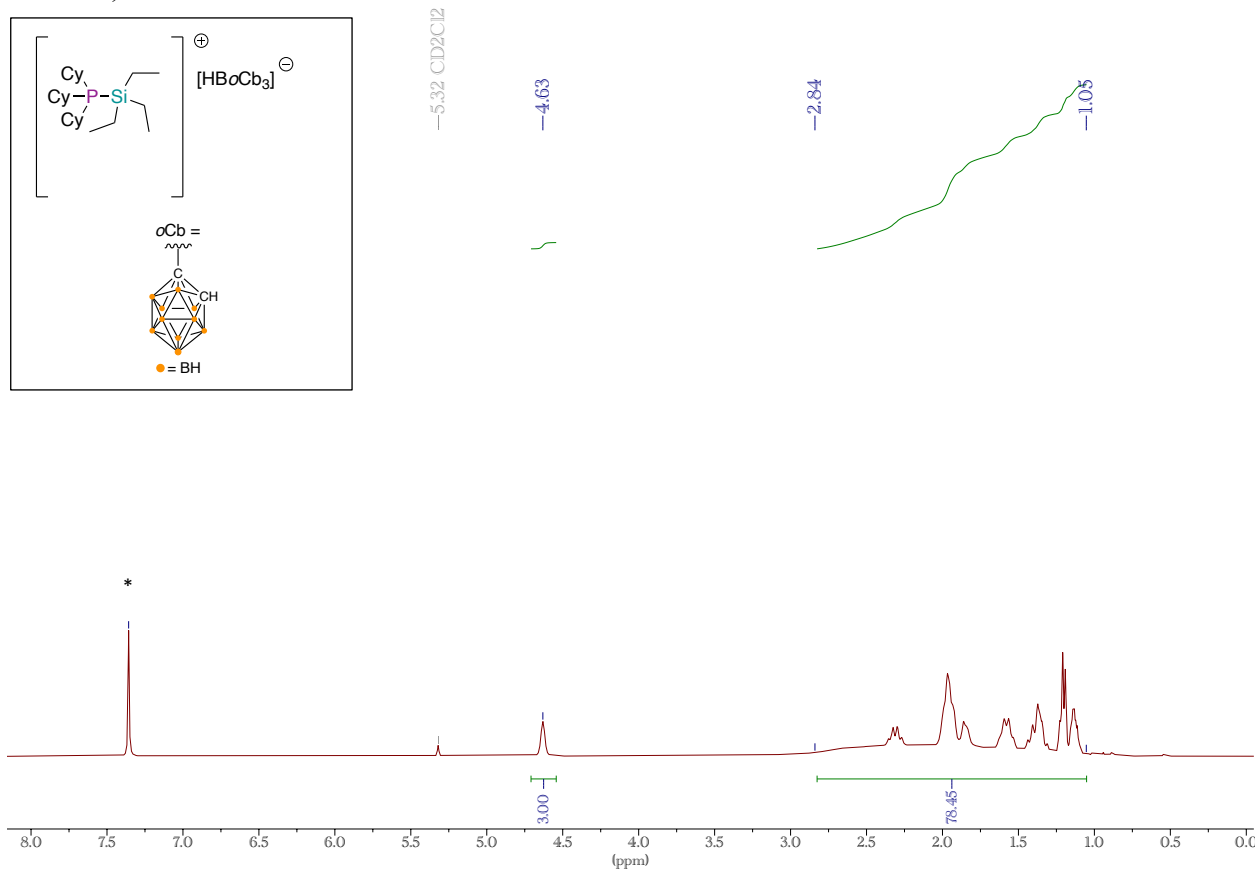


Figure S-20: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CD_2Cl_2 (* residual benzene).

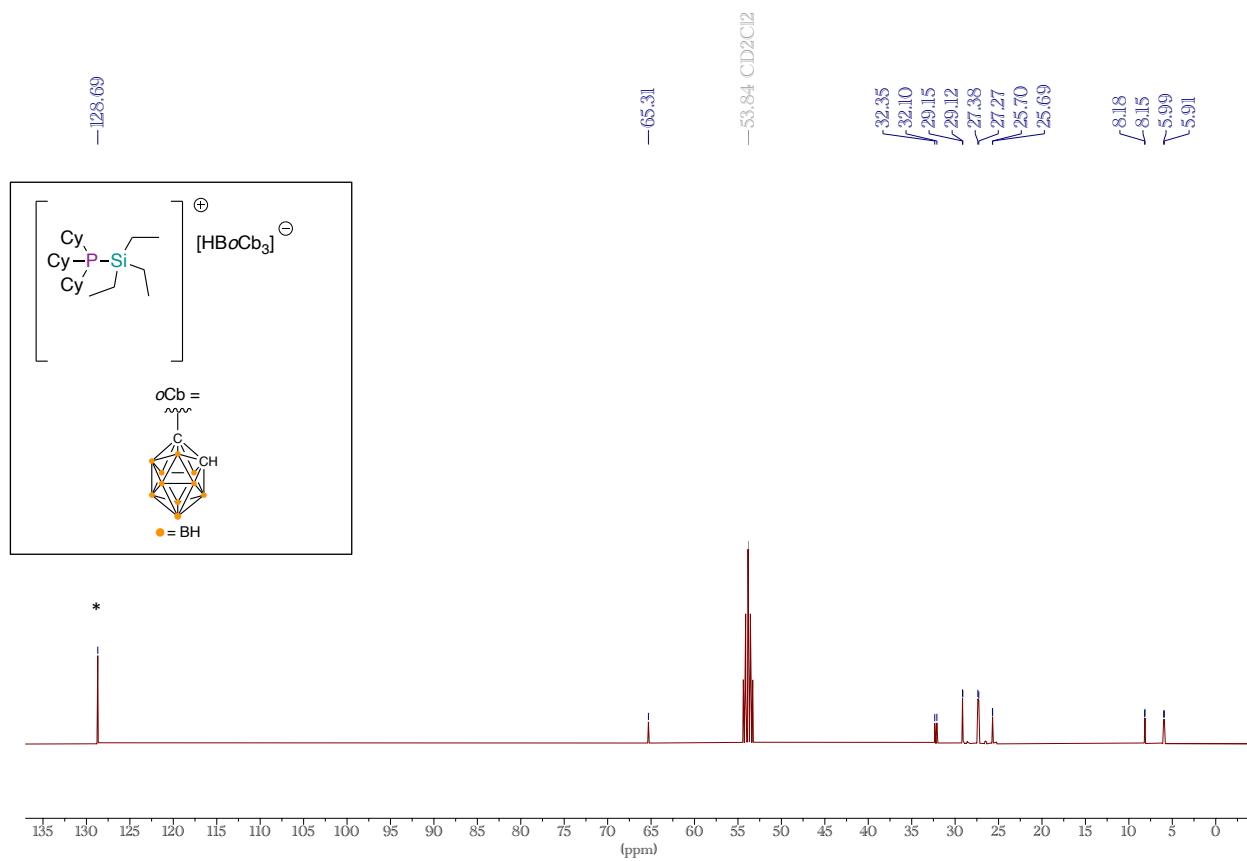


Figure S-21: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CD_2Cl_2 .

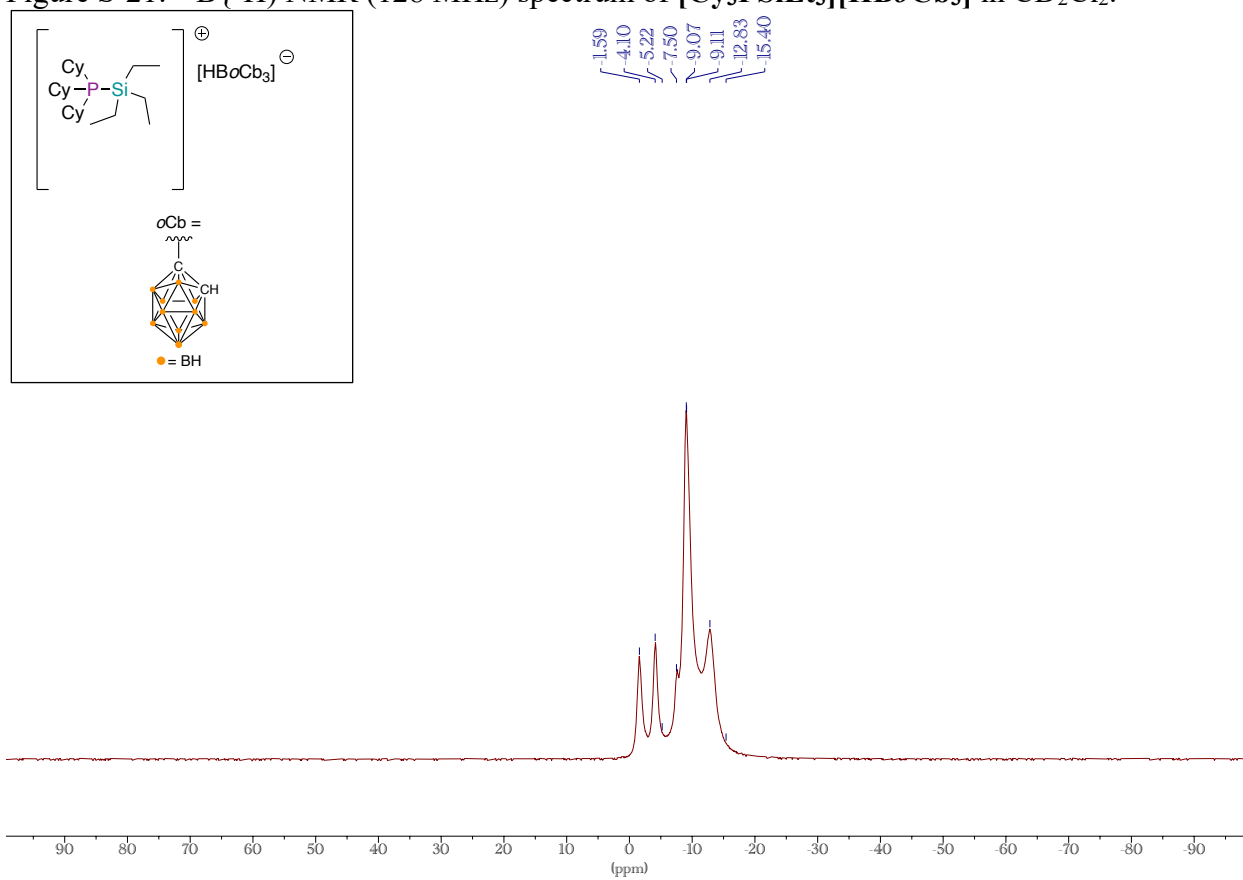


Figure S-22: ^{11}B NMR (128 MHz) spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CD_2Cl_2 .

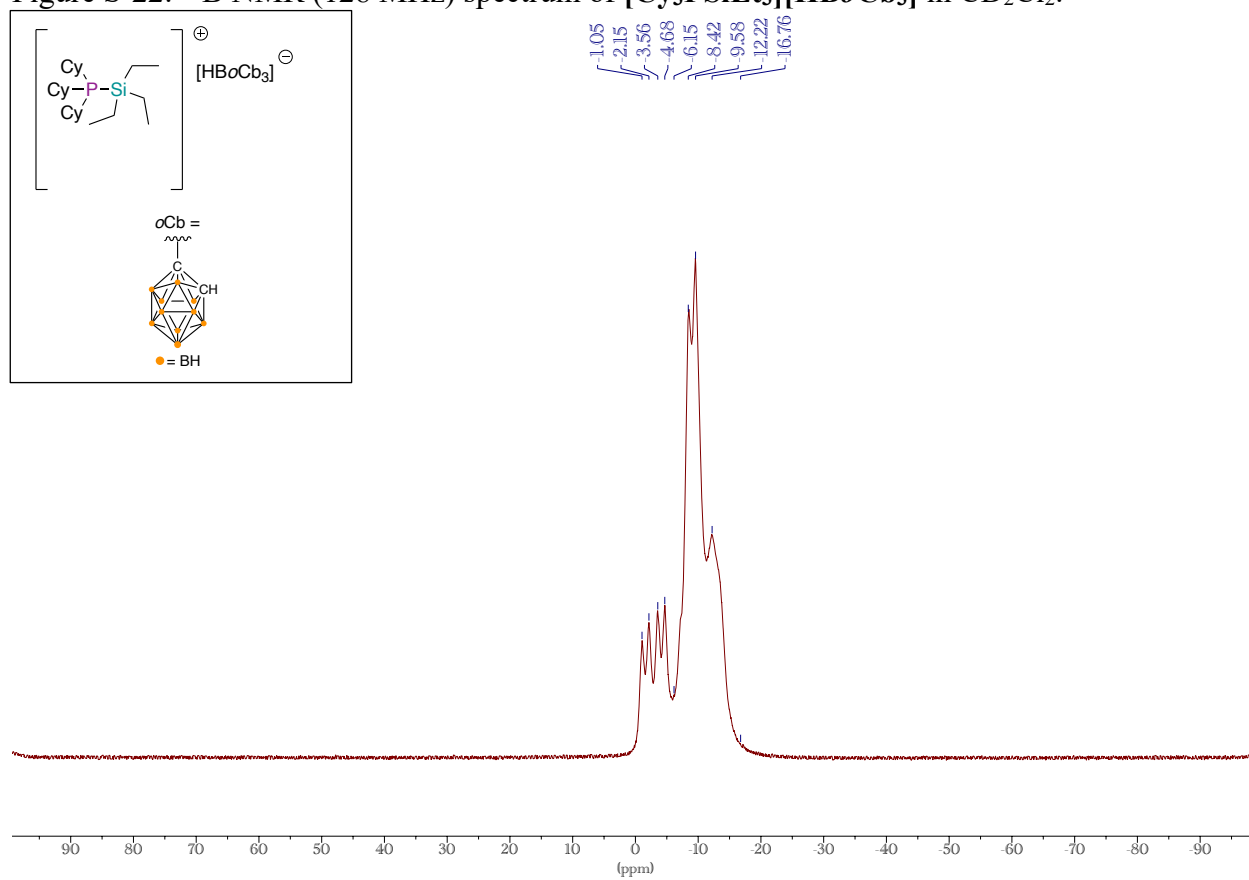


Figure S-23: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CD_2Cl_2 .

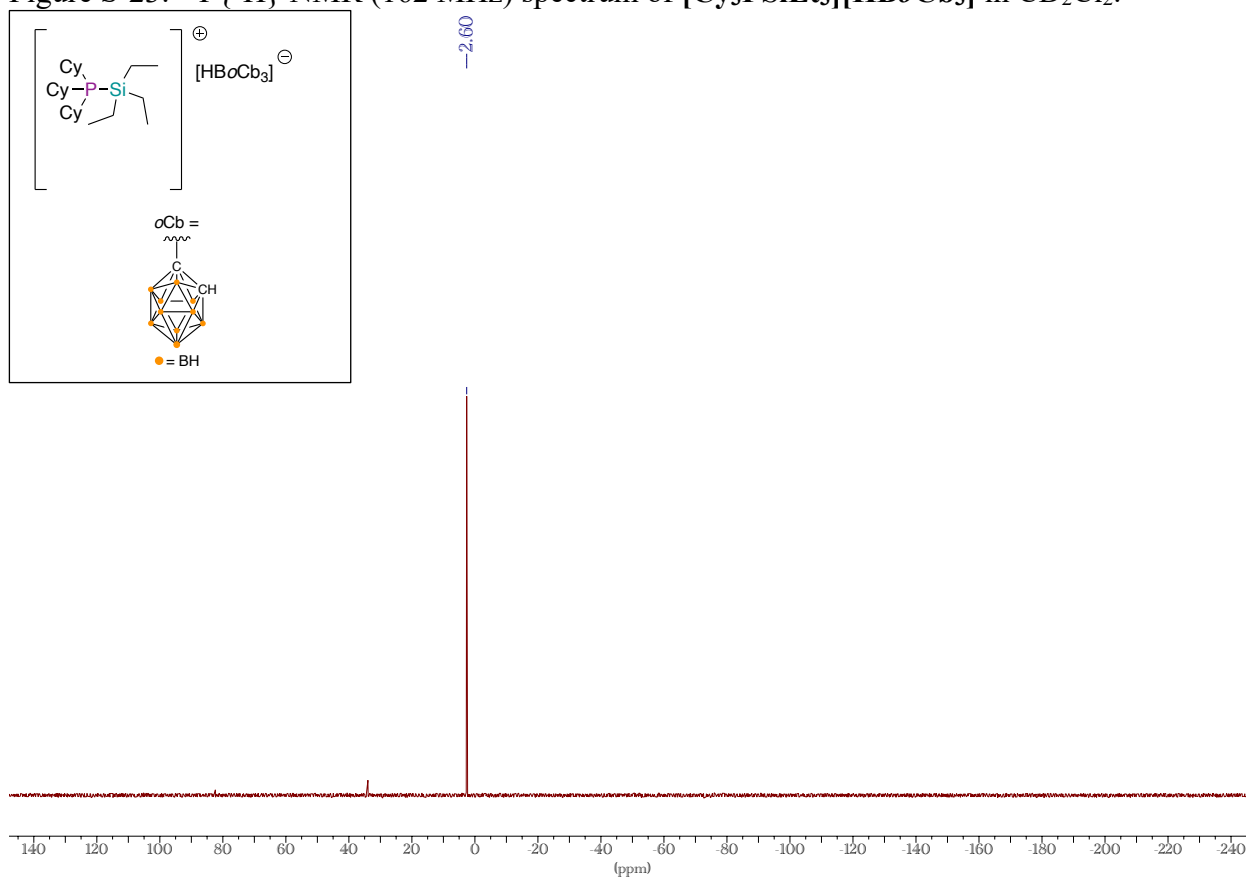


Figure S-24: FT-IR spectrum of $[\text{Cy}_3\text{PSiEt}_3][\text{HB}_0\text{Cb}_3]$.

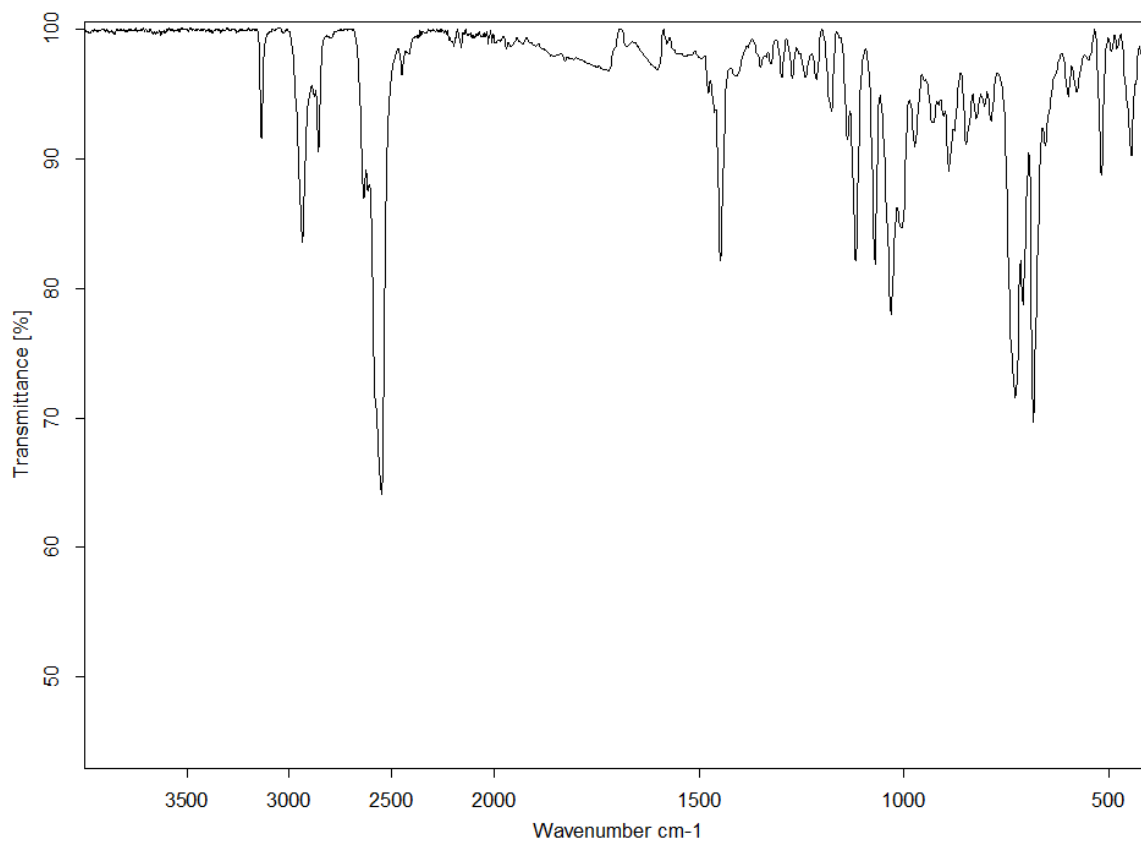


Figure S-25: ^1H NMR (400 MHz) spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HBoCb}_3]$ in CDCl_3 .

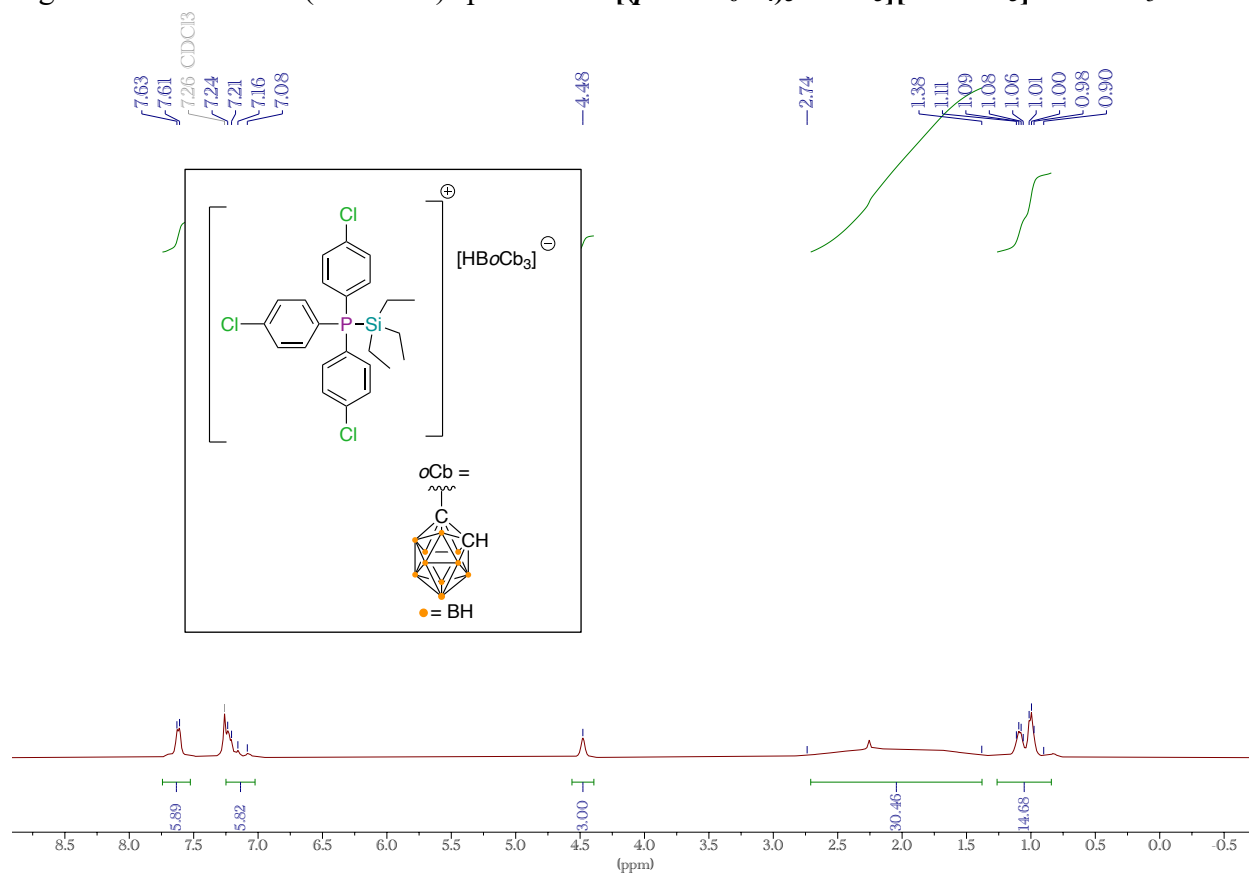


Figure S-26: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 (* residual benzene).

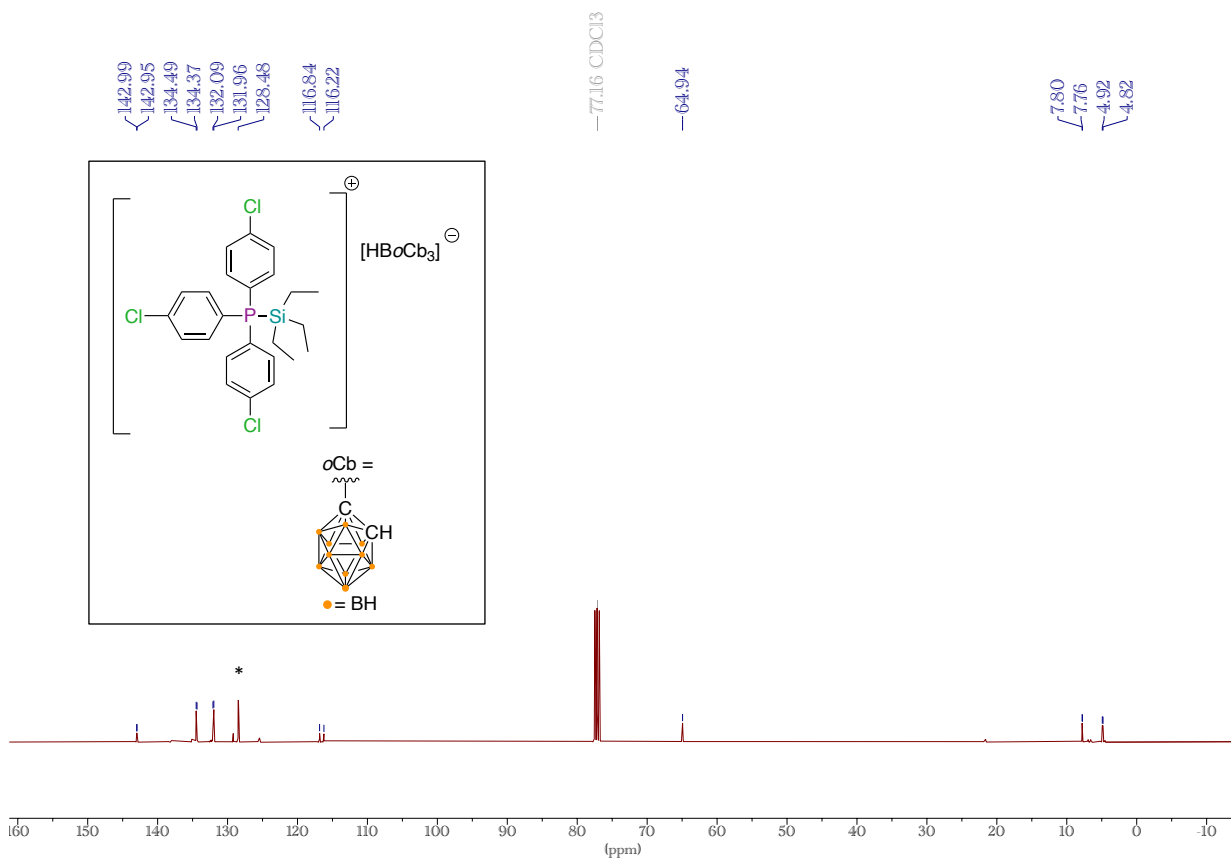


Figure S-27: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 .

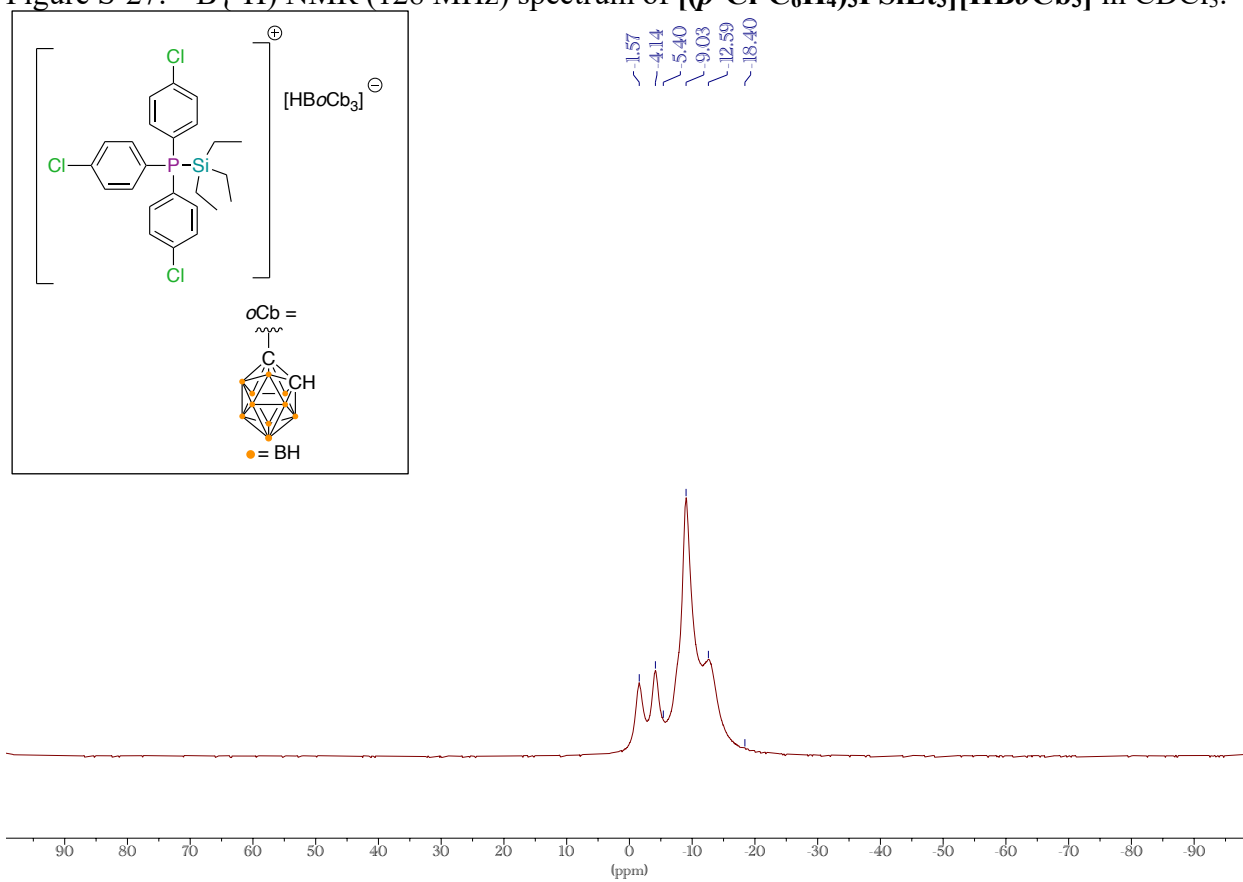


Figure S-28: ^{11}B NMR (128 MHz) spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

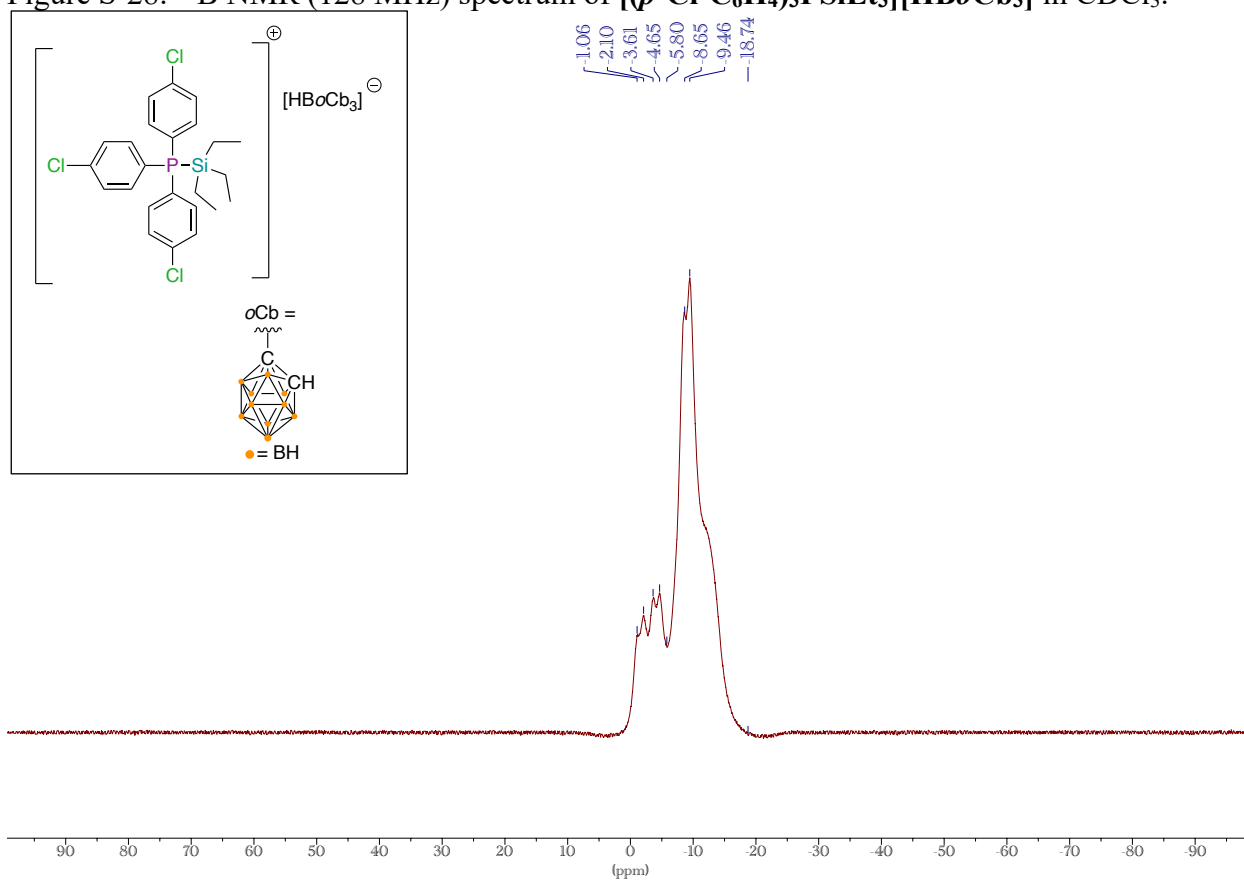


Figure S-29: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}\alpha\text{Cb}_3]$ in CDCl_3 .

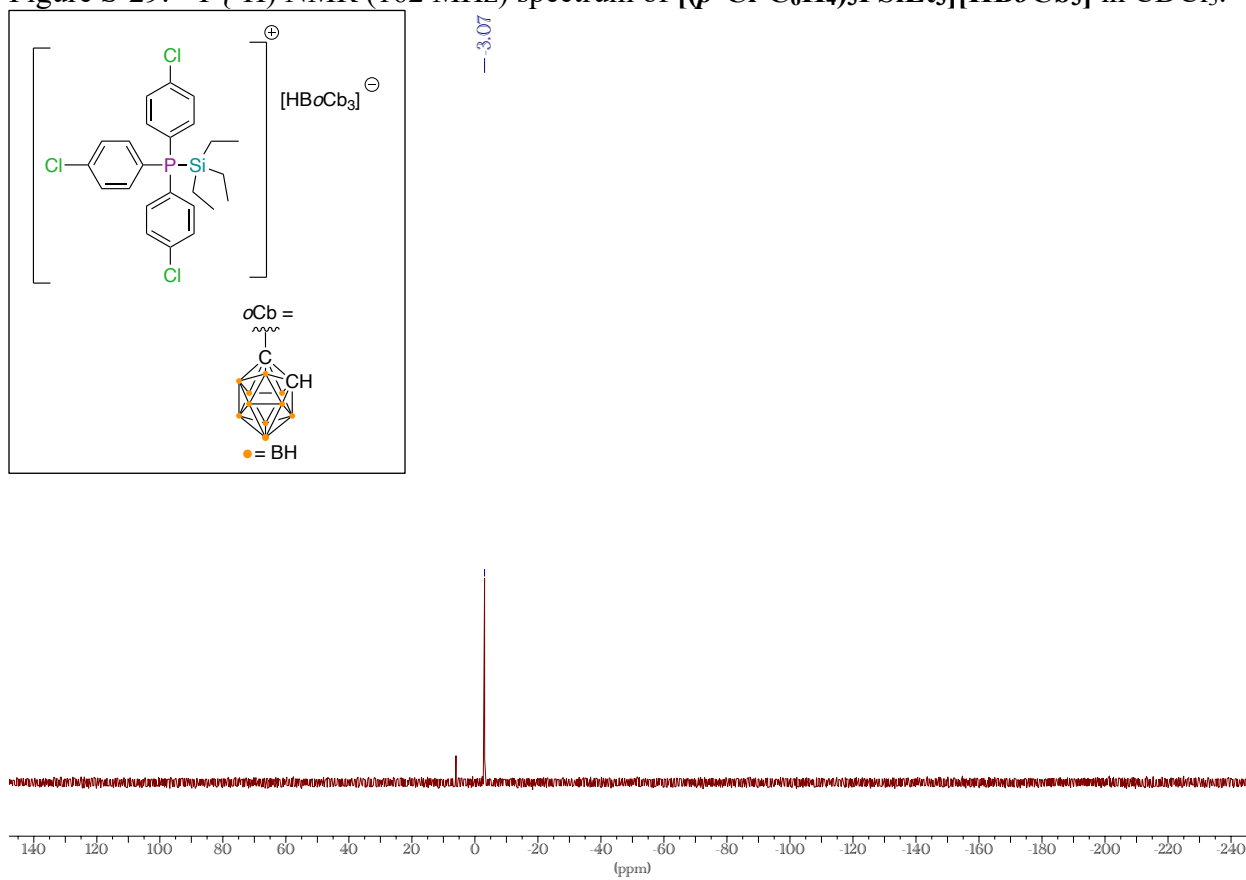


Figure S-30: FT-IR spectrum of $[(p\text{-Cl-C}_6\text{H}_4)_3\text{P SiEt}_3][\text{HB}o\text{Cb}_3]$.

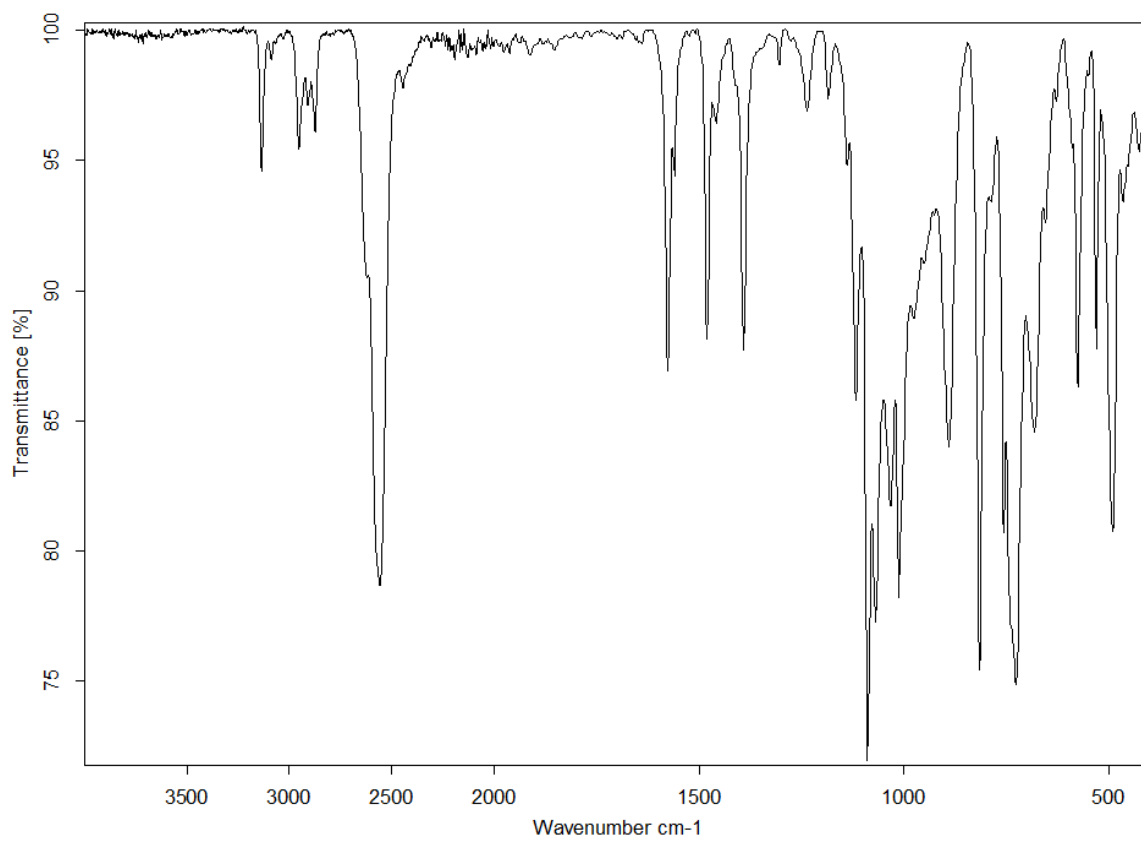


Figure S-31: ^1H NMR (400 MHz) spectrum of $[(o\text{-tol})_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 (* residual benzene and Δ residual n -pentane).

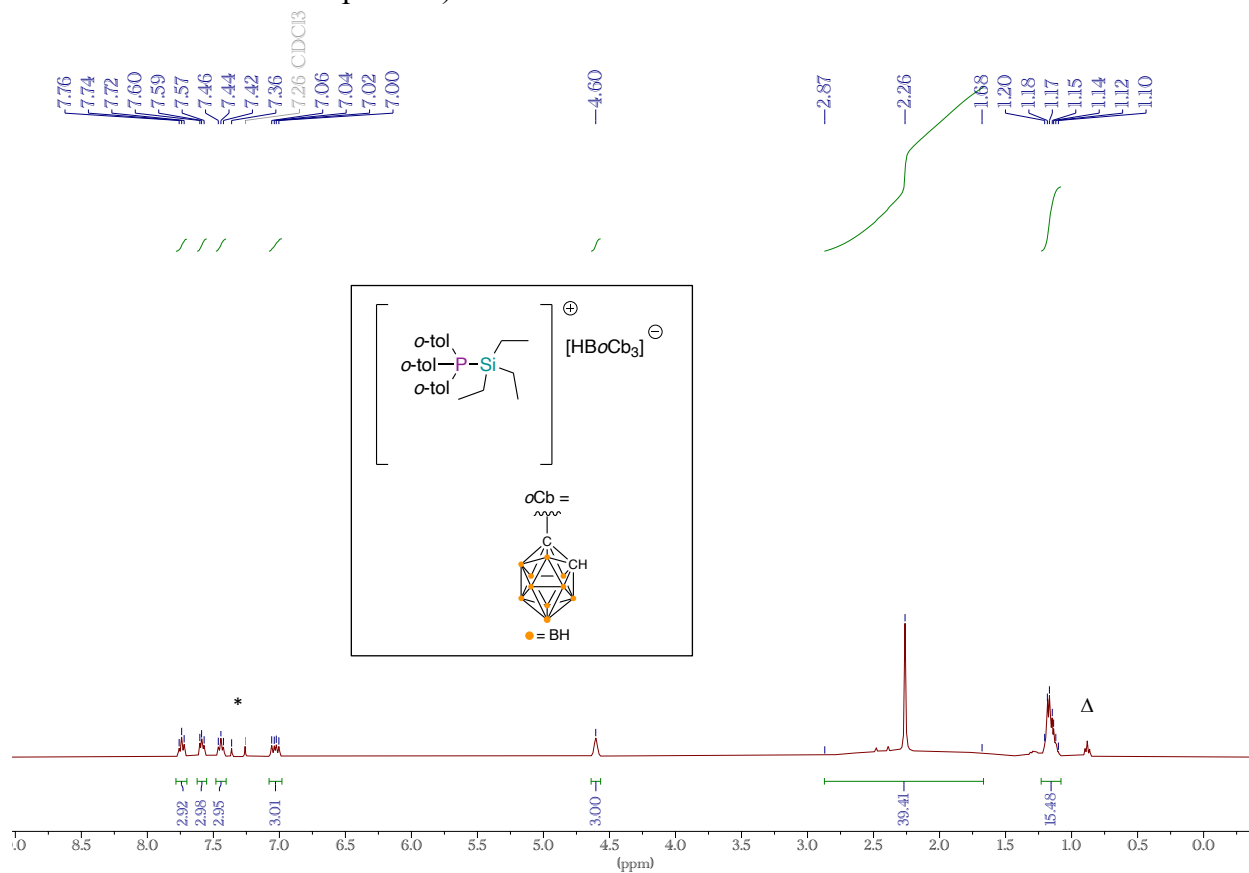


Figure S-32: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[(o\text{-tol})_3\text{PSiEt}_3][\text{H}\text{B}o\text{Cb}_3]$ in CDCl_3 (Δ residual *n*-pentane).

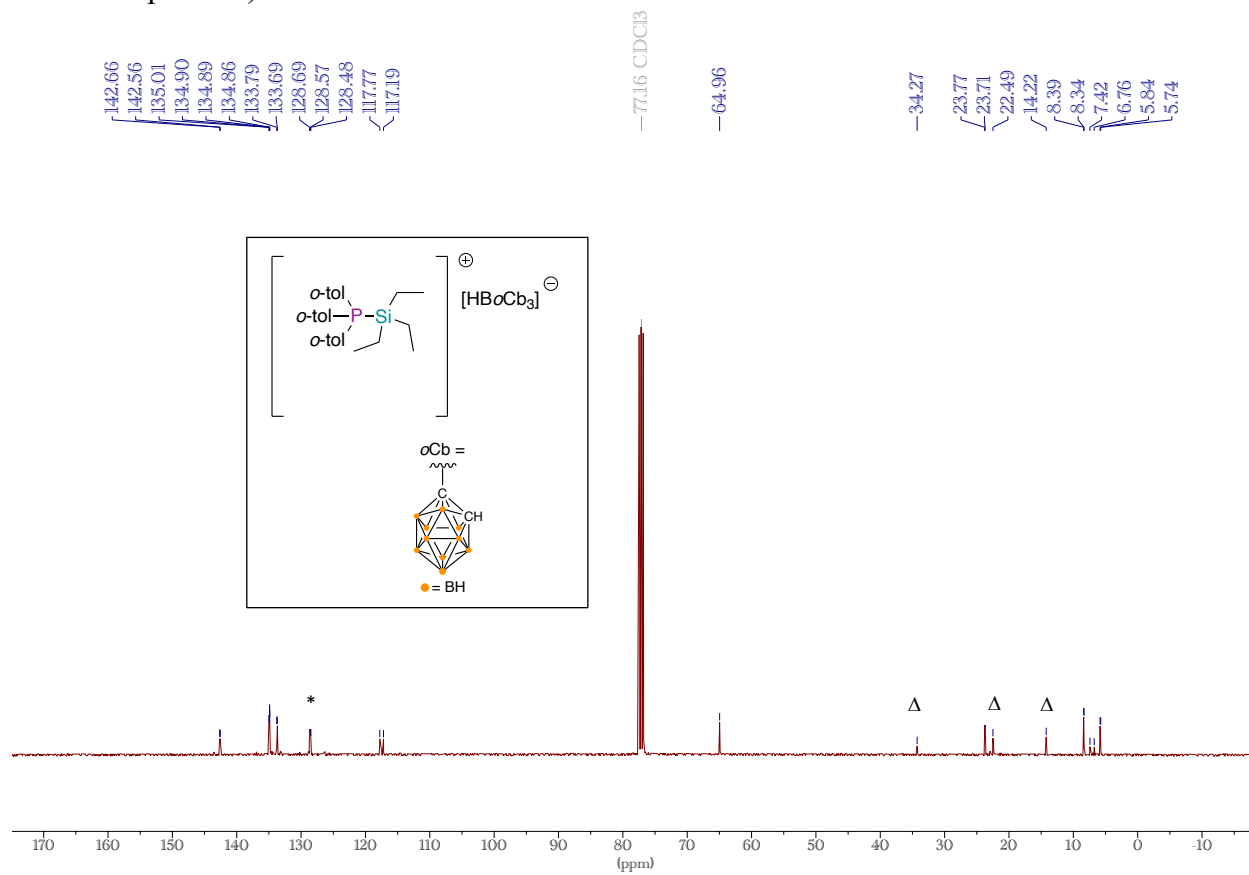


Figure S-33: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[(o\text{-tol})_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

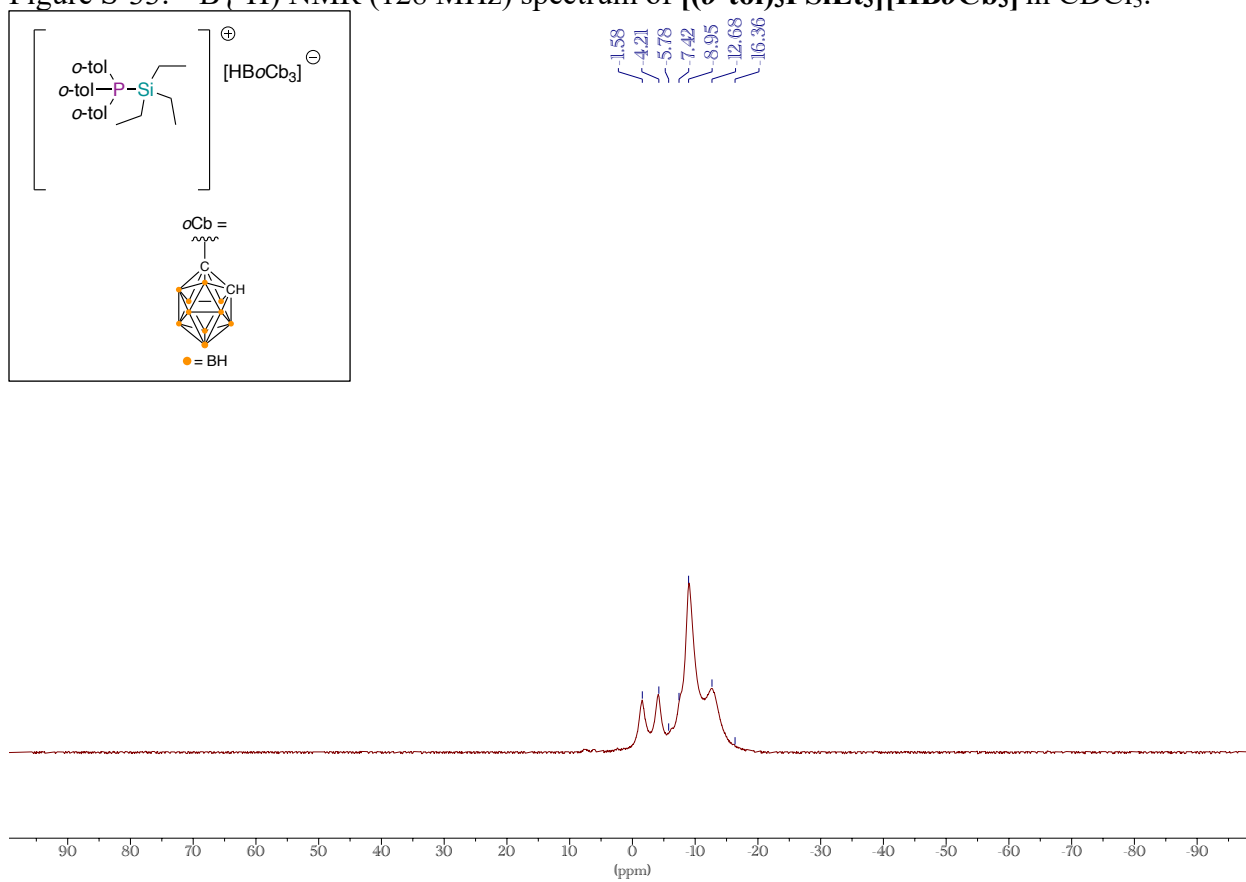


Figure S-34: ^{11}B NMR (128 MHz) spectrum of $[(o\text{-tol})_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

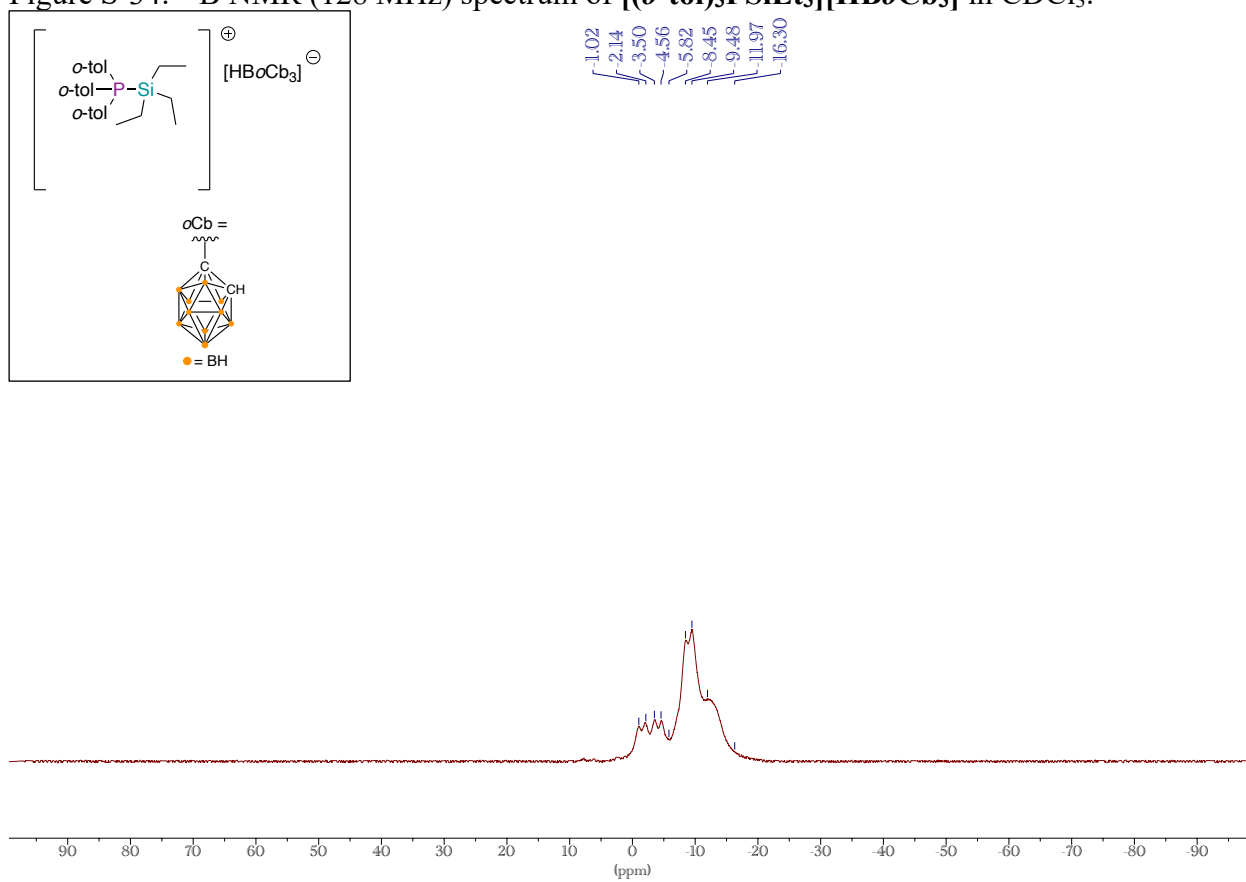


Figure S-35: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[(o\text{-tol})_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

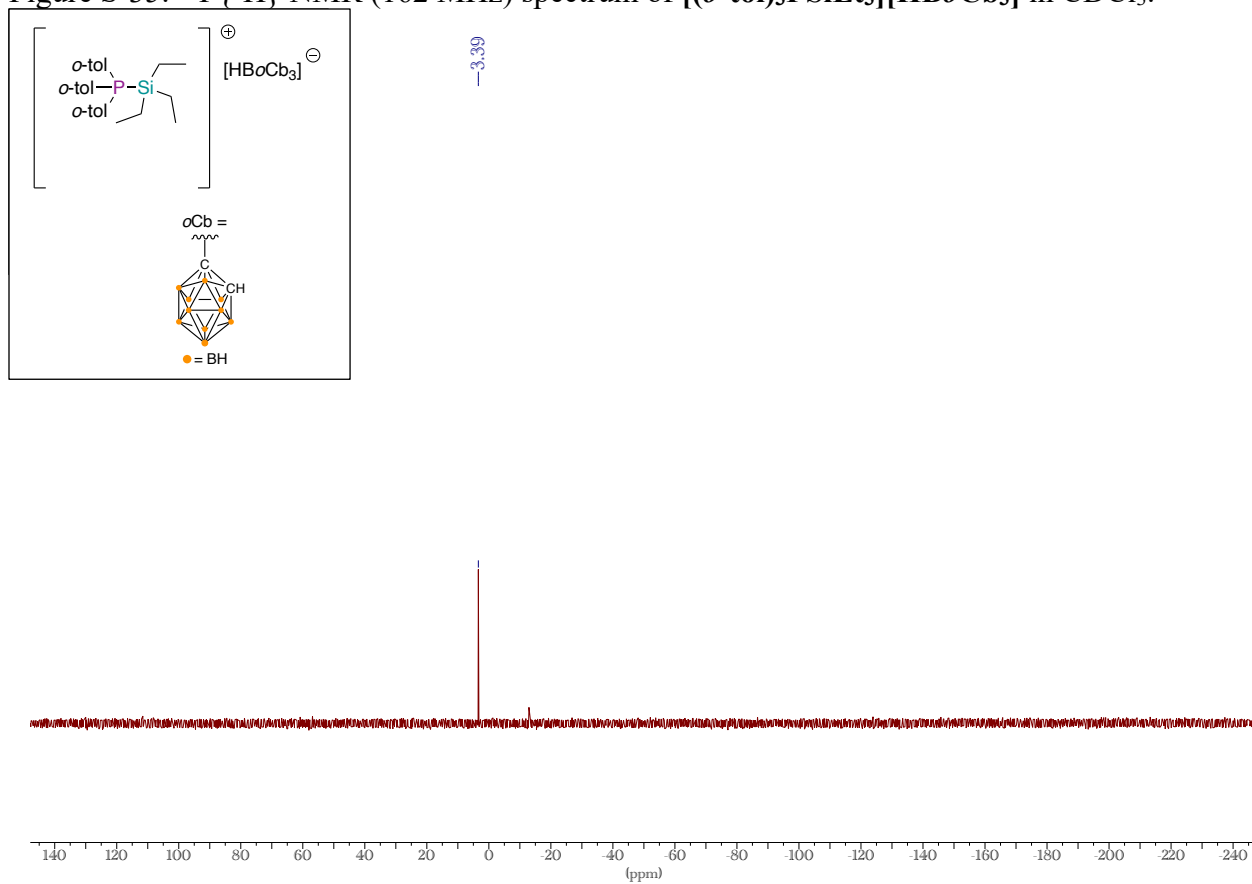


Figure S-36: FT-IR spectrum of [(*o*-tol)₃PSiEt₃][HB*o*Cb₃].

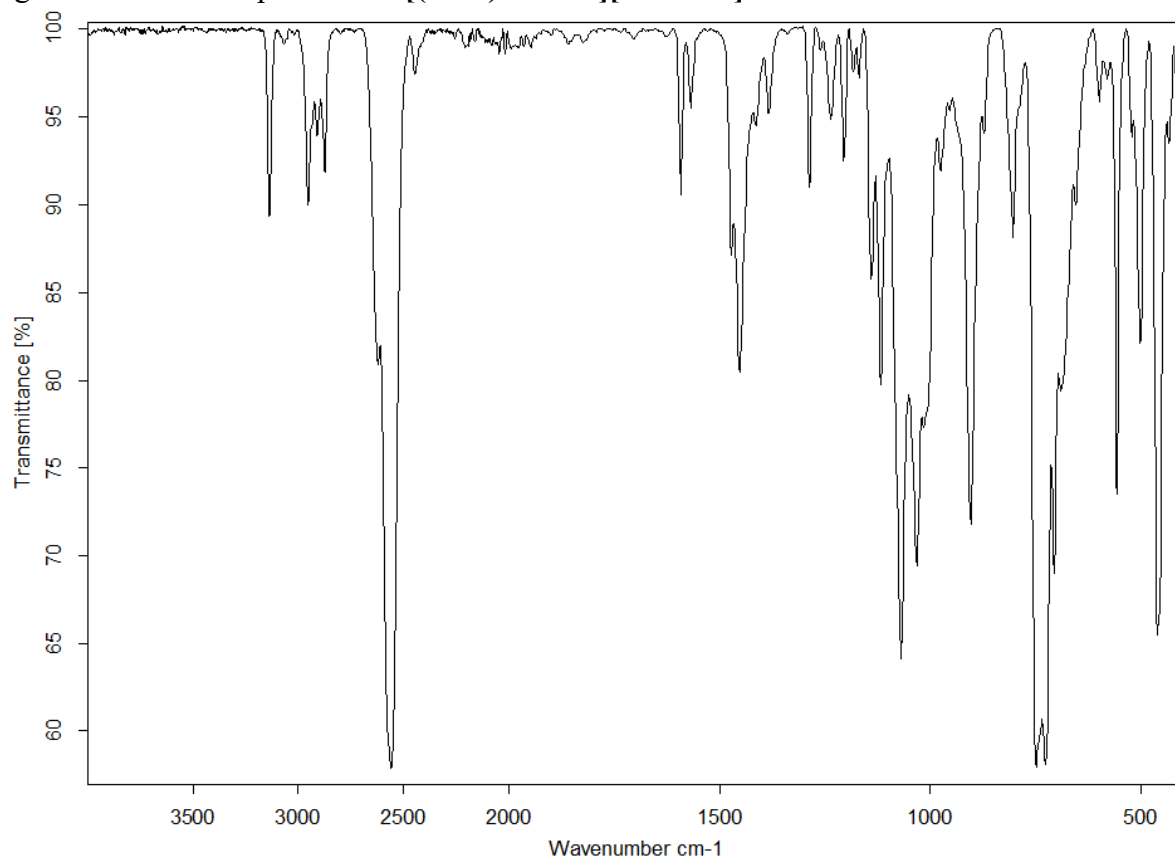


Figure S-37: ^1H NMR (400 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HBoCb}_3]$ in CDCl_3 (* residual benzene).

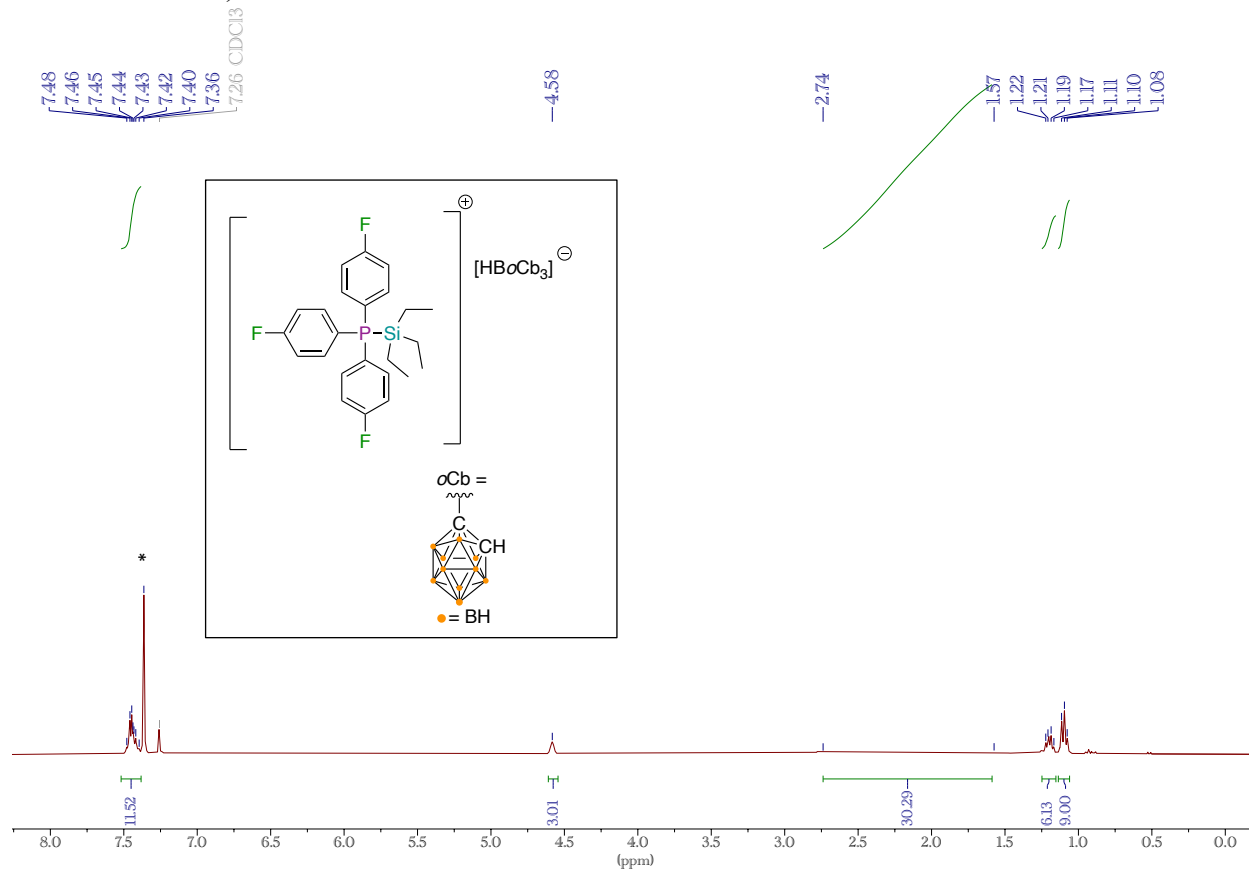


Figure S-38: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}\sigma\text{Cb}_3]$ in CDCl_3 (* residual benzene).

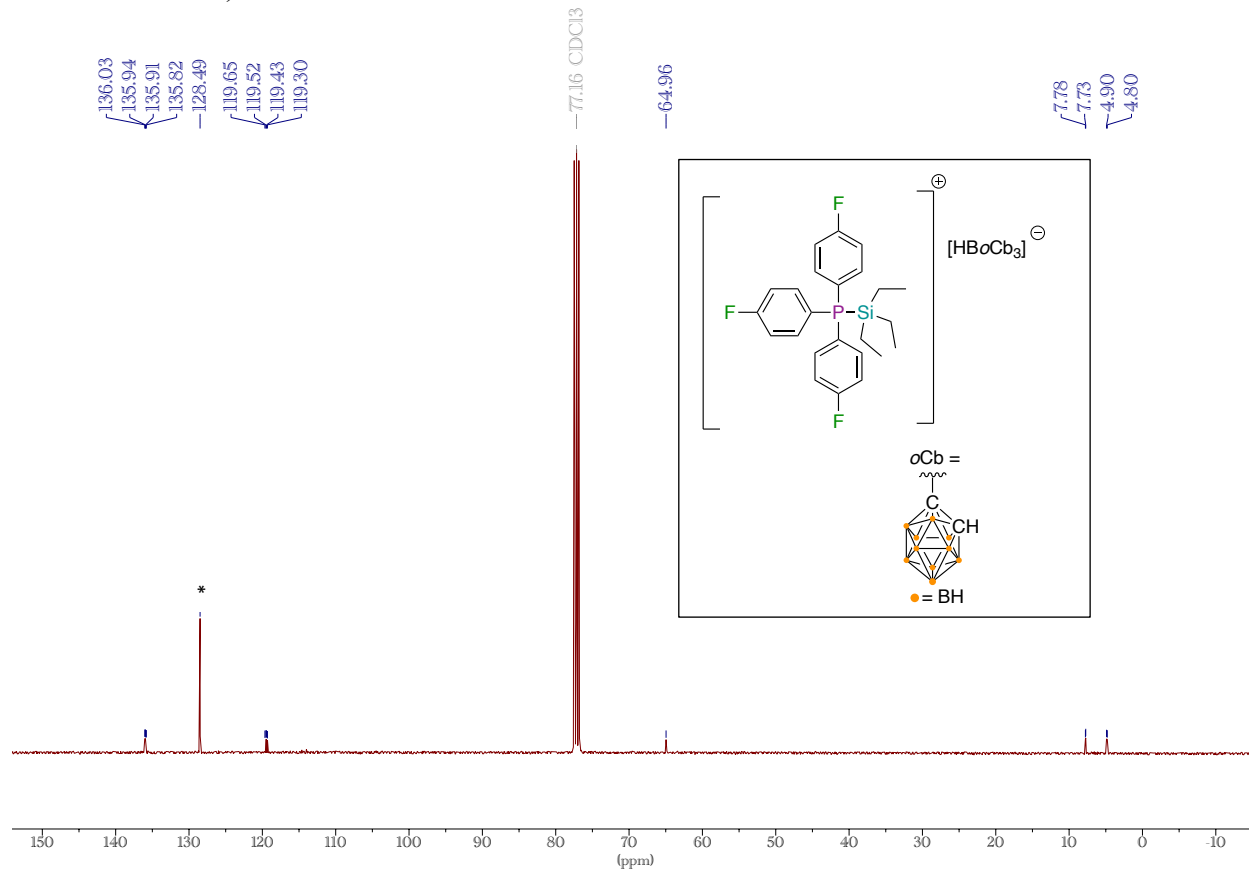


Figure S-39: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HBoCb}_3]$ in CDCl_3 .

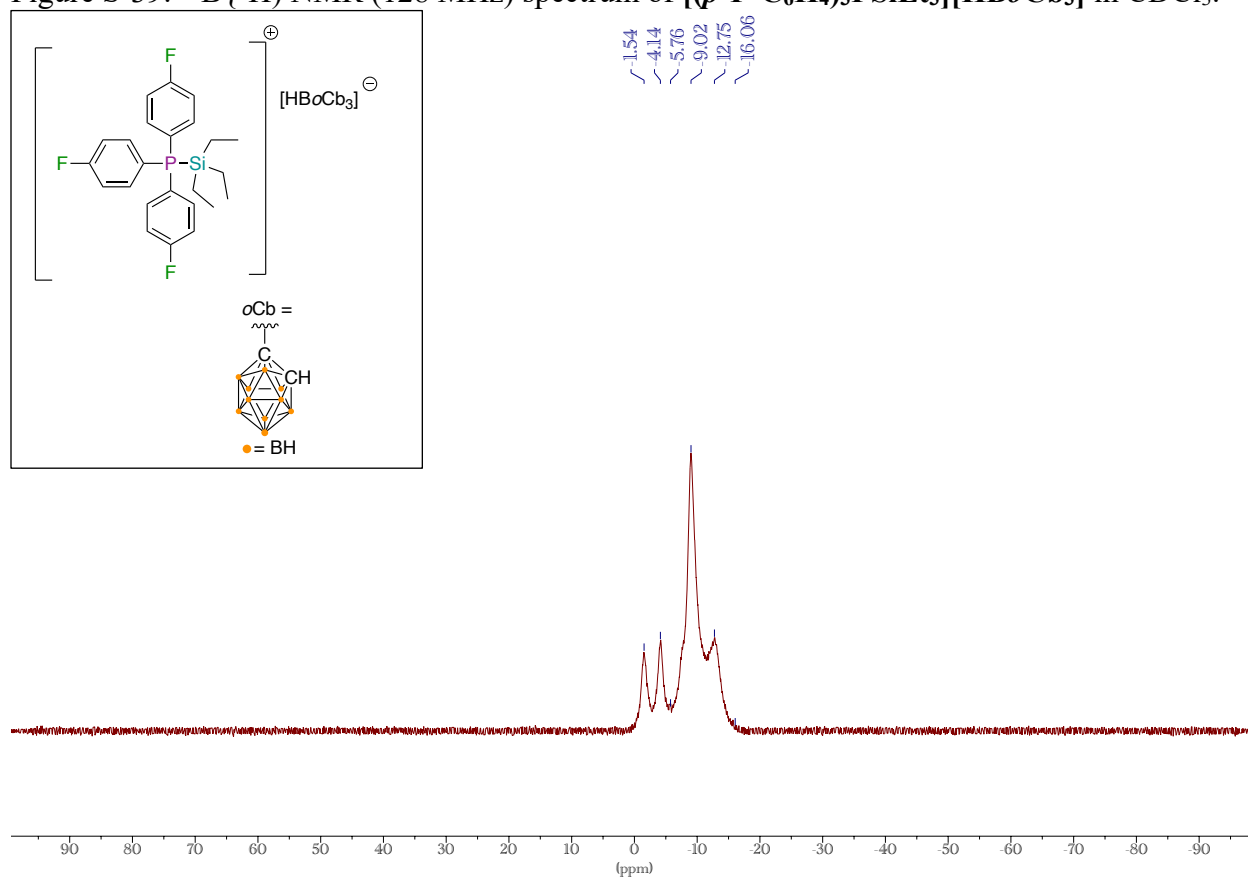


Figure S-40: ^{11}B NMR (128 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

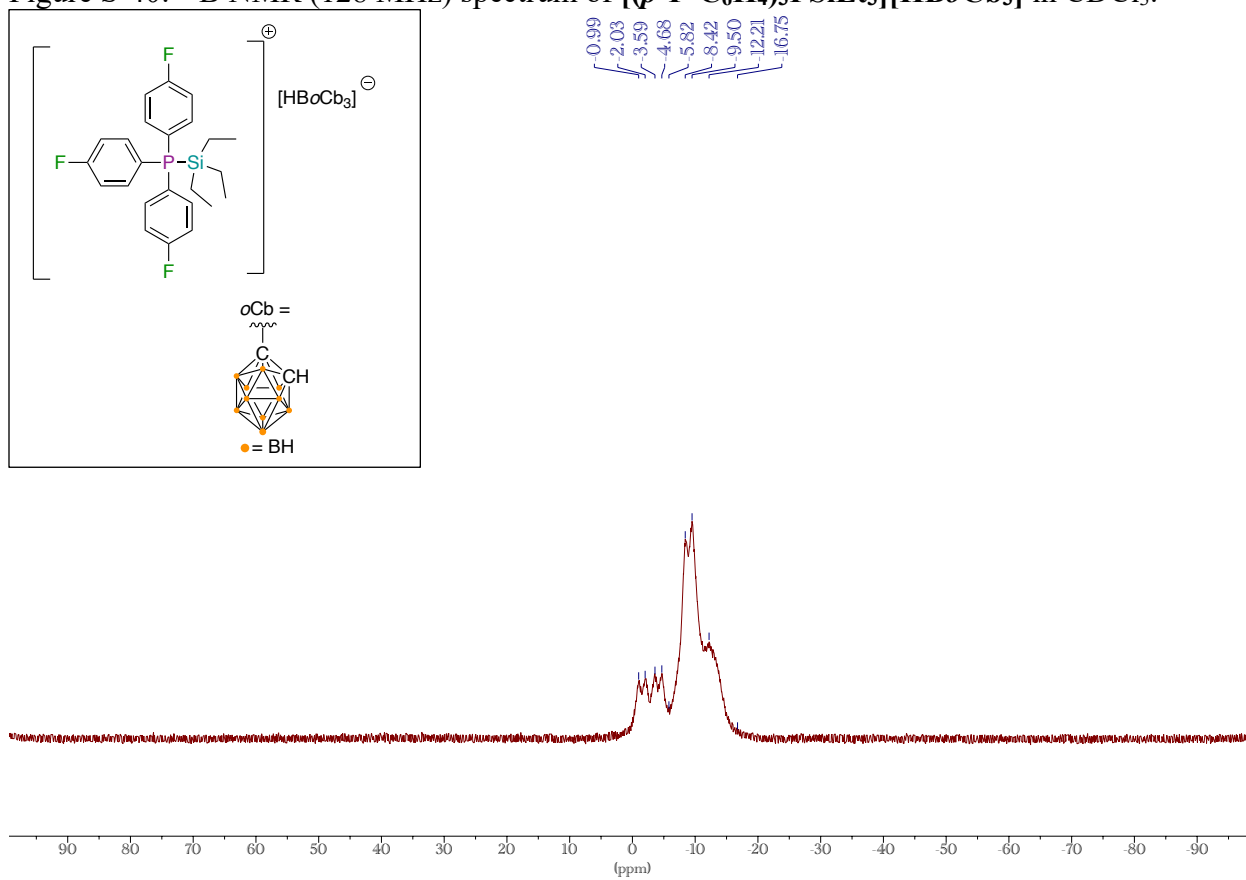


Figure S-41: $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

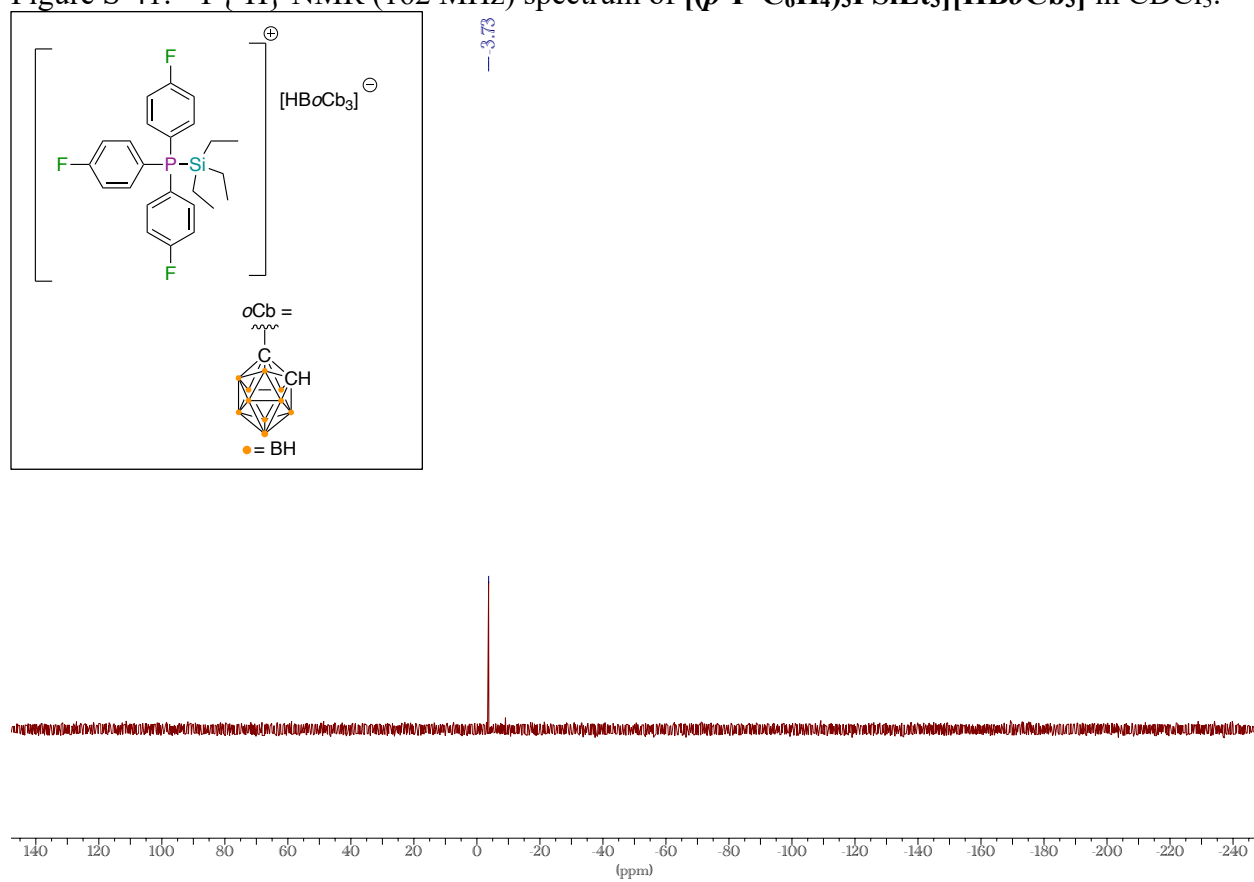


Figure S-42: $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz) spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

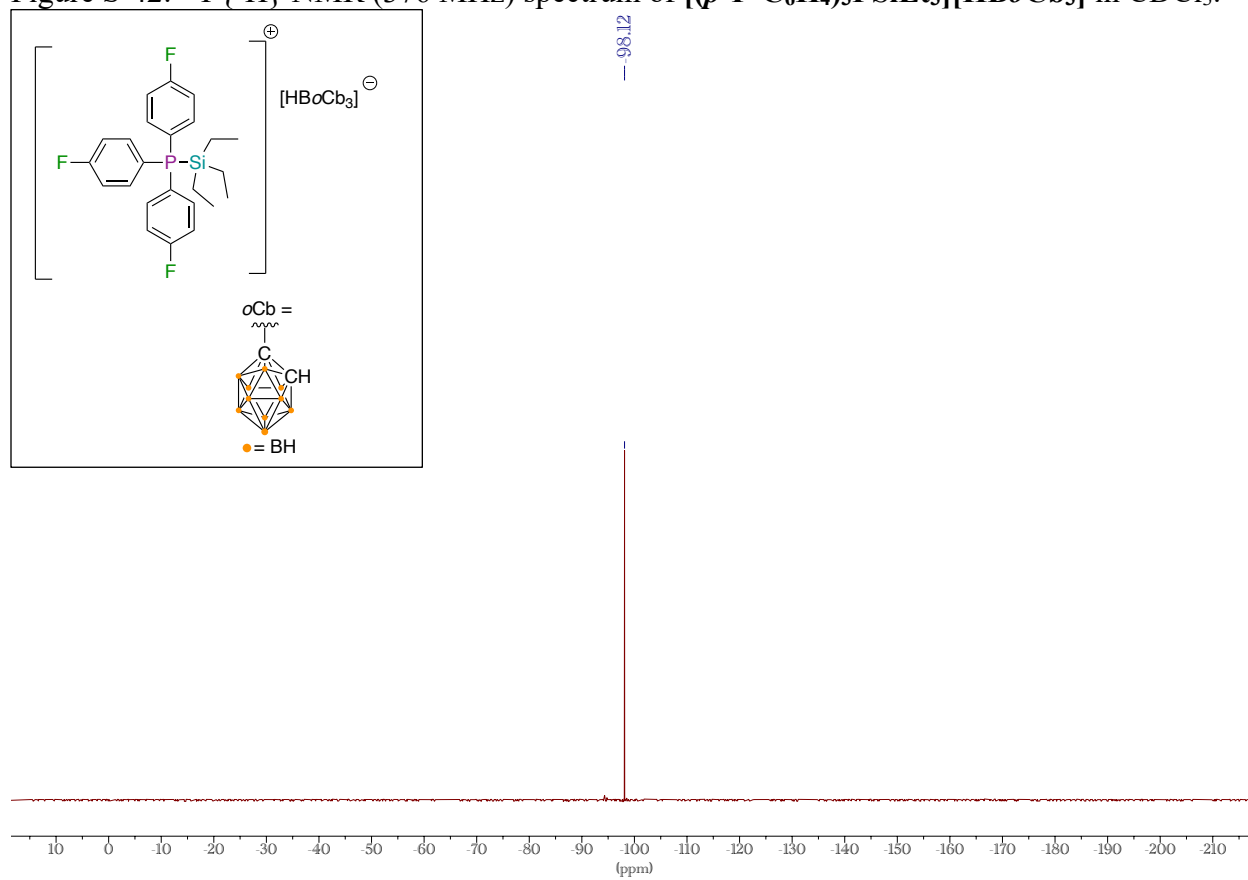


Figure S-43: FT-IR spectrum of $[(p\text{-F-C}_6\text{H}_4)_3\text{PSiEt}_3][\text{HB}o\text{Cb}_3]$.

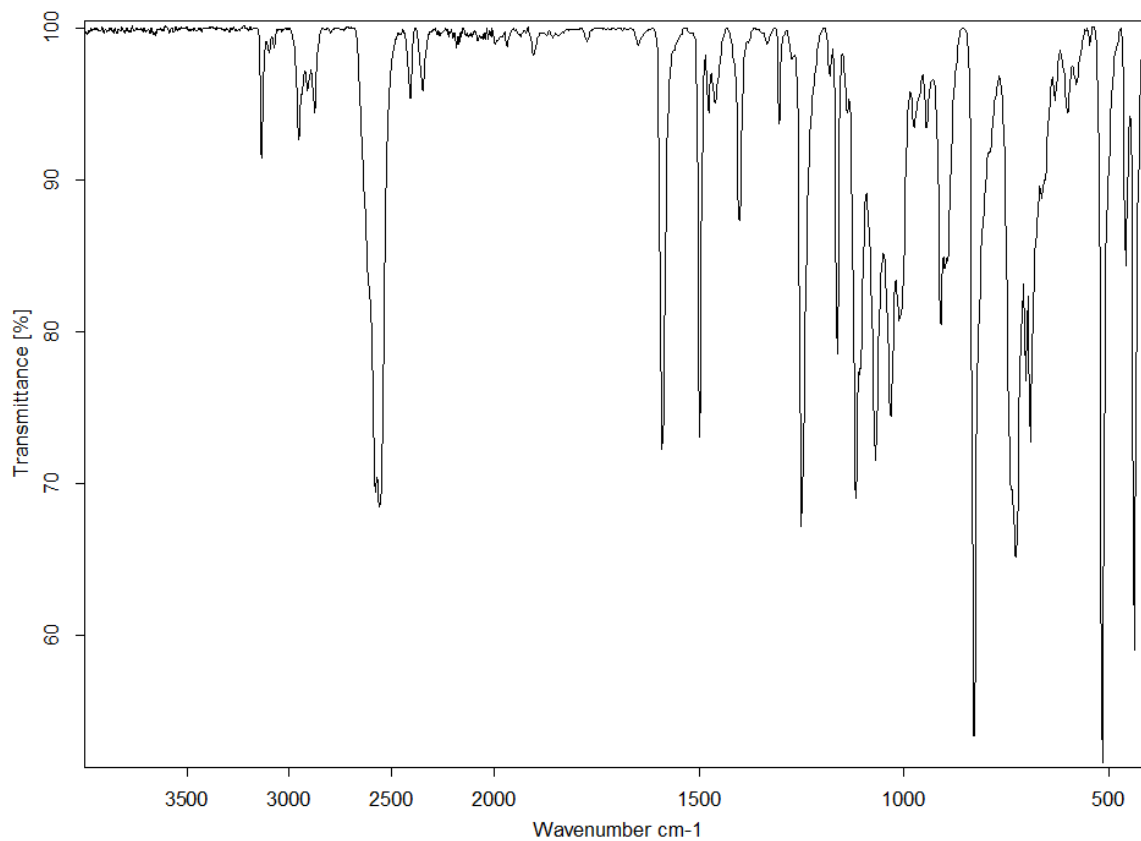


Figure S-44: ^1H NMR (400 MHz) spectrum of $[\text{Et}_3\text{NSiEt}_3][\text{HB}\alpha\text{Cb}_3]$ in CDCl_3 (∇ residual triethylamine).

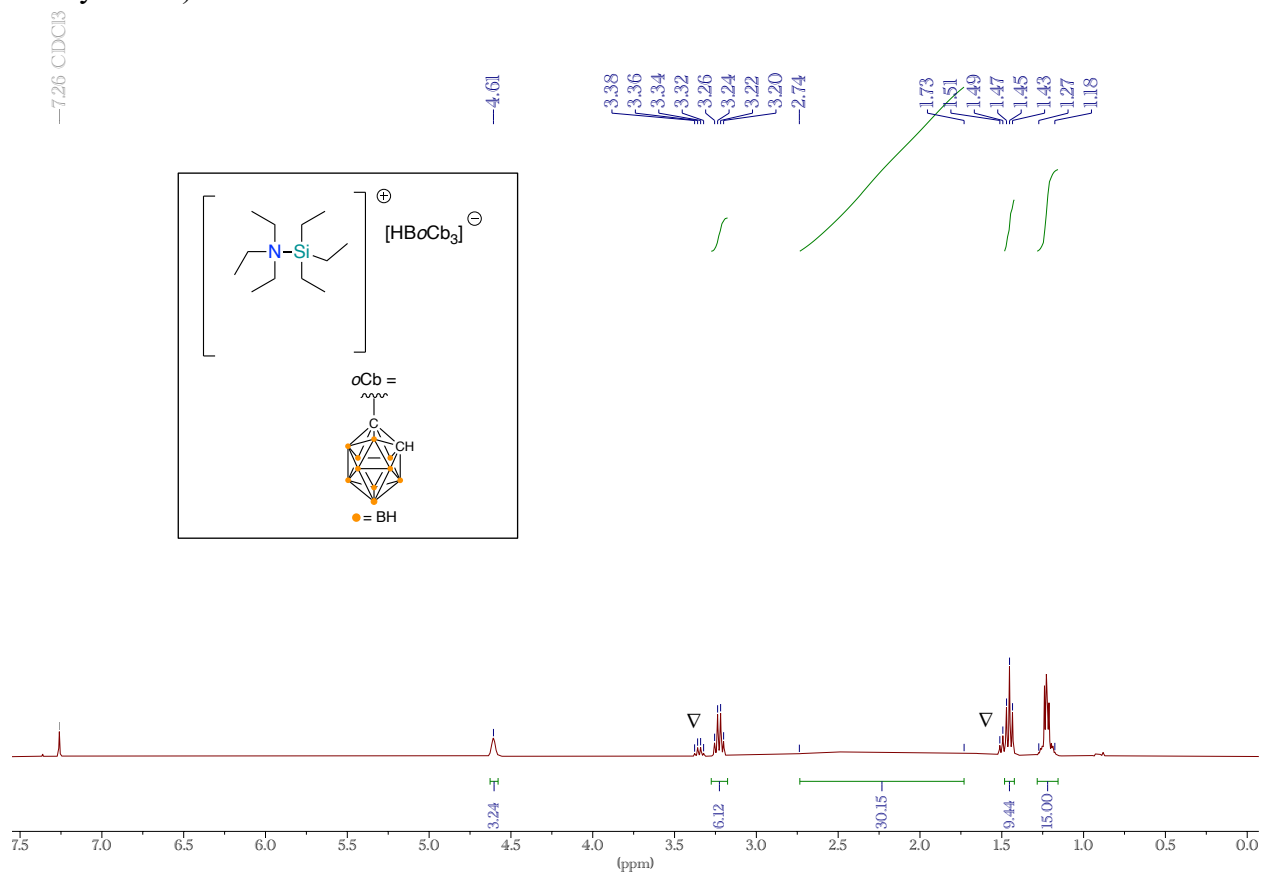


Figure S-45: $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) spectrum of $[\text{Et}_3\text{NSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

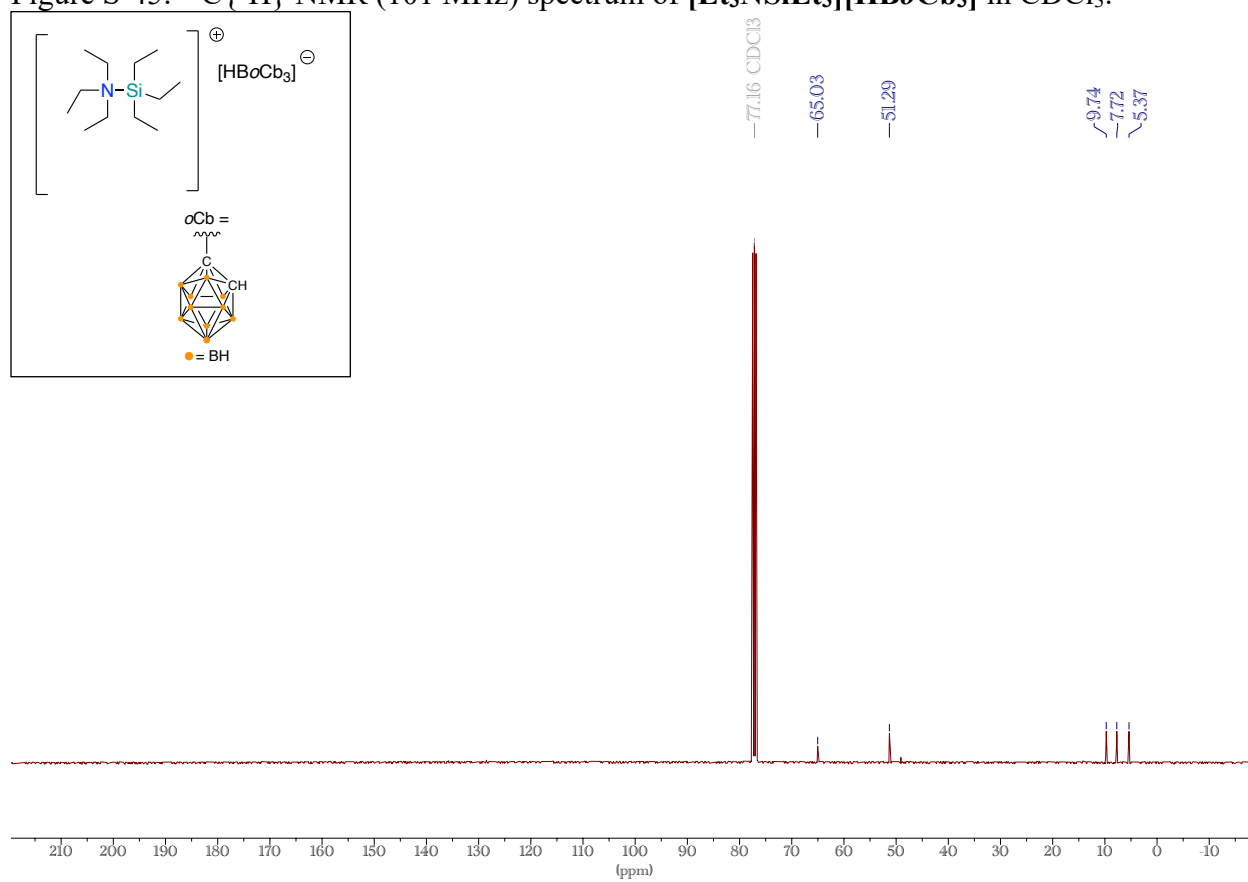


Figure S-46: $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz) spectrum of $[\text{Et}_3\text{NSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

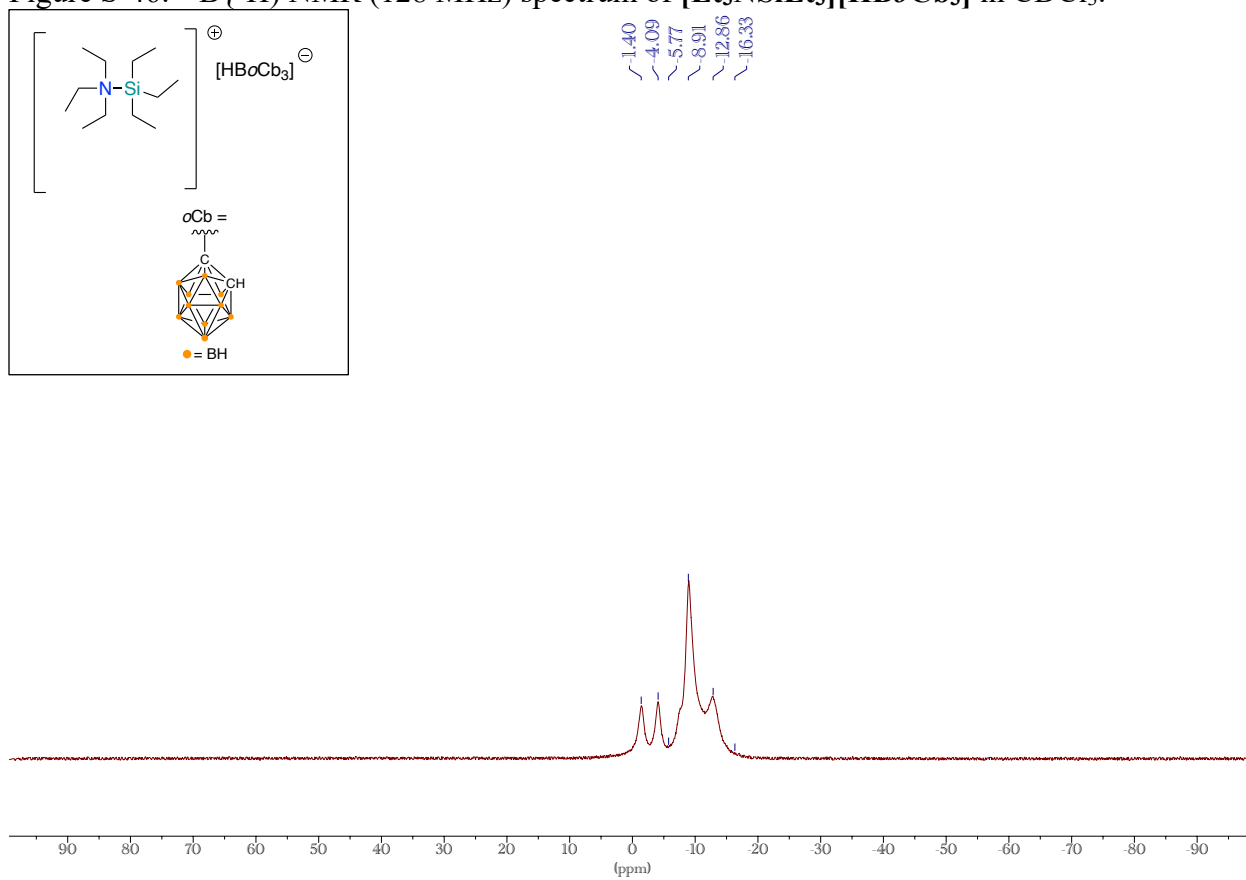


Figure S-47: ^{11}B NMR (128 MHz) spectrum of $[\text{Et}_3\text{NSiEt}_3][\text{HB}o\text{Cb}_3]$ in CDCl_3 .

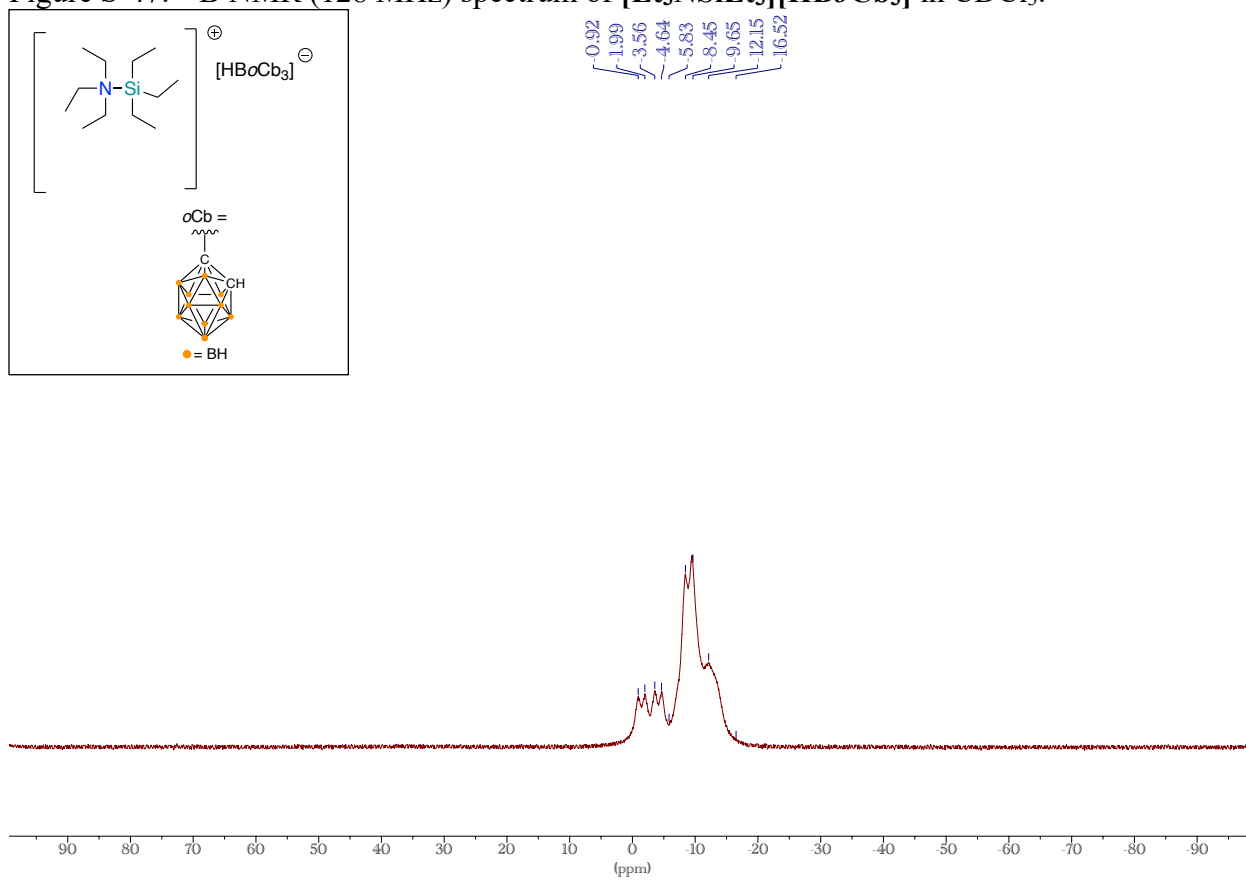


Figure S-48: FT-IR spectrum of $[\text{Et}_3\text{NSiEt}_3][\text{HB}o\text{Cb}_3]$.

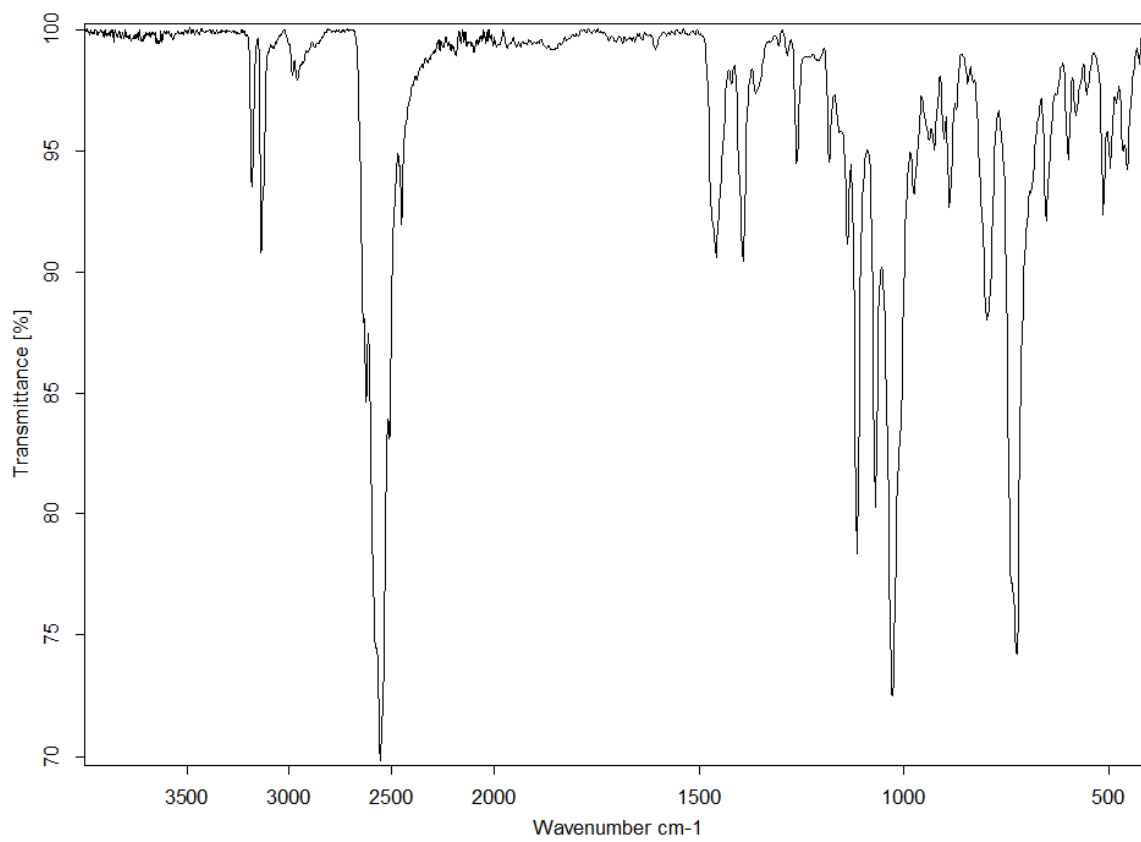


Figure S-49: $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz) spectrum obtained from the combination of $[\text{HB}o\text{Cb}_3]$ $[\text{Ph}_3\text{PSiEt}_3]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CDCl_3 . (* Corresponds to free $\text{B}(\text{C}_6\text{F}_5)_3$).

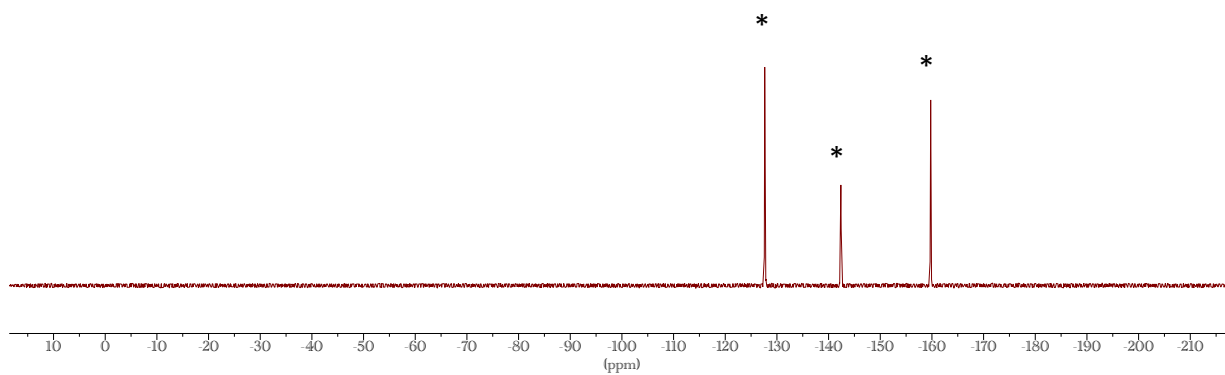


Figure S-50: ^{11}B NMR (128 MHz) spectrum obtained from the combination of $[\text{HB}o\text{Cb}_3]$ $[\text{Ph}_3\text{PSiEt}_3]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CDCl_3 .

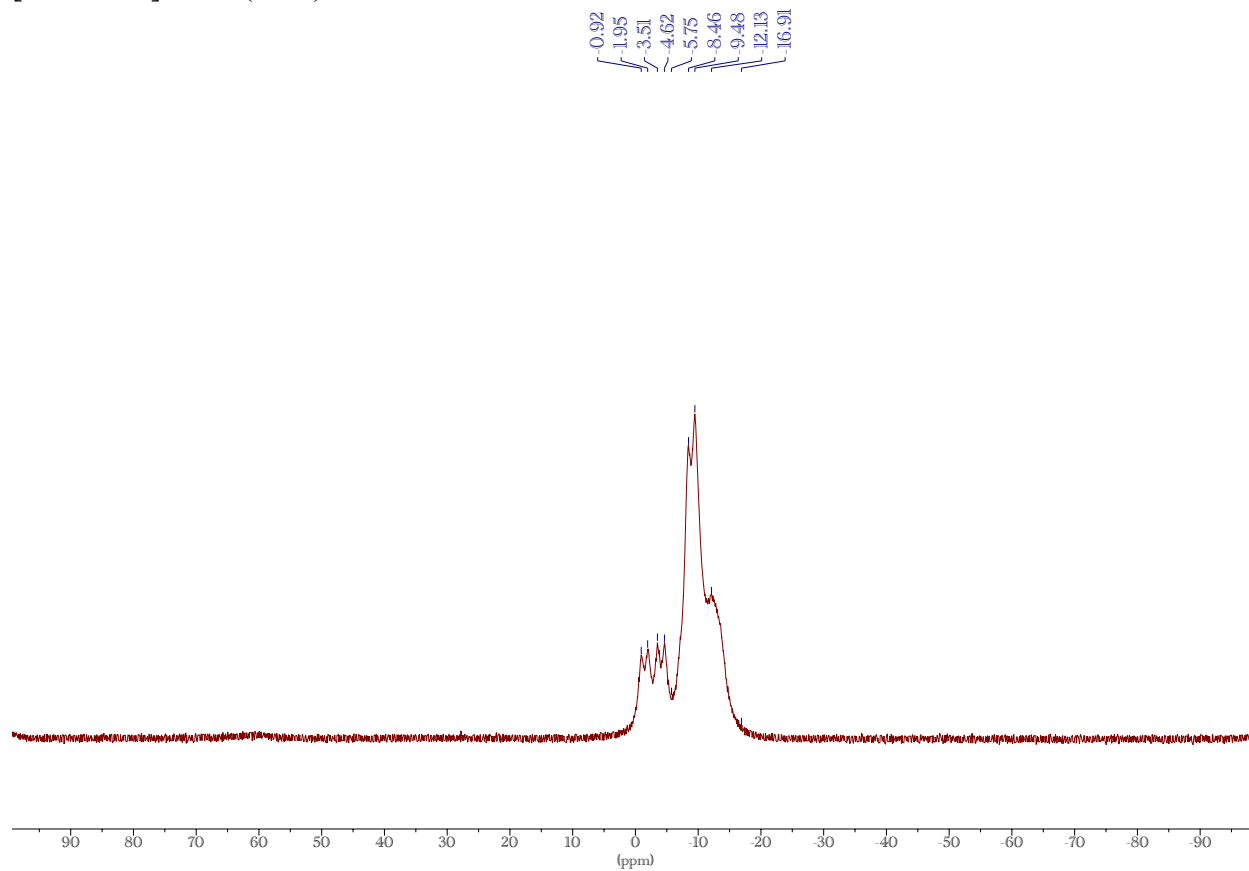


Figure S-51: Stacked ^{11}B NMR (128 MHz) spectrum obtained from the combination of $[\text{NEt}_4][\text{HB}(\text{C}_6\text{F}_5)_3]$ and $\text{B}o\text{Cb}_3$ in CDCl_3 at $23\text{ }^\circ\text{C}$. (● corresponds to the central boron of $\text{B}o\text{Cb}_3$, ● to the BH cluster of $\text{B}o\text{Cb}_3$, and ● corresponds to the central BH in $[\text{HB}(\text{C}_6\text{F}_5)_3]$).

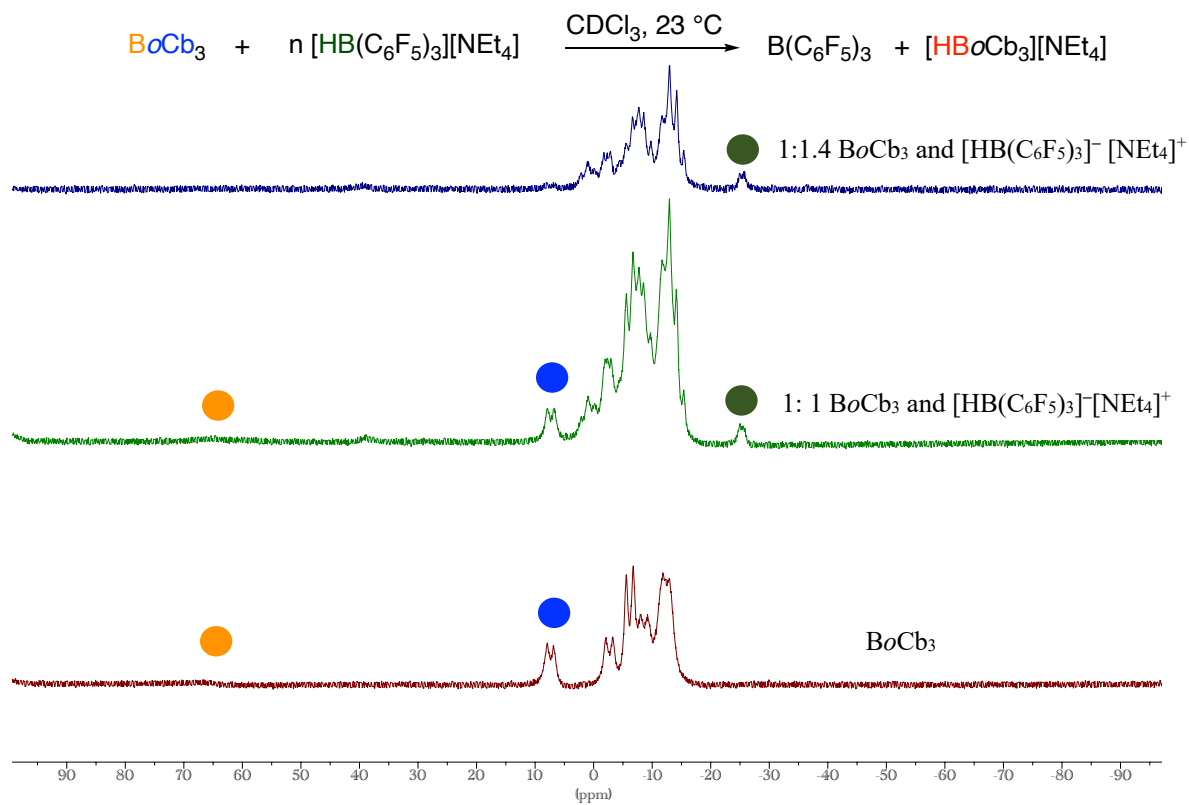


Table S-1: X-ray crystallographic details.

Compound	EtOAc·B _o Cb ₃	2,6- (CH ₃) ₂ C ₆ H ₃ NC·B _o Cb ₃	[Me ₃ PSiEt ₃][HB _o Cb ₃]	[Ph ₃ PSiEt ₃][HB _o Cb ₃]
CCDC	2259756	2259757	2259758	2259759
Empirical Formula	C ₁₀ H ₄₁ O ₂ B ₃₁	C ₁₅ H ₄₂ NB ₃₁	C ₁₅ H ₅₈ B ₃₁ PSi	C ₃₀ H ₆₄ B ₃₁ PSi
FW (g/mol)	528.54	571.60	632.78	818.98
Crystal System	triclinic	triclinic	trigonal	trigonal
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -3C ₁	<i>R</i> -3
a (Å)	10.5389(9)	11.0762(5)	13.0069(3)	15.5559(7)
b (Å)	12.0167(10)	12.7163(5)	13.0069(3)	15.5559(7)
c (Å)	13.0713(9)	12.9783(5)	25.8322(8)	36.209(3)
α (deg)	67.038(3)	87.269(2)	90	90
β (deg)	81.962(3)	66.922(2)	90	90
γ (deg)	87.400(3)	78.596(2)	120	120
V (Å ³)	1509.2(2)	1647.58(12)	3784.8(2)	7588.2(9)
Z	2	2	4	6
D _c (g cm ⁻³)	1.163	1.152	1.111	1.075
Radiation λ (Å)	0.71073	0.71073	0.71073	0.71073
Temp	150 K	150 K	150 K	150 K
R1 [I > 2(σ)I] ^a	0.0417	0.0407	0.0550	0.0677
wR2 (F ²) ^a	0.1067	0.1080	0.1373	0.1691
GOF (S) ^a	1.097	1.049	1.154	1.116

^a $R1(F[I > 2(I)]) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2(F^2 [\text{all data}]) = \{[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$) where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

