Supporting Information for:

1,4-Bromoboration of Nitroalkenes

*Kanika Vashisth and Caleb D. Martin**

Baylor University, Department of Chemistry and Biochemistry, One Bear Place #97348, Waco, TX 76798.

Author to address correspondence: Caleb D. Martin (caleb_d_martin@baylor.edu)

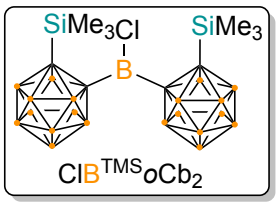
Table of Contents

1. General Considerations:

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Unilab glove box or using standard Schlenk techniques. $CDCl_3$ and C_6D_6 for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc., dried by stirring for 5 days over CaH_2, distilled, and stored over 3 Å molecular sieves. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 3 or 4 Å molecular sieves. Bis(1-trimethylsilyl-*ortho*-carboranyl)boron bromide ($BrB^{TMS}oCb_2$), bis(1-methyl-*ortho*-carboranyl)boron bromide ($BrB^{Me}oCb_2$), bis(1-methyl-*ortho*-carboranyl)boron chloride ($ClB^{Me}oCb_2$), bis(perfluorophenyl)boron bromide ($BrB(C_6F_5)_2$), and diphenylboron bromide (Ph_2BBr), trimethylsilyl-*ortho*-carborane (^{TMS}oCb) were prepared by the literature procedures.[1-5] The following substrates: *n*-BuLi (2.5 M in hexanes), 1M BCl_3 in hexanes, 3,4-methylenedioxy-*β*-nitrostyrene, 1-[(*E*)-2-nitroethynyl]naphthalene, (*E*)-1-fluoro-4-(2-nitrovinyl)benzene, (*E*)-1-methoxy-4-(2-nitrovinyl)benzene, (*E*)-2-(2-nitroethynyl)thiophene, trans-*β*-methyl-*β*-nitrostyrene and (2-nitrovinyl)benzene were purchased from commercial sources and used without further purification. Multinuclear NMR data (^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, ^{11}B, $^{11}B\{^1H\}$, $^{29}Si\{^1H\}$) were recorded on a Bruker Avance III HD 400 MHz or 600 MHz instrument. High Resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI and -ESI. Melting points were measured with a Laboratory device MEL-TEMP II capillary melting point apparatus and are uncorrected. Single crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation (λ = 0.71073 Å) or a Rigaku XtaLAB Synergy-S system using Cu radiation (λ = 1.54184 Å). Crystals were selected under paratone oil, mounted on MiTeGen

micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures produced using OLEX2.[6,7]

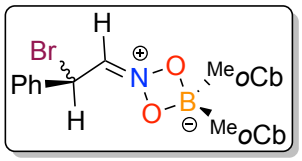
2. Experimental Section



ClB^{TMS}*o*Cb$_2$: To a stirring toluene solution of ^{TMS}*o*Cb (4.0 mmol, 0.80 g, 10 mL) at –78 ºC, *n*-BuLi (2.5 M in hexanes, 1.6 mL) was added. After 40 minutes the cold bath was removed and the mixture stirred for 4 hrs at 23 ºC. The mixture was cooled to –78 ºC and BCl_3 (1M in hexanes, 2.0 mmol, 2.0 mL) was added dropwise. After 40 minutes, the cold bath was removed and the mixture stirred for 3 days at 23 ºC (reaction completion verified by examining an aliquot by ^{11}B NMR spectroscopy). Toluene (10 mL) was added, the mixture was centrifuged, and the supernatant collected. The volatiles were removed under dynamic vacuum to give a white residue that was washed with *n*-pentane (5 mL) and dried. The powder was washed with 1:2 ether/*n*-pentane (2 × 2 mL) and dried in vacuo to obtain a white solid. Yield: 68%, 0.65 g; dp: 209 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 3.61-1.85 (m, 20H), –0.03 (s, 18H) ppm; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 81.5, 1.5 ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 59.8 (s), 5.7 (s), 1.9 (s), –1.3 to –15.1 (m) ppm; ^{11}B NMR: δ = 59.8 (s), 5.6 (d, J = 145 Hz), 1.8 (d, J = 143 Hz), –1.3 to –15.1 (m) ppm; ^{29}Si{^{1}H} NMR (119 MHz, C_6D_6): 11.5 (s) ppm; Most intense peak: HRMS (–ESI): calculated for $[C_{10}H_{38}B_{21}Si_2Cl]^-$[M+H]$^-$ 477.4373; found 477.4376. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{10}H_{38}B_{21}Si_2Cl]^-$[M]$^-$ 481.4238; found 481.4162.

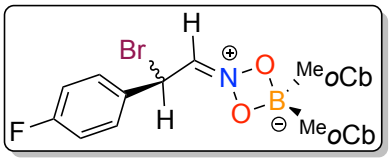
General procedure to synthesize the haloboration products 1-7:

A benzene solution (0.5 mL) of nitrostyrene [(2-nitrovinyl)benzene, (*E*)-1-fluoro-4-(2-nitrovinyl)benzene, (*E*)-1-methoxy-4-(2-nitrovinyl)benzene, 3,4-methylenedioxy-*β*-nitrostyrene, 1-[(*E*)-2-nitroethynyl]naphthalene, (*E*)-2-(2-nitroethynyl)thiophene, trans-*β*-methyl-*β*-nitrostyrene] was added to a benzene solution (0.5 mL) of haloborane ($BrB^{Me}oCb_2$) at 23 ºC and the reaction was stirred. This resulted in a color change that differed based on the substrate (Figure S-1). The reaction was monitored via $^{11}B\{^1H\}$ NMR spectroscopy, which indicated the reaction was complete within 30 minutes. The volatiles were removed in vacuo, and the residue washed with *n*-pentane (2 × 1 mL) to afford the products as powders. Amount and characterization details of each compound are listed below. Reaction attempts with other haloboranes were conducted in the same manner that gave complex mixtures (BCl_3, BBr_3, $PhBCl_2$, $PhBBr_2$, Ph_2BBr, $BrB(C_6F_5)_2$) or did not react ($ClB^{Me}oCb_2$, $ClB^{TMS}oCb_2$, $BrB^{TMS}oCb_2$). Thus, only the products with $BrB^{Me}oCb_2$ are described below.

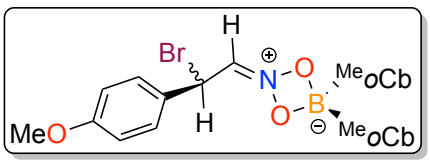


1: $BrB^{Me}oCb_2$: 0.0500 mmol, 20.2 mg; **(2-nitrovinyl)benzene**: 0.050 mmol, 7.5 mg. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **1** by vapor diffusion into hexanes. Physical state: white solid, Yield: 83%, 22.8 mg; dp: 126 °C; ^1H NMR (400 MHz, C_6D_6): δ = 6.90-6.85 (m, 3H), 6.74 (d, *J* = 4 Hz, 2H), 5.57 (d, *J* = 8 Hz, 1H), 5.12 (d, *J* = 8 Hz, 1H), 3.32-2.34 (m, 20H), 1.73 (s, 3H), 1.63 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz,

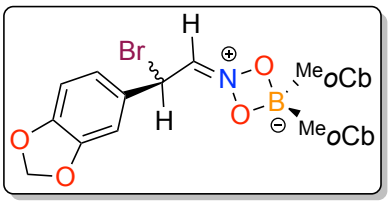
C_6D_6): δ = 133.0, 130.5, 129.7, 123.2, 78.0, 77.4, 37.4, 25.1, 24.9 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = 8.8 (s), 4.3 (s), 1.4 (s), –3.2 to –12.7 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 8.9 (s), 4.3 (d, J = 164 Hz), 1.5 (d, J = 134 Hz), –3.2 to –12.7 (m) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{14}H_{33}B_{21}NO_2Br]^-$ $[M]^-$ 553.3789; found 553.3718. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{14}H_{33}B_{21}NO_2Br]^-$ $[M]^-$ 557.3654; found 557.3674.



2: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **(*E*)-1-fluoro-4-(2-nitrovinyl)benzene**: 0.050 mmol, 8.3 mg. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **2** by vapor diffusion into hexanes. Physical state: white solid, Yield: 74%, 21.1 mg; dp: 120 °C; ^1H NMR (400 MHz, C_6D_6): δ = 6.51-6.49 (m, 2H), 6.49 (d, J = 4 Hz, 2H), 5.48 (d, J = 8 Hz, 1H), 5.02 (d, J = 8 Hz, 1H), 3.38-2.25 (m, 20H), 1.74 (s, 3H), 1.64 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6): δ = 163.7 (d, J = 252 Hz), 129.8 (d, J = 9 Hz), 128.8 (d, J = 3 Hz), 122.8, 116.8 (d, J = 23 Hz), 78.0, 77.4, 36.5, 25.1, 24.9 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6): δ = 9.1 (s), 1.6 (s), –2.9 to –12.7 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 9.2 (s), 1.6 (d, J = 138 Hz), –2.9 to –12.7 (m) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ = –109.0 (s) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{14}H_{32}B_{21}NO_2BrF]^-$ $[M\text{-}H]^-$ 571.3611; found 571.3694. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{14}H_{32}B_{21}NO_2BrF]^-$ $[M]^-$ 575.3560; found 575.3543.

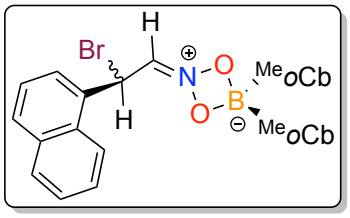


3: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **(*E*)-1-methoxy-4-(2-nitrovinyl)benzene**: 0.050 mmol, 8.9 mg. Single crystals for X-ray diffraction studies were grown from a dichloromethane solution of **3** by vapor diffusion into toluene. Physical state: yellow solid, Yield: 79%, 23.1 mg; dp: 100 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.70 (d, *J* = 8 Hz, 2H), 6.52 (d, *J* = 9 Hz, 2H), 5.70 (d, *J* = 9 Hz, 1H), 5.22 (d, *J* = 8 Hz, 1H), 3.35-2.33 (m, 23H), 1.76 (s, 3H), 1.65 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 161.6, 129.3, 124.6, 123.3, 115.2, 78.0, 77.4, 55.0, 37.6, 25.1, 24.9 ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 9.1 (s), 5.5 to –0.3 (m), –2.4 to –13.4 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 9.0 (s), 5.5 to –0.3 (m), –2.4 to –13.4 (m) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{15}H_{35}B_{21}NO_3Br]^-$ $[M]^-$ 583.3894; found 583.3847. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{15}H_{35}B_{21}NO_3Br]^-$ $[M]^-$ 587.3760; found 587.3796.

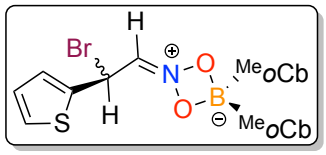


4: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **3,4-methylenedioxy-*β*-nitrostyrene**: 0.050 mmol, 9.6 mg. Physical state: yellow solid, Yield: 98%, 29.2 mg; dp: 103 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.33 (d, *J* = 4 Hz, 1H), 6.26 (d, *J* = 8 Hz, 1H), 6.08 (dd, *J* = 8 Hz, 4 Hz, 1H), 5.67 (d, *J* = 8 Hz, 1H), 5.18 (d, *J* = 1 Hz, 1H), 5.14 (d, *J* = 1 Hz, 1H), 5.11 (d, *J* = 8 Hz, 1H), 3.30-2.22 (m, 20H), 1.76 (s, 3H), 1.65 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 149.9, 149.2, 126.4, 123.0, 122.0, 108.9, 107.9, 102.0, 78.0, 77.4, 37.7, 25.1, 24.9 ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 9.0 (s), 4.0 to –0.5 (m), –3.0 to –14.1 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 9.0 (s), 4.1 to –0.5 (m), –3.0 to –14.1 (m) ppm. Most intense peak: HRMS (–ESI): calculated for

$[C_{15}H_{33}B_{21}NO_4Br]^-$ $[M]^-$ 597.3687; found 597.3630. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{15}H_{33}B_{21}NO_4Br]^-$ $[M]^-$ 601.3553; found 601.3671.

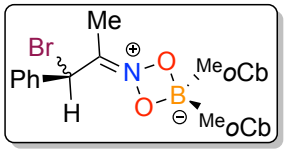


5: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **1-[(*E*)-2-nitroethynyl]naphthalene**: 0.050 mmol, 9.9 mg. Physical state: white solid, Yield: 95%, 28.7 mg; dp: 101 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.52-7.45 (m, 4H), 7.28 (d, *J* = 8 Hz, 1H), 7.22-7.18 (m, 1H), 7.03 (t, *J* = 8 Hz, 1H), 5.92 (d, *J* = 8 Hz, 1H), 5.46 (d, *J* = 8 Hz, 1H), 3.25-2.11 (m, 20H), 1.76 (s, 3H), 1.60 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 134.1, 131.5, 129.9, 129.7, 128.6, 127.3, 125.4, 123.5, 122.2, 77.9, 77.5, 36.4, 25.1, 24.8 ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ = 9.0 (s), 4.3 (s), 1.5 (s), –3.1 to –14.5 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 8.9 (s), 4.3 (d, *J* = 129 Hz), 1.6 (d, *J* = 123 Hz), –3.1 to –14.5 (m) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{20}H_{35}B_{21}NO_2Br]^-$ $[M+H]^-$ 628.4023; found 628.4070. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{20}H_{35}B_{21}NO_2Br]^-$ $[M]^-$ 632.3889; found 632.3958.



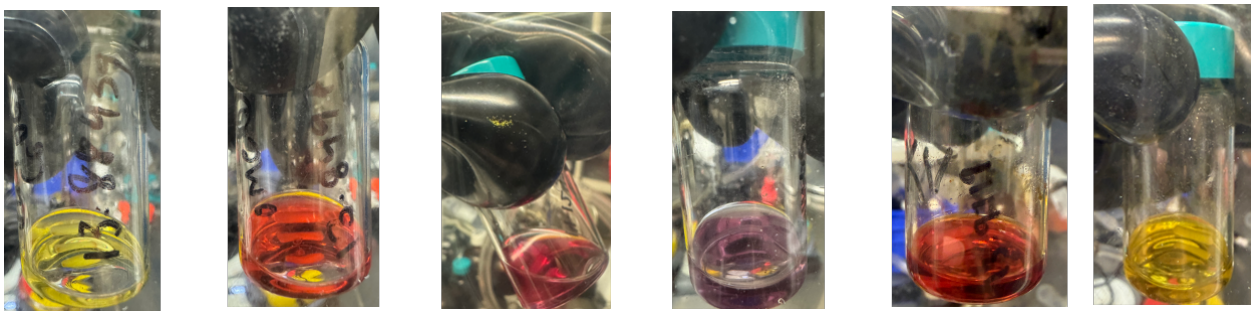
6: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **(*E*)-2-(2-nitroethynyl)thiophene**: 0.050 mmol, 7.7 mg. Physical state: orange solid, Yield: 94%, 27.9 mg; dp: 86 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.64 (d, *J* = 4 Hz, 1H), 6.40-6.35 (m, 2H), 5.55 (d, *J* = 8 Hz, 1H), 5.40 (d, *J* = 8 Hz, 1H), 3.27-2.34 (m,

20H), 1.70 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ = 135.6, 129.1, 128.8, 128.6, 122.5, 78.0, 77.4, 31.9, 25.1, 24.9 ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6): δ = 9.1 (s), 1.6 (s), –3.1 to –13.7 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 9.1 (s), 1.6 (d, *J* = 143 Hz), –3.1 to –13.7 (m) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{12}H_{31}B_{21}NO_2SBr]^-$ $[M\text{-}H]^-$ 558.3275; found 558.3270. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{12}H_{31}B_{21}NO_2SBr]^-$ $[M]^-$ 562.3878; found 562.3795.



7: BrB^{Me}*o*Cb$_2$: 0.0500 mmol, 20.2 mg; **trans-*β*-methyl-*β*-nitrostyrene**: 0.050 mmol, 8.2 mg. Physical state: yellow solid, Yield: 78%, 28.3 mg; dp: 102 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 6.98-6.90 (m, 5H), 5.56 (s, 1H), 3.39-2.29 (m, 20H), 1.71 (s, 3H), 1.64 (s, 3H), 1.17 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_6): δ = 134.3, 132.0, 130.3, 129.6, 77.9, 77.5, 41.4, 25.2, 25.0, 10.3 ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6): δ = 8.1 (s), 1.3 (s), –2.8 to –14.0 (m) ppm; ^{11}B NMR (128 MHz, C_6D_6): δ = 8.2 (s), 1.3 (d, *J* = 124 Hz), –2.8 to –14.0 (m) ppm. Most intense peak: HRMS (–ESI): calculated for $[C_{15}H_{35}B_{21}NO_2Br]^-$ $[M+H]^-$ 568.4023; found 568.3981. Peak of isotopes of highest abundance: HRMS (–ESI): calculated for $[C_{15}H_{35}B_{21}NO_2Br]^-$ $[M]^-$ 572.3878; found 572.3942.

Figure S-1: Instantaneous color changes observed during the synthesis of **2**-**7**.



2 **3** **4** **5** **6** **7**

Figure S-2: ^{1}H NMR (400 MHz) spectrum of **ClB^{TMS}*o*Cb$_2$** in C_6D_6.

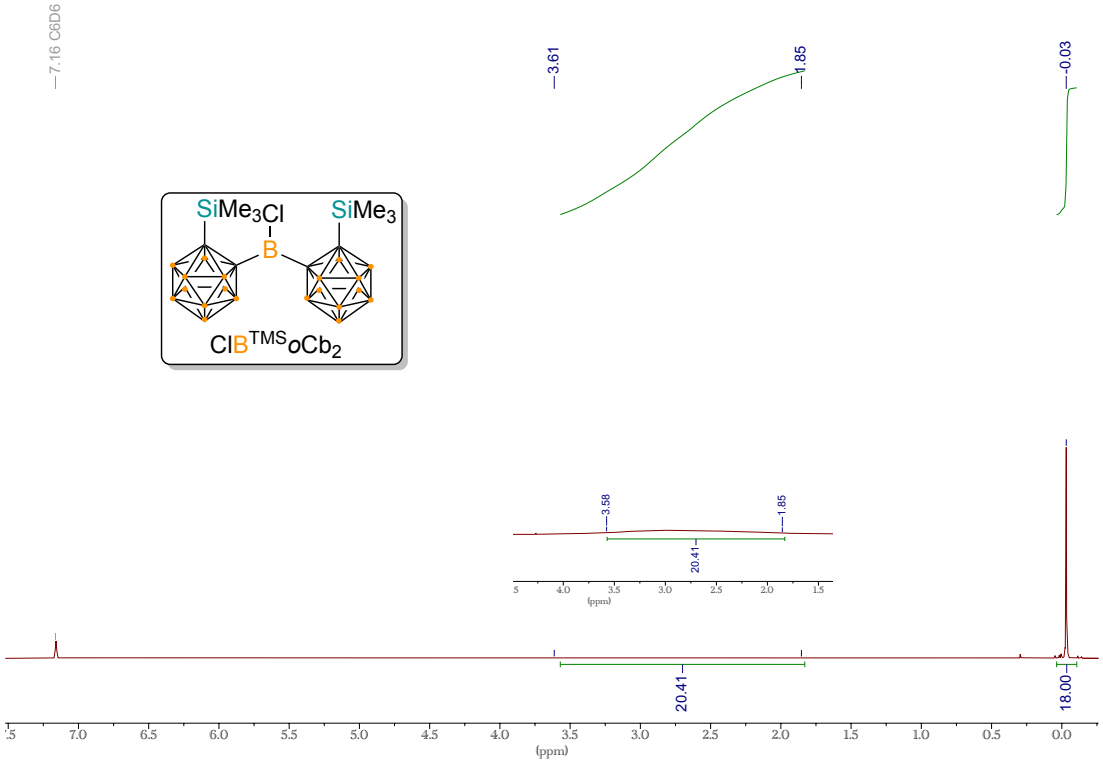


Figure S-3: ^{13}C{^{1}H} NMR (101 MHz) spectrum of **ClB^{TMS}*o*Cb$_2$** in C_6D_6.

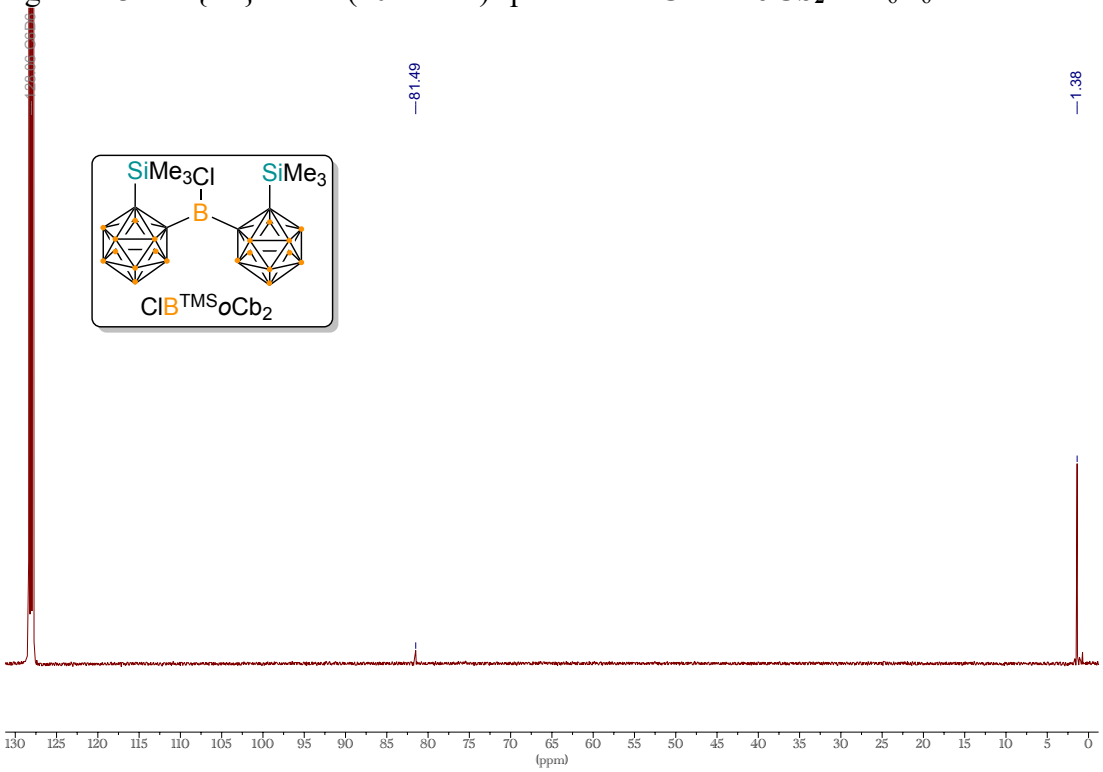


Figure S-4: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **ClB^{TMS}*o*Cb$_2$** in C_6D_6.

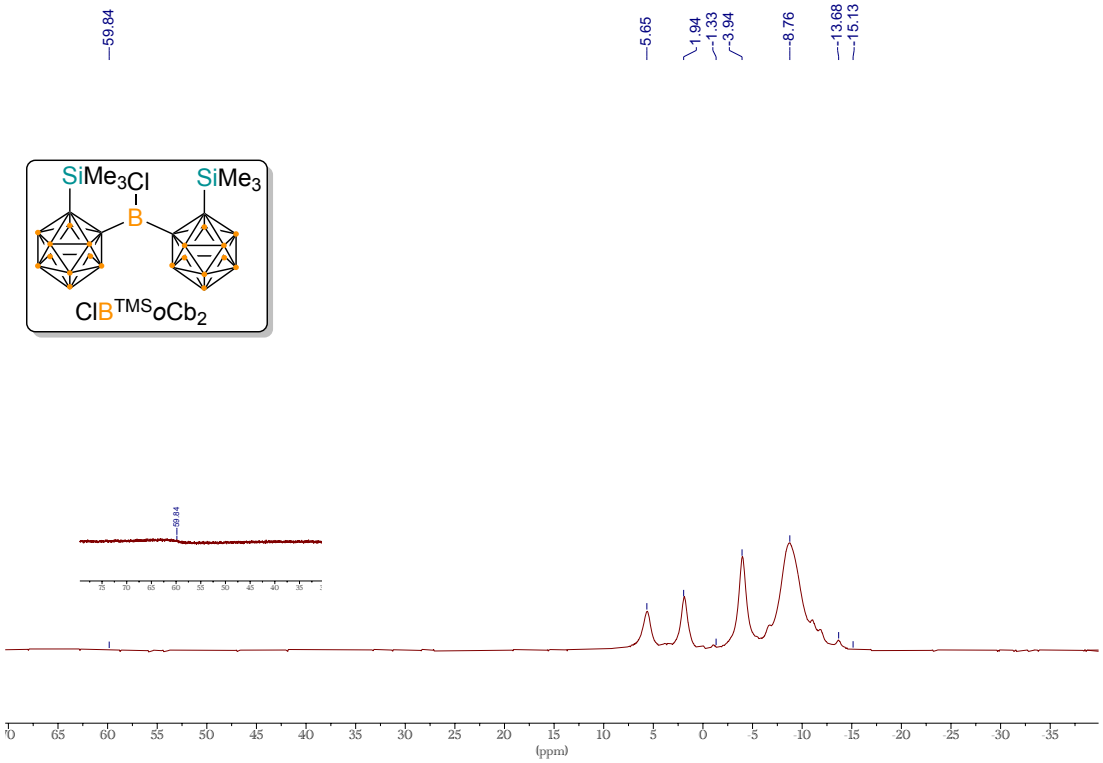


Figure S-5: ^{11}B NMR (128 MHz) spectrum of **ClB^{TMS}*o*Cb$_2$** in C_6D_6.

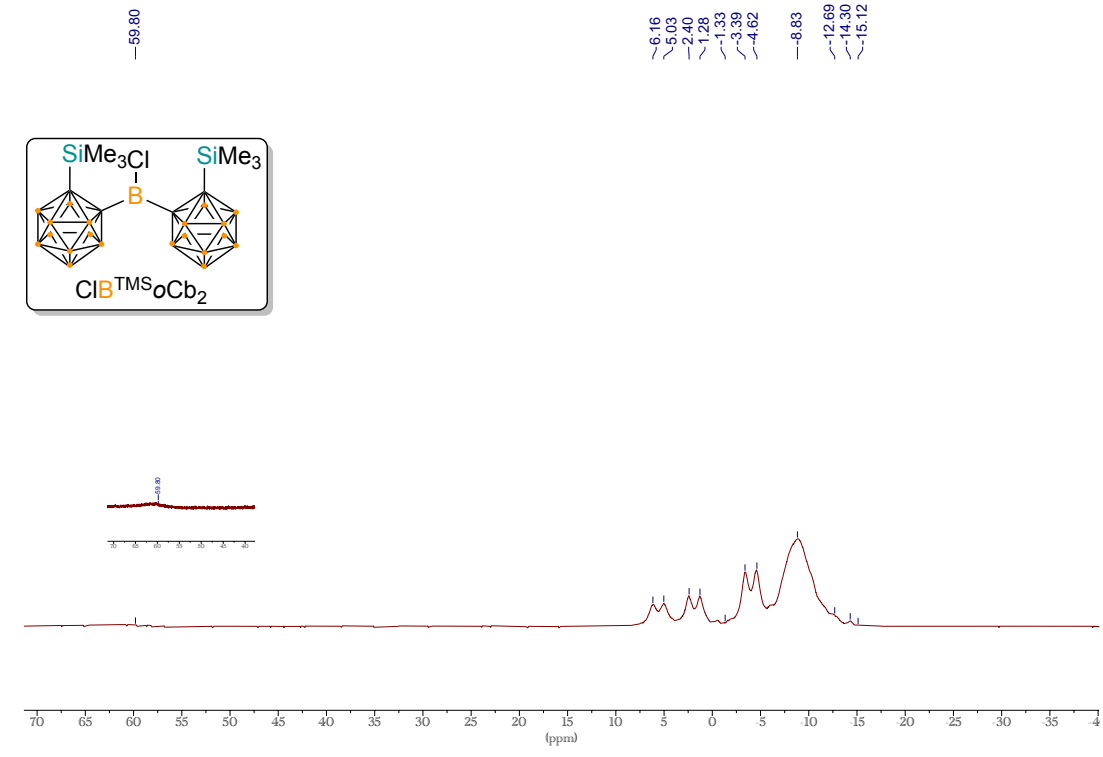


Figure S-6: $^{29}Si\{^{1}H\}$ NMR (79 MHz) spectrum of **ClB^{TMS}*o*Cb$_2$** in C_6D_6.

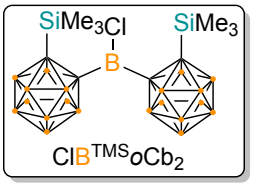


Figure S-7: ^{1}H NMR (400 MHz) spectrum of **1** in C_6D_6 (* *n*-pentane).

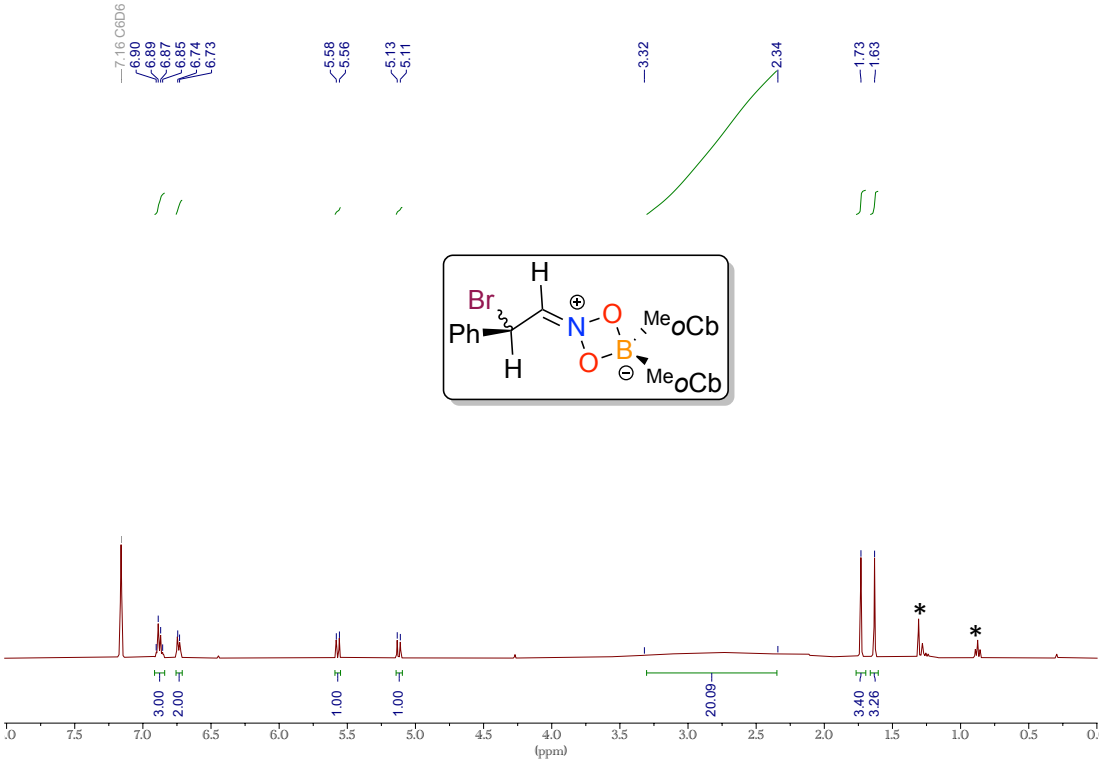


Figure S-8: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1** in C_6D_6 (* *n*-pentane).

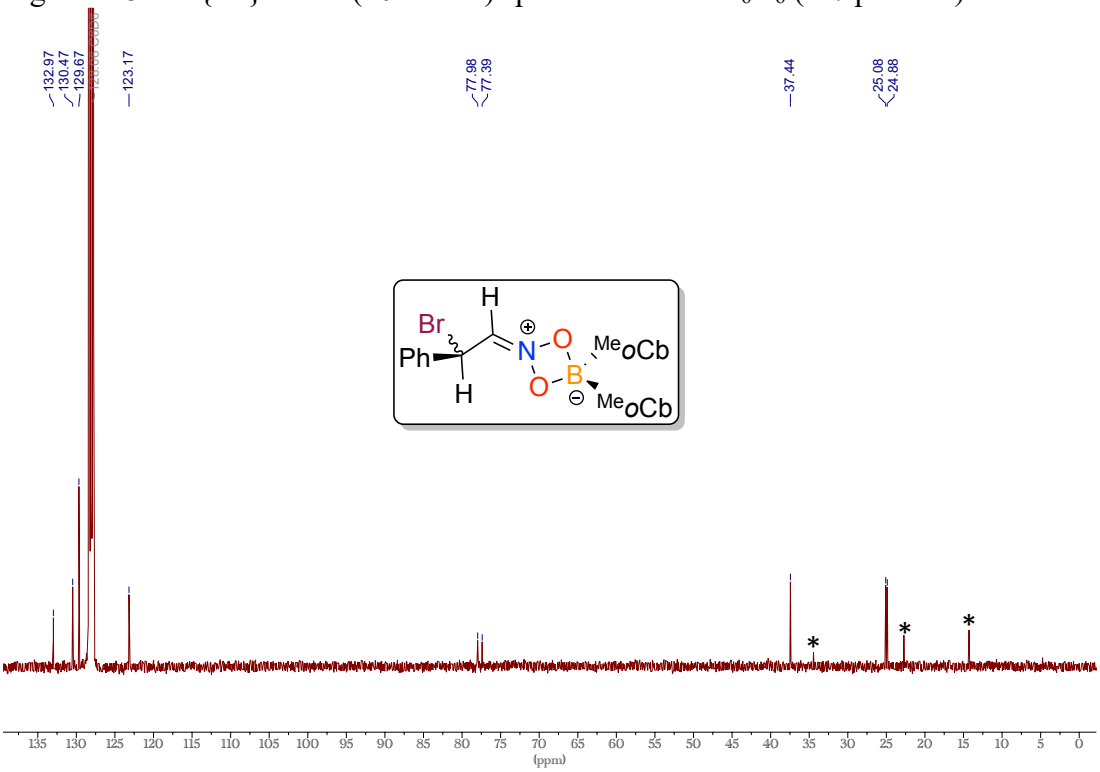


Figure S-9: Expanded aryl region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **1** in C_6D_6.

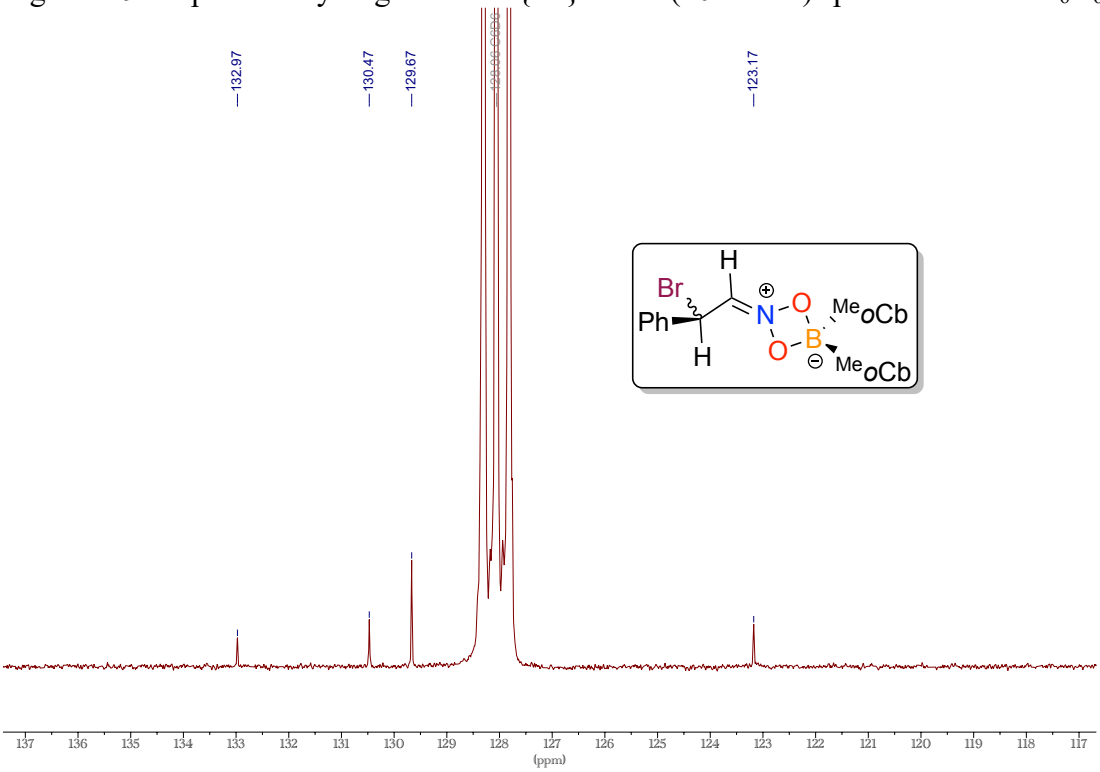


Figure S-10: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **1** in C_6D_6.

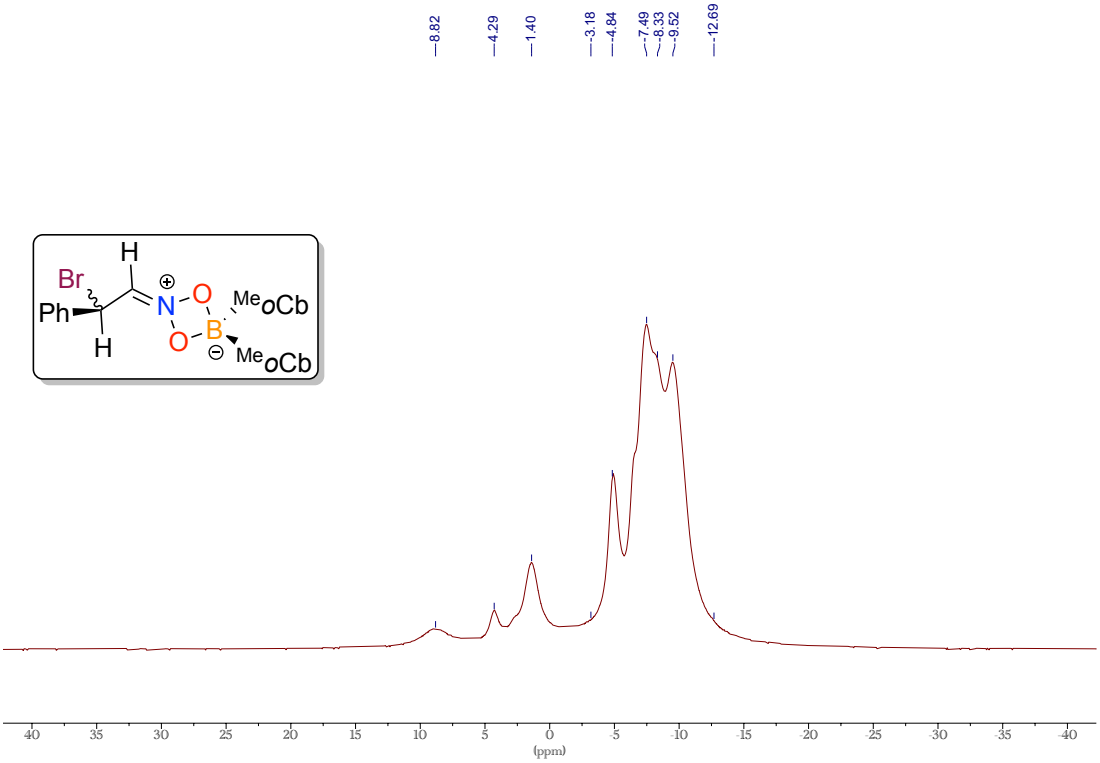


Figure S-11: ^{11}B NMR (128 MHz) spectrum of **1** in C_6D_6.

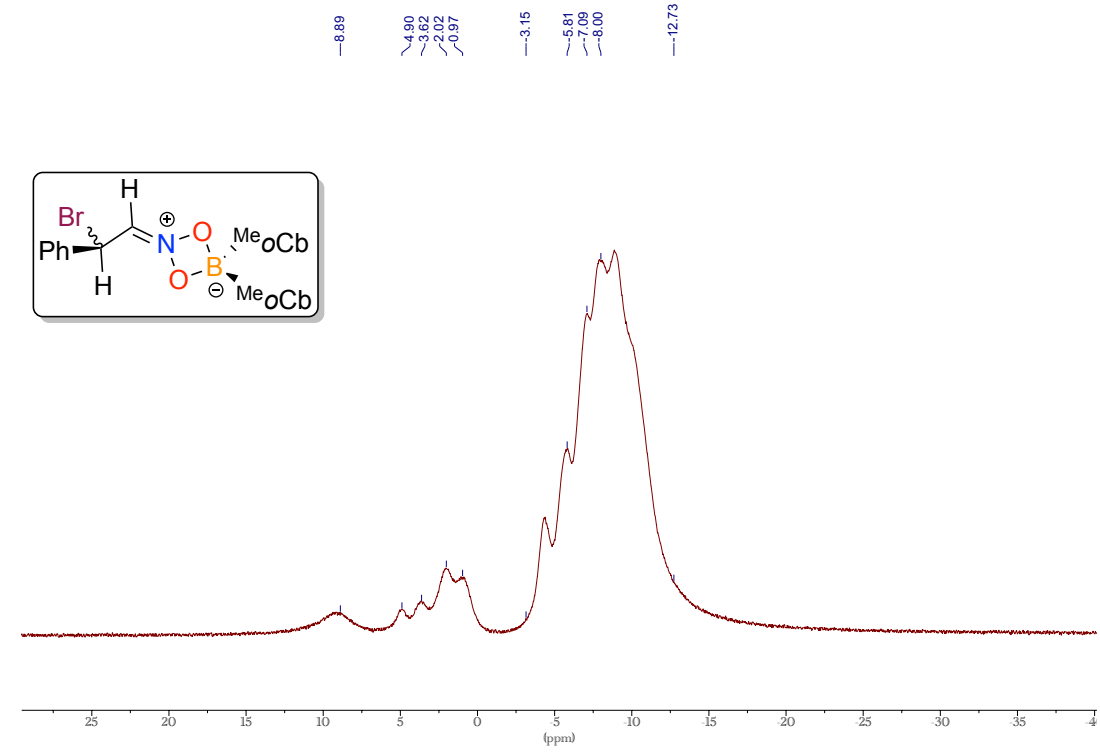


Figure S-12: ^{1}H NMR (400 MHz) spectrum of **2** in C_6D_6 (* *n*-pentane).

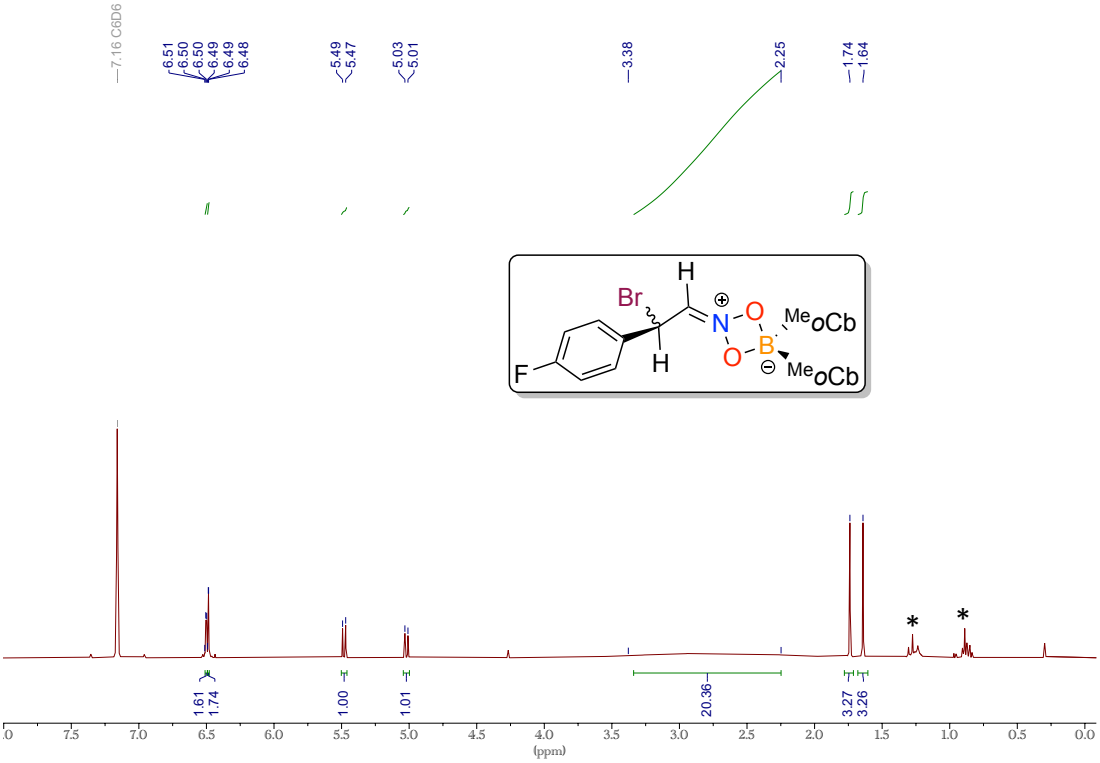


Figure S-13: $^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of **2** in C_6D_6 (* *n*-pentane).

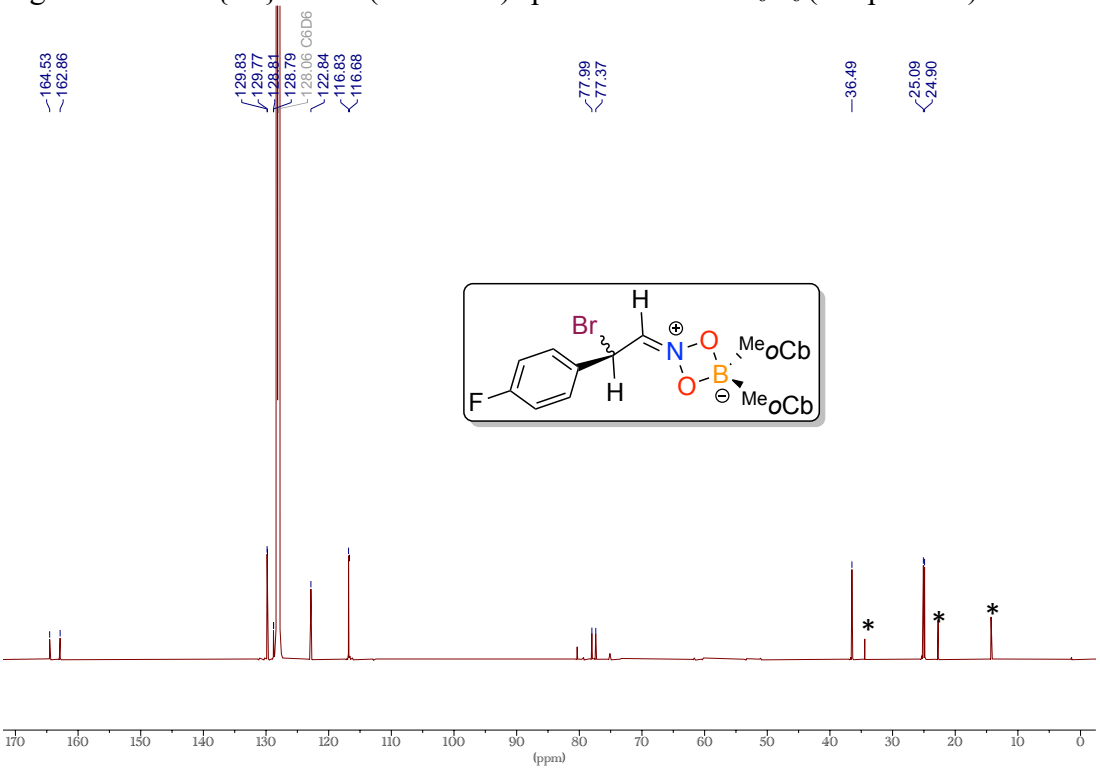


Figure S-14: Expanded ary region of $^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of **2** in C_6D_6.

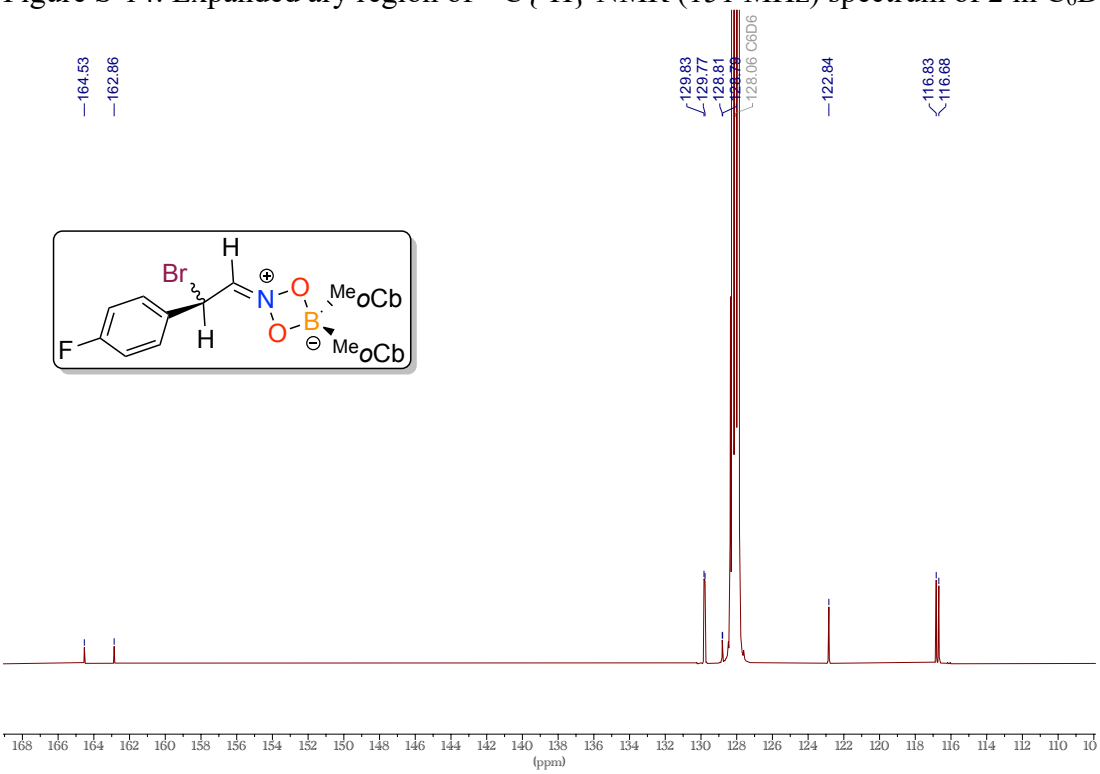


Figure S-15: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **2** in C_6D_6.

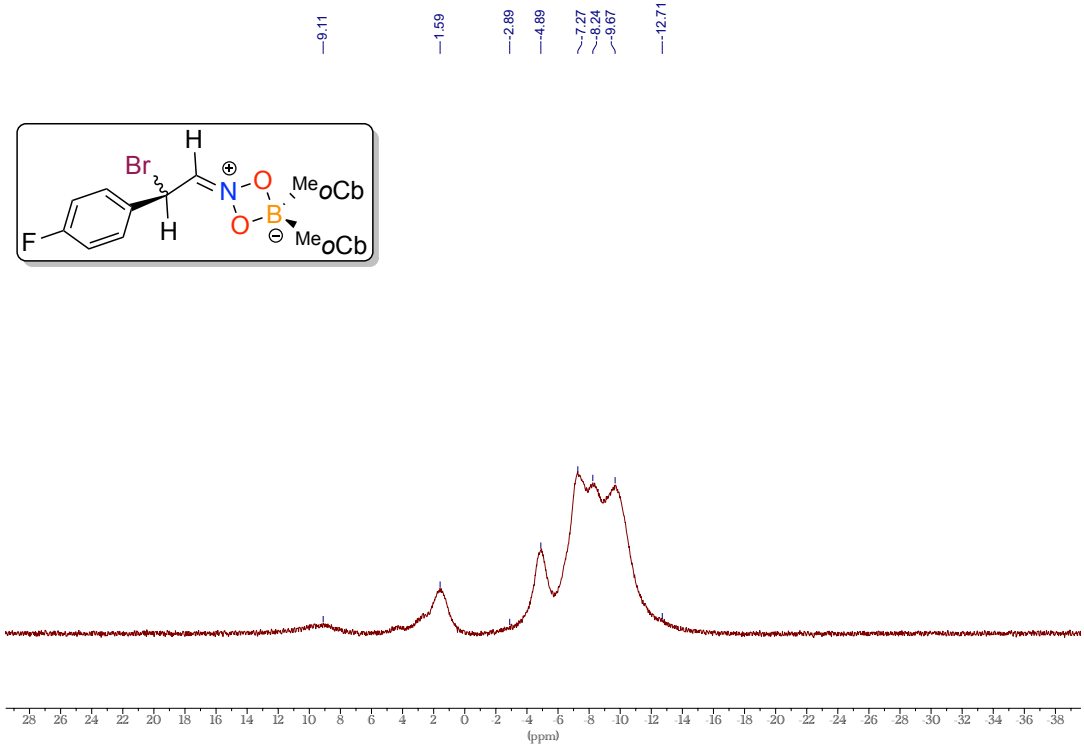


Figure S-16: ^{11}B NMR (128 MHz) spectrum of **2** in C_6D_6.

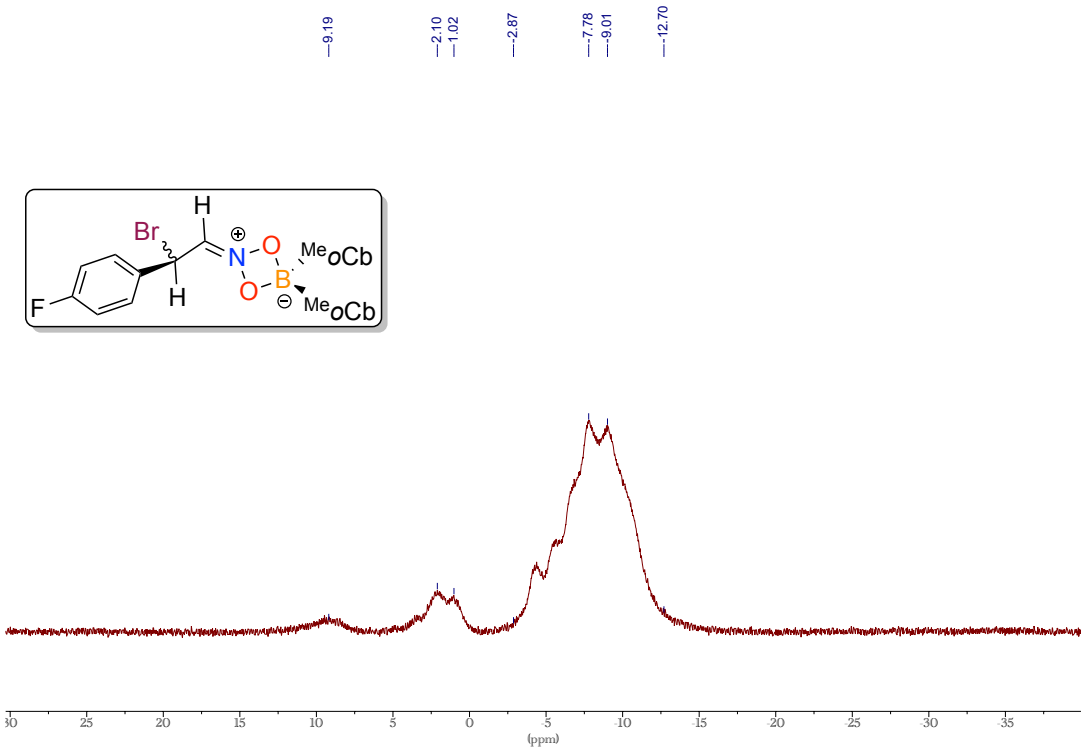


Figure S-17: ^{19}F{^{1}H} NMR (376 MHz) spectrum of **2** in C_6D_6.

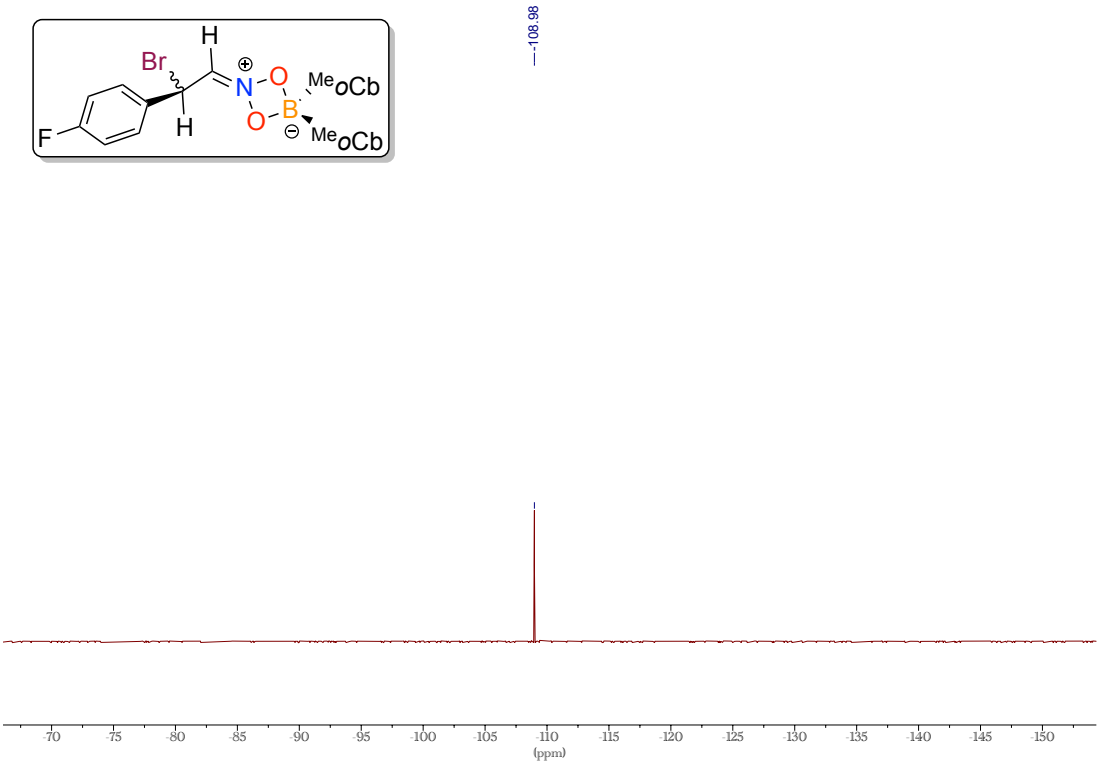


Figure S-18: ^{1}H NMR (400 MHz) spectrum of **3** in C_6D_6 (* *n*-pentane).

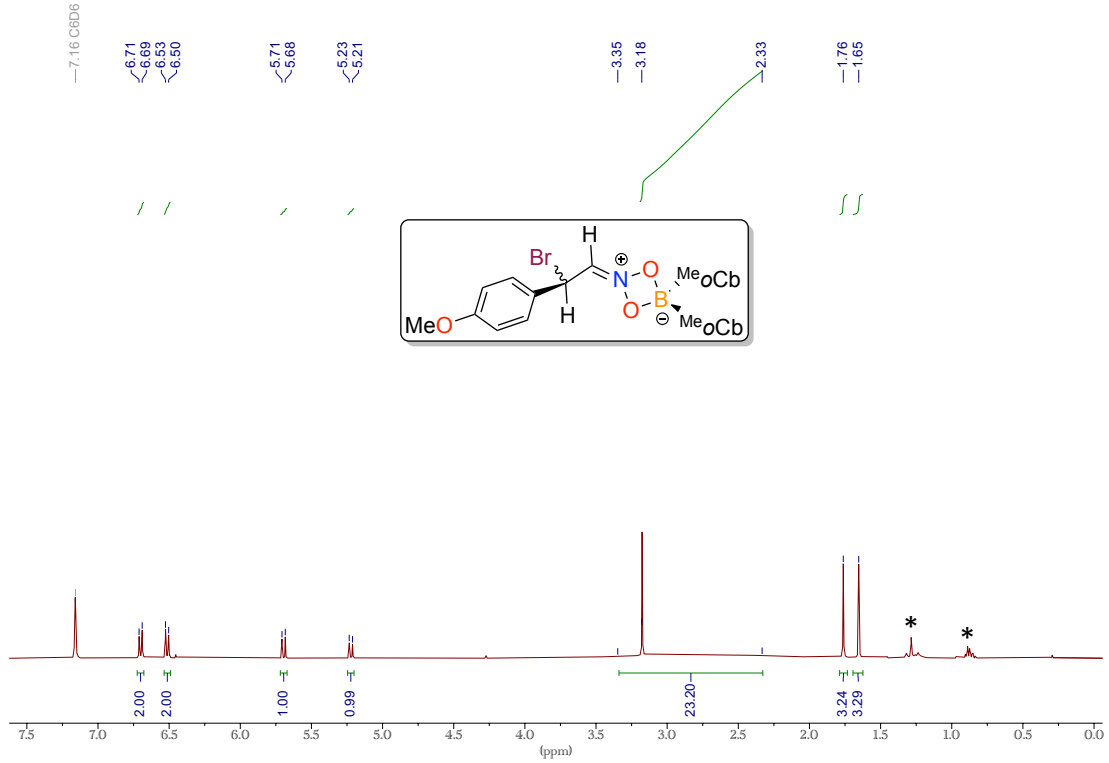


Figure S-19: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3** in C_6D_6 (* *n*-pentane).

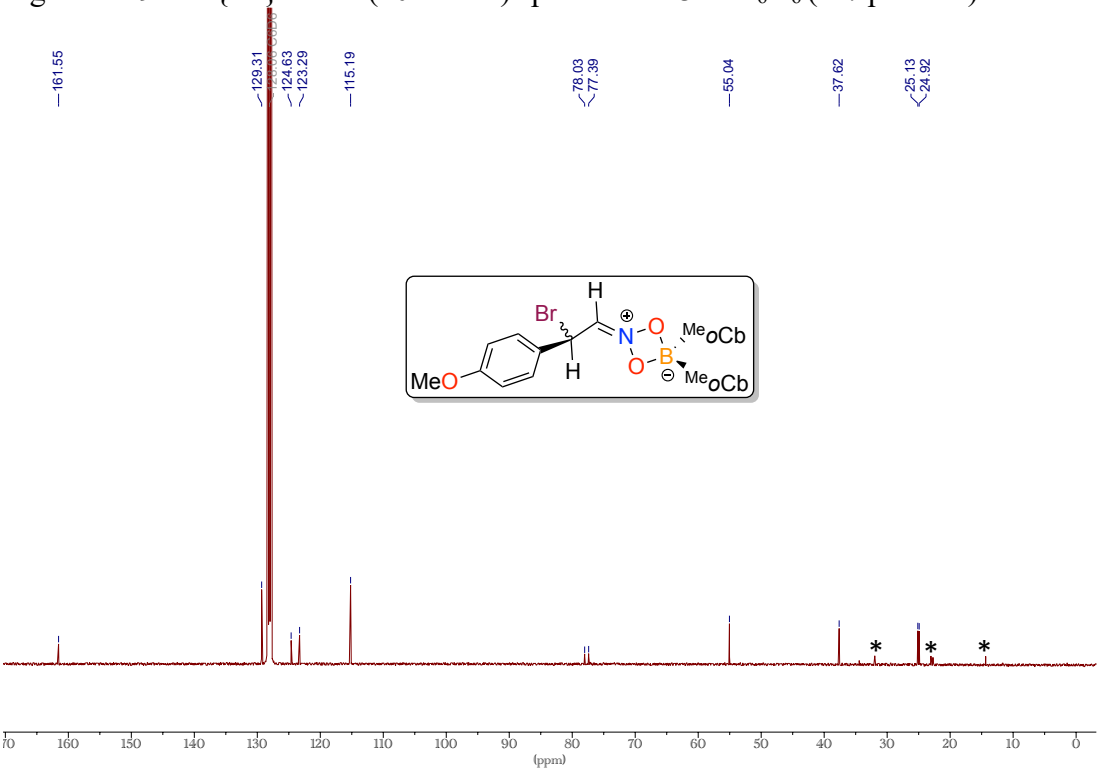


Figure S-20: Expanded aryl region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3** in C_6D_6.

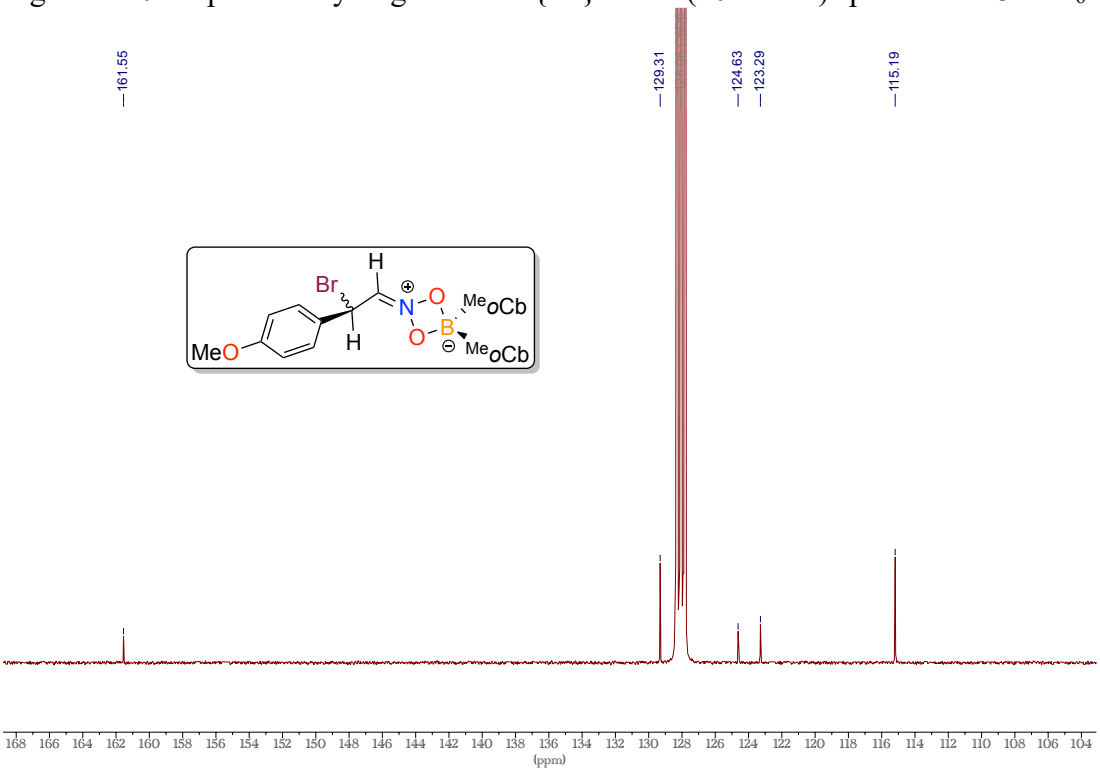


Figure S-21: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **3** in C_6D_6.

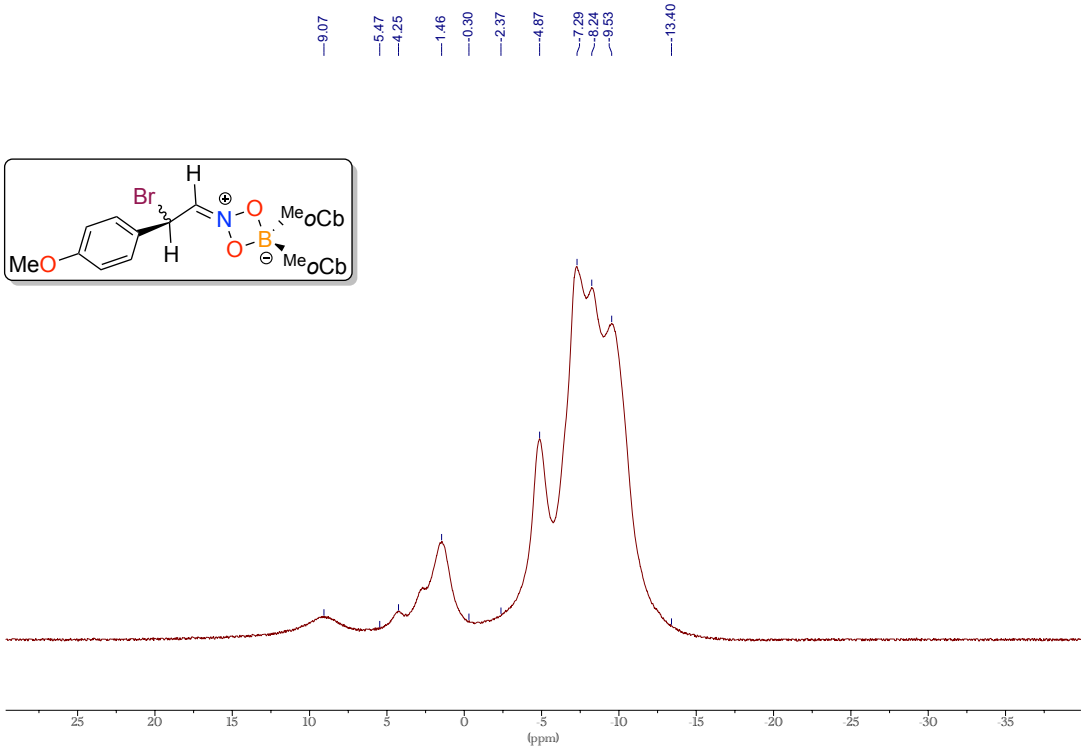


Figure S-22: ^{11}B NMR (128 MHz) spectrum of **3** in C_6D_6.

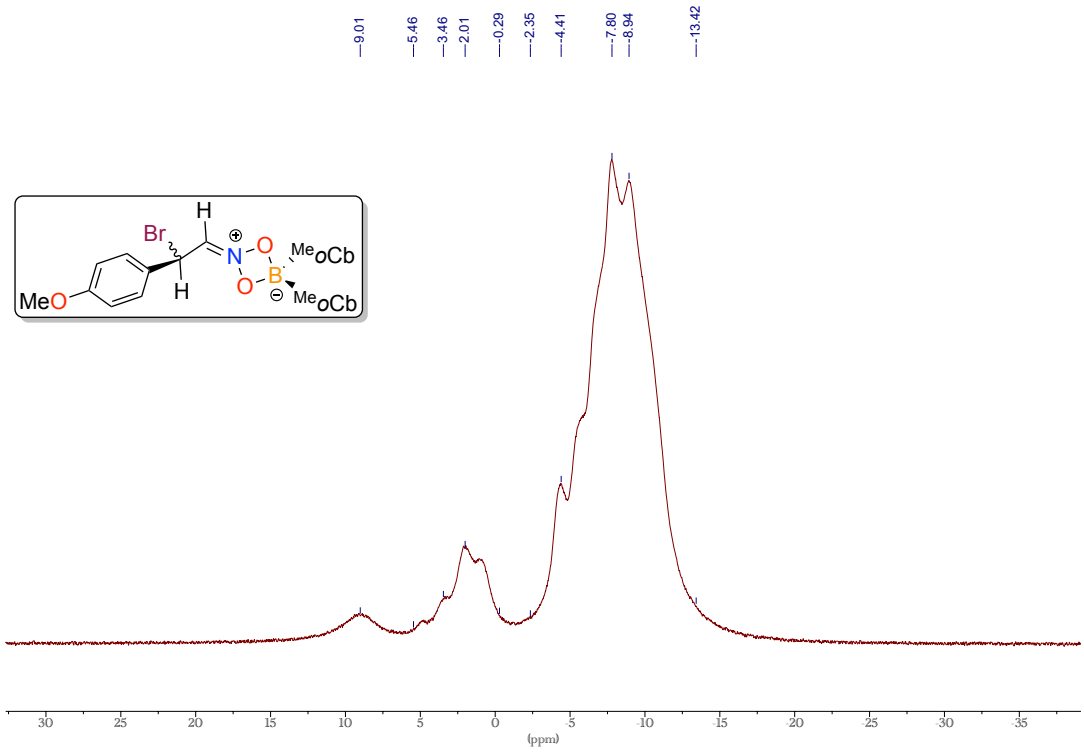


Figure S-23: ^{1}H NMR (400 MHz) spectrum of **4** in C_6D_6 (* *n*-pentane).

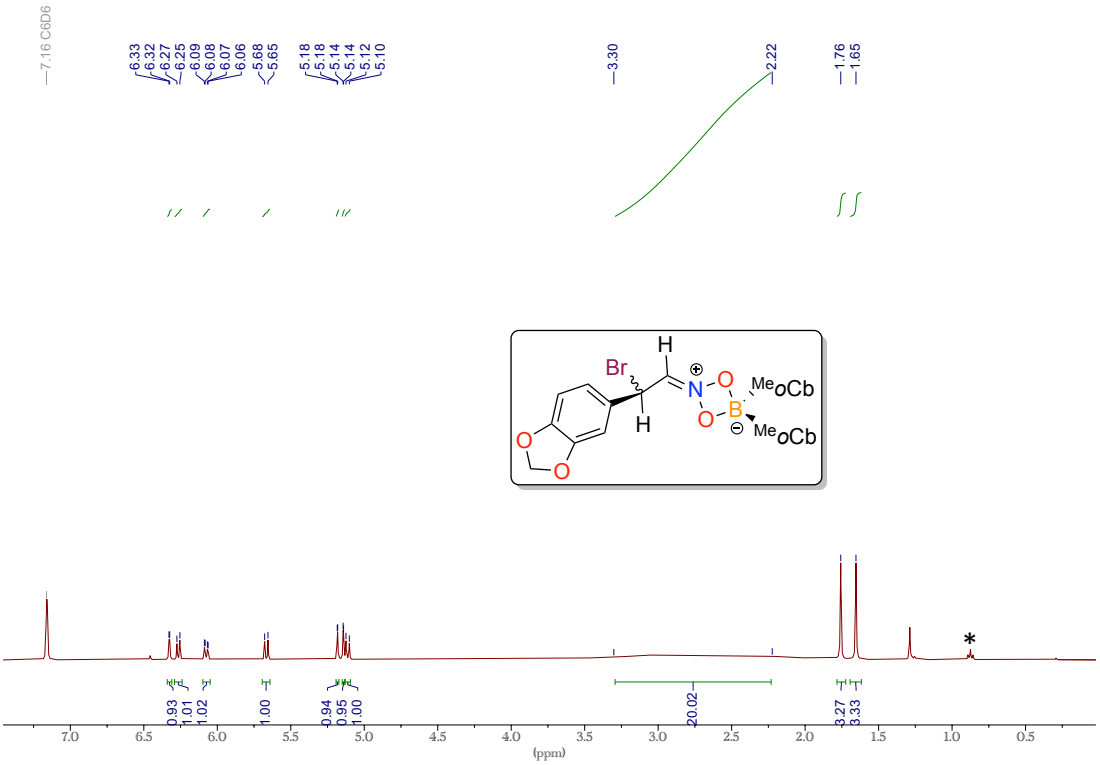


Figure S-24: Expanded aryl region and ^{1}H NMR (400 MHz) spectrum of **4** in C_6D_6.

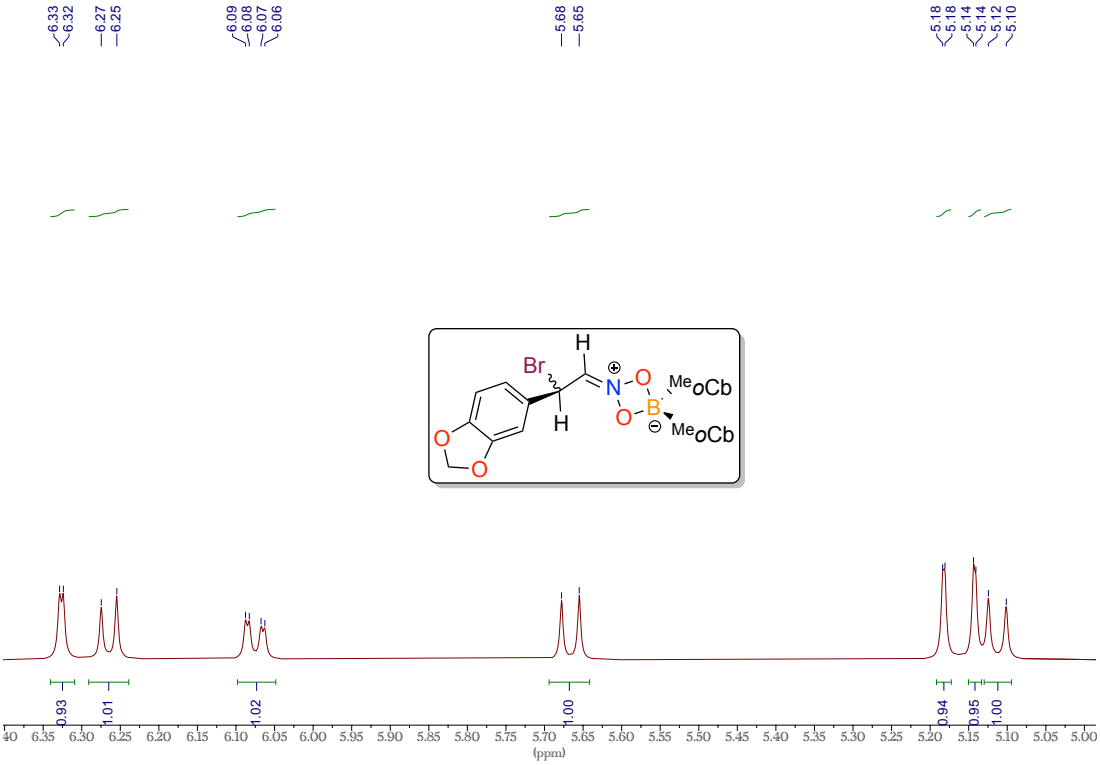


Figure S-25: ^{13}C{^{1}H} NMR (101 MHz) spectrum of **4** in C_6D_6 (* *n*-pentane).

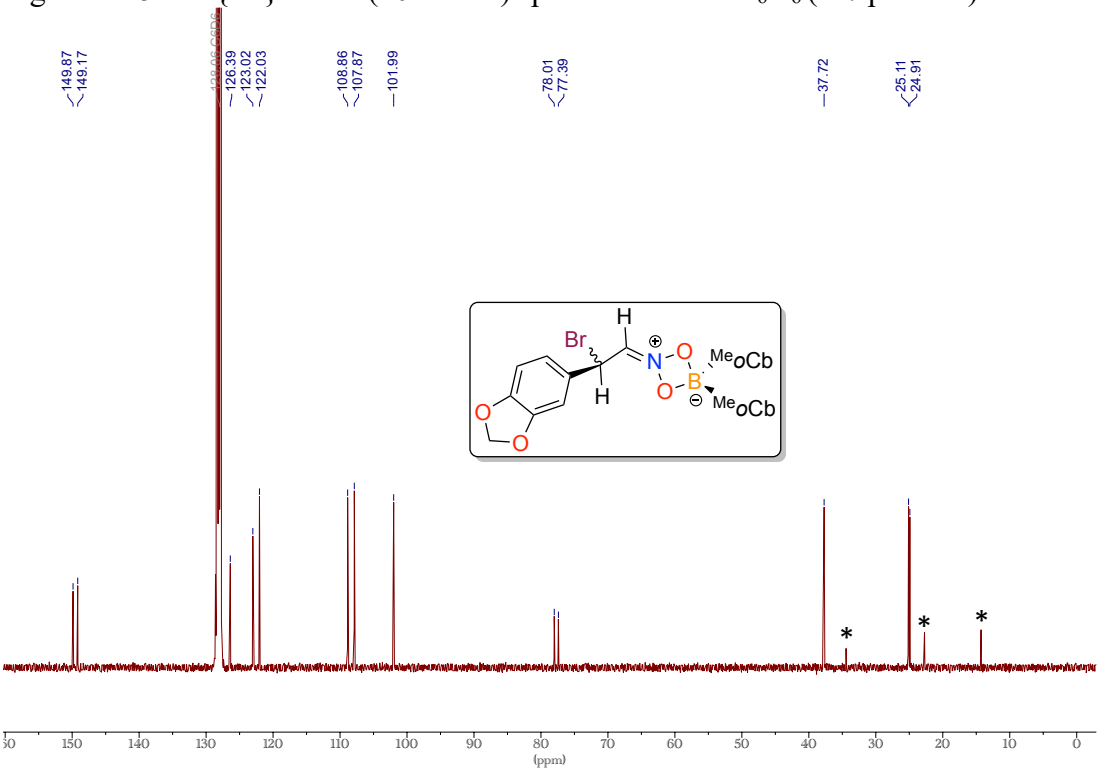


Figure S-26: Expanded aryl region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **4** in C_6D_6.

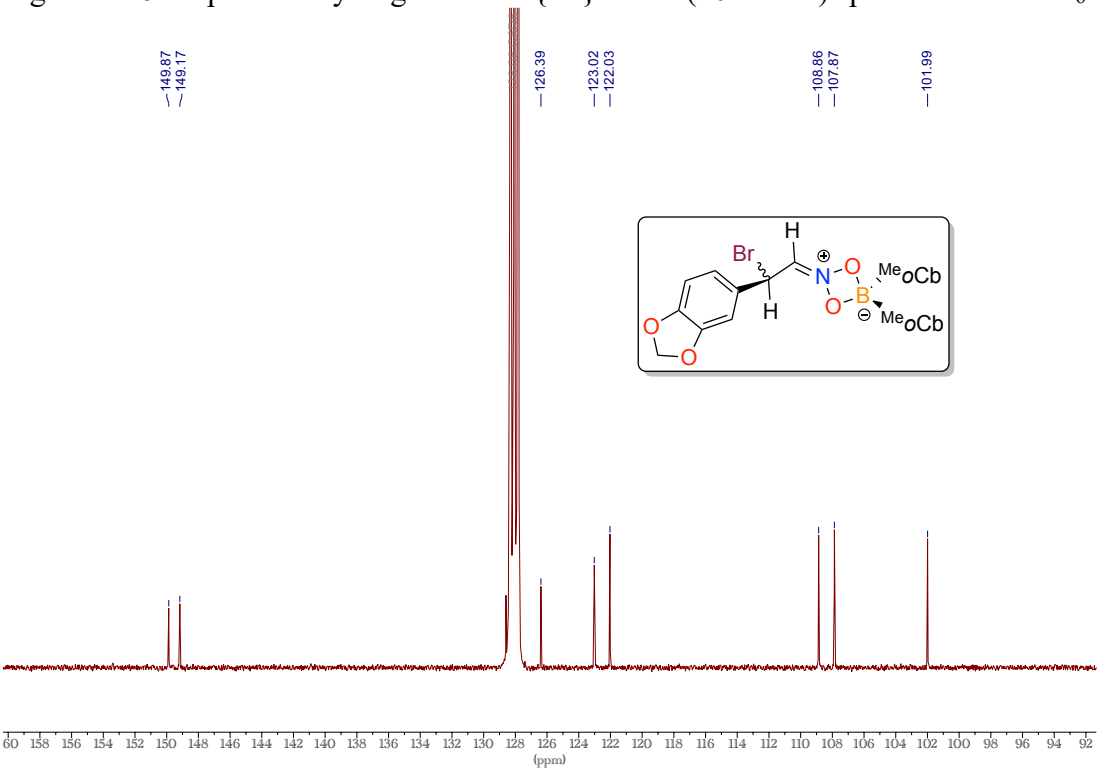


Figure S-27: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **4** in C_6D_6.

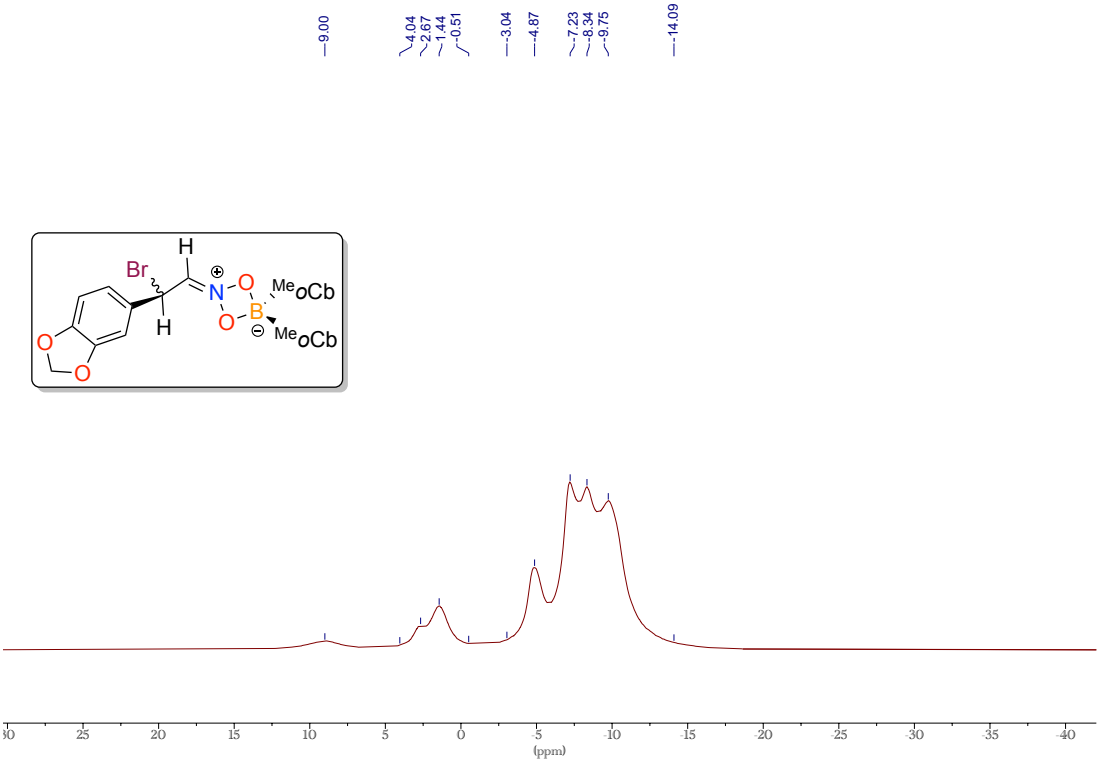


Figure S-28: ^{11}B NMR (128 MHz) spectrum of **4** in C_6D_6.

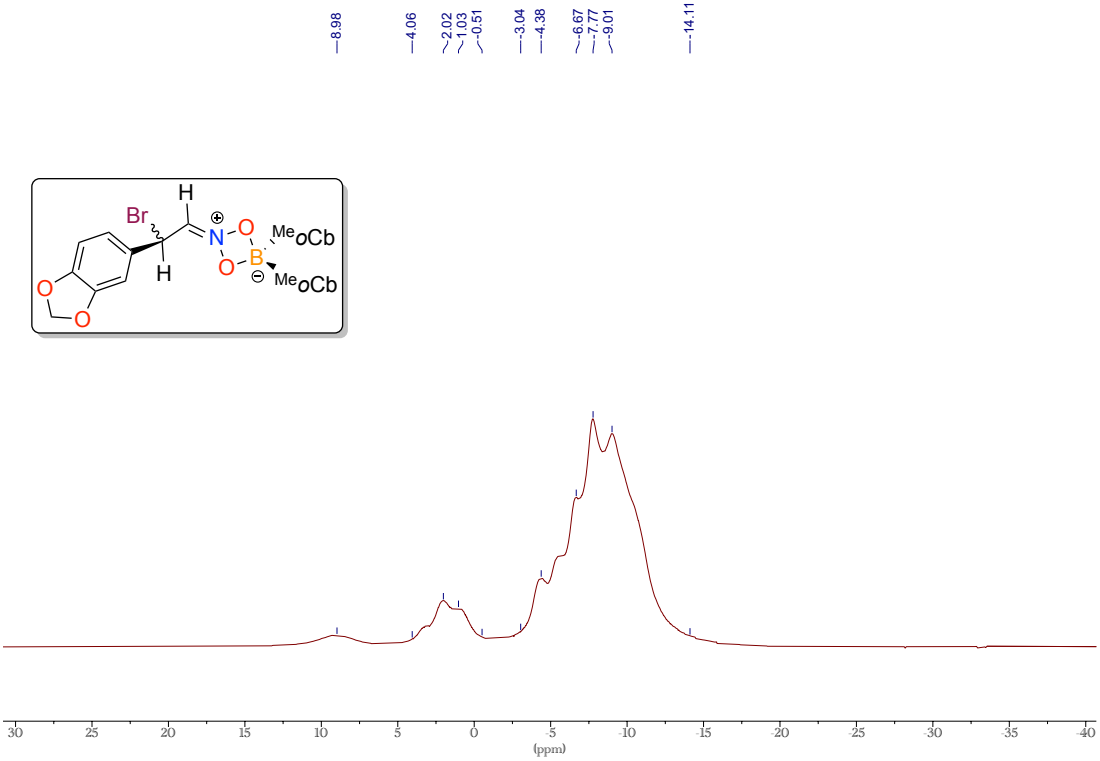


Figure S-29: ^{1}H NMR (400 MHz) spectrum of **5** in C_6D_6 (* *n*-pentane).

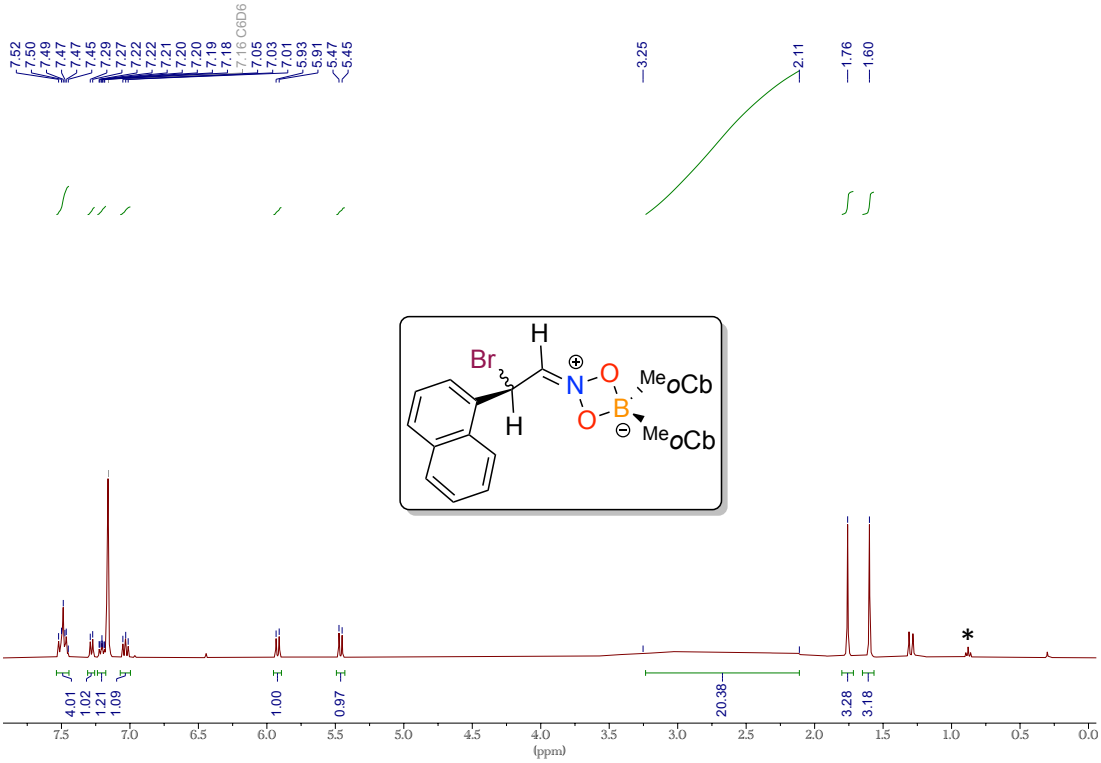


Figure S-30: ^{1}H NMR (400 MHz) spectrum of expanded aryl region **5** in C_6D_6.

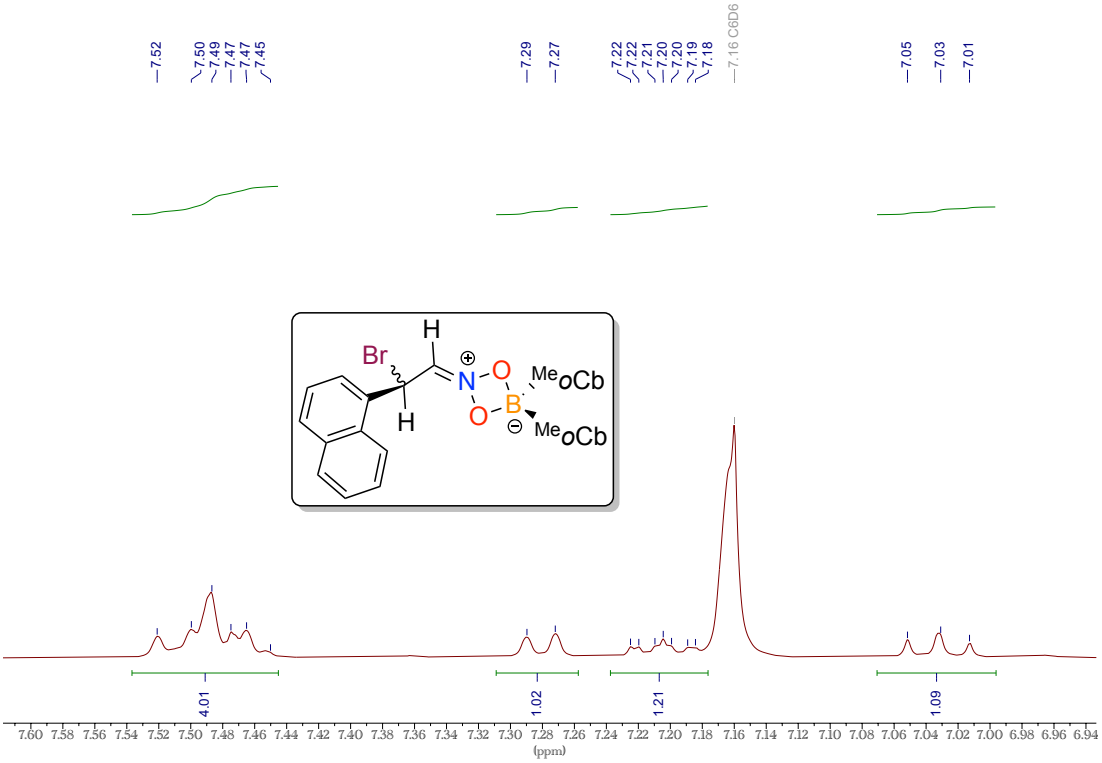


Figure S-31: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **5** in C_6D_6 (* *n*-pentane).

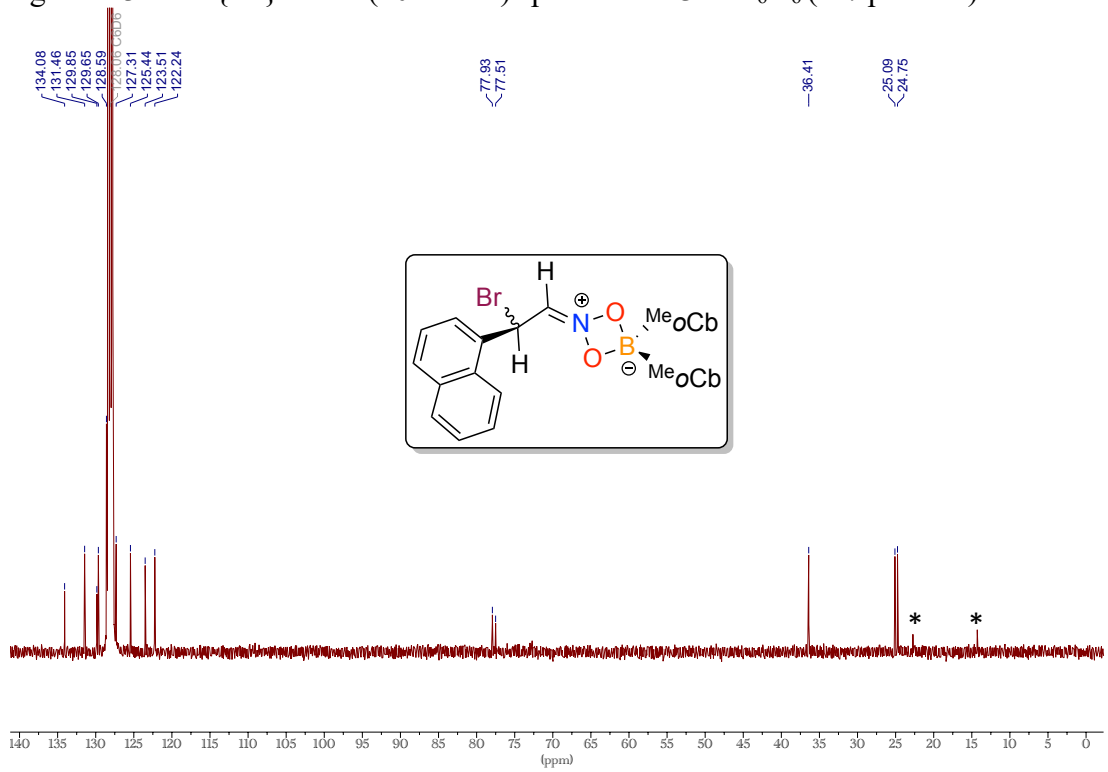


Figure S-32: Expanded aryl region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **5** in C_6D_6.

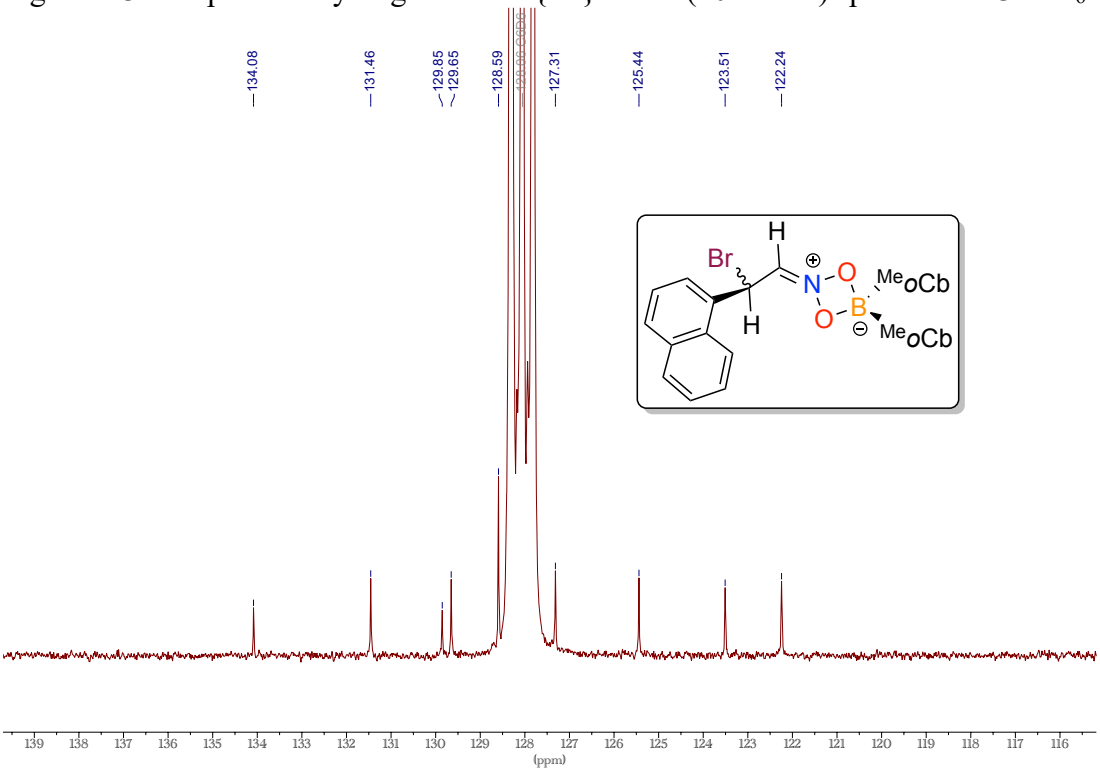


Figure S-33: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **5** in C_6D_6.

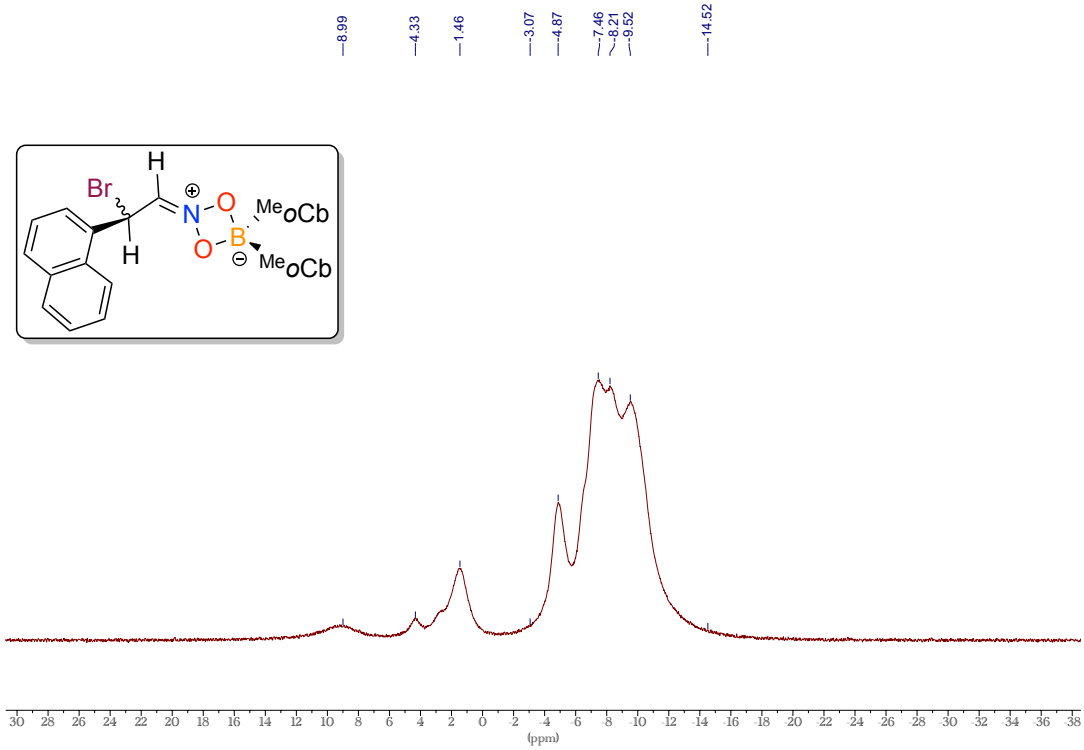


Figure S-34: ^{11}B NMR (128 MHz) spectrum of **5** in C_6D_6.

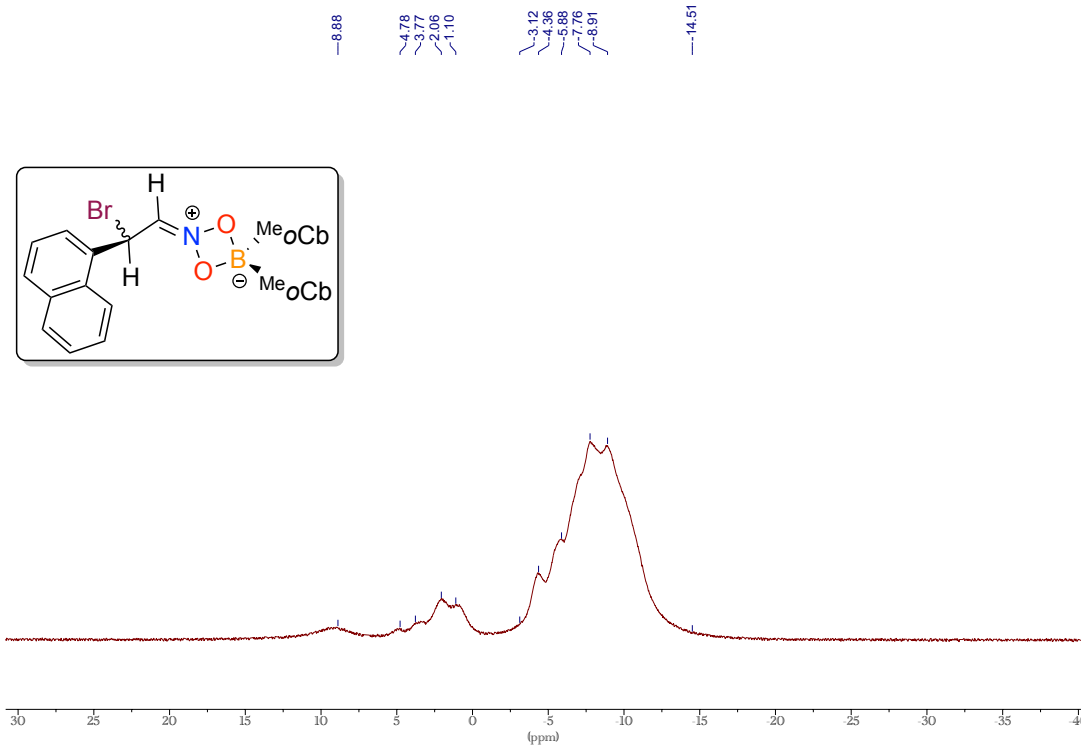


Figure S-35: ^{1}H NMR (400 MHz) spectrum of **6** in C_6D_6 (* dichloromethane).

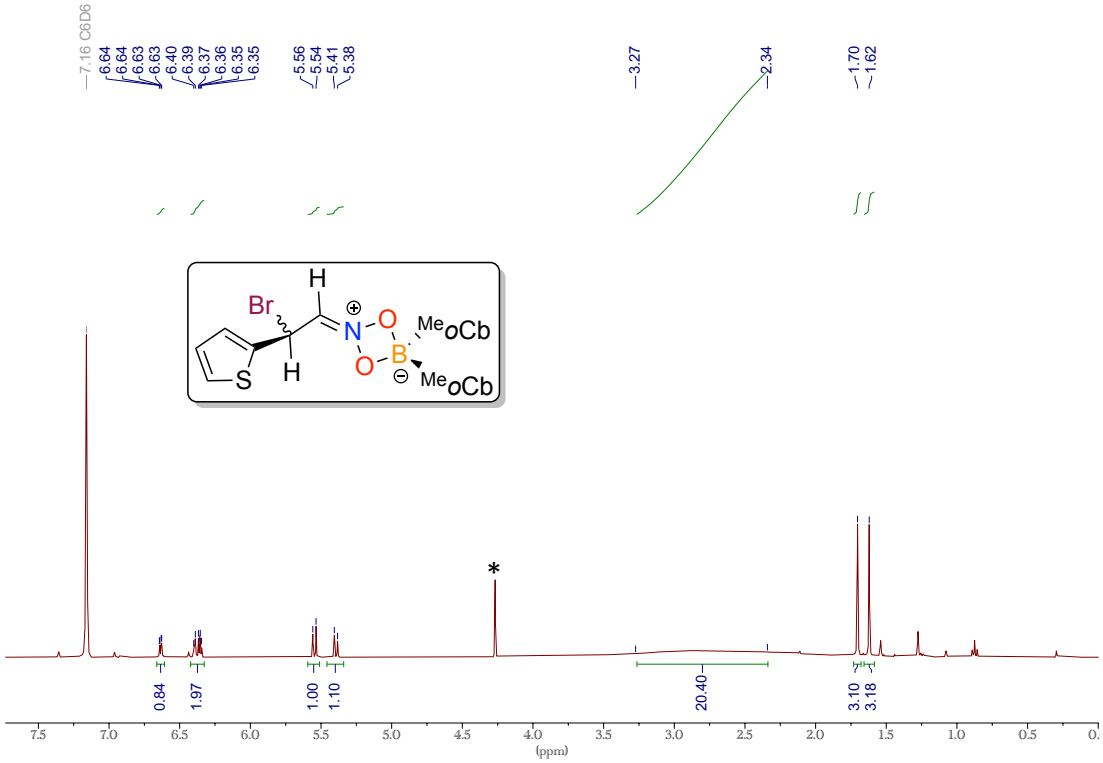


Figure S-36: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **6** in C_6D_6 (# *n*-pentane).

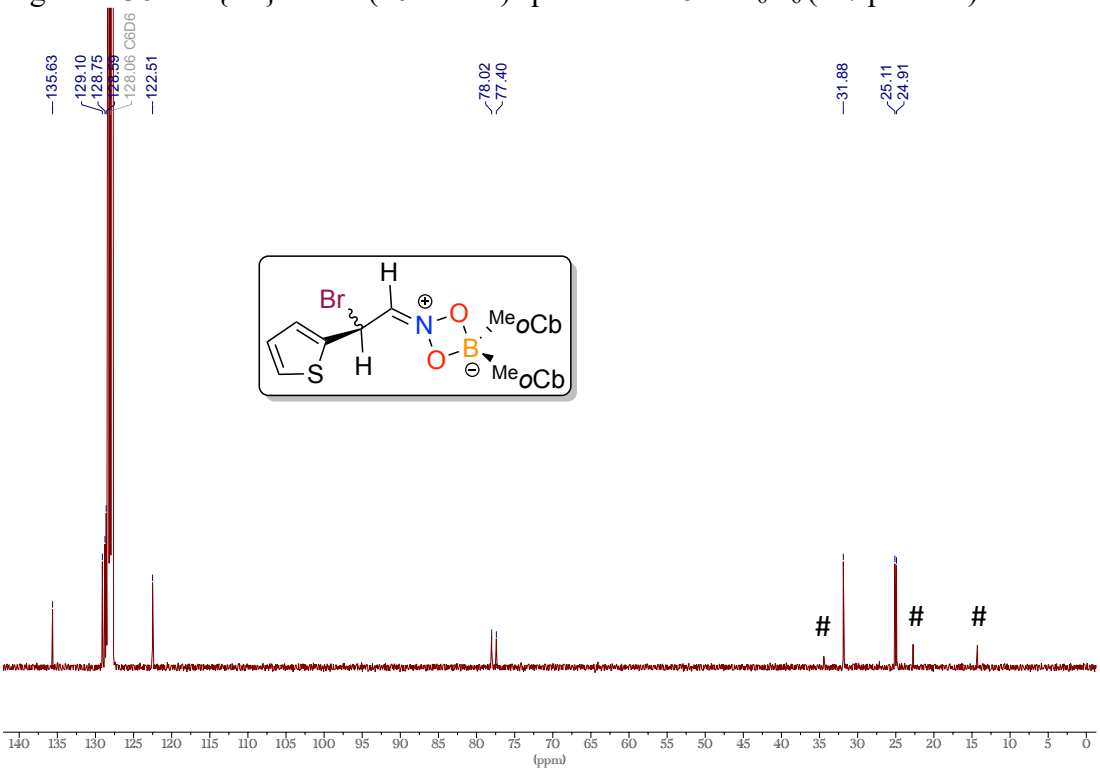


Figure S-37: Expanded ary region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **6** in C_6D_6.

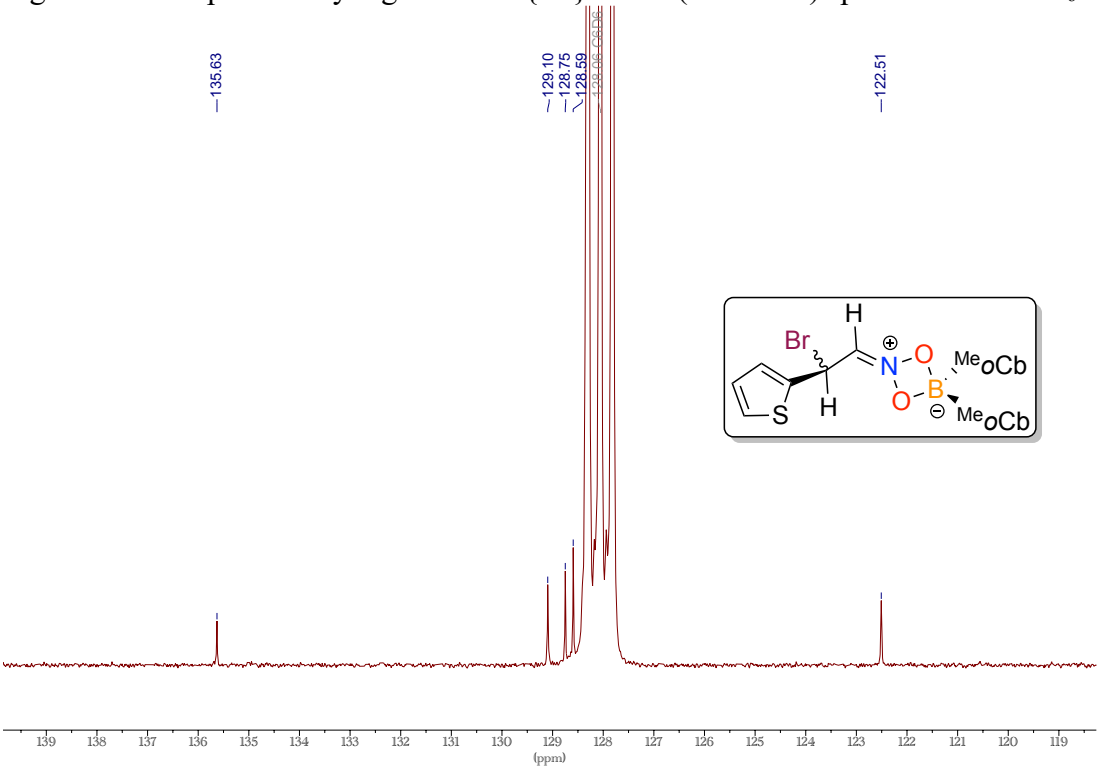


Figure S-38: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **6** in C_6D_6.

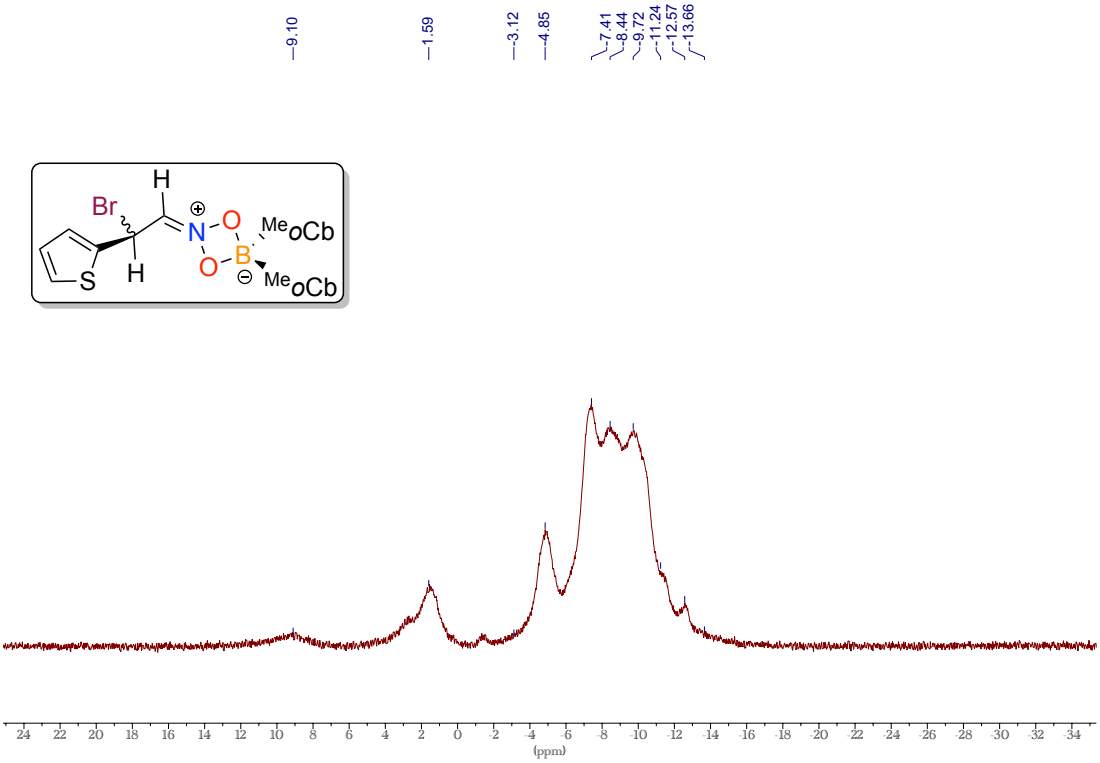


Figure S-39: ^{11}B NMR (128 MHz) spectrum of **6** in C_6D_6.

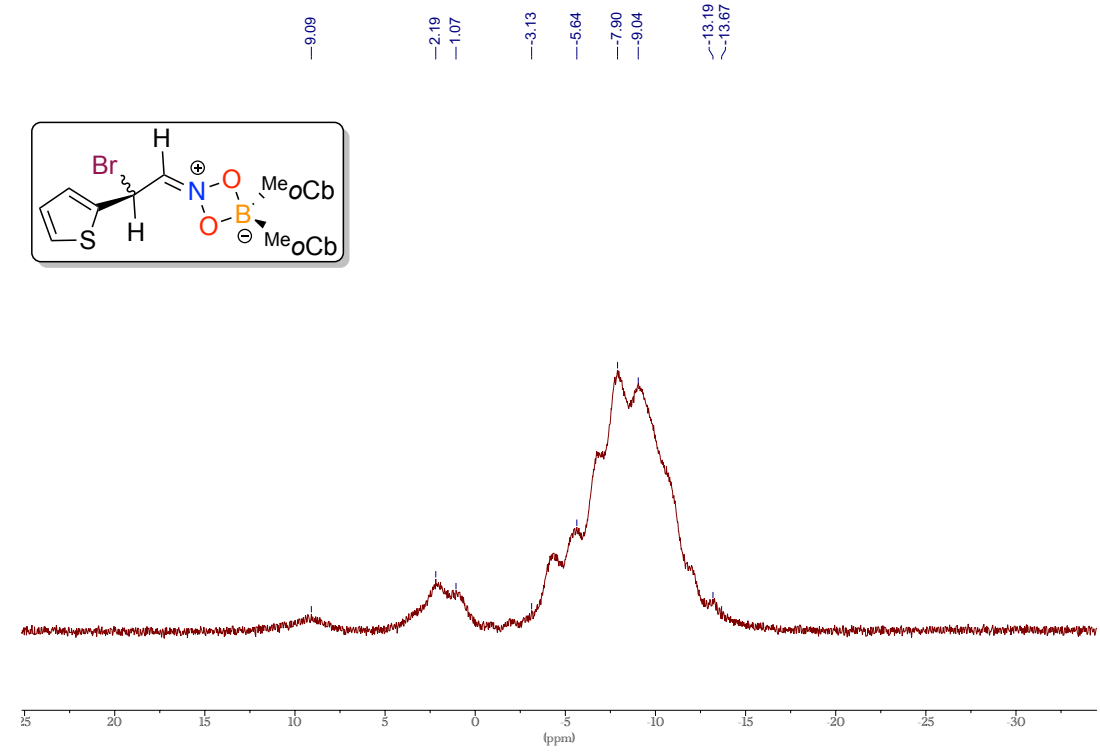


Figure S-40: ^{1}H NMR (400 MHz) spectrum of **7** in C_6D_6.

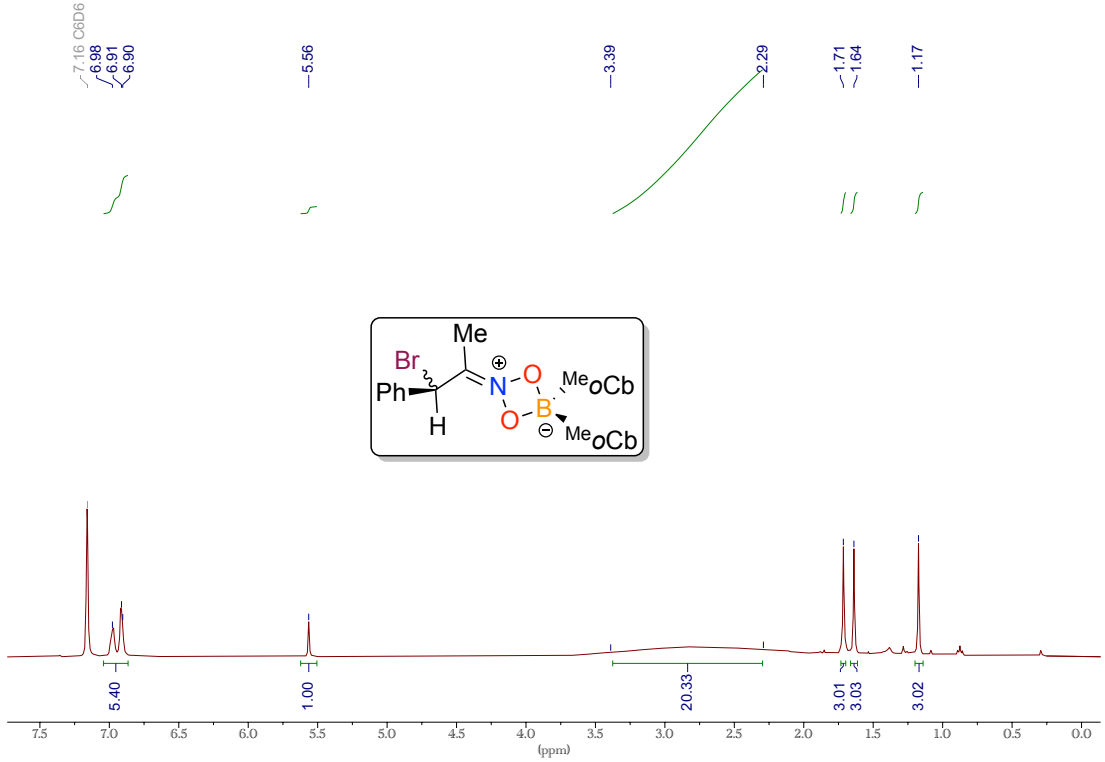


Figure S-41: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **7** in C_6D_6.

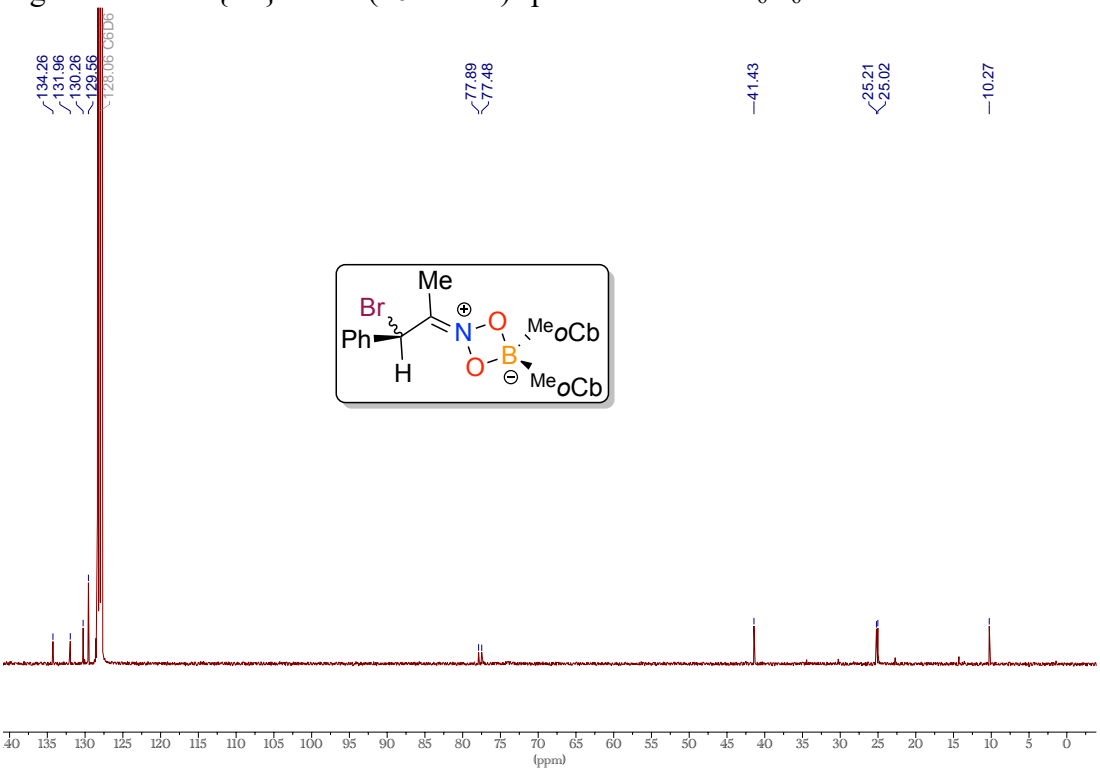


Figure S-42: Expanded ary region of $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **7** in C_6D_6.

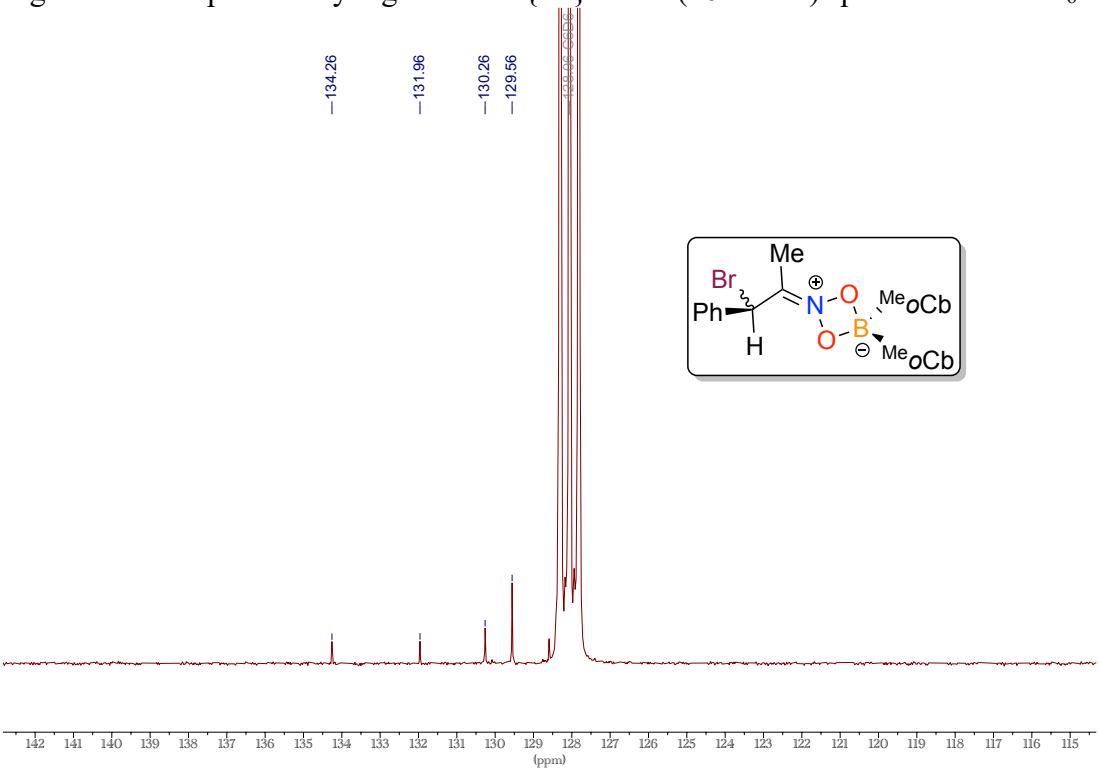


Figure S-43: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **7** in C_6D_6.

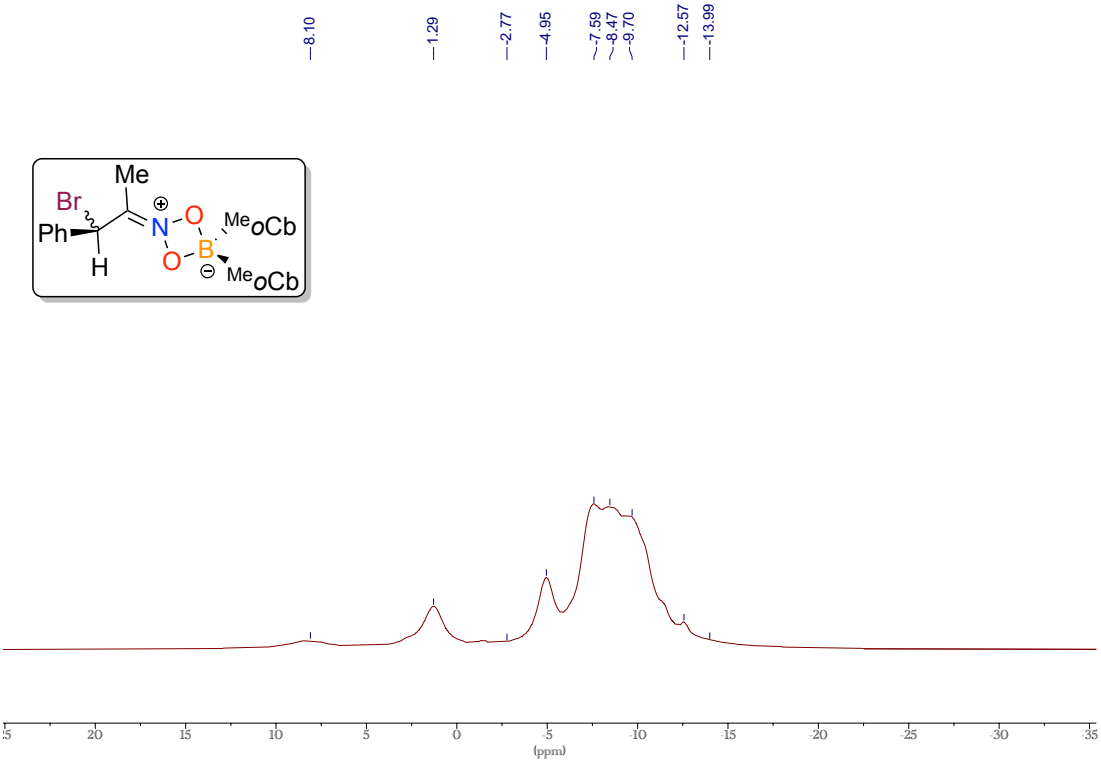


Figure S-44: ^{11}B NMR (128 MHz) spectrum of **7** in C_6D_6.

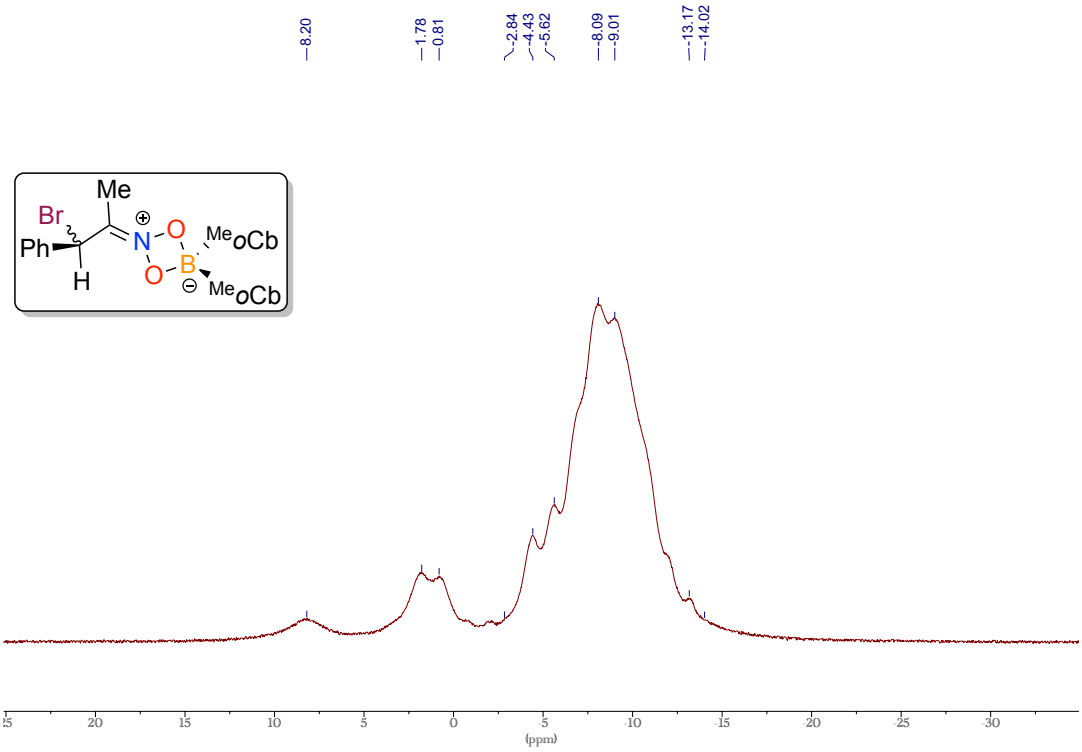


Figure S-45: Stacked ^{1}H NMR spectra of reaction of $BrB^{Me}oCb_2$ with nitrobenzene at 23 ºC after 24 h and nitrobenzene in C_6D_6.

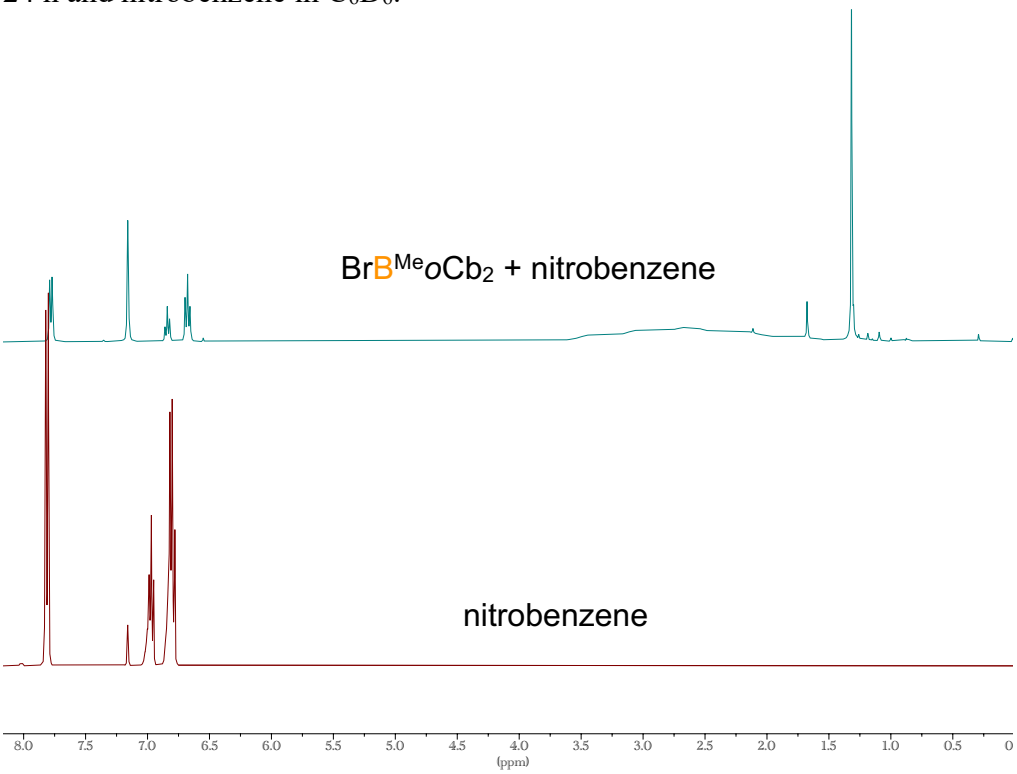


Figure S-46: Stacked ^{1}H NMR spectra of reaction of **2** with trans-β-nitrostyrene at 80 ºC after 24 h in C_6D_6.

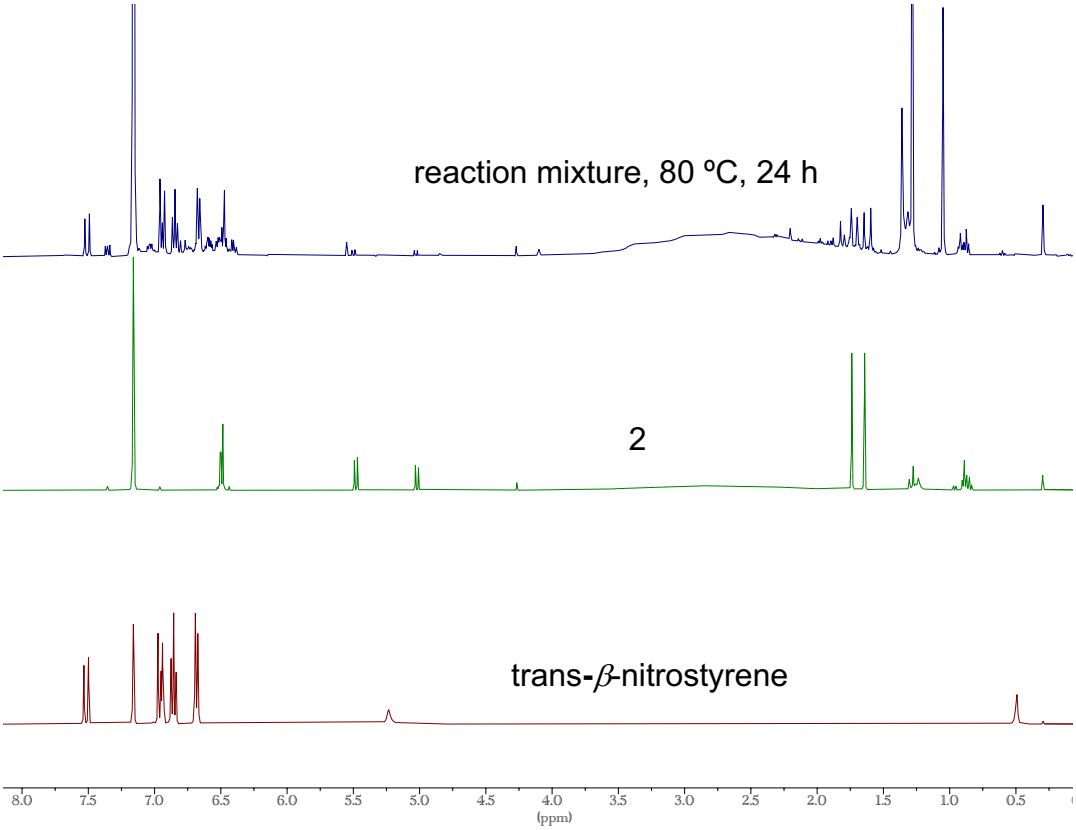


Figure S-47: X-ray structure of compound **3** exhibits two asymmetric units in the unit cell.

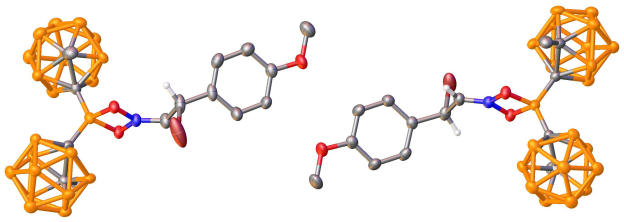


Table S-1: X-ray crystallographic details.

Compound	1	2	3
CCDC	2523539	2523540	2523541
Empirical Formula	$C_{14}H_{33}B_{21}NO_2Br$	$C_{14}H_{32}B_{21}NO_2BrF$	$C_{15}H_{35}B_{21}O_3Br_1N_1$
FW (g/mol)	554.33	572.32	584.36
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	7.7150(3)	7.6297(5)	21.6873(8)
b (Å)	19.7499(9)	19.8101(14)	14.7154(3)
c (Å)	18.9644(9)	19.2092(12)	21.3677(7)
α (deg)	90	90	90
β (deg)	93.695(2)	93.670(2)	118.883(5)
γ (deg)	90	90	90
V (Å^3)	2883.9(2)	2897.4(3)	5971.0(4)
Z	4	4	4
D_C (g cm^{-3})	1.277	1.313	1.300
Radiation λ (Å)	0.71073	0.71073	1.54184
Temp	150 K	150 K	150 K
R1 [I>2(σ)I][a]	0.0513	0.0425	0.0781
wR2 (F^2)[a]	0.1268	0.1103	0.2420
GOF (S)[a]	1.081	1.062	1.075

[a] $R1(F[I > 2(I)]) = \sum\|\|F_o| - |F_c|\|/ \sum |F_o|$; $wR2(F^2$ [all data]) = $\{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; S(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.

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