Supporting Information for:

Dearomative C2-Borylation of Indoles

*Ayesha Begum, Manjur O. Akram, and Caleb D. Martin**

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

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

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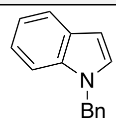
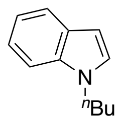
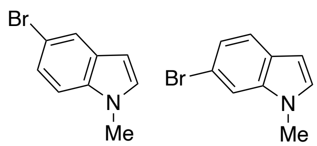
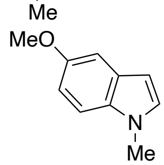
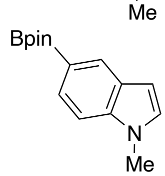
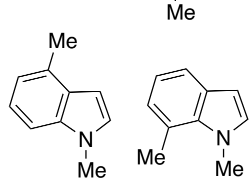
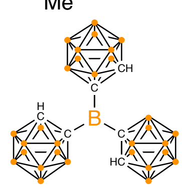
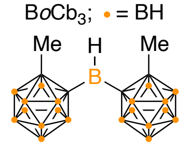
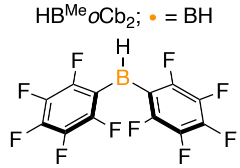
1. General Details:

All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun glove box or using standard Schlenk techniques unless specified. Chloroform-d and benzene-d_6 for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, Inc., dried by stirring for 5 days over CaH_2, distilled, and stored over 4 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. Indole, 1-methyl-1*H*-indole, 1,2-Dimethyl-1*H*-indole, 1,3-Dimethyl-1*H*-indole, $B(C_6F_5)_3$, HBpin (pin = pinacol), HBcat (cat = catechol), and $DSiEt_3$ were purchased from commercial sources and used as received. Substituted indoles, B*o*Cb_3, HB^{Me}*o*Cb_2, and $HB(C_6F_5)_2$ were prepared according to literature procedures. Multinuclear NMR spectra (^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, ^{11}B, $^{11}B\{^1H\}$, ^2H) 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. Melting or decomposition points were determined with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and developed chromatograms were analyzed by a UV lamp (λ = 254 nm). Flash column chromatography was performed with silica gel (200–300 mesh). Single crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation (λ = 0.71073 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.[1]

2. Experimental Section:

2.1 Synthesis of the Starting Materials: The compounds listed in Table S1 are known in the literature and synthesized following literature known procedures.

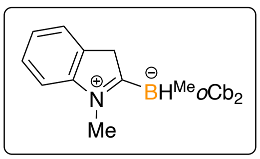
Table S1: Synthesis of starting materials: substituted indoles and boranes used in this study

Entry	Reagent	Reference
1		S. Xu, X. Huang, X. Hong, and B. Xu, *Org. Lett.*, 2012, **14**, 4614-4617
2		H. Huo, C. Fu, K. Harms, and E. Meggers, *J. Am. Chem. Soc.*, 2014, **136**, 2990-2993
3		E.-C. Elliott, J. L. Maggs, B. K. Park, P. M. O'Neill, and A. V. Stachulski, *Org. Biomol. Chem.*, 2013, **11**, 8426-8434
4		M. P. Fortes, M. M. Bassaco, T. S. Kaufman, and C. C. Silveira, *RSC. Adv.*, 2014, **4**, 34519-34530
5		A. D. Grosso, M. D. Helm, S. A. Soloman, D. C. Quintero, and M. J. Ingleson, *Chem. Commun.*, 2011, **47**, 12459-12461
6		H. F. T. Klare, M. Oestreich, J. Ito, H. Nishiyama, Y. Ohki, and K. Tatsumi, *J. Am. Chem. Soc.*, 2011, **10**, 3312-3315
7	 B*o*Cb_3; • = BH	M. O. Akram, J. R. Tidwell, J. L. Dutton, and C. D. Martin, *Angew. Chem. Int. Ed.*, 2022, **61**, e202212073
8	 HB^{Me}*o*Cb_2; • = BH	M. O. Akram, J. R. Tidwell, J. L. Dutton, and C. D. Martin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202307040
9	 $HB(C_6F_5)_2$	D. J. Parks, R. E. von H. Spence, and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809–811

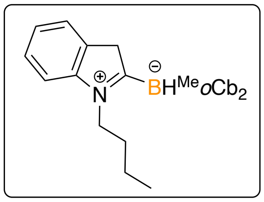
2.2 Representative Procedure for Borylation Reactions: Quantities of the indole reagents, reaction times, and characterization details for each compound are discussed below.

A benzene solution (1 mL) of indole (0.100 mmol) was added to a stirred benzene (1 mL) solution of $HB^{Me}oCb_2$ (0.100 mmol, 32.6 mg). The reaction mixture was stirred at 23 ºC and monitored by analyzing an aliquot via ^{1}H and ^{11}B NMR spectroscopy to determine completion. Upon reaction completion, the volatiles were removed under reduced pressure and the solids washed with *n*-pentane (2 mL). Drying under vacuum gave pure borylated product. Single crystals for X-ray diffraction studies of **1** and **4** were grown from their dichloromethane solution by vapor diffusion into toluene.

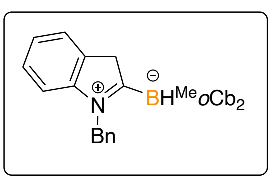
2.3 Analytical Data of Products:



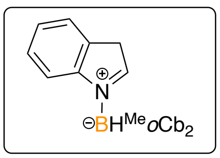
1: N-methyl indole: 13.1 mg, reaction time: 1 h; Yield: 97%, 44.0 mg; dp: 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 1H), 7.64–7.62 (m, 2H), 7.58–7.56 (m, 1H), 4.78 (s, 2H), 4.16 (s, 3H), 2.74–1.45 (m, 27H) ppm; $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 1H), 7.64–7.62 (m, 2H), 7.58–7.56 (m, 1H), 4.79 (s, 2H), 4.16 (s, 3H), 2.71–2.68 (m, 3H), 2.58 (s, 2H), 2.34–2.25 (m, 6H), 2.09–2.08 (m, 3H), 2.05 (s, 6H), 2.00–1.96 (m, 3H), 1.79 (s, 2H), 1.60 (s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 145.4, 134.0, 129.7, 129.0, 125.6, 114.2, 79.4, 49.2, 37.1, 26.1 ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.3 (s), –5.6 (s), –7.0 to –12.7 (m), –17.7 (s) ppm; ^{11}B NMR: δ = –0.3 (d, J = 154 Hz), –5.7 (d, J = 141 Hz), –7.1 to –12.8 (m), –17.8 (d, J = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2565 (2), 1468 (12), 1443 (5), 1381 (9), 1359 (11), 1214 (6), 1130 (3), 1092 (8), 1042 (15), 1020 (7), 943 (14), 793 (13), 755 (1), 669 (10), 417 (15); HRMS(–ESI): calcd 456.4863 for $C_{15}H_{36}B_{21}N$ $[M–H]^{–}$ found 456.4881.



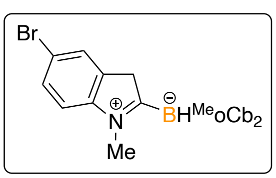
2: N-butyl indole: 17.3 mg, reaction time: 7 h; Yield: 80%, 40.0 mg; dp: 182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.73 (m, 1H), 7.63–7.58 (m, 2H), 7.56–7.52 (m, 1H), 4.69 (s, 2H), 4.61 (t, 2H, *J* = 8 Hz), 2.69–1.51 (m, 31H), 1.04 (t, 3H, *J* = 8 Hz) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 7.75–7.73 (m, 1H), 7.62–7.52 (m, 3H), 4.70 (s, 2H), 4.61 (t, 2H, *J* = 8 Hz), 2.69– 2.66 (m, 2H), 2.58 (s, 2H), 2.34–2.24 (m, 6H), 2.06–2.01 (m, 10H), 2.00 (s, 2H), 1.90–1.82 (m, 3H), 1.68 (s, 3H), 1.59–1.53 (m, 3H), 1.04 (t, 3H, *J* = 4 Hz) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.5, 134.6, 129.3, 128.9, 125.7, 114.8, 79.5, 50.4, 49.7, 31.3, 25.8, 20.6, 13.7 ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –5.6 (m), –6.8 to –13.0 (m), –17.6 (s) ppm; ^{11}B NMR: δ = –0.2 (d, *J* = 141 Hz), –5.7 (d, *J* = 141 Hz), –6.9 to –13.4 (m), –17.7 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2956 (13), 2565 (15), 2548 (1), 1461 (5), 1381 (7), 1356 (11), 1131 (3), 1103 (9), 1021 (8), 933 (14), 807 (12), 757 (2), 722 (4), 666 (10), 418 (6); HRMS(–ESI): calcd 498.5333 for $C_{18}H_{41}B_{21}N_1$ $[M–H]^-$ found 498.5344.



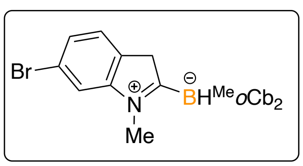
3: N-benzyl indole: 20.7 mg, reaction time: 6 h; Yield: 86%, 46.0 mg; dp: 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, 1H, *J* = 8 Hz), 7.53 (t, 1H, *J* = 8 Hz), 7.42–7.37 (m, 4H), 7.18 (d, 1H, *J* = 8 Hz), 7.05 (d, 2H, *J* = 8 Hz), 5.95 (s, 2H), 4.88 (s, 2H), 2.73–1.40 (m, 27H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, 1H, *J* = 8 Hz), 7.53 (t, 1H, *J* = 8 Hz), 7.42–7.37 (m, 4H), 7.18 (d, 1H, *J* = 8 Hz), 7.05 (d, 2H, *J* = 8 Hz), 5.95 (s, 2H), 4.88 (s, 2H), 2.72 (s, 3H), 2.56 (s, 2H), 2.35 (s, 2H), 2.29 (s, 2H), 2.21 (s, 2H), 2.09– 2.04 (m, 6H), 1.85 (s, 6H), 1.84 –1.77 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 144.8, 134.3, 132.3, 129.8, 129.3, 129.1, 128.9, 128.5, 125.9, 125.5, 116.1, 79.7, 54.0, 50.0, 25.6 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –5.6 (m), –6.7 to –14.1 (m), –17.6 (s) ppm; ^{11}B NMR: δ = –0.3 (d, J = 141 Hz), –5.7 (d, J= 154 Hz), –6.7 to –13.9 (m), –17.7 (d, J = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2641 (15), 2580 (2), 1454 (6), 1382 (13), 1357 (11), 1135 (8), 1106 (3), 1028 (12), 805 (14), 754 (7), 718 (1), 691 (5), 571 (10), 455 (9), 418 (4); HRMS(–ESI): calcd 532.5176 for $C_{21}H_{39}B_{21}N_1$ $[M–H]^-$ found 532.5196.



4: Indole: 11.7 mg, reaction time: 1 h; Yield: 90%, 40.0 mg; dp: 168 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H), 7.75 (t, 2H, J = 8 Hz), 7.63–7.57 (m, 2H), 4.31 (s, 2H), 3.24–1.44 (m, 26H) ppm; $^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H), 7.75 (t, 2H, J = 8 Hz), 7.63–7.59 (m, 2H), 4.31 (s, 2H), 3.27 (s, 1H), 2.76 (s, 2H), 2.54 (s, 2H), 2.37–2.26 (m, 6H), 2.08–2.05 (m, 10H), 1.97 (s, 2H), 1.79 (s, 2H), 1.47 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 179.9, 148.0, 132.3, 129.8, 129.4, 125.7, 118.0, 79.3, 41.8, 26.1 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –4.0 to –13.0 (m) ppm; ^{11}B NMR: δ = –0.3 (d, J = 141 Hz), –4.0 to –13.7 (m) ppm; FT-IR (ranked intensity, cm^{-1}): 2562 (1), 1454 (5), 1382 (9), 1352 (11), 1323 (7), 1117 (3), 1049 (15), 1020 (8), 937 (10), 730 (2), 683 (4), 609 (13), 494 (14), 422 (6), 413 (12); HRMS(–ESI): calcd 442.4707 for $C_{14}H_{33}B_{21}N$ $[M–H]^-$ found 442.4735.

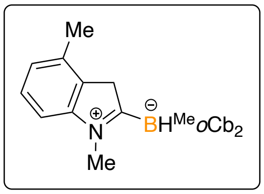


5: 5-Bromo-N-methyl indole: 21.0 mg, reaction time: 5 h; Yield: 88%, 47.0 mg; dp: 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.77 (dd, 1H, *J* = 8, 2 Hz), 7.44 (d, 1H, *J* = 8 Hz), 4.79 (s, 2H), 4.14 (s, 3H), 2.72–1.49 (m, 27H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.77 (d, 1H, *J* = 8Hz), 7.44 (d, 1H, *J* = 8 Hz), 4.79 (s, 2H), 4.14 (s, 3H), 2.66 (s, 3H), 2.57 (s, 2H), 2.35–2.29 (m, 7H), 2.24–2.07 (m, 4H), 2.05 (s, 6H), 2.01–1.98 (m, 2H), 1.74 (s, 2H), 1.58 (s, 1H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 135.9, 132.3, 129.1, 128.5, 124.4, 115.4, 79.4, 49.1, 37.2, 26.1 ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –5.6 (m), –6.9 to –12.3 (m), –17.7 (s) ppm; ^{11}B NMR: δ = –0.2 (d, *J* = 154 Hz), –5.7 (d, , *J* = 141 Hz), –6.8 to –12.9 (m), –17.7 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2580 (1), 1441 (8), 1381 (13), 1355 (9), 1214 (11), 1131 (7), 1102 (3), 1051 (12), 905 (10), 807 (4), 755 (2), 730 (6), 669 (14), 586 (15); HRMS(–ESI): calcd 535.3932 for $C_{15}H_{35}B_{21}BrN$ $[M–H]^{-}$ found 535.3971.

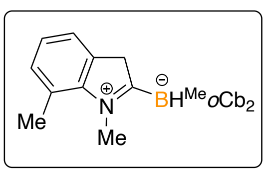


6: 6-Bromo-N-methyl indole: 21.0 mg, reaction time: 7 h; Yield: 82%, 44.0 mg; dp: 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.74 (m, 2H), 7.63 (d, 1H, *J* = 8 Hz), 4.76 (s, 2H), 4.14 (s, 3H), 2.63–1.49 (m, 27H) ppm; ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ = 7.77–7.74 (m, 2H), 7.63 (d, 1H, *J* = 8 Hz), 4.77 (s, 2H), 4.14 (s, 3H), 2.67 (s, 3H), 2.57 (s, 2H), 2.35–2.25 (m, 7H), 2.08– 2.07 (m, 3H), 2.04 (s, 6H), 2.01–1.96 (m, 2H), 1.74 (s, 2H), 1.57 (s, 2H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 146.5, 132.8, 128.5, 126.7, 122.7, 117.9, 79.4, 49.2, 37.3, 34.3, 26.1, 22.5, 14.2 ppm; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ = –0.2 (s), –5.6 (s), –6.7 to –12.0 (m), –17.7 (s) ppm; ^{11}B NMR: δ = –0.2 (d, *J* = 141 Hz), –5.7 (d, *J* = 141 Hz), –6.9 to –13.3 (m), –17.7 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2951 (13), 2576 (1), 1615 (11), 1467 (5), 1380 (12), 1261

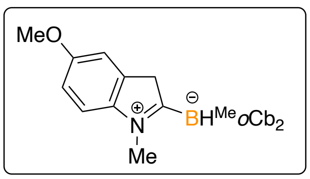
(8), 1129 (3), 1102 (14), 1063 (7), 879 (9), 852 (10), 812 (4), 729 (13), 604 (15), 420 (6); HRMS(–ESI): calcd 535.4047 for $C_{15}H_{35}B_{21}BrN$ $[M–H]^-$ found 535.4009.



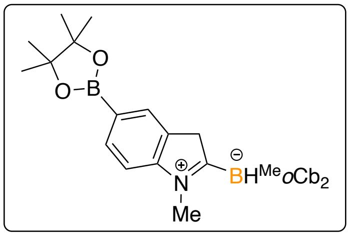
7: 4-Methyl-N-methyl indole: 14.5 mg, reaction time: 5 h; Yield: 93%, 44.0 mg; dp: 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, 1H, *J* = 8 Hz), 7.41–7.37 (m, 2H), 4.62 (s, 2H), 4.14 (s, 3H), 3.26–1.45 (m, 30H) ppm; $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, 1H, *J* = 8 Hz), 7.41–7.36 (m, 2H), 4.63 (s, 2H), 4.14 (s, 3H), 2.71–2.68 (m, 3H), 2.58–2.56 (m, 2H), 2.53 (s, 3H), 2.34–2.25(m, 6H), 2.12–2.10 (m, 3H), 2.05 (s, 7H), 2.01–1.99 (m, 2H), 1.80 (s, 2H), 1.60 (s, 2H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 145.1, 136.0, 132.8, 130.8, 129.2, 111.6, 79.5, 48.0, 37.3, 34.3, 26.1, 22.5, 18.9, 14.2 ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.3 (s), –5.6 (s), –6.7 to –12.5 (m), –17.7 (s) ppm; ^{11}B NMR: δ = –0.4 (d, *J* = 141 Hz), –5.7 (d, *J* = 154 Hz), –6.8 to –12.2 (m), –17.8 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2945 (14), 2579 (1), 1442 (6), 1380 (9), 1132 (3), 1104 (8), 1064 (7), 774 (4), 729 (5), 715 (10), 677 (2), 617 (13), 541 (11), 490 (15), 458 (15); HRMS(–ESI): calcd 470.5020 for $C_{16}H_{37}B_{21}N_1$ $[M–H]^-$ found 470.5043.



8: 7-Methyl-N-methyl indole: 14.5 mg, reaction time: 7 h; Yield: 98%, 46.0 mg; dp: 168 °C; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.56–7.54 (m, 1H), 7.44 (t, 1H, *J* = 8 Hz), 7.34 (s, 1H), 4.72 (s, 2H), 4.33 (s, 3H), 2.87–1.65 (m, 30H) ppm; $^{1}H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2): δ = 7.57–7.55 (m, 1H), 7.44 (t, 1H, *J* = 8 Hz), 7.34 (s, 1H), 4.72 (s, 2H), 4.33 (s, 3H), 2.83 (s, 3H), 2.67–2.65 (m, 2H), 2.58 (s, 2H), 2.52 (s, 1H), 2.28–2.23 (m, 6H), 2.11– 2.09 (m, 2H), 2.06 (s, 6H), 2.03–1.99 (m, 4H), 1.83 (s, 2H), 1.67 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 144.3, 135.4, 133.4, 129.6, 128.7, 126.5, 123.7, 80.3, 49.3, 41.5, 26.3, 20.9 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ = –0.6 (s), –5.9 (s), –7.2 to –12.5 (m), –17.8 (s) ppm; ^{11}B NMR: δ = –0.6 (d, *J* = 155 Hz), –5.9 (d, *J* = 154 Hz), –7.1 to –13.3 (m), –17.8 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2948 (13), 2577 (2), 1442 (6), 1379 (10), 1355 (8), 1257 (12), 1133 (11), 1105 (8), 1072 (7), 1028 (9), 942 (14), 773 (3), 730 (5), 673 (14), 617 (15); HRMS(–ESI): calcd 470.5030 for $C_{16}H_{37}B_{21}N_1$ $[M–H]^-$ found 470.5031.



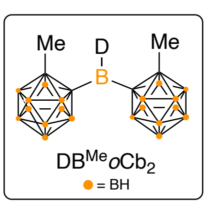
9: 5-Methoxy-N-methyl indole: 16.1 mg, reaction time: 3 h; Yield: 90%, 44.0 mg; dp: 166 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, 1H, *J* = 12 Hz), 7.24 (s, 1H), 7.10 (dd, 1H, *J* = 12, 4 Hz), 4.69 (s, 2H), 4.10 (s, 3H), 3.92 (s, 3H), 3.03–1.38 (m, 27H) ppm; $^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, 1H, *J* = 12 Hz), 7.28–7.26 (m, 1H), 7.12 (d, 1H, *J* = 12 Hz), 4.72 (s, 2H), 4.12 (s, 3H), 3.94 (s, 3H), 2.70–2.59 (m, 5H), 2.36 (s, 2H), 2.30–2.26 (m, 4H), 2.10–2.09 (m, 4H), 2.07 (s, 6H), 2.03–2.00 (m, 2H), 1.81 (s, 2H), 1.63 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 160.5, 138.9, 135.0, 115.5, 114.9, 110.3, 79.4, 56.2, 48.9, 37.0, 34.3, 26.1, 22.5, 14.2 ppm; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ = –0.3 (s), –5.7 (s), –7.0 to –12.4 (m), –17.8 (s) ppm; ^{11}B NMR: δ = –0.3 (d, *J* = 141 Hz), –5.7 (d, *J* = 154 Hz), –7.1 to –13.0 (m), –17.8 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2575 (1), 1608 (8), 1485 (5), 1443 (14), 1273 (3), 1163 (11), 1133 (4), 1108 (15), 1026 (6), 906 (12), 841 (10), 806 (7), 729 (2), 452 (9), 423 (13); HRMS(–ESI): calcd 486.4969 for $C_{16}H_{37}B_{21}NO$ $[M–H]^-$ found 486.4973.



10: 5-BPin-N-methyl indole: 25.7 mg, reaction time: 10 h; Yield: 75%, 44.0 mg; dp: 178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 8.04 (d, 1H, *J* = 8 Hz), 7.55 (d, 1H, *J* = 8 Hz), 4.77 (s, 2H), 4.16 (s, 3H), 2.85–1.62 (m, 27H), 1.37 (s, 12H) ppm; $^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 8.04 (d, 1H, *J* = 8 Hz), 7.55 (d, 1H, *J* = 8 Hz), 4.77 (s, 2H), 4.16 (s, 3H), 2.68 (s, 3H), 2.57 (s, 2H), 2.34 (s, 3H), 2.28–2.24 (m, 4H), 2.10–2.08 (m, 3H), 2.05 (s, 6H), 1.99 (s, 2H), 1.76 (s, 2H), 1.59 (s, 2H),1.37 (s, 12H) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 147.3, 135.4, 133.2, 131.8, 113.4, 84.8, 79.4, 49.1, 37.1, 26.1, 25.1 ppm; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ = 30.8 (br. s), –0.2 (s), –5.6 (s), –6.9 to –13.4 (m), –17.7 (s) ppm; ^{11}B NMR: δ = 31.7 (br), –0.2 (d, *J* = 128 Hz), –5.6 (d, *J* = 192 Hz), –7.0 to –13.7 (m), –17.7 (d, *J* = 90 Hz) ppm; FT-IR (ranked intensity, cm^{-1}): 2584 (3), 2045 (15), 1978 (12), 1430 (11), 1360 (1), 1202 (14), 1143 (4), 1105 (6), 962 (10), 856 (7), 821 (9), 729 (8), 671 (5), 475 (13), 417 (2); HRMS(–ESI): calcd 582.5716 for $C_{21}H_{46}B_{22}NO_2$ $[M–H]^-$ found 582.5734.

2.4 Preparation of DB^{Me}*o*Cb$_2$:

The compound for the mechanistic studies were synthesized based on literature procedures.[2] A comparison of the $^{1}H\{^{11}B\}$ NMR spectra with HB^{Me}*o*Cb$_2$ is shown in the Figure S66.



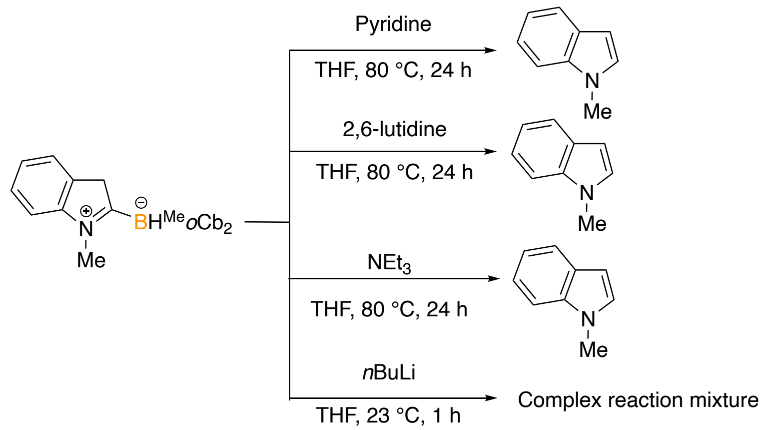
To a stirred solution of $BrB^{Me}oCb_2$ (40.5 mg, 0.10 mmol) in benzene (2 mL) taken in a vial, $DSiEt_3$ (97%-D, 0.11 mmol, 17.7 μL) was added at 23 °C and the reaction mixture stirred for 1 h. After completion of the reaction as monitored by ^1H and ^{11}B NMR spectroscopy, the volatiles removed under vacuum to afford a white solid, which was washed with cold *n*-pentane (1 mL). The residue was dried under vacuum to give pure $DB^{Me}oCb_2$ as white solid in 90% yield (29.5 mg). The product was >90% enriched with deuterium at the central boron position, as determined by $^1H\{^{11}B\}$ NMR spectrum.

2.5 Procedure for the Gram Scale Synthesis of 1 in Glovebox-free Conditions:

Compound $HB^{Me}oCb_2$ (1.60 g, 5.00 mmol) was added to a two-necked flask under nitrogen, which is equipped with a rubber septum and a stopcock connected to a Schlenk line. Then anhydrous C_6H_6 (20 mL) was added, followed by 1-methyl-1*H*-indole (0.656 g, 5.00 mmol) dissolved in C_6D_6 (10 mL) via syringe through the rubber septum. The reaction mixture was allowed to stir for 1 h at 23 °C. After completion of the reaction, as monitored by the ^1H NMR spectroscopy; The benzene was removed under vacuum and then cold *n*-pentane (20 mL) was added to the mixture and the white slurry was filtered via a fret. The solid was washed with cold *n*-pentane (3 × 5 mL). The residue was concentrated in vacuo and pure C2 borylated indole was obtained quantitatively as a pale white solid (2.25 g, 97%).

2.6 Functionalization attempts:

To a stirred solution of **1** (45.7 mg, 0.10 mmol) in THF (2 mL), the base in THF (0.12 mmol base, 1 mL THF) was added. The reactions were monitored by ^1H spectroscopy (Figure S71-S73).



Pyridine
THF, 80 °C, 24 h
2,6-lutidine
THF, 80 °C, 24 h
NEt3
THF, 80 °C, 24 h
nBuLi
THF, 23 °C, 1 h
Complex reaction mixture
BH^MeoCb2
N
Me

3. X-ray Crystallographic Data:

Table **S2**: X-ray crystallographic details for **1** and **4**

	1	**4**
CCDC	2419319	2419318
Empirical Formula	$C_{31}H_{74}B_{42}N_2Cl_2$	$C_{14}H_{34}B_{21}N_1$
FW (g/mol)	999.84	443.43
Crystal System	orthorhombic	monoclinic
Space Group	*Pbca*	*C* 2/*c*
a (Å)	15.5145(5)	32.8033(13)
b (Å)	18.9095(6)	7.9130(3)
c (Å)	38.3552(12)	22.6862(10)
α (deg)	90	90
β (deg)	90	119.452(1)
γ (deg)	90	90
V ($Å^3$)	11252.3(6)	5127.7(4)
Z	8	8
D_c (g cm^{-3})	1.180	1.149
Radiation λ (Å)	0.71073	0.71073
Temp (K)	150	150
$R1$ [I>2(σ)I][a]	0.0537	0.0419
w$R2$ (F^2)[a]	0.1543	0.1112
GOF (S)[a]	1.092	1.069

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

4. NMR and IR Spectra:

Figure S1: ^1H NMR (400 MHz) spectrum of **1** in $CDCl_3$

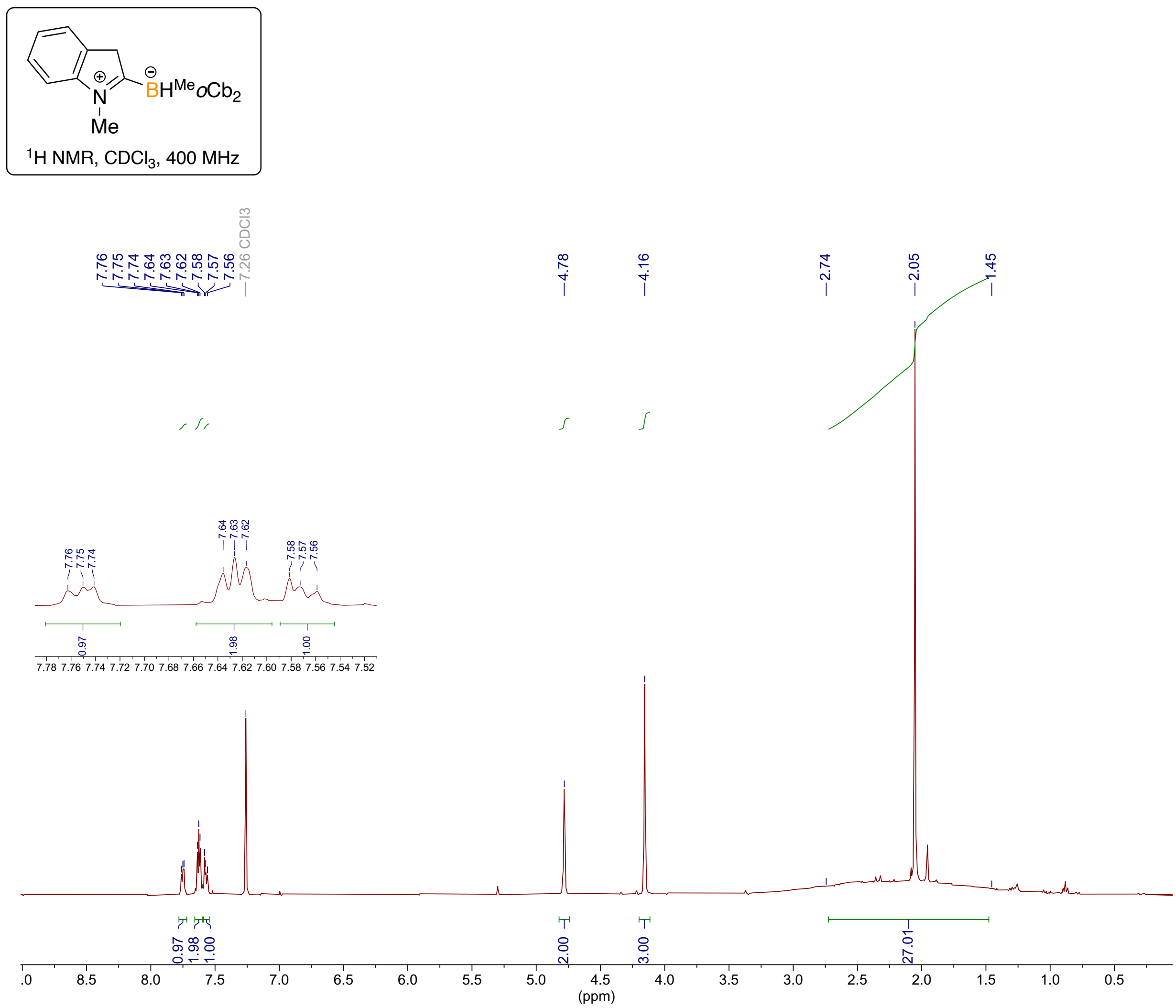


Figure S2: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **1** in $CDCl_3$

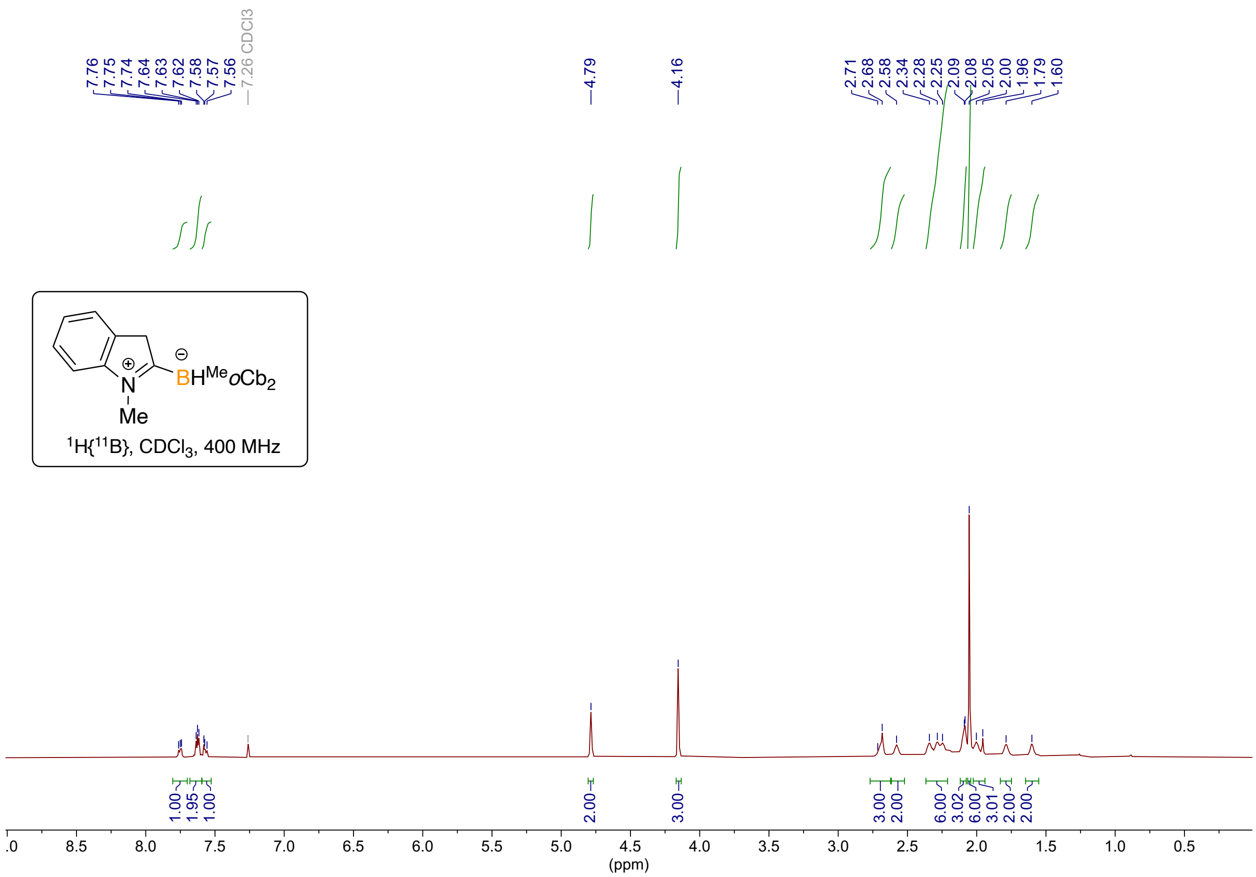


Figure S3: $^{13}C\{^1H\}$ NMR (101 MHz) spectrum of **1** in $CDCl_3$

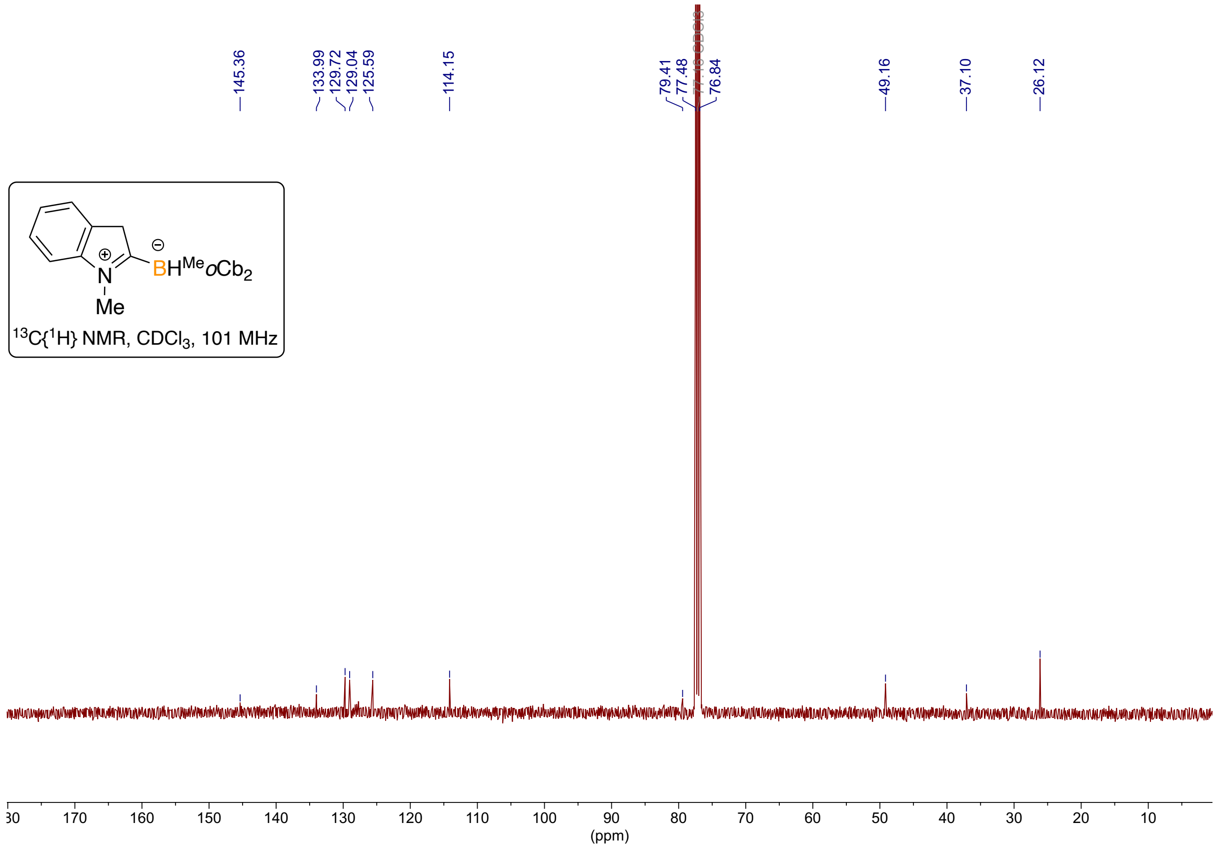


Figure S4: $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of **1** in $CDCl_3$

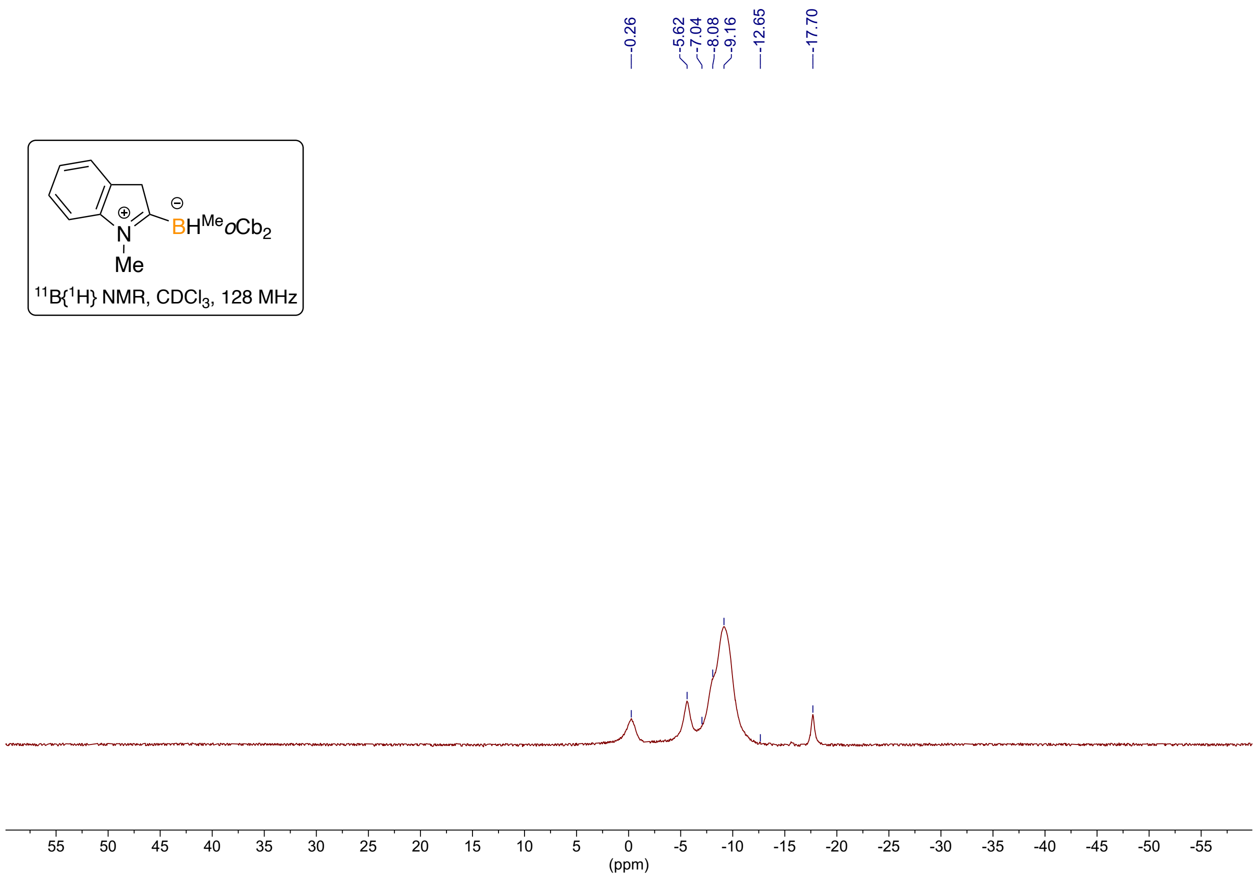
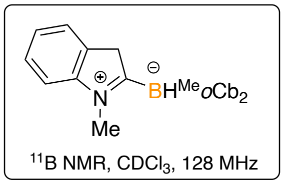


Figure S5: ^{11}B NMR (128 MHz) spectrum of **1** in $CDCl_3$



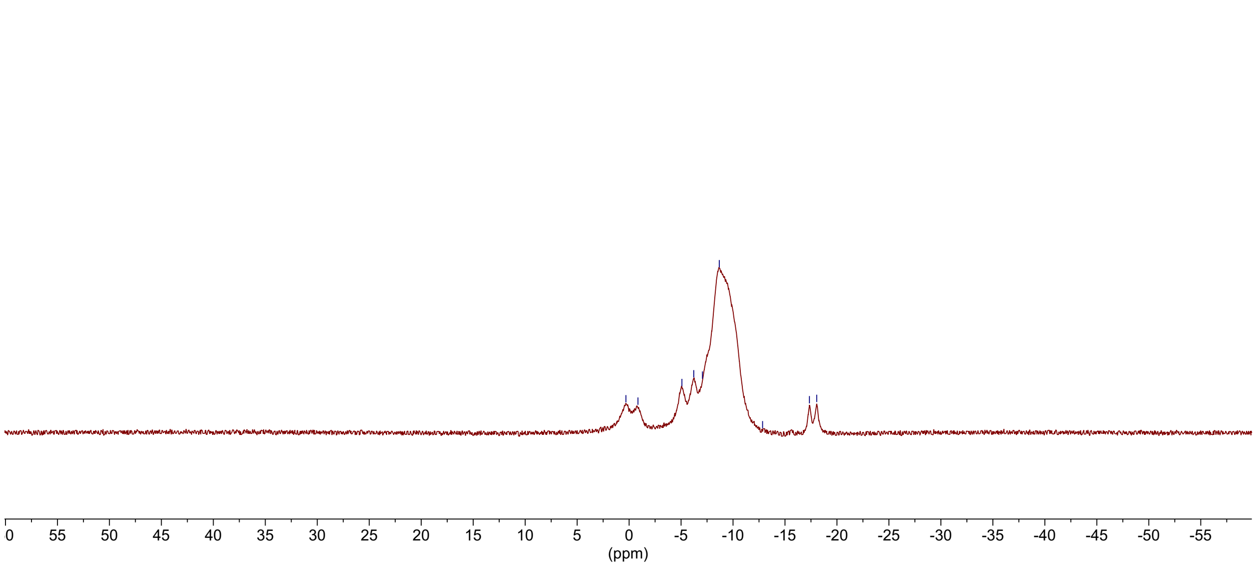


Figure S6: FT-IR spectrum of **1**

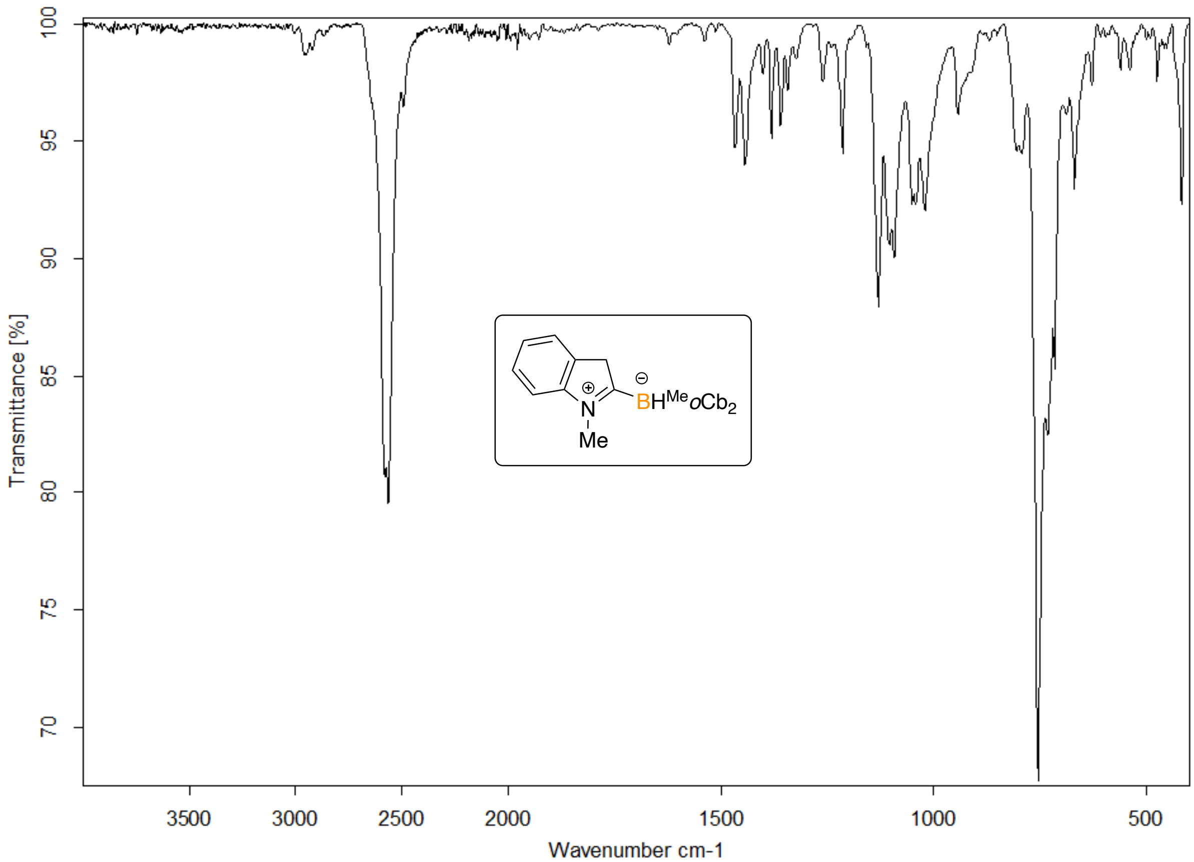


Figure S7: ^{1}H NMR (400 MHz) spectrum of **2** in $CDCl_3$

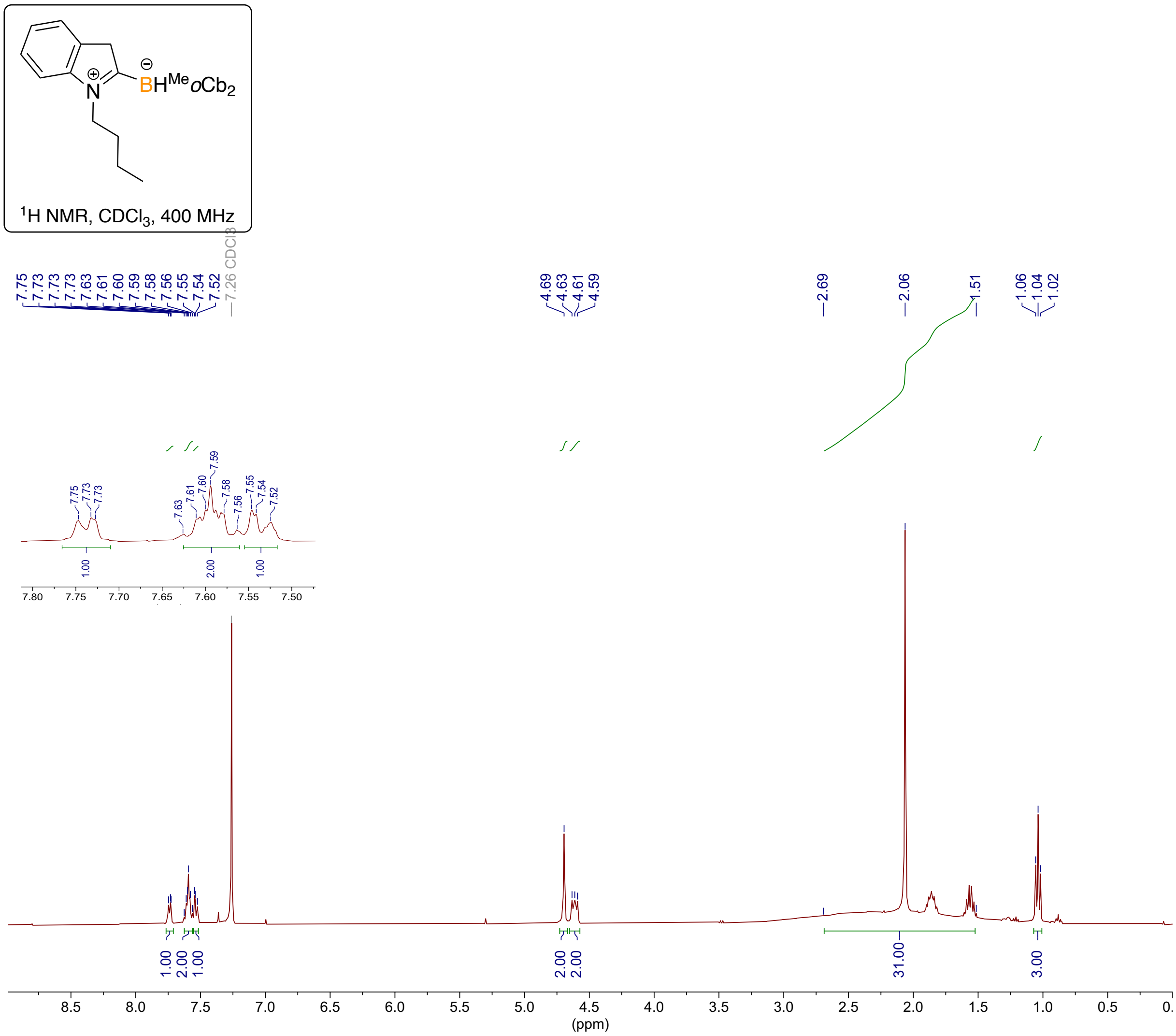


Figure S8: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **2** in $CDCl_3$

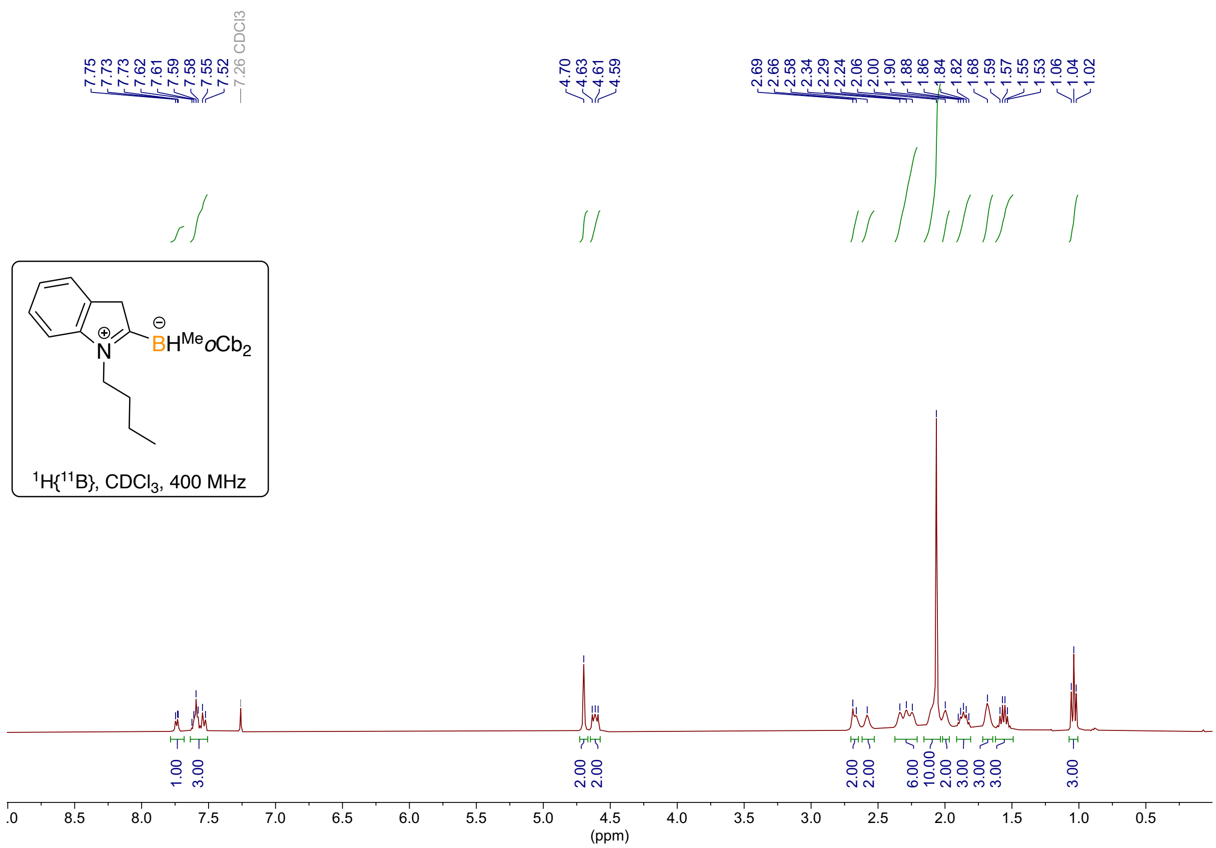


Figure S9: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **2** in $CDCl_3$

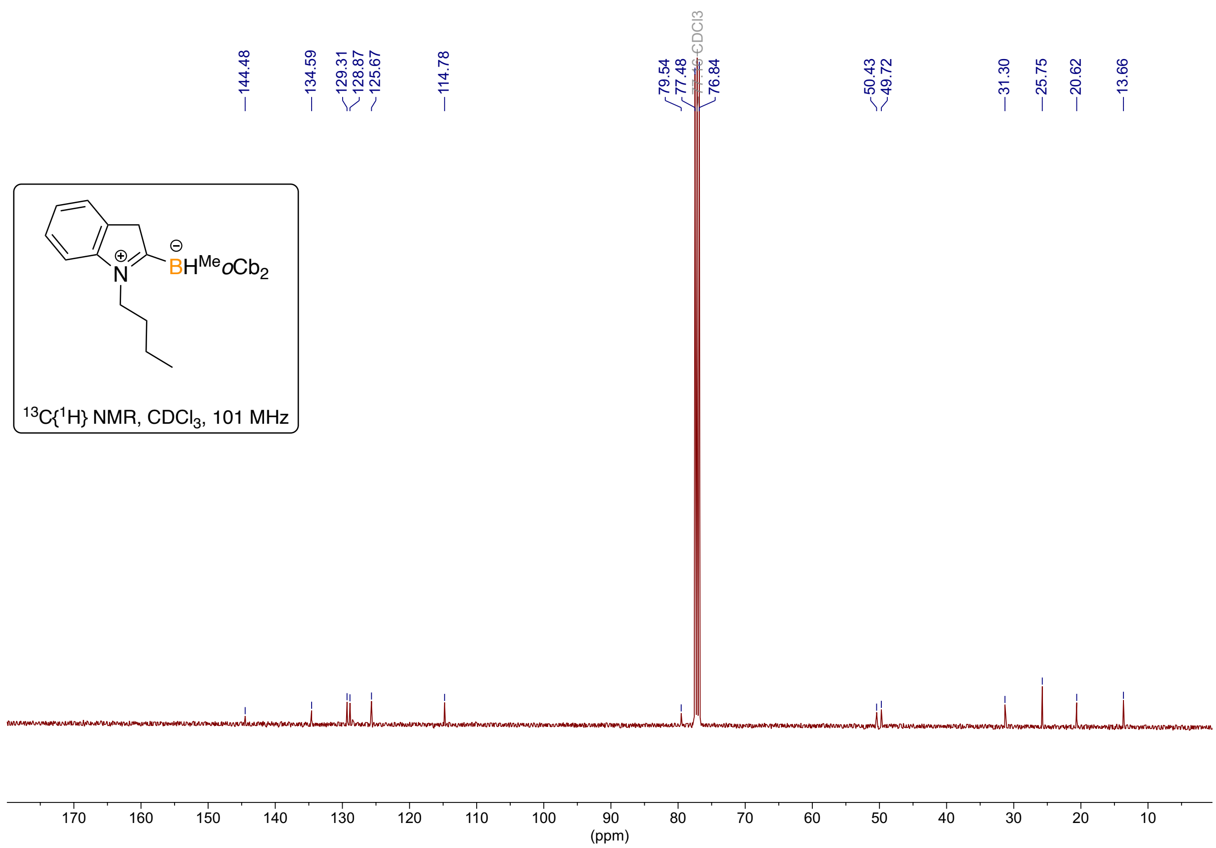


Figure S10: $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of **2** in $CDCl_3$

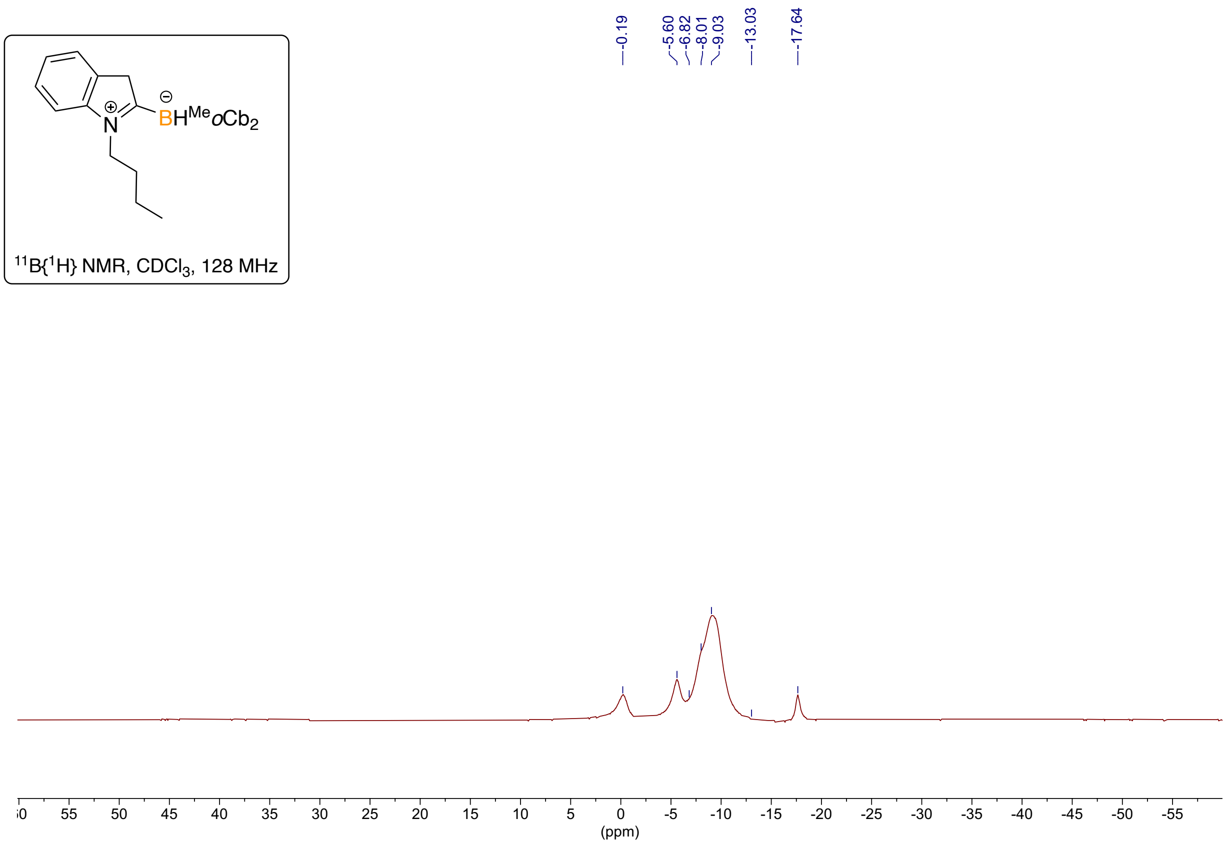


Figure S11: ^{11}B NMR (128 MHz) spectrum of **2** in $CDCl_3$

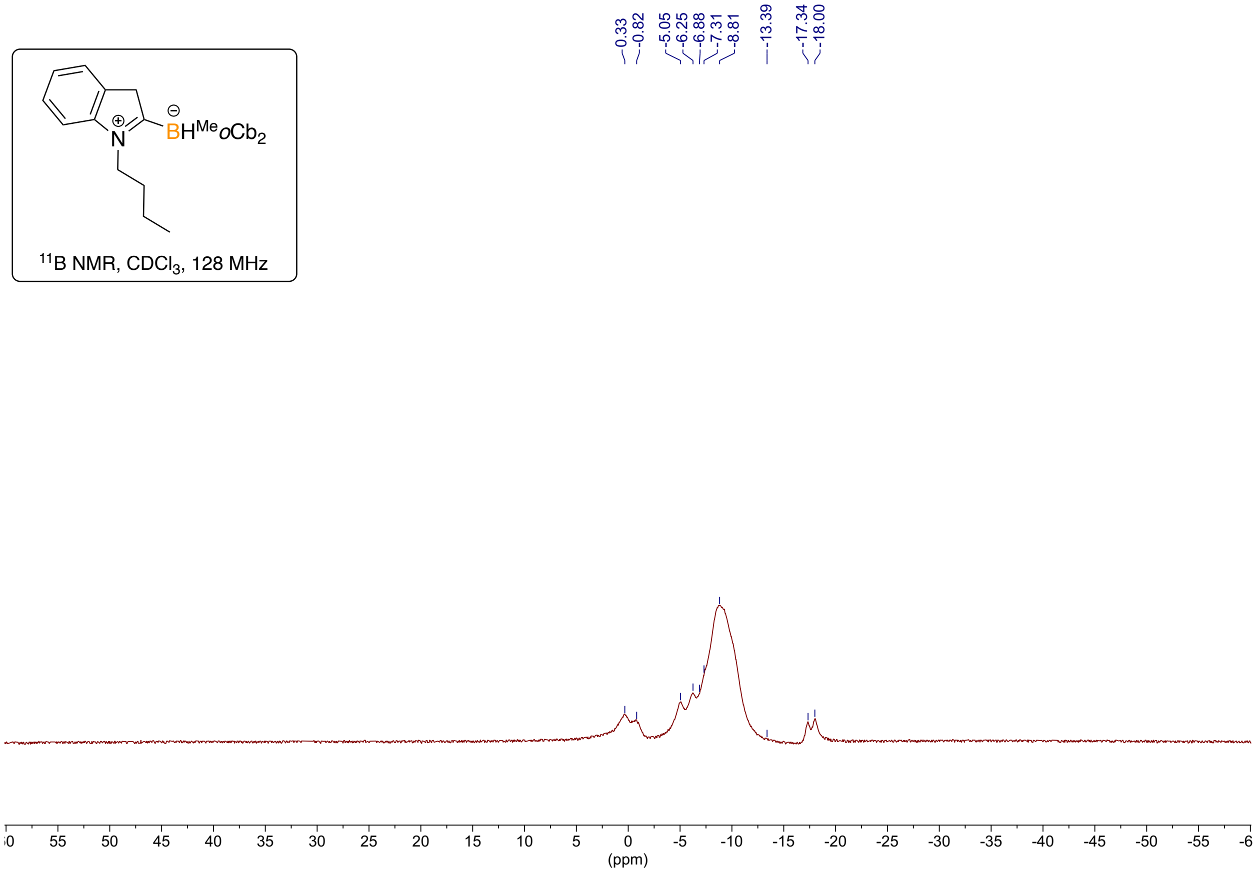


Figure S12: FT-IR spectrum of **2**

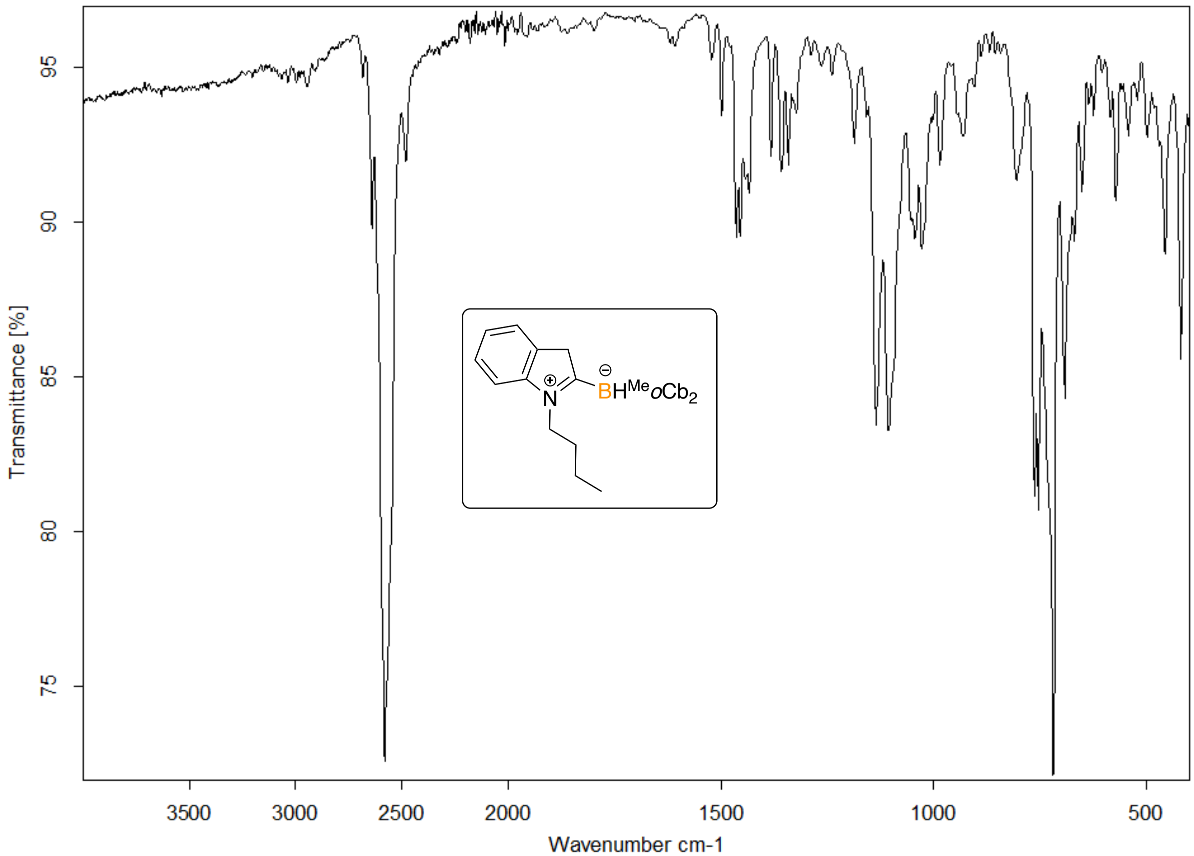


Figure S13: ^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$

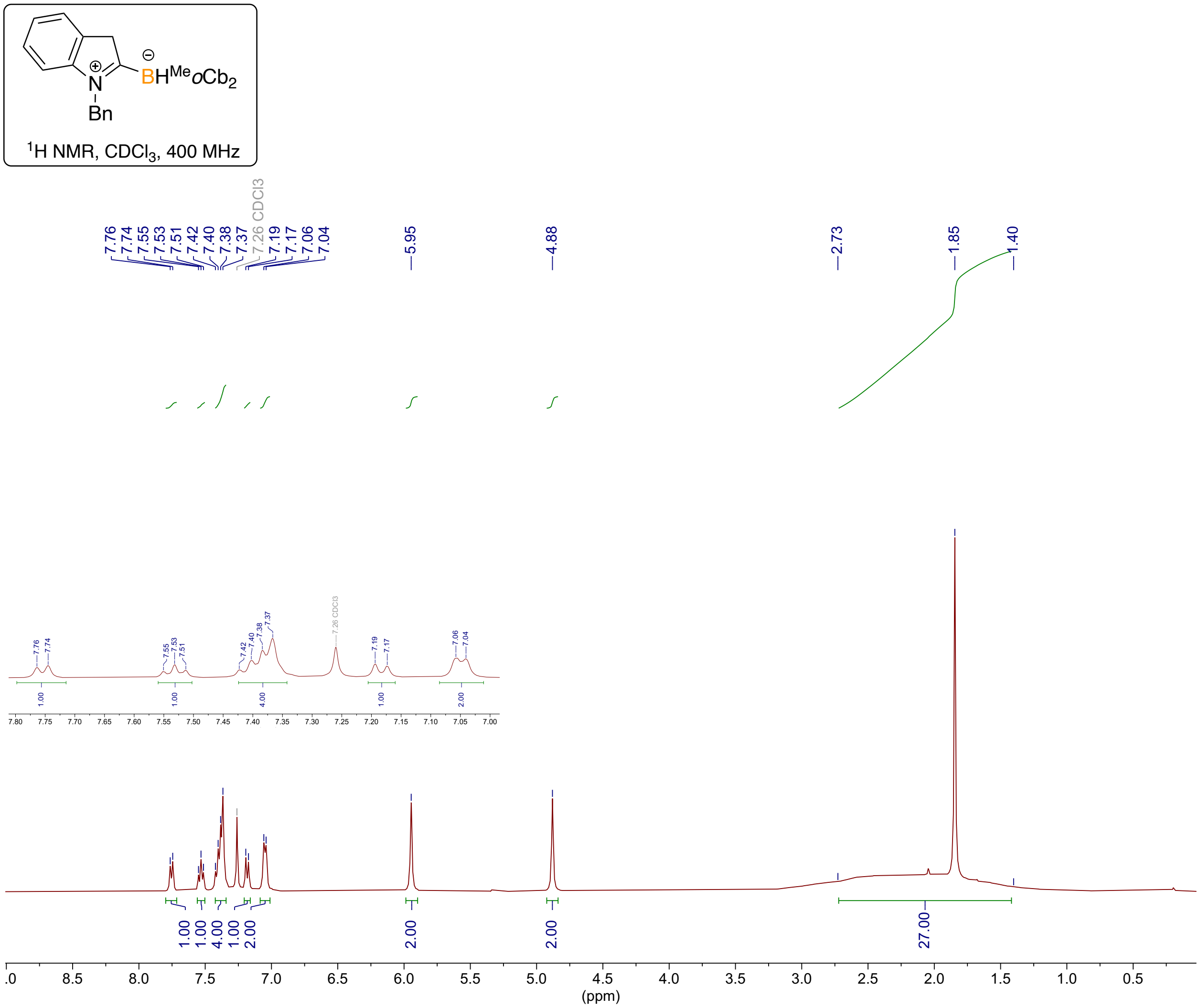


Figure S14: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **3** in $CDCl_3$

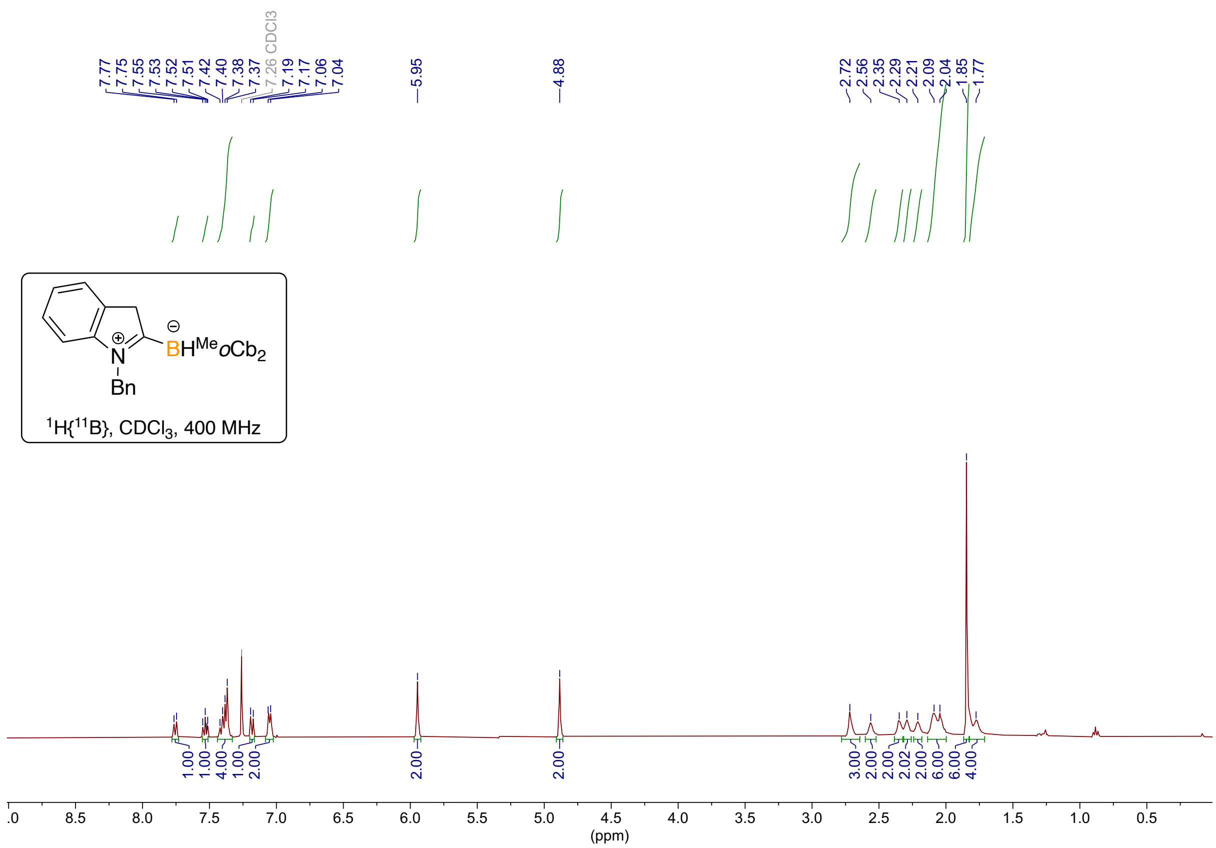


Figure S15: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **3** in $CDCl_3$

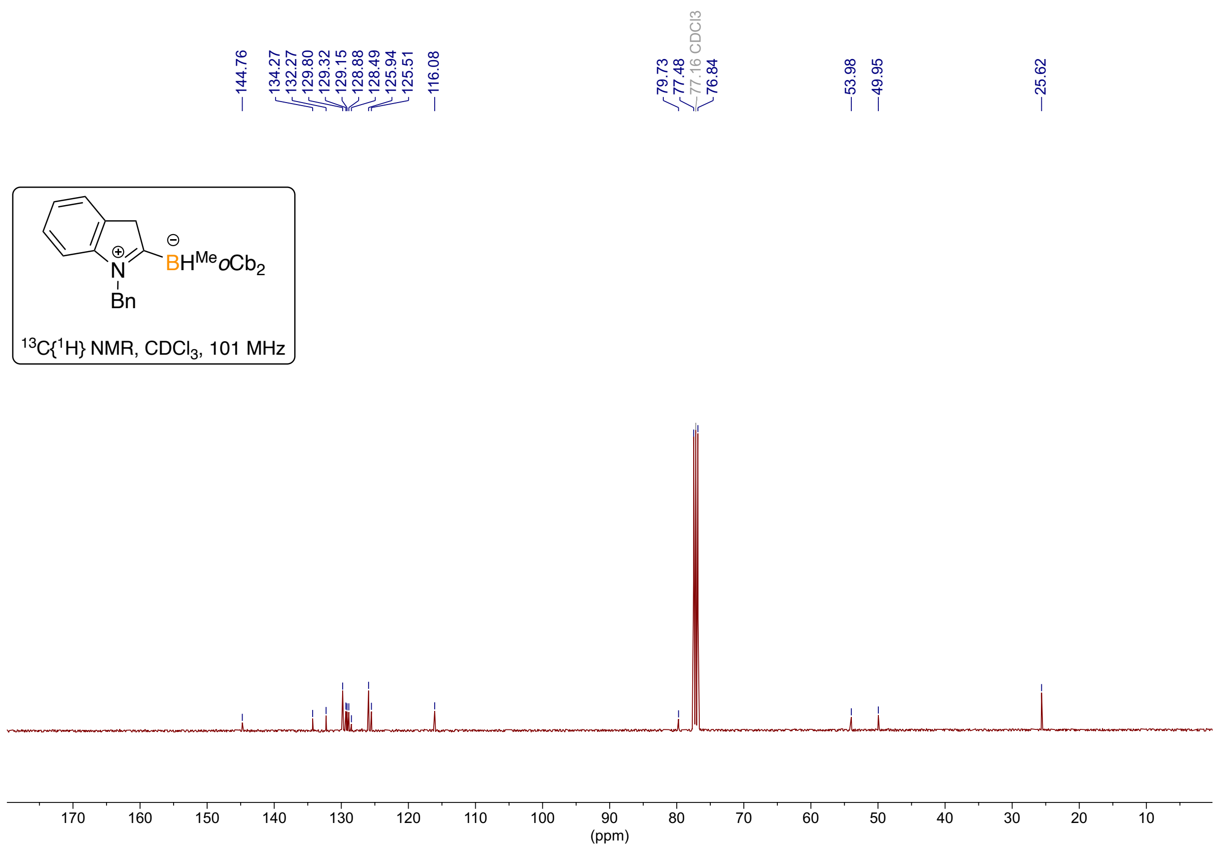


Figure S16: $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of **3** in $CDCl_3$

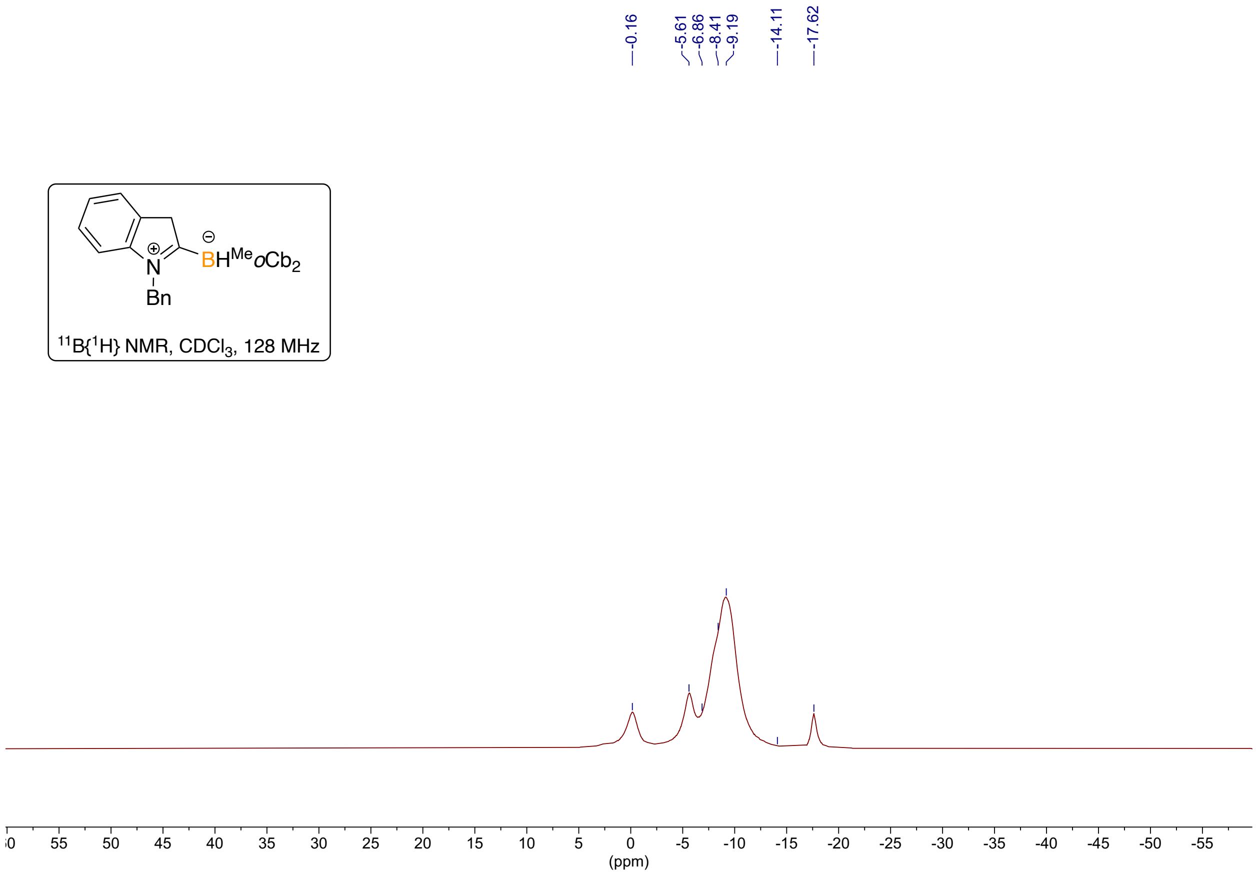


Figure S17: ^{11}B NMR (128 MHz) spectrum of **3** in $CDCl_3$

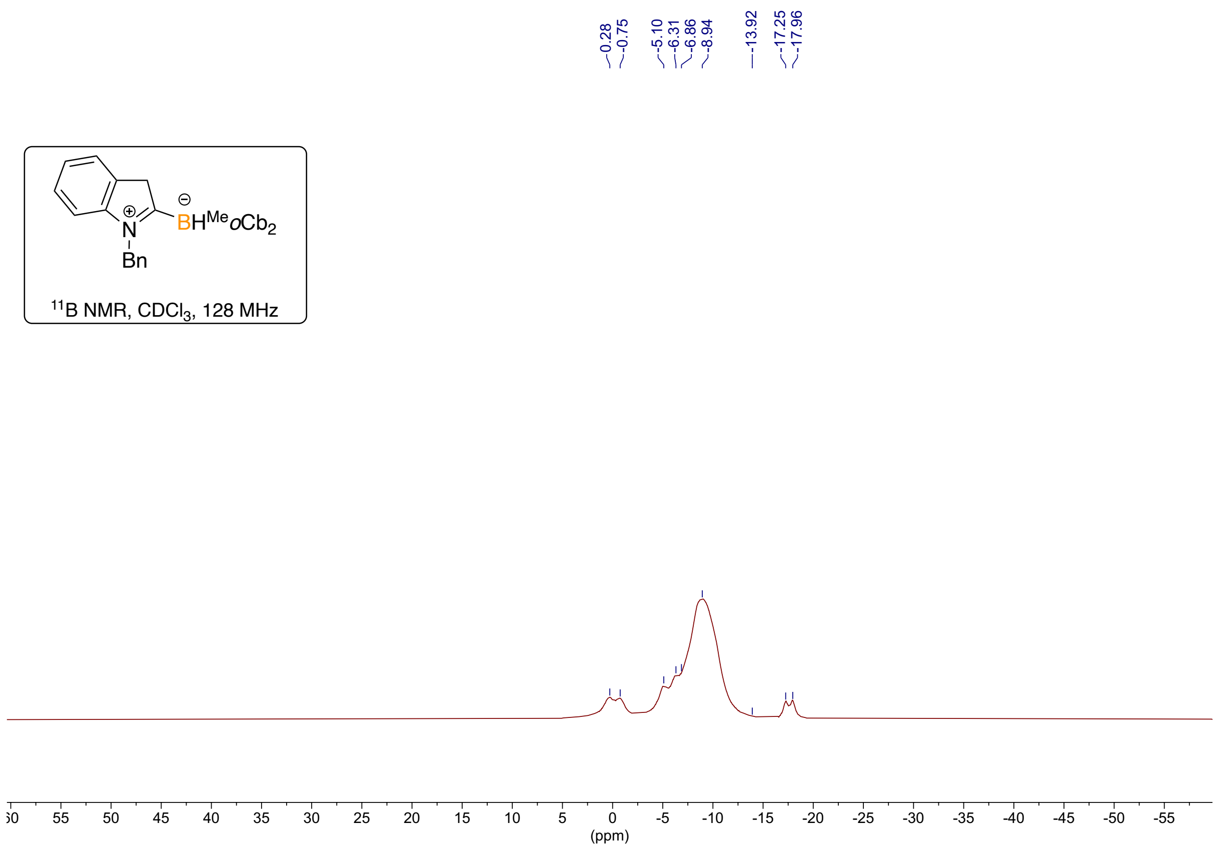


Figure S18: FT-IR spectrum of **3**

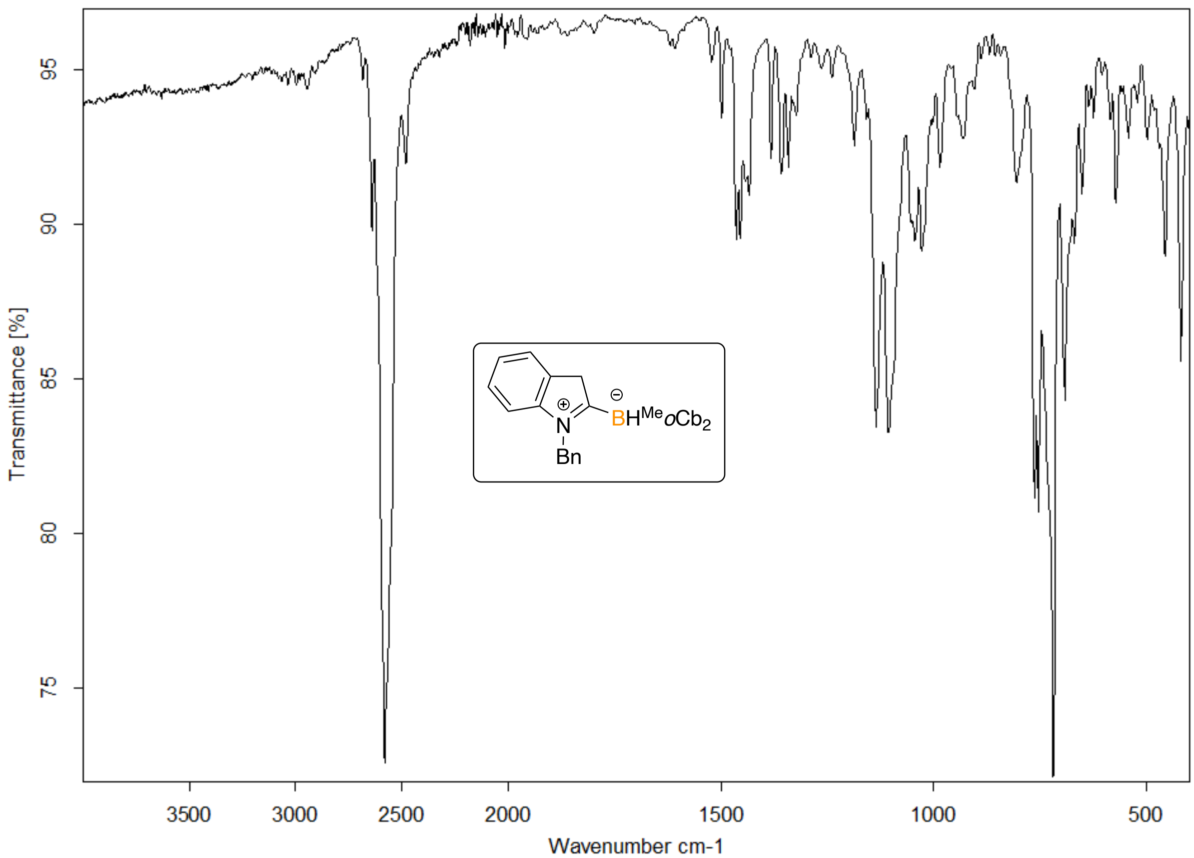
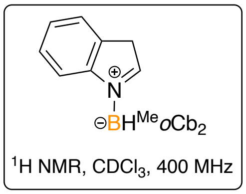


Figure S19: ^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$



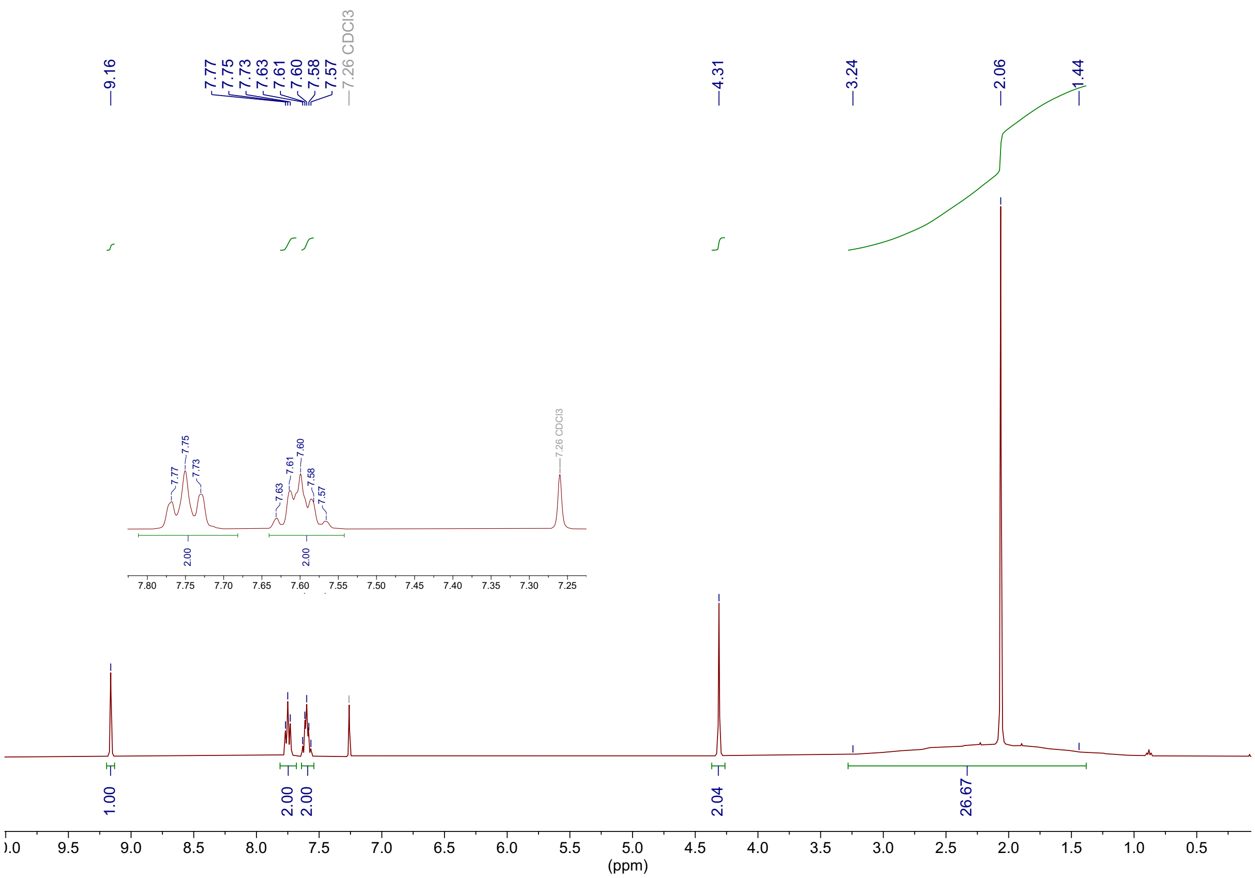


Figure S20: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **4** in $CDCl_3$

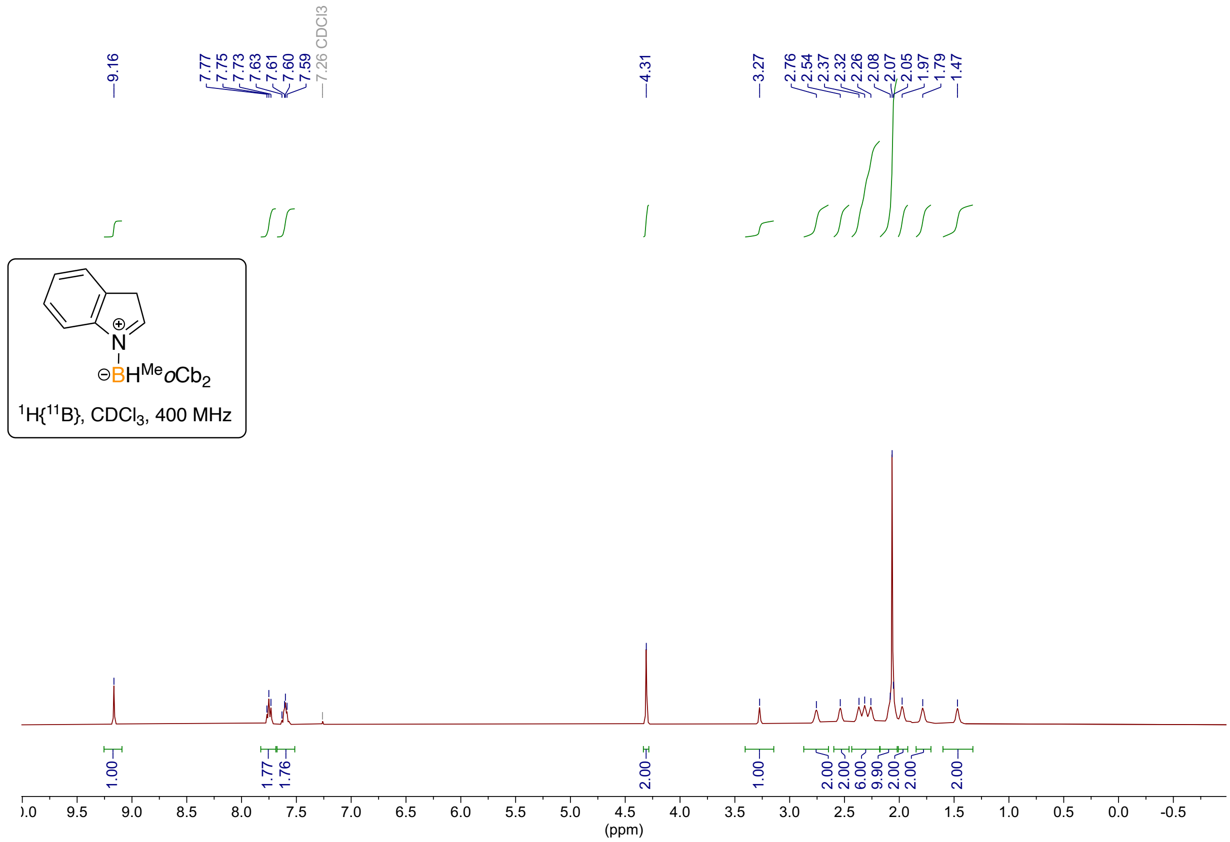


Figure S21: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **4** in $CDCl_3$

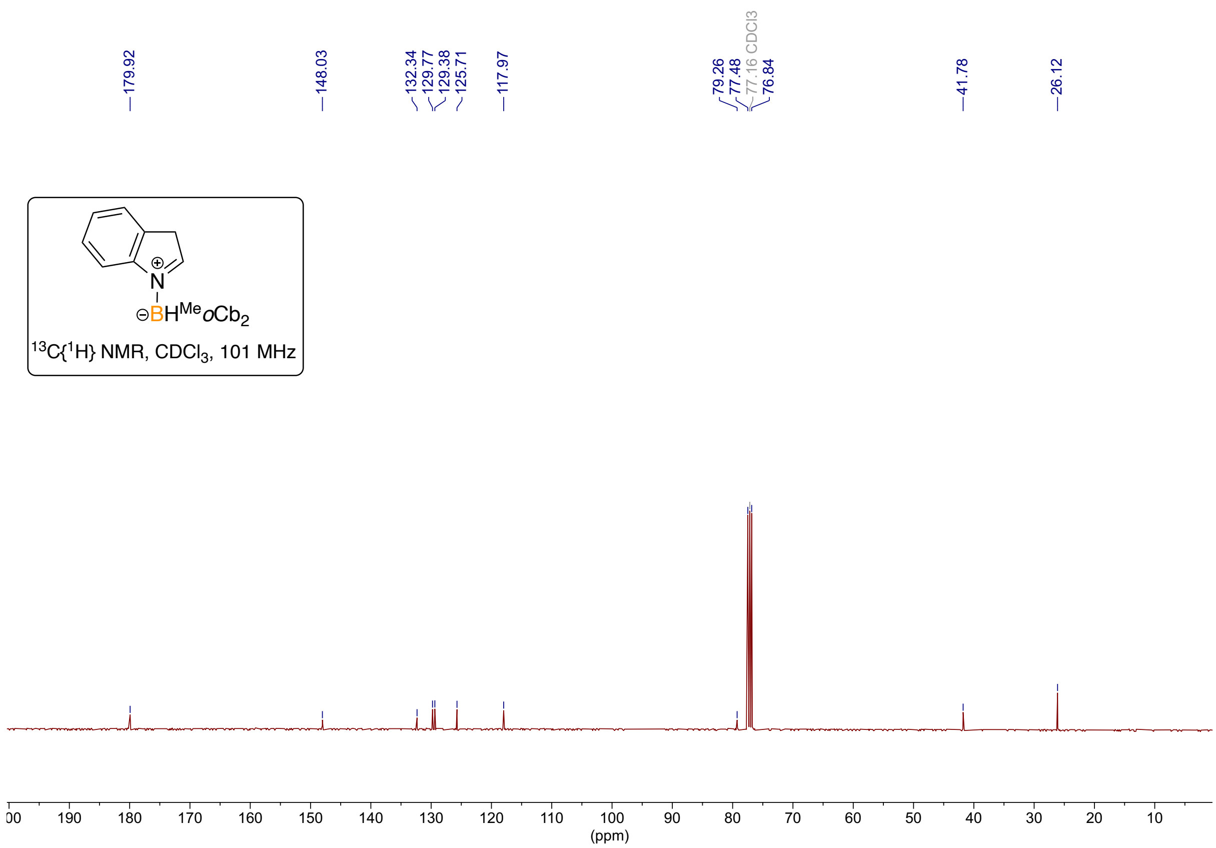
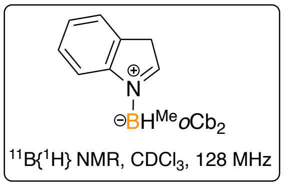


Figure S22: $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of **4** in $CDCl_3$



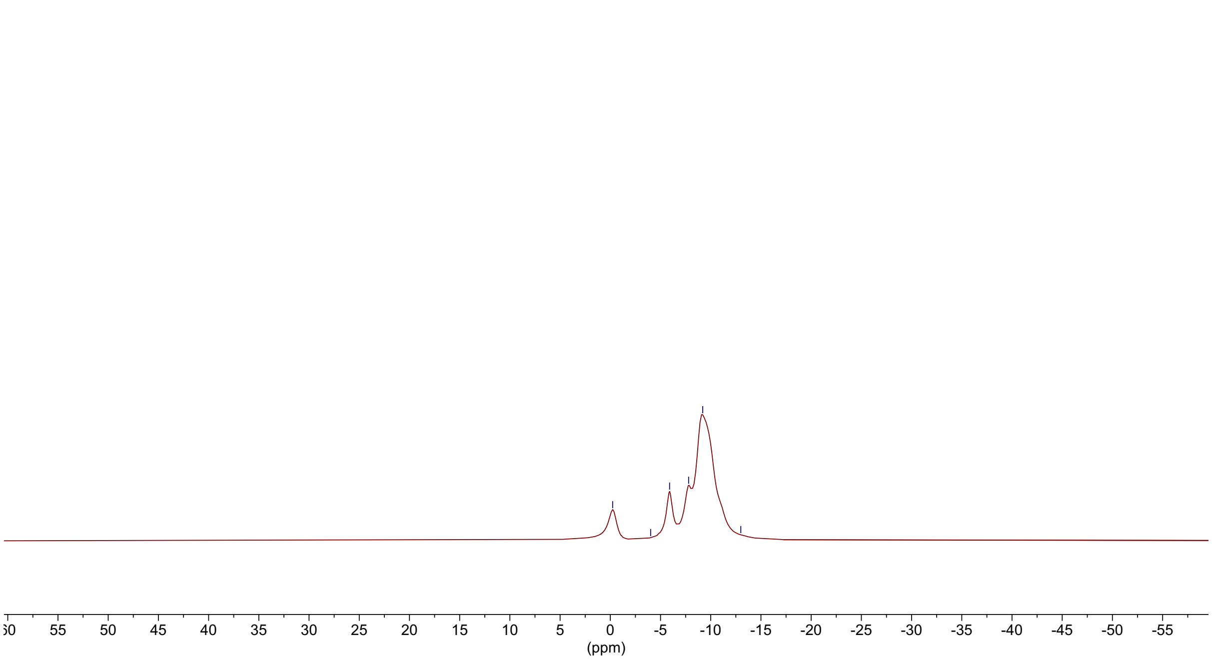
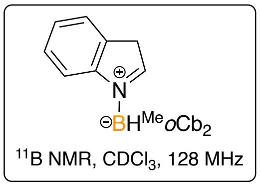


Figure S23: ^{11}B NMR (128 MHz) spectrum of **4** in $CDCl_3$



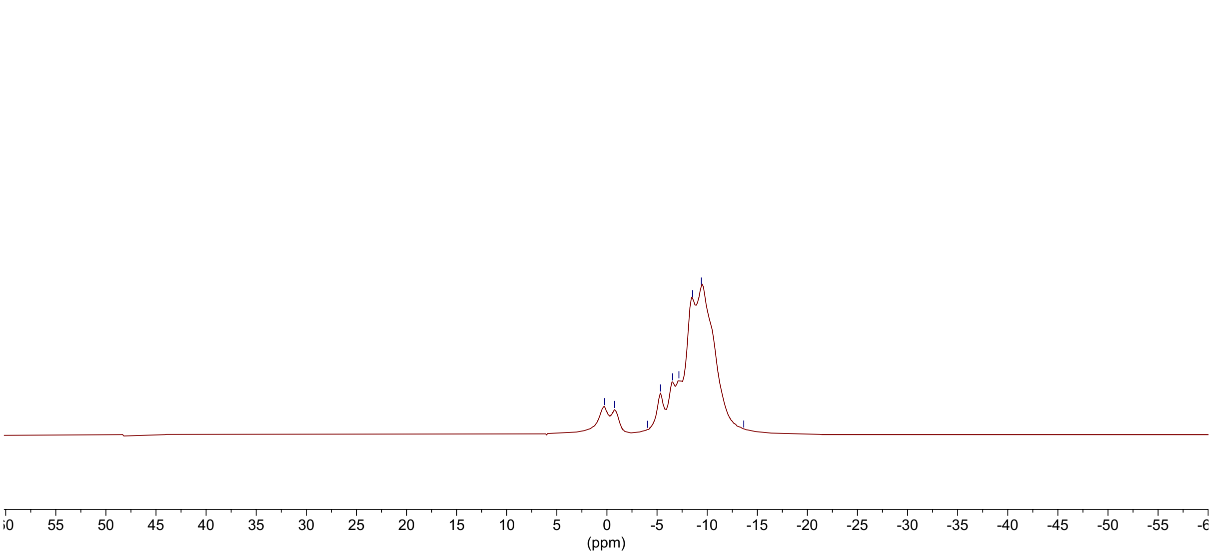


Figure S24: FT-IR spectrum of **4**

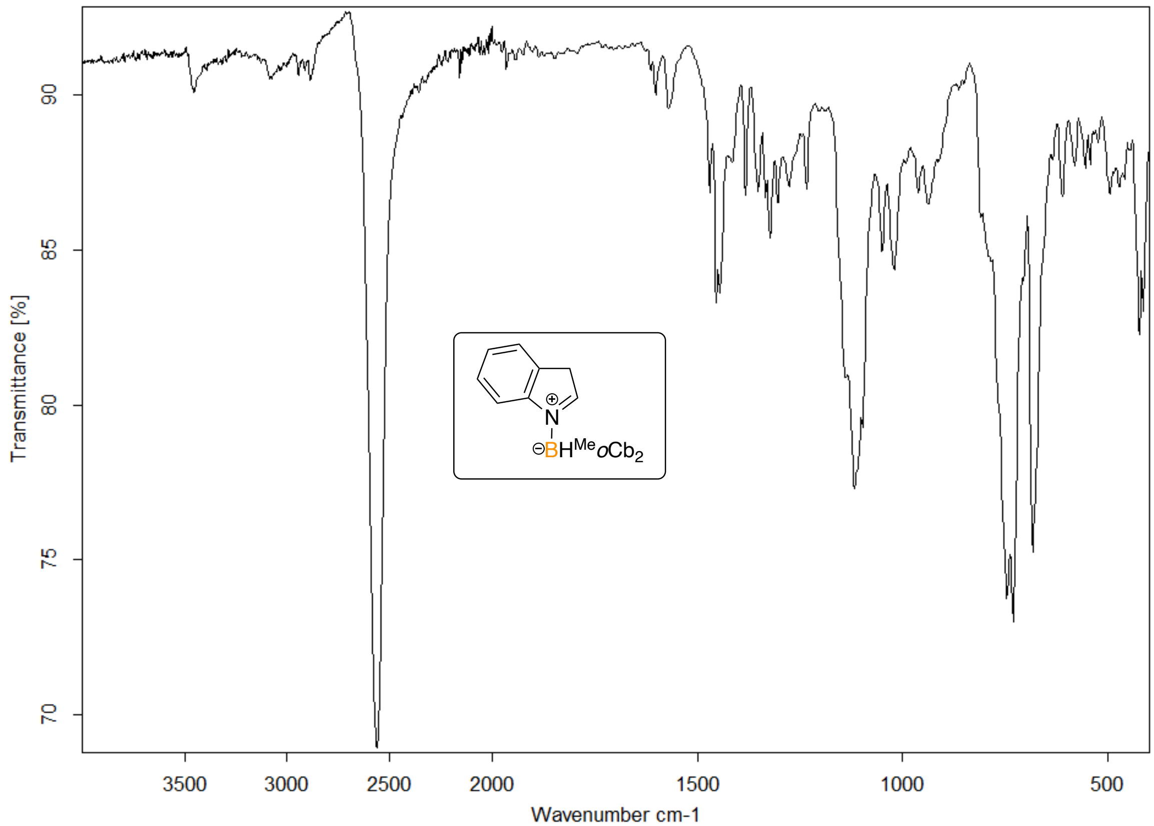


Figure S25: ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$ (* denotes residual C_6H_6)

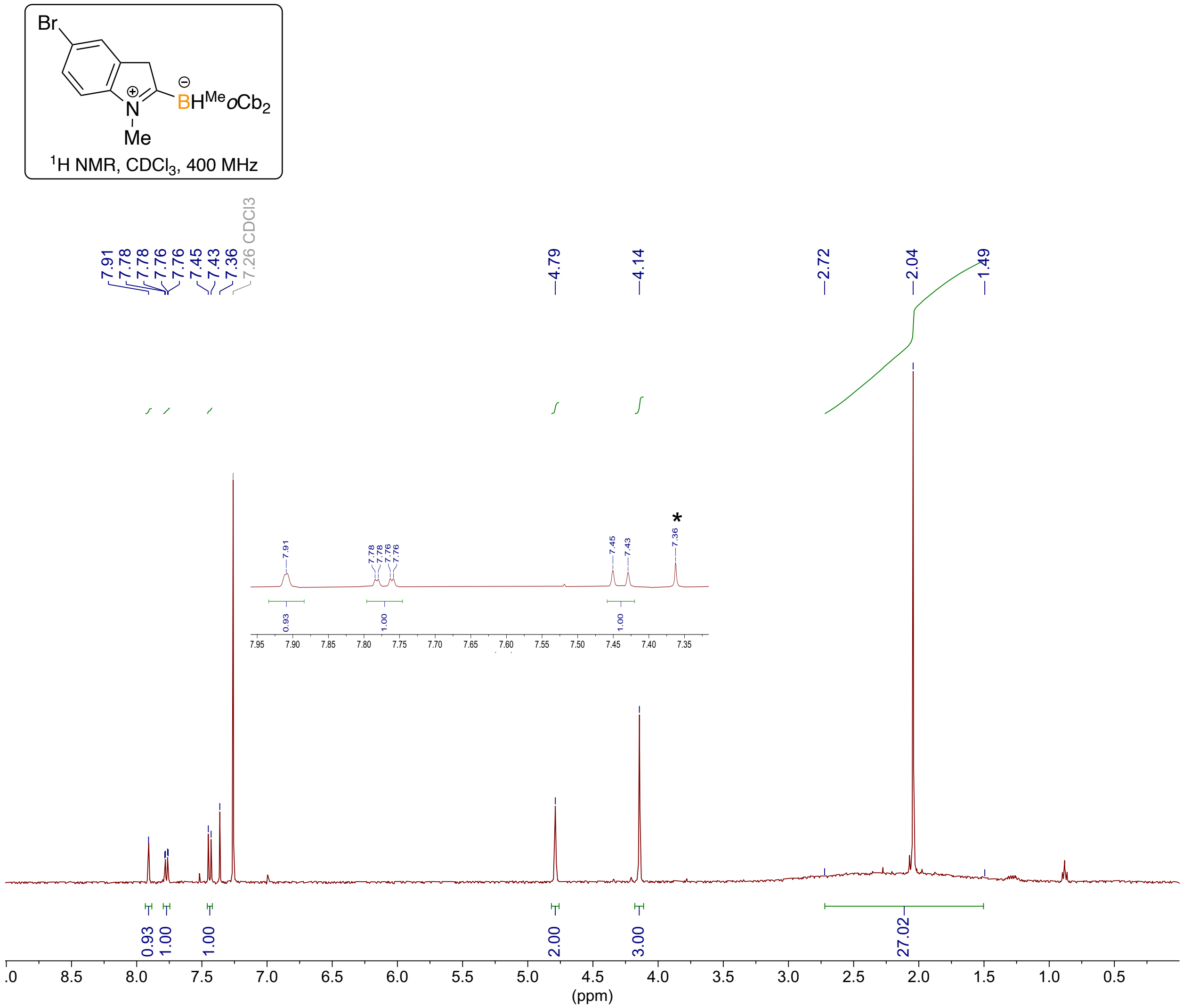


Figure S26: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **5** in $CDCl_3$

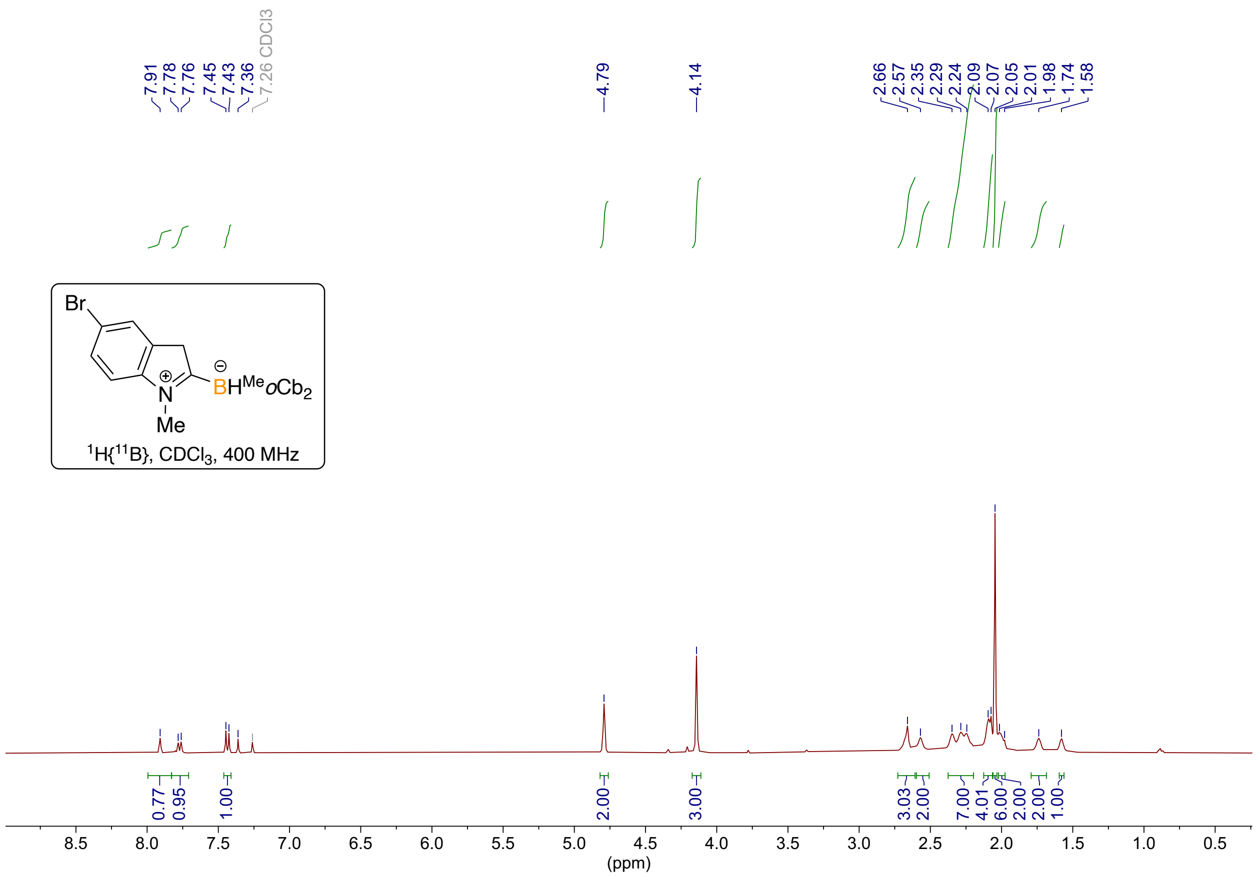


Figure S27: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **5** in $CDCl_3$

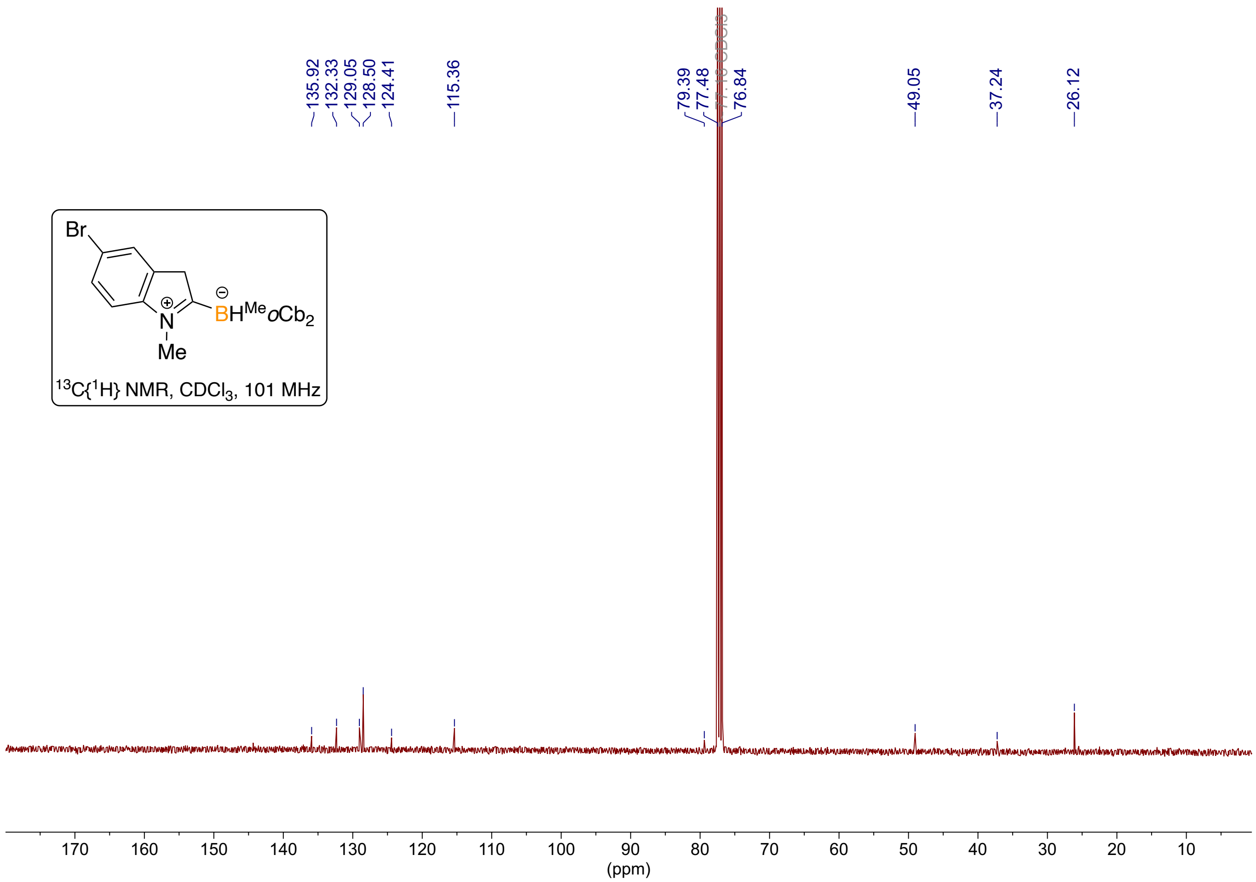
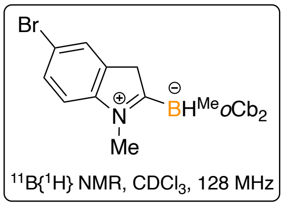


Figure S28: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **5** in $CDCl_3$



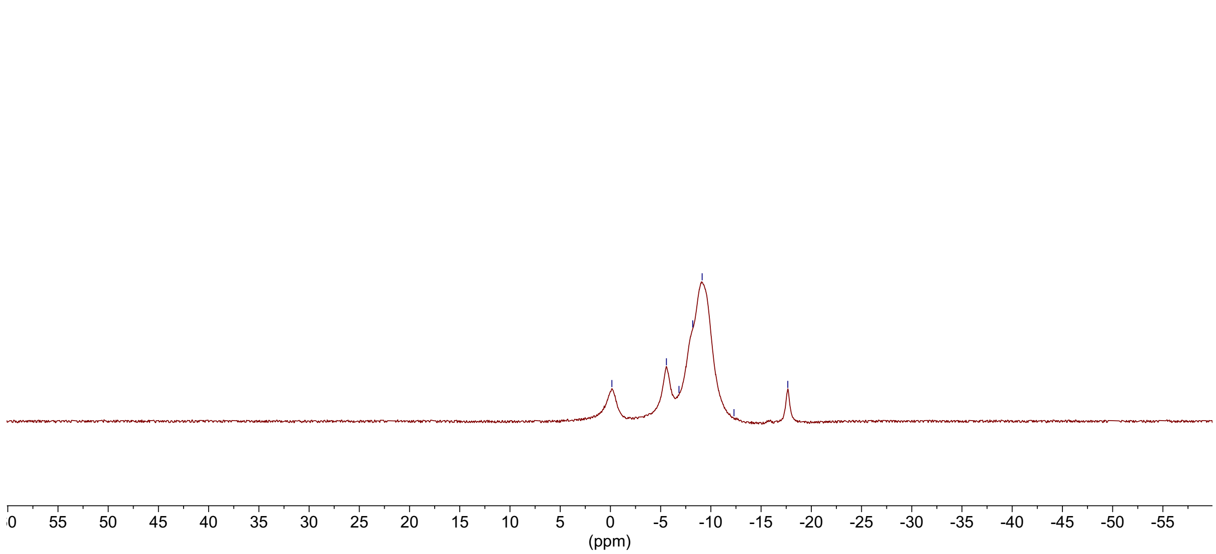
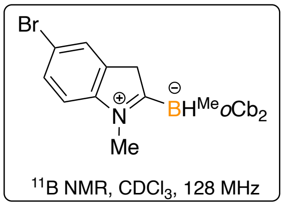


Figure S29: ^{11}B NMR (128 MHz) spectrum of **5** in $CDCl_3$



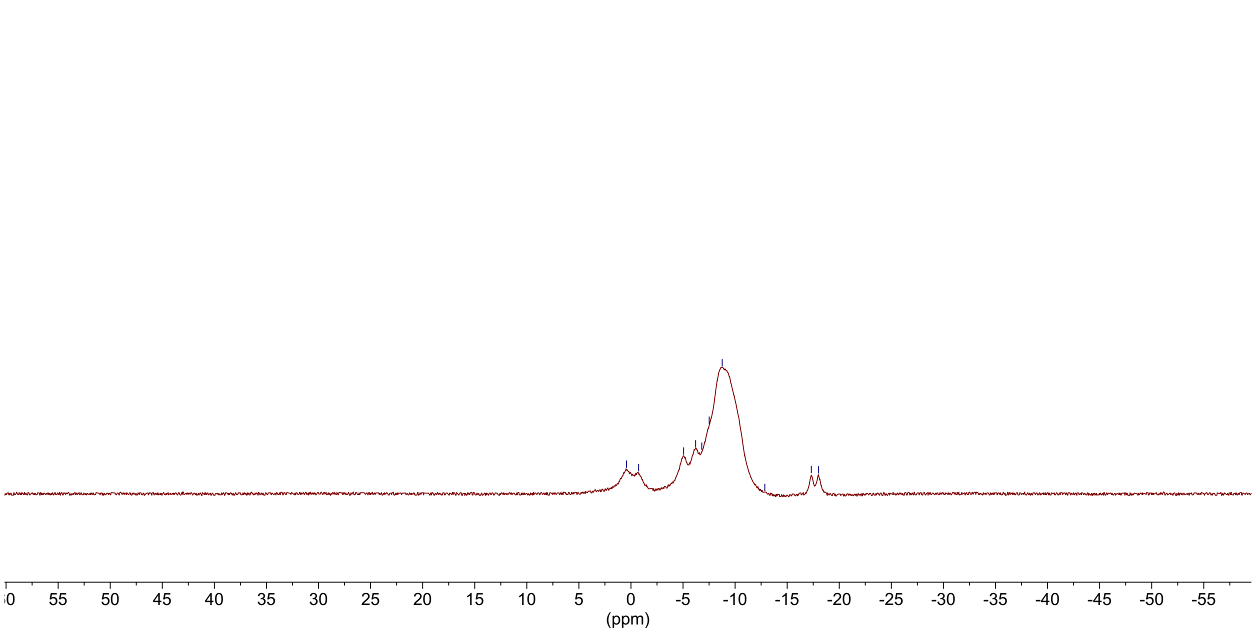


Figure S30: FT-IR spectrum of **5**

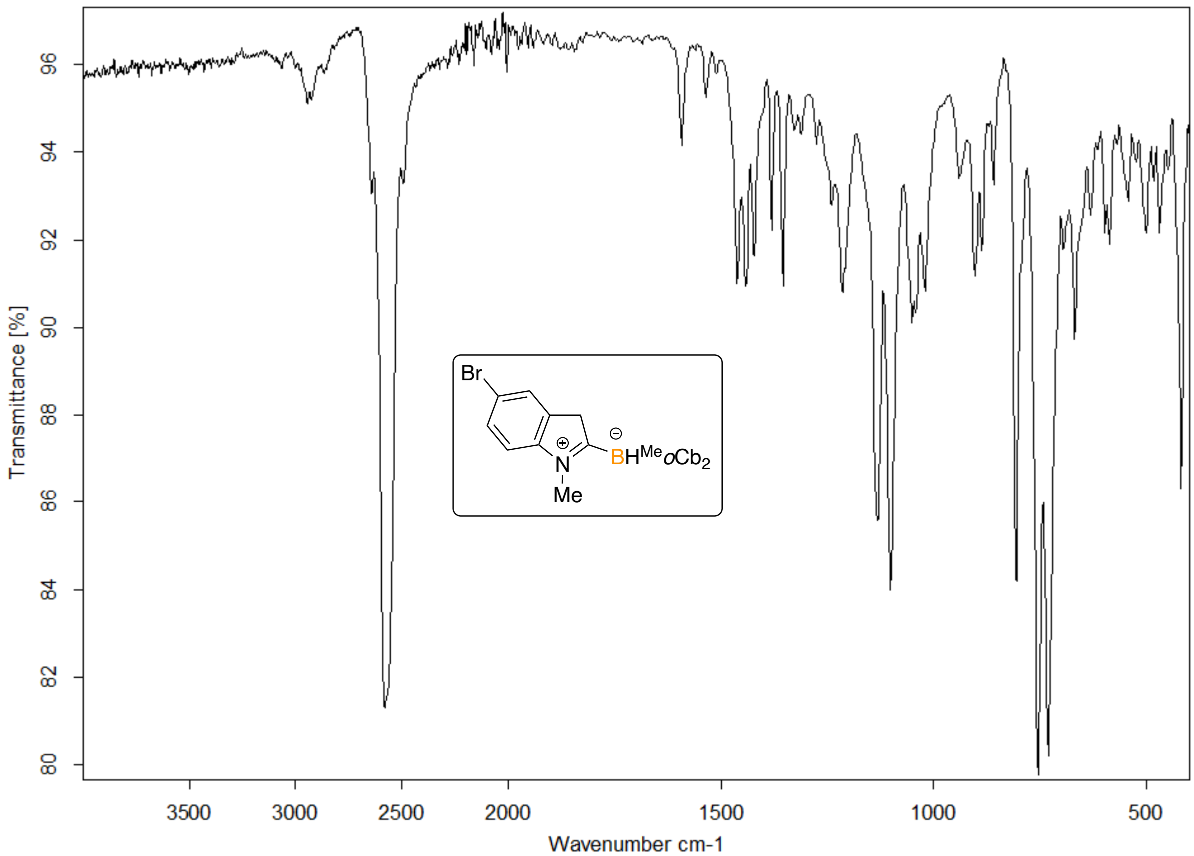


Figure S31: ^{1}H NMR (400 MHz) spectrum of **6** in $CDCl_3$

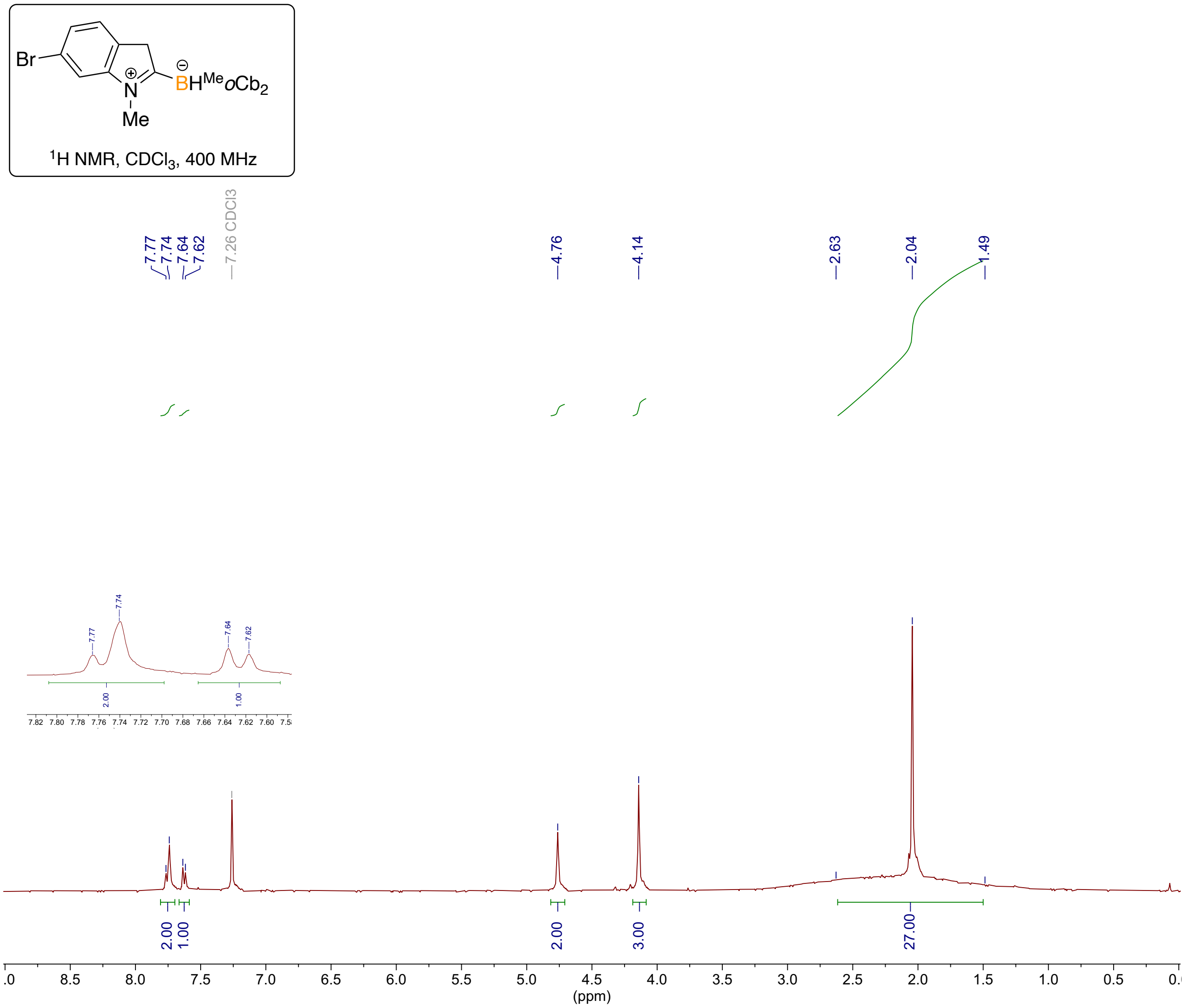


Figure S32: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **6** in $CDCl_3$

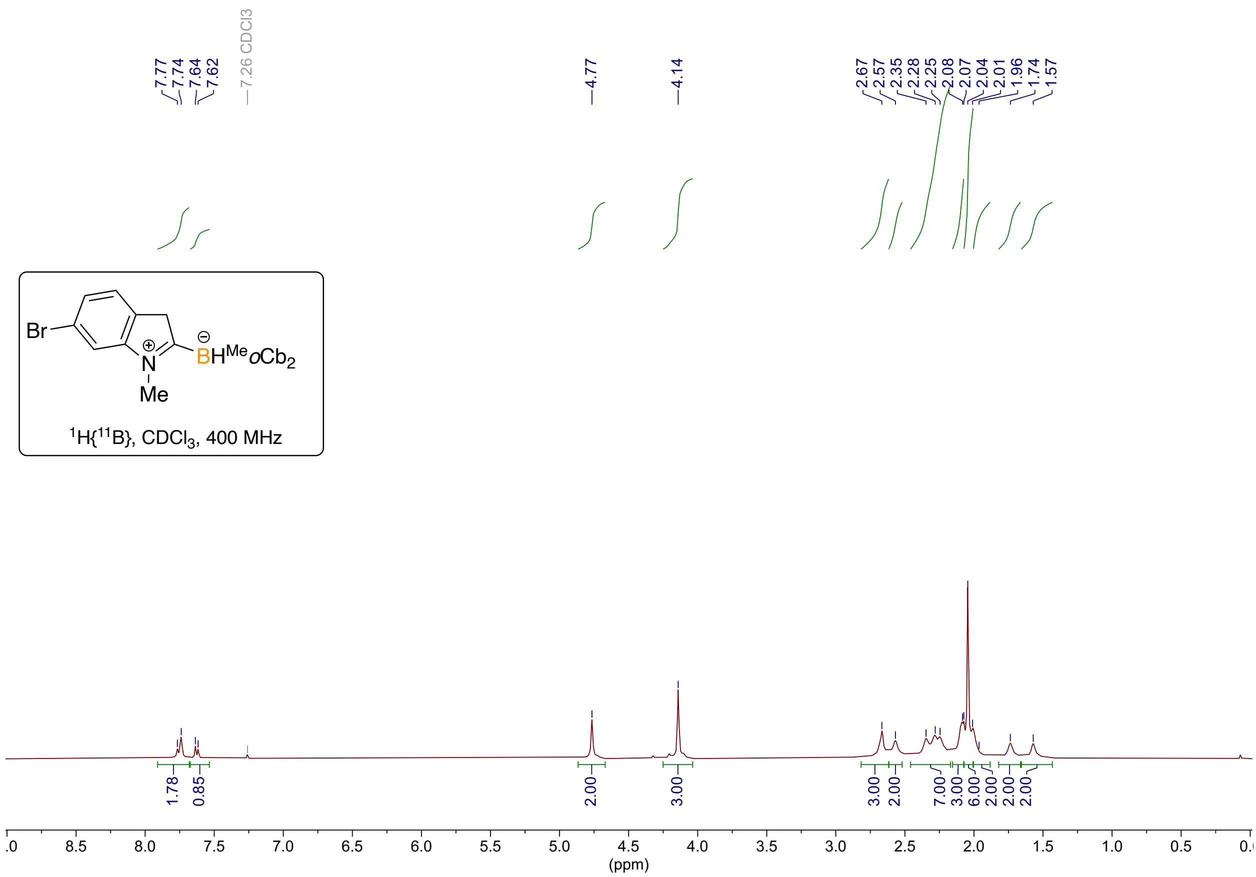


Figure S33: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **6** in $CDCl_3$

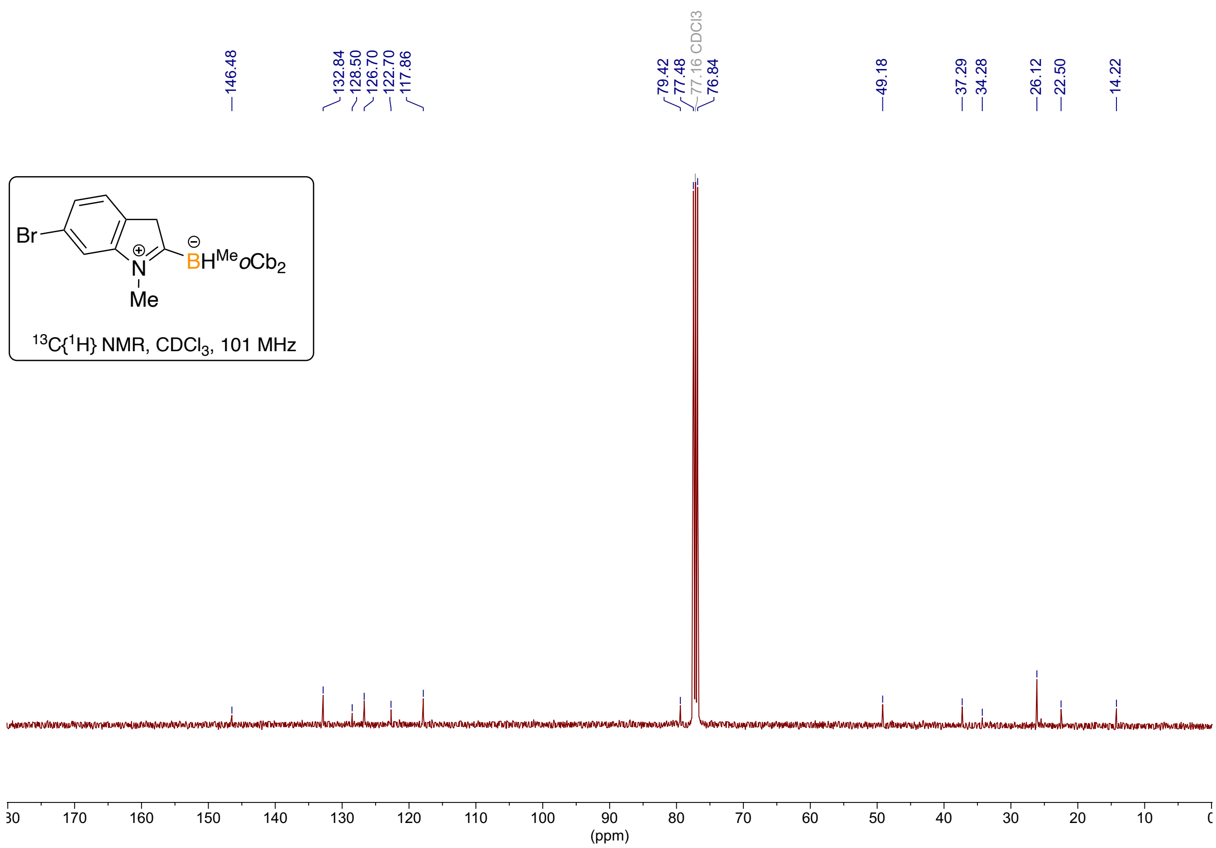


Figure S34: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **6** in $CDCl_3$

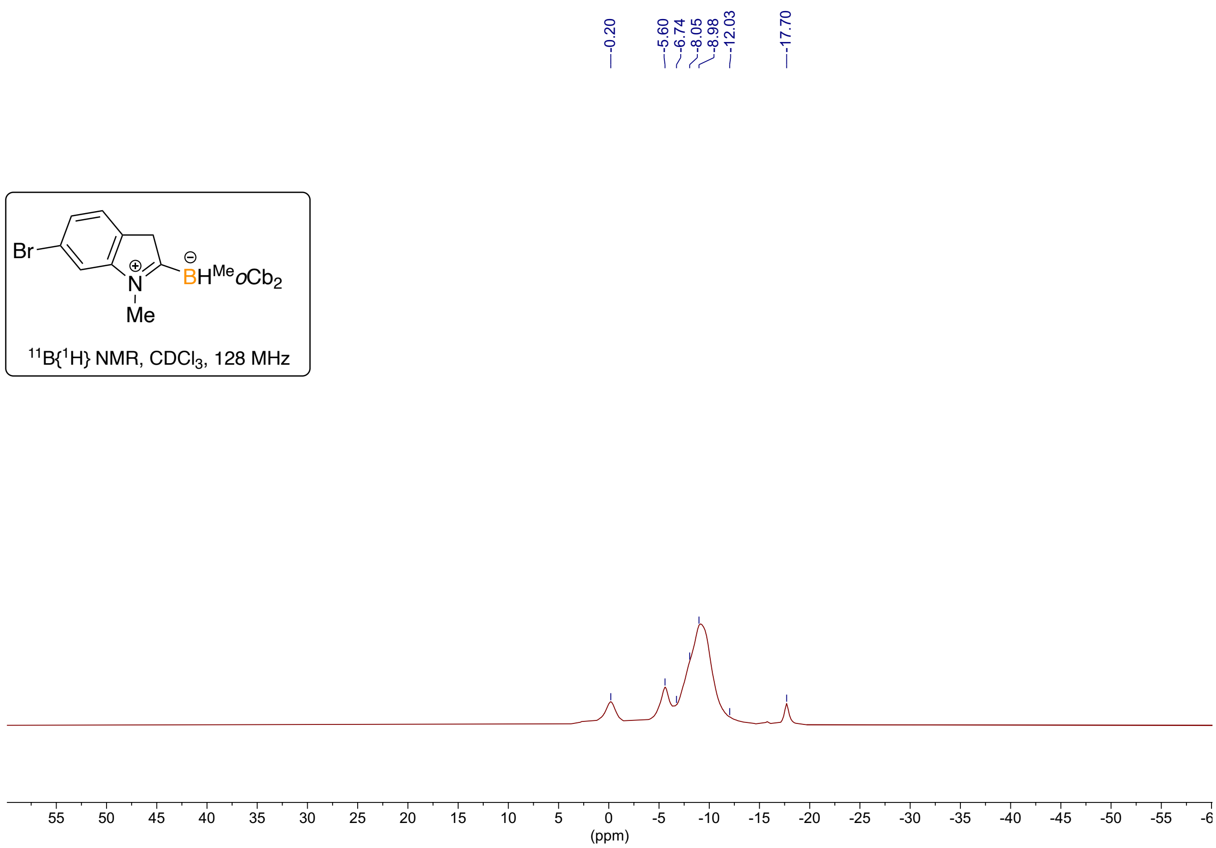
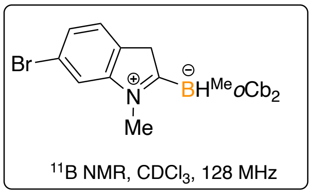


Figure S35: ^{11}B NMR (128 MHz) spectrum of **6** in $CDCl_3$



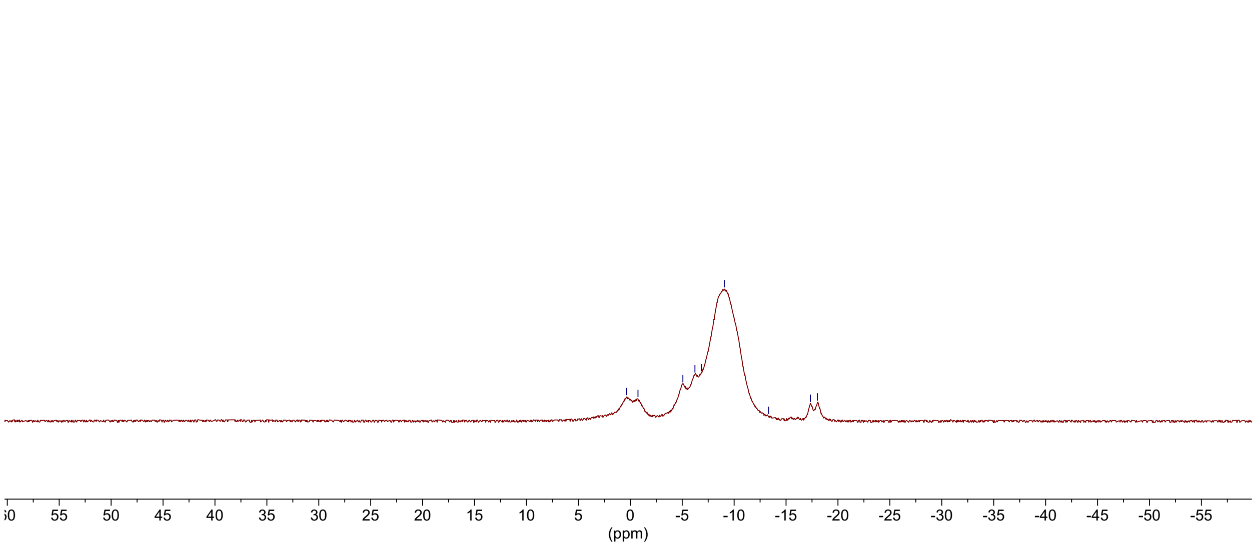


Figure S36: FT-IR spectrum of **6**

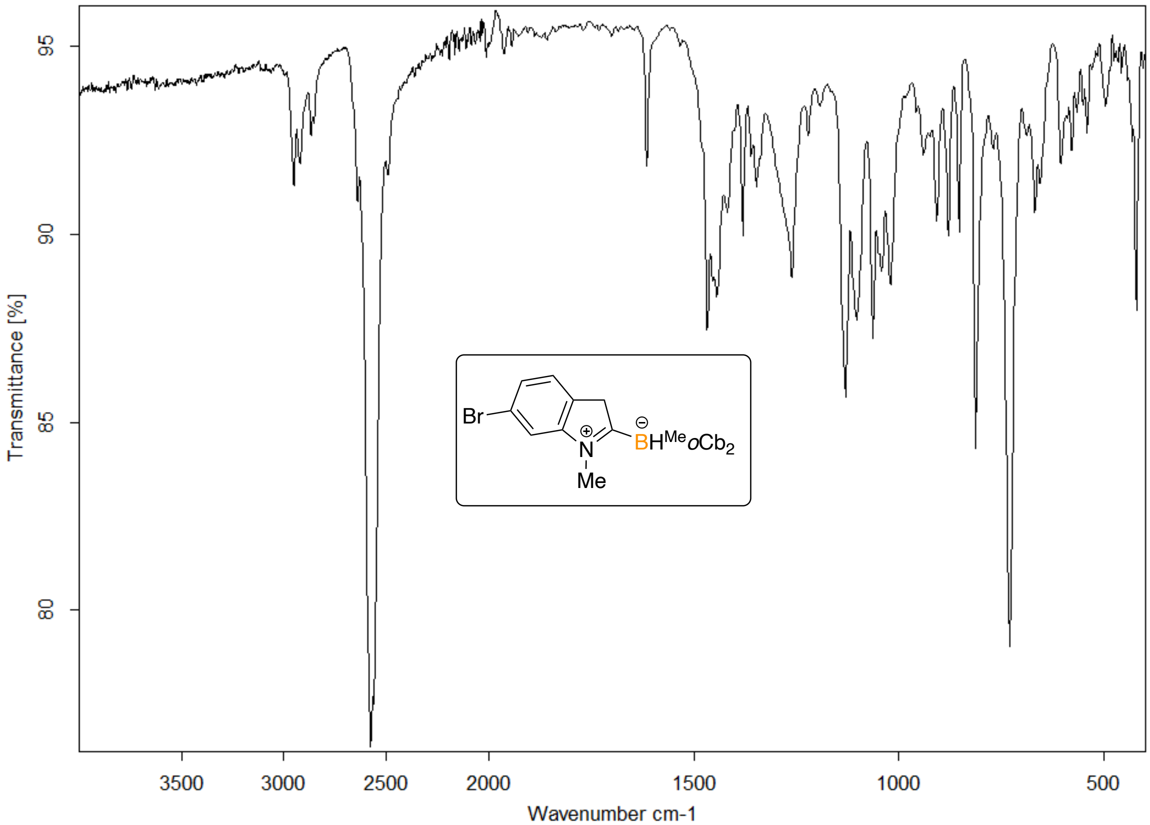


Figure S37: ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$ (*denotes residual C_6H_6)

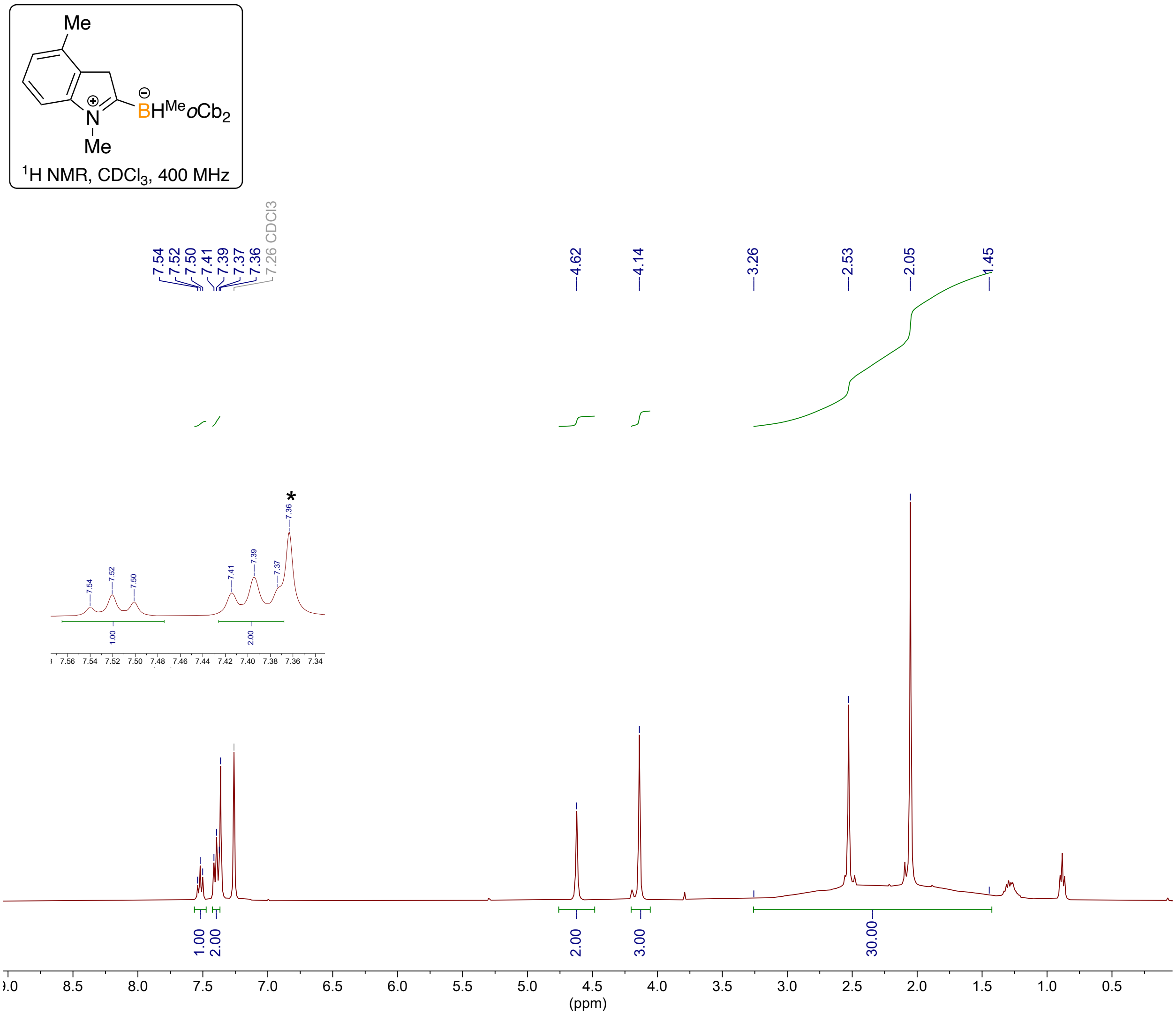


Figure S38: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **7** in $CDCl_3$

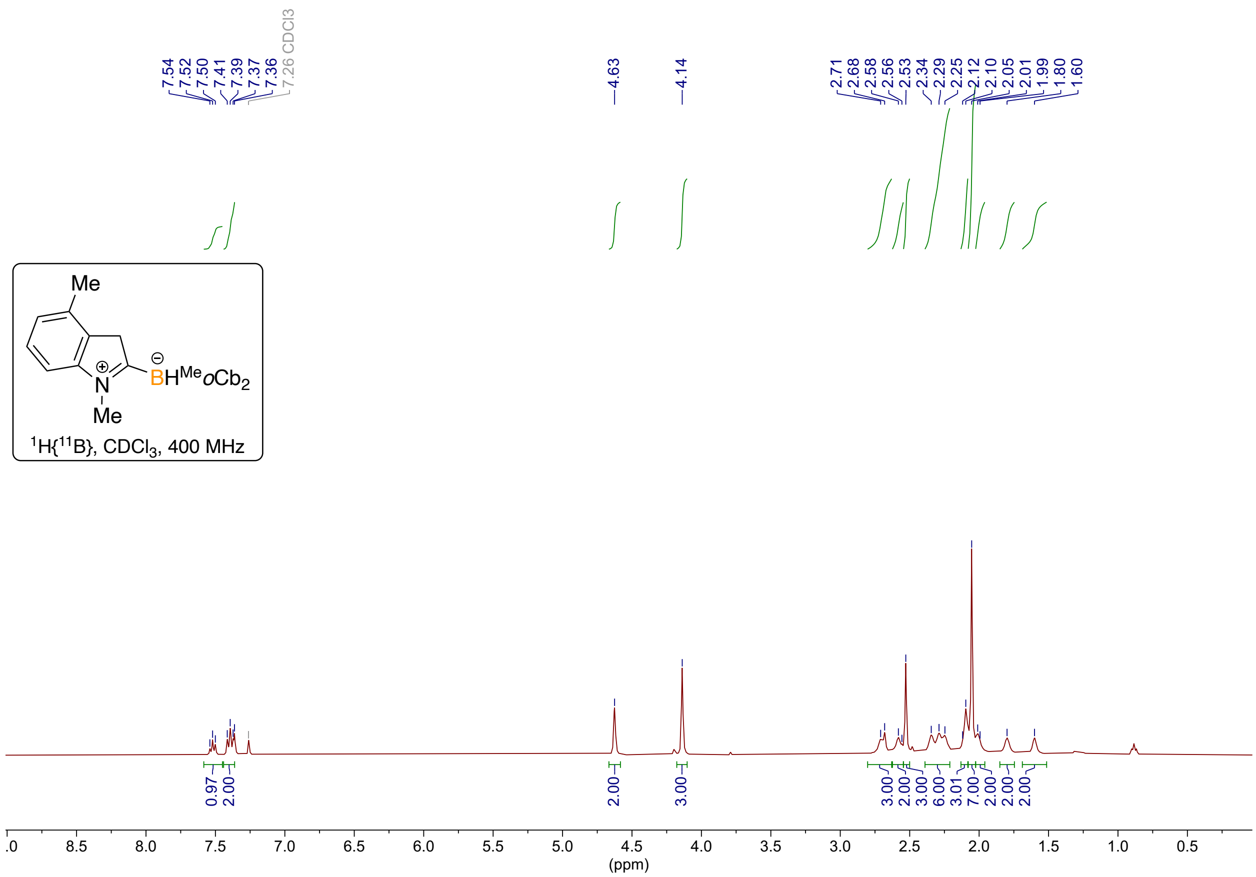


Figure S39: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **7** in $CDCl_3$ (* denotes residual C_6H_6)

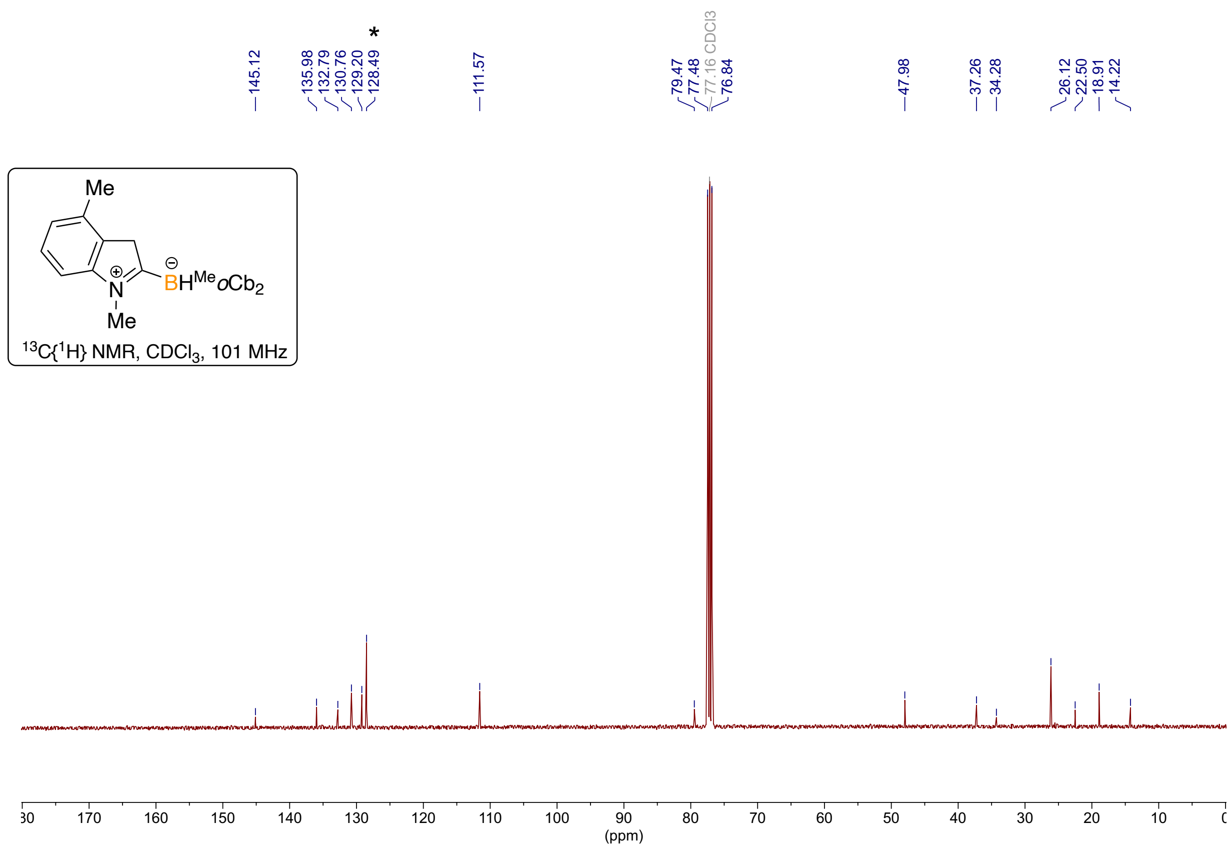
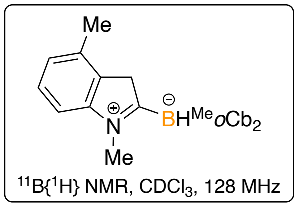


Figure S40: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **7** in $CDCl_3$



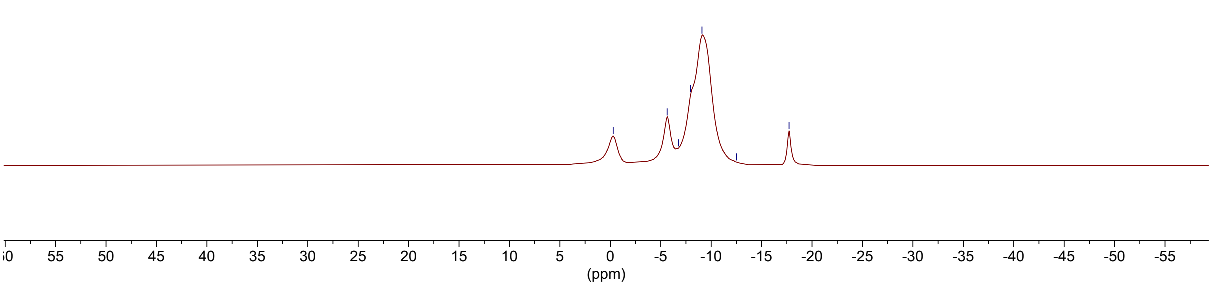
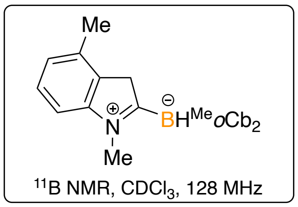


Figure S41: ^{11}B NMR (128 MHz) spectrum of **7** in $CDCl_3$



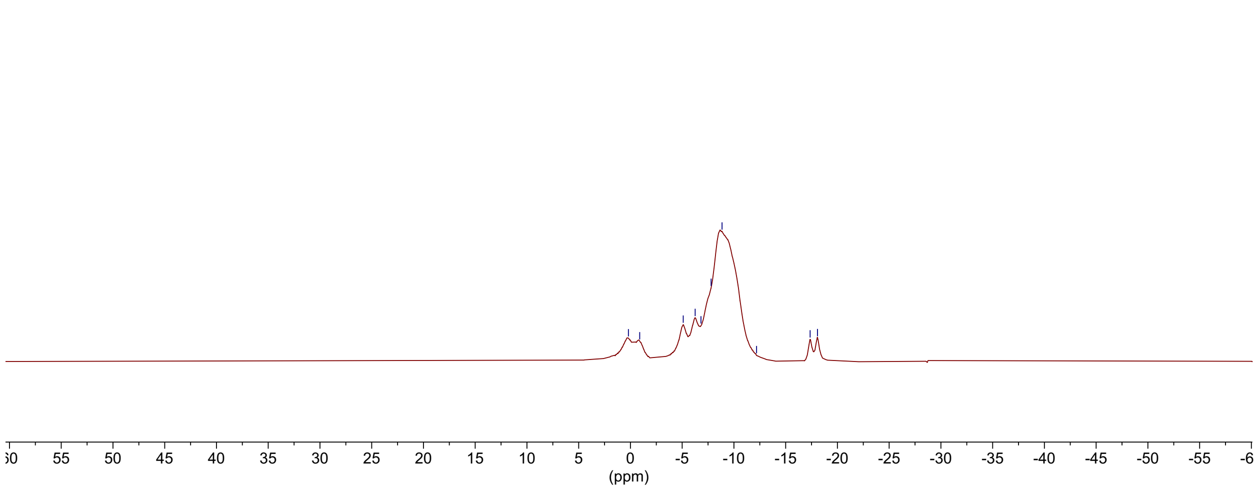


Figure S42: FT-IR spectrum of **7**

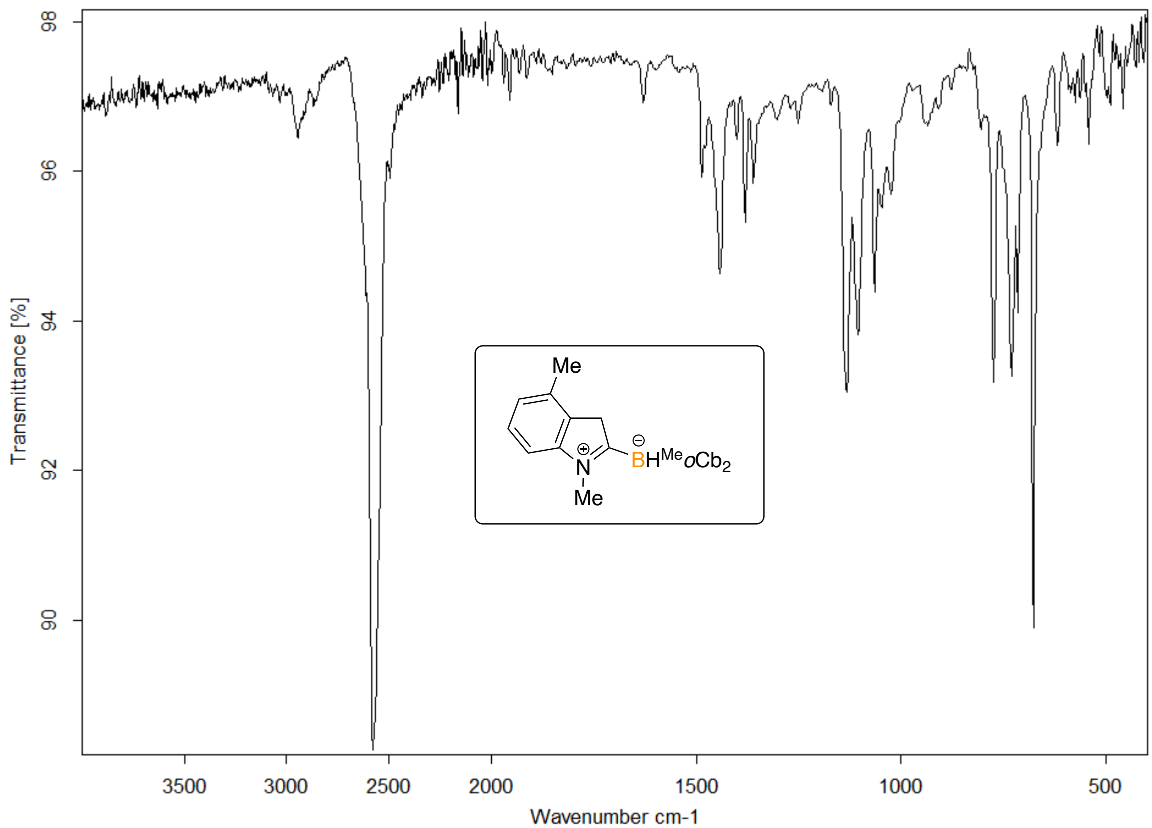
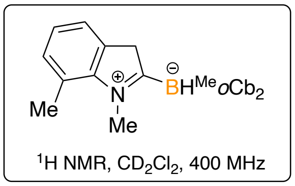


Figure S43: ^{1}H NMR (400 MHz) spectrum of **8** in CD_2Cl_2 (* denotes residual C_6H_6)



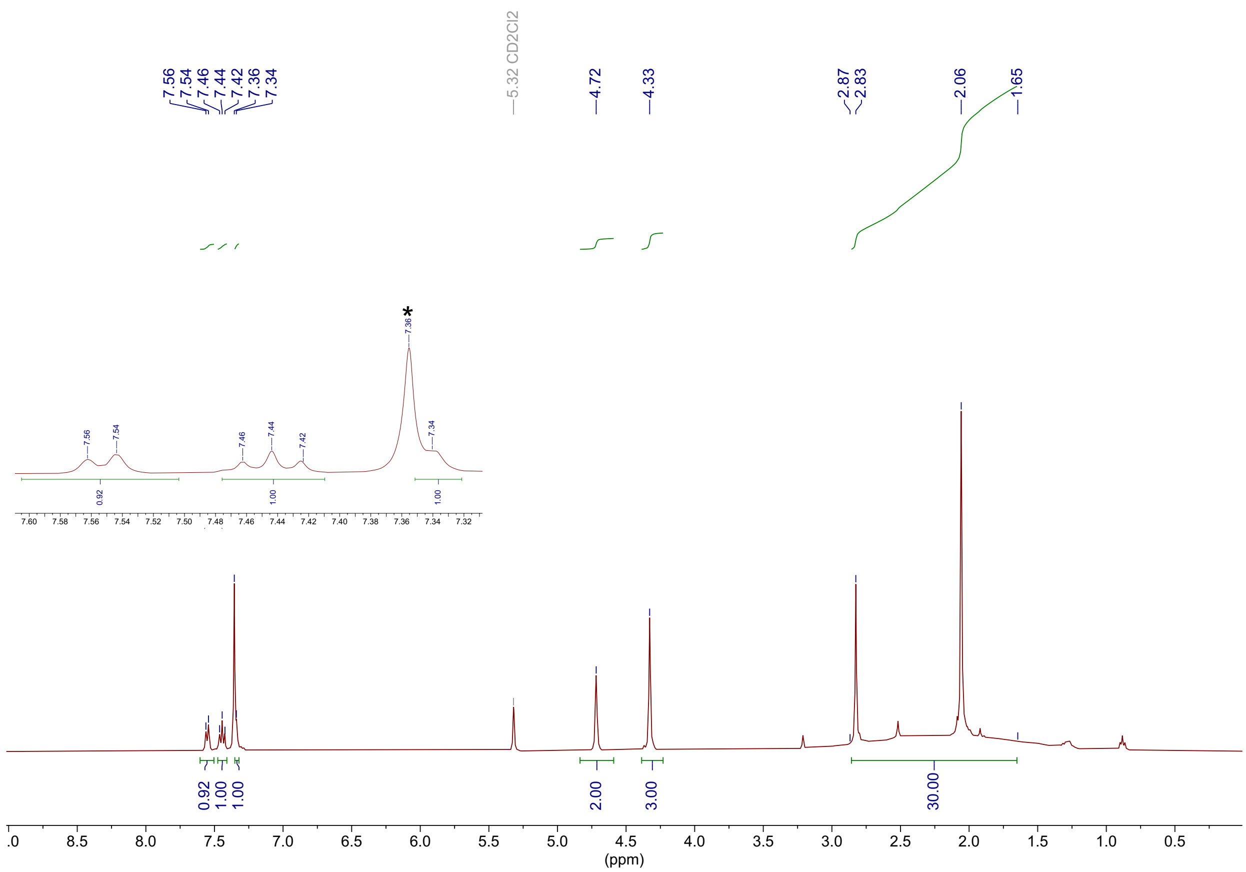


Figure S44: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **8** in CD_2Cl_2

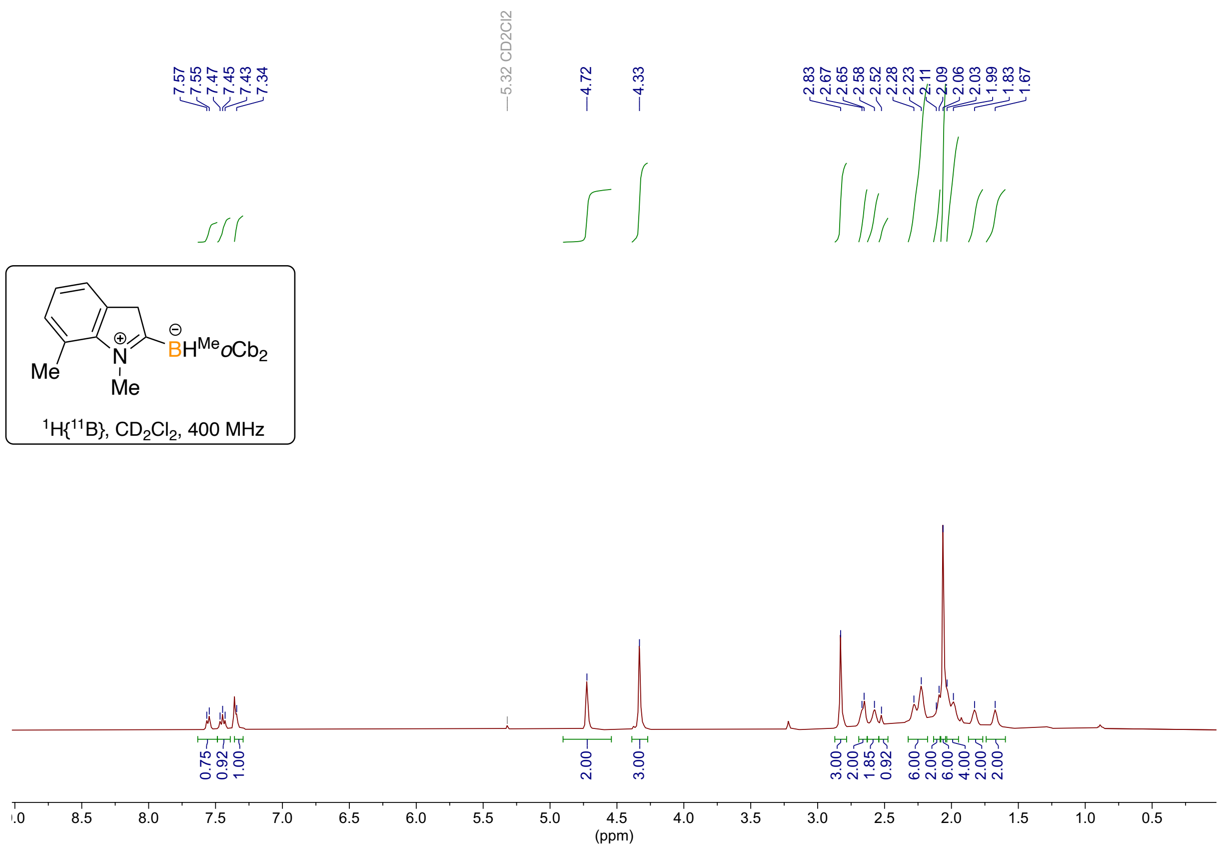


Figure S45: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **8** in CD_2Cl_2 (* denotes residual C_6H_6)

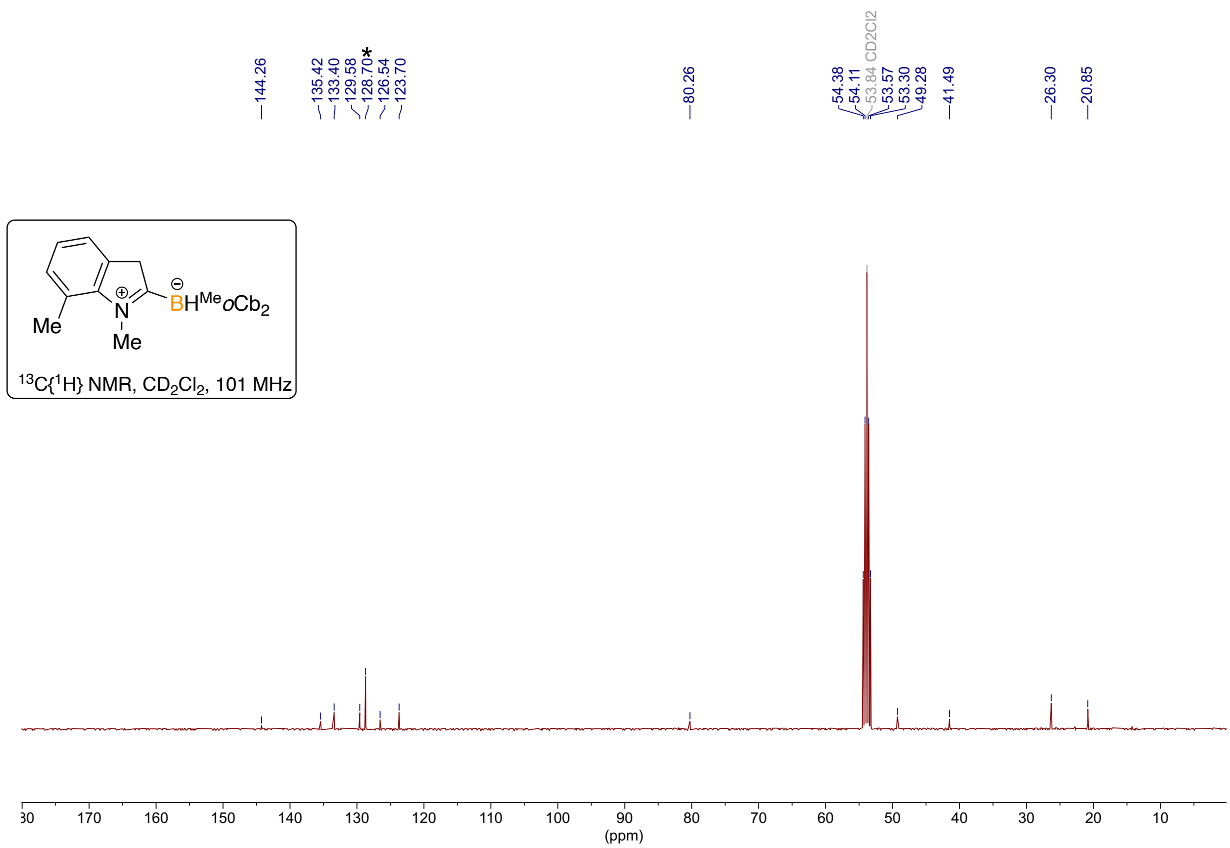


Figure S46: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **8** in CD_2Cl_2

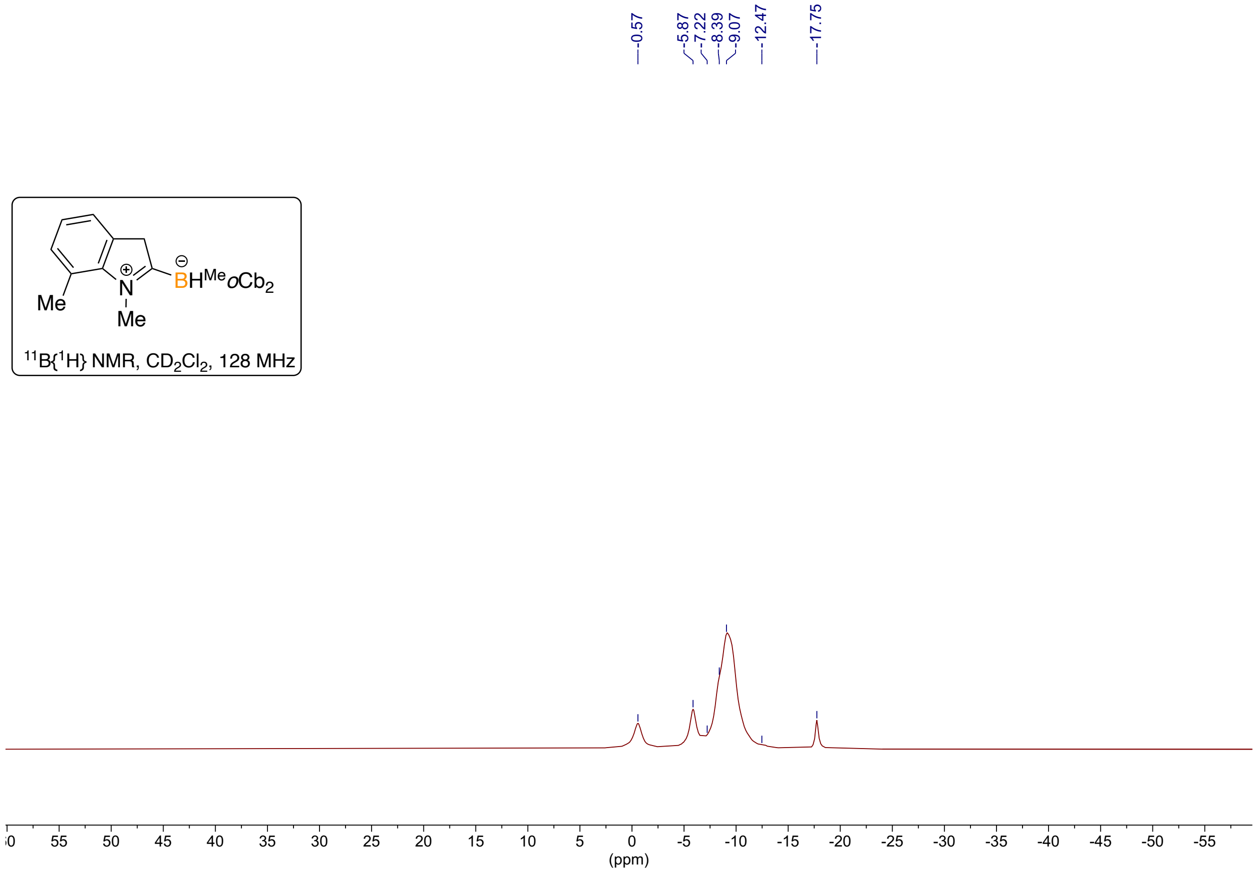
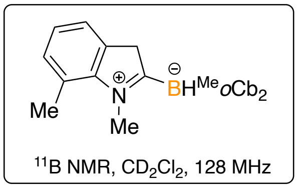


Figure S47: ^{11}B NMR (128 MHz) spectrum of **8** in CD_2Cl_2



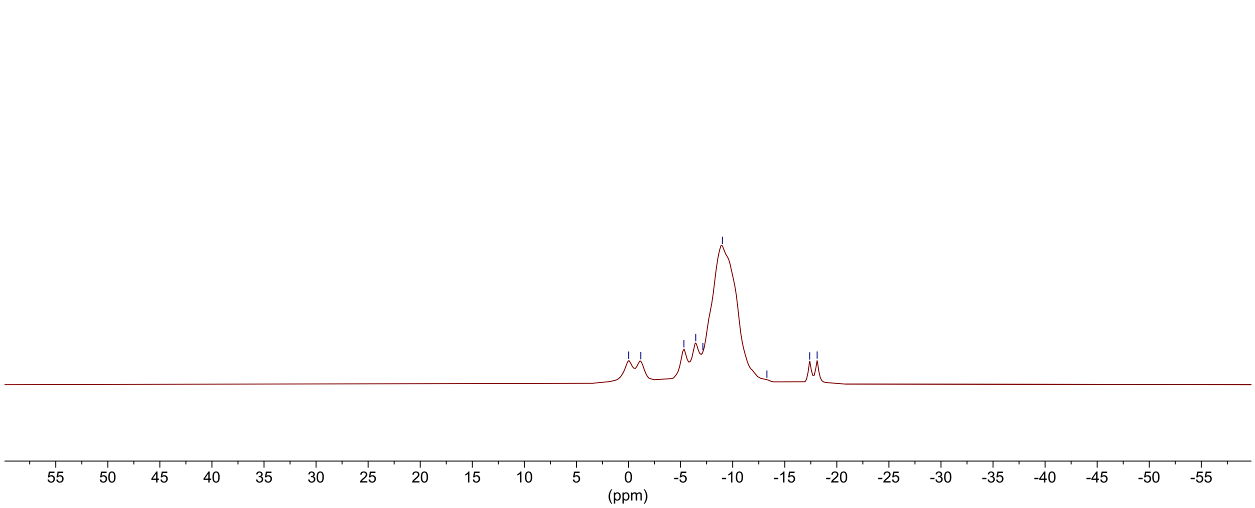


Figure S48: FT-IR spectrum of **8**

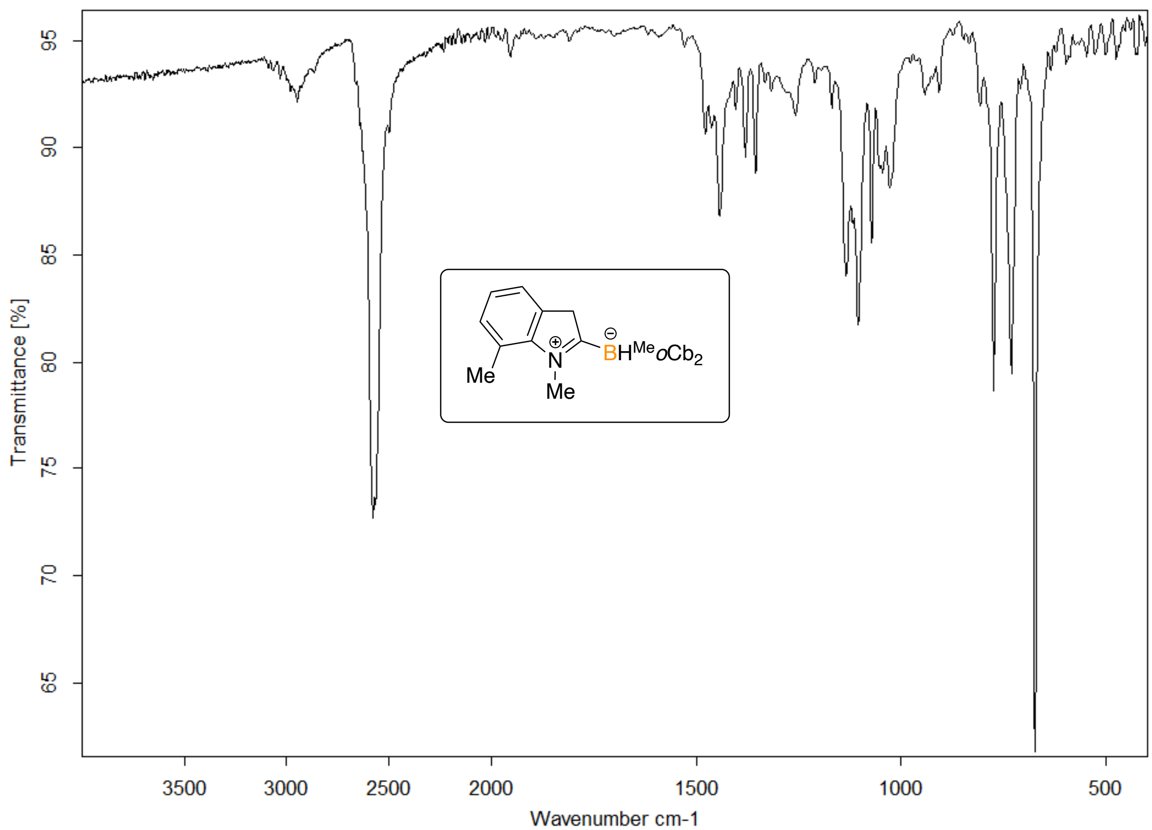
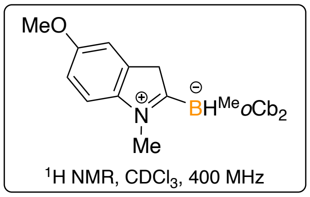


Figure S49: ^{1}H NMR (400 MHz) spectrum of **9** in $CDCl_3$



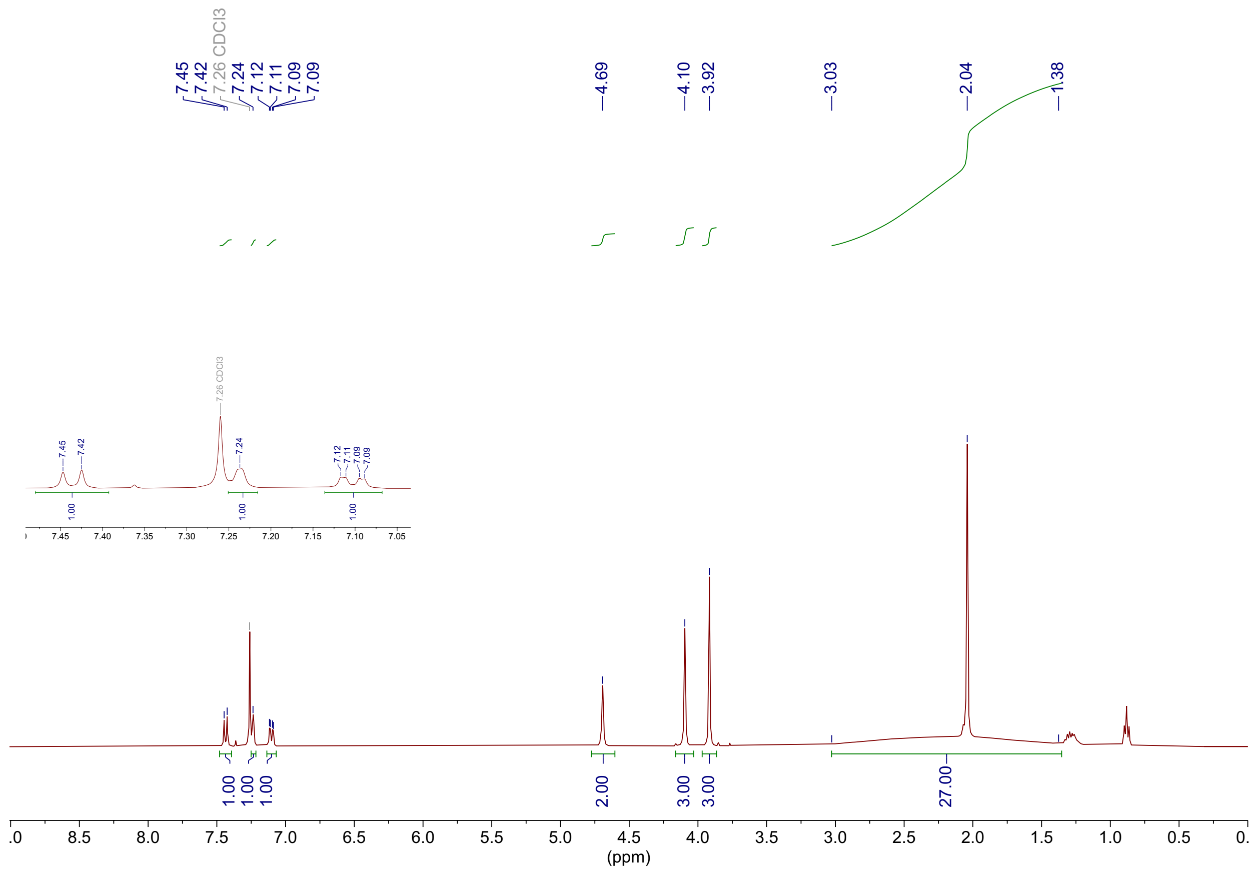


Figure S50: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **9** in $CDCl_3$

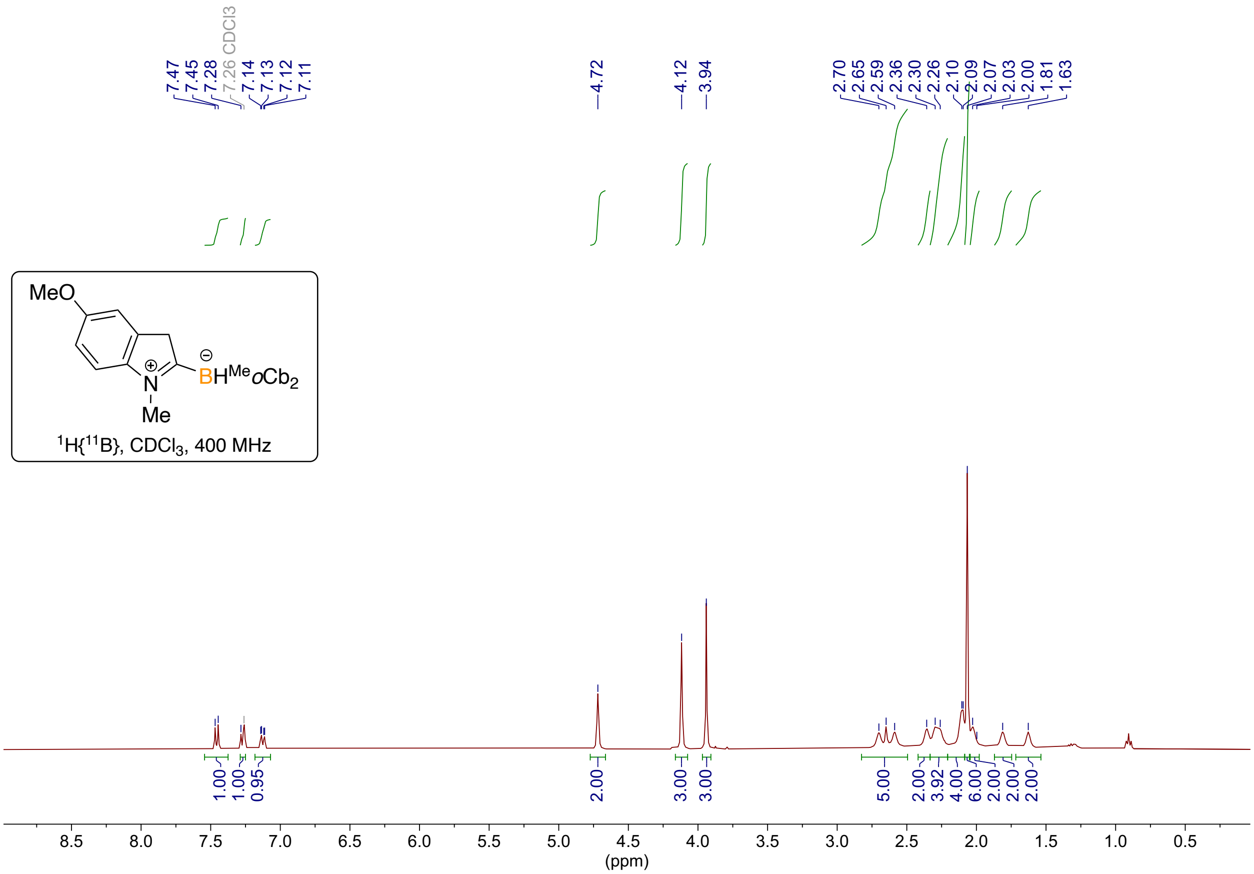


Figure S51: $^{13}C\{^1H\}$ NMR (101 MHz) spectrum of **9** in $CDCl_3$

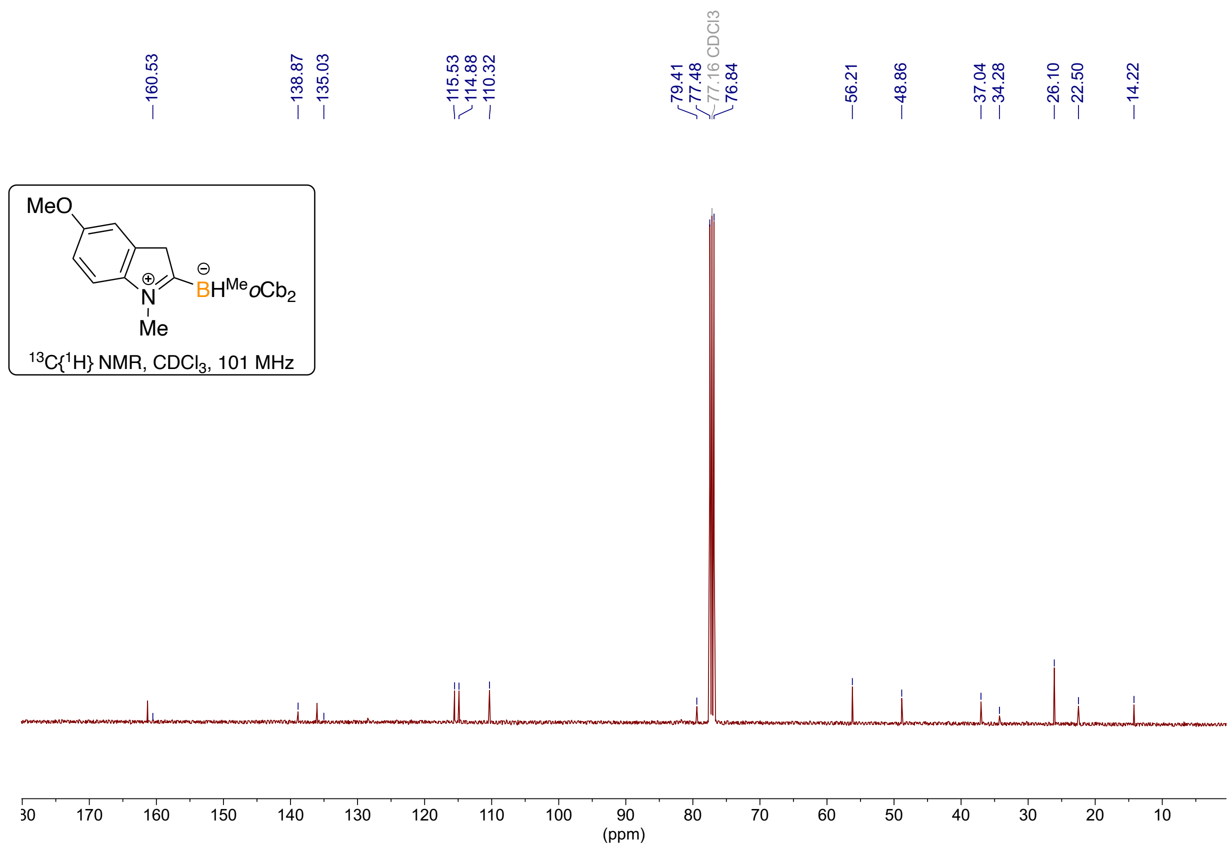
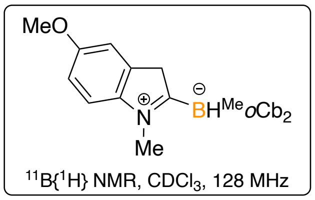


Figure S52: $^{11}B\{^{1}H\}$ NMR (128 MHz) spectrum of **9** in $CDCl_3$



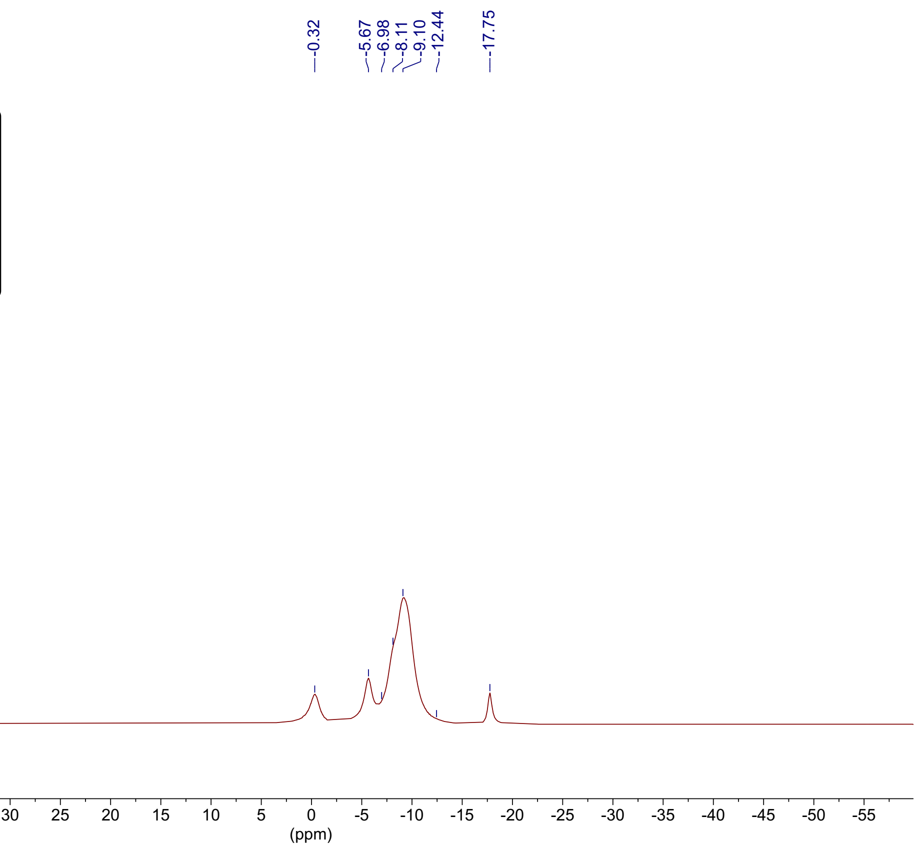
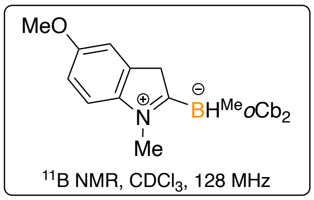


Figure S53: ^{11}B NMR (128 MHz) spectrum of **9** in $CDCl_3$



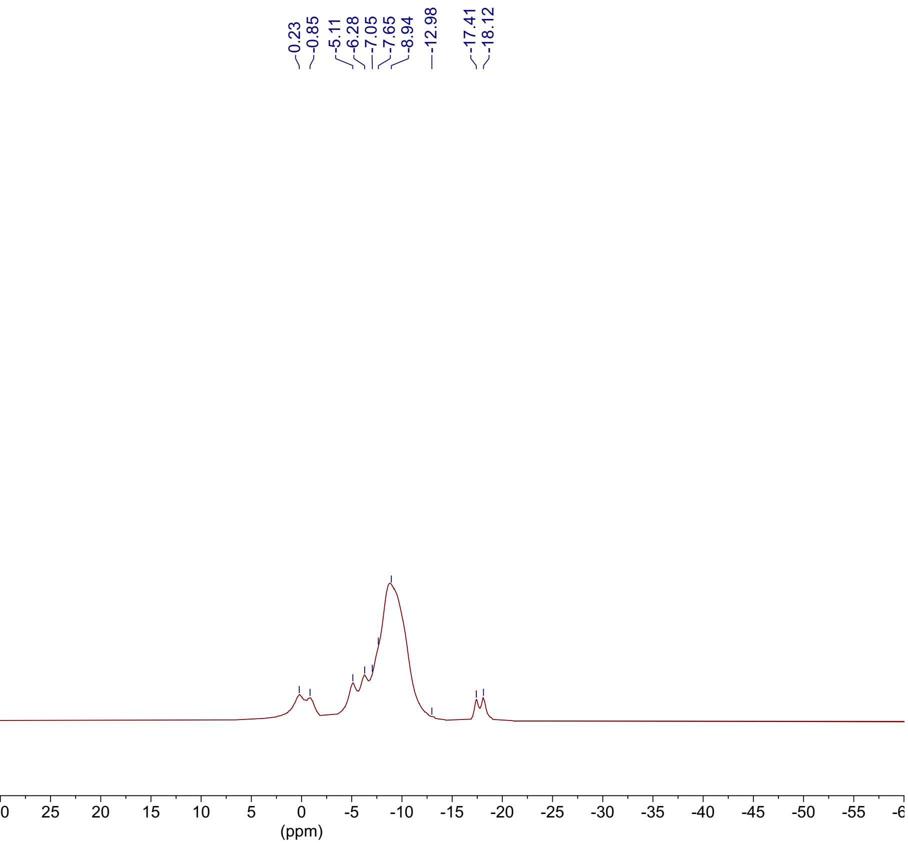


Figure S54: FT-IR spectrum of **9**

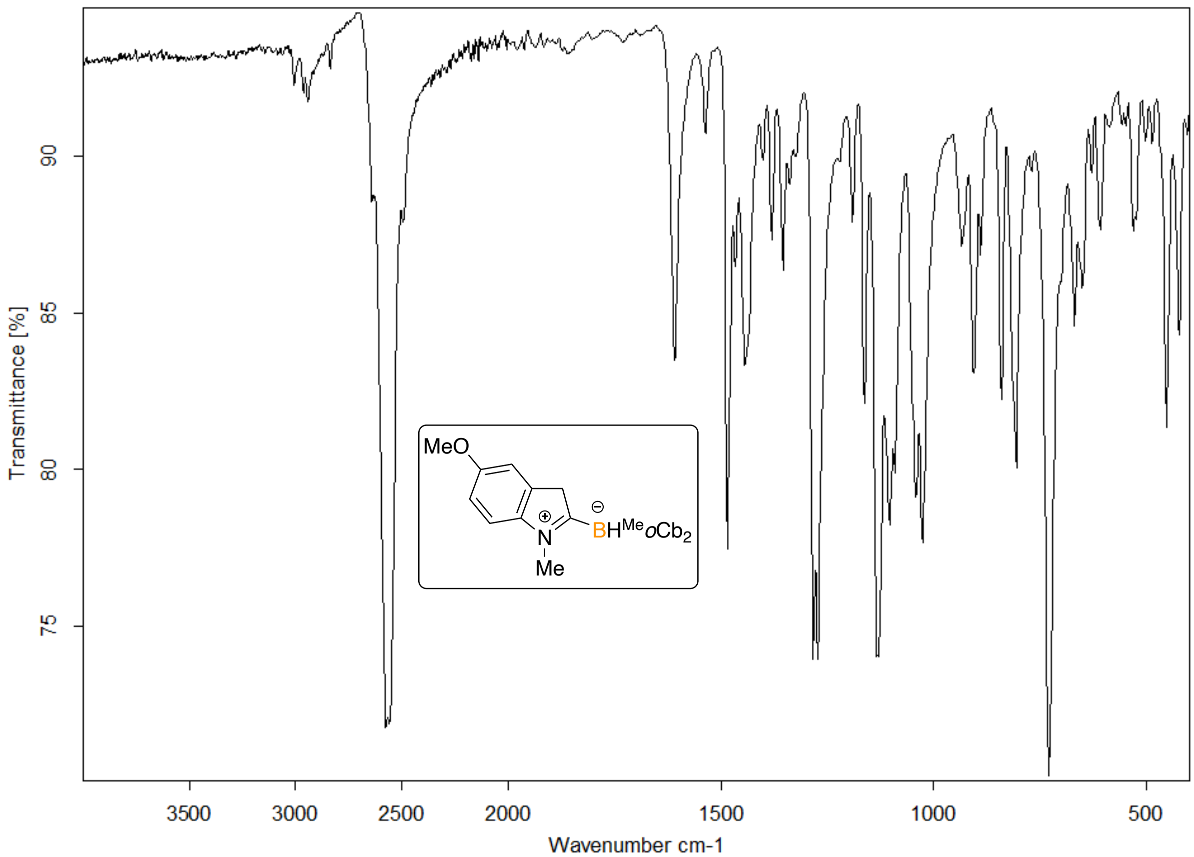
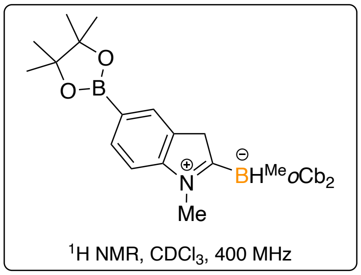


Figure S55: ^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$



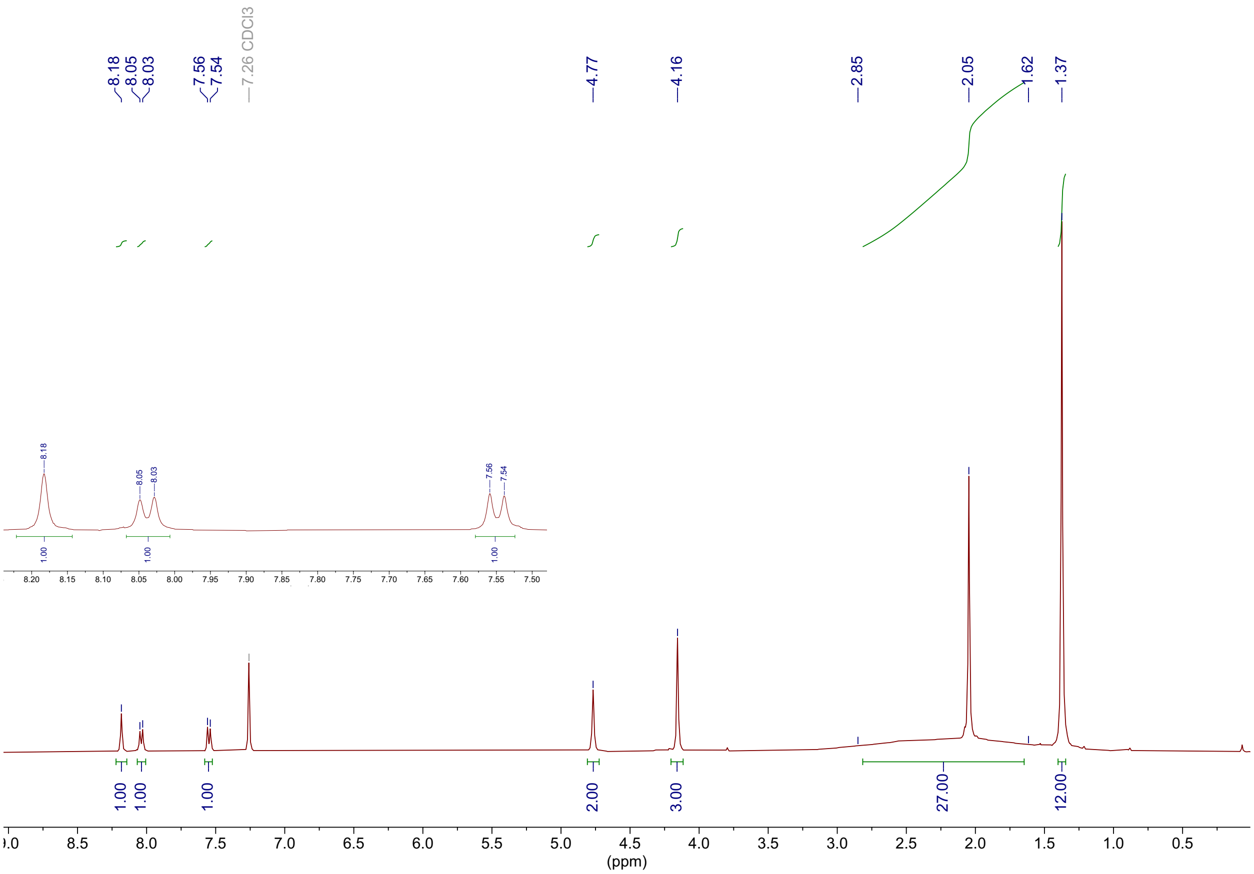


Figure S56: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of **10** in $CDCl_3$

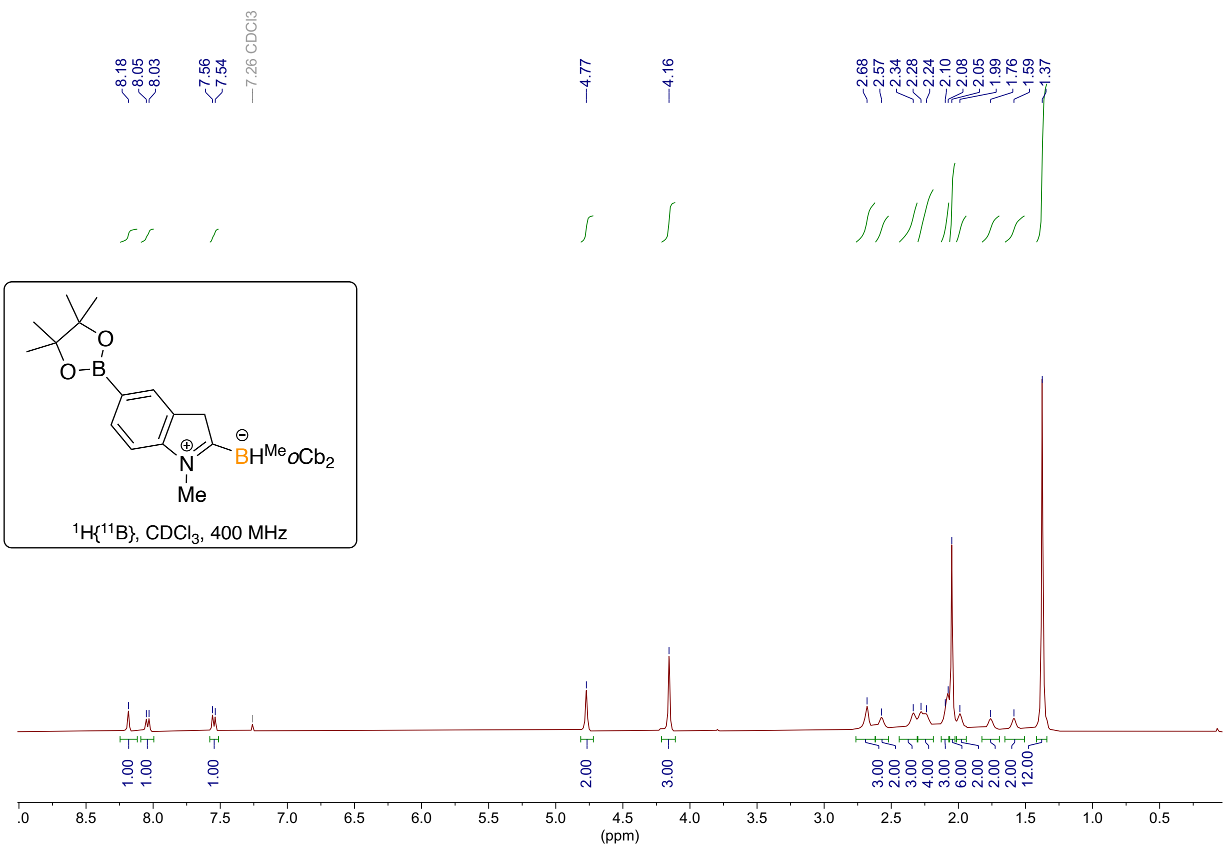


Figure S57: $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of **10** in $CDCl_3$

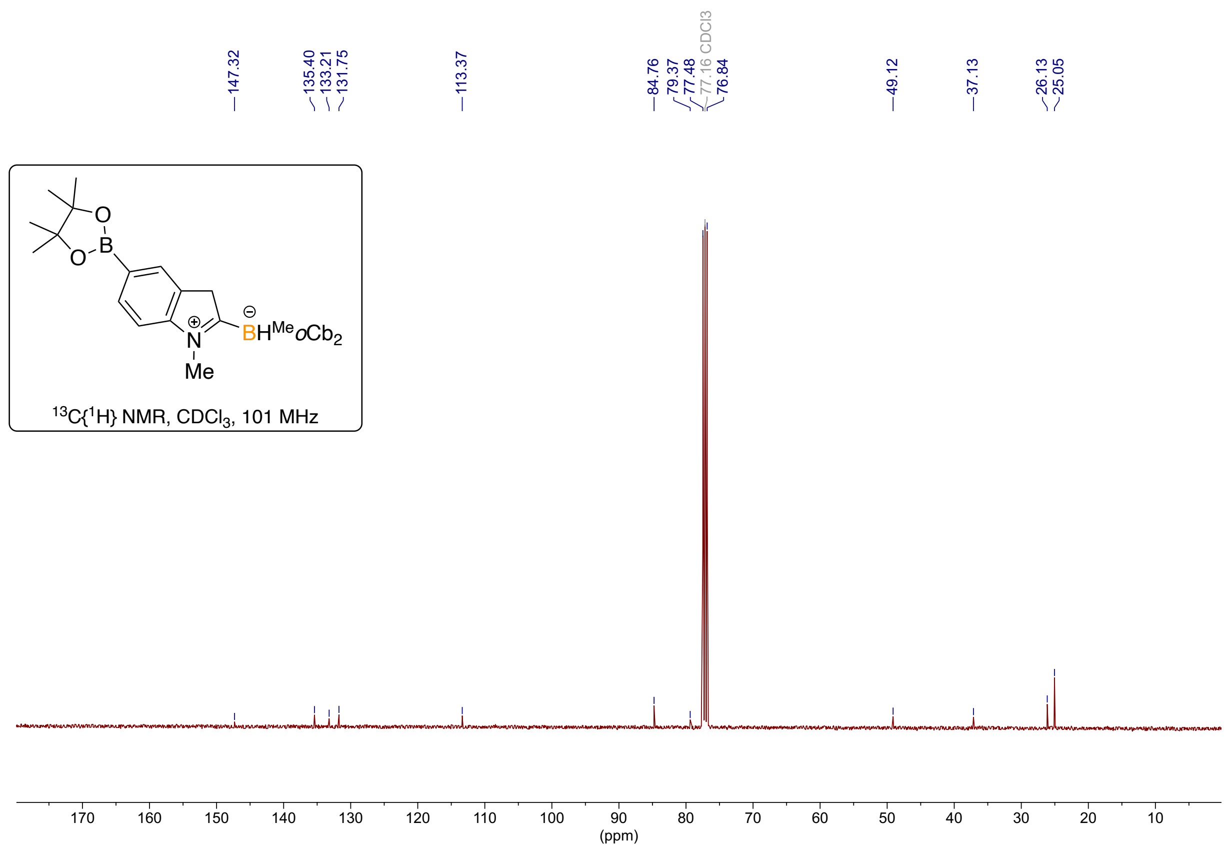


Figure S58: $^{11}B\{^1H\}$ NMR (128 MHz) spectrum of **10** in $CDCl_3$

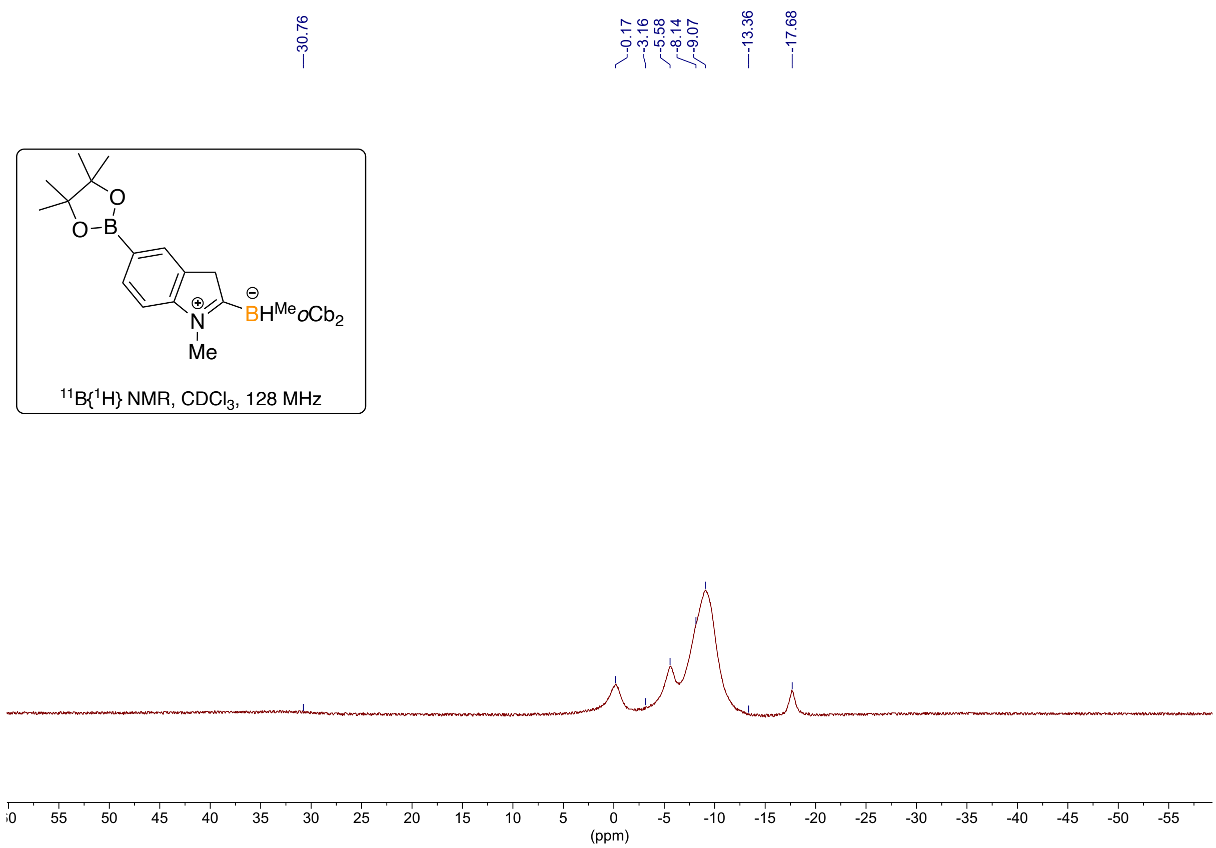


Figure S59: ^{11}B NMR (128 MHz) spectrum of **10** in $CDCl_3$

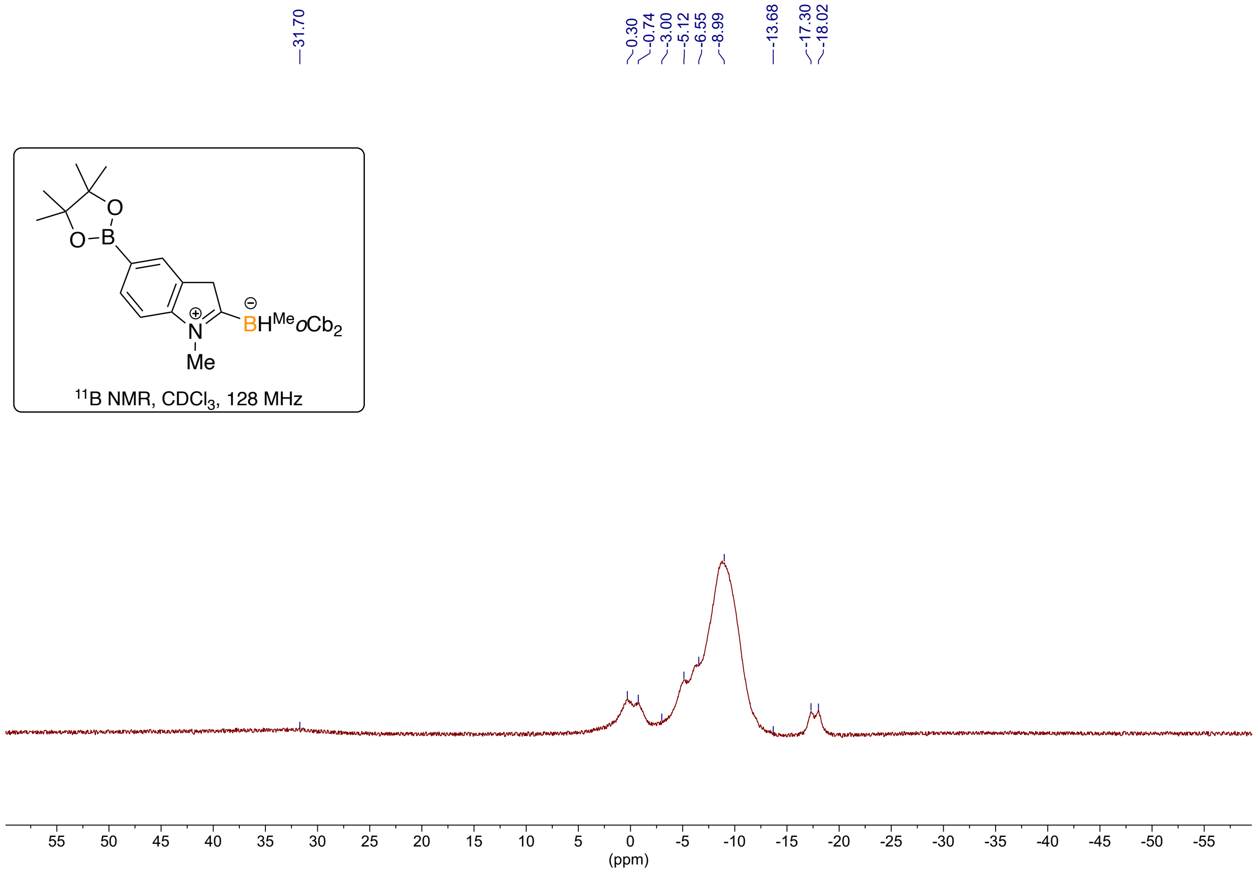


Figure S60: FT-IR spectrum of **10**

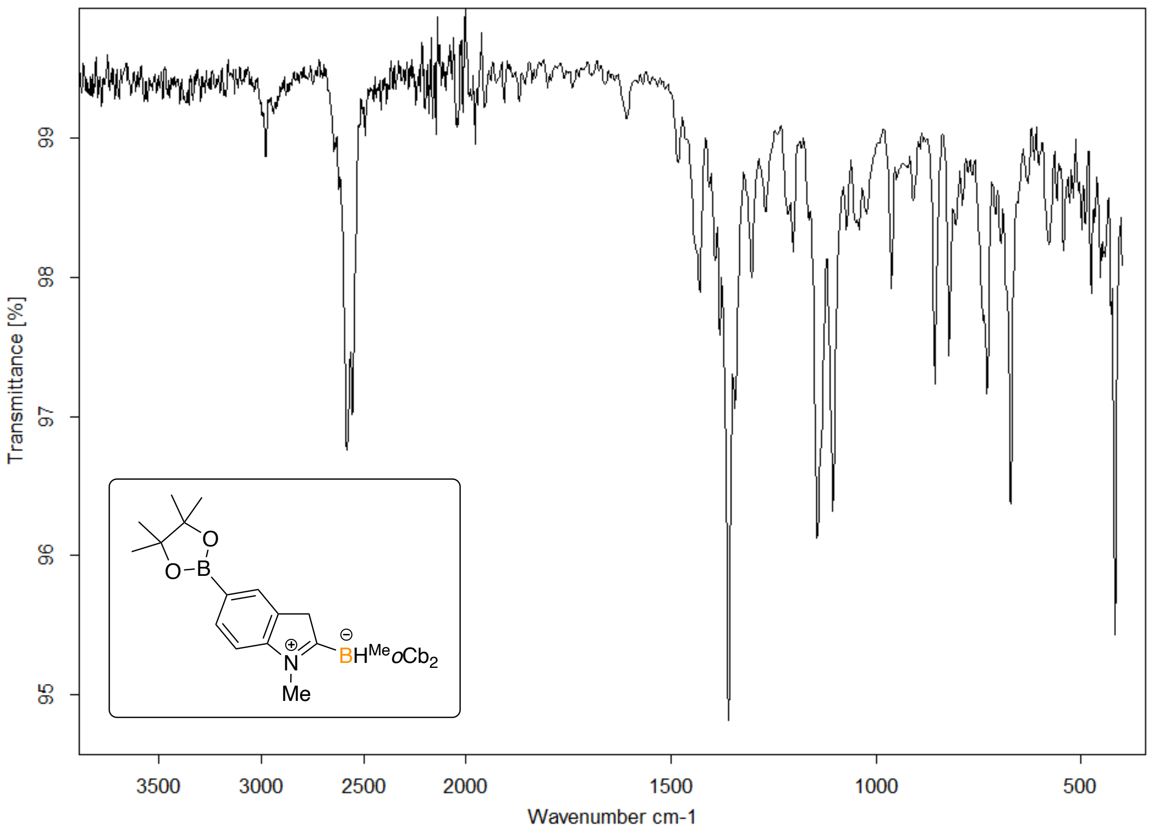


Figure S61: ^{1}H NMR (400 MHz) spectrum of $DB^{Me}oCb_2$ in C_6D_6

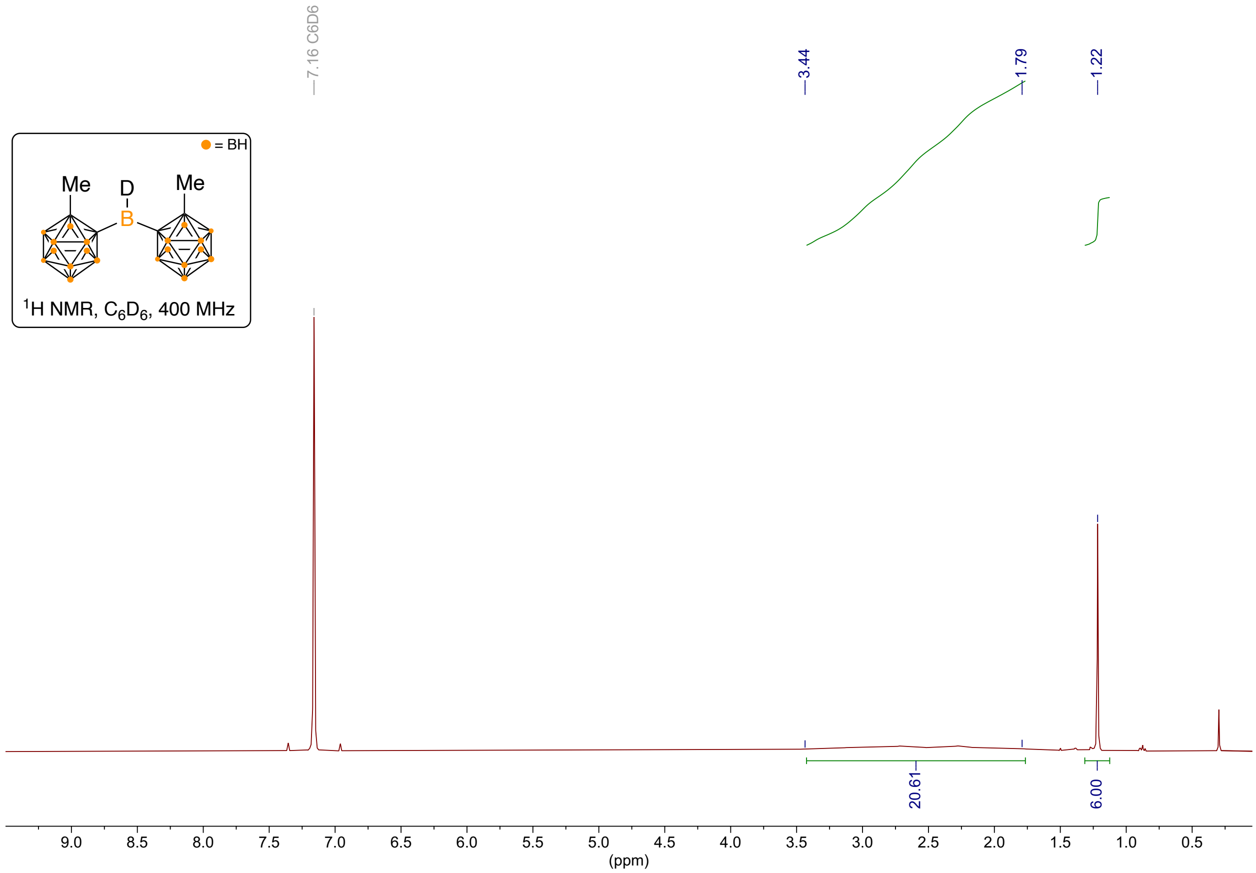
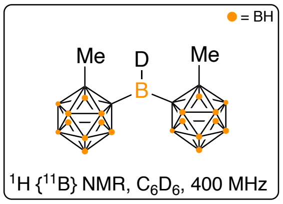


Figure S62: $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of $DB^{Me}o Cb_2$ in C_6D_6



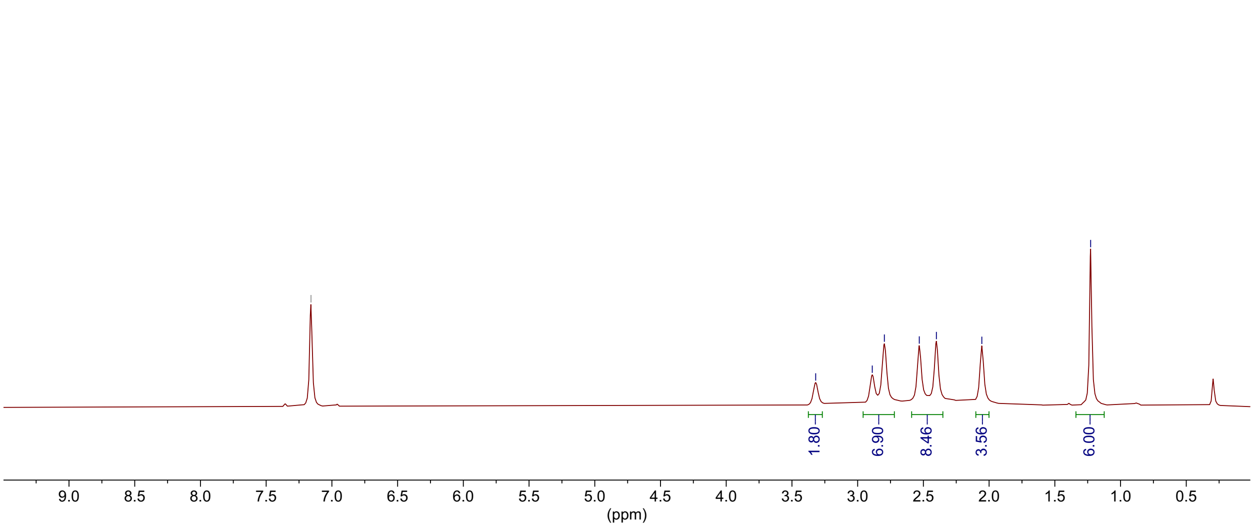


Figure S63:$^{11}B\{^1H\}$ NMR (128 MHz) spectrum of $DB^{Me}o$Cb$_2$ in C_6D_6

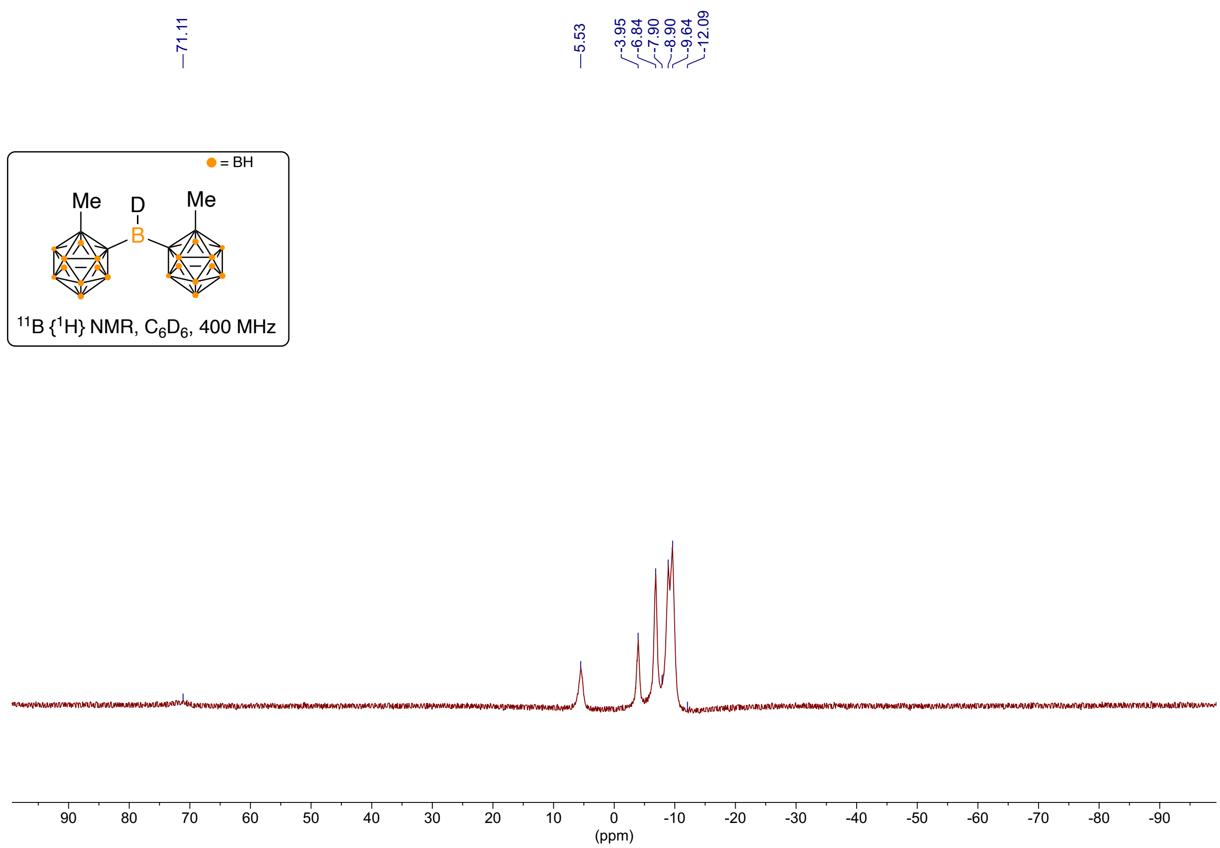


Figure S64: ^{11}B NMR (128 MHz) spectrum of DB^{Me}*o*Cb$_2$ in C_6D_6

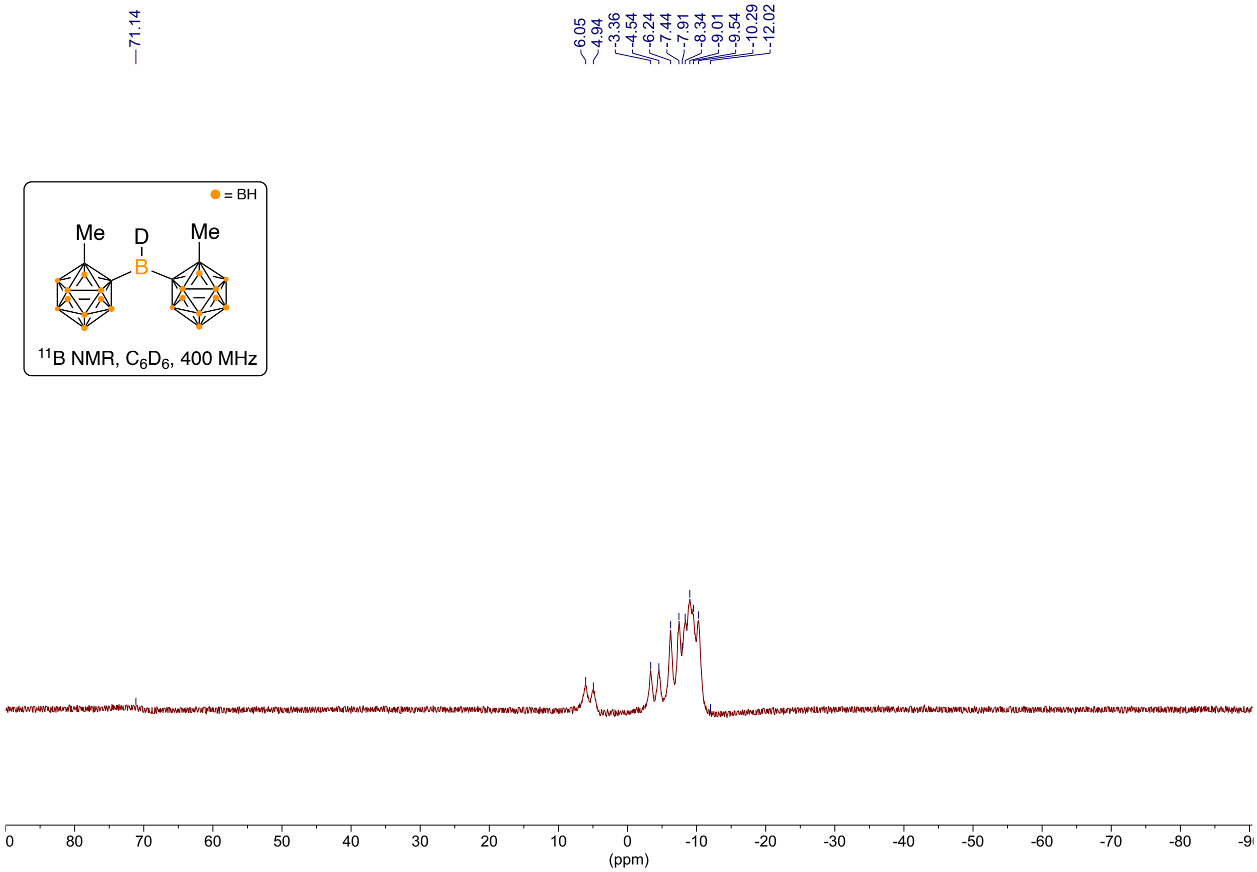


Figure S65: ^{2}H NMR (600 MHz) spectrum of $DB^{Me}\textit{o}Cb_2$ in C_6H_6

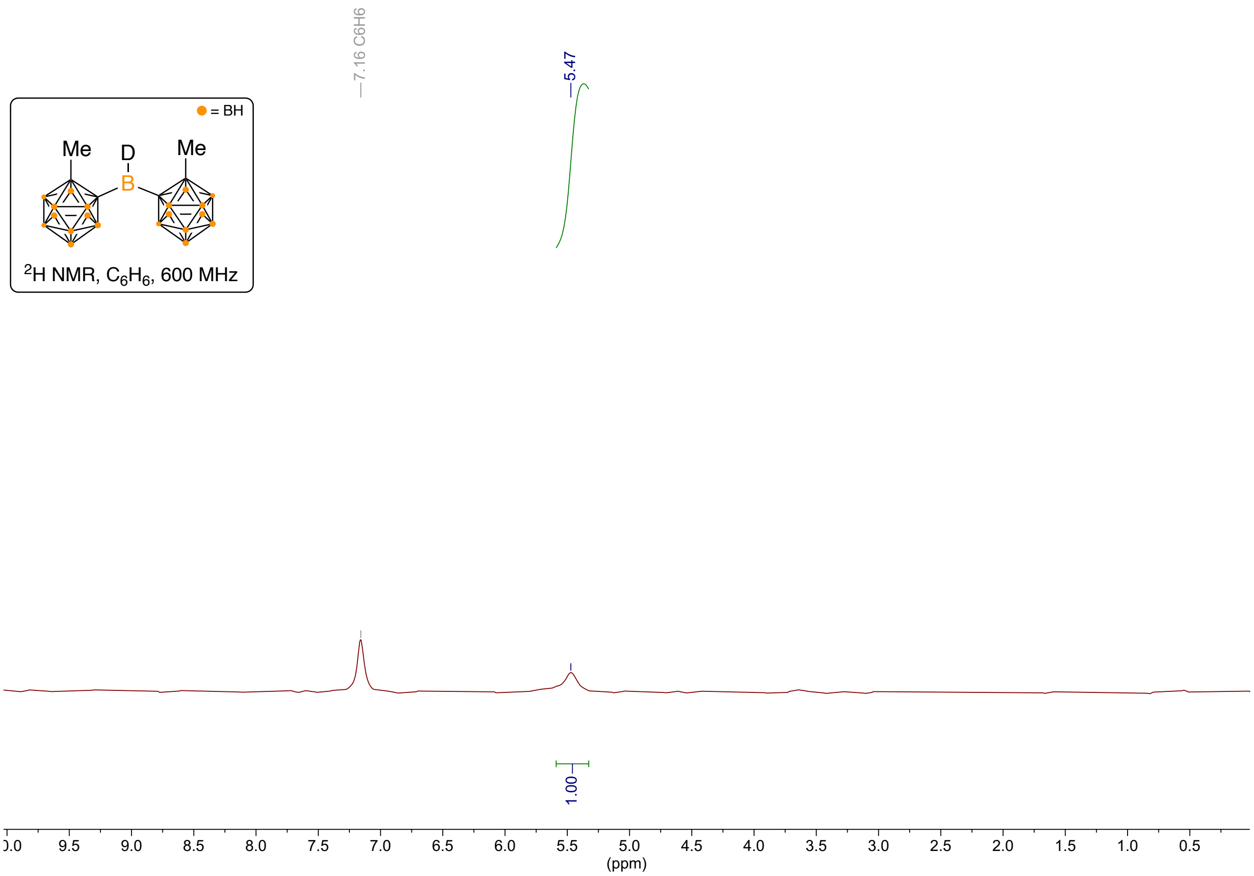


Figure S66: Stacked $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum of $HB^{Me}oCb_2$ and $DB^{Me}oCb_2$ in C_6D_6

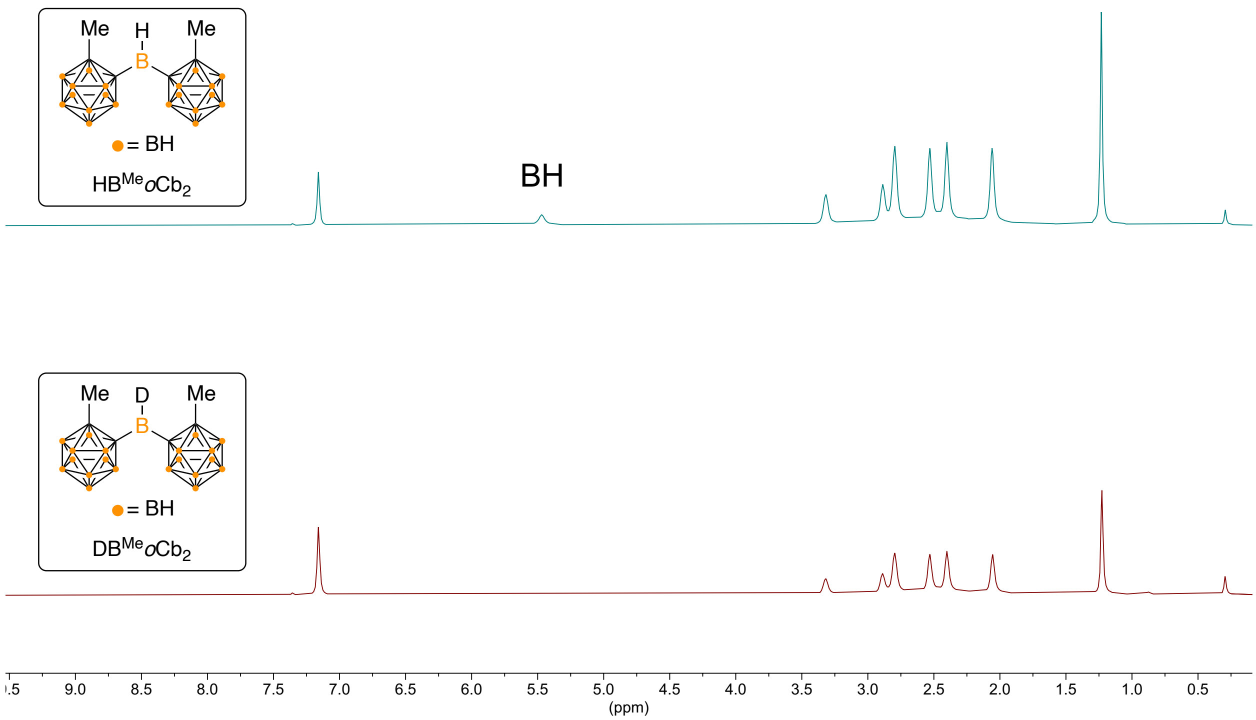


Figure S67: ^{1}H NMR (400 MHz) spectrum of **1-d** in $CDCl_3$ (* denotes C_6H_6)

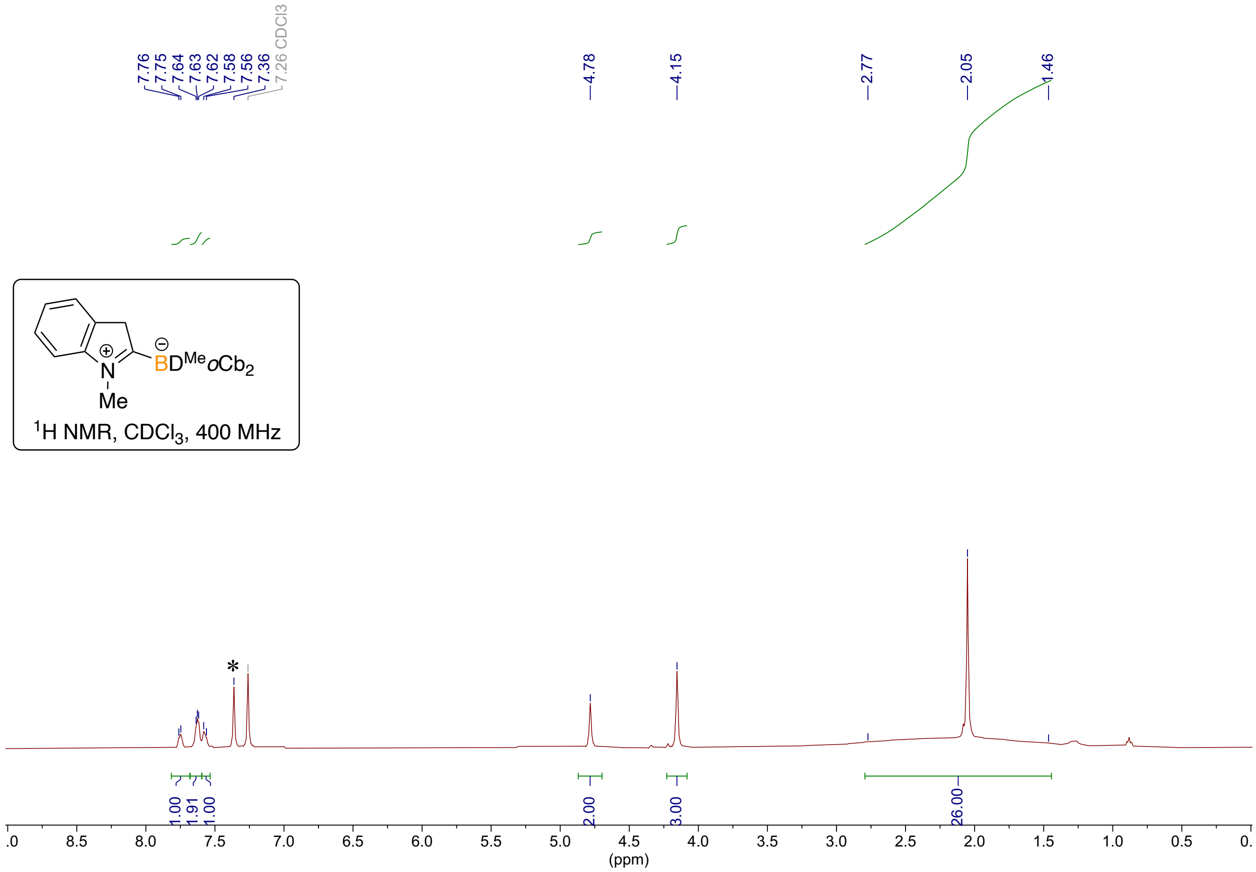


Figure S68: $^{1}H\{^{11}B\}$ NMR spectrum of **1-d** in $CDCl_3$ (400 MHz)

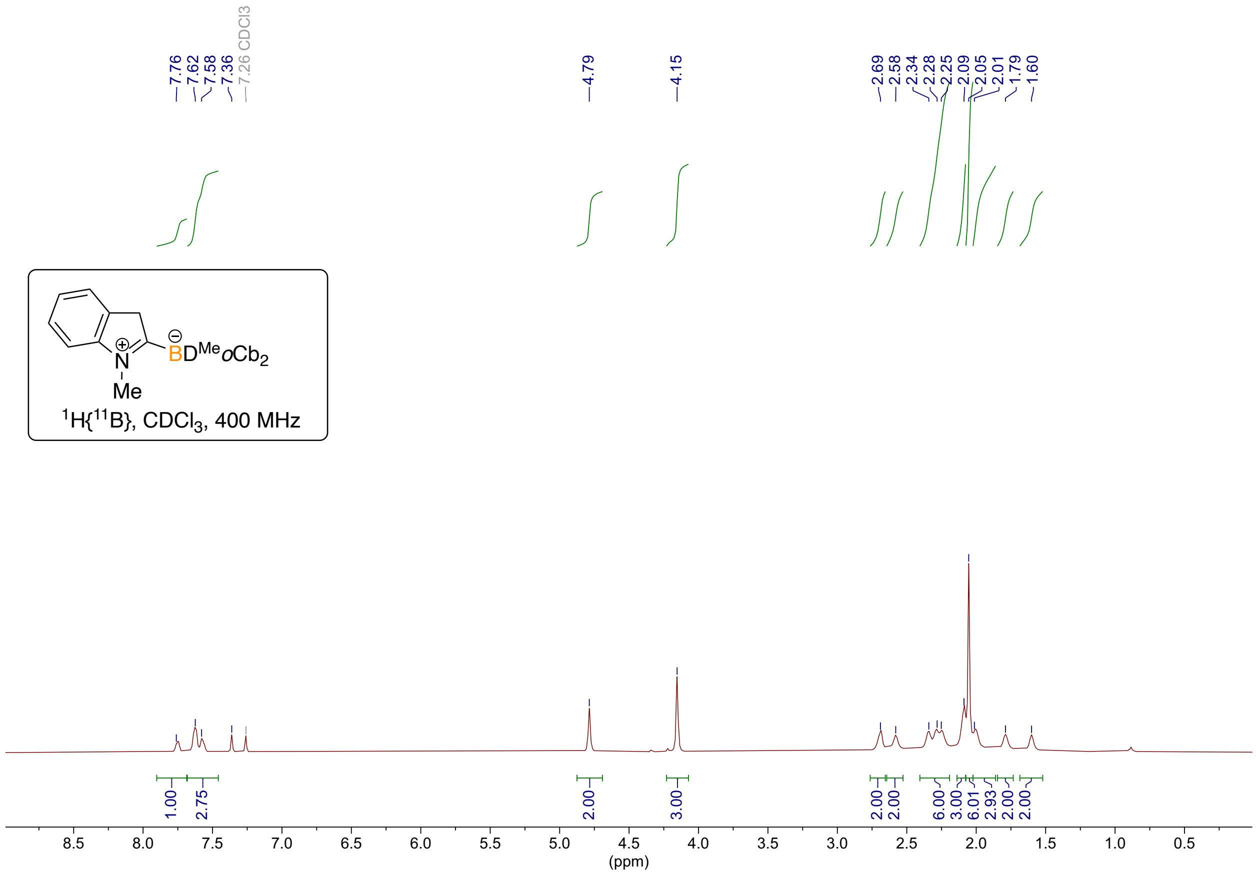


Figure S69: ^{11}B NMR spectrum of **1-d** in $CDCl_3$ (128 MHz)

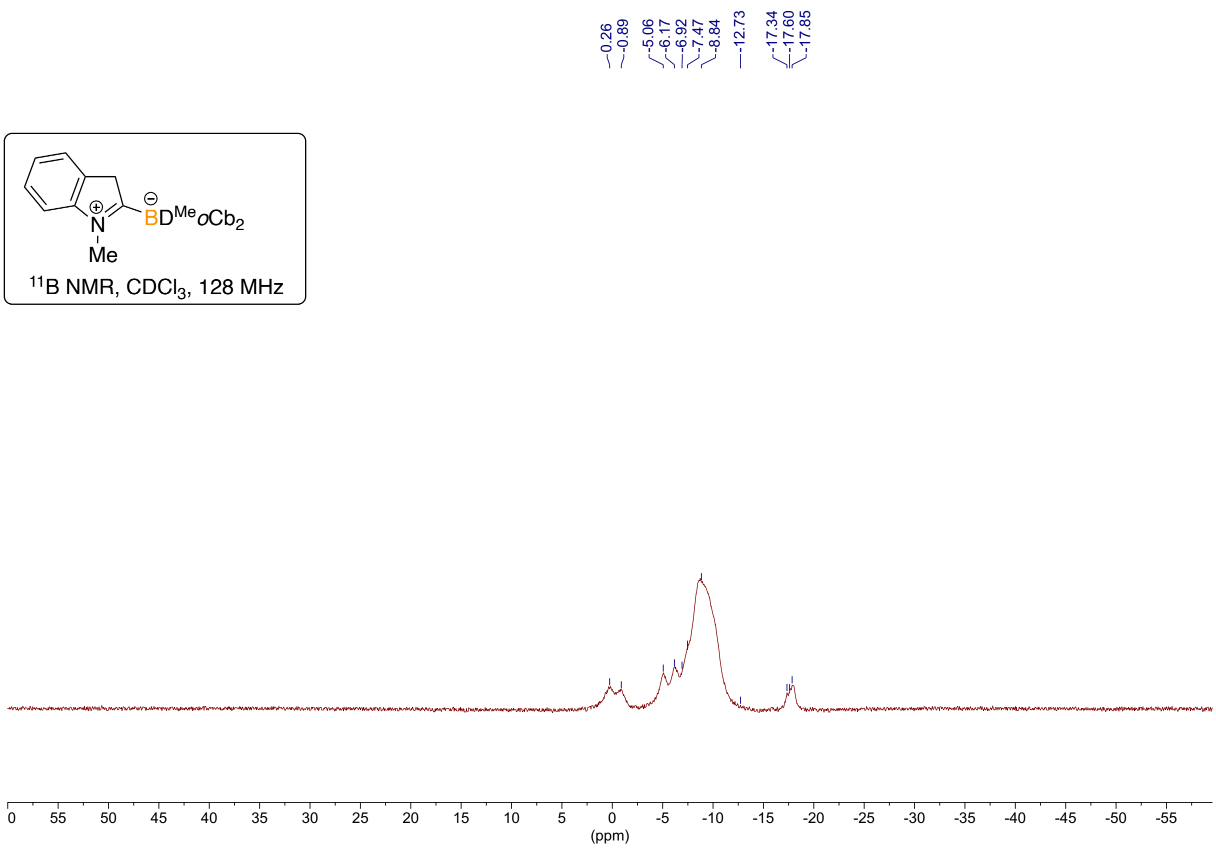


Figure S70: Low temperature $^{1}H\{^{11}B\}$ NMR (400 MHz) spectrum for the synthesis of **1** in $CDCl_3$

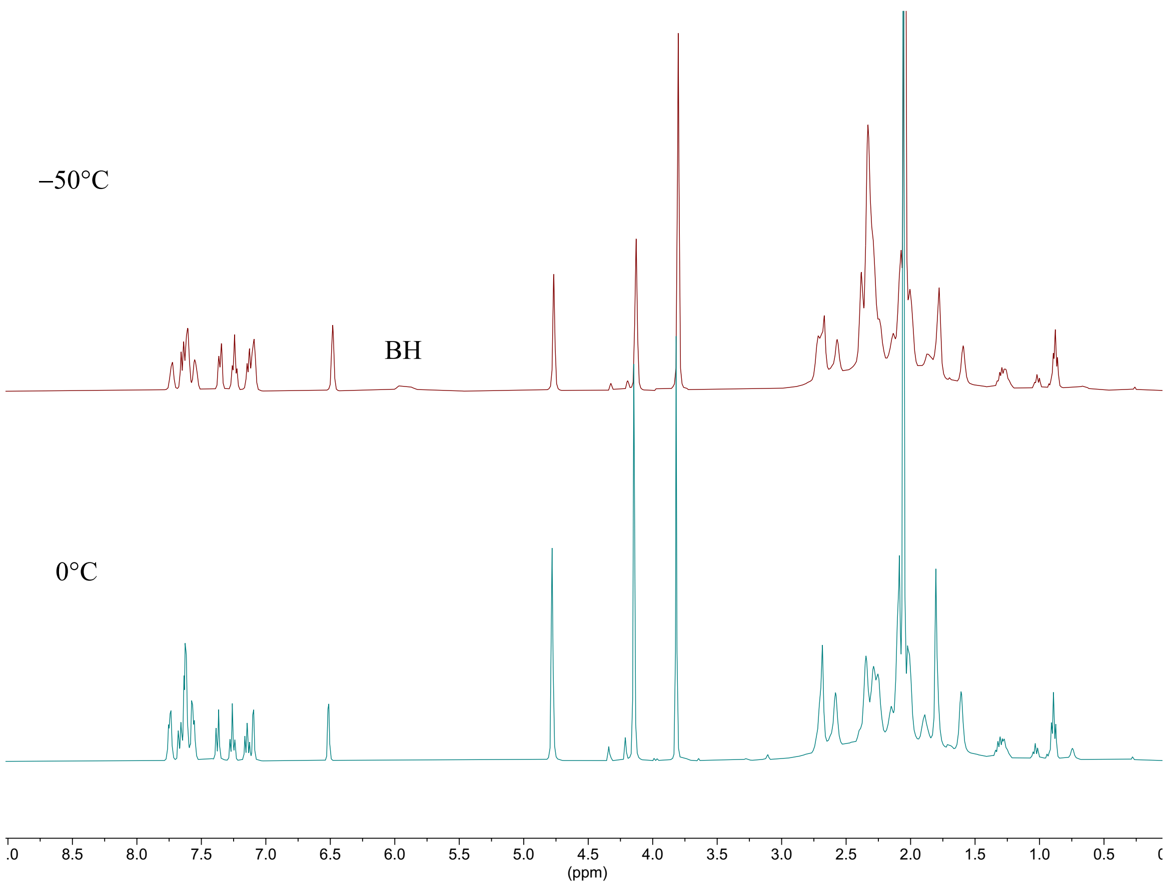


Figure S71: ^{1}H NMR spectrum of **1** and Pyridine in $CDCl_3$ (400 MHz) (* denotes peaks for 1-methyl-1*H*-indole)

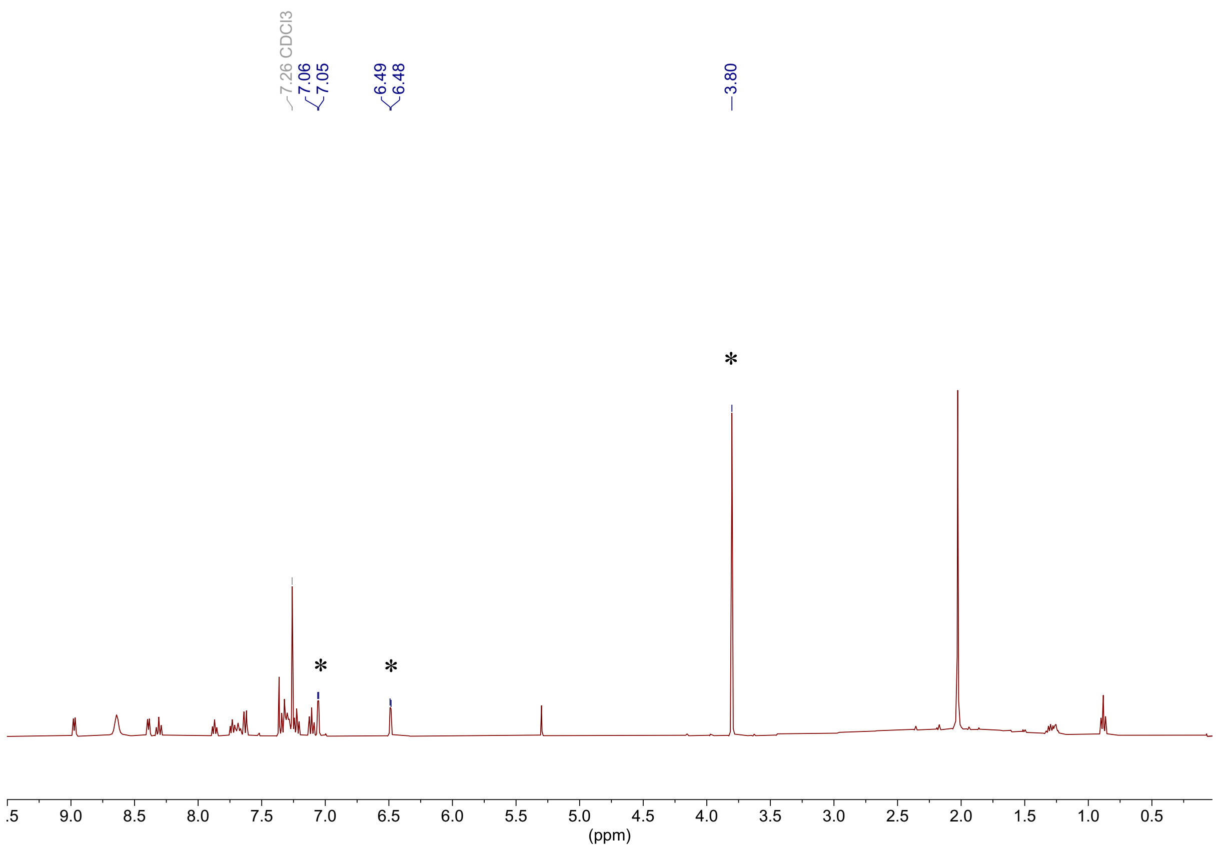


Figure S72: ^{1}H NMR spectrum of **1** and 2,6-lutidine in $CDCl_3$ (400 MHz) (* denotes peaks for 1-methyl-1*H*-indole)

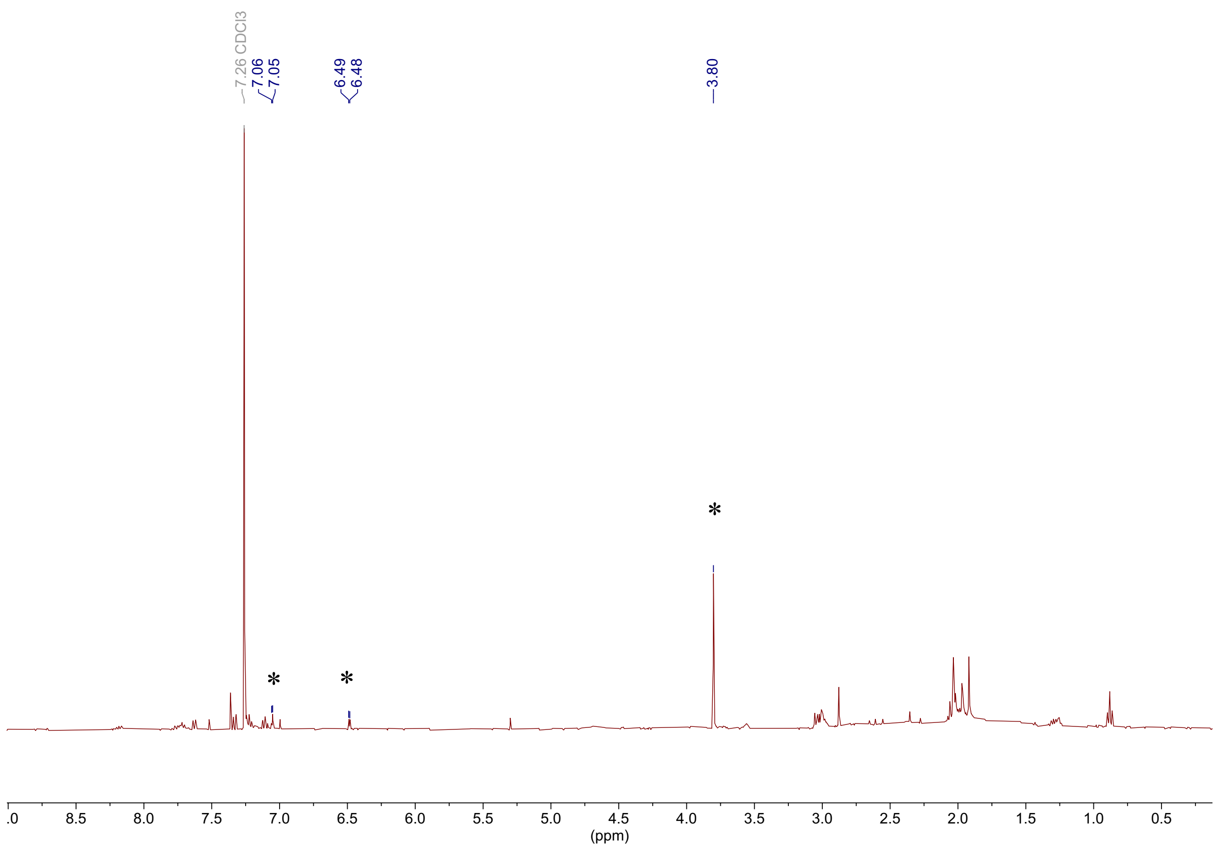
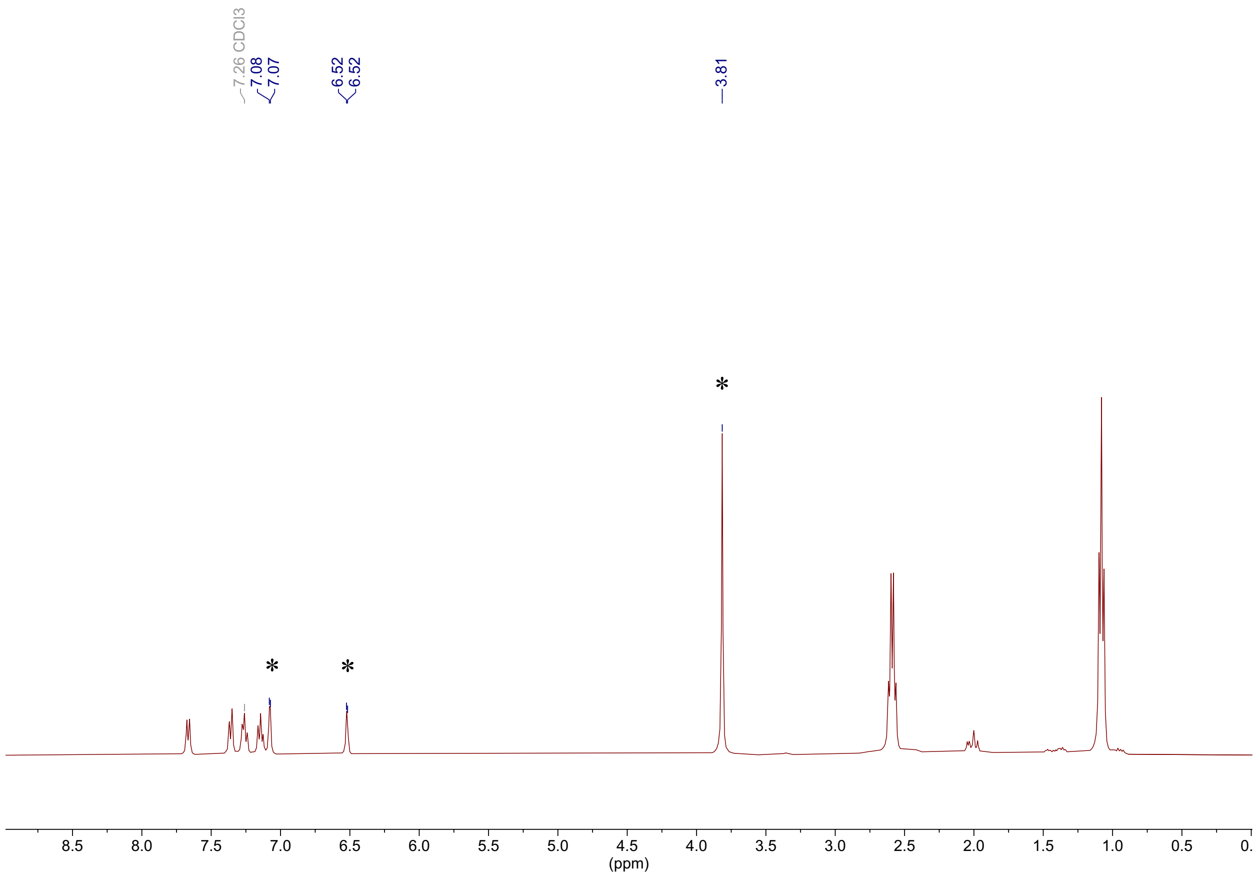


Figure S73: [1]H NMR spectrum of **1** and NEt_3 in $CDCl_3$ (400 MHz) (* denotes peaks for 1-methyl-1*H*-indole)



5. References:

1. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341; (b) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **64**, 112-122.
2. M. O. Akram, J. R. Tidwell, J. L. Dutton and C. D. Martin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202307040.