Supporting Information

Copper-Catalysed Borylation of Aryl Chlorides

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1 Experimental Section

1.1 General Considerations

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. Commercially available methylcyclohexane was degassed and dried over molecular sieves. C_6D_6, CD_2Cl_2 and $CDCl_3$ were purchased from Sigma-Aldrich. [Cu(Dipp$_2$Im)(Cl)],[S1] [Cu(Mes$_2$Im)(Cl)],[S1] [Cu(CaaC^{Me})(Cl)],[S2] [(PCy$_3$)Cu(μ-I$_2$)Cu(PCy$_3$)],[S3] [Cu(Xantphos)(Cl)],[S4] ^{i}Pr$_2$Im,[S5a-b] Me$_2$Im^{Me},[S5c] Cy$_2$Im,[S5d] and B_2cat_2[S6] were prepared according to published procedures. The diboron reagents B_2pin_2, and B_2neop_2 were a generous gift from AllyChem Co. Ltd. Anhydrous NMe_4F is commercially available; for this work, however, it was synthesized according to a literature procedure.[S7] All other reagents were purchased from Sigma-Aldrich or ABCR.

NMR spectra were recorded at 298 K using Bruker Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDHCl_2$: 5.32 ppm; $CHCl_3$: 7.26 ppm; C_6D_5H: 7.16 ppm) whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS using the natural-abundance carbon resonances (CD_2Cl_2: 53.84 ppm; $CDCl_3$: 77.16 ppm; C_6D_6: 128.0 ppm). ^{11}B and ^{19}F NMR chemical shifts are reported relative to external $BF_3{\cdot}OEt_3$ or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280

°C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

1.2 Synthesis and Characterization of the Metal Complexes

Synthesis of [Cu(^{i}Pr$_2$Im)(Cl)][S8] **1**

In a Schlenk tube, copper(I) chloride (2.00 g, 20.2 mmol,) in THF (15 mL) was cooled to -78 °C and 1,3-di-*iso*-propylimidazolin-2-ylidene (3.08 g, 20.2 mmol, 3.08 mL) was added dropwise. The mixture was allowed to warm slowly to room temperature and stirred overnight. All volatiles were removed under reduced pressure. The crude product was suspended in *n*-hexane (20 mL), collected by filtration and dried *in vacuo*. **Yield:** 4.54 g (18.1 mmol, 90%) of a grey solid. **Elemental analysis** for [$C_9H_{16}N_2CuCl$] [251.24 g/mol]: Calc. (found) C 43.03 (42.99), H 6.42 (6.45), N 11.15 (11.04). **^{1}H-NMR** (400 MHz, 25 °C, C_6D_6): δ = 0.93 (d, 12H, $^{3}J_{H-H}$ = 7 Hz, CHC*H*$_3$), 4.34 (sept, 2H, $^{3}J_{H-H}$ = 7 Hz, C*H*CH$_3$), 6.25 (s, 2H, NC*H*C*H*N). **^{13}C{^{1}H}-NMR** (100 MHz, 25 °C, C_6D_6): δ = 23.5 (CH*C*H$_3$), 53.6 (*C*HCH$_3$), 117.0 (N*CC*N), 174.5 (N*C*N). **HRMS-ASAP** (m/z): [2 M]$^{+}$ calc. for $C_{18}H_{32}Cl_2Cu_2N_4$, 502.0572 found 502.0554.

Synthesis of [Cu(Me_2Im^{Me})(Cl)][S8b] **2**

In a Schlenk tube, copper(I) chloride (198 mg, 2.00 mmol) and 1,3,4,5-tetramethylimidazolin-2-ylidene (248 mg, 2.00 mmol) was cooled to -110 °C. THF (5 mL) was added slowly down the inside of the cooled Schlenk tube. The mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed under reduced pressure. The crude product was suspended in *n*-hexane (10 mL), collected by filtration and dried *in vacuo*. **Yield:** 295 mg (1.32 mmol, 66%) of an off-white solid. **Elemental analysis** for [$C_7H_{12}N_2CuCl$] [223.18 g/mol]: Calc. (found) C 37.67 (38.04), H 5.42 (5.47), N 12.55 (12.70). **^{1}H-NMR** (400 MHz, 25 °C, C_6D_6): δ = 1.19 (s, 6H, C_qCH_3), 2.88 (s, 6H, NC*H*$_3$). **^{13}C{^{1}H}-NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 9.1 (C_qCH_3), 35.8 (N*C*H$_3$), 125.2 (N*CC*N), 174.4 (N*C*N). **HRMS-ASAP** (m/z): [M - Cl]$^{+}$ calc. for $C_7H_{12}CuN_2$, 187.0291 found, 187.0285.

Synthesis of [Cu(Cy_2Im)(Cl)][S9] **3**

In a Schlenk tube, copper(I) chloride (2.00 g, 20.2 mmol,) in THF (15 mL) was cooled to -78 °C. and 1,3-dicyclohexylimidazolin-2-ylidene (4.69 g, 20.2 mmol) was added in small portions. The mixture was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed under reduced pressure. The crude product was suspended in *n*-hexane (20 mL), collected by filtration and dried *in vacuo*. **Yield:** 5.37 g (16.2 mmol, 80%) of a white solid. **Elemental analysis** for [$C_{15}H_{24}N_2CuCl$] [331.37 g/mol]: Calc. (found) C 54.37 (54.28), H 7.30 (7.48), N 8.45 (8.33). **^{1}H-NMR** (400 MHz, 25 °C, $CDCl_3$): δ = 1.22-2.07 (m, 20H, Cy-CH_2), 4.27 (m, 2H, N-C*H*), 6.91 (s, 2H, NC*H*C*H*N). **^{13}C{^{1}H}-NMR** (100 MHz, 25 °C, $CDCl_3$): δ = 25.2 (Cy-*C*H_2), 25.5 (Cy-*C*H_2), 34.8 (Cy-*C*H_2), 61.3 (N-*C*H) 117.5 (N*CC*N), 173.7 (N*C*N). **HRMS-ASAP** (m/z): $[M]^+$ calc. for $C_{15}H_{24}N_2CuCl$, 330.0919 found, 332.0911.

1.3 Details of the Catalytic Borylation of Aryl Chlorides

1.3.1 General Procedure for Catalyst Screening

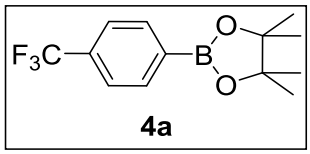
In an argon-filled glovebox, NHC-Copper-complex [Cu] (10 mol%) and the solvent were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. The base, the boron reagent, and the aryl chloride were added. The reaction mixture was stirred at 90 °C for the indicated time, then diluted with Et_2O (2 mL) and filtered through a pad of Celite (Ø 3 mm × 8 mm). Anisole was added as an internal standard and the crude reaction mixture was analysed by GC-MS.

1.3.2 General Procedures for the Synthesis of Organoboronic Esters

In an argon-filled glovebox, [Cu(Cy_2Im)(Cl)] **3** (10 mol%) and the solvent (3 mL) were added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. The base (0.75 mmol, 1.5 equiv.), the boron reagent (0.75 mmol, 1.5 equiv.) and the aryl chloride (0.5 mmol, 1.0 equiv.) were added. The reaction mixture was stirred at 90 °C for 42 h, then diluted with Et_2O (2 mL) and filtered through a pad of Celite (Ø 3 mm × 8 mm). The product was isolated by flash column chromatography (hexane/ethyl acetate (95/5); for **25a-26a** hexane/ethyl acetate (80/20)) after careful removal of the solvent *in vacuo* (especially noting that volatile arylboronates can evaporate with the solvent). The reactions were commonly performed on a 500 µmol scale in 3 mL of methylcyclohexane. The gram scale reaction of **4** was performed on a 6.00 mmol scale in 36 mL of methylcyclohexane giving a 70% yield of **4a**.

All aryl boronate products were reported previously and were unambiguously identified by comparison of HRMS and ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H} and/or ^{19}F{^{1}H} NMR spectroscopy data with literature data. The boron-bonded carbon atom was only detected for compounds **10a**, **12a** and **30a** due to quadrupolar broadening by the ^{11}B nucleus.

2-(4-Trifluoromethyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **4a**

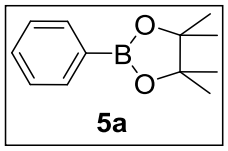


4a

Yield: 108 mg (397 µmol, 80%) of a pale yellow solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.36 (s, 12H, CH_3), 7.61 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_m), 7.91 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, CD_2Cl_2): δ = 25.1 (CH_3), 84.7 (pin-C_q), 124.7 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, CF_3), 124.7 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, aryl-C_m), 133.0 (q, $^{2}J_{C\text{-}F}$ = 32 Hz, aryl-$C_q$$CF_3$), 135.4 (aryl-$C_o$). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 30.6. **^{19}F{^{1}H} NMR** (470 MHz, 25 °C, $CDCl_3$): δ = -63.4(s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{17}BF_3O_2$ $[M+H]^+$ 273.1268 (273.1255).

The spectroscopic data for **4a** match those reported in the literature.[S10]

2-(Phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **5a**

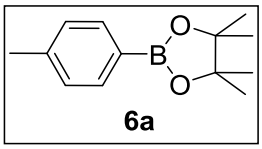


5a

Yield: 59.2 mg (290 µmol, 58%) of a colourless liquid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.37 (s, 12H, CH_3), 7.39 (m, 2H, aryl-CH_m), 7.48 (m, 1H, aryl-CH_p), 7.84 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (CH_3), 83.9 (C_q-Bpin), 127.8 (aryl-C_m), 131.4 (aryl-C_p), 134.9 (aryl-C_o). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BO_2$ $[M+H]^+$ 205.1394 (205.1386).

The spectroscopic data for **7a** match with those reported in the literature.[S11]

2-(4-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **6a**

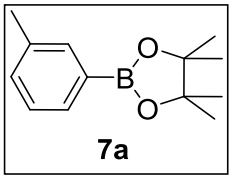


6a

Yield: 80.7 mg (370 µmol, 74%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, pin-CH_3), 2.37 (s, 3H, tolyl-CH_3), 7.19 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_m), 7.71 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 21.9 (tolyl-CH$_3$), 25.0 (pin-CH$_3$), 83.8 (pin-C_q), 128.7 (aryl-C_m), 134.9 (aryl-C_o) 141.5 (aryl-$C_q$tolyl). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1548).

The spectroscopic data for **6a** match those reported in the literature.[S12]

2-(3-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **7a**

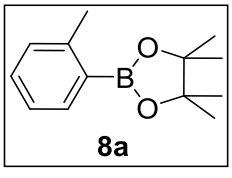


7a

Yield: 60.0 mg (275 µmol, 55%) of a colourless liquid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.35 (s, 12H, pin-CH_3), 2.36 (s, 3H, aryl-CH_3), 7.27 (m, 2H, aryl-CH), 7.62 (m, 2H, aryl-CH). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 21.4 (aryl-CH$_3$), 25.0 (pin-CH$_3$), 83.9 (pin-C_q), 127.8 (aryl-CH), 131.9 (aryl-CH), 132.2 (aryl-CH), 135.5 (aryl-CH), 137.3 (aryl-C_qCH$_3$). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1547).

The spectroscopic data for **7a** match those reported in the literature.[S13]

2-(2-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **8a**



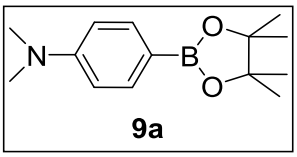
8a

Yield: 55.6 mg (255 µmol, 51%) of a colourless liquid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.35 (s, 12H, pin-CH_3), 2.55 (s, 3H, aryl-CH_3), 7.14-1.19 (m, 2H, aryl-CH), 7.33 (td, 1H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH), 7.78 (dd, 1H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 22.4 (aryl-CH$_3$), 25.0 (pin-CH$_3$), 83.5 (pin-C_q), 124.8 (aryl-CH), 129.9 (aryl-CH), 130.9

(aryl-*C*H), 136.0 (aryl-*C*H), 145.0 (aryl-$C_q$$CH_3$). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1552).

The spectroscopic data for **5a** match those reported in the literature.[S14]

2-(4-(*N*,*N*-Dimethylamino)-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **9a**

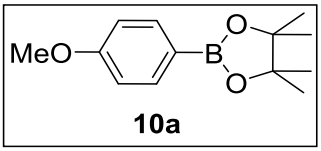


9a

Yield: 90.2 mg (365 µmol, 73%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.33 (s, 12H, pin-CH_3), 2.99 (s, 6H, N-CH_3), 6.70 (m, 2H, aryl-CH_m), 7.70 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.0 (pin-*C*H_3), 40.3 (N-*C*H_3), 83.3 (pin-C_q), 111.4 (aryl-*C*H_m), 136.3 (aryl-*C*H_o), 152.6 (aryl-C_qN). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 31.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{23}BNO_2$ $[M+H]^+$ 248.1821 (248.1820).

The spectroscopic data for **9a** match those reported in the literature.[S12]

2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **10a**

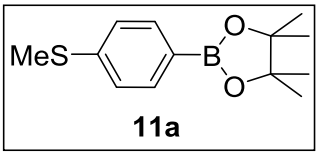


10a

Yield: 58.5 mg (250 µmol, 50%) of a pale yellow solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, pin-CH_3), 3.82 (s, 3H, OCH_3), 6.90 (d, 2H, $^3J_{H\text{-}H}$ = 9 Hz, aryl-CH_m), 7.76 (d, 2H, $^3J_{H\text{-}H}$ = 9 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.0 (pin-*C*H_3), 55.2 (O*C*H_3), 83.7 (C_q-pin), 113.4 (aryl-*C*H_m), 120.5 (br, aryl-C_qB), 136.6 (aryl-*C*H_o), 162.3 (aryl-C_qOMe). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_3$ $[M+H]^+$ 235.1500 (235.1489).

The spectroscopic data for **10a** match those reported in the literature.[S12b]

2-(4-Methylthio-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **11a**

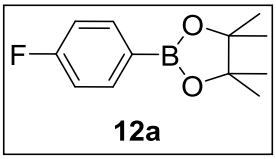


11a

Yield: 88.8 mg (355 µmol, 71%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, pin-CH_3), 2.48 (s, 3H, SCH_3), 7.23 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-CH_m), 7.72 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 15.2 (SCH_3), 25.0 (pin-CH_3), 83.8 (C_q-pin), 125.1 (aryl-CH_m), 135.2 (aryl-CH_o) 142.7 (aryl-C_qSMe). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2S$ $[M+H]^+$ 251.1272 (251.1264).

The spectroscopic data for **11a** match those reported in the literature.[S15]

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **12a**

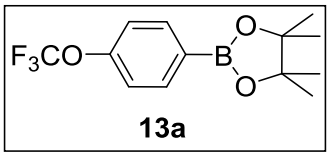


12a

Yield: 86.6 mg (390 µmol, 78%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, CH_3), 7.05 (m, 2H, aryl-CH_m), 7.81 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.0 (CH_3), 84.0 (C_q-Bpin), 115.0 (d, $^{2}J_{C\text{-}F}$ = 20 Hz, aryl-C_m), 125.1 (br, aryl-C_qB), 137.2 (d, $^{3}J_{C\text{-}F}$ = 8 Hz aryl-C_o), 165.2 (d, $^{1}J_{C\text{-}F}$ = 250 Hz, aryl-CF). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 30.6. **^{19}F{^{1}H} NMR** (470 MHz, 25 °C, $CDCl_3$): δ = -108.4 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BFO_2$ $[M+H]^+$ 223.1300 (223.1298).

The spectroscopic data for **12a** match those reported in the literature.[S16]

2-(4-(Trifluoromethoxy)phenyl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **13a**

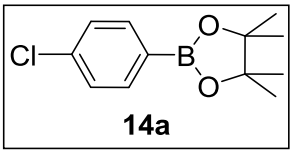


13a

Yield: 69.1 mg (240 µmol, 48%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, CH_3), 7.20 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_m), 7.84 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.0 (CH_3), 84.2 (pin-C_q), 120.0 (aryl-C_m), 120.6 (q, $^{1}J_{C\text{-}F}$ = 258 Hz, CF_3), 136.7 (aryl-C_o), 151.8 (aryl-$C_q$$CF_3$). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 30.7. **^{19}F{^{1}H} NMR** (470 MHz, 25 °C, $CDCl_3$): δ = -57.6 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{16}BF_3O_3$ $[M]^+$ 288.1139 (288.1133).

The spectroscopic data for **13a** match those reported in the literature.[S17]

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **14a**

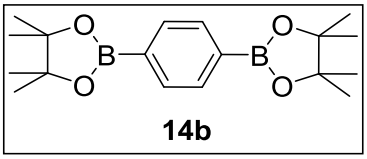


14a

Yield: 71.6 mg (300 µmol, 60%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, CH_3), 7.35 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_m), 7.74 (d, 2H, $^{3}J_{H\text{-}H}$ = 8 Hz, aryl-CH_o). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (CH_3), 84.1 (C_q-Bpin), 128.1 (aryl-CH_m), 136.3 (aryl-CH_o), 137.7 (aryl-C_qCl). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BClO_2$ $[M+H]^+$ 239.1005 (239.1001).

The spectroscopic data for **9a** match those reported in the literature.[S18]

2,2'-(1,4-Phenylene)-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **14b**

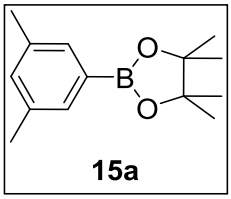


14b

Yield: 107 mg (325 µmol, 65%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.35 (s, 24H, CH_3), 7.80 (s, 4H, aryl-CH). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (CH_3), 84.0 (C_q-Bpin), 134.0 (aryl-CH). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{29}B_2O_4$ $[M+H]^+$ 331.2246 (331.2241).

The spectroscopic data for **14b** match those reported in the literature.[S19]

2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **15a**

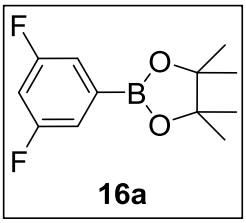


15a

Yield: 78.9 mg (340 µmol, 68%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.34 (s, 12H, pin-CH_3), 2.32 (d, 6H, $^{4}J_{H\text{-}H}$ = 1 Hz, aryl-CH_3), 7.10 (m, 1H, aryl-CH_p), 7.44 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 21.3 (aryl-CH_3), 25.0 (pin-CH_3), 83.8 (pin-C_q), 132.5 (aryl-CH_o), 133.1 (aryl-CH_p), 137.3 (aryl-$C_q$$CH_3$). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1702).

The spectroscopic data for **15a** match those reported in the literature.[S18]

2-(3,5-Difluorophenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **16a**

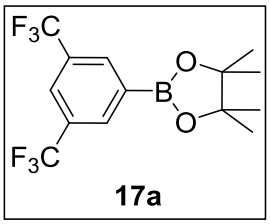


16a

Yield: 86.4 mg (360 µmol, 72%) of a colourless solid. **^{1}H NMR** (400 MHz, 25 °C, CD_2Cl_2): δ = 1.33 (s, 12H, CH_3), 6.91 (tt, 1H, $^{3}J_{F\text{-}H}$ = 9 Hz, $^{4}J_{H\text{-}H}$ = 2 Hz, aryl-CH_p), 7.27 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (100 MHz, 25 °C, CD_2Cl_2): δ = 25.1 (*C*H_3), 84.9 (C_q-Bpin), 106.7 (t, $^{2}J_{C\text{-}F}$ = 25 Hz, aryl-C_p), 117.1 (m, aryl-C_o), 163.2 (dd, $^{1}J_{C\text{-}F}$ = 249 Hz, $^{3}J_{C\text{-}F}$ = 11 Hz, aryl-*C*F). **^{11}B{^{1}H} NMR** (128 MHz, 25 °C, CD_2Cl_2): δ = 30.1. **^{19}F{^{1}H} NMR** (376 MHz, 25 °C, CD_2Cl_2): δ = -111.5 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{16}BF_2O_2$ $[M+H]^+$ 241.1206 (241.1203).

The spectroscopic data for **16a** match those reported in the literature.[S20]

2-(3,5-Trifluoromethylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **17a**

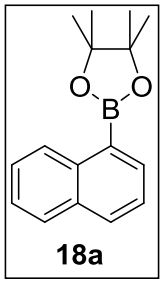


17a

Yield: 126 mg (370 µmol, 74%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.37 (s, 12 H, CH_3), 7.94 (m, 1H, aryl-CH_p), 8.24 (m, 2H, aryl-CH_o). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.0 (*C*H_3), 85.0 (pin-C_q), 123.6 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, *C*F_3), 124.9 (m, aryl-C_m), 131.0 (q, $^{2}J_{C\text{-}F}$ = 33 Hz, aryl-$C_q$$CF_3$), 134.8 (m, aryl-$C_o$). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 30.2. **^{19}F{^{1}H} NMR** (470 MHz, 25 °C, $CDCl_3$): δ = -62.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{16}BF_6O_2$ $[M+H]^+$ 341.1142 (341.1135).

The spectroscopic data for **17a** match those reported in the literature.[S21]

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene **18a**

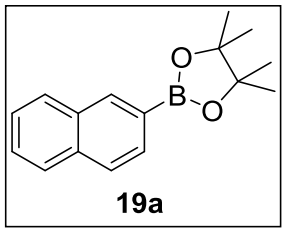


18a

Yield: 75.0 mg (295 µmol, 59%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.43 (s, 12H, CH_3), 7.45-7.57 (m, 3H, aryl-C*H*), 7.84 (m, 1H, aryl-C*H*), 7.94 (m, 1H, aryl-C*H*), 8.09 (m, 1H, aryl-C*H*), 8.77 (m, 1H, aryl-C*H*). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.1 (*C*H_3), 83.9 (C_q-Bpin), 125.1 (aryl-*C*H), 125.6 (aryl-*C*H), 126.5 (aryl-*C*H), 128.5 (aryl-*C*H), 128.6 (aryl-*C*H), 131.7 (aryl-*C*H), 133.3 (aryl- C_q), 135.8 (aryl-*C*H), 137.1 (aryl-C_q). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 31.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}BO_2$ $[M]^+$ 254.1473 (254.1468).

The spectroscopic data for **18a** match those reported in the literature.[S18]

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene **19a**

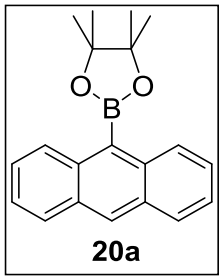


19a

Yield: 91.5 mg (360 µmol, 72%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.40 (s, 12H, CH_3), 7.49 (m, 2H, aryl-C*H*), 7.82-7.90 (m, 4H, aryl-C*H*), 8.38 (s, 1H, aryl-C*H*). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 25.1 (*C*H_3), 84.1 (C_q-Bpin), 125.9 (aryl-*C*H), 127.1 (aryl-*C*H), 127.1 (aryl-*C*H), 127.8 (aryl-*C*H), 128.8 (aryl-*C*H), 130.5 (aryl-*C*H), 133.0 (aryl-C_q), 135.2 (aryl-C_q), 136.4 (aryl-*C*H). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}BO_2$ $[M]^+$ 254.1473 (254.1471).

The spectroscopic data for 1**9a** match those reported in the literature.[S22]

9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)anthracene **20a**

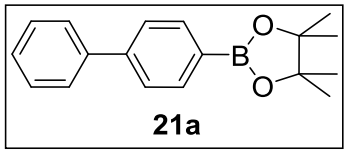


20a

Yield: 82.1 mg (270 µmol, 54%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): 1.59 (s, 12H, C*H*$_3$), 7.48 (m, 4H, aryl-C*H*), 8.01 (m, 2H, aryl-C*H*), 8.47 (m, 3H, aryl-C*H*) ppm. **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.3 (*C*H$_3$), 84.5 (*C*$_q$-Bpin), 125.0 (aryl-*C*H), 125.9 (aryl-*C*H), 128.5 (aryl-*C*H), 128.9 (aryl-*C*H), 129.6 (aryl-*C*H), 131.3 (aryl-*C*$_q$), 136.1 (aryl-*C*$_q$). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 32.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{20}H_{22}BO_2$ $[M+H]^+$ 305.1707 (305.1689).

The spectroscopic data for **20a** match those reported in the literature.[S23]

2-(Biphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **21a**

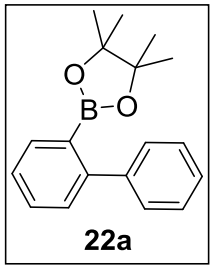


21a

Yield: 82.7 mg (295 µmol, 59%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.37 (s, 12H, C*H*$_3$), 7.36 (m, 1H, aryl-C*H*), 7.45 (m, 2H, aryl-C*H*), 7.62 (m, 4H, aryl-C*H*), 7.90 (m, 2H, aryl-C*H*). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (*C*H$_3$), 84.0 (*C*$_q$-Bpin), 126.6 (aryl-*C*H), 127.4 (aryl-*C*H), 128.9 (aryl-*C*H), 135.4 (aryl-*C*H), 141.2 (aryl-*C*$_q$), 144.0 (aryl-*C*$_q$). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{22}BO_2$ $[M+H]^+$ 281.1707 (281.1701).

The spectroscopic data for **21a** match those reported in the literature.[S22]

2-(Biphenyl-2-yl)-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane **22a**



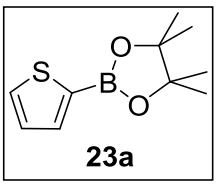
22a

Yield: 57.4 mg (205 µmol, 41%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.22 (s, 12H, C*H*$_3$), 7.32-7.49 (m, 8H, aryl-C*H*), 7.73 (m, 1H, aryl-C*H*). **^{13}C{^{1}H} NMR**

(75 MHz, 25 °C, $CDCl_3$): δ = 24.7 (CH_3), 83.8 (C_q-Bpin), 126.4 (aryl-*C*H), 127.0 (aryl-*C*H), 127.9 (aryl-*C*H), 129.1 (aryl-*C*H), 129.3 (aryl-*C*H) 130.2 (aryl-*C*H), 134.6 (aryl-*C*H), 143.4 (aryl-C_q), 147.7 (aryl-C_q). **$^{11}B\{^1H\}$ NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 31.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{22}BO_2$ $[M+H]^+$ 281.1707 (281.1702).

The spectroscopic data for **22a** match those reported in the literature.[S24]

2-(Thiophene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **23a**

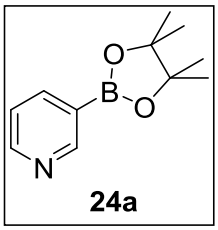


23a

Yield: 65.1mg (310 µmol, 62%) of a yellow solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.35 (s, 12H, CH_3), 7.20 (m, 1H, aryl-C*H*) 7.63-7.67 (m, 2H, aryl-C*H*). **$^{13}C\{^1H\}$ NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 24.9 (CH_3), 84.2 (C_q-Bpin), 128.4 (aryl-*C*H), 132.5 (aryl-*C*H), 137.3 (aryl-*C*H). **$^{11}B\{^1H\}$ NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 29.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{16}BO_2$ $[M+H]^+$ 211.0959 (211.0949).

The spectroscopic data for **9a** match those reported in the literature.[S25]

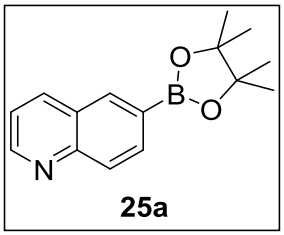
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine **24a**



24a

The yield was determined by GC-MS using biphenyl as an internal standard (68% yield). **GC/MS:** m/z: 205 $[M]^+$, 190 $[M\text{-}CH_3]^+$, 148, 120, 106.

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolone **25a**

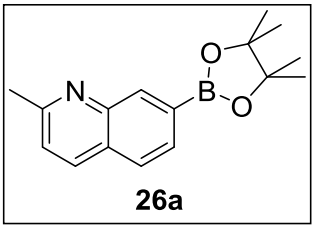


25a

Yield: 90.6 mg (355 µmol, 71%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.39 (s, 12H, CH_3), 7.40 (m, 1H, aryl-C*H*), 8.08 (m, 2H, aryl-C*H*), 8.19 (m, 1H, aryl-C*H*), 8.34 (m, 1H, aryl-C*H*), 8.94 (m, 1H, aryl-C*H*). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (*C*H_3), 84.3 (C_q-Bpin), 121.3 (aryl-*C*H), 127.8 (aryl-C_q), 128.6 (aryl-*C*H), 134.3 (aryl-*C*H), 136.2 (aryl-*C*H), 136.8 (aryl-*C*H), 149.9 (aryl-C_q), 151.5 (aryl-*C*H). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{19}BNO_2$ $[M+H]^+$ 256.1503 (256.1495).

The spectroscopic data for **9a** match those reported in the literature.[S25]

2-Methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolone **26a**

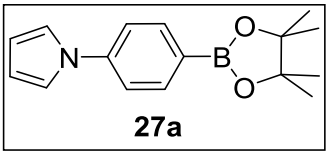


26a

Yield: 101 mg (375 µmol, 75%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.37 (s, 12H, pin-CH_3), 2.74 (s, 3H, aryl-CH_3), 7.28 (m, 1H, aryl-C*H*), 7.74 (m, 1H, aryl-C*H*), 7.83 (m, 1H, aryl-C*H*), 8.02 (m, 1H, aryl-C*H*), 8.54 (s, 1H, aryl-C*H*). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (pin-*C*H_3), 25.5 (aryl-*C*H_3), 84.1 (C_q-Bpin), 122.9 (aryl-*C*H), 126.7 (aryl-*C*H), 128.3 (aryl-C_q), 130.3 (aryl-*C*H), 136.0 (aryl-*C*H), 136.8 (aryl-*C*H), 147.4 (aryl-C_q), 159.1 (aryl-*C*H). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{21}BNO_2$ $[M+H]^+$ 270.1660 (270.1654).

The spectroscopic data for **26a** match those reported in the literature.[S26]

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-pyrrole **27a**



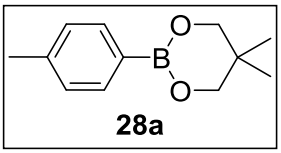
27a

Yield: 98.2 mg (365 µmol, 73%) of a colourless solid. **^{1}H NMR** (300 MHz, 25 °C, $CDCl_3$): δ = 1.36 (s, 12H, CH_3), 6.36 (t, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, pyrrole-C*H*), 7.15 (t, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, pyrrole-

C*H*), 7.41 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_m$) 7.87 (m, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_o$). **^{13}C{^{1}H} NMR** (75 MHz, 25 °C, $CDCl_3$): δ = 25.0 (*C*H$_3$), 84.0 (*C*$_q$-Bpin), 110.9 (pyrrole-*C*H) 119.2 (pyrrole-*C*H), 119.4 (aryl-*C*H$_m$), 136.4 (aryl-*C*H$_o$) 143.0 (aryl-*C*$_q$pyrrole). **^{11}B{^{1}H} NMR** (96 MHz, 25 °C, $CDCl_3$): δ = 30.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{21}BNO_2$ $[M+H]^+$ 270.1660 (270.1650).

The spectroscopic data for **27a** match those reported in the literature.[S18]

2-(4-Methyl-phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane **28a**

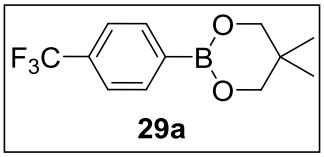


28a

Yield: 59.2 mg (290 µmol, 58%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.03 (s, 6H, neop-C*H*$_3$), 2.37 (s, 3H, tolyl-C*H*$_3$), 3.77 (s, 4H, C*H*$_2$), 7.19 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_m$), 7.72 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_o$). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 21.8 (tolyl-*C*H$_3$), 22.0 (neop-*C*H$_3$), 32.0 (neop-C$_q$), 72.4 (*C*H$_2$), 128.5 (aryl-*C*H$_m$), 134.0 (aryl-*C*H$_o$) 140.8 (aryl-*C*$_q$tolyl). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 26.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BO_2$ $[M]^+$ 204.1316 (204.1315).

The spectroscopic data for **28a** match those reported in the literature.[S27]

2-(4-Trifluoromethyl-phenyl)-5,5-dimethyl-[1,3,2]dioxaborinane **29a**

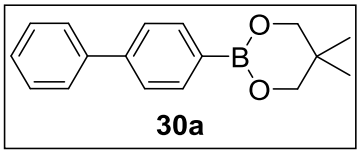


29a

Yield: 80.0 mg (310 µmol, 62%) of a pale yellow solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.03 (s, 6H, neop-C*H*$_3$), 3.79 (s, 4H, C*H*$_2$), 7.60 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_m$), 7.90 (d, 2H, $^{3}J_{H\text{-}H}$ = 9 Hz, aryl-C*H*$_o$). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 22.0 (neop-*C*H$_3$), 32.0 (neop-C$_q$), 72.5 (*C*H$_2$), 124.4 (q, $^{1}J_{C\text{-}F}$ = 272 Hz, *C*F$_3$), 124.3 (q, $^{3}J_{C\text{-}F}$ = 4 Hz, aryl-C$_m$), 132.4 (q, $^{2}J_{C\text{-}F}$ = 32 Hz, aryl-*C*$_q$CF$_3$), 134.2 (aryl-*C*$_o$). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, $CDCl_3$): δ = 26.5. **^{19}F{^{1}H} NMR** (470 MHz, 25 °C, $CDCl_3$): δ = -62.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{14}BO_2$ $[M]^+$ 258.1033 (258.1021).

The spectroscopic data for **29a** match those reported in the literature.[S28]

2-(Biphenyl-4-yl)-5,5-dimethyl-[1,3,2]dioxaborinane **30a**



30a

Yield: 49.2 mg (185 µmol, 37%) of a colourless solid. **^{1}H NMR** (500 MHz, 25 °C, $CDCl_3$): δ = 1.05 (s, 6H, neop-CH_3), 3.81 (s, 4H, CH_2), 7.36 (m, 1H, aryl-C*H*), 7.46 (m, 2H, aryl-C*H*), 7.64 (m, 4H, aryl-C*H*), 7.90 (m, 2H, aryl-C*H*). **^{13}C{^{1}H} NMR** (125 MHz, 25 °C, $CDCl_3$): δ = 22.0 (neop-CH$_3$), 32.0 (neop-C$_q$), 72.5 (CH$_2$), 126.5 (aryl-CH), 127.3 (aryl-CH), 127.5 (aryl-CH), 128.9 (aryl-CH), 131.2 (br, aryl-C_qB), 134.5 (aryl-CH), 141.3 (aryl-C_q), 143.4 (aryl-C_q). **^{11}B{^{1}H} NMR** (160 MHz, 25 °C, CD_2Cl_2): δ = 27.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{20}BO_2$ $[M+H]^+$ 267.1551 (267.1536).

The spectroscopic data for **30a** match those reported in the literature.[S29]

2 NMR Spectra

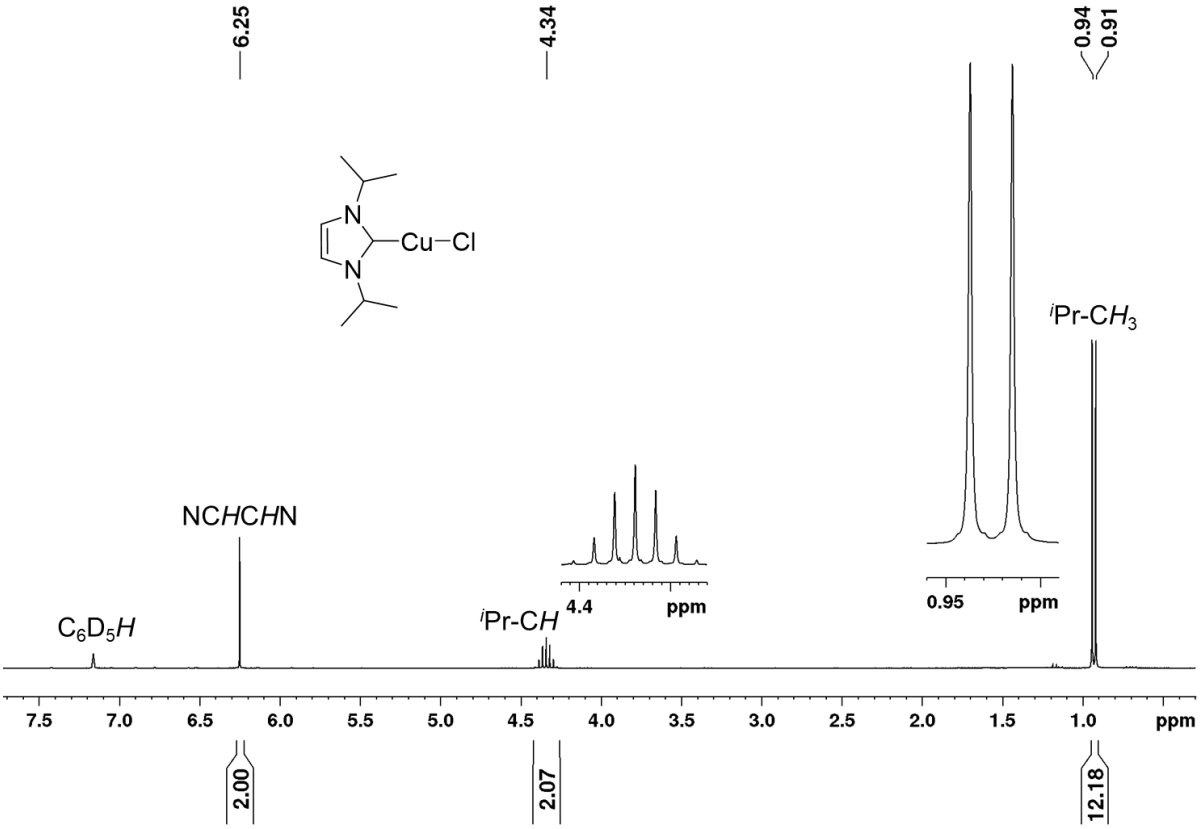


Figure S1. ^{1}H NMR spectrum of compound **1** in C_6D_6 (400 MHz).

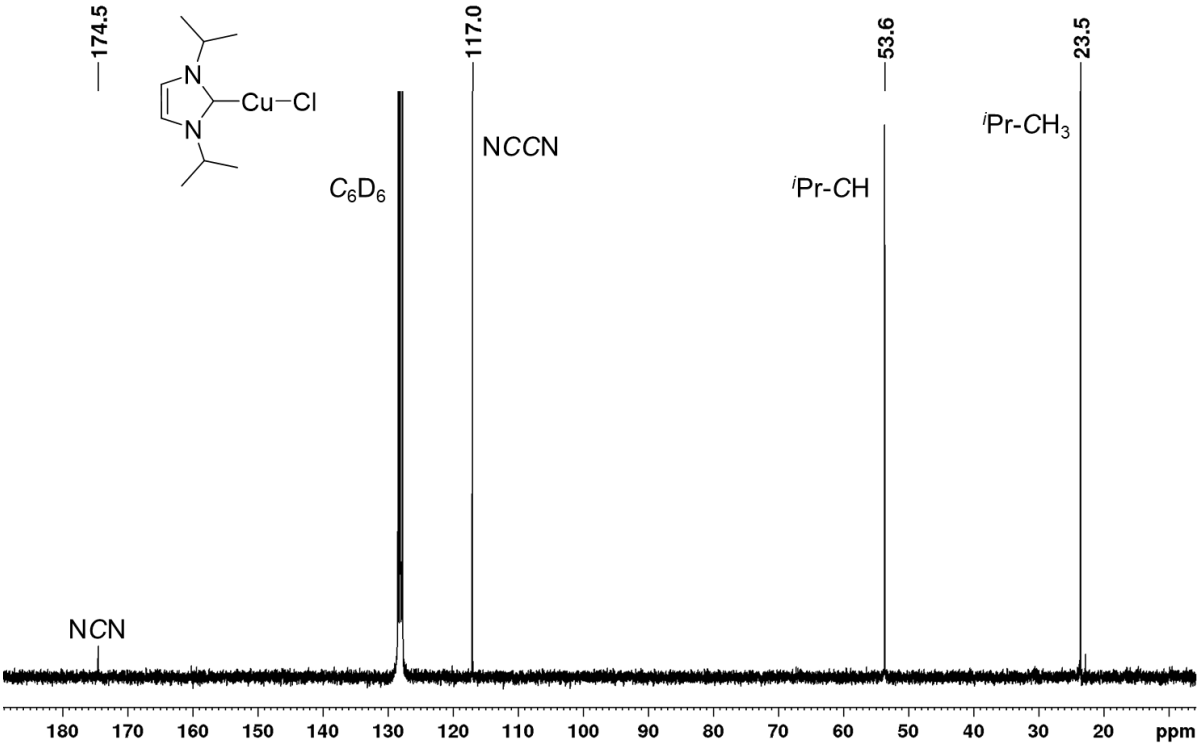


Figure S2. ^{13}C{^{1}H} NMR spectrum of compound **1** in C_6D_6 (100 MHz).

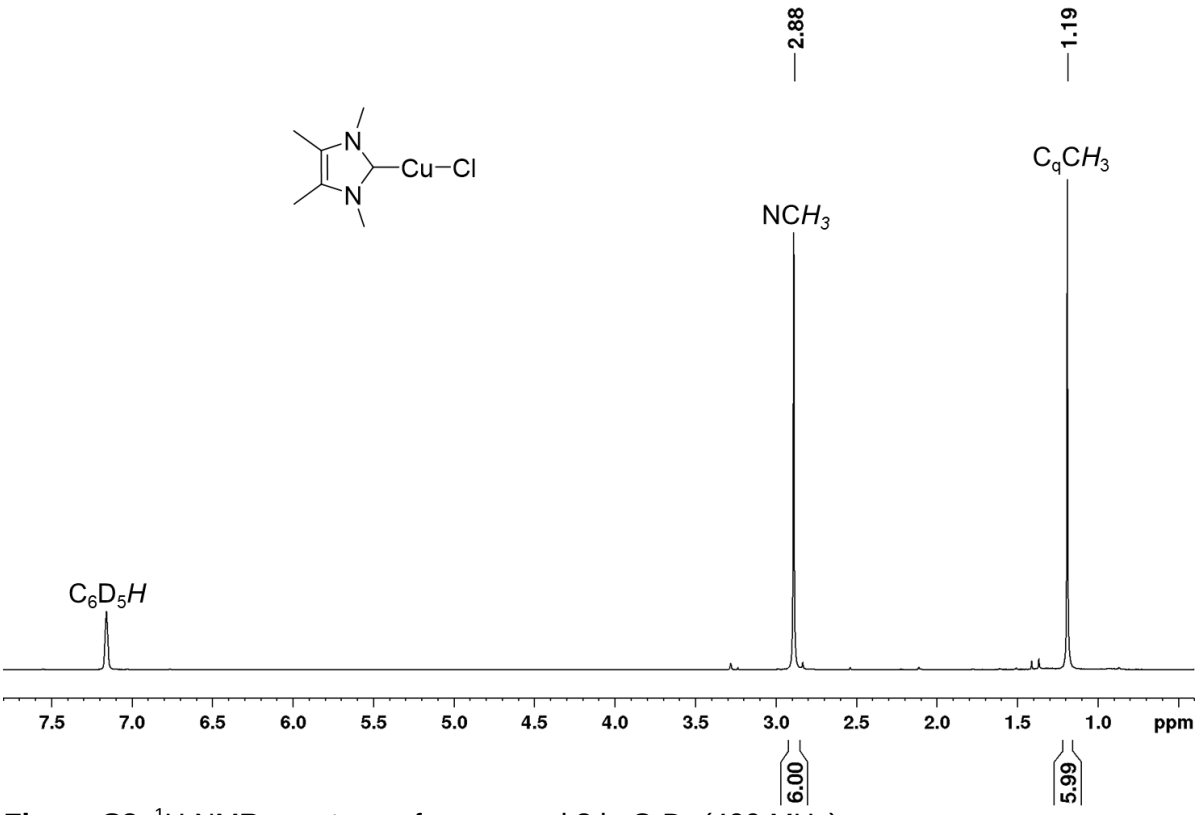


Figure S3. ^{1}H NMR spectrum of compound **2** in C_6D_6 (400 MHz).

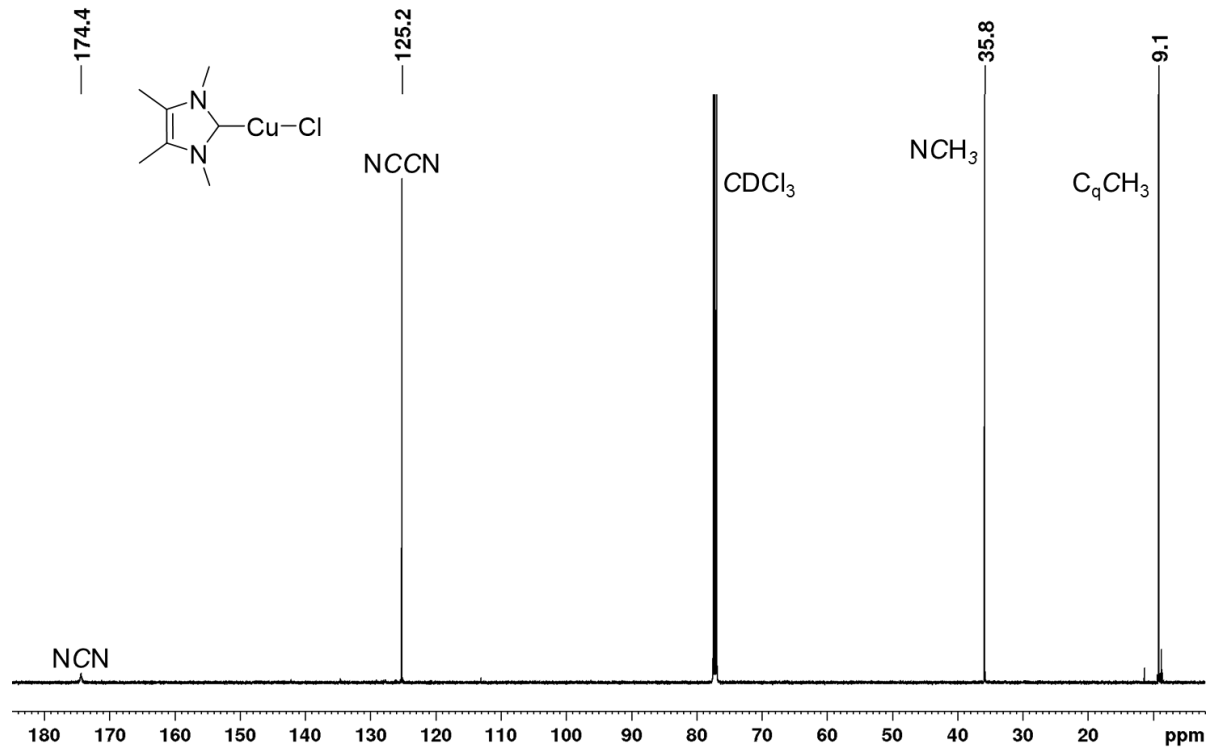


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$ (125 MHz).

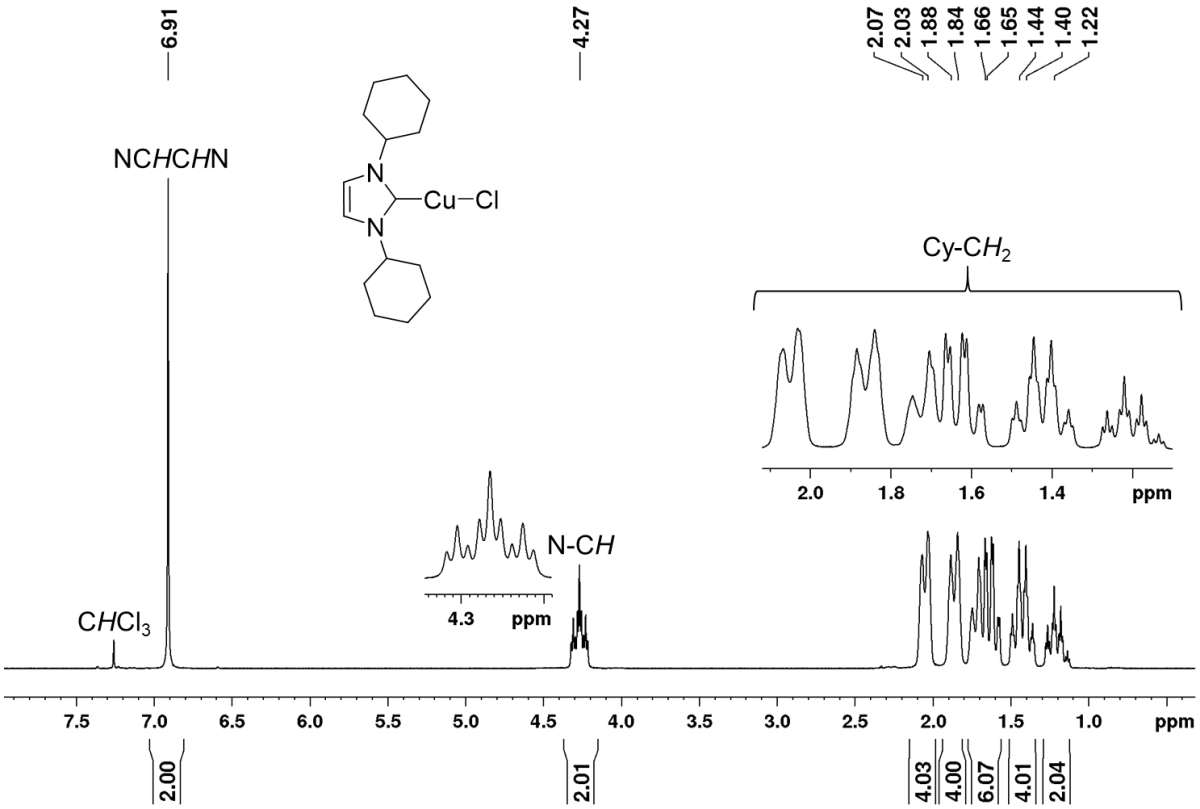


Figure S5. ^{1}H NMR spectrum of compound **3** in $CDCl_3$ (400 MHz).

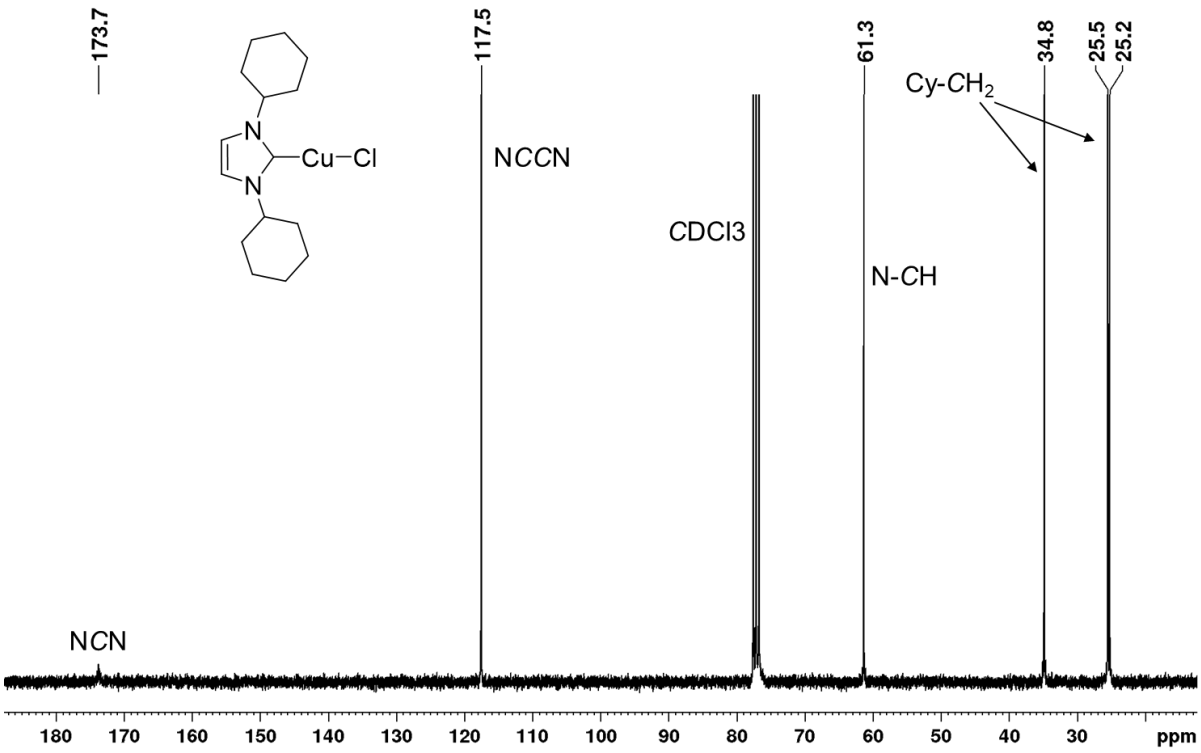


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** in $CDCl_3$ (100 MHz).

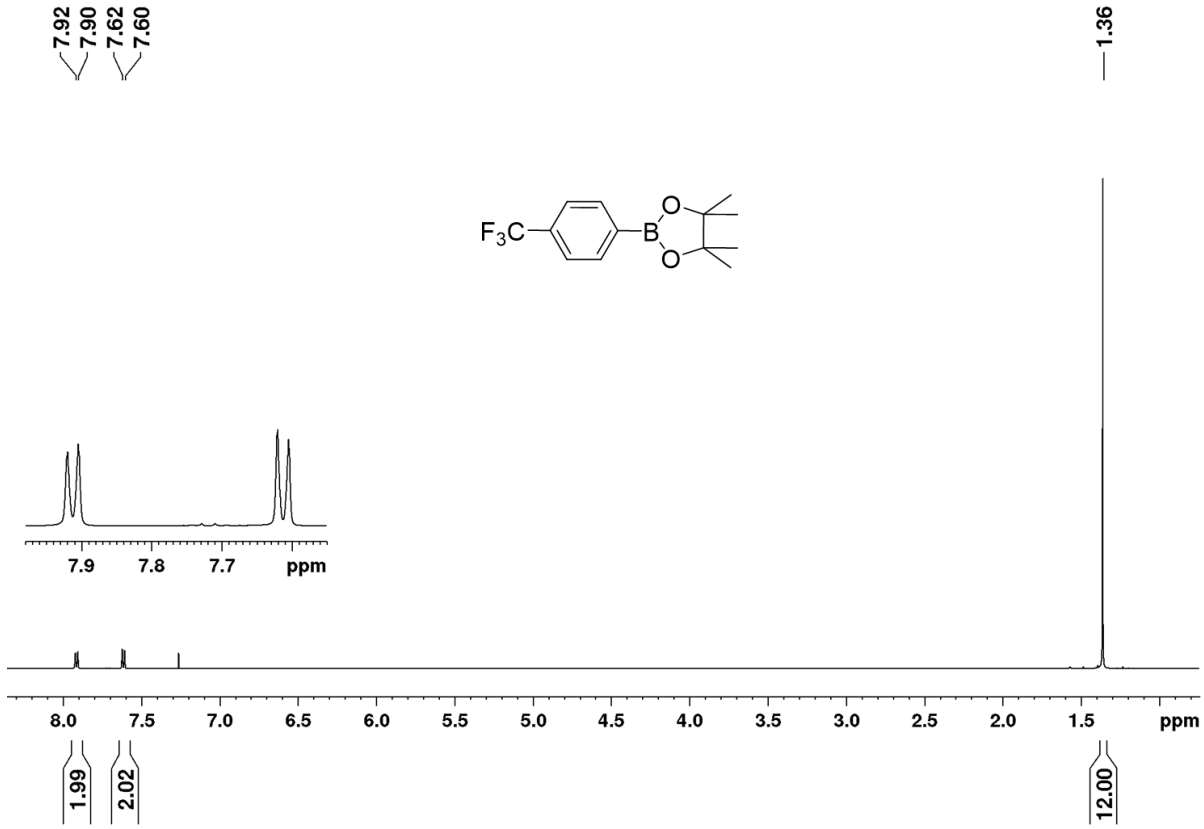


Figure S7. ^{1}H NMR spectrum of compound **4a** in $CDCl_3$ (500 MHz).

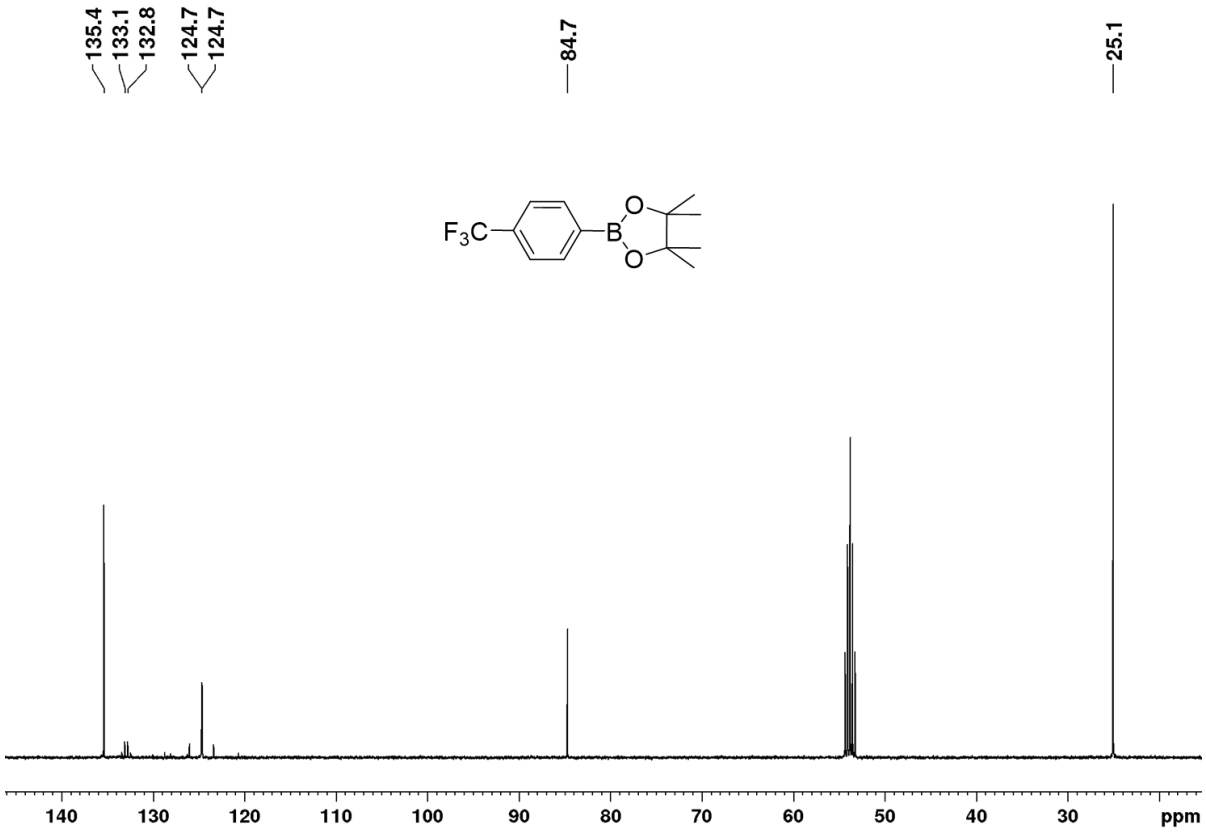


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** in CD_2Cl_2 (125 MHz).

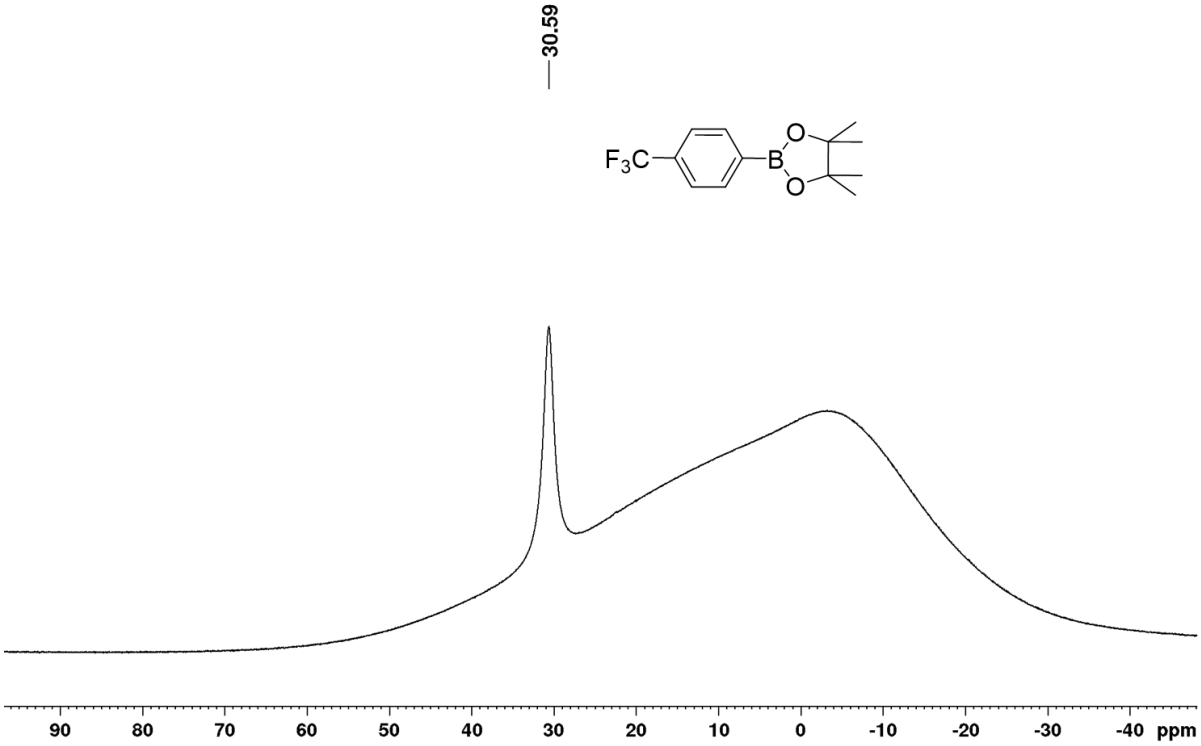


Figure S9. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4a** in $CDCl_3$ (160 MHz).

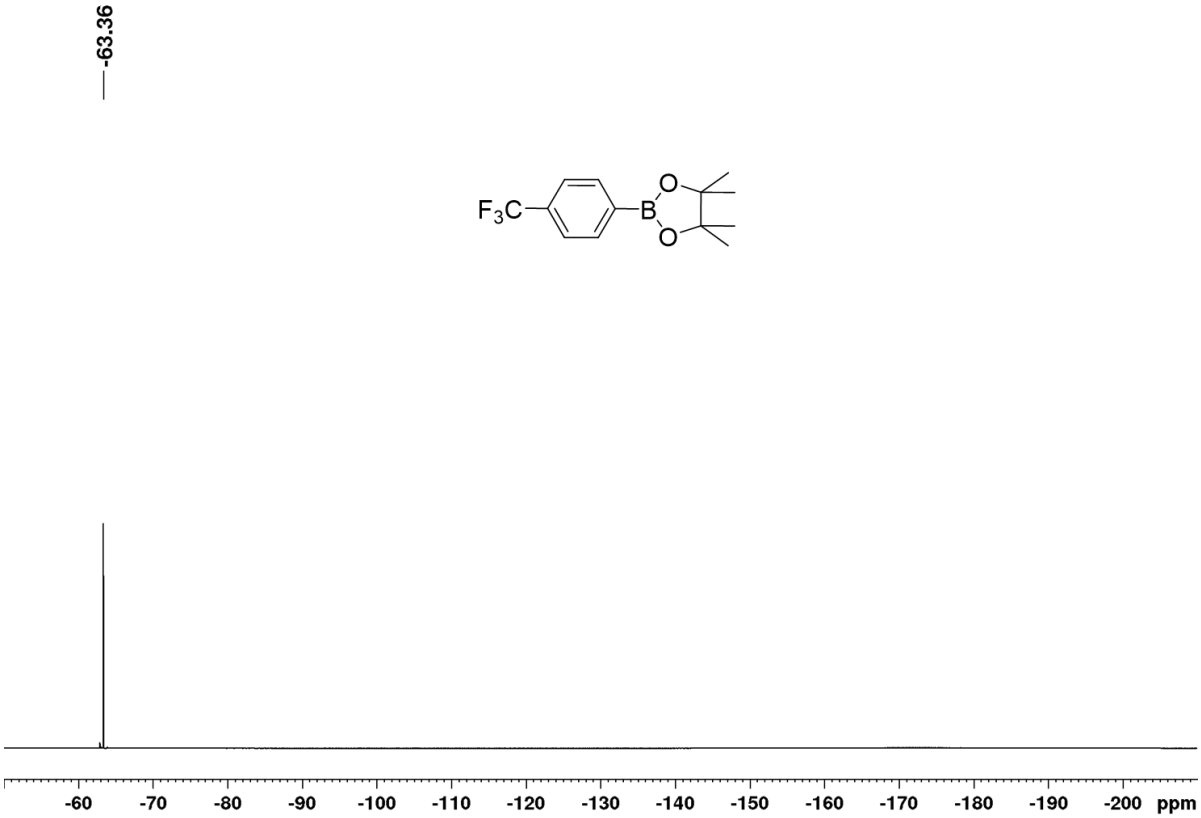


Figure S10. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4a** in $CDCl_3$ (470 MHz).

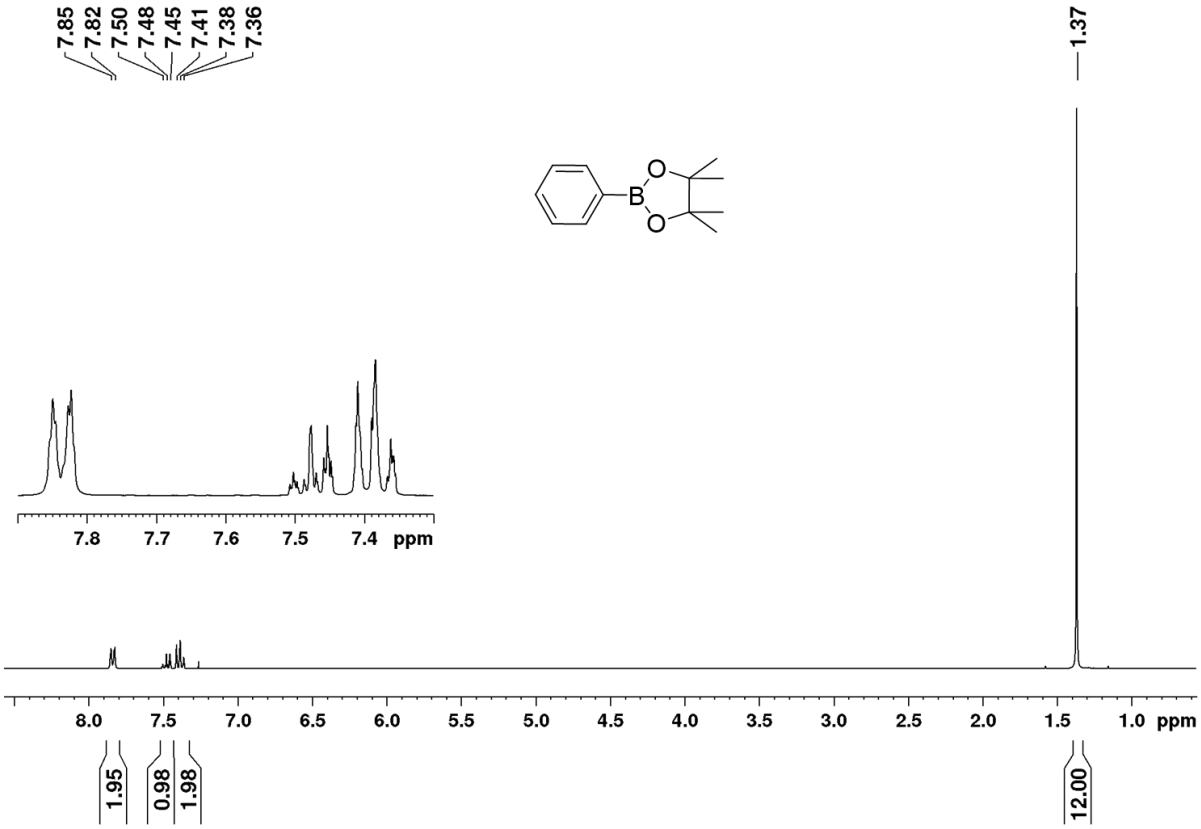


Figure S11. ^{1}H NMR spectrum of compound **5a** in $CDCl_3$ (300 MHz).

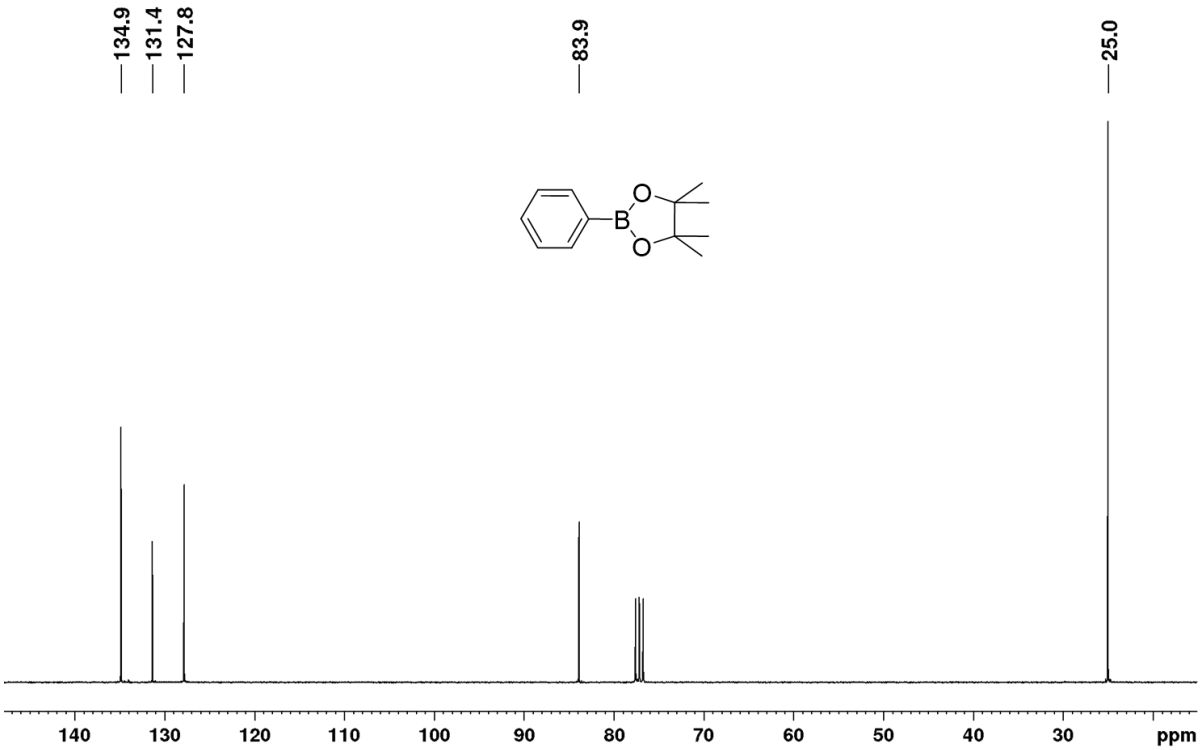


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5a** in $CDCl_3$ (75 MHz).

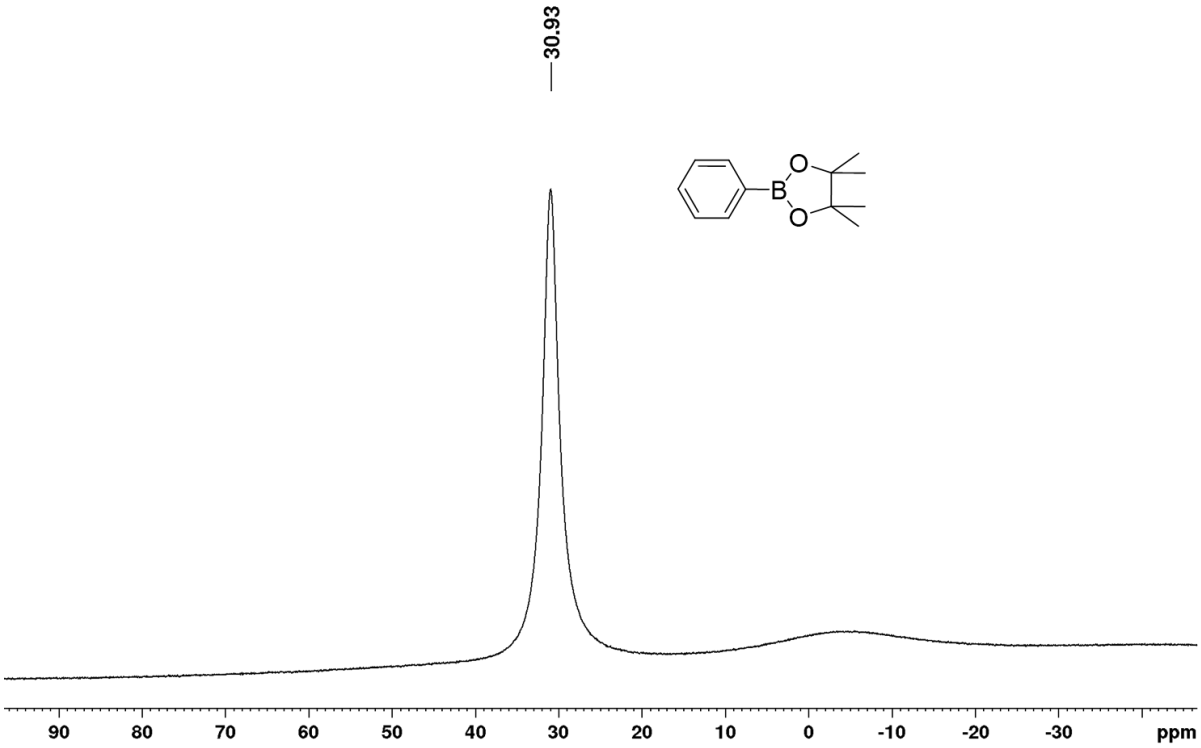


Figure S13. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5a** in $CDCl_3$ (96 MHz).

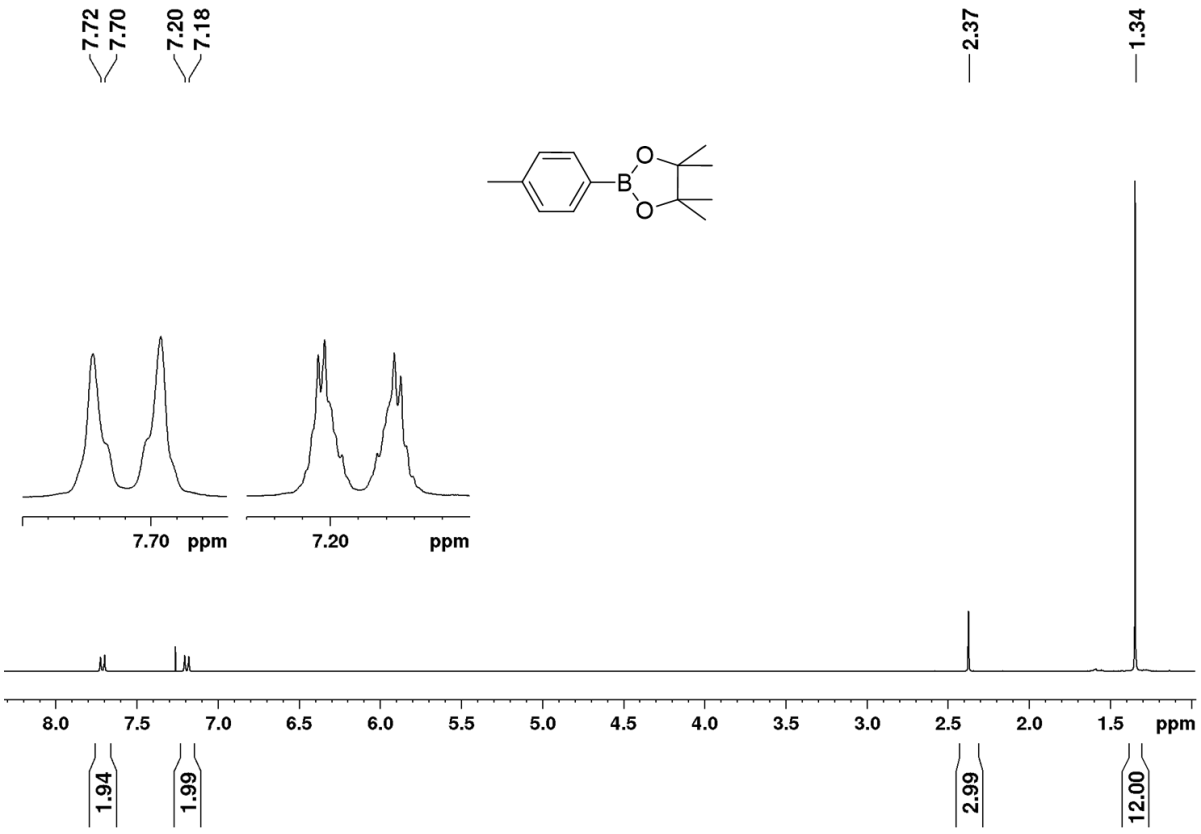


Figure S14. ^{1}H NMR spectrum of compound **6a** in $CDCl_3$ (300 MHz).

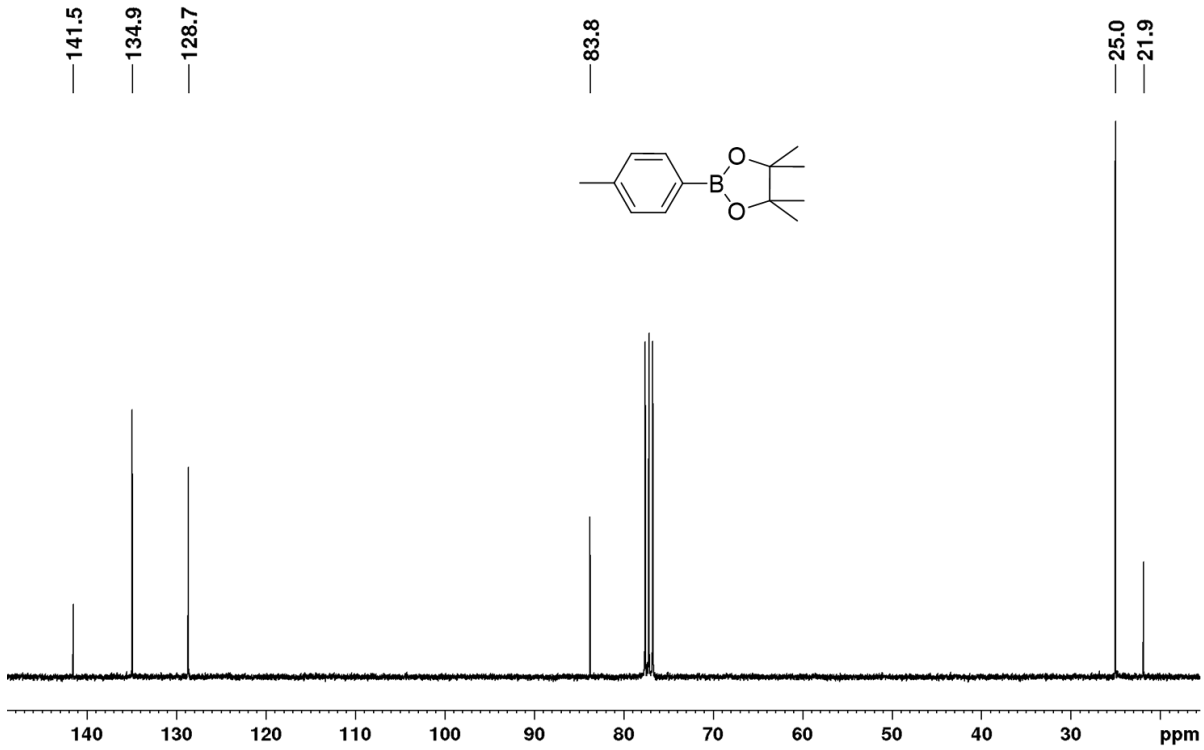


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6a** in $CDCl_3$ (75 MHz).

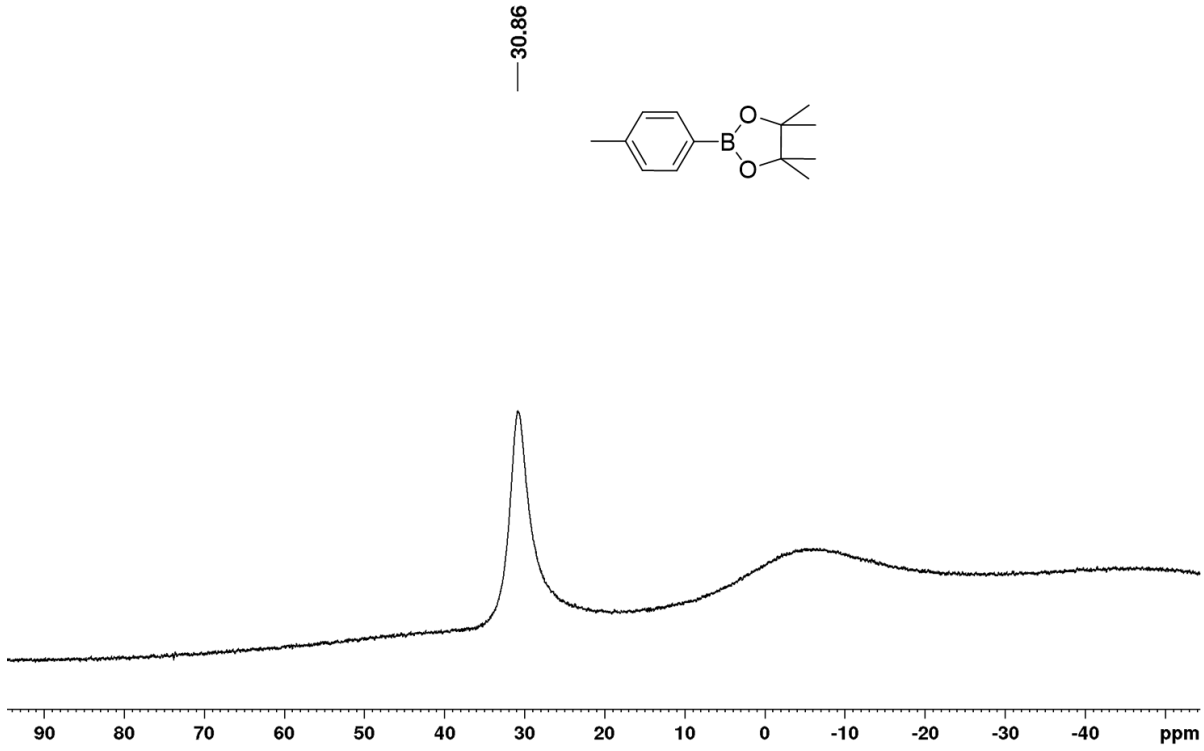


Figure S16. $^{11}B\{^{1}H\}$ NMR spectrum of compound **6a** in $CDCl_3$ (96 MHz).

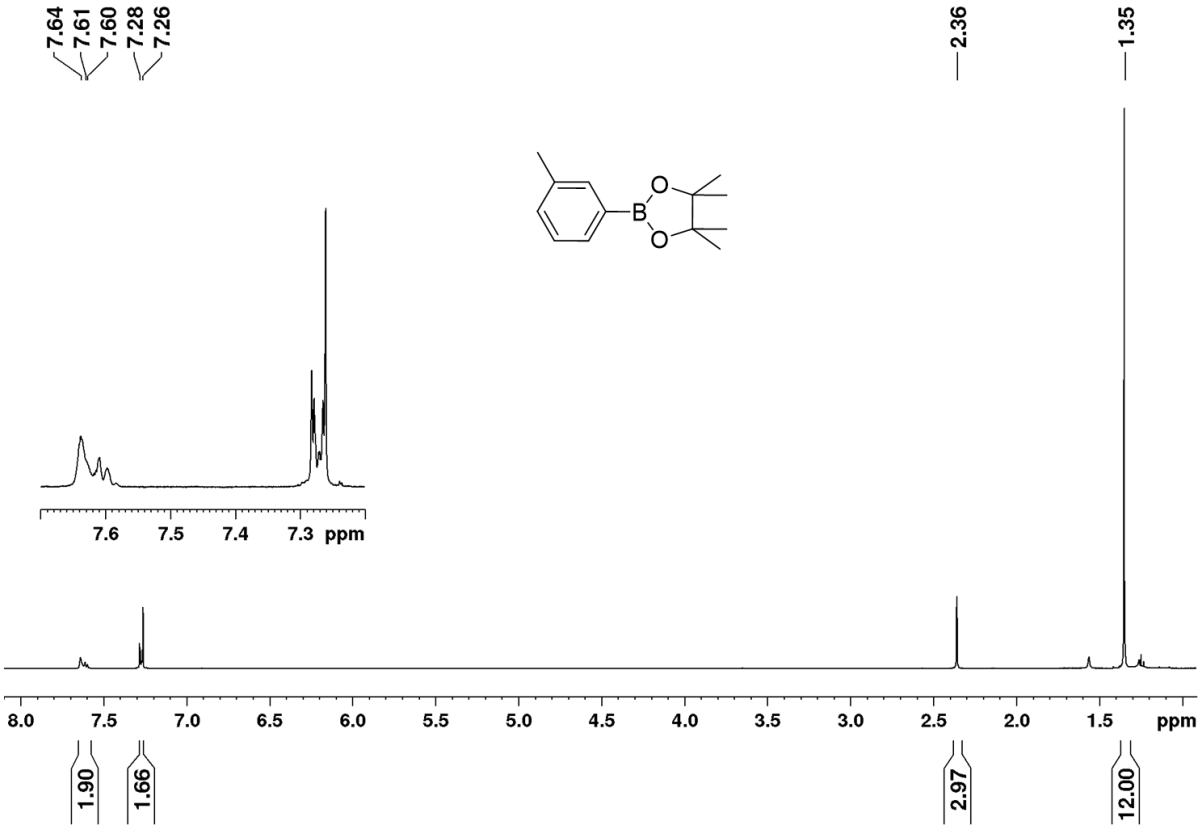


Figure S17. ^{1}H NMR spectrum of compound **7a** in $CDCl_3$ (300 MHz).

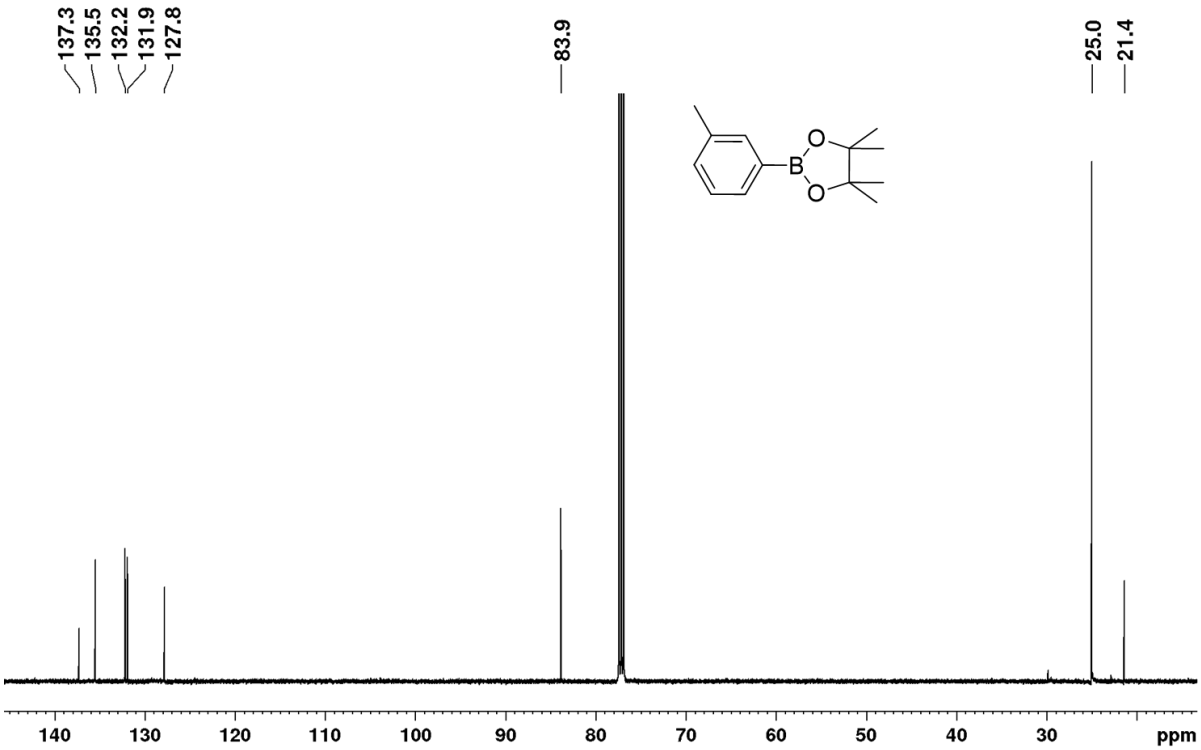


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7a** in $CDCl_3$ (75 MHz).

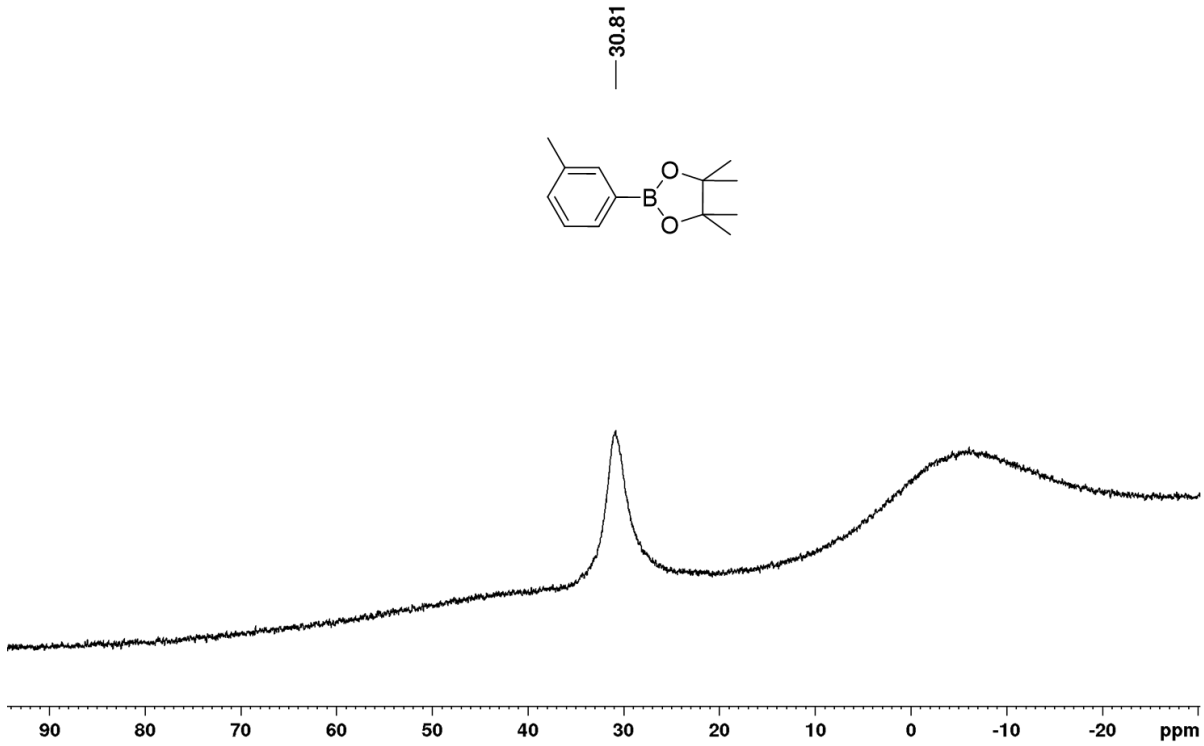


Figure S19. $^{11}B\{^{1}H\}$ NMR spectrum of compound **7a** in $CDCl_3$ (96 MHz).

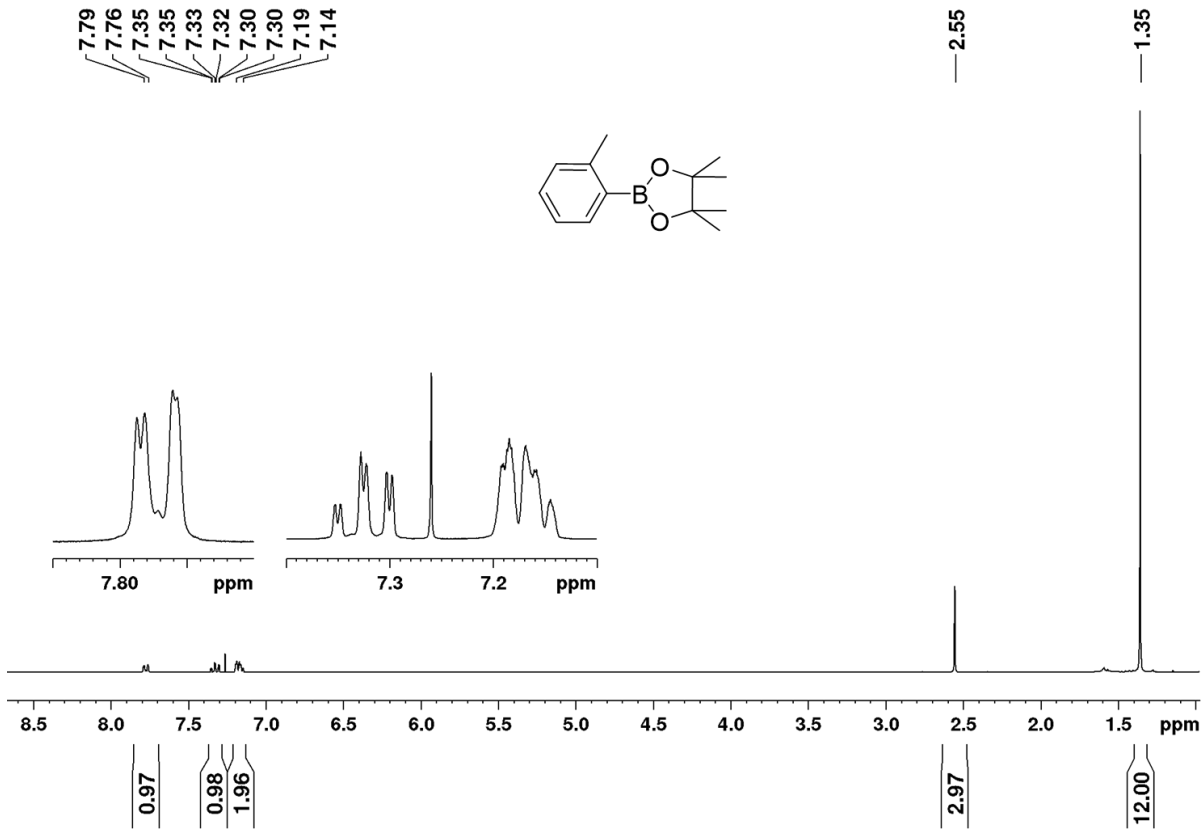


Figure S20. ^{1}H NMR spectrum of compound **8a** in $CDCl_3$ (300 MHz).

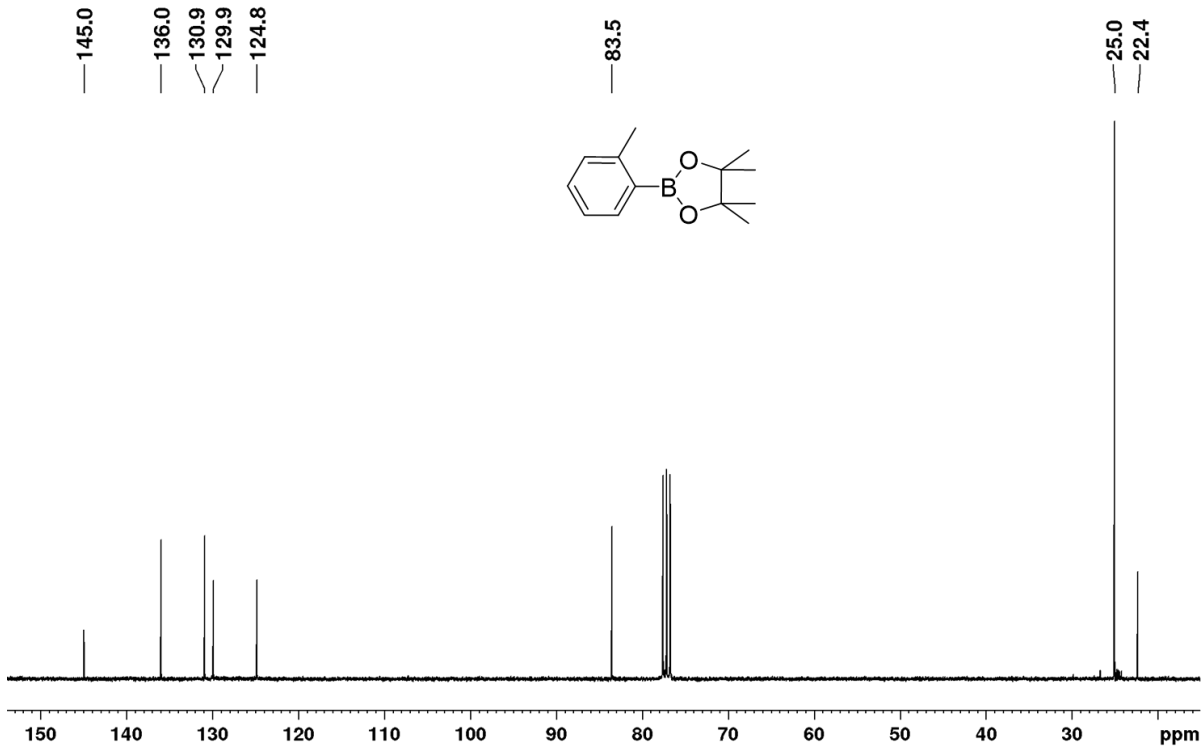


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8a** in $CDCl_3$ (75 MHz).

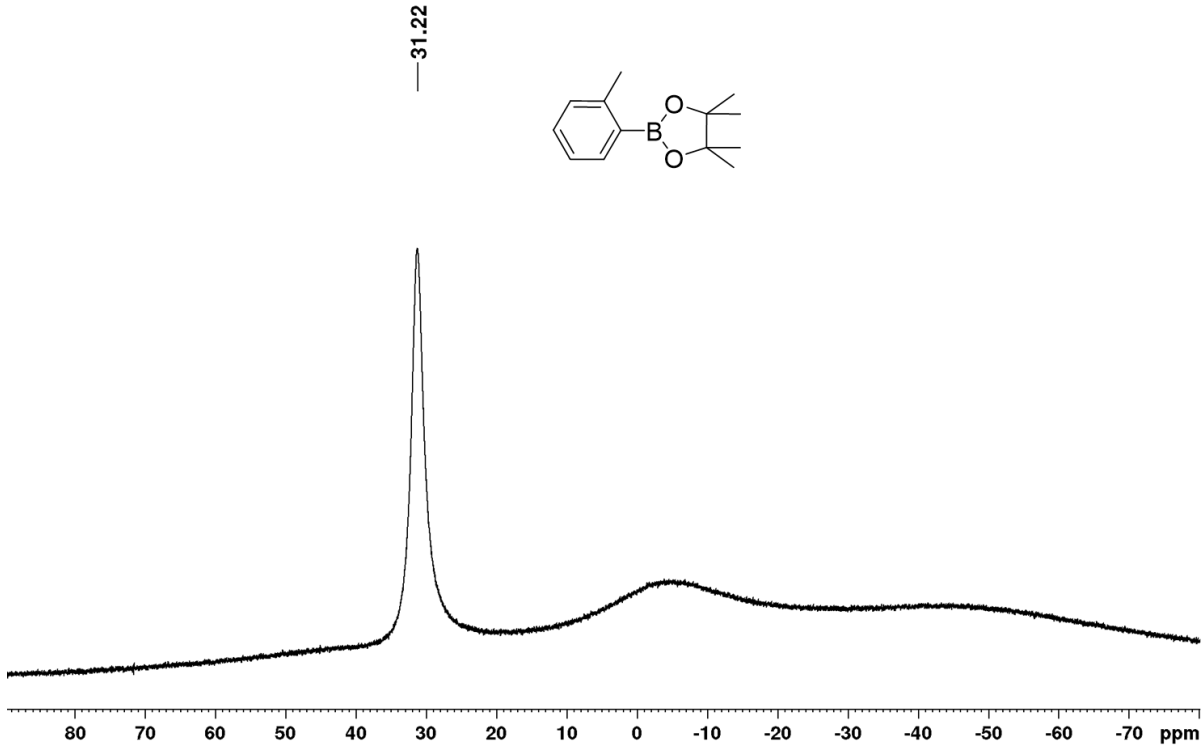


Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum of compound **8a** in $CDCl_3$ (96 MHz).

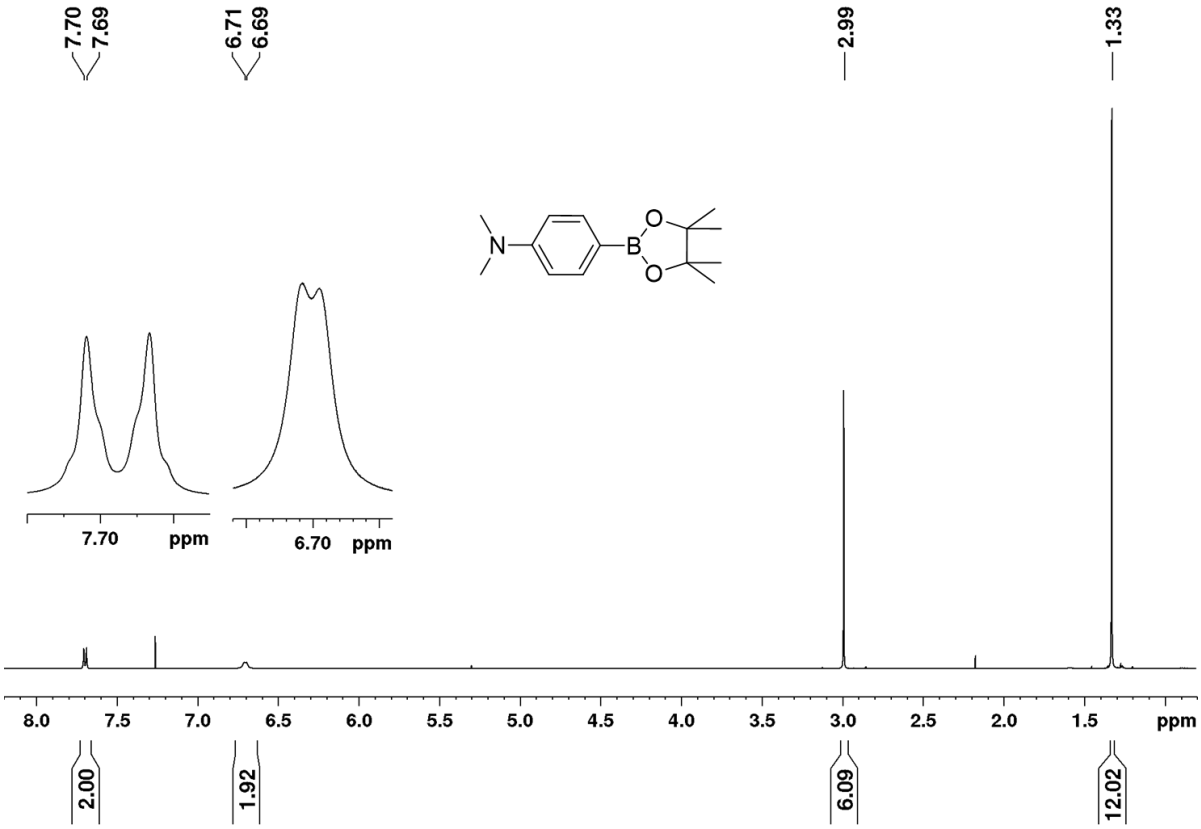


Figure S23. ^{1}H NMR spectrum of compound **9a** in $CDCl_3$ (300 MHz).

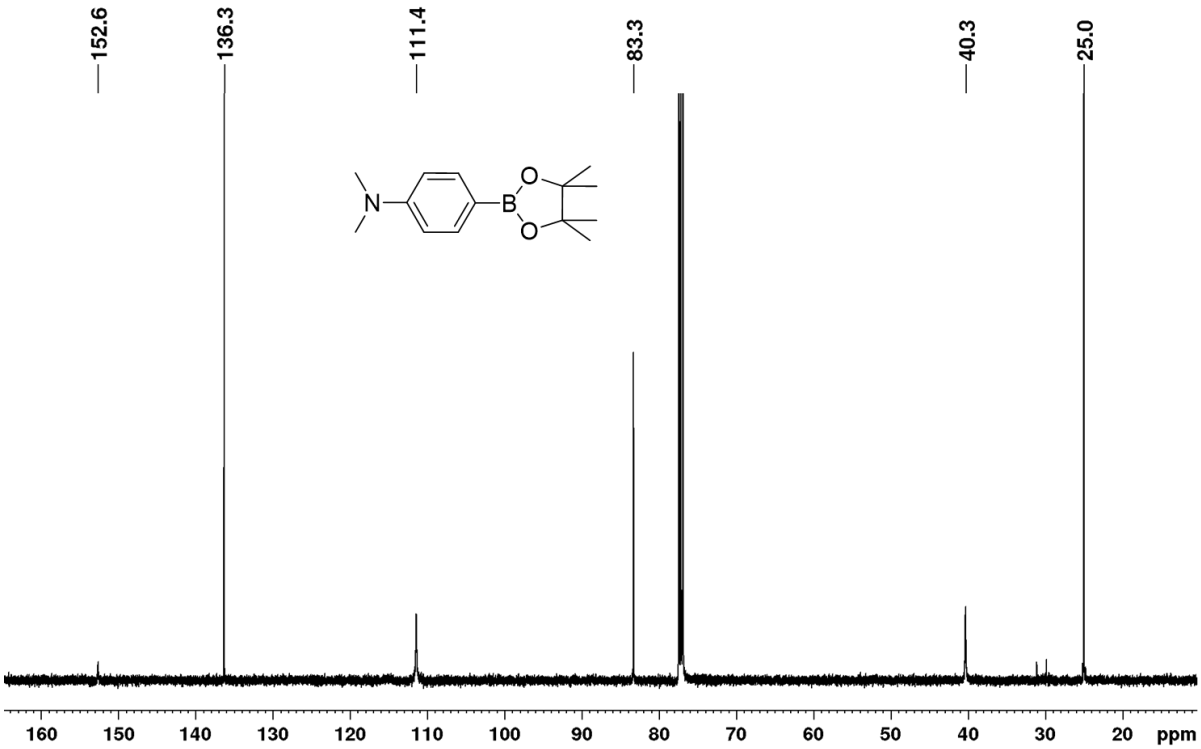


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9a** in $CDCl_3$ (75 MHz).

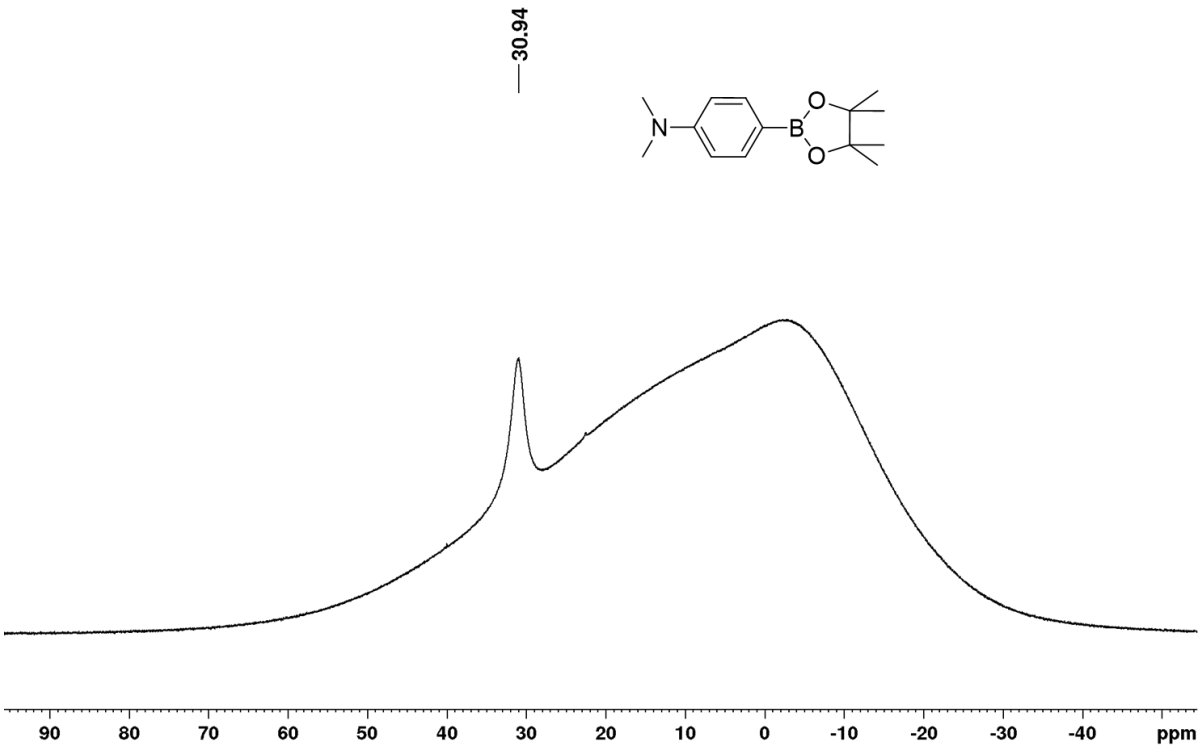


Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum of compound **9a** in $CDCl_3$ (96 MHz).

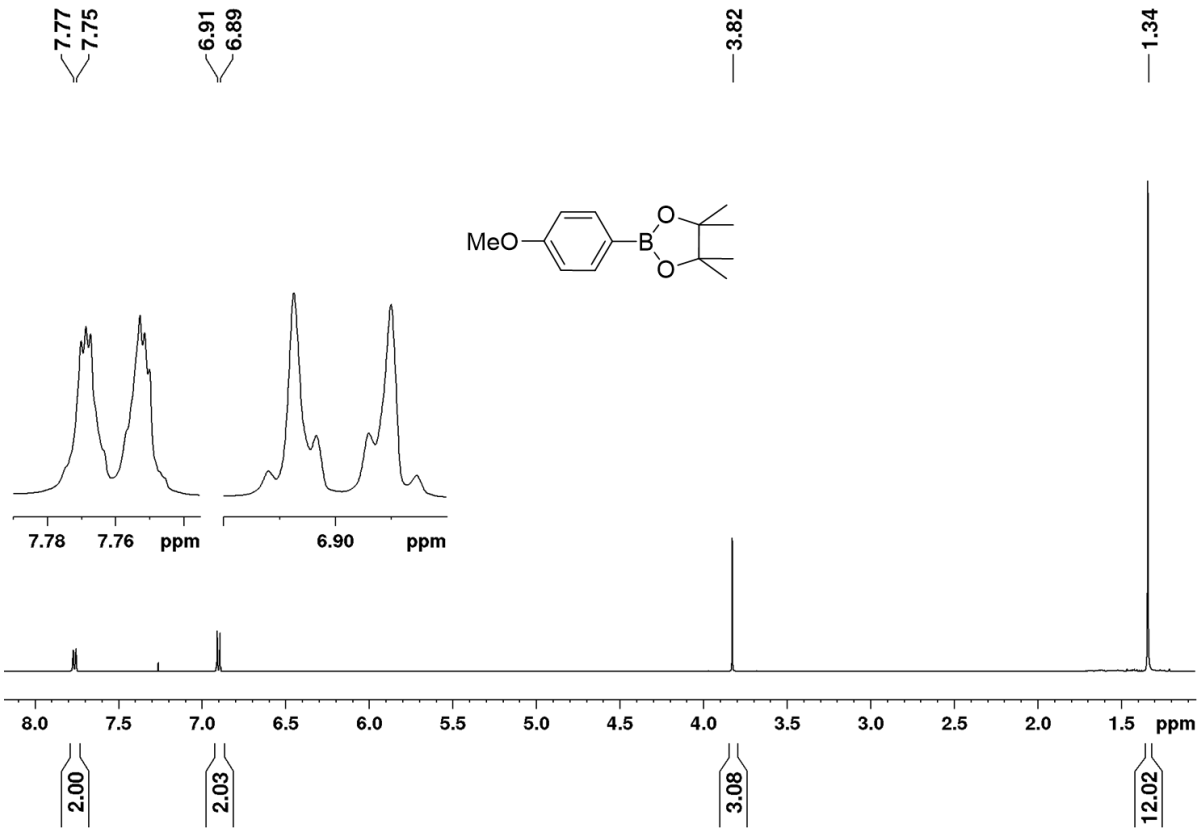


Figure S26. ^{1}H NMR spectrum of compound **10a** in $CDCl_3$ (300 MHz).

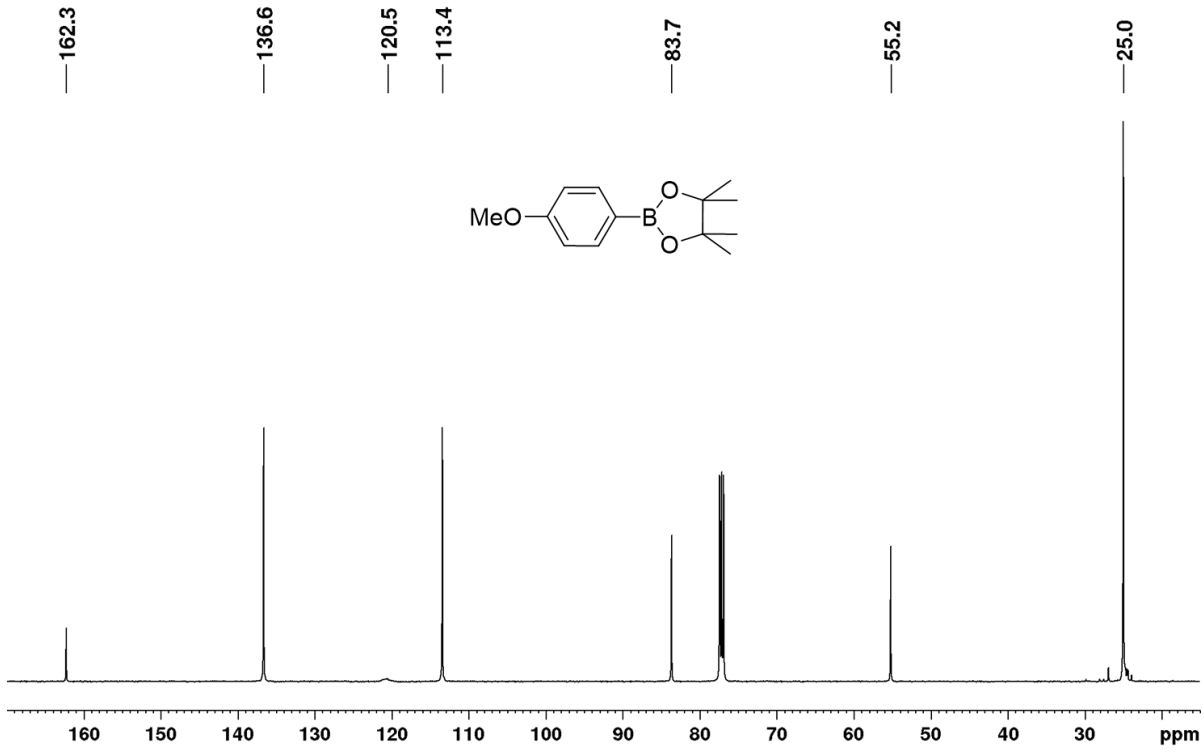


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of compound **10a** in $CDCl_3$ (75 MHz).

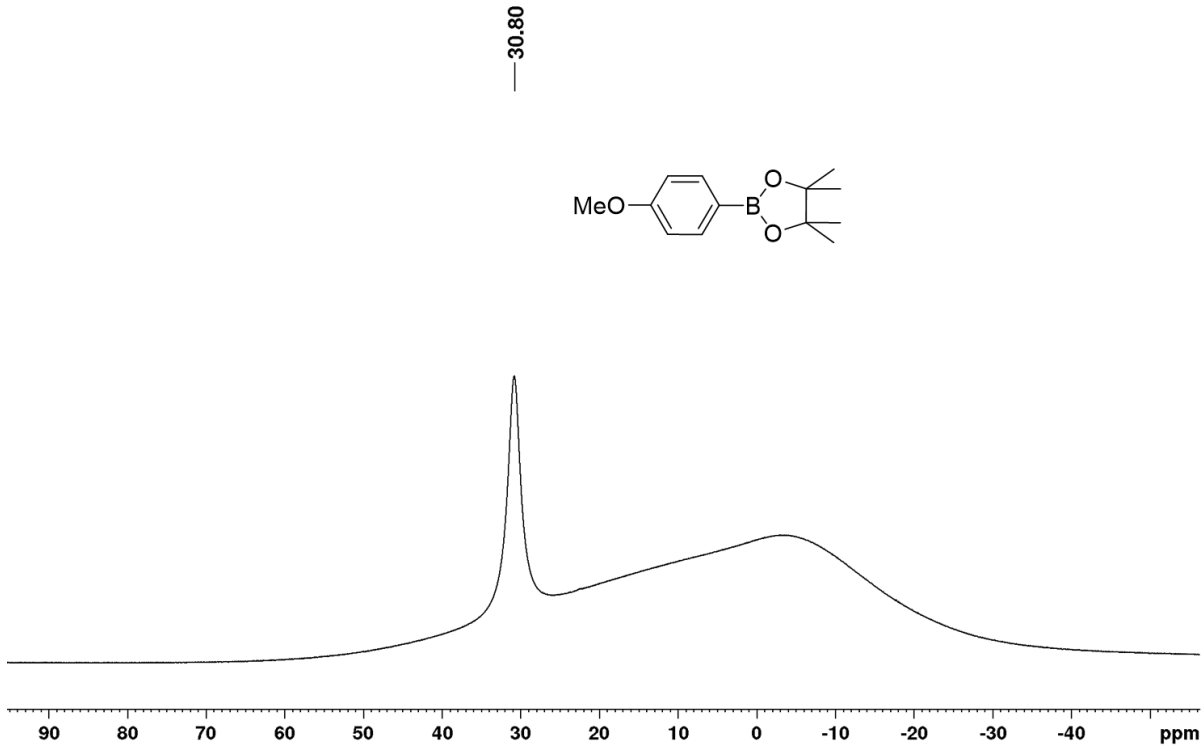


Figure S28. $^{11}B\{^{1}H\}$ NMR spectrum of compound **10a** in $CDCl_3$ (96 MHz).

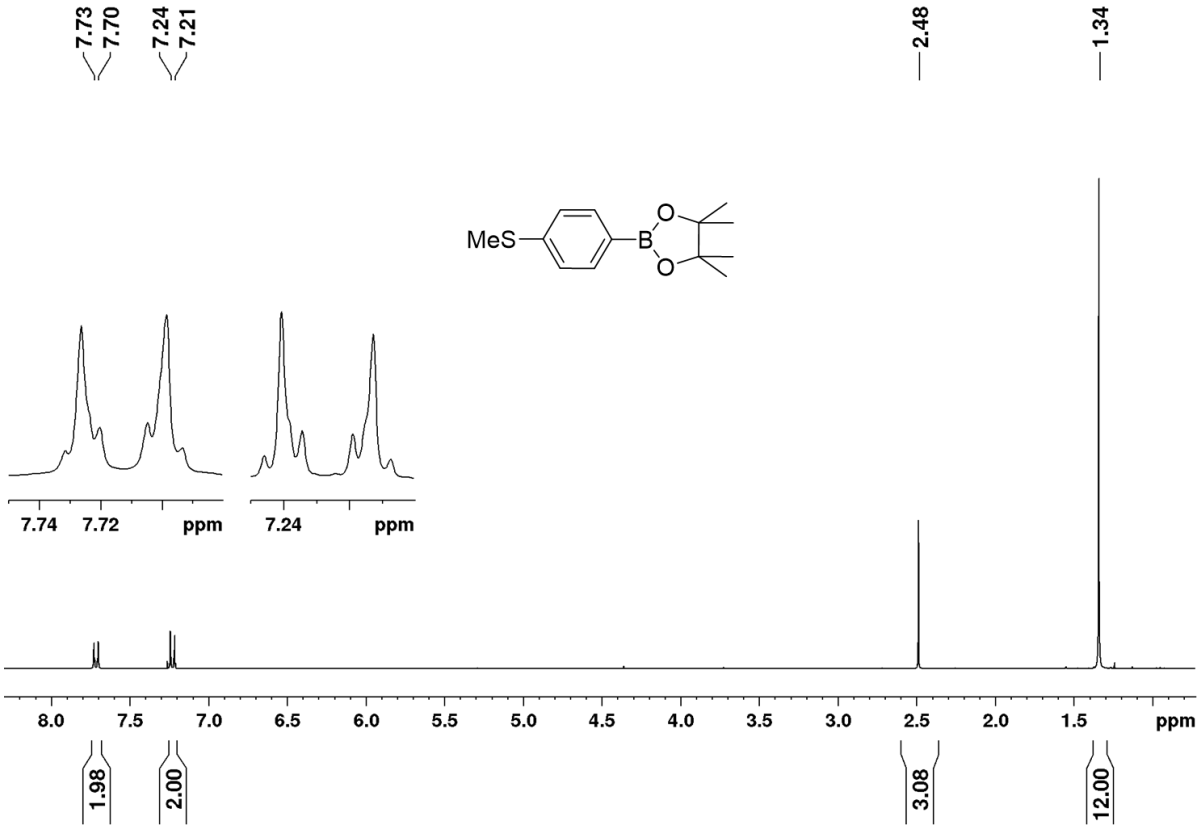


Figure S29. ^{1}H NMR spectrum of compound **11a** in $CDCl_3$ (300 MHz).

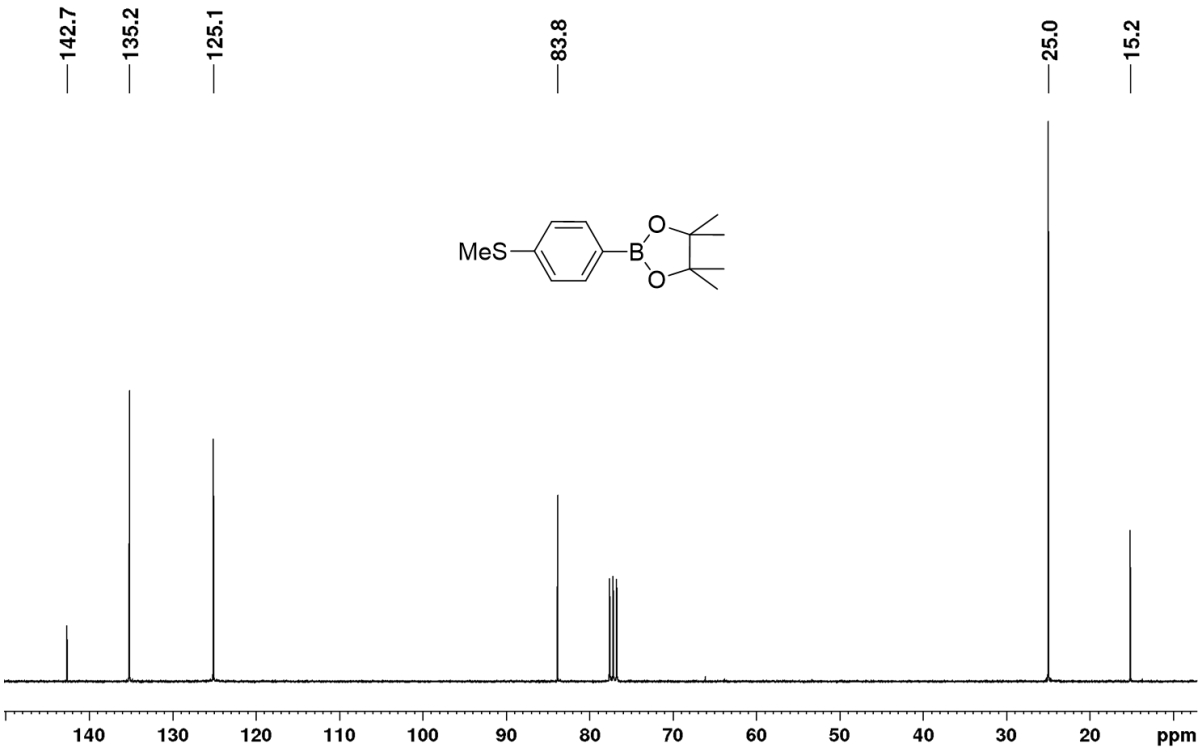


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of compound **11a** in $CDCl_3$ (75 MHz).

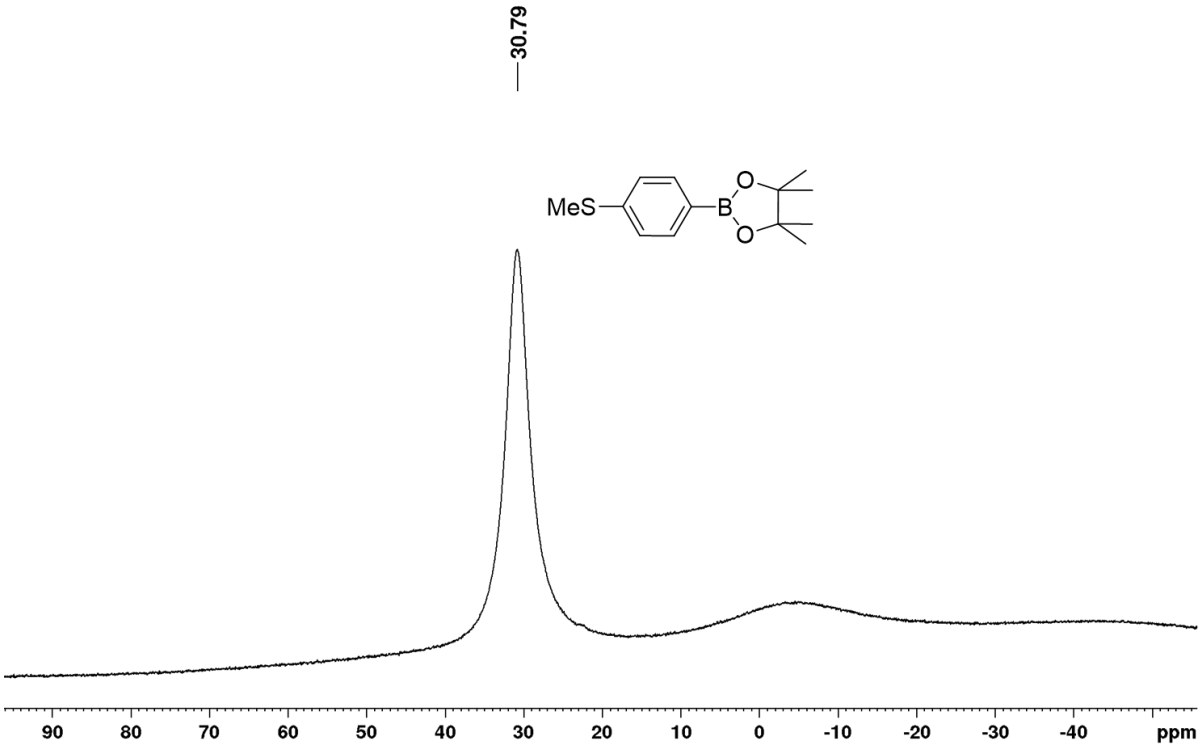


Figure S31. $^{11}B\{^{1}H\}$ NMR spectrum of compound **11a** in $CDCl_3$ (96 MHz).

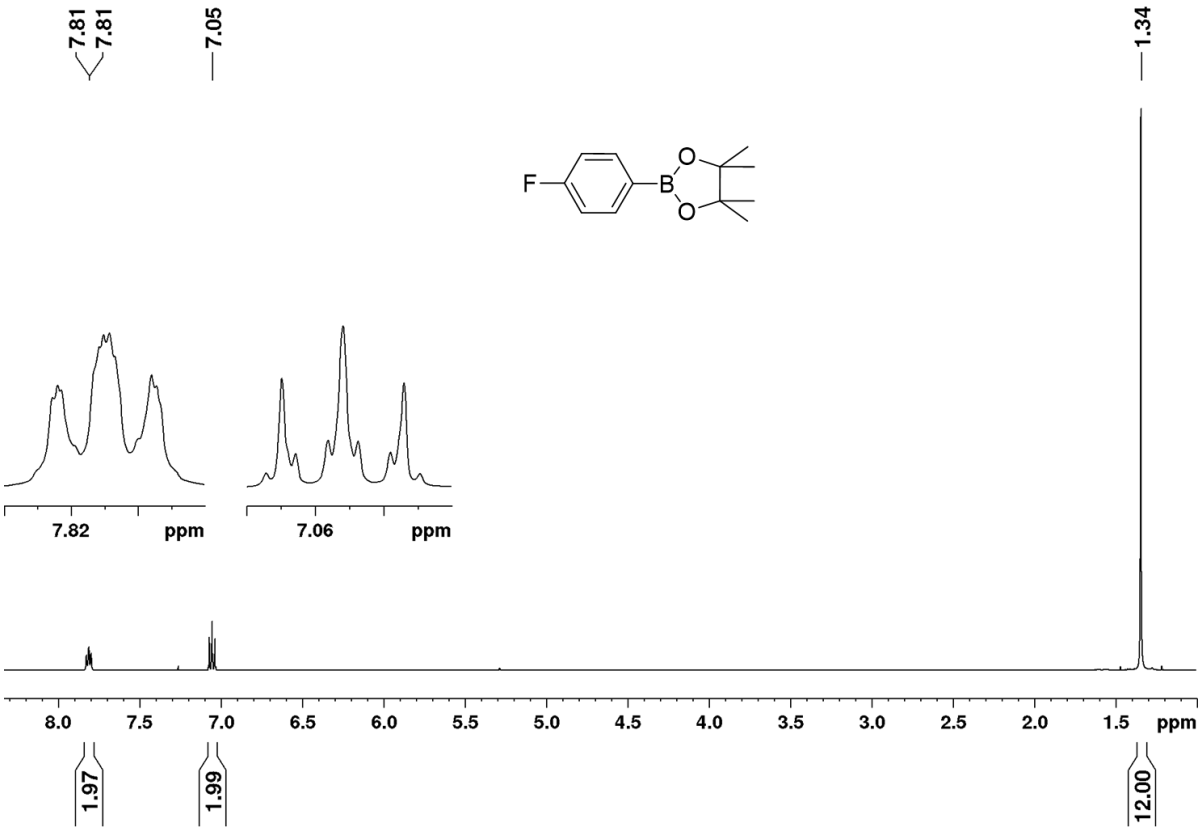


Figure S32. ^{1}H NMR spectrum of compound **12a** in $CDCl_3$ (500 MHz).

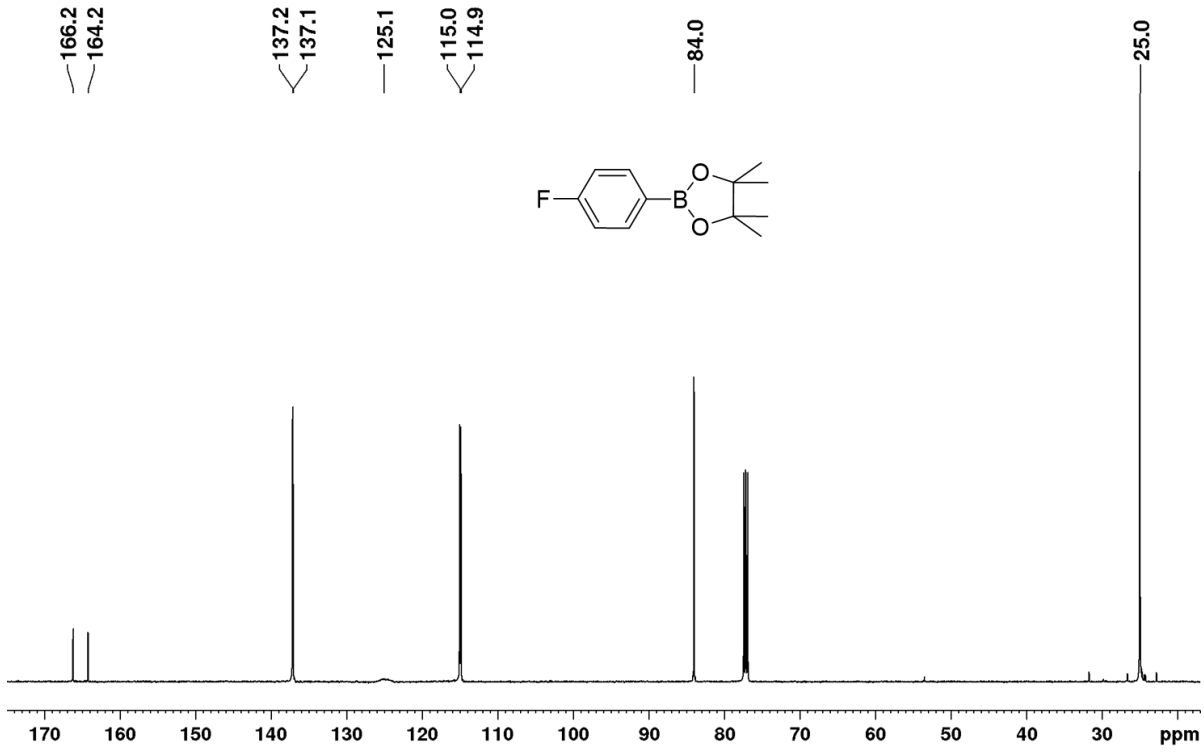


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of compound **12a** in $CDCl_3$ (125 MHz).

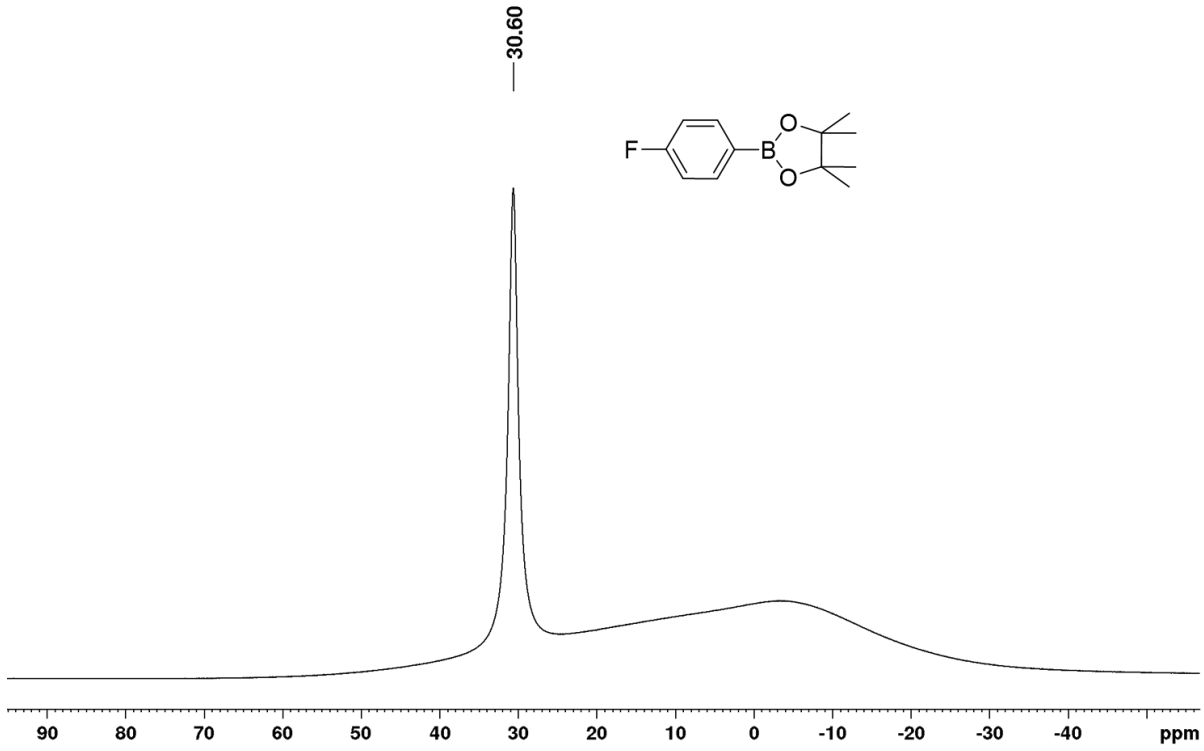


Figure S34. $^{11}B\{^{1}H\}$ NMR spectrum of compound **12a** in $CDCl_3$ (160 MHz).

Figure S35. $^{19}F\{^{1}H\}$ NMR spectrum of compound **12a** in $CDCl_3$ (470 MHz).

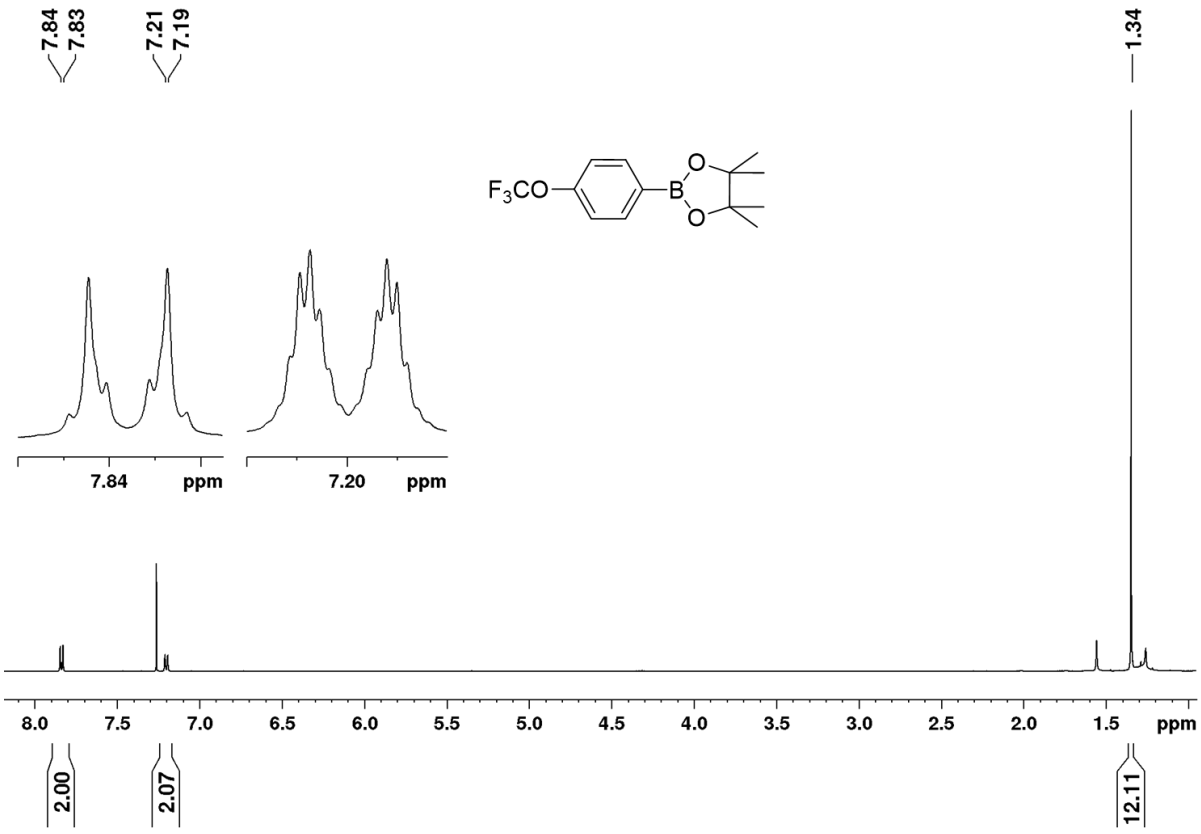


Figure S36. ^{1}H NMR spectrum of compound **13a** in $CDCl_3$ (500 MHz).

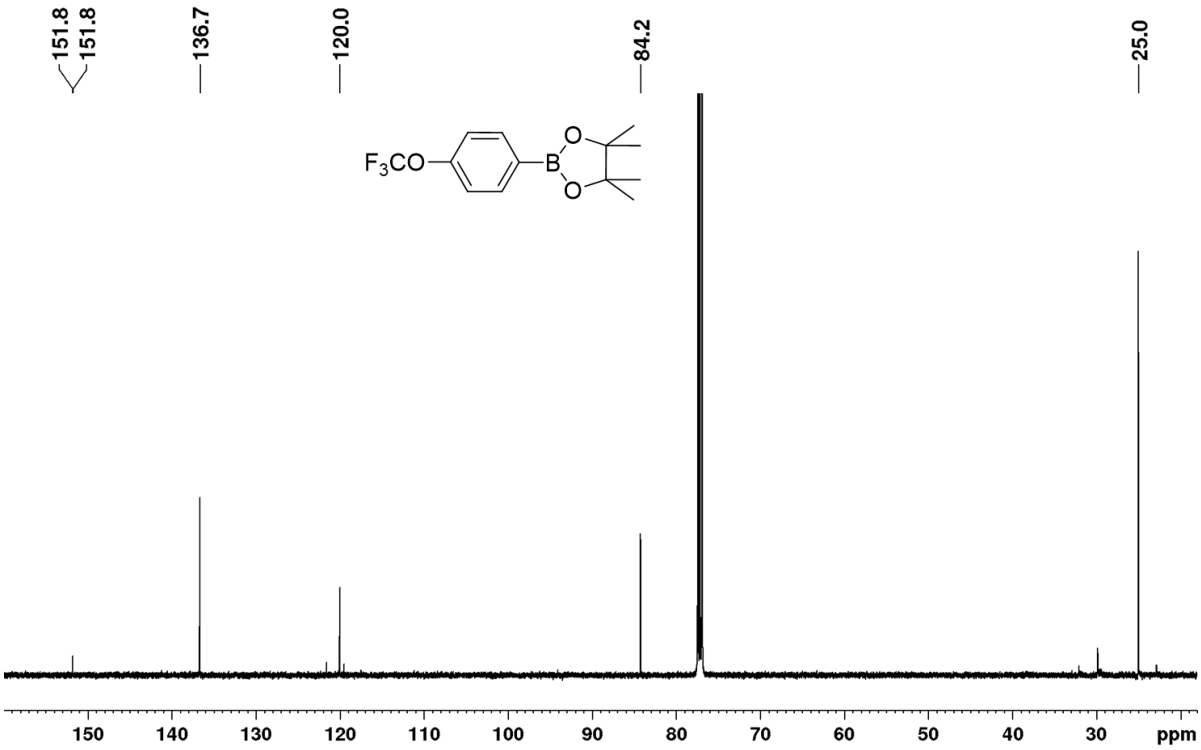


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of compound **13a** in $CDCl_3$ (125 MHz).

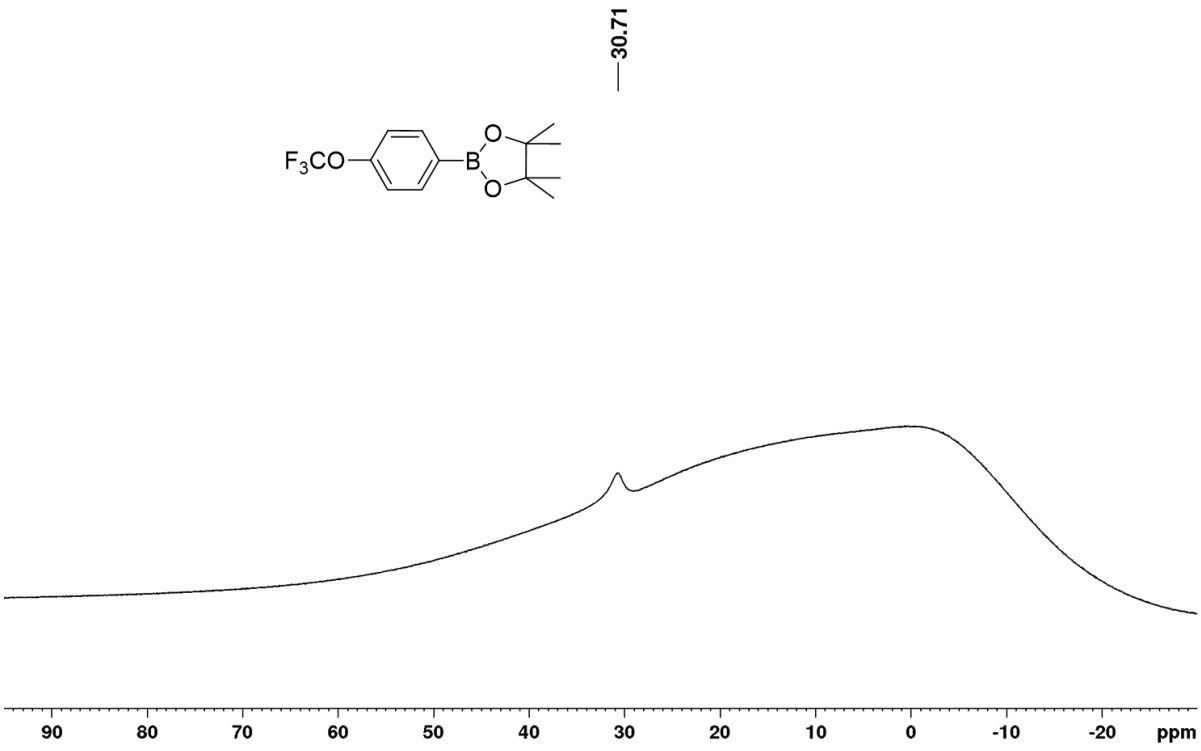


Figure S38. $^{11}B\{^{1}H\}$ NMR spectrum of compound **13a** in $CDCl_3$ (160 MHz).

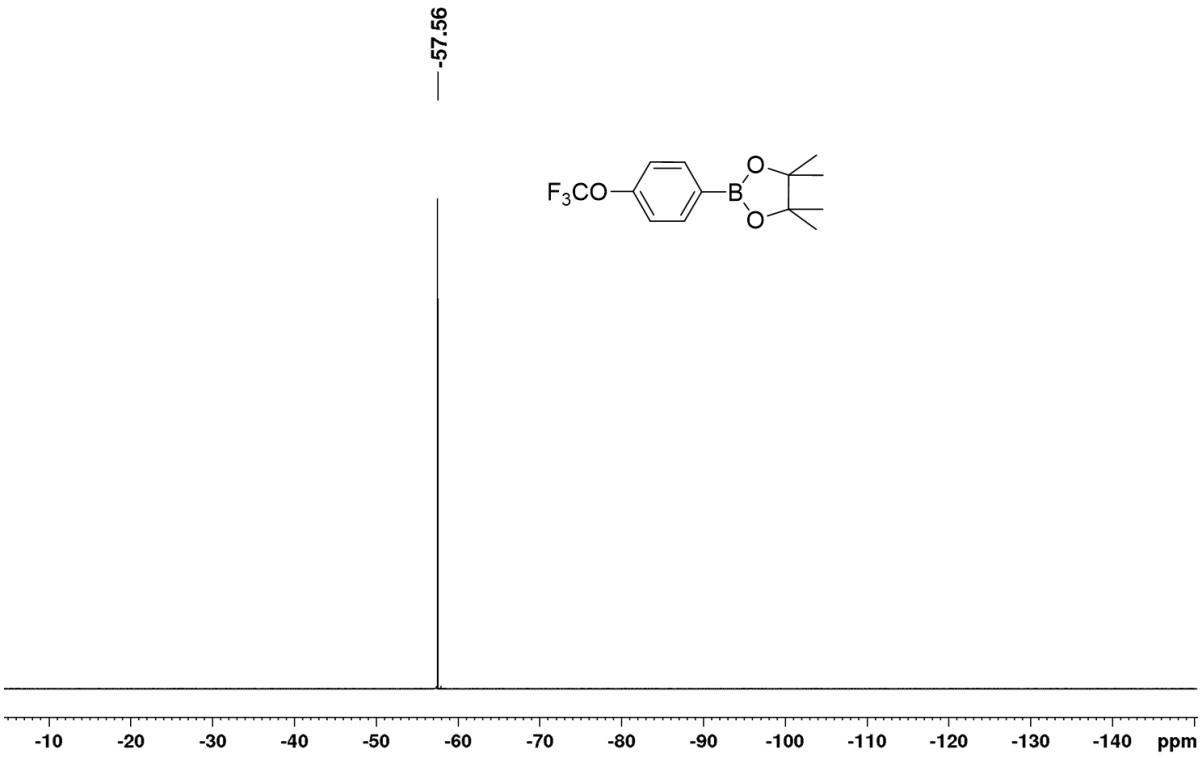


Figure S39. $^{19}F\{^{1}H\}$ NMR spectrum of compound **13a** in $CDCl_3$ (470 MHz).

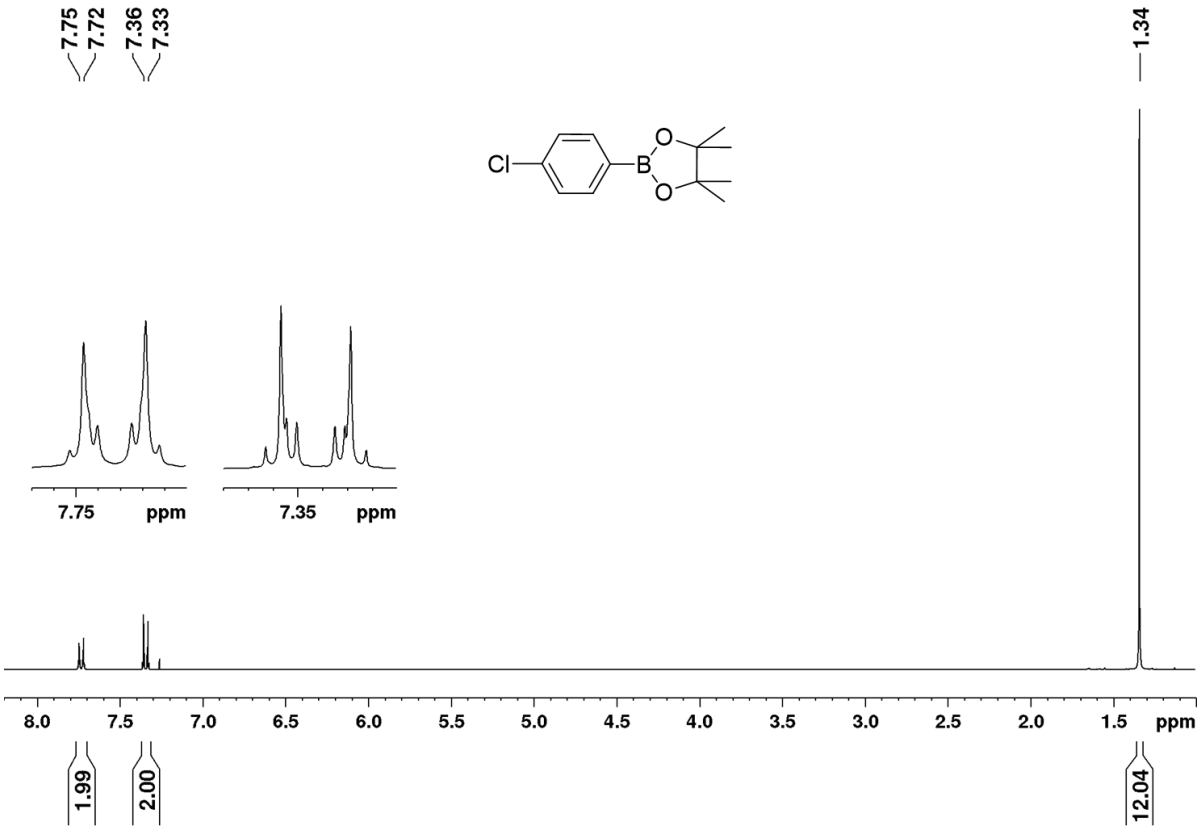


Figure S40. ^{1}H NMR spectrum of compound **14a** in $CDCl_3$ (300 MHz).

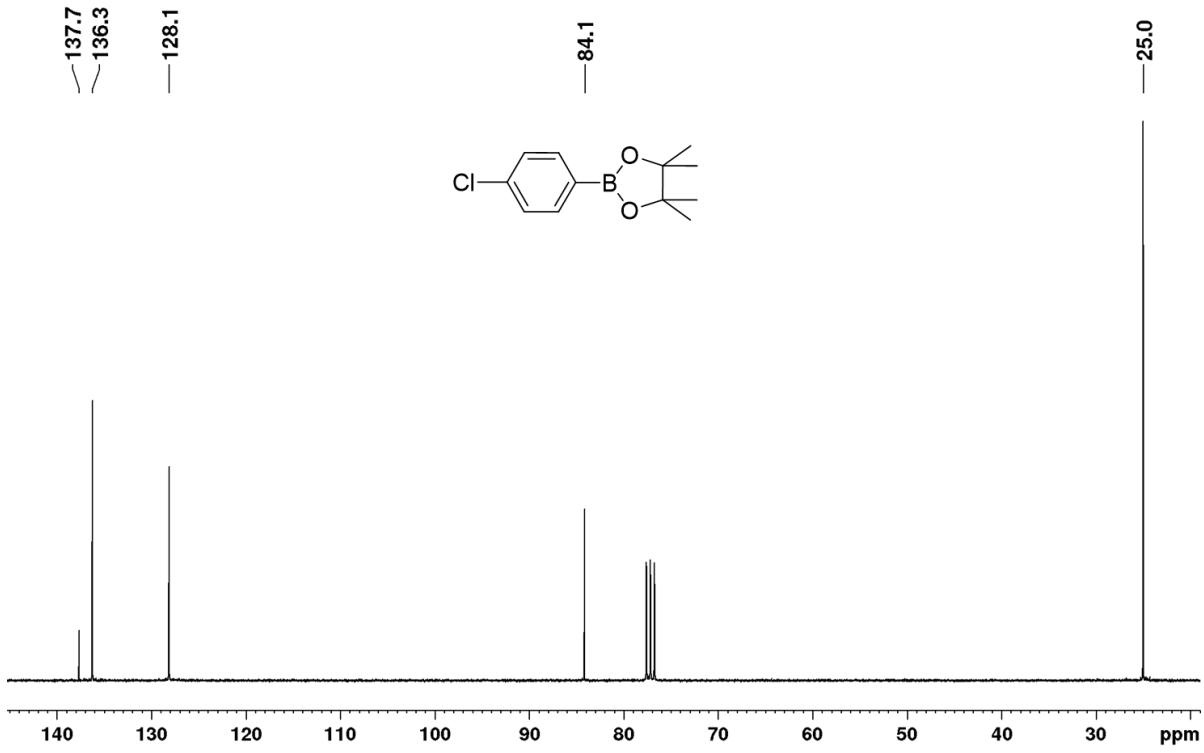


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of compound **14a** in $CDCl_3$ (75 MHz).

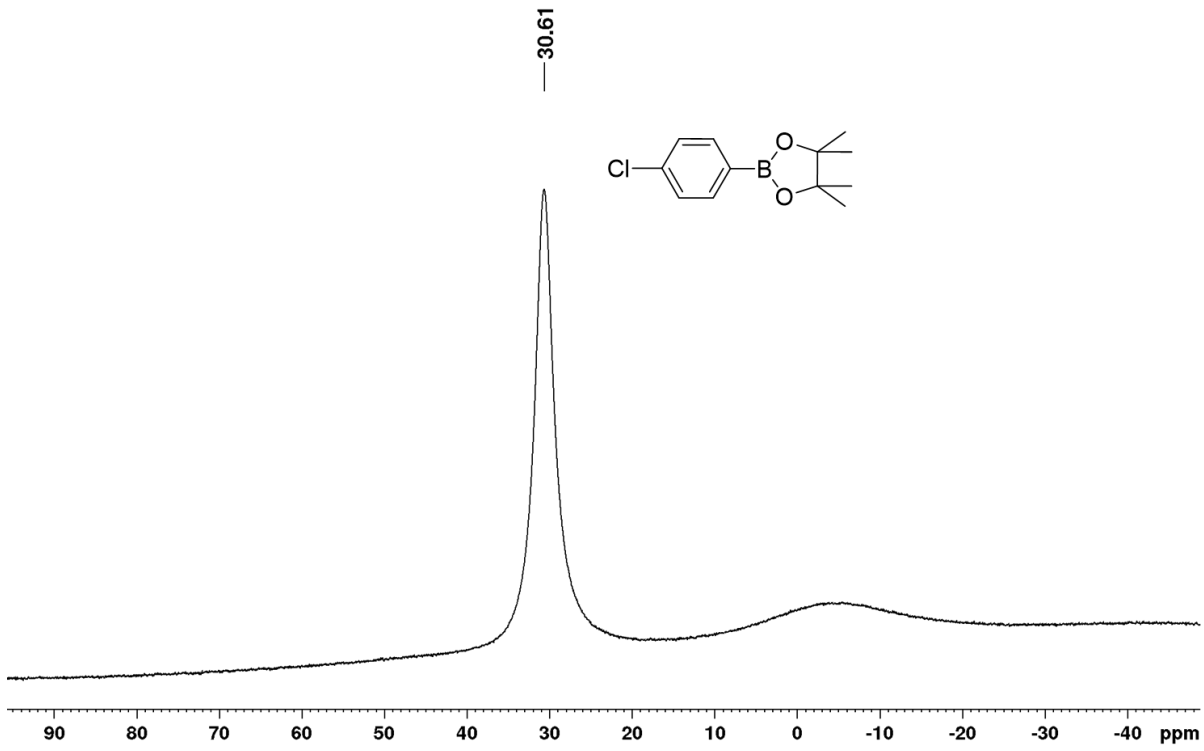


Figure S42. $^{11}B\{^{1}H\}$ NMR spectrum of compound **14a** in $CDCl_3$ (96 MHz).

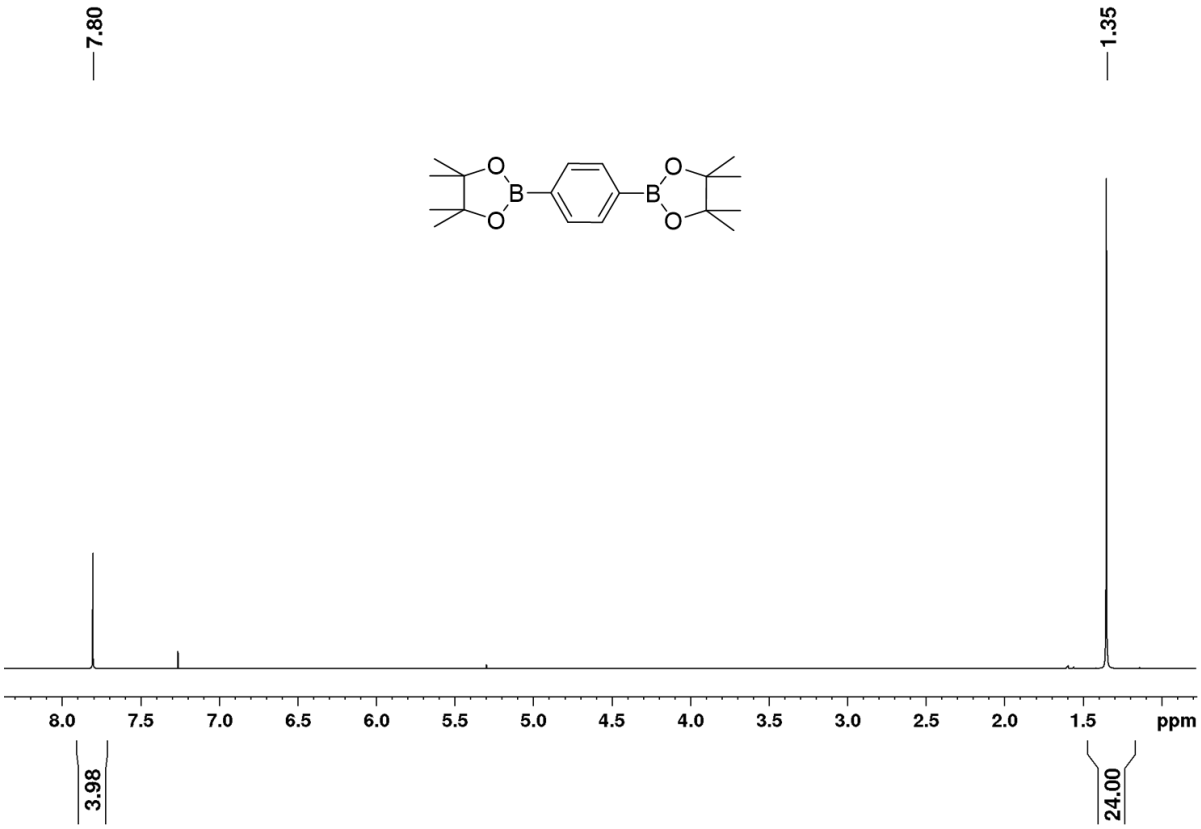


Figure S43. ^{1}H NMR spectrum of compound **14b** in $CDCl_3$ (300 MHz).

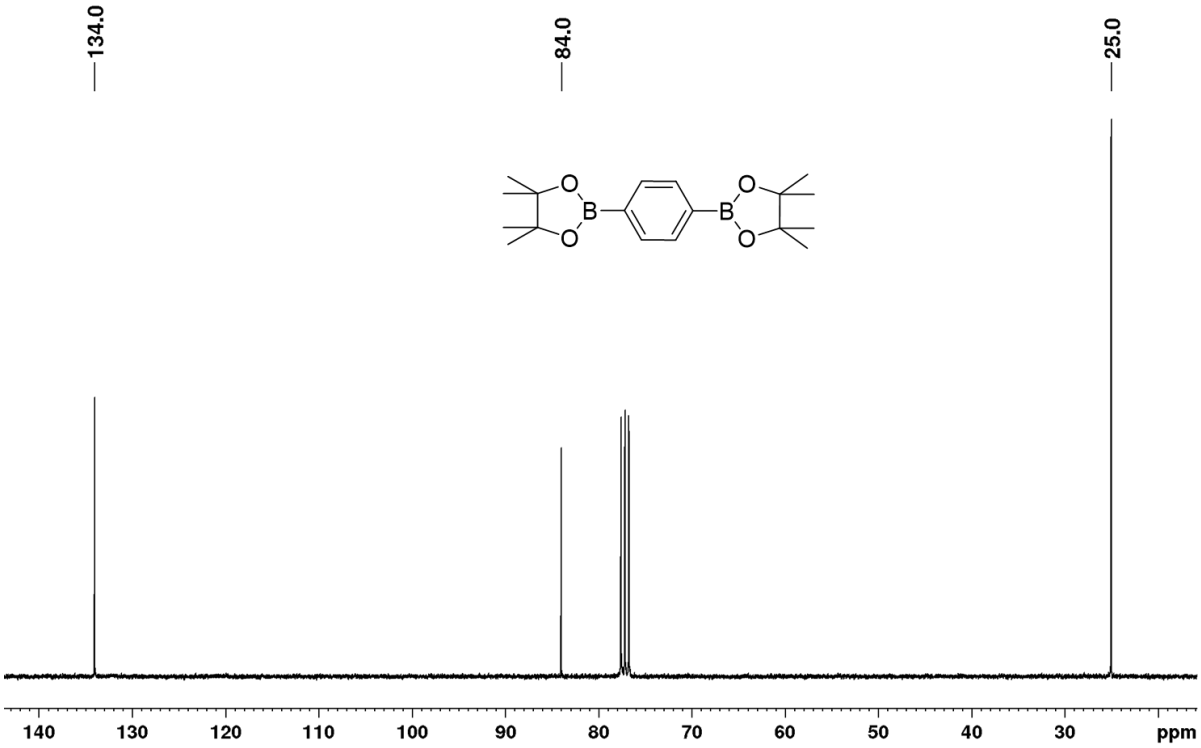


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of compound **14b** in $CDCl_3$ (75 MHz).

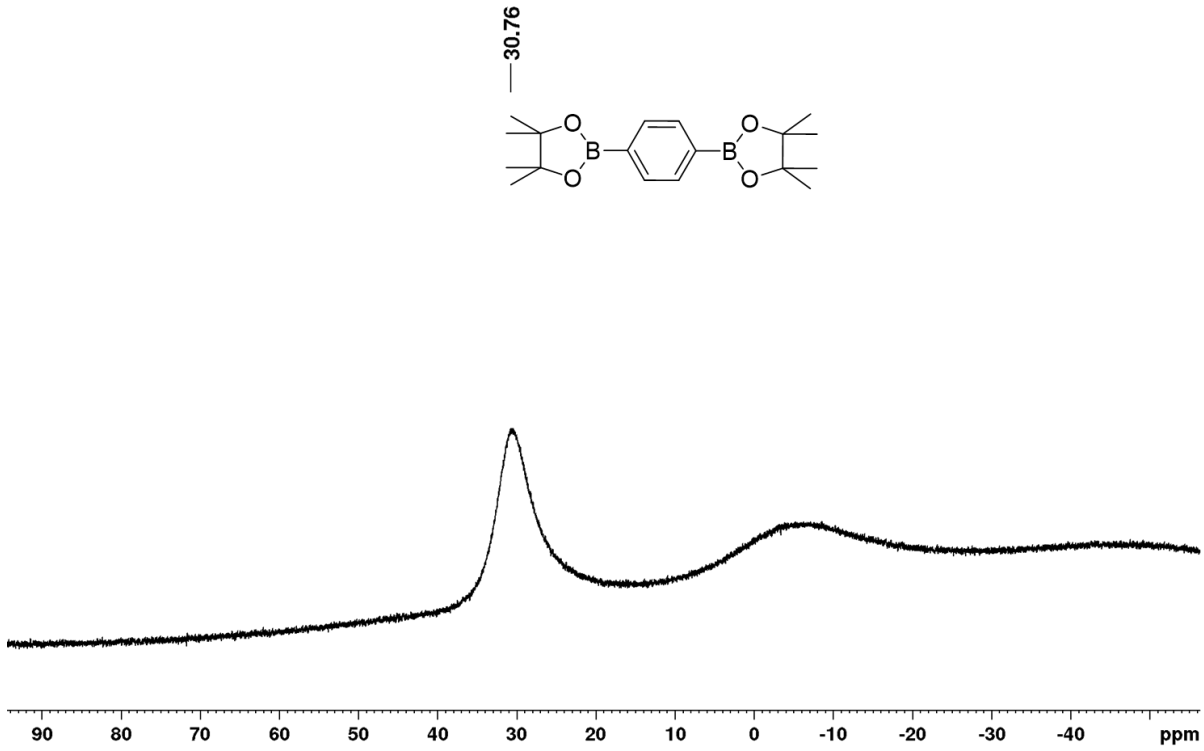


Figure S45. $^{11}B\{^{1}H\}$ NMR spectrum of compound **14b** in $CDCl_3$ (96 MHz).

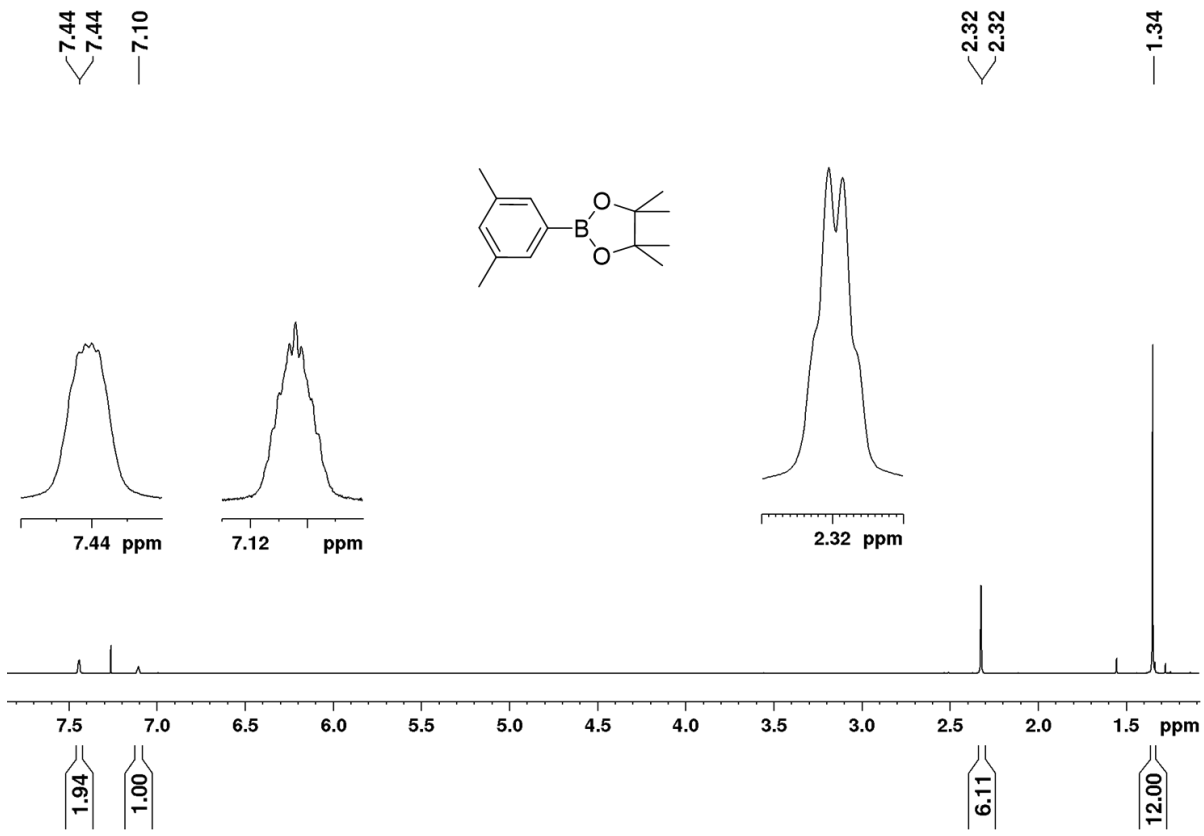


Figure S46. ^{1}H NMR spectrum of compound **15a** in $CDCl_3$ (300 MHz).

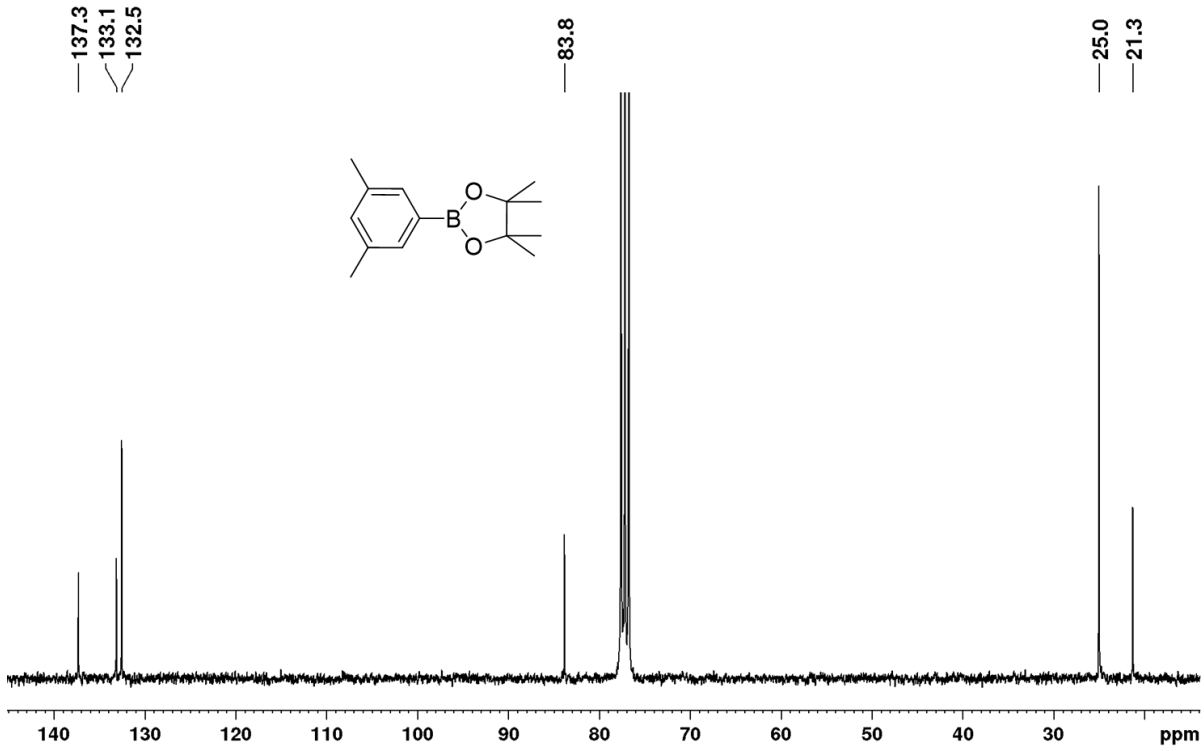


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of compound **15a** in $CDCl_3$ (75 MHz).

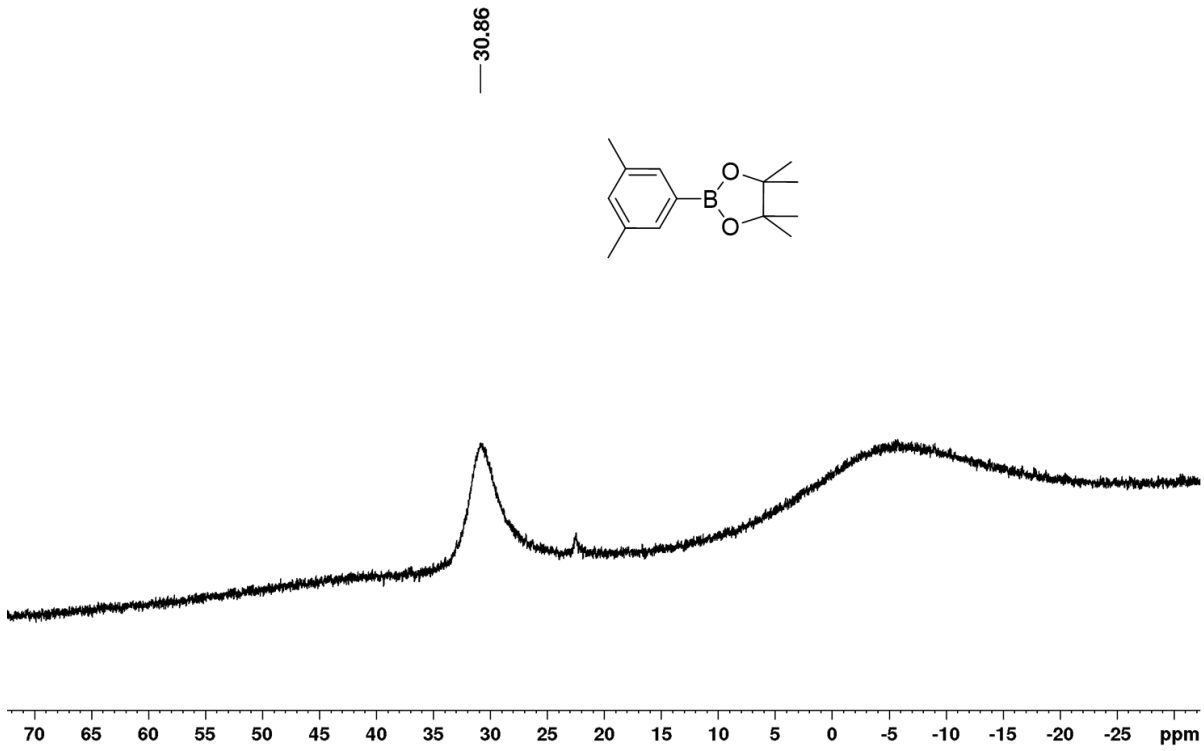


Figure S48. $^{11}B\{^{1}H\}$ NMR spectrum of compound **15a** in $CDCl_3$ (96 MHz).

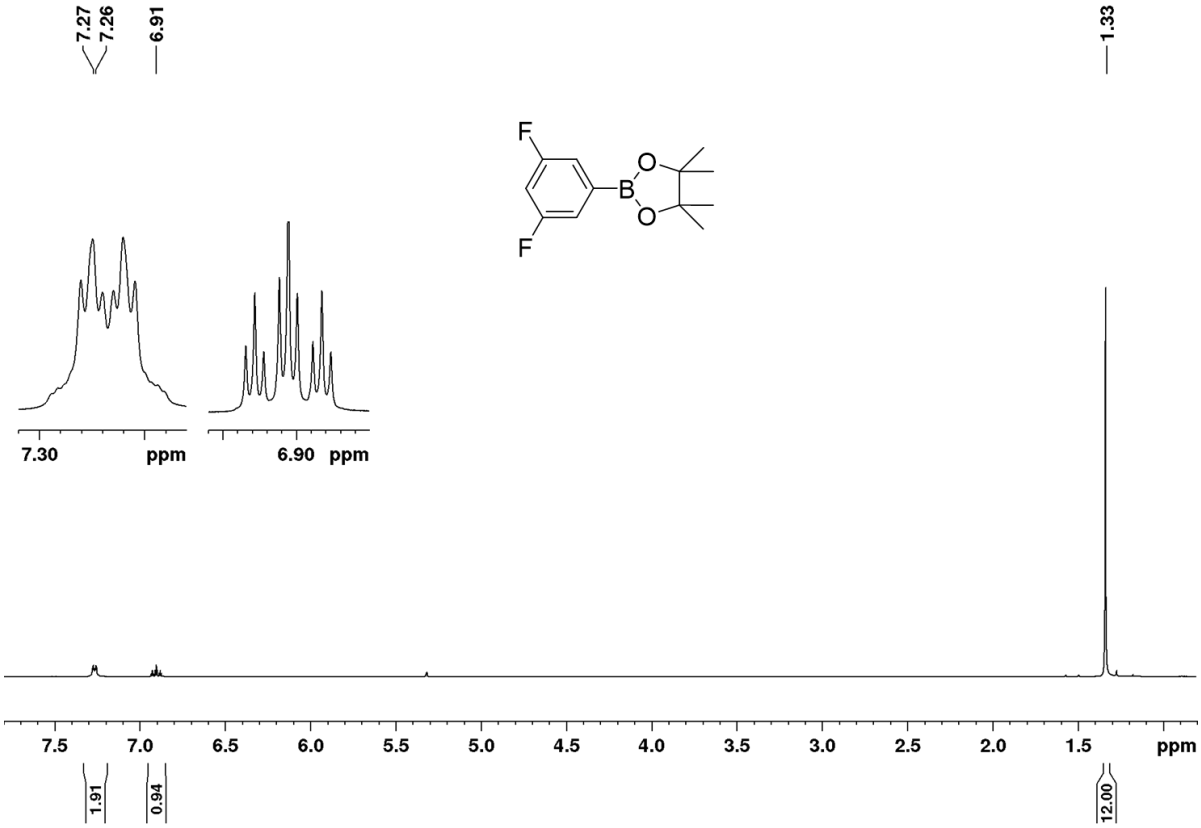


Figure S49. ^{1}H NMR spectrum of compound **16a** in CD_2Cl_2 (400 MHz).

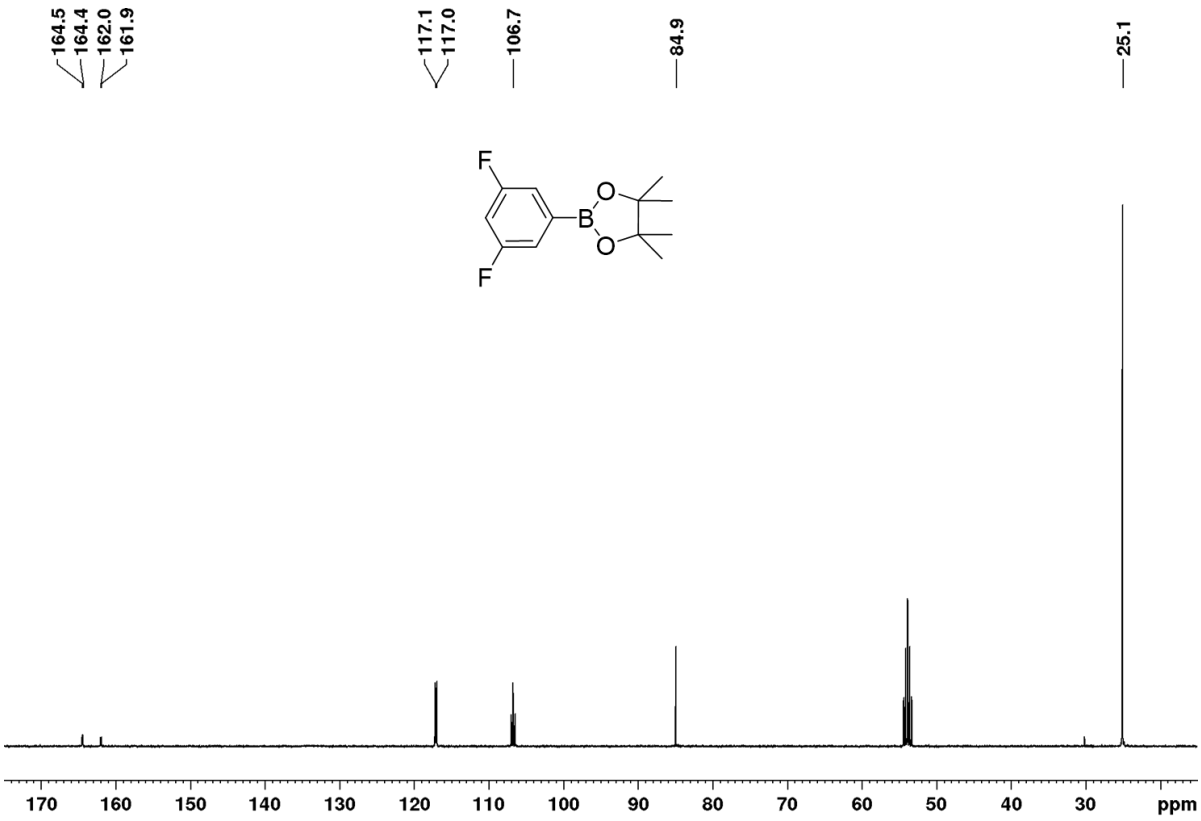


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of compound **16a** in CD_2Cl_2 (100 MHz).

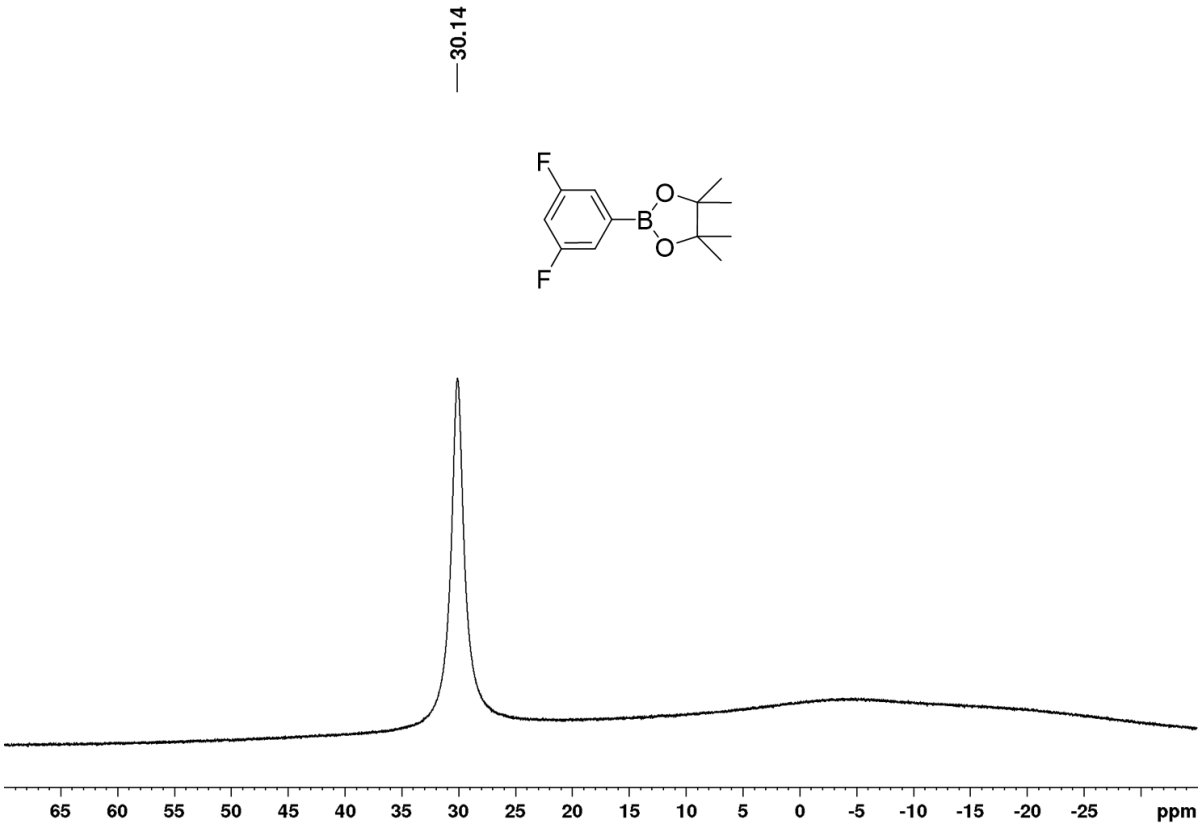


Figure S51. $^{11}B\{^{1}H\}$ NMR spectrum of compound **16a** in CD_2Cl_2 (128 MHz).

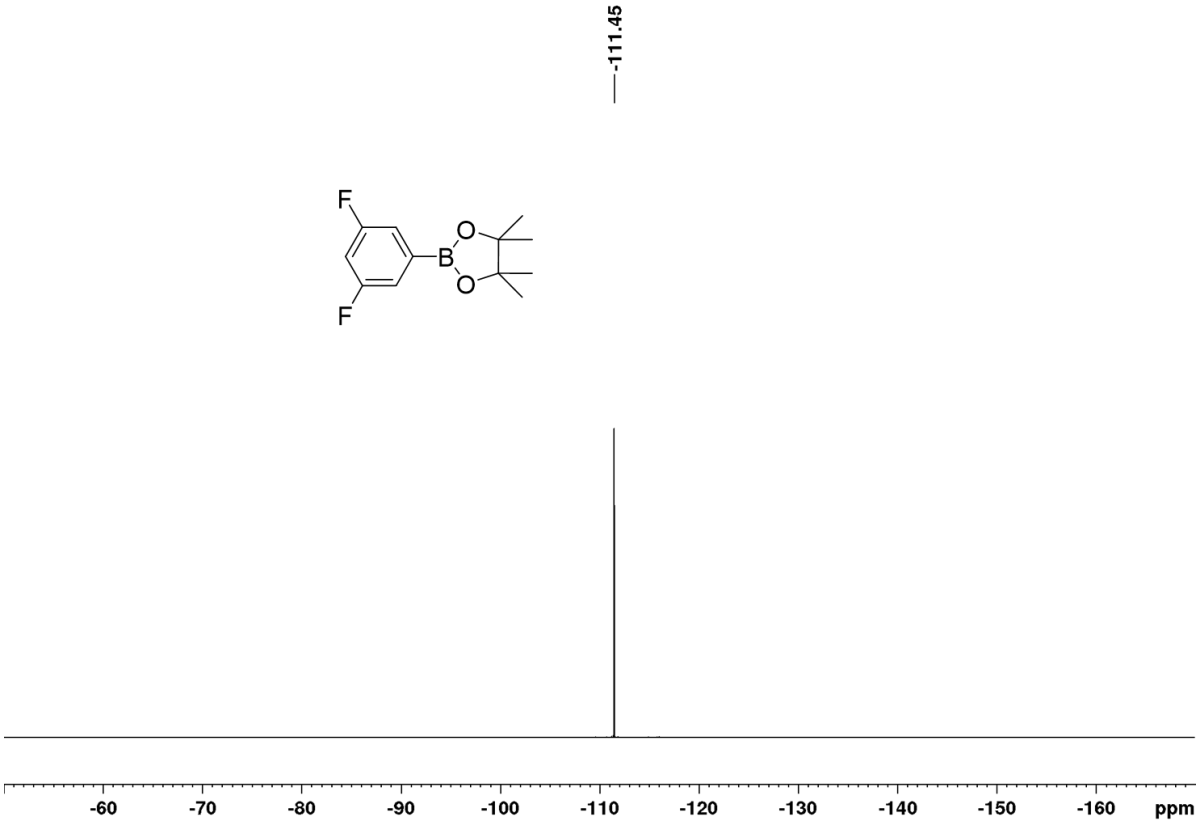


Figure S52. $^{19}F\{^{1}H\}$ NMR spectrum of compound **16a** in CD_2Cl_2 (376 MHz).

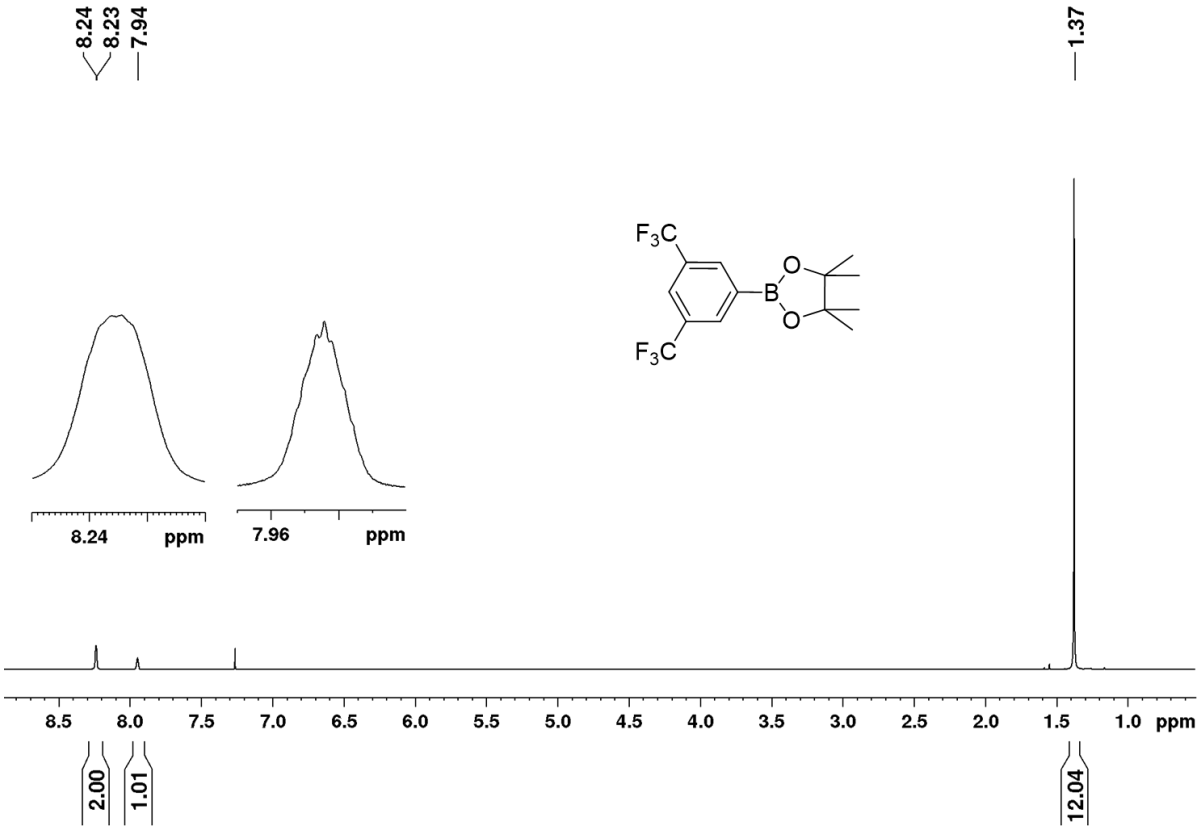


Figure S53. ^{1}H NMR spectrum of compound **17a** in $CDCl_3$ (500 MHz).

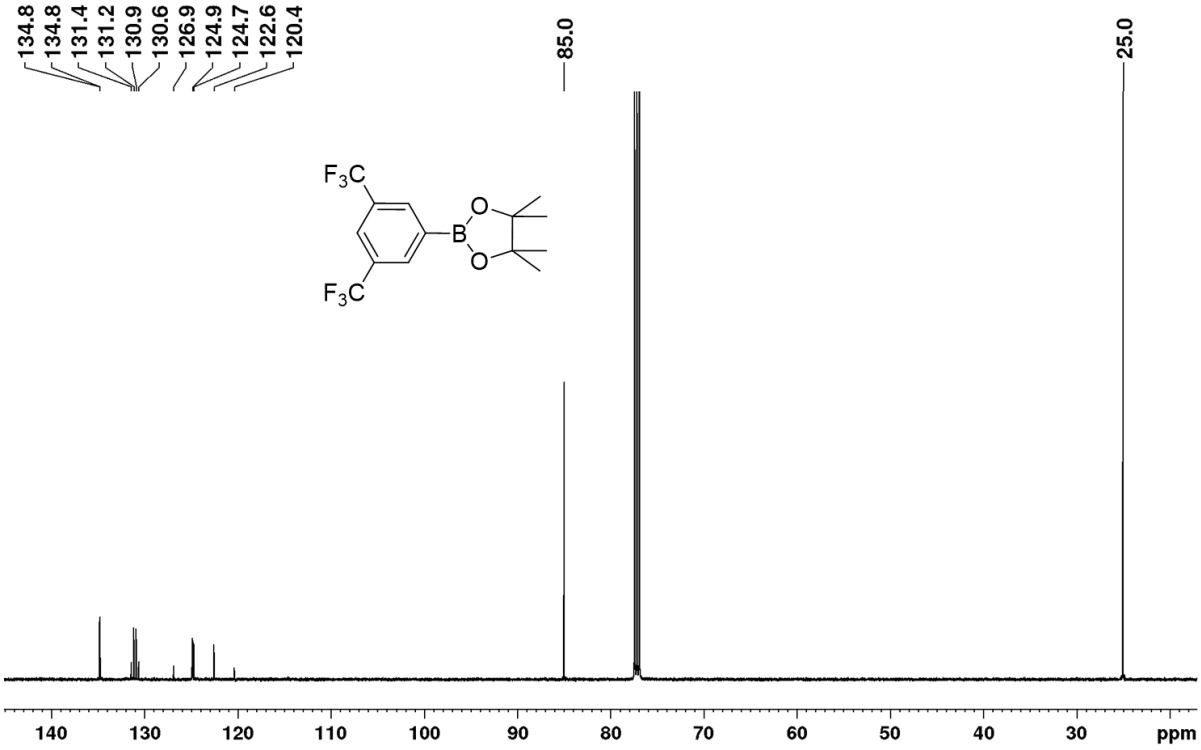


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of compound **17a** in $CDCl_3$ (125 MHz).

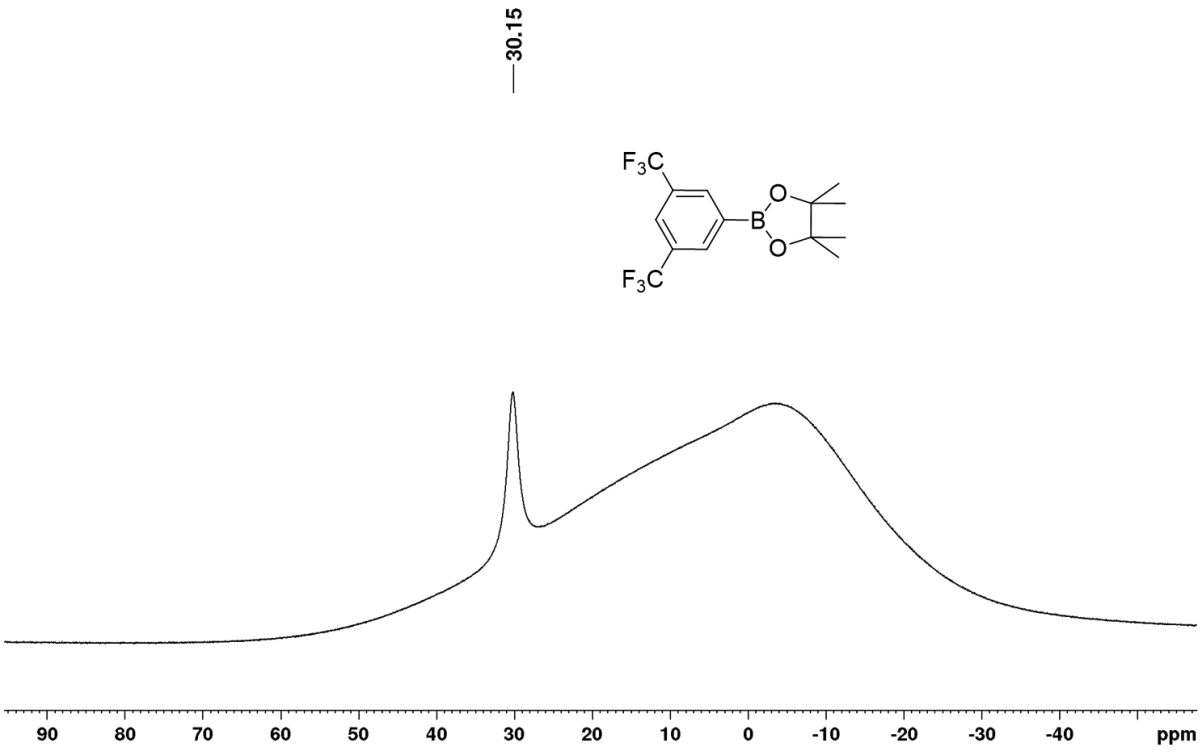


Figure S55. $^{11}B\{^{1}H\}$ NMR spectrum of compound **17a** in $CDCl_3$ (160 MHz).

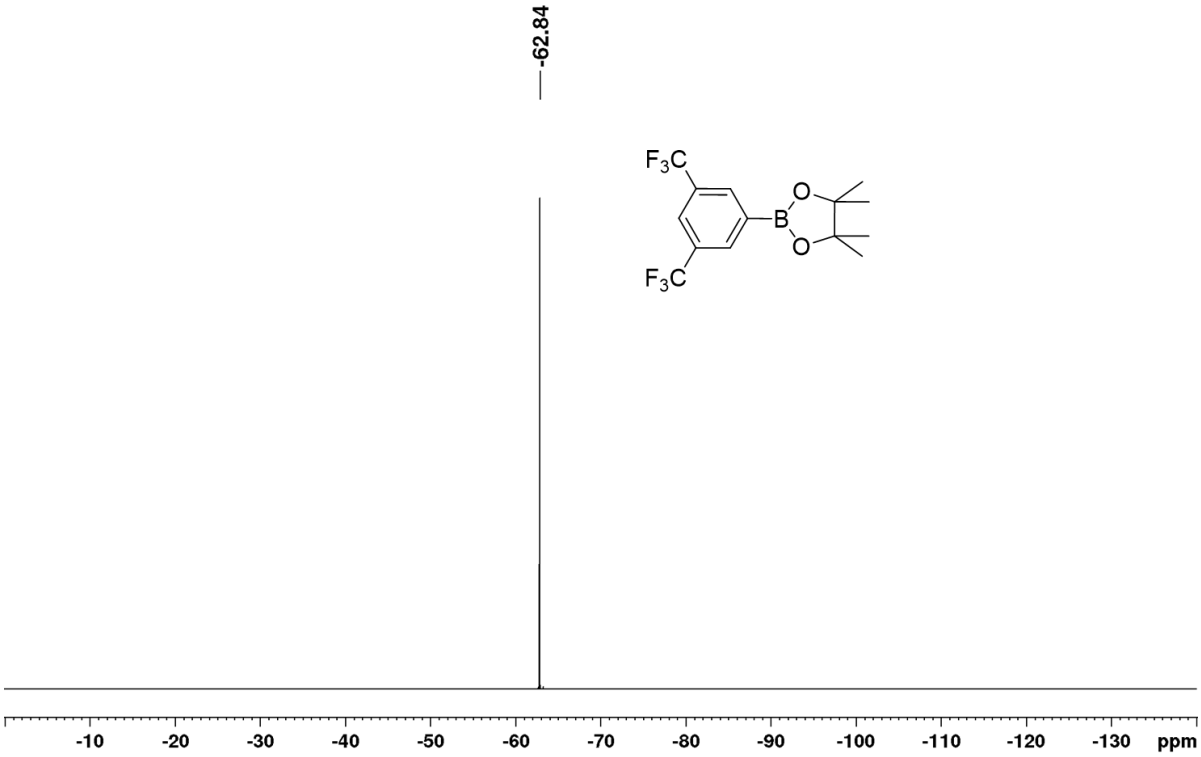


Figure S56. $^{19}F\{^{1}H\}$ NMR spectrum of compound **17a** in $CDCl_3$ (470 MHz).

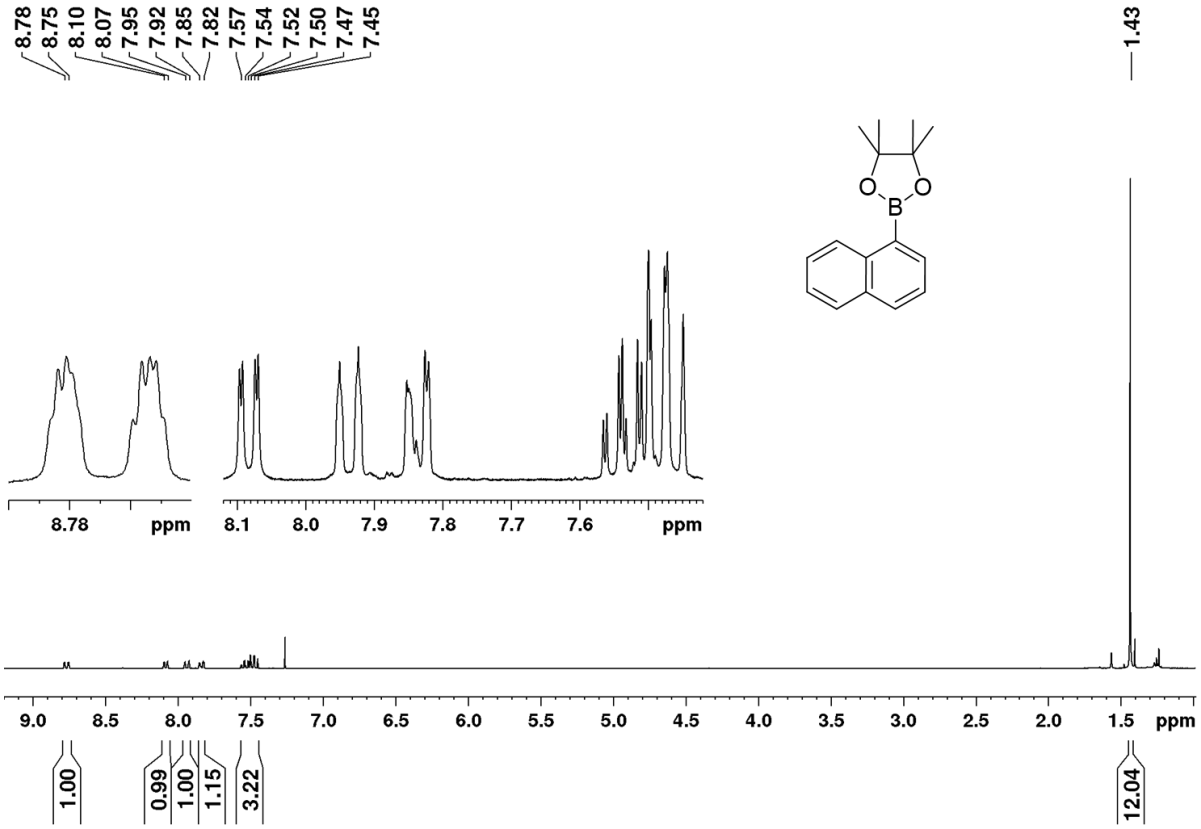


Figure S57. ^{1}H NMR spectrum of compound **18a** in $CDCl_3$ (300 MHz).

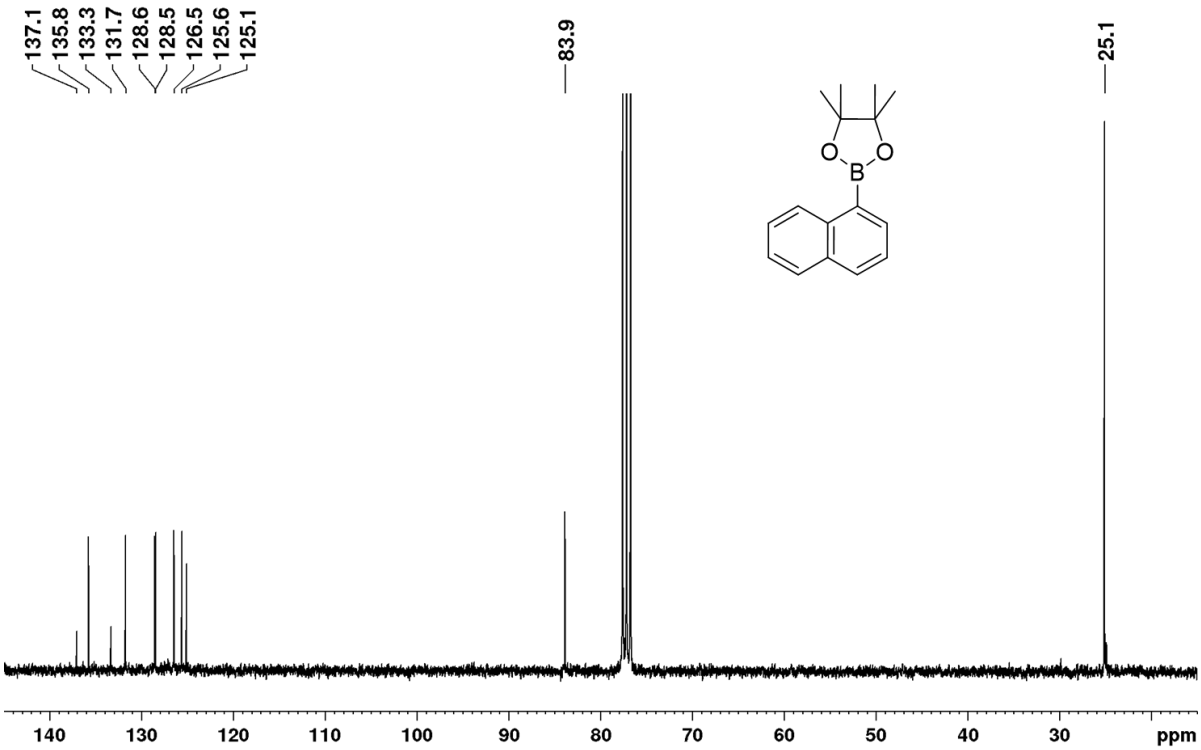


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of compound **18a** in $CDCl_3$ (75 MHz).

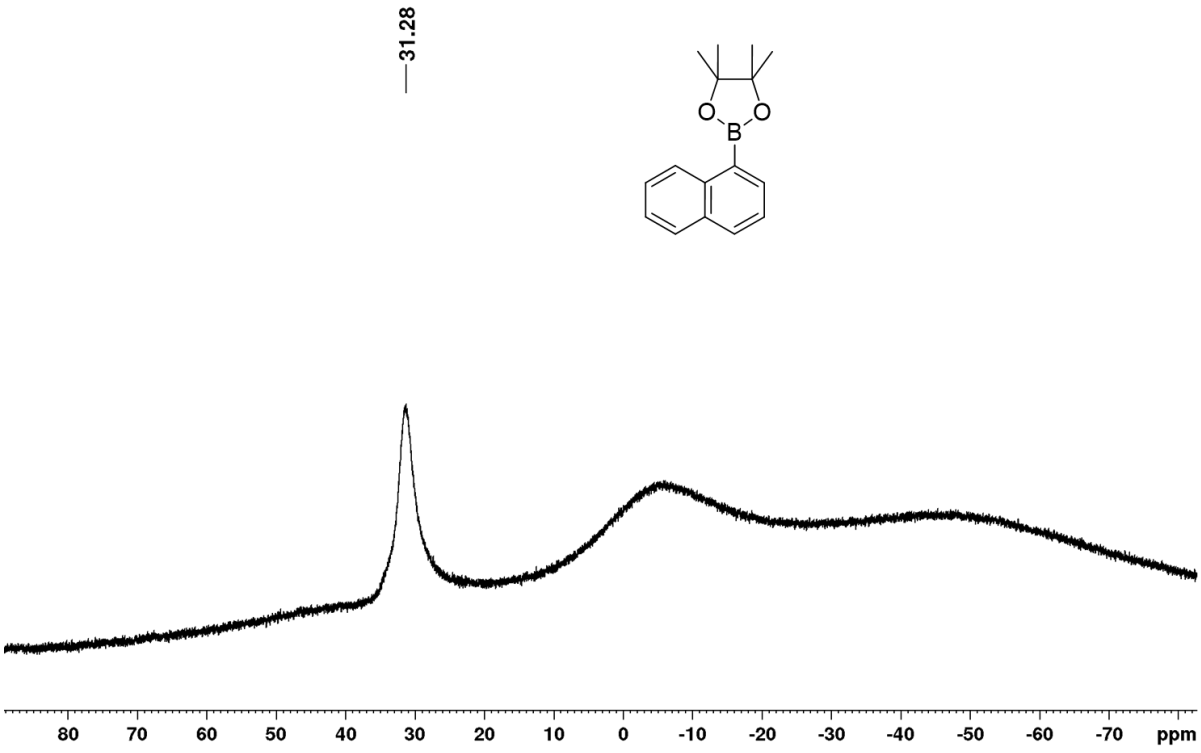


Figure S59. $^{11}B\{^{1}H\}$ NMR spectrum of compound **18a** in $CDCl_3$ (96 MHz).

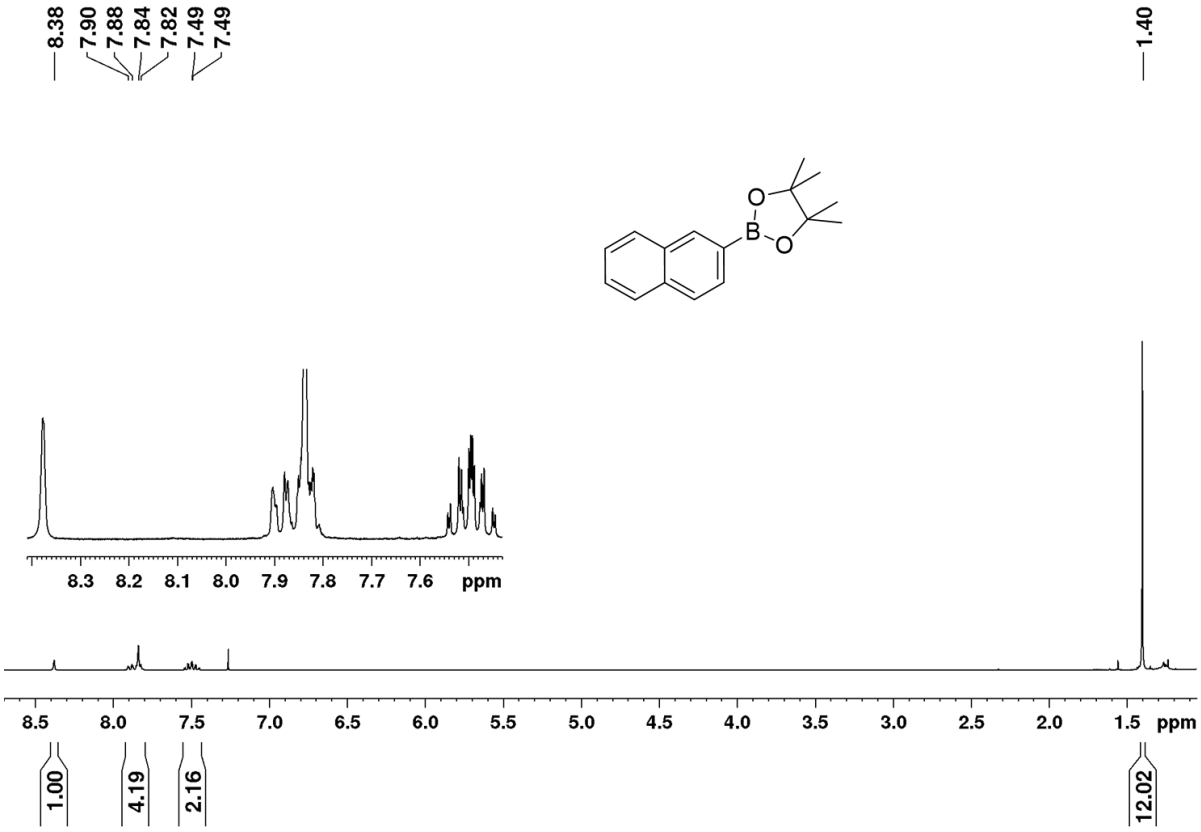


Figure S60. ^{1}H NMR spectrum of compound **19a** in $CDCl_3$ (500 MHz).

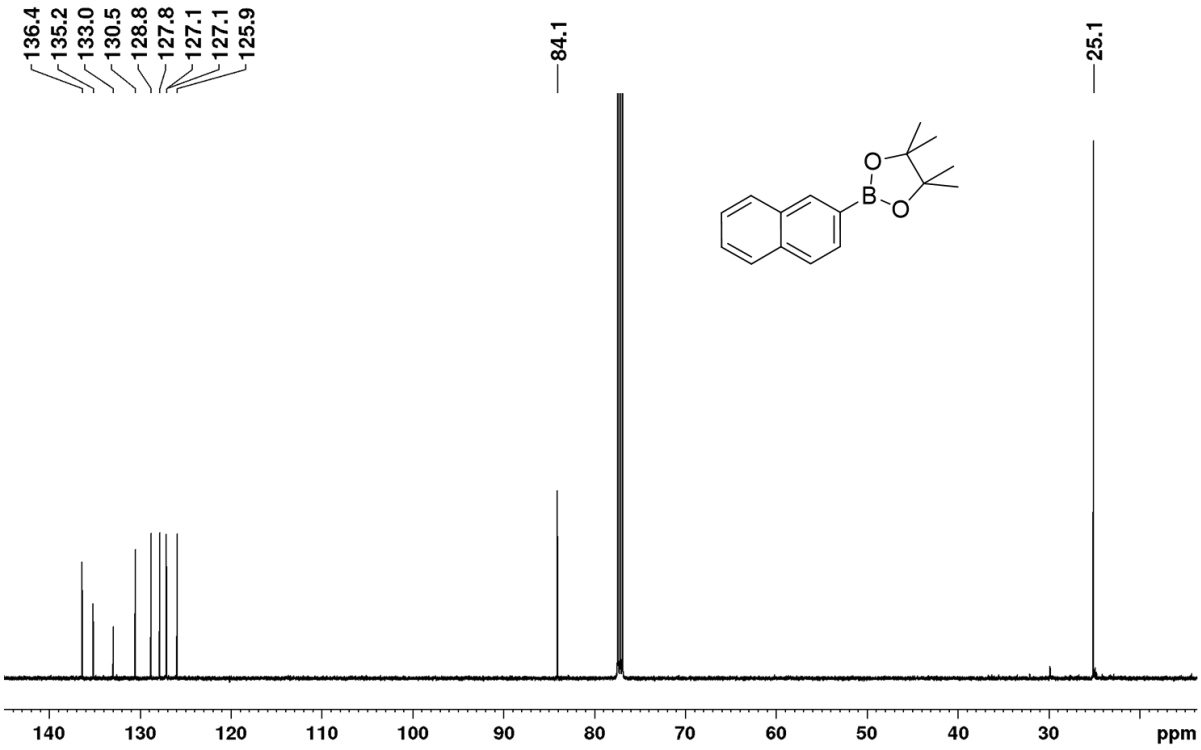


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of compound **19a** in $CDCl_3$ (125 MHz).

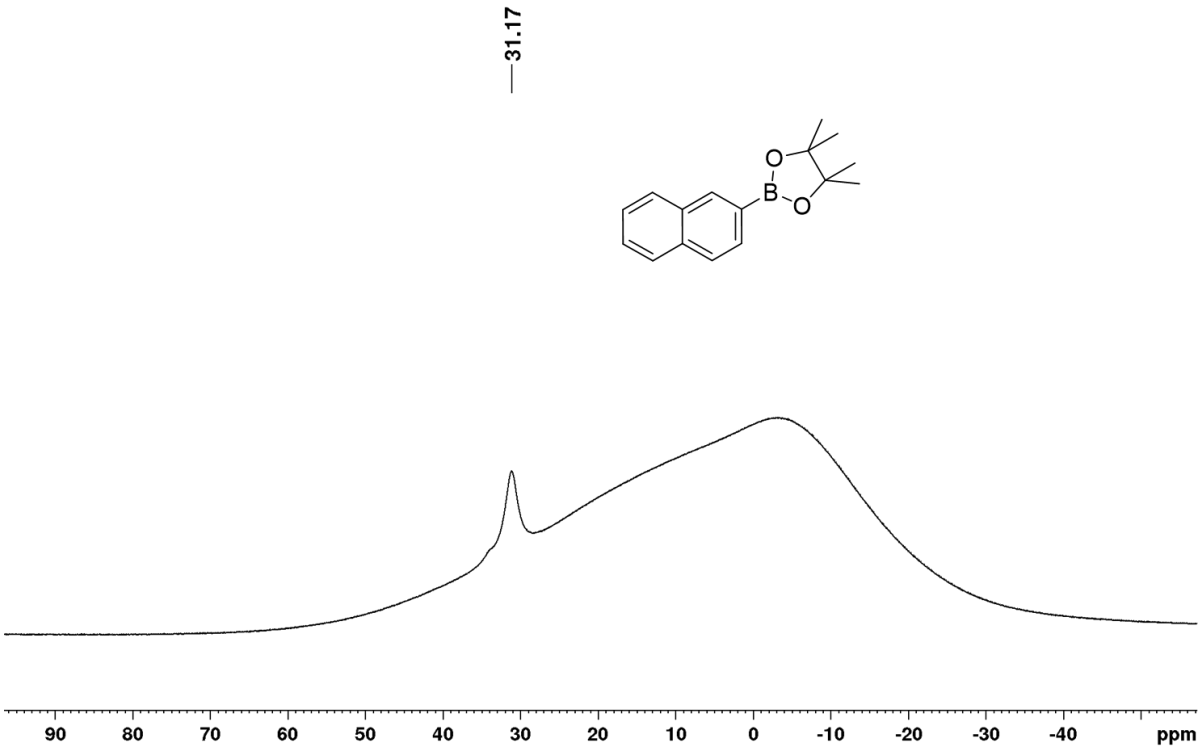


Figure S62. $^{11}B\{^{1}H\}$ NMR spectrum of compound **19a** in $CDCl_3$ (160 MHz).

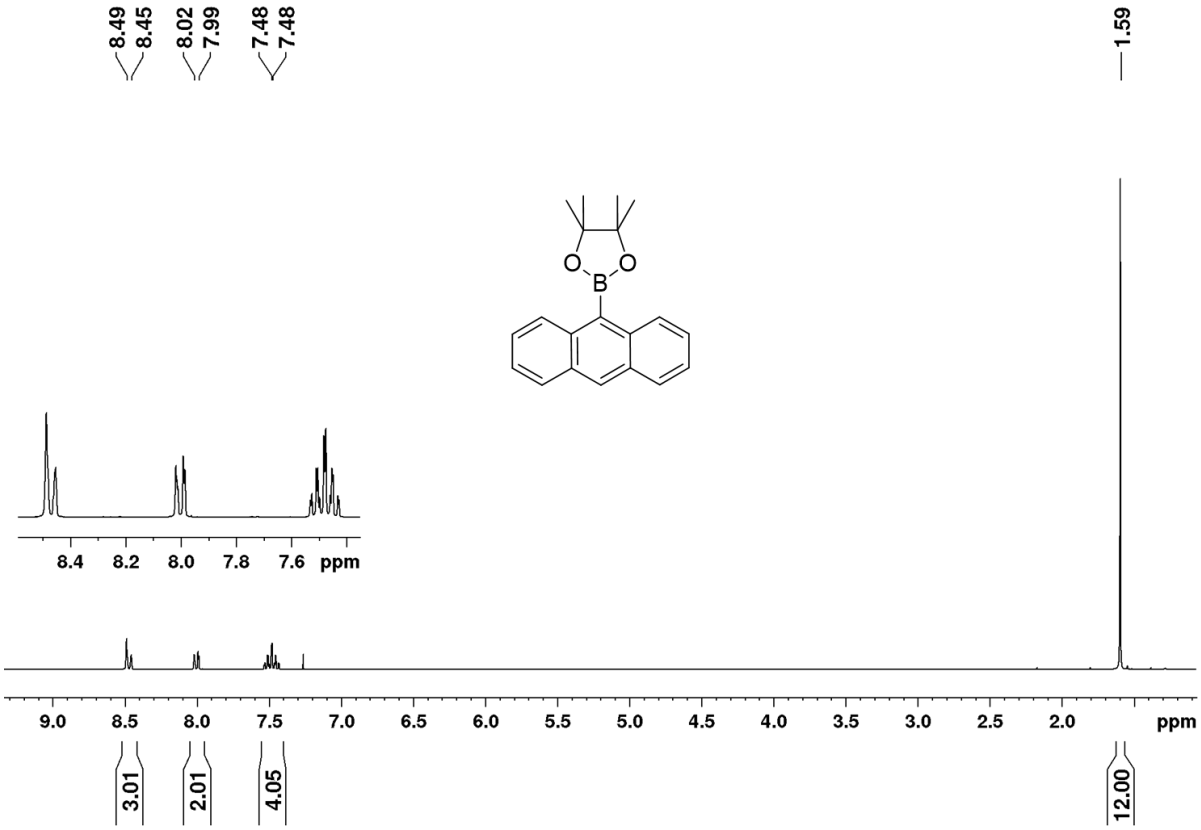


Figure S63. ^{1}H NMR spectrum of compound **20a** in $CDCl_3$ (300 MHz).

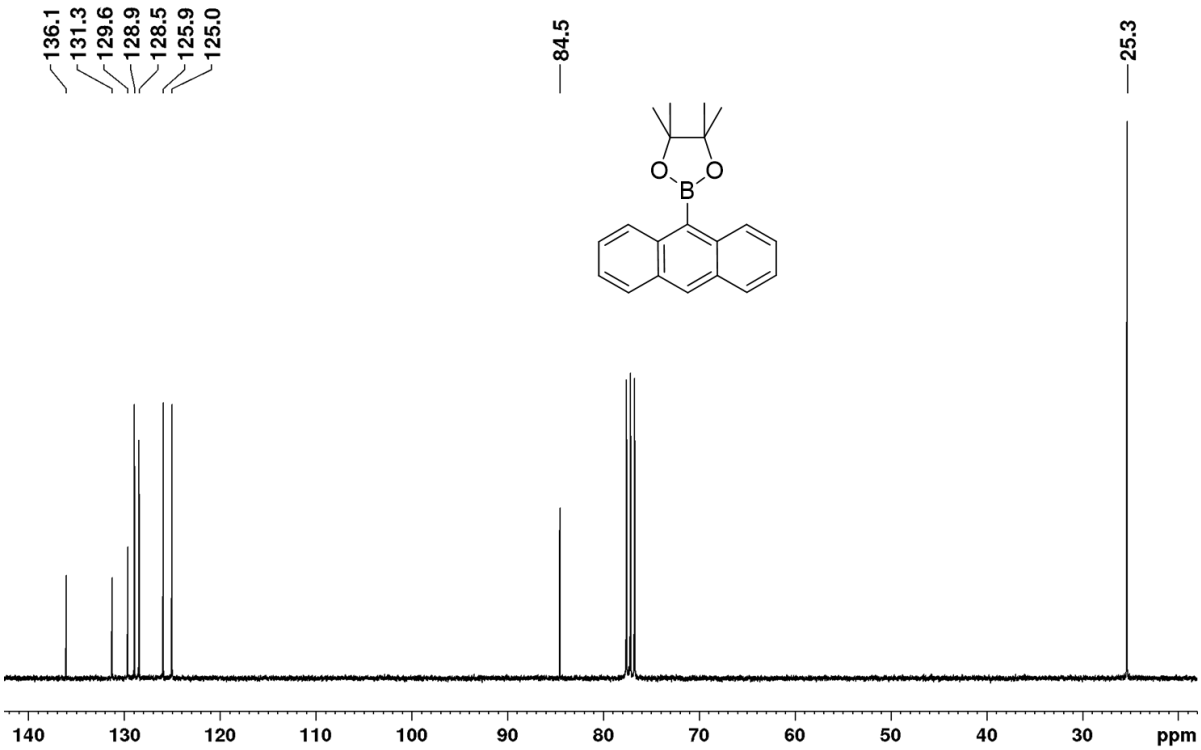


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of compound **20a** in $CDCl_3$ (75 MHz).

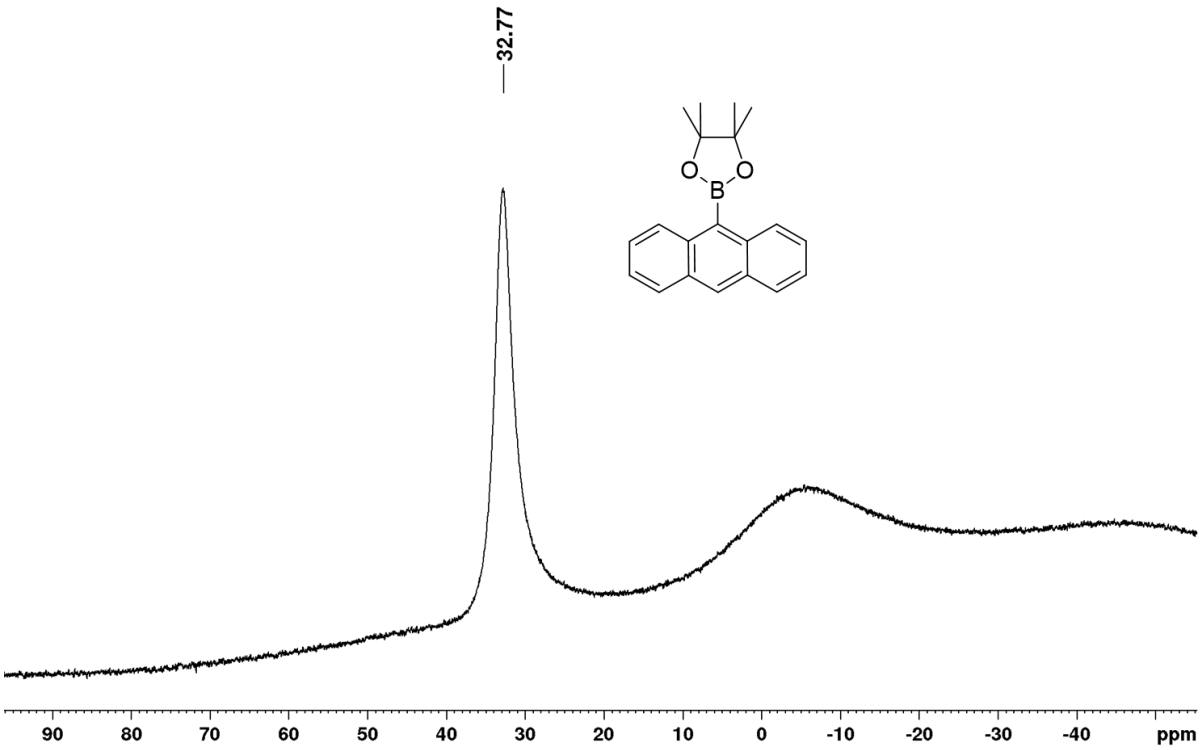


Figure S65. $^{11}B\{^{1}H\}$ NMR spectrum of compound **20a** in $CDCl_3$ (96 MHz).

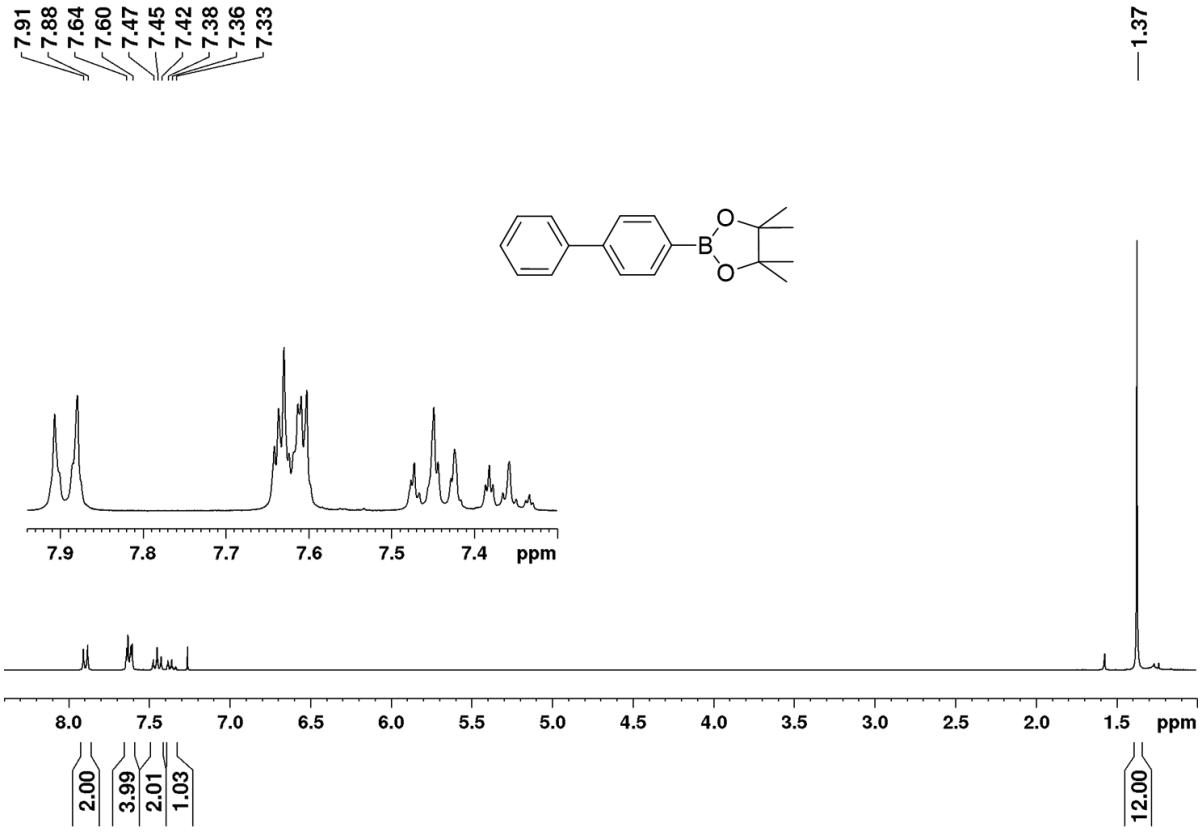


Figure S66. ^{1}H NMR spectrum of compound **21a** in $CDCl_3$ (300 MHz).

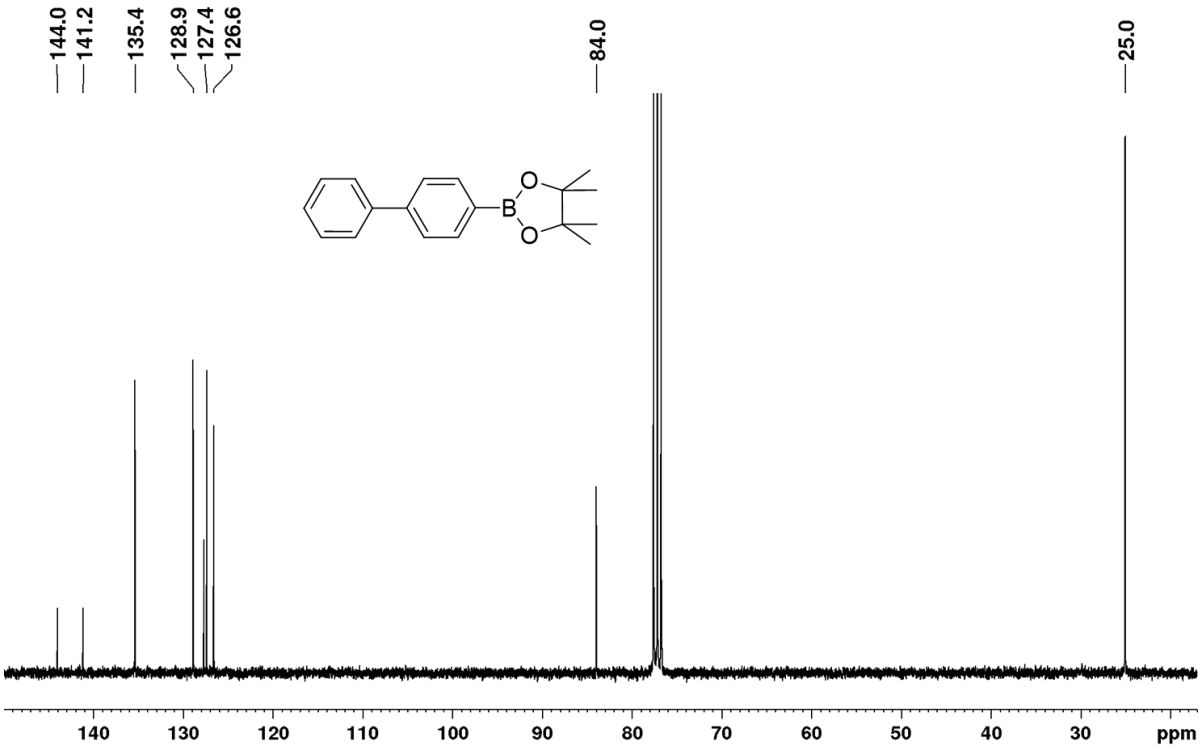


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of compound **21a** in $CDCl_3$ (75 MHz).

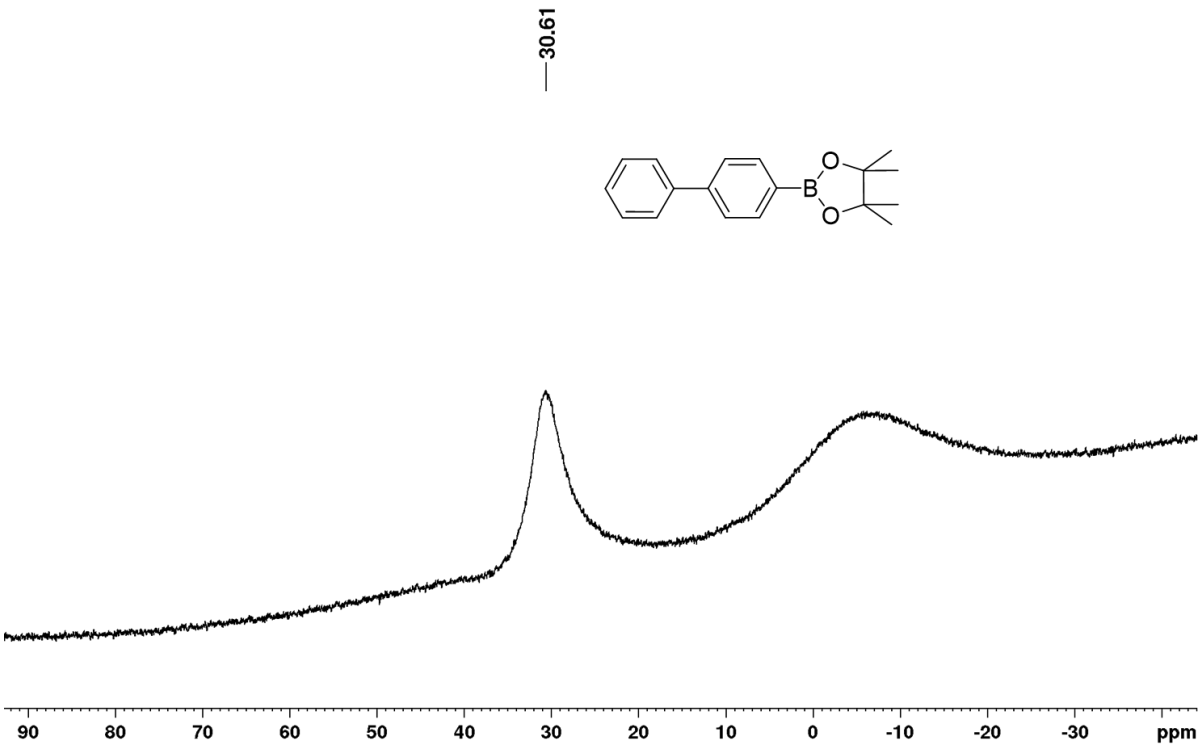


Figure S68. $^{11}B\{^{1}H\}$ NMR spectrum of compound **21a** in $CDCl_3$ (96 MHz).

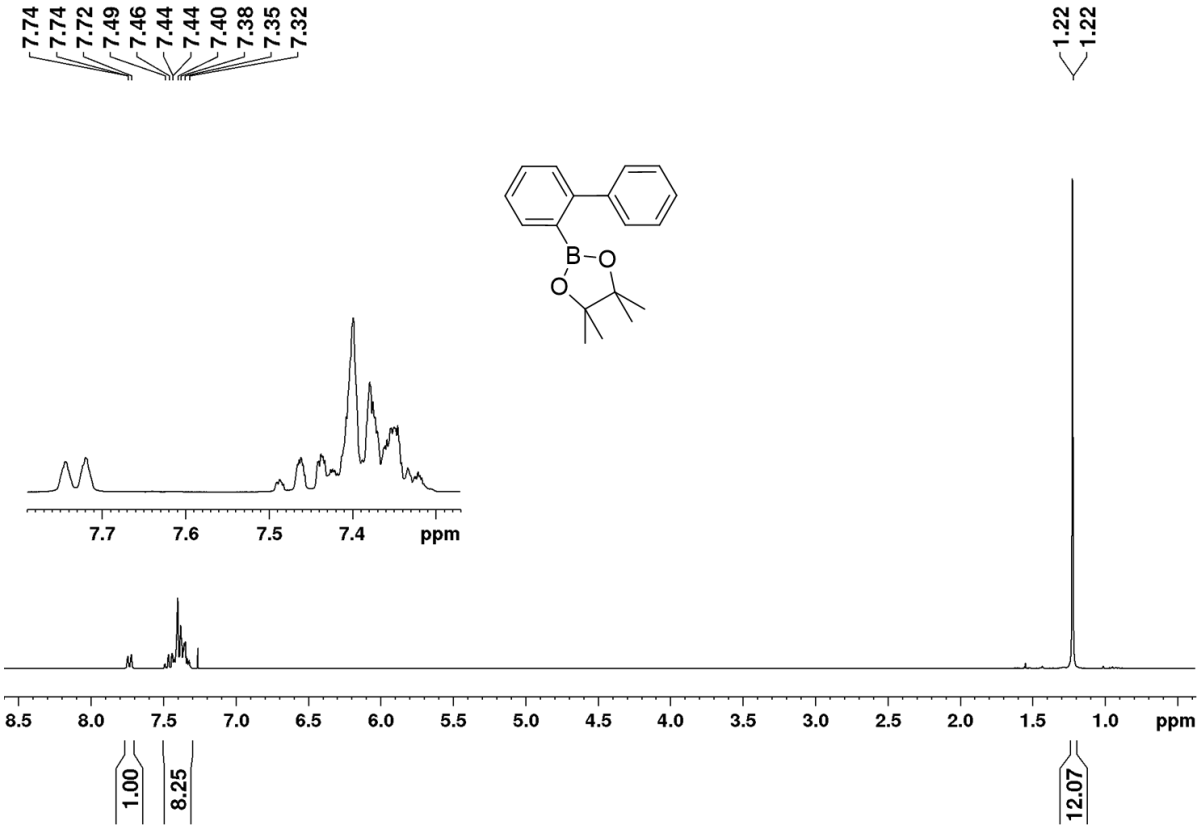


Figure S69. ^{1}H NMR spectrum of compound **22a** in $CDCl_3$ (300 MHz).

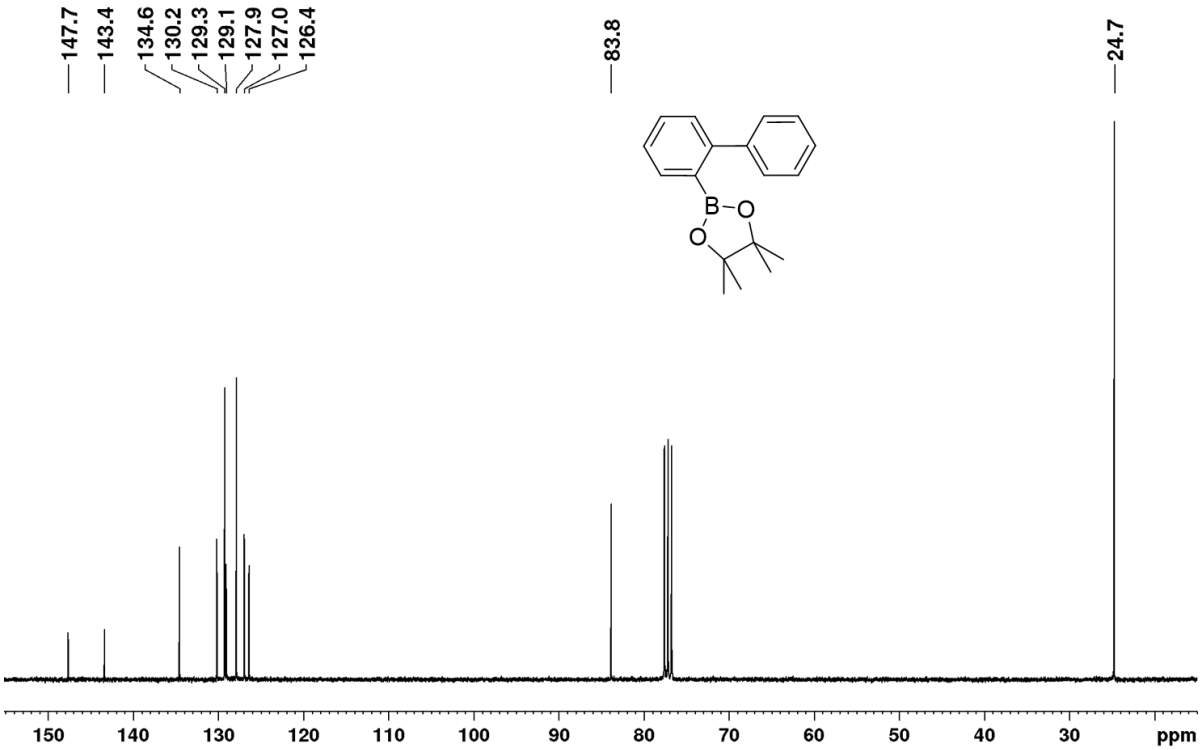


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of compound **22a** in $CDCl_3$ (75 MHz).

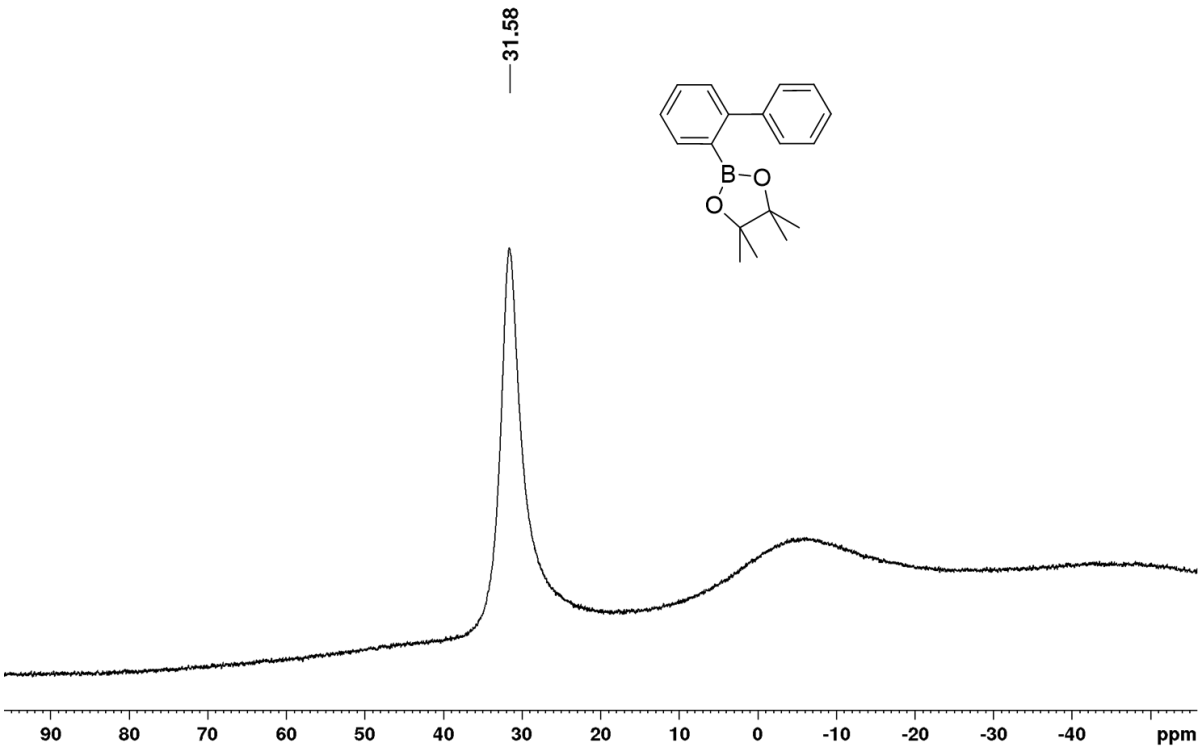


Figure S71. $^{11}B\{^{1}H\}$ NMR spectrum of compound **22a** in $CDCl_3$ (96 MHz).

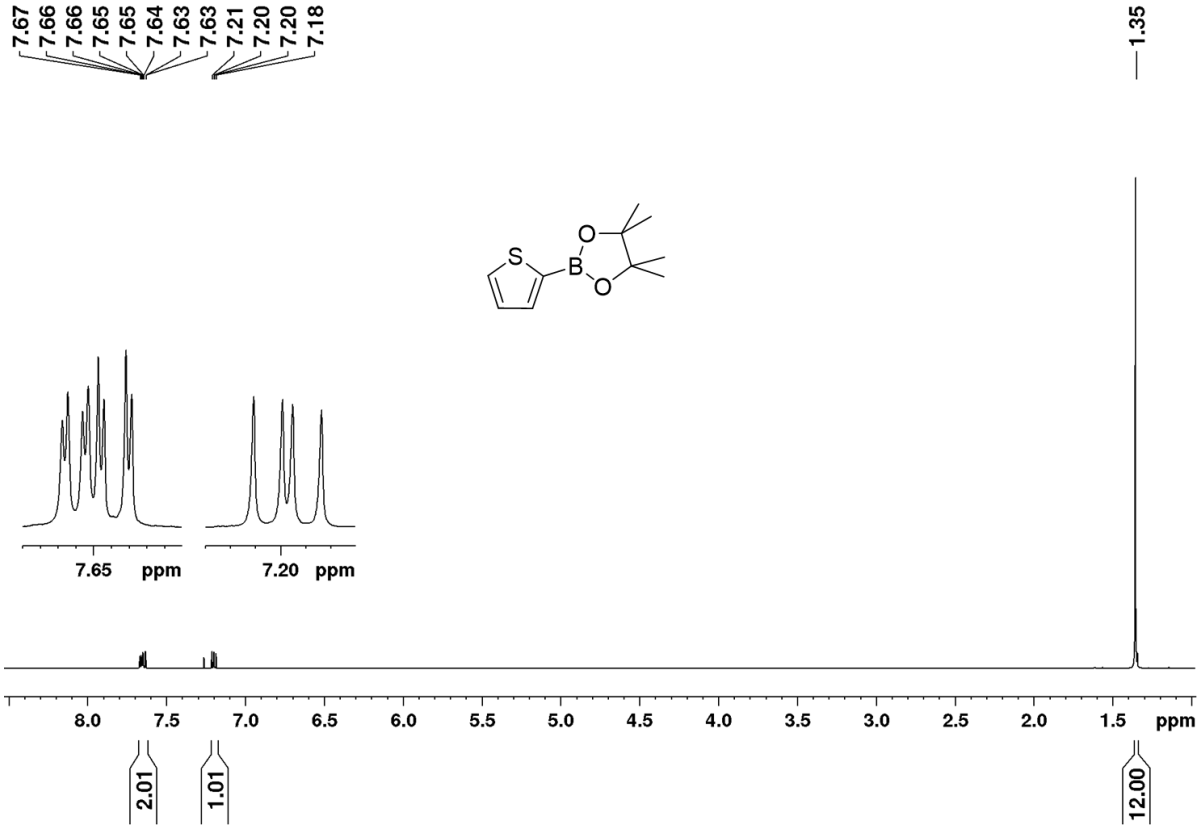


Figure S72. ^{1}H NMR spectrum of compound **23a** in $CDCl_3$ (500 MHz).

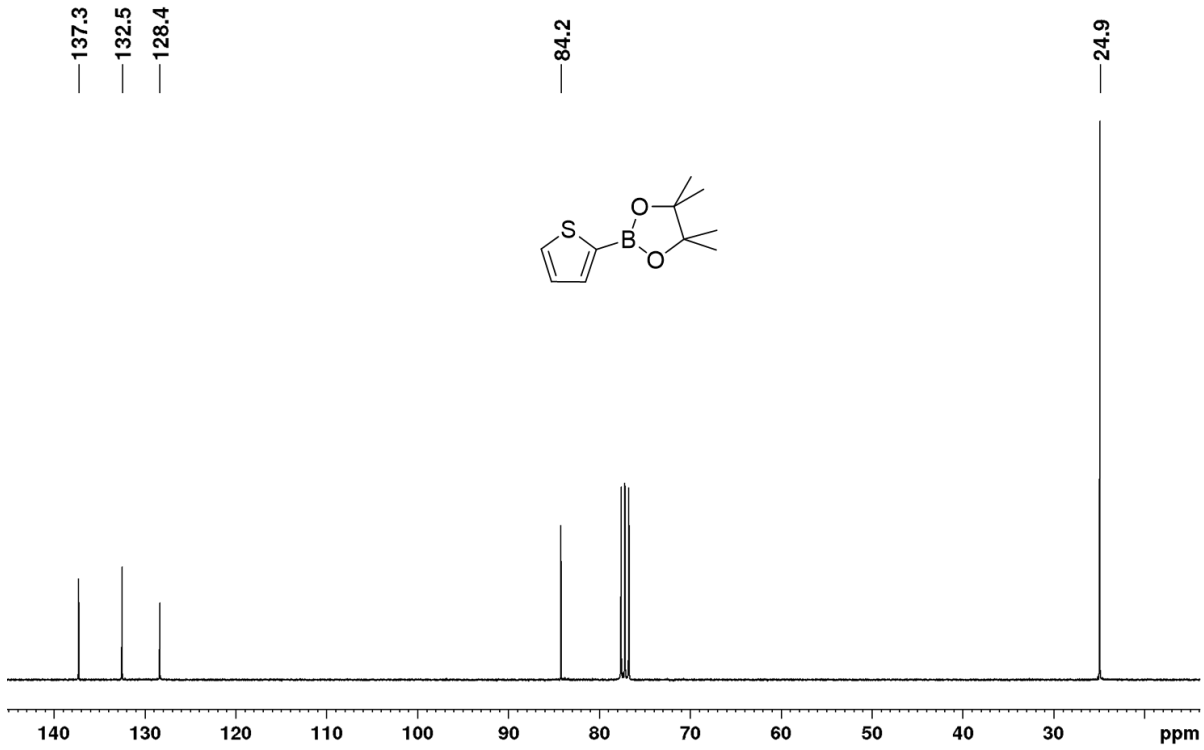


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of compound **23a** in $CDCl_3$ (125 MHz).

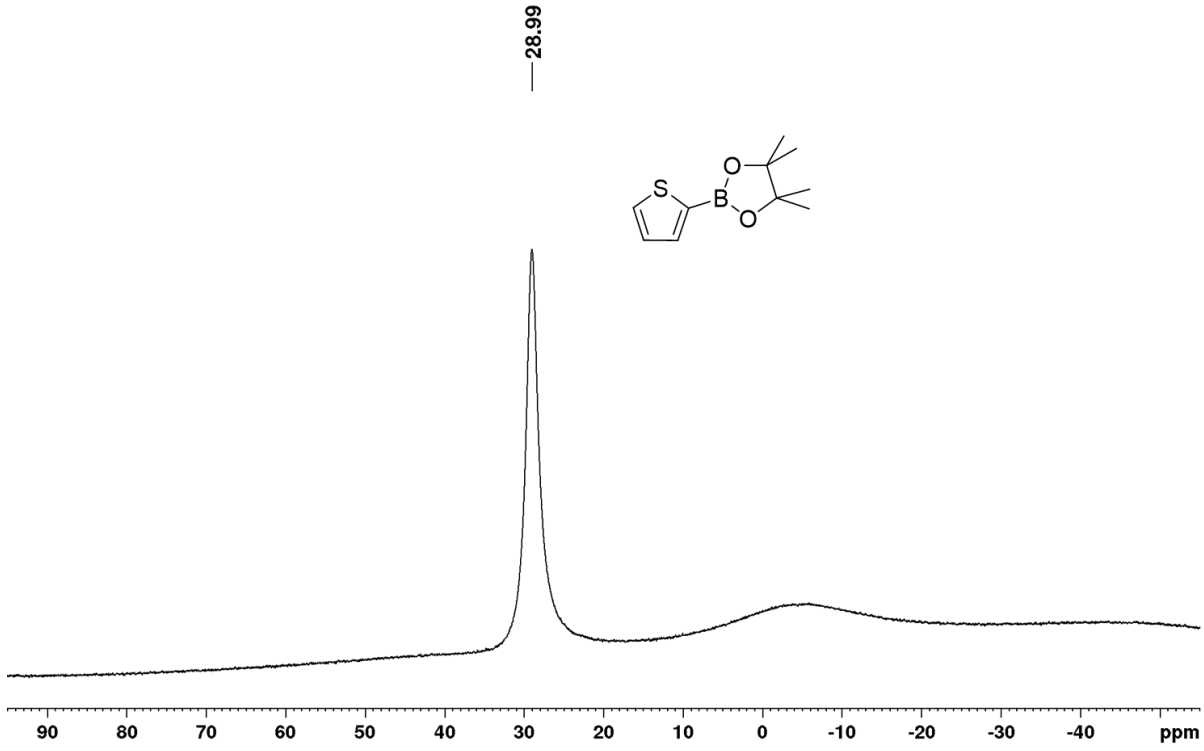


Figure S74. $^{11}B\{^{1}H\}$ NMR spectrum of compound **23a** in $CDCl_3$ (160 MHz).

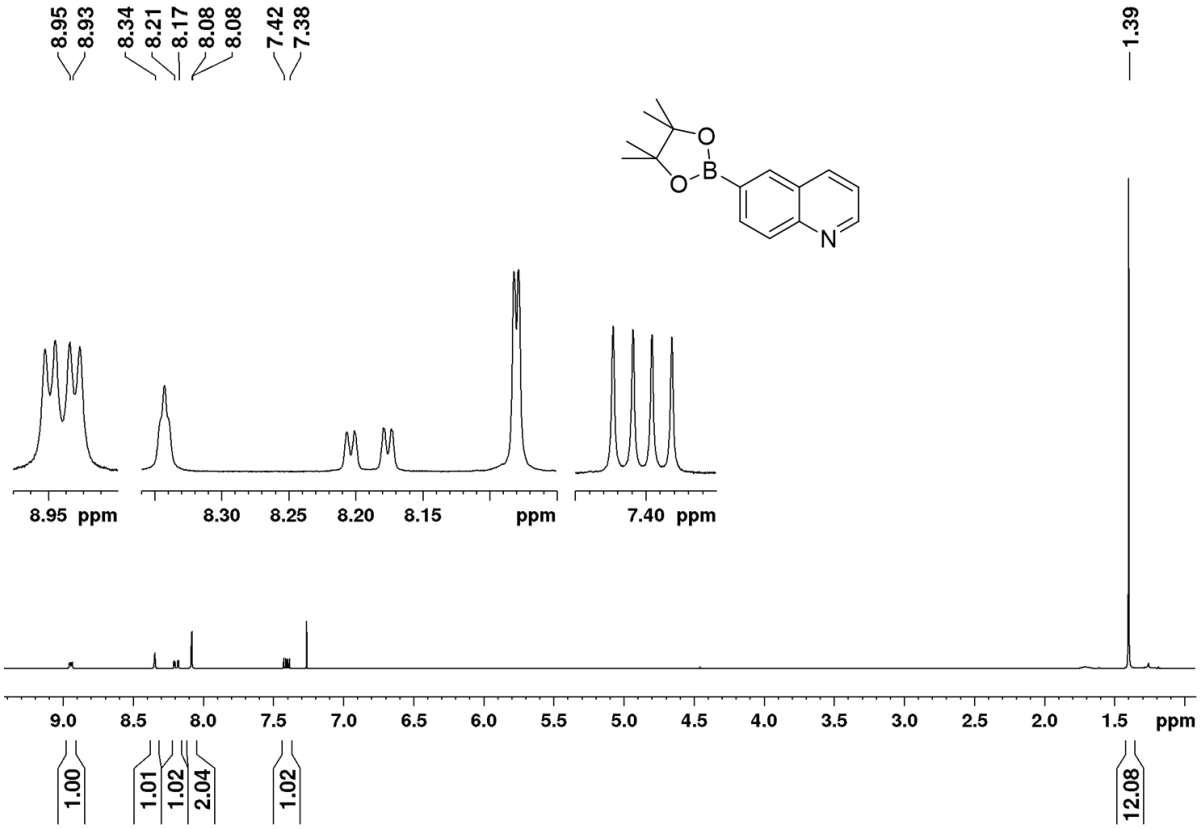


Figure S75. ^{1}H NMR spectrum of compound **25a** in $CDCl_3$ (300 MHz).

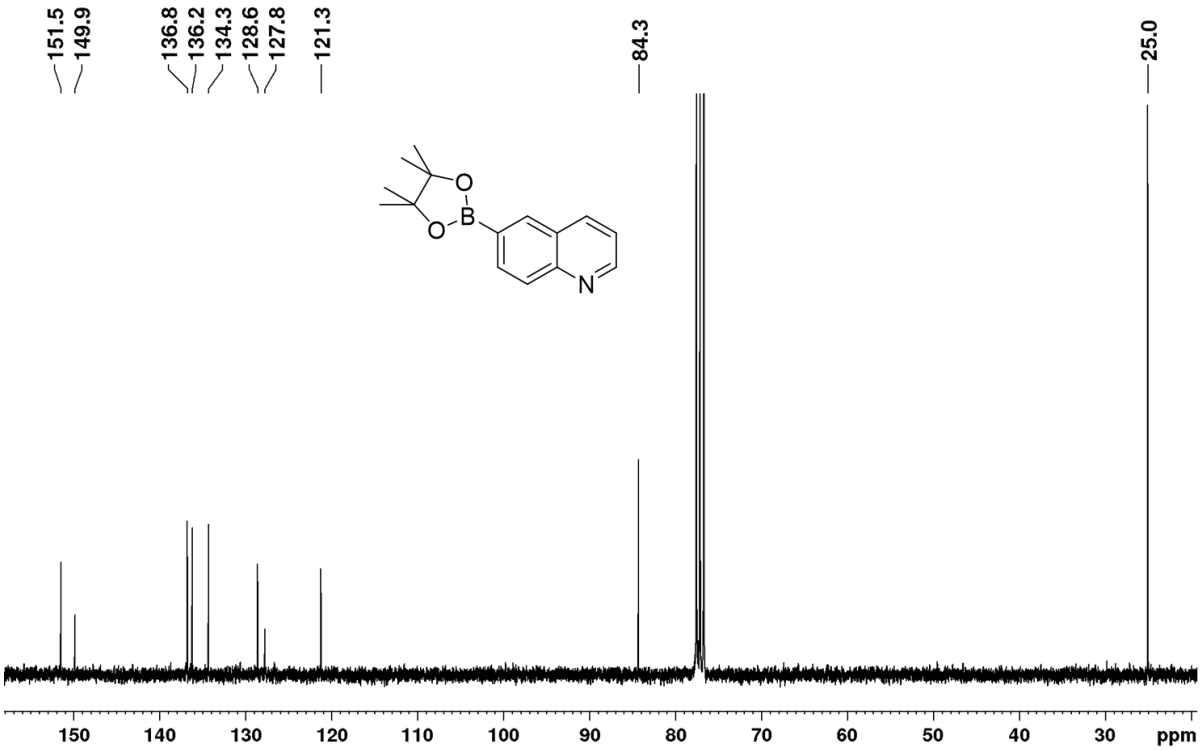


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of compound **25a** in $CDCl_3$ (75 MHz).

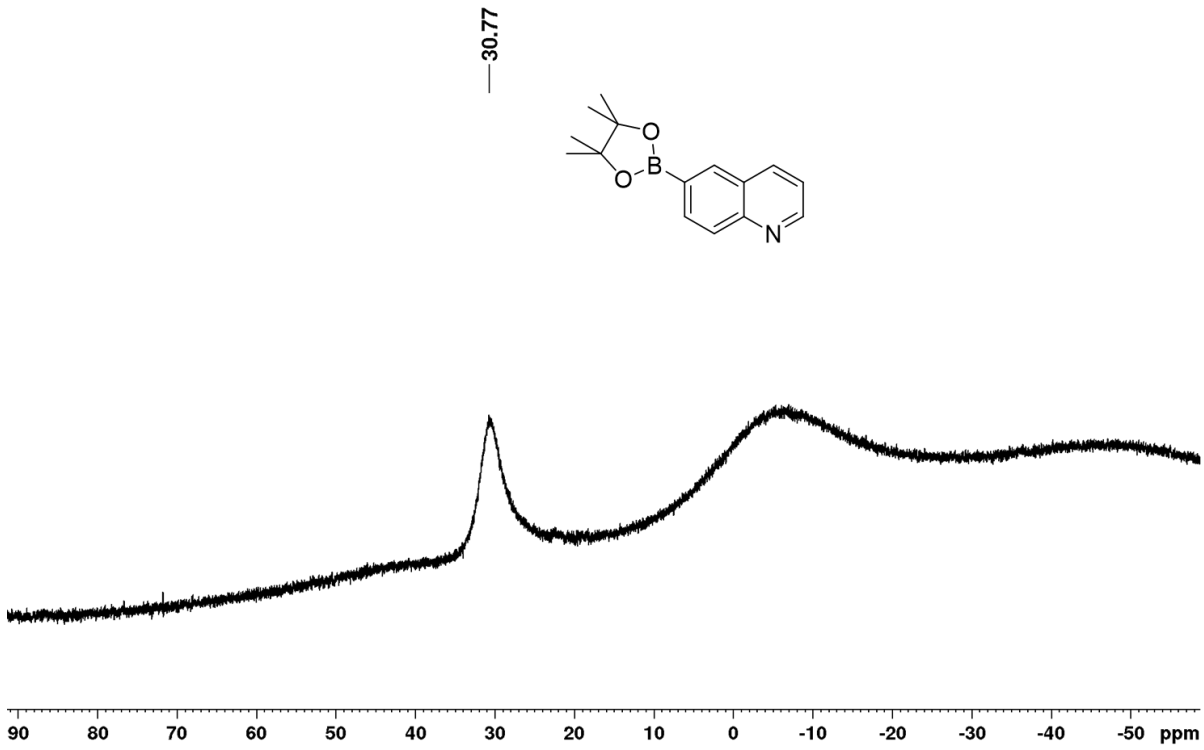


Figure S77. $^{11}B\{^{1}H\}$ NMR spectrum of compound **25a** in $CDCl_3$ (96 MHz).

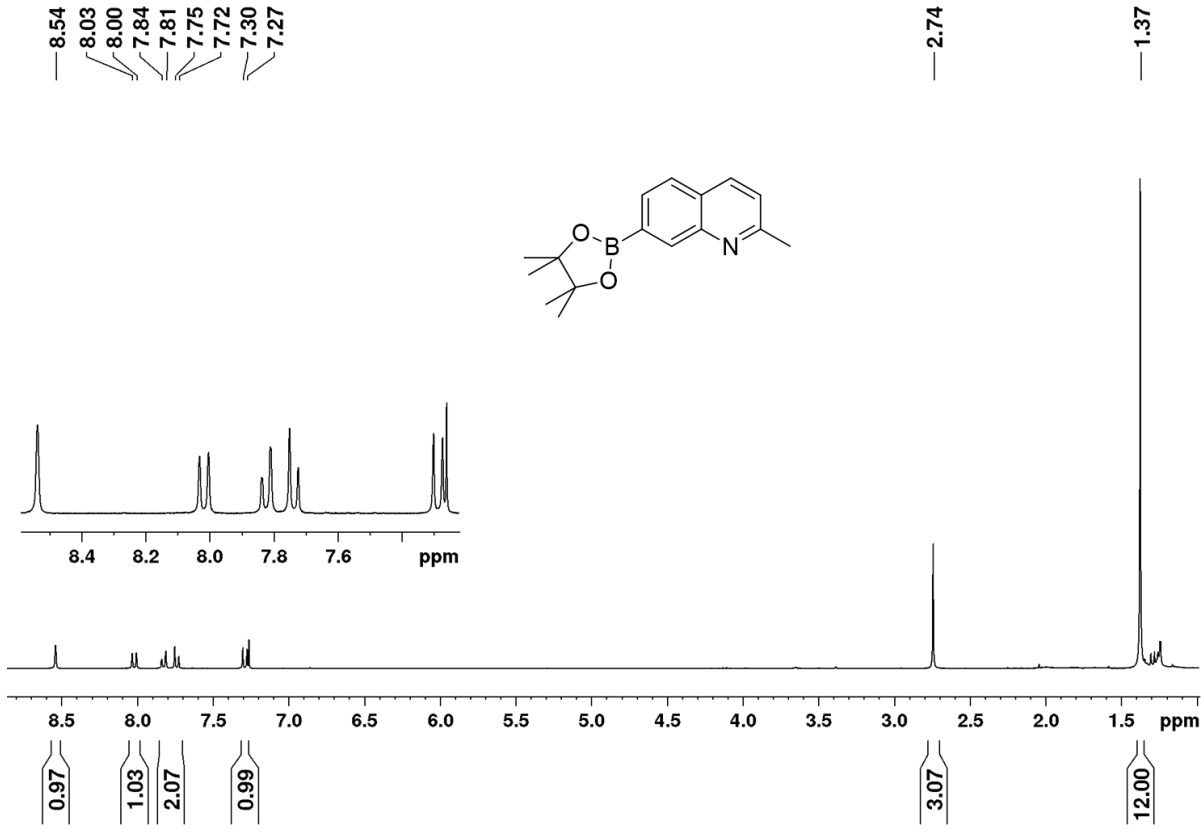


Figure S78. ^{1}H NMR spectrum of compound **26a** in $CDCl_3$ (300 MHz).

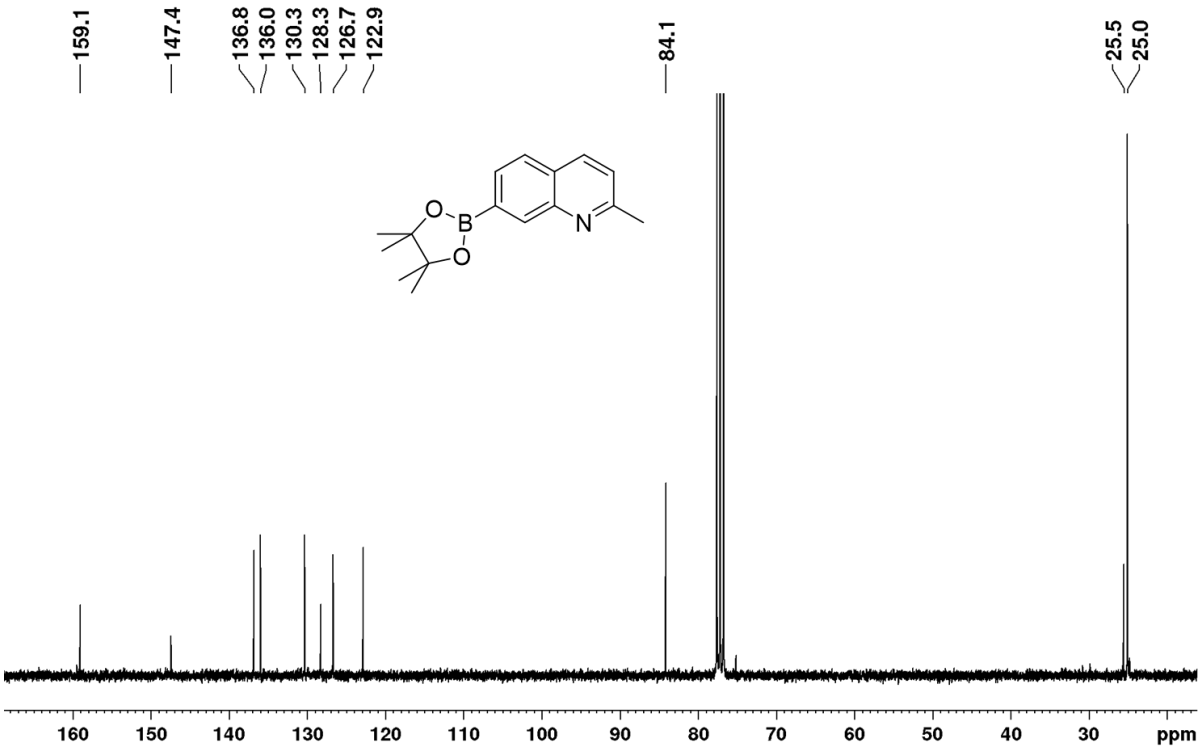


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of compound **26a** in $CDCl_3$ (75 MHz).

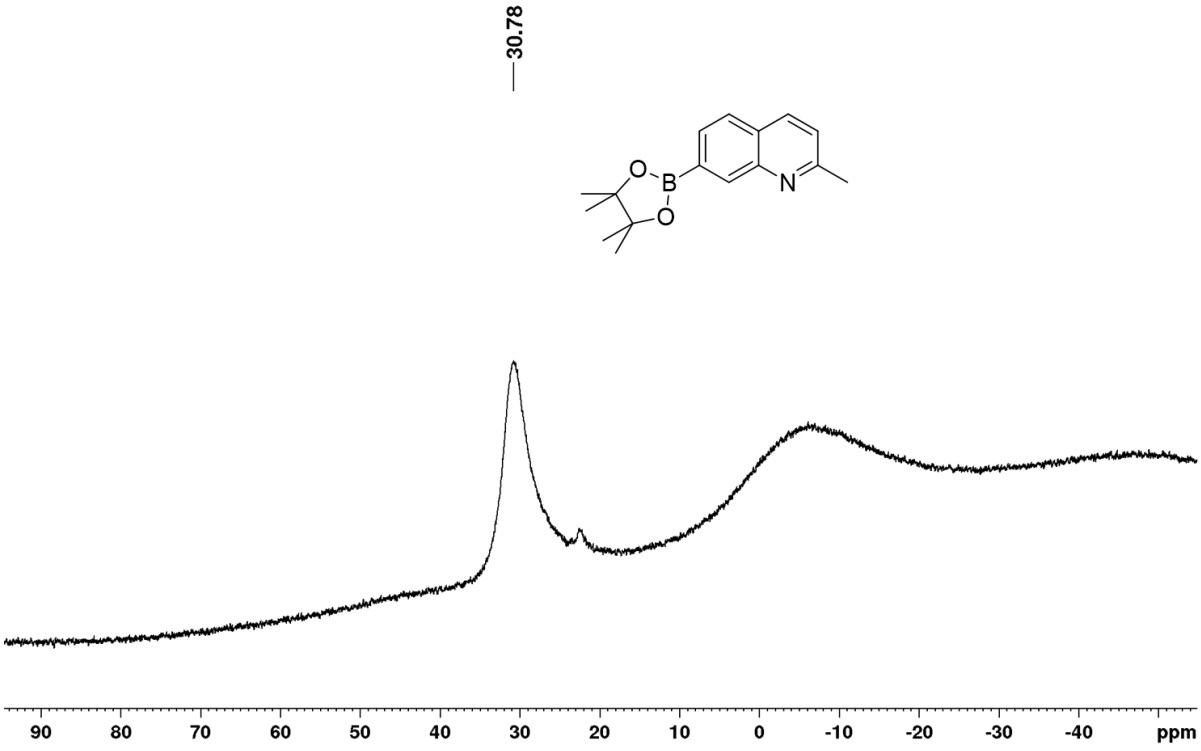


Figure S80. $^{11}B\{^{1}H\}$ NMR spectrum of compound **26a** in $CDCl_3$ (96 MHz).

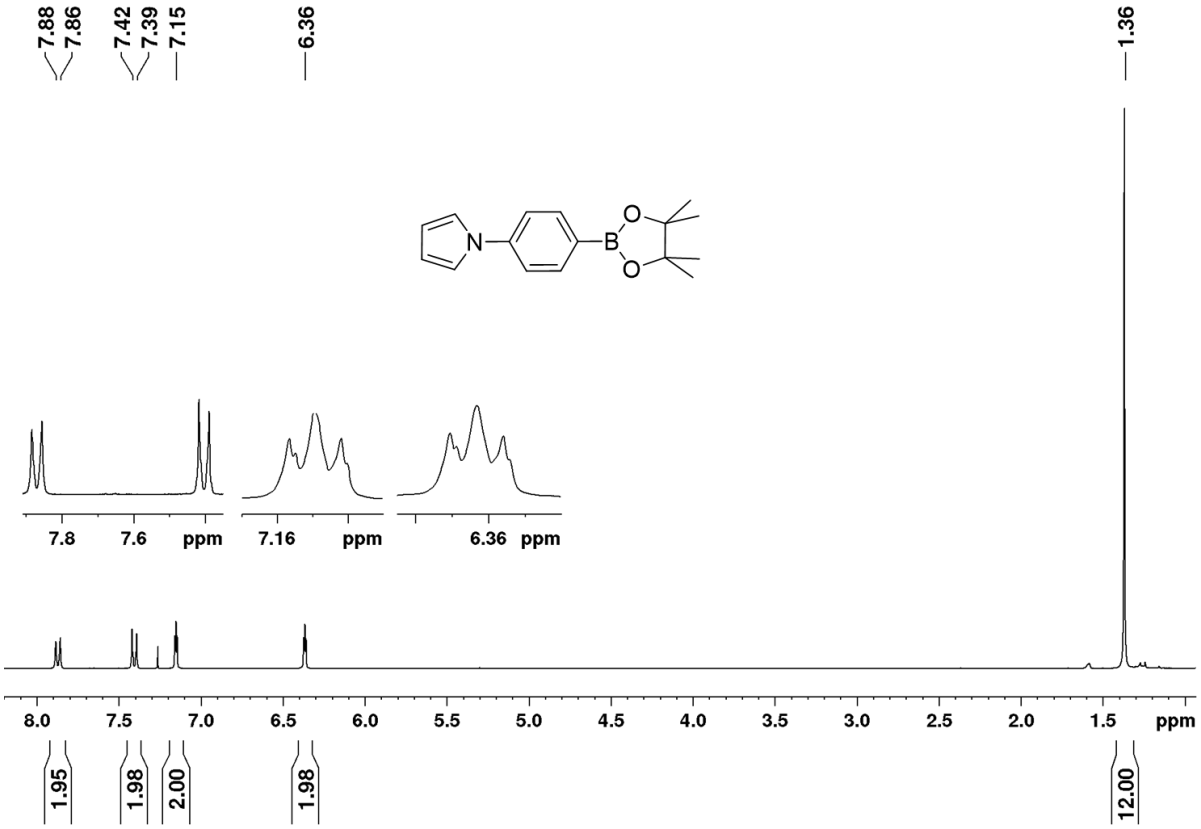


Figure S81. ^{1}H NMR spectrum of compound **27a** in $CDCl_3$ (300 MHz).

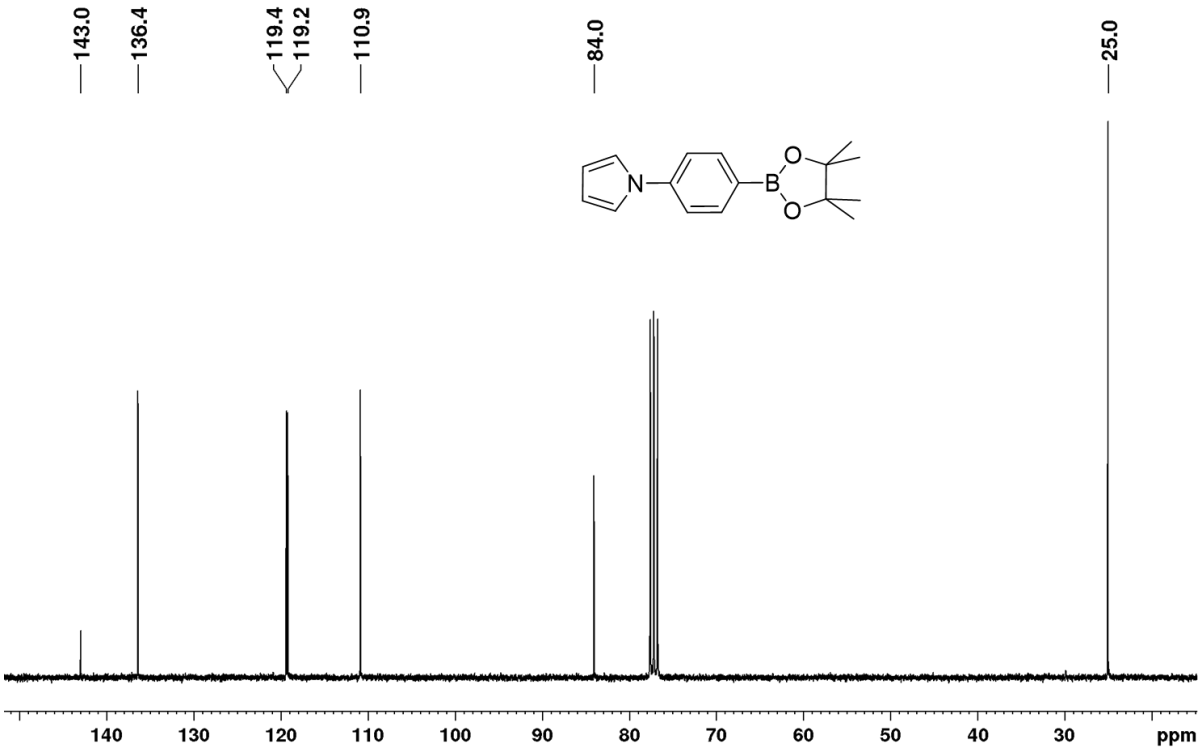


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of compound **27a** in $CDCl_3$ (75 MHz).

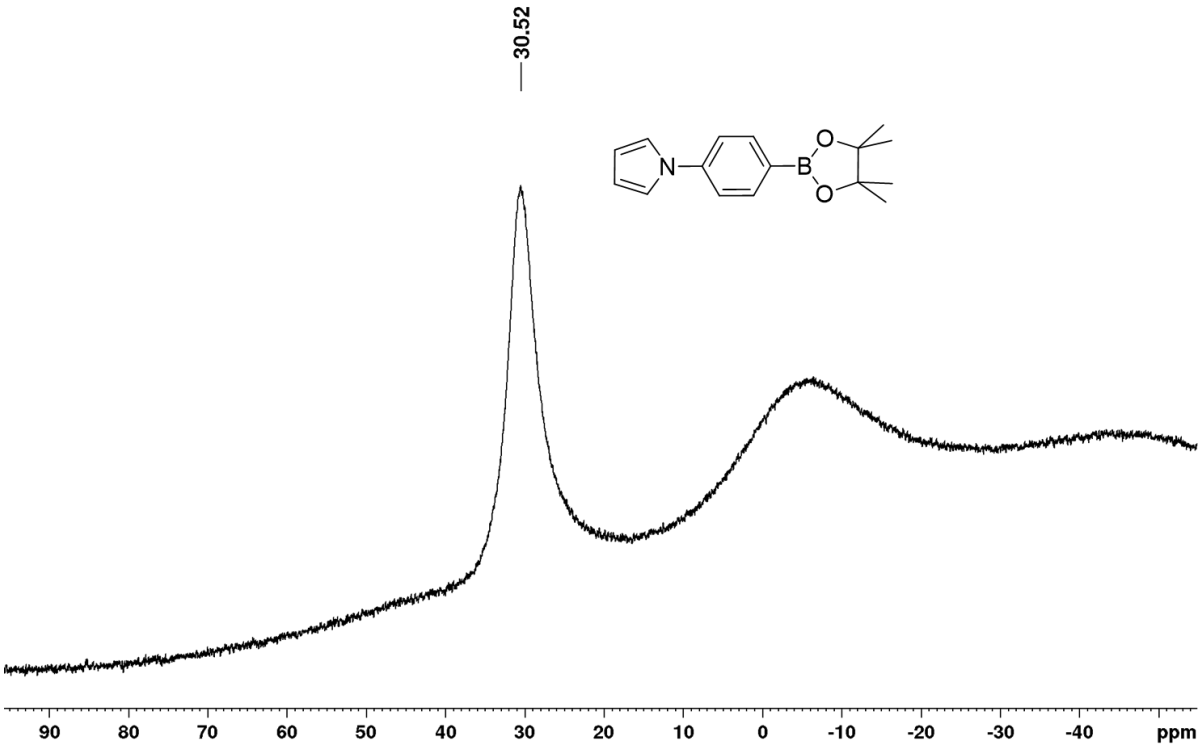


Figure S83. $^{11}B\{^{1}H\}$ NMR spectrum of compound **27a** in $CDCl_3$ (96 MHz).

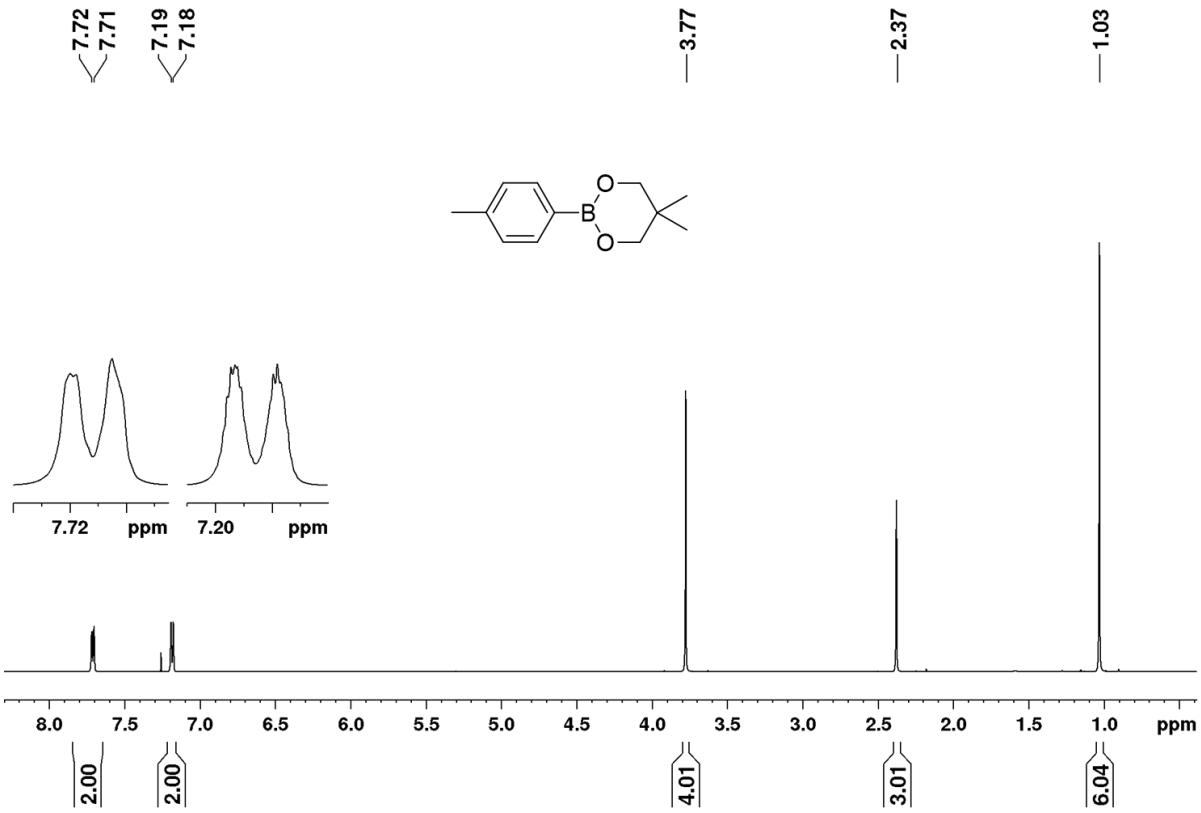


Figure S84. ^{1}H NMR spectrum of compound **28a** in $CDCl_3$ (500 MHz).

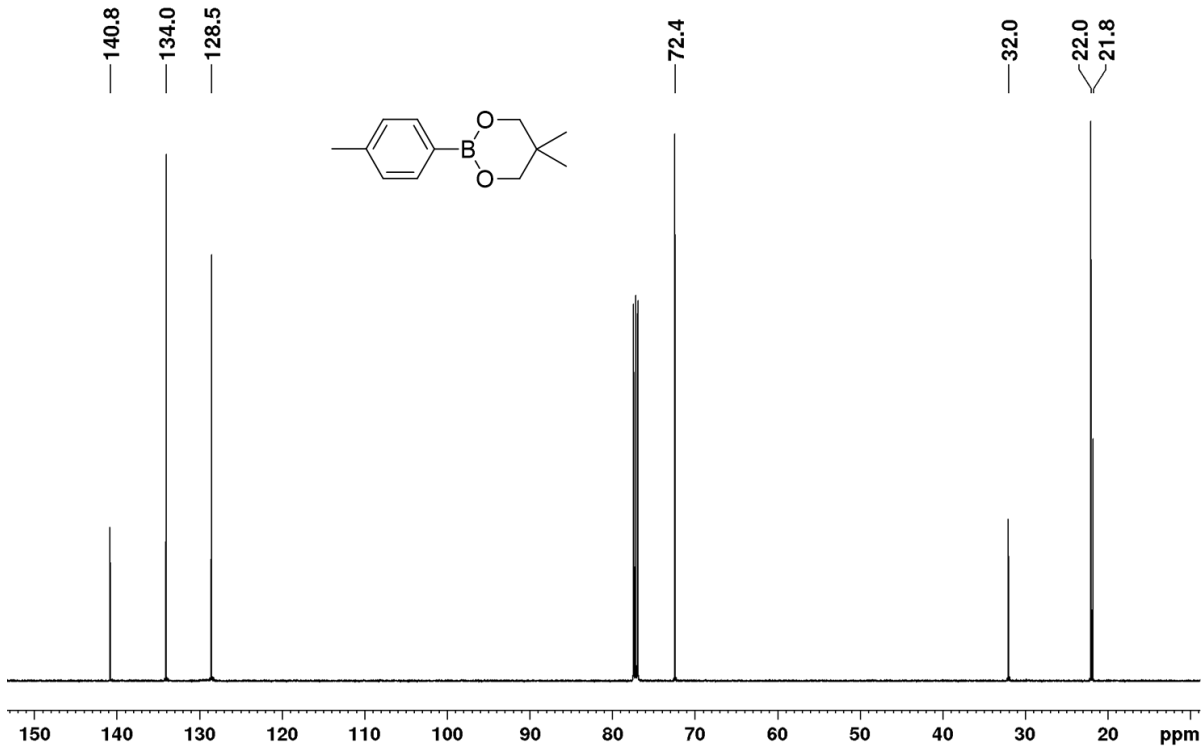


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of compound **28a** in $CDCl_3$ (125 MHz).

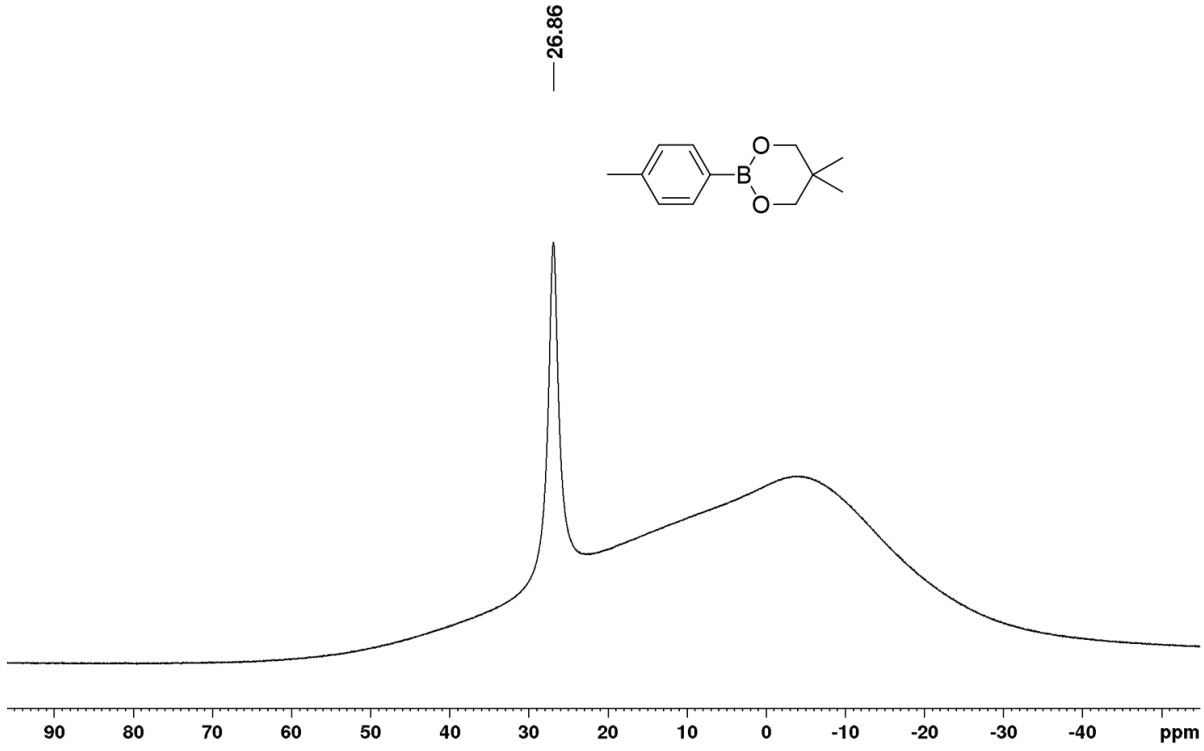


Figure S86. $^{11}B\{^{1}H\}$ NMR spectrum of compound **28a** in $CDCl_3$ (160 MHz).

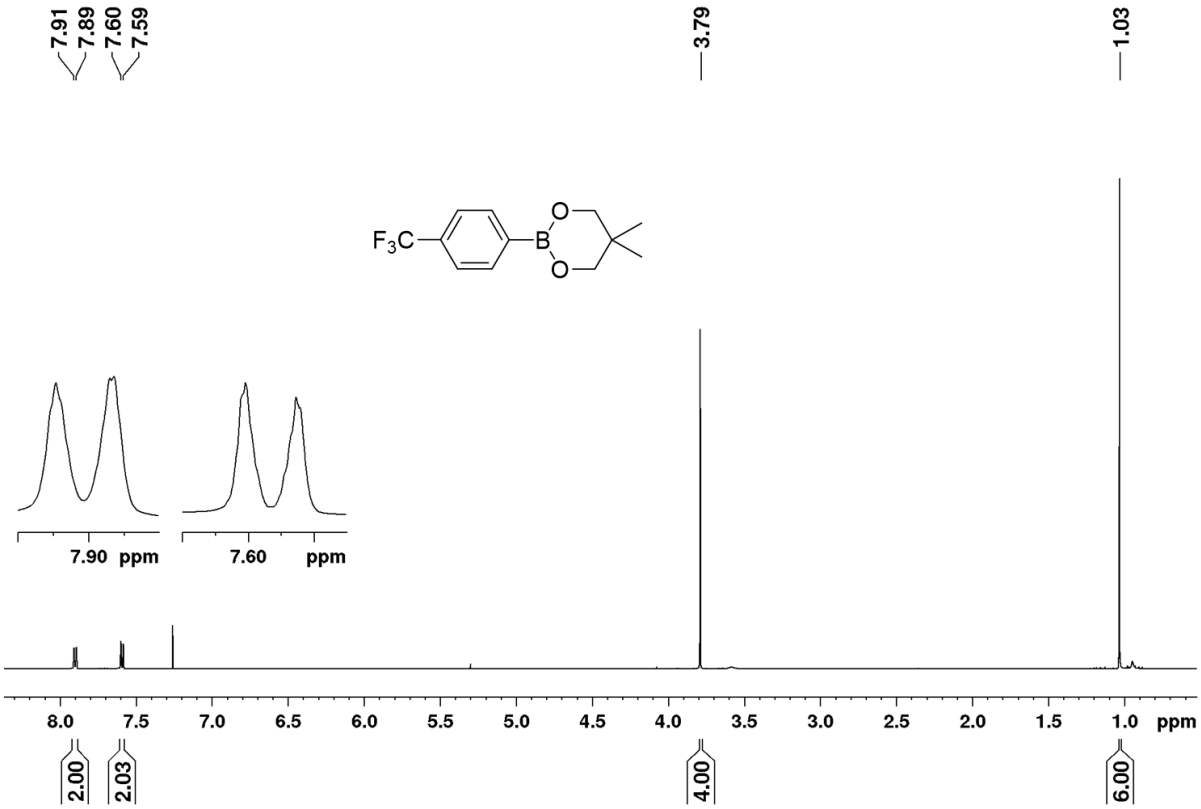


Figure S87. ^{1}H NMR spectrum of compound **29a** in $CDCl_3$ (500 MHz).

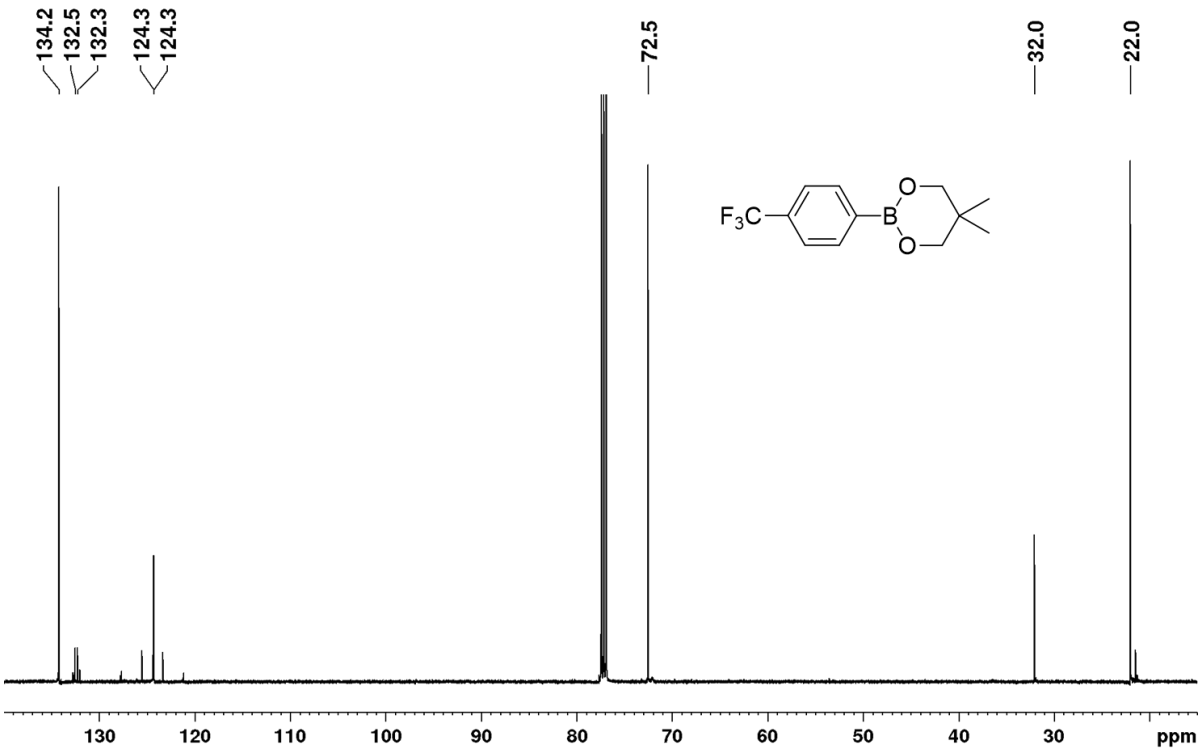


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of compound **29a** in $CDCl_3$ (125 MHz).

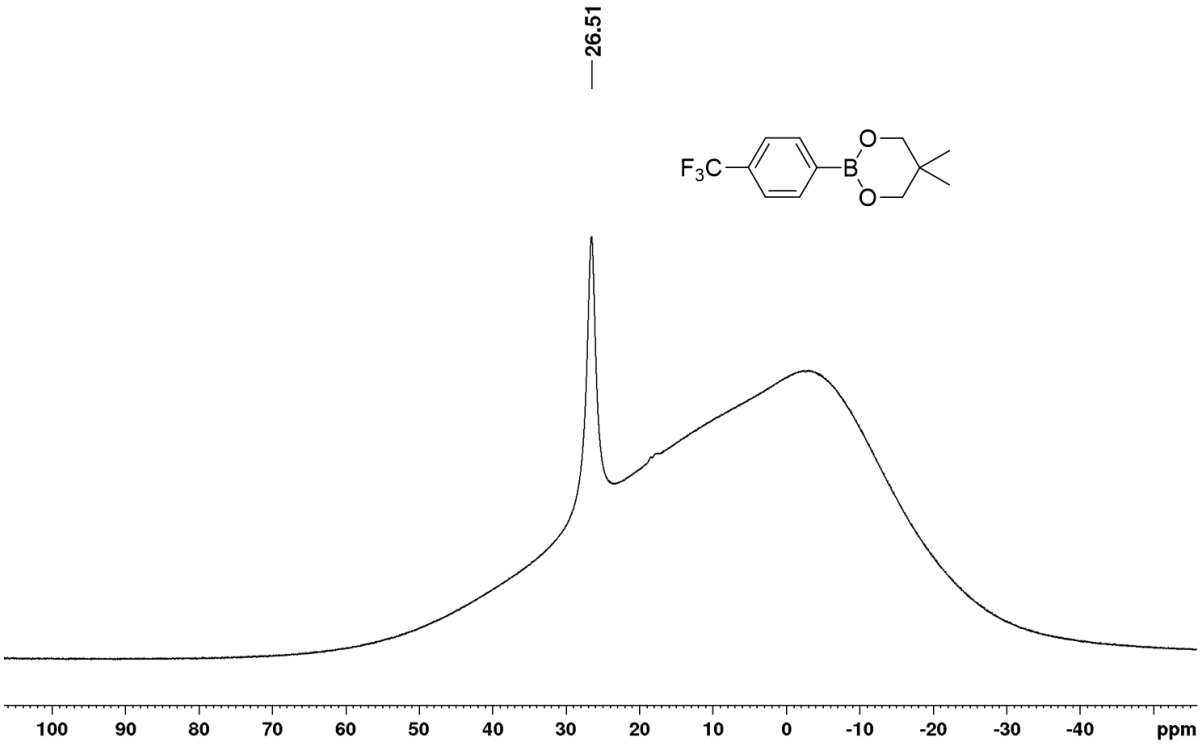


Figure S89. $^{11}B\{^{1}H\}$ NMR spectrum of compound **29a** in $CDCl_3$ (160 MHz).

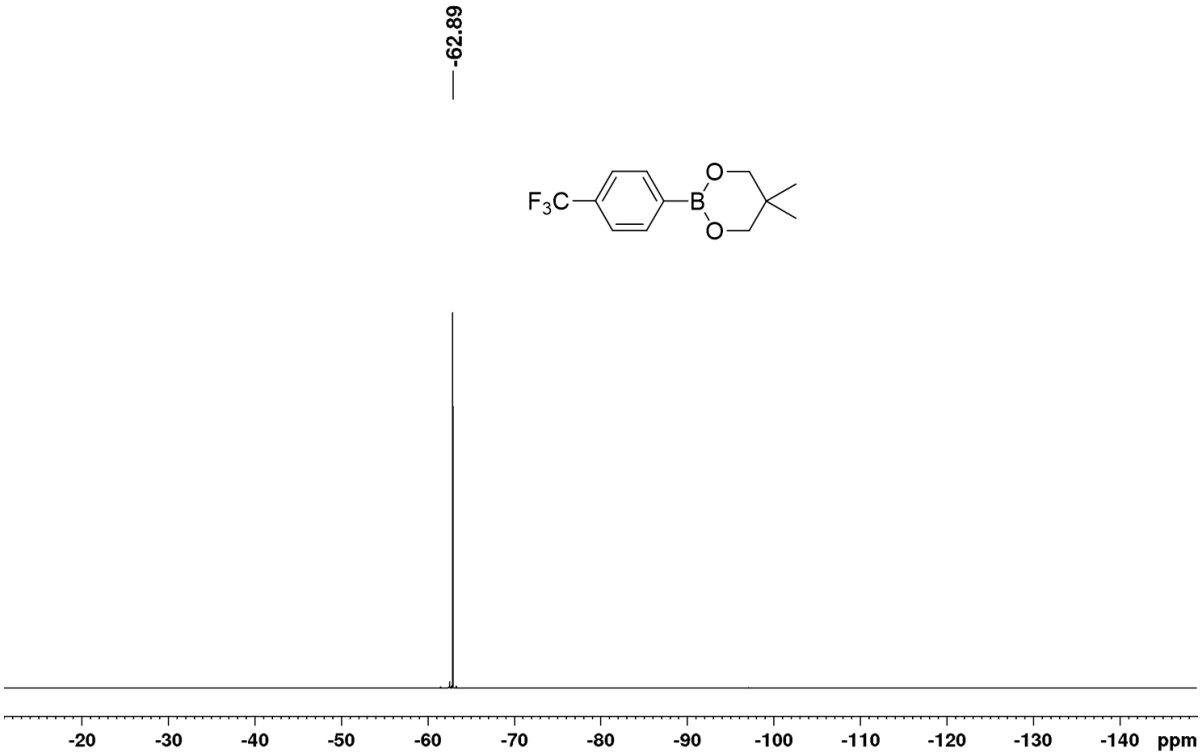


Figure S90. $^{19}F\{^{1}H\}$ NMR spectrum of compound **29a** in $CDCl_3$ (470 MHz).

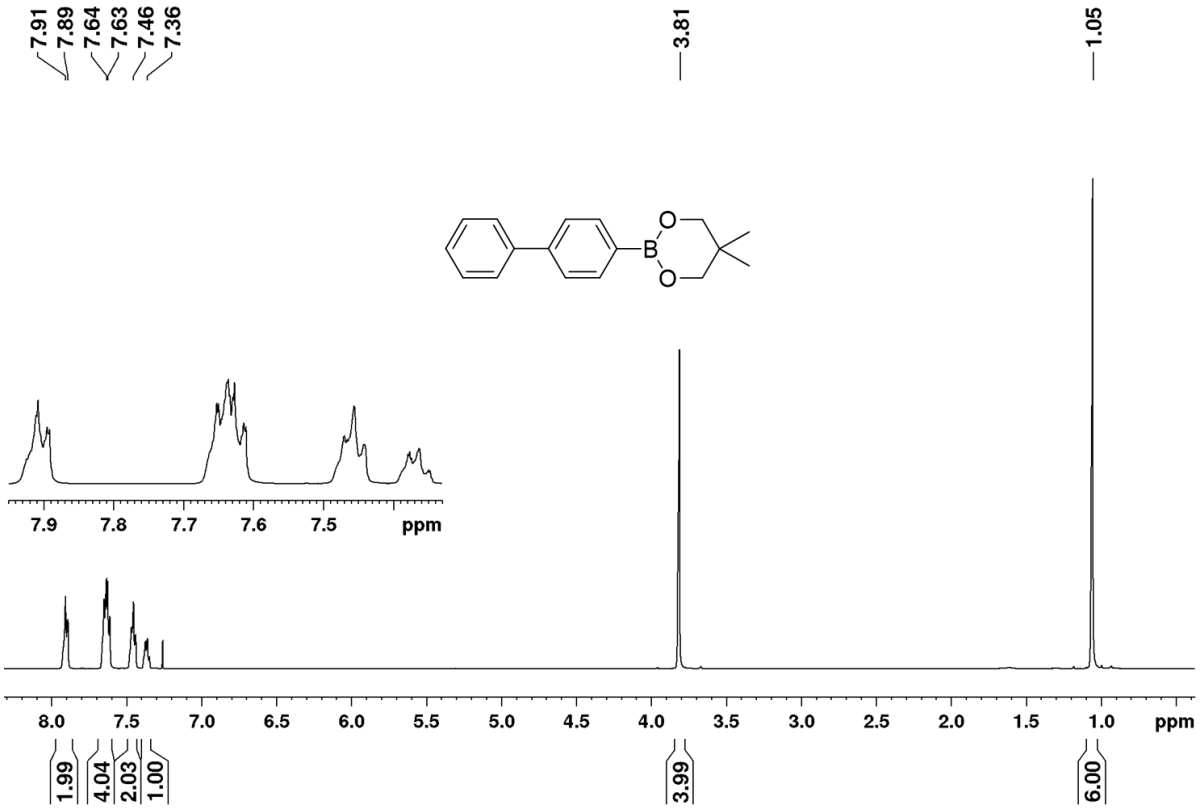


Figure S91. ^{1}H NMR spectrum of compound **30a** in $CDCl_3$ (500 MHz).

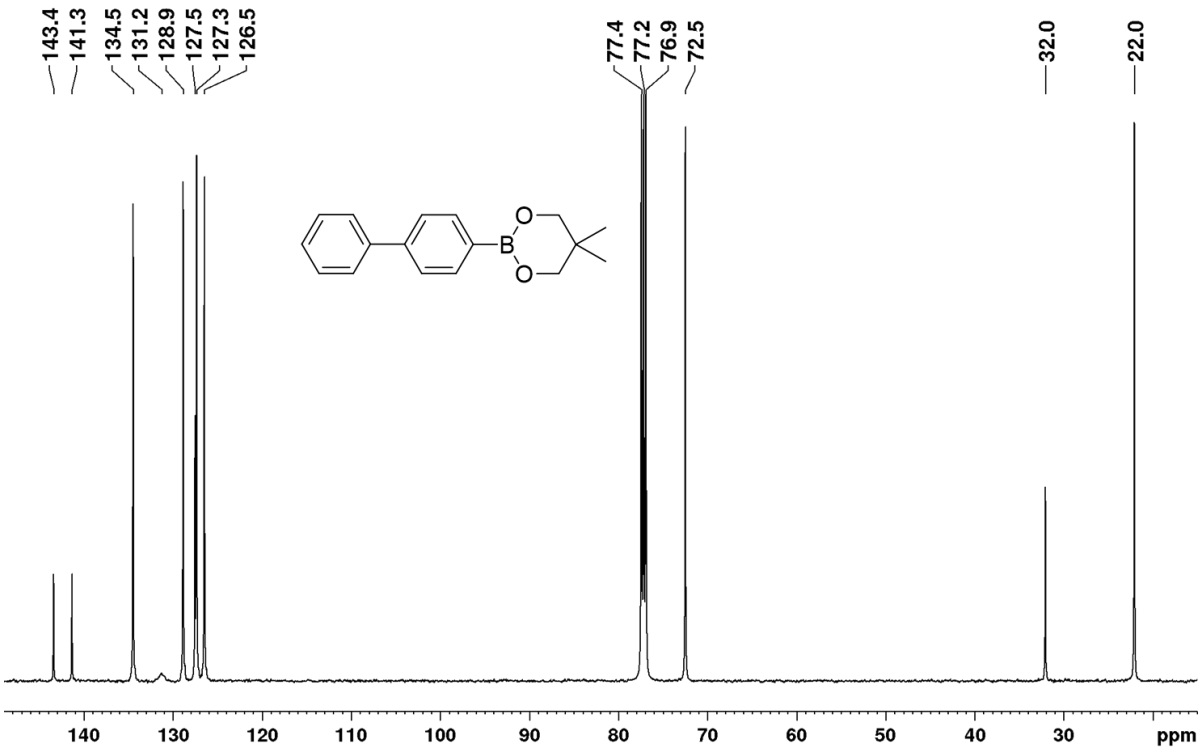


Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum of compound **30a** in $CDCl_3$ (125 MHz).

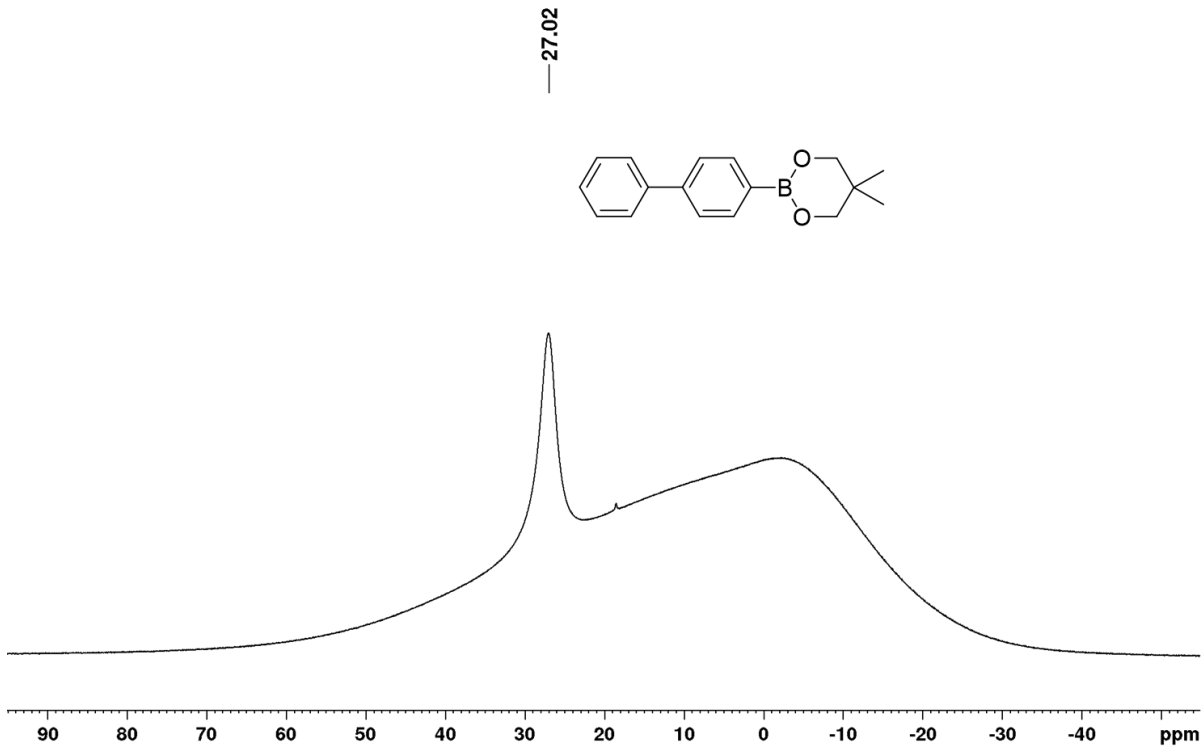


Figure S93. $^{11}B\{^{1}H\}$ NMR spectrum of compound **30a** in $CDCl_3$ (160 MHz).

3 References

[S1] C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin, C. S. J. Cazin, *Dalton Trans.*, 2010, **39**, 4489-4491.

[S2] H. Braunschweig, W. C. Ewing, T. Kramer, J. D. Mattock, A. Vargas, C. Werner, *Chem. Eur. J.*, 2015, **21**, 12347-12356.

[S3] G. A. Bowmaker, S. E. Boyd, J. V. Hanna, R. D. Hart, P. C. Healy, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.*, 2002, 2722-2730.

[S4] K. Semba, T. Fujihara, T. Xu, J. Terao, Y. Tsuji, *Adv. Synth. Catal.*, 2012, **354**, 1542-1550.

[S5] (a) T. Schaub, M. Backes, U. Radius, *Organometallics*, 2006, **25**, 4196-4206; (b) T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss, *Inorg. Synth.*, 2010, **35**, 78-83. (c) N. Kuhn, T. Kratz, *Synthesis*, 1993, 561-562. (d) C. Köcher, L. J. Gooßen, G. R. J. Artus, W. A. Herrmann, *Chem. Eur. J.*, 1996, **2**, 1627-1636.

[S6] a) H. Braunschweig, F. Guethlein, *Angew. Chem. Int. Ed.,* 2011, **50**, 12613-12616; *Angew. Chem.* 2011, **123**, 12821-12824; b) H. Braunschweig, F. Guethlein*,* EP2554547A1, 2013; c) C. N. Welch, S. G. Shore, *Inorg. Chem.*, 1968, **7**, 225-230.

[S7] K. O. Christe, W. W. Wilson, R. D. Wilson, R. Bau, J. A. Feng, *J. Am. Chem. Soc.*, 1990, **112**, 7619-7625.

[S8] a) W. Xie, S. Chang, *Angew. Chem. Int. Ed.*, 2016, **55**, 1876-1880; *Angew. Chem.*, 2016, **128**, 1908-1912; b) L. Kuehn, A. F. Eichhorn, T. B. Marder, U. Radius, *J. Organomet. Chem.*, 2019, **881**, 25-33.

[S9] S. Díez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin, S. P. Nolan, *Dalton Trans.,* 2010, **39**, 7595-7606.

[S10] a) J.-Y. Cho, C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.*, 2000, **122**, 12868-12869; b) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc.*, 2002,**124**, 390-391.

[S11] S. K. Bose, A. Deißenberger, A. Eichhorn, P. G. Steel, Z. Lin, T. B. Marder, *Angew. Chem. Int. Ed.*, 2015, **54**, 11843-11847; *Angew. Chem.*, 2015, **127**, 12009-12014.

[S12] a) A. Wolan M. Zaidlewicz, *Org. Biomol. Chem.*, 2003, **1**, 3274-3276; b) M. Murata, T. Oyama, S. Watanabe, Y. Masuda, *J. Org. Chem.*, 2000, **65**, 164-168.

[S13] H. D. S. Guerrand, L. D. Marciasini, M. Jousseaume, M. Vaultier, M. Pucheault, *Chem. Eur. J.*, 2014, **20**, 5573-5579.

[S14] W. Zhu, D. Ma, *Org. Lett.*, 2006, **8**, 261-263.

[S15] R. Moser, K. R. Voigtritter, B. H. Lipshutz, *Isr. J. Chem.*, 2010, **50**, 691-695.

[S16] H. Kinuta, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.*, 2015, **137**, 1593-1600.

[S17] L. Zhang, L. Jiao, *J. Am. Chem. Soc.,* 2017, **139**, 607-610.

[S18] P. K. Verma, S. Mandal, K. Geetharani, *ACS Catal.*, 2018, **8**, 4049-4054.

[S19] A. Bähr, B. Felber, K. Schneider, F. Diederich, *Helv. Chim. Acta.*, 2000, **83**, 1346-1376.

[S20] J. Zhou, M. W. Kuntze-Fechner, R. Bertermann, U. S. D. Paul, J. H. J. Berthel, A. Friedrich, Z. Du, T. B. Marder, U. Radius, *J. Am. Chem. Soc.*, 2016, **138**, 5250-5253.

[S21] M. K. Tse, J.-Y.Cho, M. R. Smith, *Org. Lett.*, 2001, **18**, 2831-2833

[S22] H. Ochiai, Y. Uetake, T. Niwa, T. Hosoya, *Angew. Chem. Int. Ed.*, 2017, **56**, 2482-2486; *Angew. Chem.*, 2017, **129**, 2522-2526.

[S23] F. Labre, Y. Gimbert, P. Bannwarth, S. Olivero, E. Duñach, P. Y. Chavant, *Org. Lett.*, 2014, **16**, 2366-2369.

[S24] T. Yoshida, L. Ilies, E. Nakamura, *ACS Catal.*, 2017, **7**, 3199-3203.

[S25] a) S. K. Bose, T. B. Marder, *Org. Lett.*, 2014, **16**, 4562-4565; b) E. Yamamoto, K. Izumi, Y. Horita, H. Ito, *J. Am. Chem. Soc.*, 2012, **134**, 19997-20000.

[S26] P. Li, C. Fu, S. Ma, *Org. Biomol. Chem.*, 2014, **12**, 3604-3610.

[S27] V. Derdau, R. Oekonomopulos, G. Schubert, *J. Org. Chem*., 2003, **68**, 5168-5173.

[S28] M. Tobisu, H. Kinuta, Y. Kita, E. Rémond, N. Chatani, *J. Am. Chem. Soc.*, 2012, **134**, 115-118.

[S29] X-W. Liu, J. Echavarren, C. Zarate, R. Martin, *J. Am. Chem. Soc.*, 2015, **137**, 12470-12473.