Electronic Supporting Information for

Metal-Free Borylative Dearomatization of Indoles: Exploring the Divergent Reactivity of Aminoborane C-H Borylation Catalysts

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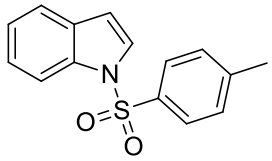
1. General Comments

All Chemicals were obtained from commercial suppliers and purified using standard procedures unless otherwise stated. Catalyst preparation, catalysis and synthesis of certain substrates were performed under a nitrogen atmosphere. All other experimental procedures including flash chromatography were carried out under ambient conditions and the solvents for flash chromatography were used as received. Solvents used in reaction or for characterization were purified. Toluene, hexanes, ethyl ether, tetrahydrofuran, and deuterated-benzene (C_6D_6) were purified by distillation over Na/benzophenone. Deuterated-chloroform ($CDCl_3$) and dichloromethane were dried by distillation over P_2O_5. Pinacolborane (HBpin) was prepared by following the literature procedure[1] for reaction optimization purposes. HBpin (containing 1% NEt_3 as stabilizer) purchased from BASF chemicals was used for the 2 gram-scale reactions. NMR spectra were recorded on Agilent Technologies NMR spectrometer at 500.00 MHz (^{1}H), 125.757 MHz (^{13}C), 160.46 MHz (^{11}B), and 470.385 MHz (^{19}F) or on Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C) and 376.29 (^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts are referenced respectively to the residual hydrogen and carbon atoms in the deuterated solvents. ^{11}B NMR calibration was performed using $F_3B{\bullet}OEt_2$ as an external reference. *Note*: In the $^{13}C\{^1H\}$ NMR spectroscopy, the carbon signal corresponds to the carbon that is directly linked to boron is obscured for most of the compounds. Mass Spectrometry analyses were carried out on an Agilent 6210 LC Time of Flight Mass Spectrometer, using electrospray ionization (ESI) method.

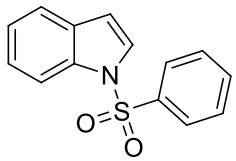
2. Synthesis of Substrates

Synthesis of 1-tosyl indole (**5a**)



The synthesis of compound 1-tosyl indole (**5a**) was achieved by modifying the literature procedure.[2] In a round-bottom flask, indole (2.50 g, 21.3 mmol), *p*-toluenesulfonyl chloride (TsCl, 4.88 g, 25.6 mmol), and benzyltriethylammonium chloride (TEBA, 485 mg, 2.13 mmol) were dissolved in CH_2Cl_2 (20 mL). Then, powdered NaOH (1.533 g, 38.3 mmol) was added and the resulting mixture was stirred at room temperature for 16 h. Afterwards, water is added, and the mixture was extracted with ethyl acetate. The organic phase is washed with water (x2), brine, and dried over Na_2SO_4. After filtration, the solvent is evaporated under reduced pressure. The resulting residue was purified by recrystallization in CH_2Cl_2/hexanes at -20 °C which gave product **5a** as white crystals. Yield: 4.88 g, 94%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (dq, J = 8.3, 0.9 Hz, 1H), 7.81 – 7.75 (m, 2H), 7.58 (d, J = 3.7 Hz, 1H), 7.54 (dt, J = 7.8, 1.0 Hz, 1H), 7.32 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.25 – 7.20 (m, 3H), 6.66 (dd, J = 3.7, 0.9 Hz, 1H), 2.34 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.05, 135.41, 134.93, 130.87, 129.99, 126.94, 126.45, 124.67, 123.39, 121.49, 113.66, 109.15, 21.70. This spectroscopic data matches previously published data.[2]

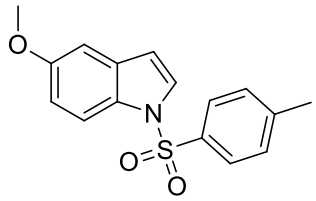
Synthesis of 1-(phenylsulfonyl) indole (**5b**)



Compound 1-(phenylsulfonyl) indole (**5b**) was synthesized from indole (2.0 g, 17.1 mmol), phenylsulfonyl chloride (3.618 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (15 mL) as described above for the synthesis of **5a**. Yield: 4.22 g, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 1H), 7.88 (dd, J = 8.5, 1.2 Hz, 2H), 7.57 (d, J = 3.7 Hz, 1H), 7.53 (dt, J = 7.4, 3.5 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.36 – 7.28 (m, 1H), 7.26 – 7.19 (m,

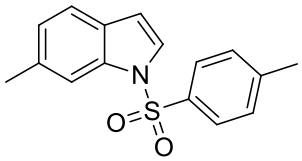
1H), 6.67 (d, *J* = 3.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 138.34, 134.94, 133.93, 130.85, 129.38, 126.87, 126.41, 124.77, 123.49, 121.53, 113.63, 109.37. This spectroscopic data matches previously published data.[3]

Synthesis of 5-methoxy-1-tosyl indole (**5c**)



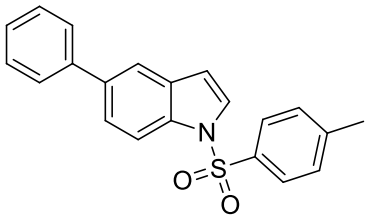
Compound 5-methoxy-1-tosyl indole (**5c**) was synthesized from 5-methoxy indole (2.52 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.59 g, 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 9.1, 0.7 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.51 (dd, *J* = 3.7, 0.5 Hz, 1H), 7.24 – 7.14 (m, 2H), 6.96 (dd, *J* = 2.5, 0.5 Hz, 1H), 6.92 (ddd, *J* = 9.0, 2.6, 0.5 Hz, 1H), 6.58 (dd, *J* = 3.6, 0.8 Hz, 1H), 3.80 (s, 3H), 2.32 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 156.49, 144.94, 135.33, 131.87, 129.94, 129.67, 127.23, 126.85, 114.53, 113.80, 109.31, 103.71, 55.74, 21.69. This spectroscopic data matches previously published data.[2]

Synthesis of 6-methyl-1-tosyl indole (**5d**)



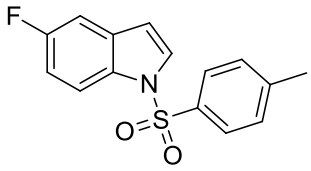
Compound 6-methyl-1-tosyl indole (**5d**) was synthesized from 6-methyl indole (2.24 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.00 g, 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.81 – 7.72 (m, 2H), 7.51 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.07 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.62 (dd, *J* = 3.6, 0.8 Hz, 1H), 2.50 (s, 3H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.92, 135.55, 135.35, 134.80, 129.96, 128.55, 126.86, 125.81, 124.95, 121.01, 113.73, 109.05, 22.08, 21.67. This spectroscopic data matches previously published data.[4]

Synthesis of 5-phenyl-1-tosyl indole (**5e**)



Compound **5e** was synthesized from 5-bromo-1-tosyl indole (**5h**) by adopting the Pd catalyzed cross-coupling protocol.[5] Compounds 5-bromo-1-tosyl indole (**5h**, 1.24 g, 3.60 mmol), $Pd(PPh_3)_4$ (200 mg, 0.16 mmol) , phenyl boronic acid (634 mg, 5.20 mmol), and Na_2CO_3 (763 mg, 7.20 mmol) were charged in a round bottom flask. To this, toluene and ethanol/H_2O (1:1, 16 mL) were added at room temperature. The reaction mixture was then stirred for an hour at 80 °C. Afterwards, the flask was cooled down to room temperature and added another portion of $Pd(PPh_3)_4$ (200 mg, 0.16 mmol). This mixture was further stirred for 12 h at 80 °C. Then, the mixture was cooled down and quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (30 mL x 3). The combined organic layer was then dried ($MgSO_4$), filtered and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, 10:90 ethyl acetate/petroleum ether v/v) to give the pure coupling product **5e**. Yield: 675 mg, 54%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dt, *J* = 8.7, 0.8 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.73 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.56 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.38 – 7.29 (m, 1H), 7.27 – 7.20 (m, 2H), 6.71 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.14, 141.38, 136.92, 135.41, 134.34, 131.44, 130.06, 128.90, 127.48, 127.17, 127.05, 126.98, 124.33, 119.94, 113.85, 109.40, 21.73. This spectroscopic data matches previously published data.[6]

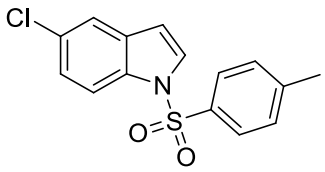
Synthesis of 5-fluoro-1-tosyl indole (**5f**)



Compound 5-fluoro-1-tosyl indole (**5f**) was synthesized from 5-fluoro indole (2.31 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.40 g, 89%. ^{1}H NMR (500

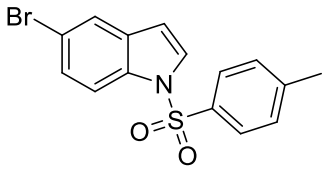
MHz, $CDCl_3$) δ 7.94 (ddt, *J* = 9.1, 4.5, 0.7 Hz, 1H), 7.81 – 7.67 (m, 2H), 7.60 (d, *J* = 3.7 Hz, 1H), 7.26 – 6.96 (m, 3H), 6.62 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.70 (d, *J* = 239.9 Hz), 131.84 (d, *J* = 10.3 Hz), 131.30 (d, *J* = 0.8 Hz), 114.66 (d, *J* = 9.5 Hz), 112.73 (d, *J* = 25.7 Hz), 109.04 (d, *J* = 4.0 Hz), 106.97 (d, *J* = 23.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -120.00 (m). This spectroscopic data matches previously published data.[7]

Synthesis of 5-chloro-1-tosyl indole (**5g**)



Compound 5-chloro-1-tosyl indole (**5g**) was synthesized from 5-chloro indole (2.59 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.50 g, 86% ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 8.8, 0.7 Hz, 1H), 7.79 – 7.72 (m, 2H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.50 (dd, *J* = 2.1, 0.6 Hz, 1H), 7.27 (ddd, *J* = 8.8, 2.1, 0.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.60 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.37, 135.07, 133.26, 132.05, 130.09, 129.22, 127.82, 126.89, 124.91, 121.08, 114.66, 108.53, 21.71. This spectroscopic data matches previously published data.[2]

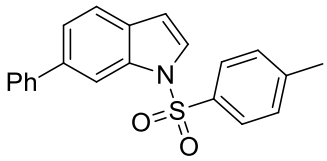
Synthesis of 5-bromo-1-tosyl indole (**5h**)



Compound 5-bromo-1-tosyl indole (**5h**) was synthesized from 5-bromo indole (3.35g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.97 g, 83%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 8.8, 0.7 Hz, 1H), 7.80 – 7.71 (m, 2H), 7.68 – 7.54 (m, 2H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.26 – 7.17 (m, 2H), 6.60 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.40, 135.05, 133.62, 132.57, 130.10, 127.67, 127.55, 126.90,

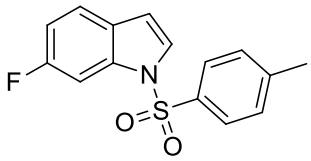
124.15, 116.88, 115.05, 108.40, 21.71. This spectroscopic data matches previously published data.[2]

Synthesis of 6-phenyl-1-tosyl indole (**5i**)



Compound **5i** was synthesized from 6-bromo-1-tosyl indole (**5l**) by adopting the Pd catalyzed cross-coupling protocol.[5] Compounds **5l** (0.827 g, 2.40 mmol), $Pd(PPh_3)_4$ (133 mg, 0.107 mmol), phenyl boronic acid (423 mg, 3.47 mmol) and Na_2CO_3 (509 mg, 4.80 mmol) were charged in a round bottom flask. To this, toluene and ethanol/H_2O (1:1, 10 mL) were added at room temperature. The reaction mixture was then stirred for an hour at 80 °C. Afterwards, the flask was cooled down to room temperature and added another portion of $Pd(PPh_3)_4$ (133 mg, 0.107 mmol). This mixture was further stirred for 12 h at 80 °C. Then, the mixture was cooled down and quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (20 mL x 3). The combined organic layer was then dried ($MgSO_4$), filtered and the solvent was evaporated. The residue was purified by flash chromatography (silica gel, 10:90 ethyl acetate/petroleum ether v/v) to give the pure coupling product **5i**. Yield: 484 mg, 58%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 1.9 Hz, 1H), 7.80 – 7.79 (m, 2H), 7.68 – 7.62 (m, 2H), 7.62 – 7.56 (m, 2H), 7.52 – 7.46 (m, 3H), 7.42 – 7.35 (m, 1H), 7.25 – 7.20 (m, 2H), 6.69 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.98, 141.39, 138.11, 135.43, 135.28, 129.93, 128.83, 127.51, 127.23, 126.82, 122.98, 121.49, 112.02, 108.83, 21.57. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{17}BNO_2S$ + H: 348.1053; Found: 348.1088.

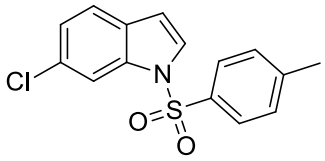
Synthesis of 6-fluoro-1-tosyl indole (**5j**)



Compound 6-fluoro-1-tosyl indole (**5j**) was synthesized from 6-fluoro indole (2.31 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in

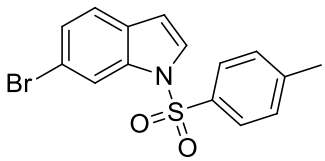
CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.65 g, 94%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.76 – 7.71 (m, 1H), 7.55 (d, *J* = 3.7 Hz, 1H), 7.45 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.27 – 7.19 (m, 2H), 6.99 (ddd, *J* = 9.2, 8.6, 2.4 Hz, 1H), 6.63 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.94 (d, *J* = 241.7 Hz), 135.08 (d, *J* = 12.5 Hz), 127.08 (d, *J* = 1.5 Hz), 126.73 (d, *J* = 4.2 Hz), 122.22 (d, *J* = 10.0 Hz), 111.91 (d, *J* = 24.3 Hz), 108.89 (d, *J* = 1.2 Hz), 101.03 (d, *J* = 28.5 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -116.48 (m).

Synthesis of 6-chloro-1-tosyl indole (**5k**)



Compound 6-chloro-1-tosyl indole (**5k**) was synthesized from 6-chloro indole (2.59 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.76 g, 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.21 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.63 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.41, 135.24, 135.13, 130.68, 130.16, 129.30, 127.00, 126.94, 124.11, 122.23, 113.82, 108.84, 21.73. This spectroscopic data matches previously published data.[2]

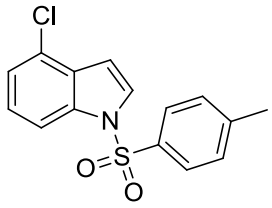
Synthesis of 6-bromo-1-tosyl indole (**5l**)



Compound 6-bromo-1-tosyl indole (**5l**) was synthesized from 6-bromo indole (3.35 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 5.27 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dt, *J* = 1.6, 0.7 Hz, 1H), 7.81 – 7.72 (m, 2H), 7.53 (d, *J* = 3.7 Hz, 1H), 7.38 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.28 – 7.22 (m, 2H), 6.61 (dd, *J* = 3.7, 0.8

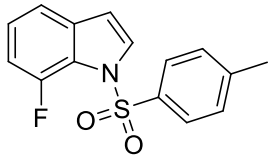
Hz, 1H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 145.42, 135.57, 135.13, 130.18, 129.65, 126.94, 126.92, 126.78, 122.59, 118.35, 116.70, 108.89, 21.74. This spectroscopic data matches previously published data.[8]

Synthesis of 4-chloro-1-tosyl indole (**5m**)



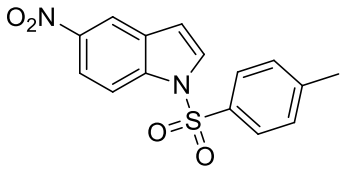
Compound 4-chloro-1-tosyl indole (**5m**) was synthesized from 4-chloro indole (2.59 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.39 g, 84%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 1H), 7.81 – 7.74 (m, 2H), 7.63 (d, *J* = 3.7 Hz, 1H), 7.27 – 7.18 (m, 4H), 6.79 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 145.44, 135.51, 135.09, 130.11, 129.64, 126.99, 126.97, 126.62, 125.37, 123.19, 112.16, 107.22, 21.71. This spectroscopic data matches previously published data.[9]

Synthesis of 7-fluoro-1-tosyl indole (**5n**)



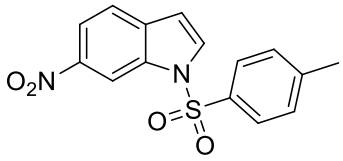
Compound 7-fluoro-1-tosyl indole (**5n**) was synthesized from 7-fluoro indole (2.31 g, 17.1 mmol)), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.11 g, 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.79 (d, *J* = 3.7 Hz, 1H), 7.33 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.13 (td, *J* = 7.9, 4.2 Hz, 1H), 6.96 (ddd, *J* = 12.2, 8.0, 0.9 Hz, 1H), 6.69 (dd, *J* = 3.7, 2.3 Hz, 1H), 2.39 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 149.81 (d, *J* = 250.4 Hz), 135.69 (d, *J* = 0.6 Hz), 135.20 (d, *J* = 3.4 Hz), 127.82 (d, *J* = 2.4 Hz), 124.06 (d, *J* = 6.7 Hz), 122.01 (d, *J* = 10.9 Hz), 117.27 (d, *J* = 3.8 Hz), 111.20 (d, *J* = 20.0 Hz), 107.74 (d, *J* = 1.9 Hz), 21.77. ^{19}F NMR (470 MHz, $CDCl_3$) δ -121.29 (m).

Synthesis of 5-nitro-1-tosyl indole (**5o**)



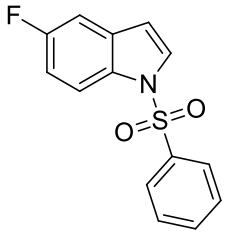
Compound 5-nitro-1-tosyl indole (**5o**) was synthesized from 5-nitro indole (2.77 g, 1.71 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.33 g, 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.2 Hz, 1H), 8.21 (dd, *J* = 9.2, 2.3 Hz, 1H), 8.09 (dt, *J* = 9.1, 0.7 Hz, 1H), 7.88 – 7.78 (m, 2H), 7.75 (d, *J* = 3.7 Hz, 1H), 7.34 – 7.28 (m, 2H), 6.82 (dd, *J* = 3.8, 0.8 Hz, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.05, 144.31, 137.70, 134.78, 130.65, 130.37, 129.34, 127.05, 119.90, 117.95, 113.76, 109.54, 21.79. This spectroscopic data matches previously published data.[10]

Synthesis of 6-nitro-1-tosyl indole (**5p**)



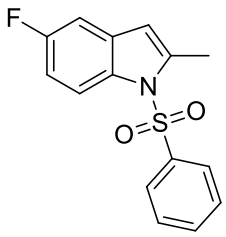
Compound 6-nitro-1-tosyl indole (**5p**) was synthesized from 6-nitro indole (2.77 g, 17.1 mmol), TsCl (3.91 g, 20.5 mmol), TEBA (390 mg, 1.71 mmol) and NaOH (1.231 g, 30.78 mmol) in CH_2Cl_2 (20 mL) as described above for the synthesis of **5a**. Yield: 4.49 g, 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (q, *J* = 0.8 Hz, 1H), 8.13 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.96 – 7.76 (m, 3H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.77 (dd, *J* = 3.6, 0.9 Hz, 1H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.02, 145.15, 135.58, 134.70, 133.62, 131.41, 130.39, 127.11, 121.68, 118.68, 109.98, 108.70, 21.76. This spectroscopic data matches previously published data.[10]

Synthesis of 5-fluoro-1-(phenylsulfonyl) indole (**5q**)



Compound 5-fluoro-1-phenylsulfonyl indole (**5q**) was synthesized from 5-fluoro indole (5.77 g, 42.7 mmol), $PhSO_2Cl$ (6.5 mL, 51.1 mmol), TEBA (972 mg, 4.27 mmol) and NaOH (3.073 g, 76.8 mmol) in CH_2Cl_2 (80 mL) as described above for the synthesis of **5a**. Yield: 9.52 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 9.0, 4.4, 0.7 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.47 – 7.40 (m, 2H), 7.18 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.04 (td, *J* = 9.1, 2.6 Hz, 1H), 6.62 (dd, *J* = 3.7, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61 (d, *J* = 240.1 Hz), 137.96, 133.99, 131.74 (d, *J* = 10.4 Hz), 131.19 (d, *J* = 1.3 Hz), 129.32, 128.00, 126.69, 114.54 (d, *J* = 9.6 Hz), 112.70 (d, *J* = 25.7 Hz), 109.13 (d, *J* = 4.2 Hz), 106.92 (d, *J* = 24.2 Hz). This spectroscopic data matches previously published data.[11]

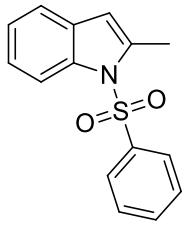
Synthesis of 5-fluoro-2-methyl-1-(phenylsulfonyl) indole (**5r**)



Compound **5r** was synthesized by modifying the literature procedure.[12] In an oven-dried Schlenk flask, 5-fluoro-1-(phenylsulfonyl)-indole **5q** (3.21 g, 11.66 mmol) was charged and dissolved in dry THF (50 mL) under nitrogen atmosphere and cooled to -78 °C. Then, lithium diisopropylamide (12.24 mL, 11.7 mmol) was added dropwise via syringe. The mixture was then stirred for 2 h at -78 °C and subsequently allowed to warm slowly to 5 °C over 1 h period. The resulting bright-red solution was cooled again to -78 °C and then methyliodide (7.98 mL, 12.83 mmol) was added. This mixture was stirred and left to warm slowly to room temperature over 12 h. Then, saturated aqueous NH_4Cl was added, followed by extracted with ethyl acetate (40 mL x 2), washed with water (50 mL x 2) and brine, and dried with Na_2SO_4. After filtration and solvent evaporation,

product **5r** was purified by flash chromatography (silica gel, 99:1 hexanes/ethyl acetate v/v). Yield: 2.90 g, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 9.1, 4.5 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.58 – 7.50 (m, 1H), 7.48 – 7.38 (m, 2H), 7.05 (dd, J = 8.6, 2.6 Hz, 1H), 6.98 (td, J = 9.1, 2.7 Hz, 1H), 6.39 – 6.27 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72 (d, J = 239.8 Hz), 139.04 (d, J = 17.6 Hz), 133.80, 133.25 (d, J = 1.0 Hz), 130.68 (d, J = 10.3 Hz), 129.32, 126.22, 115.44 (d, J = 9.3 Hz), 111.48 (d, J = 25.1 Hz), 109.56 (d, J = 3.9 Hz), 105.61 (d, J = 23.8 Hz), 15.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.01. HRMS (ESI-TOF) *m/z*: Calcd for $C_{15}H_{12}FNO_2S$ + H: 290.0646; Found: 290.0801.

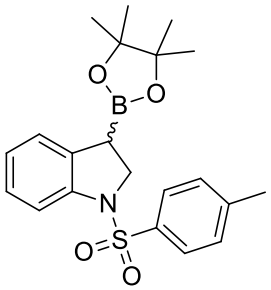
Synthesis of 2-methyl-1-(phenylsulfonyl) indole (**5s**)



Compound **5s** was synthesized by following the literature procedure.[12] In an oven-dried Schlenk flask, 1-(phenylsulfonyl)-indole **5b** (1.50 g, 5.83 mmol) was charged and dissolved in dry THF (15 mL) under nitrogen atmosphere and cooled to -78 °C. Then, lithium diisopropylamide (0.76 mL, 6.12 mmol) was added dropwise via syringe. The mixture was then stirred for 1.5 h at -78 °C and subsequently allowed to warm slowly to 5 °C over 1 h period. The resulting bright-red solution was cooled again to -78 °C and then methyliodide (0.4 mL, 6.41 mmol) was added. This mixture was stirred and left to warm slowly to room temperature over 12 h. Then, saturated aqueous NH_4Cl was added, followed by extracted with ethyl acetate (20 mL x 2), washed with water (30 mL x 2) and brine, and dried with Na_2SO_4. After filtration and solvent evaporation, product **5s** was purified by flash chromatography (silica gel, 99:1 hexanes/ethyl acetate v/v). Yield: 1.23 g, 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.3, 0.8 Hz, 1H), 7.79 (dd, J = 8.5, 1.2 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.47 – 7.39 (m, 3H), 7.32 – 7.25 (m, 1H), 7.22 (td, J = 7.5, 1.1 Hz, 1H), 6.37 (s, 1H), 2.62 (d, J = 1.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.39, 137.46, 137.16, 133.77, 129.80, 129.40, 126.41, 123.95, 123.63, 120.14, 114.60, 109.86, 15.91. This spectroscopic data matches previously published data.[13]

3. oduPreparation of Hydroborated Products and Their Characterization

Preparation of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6a**)

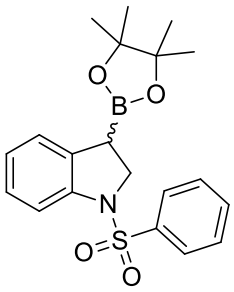


In a 5 mL microwave reactor vial containing a stir bar, precatalyst **2F** (22.9 mg, 0.1 mmol) was introduced under inert atmosphere (nitrogen). Then, 1-tosyl indole (**5a**, 285.4 mg, 1.0 mmol) followed by HBpin (218 μL, 1.5 mmol) were added and sealed. The neat reaction mixture was then stirred for 16 h at 100 °C in an oil bath. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion, **6a**). To purify the product, first the reaction crude was dissolved in ethyl ether (10 mL) and filtered through a short Celite pad, then the resulting crude after evaporation of the solvent was subjected to flash chromatography (silica gel, 5:95 ethyl ether/petroleum ether v/v) which yielded the pure product **6a**. Yield: 236 mg, 59%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.60 (dt, *J* = 8.0, 0.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.18 – 7.11 (m, 2H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 4.19 (t, *J* = 10.5 Hz, 1H), 3.92 (t, *J* = 10.6 Hz, 1H), 2.82 – 2.55 (m, 1H), 2.36 (s, 3H), 1.21 (s, 6H), 1.19 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.76, 141.73, 134.52, 133.50, 129.55, 127.27, 127.06, 124.84, 123.75, 115.14, 84.04, 52.34, 24.87, 24.55, 21.52. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.38. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{26}BNO_4S$ + H: 400.1754; Found: 400.1749.

Note: Since product **6a** undergoes slow decomposition in silica gel during the flash chromatography purification and gave only a moderate yield of pure product, we have followed another purification procedure which leads to quantitative isolation of the product but comes with a little amount of hydrolysed HBpin (< 5% by 1H NMR analysis). The procedure is after stirring the initial reaction mixture for 16 h at 100 °C, the volatiles were removed by heating at 50 °C under high vacuum for 1 h. Then, CH_2Cl_2 or ethyl ether and water mixture (1:1 ratio, 10 mL) was added at room temperature and stirred for 30 min. Then the separated organic extract was washed

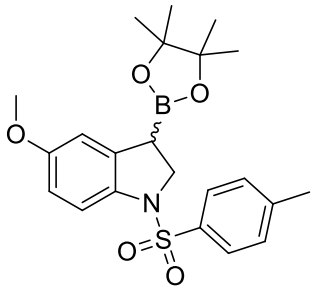
with water (3 x 10 mL) and subsequently the organic solvent was evaporated under reduced pressure to obtain product **6a**. Yield: 343 mg, 86%. This extraction procedure was followed to purify the hydroborated products that were giving either less or no yield through the flash chromatography purification procedure using silica gel stationary phase. This purification protocol was used for the 2 gram-scale reaction.

Preparation of 1-(Phenylsulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline (**6b**)



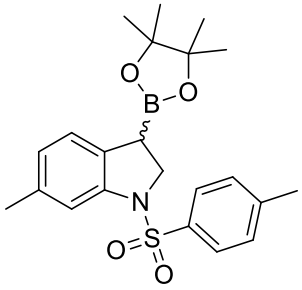
Compound **6b** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 1-(phenylsulfonyl) indole (**5b**, 257.3 mg, 1.0 mmol), and HBpin (218 μL, 1.5 mmol) under the neat condition as described above for the preparation of **6a**. Purification of the product **6b** was achieved by following the procedure mentioned above in the note of product **6a**. Yield: 277 mg, 72%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.61 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.57 – 7.48 (m, 1H), 7.48 – 7.35 (m, 2H), 7.15 (tt, *J* = 7.5, 1.3 Hz, 2H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 4.19 (t, *J* = 10.5 Hz, 1H), 3.92 (t, *J* = 10.6 Hz, 1H), 2.64 (tt, *J* = 10.4, 1.3 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.74, 137.61, 133.58, 133.09, 129.07, 127.37, 127.26, 125.01, 123.97, 115.23, 84.19, 52.48, 25.01, 24.70. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.89. HRMS (ESI-TOF) *m/z*: Calcd for $C_{20}H_{24}BNO_4S$ + H: 386.1597; Found: 386.1604.

Preparation of 5-Methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6c**)



Compound **6c** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-methoxy-1-tosyl indole (**5c**, 302 mg, 1.0 mmol), and HBpin (290 μL, 2.0 mmol) under the neat condition as described above for the preparation of **6a**. A small flash chromatography (silica gel, petroleum ether/ethyl ether 90:10 v/v) was performed to purify the product. After evaporation of the solvent to complete dryness under vacuum, **6c** was obtained as white powder. Yield: 266 mg, 62 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.82 – 6.64 (m, 2H), 4.15 (dd, *J* = 11.2, 10.1 Hz, 1H), 3.90 (t, *J* = 11.1 Hz, 1H), 3.74 (s, 3H), 2.47 (t, *J* = 10.5 Hz, 1H), 2.35 (s, 3H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.03, 143.75, 135.92, 135.45, 134.57, 129.64, 127.46, 116.95, 111.98, 111.08, 84.19, 55.69, 52.88, 25.07, 24.66, 21.67. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.39. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{29}BNO_5S$ + H: 430.1859; Found: 430.1859.

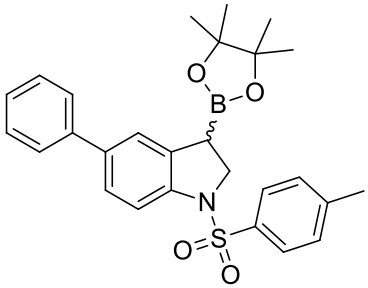
Preparation of 6-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6d**)



Compound **6d** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 6-methyl-1-tosyl indole (**6c**, 285 mg, 1.0 mmol), and HBpin (290 μL, 2.0 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Compound **6d** decomposes under the silica gel flash chromatography, so purification was achieved by following the procedure

mentioned above in the note of product **6a**. Yield: 400 mg, 97% (product comes with some unknown impurities. Since the product comes with some impurities, it was prepared and purified using the BH_3·DMS catalyst. The procedure involves treatment of **5d** (143 mg, 0.50 mmol) with HBpin (102 µL; 0.7 mmol) and BH_3·DMS (10 mol%, 4.8 µL) at 60 °C for 16 h. Afterwards, the crude reaction mix was evacuated in vacuo for 6 h at 50 °C, which afforded the product **6d** as the colorless oil with a better purity. Yield: 203 mg, > 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.43 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.02 (dd, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 7.0 Hz, 1H), 4.16 (t, *J* = 10.5 Hz, 1H), 3.89 (t, *J* = 10.7 Hz, 1H), 2.57 (t, *J* = 10.1 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.81, 141.99, 137.19, 134.78, 130.66, 129.67, 127.37, 124.65, 124.52, 116.09, 84.10, 52.79, 25.00, 24.68, 21.72, 21.66. Note: signal for the carbon that is directly attached to boron was not observed. HRMS (ESI-TOF) *m/z*: Calcd for $C_{22}H_{28}BNO_4S$ + H: 414.1910; Found: 414.1905.

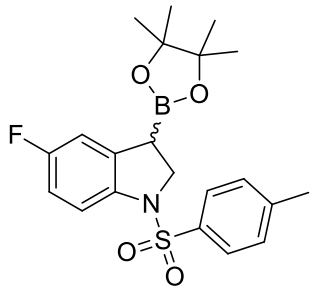
Preparation of 5-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6e**)



Compound **6e** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-phenyl-1-tosyl indole (**5e**, 347 mg, 1.0 mmol), and HBpin (218 µL, 1.5 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6e** was achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. The ethyl ether/water extraction procedure for purification gave product **6d** as white powder. Yield: 437 mg, 92 %. As the product comes with some impurities, it was prepared and purified using the BH_3·DMS catalyst. The procedure involves treatment of **5e** (174 mg, 0.50 mmol) with HBpin (102 µL; 0.7 mmol) and BH_3·DMS (10 mol%, 4.8 µL) at 60 °C for 16 h. Afterwards, the crude reaction mix was evacuated in vacuo for 6 h at 50 °C, which afforded the product **6e** as white

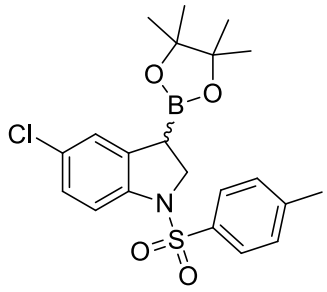
powder with a better purity. Yield: 236 mg, > 99%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.69 – 7.64 (m, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.38 (m, 4H), 7.35 – 7.29 (m, 1H), 7.26 – 7.21 (m, 2H), 4.23 (t, *J* = 10.5 Hz, 1H), 3.98 (t, *J* = 10.4 Hz, 1H), 2.74 (tt, *J* = 10.4, 1.3 Hz, 1H), 2.37 (s, 3H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.96, 141.28, 140.92, 136.96, 134.56, 134.22, 129.74, 128.82, 127.42, 127.01, 126.91, 126.26, 123.59, 115.19, 84.23, 52.65, 24.64, 24.62, 21.66. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.52. HRMS (ESI-TOF) *m/z*: Calcd for $C_{27}H_{30}BNO_4S$ + H: 476.2066; Found: 476.2068.

Preparation of 5-Fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6f**)



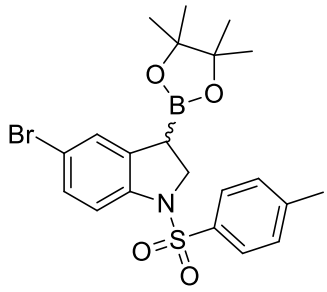
Compound **6f** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-fluoro-1-tosyl indole (**5f**, 289 mg, 1.0 mmol), and HBpin (290 μL, 2.0 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). To purify the product, first the reaction crude was dissolved in ethyl ether (10 mL) and filtered through a short Celite pad, then the resulting crude after evaporation of the solvent was subjected to flash chromatography (silica gel, 5:95 ethyl ether/petroleum ether v/v) which yielded the pure product **6f**. Yield: 376 g, 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.54 (dd, *J* = 8.8, 4.7 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.92 – 6.81 (m, 2H), 4.19 (dd, *J* = 11.1, 10.3 Hz, 1H), 3.93 (t, *J* = 10.9 Hz, 1H), 2.56 (td, *J* = 10.5, 1.3 Hz, 1H), 2.38 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.03 (d, *J* = 241.7 Hz), 138.00 (d, *J* = 2.0 Hz), 136.19 (d, *J* = 8.8 Hz), 116.57 (d, *J* = 8.6 Hz), 113.64 (d, *J* = 23.4 Hz), 112.37 (d, *J* = 24.4 Hz). Note: signal for the carbon that is directly attached to boron was not observed. ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.35 (m). ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.20. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BFNO_4S$ + H: 418.1660; Found: 418.1689.

Preparation of 5-Chloro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6g**)



Compound **6g** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-chloro-1-tosyl indole (**5g**, 306 mg, 1.0 mmol), and HBpin (334 μL, 2.3 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6g** was achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. This purification procedure gave product **6g** as white powder. Yield: 425 mg, 98 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.16 – 7.08 (m, 2H), 4.17 (t, *J* = 10.6 Hz, 1H), 3.90 (t, *J* = 10.6 Hz, 1H), 2.73 – 2.53 (m, 1H), 2.37 (s, 3H), 1.20 (s, 6H), 1.19 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.19, 140.66, 135.68, 134.34, 129.82, 129.09, 127.42, 127.23, 125.23, 116.11, 84.41, 52.65, 24.99, 24.72, 21.70. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.39. HRMS (ESI-TOF) *m/z*: $C_{21}H_{25}BClNO_4S$ + H: 434.1364; Found: 434.1357.

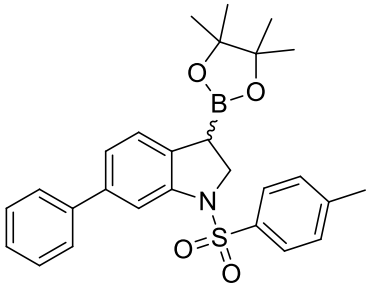
Preparation of 5-Bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6h**)



Compound **6h** was prepared from precatalyst **2F** (45.8 mg, 0.2 mmol), 5-bromo-1-tosyl indole (**5h**, 350 mg, 1.0 mmol), and HBpin (2.6 equiv, 377 μL) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). To purify the product, first the reaction crude was dissolved in ethyl ether (10 mL) and filtered through a short Celite pad, then the resulting

crude after evaporation of the solvent was subjected to flash chromatography (silica gel, 5:95 ethyl ether/petroleum ether v/v) which yielded the pure product **6h**. Yield: 425 mg, 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.28-7.22 (m, 4H), 4.16 (t, *J* = 10.6 Hz, 1H), 3.91 (t, *J* = 10.5 Hz, 1H), 2.65 (t, *J* = 10.5 Hz, 1H), 2.38 (s, 3H), 1.20 (two overlapped singlets, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.20, 141.15, 135.99, 134.30, 130.10, 129.81, 128.08, 127.38, 116.56, 116.45, 84.40, 52.55, 24.97, 24.68, 21.67. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.01. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BBrNO_4S$ + H: 478.0859; Found: 478.0841. Purification of the product **6h** was also achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. The ethyl ether/water extraction procedure for purification gave product **6h** in 89% isolated yield (426 mg).

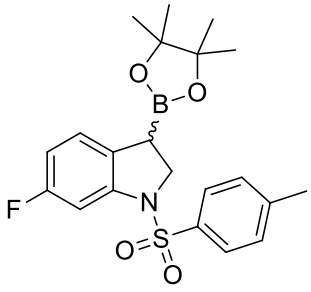
Preparation of 6-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6i**)



Compound **6i** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 6-phenyl-1-tosyl indole (**5i**, 347 mg, 1.0 mmol), and HBpin (218 µL, 1.5 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6e** was attempted by following the procedure mentioned above in the note for the alternative purification of compound **6a**. The ethyl ether/water extraction procedure for purification gave product **6i** as white powder along with trace quantity of Bpin -based impurity. Yield: 389 mg, 82%. As the product comes with some impurities, it was prepared and purified using the BH_3·DMS catalyst. The procedure involves treatment of **5e** (69.5 mg, 0.20 mmol) with HBpin (41 µL; 0.28 mmol) and BH_3·DMS (10 mol%, 1.9 µL) at 60 °C for 16 h. Afterwards, the crude reaction mix was evacuated in vacuo for 6 h at 50 °C, which afforded the product **6e** as colorless crystals with a better purity. Yield: 94 mg, > 98%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.5 Hz, 1H), 7.72 (dd, *J* = 8.3,

3.7 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.49 – 7.44 (m, 2H), 7.39 – 7.34 (m, 1H), 7.26 – 7.20 (m, 4H), 4.26 (t, *J* = 10.5 Hz, 1H), 3.98 (t, *J* = 10.6 Hz, 1H), 2.71 (td, *J* = 10.5, 1.2 Hz, 1H), 2.37 (s, 3H), 1.23 (d, *J* = 7.1 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.88, 142.42, 140.97, 140.54, 134.49, 132.69, 129.64, 128.75, 127.30, 127.18, 124.99, 122.87, 113.75, 84.13, 52.71, 24.91, 24.59, 24.56, 21.55. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.64. Note: signal for the carbon that is directly attached to boron was not seen. HRMS (ESI-TOF) *m/z*: $C_{27}H_{30}BNO_4S$ + H: 476.2062; Found: 476.2066.

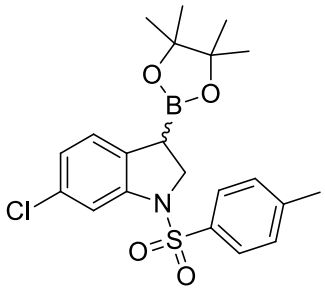
Preparation of 6-Fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6j**)



Compound **6j** was prepared from precatalyst **2F** (45.8 mg, 0.2 mmol), 6-fluoro-1-tosyl indole (**5j**, 289 mg, 1.0 mmol), and HBpin (2.6 equiv, 377 μL) under the neat condition at 120 °C as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (83% conversion). For purification, the reaction crude was dissolved in Et_2O (10 mL) and passed through a short Celite pad and eluted with more Et_2O (20 mL). The solvent was evaporated, and then a flash chromatography (silica gel, petroleum ether/ethyl ether 90:10 v/v) was performed. After evaporation of the solvent under vacuum the product **6j** was obtained as white powder. Yield: 287 mg, 69 %. By using the purification procedure noted for compound **6a** an isolated yield of 96% was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 10.1, 2.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.07 (ddd, *J* = 8.3, 5.6, 1.4 Hz, 1H), 6.63 (td, *J* = 8.7, 2.5 Hz, 1H), 4.19 (t, *J* = 10.5 Hz, 1H), 3.92 (t, *J* = 10.4 Hz, 1H), 2.63 (t, *J* = 10.4 Hz, 1H), 2.37 (s, 3H), 1.18 (two overlapped singlets, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.42 (d, J_{CF} = 243 Hz), 144.22 (d, J_{CF} = 12.6 Hz), 134.34, 129.81, 128.66 (d, J_{CF} = 2.5 Hz), 127.39, 125.42 (d, J_{CF} = 10.1 Hz), 110.12 (d, J_{CF} = 22.7 Hz), 103.11 (d, J_{CF} = 27.7 Hz), 84.25, 53.15, 24.94, 24.66, 21.66. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.03. ^{19}F NMR (470

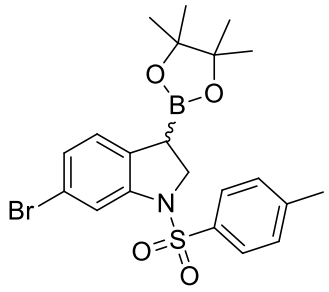
MHz, $CDCl_3$) δ -114.90. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BFNO_4S$ + H: 418.1660; Found: 418.1670.

Preparation of 6-Chloro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6k**)



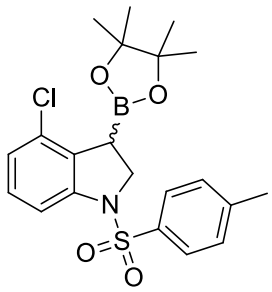
Compound **6k** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 6-chloro-1-tosyl indole (**5k**, 306 mg, 1.0 mmol), and HBpin (2.0 equiv, 290 μL) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6k** was achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. This ethyl ether/water extraction procedure for purification gave product **6k** as white powder. Yield: 382 mg, 88 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.19 (m, 2H), 7.07 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.91 (dd, *J* = 7.9, 2.0 Hz, 1H), 4.17 (t, *J* = 10.6 Hz, 1H), 3.92 (t, *J* = 10.4 Hz, 1H), 2.63 (td, *J* = 10.4, 1.5 Hz, 1H), 2.37 (s, 3H), 1.19 (s, 6H), 1.18 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.24, 142.98, 134.27, 132.83, 131.98, 129.82, 127.34, 125.66, 123.70, 115.19, 84.29, 82.87, 52.79, 24.92, 24.64, 21.66. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.95. HRMS (ESI-TOF) *m/z*: $C_{21}H_{25}BClNO_4S$ + H: 434.1364; Found: 434.1359.

Preparation of 6-Bromo-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6l**)



Compound **6l** was prepared from precatalyst **2F** (45.8 mg, 0.2 mmol), 6-chloro-1-tosyl indole (**5l**, 350 mg, 1.0 mmol), and HBpin (334 μL, 2.3 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6l** was achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. This ethyl ether/water extraction procedure for purification gave product **6l** as white powder. Yield: 454 mg, 95 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.8 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.02-6.99 (m, 1H), 4.15 (t, *J* = 10.5 Hz, 1H), 3.91 (t, *J* = 10.4 Hz, 1H), 2.61 (t, *J* = 10.5 Hz, 1H), 2.38 (s, 3H), 1.18 (two overlapped singlets, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.26, 143.28, 134.39, 132.58, 129.88, 129.88, 127.42, 126.68, 126.15, 120.67, 118.06, 84.35, 52.74, 24.98, 24.70, 21.72. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.37. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BBrNO_4S$ + H: 478.0859; Found: 478.0833.

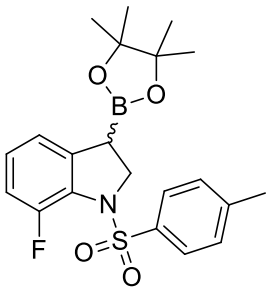
Preparation of 4-Chloro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6m**)



Compound **6m** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 4-chloro-1-tosyl indole (**5m**, 306 mg, 1.0 mmol), and HBpin (290 μL, 2.0 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Purification of the product **6m** was achieved by

following the procedure mentioned above in the note for the alternative purification of compound **6a**. This ethyl ether/water extraction procedure for purification gave product **6m** as white powder. Yield: 330 mg, 76%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.50 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.09 (td, *J* = 8.1, 0.9 Hz, 1H), 6.93 (dd, *J* = 8.1, 0.9 Hz, 1H), 4.15 (dd, *J* = 11.0, 10.4 Hz, 1H), 3.91 (dd, *J* = 10.4, 8.2 Hz, 1H), 2.76 (dd, *J* = 10.9, 8.3 Hz, 1H), 2.38 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.31, 143.34, 134.18, 132.62, 130.50, 129.84, 128.66, 127.36, 123.90, 113.08, 84.28, 52.22, 24.71, 21.67. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.24. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BClNO_4S$ + H: 434.1363; Found: 434.1338.

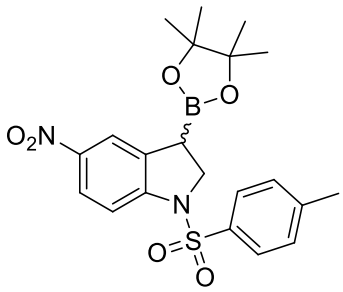
Preparation of 7-Fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6n**)



Compound **6n** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 7-fluoro-1-tosyl indole (**5n**, 290 mg, 1.0 mmol), and HBpin (2.3 equiv, 334 μL) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). For purification, the reaction crude was dissolved in Et_2O (10 mL) and passed through a short Celite pad and eluted with more Et_2O (100 mL). The solvent was evaporated, and then a flash chromatography (silica gel, petroleum ether/ethyl ether 90:10 v/v) was performed. After evaporation of the solvent under vacuum, the product **6n** was obtained as white powder. Yield: 310 mg, 74 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.00 (td, *J* = 7.8, 4,4 Hz, 1H), 6.97-6.90 (m, 2H), 4.36 (dd, *J* = 12.1, 9.0 Hz, 1H), 4.00 (t, *J* = 12.1 Hz, 1H), 2.38-2.34 (s, 3H + t, 1H overlapped), 1.21 (two overlapped singlets, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.52 (d, J_{CF} = 253 Hz), 144.02, 140.25 (d, J_{CF} = 1.3 Hz), 135.83, 129.67, 129.32 (d, J_{CF} = 10.1 Hz), 127.59, 126.74 (d, J_{CF} = 6.3 Hz), 120.38 (d, J_{CF} = 3.8 Hz), 115.58 (d, J_{CF} = 21.4 Hz), 84.32, 55.01, 25.06, 24.71,

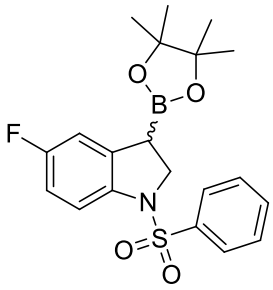
21.76. Note: signal for the carbon that is directly attached to boron was not seen. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.22. ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.30. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BFNO_4S$ + H: 418.1660; Found: 418.1679.

Preparation of 5-Nitro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosylindoline (**6o**)



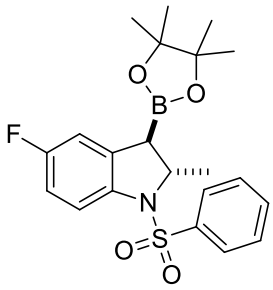
Compound **6o** was prepared from precatalyst **2F** (45.8 mg, 0.2 mmol), 5-nitro-1-tosyl indole (**5o**, 316 mg, 1.0 mmol), and HBpin (290 μL, 2.0 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (62% conversion). Increasing the amount of precatalyst and HBpin to 0.2 mmol (45.8 mg) and 2.6 mmol (377 μL), respectively, gave the quantitative conversion. Purification of the product **6o** was achieved by following the procedure mentioned above in the note for the alternative purification of compound **6a**. This ethyl ether/water extraction procedure for purification gave product **6o** as yellow powder. Yield: 235 mg, 53%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.98 (m, 2H), 7.77 – 7.69 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.34 – 7.26 (m, 2H), 4.27 (dd, *J* = 11.0, 10.2 Hz, 1H), 4.02 (t, *J* = 10.0 Hz, 1H), 2.85 (t, *J* = 10.4 Hz, 1H), 2.38 (s, 3H), 1.21 (s, 6H), 1.19 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.45, 144.87, 143.79, 134.58, 134.08, 130.02, 127.24, 124.26, 120.85, 113.04, 84.66, 52.93, 24.89, 24.59, 21.64. Note: signal for the carbon that is directly attached to boron was not observed. ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.86. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{25}BN_2O_6S$ + H: 445.1603; Found: 445.1622.

Preparation of 5-Fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylsulfonyl indoline (**6q**)



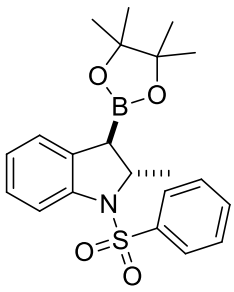
Compound **6q** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-fluoro-1-phenylsulfonyl indole (**5q**, 275 mg, 1.0 mmol), and HBpin (1.5 equiv, 218 μL) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (> 99% conversion). For purification, the reaction crude was dissolved in Et_2O (10 mL) and passed through a short Celite pad and eluted with more Et_2O (30 mL). The solvent was evaporated, and then a flash chromatography (silica gel, petroleum ether/ethyl ether 90:10 v/v) was performed. After evaporation of the solvent under vacuum the product **6q** was obtained as white powder. Yield: 358 mg, 89%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.70 (dd, *J* = 8.8, 4.7 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.00 (ddd, *J* = 8.4, 2.8, 1.4 Hz, 1H), 6.89 – 6.81 (m, 1H), 6.79 – 6.73 (m, 2H), 6.63 (tdd, *J* = 8.8, 2.7, 1.1 Hz, 1H), 4.11 (t, *J* = 10.6 Hz, 1H), 4.02 (t, *J* = 10.6 Hz, 1H), 2.30 (td, *J* = 10.5, 1.3 Hz, 1H), 0.80 (d, *J* = 1.3 Hz, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 159.90 (d, *J* = 241.3 Hz), 138.18 (d, *J* = 2.0 Hz), 137.54, 136.03 (d, *J* = 8.8 Hz), 132.42, 128.57, 128.19, 127.15, 116.25 (d, *J* = 8.6 Hz), 113.42 (d, *J* = 23.4 Hz), 112.25 (d, *J* = 24.3 Hz), 83.75, 52.67, 24.30, 24.00. Note: signal for the carbon that is directly attached to boron was not seen. ^{11}B NMR (160 MHz, C_6D_6) δ 32.05. HRMS (ESI-TOF) *m/z*: Calcd for $C_{20}H_{24}BFNO_4S$ + H: 404.1498; Found: 404.1501.

Preparation of *rac*-5-Fluoro-2-methyl-1-(phenylsulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) indoline (**6r**)



Compound **6r** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 5-fluoro-2-methyl-1-phenylsulfonyl indole (**5r**, 289 mg, 1.0 mmol), and HBpin (1.6 equiv, 233 μL) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (> 99% conversion). For purification, the reaction crude was dissolved in Et_2O (10 mL) and passed through a short Celite pad and eluted with more Et_2O (40 mL). The solvent was evaporated, and then a flash chromatography (silica gel, petroleum ether/ethyl ether 90:10 v/v) was performed. After evaporation of the solvent under vacuum the product **6r** was obtained as white powder. Yield: 342 mg, 82%. Following the purification procedure on note of compound **6a**, an isolated yield of 93% was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.57 (dd, J = 9.6, 4.7 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.42 – 7.36 (m, 2H), 6.85 – 6.80 (m, 2H), 4.41 (qd, J = 6.3, 5.3 Hz, 1H), 2.37 (dd, J = 5.4, 1.3 Hz, 1H), 1.54 (d, J = 6.3 Hz, 3H), 1.04 (d, J = 3.3 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.86 (d, J = 241.6 Hz), 137.57, 136.64 (d, J = 2.0 Hz), 134.48 (d, J = 9.0 Hz), 132.77, 128.74, 127.50, 116.03 (d, J = 8.6 Hz), 113.44 (d, J = 23.4 Hz), 112.17 (d, J = 24.3 Hz), 84.00, 61.08, 25.30, 24.69, 24.34. Note: signal for the carbon that is directly attached to boron was not seen.^{11}B NMR (160 MHz, $CDCl_3$) δ 31.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -119.81. HRMS (ESI-TOF) *m/z*: Calcd for $C_{20}H_{24}BFNO_4S$ + H: 418.1655; Found: 418.1662.

Preparation of *rac*-2-Methyl-1-(phenylsulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indoline (**6s**)



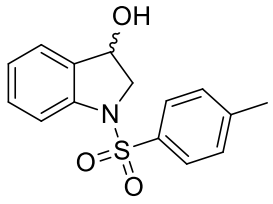
Compound **6s** was prepared from precatalyst **2F** (22.9 mg, 0.1 mmol), 2-methyl-1-(phenylsulfonyl)-indole (**5s**, 271 mg, 1.0 mmol), and HBpin (334 μL, 2.3 mmol) under the neat condition as described above for the preparation of **6a**. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (quantitative conversion). Isolation of the

product was not possible with both methods used here, so subsequent oxidation and silylation were carried out and their procedures and characterization are discussed below. ^{1}H NMR (500 MHz, crude solution in $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 737 (t, *J* = 7.8 Hz, 2H), 7.10 (m, 2H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 4.43 (m, 1H), 2.40 (d, *J* = 5.3 Hz, 1H), 1.55 (d, *J* = 6.3 Hz, 3H), 1.03 (d, *J* = 8.7 Hz, 12H). HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{26}BNO_4S$ + H: 400.1754; Found: 400.1737.

4. Hydroborated Product Functionalization Procedure and Characterization

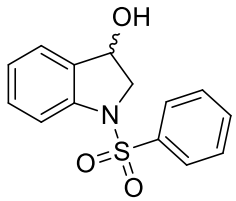
Procedure for the synthesis of derivatives of indolin-3-ol through oxidation of hydroborated products

Synthesis of 1-tosylindolin-3-ol (**6a'**)



To the reaction crude of **6a**, prepared at 1.0 mmol scale with the procedure described above, were added 10 mL of THF and 10 mL of household bleach and stirred for 24 h at room temperature. Then, the solution was extracted with ethyl acetate (15 mLx2), washed with water, brine, and dried with Na_2SO_4. The solvent was evaporated under reduce pressure and a flash chromatography (silica gel, 85:15 to 65:35 hexanes:ethyl acetate v/v) was performed to purify and obtain the product **6a'** as white powder. Yield: 289 mg, 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.38-7.29 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1H), 5.03 (dd, *J* = 6.9, 2.6 Hz, 1H), 3.95 (dd, *J* = 12.3, 6.9 Hz, 1H), 3.86 (dd, *J* = 12.3, 2.7 Hz, 1H), 2.35 (s, 3H), 1.61 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.51, 142.02, 133.70, 133.01, 130.60, 129.86, 127.45, 125.79, 125.77; 124.40, 115.60, 70.11, 58.77, 21.68. HRMS (ESI-TOF) *m/z*: Calcd for $C_{15}H_{15}NO_3S$ + H: 290.0851; Found: 290.0848.

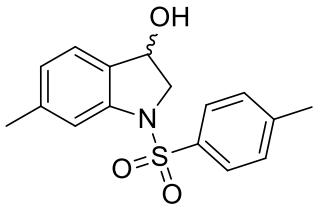
Synthesis of 1-(phenylsulfonyl) indolin-3-ol (**6b'**)



To the reaction crude of **6b**, prepared at 1.0 mmol scale with the procedure described above, were added 10 mL of THF and 10 mL of household bleach and stirred for 24 h at room temperature.

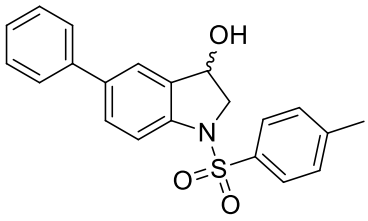
Then, the solution was extracted with ethyl acetate (15 mLx2), washed with water, brine, and dried with Na_2SO_4. The solvent was evaporated under reduce pressure and a flash chromatography (silica gel, 85:15 to 65:35 hexanes:ethyl acetate v/v) was performed to purify and obtain the product **6b'** as white powder. Yield: 207 mg, 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37-7.28 (m, 2H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 5.03 (dd, *J* = 7.0, 2.7 Hz, 1H), 3.94 (dd, *J* = 12.2, 6.9 Hz, 1H), 3.86 (dd, *J* = 12.2, 2.8 Hz, 1H), 1.87 (br s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.84, 136.62, 133.54, 132.96, 130.57, 129.23, 127.37, 125.83, 124.44; 115.39, 69.96, 58.71. HRMS (ESI-TOF) *m/z*: Calcd for $C_{14}H_{13}NO_3S$ + H: 276.0694; Found: 276.0692.

Synthesis of 6-methyl-1-tosylindolin-3-ol (**6d'**)



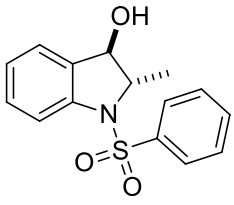
To the reaction crude of **6d**, prepared at 1.0 mmol scale with the procedure described above, were added 10 mL of THF and 10 mL of household bleach and stirred for 24 h at room temperature. Then, the solution was extracted with ethyl acetate (15 mLx2), washed with water, brine, dried with Na_2SO_4, and filtered. The solvent was evaporated under reduce pressure and the residue was dissolved in CH_2Cl_2 (1 mL) and hexanes was added until a white powder precipitates. Afterwards, the solvent was decanted, and the solids were dried under reduced pressure. This afforded the oxidized product 6-methyl-1-(phenylsulfonyl)-indolin-3-ol (**6d'**) as yellow powder. Yield: 243 mg, 80.0%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.90-6.89 (m, 1H), 4.98 (dd, *J* = 6.7, 2.2 Hz, 1H), 3.94 (dd, *J* = 12.3, 6.8 Hz, 1H), 3.86 (dd, *J* = 12.3, 2.5 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 1.23 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.44, 142.25, 141.10, 133.85, 130.33, 129.86, 127.42, 125.39, 125.36, 116.18, 69.95, 59.17, 22.04, 21.69. HRMS (ESI-TOF) *m/z*: Calcd for $C_{16}H_{17}NO_3S$ + H: 304.1007; Found: 304.1010.

Synthesis of 5-Phenyl-1-tosylindolin-3-ol (**6e'**)



To the reaction crude of **6e**, prepared at 1.0 mmol scale with the procedure described above, were added 10 mL of THF and 10 mL of household bleach and stirred for 24 h at room temperature. Then, the solution was extracted with ethyl acetate (15 mLx2), washed with water, brine, and dried with Na_2SO_4. The solvent was evaporated under reduce pressure and a flash chromatography (silica gel, 90:10 petroleum ether:ethyl acetate v/v) was performed to purify and obtain the product **6e'** as pale yellow oil. Yield: 336 mg, 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.58 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.44 – 7.39 (m, 2H), 7.35 – 7.30 (m, 1H), 7.25 – 7.20 (m, 2H), 5.09 (dd, *J* = 7.1, 2.9 Hz, 1H), 3.97 (dd, *J* = 12.1, 7.1 Hz, 1H), 3.87 (dd, *J* = 12.1, 2.9 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.54, 141.23, 140.15, 137.48, 133.66, 133.53, 129.89, 129.34, 128.93, 127.42, 127.35, 126.83, 124.33, 115.46, 69.94, 58.91, 21.62. HRMS (ESI-TOF) *m/z*: Calcd for $C_{15}H_{15}NO_3S$ + H: 366.1164; Found: 366.1159.

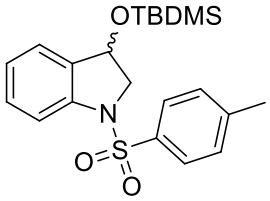
Synthesis of *rac*-2-methyl-1-tosylindolin-3-ol (**6s'**)



To the reaction crude of **6s**, prepared at 1.0 mmol scale with the procedure described above, were added 10 mL of THF and 10 mL of household bleach and stirred for 24 h at room temperature. Then, the solution was extracted with ethyl acetate (15 mLx2), washed with water, brine, and dried with Na_2SO_4. The solvent was evaporated under reduce pressure and a flash chromatography (silica gel, 85:15 to 65:35 hexanes:ethyl acetate v/v) was performed to purify and obtain the

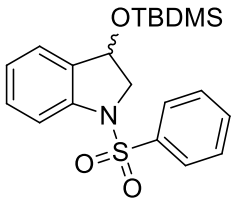
product **6s'** as white powder. Yield: 196 mg, 68%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.69 (m, 3H), 7.54-7.49 (m, 1H), 7.42-7.37 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.12 (td, *J* = 7.5, 0.9 Hz, 1H), 4.46 (s, 1H), 4.13 (qd, *J* = 6.9, 1.0 Hz, 1H), 1.39 (d, *J* = 6.9 Hz, 3H), 0.91 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 141.26, 137.52, 133.40, 132.33, 130.87, 129.12, 127.21, 126.37, 125.03, 117.26, 77.14, 67.82, 20.30. HRMS (ESI-TOF) *m/z*: Calcd for $C_{15}H_{15}NO_3S$ + H: 290.0851; Found: 290.0943.

Synthesis of **3-((tert-butyldimethylsilyl)oxy)-1-tosylindoline (6a'')**



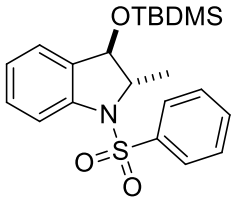
In an oven-dried 10 mL Schlenk tube, 1-tosylindolin-3-ol (**6a'**, 193 mg, 0.667 mmol), imidazole (136 mg, 2.0 mmol) and dry CH_2Cl_2 (6 mL) were added under a nitrogen atmosphere. Then, TBDMSCl (151 mg, 1.0 mmol) was added and the mixture was stirred at room temperature for 4 h. Afterwards, the resulting reaction crude was purified by flash chromatography (silica gel, short bed, 50:50 ethyl ether/dichloromethane v/v). After evaporation of the solvent under reduced pressure, the jelly-like residue was recrystallized in CH_2Cl_2/hexanes to get the pure product 3-((*tert*-butyldimethylsilyl)oxy)-1-tosylindoline (**6a''**) as white powder. Yield: 211 mg, 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (m, 3H), 7.32-7.28 (m, 1H), 7.21 (m, *3*H), 7.05 (td, *J* = 7.05, 0.9 Hz, 1H), 5.15 (dd, *J* = 7.3, 4.2 Hz), 4.05 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.68 (dd, *J* = 11.4, 4.2 Hz, 1H), 2.37 (s, 3H), 0.84 (s, 9H), 0.08 (two overlapped singlet, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.20, 141.73, 134.07, 133.48, 129.80, 129.78, 127.47, 125.47, 124.01, 115.17, 70.51, 58.80, 25.83, 21.66, 18.19, -4.42, -4.44. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{29}NO_3SSi$ + H: 404.1716; Found: 404.1697.

Synthesis of **3-((tert-butyldimethylsilyl)oxy)-1-(phenylsulfonyl)indoline (6b'')**



In an oven-dried 10 mL Schlenk tube, 1-(phenylsulfonyl)-indolin-3-ol (**6b'**, 239 mg, 0.868 mmol), imidazole (177 mg, 2.604 mmol) and dry CH_2Cl_2 (6 mL) were added under a nitrogen atmosphere. Then, TBDMSCl (193 mg, 1.302 mmol) was added and the mixture was stirred at room temperature for 4 h. Afterwards, the resulting reaction crude was purified by flash chromatography (silica gel, short bed, 50:50 ethyl ether/dichloromethane v/v). After evaporation of the solvent under reduced pressure, the jelly-like residue was recrystallized in CH_2Cl_2/hexanes to get the pure product **6b''** as white powder. Yield: 267 mg, 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.89 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.55-7.51 (m, 1H), 7.43 (t, *J* = 7.8, 2H), 7.30 (td, *J* = 8.0, 1.0 Hz), 7.20-7.18 (m, 1H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 5.14 (dd, *J* = 7.3, 4.2 Hz, 1H), 4.05 (dd, *J* = 11.4, 7.4 Hz, 1H), 3.69 (dd, *J* = 11.4, 4.2 Hz, 1H), 0.83 (s, 9H), 0.84 (s, 9H), 0.06 (two overlapped singlets, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.60, 137.11, 133.47, 133.33, 129.85, 129.17, 127.42, 125.52, 124.11, 115.10, 70.50, 58.85, 25.86, 18.21, -4.41, -4.42. HRMS (ESI-TOF) *m/z*: Calcd for $C_{20}H_{27}NO_3SSi$ + H: 390.1559; Found: 390.1539.

Synthesis of ***rac*-3-((tert-butyldimethylsilyl)oxy)-2-methyl-1-(phenylsulfonyl)indoline (6s'')**

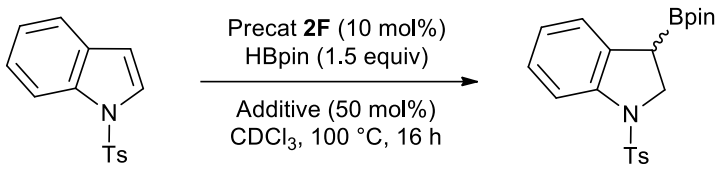


In an oven-dried 10 mL Schlenk tube, 2-methyl-1-(phenylsulfonyl)-indolin-3-ol (**6s'**, 150 mg, 0.518 mmol), imidazole (99 mg, 1.554 mmol) and dry CH_2Cl_2 (6 mL) were added under a nitrogen atmosphere. Then, TBDMSCl (109 mg, 0.777 mmol) was added and the mixture was stirred at room temperature for 4 h. Afterwards, the resulting reaction crude was purified by flash chromatography (silica gel, short bed, 50:50 ethyl ether/dichloromethane v/v). After evaporation of the solvent under reduced pressure, the resulting residue was left for crystallization in

CH_2Cl_2/hexanes at -20 °C, which gave the pure product **6s''** as white crystals. Yield: 184 mg, 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.48-7.44 (m, 1H), 7.37-7.29 (m, 3H), 7.20-7.17 (m, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 4.53 (s, 1H), 4.04 (qd, *J* = 6.9, 1.0 Hz), 1.41 (d, *J* = 6.9 Hz, 3H), 0.72 (s, 9H), 0.04 (s, 3H), -0.03 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.30, 138.24, 132.96, 132.48, 130.08, 128.94, 127.27, 126.37, 124.37, 116.34, 77.63, 68.25, 25.79, 20.61, 18.02, -4.29. HRMS (ESI-TOF) *m/z*: Calcd for $C_{21}H_{29}NO_3SSi$ + H: 404.1715; Found: 404.1695.

5. Effects due to additives on ambiphilic aminoborane 2 (in-situ generated) catalyzed borylative dearomatization

The effect in catalysis due to some additives added in 50 mol% was examined and the outcomes are shown below in Table S1. The benzoic acid, dimethylaniline and benzonitrile additives slowed down the reactivity (entry 1-3), whereas the phenol, acetopheneone and ethyl benzoate additives provided detrimental outcomes (entry 4-6) and no improvement was observed with further precatalyst increment.



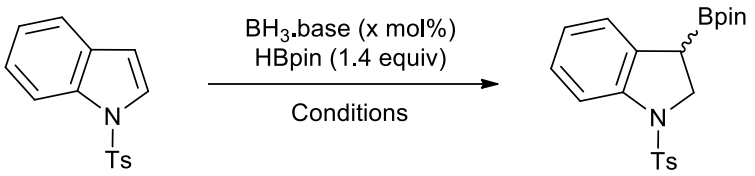
5a **6a**

Table S1. Effects due to additives on ambiphilic aminoborane **2** (in-situ generated) catalyzed borylative dearomatization.

entry	**2F** (mol%)	HBpin (equiv)	conditions[a]	additive[d]	Conv[a] (%)
1	10	1.5	$CDCl_3$, 100 °C, 16 h	benzoic acid	21
2	10	1.5	$CDCl_3$, 100 °C, 16 h	dimethylaniline	7
3	10	1.5	$CDCl_3$, 100 °C, 16 h	benzonitrile	5
4	10	1.5	$CDCl_3$, 100 °C, 16 h	phenol	0
5	10	1.5	$CDCl_3$, 100 °C, 16 h	acetophenone	0
6	10	1.5	$CDCl_3$, 100 °C, 16 h	ethyl benzoate	0

[a] Percent conversions are ^1H NMR conversions determined with an aliquot vs hexamethylbenzene as internal standard.

6. BH_3 Catalysis



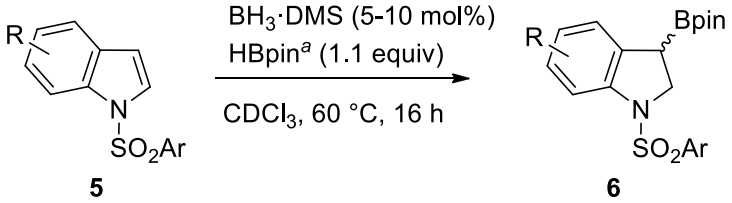
5a **6a**

Table S2. Initial results, reaction optimization for BH_3•base adduct catalysis.

entry	Catalyst	mol % of cat	conditions	Conv[a] (%)
1	BH_3•SMe_2	10	$CDCl_3$, 100 °C, 0.5 h	76
2	BH_3•THF	10	$CDCl_3$, 100 °C, 0.5 h	74
3	BH_3•N(^{t}Bu)$_3$	10	$CDCl_3$, 100 °C, 16 h	47
4	BH_3•N(Et^{i}Pr$_2$)	10	$CDCl_3$, 100 °C,16 h	31
5	BH_3•PPh_3	10	$CDCl_3$, 100 °C,16 h	0
6	BH_3•SMe_2	10	$CDCl_3$, 100 °C, 1 h	98
7	BH_3•THF	10	$CDCl_3$, 100 °C,1 h	96
8	BH_3•THF	10	$CDCl_3$, RT,16 h	70
9	BH_3•THF	10	THF, 100 °C, 16h	22
10	BH_3•THF	5	$CDCl_3$, 60 °C,6 h	98
11	BH_3•THF	5	$CDCl_3$, 60 °C, 16 h	98[b]
12	BF_3•OEt_2	10	$CDCl_3$, 50 °C, 16 h	63[c]

[a] Percent conversions are ^{1}H NMR conversions determined using hexamethylbenzene as internal standard. [b] Used commercially available HBpin that contains the 1% NEt_3 stabilizer. [c] 1.4 equiv of HBpin was used.

Table S3. Substrate scope, reaction conditions and % conversions for BH_3•DMS catalyzed borylative dearomatization.

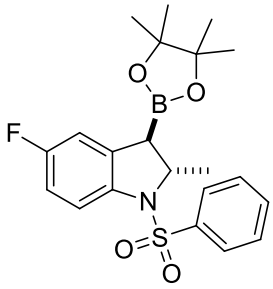


5 **6**

entry	substrate	product	Conv (%)[b]
1	**5a**	**6a**	98
2	**5b**	**6b**	97
3	**5c**	**6c**	95
4	**5d**	**6d**	>99
5	**5e**	**6e**	>99
6	**5f**	**6f**	98
7	**5g**	**6g**	96
8	**5h**	**6h**	>99
9	**5i**	**6i**	96
10	**5j**	**6j**	90
11	**5k**	**6k**	>99
12	**5l**	**6l**	97
13	**5m**	**6m**	>99
14	**5n**	**6n**	>99
15	**5o**	**6o**	>80
16	**5q**	**6q**	>99
17	**5r**	**6r**	>99
18	**5s**	**6s**	>99

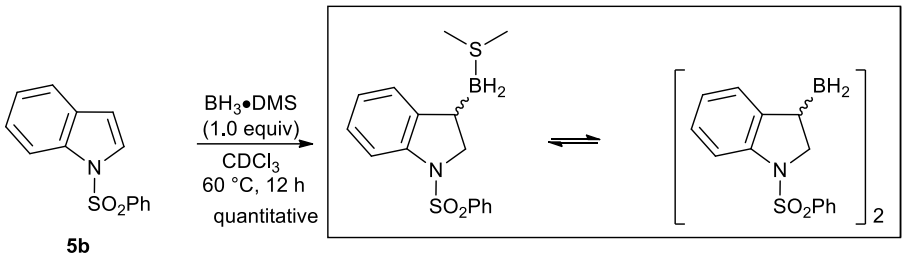
[a] Since the HBpin used contains the 1% NEt_3 stabilizer, the reaction time was extended to 16 h. [b] Percent conversions are ^1H NMR conversions determined with hexamethylbenzene as internal standard.

Prototypical borane-catalyzed two gram-scale preparation of *rac*-5-Fluoro-2-methyl-1-(phenylsulfonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) indoline (6s)



Compound **6r** was prepared from catalyst BH_3·DMS (66 µL, 10 mol%), 5-fluoro-2-methyl-1-phenylsulfonyl indole (**5r**, 2.0 g, 6.913 mmol), and HBpin (1.2 equiv, 1.203 mL) under the neat condition with heating at 60 °C for 16 h. After cooling down the resulting reaction mixture, an aliquot was taken for the ^{1}H NMR analysis (> 99% conversion). For purification, the reaction crude was simply kept in vacuo for 4 h at 50 °C, which afforded the product **6r** as white powder. Yield: 2.7 g, 93%, obtained after recrystallization from CH_2Cl_2/Hexanes at -20 °C.

Preparation of Int-BH_2 intermediate



5b **BH_2-Int**

Compound **BH_2-Int** was prepared in a J-Young NMR tube by treating 1-phenylsulfonyl indole (**5b**, 26 mg, 0.1 mmol) with BH_3•DMS complex (9.4 µL, 0.1 mmol) at 60 °C for 12 h. Note: since **BH_2-Int** is a DMS adduct, the DMS is non-volatile under high vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.62 – 7.56 (m, 1H), 7.56 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.06 (ddt, *J* = 10.3, 7.7, 1.4 Hz, 2H), 6.91 (td, *J* = 7.4, 1.1 Hz, 1H), 4.06 (t, *J* = 9.7 Hz, 1H), 3.70 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.58 (td, *J* = 7.0, 3.6 Hz, 1H), 2.17 (s, 3H), 1.89 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.23, 140.55, 132.96, 128.96, 127.44, 127.31, 125.84, 124.61, 123.40, 113.87, 57.55, 24.68, 24.49. ^{11}B NMR (160 MHz, $CDCl_3$) δ -7.12.

7. X-ray crystallography details and data of compound 6r and 6s''

Data collection was carried out on a Bruker Venture Metal-jet diffractometer using GaKα radiation (λ = 1.34139 Å). During the experiment the sample was kept at 150 K using an Oxford Cryosystem liquid N_2 device. The cell lattice parameters values were determined using reflections taken from three sets of 104 frames measured and harvested within the *APEX2* suite of programs.[14] Frame integration was performed using *SAINT* and a semi-empirical absorption correction was applied with *SADABS*.[15] The structure was solved by direct methods using XT[16] and the refinement was carried out using *SHELX2014/7*.[17] All calculations have been performed using the *OLEX2* GUI software.[18] The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. The H-atoms were included in calculated positions and treated as riding atoms using *SHELX* default parameters, except for those attached to boron atom found in the difference Fourier map and fully refined.

ORTEP diagram of compound 6s'' as a proof for syn addition

The syn addition of H and Bpin groups on indoles catalyzed by all different boron-based catalysts was ascertained through X-ray crystallographic analysis of compound **6r** and **6s''.** Compound **6s"** was derived through oxidation followed by silylation of the hydroborated product **6s**. Based on these results, the nature of addition in all other hydroborated products was surmised as a syn addition.

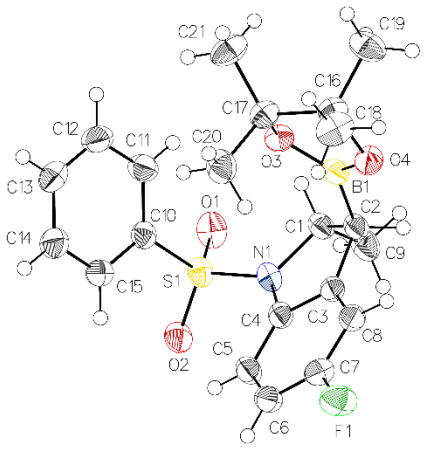


Figure S1. ORTEP diagram of compound **6r**. Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Crystal data for compound **6r**.

Empirical formula	$C_{21}H_{25}BFNO_4S$
Formula weight	417.29
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5498(5)
b/Å	19.2550(9)
c/Å	10.4914(5)
α/°	90
β/°	105.495(2)
γ/°	90
Volume/Å^3	2053.72(17)
Z	4
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	1.111
F(000)	880.0
Crystal size/mm^3	0.42 × 0.16 × 0.15
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.566 to 121.43
Index ranges	$-13 \leq h \leq 13$, $-25 \leq k \leq 24$, $-13 \leq l \leq 13$
Reflections collected	27426
Independent reflections	4699 [R_{int} = 0.0428, R_{sigma} = 0.0273]
Data/restraints/parameters	4699/0/268
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1123
Final R indexes [all data]	R_1 = 0.0494, wR_2 = 0.1172
Largest diff. peak/hole / e Å^{-3}	0.34/-0.32

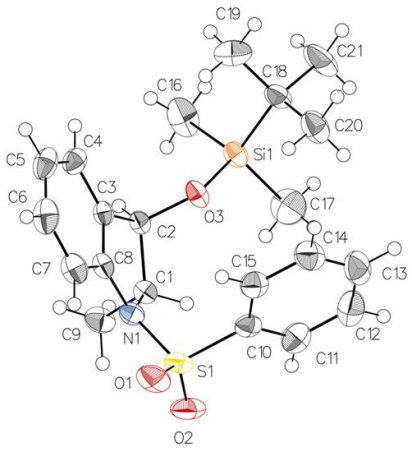


Figure S2. ORTEP diagram of compound **6s''**. Thermal ellipsoids are drawn at the 50% probability level.

Table 5. Crystal data for compound **6s''**.

Empirical formula	$C_{21}H_{29}NO_3SSi$
Formula weight	403.60
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6959(3)
b/Å	16.0600(4)
c/Å	11.9522(3)
α/°	90
β/°	91.9810(10)
γ/°	90
Volume/Å^3	2243.71(10)
Z	4
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	1.264
F(000)	864.0
Crystal size/mm^3	0.33 × 0.22 × 0.18
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.026 to 121.618
Index ranges	$-15 \le h \le 15$, $-20 \le k \le 20$, $-15 \le l \le 15$

Reflections collected	33003
Independent reflections	5160 [R_{int} = 0.0299, R_{sigma} = 0.0186]
Data/restraints/parameters	5160/0/251
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1106
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.56

8. Details of the DFT computations

Geometry optimizations and vibrational frequency calculations were performed at the ωB97XD[19]/6-31G(d,p) level of theory with Gaussian09 (C.01) software.[20] All geometry optimizations were performed without any symmetry constraints. Transition state structures were located using opt = (ts, noeigentest, calcfc) algorithms,[21] and each optimized transition state structure was subjected to a vibrational frequency analysis to ensure that the structure had only one imaginary frequency and that the magnitudes of all frequencies are greater than the residual noise of the rotational and translational frequencies. Moreover, each transition state was confirmed to be on the chosen reaction path by "plus-and-minus-displacement" minimization runs in which the optimized transition state geometry was displaced ca 0.05 Å or 5° along the imaginary frequency normal mode in both directions, and both displaced structures were optimized to the nearest minima structure. Single-point energies were computed on the ωB97XD/6-31G(d,p) optimized geometries using the ωB97XD/6-311G+(d,p) level of theory combined with the polarizable continuum model (SCRF = PCM) for inclusion of the chloroform solvent effect.[22] The energies (ΔG) given are corrected for zero-point vibrational energies (ZPVEs).

Other mechanisms envisaged initially for the borylative dearomatization reactions

For ambiphilic aminoborane catalyst: Because at room temperature majority of the ambiphilic aminoborane catalysts we studied exist as unsymmetrical dimers with the B–H bond of one aminoborane being activated by another aminoborane, we have initially envisaged another mechanism (Figure S2) involving such type intermediate. This mechanism involves: (i) monomerization of the dimeric catalyst **4** (**A1**), (ii) Then the active monomeric catalyst (**A2**)

activates the H–B bond of HBpin by the active aminoborane catalyst through the transition state **TSA(2-3)'**, leading to an HBpin activated intermediate **A3'**, and (ii) this activated intermediate delivers the H and Bpin groups across the C2-C3 double bond of the phenylsulfonyl indole through **TSA(3-4)'** and ends the cycle with the product **A4** formation. The DFT computed free energy profile as displayed in Figure S3 show, however, a high barrier for the HBpin delivery step (53.7 kcal mol^{-1}, **TSA(3-4)'**). Thus, this mechanism is considered less feasible for the borylative dearomatization catalyzed by the ambiphilic aminoboranes.

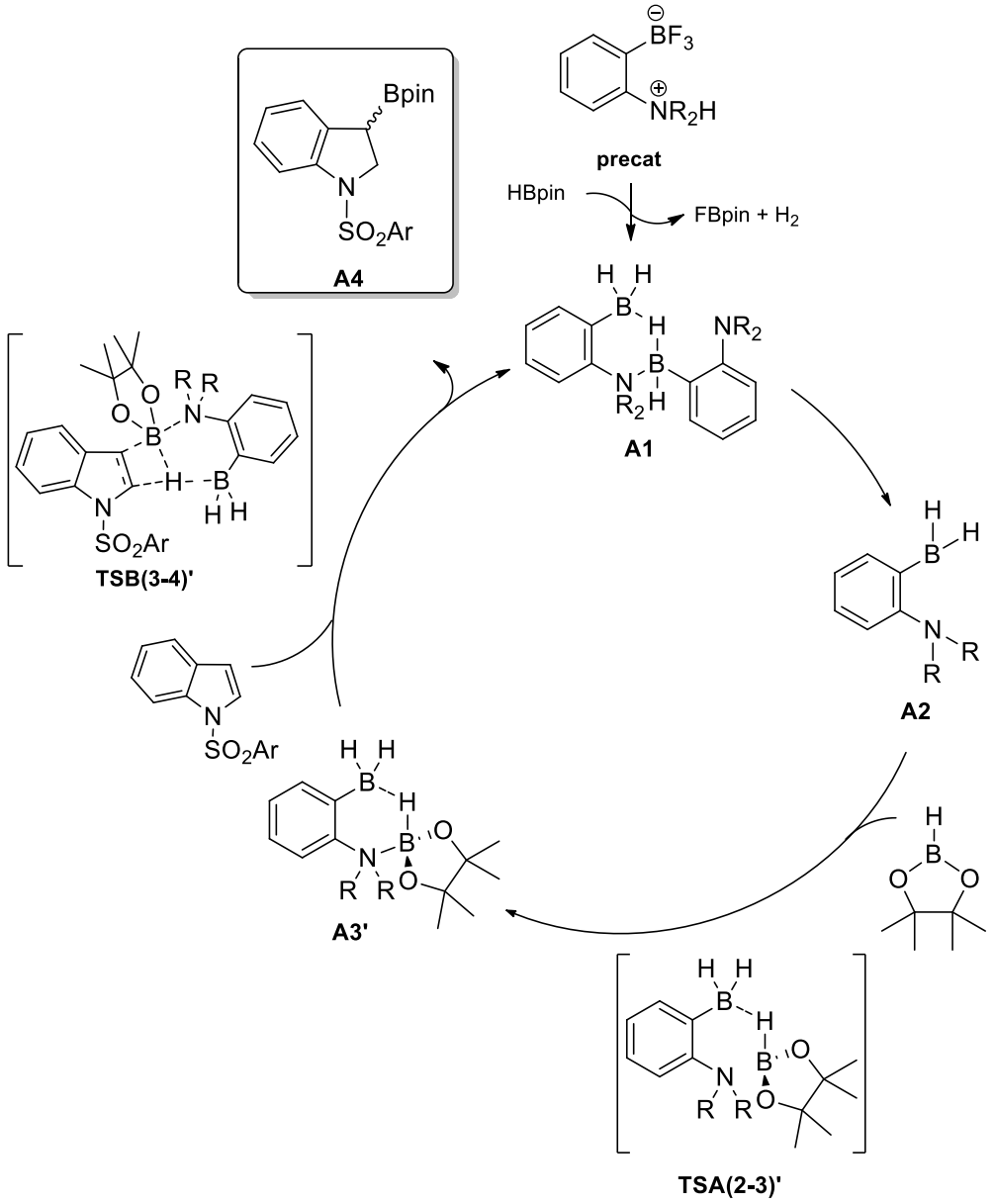


Figure S3. B-H bond activation mechanism proposed initially for the borylative dearomatization of arylsulfonyl indoles catalyzed by ambiphilic aminoboranes.

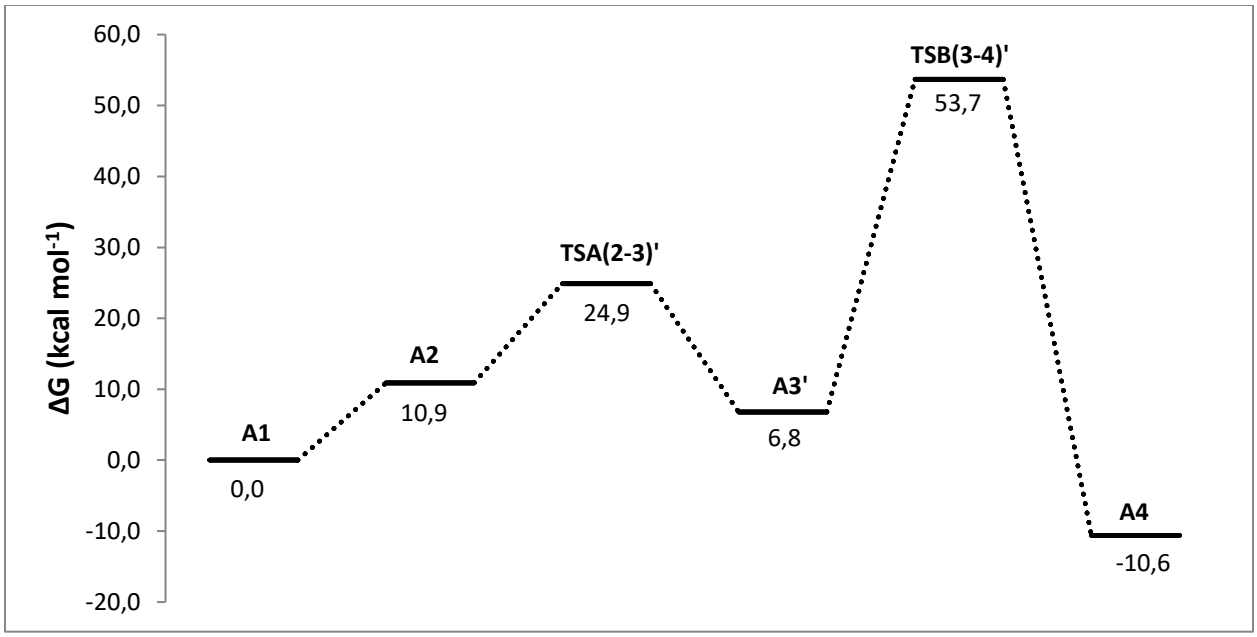


Figure S4. DFT-computed free energy profile for the HBpin activation/insertion pathway for the borylative dearomatization of 1-(phenylsulfonyl)-indole (**5b**) catalyzed by aminoborane **4**.

For the prototypical borane BH_3 as catalyst: As depicted in Figure S4, after the initial hydroboration of 1-phenylsulfonyl indole by BH_3 a direct σ-bond metathesis step between the C–B bond of **B2** and the H–B bond of HBpin, as proposed previously for C-H borylations catalyzed by aminoboranes, was also computed. Unlike the case of aminoboranes, in the BH_3 case we were able to locate the transition state for this direct metathesis step. However, to furnish the product **B5** from the hydroborated intermediate **B2** (dimer) via this direct metathesis transition state requires overcoming a free energy barrier of 34.4 kcal/mol. Thus, we consider this mechanism as a kinetically incompetent mechanism for the borylative dearomatization on indoles.

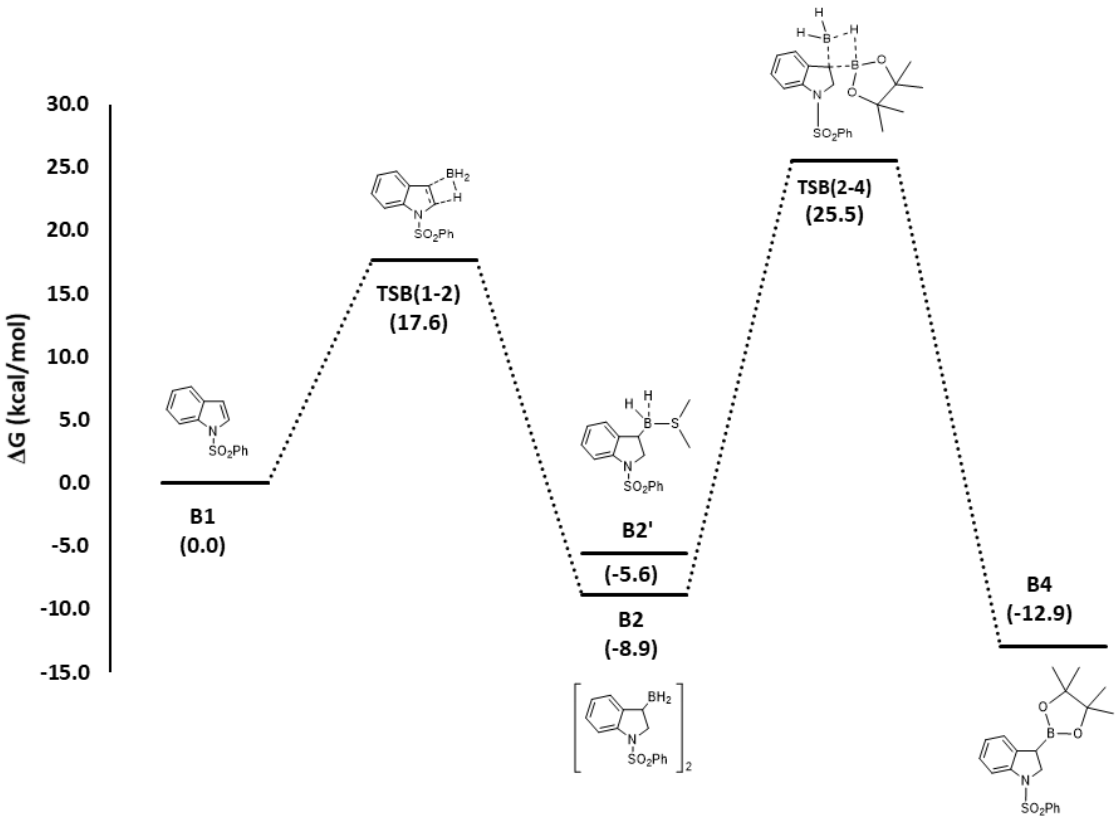
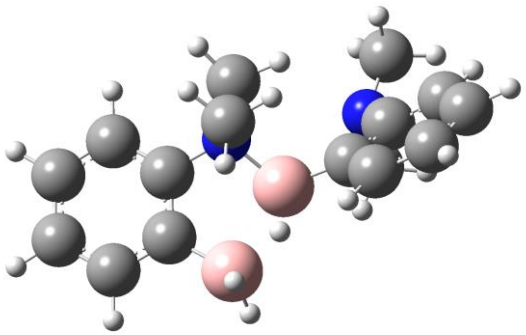


Figure S5. DFT-computed free energy profile for the hydroboration by BH_3/σ-bond metathesis pathway for the borylative dearomatization of 1-(phenylsulfonyl)-indole (**5b**) catalyzed by prototypical borane BH_3·DMS.

Optimized geometries, energies and Cartesian coordinates

Cat dimer



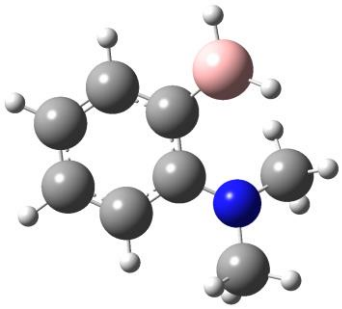
$E_{absolute}$ = -783.3028123 a.u.

G_{corr} = 0.335136 a.u.

Cartesian coordinates:

N	-2.18482100	1.65841000	0.41138700
N	0.91167200	-0.10644100	-0.75768000
C	-1.50392300	-0.69019600	0.30304200
C	-1.87498200	-2.02660500	0.10896800
H	-1.11822300	-2.80018400	0.22398900
C	-3.16912300	-2.40393800	-0.23923900
H	-3.41145900	-3.45090200	-0.39120000
C	-4.13982800	-1.42408100	-0.39431200
H	-5.15574800	-1.69313900	-0.66756800
C	-3.81629300	-0.08846800	-0.17539500
H	-4.59069500	0.66535300	-0.27196100
C	-2.51722500	0.28724300	0.17895700
C	-2.95538800	2.63793000	-0.32902300
H	-3.98391900	2.77931200	0.04815100
H	-3.01388200	2.35298700	-1.38309400
C	-2.11519500	2.00328200	1.82619900
H	-1.63340900	2.97978500	1.94115100
H	-1.52168400	1.26538200	2.36532400
C	2.69250600	-0.64858000	0.80444300
C	4.02686000	-0.53281400	1.20886500
C	4.93704200	0.25169200	0.50969000
H	5.96447800	0.32772700	0.85215300
C	4.53077800	0.94747200	-0.62502100
H	5.23289200	1.56498100	-1.17534200
C	3.21162000	0.85537000	-1.05568400
H	2.90220000	1.40258200	-1.93866200
C	2.32282200	0.06828500	-0.33185200
C	0.83985900	-1.29155800	-1.66090400
H	-0.19770500	-1.45335100	-1.95445000
H	1.46352000	-1.10963600	-2.53895800
C	0.36939800	1.07503600	-1.47592700
H	0.89294900	1.21740200	-2.42311600
H	-0.68654000	0.89637200	-1.67200800
B	0.02838700	-0.31284600	0.60083100
H	0.26053400	0.62189600	1.30681300
H	0.41514100	-1.43763400	1.08763900
B	1.64478600	-1.56616100	1.57908700
H	1.70880300	-2.74169000	1.28081200
H	1.52116600	-1.35913600	2.75720500
H	4.35173800	-1.06592100	2.09775500
H	-3.11590300	2.05338900	2.28923000
H	-2.45064900	3.60727500	-0.26183300
H	0.46815200	1.95299100	-0.84006700
H	1.21084600	-2.16502000	-1.12434000

Cat monomer



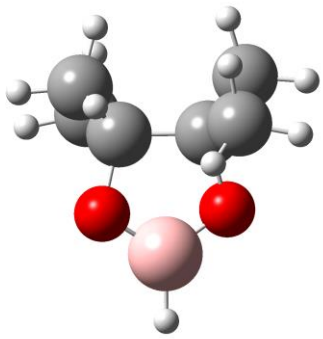
$E_{absolute}$ = -391.61894785 a.u.

G_{corr} = 0.152414 a.u.

Cartesian coordinates:

H	3.72878800	-0.38528300	0.25229400
C	2.65030400	-0.32523300	0.15363600
C	2.00650600	0.90009600	0.07435900
C	1.87485400	-1.48338200	0.09111300
C	0.60814100	1.02043000	-0.07819600
H	2.59422600	1.81437800	0.08834800
C	0.49136100	-1.41953600	-0.00897300
H	2.35177500	-2.45798800	0.14734200
C	-0.17161800	-0.17746200	-0.05953900
H	-0.07169900	-2.34522200	-0.00730800
B	0.08061500	2.39440300	-0.50760600
C	-2.29762500	0.82559400	0.71031900
H	-1.61593000	1.51554300	1.20728900
H	-3.00045800	1.40957000	0.10706300
H	-2.86173300	0.29083000	1.48896600
C	-2.30705300	-1.32668700	-0.40177100
H	-2.35502000	-2.02471900	0.45072800
H	-3.33029200	-1.04344600	-0.66234600
H	-1.87597300	-1.84590000	-1.26080100
N	-1.55676100	-0.12427000	-0.10666600
H	0.80318200	3.34823300	-0.41454600
H	-1.00184000	2.53896500	-0.99802000

HBpin



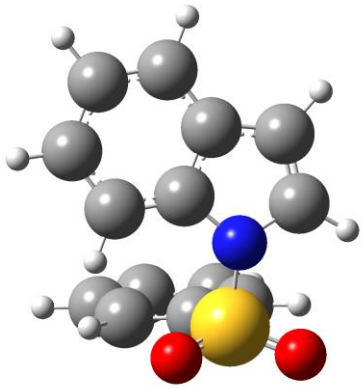
$E_{absolute}$ = -411.86180902 a.u.

G_{corr} = 0.160764 a.u.

Cartesian coordinates:

C	0.00000000	-0.78449500	-0.18409600
C	0.00000000	0.78449500	-0.18409600
B	0.00000000	0.00000000	1.93502300
O	0.33234600	1.09398400	1.18877200
O	-0.33234600	-1.09398400	1.18877200
C	1.03342500	1.42607500	-1.09852800
H	0.84833000	1.14799000	-2.14082800
H	0.96571900	2.51391900	-1.01906400
H	2.04865100	1.12989600	-0.83072100
C	-1.38114700	1.38654800	-0.44897900
H	-1.34497600	2.45833200	-0.24012600
H	-1.68509500	1.24488700	-1.48974400
H	-2.13884900	0.93939000	0.20027700
C	-1.03342500	-1.42607500	-1.09852800
H	-0.84833000	-1.14799000	-2.14082800
H	-0.96571900	-2.51391900	-1.01906400
H	-2.04865100	-1.12989600	-0.83072100
C	1.38114700	-1.38654800	-0.44897900
H	1.34497600	-2.45833200	-0.24012600
H	1.68509500	-1.24488700	-1.48974400
H	2.13884900	-0.93939000	0.20027700
H	0.00000000	0.00000000	3.12417900

1-(Phenylsulfonyl)-indole



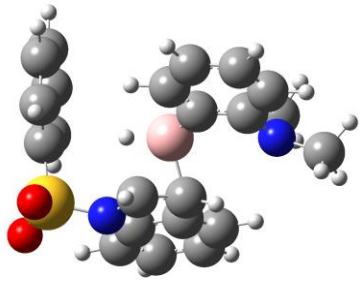
$E_{absolute}$ = -1143.38444089 a.u.

G_{corr} = 0.182133 a.u.

Cartesian coordinates:

C	-1.84889700	-1.05090300	1.93987800
C	-0.81432400	-1.69360200	1.34776000
N	-0.64957000	-1.21811300	0.03918000
C	-2.35841600	-0.08452100	0.99617500
C	-1.58522700	-0.19359900	-0.17692000
C	-1.81802800	0.59985200	-1.30056600
H	-1.23587900	0.47751700	-2.20565300
C	-3.40020400	0.84956000	1.04756400
H	-4.01232600	0.94057400	1.93938700
C	-3.63073700	1.65355900	-0.05800700
C	-2.84693600	1.52819300	-1.21750600
H	-3.05762300	2.16037700	-2.07413500
H	-4.43111600	2.38603100	-0.03431300
S	0.82954300	-1.36290400	-0.76959500
O	1.42857500	-2.57802500	-0.25263900
O	0.55264500	-1.17446800	-2.17951100
C	1.75398600	0.03783800	-0.17790200
C	2.42700300	-0.06783500	1.03739000
C	1.73765900	1.22197900	-0.90935400
C	3.09662600	1.04684300	1.53031800
H	2.43429600	-1.00948100	1.57547500
C	2.41272100	2.32938000	-0.40402800
H	1.21647800	1.26706700	-1.85855500
C	3.08587300	2.24243100	0.81264200
H	3.62794800	0.98052800	2.47374800
H	2.41208300	3.25957100	-0.96209700
H	3.60775300	3.11003200	1.20334000
H	-2.23067800	-1.24853000	2.93113700
H	-0.17298300	-2.48554000	1.70345000

TS for hydroboration by aminoborane 4 (PhSO2)



$E_{absolute}$ = -1535.00358986 a.u.

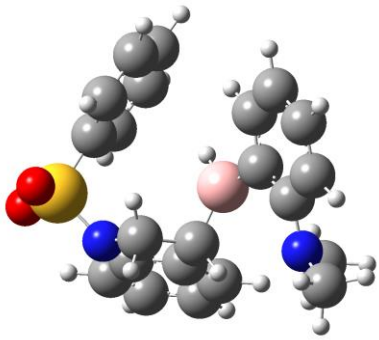
G_{corr} = 0.358784 a.u.

Cartesian coordinates:

B	0.91350900	-0.22364900	0.15293000
C	0.73785300	1.16322200	-0.84697600
C	-0.18071400	2.18617500	-0.31185600
C	-1.49563300	1.75885000	-0.52109500
H	1.69908400	1.42109900	-1.26913500
H	0.08454100	-1.05544500	-0.28465700
C	-0.10390500	0.16235300	-1.42103600
H	0.14863300	-0.52204200	-2.21932000
N	-1.44169500	0.53502600	-1.25305400
C	0.05911800	3.39006200	0.33254200
C	-1.02854100	4.14251200	0.77126900
H	-0.86054100	5.08759000	1.27691000
C	-2.33304100	3.69582300	0.56134700
H	-3.16807500	4.29959600	0.90095400
C	-2.59254000	2.49410700	-0.09664900
H	-3.60426900	2.16313700	-0.29405700
H	1.07744200	3.72909700	0.49218000
S	-2.67225300	-0.63073200	-1.33458500
O	-2.23973100	-1.55455000	-2.36378000
O	-3.91685700	0.10371400	-1.41710200
H	0.41218600	0.03142500	1.21444800
C	2.34386900	-0.90479500	-0.04498900
C	3.56936800	-0.20028400	0.05385300
C	2.41213800	-2.26250800	-0.37778000
C	4.77557900	-0.86034800	-0.20769000
C	3.61102000	-2.92085800	-0.63584100
H	1.48107800	-2.82056300	-0.45399500
C	4.79769000	-2.20699100	-0.55679600
H	5.71651700	-0.32738500	-0.12934500
H	3.61446000	-3.97339300	-0.90114000
H	5.74837300	-2.69337500	-0.75377400
N	3.55762100	1.18536400	0.38459100

C	3.11582200	1.48884600	1.73925300
H	3.86785400	1.20027000	2.49294500
H	2.93688500	2.56524100	1.83163600
H	2.18329200	0.97292800	1.96367800
C	4.73634100	1.95091800	0.03170600
H	4.50587400	3.01623700	0.13112800
H	5.61151100	1.74253800	0.67240700
H	5.01360700	1.75690100	-1.00727900
C	-2.56689100	-1.44211900	0.23917500
C	-1.90919300	-2.66568300	0.32261800
C	-3.07150700	-0.79887800	1.36730000
C	-1.75037300	-3.25586000	1.57169300
H	-1.53580300	-3.13903400	-0.57826800
C	-2.90113300	-1.39847400	2.60795800
H	-3.58512400	0.15074000	1.27307400
C	-2.23946300	-2.62082800	2.70900300
H	-1.23999100	-4.20891900	1.65527700
H	-3.28650100	-0.91210700	3.49728700
H	-2.10651800	-3.08208200	3.68200900

Hydroborated intermediate ($PhSO_2$)



$E_{absolute}$ = -1535.04405681 a.u.

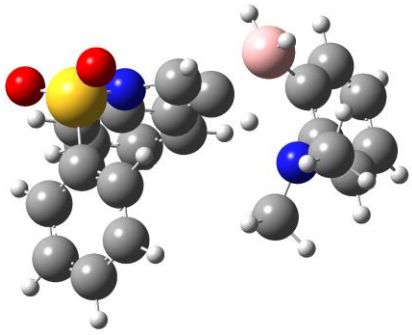
G_{corr} = 0.362399 a.u.

Cartesian coordinates:

B	1.03725100	0.02806000	0.45950400
C	0.46557600	1.18388000	-0.46547200
C	-0.61673700	2.00150700	0.19494100
C	-1.87282900	1.67105900	-0.31681800
H	1.25433900	1.81078500	-0.88456000
H	-0.09029400	-0.56667500	-1.75062700
C	-0.30829900	0.49912400	-1.63603500
H	-0.07599500	0.97726400	-2.59062400
N	-1.74833000	0.69734600	-1.34833400
C	-0.51483000	2.95386200	1.19697300

C	-1.67225700	3.56897700	1.67784900
H	-1.60063300	4.31637300	2.46126100
C	-2.91540600	3.23467400	1.14954100
H	-3.80929900	3.72507700	1.52106000
C	-3.03353400	2.28663000	0.13231600
H	-3.99358900	2.02875800	-0.29582600
H	0.45598900	3.21624200	1.60712500
S	-2.74004700	-0.65276200	-1.38455500
O	-2.37562000	-1.37943600	-2.58709700
O	-4.09339900	-0.18605900	-1.14771000
H	0.24275700	-0.55451700	1.14490400
C	2.46838000	-0.55090000	0.38656600
C	3.62513800	0.10256300	-0.12341800
C	2.54883200	-1.93179000	0.63871600
C	4.75043300	-0.66200700	-0.45792100
C	3.67050000	-2.68489500	0.31608100
H	1.67621100	-2.42132700	1.06277800
C	4.76161800	-2.03792500	-0.25151400
H	5.63978200	-0.18859700	-0.85616900
H	3.69444100	-3.75373400	0.49918700
H	5.65243400	-2.60131400	-0.51390600
N	3.62134300	1.49448500	-0.29259200
C	3.25517600	2.32428000	0.84613800
H	4.14351200	2.62868400	1.42219200
H	2.73843100	3.22875600	0.50671200
H	2.59181200	1.78117600	1.51865100
C	4.67268000	2.09632900	-1.08564900
H	4.39617800	3.13165200	-1.30340100
H	5.64980700	2.11114600	-0.57421800
H	4.78087000	1.57039000	-2.03666700
C	-2.23416100	-1.63427700	0.01522100
C	-1.40349300	-2.73060900	-0.19378700
C	-2.61136200	-1.23832800	1.29717000
C	-0.94064000	-3.44508200	0.90690500
H	-1.14370100	-3.01852600	-1.20632900
C	-2.13141700	-1.95255900	2.38794500
H	-3.26940200	-0.38747000	1.43272000
C	-1.29623600	-3.05124500	2.19366100
H	-0.30164900	-4.30926600	0.75709700
H	-2.41217900	-1.65360500	3.39216300
H	-0.92706200	-3.60583700	3.05031000

TS for C-H activation by aminoborane 4 (PhSO2)



$E_{absolute}$ = -1534.99850406 a.u.

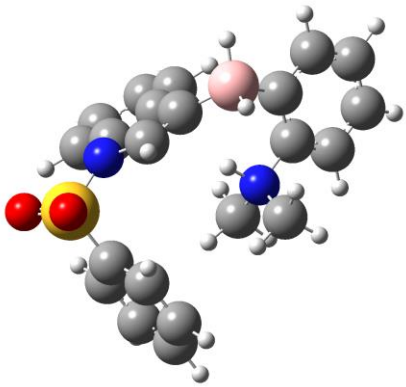
G_{corr} = 0.356675 a.u.

Cartesian coordinates:

C	5.60066200	0.31361400	0.94623600
C	5.68510300	-0.76177400	0.06581600
C	4.65928700	-1.00128300	-0.84402100
C	3.52796800	-0.17944200	-0.92281100
C	3.48527400	0.90409900	-0.03017000
C	4.49189100	1.15204000	0.90047600
N	2.30361900	1.73536000	-0.10858600
C	1.72086900	2.14374400	1.16347700
C	2.43355000	2.84056000	-1.05756300
B	2.31246500	-0.49303600	-1.92912600
C	0.79050600	-0.37658700	-0.97756200
C	0.50380200	-1.27900200	0.13736900
C	-0.85177500	-1.63705200	0.07949600
H	6.39147100	0.49971300	1.66624100
H	6.54600100	-1.42302400	0.09938400
H	4.72140700	-1.86021600	-1.50648500
H	4.41799500	1.99264100	1.58467400
H	1.38225200	0.63950800	-0.73402700
H	0.70761800	2.51686500	0.98275200
H	1.65864800	1.27639200	1.82369200
H	2.29532300	2.93636100	1.66305800
H	1.45037300	3.29203800	-1.22483600
H	2.81006900	2.45271200	-2.00458600
H	3.12067000	3.61265400	-0.68338400
H	2.17285200	0.32812100	-2.81647400
H	2.30680200	-1.63385900	-2.32873000
C	-0.41265100	-0.21178700	-1.62452300
H	-0.64797000	0.39332700	-2.48869100
N	-1.39730200	-0.97472200	-1.04341200
C	1.30537500	-1.80655200	1.15268600
C	0.72362800	-2.65594300	2.08227600
H	1.33037200	-3.07487800	2.87844300
C	-0.63322100	-3.00075400	2.00068600

H	-1.05484400	-3.68289000	2.73167900
C	-1.44642500	-2.50635400	0.99040800
H	-2.48480000	-2.79961500	0.89769000
H	2.36143600	-1.56129100	1.19605000
S	-3.05257000	-0.62725200	-1.27434000
O	-3.78345100	-1.82348300	-0.91817300
O	-3.13325100	-0.01979500	-2.58551200
C	-3.32550000	0.61793400	-0.03548400
C	-3.03502000	1.94402800	-0.34669500
C	-3.76442100	0.23664400	1.22817900
C	-3.18613700	2.90967500	0.64078600
H	-2.71529800	2.20854700	-1.34878200
C	-3.91081300	1.21446300	2.20619900
H	-3.99324500	-0.80243200	1.43306500
C	-3.61923500	2.54380300	1.91394000
H	-2.97433800	3.94921200	0.41517900
H	-4.25526600	0.93649900	3.19624000
H	-3.73561400	3.30214800	2.68119100

C-H activated intermediate ($PhSO_2$)



$E_{absolute}$ = -1535.03657402 a.u.

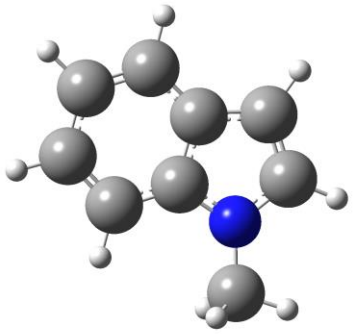
G_{corr} = 0.364414 a.u.

Cartesian coordinates:

C	5.12888100	0.97712600	0.83514300
C	5.50290600	-0.01701200	-0.06797400
C	4.57894400	-0.53841500	-0.96692300
C	3.24419100	-0.10408500	-1.01692200
C	2.93078000	0.88601500	-0.08473900
C	3.82006700	1.44089500	0.82808400
N	1.53218800	1.37867800	-0.12002000
C	0.84852400	1.39434300	1.19787000
C	1.40846200	2.66220200	-0.85571300
B	2.16120100	-0.69045500	-2.09008400

C	0.75948700	-1.09506400	-1.36602600
C	0.55965200	-1.78842500	-0.09337400
C	-0.81992700	-1.91002300	0.16133800
H	5.84634200	1.38454400	1.53941000
H	6.52348200	-0.38824000	-0.06620200
H	4.88514500	-1.31369100	-1.66284100
H	3.51199200	2.21480400	1.52562800
H	1.03409100	0.66243800	-0.69278200
H	-0.21380200	1.57211100	1.03315300
H	0.99739100	0.42322000	1.66921800
H	1.26276500	2.18927700	1.81829100
H	0.35055900	2.91908100	-0.93354300
H	1.84067600	2.51633600	-1.84549100
H	1.95090300	3.43744600	-0.31306600
H	1.91808600	0.19293600	-2.91395100
H	2.64519200	-1.65579200	-2.65098000
C	-0.49757900	-0.82425600	-1.81070500
H	-0.81535400	-0.34106000	-2.72338500
N	-1.48476400	-1.35503800	-0.94670400
C	1.47008500	-2.28010100	0.84943600
C	0.98534500	-2.84943700	2.01812300
H	1.68051500	-3.23135000	2.75904300
C	-0.39409200	-2.95443100	2.24913200
H	-0.74921400	-3.41732600	3.16431900
C	-1.32120100	-2.49707800	1.32195000
H	-2.38650500	-2.60888700	1.48133900
H	2.53592800	-2.20454700	0.66129200
S	-3.02463900	-0.69177800	-0.89845400
O	-3.84965300	-1.57289000	-0.09722900
O	-3.35671900	-0.34342400	-2.26471000
C	-2.80087700	0.83023200	0.01009200
C	-2.51757900	1.99907500	-0.69253700
C	-2.90452800	0.82091800	1.39838600
C	-2.33743900	3.18376300	0.01546400
H	-2.47087000	1.97547500	-1.77595600
C	-2.71707700	2.01119100	2.09532300
H	-3.14368200	-0.10115900	1.91546200
C	-2.43550700	3.18865900	1.40618900
H	-2.13896100	4.10700800	-0.51938000
H	-2.80420400	2.01982200	3.17649700
H	-2.30237000	4.11675300	1.95247400

1-Methyl indole



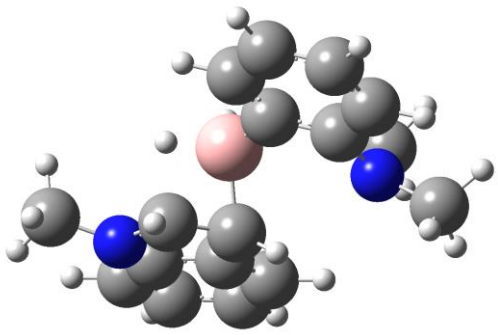
$E_{absolute}$ = -403.09285809 a.u.

G_{corr} = 0.12695 a.u.

Cartesian coordinates:

C	-0.72958800	1.88448800	0.00213900
C	-1.85637700	1.11541800	-0.00371400
N	-1.52361900	-0.22243600	-0.01158700
C	0.38551000	0.98179600	0.00116800
C	-0.15137000	-0.32738000	-0.00484200
C	0.65684600	-1.46816400	-0.00398300
H	0.22828100	-2.46552400	-0.00449900
C	1.77882900	1.14151900	0.00375400
H	2.21756400	2.13467800	0.00759700
C	2.58418800	0.01622300	0.00231600
C	2.02778100	-1.27673200	-0.00126600
H	2.68702300	-2.13906100	-0.00115800
H	3.66372900	0.12862300	0.00463100
H	-0.69527200	2.96374200	0.00419600
H	-2.89674100	1.40981300	-0.00524700
C	-2.44151500	-1.33486600	0.01059500
H	-2.23780800	-2.01925200	-0.81886700
H	-2.36693200	-1.89050800	0.95144000
H	-3.46032700	-0.95926800	-0.09398500

TS for hydroboration by aminoborane 4 (Methyl)



$E_{absolute}$ = -794.70899759 a.u.

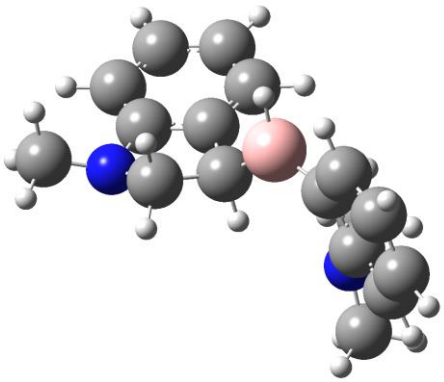
G_{corr} = 0.30325 a.u.

Cartesian coordinates:

B	-0.22217400	0.66967800	0.64533500
C	0.60887400	-0.00649800	-0.64813400
C	1.93934600	-0.56547200	-0.31920800
C	2.83879600	0.50185100	-0.19335700
H	-0.06167700	-0.52033000	-1.32561600
H	0.14599700	1.89903000	0.55152000
C	0.84748200	1.42100100	-0.76483100
H	0.25735200	2.09733700	-1.37427200
N	2.18469800	1.69432900	-0.55594900
C	2.37370700	-1.86005000	-0.09018900
C	3.70198400	-2.06954900	0.28598000
H	4.05655100	-3.07823400	0.47059900
C	4.57474300	-0.99416600	0.43911000
H	5.60101800	-1.17388300	0.74249100
C	4.15377200	0.31621000	0.20471800
H	4.84024500	1.14781200	0.32432500
H	1.68521100	-2.69342900	-0.18871000
H	0.30924000	0.38802300	1.68636900
C	-1.80623900	0.70899800	0.43231500
C	-2.57389100	-0.41494900	0.03395500
C	-2.48889700	1.91895500	0.60076200
C	-3.94767900	-0.27244600	-0.19897700
C	-3.85421700	2.06197400	0.37004200
H	-1.91942700	2.79230700	0.91260400
C	-4.58213300	0.95524300	-0.04117400
H	-4.54042100	-1.12999900	-0.49714800
H	-4.33719000	3.02466800	0.50487400
H	-5.64865200	1.03570700	-0.22963200
N	-1.93654300	-1.67010900	-0.16433800
C	-1.33845500	-2.26815500	1.02003000
H	-2.09918700	-2.68085000	1.70429800
H	-0.67321700	-3.08398100	0.71763400

H	-0.74436400	-1.53705700	1.56656500
C	-2.64569900	-2.65529100	-0.95324700
H	-1.94922100	-3.45602600	-1.22113000
H	-3.49781900	-3.12053200	-0.42617700
H	-3.01607000	-2.20403200	-1.87695000
C	2.64422200	3.00750100	-0.17387500
H	2.47325800	3.19626800	0.89478200
H	3.70972600	3.10778200	-0.38902200
H	2.10813000	3.76054300	-0.75559400

Added intermediate (Methyl)



$E_{absolute}$ = -794.73613156 a.u.

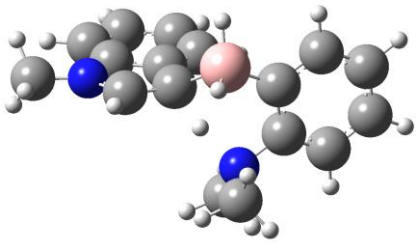
G_{corr} = 0.306349 a.u.

Cartesian coordinates:

B	-0.51160200	0.63452400	0.96111500
C	0.59259400	0.39457200	-0.14438500
C	1.85097500	-0.31694900	0.32281600
C	2.96401200	0.31477800	-0.25615400
H	0.19397900	-0.12420900	-1.02385200
H	1.23691100	2.47204900	0.20242200
C	1.19976500	1.73734400	-0.62302300
H	0.63719800	2.18129000	-1.44914300
N	2.55809000	1.38870200	-1.04814000
C	2.02790100	-1.41385500	1.14436000
C	3.32114200	-1.89256700	1.39010600
H	3.46743700	-2.74834000	2.04069200
C	4.41438000	-1.26204600	0.81026000
H	5.41593700	-1.63166500	1.00841900
C	4.25312700	-0.14624100	-0.01651000
H	5.11844800	0.34463700	-0.44932100
H	1.17446600	-1.89785900	1.61102900
H	-0.13710800	1.16166700	1.97715400
C	-2.03527400	0.43882500	0.79818700

C	-2.69148700	-0.32329300	-0.21249900
C	-2.82246900	1.31330700	1.57161200
C	-4.04802800	-0.08215800	-0.47930600
C	-4.16930100	1.53210800	1.31949000
H	-2.33335100	1.86623100	2.36918200
C	-4.76713500	0.84002800	0.27111600
H	-4.56234600	-0.64192500	-1.25157700
H	-4.74211500	2.22915300	1.92128600
H	-5.81949000	0.99321700	0.04969300
N	-1.98738600	-1.29125600	-0.92870600
C	-1.19108500	-2.27147900	-0.20565000
H	-1.70766300	-3.24256000	-0.17045600
H	-0.21226400	-2.41435900	-0.67577200
H	-1.03304300	-1.94218000	0.82088600
C	-2.56024400	-1.82706000	-2.14424000
H	-1.77448800	-2.34948400	-2.69702000
H	-3.37689800	-2.54498900	-1.95987000
H	-2.93555700	-1.02059600	-2.77793100
C	3.46633600	2.48455600	-1.28400500
H	3.74447000	3.01469200	-0.35743300
H	4.37922800	2.12178500	-1.76339600
H	2.99807900	3.19948400	-1.96569400

TS for C-H activation by aminoborane 4 (Methyl)



$E_{absolute}$ = -794.71443509 a.u.

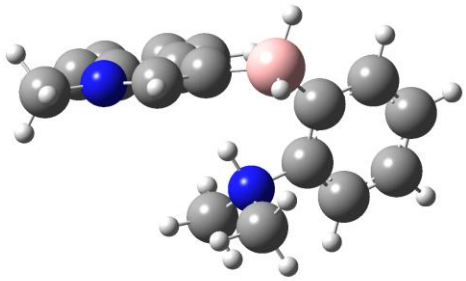
G_{corr} = 0.300465 a.u.

Cartesian coordinates:

C	-4.10267100	1.17850300	0.22171500
C	-3.81595900	1.46007200	-1.11190400
C	-2.73717600	0.84536500	-1.74033600
C	-1.91398700	-0.07736000	-1.08155000
C	-2.24436900	-0.34115900	0.25643900
C	-3.30888200	0.27110300	0.91410900
N	-1.38637300	-1.29648400	0.93566000
C	-0.99957200	-0.94960800	2.29993900
C	-1.85251600	-2.67882100	0.80627100
B	-0.63197900	-0.76372900	-1.78690600

C	0.68627000	-0.72495800	-0.67590600
C	1.30601800	0.50078500	-0.17464200
C	2.68773700	0.27467400	-0.05147800
H	-4.93866700	1.65975400	0.71968300
H	-4.43090800	2.16885000	-1.65907300
H	-2.51027000	1.08979400	-2.77451700
H	-3.52288300	0.04453100	1.95492300
H	-0.21218200	-1.14589600	0.09557900
H	-0.17483600	-1.60025800	2.60578000
H	-0.65399200	0.08553300	2.31884900
H	-1.82115700	-1.07296900	3.01704400
H	-1.07085000	-3.35849000	1.16001500
H	-2.05035600	-2.88273600	-0.24646200
H	-2.76669700	-2.84696100	1.39048400
H	-0.82003600	-1.94953300	-2.02799400
H	-0.28423300	-0.15571300	-2.77882800
C	1.75895600	-1.60284500	-0.81306000
H	1.73634600	-2.62380600	-1.17384300
N	2.93387700	-1.03437200	-0.46188300
C	4.24215800	-1.64778400	-0.50586800
H	4.67856400	-1.70008000	0.49597100
H	4.15009900	-2.65741200	-0.90711200
H	4.90824400	-1.07004800	-1.15279200
C	0.79318600	1.75406200	0.17496100
C	1.66808500	2.72536400	0.63973700
H	1.28574500	3.70458800	0.90990100
C	3.04426300	2.47176300	0.75907500
H	3.70218400	3.25389000	1.12393300
C	3.57972700	1.23964500	0.41229600
H	4.64363000	1.04368800	0.50121700
H	-0.26799700	1.95510500	0.06655800

C-H activated intermediate (Methyl)



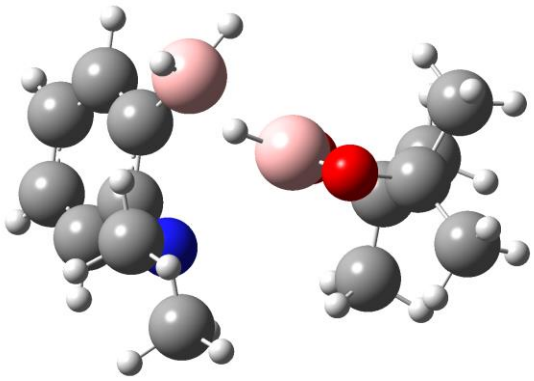
$E_{absolute}$ = -794.73580215 a.u.

G_{corr} = 0.304283 a.u.

Cartesian coordinates:

C	-4.09616400	0.87073500	0.54978700
C	-4.03759200	1.10615300	-0.82339000
C	-2.99345800	0.59280200	-1.58481500
C	-1.95971200	-0.17876600	-1.02895000
C	-2.06983500	-0.36937000	0.34963700
C	-3.09538000	0.11860700	1.15096100
N	-0.99892200	-1.19310800	0.95948800
C	-0.38413600	-0.61304000	2.17761600
C	-1.41180200	-2.60777300	1.12515800
B	-0.74965400	-0.82236800	-1.92113600
C	0.70680900	-0.59323700	-1.22338300
C	1.23778300	0.60296500	-0.59128200
C	2.54590500	0.32542000	-0.12688700
H	-4.90936500	1.26968100	1.14682300
H	-4.81422400	1.69736900	-1.29981400
H	-2.95958800	0.78803000	-2.65267200
H	-3.12594500	-0.07441000	2.21981500
H	-0.24659600	-1.18413700	0.22223800
H	0.51755300	-1.18075700	2.41246600
H	-0.12076800	0.42276300	1.96441300
H	-1.08498700	-0.66893100	3.01106700
H	-0.55329900	-3.19141200	1.46333300
H	-1.74934500	-2.96622400	0.15270900
H	-2.22018200	-2.66204300	1.85570300
H	-0.94632300	-2.03874000	-2.00049800
H	-0.78564700	-0.33149600	-3.03606600
C	1.72280400	-1.50952900	-1.09224300
H	1.75013300	-2.53580700	-1.43794000
N	2.83357100	-0.97742100	-0.45781900
C	4.07382700	-1.65557400	-0.17960400
H	4.25375800	-1.73474200	0.89891400
H	4.03001300	-2.66160700	-0.59968300
H	4.91900700	-1.12893100	-0.63479100
C	0.69322600	1.87347700	-0.35047100
C	1.44499000	2.81015500	0.34180600
H	1.03324200	3.79660000	0.53114100
C	2.74266100	2.50810300	0.79468500
H	3.30908800	3.26383400	1.33029400
C	3.31327800	1.26571300	0.56716700
H	4.31588200	1.03706900	0.91625500
H	-0.30589200	2.10840600	-0.70445800

TS for B-H activation by aminoborane 4



$E_{absolute}$ = -803.48180142 a.u.

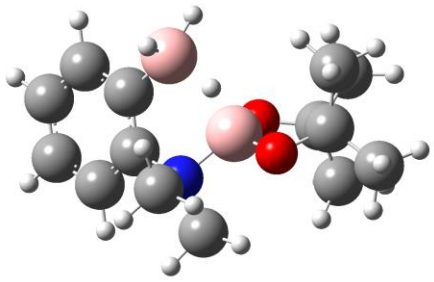
G_{corr} = 0.336636 a.u.

Cartesian coordinates:

C	-3.85319200	-1.83793800	0.25091100
C	-2.88351900	-1.77613000	-0.74514900
C	-2.04380800	-0.67025200	-0.90748400
C	-2.19885900	0.40229200	-0.00281800
C	-3.15927600	0.33584100	1.00937400
C	-3.98485100	-0.77691700	1.13608200
H	-4.48681500	-2.71450900	0.34366600
H	-2.76159600	-2.62323600	-1.41550200
H	-3.27552000	1.15830300	1.70694300
H	-4.72887600	-0.80661500	1.92627100
N	-1.32416800	1.53487700	-0.12053800
B	-0.97527100	-0.72607800	-2.07943900
H	-0.03848700	0.28031900	-1.78655200
H	-1.19486800	-0.11743200	-3.09850700
C	-1.14110700	2.32278000	1.08488600
C	-1.64862300	2.40014000	-1.25273800
B	0.81070000	0.01277800	-0.93626800
O	1.98288300	0.66201300	-1.16191300
O	0.80581700	-0.83444200	0.11724200
H	-2.58455900	2.95664600	-1.08392900
H	-2.01772100	2.94144900	1.34188400
H	-1.76308600	1.81165100	-2.16338100
H	-0.91951000	1.66600900	1.92819000
C	2.95785800	0.02957400	-0.28969500
C	2.04849100	-0.60058100	0.82453900
C	2.54250900	-1.92820400	1.37833000
H	3.52433100	-1.80482500	1.84594900
H	1.84413500	-2.28878900	2.13728500
H	2.61497900	-2.68649700	0.59787100
C	3.68142900	-1.01634600	-1.13697400
H	4.12456900	-0.52414900	-2.00568800

H	4.47838300	-1.50545500	-0.57051200
H	2.98779900	-1.78099100	-1.49736700
C	1.74109000	0.36765300	1.96457200
H	0.93519800	-0.05042400	2.57251100
H	2.61645100	0.52179800	2.60117100
H	1.41157400	1.33532300	1.58006700
C	3.93536900	1.08567800	0.19997500
H	4.63530000	0.65202600	0.92096300
H	4.51143100	1.47187200	-0.64434800
H	3.42042100	1.92369300	0.67178100
H	-0.38081100	-1.75955400	-2.24342200
H	-0.83695900	3.11872000	-1.40511600
H	-0.29439300	3.00091100	0.93657100

HBpin-activated intermediate



$E_{absolute}$ = -803.51522156 a.u.

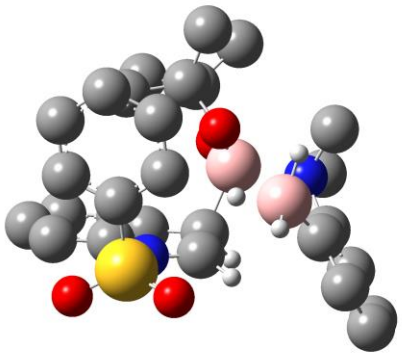
G_{corr} = 0.341124 a.u.

Cartesian coordinates:

C	-4.30463100	-1.13265200	0.46877200
C	-3.29532300	-1.63375000	-0.34479900
C	-2.13726000	-0.89925800	-0.62427300
C	-2.04953700	0.36096100	-0.03231600
C	-3.04157000	0.88963900	0.78619100
C	-4.17932200	0.13169000	1.03720900
H	-5.19000700	-1.72909000	0.66653700
H	-3.39928800	-2.62465200	-0.77741700
H	-2.94650600	1.86970100	1.23916900
H	-4.95900600	0.52805200	1.67917400
N	-0.82795000	1.13725400	-0.35682500
B	-0.98841400	-1.44734200	-1.58637400
H	0.05687400	-0.66719400	-1.51531000
H	-1.21791700	-1.28194500	-2.76625600
C	-0.46616800	2.13474200	0.68109200
C	-1.01318700	1.83752500	-1.66282500
B	0.41150300	0.10746500	-0.47695600
O	1.57218100	0.76209900	-0.94320000

O	0.68400900	-0.60042700	0.69939400
H	-1.83186500	2.55380200	-1.56802100
H	-1.19789000	2.94355300	0.70295100
H	-1.25569500	1.09870500	-2.42572600
H	-0.41900100	1.63211700	1.64583400
C	2.66686800	-0.01266500	-0.43097000
C	2.09618000	-0.53395700	0.94008700
C	2.58348400	-1.92212100	1.34031700
H	3.67326100	-1.93902400	1.44615900
H	2.14221800	-2.19999100	2.30098000
H	2.28540500	-2.67084300	0.60557300
C	2.95187200	-1.14269800	-1.42640700
H	3.13273500	-0.70135700	-2.40970800
H	3.83510900	-1.71868300	-1.13604700
H	2.10473700	-1.82816700	-1.51355600
C	2.33242600	0.44036400	2.09714500
H	1.72005700	0.12786000	2.94728200
H	3.38064900	0.44602600	2.41016700
H	2.05076800	1.46165300	1.83032300
C	3.88678700	0.89050200	-0.31417900
H	4.71464600	0.36135400	0.16827900
H	4.21396700	1.19735300	-1.31110200
H	3.66450500	1.79080500	0.26153100
H	-0.54248800	-2.53188200	-1.30599700
H	-0.08155300	2.34179400	-1.92112800
H	0.51326900	2.53535700	0.42091900

TS for B-H delivery involving aminoborane 4



Note: Only selected H atoms are shown for clarity.

$E_{absolute}$ = -1946.85109288 a.u.

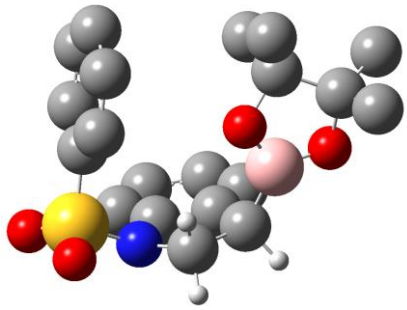
G_{corr} = 0.549487 a.u.

Cartesian coordinates:

C	-3.59304700	-3.98701900	0.40969300
C	-2.62127300	-3.59145100	-0.50167900
C	-2.32530100	-2.25125600	-0.81037400
C	-3.11863200	-1.29324800	-0.13833900
C	-4.07486100	-1.67494100	0.80764600
C	-4.31155900	-3.01619400	1.08760400
H	-3.76766900	-5.04126100	0.60132200
H	-2.02672700	-4.35238400	-0.99727800
H	-4.65932500	-0.94862700	1.35425800
H	-5.05849100	-3.28401500	1.82781100
N	-2.96150700	0.16785900	-0.44530400
B	-0.99089500	-2.01485600	-1.71164100
H	-0.22820100	-1.26633400	-1.05366600
H	-0.41578400	-3.08452600	-1.83586300
H	-1.12182200	-1.46968500	-2.79193400
C	-4.01749200	0.98485700	0.21322000
C	-3.16598900	0.33705200	-1.91606900
B	-1.43695800	0.89894100	0.02627100
O	-0.59739600	0.99839700	-1.09531400
O	-1.68007800	2.21639000	0.51774300
C	-0.11499500	2.32634800	-1.25185200
C	-1.08601100	3.18769000	-0.34952100
C	-0.86272200	-0.09182400	1.34686500
C	-0.11873700	-1.27387700	0.91556700
H	-1.75758800	-0.36034900	1.91432100
H	-0.50564100	-2.25093700	0.67481400
N	1.18205400	-1.12805000	1.20302600
C	0.16722700	0.68540500	2.09666800
C	1.41037300	0.07692200	1.92914800
C	2.58563000	0.58921600	2.45813400
H	3.53326500	0.08173900	2.34126500
C	0.07974800	1.85200600	2.84330400
H	-0.87648900	2.34517700	2.96487200
C	1.24307200	2.38341400	3.39361600
C	2.47875900	1.76606900	3.19405100
H	3.37232500	2.19682800	3.63283400
H	1.18876100	3.29332100	3.98228800
S	2.41288300	-2.22137900	0.62900900
O	3.45066900	-2.18283000	1.63736400
O	1.70135100	-3.42886800	0.29001100
C	2.96248400	-1.36709400	-0.81959800
C	4.02699100	-0.47321700	-0.70415900
C	2.29004800	-1.57458000	-2.02062800
C	4.41650900	0.24287400	-1.82742800
H	4.54356200	-0.35587800	0.24073200
C	2.68944900	-0.83921000	-3.13227300
H	1.46845600	-2.27961700	-2.08069500
C	3.74268200	0.06479500	-3.03551400
H	5.24280800	0.94192400	-1.76023300
H	2.16865200	-0.97915800	-4.07267600

H	4.04671400	0.63348200	-3.90846300
C	-2.20255500	3.89857500	-1.12573400
H	-2.90881400	4.32864100	-0.40950700
H	-1.80540600	4.71021200	-1.74158300
H	-2.75616700	3.22632800	-1.78241700
C	-0.15922100	2.66683700	-2.74023800
H	-1.15947300	2.53318800	-3.15591800
H	0.16273900	3.69757600	-2.92044900
H	0.51573000	1.99527800	-3.27716200
C	1.34680100	2.35235900	-0.79303200
H	1.44657100	2.13856500	0.27170700
H	1.88944900	1.57958000	-1.34359300
H	1.81744700	3.31945600	-0.99516300
C	-0.37800800	4.24733900	0.49379300
H	0.08904600	4.99814600	-0.15155500
H	-1.10879700	4.75566600	1.12974700
H	0.38822000	3.81566900	1.13537100
H	-2.37882000	-0.18363000	-2.45151000
H	-3.87884800	0.99229100	1.29414100
H	-4.14454500	-0.07208700	-2.17894200
H	-5.00364000	0.59154500	-0.04130200
H	-3.13101700	1.39710200	-2.15731400
H	-3.92374500	2.00794700	-0.13526700

HBpin hydroborated product (6b, A4 and B4)



Note: Only selected H atoms are shown for clarity.

$E_{absolute}$ = -1555.28889843 a.u.

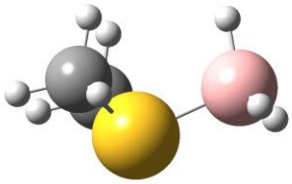
G_{corr} = 0.368679 a.u.

Cartesian coordinates:

H	0.54199300	0.38928100	-2.09616500
B	-1.57816200	-0.73412600	-0.98672000
O	-1.49650000	0.56553400	-0.56866400
O	-2.80924100	-1.29614400	-0.79028000
C	-2.67174800	0.80737100	0.23864400

C	-3.68682000	-0.23736200	-0.33995400
C	-0.33179700	-1.54185700	-1.50455900
C	0.81877200	-0.66783500	-2.05932300
H	-0.63028000	-2.30480600	-2.22943900
H	1.12501500	-0.96991900	-3.06196900
N	1.96240400	-0.86181800	-1.12949500
C	0.28195000	-2.19631100	-0.28136400
C	1.59246300	-1.75884900	-0.09432700
C	2.36731800	-2.22991900	0.95927400
H	3.39453200	-1.90928600	1.07580600
C	-0.29198600	-3.08870700	0.61069300
H	-1.31919200	-3.41061500	0.46754200
C	0.46375000	-3.55151600	1.68892100
C	1.77779300	-3.12402400	1.85373900
H	2.36526800	-3.49777500	2.68622200
H	0.02866500	-4.25197400	2.39405700
S	2.94083700	0.46314900	-0.84668400
O	4.06874800	0.00399800	-0.05721300
O	3.11576600	1.09979800	-2.13913500
C	1.96978600	1.56032100	0.17258400
C	1.87853100	1.31981300	1.54234300
C	1.30486100	2.62645300	-0.42405000
C	1.10472700	2.16913100	2.32365400
H	2.41829500	0.49165300	1.98654000
C	0.53552700	3.47105000	0.36904300
H	1.41520000	2.79703800	-1.48876600
C	0.43614600	3.24336200	1.73816000
H	1.02867700	1.99737800	3.39213100
H	0.02156400	4.31271100	-0.08319200
H	-0.16136800	3.90715200	2.35527100
C	-4.43665500	0.27129800	-1.57132000
H	-4.95340600	-0.56824200	-2.04238800
H	-5.17768000	1.02889300	-1.30254900
H	-3.74732100	0.70103700	-2.30350300
C	-3.08818300	2.26130800	0.08584800
H	-3.21531500	2.53278800	-0.96329400
H	-4.02904700	2.44699300	0.61334700
H	-2.31861700	2.90712000	0.51520600
C	-2.27314400	0.51357900	1.68493700
H	-1.97929400	-0.53296400	1.81003400
H	-1.41344100	1.13574000	1.94195000
H	-3.08898600	0.73545500	2.37846400
C	-4.66468900	-0.80877300	0.67545000
H	-5.28451600	-0.01259900	1.09960000
H	-5.32445600	-1.52959200	0.18613200
H	-4.14549800	-1.31919300	1.48796400

BH_3•DMS



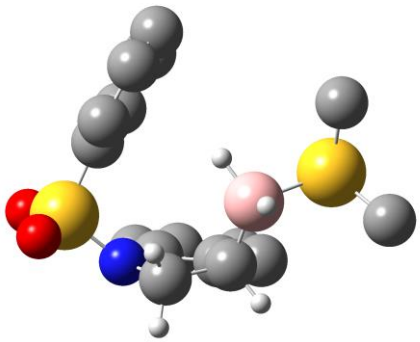
$E_{absolute}$ = -504.66907717 a.u.

G_{corr} = 0.079068 a.u.

Cartesian coordinates:

B	0.28229800	1.80341500	0.00000000
H	1.47537400	1.58248400	0.00000000
H	-0.14857900	2.29910800	1.01601200
H	-0.14857900	2.29910800	-1.01601200
S	-0.53758300	0.01293000	0.00000000
C	0.28229800	-0.80741700	1.38401600
H	-0.08037300	-0.33069200	2.29516000
H	0.03158900	-1.86930000	1.39643500
H	1.36080300	-0.65783300	1.30331000
C	0.28229800	-0.80741700	-1.38401600
H	0.03158900	-1.86930000	-1.39643500
H	-0.08037300	-0.33069200	-2.29516000
H	1.36080300	-0.65783300	-1.30331000

Hydroborated BH_2•DMS adduct (B2)



Note: Only selected H atoms are shown for clarity.

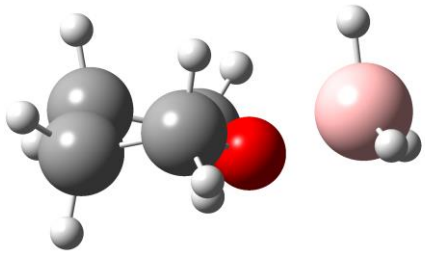
$E_{absolute}$ = -1648.08789359 a.u.

G_{corr} = 0.287681 a.u.

Cartesian coordinates:

B	-1.60655100	0.55881200	-0.99262500
C	-1.01025600	-0.88215700	-1.44819600
C	-0.68587300	-1.81740000	-0.30969200
C	0.69045800	-1.84665300	-0.07171800
H	-1.65846700	-1.37612200	-2.18203100
H	0.56135200	0.38505700	-2.37367700
C	0.38810300	-0.65341200	-2.08326300
H	0.55059600	-1.27831400	-2.96632400
N	1.36940100	-1.06505700	-1.04714600
C	-1.52664300	-2.57952500	0.48816100
C	-0.99040100	-3.34002000	1.52915900
H	-1.64543900	-3.93771300	2.15485200
C	0.38184100	-3.34417600	1.75810800
H	0.79367400	-3.94500300	2.56264700
C	1.24703400	-2.60803300	0.94753700
H	2.31864500	-2.62521400	1.09912800
H	-2.59818400	-2.59043400	0.30564200
S	2.59573100	-0.01246900	-0.62982400
O	3.09193200	0.53974900	-1.87784100
O	3.46410000	-0.72131000	0.29330200
H	-0.91672500	1.13142500	-0.18439000
C	1.80461900	1.30935200	0.26940800
C	1.57312600	2.52081300	-0.37243200
C	1.36036900	1.07632200	1.56940200
C	0.87655900	3.51924700	0.30020400
H	1.94256200	2.66911500	-1.38073900
C	0.65711200	2.07797900	2.22748800
H	1.56104000	0.12663200	2.05208800
C	0.41457000	3.29582900	1.59394200
H	0.69609100	4.47147900	-0.18728800
H	0.30547800	1.91063200	3.24029900
H	-0.12557500	4.07895200	2.11757700
H	-1.96100400	1.26400200	-1.91782700
S	-3.26762000	0.36154200	0.07938100
C	-3.59585400	2.10074300	0.43279200
H	-3.55351400	2.67323300	-0.49577900
H	-4.56550400	2.20791600	0.92058700
H	-2.79876500	2.43606500	1.09754300
C	-4.54881000	0.02204200	-1.14838000
H	-5.53615300	0.08788000	-0.68919600
H	-4.45300500	0.72594300	-1.97751500
H	-4.38392300	-0.99258600	-1.51417500

BH_3•THF



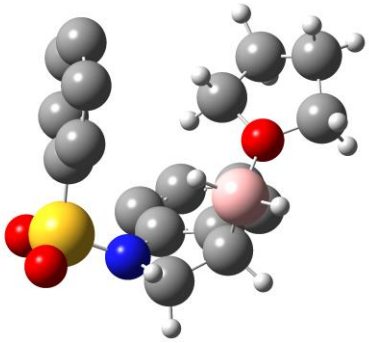
$E_{absolute}$ = -259.09091144 a.u.

G_{corr} = 0.120445 a.u.

Cartesian coordinates:

B	2.28833500	-0.00918400	0.15701100
H	2.20434700	0.13145500	1.36380800
H	2.74510700	0.94390000	-0.43061500
H	2.71132200	-1.08448600	-0.20004100
O	0.72046900	-0.03986200	-0.33313700
C	-0.02923700	1.18821400	-0.13948700
C	-0.05651200	-1.16981000	0.11161700
C	-1.43945700	0.74749000	0.26283800
H	0.48047100	1.77212800	0.62895400
H	0.00921800	1.72192100	-1.09045200
C	-1.48632300	-0.73176600	-0.14407900
H	0.28234800	-2.03039000	-0.46412000
H	0.14822900	-1.33545700	1.17561200
H	-2.21014900	1.34662400	-0.22529300
H	-1.57129500	0.84414800	1.34389900
H	-1.73006000	-0.83921700	-1.20491500
H	-2.20578500	-1.31056600	0.43787000

Hydroborated BH_2•THF adduct



Note: Only selected H atoms are shown for clarity.

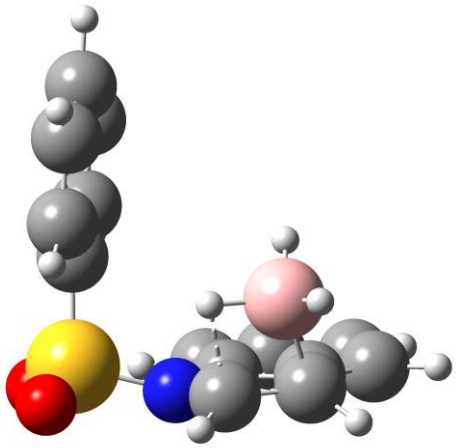
$E_{absolute}$ = -1402.51337899 a.u.

G_{corr} = 0.330522 a.u.

Cartesian coordinates:

B	1.27525900	0.00796100	2.15706700
C	0.69188200	-1.49236900	1.81095600
C	0.84574500	-1.88109100	0.36298300
C	-0.37892100	-1.78415700	-0.30642500
H	1.16956400	-2.23859100	2.45390000
H	-1.24300500	-0.76036700	2.61924000
C	-0.84299500	-1.56217600	1.99805800
H	-1.17149700	-2.51689100	2.42158200
N	-1.39888000	-1.46668100	0.62336900
C	1.98056700	-2.23202000	-0.35271200
C	1.89140900	-2.45004600	-1.73061200
H	2.77781800	-2.72843000	-2.29232700
C	0.66752100	-2.32682200	-2.38052400
H	0.60135700	-2.50660100	-3.44878000
C	-0.49331100	-2.00798700	-1.67240600
H	-1.45802400	-1.95347600	-2.16174900
H	2.93442600	-2.33677000	0.15704500
S	-2.66454600	-0.45852200	0.25112000
O	-3.40934800	-0.27852000	1.48356100
O	-3.28640700	-0.97856600	-0.95478600
H	0.42614500	0.87015700	2.08899200
C	-1.94265600	1.11689900	-0.18988700
C	-1.73876300	2.07246300	0.80105400
C	-1.58480800	1.35893700	-1.51447000
C	-1.16409700	3.29136800	0.45725500
H	-2.04179600	1.86329800	1.82028700
C	-1.00095100	2.57764200	-1.84560200
H	-1.78295800	0.60898100	-2.27071900
C	-0.79365300	3.54246300	-0.86206100
H	-1.01062400	4.04654300	1.22074400
H	-0.72698300	2.77947100	-2.87589400
H	-0.35042300	4.49756600	-1.12611000
H	1.94021800	0.06244800	3.16784700
O	2.31660100	0.44884200	0.99866300
C	3.74539500	0.53713400	1.17856000
C	1.86909400	1.15241900	-0.18354600
C	4.22062400	1.41231500	0.02185400
H	3.93447800	0.95574700	2.16784200
H	4.14389700	-0.47996100	1.13135200
C	3.12292600	1.22124100	-1.03274400
H	1.05748500	0.57181900	-0.61991800
H	1.49446700	2.13243700	0.12597100
H	5.20998100	1.11622200	-0.33137300
H	4.26947200	2.45985800	0.33343700
H	3.25480800	0.27516200	-1.56548500
H	3.08296900	2.03336400	-1.76060500

TSB(1-2)



$E_{absolute}$ = -1169.80363782 a.u.

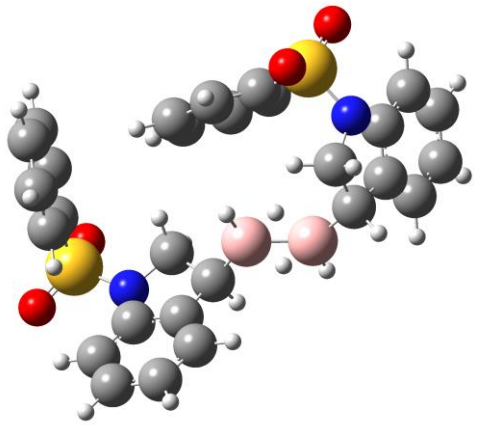
G_{corr} = 0.213170 a.u.

Cartesian coordinates:

B	0.36037700	-0.64167200	2.55581500
C	1.79061400	-1.18027000	1.75804400
C	2.38701000	-0.17562700	0.85297400
C	1.62085300	-0.12117900	-0.31532000
H	2.39779000	-1.79160900	2.41134200
H	-0.61902600	-1.10681700	1.93702300
C	0.68923900	-1.73318000	1.03780600
H	0.26759800	-2.72197200	1.14772700
N	0.60412800	-1.11296000	-0.21390500
C	3.48695900	0.65759700	0.99485000
C	3.79452700	1.54190300	-0.03651700
H	4.65048600	2.20166300	0.05830800
C	3.01502300	1.58523800	-1.19257300
H	3.27681300	2.27307800	-1.98967700
C	1.91260200	0.74859200	-1.35624700
H	1.32966700	0.75110700	-2.26870300
H	4.08769000	0.62417800	1.89780300
S	-0.84097800	-1.14739500	-1.10238800
O	-1.43139400	-2.43422000	-0.79302500
O	-0.49037400	-0.75338800	-2.45052300
H	0.25122400	0.54164500	2.41273000
C	-1.82247200	0.12656400	-0.35380600
C	-2.80284800	-0.23542100	0.56494100
C	-1.54982200	1.46001400	-0.65281000
C	-3.52364500	0.76767000	1.20360600
H	-2.99384700	-1.28340600	0.76420300
C	-2.27392700	2.45008700	-0.00222400
H	-0.79004100	1.71620600	-1.38154500
C	-3.25499200	2.10395500	0.92501900
H	-4.29066800	0.50251900	1.92266200

H	-2.07373300	3.49345200	-0.21964000
H	-3.81475500	2.88340600	1.43145600
H	0.30507800	-1.20085800	3.61471700

B2



$E_{absolute}$ = -2339.72574189 a.u.

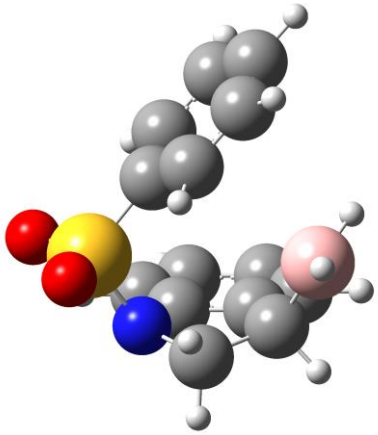
G_{corr} = 0.460185 a.u.

Cartesian coordinates:

H	-1.58632300	3.19240600	-0.79259400
H	-0.12030400	0.71320800	1.30281100
H	-0.75416600	2.60735900	0.97507300
H	-1.17531700	1.22907000	-0.35197800
B	-0.17230500	1.54824700	0.45064200
B	-1.69332400	2.37354900	0.07224200
C	-4.15509700	1.85436800	-0.30560800
C	-3.29516000	1.00530500	1.76972200
C	-4.76627300	0.62796900	-0.05130100
C	-4.52463800	2.59764000	-1.41639600
H	-2.35651000	0.49637100	2.00387900
C	-5.77047400	0.13114000	-0.87536300
C	-5.51165600	2.10345700	-2.26840700
H	-4.04740200	3.55175200	-1.61844900
C	-6.12298800	0.88217100	-1.99622200
H	-6.24938700	-0.81314000	-0.65262700
H	-5.80864900	2.67568400	-3.14093400
H	-6.89771400	0.50877400	-2.65795300
C	2.27785400	2.43592800	0.50754400
C	1.77649900	0.76977300	-1.09663000
C	3.48704300	1.91245900	0.04013700
C	2.27225200	3.31726200	1.57570000
H	1.57871100	-0.16480100	-0.55741100
C	4.70275200	2.28138800	0.60341900
C	3.48047600	3.67325200	2.17719000
H	1.33726600	3.73238400	1.94234600

C	4.67717800	3.15999100	1.68789100
H	5.63515200	1.89555100	0.21210500
H	3.48605100	4.35829400	3.01818400
H	5.61569000	3.44955200	2.14931100
C	1.13295500	1.95808000	-0.36107600
C	-3.11746700	2.16330300	0.75245600
N	3.22928300	1.05476100	-1.06537400
N	-4.24777700	0.05472300	1.14200100
H	1.43707000	0.65804300	-2.12599500
H	0.90622000	2.74668600	-1.09103400
H	-3.37355700	3.11275000	1.23913000
H	-3.72299600	1.35275200	2.71219700
S	4.22489100	-0.20380400	-1.52694400
S	-3.87337600	-1.57364400	1.24048300
O	5.59427700	0.25440200	-1.39483200
O	3.69509100	-0.67745900	-2.79338100
O	-3.49154800	-1.80944100	2.62028100
O	-4.95882100	-2.29885100	0.60819900
C	3.93181700	-1.50444800	-0.33115000
C	4.15968600	-1.27461700	1.02483200
C	3.47630700	-2.73647900	-0.79039000
C	3.90755000	-2.29693900	1.93219500
H	4.52656500	-0.31399800	1.36924800
C	3.24336200	-3.75794600	0.12624000
H	3.31644700	-2.88228300	-1.85274500
C	3.45255500	-3.53612900	1.48452000
H	4.07408800	-2.12765900	2.99047500
H	2.89075100	-4.72281200	-0.22225800
H	3.26298600	-4.33097600	2.19844500
C	-2.40888700	-1.76862200	0.23750100
C	-2.49549600	-1.59971900	-1.14493900
C	-1.20139000	-2.06785600	0.85888000
C	-1.34157300	-1.72675700	-1.90980100
H	-3.44943800	-1.38345600	-1.61318100
C	-0.05669400	-2.20854000	0.08057600
H	-1.17270700	-2.19549500	1.93508400
C	-0.12736100	-2.03750700	-1.29920800
H	-1.39335500	-1.59663700	-2.98546900
H	0.89209600	-2.44467000	0.55140200
H	0.77130700	-2.13767600	-1.90047200

3-BH_2-1-$PhSO_2$ indoline



$E_{absolute}$ = -1169.83175737 a.u.

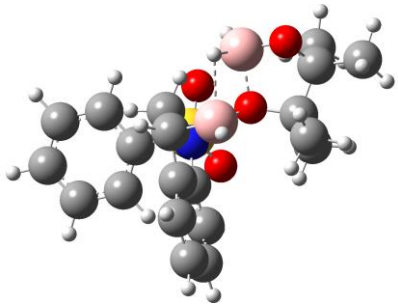
G_{corr} = 0.215873 a.u.

Cartesian coordinates:

B	-0.45274900	1.37591100	2.27951400
C	0.71949300	0.33349300	2.13777700
C	1.66775300	0.51709000	0.97775200
C	1.56748900	-0.56724200	0.10704900
H	1.24926300	0.47451900	3.09668500
H	-0.69016000	-1.40261600	2.26159300
C	0.34100000	-1.16665800	1.99872300
H	0.99567700	-1.79872600	2.60415900
N	0.60110000	-1.51391500	0.57964500
C	2.53353600	1.55831800	0.68006000
C	3.29415300	1.49312600	-0.48763400
H	3.98018700	2.29861700	-0.72886500
C	3.18764400	0.39825600	-1.34370000
H	3.79043700	0.35837800	-2.24510600
C	2.32161700	-0.65565300	-1.05406300
H	2.21963500	-1.50962700	-1.71225100
H	2.61394800	2.41371000	1.34426500
S	-0.76113700	-1.71109300	-0.40153700
O	-1.69559900	-2.52180800	0.35821500
O	-0.27559700	-2.11428600	-1.70721200
H	-0.36468700	2.46474300	1.79268000
C	-1.44834700	-0.06903800	-0.55395700
C	-2.42871000	0.34189600	0.34868800
C	-0.94738400	0.79591000	-1.52385500
C	-2.91764000	1.64366700	0.26895300
H	-2.82007900	-0.36224800	1.07472700
C	-1.44340600	2.09332200	-1.59020400
H	-0.19002100	0.44914900	-2.21699700
C	-2.42463300	2.51624300	-0.69772700
H	-3.68264700	1.97215000	0.96393900
H	-1.06208500	2.77525400	-2.34253100
H	-2.80904900	3.52913100	-0.75628600

H	-1.36200000	1.12526100	3.01828800

TSB(2-3)



$E_{absolute}$ = -1581.59933041 a.u.

G_{corr} = 0.398461 a.u.

Cartesian coordinates:

B	-1.81061100	0.85012100	1.61081900
O	-2.21672100	-0.00035800	0.58200700
H	-2.70808700	-0.58514600	2.83181000
B	-2.83002700	-1.22626400	1.79066800
H	-2.04232200	-2.12254700	1.64539700
O	-4.12591500	-1.29969700	1.26231500
C	-4.11005300	-1.16526900	-0.15239700
C	-3.32452100	0.17590600	-0.36466600
H	-2.51036700	1.71976800	2.02784000
C	-0.26188400	0.81305900	1.93168500
C	0.49622600	-0.41962700	1.41001300
C	0.20532400	1.89735100	0.97472900
H	-0.02795400	1.03671600	2.97429000
H	1.45961400	-0.52833500	1.92873300
H	-0.06172600	-1.35019300	1.48804400
C	0.72825600	1.30445100	-0.18236200
N	0.72891600	-0.10080600	-0.01771300
C	1.10409200	2.07278800	-1.27719700
C	0.97081900	3.45971800	-1.17700700
H	1.26747900	4.07514600	-2.02040300
C	0.46215800	4.06120200	-0.03119000
H	0.36516300	5.14028500	0.02040700
C	0.05992800	3.27347300	1.04942400
H	-0.36176800	3.72806500	1.94067000
H	1.47224800	1.60823500	-2.18250900
C	-4.16009300	1.39923600	-0.01447300
H	-3.53823100	2.29813600	0.00424700
H	-4.92475300	1.54157200	-0.78182000
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C	-5.55656900	-1.09432000	-0.62729200
H	-5.61188000	-0.81901900	-1.68520200
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H	-6.12891400	-0.37529900	-0.03901200
C	-3.40653800	-2.35380600	-0.82194600
H	-3.84505000	-3.27577300	-0.43244800
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H	-2.33322700	-2.37579000	-0.62274500
C	-2.66972200	0.33587100	-1.72948800
H	-2.16009400	1.30167600	-1.79098400
H	-1.93126000	-0.44604300	-1.91018000
H	-3.42998100	0.29825300	-2.51542800
S	1.63942400	-1.16425100	-0.91841600
O	1.16007400	-2.48636200	-0.56321600
O	1.62463600	-0.68709600	-2.28928400
C	3.29192600	-0.99210200	-0.27366800
C	4.10507000	0.04069900	-0.73537300
C	3.71356400	-1.85503100	0.73471800
C	5.36259400	0.21038000	-0.16813500
H	3.76103200	0.68880300	-1.53300200
C	4.97507700	-1.67531100	1.29255800
H	3.06284800	-2.66018000	1.05712600
C	5.79491000	-0.64346800	0.84439200
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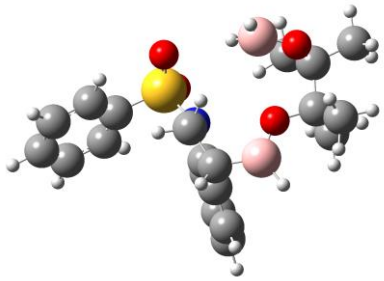
B3



$E_{absolute}$ = -1581.61487881 a.u.

G_{corr} = 0.396793 a.u.

Cartesian coordinates:

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H	-2.92943600	-3.42677900	1.92649000
B	-2.72636700	-2.72563700	0.97372200
H	-1.65826400	-2.68026800	0.43738500
O	-3.79464400	-2.02816800	0.54234900
C	-3.81039100	-1.02812900	-0.48794000
C	-3.64879100	0.34251300	0.25116500
H	-2.32655800	2.14437100	2.04457700
C	-0.19186400	1.00084400	1.86133100

C	0.38450800	-0.33400000	1.35873100
C	0.36216800	1.99117400	0.85553500
H	0.12336800	1.22904000	2.88282200
H	1.32704700	-0.56742000	1.87306300
H	-0.30013300	-1.17424300	1.45926000
C	0.78449100	1.30825000	-0.29037000
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C	1.20676700	1.99363300	-1.42268200
C	1.23603900	3.38867700	-1.36808800
H	1.57335700	3.93914800	-2.24050800
C	0.83525200	4.07896000	-0.22929300
H	0.86571600	5.16325000	-0.21178700
C	0.37728900	3.37658500	0.88689300
H	0.03683900	3.90401300	1.77276000
H	1.49257500	1.46073300	-2.32037100
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H	-4.50312100	1.44415400	1.89990900
H	-5.70269300	0.69257700	0.84942900
H	-4.77577600	-0.31304500	1.98254100
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H	-5.36029000	-0.39840900	-1.89215200
H	-5.22220800	-2.14519100	-1.65801600
H	-5.98033000	-1.15873100	-0.40620800
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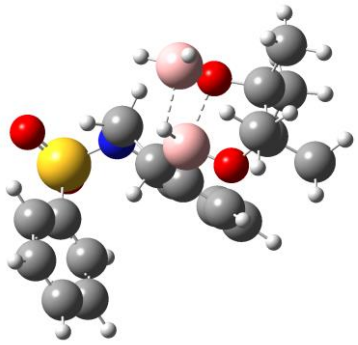
H	-2.70498700	-2.28111600	-1.85280000
H	-2.89563000	-0.61397400	-2.40044200
H	-1.71686800	-0.99926800	-1.13058800
C	-3.60254700	1.52566000	-0.71660600
H	-3.51351400	2.45769300	-0.15161700
H	-2.74207500	1.45226200	-1.38516300
H	-4.51447700	1.58459600	-1.31538700
S	1.56590200	-1.22778000	-0.88754500
O	1.05068500	-2.51518300	-0.46211500
O	1.60180000	-0.83998600	-2.28615800
C	3.20386000	-1.04490900	-0.20758900
C	4.05026500	-0.05751000	-0.70766000
C	3.58323400	-1.85626900	0.85897700
C	5.29616100	0.12135400	-0.11811400
H	3.74082100	0.54785200	-1.55139600
C	4.83370900	-1.66822500	1.43843400
H	2.90898200	-2.63046000	1.20774000
C	5.68509600	-0.67945900	0.95351200
H	5.96721300	0.88357500	-0.49939500
H	5.14386500	-2.29864900	2.26500400
H	6.65962200	-0.53562000	1.40873300

TSB(3-4)



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G_{corr} = 0.398577 a.u.

Cartesian coordinates:

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O	-2.81730100	-0.42482000	-1.42593000
C	-3.92580500	0.08992300	-0.64249400
C	-3.82389700	-0.56522700	0.79101800
H	-1.80067600	-2.27709900	-0.37140900
C	-0.12473400	-0.56994200	-0.02259000
C	0.47458900	-0.51271400	-1.44682200
C	0.10486500	0.85197300	0.44685900
H	0.49784800	-1.23571800	0.59919600
H	0.94139500	-1.43900600	-1.78147900
H	-0.28755700	-0.23325100	-2.17705200
C	1.03408200	1.47781100	-0.38790100
N	1.45989600	0.59813400	-1.43238300
C	1.44917300	2.78625300	-0.18897800
C	0.92372200	3.47220300	0.90528300
H	1.22885600	4.49759500	1.08733000
C	0.00710800	2.86043000	1.75755100
H	-0.39249700	3.41159800	2.60299300
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H	-1.12338500	1.06876700	2.19391800
H	2.16953100	3.24038600	-0.85766100
H	-1.74507300	-1.90653200	-2.62159900
H	-3.57160900	-2.52022900	-1.84995900
C	-4.47006500	-1.95092600	0.90650500
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H	-4.12229500	-2.65363300	0.15063000
C	-3.64886200	1.59200600	-0.60809600
H	-2.72091500	1.80435200	-0.07091800
H	-3.53839800	1.95183700	-1.63350600
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C	-4.41771000	0.33528000	1.87387000

H	-5.46888500	0.55722700	1.66759200
H	-4.36171200	-0.17557900	2.83826700
H	-3.86589600	1.27265000	1.95338200
C	-5.25057200	-0.19325200	-1.33911900
H	-6.07580100	0.18863800	-0.73137100
H	-5.27775700	0.31645500	-2.30543800
H	-5.41434900	-1.25910900	-1.50374800
S	3.08892900	0.15875600	-1.44052900
O	3.24640100	-0.79338500	-2.52524500
O	3.85192800	1.39179800	-1.38382200
C	3.32114400	-0.71758500	0.09651500
C	3.41869800	0.00516000	1.28392900
C	3.28820200	-2.10969900	0.09208500
C	3.46738200	-0.68641300	2.48879000
H	3.45464800	1.08834200	1.25871600
C	3.34440100	-2.78952500	1.30393000
H	3.22723200	-2.63912900	-0.85227200
C	3.42509400	-2.07869300	2.49900700
H	3.53914500	-0.13703800	3.42131600
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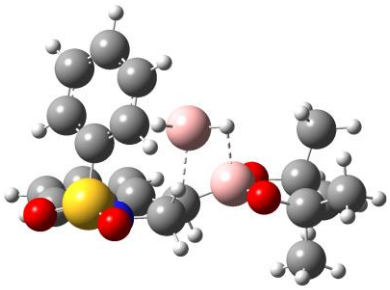
TSB(2-4)



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G_{corr} = 0.398402 a.u.

Cartesian coordinates:

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C	-0.25296300	1.81610200	0.10348400
C	0.02421700	2.88447800	0.93915200
C	-0.98793600	3.80223000	1.21538500
C	-2.24694100	3.64825800	0.64085300
C	-2.52683800	2.58855100	-0.22119200
C	-0.22038700	-0.13204800	-1.33698600
C	0.66900800	0.74479600	-0.42863600
H	1.01140800	2.98660200	1.37814700
H	-0.79061600	4.64025600	1.87532900
H	-3.02644500	4.37315000	0.85209700
H	-3.49640300	2.48063600	-0.68948300

H	0.16095300	-0.19189800	-2.35646800
H	-0.30085700	-1.15245200	-0.95293200
N	-1.53997400	0.54174400	-1.33485400
B	0.54083900	-0.29581400	1.52536500
H	-0.58649700	-0.60941600	1.31526500
H	1.36513800	-1.16094200	1.32849600
H	0.80529300	0.55045100	2.31791400
H	1.36241100	1.30196800	-1.08628800
S	-2.88952300	-0.43890600	-1.49460800
O	-4.03932100	0.43505800	-1.63245500
O	-2.53797600	-1.41436900	-2.50943200
C	-3.00587100	-1.28149000	0.06882300
C	-3.54256500	-0.60612600	1.16347700
C	-2.45876700	-2.55527400	0.19386600
C	-3.51095200	-1.21913200	2.40958100
H	-3.97603700	0.37901100	1.03598700
C	-2.43756700	-3.15884500	1.44670600
H	-2.06529300	-3.05750300	-0.68281300
C	-2.95459300	-2.48877800	2.55163300
H	-3.92247800	-0.70581400	3.27190200
H	-2.01347000	-4.15086400	1.55940000
H	-2.92978300	-2.96031700	3.52865700
C	4.25619400	0.02106200	0.59565600
C	3.98788800	-0.78857200	-0.72023100
B	2.05159300	0.03558400	0.11388500
O	2.55607100	-0.97093800	-0.68584700
O	3.02856700	0.76950900	0.74309300
C	4.40212800	-0.86918500	1.83019000
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H	3.59502200	-1.60339700	1.89401000
C	5.41501000	1.00330200	0.51605900
H	5.52861400	1.51640300	1.47417200
H	6.34940700	0.47621400	0.29935200
H	5.25016800	1.75707300	-0.25539300
C	4.65830700	-2.15263300	-0.77728600
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H	4.31131500	-2.80170700	0.02793700
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H	5.38122000	0.13221500	-2.12722400
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9. NMR Spectra of all new compounds

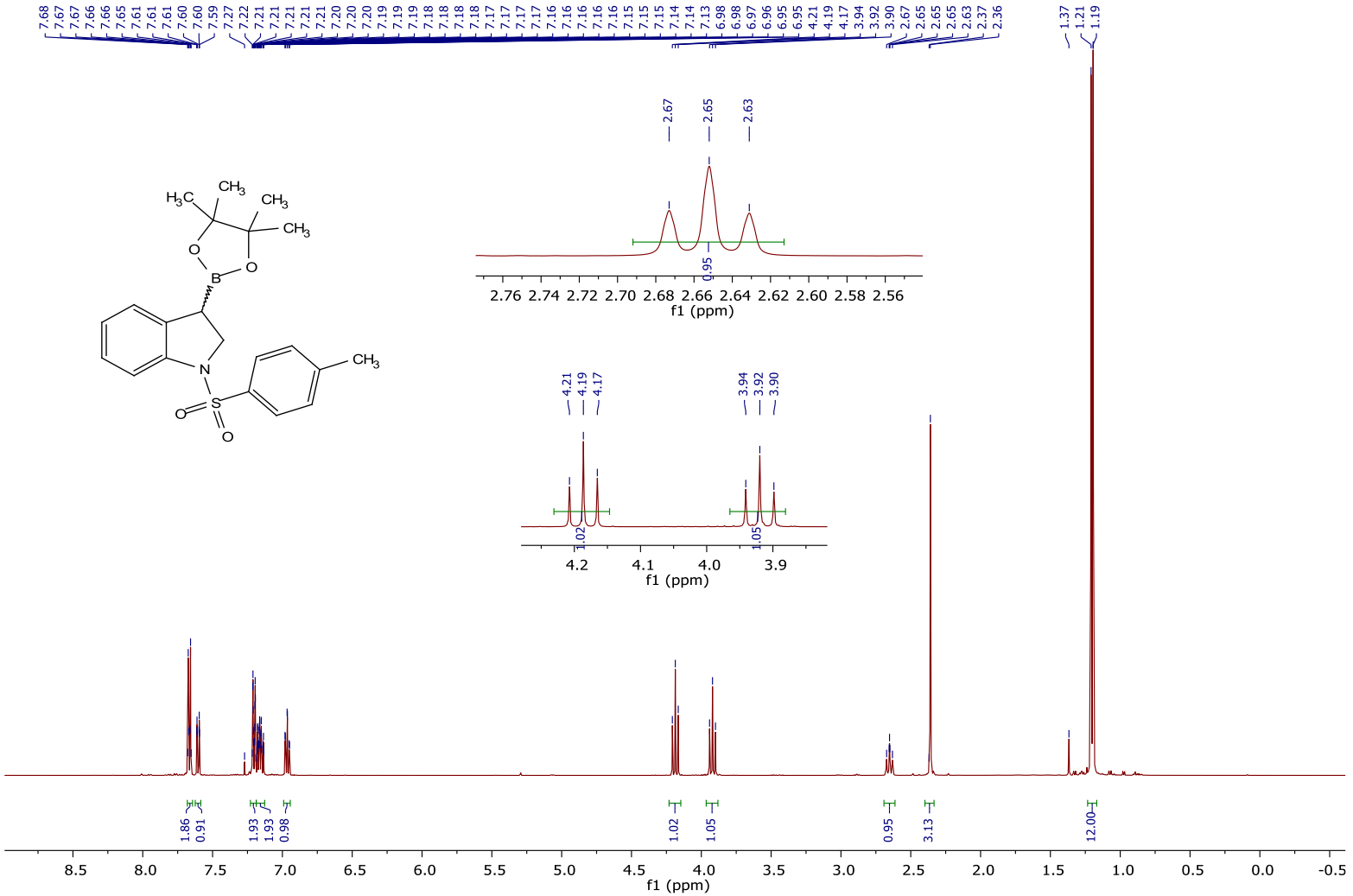

Figure S6. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6a**.

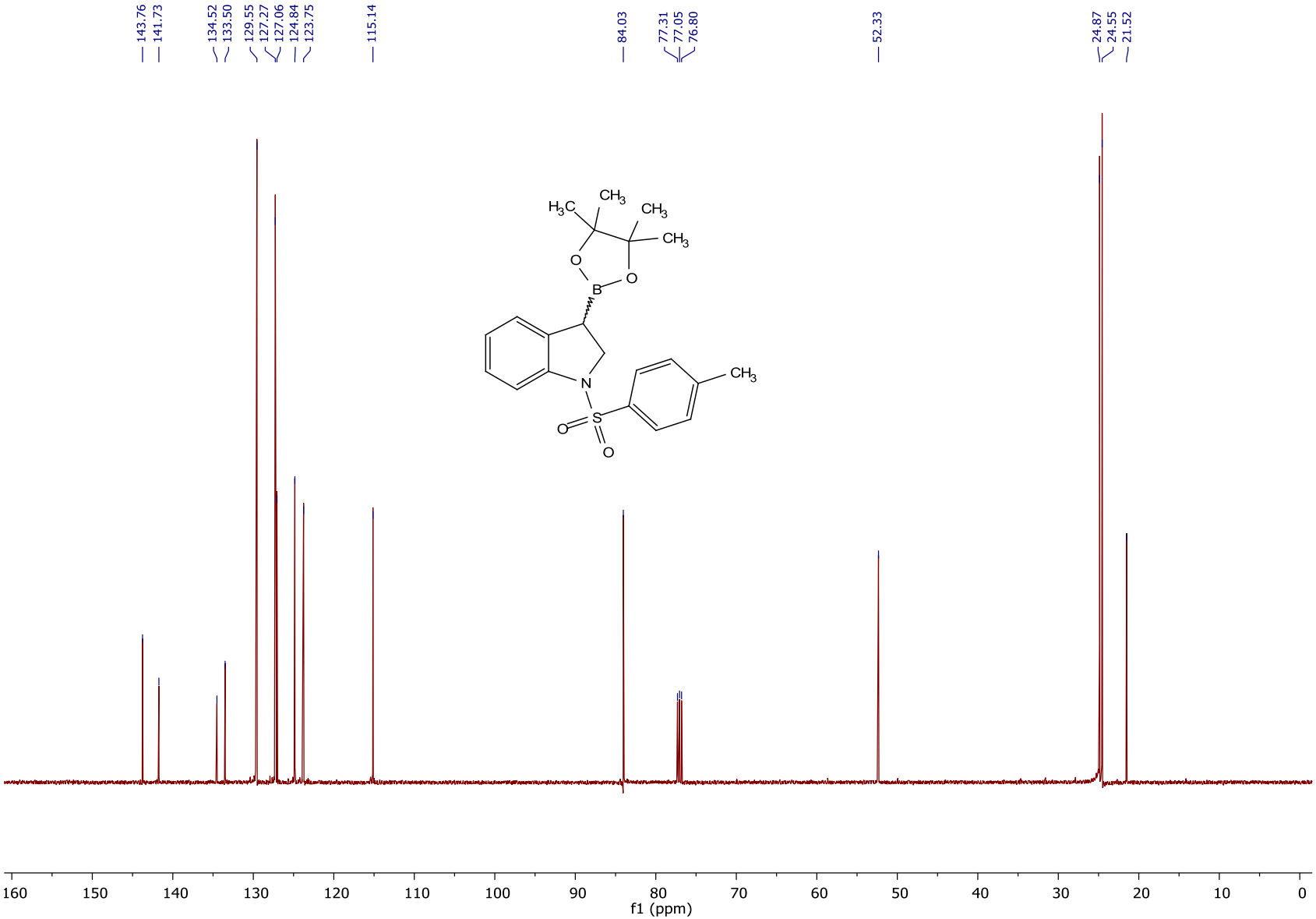

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6a**.

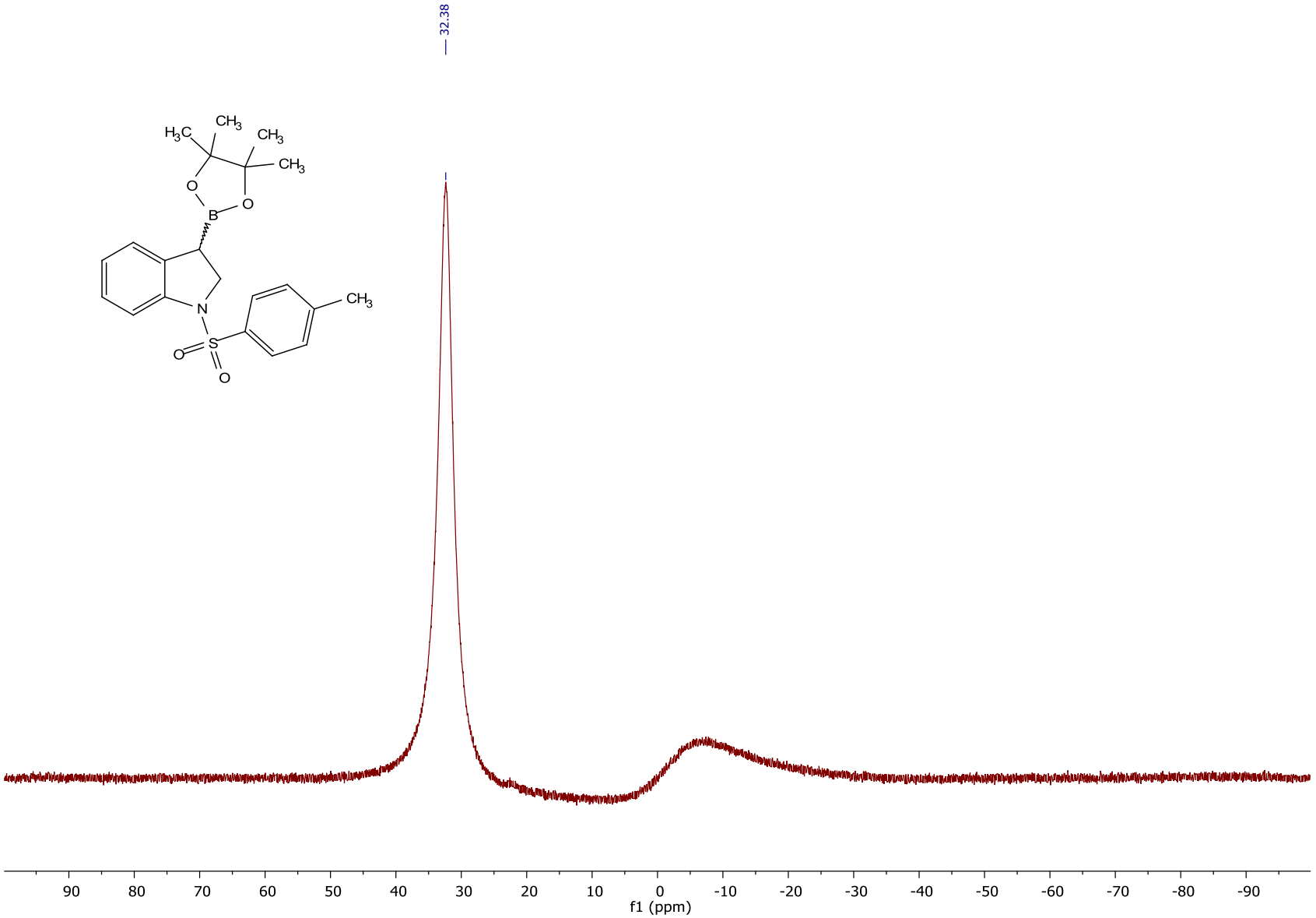

Figure S8. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6a**.

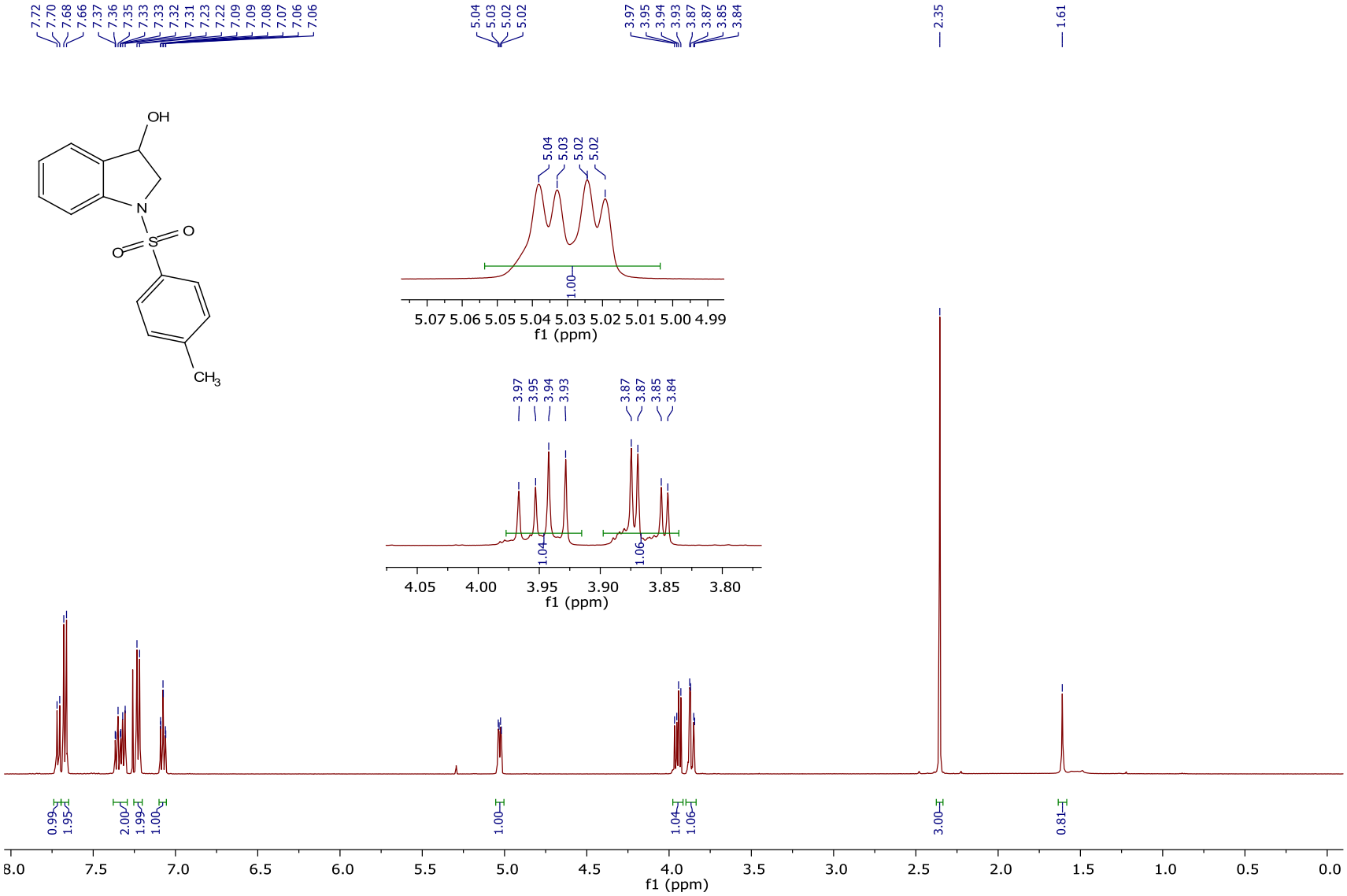

Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6a'**.

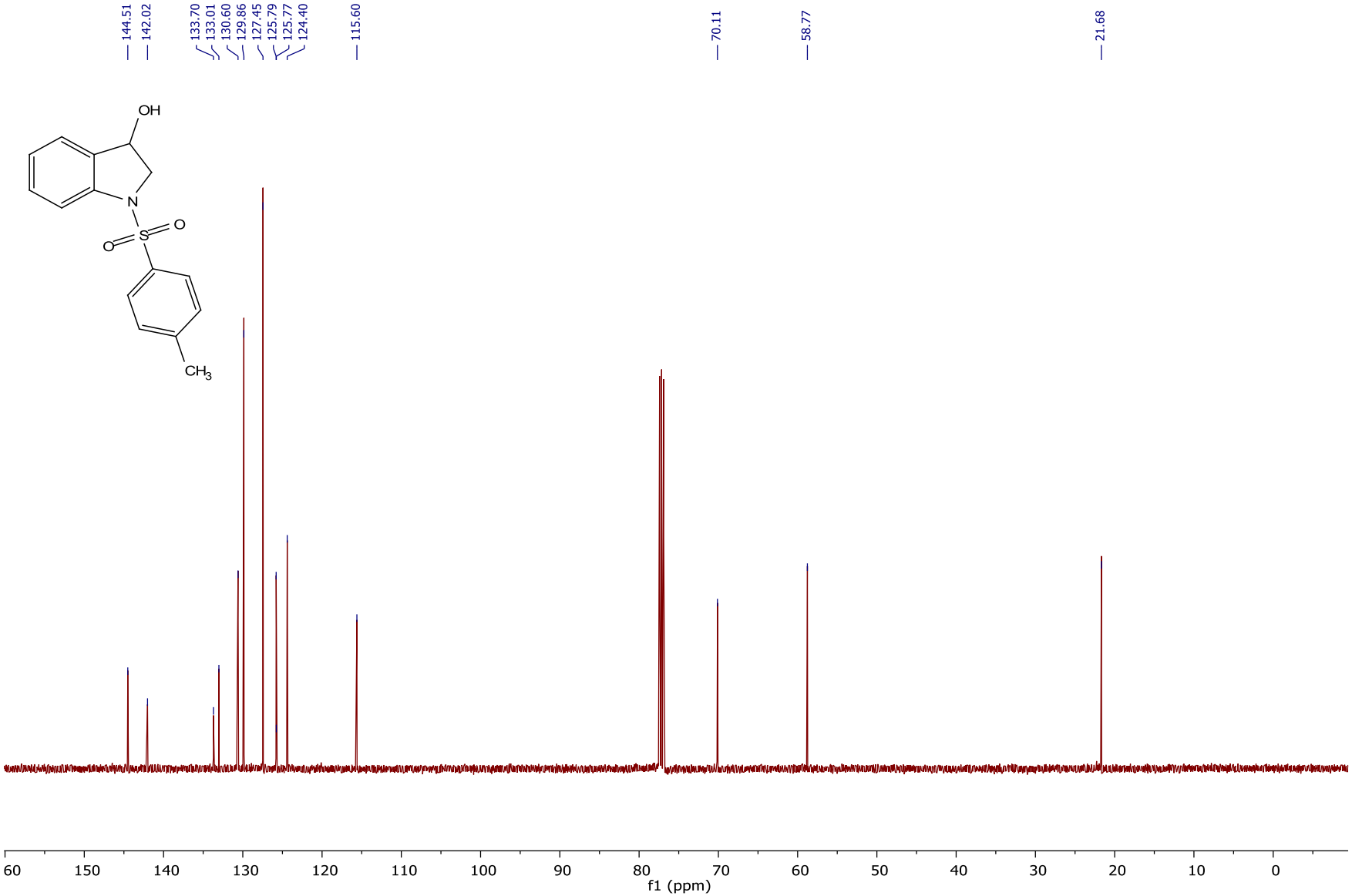

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6a'**.

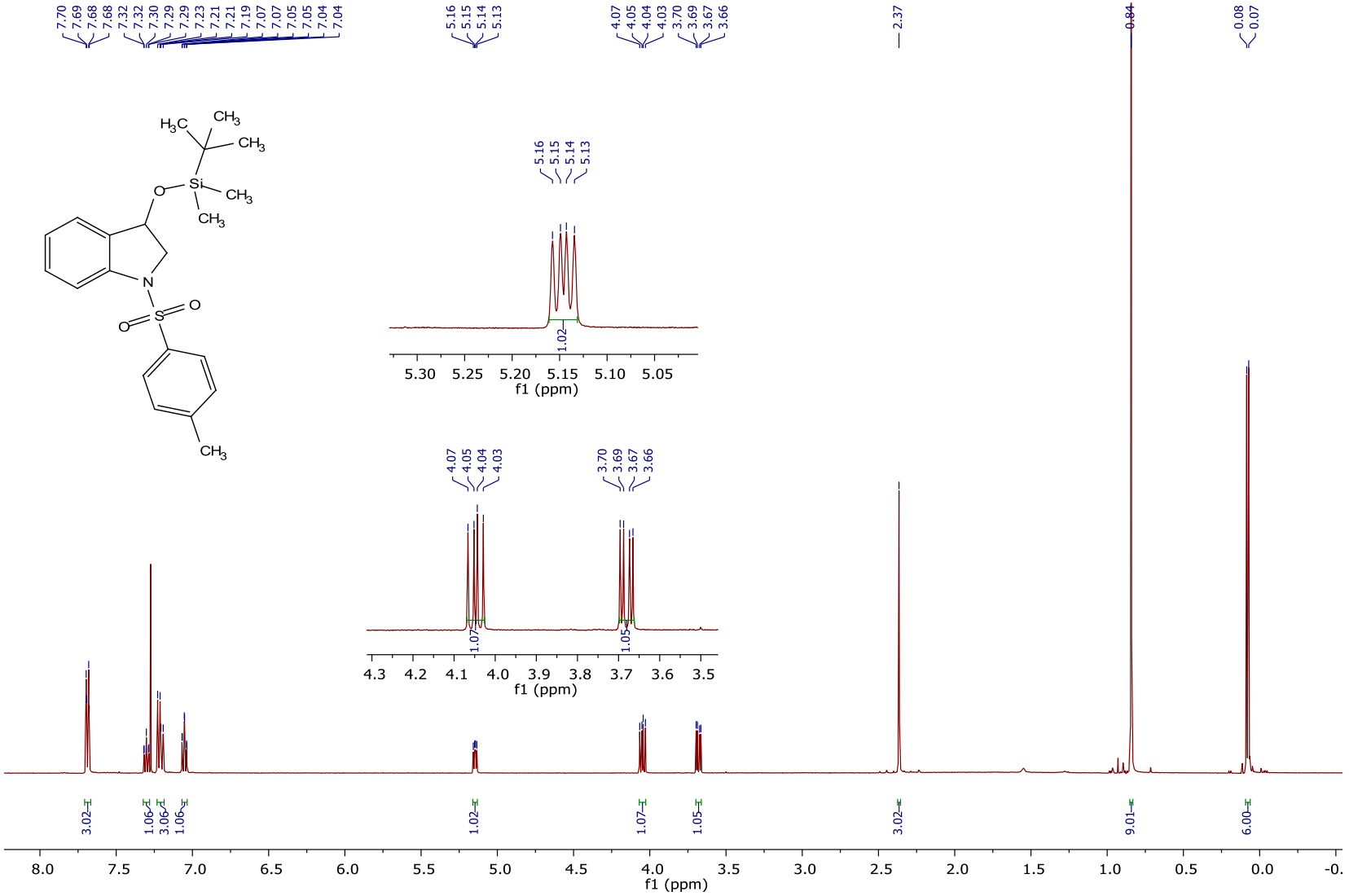

Figure S11. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6''**.

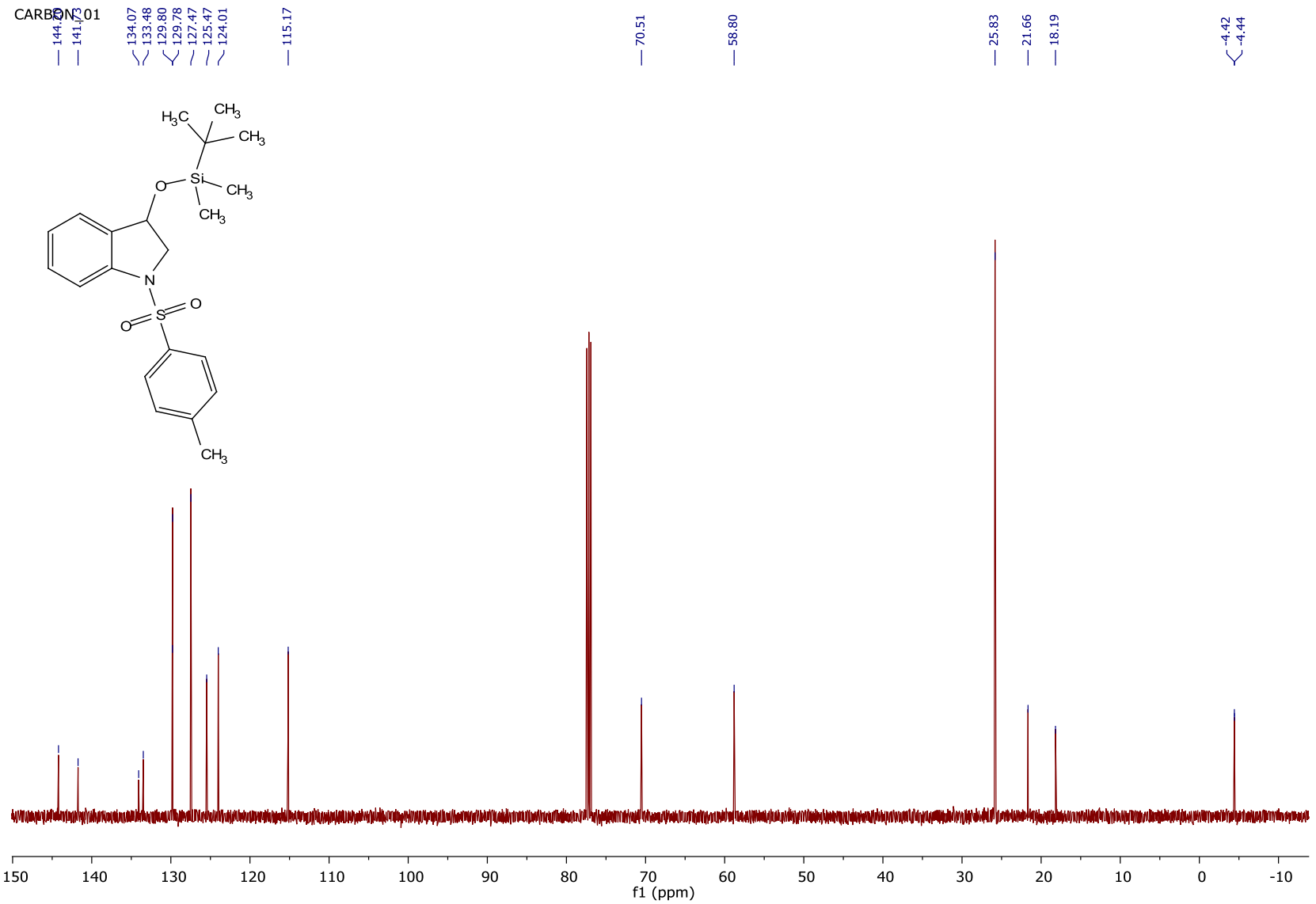

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6a''**.

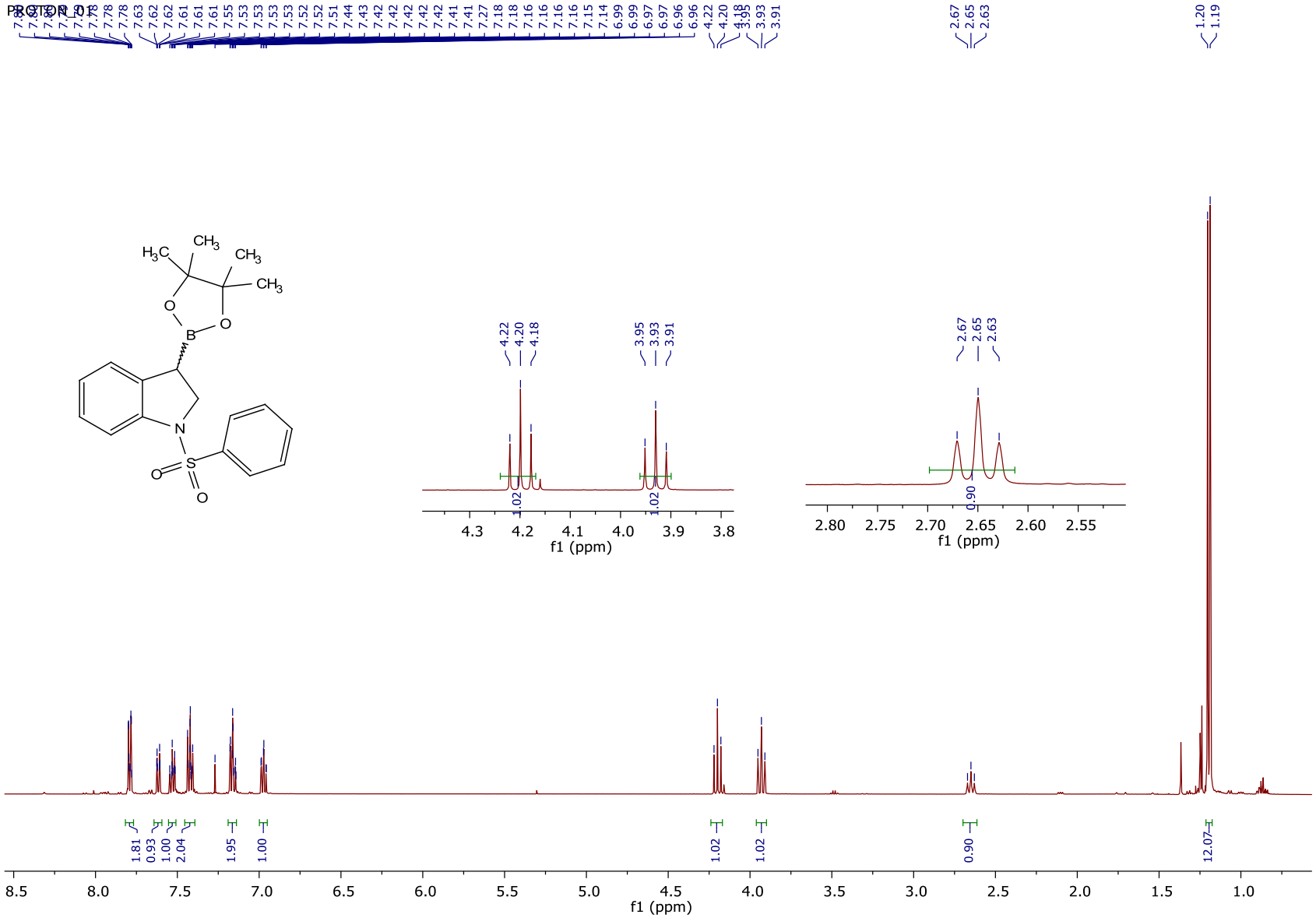

Figure S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6b**.

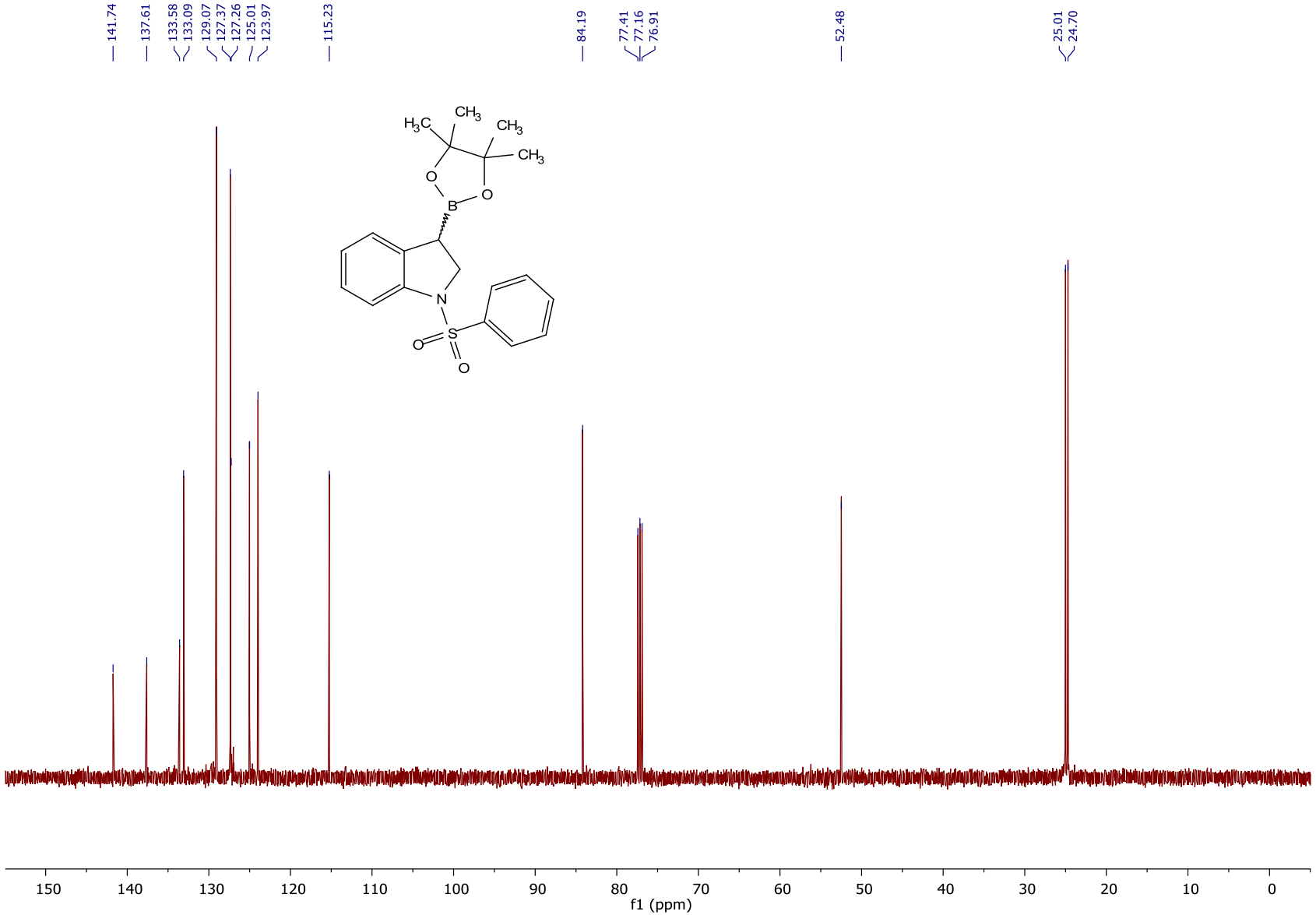

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6b**.

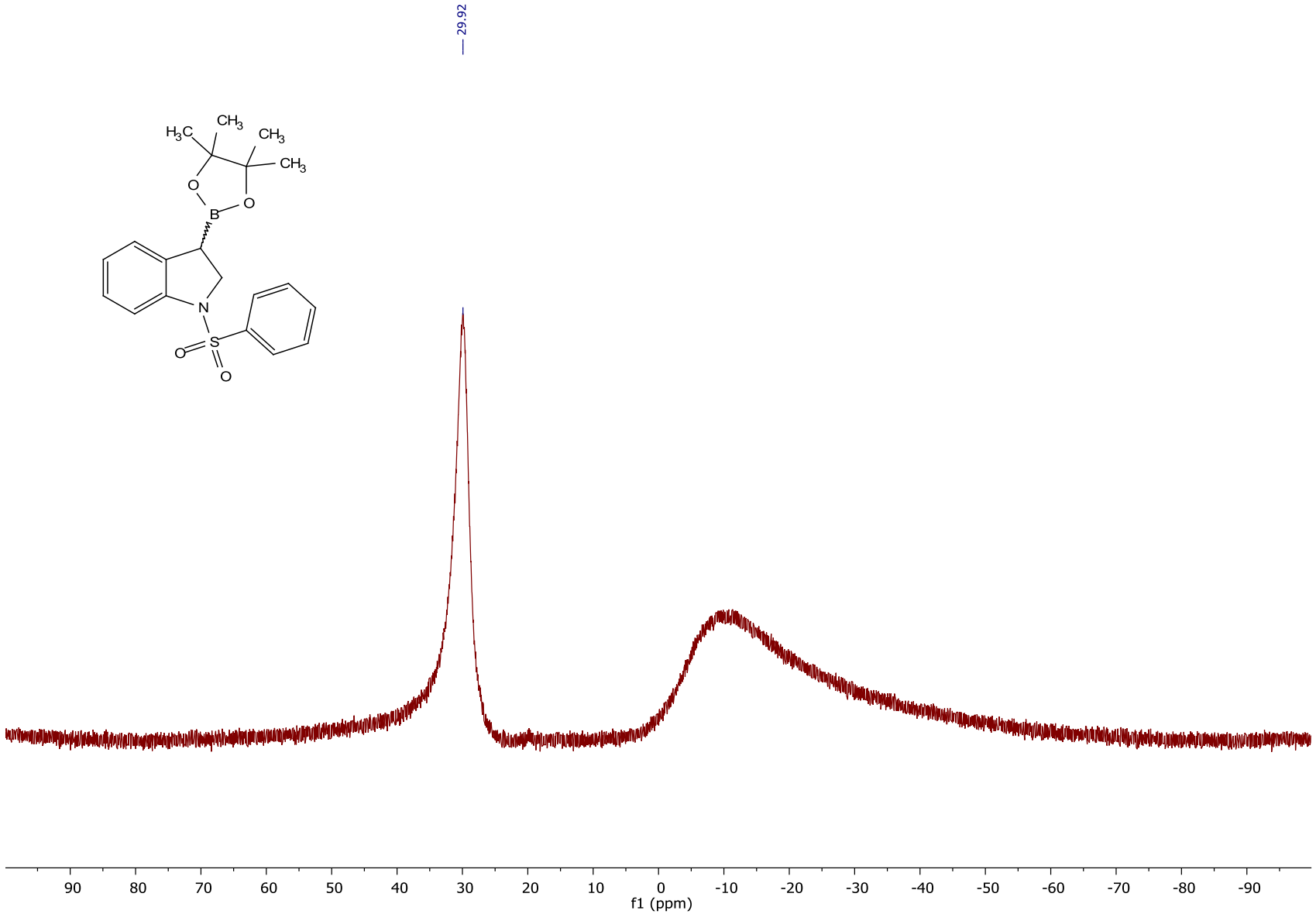

Figure S15. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6b**.

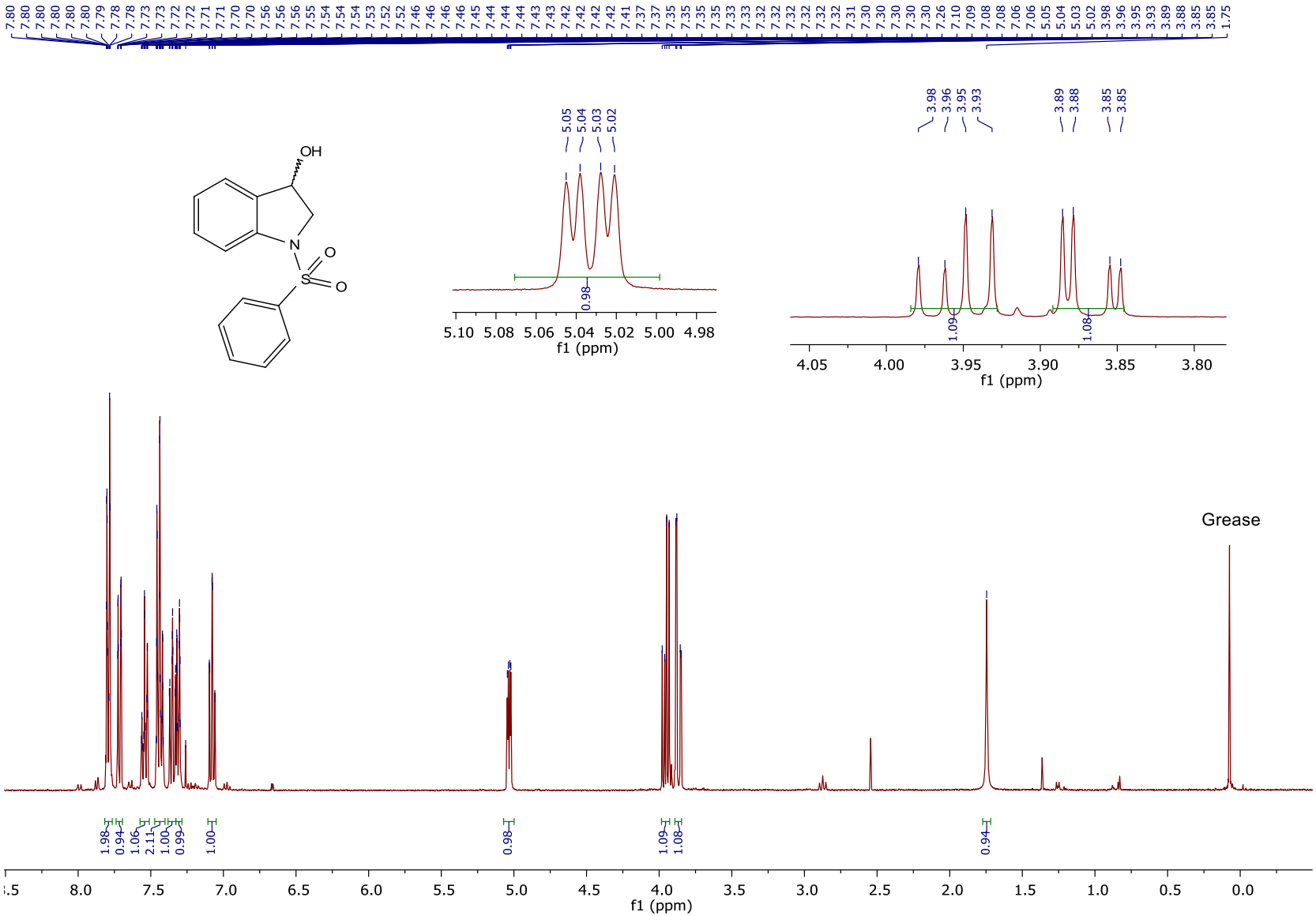

Figure S16. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6b'**.

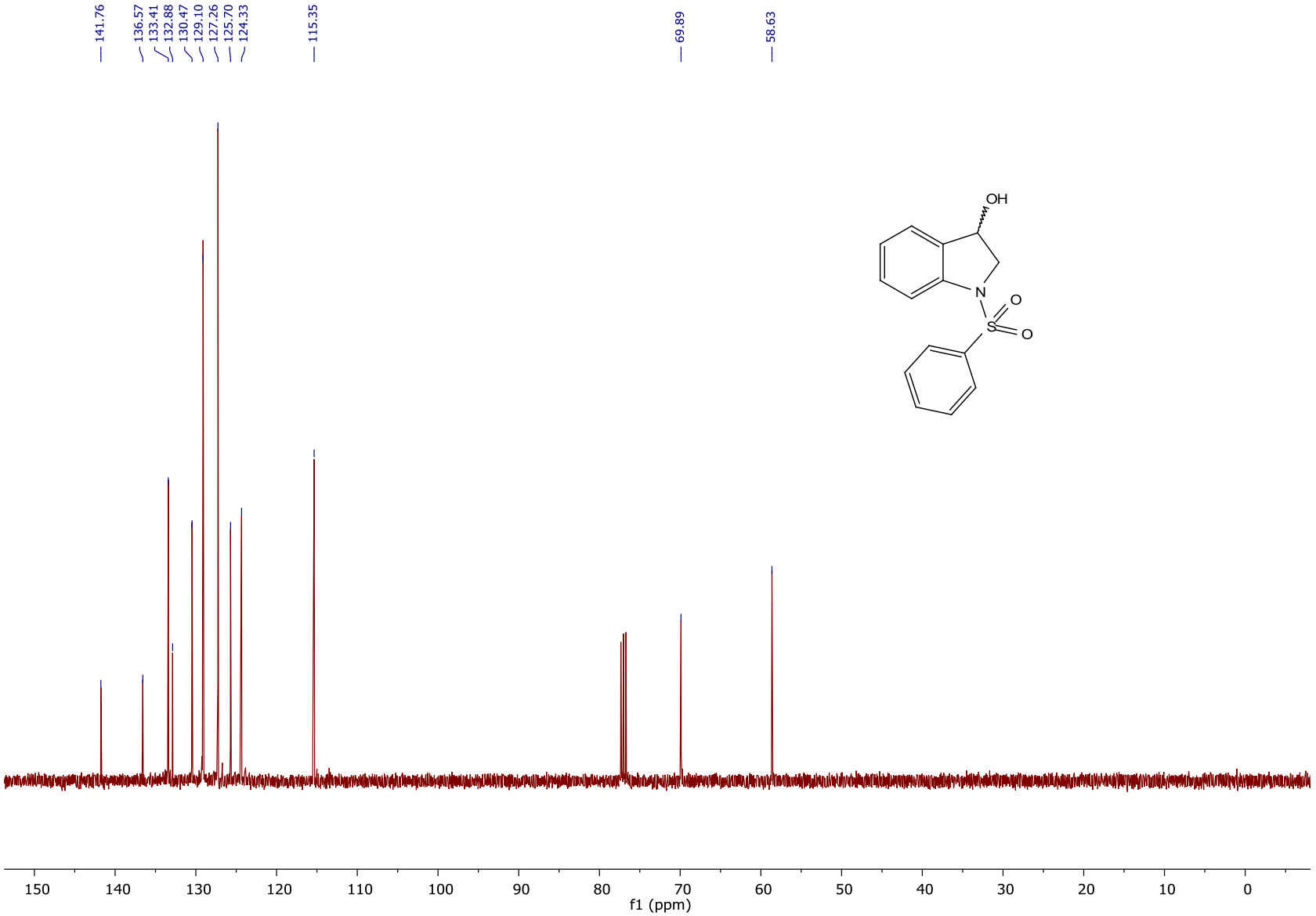

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6b'**.

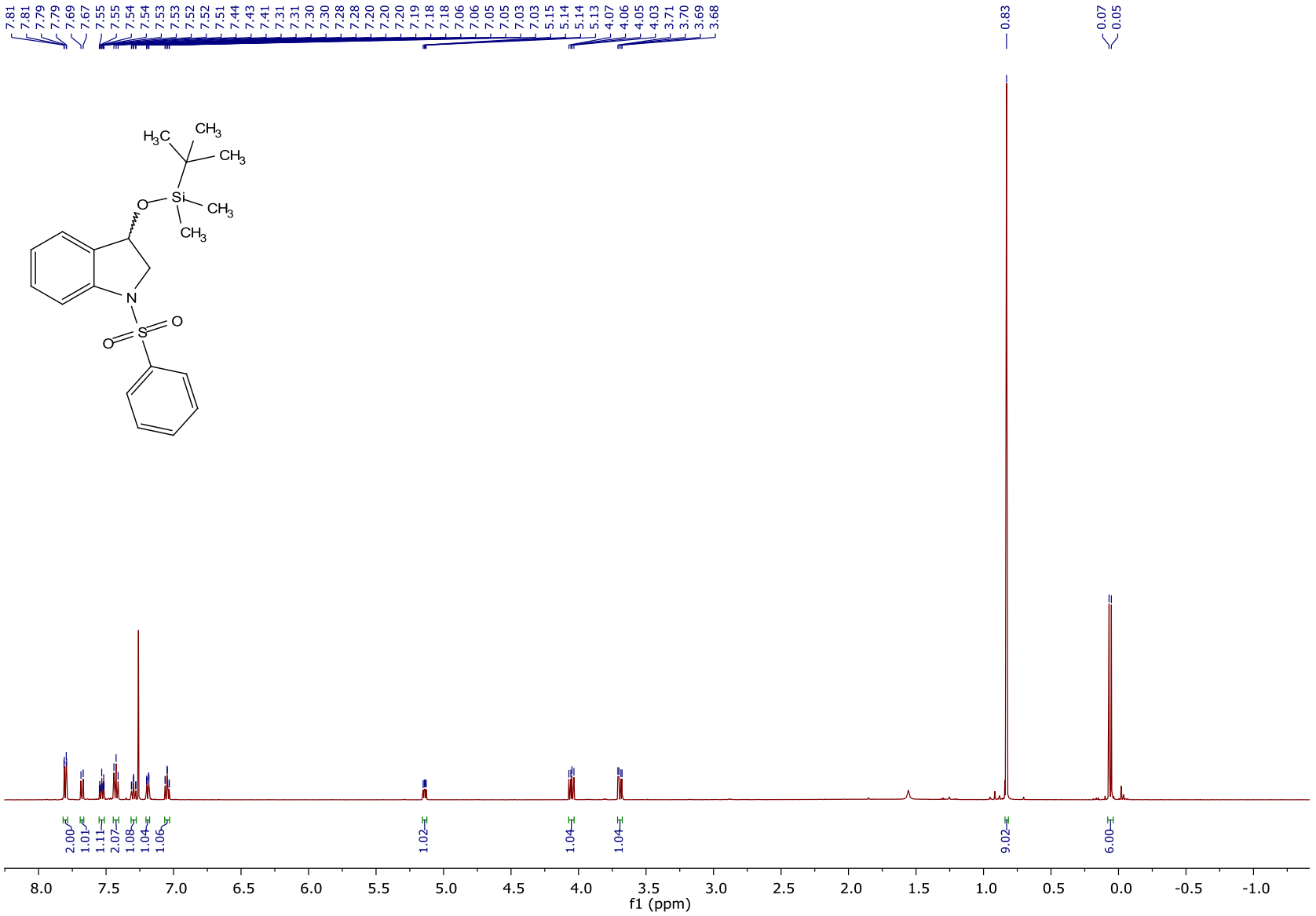

Figure S18. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6b''**.

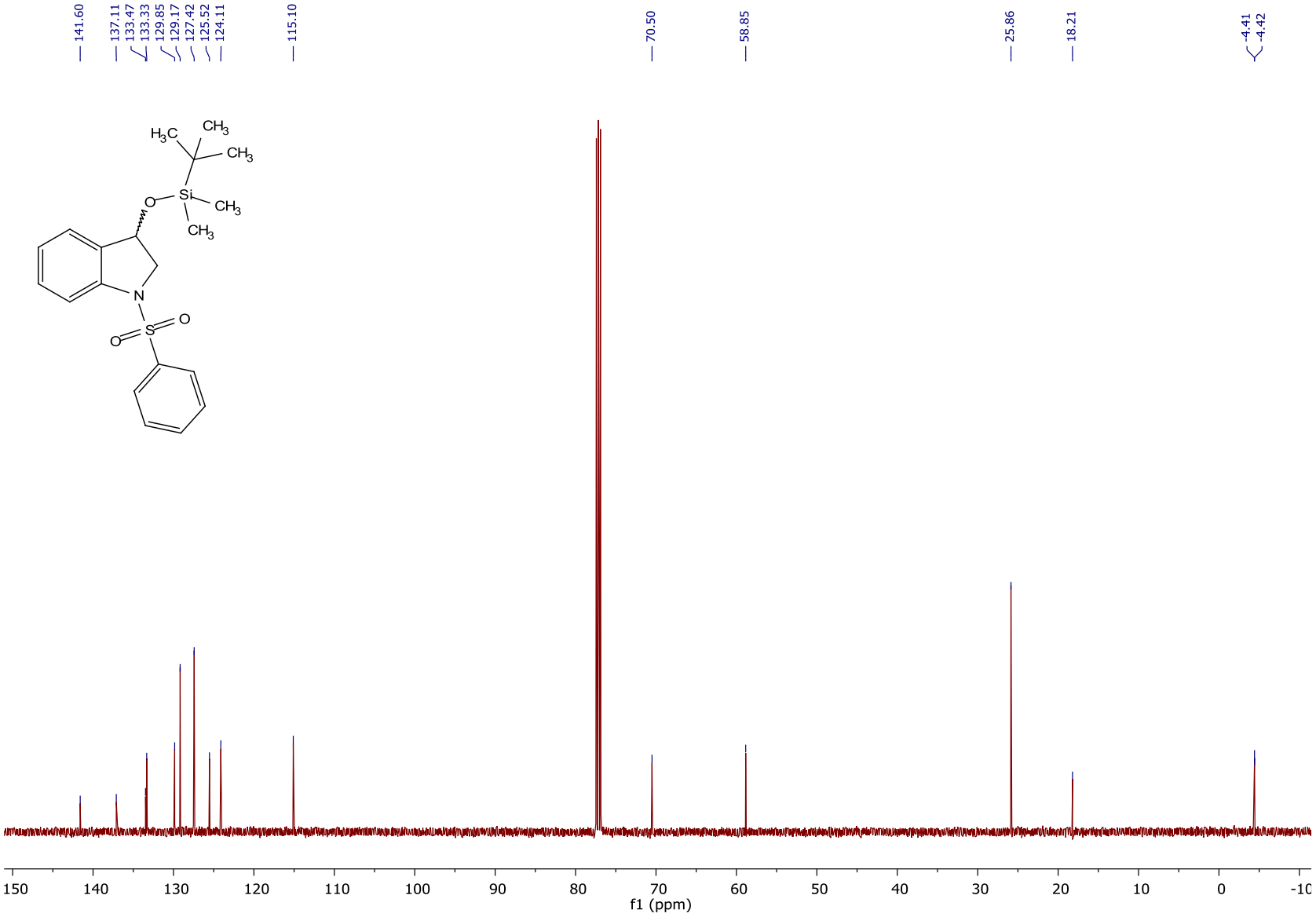

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6b''**.

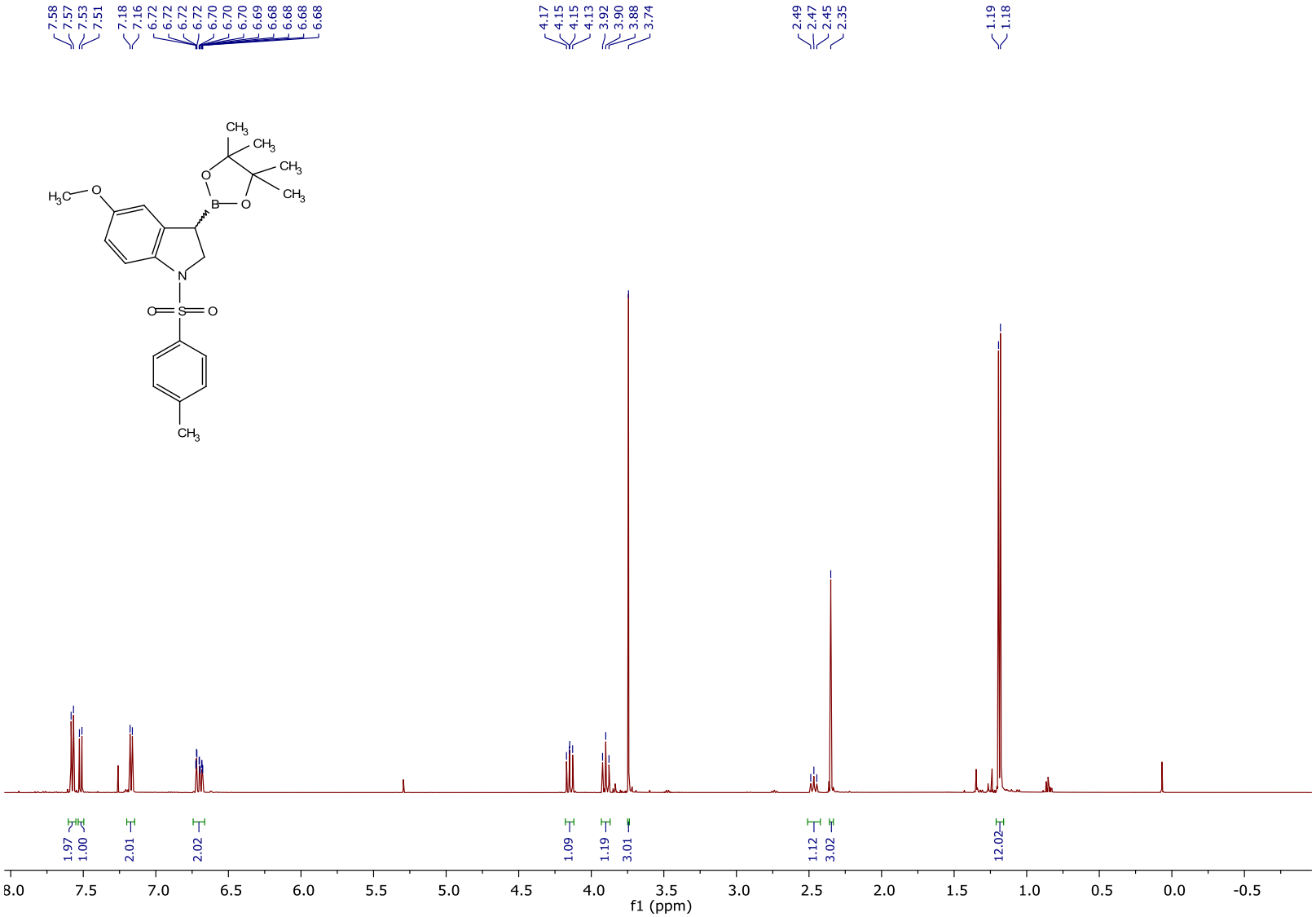

Figure S20. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6c**.

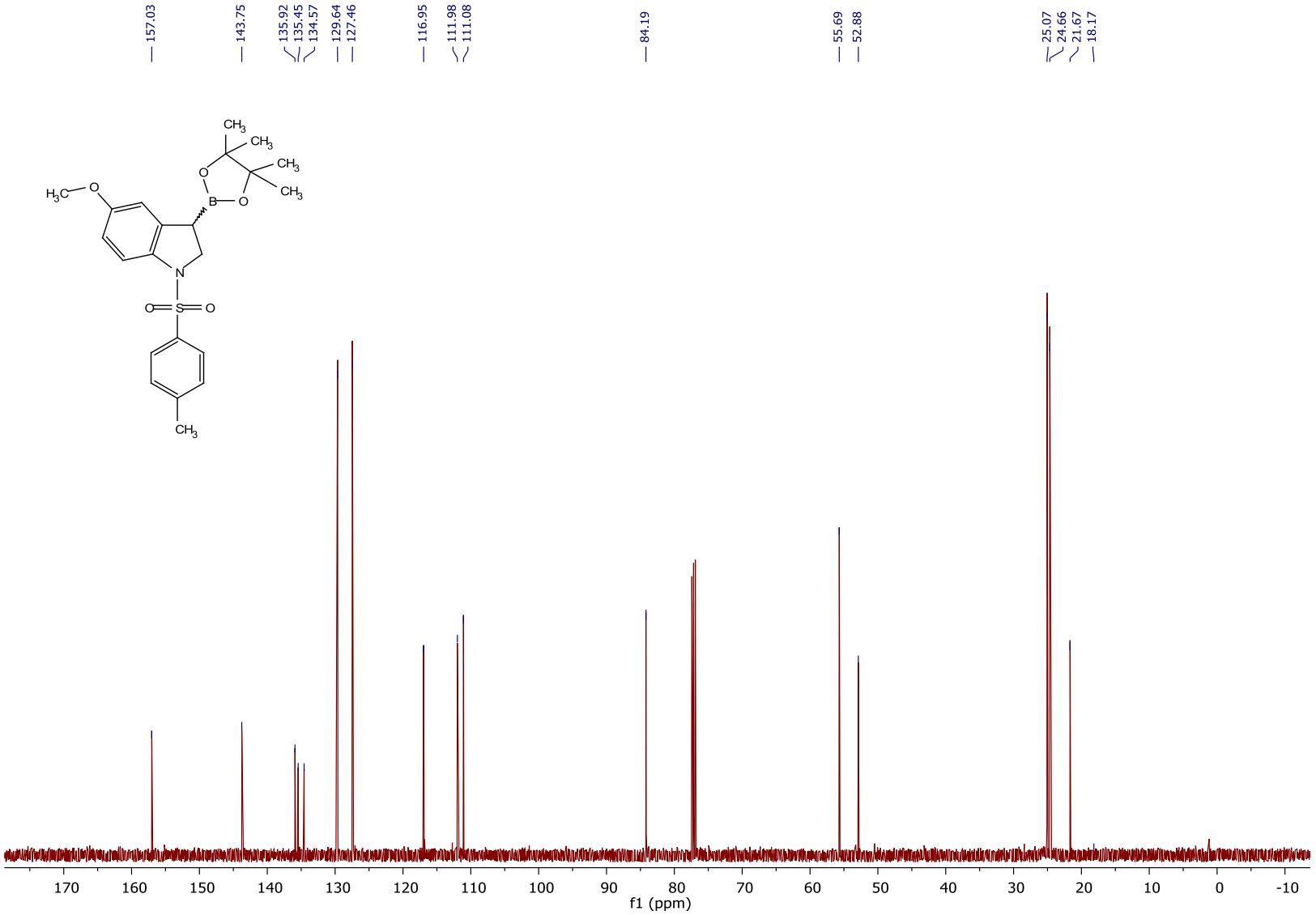

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6c**.

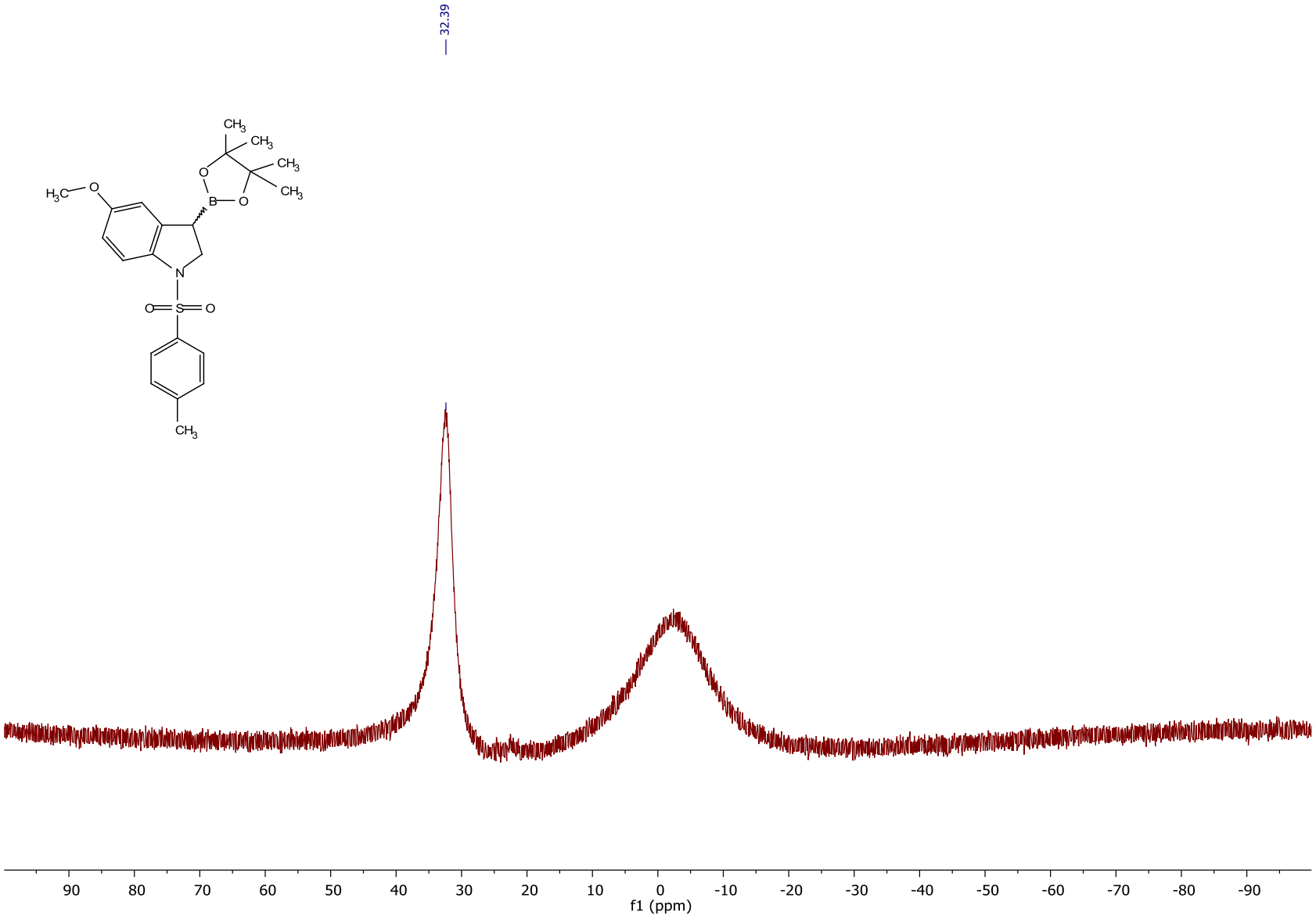

Figure S22. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6a**.

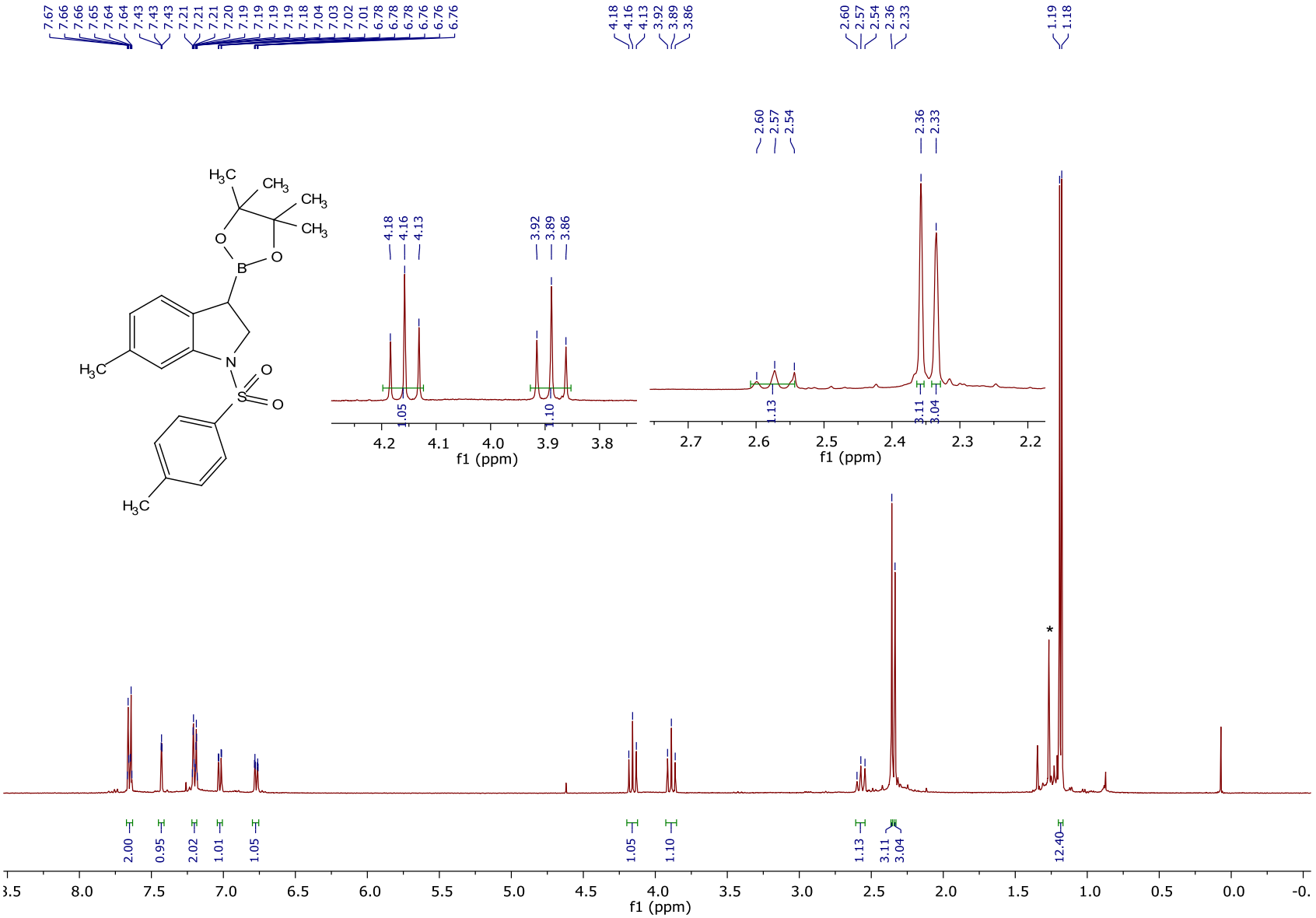

Figure S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6d**. * HBpin.

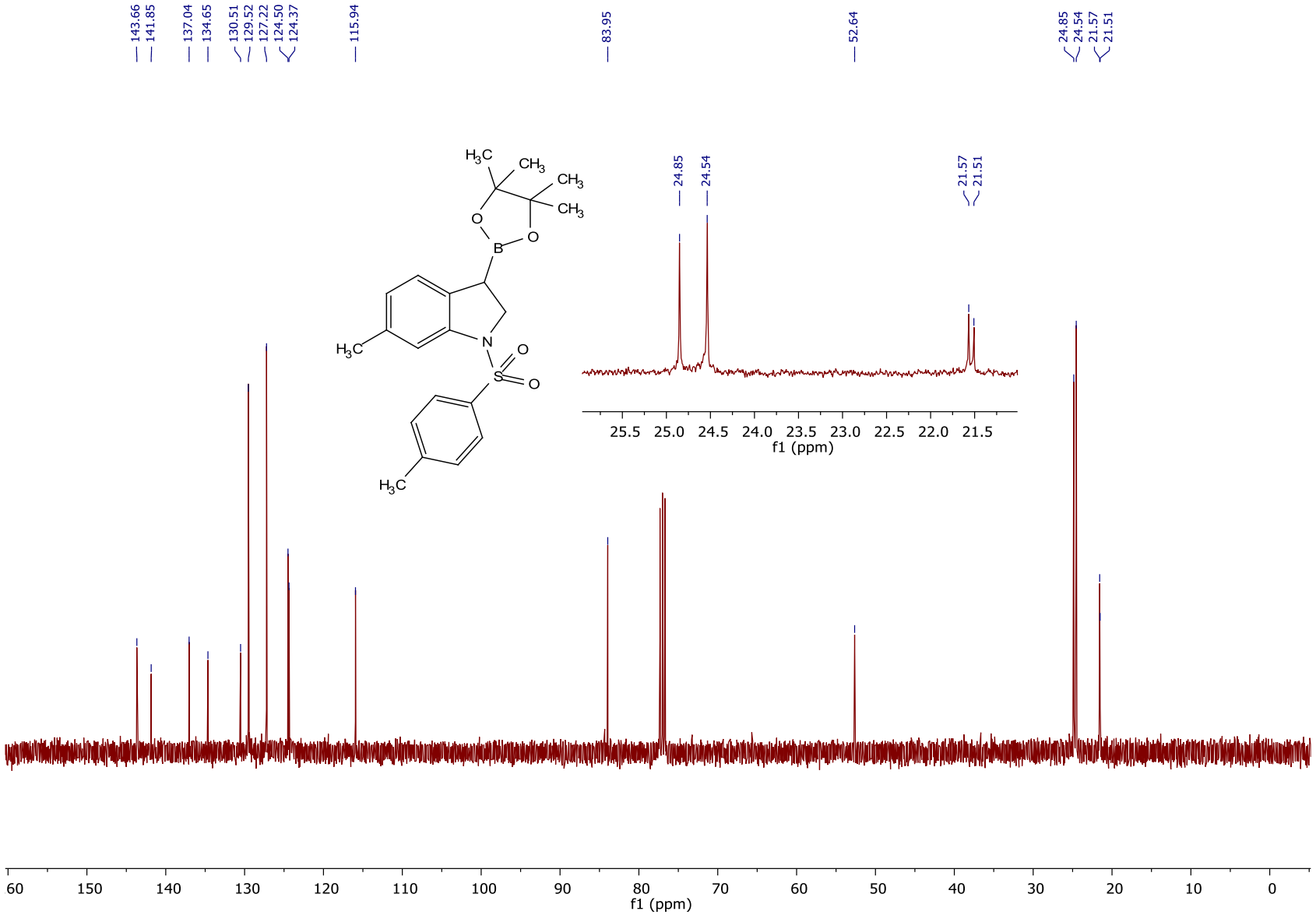

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6d**.

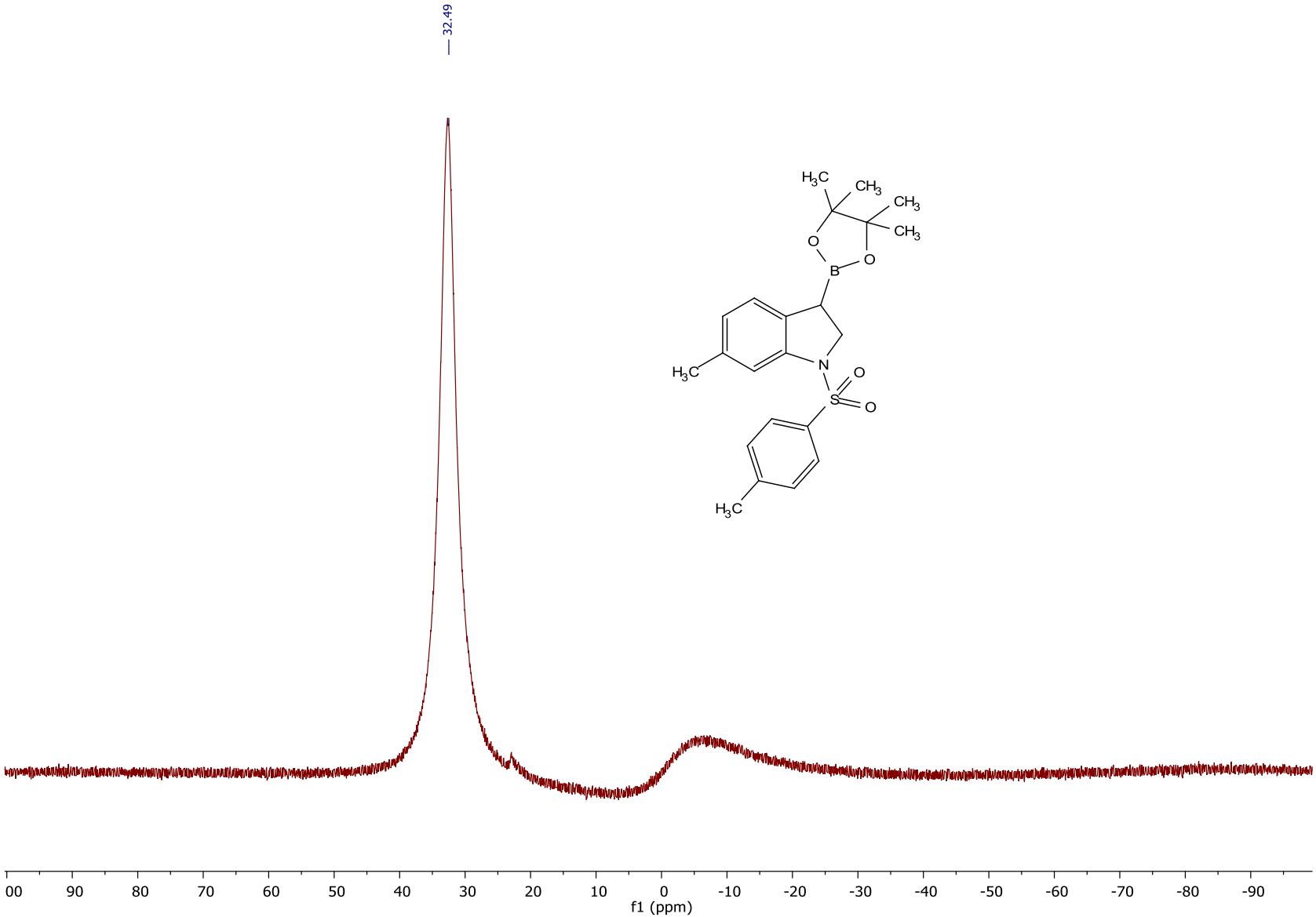

Figure S25. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6d** (reaction crude).

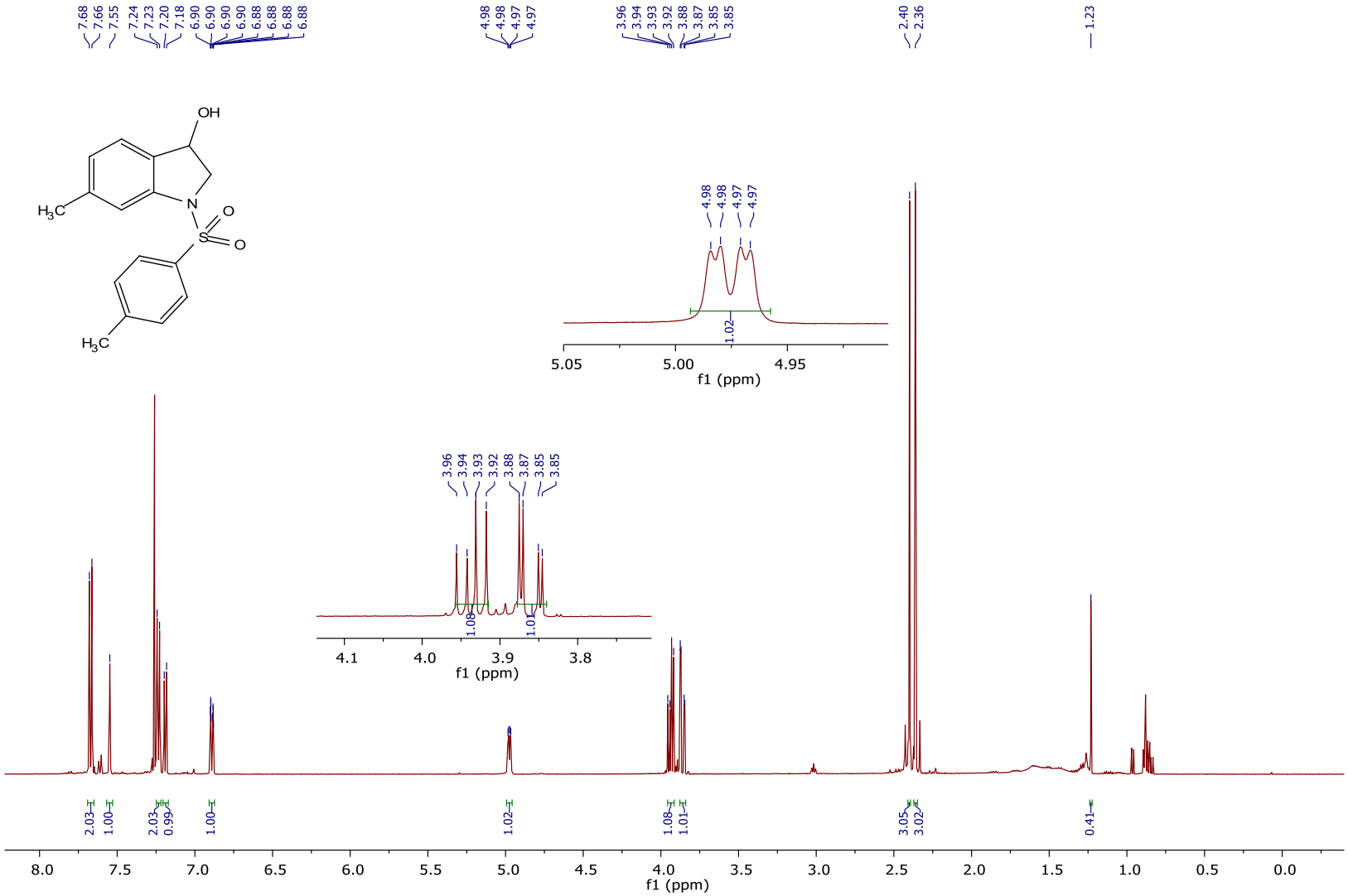

Figure S26. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6d'**.

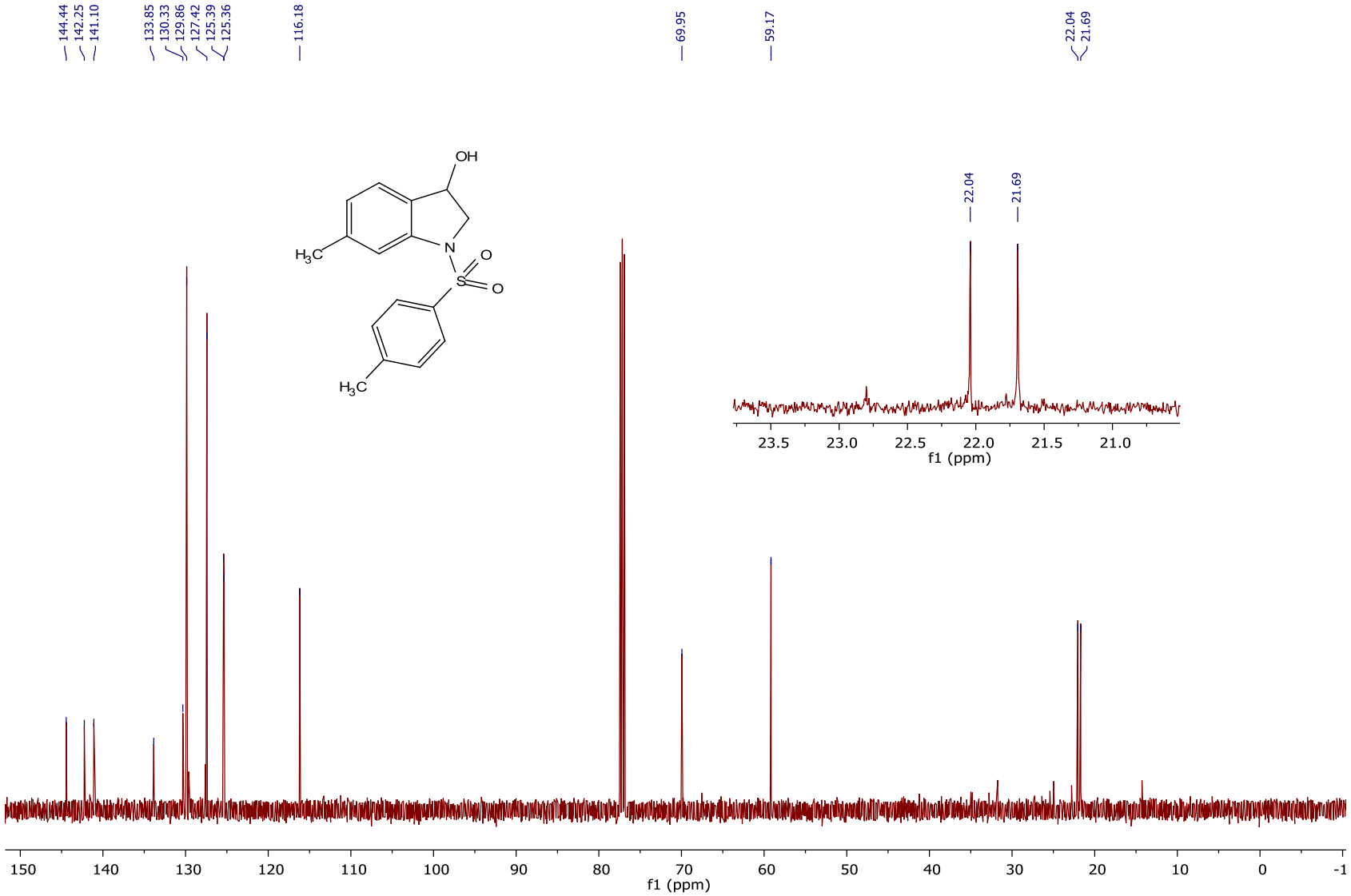

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (128.5 MHz, $CDCl_3$) of compound **6d'**.

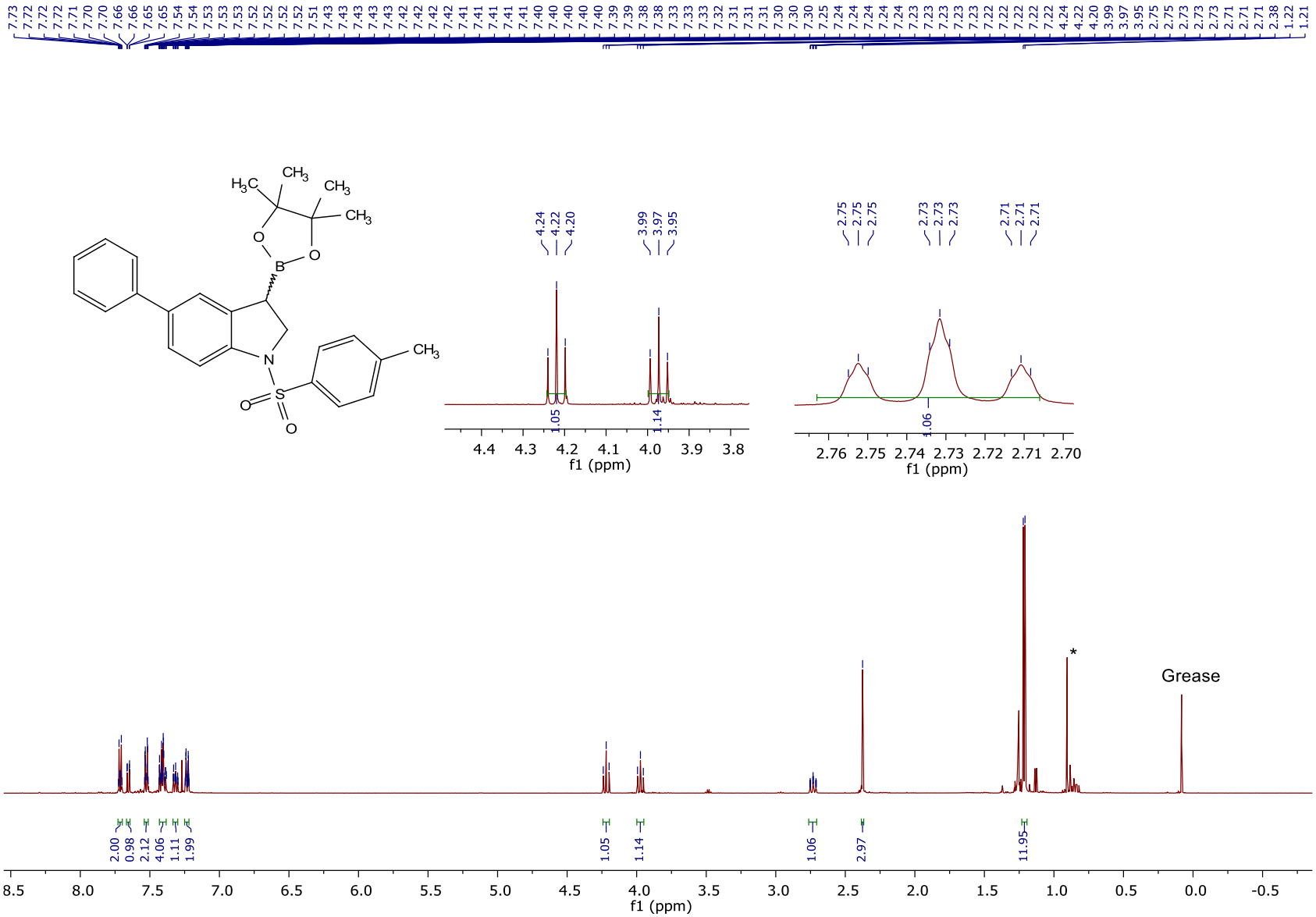

Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6e**. * Unknown impurity.

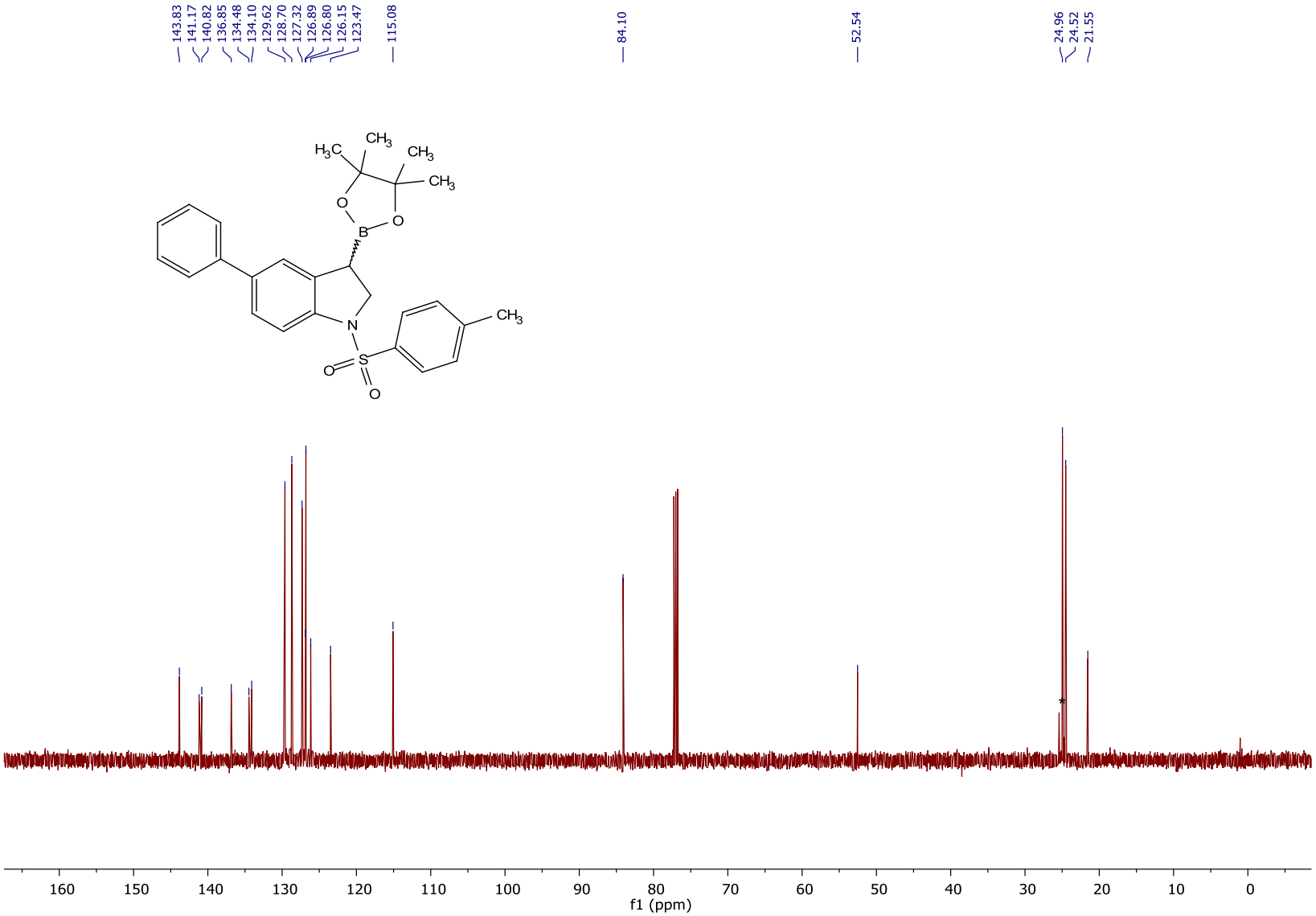

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (128.5 MHz, $CDCl_3$) of compound **6e**. * HBpin.

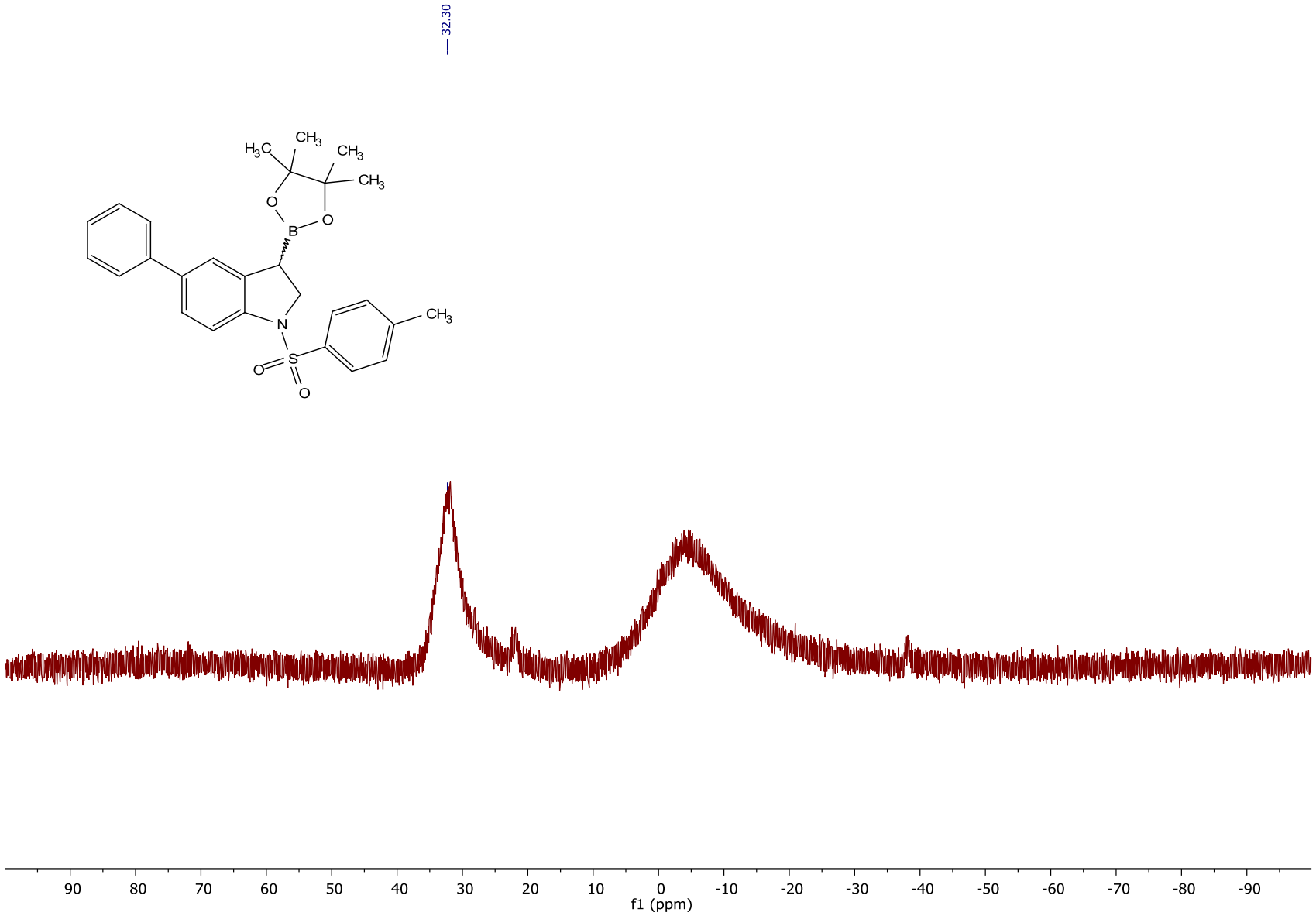

Figure S30. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6e**.

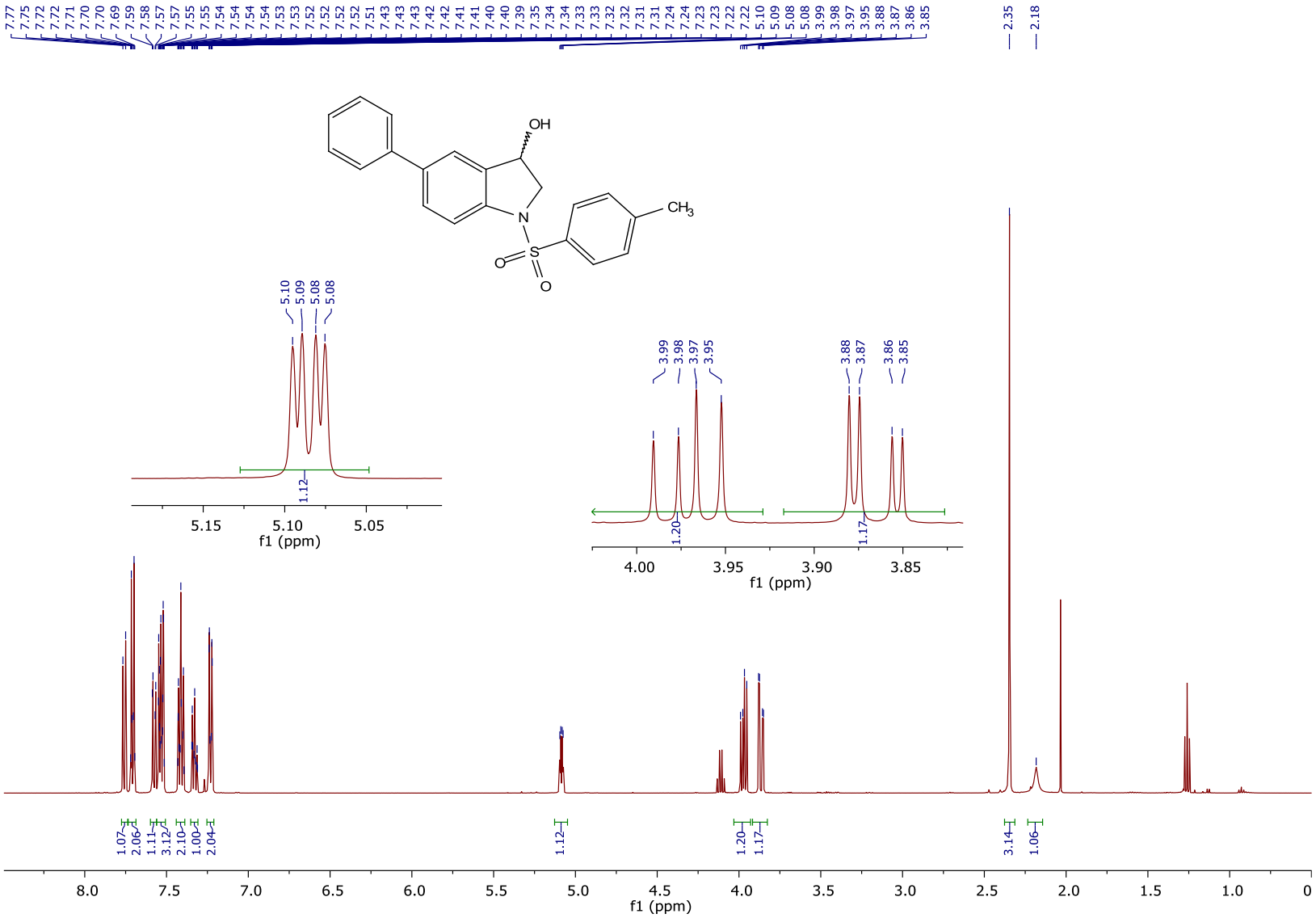

Figure S31. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6e'**.

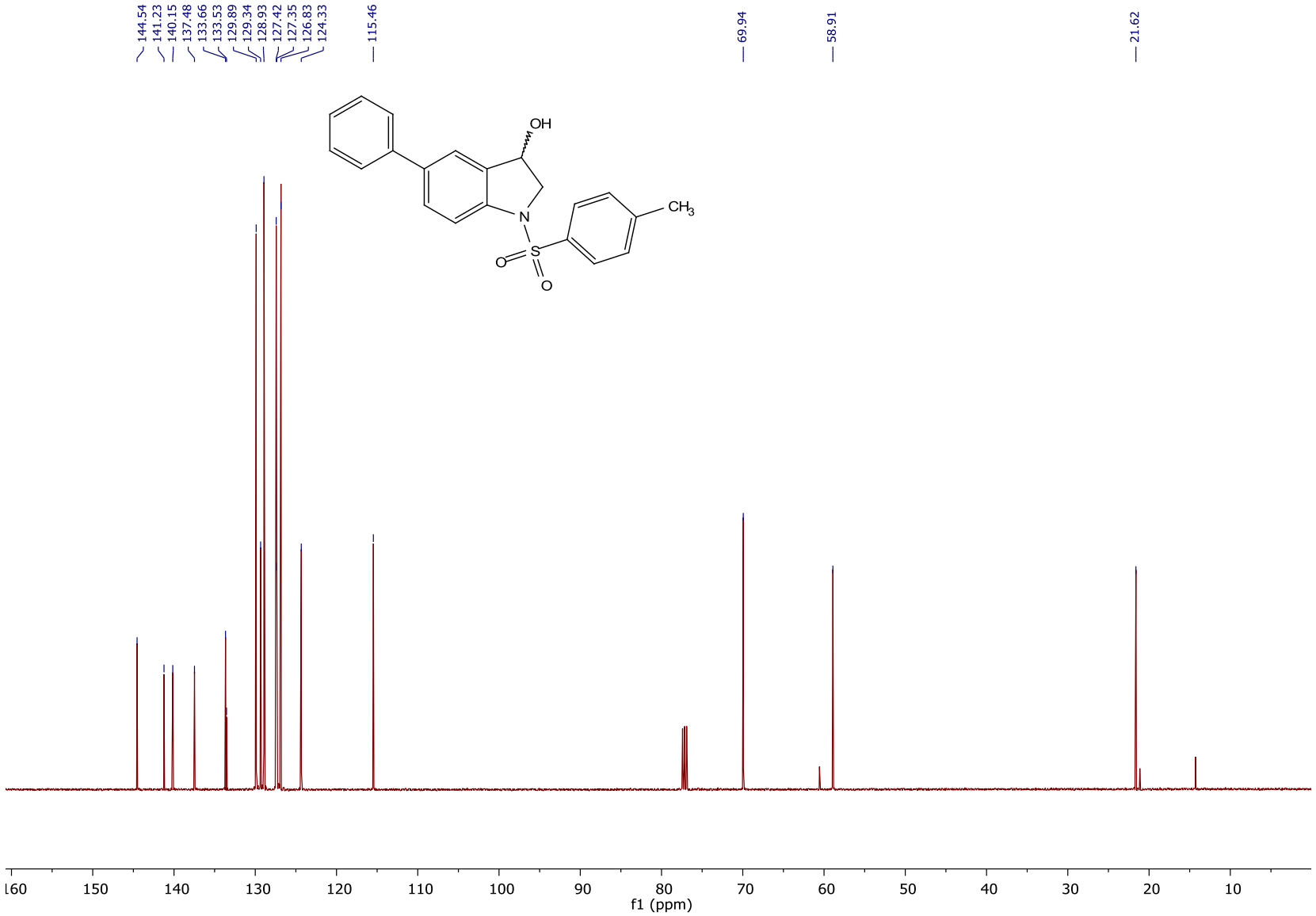

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6e'**.

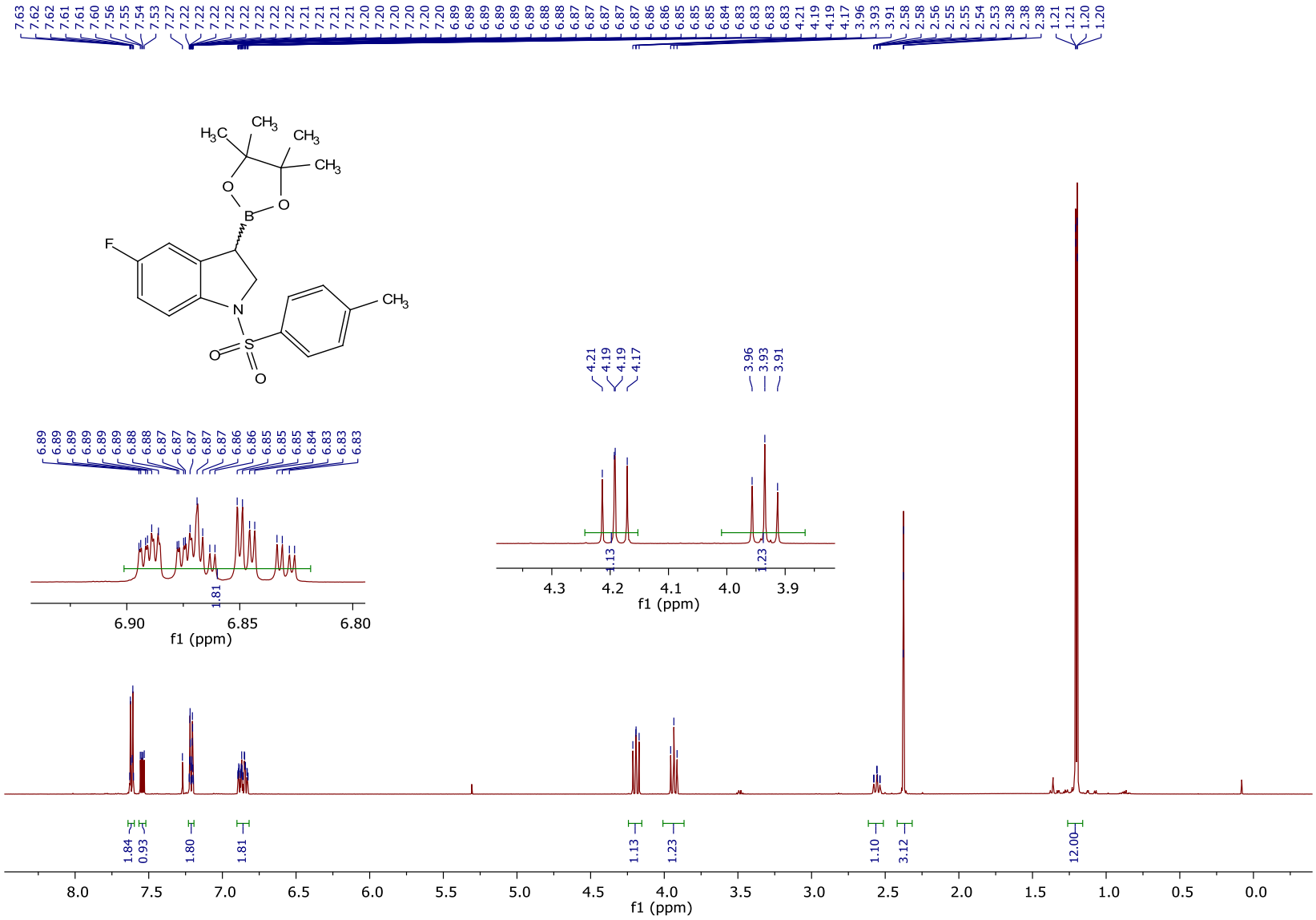

Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6f**.

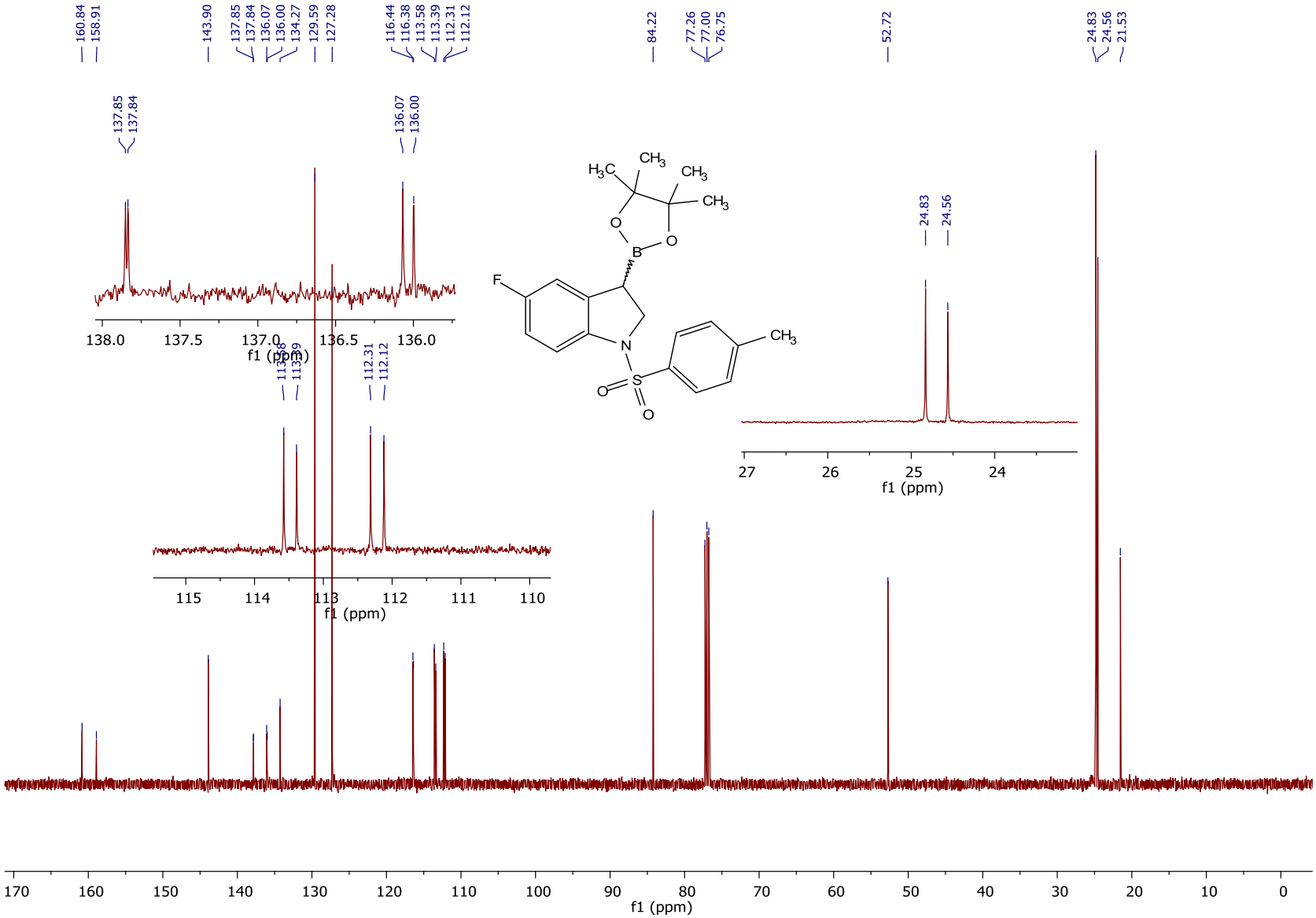

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6f**.

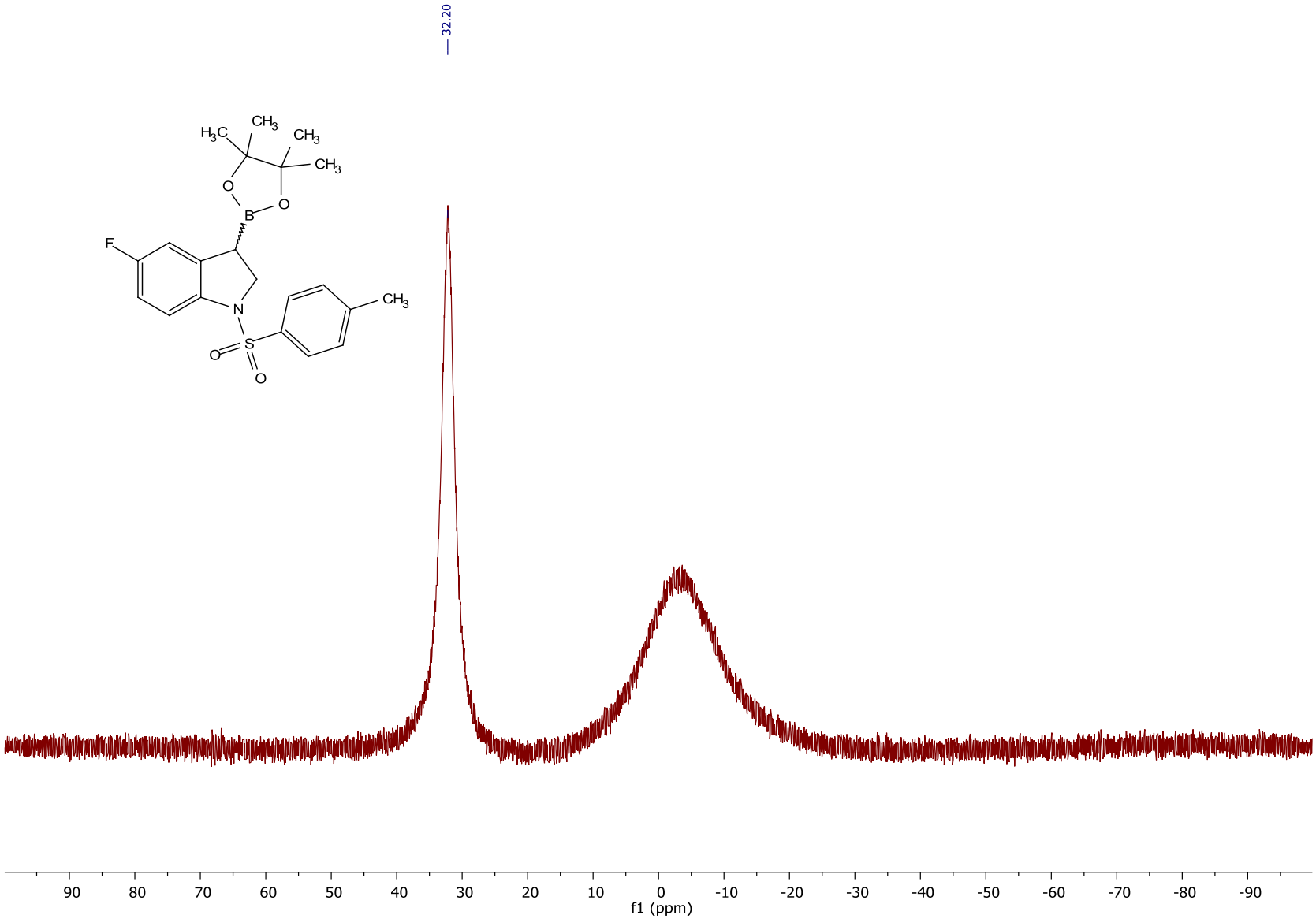

Figure S35. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6f**.

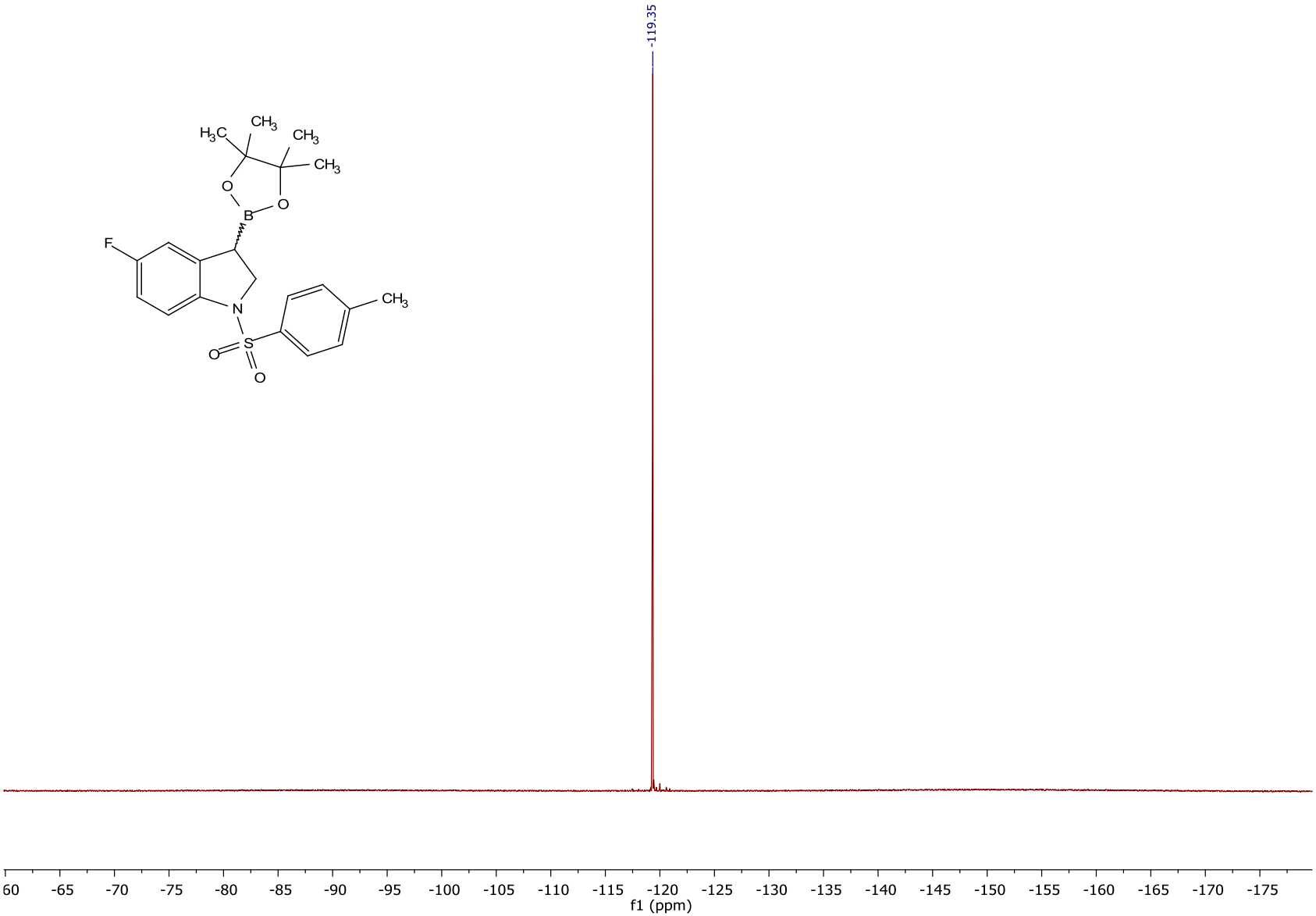

Figure S36. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **6f**.

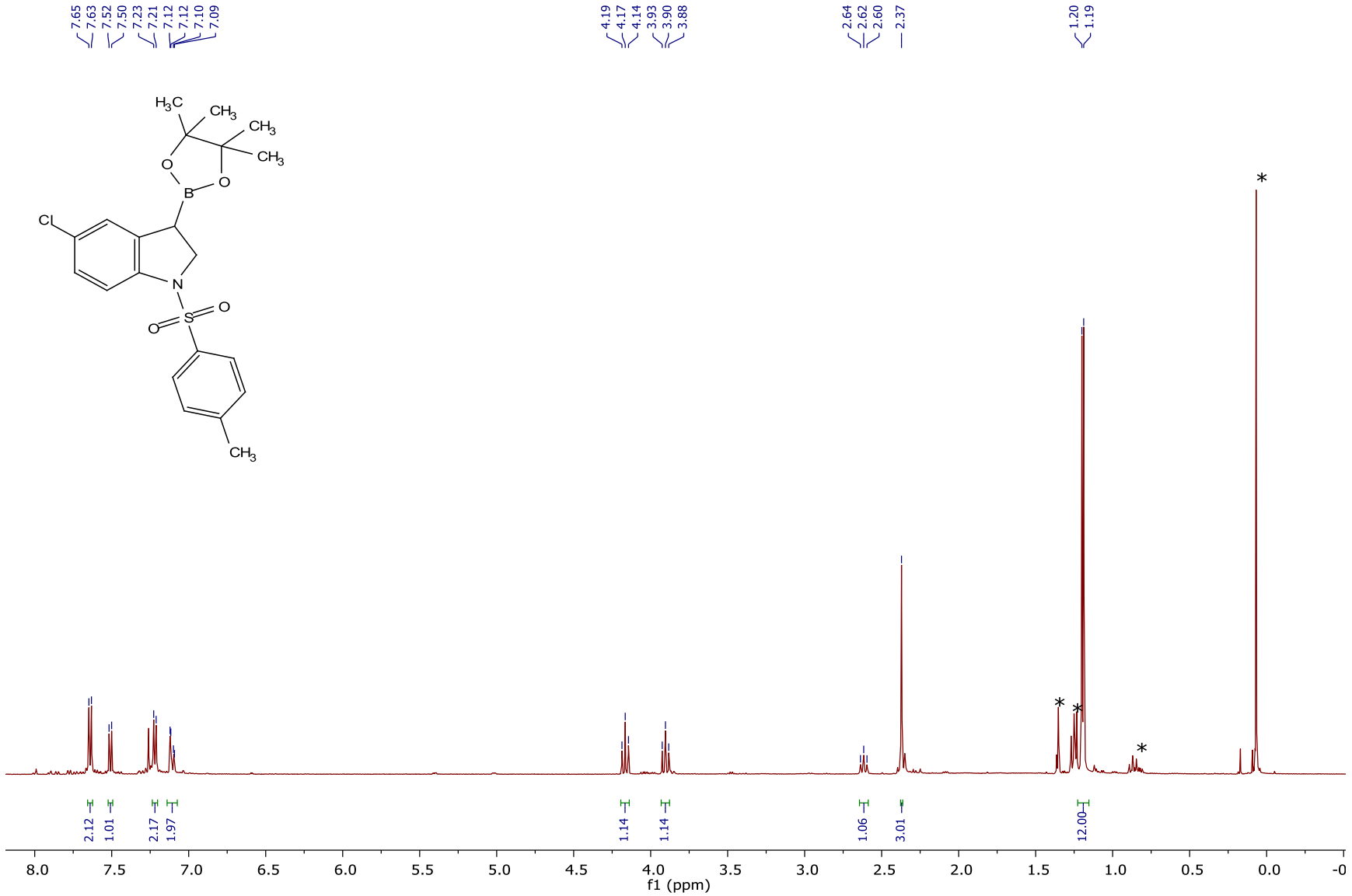

Figure S37. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6g**.

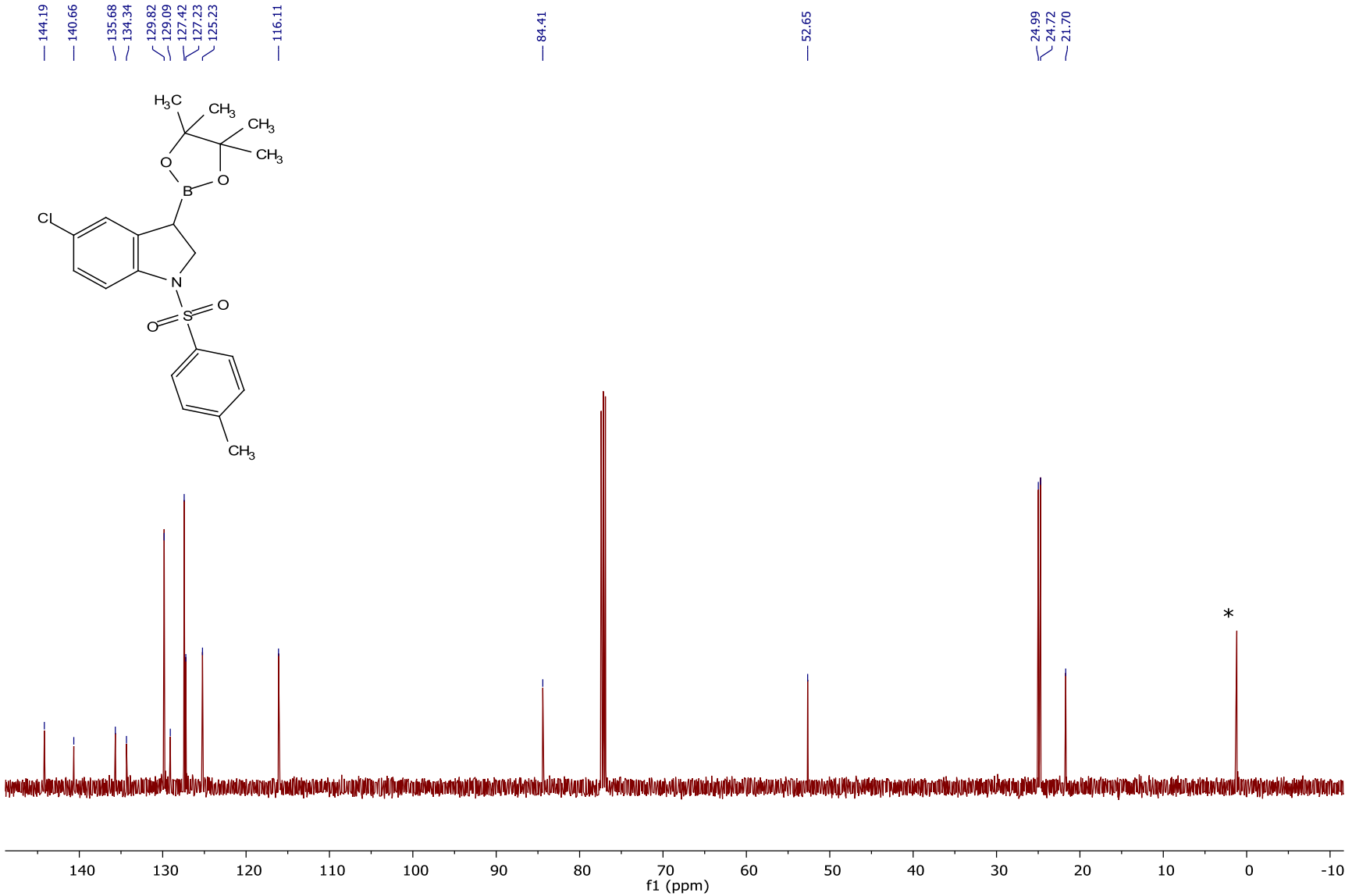

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6g**.

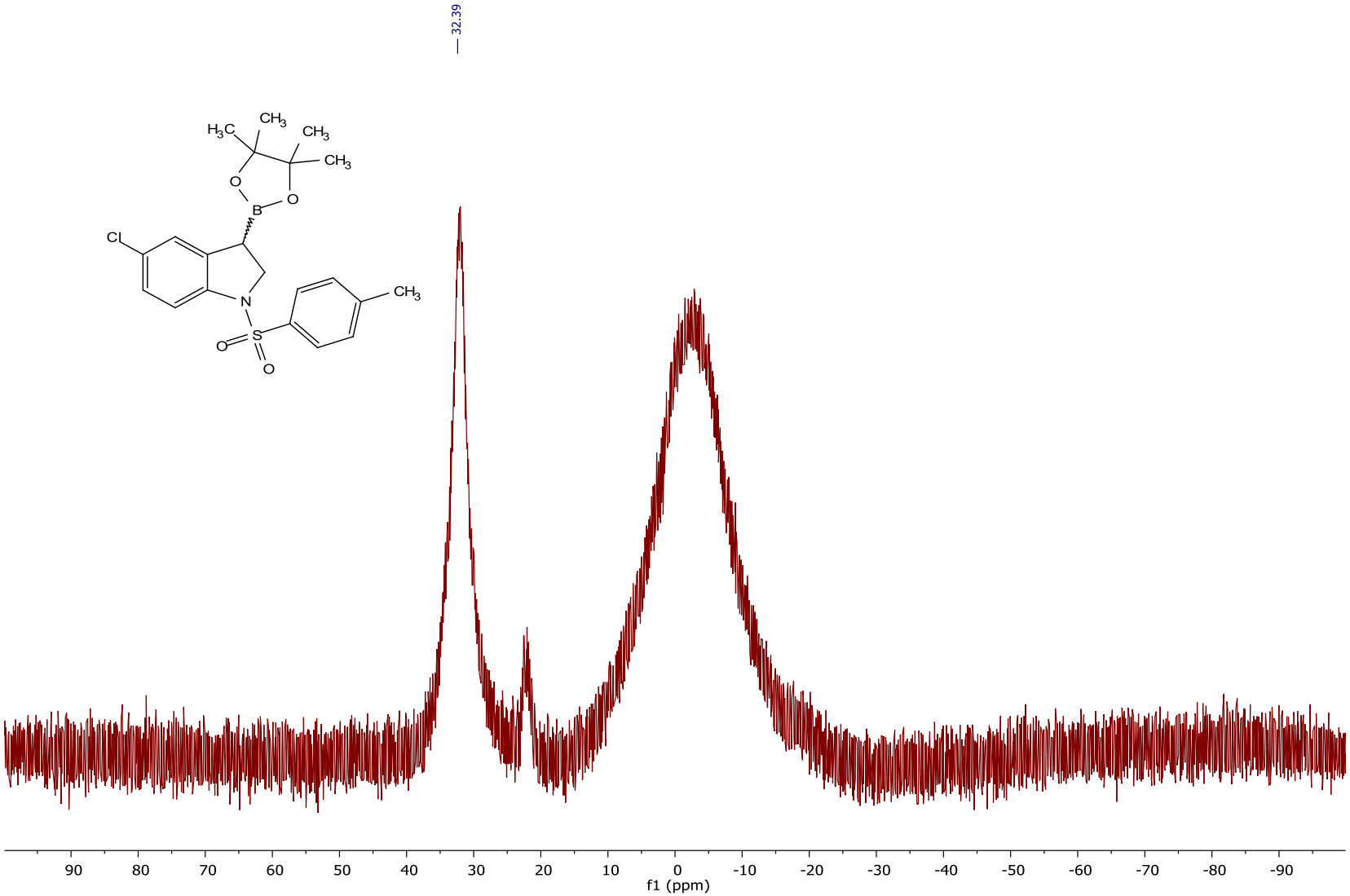

Figure S39. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6g**.

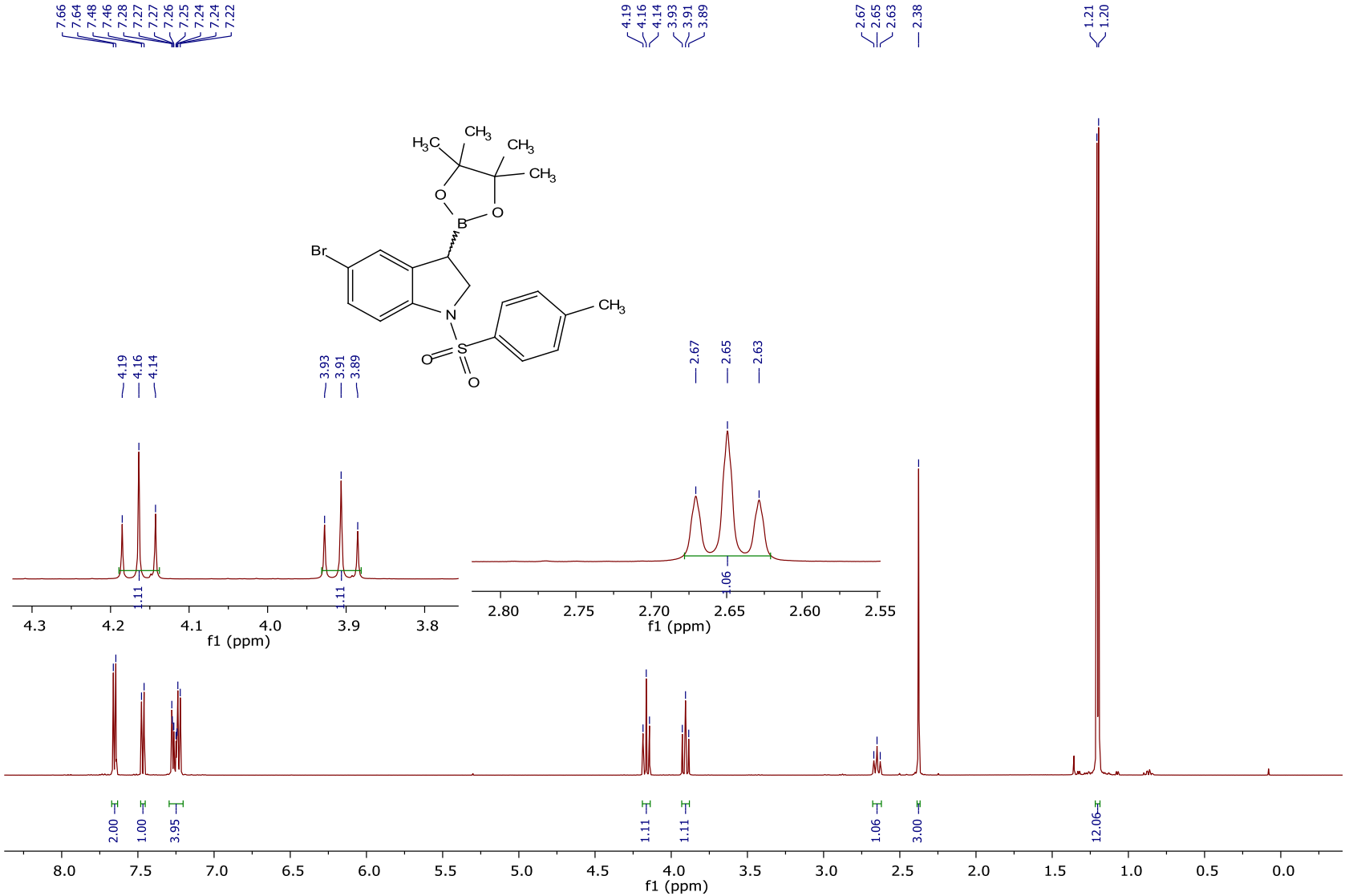

Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6h**.

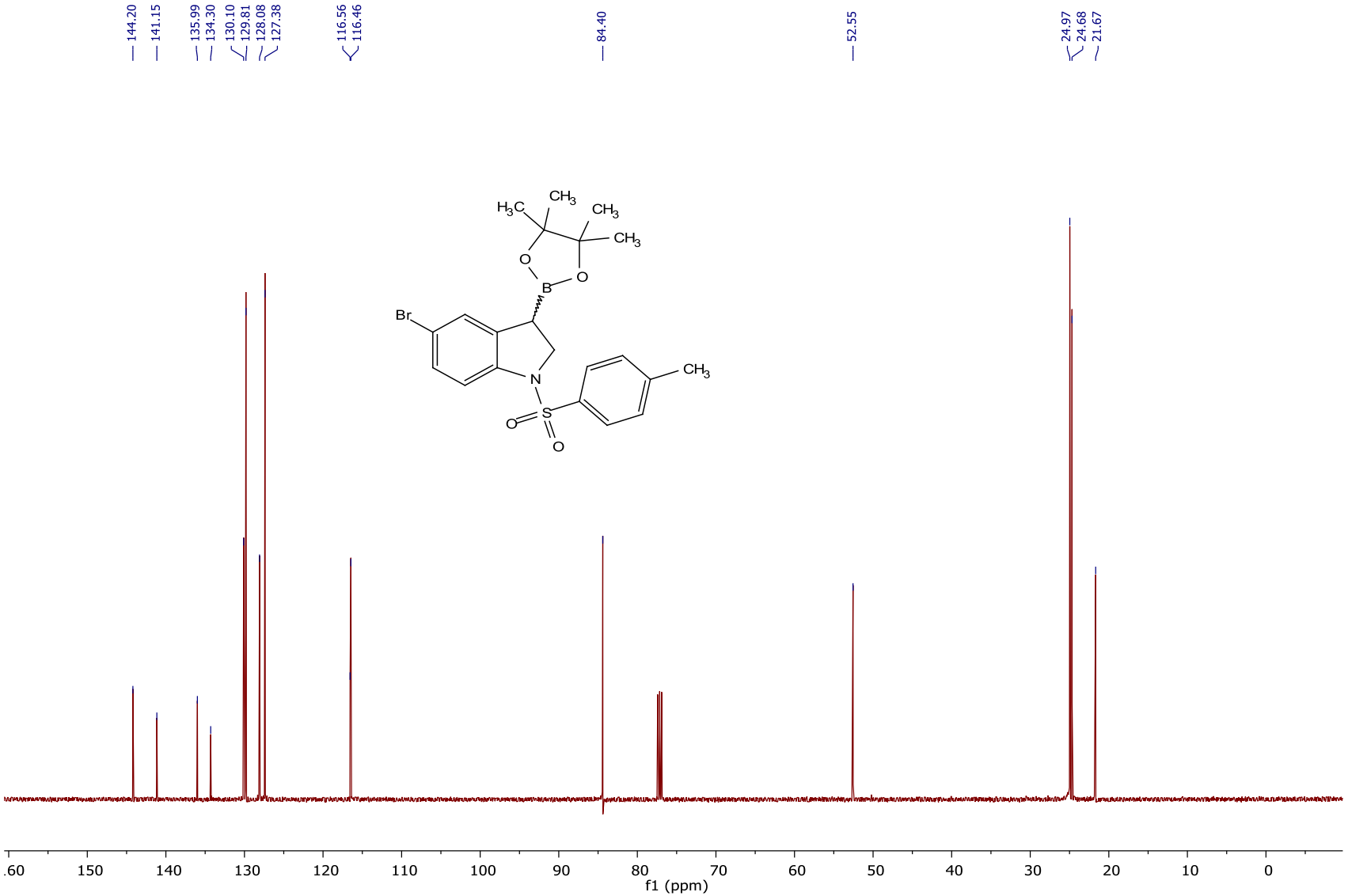

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6h**.

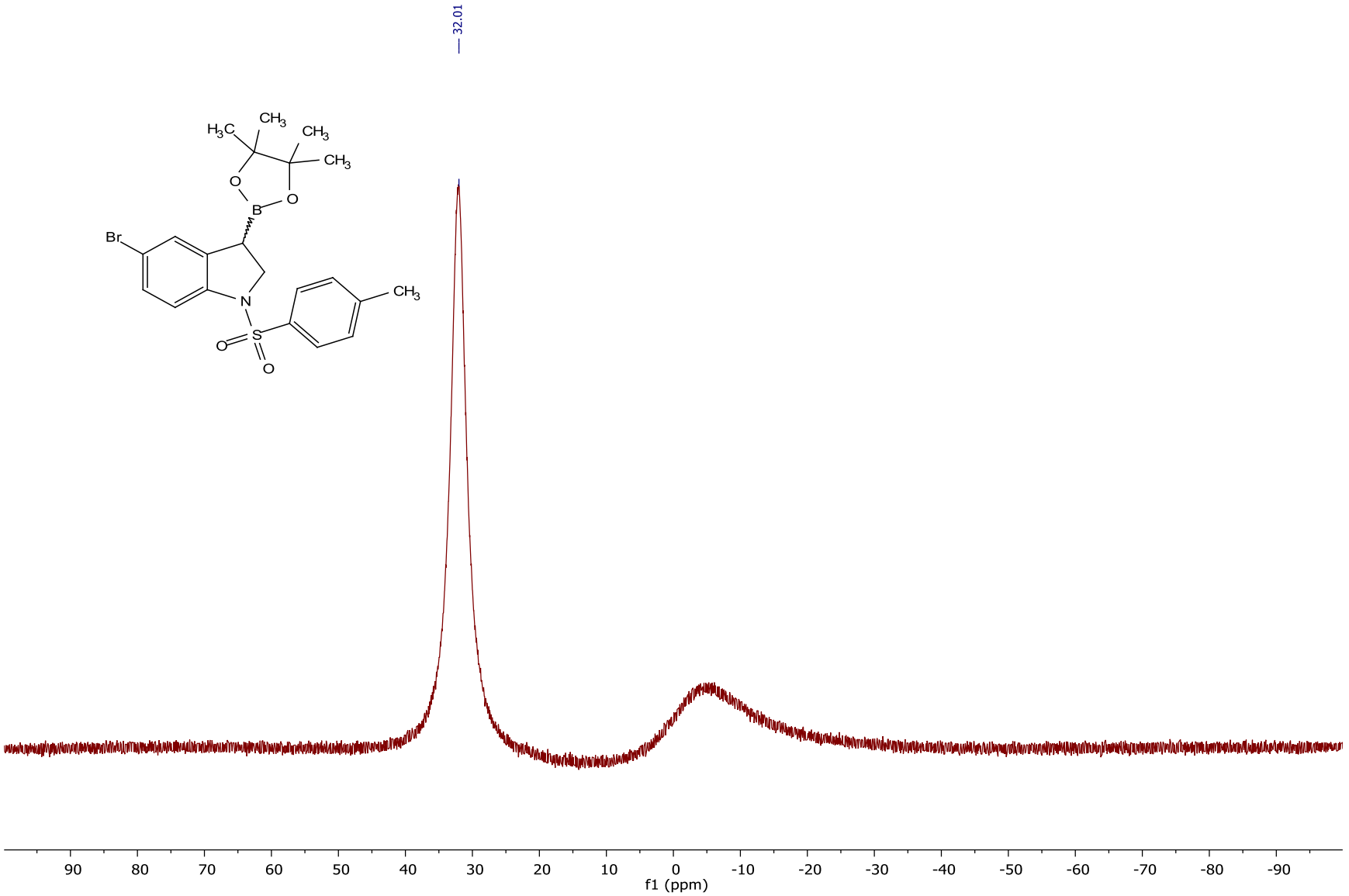

Figure S42. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6h**.

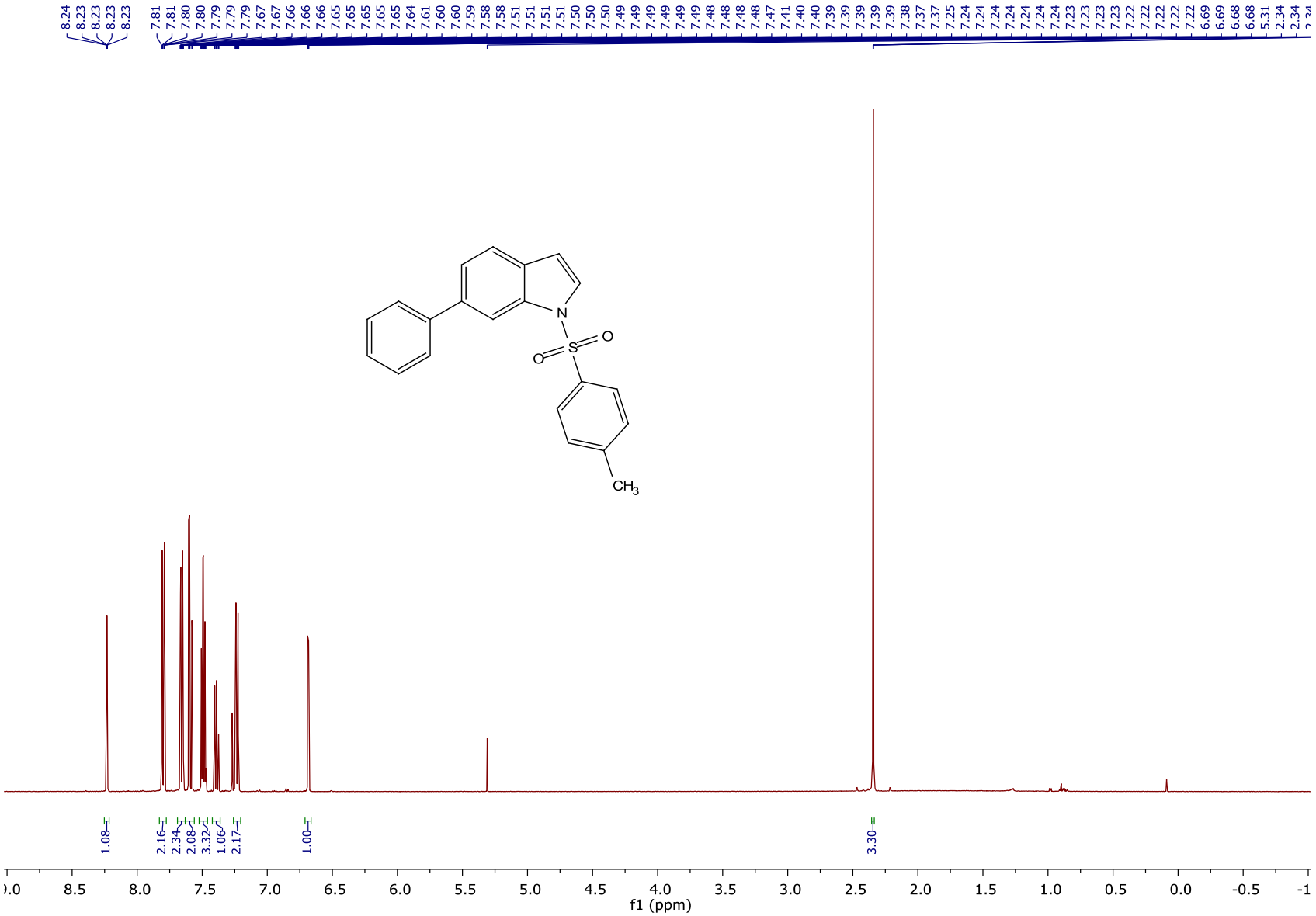

Figure S43. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5i**.

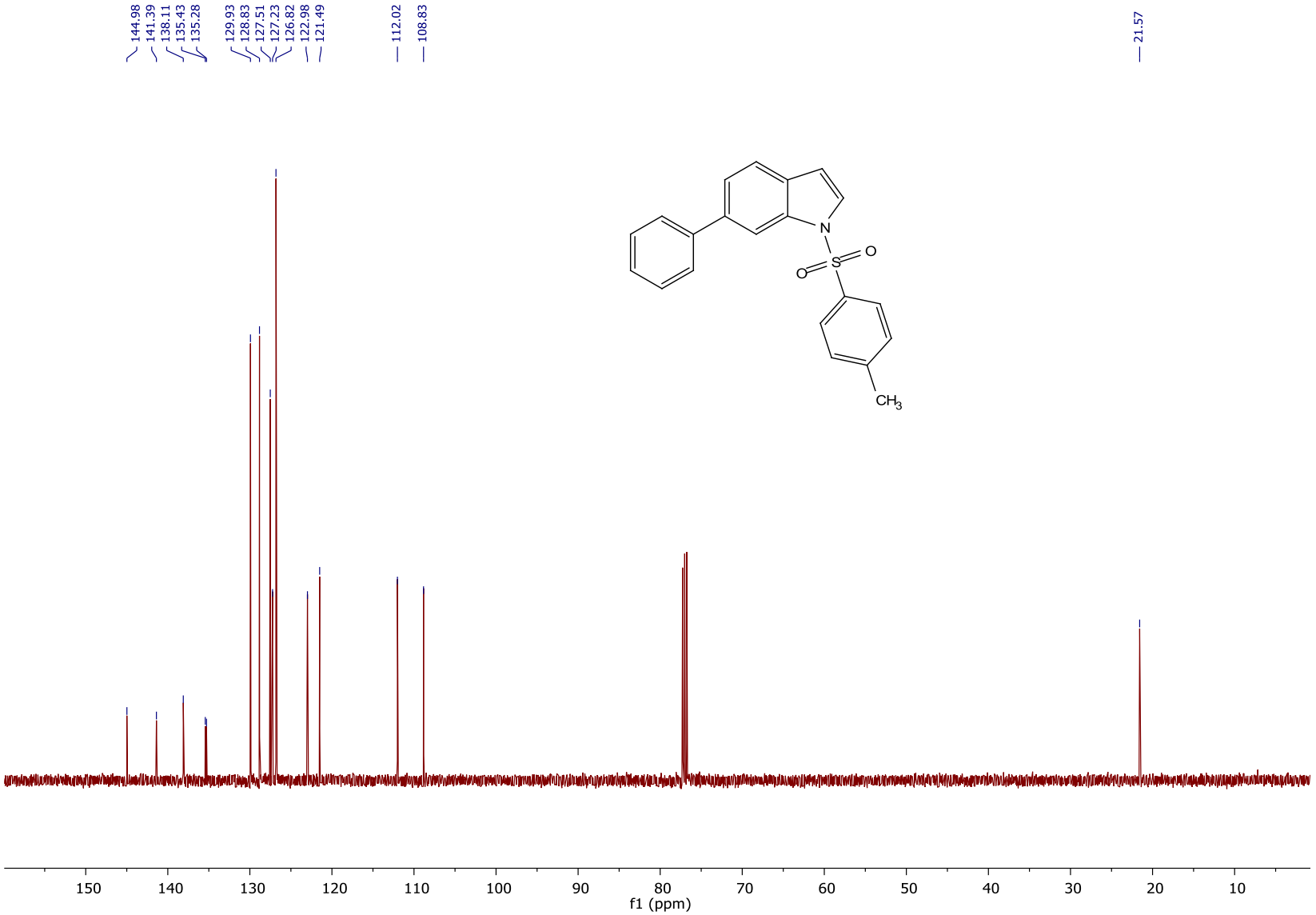

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **5i**.

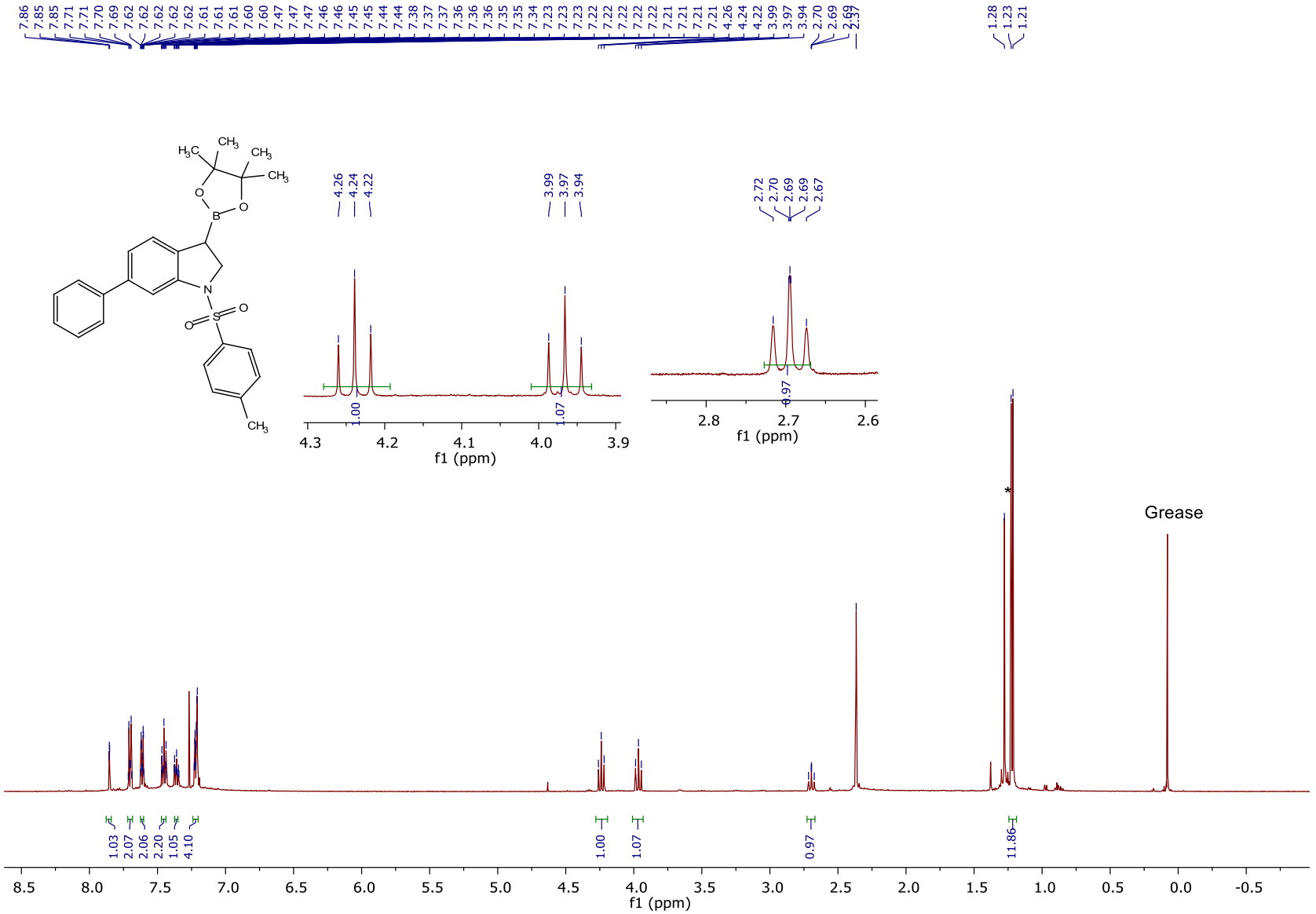

Figure S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6i**. * HBpin.

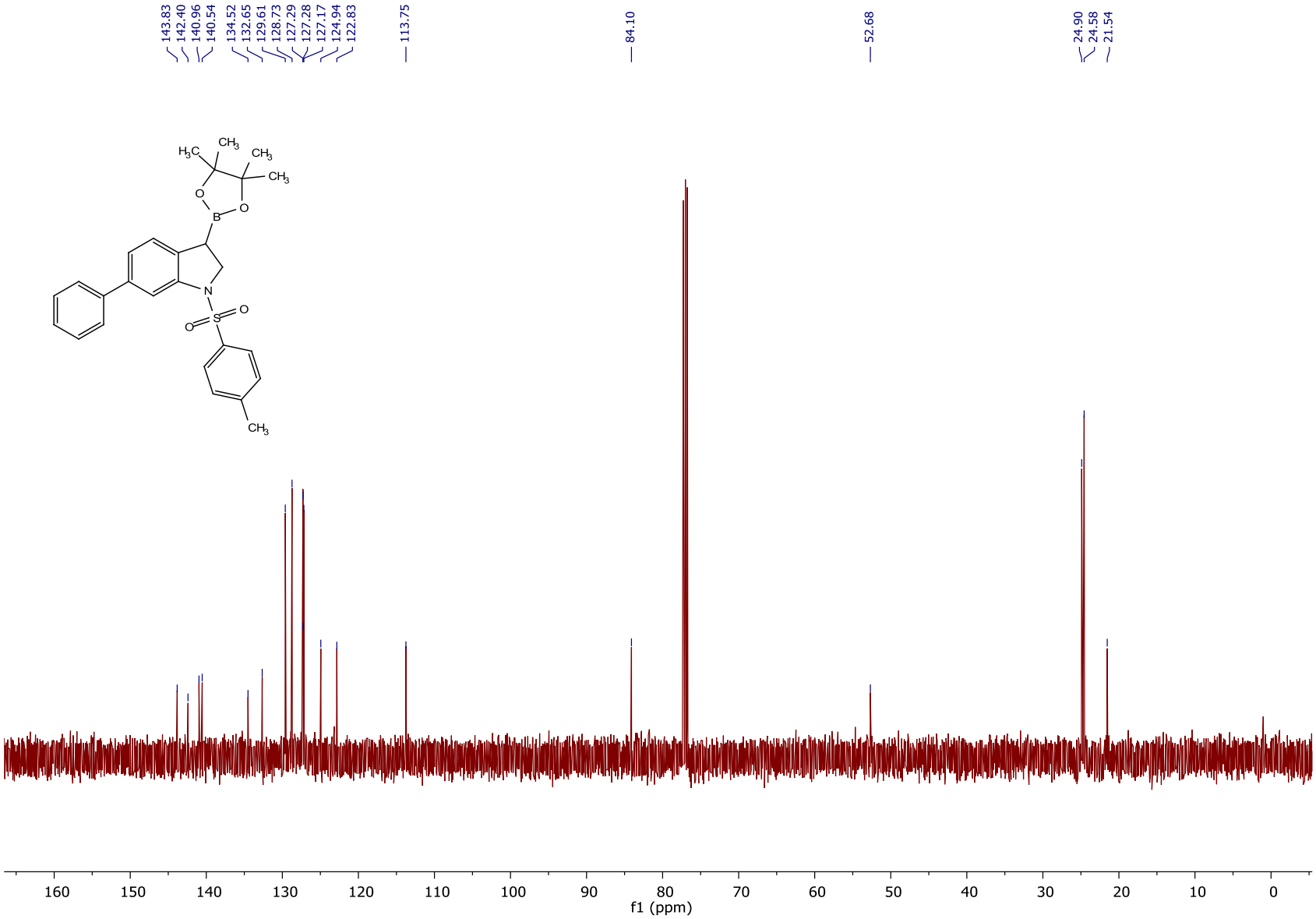

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6h**.

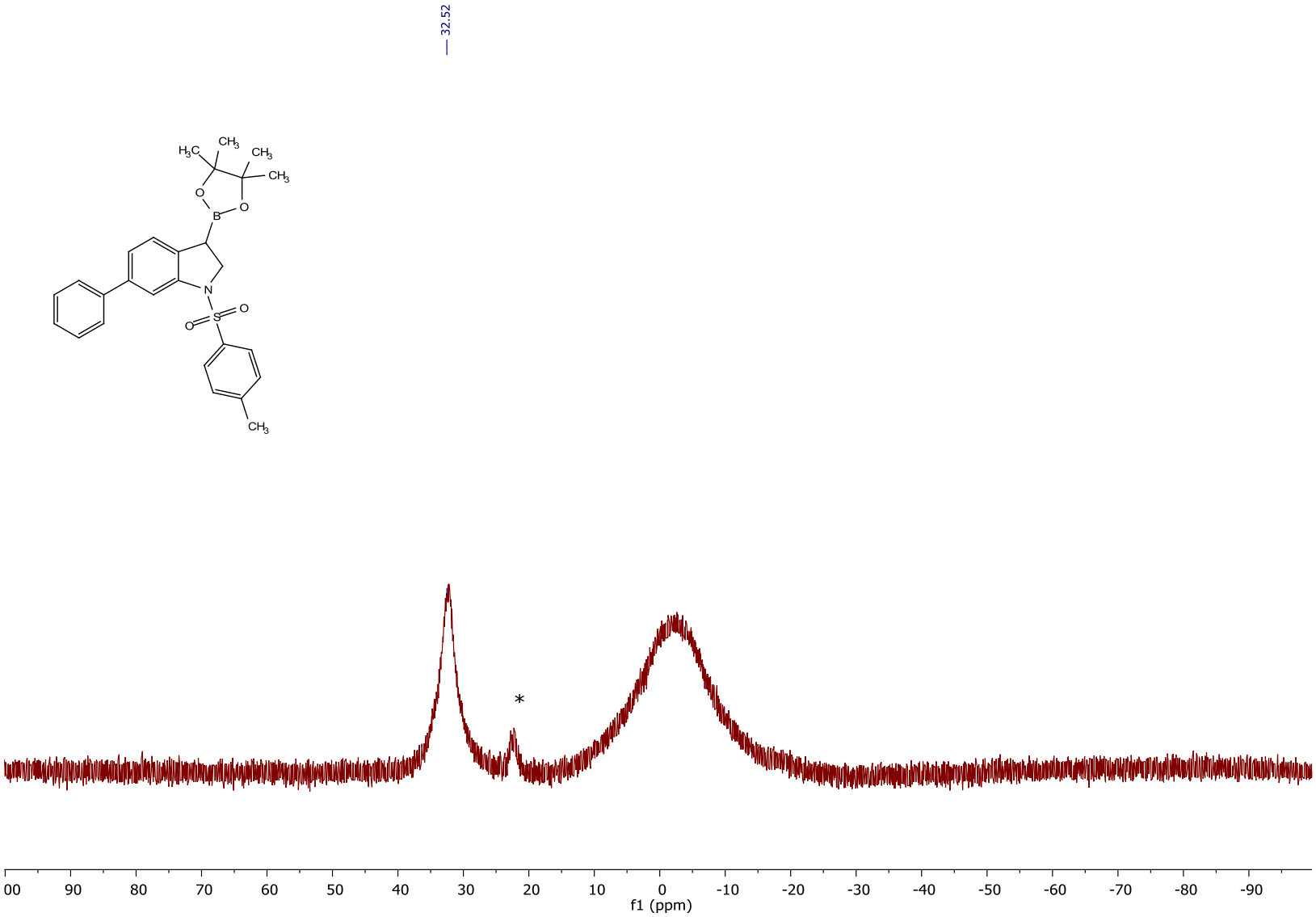

Figure S47. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6i**. * HBpin.

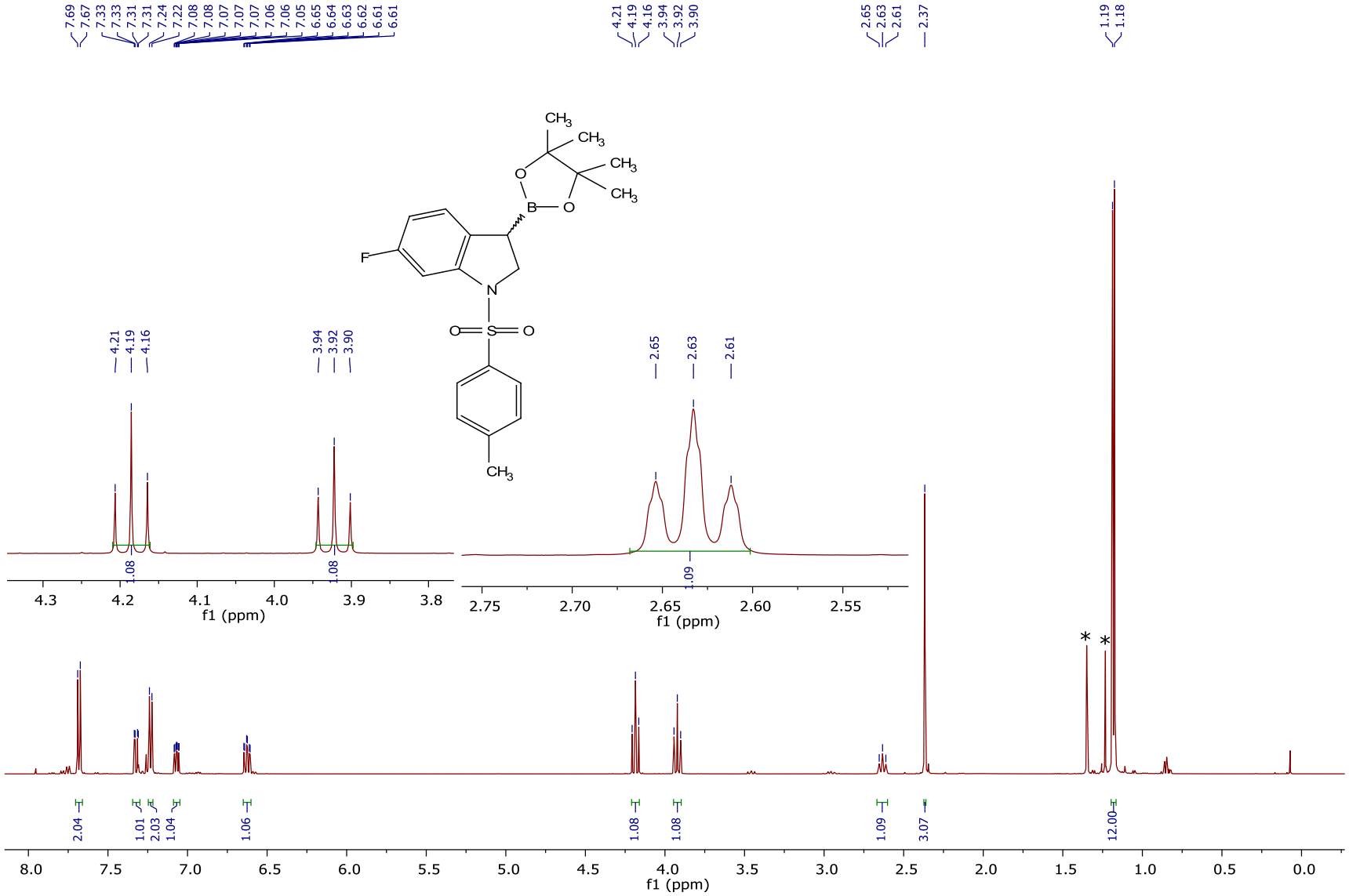

Figure S48. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6j**.

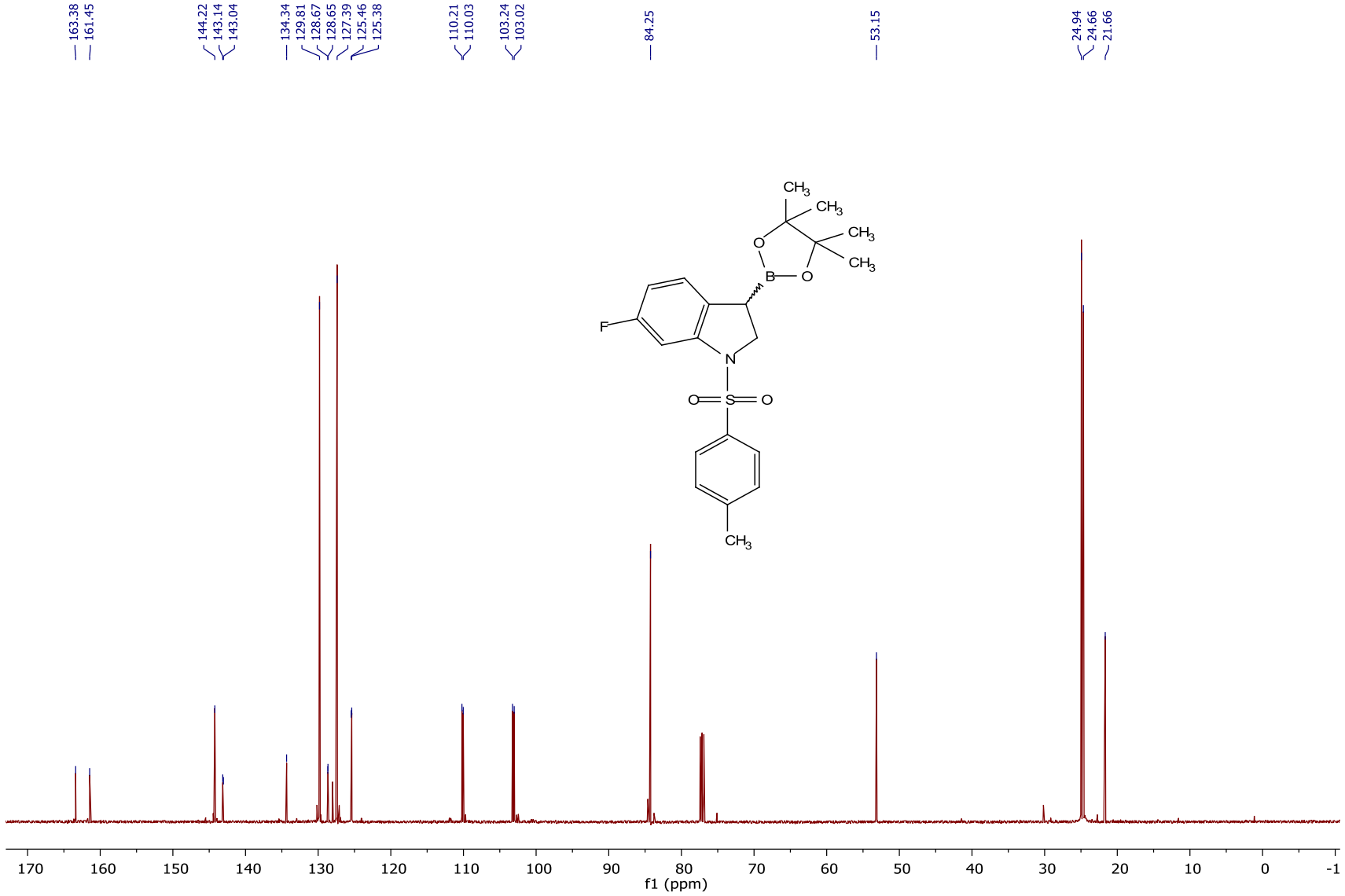

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6j**.

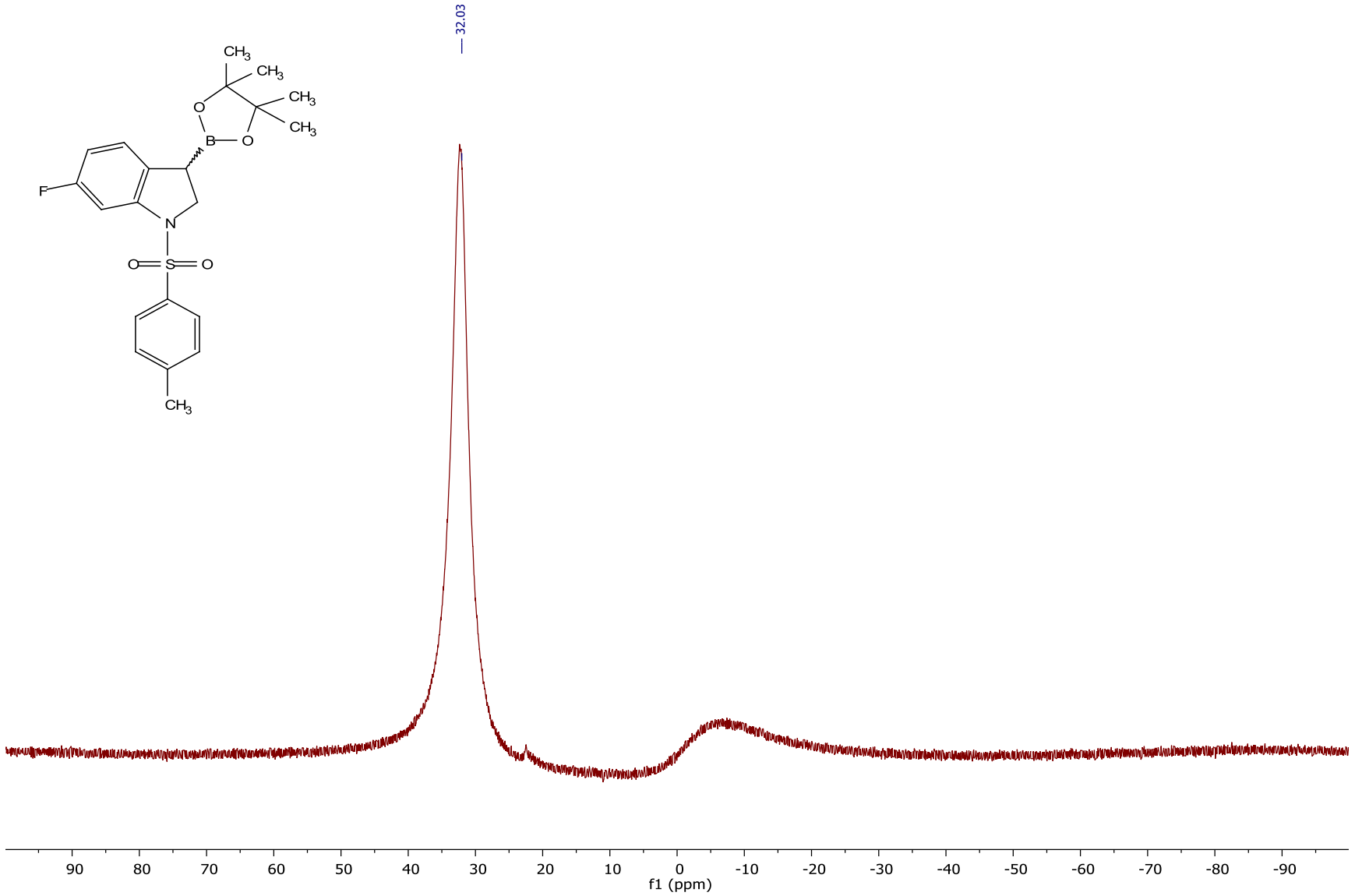

Figure S50. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6j**.

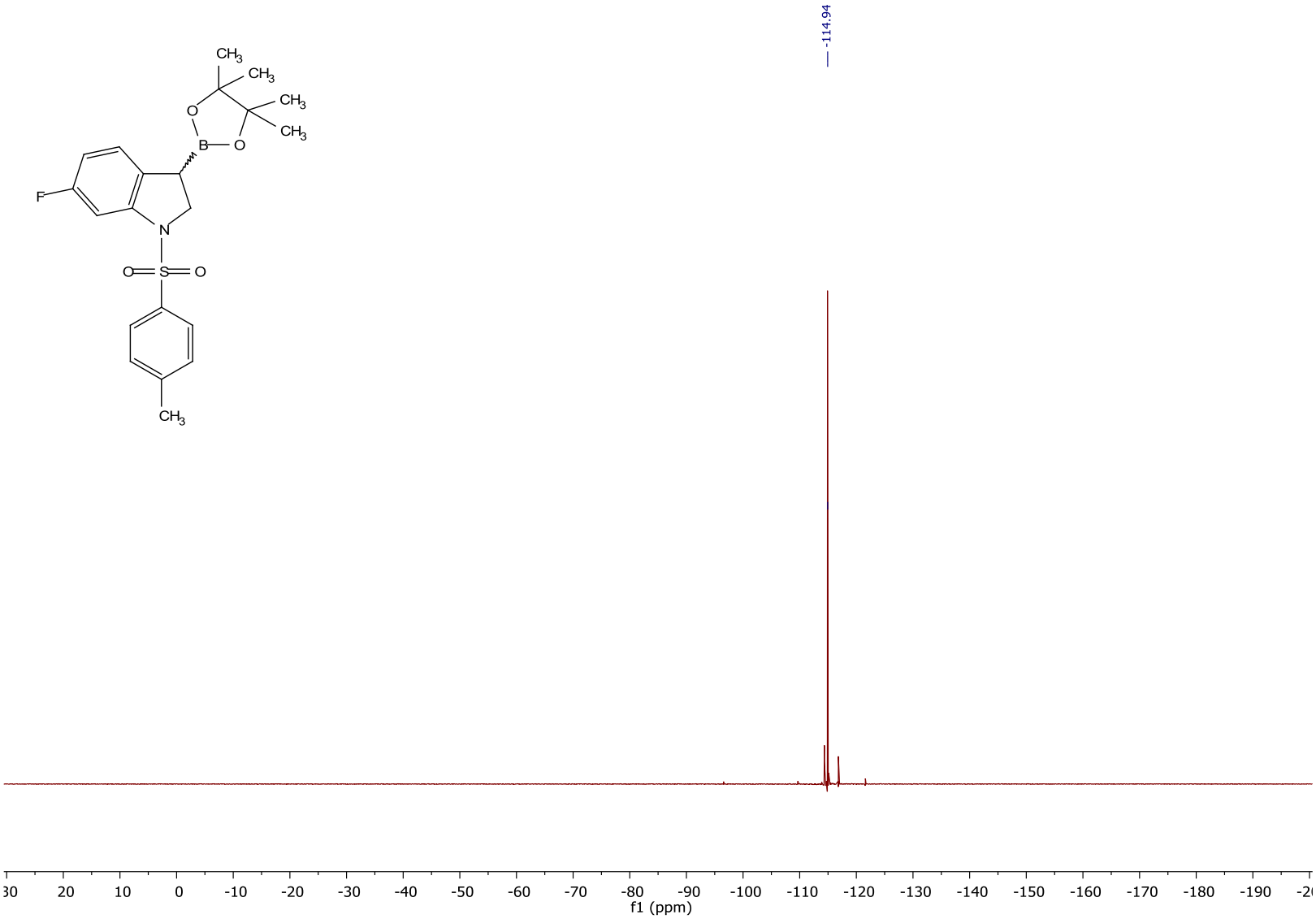

Figure S51. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **6j**.

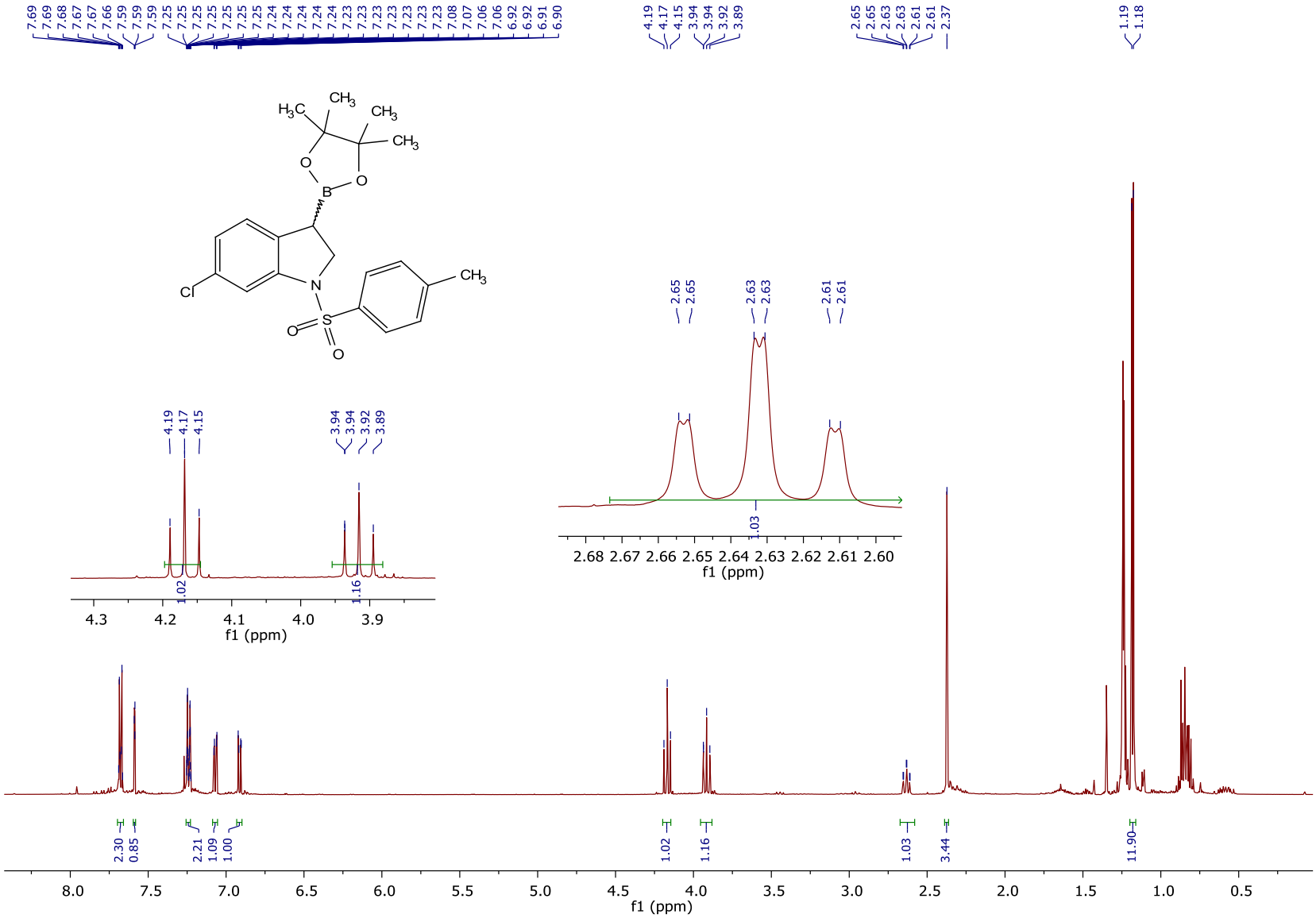

Figure S52. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6k**.

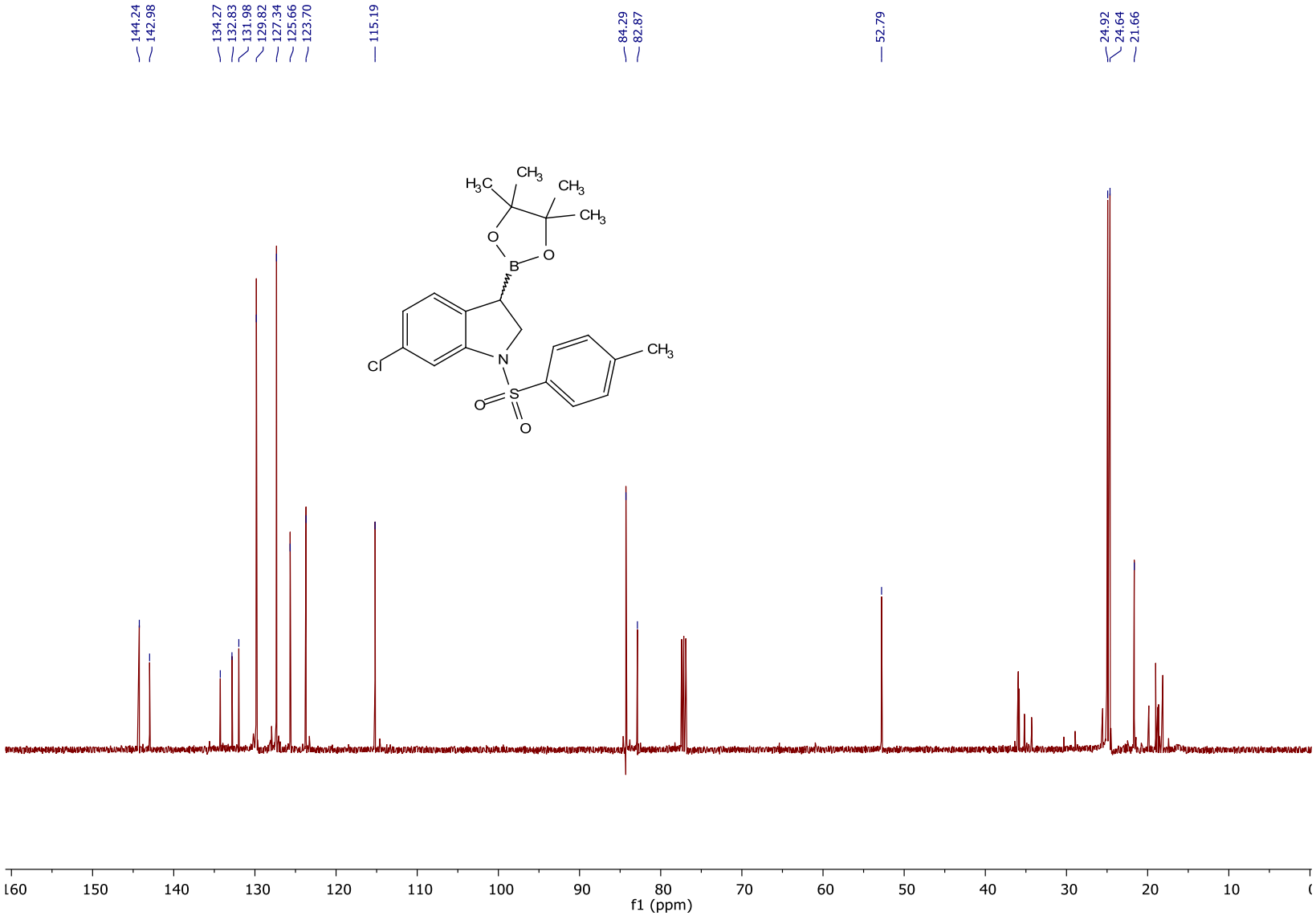

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6k**.

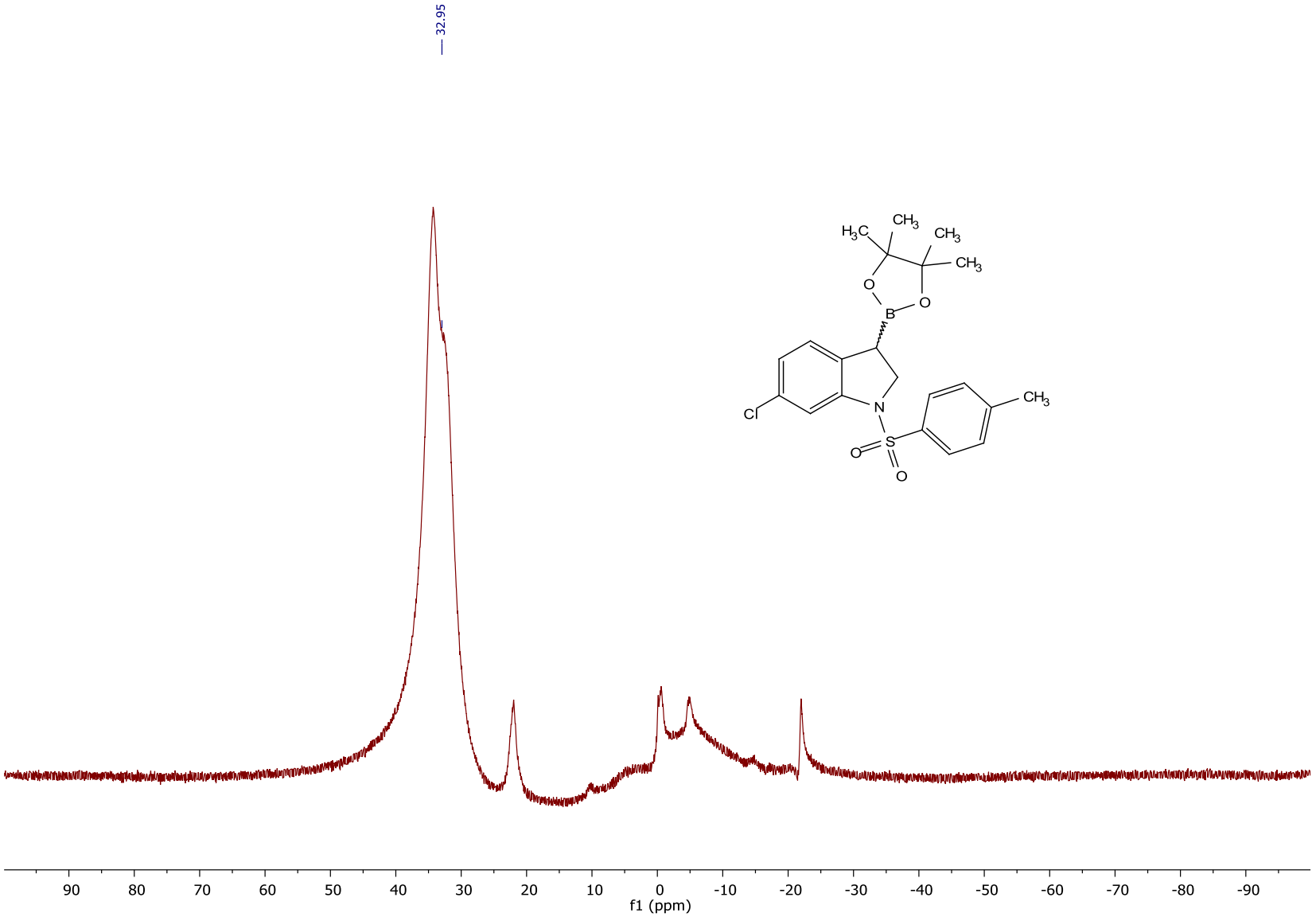

Figure S54. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6k**.

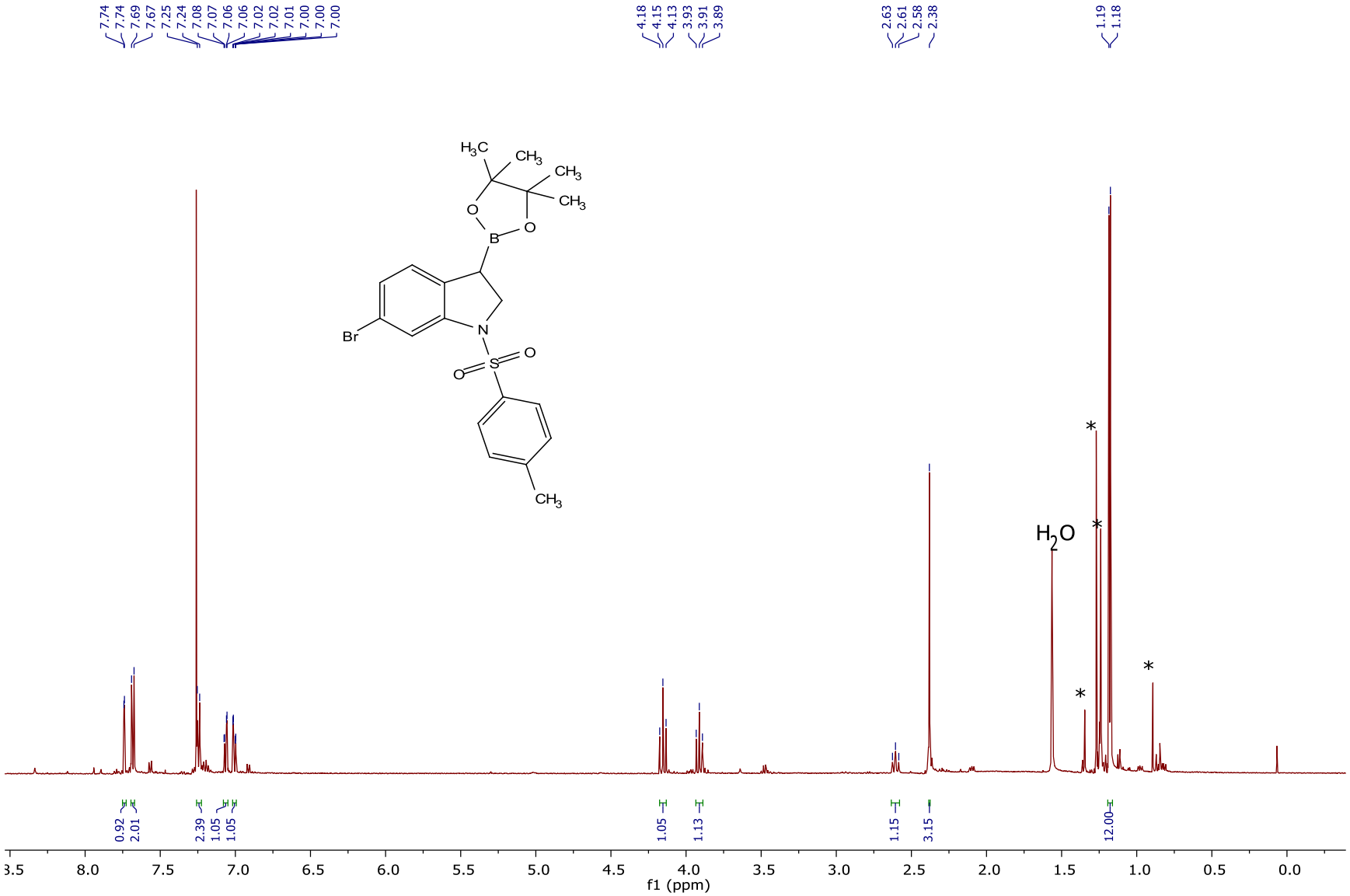

Figure S55. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6l**.

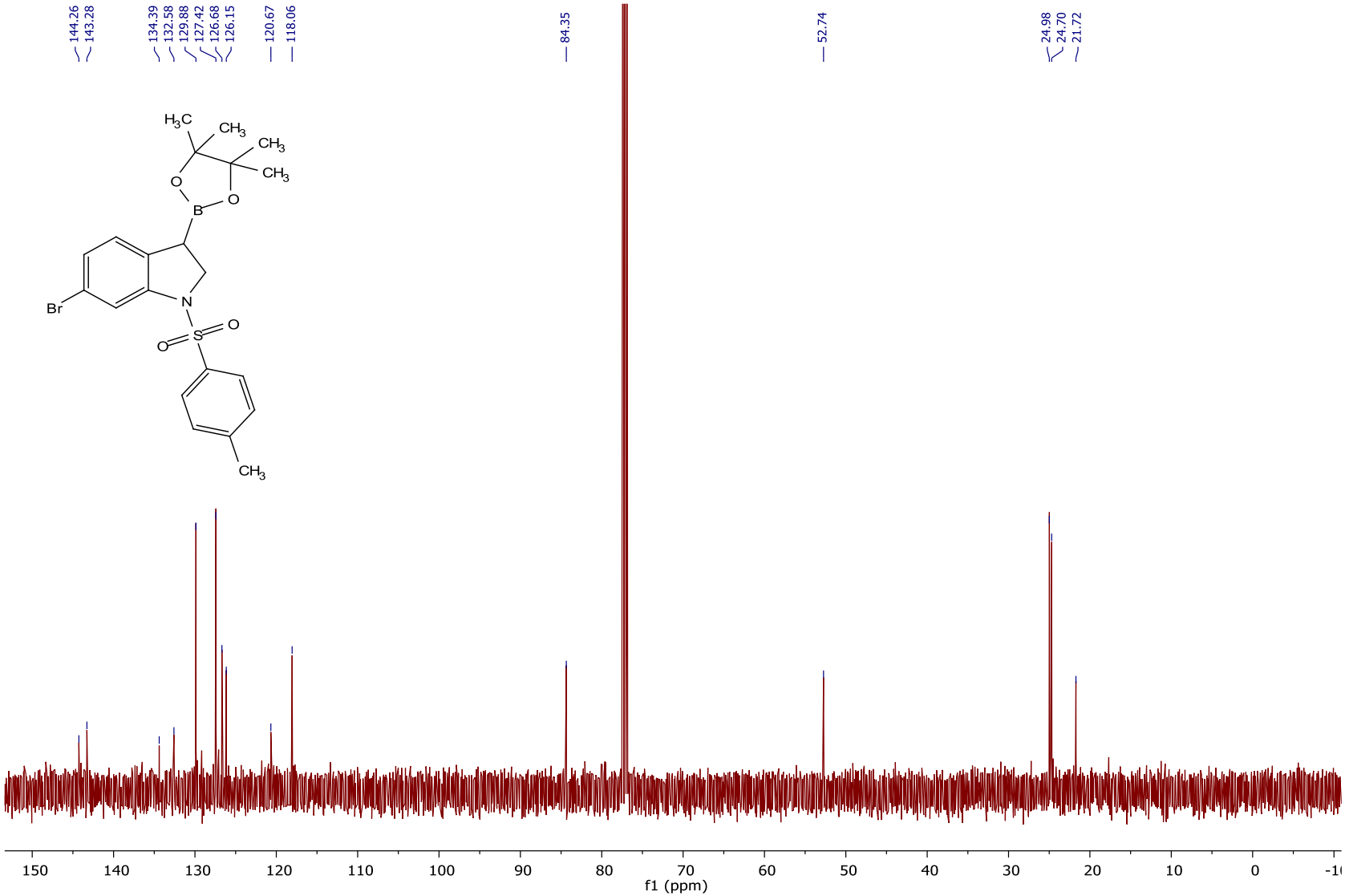

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6l**.

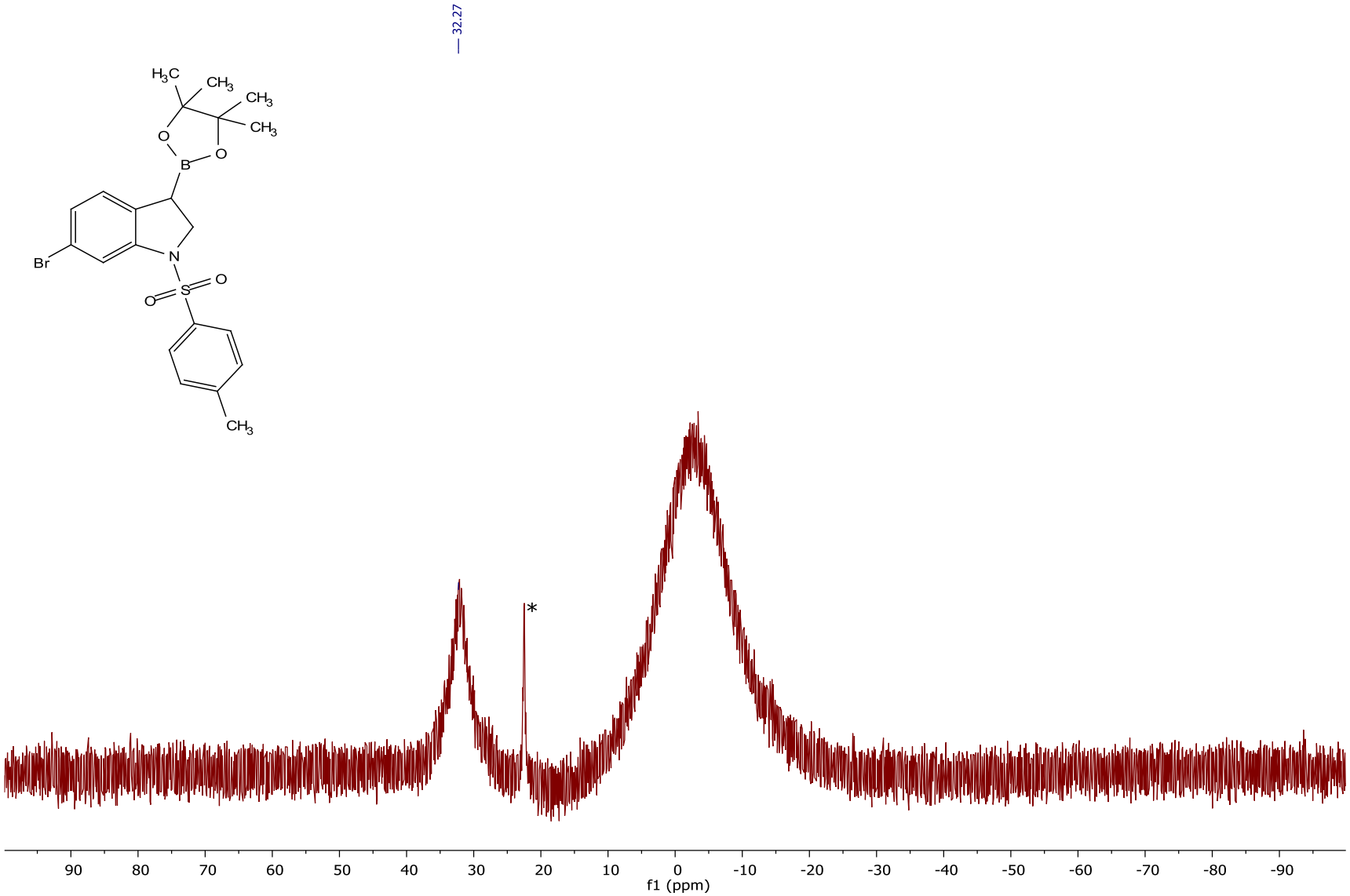

Figure S57. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6l**.

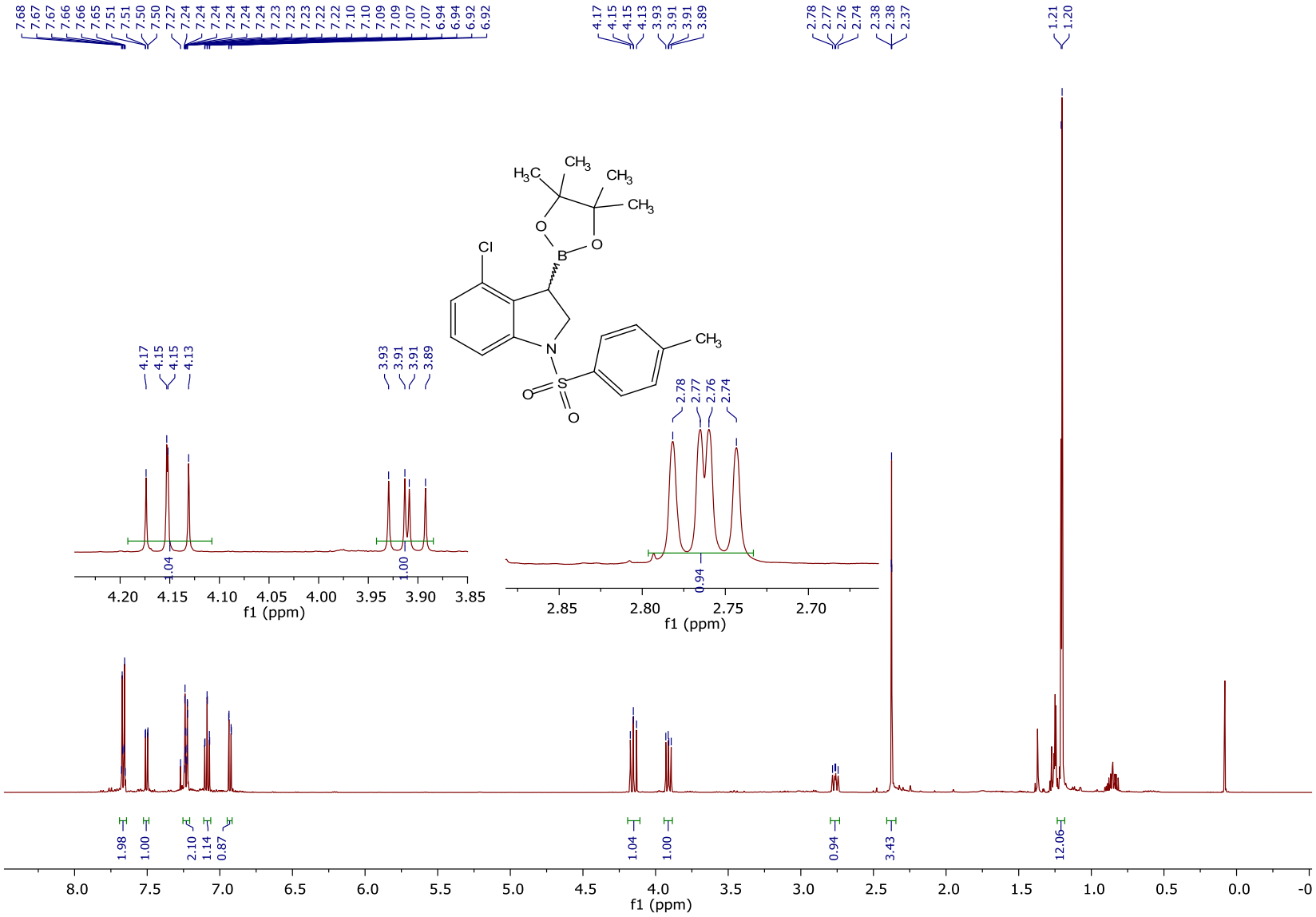

Figure S58. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6m**.

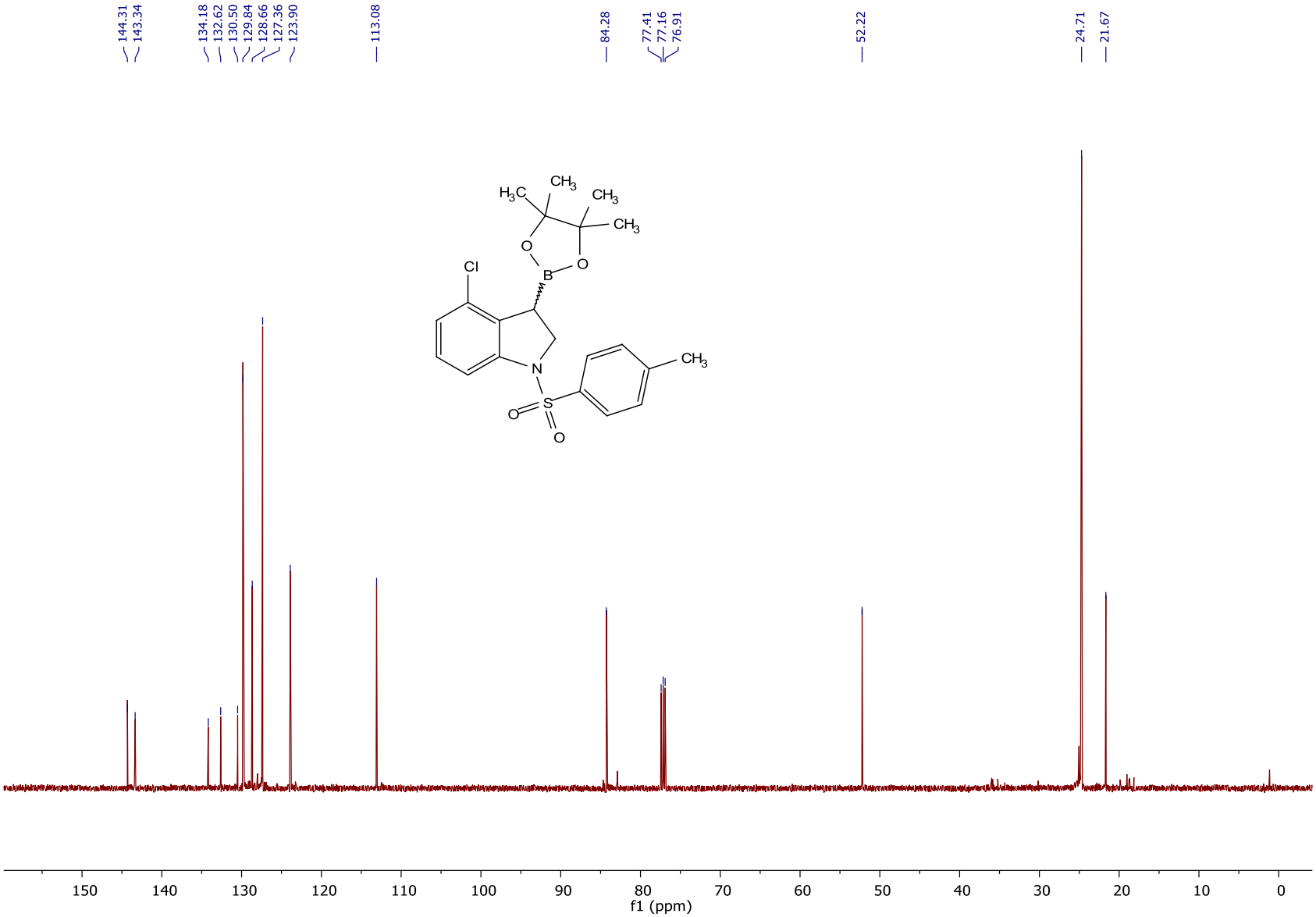

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6m**.

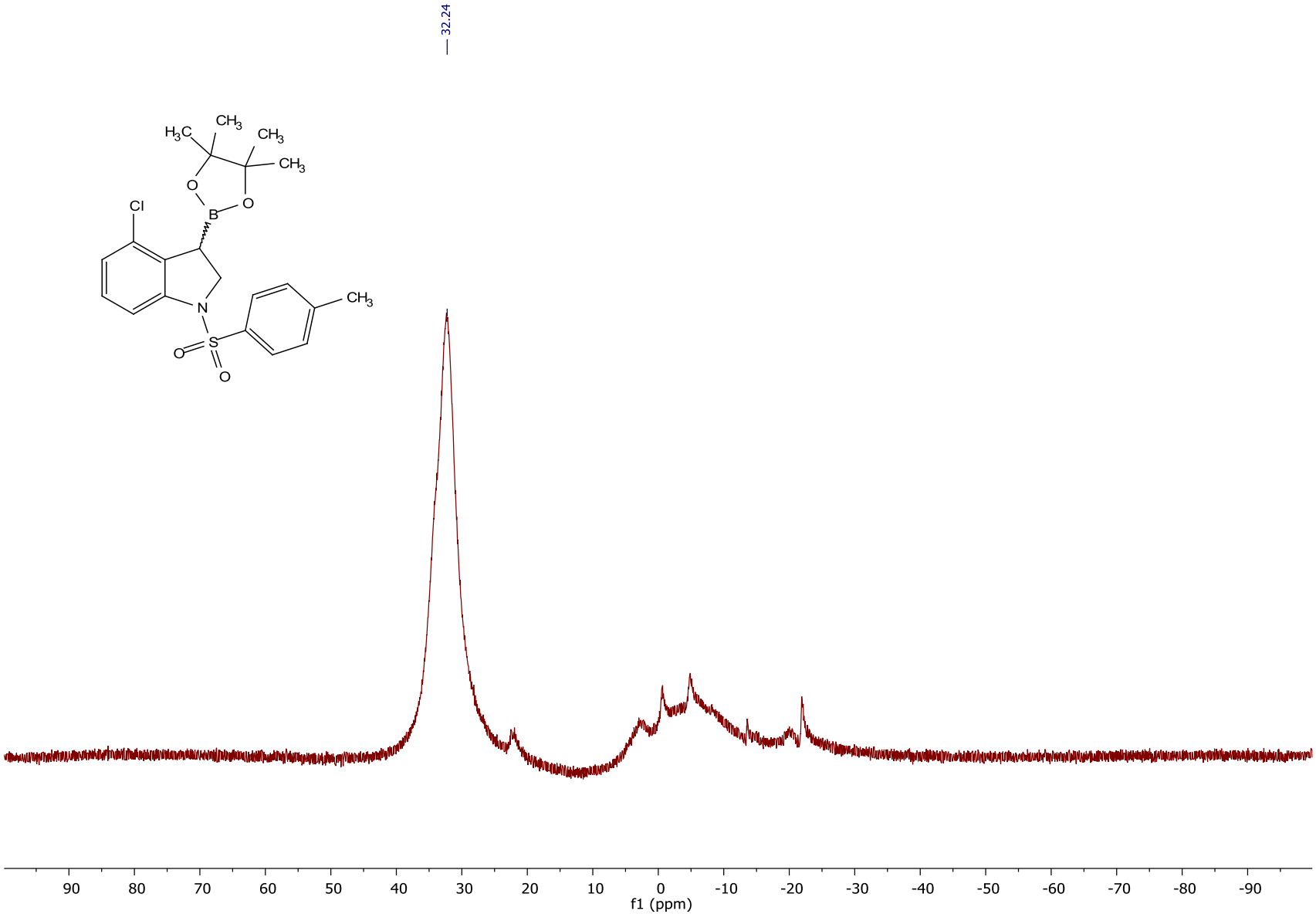

Figure S60. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6m**.

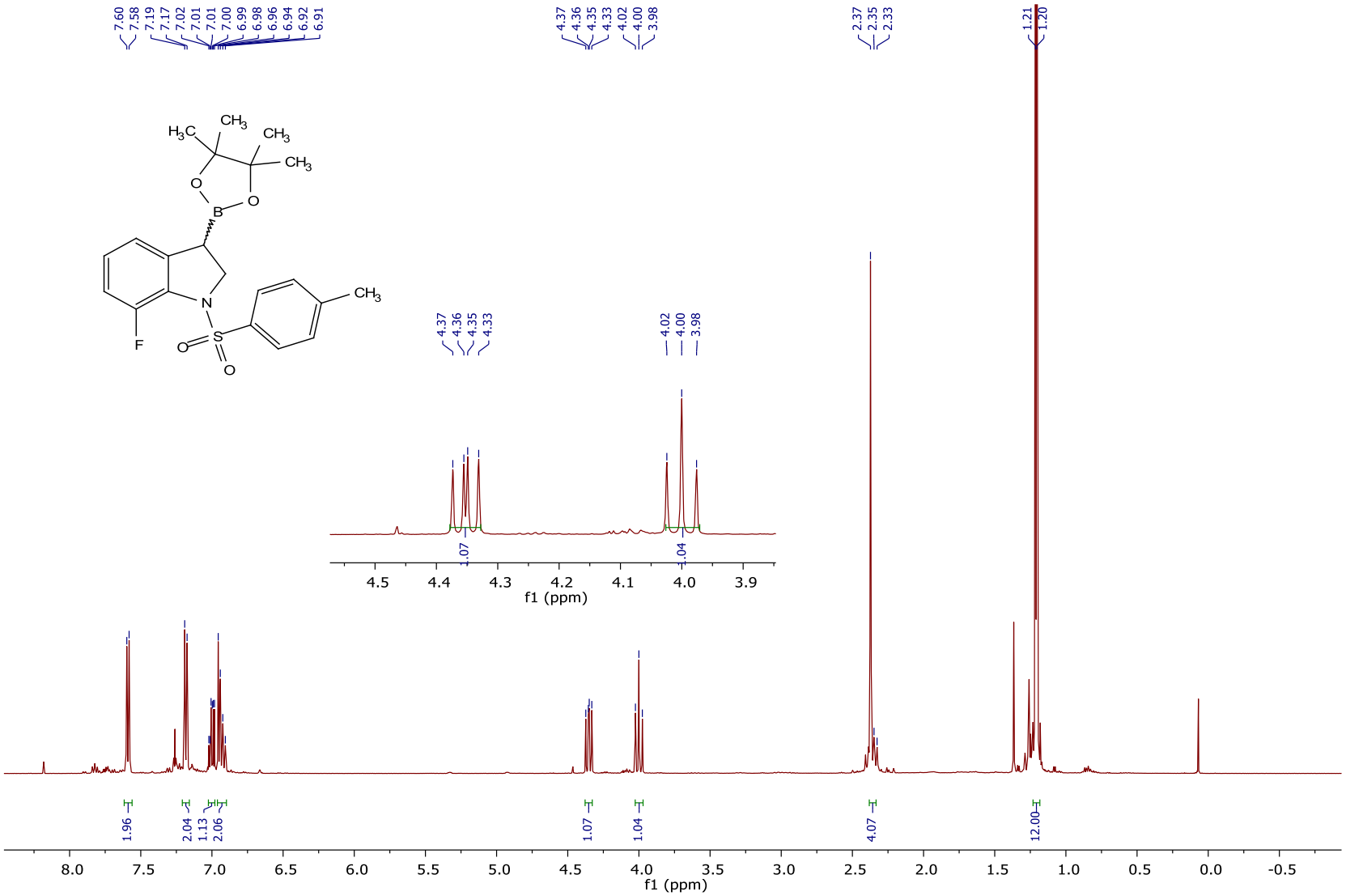

Figure S61. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6n**.

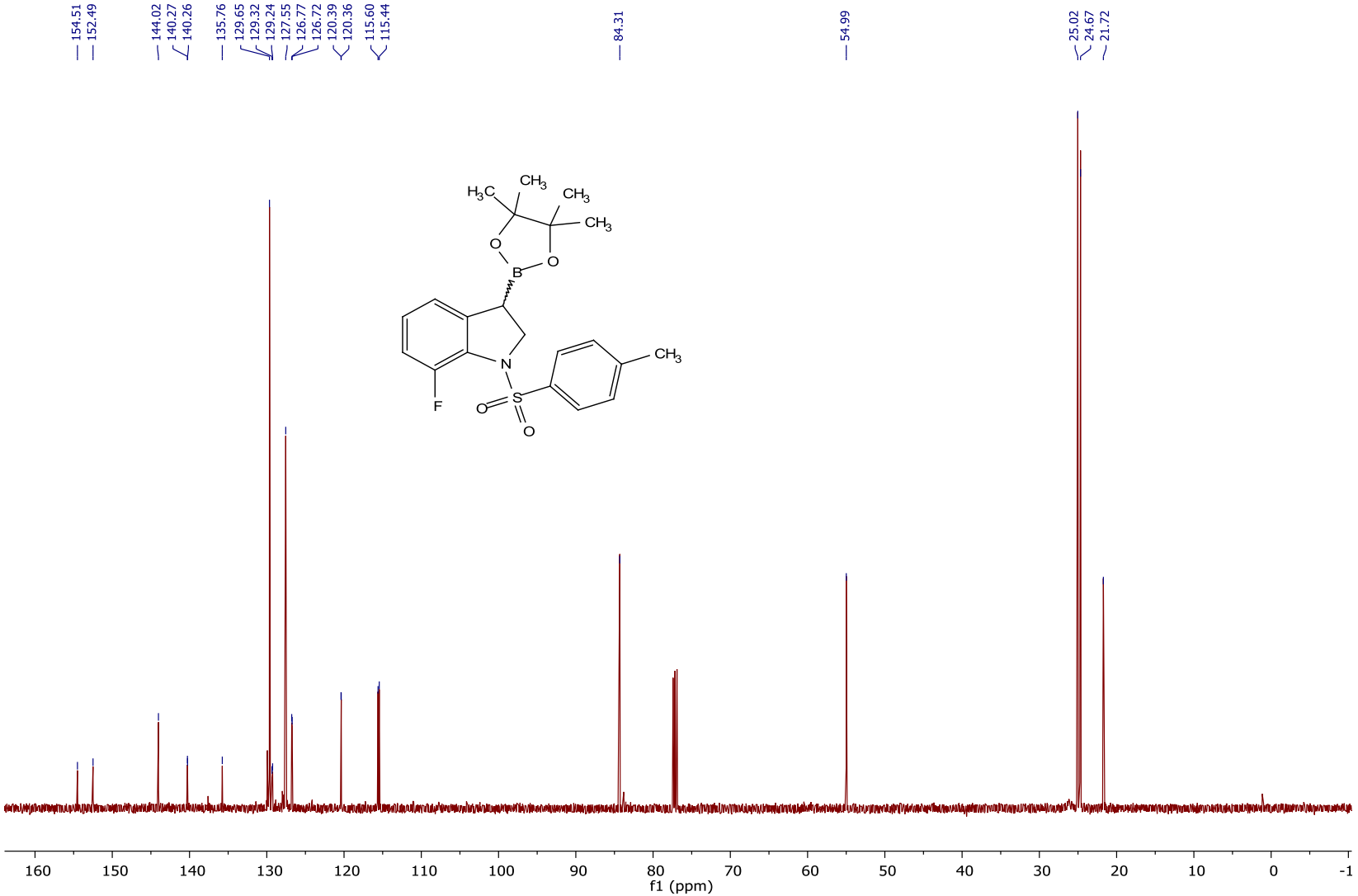

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6n**.

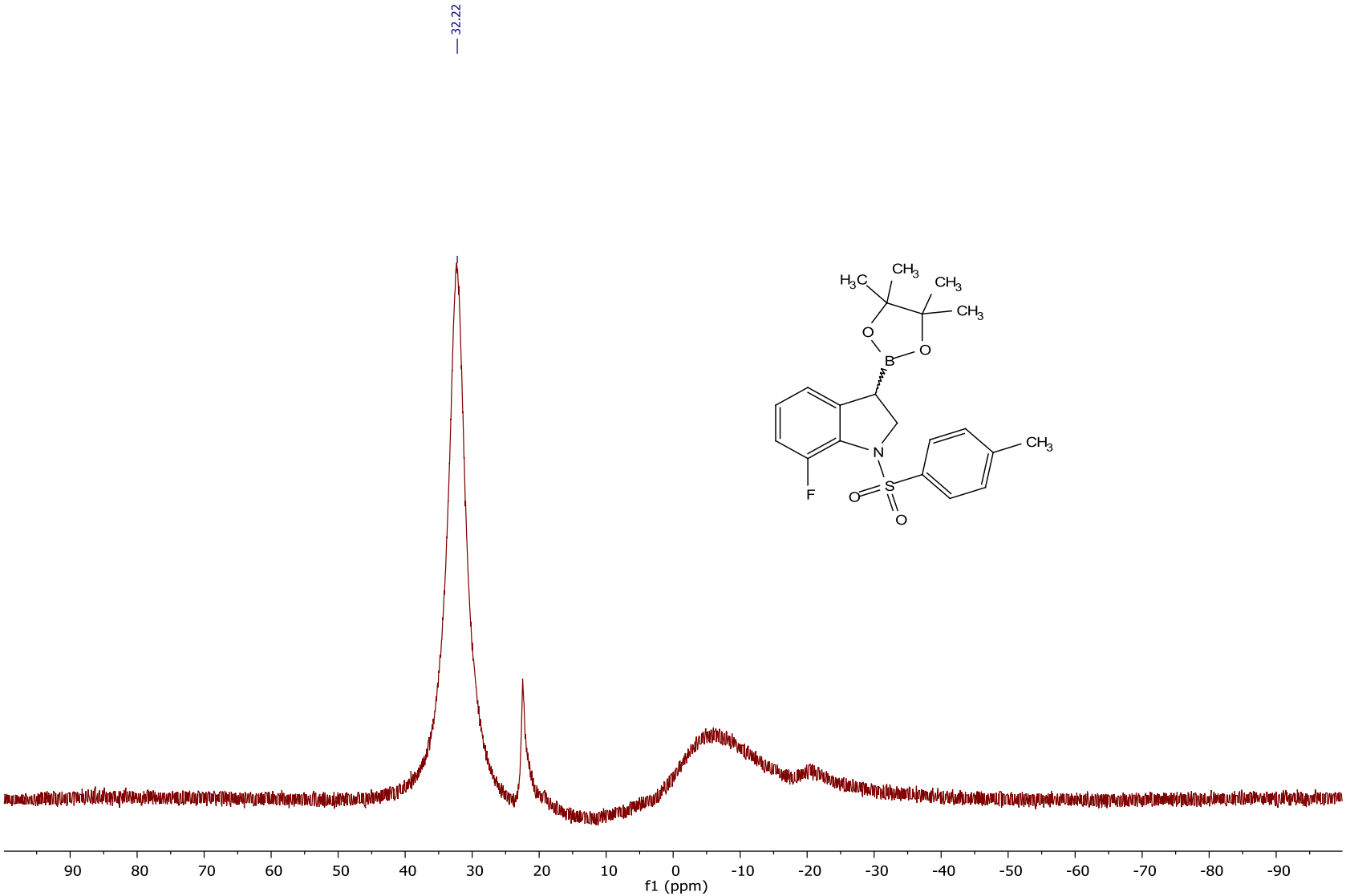

Figure S63. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6n**.

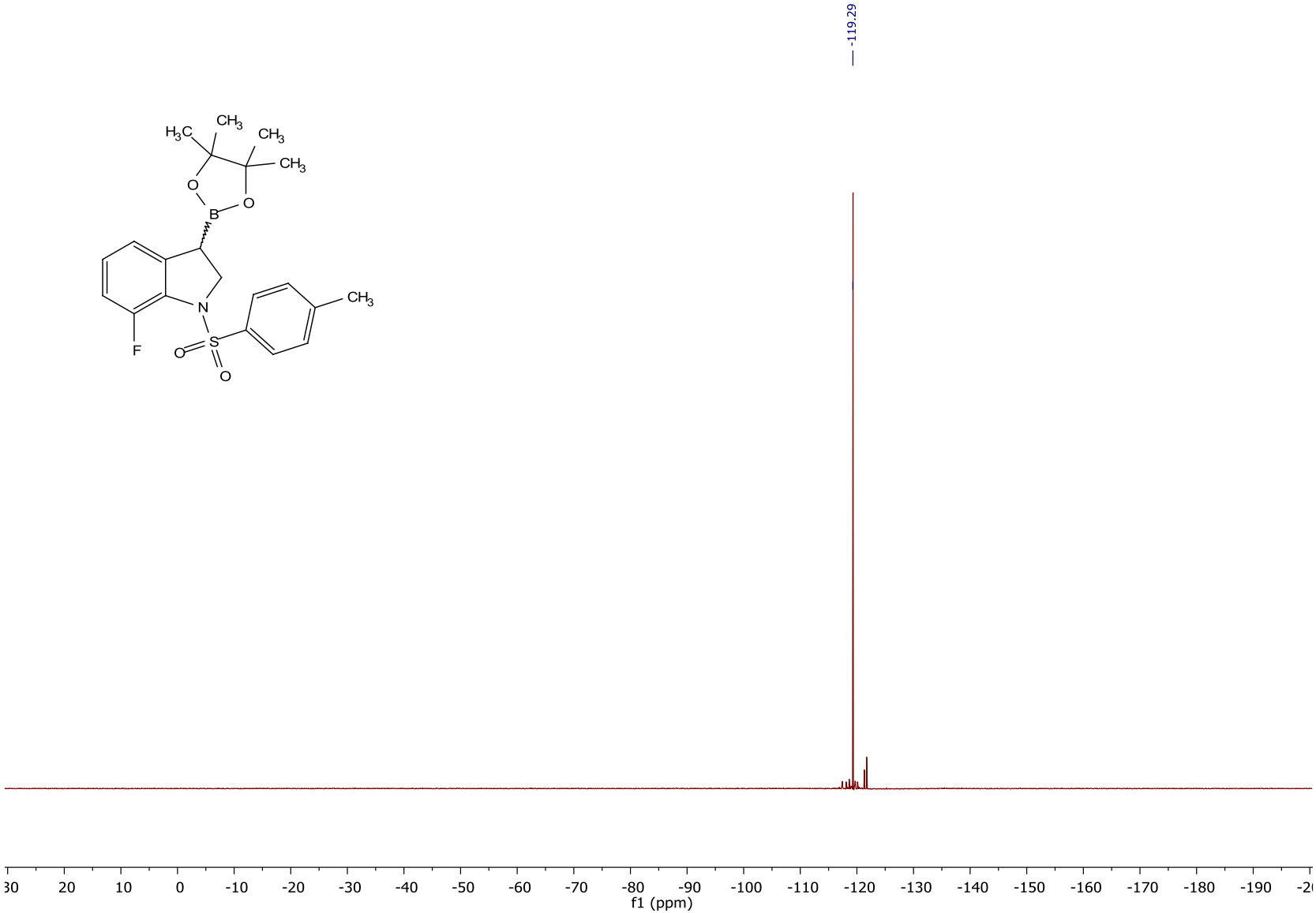

Figure S64. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **6n**.

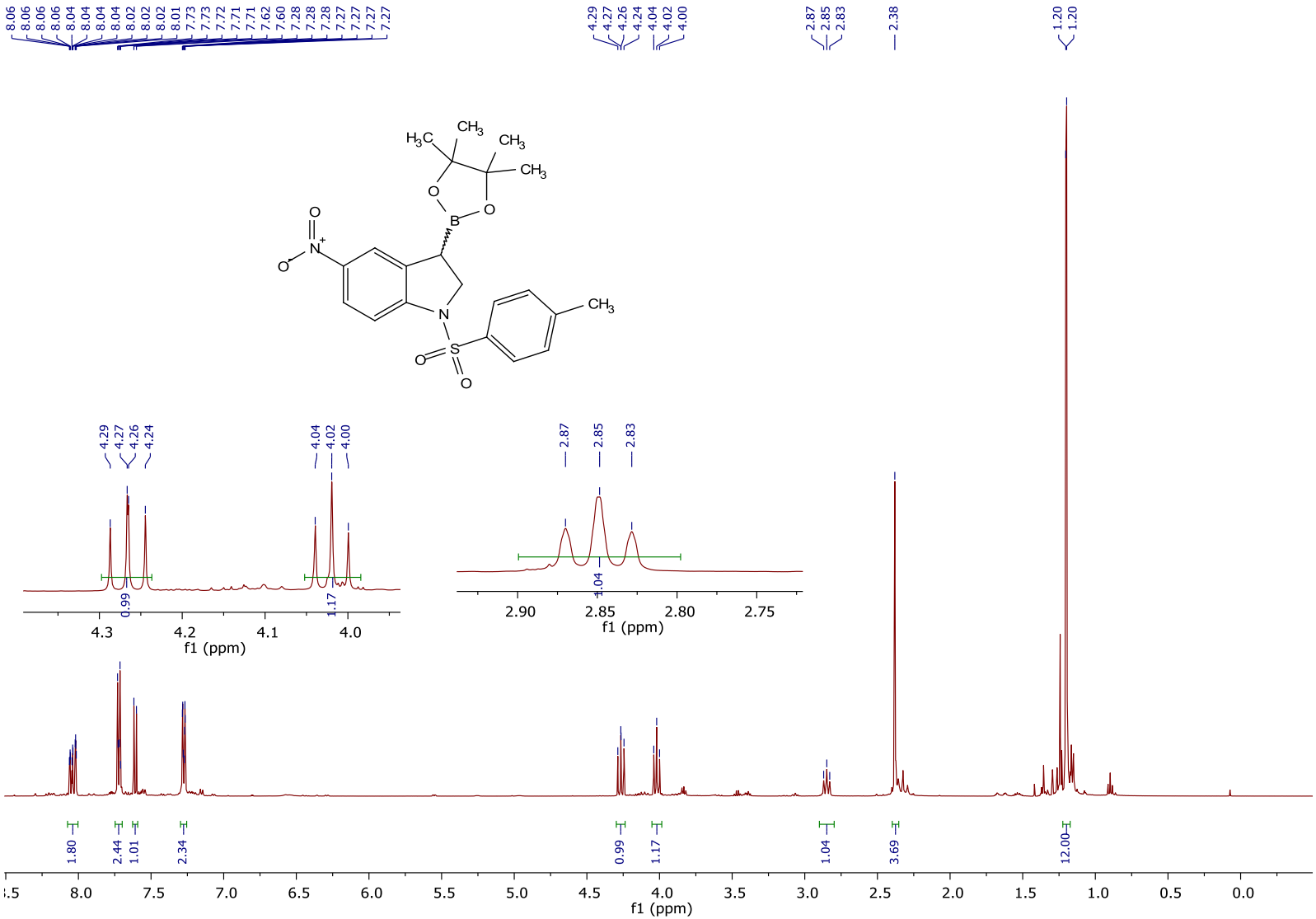

Figure S65. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6o**.

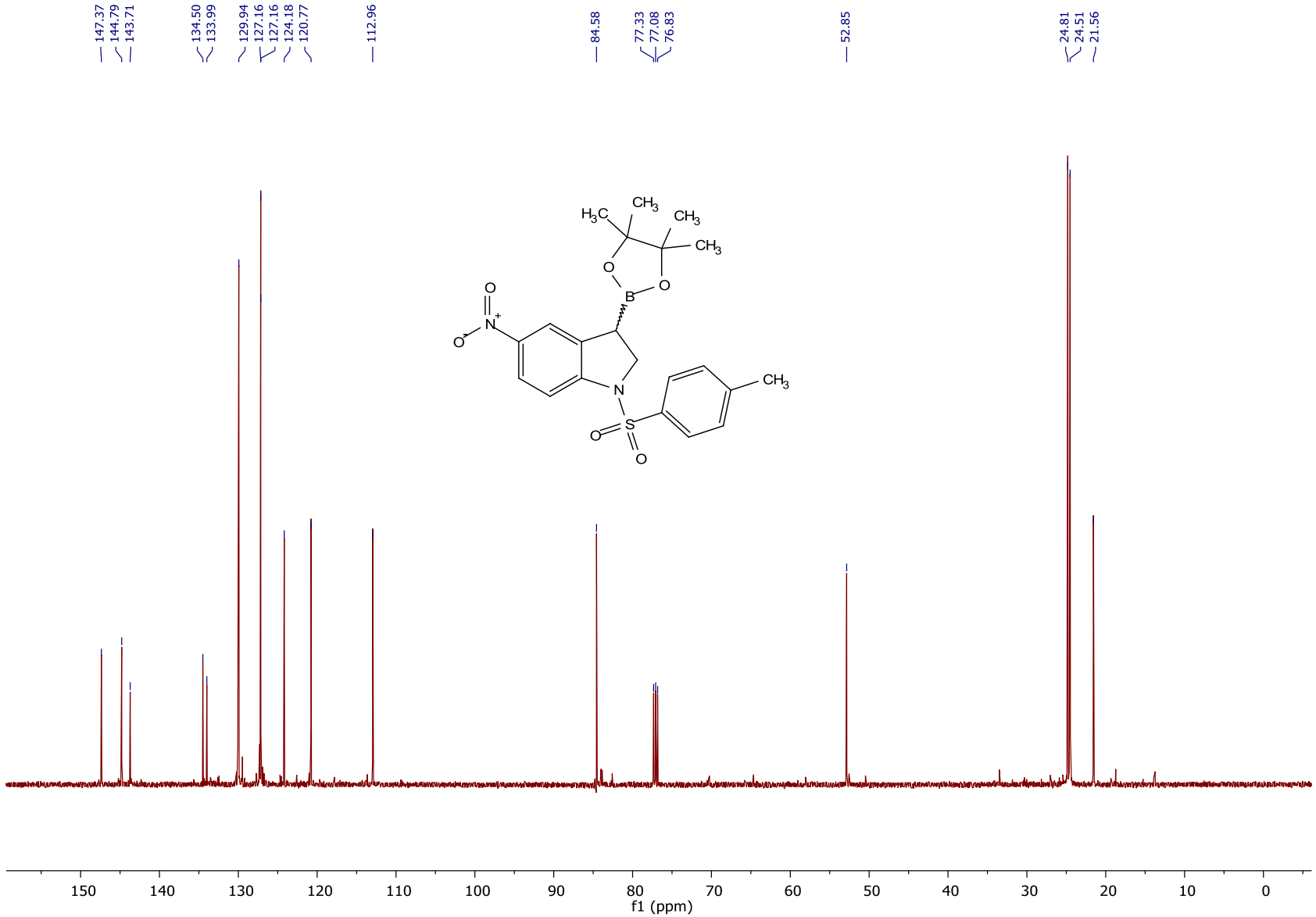

Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6o**.

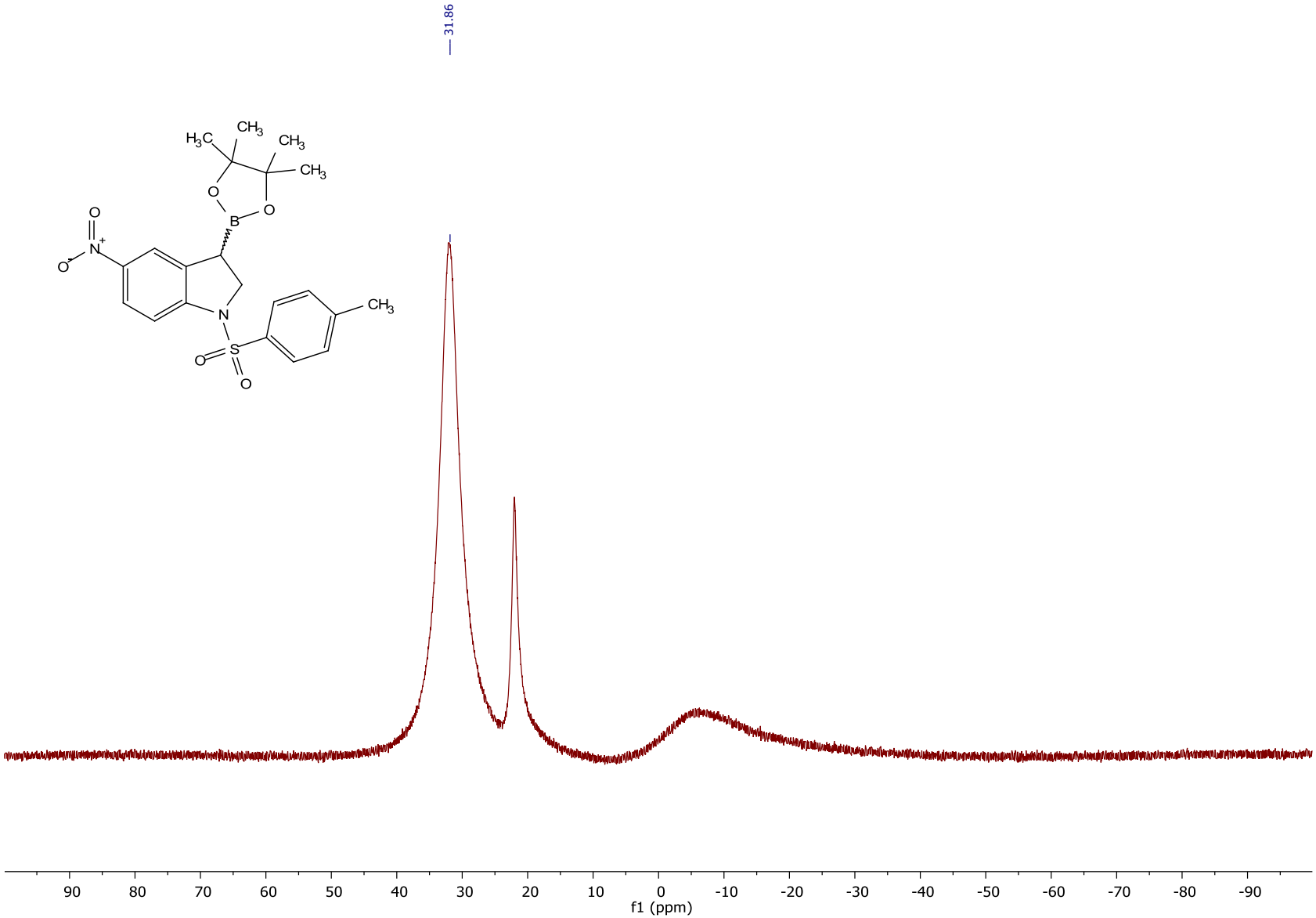

Figure S67. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6o**.

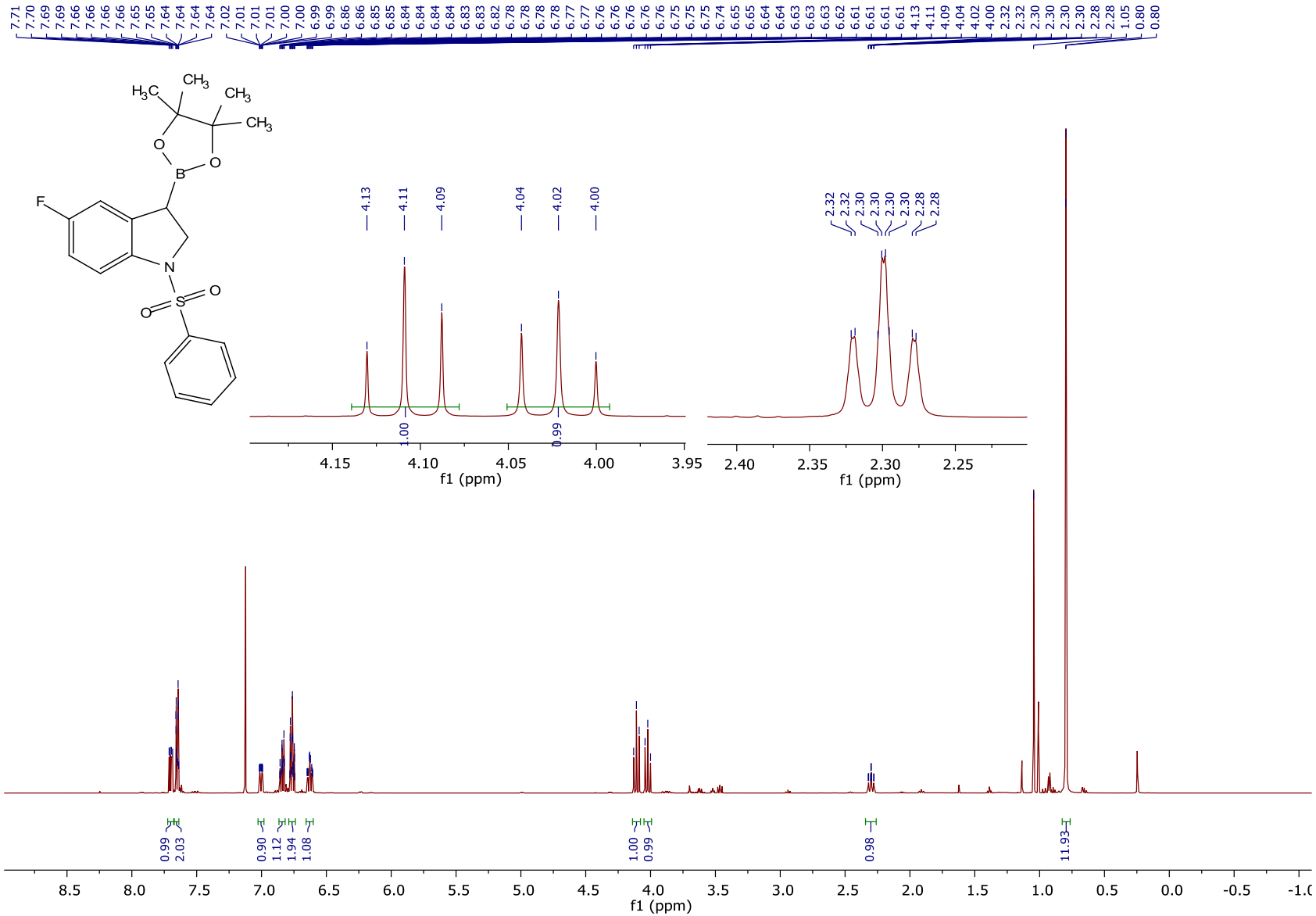

Figure S68. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6q**.

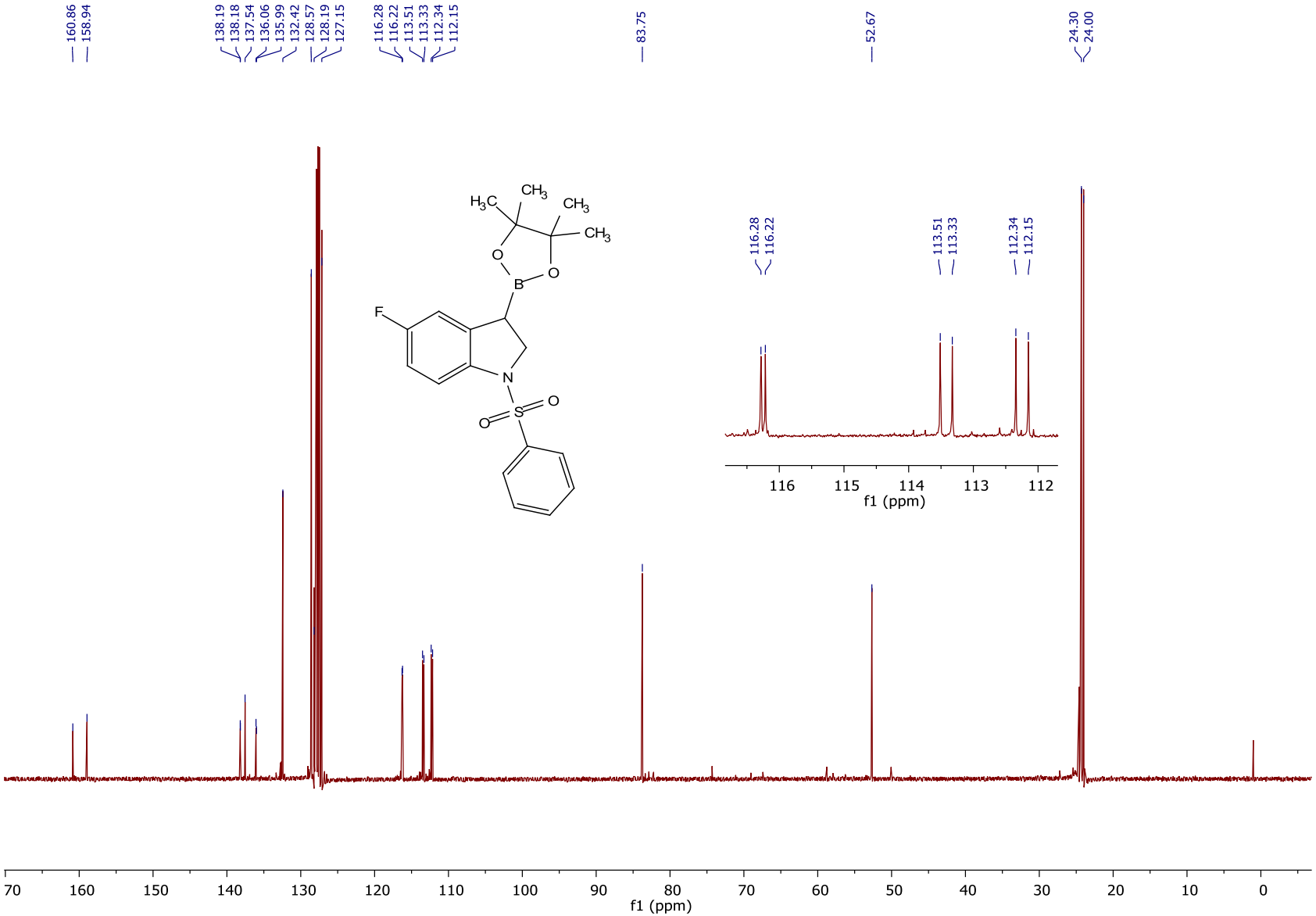

Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6q**.

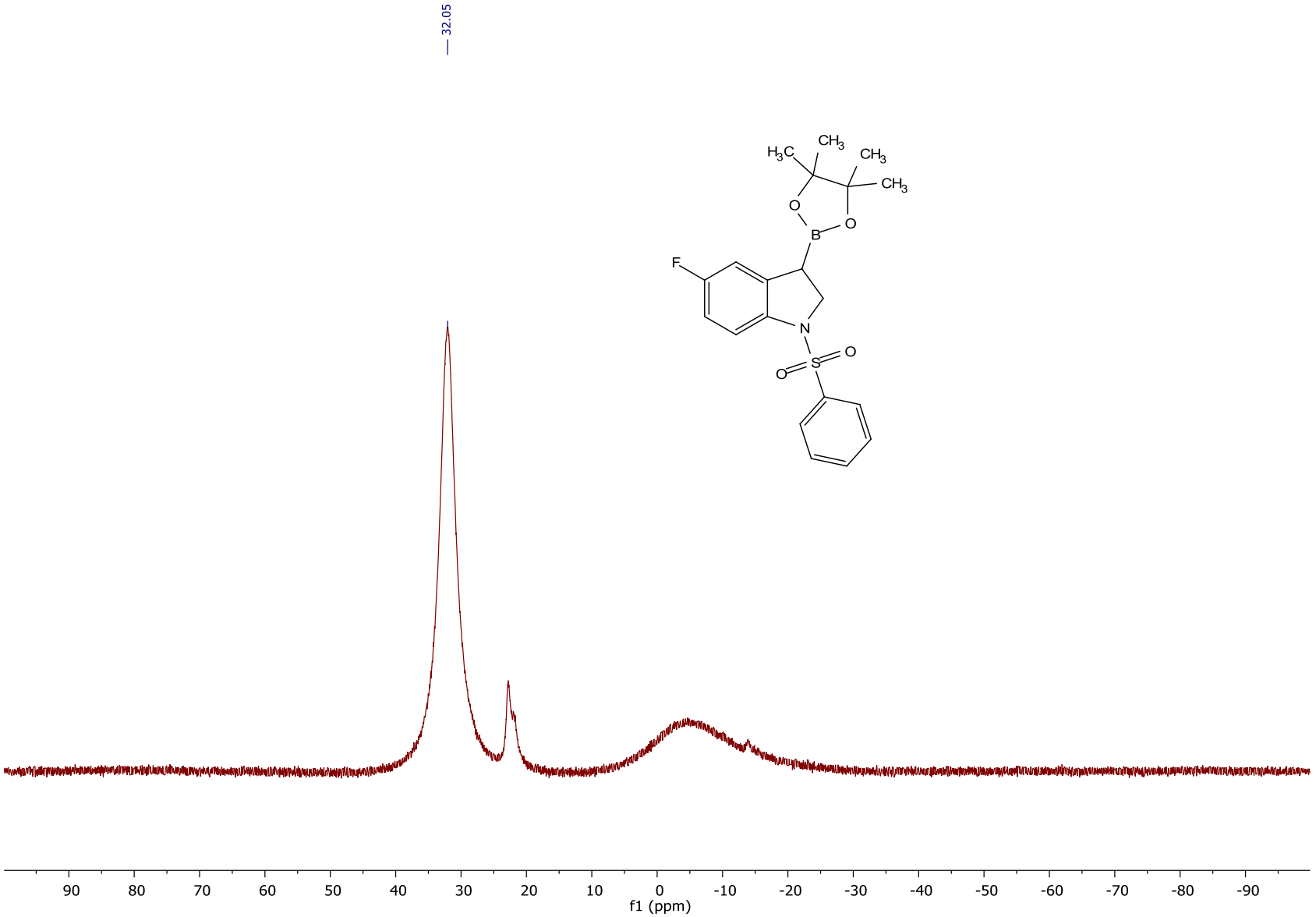

Figure S70. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6q**.

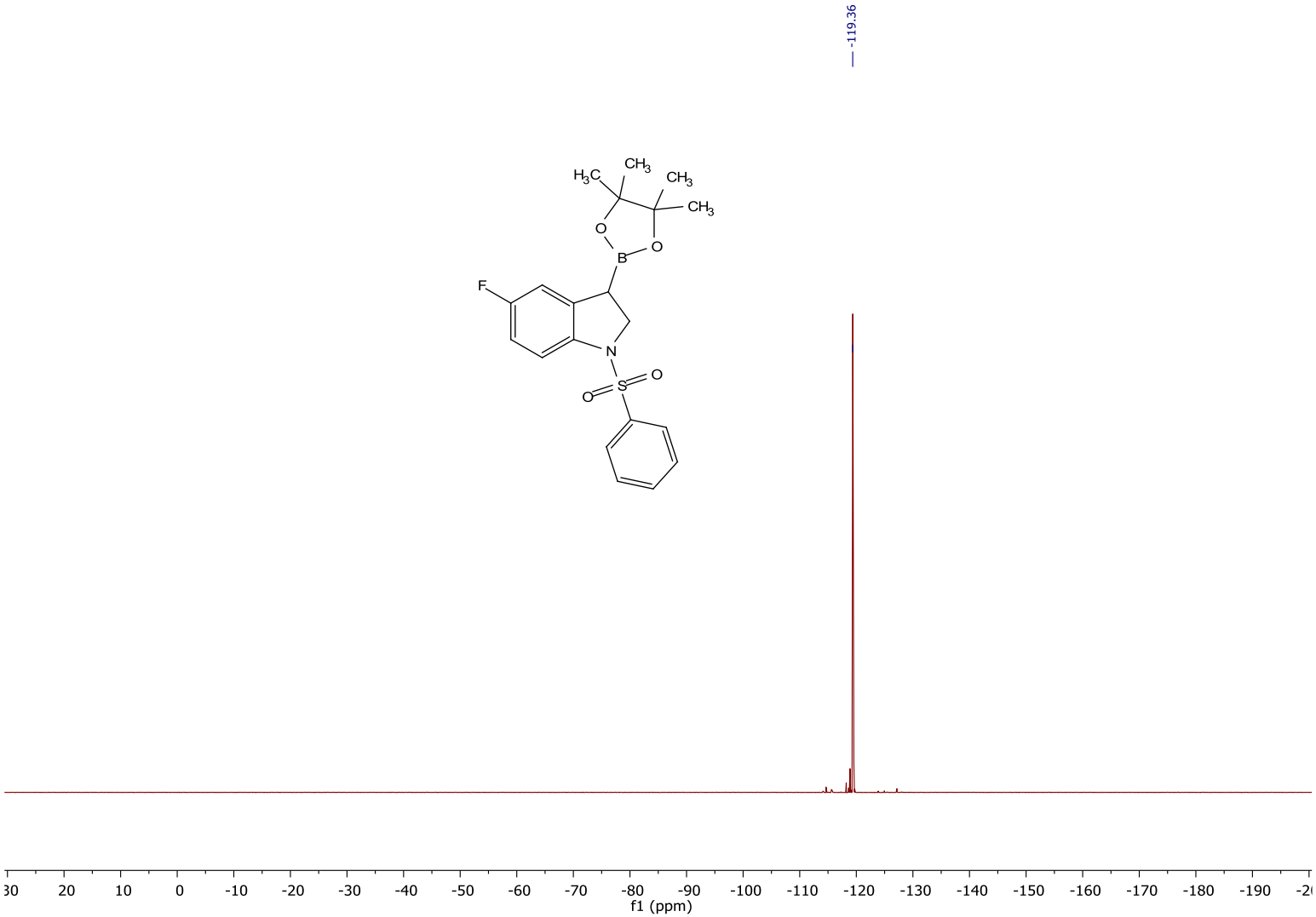

Figure S71. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **6q**.

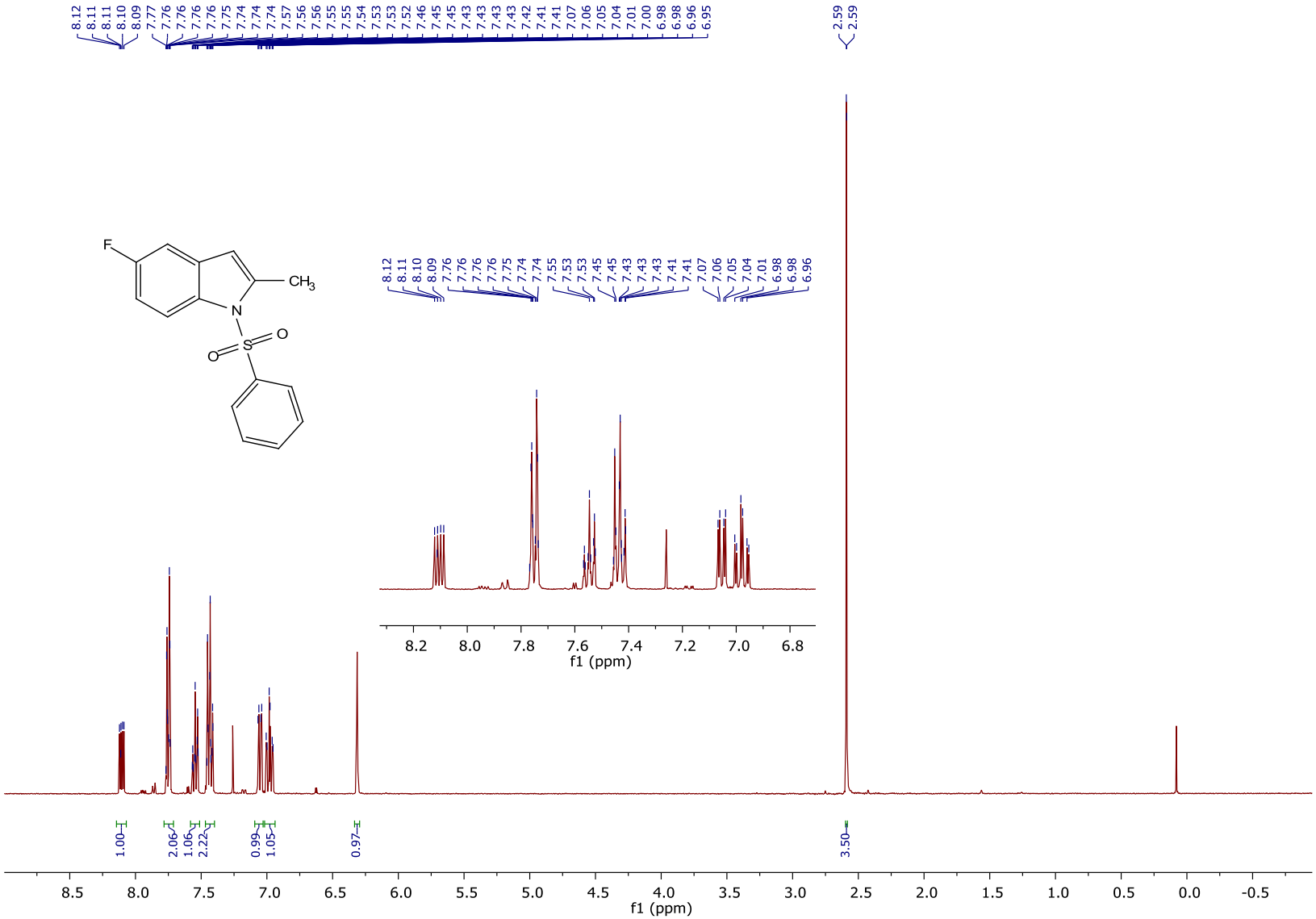

Figure S72. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5r**.

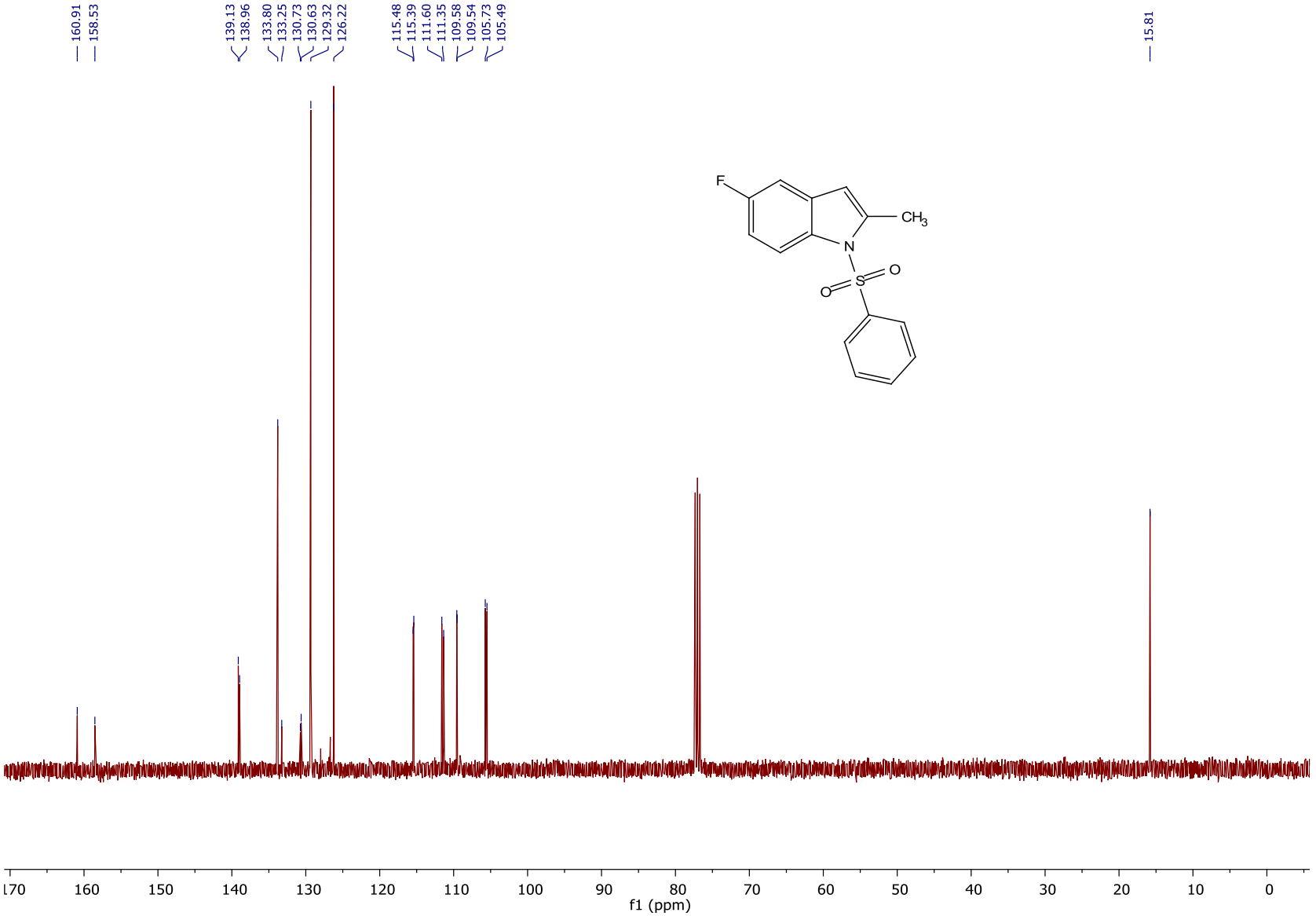

Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **5r**.

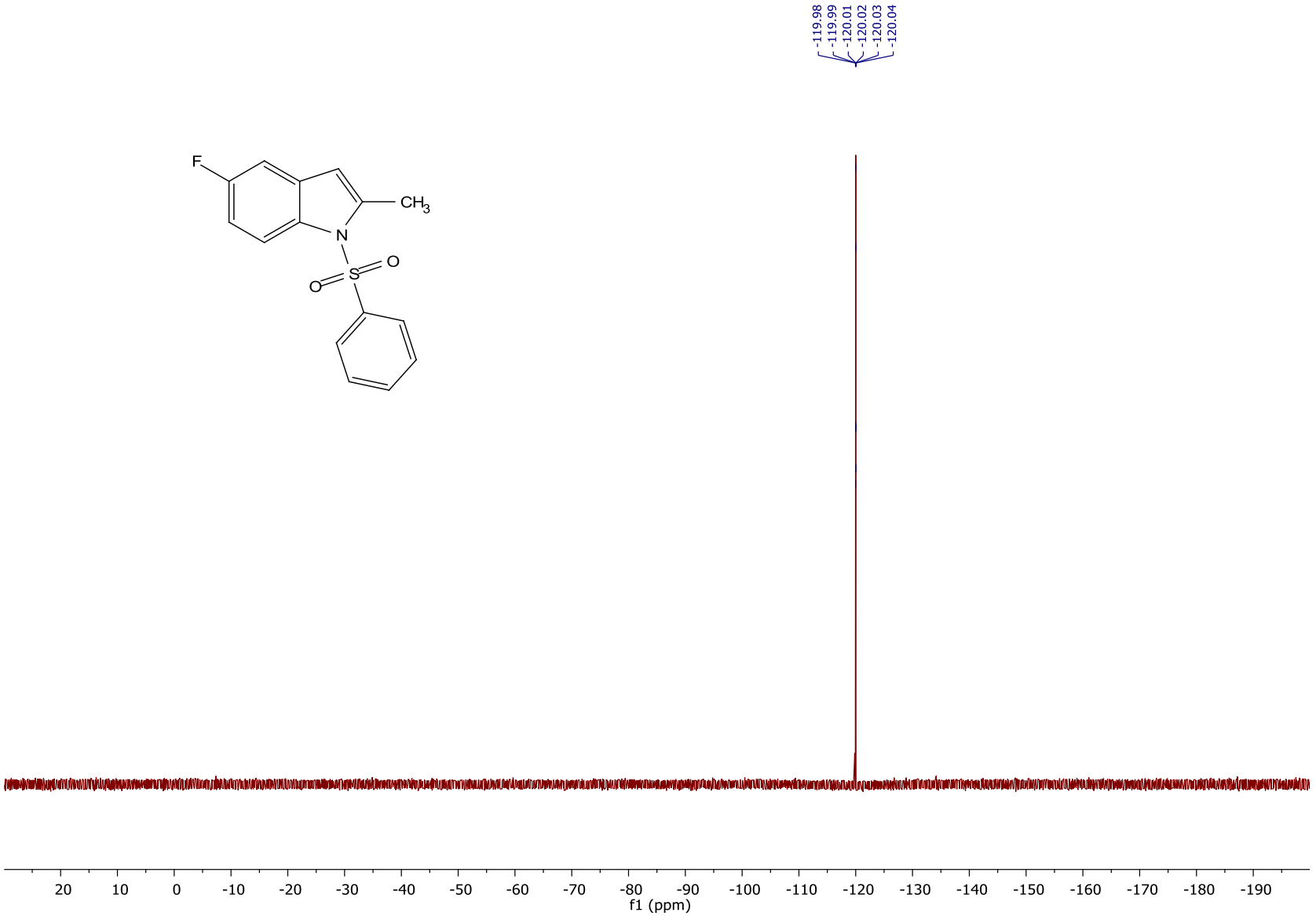

Figure S74. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **5r**.

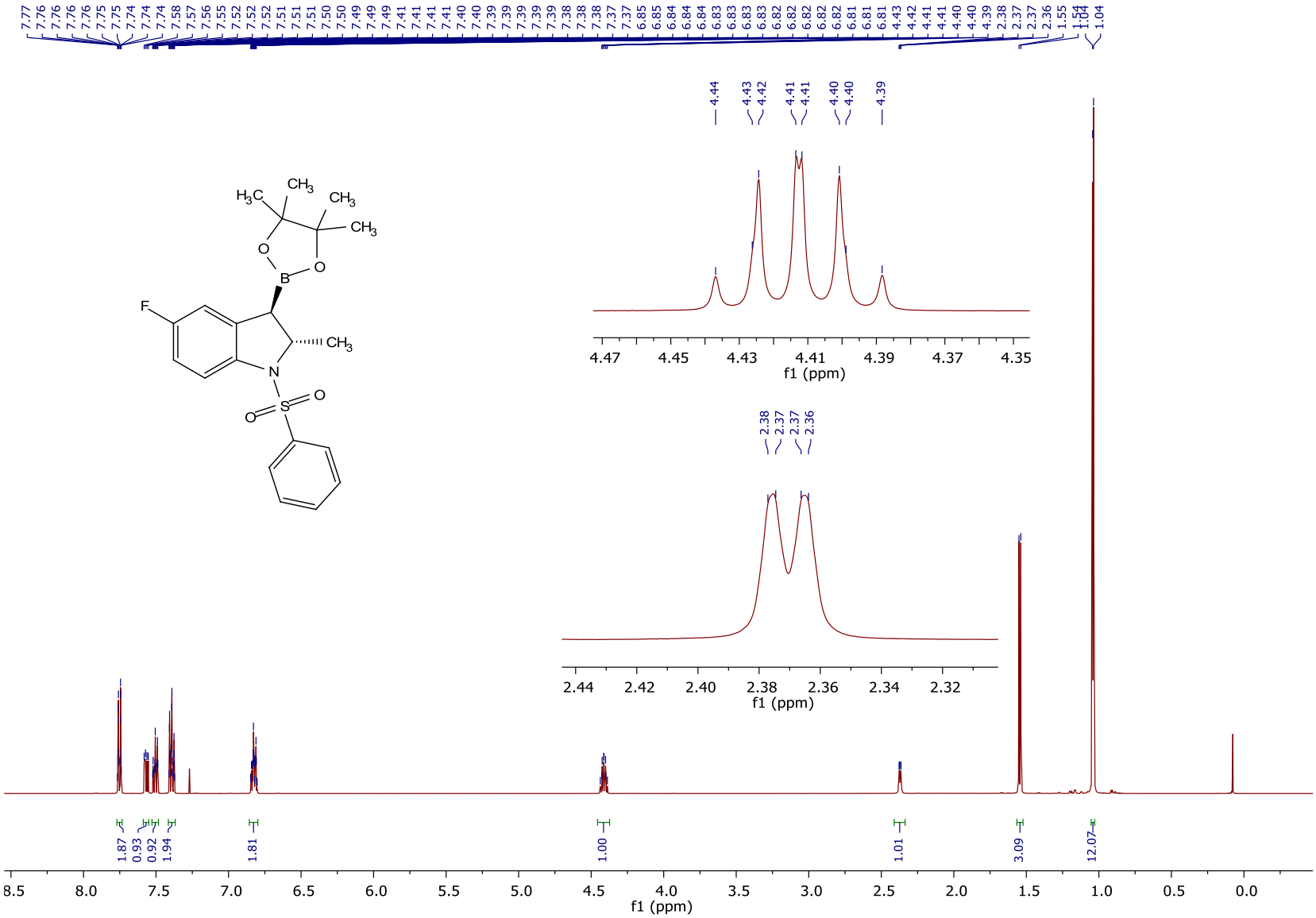

Figure S75. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6r**.

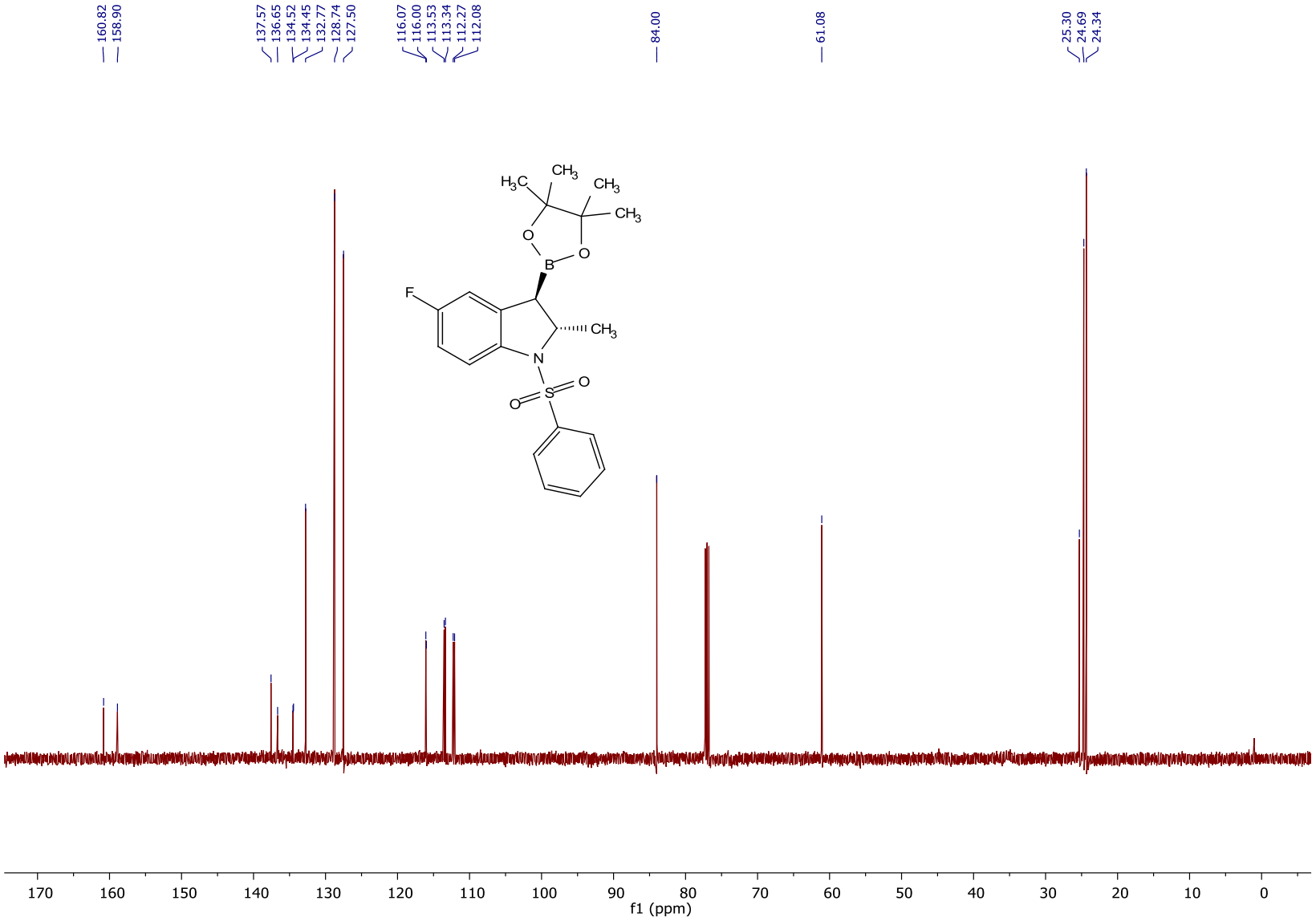

Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6r**.

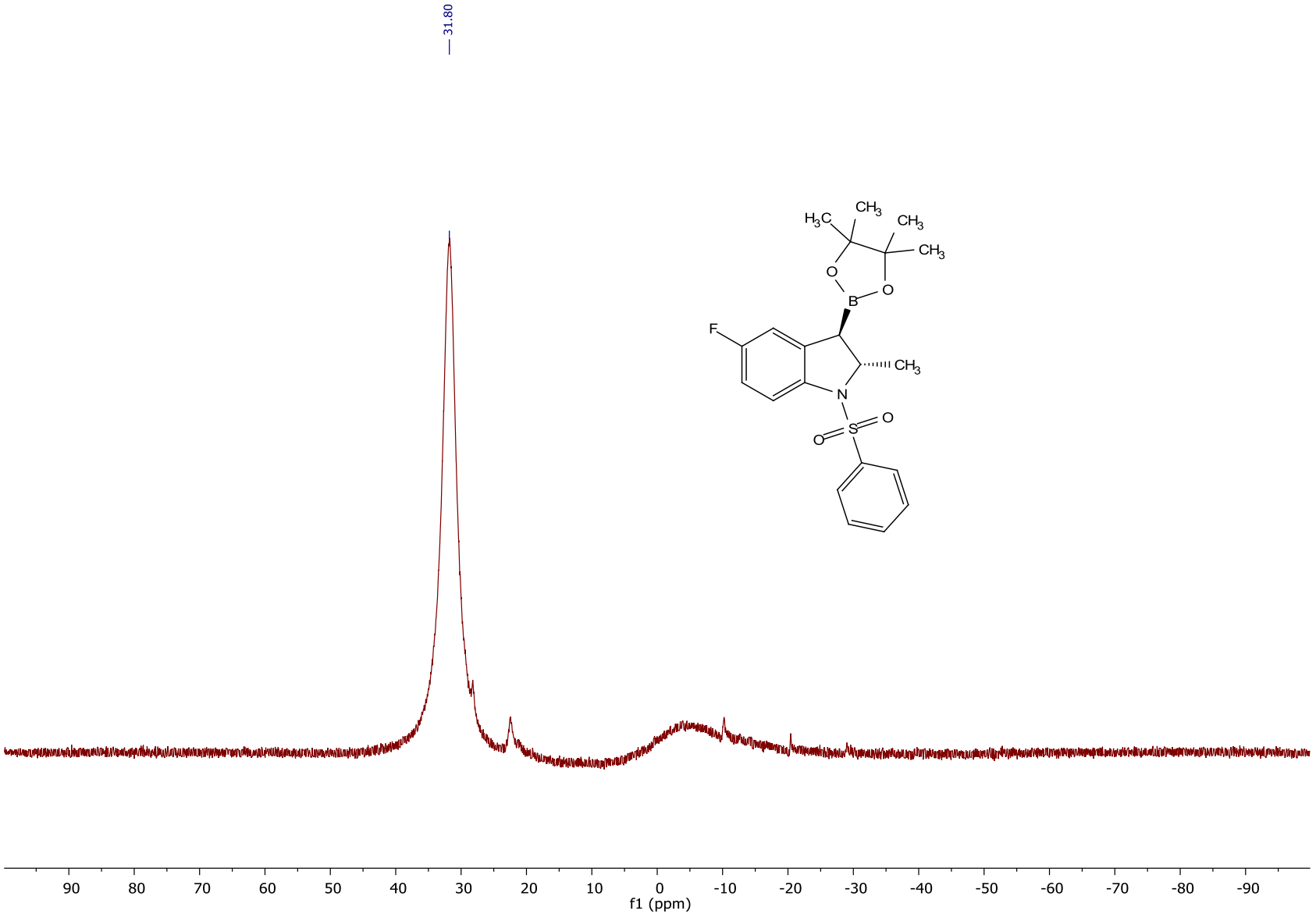

Figure S77. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of compound **6r**.

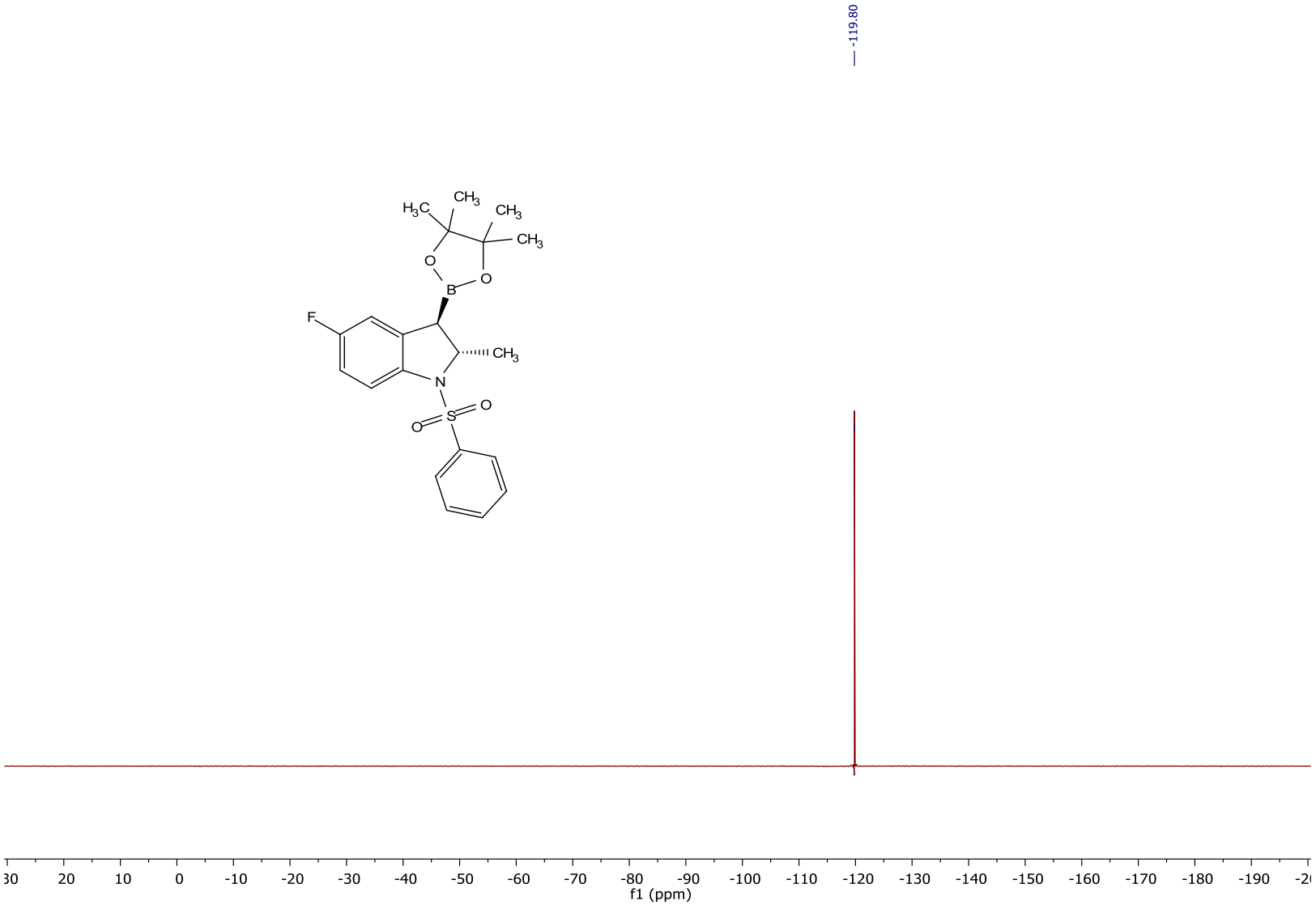

Figure S78. ^{19}F NMR spectrum (470.4 MHz, $CDCl_3$) of compound **6r**.

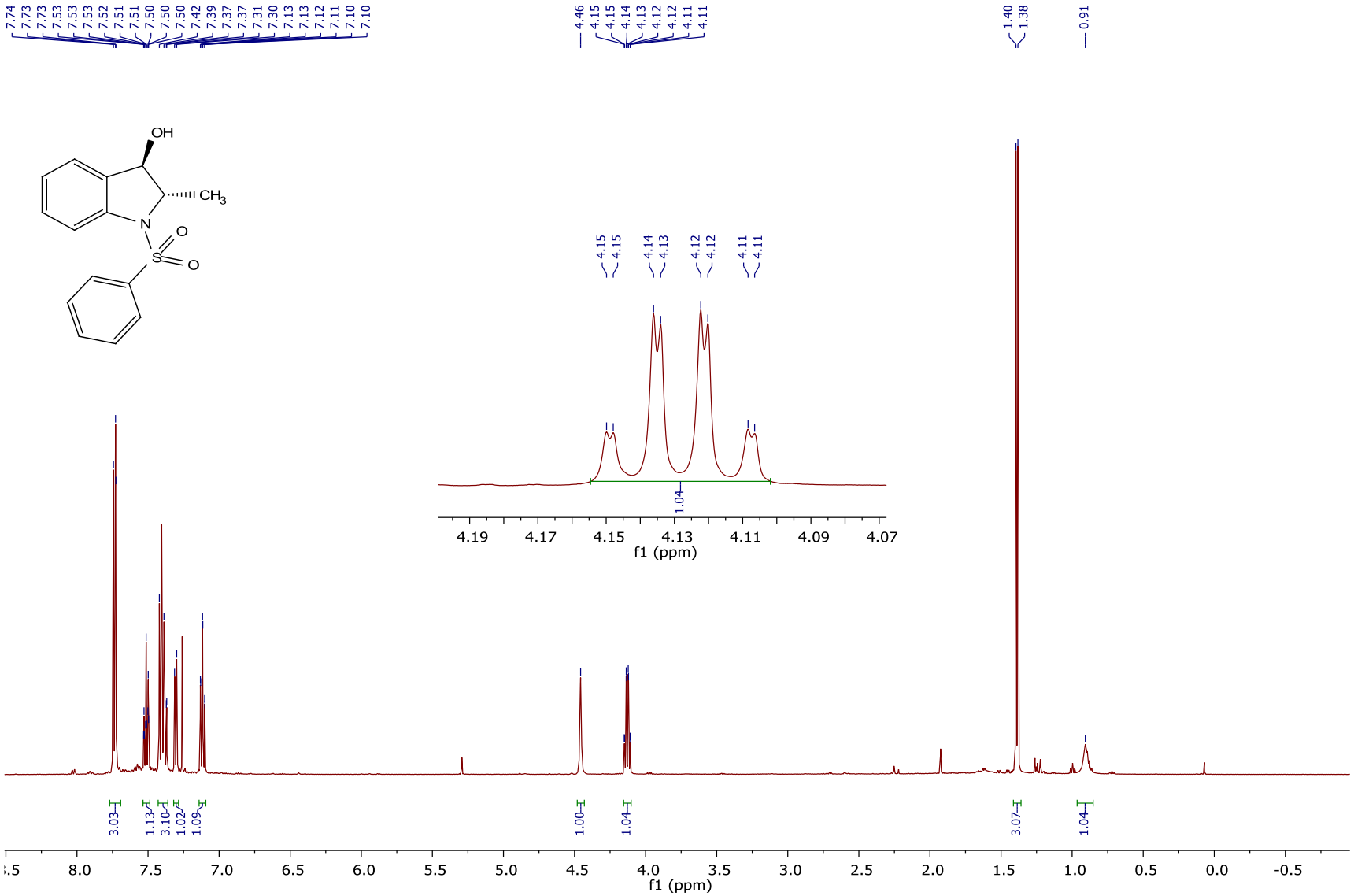

Figure S79. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6s'**.

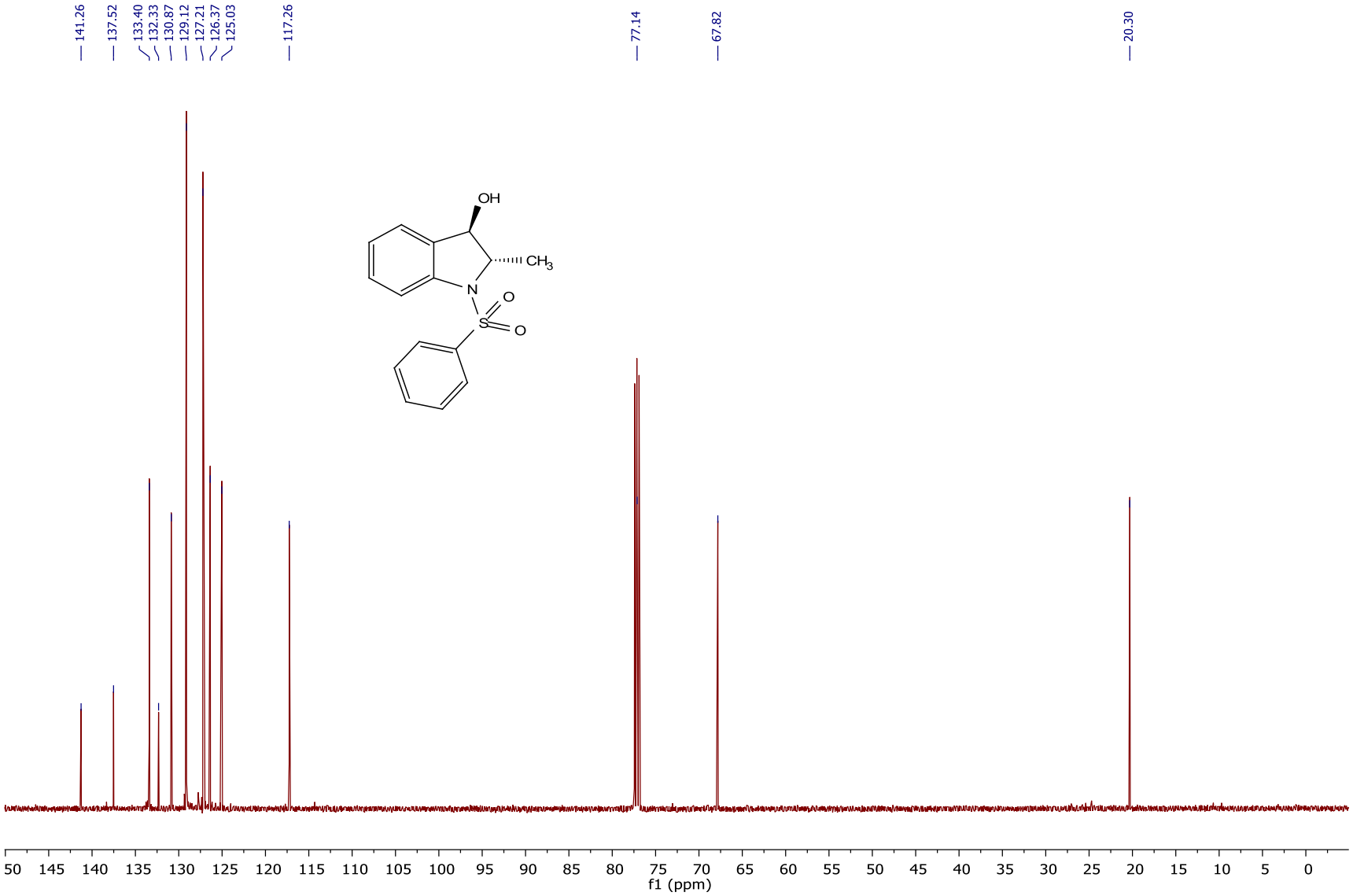

Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6s'**.

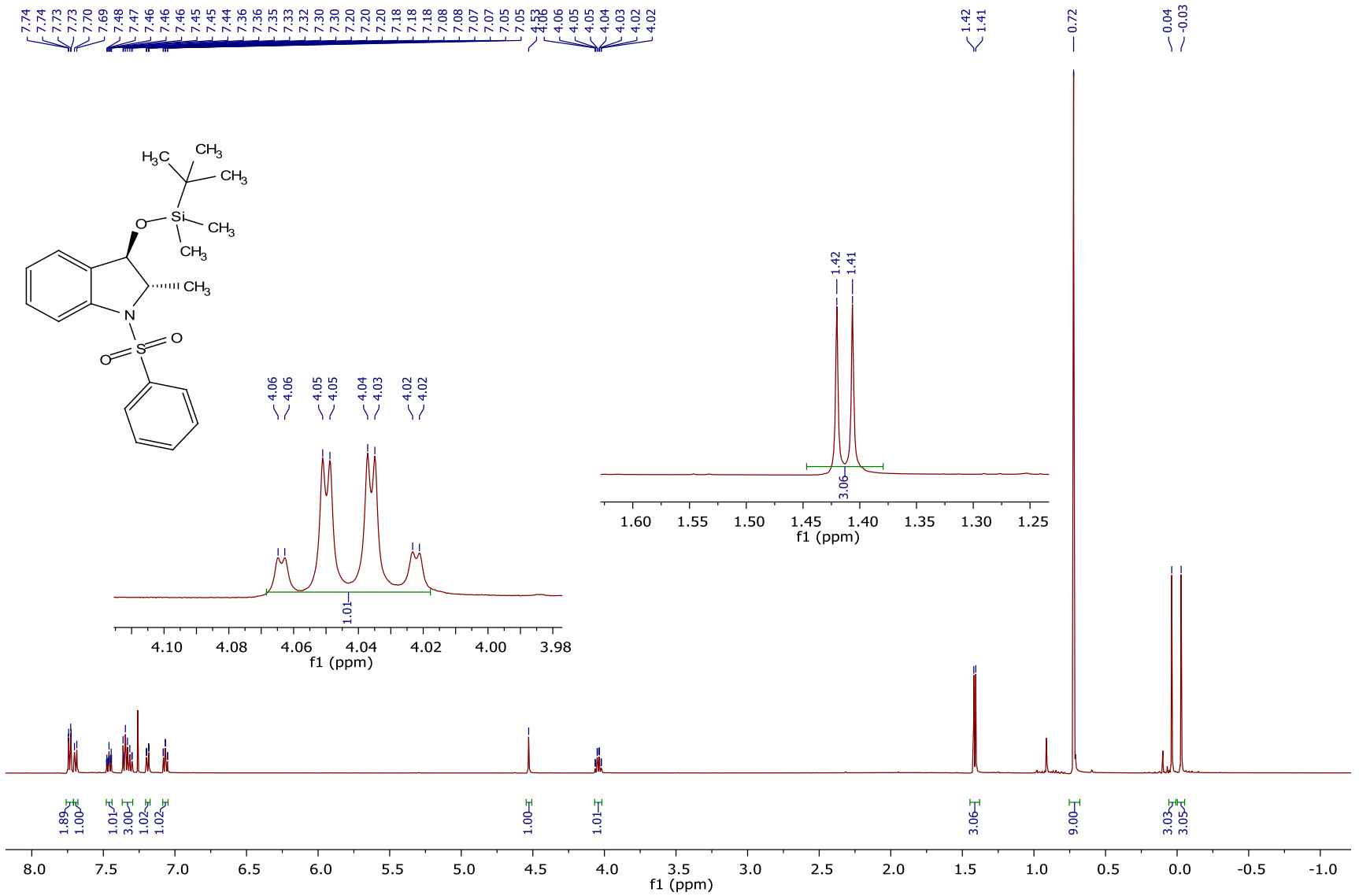

Figure S81. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6s''**.

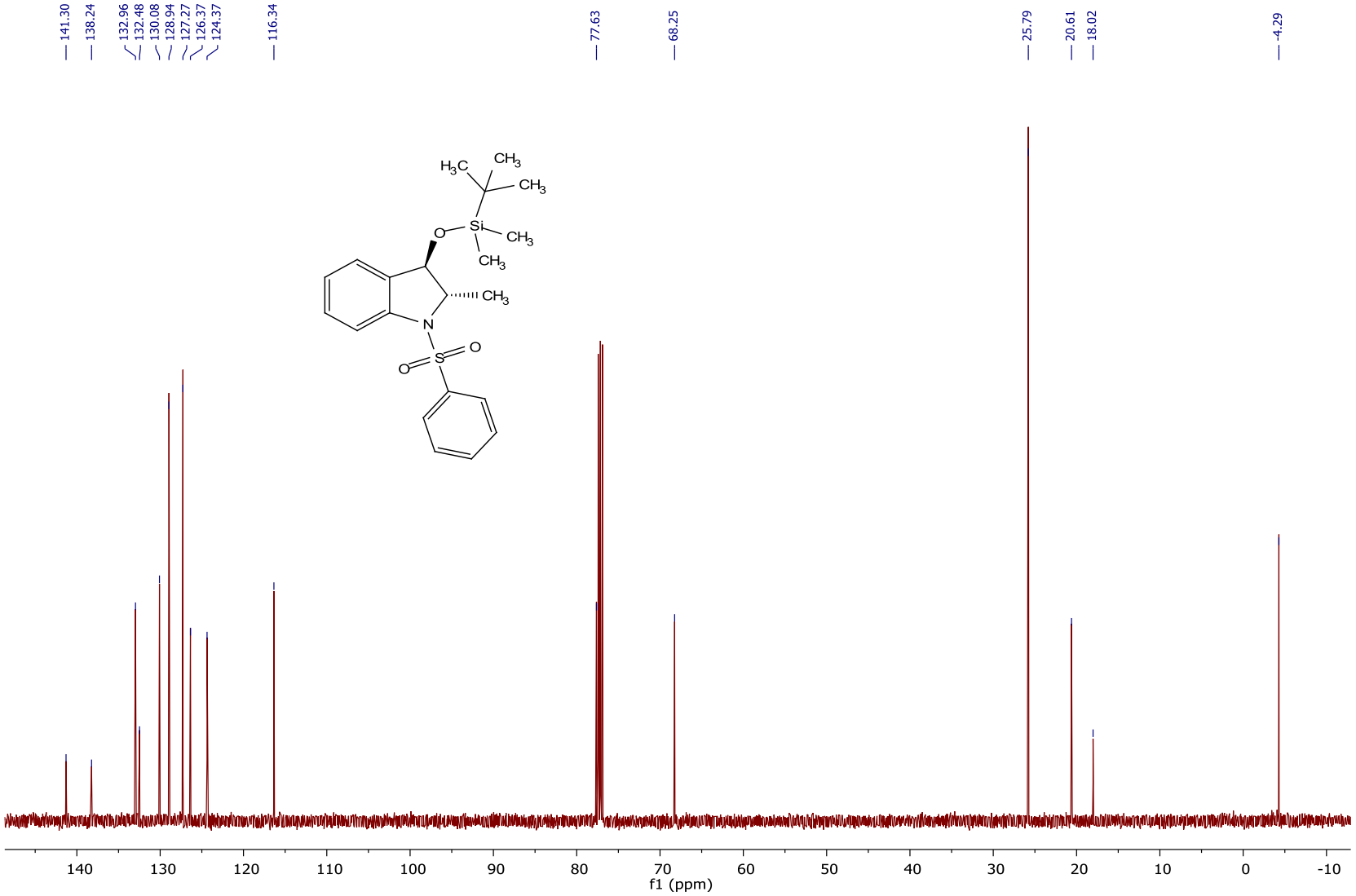

Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of compound **6s''**.

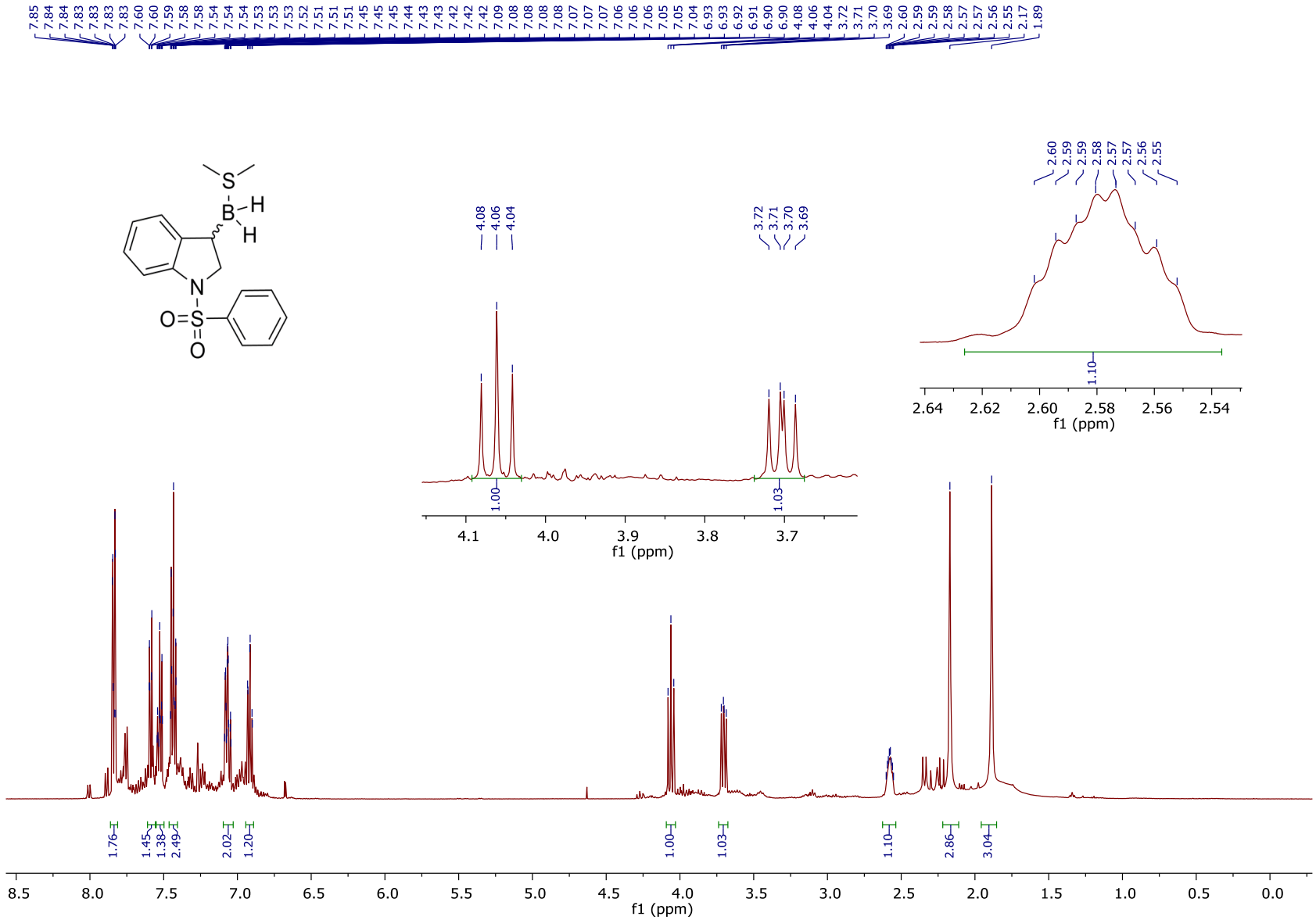

Figure S83. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the highly sensitive **BH_2-Int** compound.

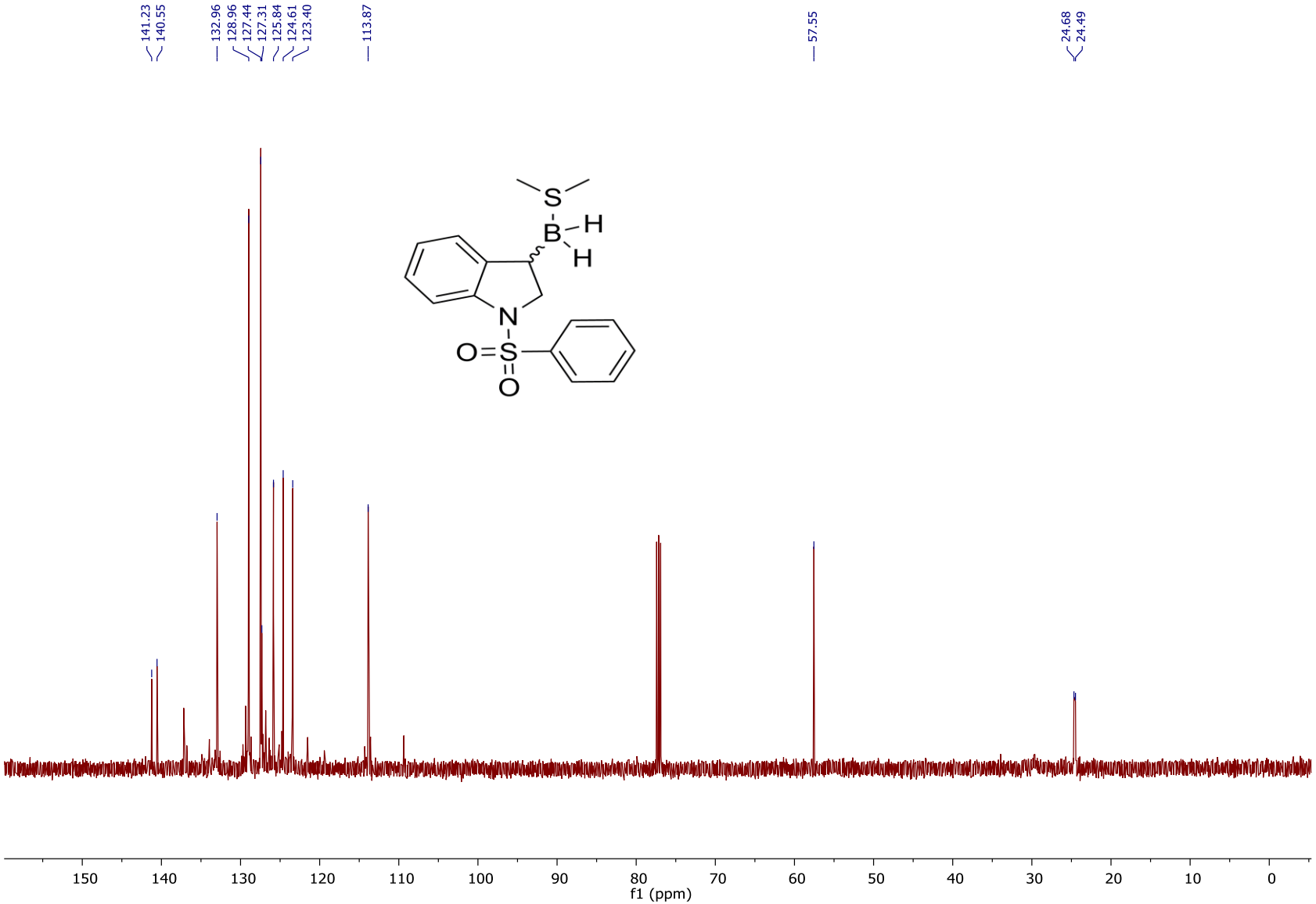

Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, $CDCl_3$) of the highly sensitive **BH_2-Int** compound.

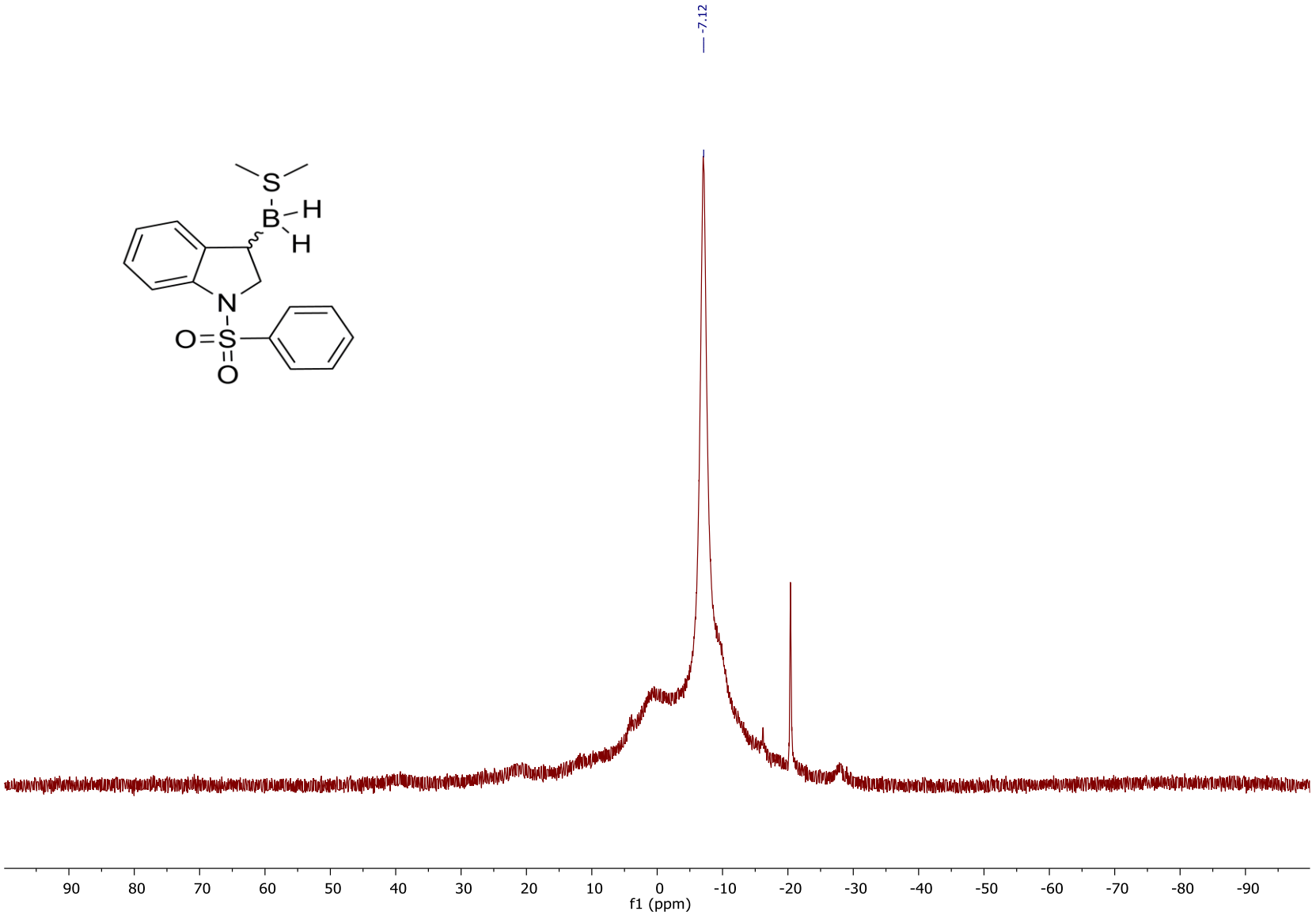

Figure S85. $^{11}B\{^{1}H\}$ NMR spectrum (160.5 MHz, $CDCl_3$, borosilicate NMR tube) of the highly sensitive **BH_2-Int** compound.

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