Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cu-mediated *vs* Cu-free Selective Borylation of Aryl Alkyl Sulfones

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1 Experimental Section

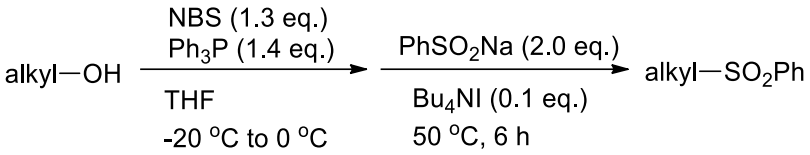
1.1 General Considerations

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Reagent grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated and were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze-pump-thaw method. $CDCl_3$ was purchased from Sigma-Aldrich. The diboron reagents B_2neop_2, B_2cat_2 and B_2pin_2 were a generous gift from AllyChem Co. Ltd. All other reagents were purchased from Alfa-Aesar, Sigma-Aldrich or ABCR, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received.

NMR spectra were recorded at 298 K using Bruker Avance 300 (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz), Bruker DPX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz, ^{11}B, 128 MHz; ^{19}F, 376 MHz), or Bruker Avance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz, ^{11}B, 160 MHz; ^{19}F, 470 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^1H\}$ NMR spectra are reported relative to TMS using the natural-abundance carbon resonances ($CDCl_3$: 77.16 ppm). However, signals for the carbon attached to boron, C-B, are usually too broad to observe in the $^{13}C\{^1H\}$ NMR spectra. ^{11}B and ^{19}F NMR chemical shifts are reported relative to external BF_3•OEt_3 or $CFCl_3$, respectively. Coupling constants are given in Hertz. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry, Universität Würzburg, using an Elementar vario micro cube instrument. Automated flash chromatography was performed using a Biotage® Isolera Four system, on silica gel (Biotage SNAP cartridge KP-Sil 10 g and KP-Sil 25 g). Commercially available, precoated TLC plates (Polygram® Sil G/UV254) were purchased from Machery-Nagel. The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 30 °C. GC-MS analyses were performed using a Thermo Fisher Scientific Trace 1310 gas chromatograph (column: TG-SQC 5% phenyl methyl siloxane, 15 m, ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C; carrier gas: He (1.2 mL min^{-1}) or an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, Ø 0.25 mm, film 0.25 µm; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C min^{-1}); carrier gas: He (1.2 mL min^{-1}) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. High-resolution mass spectra were obtained using a Thermo Scientific Exactive Plus spectrometer equipped with an Orbitrap Mass Analyzer. Measurements were accomplished using an ASAP/APCI source with a corona needle, and a carrier-gas (N_2) temperature of 250 °C.

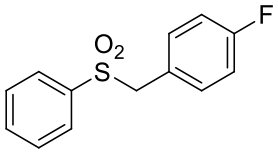
1.2 Synthesis of Sulfone Substrates

General procedure 1:



The compound was synthesized according to the literature.[1] Alkyl alcohol (3.0 mmol), Ph_3P (4.2 mmol) and THF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at –20 °C under argon. NBS (3.9 mmol) was added in small portions over 15 min. The reaction mixture was stirred while warming from –20 °C to 0 °C for 30 min. A mixture of $PhSO_2Na$ (6.0 mmol) and Bu_4NI (0.3 mmol) was added in 3 portions over 10 min to this solution. The mixture was stirred for 6 h at 50 °C, then diluted with EtOAc (20 mL) and 3% aqueous $Na_2S_2O_3$ (20 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

1-Fluoro-4-({phenylsulfonyl}methyl)benzene 2a

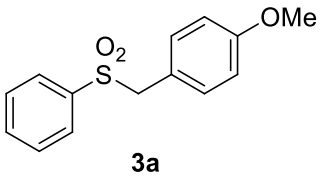


2a

According to **General procedure 1** with (4-fluorophenyl)methanol (378 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **2a** as a white solid (630 mg, 2.52 mmol, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 – 7.60 (m, 3H), 7.47 (t, J = 8 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.95 (t, J = 8 Hz, 2H), 4.28 (s, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.1 (d, J = 247 Hz), 137.6, 134.0, 132.7 (d, J = 8 Hz), 129.1, 128.7, 124.0 (d, J = 3 Hz), 115.8 (d, J = 22 Hz), 62.1. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -112.3 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{12}FO_2S$ $[M+H]^+$ 251.0537 (251.0534).

The spectroscopic data for **2a** match those reported in the literature.[2]

1-Methoxy-4-({phenylsulfonyl}methyl)benzene 3a

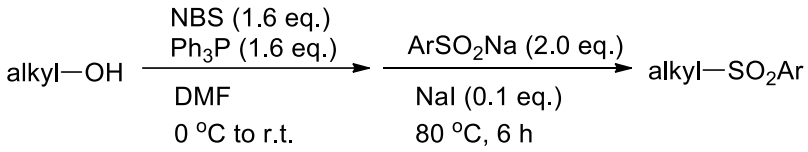


3a

According to **General procedure 1** with (4-methoxyphenyl)methanol (414 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **3a** as a white solid (684 mg, 2.61 mmol, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7 Hz, 2H), 7.60 (t, *J* = 7 Hz, 1H), 7.45 (t, *J* = 7 Hz, 2H), 6.99 (d, *J* = 9 Hz, 2H), 6.78 (d, *J* = 9 Hz, 2H), 4.25 (s, 2H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 160.0, 137.9, 133.8, 132.1, 129.0, 128.7, 120.0, 114.1, 62.3, 55.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{15}O_3S$ $[M+H]^+$ 263.0736 (263.0728).

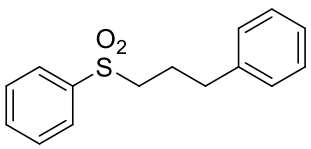
The spectroscopic data for **3a** match those reported in the literature.[2]

General procedure 2:



This method was based on the literature.[1] The alkyl alcohol (3.0 mmol), Ph_3P (4.8 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar at 0 °C under Ar. NBS (4.8 mmol) was added in small portions over 15 min. The reaction mixture was stirred while worming from 0 °C to r.t. over 30 min. To this solution was added a mixture of $PhSO_2Na$ (6.0 mmol) and NaI (0.3 mmol) in 3 portions over 10 min. The mixture was stirred for 6 h at 80 °C, then diluted with EtOAc (20 mL) and 3% aq $Na_2S_2O_3$ (20 mL). The layers were separated, and the aqueous phase was extracted with EtOAc (2 x 30 mL). The organic layer was washed with water and brine, and then dried over anhydrous Na_2SO_4, filtred and the solvent removed under vacuum. The crude product was purified by recrystallization or flash column chromatography on silica gel with hexane/EtOAc to afford the sulfone.

({3-Phenylpropyl}sulfonyl)benzene 4a

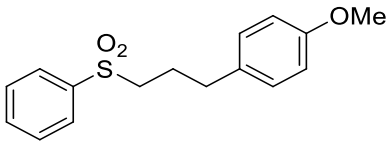


4a

According to **General procedure 2** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and $PhSO_2Na$ (985 mg, 6.0 mmol, 2.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **4a** as a white solid (633 mg, 2.43 mmol, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.87 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.54 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 7.11 – 7.09 (m, 2H), 3.10 – 3.06 (m, 2H), 2.70 (t, *J* = 7 Hz, 2H), 2.09 – 2.01 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 139.9, 139.0, 133.8, 129.4, 128.7, 128.5, 128.1, 126.5, 55.5, 34.2, 24.3. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{17}O_2S$ $[M+H]^+$ 261.0944 (261.0943).

The spectroscopic data for **4a** match those reported in the literature.[3]

1-Methoxy-4-(3-{phenylsulfonyl}propyl)benzene 5a

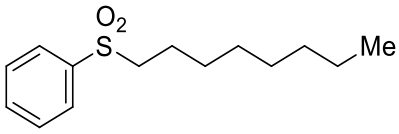


5a

According to **General procedure 2** with 3-(4-methoxyphenyl)propan-1-ol (499 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by recrystallization (hexane/EtOAc) to yield the product **5a** as a white solid (653 mg, 2.25 mmol, 75% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.91 – 7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.03 – 6.99 (m, 2H), 6.82 – 6.78 (m, 2H), 3.78 (s, 3H), 3.08 – 3.03 (m, 2H), 2.64 (t, *J* = 7 Hz, 2H), 2.06 – 1.96 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 158.3, 139.3, 133.8, 132.0, 129.5, 129.4, 128.2, 114.1, 55.6, 55.4, 33.3, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1045).

The spectroscopic data for **5a** match those reported in the literature.[4]

(Octylsulfonyl)benzene 6a

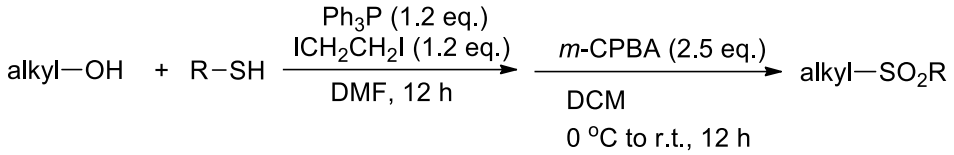


6a

According to **General procedure 1** with octan-1-ol (390 mg, 3.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **6a** as a white solid (587 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.93 – 7.89 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.10 – 3.05 (m, 2H), 1.75 – 1.65 (m, 2H), 1.36 – 1.22 (m, 10H), 0.85 (t, *J* = 7 Hz, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.4, 133.8, 129.4, 128.2, 56.5, 31.8, 29.1, 29.0, 28.4, 22.8, 22.7, 14.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{23}O_2S$ $[M+H]^+$ 255.1413 (255.1409).

The spectroscopic data for **6a** match those reported in the literature.[5]

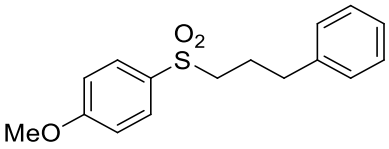
General procedure 3:



This method was based on the literature.[6] The alkyl alcohol (3.0 mmol), Ph_3P (3.6 mmol) and anhydrous DMF (10 mL) were added to a Schlenk flask equipped with a magnetic stirring bar under argon. The compound 1,2-diiodoethane (3.6 mmol) was then added and the mixture was stirred for 2 min until the 1,2-diiodoethane was completely dissolved. Thiol (9.0 mmol) was added subsequently and the mixture was stirred at room temperature for 12 h, then diluted with CH_2Cl_2 (20 mL). The mixture was washed with water (3 x 20 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtred and the solvent was removed under vacuum.

The crude aryl sulfide was dissolved in CH_2Cl_2 (10 mL) in an ice-water bath before *m*-CPBA (contains *ca*. 23 wt%, 7.5 mmol, 1.68 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 was added and the resulting solution was extracted with EtOAc (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/ethyl acetate: 10/1).

1-Methoxy-4-({3-phenylpropyl}sulfonyl)benzene 9c

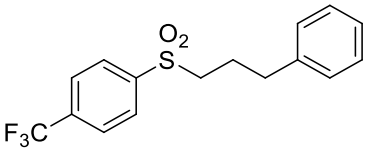


9c

According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-OMePhSH (1.262 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **9c** as a white solid (633 mg, 2.31 mmol, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 9 Hz, 2H), 7.27 (dd, *J* = 6, 9 Hz, 2H), 7.20 (dd, *J* = 6, 9 Hz, 1H), 7.12 – 7.10 (m, 2H), 7.00 (d, *J* = 9 Hz, 2H), 3.87 (s, 3H), 3.08 – 3.04 (m, 2H), 2.69 (t, *J* = 7 Hz, 2H), 2.07 – 1.99 (m, 2H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 163.7, 140.0, 130.5, 130.2, 128.6, 128.4, 126.4, 114.5, 55.77, 55.75, 34.1, 24.5. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}O_3S$ $[M+H]^+$ 291.1049 (291.1044).

The spectroscopic data for **9c** match those reported in the literature.[7]

1-({3-Phenylpropyl}sulfonyl)-4-(trifluoromethyl)benzene 10c

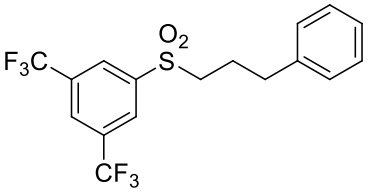


10c

According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 4-CF_3PhSH (1.603 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **10c** as a white solid (630 mg, 1.92 mmol, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 2H), 7.27 (t, J = 7 Hz, 2H), 7.21 (dd, J = 6, 9 Hz, 1H), 7.10 (d, J = 7 Hz, 2H), 3.11 – 3.08 (m, 2H), 2.72 (t, J = 7 Hz, 2H), 2.10 – 2.03 (m, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 142.7, 139.7, 135.6 (q, J = 33 Hz), 128.9, 128.8, 128.5, 126.7, 126.6 (q, J = 4 Hz), 123.2 (q, J = 273 Hz), 55.4, 34.2, 24.2. **^{19}F{^{1}H} NMR** (376 MHz, $CDCl_3$): δ = -63.2 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{16}F_3O_2S$ $[M+H]^+$ 329.0818 (329.0814).

The spectroscopic data for **10c** match those reported in the literature.[7]

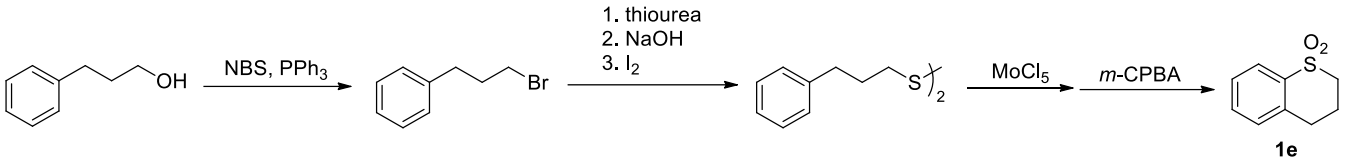
1-({3-Phenylpropyl}sulfonyl)-3,5-bis(trifluoromethyl)benzene 11c



11c

According to **General procedure 3** with 3-phenyl-1-propanol (409 mg, 3.0 mmol, 1.0 equiv.) and 3,5-CF_3PhSH (2.215 g, 9.0 mmol, 3.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to yield the product **11c** as a white solid (654 mg, 1.65 mmol, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.33 (s, 2H), 8.15 (s, 1H), 7.30 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.11 – 7.09 (m, 2H), 3.15 – 3.12 (m, 2H), 2.76 (t, J = 8 Hz, 2H), 2.15 – 2.09 (m, 2H). **^{13}C{^{1}H} NMR** (120 MHz, $CDCl_3$): δ = 142.2, 139.3, 133.5 (q, J = 34 Hz), 128.9, 128.6 (q, J = 4 Hz), 128.5, 127.6, 126.9, 122.5 (q, J = 273 Hz), 55.4, 34.0, 23.9. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{15}F_6O_2S$ $[M+H]^+$ 397.0691 (397.0687).

The synthesis of thiochroman 1,1-dioxide 1e



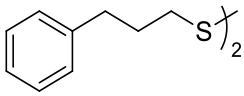
1e

3-Phenylpropan-1-ol (1.36 g, 10 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (20 mL) under an argon atmosphere. Triphenylphosphine (3.15 g, 12 mmol, 1.2 equiv.) and *N*-bromosuccinimide (2.14 g, 12 mmol, 1.2 equiv.) were added to the solution at 0 °C and the mixture was stirred for 2 h. A saturated aqueous solution of $NaHCO_3$ (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford (3-bromopropyl)benzene (1.83 g, 9.2 mmol, 92%).

(3-Bromopropyl)benzene (1.19 g, 6 mmol, 1.0 equiv.) was dissolved in ethanol (10 mL) and thiourea (0.5 g, 6.6 mmol, 1.1 equiv.) was added. The mixture was heated to reflux for 16 h and subsequently cooled to room temperature. Then, 2 N NaOH (20 mL) was added, and the reaction was stirred at room temperature for 20 min. Afterwards, the solution was acidified with a 2 N H_2SO_4 and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude thiol was dissolved in methanol (20 mL) and a saturated solution of iodine in methanol was added until the colour of the solution maintained yellow. A saturated aqueous solution of $Na_2S_2O_3$ (20 mL) was added to remove the excess iodine and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford the disulfide (1.54 g, 5.1 mmol, 85%).

The disulfide (1.54 g, 5.1 mmol, 1.0 equiv.) was dissolved in anhydrous CH_2Cl_2 (10 mL) at argon atmosphere. $MoCl_5$ (2.79 g, 10.2 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at room temperature for the 5 min. After 5 min, the reaction mixture was filtred through a pad of Celite (Ø 3 mm x 8 mm) and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexane/ethyl acetate: 100/1) to afford the sulfide (0.53 g, 3.5 mmol, 69%). The sulfide (0.53 g, 3.5 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (9 mL) in an ice-water bath before *m*-CPBA (*ca*. 23 wt%, 8.75 mmol, 1.96 g) was added in portions. The mixture was allowed to warm to room temperature. After 12 h, saturated aqueous Na_2CO_3 were added, and the resulting solution was extracted with EtOAc (3 x 30 mL). The combined organic layer was dried over Na_2SO_4 and filtred through a pad of Celite (Ø 3 mm x 8 mm). The reaction mixture was purified by recrystallisation (hexane/EtOAc) to yield the product **1e** as a white solid (492 mg, 2.70 mmol, 77% yield).

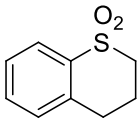
1,2-Bis(3-phenylpropyl)disulfane



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.26 (m, 4H), 7.22 – 7.16 (m, 6H), 2.75 – 2.66 (m, 8H), 2.06 – 1.97 (m, 4H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.5, 128.63, 128.56, 126.1, 38.3, 34.5, 30.7. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}O_2S$ $[M+H]^+$ 303.1236 (303.1226).

The spectroscopic data match those reported in the literature.[8]

Thiochroman 1,1-dioxide 1e



1e

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 – 7.90 (m, 1H), 7.49 – 7.37 (m, 2H), 7.25 – 7.22 (m, 1H), 3.38 – 3.34 (m, 2H), 3.03 (t, J = 6 Hz, 2H), 2.54 – 2.46 (m, 2H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 139.1, 136.5, 132.4, 129.7, 127.8, 123.8, 50.9, 28.5, 21.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_9H_{11}O_2S$ $[M+H]^+$ 183.0474 (183.0467).

The spectroscopic data for **1e** match those reported in the literature.[8]

1.3 Details of the Borylation of Aryl Alkyl Sulfones

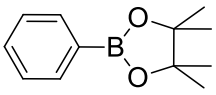
General procedure of optimization:

In an argon-filled glovebox, the aryl sulfone **1a** (0.5 mmol, 1.0 equiv.), dissolved in solvent (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. Base, catalyst and the boron source were added. The reaction mixture was stirred at 100 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The solvent was evaporated under reduced pressure and dodecane was added as an internal standard and the crude reaction mixture was analysed by GC-MS.

General procedures 4:

In an argon-filled glovebox, the sulfone (0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), and B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product was purified by flash column chromatography (hexane/EtOAc) after careful removal of the solvent *in vacuo*. All aryl boronate products were unambiguously identified by comparison of HRMS and ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$ and/or $^{19}F\{^1H\}$ NMR spectra with literature data.

2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1b

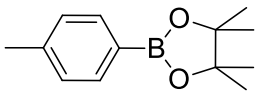


1b

According to **General procedure 4**, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **1b** as a colourless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.85 – 7.82 (m, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.36 (m, 2H), 1.37 (s, 12H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 134.9, 131.4, 127.8, 83.9, 25.0. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{18}BO_2$ $[M+H]^+$ 205.1394 (205.1386).

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

2-(*p*-Tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1d

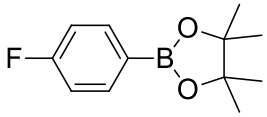


1d

According to **General procedure 4** with 1-methyl-4-(methylsulfonyl)benzene **1c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **1d** as a colourless solid (96.0 mg, 440 µmol, 88% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 2.37 (s, 3H) 1.34 (s, 12H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 141.5, 134.9, 128.7, 83.8, 25.0, 21.9. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1548).

The spectroscopic data for **1d** match those reported in the literature.[10]

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 2d

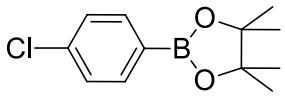


2d

According to **General procedure 4** with 1-fluoro-4-(methylsulfonyl)benzene **2c** (87.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **2d** as a colourless solid (92.2 mg, 415 µmol, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.83 – 7.79 (m, 2H), 7.07 – 7.03 (m, 2H), 1.34 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 165.2 (d, J = 250 Hz), 137.2 (d, J = 8 Hz), 125.1 (br), 115.0 (d, J = 20 Hz), 114.8 (d, J = 21 Hz), 84.0, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.7. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -108.4 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BFO_2$ $[M+H]^+$ 223.1300 (223.1298).

The spectroscopic data for **2d** match those reported in the literature.[11]

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3d



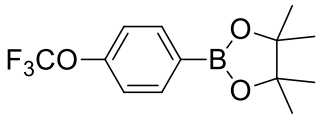
3d

According to **General procedure 4** with 1-chloro-4-(methylsulfonyl)benzene **3c** (95.3 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **3d** as a colourless solid (102.5 mg, 430 µmol, 86% yield). **^{1}H NMR** (300 MHz,

$CDCl_3$): δ = 7.73 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 1.34 (s, 12H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 137.7, 136.3, 128.1, 84.1, 25.0. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 30.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{12}H_{17}BClO_2$ $[M+H]^+$ 239.1005 (239.1001).

The spectroscopic data for **3d** match those reported in the literature.[12]

2-(4-(Trifluoromethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4d

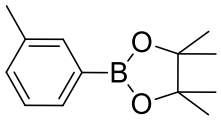


4d

According to **General procedure 4** with 1-trifluoromethoxy-4-(methylsulfonyl)benzene **4c** (120.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **4d** as a colourless solid (128.2 mg, 445 µmol, 89% yield). **^1H NMR** (500 MHz, $CDCl_3$): δ = 7.84 (d, J = 8 Hz, 2H), 7.20 (d, J = 8 Hz, 2H), 1.34 (s, 12H). **$^{13}C\{^1H\}$ NMR** (125 MHz, $CDCl_3$): δ = 151.8, 136.7, 120.6 (q, J = 258 Hz), 120.0, 84.2, 25.0. **$^{11}B\{^1H\}$ NMR** (160 MHz, $CDCl_3$): δ = 30.6. **$^{19}F\{^1H\}$ NMR** (470 MHz, $CDCl_3$): δ = -57.6 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{16}BF_3O_3$ $[M]^+$ 288.1139 (288.1133).

The spectroscopic data for 4**d** match those reported in the literature.[13]

2-(3-Methyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 5d

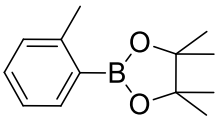


5d

According to **General procedure 4** with 1-methyl-3-(methylsulfonyl)benzene **5c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **5d** as a colourless solid (77.4 mg, 355 µmol, 71% yield). **^1H NMR** (300 MHz, $CDCl_3$): δ = 7.64 – 7.58 (m, 2H), 7.28 – 7.26 (m, 2H), 2.36 (s, 3H), 1.35 (s, 12H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ = 137.3, 135.5, 132.2, 131.9, 127.8, 83.9, 25.0, 21.4. **$^{11}B\{^1H\}$ NMR** (96 MHz, $CDCl_3$): δ = 31.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1547).

The spectroscopic data for **5d** match those reported in the literature.[14]

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

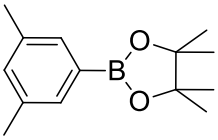


6d

According to **General procedure 4** with 1-methyl-2-(methylsulfonyl)benzene **6c** (85.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **6d** as a colourless solid (57.8 mg, 265 µmol, 53% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.79 – 7.76 (m, 1H), 7.33 (td, J = 8, 2 Hz, 1H), 7.19 – 7.14 (m, 2H), 2.55 (s, 3H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 145.0, 136.0, 130.9, 129.9, 124.8, 83.5, 25.0, 22.4. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1551 (219.1552).

The spectroscopic data for **6d** match those reported in the literature.[19]

2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 7d

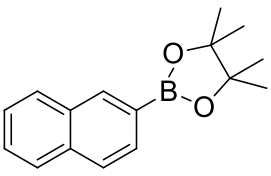


7d

According to **General procedure 4** with 1,3-dimethyl-5-(methylsulfonyl)benzene **7c** (92.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **7d** as a colourless solid (80.1 mg, 345 µmol, 69% yield). **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.44 (m, 2H). 7.10 (m, 1H), 2.32 (d, J = 1 Hz, 6H),1.34 (s, 12H), **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 137.3, 133.1, 132.5, 83.8, 25.0, 21.3. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.9. **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1707 (233.1702).

The spectroscopic data for **7d** match those reported in the literature.[12]

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene 8d

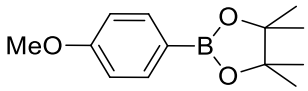


8d

According to **General procedure 4** with 2-(methylsulfonyl)naphthalene **8c** (103.1 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **8d** as a colourless solid (99.1 mg, 390 µmol, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.90 – 7.82 (m, 4H), 7.54 – 7.45 (m, 2H), 1.40 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 136.4, 135.2, 133.0, 130.5, 128.8, 127.8, 127.1, 127.1, 125.9, 84.1, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.2. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{19}BO_2$ $[M]^+$ 254.1473 (254.1471).

The spectroscopic data for **8d** match those reported in the literature.[15]

2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 9d

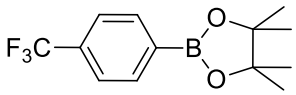


9d

According to **General procedure 4** with 1-methoxy-4-((3-phenylpropyl)sulfonyl)benzene **9c** (145.2 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **9d** as a colourless solid (86.6 mg, 370 µmol, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.76 (d, J = 9 Hz, 2H), 6.90 (d, J = 9 Hz, 2H), 3.82 (s, 3H), 1.34 (s, 12H),. **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 162.3, 136.6, 120.5 (br), 113.4, 83.7, 55.2, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{20}BO_3$ $[M+H]^+$ 235.1500 (235.1489).

The spectroscopic data for **9d** match those reported in the literature.[10]

2-(4-Trifluoromethyl-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 10d

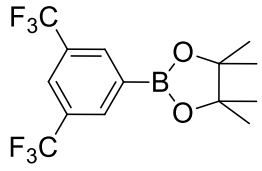


10d

According to **General procedure 4** with 1-((3-phenylpropyl)sulfonyl)-4-(trifluoromethyl)benzene **10c** (164.2mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **10d** as a colourless solid (111.5 mg, 410 µmol, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 8 Hz, 2H), 7.61 (d, J = 8 Hz, 2H), 1.36 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 135.2, 133.0 (q, J = 32 Hz), 124.7 (q, J = 4 Hz), 124.7 (q, J = 272 Hz), 84.7, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.7. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -63.0(s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{13}H_{17}BF_3O_2$ $[M+H]^+$ 273.1268 (273.1255).

The spectroscopic data for **10d** match those reported in the literature.[16]

2-(3,5-Trifluoromethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11d

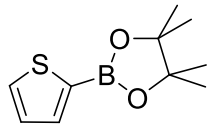


11d

According to **General procedure 4** with 1-((3-phenylpropyl)sulfonyl)-3,5-bis(trifluoromethyl)benzene **11c** (198.2 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **11d** as a colourless solid (131.0 mg, 385 µmol, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.23 (m, 2H), 7.94 (m, 1H), 1.37 (s, 12 H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 134.8 (m), 131.0 (q, J = 33 Hz), 124.9 (m), 123.6 (q, J = 272 Hz), 85.0, 25.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -62.8 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{16}BF_6O_2$ $[M+H]^+$ 341.1142 (341.1135).

The spectroscopic data for **11d** match those reported in the literature.[17]

2-(Thiophene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane 12d

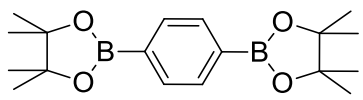


12d

According to **General procedure 4** with 2-(methylsulfonyl)thiophene **12c** (81.5 mg, 0.5 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc = 98/2) to yield the product **12d** as a yield solid (75.6 mg, 360 µmol, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.63 – 7.67 (m, 2H), 7.20 (m, 1H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 137.3, 132.5, 128.4, 84.2, 24.9. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 29.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{10}H_{16}BO_2$ $[M+H]^+$ 211.0959 (211.0949).

The spectroscopic data for **12d** match those reported in the literature.[19]

2,2'-(1,4-Phenylene)-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) 13d

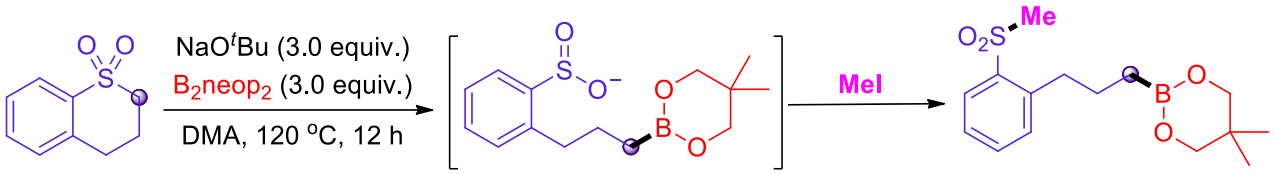


13d

Yield: 117.2 mg (325 µmol, 71%) of a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.80 (s, 4H), 1.35 (s, 24H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ = 134.0, 84.0, 25.0. **^{11}B{^{1}H} NMR** (96 MHz, $CDCl_3$): δ = 30.8. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{29}B_2O_4$ $[M+H]^+$ 331.2246 (331.2241).

The spectroscopic data for **13d** match those reported in the literature.[18]

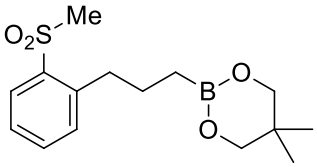
2 Ring-opening Borylation of Cyclic Sulfones



1e **1f**

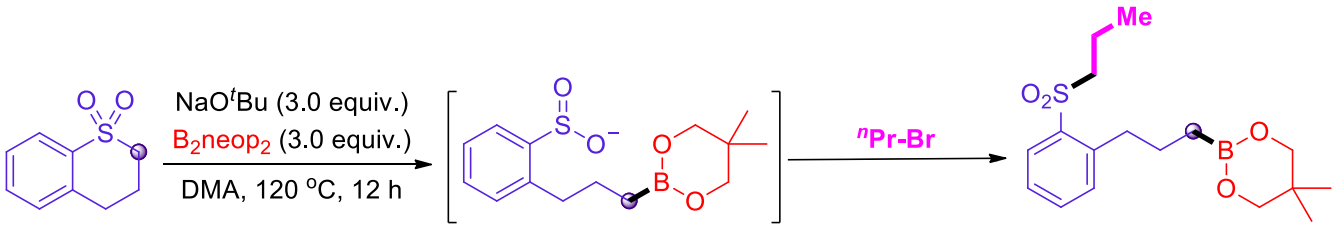
In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 12 h. After 12 h, iodomethane (85.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for extra 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **1f**.

2-(3-(2-(Methylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 1f



1f

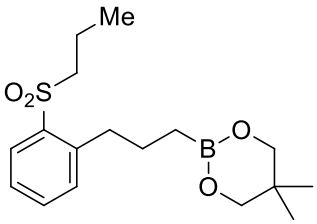
Yield: 62.3 mg (201 µmol, 67%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.03 – 8.01 (m, 1H), 7.55 – 7.51 (m, 1H), 7.42 – 7.40 (m, 1H), 7.36 – 7.32 (m, 1H), 3.58 (s, 4H), 3.11 (s, 3H), 3.06 – 3.02 (m, 2H), 1.81 – 1.74 (m, 2H), 0.95 (s, 6H), 0.87 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.1, 138.6, 133.6, 131.9, 129.4, 126.5, 72.1, 44.7, 35.2, 31.8, 26.7, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.0. **HRMS-ASAP** (m/z): Calculated (found) for $C_{15}H_{24}BO_4S$ $[M+H]^+$ 311.1483 (311.1471). **Anal.** for $C_{15}H_{23}BO_4S$ calcd: C, 58.08; H, 7.47; S, 10.34. found: C, 58.22; H, 7.58; S, 10.52.



1e **2f**

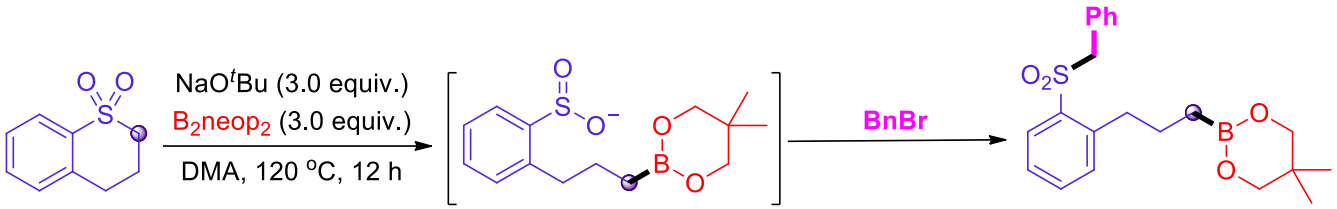
In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 12 h. After 12 h, 1-bromopropane (73.8 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for extra 12 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **2f**.

2-(3-(2-(Propylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 2f



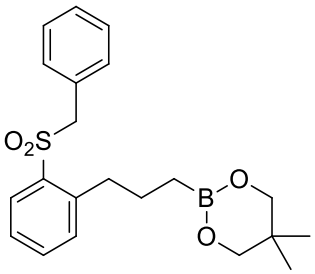
2f

Yield: 52,8 mg (156 µmol, 52%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.99 – 7.97 (m, 1H), 7.54 – 7.50 (m, 1H), 7.41 – 7.39 (m, 1H), 7.35 – 7.32 (m, 1H), 3.59 (s, 4H), 3.15 – 3.12 (m, 2H), 3.03 – 3.00 (m, 2H), 1.79 – 1.68 (m, 4H), 0.99 (t, J = 8 Hz, 3H), 0.96 (s, 6H), 0.87 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.4, 137.1, 133.5, 131.9, 130.4, 126.3, 72.1, 58.1, 35.4, 31.8, 26.9, 22.0, 16.6, 13.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{17}H_{28}BO_4S$ $[M+H]^+$ 339.1796 (339.1784). **Anal.** for $C_{17}H_{27}BO_4S$ calcd: C, 60.36; H, 8.05; S, 9.48. found: C, 60.51; H, 7.92; S, 9.61.



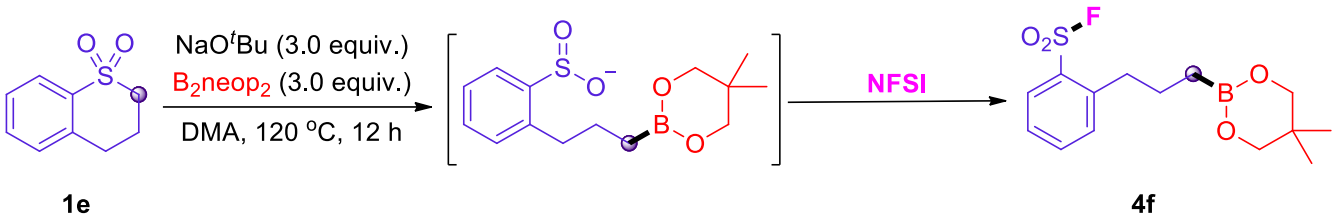
In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 12 h. After 12 h, (bromomethyl)benzene (102.6 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 12 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (5/1)) to yield the product **3f**.

2-(3-(2-(Benzylsulfonyl)phenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane 3f



3f

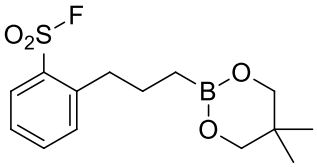
Yield: 51.0 mg (132 µmol, 44%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.64 – 7.62 (m, 1H), 7.49 – 7.46 (m, 1H), 7.38 – 7.36 (m, 1H), 7.30 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.16 (m, 1H), 7.09 – 7.07 (m, 2H), 4.36 (s, 2H), 3.59 (s, 4H), 2.95 – 2.92 (m, 2H), 1.80 – 1.74 (m, 2H), 0.96 (s, 6H), 0.85 (t, J = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 143.9, 135.9, 133.6, 131.7, 131.1, 131.0, 128.8, 128.6, 128.3, 126.1, 72.1, 62.9, 35.4, 31.8, 26.7, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.1. **HRMS-ASAP** (m/z): Calculated (found) for $C_{21}H_{28}BO_4S$ $[M+H]^+$ 387.1796 (387.1786). **Anal.** for $C_{21}H_{27}BO_4S$ calcd: C, 65.29; H, 7.04; S, 8.30. found: C, 65.46; H, 7.19; S, 8.33.



1e **4f**

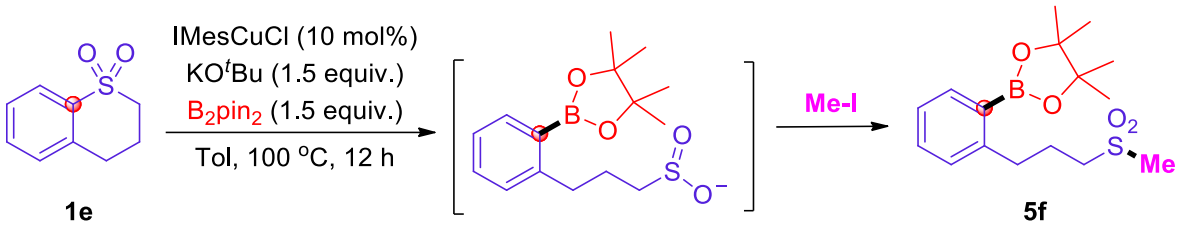
In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in DMA (1 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. NaO^{t}Bu (86.5 mg, 0.9 mmol, 3.0 equiv.) and B_2neop_2 (203.3 mg, 0.9 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 120 °C for 12 h. After 12 h, N-fluorobenzenesulfonimide (189.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **4f**.

2-(3-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)propyl)benzene-1-sulfonyl fluoride 4f



4f

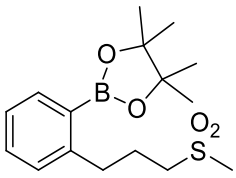
Yield: 67.0 mg (213 µmol, 71%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.48 (d, *J* = 8 Hz, 1H), 7.40 – 7.36 (m, 1H), 3.59 (s, 4H), 3.02 – 2.99 (m, 2H), 1.80 – 1.74 (m, 2H), 0.96 (s, 6H), 0.85 (t, *J* = 8 Hz, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 144.3, 135.2, 132.2, 132.15 (d, *J* = 23 Hz), 130.2, 126.5, 72.1, 35.6, 31.8, 26.0, 22.0. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 30.3. **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$): δ = -150.0 (s). **HRMS-ASAP** (m/z): Calculated (found) for $C_{14}H_{21}BFO_4S$ $[M+H]^+$ 315.1232 (339.1221). **Anal.** for $C_{14}H_{20}BFO_4S$ calcd: C, 53.52; H, 6.42; S, 10.21. found: C, 53.66; H, 6.38; S, 10.28.



1e **5f**

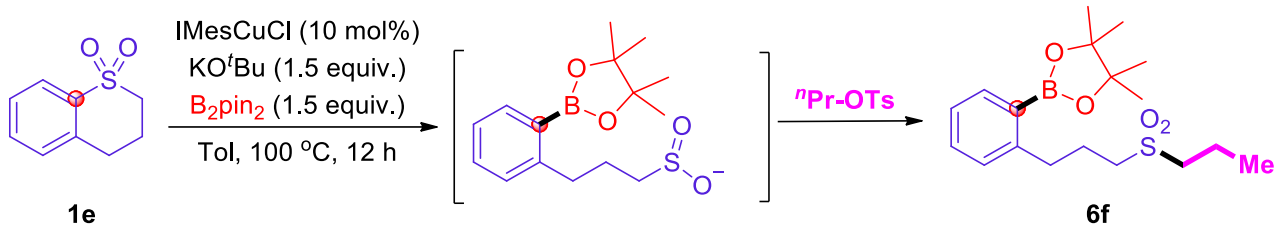
In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (12.1 mg, 10 mol%), KO^{t}Bu (50.5 mg, 0.45 mmol, 1.5 equiv.) and B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 °C for 12 h. After 12 h, iodomethane (85.2 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at room temperature for an additional 6 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **5f**.

4,4,5,5-Tetramethyl-2-(2-(3-(methylsulfonyl)propyl)phenyl)-1,3,2-dioxaborolane 5f



5f

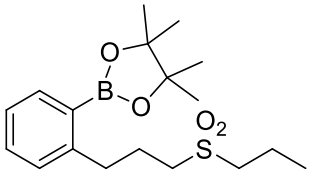
Yield: 47.7 mg (147 µmol, 49%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.84 – 7.82 (m, 1H), 7.39 – 7.36 (m, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.16 (m, 1H), 3.04 – 3.01 (m, 4H), 2.84 (s, 3H), 2.17 – 2.11 (m, 2H), 1.35 (s, 12H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.2, 136.8, 131.4, 129.4, 126.0, 83.8, 54.7, 40.4, 34.2, 25.9, 25.1. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.4. **HRMS-ASAP** (m/z): Calculated (found) for $C_{16}H_{26}BO_4S$ $[M+H]^+$ 325.1639 (325.1629). **Anal.** for $C_{16}H_{25}BO_4S$ calcd: C, 59.27; H, 7.77; S, 9.89. found: C, 59.34; H, 7.66; S, 9.73.



1e **6f**

In an argon-filled glovebox, the cyclic sulfone **1e** (54.7 mg, 0.3 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (12.1 mg, 10 mol%), KO^{t}Bu (50.5 mg, 0.45 mmol, 1.5 equiv.) and B_2pin_2 (114.3 mg, 0.45 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at 100 °C for 12 h. After 12 h, propyl 4-methylbenzenesulfonate (128.6 mg, 0.6 mmol, 2.0 equiv.) was added into the reaction tube under argon. The reaction mixture was stirred at 100 °C for extra 3 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). After careful removal of the solvent *in vacuo*, the reaction mixture was purified by column chromatography on silica gel (hexane/EtOAc (10/1)) to yield the product **6f**.

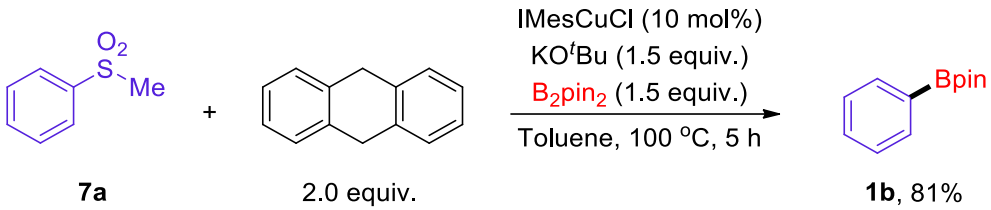
4,4,5,5-Tetramethyl-2-(2-(3-(propylsulfonyl)propyl)phenyl)-1,3,2-dioxaborolane 6f



6f

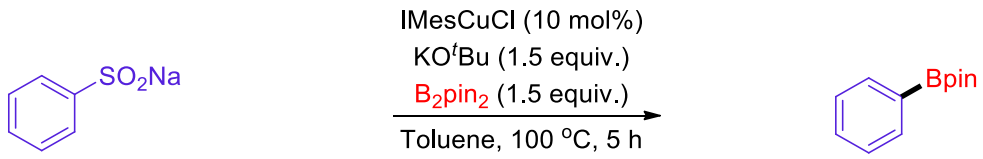
Yield: 60.2 mg (171 µmol, 57%) of a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.83 – 7.81 (m, 1H), 7.39 – 7.35 (m, 1H), 7.24 – 7.21 (m, 1H), 7.18 – 7.16 (m, 1H), 3.01 (t, *J* = 8 Hz, 2H), 2.98 – 2.94 (m, 2H), 2.89 – 2.86 (m, 2H), 2.15 – 2.08 (m, 2H), 1.86 – 1.78 (m, 2H), 1.35 (s, 12H), 1.04 (t, *J* = 8 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ = 147.2, 136.8, 131.4, 129.4, 125.9, 83.8, 54.3, 52.5, 34.3, 25.4, 25.1, 15.9, 13.3. **^{11}B{^{1}H} NMR** (160 MHz, $CDCl_3$): δ = 31.6. **HRMS-ASAP** (m/z): Calculated (found) for $C_{18}H_{30}BO_4S$ $[M+H]^+$ 353.1952 (353.1942). **Anal.** for $C_{18}H_{29}BO_4S$ calcd: C, 61.37; H, 8.30; S, 9.10. found: C, 61.42; H, 8.15; S, 9.18.

3 Preliminary Mechanistic Investigations



7a 2.0 equiv. **1b**, 81%

In an argon-filled glovebox, (methylsulfonyl)benzene **7a** (78.1 mg, 0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.), and 9,10-dihydroanthracene (180.2 mg,1.0 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 100 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product **1b** was isolated in 81% yield following flash column chromatography (hexane/EtOAc (98/2)) after careful removal of the solvent *in vacuo*.



1g **1b**, 0%

In an argon-filled glovebox, benzenesulfinic acid sodium salt **1g** (82.1 mg, 0.5 mmol, 1.0 equiv.), dissolved in toluene (2 mL), was added to a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar. IMesCuCl (20.2 mg, 10 mol%), KO^{t}Bu (84.2 mg, 0.75 mmol, 1.5 equiv.), B_2pin_2 (190.5 mg, 0.75 mmol, 1.5 equiv.), and 9,10-dihydroanthracene (180.2 mg,1.0 mmol, 2.0 equiv.) were added. The reaction mixture was stirred at 100 °C for 5 h, then diluted with Et_2O (2 mL) and filtred through a pad of Celite (Ø 3 mm x 8 mm). The product **1b** was not observed by GC-MS

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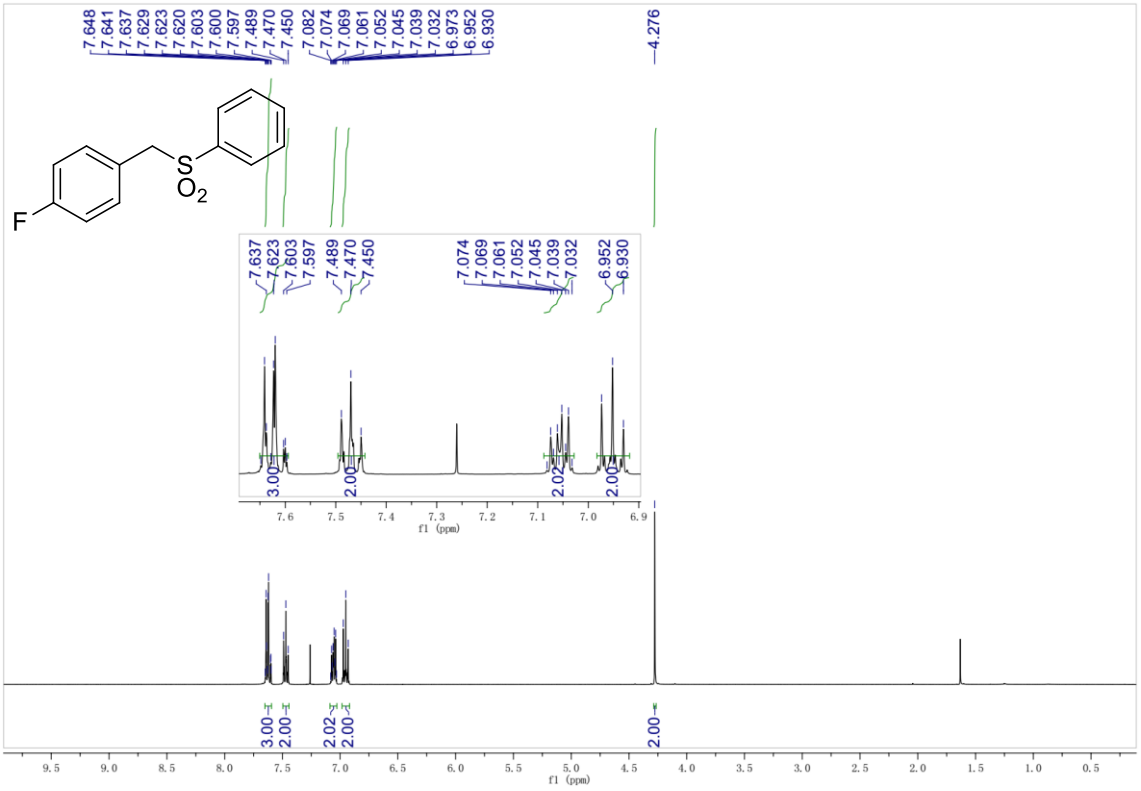
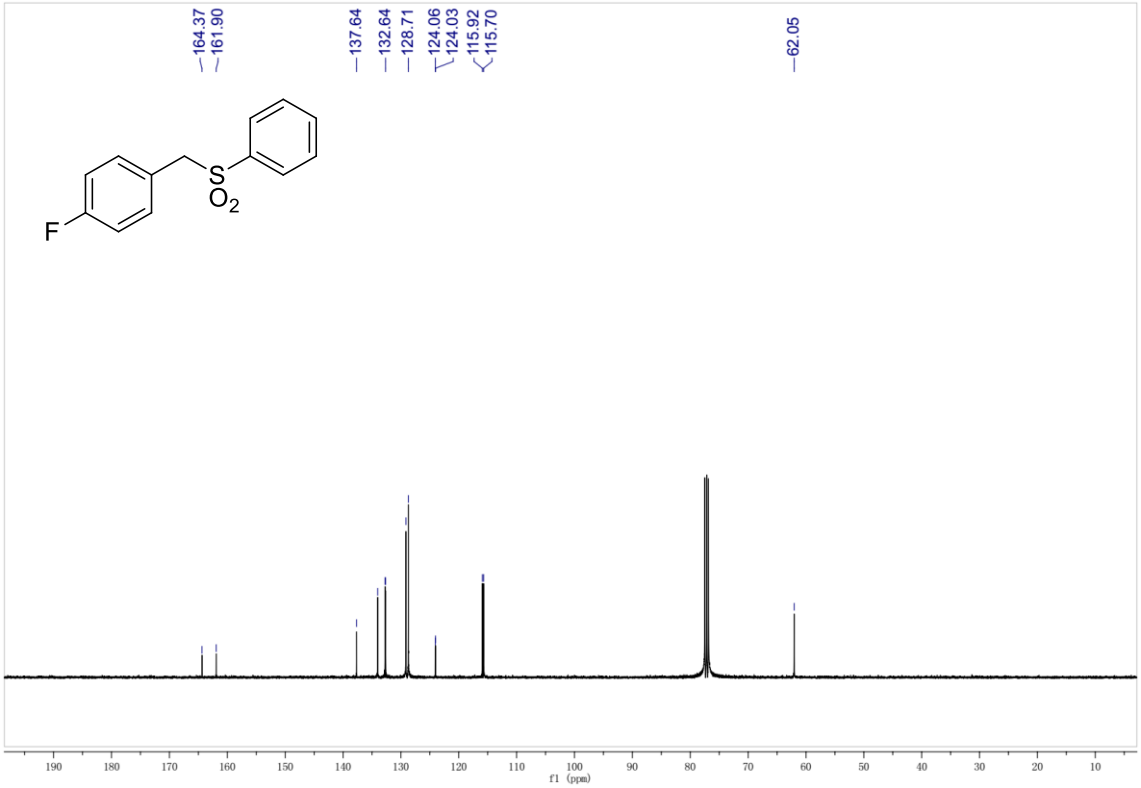
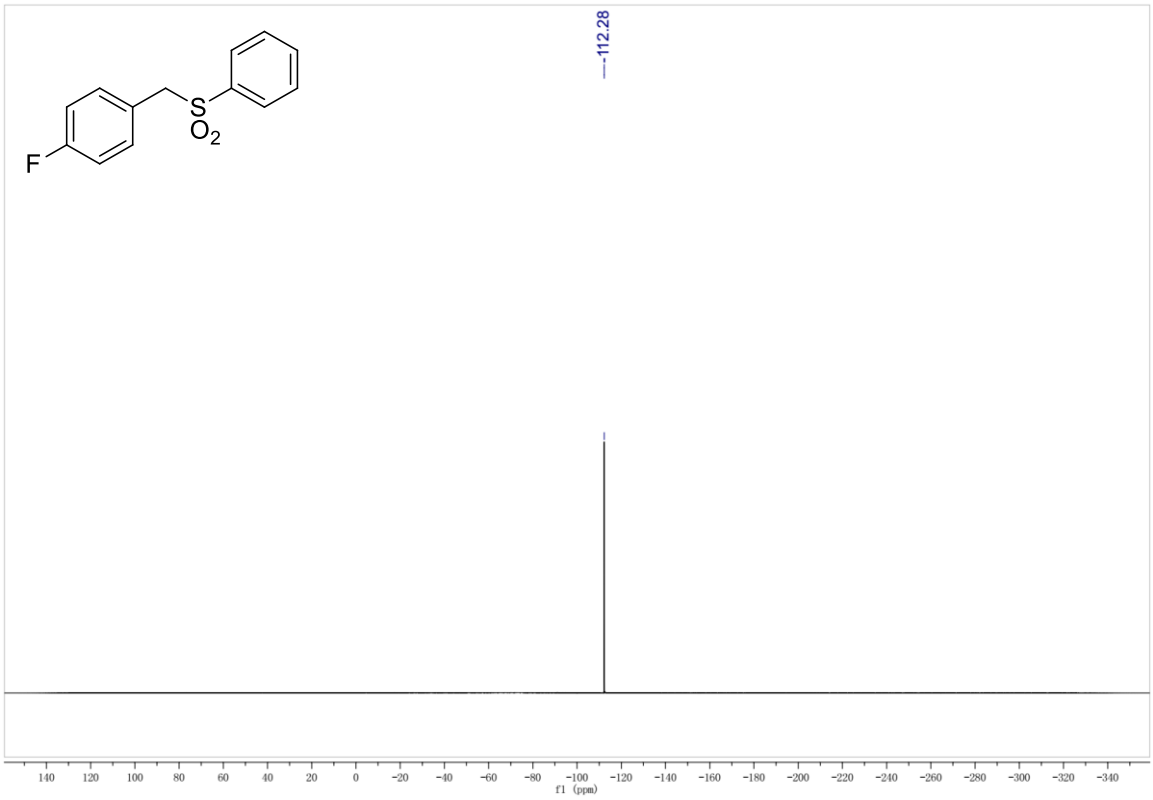
5 NMR Spectra



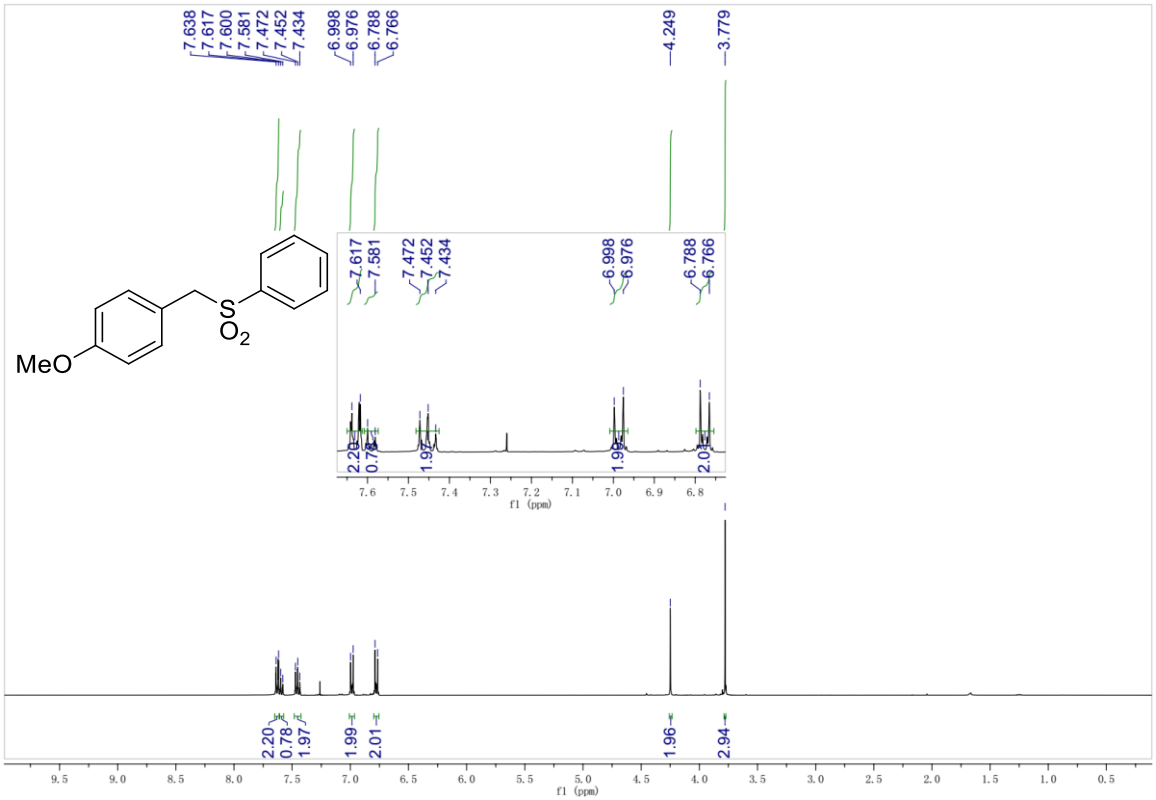
^{1}H NMR spectrum of compound **2a** in $CDCl_3$ (400 MHz).



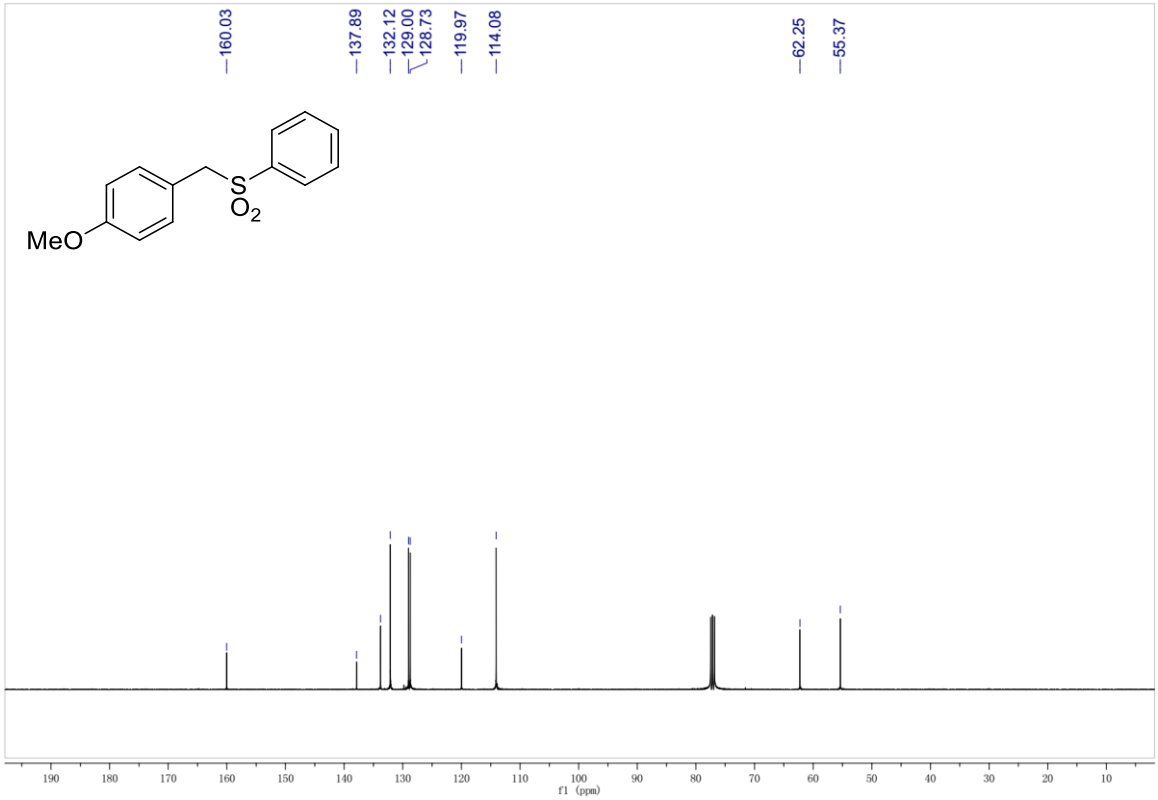
^{13}C{^{1}H} NMR spectrum of compound **2a** in $CDCl_3$ (100 MHz).



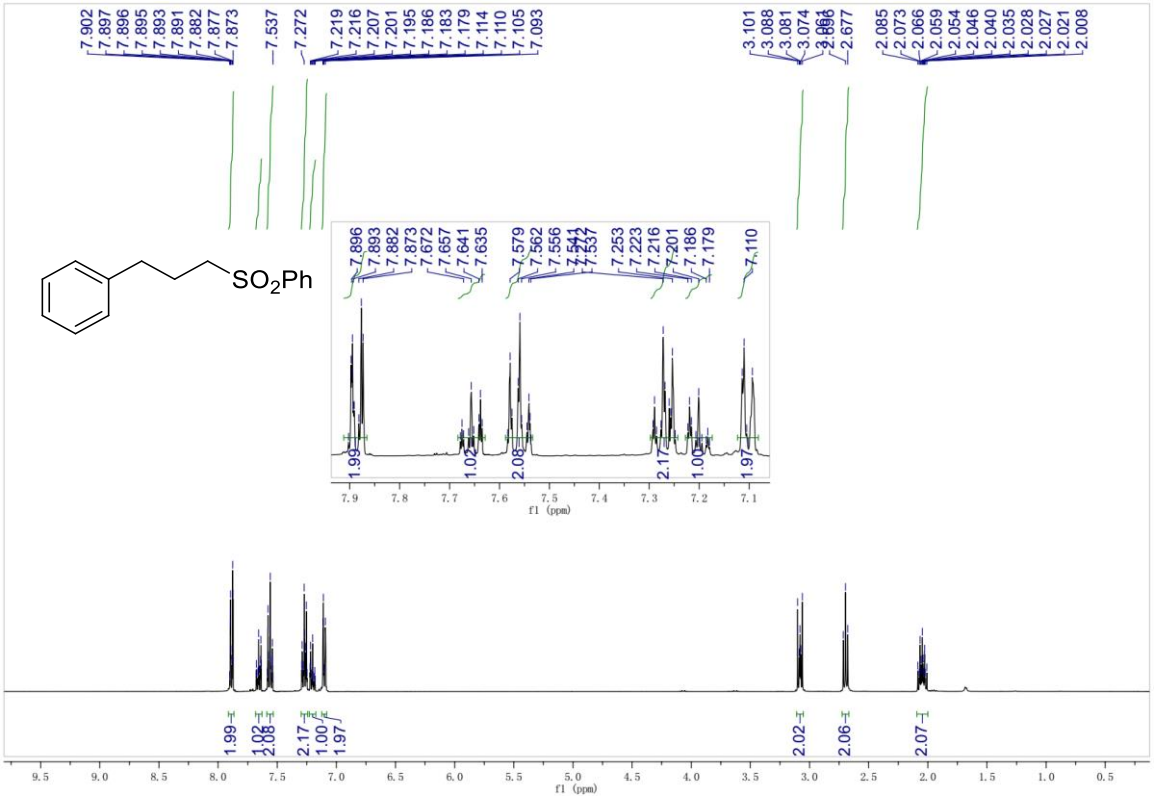
$^{19}F\{^{1}H\}$ NMR spectrum of compound **2a** in $CDCl_3$ (376 MHz).



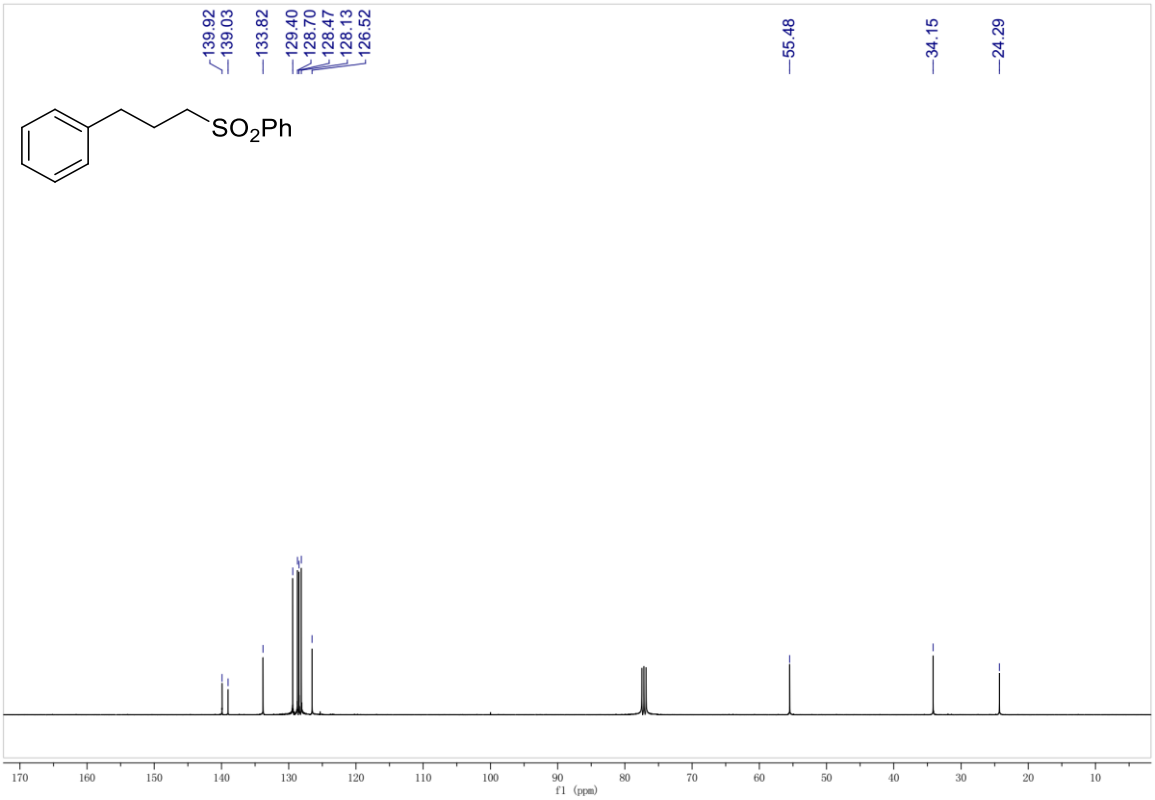
^{1}H NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz).



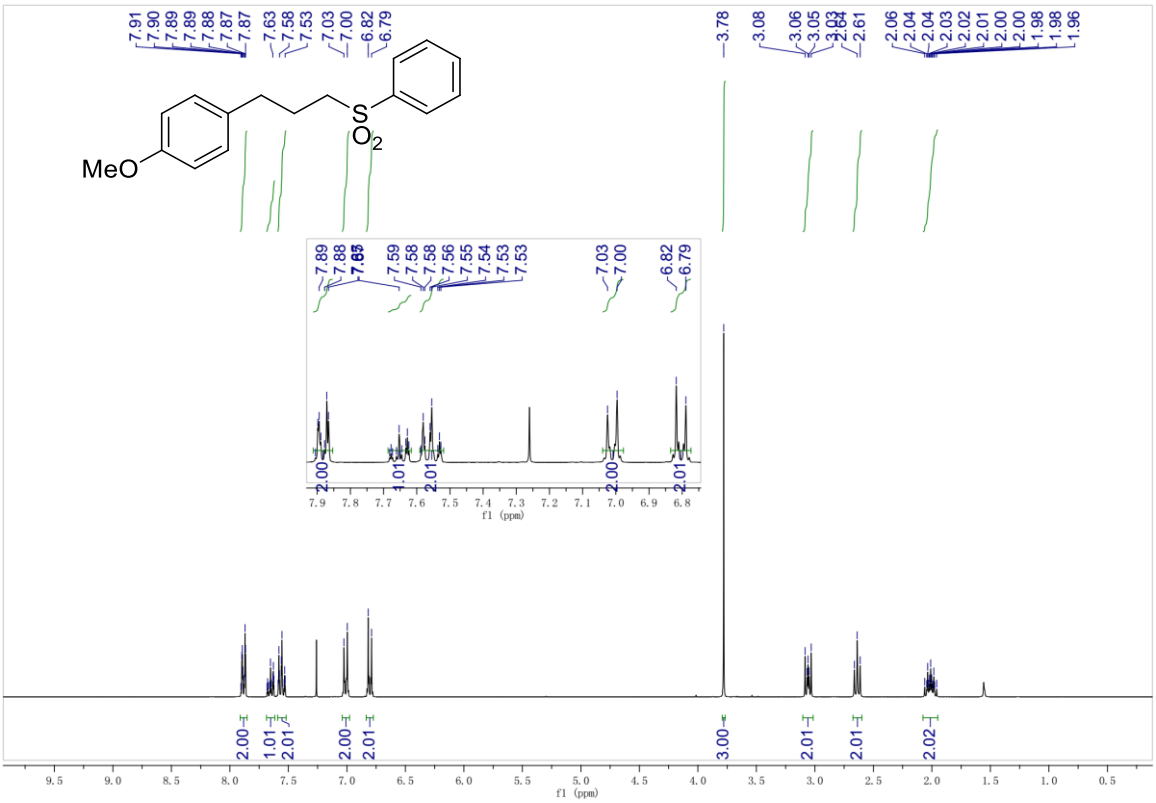
$^{13}C\{^{1}H\}$ NMR spectrum of compound **3a** in $CDCl_3$ (100 MHz).



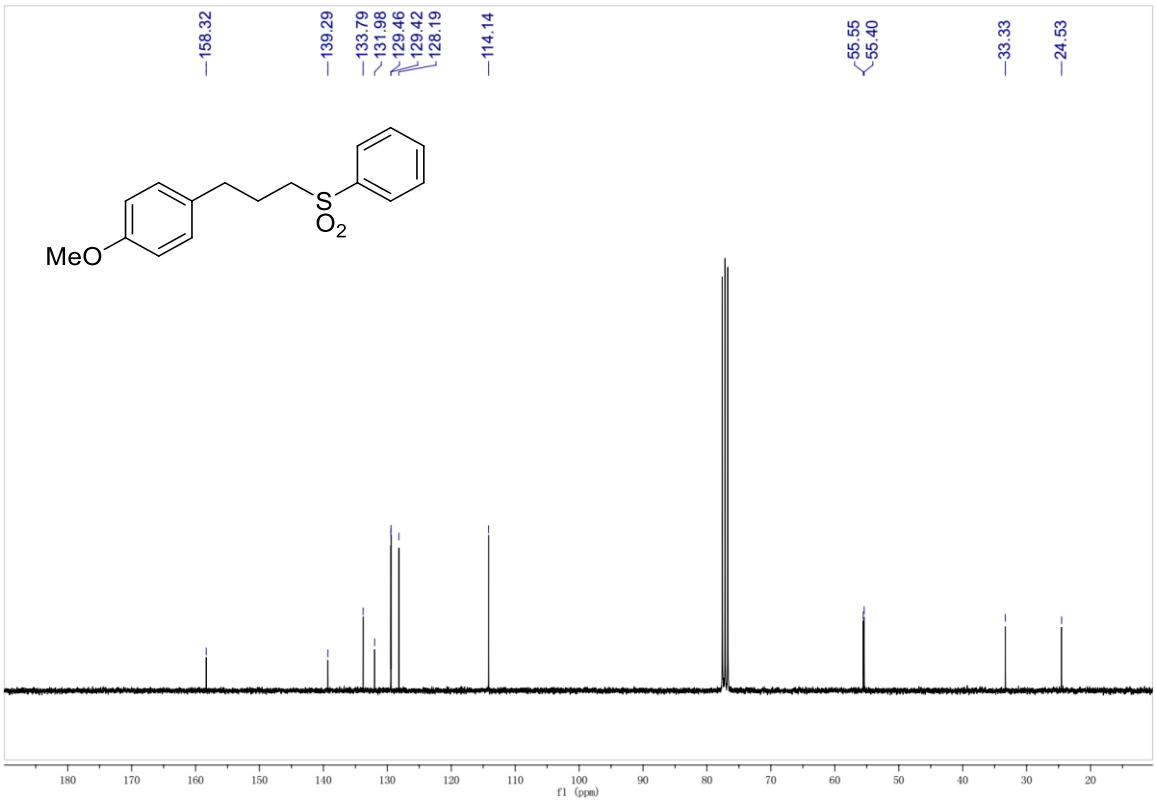
^{1}H NMR spectrum of compound **4a** in $CDCl_3$ (400 MHz).



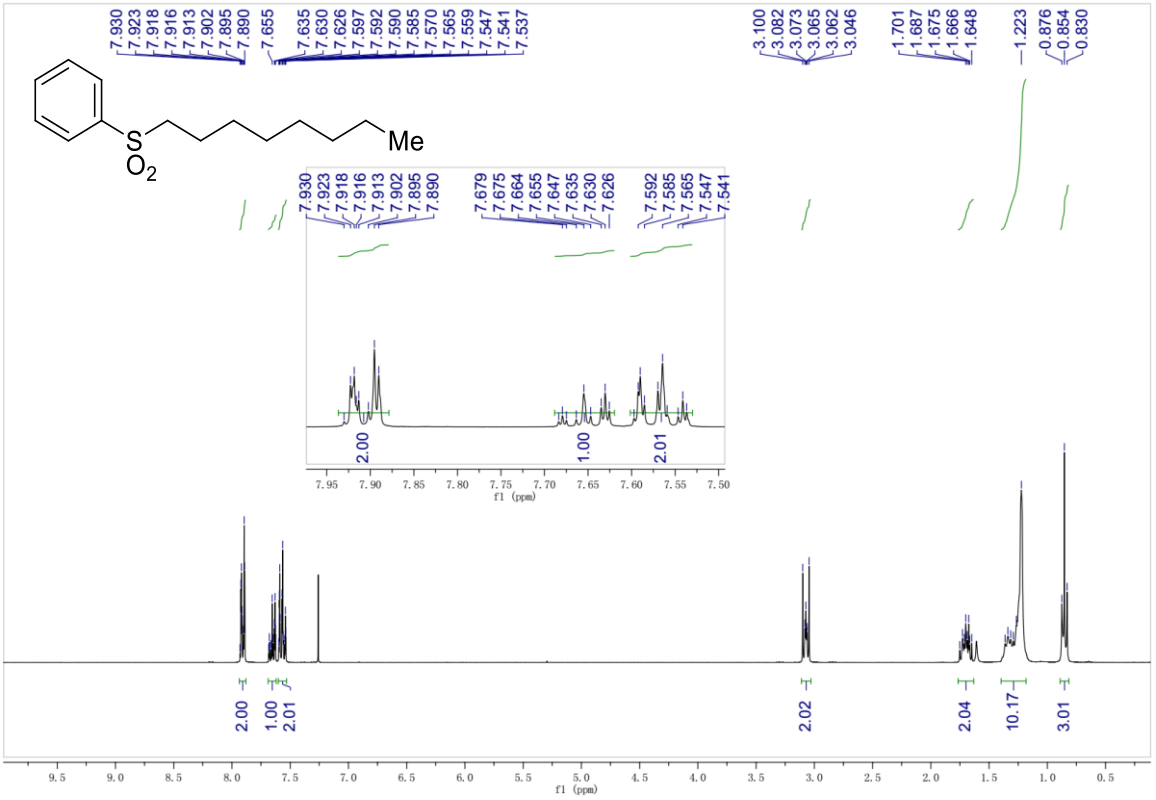
$^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** in $CDCl_3$ (100 MHz).



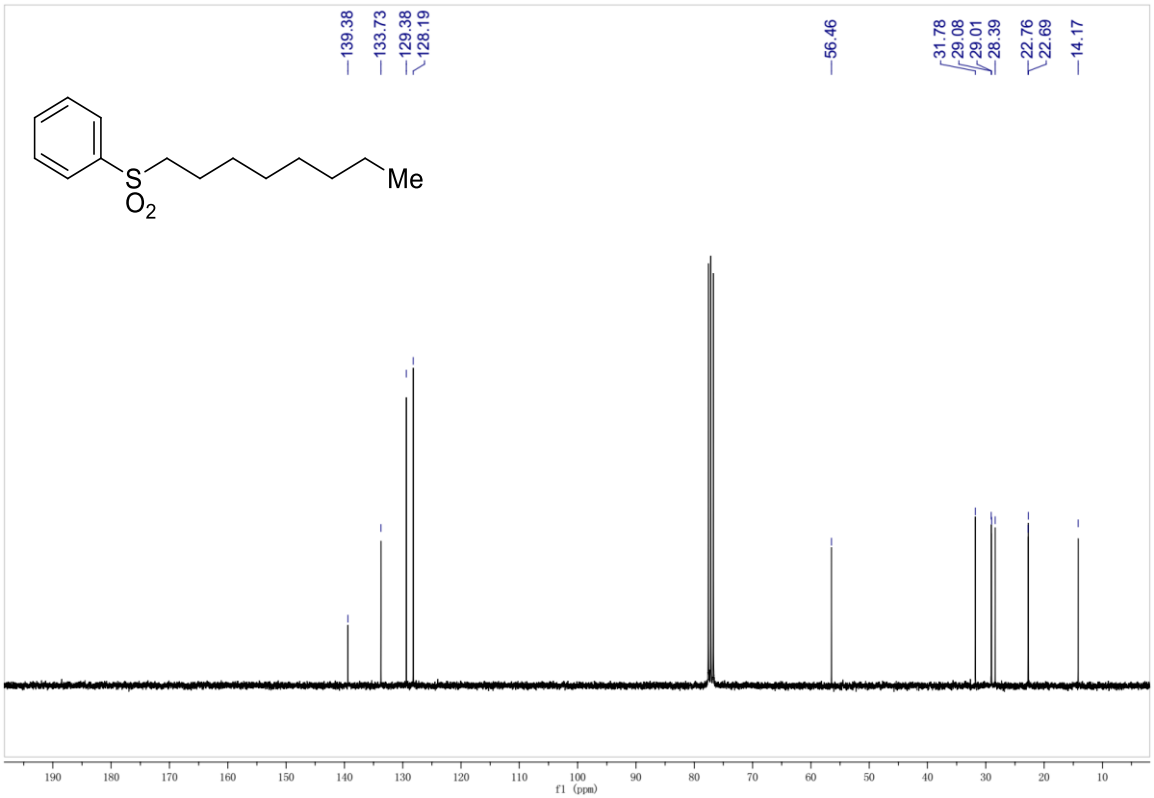
^{1}H NMR spectrum of compound **5a** in $CDCl_3$ (300 MHz).



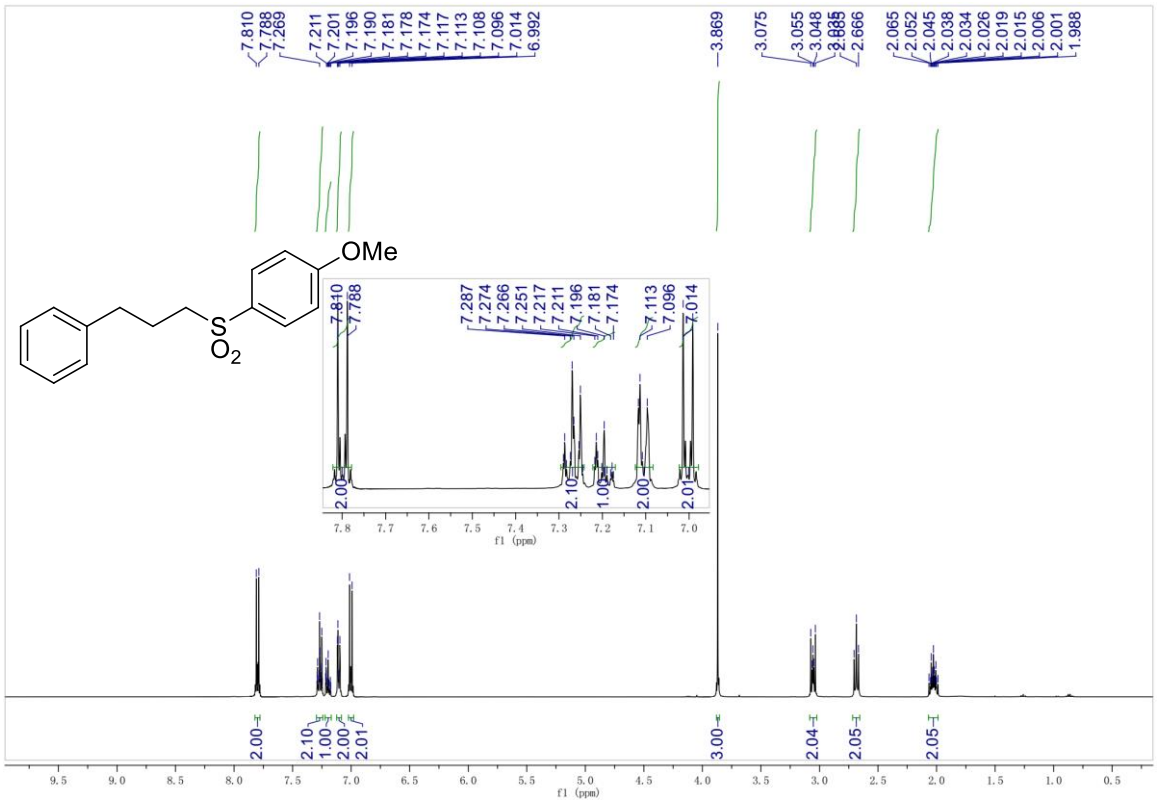
$^{13}C\{^{1}H\}$ NMR spectrum of compound **5a** in $CDCl_3$ (75 MHz).



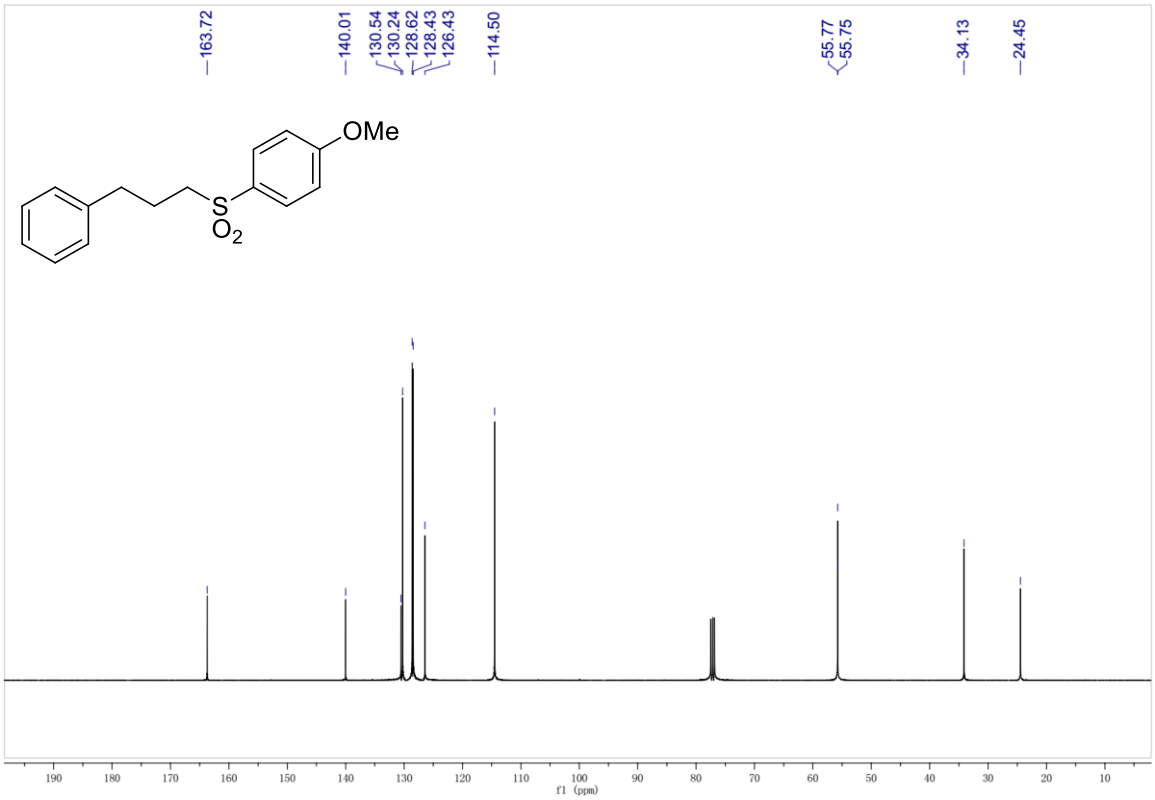
^{1}H NMR spectrum of compound **6a** in $CDCl_3$ (300 MHz).



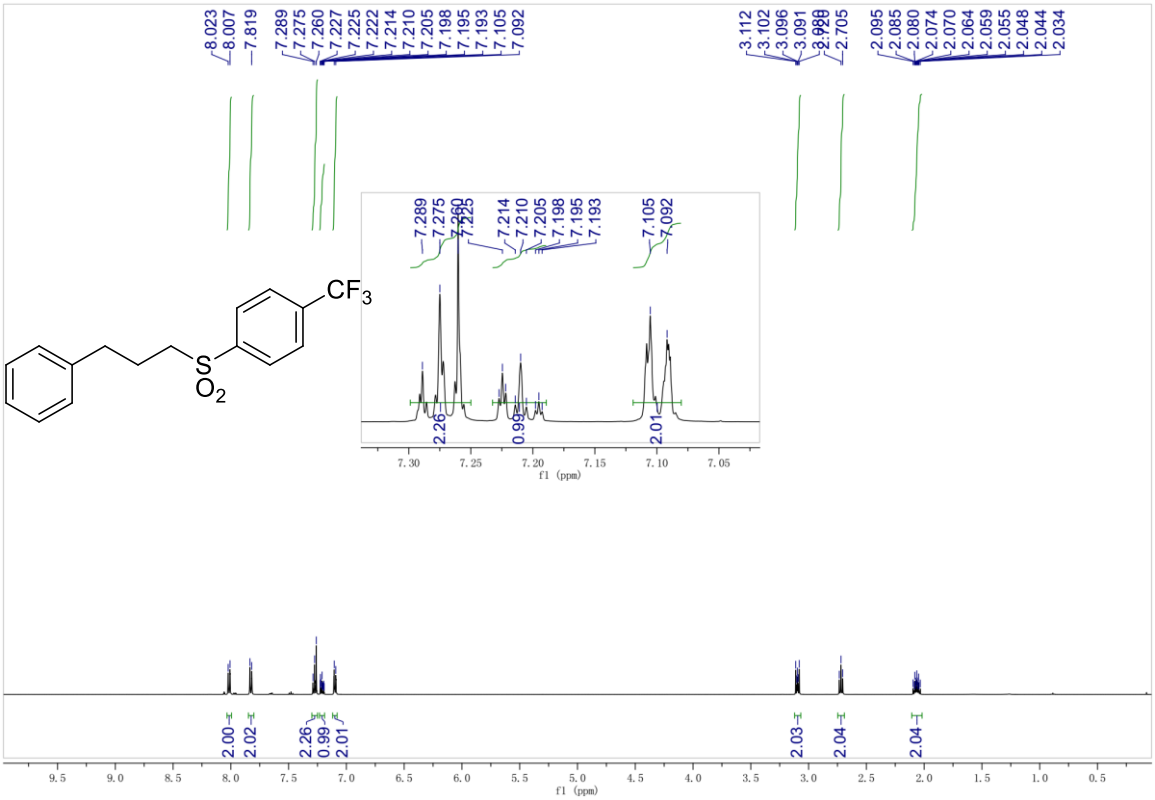
$^{13}C\{^{1}H\}$ NMR spectrum of compound **6a** in $CDCl_3$ (75 MHz).



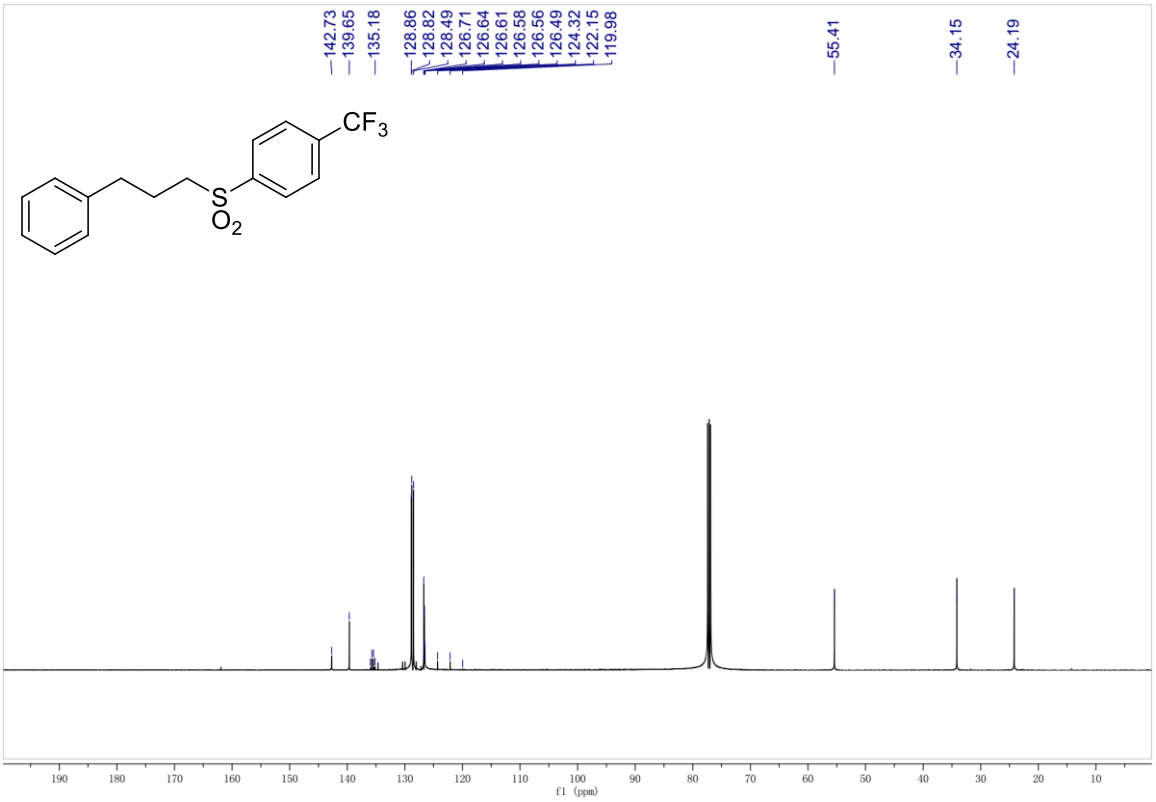
^{1}H NMR spectrum of compound **9c** in $CDCl_3$ (400 MHz).



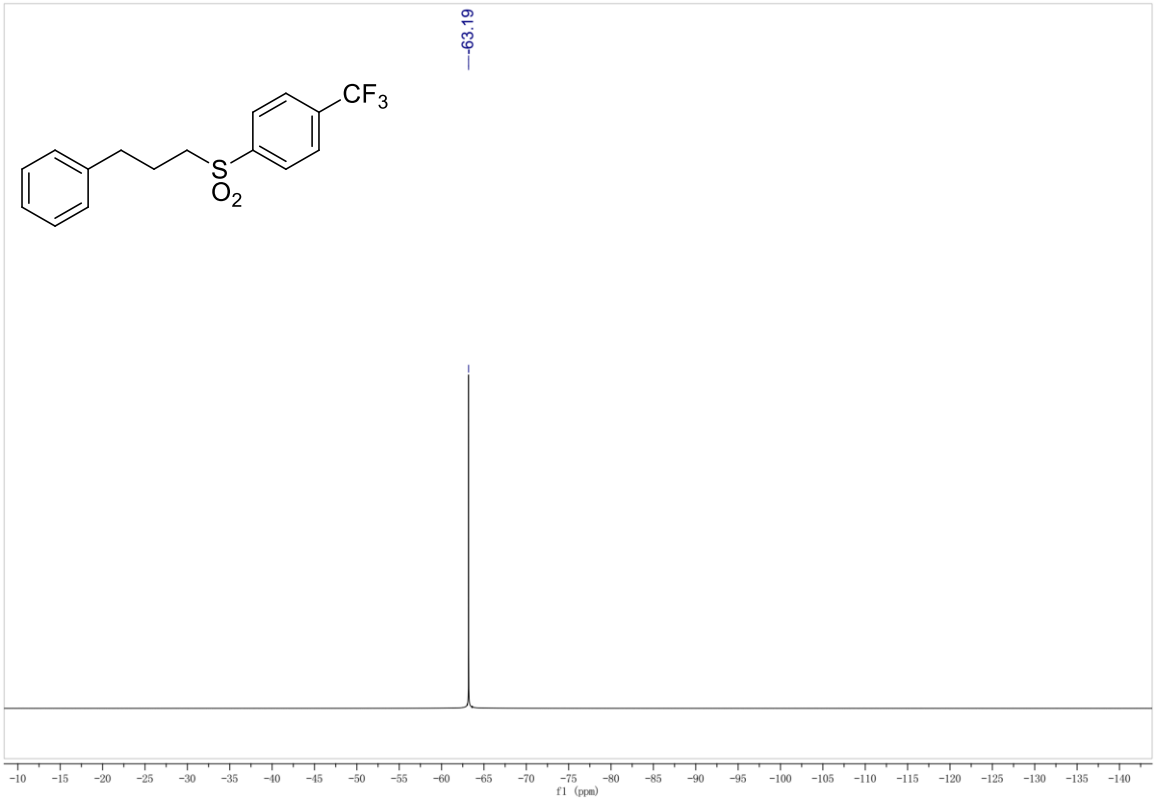
$^{13}C\{^{1}H\}$ NMR spectrum of compound **9c** in $CDCl_3$ (100 MHz).



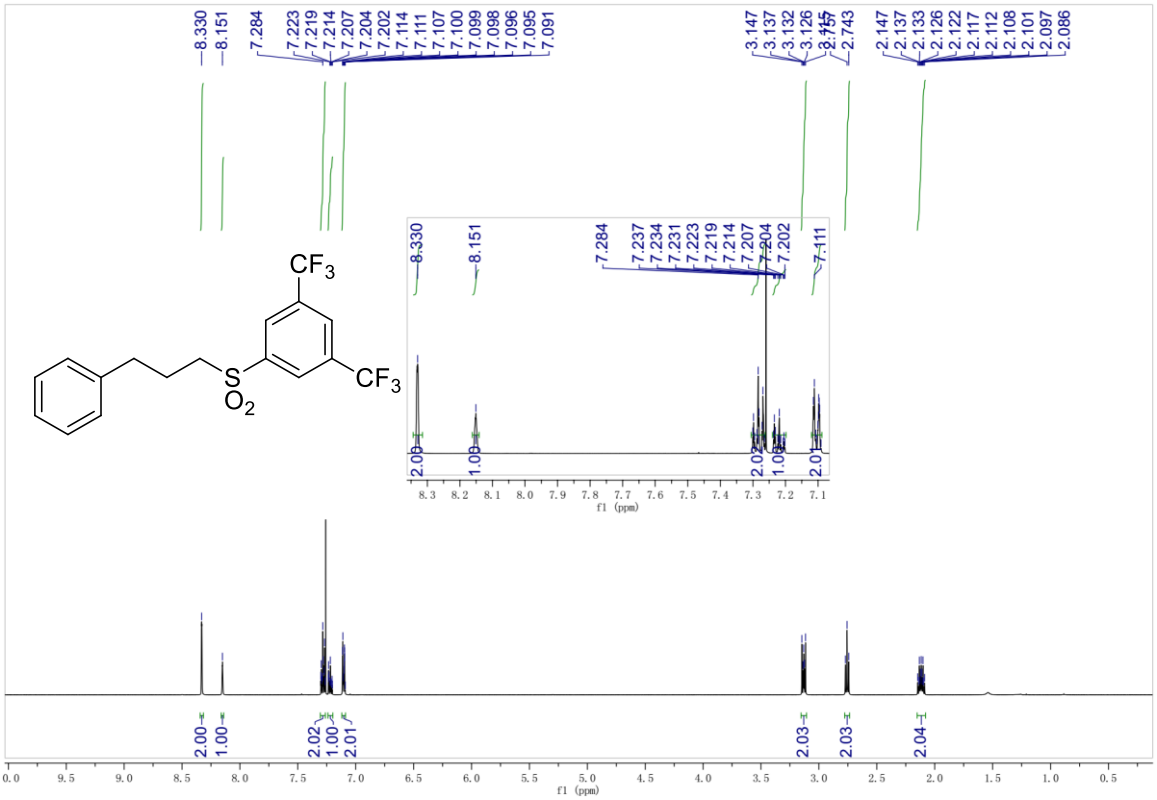
^{1}H NMR spectrum of compound **10c** in $CDCl_3$ (500 MHz).



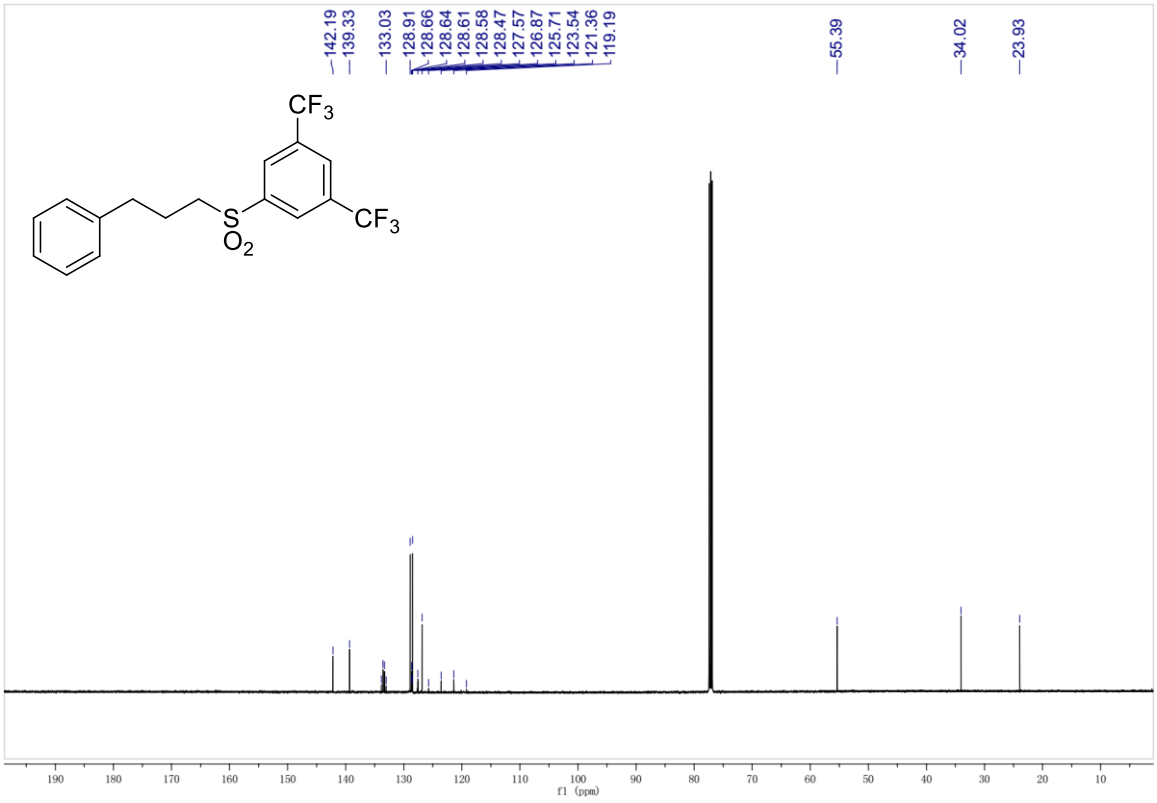
$^{13}C\{^{1}H\}$ NMR spectrum of compound **10c** in $CDCl_3$ (125 MHz).



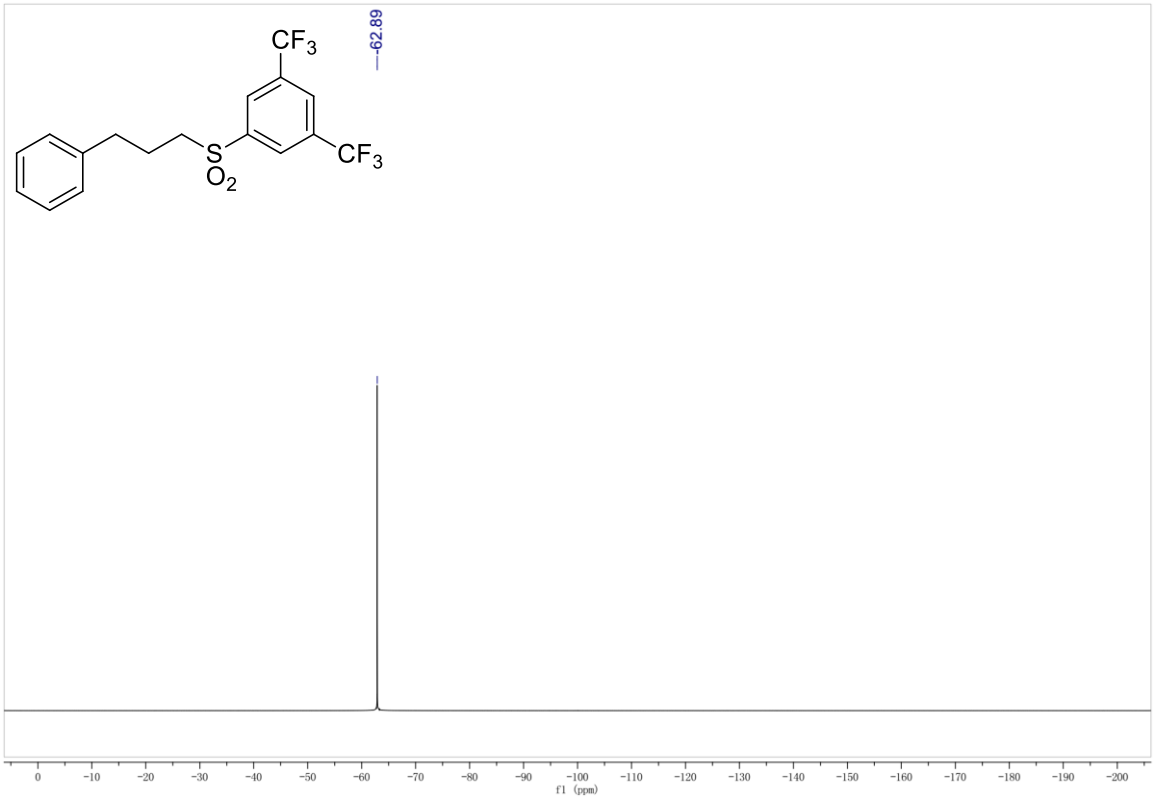
$^{19}F\{^{1}H\}$ NMR spectrum of compound **10c** in $CDCl_3$ (470 MHz).



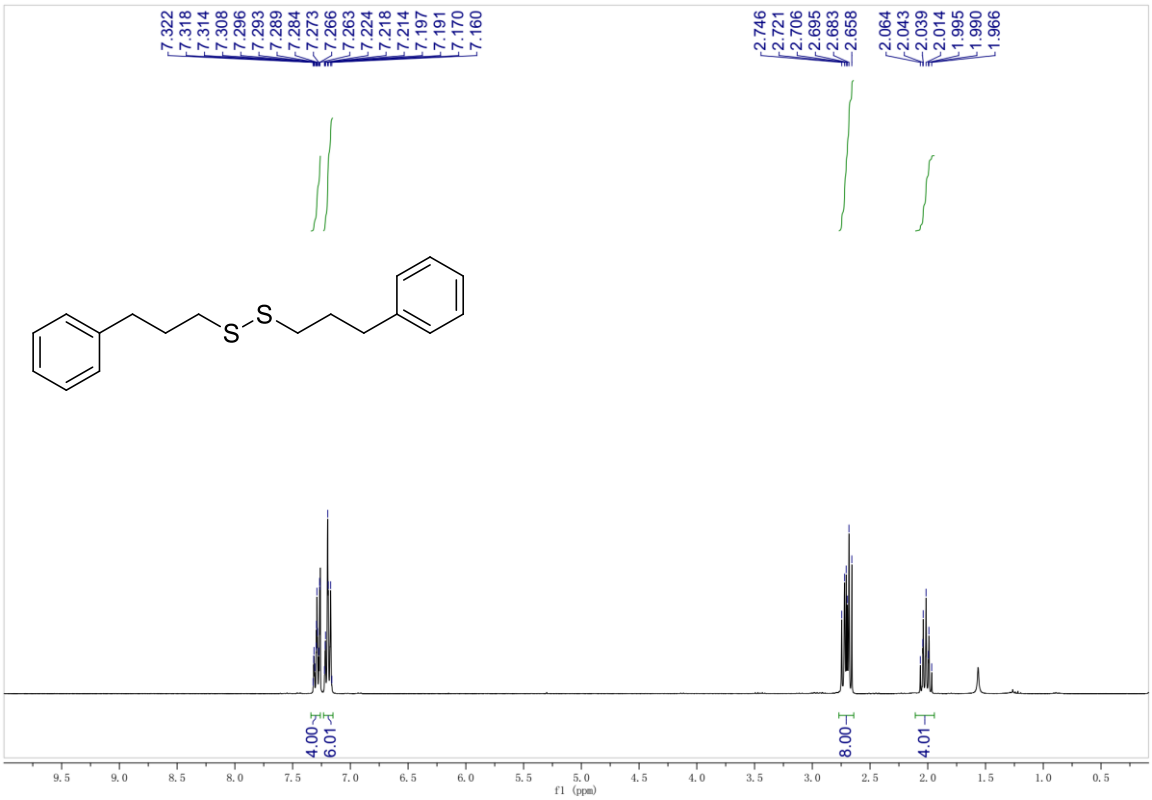
^{1}H NMR spectrum of compound **11c** in $CDCl_3$ (500 MHz).



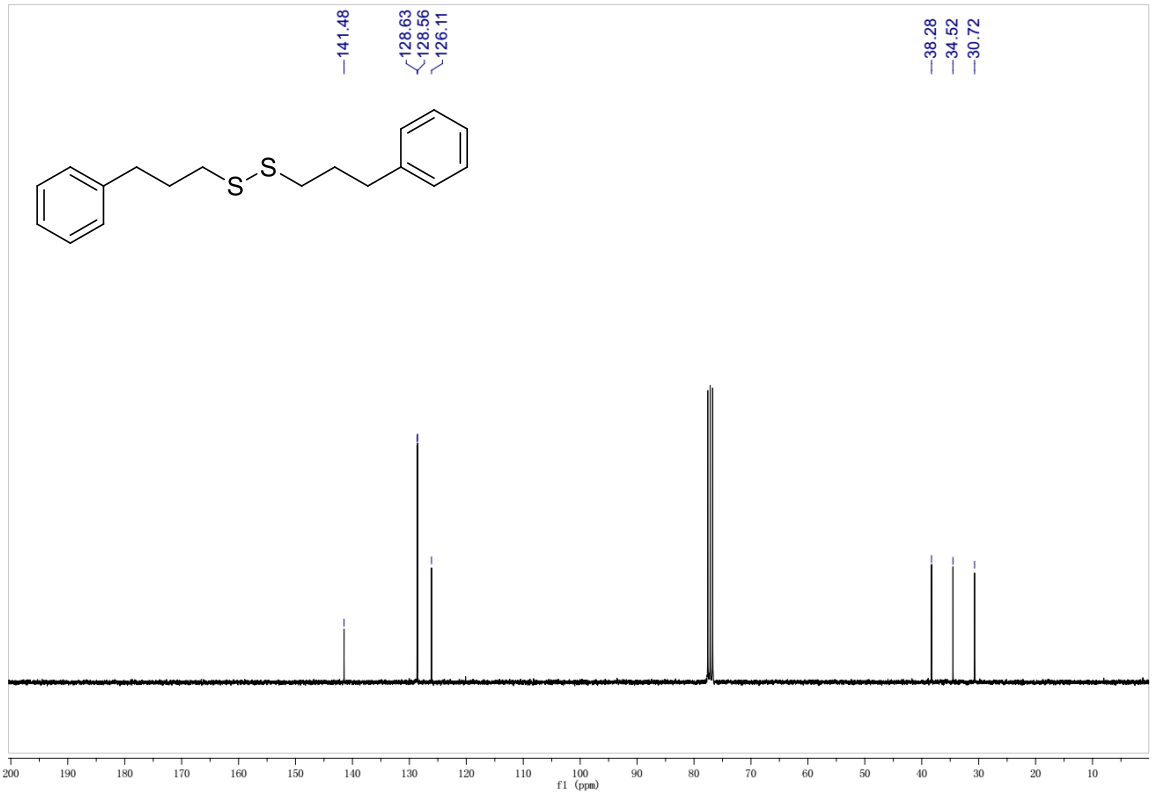
$^{13}C\{^{1}H\}$ NMR spectrum of compound **11c** in $CDCl_3$ (125 MHz).



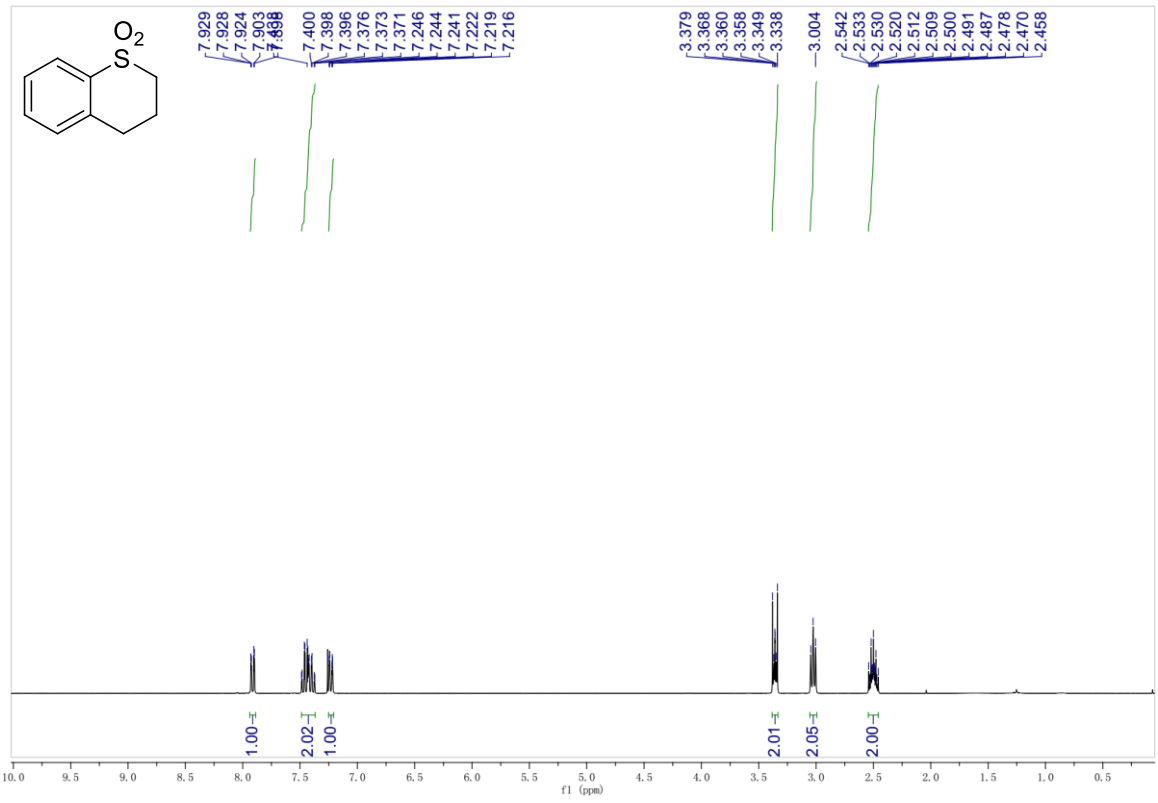
$^{19}F\{^{1}H\}$ NMR spectrum of compound **11c** in $CDCl_3$ (470 MHz).



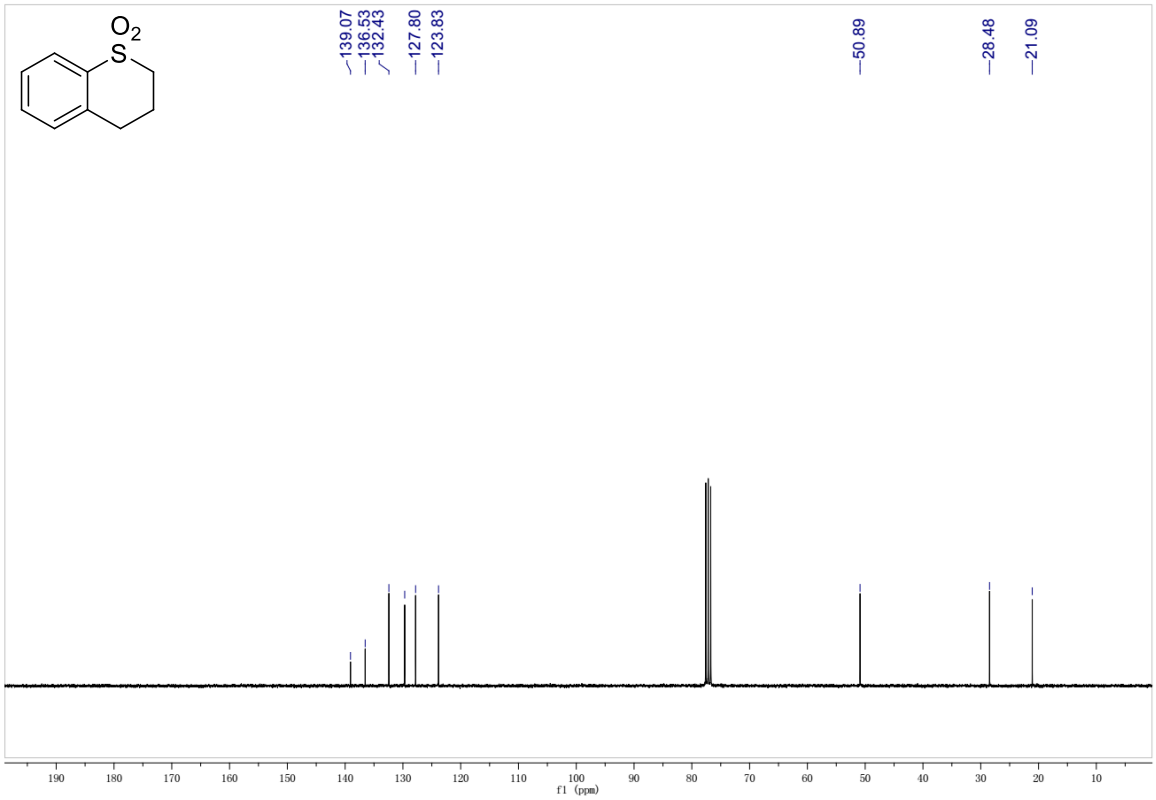
^{1}H NMR spectrum of **1,2-bis(3-phenylpropyl)disulfane** in $CDCl_3$ (300 MHz).



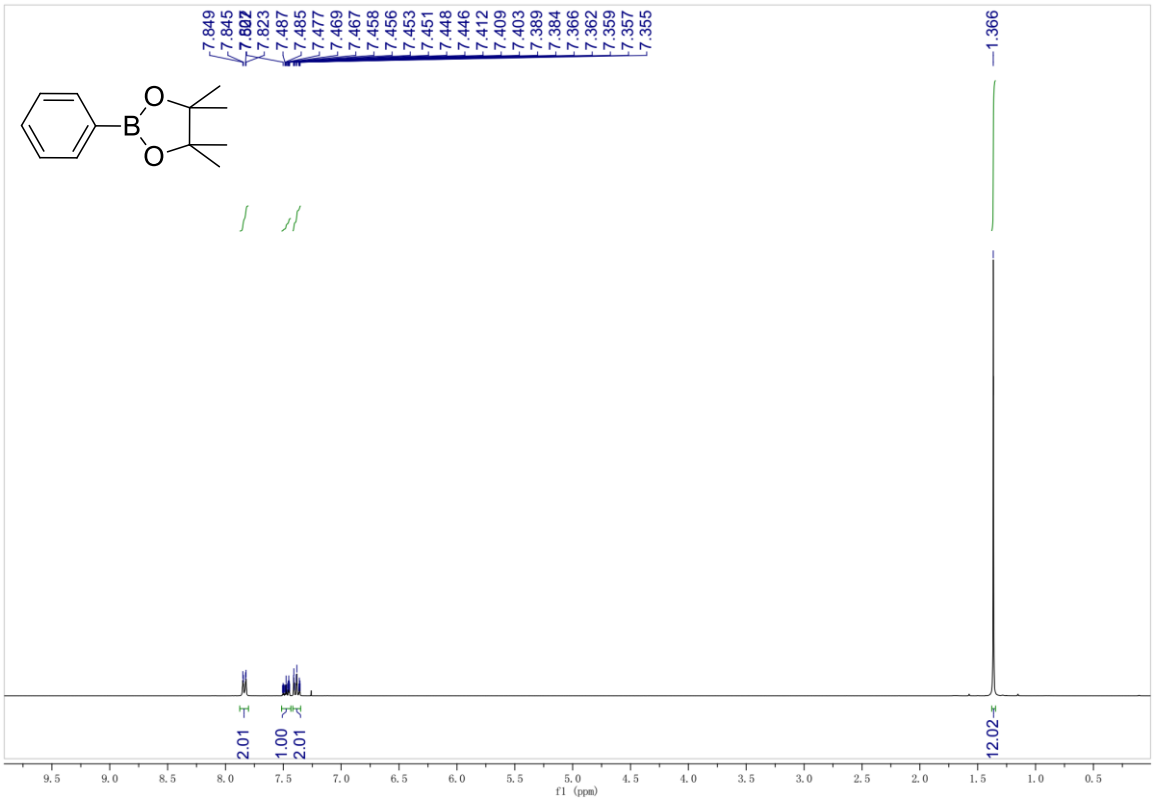
$^{13}C\{^{1}H\}$ NMR spectrum of **1,2-bis(3-phenylpropyl)disulfane** in $CDCl_3$ (75 MHz).



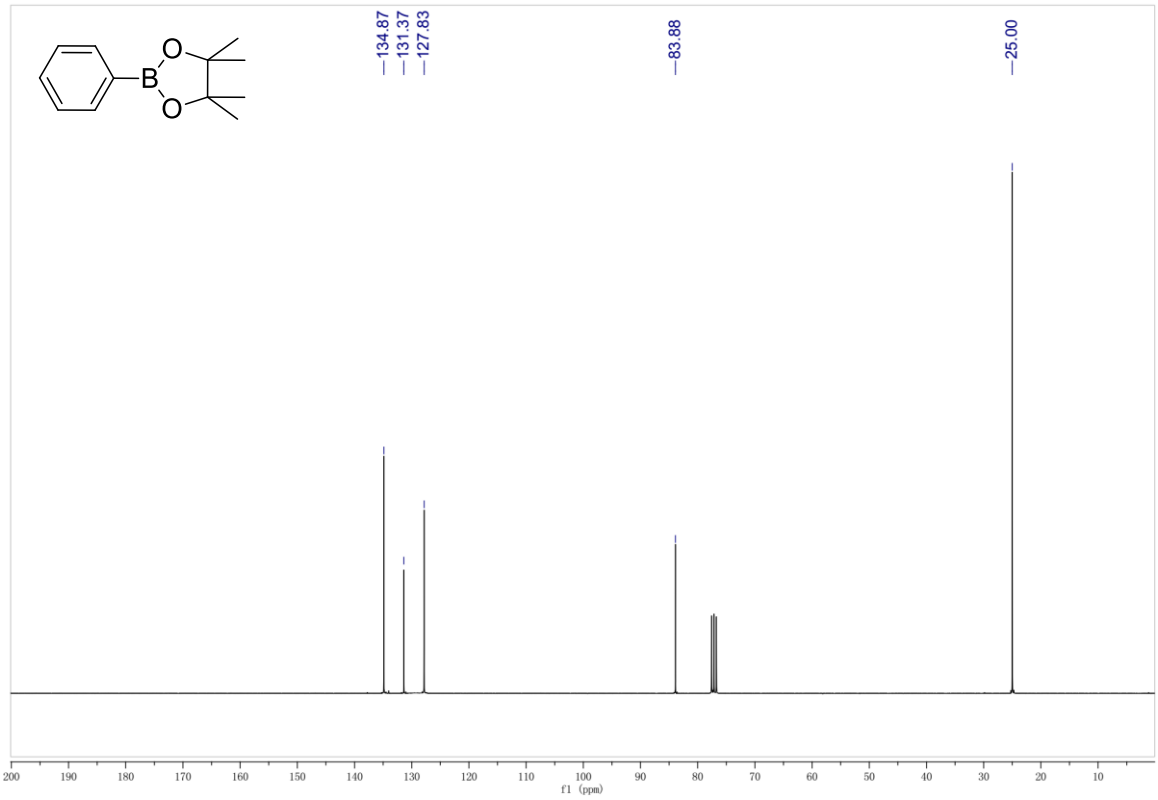
^{1}H NMR spectrum of compound **1e** in $CDCl_3$ (300 MHz).



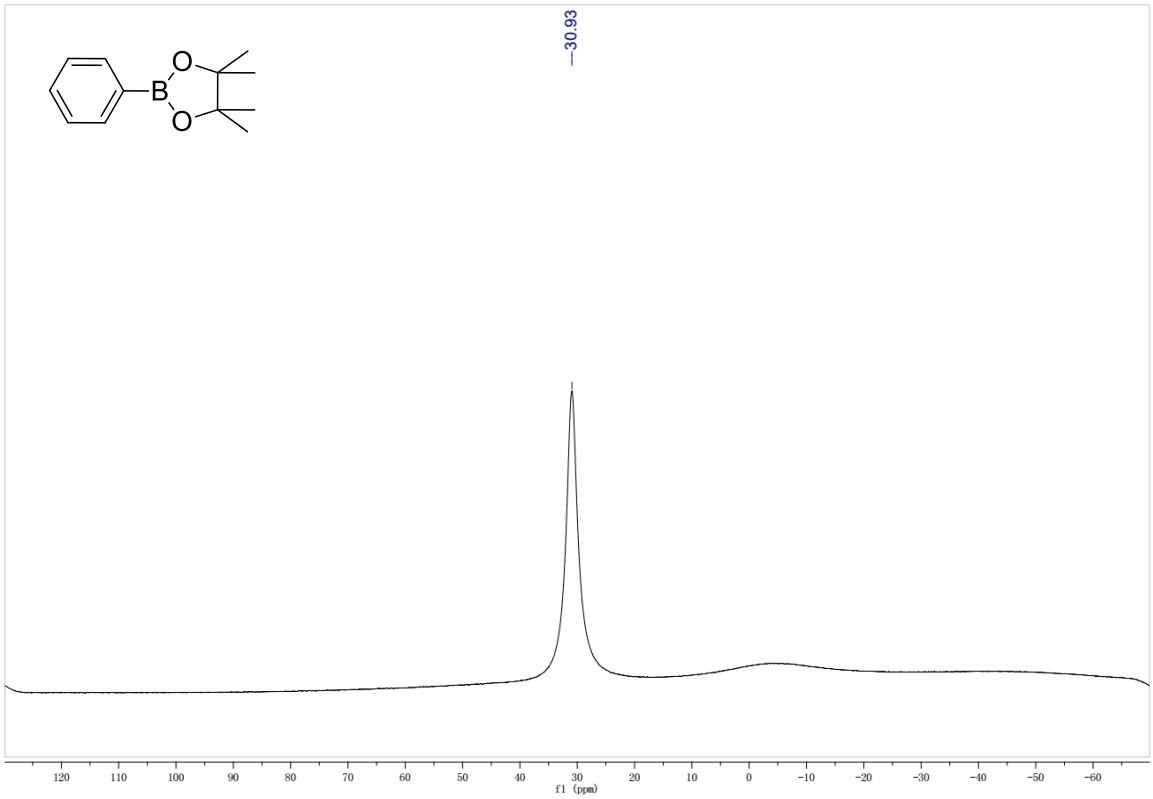
$^{13}C\{^{1}H\}$ NMR spectrum of compound **1e** in $CDCl_3$ (75 MHz).



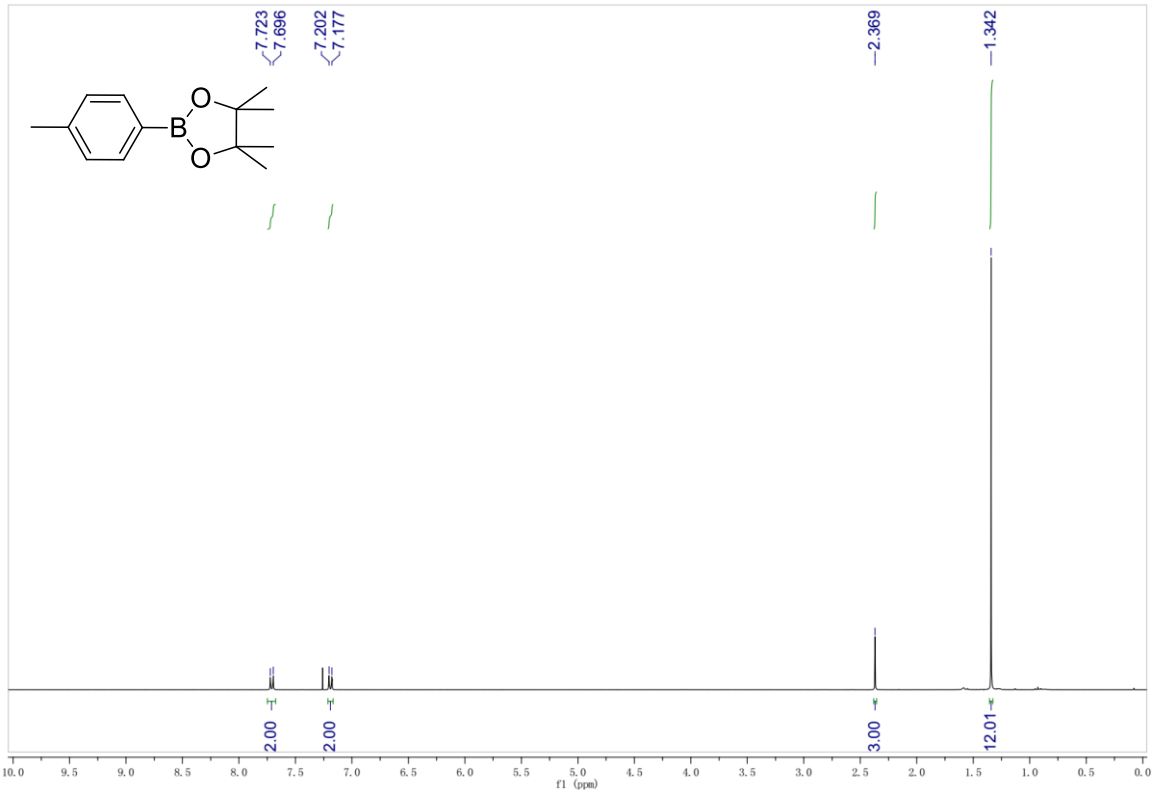
^{1}H NMR spectrum of compound **1b** in $CDCl_3$ (300 MHz).



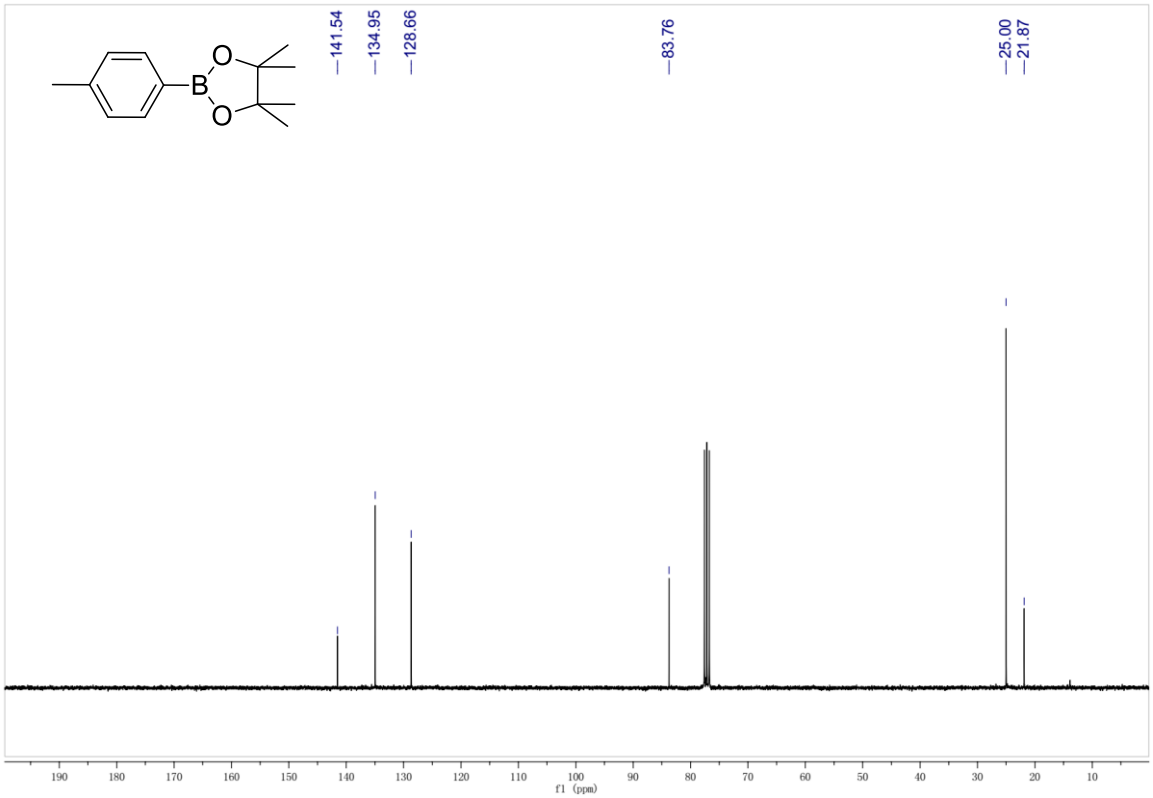
$^{13}C\{^{1}H\}$ NMR spectrum of compound **1b** in $CDCl_3$ (75 MHz).



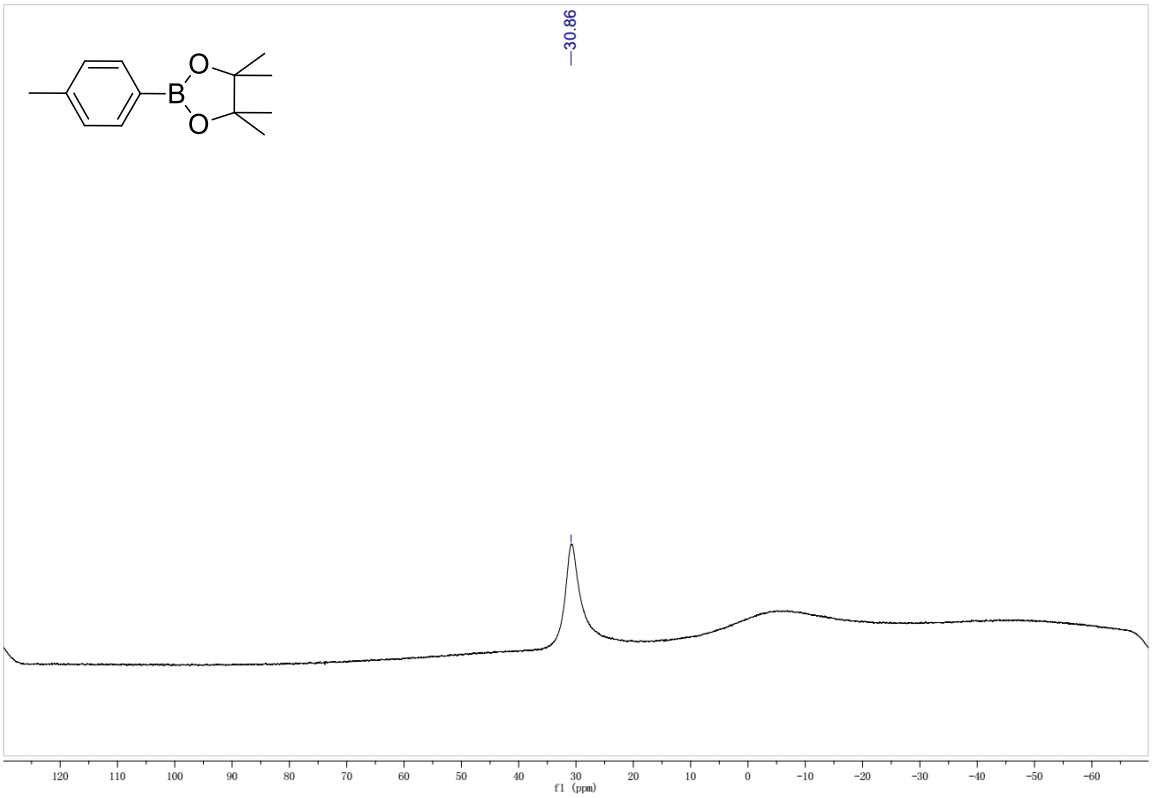
$^{11}B\{^{1}H\}$ NMR spectrum of compound **1b** in $CDCl_3$ (96 MHz).



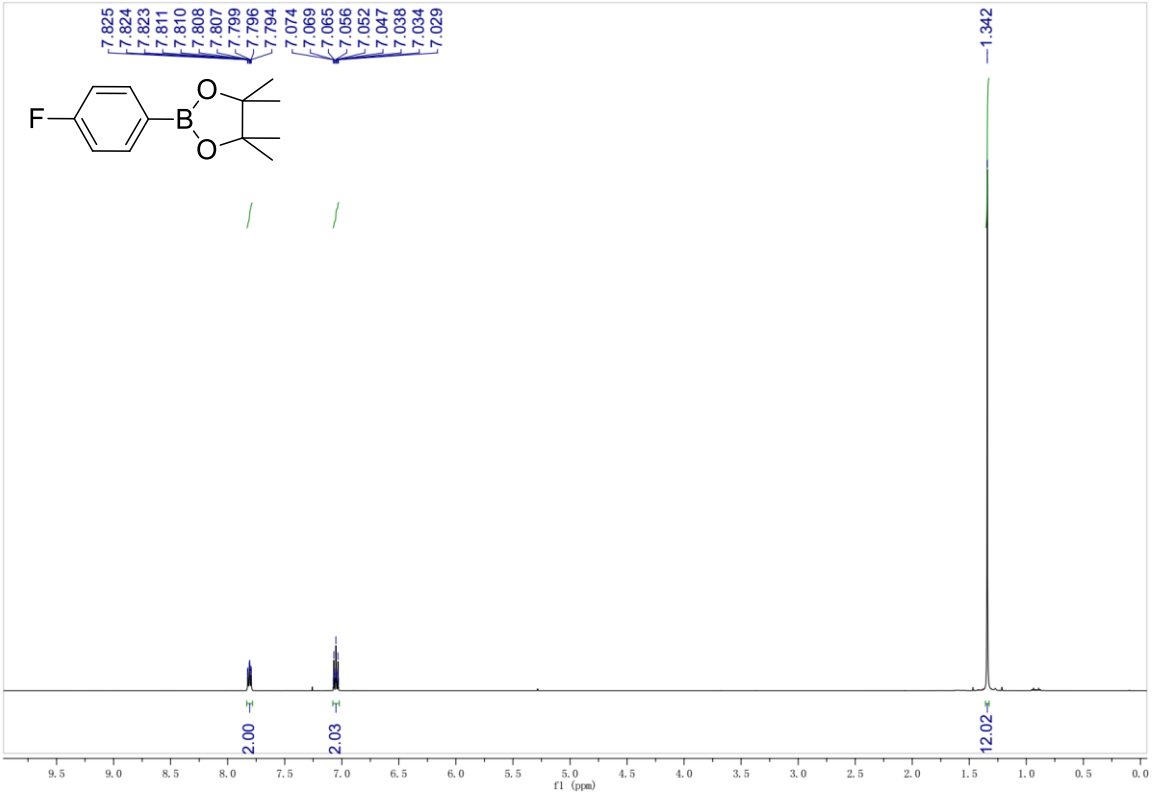
^{1}H NMR spectrum of compound **1d** in $CDCl_3$ (300 MHz).



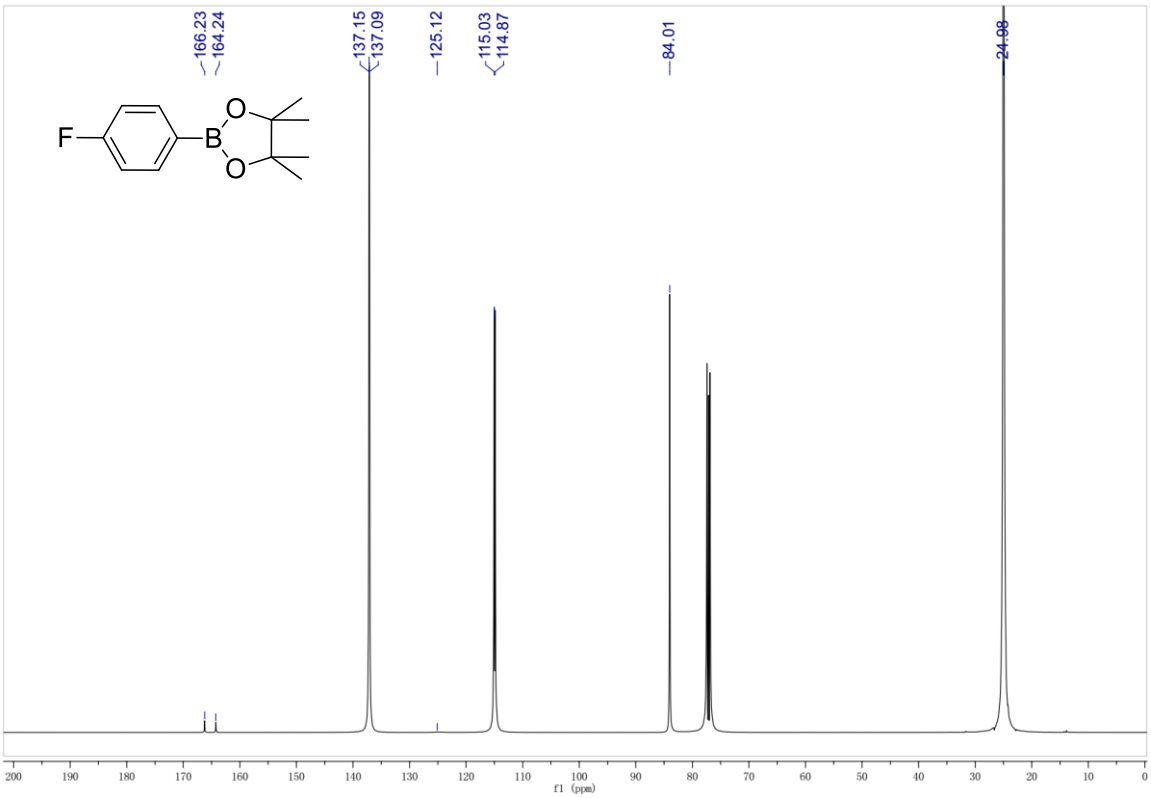
^{13}C{^{1}H} NMR spectrum of compound **1d** in $CDCl_3$ (75 MHz).



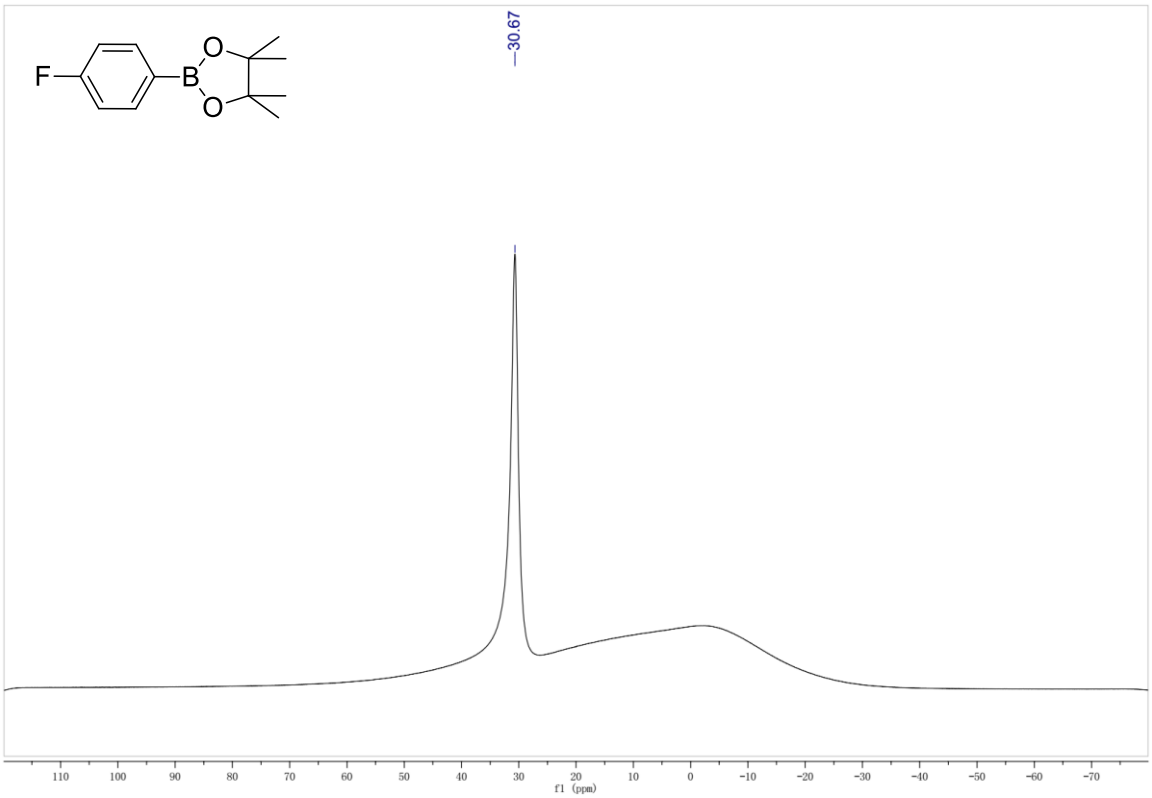
$^{11}B\{^{1}H\}$ NMR spectrum of compound **1d** in $CDCl_3$ (96 MHz).



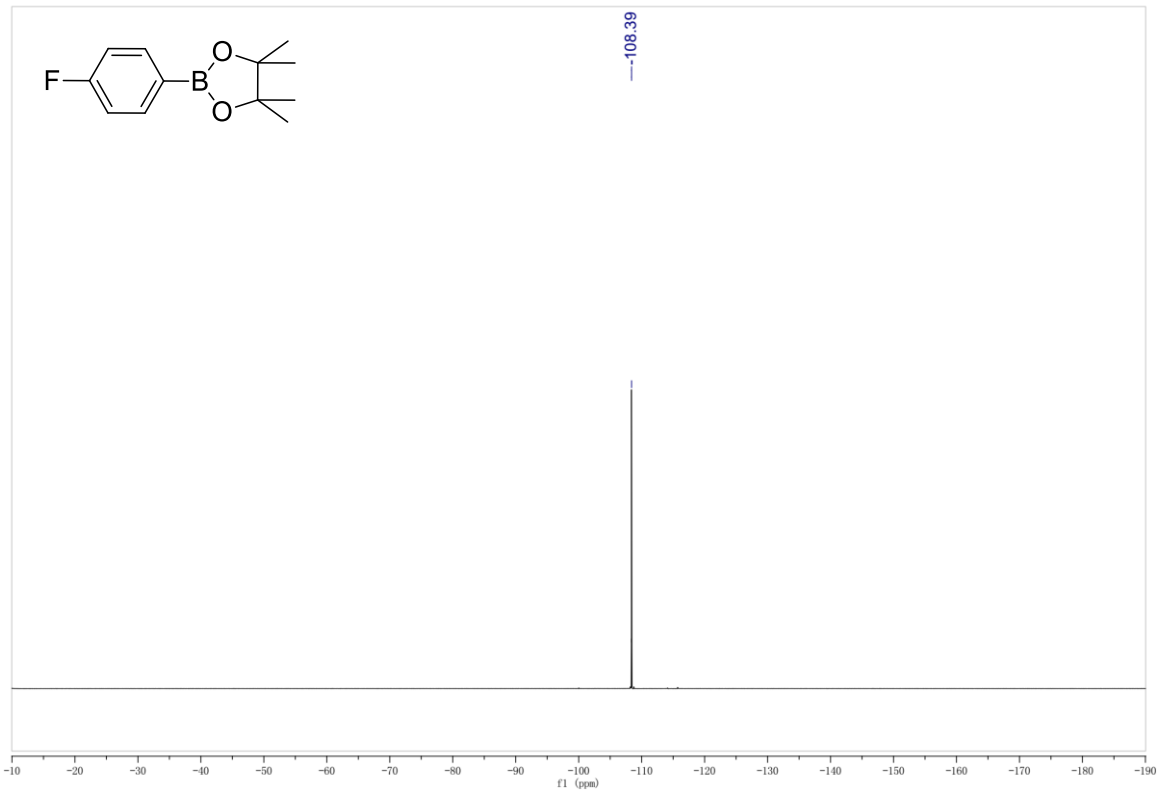
^{1}H NMR spectrum of compound **2d** in $CDCl_3$ (500 MHz).



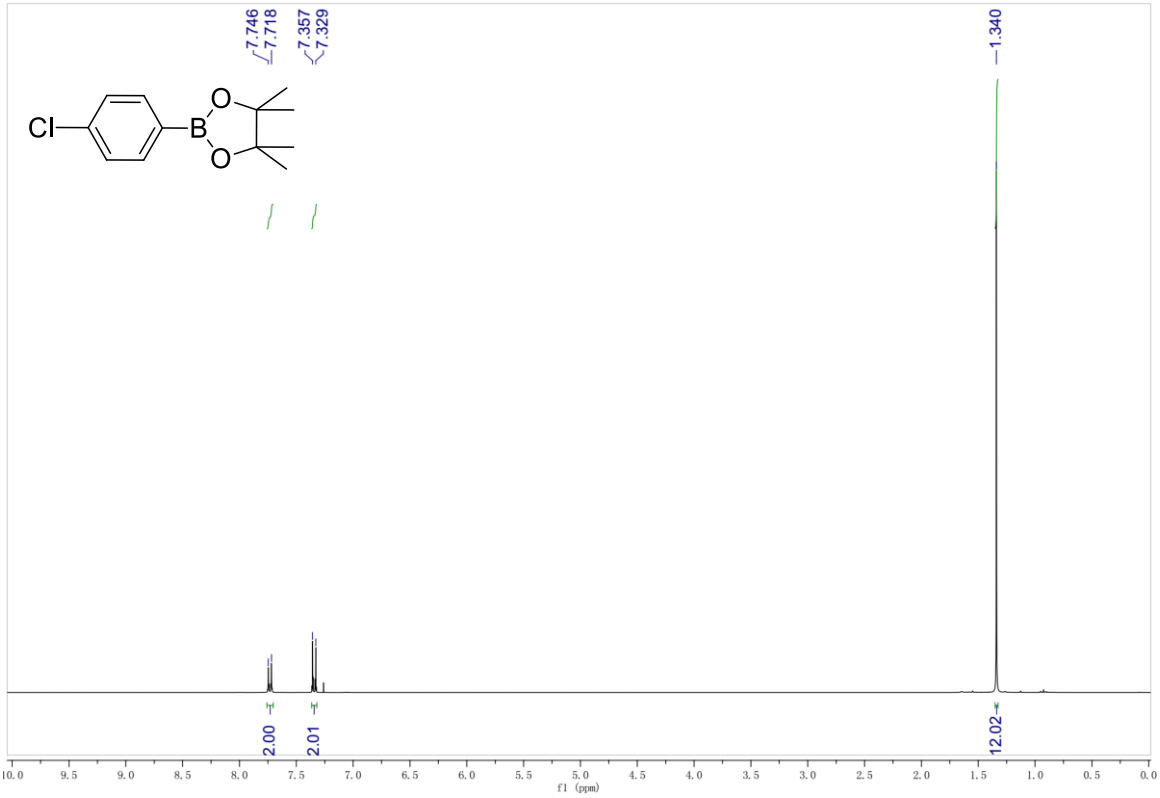
$^{13}C\{^{1}H\}$ NMR spectrum of compound **2d** in $CDCl_3$ (125 MHz).



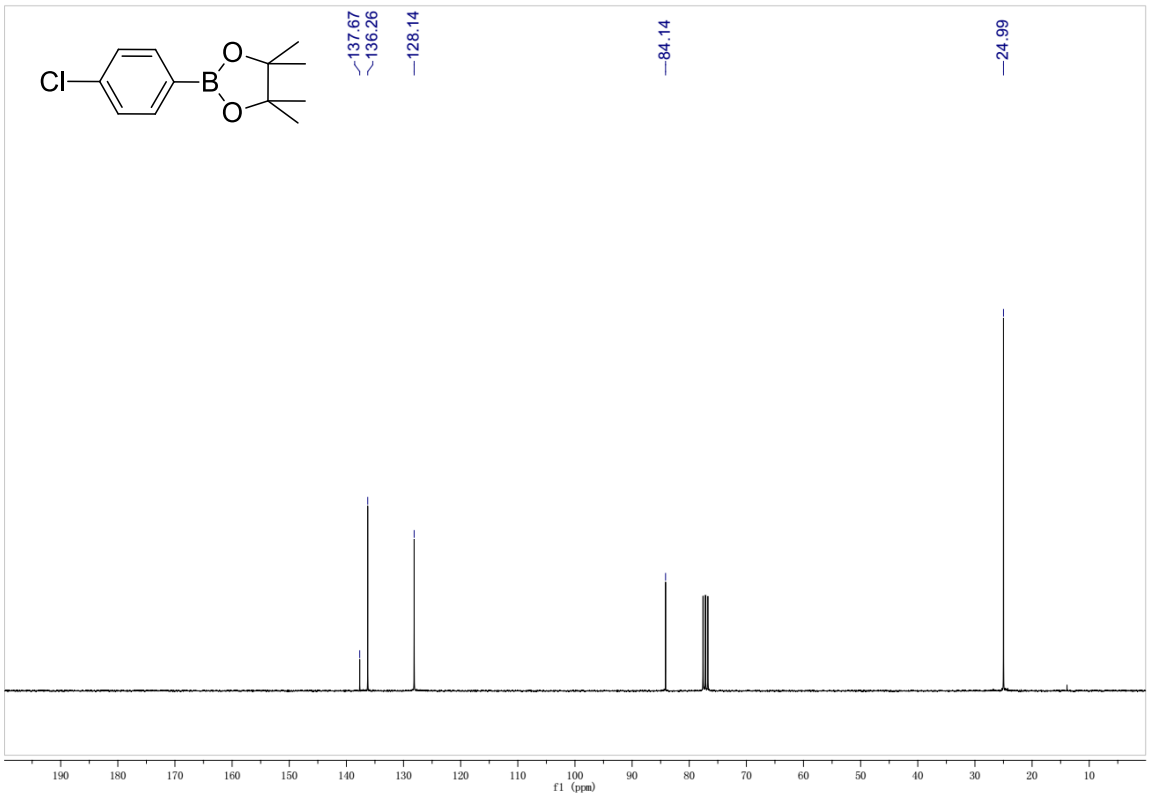
$^{11}B\{^{1}H\}$ NMR spectrum of compound **2d** in $CDCl_3$ (160 MHz).



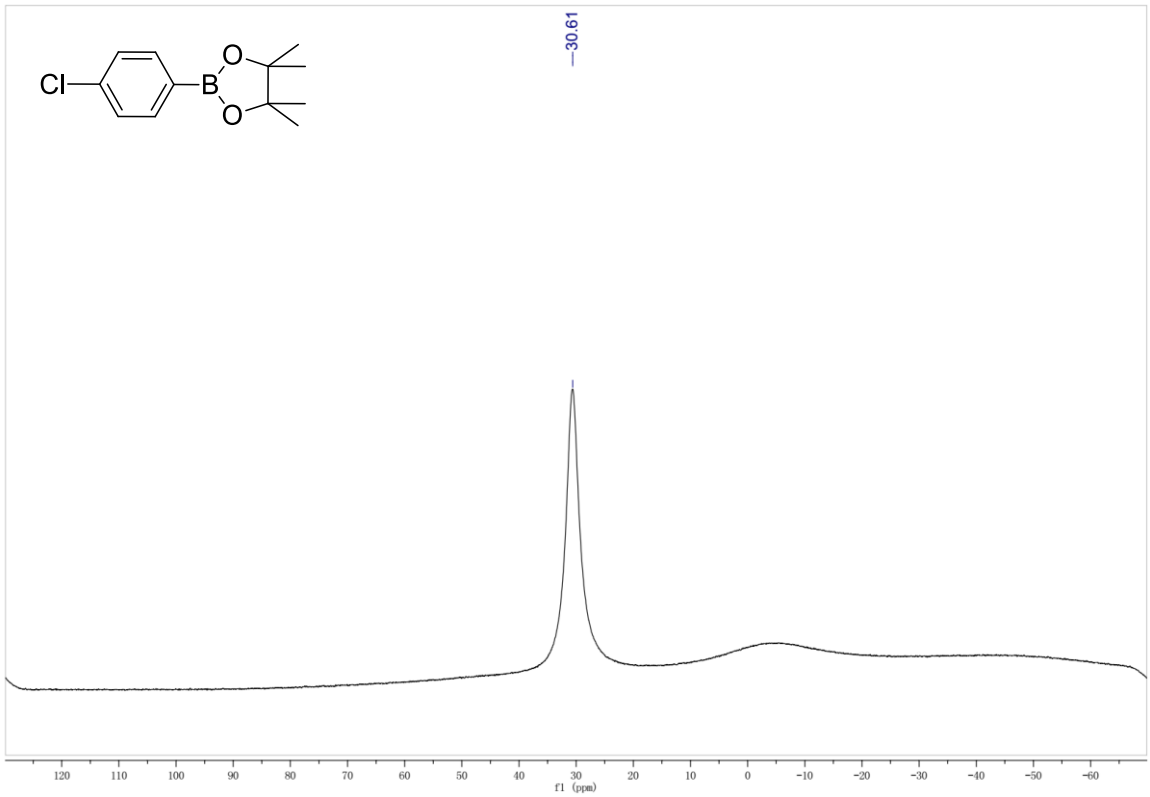
$^{19}F\{^{1}H\}$ NMR spectrum of compound **2d** in $CDCl_3$ (470 MHz).



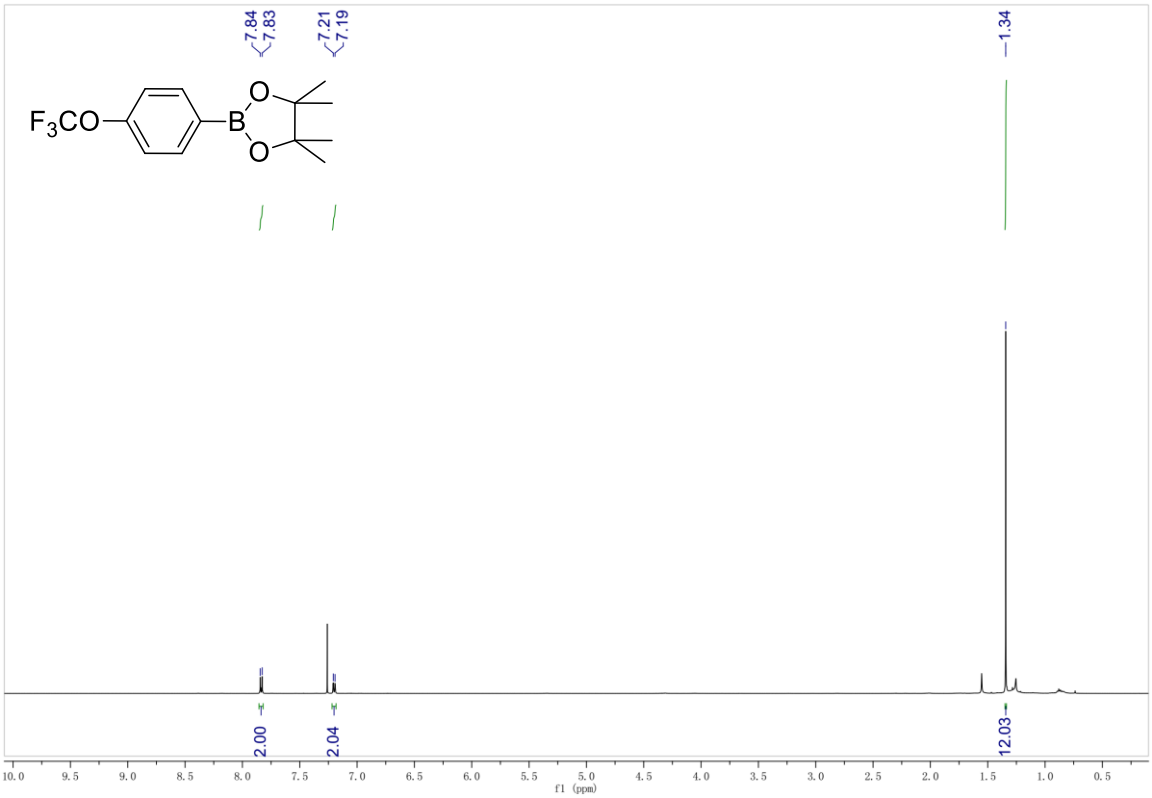
^{1}H NMR spectrum of compound **3d** in $CDCl_3$ (300 MHz).



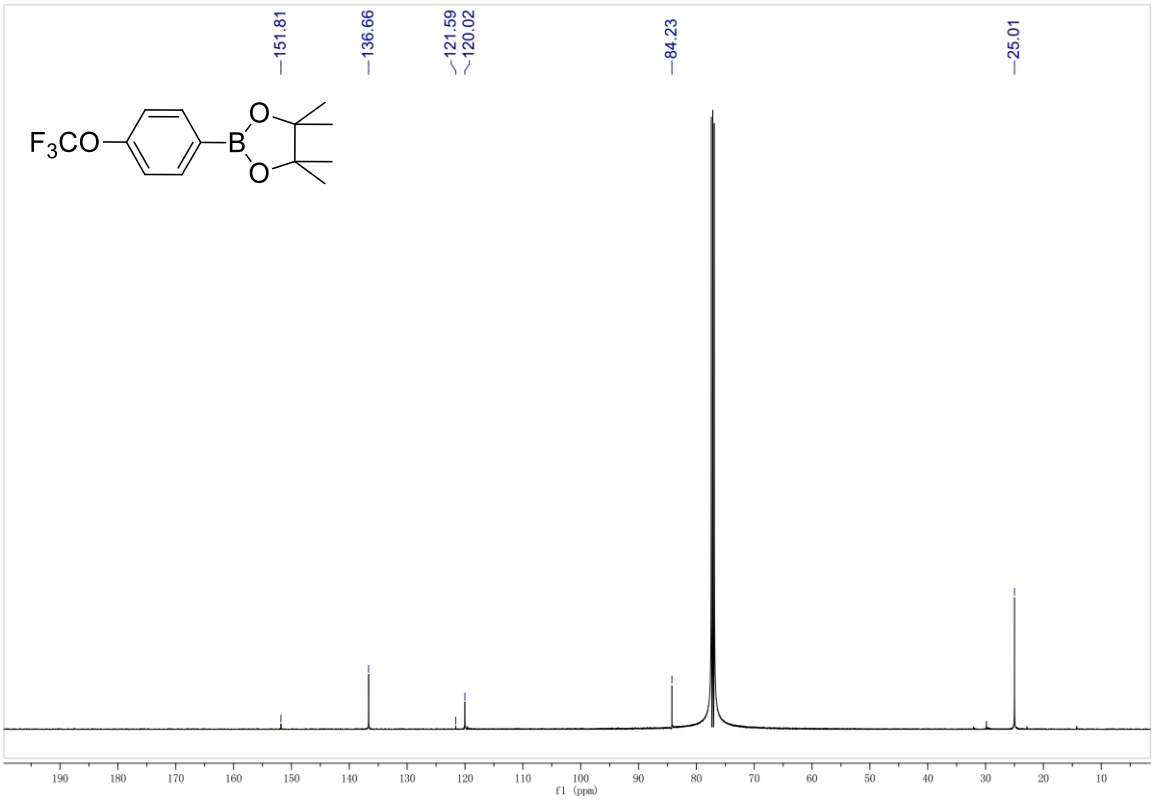
$^{13}C\{^{1}H\}$ NMR spectrum of compound **3d** in $CDCl_3$ (75 MHz).



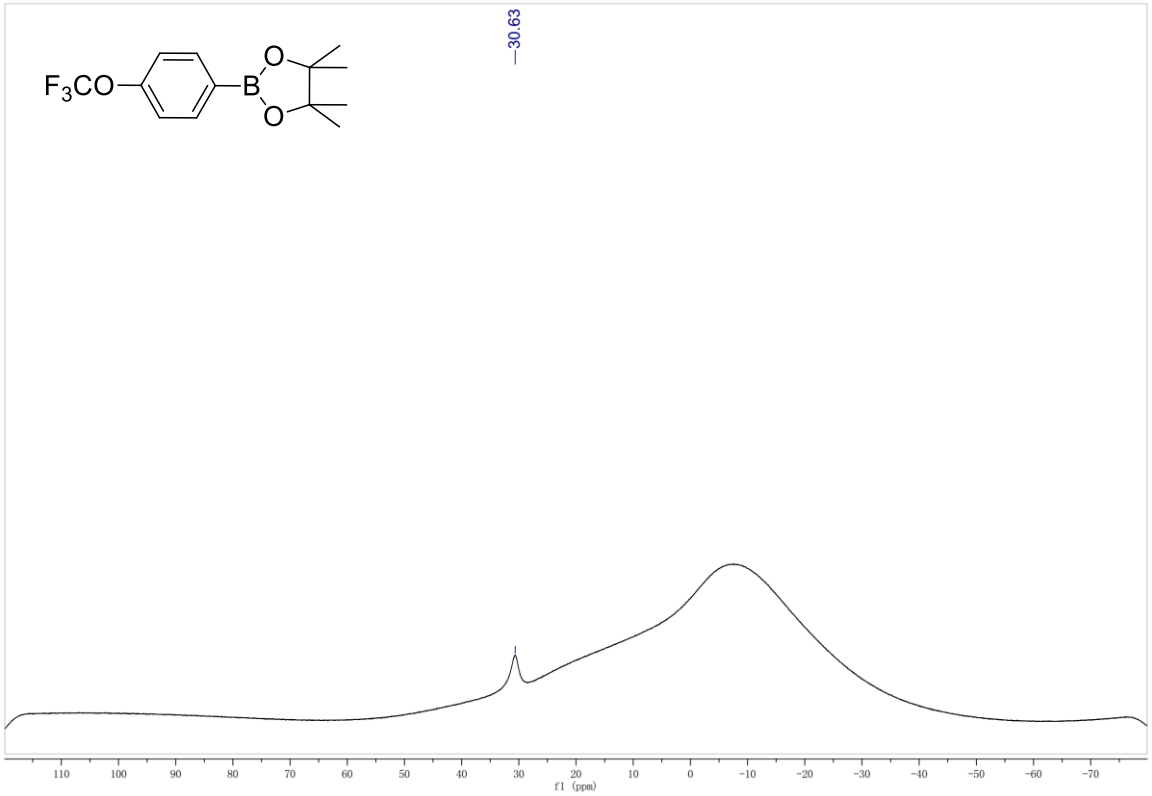
$^{11}B\{^{1}H\}$ NMR spectrum of compound **3d** in $CDCl_3$ (96 MHz).



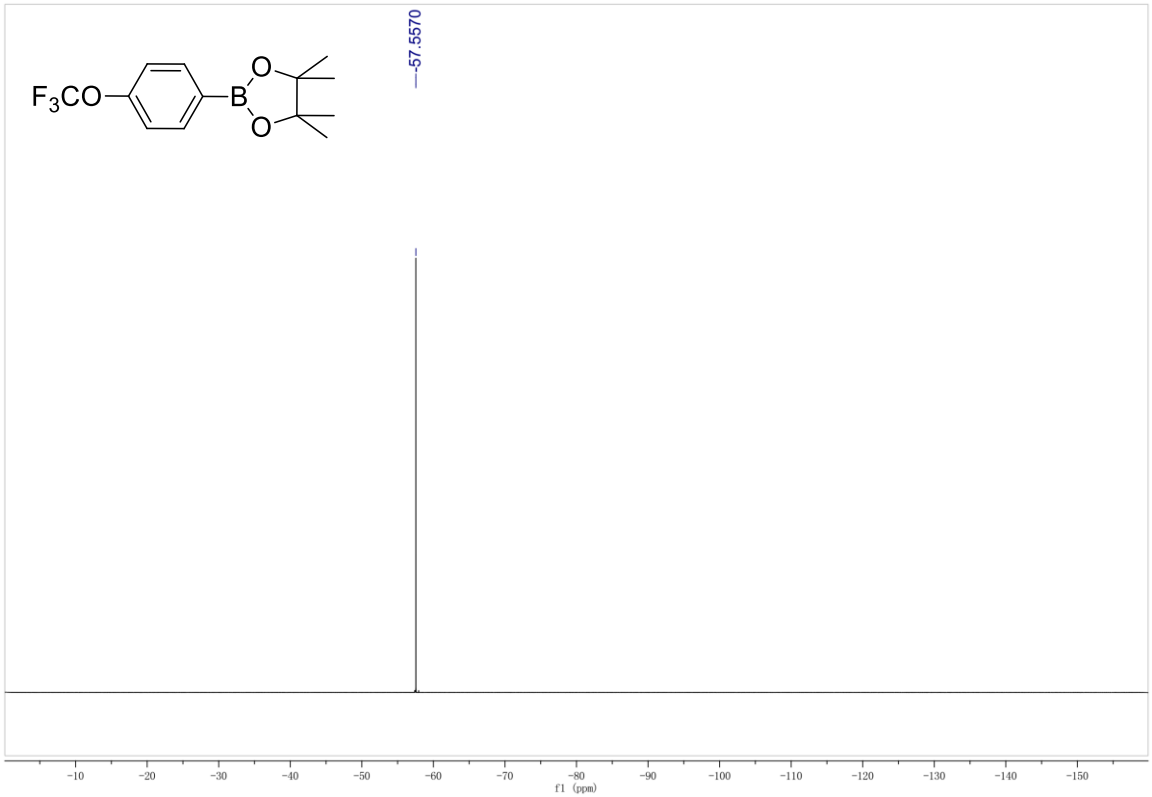
^{1}H NMR spectrum of compound **4d** in $CDCl_3$ (500 MHz).



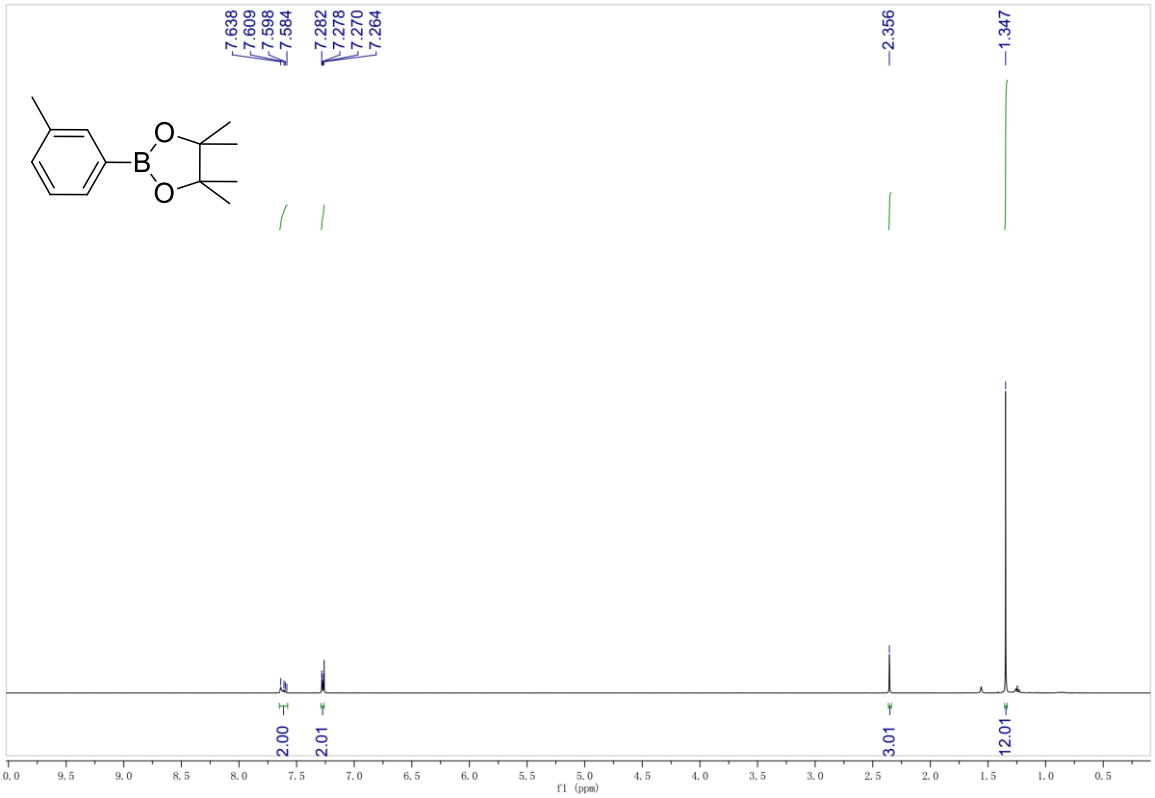
$^{13}C\{^{1}H\}$ NMR spectrum of compound **4d** in $CDCl_3$ (125 MHz).



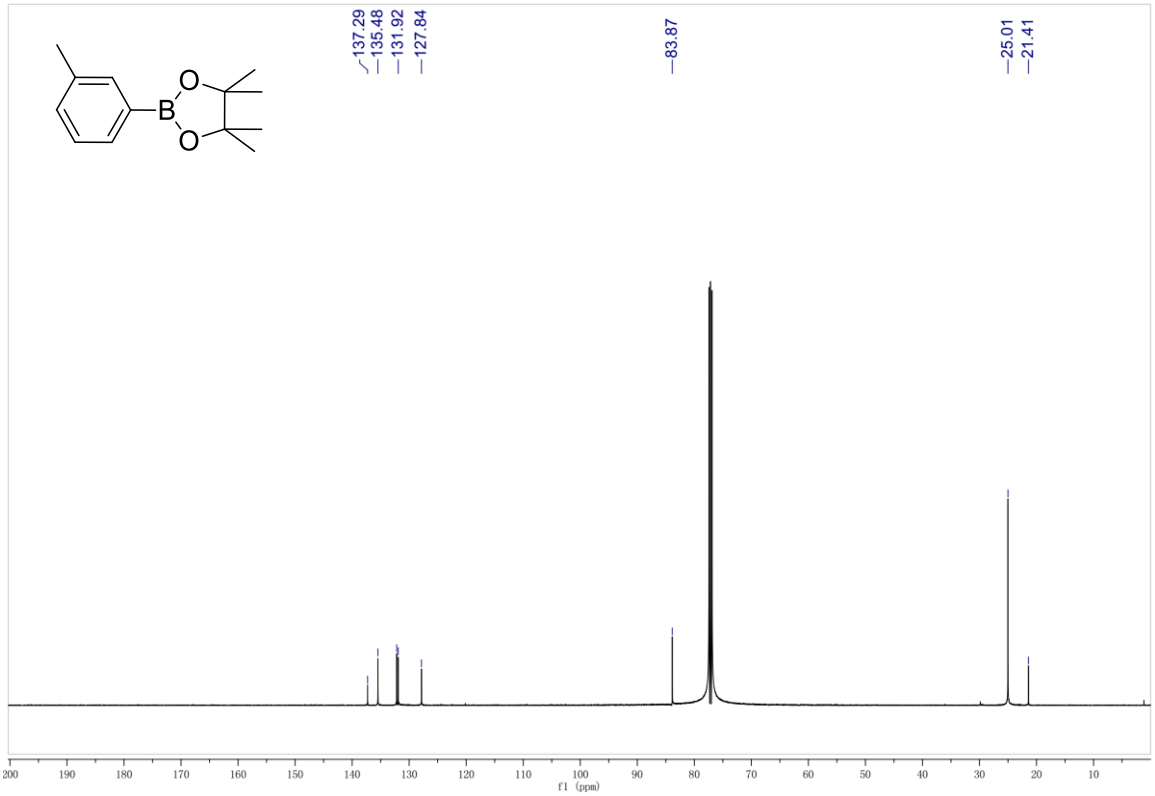
$^{11}B\{^{1}H\}$ NMR spectrum of compound **4d** in $CDCl_3$ (160 MHz).



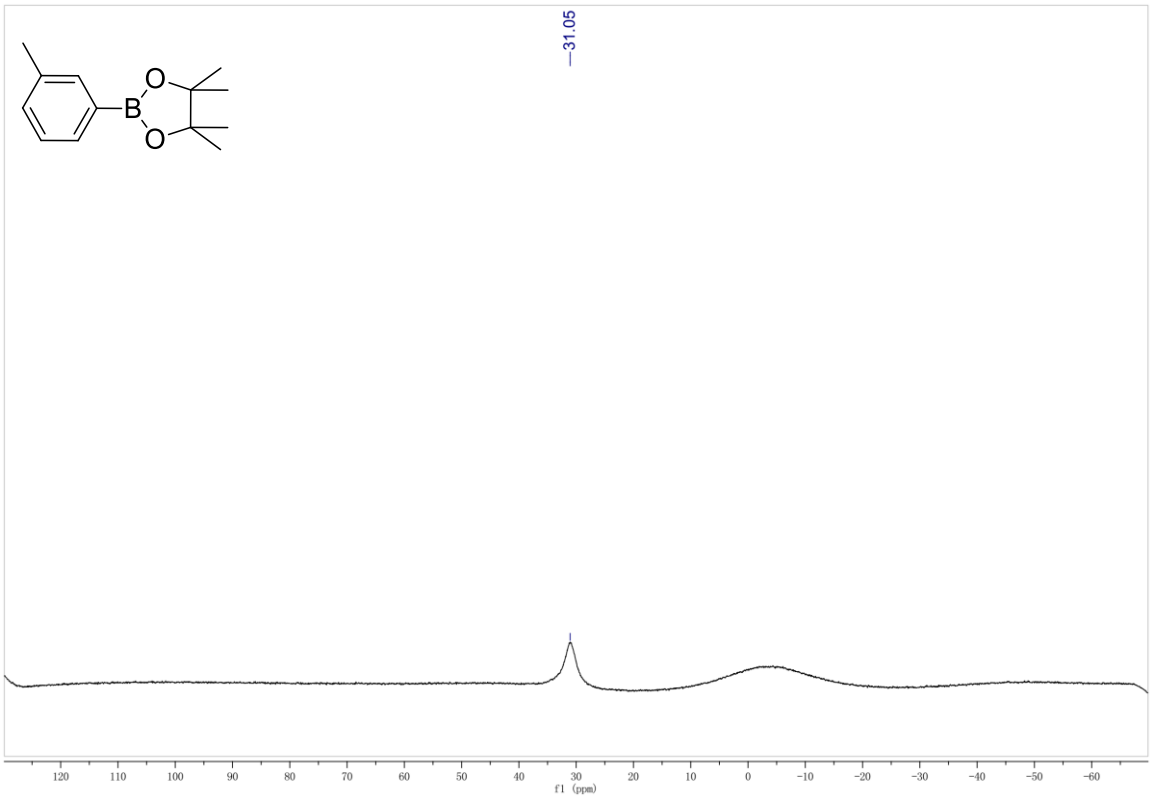
$^{19}F\{^{1}H\}$ NMR spectrum of compound **4d** in $CDCl_3$ (470 MHz).



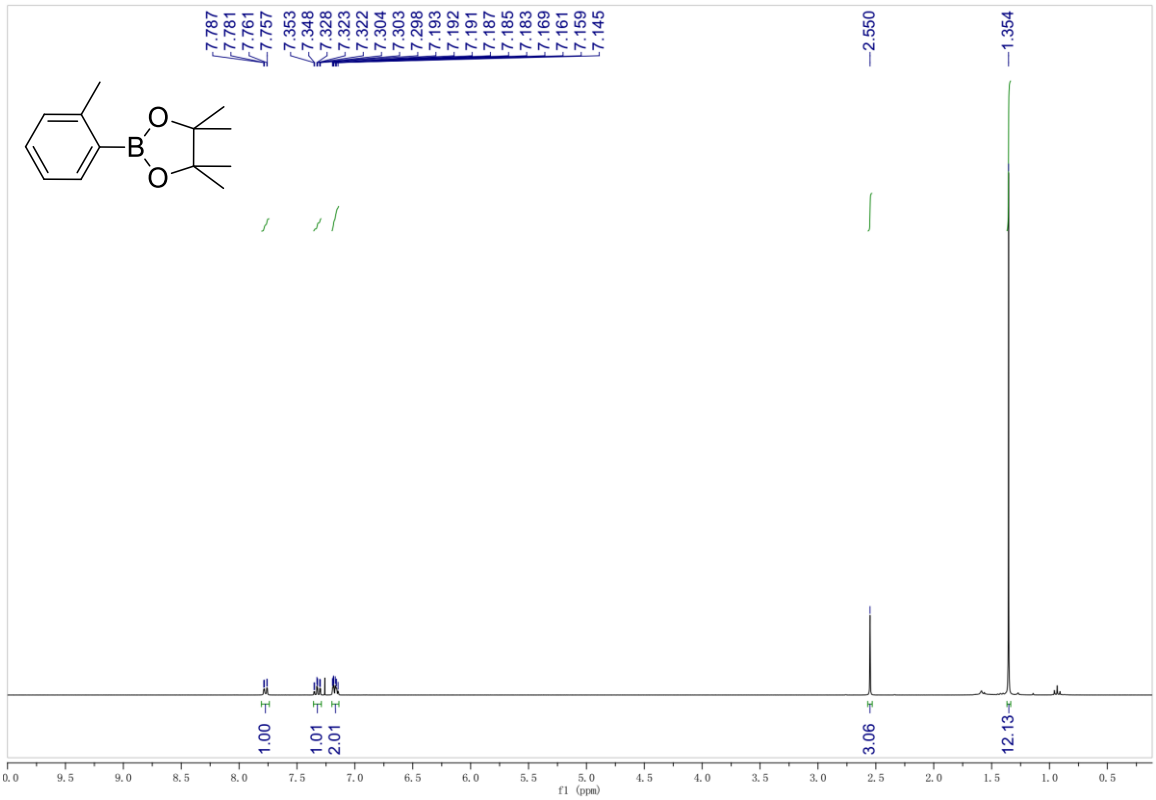
^{1}H NMR spectrum of compound **5d** in $CDCl_3$ (300 MHz).



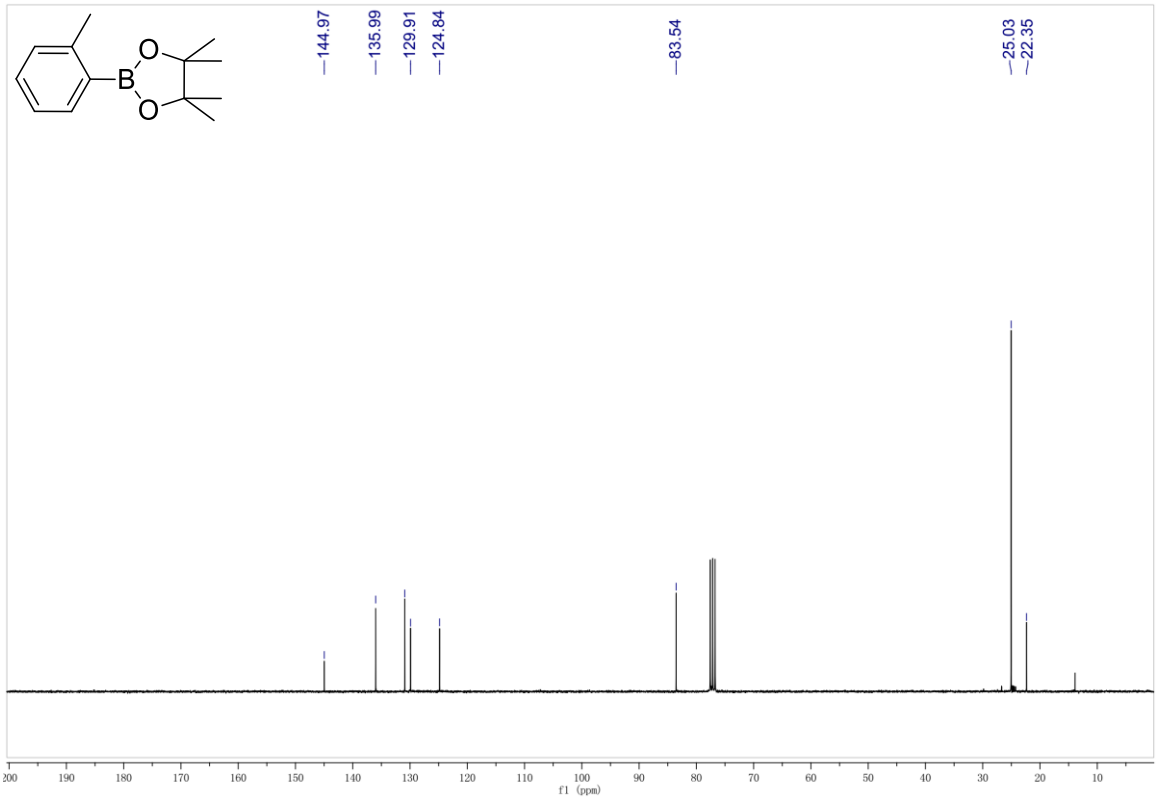
^{13}C{^{1}H} NMR spectrum of compound **5d** in $CDCl_3$ (75 MHz).



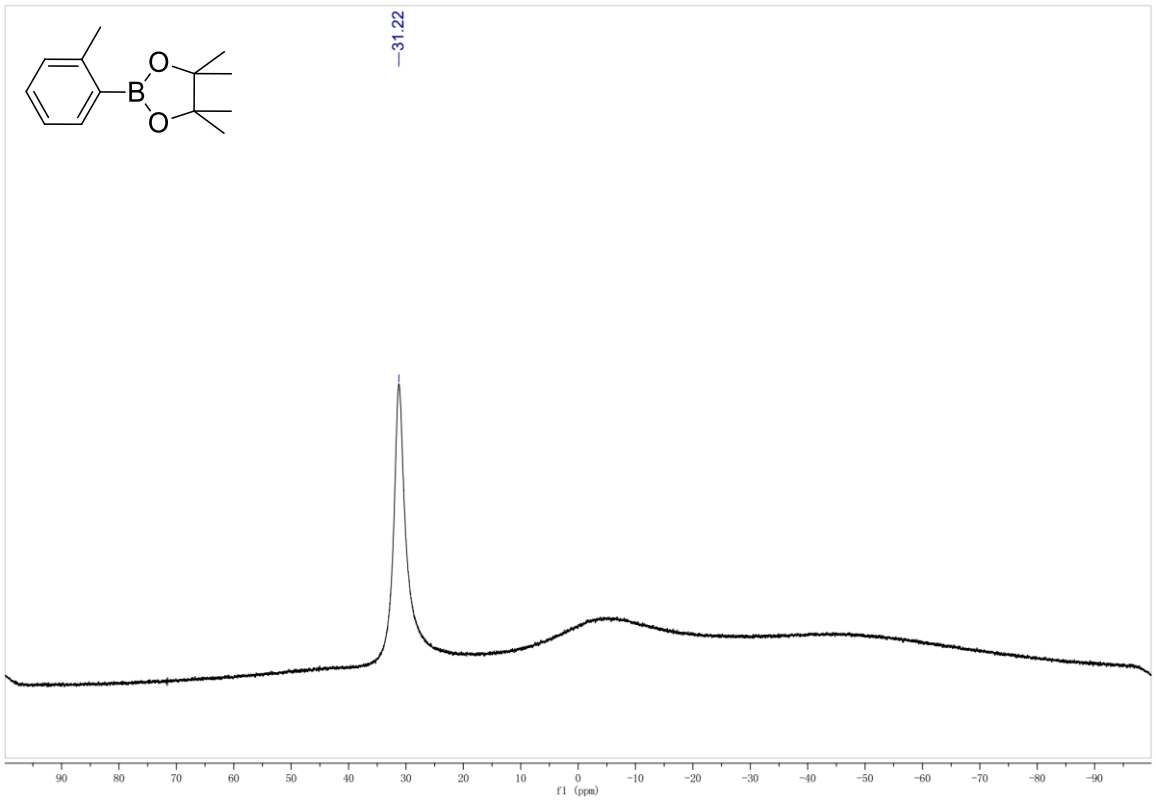
$^{11}B\{^{1}H\}$ NMR spectrum of compound **5d** in $CDCl_3$ (96 MHz).



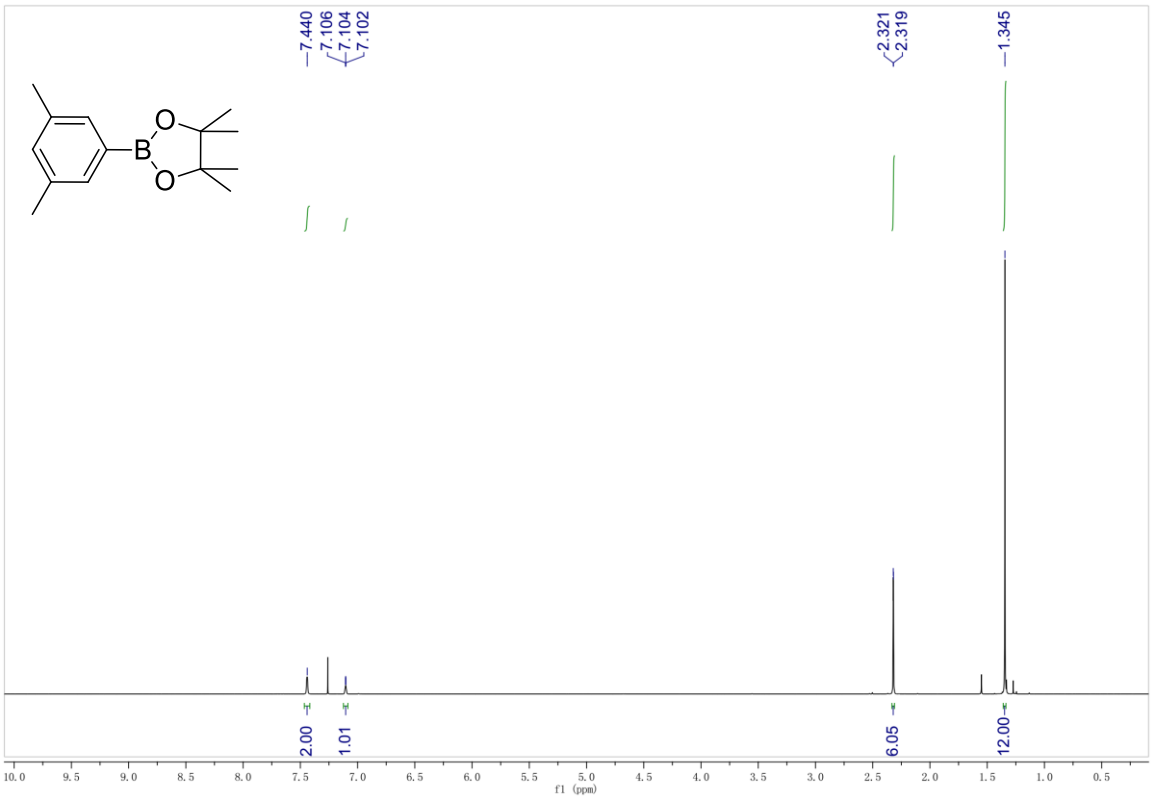
^{1}H NMR spectrum of compound **6d** in $CDCl_3$ (300 MHz).



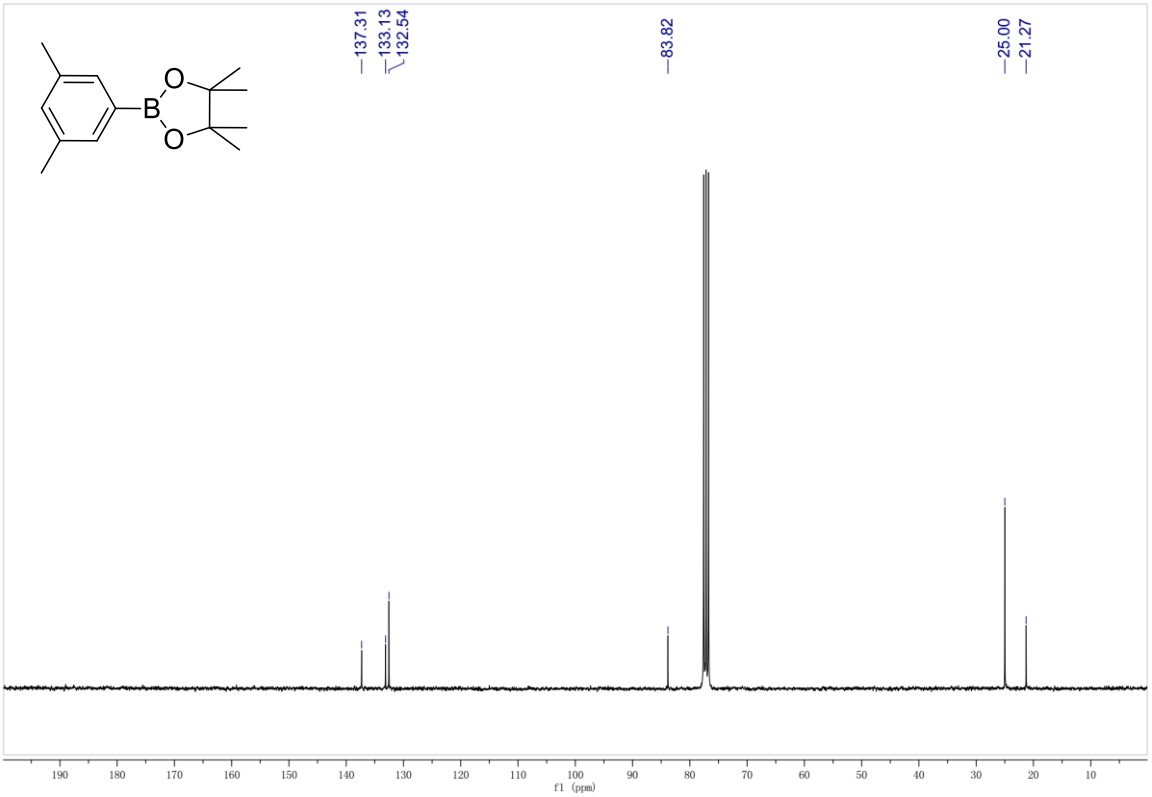
$^{13}C\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$ (75 MHz).



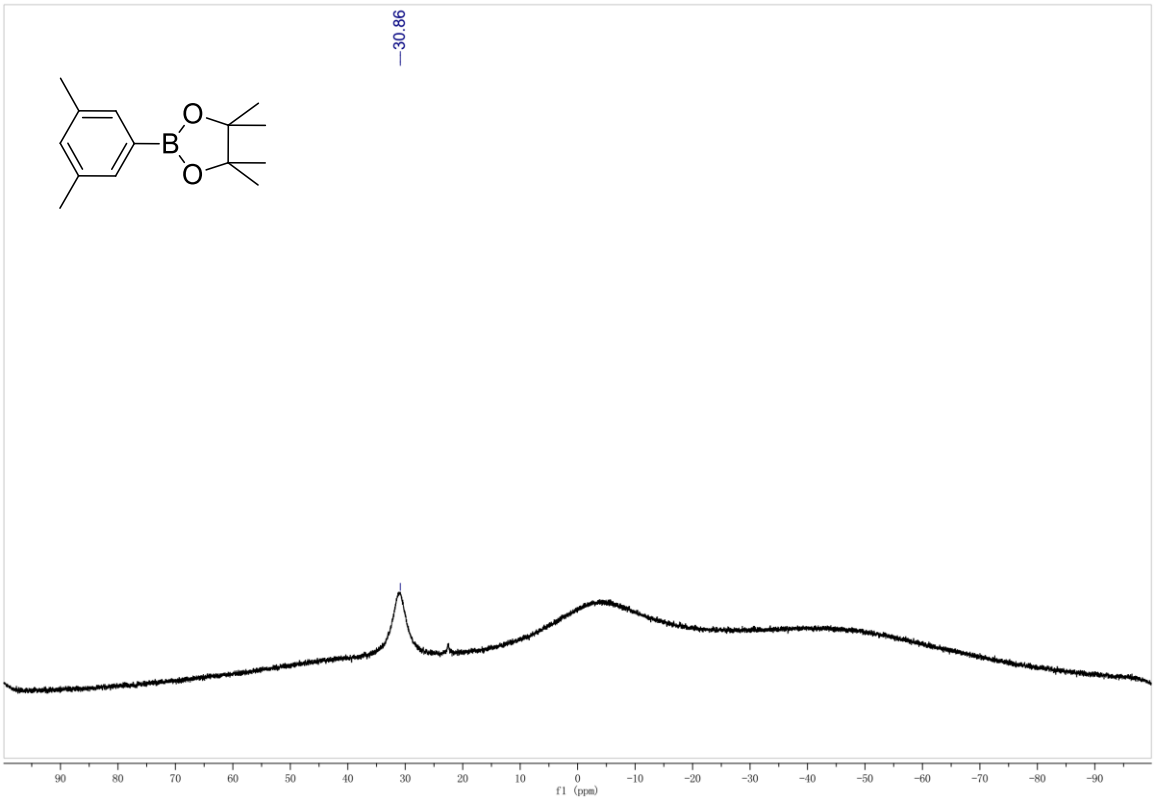
$^{11}B\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$ (96 MHz).



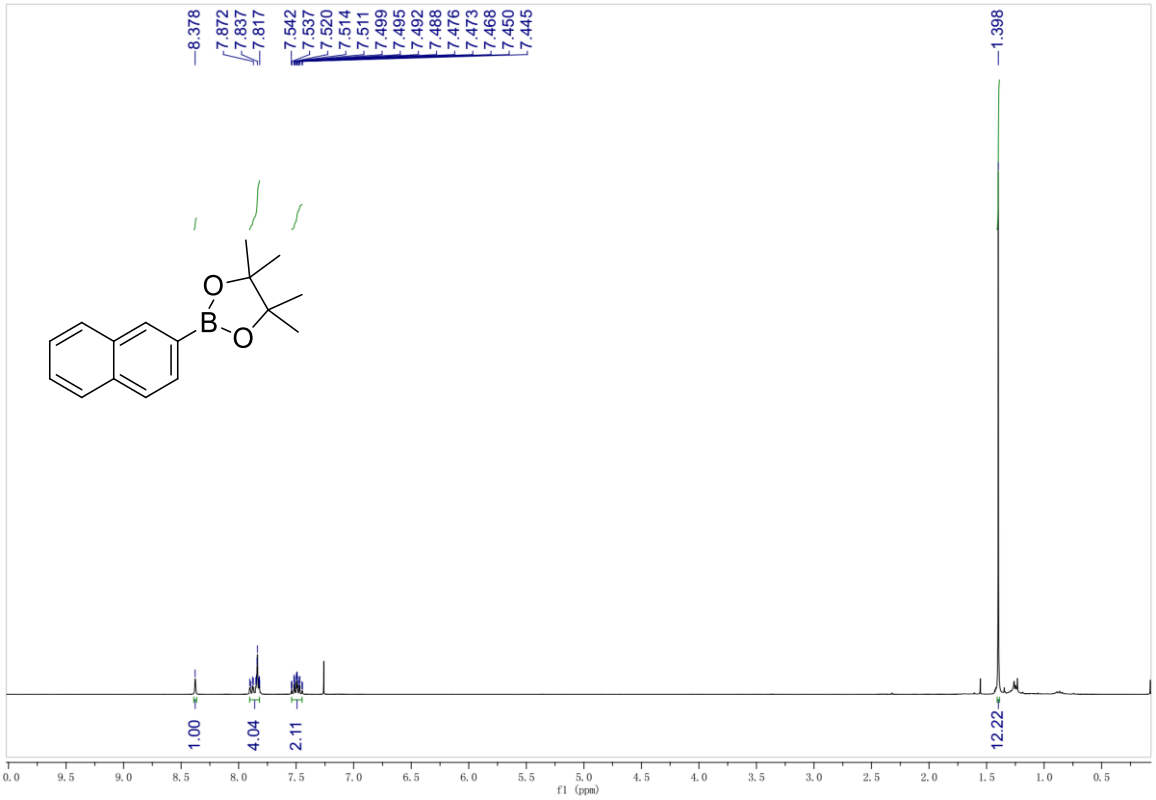
^{1}H NMR spectrum of compound **7d** in $CDCl_3$ (300 MHz).



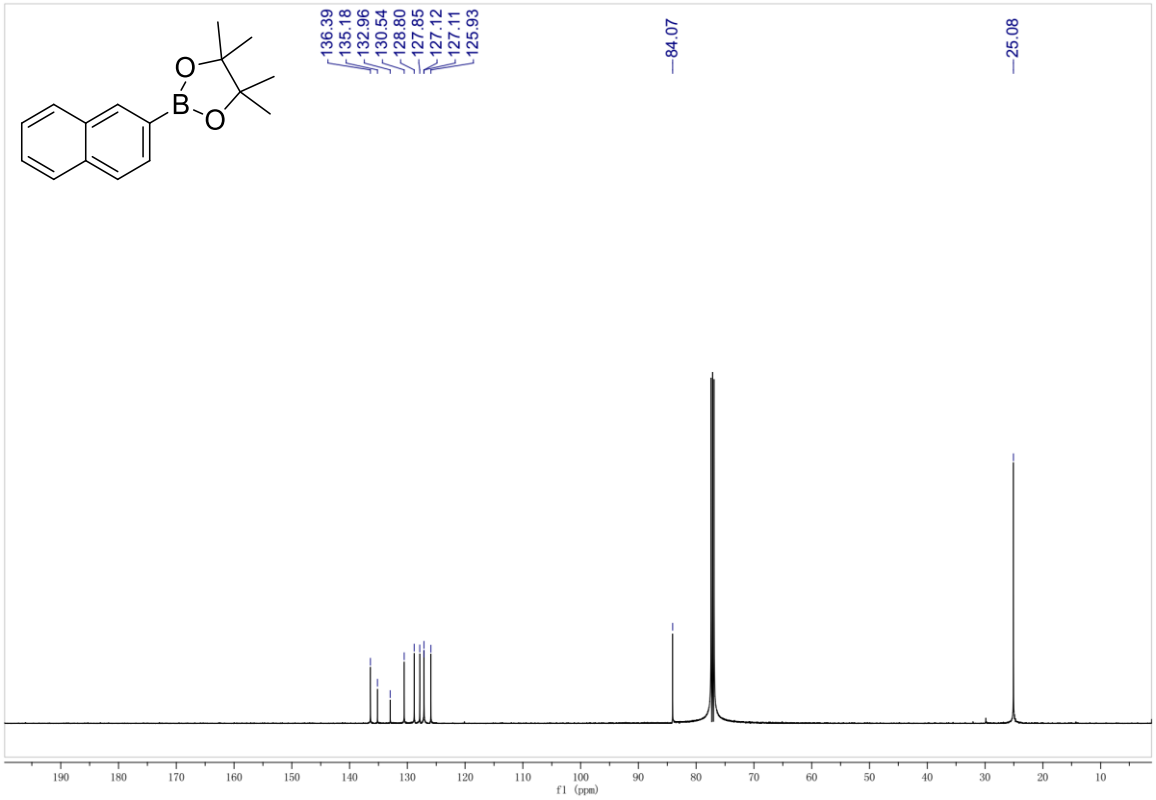
^{13}C{^{1}H} NMR spectrum of compound **7d** in $CDCl_3$ (75 MHz).



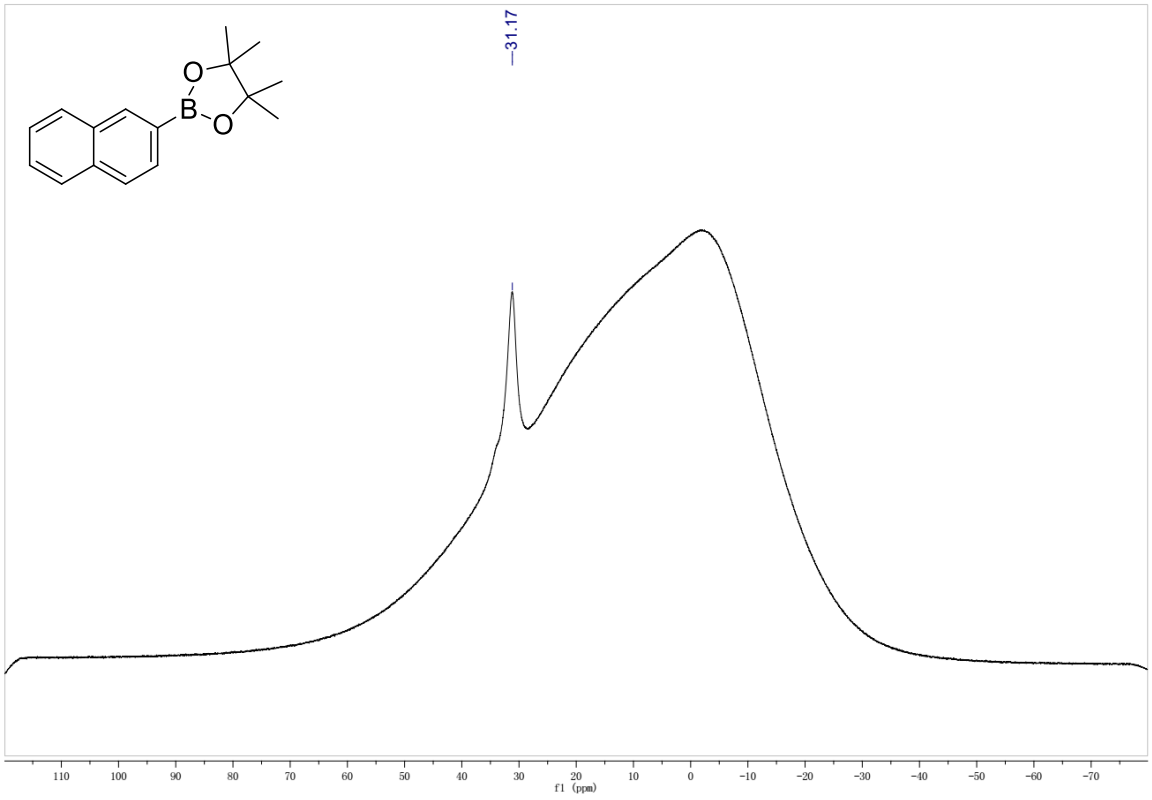
$^{11}B\{^{1}H\}$ NMR spectrum of compound **7d** in $CDCl_3$ (96 MHz).



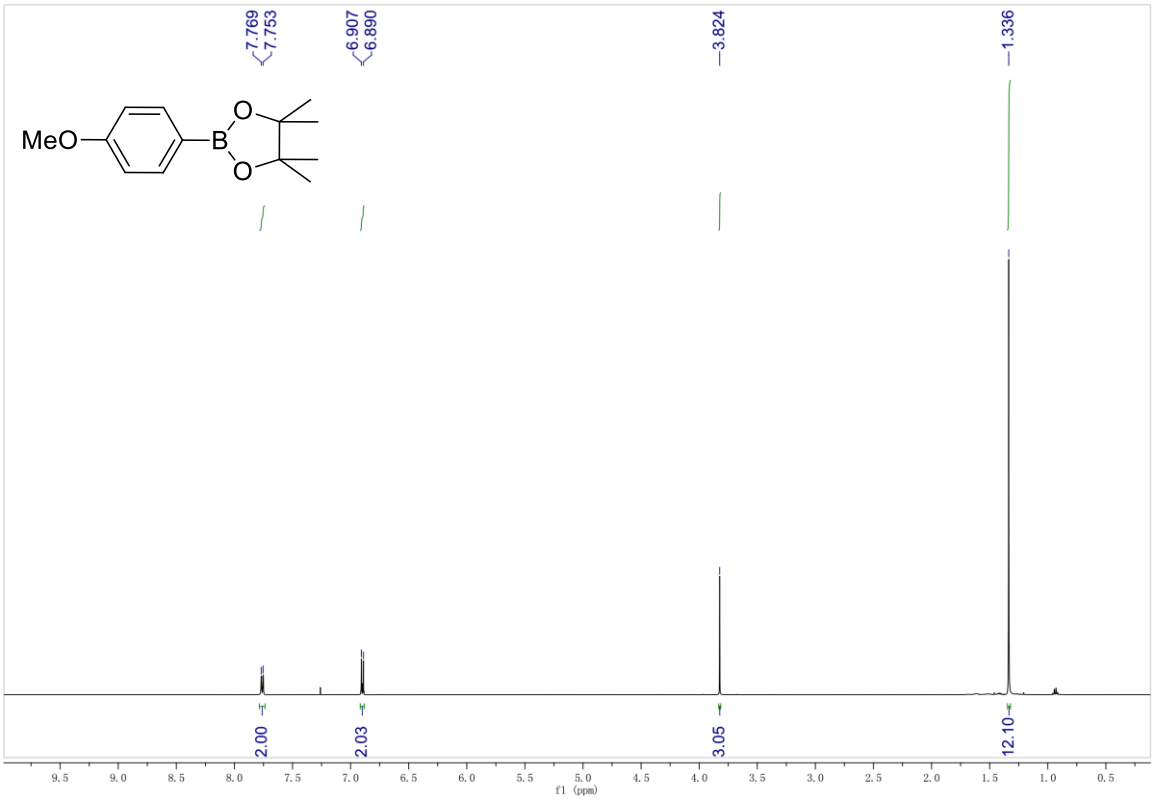
^{1}H NMR spectrum of compound **8d** in $CDCl_3$ (500 MHz).



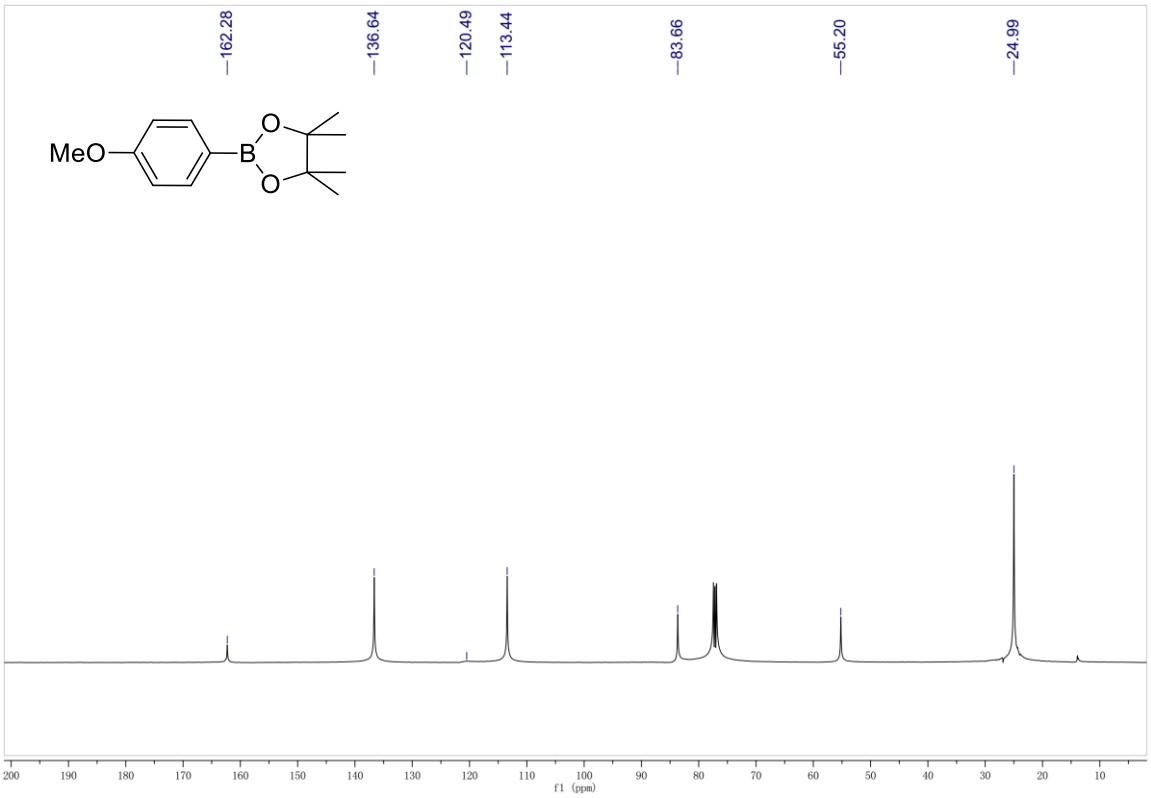
$^{13}C\{^{1}H\}$ NMR spectrum of compound **8d** in $CDCl_3$ (125 MHz).



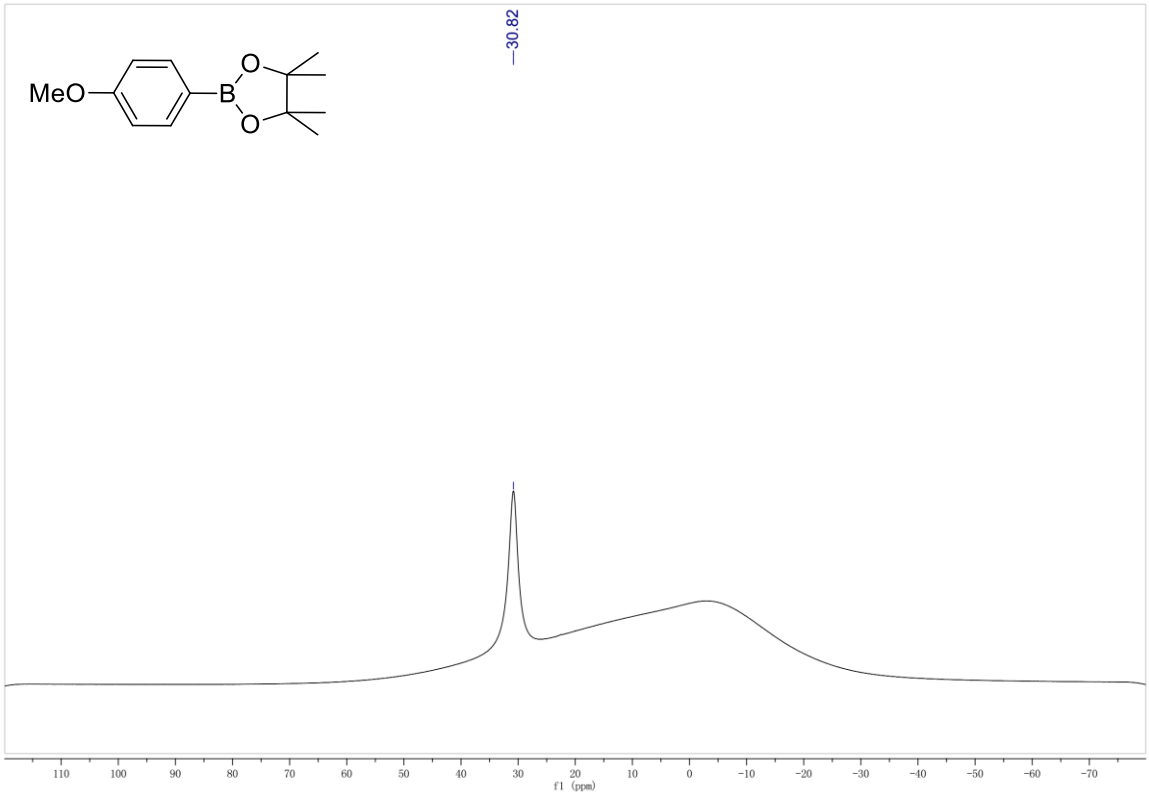
$^{11}B\{^{1}H\}$ NMR spectrum of compound **8d** in $CDCl_3$ (160 MHz).



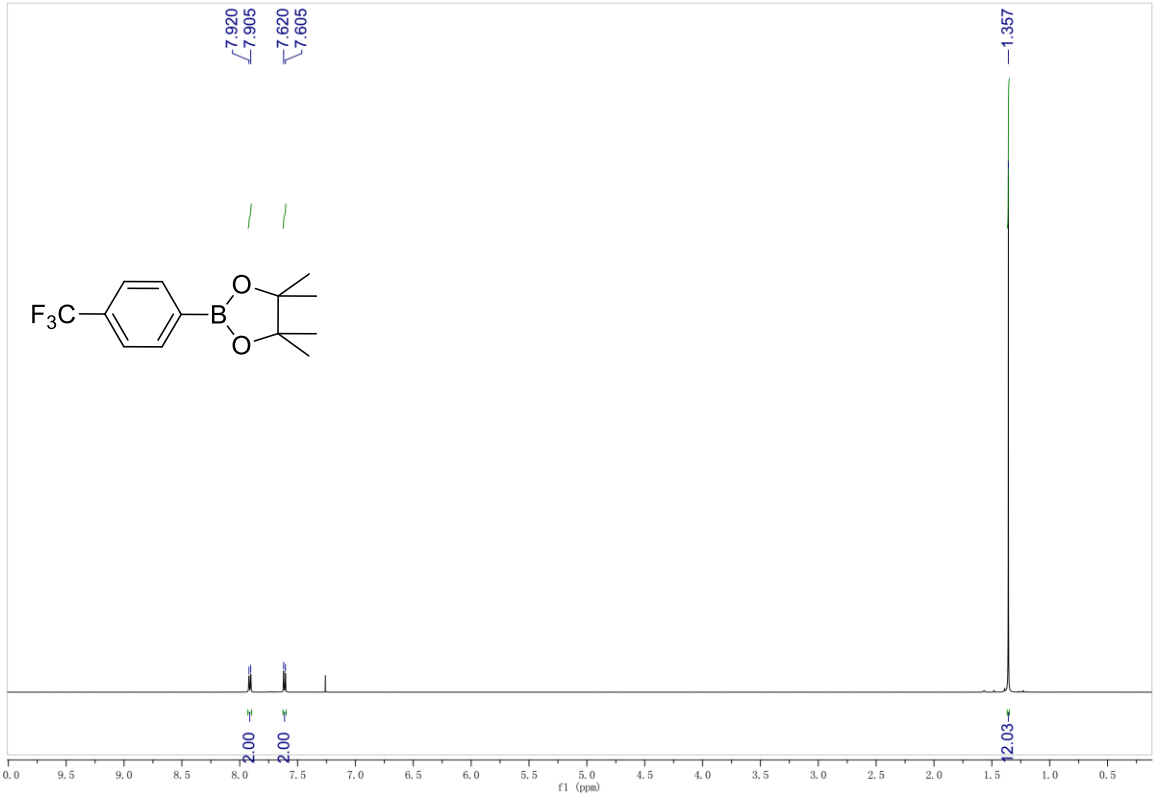
^{1}H NMR spectrum of compound **9d** in $CDCl_3$ (500 MHz).



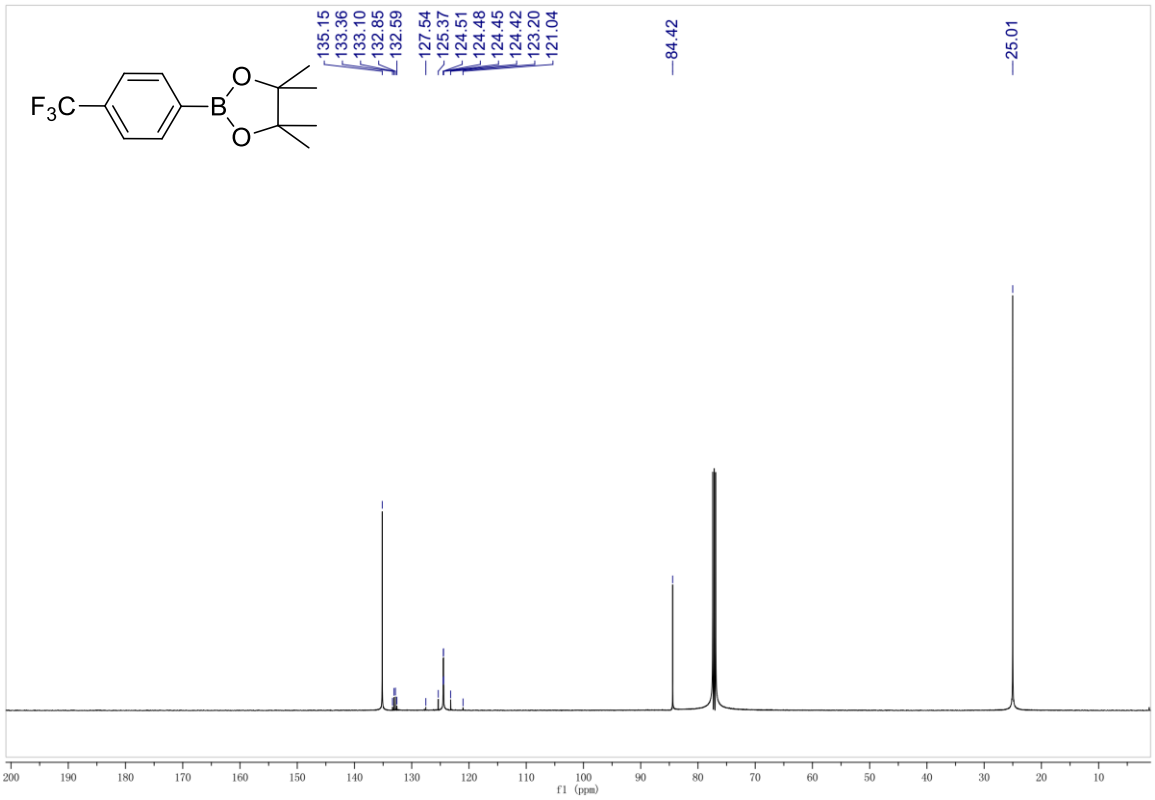
^{13}C{^{1}H} NMR spectrum of compound **9d** in $CDCl_3$ (125 MHz).



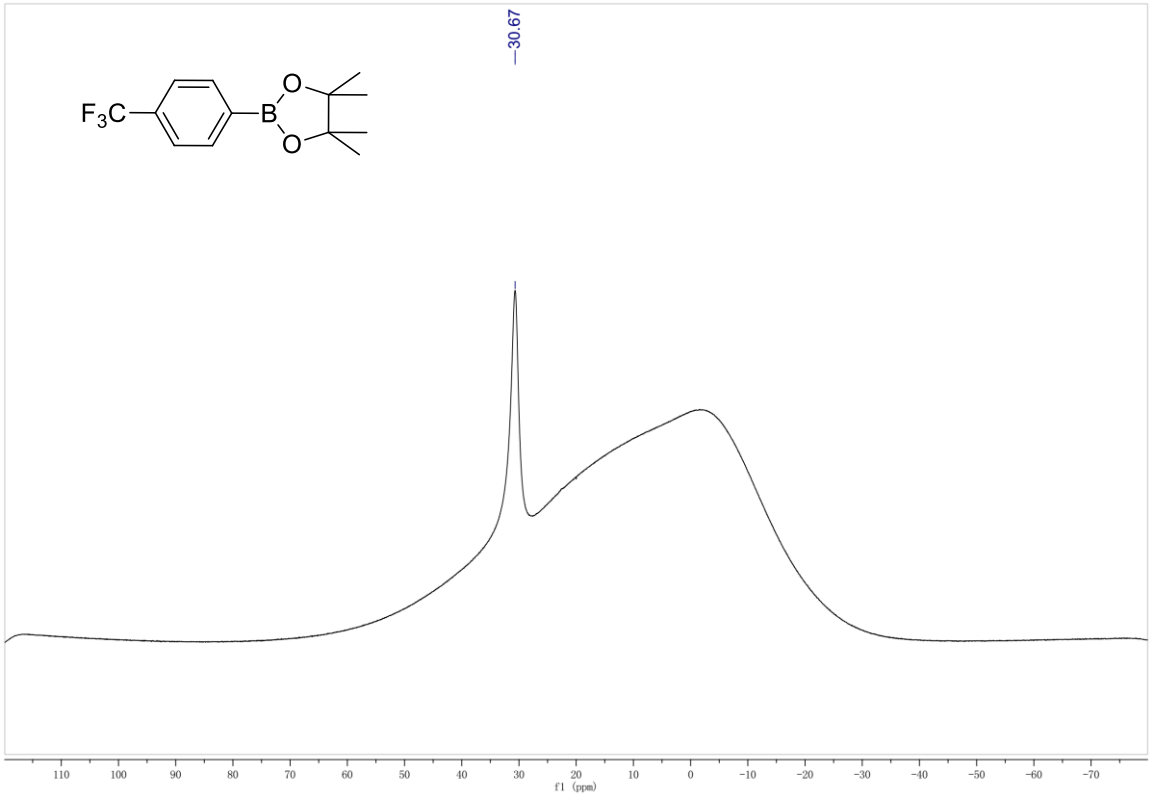
$^{11}B\{^{1}H\}$ NMR spectrum of compound **9d** in $CDCl_3$ (160 MHz).



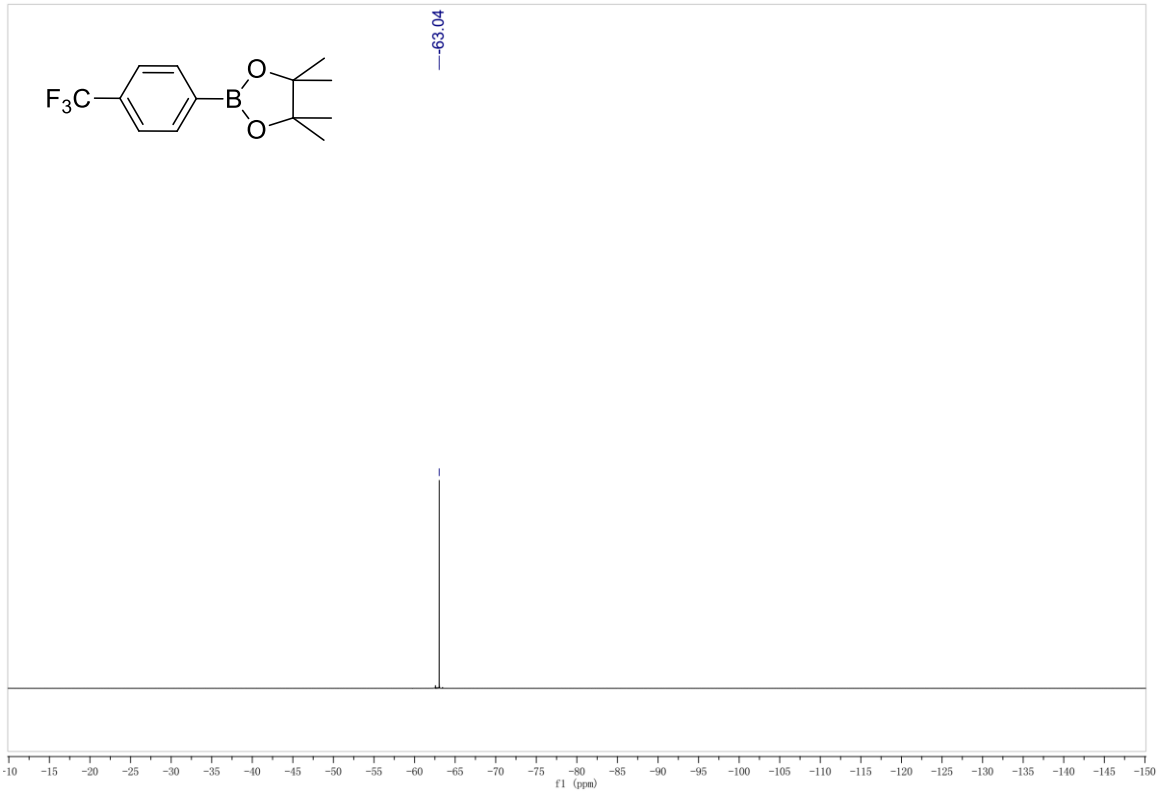
^{1}H NMR spectrum of compound **10d** in $CDCl_3$ (500 MHz).



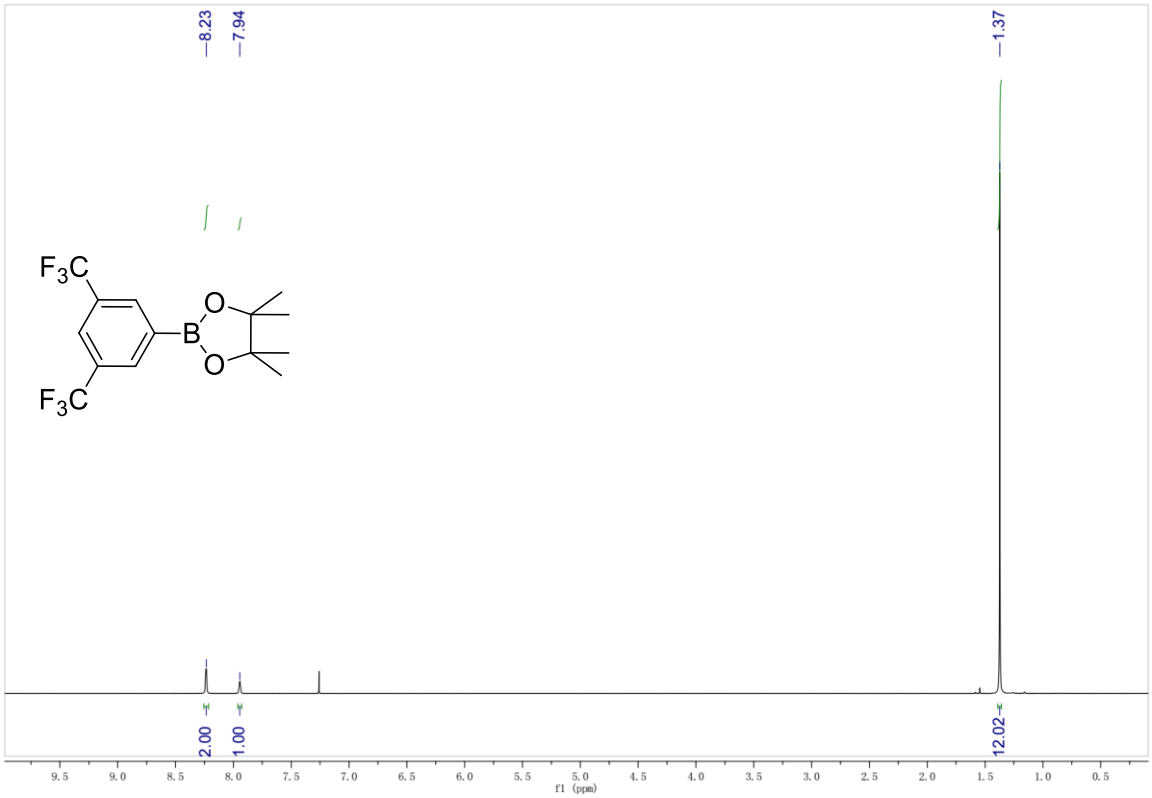
$^{13}C\{^{1}H\}$ NMR spectrum of compound **10d** in $CDCl_3$ (125 MHz).



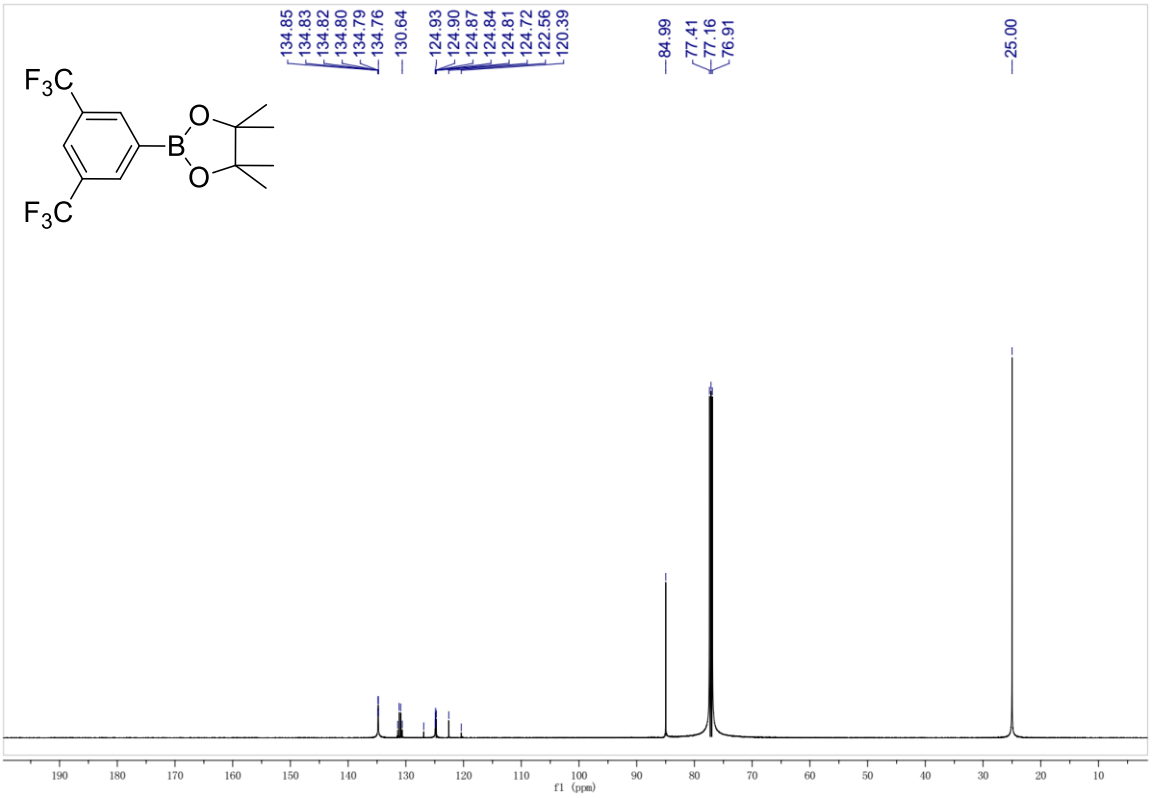
$^{11}B\{^{1}H\}$ NMR spectrum of compound **10d** in $CDCl_3$ (160 MHz).



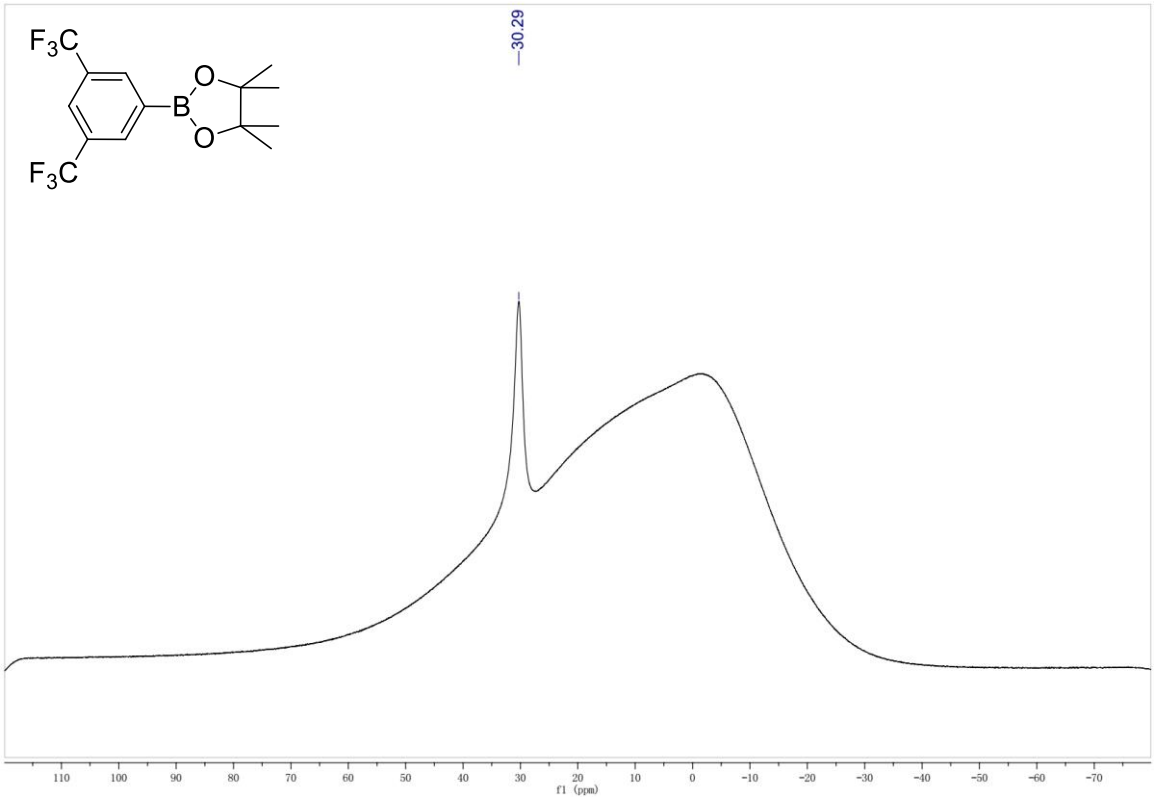
$^{19}F\{^{1}H\}$ NMR spectrum of compound **10d** in $CDCl_3$ (470 MHz).



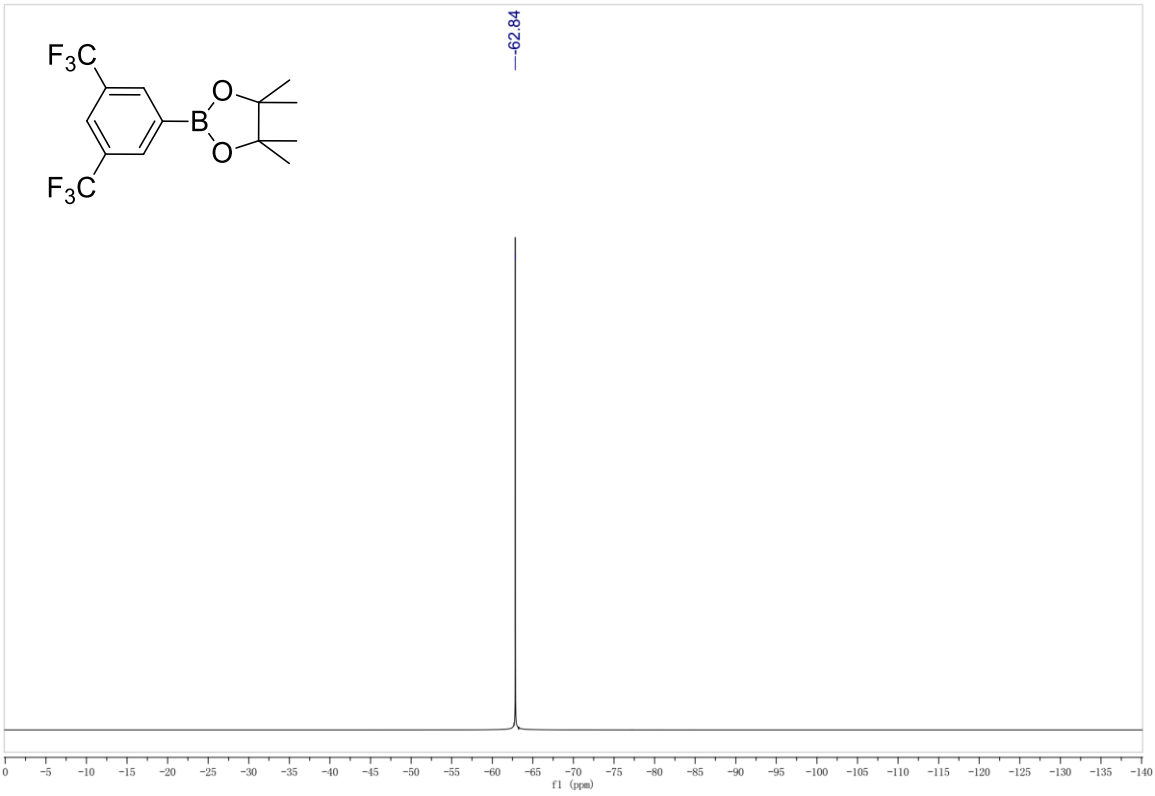
^{1}H NMR spectrum of compound **11d** in $CDCl_3$ (500 MHz).



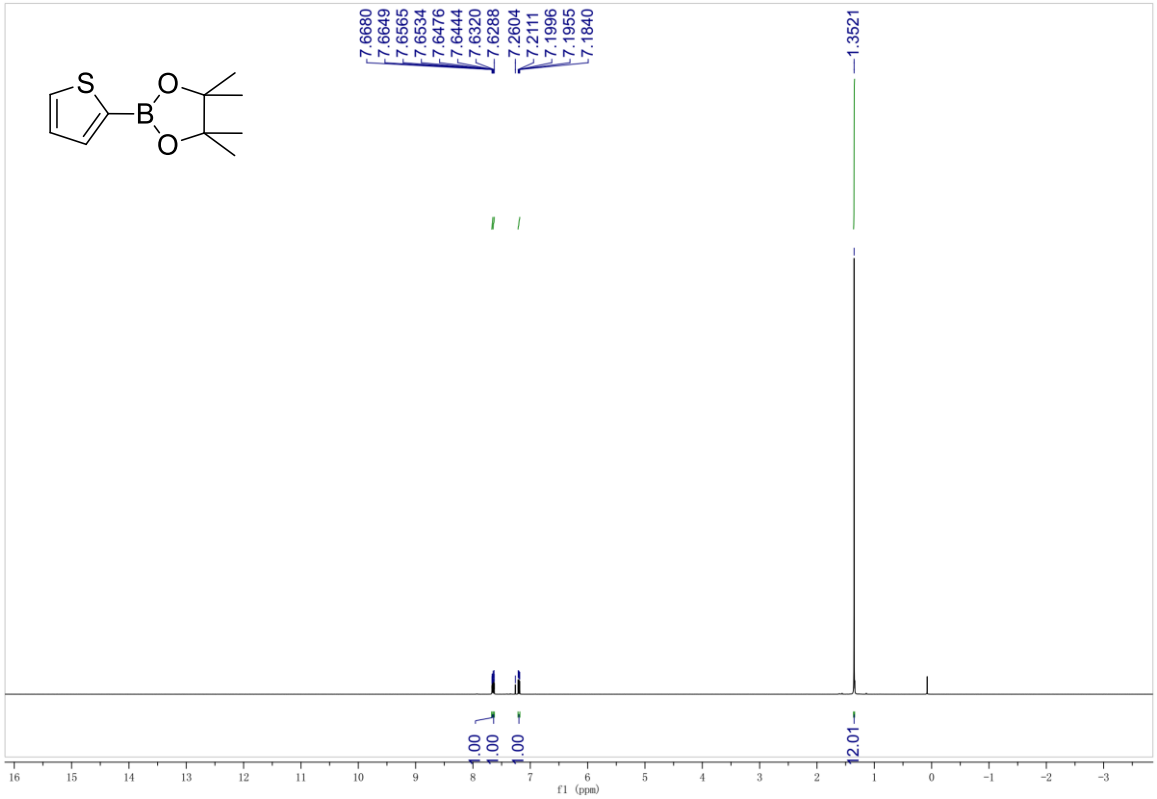
$^{13}C\{^{1}H\}$ NMR spectrum of compound **11d** in $CDCl_3$ (125 MHz).



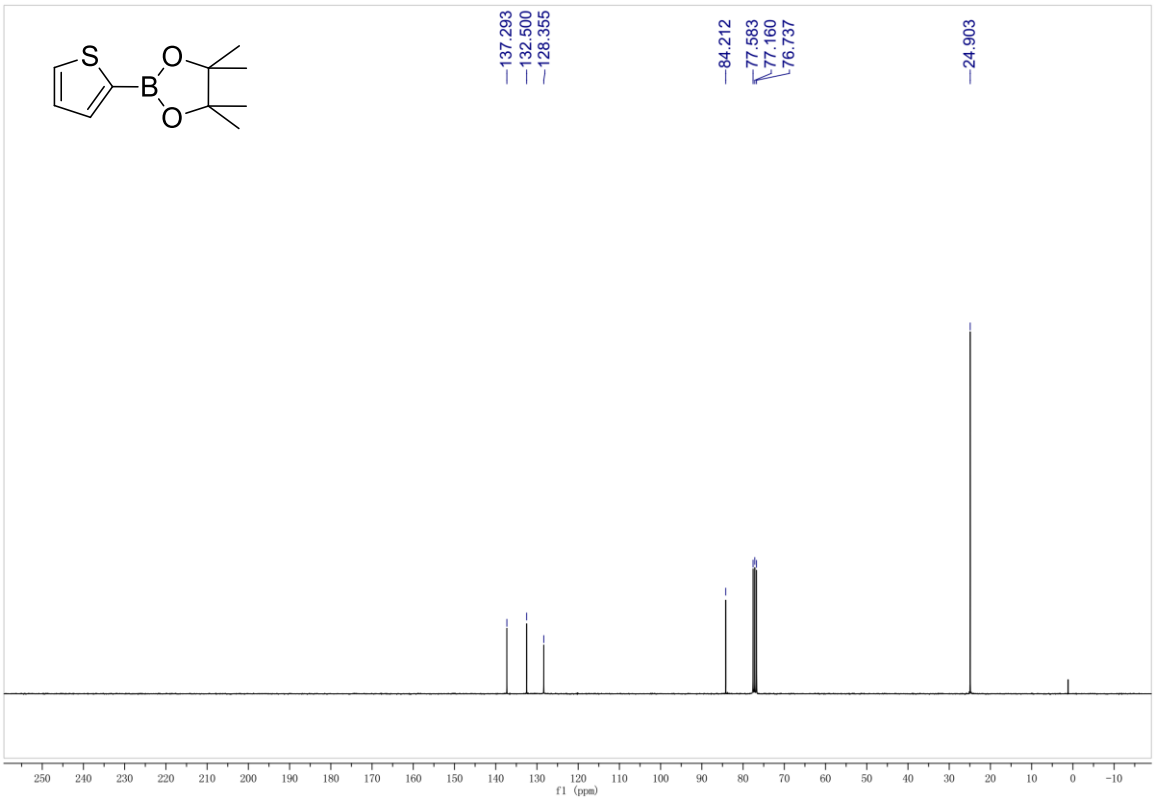
$^{11}B\{^{1}H\}$ NMR spectrum of compound **11d** in $CDCl_3$ (160 MHz).



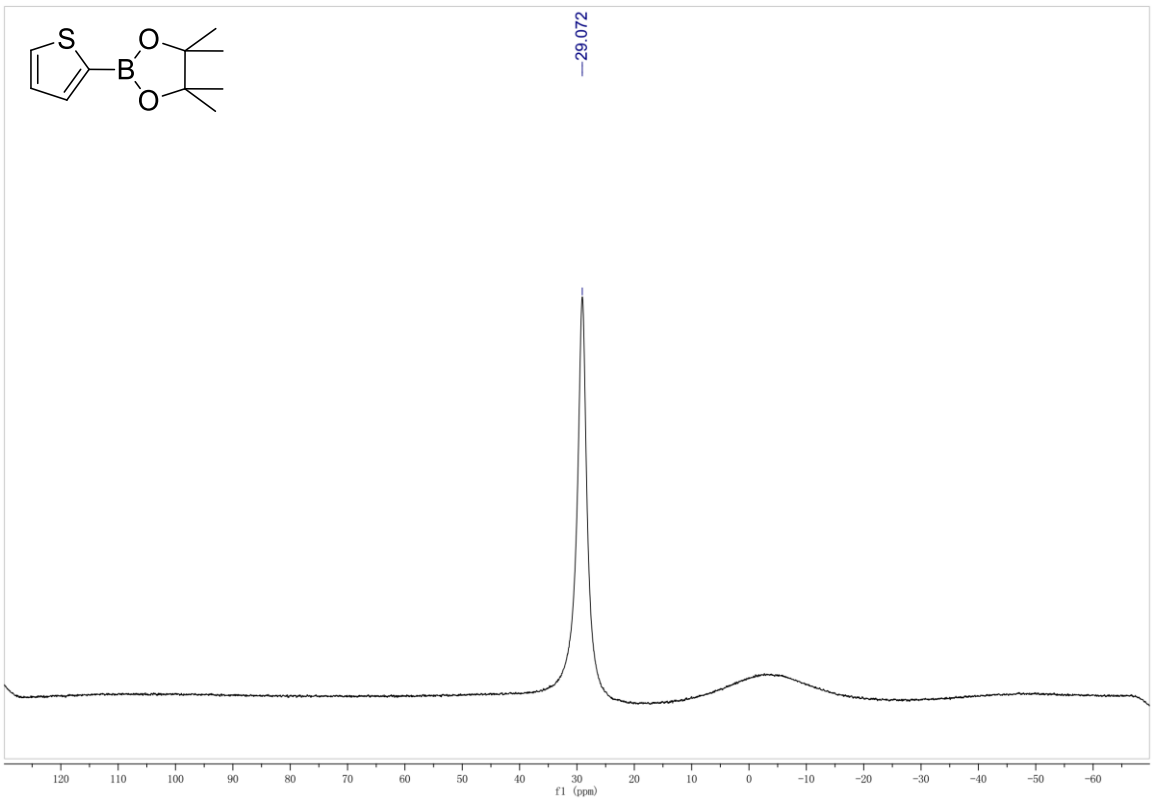
$^{19}F\{^{1}H\}$ NMR spectrum of compound **11d** in $CDCl_3$ (470 MHz).



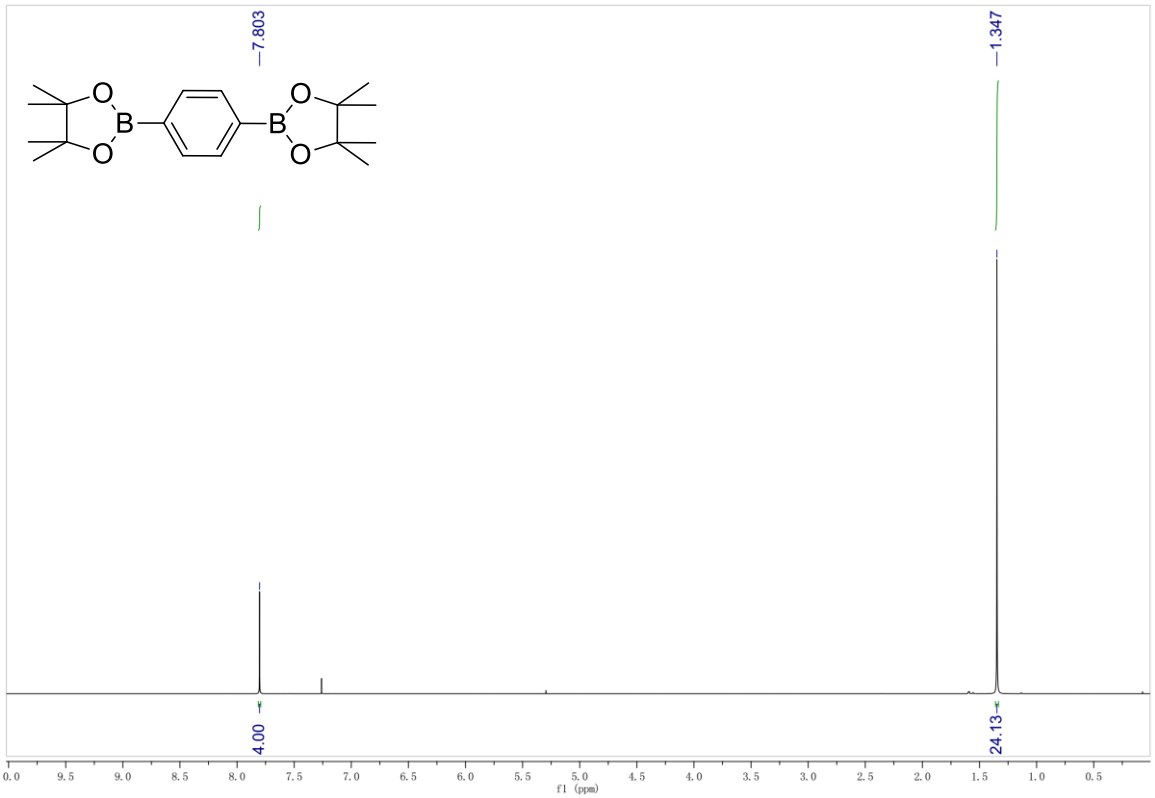
^{1}H NMR spectrum of compound **12d** in $CDCl_3$ (500 MHz).



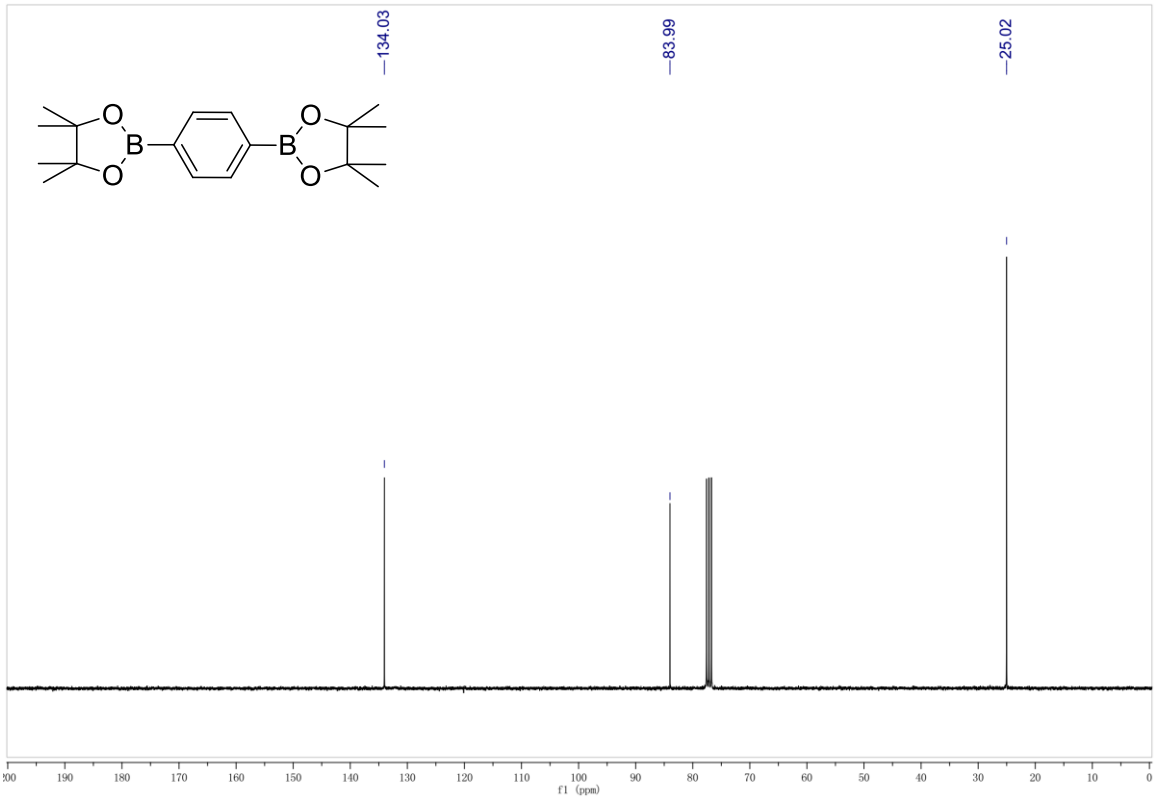
$^{13}C\{^{1}H\}$ NMR spectrum of compound **12d** in $CDCl_3$ (125 MHz).



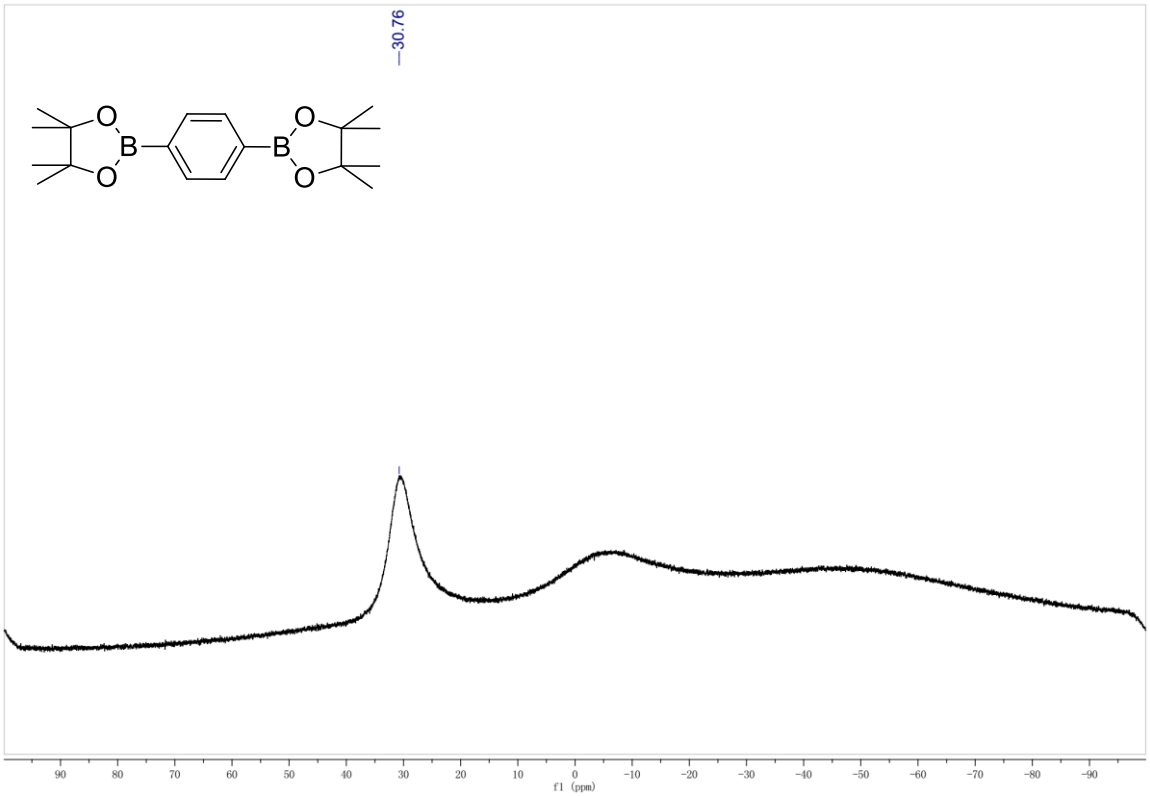
$^{11}B\{^{1}H\}$ NMR spectrum of compound **12d** in $CDCl_3$ (160 MHz).



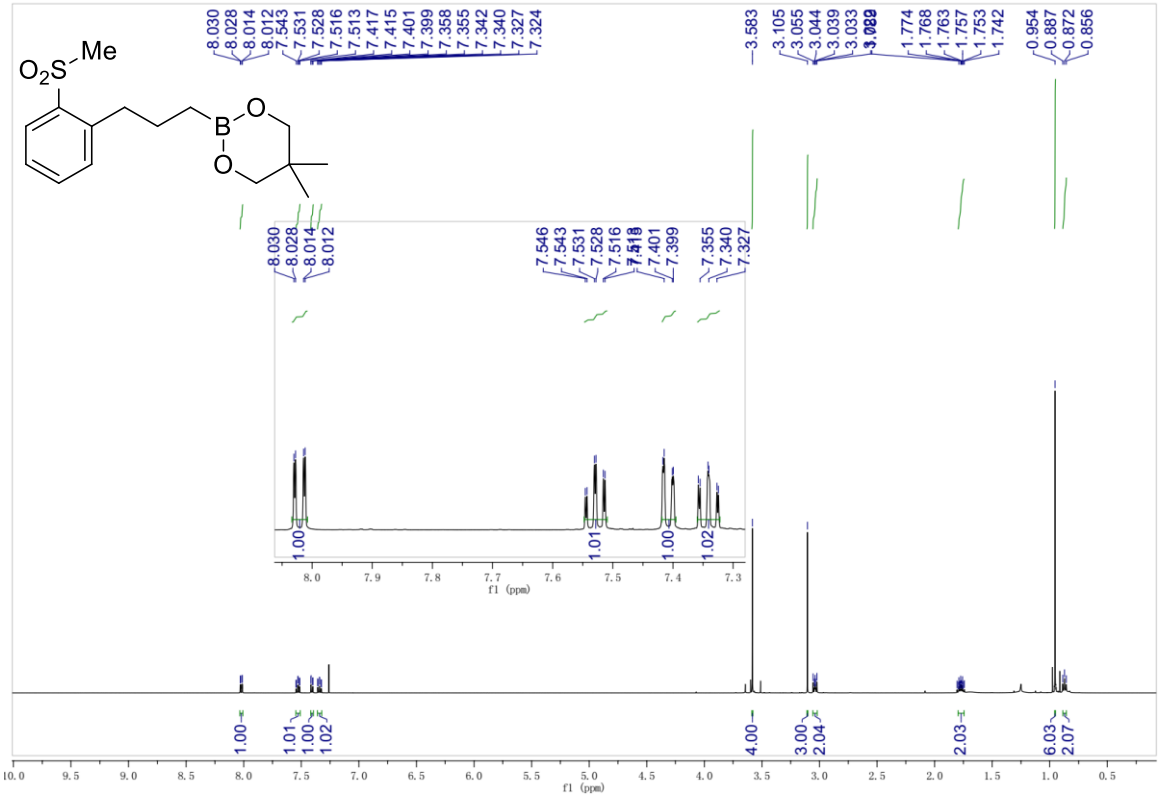
^{1}H NMR spectrum of compound **13d** in $CDCl_3$ (300 MHz).



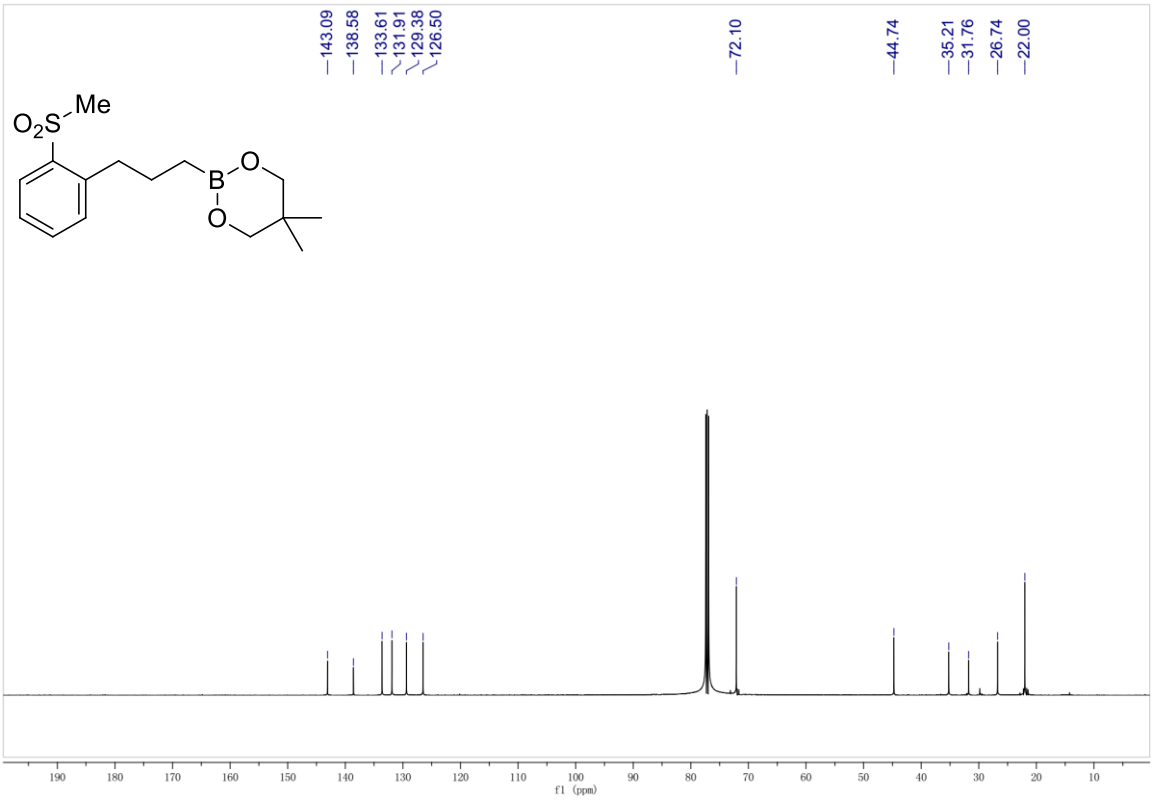
$^{13}C\{^{1}H\}$ NMR spectrum of compound **13d** in $CDCl_3$ (75 MHz).



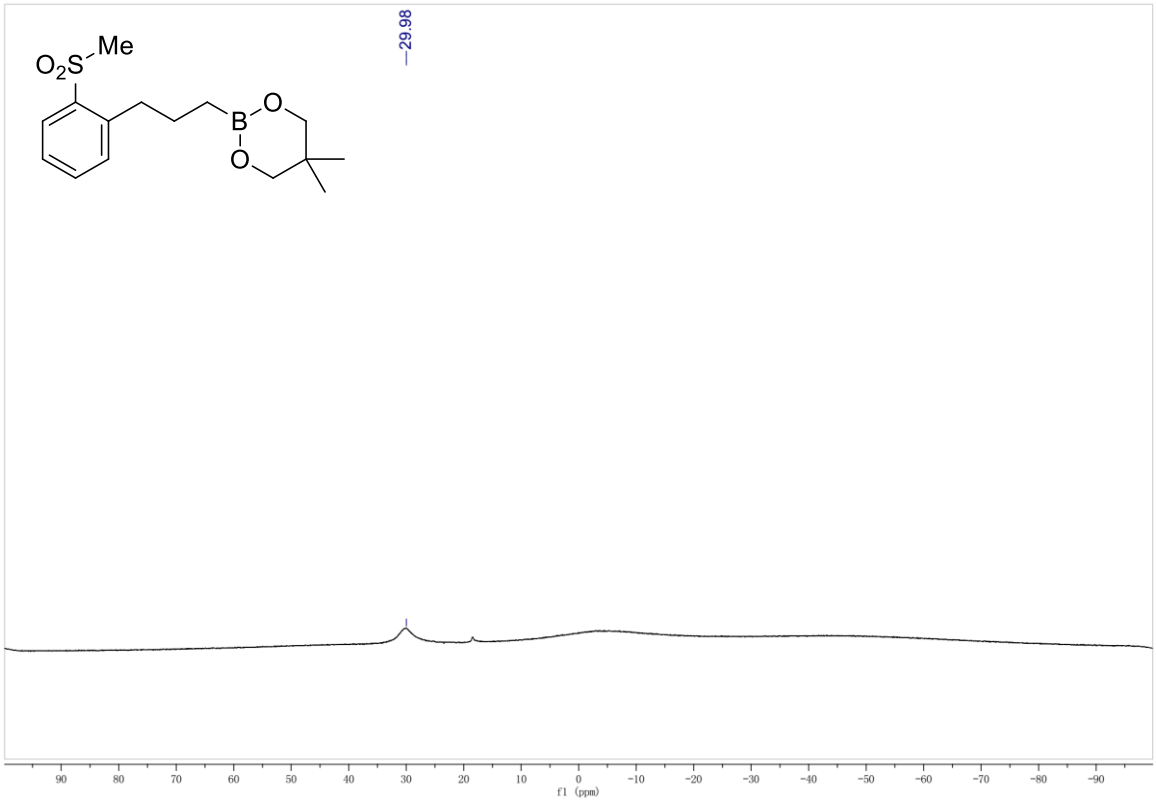
$^{11}B\{^{1}H\}$ NMR spectrum of compound **13d** in $CDCl_3$ (96 MHz).



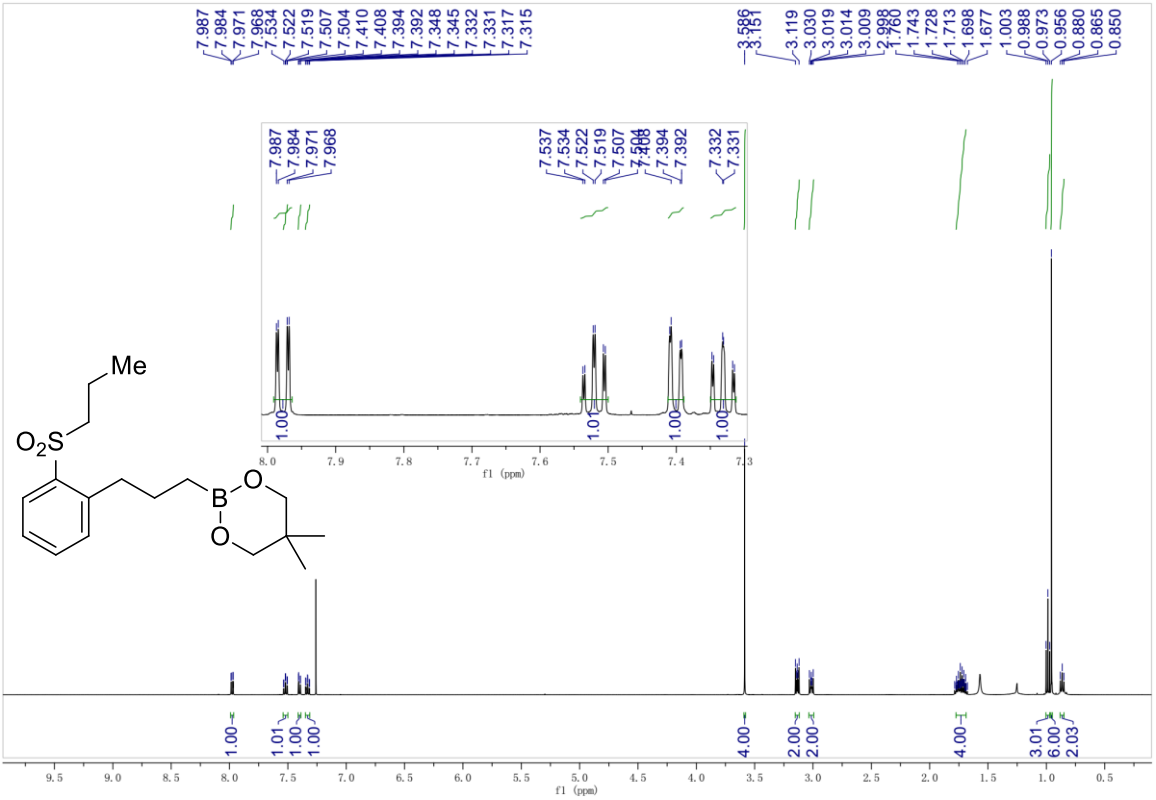
^{1}H NMR spectrum of compound **1f** in $CDCl_3$ (500 MHz).



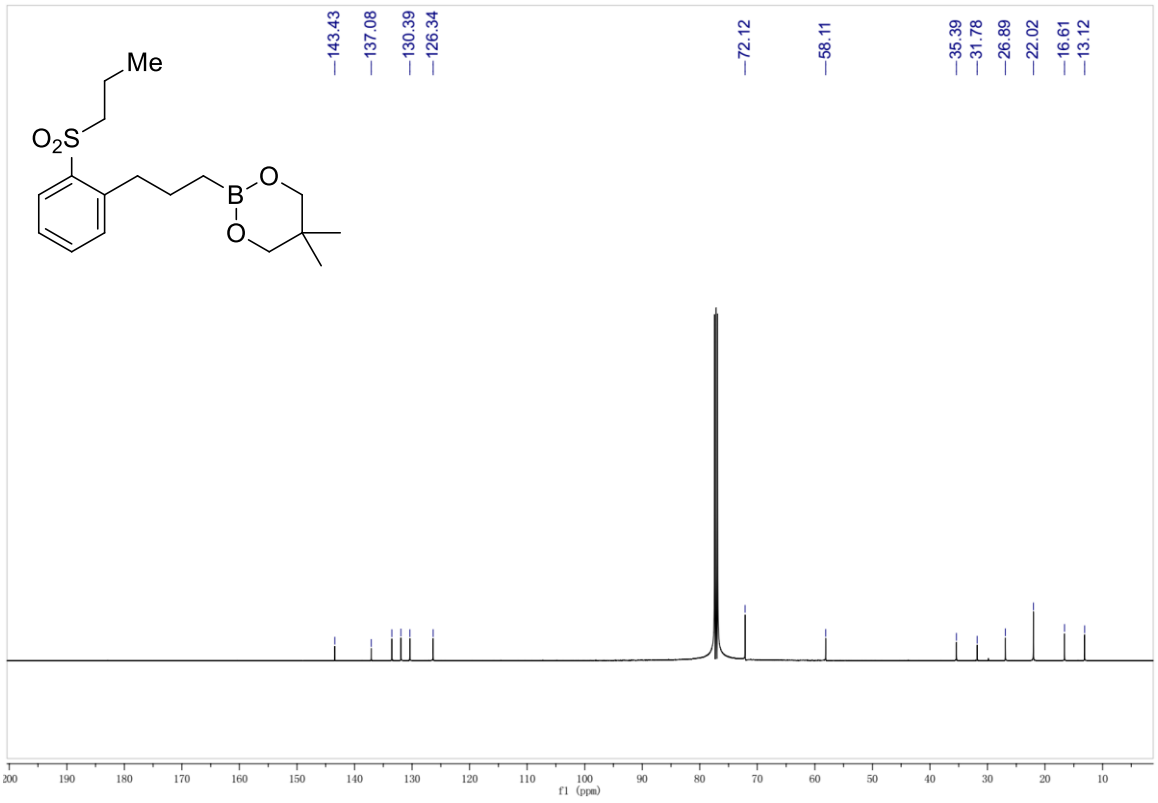
$^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** in $CDCl_3$ (125 MHz).



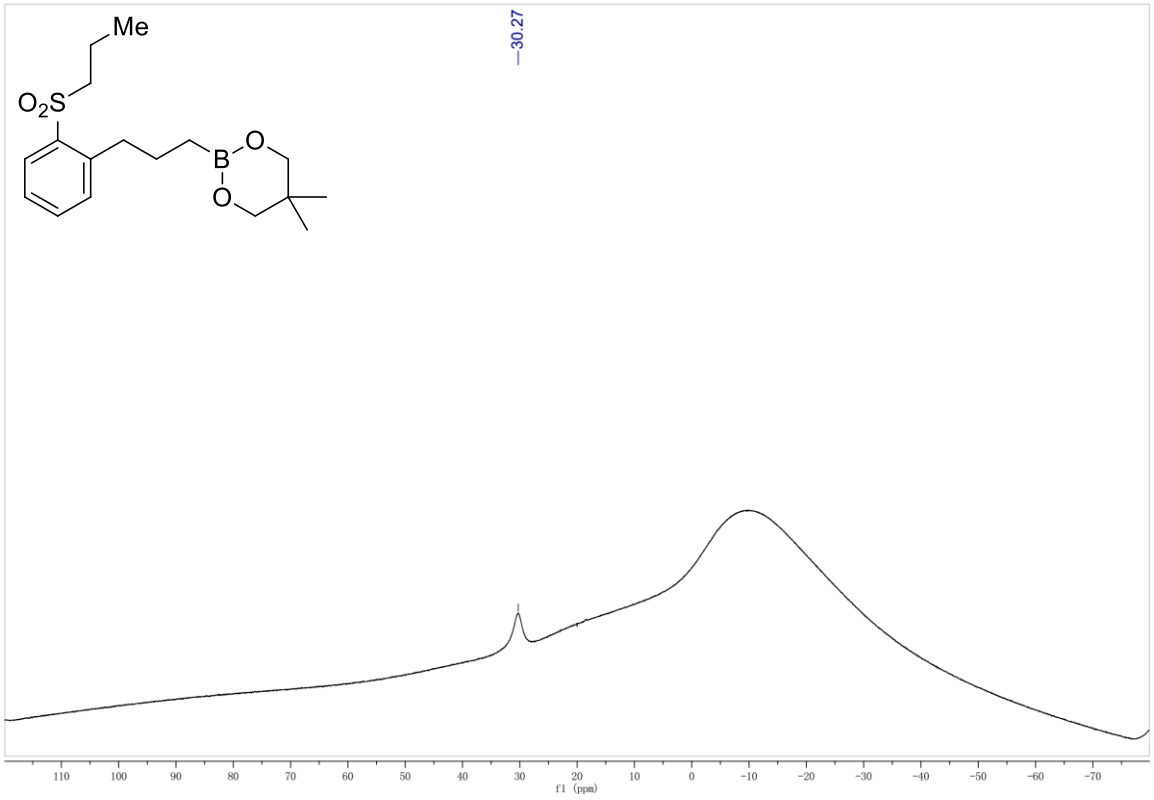
$^{11}B\{^{1}H\}$ NMR spectrum of compound **1f** in $CDCl_3$ (160 MHz).



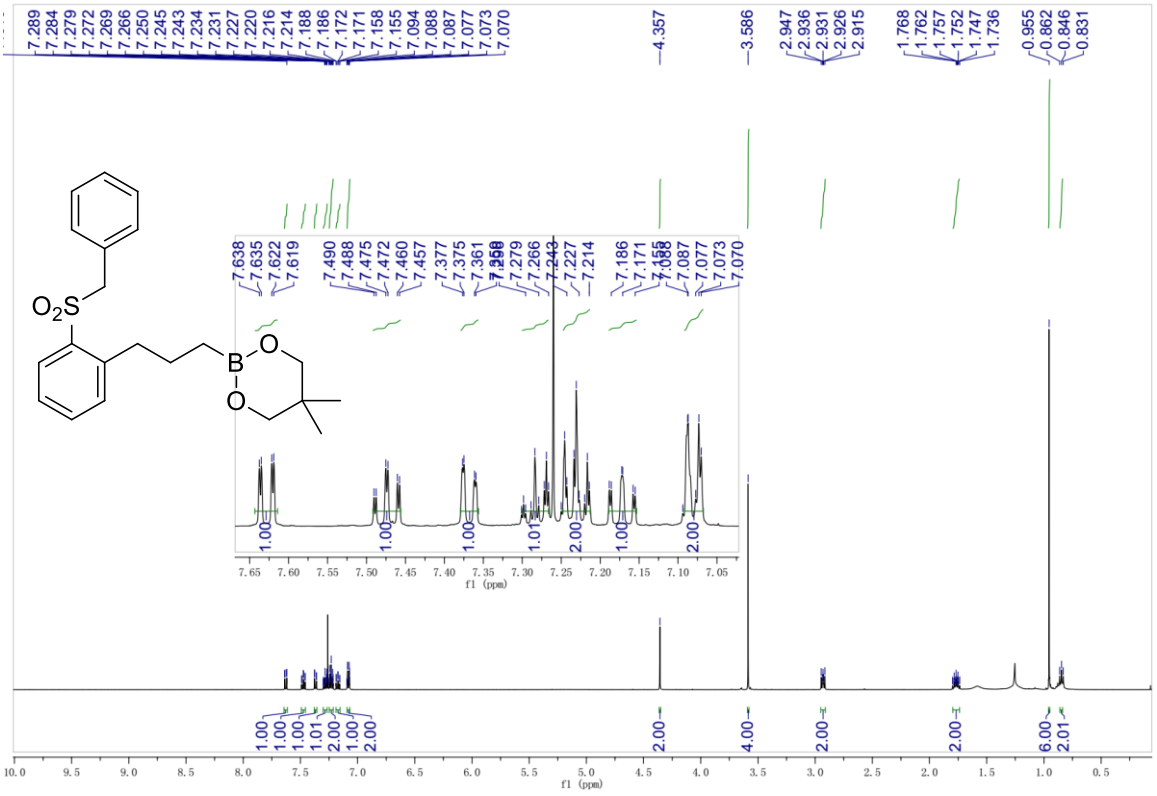
^{1}H NMR spectrum of compound **2f** in $CDCl_3$ (500 MHz).



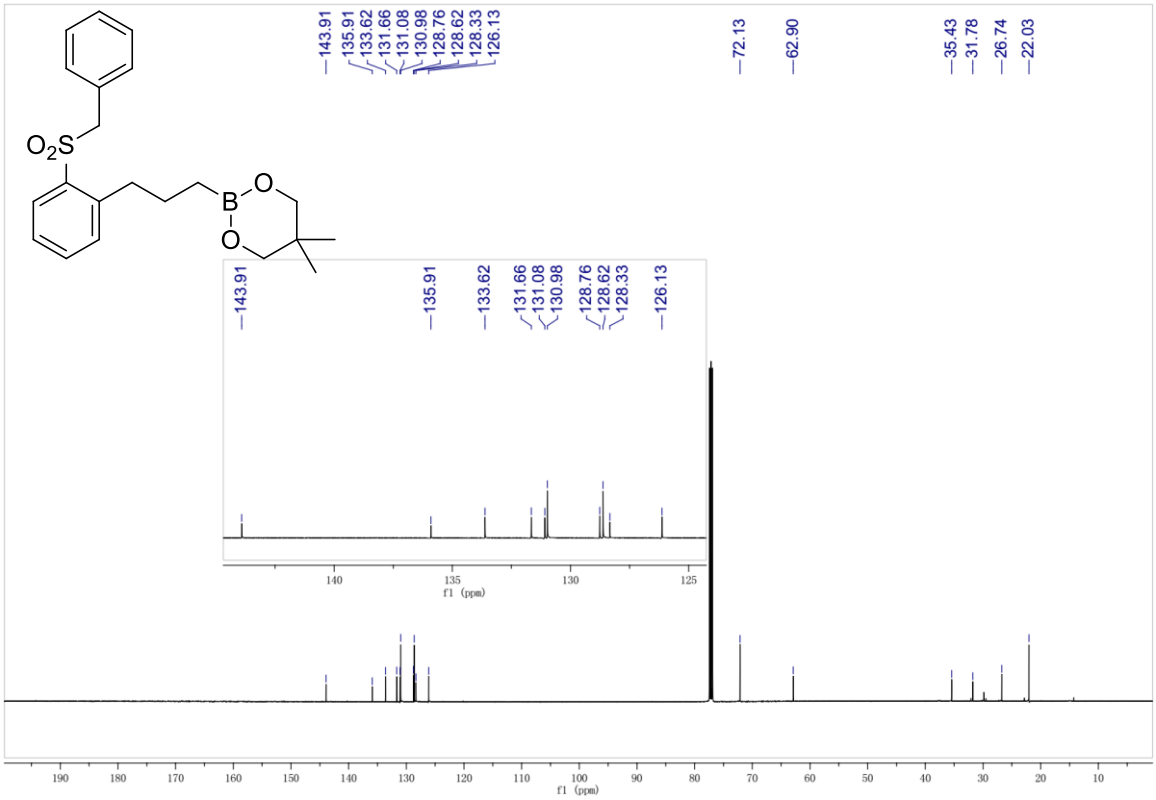
$^{13}C\{^{1}H\}$ NMR spectrum of compound **2f** in $CDCl_3$ (125 MHz).



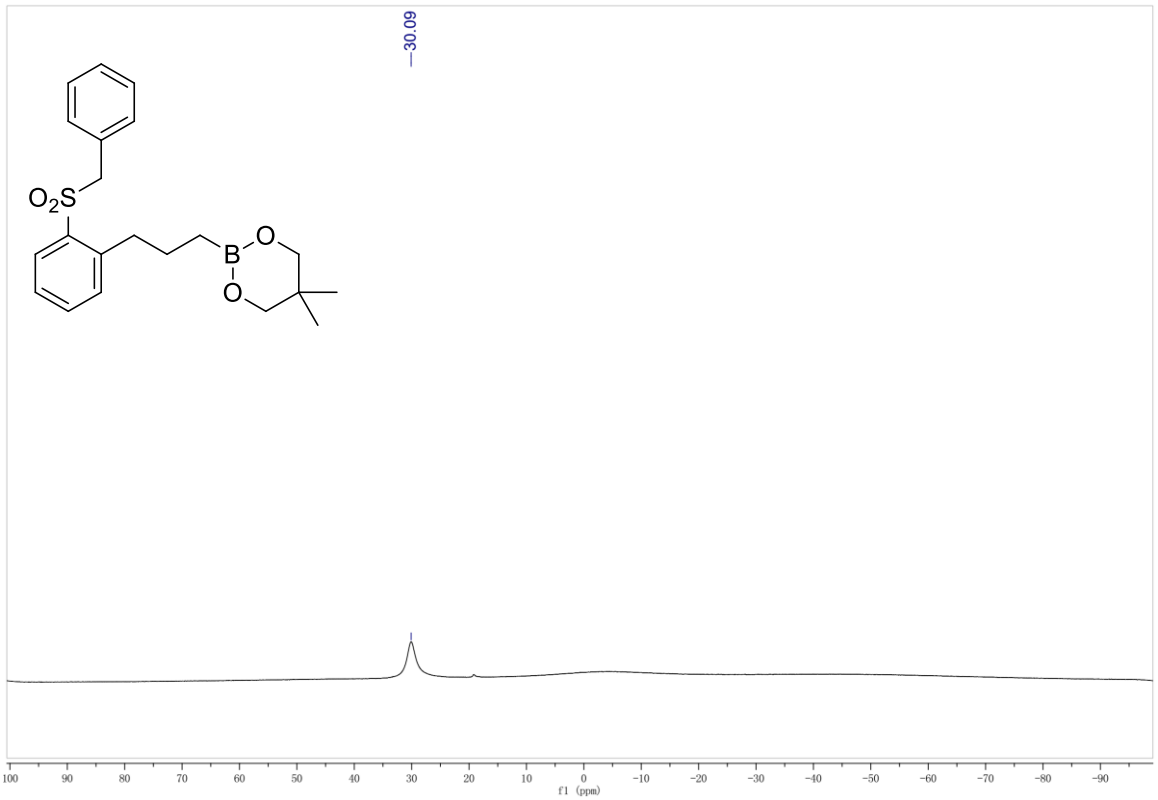
$^{11}B\{^{1}H\}$ NMR spectrum of compound **2f** in $CDCl_3$ (160 MHz).



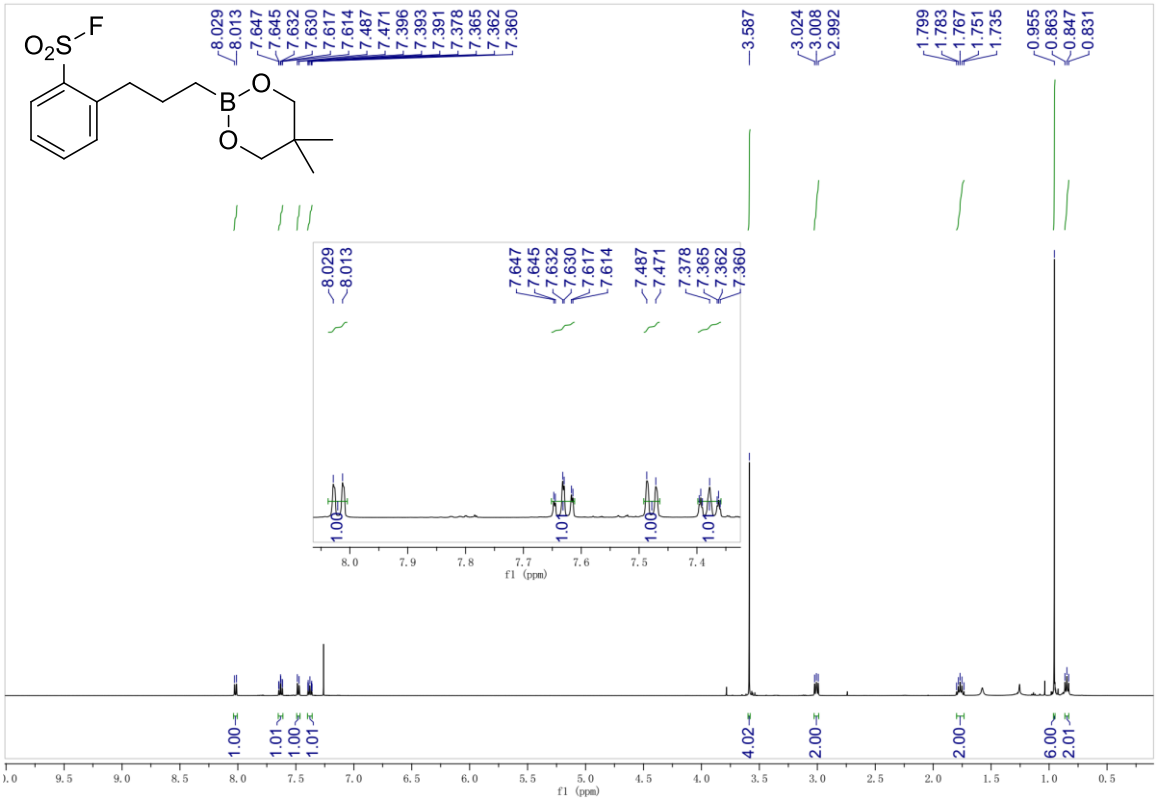
^{1}H NMR spectrum of compound **3f** in $CDCl_3$ (500 MHz).



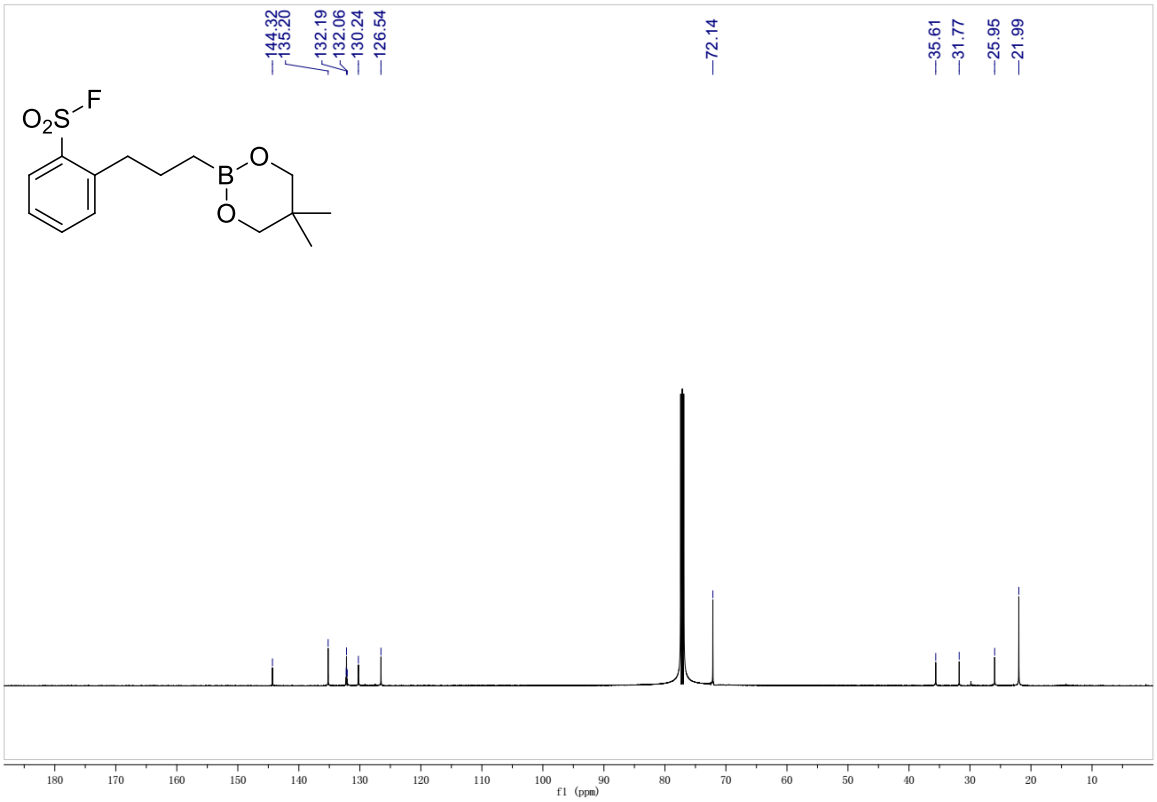
$^{13}C\{^{1}H\}$ NMR spectrum of compound **3f** in $CDCl_3$ (125 MHz).



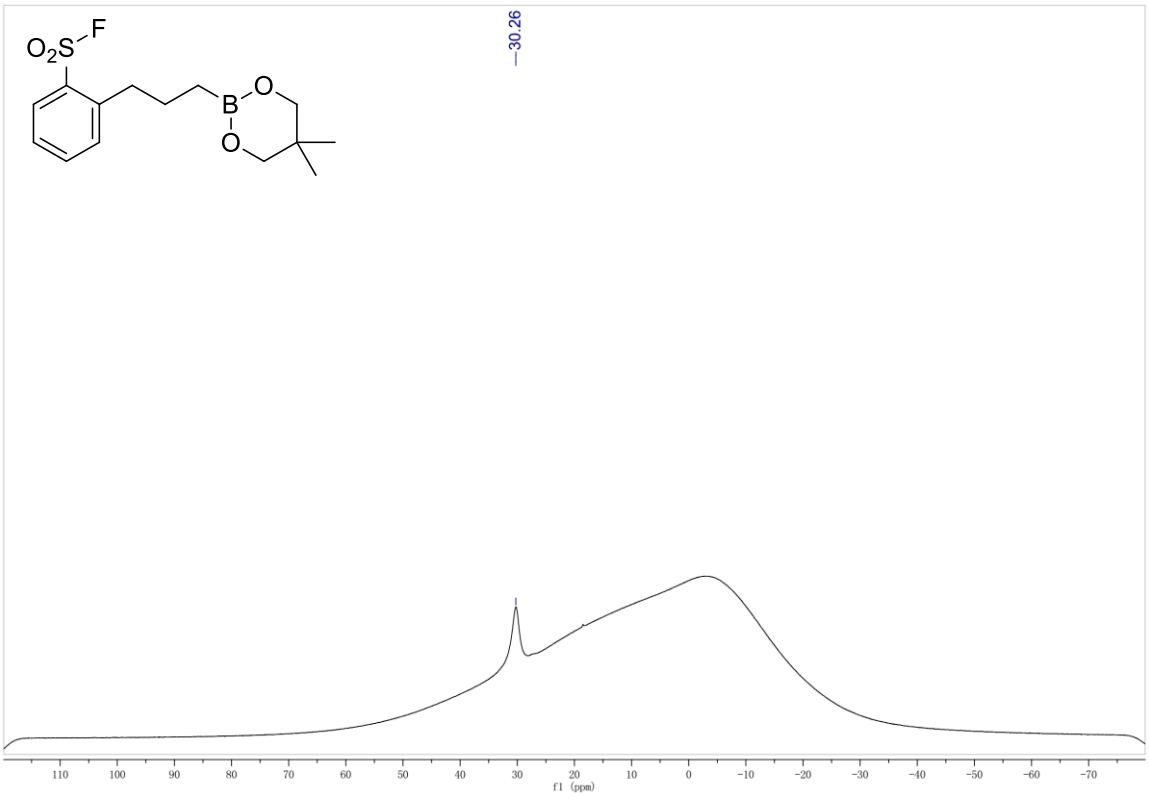
$^{11}B\{^{1}H\}$ NMR spectrum of compound **3f** in $CDCl_3$ (160 MHz).



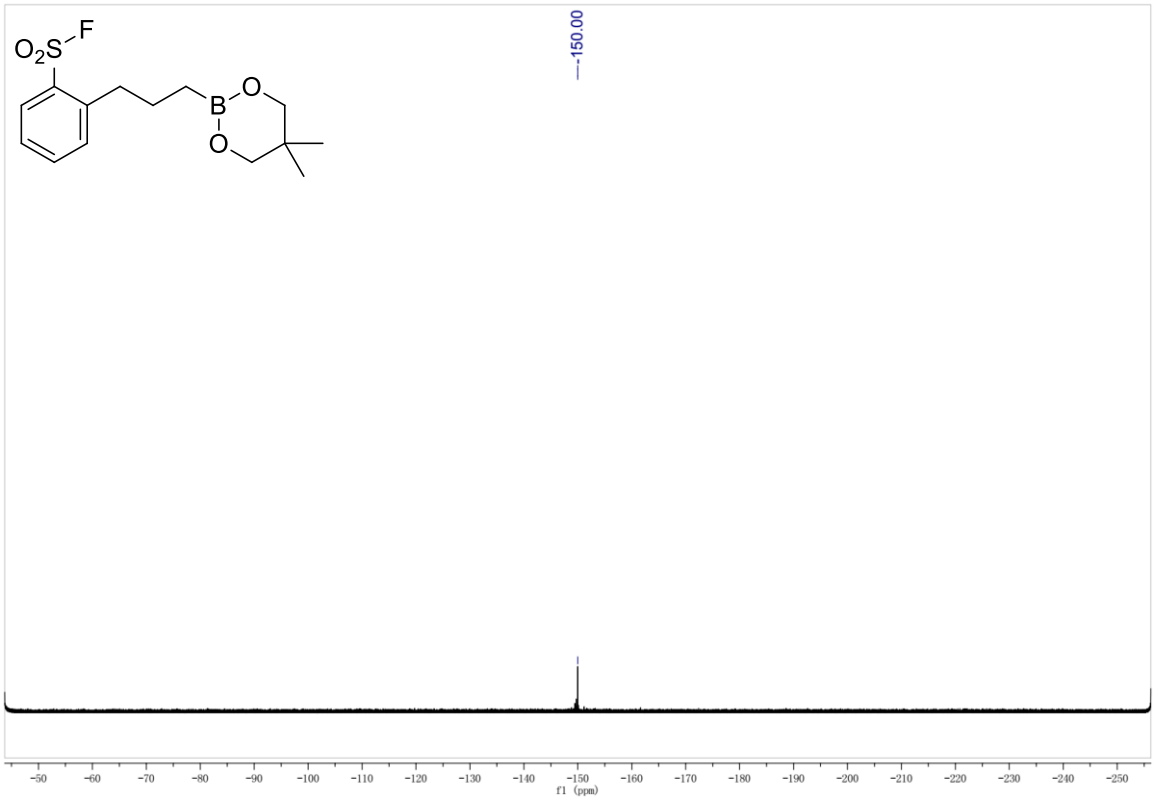
^{1}H NMR spectrum of compound **4f** in $CDCl_3$ (500 MHz).



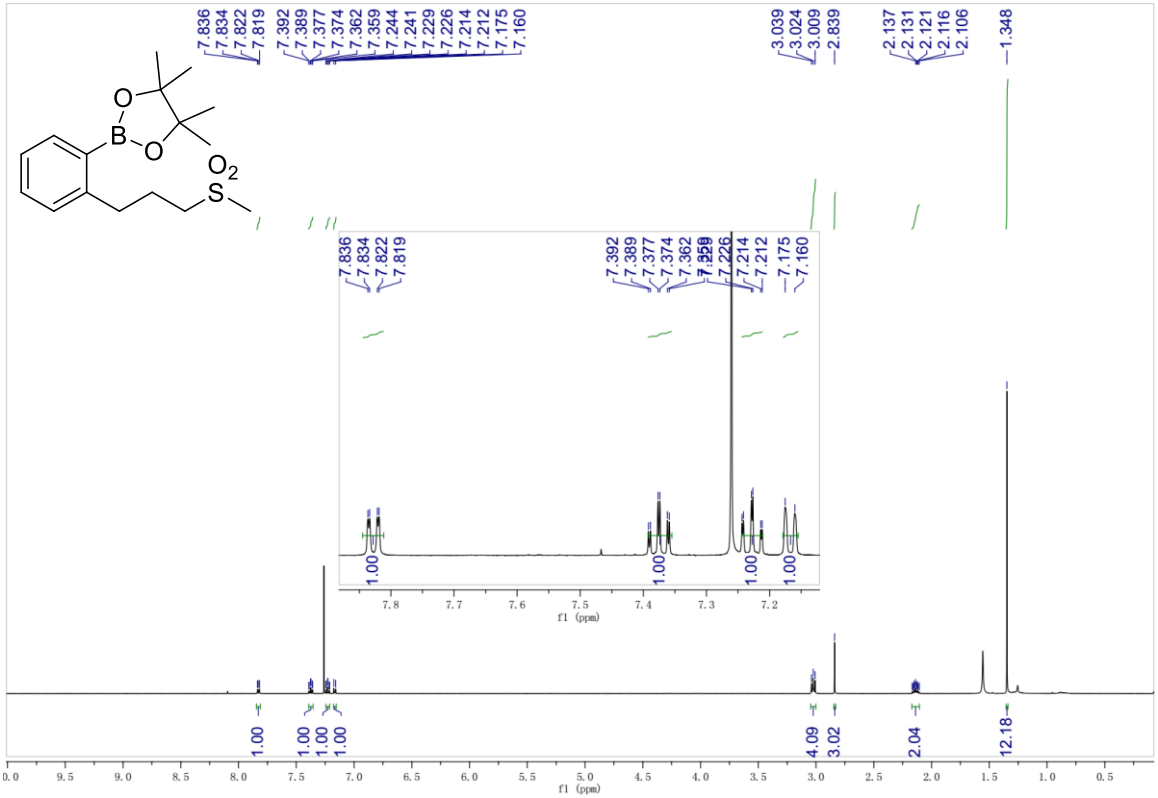
^{13}C{^{1}H} NMR spectrum of compound **4f** in $CDCl_3$ (125 MHz).



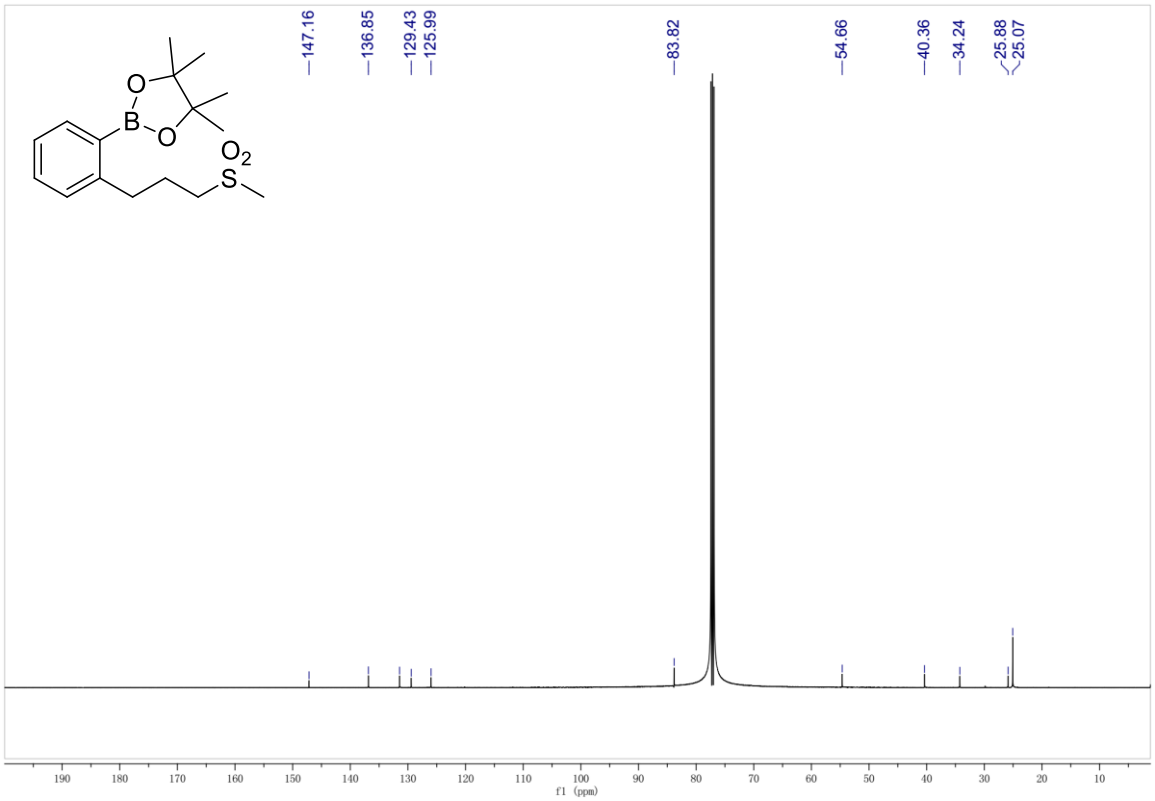
$^{11}B\{^{1}H\}$ NMR spectrum of compound **4f** in $CDCl_3$ (160 MHz).



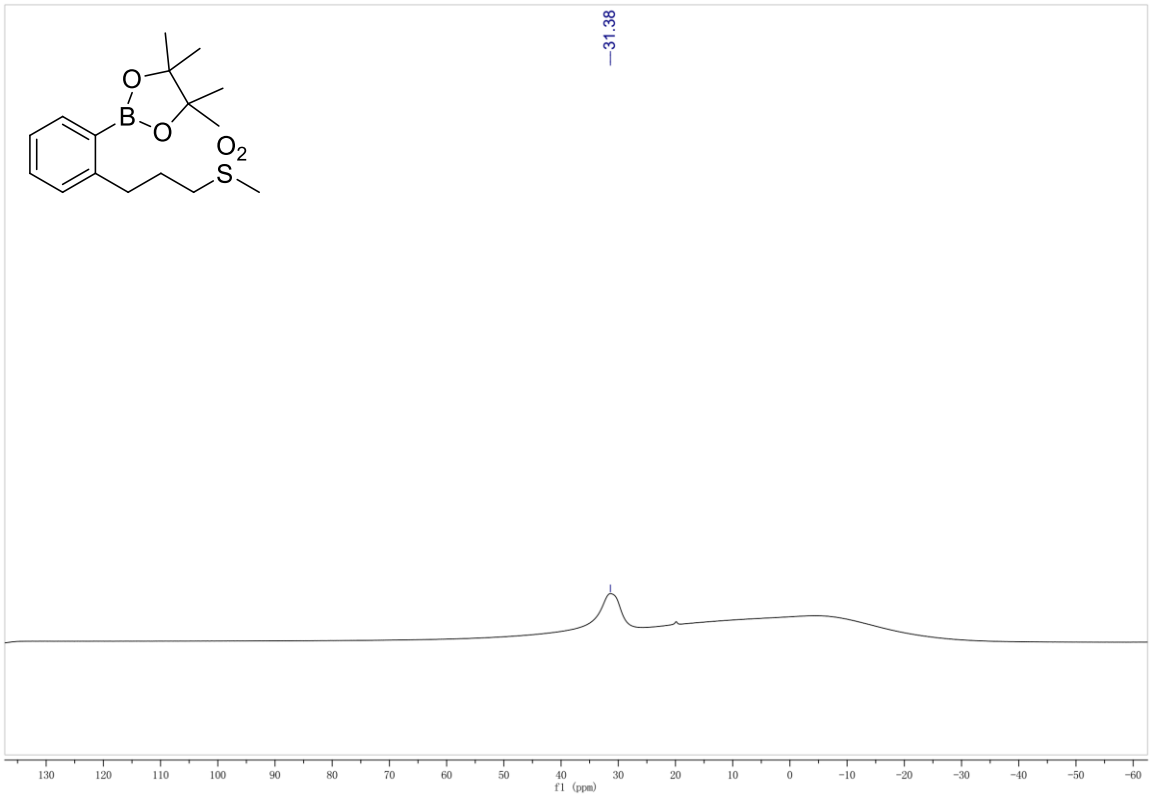
$^{19}F\{^{1}H\}$ NMR spectrum of compound **4f** in $CDCl_3$ (470 MHz).



^{1}H NMR spectrum of compound **5f** in $CDCl_3$ (500 MHz).

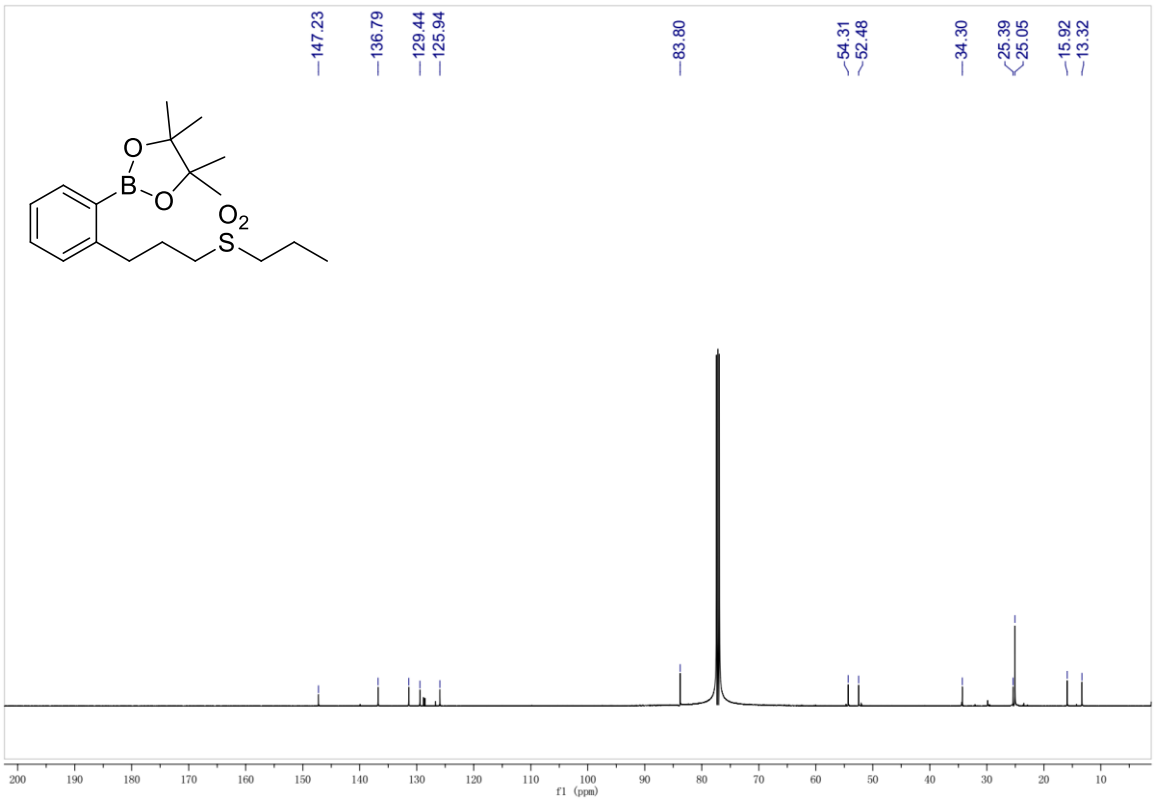


$^{13}C\{^{1}H\}$ NMR spectrum of compound **5f** in $CDCl_3$ (125 MHz).

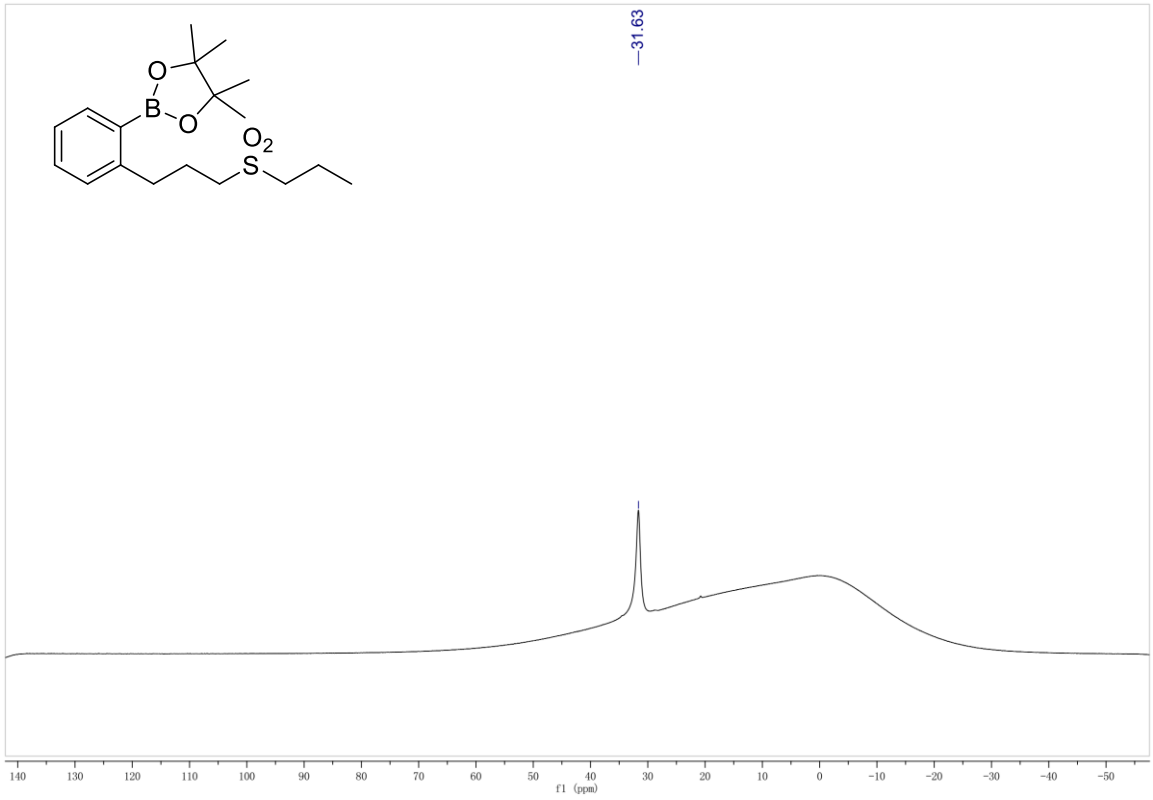


$^{11}B\{^{1}H\}$ NMR spectrum of compound **5f** in $CDCl_3$ (160 MHz).

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



$^{13}C\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$ (125 MHz).



$^{11}B\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$ (160 MHz).