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Supporting Information

Boryl (Hetero)aryne Precursors as Versatile Arylation Reagents: Synthesis through C–H Activation and Orthogonal Reactivity

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Supporting Information

1 General Considerations

Unless otherwise stated, all reactions were carried out under an Ar atmosphere using magnetic stirring. Substrate and complex syntheses are described below.

^{1}H, ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Unity 400 MHz spectrometer (^{1}H 399.5 MHz, ^{11}B 128 MHz, ^{13}C 100.6 MHz, ^{19}F 376 MHz). ^{1}H and ^{13}C chemical shifts are referenced indirectly to tetramethylsilane *via* the residual solvent signals (^{1}H: $CHCl_3$ at 7.26, ^{13}C: $CDCl_3$ at 77.0 ppm). ^{11}B ($BF_3{\cdot}Et_2O$) and ^{19}F ($CFCl_3$) chemical shifts were calibrated to an external standard at 0.00 ppm.

High resolution accurate Electron Ionisation (EI) mass spectrometry was performed on a VG Autospec mass spectrometer at 70eV. Electrospray Ionisation (ESI) mass spectrometry was performed on a Bruker Daltonics micrOTOF II mass spectrometer.

THF was freshly distilled from Na^0/benzophenone and stored over 4Å molecular sieves under Argon. MeCN was freshly distilled after being dried over K_2CO_3 and 4Å molecular sieves, and stored over 4Å molecular sieves under Argon. All other solvents used were pre-dried over 4Å molecular sieves and stored under Argon prior to use. All H_2O used was deionized and degassed (Ar). Purification by chromatography was performed using Kiesel gel 60 H silica gel (particle size 0.063-0.100 mm). Thin layer chromatography (TLC) was carried out using aluminium-backed plates coated with Kieselgel 60 (0.20 mm, UV 254) and visualized under ultraviolet light (λ = 254 nm).

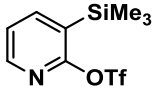
X-ray diffraction data: All the measurements were performed using graphite-monochromatized Mo K□ radiation at 100K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F^2 (SHELXL-2014/7).[1] The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry and C-H distances of 0.98 Å. Aromatic H atoms are place at idealized positions at a distance of 0.95 Å.

2 Origin and Synthesis of Starting Materials

(Hetero)aryne precursors **1a-c** and **h,** 4,4'-Di-*tert*-butyl-2,2'-dipyridyl, [{Ir(μ-OMe)COD}$_2$], $Pd(dba)_2$, $Pd(OAc)_2$, [{RhCl(COD)}$_2$], $Cu(OAc)_2$, CuI, X-Phos, 1,10-phenanthroline, inorganic salts compounds and, unless stated, all other organic reagents were obtained commercially and used without further purification. Bis(pinacolato)diboron was dried under vacuum at 50 °C overnight before use. Aryne precursors **1d**, **1g**[2] and **1e**[3] and *N*-*tert*-butyl-*α*-phenylnitrone[4] were prepared according to literature procedures. Aryne precursor **1f** was prepared using a modified literature procedure (*see below*).

Synthesis of 3-(trimethylsilyl)pyridin-2-yl-trifluoromethansulfonate (**1f**)

This compound was synthesised using a modified literature procedure.[5]



To a solution of 2-hydroxypyridine (5 g, 53 mmol) in THF (130 mL, 0.4 M) under argon, was added dropwise a 1M THF solution of LDA (117 mL, 117 mmol) at 0 °C over 20 min. The solution was allowed to warm up to 20 °C, stirred for 1 h, then cooled again to 0 °C. Chlorotrimethylsilane (7.4 mL, 58 mmol) was added dropwise over 10 min. The solution was allowed to warm up to 20 °C and stirred for 2 h. The reaction was quenched with a saturated $NH_4Cl_{(aq)}$ (80 mL) and extracted with Et_2O (3 × 80 mL). The organic phase was washed sequentially with sat. $NH_4Cl_{(aq)}$ (50 mL) and brine (50 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure to give an orange solid. The solid was then dissolved in pyridine (53 mL, 1

M), cooled to 0 °C and Tf_2O (9.8 mL, 58.3 mmol) was added dropwise over 10 min. The reaction mixture was stirred overnight at 20 °C, concentrated under reduced pressure, diluted with Et_2O (100 mL) and washed with H_2O (2 × 30 mL). Aqueous phases were extracted again with Et_2O (3 × 30 mL). The combined organic phases were washed with brine (30 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude material was purified by silica gel flash chromatography (50:1 pentane/Et_2O) to give the title compound as a colourless oil (12.25 g, 41 mmol, 77%). The identity of the compound was confirmed by comparison of ^1H, ^{13}C and ^{19}F NMR shifts to literature values.

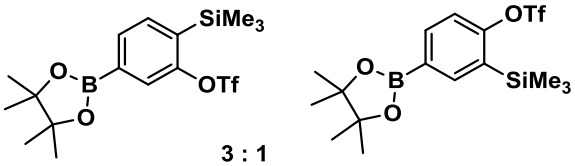
3 Borylation of Aryne Precursors

3.1 General Procedure for Borylation

To a 6 mL glass flask equipped with a Teflon tap and magnetic stirrer bar under argon were added [{Ir(μ-OMe)COD}$_2$] (2.5 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (5 mol%) and $B_2(pin)_2$ (mmol, 0.2 equiv.) Anhydrous THF (concentration = 0.5 mmol/mL) was added and the solution stirred at room temperature for 0.5 h (until the solution acquired a deep red colour). Under a flow of argon, additional $B_2(pin)_2$ (mmol, 1 equiv.) was added then precursor **1** (1 equiv.) was added with a pipette and the pipette was washed with THF (final concentration 0.5 M). The reaction mixture was sealed under argon and heated at 50 °C for 18 h, cooled to 20 °C, diluted with Et_2O (30 mL) and concentrated under reduced pressure. Pentane (50 mL) was added to the deep red oil and concentrated again under reduced pressure. The crude material was purified by twice filtering through a thin pad of silica gel (9:1 pentane/Et_2O).

3.2 Data for Borylated Compounds.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2a'**)



Yield = 99% (based on 3 mmol scale of **1a**), colorless solid. The regioisomers were identified by C-H correlation NMR. See page S23.

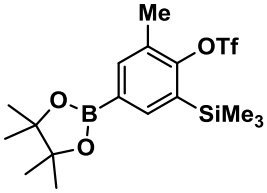
Major isomer (2a'): ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.2 Hz, 1H), 7.69 (s, 1H), 7.53 (d, J = 7.2 Hz, 1H), 1.34 (s, 12H), 0.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 135.9, 135.7, 133.5, 125.0, 125.0, 123.2, 120.0, 118.5, 116.9, 113.7, 84.3, 24.8, -0.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.9. ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

Minor isomer (2a''): 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.87 (dd, J = 8.5, 1.3 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 1.34 (s, 12H), 0.38 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 142.9, 137.9, 118.5 (q, J_{CF} = 321.2 Hz), 116.9, 84.1, 24.8, -0.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.9; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

Both isomers: HRMS (ESI+): m/z calcd for $C_{16}H_{24}BF_3NaO_5SSi$ 447.1050; found 447.1047.

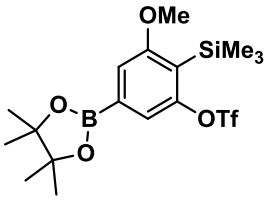
The above general procedure can be scaled up to 6 mmol of precursor **1a** (Yield = 85%).

2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2b**)



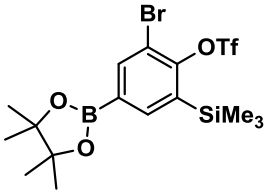
Yield = 98% (based on 3.2 mmol scale of **1b**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.75 (s, 1H), 2.39 (s, 3H), 1.35 (s, 12H), 0.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 141.1, 140.3, 133.8, 130.4, 118.6 (q, J_{CF} = 319.8 Hz), 84.1, 24.8, 17.0 (q, J_{CF} = 1.5 Hz), 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6. HRMS (ESI+): m/z calcd for $C_{17}H_{26}BF_3NaO_5SSi$ 461.1211; found 461.1212.

2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2c**)



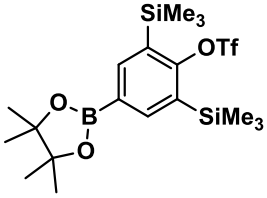
Yield = 93% (based on 3.05 mmol scale of **1c**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.22 (s, 1H), 3.87 (s, 3H), 1.34 (s, 12H), 0.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 154.3, 124.2, 118.6 (d, J_{CF} = 1.4 Hz), 118.6 (q, J_{CF} = 320.7 Hz), 114.9, 84.3, 55.7, 24.8, 0.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.2. HRMS (ESI+): m/z calcd for $C_{17}H_{26}BF_3NaO_6SSi$ 477.1162; found 477.1160.

2-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2d**)



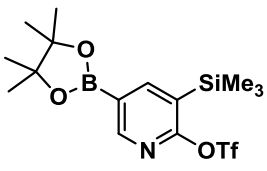
Yield = 97% (based on 2 mmol scale of **1d**), pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.88 (s, 1H), 1.34 (s, 12H), 0.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.8, 142.1, 142.0, 136.9, 118.6 (q, J_{CF} = 320.9 Hz), 116.1, 84.5, 24.8, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.6; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6. HRMS (ESI+): m/z calcd for $C_{16}H_{23}BBrF_3NaO_5SSi$ 525.0160; found 525.0174.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,6-bis(trimethylsilyl)phenyl trifluoromethanesulfonate (**2e**)



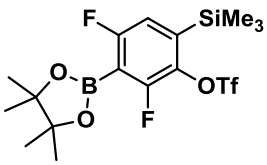
Yield = 92% (based on 1.7 mmol scale of **1e**), colorless solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 2H), 1.35 (s, 12H), 0.37 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 144.9, 142.0 (d, J_{CF} = 10.1 Hz), 133.7, 118.4 (q, J_{CF} = 319.9 Hz), 84.1, 24.8, 0.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.4. HRMS (ESI+): m/z calcd for $C_{19}H_{32}BF_3NaO_5SSi_2$ 519.1451; found 519.1447.

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)pyridin-2-yl trifluoromethanesulfonate (**2f**)



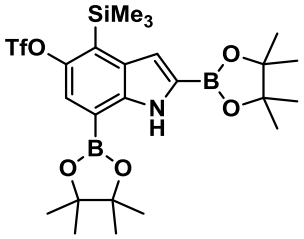
Yield = 69% (based on 6.1 mmol scale of **1f**), colorless solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, J = 2.0 Hz, 1H), 8.23 (d, J = 2.0 Hz, 1H), 1.34 (s, 12H), 0.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 155.2, 153.2, 123.8, 118.5 (q, J_{CF} = 320.8 Hz), 84.5, 24.8, -1.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.4. HRMS (ESI+): m/z calcd for $C_{15}H_{23}BF_3NNaO_5SSi$ 448.1007; found 448.1004.

2,4-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**2g**)



Yield = 96% (based on 1 mmol scale of **1g**), colorless solid.[1]H NMR (400 MHz, $CDCl_3$): δ 6.96 (dd, J = 8.0, 1.6 Hz, 1H), 1.37 (s, 12H), 0.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.2 (dd, J_{CF} = 256.3, 10.2 Hz), 156.5 (dd, J_{CF} = 259.8, 12.5 Hz), 141.70 (dd, J_{CF} = 6.3, 2.4 Hz), 136.6 (dd, J_{CF} = 13.9, 3.8 Hz), 118.6 (q, J_{CF} = 320.9 Hz), 117.0 (dd, J_{CF} = 24.4, 3.9 Hz), 84.6, 24.7, -0.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.0 (d, J_{FF} = 21.7 Hz), -99.8 – -100.0 (m), -112.1 (qd, J_{FF} = 21.7, 4.6 Hz); ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.1.

2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)-1H-indol-5-yl trifluoromethanesulfonate (**2h**)



Using 2 equiv of B_2Pin_2. In a mixture with B_2Pin_2 (about 2 : 1). Yield = 54% (based on 3.05 mmol scale of **1h**), colorless solid. ^{1}H NMR (400 MHz, C_6D_6): δ 9.92 (br s, 1H), 8.09 (s, 1H), 7.74 (d, J = 2.1 Hz, 1H), 1.09 (s, 12H), 0.95 (s, 12H), 0.52 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.4, 140.6, 132.1, 129.0, 122.5, 118.7 (q, J_{CF} = 320.6 Hz), 115.3, 84.4, 84.3, 24.9, 24.8, 1.1; ^{19}F NMR (376 MHz, C_6D_6): δ -73.5; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5. HRMS (EI+): m/z calcd for $C_{24}H_{36}B_2NO_7F_3SSi$ 589.2120; found 589.2136.

Procedures for the Capture of Boryl Arynes

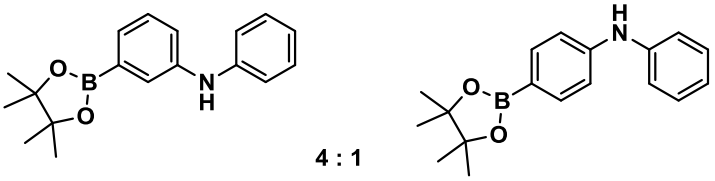
3.3 General Procedure

A 6 mL glass flask equipped with a Teflon tap and magnetic stirrer was charged with the appropriate aryne precursor (**2**) (0.2 mmol, unless otherwise noted), trapping reagent (indicated in each case below), CsF (as indicated below) and 18-crown-6 (53 mg, 0.2 mmol, 1 equiv.). The flask was evacuated and backfilled with argon. MeCN (2 mL) was then added and the resulting suspension stirred at the indicated temperature. The reaction was monitored by ^{19}F NMR. Upon complete consumption of **2**, the reaction mixture was diluted with Et_2O (20 mL) and washed with brine (2 × 15 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography using the indicated eluent system.

3.4 Data for Aryne Capture Compounds

N-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**4a**)

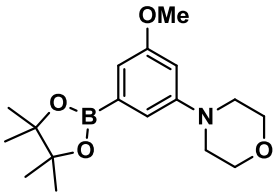
Aryne precursor: **2a**, capture reagent: aniline (93 mg, 1 mmol, 5 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 60 °C, reaction time: 7 h. Column chromatography eluent: pentane/Et_2O (8 : 1), R_f = 0.2. Yield = 83% (based on **2a**), yellow oil.



Major isomer: ^{1}H NMR (400 MHz, C_6D_6): 7.81 (ddd, J = 7.2, 1.1, 1.1 Hz, 1H), 7.78 (br d, J = 2.4 Hz, 1H), 7.09 – 6.99 (m, 3H), 6.89 – 6.83 (m, 3H, partially obscured by minor isomer), 6.78 (tt, J = 7.4,

1.1 Hz, 1H), 5.11 (s, 1H), 1.13 (s, 12H); ^{13}C NMR (101 MHz, C_6D_6): δ 143.4, 142.6, 129.1, 128.7, 127.7, 124.9, 120.5, 119.0, 117.5, 83.4, 24.6; ^{11}B NMR (128 MHz, C_6D_6): δ 31.4.
Minor isomer: N-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline. ^{1}H NMR (400 MHz, C_6D_6): δ 8.15 (m, 2H), 7.21 – 7.13 (m, 4H, partially obscured by C_6D_6), 7.02 (ddd, J = 8.1, 2.5, 1.1 Hz, 2H), 6.85 – 6.81 (m, 1H, partially obscured by major isomer), 5.18 (s, 1H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, C_6D_6): δ 146.3, 142.0, 136.6, 129.1, 121.5, 120.9, 115.7, 83.1, 24.6; ^{11}B NMR (128 MHz, C_6D_6): δ 31.4.
Both isomers: HRMS (EI+): m/z calcd for $C_{18}H_{22}NO_2B$ 295.1744; found 295.1750.

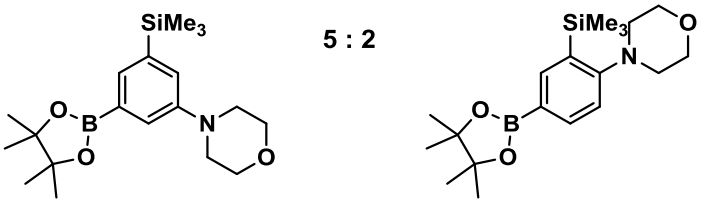
4-(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (**4b**)



Aryne precursor: **2c**, capture reagent: morpholine (52 mg, 0.6 mmol, 3 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 60 °C, reaction time: 6 h. Column chromatography eluent: pentane/Et_2O (2.5 : 1), R_f = 0.2. Yield = 67% (based on **2c**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J = 2.1 Hz, 1H), 6.87 (d, J = 1.7 Hz, 1H), 6.56 (br s, 1H), 3.88 – 3.83 (m, 4H), 3.82 (s, 3H), 3.22 – 3.15 (m, 4H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.1, 125.5, 115.0, 109.7, 106.0, 83.8, 66.8, 55.3, 49.4, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7. HRMS (EI+): m/z calcd for $C_{17}H_{26}NO_4B$ 319.1955; found 319.1951.

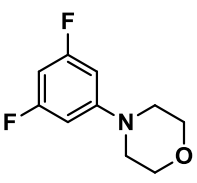
4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)phenyl)morpholine (**4c**)

Aryne precursor: **2e**, capture reagent: morpholine (52 mg, 0.6 mmol, 3 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 60 °C, reaction time: 5 h. Column chromatography eluent: pentane/Et_2O (6 : 1). R_f = 0.2. Yield = 62% (based on **2e**), colorless solid.



Major regioisomer: R_f = 0.2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 1H), 7.37 (d, J = 2.0 Hz, 1H), 7.19 (br s, 1H), 3.93 – 3.84 (m, 4H), 3.28 – 3.18 (m, 4H), 1.35 (s, 12H), 0.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 140.5, 131.6, 123.9, 122.5, 83.7, 67.0, 49.7, 24.8, -1.0; ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0. HRMS (ESI+): m/z calcd for $C_{19}H_{33}BNO_3Si$ 362.2321; found 362.2314.
Minor regioisomer: 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenyl)morpholine. R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 1.3 Hz, 1H), 7.86 (dd, J = 8.0, 1.3 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 3.89 – 3.80 (m, 4H), 2.93 – 2.83 (m, 4H), 1.33 (s, 12H), 0.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 142.2, 137.6, 137.1, 121.8, 83.7, 67.2, 54.1, 24.8, 0.1; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9. HRMS (EI+): m/z calcd for $C_{19}H_{32}BNO_3Si$ 361.2245; found 361.2250.

4-(3,5-difluorophenyl)morpholine (**4d**)

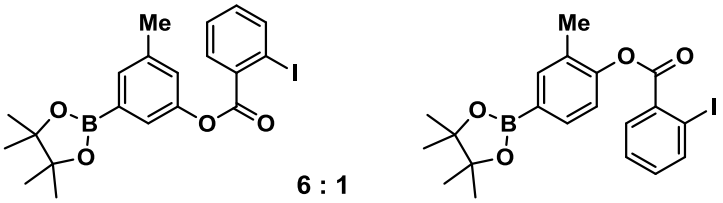


Aryne precursor: **2g** (scale: 0.3 mmol), capture reagent: morpholine (78 mg, 0.9 mmol, 3 equiv.), CsF (228 mg, 1 mmol, 5 equiv.), reaction temperature: 60 °C, reaction time: 5 h. Column chromatography eluent: pentane/Et_2O (8 : 1). R_f = 0.2. Yield = 64% (based on **2g**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 – 6.32 (m, 2H), 6.29 (tt, J = 8.8, 2.2 Hz, 1H), 3.86 – 3.80 (m, 4H), 3.18 – 3.09 (m,

4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.2 (d, J_{CF} = 15.8 Hz), 162.8 (d, J_{CF} = 15.9 Hz), 153.2 (t, J_{CF} = 12.2 Hz), 98.0 – 97.5 (m), 94.5 (t, J_{CF} = 26.1 Hz), 66.5 (s), 48.3 (s); ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.7 – -109.8 (m). HRMS (EI+): m/z calcd for $C_{10}H_{11}NOF_2$ 199.0809; found 199.0804.

3-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 2-iodobenzoate (**4e**)

Aryne precursor: **2b**, capture reagent: 2-iodobenzoic acid (88 mg, 0.24 mmol, 1.2 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), 18-crown-6 (158 mg, 0.6 mmol, 3 equiv.), reaction temperature: 60 °C, reaction time: 24 h. Column chromatography eluent: pentane/Et_2O (12 : 1), R_f = 0.6. Yield = 61% (based on **2b**), colorless oil.

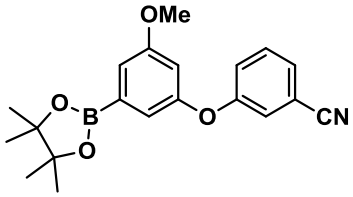


Major regioisomer: ^{1}H NMR (400 MHz, C_6C_6): δ 7.98 – 7.94 (m, 1H), 7.84 – 7.81 (m, 1H), 7.70 (dd, J = 7.7, 1.7 Hz, 1H), 7.69 (dd, J = 7.9, 1.1 Hz, 1H), 7.13 – 7.11 (m, 1H), 6.82 (td, J = 7.7, 1.1 Hz, 1H), 6.51 (td, J = 7.9, 1.7 Hz, 1H), 2.05 (d, J = 0.5 Hz, 3H), 1.12 (s, 12H); ^{13}C NMR (101 MHz, C_6C_6): δ 164.5, 150.8, 141.2, 138.9, 133.4, 132.3, 131.2, 129.7, 127.4, 125.4, 124.9, 94.4, 83.5, 24.5, 20.6; ^{11}B NMR (128 MHz, C_6C_6): δ 30.7.

Minor regioisomer: 2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl 2-iodobenzoate ^{1}H NMR (400 MHz, C_6C_6): δ 8.03 – 8.01 (m, 1H), 7.77 (dd, J = 7.8, 1.7 Hz, 1H), 7.72 – 7.70 (m, 1H, partially obscured by major isomer), 7.14 (s, 1H), 6.83 (td, J = 7.6, 1.2 Hz, 1H), 6.54 – 6.49 (m, 1H, partially obscured by major isomer), 2.12 (s, 3H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, C_6C_6): δ 163.7, 152.3, 141.5, 138.3, 134.5, 134.0, 132.5, 131.1, 129.7, 127.5, 121.6, 94.6, 83.4, 24.6, 15.9; ^{11}B NMR (128 MHz, C_6C_6): δ 30.7.

Both isomers: HRMS (ESI+): m/z calcd for $C_{20}H_{22}BINaO_4$ 487.0552; found 487.0561.

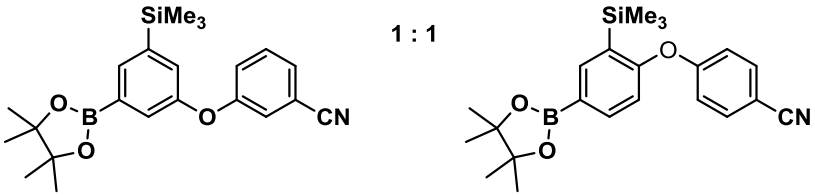
3-(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)benzonitrile (**4f**)



Aryne precursor: **2c**, capture reagent: 3-cyanophenol (36 mg, 0.3 mmol, 1.5 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), reaction temperature: 60 °C, reaction time: 7 h. Column chromatography eluent: pentane/Et_2O (8 : 1), R_f = 0.2. Yield = 63% (based on **2c**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.05 (s, 1H), 6.71 – 6.66 (m, 1H), 3.83 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.7, 158.3, 156.0, 130.9, 126.2, 122.7, 120.9, 118.0, 115.4, 113.4, 109.8, 84.1, 55.6, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9. HRMS (ESI+): m/z calcd for $C_{20}H_{22}BNNaO_4$ 374.1538; found 374.1531.

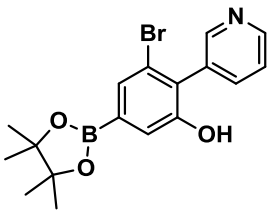
3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)phenoxy)benzonitrile and 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)phenoxy)benzonitrile (**4g**)

Aryne precursor: **2e**, capture reagent: 3-cyanophenol (71 mg, 0.6 mmol, 3 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), reaction temperature: 40 °C, reaction time: 20 h. Column chromatography eluent: pentane/Et_2O (30 : 1), R_f = 0.2. Yield = 62% (based on **2e**), colorless oil.



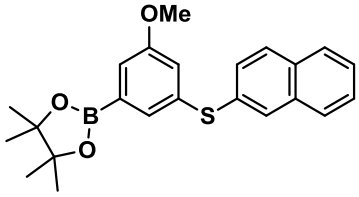
^{1}H NMR (400 MHz, C_6D_6): δ 8.44 (d, J = 1.4 Hz, 1H), 8.25 (s, 1H), 8.05 (dd, J = 8.2, 1.6 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.44 – 7.39 (m, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 6.78 – 6.70 (m, 2H), 6.66 (d, J = 7.8 Hz, 2H), 6.57 (t, J = 8.0 Hz, 1H), 6.54 – 6.45 (m, 2H), 1.16 (s, 12H), 1.09 (s, 12H), 0.23 (s, 9H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6): δ 163.5, 158.0, 157.4, 155.2, 143.8, 143.1, 142.9, 138.3, 136.1, 130.2, 130.1, 130.1, 126.2, 126.0, 125.9, 122.4, 121.6, 121.3, 121.0, 117.8, 117.8, 117.0, 114.0, 113.9, 83.7, 83.5, 24.6, 24.5, -1.2, -1.7; ^{11}B NMR (128 MHz, C_6D_6): δ 30.9. HRMS (ESI+): m/z calcd for $C_{22}H_{28}BNNaO_3Si$ 416.1828; found 416.1832.

3-bromo-2-(pyridin-3-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**4h**)



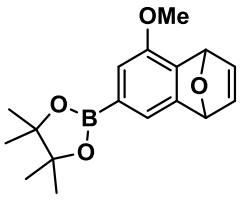
Aryne precursor: **2d**, capture reagent: pyridine *N*-oxide (29 mg, 0.3 mmol, 1.5 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), reaction temperature: 60 °C, reaction time: 24 h. Column chromatography eluent: DCM/MeOH (100 : 2), R_f = 0.2. Yield = 41% (based on **2d**), yellow solid. ^{1}H NMR (400 MHz, C_6D_6): δ 8.47 (s, 1H), 8.12 (s, 1H), 8.04 (d, J = 3.2 Hz, 1H), 7.77 (s, 1H), 7.34 (d, J = 7.8 Hz, 1H), 6.60 (dd, J = 6.9, 5.5 Hz, 1H), 1.09 (s, 12H); ^{13}C NMR (101 MHz, C_6D_6): δ 155.9, 149.9, 146.9, 138.8, 133.8, 130.3, 128.9, 124.2, 123.0, 121.7, 83.8, 24.5; ^{11}B NMR (128 MHz, C_6D_6): δ 29.9. HRMS (ESI+): m/z calcd for $C_{17}H_{20}BBrNO_3$ 376.0717; found 376.0726. For crystallographic data, see page S17.

2-(3-methoxy-5-(naphthalen-2-ylthio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4i**)



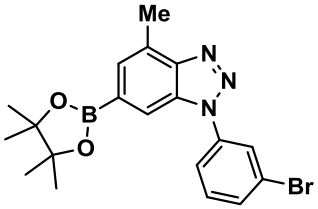
Aryne precursor: **2c**, capture reagent: 2-Naphtalenethiol (48 mg, 0.3 mmol, 1.5 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), reaction temperature: 60 °C, reaction time: 7 h. Column chromatography eluent: pentane/Et_2O (19 : 1), R_f = 0.35. Yield = 74% (based on **2c**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.71 (m, 4H), 7.56 (s, 1H), 7.50 – 7.43 (m, 2H), 7.41 (d, J = 8.6 Hz, 1H), 7.26 (d, J = 1.7 Hz, 1H), 7.00 (s, 1H), 3.77 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 136.3, 133.8, 133.3, 132.2, 130.1, 129.4, 128.8, 128.5, 127.7, 127.4, 126.5, 126.1, 120.3, 118.1, 84.1, 55.4, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0. HRMS (ESI+): m/z calcd for $C_{23}H_{25}BNaO_3S$ 415.1514; found 415.1508.

2-(8-methoxy-1,4-dihydro-1,4-epoxynaphthalen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4j**)



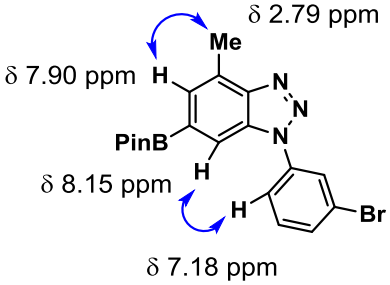
Aryne precursor: **2c**, capture reagent: Furan (68 mg, 1 mmol, 5 equiv.), CsF (91 mg, 0.6 mmol, 3 equiv.), reaction temperature: 40 °C, reaction time: 17h h. Column chromatography eluent: pentane/Et_2O (6 : 1), R_f = 0.2. Yield = 83% (based on **2c**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H), 7.07 (s, 1H), 7.07 – 6.99 (m, 2H), 5.94 (s, 1H), 5.69 (s, 1H), 3.87 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 150.9, 143.1, 142.5, 138.7, 119.2, 116.8, 83.7, 82.4, 79.9, 55.62, 24.8, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5. HRMS (ESI+): m/z calcd for $C_{17}H_{21}BNaO_4$ 323.1428; found 323.1431.

1-(3-bromophenyl)-4-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[d][1,2,3]triazole (**4k**)



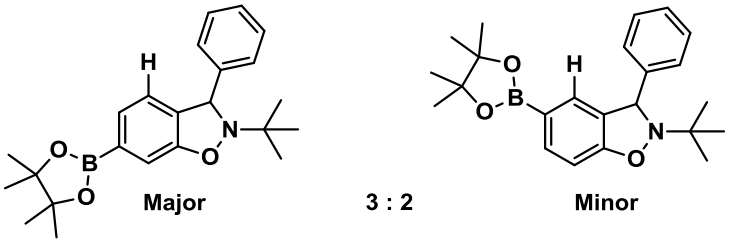
Aryne precursor: **2b**, capture reagent: 1-azido-3-bromobenzene (0.5 M in *tert*-butyl methyl ether) (0.6 mL, 59 mg, 0.3 mmol, 1.5 equiv.), CsF (152 mg, 1 mmol, 5 equiv.), reaction temperature: 60 °C, reaction time: 6 h. Column chromatography eluent: pentane/Et_2O (8 : 1), R_f = 0.3. Yield = 44% (based on **2b**), colorless solid. ^{1}H NMR (400 MHz, c_6d_6): δ 8.15 (s, 1H), 7.90 (s, 1H), 7.81 (dd, J = 1.7, 1.7 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 6.52 (t, J = 8.1 Hz, 1H), 2.79 (s, 3H), 1.16 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 138.2, 131.9, 131.6, 131.0, 130.4, 129.9, 126.3, 123.3, 121.6, 114.2, 84.3, 24.9, 16.6; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9. HRMS (EI+): m/z calcd for $C_{19}H_{21}BN_3O_2Br$ 413.0910; found 413.0915.

NOESY NMR analysis (see page S85) indicates only one correlation of the methyl group to an ArH signal, plus a correlation between the two rings, as indicated below:



2-(tert-butyl)-3-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzo[d]isoxazole (**4l**)

Aryne precursor: **2a**, capture reagent: benzylidene-tert-butylamine *N*-oxide (53 mg, 0.3 mmol, 1.5 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 60 °C, reaction time: 22 h. Column chromatography eluent: pentane/Et_2O (40 : 1), R_f = 0.3. Yield = 70% (based on **2a**), colorless solid. The regioisomers were identified by C-H correlation NMR. See page S89.



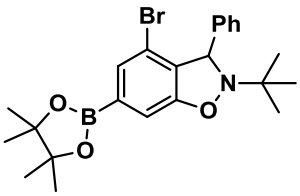
Major regioisomer: ^{1}H NMR (400 MHz, C_6D_6): 7.64 (s, 1H), 7.59 (dd, J = 7.4, 0.8 Hz, 1H), 7.35 – 7.28 (m, 2H, partially obscured by minor regioisomer), 7.08 – 7.02 (m, 2H), 7.02 – 6.95 (m, 1H, partially obscured by minor regioisomer), 6.76 (dd, J = 7.4, 0.6 Hz, 1H), 5.36 (s, 1H), 1.02 (s, 9H, partially obscured by minor regioisomer), 1.01 (s, 12H, partially obscured by minor regioisomer); ^{13}C NMR (101 MHz, C_6D_6): δ 156.3, 144.2, 133.5, 128.4, 127.7, 127.1, 127.2, 123.2, 112.6, 83.4, 67.0, 60.5, 25.1, 25.1, 24.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

Minor regioisomer: 2-(tert-butyl)-3-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzo[d]isoxazole

^{1}H NMR (400 MHz, C_6D_6): δ 7.89 (dd, J = 8.7, 1.0 Hz, 1H), 7.74 (s, 1H), 7.35 – 7.28 (m, 2H, partially obscured by major regioisomer), 7.02 – 6.95 (m, 2H, partially obscured by major regioisomer), 6.95 – 6.89 (m, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.40 (s, 1H), 1.02 (s, 9H, partially obscured by major

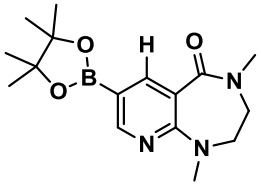
regioisomer), 1.01 (s, 12H, partially obscured by major regioisomer); ^{13}C NMR (101 MHz, C_6D_6): δ 159.0, 144.2, 136.4, 130.7, 130.2, 128.4, 127.3, 127.1, 106.3, 83.1, 66.7, 60.6, 24.6, 24.5, 24.5; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.
Both isomers: HRMS (EI+): m/z calcd for $C_{23}H_{30}BNO_3$ 379.2319; found 379.2314.

4-bromo-2-(tert-butyl)-3-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydrobenzo[d]isoxazole (**4m**)



Aryne precursor: **2d**, capture reagent: Benzylidene-tert-butylamine-*N*-oxide (53 mg, 0.3 mmol, 1.5 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 60 °C, reaction time: 30h. Column chromatography eluent: pentane/Et_2O (40 : 1), R_f = 0.2. Yield = 45% (based on **2d**), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.33 – 7.20 (m, 6H), 5.53 (s, 1H), 1.34 (s, 12H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2, 141.3, 132.4, 130.6, 128.5, 128.1, 127.6, 117.7, 111.4, 84.2, 67.8, 61.7, 25.3, 24.9, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.1. HRMS (ESI+): m/z calcd for $C_{23}H_{30}BBrNO_3$ 458.1501; found 458.1493. For crystallographic data, see page S17.

1,4-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydro-5H-pyrido[2,3-e][1,4]diazepin-5-one (**4n**)

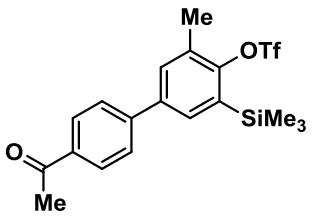


Aryne precursor: **2f**, capture reagent: pyridine *N*-oxide (114 mg, 1 mmol, 5 equiv.), CsF (122 mg, 0.8 mmol, 4 equiv.), reaction temperature: 20 °C, reaction time: 5 days. Column chromatography eluent: DCM/MeOH (19 : 1), R_f = 0.3. Yield = 39% (based on **2f**), colorless solid. The regioisomer was identified by C-H correlation NMR. See page S96. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 1.6 Hz, 1H), 8.38 (d, J = 1.6 Hz, 1H), 3.64 – 3.57 (m, 2H), 3.55 – 3.48 (m, 2H), 3.15 (s, 3H), 3.10 (s, 3H), 1.29 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.1, 157.0, 156.6, 147.3, 117.5, 83.6, 55.8, 47.7, 38.8, 35.5, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7. HRMS (EI+): m/z calcd for $C_{16}H_{24}N_3O_3B$ 317.1911; found 317.1919.

4 Suzuki-Miyaura Reactions

A 6 mL glass flask equipped with a Teflon cap and magnetic stirrer was charged with the appropriate boronate (0.2 mmol, 1 equiv.), aryl bromide (0.24 mmol, 1.2 equiv.), $Pd(OAc)_2$ (2 mg, 0.004 mmol, 2 mol%), X-Phos (3.8 mg, 0.008 mmol, 4 mol%) and K_3PO_4 (85 mg, 0.4 mmol, 2 equiv.). The flask was evacuated and backfilled with argon. Toluene (1 mL) and H_2O (0.1 ml) were added and the resulting suspension was stirred for 18 h at 80 °C. The reaction mixture was diluted with Et_2O (20 mL) and washed with brine (15 ml), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography using the indicated eluent system.

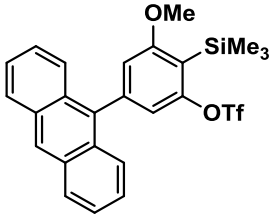
4'-acetyl-3-methyl-5-(trimethylsilyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (**5a**)



Boronate: **2b**, coupling partner: 4-bromoacetophenone (48 mg, 0.24 mmol). Column chromatography eluent: pentane/Et_2O (18 : 1), R_f = 0.2. Yield = 86% (based on **2b**), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 2.3 Hz, 1H), 7.51 (d, J = 2.3 Hz, 1H), 2.65 (s, 3H), 2.46 (s, 3H), 0.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.5, 151.0, 144.3, 139.6, 136.3, 135.6,

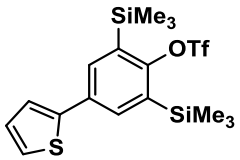
133.3, 132.5, 131.9, 128.9, 127.4, 118.6 (q, J_{CF} = 319.9 Hz), 26.7, 17.5 (m), 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.3. HRMS (EI+): m/z calcd for $C_{19}H_{21}O_4F_3SSi$ 430.0882; found 430.0879.

5-(anthracen-9-yl)-3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**5b**)



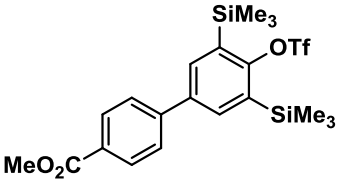
Boronate: **2c**, coupling partner: 9-bromoanthracene (62 mg, 0.24 mmol). Column chromatography eluent: pentane/Et_2O (18 : 1), R_f = 0.2. Yield = 97% (based on **2c**), yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.44 – 7.36 (m, 2H), 7.03 (s, 1H), 6.89 (d, J = 0.7 Hz, 1H), 3.78 (s, 3H), 0.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 154.6, 143.0, 134.6, 131.2, 129.8, 128.4, 127.3, 126.1, 125.9, 125.3, 120.1, 118.6 (q, J_{CF} = 320.9 Hz), 115.9 (m), 112.6, 55.7, 0.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.6. HRMS (EI+): m/z calcd for $C_{25}H_{23}O_4F_3SSi$ 504.1038; found 504.1024.

4-(thiophen-2-yl)-2,6-bis(trimethylsilyl)phenyl trifluoromethanesulfonate (**5c**)



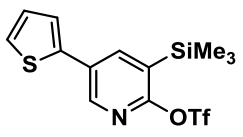
Boronate: **2e**, coupling partner: 2-bromothiophene (39 mg, 0.24 mmol). Column chromatography eluent: pentane, R_f = 0.3. Yield = 80% (based on **2e**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 2H), 7.34 (d, J = 5.1 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 7.11 (dd, J = 5.1, 3.6 Hz, 1H), 0.41 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1, 142.7, 135.6, 135.6, 133.4, 128.2, 125.7, 124.1, 118.4 (q, J_{CF} = 320.1 Hz), 0.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.3. HRMS (EI+): m/z calcd for $C_{17}H_{23}O_3F_3Si_2S_2$ 452.0579; found 452.0571.

Methyl 4'-(((trifluoromethyl)sulfonyl)oxy)-3',5'-bis(trimethylsilyl)-[1,1'-biphenyl]-4-carboxylate (**5d**)



Boronate **2e**, coupling partner: Methyl-4-bromobenzoate (52 mg, 0.24 mmol). Column chromatography eluent: pentane/Et_2O (75 : 1), R_f = 0.2. Yield = 84% (based on **2e**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.2 Hz, 2H), 7.75 (s, 2H), 7.61 (d, J = 8.3 Hz, 2H), 3.96 (s, 3H), 0.42 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.8, 154.9, 144.4, 139.0, 137.0, 135.7, 130.2, 129.4, 127.3, 118.4 (q, J_{CF} = 320.1 Hz), 52.2, 0.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.3. HRMS (EI+): m/z calcd for $C_{21}H_{27}O_5F_3Si_2S$ 504.1070; found 504.1059.

5-(thiophen-2-yl)-3-(trimethylsilyl)pyridin-2-yl trifluoromethanesulfonate (**5e**)



Boronate **2f**, coupling partner: 2-bromothiophene (39 mg, 0.24 mmol). Column chromatography eluent: pentane/Et_2O (100 : 1), R_f = 0.3. Yield = 60% (based on **2f**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 2.6 Hz, 1H), 8.02 (d, J = 2.6 Hz, 1H), 7.40 (dd, J = 5.1, 1.0 Hz, 1H), 7.33 (dd, J = 3.6, 1.0 Hz, 1H), 7.14 (dd, J = 5.1, 3.7 Hz, 1H), 0.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.7, 145.5, 143.9, 138.7, 130.3, 128.4, 126.7, 125.4, 124.9, 118.4 (q, J_{CF} = 320.5 Hz), -1.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.7. HRMS (EI+): m/z calcd for $C_{13}H_{14}NO_3F_3SiS_2$ 381.0137; found 381.0140.

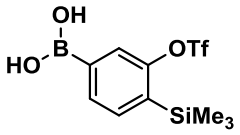
5 Deprotection of B(pin) Boronates

5.1 General Procedure

Based on a modified literature procedure.[6] Diethanolamine (115 µL, 1.2 mmol, 1.2 equiv.) was added at room temperature to a stirring solution of boronate **2** (1 mmol) in Et_2O (10 mL) in a round-bottomed flask under air. The mixture was stirred vigorously for 18 h and the resulting colorless precipitate collected by filtration, washed with Et_2O (2 x 5 mL) and dried with filter paper. The residue was resuspended in Et_2O (20 mL) under air, treated with 0.5 M $HCl_{(aq)}$ (8 mL, 4 mmol, 4 equiv.) and stirred vigorously for 1 to 3 h (or until the reaction mixture became homogeneous). The solution was then diluted with Et_2O (20 mL) and washed with brine (2 × 20 mL). The aqueous layer was extracted once more with Et_2O (30 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated under reduced pressure to afford the products as a colourless solid.

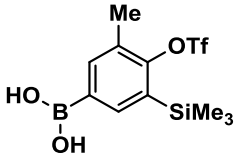
5.2 Data for Deprotected Boronates

(4-(((trifluoromethyl)sulfonyl)oxy)-3-(trimethylsilyl)phenyl)boronic acid (**6a**)



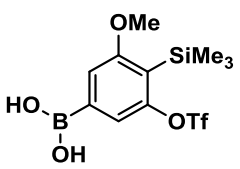
10 to 1 mixture of boronic acid and boroxine. Yield = 59% (based on **2a**), colorless solid. The regioisomer was identified by Si-H correlation NMR. See page S116. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 7.2 Hz, 1H), 8.09 (s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 0.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3, 138.6, 136.3, 134.1, 125.6, 118.5 (q, J_{CF} = 319.9 Hz), -0.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.1; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.5. HRMS (CI+): m/z calcd for $C_{10}H_{15}BO_5F_3SSi$ 343.0455; found 343.0461. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 0.46 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -74.1; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.5.

(3-methyl-4-(((trifluoromethyl)sulfonyl)oxy)-5-(trimethylsilyl)phenyl)boronic acid (**6b**)



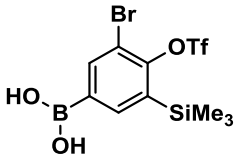
7 to 2 mixture of boronic acid and boroxine. Yield = 88% (based on **2b**), colorless solid. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.08 (s, 1H), 2.51 (s, 3H), 0.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.7, 142.3, 141.0, 134.5, 131.0, 118.6 (q, J_{CF} = 319.7 Hz), 17.4, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.2; ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.0. HRMS (CI+): m/z calcd for $C_{11}H_{17}BO_5F_3SSi$ 357.0611; found 357.0612. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.66 (s, 1H), 2.4 (s, 3H), 0.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 140.0, 139.2, 134.2, 130.7, 118.6 (q, J_{CF} = 319.7 Hz), 30.9, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.3; ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.0.

(3-methoxy-5-(((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)boronic acid (**6c**)



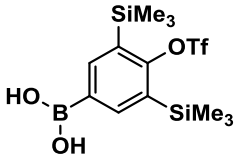
5 to 1 mixture of boronic acid and boroxine. Yield = 84% (based on **2c**) , colorless solid. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.56 (s, 1H), 3.95 (s, 3H), 0.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 154.8, 126.8, 119.1, 118.7 (q, J_{CF} = 320.7 Hz), 115.0, 55.4, 0.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.0; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.6. HRMS (CI+): m/z calcd for $C_{11}H_{17}BO_6F_3SSi$ 373.0560; found 373.0563. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 1H), 7.19 (s, 1H), 3.87 (s, 3H), 0.37 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.8; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.6.

(3-bromo-4-(((trifluoromethyl)sulfonyl)oxy)-5-(trimethylsilyl)phenyl)boronic acid (**6d**)



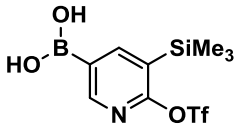
13 to 1 mixture of boronic acid and boroxine. Yield = 80% (based on **2d**), colorless solid. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 1.6 Hz, 1H), 8.32 (d, J = 1.6 Hz, 1H), 0.50 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 143.2, 142.7, 137.8, 118.6 (q, J_{CF} = 321.0 Hz), 116.9, 0.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.4; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.3. HRMS (CI+): m/z calcd for $C_{10}H_{14}BO_5F_3SSiBr$ 420.9560; found 420.9555. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.86 (s, 1H), 0.42 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.6; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.3.

(4-(((trifluoromethyl)sulfonyl)oxy)-3,5-bis(trimethylsilyl)phenyl)boronic acid (**6e**)



6 to 1 mixture of boronic acid and boroxine. Yield = 53% (based on **2e**), colorless solid. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 2H), 0.46 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 145.8, 134.6, 118.4 (q, J_{CF} = 320.2 Hz), 0.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.3; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.2. HRMS (CI+): m/z calcd for $C_{13}H_{23}BO_5F_3SSi_2$ 415.0850; found 415.0844. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 2H), 0.46 (s, 18H, partially obscured by boronic acid); ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.3; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.2.

(6-(((trifluoromethyl)sulfonyl)oxy)-5-(trimethylsilyl)pyridin-3-yl)boronic acid (**6f**)

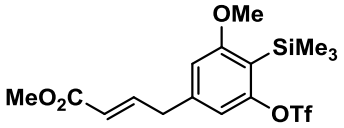


10 to 1 mixture of boronic acid and boroxine. Yield = 85% (based on **2f**), colorless solid. **Boronic acid**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 8.61 (s, 1H), 0.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 156.2, 154.1, 124.7, 118.4 (q, J_{CF} = 320.5 Hz), -1.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.0; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.7. HRMS: Product degrades. **Boroxine**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H, partially obscured by boronic acid), 8.26 (d, J_{CF} = 1 Hz, 1H), 0.43 (s, 9H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.0; ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.7.

6 Derivatization of Boronic Acids

6.1 Tsuji-Trost Coupling

Methyl-4-(3-methoxy-5-(((trifluoromethyl)sulfonyl)oxy)-4-(trimethylsilyl)phenyl)but-2-enoate (**7a**)

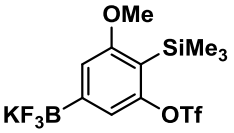


A 6 mL glass flask equipped with a Teflon cap and magnetic stirrer was charged with boronic acid **6c** (74 mg, 0.2 mmol, 1.2 equiv.), $Pd(OAc)_2$ (1 mg, 0.005 mmol, 2.5 mol%) and KF (46 mg, 0.8 mmol, 4 equiv.). The flask was evacuated and backfilled with argon. 1,4-dioxane (1 mL) was added then methyl-4-bromocrotonate (43 mg, 0.24 mmol, 1.2 equiv.). The resulting suspension was stirred for 18 h at 20 °C. The reaction mixture was diluted with Et_2O (20 mL) and washed with brine (2 × 15 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography; eluent system: pentane/Et_2O (8 : 1). R_f = 0.2. Yield = 65% (based on **6c**), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (dt, J = 15.6, 6.7 Hz, 1H), 6.75 (s, 1H), 6.62 (s, 1H), 5.84 (dt, J = 15.6, 1.4 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.52 (dd, J = 6.7, 1.4 Hz, 2H), 0.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 165.7, 154.7, 145.7, 142.1, 122.7, 119.1, 118.6 (q, J_{CF} = 320.8 Hz), 113.2 (q, J_{CF} = 1.4 Hz), 110.0, 55.6, 51.6, 38.2, 0.7; ^{19}F

NMR (376 MHz, $CDCl_3$): δ -72.8. HRMS (EI+): m/z calcd for $C_{16}H_{21}O_6F_3SiS$ 426.0780; found 426.0794.

6.2 Trifluoroboronate Potassium Salt

3-methoxy-5-(trifluoroboranyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate potassium salt (**7b**)

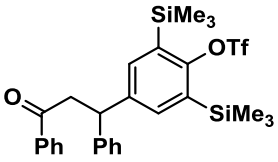


Synthesis based on a literature procedure.[7] Boronic acid **6c** (186 mg, 0.5 mmol). Yield = 99% (based on **6c**), colorless solid. ^{1}H NMR (400 MHz, CD_3CN): δ 7.07 (s, 1H), 6.95 (s, 1H), 3.83 (s, 3H), 0.33 (s, 10H); ^{13}C NMR (101 MHz, CD_3CN): δ 165.8, 155.4, 119.6 (q, J_{CF} = 319.8 Hz), 117.1, 116.0 – 115.9 (m), 113.8 (q, J_{CF} = 1.6 Hz), 77.4, 56.1, 1.1; ^{19}F NMR (376 MHz, CD_3CN): δ -73.8, -143.5 (m); ^{11}B NMR (128 MHz, CD_3CN): δ 2.64 (q, J = 39.7 Hz). HRMS (ESI+): m/z calcd for $C_{11}H_{14}BF_6O_4SSi$ 395.0387; found 395.0377.

6.3 Rh-Catalyzed Conjugate Addition

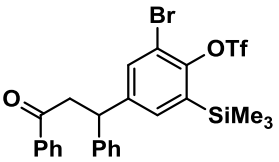
A 6 mL glass flask equipped with a Teflon cap and magnetic stirrer was charged with the appropriate boronic acid (0.2 mmol, 1.2 equiv.), chalcone (42 mg, 0.2 mmol, 1 equiv.), [{RhCl(COD)}$_2$] (3 mg, 0.006 mmol, 3 mol%) and $NaHCO_3$ (3.4 mg, 0.04 mmol, 0.2 equiv.). The flask was evacuated and backfilled with argon. 1,4-dioxane (2 mL) and H_2O (0.4 ml) were added and the resulting suspension was stirred for 24 h at 50 °C. The crude mixture was purified by silica gel flash chromatography using the indicated eluent system.

4-(3-oxo-1,3-diphenylpropyl)-2,6-bis(trimethylsilyl)phenyl trifluoromethanesulfonate (**7c**)



Boronic acid **6e** (99 mg). Column chromatography eluent: pentane/Et_2O (50 : 1), R_f = 0.2. Yield = 86% (based on **6e**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.89 (m, 2H), 7.63 – 7.53 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 (s, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 4.87 (t, J = 7.3 Hz, 1H), 3.73 (dd, J = 16.9, 7.3 Hz, 1H), 3.69 (dd, J = 16.9, 7.3 Hz, 1H), 0.28 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.8, 153.4, 143.2, 142.8, 137.7, 136.9, 134.8, 133.2, 128.7, 128.6, 128.0, 127.7, 126.7, 118.4 (q, J_{CF} = 320.0 Hz), 45.4, 44.7, 0.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.5. HRMS (EI+): m/z calcd for $C_{28}H_{33}O_4F_3Si_2S$ 578.1590; found 578.1586.

2-bromo-4-(3-oxo-1,3-diphenylpropyl)-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**7d**)



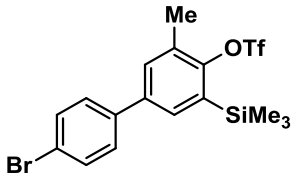
Boronic acid **6b** (101 mg). Column chromatography eluent: pentane/Et_2O (40 : 1), R_f = 0.2. Yield = 93% (based on **6b**), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 2H), 7.59 – 7.53 (m, 1H), 7.51 (d, J = 2.3 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.35 (d, J = 2.3 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.22 (m, 3H), 4.83 (t, J = 7.2 Hz, 1H), 3.73 (dd, J = 17.3, 7.2 Hz, 1H), 3.67 (dd, J = 17.3, 7.2 Hz, 1H), 0.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.2, 147.2, 145.5, 142.5, 137.4, 136.7, 135.2, 135.0, 133.4, 128.9, 128.7, 128.0, 127.7, 127.0, 118.5 (q, J_{CF} = 320.8 Hz), 116.5, 45.0, 44.5, -0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.8. HRMS (EI+): m/z calcd for $C_{25}H_{24}O_4BrSSiF_3$ 584.0300; found 584.0309.

6.4 Iodonium Suzuki Coupling

A 6 mL glass flask equipped with a Teflon cap and magnetic stirrer was charged with the appropriate boronic acid (0.2 mmol, 1 equiv.), iodonium salt (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (1 mg, 0.004 mmol,

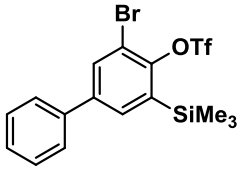
2 mol%) and Na_2CO_3 (25 mg, 0.24 mmol, 0.2 equiv.). The flask was evacuated and backfilled with argon. Diglyme (0.8 mL) and H_2O (0.2 ml) were added and the resulting suspension was stirred for 20 h at 20 °C. The reaction mixture was diluted with Et_2O (20 mL) and washed with a saturated solution of NH_4Cl (2 × 15 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography using the indicated eluent system.

4'-bromo-3-methyl-5-(trimethylsilyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (**7e**)



Boronic acid **6b** (71 mg), bis(4-bromophenyl)iodonium triflate (118 mg). Column chromatography eluent: pentane/Et_2O (40 : 1), R_f = 0.2. Yield = 67% (based on **6b**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.55 (m, 2H), 7.54 – 7.51 (dd, J = 2.4, 0.5 Hz, 1H), 7.45 (dd, J = 2.4, 0.5 Hz, 1H), 7.44 – 7.38 (m, 2H), 2.46 (s, 3H), 0.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7, 139.7, 138.7, 135.5, 132.9, 132.2, 132.0, 131.8, 128.8, 122.2, 118.6 (q, J_{CF} = 319.8 Hz), 17.4 (q, J_{CF} = 1.4 Hz), 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.3. HRMS (EI+): m/z calcd for $C_{17}H_{18}O_3F_3BrSSi$ 465.9881; found 465.9873.

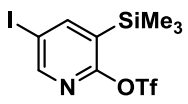
3-bromo-5-(trimethylsilyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (**7f**)



Boronic acid **6d** (84 mg), diphenyliodonium *para*-toluenesulfonate (90 mg). Column chromatography eluent: pentane. R_f = 0.4. Yield = 87% (based on **6d**), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 2.3 Hz, 1H), 7.65 (d, J = 2.3 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 1H), 0.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 142.3, 138.4, 137.8, 134.2, 129.0, 128.4, 127.2, 118.6 (q, J_{CF} = 321.0 Hz), 116.7, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.6. HRMS (EI+): m/z calcd for $C_{16}H_{16}O_3F_3SiSBr$ 451.9725; found 451.9727.

6.5 Iodination

5-iodo-3-(trimethylsilyl)pyridin-2-yl trifluoromethanesulfonate (**7g**)



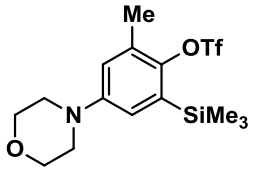
A 6 mL glass flask equipped with a Teflon cap and magnetic stirrer was charged with boronic acid **6f** (69 mg, 0.2 mmol, 1 equiv.), *N*-iodosuccinimide (135 mg, 0.6 mmol, 3 equiv.), CuI (4 mg, 0.02 mmol, 10 mol%), 1,10-phenanthroline (7 mg, 0.02 mmol, 10 mol%) and K_2CO_3 (56 mg, 0.4 mmol, 2 equiv.). The flask was evacuated and backfilled with argon. Diglyme (1 mL) was added and the resulting suspension was stirred for 16 h at 40 °C. The reaction mixture was diluted with Et_2O (20 mL) and washed with a 1 to 1 solution of saturated aqueous NH_4Cl and saturated aqueous Na_2SO_3 (15 mL) then wash with brine (10 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography; eluent system: pentane/Et_2O (50 : 1). R_f = 0.5. Yield = 93% (based on **6f**), pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, J = 2.4 Hz, 1H), 8.12 (d, J = 2.4 Hz, 1H), 0.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.0, 154.5, 154.5, 128.7, 118.4 (q, J_{CF} = 321.0 Hz), 92.0, -1.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -72.6. HRMS (EI+): m/z calcd for $C_9H_{11}NO_3F_3SiSI$ 424.9226; found 424.9220.
Note: For the identical reaction run without CuI, the conversion after 16 h is 70 %.

6.6 Chan-Lam Coupling

A 6 mL glass flask equipped with a rubber septum and magnetic stirrer was charged with the appropriate boronate (1.2 equiv.), $Cu(OAc)_2 \cdot H_2O$ (0.1 equiv.) and pre-dried 4Å molecular sieves (375 mg/mmol). The flask was evacuated and backfilled with O_2. CH_2Cl_2 (1 mL) was added and the resulting suspension was stirred for 5 min at 20 °C. Morpholine (1 equiv.) was then added and the

mixture was stirred for 20 h at 40 °C. The crude mixture was purified by silica gel flash chromatography using the indicated eluent system.

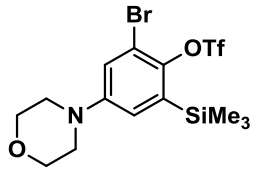
2-methyl-4-morpholino-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**7h**)



Boronic acid **6b** (71 mg, 0.2 mmol), copper (3.2 mg, 0.016 mmol), 4Å MS (75mg), morpholine (14.3 mg, 0.16 mmol). Column chromatography eluent: petroleum ether/EtOAc (10 : 1), R_f = 0.4. Yield = 93% (based on morpholine), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, J = 2.9 Hz, 1H), 6.76 (d, J = 2.9 Hz, 1H), 3.94 – 3.80 (m, 4H), 3.22 – 3.10 (m, 4H), 2.34 (s, 3H), 0.37 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 144.1, 135.1, 131.9, 120.7, 119.9, 118.6 (q, J_{CF} = 319.8 Hz), 66.7, 49.1, 17.7 (q, J_{CF} = 1.4 Hz), 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.5. HRMS (CI+): m/z calcd for $C_{15}H_{23}NO_4SSiF_3$ 398.1069; found 398.1070.

2-bromo-4-morpholino-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (**7i**)

Boronic acid **6d** (71 mg, 0.24 mmol), copper (3.2 mg, 0.02 mmol), 4Å MS (75mg), morpholine (14.3 mg, 0.2 mmol). Column chromatography eluent: pentane/Et_2O (9 : 1), R_f = 0.2. Yield = 72% (based on morpholine), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 1H), 6.92 (s, 1H), 3.85 (s, 4H), 3.17 (s, 4H), 0.39 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7, 141.3, 137.3, 121.4, 121.2, 118.5 (q, J_{CF} = 320.4 Hz), 117.0, 66.6, 48.5, 0.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.8. HRMS (EI+): m/z calcd for $C_{14}H_{19}NO_4F_3SiSBr$ 460.9940; found 460.9956.



7 Crystallographic Data

Crystal data	Compound **4m**	Compound **4h**
CCDC-No.	-	-
Empirical formula	$C_{23}H_{29}BBrNO_3$	$C_{17}H_{19}BBrNO_3$, $CHCl_3$
Formula weight	458.19	495.42
Crystal description	Colorless block	Colorless block
Crystal size	0.35 x 0.22 x 0.21	0.45 x 0.23 x 0.2
Crystal system, space group	Triclinic P_1	Orthorhombic, P b c a
Unit cell dimensions:		
a	5.9629(3)	13.0653(7)
b	9.6761(5)	11.0099(6)
c	9.6943(5)	29.9093(17)
α	83.833(3)	90
β	82.215(3)	90
Γ	89.828(3)	90
Volume	550.94(5)	4302.4(4)
Z	1	8
Calculated density	1.381 Mg/m³	1.530 Mg/m³
F(000)	238	2000
Linear absorption coefficient μ	1.889 mm^{-1}	2.301 mm^{-1}
Absorption correction	multi-scan, SADABS 2008	multi-scan, SADABS 2008
Max. and min. transmission	0.6257 and 0.7455	0.5929 and 0.7455
Unit cell determination	2.1 < Θ < 27.4°	1.4 < Θ < 27.2°
	4282 reflections used at 100K	3607 reflections used at 100K
Data collection	-	-
Temperature	100(2)K	100(2)K
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube	fine-focus sealed tube
Radiation and wavelength	MoK_α, 0.71073Å	MoK_α, 0.71073Å
Monochromator	Graphite	Graphite
Scan type	ω scans	ω scans
Θ range for data collection	2.1 < Θ < 27.4°	1.4 < Θ < 27.2°
Index ranges	$-7 \le h \le 7, -12 \le k \le 12, -12 \le l \le 12$	$-16 \le h \le 16, -14 \le k \le 11, -29 \le l \le 38$
Reflections collected / unique	8642/ 4395	34995/ 4781
Significant unique reflections	4282 with I > 2σ(I)	3607 with I > 2σ(I)
R(int), R(sigma)	0.0294, 0.0479	0.0429, 0.0583
Completeness to Θ_{max}	99.7%	99.3%
Refinement	-	-
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / parameters / restraints	4395/ 270/ 3	4781/ 249/ 0
Goodness-of-fit on F^2	1.015	1.015
Final R indices [I > 2σ(I)]	R1 = 0.0299, wR2 = 0.0623	R1 = 0.0327, wR2 = 0.0653
R indices (all data)	R1 = 0.0313, wR2 = 0.0618	R1 = 0.0557, wR2 = 0.0719
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(aP)^2]$ where $P=(F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$
Weighting scheme parameters a	0.0302	a = 0.0291, b = 2.1499
Largest Δ/σ in last cycle	0.000	0.001
Largest difference peak and hole	0.527 and -0.248 e/Å³	0.468 and -0.411 e/Å³
Structure Solution Program	SHELXS-2014 (Sheldrick, 2008)	SHELXS-2014 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-2014 (Sheldrick, 2008)	SHELXL-2014 (Sheldrick, 2008)

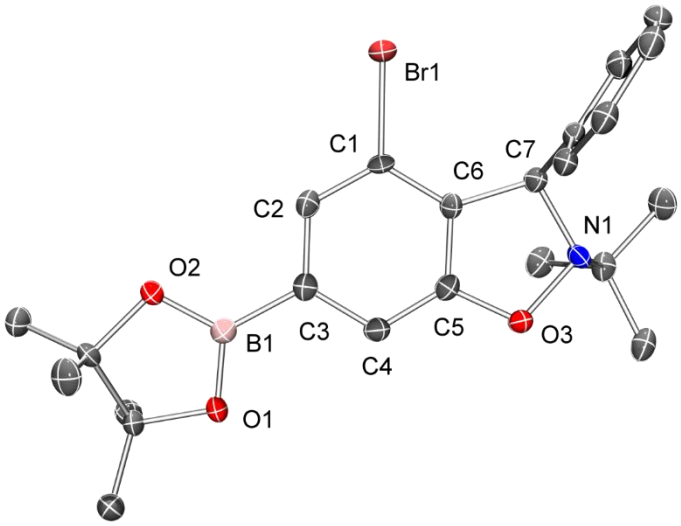


Figure S1. ORTEP drawing of **4m** at 50% probability levels. Hydrogen atoms are omitted for clarity. 4m was refined as an inversion twin with a BASF of 0.53.

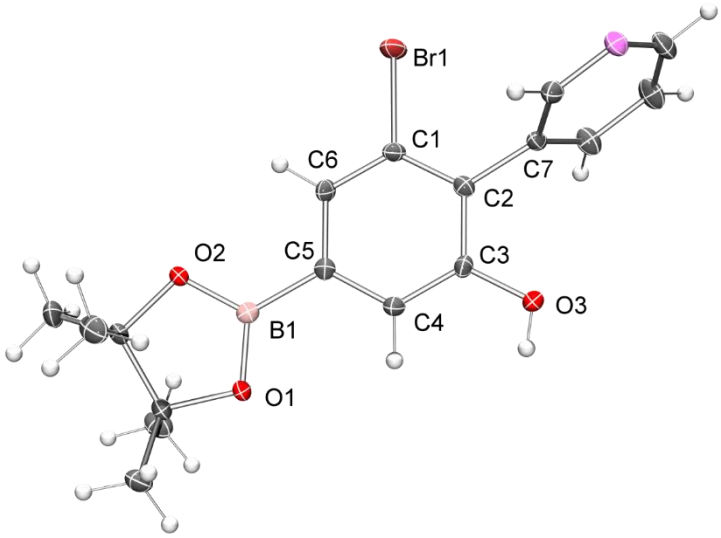


Figure S2. ORTEP drawing of **4h** at 50% probability levels. The chloroform solvate is omitted for clarity.

8 References

[1] G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112-122.
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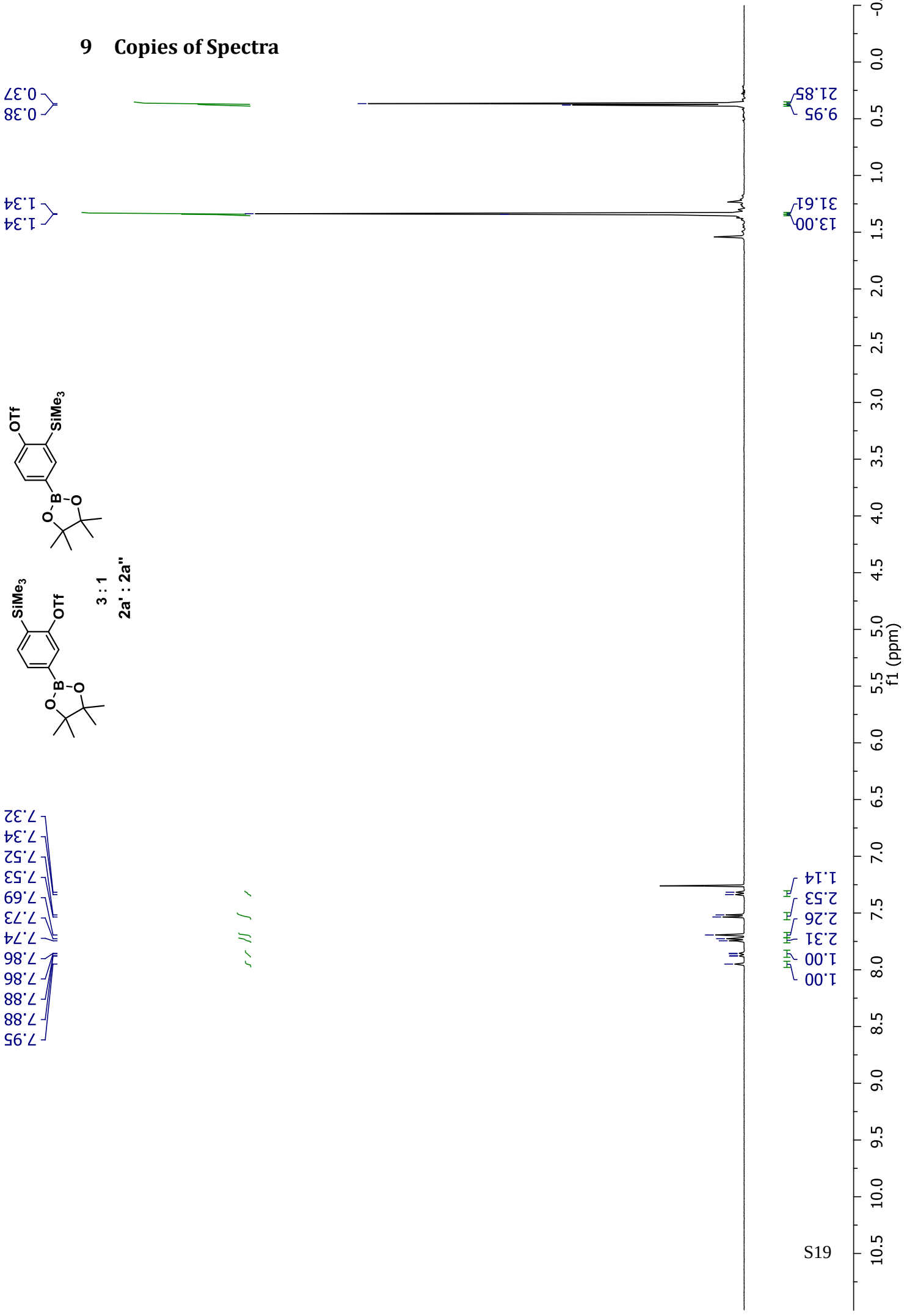
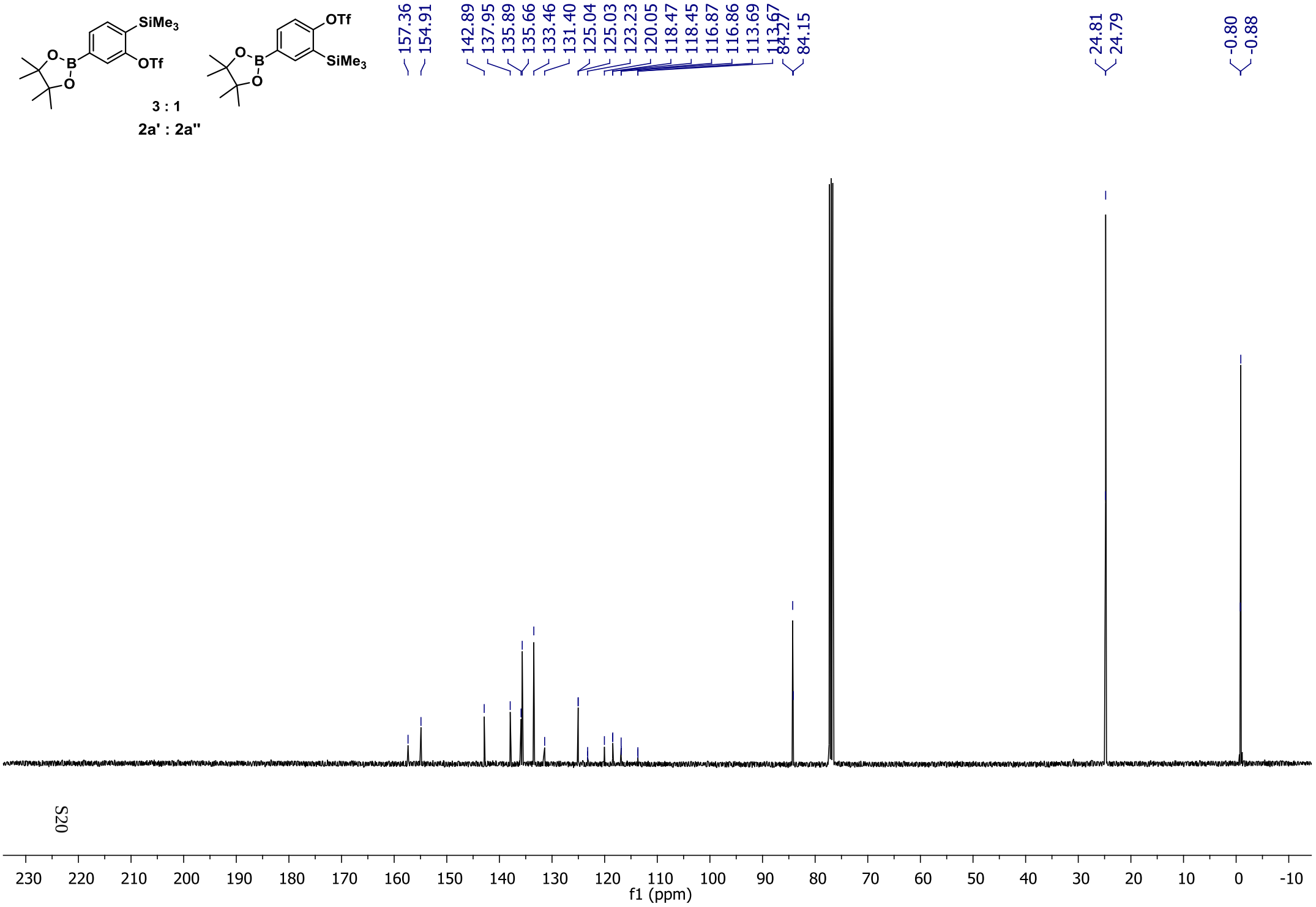
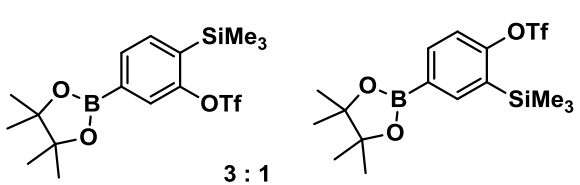
9 Copies of Spectra

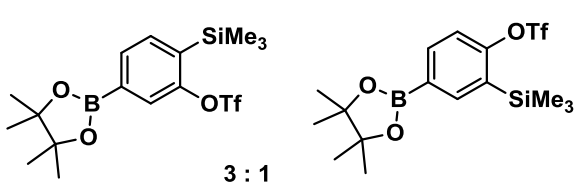



SiMe3
OTf
3 : 1
2a' : 2a''
OTf
SiMe3
157.36
154.91
142.89
137.95
135.89
135.66
133.46
131.40
125.04
125.03
123.23
120.05
118.47
118.45
116.87
116.86
113.69
113.67
84.27
84.15
24.81
24.79
-0.80
-0.88
S20
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



-73.89
-73.94

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



3 : 1

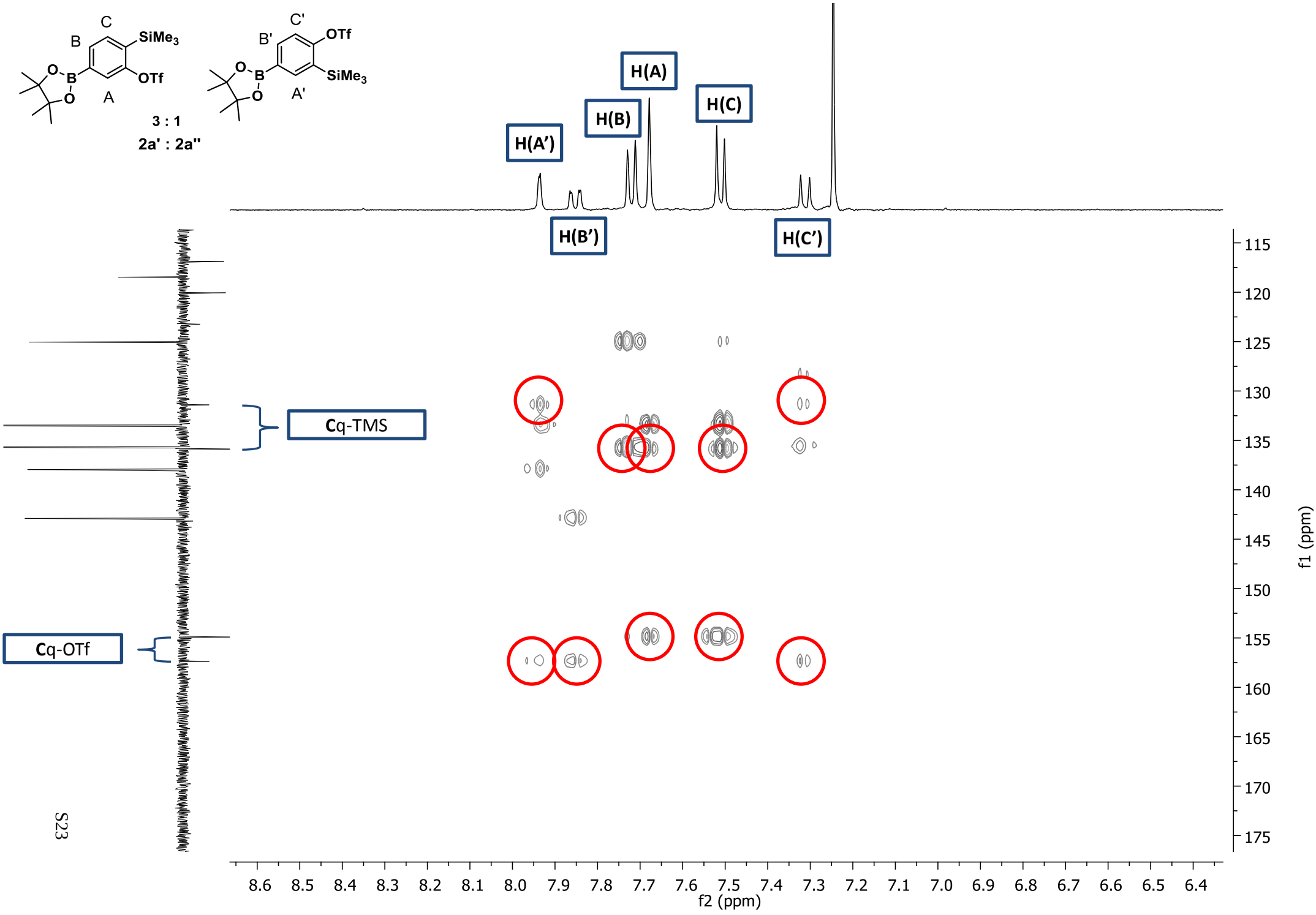
2a' : 2a''

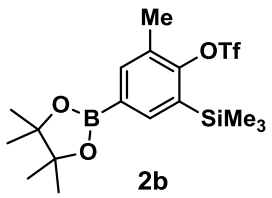
30.46

S22

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

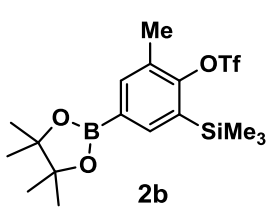
f1 (ppm)


C
B
SiMe3
O
B
O
OTf
A
C'
B'
OTf
O
B
O
SiMe3
A'
3 : 1
2a' : 2a''
H(A)
H(B)
H(C)
H(A')
H(B')
H(C')
Cq-TMS
Cq-OTf
f2 (ppm)
f1 (ppm)
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
115
120
125
130
135
140
145
150
155
160
165
170
175


Me
OTf
O
B
O
SiMe3

2b

7.83
7.75
2.39
1.35
0.40
0.93
0.94
3.00
12.77
8.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

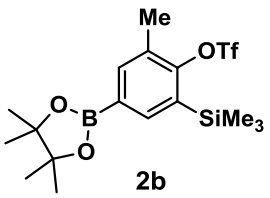


2b

153.47
141.13
140.34
133.83
130.39
123.38
120.20
117.02
113.84
84.12
24.82
17.03
17.02
17.00
0.14

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



2b

-73.38

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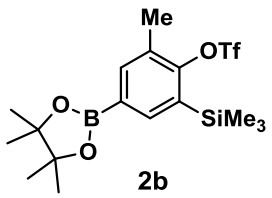
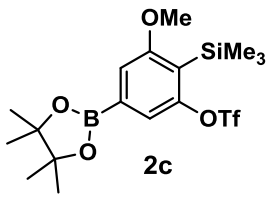
f1 (ppm)



2b

30.56

f1 (ppm)


OMe
SiMe3
O
B
O
OTf

2c

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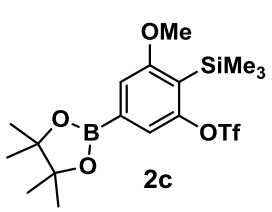
3.87
1.34
0.36
0.90
0.94
3.00
12.58
9.10
S28
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OMe
SiMe3
O
B
O
OTf

2c

165.19
154.48
124.41
123.56
120.37
118.83
118.81
117.18
115.08
113.99
84.47
55.86
24.96
0.86
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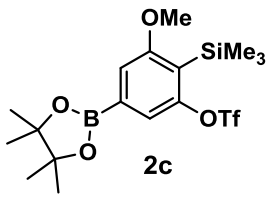
f1 (ppm)



2c

-72.80

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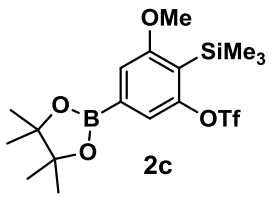
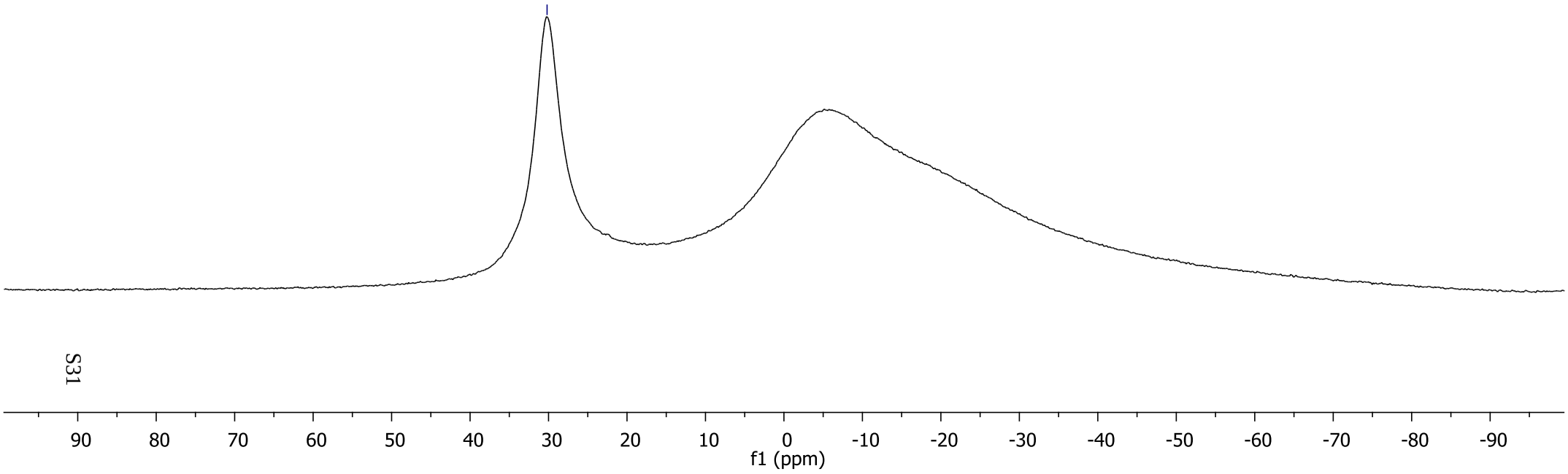
f1 (ppm)


OMe
SiMe3
O
B
O
OTf

2c

30.19


90
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70
60
50
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0
-10
-20
-30
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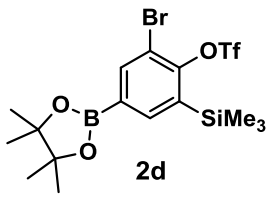
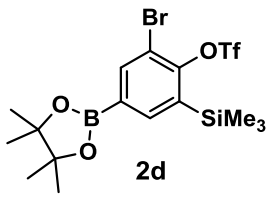
-50
-60
-70
-80
-90
f1 (ppm)

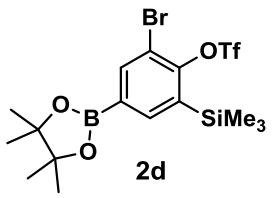


2d


Br
OTf
O
B
O
SiMe3

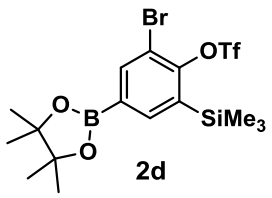
2d

150.81
142.07
141.96
136.88
123.36
120.17
116.98
116.12
113.79
84.49
24.80
0.10
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
OTf
O
B
O
SiMe3

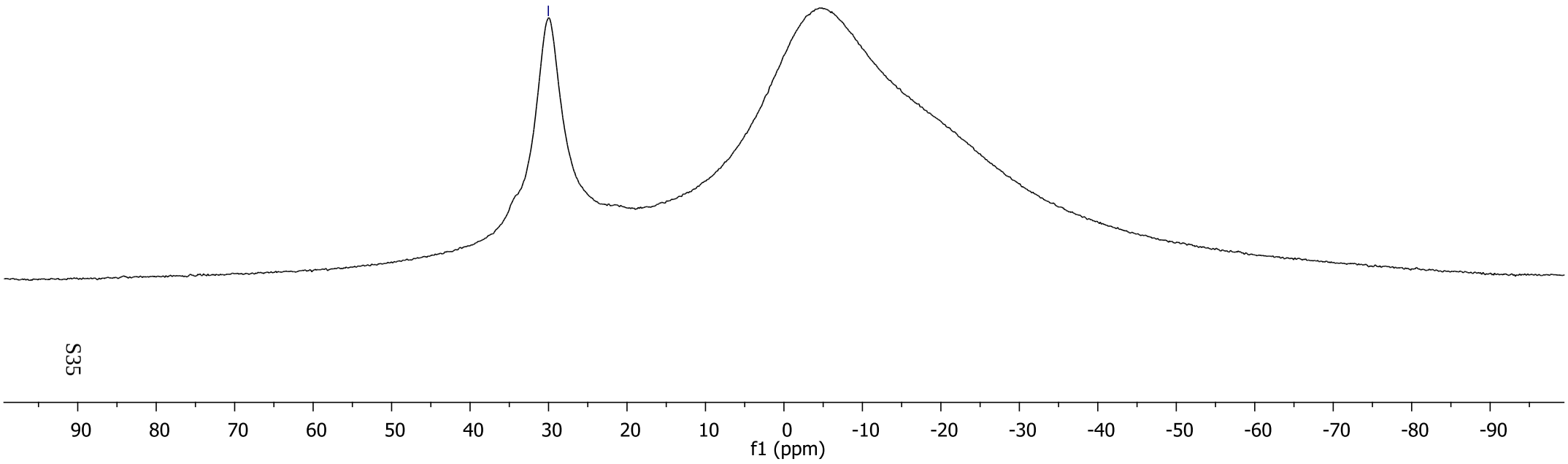
2d

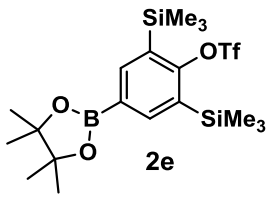
-71.60
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


Br
OTf
O
B
O
SiMe3

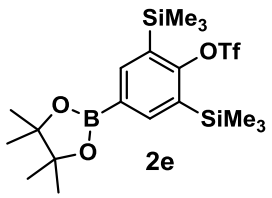
2d

30.02


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


SiMe3
OTf
SiMe3
O
B
O
2e

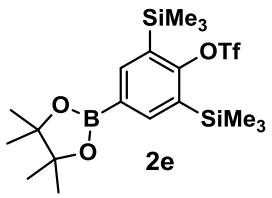
7.99
1.35
0.37
2.00
13.43
18.33
S36
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



157.45
144.87
142.07
141.97
133.74
123.18
120.00
116.81
113.63
84.07
24.84
0.39

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

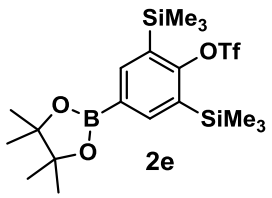


2e

-72.35

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)



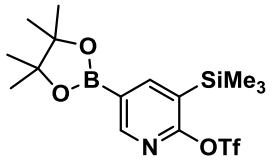
2e

30.55

S39

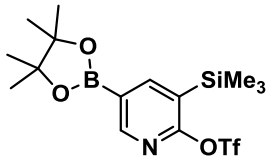
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)


O
B
O
SiMe3
N
OTf

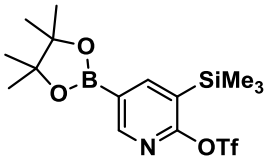
2f

8.65
8.65
8.24
8.23
1.34
0.37
0.95
1.01
14.00
9.49
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
B
O
SiMe3
N
OTf

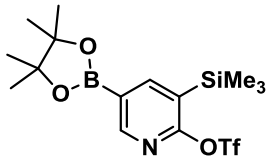
2f

162.77
155.17
153.17
123.78
123.24
120.05
116.87
113.68
84.48
24.78
-1.54
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
B
O
SiMe3
N
OTf

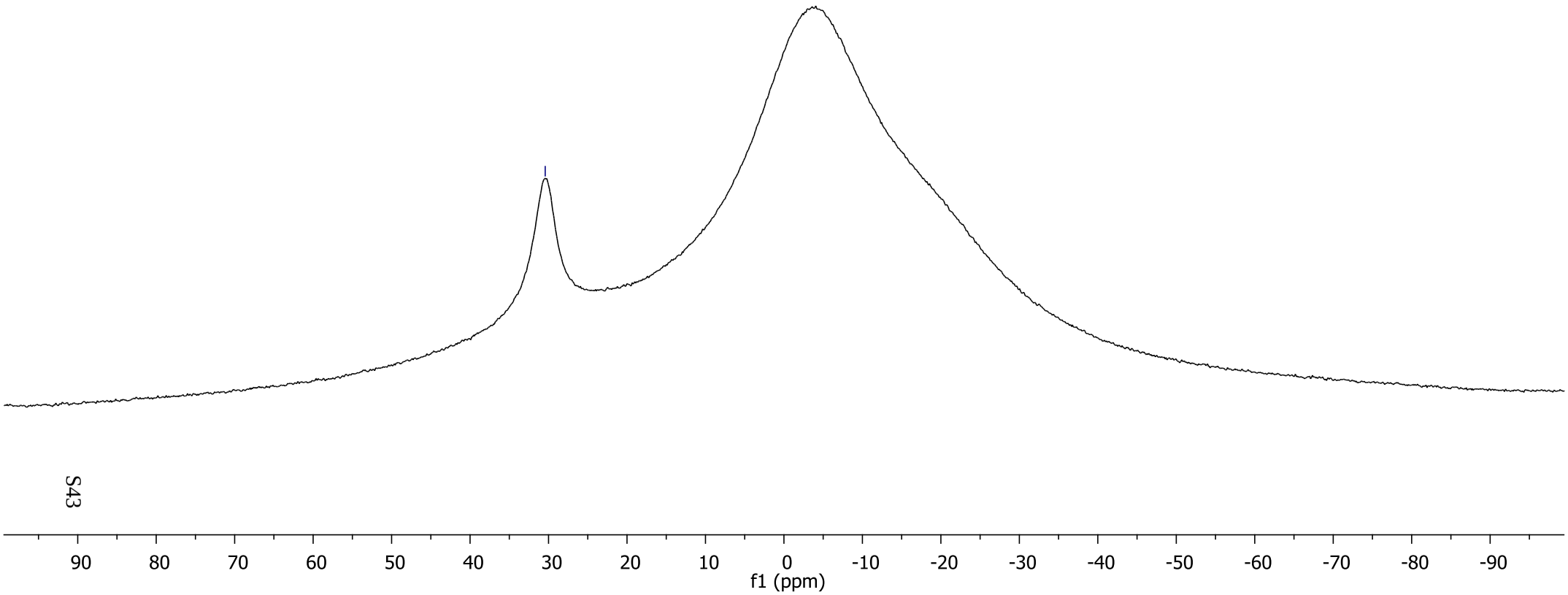
2f

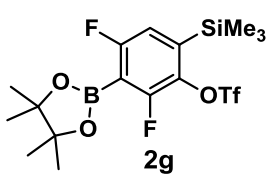
-72.82
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


O
B
O
SiMe3
N
OTf

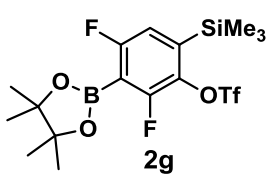
2f

30.42


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

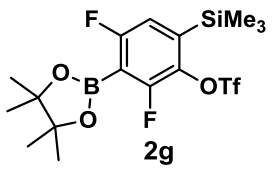


2g


F
SiMe3
O
B
OTf
O
F

2g

165.56
165.45
163.01
162.91
157.90
157.77
155.31
155.19
141.74
141.72
141.68
141.65
123.39
120.20
117.14
117.10
117.01
116.89
116.86
113.82
84.64
24.67
-0.82
S45
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

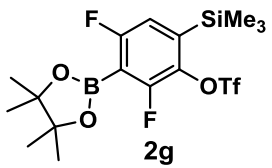


2g

-71.99
-72.05
-99.88
-99.89
-99.89
-99.90
-99.92
-112.06
-112.08
-112.12
-112.13

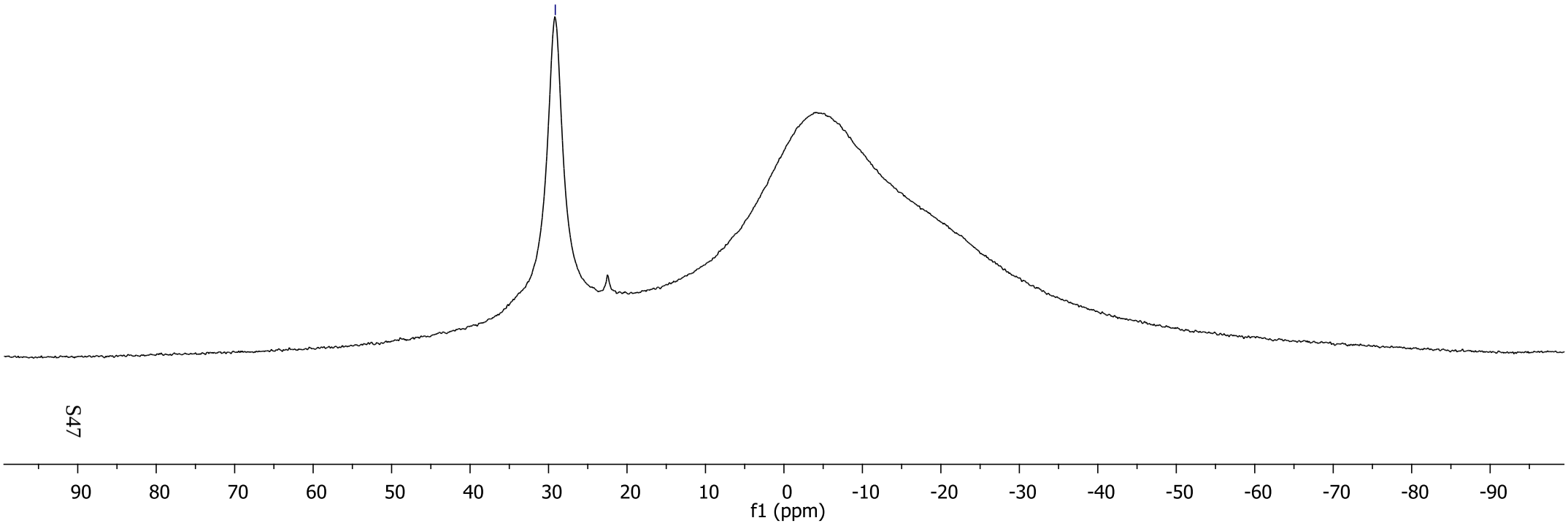
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

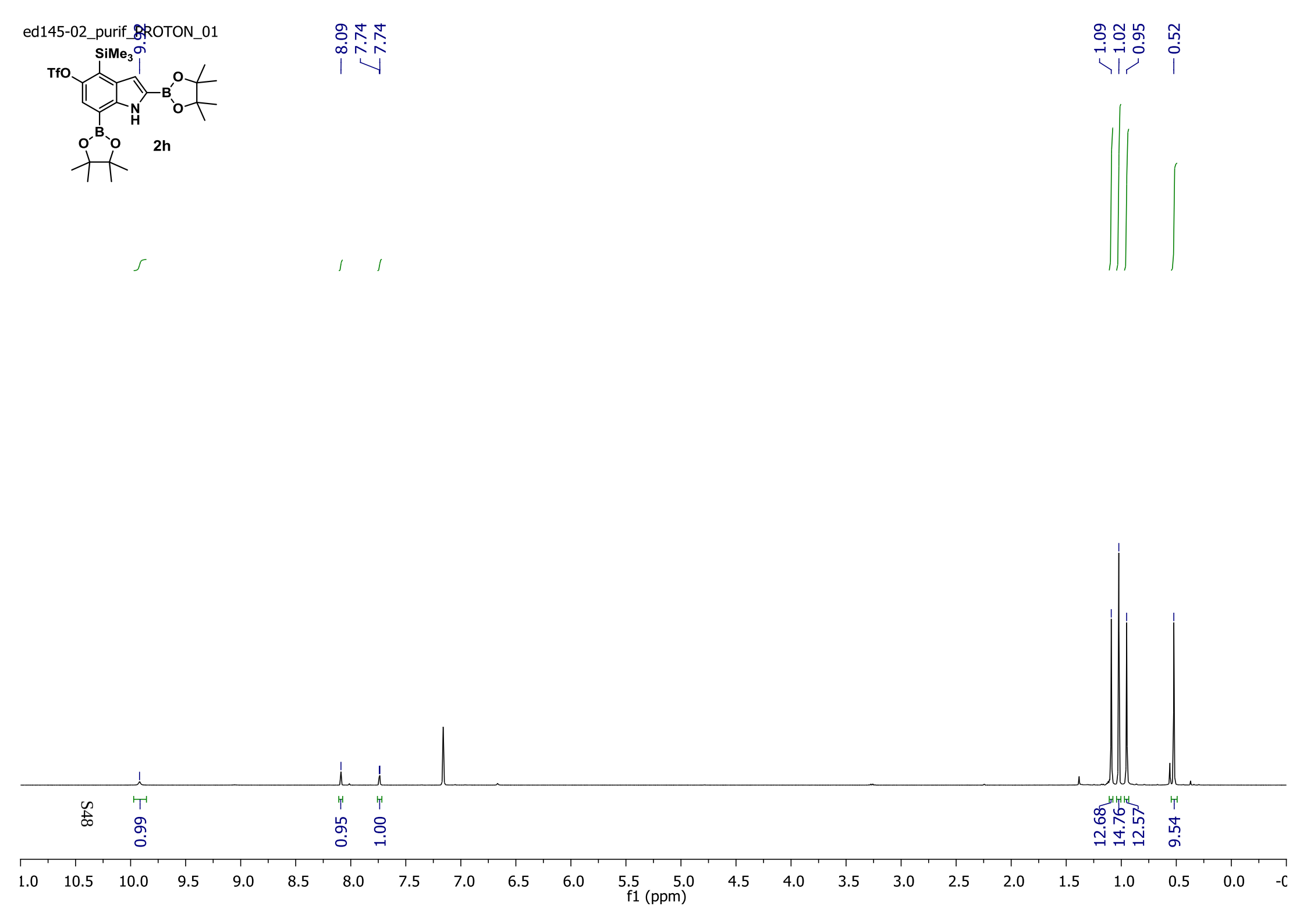
f1 (ppm)


F
SiMe3
O
B
O
OTf
F

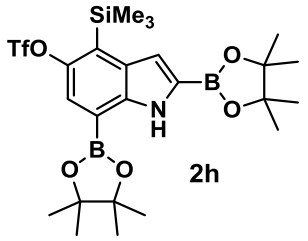
2g

29.14


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


ed145-02_purif_2_PROTON_01
SiMe3
TfO
B
O
N
H
2h
9.97
8.09
7.74
7.74
1.09
1.02
0.95
0.52
0.99
0.95
1.00
12.68
14.76
12.57
9.54
f1 (ppm)

ed145-02_anal_CARBON_01



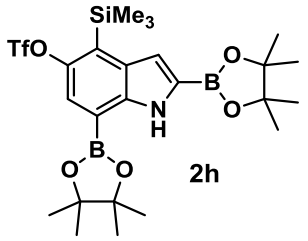
2h

148.44
140.58
132.11
128.98
123.43
122.51
120.25
117.06
115.28
113.87
84.37
84.27
24.90
24.78
1.07

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

ed145-02_purif_FLUORINE_01



2h

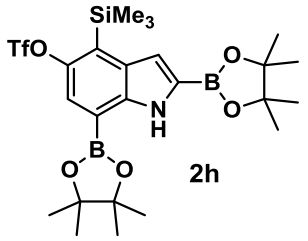
-73.50

S50

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

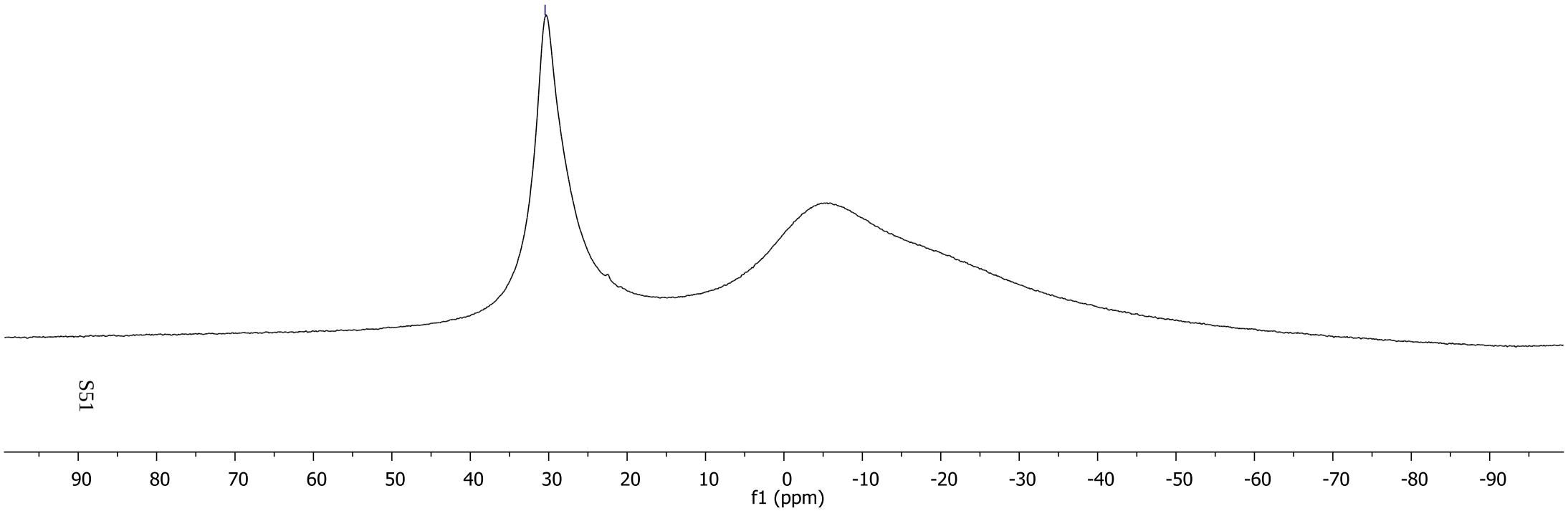
f1 (ppm)

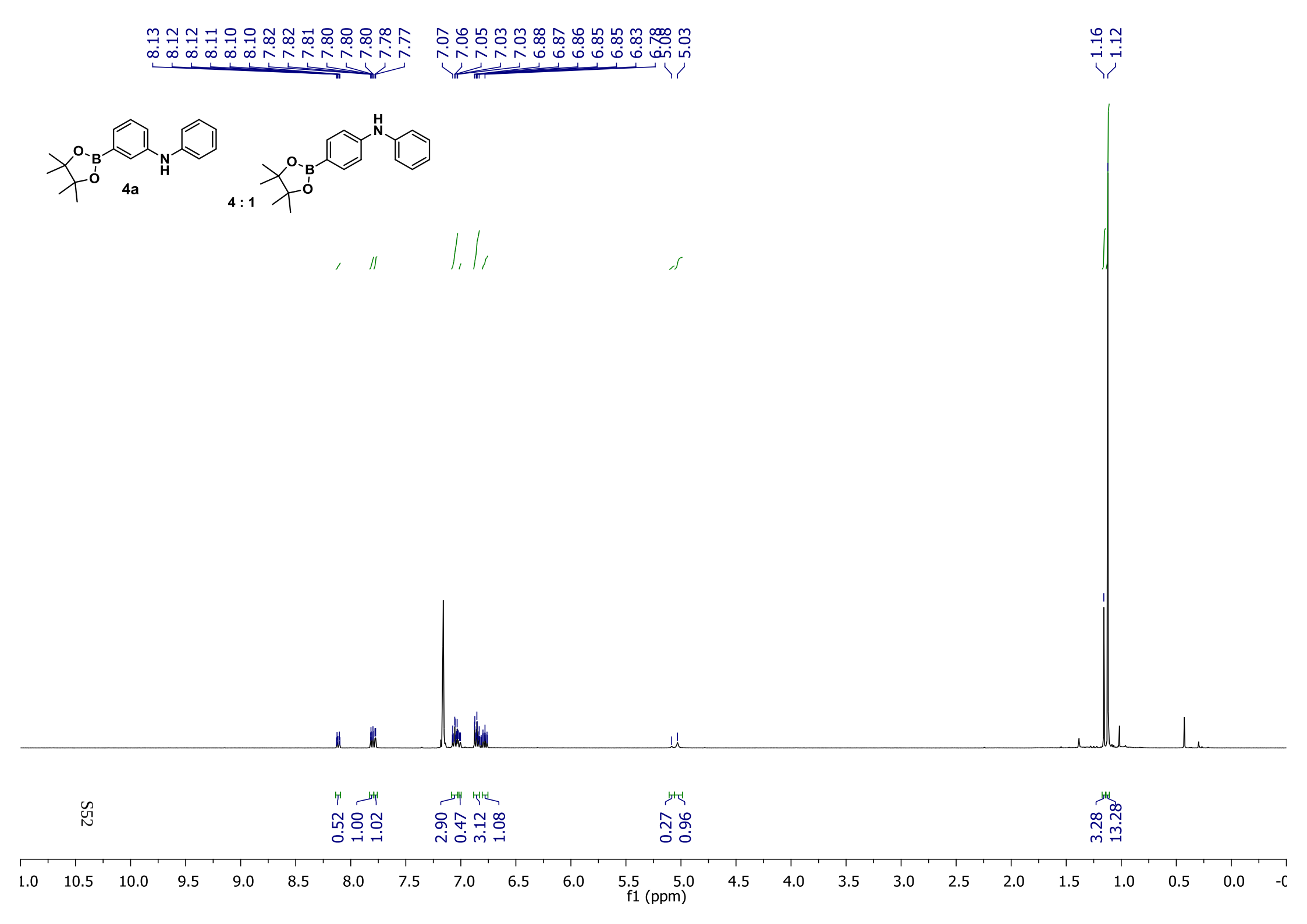
ed145-02_anal_BORON_11_01

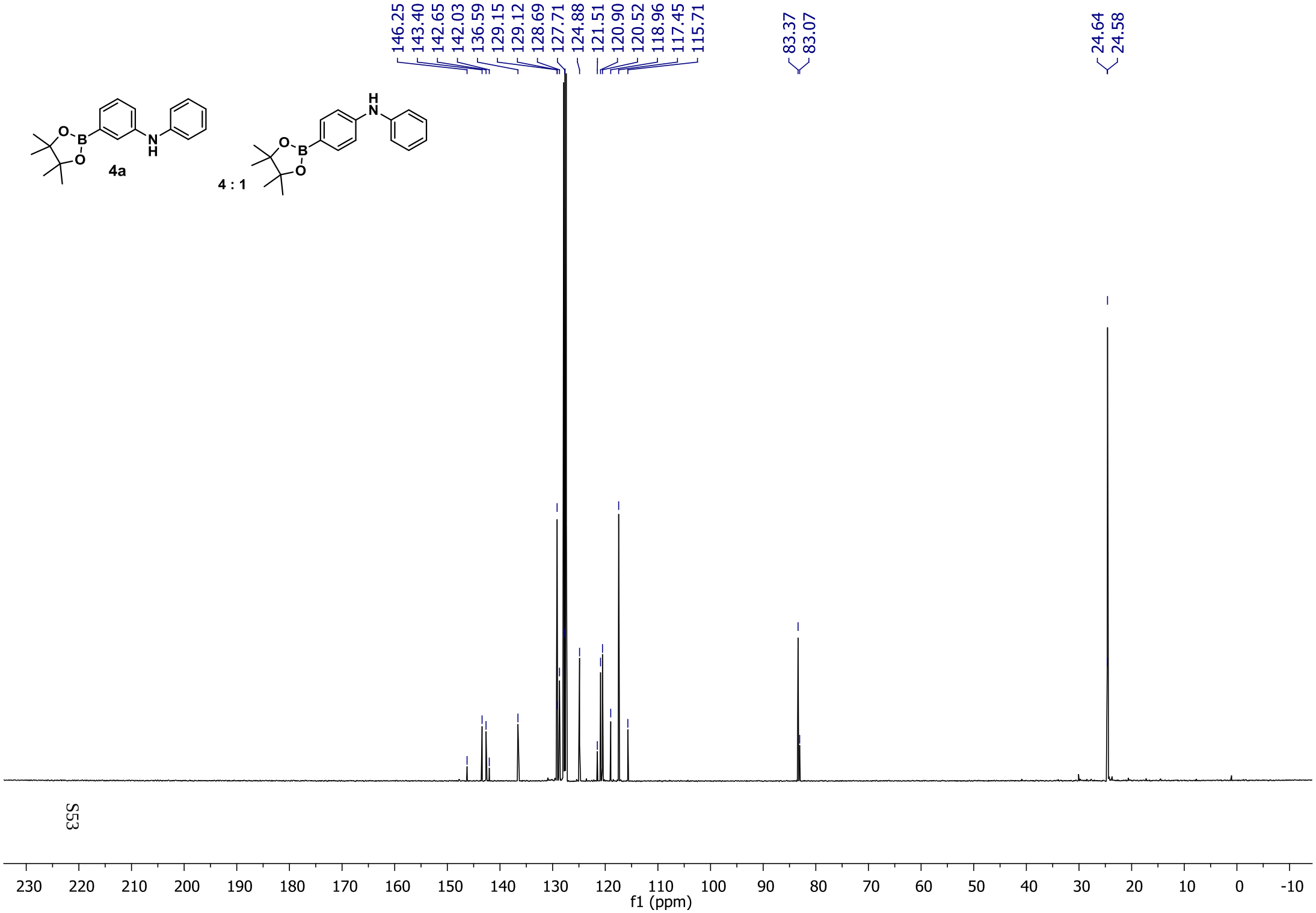


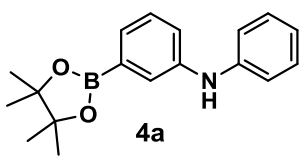
2h

30.46



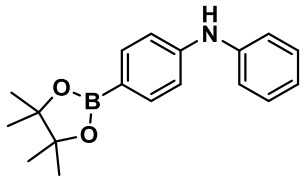

8.13
8.12
8.12
8.11
8.10
8.10
7.82
7.82
7.81
7.80
7.80
7.80
7.78
7.77
7.07
7.06
7.05
7.03
7.03
6.88
6.87
6.86
6.85
6.85
6.83
6.78
5.08
5.03
1.16
1.12
4a
4 : 1
S52
0.52
1.00
1.02
2.90
0.47
3.12
1.08
0.27
0.96
3.28
13.28
f1 (ppm)


146.25
143.40
142.65
142.03
136.59
129.15
129.12
128.69
127.71
124.88
121.51
120.90
120.52
118.96
117.45
115.71
83.37
83.07
24.64
24.58
4a
4 : 1
S53
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

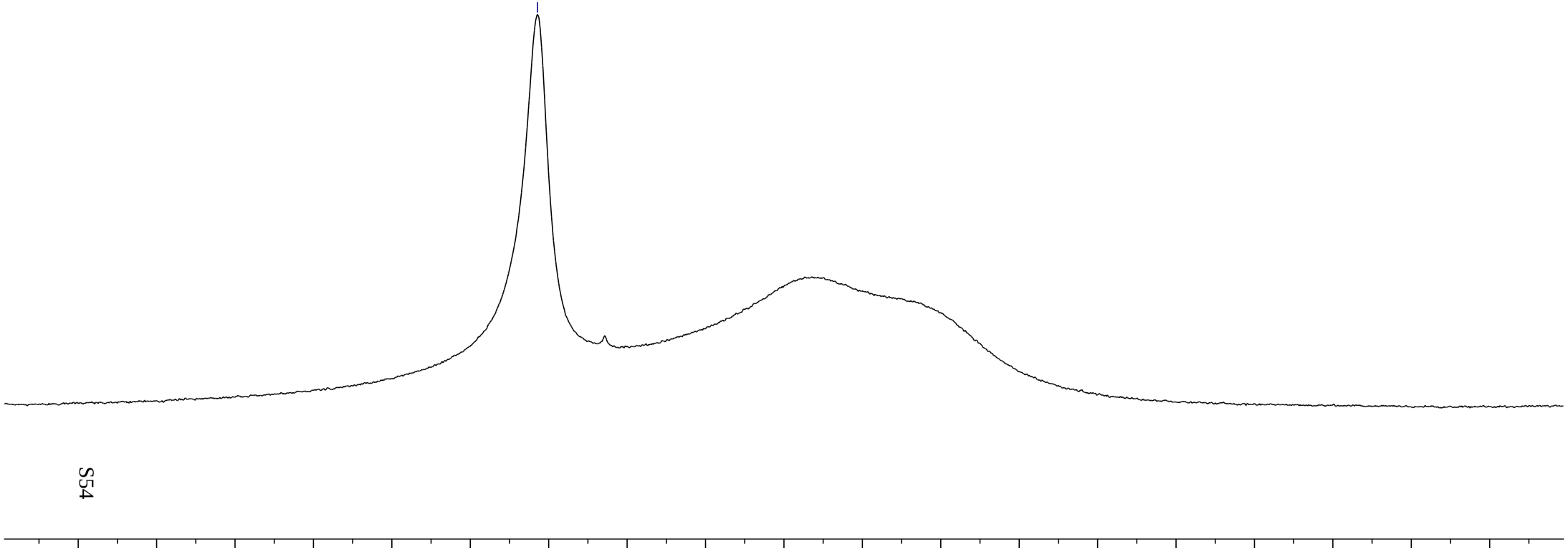

O
B
O
N
H

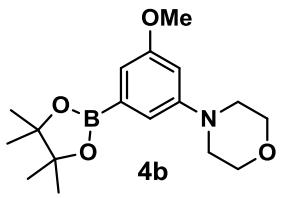
4a

4 : 1


H
N
O
B
O

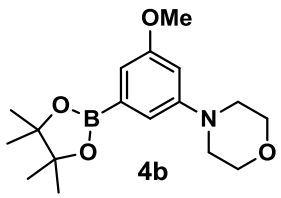
31.43


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


OMe
O
B
O
N
O

4b

7.02
7.01
6.87
6.87
6.56
3.86
3.85
3.84
3.82
3.20
3.18
3.17
1.34
1.00
0.98
0.96
4.04
3.17
4.29
13.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



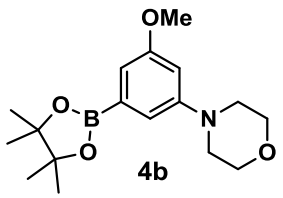
4b

160.15
125.47
115.04
109.66
105.95
83.78
66.84
55.33
49.42
24.81

S56

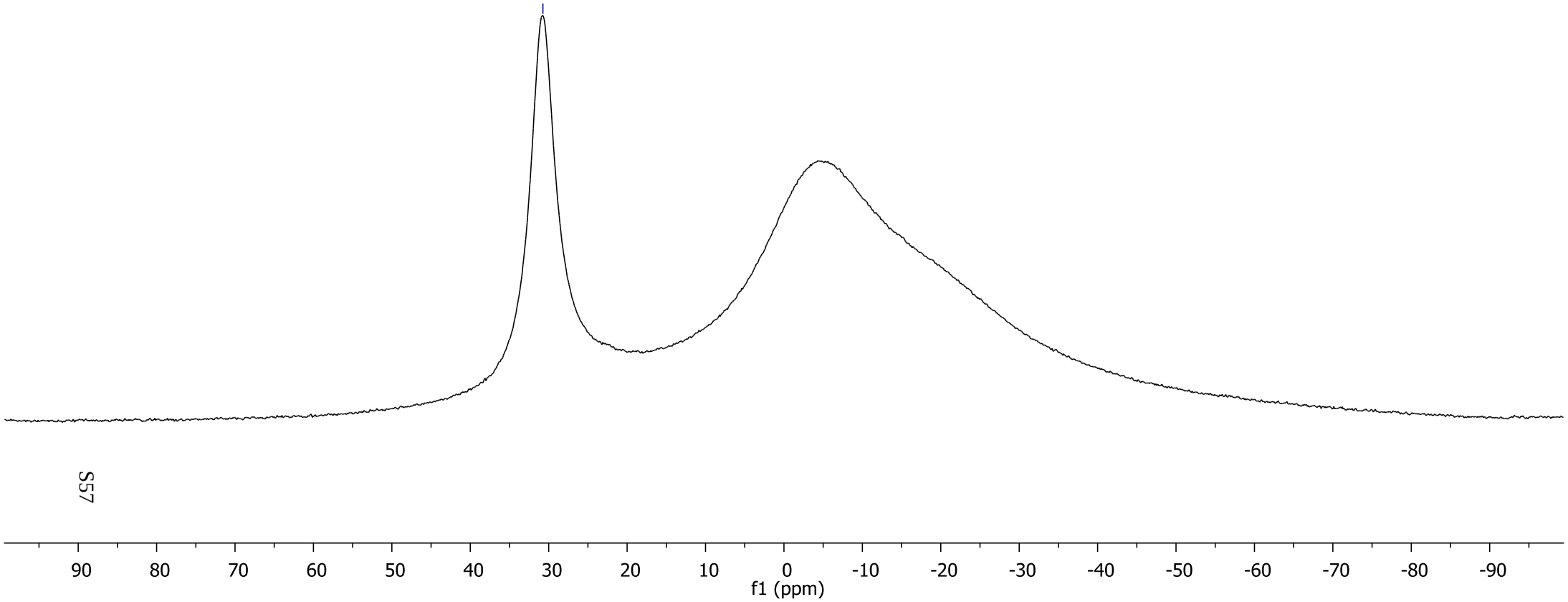
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

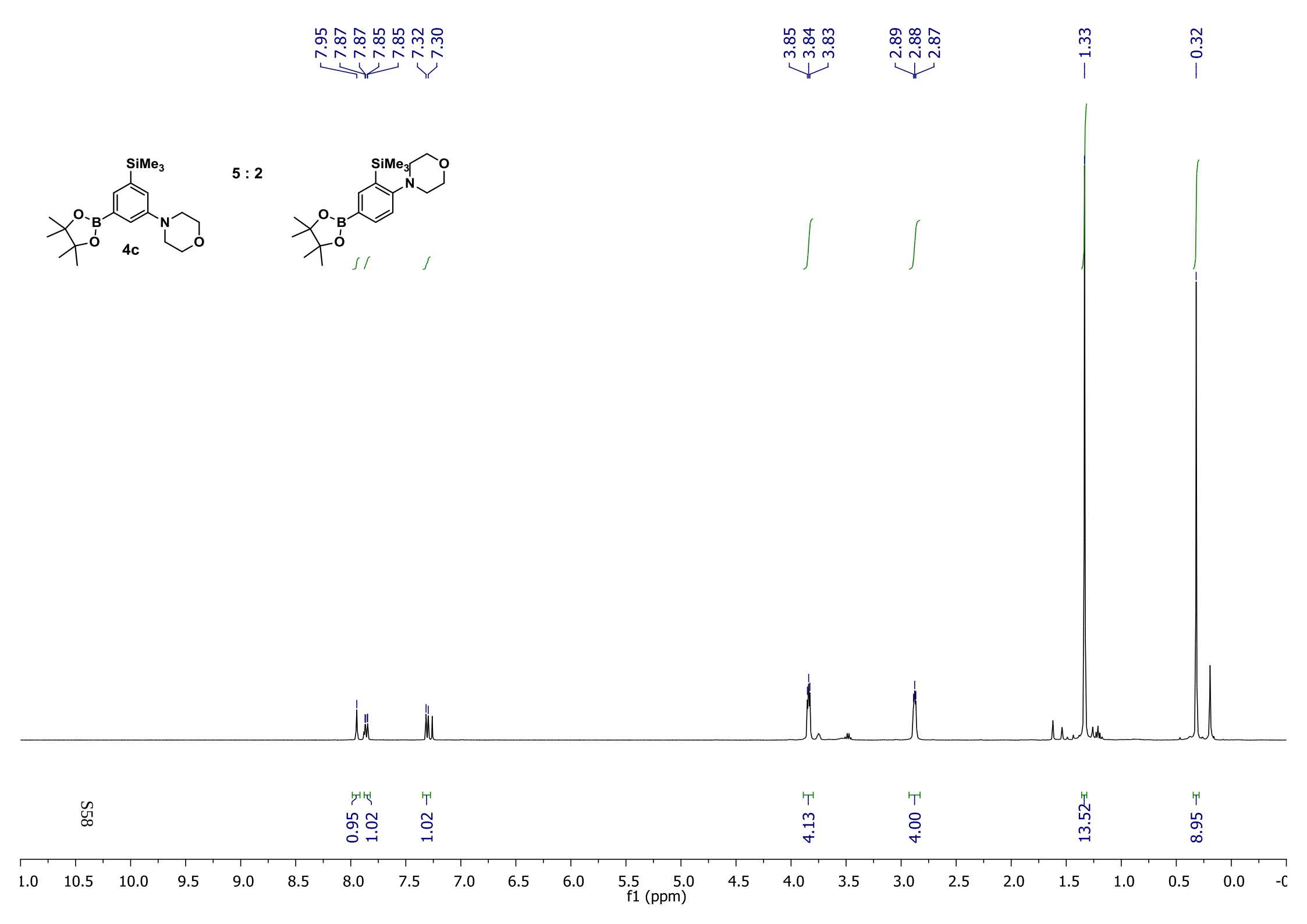
f1 (ppm)

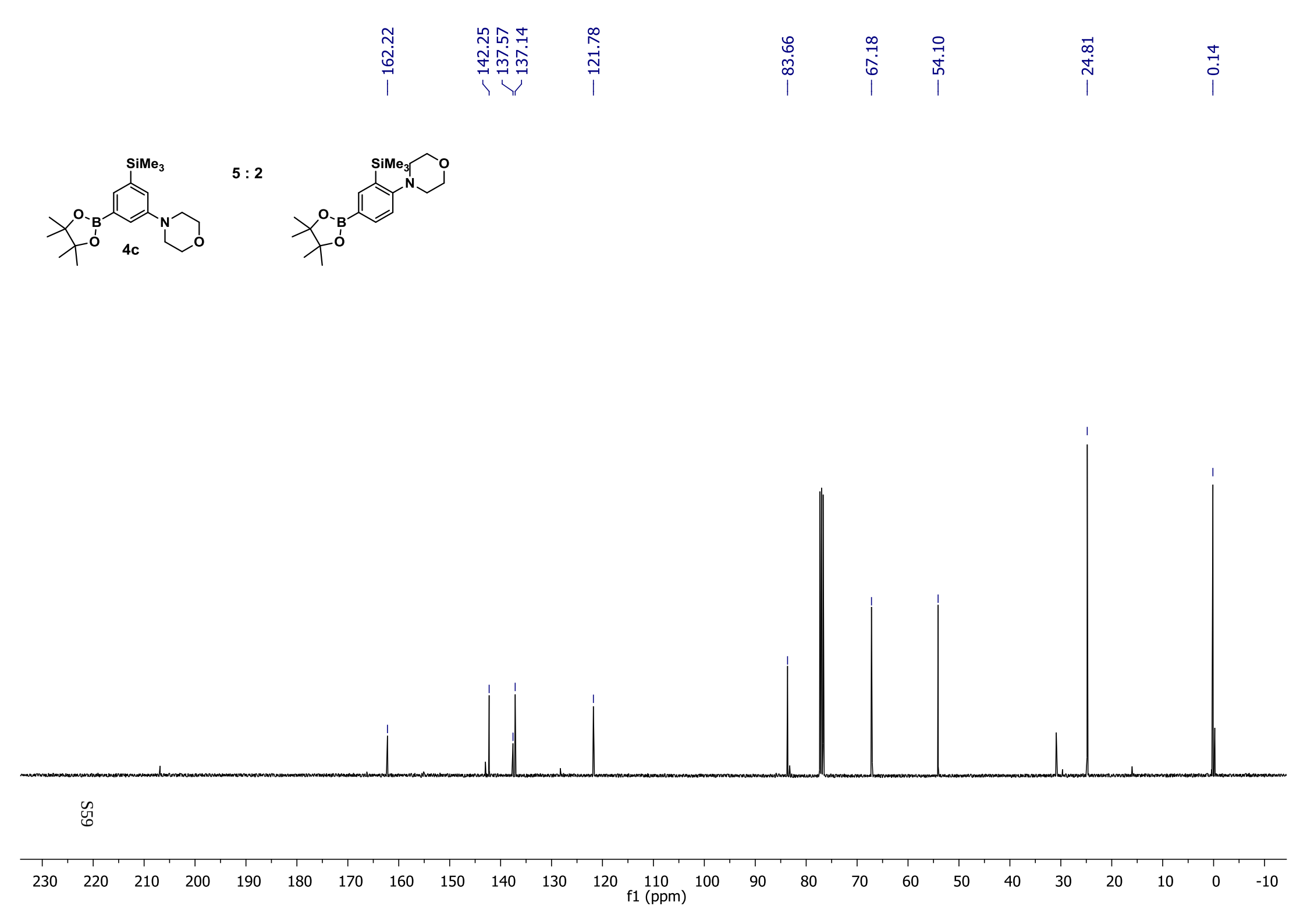

OMe
O
B
O
N
O

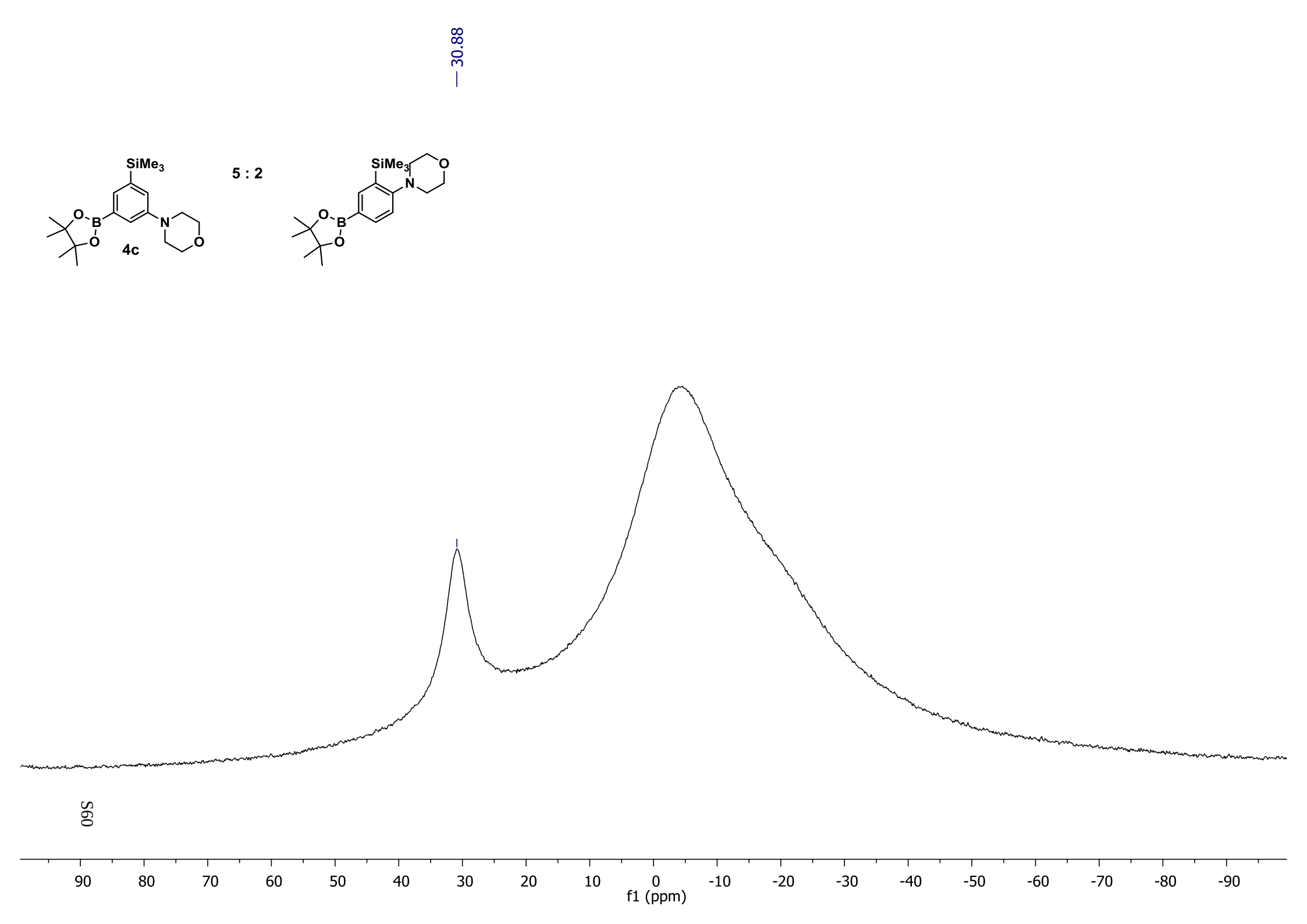
4b

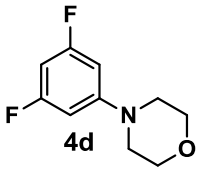
30.74


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


7.95
7.87
7.87
7.85
7.85
7.32
7.30
3.85
3.84
3.83
2.89
2.88
2.87
1.33
0.32
SiMe3
O
B
O
N
O
4c
5 : 2
SiMe3
O
N
O
B
O
S58
0.95
1.02
1.02
4.13
4.00
13.52
8.95
f1 (ppm)

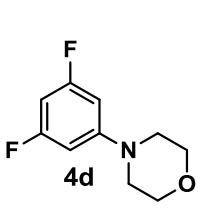

162.22
142.25
137.57
137.14
121.78
83.66
67.18
54.10
24.81
0.14
SiMe3
O
B
O
N
O
4c
5 : 2
SiMe3
O
N
O
B
O
S59
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


30.88
SiMe3
O
B
O
N
O
4c
5 : 2
SiMe3
O
N
O
B
O
S60
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


F
F
N
O

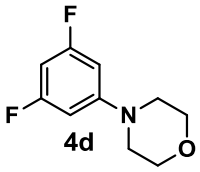
4d

6.40
6.39
6.38
6.38
6.37
6.35
6.34
6.34
6.33
6.32
6.31
6.31
6.30
6.29
6.29
6.28
6.27
6.26
6.26
3.85
3.84
3.82
3.16
3.15
3.14
2.00
0.92
4.15
4.22
f1 (ppm)



165.25
165.10
162.82
162.67
153.35
153.23
153.11
97.87
97.78
97.67
97.58
94.71
94.45
94.19
66.47
48.25

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

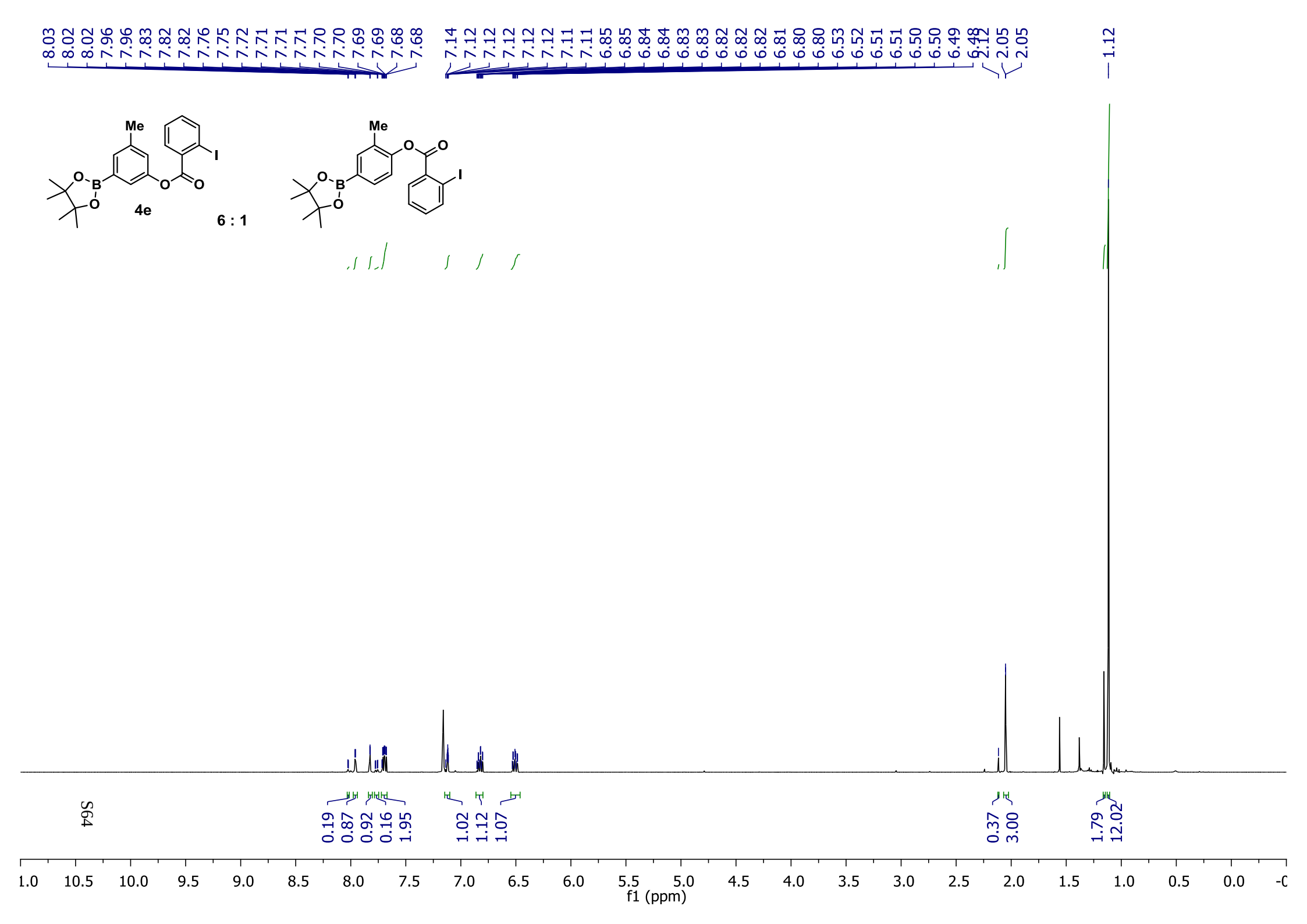


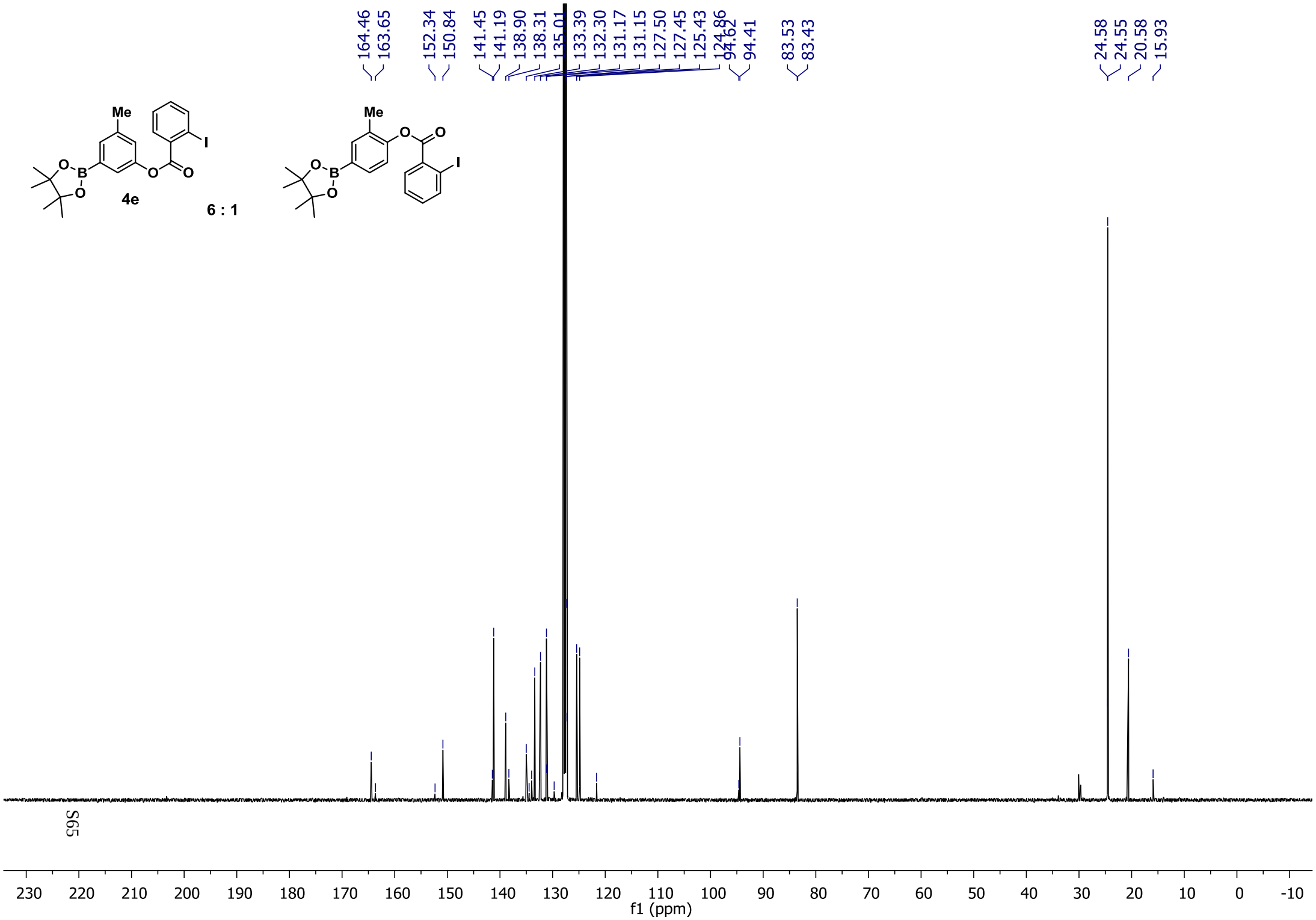
4d

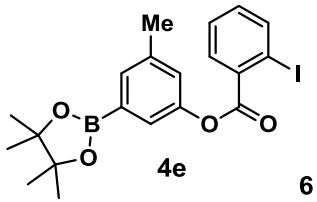
-109.70
-109.71
-109.72
-109.73
-109.74
-109.75
-109.76
-109.77
-109.78
-109.79

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

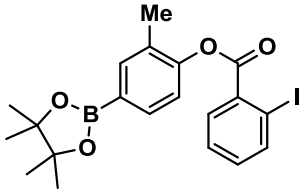

8.03 8.02 8.02 7.96 7.96 7.83 7.82 7.82 7.76 7.75 7.72 7.71 7.71 7.71 7.70 7.70 7.69 7.69 7.68 7.68
7.14 7.12 7.12 7.12 7.12 7.11 7.11 6.85 6.85 6.84 6.84 6.83 6.83 6.82 6.82 6.82 6.81 6.80 6.80 6.53 6.52 6.51 6.51 6.50 6.50 6.49 6.48 2.12 2.05 2.05
1.12
Me
I
O
B
O
O
O
4e
6 : 1
Me
O
O
I
O
B
O
0.19 0.87 0.92 0.16 1.95 1.02 1.12 1.07 0.37 3.00 1.79 12.02
S64
f1 (ppm)


164.46
163.65
152.34
150.84
141.45
141.19
138.90
138.31
135.01
133.39
132.30
131.17
131.15
127.50
127.45
125.43
124.86
94.62
94.41
83.53
83.43
24.58
24.55
20.58
15.93
Me
I
O
B
O
O
O
4e
6 : 1
Me
O
O
I
O
B
O
S65
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4e

6 : 1

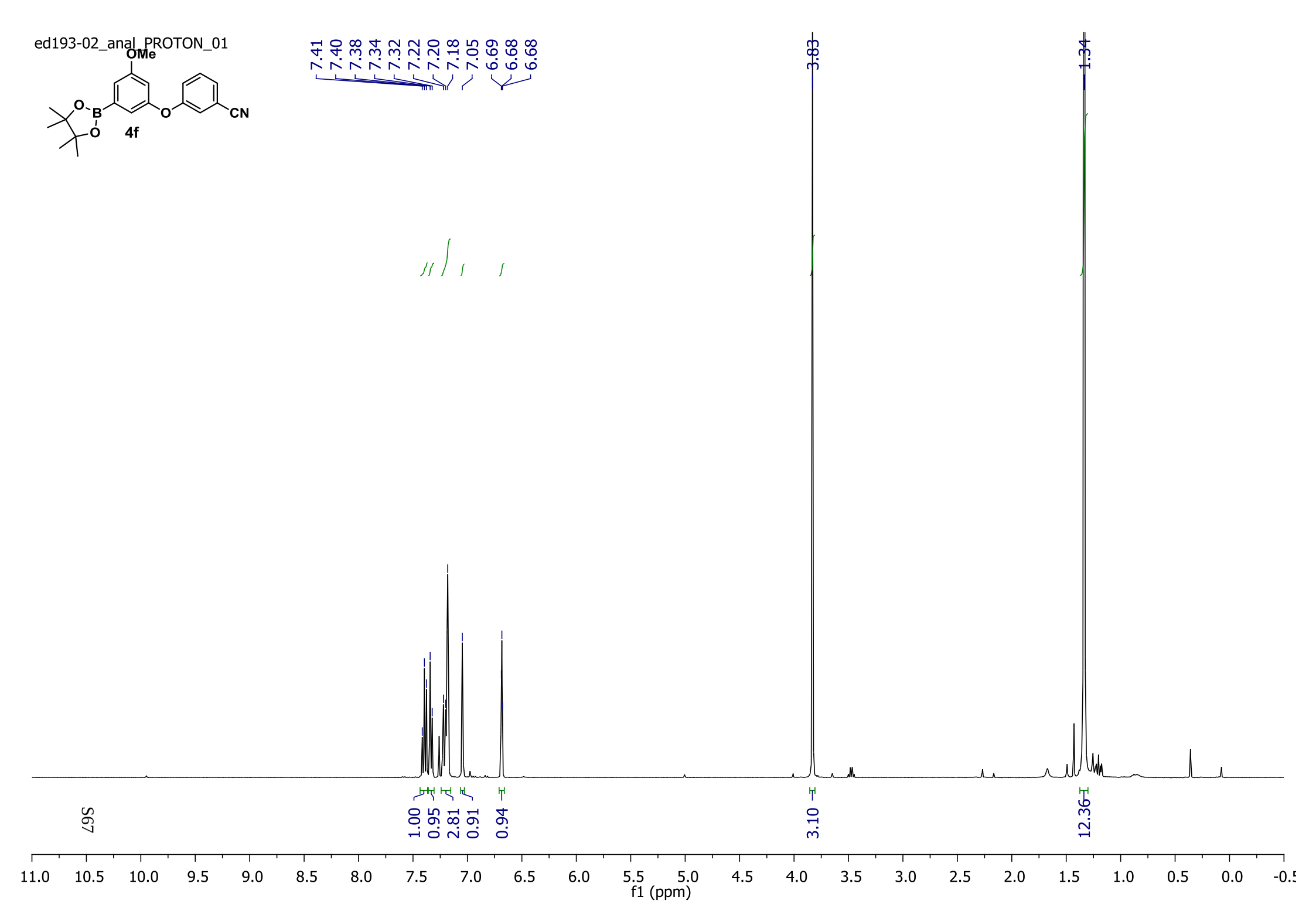


30.75

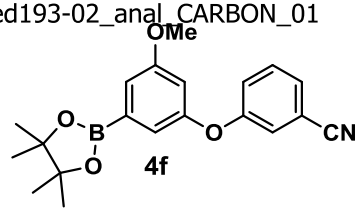
S66

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)


ed193-02_anal_PROTON_01
OMe
O
B
O
O
CN
4f
7.41
7.40
7.38
7.34
7.32
7.22
7.20
7.18
7.05
6.69
6.68
6.68
3.83
1.34
1.00
0.95
2.81
0.91
0.94
3.10
12.36
S67
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

ed193-02_anal_CARBON_01

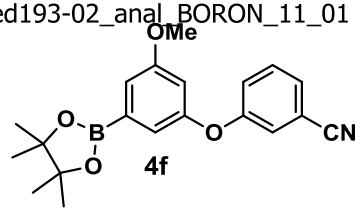


4f

160.73
158.25
155.99
130.58
126.24
122.65
120.90
117.98
115.38
113.43
109.76
84.13
55.56
24.83

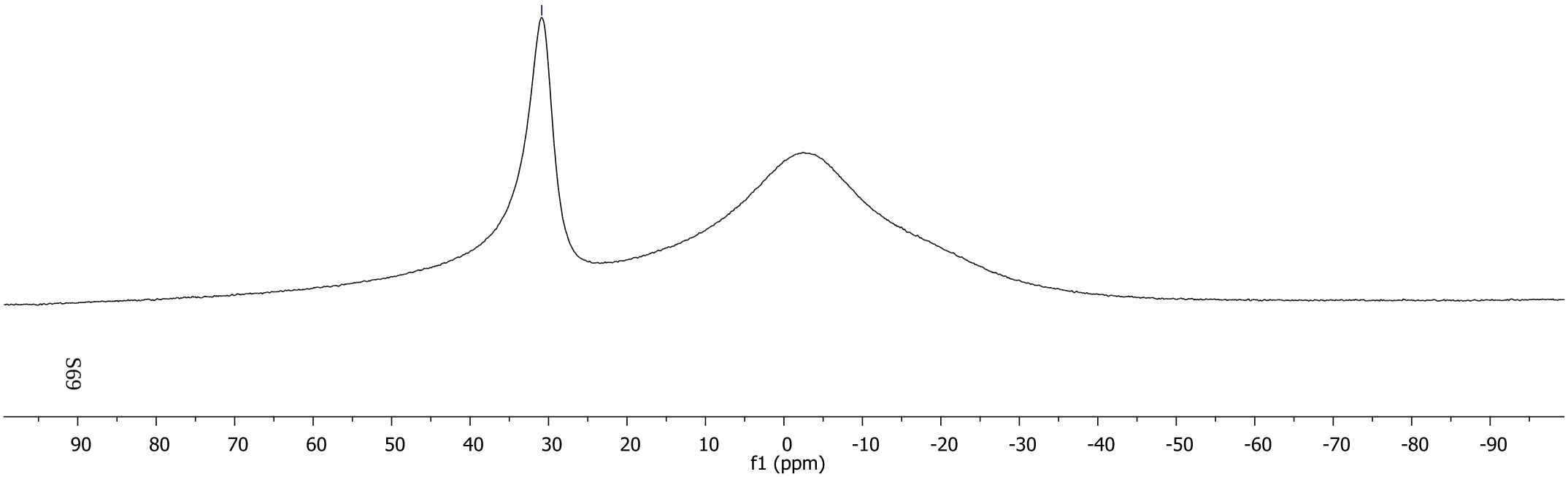
f1 (ppm)

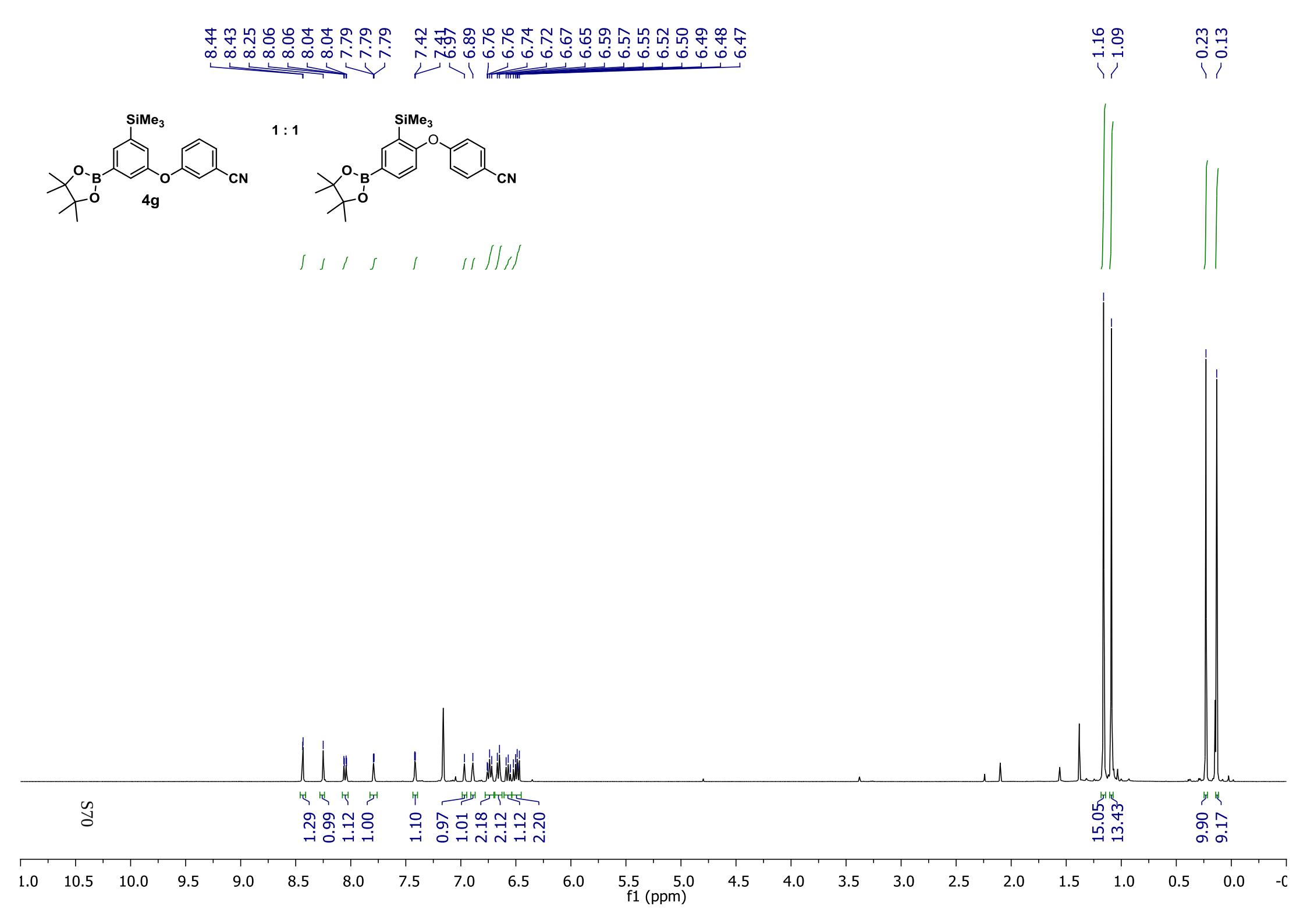
ed193-02_anal_BORON_11_01

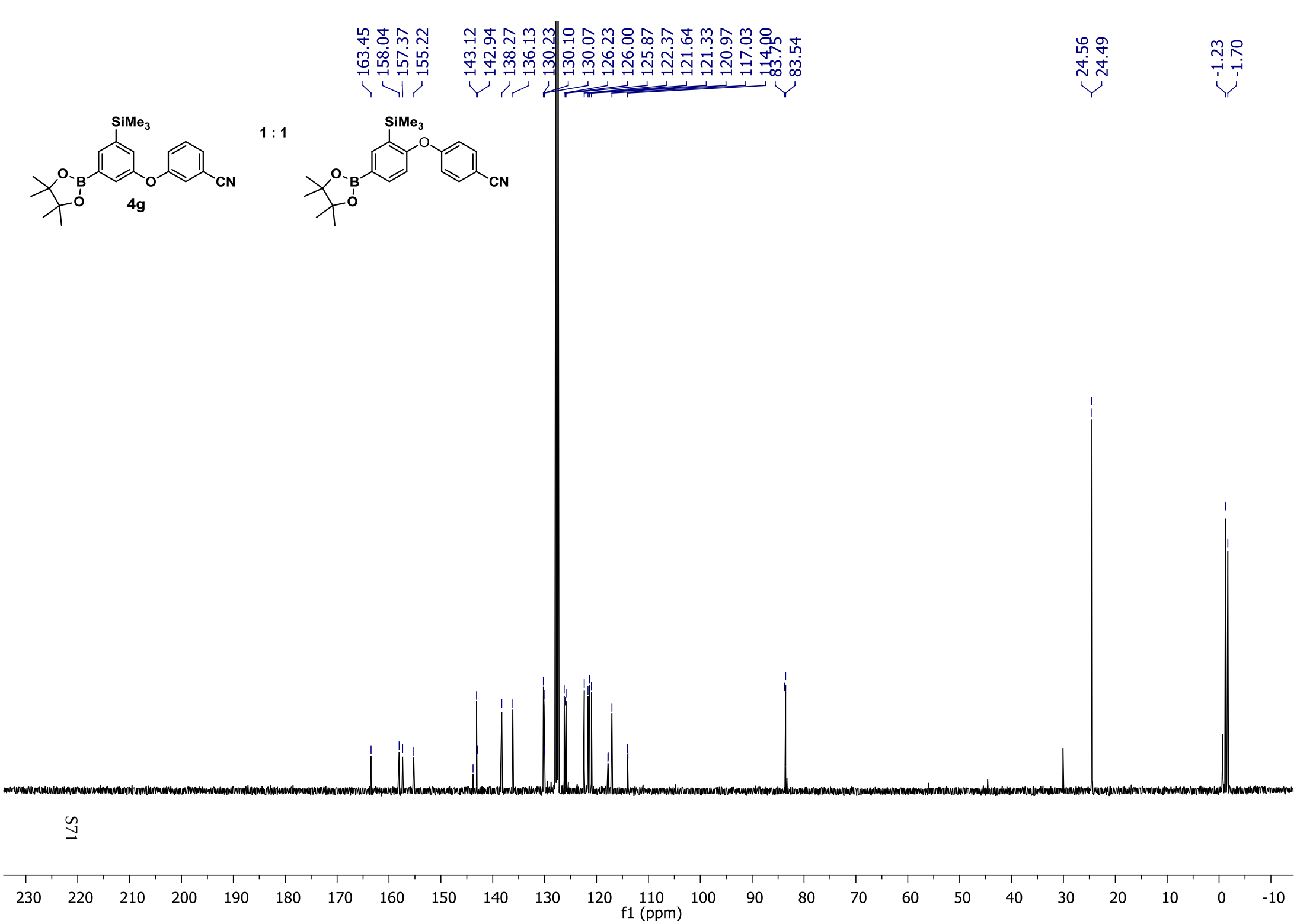


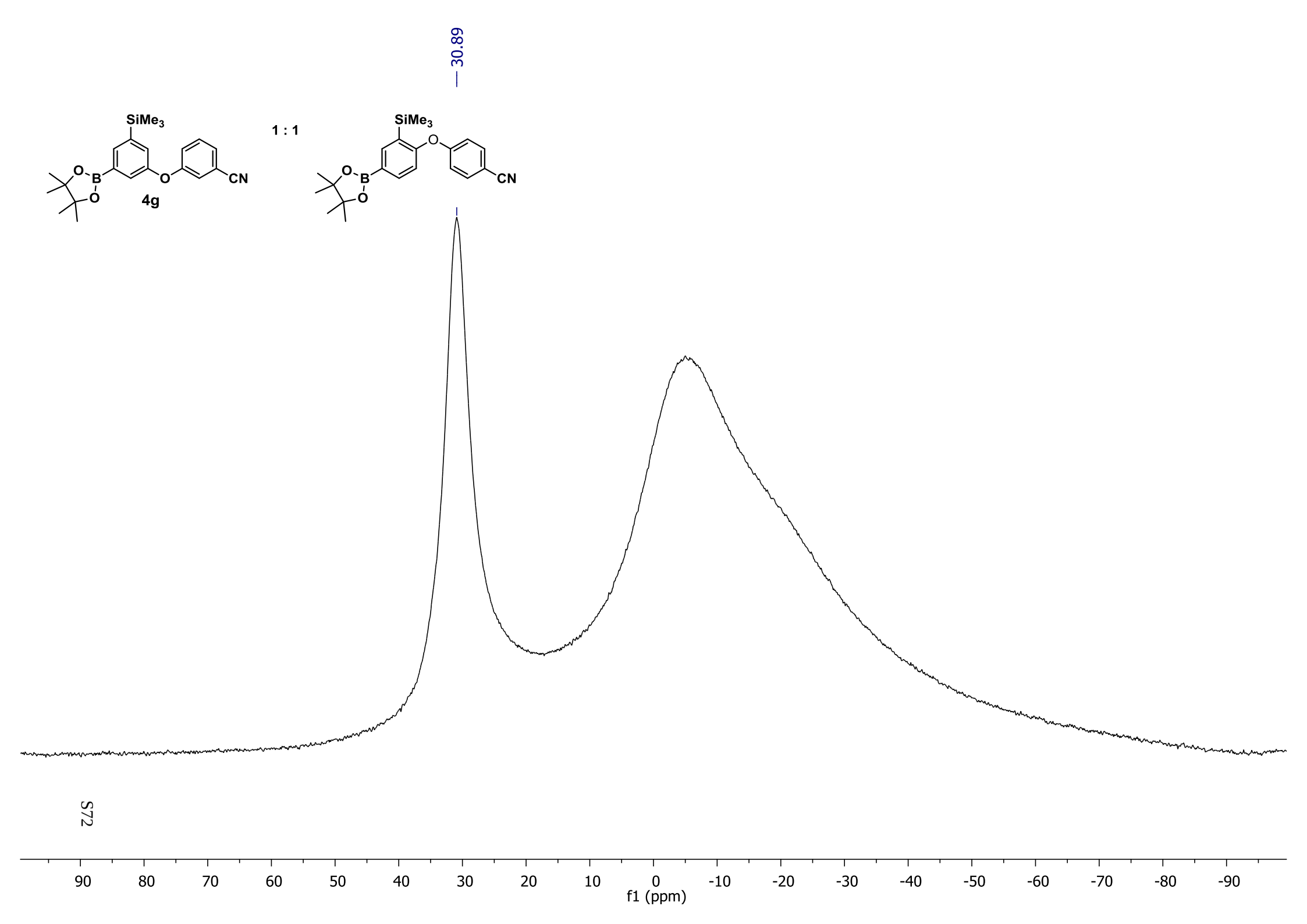
4f

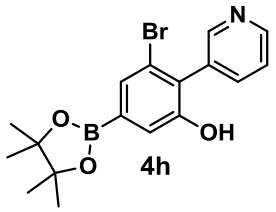
30.87




8.44
8.43
8.25
8.06
8.06
8.04
8.04
7.79
7.79
7.79
7.42
7.41
6.97
6.89
6.76
6.76
6.74
6.72
6.67
6.65
6.59
6.57
6.55
6.52
6.50
6.49
6.48
6.47
1.16
1.09
0.23
0.13
SiMe3
O
B
O
O
CN
4g
1 : 1
SiMe3
O
B
O
O
CN
S70
1.29
0.99
1.12
1.00
1.10
0.97
1.01
2.18
2.12
1.12
2.20
15.05
13.43
9.90
9.17
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

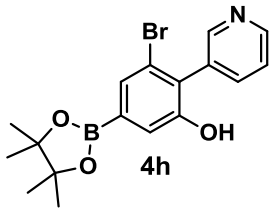

163.45
158.04
157.37
155.22
143.12
142.94
138.27
136.13
130.23
130.10
130.07
126.23
126.00
125.87
122.37
121.64
121.33
120.97
117.03
114.00
83.75
83.54
24.56
24.49
-1.23
-1.70
SiMe3
1 : 1
SiMe3
O
B
O
O
CN
4g
S71
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


30.89
SiMe3
1 : 1
SiMe3
O
B
O
O
CN
4g
O
B
O
O
CN
S72
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


Br
N
O
B
O
OH

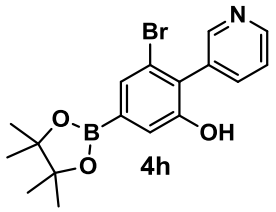
4h

8.47
8.12
8.05
8.04
7.77
7.35
7.33
6.61
6.60
6.60
6.58
1.09
1.00
1.05
1.08
1.07
1.09
1.11
13.04
f1 (ppm)



155.90
149.94
146.91
138.82
133.78
130.29
128.92
124.24
123.00
121.70
83.79
24.46

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



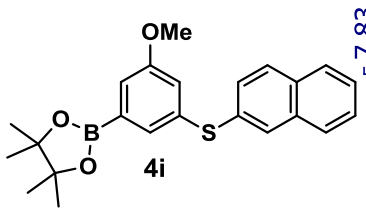
4h

29.86

S75

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)



7.83 7.81 7.79 7.79 7.77 7.75 7.73 7.56 7.49 7.48 7.47 7.46 7.44 7.42 7.40 7.26 7.26 7.00

3.77

1.35

4.09 0.96 2.01 0.99 1.09 1.00

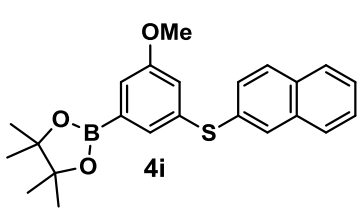
3.14

12.73

S76

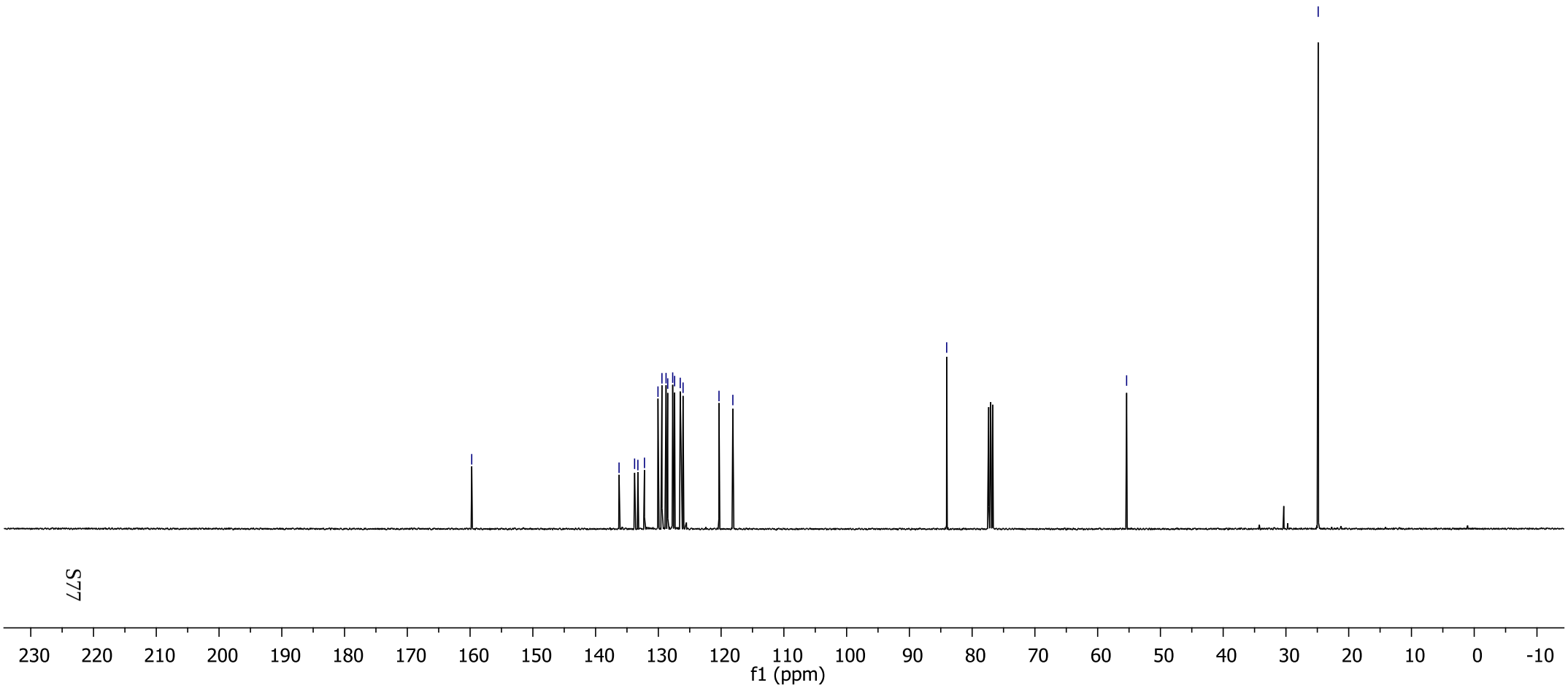
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

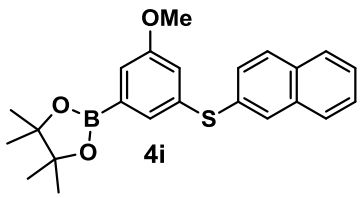
f1 (ppm)



4i

159.74
136.26
133.79
133.26
132.21
130.06
129.43
128.77
128.50
127.71
127.41
126.51
126.06
120.34
118.13
84.06
55.39
24.86





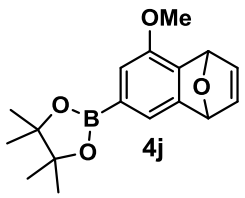
4i

31.04

S78

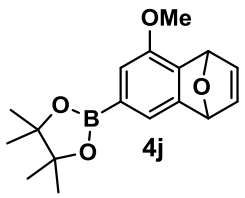
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)


OMe
O
B
O
O

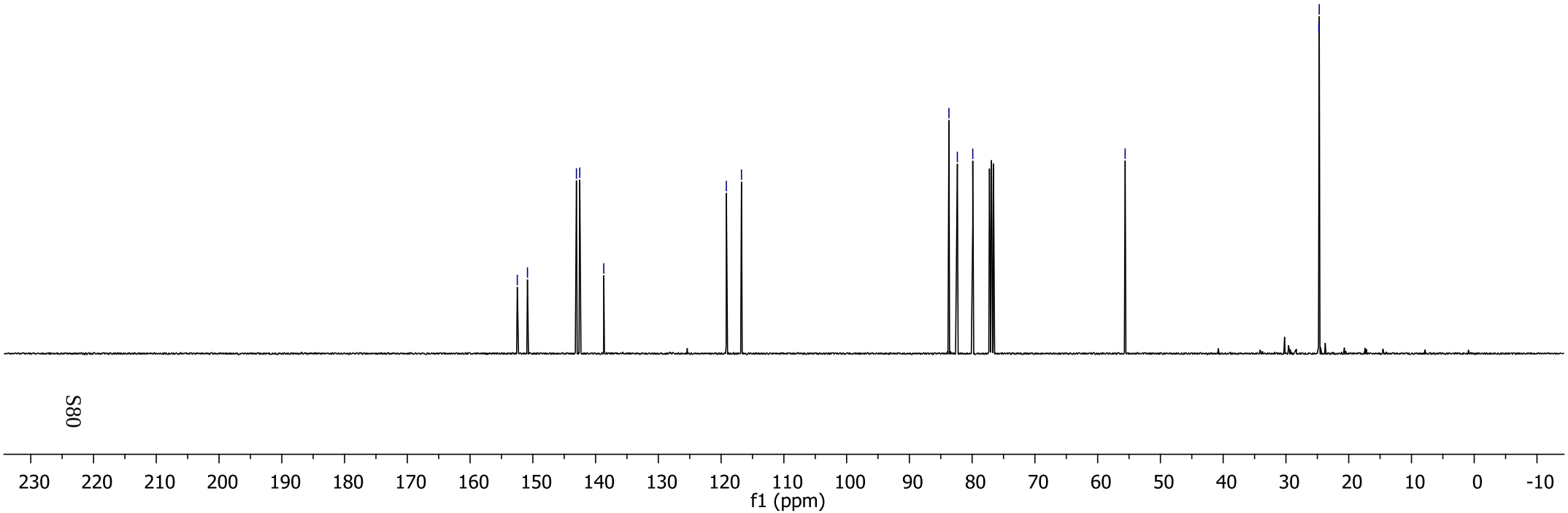
4j

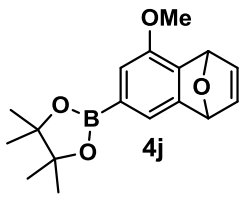
7.36
7.07
7.05
7.03
7.02
7.00
5.94
5.69
3.87
1.33
0.98
1.00
2.08
0.97
1.00
3.29
12.89
S79
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



4j

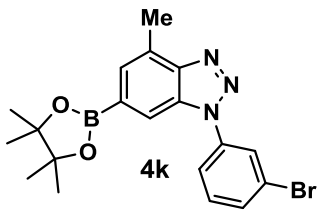
152.48
150.86
143.05
142.53
138.70
119.17
116.75
83.70
82.36
79.90
55.62
24.76
24.70





4j

30.47



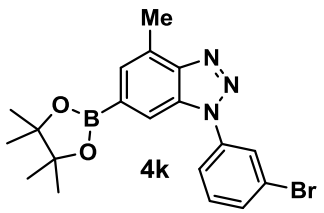
8.15 7.90 7.81 7.81 7.80 7.18 7.07 7.05 7.05 6.54 6.52 6.50 2.79 1.16

1.00 1.01 0.94 0.51 0.98 1.02 3.14 13.48

S82

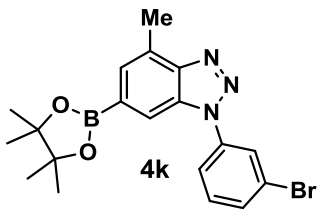
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f1 (ppm)

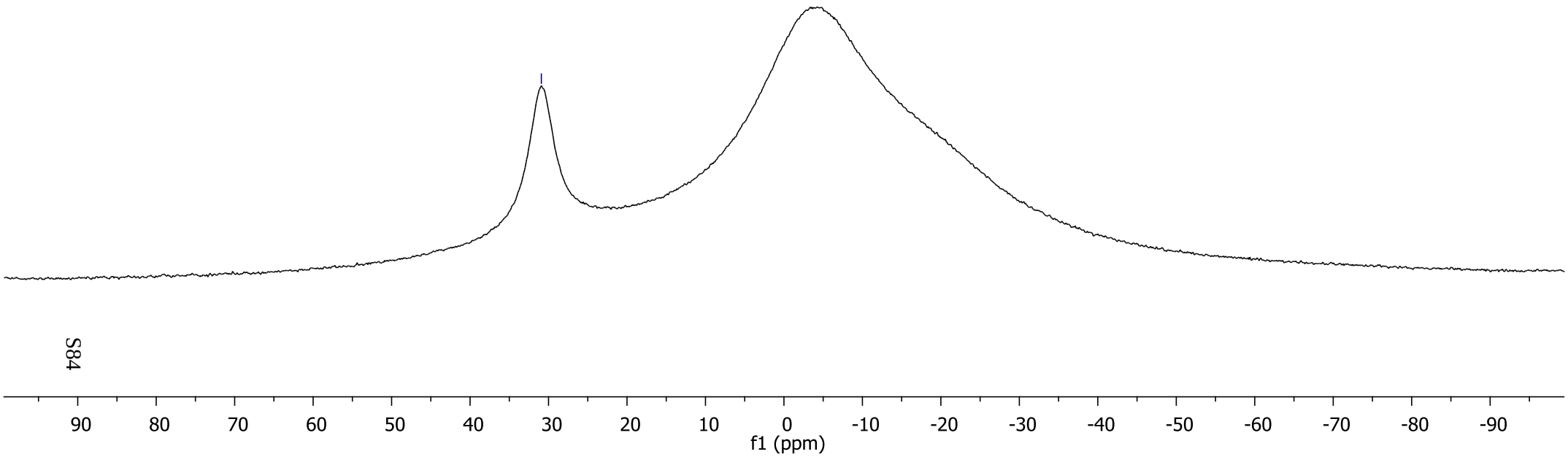


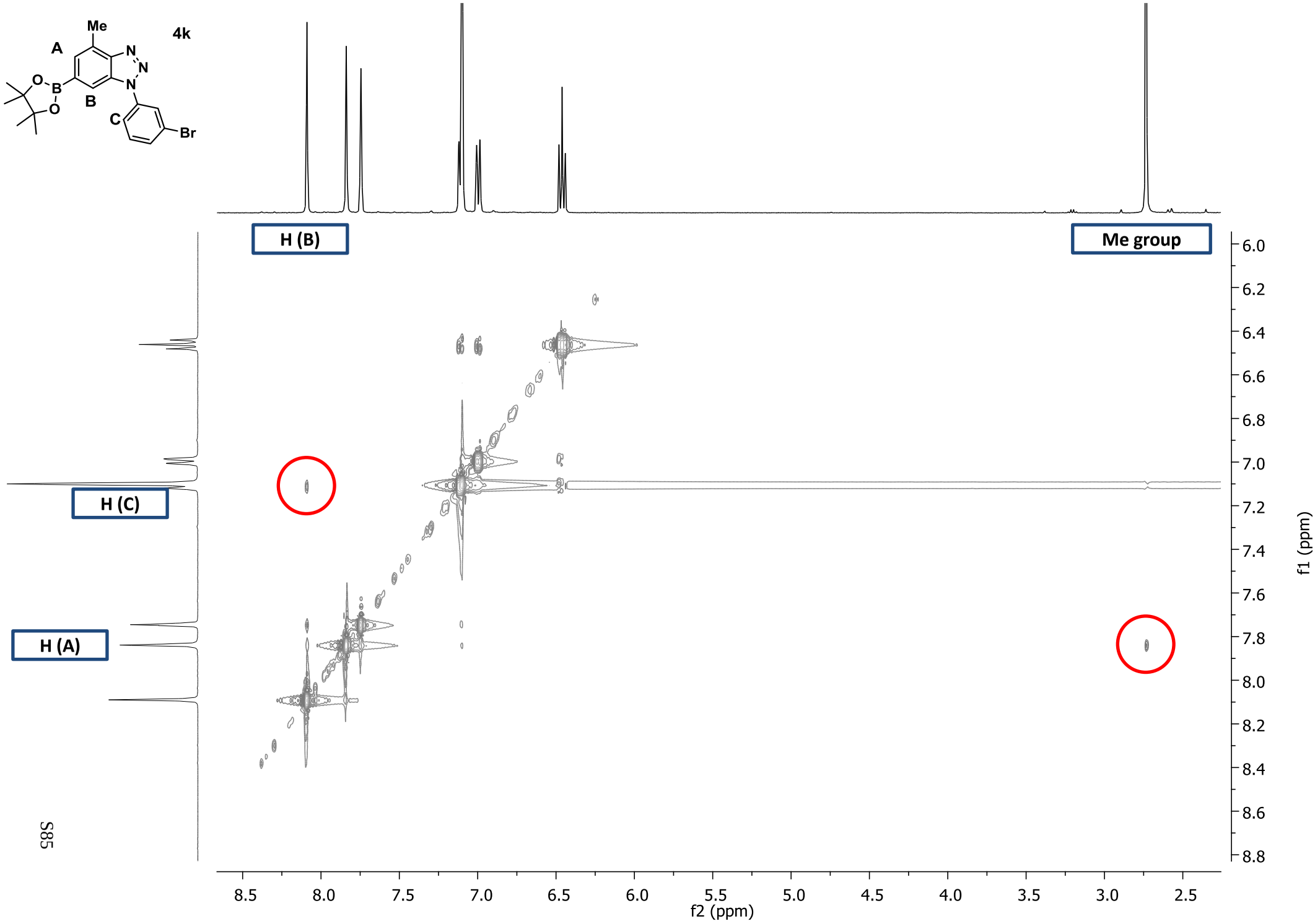
148.01
138.19
131.95
131.63
131.02
130.39
129.94
126.27
123.30
121.55
114.15
84.34
24.85
16.63

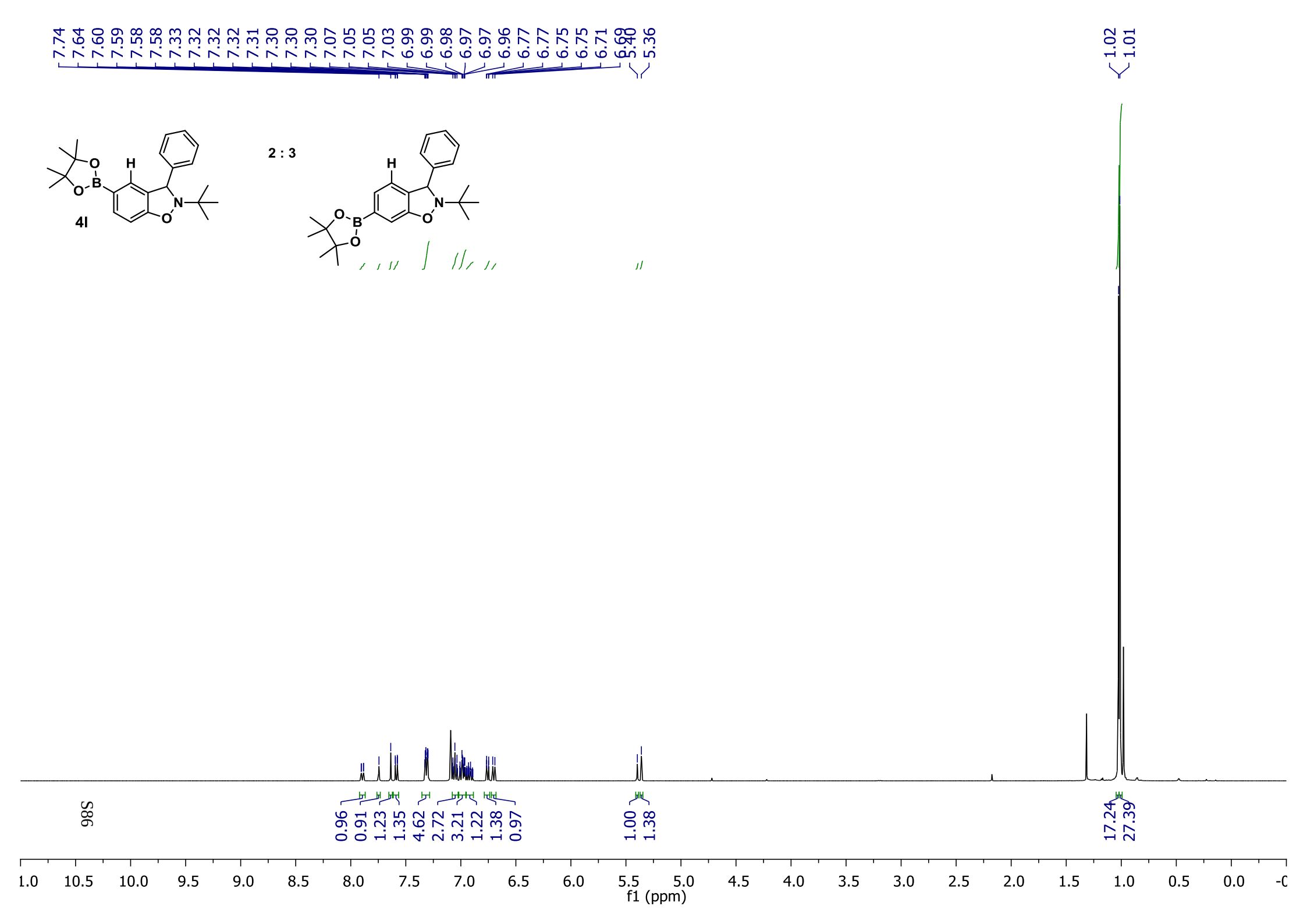
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

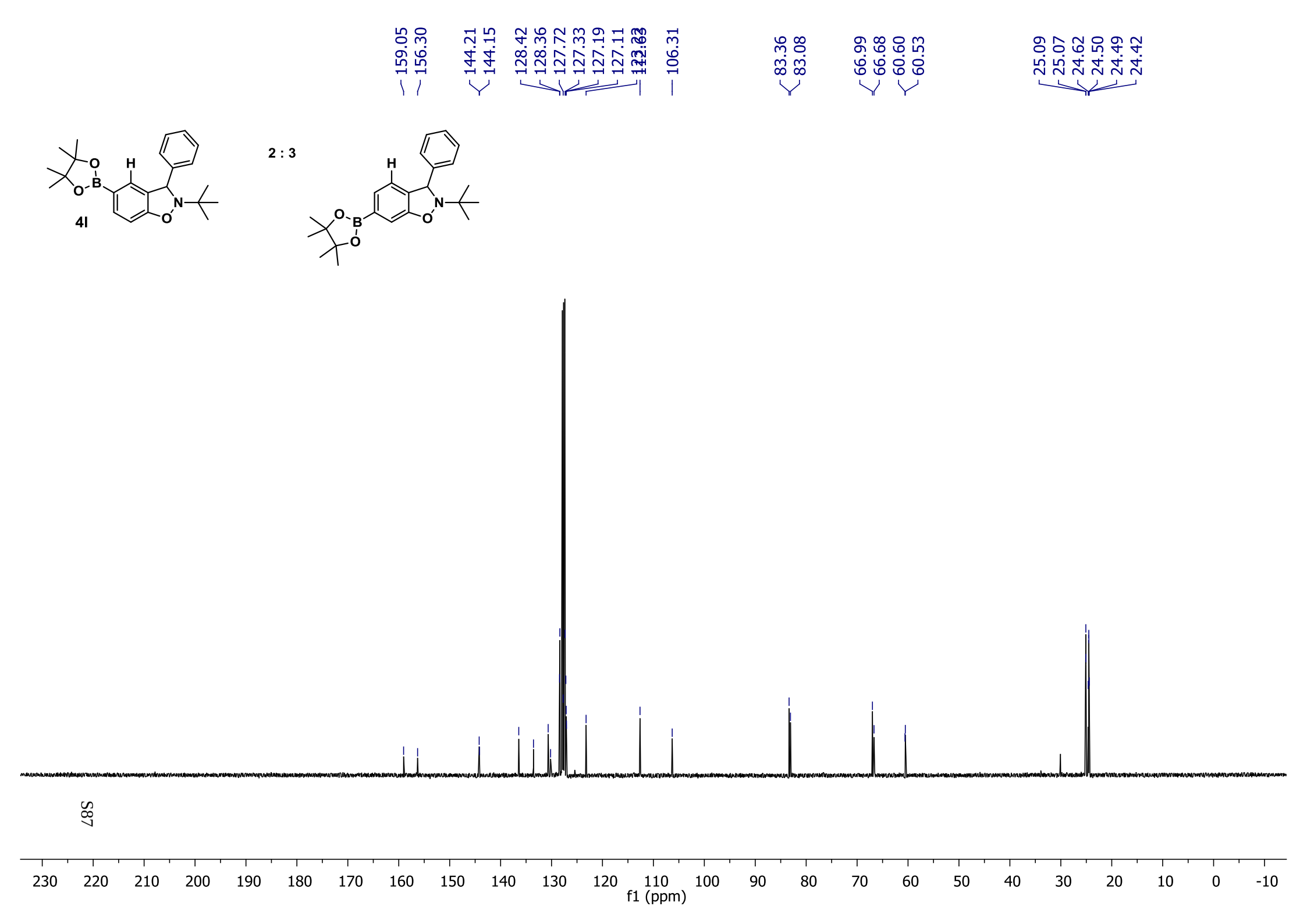

Me
N
N
N
O
B
O
4k
Br

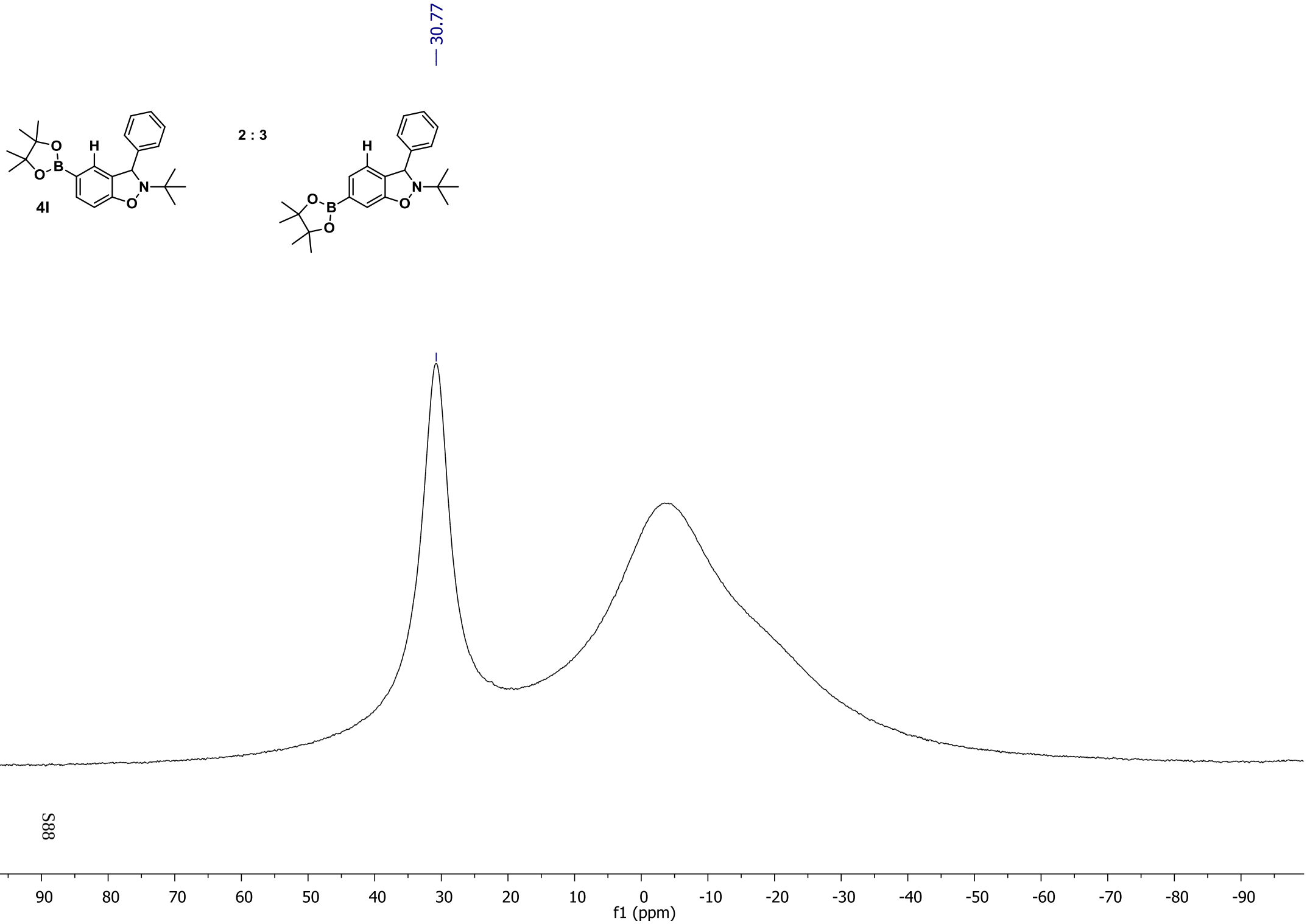
30.92

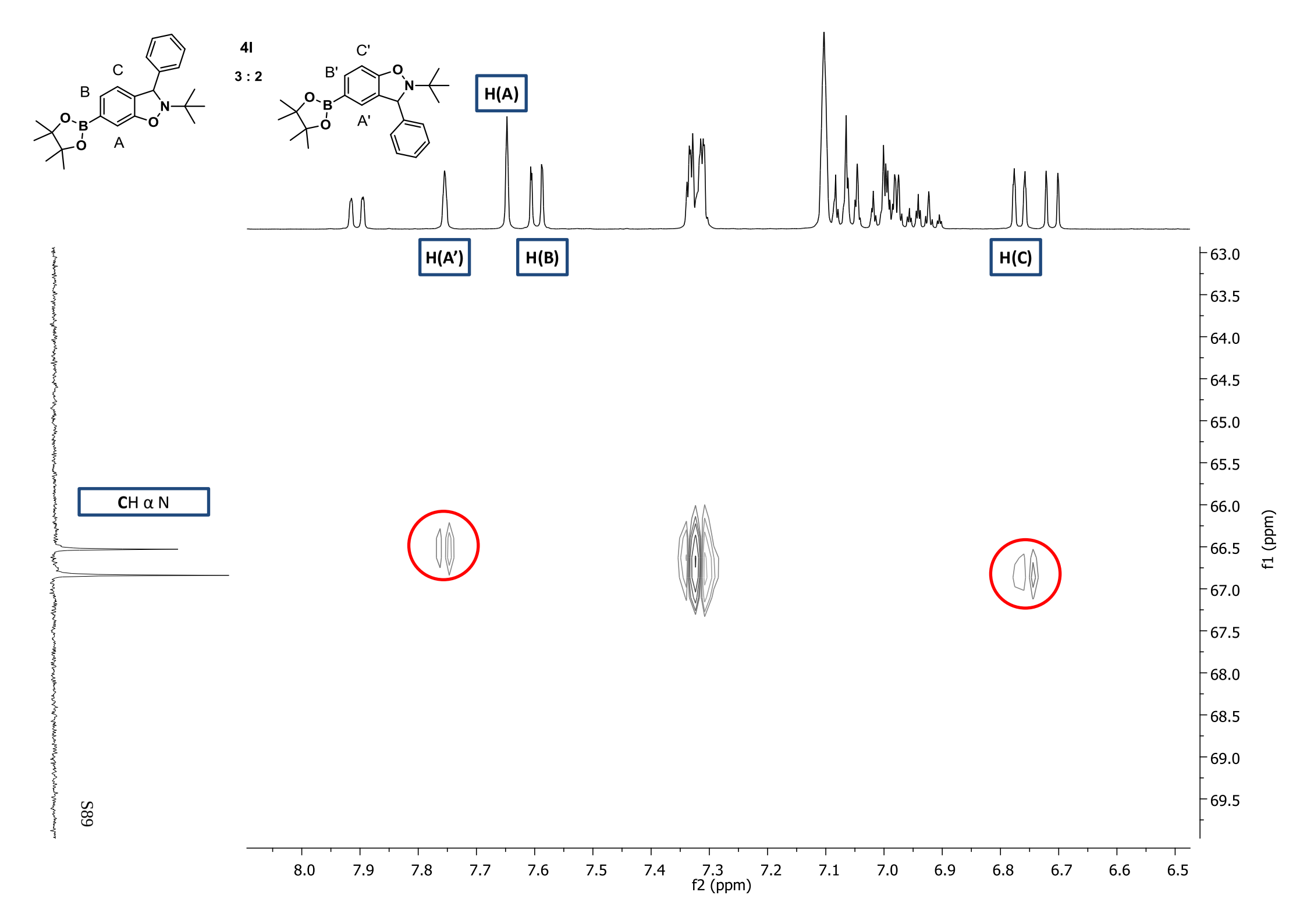

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

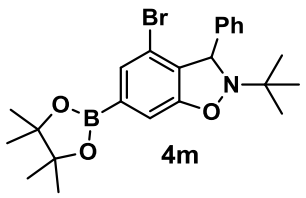

4k
Me
A
B
C
Br
H (B)
Me group
H (C)
H (A)
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8


7.74
7.64
7.60
7.59
7.58
7.58
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.30
7.07
7.05
7.05
7.03
6.99
6.99
6.98
6.97
6.97
6.96
6.77
6.77
6.75
6.75
6.71
6.69
5.40
5.36
1.02
1.01
4l
2 : 3
0.96
0.91
1.23
1.35
4.62
2.72
3.21
1.22
1.38
0.97
1.00
1.38
17.24
27.39
f1 (ppm)

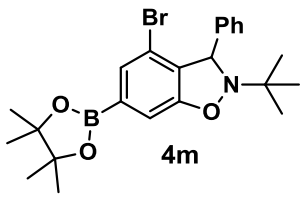

159.05
156.30
144.21
144.15
128.42
128.36
127.72
127.33
127.19
127.11
106.31
83.36
83.08
66.99
66.68
60.60
60.53
25.09
25.07
24.62
24.50
24.49
24.42
4l
2 : 3
S87
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


30.77
4l
2 : 3
S88
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

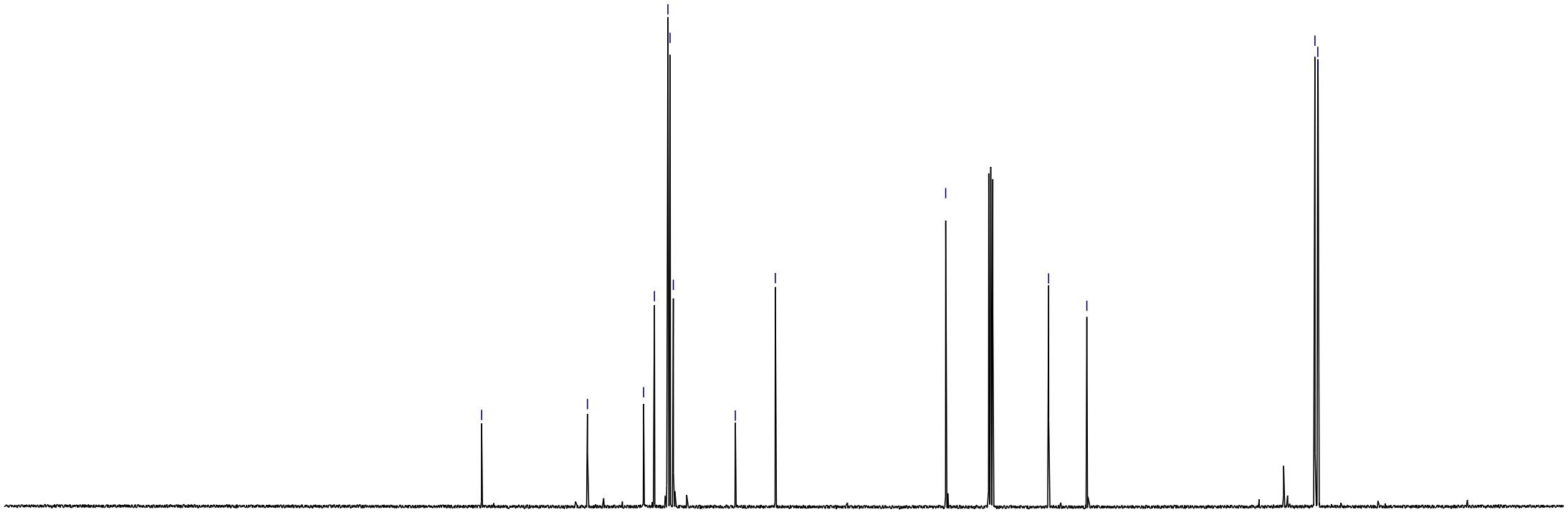

4l
3 : 2
C
B
A
B'
C'
A'
H(A)
H(A')
H(B)
H(C)
CH α N
S89
f2 (ppm)
f1 (ppm)
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
63.0
63.5
64.0
64.5
65.0
65.5
66.0
66.5
67.0
67.5
68.0
68.5
69.0
69.5


Br
Ph
N
O
B
O
O
4m

7.46
7.32
7.30
7.28
7.26
7.26
7.23
5.53
0.90
6.11
1.00
12.46
9.56
S90
f1 (ppm)

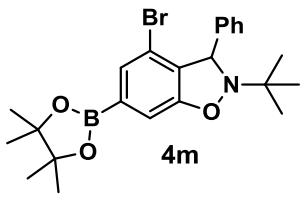


158.19
141.32
132.36
130.64
128.49
128.15
127.62
117.74
111.36
84.20
67.79
61.69
25.33
24.87
24.82



230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

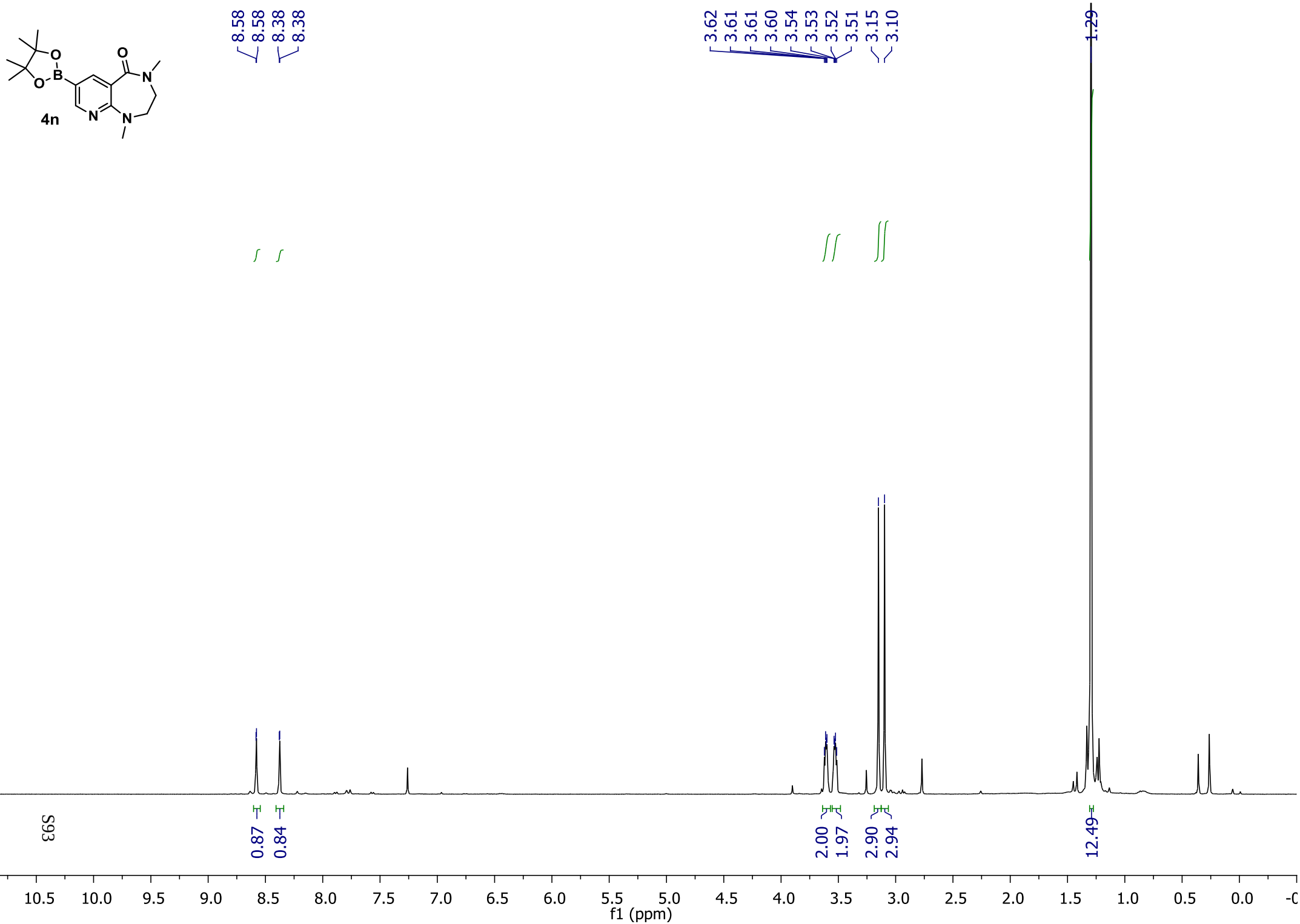


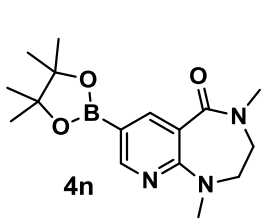
4m

30.12

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)


4n
8.58
8.58
8.38
8.38
3.62
3.61
3.61
3.60
3.54
3.53
3.52
3.51
3.15
3.10
1.29
0.87
0.84
2.00
1.97
2.90
2.94
12.49
f1 (ppm)

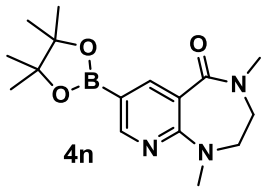


4n

169.06
156.99
156.56
147.30
117.47
83.59
55.81
47.75
38.79
35.54
24.79

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



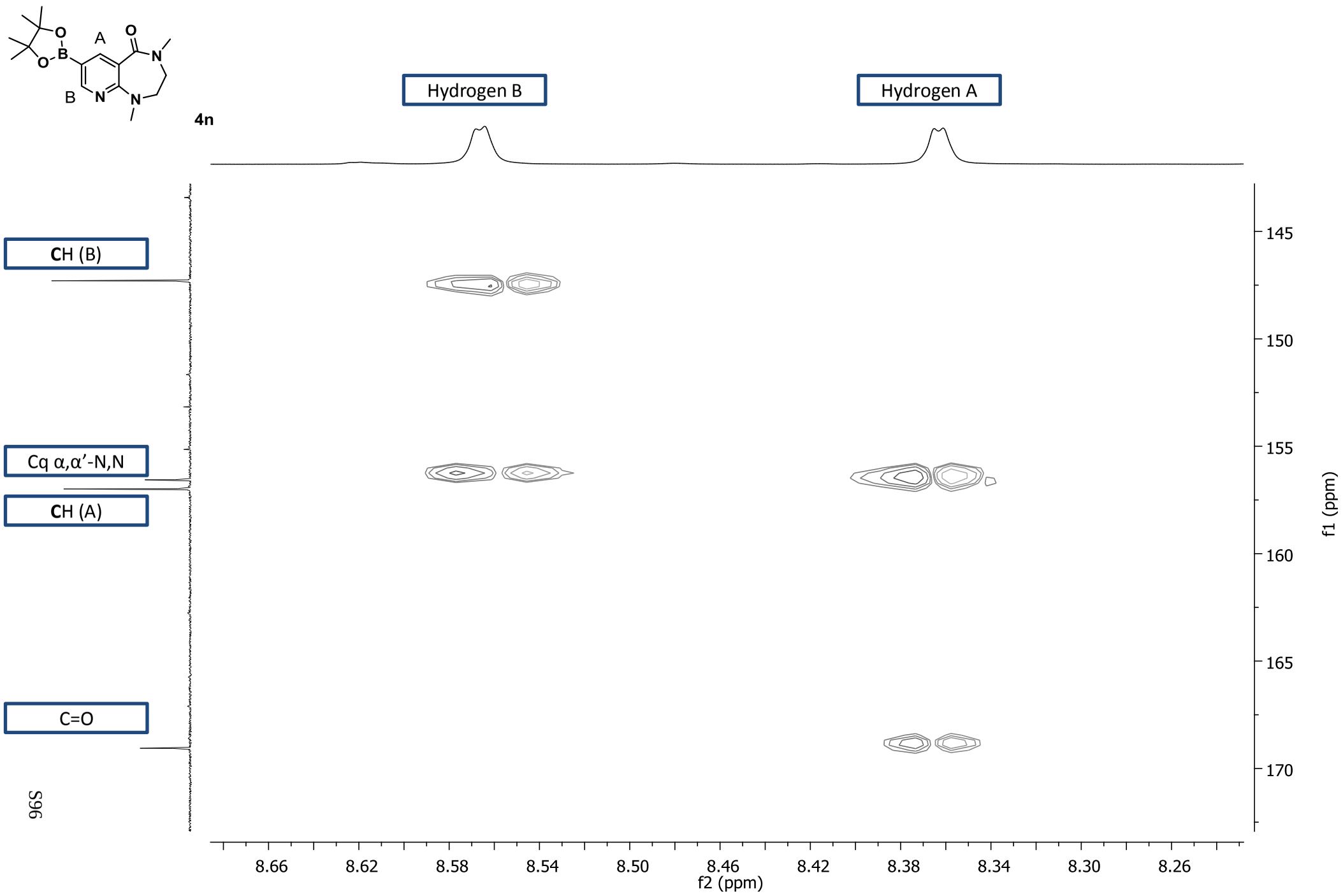
4n

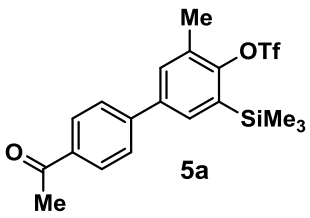
30.67

S95

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

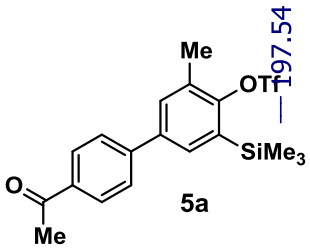
f1 (ppm)


A
B
4n
Hydrogen B
Hydrogen A
CH (B)
Cq α,α'-N,N
CH (A)
C=O
S96
8.66
8.62
8.58
8.54
8.50
8.46
8.42
8.38
8.34
8.30
8.26
f2 (ppm)
145
150
155
160
165
170
f1 (ppm)


Me
OTf
SiMe3
O
Me

5a

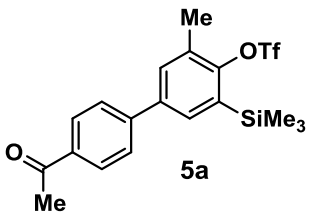
8.06
8.04
7.65
7.63
7.58
7.58
7.51
7.51
2.65
2.46
0.43
2.03
2.10
1.00
1.01
3.00
2.98
9.07
S97
f1 (ppm)



5a

197.54
151.03
144.27
139.60
136.26
135.62
133.26
132.48
131.94
128.94
127.38
123.37
120.19
117.01
113.83
26.65
17.47
17.46
0.08

f1 (ppm)



5a

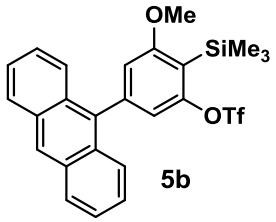
-73.26

S99

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

ed234-01_purif_PROTON_01



5b

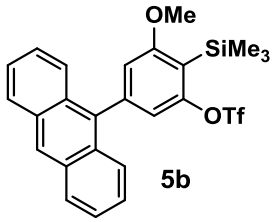
8.52 8.06 8.04 7.65 7.63 7.49 7.49 7.47 7.46 7.45 7.42 7.42 7.40 7.40 7.39 7.38 7.38 7.03 6.89 6.89 3.78 0.48

S100

1.00 2.03 2.08 2.10 2.19 0.94 1.03 3.11 8.96

f1 (ppm)

ed234-01_purif_CARBON_01



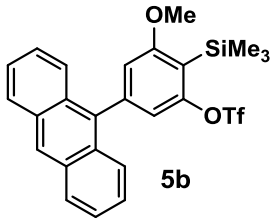
5b

165.38
154.56
143.02
134.55
131.22
129.83
128.43
127.35
126.13
125.93
125.27
123.37
120.17
120.08
116.98
115.88
115.86
113.79
112.63
55.75
0.90

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

ed234-01_purif_FLUORINE_01



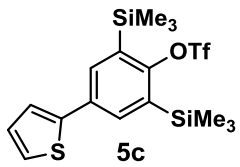
5b

-72.65

S102

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)



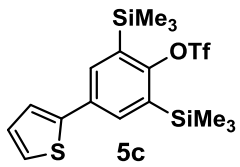
7.75
7.35
7.33
7.31
7.30
7.13
7.12
7.11
7.10

0.41

1.93
0.96
1.00
1.00

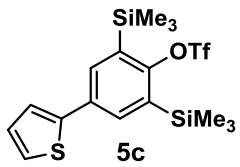
18.30

f1 (ppm)



154.11
142.67
135.63
135.61
133.43
128.18
125.74
124.08
123.18
120.00
116.82
113.64
0.30

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

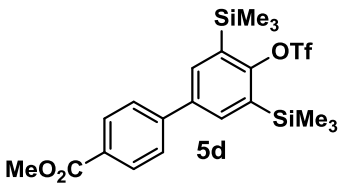


5c

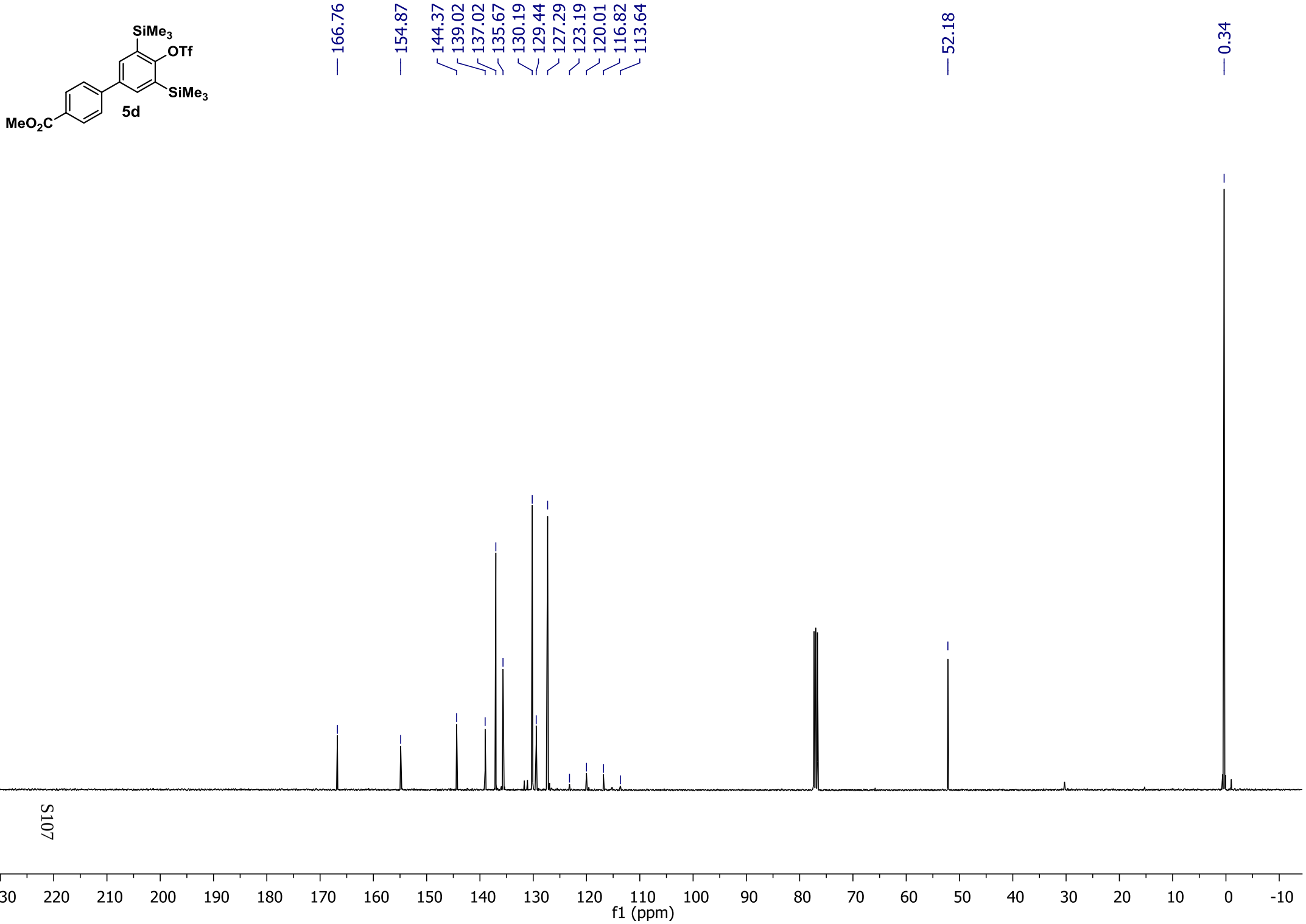
-72.35

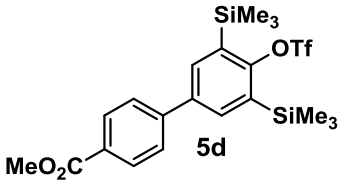
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)


SiMe3
OTf
SiMe3
MeO2C
5d

8.15
8.13
7.75
7.62
7.60
3.96
0.42
1.97
1.95
2.11
3.00
17.87
f1 (ppm)


SiMe3
OTf
SiMe3
MeO2C
5d
166.76
154.87
144.37
139.02
137.02
135.67
130.19
129.44
127.29
123.19
120.01
116.82
113.64
52.18
0.34
S107
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SiMe3
OTf
SiMe3
MeO2C

5d

-72.31
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

ed235-01_F1_PROTON_01

5e

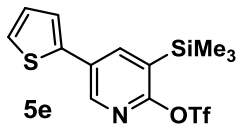
8.53
8.53
8.03
8.02
7.41
7.40
7.39
7.39
7.34
7.34
7.33
7.33
7.15
7.14
7.14
7.13
0.41

S109

1.00
1.05
1.03
1.09
1.10
9.17

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

ed235-01_anal_CARBON_01



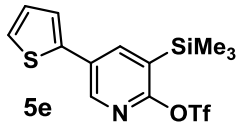
5e

159.68
145.47
143.90
138.65
130.34
128.43
126.67
125.45
124.89
123.27
120.08
116.89
113.71
-1.62

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

ed235-01_F1_FLUORINE_01

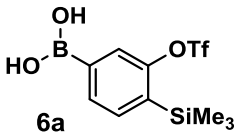


5e

-72.73

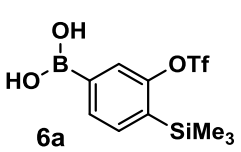
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)


OH
HO
B
OTf
SiMe3

6a

8.40
8.27
8.25
8.12
8.11
8.09
7.73
7.71
7.53
7.51
0.46
0.44
0.90
1.00
12.50
21.25
8.53
11.63
1.22
8.55
97.86
f1 (ppm)

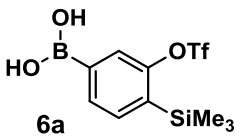


6a

155.29
138.63
136.27
134.06
125.62
123.31
120.13
116.95
113.77
-0.92

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

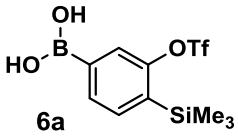


6a

-74.06

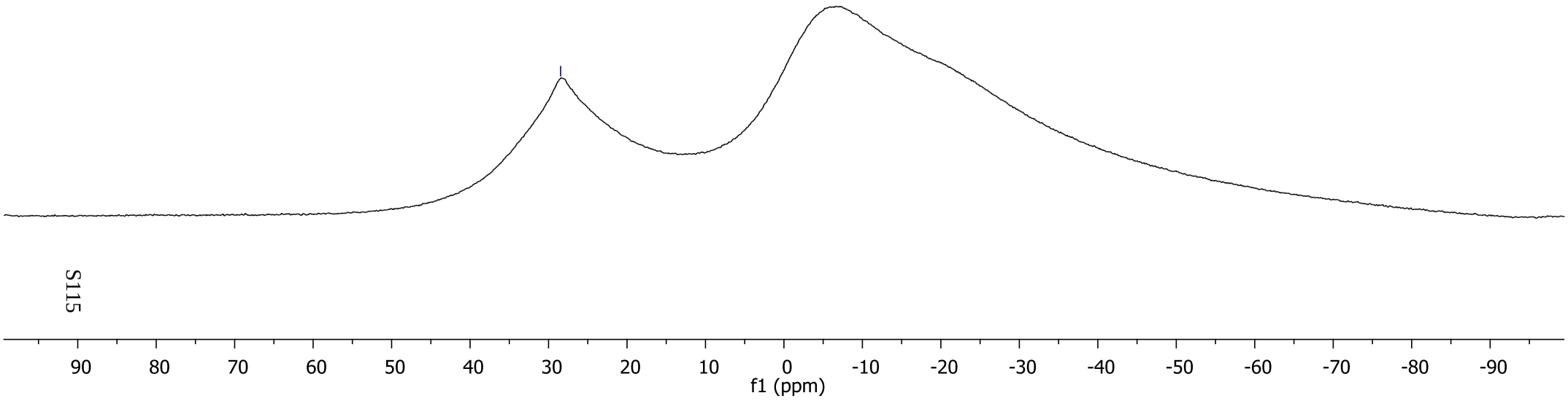
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

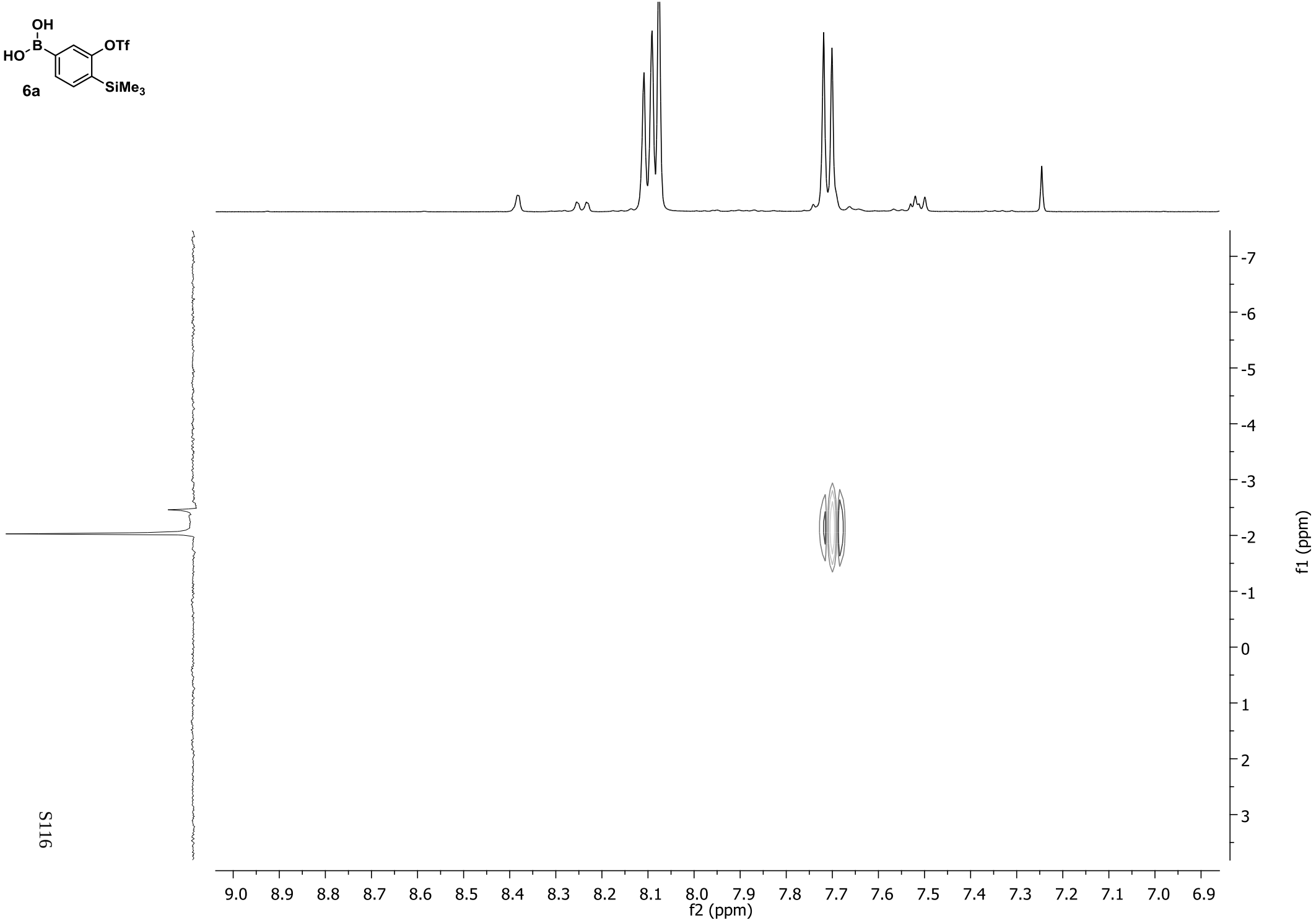
f1 (ppm)

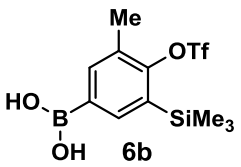

OH
HO
B
OTf
SiMe3

6a

28.46

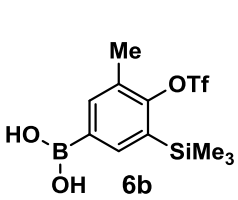

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


OH
HO
B
OTf
SiMe3
6a
f2 (ppm)
f1 (ppm)


Me
OTf
HO
B
OH
SiMe3

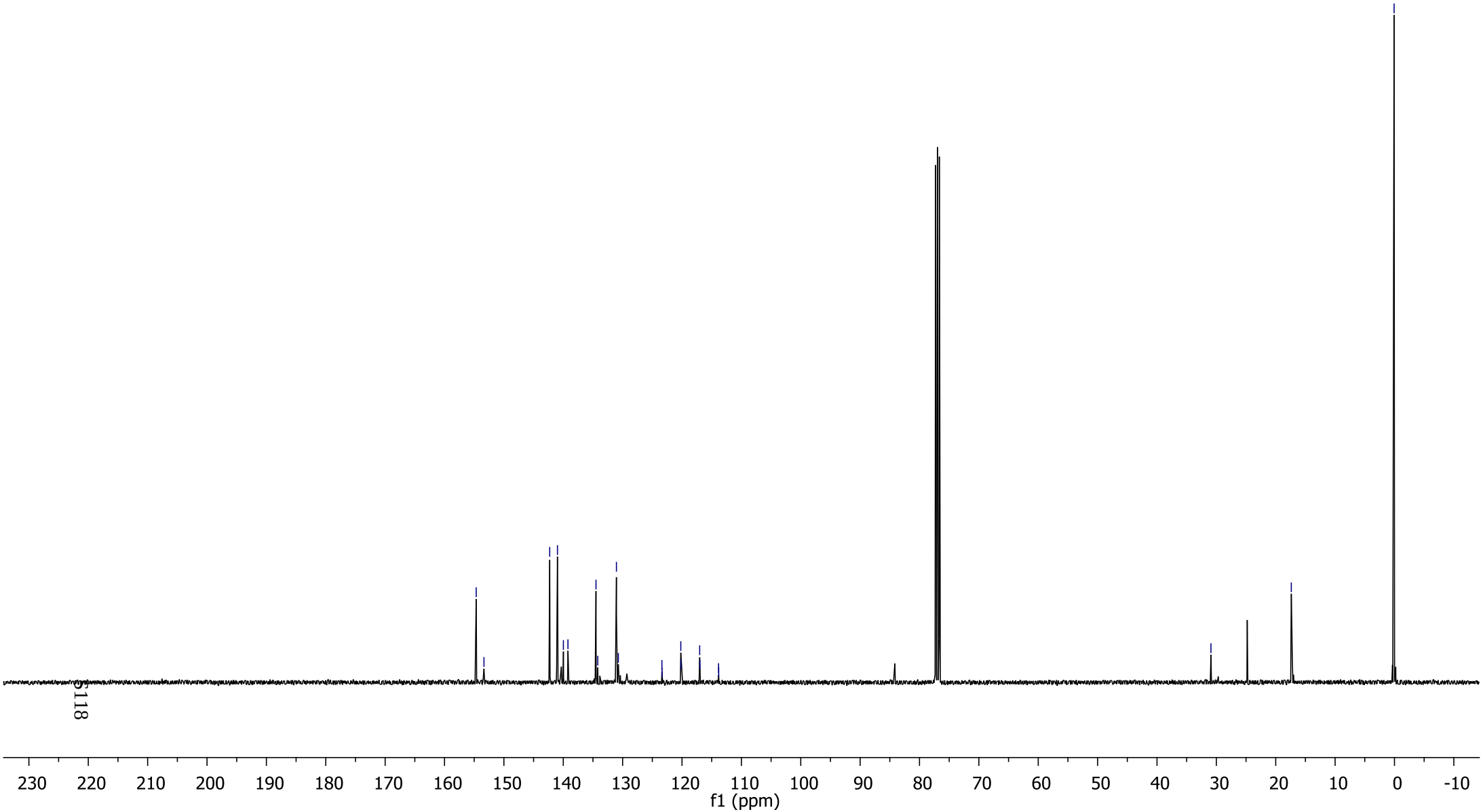
6b

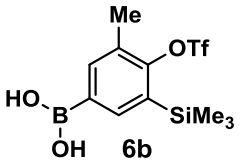
8.26
8.08
7.75
7.66
2.51
0.47
0.40
3.35
3.33
1.00
1.03
10.15
3.04
30.10
10.52
S117
f1 (ppm)



154.66
153.36
142.29
140.98
139.98
139.21
134.49
134.19
131.04
130.72
123.38
123.36
120.20
120.18
117.02
117.00
113.85
113.82

30.91
17.38
0.06





6b

-73.19
-73.31

S119

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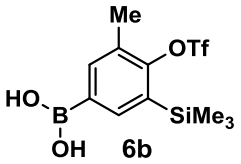
f1 (ppm)



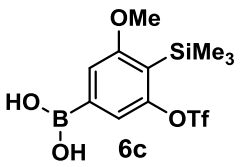
6b

28.95

S120

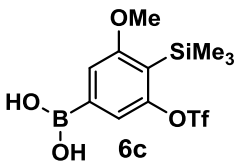
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)


OMe
SiMe3
HO
B
OH
OTf

6c

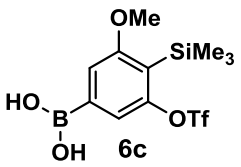
7.73
7.56
3.95
0.42
0.37
4.80
5.02
1.00
1.08
15.27
3.42
44.66
9.30
f1 (ppm)



165.40
154.85
126.75
123.44
120.25
119.13
117.06
114.99
55.41
0.64

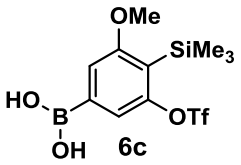
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


OMe
SiMe3
HO
B
OH
OTf

6c

-72.82
-72.98
S123
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

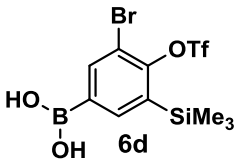


6c

28.62

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)



8.42
8.42
8.33
8.32
8.04
7.86

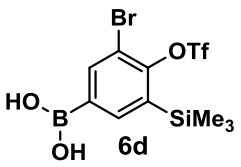
0.50
0.42

S125

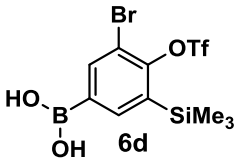
12.70
13.15
1.00
0.93

107.07
9.81

f1 (ppm)

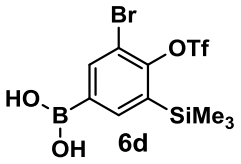

Br
OTf
HO
B
OH
SiMe3
6d

152.34
143.16
142.66
137.77
123.38
120.19
117.00
116.94
113.81
0.02
S126
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



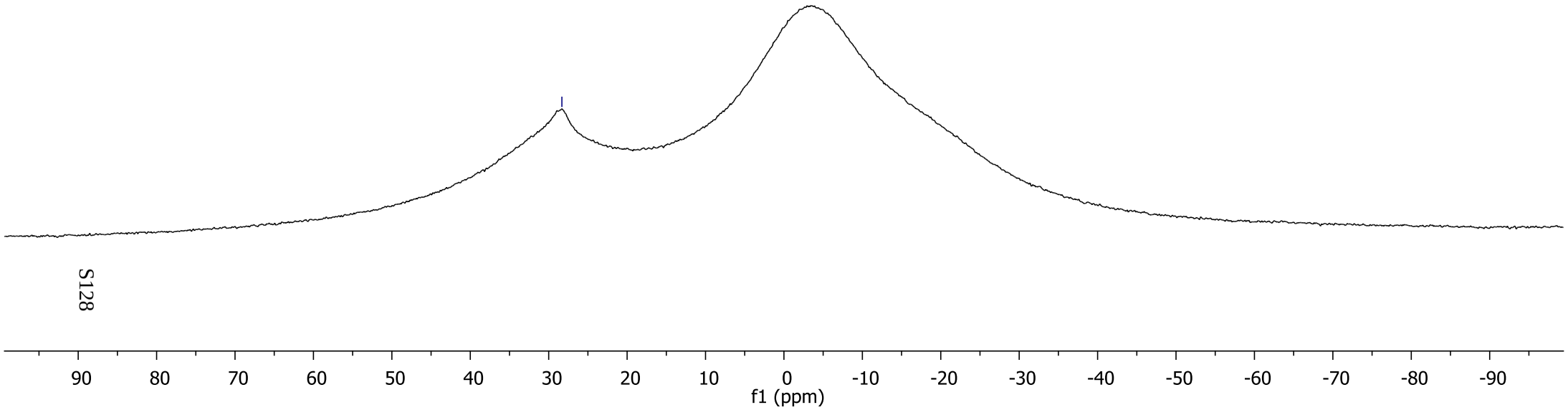
-71.41
-71.61

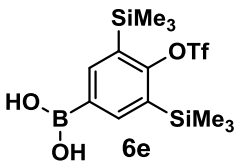
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Br
OTf
HO
B
OH
SiMe3

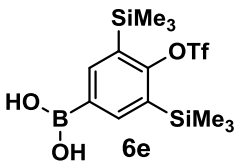
6d

28.32


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


SiMe3
OTf
HO
B
OH
SiMe3
6e

8.44
8.42
0.46
S129
2.00
0.34
20.71
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

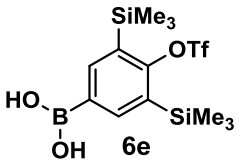


6e

158.59
145.81
134.57
123.19
120.01
116.82
0.29

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

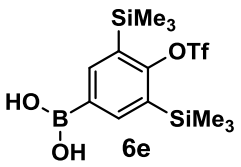


6e

-72.28
-72.32

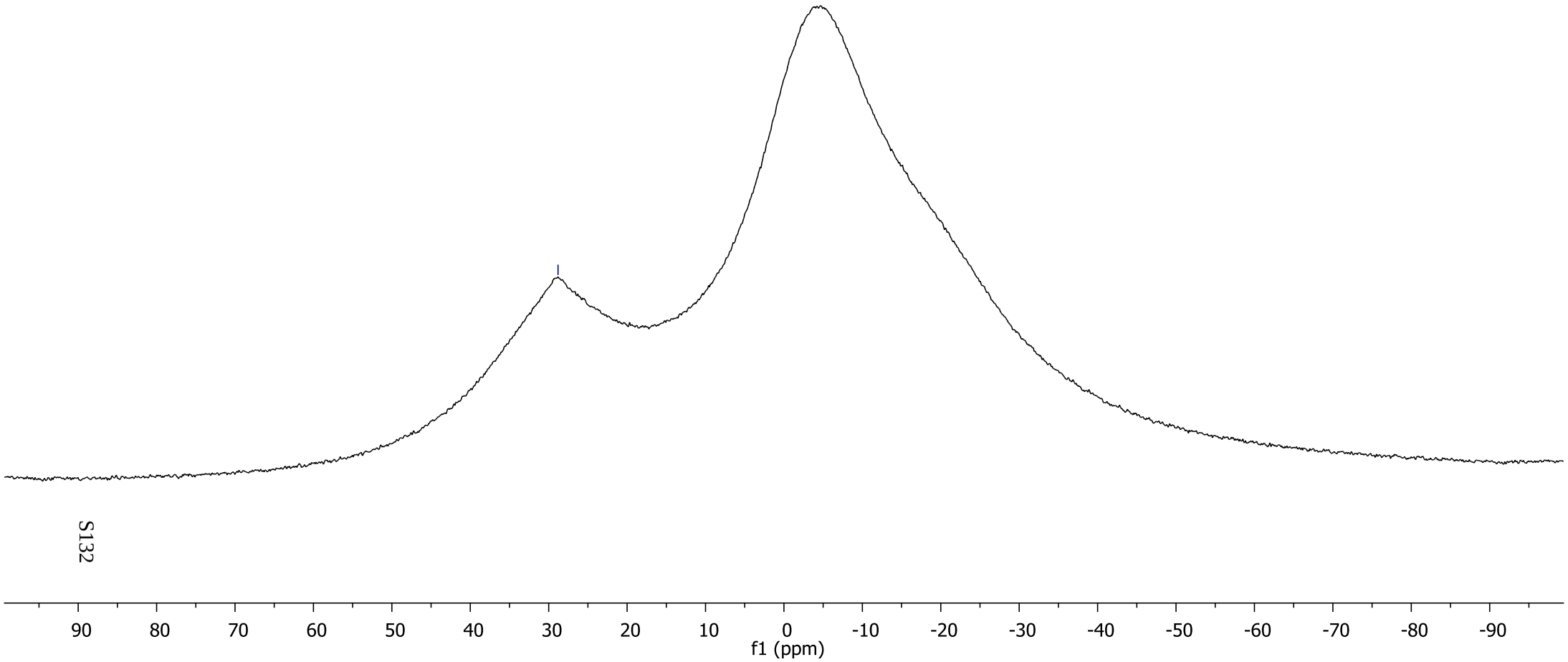
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

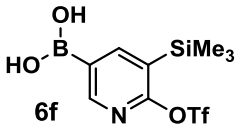
f1 (ppm)


SiMe3
OTf
HO
B
OH
SiMe3

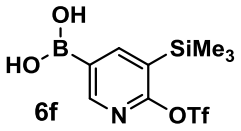
6e

28.81

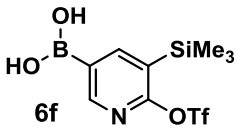

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


OH
HO
B
SiMe3
6f
N
OTf

9.02
8.61
8.27
8.26
0.44
1.00
1.14
0.11
9.44
1.11
f1 (ppm)


OH
HO
B
SiMe3
6f
N
OTf

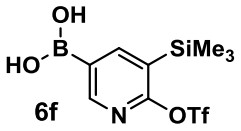
163.87
156.18
154.06
124.66
123.18
120.00
116.81
113.62
-1.66
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



-72.96

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

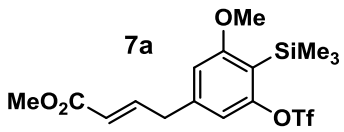
f1 (ppm)



28.65

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

f1 (ppm)



7.08 7.06 7.05 7.04 7.02 7.01 6.75 6.62 5.86 5.86 5.86 5.83 5.82 5.82

3.81 3.73 3.53 3.52 3.51 3.51

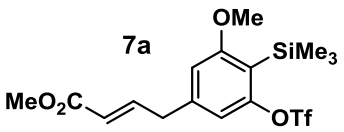
0.35

S137

1.00 1.00 1.05 0.98 3.14 3.16 2.15 9.63

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

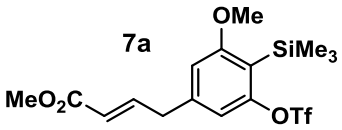
f1 (ppm)



166.52
165.66
154.68
145.71
142.10
123.33
122.74
120.14
119.09
116.95
113.76
113.18
113.16
109.98
55.56
51.55
38.20
0.68

S138

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

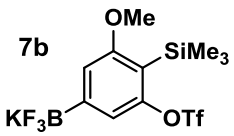


-72.80

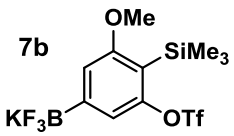
S139

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

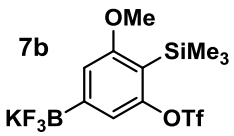

7b
OMe
SiMe3
KF3B
OTf

7.07
6.95
3.83
0.33
1.00
0.81
3.16
10.15
f1 (ppm)



165.77
155.41
124.40
121.22
118.04
117.10
115.97
115.95
115.93
115.92
115.90
114.87
113.82
113.81
77.44
56.15
1.09

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

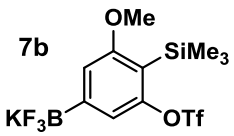


-73.77

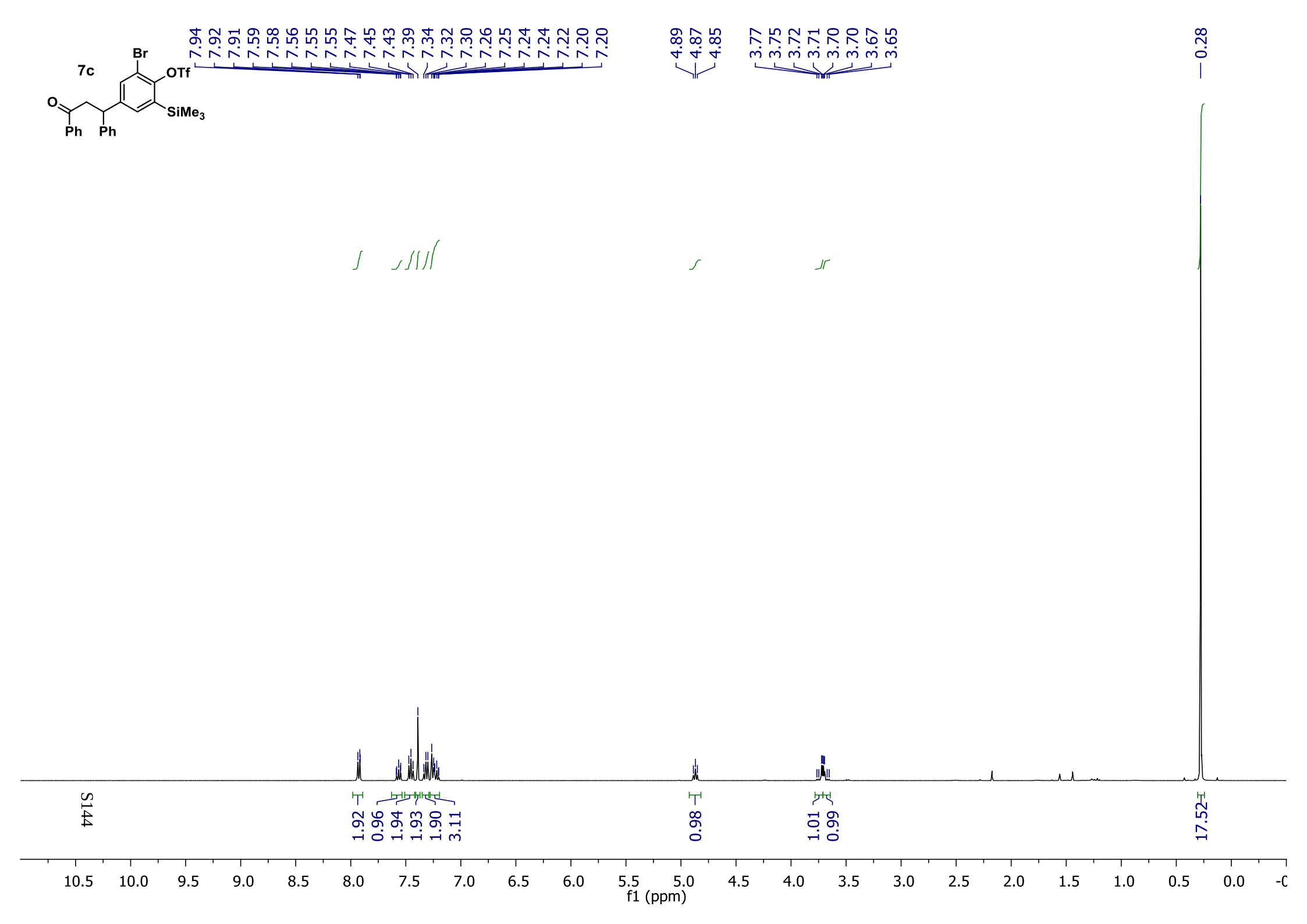
-143.51

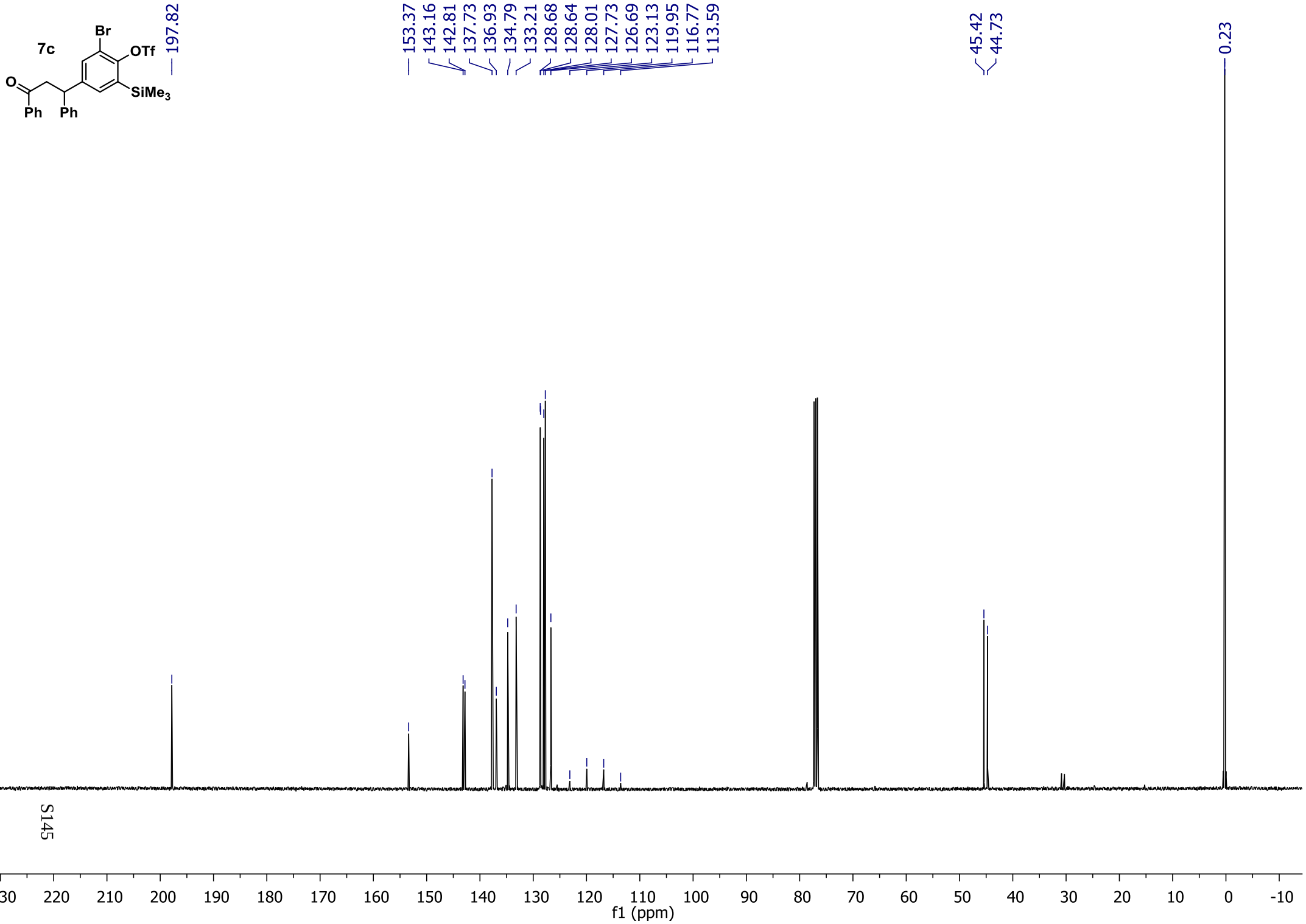
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

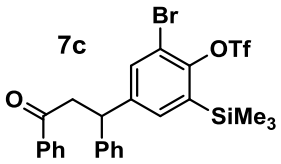
f1 (ppm)


7b
OMe
SiMe3
KF3B
OTf

2.79
2.48
S143
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


7c
Br
OTf
SiMe3
O
Ph
Ph
7.94
7.92
7.91
7.59
7.58
7.56
7.55
7.55
7.47
7.45
7.43
7.39
7.34
7.32
7.30
7.26
7.25
7.24
7.24
7.22
7.20
7.20
4.89
4.87
4.85
3.77
3.75
3.72
3.71
3.70
3.70
3.67
3.65
0.28
1.92
0.96
1.94
1.93
1.90
3.11
0.98
1.01
0.99
17.52
f1 (ppm)

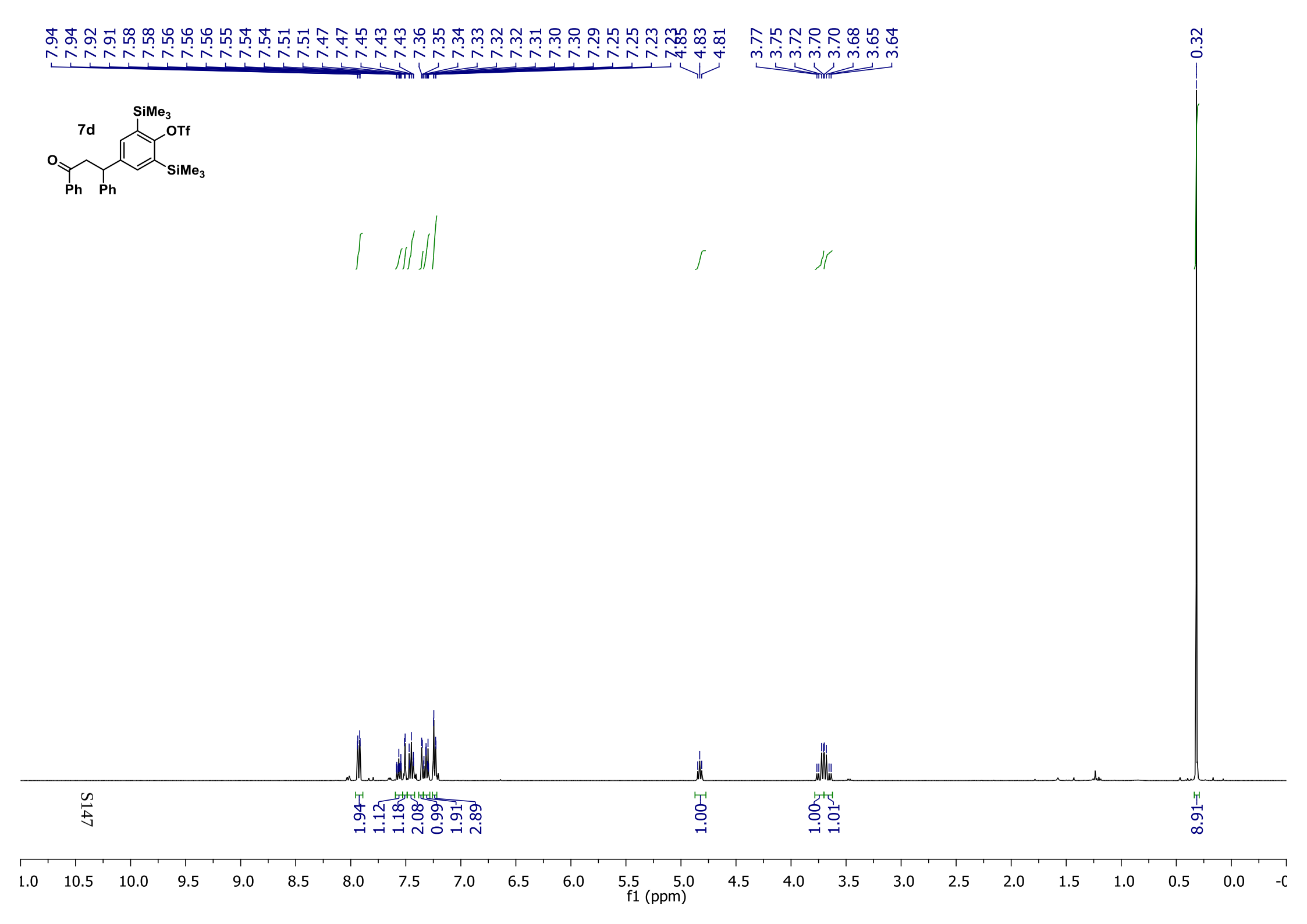

7c
Br
OTf
SiMe3
O
Ph
Ph
197.82
153.37
143.16
142.81
137.73
136.93
134.79
133.21
128.68
128.64
128.01
127.73
126.69
123.13
119.95
116.77
113.59
45.42
44.73
0.23
f1 (ppm)

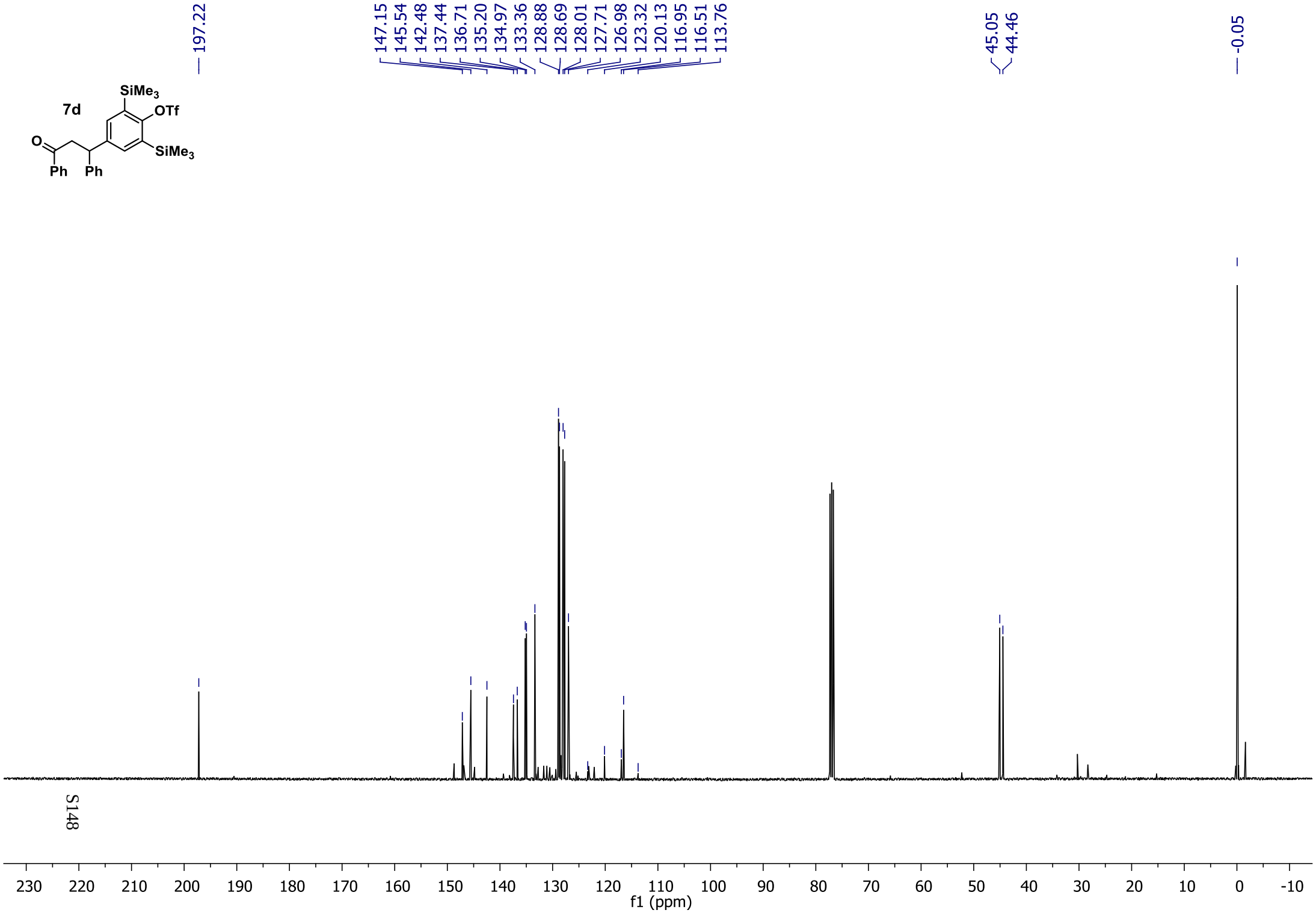


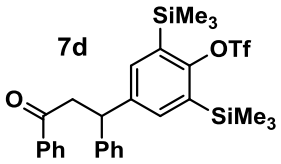
-72.53

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)


7.94
7.94
7.92
7.91
7.58
7.58
7.56
7.56
7.56
7.55
7.54
7.54
7.51
7.51
7.47
7.47
7.45
7.43
7.43
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.25
7.25
7.23
4.85
4.83
4.81
3.77
3.75
3.72
3.70
3.70
3.68
3.65
3.64
0.32
7d
SiMe3
OTf
SiMe3
O
Ph
Ph
1.94
1.12
1.18
2.08
0.99
1.91
2.89
1.00
1.00
1.01
8.91
S147
f1 (ppm)

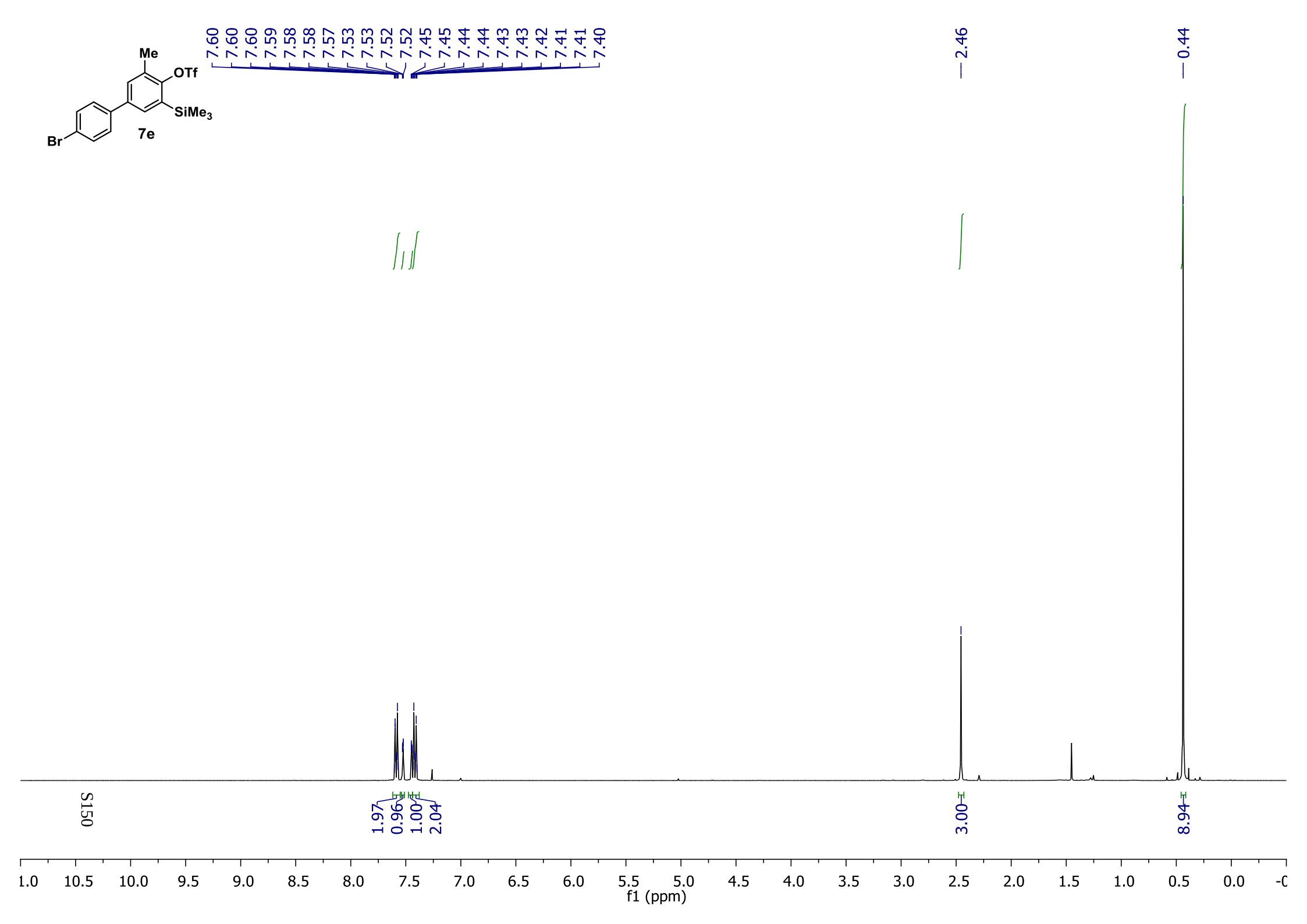

197.22
147.15
145.54
142.48
137.44
136.71
135.20
134.97
133.36
128.88
128.69
128.01
127.71
126.98
123.32
120.13
116.95
116.51
113.76
45.05
44.46
-0.05
7d
SiMe3
OTf
SiMe3
O
Ph
Ph
S148
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

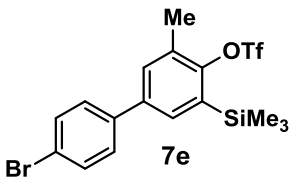


-71.76

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)


Me
OTf
SiMe3
Br
7e
7.60
7.60
7.60
7.59
7.58
7.58
7.57
7.53
7.53
7.52
7.52
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.41
7.41
7.40
2.46
0.44
S150
1.97
0.96
1.00
2.04
3.00
8.94
f1 (ppm)



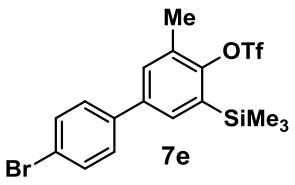
150.67
139.71
138.68
135.48
132.94
132.18
131.98
131.84
128.81
123.39
122.16
120.21
117.03
113.85

17.45
17.43

0.08

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

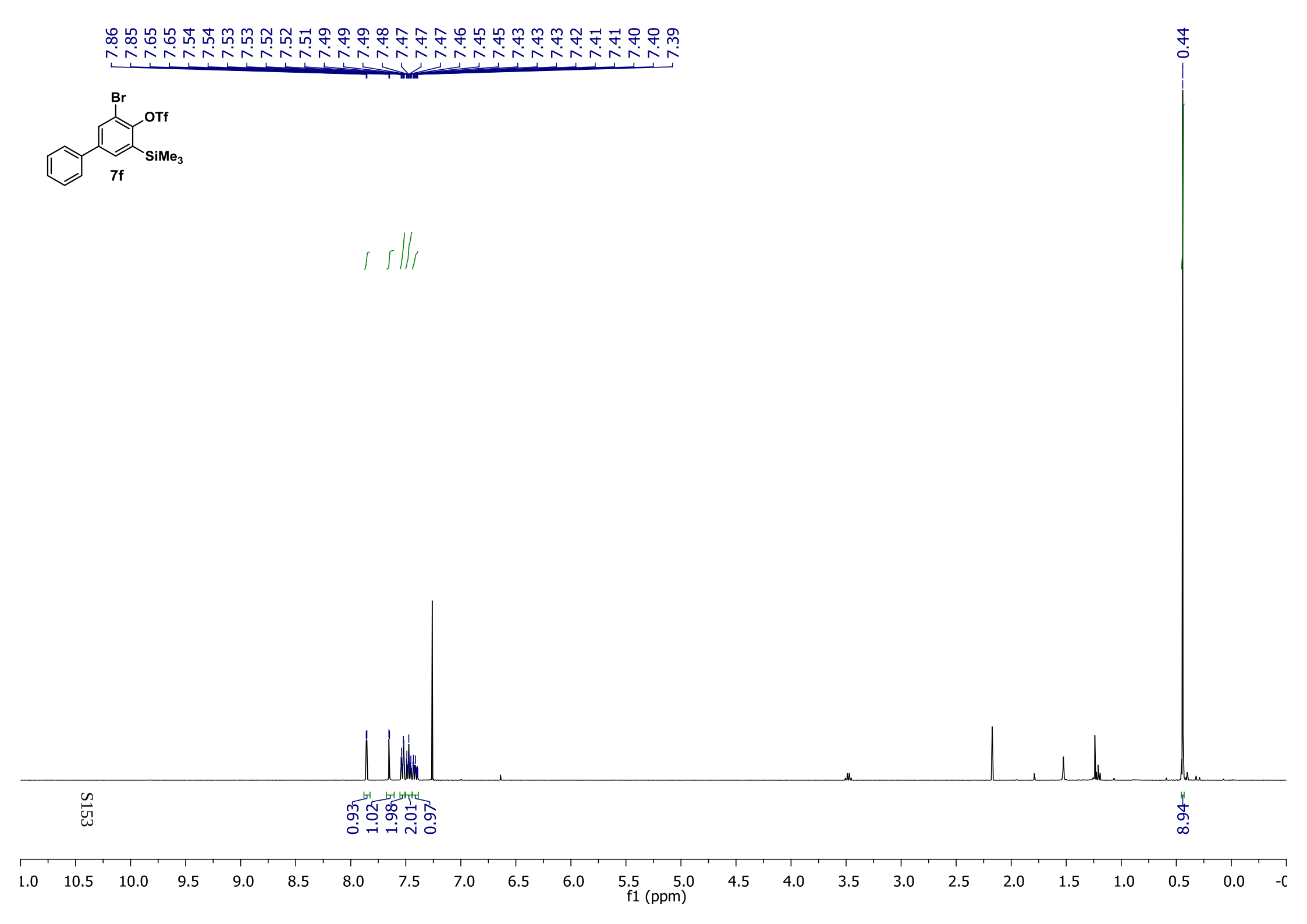
f1 (ppm)

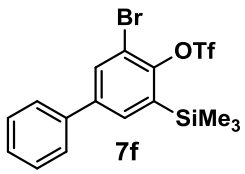


-73.30

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

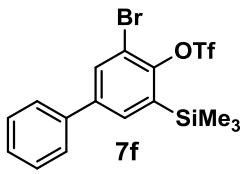
f1 (ppm)


7.86
7.85
7.65
7.65
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.49
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.43
7.43
7.43
7.42
7.41
7.41
7.40
7.40
7.39
0.44
Br
OTf
SiMe3
7f
S153
0.93
1.02
1.98
2.01
0.97
8.94
f1 (ppm)


Br
OTf
SiMe3

7f

148.02
142.33
138.38
137.83
134.23
129.02
128.37
127.23
123.39
120.20
117.01
116.72
113.81
0.07
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



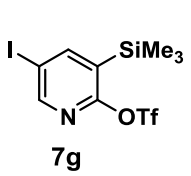
7f

-71.62

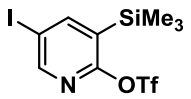
S155

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

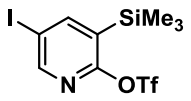


7g


I
SiMe3
N
OTf

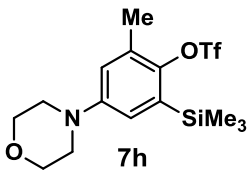
7g

160.04
154.52
154.46
128.71
123.20
120.01
116.82
113.63
92.00
-1.74
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


I
SiMe3
N
OTf

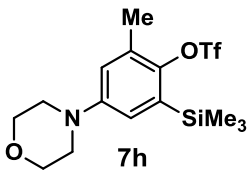
7g

-72.62
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


Me
OTf
SiMe3
N
O

7h

6.86
6.86
6.77
6.76
3.87
3.86
3.85
3.17
3.16
3.15
2.34
0.37
S159
1.00
1.01
4.12
4.10
3.04
9.10
f1 (ppm)

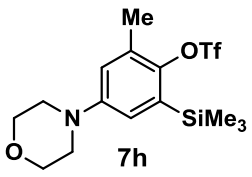


7h

150.02
144.09
135.09
131.95
123.36
120.67
120.18
119.89
117.01
113.83
66.74
49.07
17.68
17.67
0.07

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

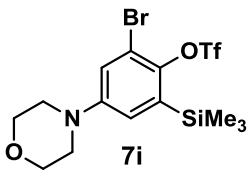


7h

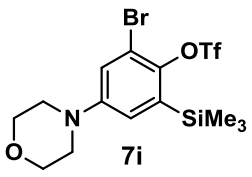
-73.52

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

f1 (ppm)

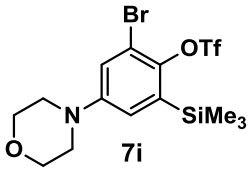


7i


Br
OTf
SiMe3
N
O

7i

150.69
141.27
137.30
123.36
121.42
121.25
120.17
116.98
113.79
66.55
48.49
0.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
OTf
N
O
SiMe3

7i

-71.81
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)