Nickel-Catalyzed Borylation of Benzylic Ammonium Salts: Stereospecific Synthesis of Enantioenriched Benzylic Boronates

Corey H. Basch, Kelsey M. Cobb, Mary P. Watson*

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

mpwatson@udel.edu

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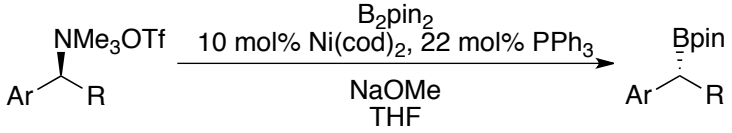
General Information

Reactions were performed in oven-dried vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. Flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of N_2. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, 60Å) unless otherwise noted. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, or Cambridge Isotopes Laboratories and used as received with the following exceptions: Bis(pinacolato)diboron, bis(neopentyl glycolato)diboron, and bis(hexylene glycolato)diboron were purchased from Sigma Aldrich and immediately placed in a N_2-atmosphere glovebox for storage. $Ni(OAc)_2 \cdot 4H_2O$ was purchased from Alfa Aesar and donated by Astra Zeneca. Methyl trifluoromethanesulfonate (MeOTf) was purchased from TCI and used directly. 1,3-Bis(cyclohexyl)imidazolium tetrafluoroborate ($ICy \cdot HBF_4$) was purchased from Sigma Aldrich and used as received.. THF was dried by passing through drying columns, then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox.[1] Commercially available enantioenriched amines were purchased from Alfa Aesar or Sigma Aldrich and used as received. Enantioenriched amines that were not commercially available were obtained through Grignard or hydride additions of Ellman's sulfinimines.[2] Dimethyl benzyl amines were prepared using Escheweiler-Clarke conditions or reductive amination of the corresponding primary benzyl amine with formaldehyde.[3] In some instances oven-dried potassium carbonate was added into $CDCl_3$ to remove trace amount of acid. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, fluorine nuclear magnetic resonance spectra (^{19}F NMR), and silicon nuclear magnetic resonance spectra (^{29}Si NMR) were recorded on both 400 MHz and 600 MHz spectrometers. Boron nuclear magnetic resonance spectra (^{11}B NMR) were recorded on a 600 MHz spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.2). Data are represented as follows: chemical shift, multiplicity

(br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using FTIR spectrophotometers with material loaded onto a KBr plate. The mass spectral data were obtained at the University of Delaware mass spectrometry facility. Optical rotations were measured using a 2.5 mL cell with a 0.1 dm path length. Melting points were taken on a Stuart SMP10 instrument.

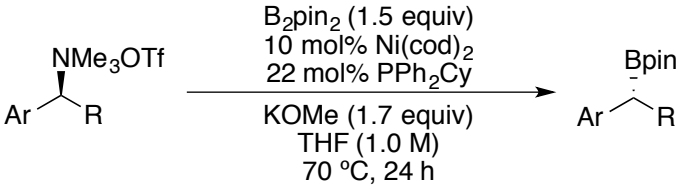
Stereospecific Borylation of Benzylic Ammonium Salts

General Procedure A: Borylation of Naphthyl-Substituted Benzylic Ammonium Salts



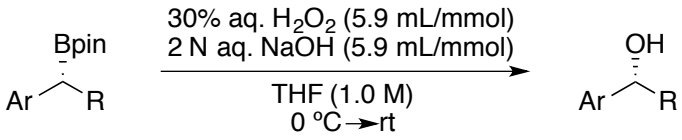
In a N_2-atmosphere glovebox, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 10 mol %), PPh_3 (4.4 mg, 0.066 mmol, 22 mol %), NaOMe (24 mg, 0.45 mmol, 1.5 equiv), B_2pin_2 (114 mg, 0.45 mmol, 1.5 equiv), and ammonium salt **1** (0.30 mmol, 1.0 equiv) were weighed into a 1-dram vial equipped with a magnetic stir bar. THF (1.5 mL, 0.2 M) was added, and the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a short plug of Celite®, which was then rinsed with Et_2O (~ 10 mL). The filtrate was concentrated and purified by silica gel chromatography to give the benzylic boronate product. The benzylic boronate was then converted to the corresponding benzylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure B: Borylation of Non-Naphthyl-Substituted Benzylic Ammonium Salts



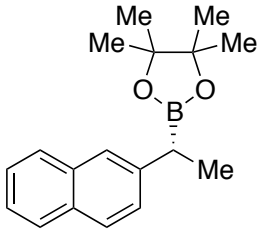
In a N_2-atmosphere glovebox, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 10 mol %), PPh_2Cy (18 mg, 0.066 mmol, 22 mol %), KOMe (38 mg, 0.45 mmol, 1.7 equiv), B_2pin_2 (114 mg, 0.45 mmol, 1.5 equiv), and ammonium salt **1** (0.30 mmol, 1.0 equiv) were weighed into a 1-dram vial equipped with a magnetic stir bar. THF (0.3 mL, 1.0 M) was added and the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 70 ºC for 24 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a plug of Celite®, which was then rinsed with Et_2O (~ 10 mL). The filtrate was concentrated and then purified by silica gel chromatography to give the benzylic boronate product. The benzylic boronate was then converted to the corresponding benzylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure C: Oxidation of Benzylic Boronates to Benzylic Alcohols for Determination of Enantiomeric Excess (ee).



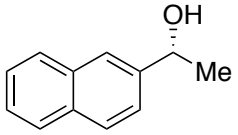
A solution of the benzylic boronate **2** (1.0 equiv) and Et_2O (0.017 M) was cooled to 0 ˚C. Aqueous NaOH (2 N, 5.9 mL/mmol of **2**) was added, followed by aq. H_2O_2 (30%, 5.9 mL/mmol of **2**). The mixture was stirred and allowed to warm slowly to room temperature overnight. The reaction mixture was diluted with H_2O and Et_2O, and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The crude mixture was purified via silica gel chromatography to afford benzylic alcohol **3** for ee

determination. For duplicate experiments, alcohol **3** was isolated once via column chromatography (to verify high yield in the oxidation) and once via preparatory thin-layer chromatography under the same mobile-phase conditions.



(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (2a). Prepared via General Procedure A using ammonium salt **1a** (amine purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2a** (run 1: 69 mg, 82%; run 2: 79%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 3H), 7.67 (s, 1H), 7.48 – 7.37 (m, 3H), 2.64 (q, J = 7.4 Hz, 1H), 1.46 (d, J = 7.6 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 134.0, 131.8, 127.8, 127.7, 127.6, 127.4, 125.8, 125.4, 124.9, 83.5, 24.8, 24.8, 17.0.[4] The spectral data match that previously reported in the literature.[5]

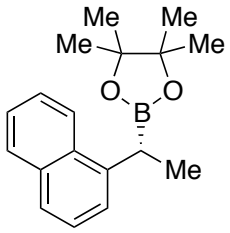
Boronate **2a** was oxidized to alcohol **3a** via General Procedure C. The enantiomeric excess was determined to be 99% (run 1: 99% ee; run 2: 99% ee) by chiral HPLC analysis. See alcohol **3a** below.



(*R*)-1-(naphthalen-2-yl)ethanol (3a). Prepared via General Procedure C using benzylic boronate **2a**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3a** (run 1 (66 mg of **2a**): 38 mg, 95%) as a white solid. The enantiomeric excess was determined to be 99% (run 1: 99% ee; run 2: 99% ee) by chiral

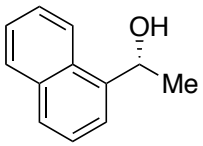
HPLC analysis (CHIRAPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 43.70 min, t_R(minor) = 45.74 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 4H), 7.56 – 7.42 (m, 3H), 5.06 (q, *J* = 6.2 Hz, 1H), 2.07 (s, 1H), 1.58 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 133.4, 133.0, 128.5, 128.1, 127.8, 126.3, 126.0, 123.97, 123.95 70.7, 25.3. The spectral data match that previously reported in the literature.[6]

The absolute configuration of alcohol **3a** was determined to be *R* by comparison of its HPLC trace to that of commercially available, enantioenriched **3a**.

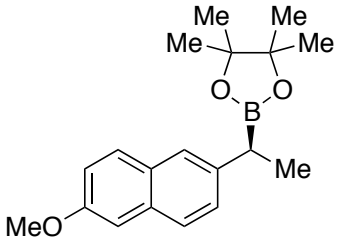


(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)ethyl)-1,3,2-dioxaborolane ((*R*)-2b). Prepared via General Procedure A using ammonium salt **1b** (amine purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2b** (run 1: 47 mg, 56%; run 2: 47 mg, 56%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.39 (m, 4H), 3.14 (q, *J* = 7.4 Hz, 1H), 1.52 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 134.0, 132.1, 128.9, 126.0, 125.5, 125.4, 124.4, 124.2, 83.6, 24.8, 24.7, 16.6.[4] The spectral data matches that previously reported in the literature.[5]

Boronate **2b** was oxidized to alcohol **3b** via General Procedure C. The enantiomeric excess was determined to be 92% (run 1: 92%, run 2: 91%) by chiral HPLC analysis. See alcohol **3b** below.

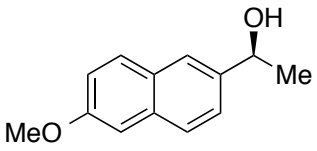


(*R*)-1-(naphthalen-1-yl)ethanol (3b). Prepared via General Procedure C using benzylic boronate **2b**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3b** (run 1 (47 mg of **2b**): 21 mg, 72%) as a colorless oil. The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 91% ee) by chiral HPLC analysis (CHIRAPAK IC, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 23.87 min, t_R(minor) = 18.43 min): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.45 (m, 3H), 5.69 (q, *J* = 6.3 Hz, 1H), 1.96 (s, 1H), 1.68 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 133.9, 130.4, 129.1, 128.1, 126.2, 125.73, 125.70, 123.3, 122.1, 67.3, 24.5. The spectral data of this compound match that previously reported in the literature.[6]

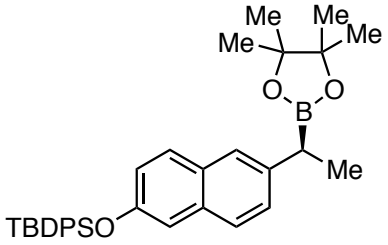


(*S*)-2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c). Prepared via General Procedure A using ammonium salt **1c** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2c** (run 1: 78 mg, 83%; run 2: 78 mg, 83%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.1 Hz, 2H), 7.60 (s, 1H), 7.38 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 2.60 (q, *J* = 7.5 Hz, 1H), 1.44 (d, *J* = 7.5 Hz, 3H), 1.23 (s, 6H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 140.3, 132.7, 129.5, 129.1, 127.8, 126.7, 125.3, 118.5, 105.7, 83.5, 55.4, 24.8, 24.7, 17.1.[4] The spectral data match that previously reported in the literature.[7]

Boronate **2c** was oxidized to alcohol **3c** via General Procedure C. The enantiomeric excess was determined to be 99% (run 1: 98% ee; run 2: 99% ee) by chiral HPLC analysis. See alcohol **3c** below.



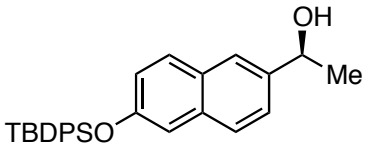
(*S*)-1-(6-methoxynaphthalen-2-yl)ethanol (3c). Prepared via General Procedure C using benzylic boronate **2c**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3c** (run 1 (67 mg of **2c**): 31 mg, 72%) as a white solid; the enantiomeric excess was determined to be 99% (run 1: 98% ee; run 2: 99% ee) by chiral HPLC analysis (CHIRAPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 19.99 min, t_R(minor) = 25.84 min): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 3H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.18 – 7.11 (m, 2H), 5.02 (q, *J* = 6.5 Hz, 1H), 3.92 (s, 3H), 2.03 (s, 1H), 1.57 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 141.1, 134.2, 129.6, 128.9, 127.3, 124.5, 123.9, 119.1, 105.9, 70.6, 55.5, 25.2. The spectral data match that previously reported in the literature.[8]



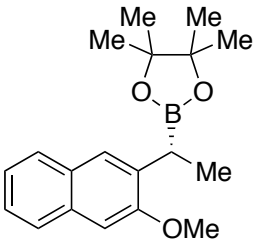
(*S*)-*tert*-butyldiphenyl((6-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)naphthalen-2-yl)oxy)silane (2d). Prepared via General Procedure A using ammonium salt **1d** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2d** (76 mg, 47%) as a white solid (mp 84–86 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.62 – 7.53 (m, 2H),

7.49 – 7.37 (m, 7H), 7.29 (dd, J = 8.5, 1.5 Hz, 1H), 7.10 – 7.03 (m, 2H), 2.57 (q, J = 7.4 Hz, 1H), 1.42 (d, J = 7.5 Hz, 3H), 1.25 (s, 6H), 1.23 (s, 6H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 140.4, 135.7, 133.2, 132.7, 130.0, 129.6, 128.8, 128.0, 127.6, 126.8, 125.2, 121.5, 114.5, 83.5, 26.8, 24.82, 24.79, 19.7, 17.2;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; ^{29}Si NMR (79 MHz, $CDCl_3$) δ –6.4; FTIR (neat) 2960, 2858, 1603, 1500, 1352, 1143, 975, 701 cm^{-1}; HRMS (LIFDI) calculated for $C_{34}H_{41}BO_3Si$: 536.2887, found: 536.2894.

Boronate **2d** was oxidized to alcohol **3d** via General Procedure C. The enantiomeric excess was determined to be 92% by chiral HPLC analysis. See alcohol **3d** below.

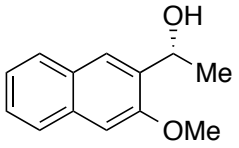


(*S*)-1-(6-((tert-butyldiphenylsilyl)oxy)naphthalen-2-yl)ethanol (3d). Prepared via General Procedure C using benzylic boronate **2d**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3d** (run 1 (71 mg of **2d**): 54 mg, 95%) as a colorless semi-solid. The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 35.70 min, t_R(minor) = 33.76 min. $[\alpha]_D^{24}$ = –20.2º (c 2.2, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 4H), 7.67 (s, 1H), 7.63 – 7.59 (m, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.47 – 7.34 (m, 7H), 7.12 – 7.05 (m, 2H), 4.98 (q, J = 6.4 Hz, 1H), 1.99 (bs, 1H), 1.54 (d, J = 6.5 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 141.1, 135.7, 134.0, 133.0, 130.1, 129.3, 128.9, 128.0, 127.3, 124.2, 123.7, 122.0, 114.7, 70.6, 26.7, 25.2, 19.7; ^{29}Si NMR (119 MHz, $CDCl_3$) δ –5.9; FTIR (neat) 3347 (broad), 3051, 2931, 2858, 1606, 1482, 1263, 1175, 114, 76, 701, 504 cm^{-1}; HRMS (CI+) calculated for $C_{28}H_{30}BO_2Si$: 427.2093, found: 427.2090.



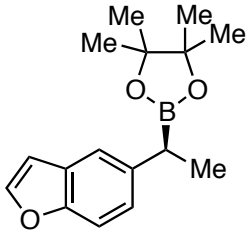
(*R*)-2-(1-(3-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e). Prepared via General Procedure A using ammonium salt **1e** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2e** (46 mg, 49%) as an opaque semi-solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.60 (s, 1H), 7.38 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.31 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.08 (s, 1H), 3.93 (s, 3H), 2.63 (q, *J* = 7.5 Hz, 1H), 1.43 (d, *J* = 7.5 Hz, 3H), 1.26 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 135.7, 133.1, 129.4, 127.3, 126.5, 126.3, 125.3, 123.5, 104.4, 83.2, 55.1, 24.80, 24.77, 14.8;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; FTIR (neat) 2976, 1472, 1388, 1251, 1144, 847, 746 cm^{-1}; HRMS (LIFDI) calculated for $C_{19}H_{25}BO_3$: 312.1897, found: 312.1884.

Boronate **2e** was oxidized to alcohol **3e** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **3e** below.



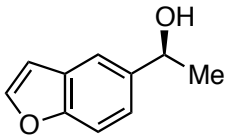
(*R*)-1-(3-methoxynaphthalen-2-yl)ethanol (3e). Prepared via General Procedure C using benzylic boronate **2e**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3e** (run 1 (46 mg of **2e**): 25 mg, 83%) as a clear oil. The enantiomeric excess was determined to be 95% (CHIRALPAK IB, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.47 min, t_R(minor) = 14.96 min. $[\alpha]_D^{24}$ = –35.7º (c 0.11, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.13 (s, 1H), 5.22 (q, *J* = 6.0 Hz,

1H), 3.97 (s, 3H), 2.77 (s, 1H), 1.61 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.6, 135.0, 133.9, 128.9, 127.9, 126.5, 126.4, 125.3, 124.1, 105.6, 67.0, 55.5, 23.1. The spectral data match that previously reported in the literature for the racemic compound.[9]

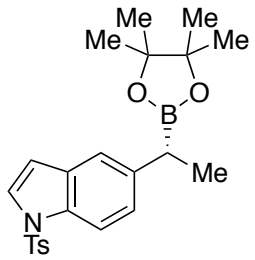


(*S*)-2-(1-(benzofuran-5-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f). Prepared via General Procedure A, except that the reaction temperature was 50 ºC, using ammonium salt **1f** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2f** (run 1: 48 mg, 59%; run 2: 55 mg, 67%) as a white solid (mp 58–59 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.2 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.17 (dd, J = 8.6, 1.9 Hz, 1H), 6.71 (dd, J = 2.2, 1.0 Hz, 1H), 2.54 (q, J = 7.5 Hz, 1H), 1.39 (d, J = 7.5 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 144.9, 139.6, 127.7, 124.7, 119.8, 111.1, 106.7, 83.4, 24.79, 24.75, 17.9;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.6; FTIR (neat) 2976, 1467, 1319, 1144, 843, 737 cm^{-1}; HRMS (LIFDI) calculated for $C_{16}H_{21}BO_3$: 272.1584, found: 272.1611.

Boronate **2f** was oxidized to alcohol **3f** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis. See alcohol **3f** below.



(*S*)-1-(benzofuran-5-yl)ethanol (3f). Prepared via General Procedure C using benzylic boronate **2f**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3f** (run 1 (41 mg of **2f**): 15 mg, 61%) as a clear oil. The enantiomeric excess was determined to be 98% (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRALPAK IC, 0.5 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 45.76 min, t_R(minor) = 43.97 min. $[\alpha]_D^{24}$ = –33.0º (c 0.79, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.76 (d, *J* = 1.1 Hz, 1H), 5.01 (q, *J* = 6.4 Hz, 1H), 1.92 (bs, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 145.6, 140.7, 127.6, 122.2, 118.1, 111.5, 106.8, 70.8, 25.7; FTIR (neat) 3344 (broad), 2921, 1444, 1261, 1129, 1072, 891, 813, 738 cm^{-1}; HRMS (CI+) calculated for $C_{10}H_{11}O_2$: 163.0759, found: 163.0756.

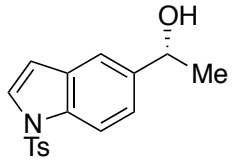


(*R*)-5-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-tosyl-1*H*-indole (2g). Prepared via General Procedure A using ammonium salt **1g** (prepared in ≥95% ee). Instead of filtering through Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield was determined by ^{1}H NMR to be 44% (run 1: 46%, run 2: 41%). The reaction mixture was complicated, preventing effective purification and isolation on scale. However, an analytical sample of **2g** (contaminated with ~15% B_2pin_2) was purified by silica gel chromatography (prep TLC, 30% EtOAc/hexanes) to enable characterization: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 3.6 Hz, 1H), 7.34 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.17 (dd, *J* = 8.6, 1.3 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 2.48 (q, *J* = 7.5 Hz, 1H), 2.33 (s, 3H), 1.32 (d, *J* = 7.5 Hz, 3H), 1.20 (s, 6H), 1.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.2, 135.6, 133.1, 131.2, 130.0, 127.0, 126.3, 125.2, 120.0, 113.4, 109.3, 83.5, 24.79, 24.76,

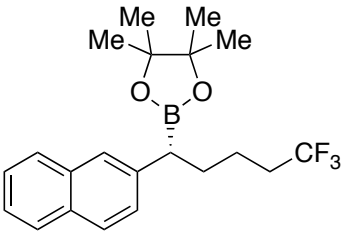
21.7, 17.6;[4] ^{11}B (193 MHz, $CDCl_3$) δ 33.8; FTIR (neat, cm^{-1}) 2977, 2930, 1459, 1372, 1173, 676, 583; HRMS (CI) calculated for $C_{23}H_{28}BNO_4S$: 425.1832, found: 425.1840.

The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2g** was oxidized to alcohol **3g** via General Procedure C. The enantiomeric excess was determined to be 96% by chiral HPLC analysis. See alcohol **3g** below.

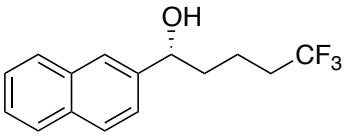


(*R*)-1-(1-tosyl-1*H*-indol-5-yl)ethanol (3g). Prepared via General Procedure C using benzylic boronate **2g**. The crude mixture was purified by silica gel chromatography (40% EtOAc/hexanes) to give **3g** (run 1 (43 mg of **2g**): 34 mg, 79%) as a pale yellow semi-solid. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 58.15 min, t_R(minor) = 53.38 min. $[\alpha]_D^{24}$ = -18.7º (c 0.165, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 3.6 Hz, 1H), 7.52 (s, 1H), 7.31 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 3.6 Hz, 1H), 4.94 (q, *J* = 6.4 Hz, 1H), 2.32 (s, 3H), 1.99 (s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 141.2, 135.3, 134.3, 131.0, 130.0, 126.9, 126.9, 122.5, 118.2, 113.7, 109.2, 70.6, 25.5, 21.7; FTIR (neat) 3379 (broad), 2971, 1596, 1369, 1173, 1128, 676, 579 cm^{-1}; HRMS (CI+) $[M+H]^+$ calculated for $[C_{17}H_{18}NO_3S]^+$: 316.1007, found: 316.1017.



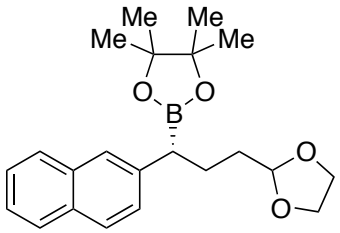
(*R*)-4,4,5,5-tetramethyl-2-(5,5,5-trifluoro-1-(naphthalen-2-yl)pentyl)-1,3,2-dioxaborolane (2h). Prepared via General Procedure A using ammonium salt **1h** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2h** (run 1: 73 mg, 64%; run 2: 69 mg, 60%) as a white solid (mp 74–76 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 3H), 7.65 (s, 1H), 7.50 – 7.33 (m, 3H), 2.50 (t, J = 7.9 Hz, 1H), 2.19 – 1.96 (m, 3H), 1.91 – 1.78 (m, 1H), 1.65 – 1.50 (m, 2H), 1.23 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.2, 134.0, 132.1, 128.1, 127.7, 127.6, 127.4 (q, $J_{C\text{-}F}$ = 276.4 Hz), 127.3, 126.5, 126.0, 125.2, 83.7, 33.9 (q, $J_{C\text{-}F}$ = 28.4 Hz), 31.6, 24.8, 24.7, 21.7 (q, $J_{C\text{-}F}$ = 2.7 Hz);[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –66.3; FTIR (neat) 2978, 1361, 1259, 1141, 857, 749 cm^{-1}; HRMS (CI+) calculated for $C_{21}H_{26}BF_3O_2$: 379.2049, found: 379.2034.

Boronate **2h** was oxidized to alcohol **3h** via General Procedure C. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis. See alcohol **3h** below.



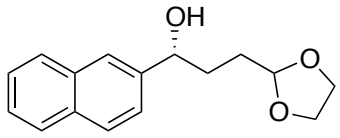
(*R*)-5,5,5-trifluoro-1-(naphthalen-2-yl)pentan-1-ol (3h). Prepared via General Procedure C using benzylic boronate **2h**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3h** (run 1 (61 mg of **2h**): 40 mg, 93%) as a white solid (mp 48–50 ºC). The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 96% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 28.25 min, t_R(minor) = 25.09 min. $[\alpha]_D^{24}$ =

+38.4º (c 0.75, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 3H), 7.76 (s, 1H), 7.55 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.87 – 4.79 (m, 1H), 2.20 – 2.02 (m, 3H), 1.99 – 1.67 (m, 3H), 1.68 – 1.52 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 133.4, 133.2, 128.7, 128.1, 127.9, 127.2 (q, $J_{C\text{-}F}$ = 277.5 Hz), 126.5, 126.2, 124.7, 123.9, 74.4, 37.8, 33.7 (q, $J_{C\text{-}F}$ = 28.6 Hz), 18.6 (q, $J_{C\text{-}F}$ = 3.0 Hz); ^{19}F NMR (376.5 Hz, $CDCl_3$) δ –66.3; FTIR (neat) 3350 (broad), 2947, 1391, 1259, 1134, 1028, 821, 749, 479 cm^{-1}; HRMS (CI+) calculated for $C_{15}H_{16}F_3O$: 269.1153, found: 269.1158.

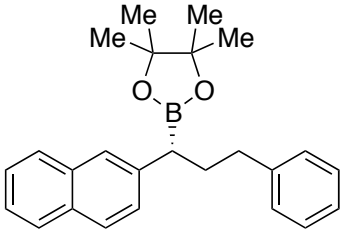


(*R*)-2-(3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i). Prepared via General Procedure A using ammonium salt **1i** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (10% EtOAc/hexanes) to give **2i** (64 mg, 58%) as a white solid (mp 82–84 ºC) (note: a 10:1 mixture of product to B_2pin_2 was observed): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 3H), 7.65 (s, 1H), 7.47 – 7.36 (m, 3H), 4.86 (t, *J* = 4.8 Hz, 1H), 3.98 – 3.77 (m, 4H), 2.51 (t, *J* = 8.0 Hz, 1H), 2.15 – 2.01 (m, 1H), 1.99 – 1.84 (m, 1H), 1.76 – 1.59 (m, 2H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 133.9, 131.9, 127.9, 127.63, 127.59 127.5, 126.5, 125.8, 125.0, 104.7, 83.5, 64.9, 33.5, 26.8, 24.8, 24.7; ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (neat) 2977, 2882, 1371, 1324, 1141, 857, 750 cm^{-1}; HRMS (LIFDI) calculated for $C_{22}H_{29}BO_4$: 368.2140, found: 368.2143.

Boronate **2i** was oxidized to alcohol **3i** via General Procedure C. The enantiomeric excess was determined to be 98% by chiral HPLC analysis. See alcohol **3i** below.



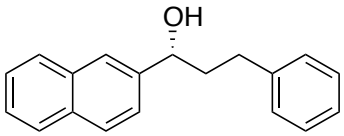
(*R*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-ol (3i). Prepared via General Procedure C using benzylic boronate **2i**. The crude mixture was purified by silica gel chromatography (40% EtOAc/hexanes) to give **3i** (36 mg, 84%) as a white solid (mp 67–69 ºC). The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 31.06 min, t_R(minor) = 27.49 min. $[\alpha]_D^{24}$ = –18.4º (c 1.78, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 4H), 7.53 – 7.40 (m, 3H), 4.96 – 4.85 (m, 2H), 4.03 – 3.81 (m, 4H), 2.74 (d, *J* = 3.5 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.91 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 133.4, 133.0, 128.4, 128.1, 127.8, 126.2, 125.9, 124.6, 124.2, 104.4, 74.3, 65.2, 65.1, 33.1, 30.1; FTIR (neat) 3434 (broad), 2882, 1409, 1139, 1031, 822, 751, 479 cm^{-1}; HRMS (CI+) calculated for $C_{16}H_{18}O_3$: 241.1229, found: 241.1225.



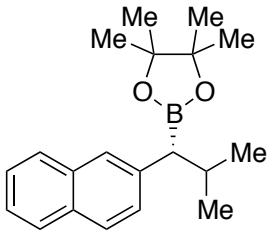
(*R*)-4,4,5,5-tetramethyl-2-(1-(naphthalen-2-yl)-3-phenylpropyl)-1,3,2-dioxaborolane (2j). Prepared via General Procedure A using ammonium salt **1j** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2j** (80 mg, 72%) as a white solid (mp 77–79 ºC): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 3H), 7.71 (s, 1H), 7.52 – 7.41 (m, 3H), 7.34 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 2.65 (t, *J* = 7.9 Hz, 2H), 2.60 (t, *J* = 7.9 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.21 – 2.10 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 140.6, 133.9, 131.9, 128.7, 128.4, 128.0, 127.7, 127.6, 127.5, 126.5, 125.84, 125.81, 125.0, 83.6, 35.6, 34.3, 24.84, 24.76;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.7; FTIR

(neat) 2977, 2930, 1323, 1141, 857, 748, 699 cm^{-1}; HRMS (LIFDI) calculated for $C_{25}H_{29}BO_2$: 372.2261, found: 372.2270.

Boronate **2j** was oxidized to alcohol **3j** via General Procedure C. The enantiomeric excess was determined to be 98% by chiral HPLC analysis. See alcohol **3j** below.



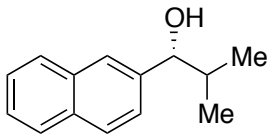
(*R*)-1-(naphthalen-2-yl)-3-phenylpropan-1-ol (3j). Prepared via General Procedure C using benzylic boronate **2j**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3j** (43 mg, 94%) as a white solid (mp 85–86 ºC). The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 35.44 min, t_R(minor) = 38.33 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 3H), 7.79 (s, 1H), 7.55 – 7.44 (m, 3H), 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 4.87 (ddd, *J* = 8.1, 5.5, 2.9 Hz, 1H), 2.85 – 2.65 (m, 2H), 2.30 – 2.06 (m, 2H), 2.02 (d, *J* = 3.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 141.9, 133.5, 133.2, 128.56, 128.59, 128.63, 128.1, 127.9, 126.4, 126.1, 126.0, 124.9, 124.2, 74.2, 40.5, 32.2. The spectral data match that of the literature.[10]



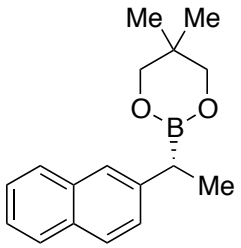
(*R*)-4,4,5,5-tetramethyl-2-(2-methyl-1-(naphthalen-2-yl)propyl)-1,3,2-dioxaborolane (2k). Prepared via General Procedure A using ammonium salt **1k** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2k** (run 1: 46 mg, 49%; run 2: 47 mg, 50%) as a white solid (mp 85–86 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 3H), 7.66 (s, 1H), 7.47 – 7.36

(m, 3H), 2.33 – 2.19 (m, 1H), 2.16 (d, J = 10.5 Hz, 1H), 1.21 (s, 6H), 1.18 (s, 6H), 1.10 (d, J = 6.4 Hz, 3H), 0.77 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 133.9, 132.0, 128.1, 127.7, 127.6, 127.3, 125.7, 124.9, 83.4, 31.1, 24.8, 24.7, 23.4, 22.3;[4] ^{13}C NMR (151 MHz, $C(O)(CD_3)_2$) δ 141.2, 134.7, 132.9, 128.7, 128.3, 128.3, 128.2, 127.9, 126.6, 125.7, 83.9, 31.7, 25.0, 24.9, 23.5, 22.4;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (neat) 2922, 2850, 1382, 1323, 1143, 1103 cm^{-1}; HRMS (LIFDI) calculated for $C_{20}H_{27}BO_2$: 310.2104, found: 310.2126.

Boronate **2k** was oxidized to alcohol **3k** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 97%, run 2: 98%) by chiral HPLC analysis. See alcohol **3k** below.

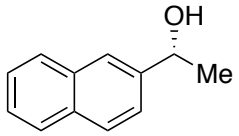


(*R*)-2-methyl-1-(naphthalen-2-yl)propan-1-ol (3k). Prepared via General Procedure C using benzylic boronate **2k**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3k** (run 1 (39 mg of **2k**): 7 mg, 28%) as a clear oil. The enantiomeric excess was determined to be 98% (run 1: 97%, run 2: 98%) by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 17.49 min, t_R(minor) = 16.15 min; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 3H), 7.76 (s, 1H), 7.51 – 7.44 (m, 3H), 4.54 (d, J = 6.9 Hz, 1H), 2.12 – 2.03 (m, J = 6.7 Hz, 1H), 1.93 (s, 1H), 1.05 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 133.3, 133.1, 128.2, 128.1, 127.8, 126.2, 125.9, 125.6, 124.8, 80.4, 35.4, 19.3, 18.4. The spectral data match that previously reported in the literature.[11]

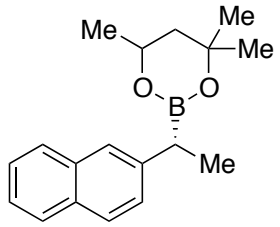


(*R*)-5,5-dimethyl-2-(1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborinane (2l). Prepared via General Procedure A using ammonium salt **1a** (amine purchased in >99% ee) and bis(neopentyl glycolato)diboron (B_2neop_2) instead of B_2pin_2. Instead of filtering through Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield of the reaction was determined by ^1H NMR analysis to be 61%. The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2l** was oxidized to alcohol **3a** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **3a** below.



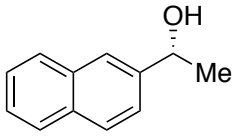
(*R*)-1-(naphthalen-2-yl)ethanol (3a). Prepared via General Procedure C using benzylic boronate **2l**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3a** (29 mg, 93%) as a white solid. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 45.06 min, t_R(minor) = 47.29 min. The spectral data match that of alcohol **3a** above.



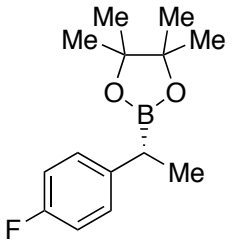
4,4,6-trimethyl-2-((*R*)-1-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborinane (2m). Prepared via General Procedure A using ammonium salt **1a** (amine purchased in >99% ee) and bis(hexylene glycolato)diboron (B_2hex_2) instead of B_2pin_2. Instead of filtering through

Celite®, the diluted mixture was filtered through a small plug of silica gel and then concentrated. 1,3,5-Trimethoxybenzene was added as internal standard, and the yield of the reaction was determined by ^{1}H NMR analysis to be 74%. The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2m** was oxidized to alcohol **3a** via General Procedure C. The enantiomeric excess was determined to be 95% by chiral HPLC analysis. See alcohol **3a** below.



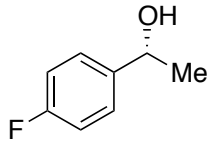
(*R*)-1-(naphthalen-2-yl)ethanol (3a). Prepared via General Procedure C using benzylic boronate **2m**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3a** (35 mg, quant.) as a white solid. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 44.64 min, t_R(minor) = 46.84 min. The spectral data match that of alcohol **3a** above.



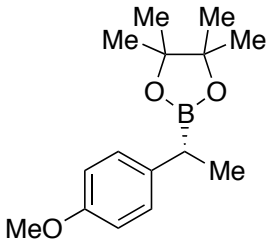
(*R*)-2-(1-(4-fluorophenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n). Prepared via General Procedure B on a 0.5-mmol scale using ammonium salt **1n** (amine purchased in >99% ee) and ICy·HBF_4 (19.2 mg, 0.060 mmol, 12 mol %) instead of PPh_2Cy. The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2n** (66 mg, 53%) as a clear oil (please note that **2n** was not

subjected to high vacuum due to its volatility): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 6.98 – 6.91 (m, 2H), 2.42 (q, J = 7.5 Hz, 1H), 1.31 (d, J = 7.5 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, $J_{C\text{-}F}$ = 243.2 Hz), 140.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 83.5, 24.8, 17.4. The spectral data match that reported in the literature.[12] The sample was then concentrated and subjected to General Procedure C for oxidation and determination of enantiomeric excess.

Boronate **2n** was oxidized to alcohol **3n** via General Procedure C. The enantiomeric excess was determined to be 86% (run 1 from oxidation of isolated **2n**: 87% ee; run 2 from oxidation of crude **2n**: 85% ee) by chiral HPLC analysis. See alcohol **3n** below.

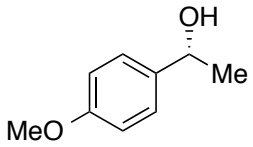


(*R*)-1-(4-fluorophenyl)ethanol (3n). Prepared via General Procedure C using benzylic boronate **2n**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3n** (16 mg, 62%) as a clear oil. The enantiomeric excess was determined to be 86% (run 1 from oxidation of isolated **2n**: 87% ee; run 2 from oxidation of crude **2n**: 85% ee) by chiral HPLC analysis (CHIRALPAK IF, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 16.25 min, t_R(minor) = 17.65 min: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.3, 5.6 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 4.89 (q, J = 6.4 Hz, 1H), 1.87 (s, 1H), 1.48 (d, J = 6.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3 (d, $J_{C–F}$ = 244.6 Hz), 141.7, 127.2 (d, $J_{C–F}$ = 7.6 Hz), 115.4 (d, $J_{C–F}$ = 22.7 Hz), 70.0, 25.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ –115.4. The spectral data match that of the literature.[13]

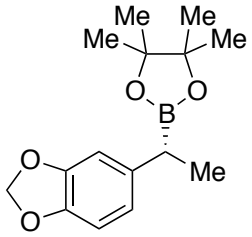


(*R*)-2-(1-(4-methoxyphenyl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o). Prepared via General Procedure B using ammonium salt **1o** (amine precursor purchased in >99% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2o** (run 1: 45 mg, 57%; run 2: 41 mg, 52%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 137.0, 128.6, 113.8, 83.2, 55.2, 24.7, 24.6, 17.4.[4] The spectral data matches that previously reported in the literature.[14]

Boronate **2o** was oxidized to alcohol **3o** via General Procedure C. The enantiomeric excess was determined to be 86% (run 1: 85% ee; run 2: 87% ee) by chiral HPLC analysis. See alcohol **3o** below.

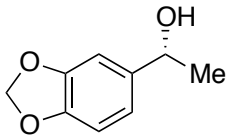


(*R*)-1-(4-methoxyphenyl)ethanol (3o). Prepared via General Procedure C using benzylic boronate **2o**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3o** (run 1 (45 mg of **2o**): 19 mg, 72%) as a clear oil. The enantiomeric excess was determined to be 86% (run 1: 85%, run 2: 87%) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 20.16 min, t_R(minor) = 22.24 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.86 (q, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 1.84 (bs, 1H), 1.48 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 138.1, 126.8, 114.0, 70.2, 55.5, 25.2. The spectral data match that previously reported in the literature.[15]



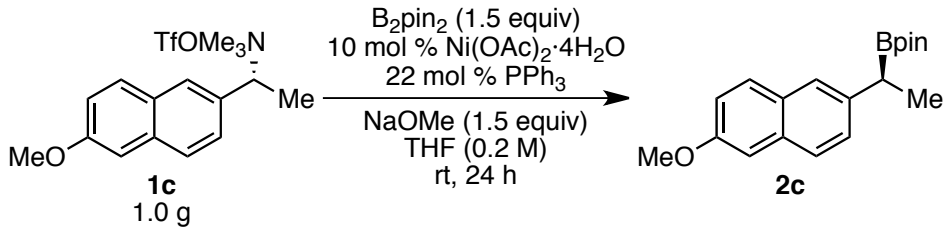
(*R*)-2-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p). Prepared via General Procedure B using ammonium salt **1p** (amine prepared in ≥95% ee). The crude mixture was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2p** (run 1: 48 mg, 58%; run 2: 53 mg, 63%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 1.7 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.90 (s, 2H), 2.35 (q, *J* = 7.5 Hz, 1H), 1.28 (d, *J* = 7.5 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.2, 139.0, 120.5, 108.6, 108.3, 100.8, 83.5, 24.8, 24.8, 17.7;[4] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3; FTIR (neat) 2977, 1487, 1321, 1237, 1144, 1041, 938, 811 cm^{-1}; HRMS (CI) calculated for $C_{15}H_{21}BO_4$: 277.1611, found: 277.1609.

Boronate **2p** was oxidized to alcohol **3p** via General Procedure C. The enantiomeric excess was determined to be 85% (run 1: 84% ee; run 2: 85% ee) by chiral HPLC analysis. See alcohol **3p** below.



(*R*)-1-(benzo[*d*][1,3]dioxol-5-yl)ethanol (3p). Prepared via General Procedure C using benzylic boronate **2p**. The crude mixture was purified by silica gel chromatography (20% EtOAc/hexanes) to give **3p** (run 1 (40 mg of **2o**): 21 mg, 87%) as a clear oil. The enantiomeric excess was determined to be 85% (run 1: 85%, run 2: 84%) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=210 nm); t_R(major) = 19.60 min, t_R(minor) = 22.01 min: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.88 (m, 1H), 6.85 – 6.75 (m, 2H), 5.95 (s, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 1.76 (bs, 1H), 1.46 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.0, 140.1, 118.9, 108.3, 106.2, 101.2, 70.5, 25.3. The spectral data match that previously reported in the literature.[15]

Gram-Scale Synthesis of (*S*)-2-(1-(6-methoxynaphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



An oven-dried, 50-mL Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with N_2 (x 4). $Ni(OAc)_2{\cdot}4H_2O$ (63 mg, 0.254 mmol, 10 mol %), PPh_3 (147 mg, 0.559 mmol, 22 mol %), B_2pin_2 (0.968 g, 3.81 mmol, 1.5 equiv), and ammonium salt **1c** (≥95% ee, 1.00 g, 2.54 mmol. 1.0 equiv) were added. NaOMe (0.206 g, 3.81 mmol, 1.5 equiv) was quickly added and the flask was sealed with a rubber septum. The flask was evacuated and then backfilled with N_2 (x 4). THF (13 mL, 0.2 M) was then added. The mixture was stirred vigorously at room temperature for 24 h. Over the course of the reaction, the solution turned from light yellow to dark orange. Et_2O (~ 40 mL) was added, and the mixture was stirred for five minutes. The mixture was filtered through a pad of Celite®, which was then washed multiple times with Et_2O (~ 120 mL total volume). The filtrate was concentrated, and the crude material was purified by silica gel chromatography (5% EtOAc/hexanes) to give **2c** (68%, 99% ee) as a white solid. The spectra of this material match that of **2c** prepared on 0.3 mmol scale, as described above.

Boronate **2c** was oxidized to alcohol **3c** via General Procedure C. The enantiomeric excess was determined to be 99% by chiral HPLC analysis. The spectral data of this alcohol match that of alcohol **2c** as described above.

Preparation of Benzyl Ammonium Salts

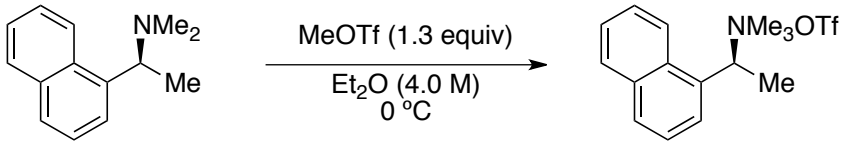
Enantioenriched amines that were not commercially available were obtained through Grignard or hydride additions to Ellman's sulfinimines.[2] Via these reactions, a single diastereomer of each sulfinamine was isolated (as determined by ^1H NMR analysis). We thus assume ≥95% ee of the subsequent amine after removal of Ellman's

auxiliary. Dimethyl benzyl amines were then prepared using Escheweiler-Clarke conditions or reductive amination of the corresponding primary benzyl amine with formaldehyde.[3] We assume no loss of ee in the formation of the trimethyl ammonium triflates from this intermediate. For enantioenriched amines that were commercially available, we also assume no loss of ee in the formation of the trimethyl ammonium triflates.

Ammonium triflates **1a**, **1b**, **1k**, **1n**, and **1o** have been previously prepared in our laboratory.[16]

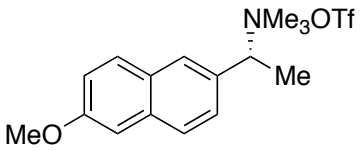
Ammonium triflates prepared via these procedures were used as is in the stereospecific borylation reaction, without further purification. In some cases, impurities are present in the ammonium triflates.

General Procedure D: Preparation of (*S*)-*N*,*N*,*N*-trimethyl-1-(naphthalen-1-yl)ethanaminium trifluoromethanesulfonate (1b)

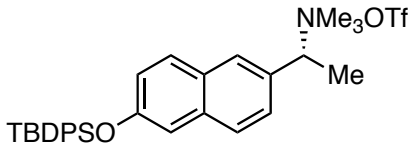


(*S*)-*N*,*N*-Dimethyl-1-(naphthalen-1-yl)ethanamine (0.806 g, 4.04 mmol, 1.0 equiv), which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-(-)-1-(1-naphthyl)ethylamine (purchased in >99% ee), was dissolved in Et_2O (1.01 mL, 4.0 M). MeOTf (0.58 mL, 5.25 mmol, 1.3 equiv) was added dropwise at 0 ºC. After complete addition, the mixture was allowed to stir for an additional 30 minutes at 0 ºC. The mixture was diluted with Et_2O (~ 2 mL), taken out of the ice bath, and allowed to warm to room temperature while stirring. The white precipitate was filtered and washed with Et_2O (3 x 15 mL). The solid was dried under high vacuum to afford salt **1b** (1.377 g,

94%) as a white solid, which was used directly in the benzylic borylation. This compound was previously prepared in our laboratory via this method.[15]

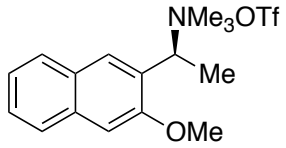


(*R*)-1-(6-methoxynaphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1c). Prepared according to General Procedure D on a 5.64 mmol scale from (*R*)-1-(6-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[3a] from (*R*)-1-(6-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[2]), to afford salt **1c** (2.085 g, 94%) as a white solid (mp 109–111 ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84-7.74 (m, 2H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H), 4.98 (q, *J* = 6.9 Hz, 1H), 3.92 (s, 3H), 3.15 (s, 9H), 1.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 135.6, 130.2, 128.4, 128.1, 127.2, 121.0 (q, $J_{C\text{-}F}$ = 320.1 Hz), 120.4, 105.7, 74.5, 55.6, 51.2, 15.2; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3043, 1608, 1488, 1270, 1160, 846, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.



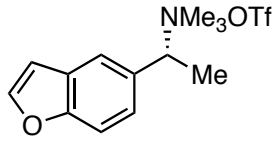
(*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1d). Prepared according to General Procedure D on a 1.50 mmol scale from (*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared by reductive amination[3b] from (*R*)-1-(6-((*tert*-butyldiphenylsilyl)oxy)naphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[2]). In this case, stirring ceased as a

result of precipitate formation. The solution was diluted with Et_2O to 2.0 M and the stir bar was agitated with a spatula to resume stirring. The reaction afforded salt **1d** (0.698 g, 75%) as a white solid (mp 180–182 ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74 (d, *J* = 6.9 Hz, 4H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 5H), 7.13 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 4.92 (q, *J* = 6.9 Hz, 1H), 3.13 (s, 9H), 1.84 (d, *J* = 6.9 Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 135.6, 135.4, 132.6, 130.3, 130.1, 128.5, 128.14, 128.09, 127.2, 123.3, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 114.6, 74.6, 51.2, 26.7, 19.7, 15.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; ^{29}Si NMR (119 MHz, $CDCl_3$) δ –5.0; FTIR (neat) 3051, 2933, 2859, 1605, 1483, 1266, 1161, 1031, 879, 703, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{31}H_{38}NOSi^+]$: 468.3, found: 468.4.

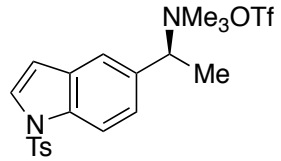


(*S*)-1-(3-methoxynaphthalen-2-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1e) Prepared according to General Procedure D on a 1.45 mmol scale from (*S*)-1-(3-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-1-(3-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[2]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **1e** (0.359 g, 63%) as a clear viscous oil. By NMR, an ~8:1 mixture of rotamers was observed: ^{1}H NMR (600 MHz, $CDCl_3$, major rotamer) δ 7.97 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 5.29 (q, *J* = 7.1 Hz, 1H), 3.98 (s, 3H), 3.11 (s, 9H), 1.85 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, major rotamer) δ 154.8, 135.3, 130.7, 128.7, 128.5, 128.1, 126.6, 125.1, 122.5, 120.7 (q, $J_{C\text{-}F}$ = 320.0 Hz), 106.8, 65.9, 56.0, 51.09, 51.07, 51.05, 15.4;[17] ^{19}F NMR (376.5 MHz,

$CDCl_3$) δ –78.4; FTIR (neat) 3048, 1634, 1474, 1260, 1163, 1031, 756, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.

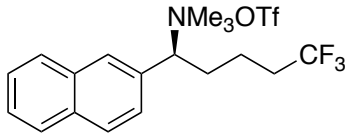


(*R*)-1-(benzofuran-5-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1f). Prepared according to General Procedure D on a 6.12 mmol scale from (*R*)-1-(benzofuran-5-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[3a] from (*R*)-1-(benzofuran-5-yl)ethanamine (prepared using Ellman's auxiliary[2]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (2 mL), which caused white precipitate to form. The precipitate was filtered and washed with Et_2O (3 x 15 mL) and dried under high vacuum to afford salt **1f** (2.076 g, 96%) as a white solid (mp 106–108 ºC): ^1H NMR (600 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 6.85 – 6.81 (m, 1H), 4.98 (q, *J* = 7.0 Hz, 1H), 3.13 (s, 9H), 1.85 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 146.9, 128.5, 127.1, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 112.4, 107.0, 74.4, 51.18, 51.15, 51.1, 15.5;[17] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3042, 1472, 1263, 1158, 1030, 838, 750, 639, 518 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{13}H_{18}NO^+]$: 204.1, found: 204.2.

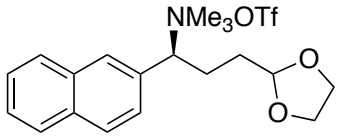


(*S*)-*N*,*N*,*N*-trimethyl-1-(1-tosyl-1*H*-indol-5-yl)ethanaminium trifluoromethanesulfonate (1g). Prepared according to General Procedure D on a 2.97 mmol scale from (*S*)-*N*,*N*-dimethyl-1-(1-tosyl-1*H*-indol-5-yl)ethanamine, which was

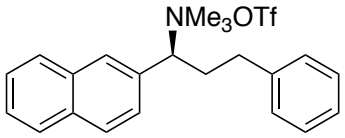
prepared using Escheweiler-Clarke conditions[3a] from (*S*)-1-(1-tosyl-1*H*-indol-5-yl)ethanamine (prepared using Ellman's auxiliary[2]) to afford salt **1g** (1.277 g, 85%) as a white solid (mp 73-75 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.62 (d, J = 3.7 Hz, 1H), 7.42 (d, J = 8.6 Hz, 1H), 7.25 (s, 1H), 6.71 (d, J = 3.6 Hz, 1H), 4.91 (q, J = 6.9 Hz, 1H), 3.09 (s, 9H), 2.34 (s, 3H), 1.80 (d, J = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.8, 135.6, 135.0, 131.3, 130.4, 128.0, 127.4, 127.1, 120.9 (q, $J_{C\text{-}F}$ = 320.12 Hz), 114.2, 109.1, 74.3, 51.2, 21.8, 15.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3051, 1464, 1373, 1273, 1175, 1031, 639, 581 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{20}H_{25}N_2O_2S^+]$: 357.2, found: 357.3.



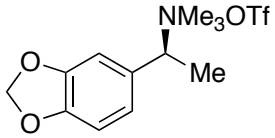
(*S*)-5,5,5-trifluoro-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)pentan-1-aminium trifluoromethanesulfonate (1h). Prepared according to General Procedure D on a 3.47 mmol scale from (*S*)-5,5,5-trifluoro-*N*,*N*-dimethyl-1-(naphthalen-2-yl)pentan-1-amine, which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-5,5,5-trifluoro-1-(naphthalen-2-yl)pentan-1-amine (prepared using Ellman's auxiliary[2]). In this case, a precipitate did not form upon addition of MeOTf. Instead, two distinct layers were observed. The top layer was decanted. The bottom layer was washed with a 1:1 (v/v) solution of Et_2O/hexanes (5 x 4 mL) and dried under high vacuum at 50 ºC to afford salt **1h** (1.492 g, 94%) as a sticky solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.88 (m, 3H), 7.86 (d, J = 8.2 Hz, 1H), 7.64 – 7.44 (m, 3H), 4.87 – 4.76 (m, 1H), 3.16 (s, 9H), 2.41 (s, 2H), 2.29 – 2.03 (m, 2H), 1.53 – 1.36 (m, 1H), 1.32 – 1.13 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.1, 133.1, 130.0, 129.6, 128.7, 128.2, 127.9, 127.5, 126.9 (q, $J_{C\text{-}F}$ = 277.5 Hz), 122.9, 120.7 (q, $J_{C\text{-}F}$ = 320.1 Hz), 78.7, 51.8, 32.8 (q, $J_{C\text{-}F}$ = 29.0 Hz) 26.3, 19.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4, –66.2; FTIR (neat) 3053, 2957, 1491, 1260, 1154, 1031, 831, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{18}H_{23}F_3N^+]$: 310.2, found: 310.4. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.



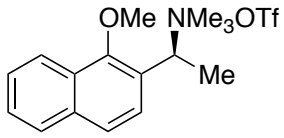
(*S*)-3-(1,3-dioxolan-2-yl)-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)propan-1-aminium trifluoromethanesulfonate (1i). Prepared according to General Procedure D on a 1.93 mmol scale from (*S*)-3-(1,3-dioxolan-2-yl)-*N*,*N*-dimethyl-1-(naphthalen-2-yl)propan-1-amine, which was prepared by reductive amination[3b] from (*S*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-amine (prepared using Ellman's auxiliary[2]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **1i** (0.854 g, 98%) as a sticky white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 7.89 (m, 3H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.41 (m, 3H), 4.89 – 4.83 (m, 1H), 4.81 (t, *J* = 4.0 Hz, 1H), 3.97 – 3.86 (m, 2H), 3.82 – 3.63 (m, 2H. Please note: this peak is contaminated with an unknown impurity. At 50 ºC the peak corresponding to the impurity shifts and an accurate integration of two protons is obtained), 3.17 (s, 9H), 2.50 – 2.29 (m, 2H), 1.60 – 1.24 (m, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 8.14 – 7.99 (m, 1H), 7.99 – 7.90 (m, 2H), 7.90 – 7.82 (m, 1H), 7.62 – 7.46 (m, 3H), 4.97 – 4.74 (m, 2H), 4.00 – 3.67 (m, 4H), 3.18 (s, 9H), 2.59 – 2.26 (m, 2H), 1.61 – 1.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 134.1, 133.1, 129.9, 129.5, 128.8, 128.1, 127.8, 127.4, 123.0, 120.8 (q, $J_{C\text{-}F}$ = 321.1 Hz), 102.8, 78.9, 65.1, 65.0, 51.8, 30.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; FTIR (neat) 3054, 2890, 1489, 1264, 1159, 1031, 830, 639, 518 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{19}H_{26}NO_2^+]$: 300.2, found: 300.3. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.



(*S*)-*N*,*N*,*N*-trimethyl-1-(naphthalen-2-yl)-3-phenylpropan-1-aminium trifluoromethanesulfonate (1j). Prepared according to General Procedure D on a 1.93 mmol scale from (*S*)-*N*,*N*-dimethyl-1-(naphthalen-2-yl)-3-phenylpropan-1-amine, which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-3-(1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)propan-1-amine (prepared using Ellman's auxiliary[2]). In this case, a white precipitate did not form upon addition of MeOTf. Instead, two distinct layers formed. The top layer was decanted off. The bottom layer was washed with Et_2O (5 x 2 mL) and then hexanes (5 x 2 mL, HPLC grade) and then dried under high vacuum to give salt **1j** (0.854 g, 98%) as a beige solid that slowly turned yellow (mp 65–68ºC): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.53 (s, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 2H), 4.78 – 4.65 (m, 1H. Please note: this peak is contaminated with an unknown impurity; however at 50 ºC the peak corresponding to the impurity shifts and a more accurate integration is obtained.), 3.12 (s, 9H), 2.60 (d, *J* = 6.7 Hz, 2H), 2.49 – 2.27 (m, 2H); ^{1}H NMR (400 MHz, $CDCl_3$, 50 ºC) δ 8.05 (s, 1H), 8.02 – 7.93 (m, 2H), 7.93 – 7.87 (m, 1H), 7.64 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.25 – 7.18 (m, 2H), 7.17 – 7.11 (m, 1H), 7.08 – 7.02 (m, 2H), 4.77 – 4.60 (m, 1H), 3.13 (s, 9H), 2.66 – 2.55 (m, 2H), 2.51 – 2.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.1, 134.1, 133.1, 130.0, 129.5, 128.8, 128.4, 128.2, 127.9, 127.5, 127.3, 126.7, 123.0, 120.8 (q, $J_{C\text{-}F}$ = 320.9 Hz), 78.9, 51.7, 32.3, 29.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.3; FTIR (neat) 3058, 2969, 1490, 1262, 1160, 1030, 829, 638 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{22}H_{26}N^+]$: 304.2, found: 304.3. Two-dimensonal NMR experiments were used to verify ^{1}H and ^{13}C assignments due to the complex nature of the spectra.



(*S*)-1-(benzo[d][1,3]dioxol-5-yl)-*N*,*N*,*N*-trimethylethanaminium trifluoromethanesulfonate (1p). Prepared according to General Procedure D on a 1.52 mmol scale from (*S*)-1-(benzo[d][1,3]dioxol-5-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-1-(benzo[d][1,3]dioxol-5-yl)ethanamine (prepared using Ellman's auxiliary[2]), to afford salt **1p** (0.471 g, 87%) as an off-white solid (mp 136–138 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 7.8 Hz, 1H), 6.95 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H), 4.80 (q, *J* = 7.0 Hz, 1H), 3.11 (s, 9H), 1.76 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.8, 148.6, 125.9, 120.9 (q, $J_{C\text{-}F}$ = 320.1 Hz), 109.0, 102.1, 74.1, 51.13, 51.11, 51.08, 15.3;[17] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.5; FTIR (neat) 3045, 2909, 1493, 1256, 1159, 1031, 835, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{12}H_{18}NO_2^+]$: 208.1, found: 208.2.



(S)-1-(1-methoxynaphthalen-2-yl)-N,N,N-trimethylethanaminium trifluoromethanesulfonate (1q) Prepared according to General Procedure D on a 5.64 mmol scale from (*S*)-1-(1-methoxynaphthalen-2-yl)-*N*,*N*-dimethylethanamine, which was prepared using Escheweiler-Clarke conditions[3a] from (*S*)-1-(1-methoxynaphthalen-2-yl)ethanamine (prepared using Ellman's auxiliary[2]), to afford salt **1l** (2.085 g, 94%) as a white solid (mp 123–124 ºC); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 1H), 7.91 – 7.86 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.50 (d, *J* = 8.7 Hz, 1H), 5.30 (q, *J* = 7.1 Hz, 1H), 4.00 (s, 3H), 3.16 (s, 9H), 1.94 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 135.9, 128.5, 128.3, 127.5, 127.4, 125.6, 124.4, 123.3, 120.94, 120.90 (q, $J_{C\text{-}F}$ = 320.1 Hz), 67.1, 63.9, 51.38, 51.36 51.34, 15.4;[17] ^{19}F NMR (565 MHz, $CDCl_3$) δ –78.4; FTIR (neat) 3051, 1471, 1272, 1158, 1031, 827, 639 cm^{-1}; LRMS (ESI+) $[M\text{-}OTf]^+$ calculated for $[C_{16}H_{22}NO^+]$: 244.2, found: 244.2.

References

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4. In some cases, the benzylic carbon is not observed to to quadrupolar broadening caused by ^{11}B.
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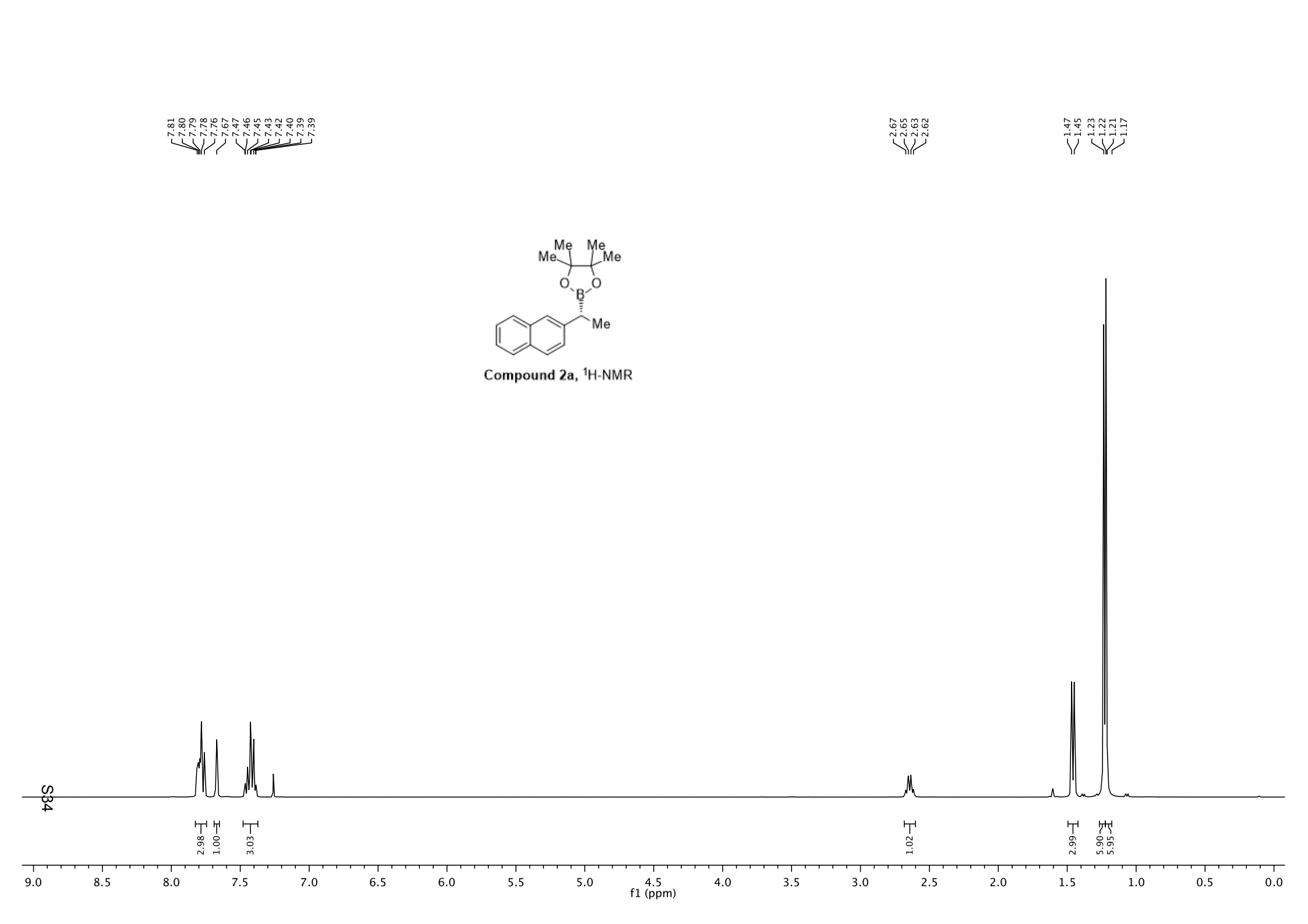
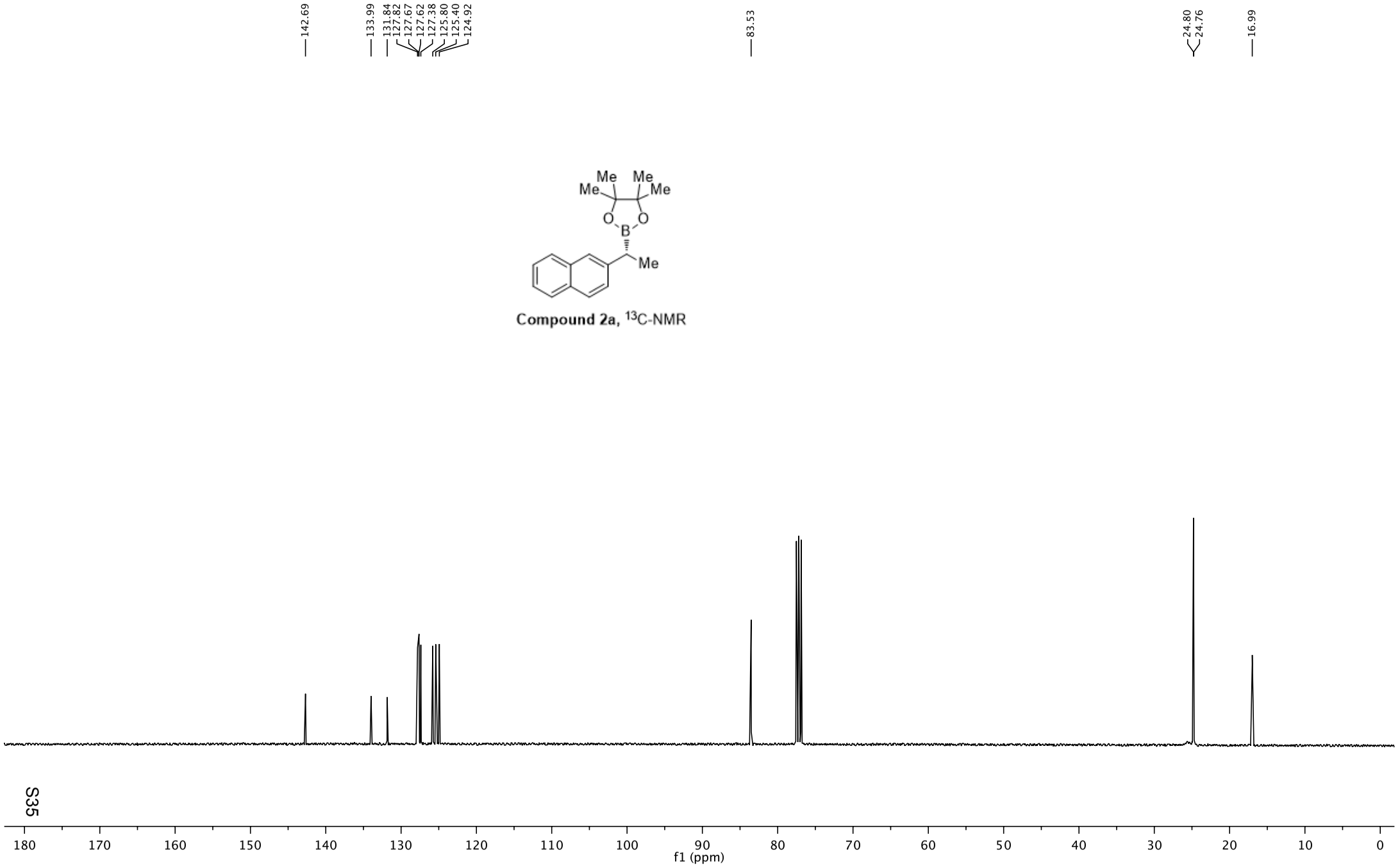
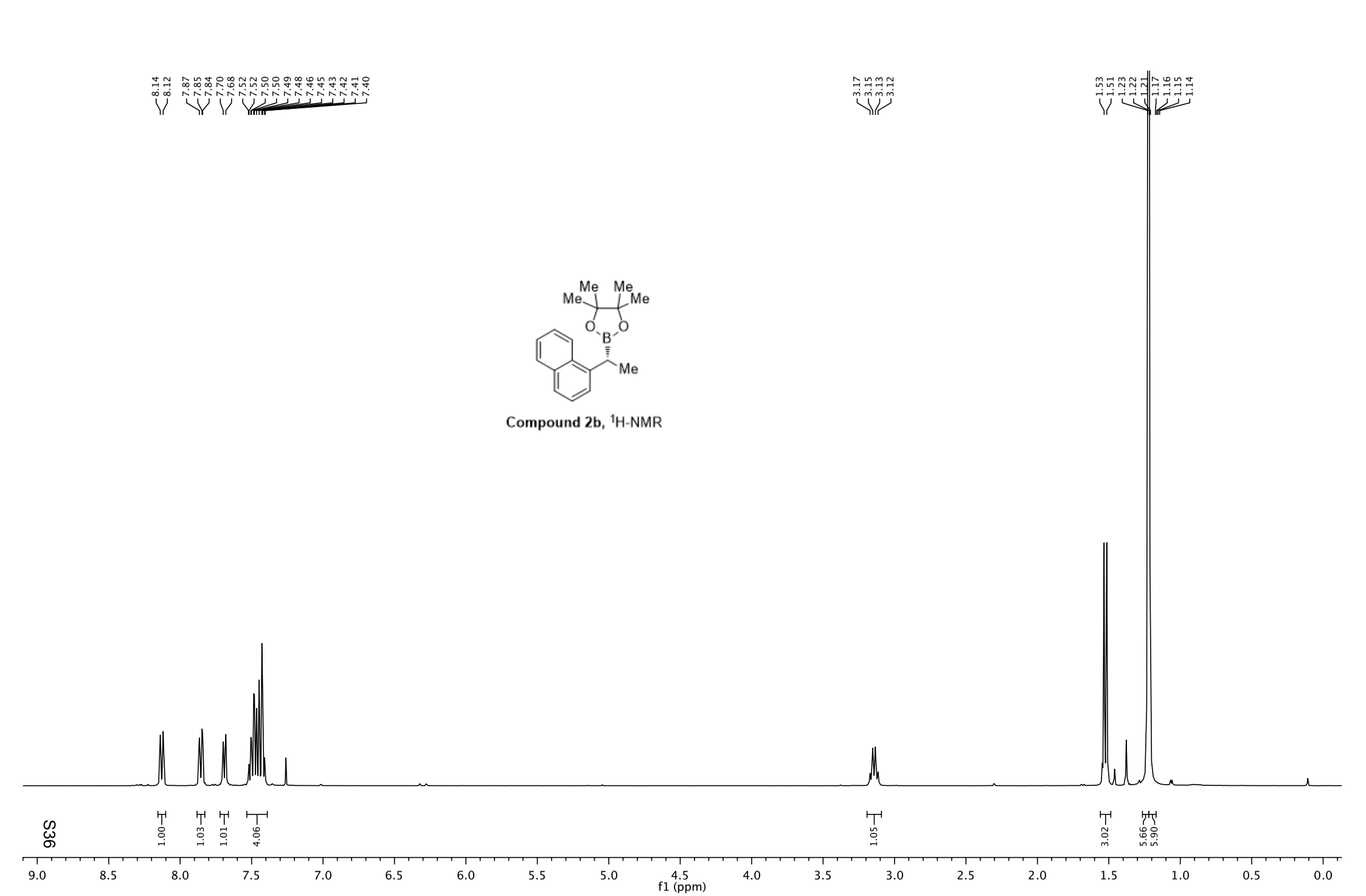
17. In several of the ammonium triflates, the methyl groups of the NMe_3 fragment appear as three, nearly coincident peaks. We hypothesize that this may be due to hindered rotation about the benzylic C–N bond. rotation.



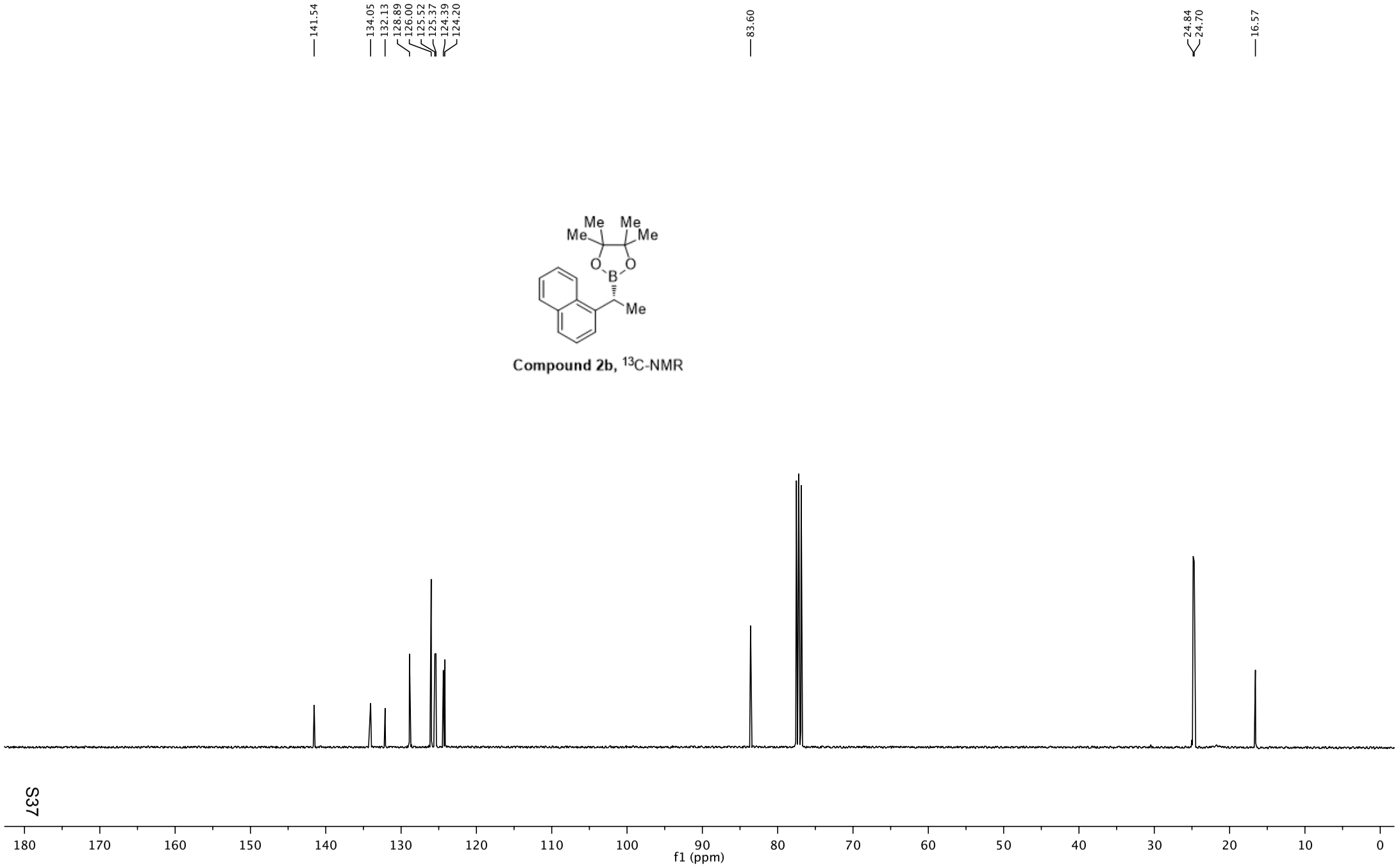
Compound 2a, ^{1}H-NMR



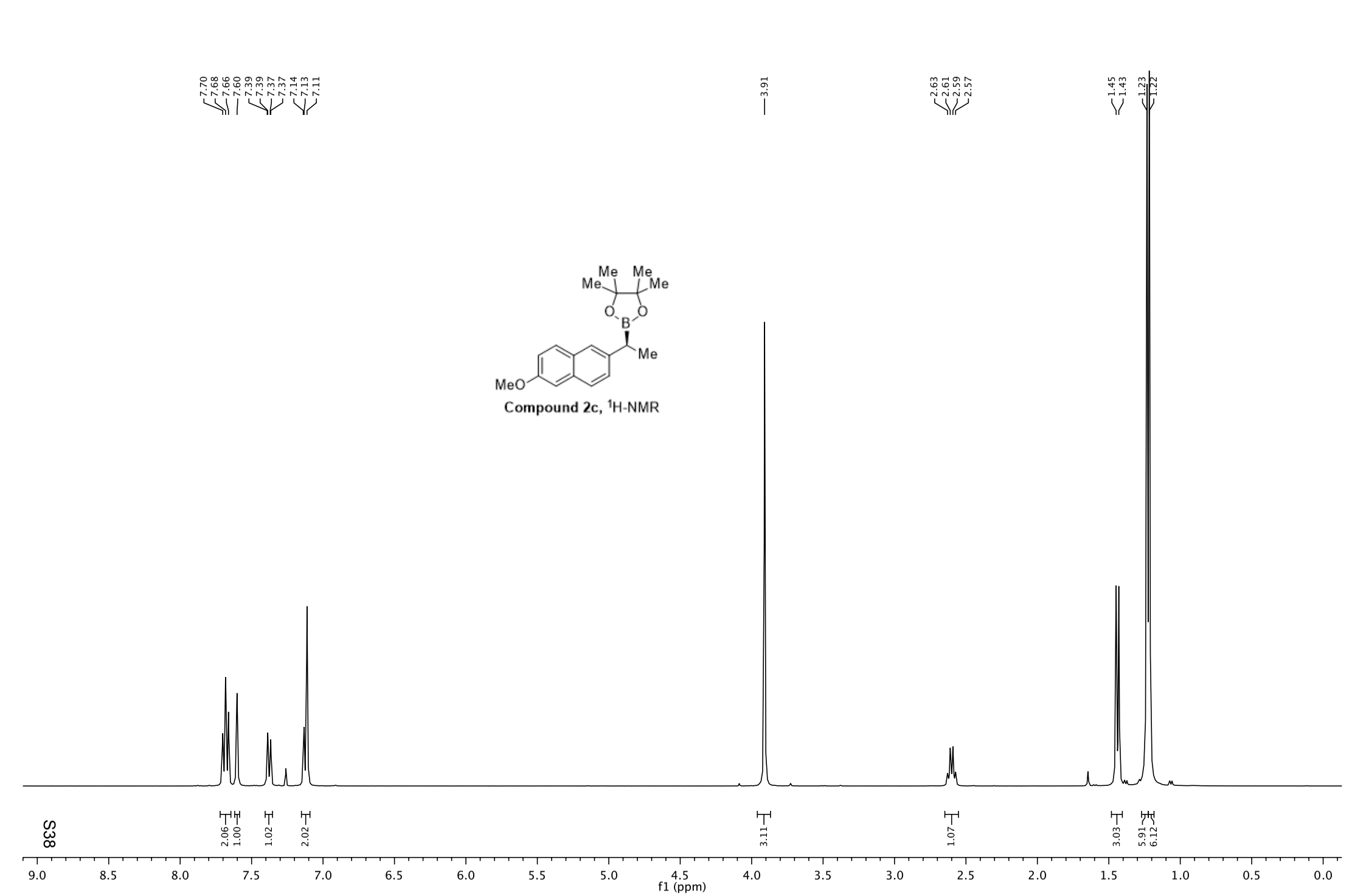
Compound 2a, ^{13}C-NMR



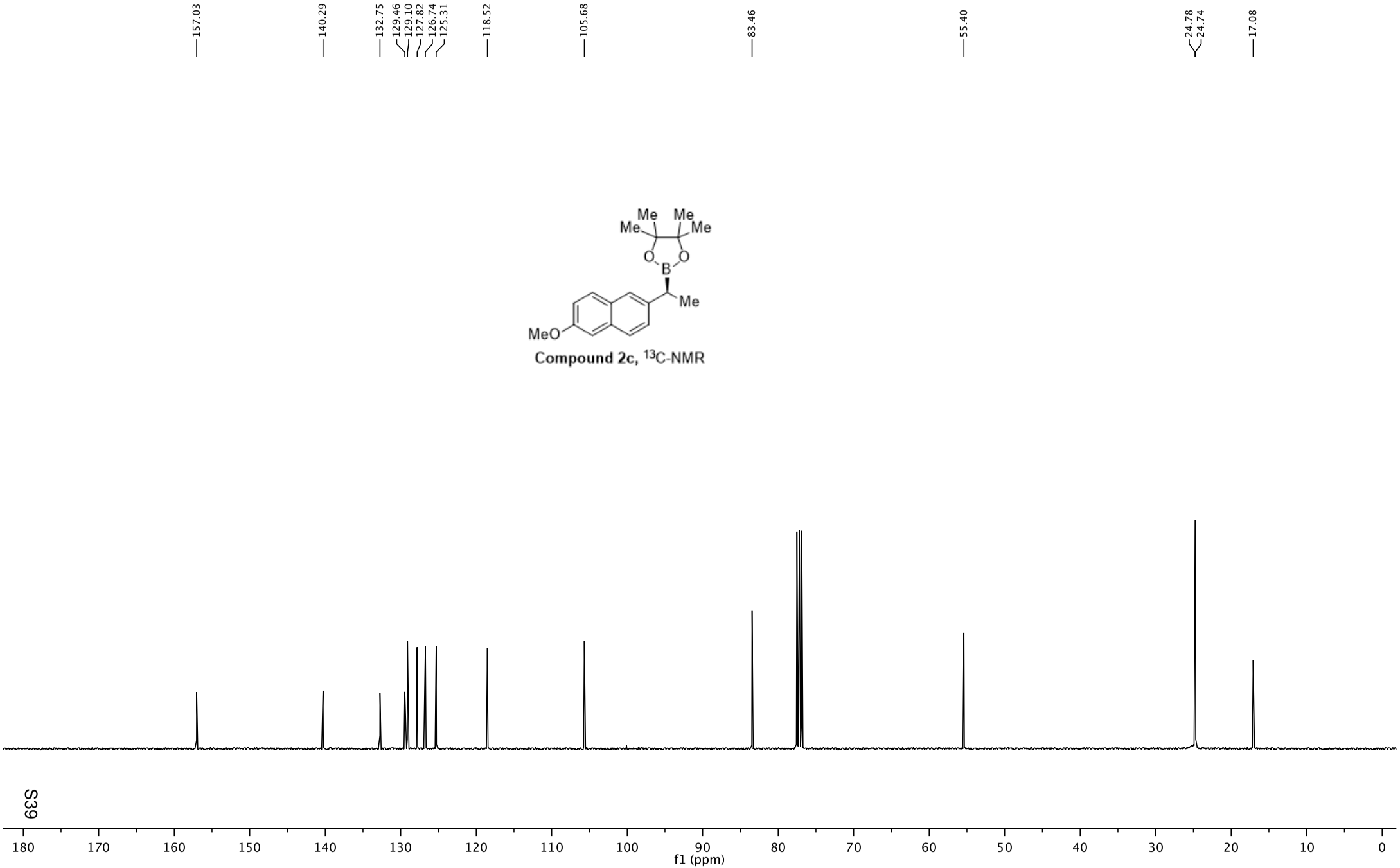
Compound 2b, ^{1}H-NMR



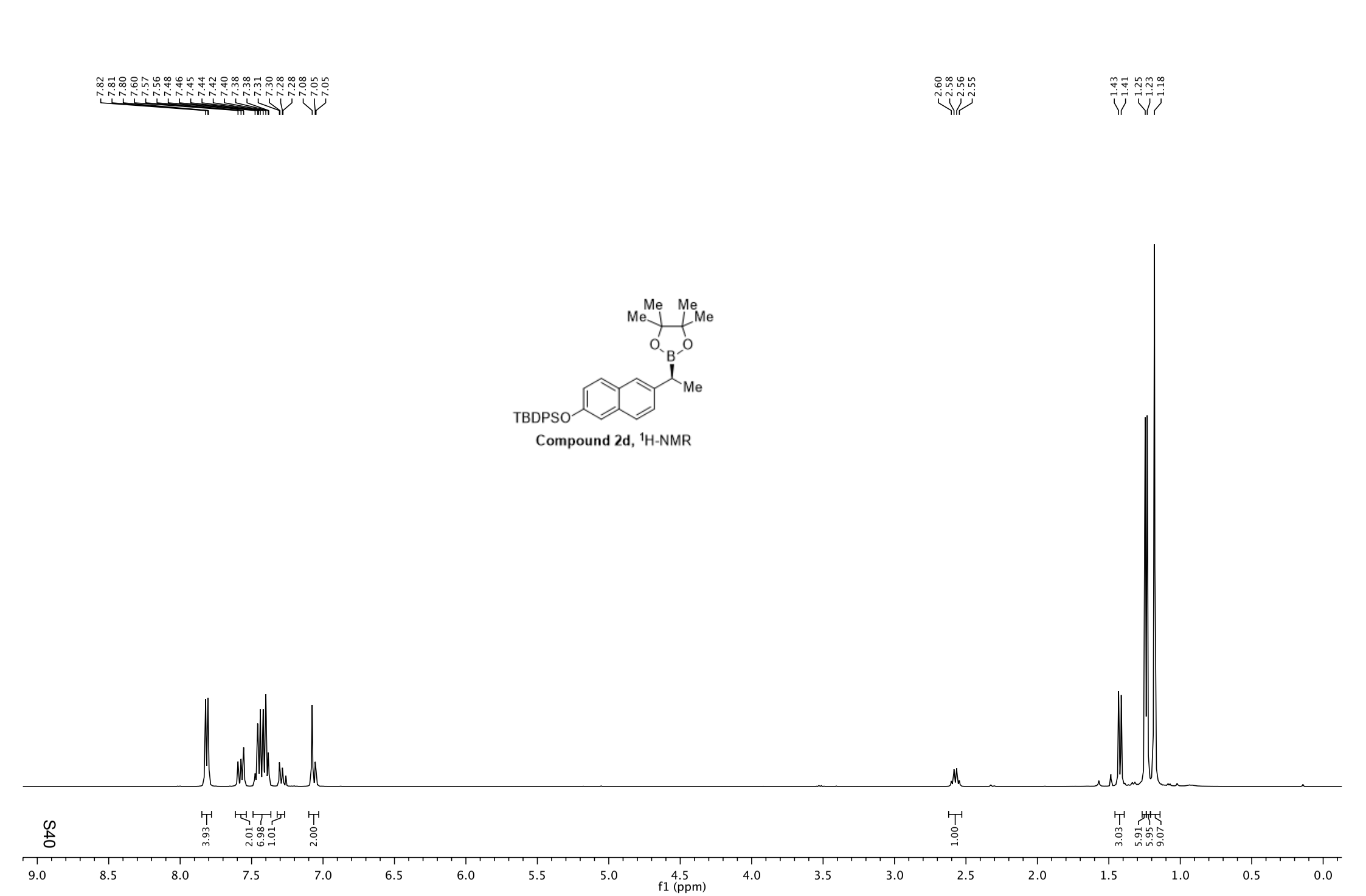
Compound 2b, ^{13}C-NMR



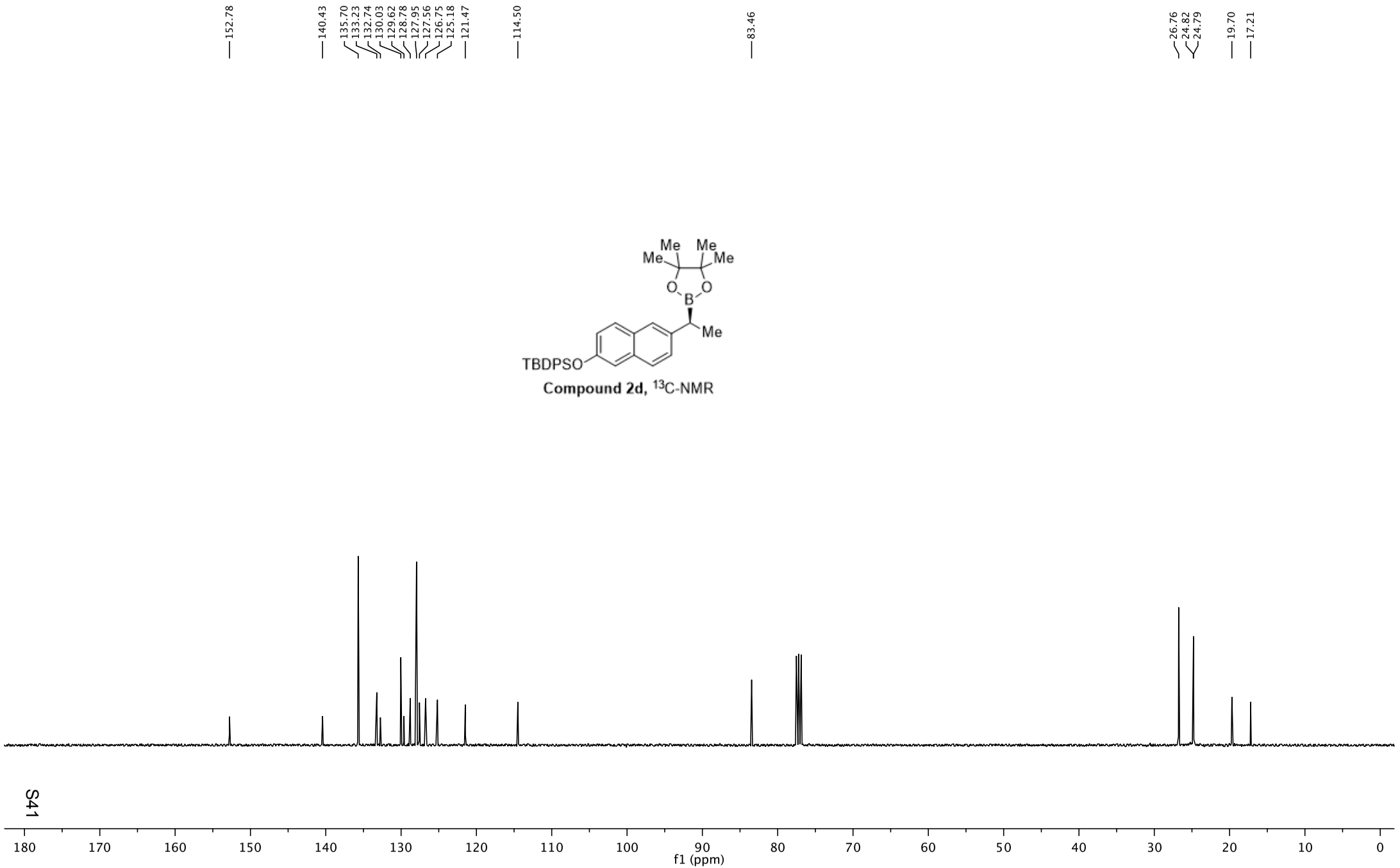
Compound 2c, ^{1}H-NMR



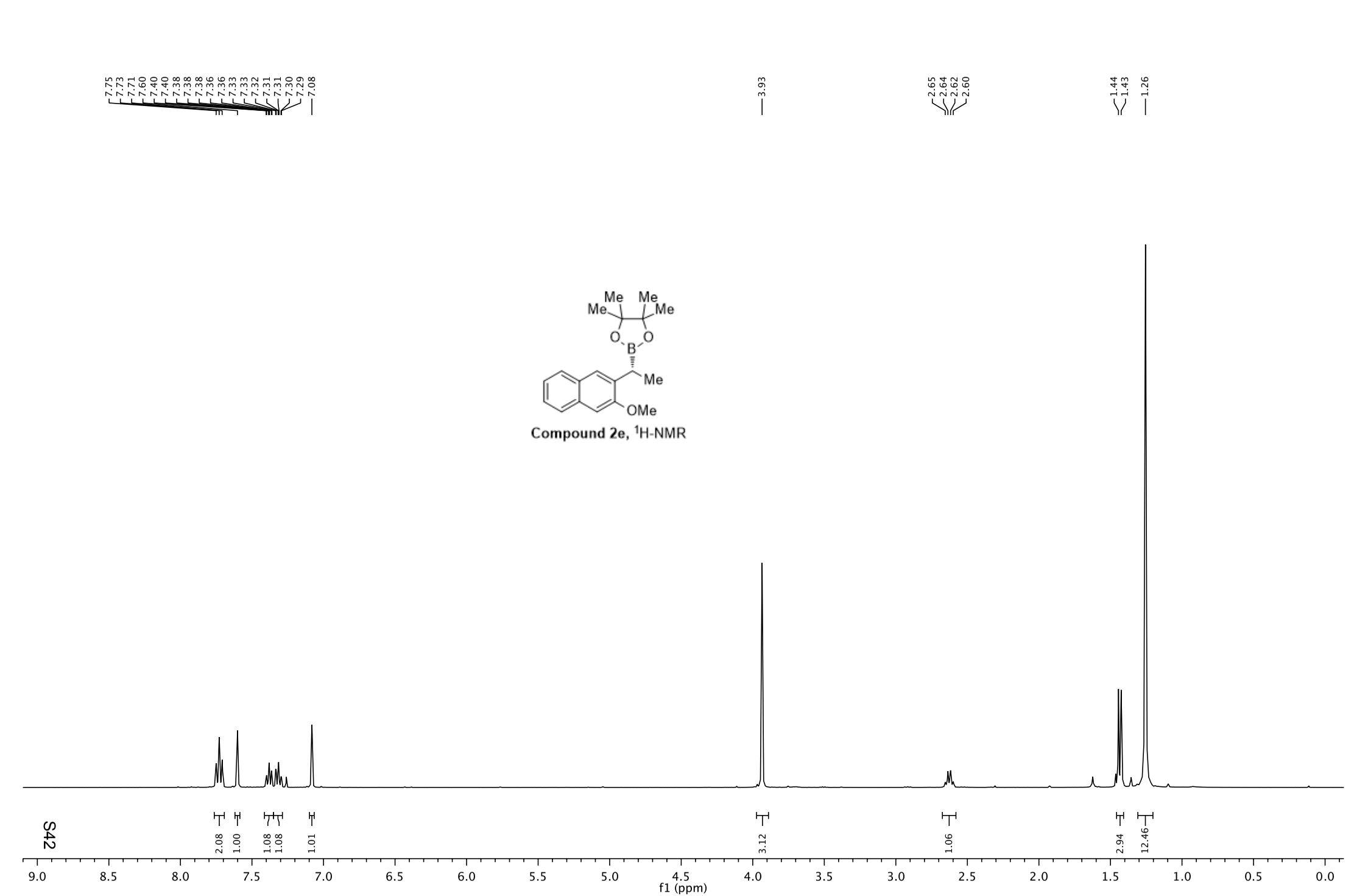
Compound 2c, ^{13}C-NMR



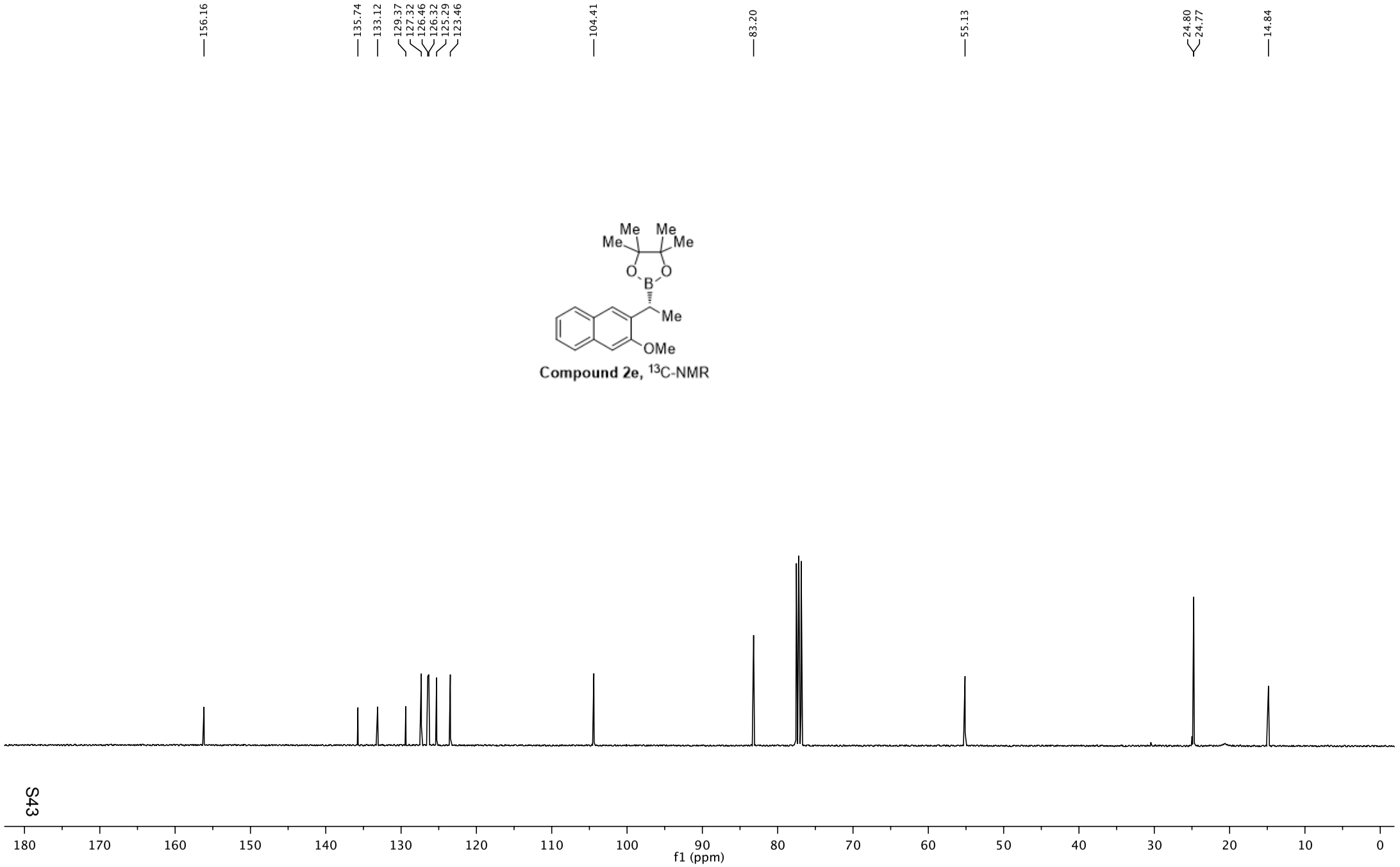
Compound 2d, ^{1}H-NMR



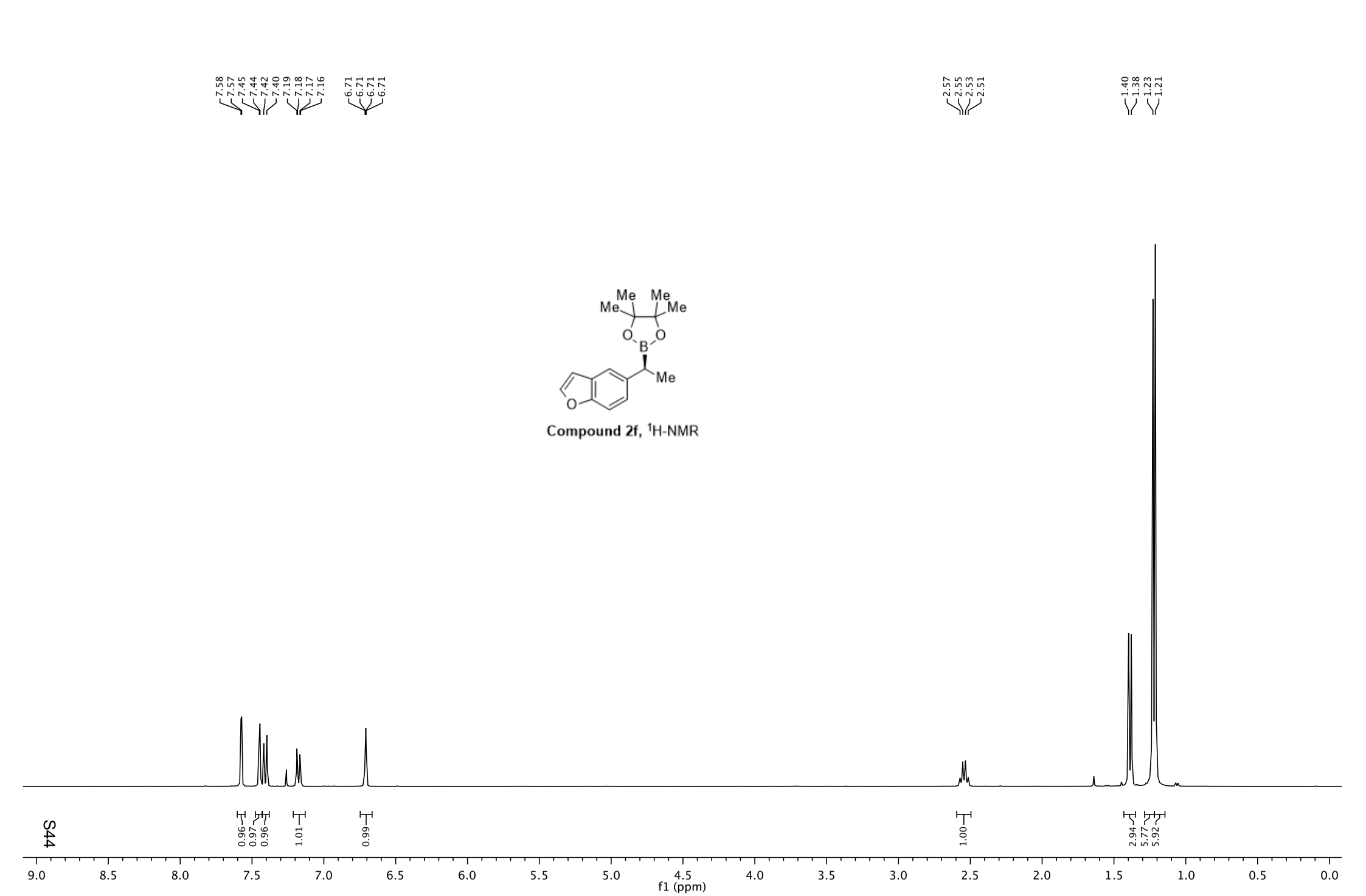
Compound 2d, ^{13}C-NMR



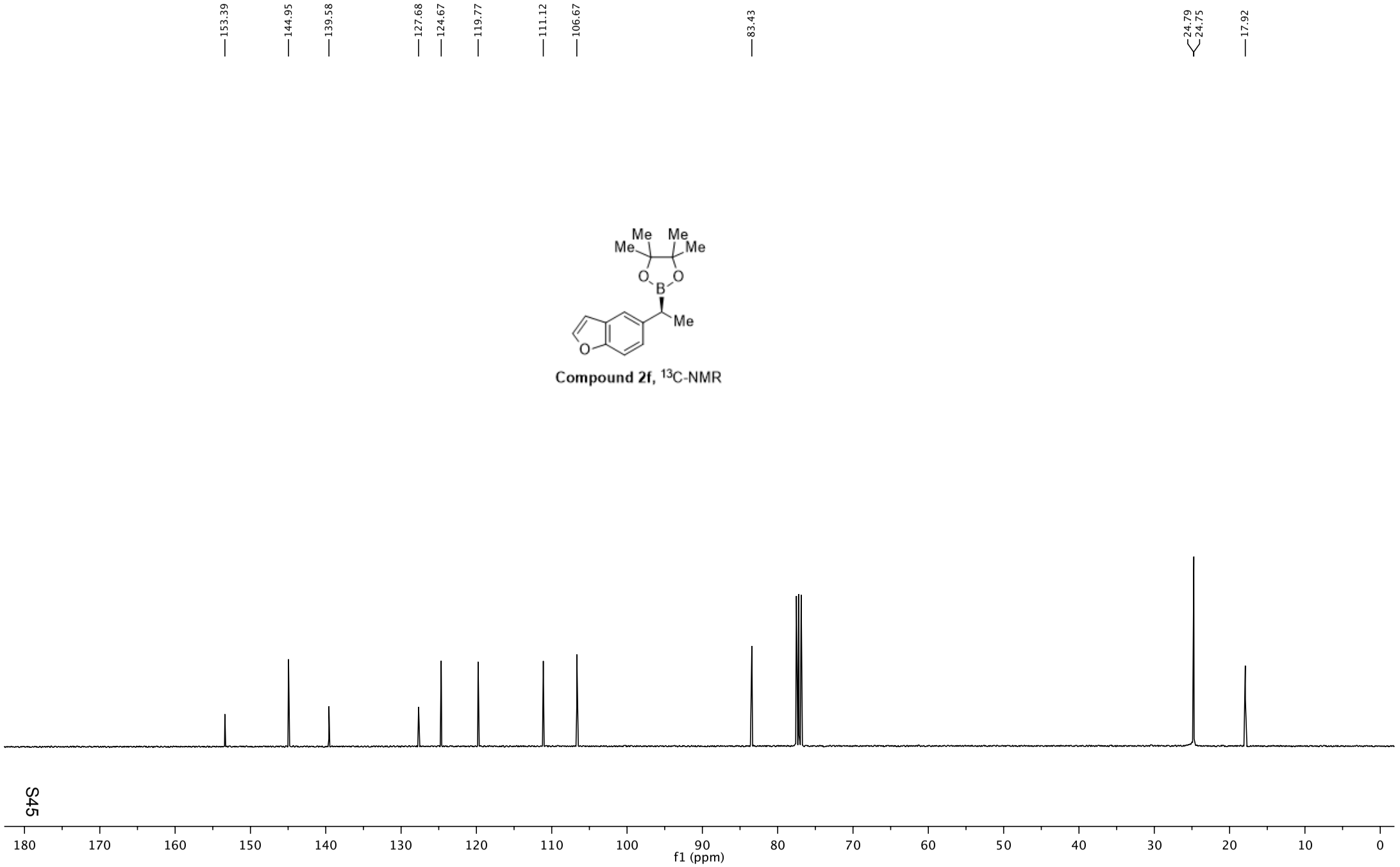
Compound 2e, ^{1}H-NMR

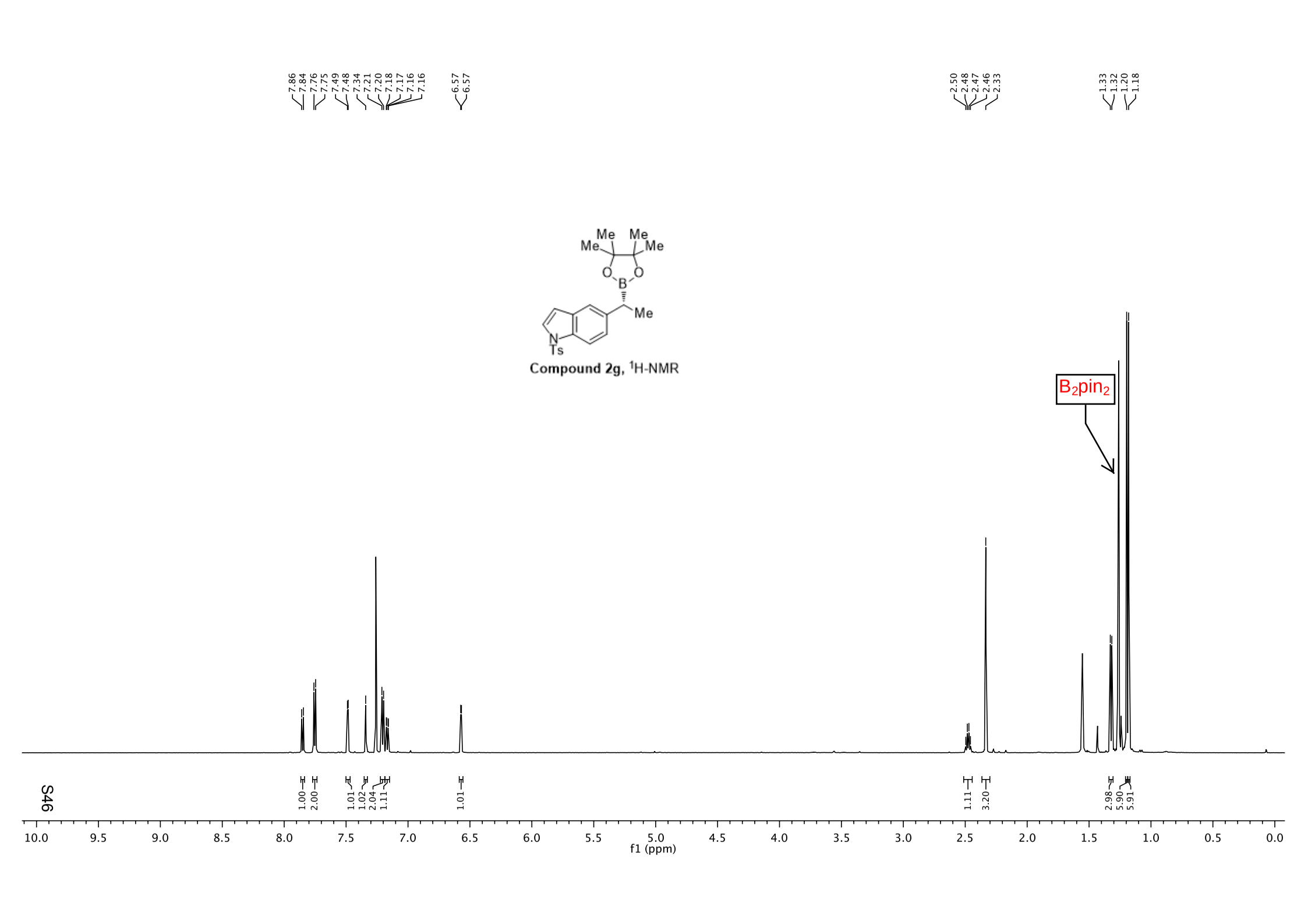


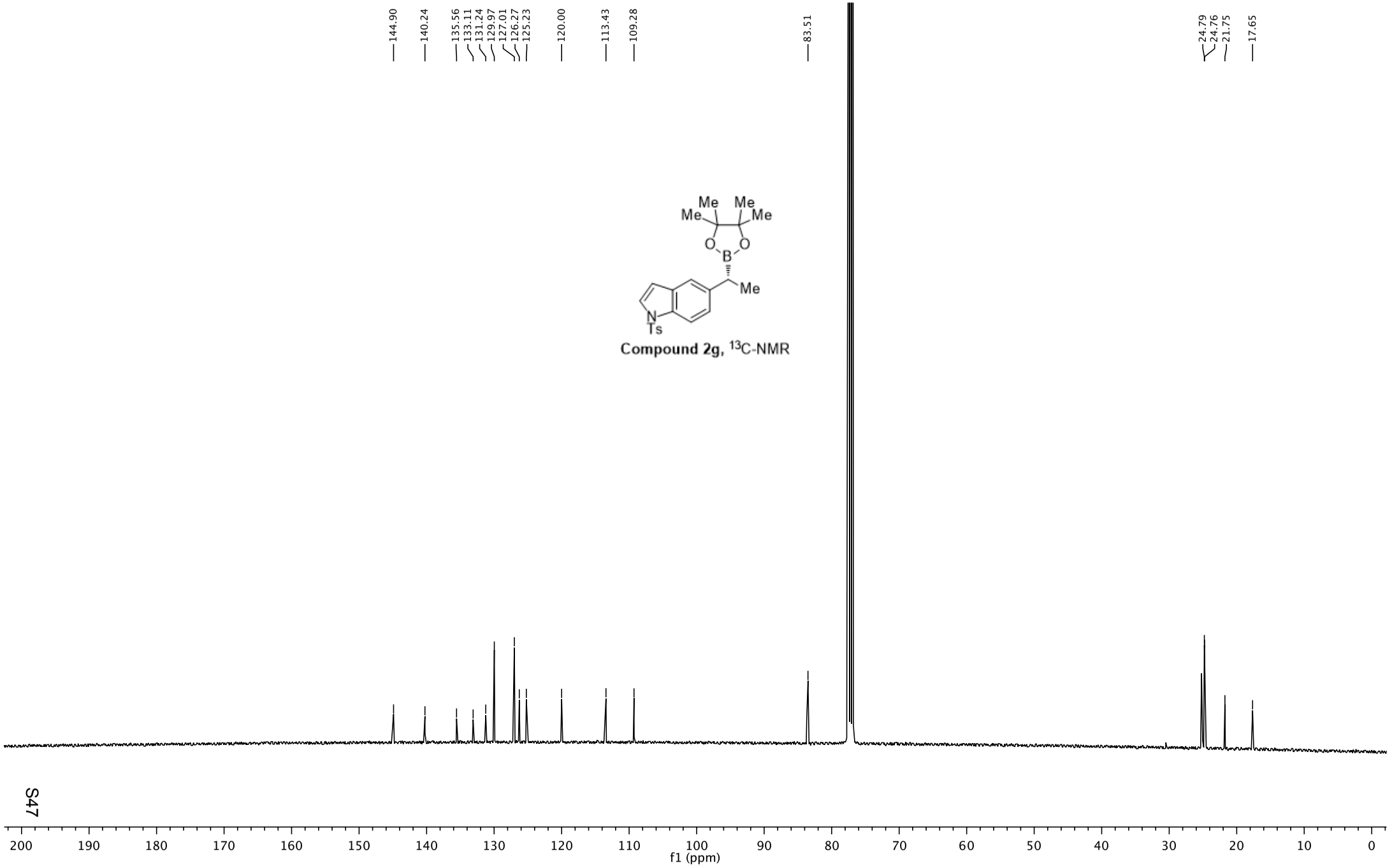
Compound 2e, ^{13}C-NMR



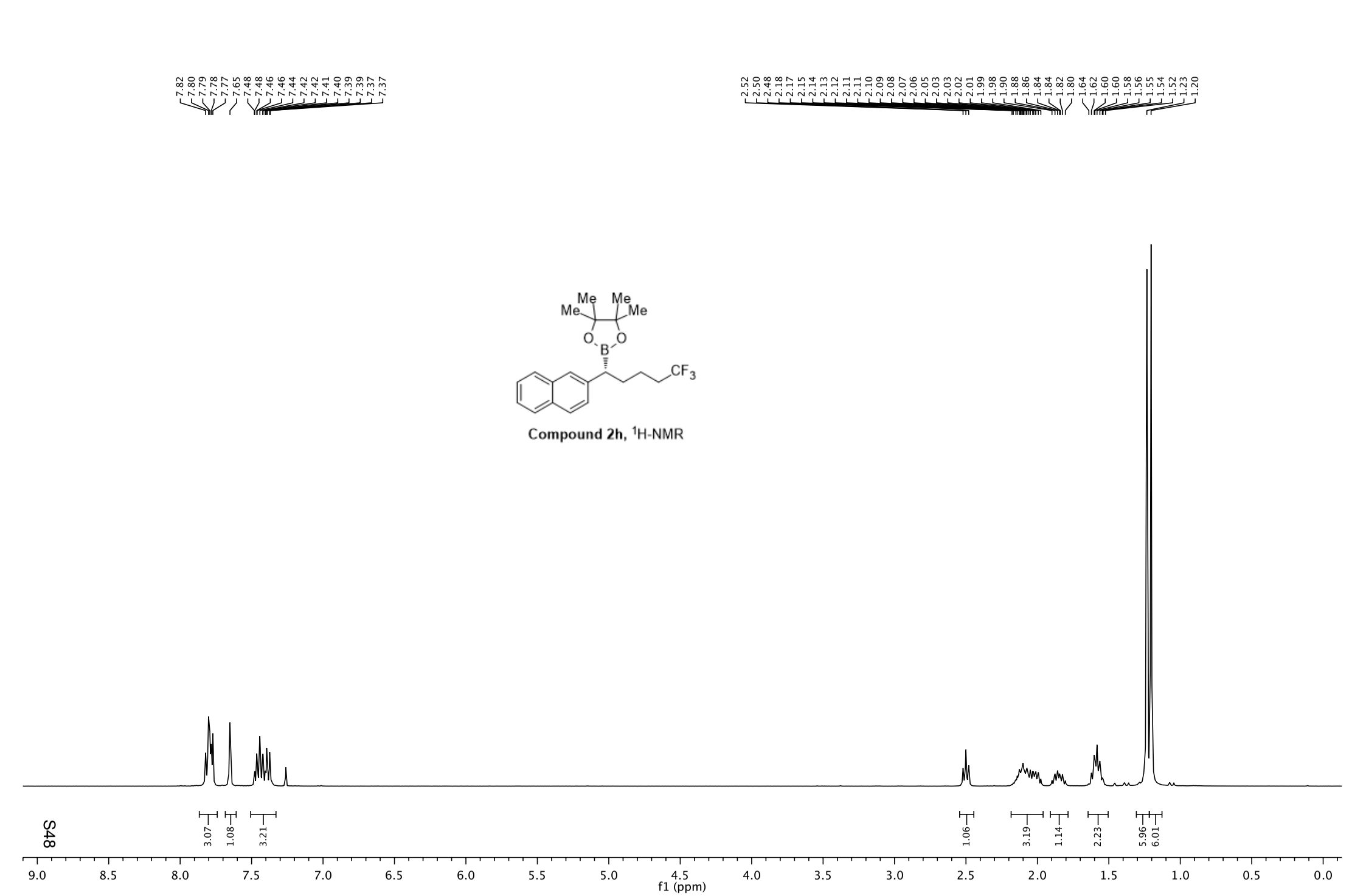
Compound 2f, ^{1}H-NMR

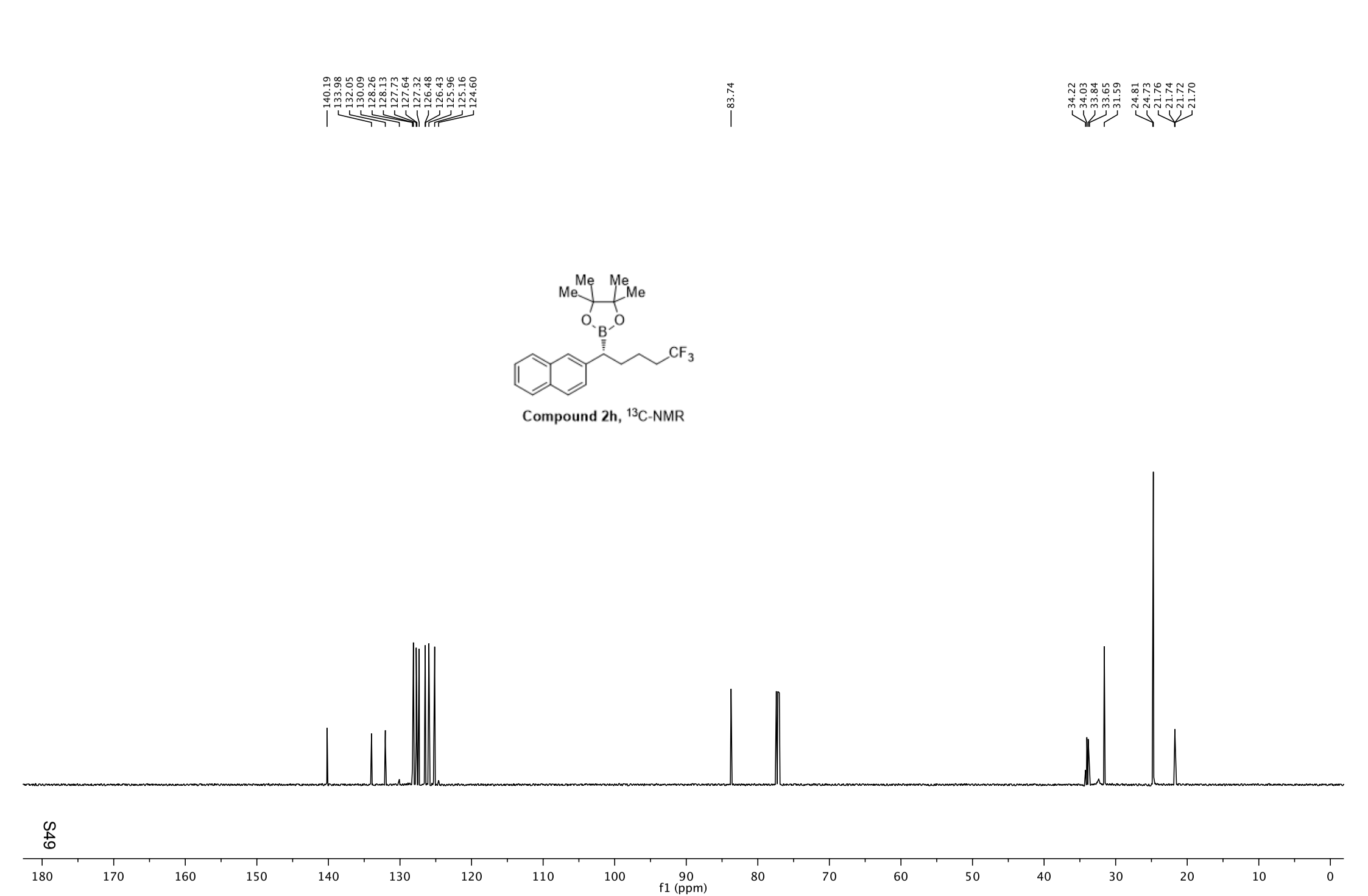

153.39
144.95
139.58
127.68
124.67
119.77
111.12
106.67
83.43
24.79
24.75
17.92
Me
Me
Me
Me
O
O
B
Me
O
Compound 2f, 13C-NMR
S45
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

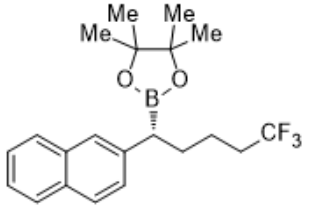

7.86
7.84
7.76
7.75
7.49
7.48
7.34
7.21
7.20
7.18
7.17
7.16
7.16
6.57
6.57
2.50
2.48
2.47
2.46
2.33
1.33
1.32
1.20
1.18
Me
Me
Me
Me
O
O
B
Me
N
Ts
Compound 2g, 1H-NMR
B2pin2
1.00
2.00
1.01
1.02
2.04
1.11
1.01
1.11
3.20
2.98
5.90
5.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



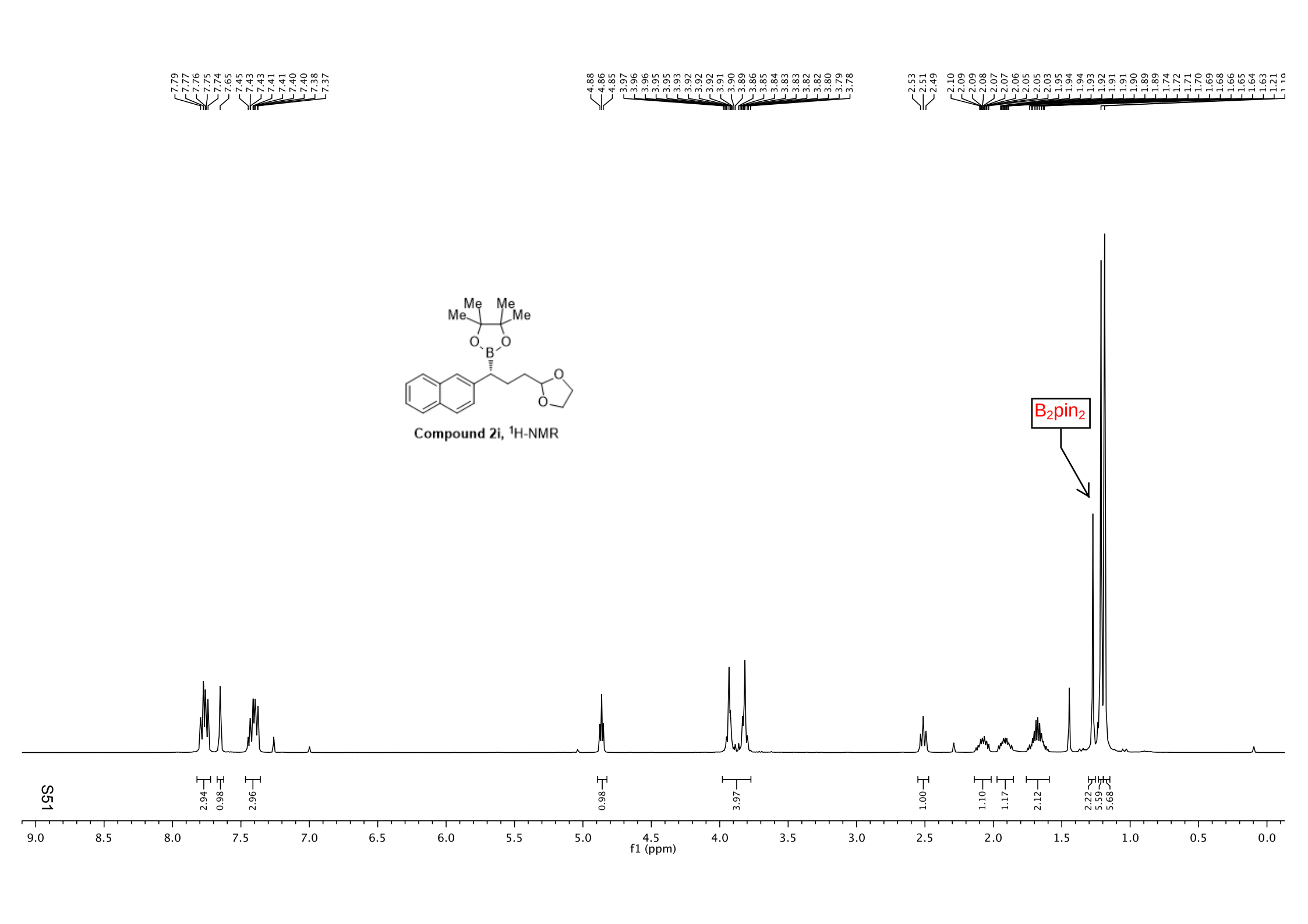
Compound 2g, ^{13}C-NMR

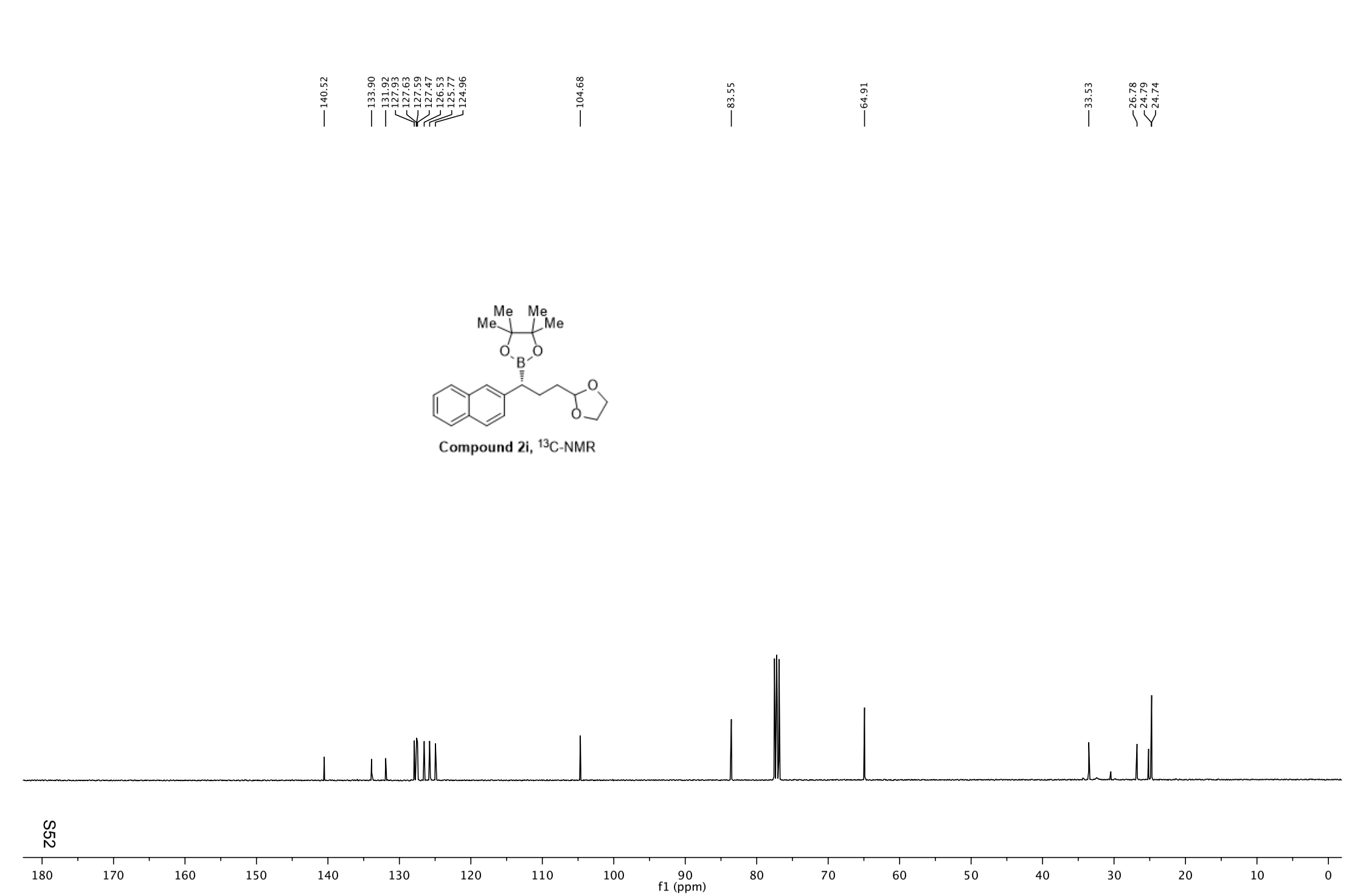

7.82
7.80
7.79
7.78
7.77
7.65
7.48
7.48
7.46
7.46
7.44
7.42
7.42
7.41
7.40
7.39
7.39
7.37
7.37
2.52
2.50
2.48
2.18
2.17
2.15
2.14
2.13
2.12
2.11
2.11
2.10
2.09
2.08
2.07
2.06
2.05
2.03
2.03
2.02
2.01
1.99
1.98
1.90
1.88
1.86
1.84
1.84
1.82
1.80
1.64
1.62
1.60
1.60
1.58
1.56
1.55
1.54
1.52
1.23
1.20
Me
Me
Me
Me
O
O
B
CF3
Compound 2h, 1H-NMR
3.07
1.08
3.21
1.06
3.19
1.14
2.23
5.96
6.01
S48
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)

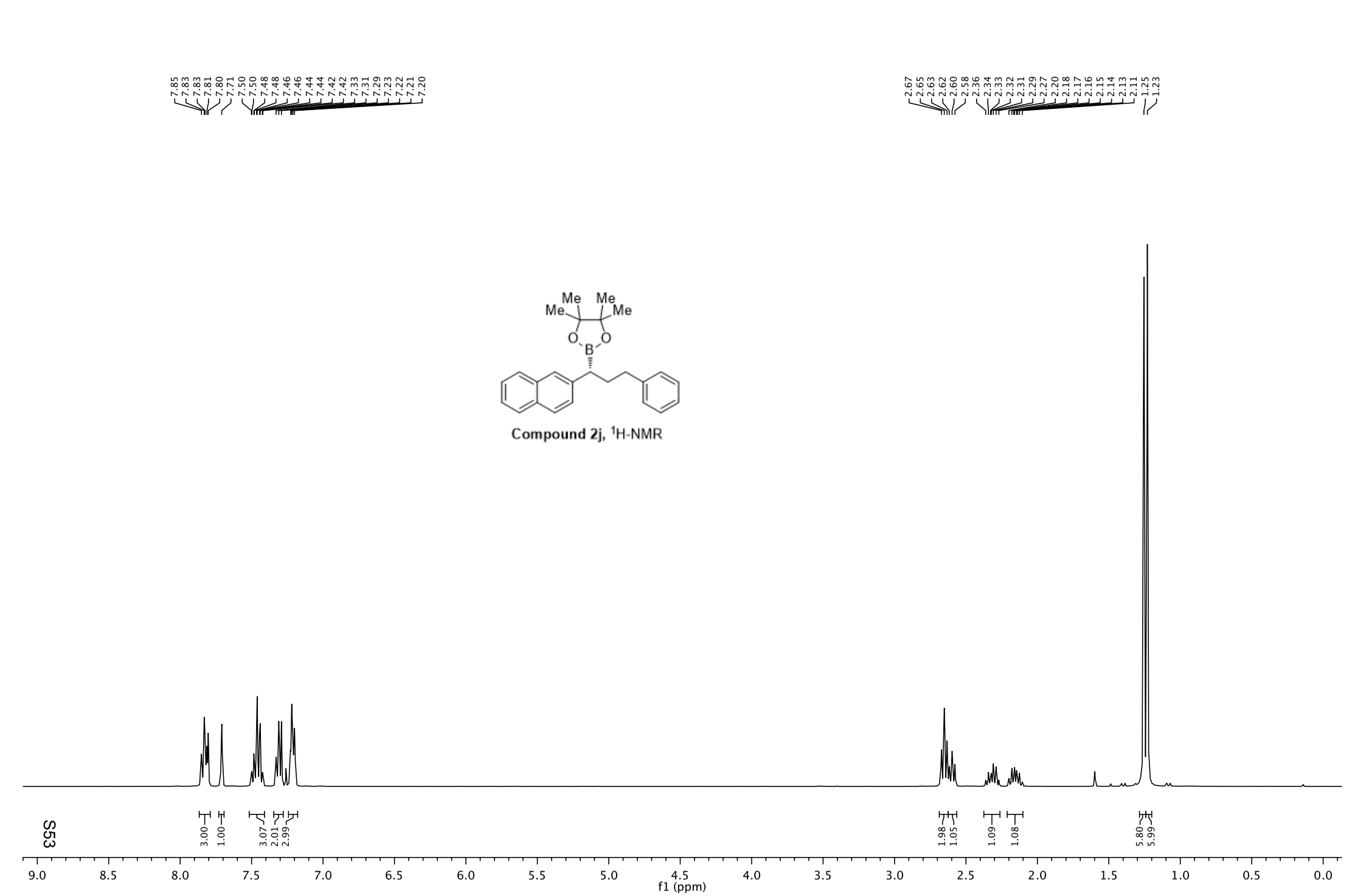

140.19
133.98
132.05
130.09
128.26
128.13
127.73
127.64
127.32
126.48
126.43
125.96
125.16
124.60
83.74
34.22
34.03
33.84
33.65
31.59
24.81
24.73
21.76
21.74
21.72
21.70
Me
Me
Me
Me
O
O
B
CF3
Compound 2h, 13C-NMR
S49
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



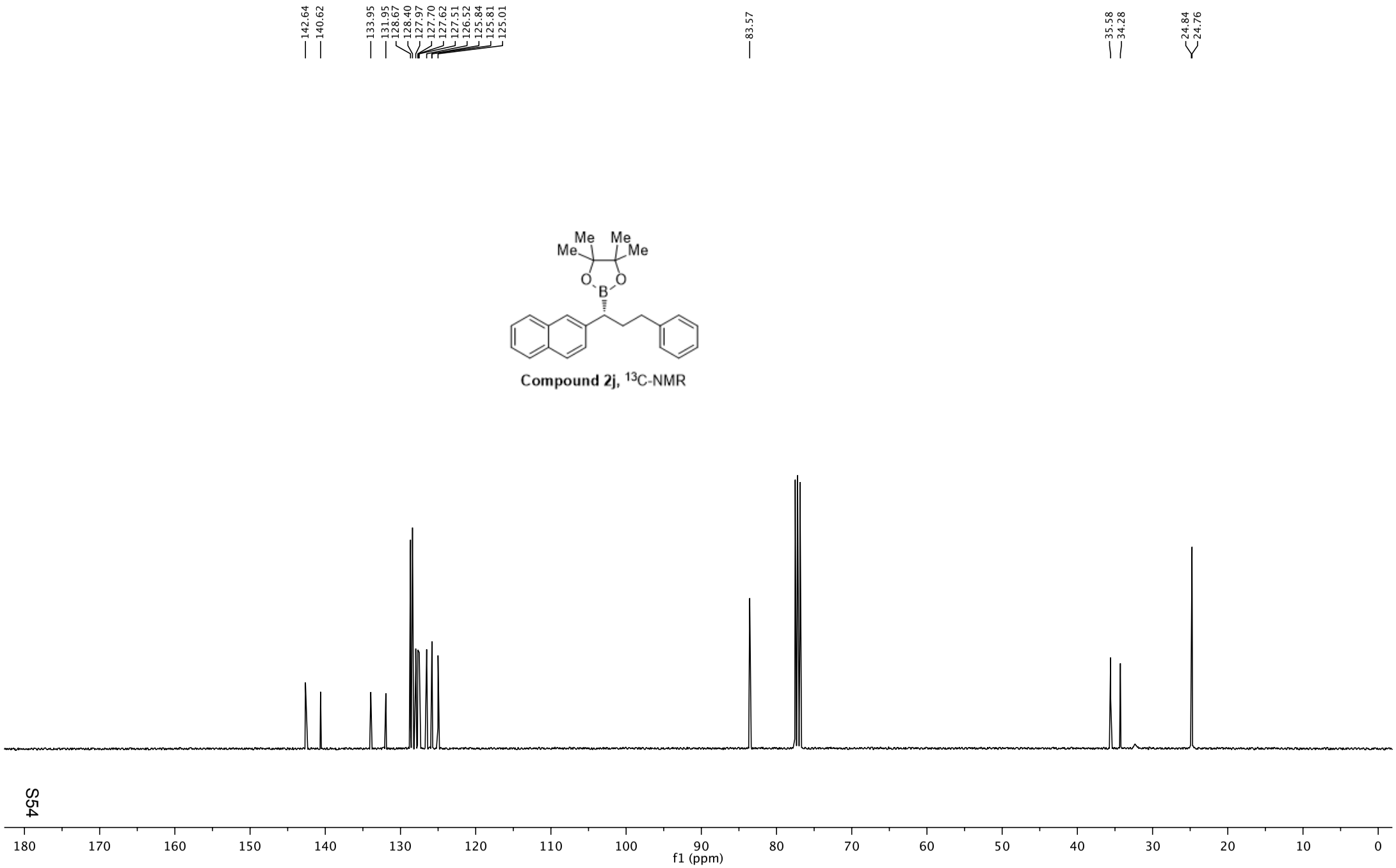
Compound 2h, ^{19}F-NMR


Me
Me
Me
Me
O
O
B
O
O
Compound 2i, 1H-NMR
B2pin2
S51
f1 (ppm)

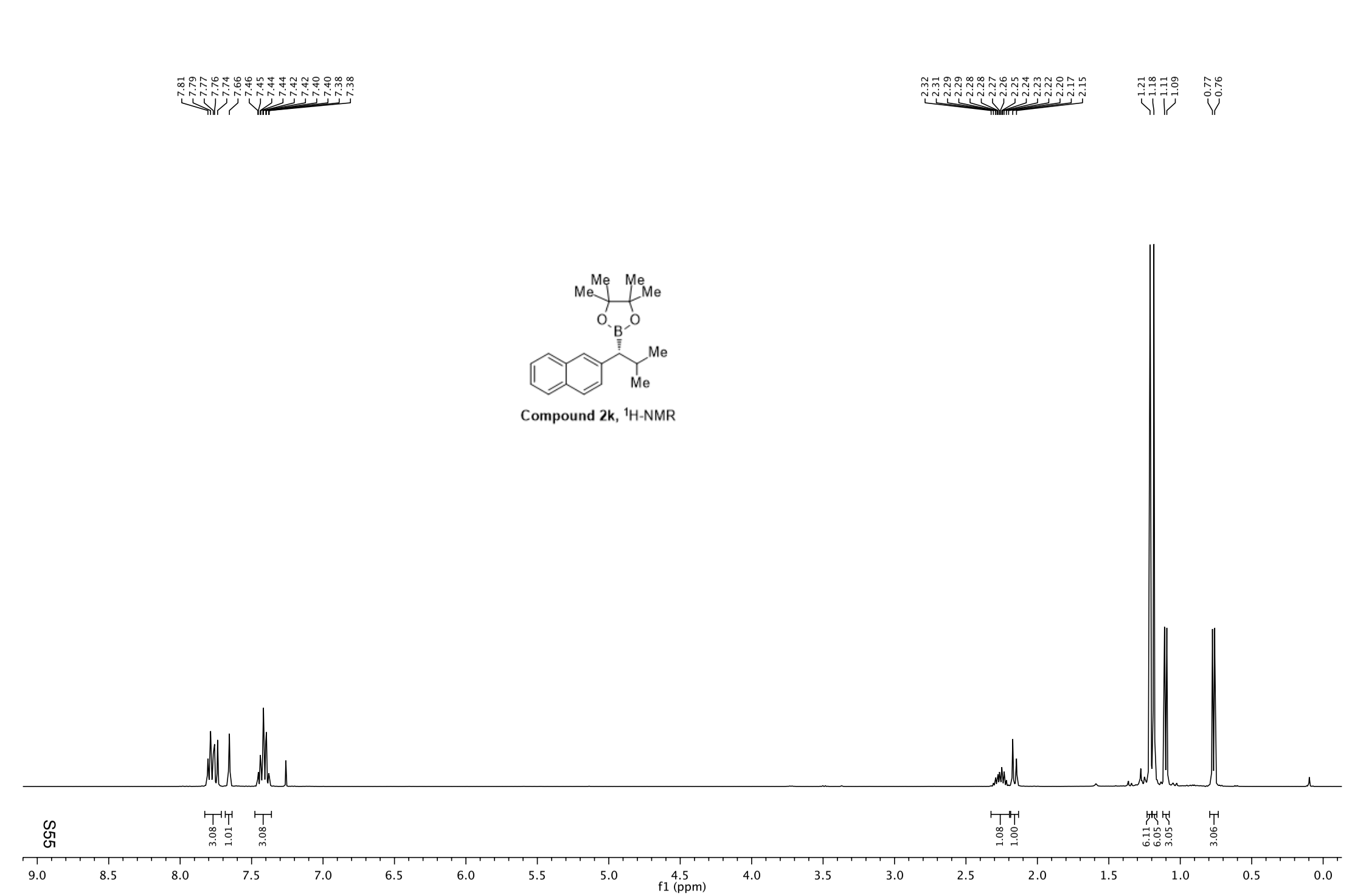

140.52
133.90
131.92
127.93
127.63
127.59
127.47
126.53
125.77
124.96
104.68
83.55
64.91
33.53
26.78
24.79
24.74
Me
Me
Me
Me
O
O
B
O
O
Compound 2i, 13C-NMR
S52
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

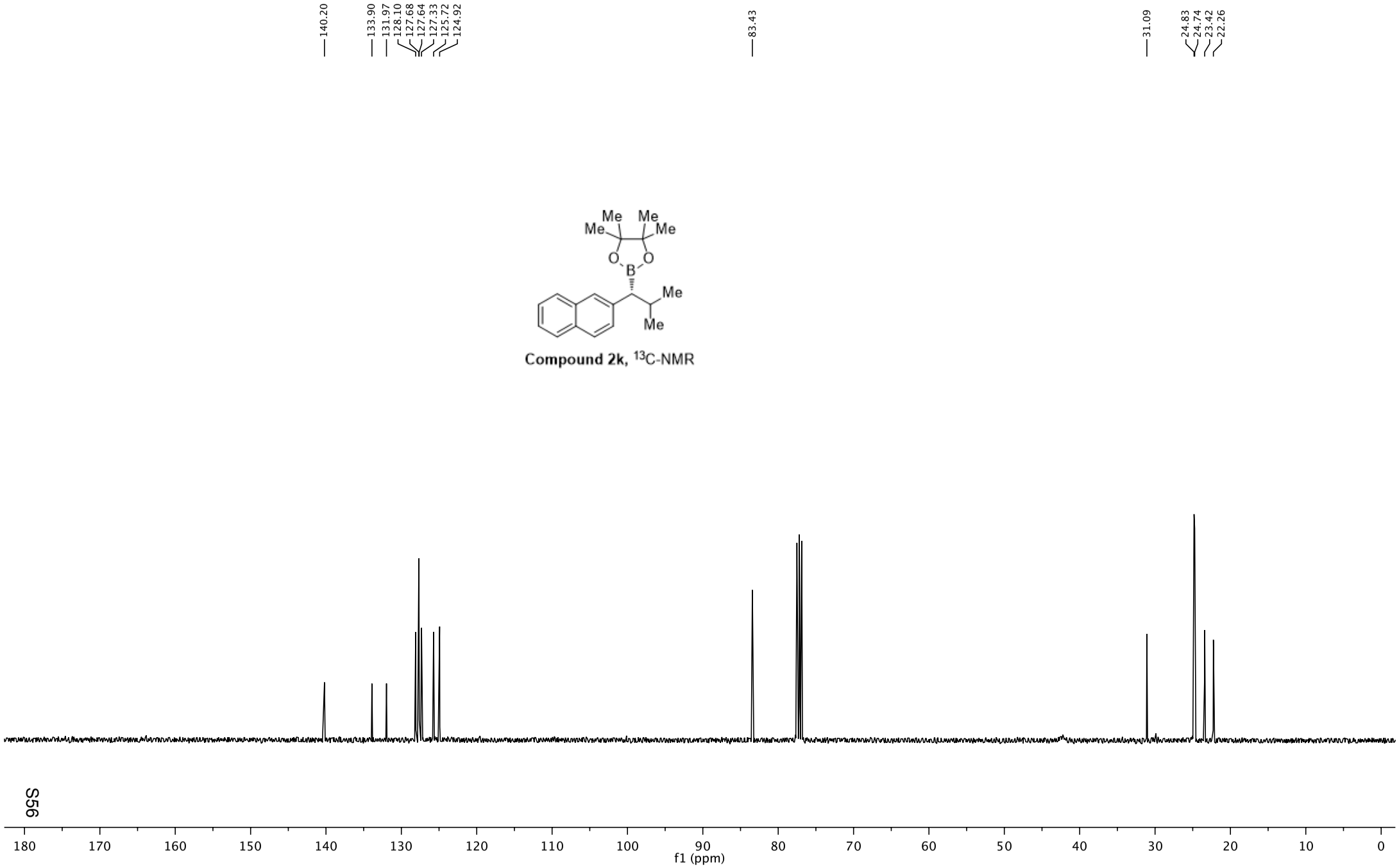


Compound 2j, ^{1}H-NMR

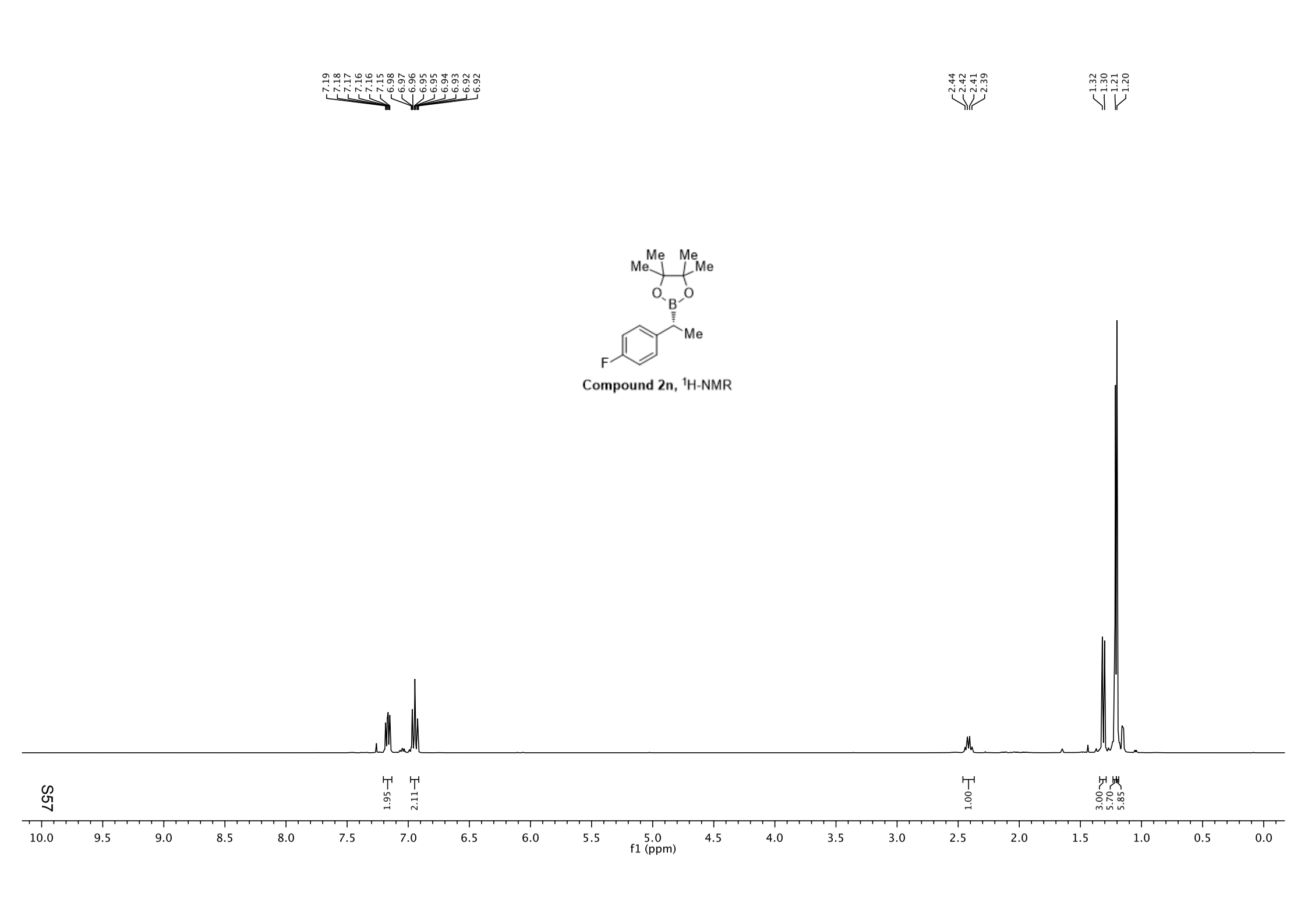


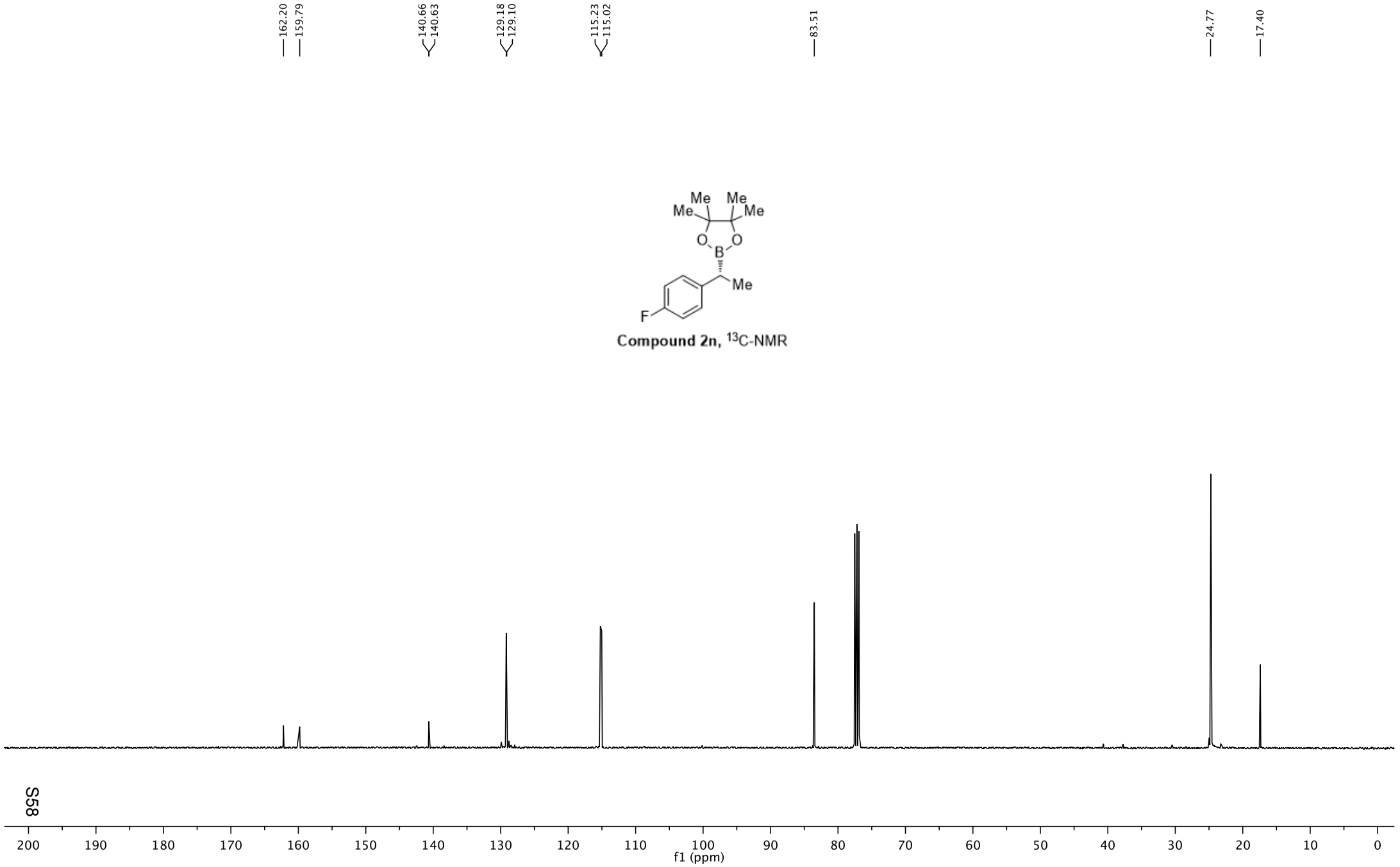
Compound 2j, ^{13}C-NMR


7.81
7.79
7.77
7.76
7.74
7.66
7.46
7.45
7.44
7.44
7.42
7.42
7.40
7.40
7.38
7.38
2.32
2.31
2.29
2.29
2.28
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.20
2.17
2.15
1.21
1.18
1.11
1.09
0.77
0.76
Me
Me
Me
Me
O
O
B
Me
Me
Compound 2k, 1H-NMR
S55
3.08
1.01
3.08
1.08
1.00
6.11
6.05
3.05
3.06
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)

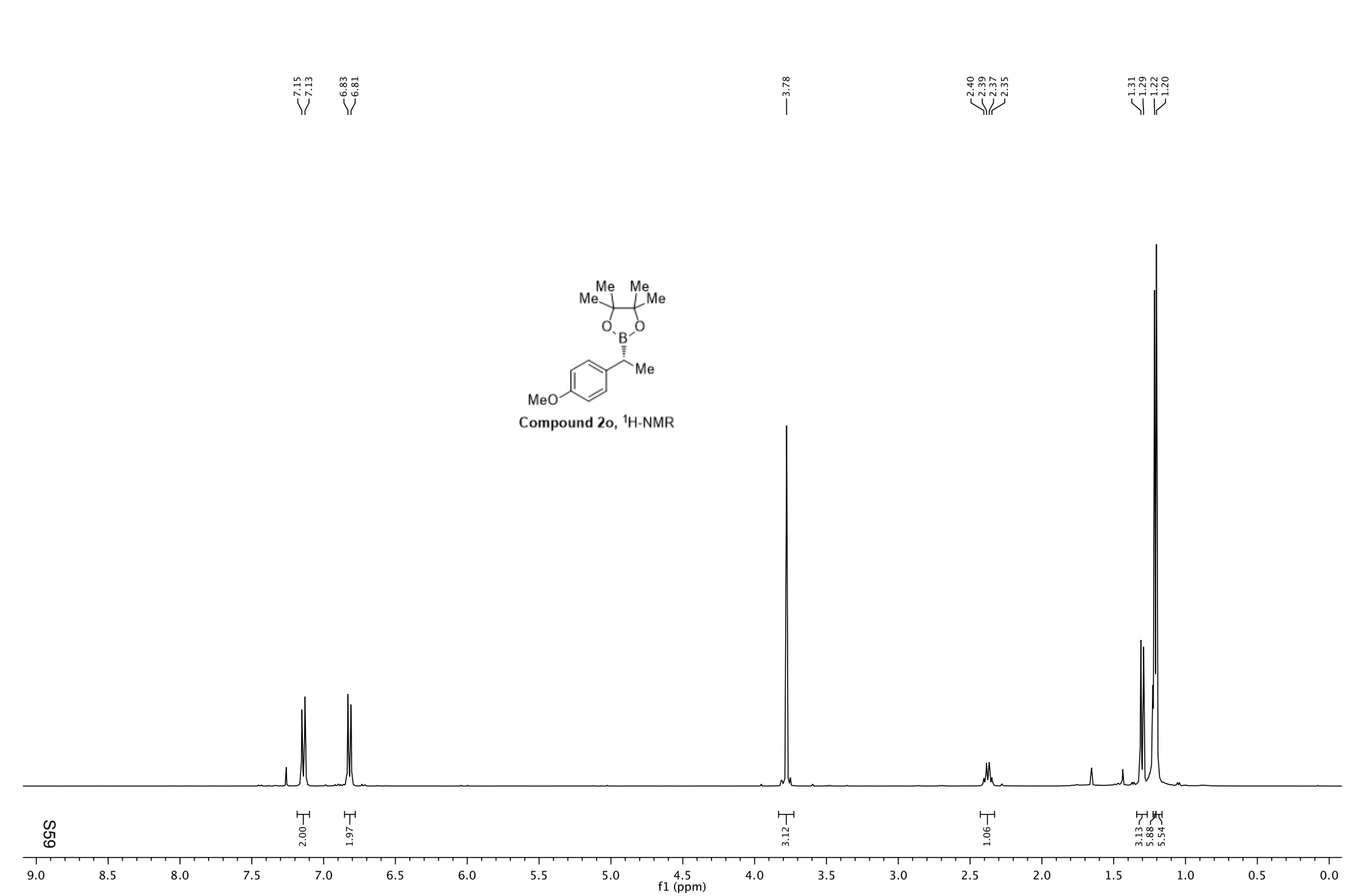


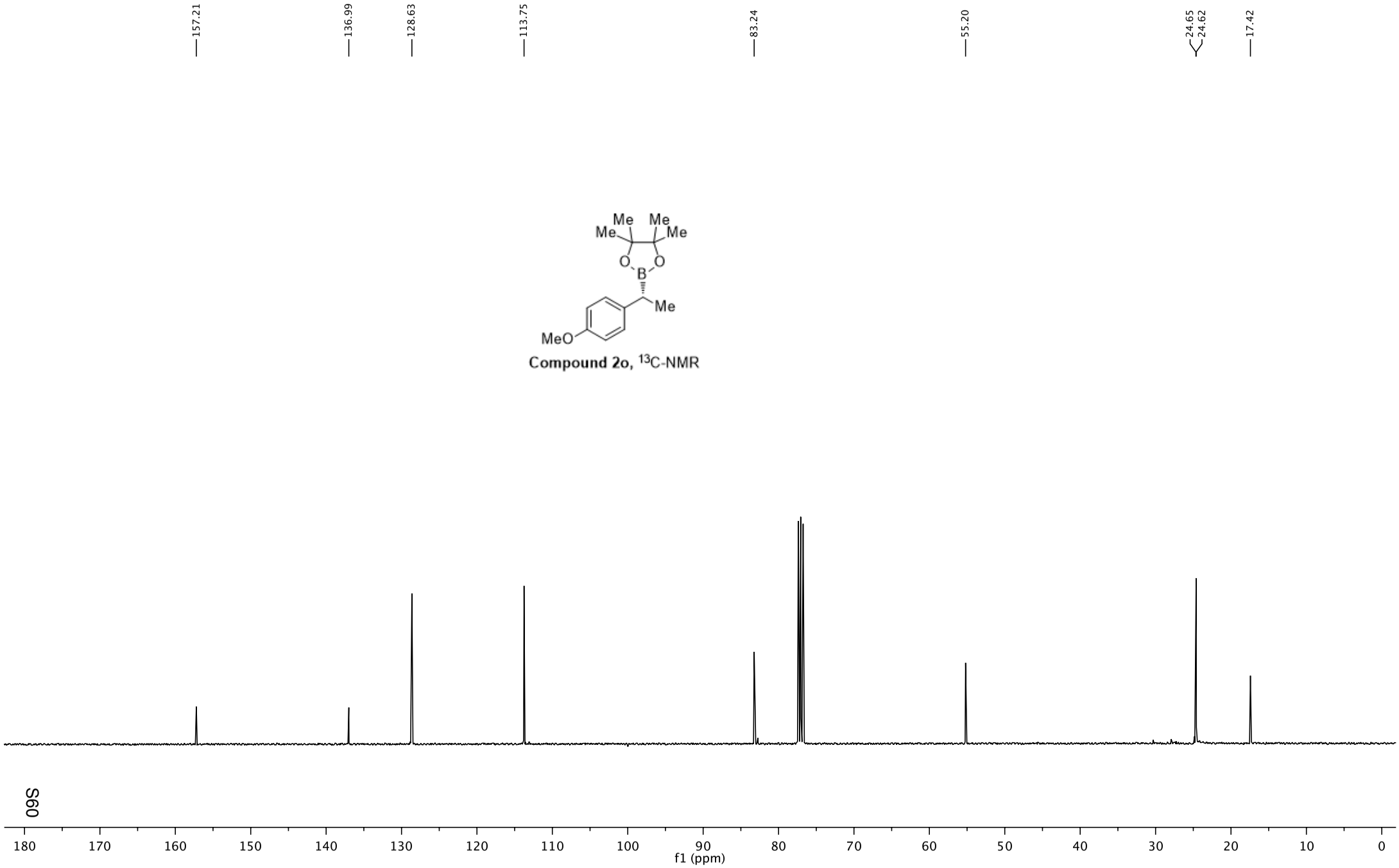
Compound 2k, ^{13}C-NMR

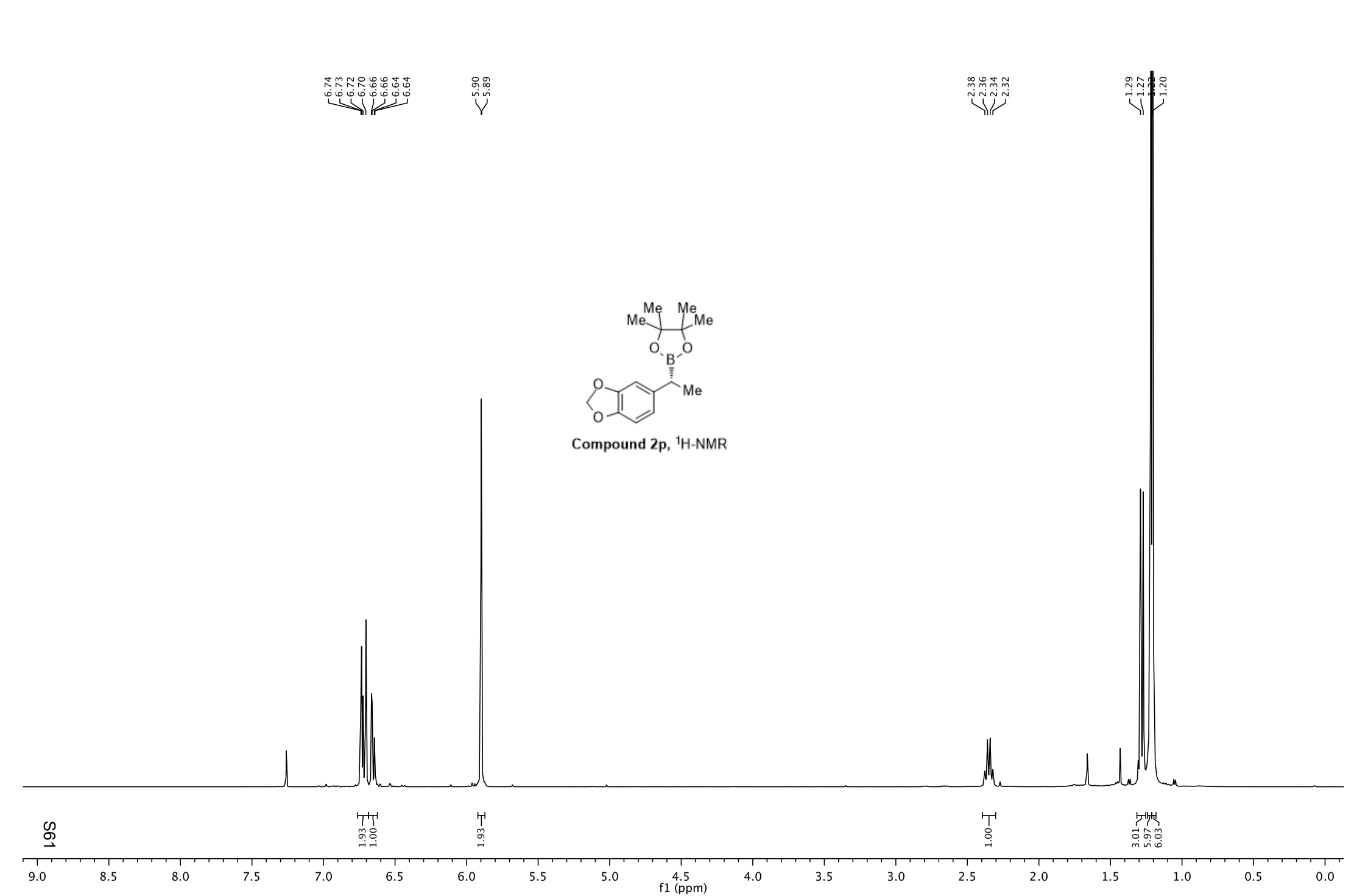

7.19
7.18
7.17
7.16
7.16
7.15
6.98
6.97
6.96
6.95
6.95
6.94
6.93
6.92
6.92
2.44
2.42
2.41
2.39
1.32
1.30
1.21
1.20
Me
Me
Me
Me
O
O
B
Me
F
Compound 2n, 1H-NMR
1.95
2.11
1.00
3.00
5.70
5.85
S57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



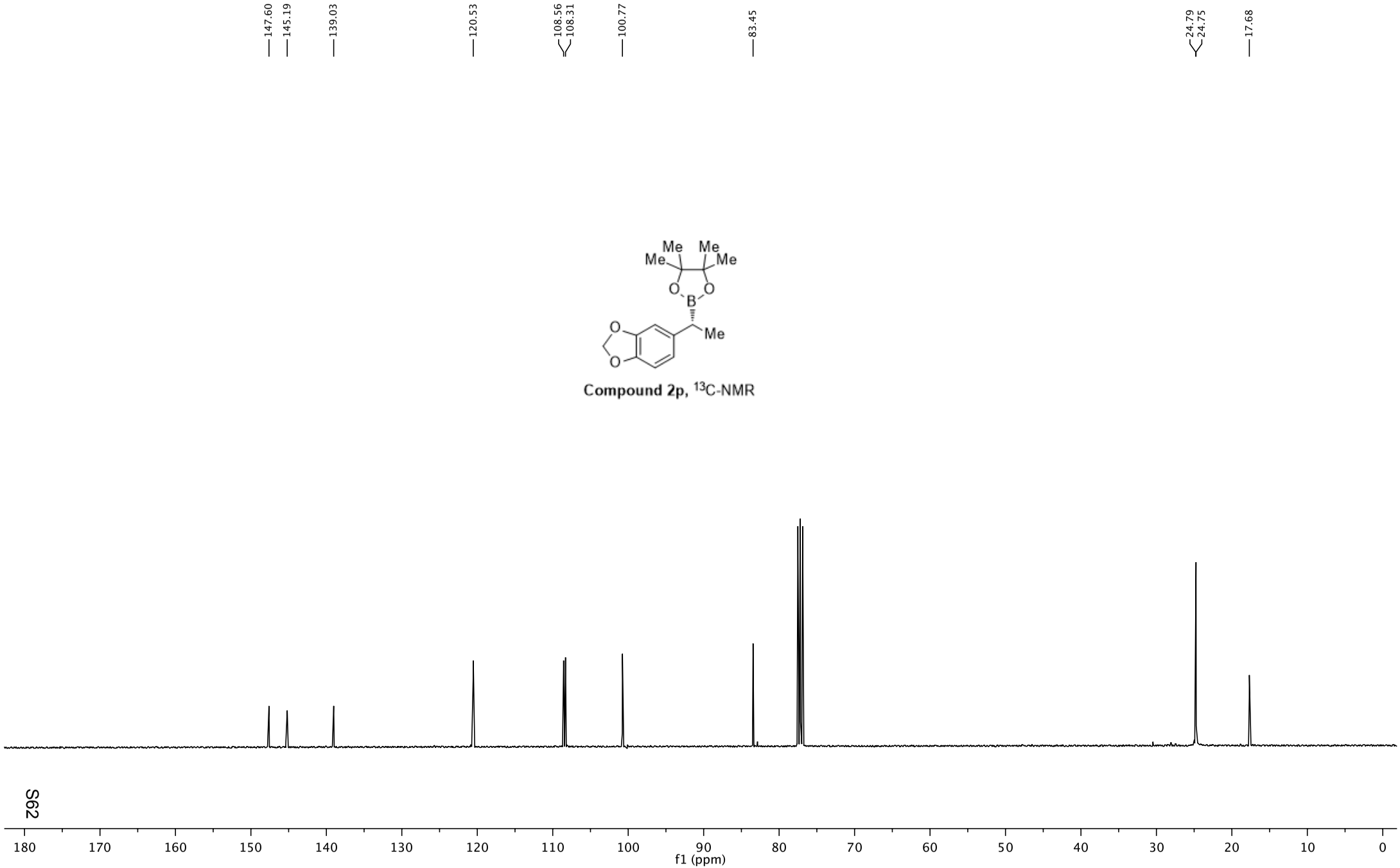
Compound 2n, ^{13}C-NMR


7.15
7.13
6.83
6.81
3.78
2.40
2.39
2.37
2.35
1.31
1.29
1.22
1.20
Me
Me
Me
Me
O
B
O
Me
MeO
Compound 2o, 1H-NMR
2.00
1.97
3.12
1.06
3.13
5.88
5.54
S59
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)

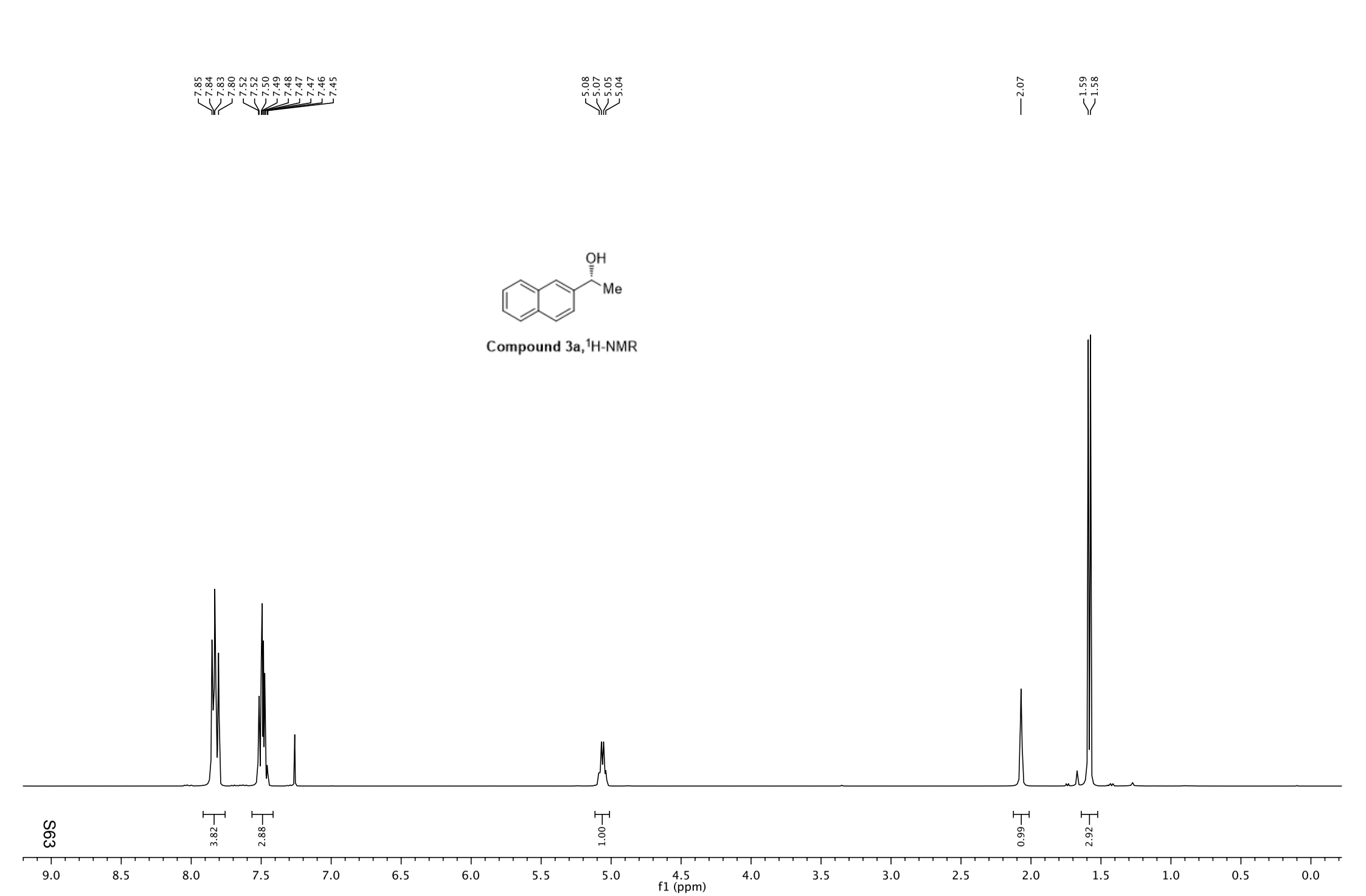

157.21
136.99
128.63
113.75
83.24
55.20
24.65
24.62
17.42
Me
Me
Me
Me
O
O
B
Me
MeO
Compound 2o, 13C-NMR
S60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

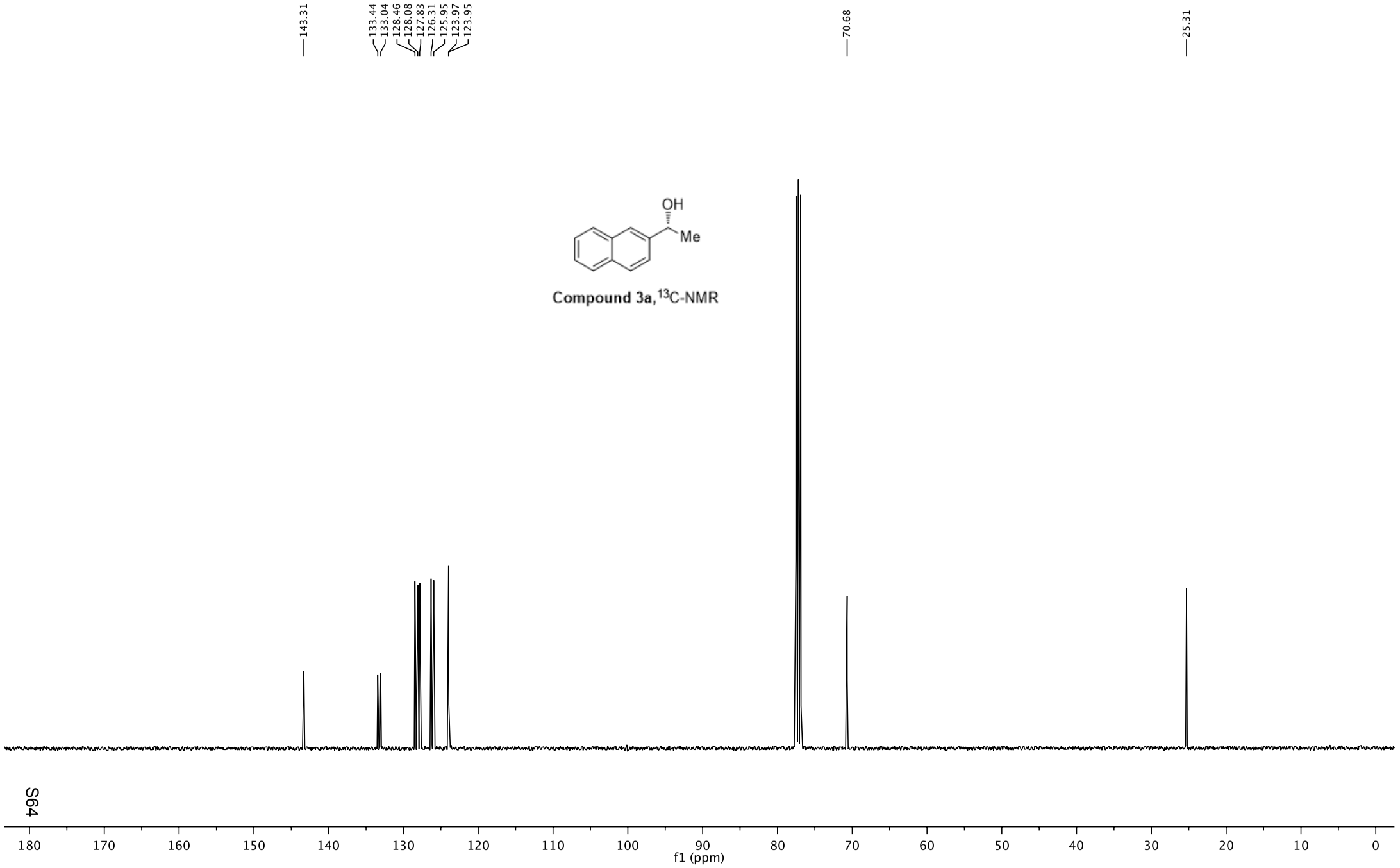


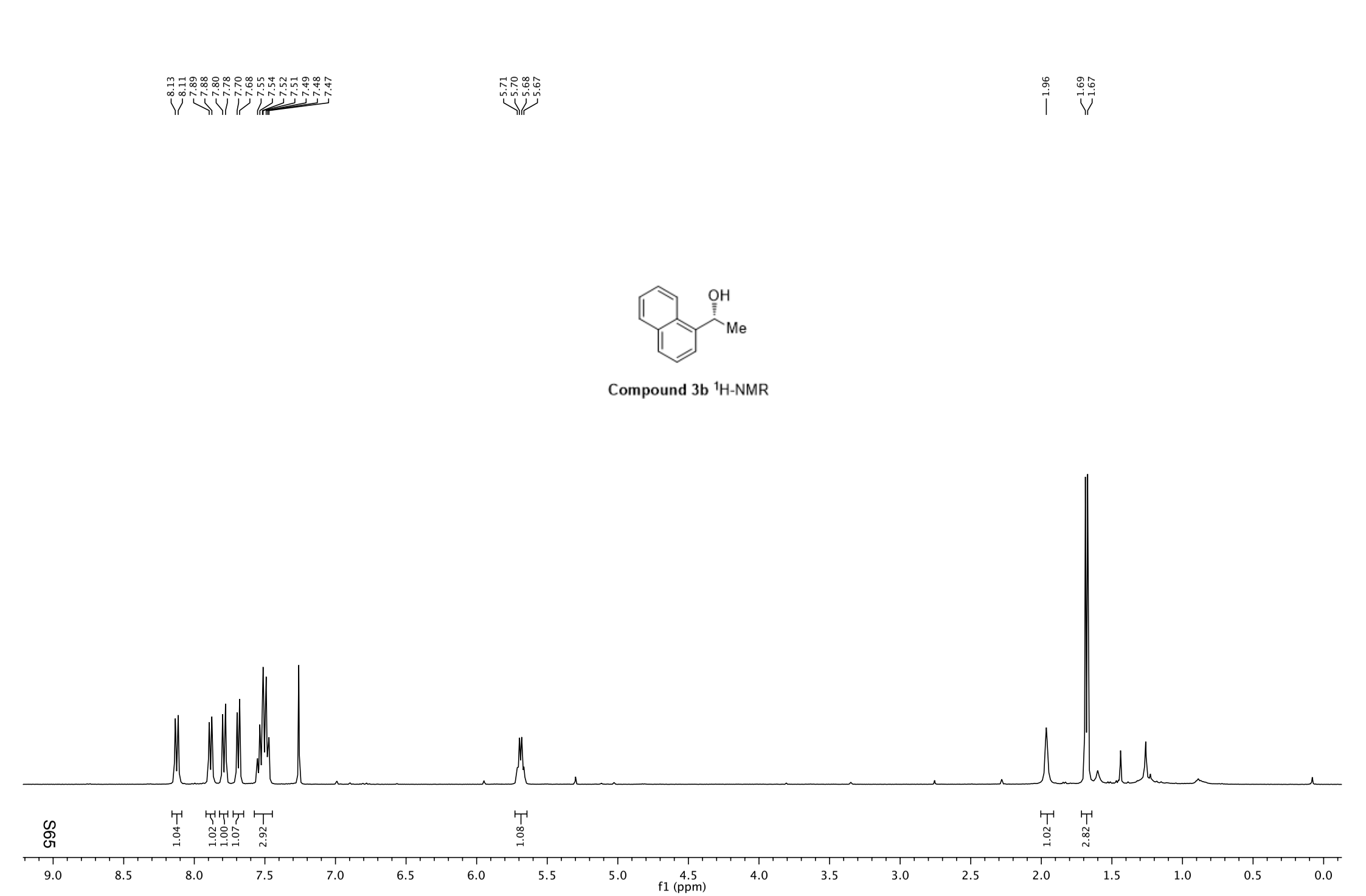
Compound 2p, ^{1}H-NMR



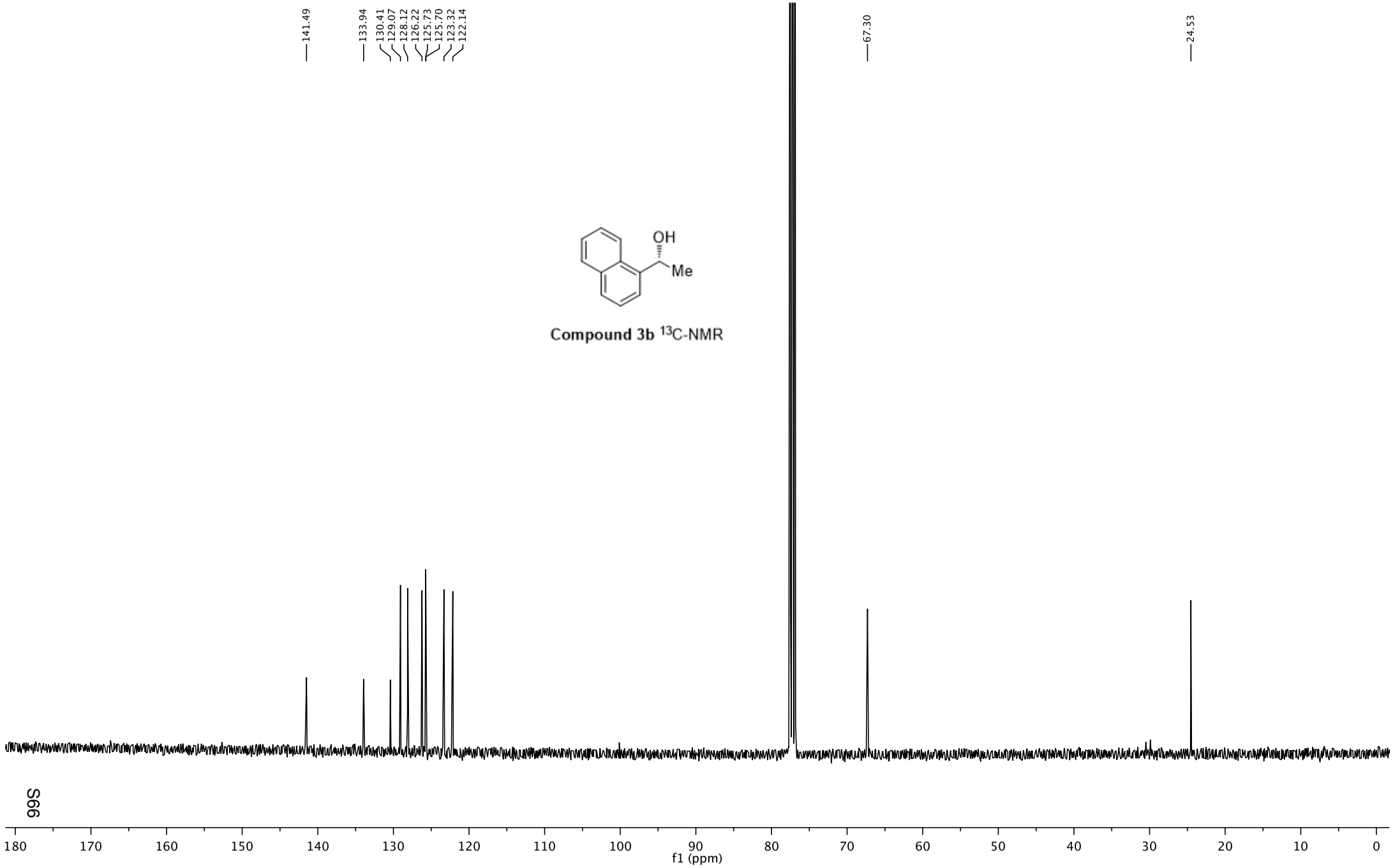
Compound 2p, ^{13}C-NMR

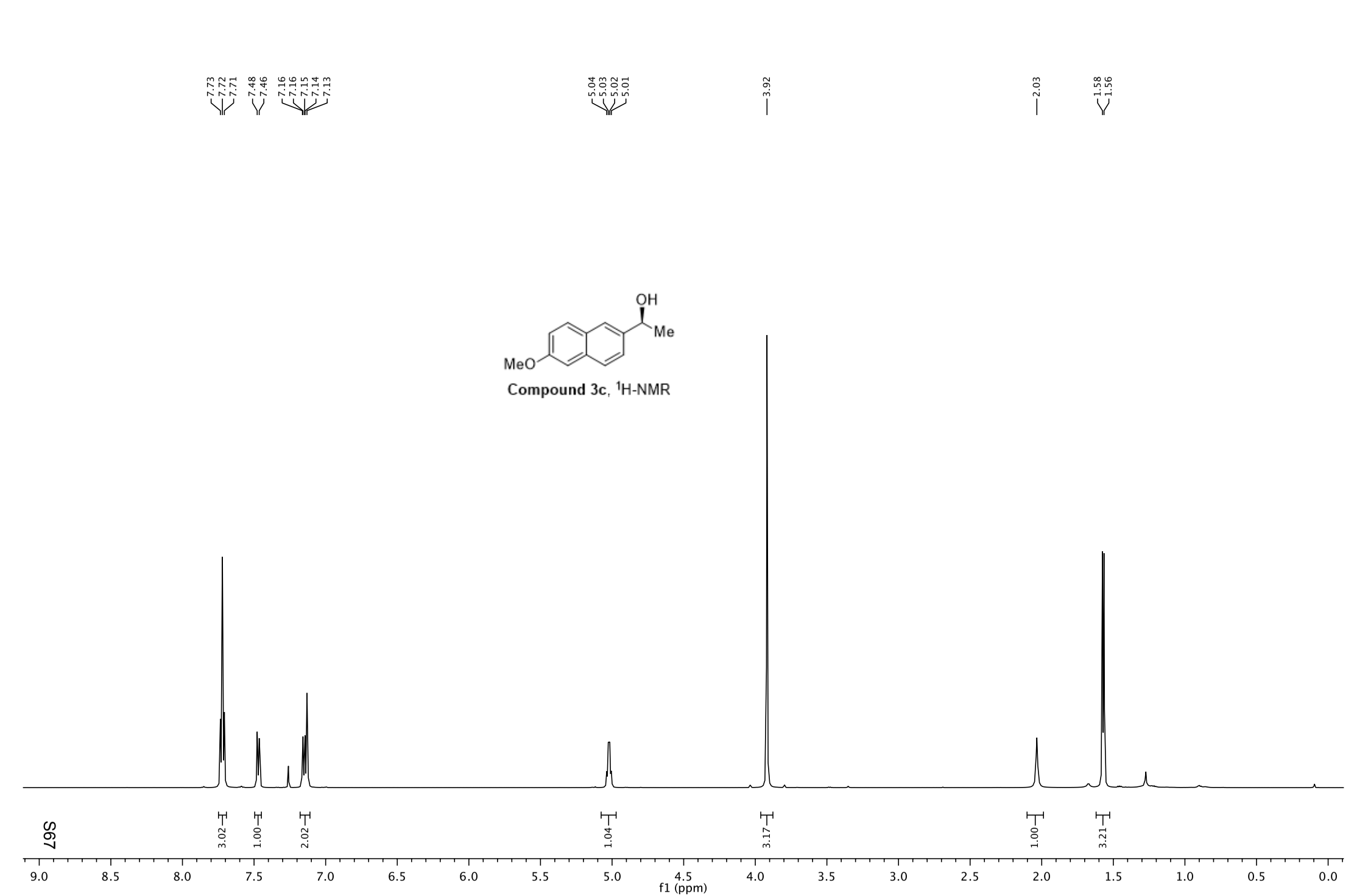

7.85
7.84
7.83
7.80
7.52
7.52
7.50
7.49
7.48
7.47
7.47
7.46
7.45
5.08
5.07
5.05
5.04
2.07
1.59
1.58
OH
Me
Compound 3a, 1H-NMR
3.82
2.88
1.00
0.99
2.92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

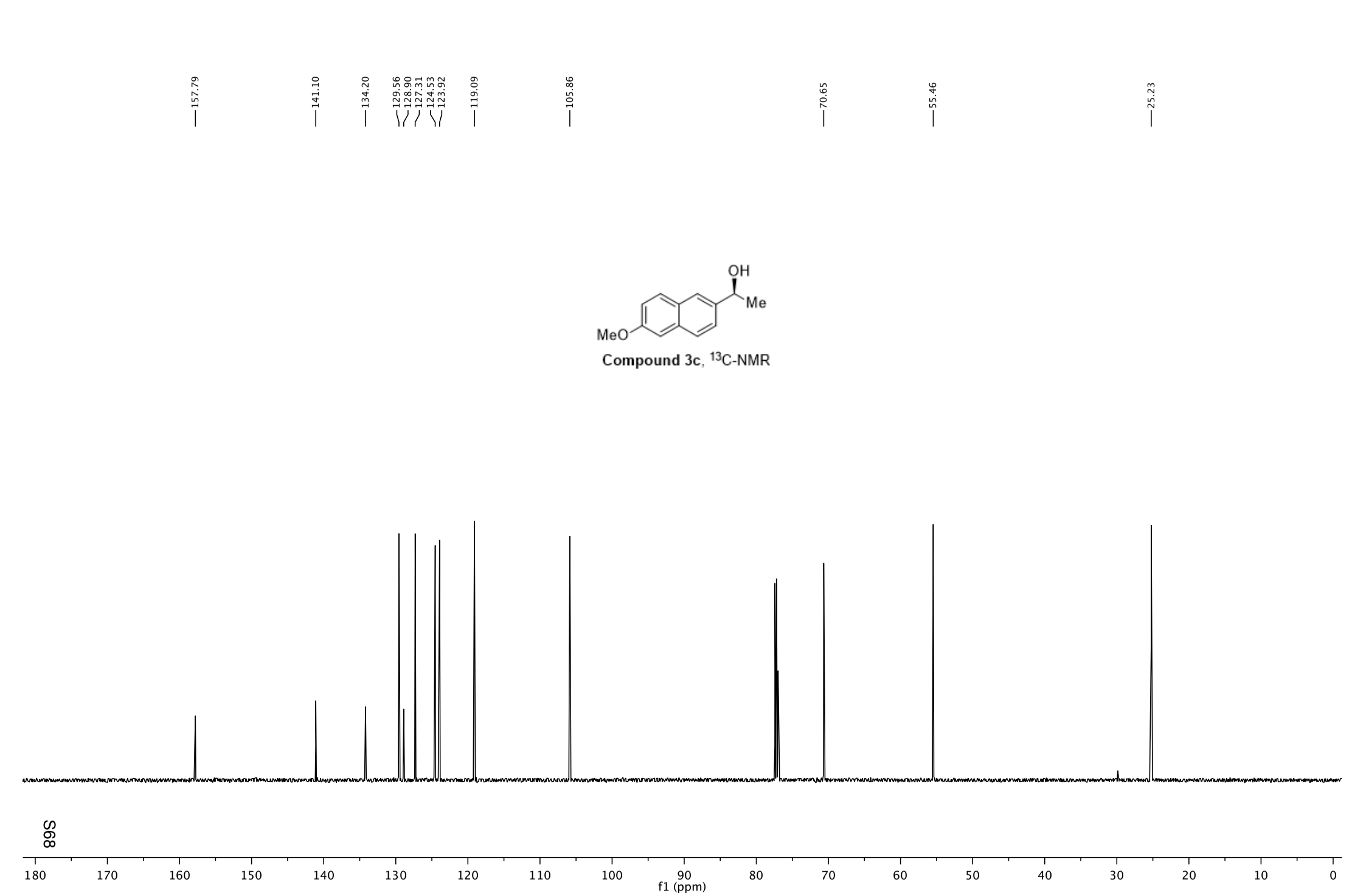

143.31
133.44
133.04
128.46
128.08
127.83
126.31
125.95
123.97
123.95
70.68
25.31
OH
Me
Compound 3a, 13C-NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



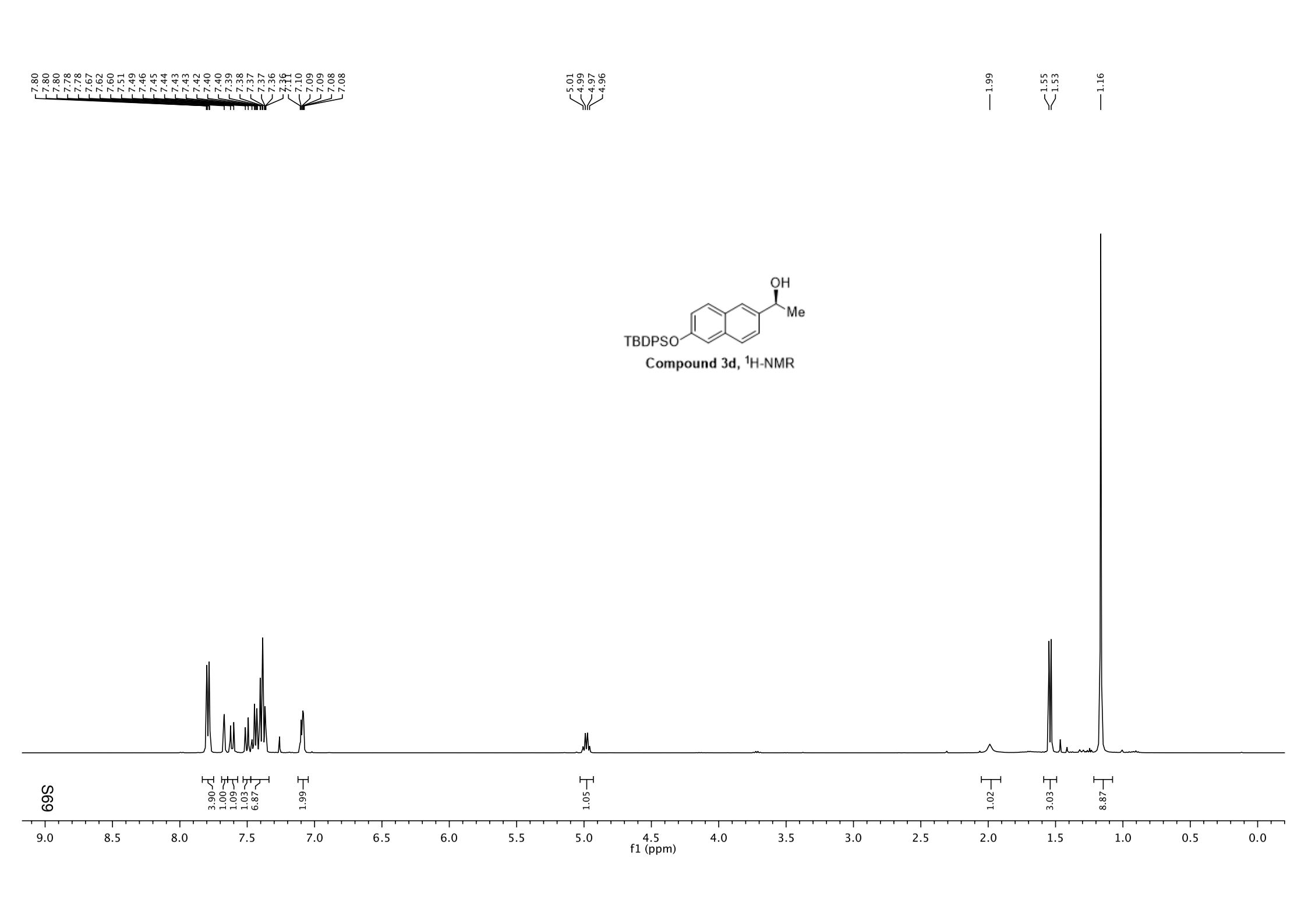
Compound 3b ^{1}H-NMR

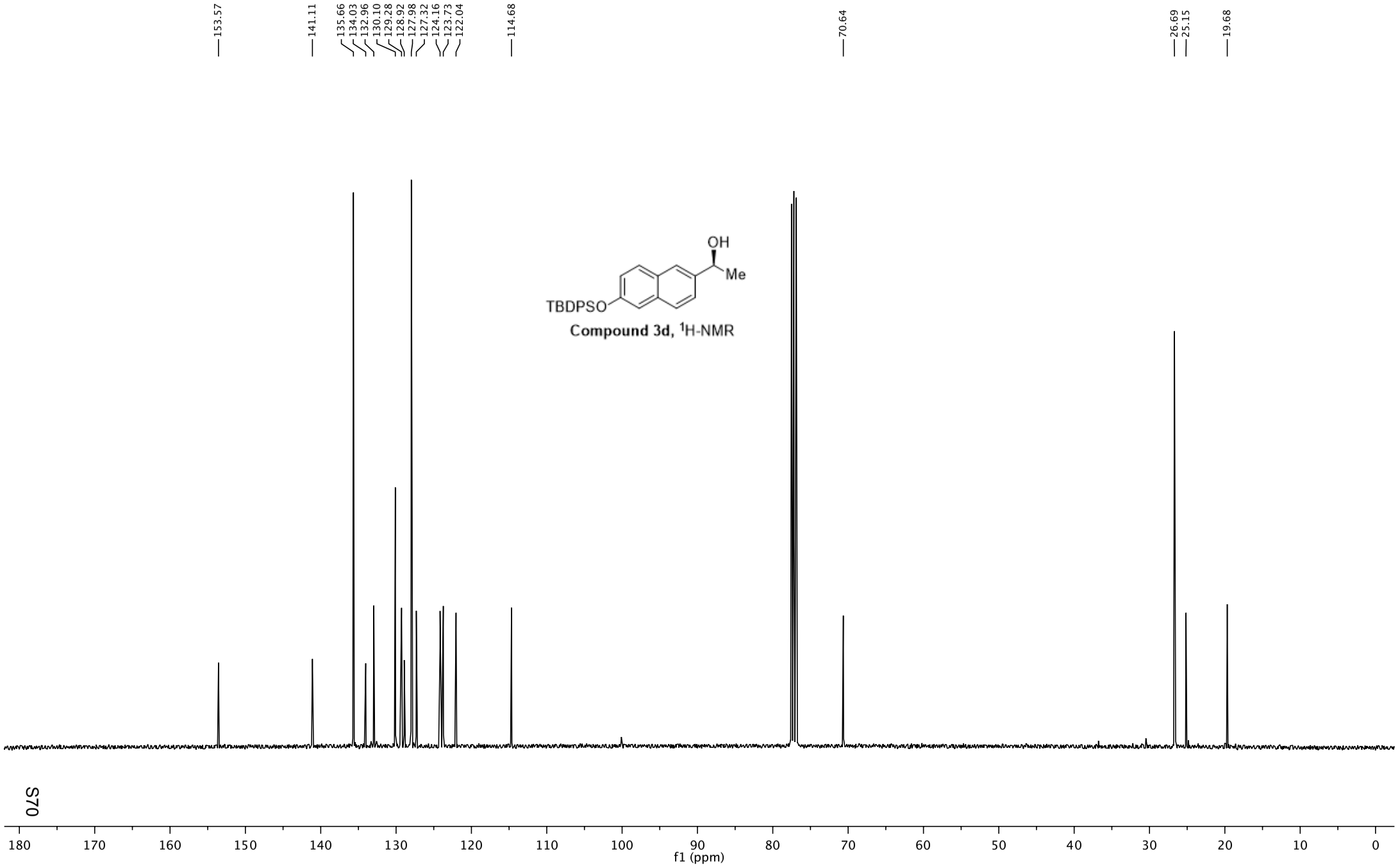

141.49
133.94
130.41
129.07
128.12
126.22
125.73
125.70
123.32
122.14
67.30
24.53
OH
Me
Compound 3b ^{13}C-NMR
S66
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

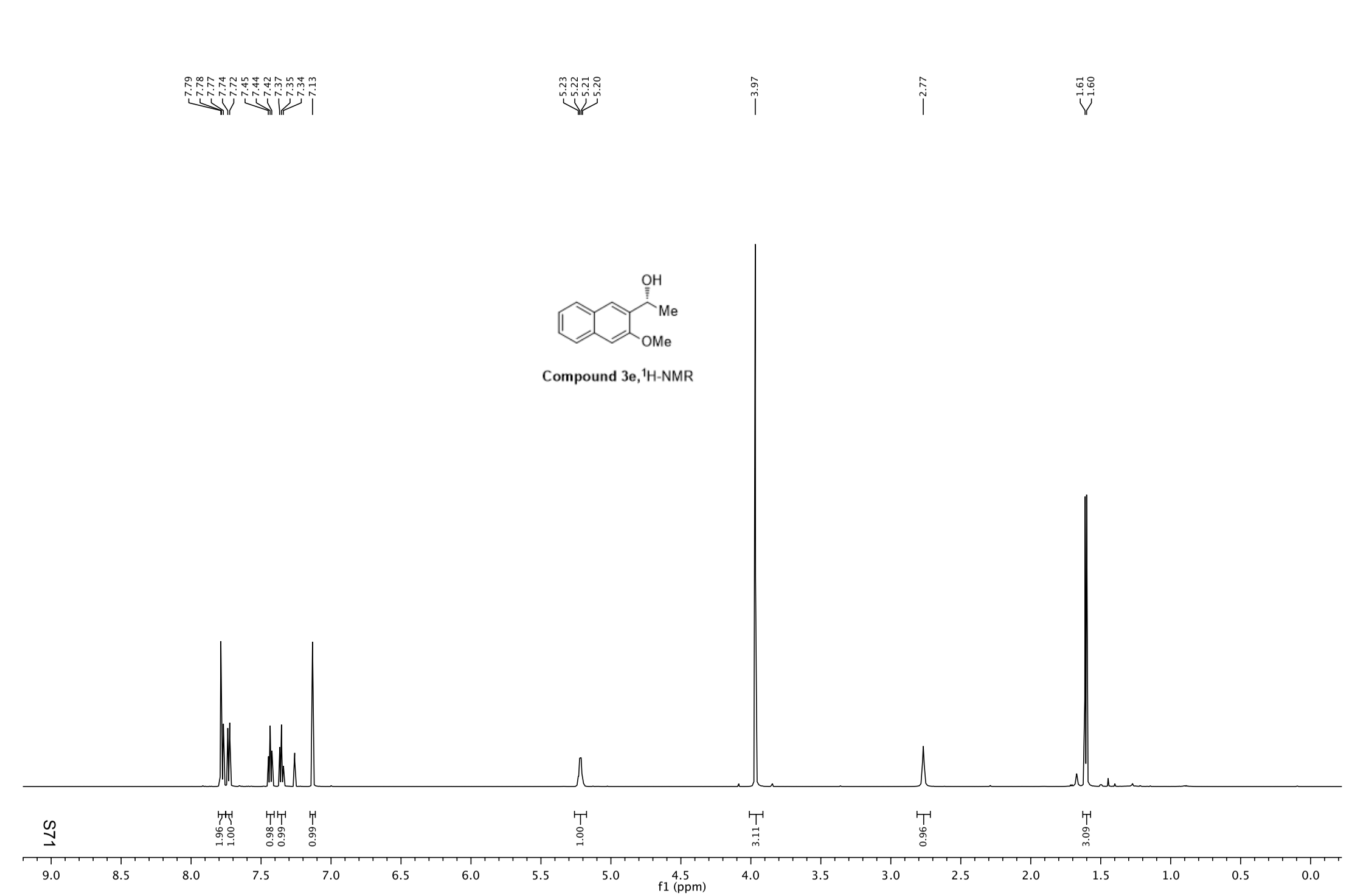

7.73
7.72
7.71
7.48
7.46
7.16
7.16
7.15
7.14
7.13
5.04
5.03
5.02
5.01
3.92
2.03
1.58
1.56
OH
Me
MeO
Compound 3c, 1H-NMR
3.02
1.00
2.02
1.04
3.17
1.00
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

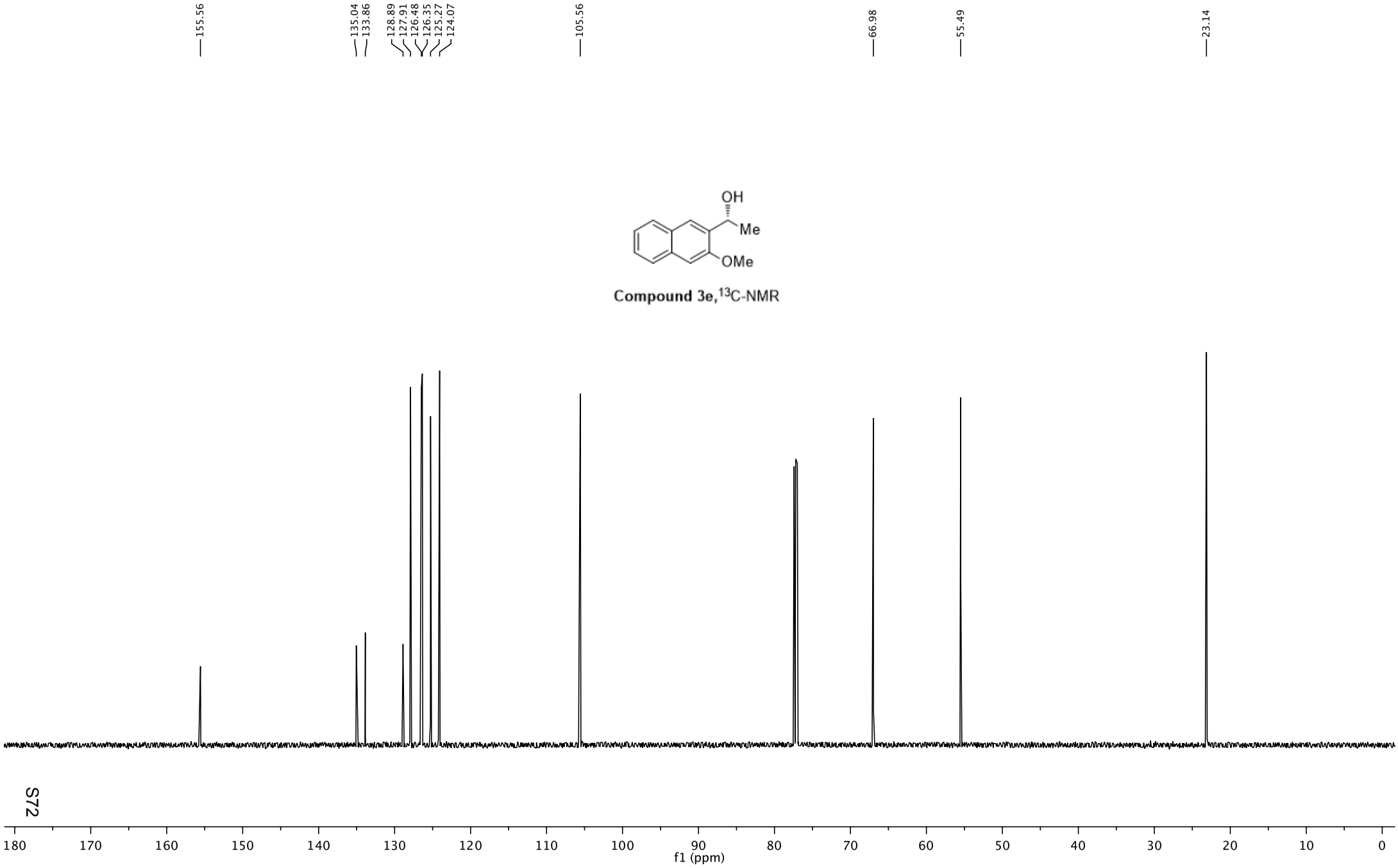


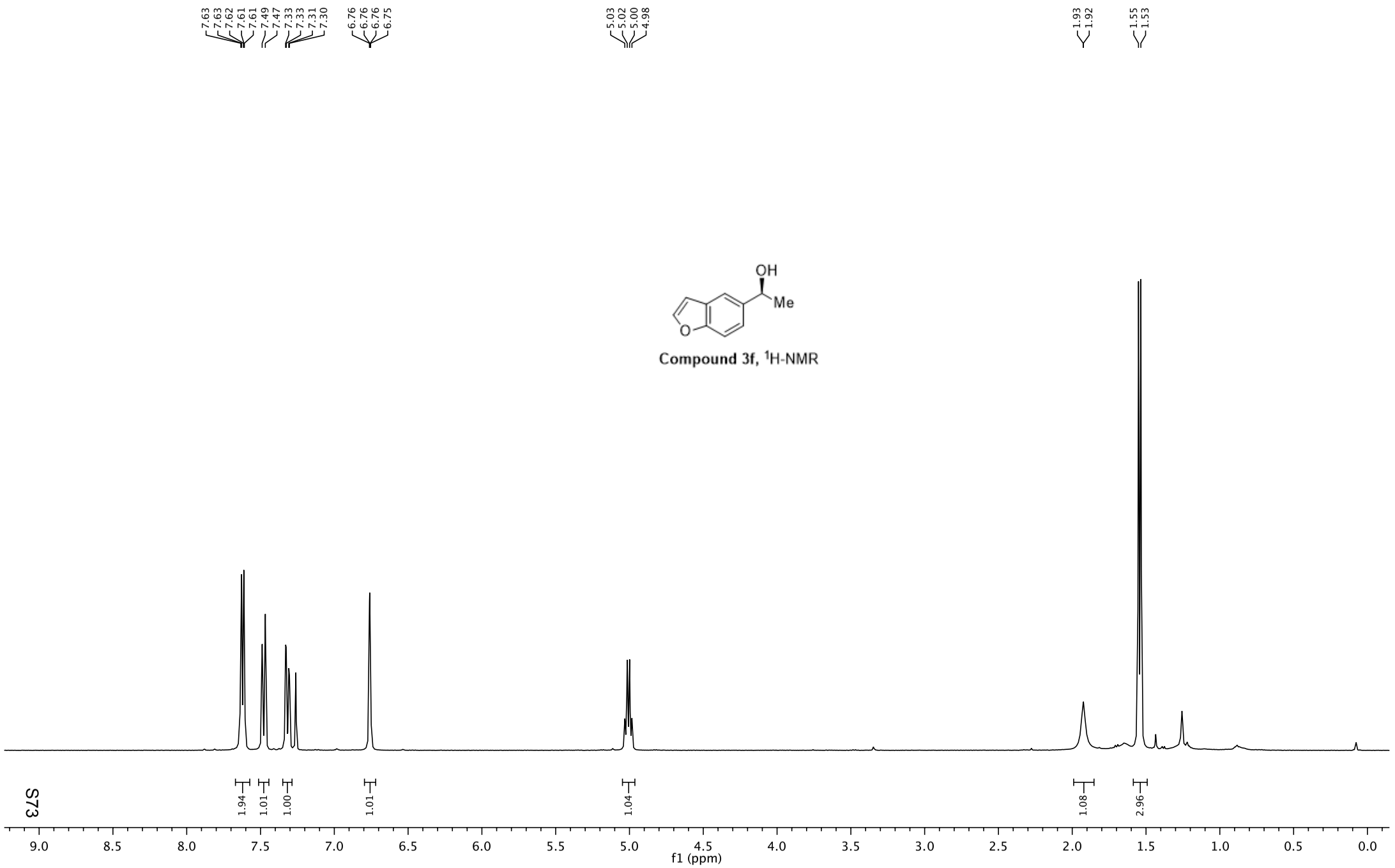
Compound 3c, ^{13}C-NMR

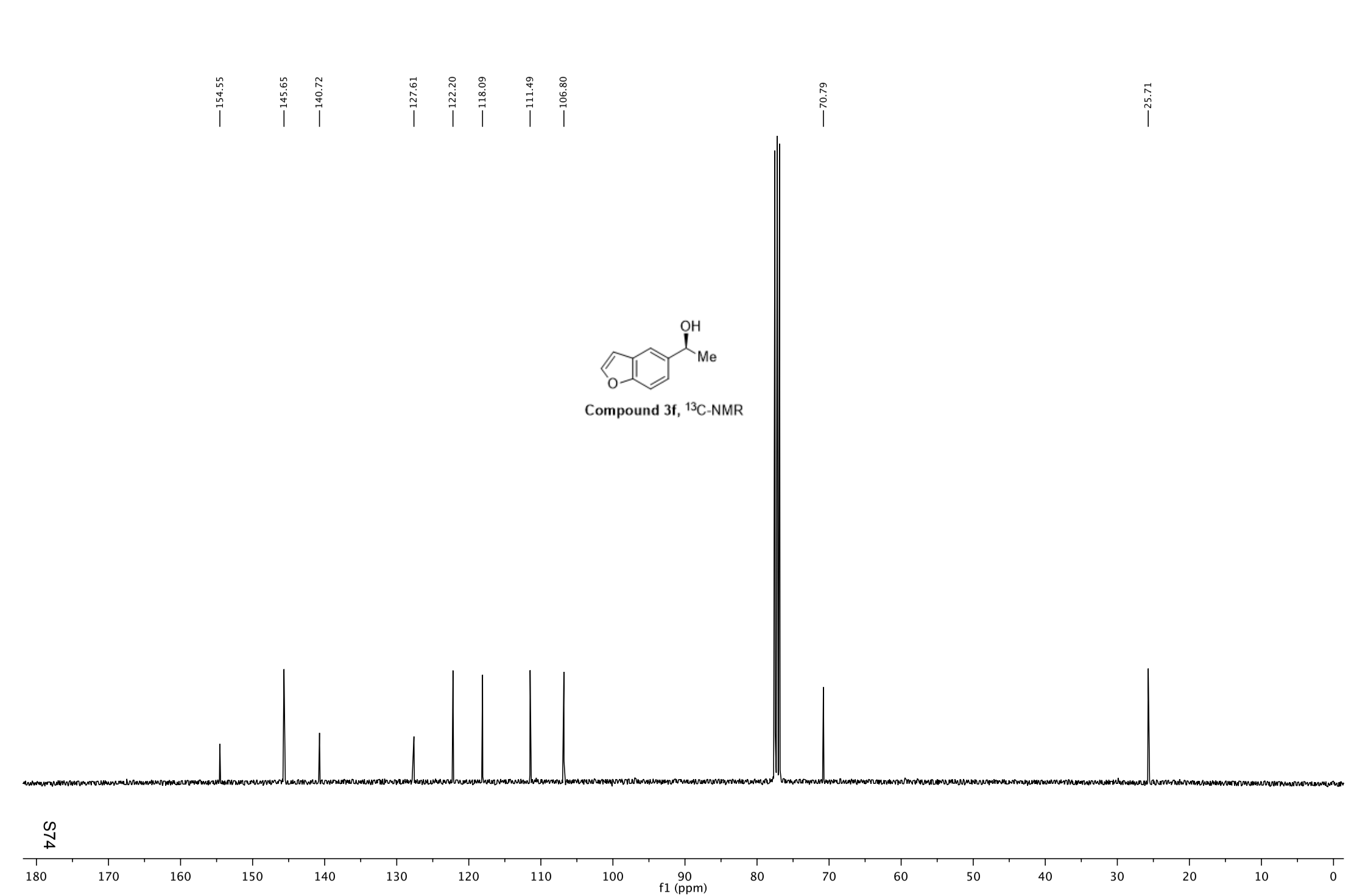

7.80
7.80
7.80
7.78
7.78
7.67
7.62
7.60
7.51
7.49
7.46
7.45
7.44
7.43
7.43
7.42
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.11
7.10
7.09
7.09
7.08
7.08
5.01
4.99
4.97
4.96
1.99
1.55
1.53
1.16
OH
Me
TBDPSO
Compound 3d, 1H-NMR
3.90
1.00
1.09
1.03
6.87
1.99
1.05
1.02
3.03
8.87
S69
9.0
8.5
8.0
7.5
7.0
6.5
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)

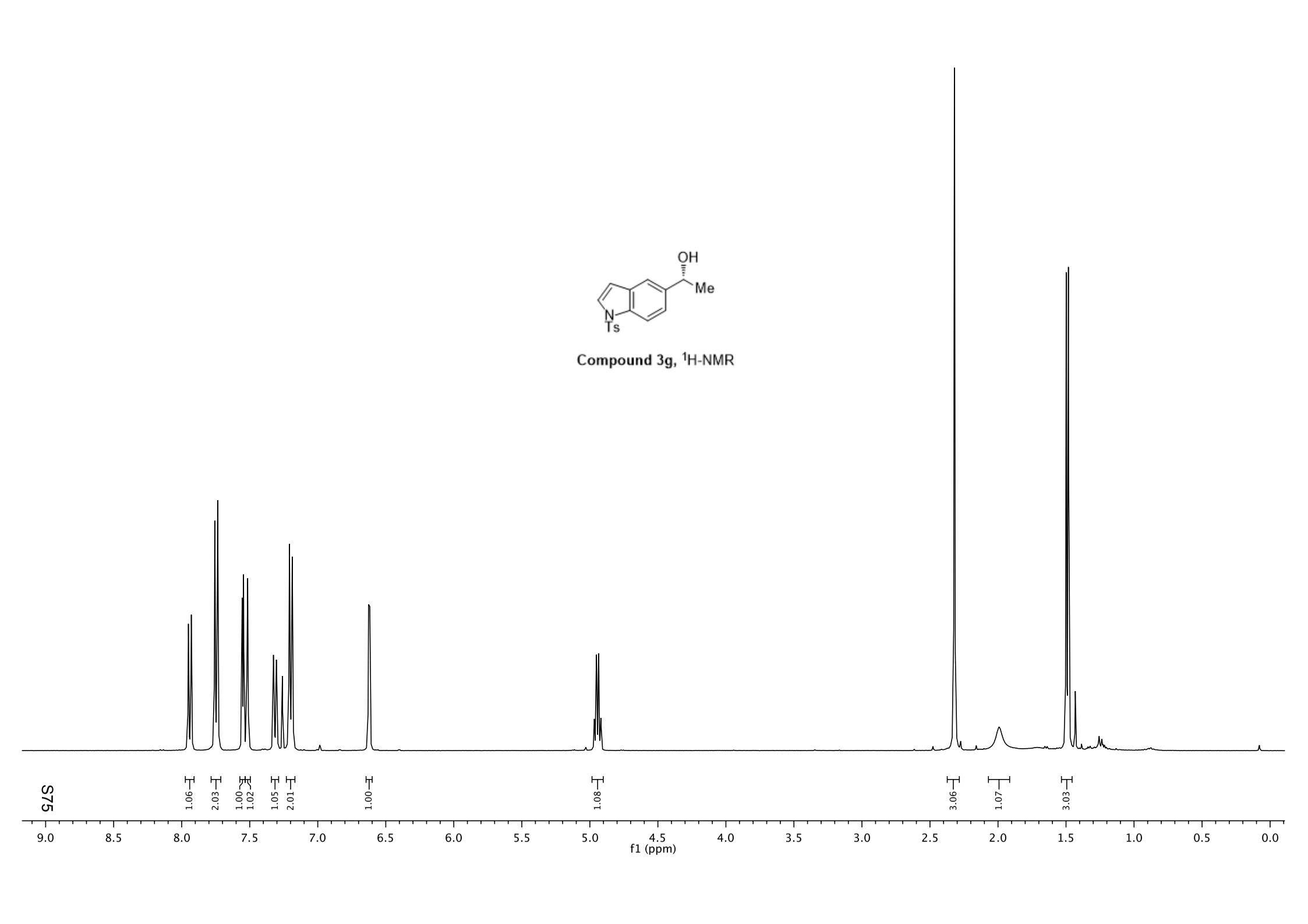

153.57
141.11
135.66
134.03
132.96
130.10
129.28
128.92
127.98
127.32
124.16
123.73
122.04
114.68
70.64
26.69
25.15
19.68
OH
Me
TBDPSO
Compound 3d, 1H-NMR
S70
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

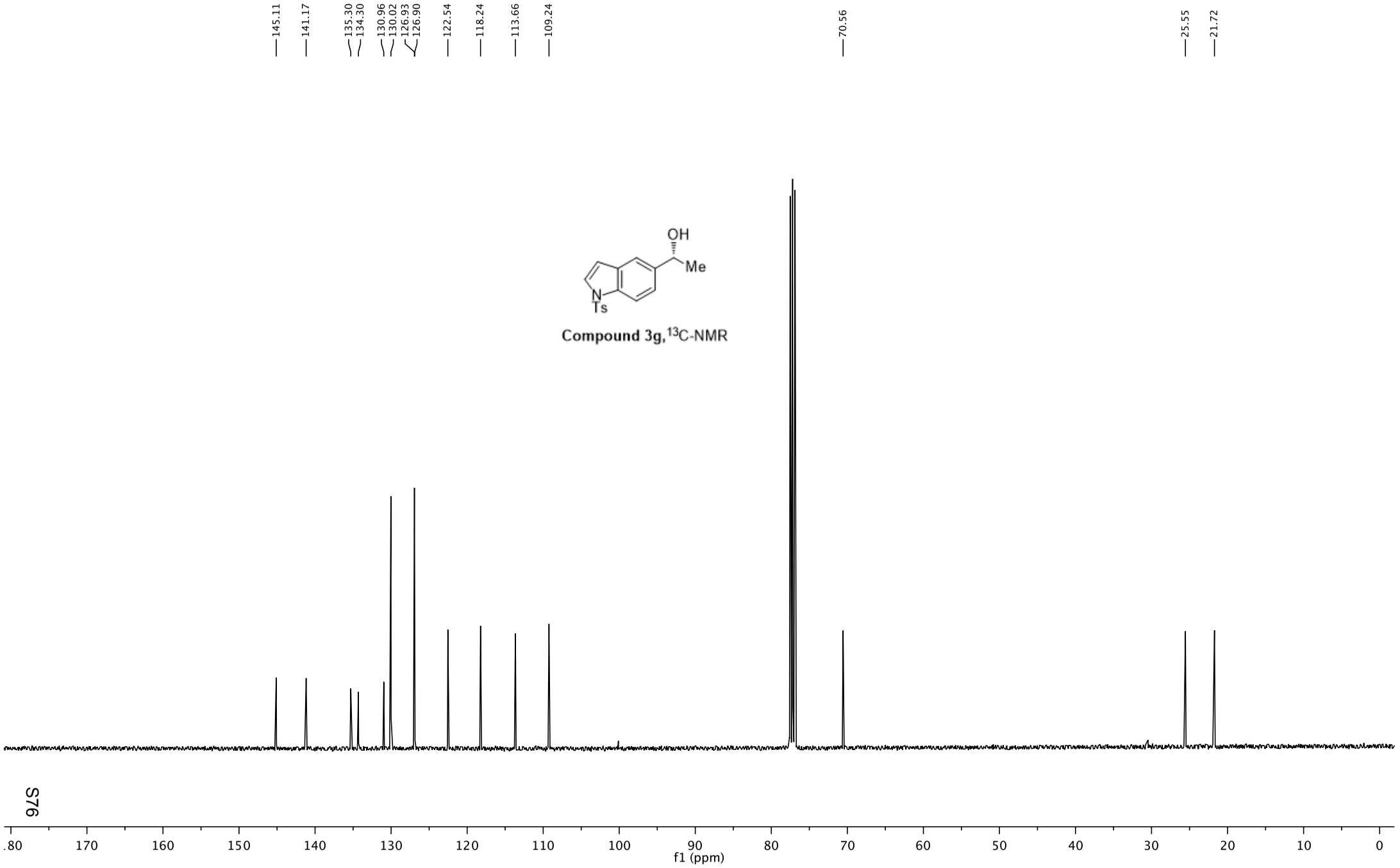

7.79
7.78
7.77
7.74
7.72
7.45
7.44
7.42
7.37
7.35
7.34
7.13
5.23
5.22
5.21
5.20
3.97
2.77
1.61
1.60
OH
Me
OMe
Compound 3e, 1H-NMR
1.96
1.00
0.98
0.99
0.99
1.00
3.11
0.96
3.09
f1 (ppm)

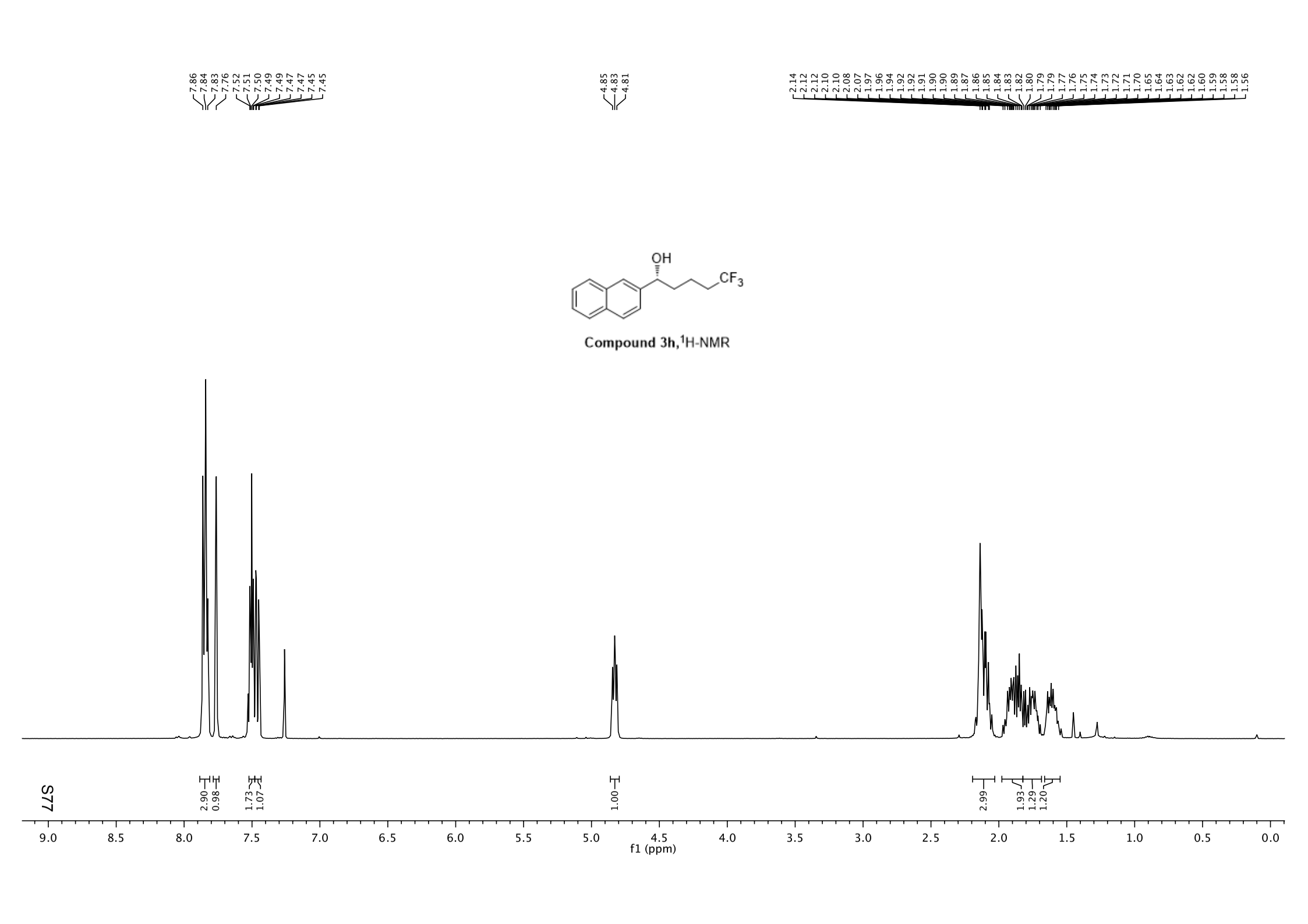

155.56
135.04
133.86
128.89
127.91
126.48
126.35
125.27
124.07
105.56
66.98
55.49
23.14
OH
Me
OMe
Compound 3e, 13C-NMR
S72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

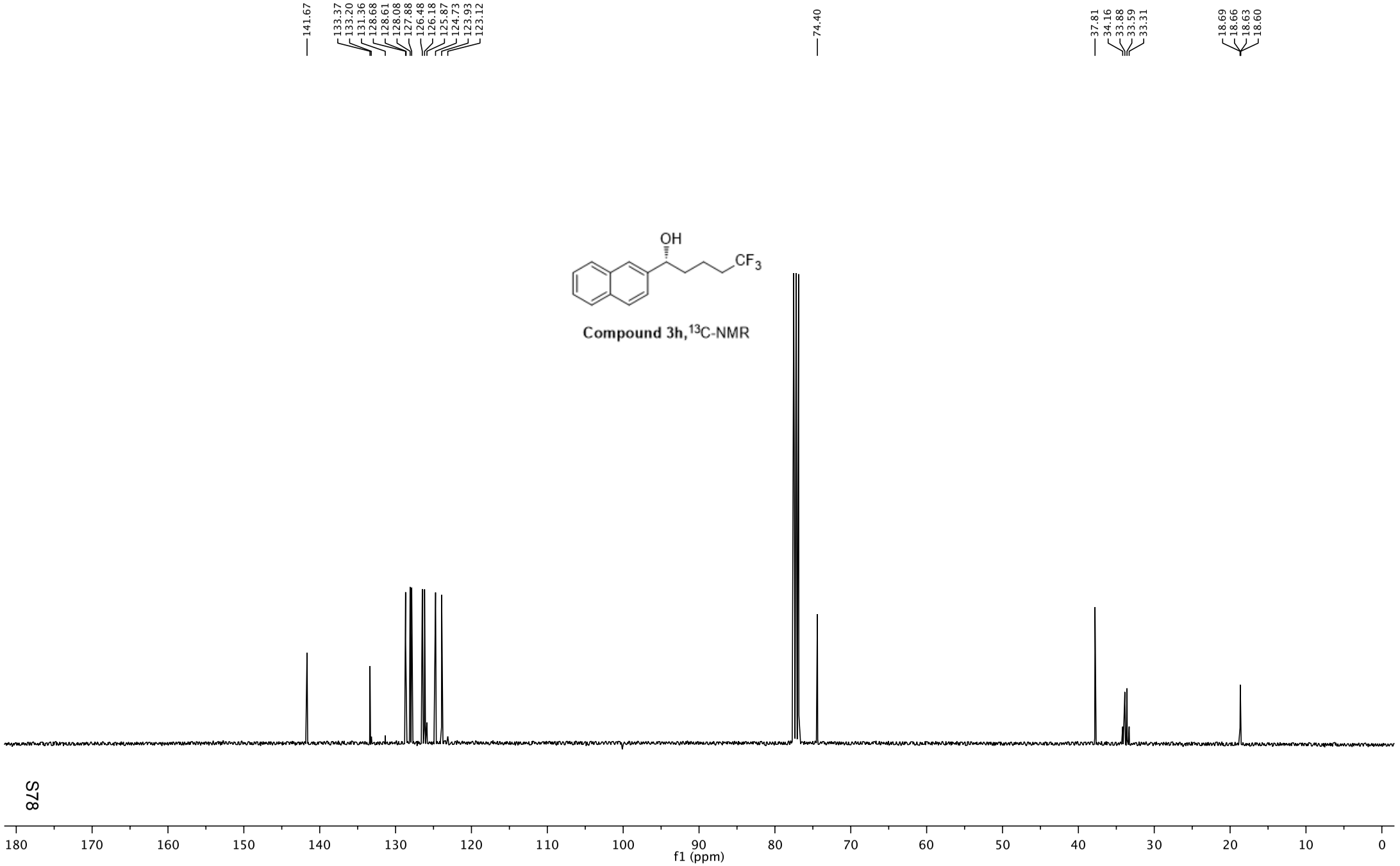

7.63
7.63
7.62
7.61
7.61
7.49
7.47
7.33
7.33
7.31
7.30
6.76
6.76
6.76
6.75
5.03
5.02
5.00
4.98
1.93
1.92
1.55
1.53
OH
Me
O
Compound 3f, 1H-NMR
1.94
1.01
1.00
1.01
1.04
1.08
2.96
S73
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

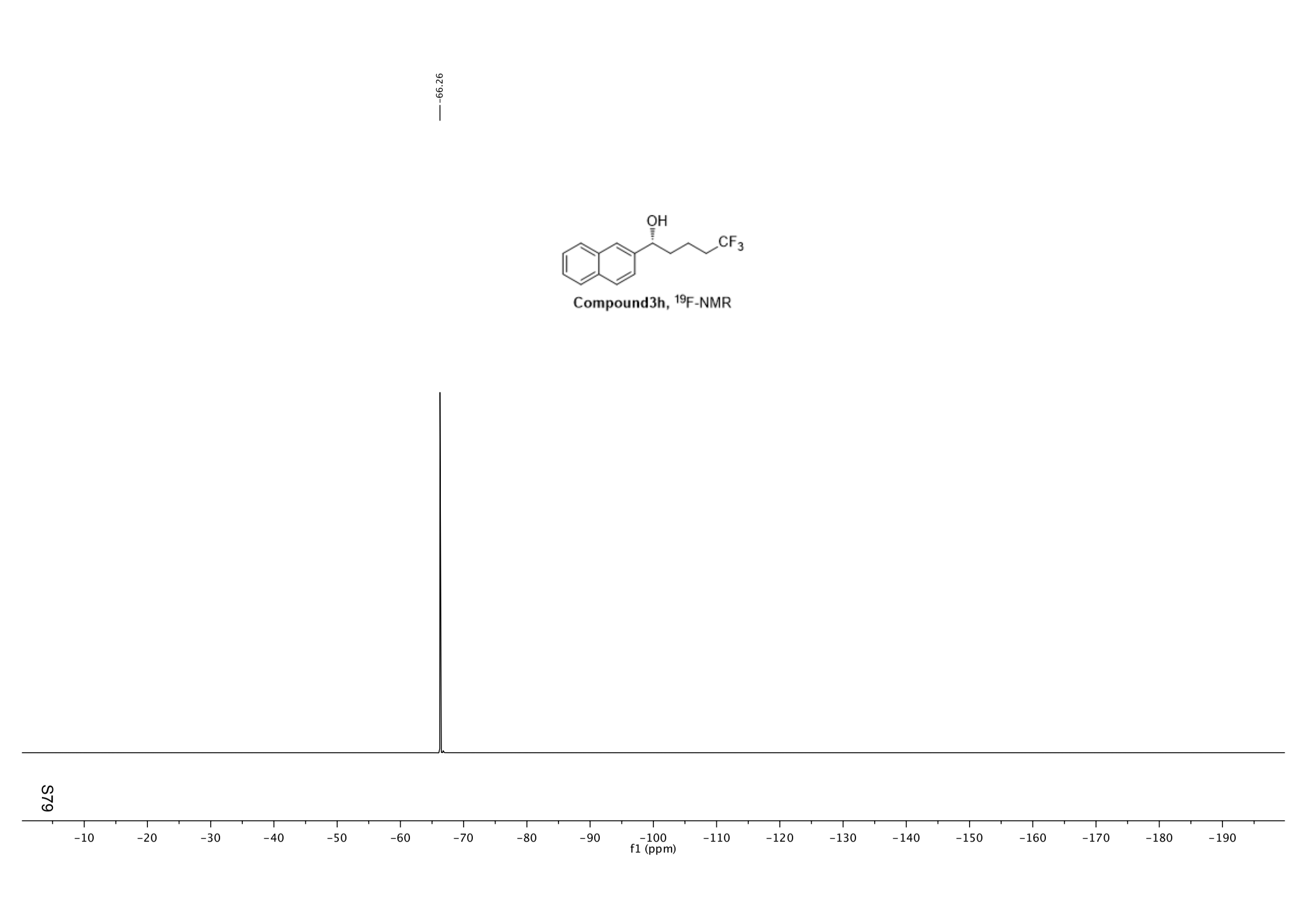

154.55
145.65
140.72
127.61
122.20
118.09
111.49
106.80
70.79
25.71
OH
Me
O
Compound 3f, 13C-NMR
f1 (ppm)

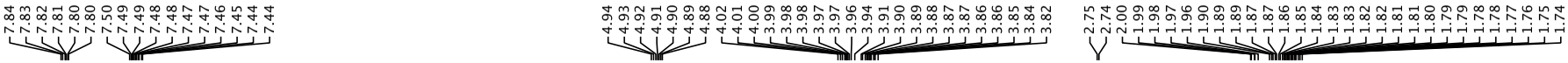

OH
Me
N
Ts
Compound 3g, 1H-NMR
S75
1.06
2.03
1.00
1.02
1.05
2.01
1.00
1.08
3.06
1.07
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

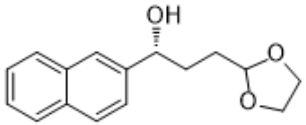

145.11
141.17
135.30
134.30
130.96
130.02
126.93
126.90
122.54
118.24
113.66
109.24
70.56
25.55
21.72
OH
Me
N
Ts
Compound 3g, 13C-NMR
S76
f1 (ppm)


7.86
7.84
7.83
7.76
7.52
7.51
7.50
7.49
7.49
7.47
7.47
7.45
7.45
4.85
4.83
4.81
2.14
2.12
2.12
2.10
2.10
2.08
2.07
1.97
1.96
1.94
1.92
1.92
1.91
1.90
1.90
1.89
1.87
1.86
1.85
1.84
1.83
1.82
1.80
1.79
1.79
1.77
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.65
1.64
1.63
1.62
1.62
1.60
1.59
1.58
1.58
1.56
OH
CF3
Compound 3h,1H-NMR
S77
2.90
0.98
1.73
1.07
1.00
2.99
1.93
1.29
1.20
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)

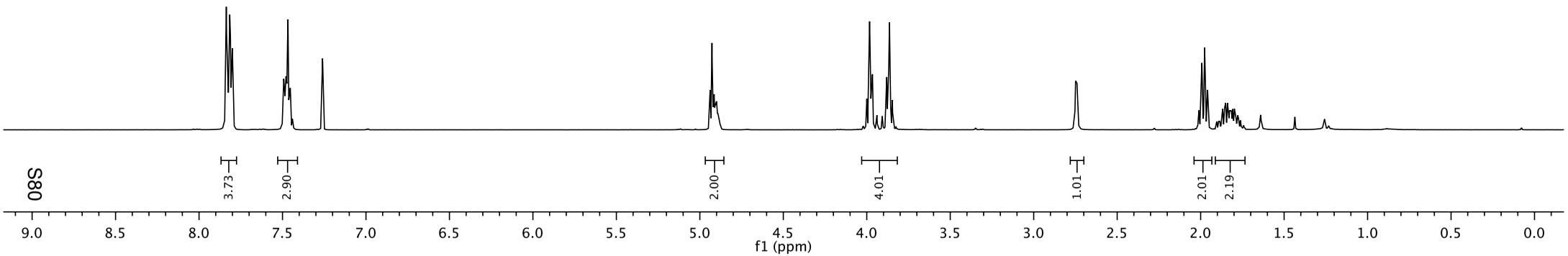

141.67
133.37
133.20
131.36
128.68
128.61
128.08
127.88
126.48
126.18
125.87
124.73
123.93
123.12
74.40
37.81
34.16
33.88
33.59
33.31
18.69
18.66
18.63
18.60
OH
CF3
Compound 3h, 13C-NMR
S78
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

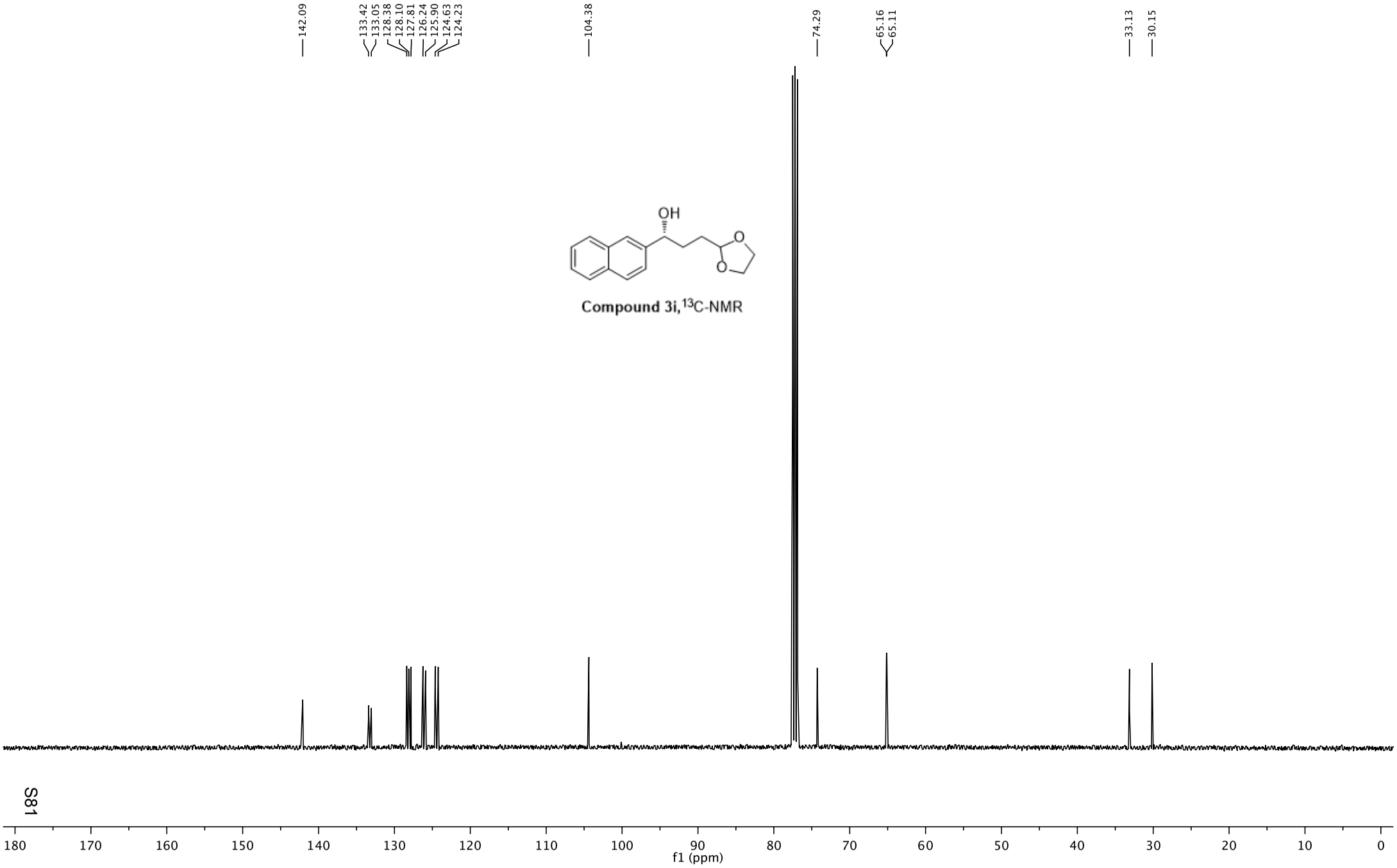

-66.26
OH
CF3
Compound3h, 19F-NMR
S79
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

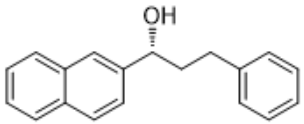




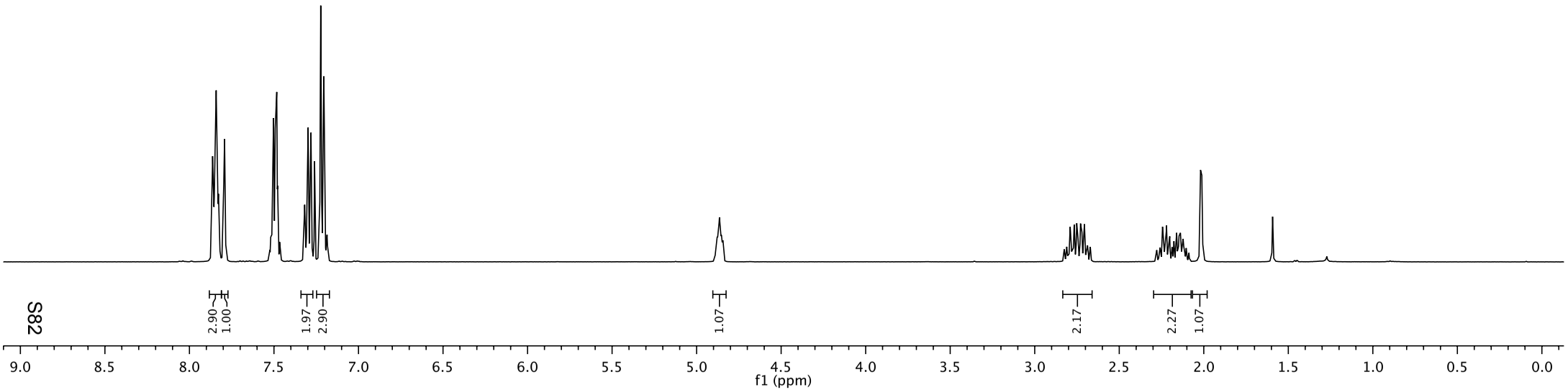
Compound 3i, ^{1}H-NMR

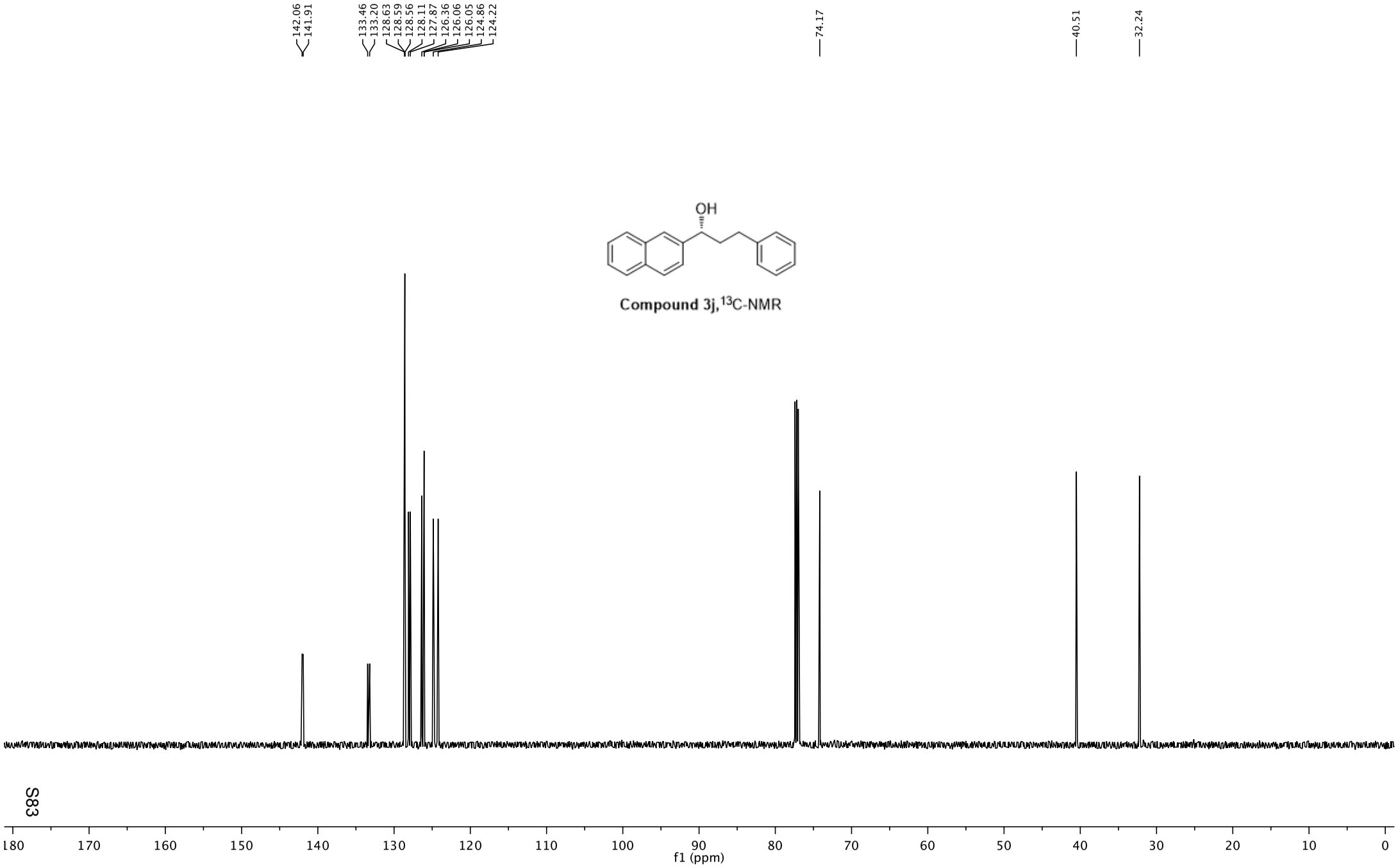


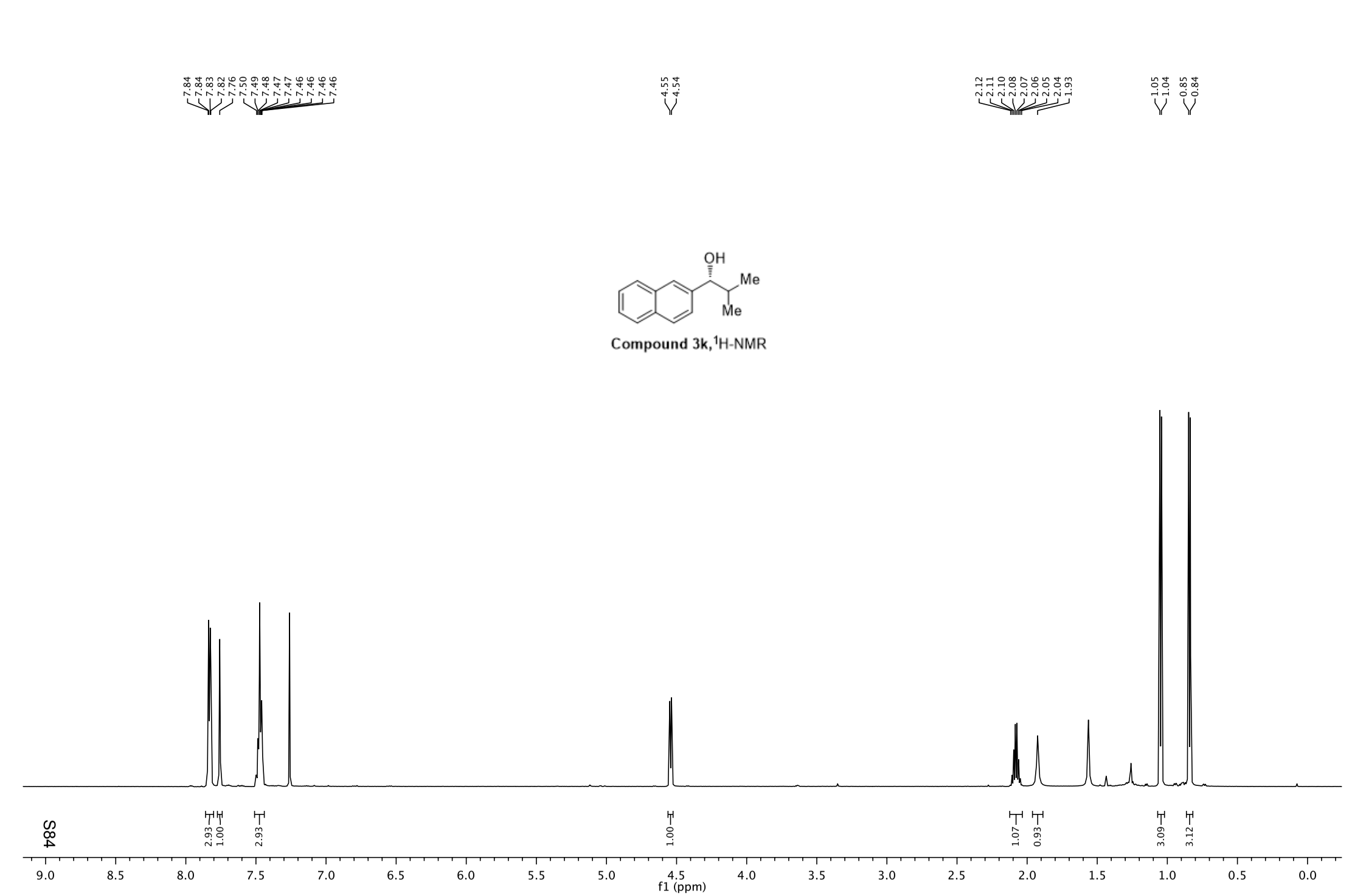

142.09
133.42
133.05
128.38
128.10
127.81
126.24
125.90
124.63
124.23
104.38
74.29
65.16
65.11
33.13
30.15
OH
O
O
Compound 3i, 13C-NMR
f1 (ppm)

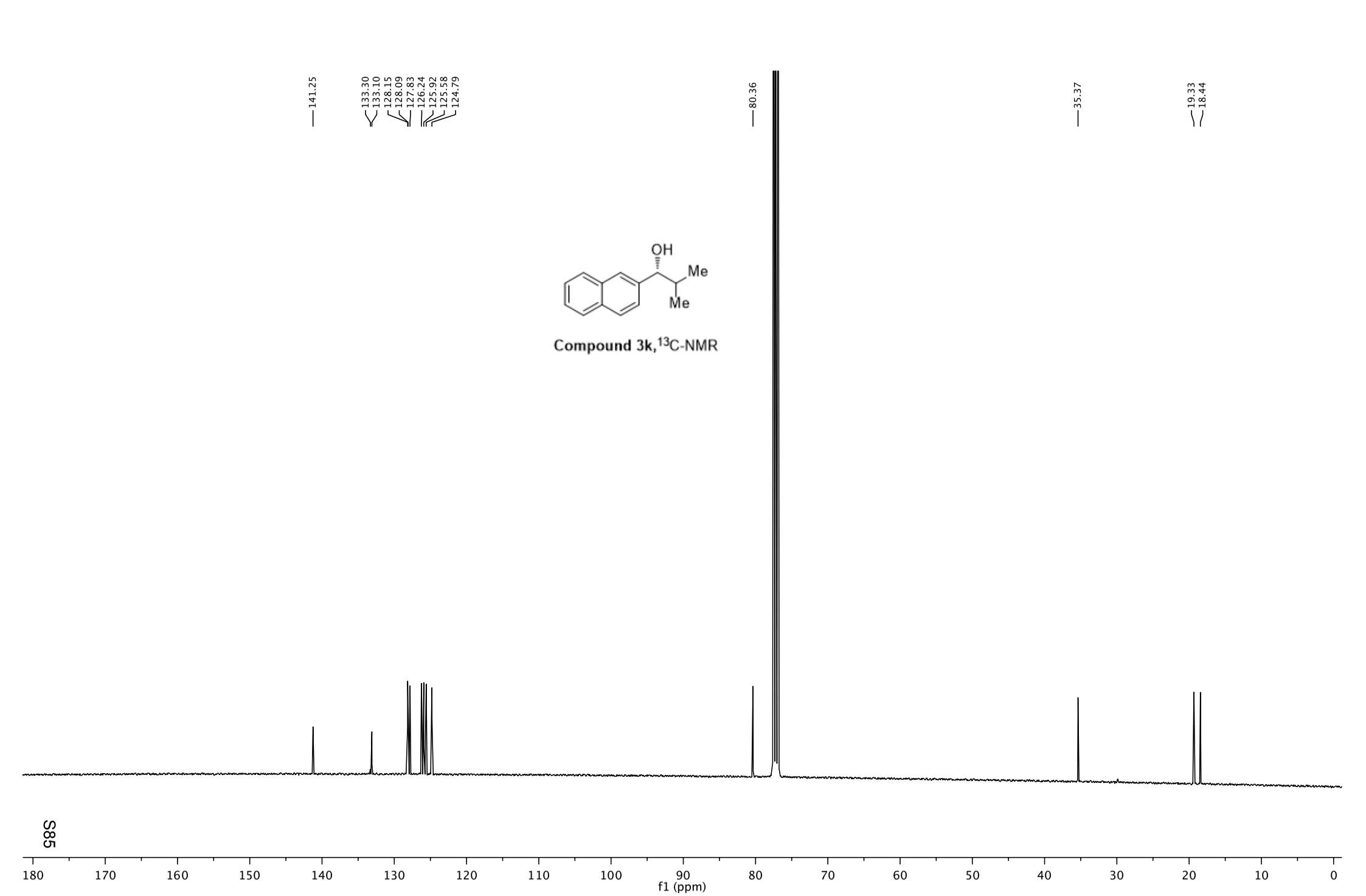


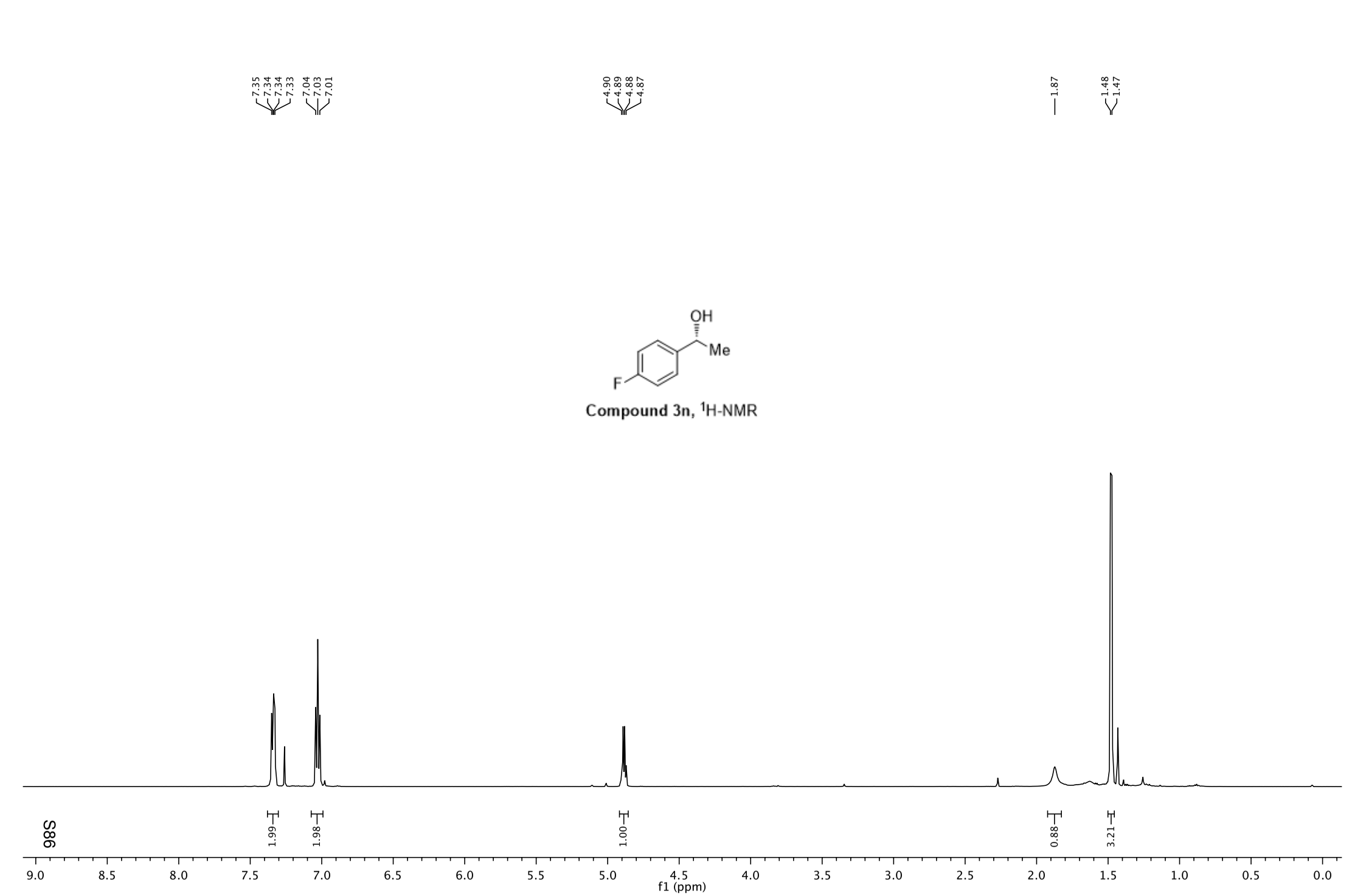
Compound 3j, ^{1}H-NMR



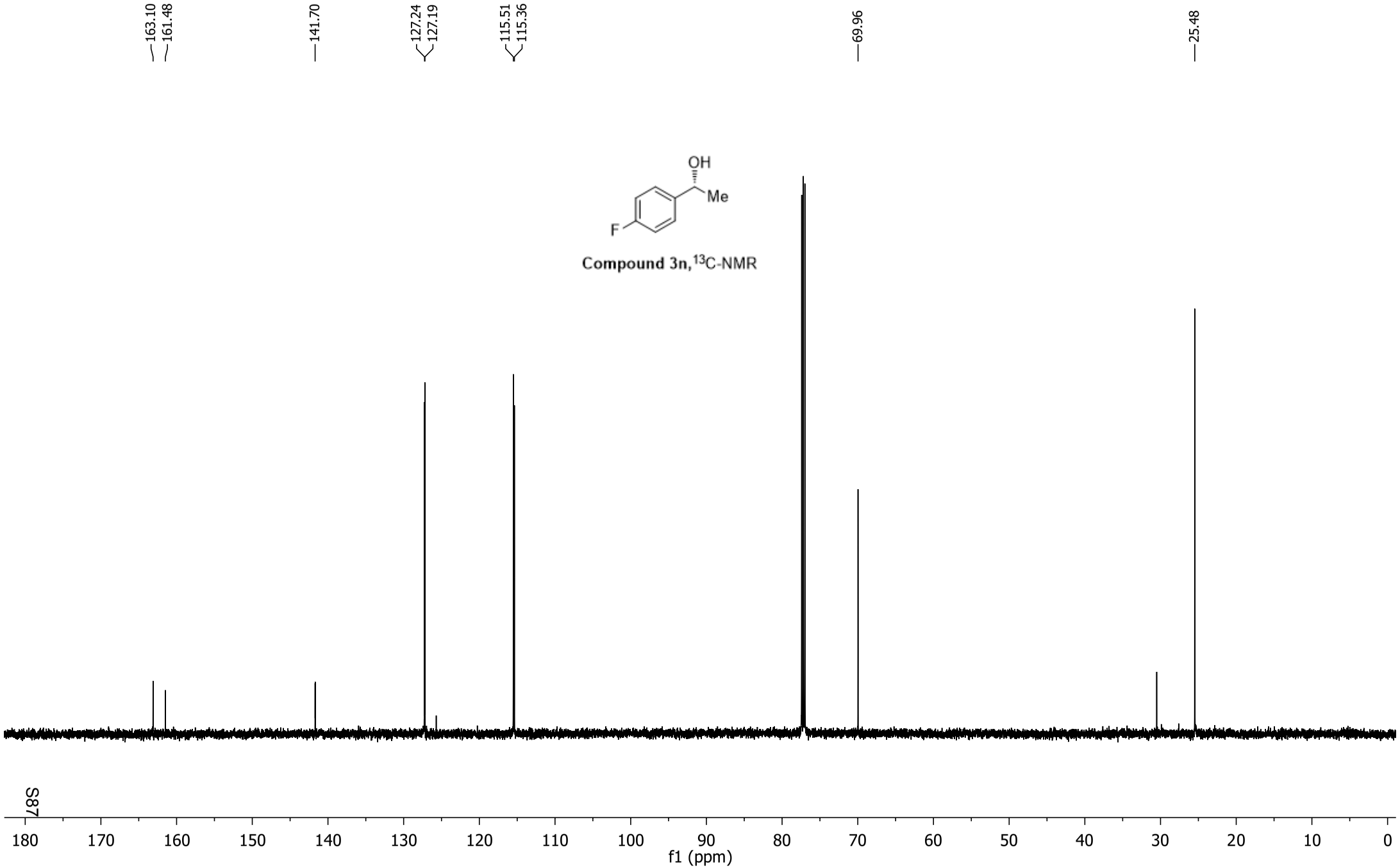

142.06
141.91
133.46
133.20
128.63
128.59
128.56
128.11
127.87
126.36
126.06
126.05
124.86
124.22
74.17
40.51
32.24
OH
Compound 3j, 13C-NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

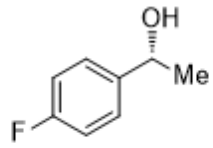

7.84
7.84
7.83
7.82
7.76
7.50
7.49
7.48
7.47
7.47
7.46
7.46
7.46
7.46
4.55
4.54
2.12
2.11
2.10
2.08
2.07
2.06
2.05
2.04
1.93
1.05
1.04
0.85
0.84
OH
Me
Me
Compound 3k, 1H-NMR
2.93
1.00
2.93
1.00
1.07
0.93
3.09
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.25
133.30
133.10
128.15
128.09
127.83
126.24
125.92
125.58
124.79
80.36
35.37
19.33
18.44
OH
Me
Me
Compound 3k, 13C-NMR
S85
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

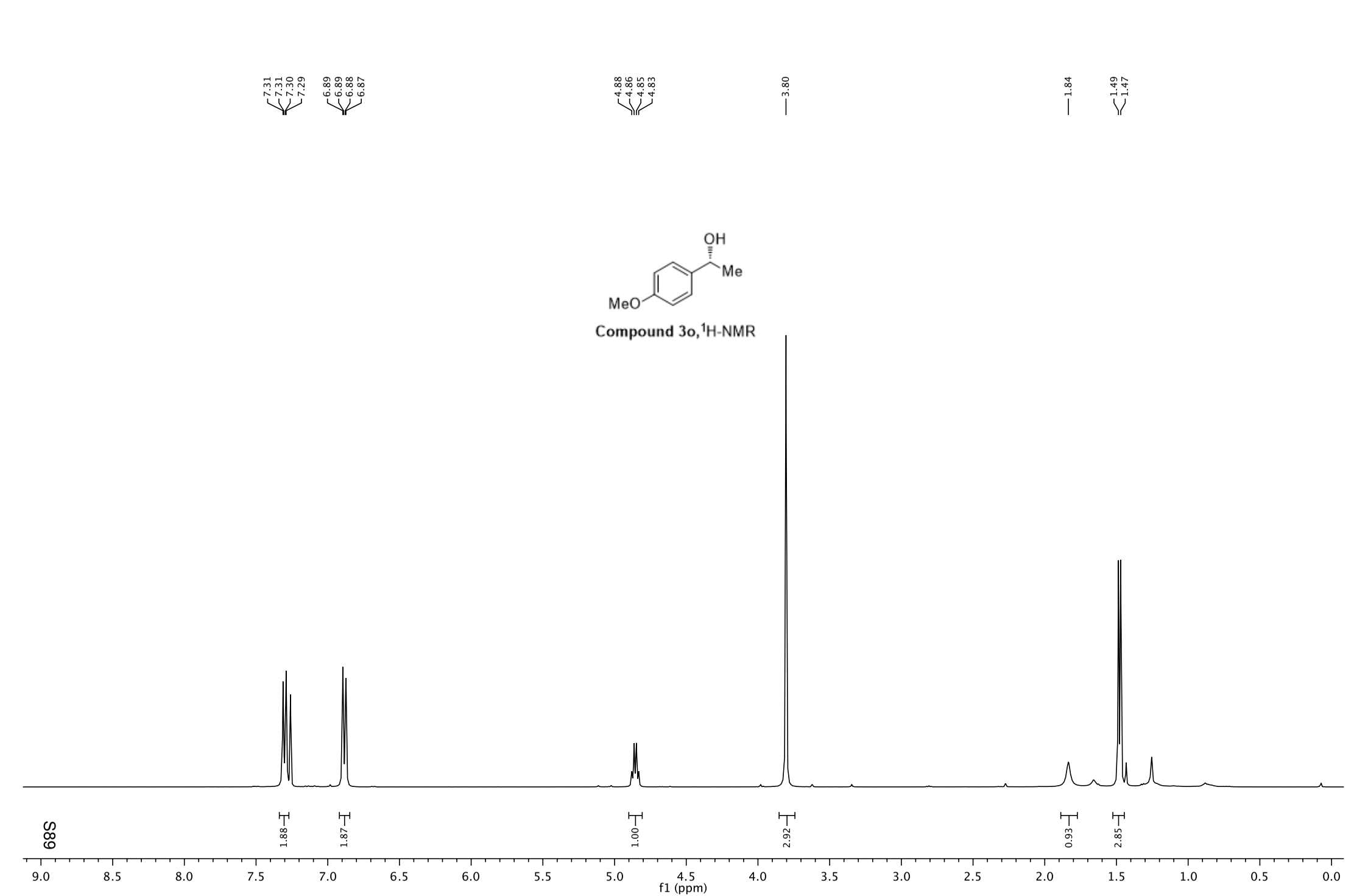


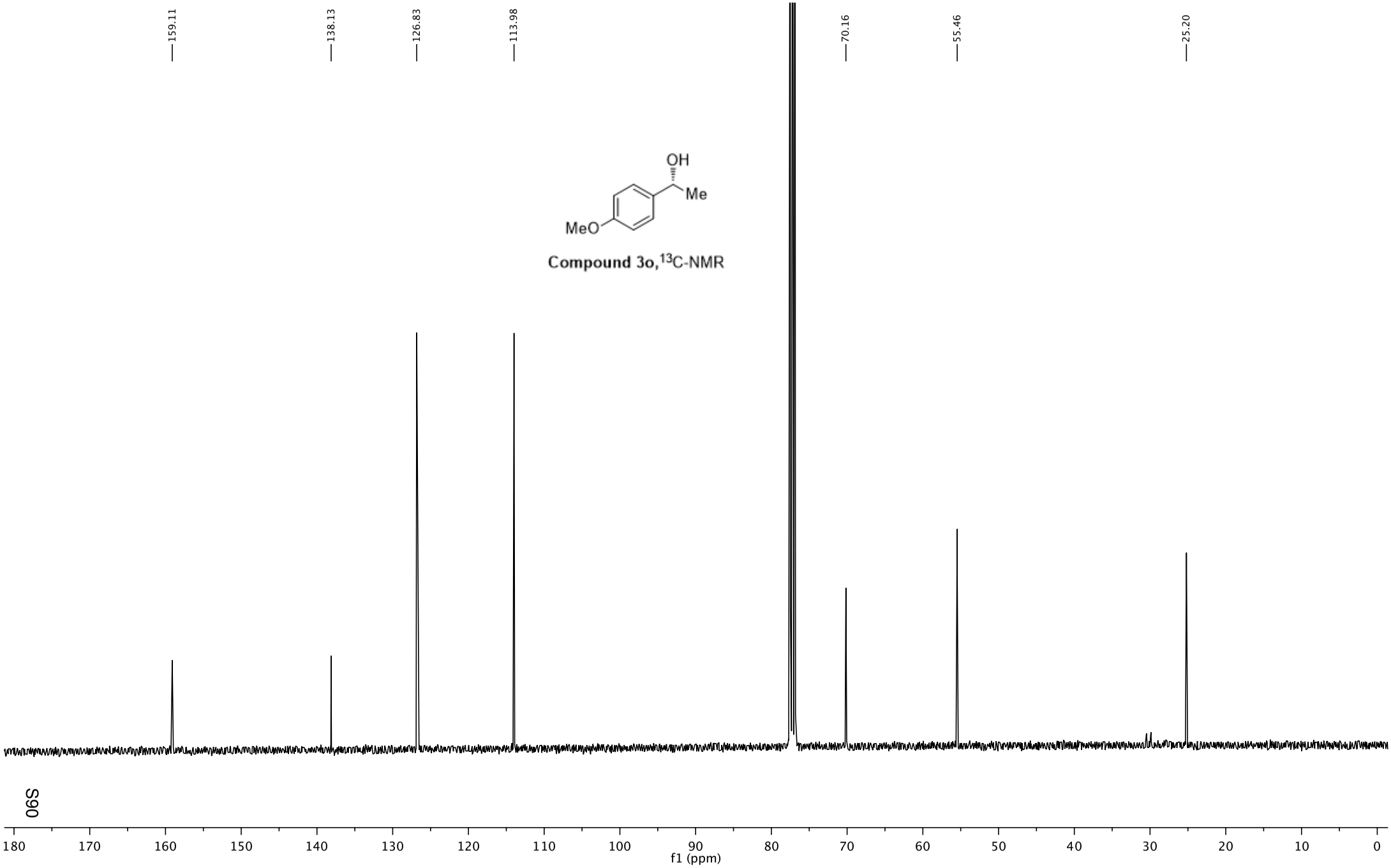
Compound 3n, ^{1}H-NMR

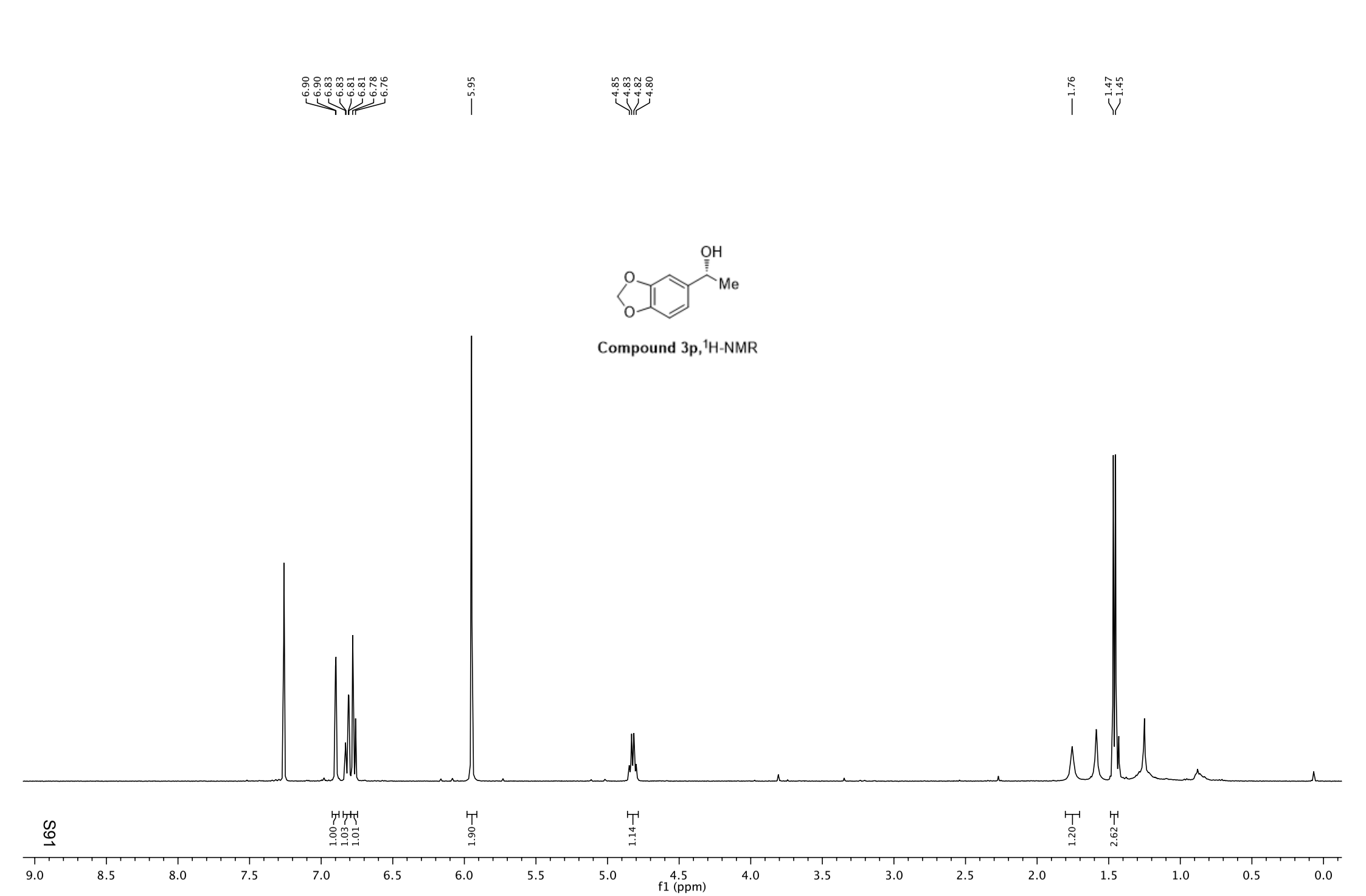

163.10
161.48
141.70
127.24
127.19
115.51
115.36
69.96
25.48
OH
Me
F
Compound 3n, 13C-NMR
S87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

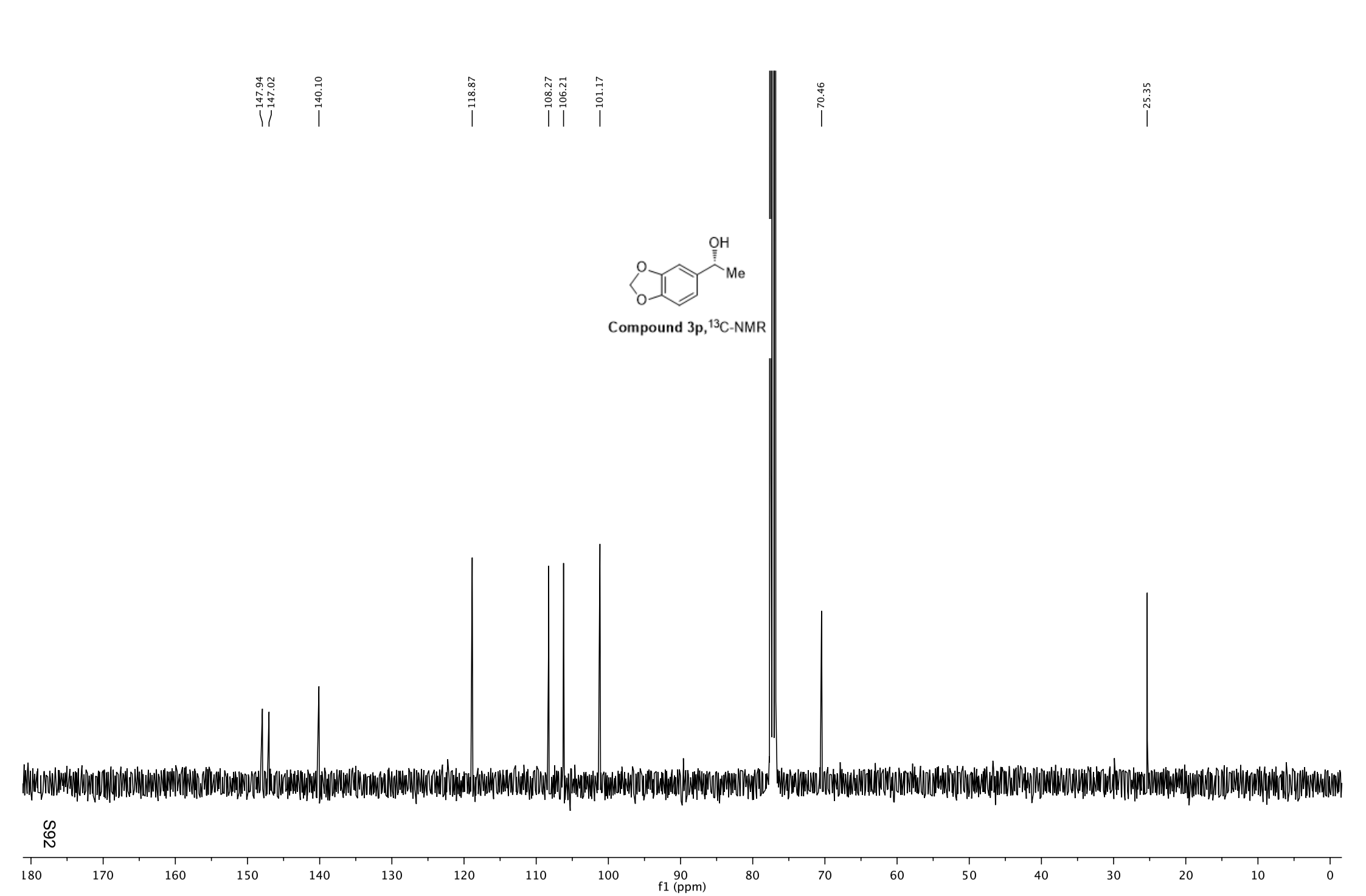


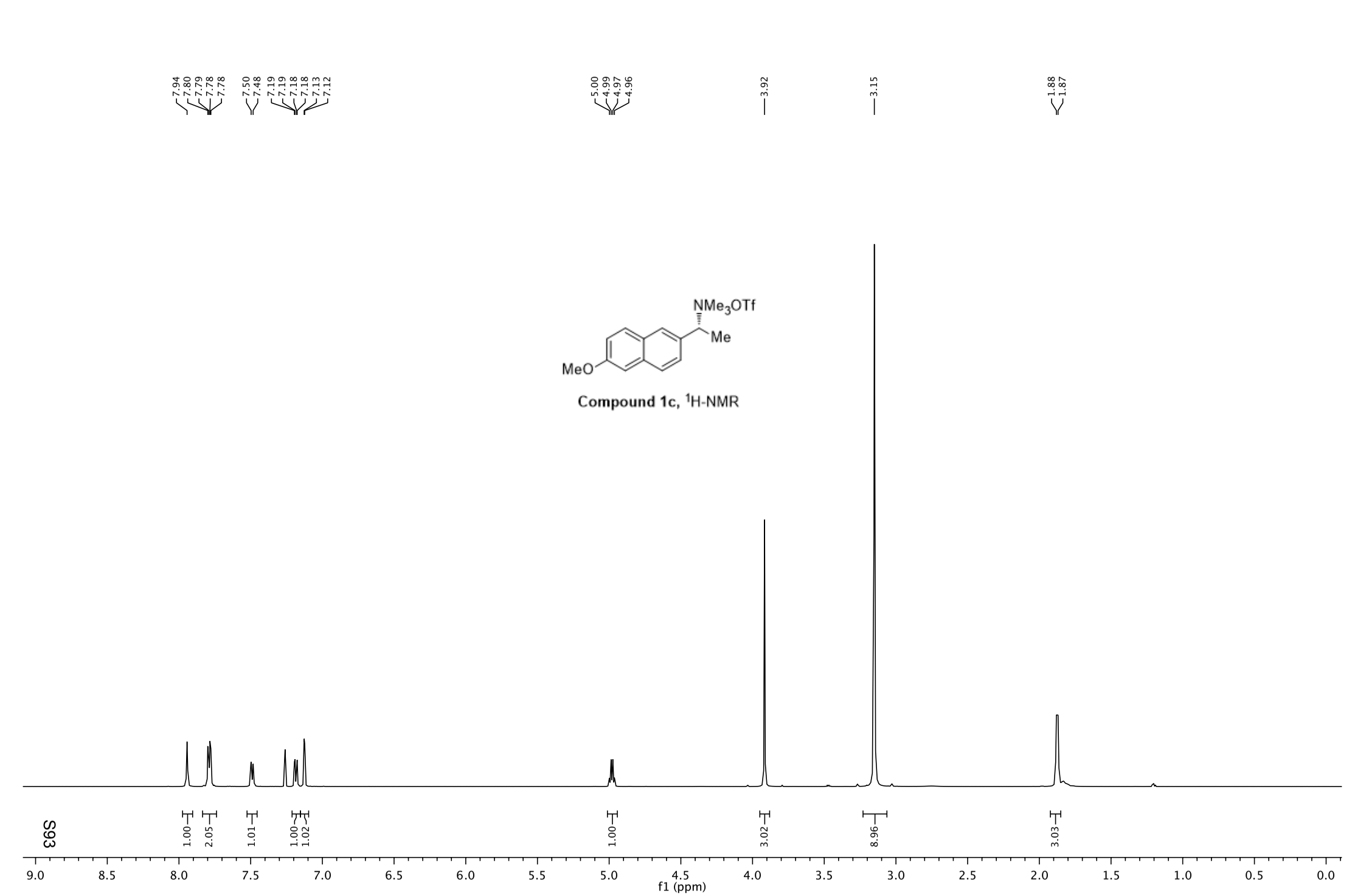
Compound 3n, ^{19}F-NMR

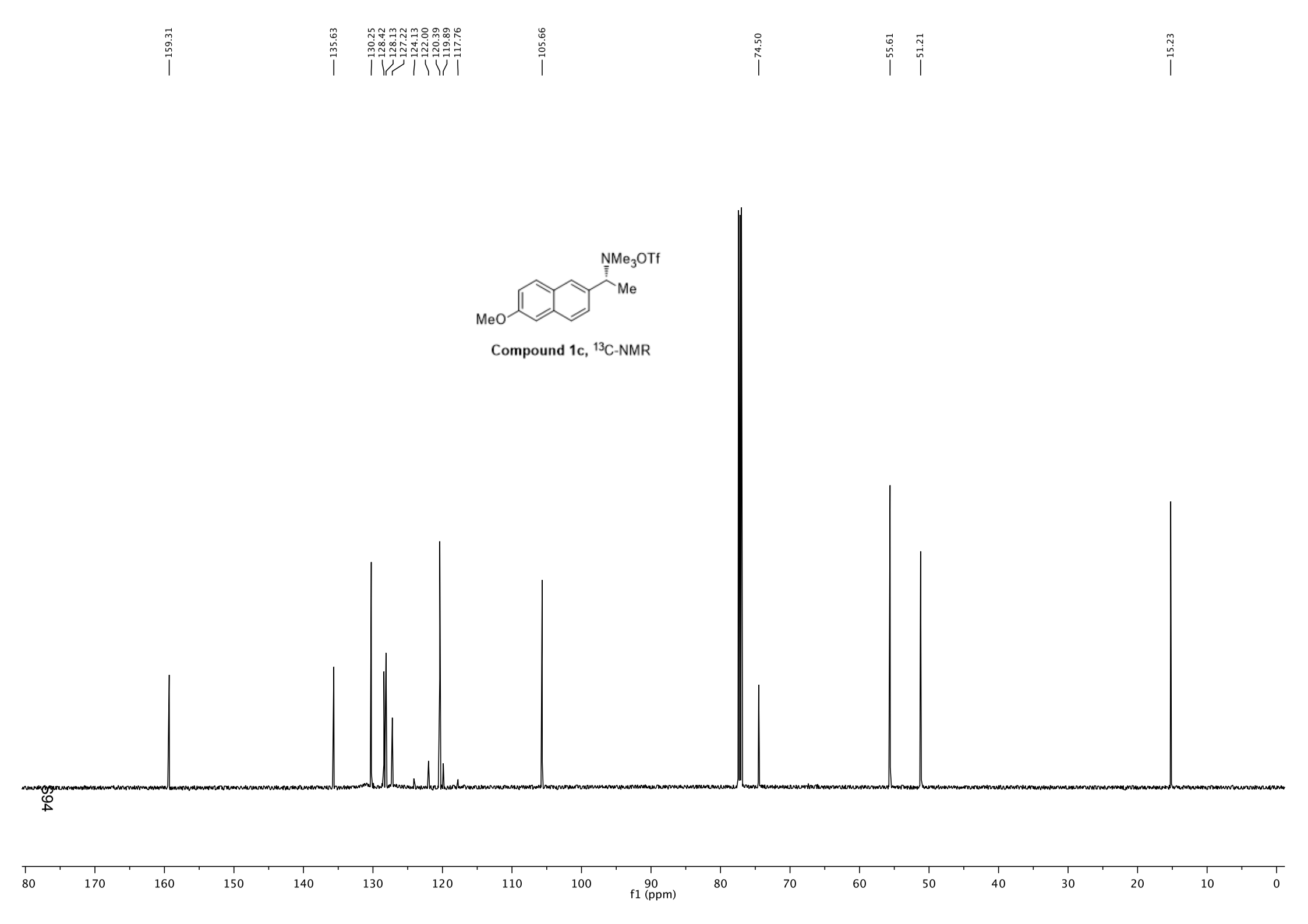

7.31
7.31
7.30
7.29
6.89
6.89
6.88
6.87
4.88
4.86
4.85
4.83
3.80
1.84
1.49
1.47
OH
Me
MeO
Compound 3o, 1H-NMR
S89
1.88
1.87
1.00
2.92
0.93
2.85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

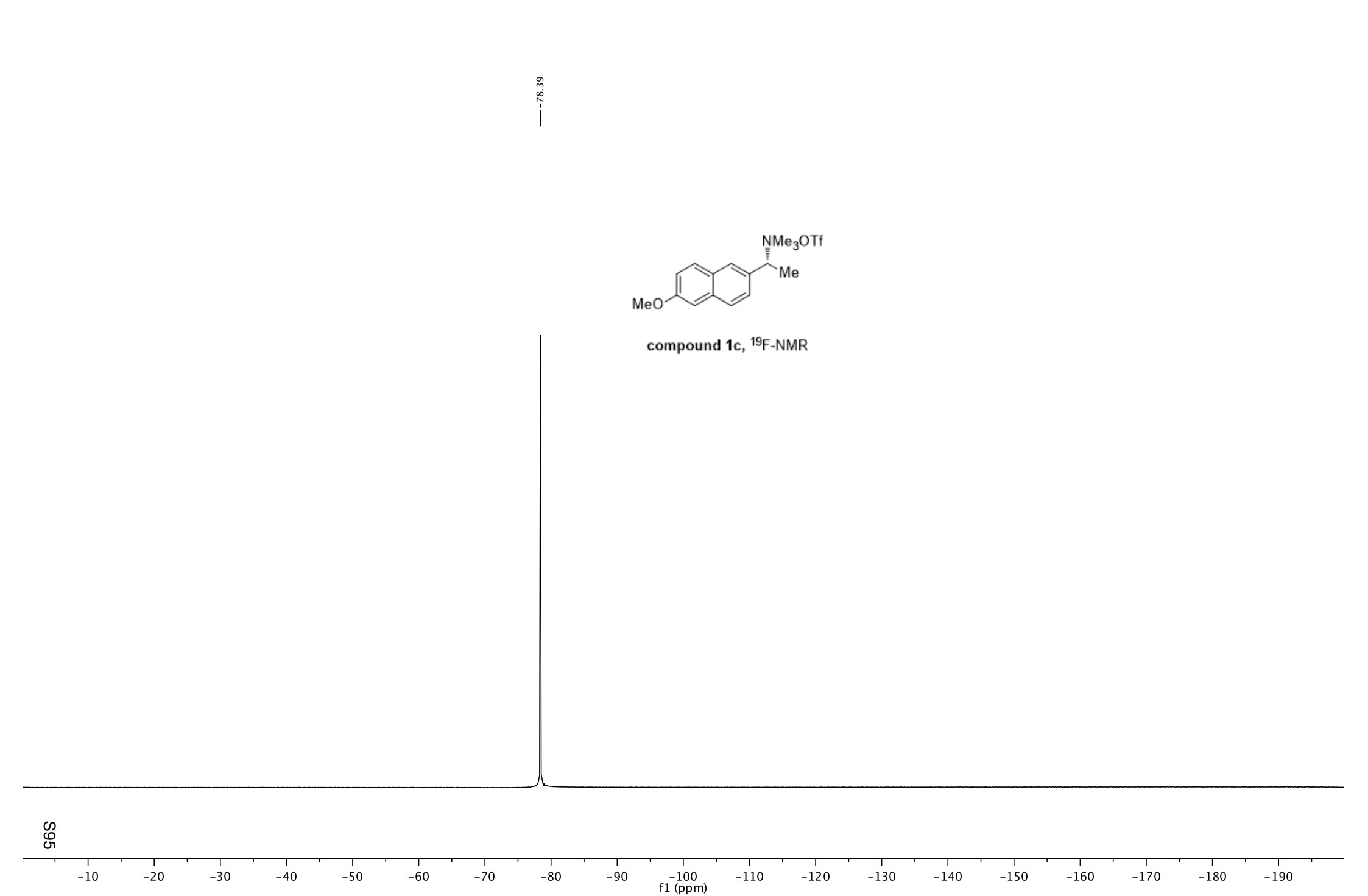

159.11
138.13
126.83
113.98
70.16
55.46
25.20
OH
Me
MeO
Compound 3o, 13C-NMR
S90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


6.90
6.90
6.83
6.83
6.81
6.81
6.78
6.76
5.95
4.85
4.83
4.82
4.80
1.76
1.47
1.45
OH
Me
O
O
O
Compound 3p, 1H-NMR
1.00
1.03
1.01
1.90
1.14
1.20
2.62
f1 (ppm)

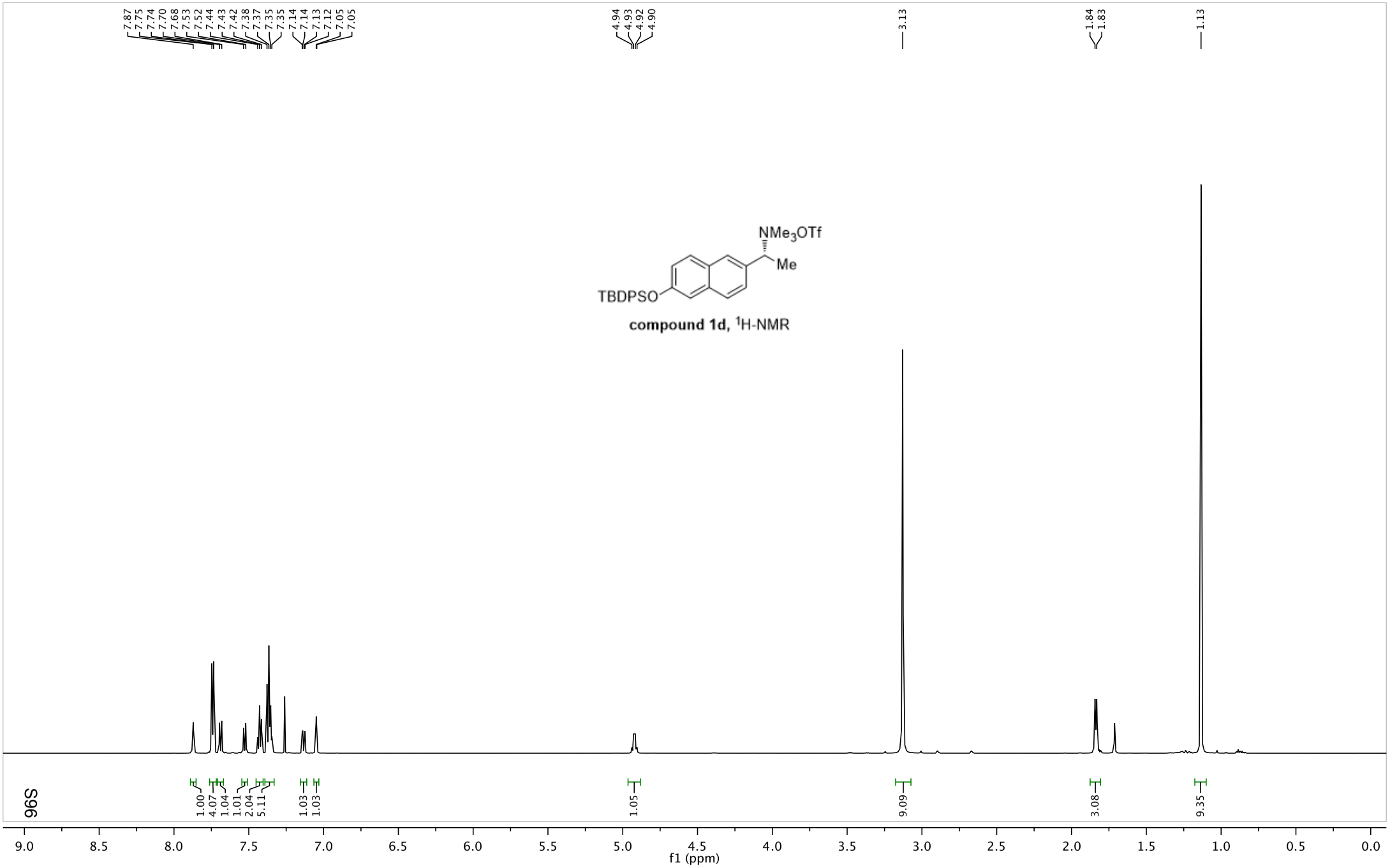

147.94
147.02
140.10
118.87
108.27
106.21
101.17
70.46
25.35
OH
Me
O
O
Compound 3p, 13C-NMR
S92
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

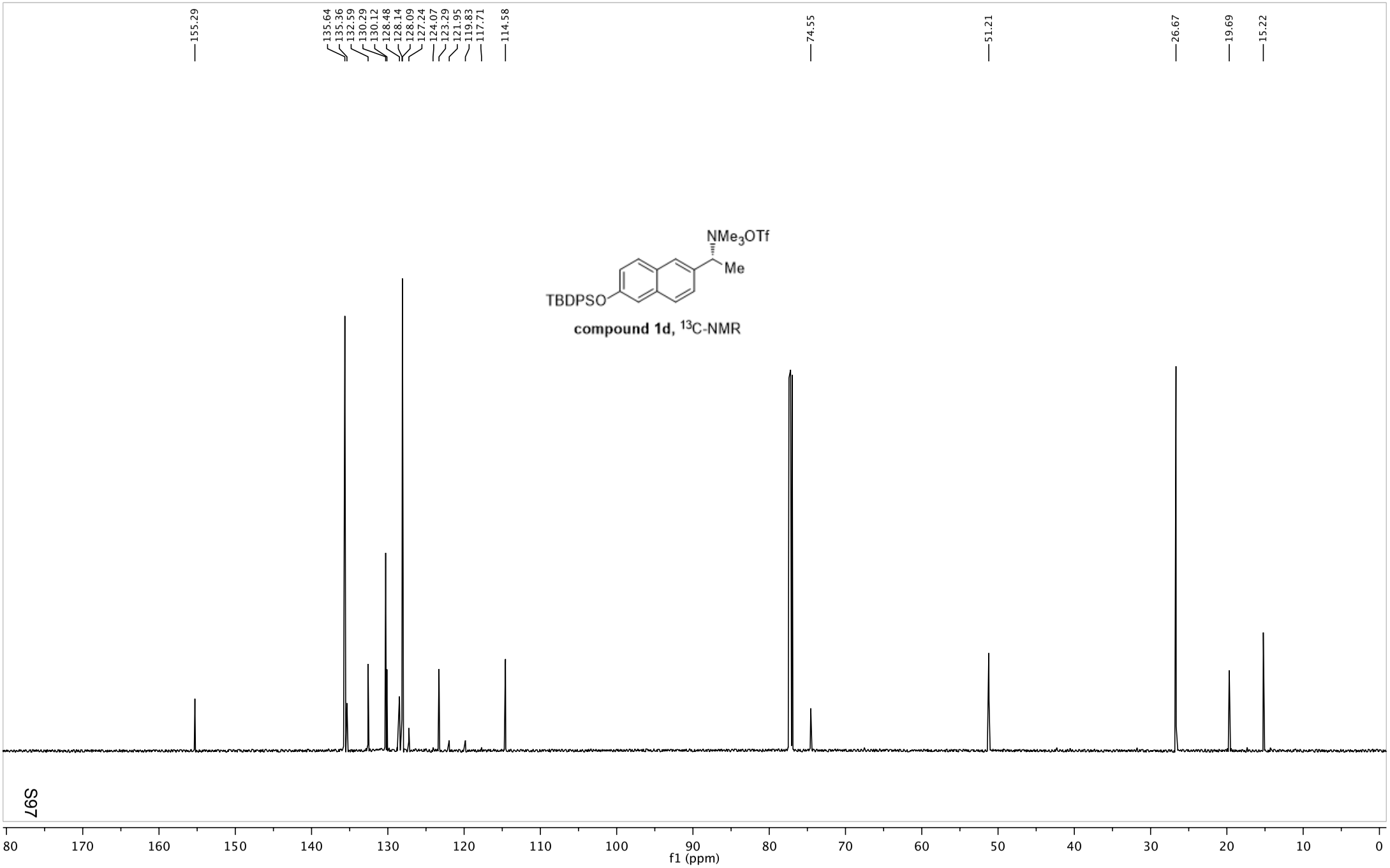

7.94
7.80
7.79
7.78
7.78
7.50
7.48
7.19
7.19
7.18
7.18
7.13
7.12
5.00
4.99
4.97
4.96
3.92
3.15
1.88
1.87
NMe3OTf
Me
MeO
Compound 1c, 1H-NMR
1.00
2.05
1.01
1.00
1.02
1.00
3.02
8.96
3.03
S93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

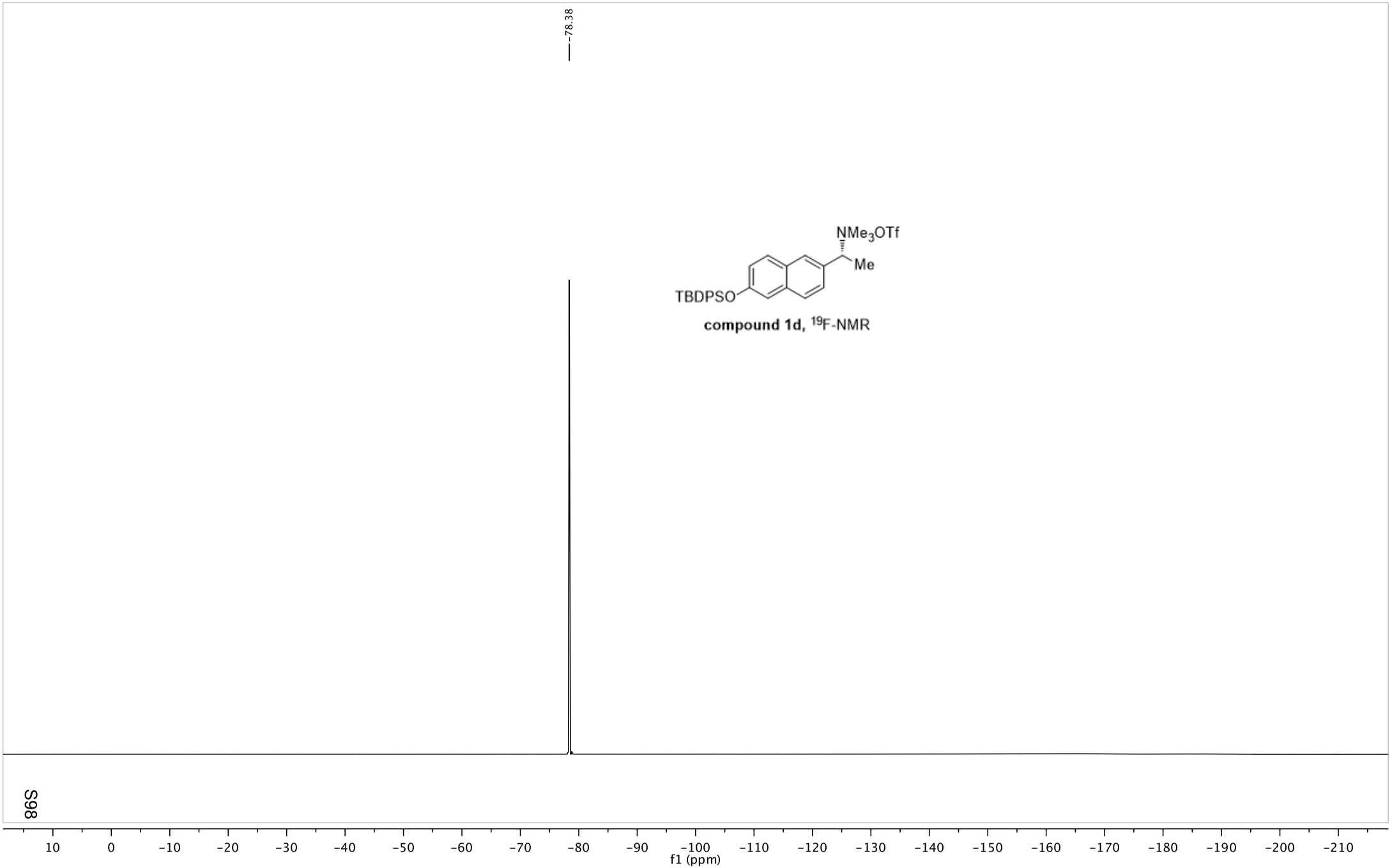

159.31
135.63
130.25
128.42
128.13
127.22
124.13
122.00
120.39
119.89
117.76
105.66
74.50
55.61
51.21
15.23
NMe3OTf
Me
MeO
Compound 1c, 13C-NMR
394
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

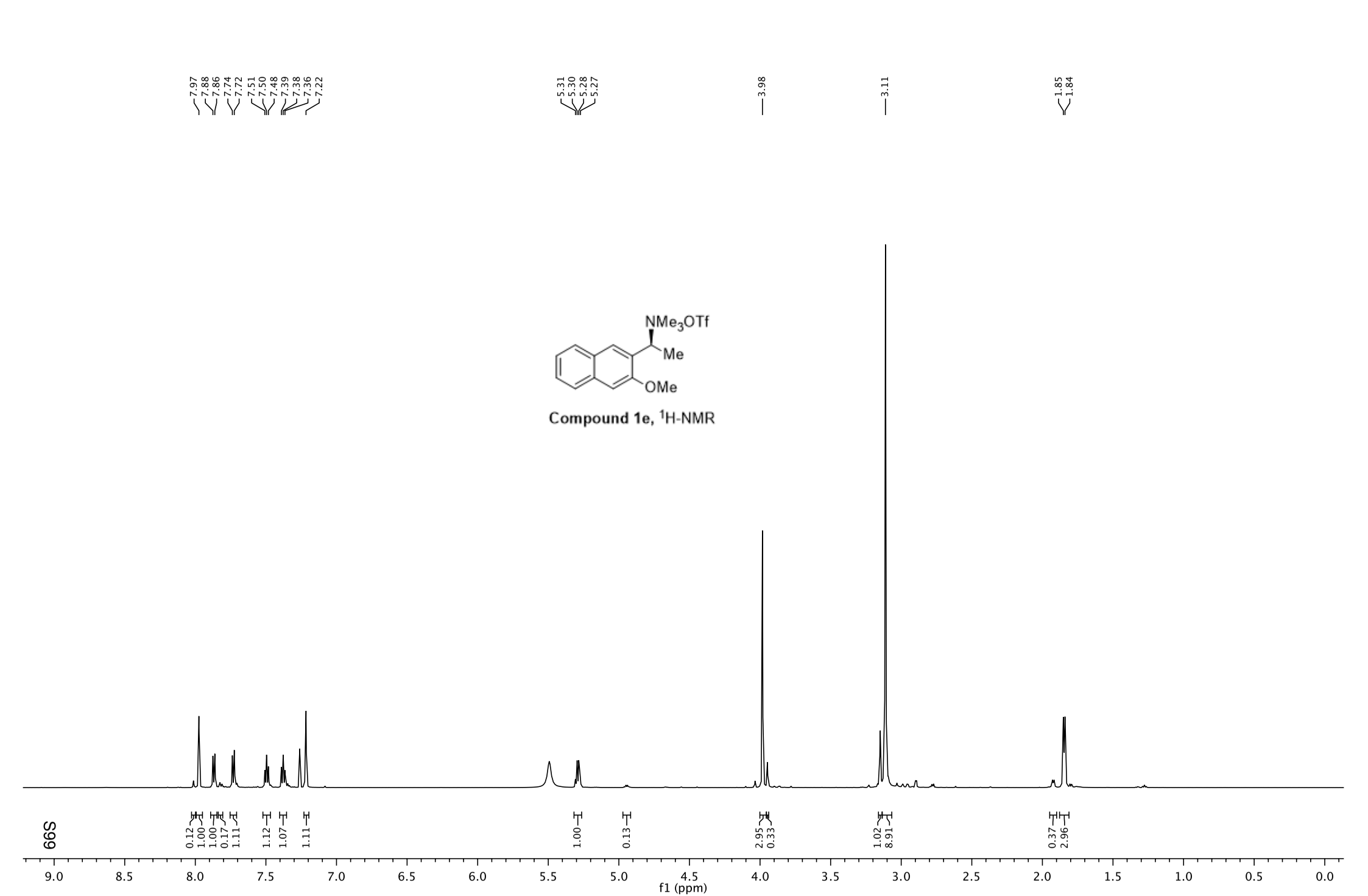


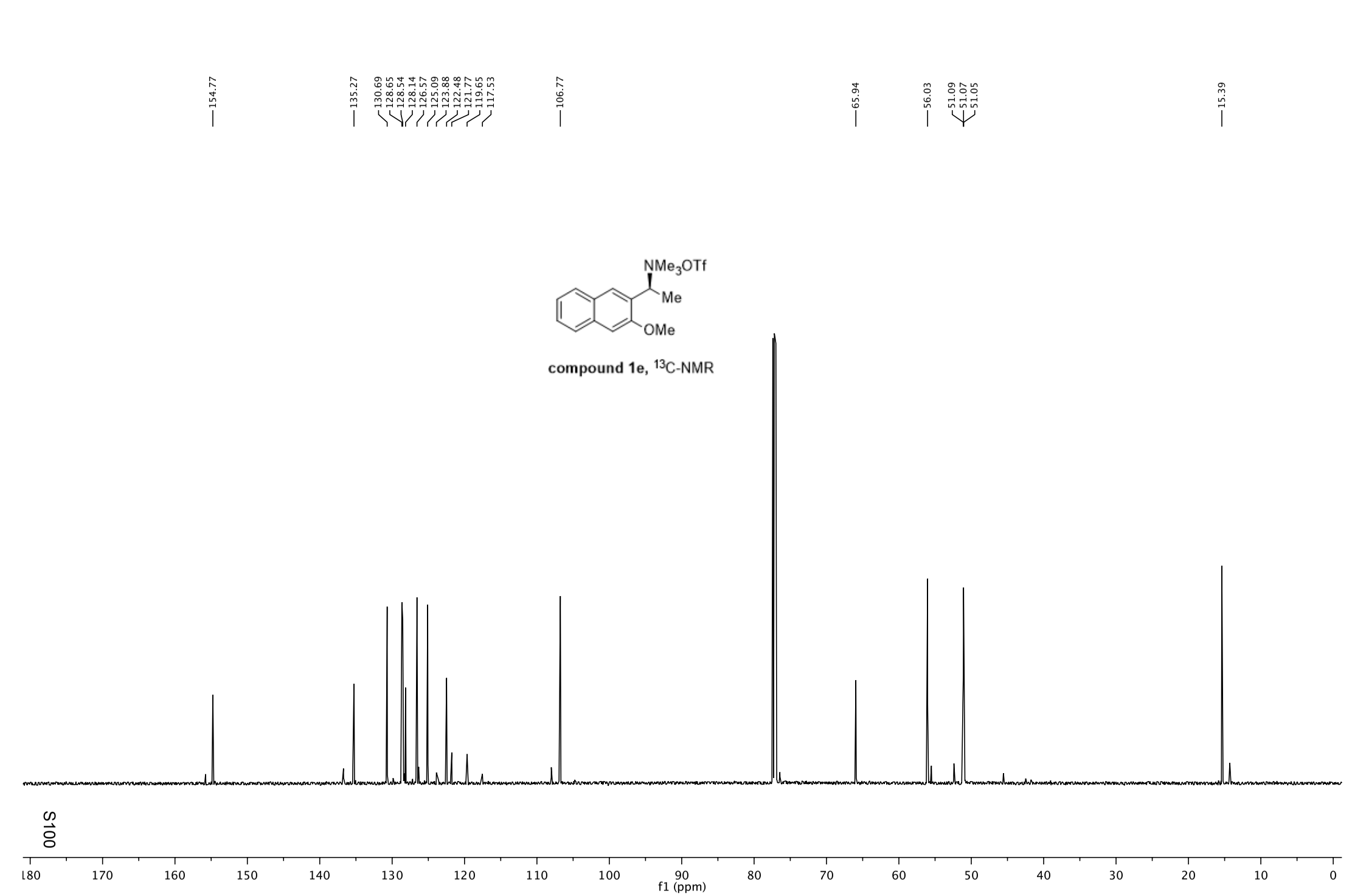
compound 1c, ^{19}F-NMR

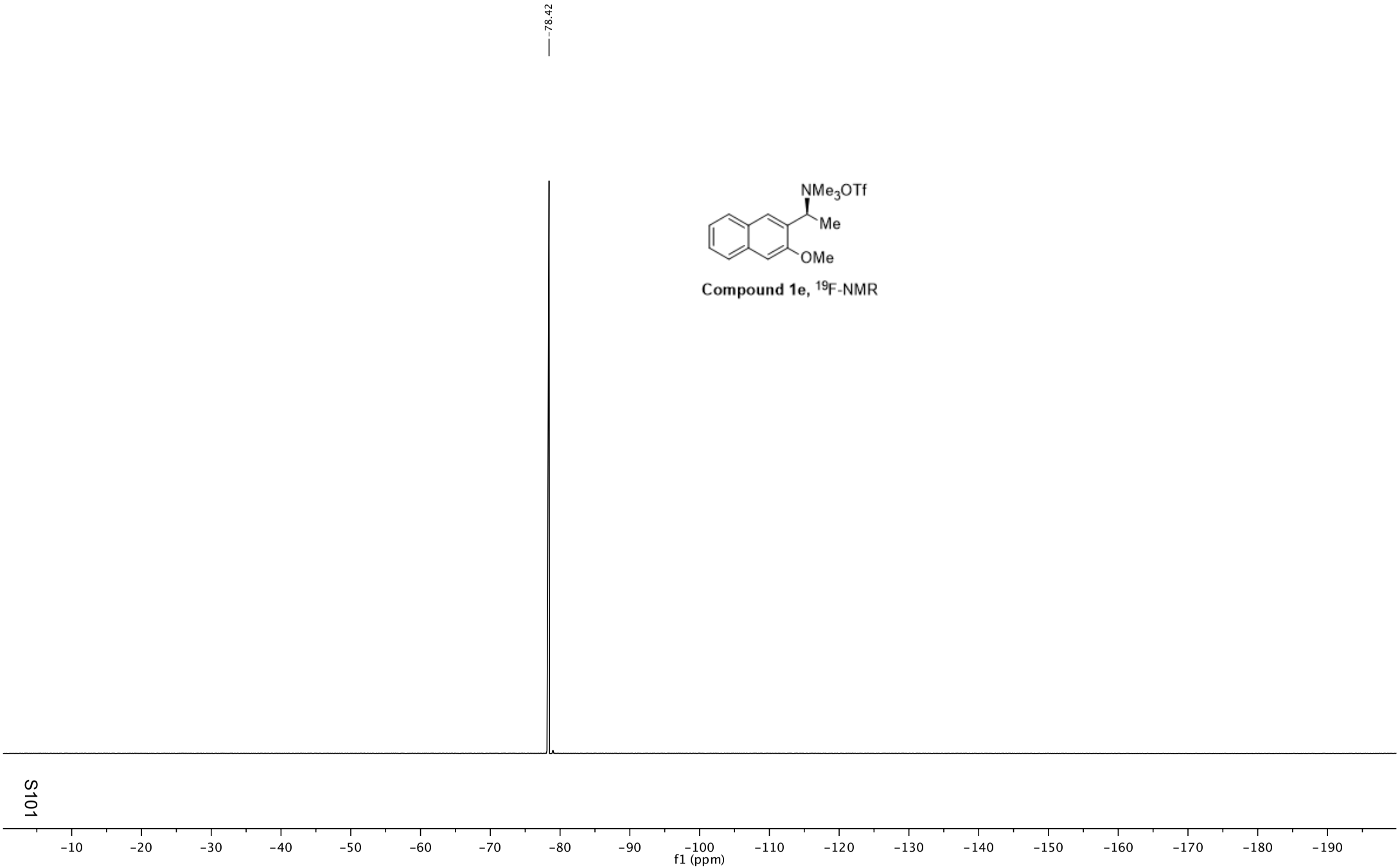

7.87
7.75
7.74
7.70
7.68
7.53
7.52
7.44
7.43
7.42
7.38
7.37
7.35
7.35
7.14
7.14
7.13
7.12
7.05
7.05
4.94
4.93
4.92
4.90
3.13
1.84
1.83
1.13
NMe3OTf
Me
TBDPSO
compound 1d, 1H-NMR
S96
1.00
4.07
1.04
1.01
2.04
5.11
1.03
1.03
1.05
9.09
3.08
9.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

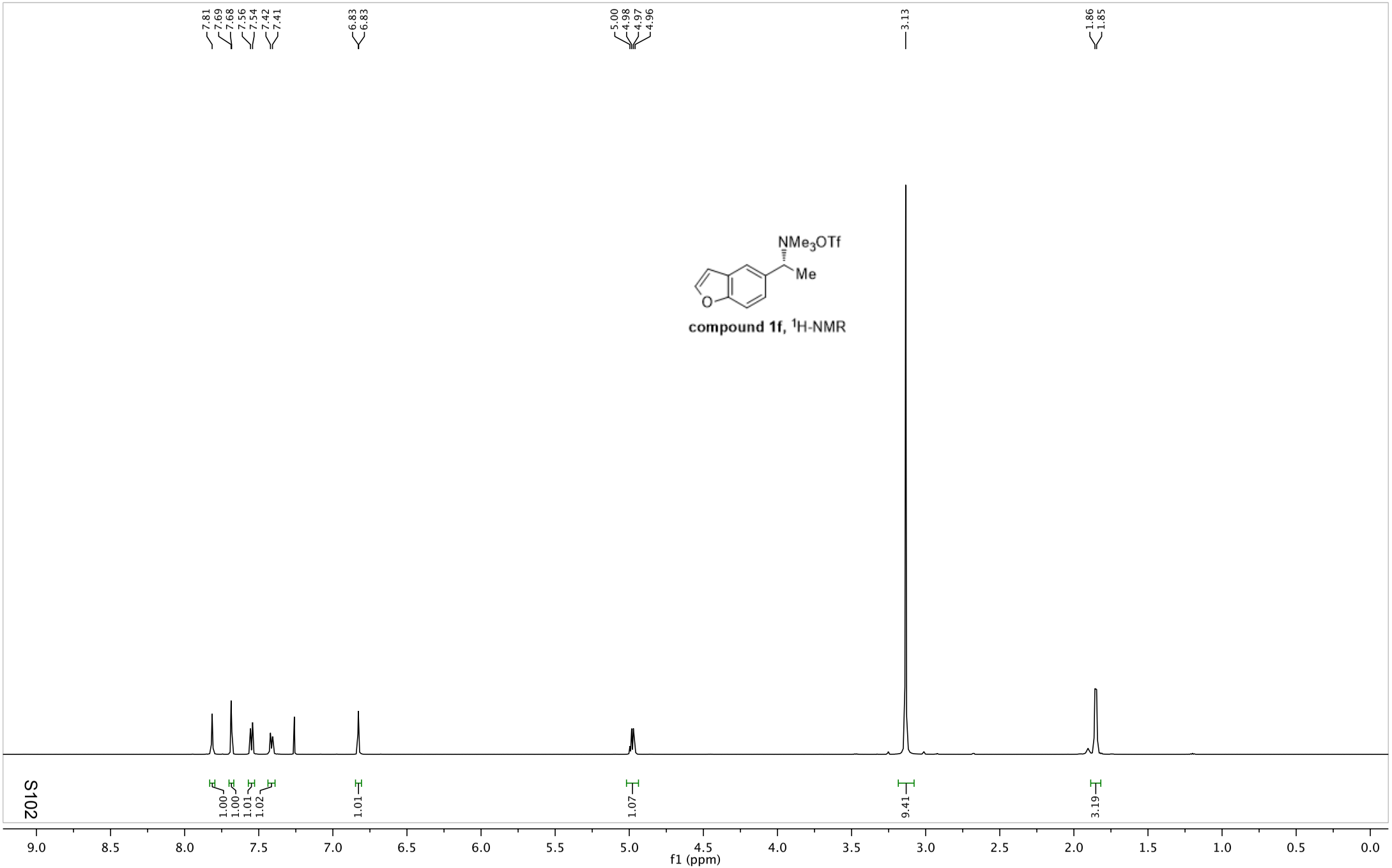

155.29
135.64
135.36
132.59
130.29
130.12
128.48
128.14
128.09
127.24
124.07
123.29
121.95
119.83
117.71
114.58
74.55
51.21
26.67
19.69
15.22
NMe3OTf
Me
TBDPSO
compound 1d, 13C-NMR
S97
f1 (ppm)

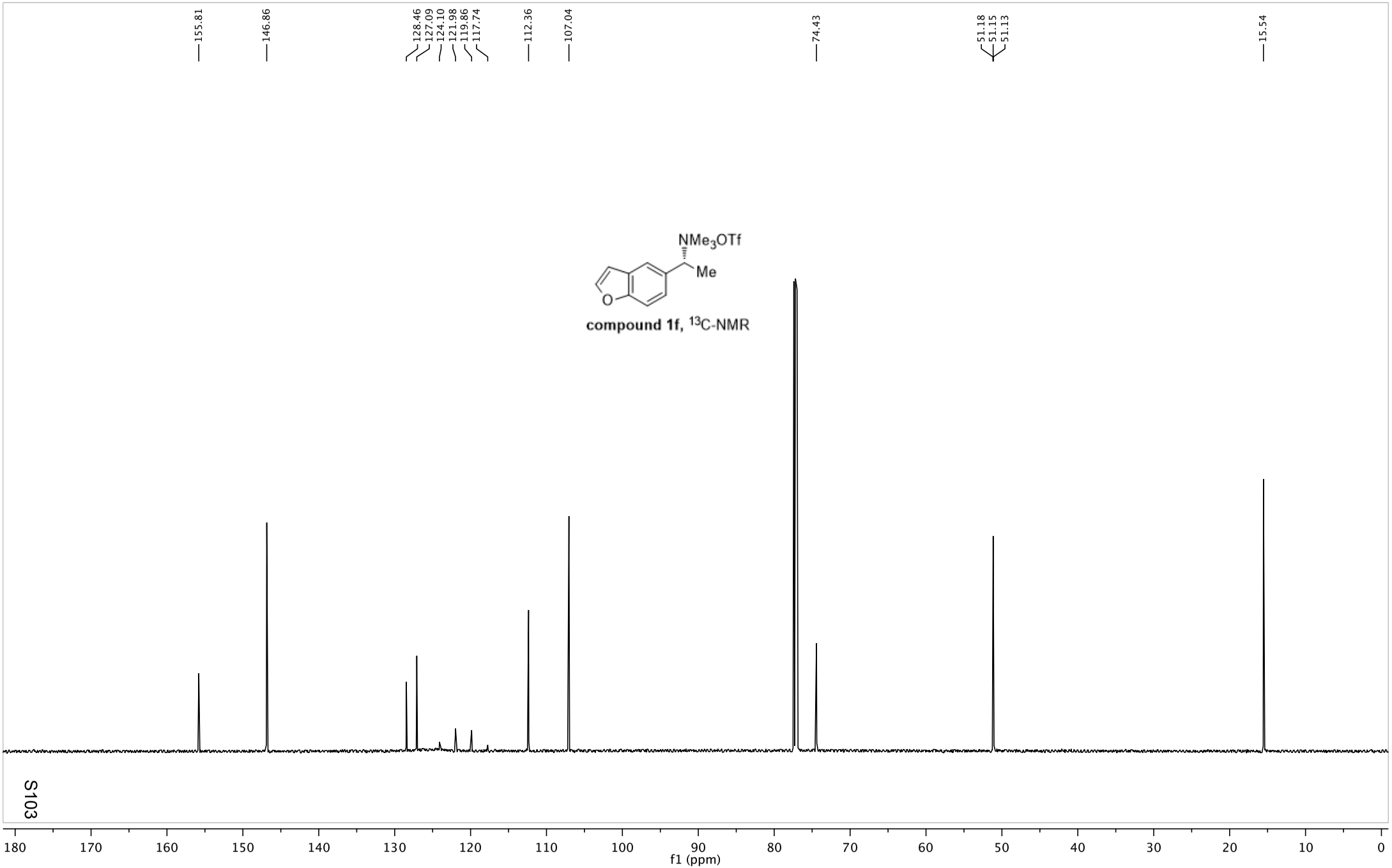

-78.38
NMe3OTf
Me
TBDPSO
compound 1d, 19F-NMR
S98
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

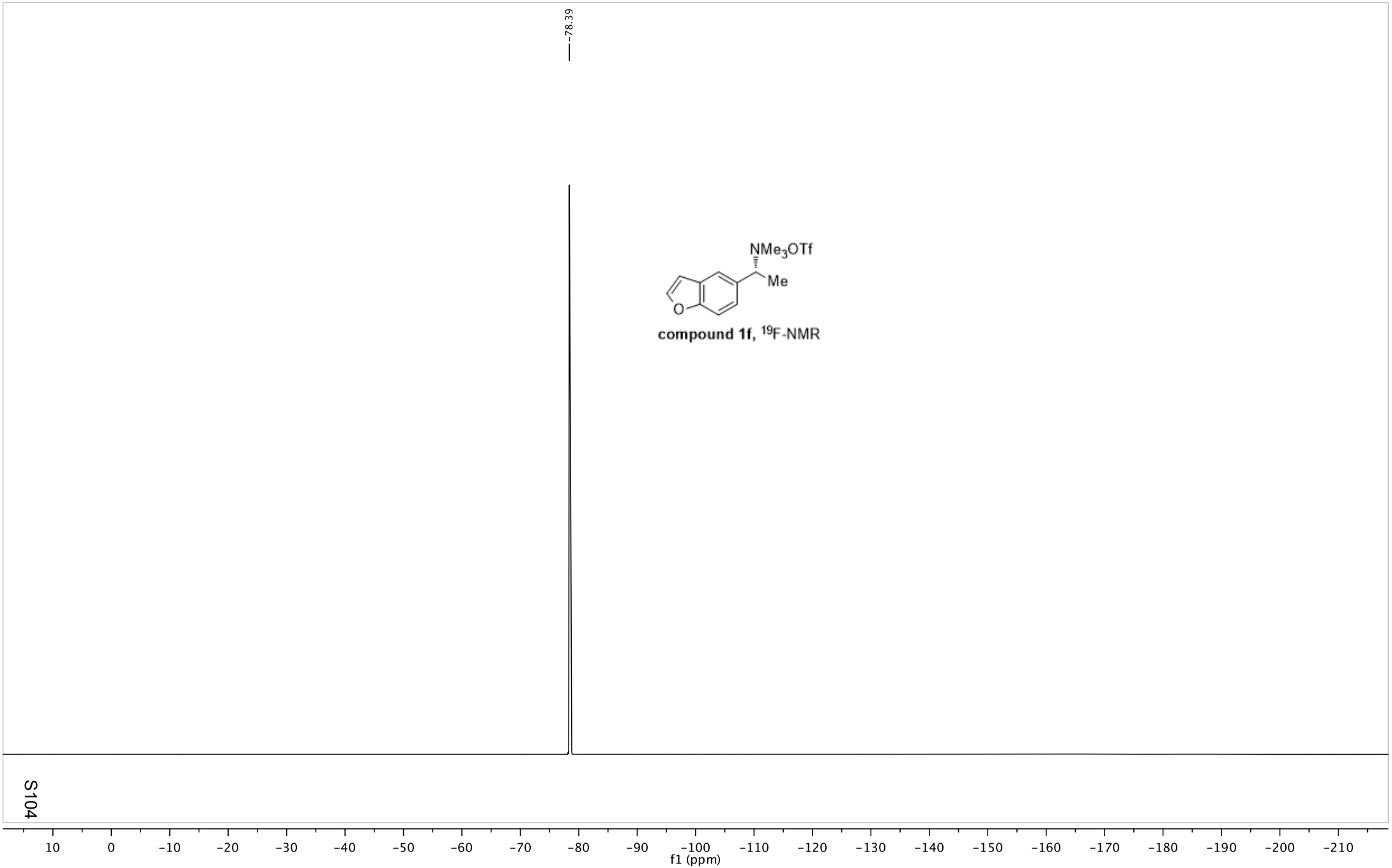

7.97
7.88
7.86
7.74
7.72
7.51
7.50
7.48
7.39
7.38
7.36
7.22
5.31
5.30
5.28
5.27
3.98
3.11
1.85
1.84
NMe3OTf
Me
OMe
Compound 1e, 1H-NMR
S99
0.12
1.00
1.00
0.17
1.11
1.12
1.07
1.11
1.00
0.13
2.95
0.33
1.02
8.91
0.37
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


154.77
135.27
130.69
128.65
128.54
128.14
126.57
125.09
123.88
122.48
121.77
119.65
117.53
106.77
65.94
56.03
51.09
51.07
51.05
15.39
NMe3OTf
Me
OMe
compound 1e, 13C-NMR
S100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

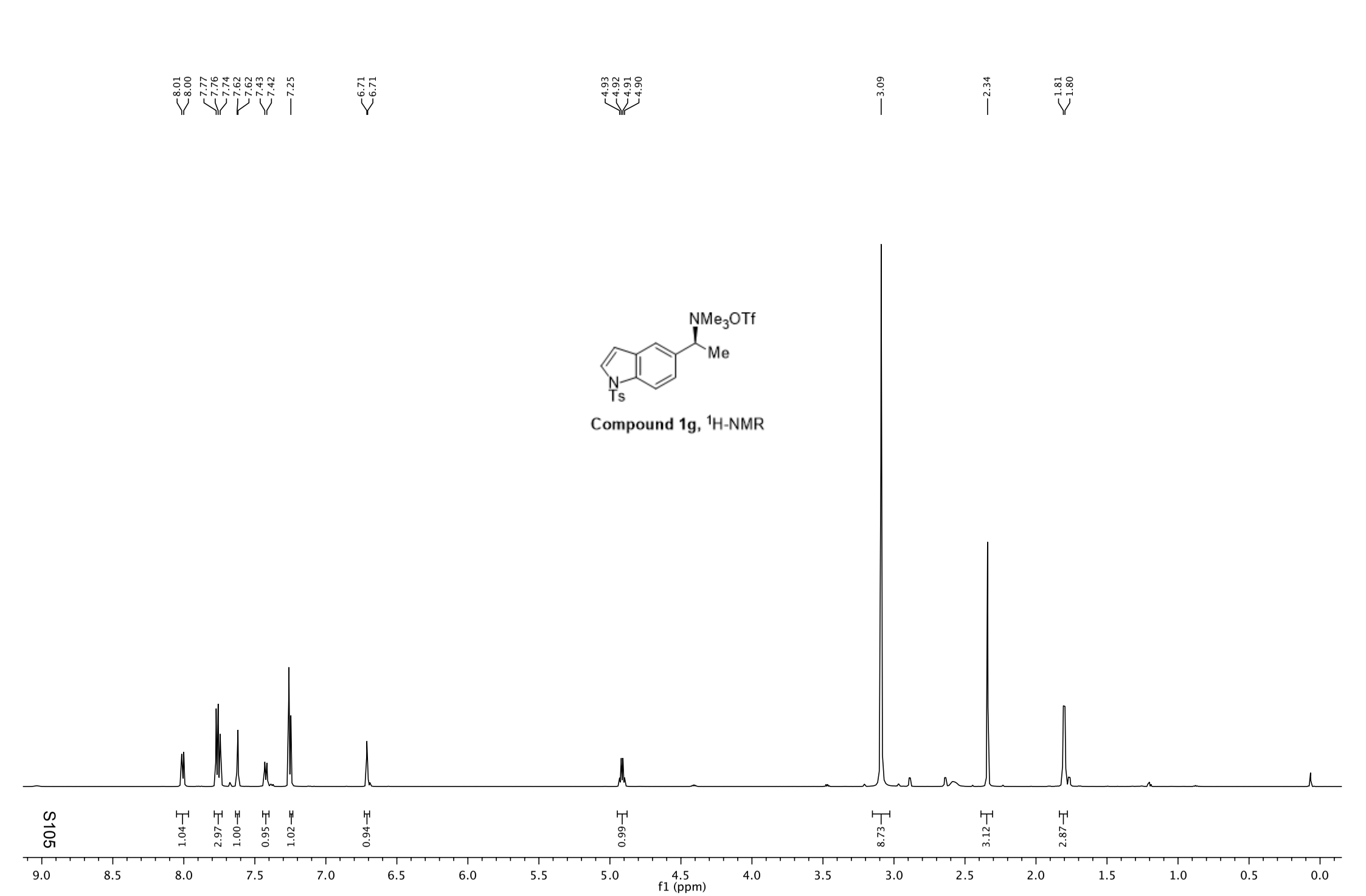

-78.42
NMe3OTf
Me
OMe
Compound 1e, 19F-NMR
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


7.81
7.69
7.68
7.56
7.54
7.42
7.41
6.83
6.83
5.00
4.98
4.97
4.96
3.13
1.86
1.85
NMe3OTf
Me
O
compound 1f, 1H-NMR
1.00
1.00
1.01
1.02
1.01
1.07
9.41
3.19
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)

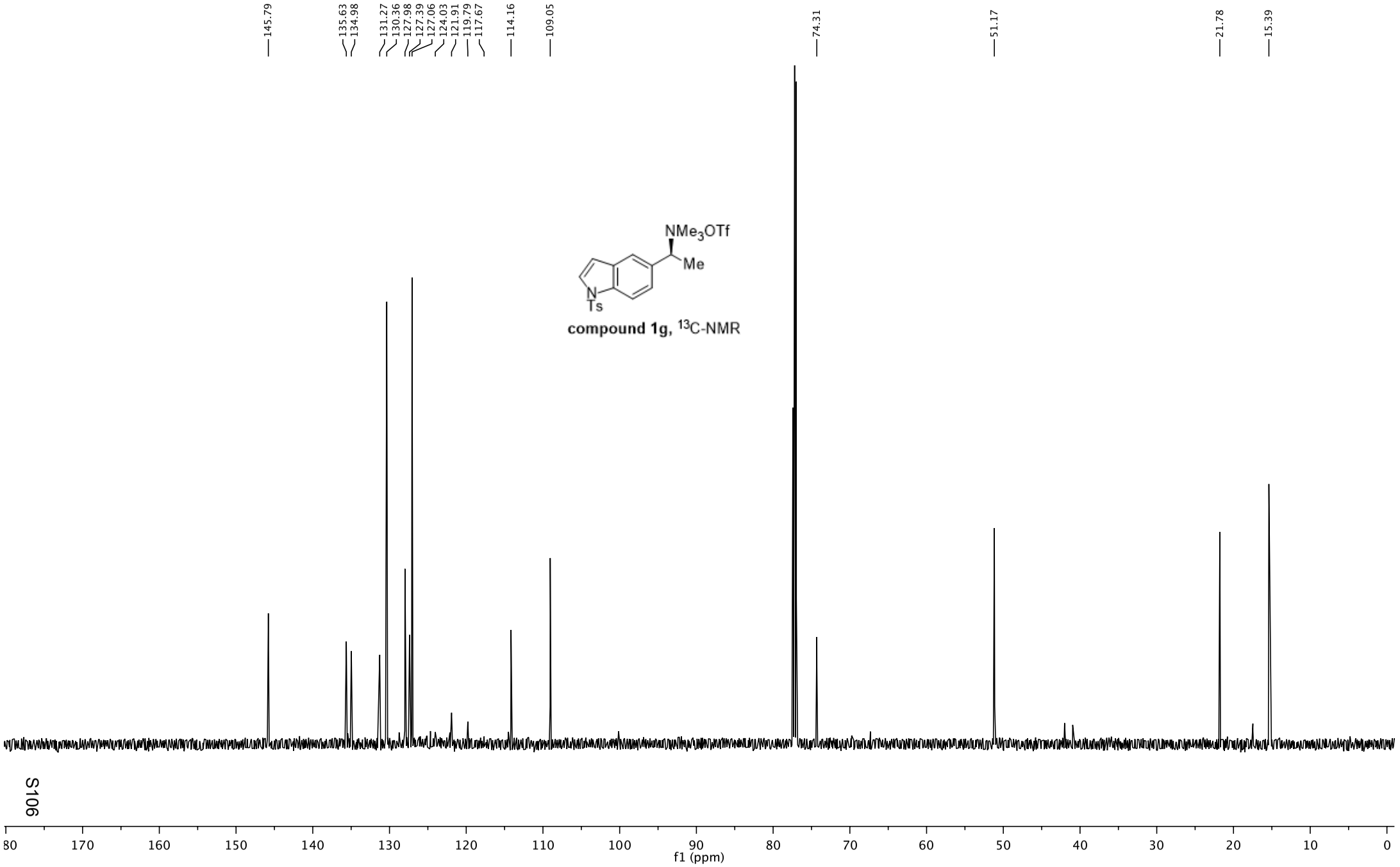

155.81
146.86
128.46
127.09
124.10
121.98
119.86
117.74
112.36
107.04
74.43
51.18
51.15
51.13
15.54
NMe3OTf
Me
O
compound 1f, 13C-NMR
S103
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

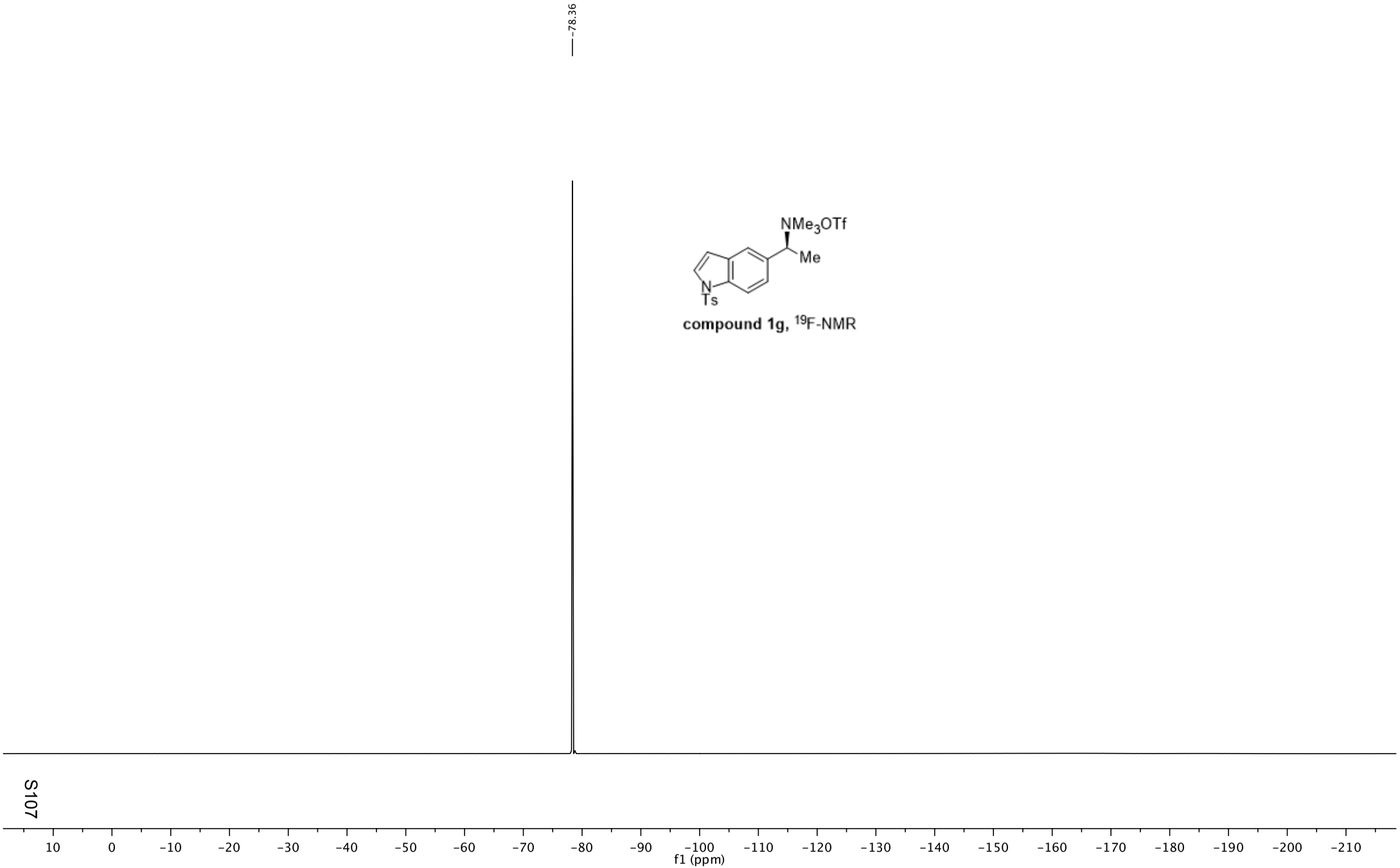


compound 1f, ^{19}F-NMR

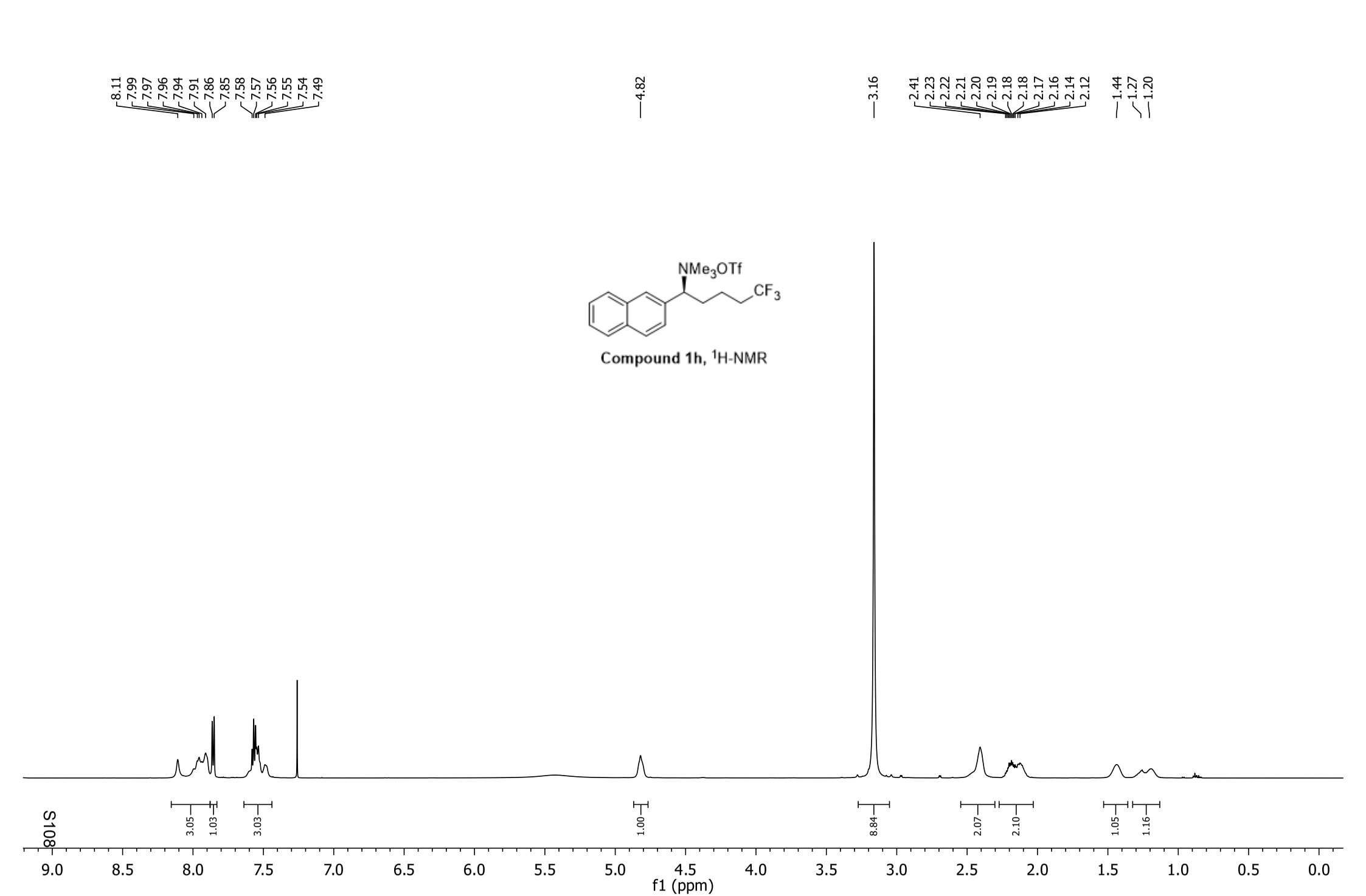


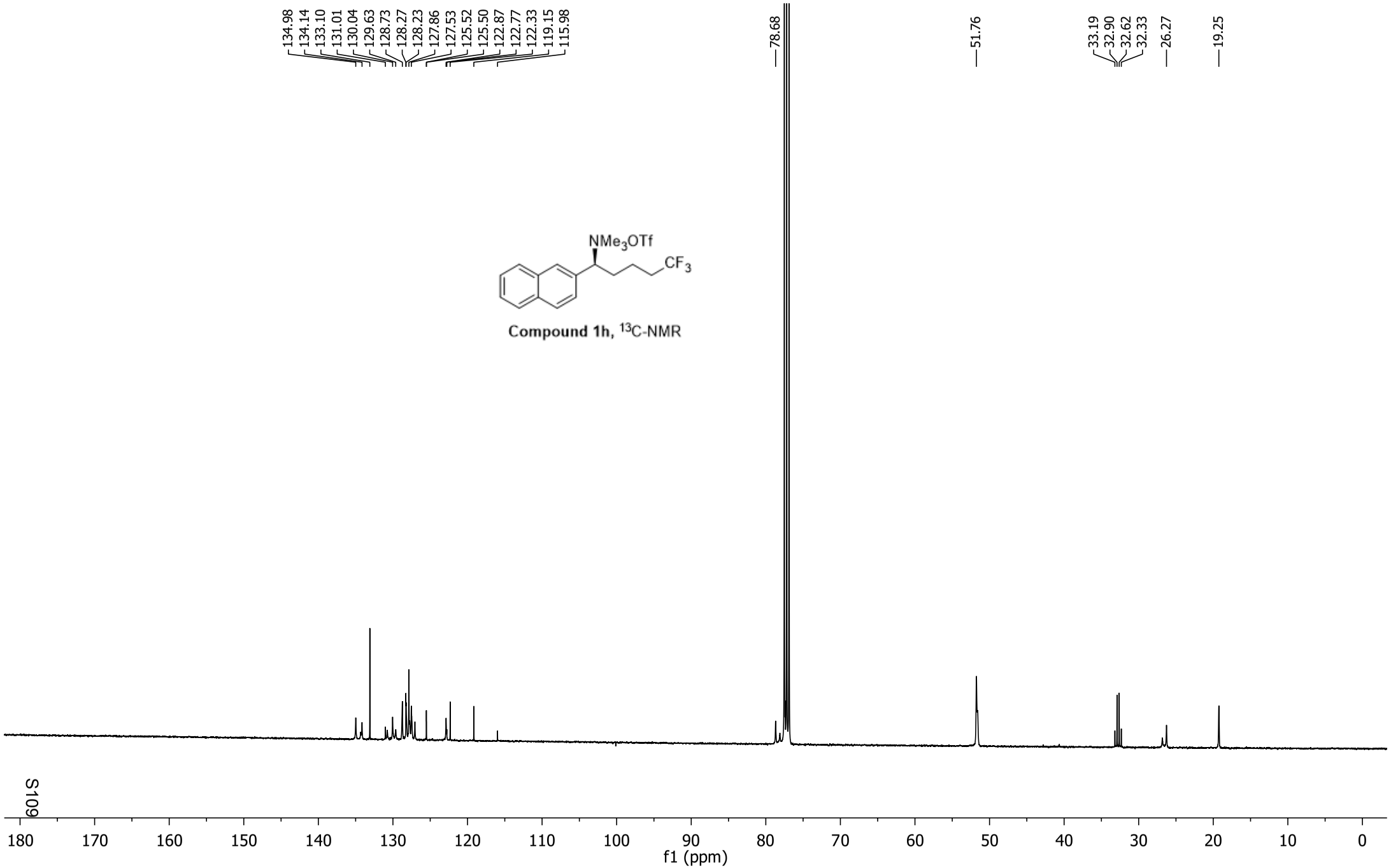
Compound 1g, ^{1}H-NMR

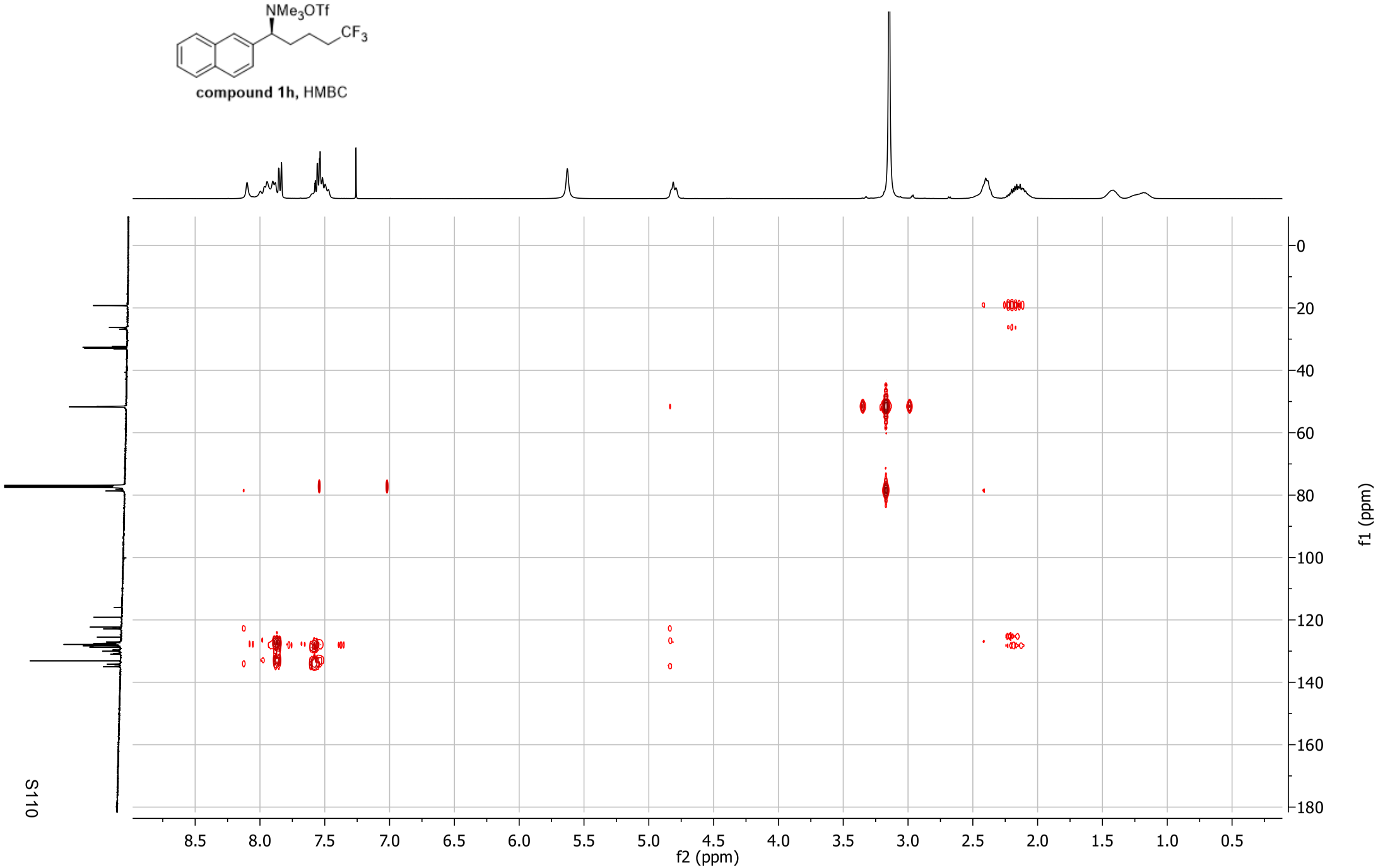

145.79
135.63
134.98
131.27
130.36
127.98
127.39
127.06
124.03
121.91
119.79
117.67
114.16
109.05
74.31
51.17
21.78
15.39
NMe3OTf
Me
N
Ts
compound 1g, 13C-NMR
f1 (ppm)

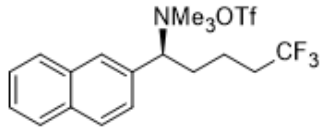


compound 1g, ^{19}F-NMR

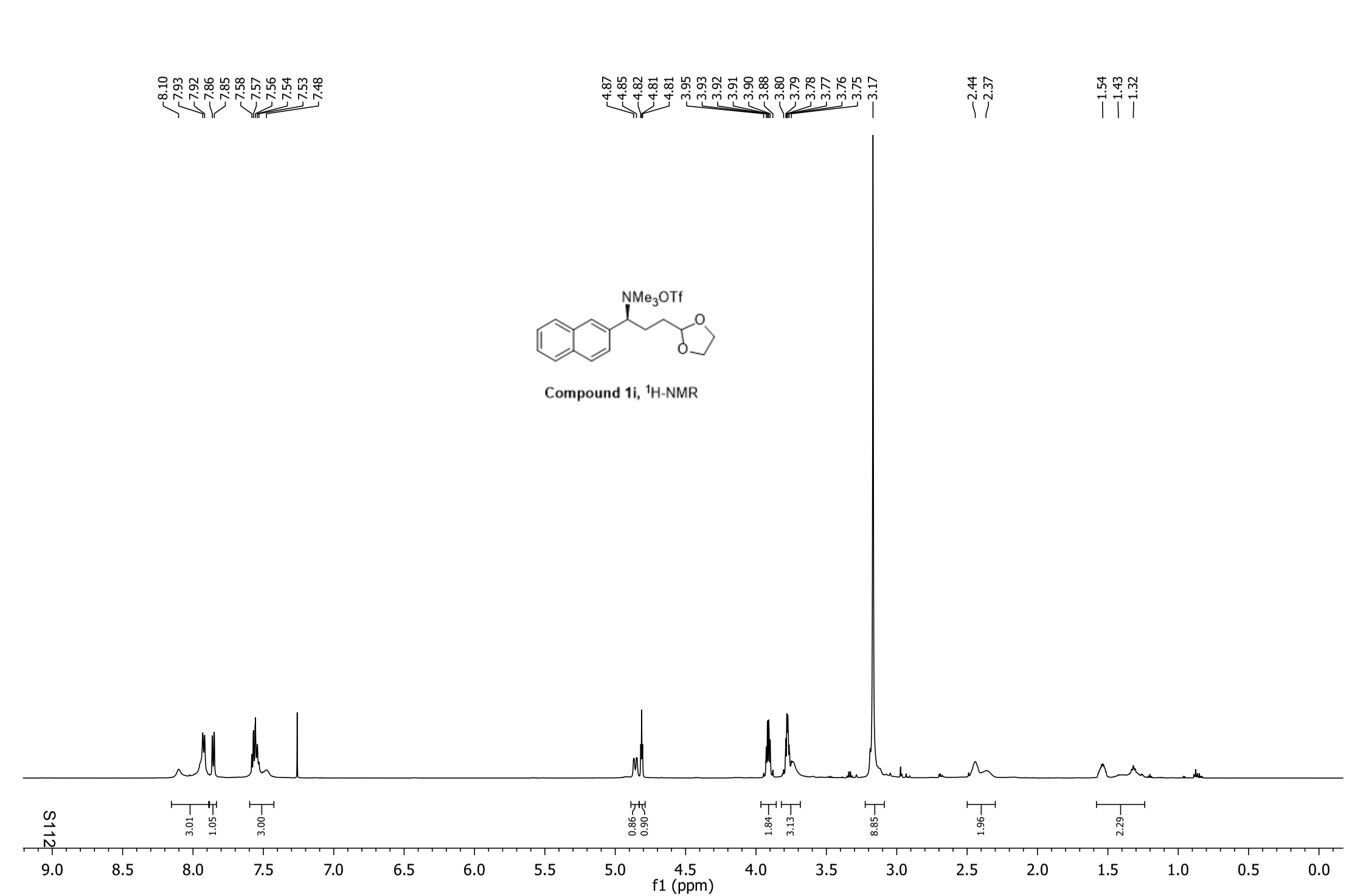

8.11
7.99
7.97
7.96
7.94
7.91
7.86
7.85
7.58
7.57
7.56
7.55
7.54
7.49
4.82
3.16
2.41
2.23
2.22
2.21
2.20
2.19
2.18
2.18
2.17
2.16
2.14
2.12
1.44
1.27
1.20
NMe3OTf
CF3
Compound 1h, 1H-NMR
3.05
1.03
3.03
1.00
8.84
2.07
2.10
1.05
1.16
S108
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

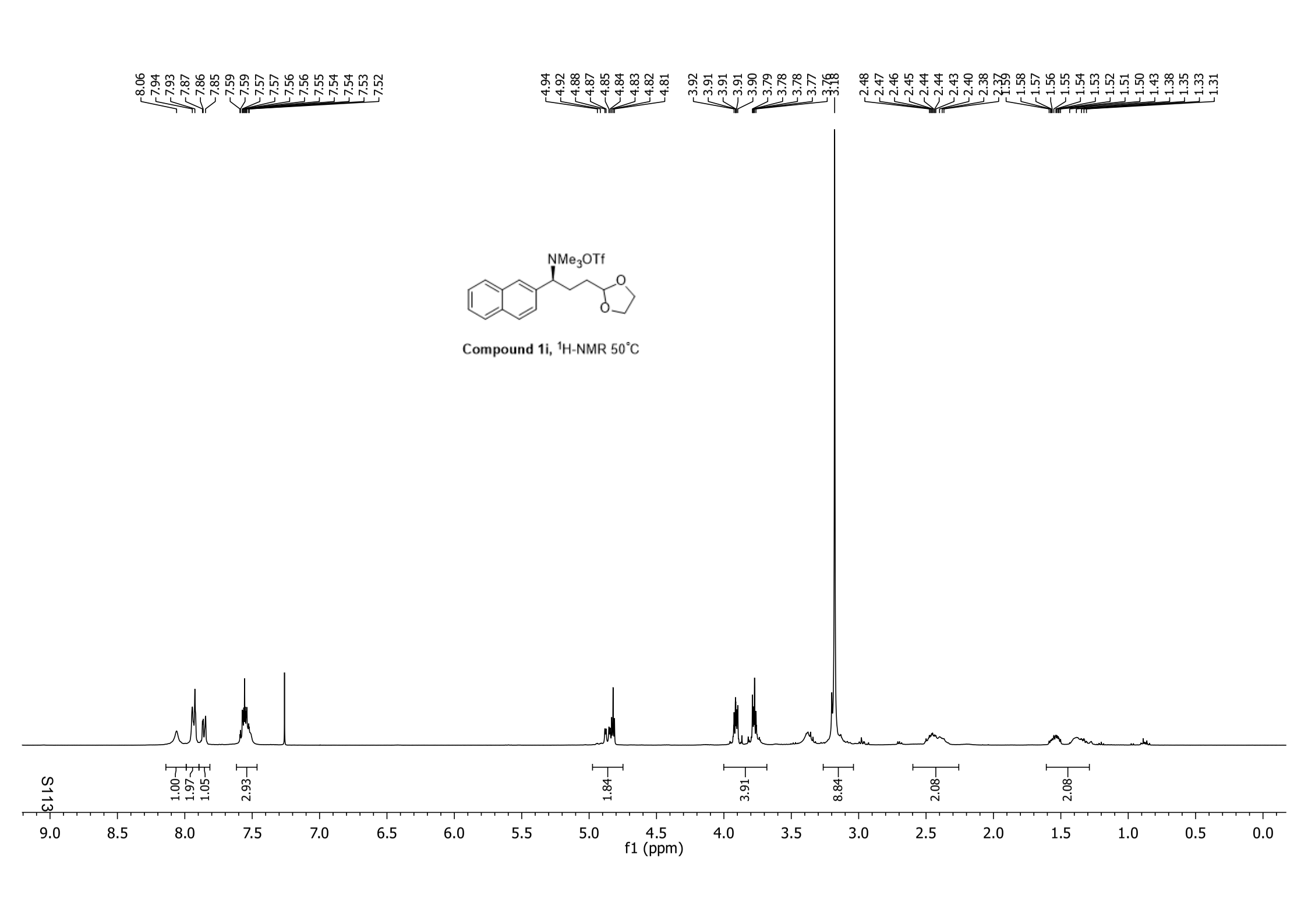

134.98
134.14
133.10
131.01
130.04
129.63
128.73
128.27
128.23
127.86
127.53
125.52
125.50
122.87
122.77
122.33
119.15
115.98
78.68
51.76
33.19
32.90
32.62
32.33
26.27
19.25
NMe3OTf
CF3
Compound 1h, 13C-NMR
S109
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

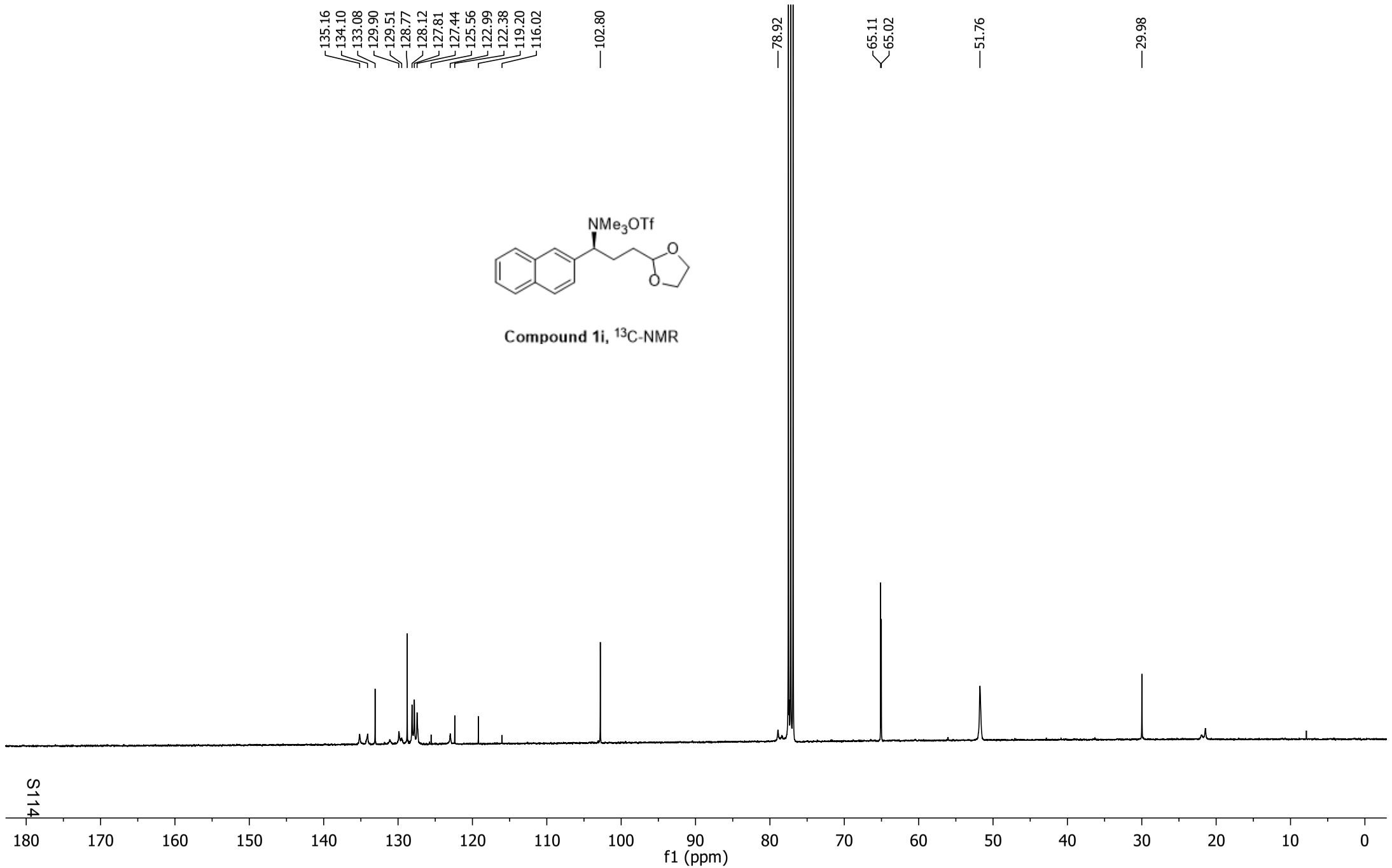

NMe3OTf
CF3
compound 1h, HMBC
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
20
40
60
80
100
120
140
160
180

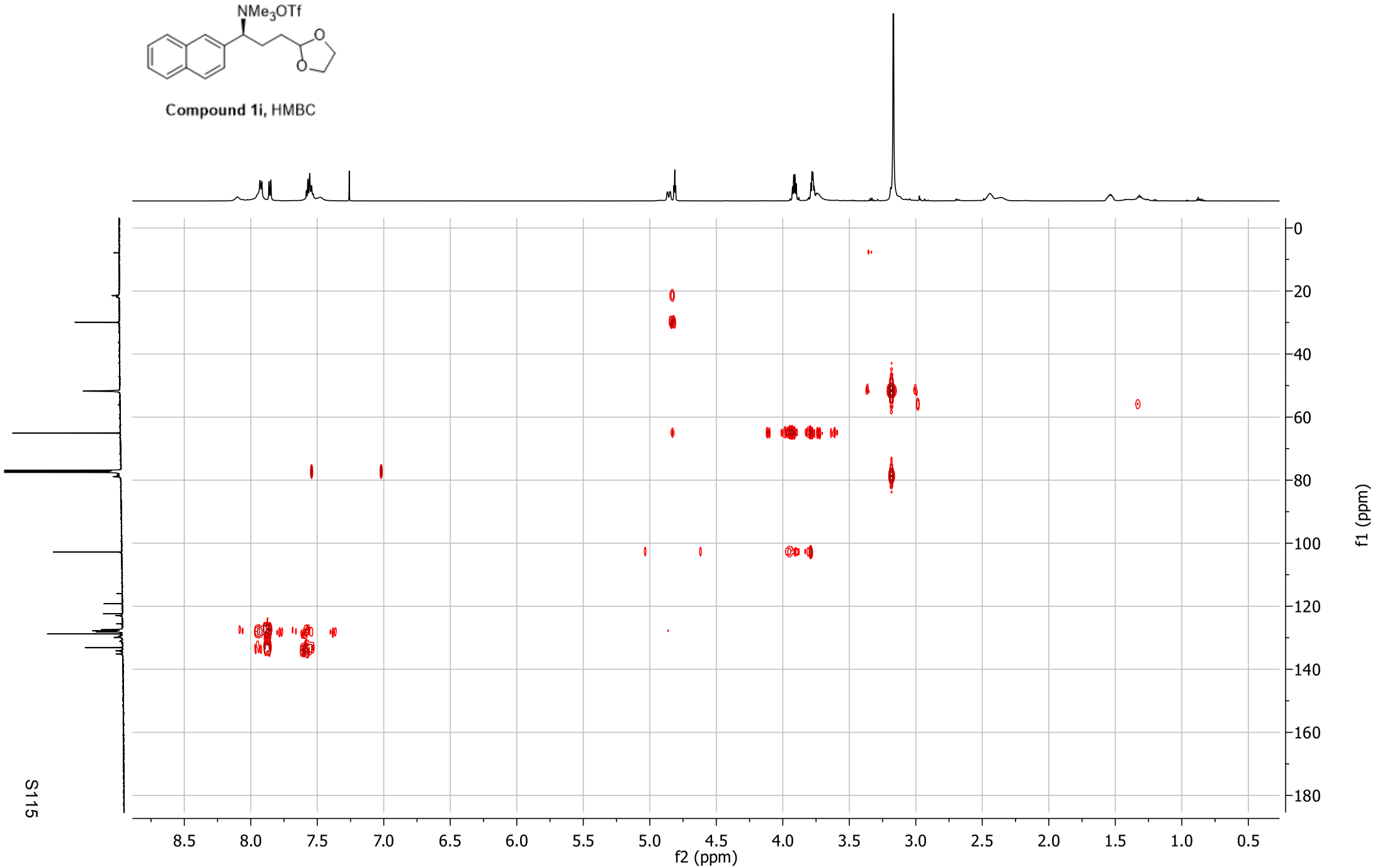


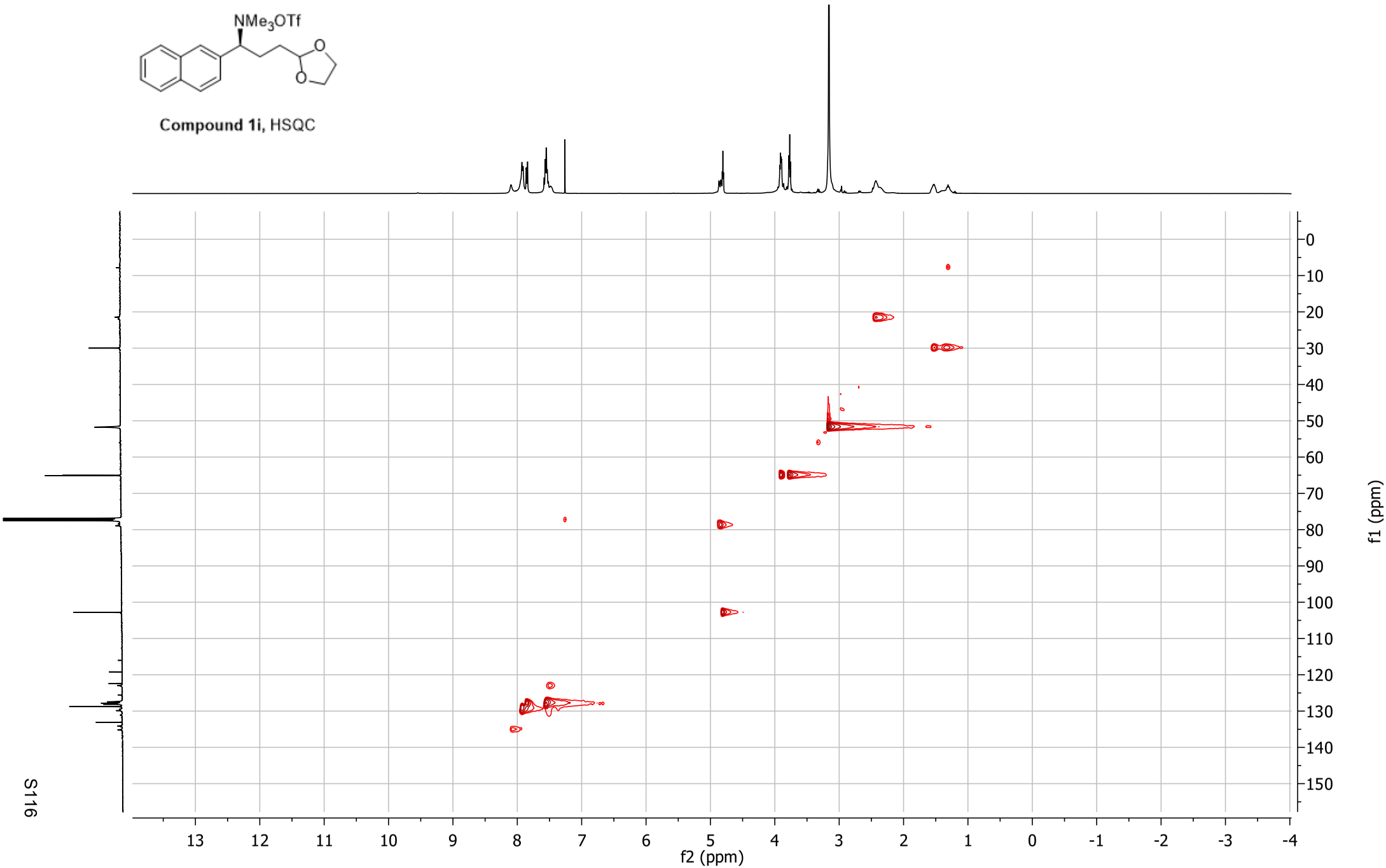
Compound 1h, HSQC

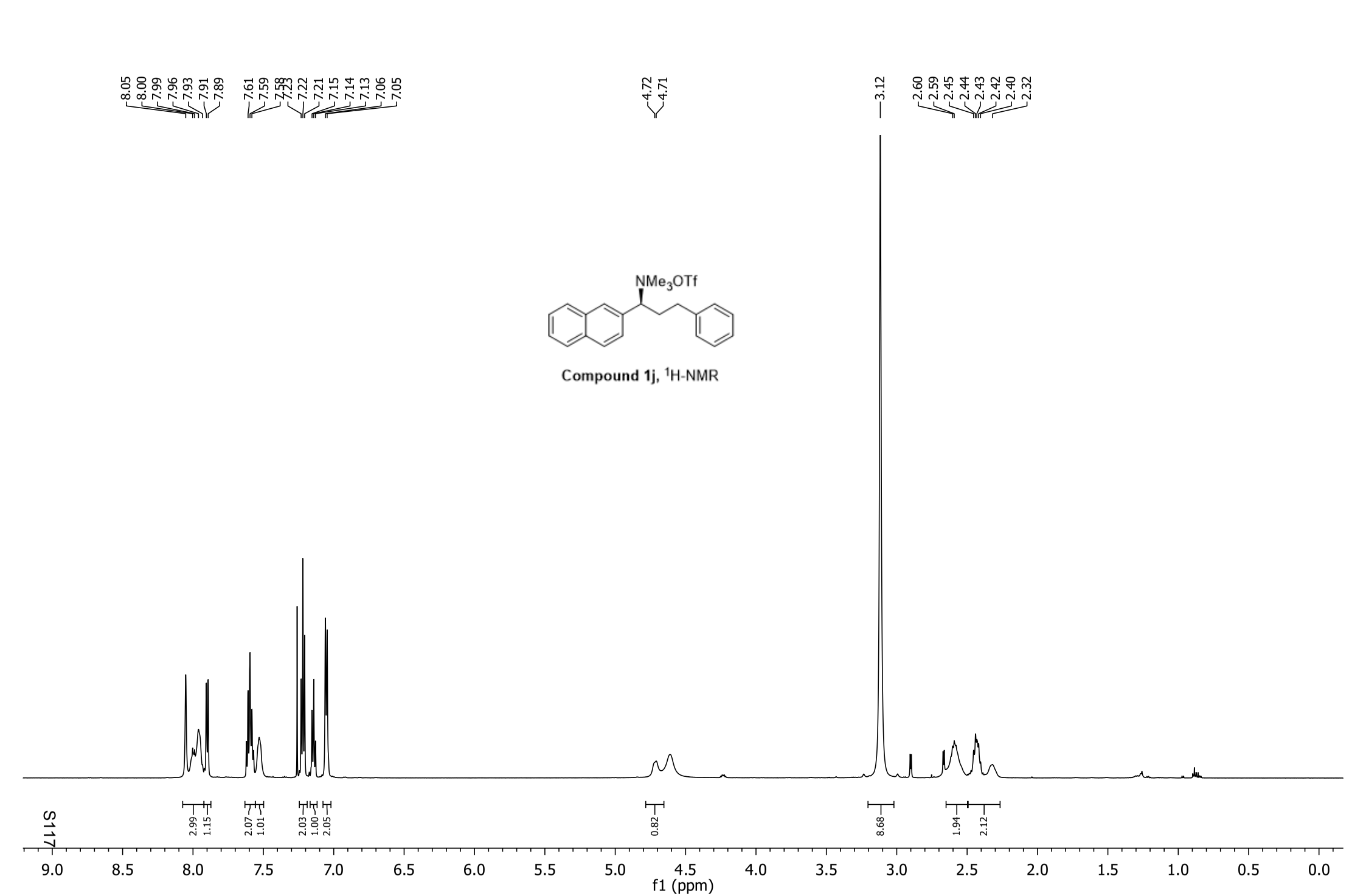

8.10
7.93
7.92
7.86
7.85
7.58
7.57
7.56
7.54
7.53
7.48
4.87
4.85
4.82
4.81
4.81
3.95
3.93
3.92
3.91
3.90
3.88
3.80
3.79
3.78
3.77
3.76
3.75
3.17
2.44
2.37
1.54
1.43
1.32
NMe3OTf
O
O
Compound 1i, 1H-NMR
3.01
1.05
3.00
0.86
0.90
1.84
3.13
8.85
1.96
2.29
S112
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8.06
7.94
7.93
7.87
7.86
7.85
7.59
7.59
7.57
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.52
4.94
4.92
4.88
4.87
4.85
4.84
4.83
4.82
4.81
3.92
3.91
3.91
3.91
3.90
3.79
3.78
3.78
3.77
3.76
3.18
2.48
2.47
2.46
2.45
2.44
2.44
2.43
2.40
2.38
2.37
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.51
1.50
1.43
1.38
1.35
1.33
1.31
NMe3OTf
O
O
Compound 1i, 1H-NMR 50°C
S113
1.00
1.97
1.05
2.93
1.84
3.91
8.84
2.08
2.08
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)

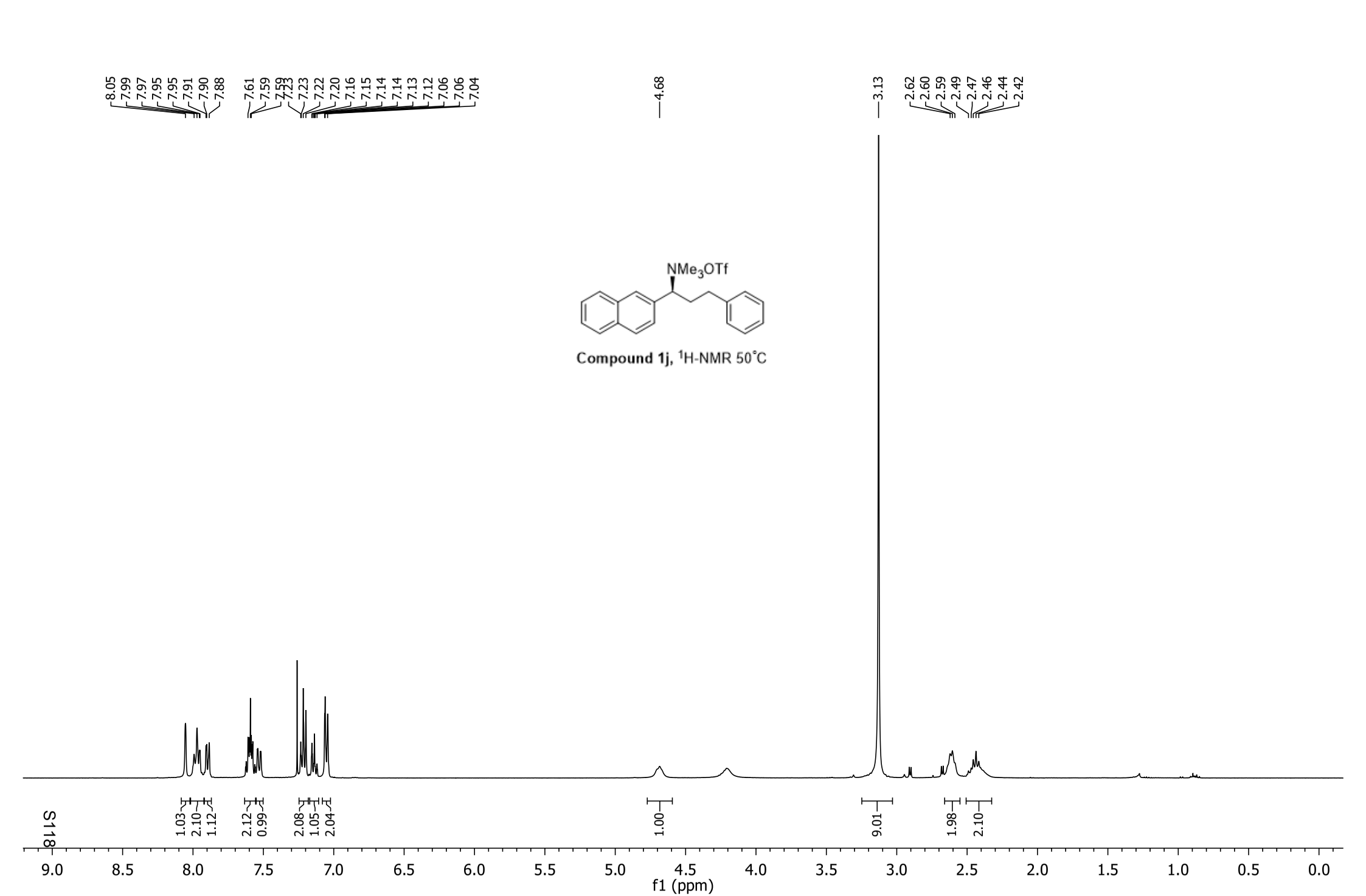

135.16
134.10
133.08
129.90
129.51
128.77
128.12
127.81
127.44
125.56
122.99
122.38
119.20
116.02
102.80
78.92
65.11
65.02
51.76
29.98
NMe3OTf
O
O
Compound 1i, 13C-NMR
S114
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

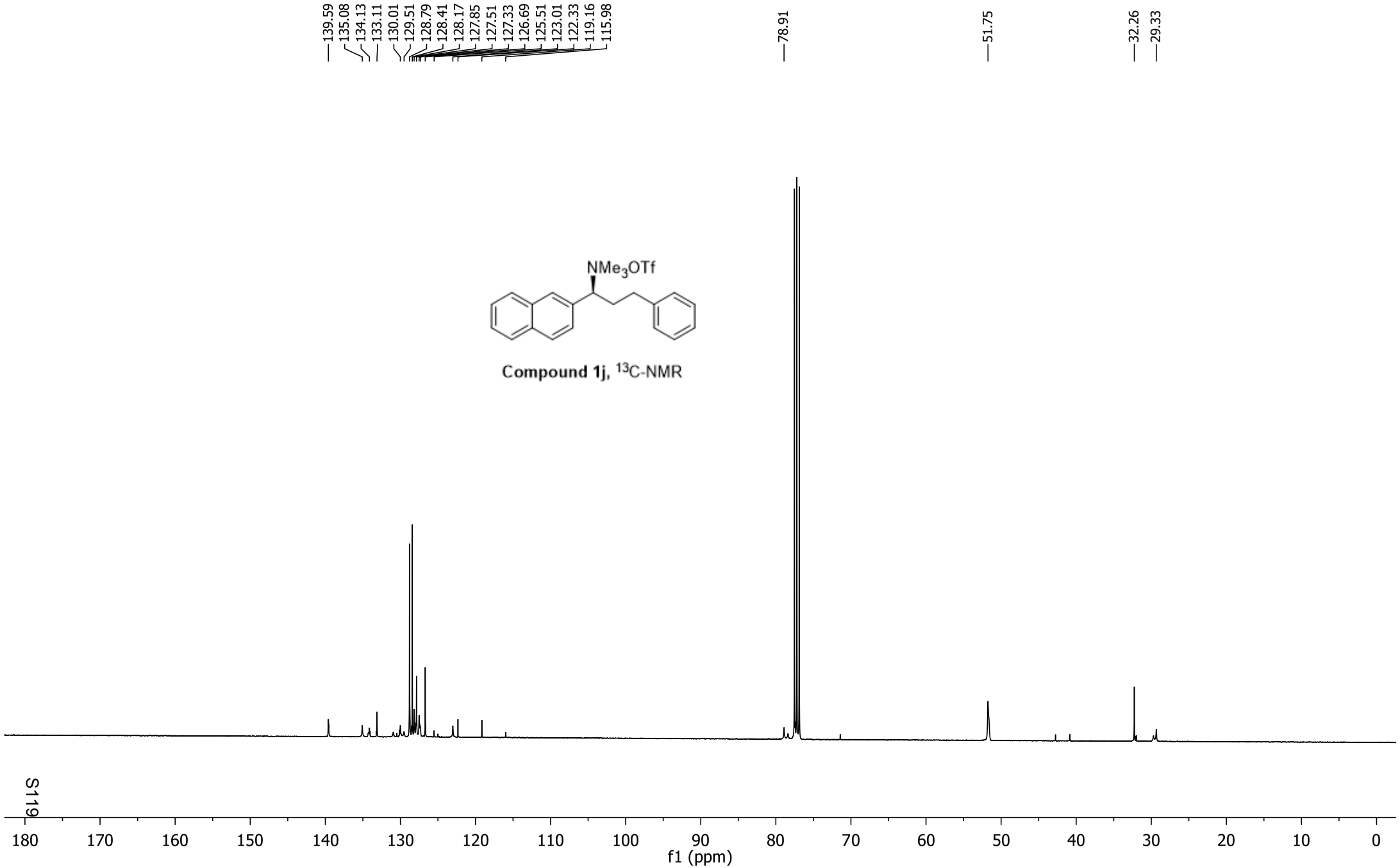

NMe3OTf
O
O
Compound 1i, HMBC
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

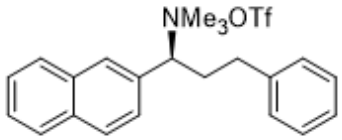

NMe3OTf
O
O
Compound 1i, HSQC
f2 (ppm)
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150



Compound 1j, ^{1}H-NMR


8.05
7.99
7.97
7.95
7.95
7.91
7.90
7.88
7.61
7.59
7.59
7.23
7.23
7.22
7.20
7.16
7.15
7.14
7.14
7.13
7.12
7.06
7.06
7.04
4.68
3.13
2.62
2.60
2.59
2.49
2.47
2.46
2.44
2.42
NMe3OTf
Compound 1j, 1H-NMR 50˚C
1.03
2.10
1.12
2.12
0.99
2.08
1.05
2.04
1.00
9.01
1.98
2.10
S118
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)

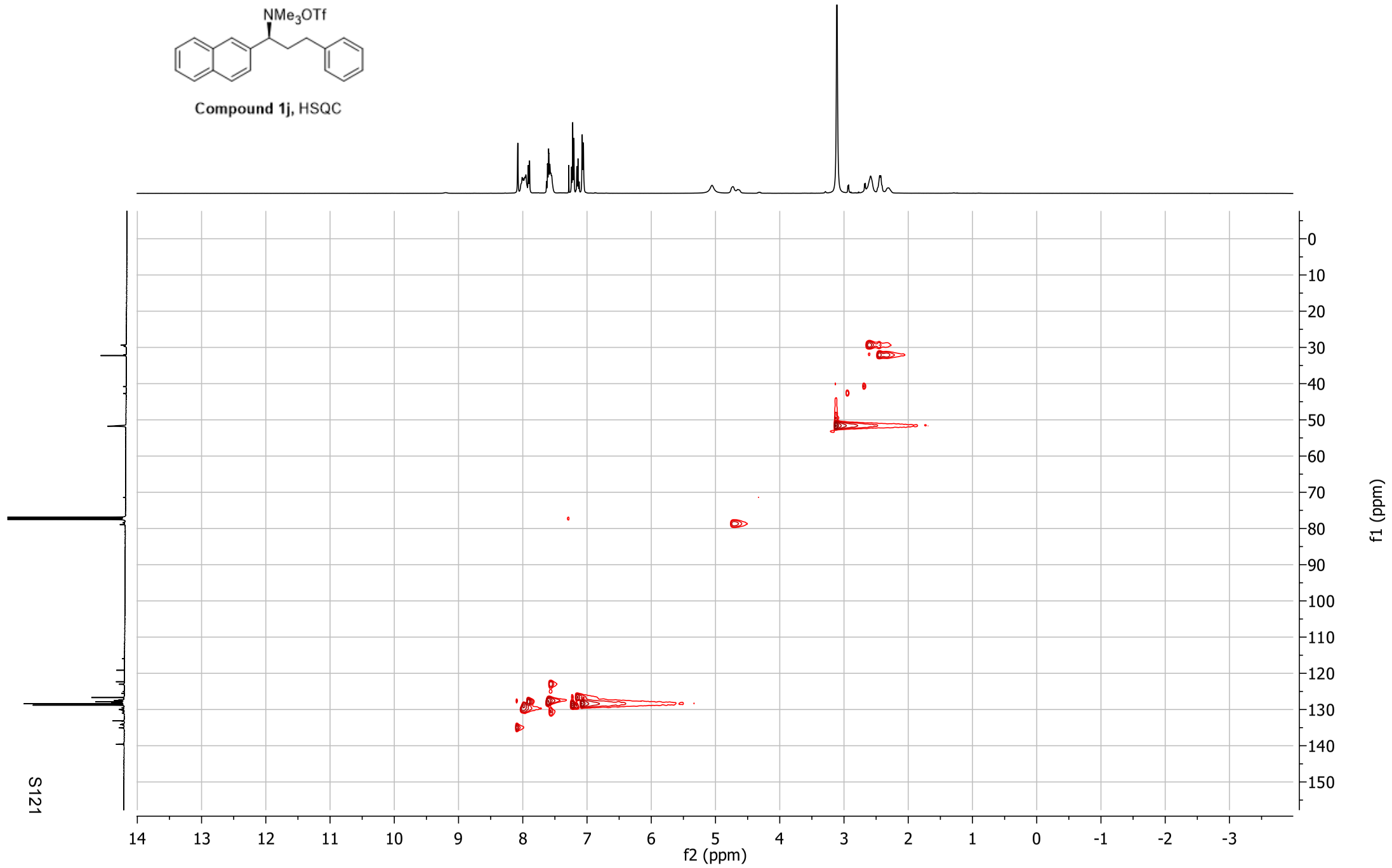

139.59
135.08
134.13
133.11
130.01
129.51
128.79
128.41
128.17
127.85
127.51
127.33
126.69
125.51
123.01
122.33
119.16
115.98
78.91
51.75
32.26
29.33
NMe3OTf
Compound 1j, 13C-NMR
S119
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

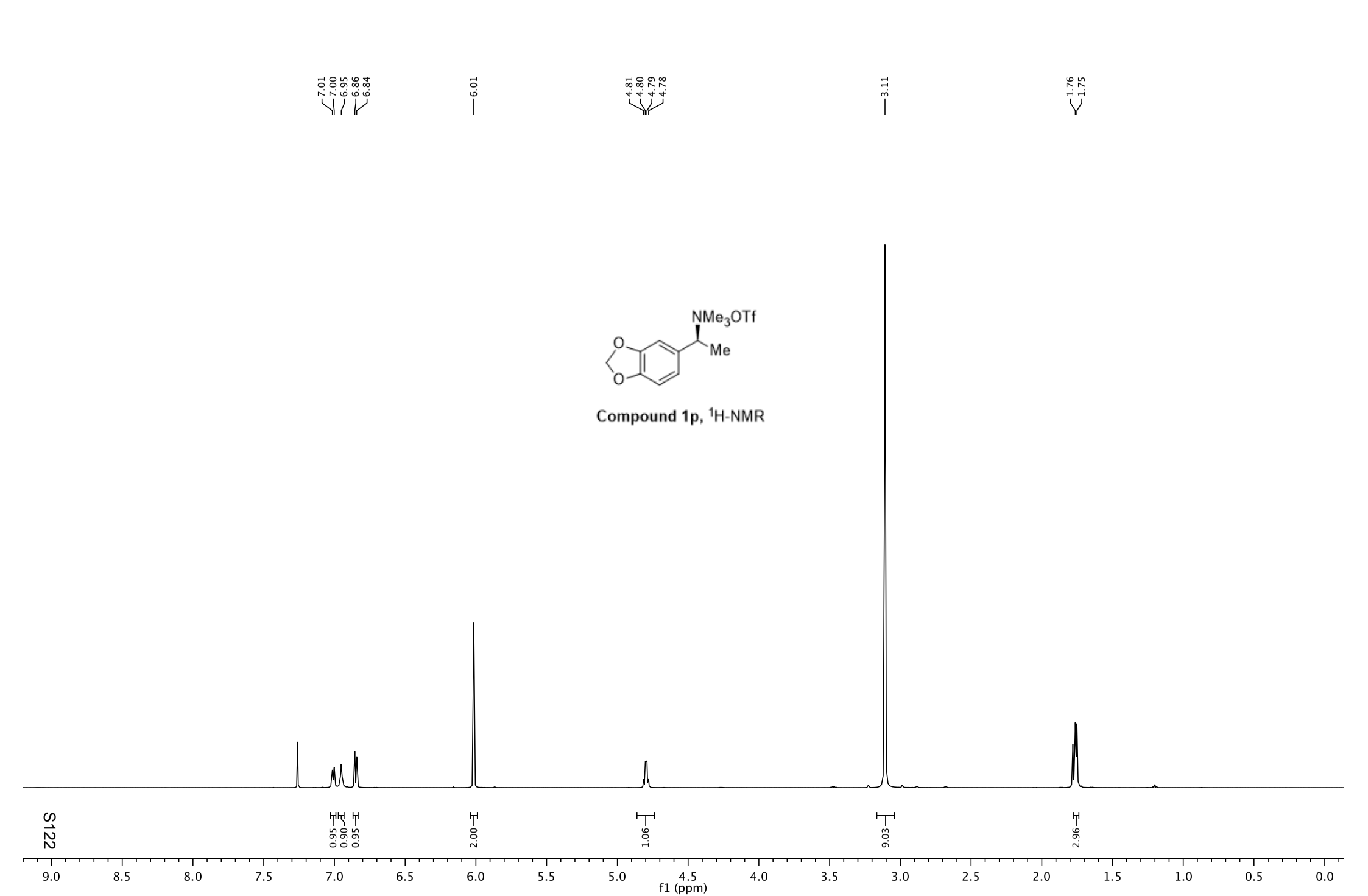


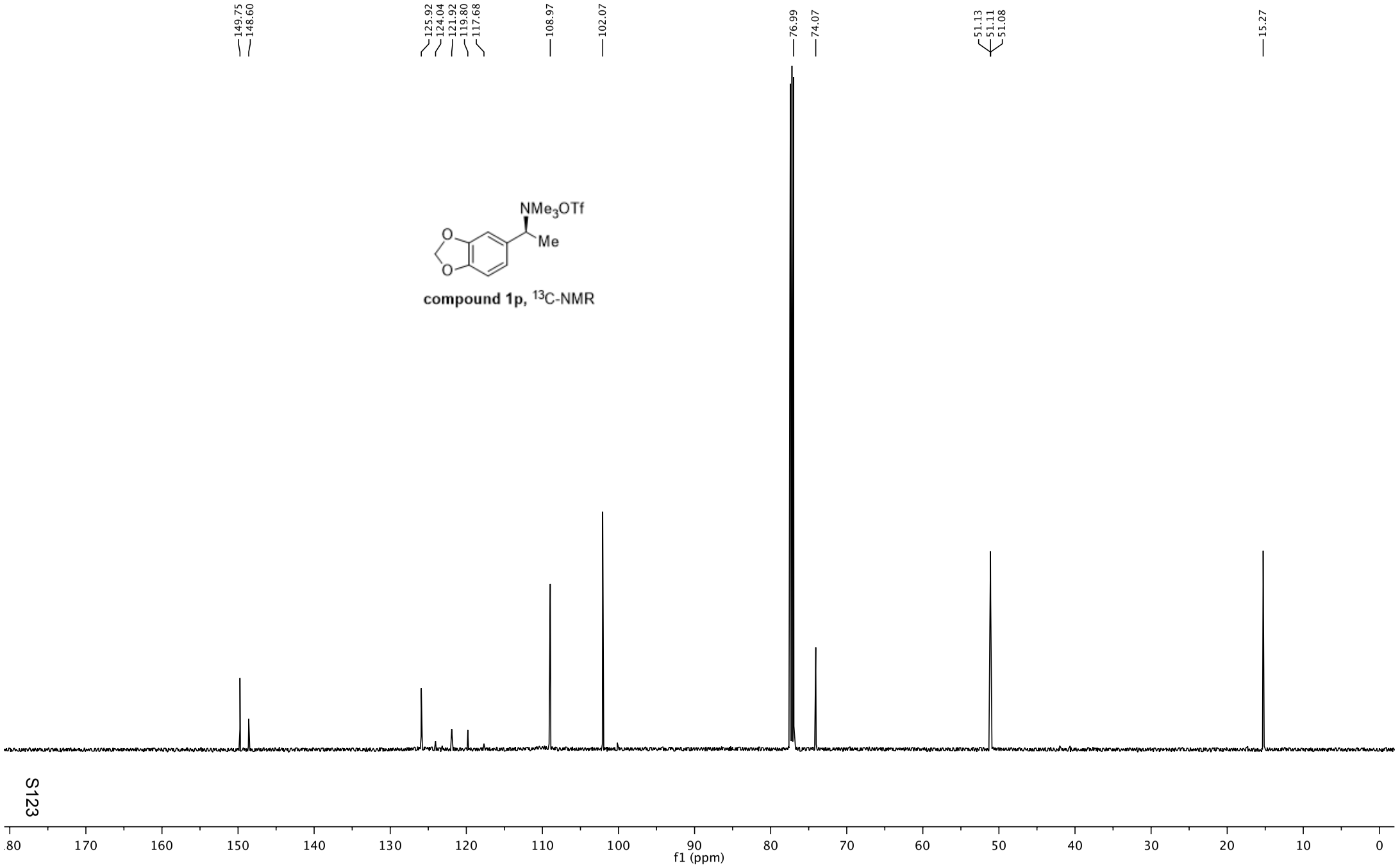
Compound 1j, HMBC

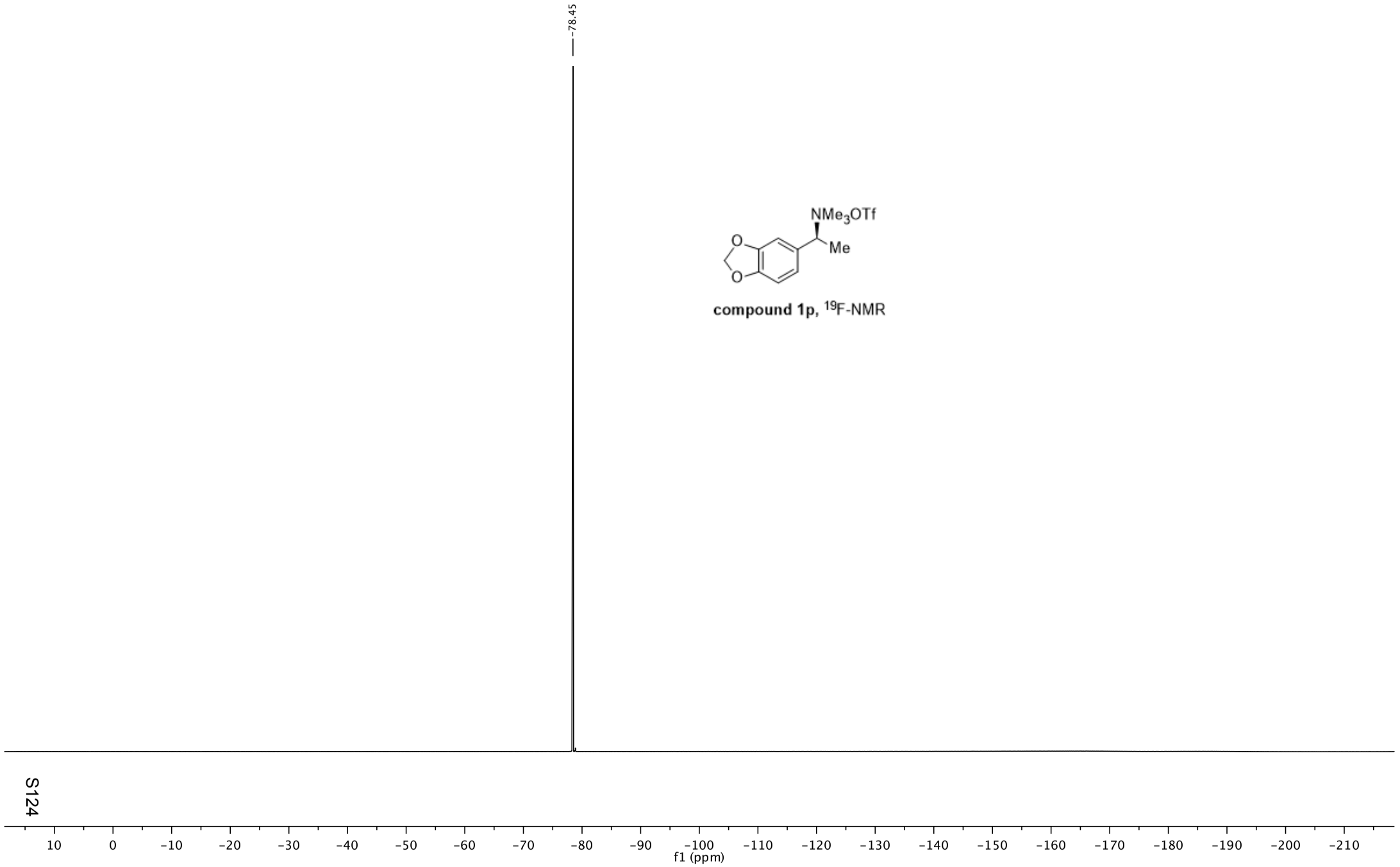
f2 (ppm)

f1 (ppm)

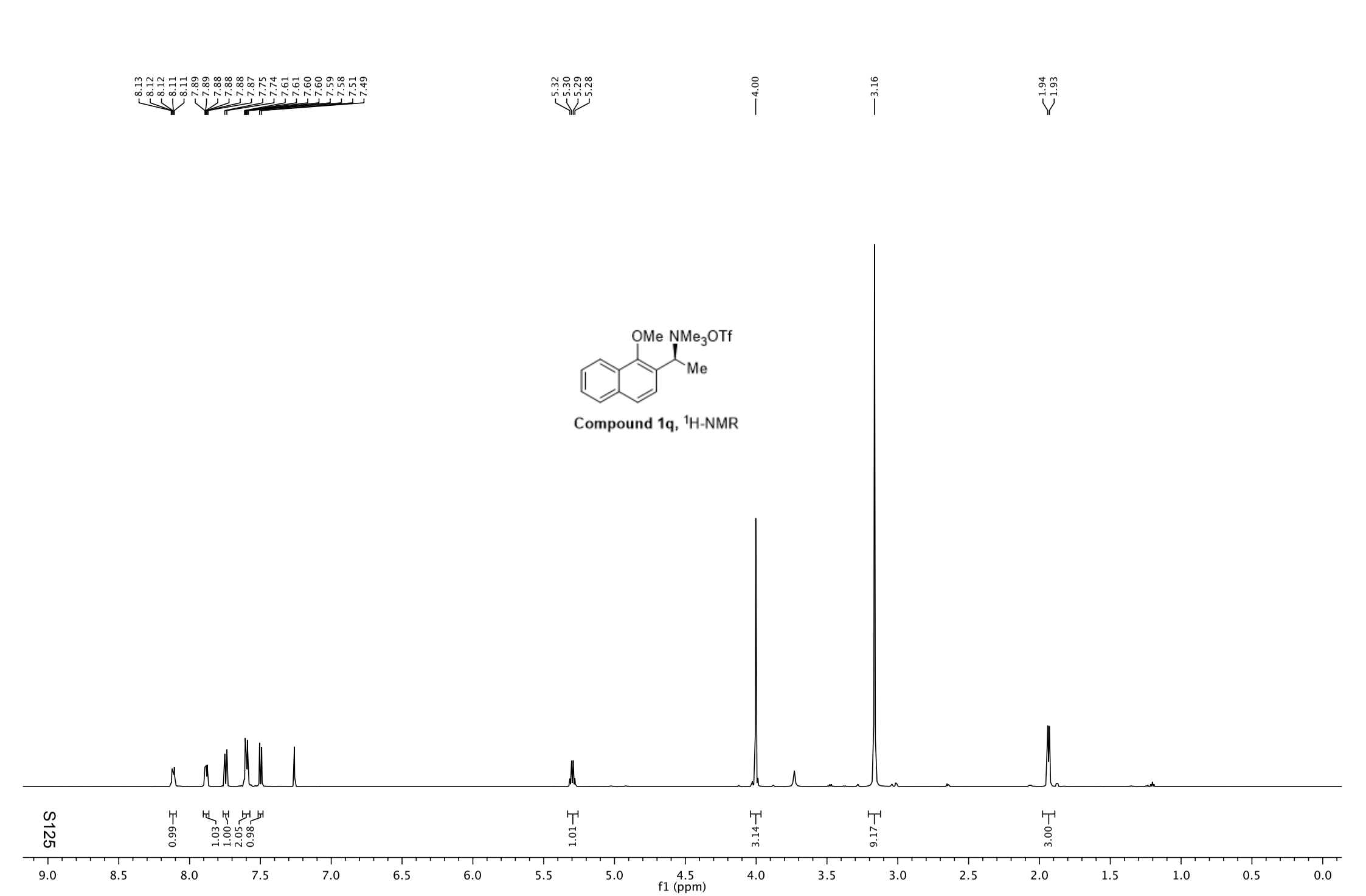

NMe3OTf
Compound 1j, HSQC
f2 (ppm)
f1 (ppm)
S121

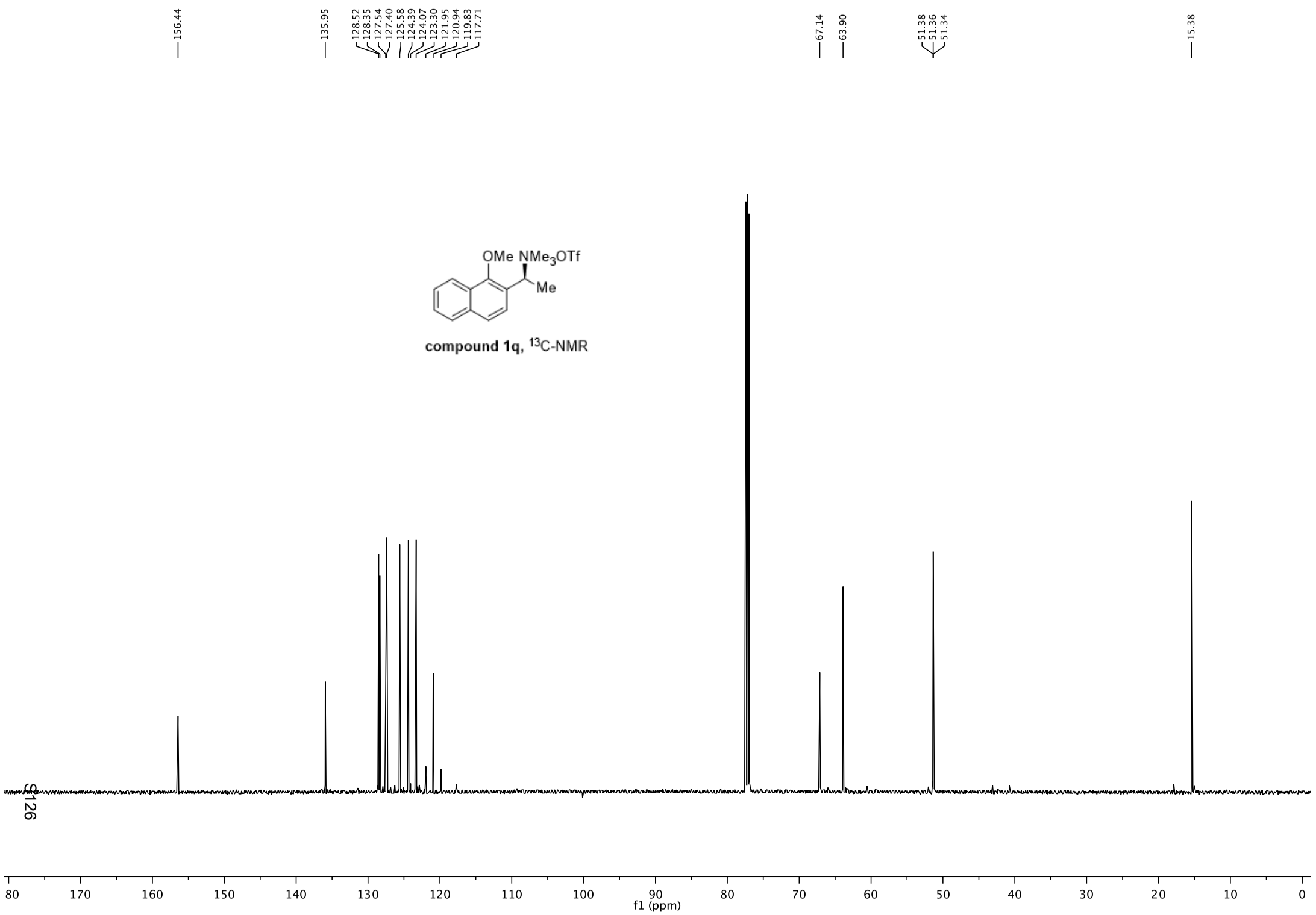

7.01
7.00
6.95
6.86
6.84
6.01
4.81
4.80
4.79
4.78
3.11
1.76
1.75
NMe3OTf
Me
O
O
Compound 1p, 1H-NMR
S122
0.95
0.90
0.95
2.00
1.06
9.03
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

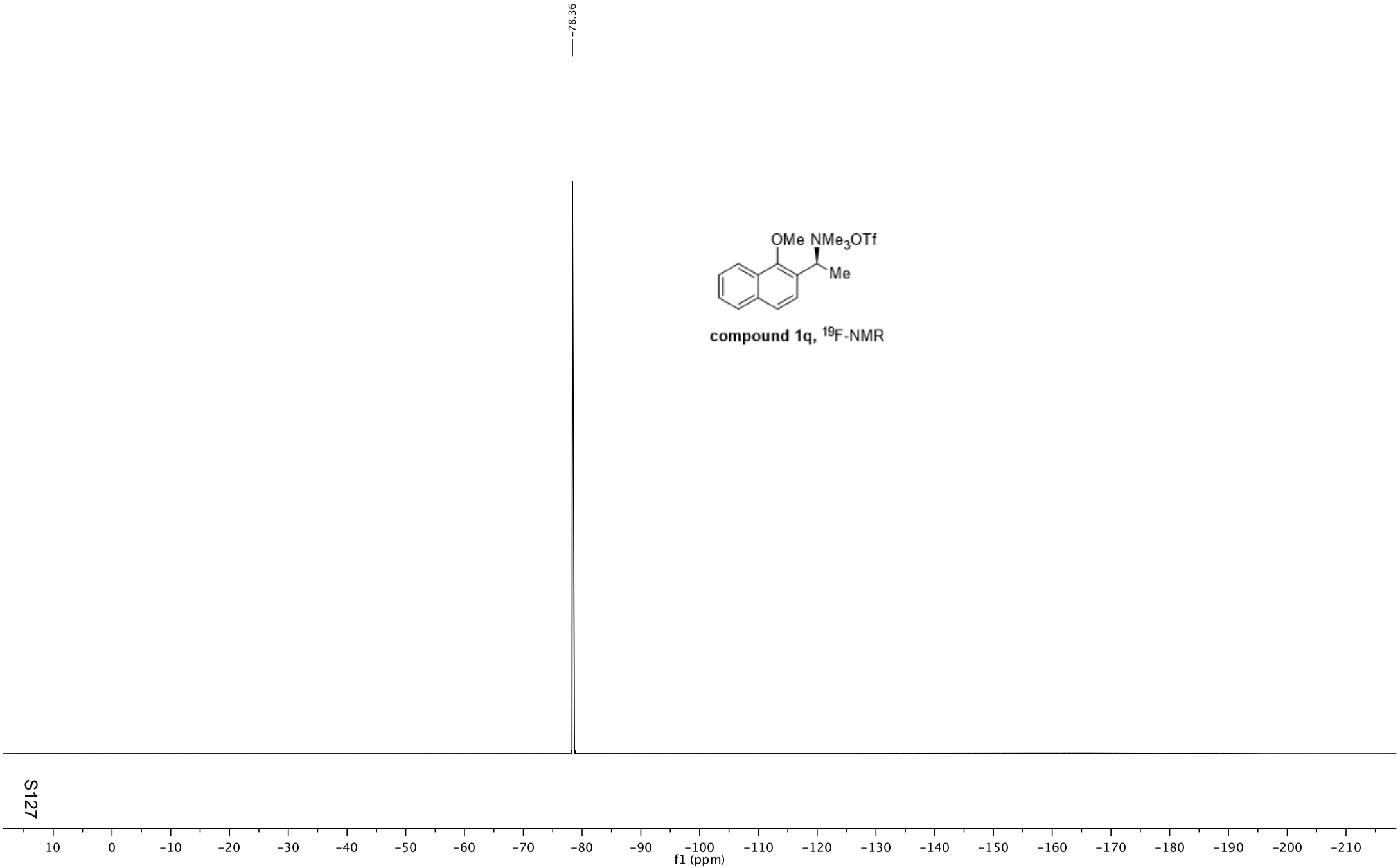

149.75
148.60
125.92
124.04
121.92
119.80
117.68
108.97
102.07
76.99
74.07
51.13
51.11
51.08
15.27
NMe3OTf
Me
O
O
compound 1p, 13C-NMR
f1 (ppm)



compound 1p, ^{19}F-NMR

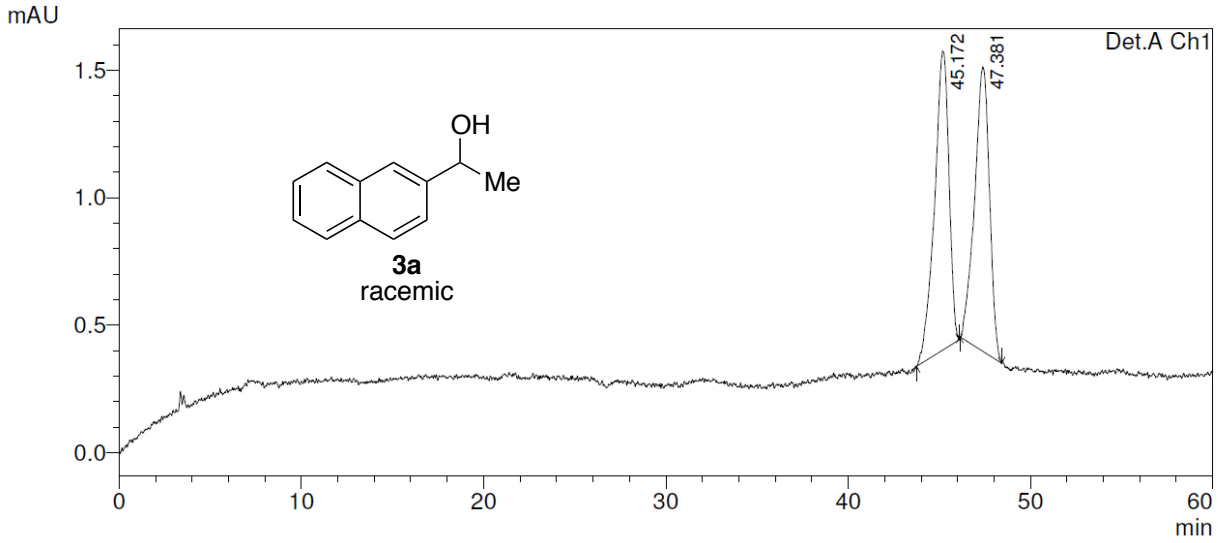

8.13
8.12
8.12
8.11
8.11
7.89
7.89
7.88
7.88
7.88
7.87
7.75
7.74
7.61
7.60
7.60
7.59
7.58
7.51
7.49
5.32
5.30
5.29
5.28
4.00
3.16
1.94
1.93
OMe NMe3OTf
Me
Compound 1q, 1H-NMR
S125
0.99
1.03
1.00
2.05
0.98
1.01
3.14
9.17
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.44
135.95
128.52
128.35
127.54
127.40
125.58
124.39
124.07
123.30
121.95
120.94
119.83
117.71
67.14
63.90
51.38
51.36
51.34
15.38
OMe NMe3OTf
Me
compound 1q, 13C-NMR
6126
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



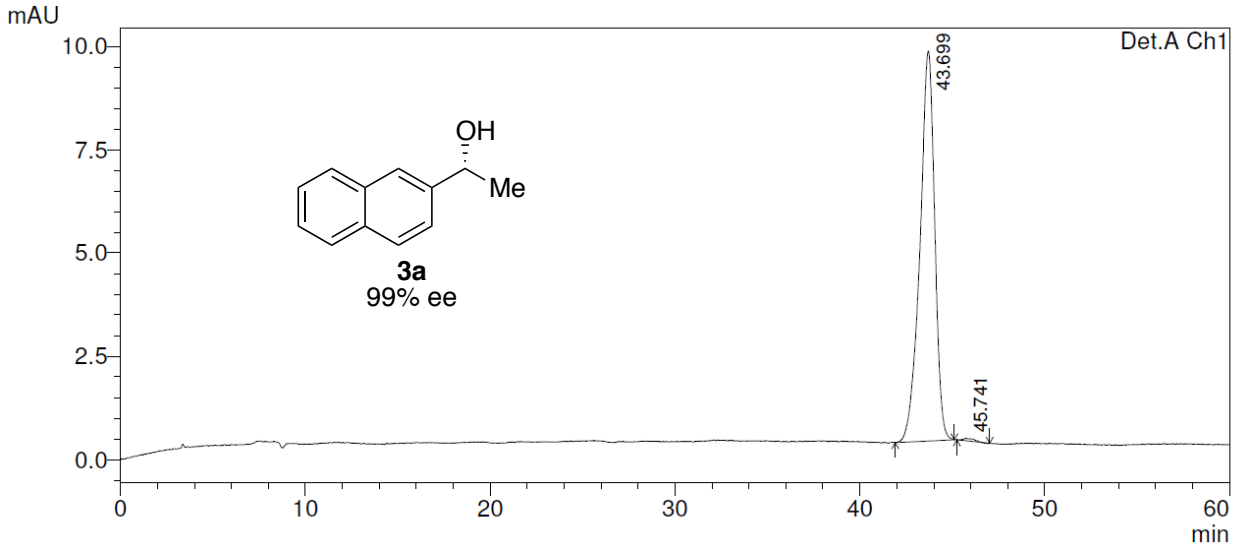
compound 1q, ^{19}F-NMR

Compound **3a**, racemic (254 nm)



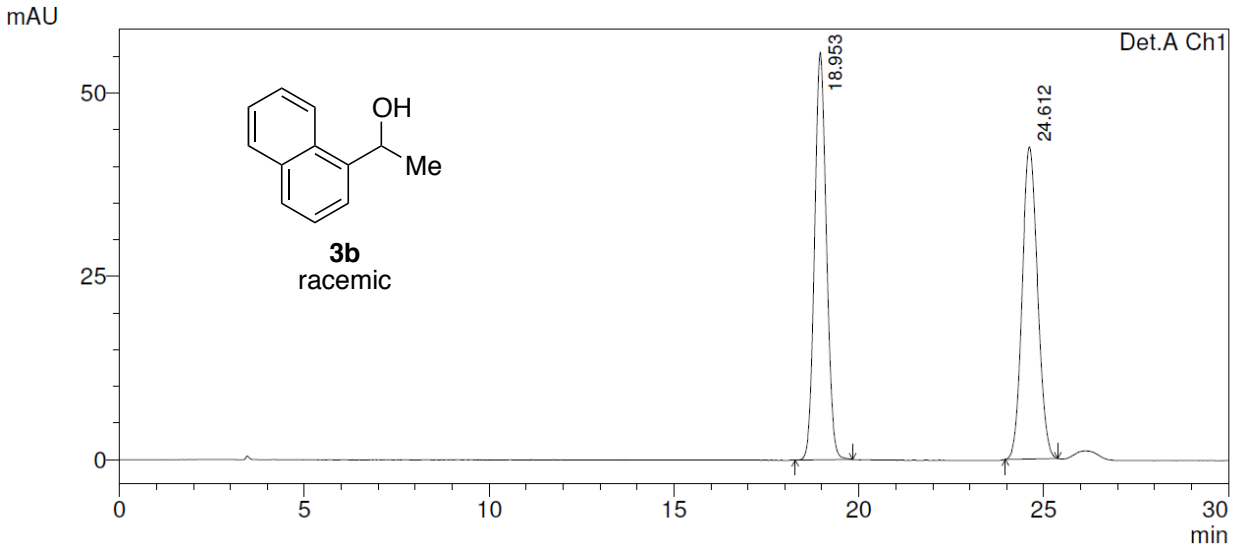
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound **3a**, 99% ee (254 nm)



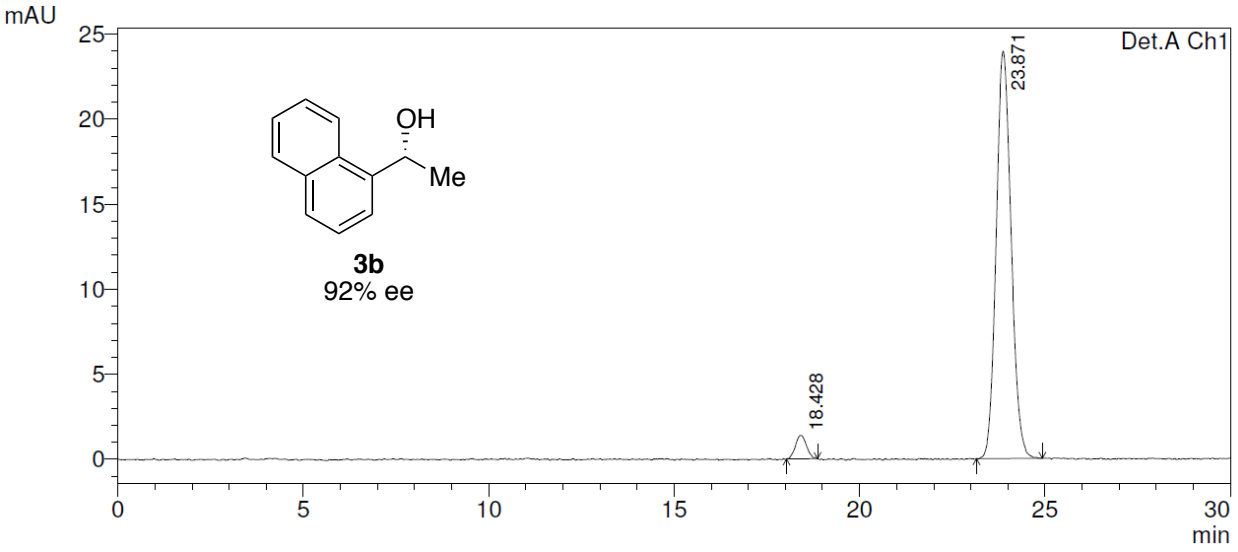
Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.699	524955	9434	99.543	99.356
2	45.741	2408	61	0.457	0.644
Total		527362	9495	100.000	100.000

Compound **3b**, racemic (254 nm)



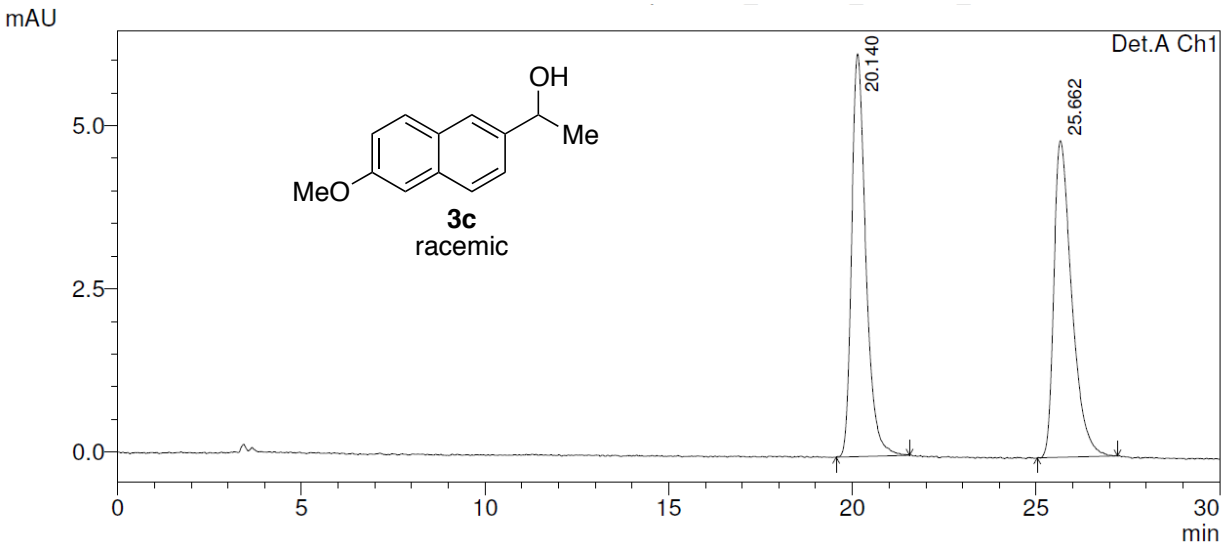
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.953	1239231	55611	50.146	56.632
2	24.612	1232017	42586	49.854	43.368
Total		2471248	98197	100.000	100.000

Compound **3b**, 92% ee (254 nm)



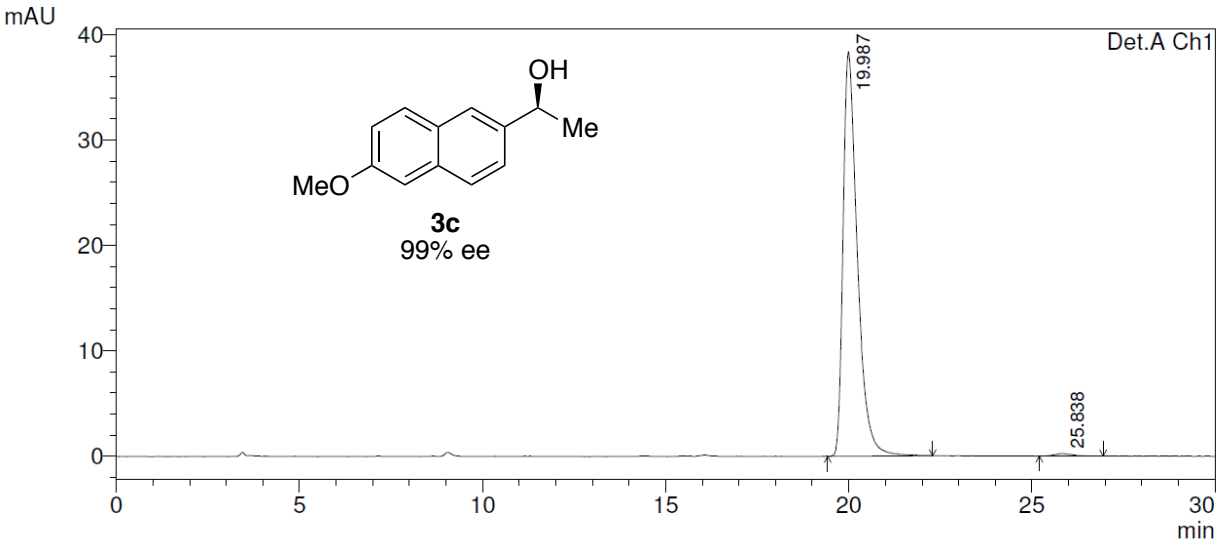
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.428	28226	1362	4.034	5.381
2	23.871	671567	23948	95.966	94.619
Total		699793	25310	100.000	100.000

Compound **3c**, racemic (254 nm)



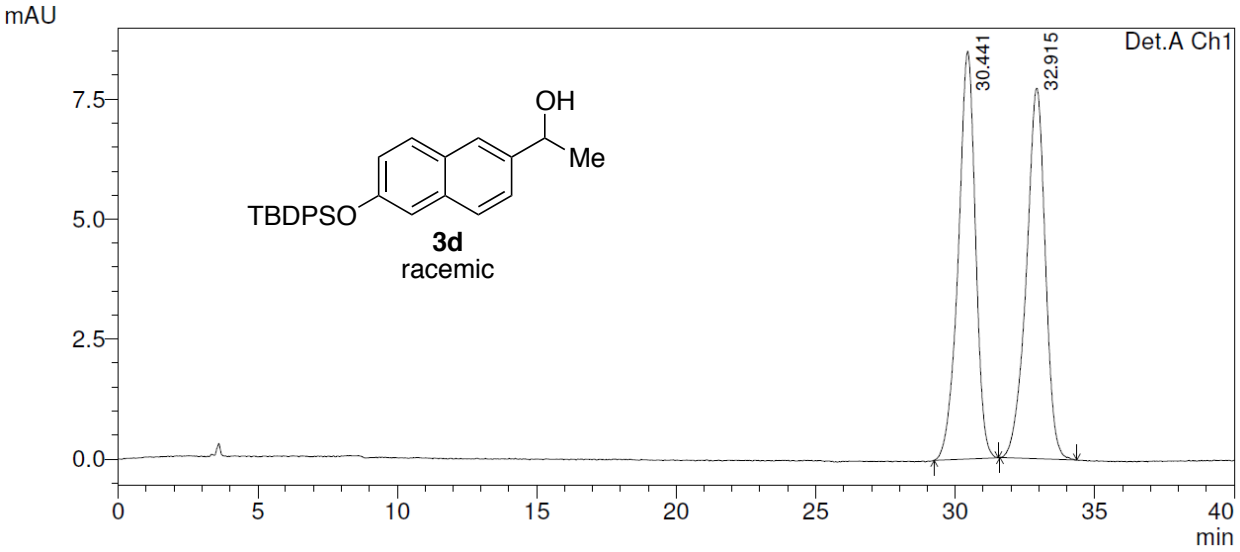
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.140	165137	6165	50.153	55.982
2	25.662	164128	4848	49.847	44.018
Total		329266	11013	100.000	100.000

Compound **3c**, 99% ee (254 nm)



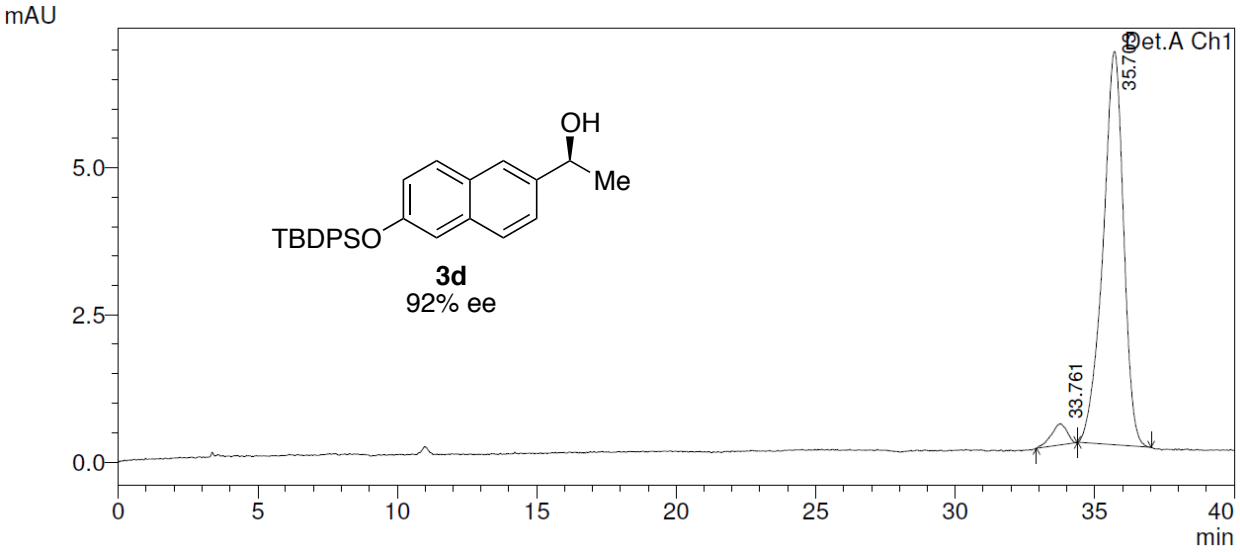
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.987	1037849	38360	99.309	99.372
2	25.838	7220	242	0.691	0.628
Total		1045069	38602	100.000	100.000

Compound **3d**, racemic (254 nm)



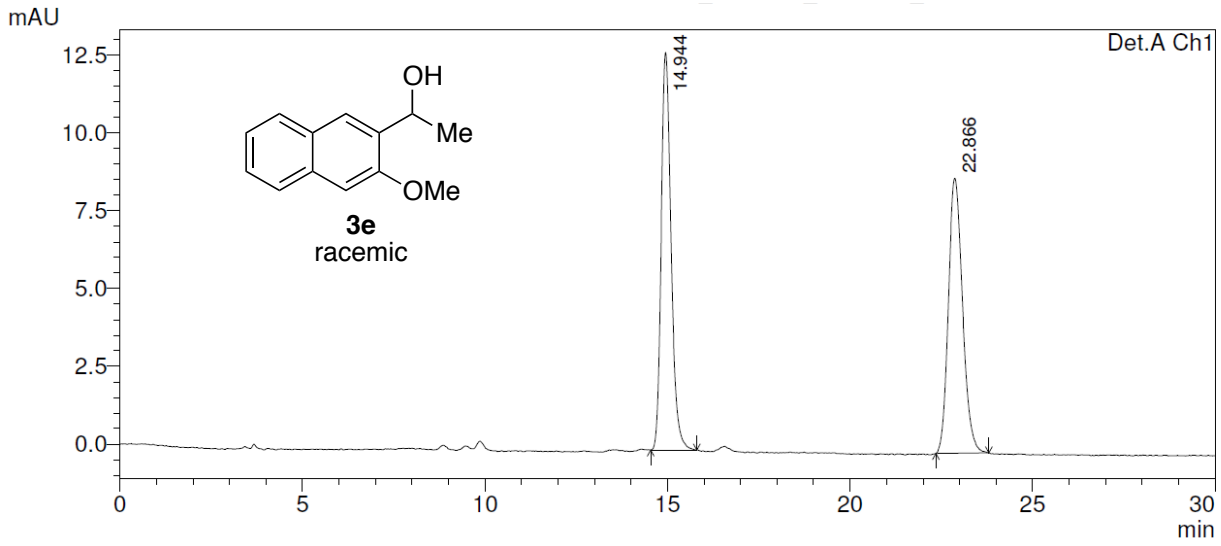
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.441	364152	8496	49.958	52.369
2	32.915	364762	7727	50.042	47.631
Total		728913	16223	100.000	100.000

Compound **3d**, 92% ee (254 nm)



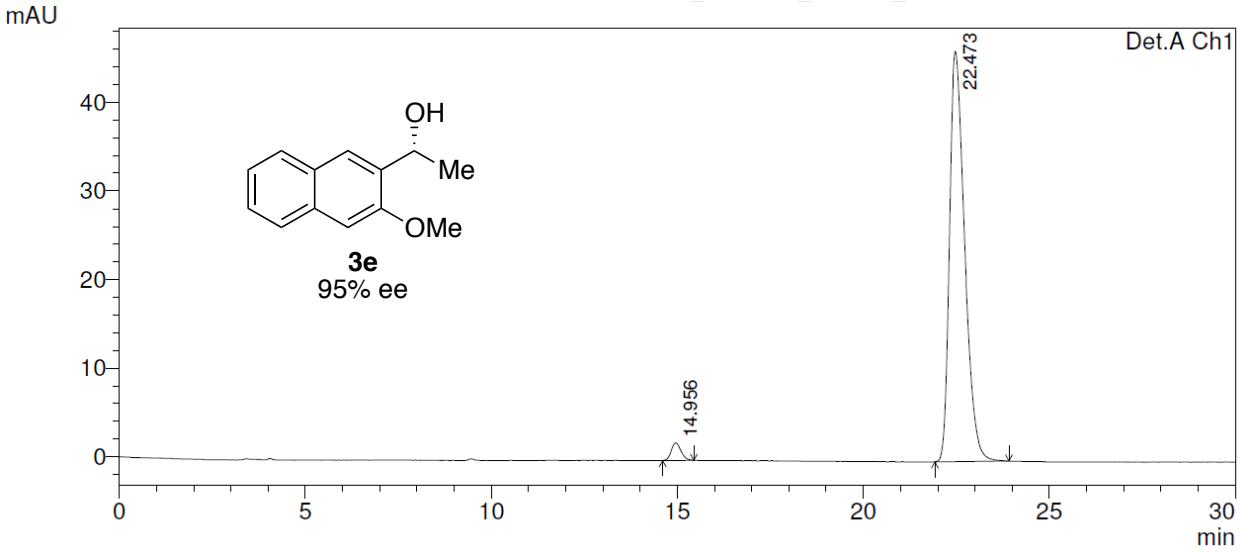
Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.761	14125	358	3.958	5.084
2	35.703	342763	6682	96.042	94.916
Total		356888	7040	100.000	100.000

Compound **3e**, racemic (254 nm)



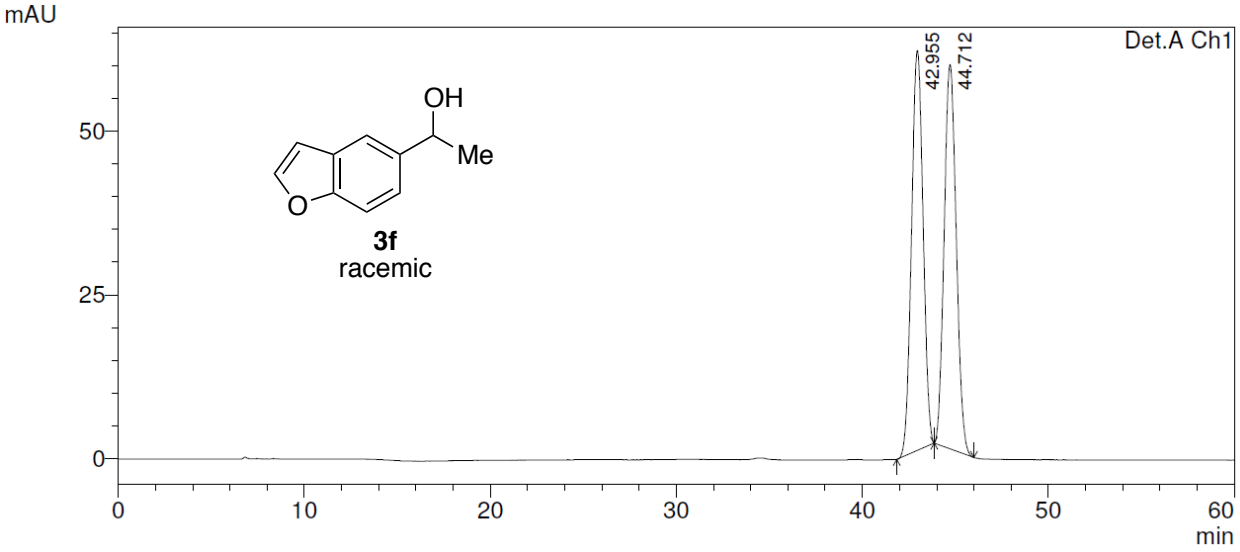
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.944	239370	12773	50.150	59.107
2	22.866	237935	8837	49.850	40.893
Total		477305	21610	100.000	100.000

Compound **3e**, 95% ee (254 nm)



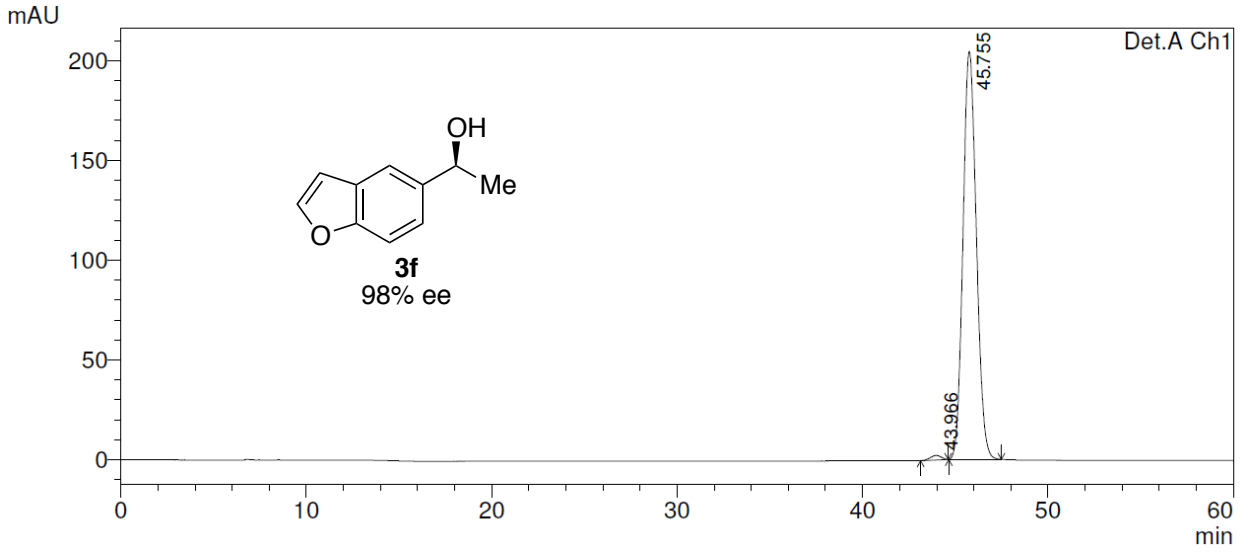
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.956	35963	1982	2.675	4.104
2	22.473	1308675	46315	97.325	95.896
Total		1344638	48297	100.000	100.000

Compound **3f**, racemic (254 nm)



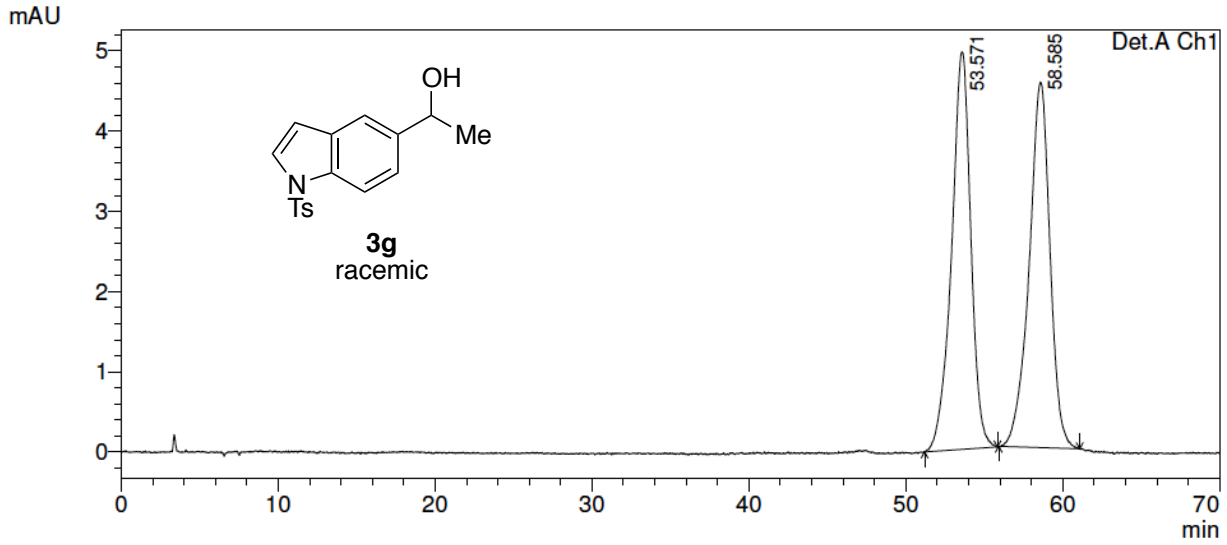
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.955	2640838	61031	49.950	51.012
2	44.712	2646127	58610	50.050	48.988
Total		5286965	119641	100.000	100.000

Compound **3f**, 98% ee (254 nm)



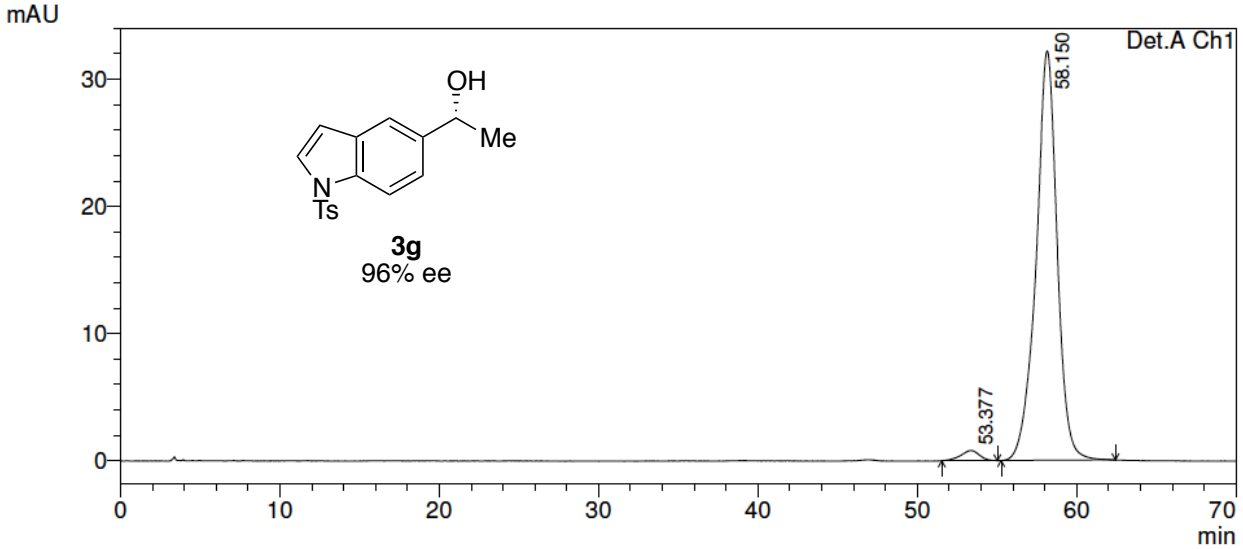
Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.966	90232	2245	0.873	1.086
2	45.755	10242584	204407	99.127	98.914
Total		10332816	206652	100.000	100.000

Compound **3g**, racemic (254 nm)



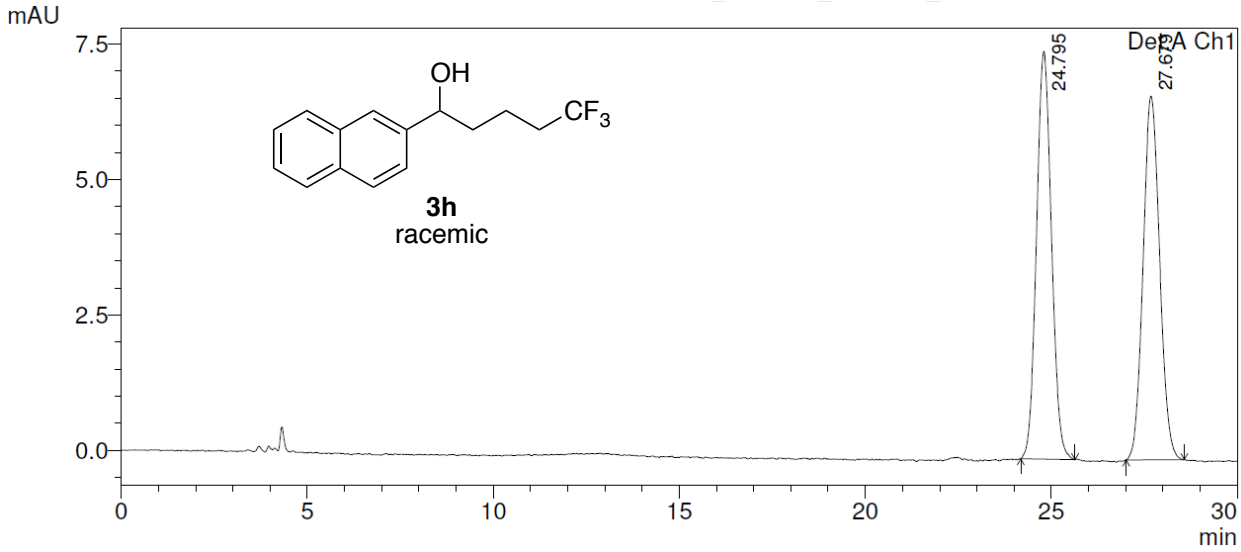
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.571	422898	4957	50.129	52.089
2	58.585	420722	4559	49.871	47.911
Total		843620	9516	100.000	100.000

Compound **3g**, 96% ee (254 nm)



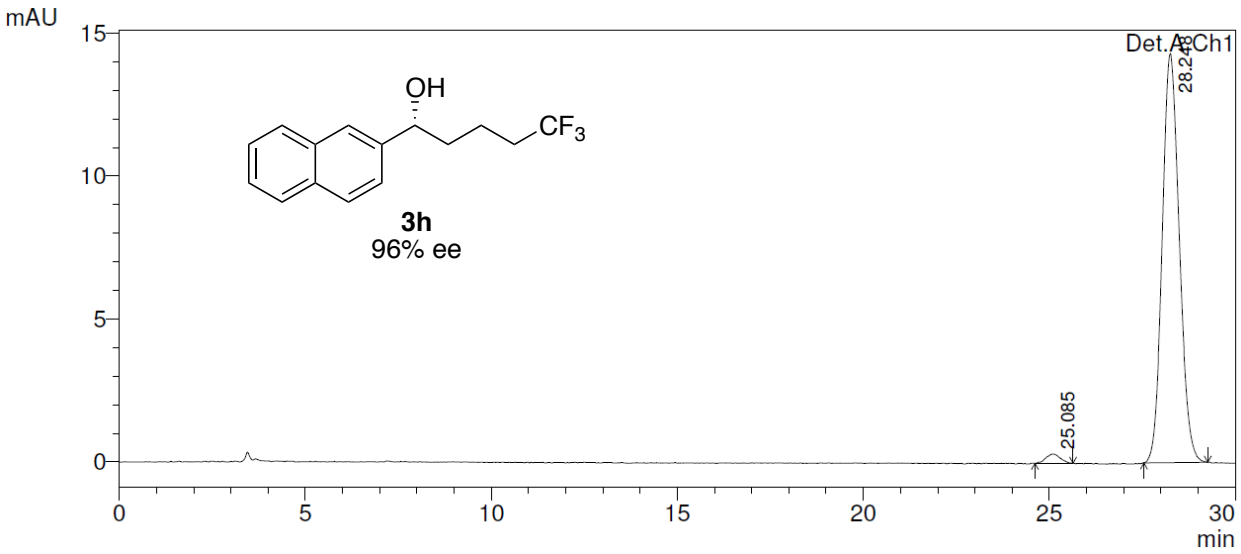
Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.377	64936	808	2.149	2.450
2	58.150	2956179	32179	97.851	97.550
Total		3021114	32987	100.000	100.000

Compound **3h**, racemic (254 nm)



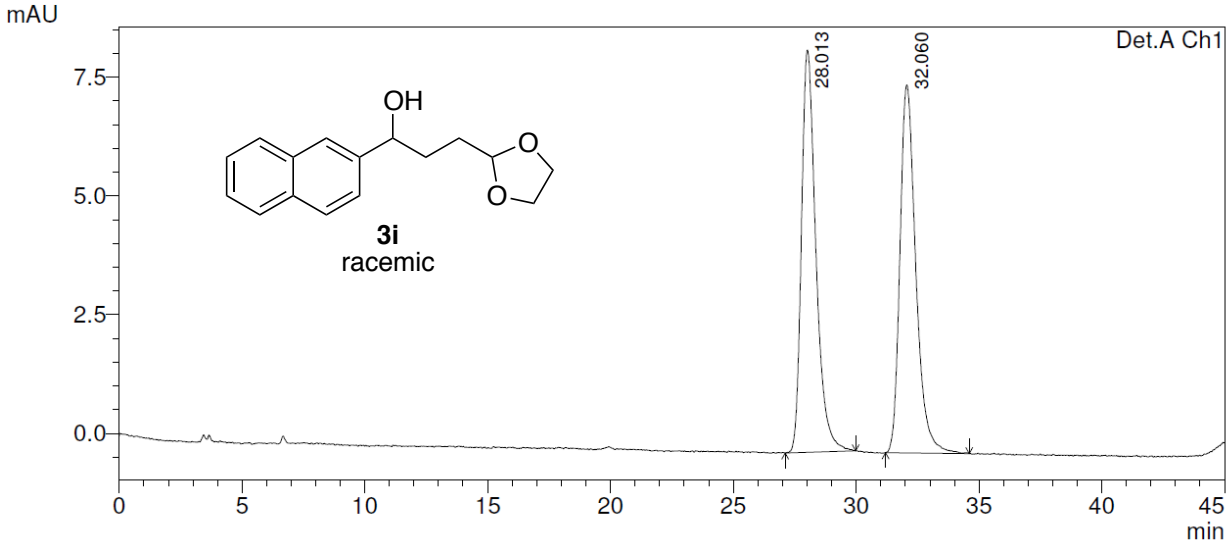
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.795	210483	7521	50.324	52.855
2	27.679	207772	6708	49.676	47.145
Total		418255	14229	100.000	100.000

Compound **3h**, 96% ee (254 nm)



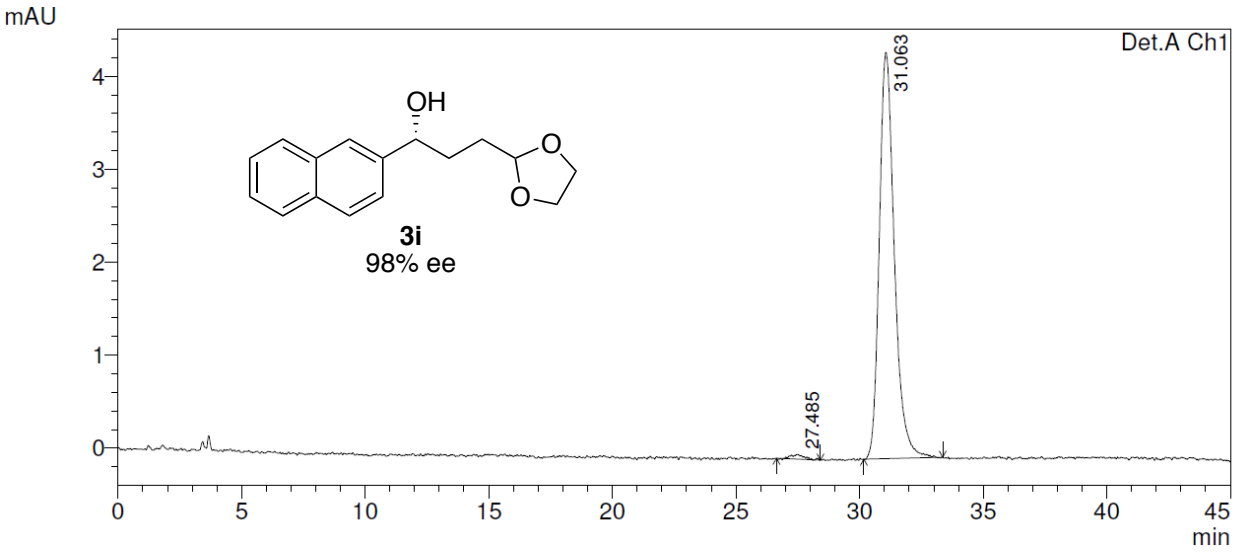
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.085	8553	324	1.840	2.212
2	28.248	456259	14308	98.160	97.788
Total		464812	14632	100.000	100.000

Compound **3i**, racemic (254 nm)



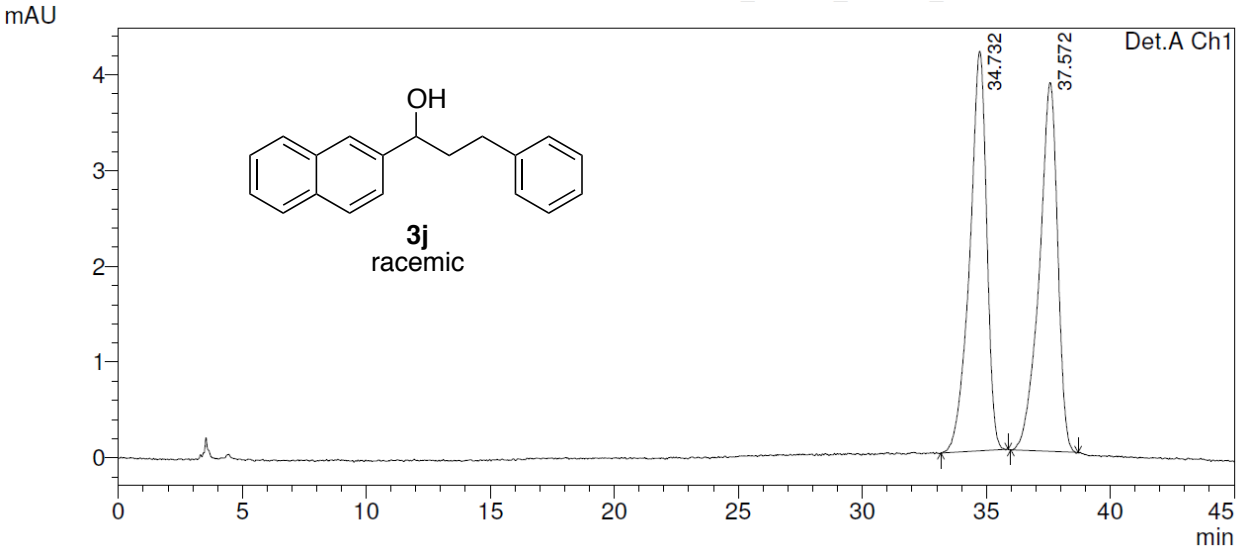
Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.013	346583	8466	49.977	52.224
2	32.060	346898	7745	50.023	47.776
Total		693481	16211	100.000	100.000

Compound **3i**, 98% ee (254 nm)



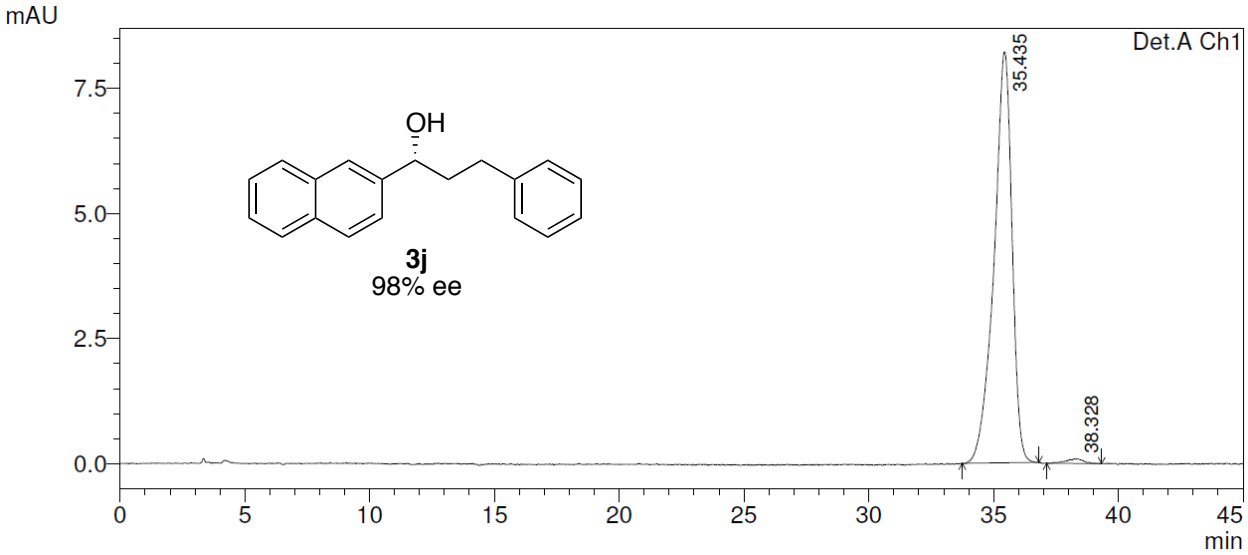
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.485	1806	53	0.968	1.191
2	31.063	184751	4374	99.032	98.809
Total		186557	4426	100.000	100.000

Compound **3j**, racemic (254 nm)



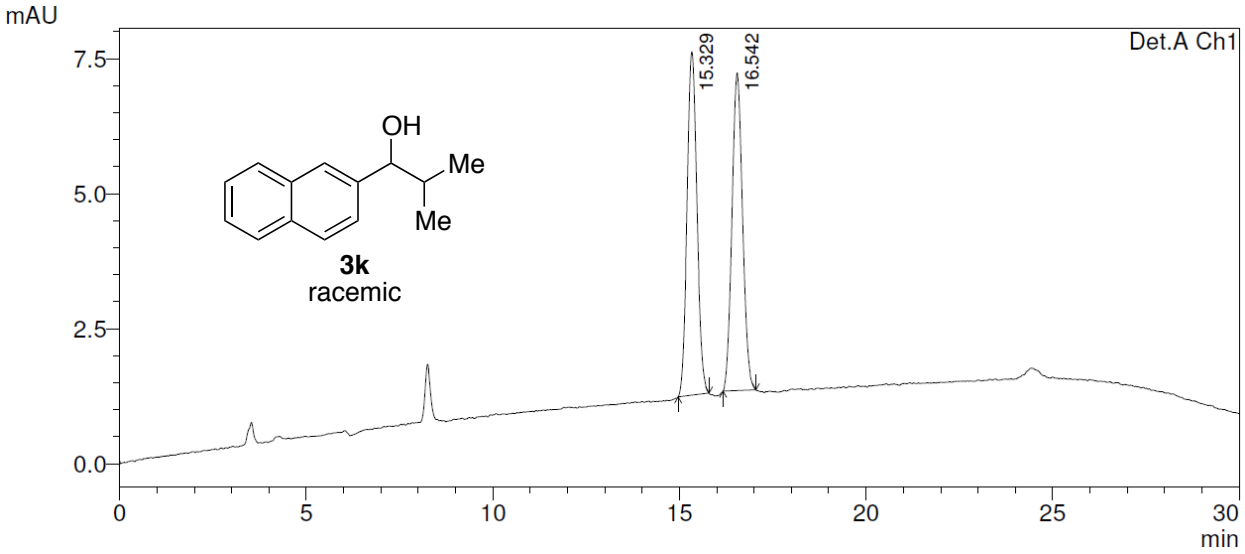
Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.732	198596	4170	50.141	51.978
2	37.572	197482	3853	49.859	48.022
Total		396078	8023	100.000	100.000

Compound **3j**, 98% ee (254 nm)



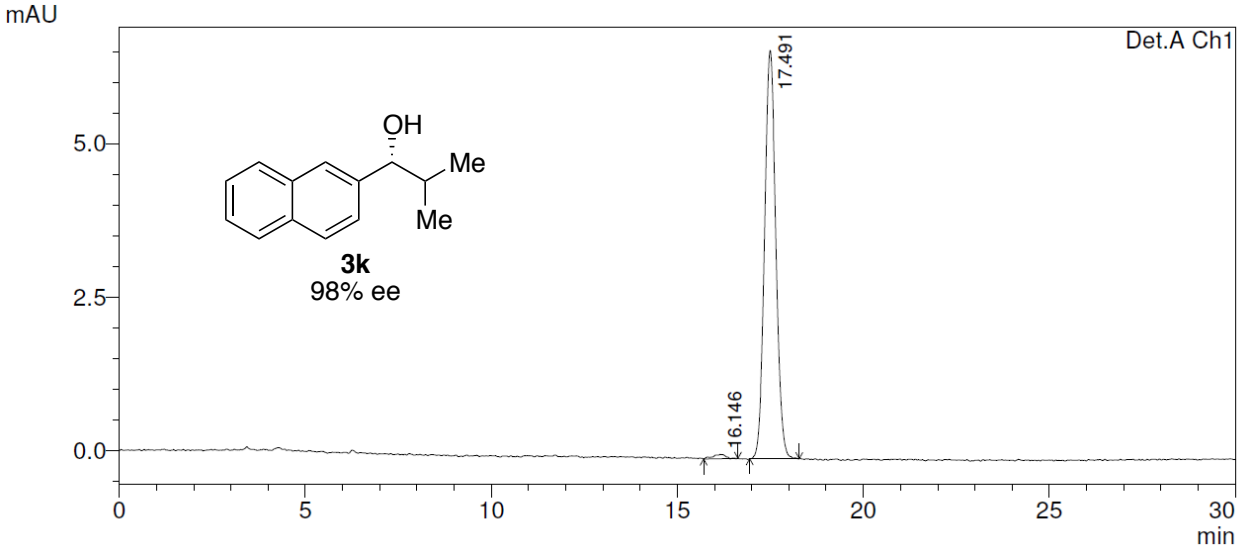
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.435	412336	8222	98.853	98.861
2	38.328	4783	95	1.147	1.139
Total		417119	8317	100.000	100.000

Compound **3k**, racemic (254 nm)



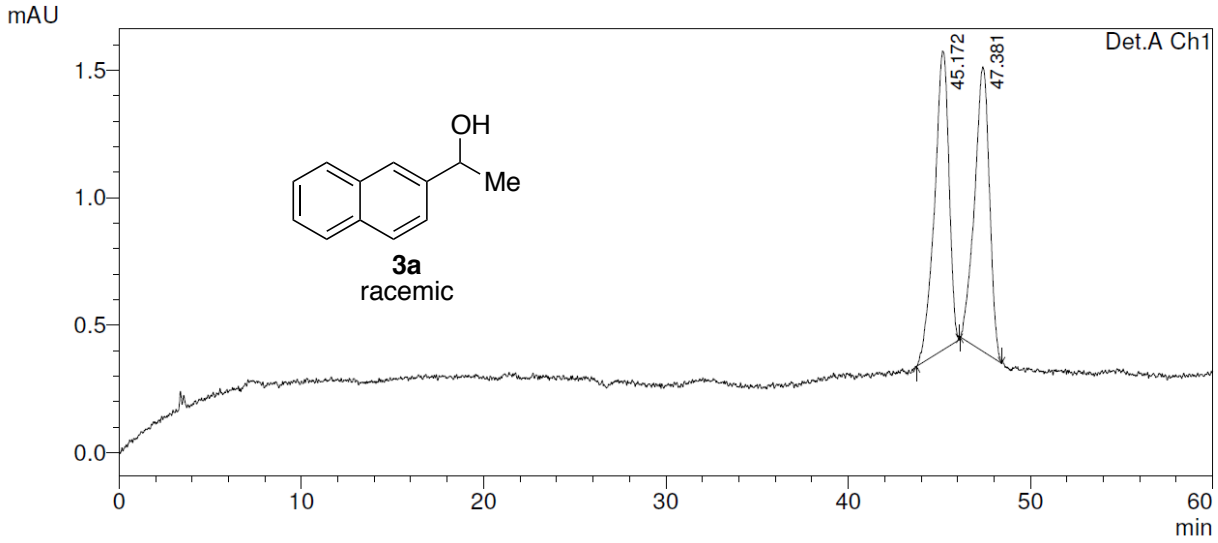
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.329	116684	6363	50.105	51.956
2	16.542	116193	5884	49.895	48.044
Total		232877	12246	100.000	100.000

Compound **3k**, 98% ee (254 nm)



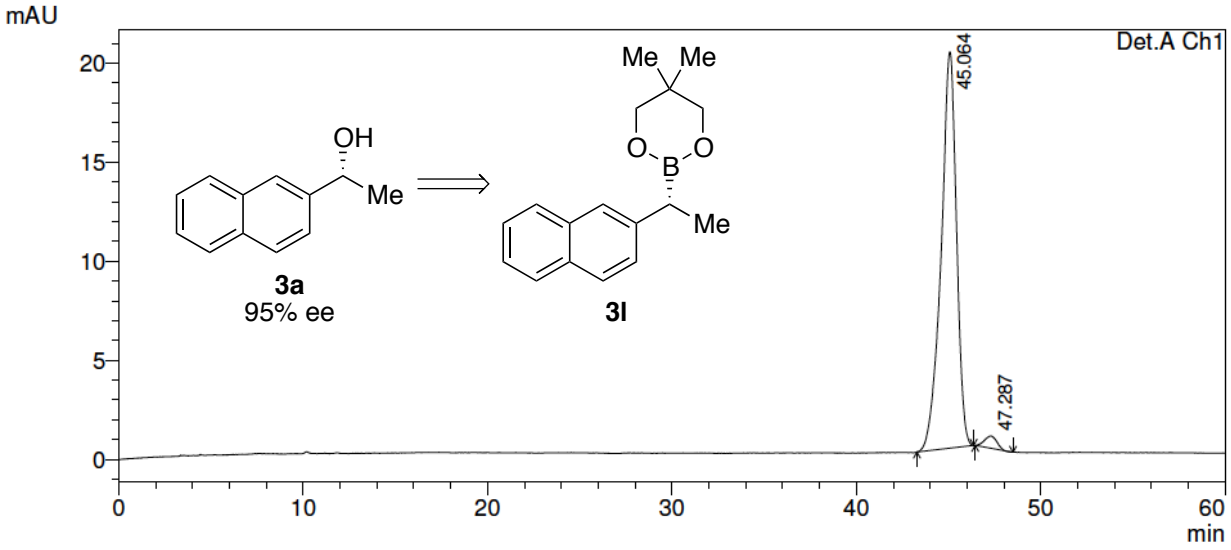
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.146	1594	70	1.126	1.034
2	17.491	140016	6657	98.874	98.966
Total		141610	6726	100.000	100.000

Compound **3a**, racemic (254 nm)



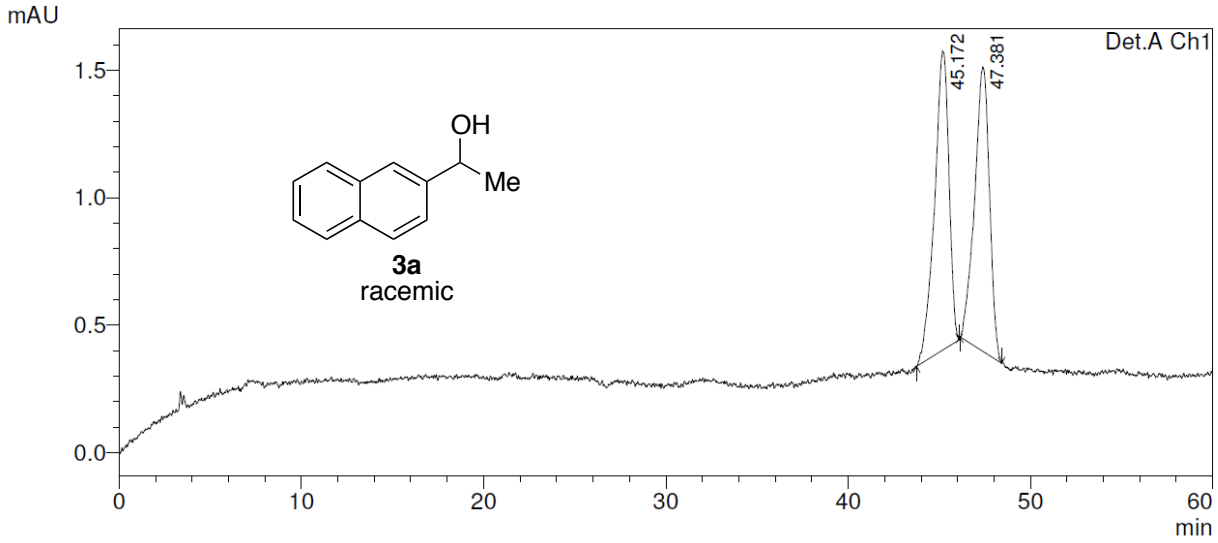
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound **3a**, 95% ee (254 nm)



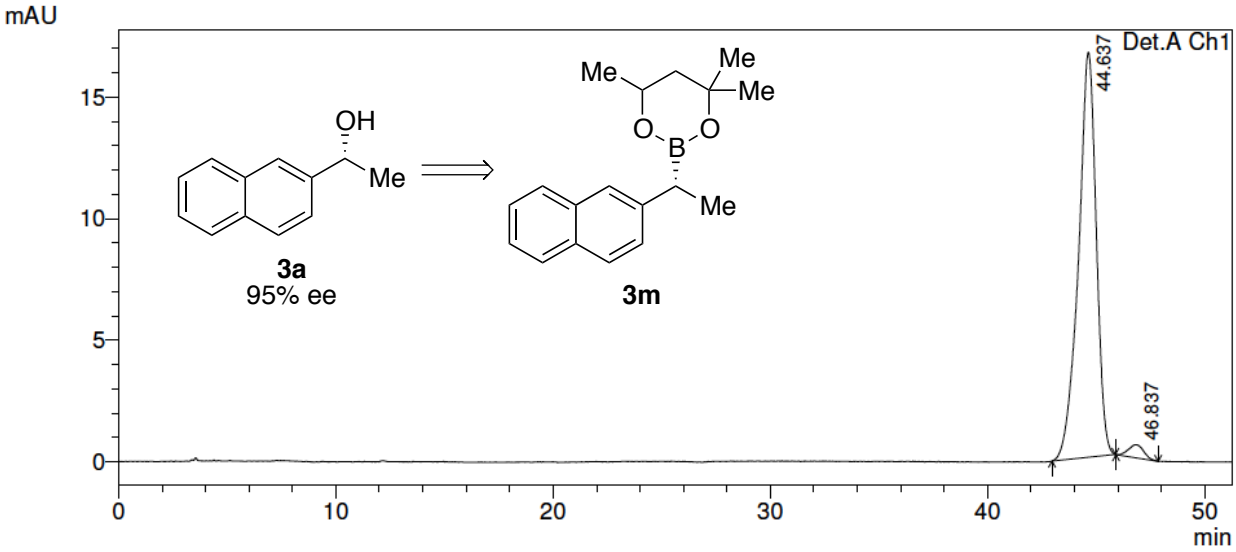
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.064	1159668	20005	97.571	97.019
2	47.287	28864	615	2.429	2.981
Total		1188532	20620	100.000	100.000

Compound **3a**, racemic (254 nm)



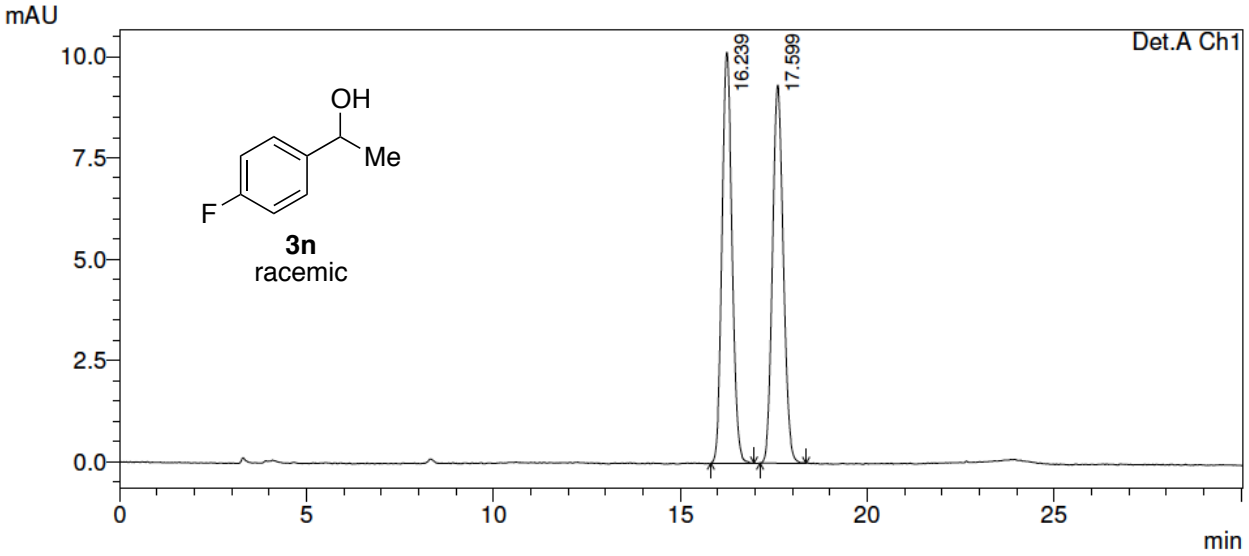
Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.172	64627	1174	50.417	51.245
2	47.381	63558	1117	49.583	48.755
Total		128185	2292	100.000	100.000

Compound **3a**, 95% ee (254 nm)



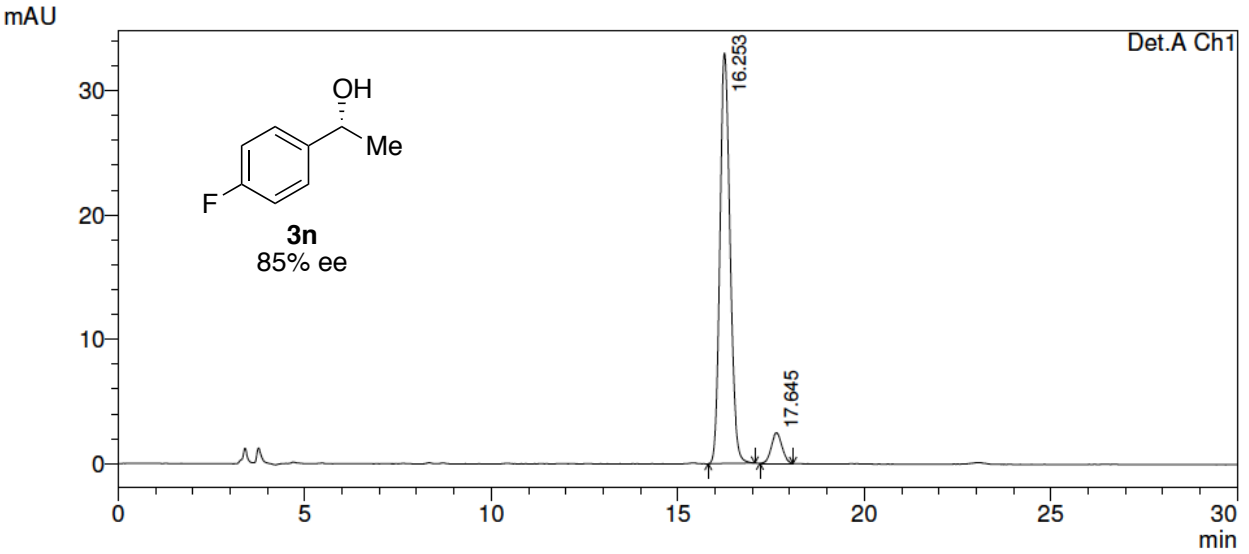
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.637	946536	16673	97.303	96.868
2	46.837	26234	539	2.697	3.132
Total		972770	17212	100.000	100.000

Compound **3n**, racemic (254 nm)



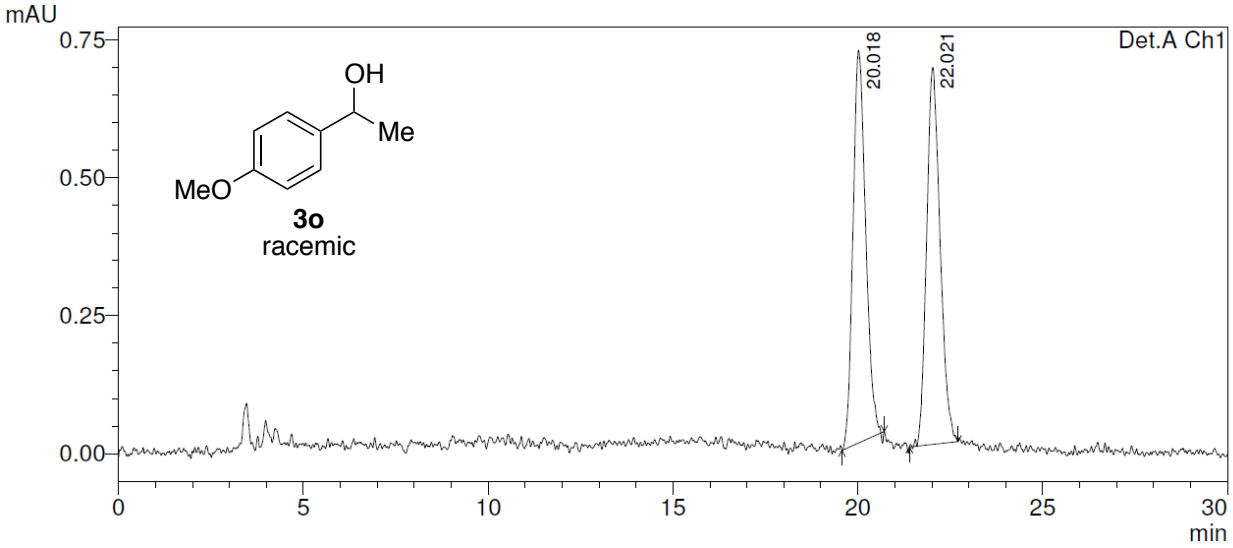
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.239	189291	10142	50.049	52.077
2	17.599	188917	9333	49.951	47.923
Total		378208	19476	100.000	100.000

Compound **3n**, 85% ee (254 nm)



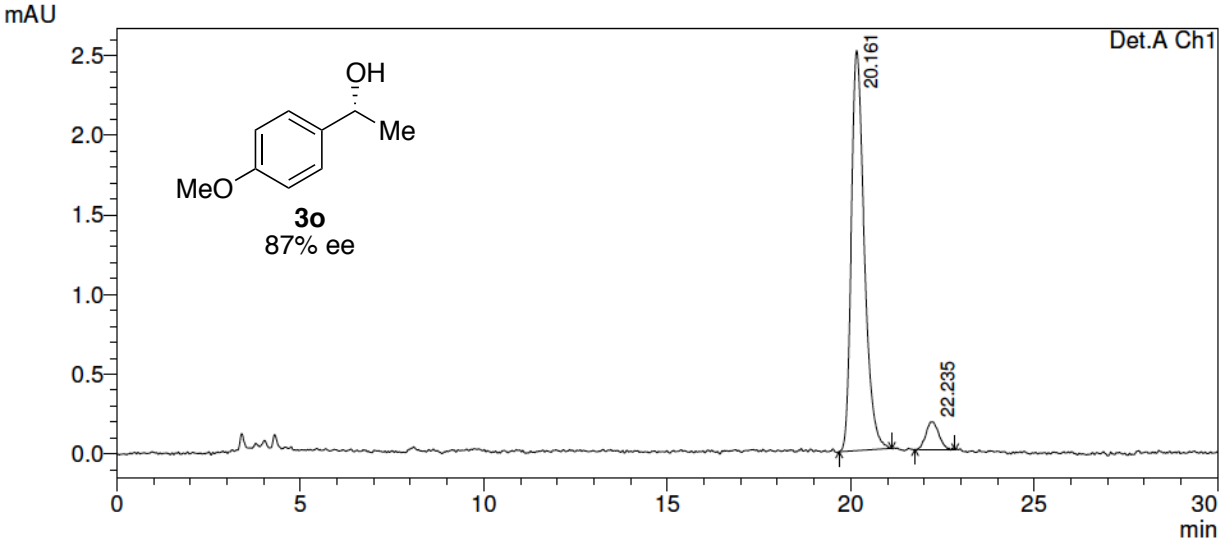
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.253	625785	33025	92.796	93.094
2	17.645	48585	2450	7.204	6.906
Total		674370	35475	100.000	100.000

Compound **3o**, racemic (254 nm)



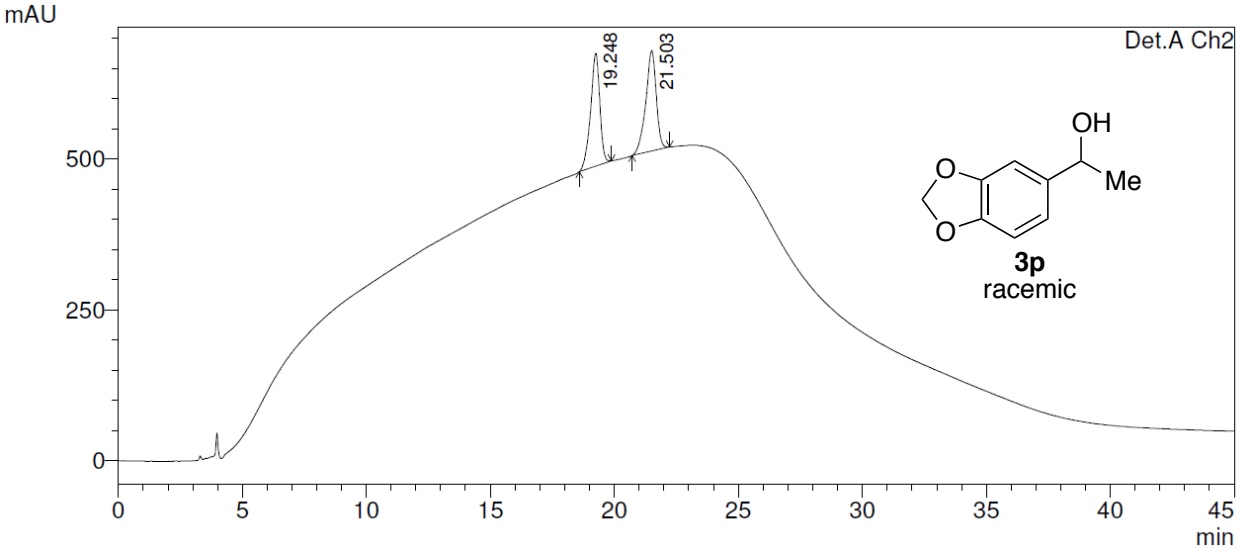
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.018	16955	713	49.424	51.024
2	22.021	17351	684	50.576	48.976
Total		34306	1397	100.000	100.000

Compound **3o**, 87% ee (254 nm)



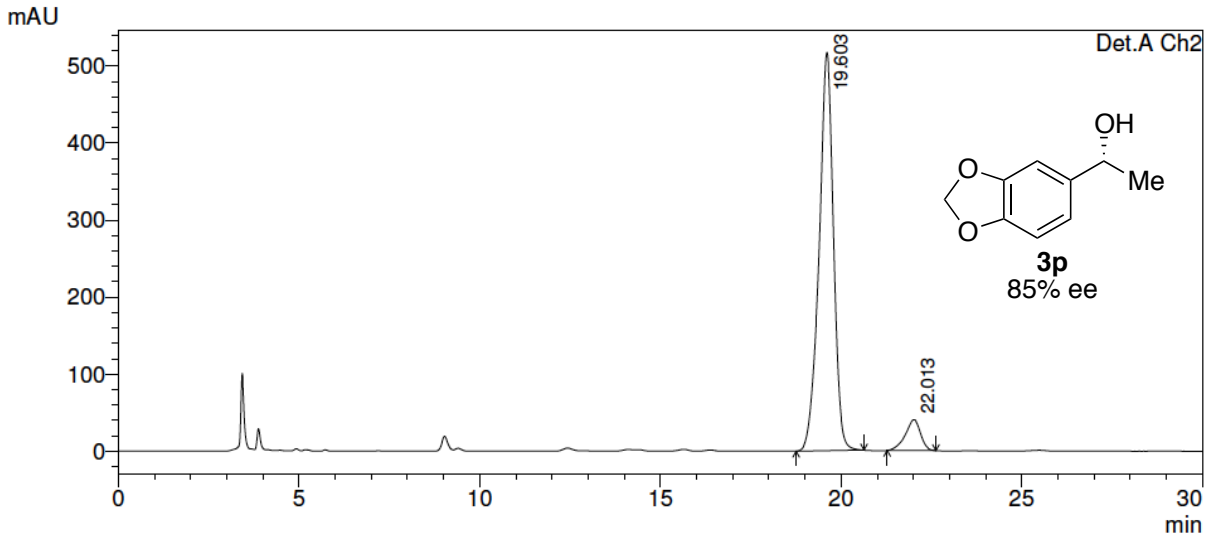
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.161	61611	2512	93.425	93.488
2	22.235	4336	175	6.575	6.512
Total		65947	2687	100.000	100.000

Compound **3p**, racemic (210 nm)



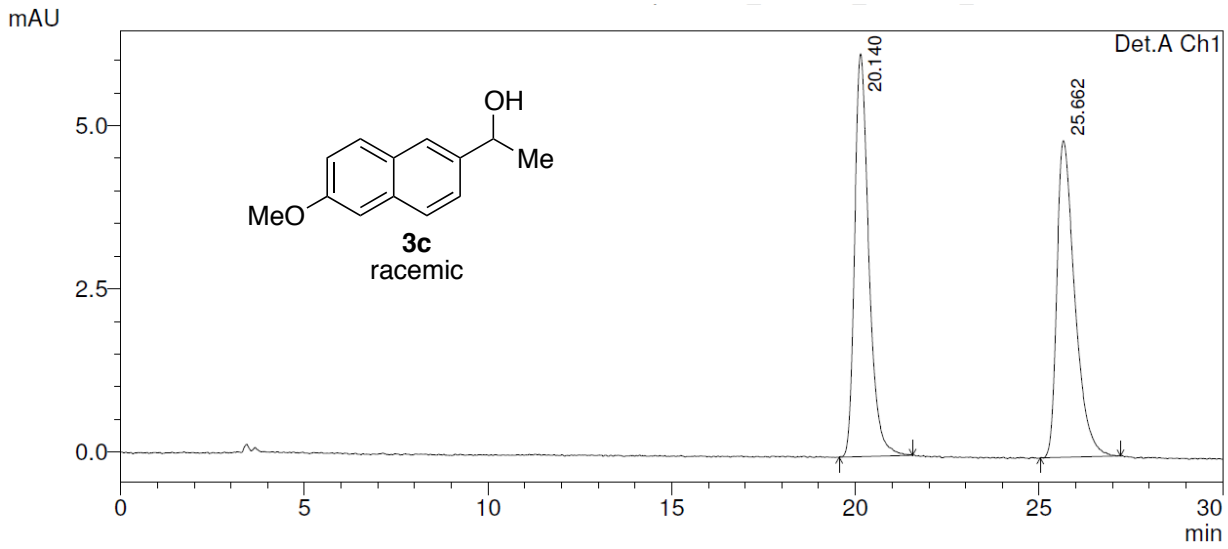
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.248	4853386	187177	49.816	52.913
2	21.503	4889175	166570	50.184	47.087
Total		9742560	353746	100.000	100.000

Compound **3p**, 85% ee (210 nm)



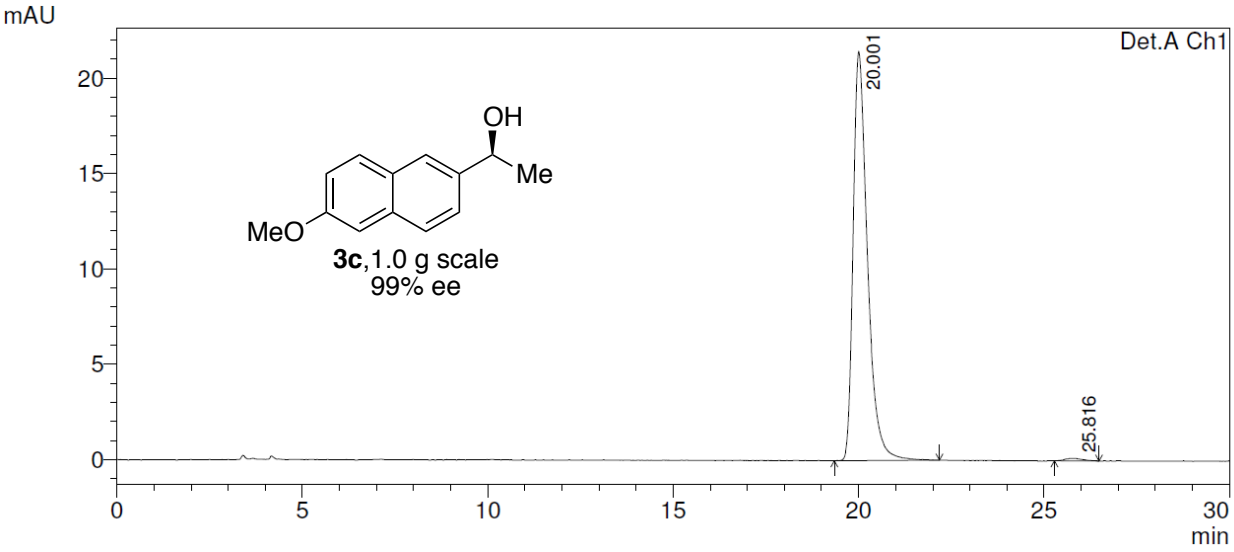
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.603	14324275	516565	92.465	92.804
2	22.013	1167262	40056	7.535	7.196
Total		15491537	556621	100.000	100.000

Compound **3c**, racemic (254 nm)



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.140	165137	6165	50.153	55.982
2	25.662	164128	4848	49.847	44.018
Total		329266	11013	100.000	100.000

Compound **3c**, 99% ee (254 nm)



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.001	574869	21457	99.271	99.399
2	25.816	4222	130	0.729	0.601
Total		579091	21587	100.000	100.000