Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Formal Deoxygenative Hydrofluorination of Aromatic Aldehydes by (Difluoroiodo)toluene

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Supporting Information

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Experimental Details and Characterization Data

General details:

Reactions were carried out in oven-dried glassware under a positive nitrogen atmosphere, or in 4 mL PFA vials purchased from Elemental Scientific. Transfer of anhydrous solvents and reagents was accomplished with oven-dried syringes. Solvents were dried and purified using a JC Meyer solvent purification system, and were used without further purification. Thin layer chromatography was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F254 (Silicycle). Flash chromatography columns were packed with 230-400 mesh silica gel (Silicycle). Proton NMR spectra (^{1}H NMR) were recorded at 300 or 500 MHz, and are reported (ppm) relative to the residual chloroform peak (7.26 ppm) or dimethylsulfoxide peak (2.50 ppm), and coupling constants (J) are reported in hertz (Hz). Carbon NMR spectra (^{13}C NMR) were recorded at 125 or 75 MHz and are reported (ppm) relative to the center line of the triplet from chloroform-d (77.16 ppm). Positive ion electrospray (ESI) and Direct Analysis in Real Time (DART) experiments were performed with a ThermoFisher Scientific Q-Exactive hybrid mass spectrometer. Accurate mass determinations were performed at a mass resolution of 70,000. For ESI, samples were infused at 5mL/min in 1:1 CH_3OH/H_2O+0.1% formic acid. Low-resolution mass determinations were carried out on an Agilent 5975B GCMS system.

General procedure for hydrazone synthesis:

Hydrazones (**13a-o**) were prepared as described in the literature.[1-3] The aldehyde (20mmol) was added to a solution of $H_2NNH_2 \bullet H_2O$ (200 mmol, 10 equiv) in ethyl alcohol (20 mL). The reaction mixture was stirred at room temperature for 3 h (unless otherwise mentioned), then the resulting mixture was poured over ice to obtain a precipitate. Suction filtration gave a solid that was air-dried and used in benzylic fluorination reactions without further purification. The hydrazones were identified by comparison of the spectral data and the melting point described in the literature.

4-nitrobenzylidene hydrazone (13a) Reaction heated at 50 °C for 1h. Obtained as a yellow solid. Yield 88%, mp 134-136 °C (lit.[2] 134 °C).

3-nitrobenzylidene hydrazone (13b) Reaction heated at 50 °C for 1h. Obtained as yellow solid. Yield 87%, mp 107-108 °C (lit.[4] 107 °C).

2-nitrobenzylidene hydrazone (13c) Obtained as a yellow solid. Yield 88%, mp 150-152 °C (lit.[5] 152-153 °C).

4-methyl-3-nitrobenzylidene hydrazone (13d) Obtained as yellow solid. Yield 91%, mp 186-188 °C; IR (neat); 2979, 1626, 1531, 1447, 1380, 1337, 1292, 1200, 956 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): 5.74 (br s, 2H); 7.30 (d, J = 7.9 Hz, 1H); 7.68 (d J = 7.9 Hz, 1H); 7.71 (s, 1H); 8.08 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 20.3; 122.0; 129.8; 133.0; 133.3; 134.8; 139.6; 149.4; HRMS (ESI): calcd for $C_8H_9N_3O_2$ $[M + H]^+$: 180.0767 found 180.0767.

4-bromo-3-nitrobenzylidene hydrazone (13e) Obtained as orange solid. Yield 82%; mp 108-110 °C; IR (neat): 3393, 3286, 1622, 1586, 1528, 1349, 1290, 1219, 955 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): 5.84 (br s, 2H); 7.58 (d, J = 8.1Hz, 1H); 7.67 (s, 1H); 7.69 (d, J = 8.3 Hz, 1H); 7.99 (s 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 113.3; 122.5; 129.9; 135.1; 136.3; 137.9; 150.1; HRMS (ESI): calcd for $C_7H_7BrN_3O_2$ $[M + H]^+$: 243.9716 found 243.9716.

4-carbmethoxybenzylidene hydrazone (13f) Obtained as white solid. Yield 78%, mp 97-98 °C (lit.[3] 96-97 °C).

4-cyanobenzylidene hydrazone (13g) Obtained as white solid. Yield 89%, mp 64-66 °C (lit.[4] 66-67 °C).

3-cyanobenzylidene hydrazone (13h) Obtained as white crystals. Yield 77%, mp 80-82 °C (lit.[2] 83-84 °C).

4-tosyloxybenzylidene hydrazone (13i) Obtained as brown solid. Yield 92%, mp 172-174°C; IR (neat): 3421, 3300, 2906, 1596, 1498, 1334, 1194, 1180, 1090, 917 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): 2.46 (s, 3H); 5.59 (br s, 2H); 6.97 (d, J = 8.6 Hz, 2H); 7.32 (d, J = 8.1 Hz, 2H); 7.46 (d, J = 8.6 Hz, 2H); 7.7 (d, J = 8.3 Hz, 2H); 7.72 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 21.7; 122.6; 122.9; 127.2; 128.5; 129.8; 129.9; 132.3; 134.2; 141.1; 145.4; 149.6; HRMS (ESI): $C_{14}H_{15}N_2O_3S$ $[M + H]^+$: 291.0796 found 291.0796.

4-phenylbenzylidene hydrazone (13j) Obtained as yellow solid. Yield 95%; IR (neat): 3348, 3182, 2914, 1620, 1555, 1484, 1402, 1252, 1076925, 832 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): 5.59 (br s, 1H); 7.38 (t, J = 7.5 Hz, 1H); 7.48 (t, J = 7.5 Hz, 2H); 7.63 (q, J = 14.4, 8.3 Hz, 6H); 7.82 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 126.6; 127.0; 127.3; 127.5; 128.8; 134.2; 140.6; 141.4; 142.7; HRMS (ESI): calcd for $C_{13}H_{13}N_2$ $[M + H]^+$: 197.1073 found 197.1074.

3,4-dichlorobenzylidene hydrazone (13k) Obtained as a white solid. Yield 86%; IR (neat): 3176; 1737; 1594; 174; 1372; 121; 1132; 1027 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.63 (br s, 2H); 7.41-7.32 (m, 2H); 7.61 (s, 2H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 125.2; 127.6; 130.5; 132.1; 132.8; 135.4; 139.8.

3-benzyloxybenzylidene hydrazone (13o) Obtained as white crystals. Yield 82%; mp 62-64 °C; IR (neat): 3348, 3183, 3034, 1620, 1650, 1590, 185, 103, 1070, 925, 832 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): 5.12 (s, 2H); 5.56 (br s, 2H); 6.96 (dd, J = 6, 5 Hz, 1H); 7.13 (d, J = 8 Hz, 1H); 7.28 (s, 1H); 7.29 (d, J = 0.5 Hz, 1H); 7.37 (d, J = 7.5 Hz, 1H); 7.42 (t, J = 7.5 Hz, 2H); 7.48 (d, J = 6 Hz, 2H); 7.75 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 70.0; 111.3; 116; 119.5; 127.6; 128.0; 128.6; 129.6; 136.6; 136.9; 142.9; 159.1; HRMS (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$: 227.1178 found 227.1178.

2-bromo-5-methoxybenzylidene hydrazone (13p): Obtained as a white solid. Yield 69%; IR (neat): 3292, 2937; 2837; 1616; 1592; 177; 1407; 1317; 1264; 1181; 1128; 1025 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 3.82 (s, 3H); 5.63 (br s, 2H); 6.74 (d, J = 8.4 Hz, 1H); 7.34 (d, J = 8.4 Hz, 1H); 7.91 (s, 1H); 8.04 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 55.8; 112.7; 113.5; 125.7; 128.3; 132.0 137.2; 155.8.

General procedure for benzyl fluoride synthesis:

A 4 mL PFA (Teflon) vial containing (difluoroiodo)toluene (1.7 equiv) was placed under nitrogen and immersed in a pre-heated 40 °C bath. To this was added a pre-made solution of hydrazone **13** (50 mg, 1.0 equiv) in CH_2Cl_2 (1.5 mL) via a syringe pump over ~10 minutes. The reaction was monitored by TLC analysis, and upon consumption of the hydrazone (5-10 min), the reaction mixture was cooled to RT and concentrated by rotary evaporation. The resulting crude reaction mixture was purified by flash silica gel chromatography (EtOAc in hexanes or EtOAc in benzene) to provide the benzyl fluorides **10**.

1-(fluoromethyl)-4-nitrobenzene (10a):[6] Obtained as a white crystalline solid (35 mg, 74 %); R_f: 0.3 (1/9 Ethyl acetate/Hexane); IR (neat): 3115; 3086; 1935; 1605; 1504; 1347; 1012; 838 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): 5.49 (d, J = 46.7 Hz, 2H); 7.51 (d, J = 8.1 Hz, 2H); 8.23 (d, J= 8.1 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$, δ ppm): 82.8 (d, J = 170.5 Hz, 1C); 123.7; 126.9 (d, J = 7.1 Hz, 2C); 143.3 (d, J = 17.7 Hz, 1C); 147.8; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -215.91; GC-MS (EI) 153.9 $(M-H)^+$.

1-(fluoromethyl)-3-nitrobenzene (10b): Obtained as a yellow liquid (33 mg, 71 %); IR (neat): 3094; 2960; 1526; 1349; 1218; 989; 892; 804 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.48 (d, J = 46.9 Hz, 2H); 7.59 (t, J = 7.8 Hz, 1H); 7.69 (d, J = 7.8 Hz, 1H); 8.21 (apparent d, J = Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 83.0 (d, J = 170.5 Hz, 1C); 121.8 (d, J = 7.2 Hz, 1C); 123.5 (d, J = 1.8 Hz, 1C); 129.7; 132.5 (d, J = 6.3 Hz, 1C); 138.3 (d, J = 18.4 Hz, 1C); 148.4; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -212.59; GC-MS (EI) 153.9 $(M-H)^+$.

1-(fluoromethyl)-2-nitrobenzene (10c)[6]: Obtained as a white solid (30 mg, 64%); IR (neat): 2925; 1616; 1522; 1341; 1009; 858 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.89 (d, J = 47.9 Hz, 2H); 7.53 (t, J = 8.0 Hz, 1H); 7.77 (t, J = 7.7 Hz, 1H); 7.83 (d, J = 7.7 Hz, 1H); 8.24 (d, J = 8.1 Hz, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 81.3 (d, J = 172.8 Hz, 1C); 124.9, 126.8 (d, J = 17.6 Hz, 1C); 128.6, 134.3, 134.4, 145.6; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -219.4; GC-MS (EI) 155.0 $(M)^+$.

4-(fluoromethyl)-1-methyl-2-nitrobenzene (10d): Obtained as a colourless liquid (24mg, 51%); IR (neat): 2933; 1527; 1497; 1344; 1221; 986; 812 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 2.6 (s, 3H); 5.40 (d, J = 47.2 Hz, 2H); 7.37 (d, J = 7.8 Hz, 1H); 7.50 (d, J = 7.8 Hz, 1H); 7.97 (s, 1H);); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 20.2, 82.9 (d, J = 169.2Hz, 1C); 123.3 (d, J = 6.8 Hz, 1C); 131.5 (d, J = 5.9

Hz, 1C); 133.2; 133.9 (d, J = 2.5 Hz, 1C); 135.6 (d, J = 18.3 Hz, 1C); 149.2; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -210.66; GC-MS (EI) 169.1 (M^+).

1-bromo-4-(fluoromethyl)-2-nitrobenzene (10e): Obtained as a yellow liquid (34 mg, 71%); IR (neat): 3073; 2959; 1606; 1532; 1475; 1352; 1031; 891; 827; 804 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.39 (d, J = 46.8 Hz, 2H); 7.41 (d, J = 8.2 Hz, 1H); 7.75 (d, J = 8.2 Hz, 1H); 7.97 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 82.2 (d, J = 171.2 Hz, 1C); 114.46, 123.8, 131.2, 135.4, 137.5, 149.9; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -213.86; HRMS (DART 300 °C): calcd for $C_7H_6O_2NBrF$ $[M+H]^+$: 233.9561 found 233.9559.

methyl 4-(fluoromethyl)benzoate (10f)[7]: Obtained as a pale yellow liquid (30 mg, 64%); IR (neat): 2926; 2854; 1720; 1435; 1275; 1177; 1106; 1016 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 3.90 (s, 3H); 5.43 (d, J = 47.2 Hz, 2H); 7.41 (d, J = 7.8 Hz, 2H); 8.04 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 52.1; 86.6 (d, J = 168.8 Hz, 1C); 126.6 (d, J = 6.7 Hz, 2C); 129.8 (d, J = 2.3 Hz, 2C); 130.4; 141.2 (d, J = 17.2 Hz, 1C); 166.6; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -213.13; GC-MS (EI) 168.12 (M^+).

4-(fluoromethyl)benzonitrile (10g):[7] Obtained as a yellow liquid (33 mg, 71%). IR (neat): 2926; 2230; 1416; 1378; 1214; 1012; 817 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.44 (d, J = 46.8 Hz, 2H); 7.45 (d, J = 7.8 Hz, 2H); 7.67 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 83.1 (d, J = 170.5 Hz, 1C); 112.5; 118; 127.5 (d, J = 65.4 Hz, 2C); 132.4; 141.5 (d, J = 17.9 Hz, 1C); ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -215.44; GC-MS (EI): 135.15 (M^+).

3-(fluoromethyl)benzonitrile (10h):[8] Obtained as a yellow liquid; 20:1 mixture of **10h**:**16h** (34 mg, 73 %). IR (neat): 2923; 2231; 1485; 1378; 1151; 985; 891 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): 5.41 (d, J = 47.1 Hz, 2H); 6.67* (t, J = 56.1 Hz, 0.06H); 7.49 (t, J = 7.7 Hz, 1H); 7.59 (d, J = 7.7 Hz, 1H); 7.63 (d, J = 3.2 Hz, 2H); 7.76 (t, J = 8.8 Hz, 0.09H); 7.81 (s, 0.05H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 82.9 (d, J = 170.2 Hz, 1C); 113.0; 118.3; 129.5; 130.4; 131.1; 132.2; 137.9 (d, J = 18.0 Hz, 1C); ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -212.64 (**16h**: -112.73); GC-MS (EI): 135.15 (M^+).

4-(fluoromethyl)phenyl 4-methylbenzenesulfonate (10i): Obtained as a colourless gum (29 mg, 60%), IR (neat): 2926; 1597; 1504; 1370; 1197; 117; 1152; 1092 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 2.43 (s, 3H); 5.32 (d, J = 47.5 Hz, 2H); 6.99 (d, J = 8.3 Hz, 2H); 7.31-7.24 (m, 4H); 7.68 (d, J = 8.3 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 21.7; 83.6 (d, J = 167.4 Hz, 1C); 122.6; 128.5; 128.6 (d, J = 5.9 Hz, 2C); 129.8; 132.3; 135.2 (d, J = 17.5 Hz, 1C); 145.5; 149.7; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -208.45; GC-MS (EI) 280.1 (M^+).

4-(fluoromethyl)-1,1'-biphenyl (10j)[7]: Obtained as a white solid (24mg, 51%); IR (neat): 2921; 180; 1686; 1486; 1077; 1005; 823 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.43 (d, J = 47.1Hz, 2H); 7.37 (t, J = 7.4 Hz, 1H); 7.46 (t, J = 7.8 Hz, 4H); 7.62 (t, J = 7.8 Hz, 4H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 84.4 (d, J = 166Hz, 1C); 127.2, 127.4 (d, J =1.7 Hz, 2C); 127.6; 128.1 (d, J = 6.0 Hz, 1C); 128.9; 135.1; 140.6; 141.8; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -206.39; GC-MS (EI pos.): 186.1 (M^+).

1,2-dichloro-4-(fluoromethyl)benzene (10k)[8]: Obtained as a colourless liquid (32mg, 68%); IR (neat): 2924; 1598; 1473; 1212; 1131; 1032; 1007; 874; 816 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.31 (d, J = 47.3 Hz, 2H); 7.18 (d, J = 2.2 Hz, 1H); 7.44 (s,1H); 7.5 (d, J = 2.2 Hz, 1H); ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -210.38; GC-MS (EI) 178.0 (M^+).

1-(methoxy)-3-(fluoromethyl)benzene (10n)[7]: Obtained as a colourless liquid (16 mg, 33%); IR (neat): 3008; 2959; 2838; 1598; 1587; 1457; 1266; 1156; 1040 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 3.82 (s,

3H); 5.36 (d, J = 47.7 Hz, 2H); 6.92 (m, 3H); 7.30 (app. t, J = 7.6 Hz, 1H); ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -207.93; GC-MS (EI pos.): 140.05 (M^+).

1-(benzyloxy)-3-(fluoromethyl)benzene (10o): Obtained as a white solid (30 mg, 45%); IR (neat): 3033; 2973; 2852; 1693; 1594; 1583; 1447; 1258; 1166; 1025 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 5.34 (d, J = 47.7 Hz, 2H); 6.97 (apparent t, 3H); 7.42-7.29 (m, 6H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 70.1; 84.4 (d, J = 166.8 Hz, 1C); 113.7 (d, J = 6.4 Hz, 1C); 115.2 (d, J = 3.0 Hz,1C); 119.8 (d, J = 5.5 Hz, 1C); 127.5; 128.1; 128.7; 129.8; 136.9; 137.8 (d, J = 17.4 Hz, 1C); ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -208.03; GC-MS (EI pos.): 216.1 (M^+).

1-bromo-2-(fluoromethyl)-4-methoxybenzene (10p): Obtained as yellow liquid (22 mg, 47%); IR (neat): 3019; 2920; 1482; 1208; 1111; 1059; 1006 cm^{-1}; ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 3.81 (s, 3H); 5.38 (d, J = 47.5 Hz, 2H); 6.75 (d, J = 8.7 Hz, 1H); 7.4 (d, J = 8.7Hz, 1H); 7.47 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$, δ ppm): 55.6; 79.6 (d, J = 166.1 Hz, 1C); 112.0; 112.7; 127.0 (d, J = 17.4 Hz, 1C); 131.2 (d, J = 8.9 Hz, 1C); 132.3 (d, J = 3.9 Hz, 1C); 155.9; ^{19}F NMR (300MHz, $CDCl_3$, δ ppm): -217.59; GC-MS (EI pos.): 218.0 (M^+).

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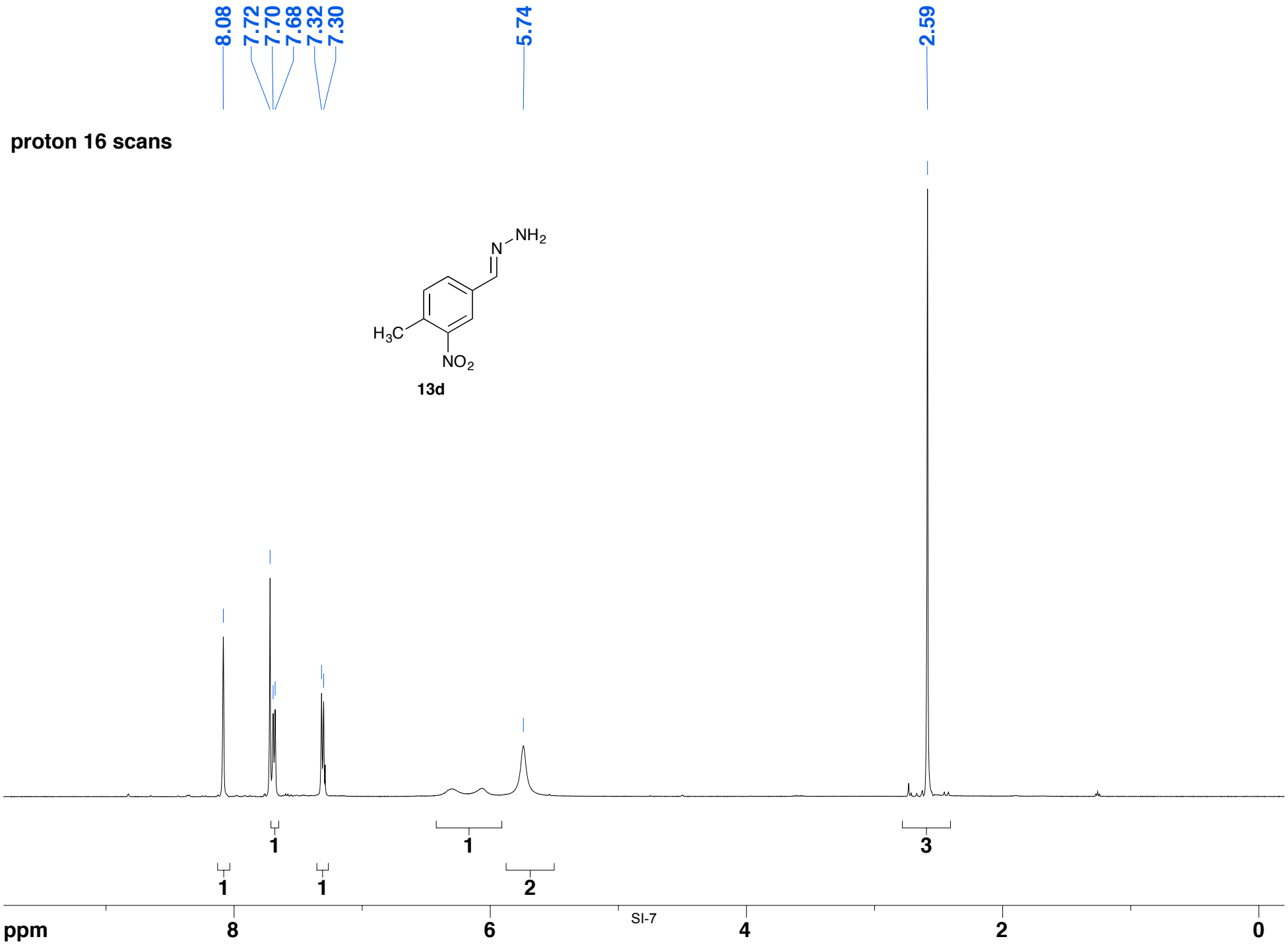
^{1}H, ^{13}C and ^{19}F NMR spectra of new compounds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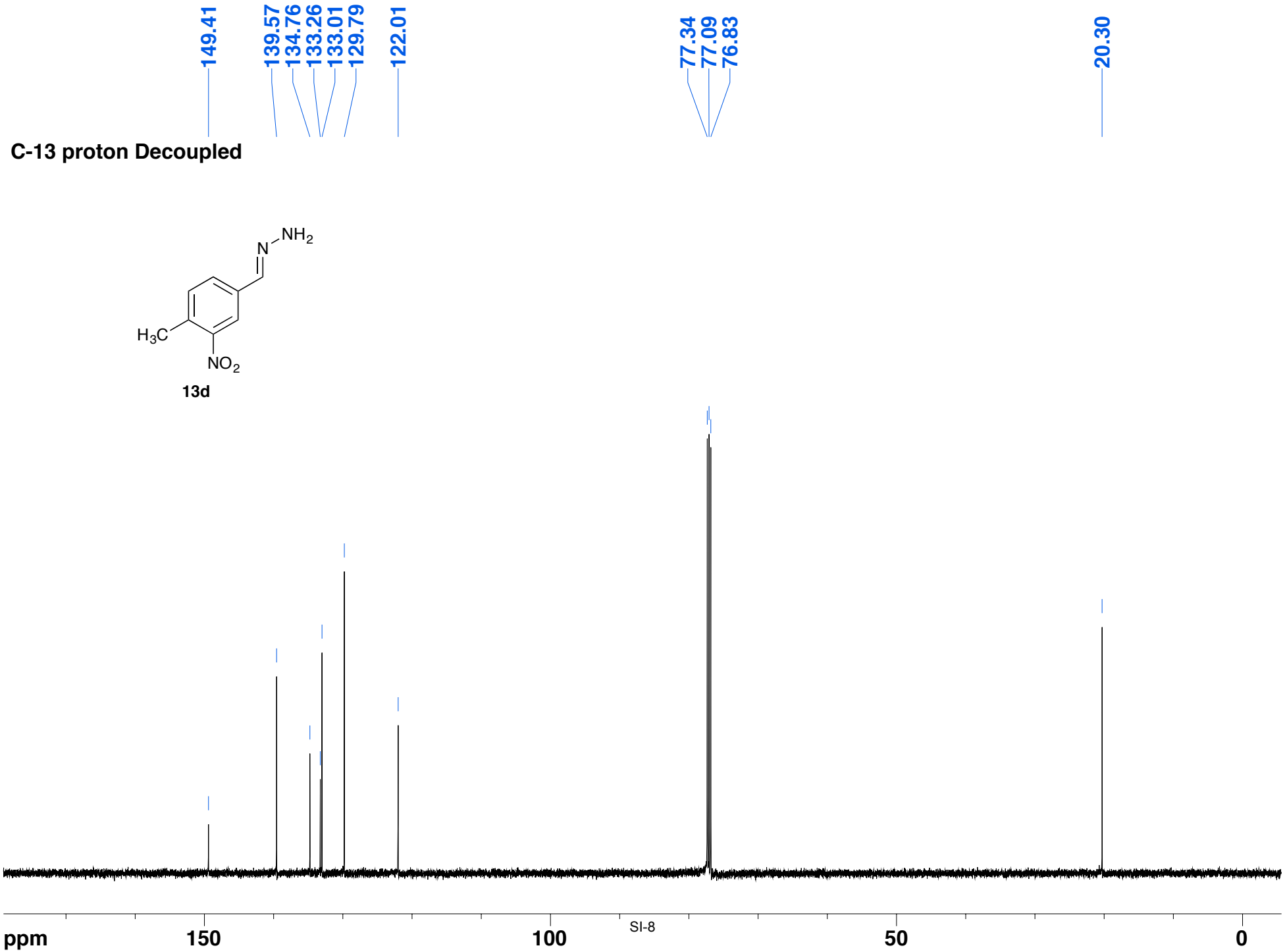
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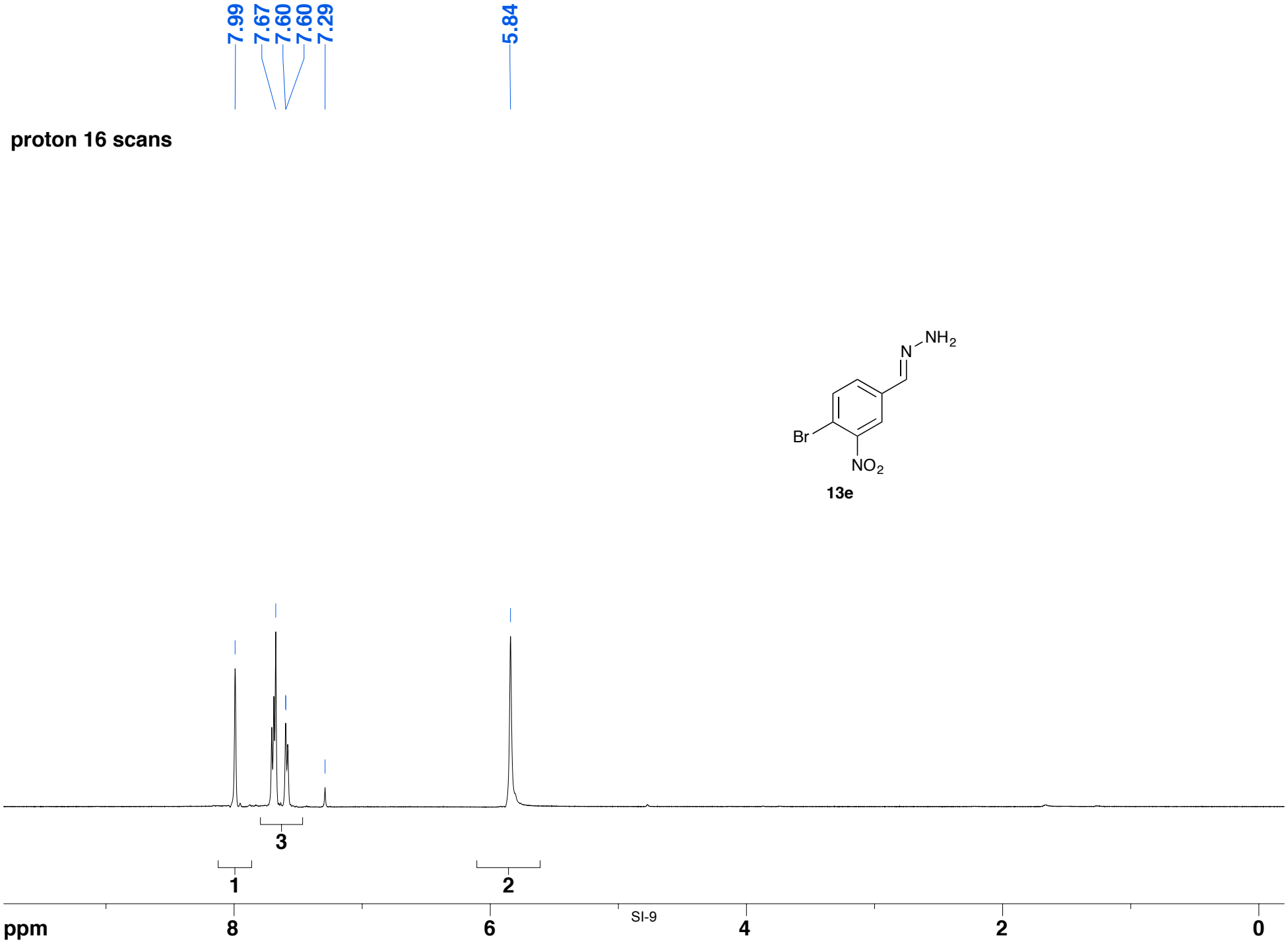
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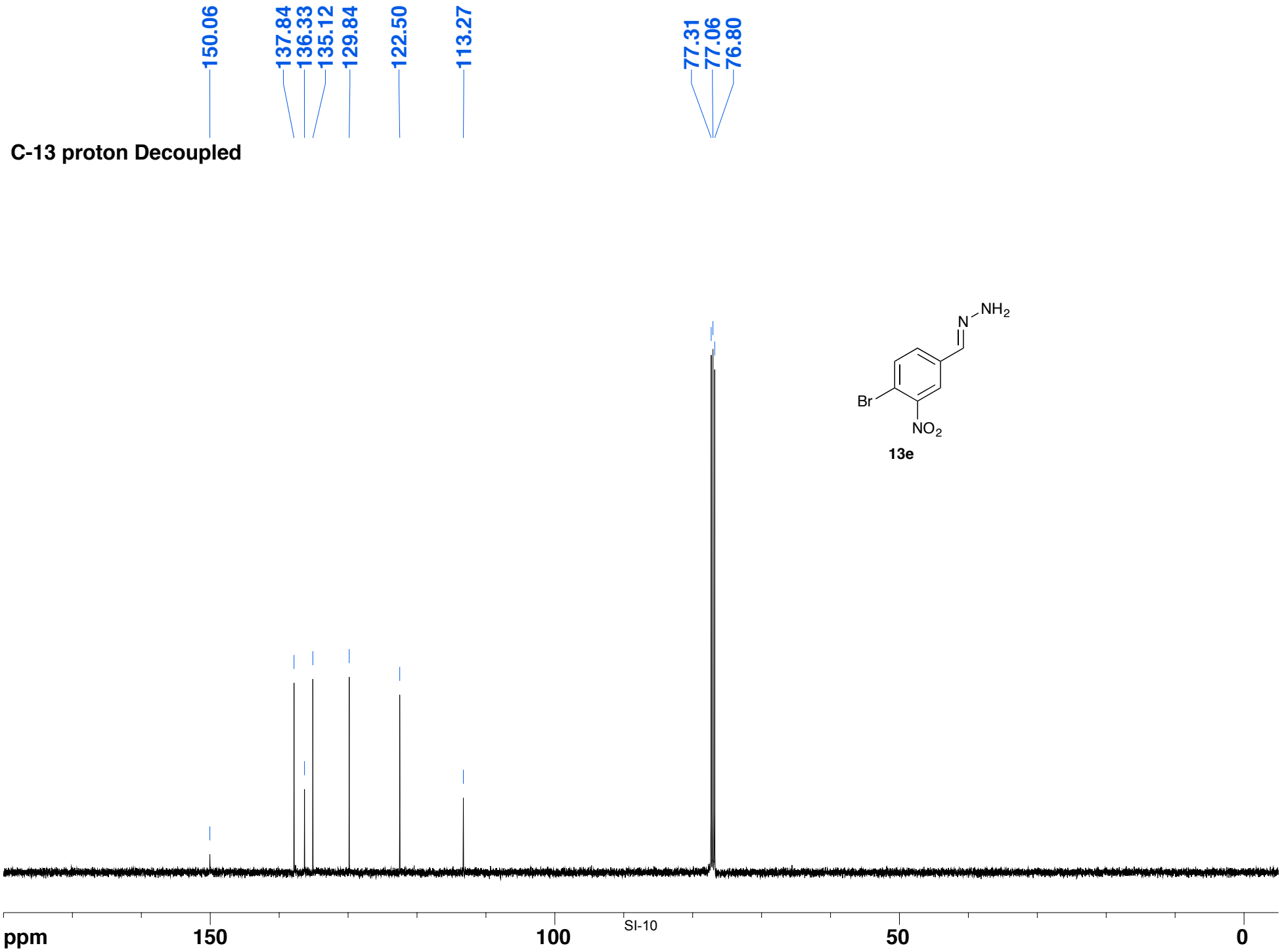
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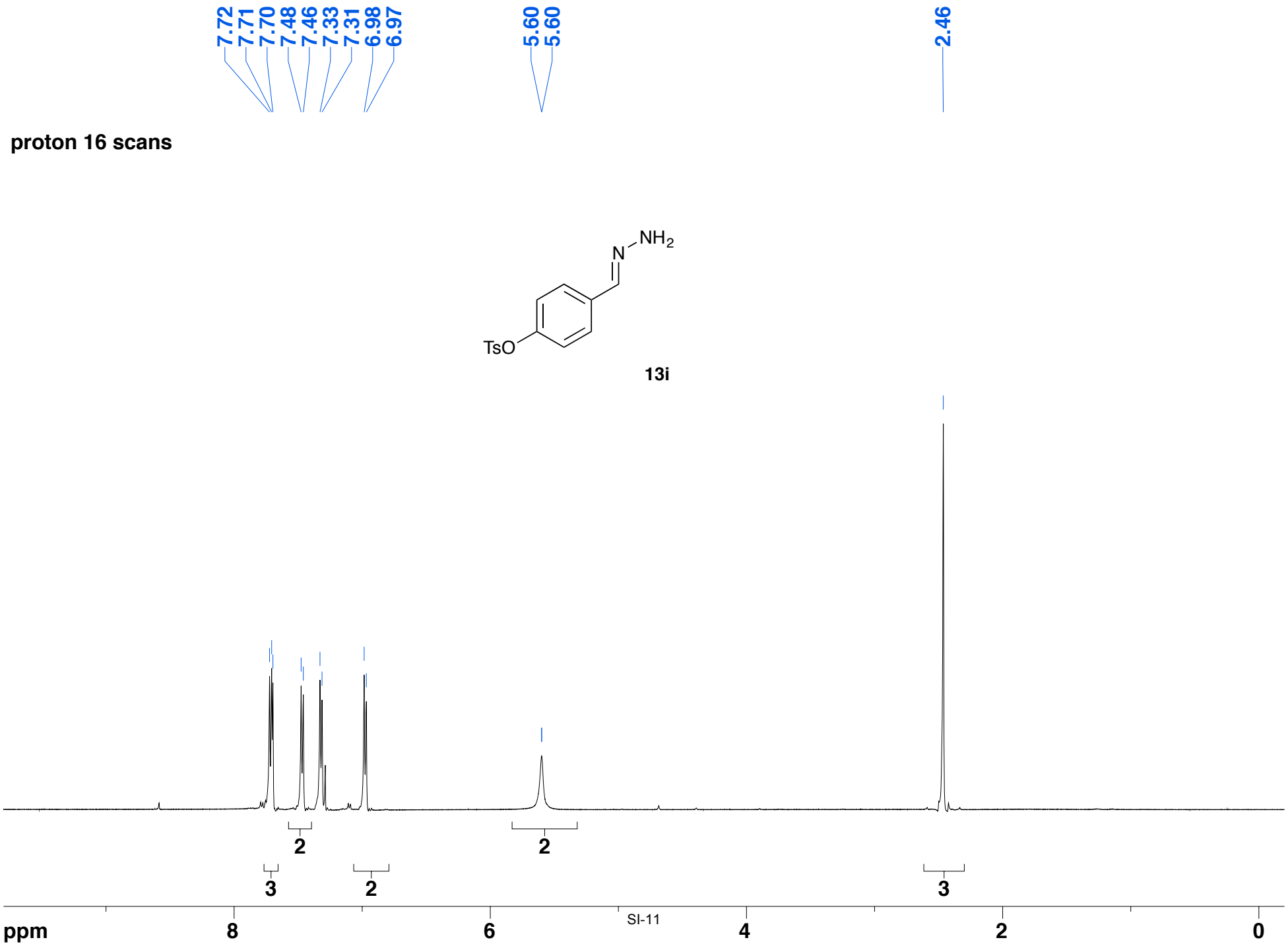
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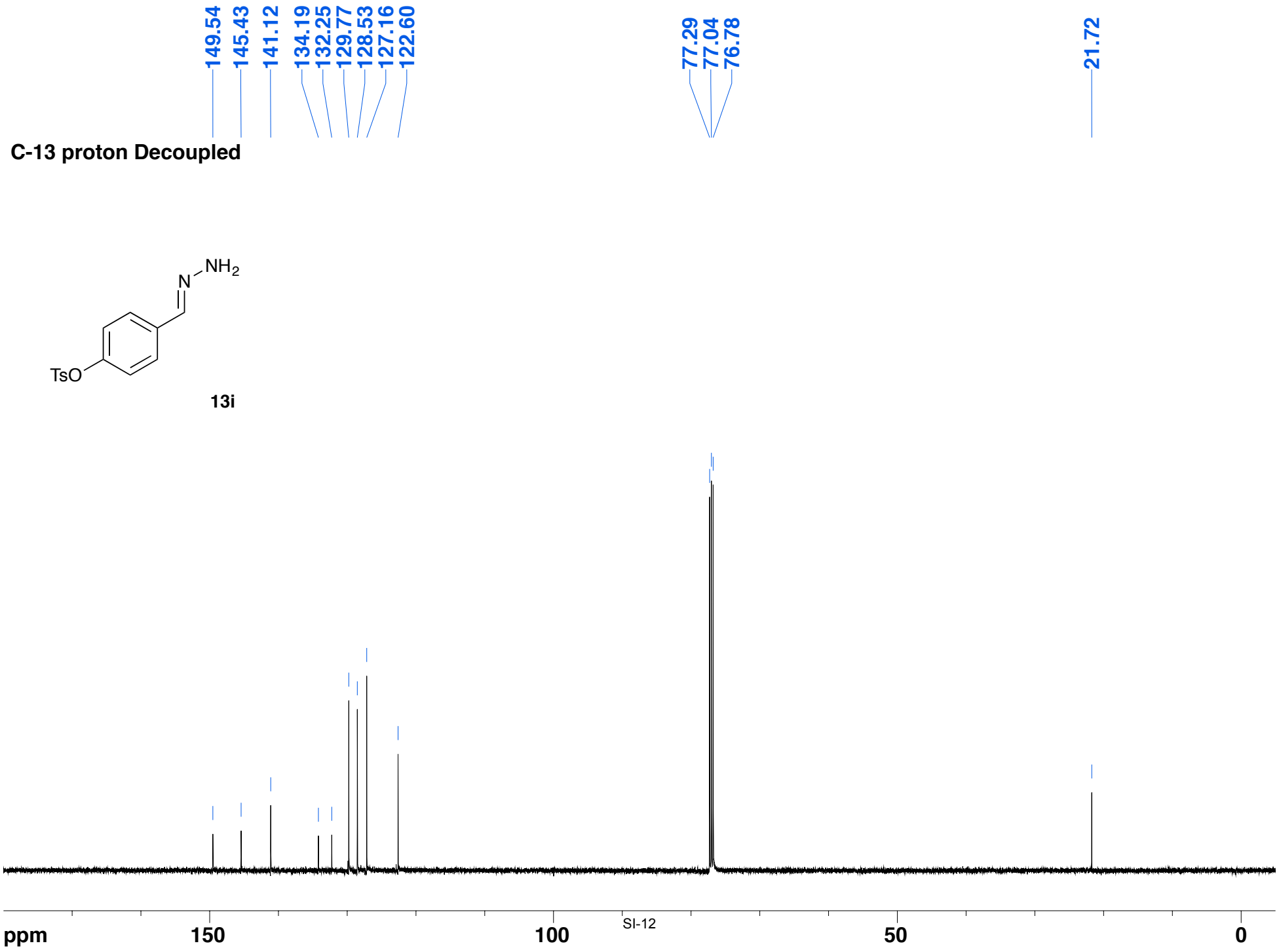
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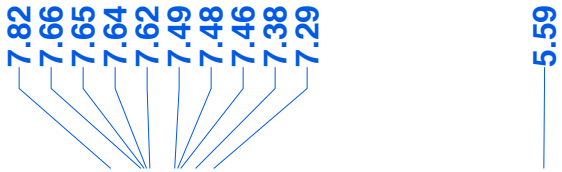
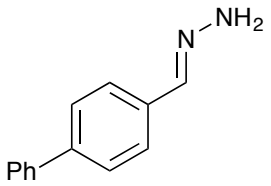
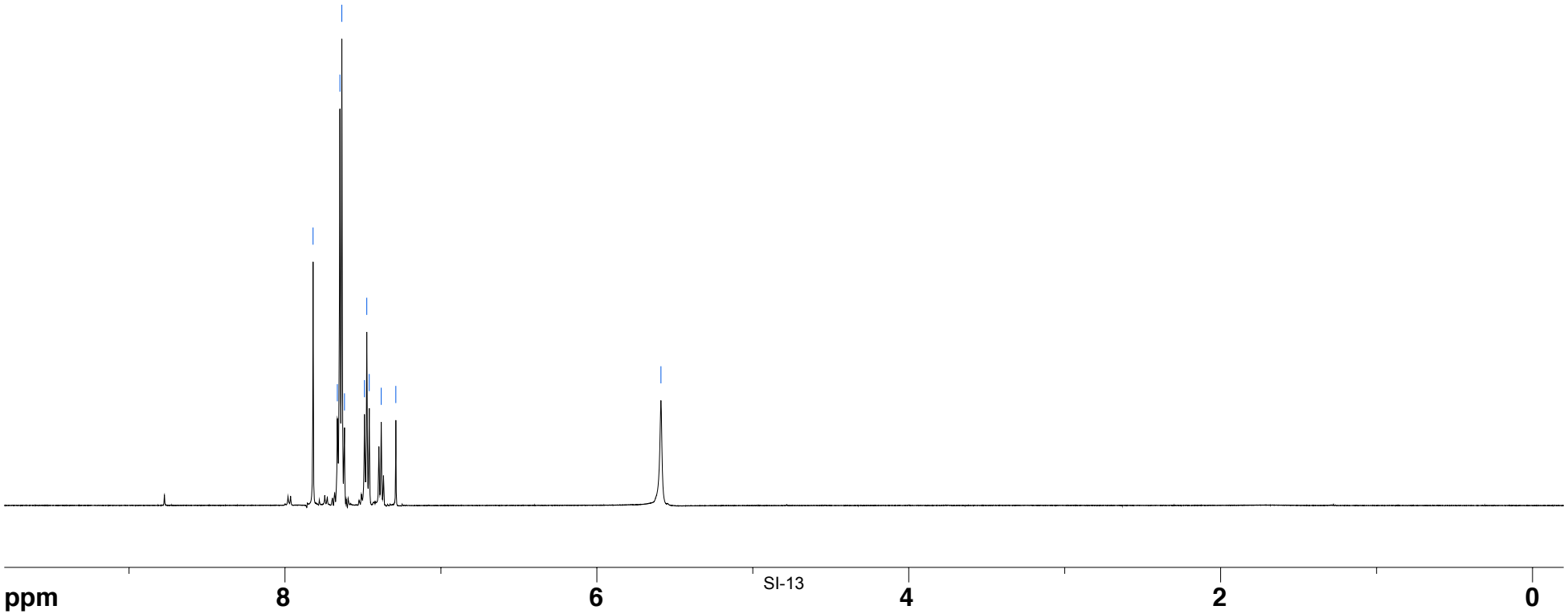
127.16
122.60
77.29
77.04
76.78
21.72
C-13 proton Decoupled
NH2
N
TsO
13i
ppm
150
100
50
0

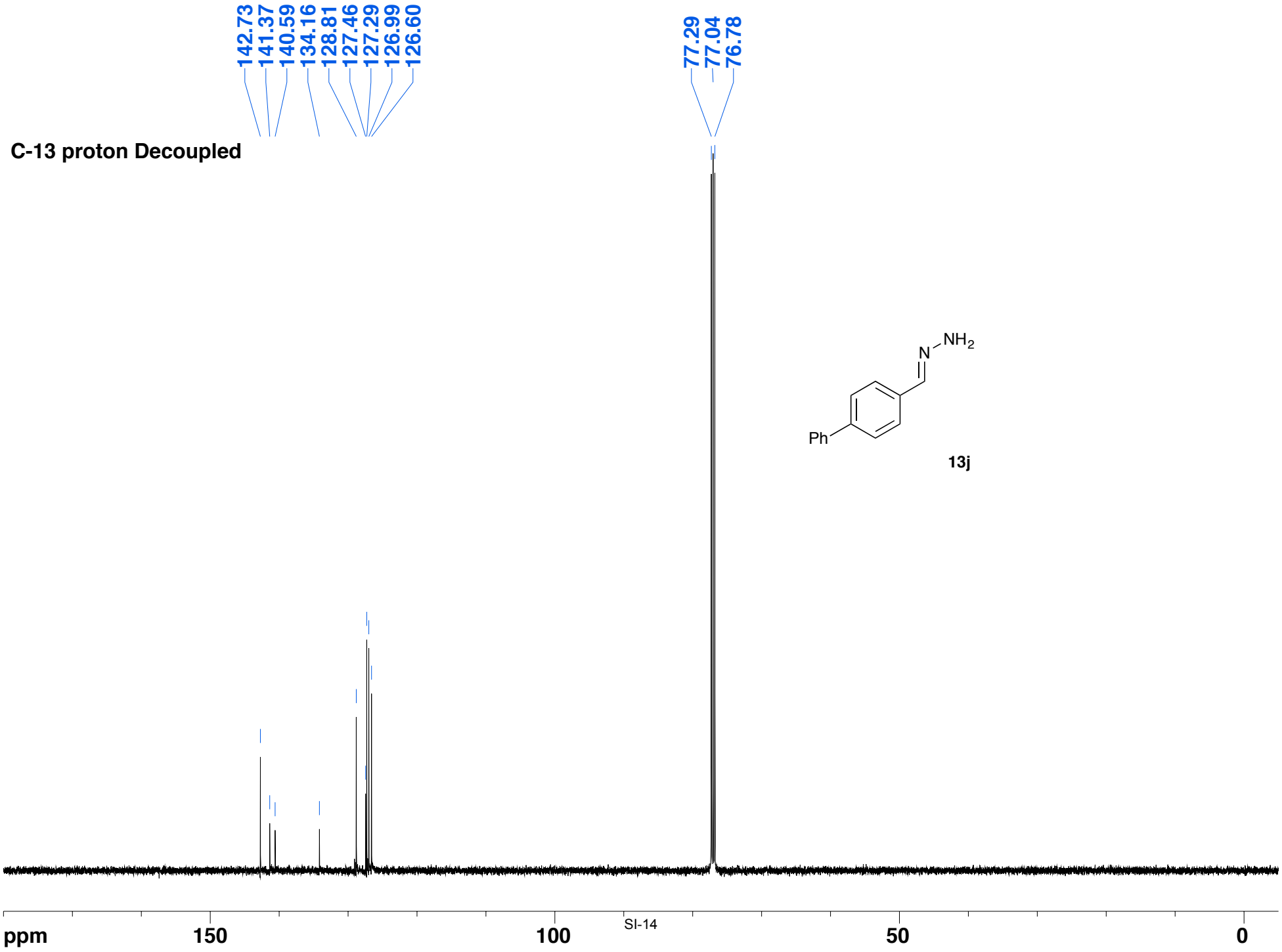


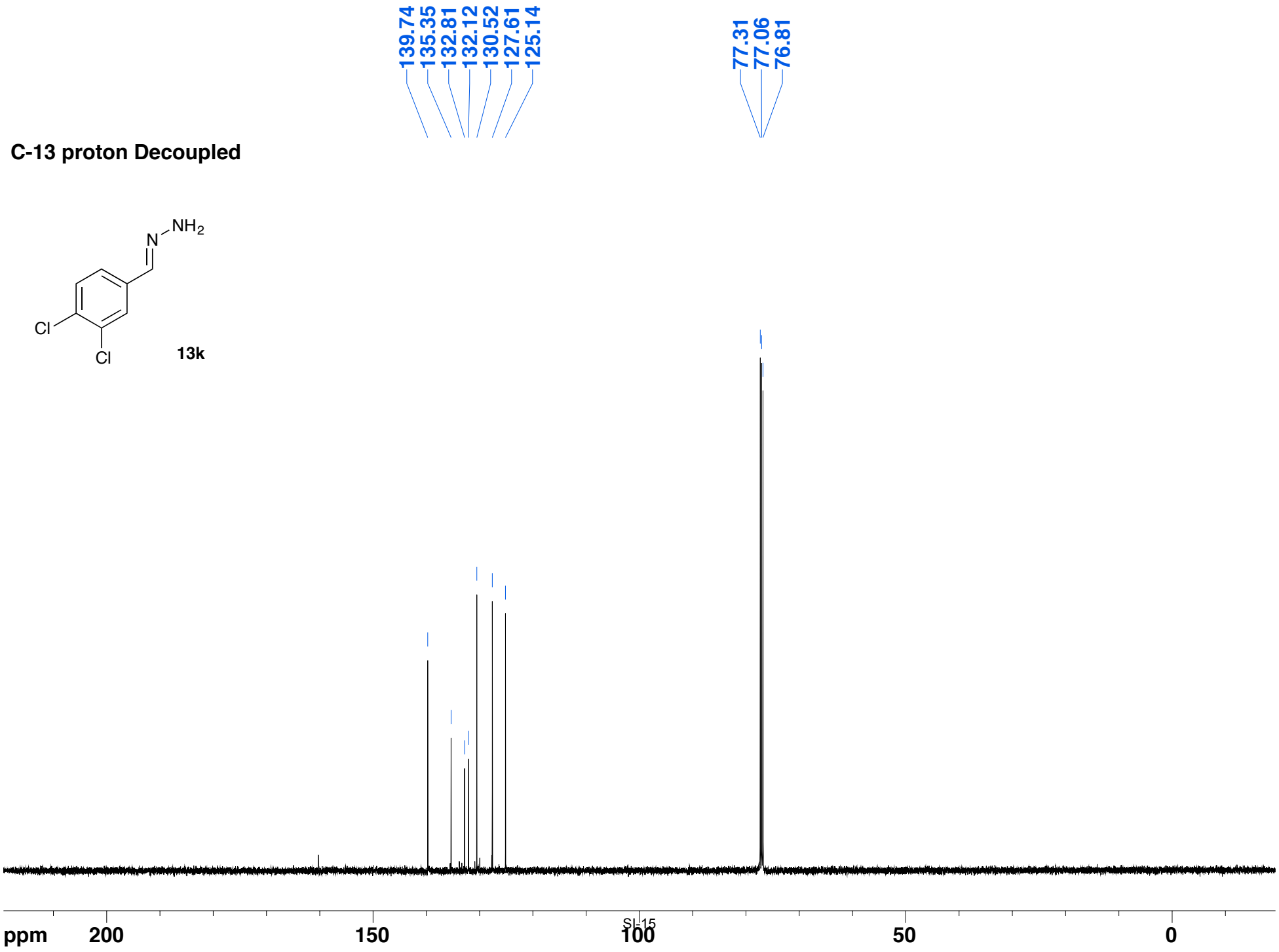
proton 16 scans

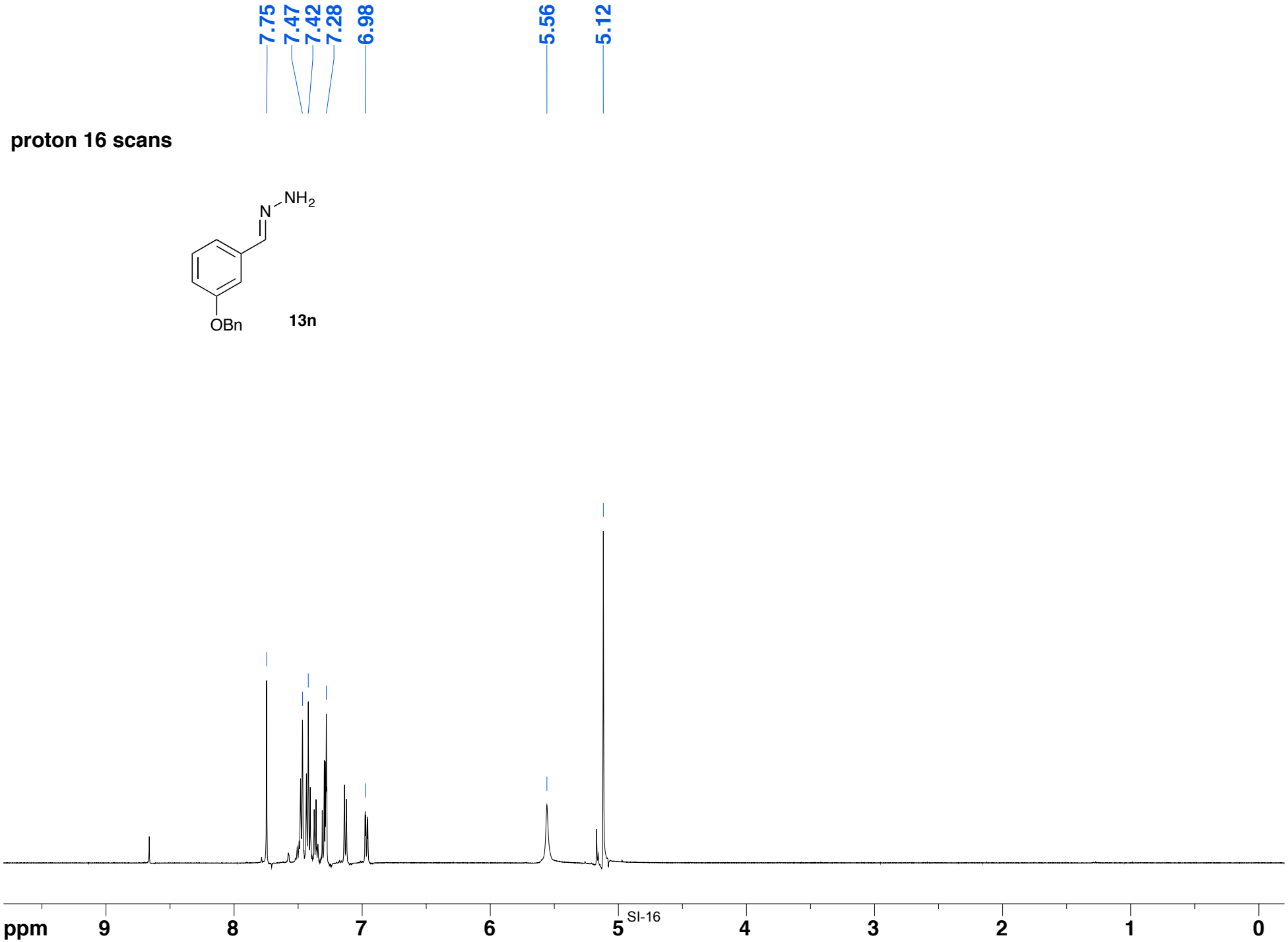


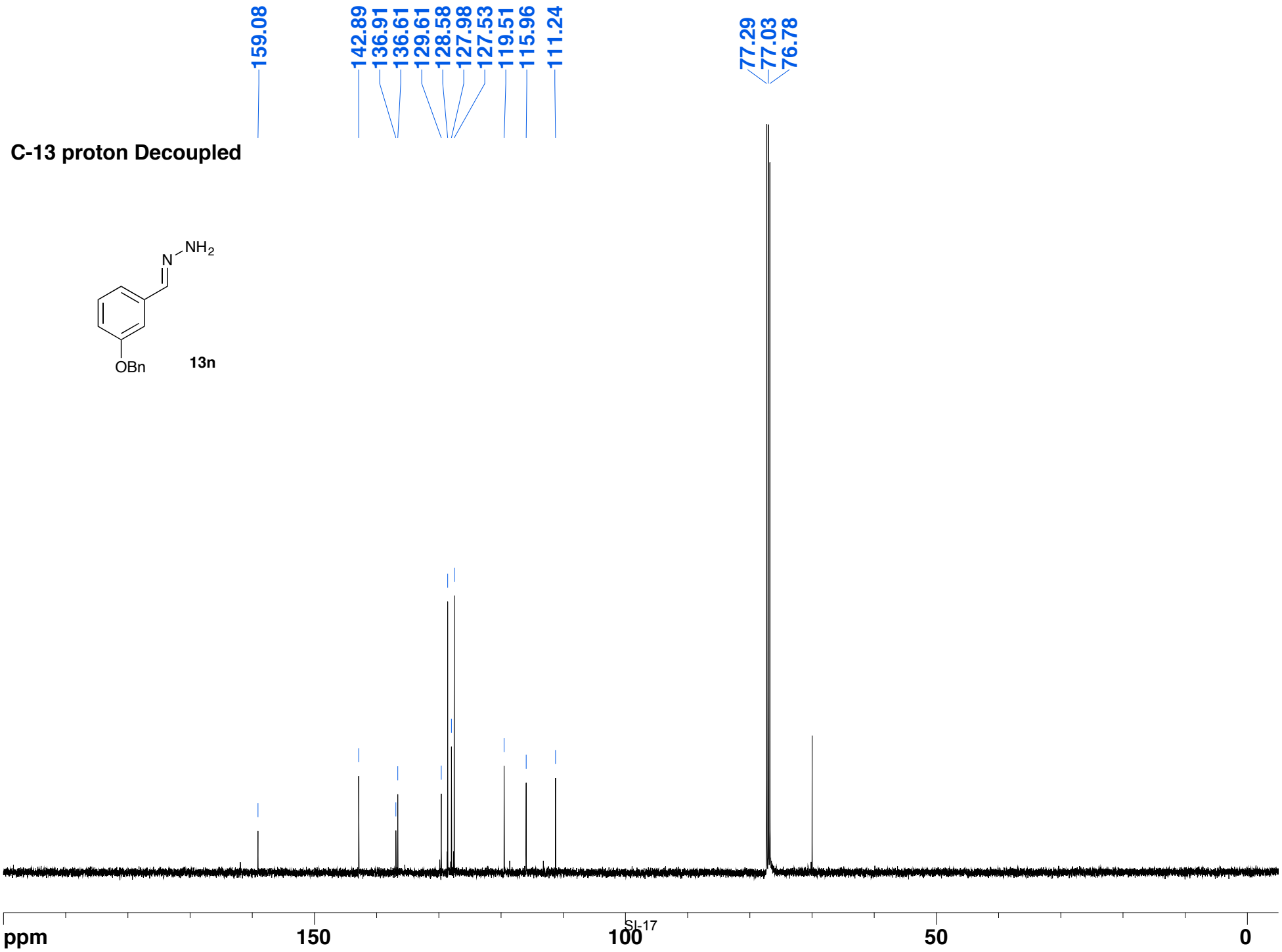
13j

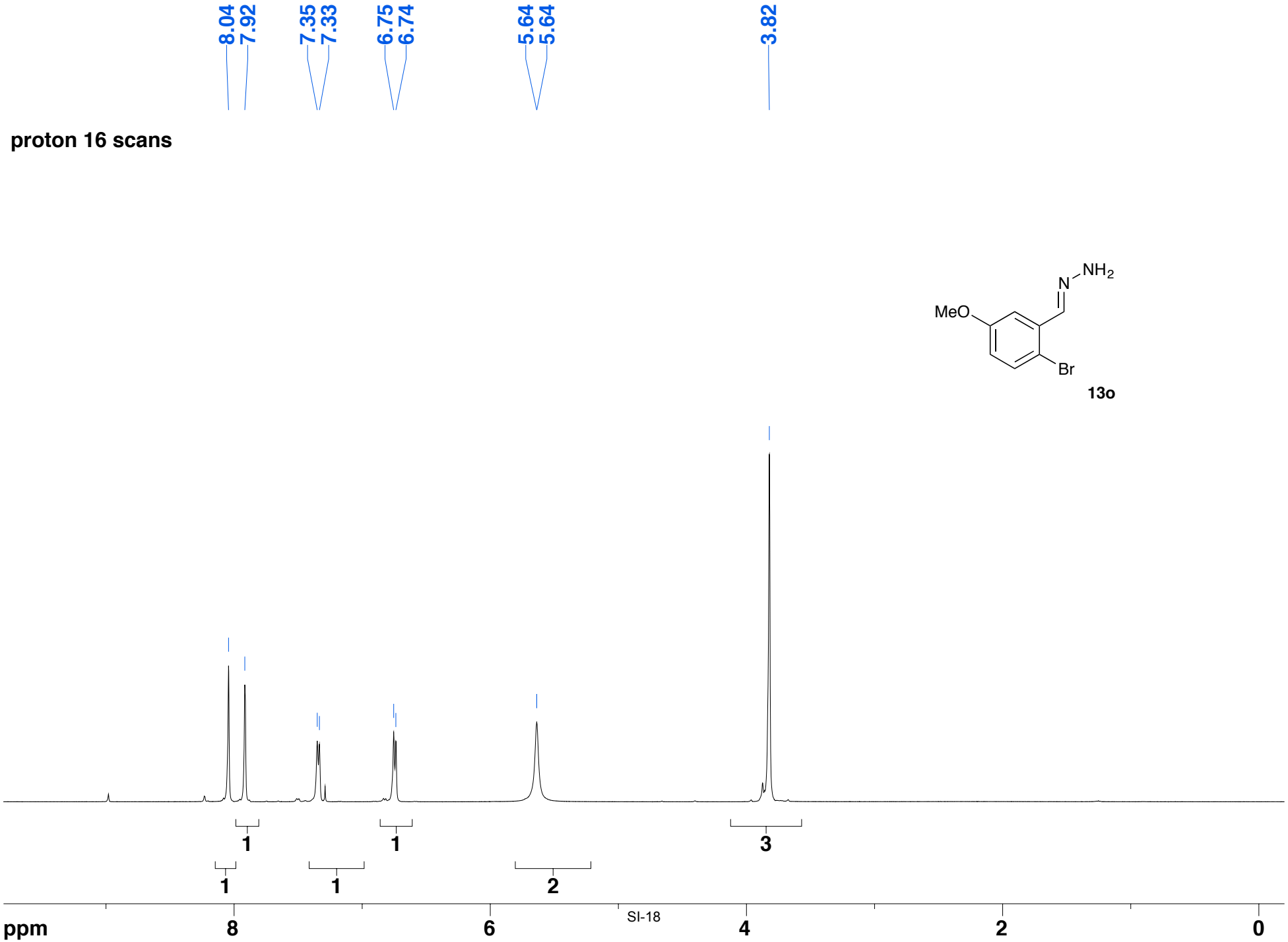


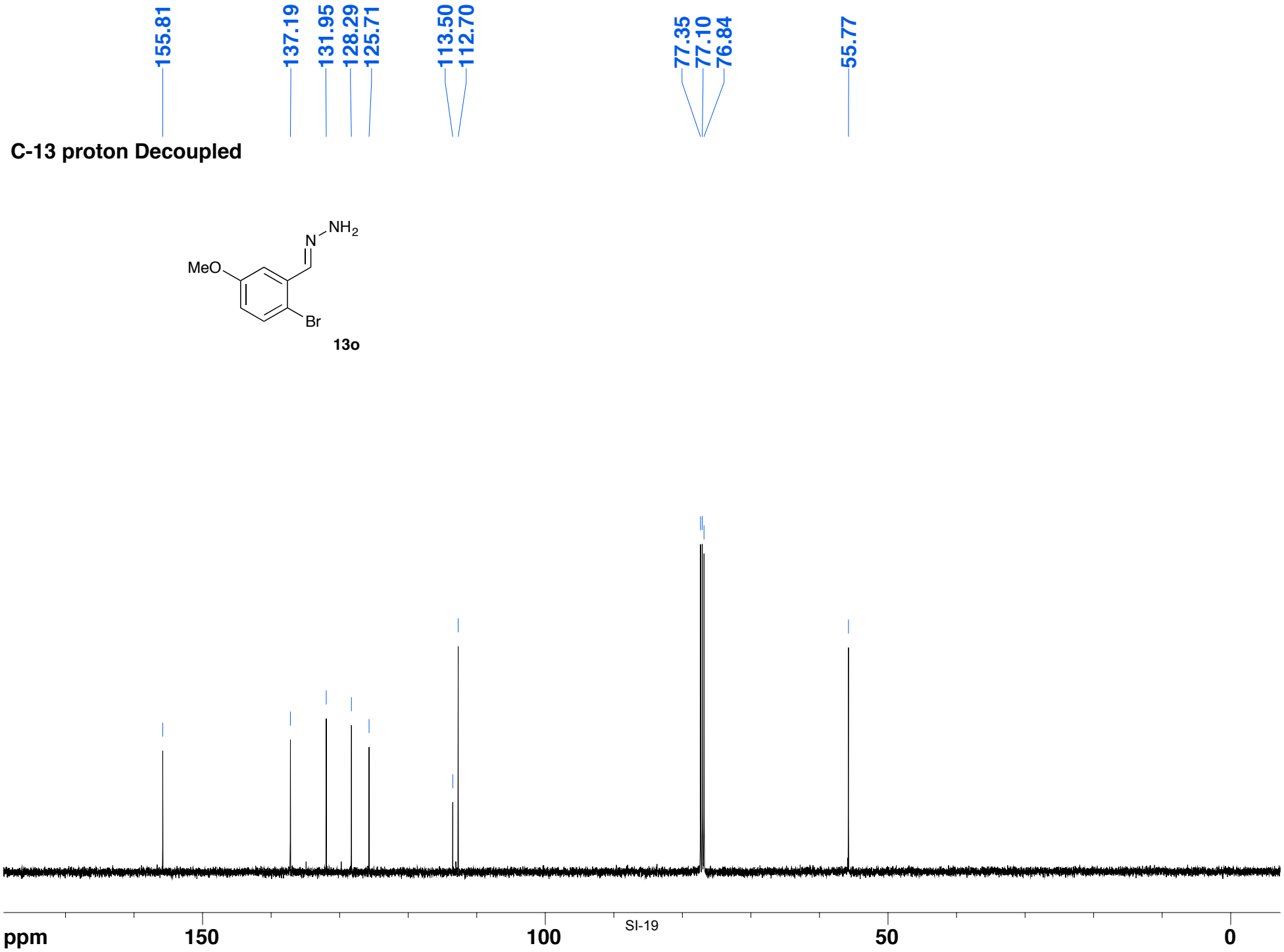

142.73
141.37
140.59
134.16
128.81
127.46
127.29
126.99
126.60
77.29
77.04
76.78
C-13 proton Decoupled
NH2
N
Ph
13j
ppm
150
100
50
0

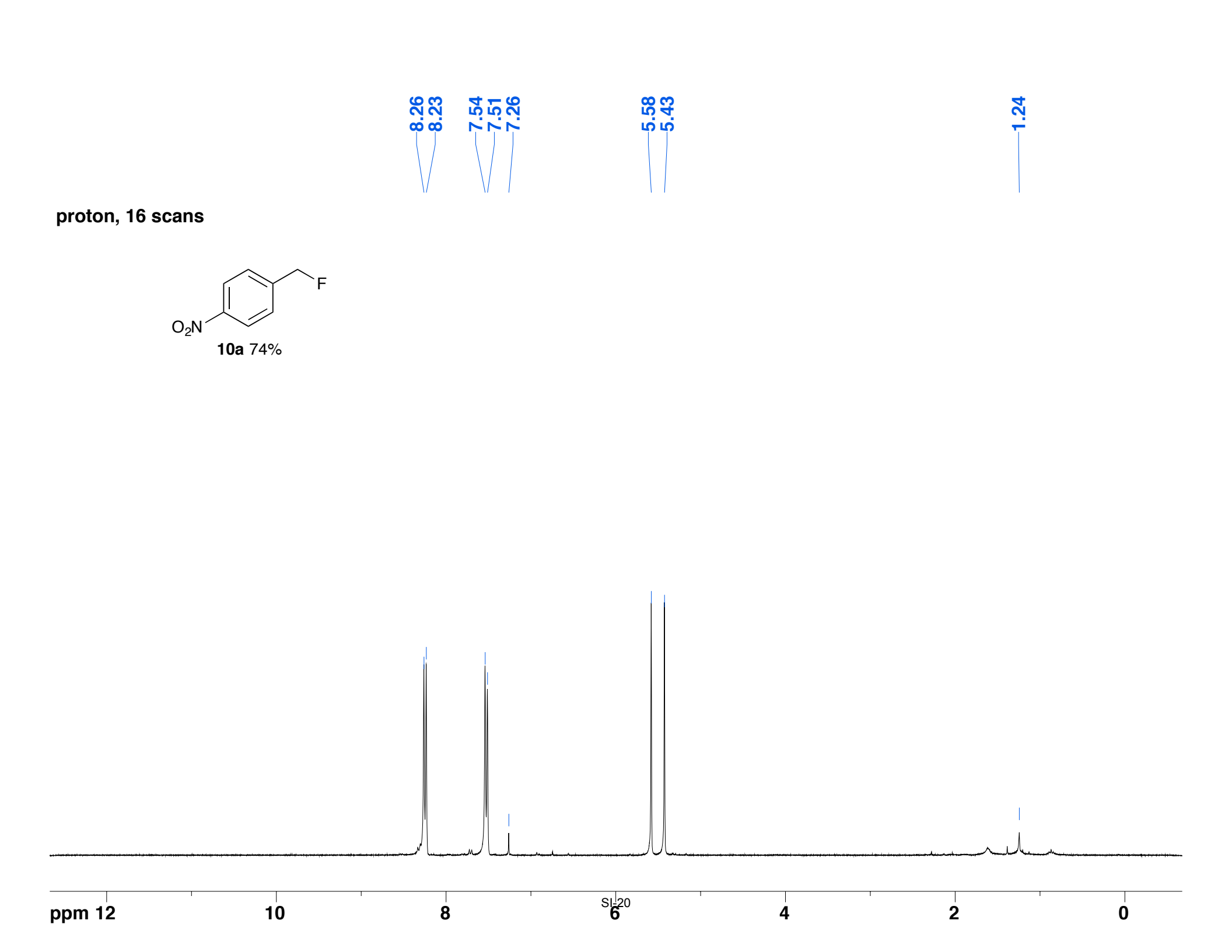

139.74
135.35
132.81
132.12
130.52
127.61
125.14
77.31
77.06
76.81
C-13 proton Decoupled
NH2
N
Cl
Cl
13k
ppm
200
150
100
50
0
SI-15

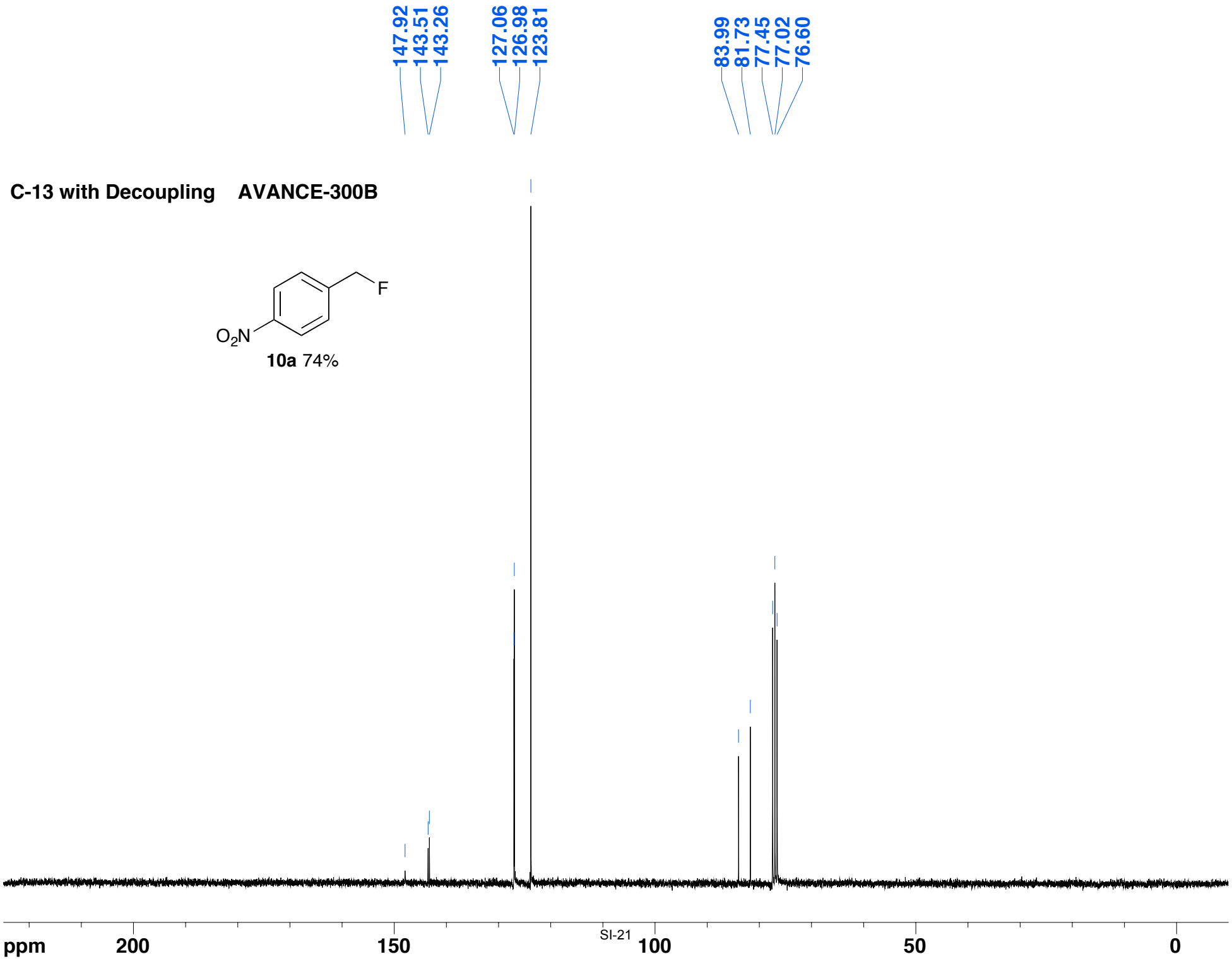

7.75
7.47
7.42
7.28
6.98
5.56
5.12
proton 16 scans
N
NH2
OBn
13n
ppm
9
8
7
6
5
4
3
2
1
0

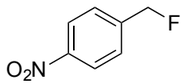

159.08
142.89
136.91
136.61
129.61
128.58
127.98
127.53
119.51
115.96
111.24
77.29
77.03
76.78
C-13 proton Decoupled
NH2
N
OBn
13n
ppm
150
100
50
0


8.04
7.92
7.35
7.33
6.75
6.74
5.64
5.64
3.82
proton 16 scans
NH2
N
MeO
Br
13o
1
1
3
1
1
2
ppm
8
6
4
2
0


155.81
137.19
131.95
128.29
125.71
113.50
112.70
77.35
77.10
76.84
55.77
C-13 proton Decoupled
NH2
N
MeO
Br
13o
ppm
150
100
50
0


8.26
8.23
7.54
7.51
7.26
5.58
5.43
1.24
proton, 16 scans
F
O2N
10a 74%
ppm 12
10
8
6
4
2
0
SI-20

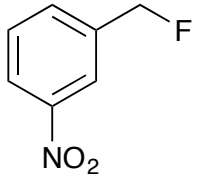

147.92
143.51
143.26
127.06
126.98
123.81
83.99
81.73
77.45
77.02
76.60
C-13 with Decoupling AVANCE-300B
F
O2N
10a 74%
ppm
200
150
100
50
0



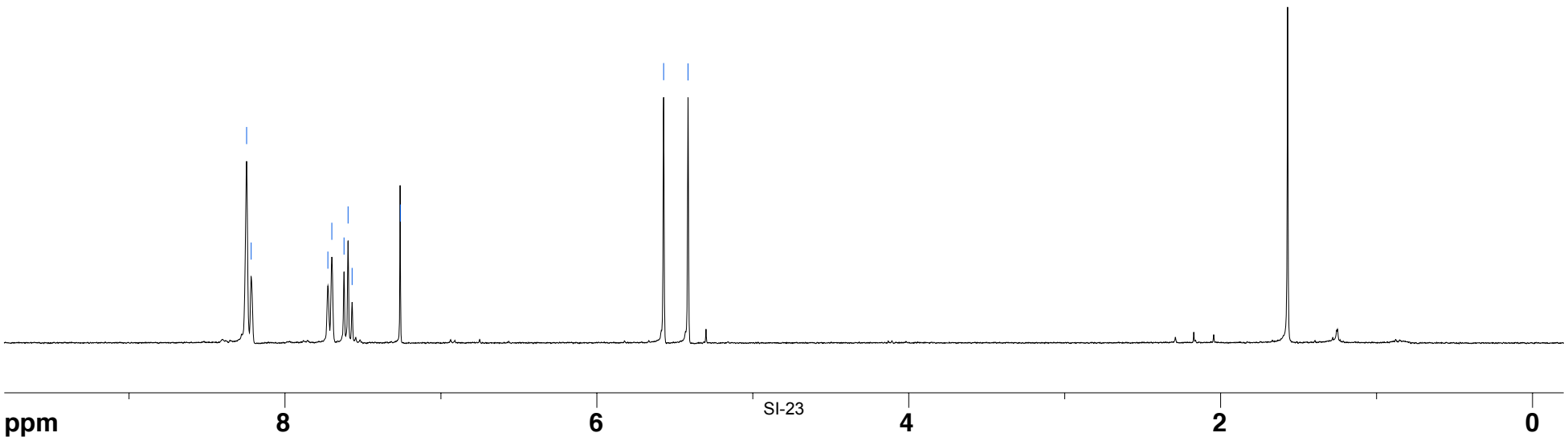
-215.635

ppm -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220

proton, 16 scans



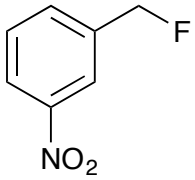
10b 71%



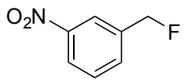
148.37
138.35
138.21
137.20
132.77
132.72
131.19
129.72
123.50
121.84
121.79

83.63
82.28
77.31
77.05
76.80

C-13 proton Decoupled

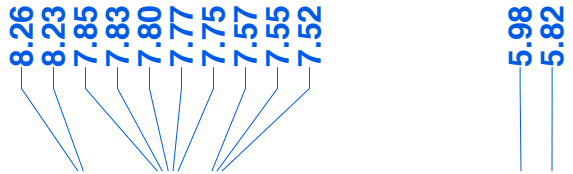


10b 71%

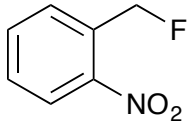


-212.404
-212.500
-212.596

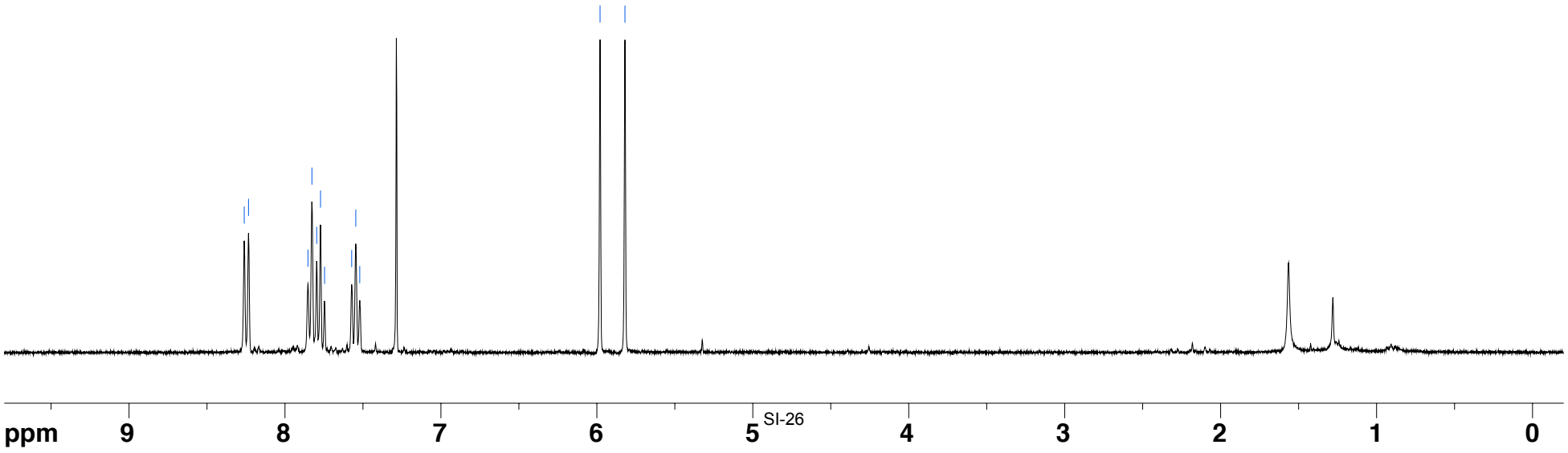
ppm -0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220



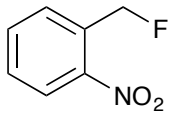
proton 16 scans AVANCE 300B



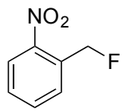
10c 64%



C-13 proton Decoupled

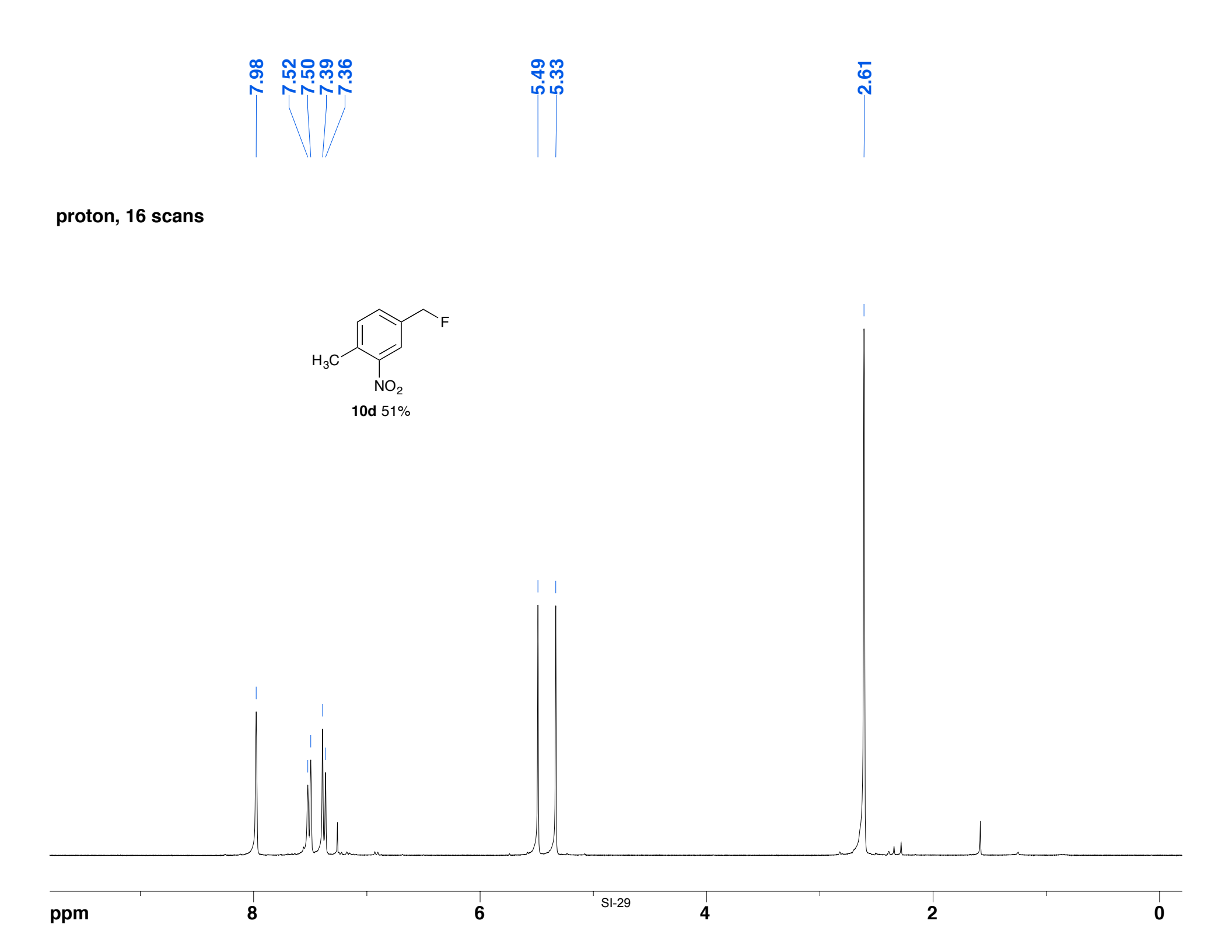


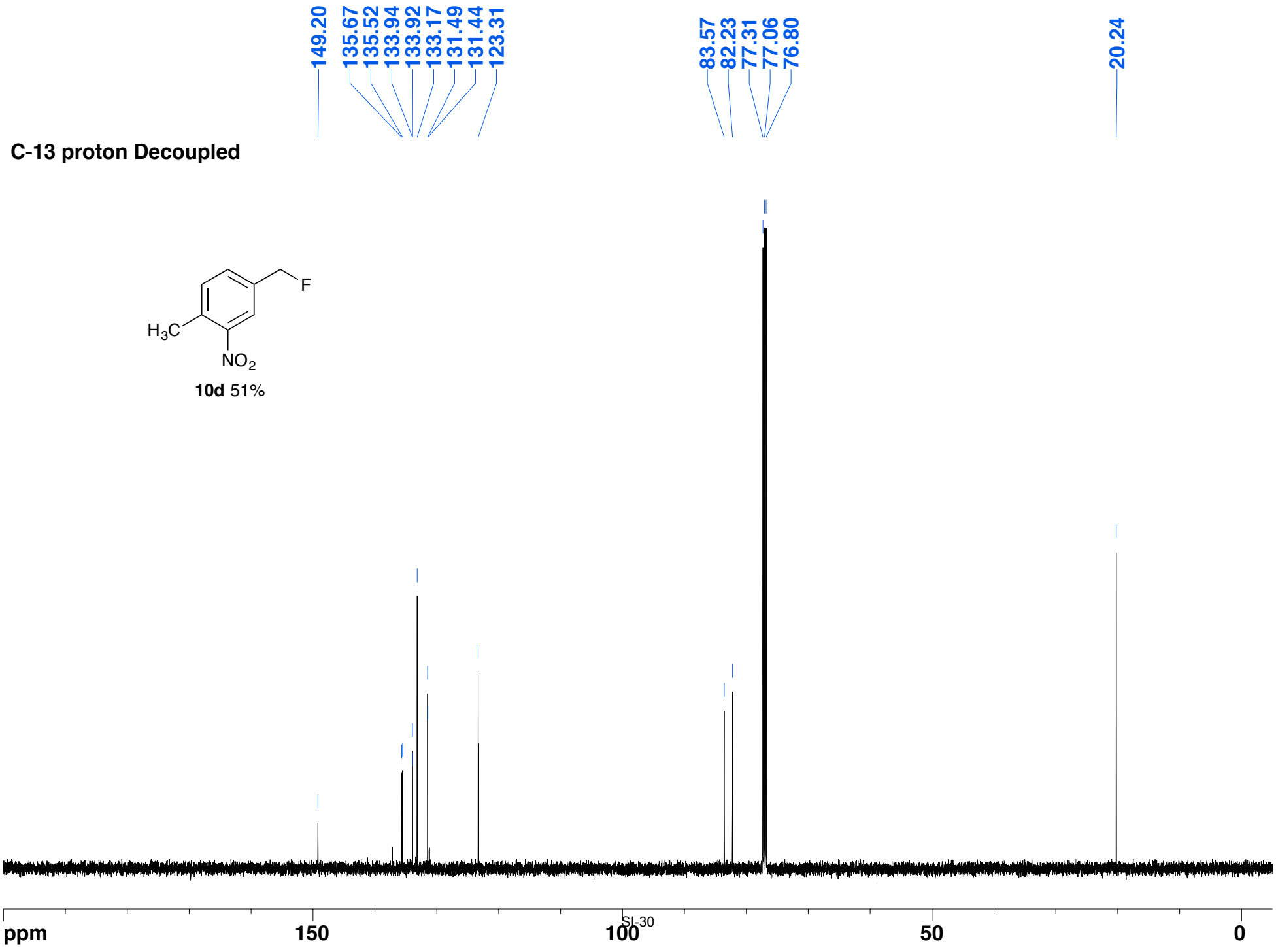
10c 64%

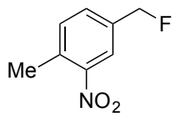


-219.309

ppm -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220

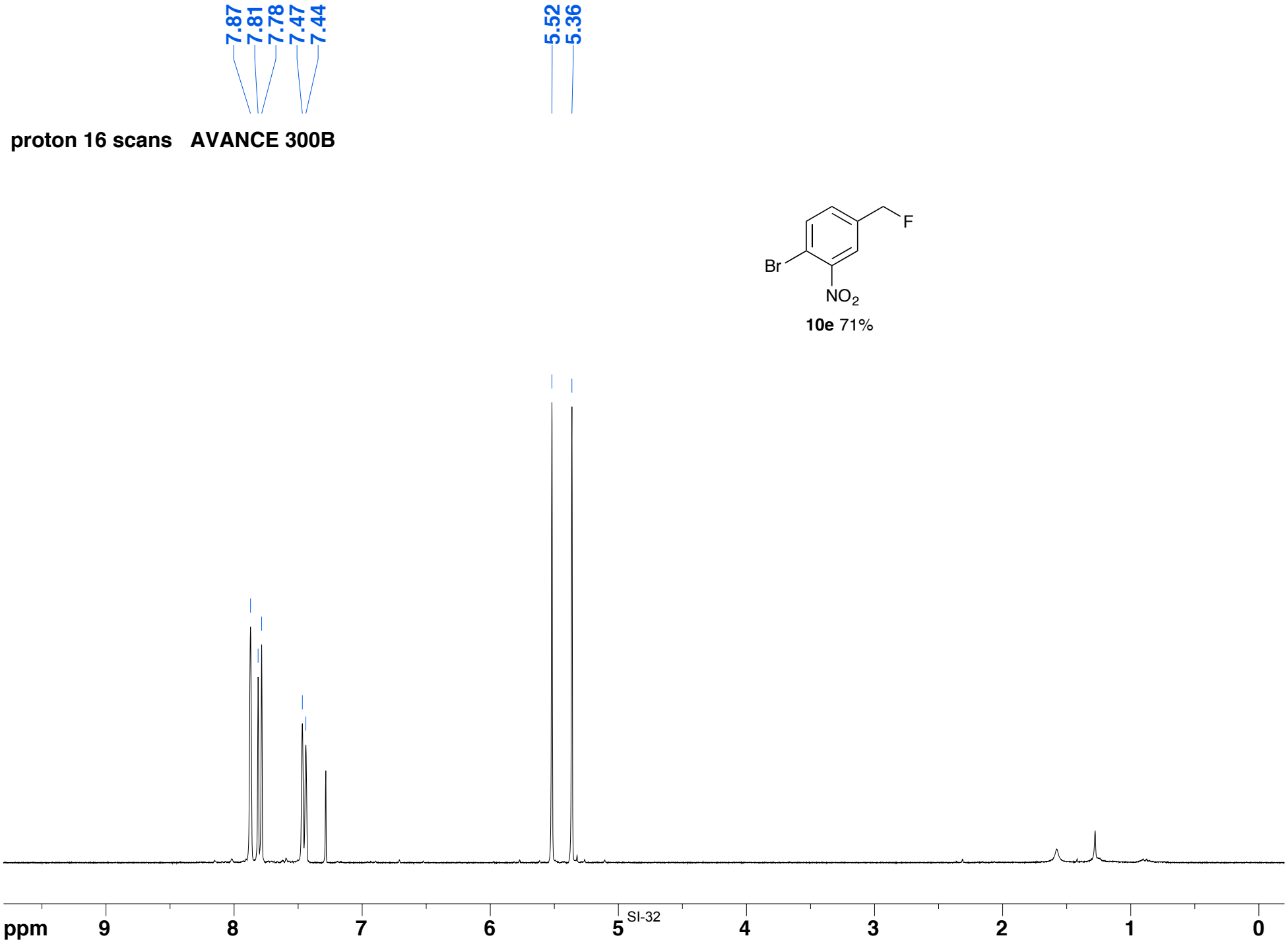

7.98
7.52
7.50
7.39
7.36
5.49
5.33
2.61
proton, 16 scans
F
H3C
NO2
10d 51%
ppm
8
6
4
2
0


149.20
135.67
135.52
133.94
133.92
133.17
131.49
131.44
123.31
83.57
82.23
77.31
77.06
76.80
20.24
C-13 proton Decoupled
F
H3C
NO2
10d 51%
ppm
150
100
50
0



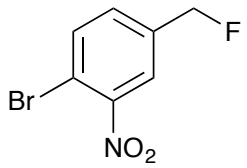
-210.650

ppm -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220

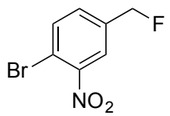

7.87
7.81
7.78
7.47
7.44
5.52
5.36
proton 16 scans AVANCE 300B
Br
F
NO2
10e 71%
ppm
9
8
7
6
5
4
3
2
1
0

149.90
137.47
137.32
135.40
131.15
131.10
123.78
123.73
114.45
114.43
82.92
77.28
77.02
76.77

C-13 proton Decoupled

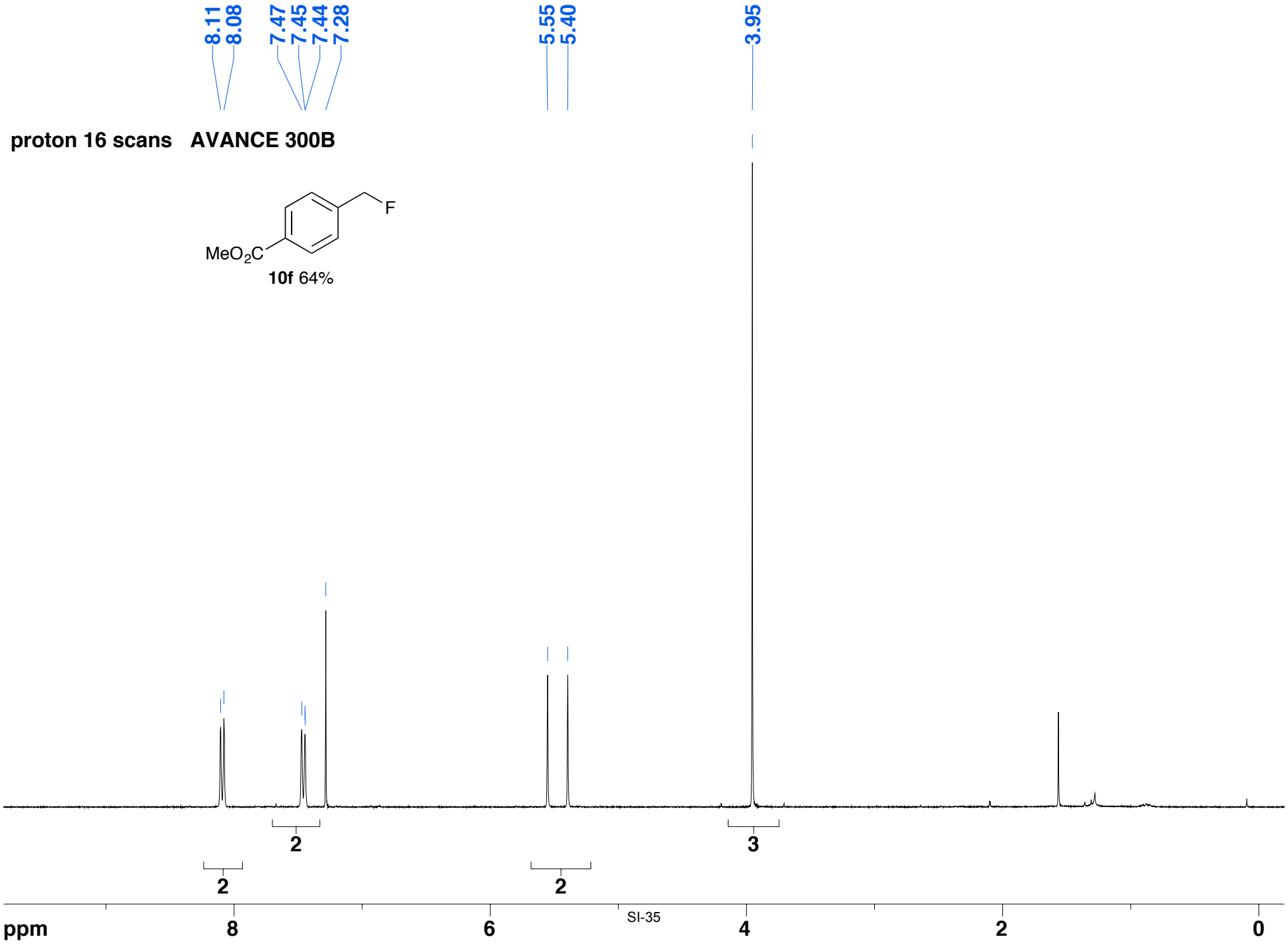


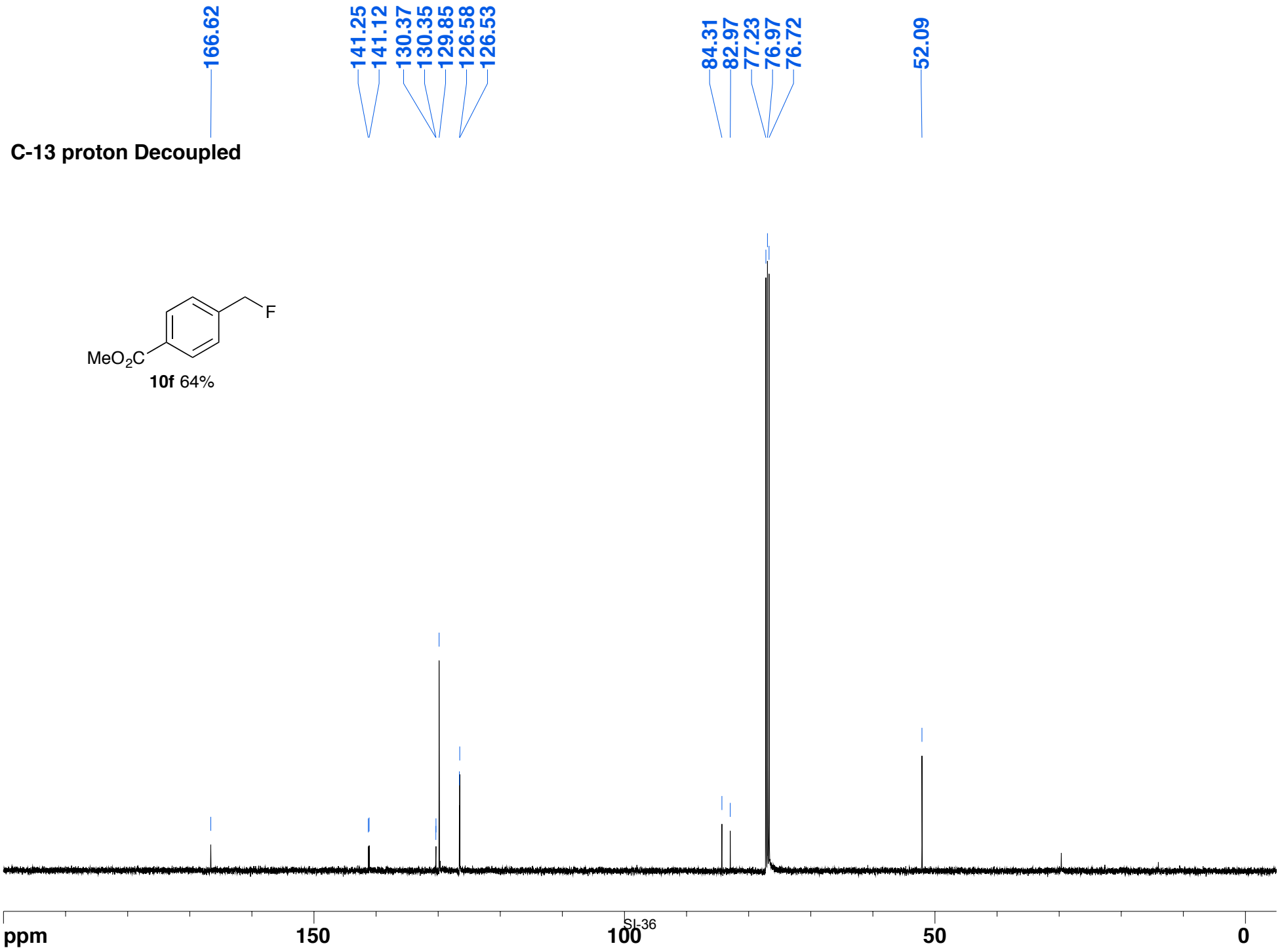
10e 71%



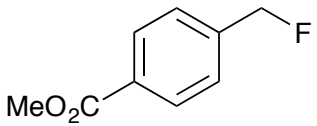
-213.678

ppm -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230

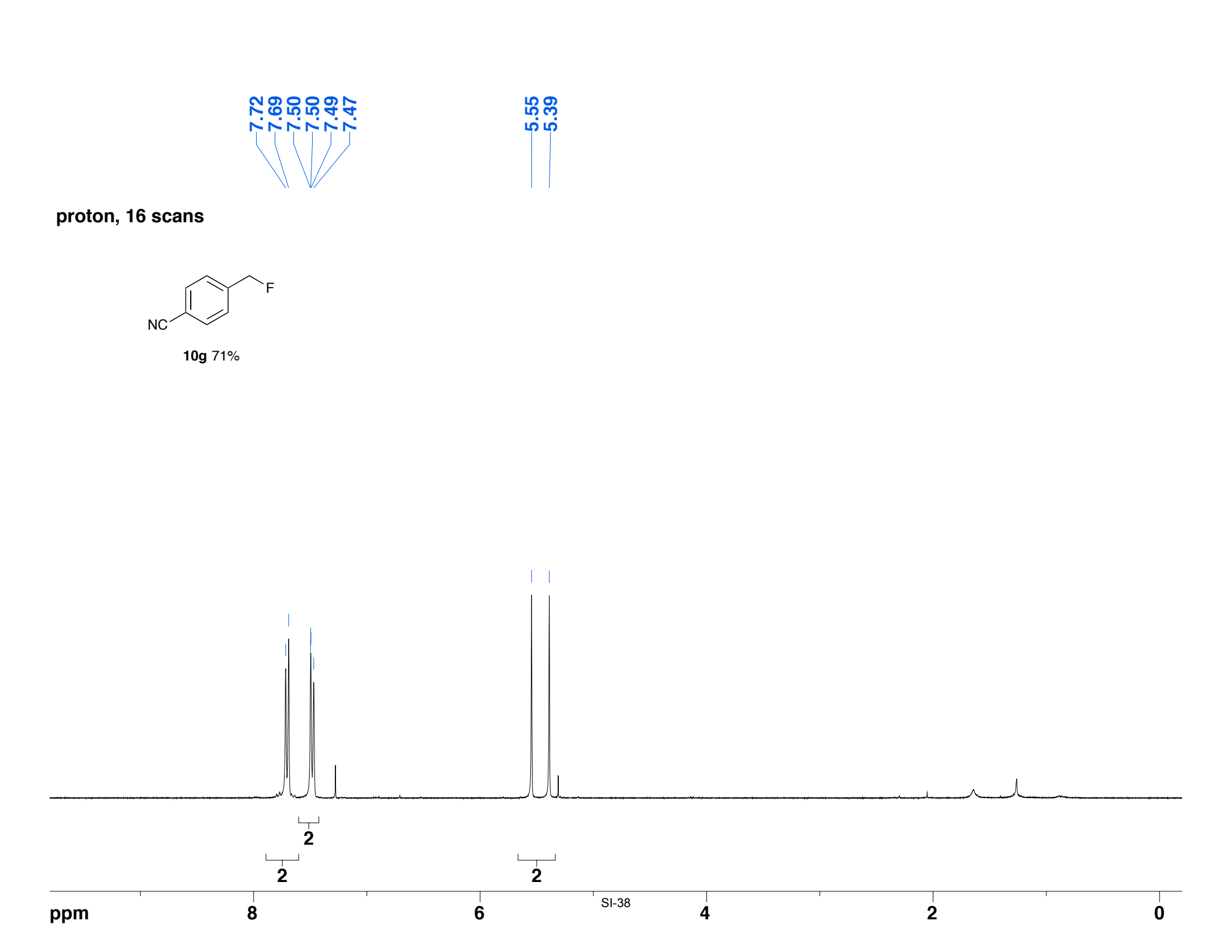

8.11
8.08
7.47
7.45
7.44
7.28
5.55
5.40
3.95
proton 16 scans AVANCE 300B
F
MeO2C
10f 64%
2
2
2
3
ppm
8
6
4
2
0

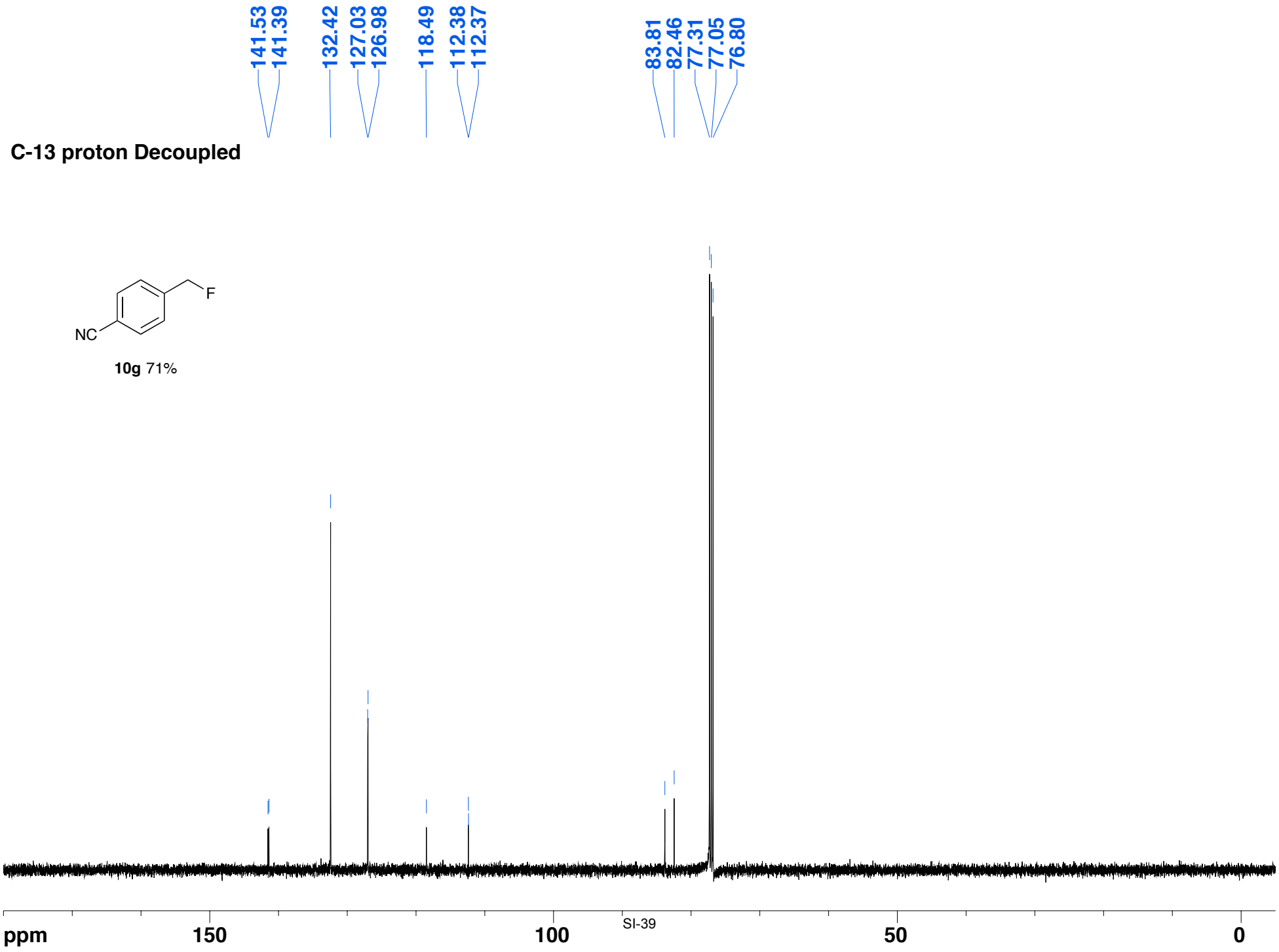

166.62
141.25
141.12
130.37
130.35
129.85
126.58
126.53
84.31
82.97
77.23
76.97
76.72
52.09
C-13 proton Decoupled
F
MeO2C
10f 64%
ppm
150
100
50
0

F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm

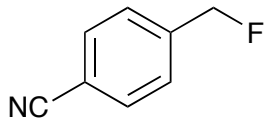


10f 64%

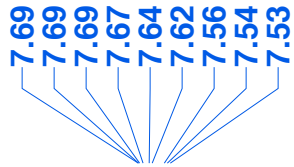

7.72
7.69
7.50
7.50
7.49
7.47
5.55
5.39
proton, 16 scans
F
NC
10g 71%
2
2
2
ppm
8
6
4
2
0


141.53
141.39
132.42
127.03
126.98
118.49
112.38
112.37
83.81
82.46
77.31
77.05
76.80
C-13 proton Decoupled
F
NC
10g 71%
ppm
150
100
50
0

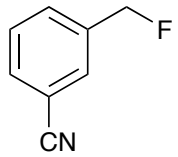
F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm



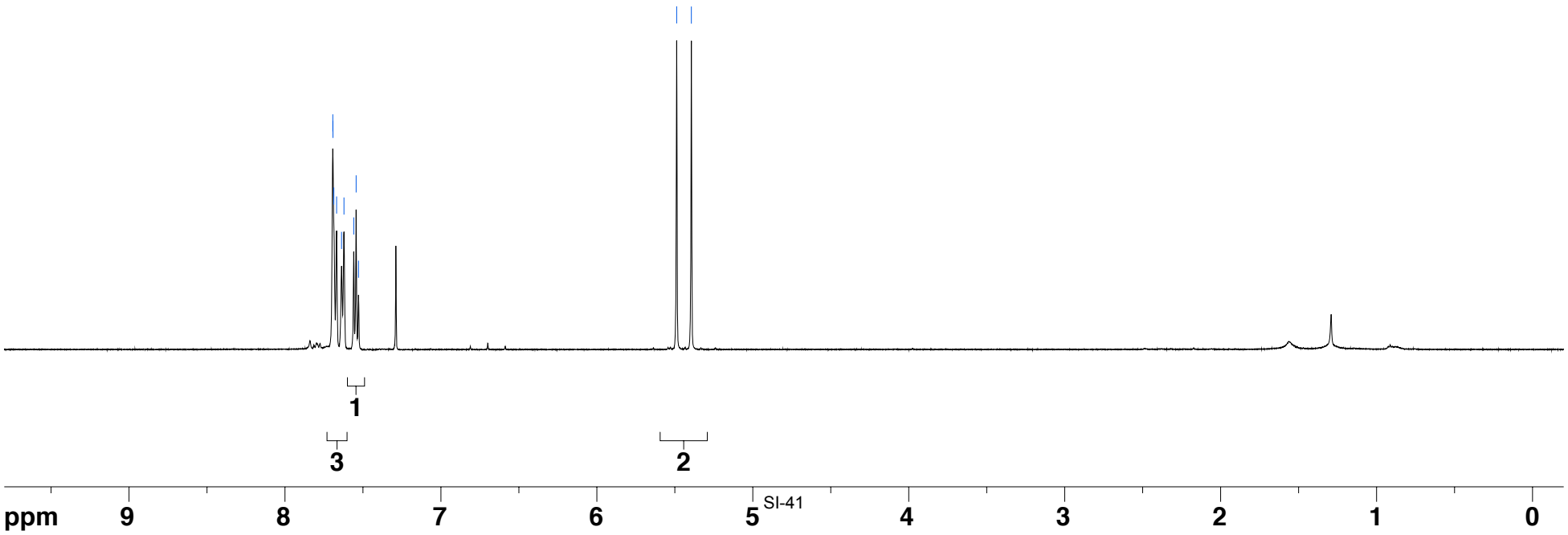
10g 71%

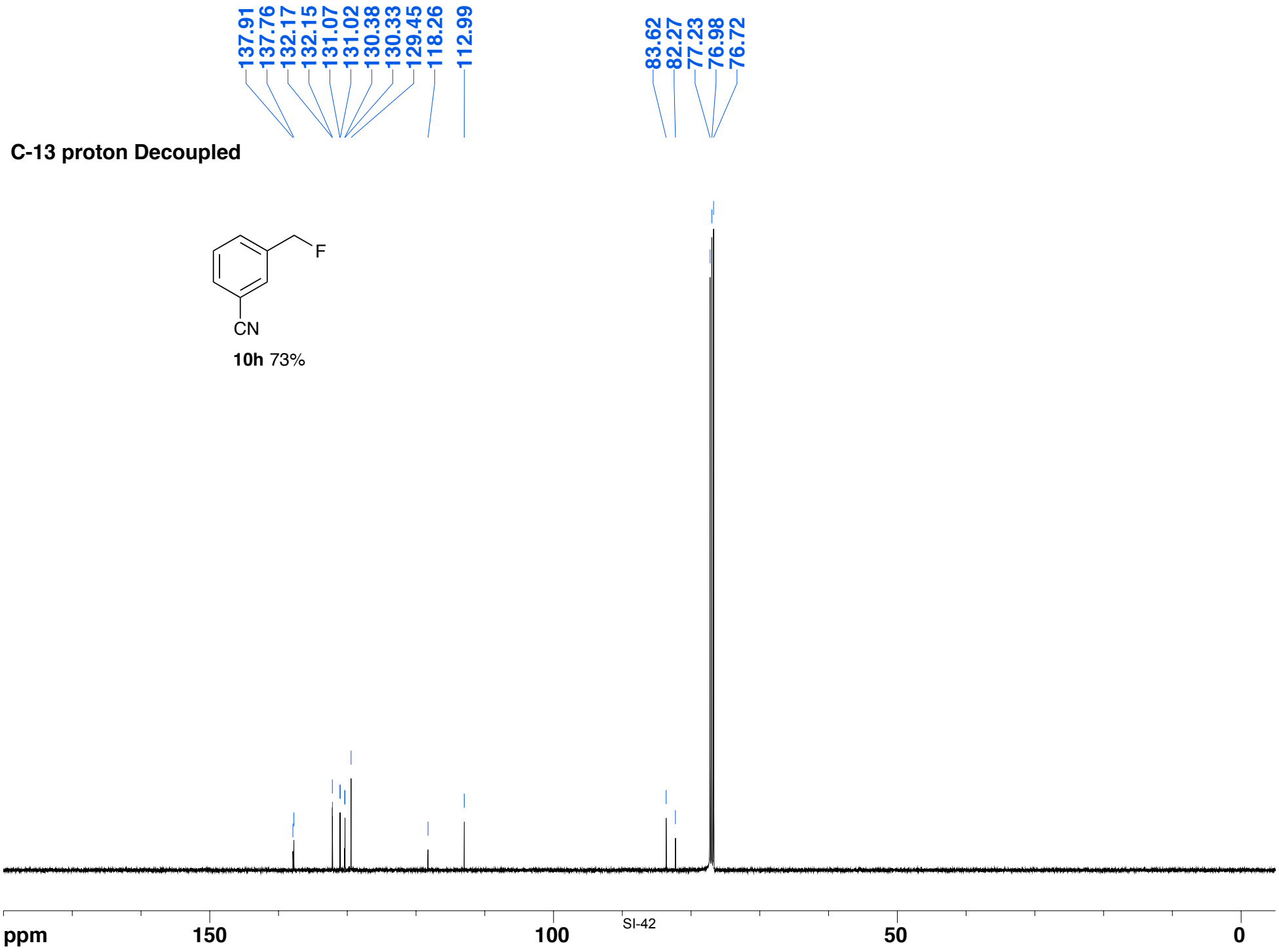


Proton, 16 Scans AVANCE 500

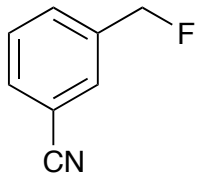


10h 73%

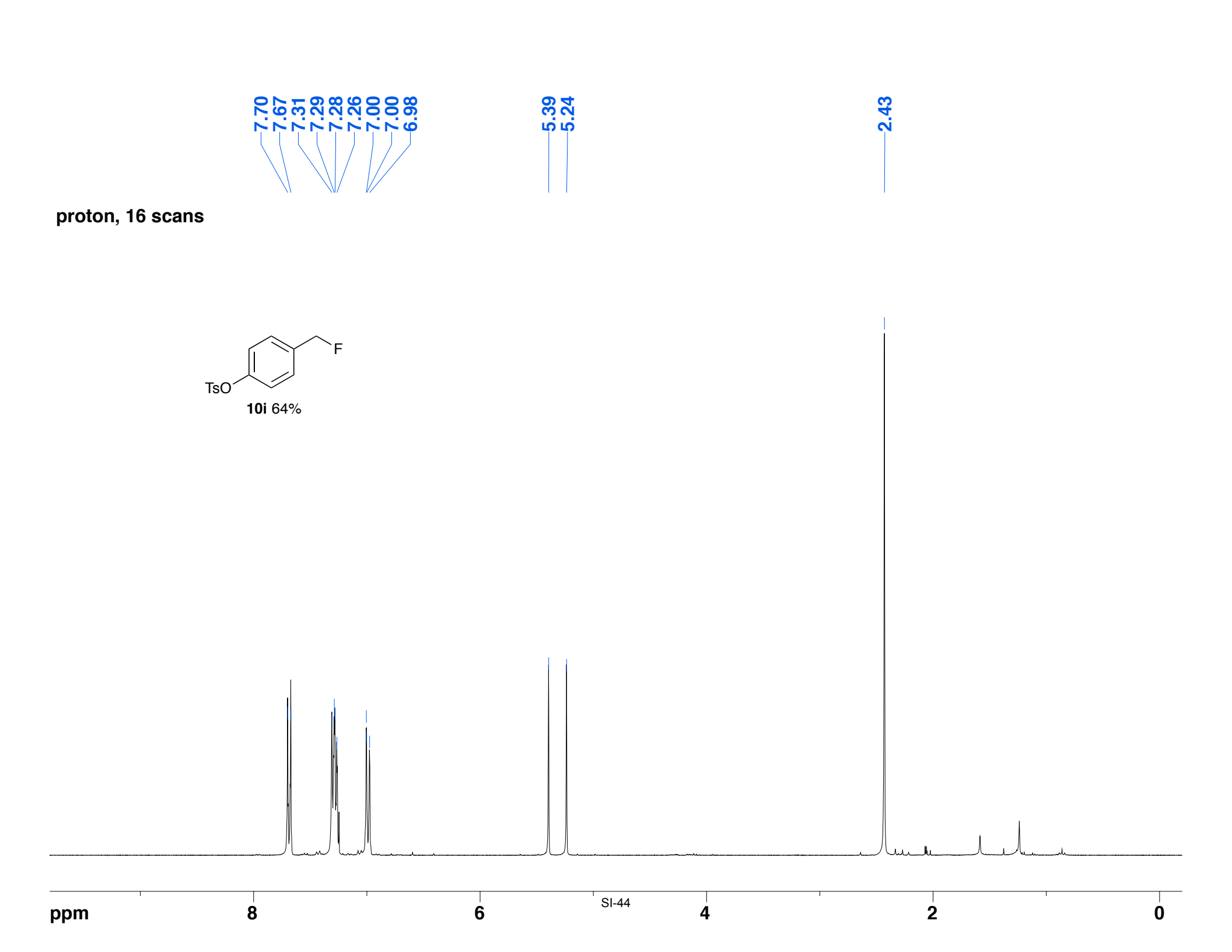


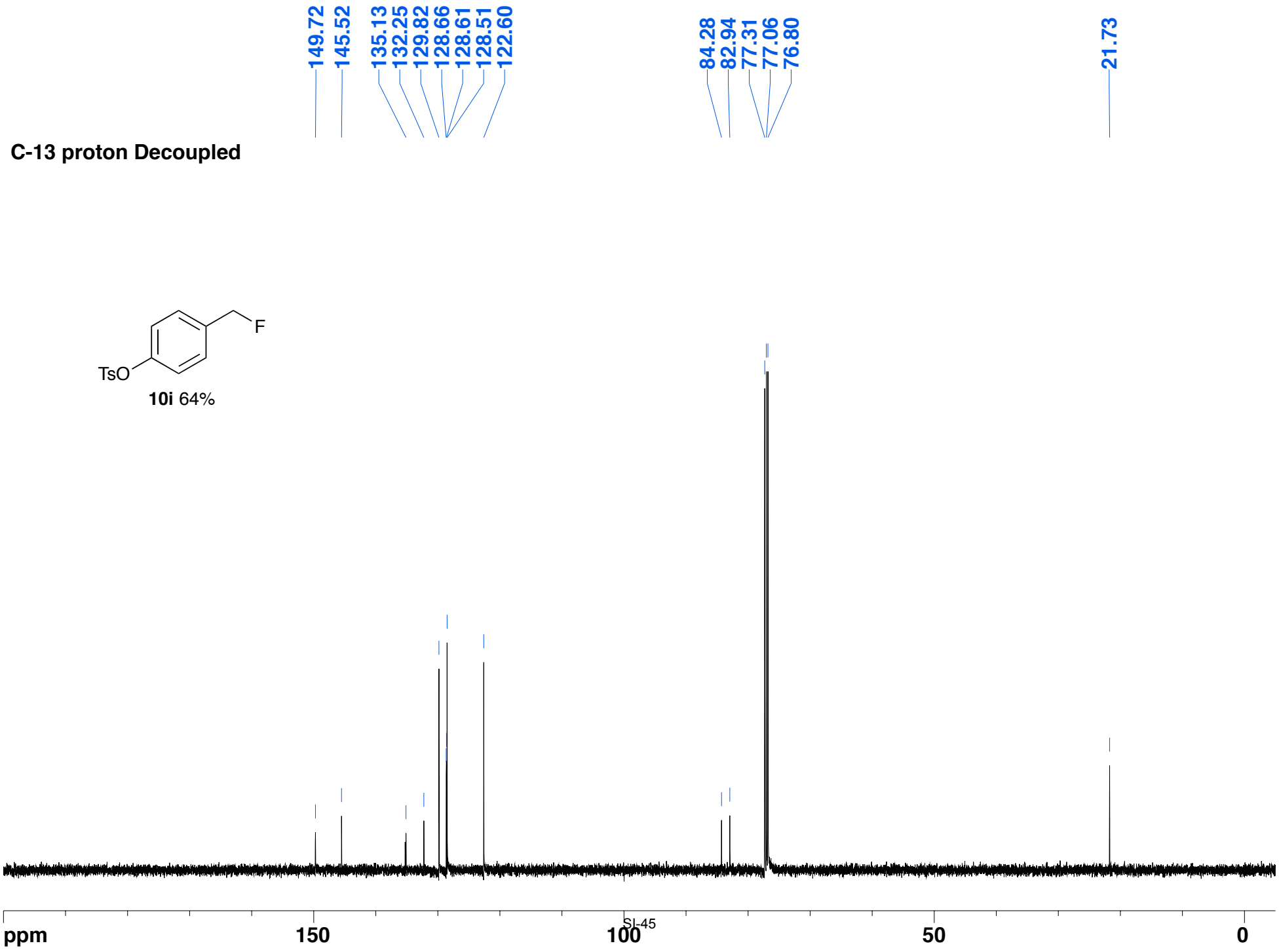

137.91
137.76
132.17
132.15
131.07
131.02
130.38
130.33
129.45
118.26
112.99
83.62
82.27
77.23
76.98
76.72
C-13 proton Decoupled
F
CN
10h 73%
ppm
150
100
50
0

F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm

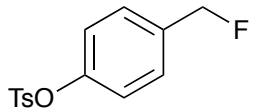


10h 73%

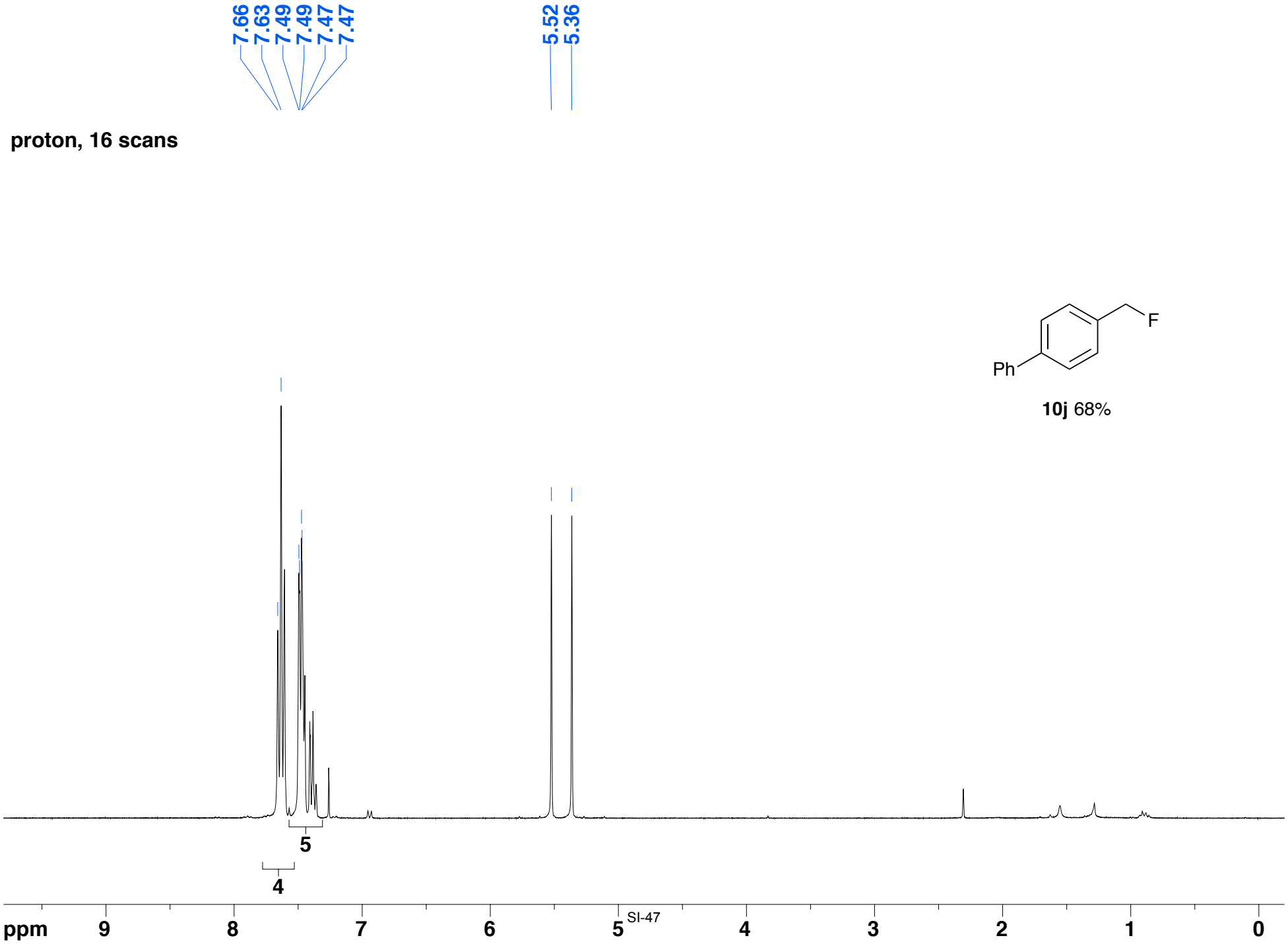

7.70
7.67
7.31
7.29
7.28
7.26
7.00
7.00
6.98
5.39
5.24
2.43
proton, 16 scans
F
TsO
10i 64%
ppm
8
6
4
2
0

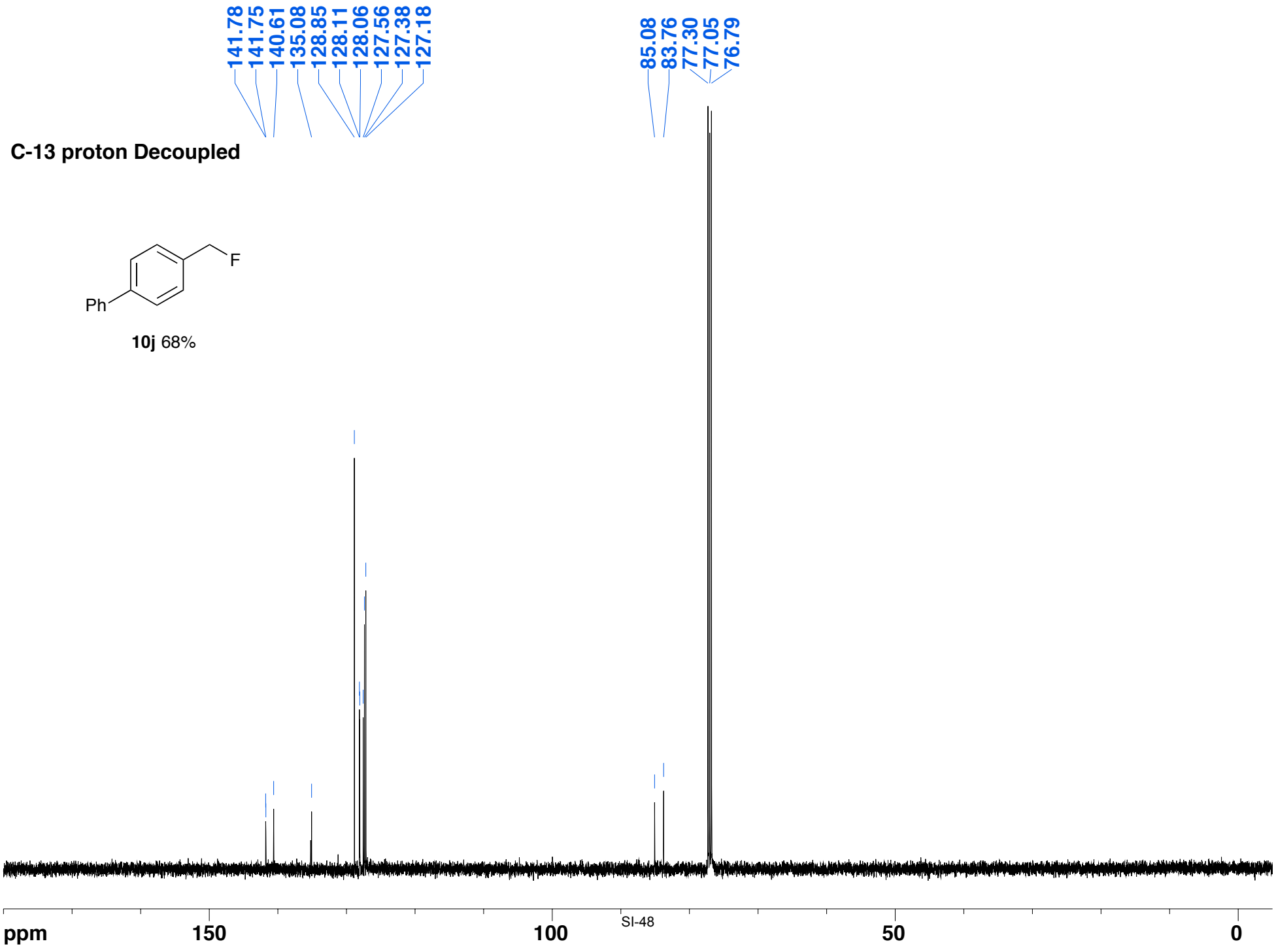

149.72
145.52
135.13
132.25
129.82
128.66
128.61
128.51
122.60
84.28
82.94
77.31
77.06
76.80
21.73
C-13 proton Decoupled
F
TsO
10i 64%
ppm
150
100
50
0

F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm

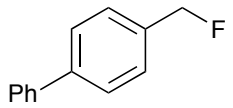


10i 64%

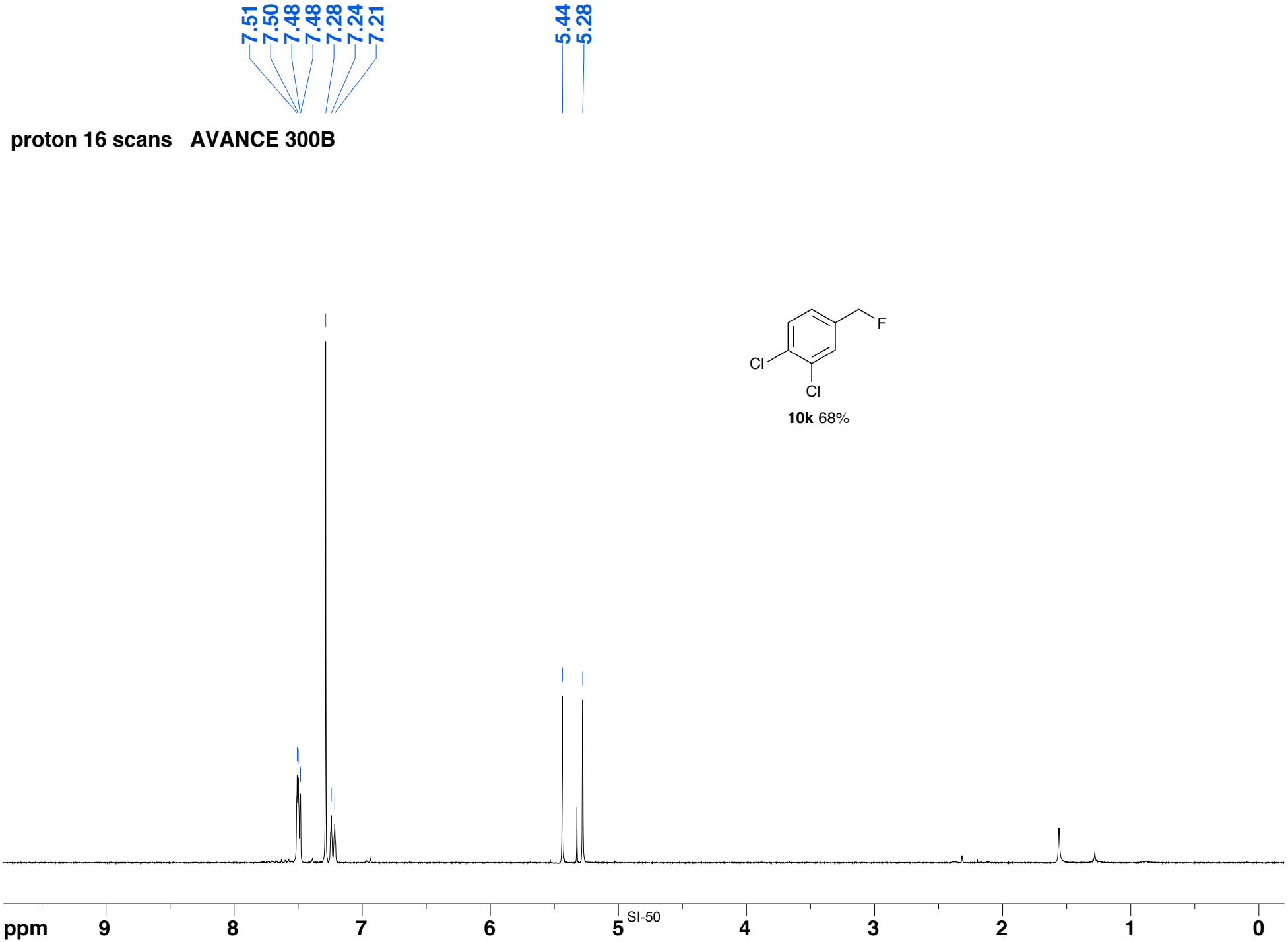

7.66
7.63
7.49
7.49
7.47
7.47
5.52
5.36
proton, 16 scans
F
Ph
10j 68%
5
4
ppm
9
8
7
6
5
4
3
2
1
0


141.78
141.75
140.61
135.08
128.85
128.11
128.06
127.56
127.38
127.18
85.08
83.76
77.30
77.05
76.79
C-13 proton Decoupled
F
Ph
10j 68%
ppm
150
100
50
0

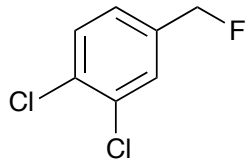
F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm



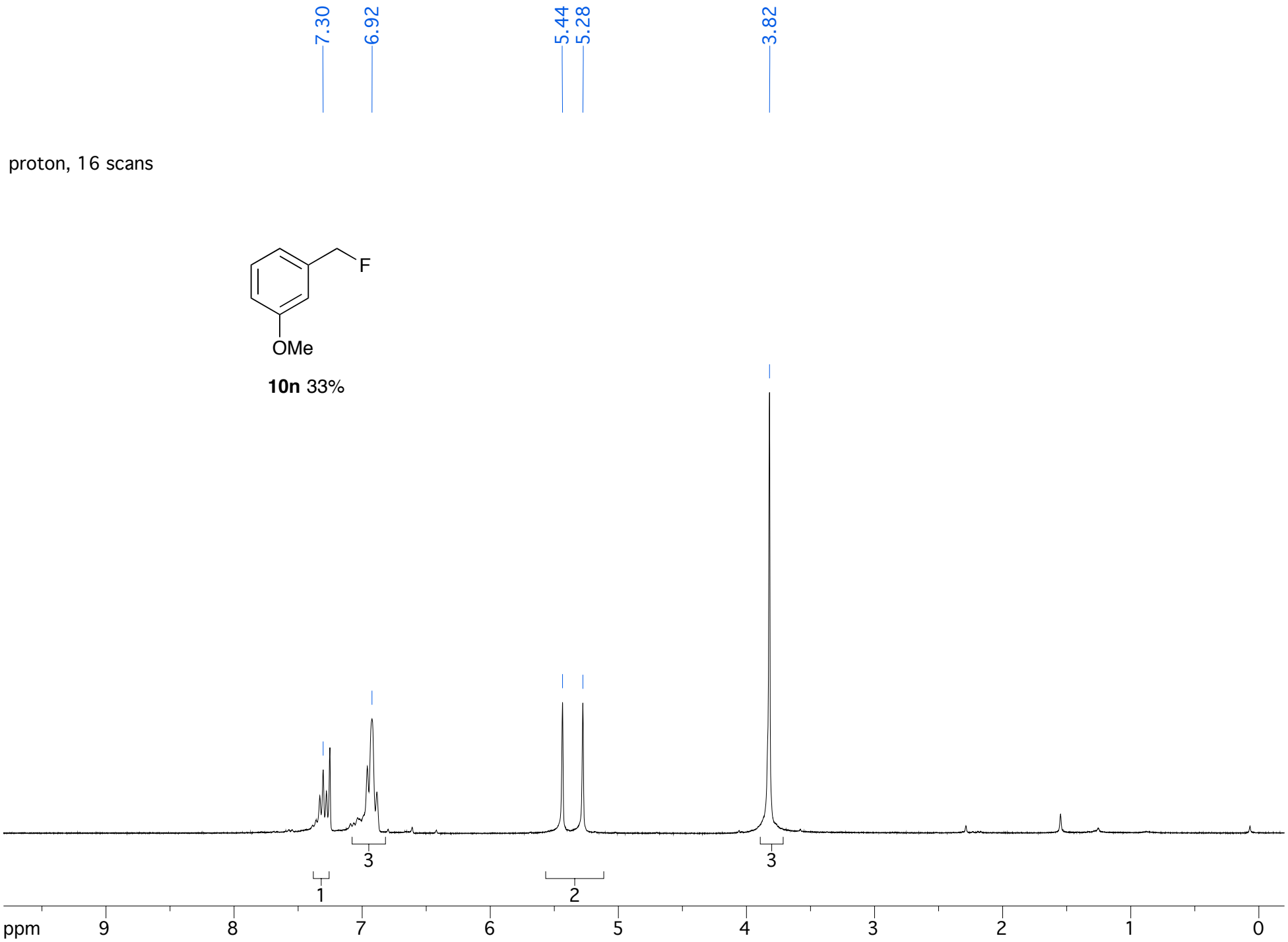
10j 68%


7.51
7.50
7.48
7.48
7.28
7.24
7.21
5.44
5.28
proton 16 scans AVANCE 300B
Cl
Cl
F
10k 68%
ppm
9
8
7
6
5
4
3
2
1
0

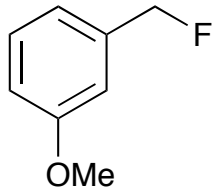
19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm



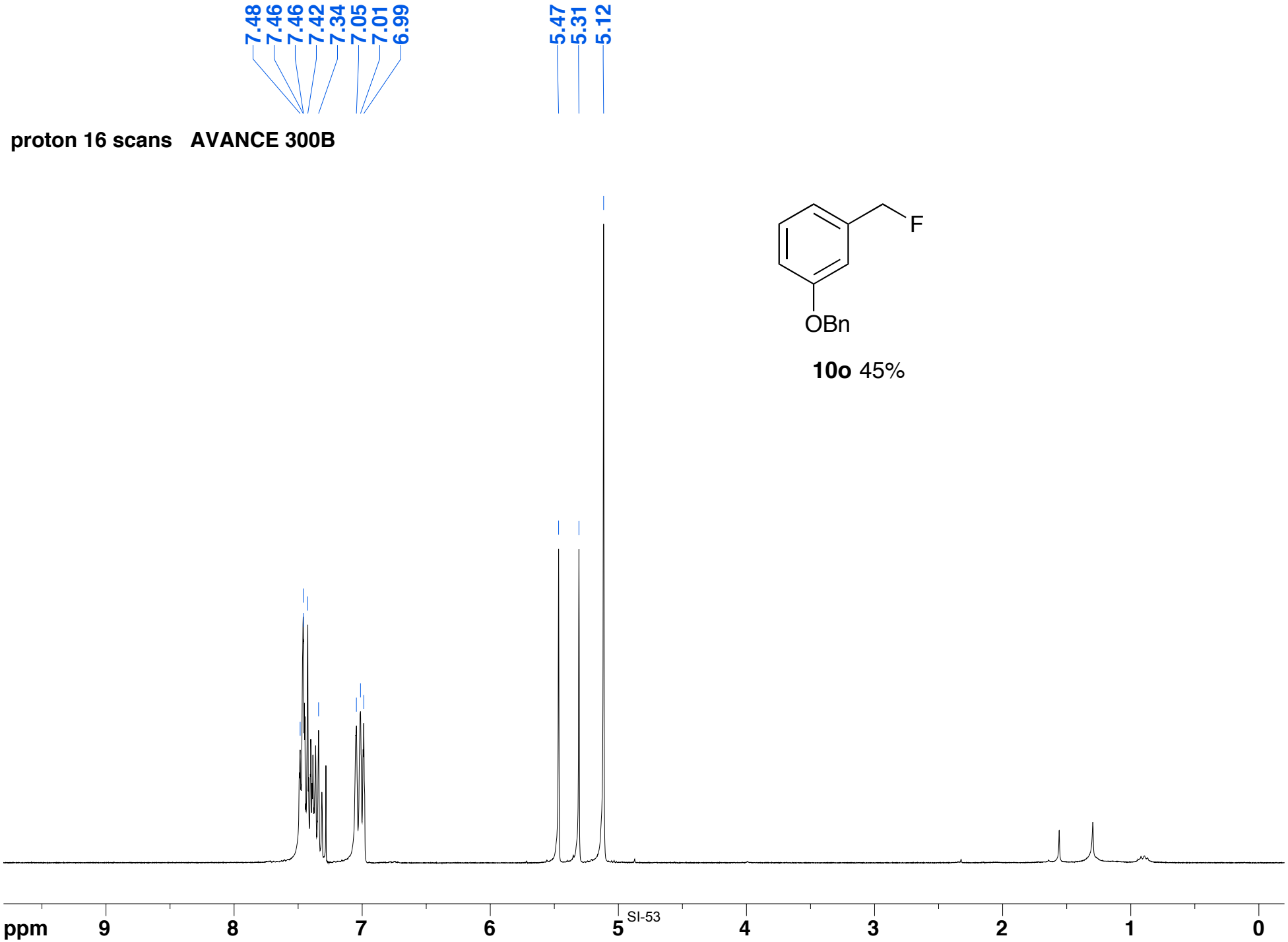
10k 68%

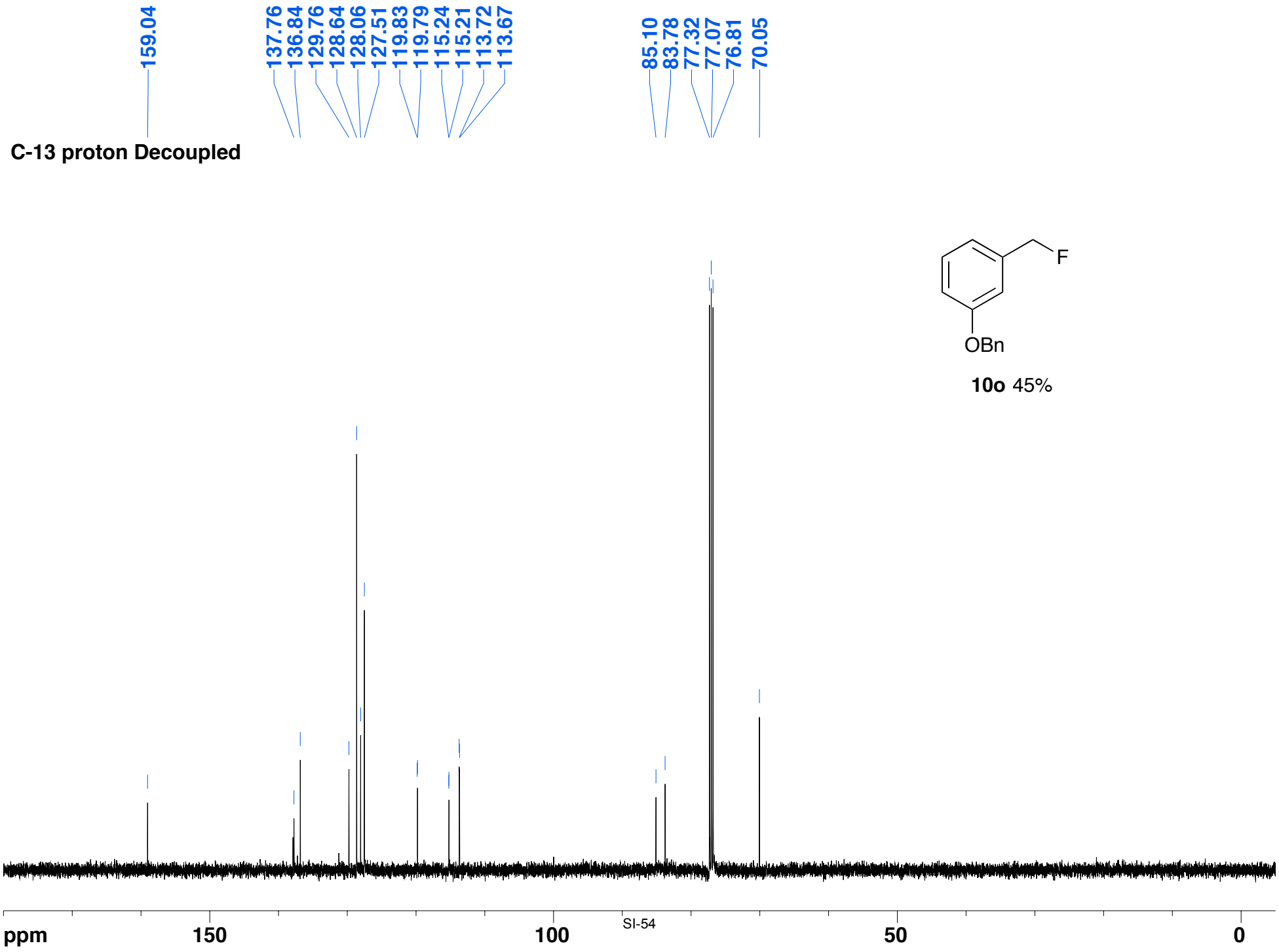

7.30
6.92
5.44
5.28
3.82
proton, 16 scans
F
OMe
10n 33%
3
3
1
2
ppm
9
8
7
6
5
4
3
2
1
0

F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm

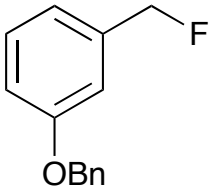


10n 33%

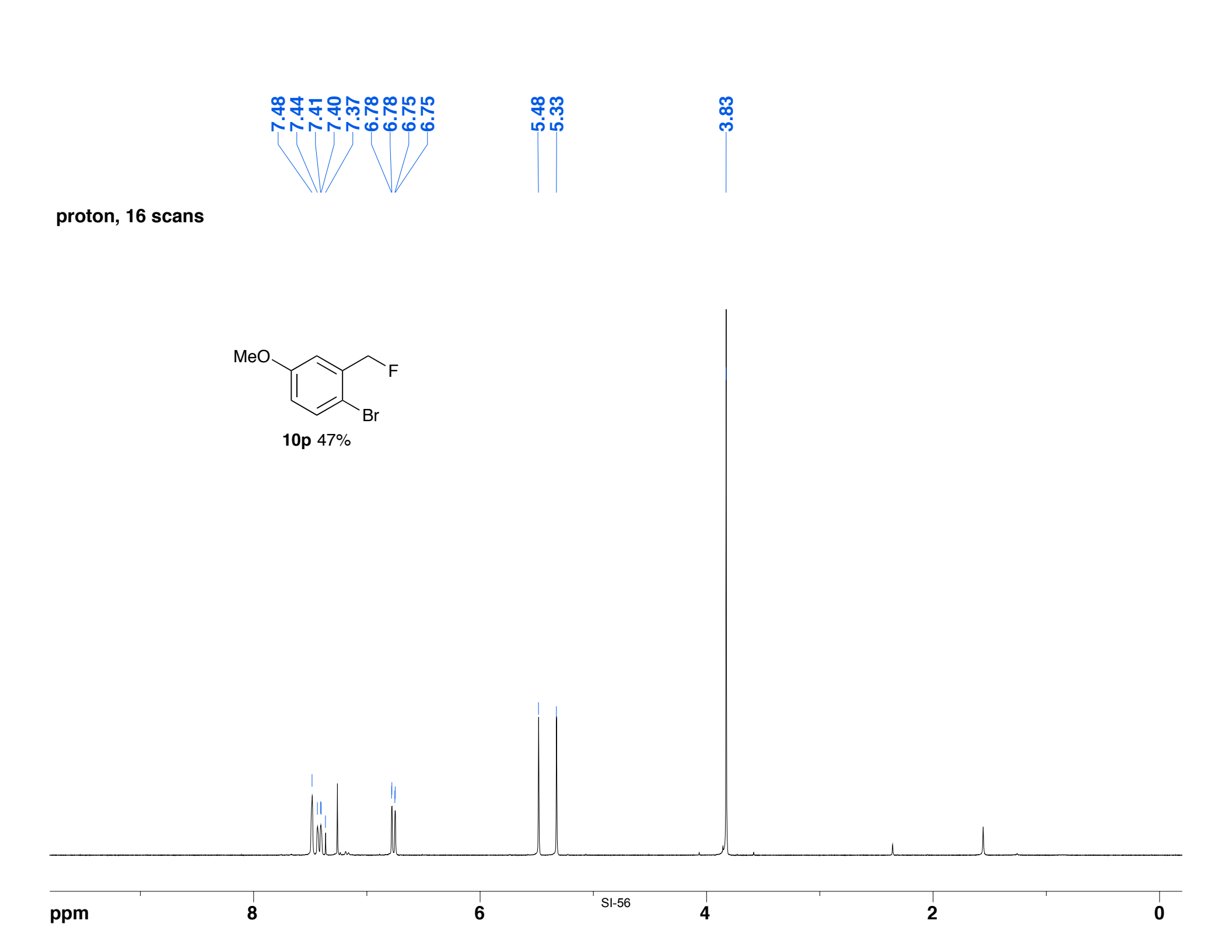

7.48
7.46
7.46
7.42
7.34
7.05
7.01
6.99
5.47
5.31
5.12
proton 16 scans AVANCE 300B
F
OBn
10o 45%
ppm
9
8
7
6
5
4
3
2
1
0


159.04
137.76
136.84
129.76
128.64
128.06
127.51
119.83
119.79
115.24
115.21
113.72
113.67
85.10
83.78
77.32
77.07
76.81
70.05
C-13 proton Decoupled
F
OBn
10o 45%
ppm
150
100
50
0

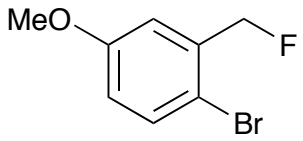
F-19 Observed H1 Decoupled Sweep Width 210 ppm



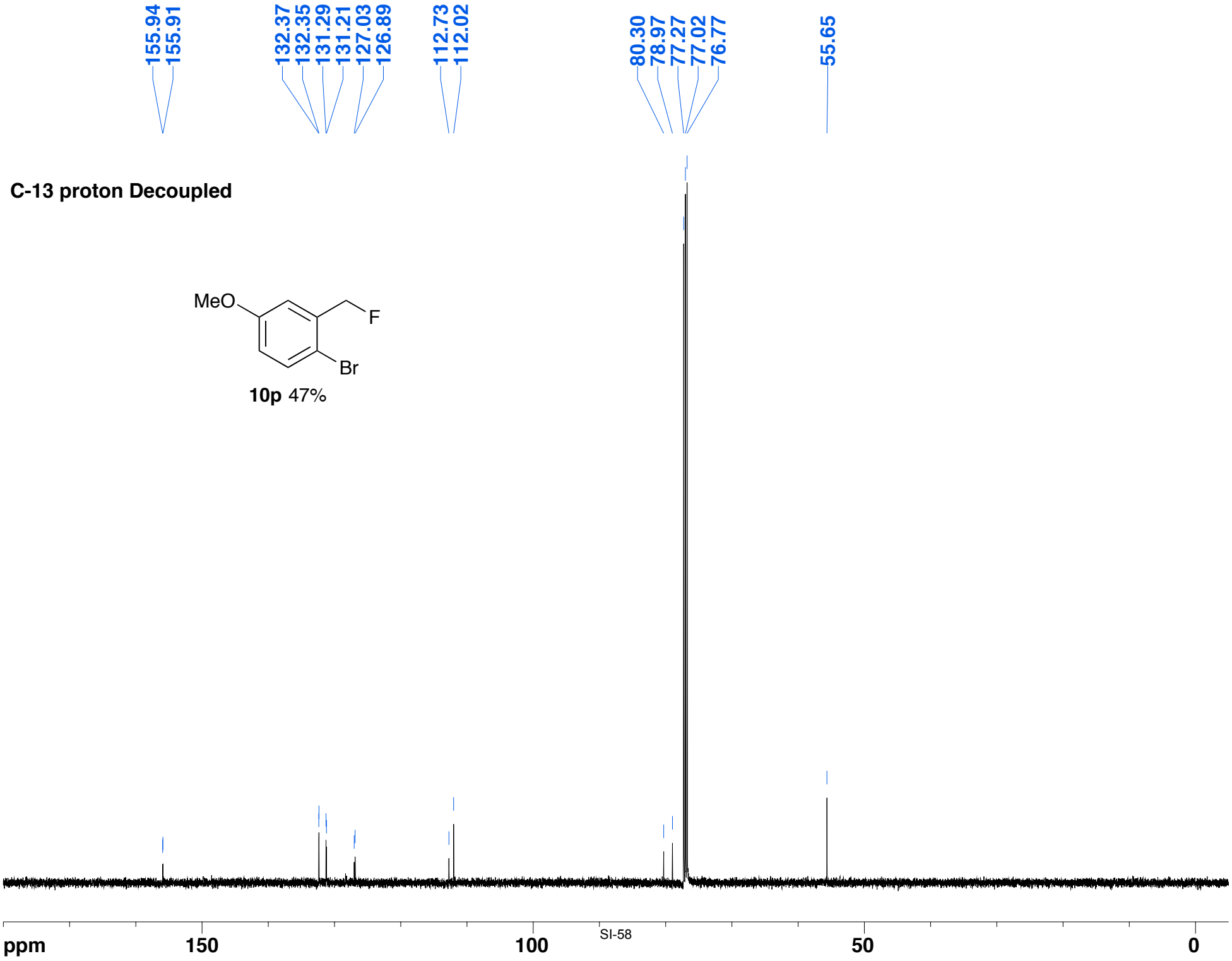
10o 45%


7.48
7.44
7.41
7.40
7.37
6.78
6.78
6.75
6.75
5.48
5.33
3.83
proton, 16 scans
MeO
F
Br
10p 47%
ppm
8
6
4
2
0

F19CPD- 300 ppm Sweep Width referenced to TFA=-76.53 ppm



10p 47%


155.94
155.91
132.37
132.35
131.29
131.21
127.03
126.89
112.73
112.02
80.30
78.97
77.27
77.02
76.77
55.65
C-13 proton Decoupled
MeO
F
Br
10p 47%
ppm
150
100
50
0