SUPPORTING INFORMATION

Synthesis of 1,2-Bis(Trifluoromethylthio)arenes via Aryne Intermediates

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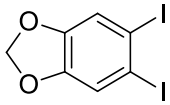
General considerations:

Reactions were performed either in 2-dram vials or 200 mL flasks. Column chromatography was performed on 60Å silica gel (Sorbent Technologies). GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). The ^{1}H, ^{19}F and ^{13}CNMR were recorded on JEOL EC-500 or JEOL EC-600 spectrometers using TMS or residual solvent peak as a reference. Compounds for HRMS were analyzed by positive mode electrospray ionization (CI or ESI) using Agilent QTOF mass spectrometer in the Mass Spectrometry Facility (MSF) of the Department of Chemistry and Biochemistry of University of Texas-Austin. IR spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Temperature was monitored by Fluke 54 II B Dual Input Digital Thermometer with Data Logging. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker. Low temperature reactions were performed using Cryo Immersion Cooler FC100 with Flexi Probe from SP Scientific. All procedures were performed under nitrogen atmosphere unless otherwise noted. Room temperature is 23 °C. All silyl aryl triflates except ones used in Table 1, entries 3 and 14 and Scheme 1 are known.[1] Preparation of the unknown silyl aryl triflates is reported below.

TMPLi: A 500 mL oven-dried Schlenk flask equipped with a magnetic stir bar and a septum was evacuated and backfilled with nitrogen 5 times. TMPH (2,2,6,6-tetramethylpiperidine; 35.4 g, 42.3 mL, 250 mmol) was added via syringe, followed by anhydrous pentane to give approximately 100 mL of solution. The mixture was cooled to -78 °C (dry ice-acetone bath) and stirred for 10 minutes. n-BuLi (1.6 M in hexanes, 180 mL, 288 mmol) was added dropwise and reaction mixture was stirred for 30 minutes at -78 °C, then warmed to room temperature (23 °C) and stirred overnight. The solvent was cannula transferred away from the solid. The solid was washed with pentane 3 times using cannula to remove the supernatant solution and then dried under vacuum to remove all solvent. Residue was dried under vacuum for at least 5 hours. A light yellow powder of solid TMPLi (33.1 g) was obtained.

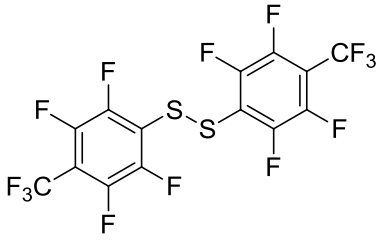
5,6-Diiodo-1,3-benzodioxole (SM for Table 2, entry 5)



5,6-Diiodo-1,3-benzodioxole was synthesized by a modified literature procedure.[2] A mixture of 1,3-benzodioxole (1.22 g, 10 mmol), periodic acid (1.82 g, 8 mmol) and iodine (5.08 g, 20 mmol) was warmed in a mixture of acetic acid, water, and sulfuric acid (12.3 mL, 10:2:0.3) to 70 °C . The mixture was stirred for 48 h at 70 °C, cooled, and then diluted with ethyl acetate (20 mL). Aqueous sodium bisulfite solution (100 mL) was added to the mixture and it was shaken for a couple of minutes. The mixture was transferred to a separatory funnel and was extracted with dichloromethane (3 x 100 mL). Solvent was evaporated in vacuo, and the product was purified by chromatography on a silica gel column to provide 2.05 g (55%) of 5,6-diiodo-1,3-benzodioxole as a white solid. R_f = 0.50, hexanes. ^{1}H NMR (600 MHz) δ 7.29 (s, 2H), 5.96 (s, 2H). ^{13}C NMR (151 MHz) δ 149.0, 118.8, 102.2, 96.4. This compound is known.[3]

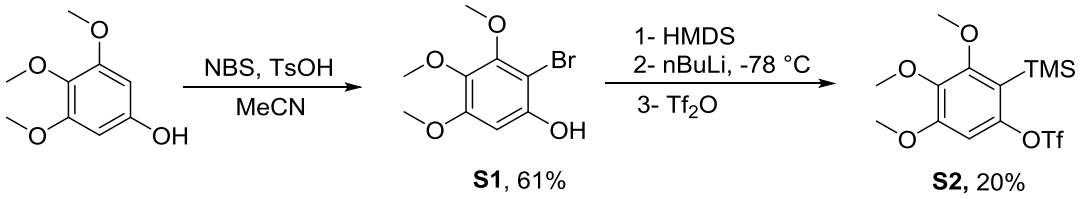
Bis[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]disulfide (SM for product 22)

This compound was synthesized by using a modified literature procedure.[4] 2,3,5,6-



Tetrafluoro-4-(trifluoromethyl)benzenethiol, (4.95 g, 19.8 mmol) was added to a solution of sodium perborate tetrahydrate (6.1 g, 39.6 mmol) in HOAc/H_2O (62.5 mL HOAc + 25 mL H_2O) at room temperature. After stirring for 4 h, reaction was quenched by adding EtOAc (100 mL) and water (100 mL). The organic layer was washed with water, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane, R_f = 0.60) to afford the product in 92% yield as a yellow oil (4.54 g). ^{19}F NMR (565 MHz) δ -56.4 (t, *J* = 22.0 Hz, 6F), -129.6 (dd, *J* = 22.0, 11.0 Hz, 4F), -136.7 – -139.3 (m, 4F). This compound is known.[5]

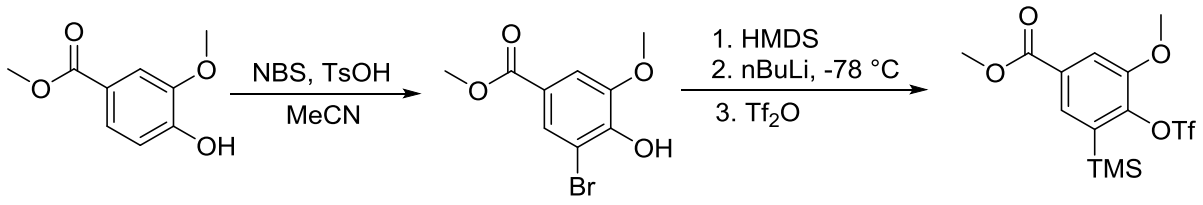
3,4,5-Trimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (Table 1, entry 3)



S1, 61% **S2**, 20%

3,4,5-Trimethoxyphenol (20 mmol, 3.68 g) and TsOH (10 mmol, 1.9 g) were dissolved in acetonitrile (40 mL) at room temperature and NBS (20 mmol, 3.56 g) was added to the solution. After 30 minutes, reaction was stopped and volatiles were evaporated. The residue was subjected to column chromatography (hexanes/CH_2Cl_2 1:1). After column chromatography, a red oil was obtained (3.15 g, 61%). R_f = 0.25 (hexanes/CH_2Cl_2 1:1). Following the reported procedure,[1] **S1** was converted to **S2** in 20% overall yield (0.93 g). Product was isolated as a light yellow oil. R_f = 0.30, hexanes/CH_2Cl_2 6/1. FT-IR (neat, cm^{-1}) ν 2965, 2842, 1601, 1509, 1416, 1244, 1206. HRMS (CI) calc. For $C_{13}H_{19}O_6SF_3Si$ $[M]^+$: 388.0624; found: 388.0629.

3-Methoxy-4-(trifluoromethylsulfonyloxy)-5-(trimethylsilyl)methyl benzoate (Table 1, entry 14)



S3, 55% **S4**, 25%

Methyl vanillate (3.5 mmol, 0.637 g) and TsOH (3.5 mmol, 0.665 g) were dissolved in acetonitrile (20 mL) at room temperature and solid *N*-bromosuccinimide (3.5 mmol, 0.62 g) was added to the solution. After stirring for 4 hours, reaction was stopped and volatiles were evaporated. The residue was subjected to column chromatography (hexanes/ethyl acetate 3:1). After column chromatography, compound **S3** was obtained as a yellow solid

(743 mg, 55 %). R_f = 0.25 (hexanes/ethyl acetate 3:1). Substance **S3** was converted to **S4** by following the procedure of Garg[1] in 25% yield. Product **S4** was isolated as a colorless oil (hexane:ethyl acetate/10:1, R_f = 0.30). ^{1}H NMR (500 MHz) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 0.40 (s, 9H).^{13}C NMR (126 MHz) δ 166.1, 150.2, 146.3, 135.7, 130.3, 128.4, 121.5 (q, *J* = 322.2 Hz), 115.0, 56.0, 52.6, -0.6. FT-IR (neat, cm^{-1}) ν 2955, 1725 (C=O), 1585, 1402, 1313, 1293, 1201. HRMS (CI) calc. For $C_{13}H_{17}O_6SF_3Si$ $[M]^+$: 386.0467; found: 386.0463.

General procedure for silyl aryl iodide and bromide synthesis:

A. Deprotonative silylation of aryl iodides or bromides:

Outside the glovebox a 200 mL round bottom flask was equipped with a magnetic stir bar (1 x 3 cm). The flask was placed inside the glovebox. To the flask was added solid TMPLi (10 mmol, 1.47 g). The flask was then taken out of the glovebox and placed into cooling bath (ethanol/liquid N_2) at -110 °C. The reaction temperature was monitored by immersing a digital thermometer into the ethanol/nitrogen cooling bath. Precise temperature regime is extremely important for reproducibility of the silylation reactions. Solvent or solvent mixture (45 mL of Et_2O/THF:3/1) was added via syringe to the reaction flask. Solution was stirred for 10 - 15 minutes at -110 °C. In one 10 dram vial, aryl iodide or bromide (10 mmol) was dissolved in solvent (5 - 10 mL) and in another 10 dram vial, silyl chloride was dissolved in solvent (5 mL). Both 10 dram vials were placed in cooling bath (10 - 15 minutes) to reach reaction temperature. Aryl iodide solution was rapidly (5 seconds) added to TMPLi solution via syringe following by rapid addition of silyl chloride solution. Reaction mixture was warmed to appropriate temperature and either kept at that temperature for 19 h or quenched immediately. Water (10 - 20 mL) was added dropwise to reaction mixture to quench the remaining TMPLi. The crude mixture was extracted with ethyl acetate (3 x 20 mL) and volatiles were evaporated. Residue was subjected to flash chromatography on silica gel.

B. Lithiation/quench of 1,2-diiodoarenes:

Lithiation/silylation of 1,2-diiodoarenes was performed using a modified procedure reported earlier.[6] A 250 mL oven-dried flask equipped with a magnetic stir bar (1 x 3 cm) and a septum was evacuated and backfilled with nitrogen 5 times. A solution of 1,2-diiodooarene (10 - 20 mmol) in 3/1 mixture of Et_2O/THF (80 - 100 mL) was injected via syringe into the flask. Solution was stirred at - 110 °C for 10 - 15 minutes. n-BuLi (1.6 M in hexane, 1.2 equiv) was cooled to -90 °C in a separate vial and was dropwise added via syringe to the solution of 1,2-diiodoarene in 10 minutes. It is important to add nBuLi solution by the wall of flask as opposed to adding it into reaction solution directly. Mixture was warmed up to -95 °C and kept at this temperature for 15 - 20 minutes. A cooled solution (-95 °C) of dimethyl silyl chloride (15 equiv) in 3/1 mixture of Et_2O/THF (10 mL) was rapidly (10 - 15 sec) added into the reaction mixture via syringe. Reaction mixture was warmed to -65 °C and then was quenched dropwise with water (20 mL). The crude mixture was extracted with ethyl acetate (3 x 20 mL) and the volatiles were evaporated. Residue was subjected to flash chromatography on silica gel.

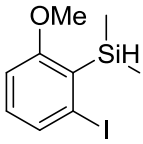
Note: Procedure B is extremely sensitive to temperature and time. If temperature does not reach -95 °C or if it is kept at -95 °C less than 15 - 20 minutes, the reaction will be incomplete and the separation of starting material and product is very difficult.

C. Iodine/bromine exchange in silyl aryl bromides

Lithiation/iodination of silyl aryl bromides was performed using the following procedure. A 200 mL oven-dried flask equipped with a magnetic stir bar (1 x 3 cm) and a septum was evacuated and backfilled with nitrogen 5 times. A solution of silyl aryl bromides (10 - 20 mmol) in 3/1 mixture of Et_2O/THF (80 - 100 mL) or pure THF or Et_2O was injected via syringe into the flask. Solution was stirred at - 78 °C for 10 - 15 minutes. n-BuLi (1.6 M in hexane) was cooled to -78 °C in a separate vial and then was dropwise added via syringe to the solution of silyl aryl bromides in 10 minutes. It is important to add nBuLi

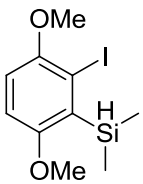
solution by the wall of flask as opposed to adding it into reaction solution directly. Mixture was stirred at -78 °C for 15 minutes, warmed up to - 60 °C and subsequently cooled down to -78 °C. A precooled solution of ICH_2CH_2I was injected into reaction mixture via syringe. Reaction mixture was kept at -78 °C for 45 minutes and then warmed to - 60 °C. Reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (20 mL) and was shaken strongly. Cooling bath was removed and mixture was stirred for 1 hour. The mixture was extracted with ether (3 x 20 mL) and the volatiles were evaporated. Residue was subjected to flash chromatography on silica gel or neutral alumina.

1-Iodo-3-methoxy-2-(dimethylsilyl) benzene (Table 2, SM for entry 1)



Method A: 1-Iodo-3-methoxybenzene (10 mmol, 2.34 g), chlorodimethylsilane (100 mmol, 9.46 g), TMPLi (25 mmol, 3.69 g), Et_2O (45 mL), THF (15 mL), -110 °C to -30 °C and keep at this temperature for 19 hours. After column chromatography (hexanes), 2.77 g (95 %) of colorless oil was obtained. R_f = 0.60 (hexanes). ^{1}H NMR (600 MHz) δ 7.49 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.86 (septet, *J* = 3.6 Hz, 1H), 3.77 (s, 3H), 0.36 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (151 MHz) δ 164.7, 133.1, 132.0, 131.2, 109.6, 105.6, 55.6, -2.7. FT-IR (neat, cm^{-1}) ν 2957, 2155 (Si-H), 1572, 1552, 1449, 1415, 1240. HRMS (CI) calc. For $C_9H_{12}IOSi$ [M-H] +: 290.9702; found: 290.9697.

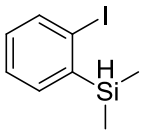
(2-Iodo-3,6-dimethoxyphenyl)dimethylsilane (Table 2, SM for entry 2)



Method A: 2-iodo-1,4-dimethoxybenzene (5.17 mmol, 1.37 g), chlorodimethylsilane (51.5 mmol, 4.89 g), TMPLi (10.34 mmol, 1.52 g), Et_2O (30 mL), THF (10 mL), -110 °C to -75 °C. After column chromatography (hexanes), 1.35 g (81 %) of yellow-to-colorless oil was obtained. R_f = 0.30 (hexane). ^{1}H NMR (600 MHz) δ 6.79 (s, 1H), 6.78 (s, 1H), 4.91 (Septet, *J* = 3.8 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 0.35 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (151 MHz) δ 159.0, 152.4, 133.6, 112.8, 110.6, 98.3, 57.3, 56.2, -2.6. FT-IR (neat, cm-1)

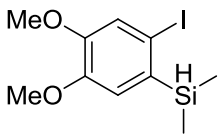
ν 2946, 2156 (Si-H), 1559, 1455, 1416, 1404, 1245. HRMS (CI) calc. For $C_{10}H_{15}O_2SiI$ $[M]^+$: 321.9886; found: 321.9883.

1-Iodo-2-(dimethylsilyl)benzene (Table 2, SM for entry 3)



Method B: 1,2-diiodobenzene (10 mmol, 3.3 g), nBuLi (11 mmol, 6.88 mL of 1.6 M in hexane), Et_2O (60 mL), THF (20 mL), -110 °C to -100 °C, chlorodimethylsilane (100 mmol, 9.46 g), warm up to -55 °C. After column chromatography (hexanes), 1.34 g (51 %) of colorless oil was obtained. R_f = 0.90 (hexane). ^{1}H NMR (600 MHz) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.47 (septet, *J* = 3.7 Hz, 1H), 0.42 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (151 MHz) δ143.8, 139.3, 136.6, 131.1, 127.3, 105.0, -3.4. FT-IR (neat, cm-1) ν 2956, 2153 (Si-H), 1571, 1549, 1445, 1415, 1248. HRMS (CI) calc. For $C_8H_{10}SiI$ $[M-H]^+$: 260.9597; found: 260.9595.

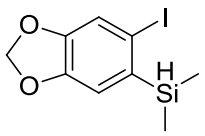
(2-Iodo-4,5-dimethoxyphenyl)dimethylsilane (Table 2, SM for entry 4)



Method C: (2-bromo-4,5-dimethoxyphenyl)dimethylsilane (3.0 mmol, 0.826 g), nBuLi (4.5 mmol, 2.8 mL, 1.6 M in hexane), THF (30 mL), ICH_2CH_2I (6.0 mmol, 1.68 g in 10 mL of THF). Column chromatography on alumina (hexanes followed by hexane/ethyl acetate 20:1) gave 194 mg (21 %) of a green-yellow oil. R_f = 0.40 (hexane/ethyl acetate 20:1). ^{1}H NMR (600 MHz) δ 7.25 (s, 1H), 6.87 (s, 1H), 4.43 (septet, *J* = 3.8 Hz, 1H), 3.84 (s, 3H), 3.84 (s, 3H), 0.40 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (151 MHz) δ 150.5, 148.7, 134.6, 122.4, 119.0, 93.4, 56.0, 56.0, -3.13. FT-IR (neat, cm-1) ν 2954, 2835, 2114 (Si-H), 1577, 1553, 1508, 1463, 1435. HRMS (CI) calc. For $C_{10}H_{15}O_2SiI$ $[M]^+$: 321.9886; found: 321.9886.

Note: neutral alumina was used instead of silica for column chromatography. Attempt to run the reaction on a 10 mmol scale was not successful.

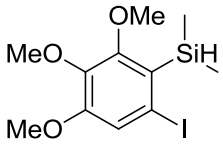
(6-Iodobenzo[d][1,3]dioxol-5-yl)dimethylsilane (Table 2, SM for entry 5)



Method B: 5,6-diiodobenzo[d][1,3]dioxole (0.25 mmol, 94 mg), nBuLi (0.238 mmol, 0.15 mL of 1.6 M in hexane), Et_2O (1 mL), THF (1 mL), -110 °C to -100 °C; then chlorodimethylsilane (1.5 mmol, 145 mg in 0.5 mL of solvent), warm up to -91 °C. Reaction was quenched with aqueous saturated $Na_2S_2O_3$ solution (3 mL). After column chromatography on alumina neutral (hexanes/ethyl acetate 20:1), 37 mg (48 %) of colorless oil was obtained. R_f = 0.70 (hexane). ^{1}H NMR (500 MHz) δ 7.29 (s, 1H), 6.89 (s, 1H), 5.95 (s, 2H), 4.45 (septet, *J* = 3.7 Hz, 1H), 0.40 (d, *J* = 3.7 Hz, 6H).^{13}C NMR (151 MHz) δ 149.6, 148.0, 135.7, 119.9, 115.8, 101.4, 93.0, -3.12. FT-IR (neat, cm-1) ν 2956, 2894, 2127 (Si-H), 1602, 1500, 1489, 1354, 1299. HRMS (CI) calc. For $C_9H_{11}O_2SiI$ $[M]^+$: 305.9573; found: 305.9570.

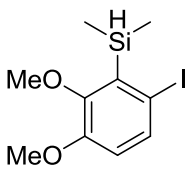
Note: neutral alumina was used instead of silica for column chromatography. Attempt to run the reaction on a 10 mmol scale was not successful.

(6-Iodo-2,3,4-trimethoxyphenyl)dimethylsilane (Table 2, SM for entry 6)



Method A: 5-iodo-1,2,3-trimethoxybenzene (5.15 mmol, 1.51 g), chlorodimethylsilane (51.5 mmol, 4.87 g), TMPLi (15.96 mmol, 2.35 g), Et_2O (30 mL), THF (10 mL), -110 °C to -30 °C. After column chromatography (hexanes followed by hexane/ ethyl acetate 50:1), 0.64 g (56 %) of yellow oil was obtained. R_f = 0.40 (hexane/EtOAc 50:1). ^{1}H NMR (600 MHz) δ 7.15 (s, 1H), 4.74 (septet, *J* = 3.8 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 0.35 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (151 MHz) δ 158.6, 155.3, 141.8, 128.1, 120.2, 96.5, 61.2, 60.6, 56.2, -2.2. FT-IR (neat, cm^{-1}) ν 2935, 2153 (Si-H), 1567, 1469, 1423, 1351, 1285. HRMS (CI) calc. For $C_{11}H_{17}O_3SiI$ $[M]^+$: 351.9992; found: 351.9994.

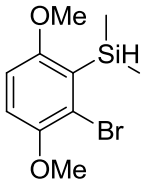
(6-Iodo-2,3-dimethoxyphenyl)dimethylsilane (Table 2, SM for entry 7)



Method A: 4-iodo-1,2-dimethoxybenzene (10.0 mmol, 2.64 g), chlorodimethylsilane (50.0 mmol, 4.73 g), TMPLi (15.0 mmol, 2.21 g),

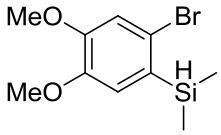
Et_2O (20 mL), THF (40 mL), -110 °C to -35 °C and keep at -35 °C for 2 h. After column chromatography (hexanes followed by hexane/Et_2O 50:1), 1.74 g (54 %) of a light yellow oil was obtained. R_f = 0.50 (hexane/Et_2O 50:1). ^{1}H NMR (500 MHz) δ 7.55 (d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 4.80 (septet, 3.8 Hz, 1H), 3.82 (s, 6H), 0.39 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (126 MHz) δ 154.6, 152.5, 136.1, 136.0, 115.8, 92.4, 61.2, 55.7, -2.4. FT-IR (neat, cm^{-1}) ν 2962, 2935, 2154 (Si-H), 1560, 1451, 1414, 1371, 1283. HRMS (CI) calc. For $C_{10}H_{15}O_2SiI$ $[M]^+$: 321.9886; found: 321.9881.

2-Bromo-1,4-dimethoxy-3-(dimethylsilyl)benzene (Scheme 3, compound 10)



Method A: 2-Bromo-1,4-dimethoxybenzene (20 mmol, 5.51 g), chlorodimethylsilane (200 mmol, 18.9 g), TMPLi (40 mmol, 5.89 g), Et_2O (90 mL), THF (30 mL), -110 °C to -80 °C. After column chromatography (hexanes followed by hexanes/dichloromethane 4:1), 5.15 g (94 %) of a colorless oil was obtained. R_f = 0.50 (hexanes/dichloromethane 4:1). ^{1}H NMR (600 MHz) δ 6.86 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 8.9 Hz, 1H), 4.83 (septet, J = 3.8 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 0.37 (d, J = 3.8 Hz, 6H). ^{13}C NMR (151 MHz) δ 159.0, 150.4, 129.3, 120.5, 113.9, 109.8, 57.0, 56.2, -2.8. FT-IR (neat, cm^{-1}) ν 2955, 2159 (Si-H), 1563, 1457, 1421, 1251, 1033. HRMS (CI) calc. For $C_{10}H_{12}BrOSi$ $[M-H]^+$: 272.9946; found: 272.9949.

4-Bromo-1,2-dimethoxyphenyl-5-(dimethylsilyl)benzene (Scheme 3, compound 13)

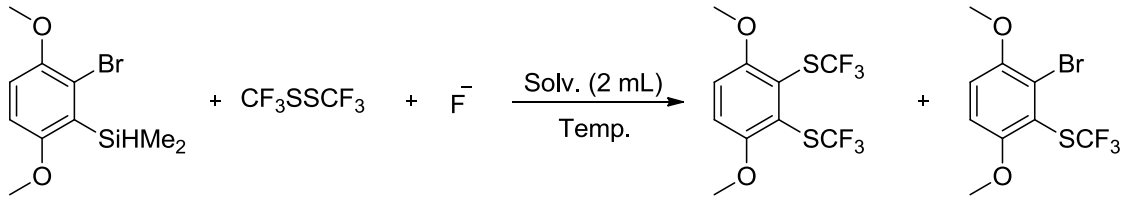


Method B: 1,2-dibromo-4,5-dimethoxybenzene (20.0 mmol, 5.92 g), nBuLi (23 mmol, 14.38 mL, 1.6 M in hexane), Et_2O (75 mL), THF (25 mL), -110 °C to -90 °C then chlorodimethylsilane (200 mmol, 18.9 g in 20 mL of solvent), warm up to -60 °C. After column chromatography (hexanes/CH_2Cl_2 6:1 followed by hexanes/CH_2Cl_2 2:1), 1.74 g (54 %) of colorless oil was obtained. R_f = 0.50 (hexane/CH_2Cl_2 4:1). ^{1}H NMR (500 MHz) δ 7.02 (s, 1H), 6.91 (s, 1H), 4.46 (Septet, *J* = 3.7 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 0.40 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (126 MHz) δ 150.8, 147.9, 129.7, 121.4, 118.6, 115.9, 56.1, 56.1 -3.3. FT-IR (neat, cm-1) ν 2956,

2836, 2122 (Si-H), 1583, 1557, 1495, 1463, 1435. HRMS (CI) calc. For $C_{10}H_{15}O_2Si^{79}Br$ $[M]^+$: 274.0025; found: 274.0026. For $C_{10}H_{15}O_2Si^{81}Br$ $[M]^+$: 274.0004; found: 274.0007.

Optimization reactions:

Outside the glovebox, a 2 dram vial was equipped with a magnetic stir bar (0.2 x 0.5 cm) and aryne precursor (0.25 mmol, 1.0 equiv). Vial was transferred to the glovebox. Inside the glovebox, solvent and then F^- source were added to the vial. Liquid, cold CF_3SSCF_3 (0.875 mmol, 3.5 equiv) was subsequently added quickly. The vial was sealed and taken out from the glovebox. Vials were stirred at different temperature for 24 h. After 24 h, methanol (2 mL) was added to the reaction mixture. The yield and ratio of products were determined by GC.

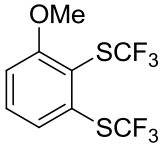


Entry	F^-	Solv.	Temp. (°C)	%Yield of A	**A:B**
1	KF/18-crown-6	Et_2O	rt	4	1:20
2	KF/18-crown-6	Et_2O	50	5	1:17
3	KF/18-crown-6	DME	rt	7	1:15
4	KF/18-crown-6	DME	85	35	5:7
5	KF/18-crown-6	THF	70	26	2:5
6	TMAF	Et_2O:THF(1:3)	60	17	1:6
7	TMAF	Et_2O:THF(1:1)	60	12	3:6
8	TMAF	Et_2O:THF(3:1)	60	8	3:6
9	**CsF**	**DME**	**85**	**68**	**3:1**
10	CsF	MeCN	85	61	2.5:1

General procedure for aryne reactions with CF_3SSCF_3:

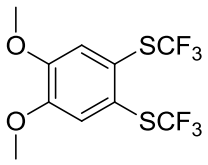
Outside the glovebox, a 2 dram vial was equipped with a magnetic stir bar (0.2 x 0.5 cm) and aryne precursor (0.3 or 0.5 mmol, 1.0 equiv). Vial was transferred to the glovebox. Inside the glovebox, dimethoxyethane (DME) or MeCN (2 mL) and then CsF (0.9 or 1.5 mmol, 3 equiv) were added to the vial. Liquid, cold CF_3SSCF_3 (1.05 or 1.75 mmol, 3.5 equiv) was subsequently added quickly. The vial was sealed and taken out from the glovebox. Vials were stirred at 110 (for DME) or 85 °C (for MeCN) for 24 - 48 h. After appropriate reaction time, methanol (2 mL) was added to the reaction mixture. The crude mixture was concentrated and purified by column chromatography on silica gel.

3-Methoxy-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 1)



2-Methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.5 mmol, 165 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. After column chromatography (hexanes), 118 mg (75 %) of a light yellow oil was obtained. R_f = 0.30 (hexanes/ CH_2Cl_2 10:1). ^{1}H NMR (500 MHz) δ 7.53-7.49 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (126 MHz) δ 162.5, 136.0, 133.4, 129.4 (q, *J* = 309 Hz), 129.1 (q, *J* = 311 Hz), 127.3, 116.7, 113.3, 56.6. ^{19}F NMR (470 MHz) δ -41.4, -41.6. FT-IR (neat, cm-1) ν 2945, 1573, 1464, 1434, 1417, 1277, 1090. HRMS (CI) calc. For $C_9H_6OF_6S_2$ $[M]^+$: 307.9764; found: 307.9764.

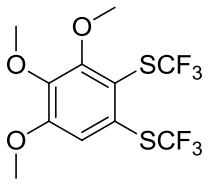
4,5-Dimethoxy-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 2)



3,4-Dimethoxy-6-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.5 mmol, 180 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. After column chromatography (hexane/ether 10:1), 140 mg (76 %) of a yellow oil was obtained. R_f = 0.50 (hexane/ether 10:1). Product contains 8% mono-thiolation product as an impurity. ^{1}H NMR (600 MHz) δ 7.28 (s, 2H), 3.91 (s, 6H). ^{13}C NMR (151 MHz) δ 151.4, 130.4 (q, *J* = 309 Hz), 123.2, 120.1, 56.3. ^{19}F NMR (565 MHz) δ -42.8. FT-IR (cm^{-1}) ν 2936, 2844,

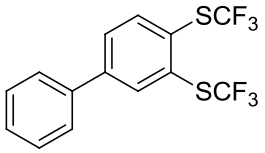
1580, 1497, 1439, 1261, 1095. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9868.

3,4,5-Trimethoxy-1,2-bis(trifluoromethylthio)benzene (Table 1, entry 3)



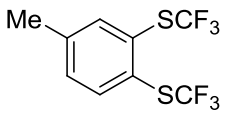
2,3,4-Trimethoxy-6-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.43 mmol, 165 mg), CsF (1.3 mmol, 194 mg), CF_3SSCF_3 (1.5 mmol, 300 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. After column chromatography (hexanes followed by hexanes/CH_2Cl_2 15:1), 128 mg (84 %) of a colorless oil was obtained. R_f = 0.20 (hexanes/CH_2Cl_2).^{1}H NMR (600 MHz) δ 7.16 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz) δ 157.4, 156.4, 144.7, 130.4 (q, *J* = 309 Hz), 130.1 (q, *J* = 311 Hz), 128.7, 115.9, 115.6, 61.7, 61.0, 56.4. ^{19}F NMR (565 MHz) δ -42.1, -42.5. FT-IR (neat, cm^{-1}) ν 2943, 2852, 1564, 1478, 1426, 1374, 1303, 1240, 1094. HRMS (CI) calc. For $C_{11}H_{10}O_3F_6S_2$ $[M]^+$: 367.9976; found: 367.9981.

4-Phenyl-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 4)



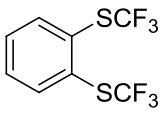
4-Phenyl-2-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.5 mmol, 188 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. After column chromatography (pentane), 138 mg (78 %) of a colorless oil was obtained. R_f = 0.80 (hexanes). Two columns may be necessary for complete purification. ^{1}H NMR (500 MHz) δ 8.09 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.74 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.60 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.48 – 7.43 (m, 1H). ^{13}C NMR (151 MHz) δ 145.0, 138.3, 138.0, 136.2, 131.9, 130.2, 129.6, 129.33 (q, *J* = 310 Hz), 129.30, 129.28 (q, *J* = 310 Hz), 128.9, 127.3. ^{19}F NMR (470 MHz) δ -41.6, -41.8. FT-IR (neat, cm^{-1}) ν 3075, 3045, 1584, 1459, 1373, 1126, 1095. HRMS (CI) calc. For $C_{14}H_8F_6S_2$ $[M]^+$: 353.9972; found: 353.9975.

4-Methyl-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 5)



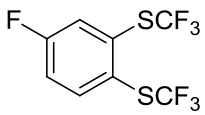
3-Methyl-6-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.5 mmol, 157 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. The crude mixture was passed through a short pad of celite and concentrated on a rotary evaporator. NMR yield of 64% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR (600 MHz) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H). ^{19}F NMR δ -42.3, -41.8. HRMS (CI) calc. For $C_9H_6F_6S_2$ $[M]^+$: 291.9815; found: 291.9810.

1, 2-Bis(trifluoromethylthio)benzene (Table 1, entry 6)



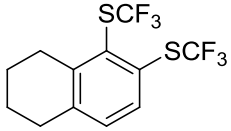
Trimethylsilylphenyltrifluoromethanesulfonate (0.5 mmol, 150 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. The crude mixture was passed through a short pad of celite and concentrated on a rotary evaporator. NMR yield of 71% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR δ 7.85 (dd, *J* = 6, 4 Hz, 2H), 7.52 (dd, *J* = 6, 4 Hz, 2H). ^{13}C NMR δ 138.3, 133.1, 131.2, 126.8 (q, *J* = 314 Hz). ^{19}F NMR δ -42.1. This compound is known.[7]

4-Fluoro-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 7)



3-Fluoro-6-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.5 mmol, 159 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. The crude mixture was passed through a short pad of celite and concentrated on a rotary evaporator. NMR yield of 56% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR (600 MHz) δ 7.88 (s, 1H), 7.61 (s, 1H), 7.26 (s, 1H). ^{19}F NMR (565 MHz) δ -41.3, -42.4, -105.6.

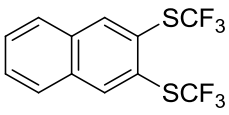
1,2-Bis((trifluoromethyl)thio)-5,6,7,8-tetrahydronaphthalene (Table 1, entry 8)



1-(Trimethylsilyl)-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethane-sulfonate (0.3 mmol, 106 mg), CsF (1.8 mmol, 260 mg), CF_3SSCF_3 (1.05 mmol, 212 mg), dimethoxyethane (2.0 mL), 110 °C for 48 h. After column chromatography (hexanes), 74 mg (74 %) of a colorless oil was obtained. R_f = 0.70 (hexanes). ^{1}H NMR (600 MHz) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 3.06 (t, *J* = 6.2 Hz, 2H), 2.83 (t, *J* = 6.2 Hz, 2H), 1.80 (m, 4H). ^{13}C NMR (151 MHz) δ 146.3, 142.3, 133.7, 133.4, 131.8, 129.5 (q, *J* = 310 Hz), 129.4 (q, *J* = 311 Hz), 129.0, 30.1, 29.9, 22.9, 22.0. ^{19}F NMR (470 MHz) δ -42.1, -41.2. FT-IR (neat, cm^{-1}) ν 2939, 1452, 1434, 1262, 1122, 1090. HRMS (CI) calc. For $C_{12}H_{10}F_6S_2$ $[M]^+$: 332.0128; found: 332.0129.

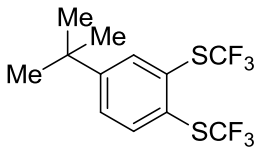
A 1.0 mmol scale reaction (1.0 mmol substrate, 6.0 mmol CsF, 3.5 mmol CF_3SSCF_3, 3 mL dimethoxyethane in a 2 dram vial) at 110 °C for 46 hours gave 268 mg (81%) of product as a colorless oil.

2, 3-Bis(trifluoromethylthio)naphthalene (Table 1, entry 9)



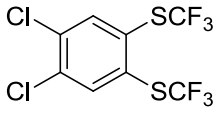
3-Trimethylsilyl-2-naphthyl trifluoromethanesulfonate (0.3 mmol, 105 mg), CsF (1.8 mmol, 260 mg), CF_3SSCF_3 (1.05 mmol, 212 mg), dimethoxyethane (2.0 mL), 110 °C for 48 h. After column chromatography (hexane), 68 mg (69 %) of a white solid was obtained. R_f = 0.80 (hexane). Melting point 55-57 °C (from hexane). Two columns may be necessary for complete purification. ^{1}H NMR (600 MHz) δ 8.40 (s, 2H), 7.93-7.90 (m, 2H), 7.68-7.65 (m, 2H). ^{13}C NMR (126 MHz) δ 139.2, 134.1, 129.6 (q, *J* = 311 Hz), 129.1, 128.18, 128.16. ^{19}F NMR (470 MHz) δ -42.3. FT-IR (neat, cm^{-1}) ν 2923, 2852, 1488, 1156, 1140, 1092. HRMS (CI) calc. For $C_{12}H_6F_6S_2$ $[M]^+$: 327.9815; found: 327.9821.

4-t-Butyl-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 10)



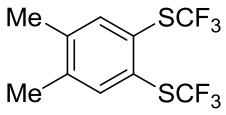
3-t-Butyl-6-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.5 mmol, 177 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 48 h. The crude mixture was passed through a short pad of celite and concentrated on a rotary evaporator. NMR yield of 66% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR (600 MHz) δ 7.86 (s, 1H), 7.78 (d, *J* = 8.3, 1H), 7.53 (d, *J* = 8.3, 1H), 1.34 (s, 9H). ^{19}F NMR (376 MHz) δ -41.91, -42.03. HRMS (CI) calc. For $C_{12}H_{12}F_6S_2$ $[M]^+$: 334.0285; found: 334.0283.

4,5-Dichloro-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 11)



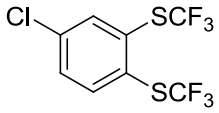
3,4-Dichloro-6-(trimethylsilyl) phenyl trifluoromethanesulfonate (0.3 mmol, 111 mg), CsF (0.9 mmol, 140 mg), CF_3SSCF_3 (1.05 mmol, 212 mg), dimethoxyethane (2.0 mL), 110 °C for 48 h. After column chromatography (hexanes), 45 mg (44 %) of a colorless oil was obtained. R_f = 0.80 (hexane). ^{1}H NMR (600 MHz) δ 7.94 (s, 1H). ^{13}C NMR (151 MHz) δ 138.3, 136.5, 130.7, 129.8, 127.7. ^{19}F NMR (565 MHz) δ -41.5. FT-IR (neat, cm^{-1}) ν 2995, 1561, 1525, 1442, 1310, 1133. HRMS (CI) calc. For $C_8H_2F_6S_2{}^{35}Cl^{35}Cl$ $[M]^+$: 345.8879; found: 345.8883. HRMS (CI) calc. For $C_8H_2F_6S_2{}^{35}Cl^{37}Cl$ $[M]^+$: 347.8850; found: 347.8856. HRMS (CI) calc. For $C_8H_2F_6S_2{}^{37}Cl^{37}Cl$ $[M]^+$: 349.8820; found: 349.8819.

4,5-Dimethyl-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 12)



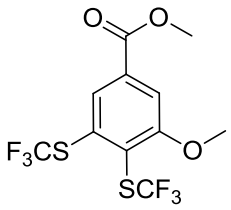
3,4-Dimethyl-6-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.25 mmol, 82 mg), CsF (1.25 mmol, 190 mg), CF_3SSCF_3 (0.875 mmol, 177 mg), dimethoxyethane (0.5 mL), 85 °C for 43 h. NMR yield of 68% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR (500 MHz) δ 7.63 (s, 2H), 2.32 (s, 6H). ^{19}F NMR (470 MHz) δ -42.2. HRMS (CI) calc. For $C_{10}H_8F_6S_2$ $[M]^+$: 305.9972; found: 305.9981.

4-Chloro-1, 2-bis(trifluoromethylthio)benzene (Table 1, entry 13)



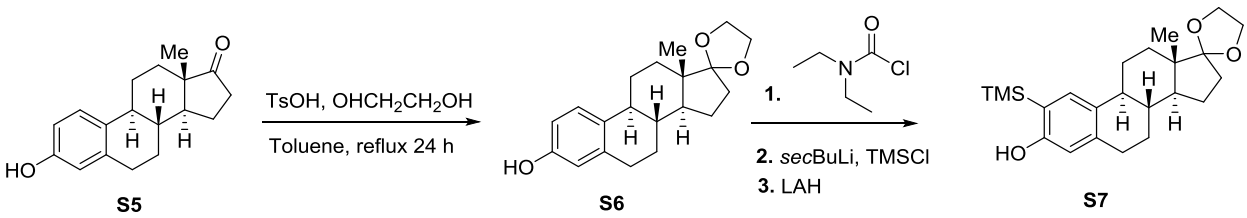
3-Chloro-6-(trimethylsilyl)phenyltrifluoromethanesulfonate (0.5 mmol, 159 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. NMR yield of 65% was determined by using trifluoromethylbenzene internal standard. ^{1}H NMR (600 MHz) δ 7.82 (s, 1H), 7.80-7.76 (m, 1H), 7.53 - 7.47 (m, 1H). ^{19}F NMR (565 MHz) δ -41.4, -41.9. HRMS (CI) calc. For $C_8H_3F_6S_2{}^{37}Cl$ $[M]^+$: 313.9239; found: 313.9236.

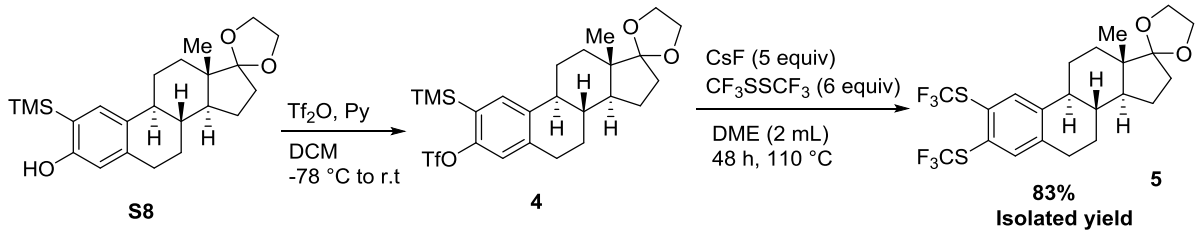
Methyl 3-methoxy-4,5-bis((trifluoromethyl)thio)benzene (Table 1, entry 14)



3-Methoxy-4-(trifluoromethylsulfonyloxy)-5-(trimethylsilyl)methyl benzoate (0.33 mmol, 127 mg), CsF (1.0 mmol, 150 mg), CF_3SSCF_3 (1.16 mmol, 230 mg), dimethoxyethane (2.0 mL), 110 °C for 42 h. After column chromatography (hexane/ethyl acetate 15:1), 48 mg (41 %) of a brown oil was obtained. Two columns may be necessary for complete purification. R_f = 0.40 (hexane/ ethyl acetate 15:1). ^{1}H NMR (500 MHz) δ 8.07 (s, 1H), 7.71 (s, 1H), 4.00 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (126 MHz) δ 165.2, 162.2, 136.2, 134.7, 129.2 (q, *J* = 310 Hz), 128.8 (q, *J* = 311 Hz), 127.8, 121.8, 113.9, 56.9, 53.1. ^{19}F NMR (470 MHz) δ -40.8, -41.3. FT-IR (neat, cm^{-1}) ν 2956, 1729 (C=O), 1558, 1397, 1244, 1129, 1095. HRMS (CI) calc. For $C_{11}H_8O_3F_6S_2$ $[M]^+$: 365.9819; found: 365.9815.

(8R, 9S, 13S, 14S) -13-Methyl-2,3-bis((trifluoromethyl)thio)-6, 7, 8, 9, 11, 12, 13, 14, 15, 16-decahydrospiro[cyclopenta[a]phenanthrene-17, 2'-[1,3]dioxolane] 5





Synthesis of 4

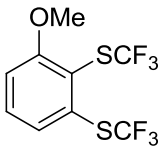
Compound **S8** was synthesized by employing a previously reported procedure.[8] To synthesize compound **4**, reaction conditions of previously reported procedure were applied and a foam was obtained in 86% isolated yield.[9] ^{1}H NMR (500 MHz) δ 7.41 (s, 1H), 7.01 (s, 1H), 3.98-3.88 (m, 4H), 2.88-2.84 (m, 2H), 2.37-2.22 (m, 2H), 2.06-2.0 (s, 1H), 1.94-1.89 (m, 1H), 1.88-1.74 (m, 3H), 1.67-1.60 (m, 1H), 1.58-1.47 (m, 2H), 1.42-1.32 (s, 2H), 0.88 (s, 3H), 0.33 (s, 9H). ^{19}F NMR (470 MHz) δ -73.9.

Synthesis of 5

Outside the glovebox, a 2 dram vial was equipped with a magnetic stir bar (0.2 x 0.5 cm) and compound **4** (0.1 mmol, 52 mg, 1.0 equiv). Vial was transferred to the glovebox. Inside the glovebox, DME (2 mL) and then CsF (0.5 mmol, 80 mg, 5.0 equiv) were added to the vial. Subsequently, cold CF_3SSCF_3 (0.6 mmol, 120 mg, 6.0 equiv) was added. The vial was sealed and taken out from the glovebox. Vial was stirred at 110 °C for 48 h. After 48 h, methanol (2 mL) was added to the reaction mixture. The crude mixture was concentrated and purified by column chromatography on silica gel. After column chromatography (hexanes/ethyl acetate 20:1), 50 mg (83 %) of a yellow oil was obtained. R_f = 0.40 (hexanes/ethyl acetate 20:1). ^{1}H NMR (600 MHz) δ 7.75 (s, 1H), 7.55 (s, 1H), 3.97-3.86 (m, 4H), 2.95-2.83 (m, 2H), 2.35-2.25 (m, 2H), 2.02 (t, 1H), 1.97-192 (m, 1H), 1.87-1.75 (m, 3H), 1.66 – 1.60 (m, 1H), 1.58-1.32 (m, 5H), 0.88 (s, 3H). ^{13}CNMR (126 MHz) δ 145.2, 141.9, 138.5, 135.9, 129.42 (q, *J* = 310 Hz), 129.39 (q, *J* = 310 Hz), 127.9, 127.4, 119.2, 65.4, 64.7, 49.4, 46.1, 43.9, 38.2, 34.2, 30.5, 29.2, 26.4, 25.7, 22.4, 14.4. ^{19}F NMR (565 MHz) δ -42.1, -42.3. FT-IR (neat, cm^{-1}) ν 2938, 2872,

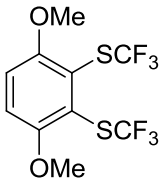
1466, 1380, 1309, 1128, 1096. HRMS (CI) calc. For $C_{22}H_{24}O_2F_6S_2$ $[M]^+$: 498.1122; found: 498.1125.

3-Methoxy-1, 2-bis(trifluoromethylthio)benzene (Table 2, entry 1)

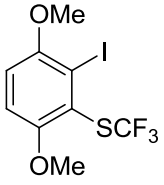


1-Iodo-3-methoxy-2-(dimethylsilyl)benzene (0.3 mmol, 88 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 37 h. After column chromatography (hexanes followed by hexanes/CH_2Cl_2 10:1), 69 mg (74 %) of a light yellow oil was obtained. R_f = 0.30 (hexanes/CH_2Cl_2 10:1). Crude NMR ratio of A (product):B ($ArISCF_3$) = 3.7:1.0. ^{1}H NMR (500 MHz) δ 7.53 – 7.49 (t, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (126 MHz) δ 162.5, 136.0, 133.4, 129.4 (q, *J* = 309 Hz), 129.1 (q, *J* = 311 Hz), 127.3, 116.7, 113.3, 56.6. ^{19}F NMR (470 MHz) δ -41.4, -41.6. FT-IR (neat, cm^{-1}) ν 2945, 2849, 1573, 1463, 1434, 1277, 1090. HRMS (CI) calc. For $C_9H_6OF_6S_2$ $[M]^+$: 307.9764; found: 307.9764.

3,6-Dimethoxy-1, 2-bis(trifluoromethylthio)benzene (Table 2, entry 2)



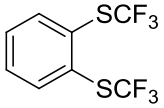
1-Iodo-3,6-dimethoxy-2-(dimethylsilyl)benzene (0.3 mmol, 97 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 37 h. After column chromatography (hexanes followed by hexanes/CH_2Cl_2 10:1), 69 mg (71 %) of a yellow solid was obtained. R_f = 0.20 (hexanes/CH_2Cl_2 10:1). ^{1}H NMR (500 MHz) δ 7.15 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz) δ 156.3, 129.2 (q, *J* = 310 Hz), 121.3, 116.1, 56.8. ^{19}F NMR (470 MHz) δ -41.5. FT-IR (neat, cm^{-1}) ν 2919, 2849, 1558, 1464, 1431, 1265, 1095. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9877.



Note: The following byproduct was isolated in 23% yield as a brown oil. ^{1}H NMR (500 MHz) δ 6.96 (m, 2H), 3.86 (d, 6H). ^{13}C NMR (126 MHz) δ 156.3, 153.9, 136.8, 129.5 (q, *J* = 310 Hz), 115.3, 112.1, 105.6, 57.4, 56.9. ^{19}F NMR (470 MHz) δ -41.33. HRMS (CI) calc. For $C_9H_8O_2F_3SI$ $[M]^+$: 363.9242;

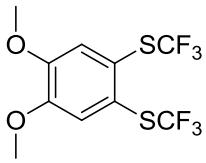
found: 363.9236.

1, 2-Bis(trifluoromethylthio)benzene (Table 2, entry 3)



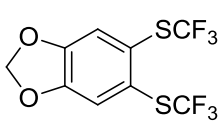
1-Iodo-2-(dimethylsilyl)benzene (0.5 mmol, 131 mg), CsF (1.5 mmol, 228 mg), CF_3SSCF_3 (1.75 mmol, 354 mg), dimethoxyethane (1.0 mL), 85 °C for 24 h. The crude mixture was passed through a short path of celite and concentrated on a rotary evaporator. The crude mixture was passed through a short path of celite and concentrated on a rotary evaporator. NMR yield of 58% was determined by using trifluoromethylbenzene internal standard. Crude NMR ratio of A (product):B ($ArISCF_3$) = 2.4:1.0. ^{1}H NMR δ 7.85 (dd, *J* = 6, 4 Hz, 2H), 7.52 (dd, *J* = 6, 4 Hz, 2H). ^{13}C NMR δ 138.3, 133.1, 131.2, 126.8 (q, *J* = 314 Hz). ^{19}F NMR δ -42.1. This compound is known.[7]

4,5-Dimethoxy-1, 2-bis(trifluoromethylthio)benzene (Table 2, entry 4)



1-Iodo-4,5-dimethoxy-2-(dimethylsilyl) benzene (0.22 mmol, 71 mg), CsF (0.65 mmol, 100 mg), CF_3SSCF_3 (0.76 mmol, 152 mg), dimethoxyethane (2.0 mL), 110 °C for 46 h. After column chromatography (hexane/ether 10:1), 46 mg (63 %) of a yellow oil was obtained. R_f = 0.50 (hexane/ether 10:1). Crude NMR ratio of A (product):B ($ArISCF_3$) = 2.9:1.0. ^{1}H NMR (600 MHz) δ 7.28 (s, 2H), 3.91 (s, 6H). ^{13}C NMR (151 MHz) δ 151.4, 130.4 (q, *J* = 309 Hz), 123.2, 120.1, 56.3. ^{19}F NMR (565 MHz) δ -42.8. FT-IR (neat, cm^{-1}) ν 2936, 2844, 1580, 1497, 1439, 1261, 1095. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9868.

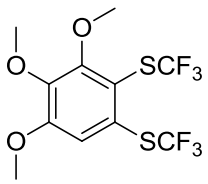
5,6-Bis((trifluoromethyl)thio) benzo[d][1,3]dioxole (Table 2, entry 5)



(6-Iodobenzo[d][1,3]dioxol-5-yl)dimethylsilane (0.3 mmol, 92 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 37 h. After column chromatography (hexanes followed by hexanes/ether 10:1), 56 mg (58 %) of a brown oil

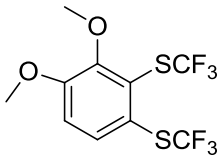
was obtained. R_f = 0.60 (hexanes/ether 10:1). Crude NMR ratio of A (product):B ($ArISCF_3$) = 2.8:1.0. ^{1}H NMR (600 MHz) δ 7.29 (s, 2H), 6.12 (s, 2H). ^{13}C NMR (151 MHz) δ 150.7, 129.2 (q, *J* = 310 Hz), 124.7, 117.4, 103.1. ^{19}F NMR (470 MHz) δ -42.6. FT-IR (neat, cm^{-1}) ν 2923, 2854, 1505, 1470, 1324, 1234, 1093. HRMS (CI) calc. For $C_9H_4O_2F_6S_2$ $[M]^+$: 321.9557; found: 321.9564.

3,4,5-Trimethoxy-1,2-bis(trifluoromethylthio)benzene (Table 2, entry 6)



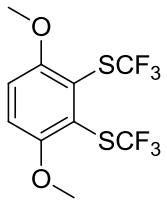
1-Iodo-3,4,5-trimethoxy-2-(dimethylsilyl)benzene (0.3 mmol, 106 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 37 h. After column chromatography (hexanes followed by hexanes/CH_2Cl_2 15:1), 90 mg (82 %) of a colorless oil was obtained. R_f = 0.20 (hexanes/CH_2Cl_2). Crude NMR ratio of A (product):B ($ArISCF_3$) = 4.5:1.0. ^{1}H NMR (600 MHz) δ 7.16 (s, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (151 MHz) δ 157.4, 156.4, 144.7, 130.4 (q, *J* = 309 Hz), 130.1 (q, *J* = 311 Hz), 128.7, 115.8, 115.6, 61.7, 61.0, 56.4. ^{19}F NMR (565 MHz) δ -42.1, -42.5. FT-IR (neat, cm^{-1}) ν 2943, 2852, 1564, 1478, 1426, 1374, 1303, 1240, 1094. HRMS (CI) calc. For $C_{11}H_{10}O_3F_6S_2$ $[M]^+$: 367.9976; found: 367.9981.

3,4-Dimethoxy-1,2-bis(trifluoromethylthio)benzene (Table 2, entry 7)



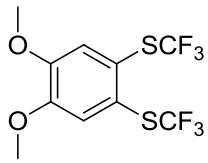
1-Iodo-3,4-dimethoxy-2-(dimethylsilyl)benzene (0.3 mmol, 97 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 37 h. After column chromatography (hexanes followed by hexanes/ethyl acetate 17:1), 60 mg (60 %) of a brown oil was obtained. R_f = 0.40 (hexanes/ethyl acetate 17:1). Crude NMR ratio of A (product):B ($ArISCF_3$) = 2.8:1.0. ^{1}H NMR (600 MHz) δ 7.62 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (126 MHz) δ 155.8, 153.4, 135.0, 134.1, 129.4 (q, *J* = 371 Hz), 129.1 (q, *J* = 371 Hz), 123.1, 115.4, 61.4, 56.2. ^{19}F NMR (470 MHz) δ -43.0, -41.3. FT-IR (neat, cm^{-1}) ν 2917, 2848, 1568, 1471, 1428, 1299, 1259, 1093. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9865.

3,6-Dimethoxy-1, 2-bis(trifluoromethylthio)benzene (Scheme 3, product 11)



1-Bromo-3,6-dimethoxy-2-(dimethylsilyl)benzene (0.3 mmol, 83 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 46 h. After column chromatography (hexanes followed by hexanes/ether 3:1), 61 mg (61 %) of a yellow solid was obtained. R_f = 0.20 (hexanes/CH_2Cl_2 10:1). Crude NMR ratio of A (product **11**):B ($ArBrSCF_3$ **12**) = 3.0:1.0. ^{1}H NMR (500 MHz) δ 7.15 (s, 2H), 3.89 (s, 6H). ^{13}C NMR (126 MHz) δ 156.3, 129.2 (q, *J* = 371 Hz), 121.3, 116.1, 56.8. ^{19}F NMR (470 MHz) δ -41.5. FT-IR (neat, cm^{-1}) ν 2919, 2849, 1558, 1464, 1431, 1265, 1095. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9877.

4,5-Dimethoxy-1, 2-bis(trifluoromethylthio) benzene (Scheme 3, product 14)



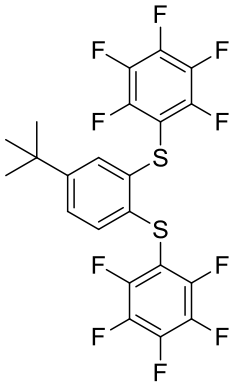
1-Bromo-3,4-dimethoxy-6-(dimethylsilyl) benzene (0.3 mmol, 83 mg), CsF (0.9 mmol, 137 mg), CF_3SSCF_3 (1.05 mmol, 210 mg), dimethoxyethane (2.0 mL), 110 °C for 46 h. After column chromatography (hexane/ether 5:1), 53 mg (53 %) of a yellow oil was obtained. R_f = 0.50 (hexane/ether 5:1). Crude NMR ratio of A (product **14**):B ($ArBrSCF_3$ **15**) = 2.7:1.0. ^{1}H NMR (600 MHz) δ 7.28 (s, 2H), 3.91 (s, 6H). ^{13}C NMR (151 MHz) δ 151.4, 130.4 (q, *J* = 309 Hz), 123.2, 120.1, 56.3. ^{19}F NMR (565 MHz) δ -42.8. FT-IR (neat, cm^{-1}) ν 2936, 2844, 1580, 1497, 1439, 1261, 1095. HRMS (CI) calc. For $C_{10}H_8O_2F_6S_2$ $[M]^+$: 337.9870; found: 337.9868.

General procedure for aryne reactions with $F_5PhSSPhF_5$ and $CF_3F_4PhSSPhF_4CF_3$:

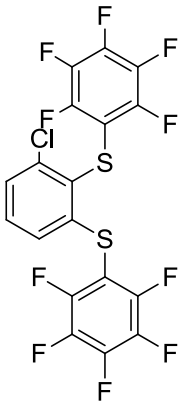
Outside the glovebox, a 2 dram vial was equipped with a magnetic stir bar (0.2 x 0.5 cm) and aryne precursor (0.2 mmol, 1.0 equiv). Vial was transferred to the glovebox. Inside the glovebox, MeCN (2 mL) and then CsF (0.6 mmol, 3.0 equiv) were added to the vial. Disulfide $F_5PhSSPhF_5$ or $F_3CF_4PhSSPhF_4CF_3$ (0.6 mmol, 3.0 equiv) was added subsequently. The vial was sealed and taken out from the glovebox. Vials were stirred at

85 °C for 46 h. After 46 h, methanol (2 mL) was added to the reaction mixture. The crude mixture was concentrated and purified by column chromatography on silica gel.

4-tert-Butyl-1, 2-bis(perfluorophenyl)benzene (Scheme 4, product 20)



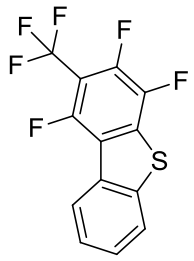
4-tert-Butyl-2-(trimethylsilyl)phenyltrifluoromethanesulfonate **18** (0.2 mmol, 71 mg), CsF (0.6 mmol, 100 mg), $F_5PhSSPhF_5$ (0.6 mmol, 233 mg), MeCN (2.0 mL), 85 °C for 47 h. After column chromatography (hexane/CH_2Cl_2 20:1), 27 mg (26 %) of a white solid was obtained. R_f = 0.80 (hexane/CH_2Cl_2 20:1). ^{1}H NMR (600 MHz) δ 7.28 (m, 1H), 7.20 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 1.21 (s, 9H). ^{19}F NMR (565 MHz) δ -131.1 (d, *J* = 18.1 Hz, 2F), -131.4 (d, *J* = 18.1 Hz, 2F), -150.6 (t, *J* = 21.0 Hz, 1F), -151.0 (t, *J* = 21.0 Hz, 1F), -159.9 (s, 2F), -160.2 (s, 2F). FT-IR (neat, cm^{-1}) ν 2956, 2845, 2119, 1641, 1578, 1515, 1486, 1459, 1247. HRMS (CI) calc. For $C_{22}H_{12}F_{10}S_2$ $[M]^+$: 530.0221; found: 530.0219.



3-Chloro-1, 2-bis(perfluorophenyl)benzene (Scheme 4, product 21)

3-Chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **19** (0.2 mmol, 67 mg), CsF (0.54 mmol, 80 mg), $F_5PhSSPhF_5$ (0.6 mmol, 233 mg), MeCN (2.0 mL), 85 °C for 46 h. After column chromatography (hexane/CH_2Cl_2 20:1), 21 mg (21 %) of a white solid was obtained. R_f = 0.70 (hexane/CH_2Cl_2 20:1). ^{1}H NMR (600 MHz) δ 7.28 (s, 1H), 7.15 (s, 1H), 6.63 (s, 1H). ^{19}F NMR (565 MHz) δ -130.2 (d, *J* = 18.2 Hz, 2F), -133.1 (d, *J* = 18.2 Hz, 2F), -148.4 (t, *J* = 21.0 Hz, 1F), -152.6 (t, *J* = 21.0 Hz, 1F), -158.8 (s, 2F), -160.7 (s, 2F). FT-IR (neat, cm^{-1}) ν 2925, 2850, 1637, 1510, 1482, 1428, 1087. HRMS (CI) calc. For $C_{18}H_3F_{10}S_2Cl$ $[M]^+$: 507.9205; found: 507.9215.

1,3,4-Trifluoro-2-(trifluoromethyl)dibenzo[b,d]thiophene (Scheme 5, product 23)



2-(Trimethylsilyl)phenyltrifluoromethanesulfonate (0.2 mmol, 60 mg), CsF (0.54 mmol, 80 mg), $F_5PhSSPhF_5$ (0.6 mmol, 233 mg), MeCN (2.0 mL), 85 °C for 47 h. After column chromatography (hexane/CH_2Cl_2 20:1), 41 mg (67 %) of a white solid was obtained. R_f = 0.80 (hexane/CH_2Cl_2 20:1). ^{1}H NMR (600 MHz) δ 8.35 (d, *J* = 9.9 Hz, 1H), 7.87 (d, *J* = 9.9 Hz, 1H), 7.59 – 7.52 (m, 2H). ^{19}F NMR (565 MHz) δ -55.2 – -55.4 (m, 3F), -119.8 – -119.9 (m, 1F), -139.0 – -139.3 (m, 1F), -141.6 (dd, *J* = 20.4, 16.9 Hz, 1F). FT-IR (neat, cm^{-1}) ν 2922, 2852, 1636, 1591, 1490, 1448, 1363, 1268, 1222. HRMS (CI) calc. For $C_{13}H_4F_6S$ [M-H] +: 305.9938; found: 305.9943

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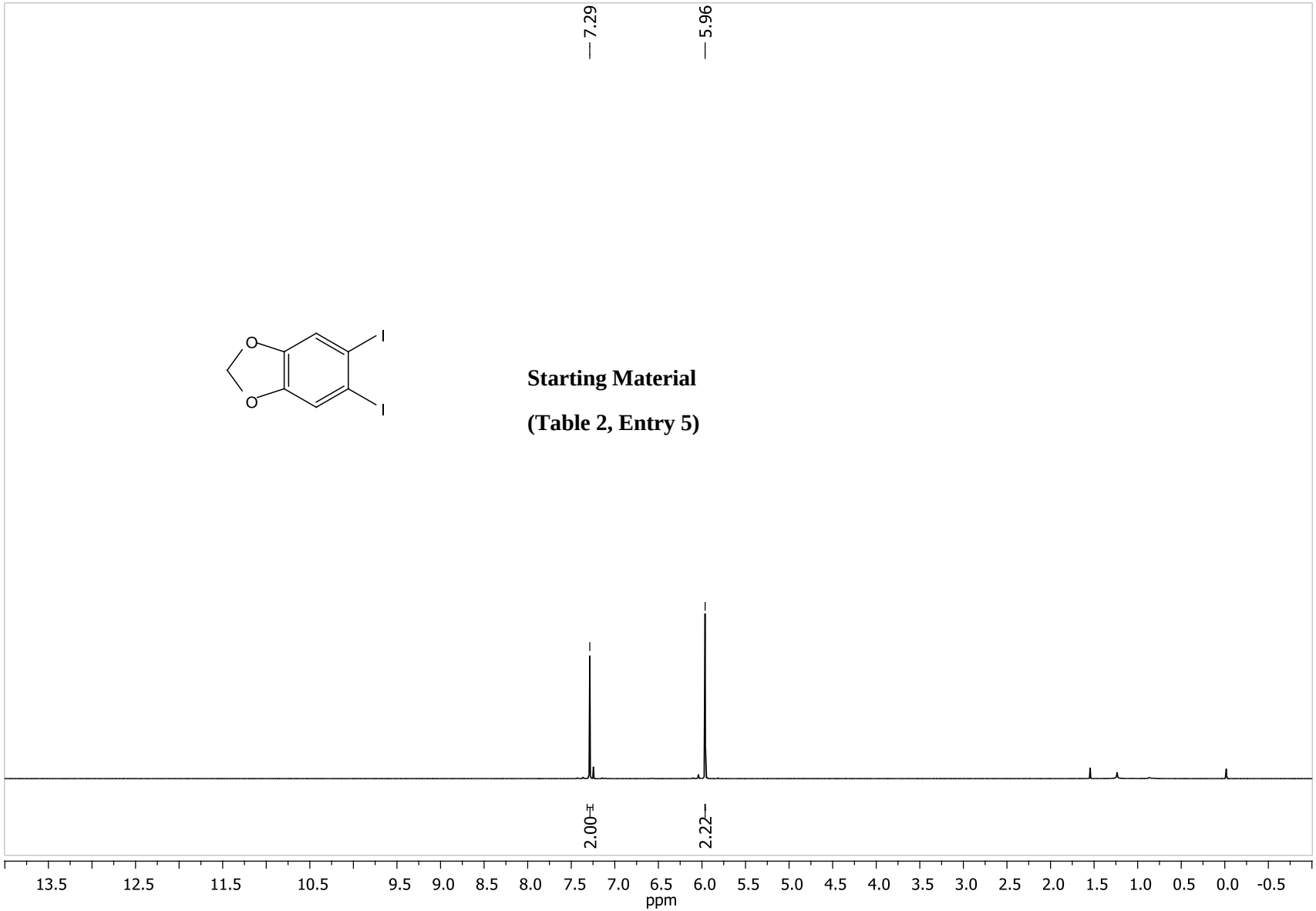
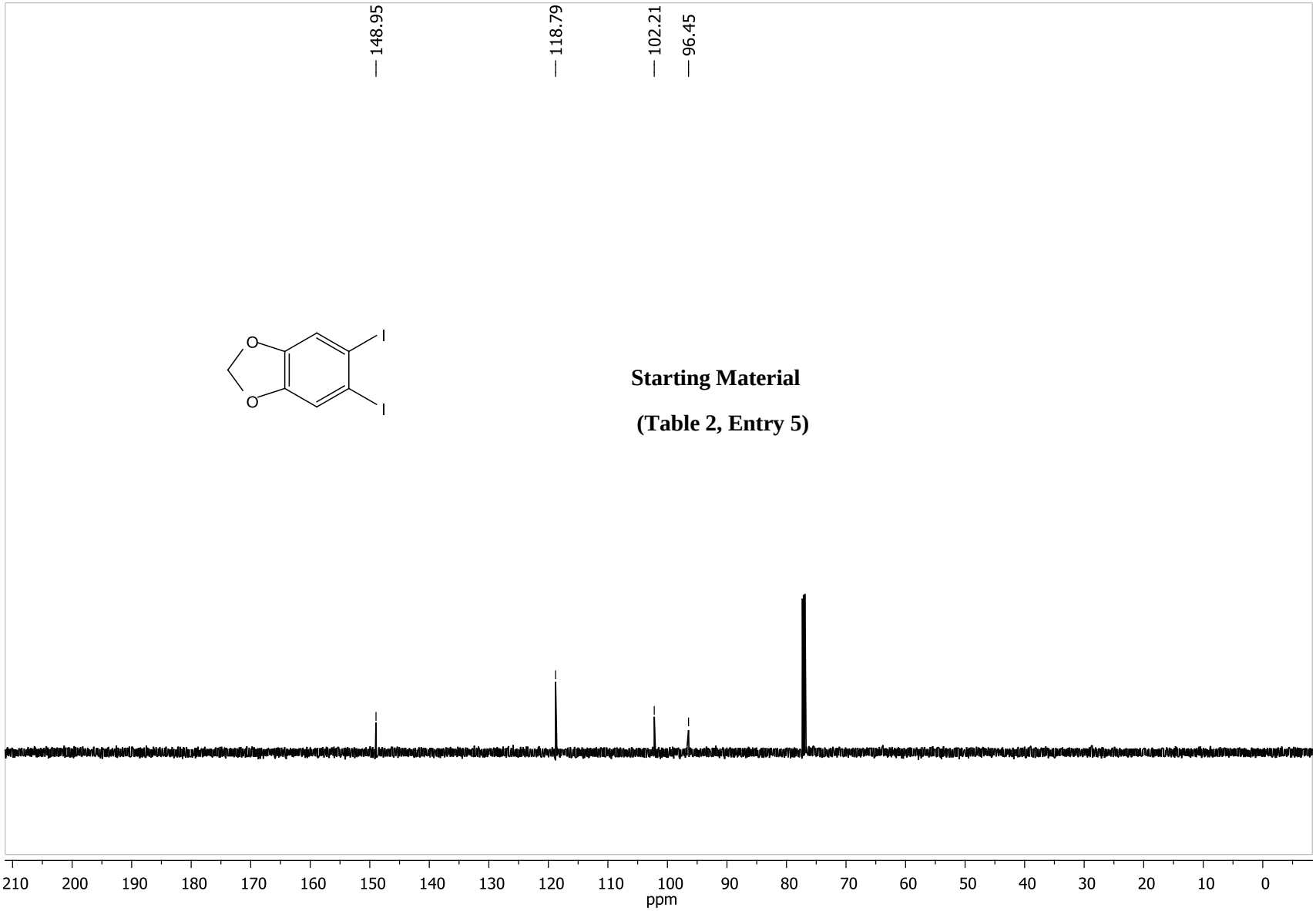


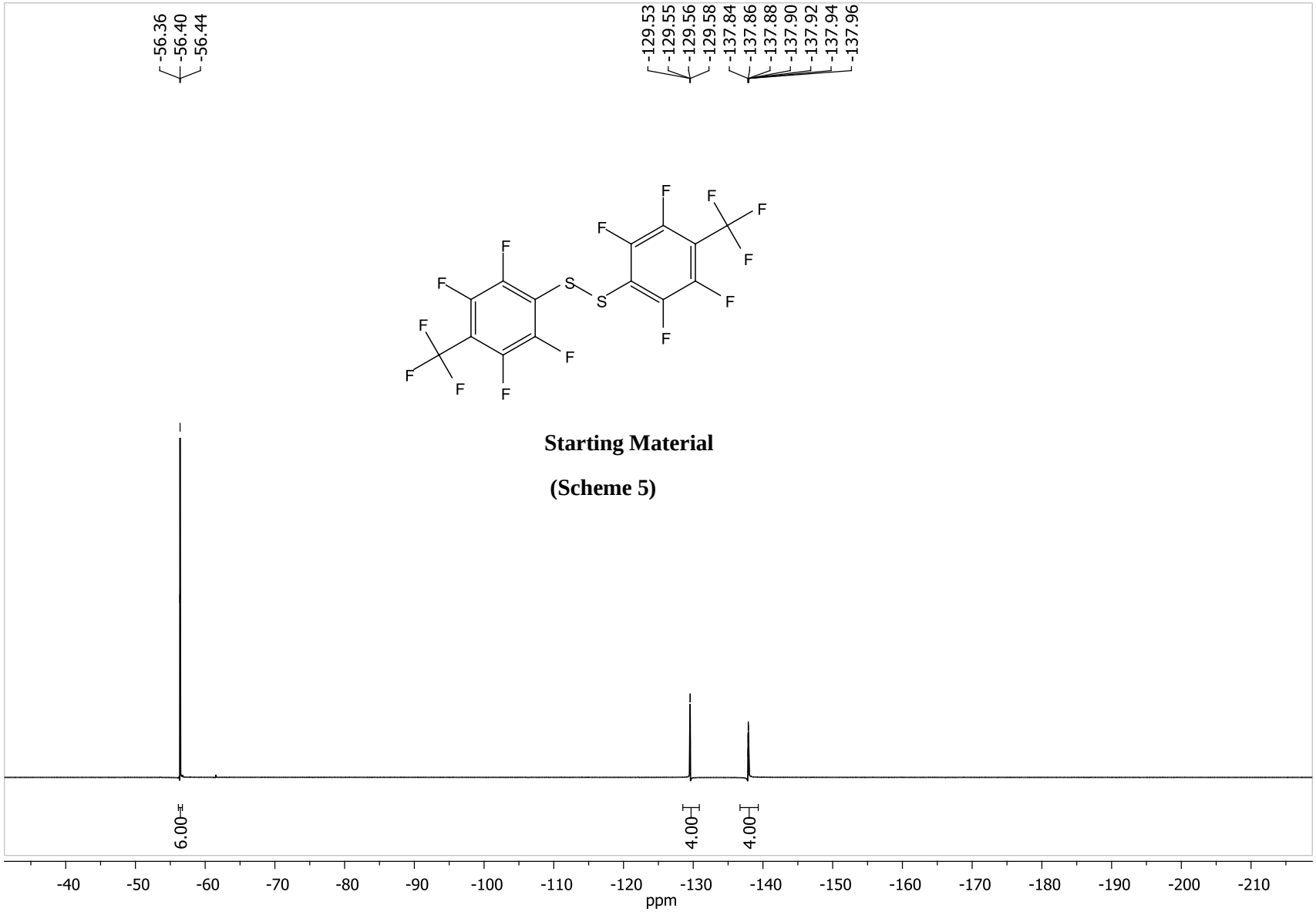
Starting Material

(Table 2, Entry 5)



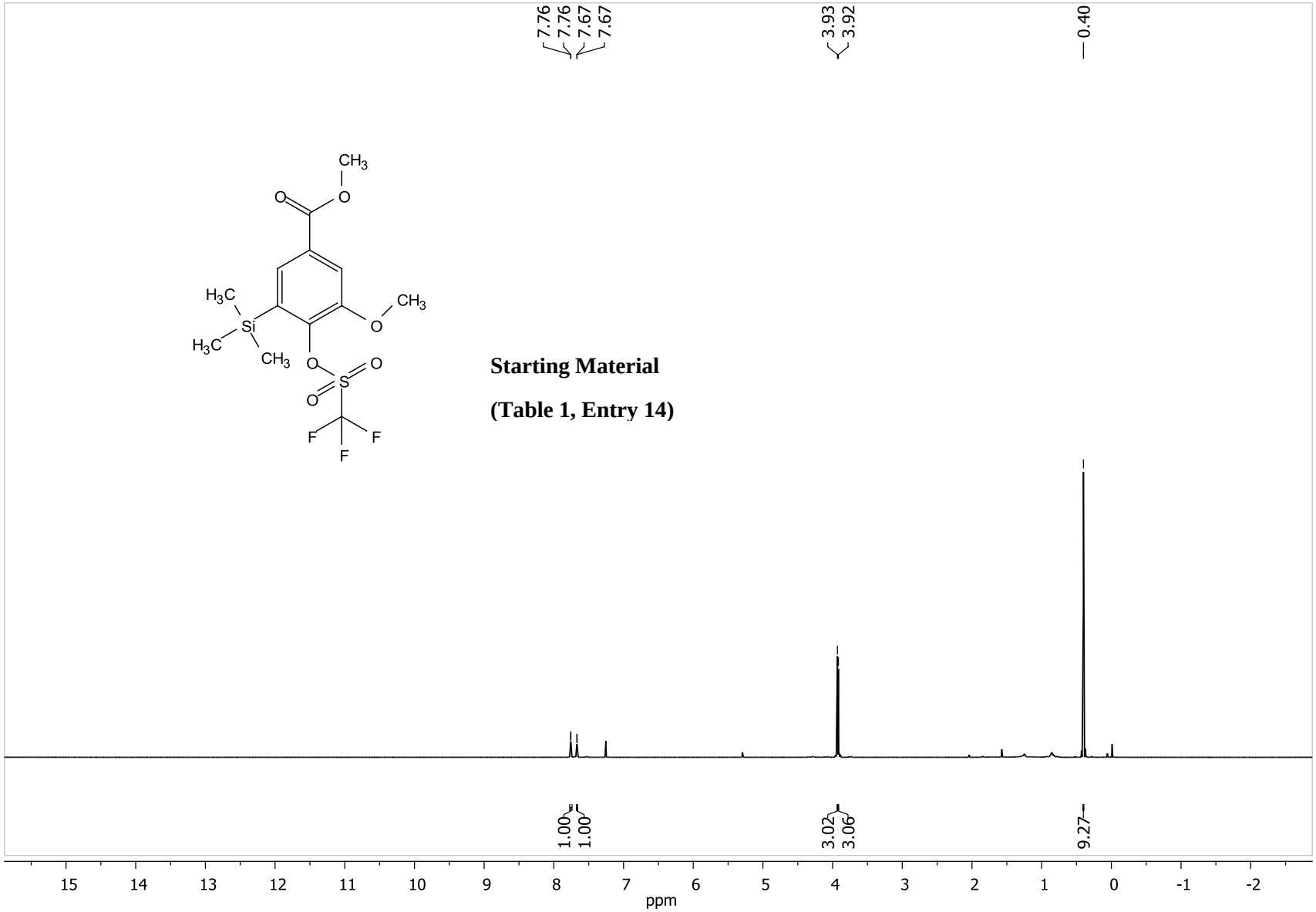
Starting Material

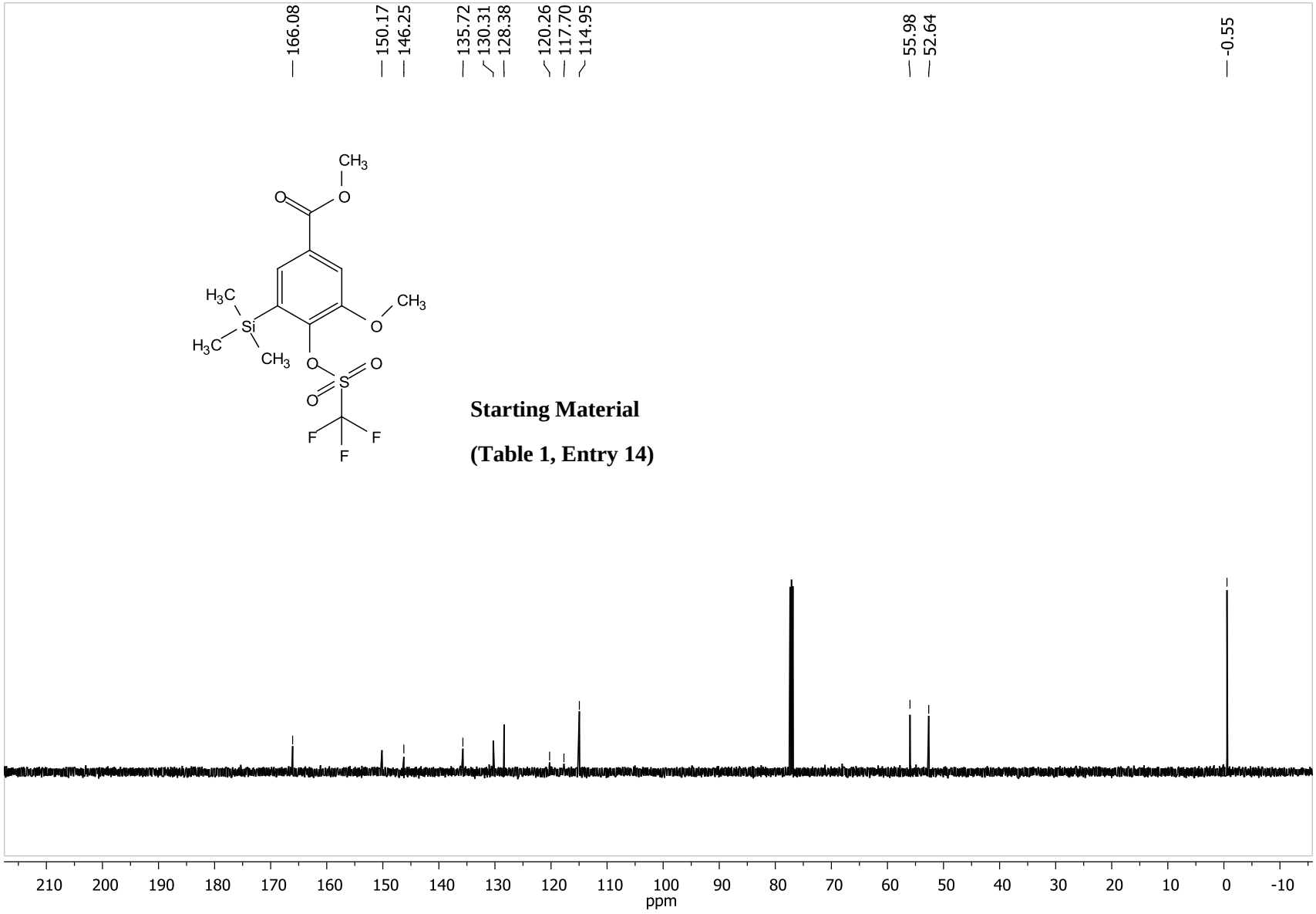
(Table 2, Entry 5)

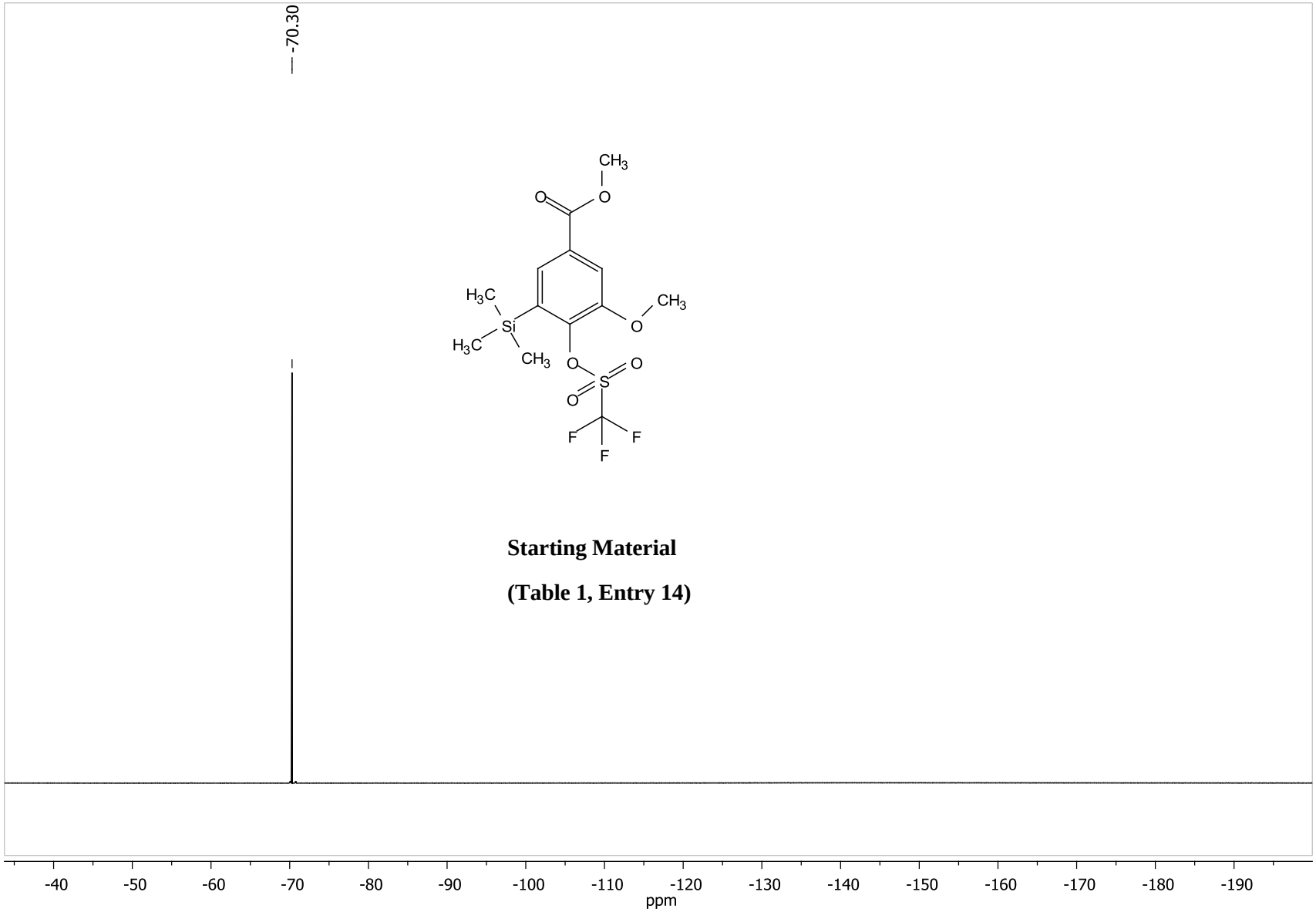


Starting Material

(Scheme 5)

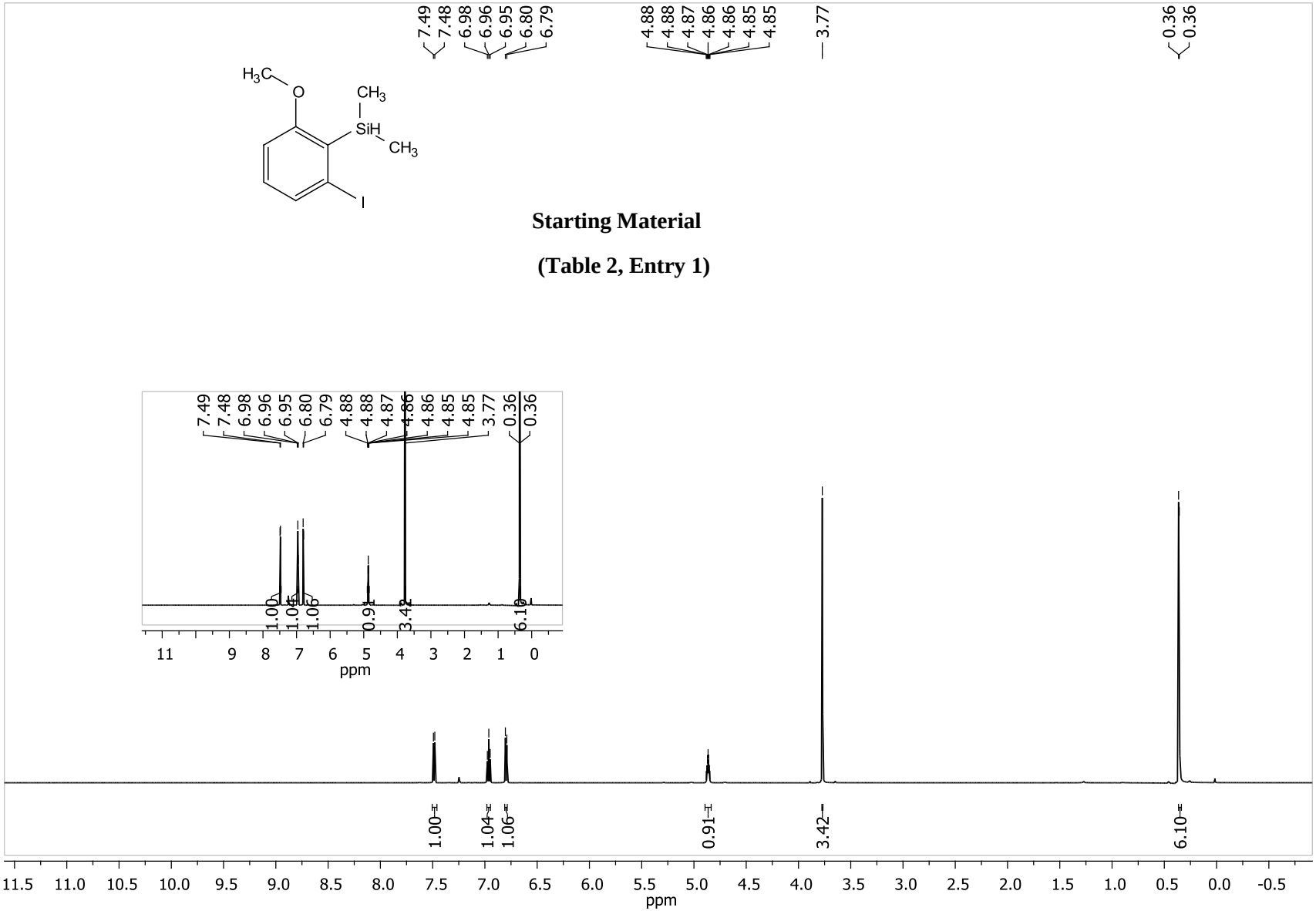

7.76
7.76
7.67
7.67
3.93
3.92
0.40
CH3
O
O
H3C
Si
H3C
CH3
CH3
O
O
O
O
S
F
F
F
Starting Material
(Table 1, Entry 14)
1.00
1.00
3.02
3.06
9.27
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


166.08
150.17
146.25
135.72
130.31
128.38
120.26
117.70
114.95
55.98
52.64
-0.55
CH3
O
O
H3C
Si
H3C
CH3
CH3
O
O
O
S
O
F
F
F
Starting Material
(Table 1, Entry 14)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



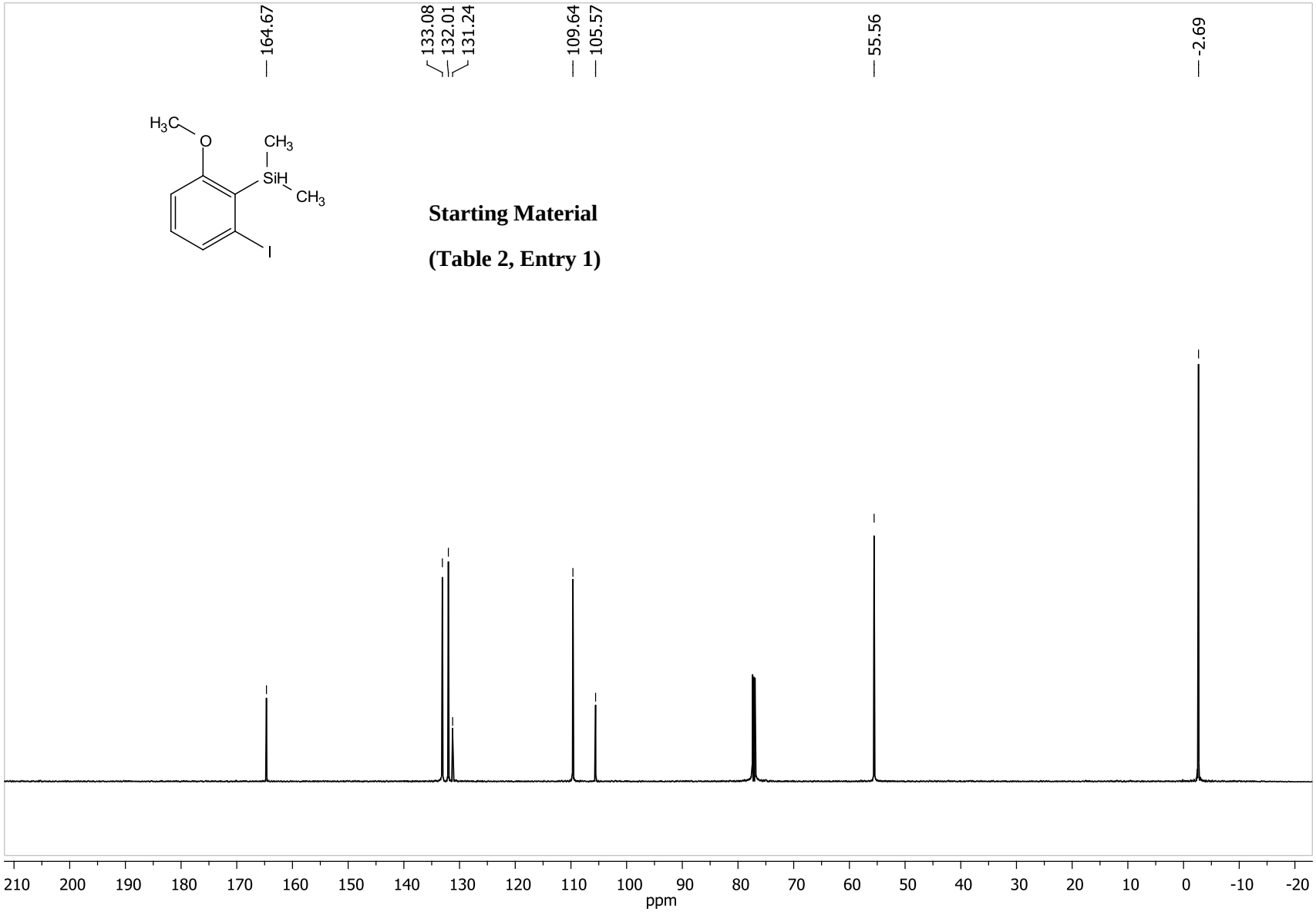
Starting Material

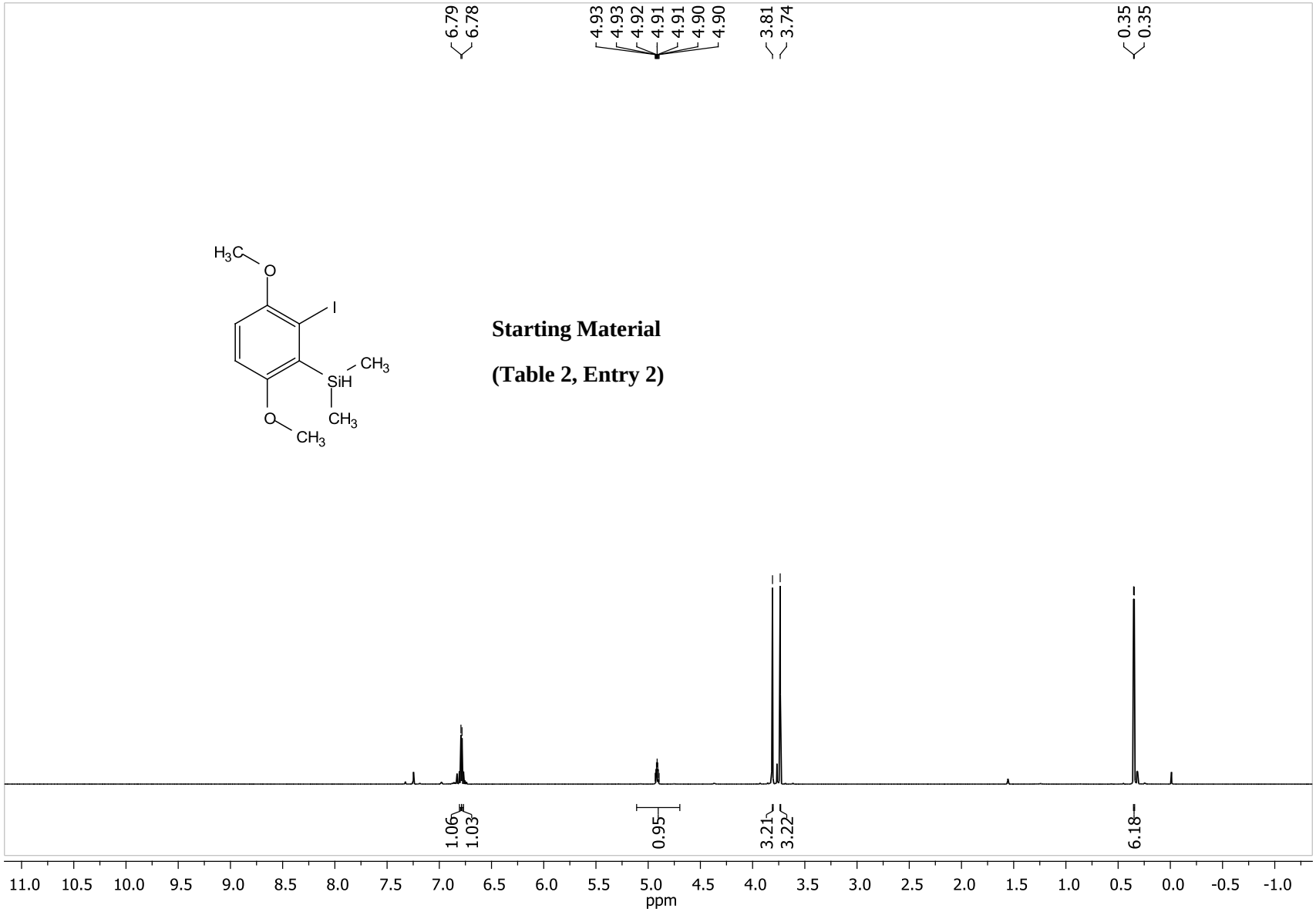
(Table 1, Entry 14)

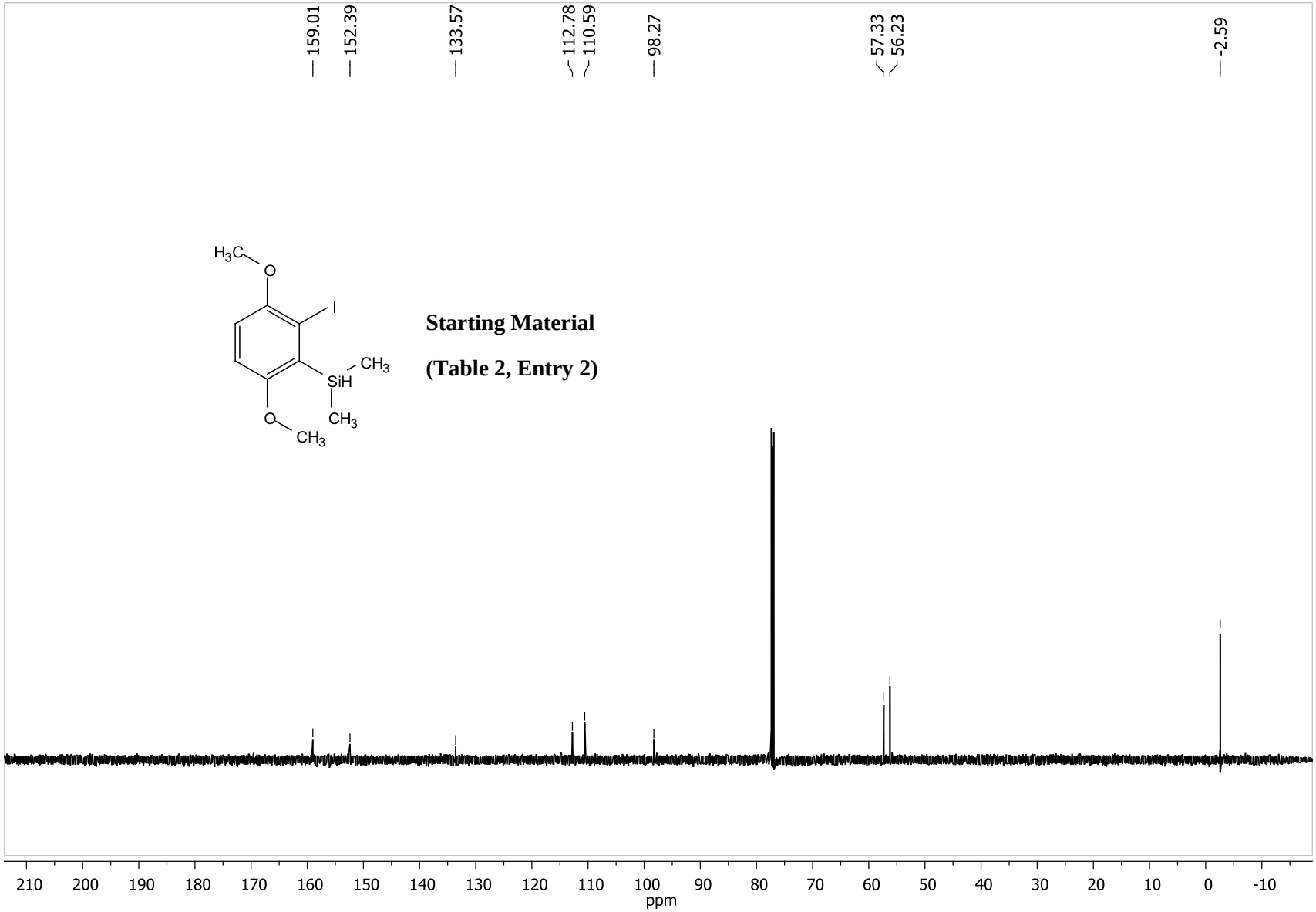


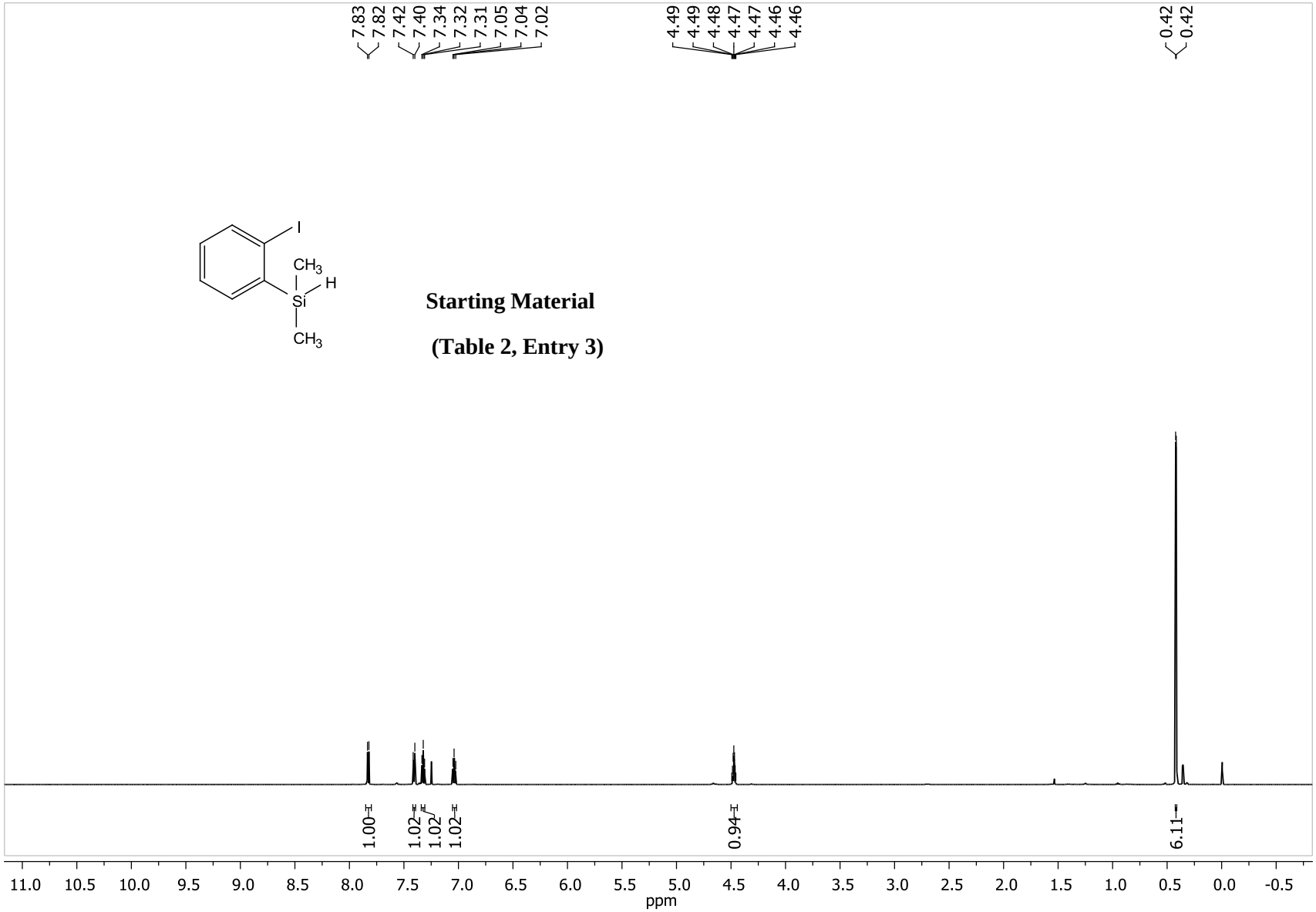
Starting Material

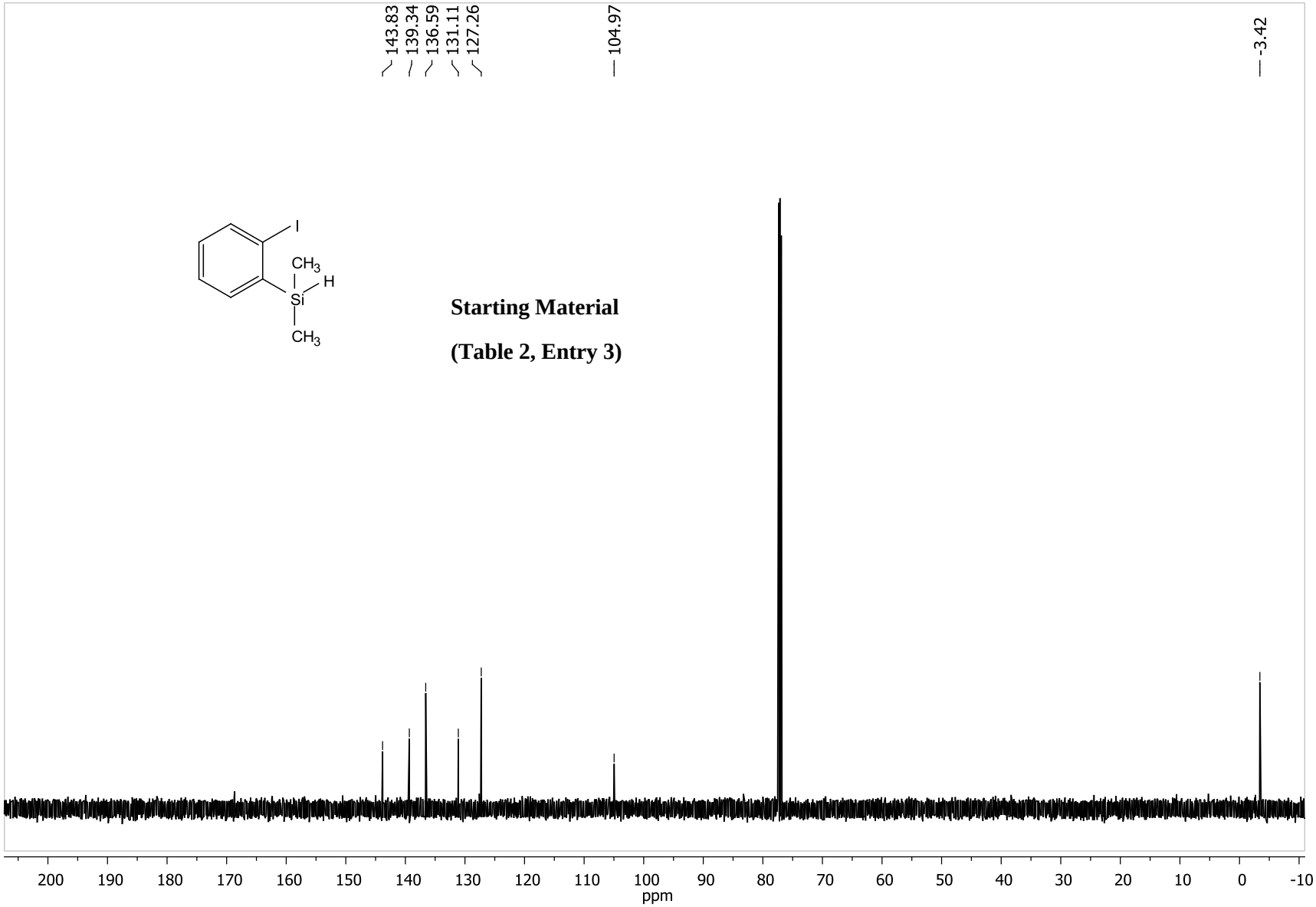
(Table 2, Entry 1)

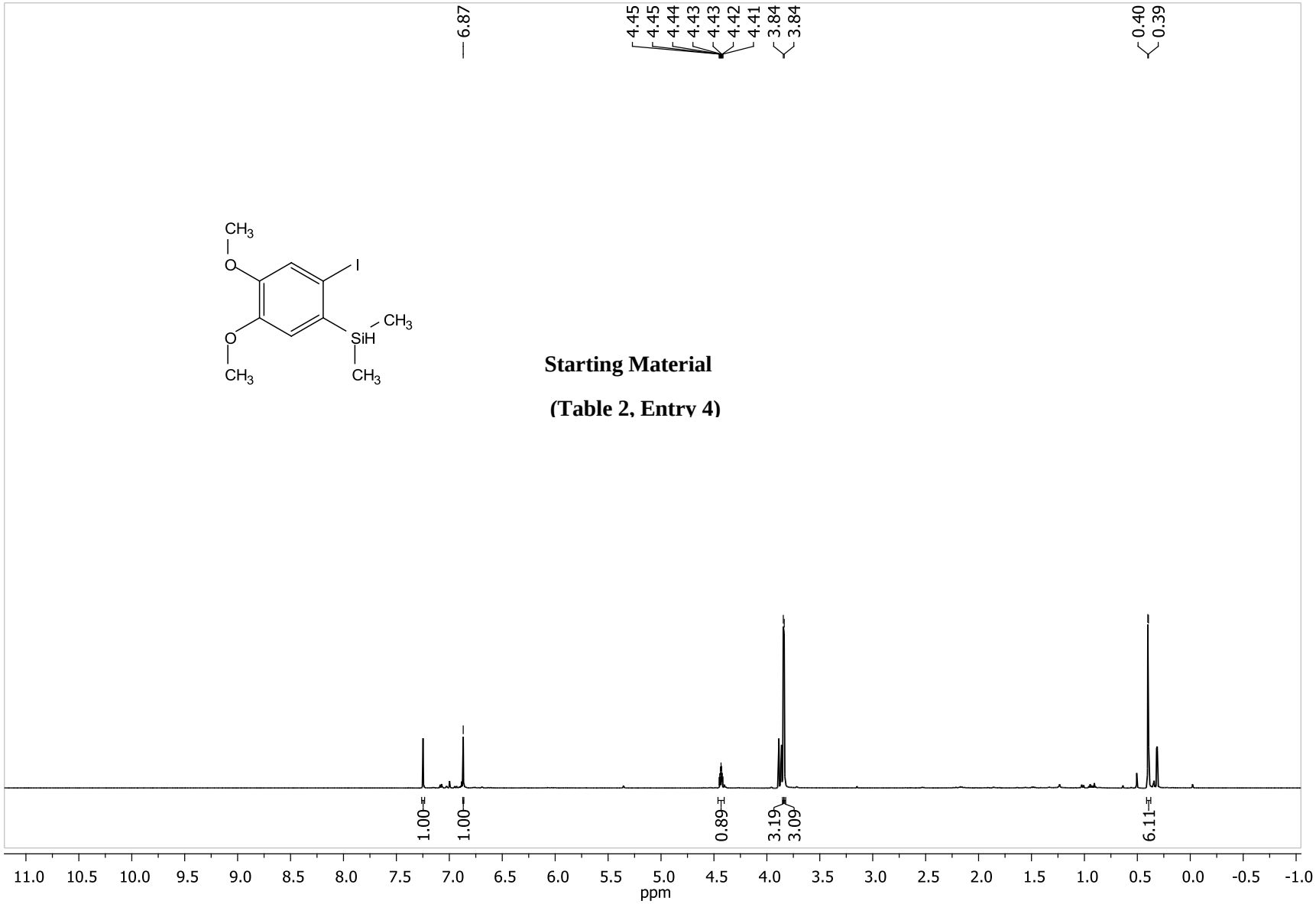

164.67
133.08
132.01
131.24
109.64
105.57
55.56
-2.69
H3C
O
CH3
SiH
CH3
I
Starting Material
(Table 2, Entry 1)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm


6.79
6.78
4.93
4.93
4.92
4.91
4.91
4.90
4.90
3.81
3.74
0.35
0.35
H3C
O
I
CH3
SiH
CH3
O
CH3
Starting Material
(Table 2, Entry 2)
1.06
1.03
0.95
3.21
3.22
6.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


159.01
152.39
133.57
112.78
110.59
98.27
57.33
56.23
-2.59
H3C
O
I
CH3
SiH
CH3
O
CH3
Starting Material
(Table 2, Entry 2)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

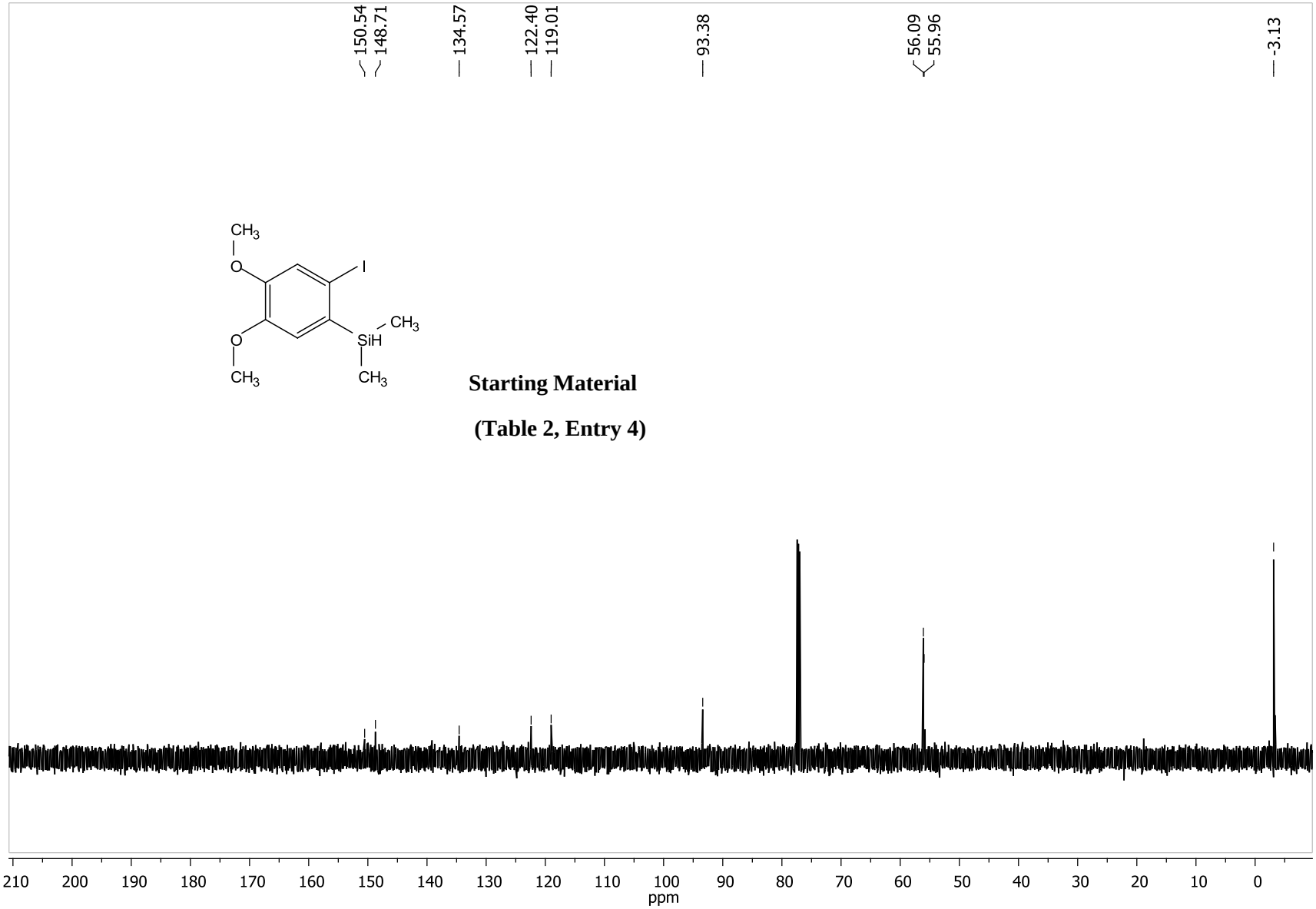

7.83
7.82
7.42
7.40
7.34
7.32
7.31
7.05
7.04
7.02
4.49
4.49
4.48
4.47
4.47
4.46
4.46
0.42
0.42
I
CH3
H
Si
CH3
Starting Material
(Table 2, Entry 3)
1.00
1.02
1.02
1.02
0.94
6.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


143.83
139.34
136.59
131.11
127.26
104.97
-3.42
I
CH3
H
Si
CH3
Starting Material
(Table 2, Entry 3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



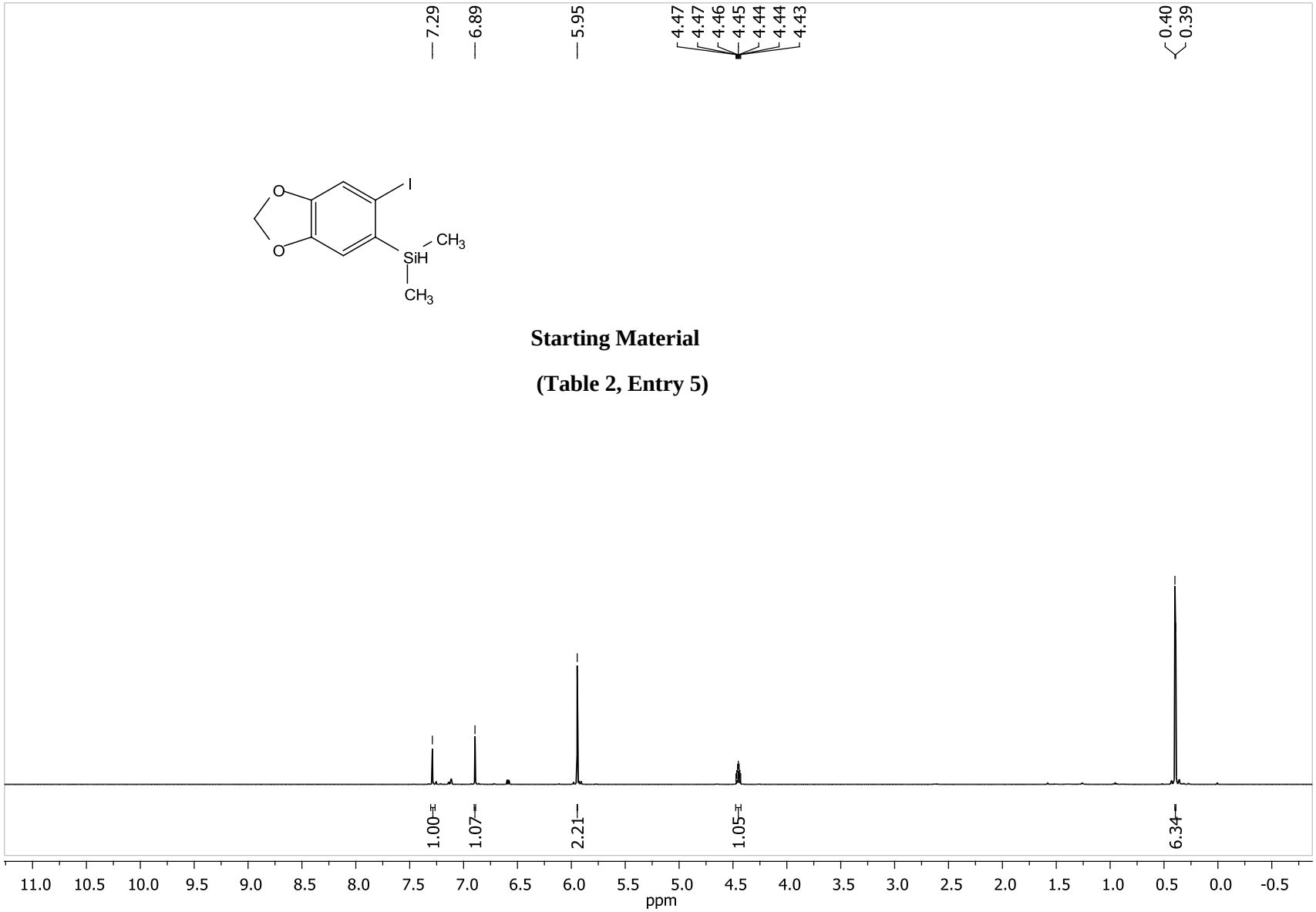
Starting Material

(Table 2, Entry 4)



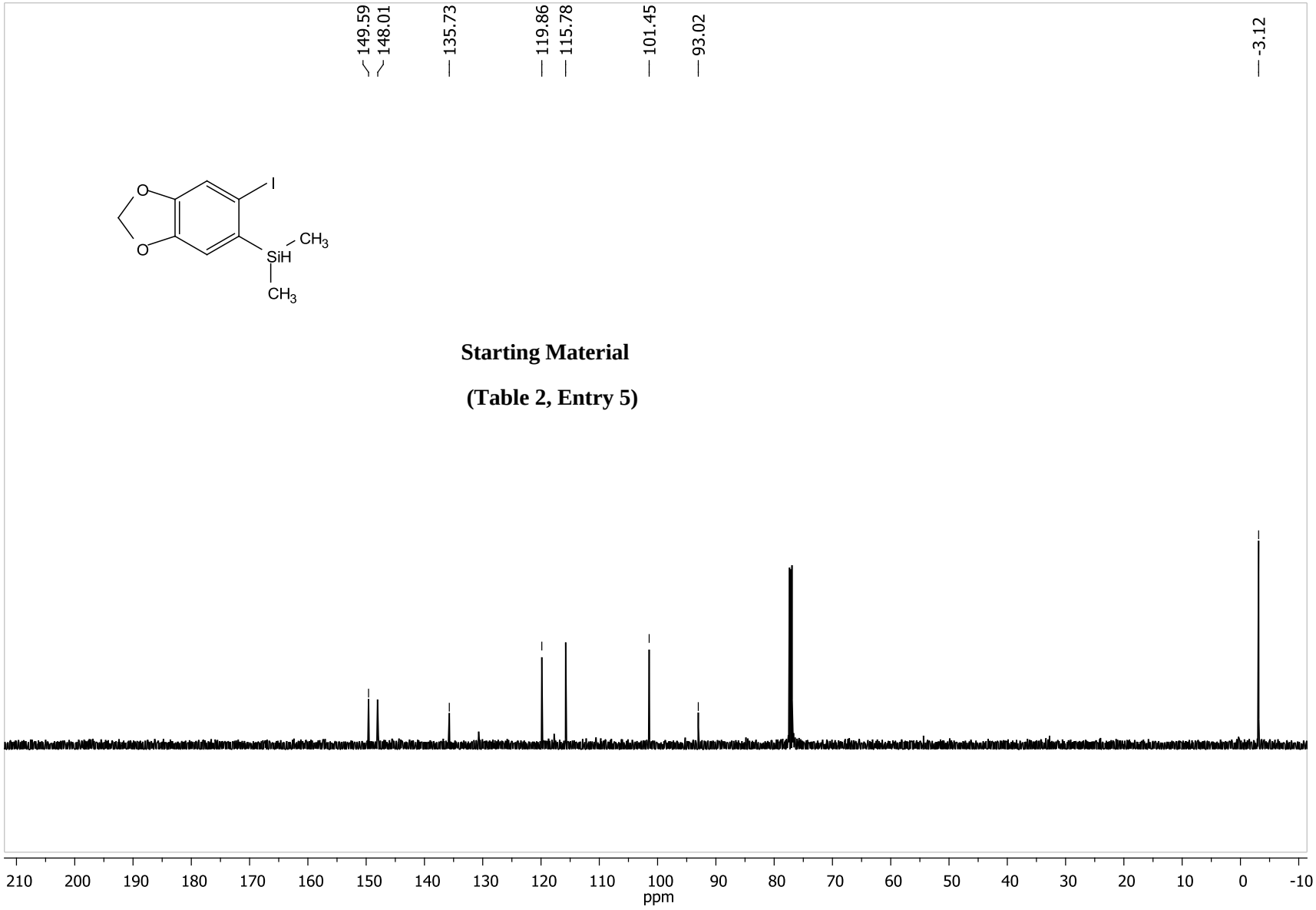
Starting Material

(Table 2, Entry 4)



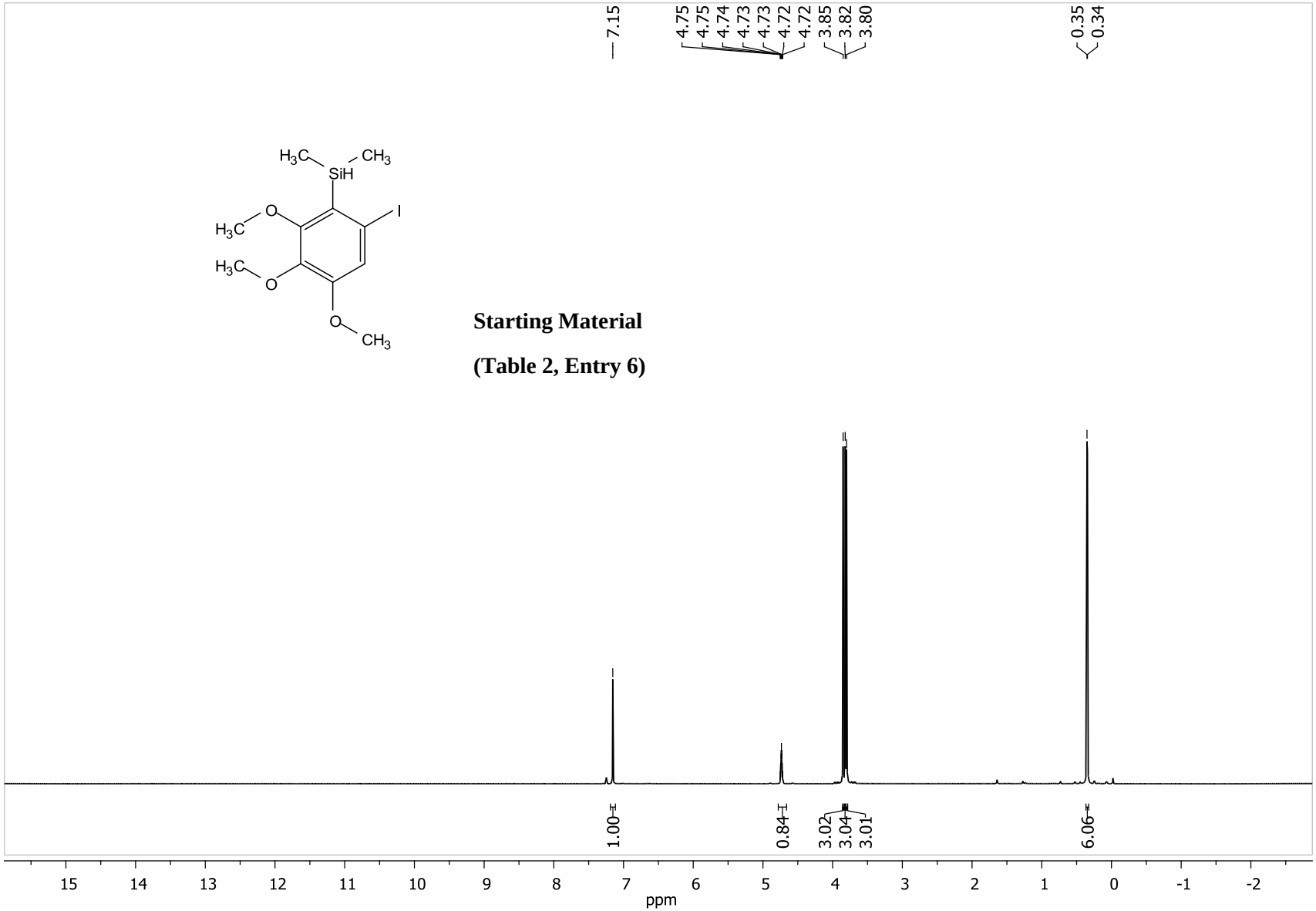
Starting Material

(Table 2, Entry 5)



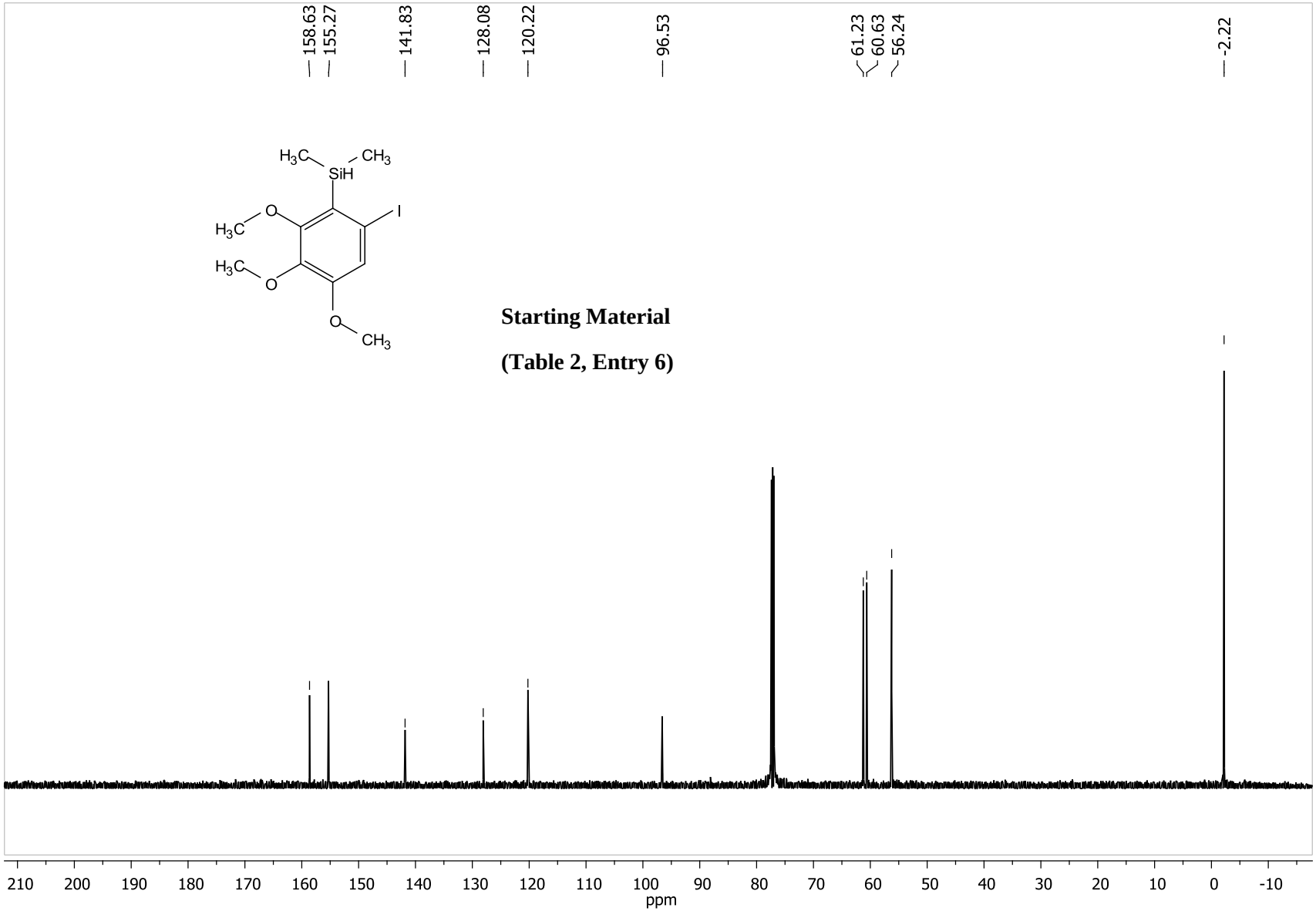
Starting Material

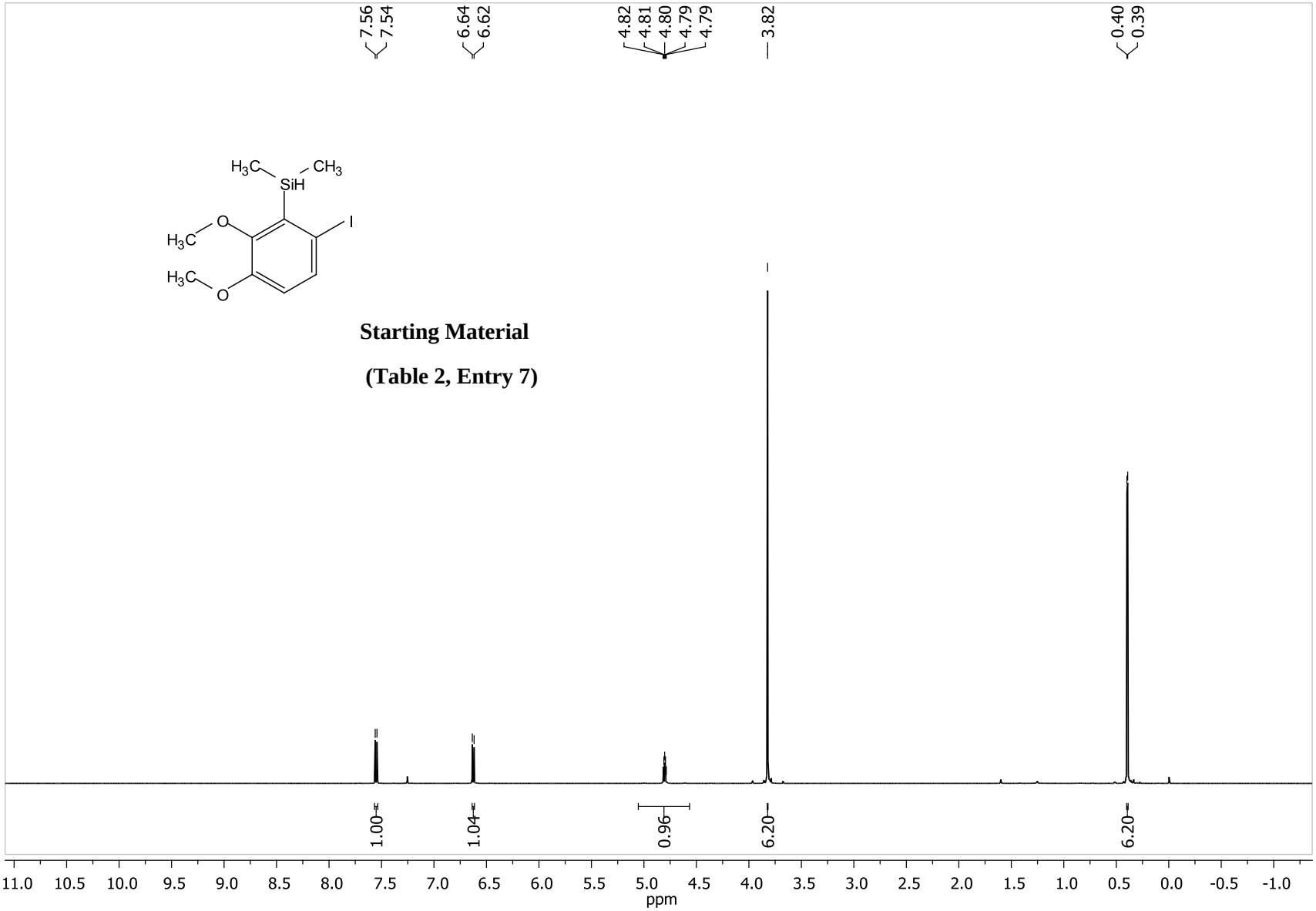
(Table 2, Entry 5)



Starting Material

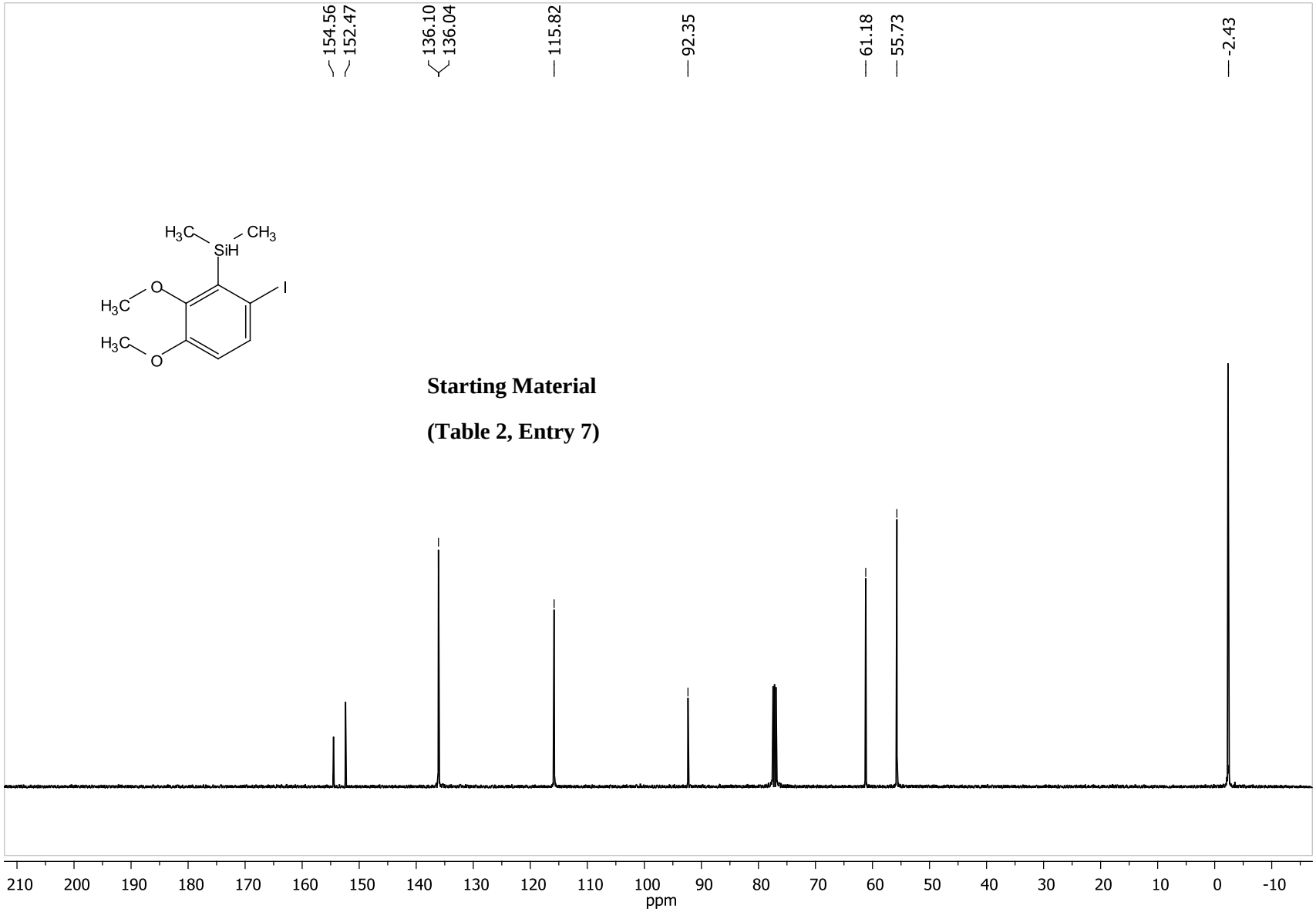
(Table 2, Entry 6)

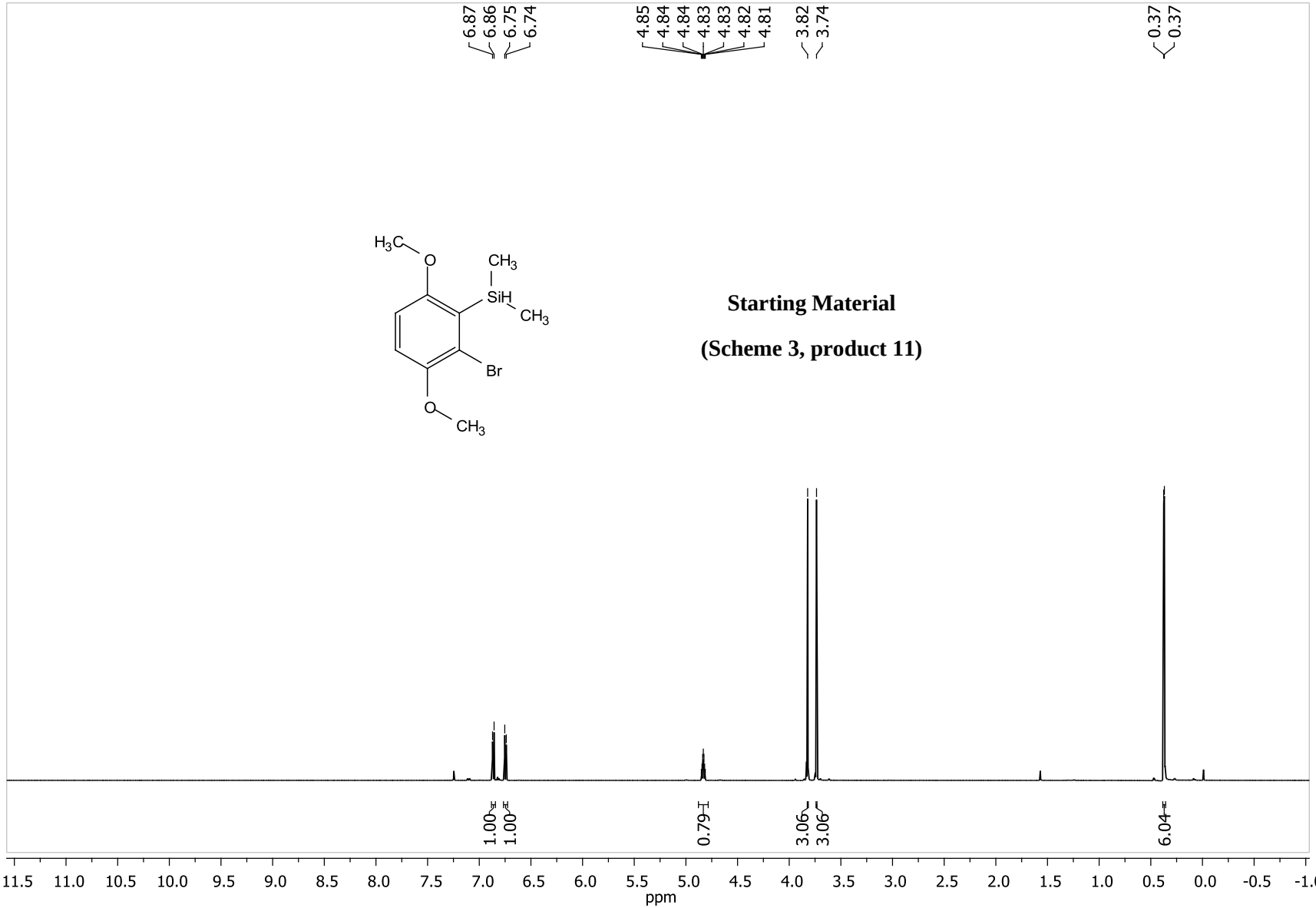

158.63
155.27
141.83
128.08
120.22
96.53
61.23
60.63
56.24
-2.22
H3C
CH3
SiH
O
H3C
I
H3C
O
O
CH3
Starting Material
(Table 2, Entry 6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

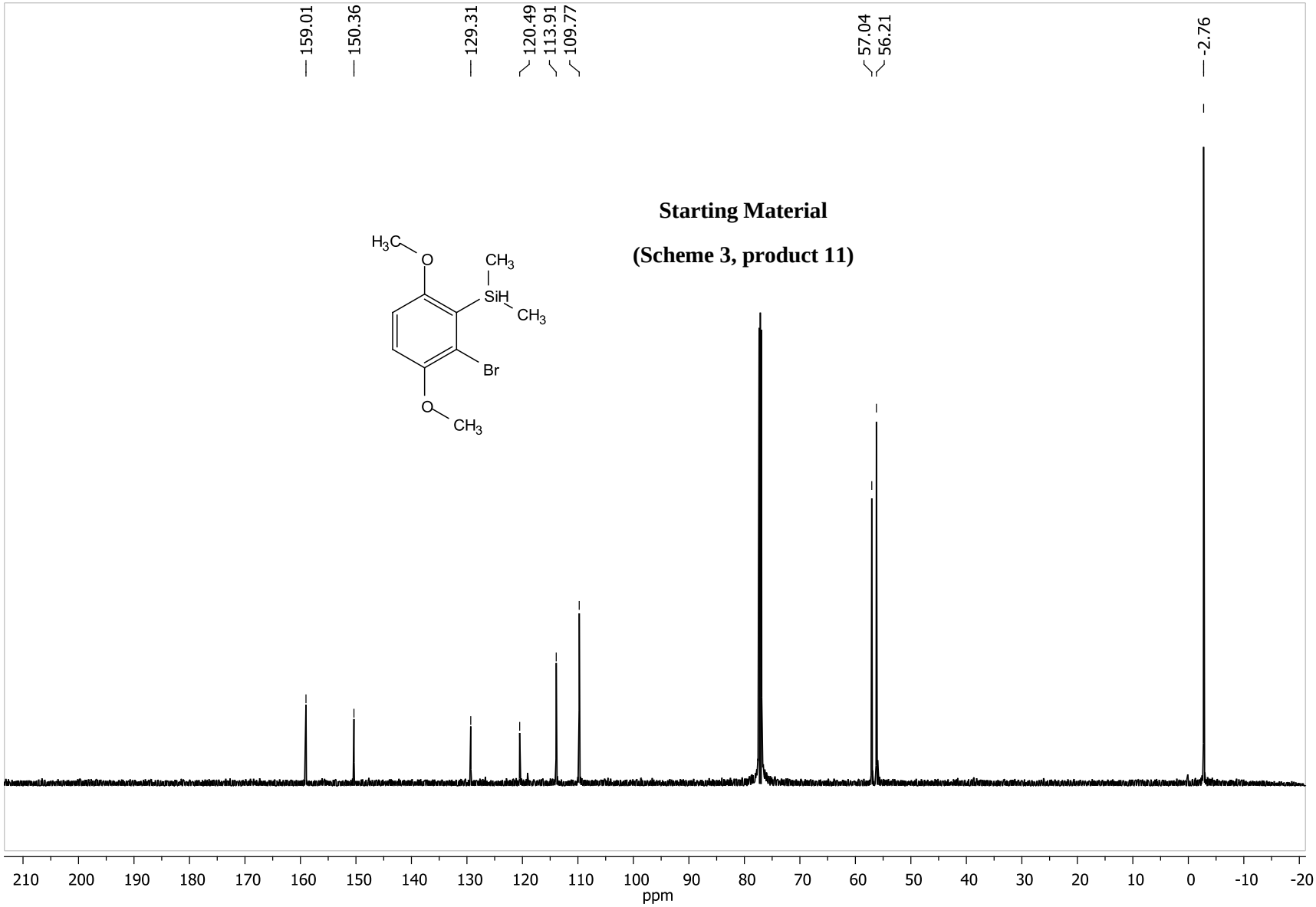


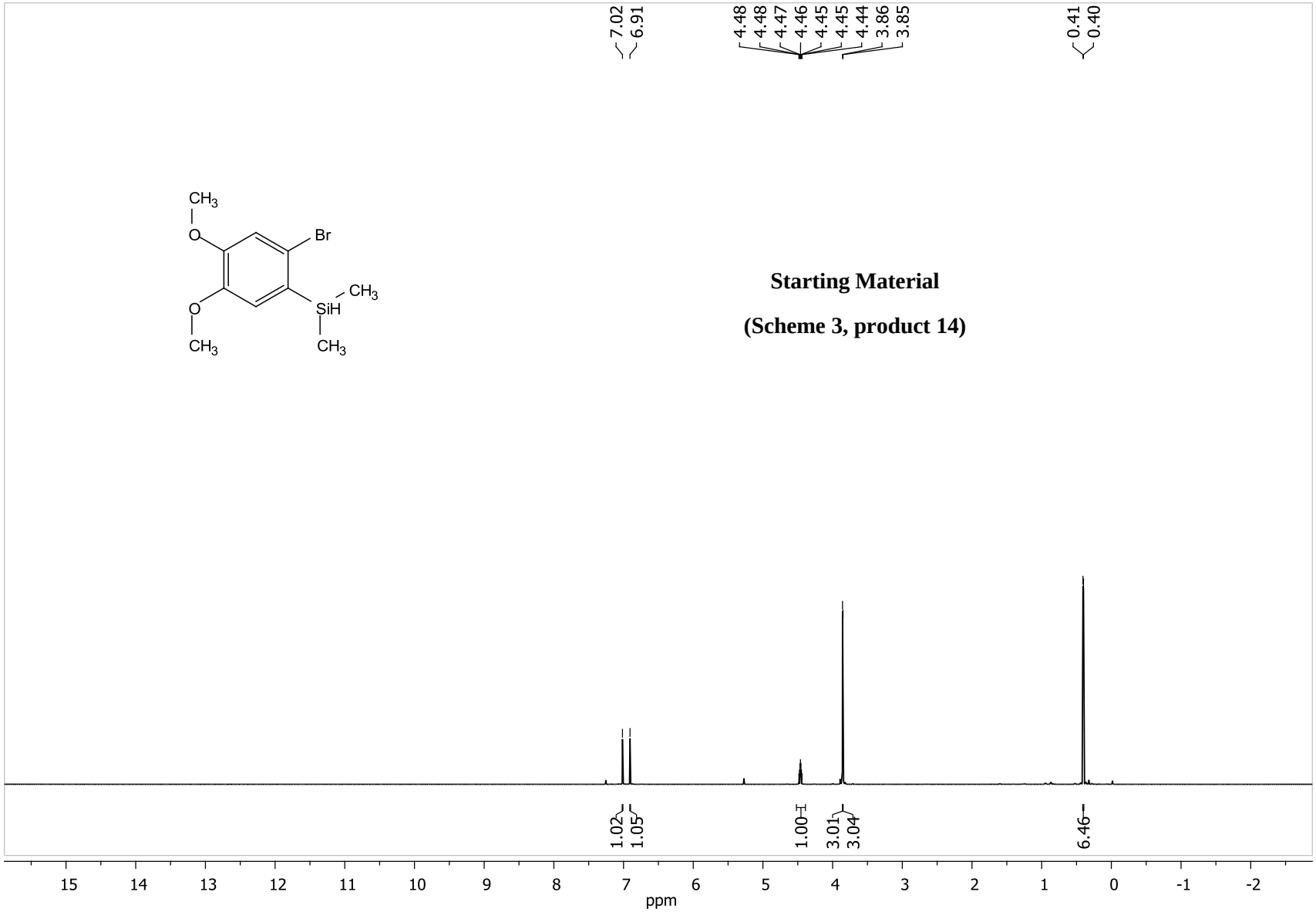
Starting Material

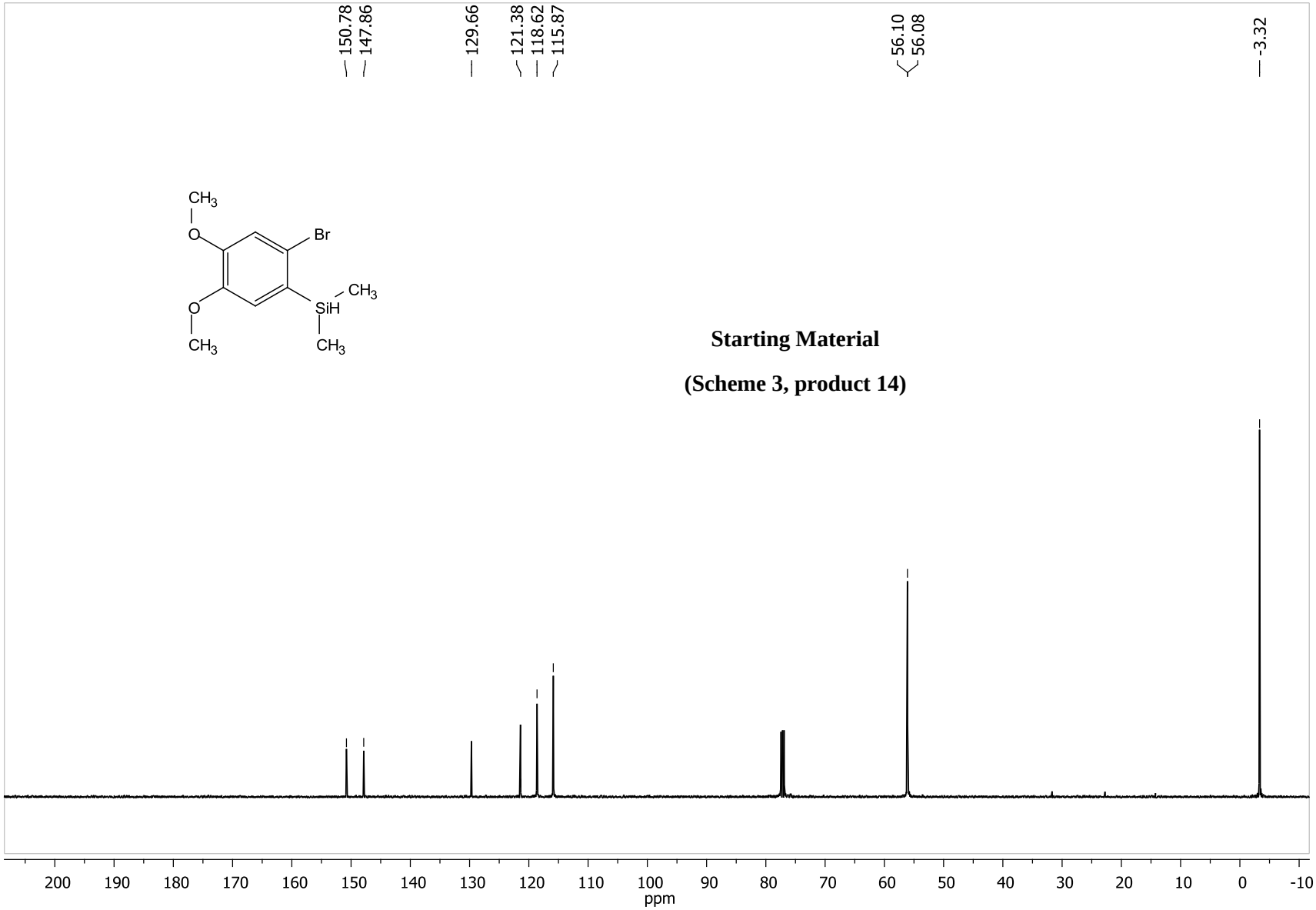
(Table 2, Entry 7)


154.56
152.47
136.10
136.04
115.82
92.35
61.18
55.73
-2.43
H3C
CH3
SiH
O
H3C
I
H3C
O
Starting Material
(Table 2, Entry 7)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


6.87
6.86
6.75
6.74
4.85
4.84
4.84
4.83
4.83
4.82
4.81
3.82
3.74
0.37
0.37
H3C
O
CH3
SiH
CH3
Br
O
CH3
Starting Material
(Scheme 3, product 11)
1.00
1.00
0.79
3.06
3.06
6.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

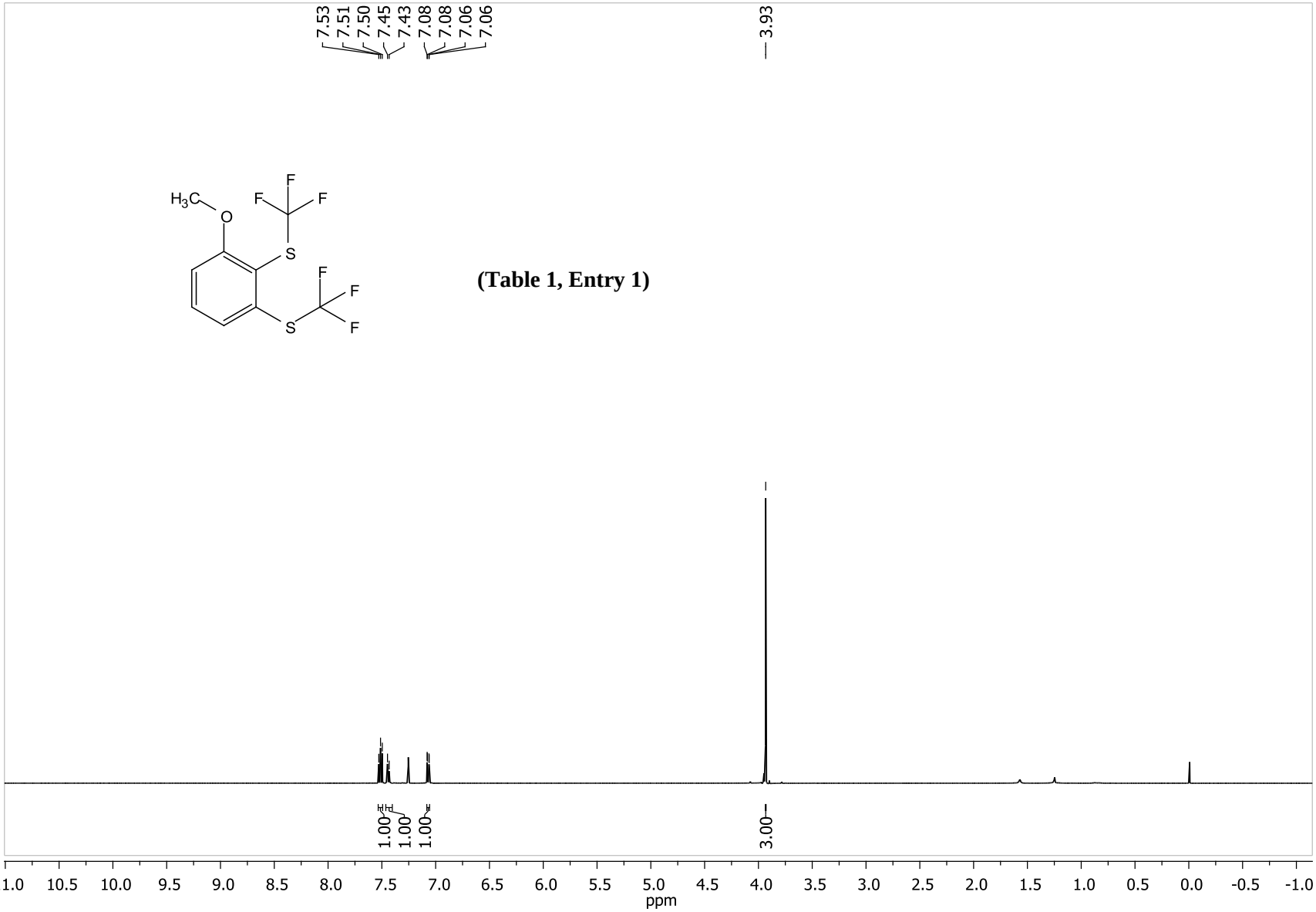

159.01
150.36
129.31
120.49
113.91
109.77
57.04
56.21
-2.76
Starting Material
(Scheme 3, product 11)
H3C
O
CH3
SiH
CH3
Br
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm

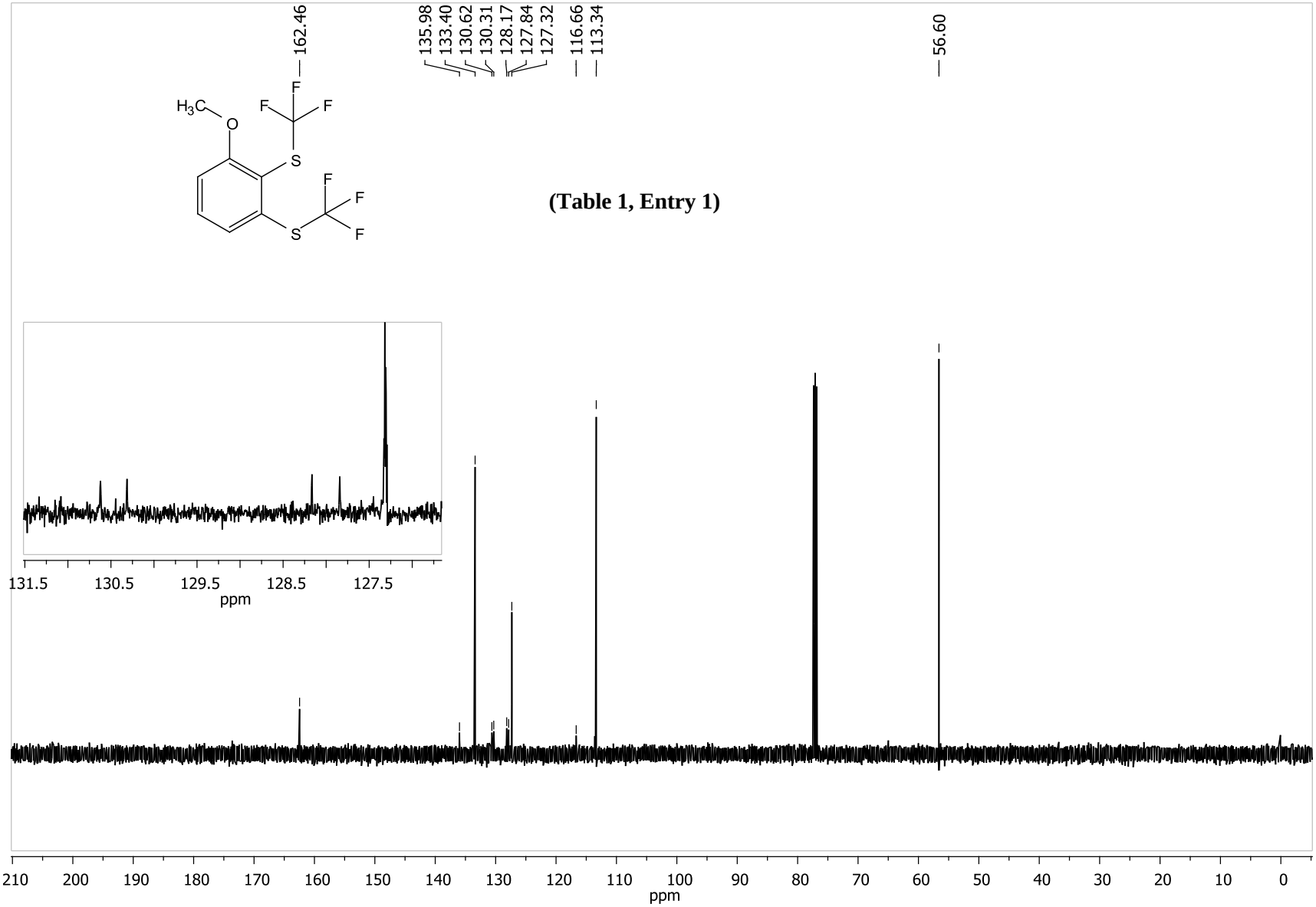

7.02
6.91
4.48
4.48
4.47
4.46
4.45
4.45
4.44
3.86
3.85
0.41
0.40
CH3
O
Br
CH3
O
SiH
CH3
CH3
CH3
Starting Material
(Scheme 3, product 14)
1.02
1.05
1.00
3.01
3.04
6.46
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

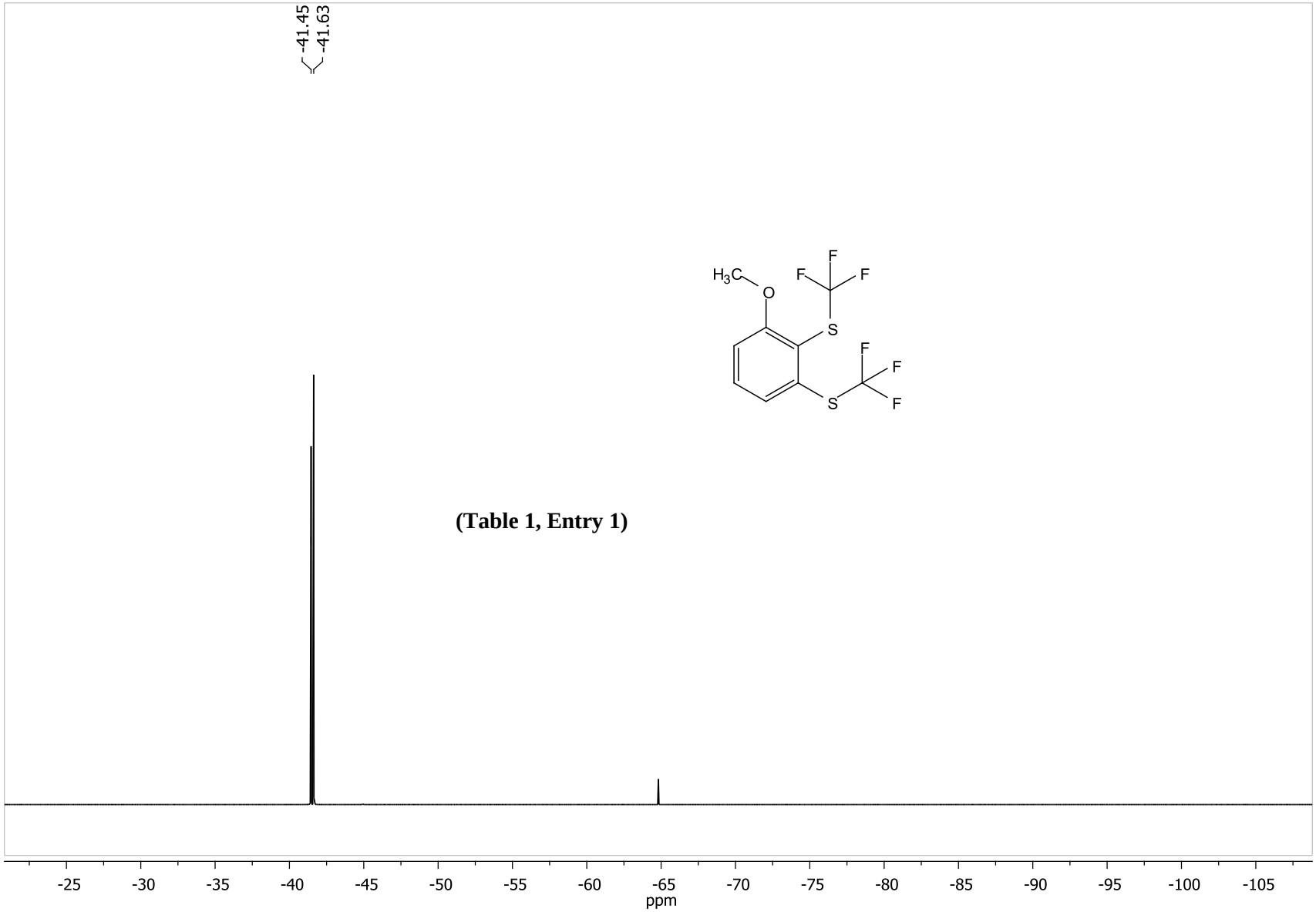


Starting Material

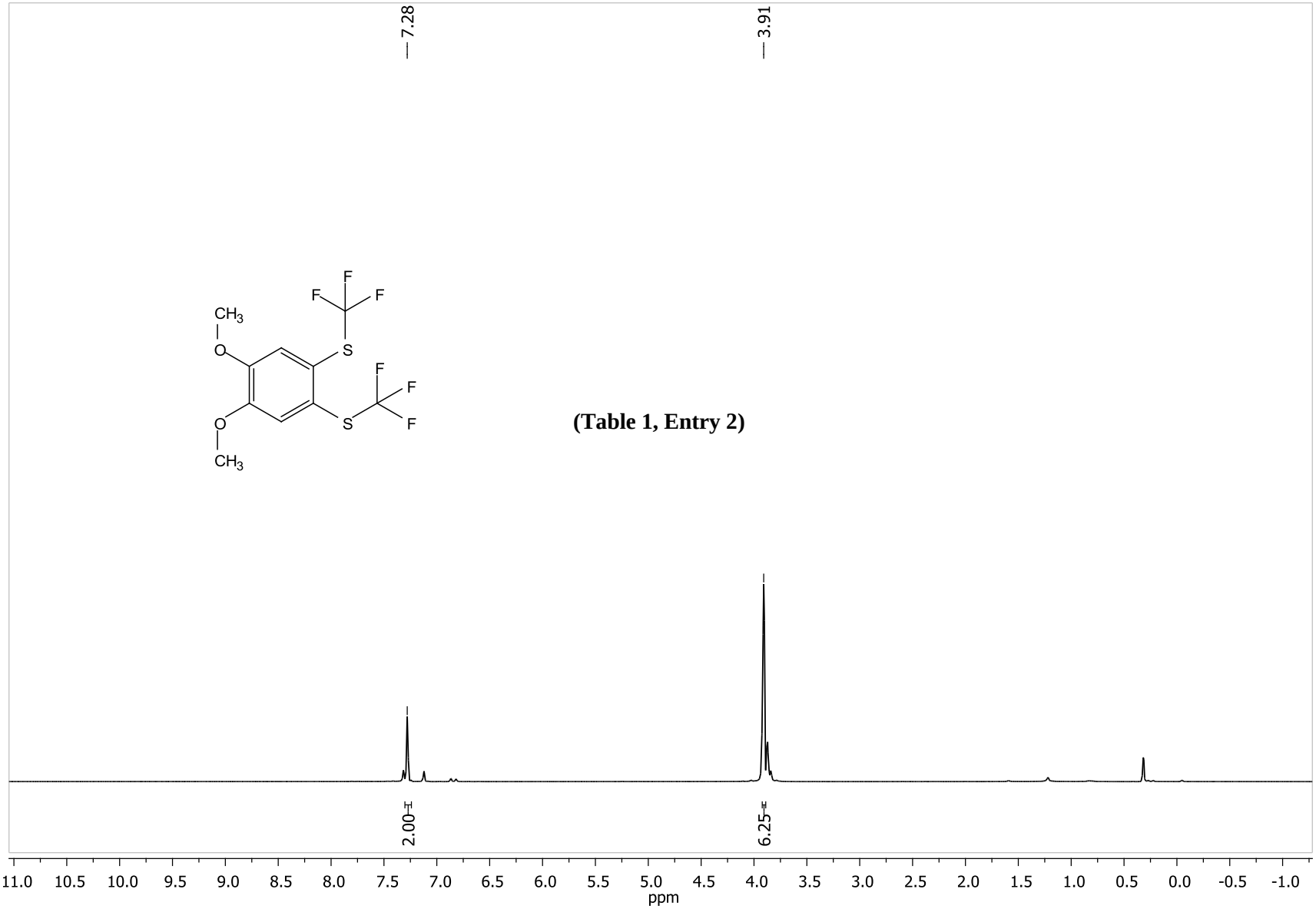
(Scheme 3, product 14)

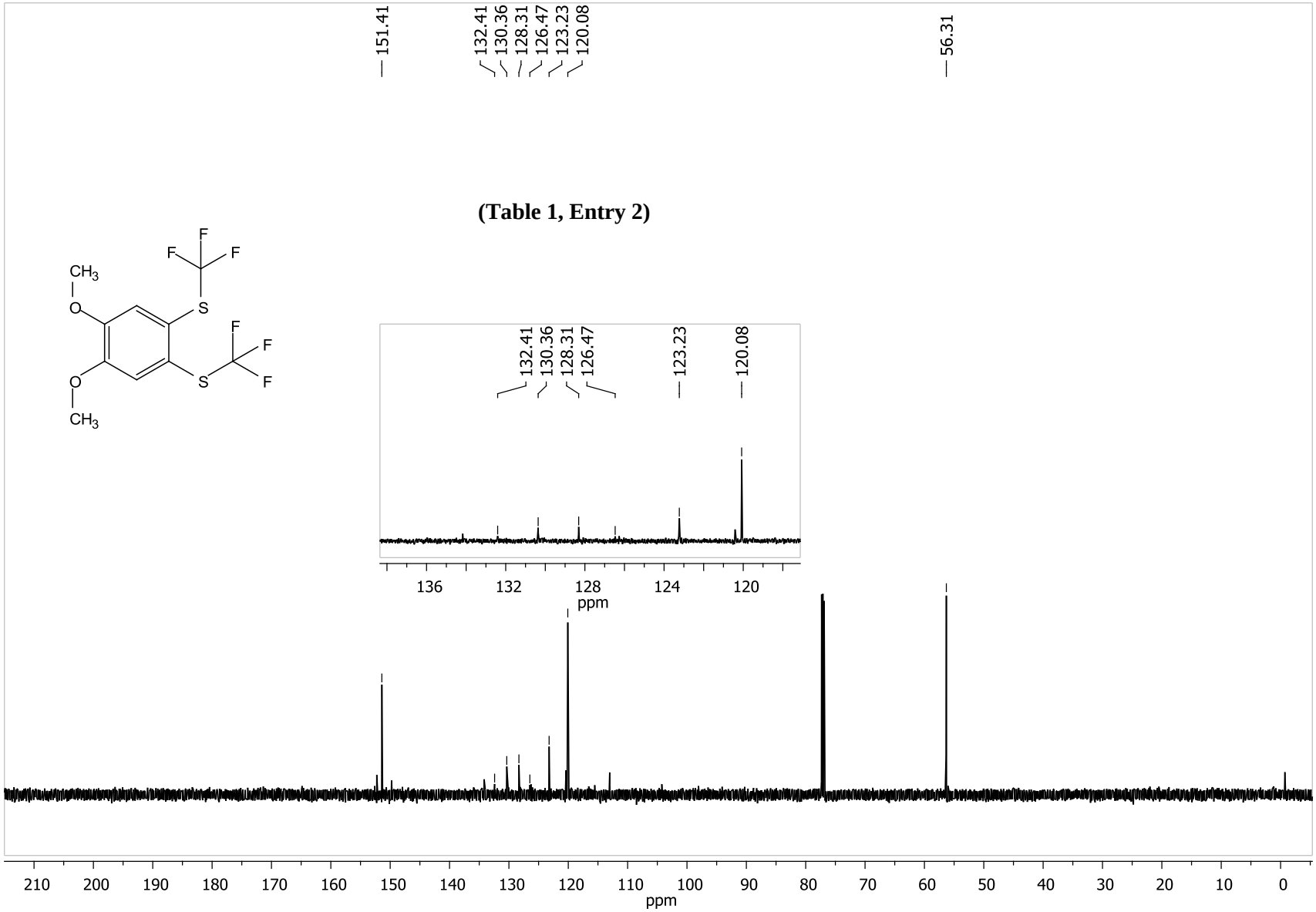

7.53
7.51
7.50
7.45
7.43
7.08
7.08
7.06
7.06
3.93
H3C
O
F
F
F
S
F
F
F
S
(Table 1, Entry 1)
1.00
1.00
1.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

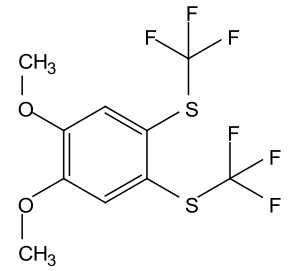

162.46
135.98
133.40
130.62
130.31
128.17
127.84
127.32
116.66
113.34
56.60
H3C
O
F
F
F
S
F
F
S
F
(Table 1, Entry 1)
131.5
130.5
129.5
128.5
127.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



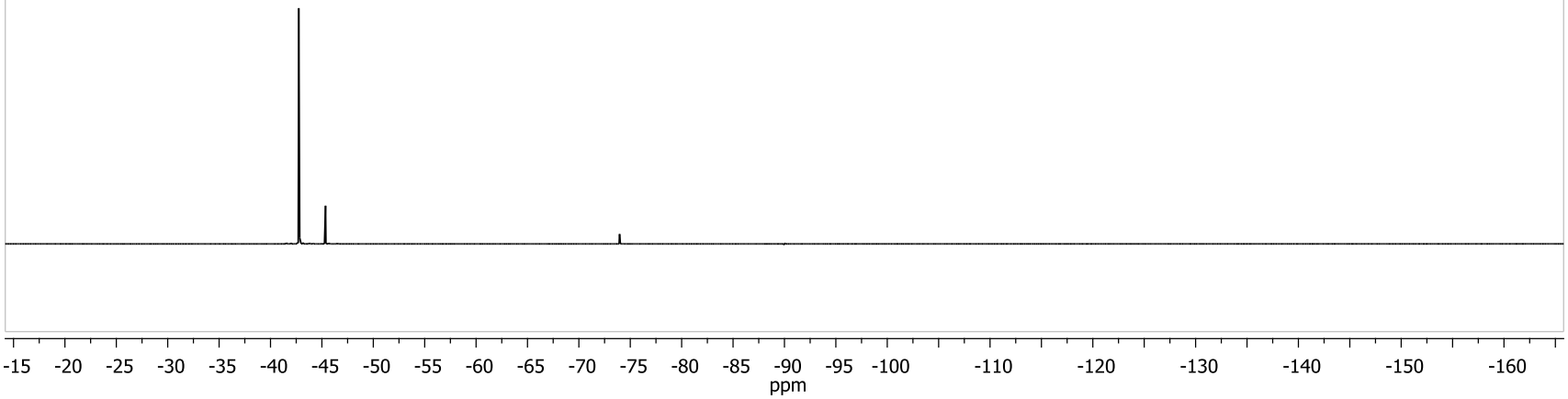
(Table 1, Entry 1)

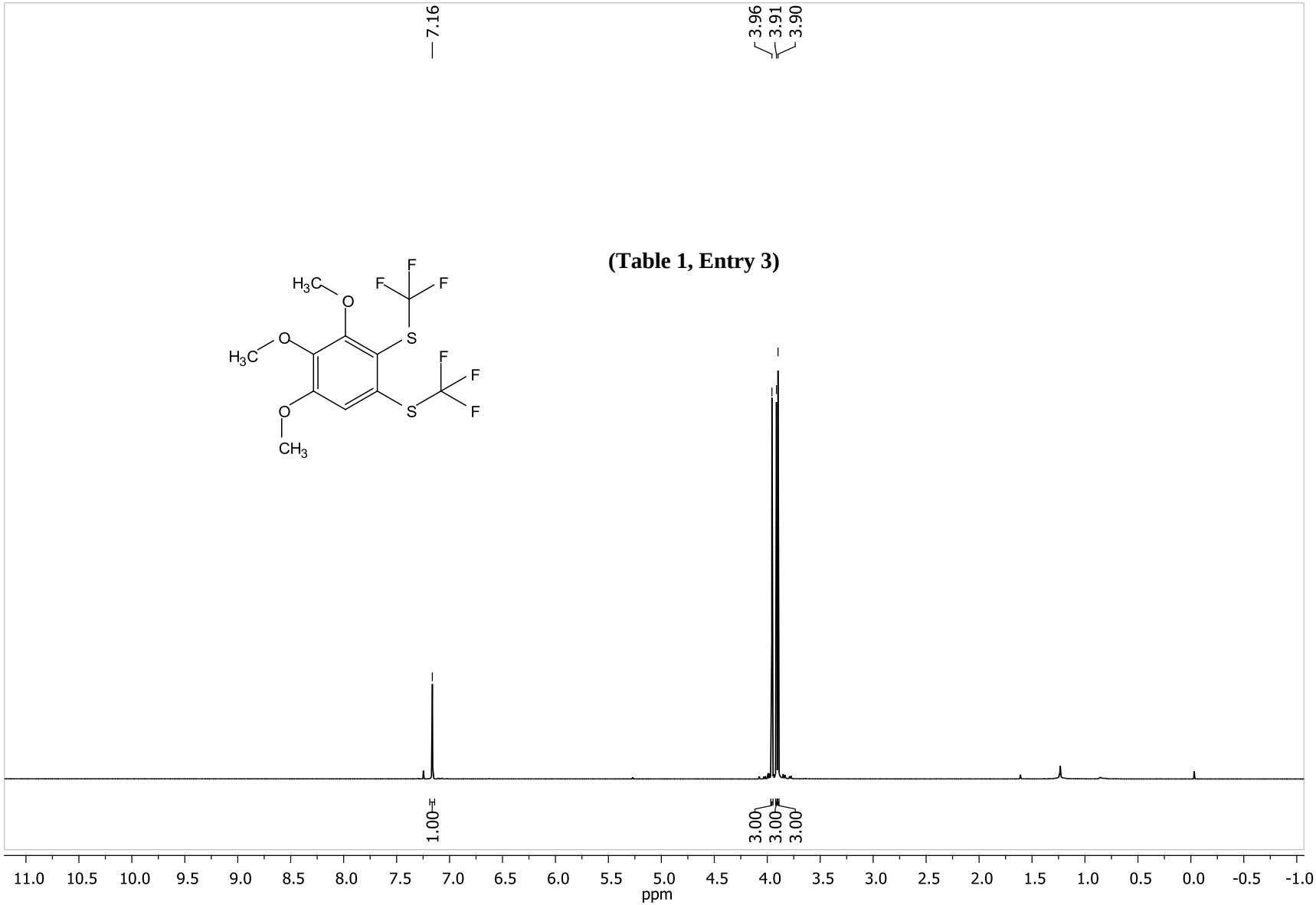

7.28
3.91
F
F
F
CH3
O
S
F
F
F
S
O
CH3
(Table 1, Entry 2)
2.00
6.25
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

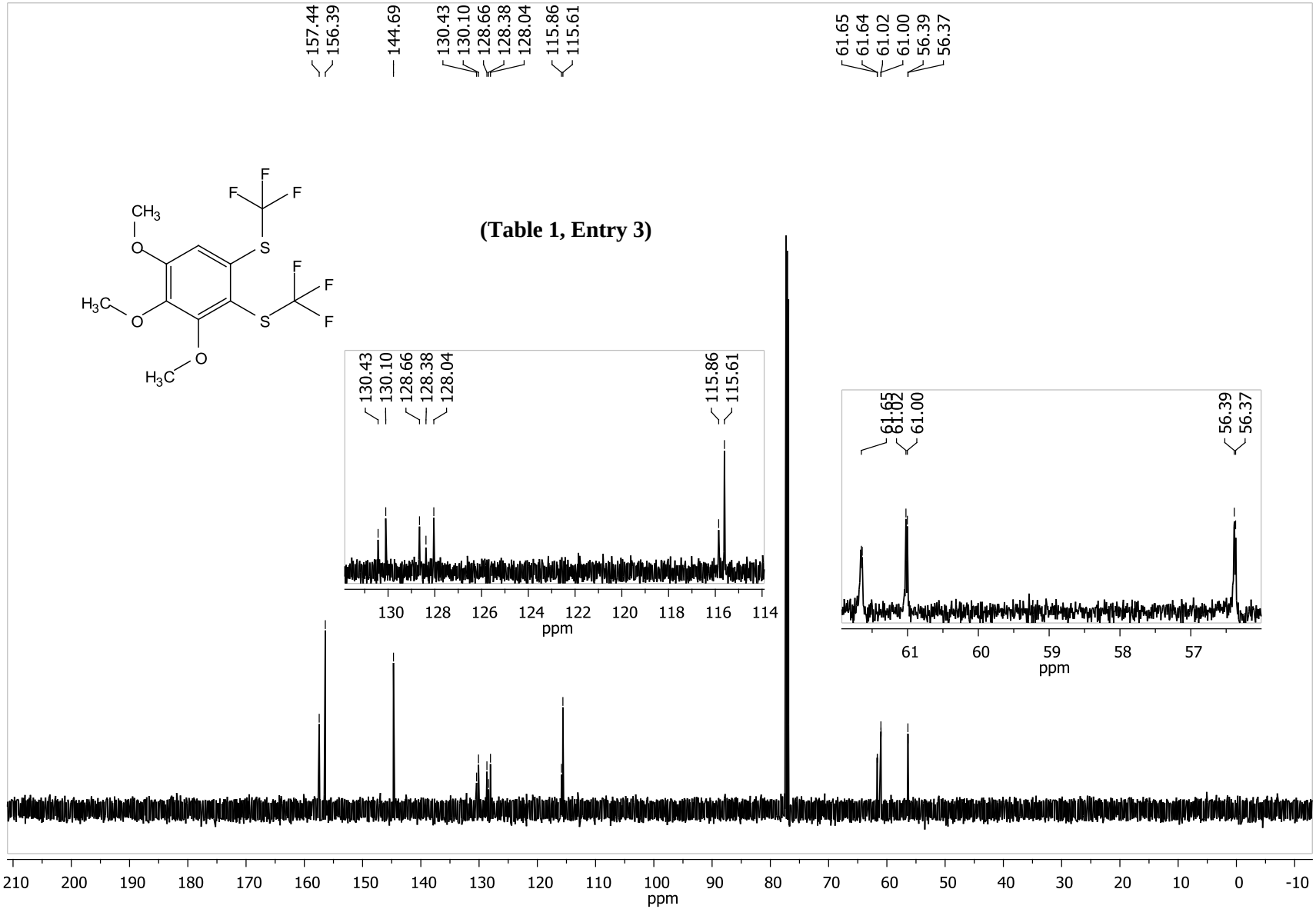

151.41
132.41
130.36
128.31
126.47
123.23
120.08
56.31
(Table 1, Entry 2)
CH3
O
S
F
F
F
F
F
F
S
O
CH3
132.41
130.36
128.31
126.47
123.23
120.08
136
132
128
124
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



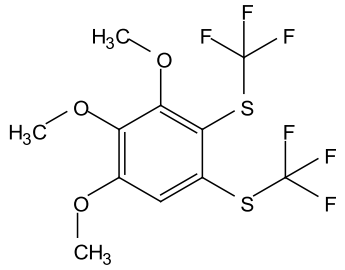
(Table 1, Entry 2)

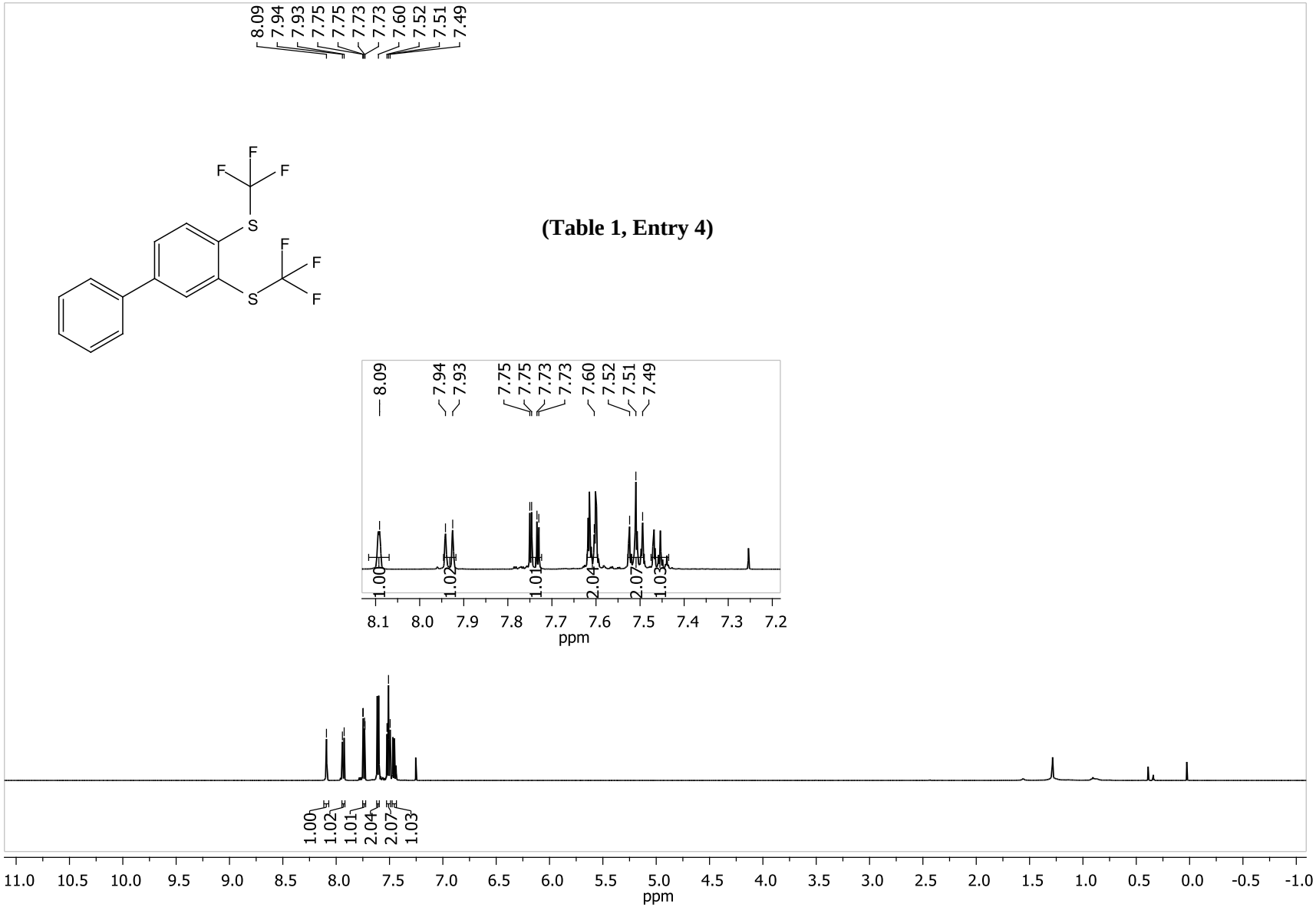


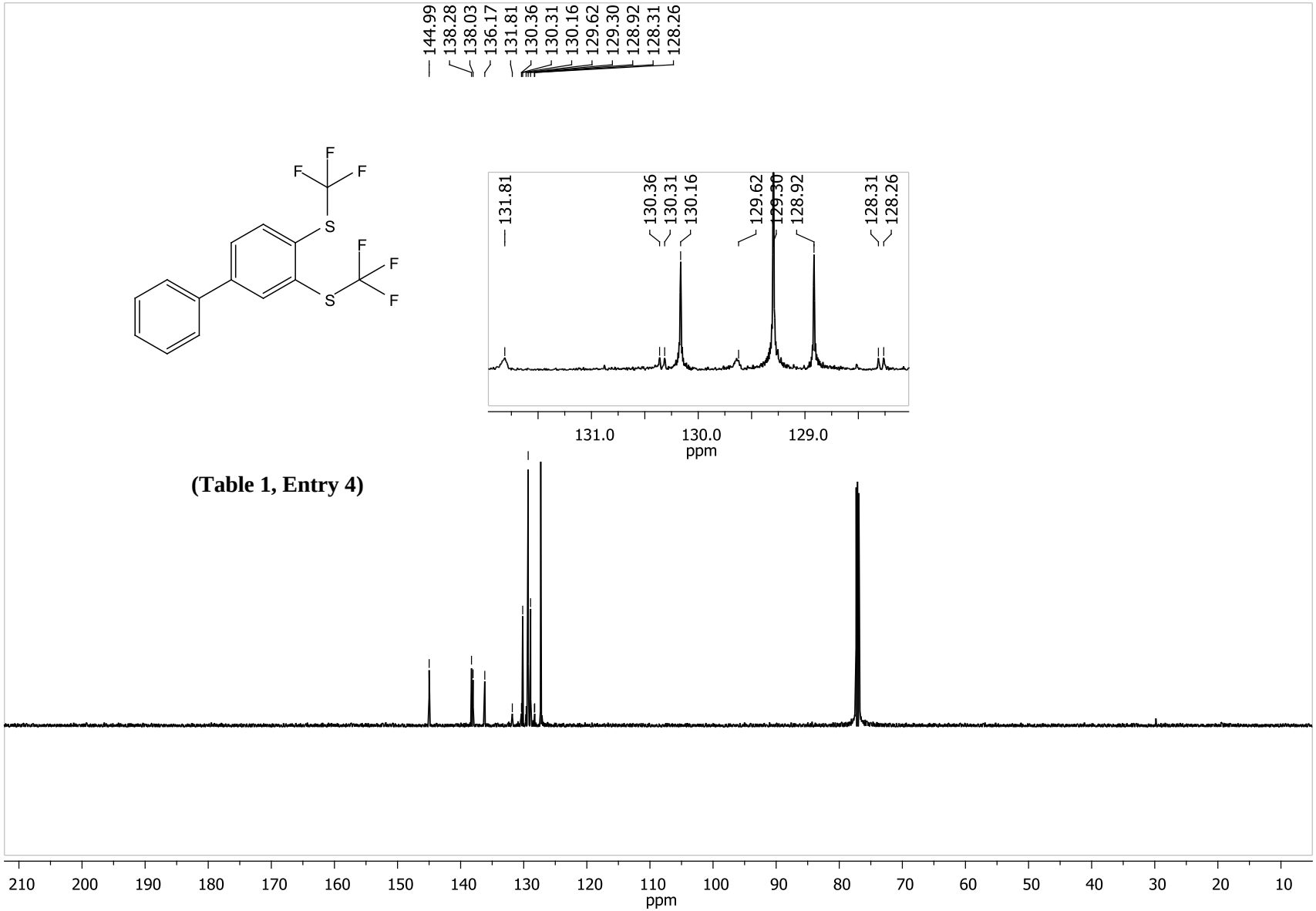

7.16
3.96
3.91
3.90
(Table 1, Entry 3)
1.00
3.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

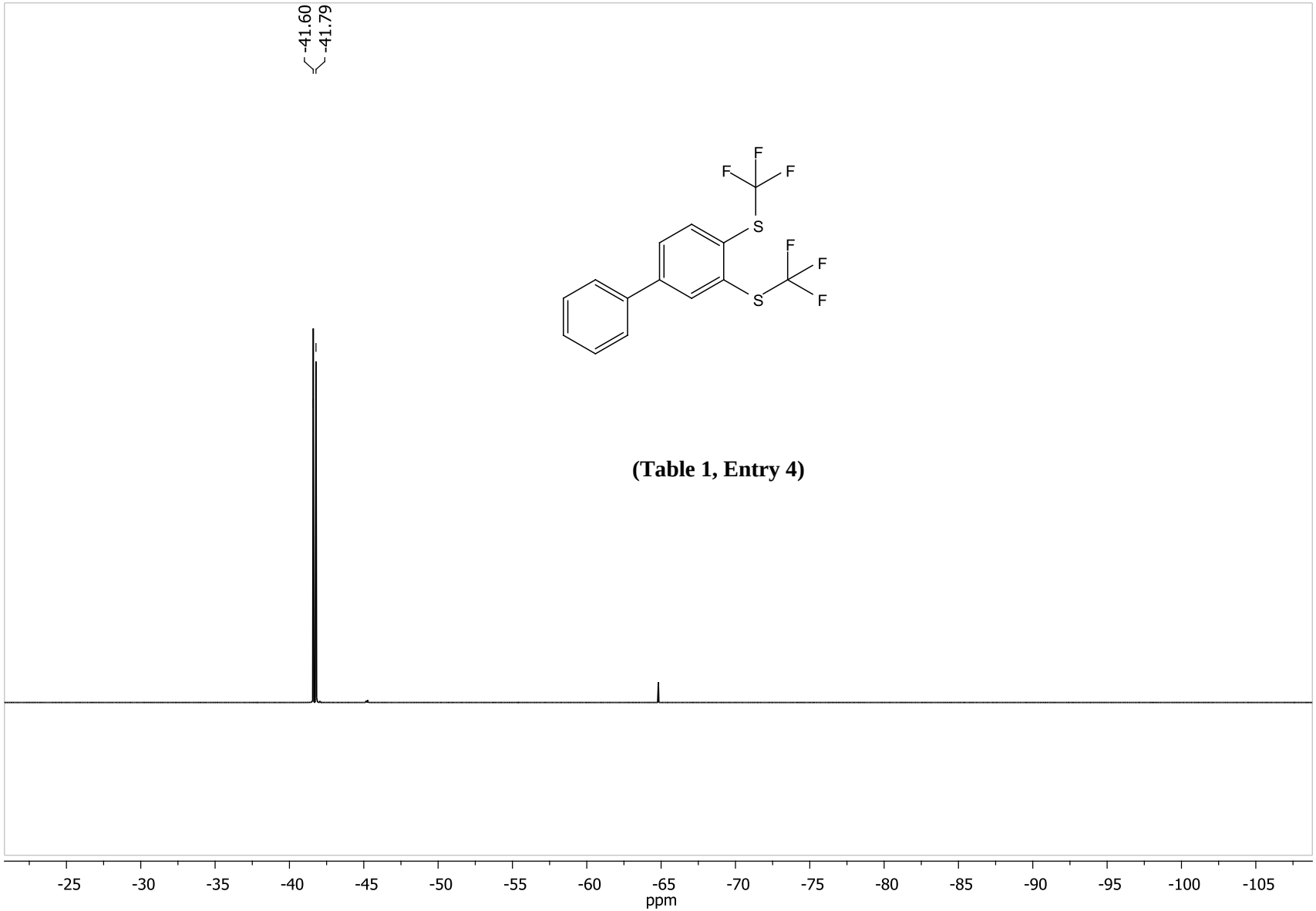

157.44
156.39
144.69
130.43
130.10
128.66
128.38
128.04
115.86
115.61
61.65
61.64
61.02
61.00
56.39
56.37
(Table 1, Entry 3)
ppm
ppm
ppm

(Table 1, Entry 3)

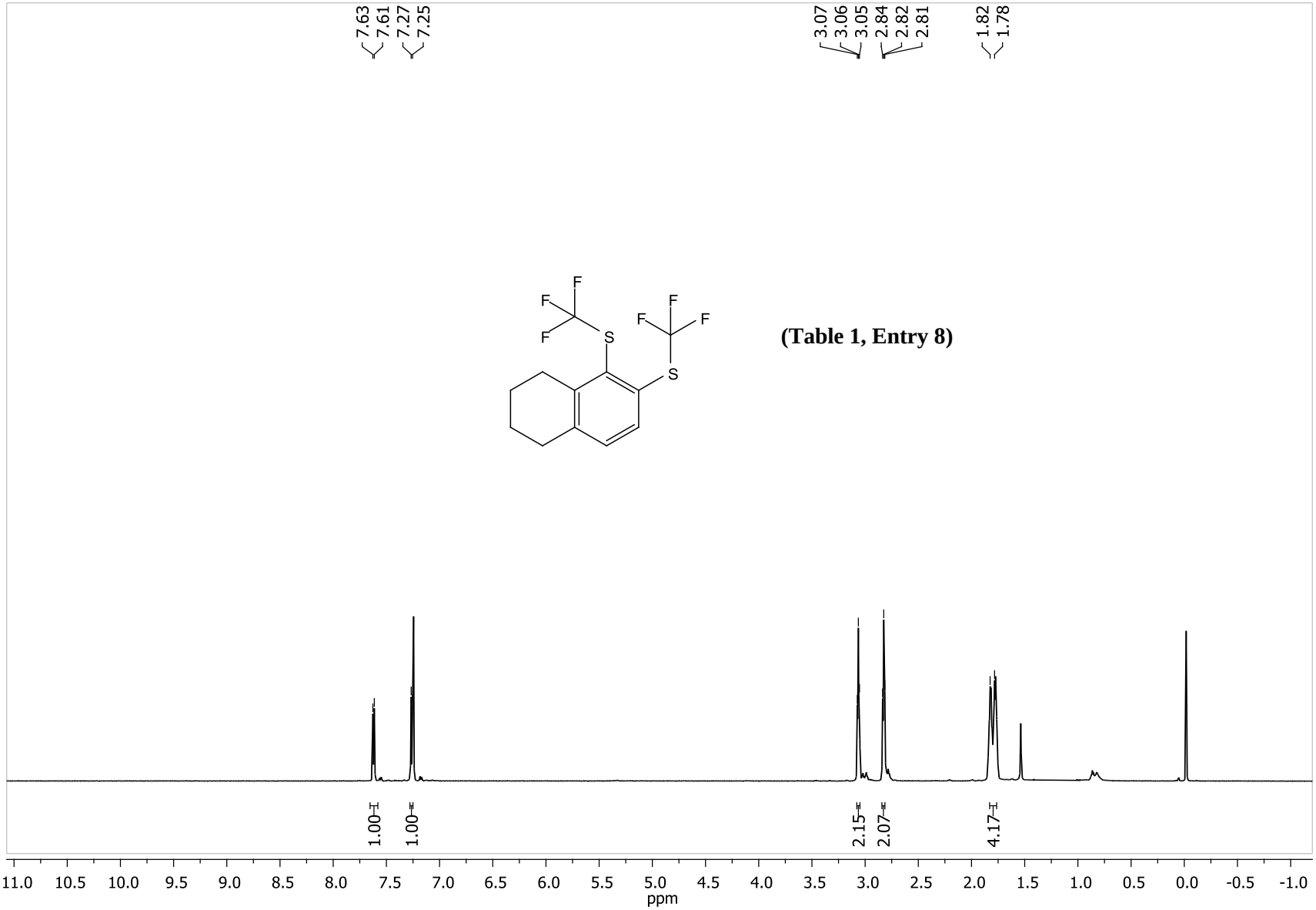


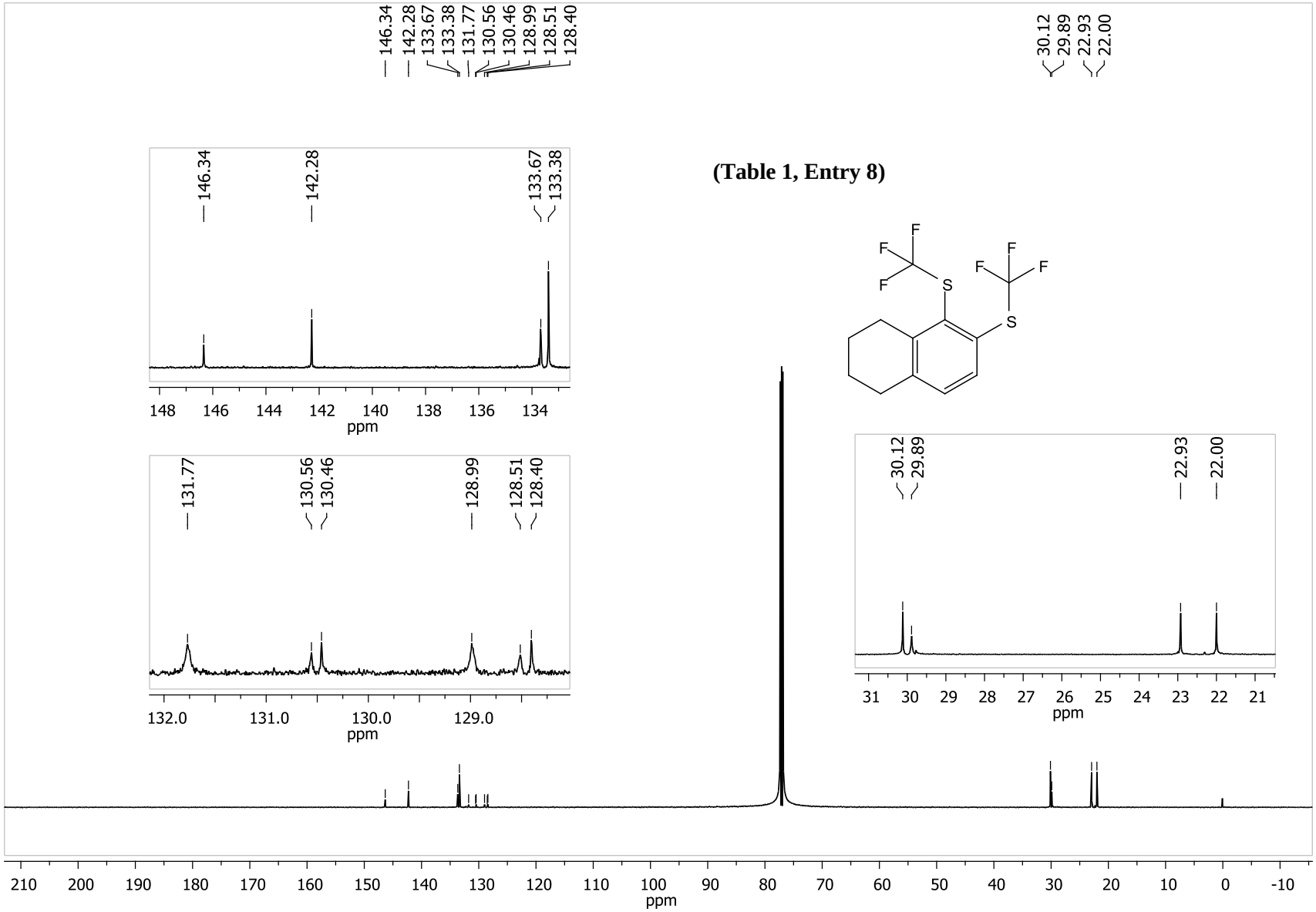

8.09
7.94
7.93
7.75
7.75
7.73
7.73
7.60
7.52
7.51
7.49
F
F
F
S
F
F
F
S
(Table 1, Entry 4)
1.00
1.02
1.01
2.04
2.07
1.03
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

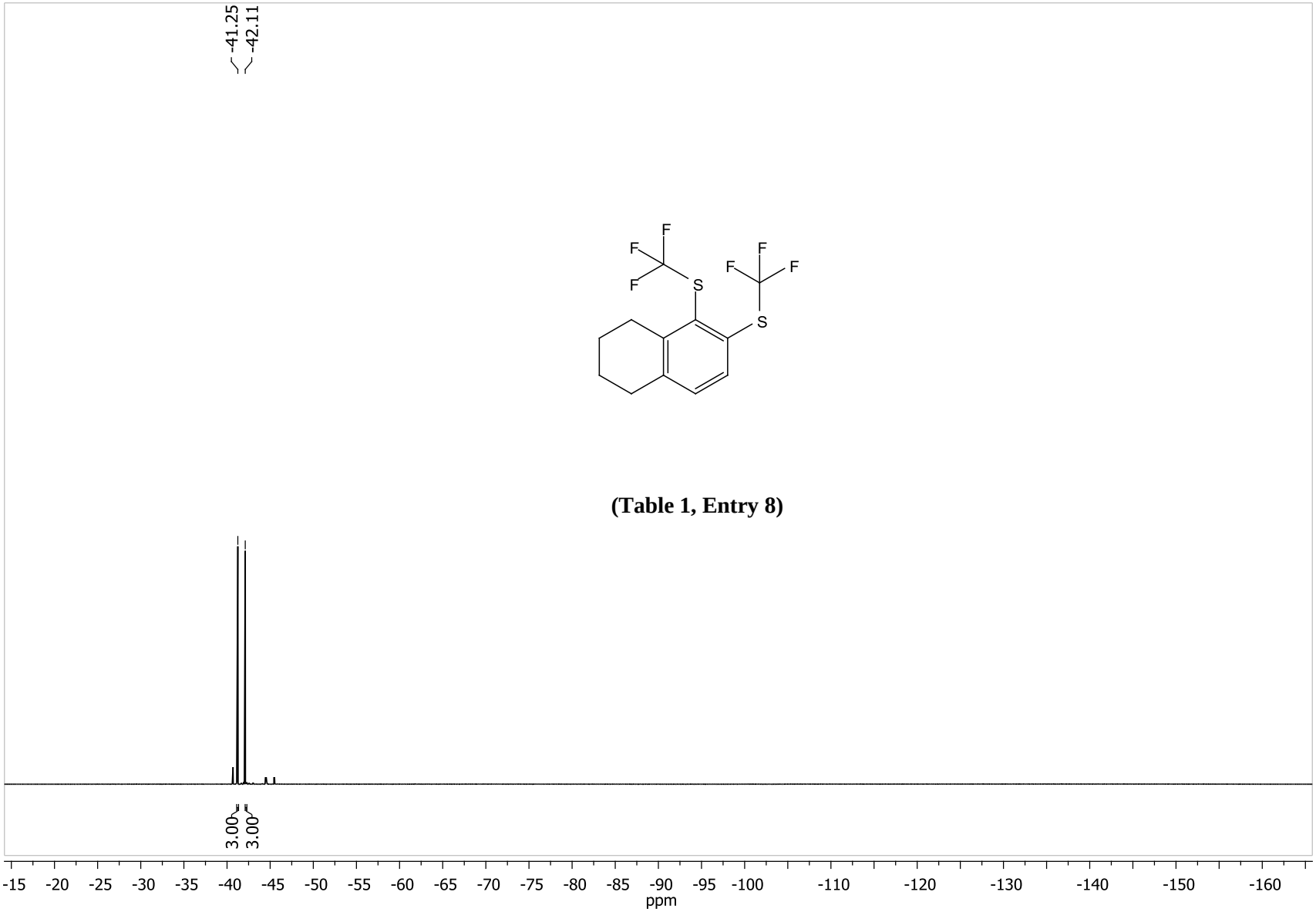

144.99
138.28
138.03
136.17
131.81
130.36
130.31
130.16
129.62
129.30
128.92
128.31
128.26
F
F
F
S
F
F
F
S
131.81
130.36
130.31
130.16
129.62
129.30
128.92
128.31
128.26
131.0
130.0
129.0
ppm
(Table 1, Entry 4)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



(Table 1, Entry 4)

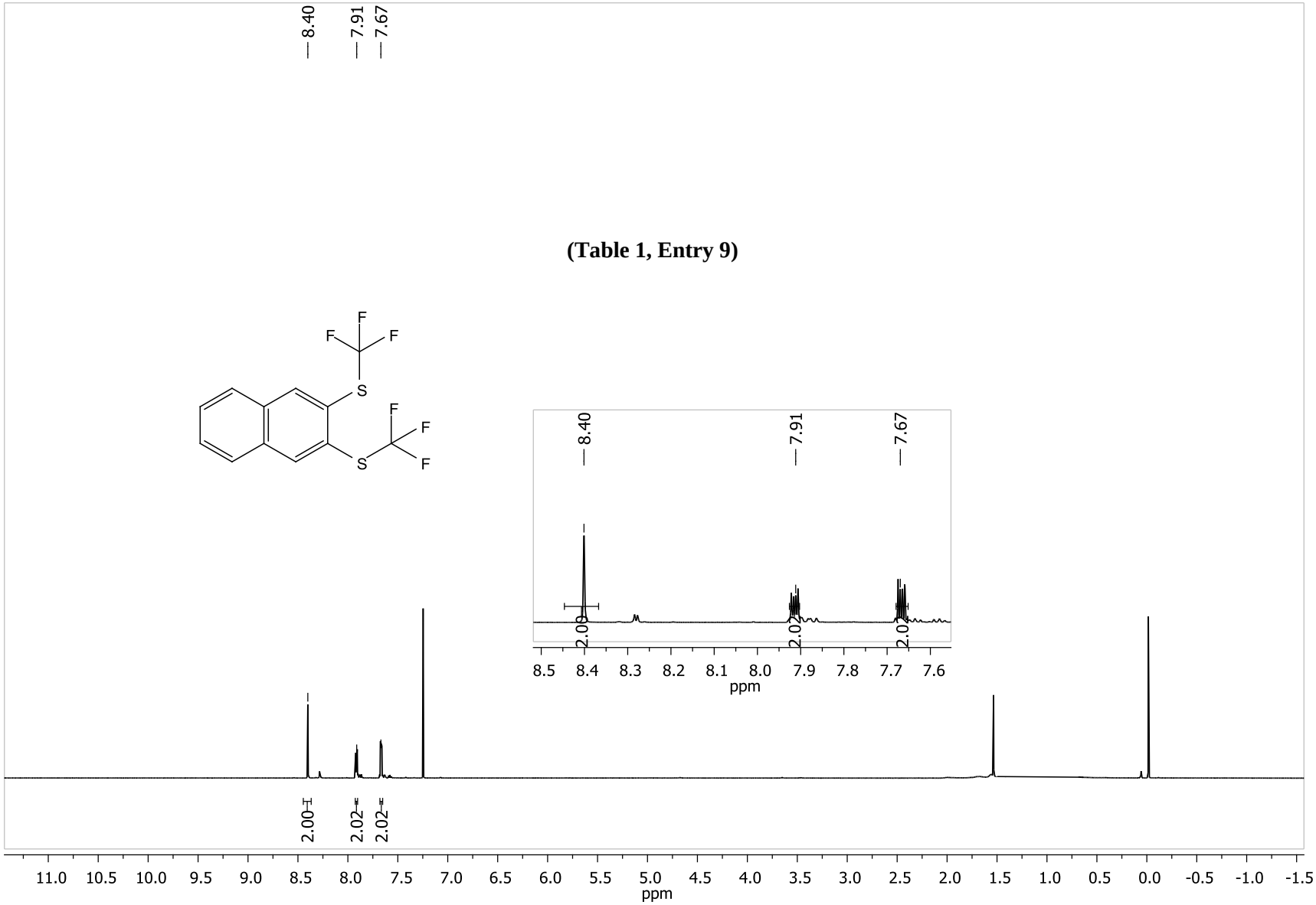

7.63
7.61
7.27
7.25
3.07
3.06
3.05
2.84
2.82
2.81
1.82
1.78
F
F
F
S
F
F
F
S
(Table 1, Entry 8)
1.00
1.00
2.15
2.07
4.17
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

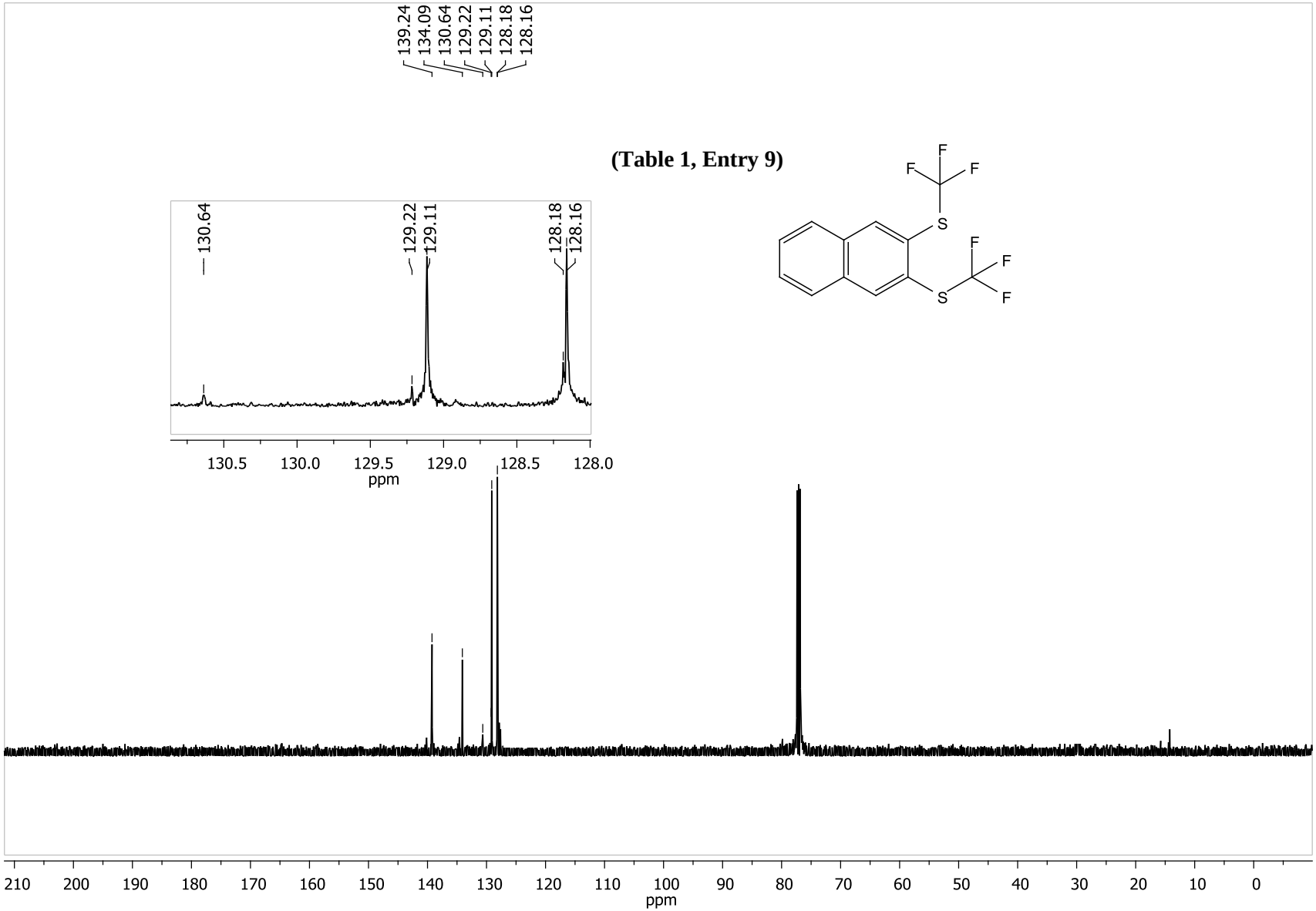

146.34
142.28
133.67
133.38
131.77
130.56
130.46
128.99
128.51
128.40
30.12
29.89
22.93
22.00
(Table 1, Entry 8)
F
F
F
S
F
F
F
S
148 146 144 142 140 138 136 134
ppm
132.0 131.0 130.0 129.0
ppm
31 30 29 28 27 26 25 24 23 22 21
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

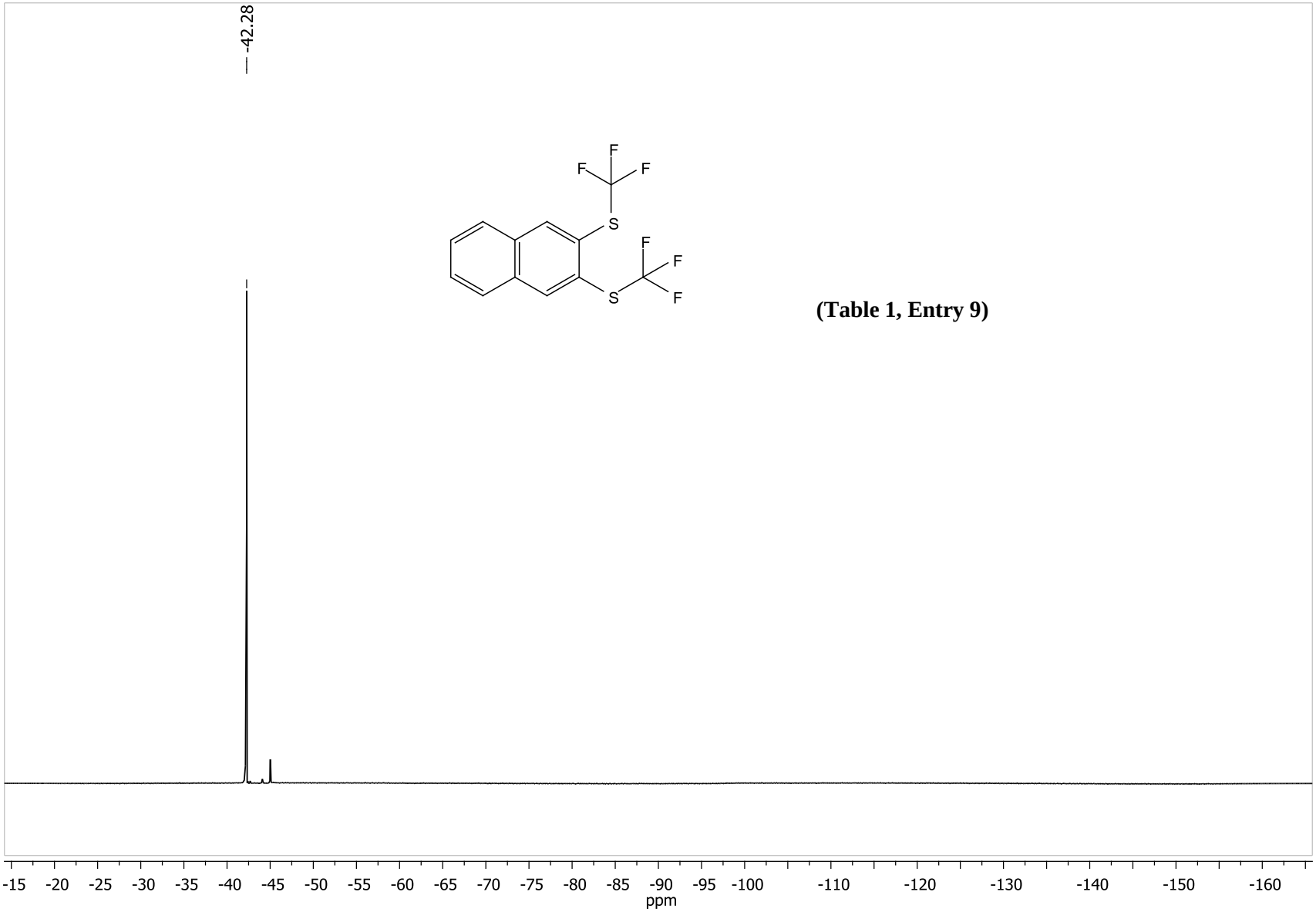


(Table 1, Entry 8)

(Table 1, Entry 9)

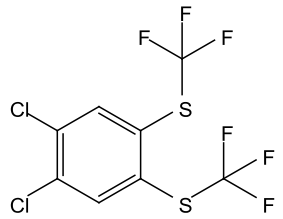


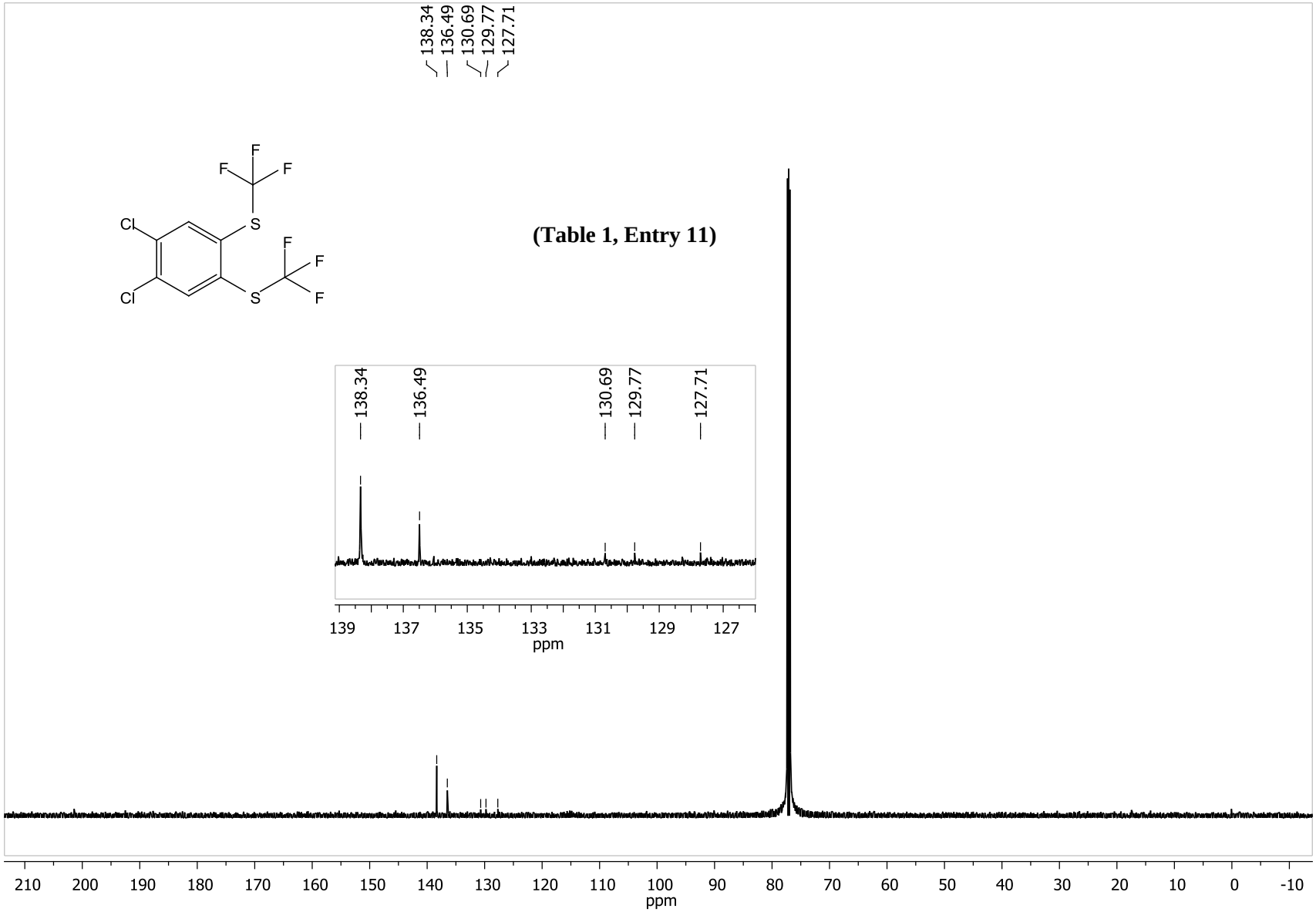

139.24
134.09
130.64
129.22
129.11
128.18
128.16
(Table 1, Entry 9)
F
F
F
S
F
F
F
S
130.64
129.22
129.11
128.18
128.16
130.5
130.0
129.5
129.0
128.5
128.0
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

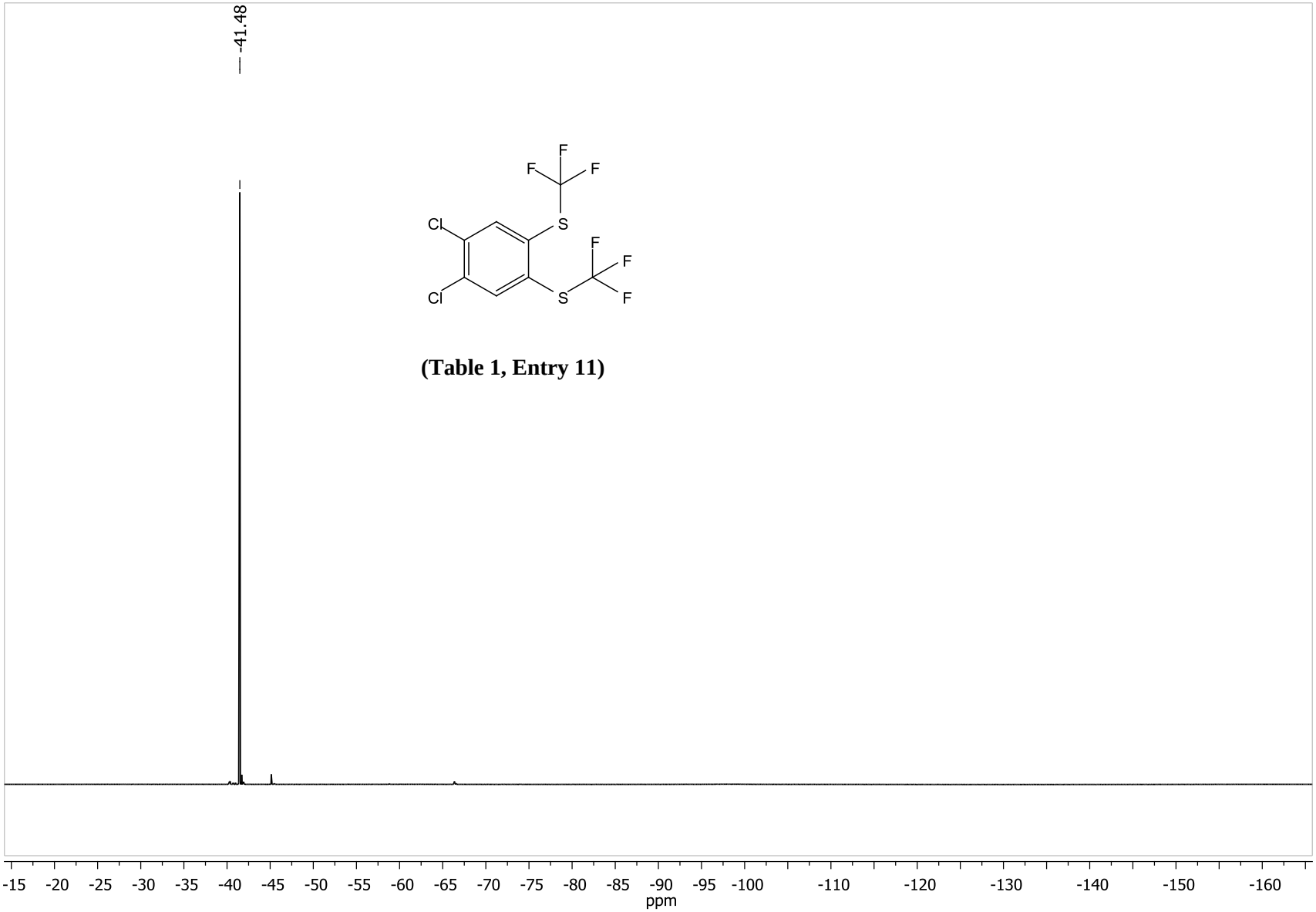


(Table 1, Entry 9)

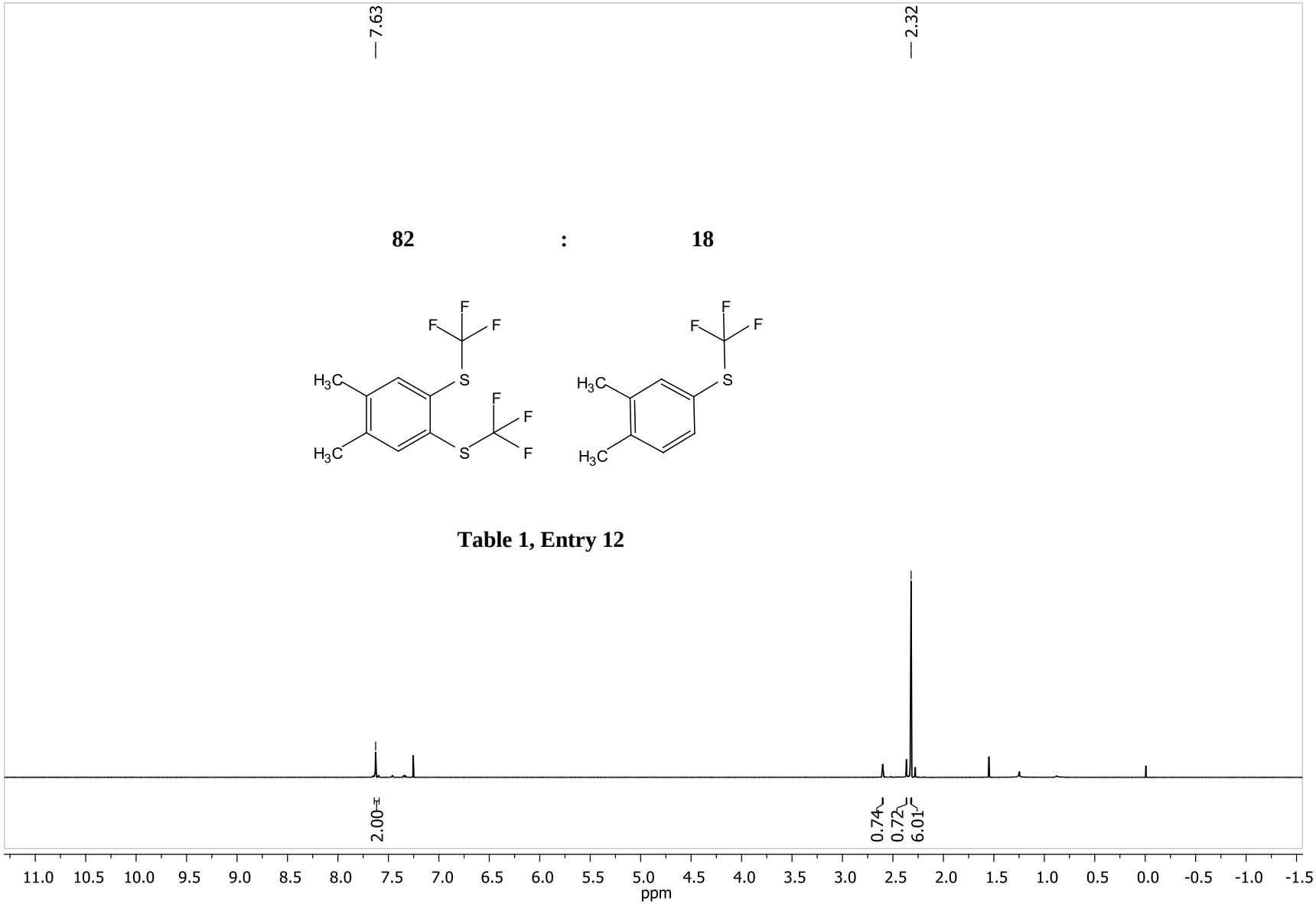
(Table 1, Entry 11)




138.34
136.49
130.69
129.77
127.71
F
F
F
Cl
S
F
F
Cl
S
F
(Table 1, Entry 11)
138.34
136.49
130.69
129.77
127.71
139
137
135
133
131
129
127
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



(Table 1, Entry 11)


7.63
2.32
82 : 18
F
F
F
S
H3C
H3C
F
F
F
S
F
F
F
S
H3C
H3C
Table 1, Entry 12
2.00
0.74
0.72
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
ppm

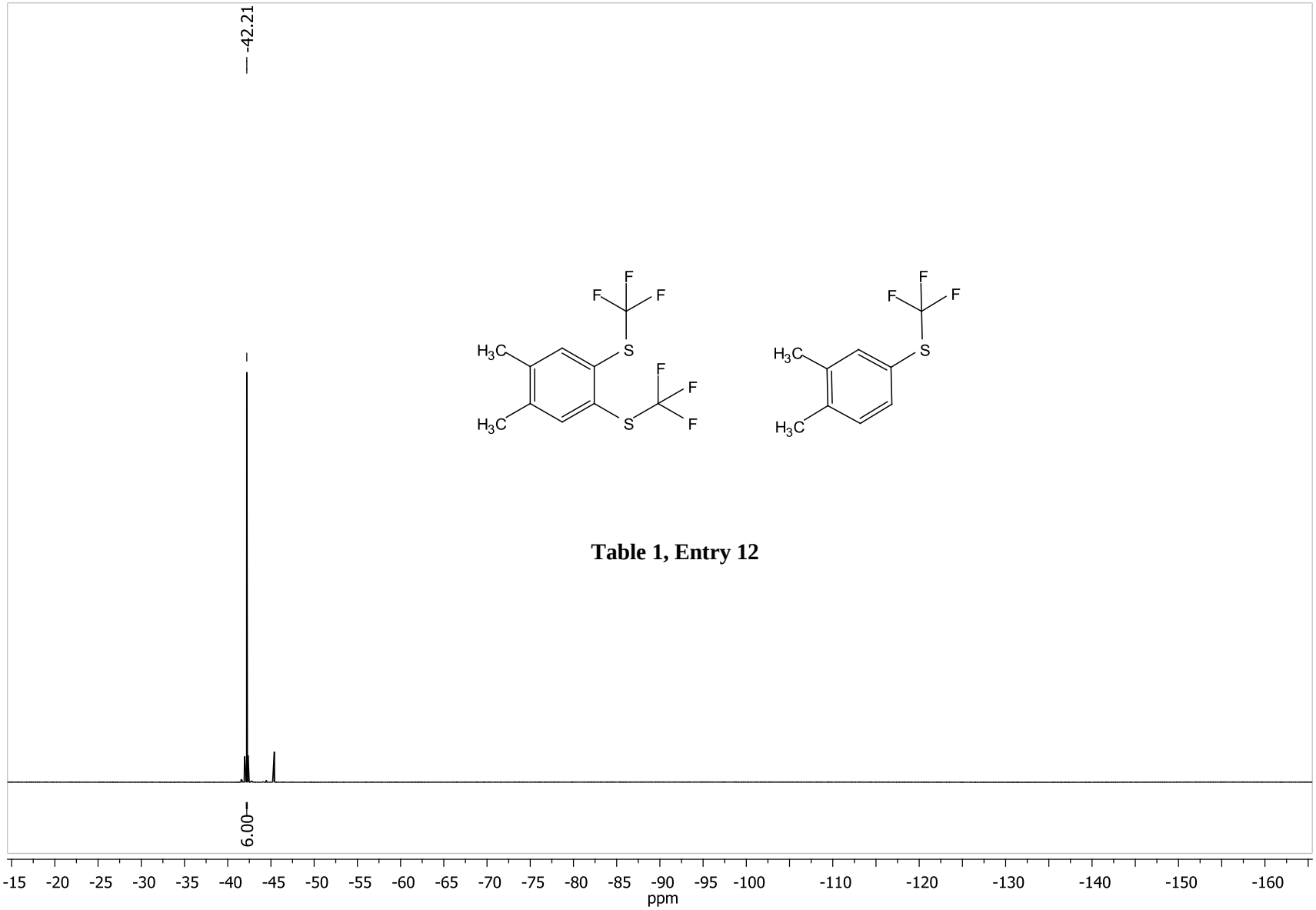


Table 1, Entry 12

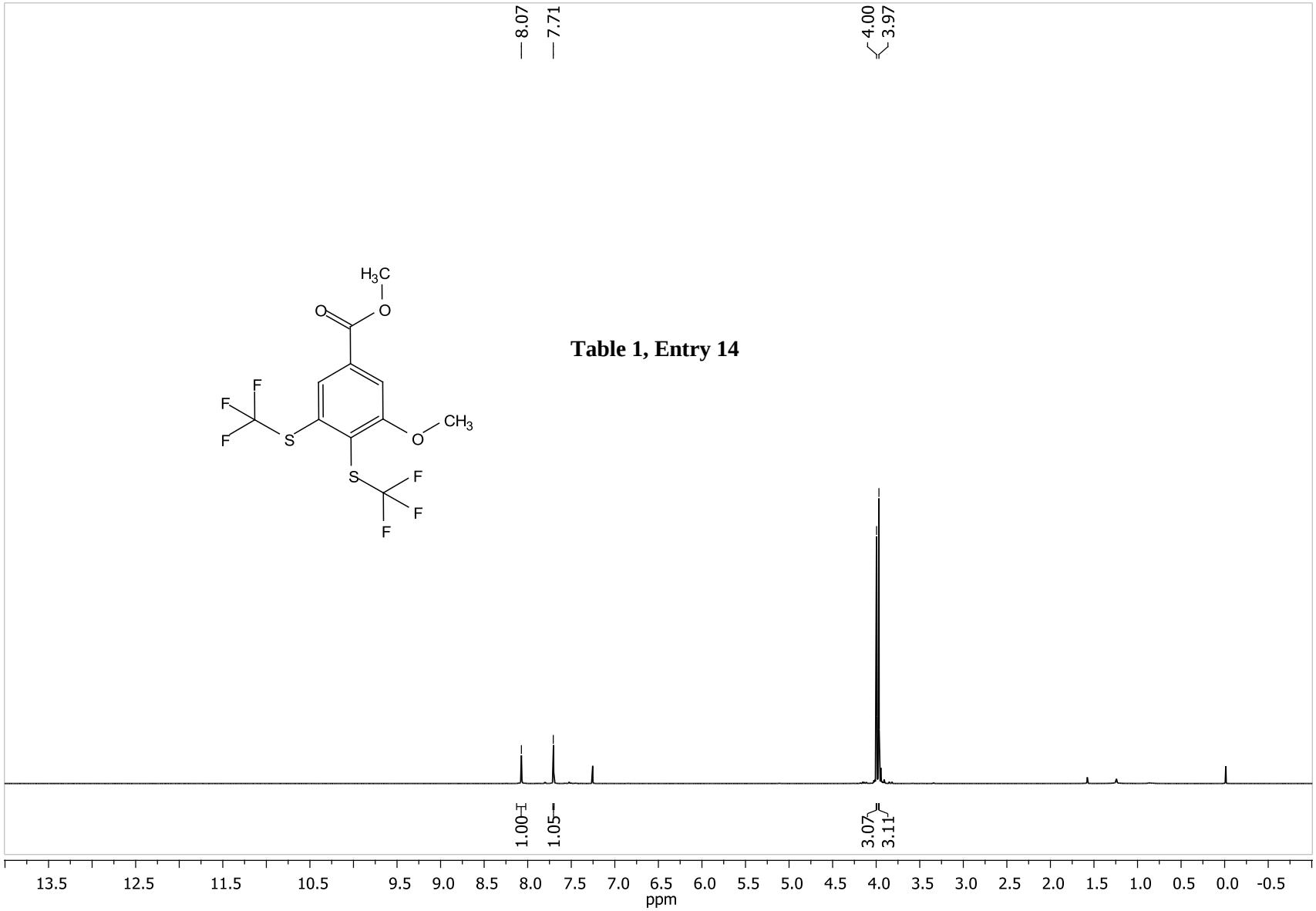
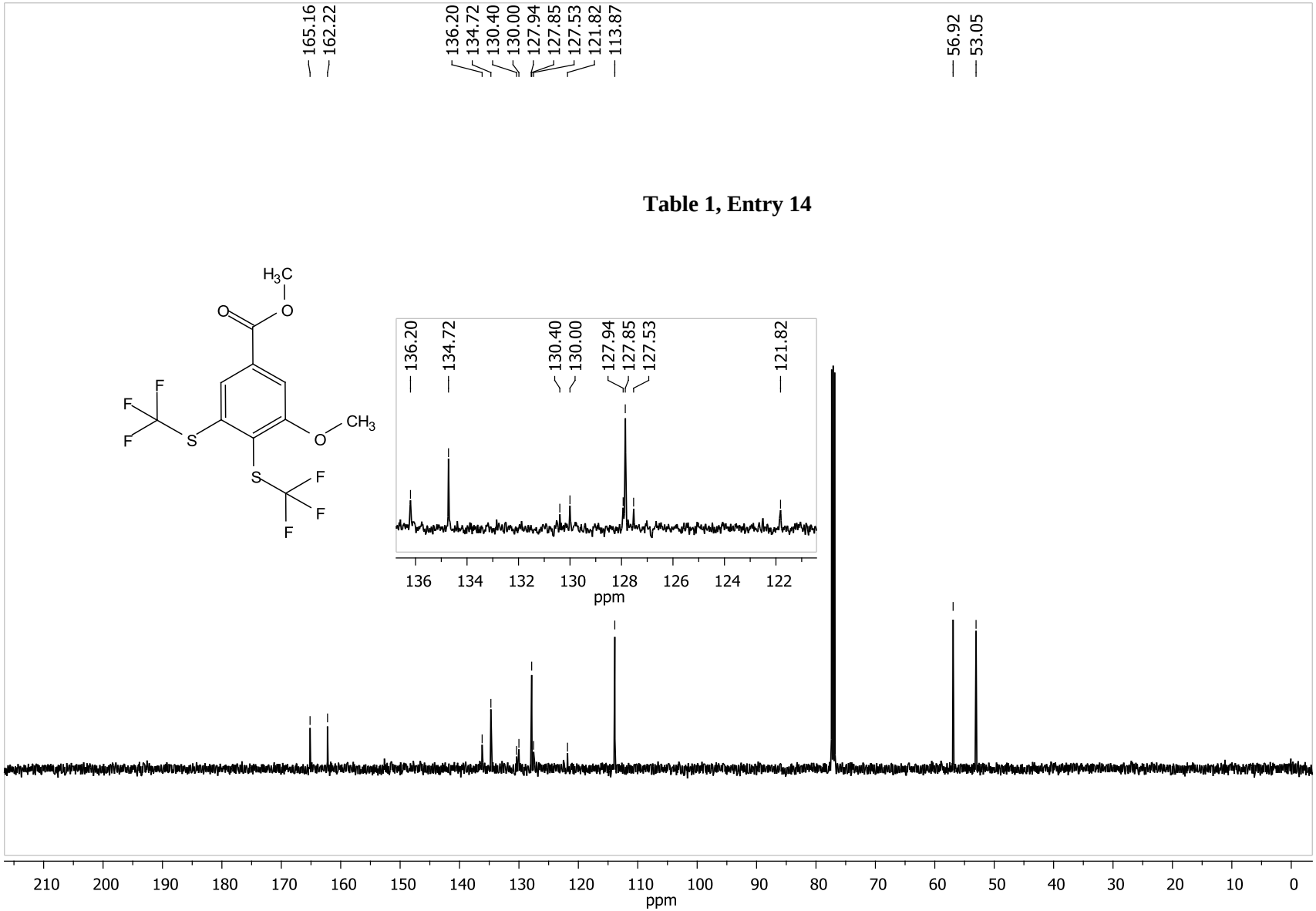


Table 1, Entry 14

Table 1, Entry 14



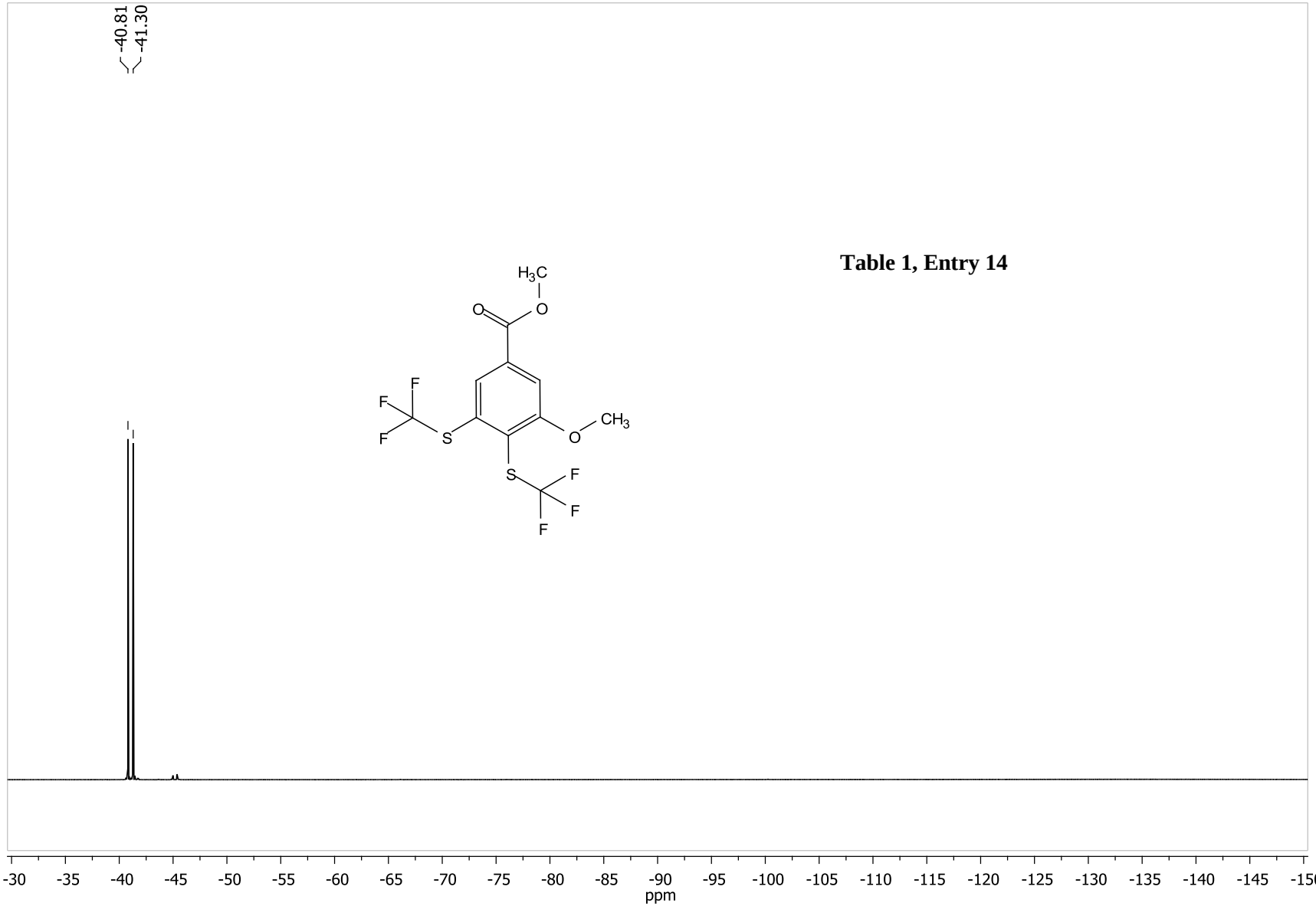
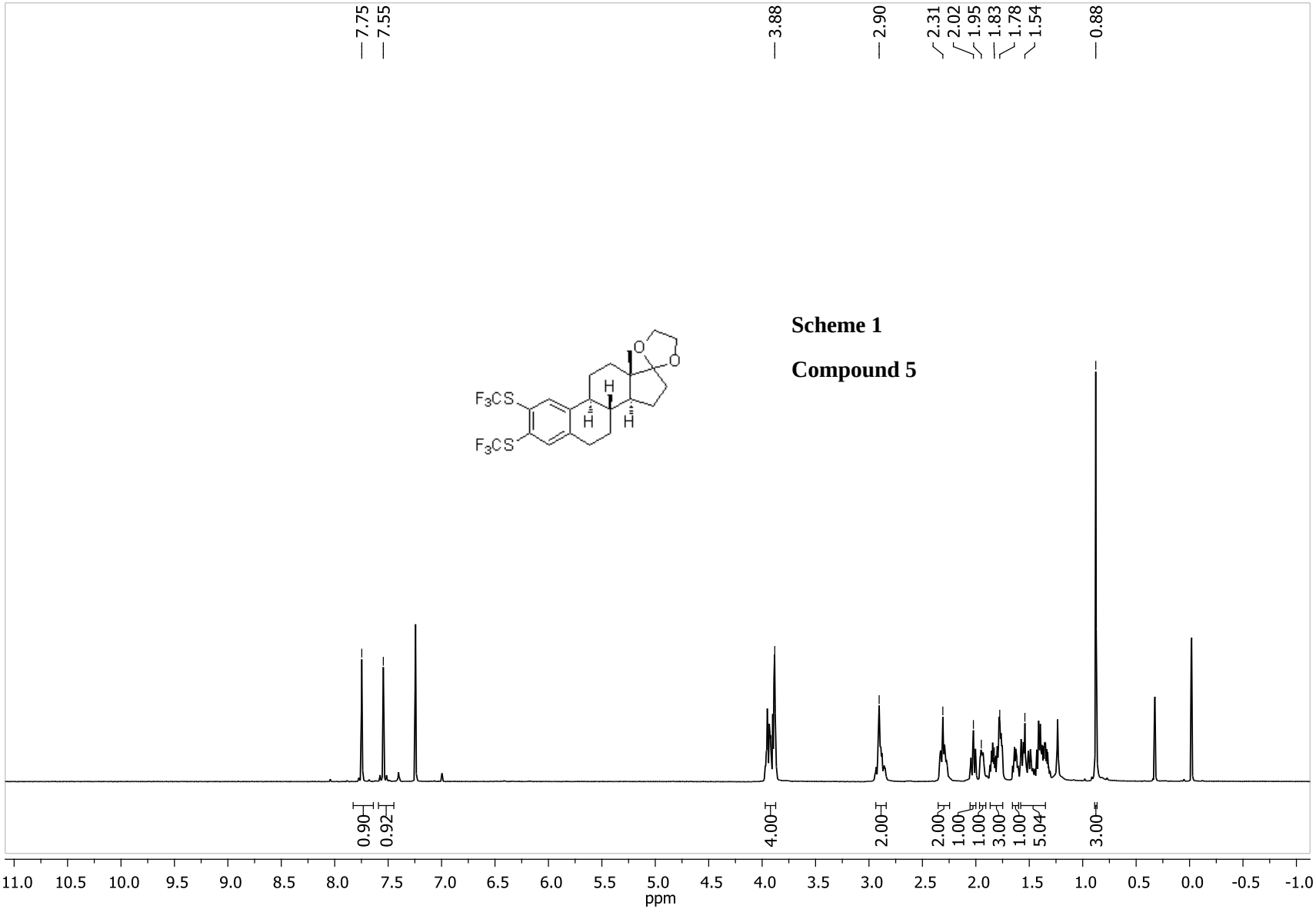
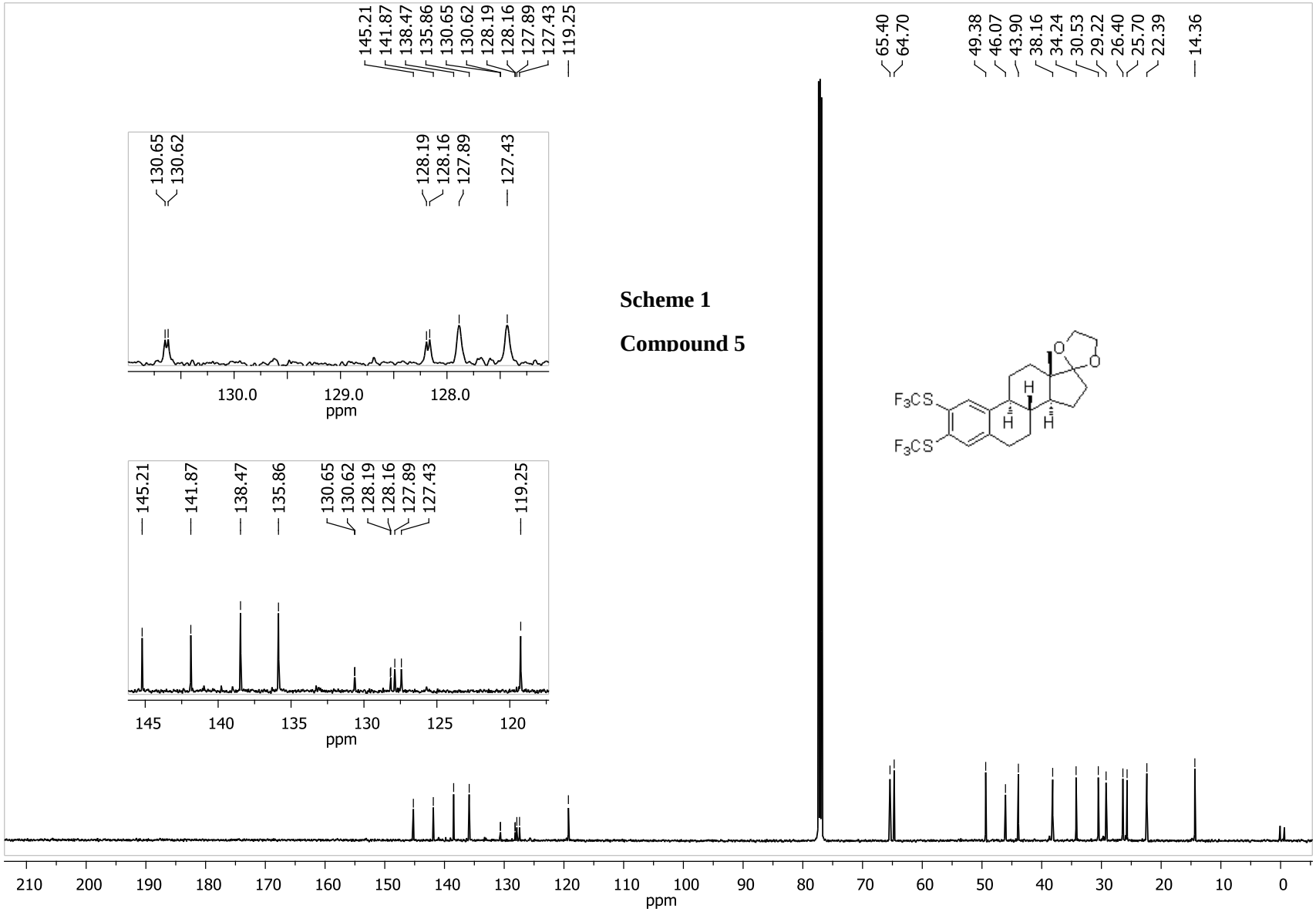
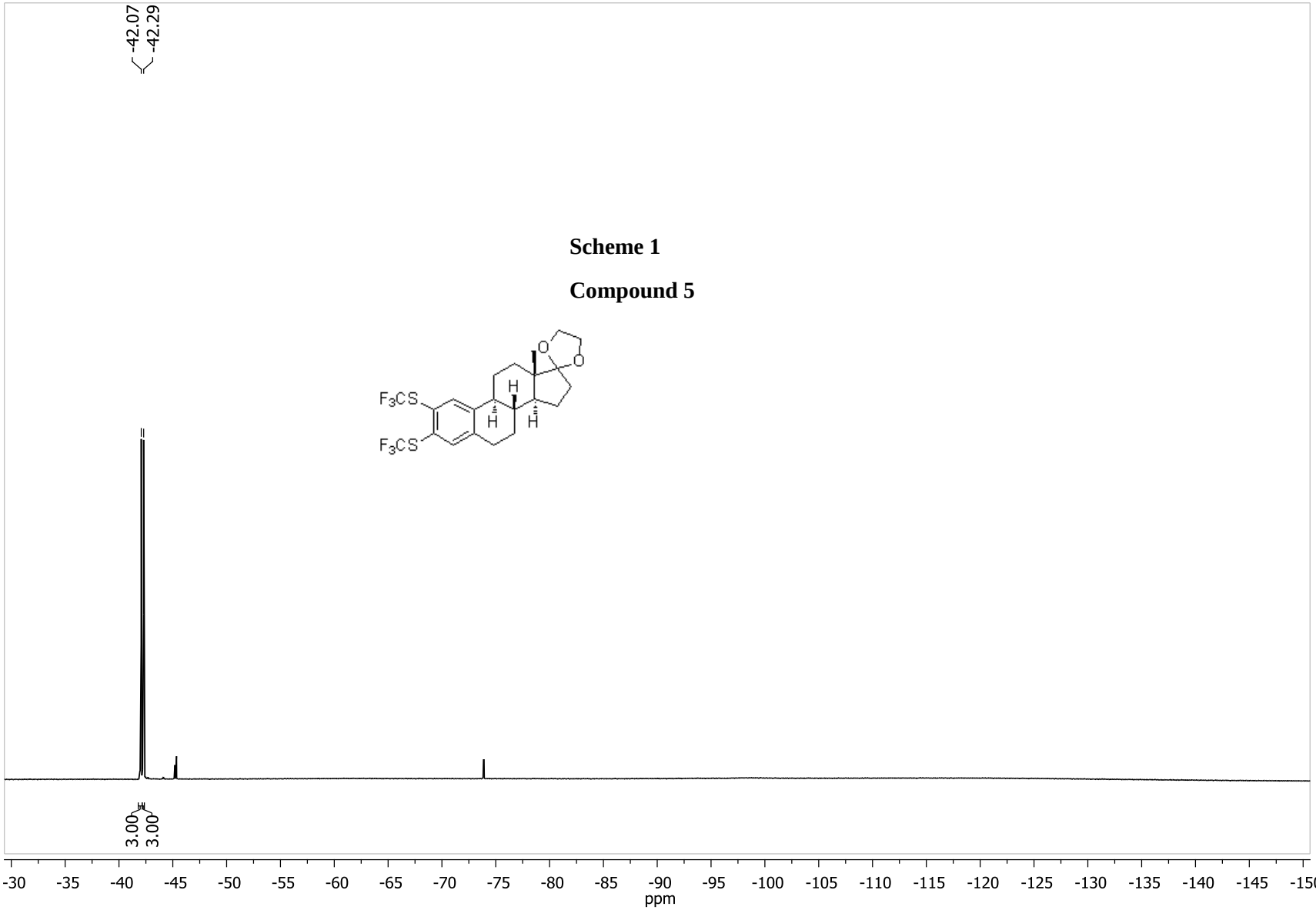


Table 1, Entry 14

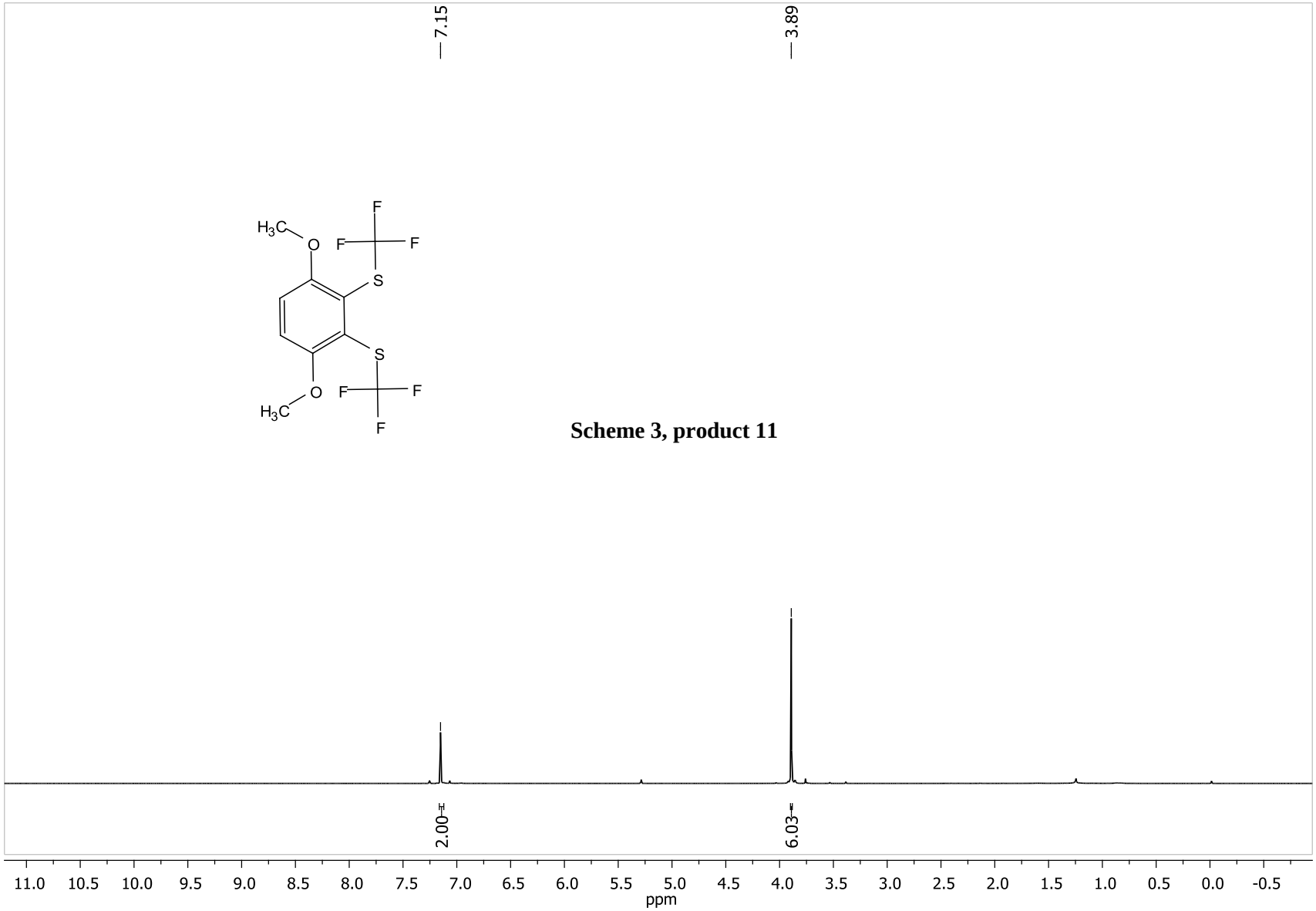

7.75
7.55
3.88
2.90
2.31
2.02
1.95
1.83
1.78
1.54
0.88
Scheme 1
Compound 5
F3CS
F3CS
O
O
H
H
H
0.90
0.92
4.00
2.00
2.00
1.00
1.00
3.00
1.00
5.04
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


145.21
141.87
138.47
135.86
130.65
130.62
128.19
128.16
127.89
127.43
119.25
65.40
64.70
49.38
46.07
43.90
38.16
34.24
30.53
29.22
26.40
25.70
22.39
14.36
130.0
129.0
128.0
ppm
145
140
135
130
125
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scheme 1
Compound 5
F3CS
F3CS
O
O
H
H
H

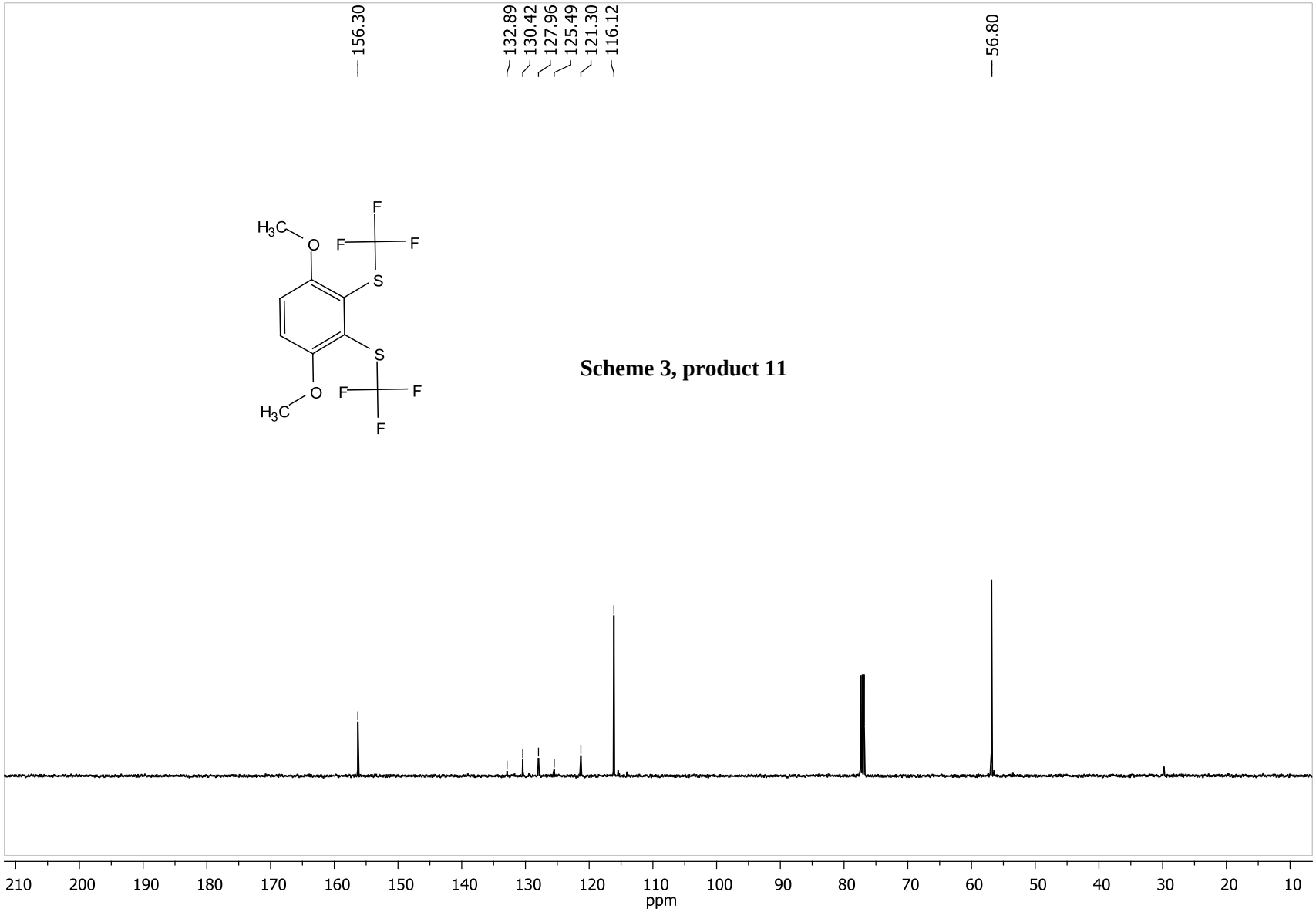


Scheme 1

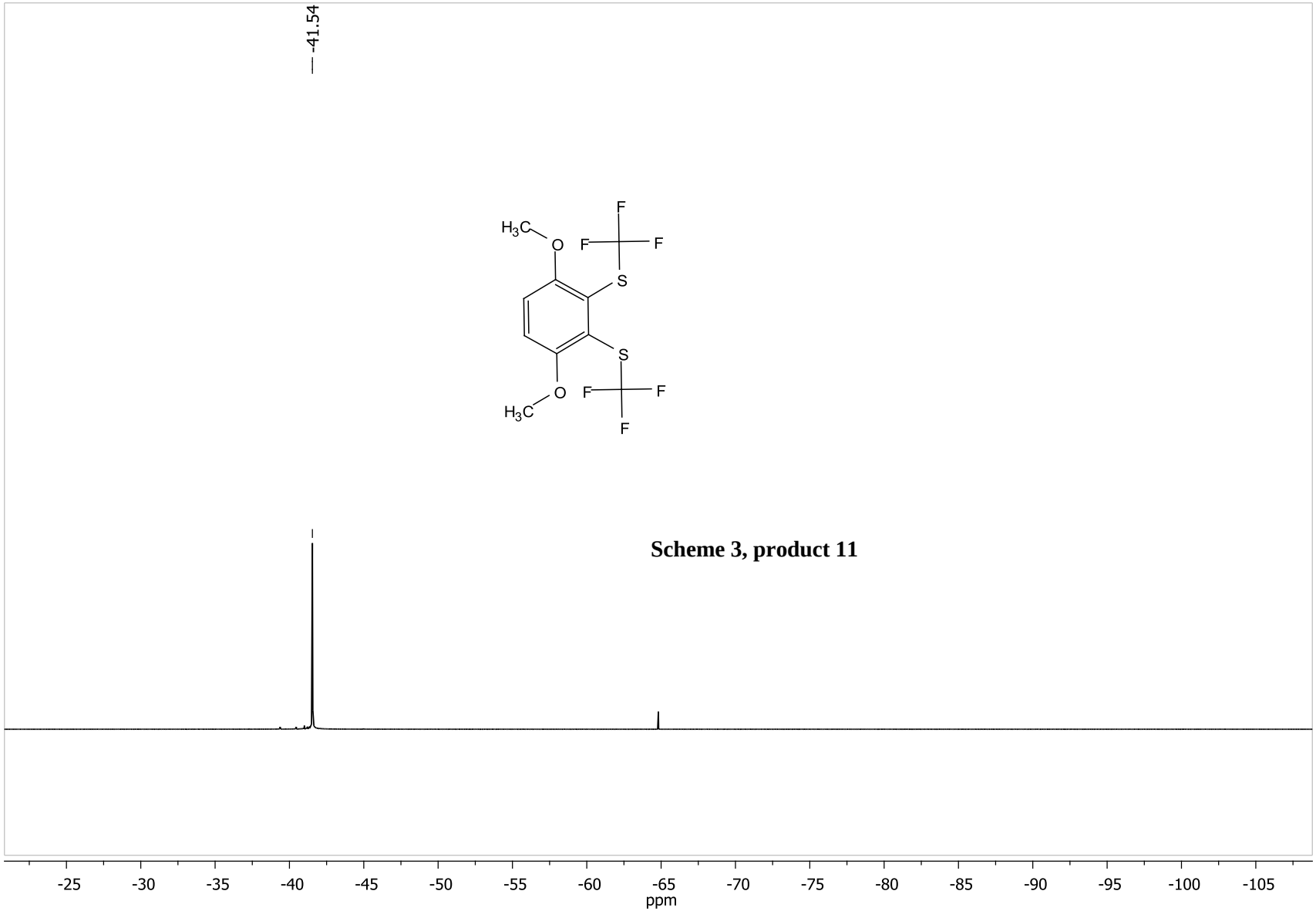
Compound 5



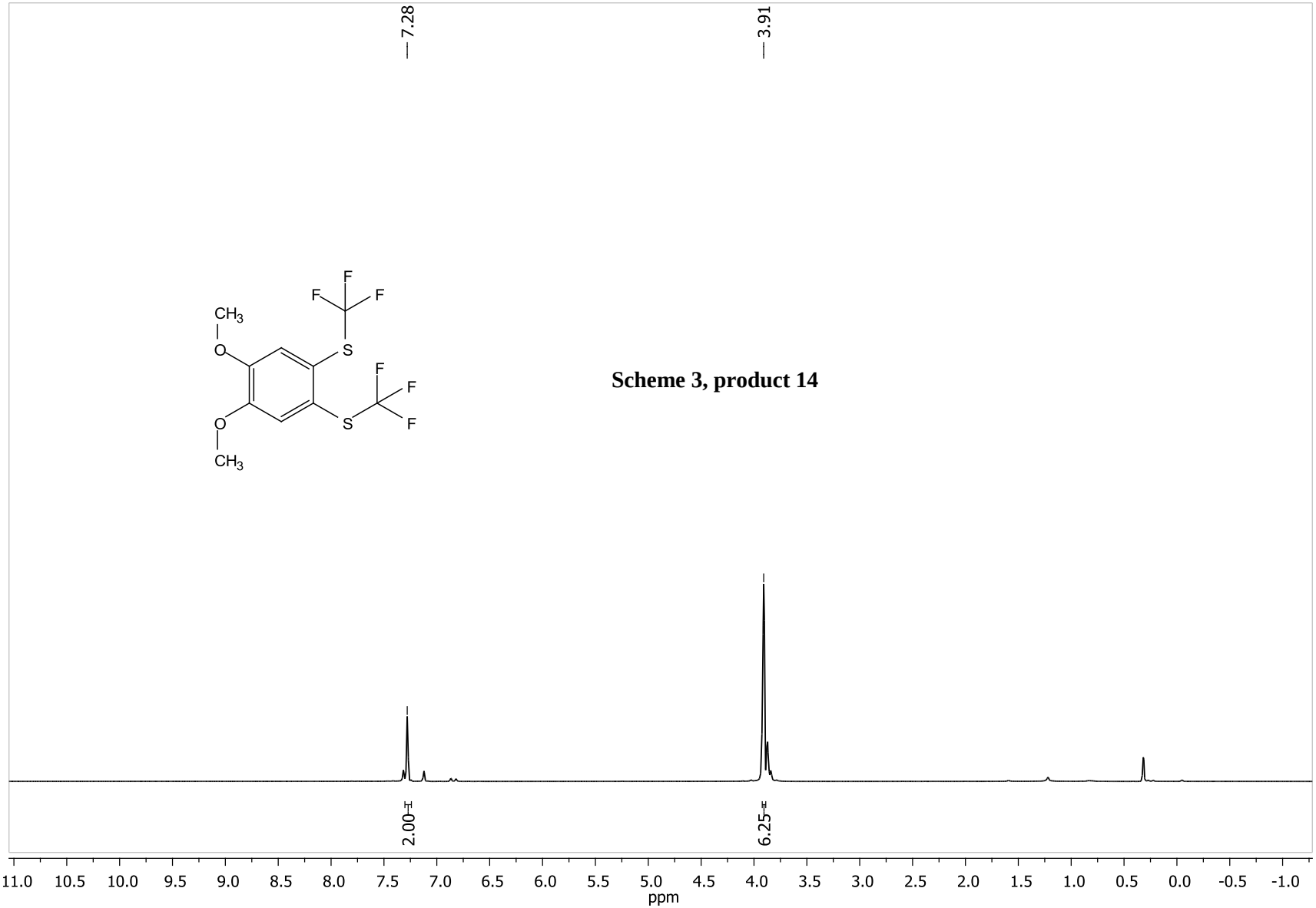
Scheme 3, product 11



Scheme 3, product 11

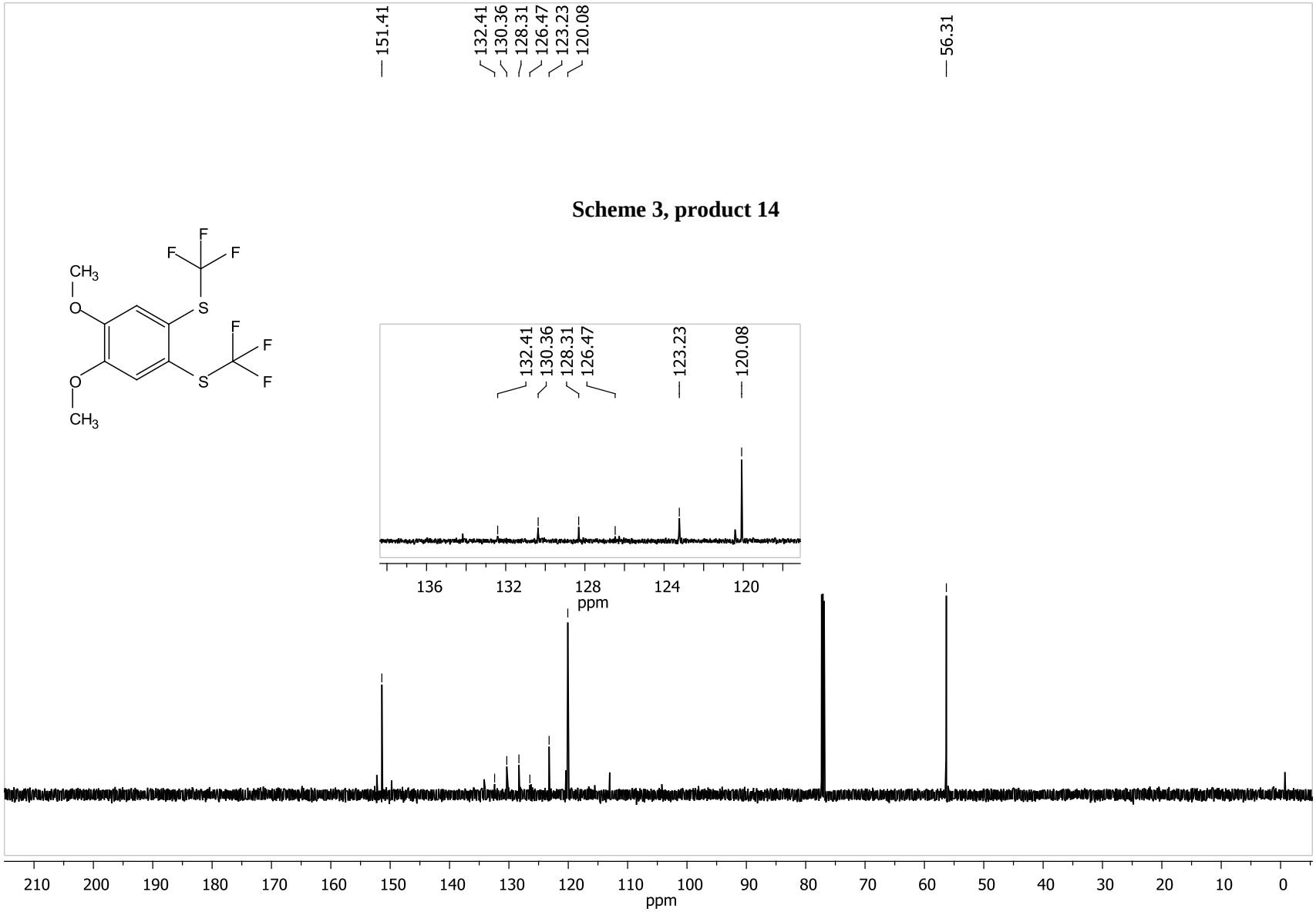


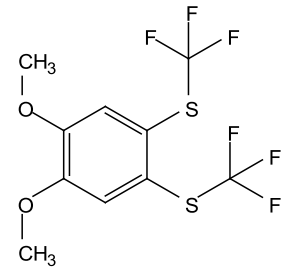
Scheme 3, product 11



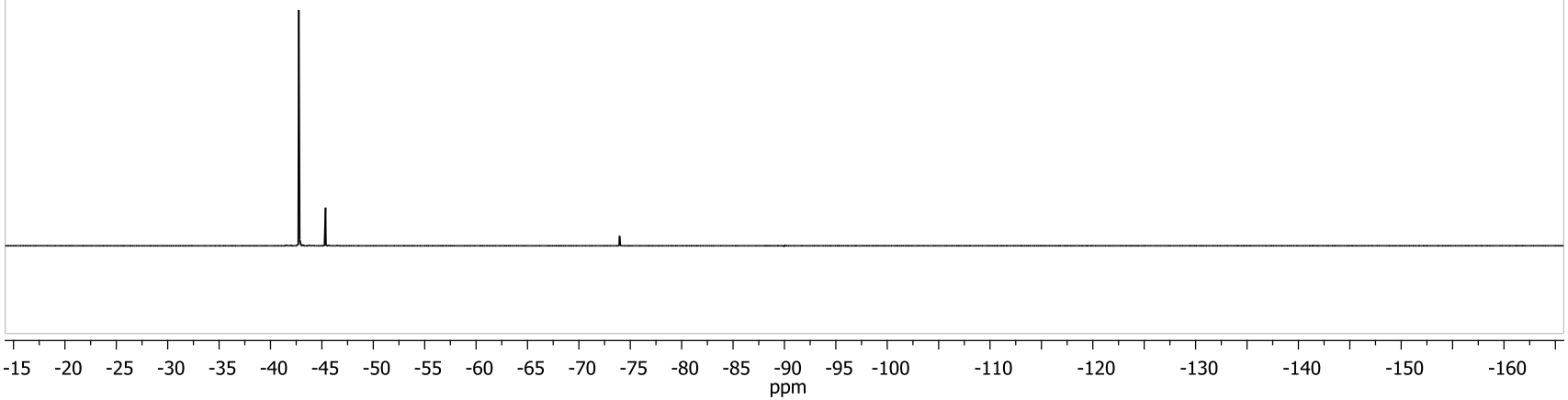
Scheme 3, product 14

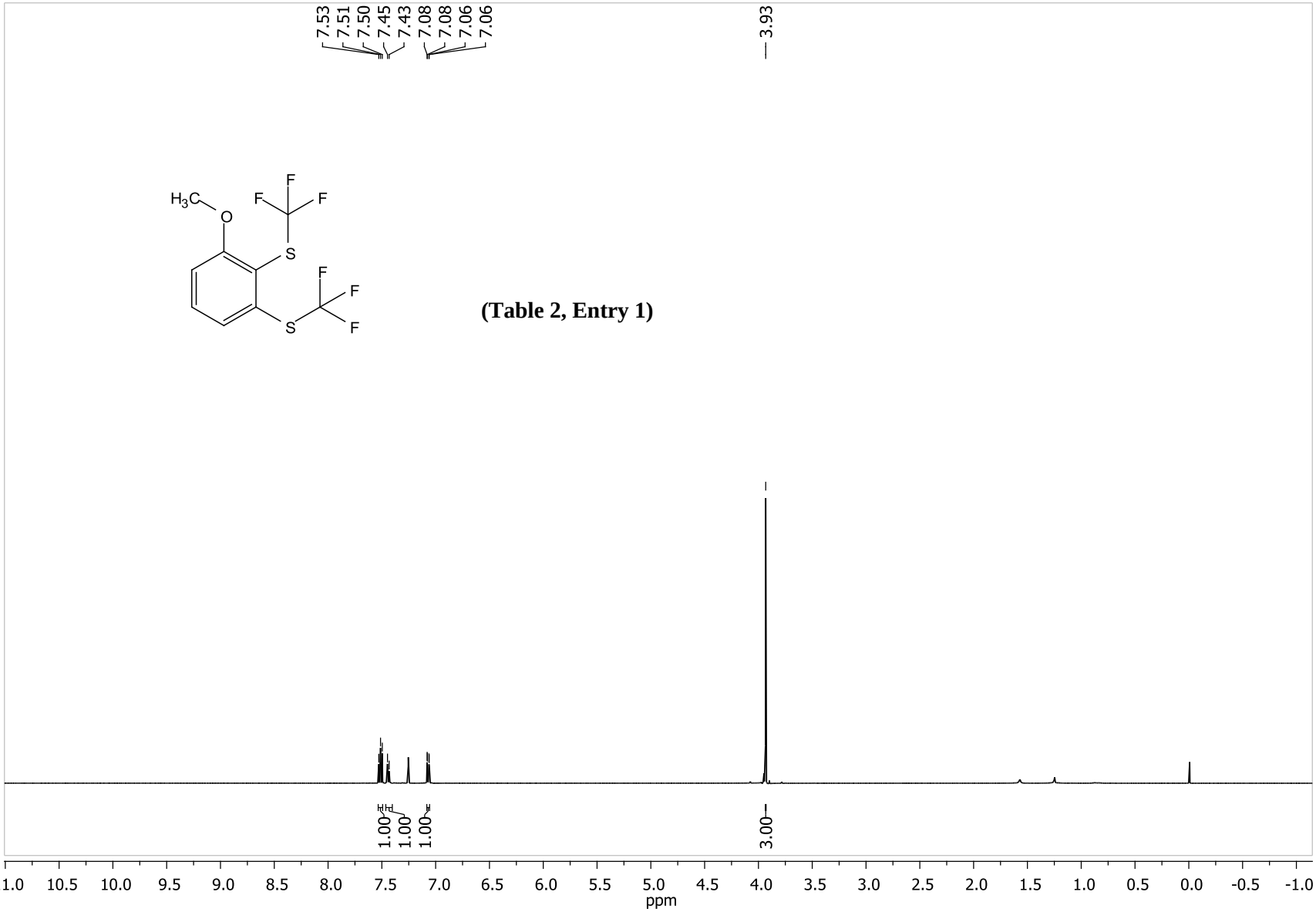
Scheme 3, product 14

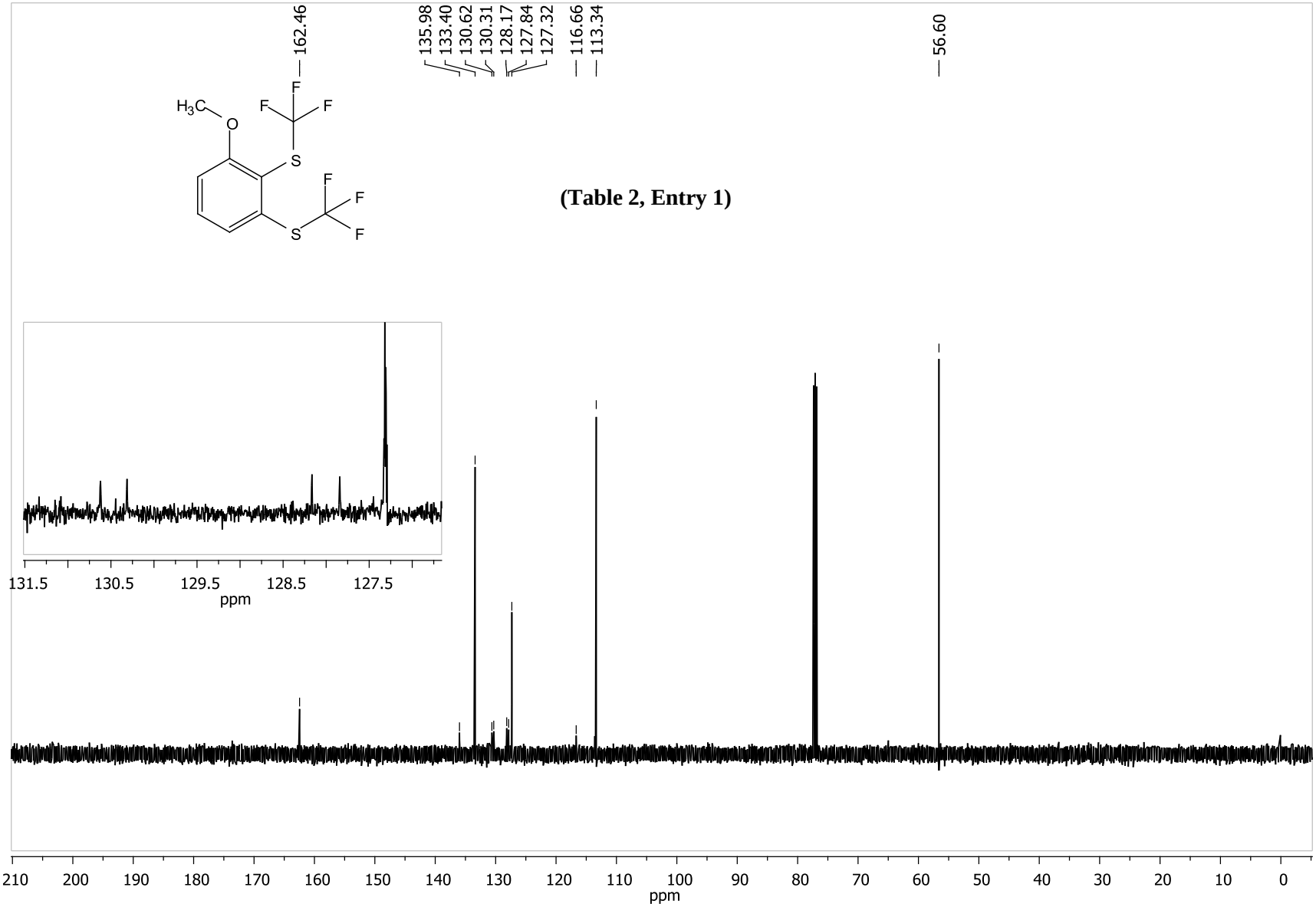


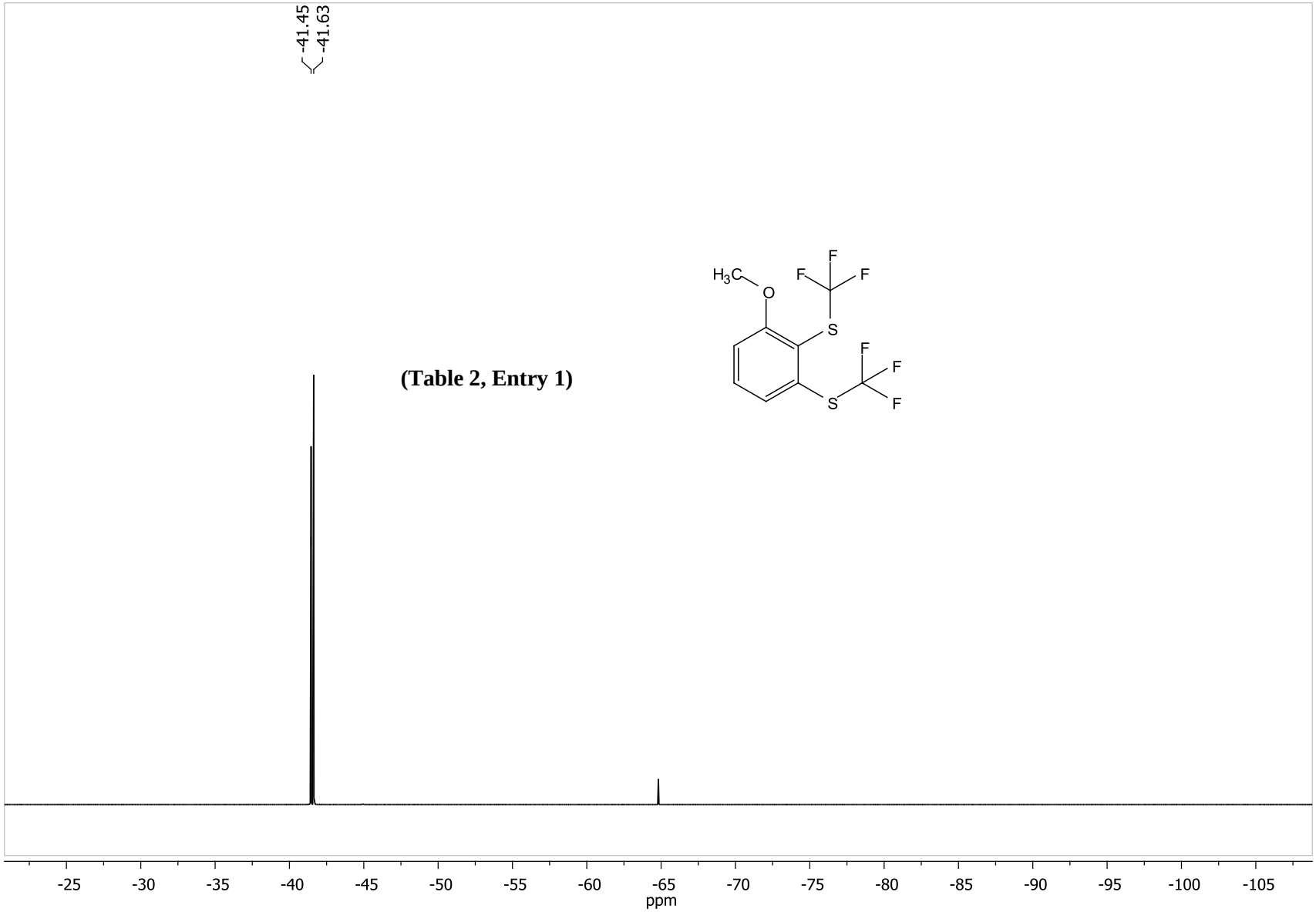


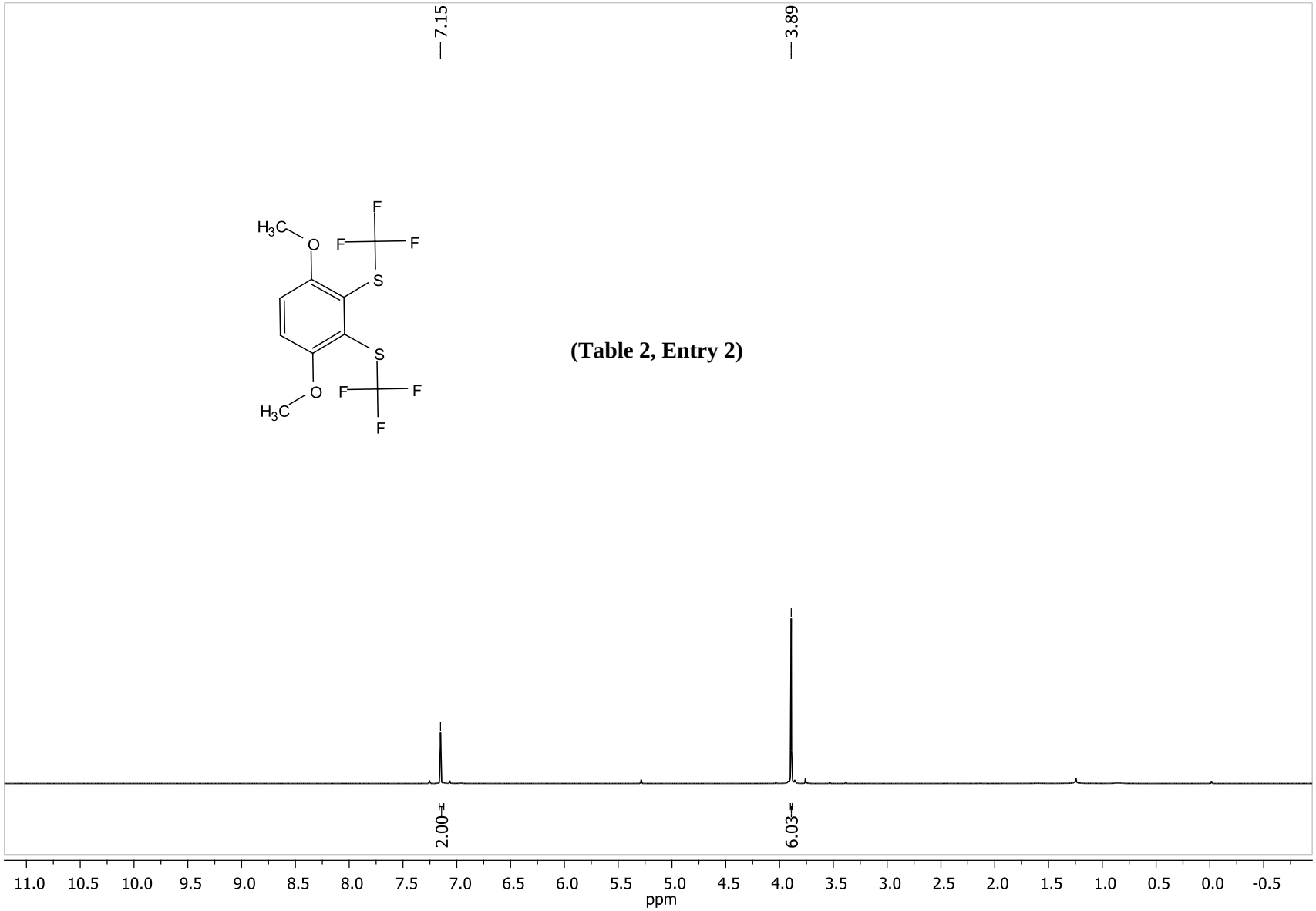
Scheme 3, product 14



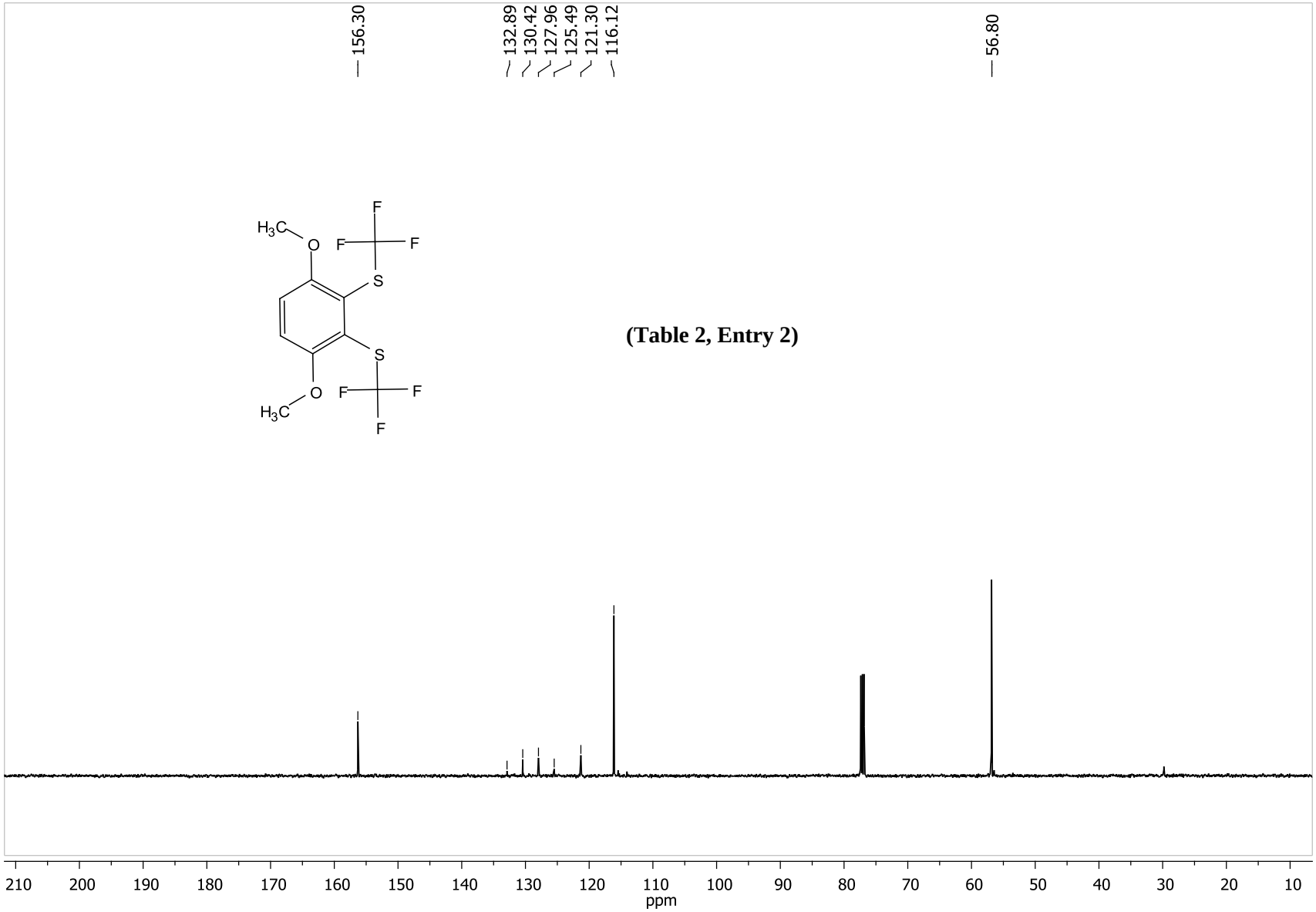

7.53
7.51
7.50
7.45
7.43
7.08
7.08
7.06
7.06
3.93
H3C
O
F
F
F
S
F
F
F
S
(Table 2, Entry 1)
1.00
1.00
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

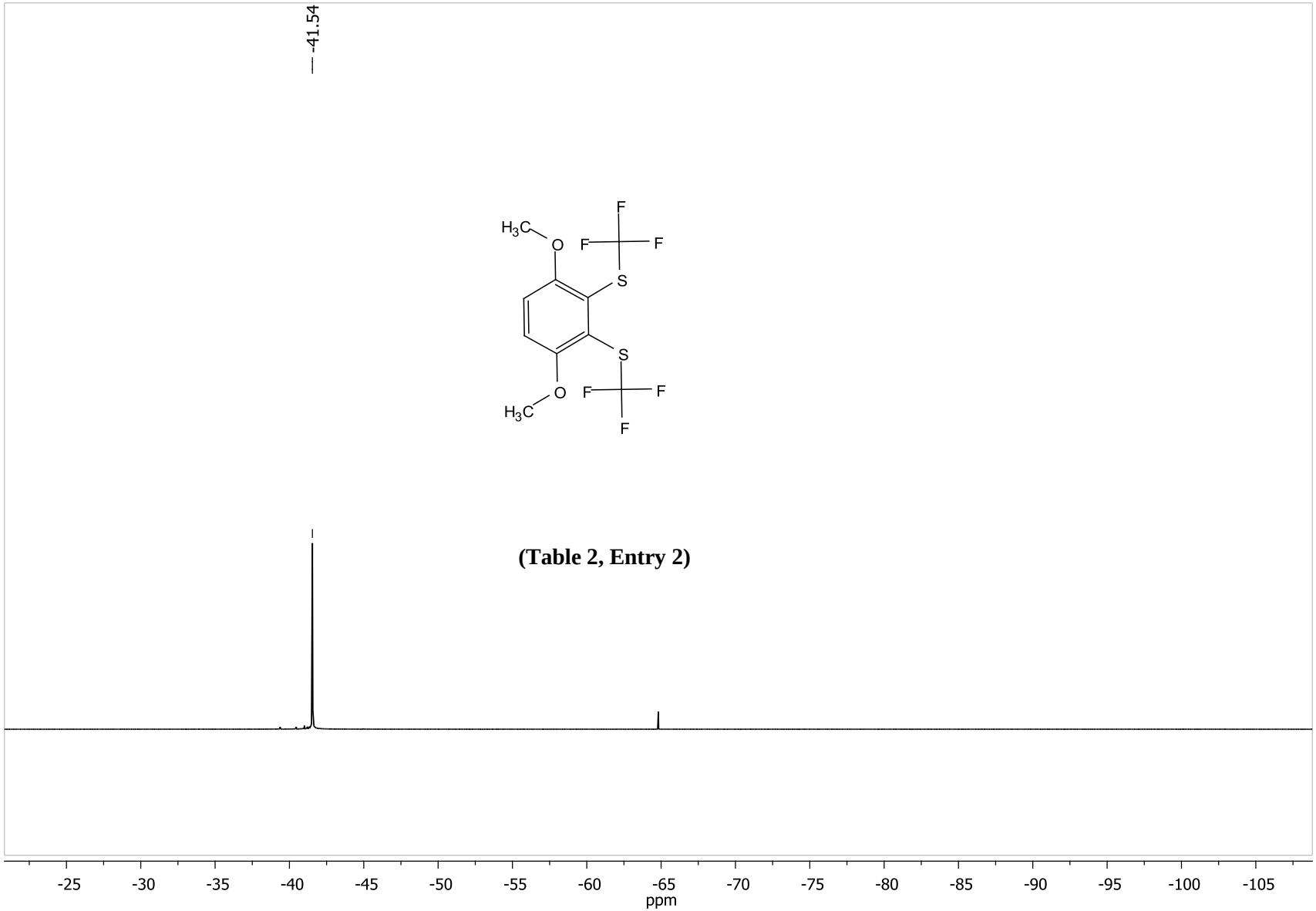

162.46
135.98
133.40
130.62
130.31
128.17
127.84
127.32
116.66
113.34
56.60
H3C
O
F
F
F
S
F
F
S
F
(Table 2, Entry 1)
131.5
130.5
129.5
128.5
127.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-41.45
-41.63
(Table 2, Entry 1)
H3C
O
F
F
F
S
F
F
F
S
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
ppm

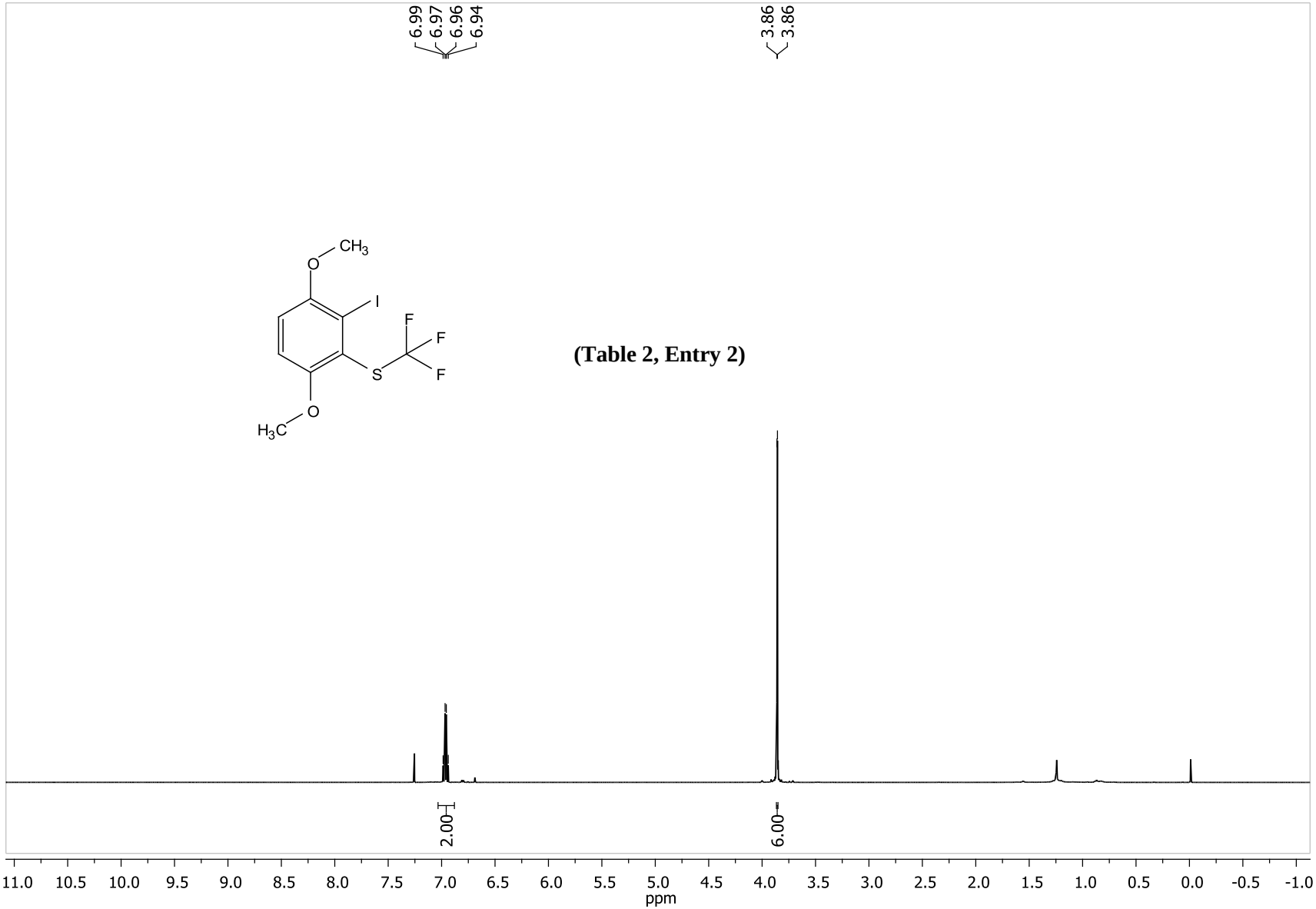


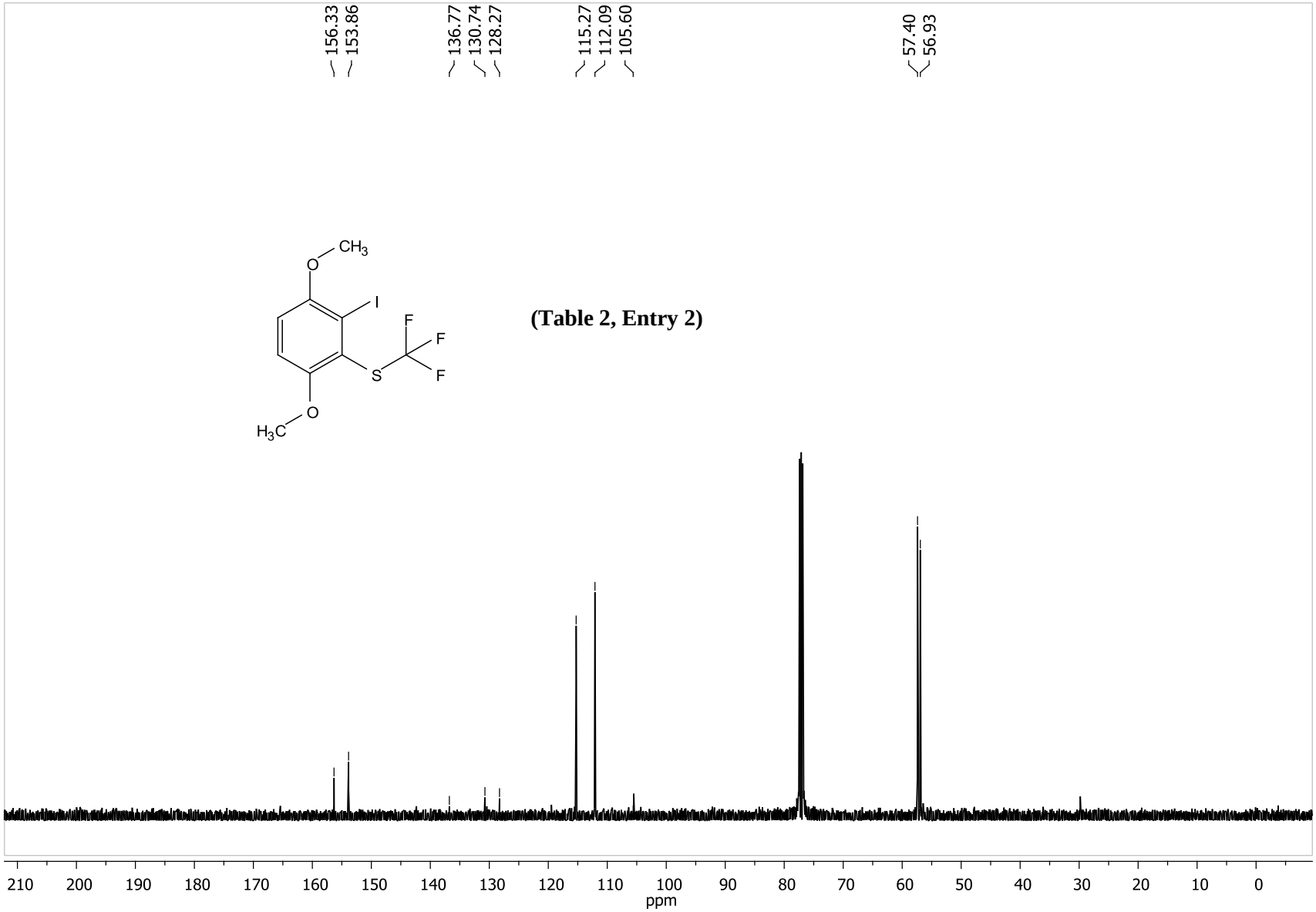
(Table 2, Entry 2)

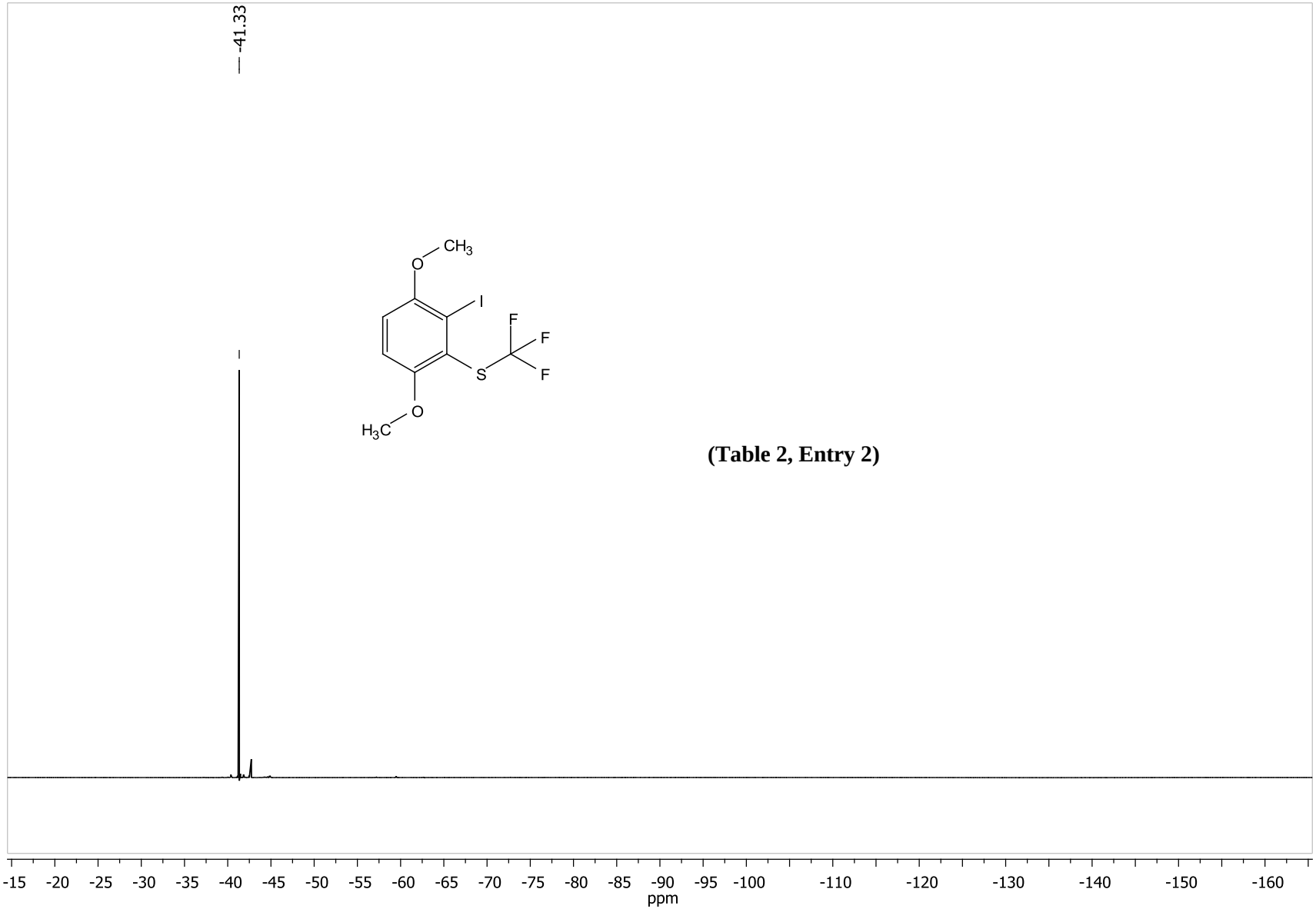

156.30
132.89
130.42
127.96
125.49
121.30
116.12
56.80
H3C
O
F
F
F
S
S
O
F
F
F
H3C
(Table 2, Entry 2)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



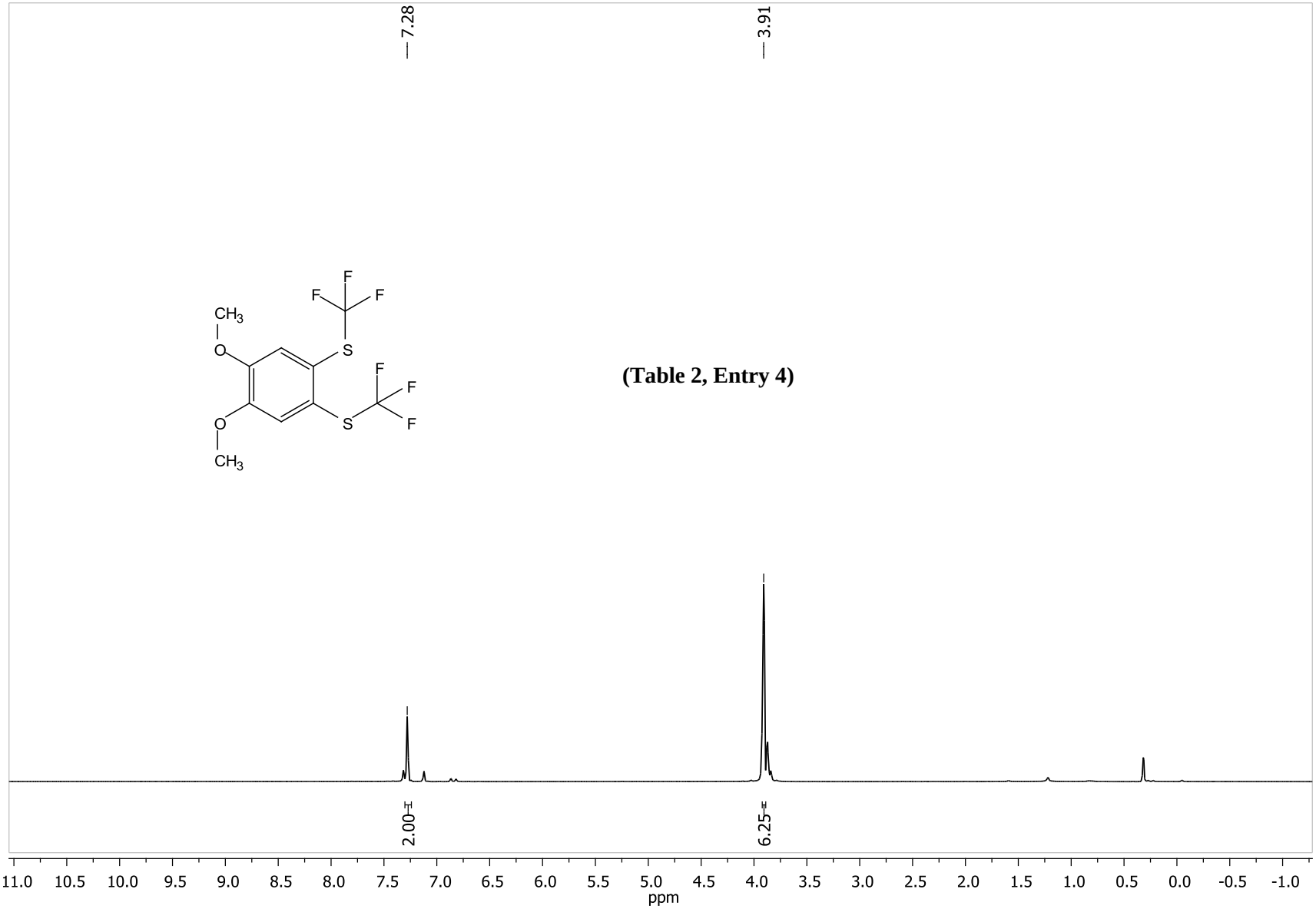
(Table 2, Entry 2)

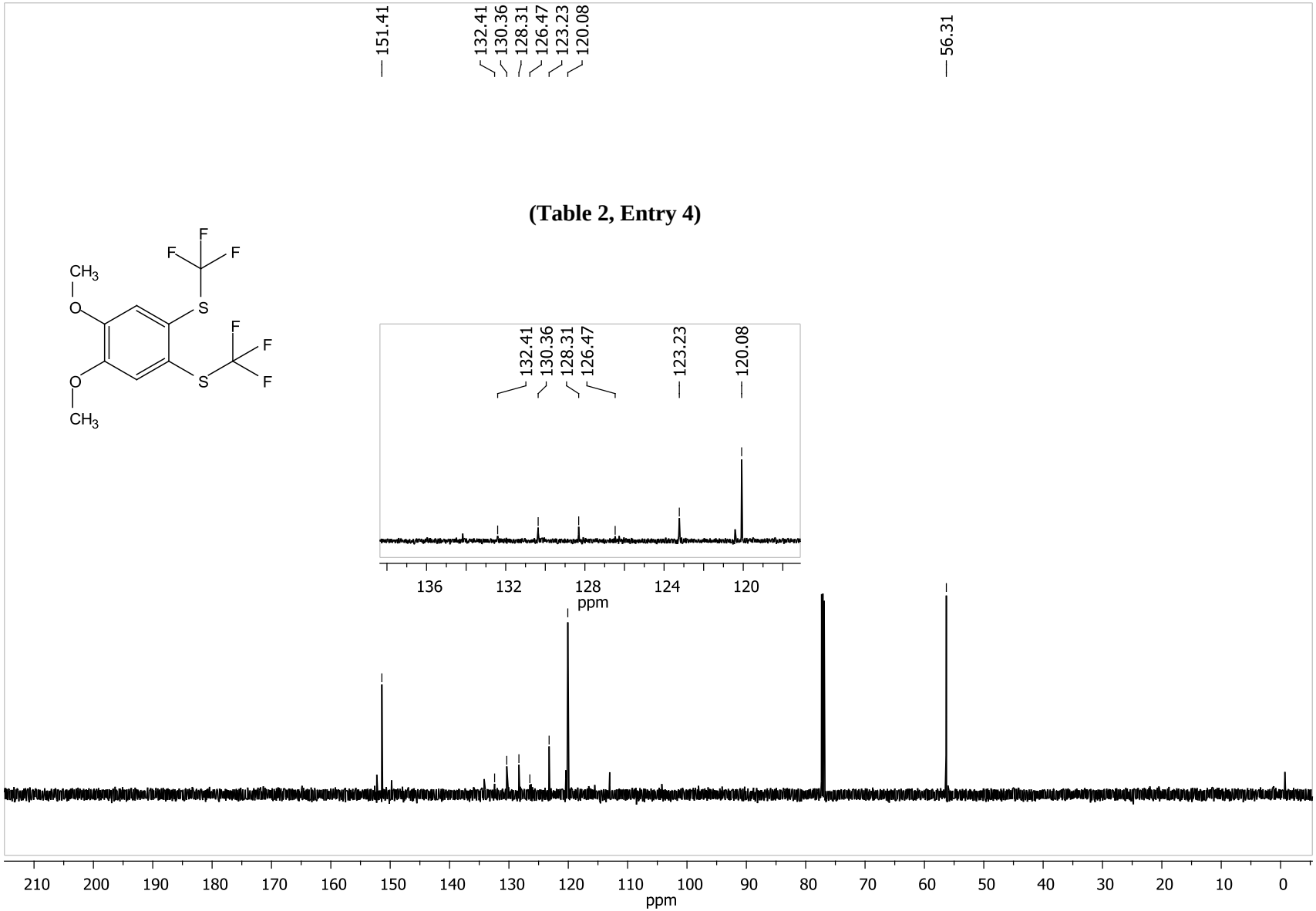

6.99
6.97
6.96
6.94
3.86
3.86
CH3
O
I
F
F
F
S
O
H3C
(Table 2, Entry 2)
2.00
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


156.33
153.86
136.77
130.74
128.27
115.27
112.09
105.60
57.40
56.93
CH3
O
I
F
F
F
S
O
H3C
(Table 2, Entry 2)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

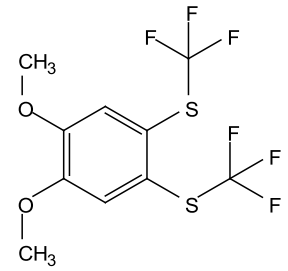


(Table 2, Entry 2)

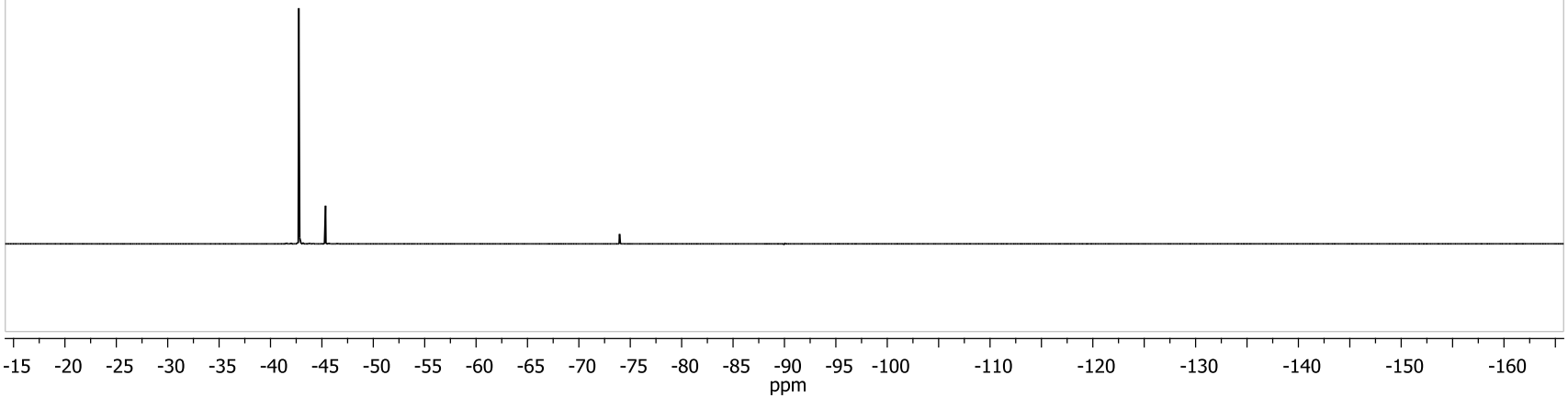

7.28
3.91
F
F
F
CH3
O
S
F
F
F
S
O
CH3
(Table 2, Entry 4)
2.00
6.25
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

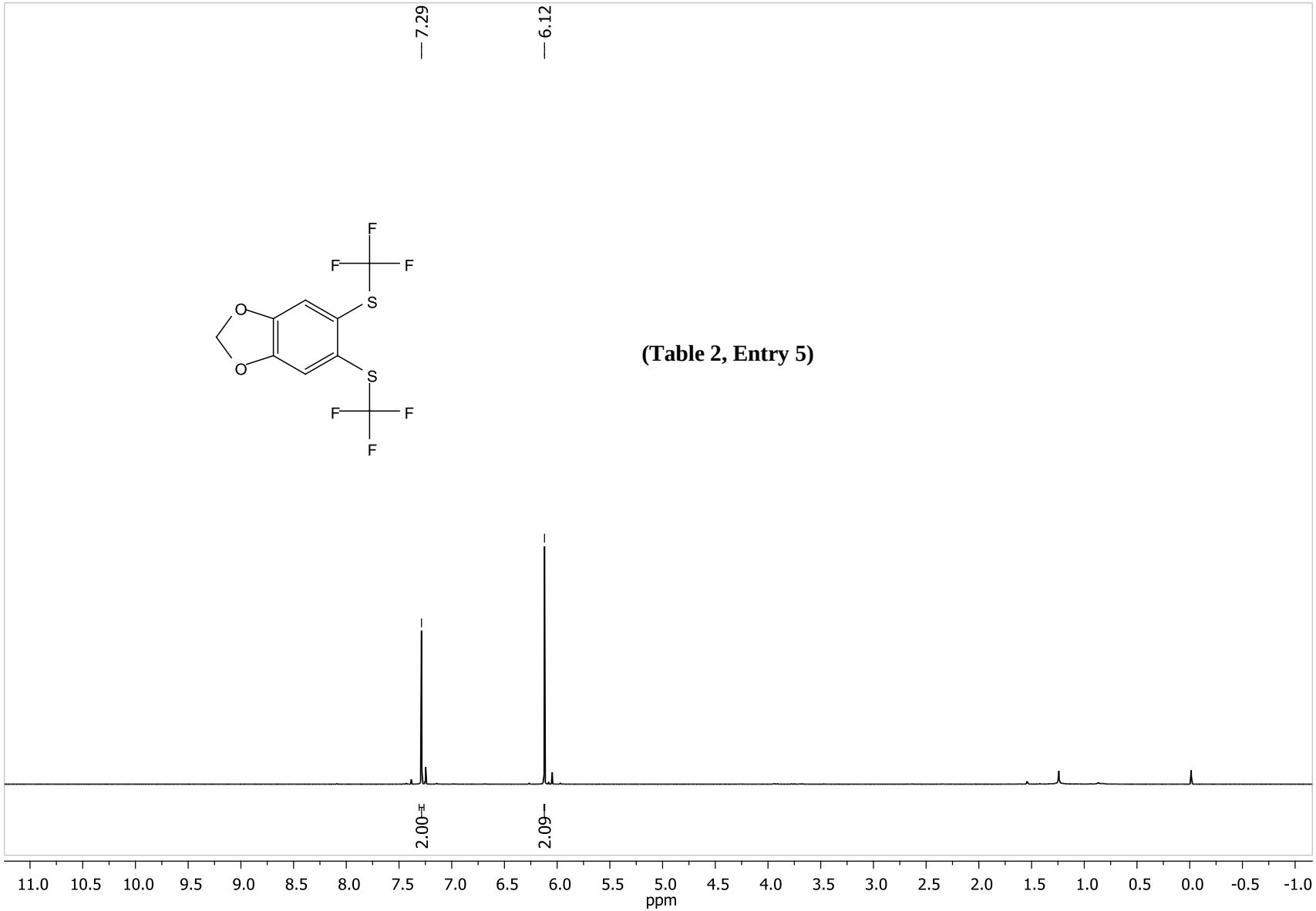


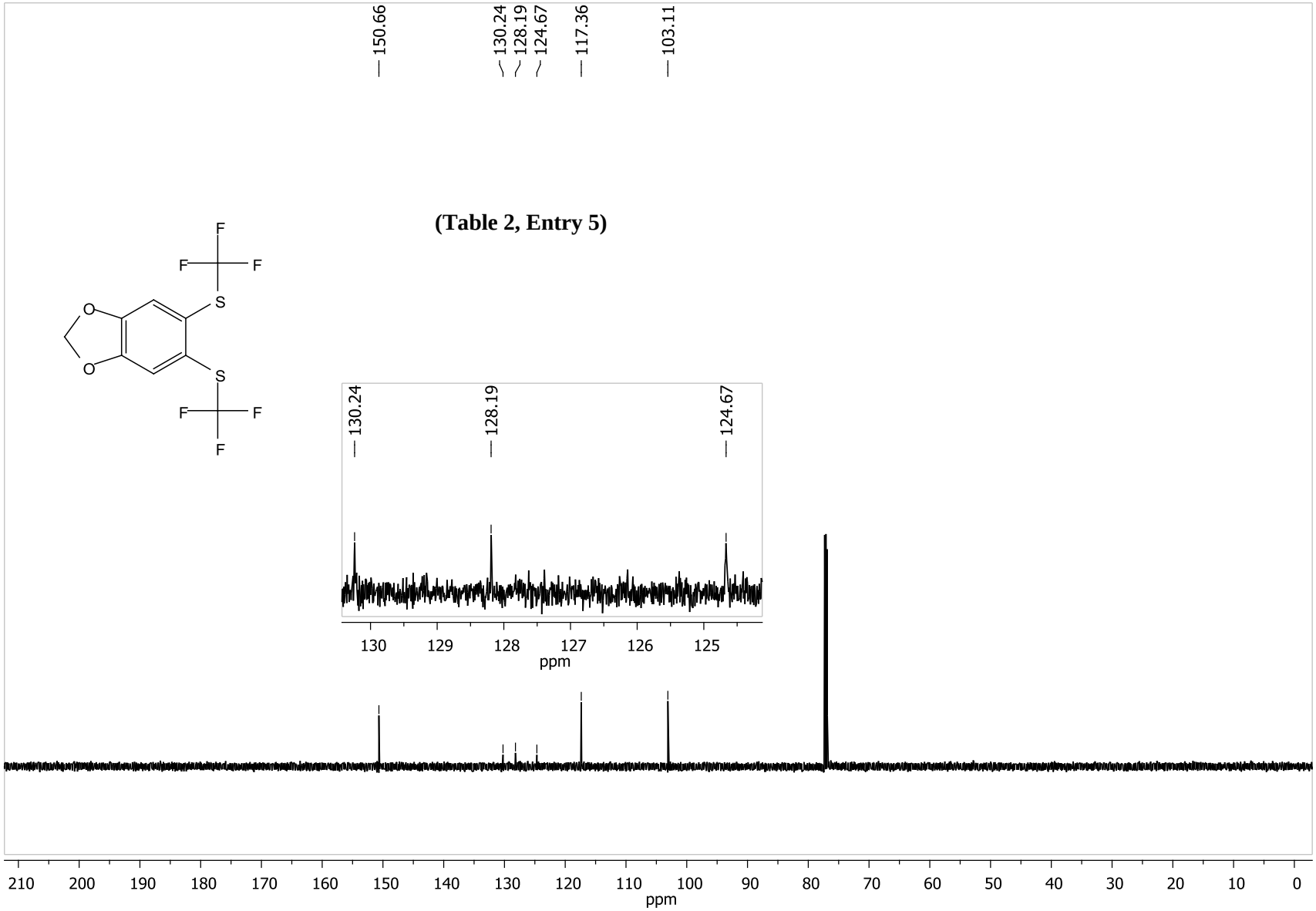
(Table 2, Entry 4)

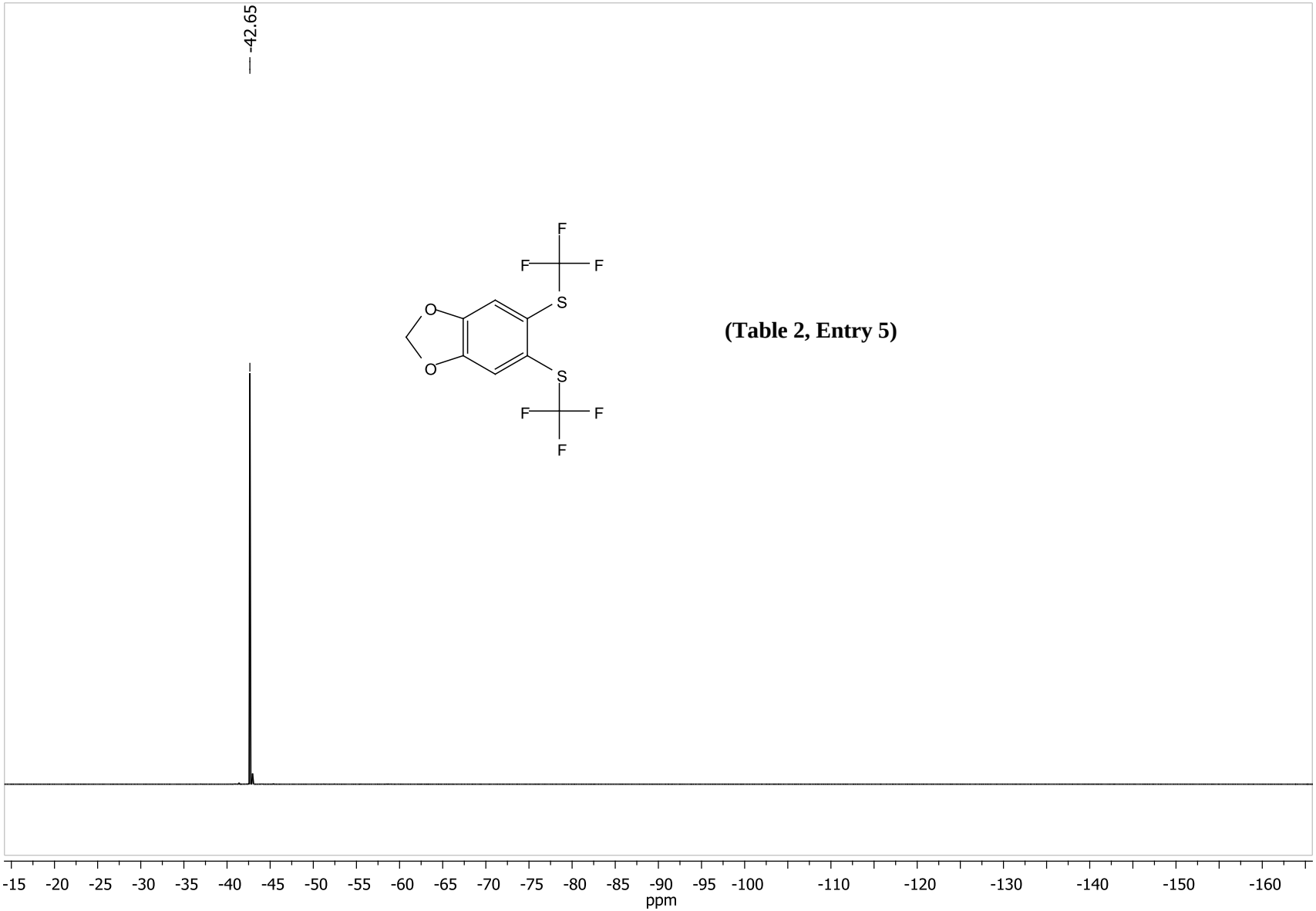


(Table 2, Entry 4)

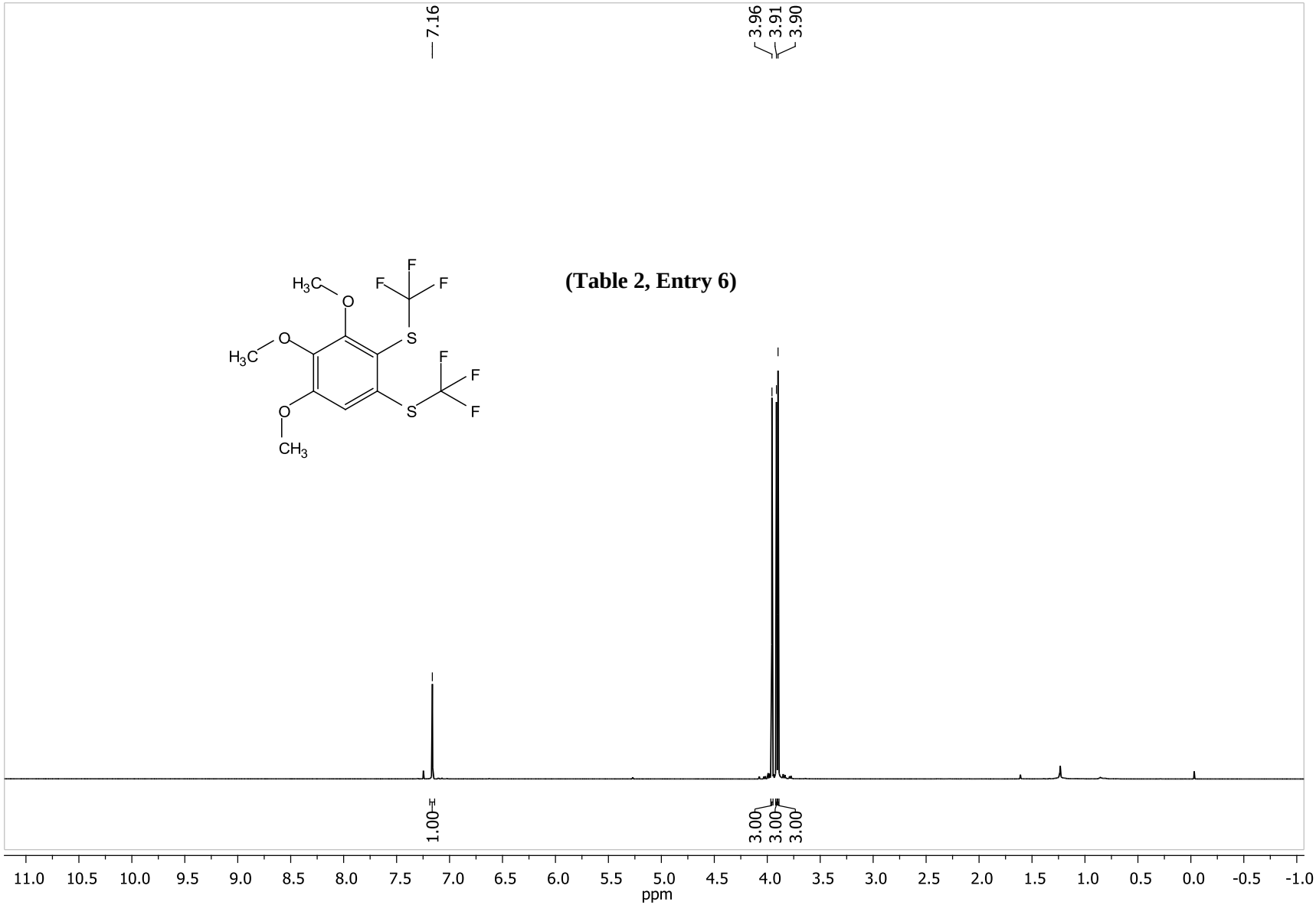


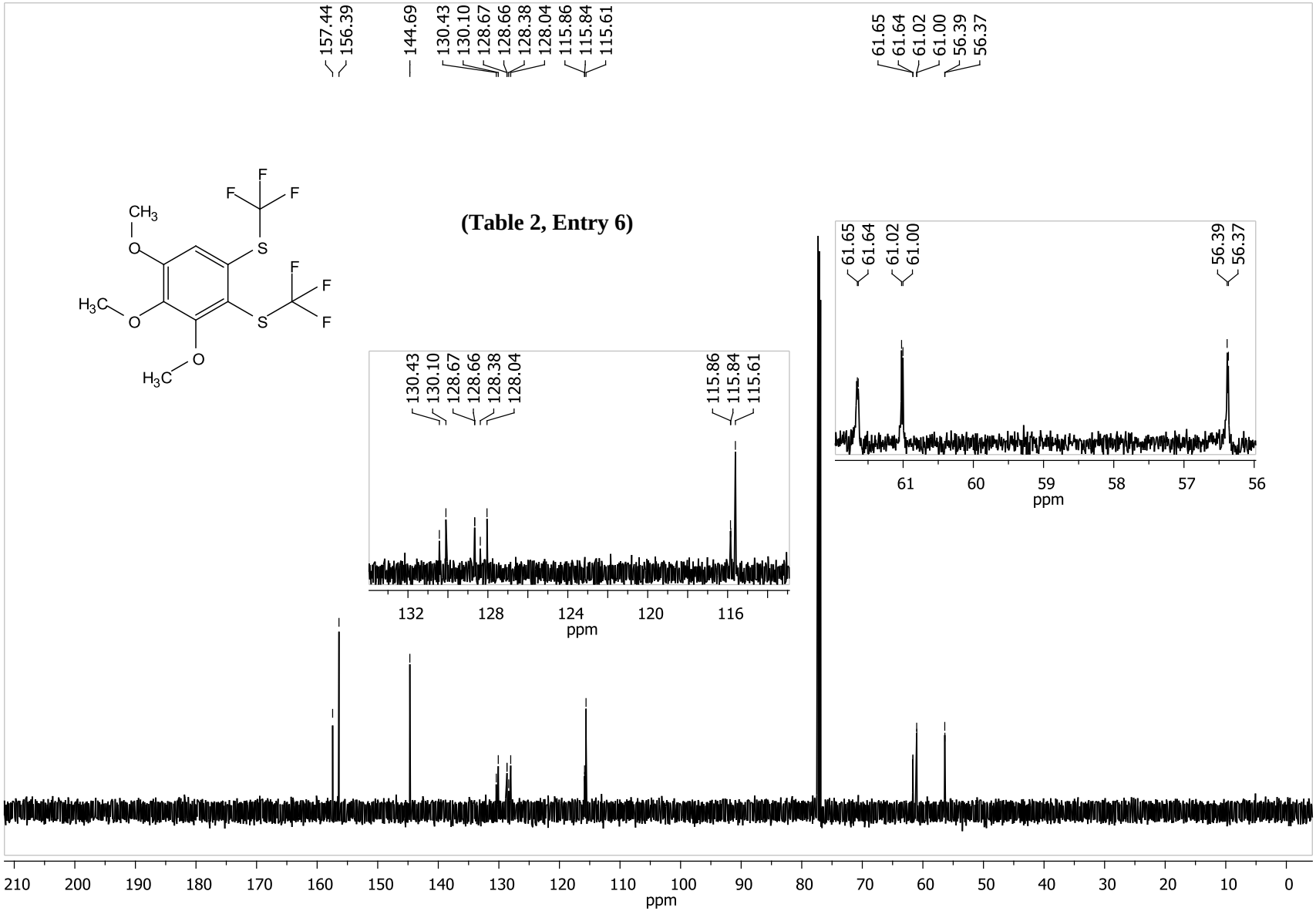

7.29
6.12
F
F
F
S
O
O
S
F
F
F
(Table 2, Entry 5)
2.00
2.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


150.66
130.24
128.19
124.67
117.36
103.11
(Table 2, Entry 5)
F
F
F
S
O
O
S
F
F
F
130.24
128.19
124.67
130
129
128
127
126
125
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

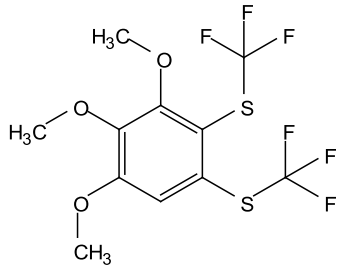


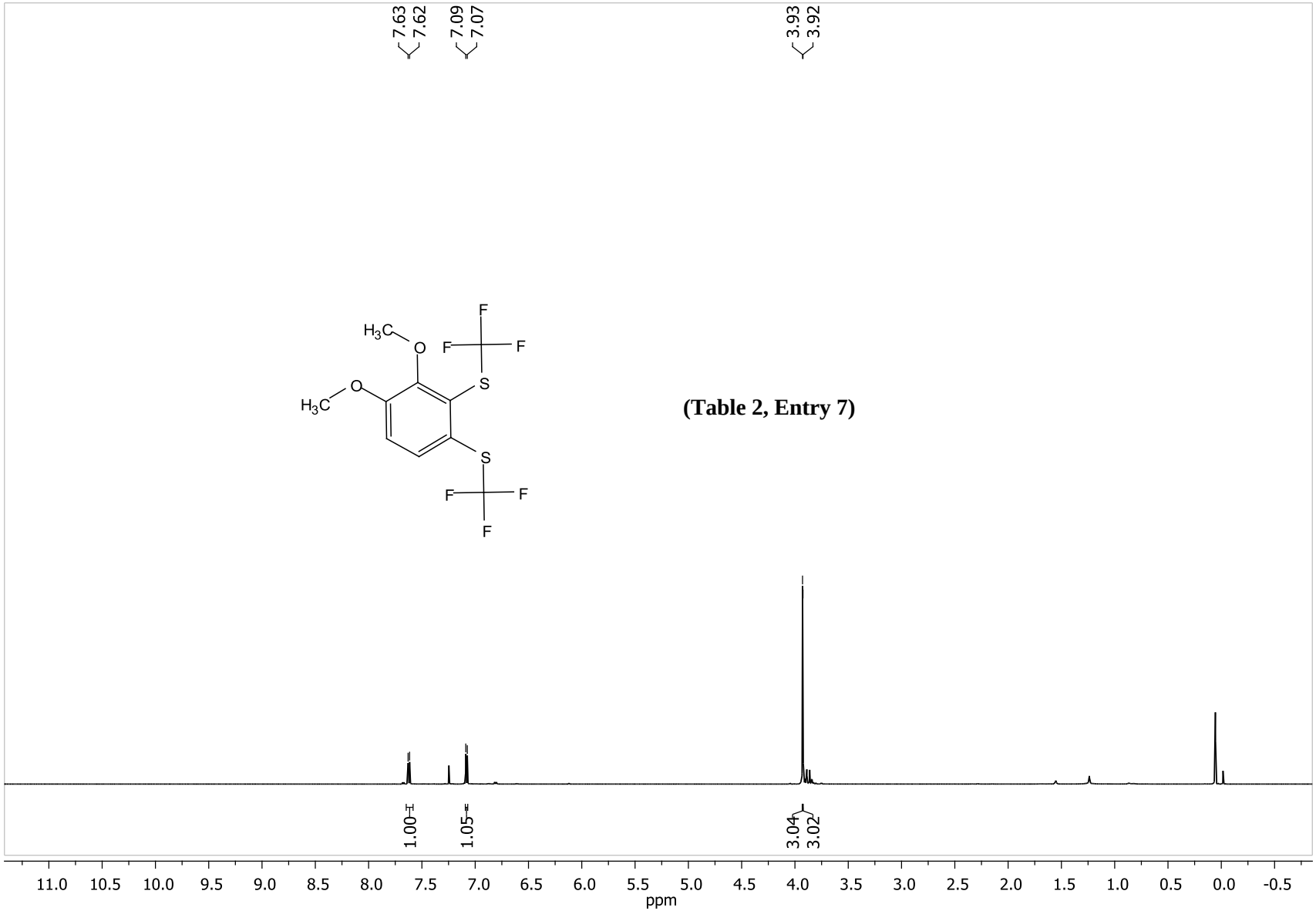
(Table 2, Entry 5)


7.16
3.96
3.91
3.90
(Table 2, Entry 6)
1.00
3.00
3.00
3.00
ppm

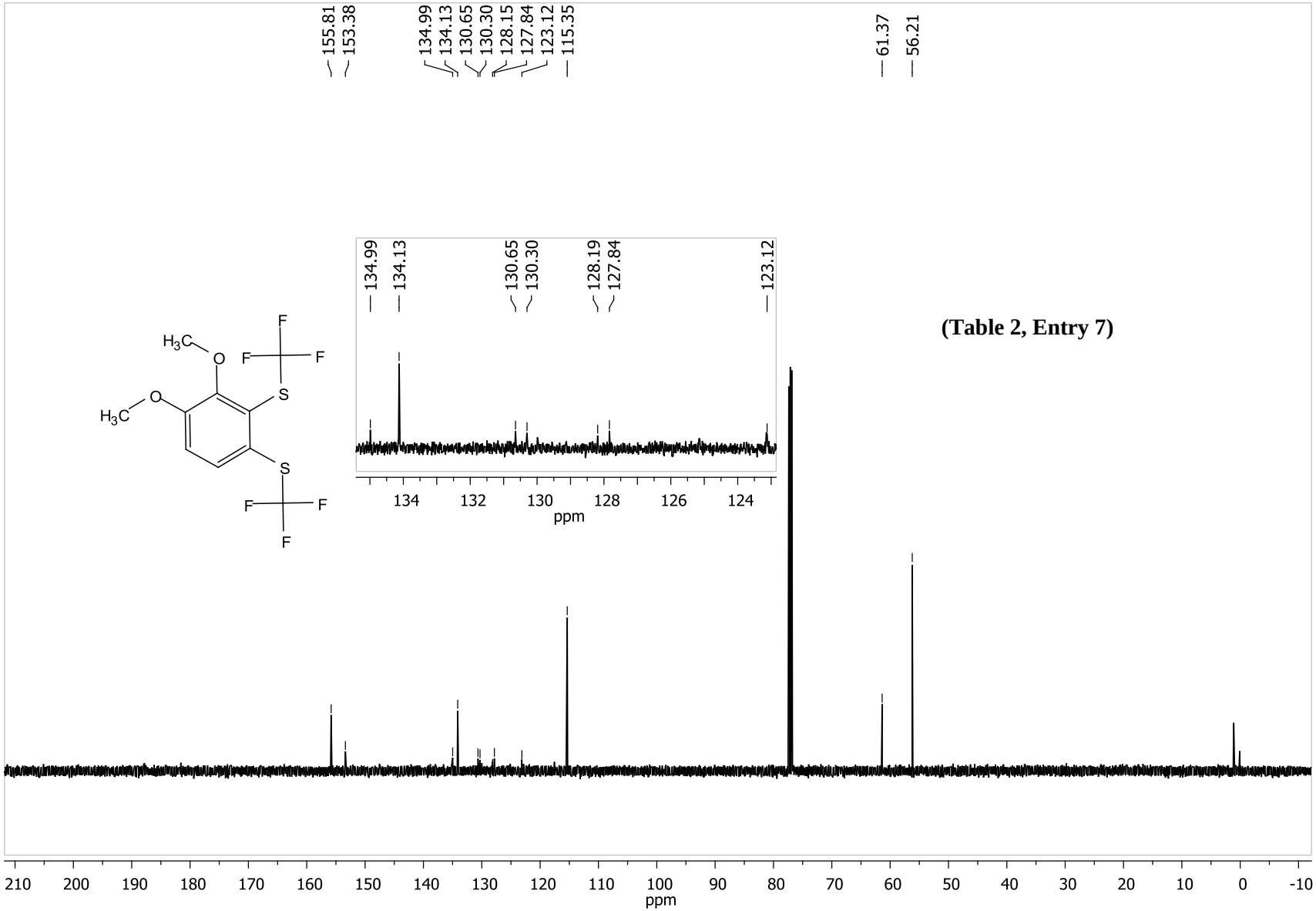

157.44
156.39
144.69
130.43
130.10
128.67
128.66
128.38
128.04
115.86
115.84
115.61
61.65
61.64
61.02
61.00
56.39
56.37
(Table 2, Entry 6)
F
F
F
CH3
O
S
F
F
F
H3C
O
S
O
H3C
130.43
130.10
128.67
128.66
128.38
128.04
115.86
115.84
115.61
132
128
124
120
116
ppm
61.65
61.64
61.02
61.00
56.39
56.37
61
60
59
58
57
56
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

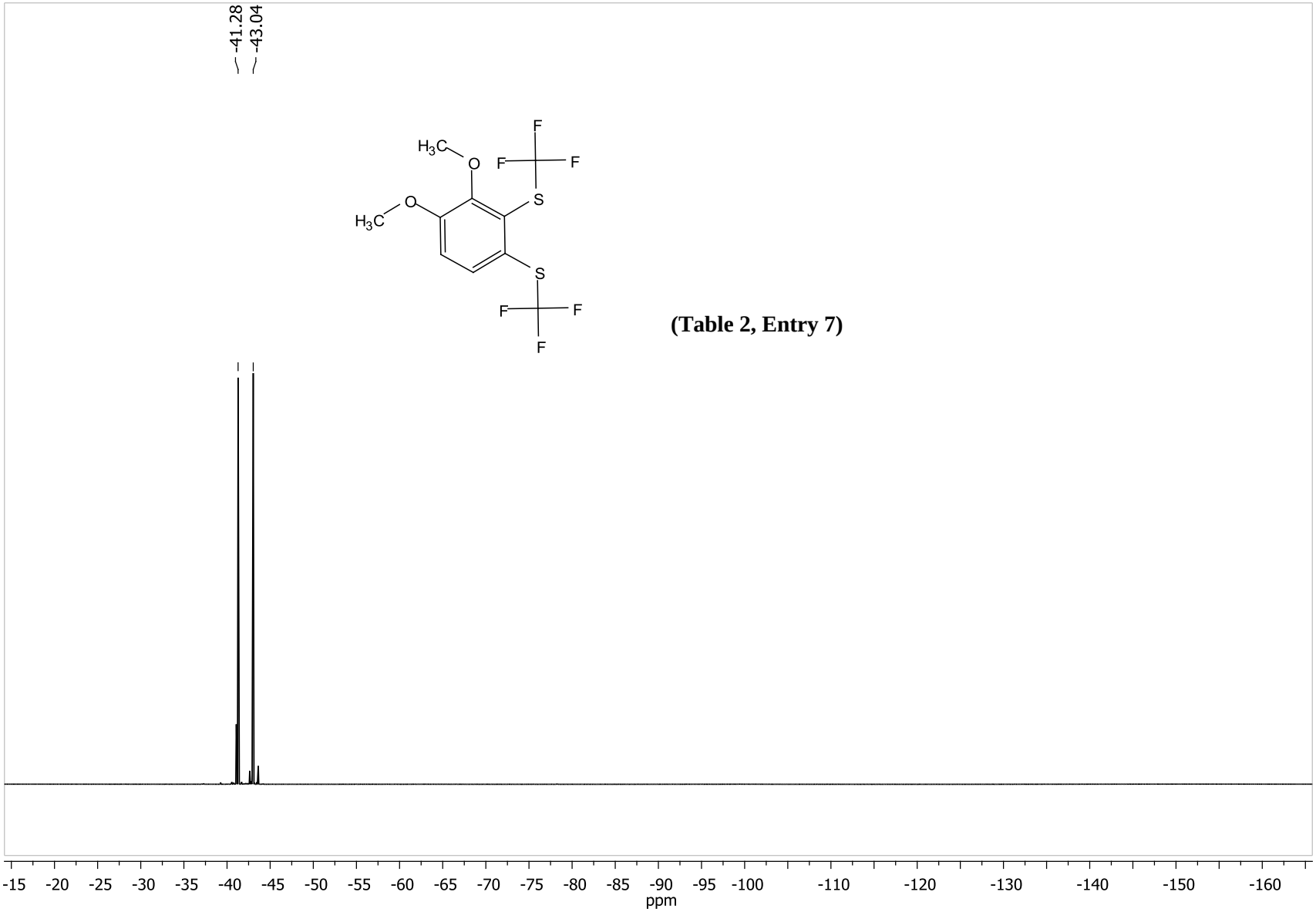
(Table 2, Entry 6)

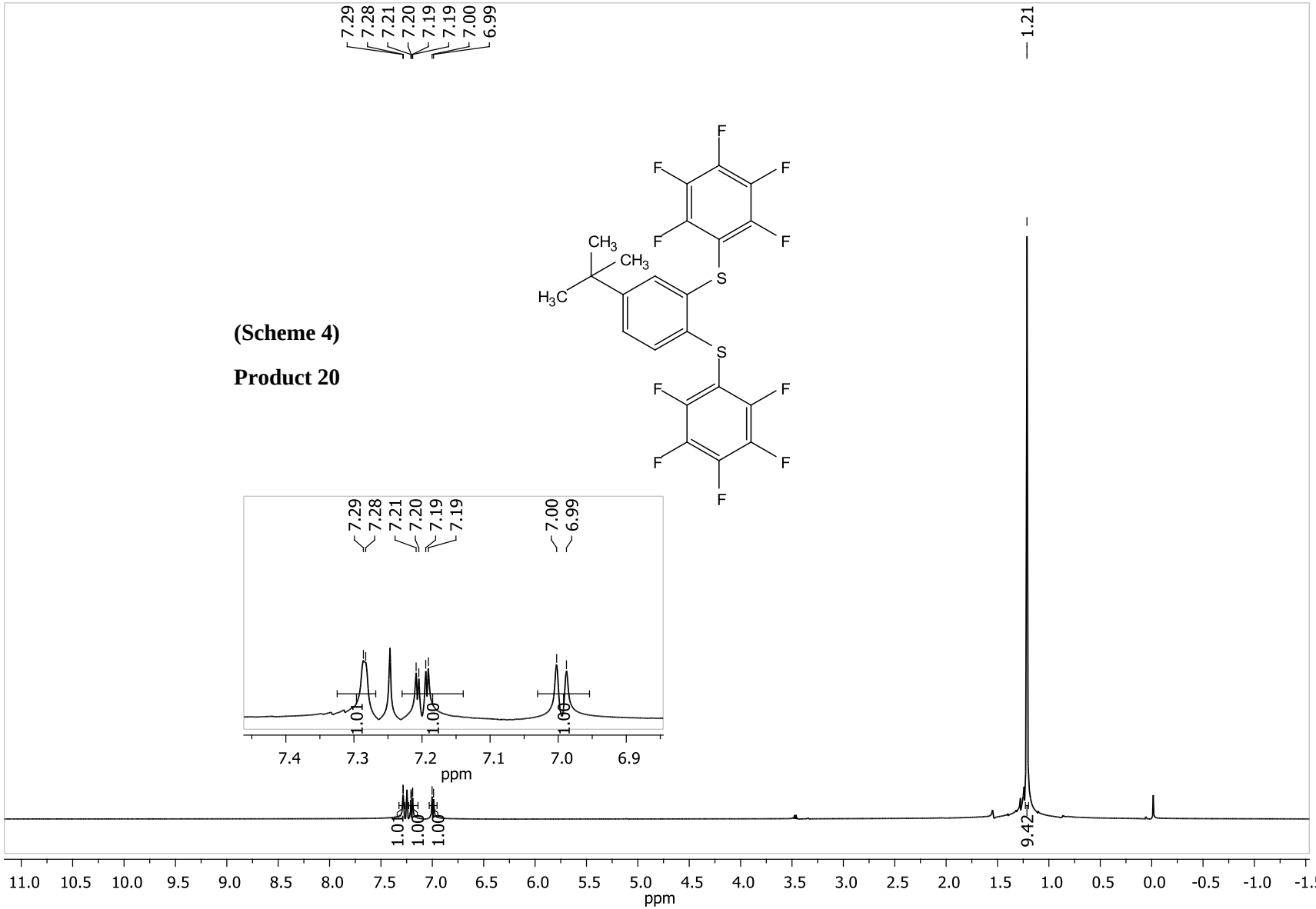


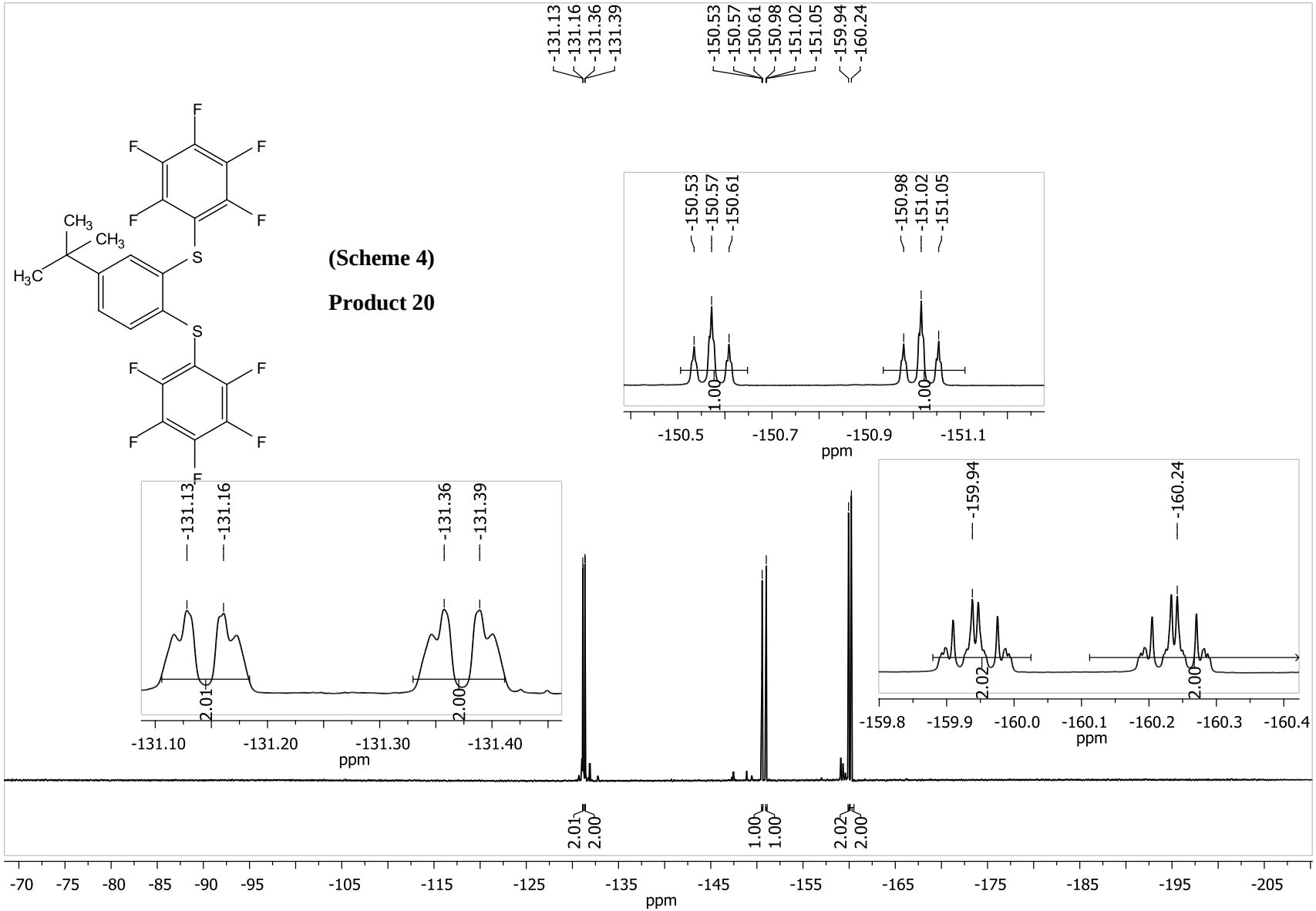


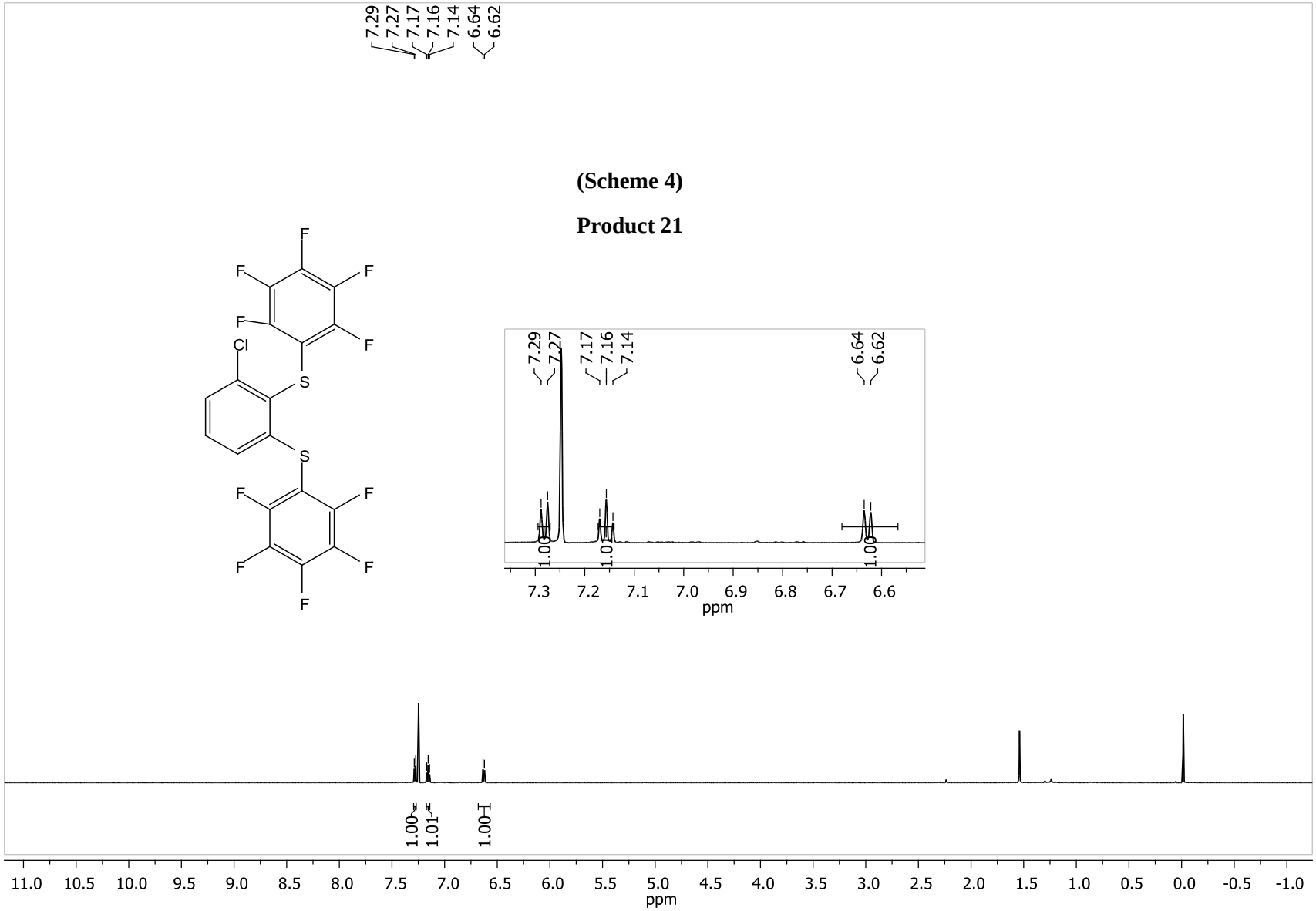
(Table 2, Entry 7)

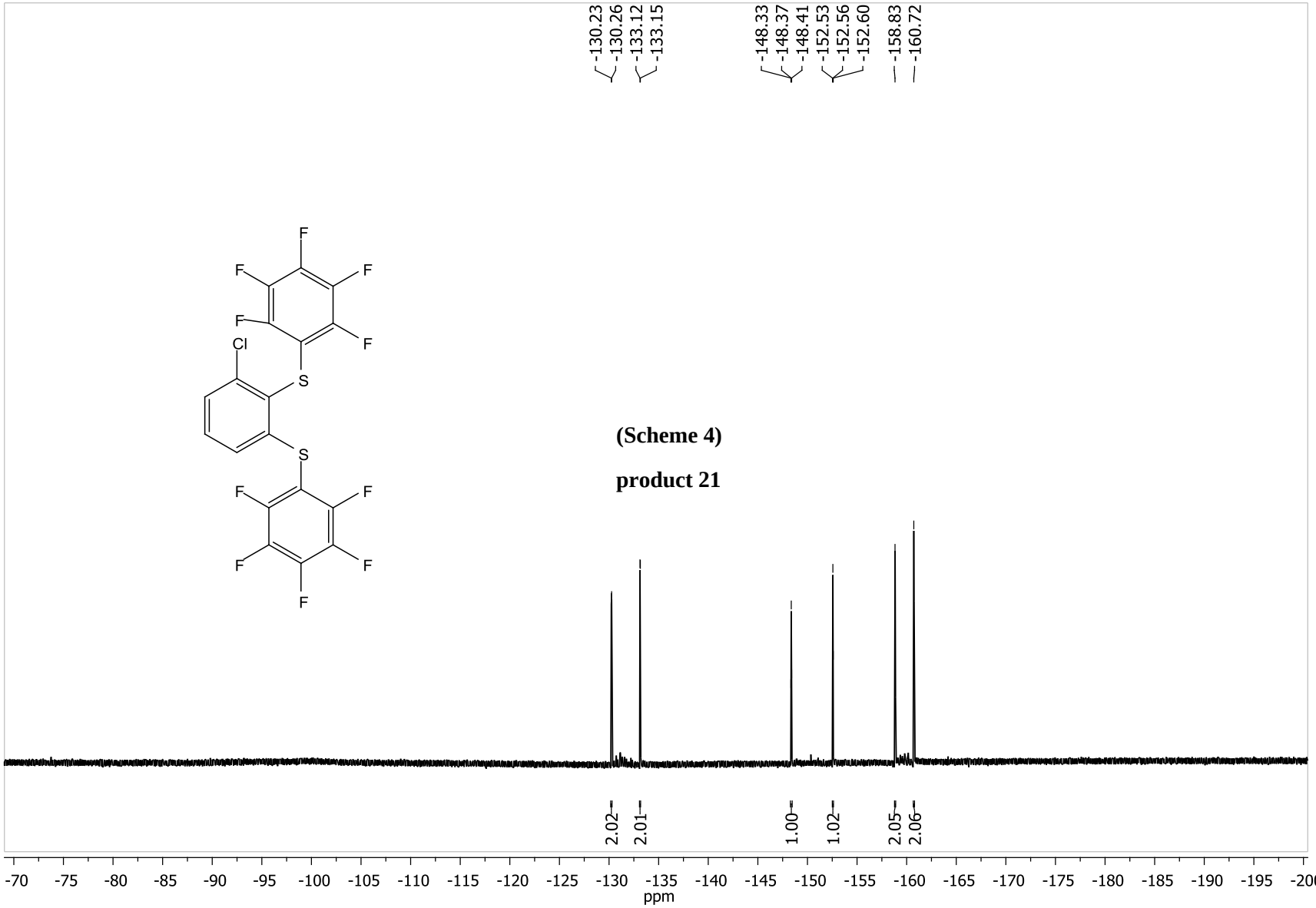

155.81
153.38
134.99
134.13
130.65
130.30
128.15
127.84
123.12
115.35
61.37
56.21
134.99
134.13
130.65
130.30
128.19
127.84
123.12
134
132
130
128
126
124
ppm
(Table 2, Entry 7)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

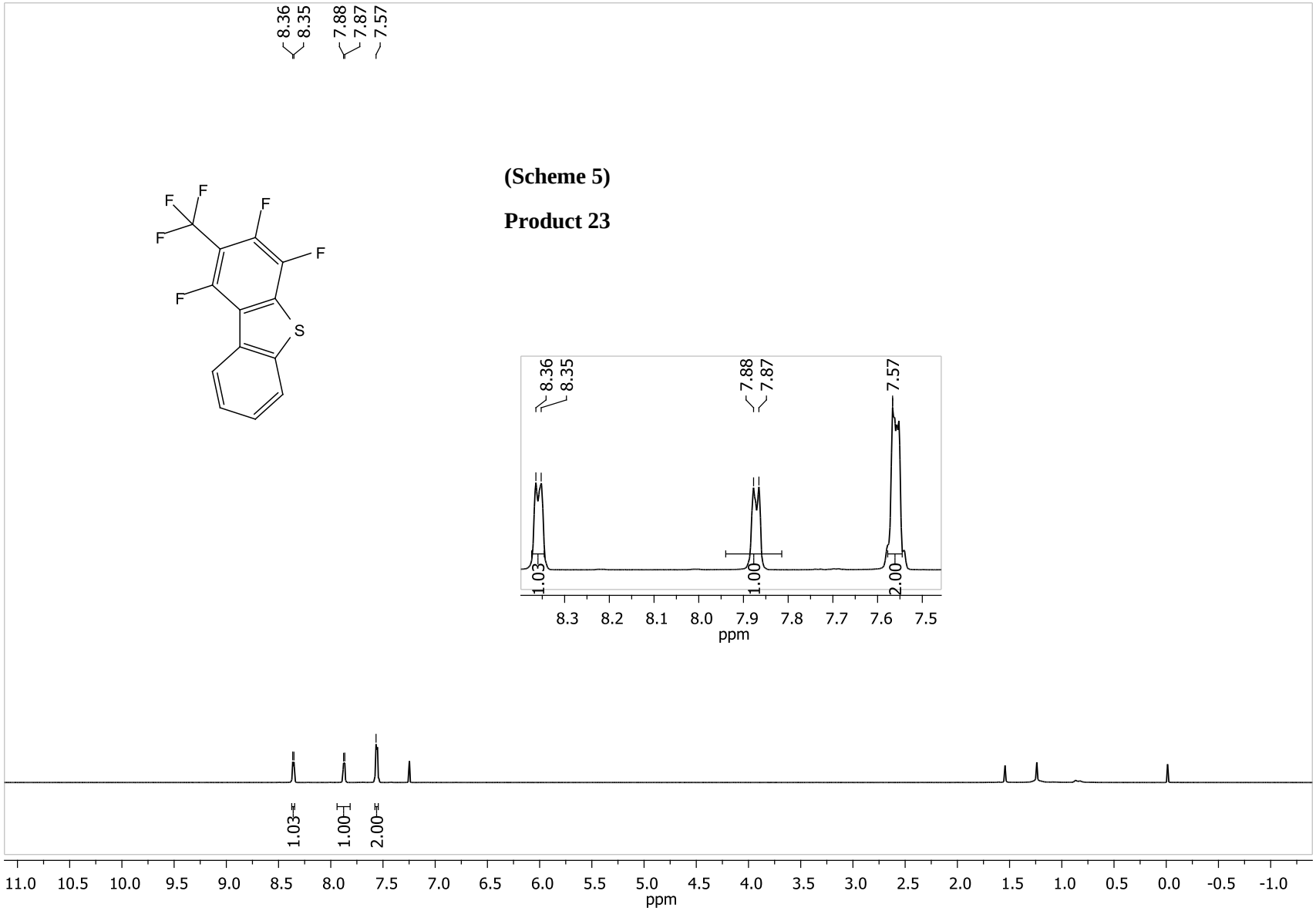

-41.28
-43.04
H3C
O
F
F
F
S
O
H3C
S
F
F
F
(Table 2, Entry 7)
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120 -130 -140 -150 -160
ppm


7.29
7.28
7.21
7.20
7.19
7.19
7.00
6.99
1.21
(Scheme 4)
Product 20
F
F
F
F
F
CH3
CH3
H3C
S
S
F
F
F
F
F
1.01
1.00
1.00
1.01
1.00
1.00
9.42
7.4
7.3
7.2
7.1
7.0
6.9
ppm
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
ppm


-131.13
-131.16
-131.36
-131.39
-150.53
-150.57
-150.61
-150.98
-151.02
-151.05
-159.94
-160.24
F
F
F
F
F
CH3
CH3
H3C
S
S
F
F
F
F
F
(Scheme 4)
Product 20
-150.53
-150.57
-150.61
-150.98
-151.02
-151.05
1.00
1.00
-150.5
-150.7
-150.9
-151.1
ppm
-131.13
-131.16
-131.36
-131.39
2.01
2.00
-131.10
-131.20
-131.30
-131.40
ppm
-159.94
-160.24
2.02
2.00
-159.8
-159.9
-160.0
-160.1
-160.2
-160.3
-160.4
ppm
2.01
2.00
1.00
1.00
2.02
2.00
-70
-75
-80
-85
-90
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
-205
ppm

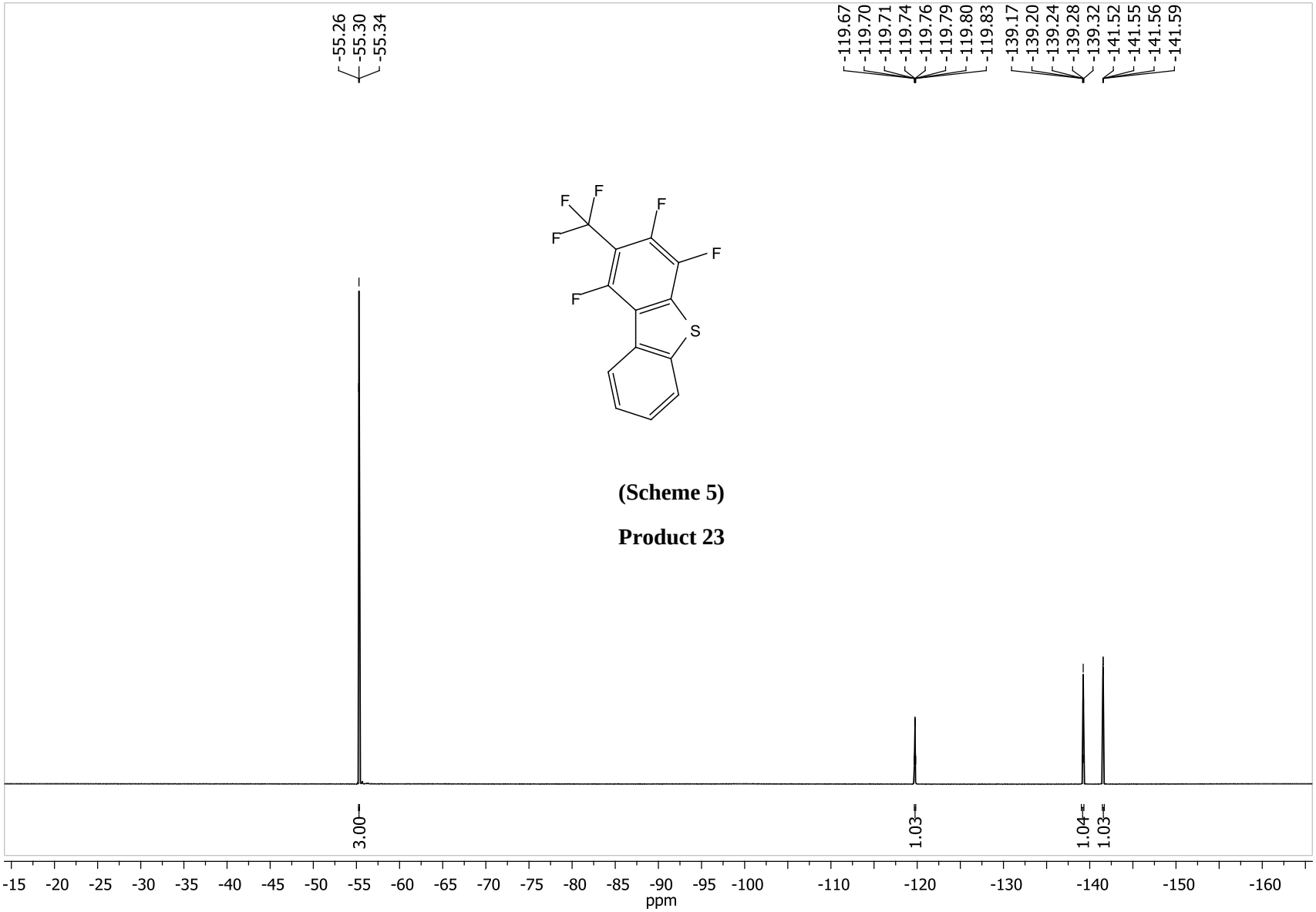

7.29
7.27
7.17
7.16
7.14
6.64
6.62
(Scheme 4)
Product 21
F
F
F
F
F
Cl
S
S
F
F
F
F
F
7.29
7.27
7.17
7.16
7.14
6.64
6.62
1.00
1.01
1.00
1.00
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
1.00
1.01
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


-130.23
-130.26
-133.12
-133.15
-148.33
-148.37
-148.41
-152.53
-152.56
-152.60
-158.83
-160.72
F
F
F
F
F
Cl
S
S
F
F
F
F
F
(Scheme 4)
product 21
2.02
2.01
1.00
1.02
2.05
2.06
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200
ppm



(Scheme 5)

Product 23



(Scheme 5)

Product 23