Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

1,2-Bis(arylthio)arene Synthesis via Aryne Intermediates

Milad Mesgar, Justin Nguyen-Le, and Olafs Daugulis*

Department of Chemistry, University of Houston, Houston, TX 77204-5003

Table of Contents

General considerations:

Reactions were performed either in 2-dram vials. 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}C NMR 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.

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.

Di-1-Adamantylamine

Method used previously was employed.[1] A thick-walled glass tube (12-inch diameter and 800 ml volume) was filled with powdered 1-adamantyl bromide (215 g, 1.0 mol) and 1-adamantylamine (272 g, 1.8 mol). Tube was evacuated for 24 h and then vacuum-sealed and placed into a metal container. The metal container was placed in furnace. The temperature was increased from room temperature to 240 °C over 5 hours and maintained at 240 °C for 72 h. The mass inside the tube (487 g) converted to a hard solid by cooling to 25 °C. The solid was carefully crushed with a mortar and pestle. About 3.3 % of the powder (16 g) was dissolved in a mixture of hot aqueous NaOH (20%, 250 mL) and ether (250 mL). It is important to dissolve powder in NaOH solution first and then add ether. The solution was placed into separatory funnel. It was shaken vigorously only after the reaction mixture cooled down. The ether layer was separated and shaken with aqueous HCl solution (300 mL, 10 %) to precipitate di-1-adamantylamine as the hydrochloride salt which is insoluble. The precipitate was collected by filtration and washed twice with water. The resulting white solid was shaken with warm aqueous NaOH (20 %, 200 mL) and after 3 minutes, ether (250 mL) solution to regenerate di-1-adamantylamine. The ether layer was separated and dried over anhydrous K_2CO_3. After filtering off the drying agent and evaporating the solvent in vacuo, 7.02 g (75%) of di-1-adamantylamine was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99 (apparent s, 6H), 1.75 (d, 12H), 1.59 (apparent s, 12H). 13C NMR (100 MHz) δ 52.6, 46.6, 36.6, 30.1. This compound is known.[2]

Lithium di-1-admantylamide (LDAM, 3)

Di-1-adamantylamine (14 g) was placed in oven-dried 500 ml Schlenk flask equipped with a stir bar. Flask was sealed with rubber septum and Teflon tape. Flask was filled with N_2 gas and evacuated at least 5 times (each time 10 minutes). Anhydrous pentane (240 mL) was added to the flask via syringe. n-BuLi (1.6 M in hexane, 36.0 mL) was injected dropwise via syringe into the suspension at room temperature. After injecting

about 23 ml of n-BuLi, suspension became completely transparent as amine dissolved and after 2 to 3 hours it turned into a white suspension. Stirring was continued for 24 hours and then the suspension was allowed to settle. The transparent supernatant solution was removed via syringe and anhydrous pentane (100 mL) was added to the suspension. Suspension was stirred for 5 minutes and after settling, the transparent supernatant was removed via syringe. The same procedure was repeated once more. The residue was dried under vacuum for 8 hours. The product (12.2 g, 86 %) was used without further purification. The NMR experiment was run at – 60 °C in THF-d8.

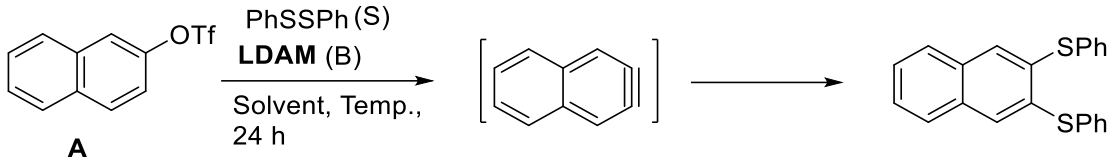
^{1}H NMR (600 MHz, – 60 °C in THF-d_8.) δ 1.87 (apparent s, 6H), 1.65 – 1.40 (m, 24H). ^{13}C NMR (151 MHz) δ 54.0, 51.7, 37.9, 31.2. This compound is known.[1]

General procedure for reactions:

Outside the glovebox a 2-dram vial was equipped with two magnetic stirring bars (size: 5x1x1 mm). The vial was placed inside the glovebox. To the vial was added solid LDAM (0.291 g, 1.0 mmol). The sealed vial was then taken out of the glovebox and placed into oil bath/cooling bath at reaction temperature. Two thirds of solvent or solvent mixture (1.3 mL out of 2.0 mL) was added via syringe to the reaction vial. Vial was stirred for 5-10 minutes at reaction temperature. In another vial, haloarene or aryl triflate (0.5 mmol) was mixed with disulfide compound (0.75 mmol, 1.25 equiv). Subsequently, one third of reaction solvent (0.7 mL) was added to this vial. The vial with reactants was kept at the reaction temperature for 5-10 minutes. Subsequently, solution of reactants was added to the reaction vial containing base in 1 minute by syringe. After stirring at indicated temperature for indicated time, reactions were quenched with methanol (0.5 mL, unless otherwise stated), followed by dilution with dichloromethane (0.5 mL). To the diluted reaction mixture was added silica gel and then mixture was dried on rotary evaporator and subjected to flash chromatography in hexanes followed by appropriate solvent to elute the products. After concentrating the fractions containing the product, the residue was dried under reduced pressure to yield

pure product. If necessary, purification by preparative HPLC was performed.

Table S1. Optimization of ArOTf reaction with PhSSPh

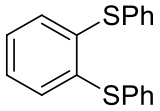


Entry	(**A**/**S**/**B**)	Solvent	Temp.(˚C)	Time (h)	Total yield (%)[a]
1	1/1/1.2	THF	0	38	35
2	1/1/1.2	THF	25	38	25
3	1/2/2	Et_2O/THF (49/1)	0	24	70
4	1/1/1.2	Et_2O/THF (49/1)	25	38	20
5	1/1.2/2	Et_2O/C_6H_{12} (1/1)	0	47	74
6	1/1.2/1.2	Et_2O/C_6H_{12} (1/1)	0	47	69
7	1/1.2/1.2	Et_2O/THF (49/1)	0	47	72
8	**1/1.2/1.5**	**Et_2O/THF (49/1)**	**0**	**47**	**80 (71[b])**
9	1/1.2/2	Et_2O/THF (49/1)	0	47	78

[a] Aryne precursor (0.25 mmol), solvent (1.5 mL). Yields determined by GC analysis with n-decane as an internal standard.

[b] Isolated yield.

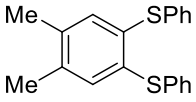
1,2-Bis(phenylthio)benzene (Table 2, entry 1)



Phenyl triflate (57 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 25:1), 67 mg (91 %) of a yellow oil was obtained. R_f = 0.30 (hexanes). This compound is known.[3]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 8H), 7.31 – 7.27 (m, 2H), 7.15 – 7.10 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 134.6, 131.9, 131.5, 129.5, 127.63, 127.61. FT-IR (neat, cm^{-1}) ν 3054, 2916, 2849, 1581, 1570, 1475, 1439, 1433. HRMS (APCI-MS) calc. For $C_{18}H_{14}S_2$ $[M+H]^+$: 295.0610; found: 295.0608.

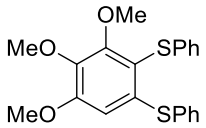
4,5-Dimethyl-1,2-bis(phenylthio)benzene (Table 2, entry 2)



3,4-Dimethylphenyl triflate[4] (64 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes), 67 mg (84 %) of a yellow solid was obtained. R_f = 0.50 (hexanes). This compound is known.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 7.02 (s, 2H), 2.14 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.8, 134.2, 133.7, 130.8, 129.3, 127.0, 19.5. FT-IR (neat, cm^{-1}) ν 3057, 2958, 2931, 2904, 1580, 1567, 1470, 1437, 1423, 1394. HRMS (APCI-MS) calc. For $C_{20}H_{18}S_2$ $[M+H]^+$: 323.0923; found: 323.0928.

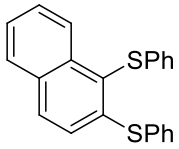
1,2-Bis(phenylthio)-3,4,5-trimethoxybenzene (Table 2, entry 3)



3,4,5-Trimethoxyphenyl triflate[6] (79 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ether 10:1 followed by hexanes/ether 5:1), 54 mg (56 %) of an off-white solid was obtained. R_f = 0.10 (hexanes/dichloromethane 5:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.8 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.24 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 155.2, 141.6, 140.9, 138.0, 134.3, 133.6, 129.6, 128.9, 128.6, 126.7, 125.4, 115.8, 107.4, 61.6, 61.1, 55.8. HRMS (APCI-MS) calc. For $C_{21}H_{20}O_3S_2$ $[M+H]^+$: 385.0927; found: 385.0929.

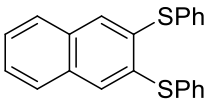
1,2-Bis(phenylthio)naphthalene (Table 2, entry 4)



1-Naphthyl triflate (69 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes), 53 mg (61 %) of a yellow oil was obtained. R_f = 0.30 (hexanes). This compound is known.[7]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.45 – 7.39 (m, 4H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.11 – 7.06 (m, 3H), 7.02 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.2, 137.2, 135.8, 134.9, 133.3, 132.2, 130.7, 129.8, 129.1, 128.9, 128.5, 128.1, 126.6, 125.9, 125.8, 125.4, 125.3, 124.5. FT-IR (neat, cm^{-1}) ν 3063, 2919, 1613, 1579, 1547, 1476, 1337, 1310. HRMS (APCI-MS) calc. For $C_{22}H_{16}S_2$ $[M+H]^+$: 345.0766; found: 345.0770.

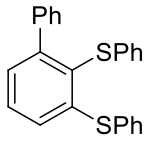
2,3-Bis(phenylthio)naphthalene (Table 2, entry 5)



2-Naphthyl triflate (69 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/dichloromethane 8:1), 67 mg (71 %) of a white solid was obtained. R_f = 0.35 (hexanes/dichloromethane 8:1). This compound is known.[8]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.63 – 7.60 (m, 2H), 7.42 – 7.38 (m, 6H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.32 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 134.9, 132.8, 131.8, 130.7, 129.5, 127.7, 127.2, 126.6. FT-IR (neat, cm^{-1}) ν 3053, 2922, 2875, 1577, 1475, 1438, 1419, 1307. HRMS (APCI-MS) calc. For $C_{22}H_{16}S_2$ $[M+H]^+$: 345.0766; found: 345.0768.

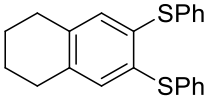
3-Phenyl-1,2-bis(phenylthio)benzene (Table 2, entry 6)



2-Biphenyl triflate[4] (76 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 20:1), 65 mg (68 %) of a yellow solid was obtained. R_f = 0.50 (hexanes/ethyl acetate 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.42 – 7.38 (m, 3H), 7.28 – 7.26 (m, 3H), 7.25 – 7.21 (m, 3H), 7.16 – 7.12 (m, 3H), 7.07 – 7.05 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 148.0, 141.2, 137.7, 135.2, 133.2, 129.8, 129.7, 129.2, 129.0, 128.8, 127.8, 127.7, 127.3, 127.0, 126.5, 125.3. Signal for one carbon could not be located. FT-IR (neat, cm^{-1}) ν 3049, 2918, 1578, 1548, 1475, 1438, 1385. HRMS (APCI-MS) calc. For $C_{24}H_{18}S_2$ $[M+H]^+$: 371.0923; found: 371.0922.

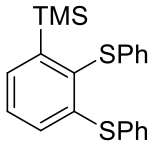
2,3-Bis(phenylthio)-1,2,3,4-tetrahydronaphthalene (Table 2, entry 7)



5,6,7,8-Tetrahydronaphthalen-2-yl trifluoromethanesulfonate[6] (70 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/dichloromethane 5:1), 71 mg (82 %) of a white solid was obtained. R_f = 0.60 (hexanes/dichloromethane 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 8H), 7.25 – 7.22 (m, 2H), 6.95 (s, 2H), 2.70 – 2.6 (m, 4H), 1.70-1.60 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 135.8, 133.9, 133.2, 130.9, 129.3, 127.0, 29.0, 23.0. FT-IR (neat, cm^{-1}) ν 3058, 2925, 2854, 1579, 1474, 1452, 1437, 1377. HRMS (APCI-MS) calc. For $C_{22}H_{20}S_2$ $[M+H]^+$: 349.1079; found: 349.1085.

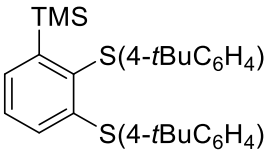
2,3-Bis(phenylthio)trimethylsilyl benzene (Table 2, entry 8)



2-(Trimethylsilyl)phenyl triflate (75 mg, 0.25 mmol), diphenyldisulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes), 83 mg (91 %) of a yellow oil was obtained. R_f = 0.20 (hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.37 – 7.34 (m, 4H), 7.24 – 7.19 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.99 – 6.96 (m, 2H), 6.86 (dd, *J* = 8.0, 1.4 Hz, 1H), 0.3 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 147.8, 138.3, 135.0, 133.6, 133.2, 132.4, 129.6, 129.5, 129.0, 128.82, 128.78, 125.7, 125.0, 0.5. FT-IR (neat, cm^{-1}) ν 3020, 2943, 2906, 1582, 1544, 1475, 1366, 1245, 1130. HRMS (APCI-MS) calc. For $C_{20}H_{19}S_2Si$ $[M\text{-}CH_3]^+$: 351.0694; found: 351.0692.

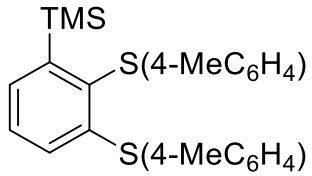
2,3-Bis(4,4'-t-butylphenylthio)trimethylsilylbenzene (Table 2, entry 9)



2-(Trimethylsilyl)phenyl triflate (75 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 113 mg (94 %) of a yellow solid was obtained. R_f = 0.30 (hexanes).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 7.24 – 7.22 (m, 2H), 7.19 – 7.16 (m, 1H), 6.91 – 6.88 (m, 2H), 6.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 1.31 (s, 9H), 1.27 (s, 9H), 0.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1, 148.9, 148.1, 147.9, 134.9, 134.6, 133.9, 132.0, 129.5, 129.2, 128.4, 126.7, 125.9, 125.8, 34.8, 34.4, 31.4, 31.3, 0.5. FT-IR (neat, cm^{-1}) ν 2968, 2904, 1544, 1490, 1463, 1400, 1364, 1270, 1246. HRMS (CI-MS) calc. For $C_{29}H_{38}S_2Si$ $[M]^+$: 478.2184; found: 478.2193.

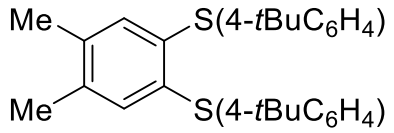
2,3-Bis(4,4'-methylphenylthio)trimethylsilylbenzene (Table 2, entry 10)



2-(Trimethylsilyl)phenyl triflate (75 mg, 0.25 mmol), bis(4-methylphenyl)disulfide[9] (74 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 113 mg (68 %) of a yellow solid was obtained. R_f = 0.30 (hexanes).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, J = 7.2 Hz, 3H), 7.16 (t, J = 7.8 Hz, 3H), 7.03 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 0.29 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.0, 148.3, 139.1, 135.4, 134.61, 134.57, 131.9, 130.4, 129.9, 129.7, 129.2, 128.6, 128.3, 125.7, 21.4, 21.1, 0.5.

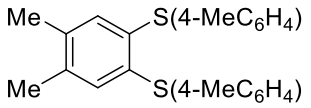
4,5-Dimethyl-1,2-bis(4,4'-tert-butylphenylthio)benzene (Table 2, entry 11)



3 ,4-Dimethylphenyl triflate[4] (64 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1), 102 mg (94 %) of a brown solid was obtained. R_f = 0.30 (hexanes).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 4H), 7.24 (d, *J* = 8.1 Hz, 4H), 6.97 (s, 2H), 2.12 (s, 6H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 136.8, 134.5, 133.2, 132.0, 131.0, 126.3, 34.6, 31.4, 19.4. FT-IR (neat, cm^{-1}) ν 2960, 2902, 2866, 1593, 1488, 1458, 1394, 1362, 1267. HRMS (CI-MS) calc. For $C_{28}H_{34}S_2$ $[M]^+$: 434.2101; found: 434.2096.

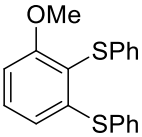
4,5-Dimethyl-1,2-bis(4,4'-methylphenylthio)benzene (Table 2, entry 12)



3,4-Dimethylphenyl triflate[4] (64 mg, 0.25 mmol), di(p-tolyl) disulfide[9] (74 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 7:1), 89 mg (quantitative yield) of a white solid was obtained. R_f = 0.55 (hexanes/ethyl acetate: 7/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.7 Hz, 4H), 6.87 (d, *J* = 8.7 Hz, 4H), 6.81 (s, 2H), 3.80 (s, 6H), 2.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 136.1, 134.7, 134.3, 131.8, 125.3, 115.0, 55.4, 19.4. FT-IR (neat, cm^{-1}) ν 3003, 2959, 2917, 1613, 1575, 1547, 1490, 1447. HRMS (APCI-MS) calc. For $C_{22}H_{22}S_2$ $[M+H]^+$: 351.1236; found: 351.1236.

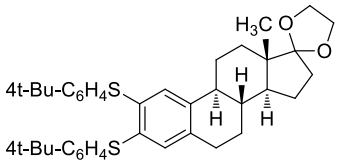
2,3-Bis(phenylthio)anisole (Table 2, entry 13)



2-Methoxyphenyl *N*,*N*-dimethylsulfamate[10] (58 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 25 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 15:1), 41 mg (55 %) of a yellow oil was obtained. R_f = 0.30 (hexane/ethyl acetate 20:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.39 – 7.36 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.18 – 7.08 (m, 4H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 148.6, 136.9, 135.2, 133.0, 131.0, 129.7, 128.9, 128.8 126.8, 125.3, 119.6, 116.7, 108.1, 56.4. FT-IR (neat, cm^{-1}) ν 3051, 2965, 2936, 1576, 1563, 1475, 1454, 1438, 1189. HRMS (APCI-MS) calc. For $C_{19}H_{16}OS_2$ $[M+H]^+$: 325.0715; found: 325.0719.

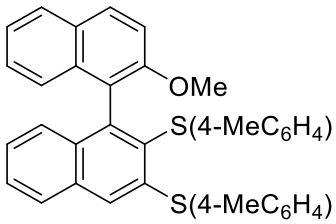
(8R, 9S, 13S, 14S) -13-Methyl-2,3-bis(phenylthio)-6, 7, 8, 9, 11, 12, 13, 14, 15, 16-decahydrospiro[cyclopenta[a]phenanthrene-17, 2'-[1,3]dioxolane] (Scheme 1, compound 5a)



(8R,9S,13S,14S)-13-Methyl-6, 7, 8, 9, 11, 12, 13, 14, 15, 16 decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]-dioxolan]-3-yl trifluoromethanesulfonate[11] (112 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 15:1), 112 mg (72 %) of a white solid was obtained. R_f = 0.40 (hexanes/ethyl acetate 15:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 4H), 7.29 – 7.23 (m, 4H), 7.12 (s, 1H), 6.86 (s, 1H), 3.96 – 3.85 (m, 4H), 2.70 (dd, J = 8.1, 3.8 Hz, 2H), 2.15 (t, J = 12.9 Hz, 1H), 2.00 (t, J = 11.5 Hz, 2H), 1.85 – 1.57 (m, 5H), 1.44 (d, J = 12.7 Hz, 1H), 1.35 – 1.30 (m, 4H) 1.31 (s, 9H), 1.30 (s, 9H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 150.1, 140.3, 137.2, 135.6, 133.3, 132.3, 131.8, 131.5, 130.6, 130.0, 129.9, 126.4, 126.3, 119.4, 65.3, 64.6, 49.4, 46.1, 43.9, 38.6, 34.7, 34.6, 34.2, 31.39, 31.38, 30.6, 29.1, 26.8, 25.7, 22.4, 14.4. FT-IR (neat, cm^{-1}) ν 2959, 2929, 2866, 1576, 1489, 1459, 1433, 1393, 1362. HRMS (CI-MS) calc. For $C_{40}H_{50}O_2S_2$ $[M]^+$: 626.3252; found: 626.3270.

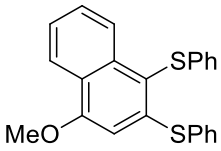
1-(2-Methoxynaphthyl)-2,3-Bis(4,4'-methylphenylthio)naphthalene (Scheme 1, compound 6a)



1-(2-Methoxynaphthyl)naphthyl triflate[12] (108 mg, 0.25 mmol), bis(4-methylphenyl)disulfide[9] (74 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 30 hours. After column chromatography (hexanes/ethyl acetate 10:1), 78 mg (59 %) of a yellow solid was

obtained. R_f = 0.50 (hexanes/ethyl acetate 10:1). ^{1}H NMR (400 MHz, methylene chloride-d2) δ 7.97 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.37-7.25 (m, 6H), 7.14 (q, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.93-6.85 (m, 5H), 3.54 (s, 3H), 2.43 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, methylene chloride-d2) δ 154.4, 143.9, 142.5, 139.4, 135.2, 135.1, 134.2, 133.8, 133.6, 131.5, 130.7, 129.8, 129.5, 129.4, 129.2, 128.7, 128.0, 127.7, 127.3, 127.0, 126.8, 126.5, 125.7, 125.2, 124.8, 123.4, 121.2, 112.8, 55.7, 21.2, 20.7.

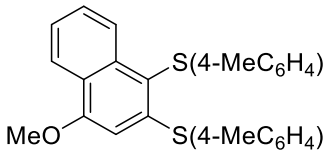
4-Methoxy-1,2-bis(phenylthio)naphthalene (Table 3, entry 1)



4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/dichloromethane 5:1 followed by hexanes/dichloromethane 4:1), 84 mg (89 %) of a yellow solid was obtained. R_f = 0.55 (hexanes/dichloromethane 5:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.40 (m, 4H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 3H), 6.40 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 146.9, 137.9, 136.5, 134.9, 133.6, 129.7, 129.0, 128.9, 128.6, 126.1, 125.7, 125.2, 125.1, 124.9, 122.6, 115.6, 104.0, 55.4. FT-IR (neat, cm^{-1}) ν 2959, 2939, 1612, 1568, 1548, 1497, 1459, 1426. HRMS (APCI-MS) calc. For $C_{23}H_{18}OS_2$ $[M+H]^+$: 375.0872; found: 375.0873.

4-Methoxy-1,2-bis(4,4'-methylphenylthio)naphthalene (Table 3, entry 2)

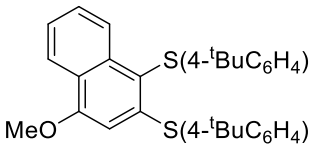


4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), di(*p*-tolyl) disulfide (74 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 7:1), 89 mg (88

%) of a white foam was obtained. R_f = 0.50 (hexanes/ethyl acetate 7:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.37 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.97 (q, *J* = 8.2 Hz, 4H), 6.34 (s, 1H), 3.67 (s, 3H), 2.39 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 147.4, 139.2, 136.5, 135.2, 134.8, 134.3, 130.4, 129.8, 129.7, 128.4, 126.3, 125.6, 124.9, 124.8, 122.5, 115.4, 103.6, 55.4, 21.4, 21.0. FT-IR (neat, cm^{-1}) ν 2917, 1614, 1576, 1548, 1491, 1448, 1407, 1372, 1334, 1259. HRMS (CI-MS) calc. For $C_{25}H_{22}OS_2$ $[M]^+$: 402.1112; found: 402.1106.

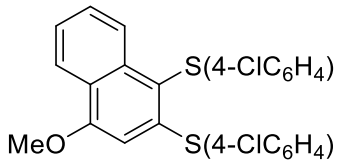
4-Methoxy-1,2-bis(4,4'-tert-butylphenylthio)naphthalene (Table 3, entry 3)



4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 20:1 and hexanes/ethyl acetate 10:1), 115 mg (95 %) of a yellow solid was obtained. R_f = 0.10 (hexanes).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.43 – 7.37 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 3.65 (s, 3H), 1.33 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 152.4, 148.0, 147.4, 136.5, 135.0, 134.3, 129.9, 128.4, 126.6, 126.1, 126.0, 125.8, 124.9, 124.8, 122.4, 115.6, 103.8, 55.2, 34.9, 34.4, 31.4, 31.4. FT-IR (neat, cm^{-1}) ν 2962, 2868, 1614, 1575, 1549, 1499, 1487, 1448. HRMS (CI-MS) calc. For $C_{31}H_{34}OS_2$ $[M]^+$: 486.2051; found: 486.2055.

4-Methoxy-1,2-bis(4,4'-chlorophenylthio)naphthalene (Table 3, entry 4)

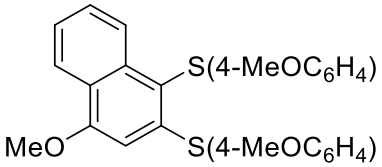


4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), 4,4'-dichlorodiphenyl disulfide (86 mg, 0.3 mmol), LDAM

(146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate 15:1), 80 mg (72 %) of a yellow solid was obtained. R_f = 0.60 (hexanes/ethyl acetate 10:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.46 – 7.43 (m, 3H), 7.39 – 7.36 (m, 2H), 7.14 – 7.11 (m, 2H), 6.95 – 6.93 (m, 2H), 6.39 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 146.0, 136.4, 136.3, 135.7, 135.1, 132.1, 131.0, 129.9, 129.1, 128.8, 127.4, 125.53, 125.49, 125.1, 122.7, 115.8, 104.0, 55.6. FT-IR (neat, cm^{-1}) ν 3078, 2903, 1615, 1577, 1504, 1474, 1448, 1434. HRMS (CI-MS) calc. For $C_{23}H_{16}Cl_2OS_2$ $[M]^+$: 443.9990; found: 443.9989.

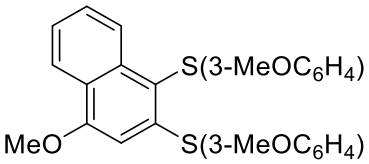
4-Methoxy-1,2-bis(4,4'-dimethoxyphenylthio)naphthalene (Table 3, entry 5)



4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), 4,4'-dimethoxyphenyl disulfide (84 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 7:1), 72 mg (68 %) of a yellow solid was obtained. R_f = 0.40 (hexanes/ethyl acetate 7:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 157.8, 156.9, 147.8, 137.5, 137.4, 136.4, 128.5, 128.4, 124.8, 124.6, 123.5, 115.6, 115.3, 115.2, 114.8, 114.7, 103.0, 55.5, 55.4, 55.3. FT-IR (neat, cm^{-1}) ν 3004, 2931, 2836, 1613, 1589, 1575, 1548, 1490, 1448. HRMS (CI-MS) calc. For $C_{25}H_{22}O_3S_2$ $[M]^+$: 434.1010; found: 434.1011.

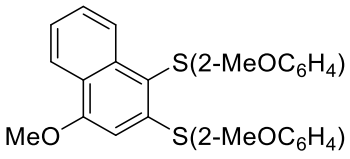
4-Methoxy-1,2-bis(3,3'-dimethoxyphenylthio)naphthalene (Table 3, entry 6)



4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), 3,3'-dimethoxyphenyl disulfide[9] (84 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 10:1), 69 mg (64 %) of a brown oil was obtained. R_f = 0.50 (hexanes/ethyl acetate 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.10 (m, 2H), 6.80 (d, *J* = 2.7 Hz, 1H), 6.53 (d, *J* = 2.7 Hz, 1H), 6.62– 6.61 (m, 3H), 6.38 (s, 1H), 3.71 (s, 3H), 2.53 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.2, 160.0, 157.2, 146.6, 139.3, 136.4, 134.7, 130.4, 129.8, 128.5, 126.8, 125.7, 125.2, 125.0, 122.5, 119.3, 118.4, 115.7, 115.0, 111.8, 110.5, 104.2, 55.51, 55.46, 55.2. FT-IR (neat, cm^{-1}) ν 3001, 2932, 2833, 1610, 1584, 1575, 1550, 1501, 1475. HRMS (CI-MS) calc. For $C_{25}H_{22}O_3S_2$ $[M]^+$: 434.1010; found: 434.1001.

4-Methoxy-1,2-bis(2,2'-dimethoxyphenylthio)naphthalene (Table 3, entry 7)

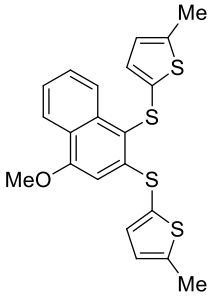


4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), 2,2'-dimethoxyphenyl disulfide[9] (84 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 20:1 followed by hexanes/ethyl acetate 10:1), 67 mg (62 %) of a yellow solid was obtained. R_f = 0.20 (hexanes/ethyl acetate 20:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H),7.06 – 6.94 (m, 3H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.69 – 6.61 (m, 1H), 6.40 (dd, *J* = 7.9, *J* = 1.7 Hz, 1H), 6.36 (s, 1H), 3.99 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 156.9, 155.6, 154.5, 146.8,

136.7, 136.6, 130.9, 128.3, 126.2, 125.72, 125.69, 125.5, 125.0, 124.9, 122.3, 121.4, 121.2, 114.3, 111.4, 110.3, 103.7, 56.02, 55.96, 55.4. FT-IR (neat, cm^{-1}) ν 3064, 2953, 2915, 2850, 1615, 1580, 1553, 1504. HRMS (CI-MS) calc. For $C_{25}H_{22}O_3S_2$ $[M]^+$: 434.1010; found: 434.1007.

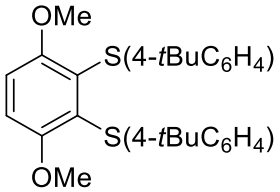
4-Methoxy-1,2-bis[5,5'-bis(2-methylthiophene)-sulfanyl]naphthalene (Table 3, entry 8)



4-Methoxy-1-naphthyl triflate[8] (76 mg, 0.25 mmol), 2,2'-dithiobis(5-methylthiophene)[9] (78 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47hours. After column chromatography (hexanes), 60 mg (58 %) of a yellow oil was obtained. R_f = 0.20 (hexane). Two chromatographic purifications may be necessary for obtaining pure material.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.46 – 7.36 (m, 1H), 7.21 (d, *J* = 3.7 Hz, 1H), 7.09 (d, *J* = 3.7 Hz, 1H), 6.82 (d, *J* = 4.8 Hz, 1H), 6.54 (d, *J* = 4.9 Hz, 1H), 6.39 (s, 1H), 3.73 (s, 3H), 2.54 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 147.4, 146.7, 142.6, 138.2, 135.7, 132.5, 131.6, 128.3, 127.7, 126.6, 125.4, 125.2, 124.9, 124.8, 122.6, 117.7, 102.1, 55.4, 16.1, 15.7. FT-IR (neat, cm^{-1}) ν 3002, 2929, 2841, 1614, 1575, 1551, 1499, 1464. HRMS (CI-MS) calc. For $C_{21}H_{18}OS_4$ $[M]^+$: 414.0241; found: 414.0236.

3,6-Dimethoxy-1,2-bis(4,4'-tert-butylphenylthio)benzene (Scheme 2, compound 8)

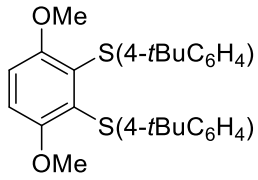


1-Chloro-2,5-dimethoxybenzene (44 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.90 mL), tetrahydrofuran (0.10 mL), 25 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 10:1 followed by hexanes/ethyl acetate 7:1), 60 mg (51 %) of a pale-yellow solid was

obtained. R_f = 0.40 (hexanes/ethyl acetate 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 4H), 6.99 (d, *J* = 8.4 Hz, 4H), 6.95 (s, 2H), 3.70 (s, 6H), 1.23 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 148.4, 134.2, 128.9, 127.6, 125.7, 113.3, 56.7, 34.4, 31.3. FT-IR (neat, cm^{-1}) ν 2941, 2783, 1552, 1518, 1401, 1333, 1249, 1181. HRMS (CI-MS) calc. For $C_{28}H_{34}O_2S_2$ $[M]^+$: 466.2000; found: 466.2007.

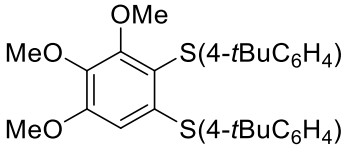
3,6-Dimethoxy-1,2-bis(4,4'-tert-butylphenylthio)benzene (Scheme 2, compound 8)



1-Bromo-2,5-dimethoxybenzene (55 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.90 mL), tetrahydrofuran (0.10 mL), 25 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 10:1 followed by hexanes/ethyl acetate 7:1), 74 mg (65 %) of a pale-yellow solid was obtained. R_f = 0.40 (hexanes/ethyl acetate 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 4H), 6.99 (d, *J* = 8.4 Hz, 4H), 6.95 (s, 2H), 3.70 (s, 6H), 1.23 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 148.4, 134.2, 128.9, 127.6, 125.7, 113.3, 56.7, 34.4, 31.3. FT-IR (neat, cm^{-1}) ν 2956, 2902, 2866, 1566, 1494, 1458, 1426, 1397, 1362, 1255. HRMS (CI-MS) calc. For $C_{28}H_{34}O_2S_2$ $[M]^+$: 466.2000; found: 466.2007.

3,4,5-Trimethoxy-1,2-bis(4,4'-tert-butylphenylthio)benzene (Scheme 2, compound 11)

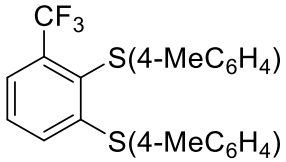


3,4,5-Trimethoxyphenyl bromide (62 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 25 °C, 47 hours. After column chromatography

(hexanes/ethyl acetate 10:1 followed by hexanes/ethyl acetate 7:1), 96 mg (78 %) of a pale-yellow solid was obtained. Rf = 0.45 (hexane/ethyl acetate 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 4H), 7.09 (d, *J* = 9.0 Hz, 4H), 6.15 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.55 (s, 3H), 1.31 (s, 9H), 1.26 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 155.0, 152.2, 148.4, 142.3, 140.6, 134.5, 134.3, 129.9, 126.7, 126.6, 126.0, 115.9, 106.9, 61.6, 61.1, 55.7, 34.8, 34.4, 31.4, 31.3. FT-IR (neat, cm^{-1}) ν 2959, 2739, 2918, 1568, 1549, 1471, 1460, 1436, 1422.

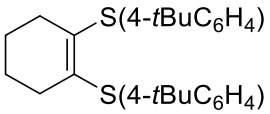
3-Trifluoromethyl-1,2-bis(4,4'-methylphenylthio)benzene (Scheme 2, compound 13)



In a 1-dram vial 1-bromo-3-trifluoromethylbenzene (56 mg, 0.25 mmol), di(*p*-tolyl) disulfide (74 mg, 0.3 mmol), and diethyl ether/THF mixture (49/1, 0.5 mL) were mixed. In a separate 2-dram vial, LDAM (182 mg, 0.625 mmol) and diethyl ether/THF mixture (49/1, 1.5 mL) were mixed. The solution of 1-dram vial was then added to base solution via syringe and stirred at 50 °C for 47 hours. Reaction was quenched with methanol (0.50 mL). After column chromatography (hexanes), 70 mg (72 %) of a white solid was obtained. Rf = 0.50 (hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.33-7.28 (m, 3H), 7.25-7.18 (m, 5H), 6.91-6.89 (m, 1H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 139.5, 138.6, 136.2, 134.6, 132.6, 130.8, 130.6, 129.2, 128.2 (q, *J* = 32.8 Hz), 128.1, 128.0, 127.1 (q, *J* = 2.8 Hz), 123.9 (q, *J* = 271.7 Hz), 123.6 (q, *J* = 3.9 Hz), 21.4, 21.3. ^{19}F NMR (376 MHz) δ -62.4. FT-IR (neat, cm^{-1}) ν 2922, 1900, 1592, 1318, 1253, 1104, 1079, 1035. HRMS (CI-MS) calc. For $C_{21}H_{17}F_3S_2$ $[M]^+$: 390.0723; found: 390.0724.

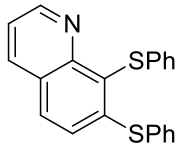
1,2-Bis(4,4'-tert-butylphenylsulfanyl)cyclohexene (Scheme 3, compound 15)



1-Cyclohexenyl triflate[3] (58 mg, 0.25 mmol), bis(4-tert-butylphenyl)disulfide[9] (99 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes), 96 mg (94 %) of a yellow solid was obtained. R_f = 0.30 (hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 8H), 2.22 – 2.13 (m, 4H), 1.66 – 1.56 (m, 4H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 133.4, 131.6, 130.5, 126.0, 34.6, 32.2, 31.4, 23.6. FT-IR (neat, cm^{-1}) ν 2957, 2903, 2865, 1592, 1566, 1489, 1463, 1427, 1393. HRMS (CI-MS) calc. For $C_{26}H_{34}S_2$ $[M]^+$: 410.2102; found: 410.2105.

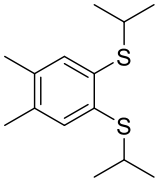
6,7-Bis(phenylthio)quinoline (Scheme 3, compound 17)



Quinolin-8-yl trifluoromethanesulfonate[13] (69 mg, 0.25 mmol), diphenyl disulfide (66 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.96 mL), tetrahydrofuran (0.04 mL), 0 °C, 47 hours. After column chromatography (hexanes/ethyl acetate 10:1 followed by (hexanes/ethyl acetate 6:1 and then (hexanes/ethyl acetate 1:1), 25 mg (29 %) of a yellow solid was obtained. R_f = 0.30 hexanes/ethyl acetate 10:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.45 – 7.42 (m, 3H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.18 – 7.12 (m, 4H), 7.10 – 7.06 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 150.6, 149.2, 137.1, 136.6, 135.5, 132.5, 129.91, 129.89, 129.4, 128.8, 127.2, 126.7, 126.3, 125.4, 125.3, 120.9. FT-IR (neat, cm^{-1}) ν 3060, 3034, 2914, 1597, 1577, 1474, 1440, 1435. HRMS (APCI-MS) calc. For $C_{21}H_{15}NS_2$ $[M+H]^+$: 346.0719; found: 346.0722.

4,5-Dimethyl-1,2-bis(isopropylthio)benzene (Scheme 3, Compound 19)



3,4-Dimethylphenyltriflate (64 mg, 0.25 mmol), diisopropyl disulfide (45 mg, 0.3 mmol), LDAM (146 mg, 0.5 mmol), diethyl ether (1.0 mL), tetrahydrofuran (1.0 mL), 23 °C, 7 hours. After column chromatography (hexanes/toluene 10:1), 36 mg (56 %) of a colorless oil was obtained. R_f = 0.55 (hexanes/toluene 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 3.44 (septet, *J* = 6.9 Hz, 2H), 2.21 (s, 6H), 1.29 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.4, 143.6, 132.8, 37.4, 23.1, 19.5. FT-IR (neat, cm^{-1}) ν 2959, 2920, 2862, 1588, 1447, 1380, 1236, 1152, 1050, 941, 883. HRMS (ESI-MS) calc. For $C_{14}H_{22}S_2$ $[M+1]^+$: 255.1236; found: 255.1245.

Base Comparison (Scheme 4):

In a 1-dram vial 1-bromo-3-trifluoromethylbenzene (56 mg, 0.25 mmol), di(*p*-tolyl) disulfide (74 mg, 0.3 mmol), and diethyl ether/THF mixture (49/1, 0.5 mL) were combined. In a separate 2-dram vial, LDAM (182 mg, 0.625 mmol) and diethyl ether/THF mixture (49/1, 1.5 mL) were combined. The solution of 1-dram vial was then added to base solution via syringe and stirred at 50 °C for 47 hours.

The same reaction was conducted with TMPLi (92 mg, 0.625 mmol).

Reactions were quenched with methanol (0.50 mL). The crude mixtures were analyzed by ^{19}F-NMR using fluorobenzene (23.6 μL, 0.25 mmol) as the internal standard. ^{1}H NMR analysis of the crude reaction mixture showed 77% and 42% yield of **13** for LDAM and LiTMP bases, respectively.

References.

1- M. Mesgar, J. Nguyen-Le, O. Daugulis, *J. Am. Chem. Soc.* 2018, **140**, 13703.

2- E. V. Krumkalns, W. Pfeifer, *J. Med. Chem.* 1968, **11**, 1103.

3- F. T. Toledo, H. Marques, J. V. Comasseto, C. Raminelli, *Tetrahedron Lett.* 2007, **48**, 8125.

4- A. J. Kendall, L. N. Zakharov, D. R. Tyler, *Inorg. Chem.* 2016, **55**, 3079.

5- M. Novi, G. Garbarino, G. Petrillo, C. Dell'Erba, *J. Chem. Soc., Perkin Trans. 2* 1987, 623.

6- H. Sajiki, A. Mori, T. Mizusaki, T. Ikawa, T. Maegawa, K. Hirota, *Org. Lett.* 2006, **8**, 987.

7- M. Novi, G. Garbarino, G. Petrillo, C. Dell'Erba, *Tetrahedron* 1990, **46**, 2205.

8- E. T. Akin, M. Erdogan, A. Dastan, N. Saracoglu, *Tetrahedron* 2017, **73**, 5537.

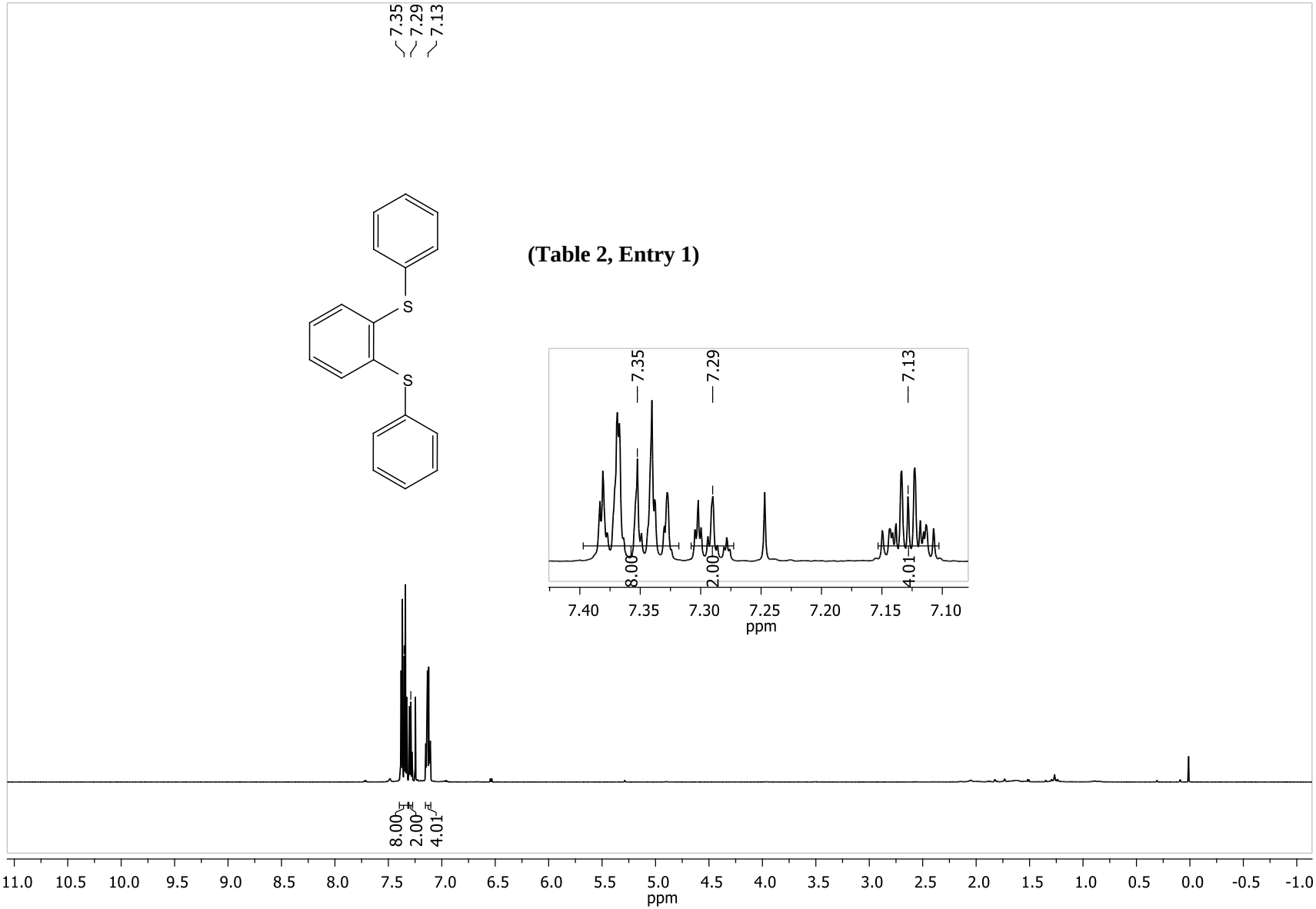
9- G. W. Kabalka, M. S. Reddy, M-L Yao, *Tetrahedron Lett. 2009*, **50**, 7340.

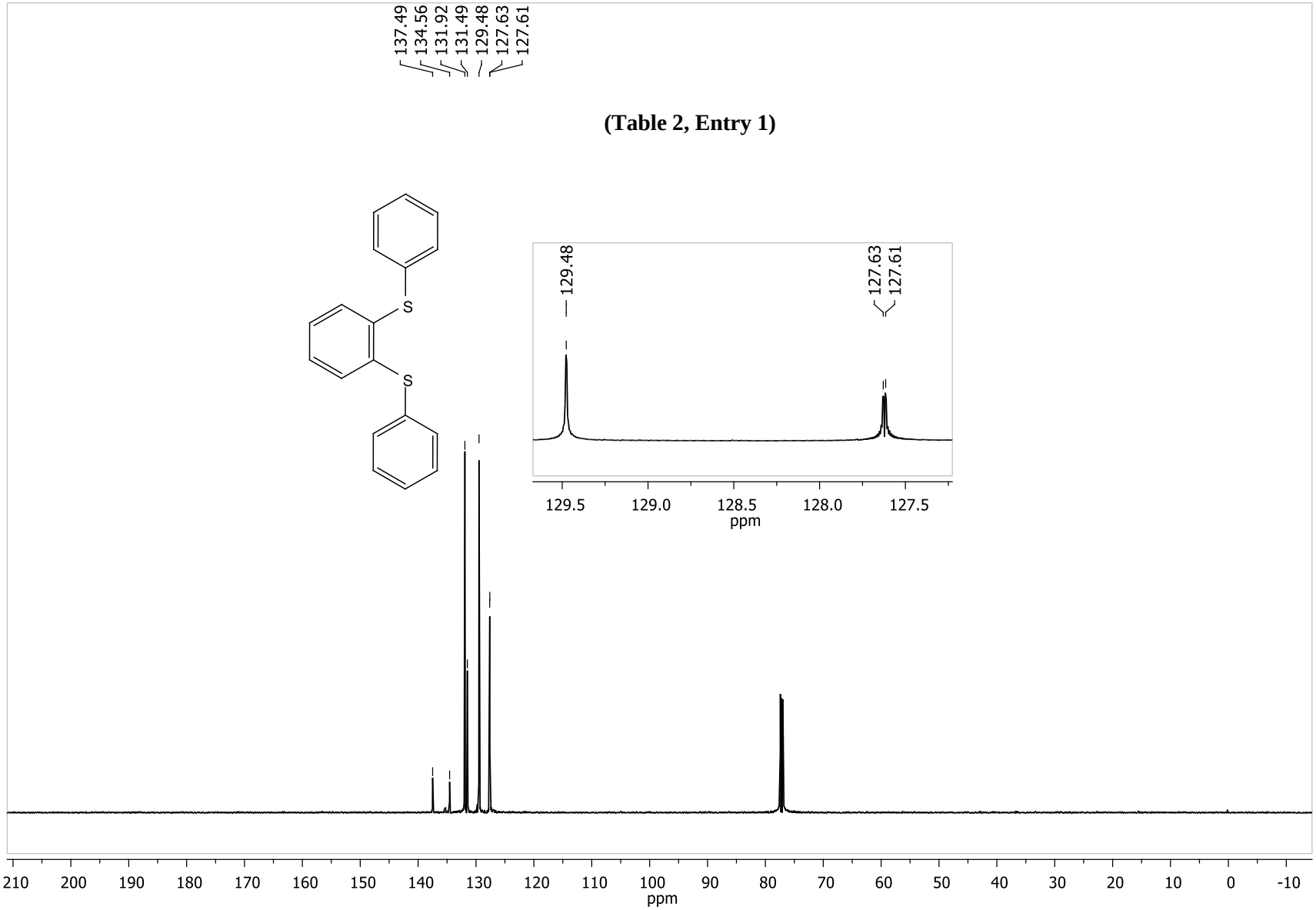
10- M. Mesgar, O. Daugulis, *Org. Lett.* 2016, **18**, 3910.

11- E. V. Vinogradova, N. H. Park, B. P. Fors, S. L. Buchwald, *Org. Lett.* 2013, **15**, 1394.

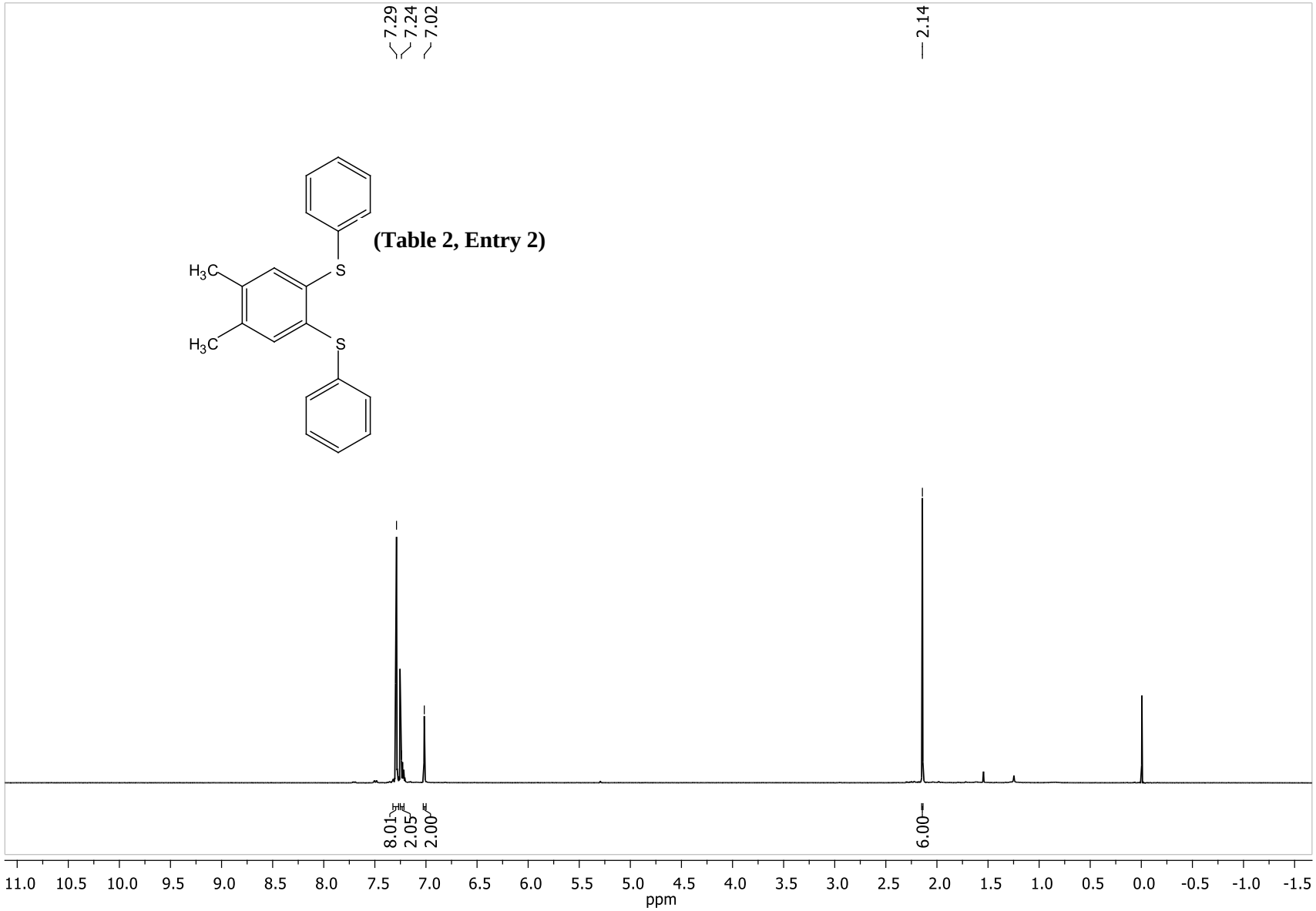
12- A. Ficks, C. Sibbald, S. Ojo, R. W. Harrington, W. Clegg, L. J. Higham, *Synthesis* 2013, **45**, 265.

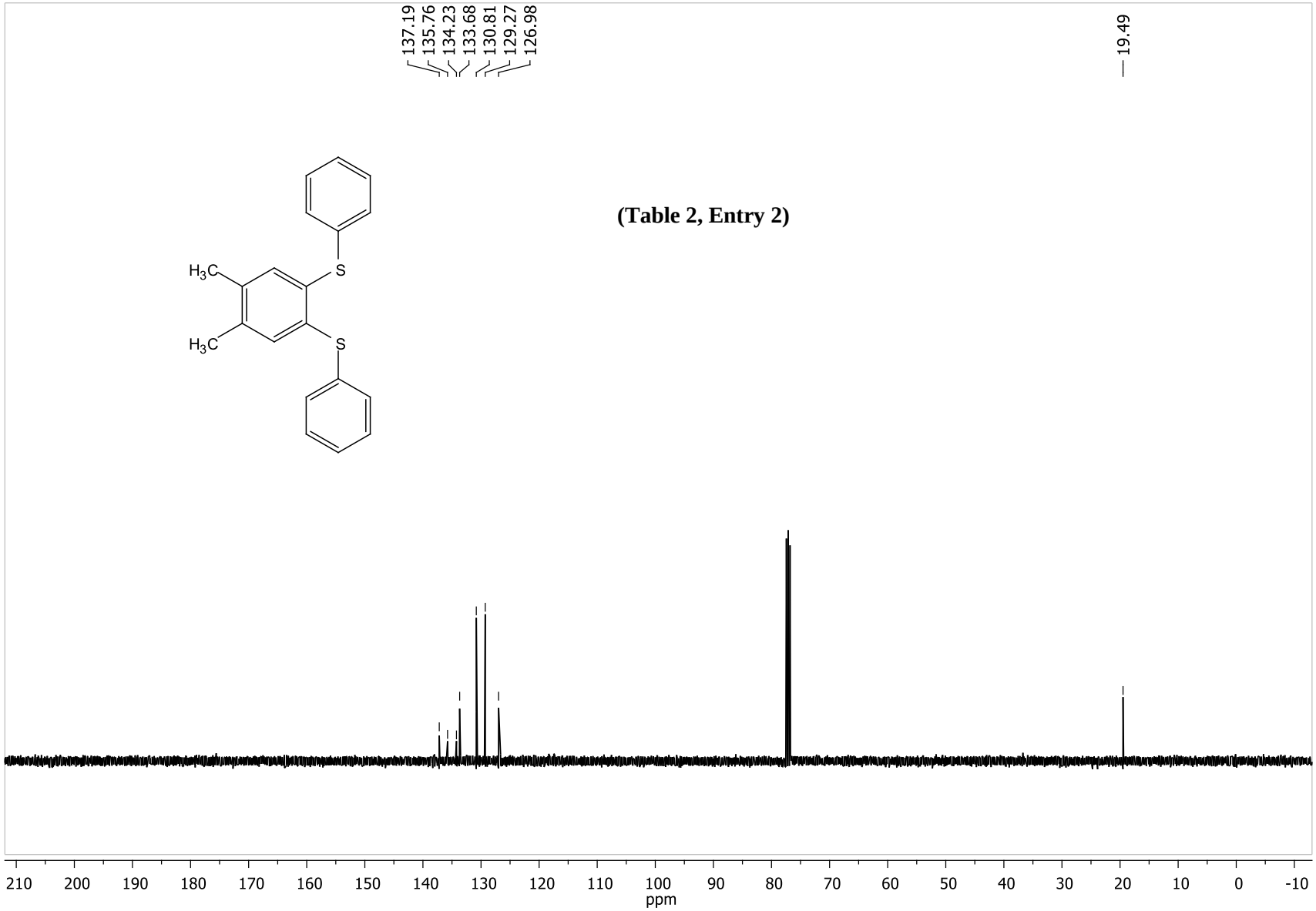
13- J.-C. Hsieh, Y.-H. Chu, K. Muralirajan, C.-H. Cheng, *Chem. Commun.* 2017, **53**, 11584.

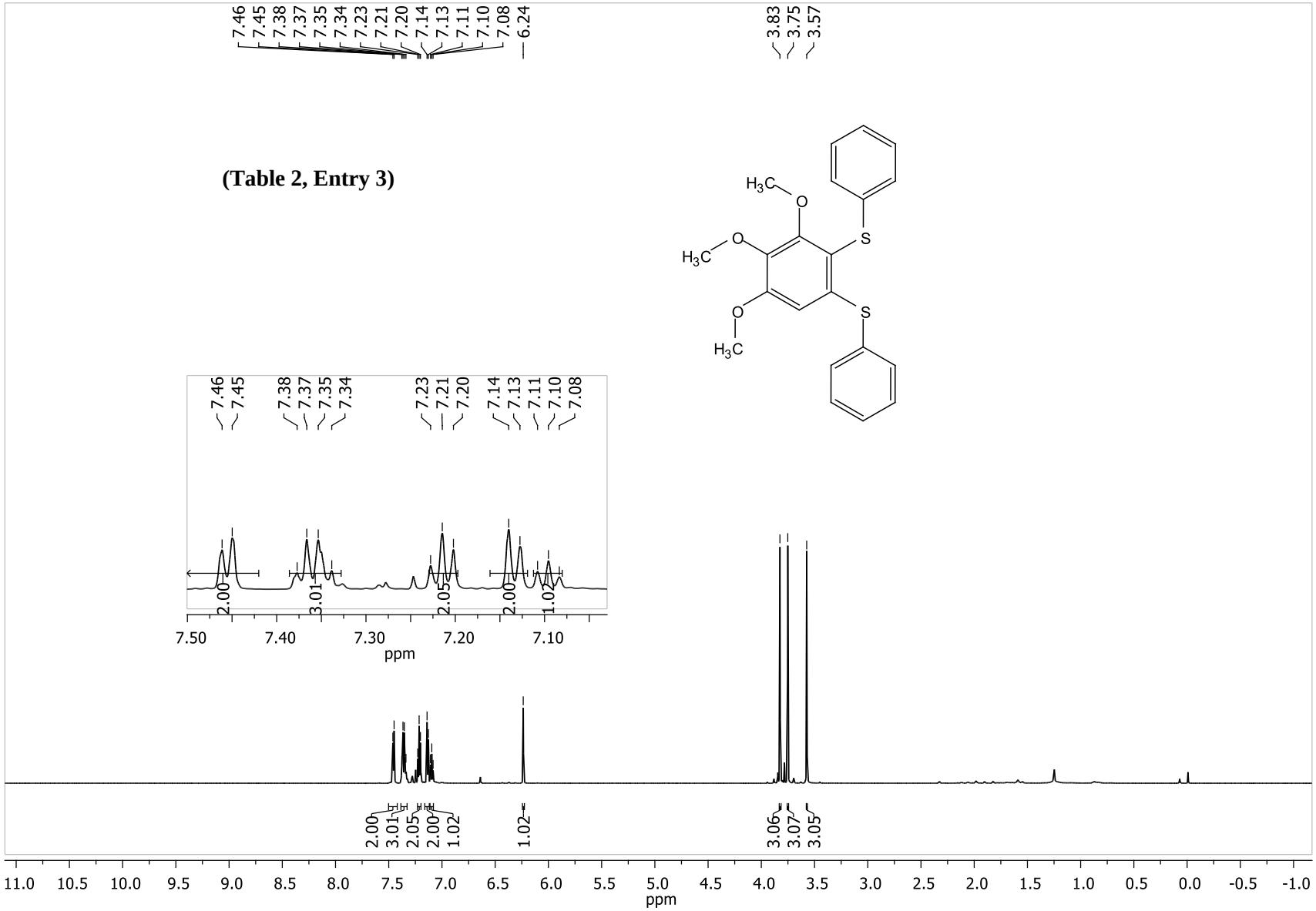

7.35
7.29
7.13
S
S
(Table 2, Entry 1)
7.35
7.29
7.13
8.00
2.00
4.01
7.40 7.35 7.30 7.25 7.20 7.15 7.10
ppm
8.00
2.00
4.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

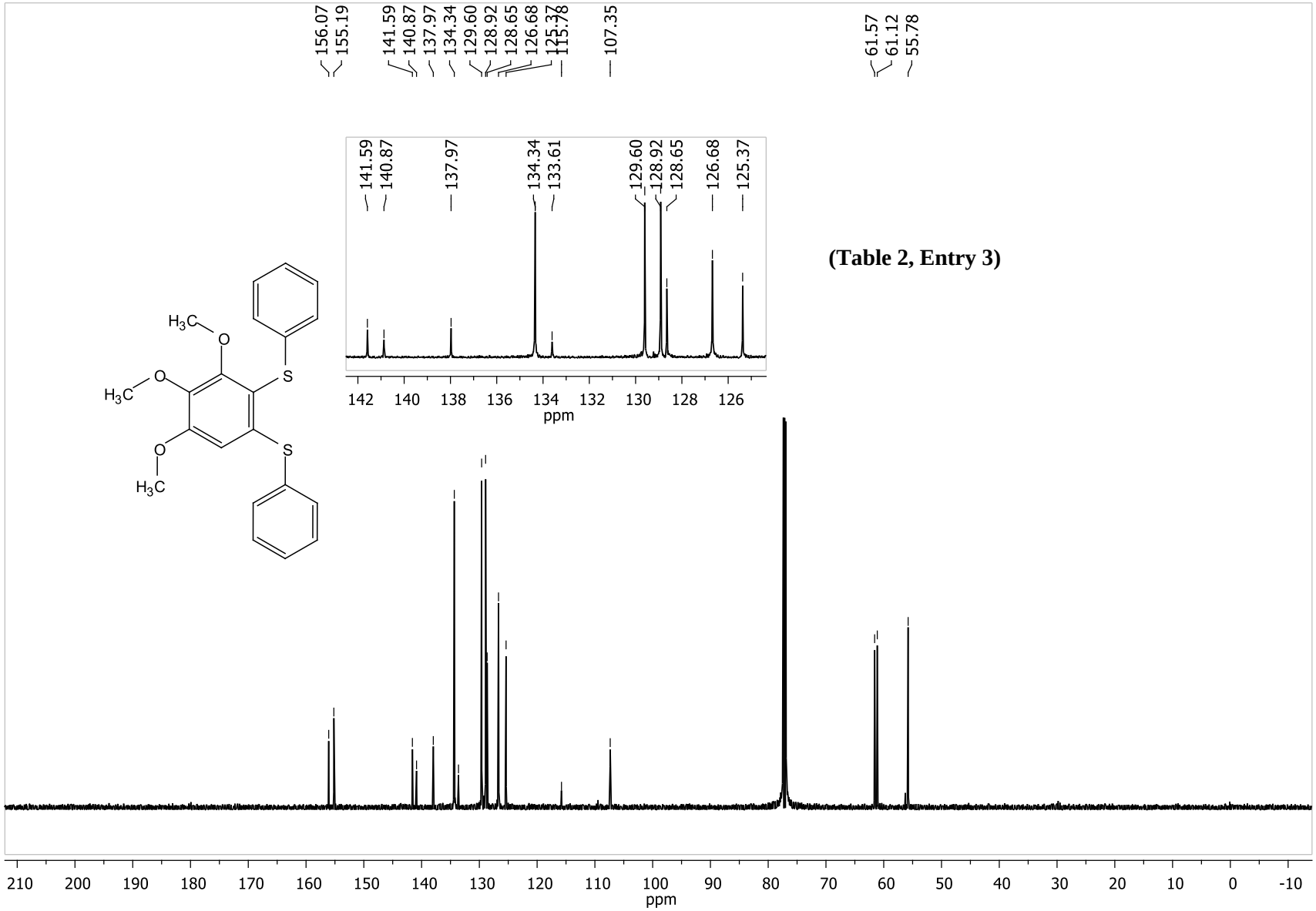


(Table 2, Entry 1)


7.29
7.24
7.02
2.14
H3C
S
H3C
S
(Table 2, Entry 2)
8.01
2.05
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 -1.5
ppm

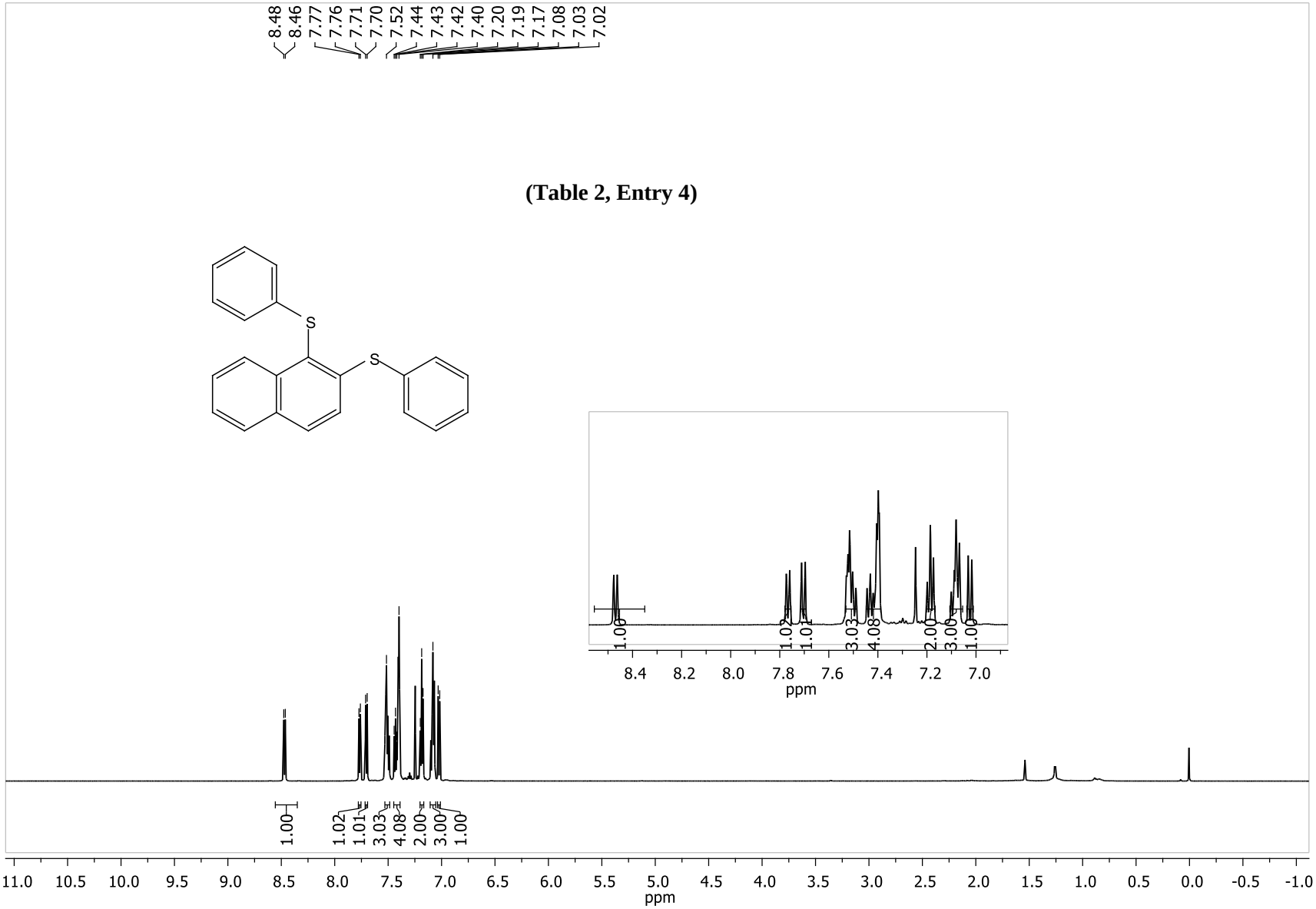

137.19
135.76
134.23
133.68
130.81
129.27
126.98
19.49
H3C
S
H3C
S
(Table 2, Entry 2)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

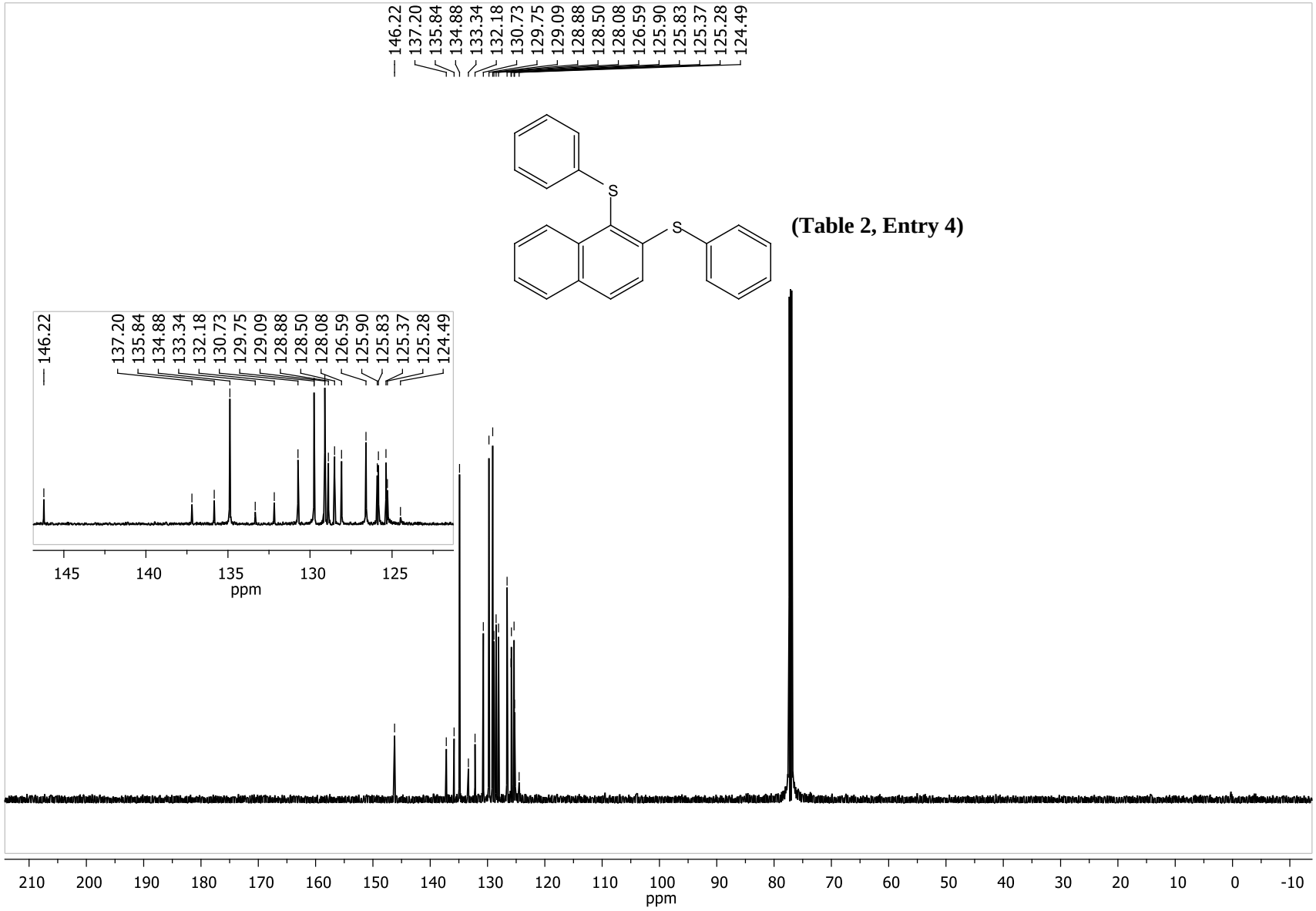

7.46
7.45
7.38
7.37
7.35
7.34
7.23
7.21
7.20
7.14
7.13
7.11
7.10
7.08
6.24
3.83
3.75
3.57
(Table 2, Entry 3)
H3C
O
O
H3C
S
O
H3C
S
2.00
3.01
2.05
2.00
1.02
7.50
7.40
7.30
7.20
7.10
ppm
1.02
3.06
3.07
3.05
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

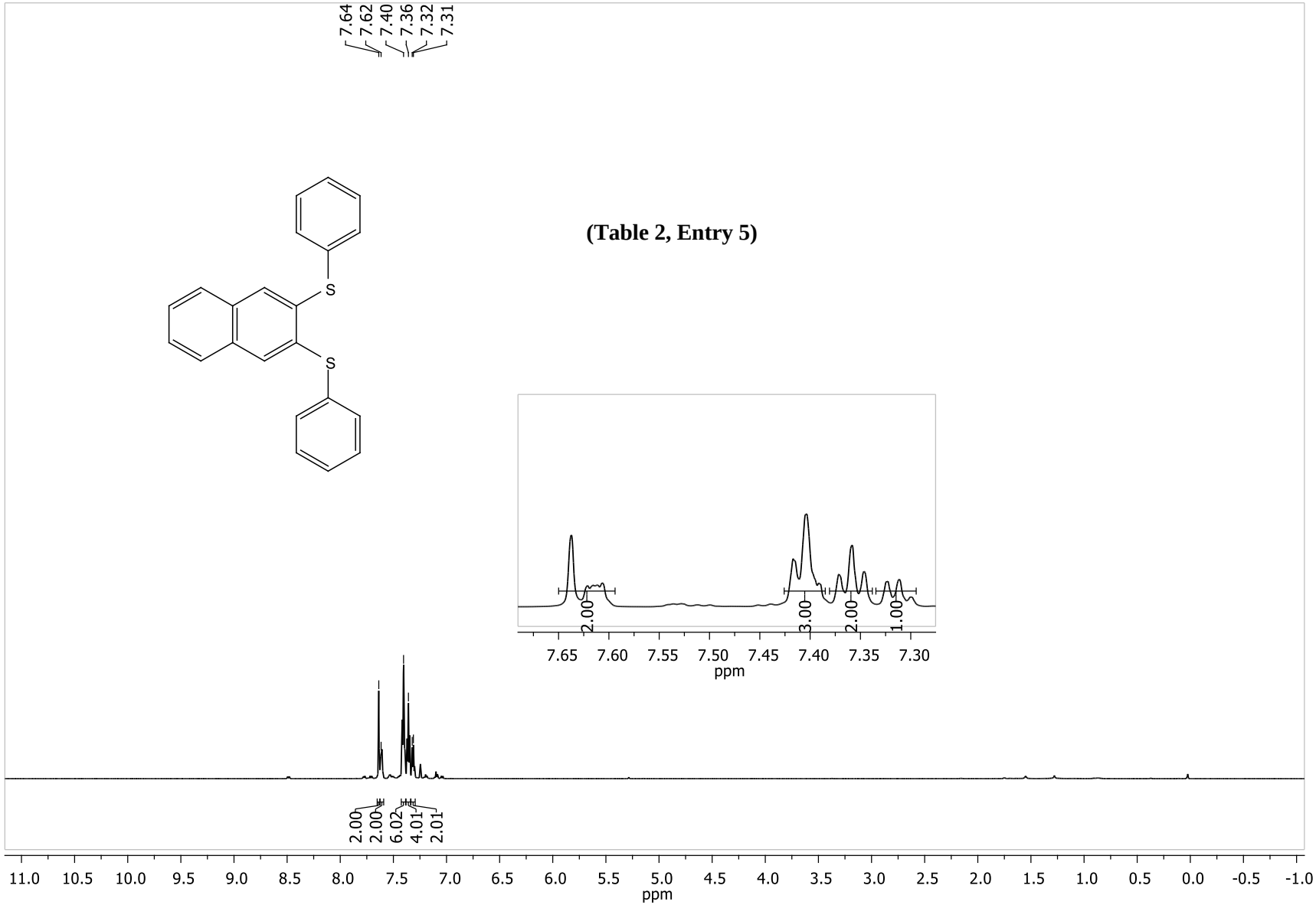


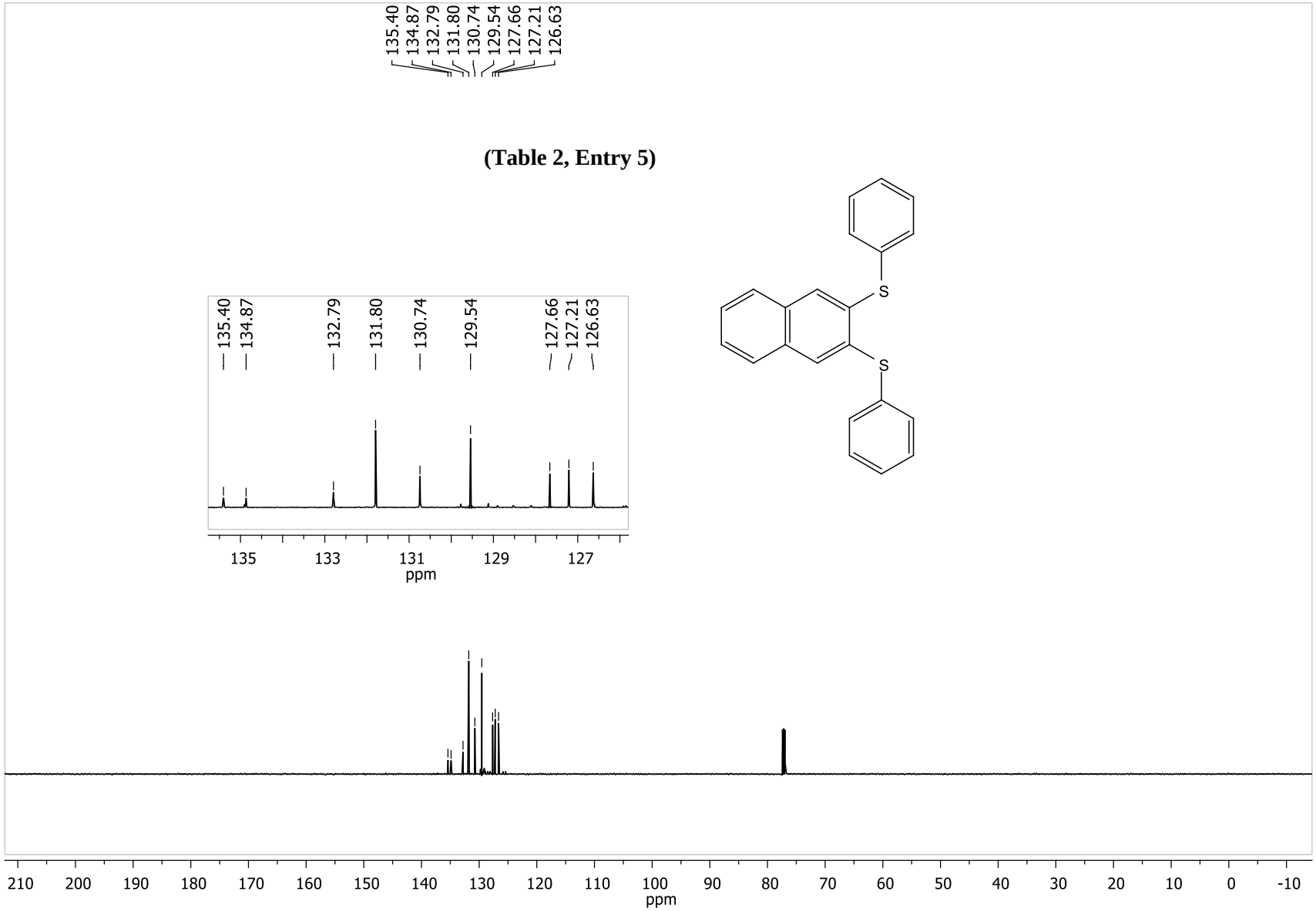
(Table 2, Entry 3)

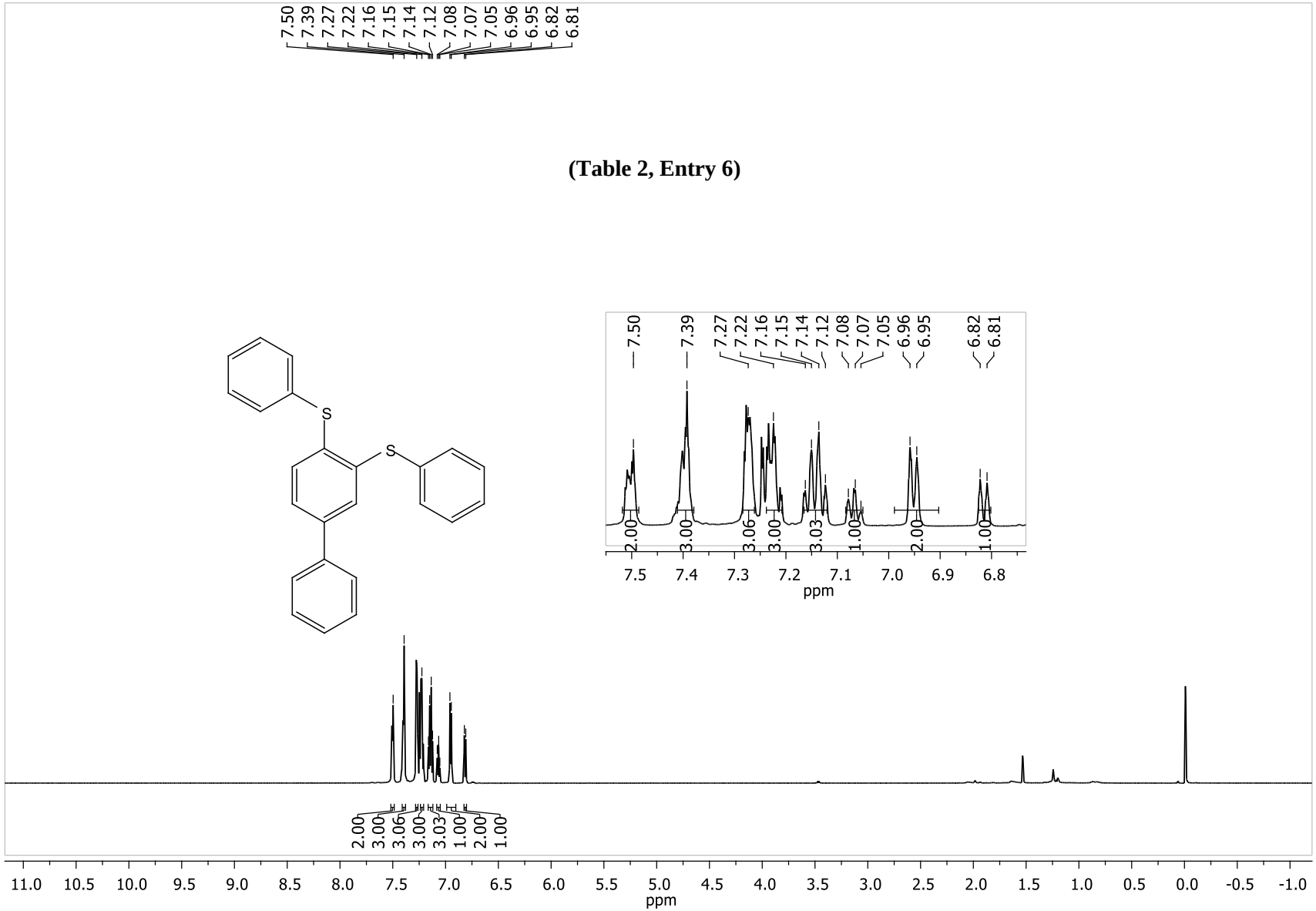
(Table 2, Entry 4)



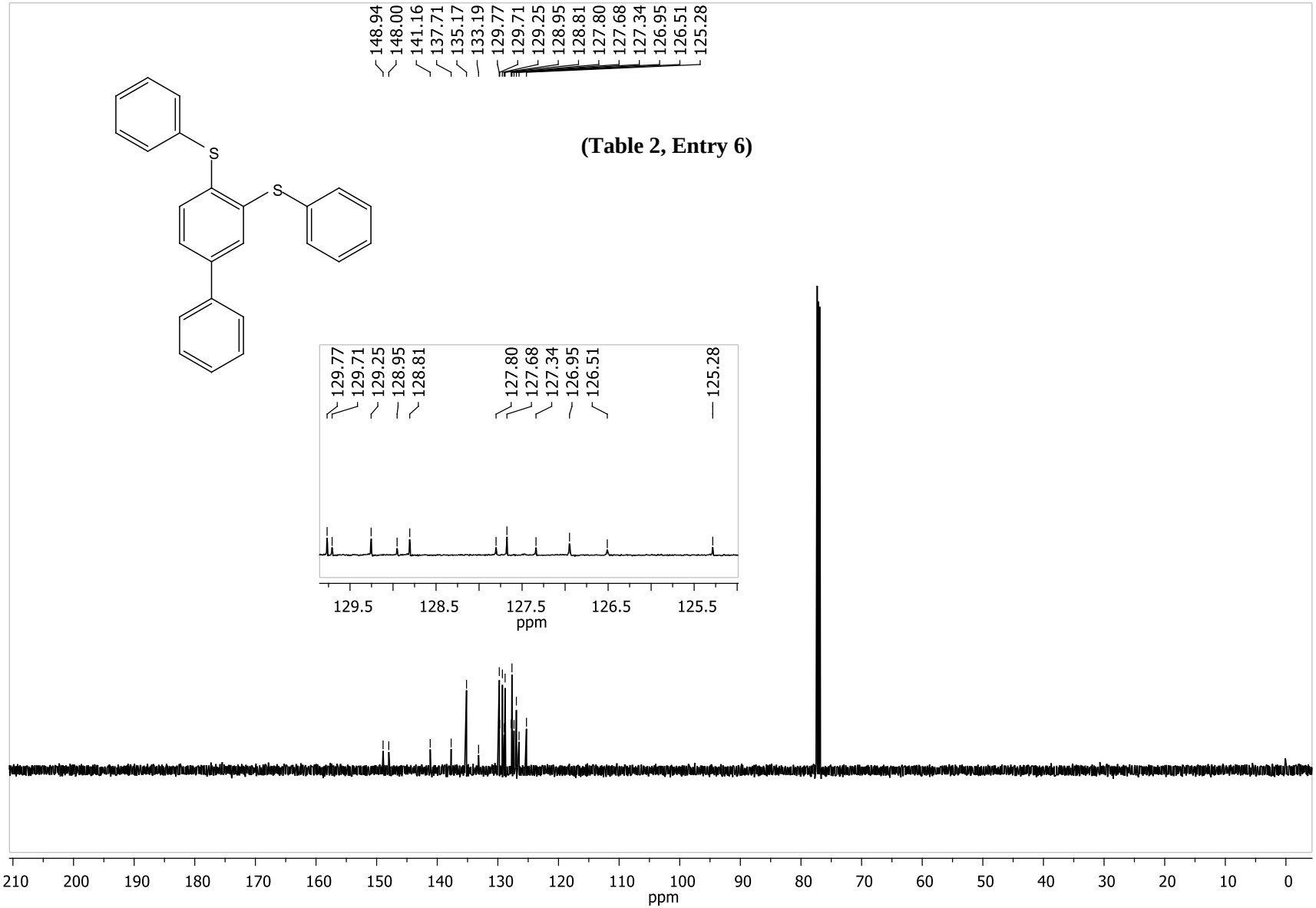

146.22
137.20
135.84
134.88
133.34
132.18
130.73
129.75
129.09
128.88
128.50
128.08
126.59
125.90
125.83
125.37
125.28
124.49
S
S
(Table 2, Entry 4)
145
140
135
130
125
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

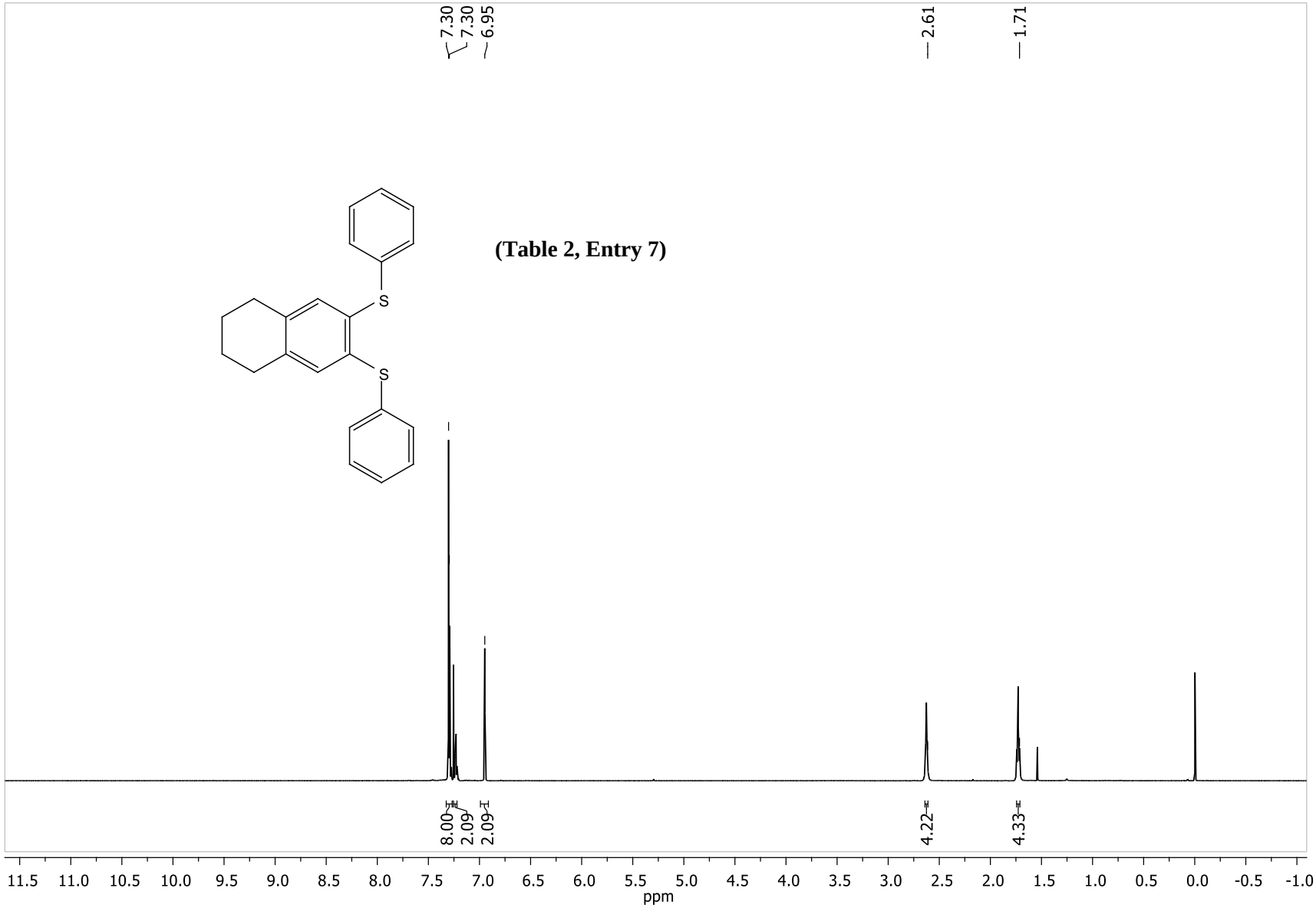

7.64
7.62
7.40
7.36
7.32
7.31
S
S
(Table 2, Entry 5)
2.00
3.00
2.00
1.00
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
ppm
2.00
2.00
6.02
4.01
2.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

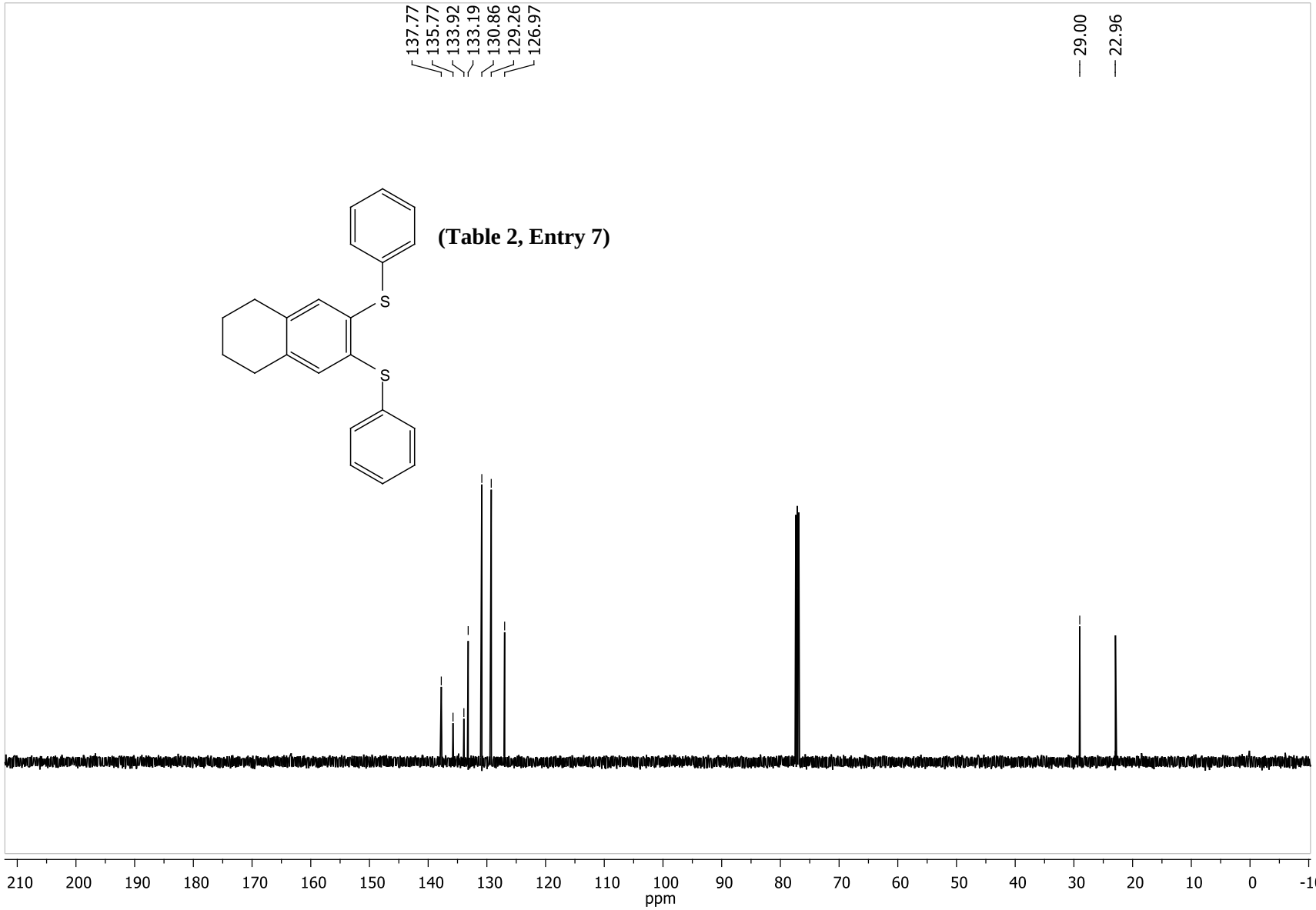

135.40
134.87
132.79
131.80
130.74
129.54
127.66
127.21
126.63
(Table 2, Entry 5)
S
S
135
133
131
129
127
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

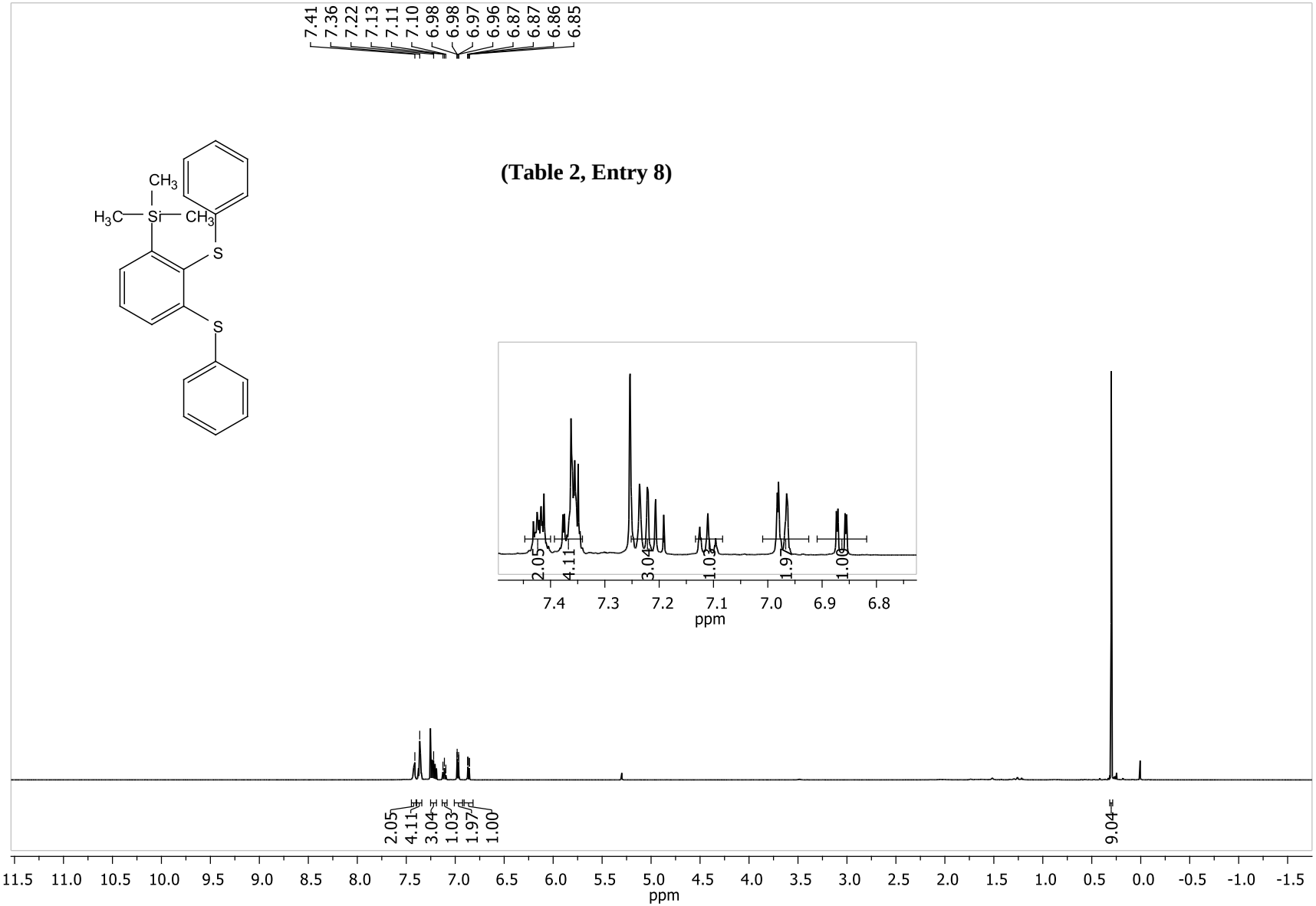


(Table 2, Entry 6)

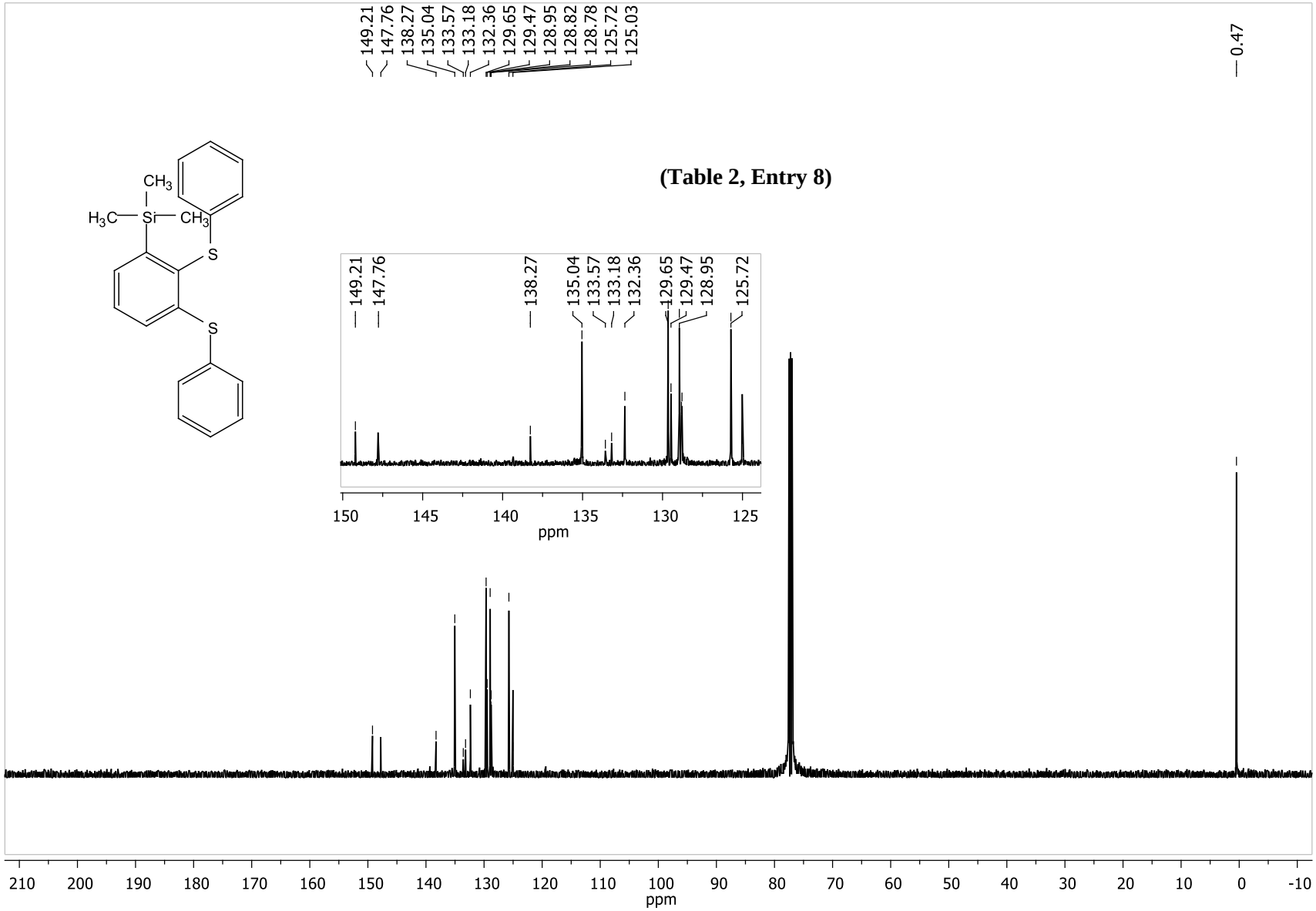

148.94
148.00
141.16
137.71
135.17
133.19
129.77
129.71
129.25
128.95
128.81
127.80
127.68
127.34
126.95
126.51
125.28
S
S
(Table 2, Entry 6)
129.5
128.5
127.5
126.5
125.5
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.30
7.30
6.95
2.61
1.71
S
S
(Table 2, Entry 7)
8.00
2.09
2.09
4.22
4.33
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

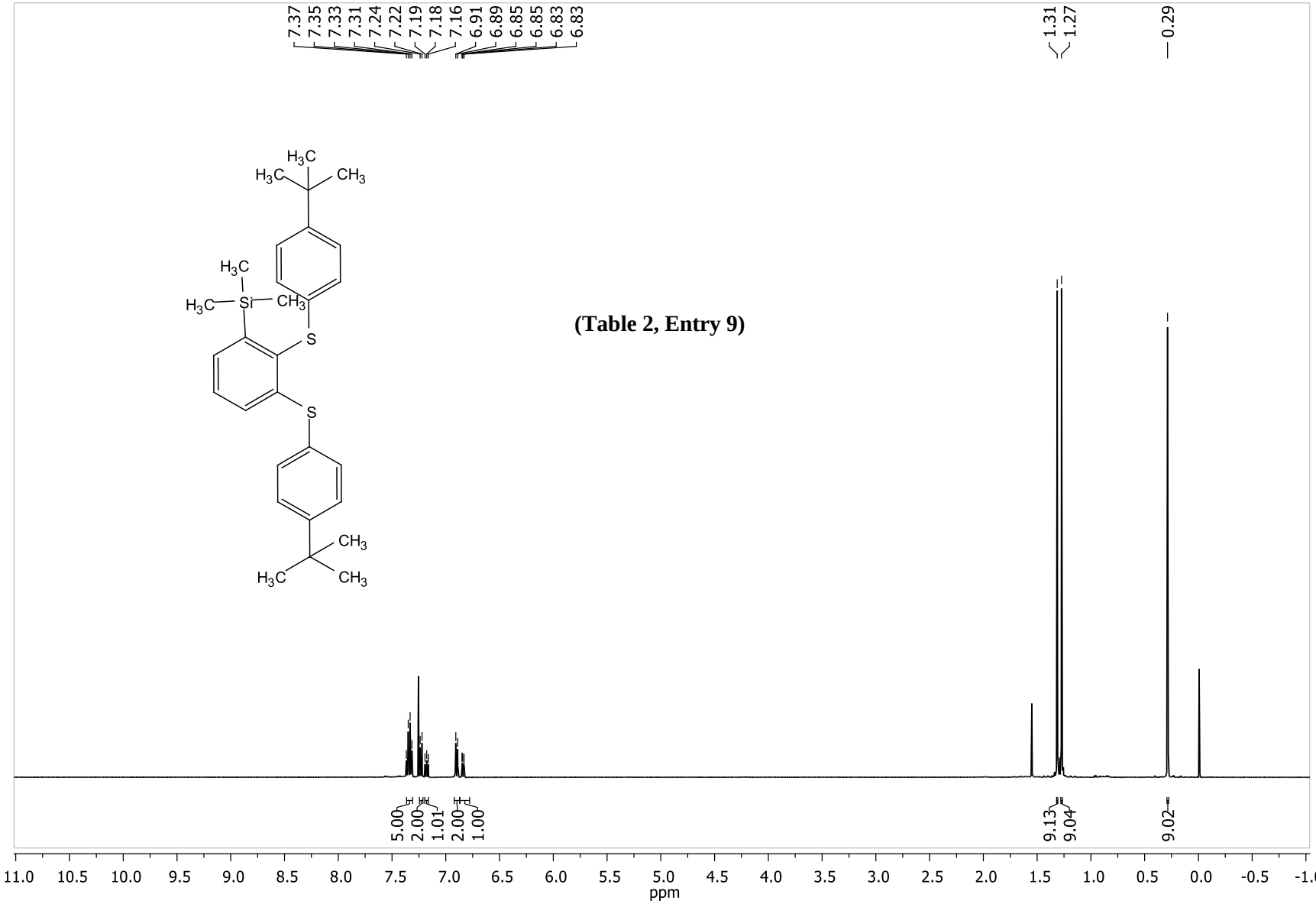

137.77
135.77
133.92
133.19
130.86
129.26
126.97
29.00
22.96
S
S
(Table 2, Entry 7)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

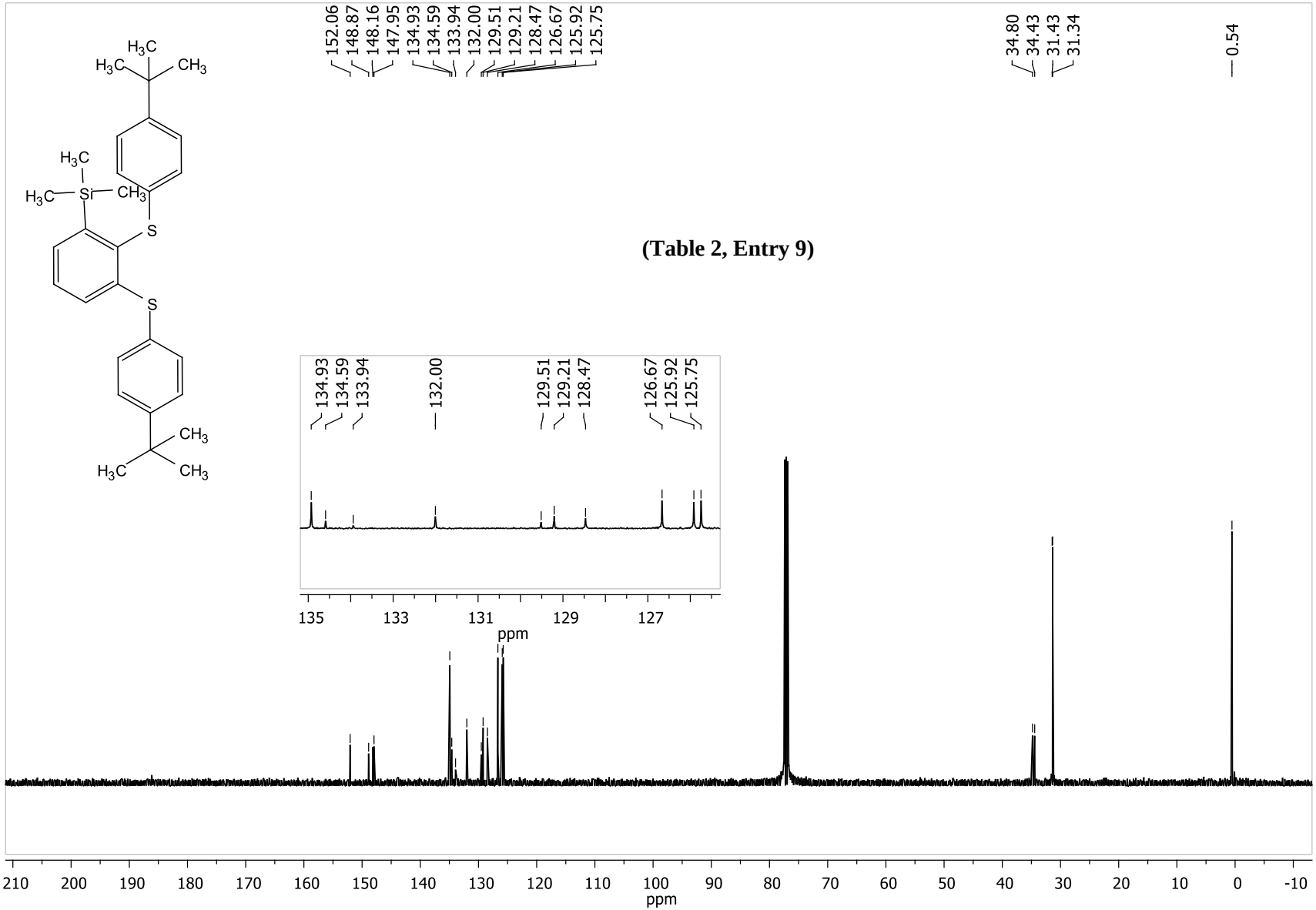


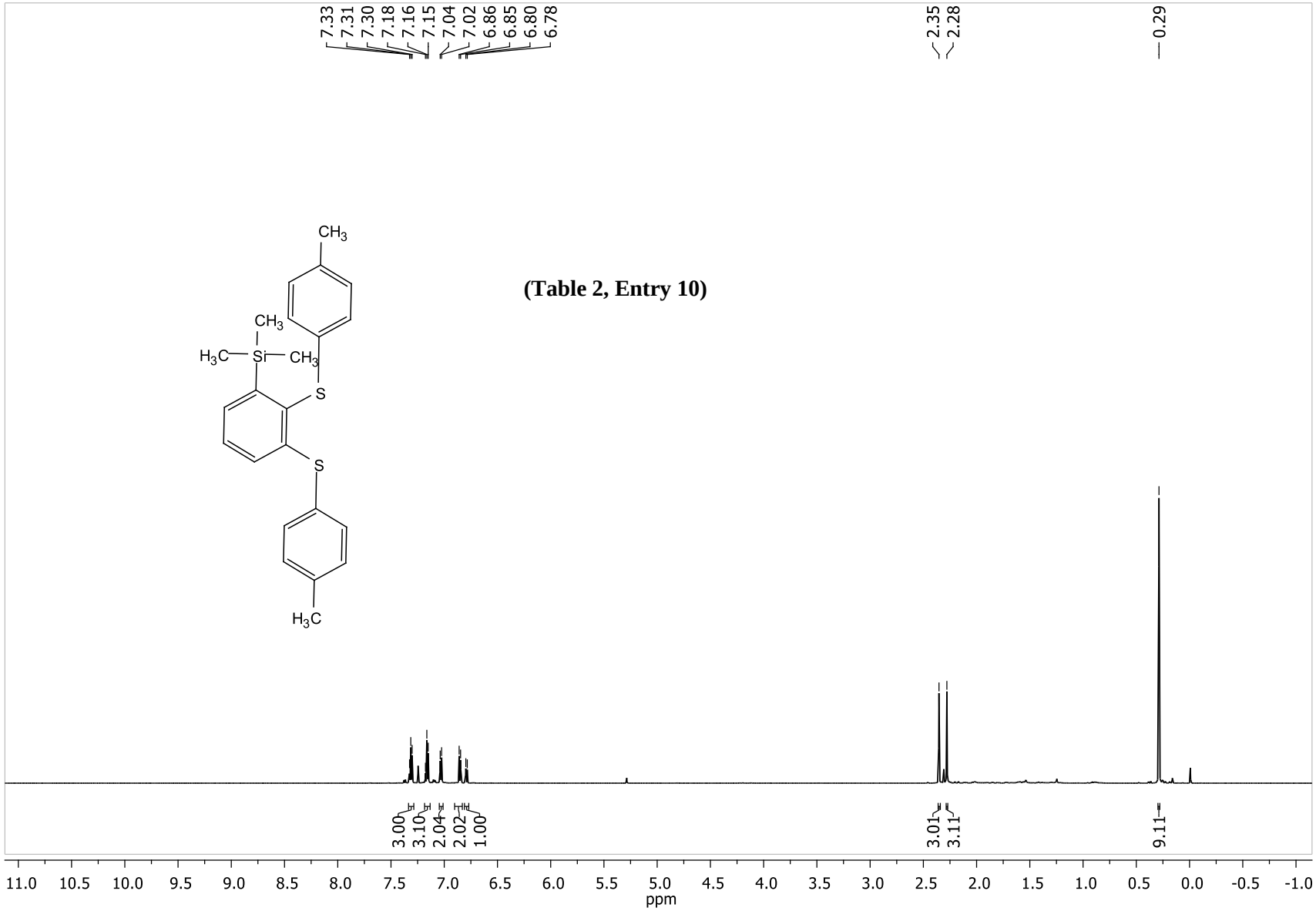
(Table 2, Entry 8)



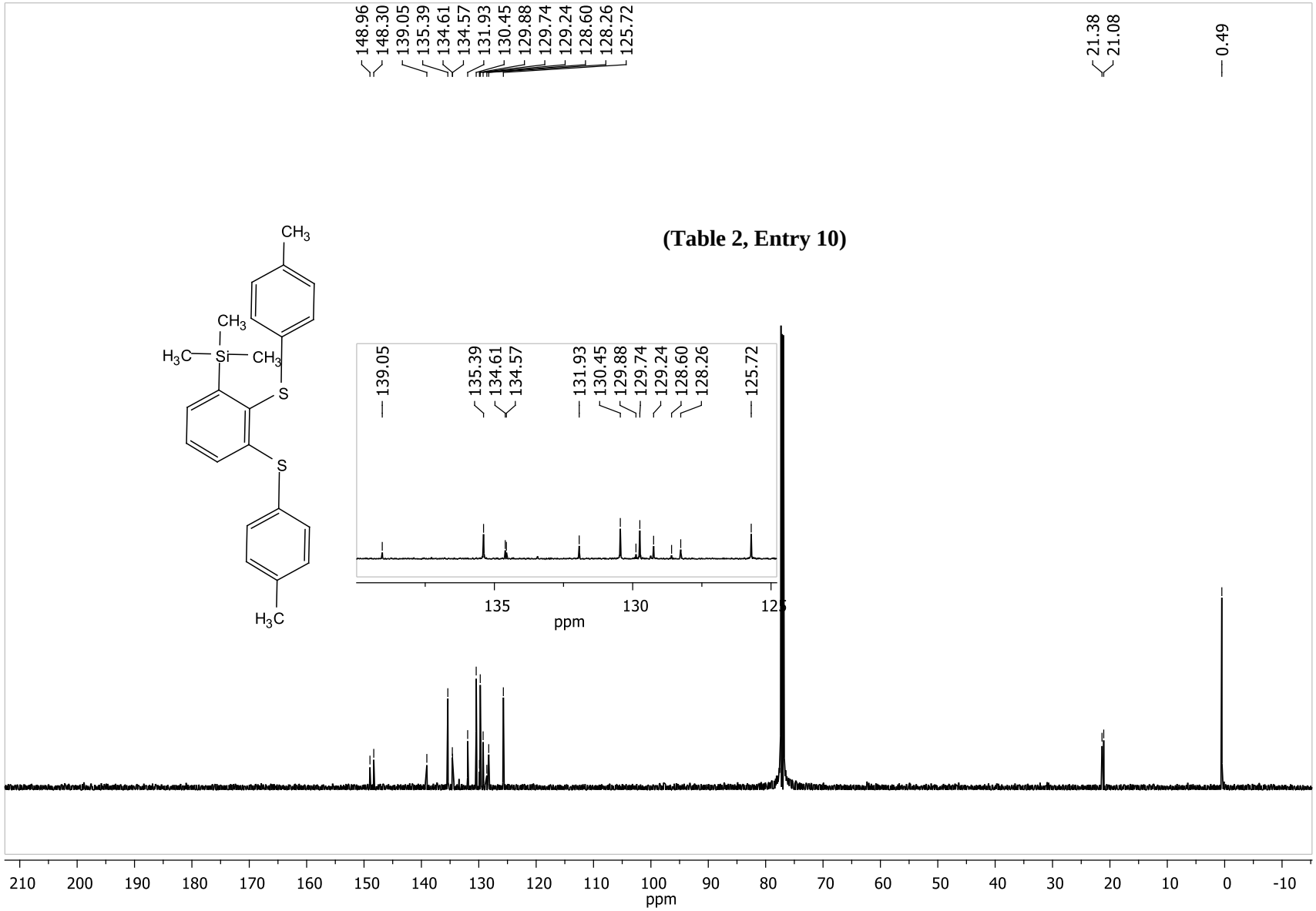
(Table 2, Entry 8)

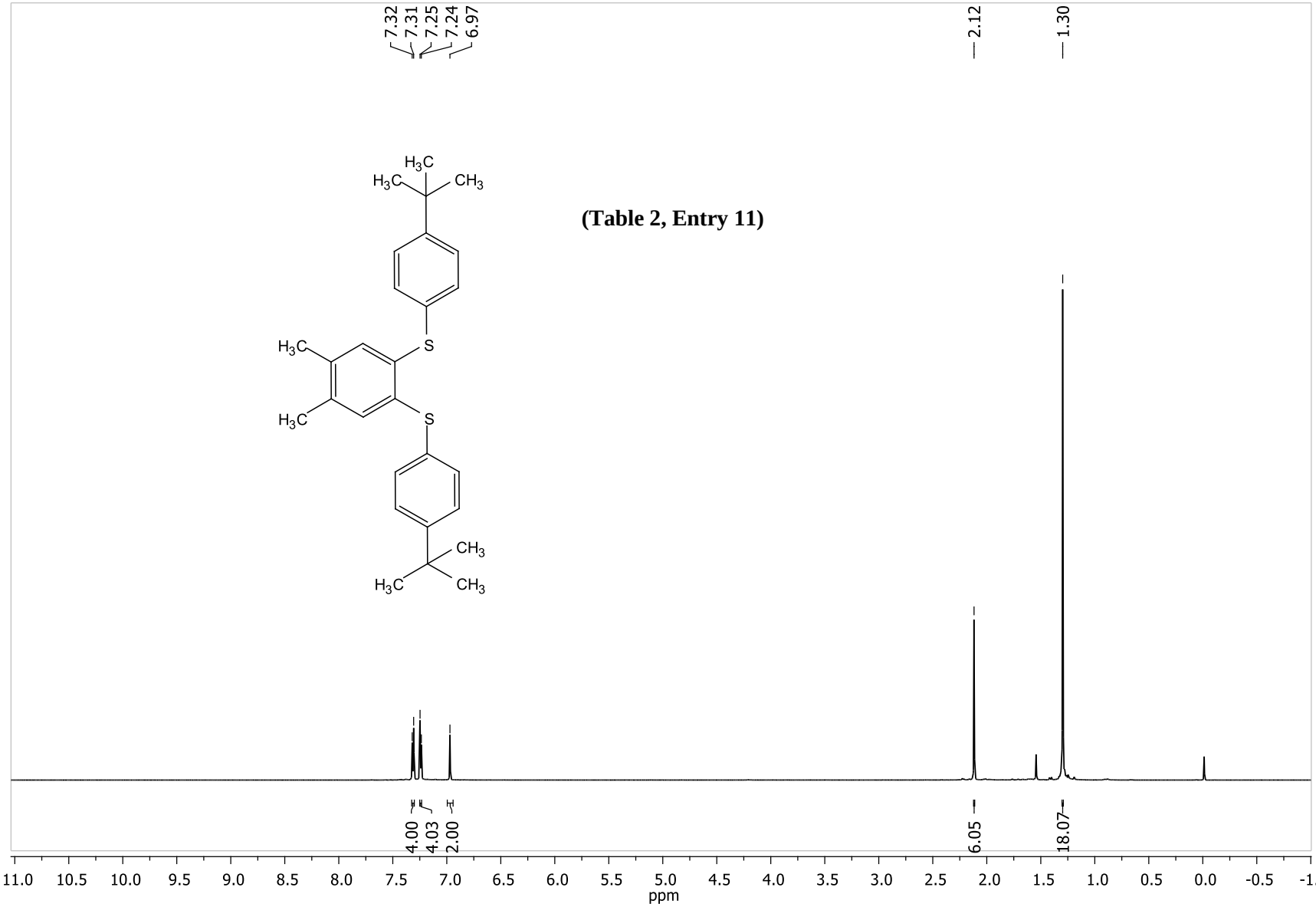

7.37
7.35
7.33
7.31
7.24
7.22
7.19
7.18
7.16
6.91
6.89
6.85
6.85
6.83
6.83
1.31
1.27
0.29
H3C
H3C
CH3
H3C
H3C
Si
CH3
S
S
CH3
H3C
CH3
(Table 2, Entry 9)
5.00
2.00
1.01
2.00
1.00
9.13
9.04
9.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

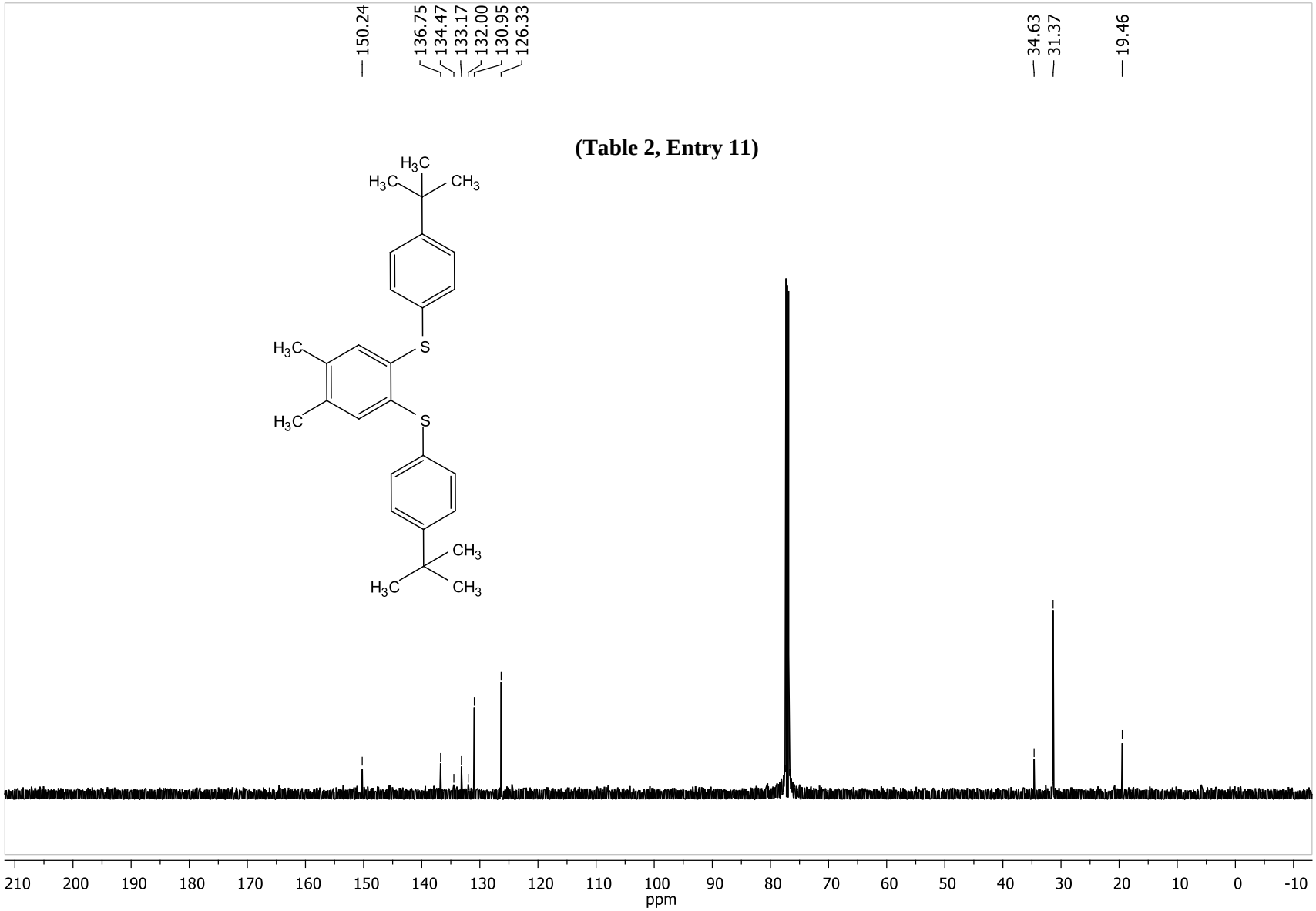

152.06
148.87
148.16
147.95
134.93
134.59
133.94
132.00
129.51
129.21
128.47
126.67
125.92
125.75
34.80
34.43
31.43
31.34
0.54
(Table 2, Entry 9)
134.93
134.59
133.94
132.00
129.51
129.21
128.47
126.67
125.92
125.75
135
133
131
129
127
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

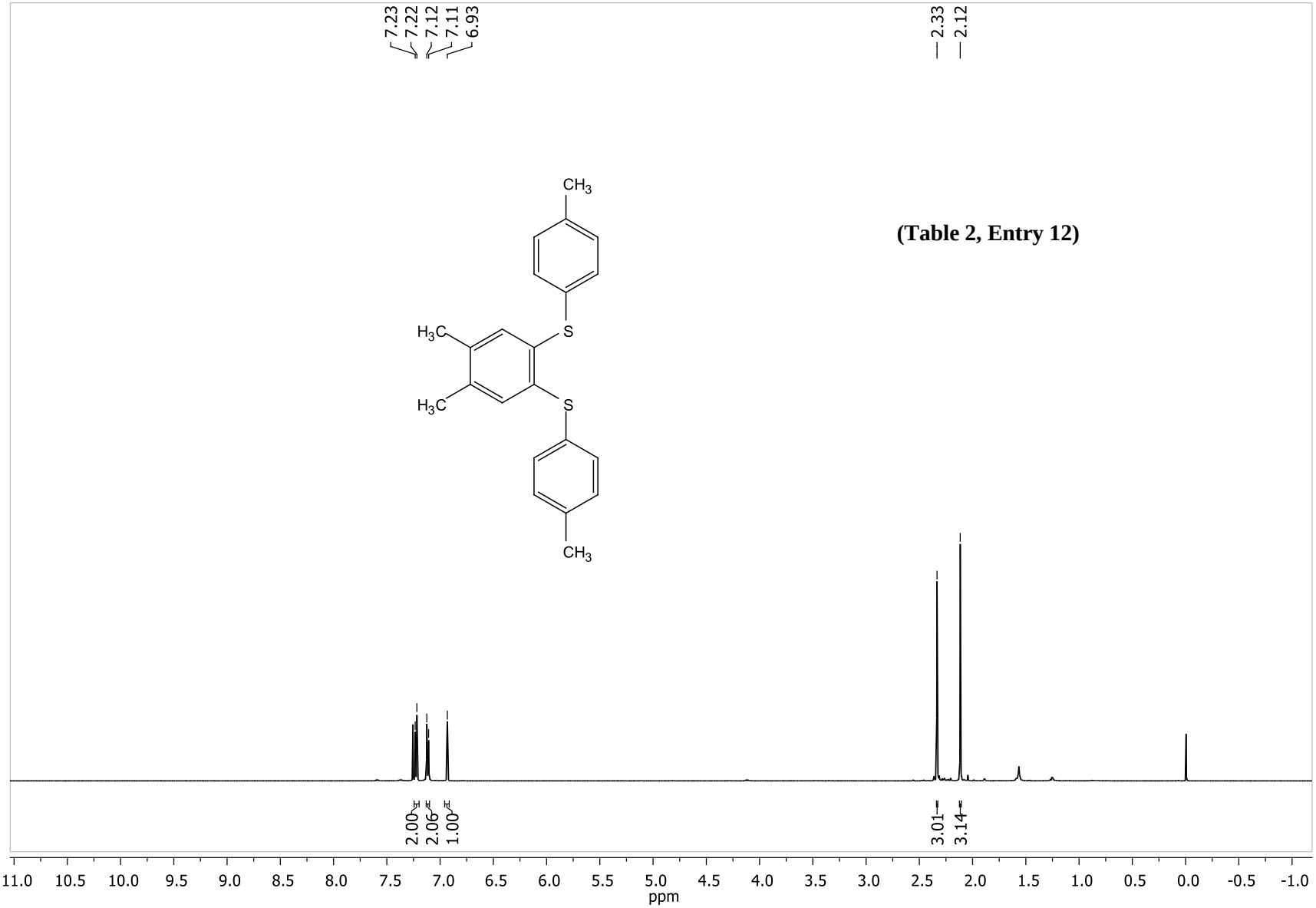


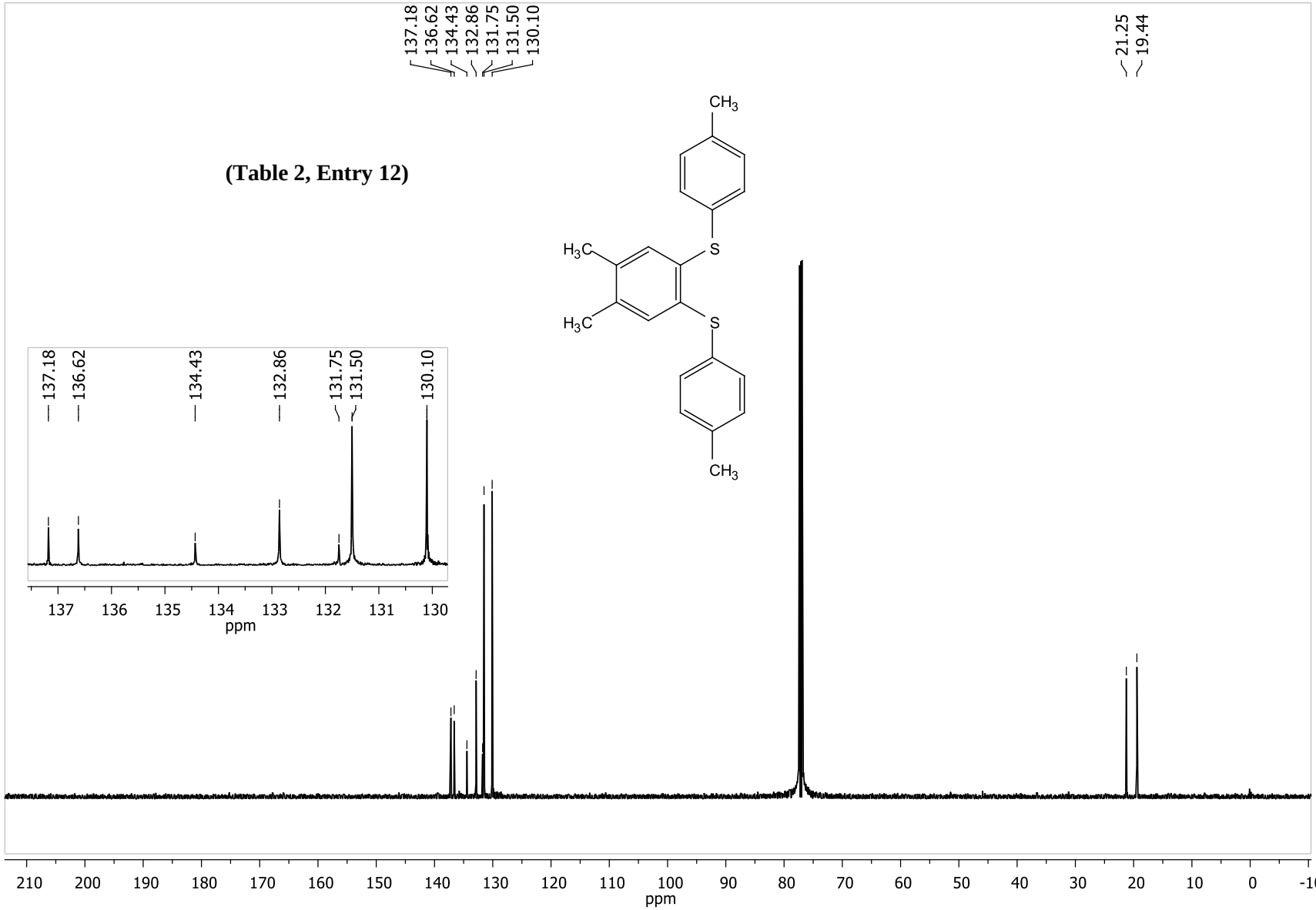
(Table 2, Entry 10)

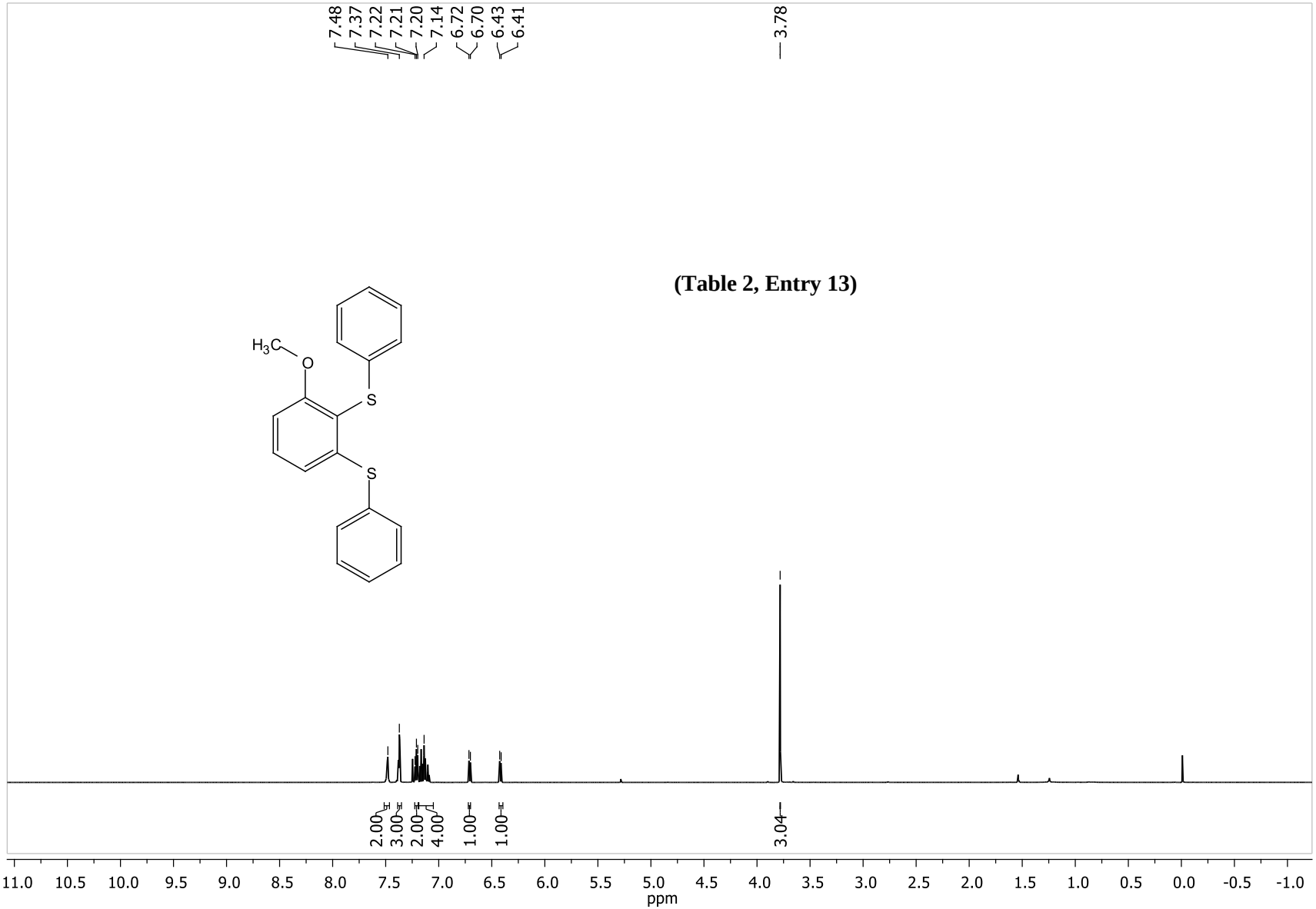

148.96
148.30
139.05
135.39
134.61
134.57
131.93
130.45
129.88
129.74
129.24
128.60
128.26
125.72
21.38
21.08
0.49
(Table 2, Entry 10)
CH3
H3C
Si
CH3
CH3
S
S
H3C
139.05
135.39
134.61
134.57
131.93
130.45
129.88
129.74
129.24
128.60
128.26
125.72
135
130
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.32
7.31
7.25
7.24
6.97
2.12
1.30
(Table 2, Entry 11)
4.00
4.03
2.00
6.05
18.07
ppm

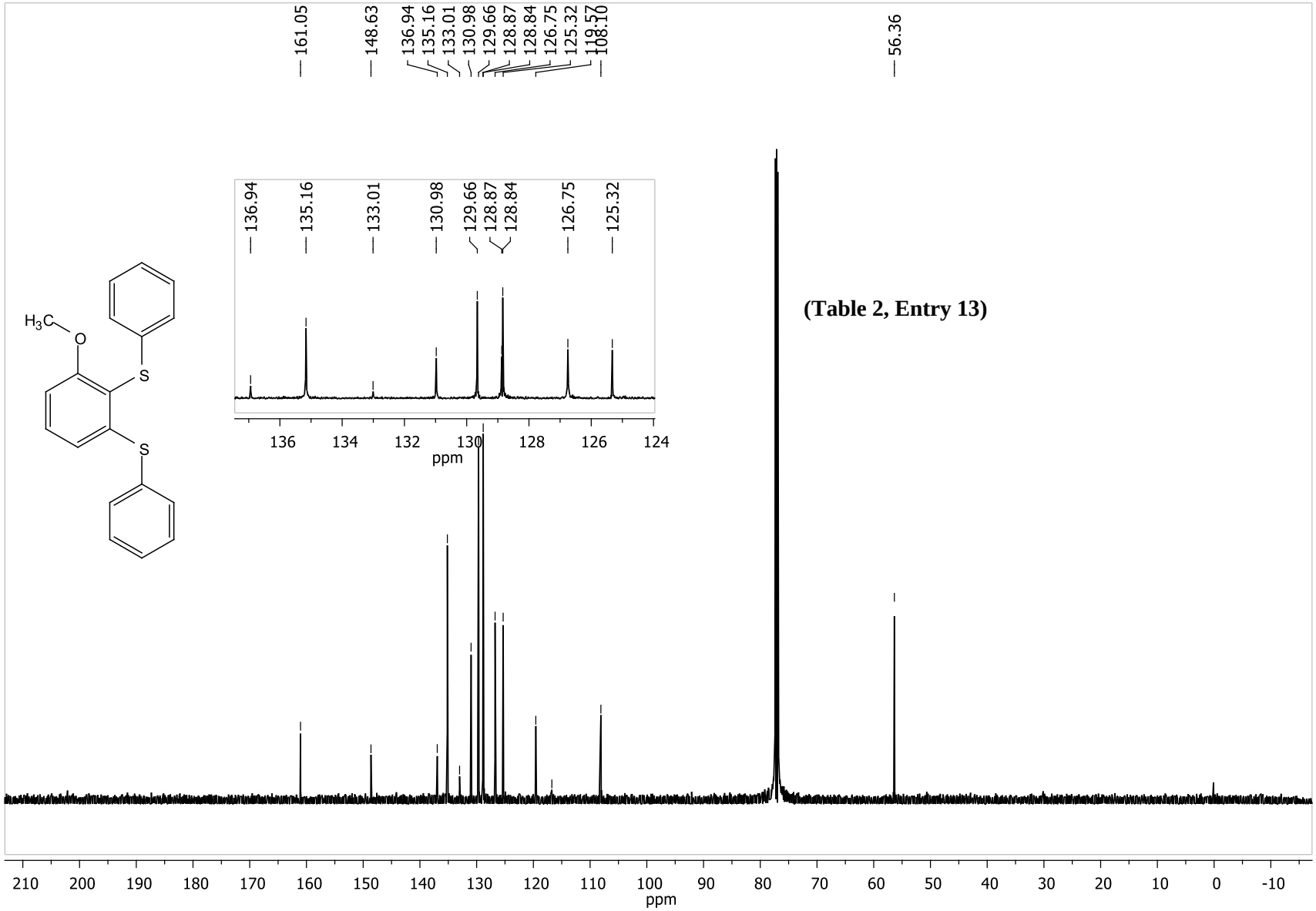

150.24
136.75
134.47
133.17
132.00
130.95
126.33
34.63
31.37
19.46
(Table 2, Entry 11)
H3C
H3C
CH3
H3C
S
H3C
S
CH3
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

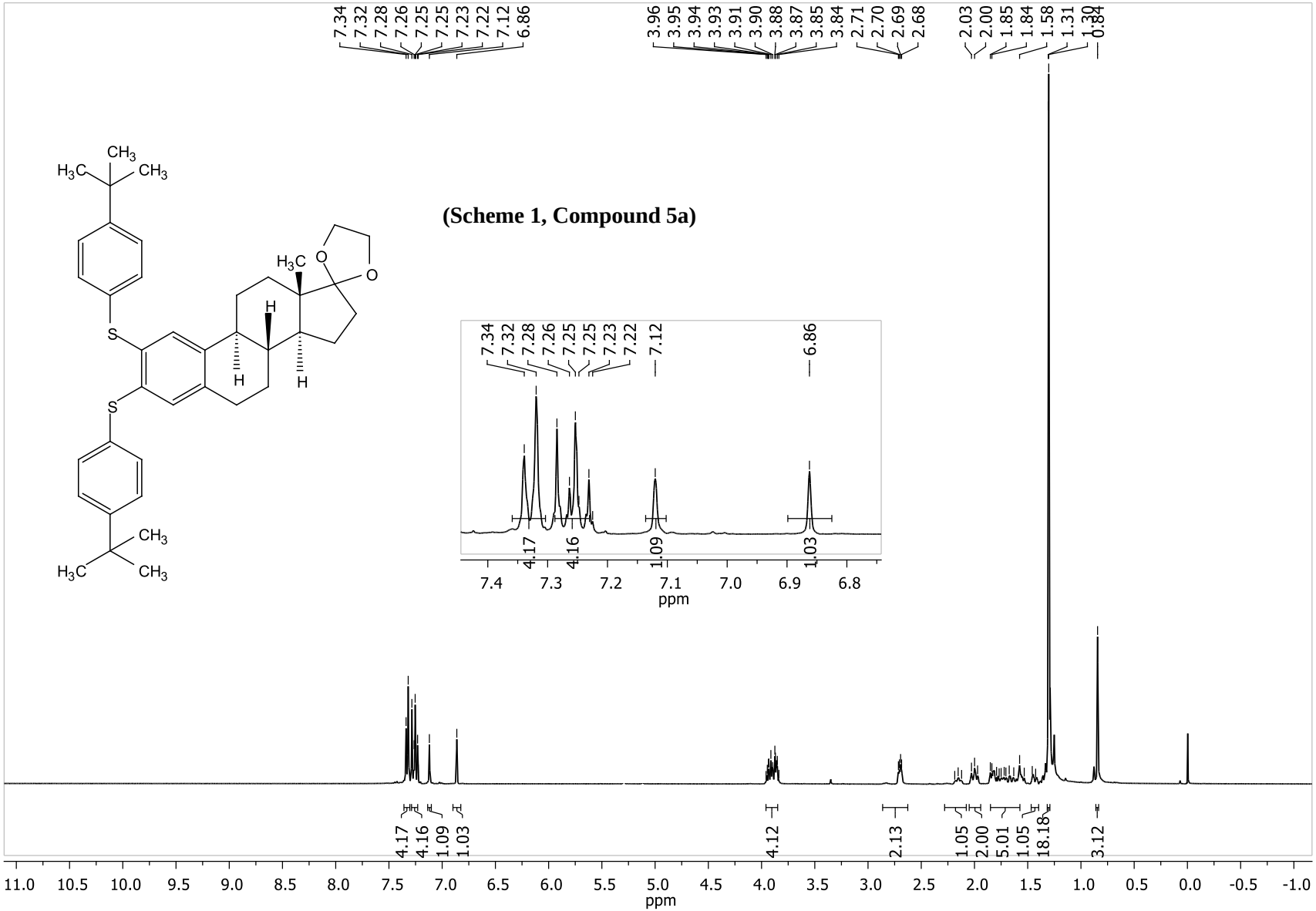

7.23
7.22
7.12
7.11
6.93
2.33
2.12
CH3
H3C
S
H3C
S
CH3
(Table 2, Entry 12)
2.00
2.06
1.00
3.01
3.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

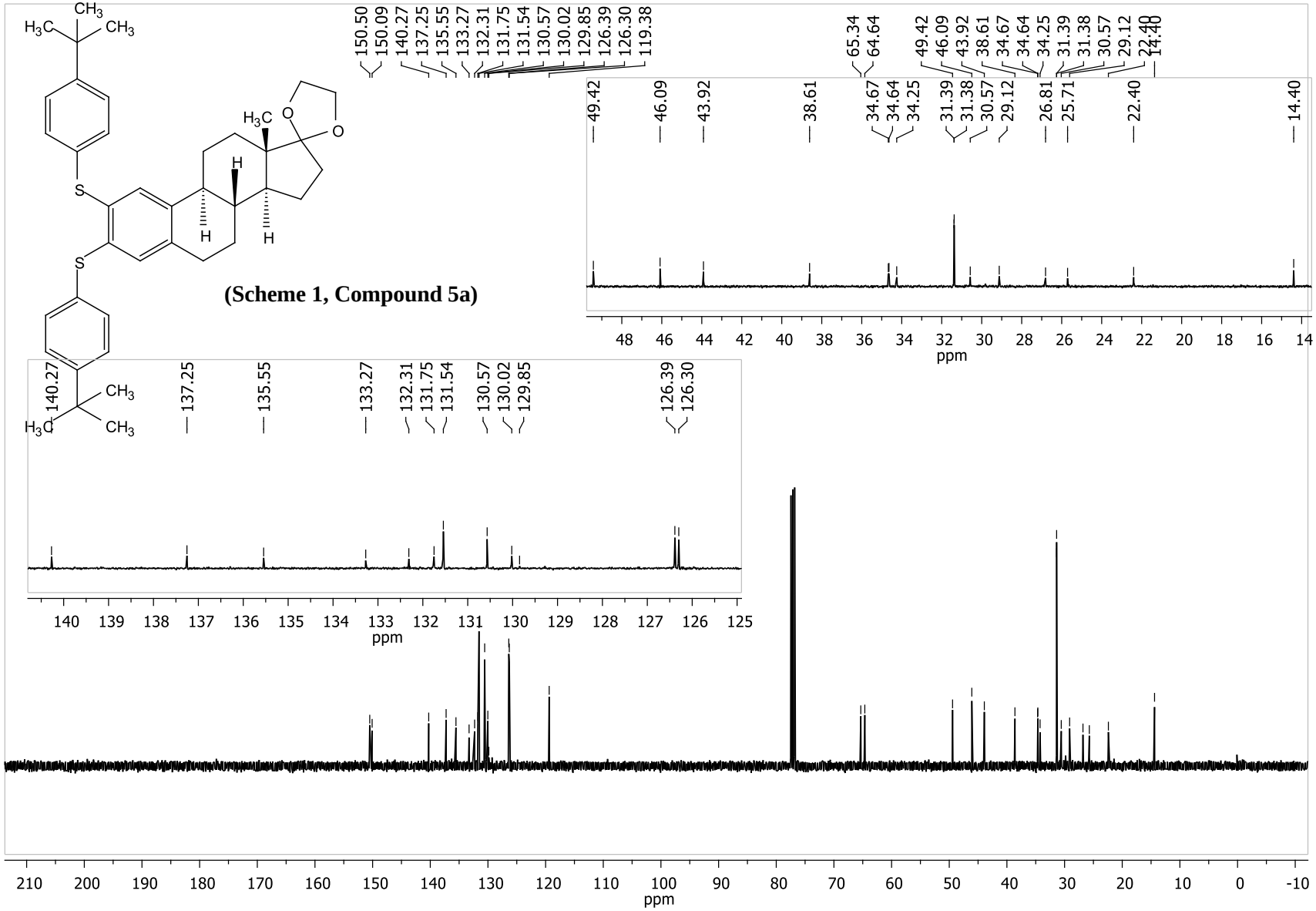

137.18
136.62
134.43
132.86
131.75
131.50
130.10
21.25
19.44
(Table 2, Entry 12)
CH3
H3C
S
H3C
S
CH3
137.18
136.62
134.43
132.86
131.75
131.50
130.10
137 136 135 134 133 132 131 130
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

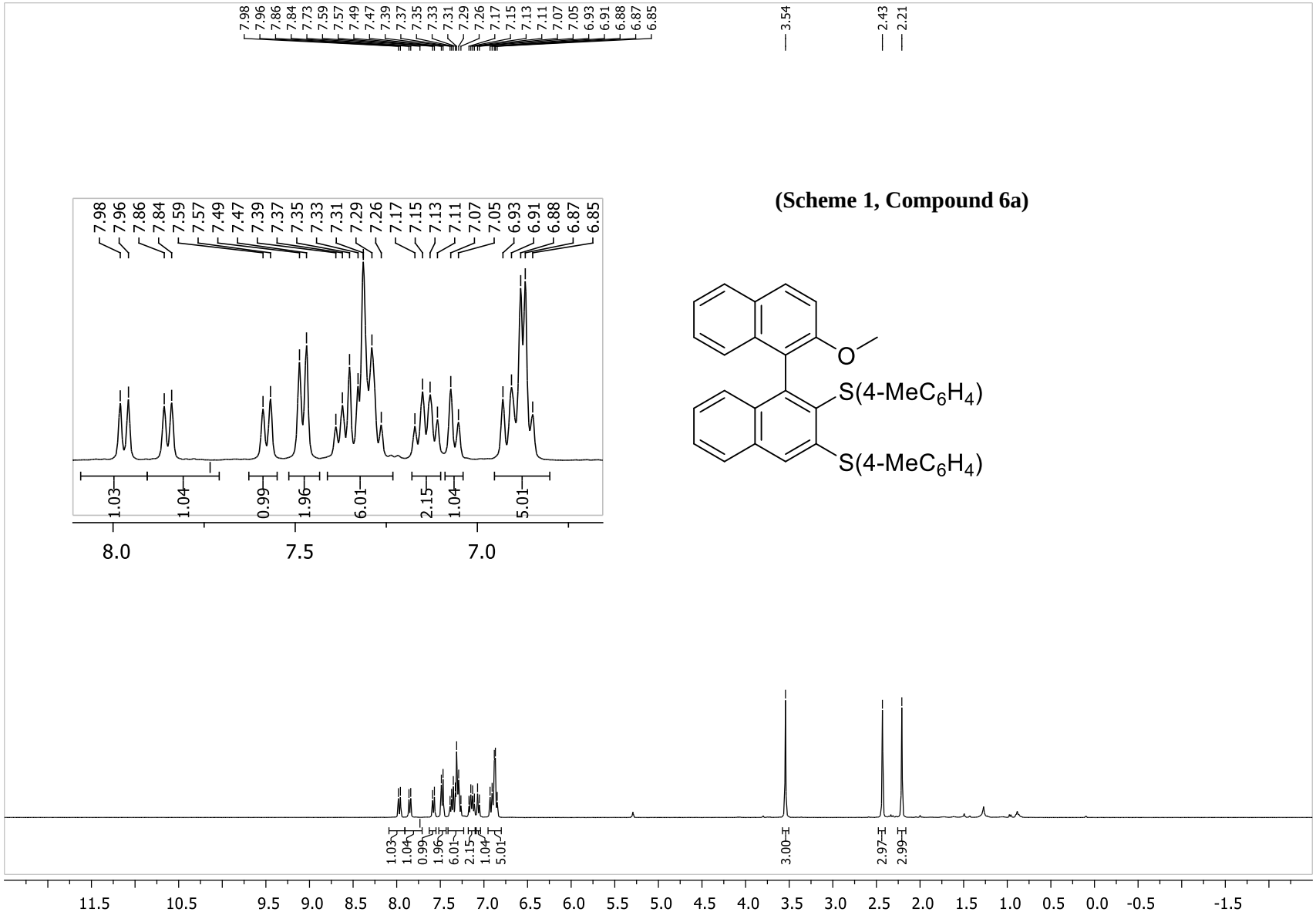


(Table 2, Entry 13)

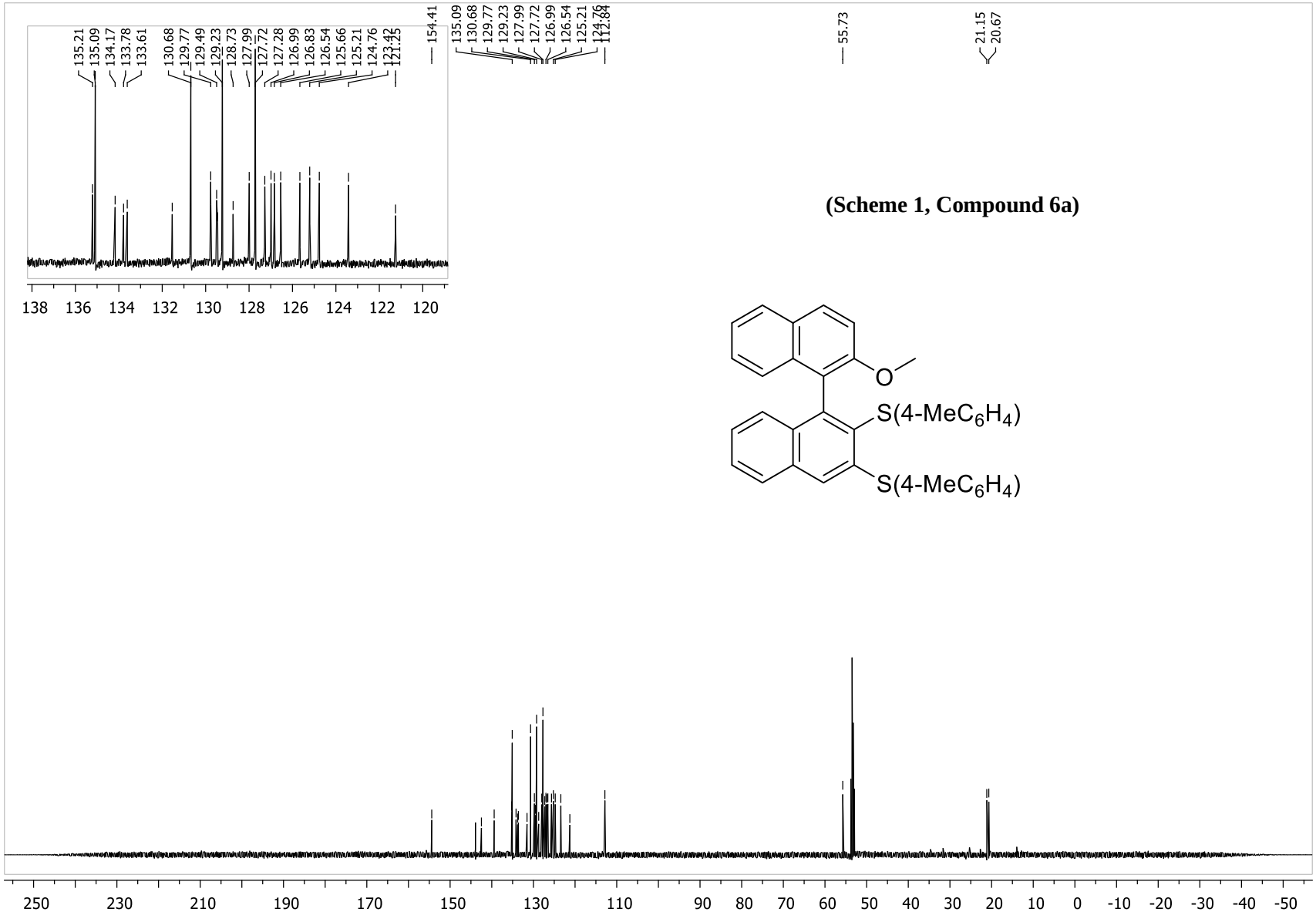

161.05
148.63
136.94
135.16
133.01
130.98
129.66
128.87
128.84
126.75
125.32
56.36
H3C
O
S
S
136
134
132
130
128
126
124
ppm
(Table 2, Entry 13)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.34 7.32 7.28 7.26 7.25 7.25 7.23 7.22 7.12 6.86
3.96 3.95 3.94 3.93 3.91 3.90 3.88 3.87 3.85 3.84 2.71 2.70 2.69 2.68
2.03 2.00 1.85 1.84 1.58 1.31 1.30 0.84
(Scheme 1, Compound 5a)
4.17 4.16 1.09 1.03 4.12 2.13 1.05 2.00 5.01 1.05 18.18 3.12
ppm

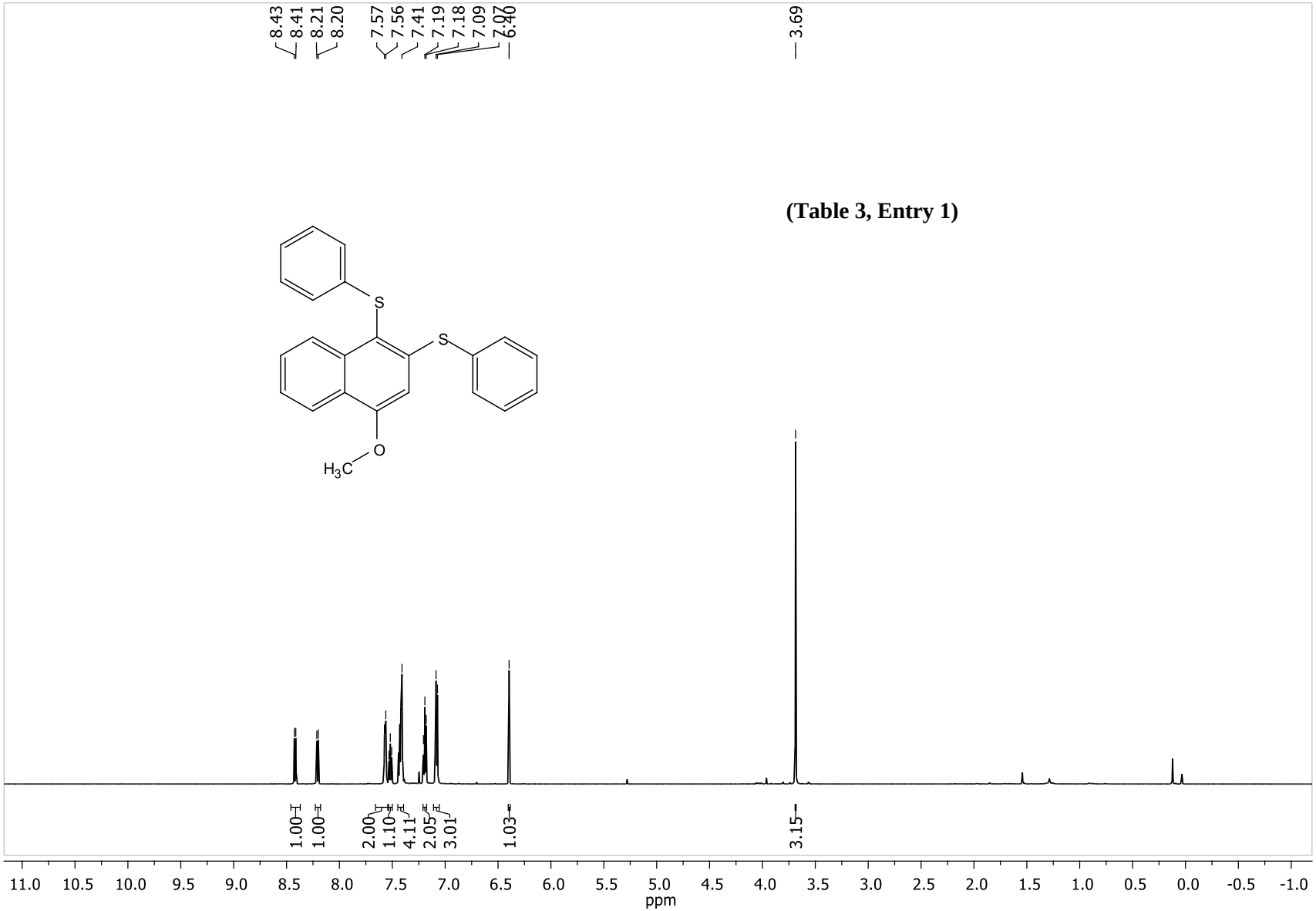

(Scheme 1, Compound 5a)
ppm



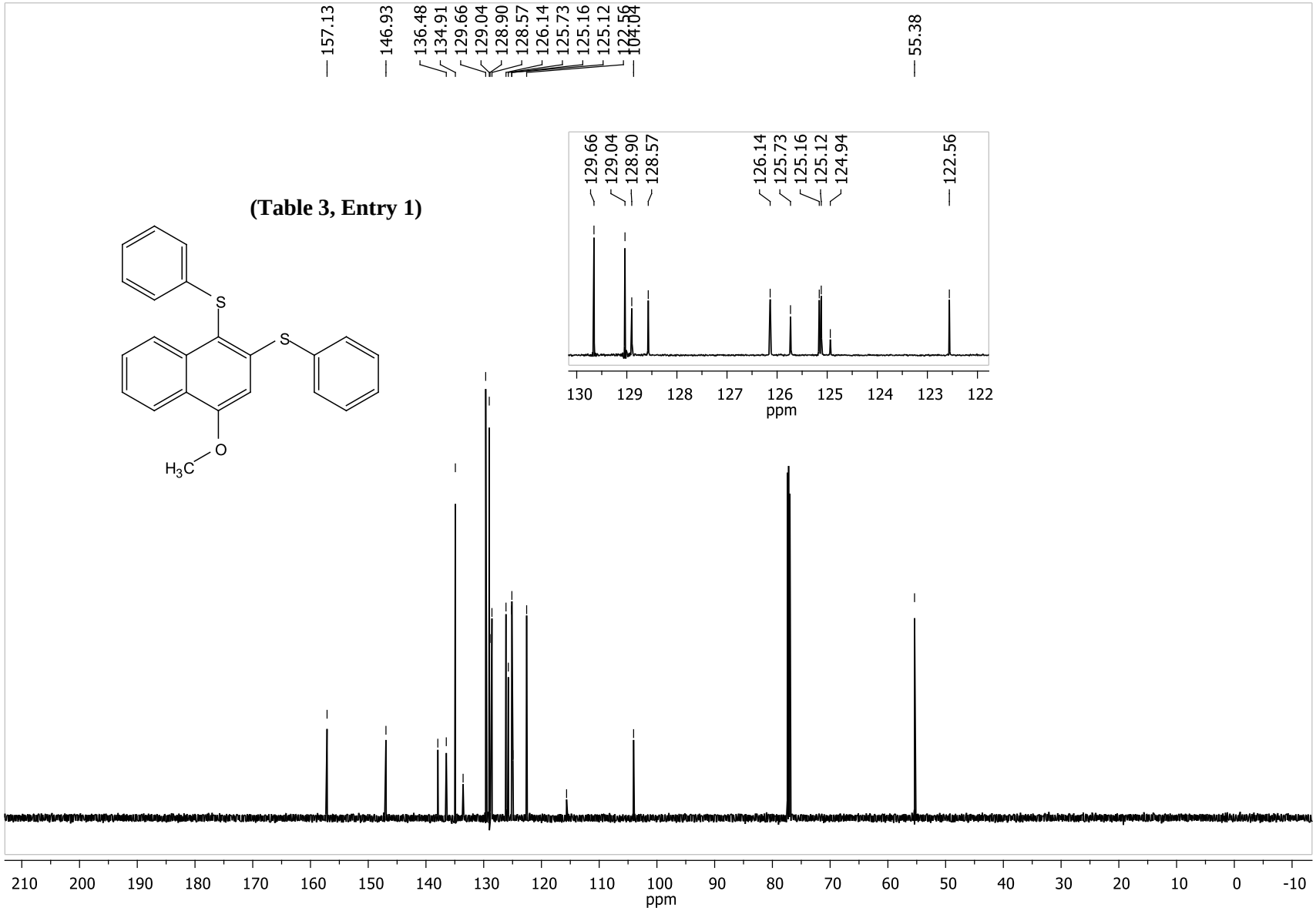
(Scheme 1, Compound 6a)



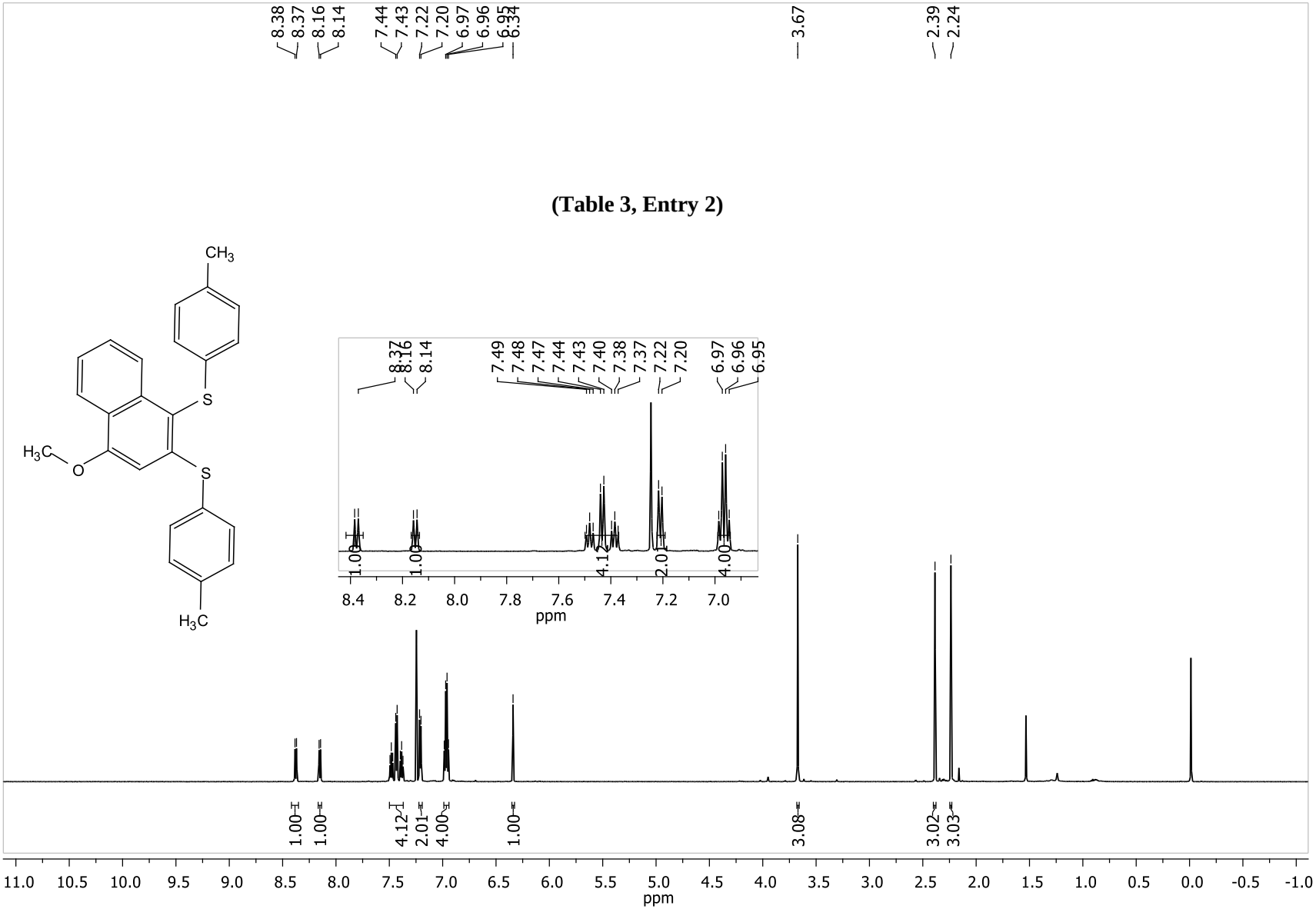
(Scheme 1, Compound 6a)

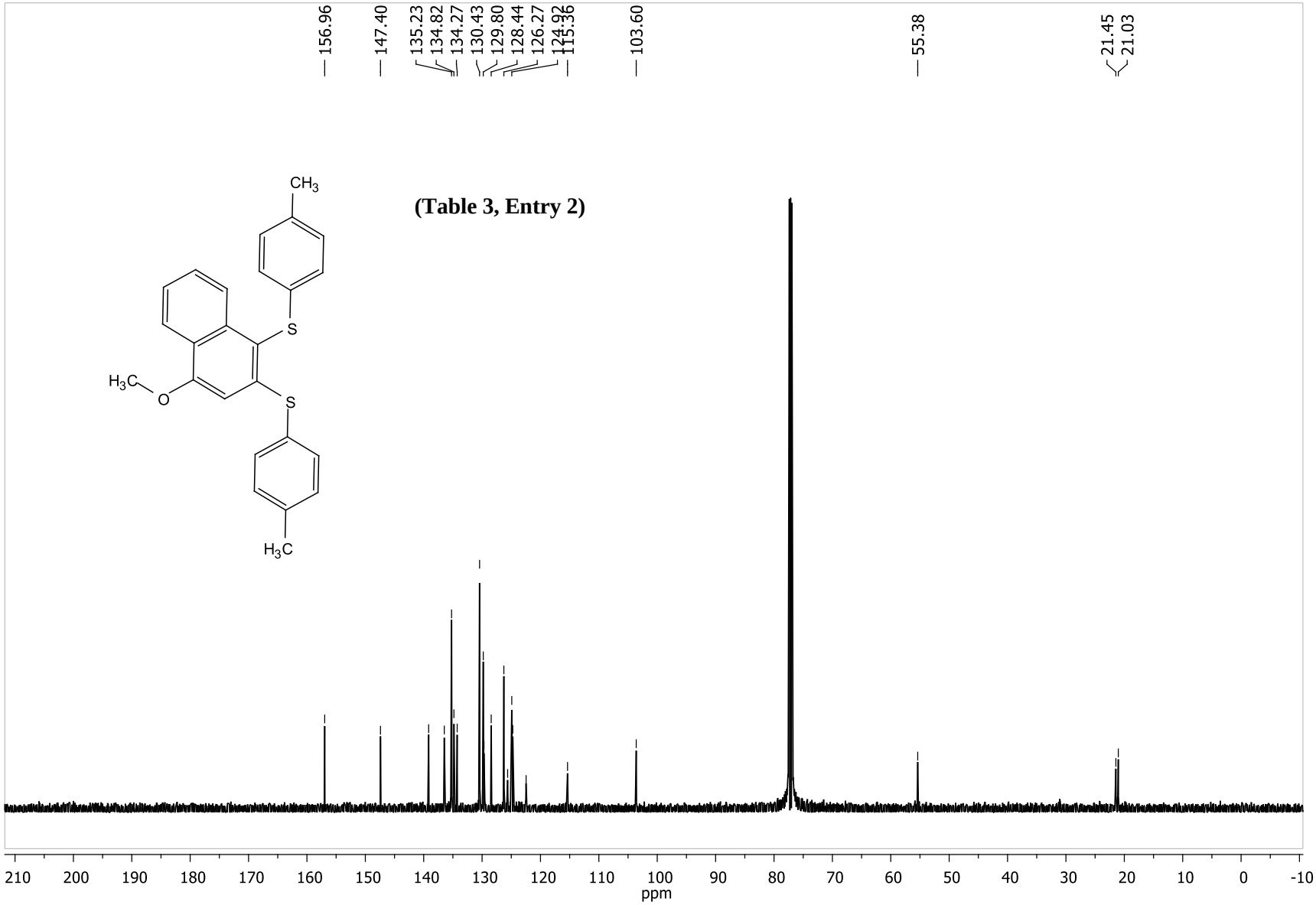


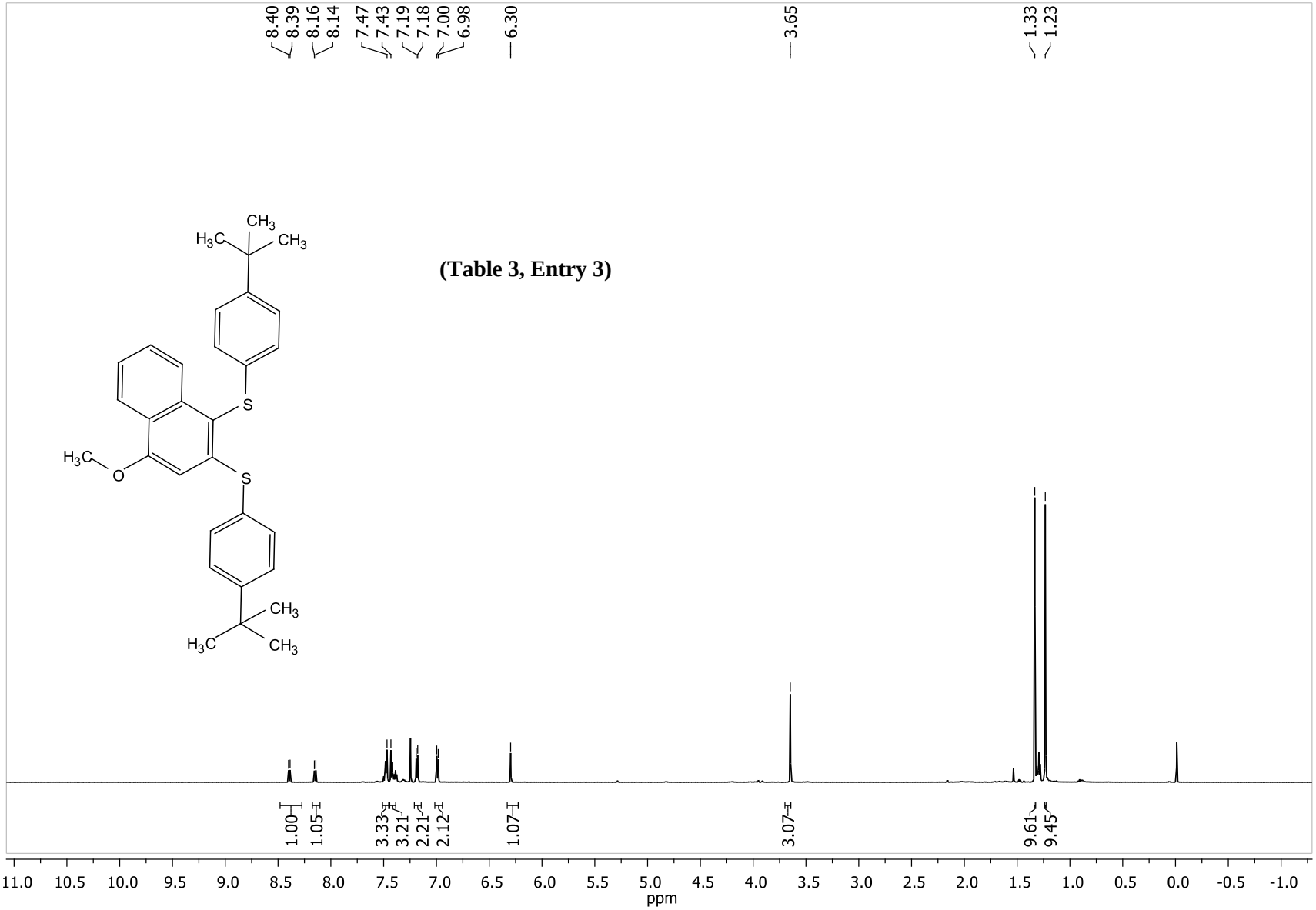
(Table 3, Entry 1)


157.13
146.93
136.48
134.91
129.66
129.04
128.90
128.57
126.14
125.73
125.16
125.12
122.56
104.04
55.38
(Table 3, Entry 1)
S
S
O
H3C
129.66
129.04
128.90
128.57
126.14
125.73
125.16
125.12
124.94
122.56
130 129 128 127 126 125 124 123 122
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

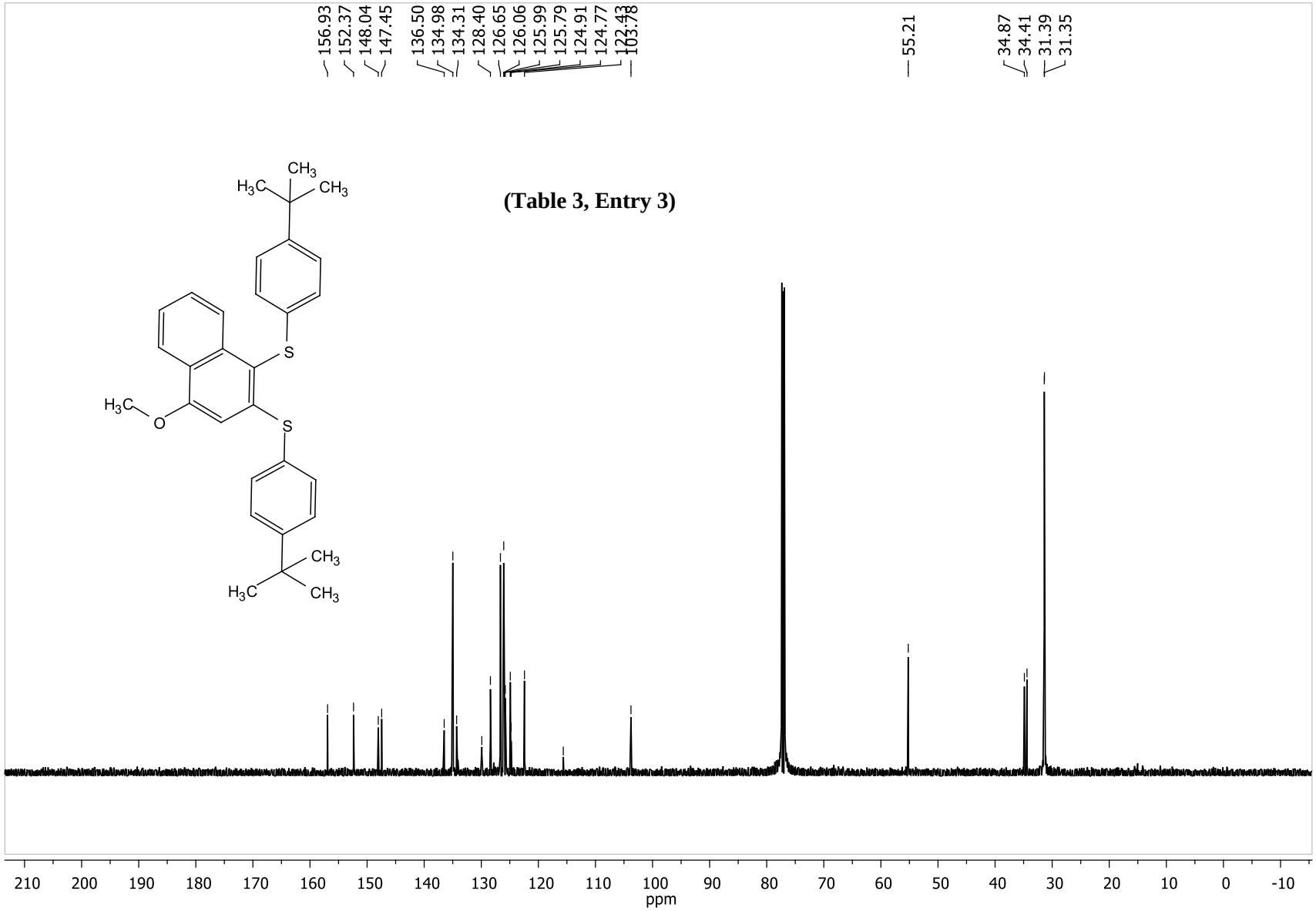
(Table 3, Entry 2)

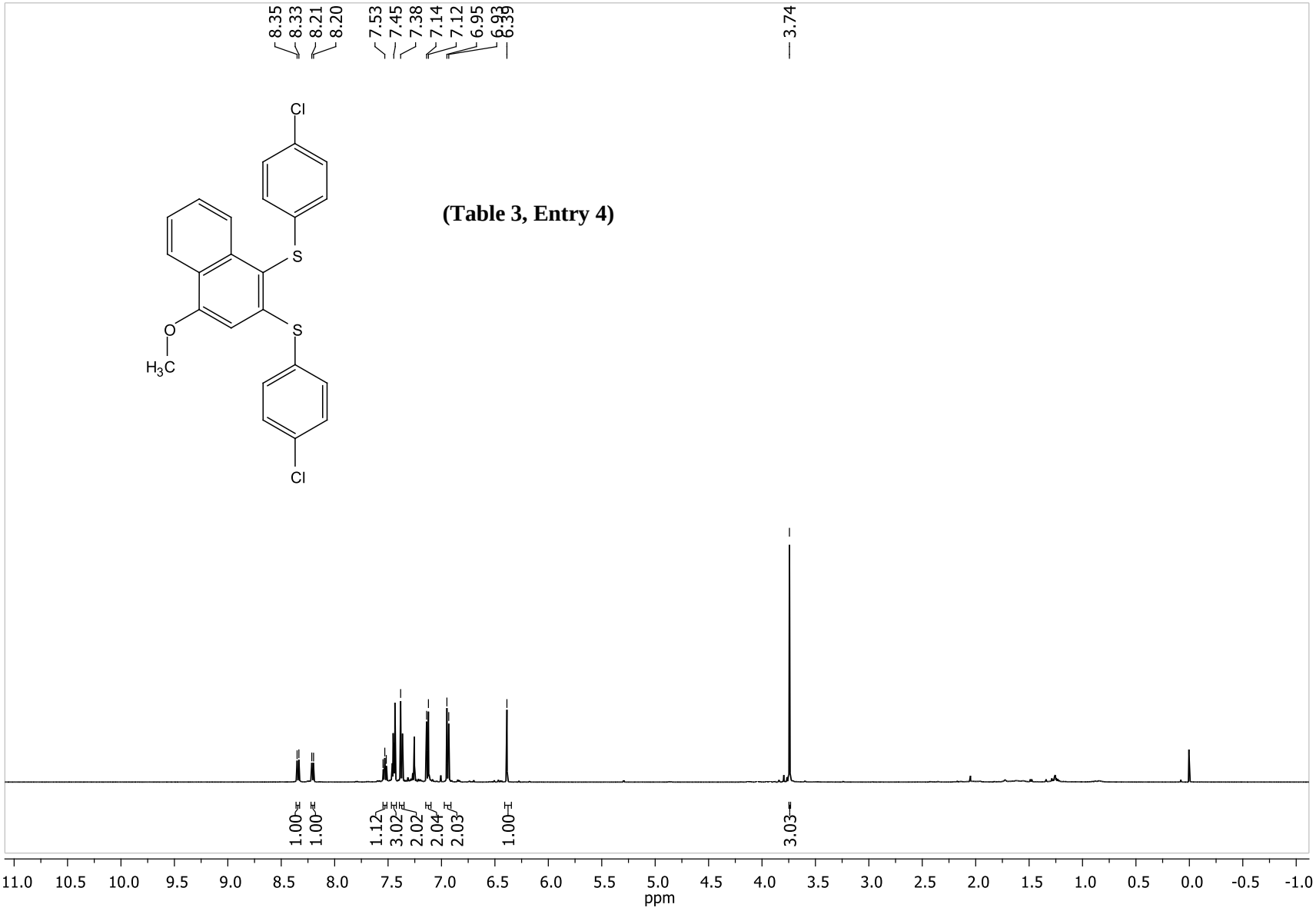


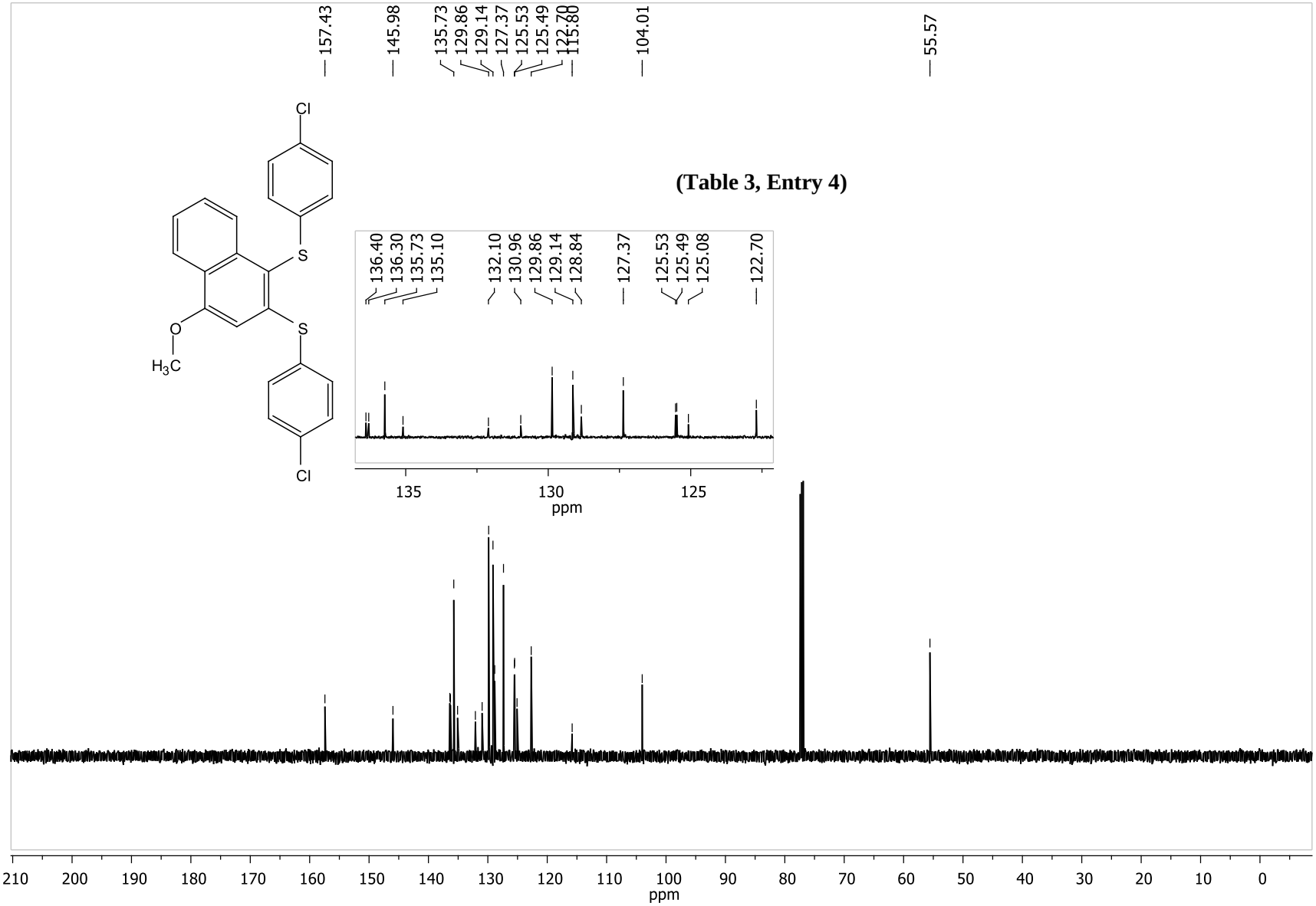

156.96
147.40
135.23
134.82
134.27
130.43
129.80
128.44
126.27
124.92
115.36
103.60
55.38
21.45
21.03
(Table 3, Entry 2)
CH3
S
H3C
O
S
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



(Table 3, Entry 3)

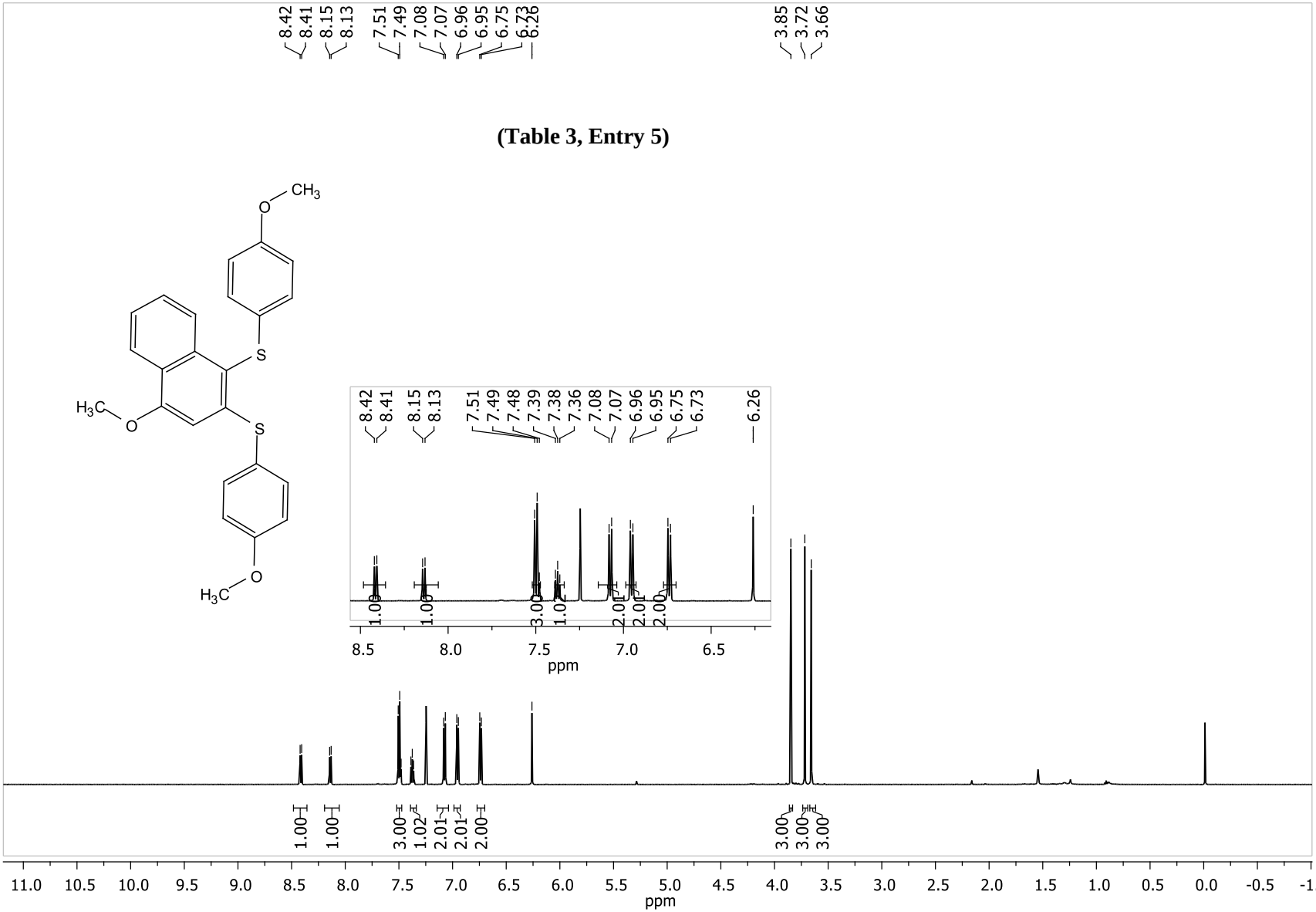

156.93
152.37
148.04
147.45
136.50
134.98
134.31
128.40
126.65
126.06
125.99
125.79
124.91
124.77
122.43
103.78
55.21
34.87
34.41
31.39
31.35
(Table 3, Entry 3)
CH3
H3C
CH3
S
H3C
O
S
CH3
H3C
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

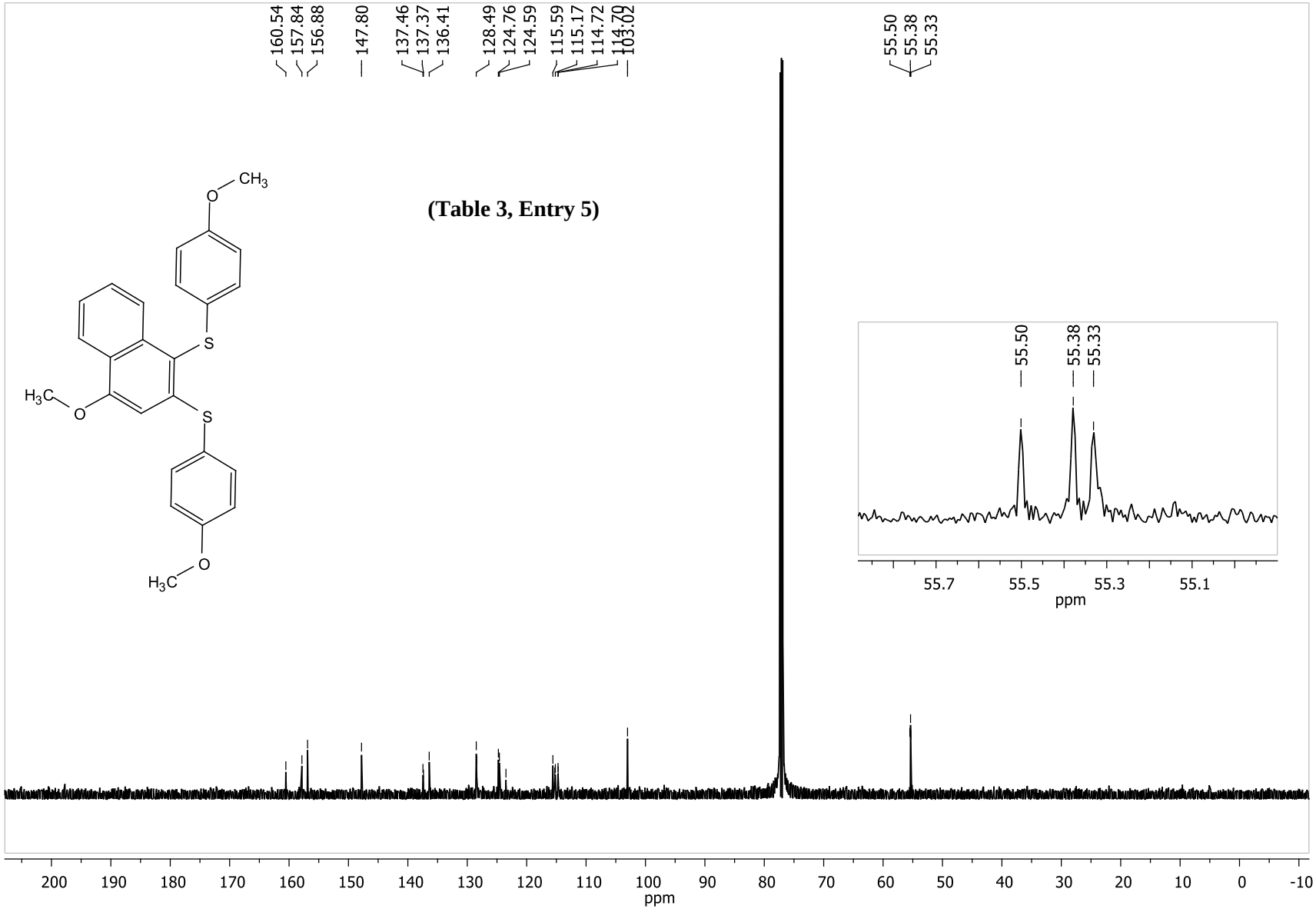

8.35
8.33
8.21
8.20
7.53
7.45
7.38
7.14
7.12
6.95
6.93
6.39
3.74
Cl
S
S
O
H3C
Cl
(Table 3, Entry 4)
1.00
1.00
1.12
3.02
2.02
2.04
2.03
1.00
3.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

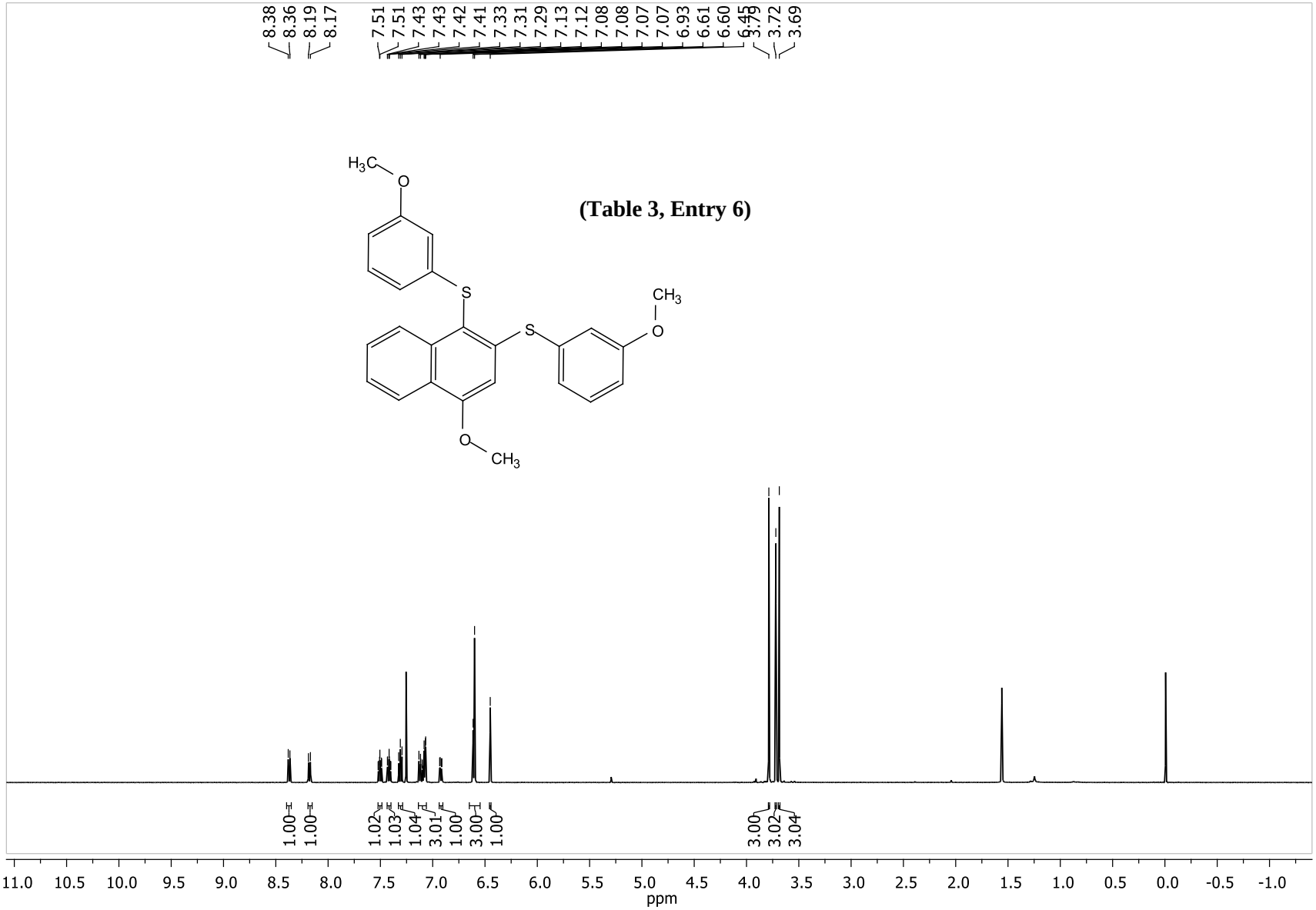


(Table 3, Entry 4)

(Table 3, Entry 5)

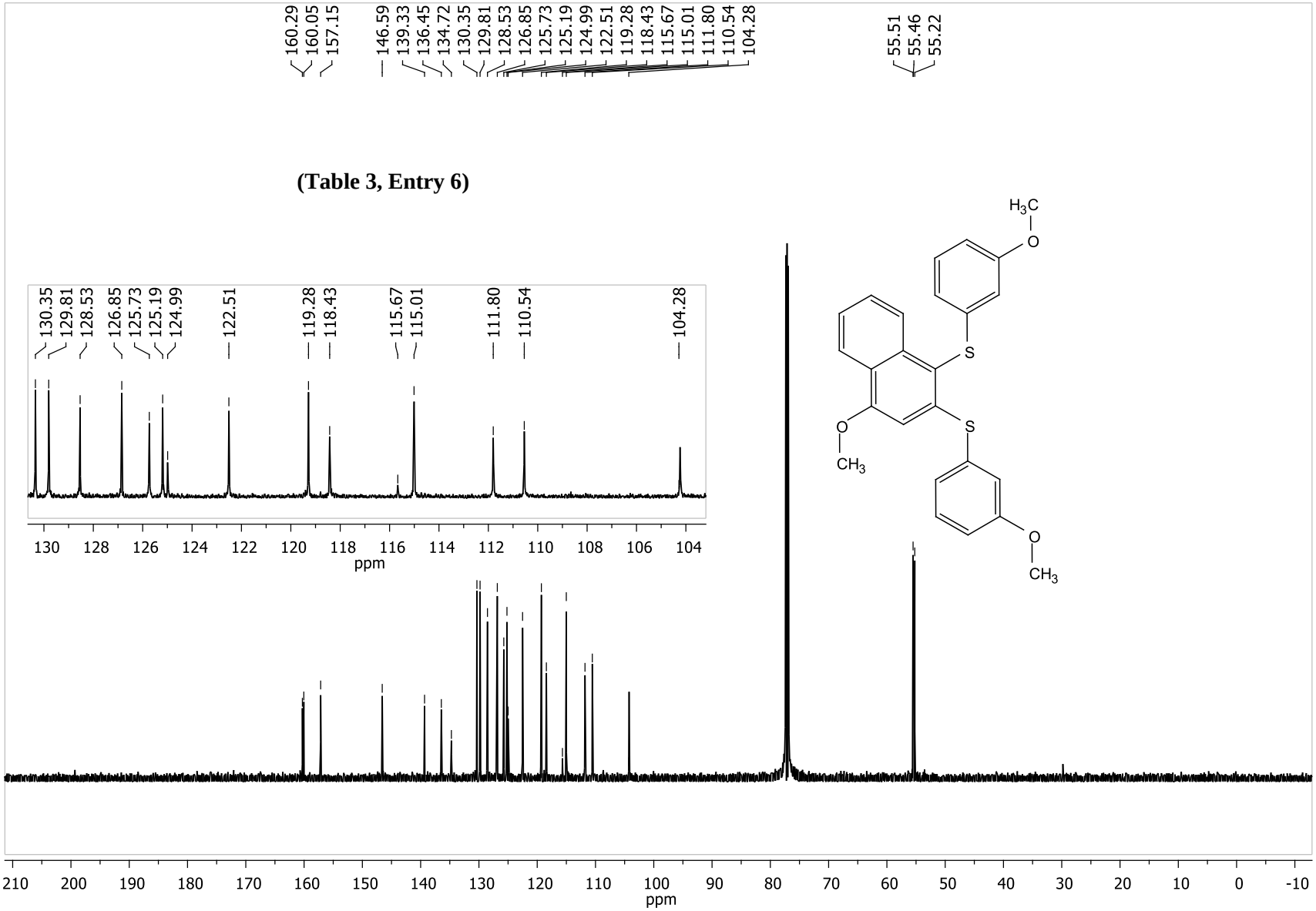



160.54
157.84
156.88
147.80
137.46
137.37
136.41
128.49
124.76
124.59
115.59
115.17
114.72
114.70
103.02
55.50
55.38
55.33
(Table 3, Entry 5)
CH3
O
S
S
H3C
O
O
H3C
55.50
55.38
55.33
55.7
55.5
55.3
55.1
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

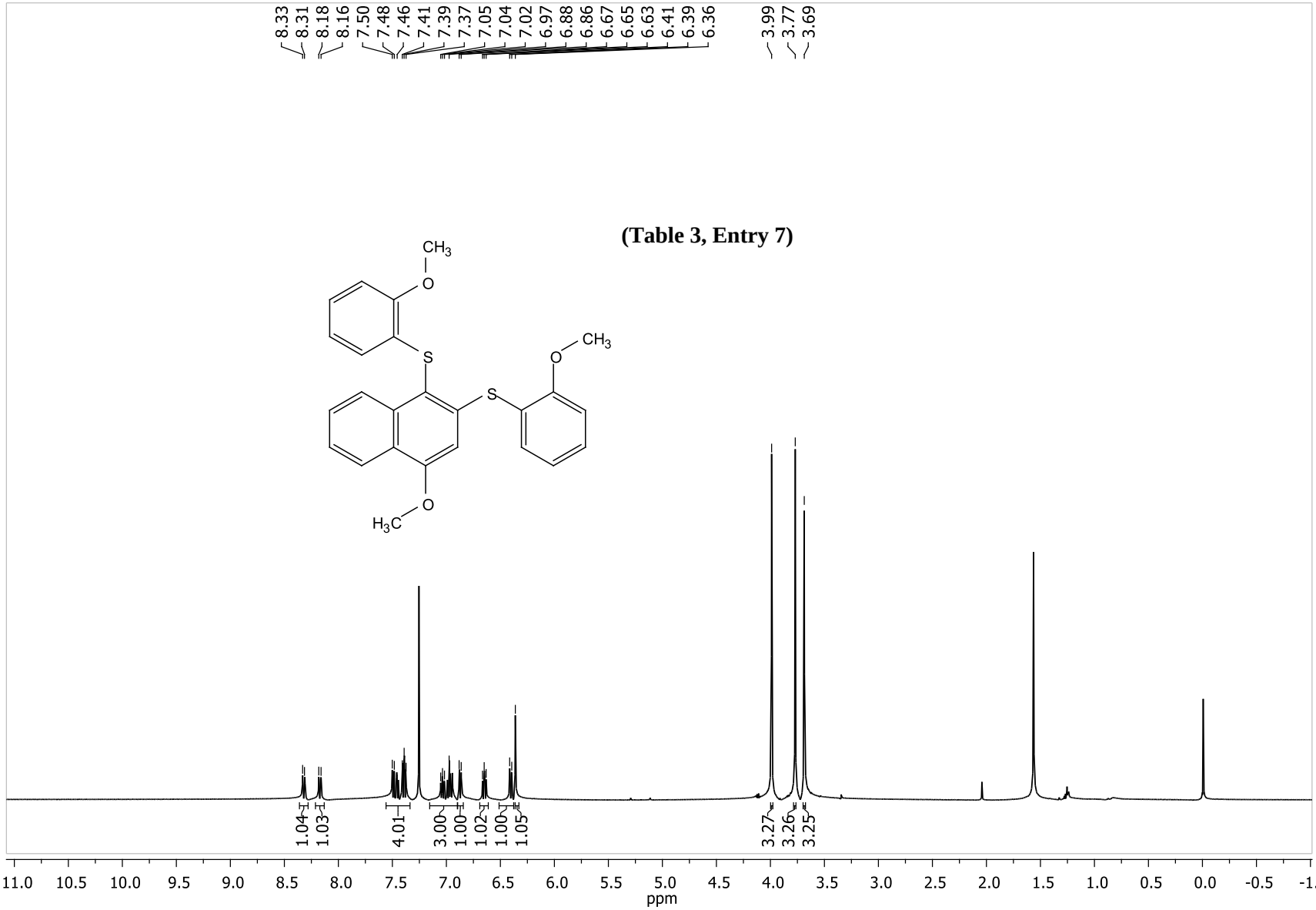


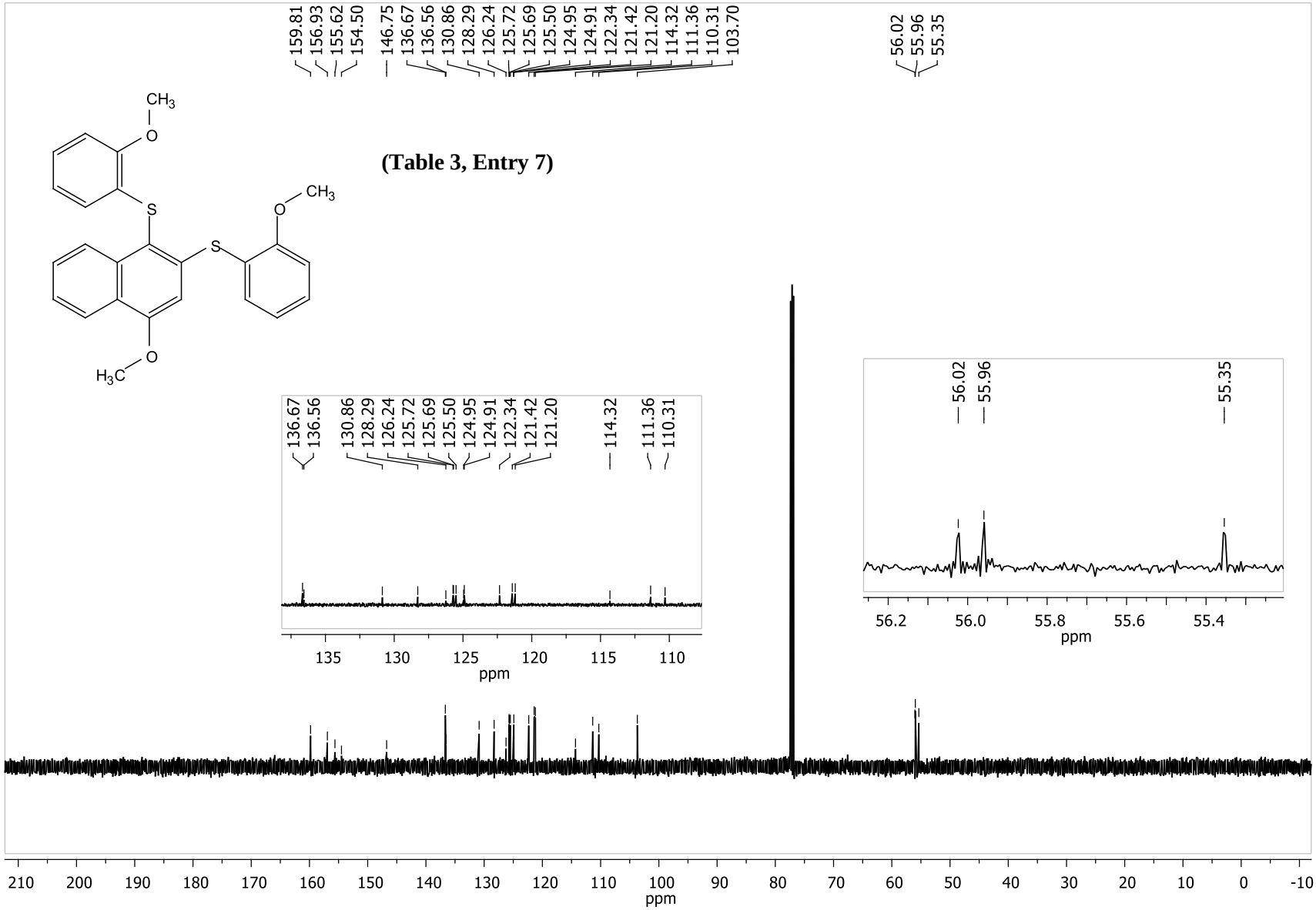
(Table 3, Entry 6)

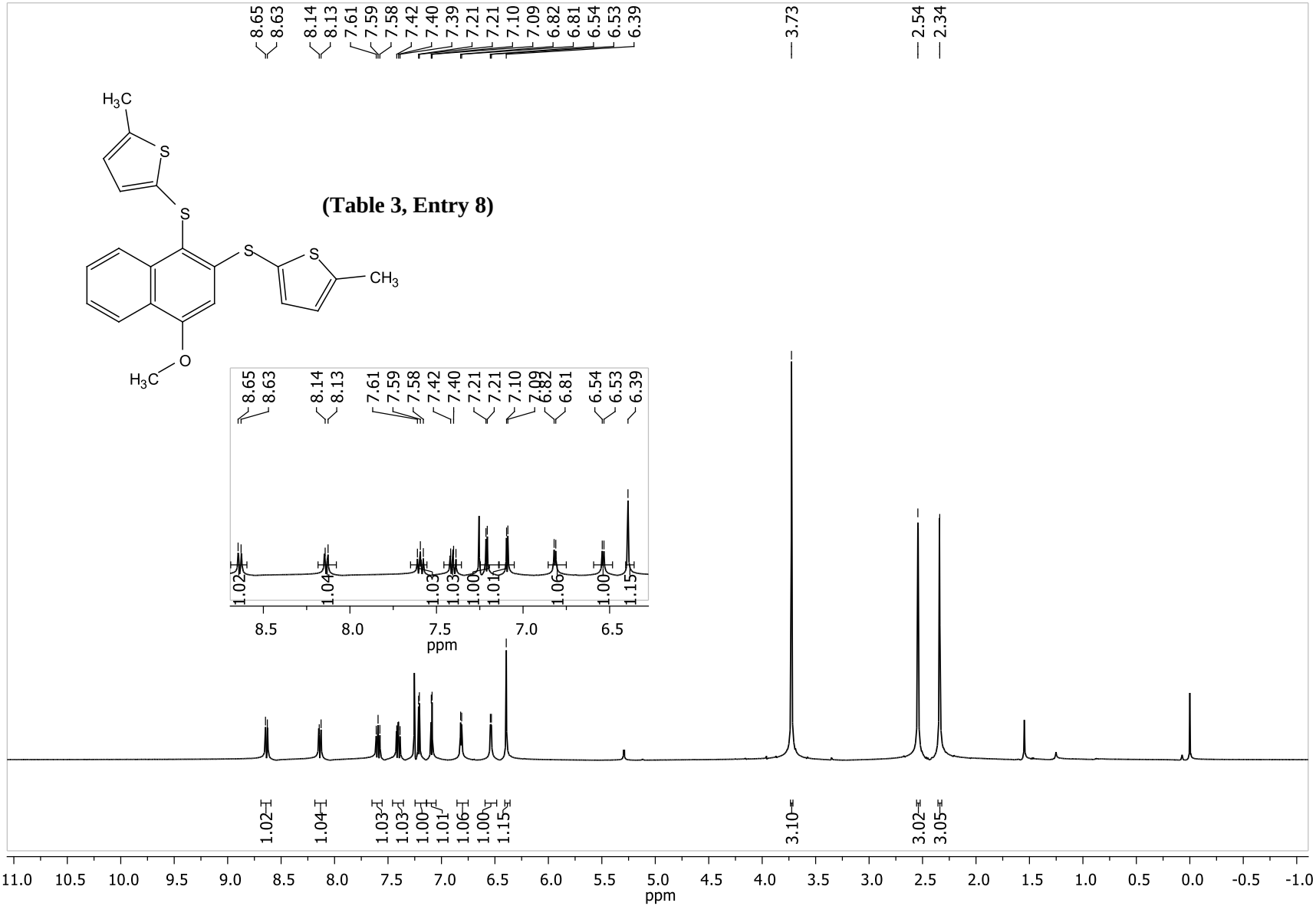
(Table 3, Entry 6)

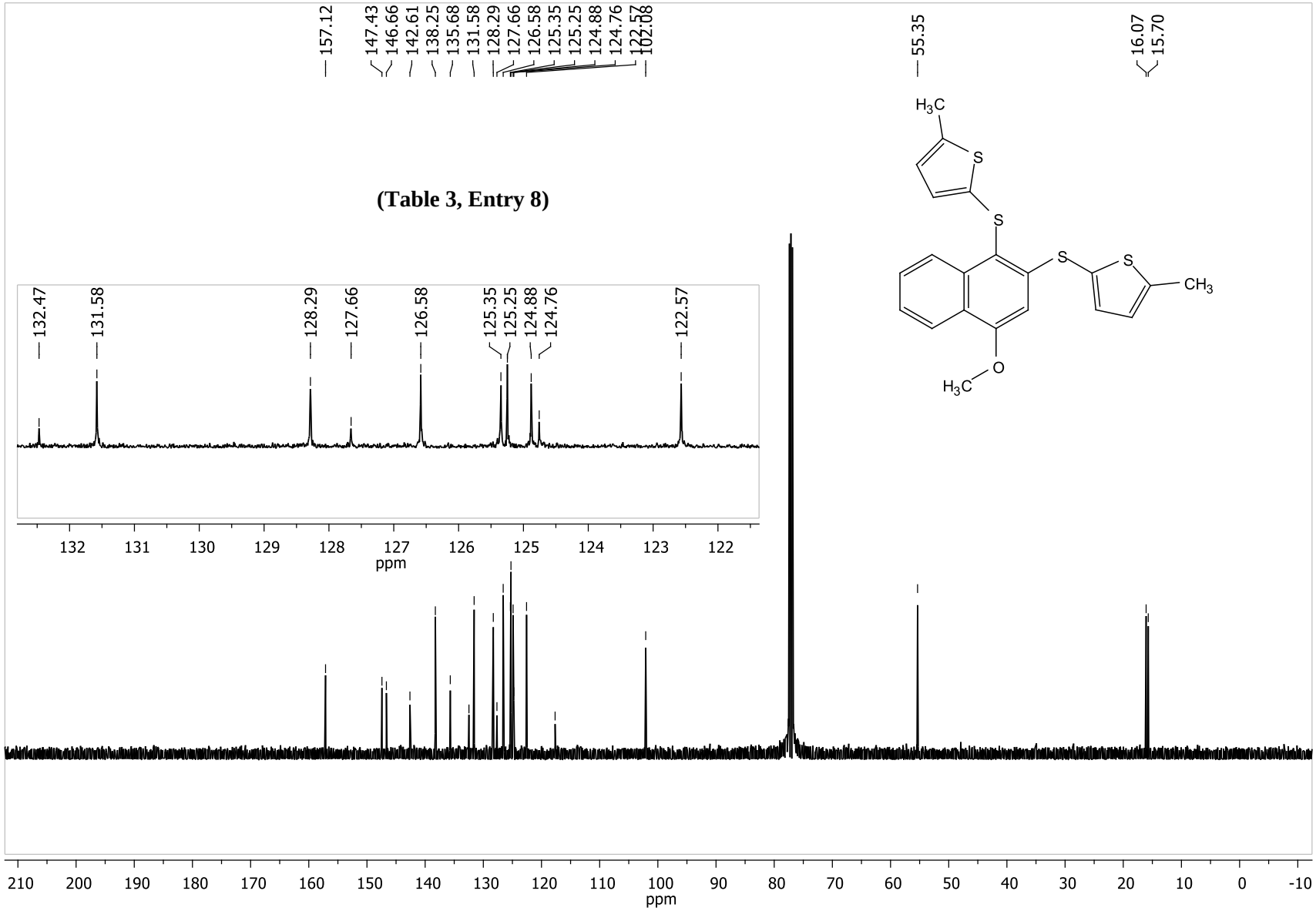


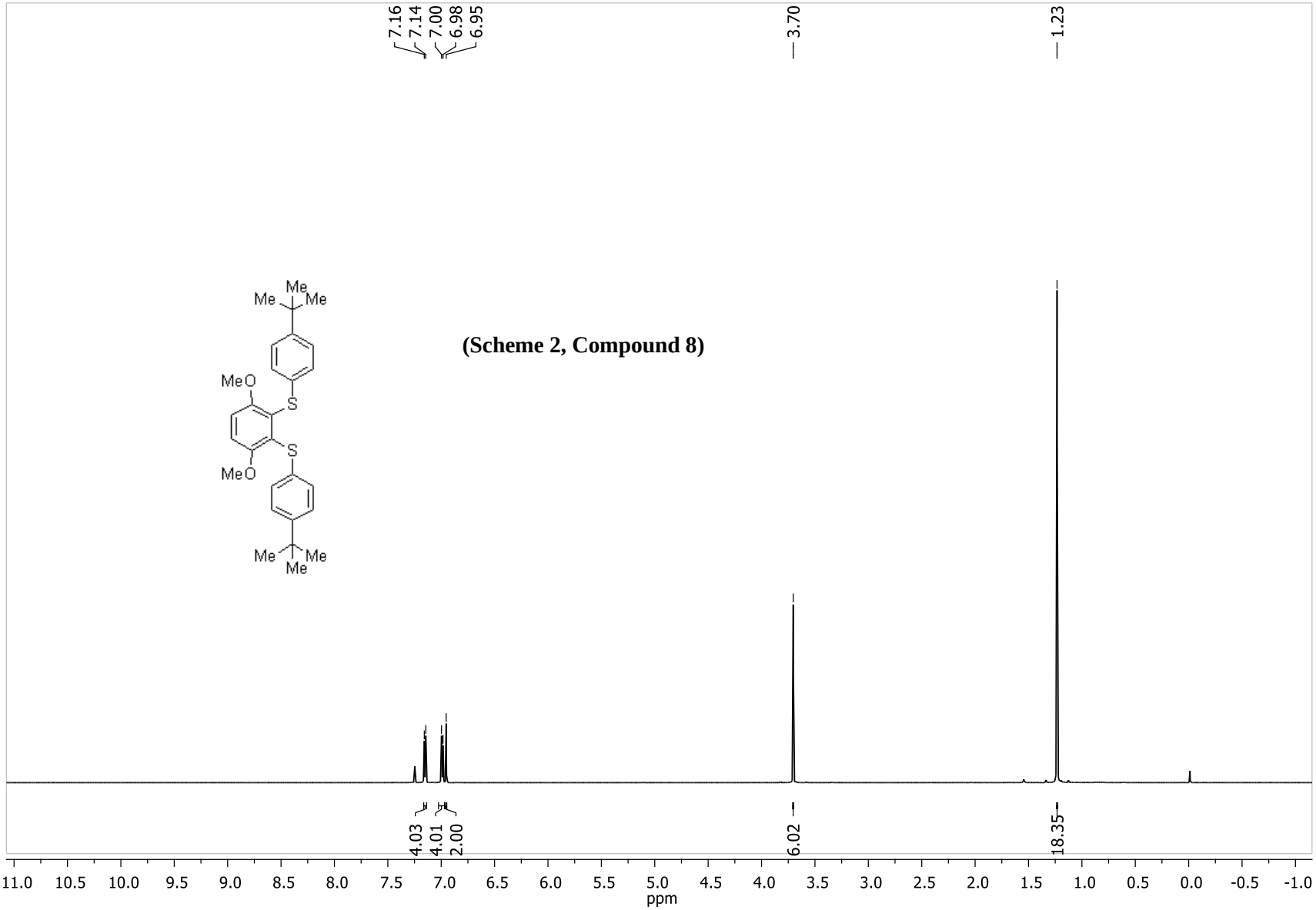
(Table 3, Entry 7)

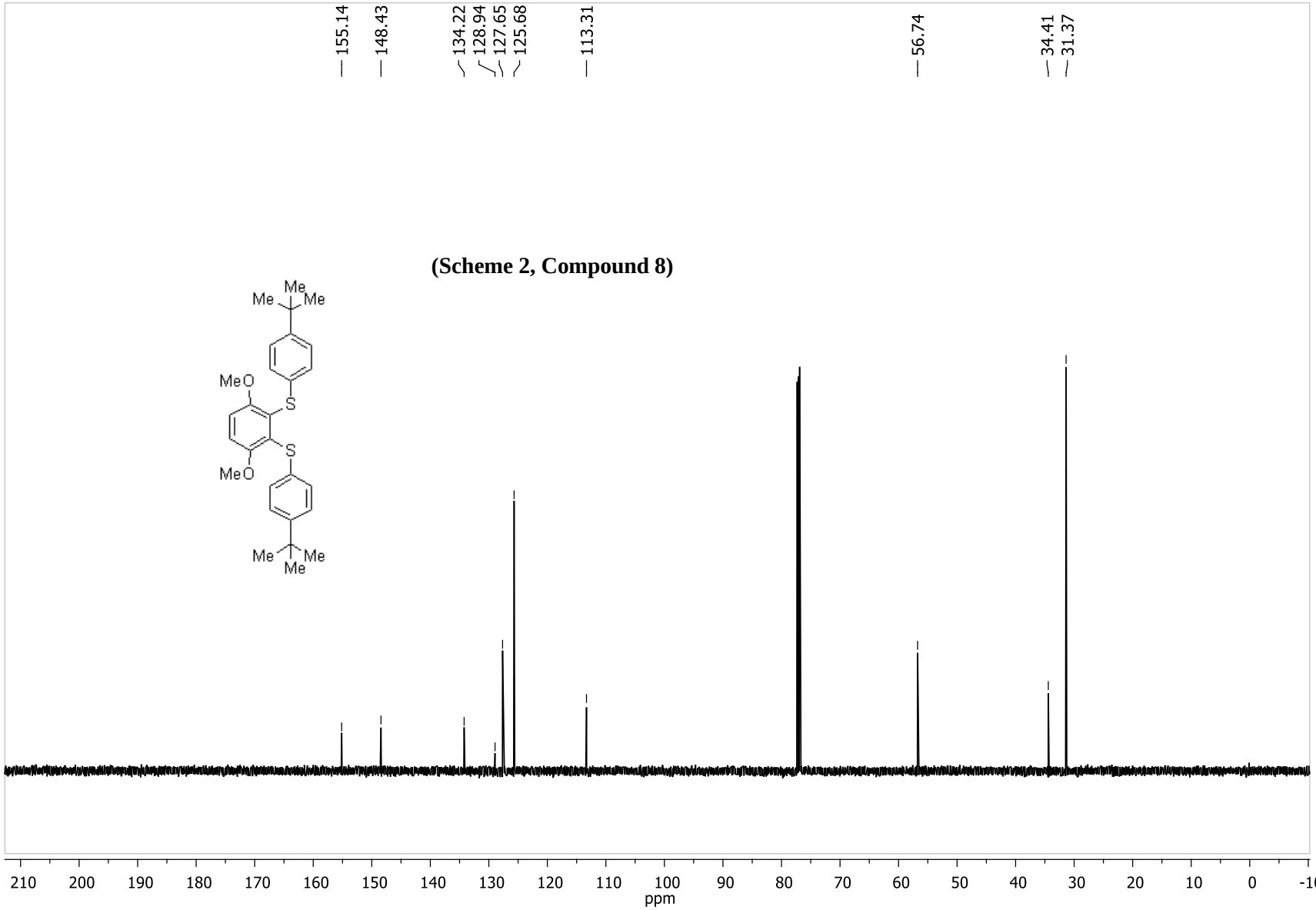



159.81
156.93
155.62
154.50
146.75
136.67
136.56
130.86
128.29
126.24
125.72
125.69
125.50
124.95
124.91
122.34
121.42
121.20
114.32
111.36
110.31
103.70
56.02
55.96
55.35
CH3
O
S
S
O
CH3
O
H3C
(Table 3, Entry 7)
135
130
125
120
115
110
ppm
56.2
56.0
55.8
55.6
55.4
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

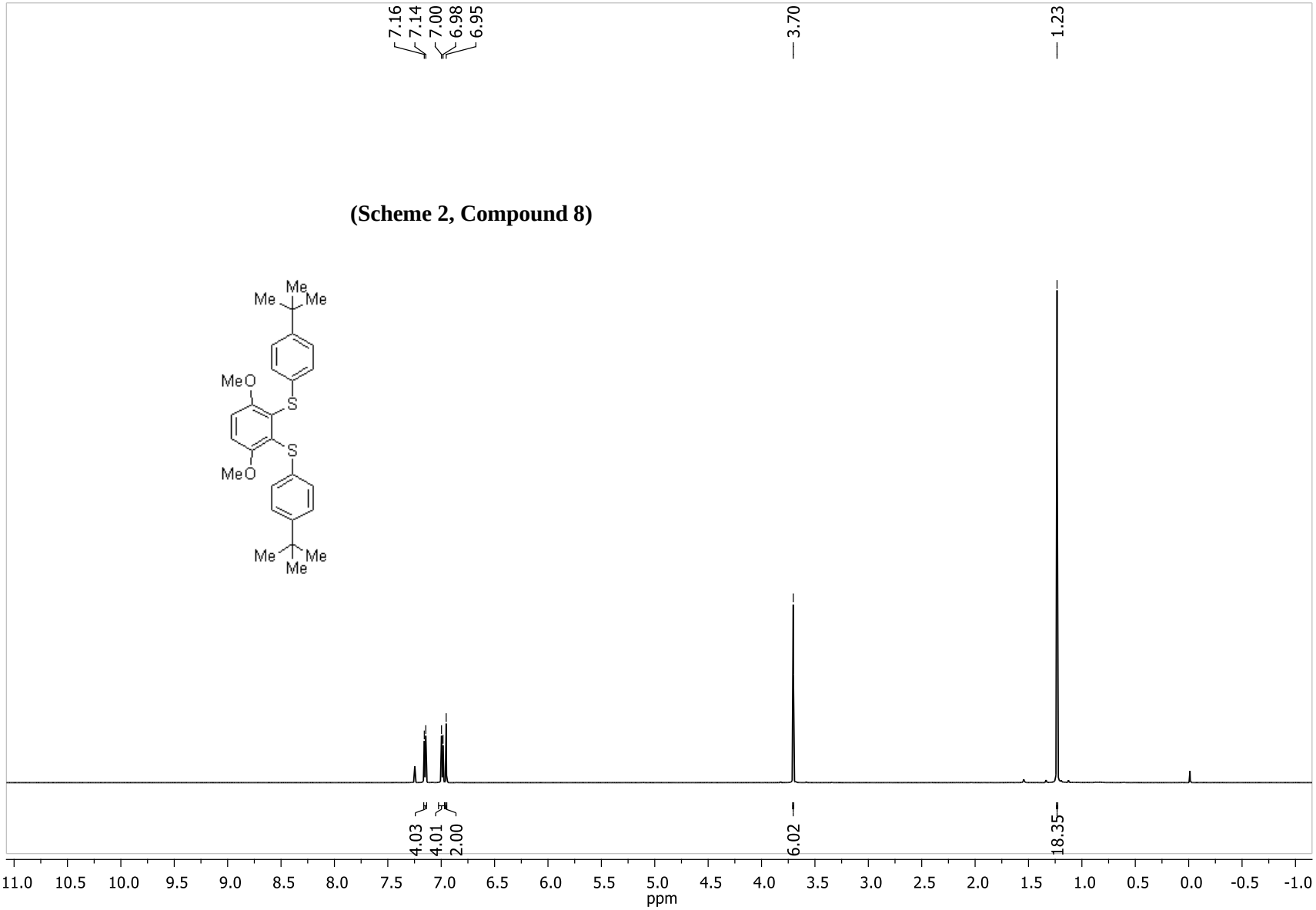

8.65
8.63
8.14
8.13
7.61
7.59
7.58
7.42
7.40
7.39
7.21
7.21
7.10
7.09
6.82
6.81
6.54
6.53
6.39
3.73
2.54
2.34
H3C
S
S
S
S
CH3
O
H3C
(Table 3, Entry 8)
1.02
1.04
1.03
1.03
1.00
1.01
1.06
1.00
1.15
3.10
3.02
3.05
ppm

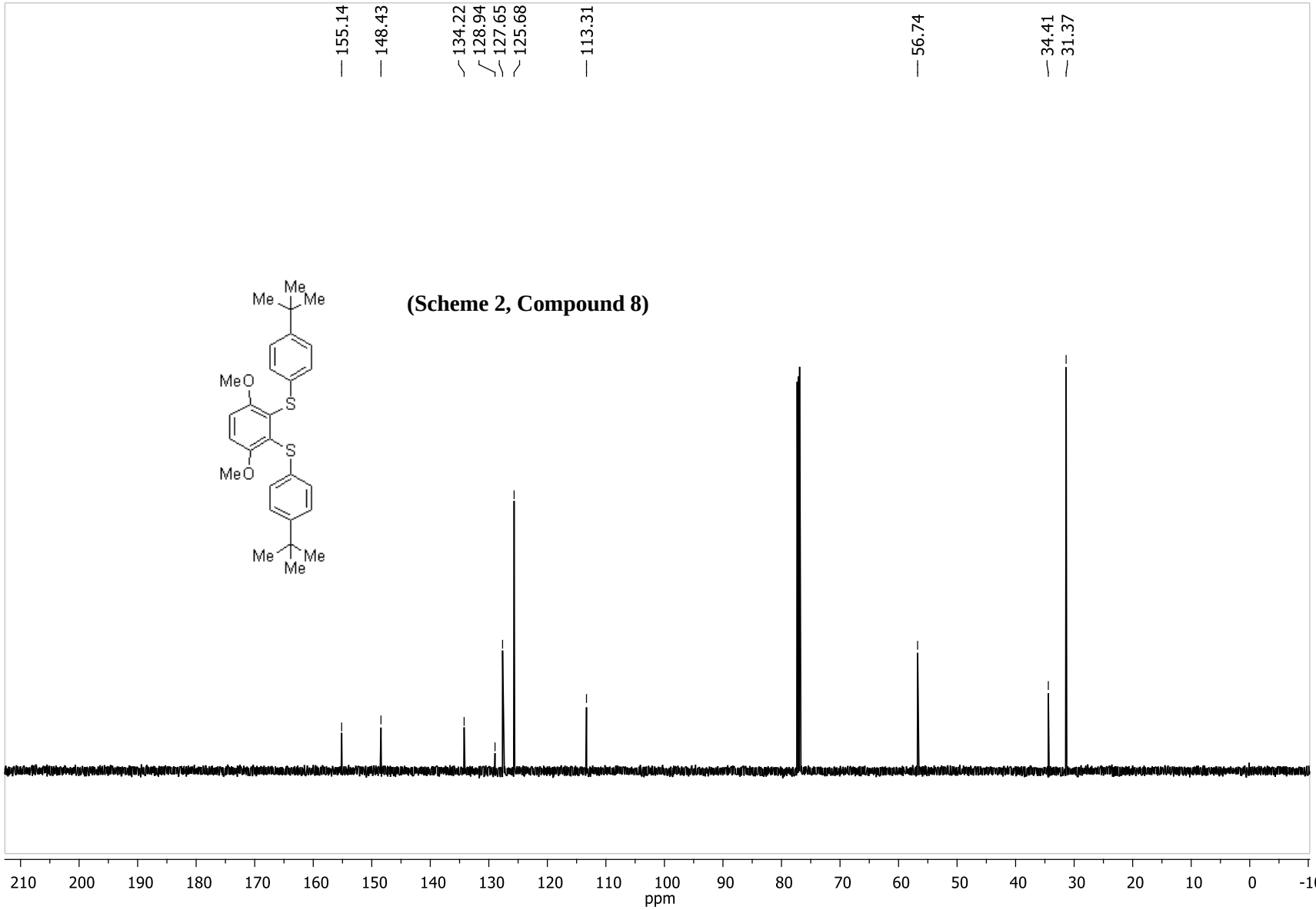

157.12
147.43
146.66
142.61
138.25
135.68
131.58
128.29
127.66
126.58
125.35
125.25
124.88
124.76
122.57
122.08
55.35
16.07
15.70
(Table 3, Entry 8)
132.47
131.58
128.29
127.66
126.58
125.35
125.25
124.88
124.76
122.57
ppm
ppm

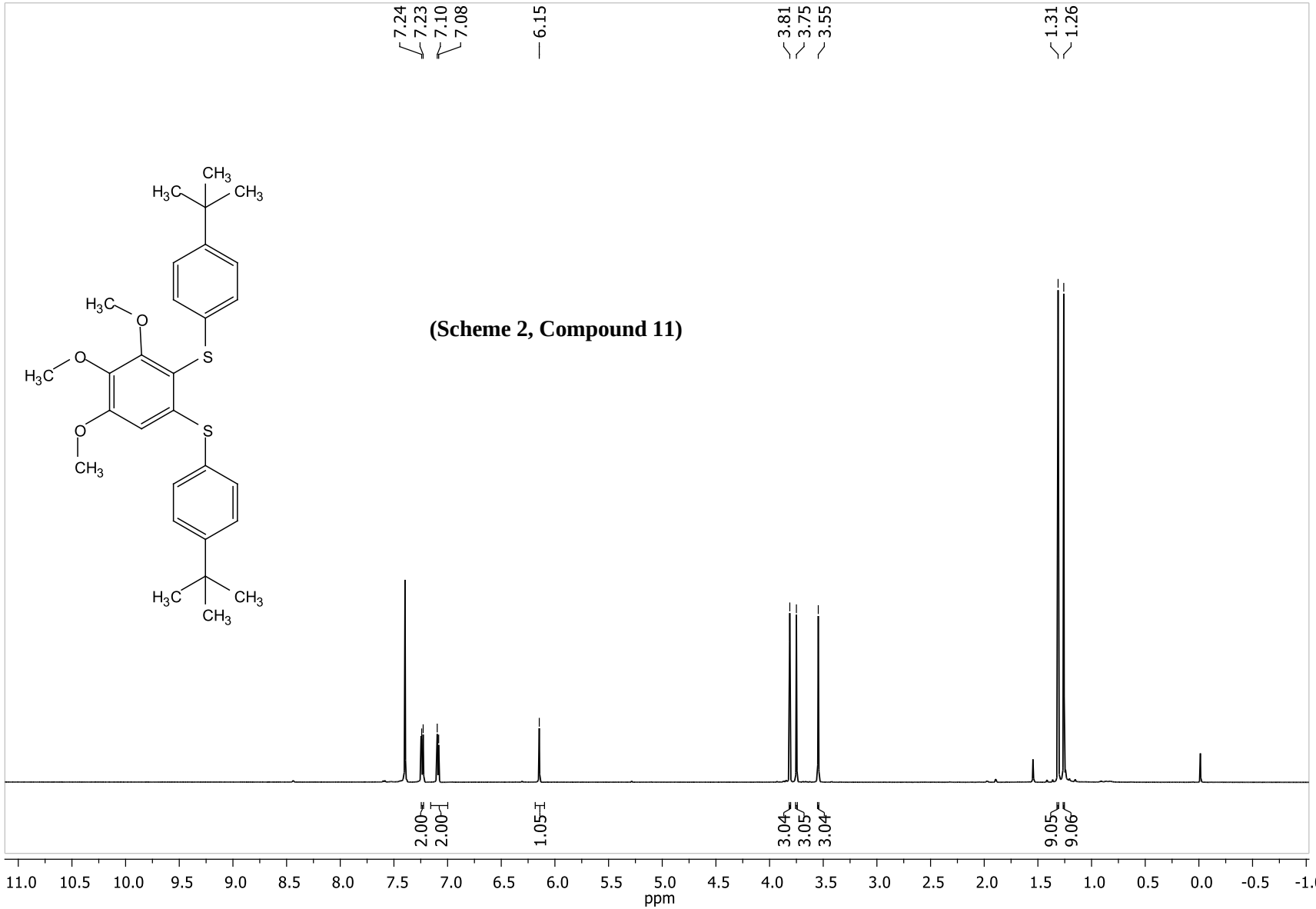

7.16
7.14
7.00
6.98
6.95
3.70
1.23
Me
Me
Me
MeO
S
S
MeO
Me
Me
Me
(Scheme 2, Compound 8)
4.03
4.01
2.00
6.02
18.35
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

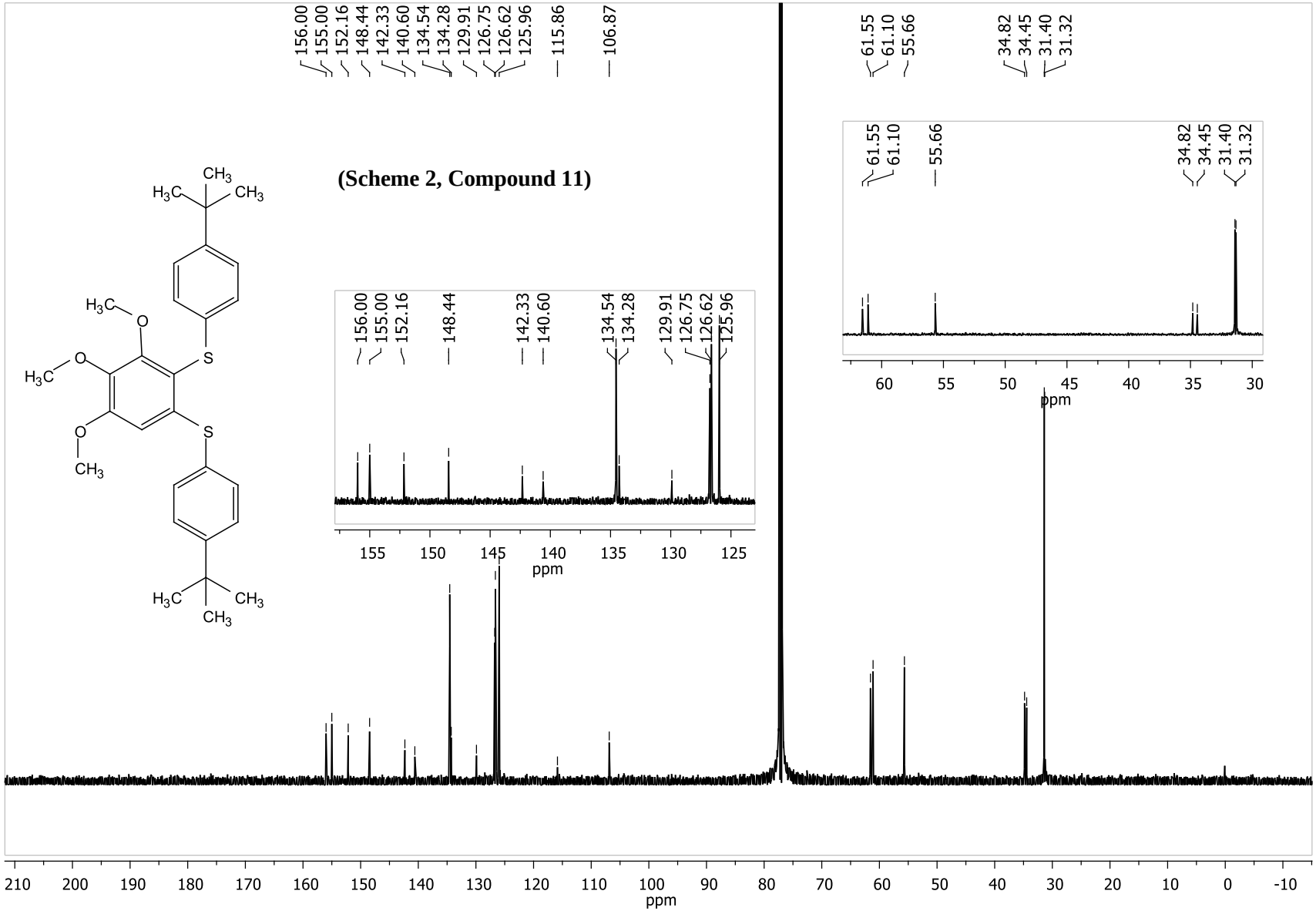

155.14
148.43
134.22
128.94
127.65
125.68
113.31
56.74
34.41
31.37
(Scheme 2, Compound 8)
Me
Me
Me
MeO
S
S
MeO
Me
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

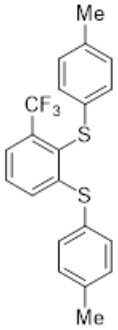
(Scheme 2, Compound 8)



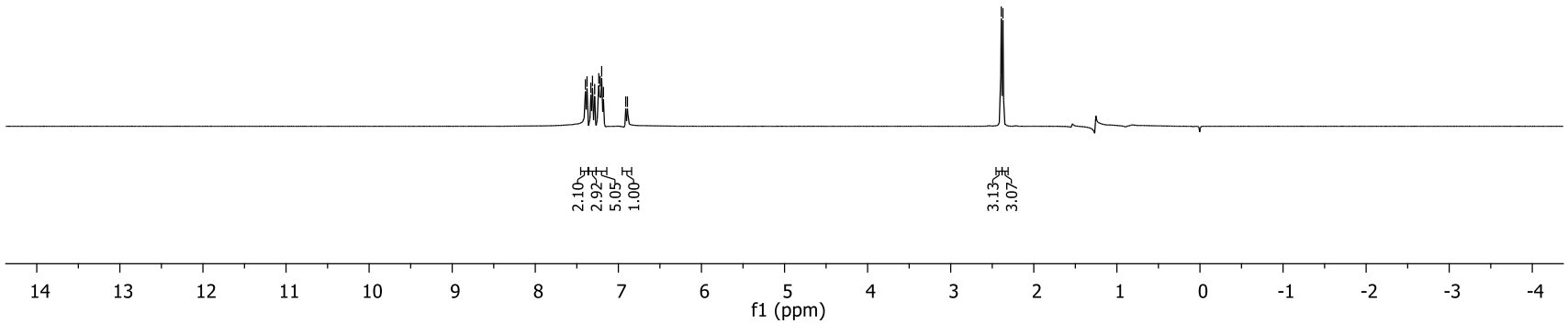

155.14
148.43
134.22
128.94
127.65
125.68
113.31
56.74
34.41
31.37
(Scheme 2, Compound 8)
Me
Me
Me
MeO
S
S
MeO
Me
Me
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

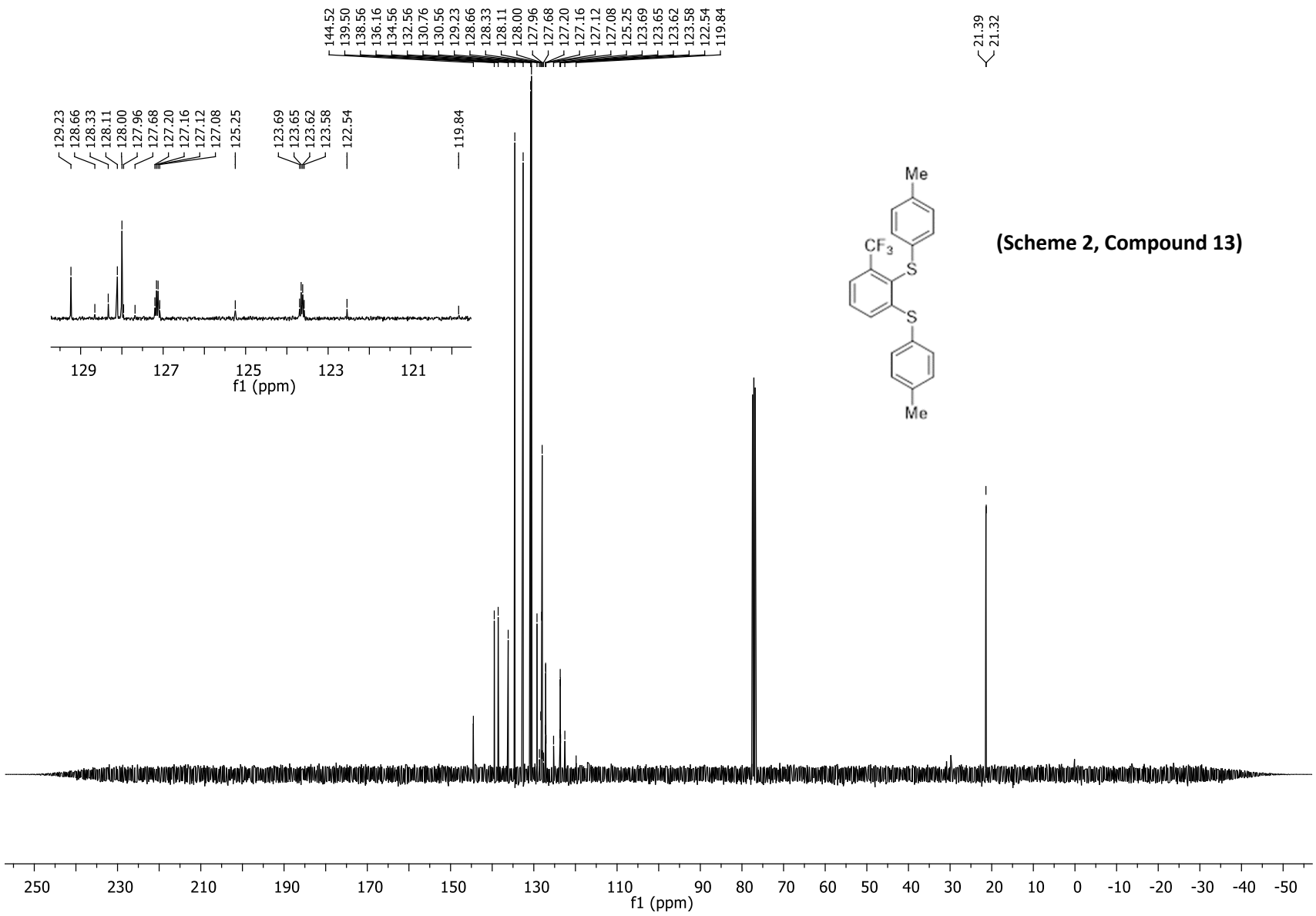

7.24
7.23
7.10
7.08
6.15
3.81
3.75
3.55
1.31
1.26
(Scheme 2, Compound 11)
2.00
2.00
1.05
3.04
3.05
3.04
9.05
9.06
ppm


156.00
155.00
152.16
148.44
142.33
140.60
134.54
134.28
129.91
126.75
126.62
125.96
115.86
106.87
61.55
61.10
55.66
34.82
34.45
31.40
31.32
(Scheme 2, Compound 11)
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

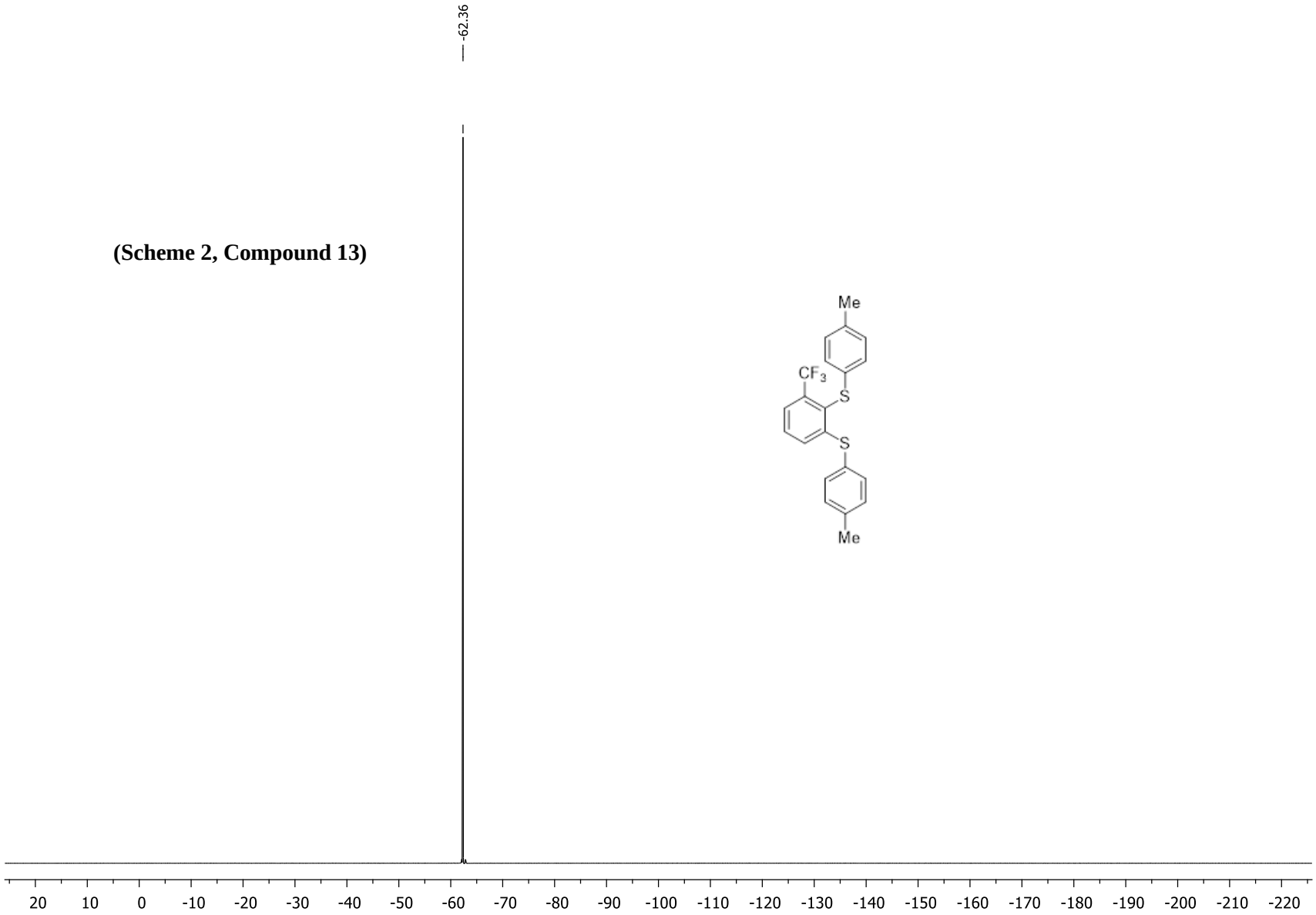


(Scheme 2, Compound 13)

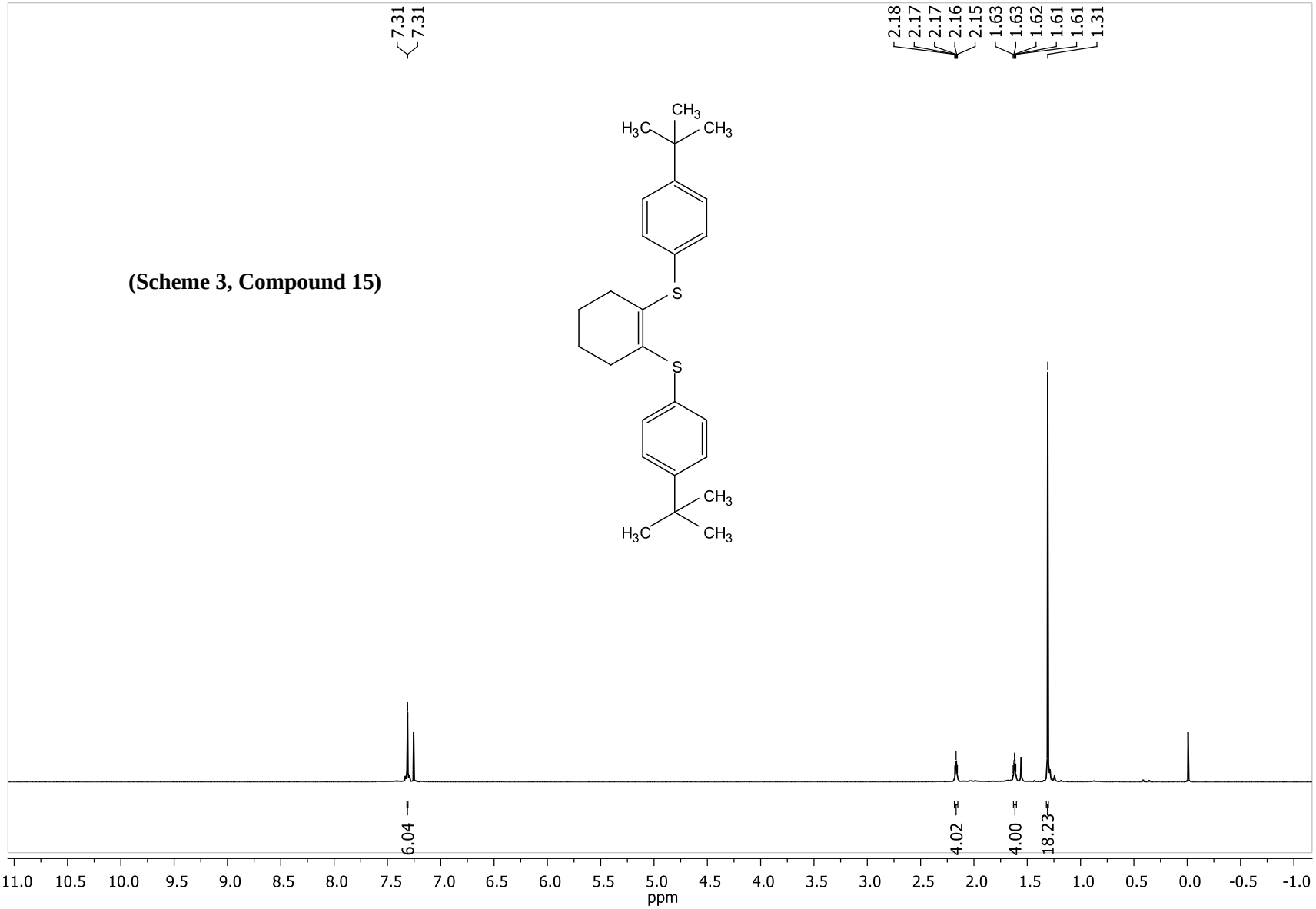


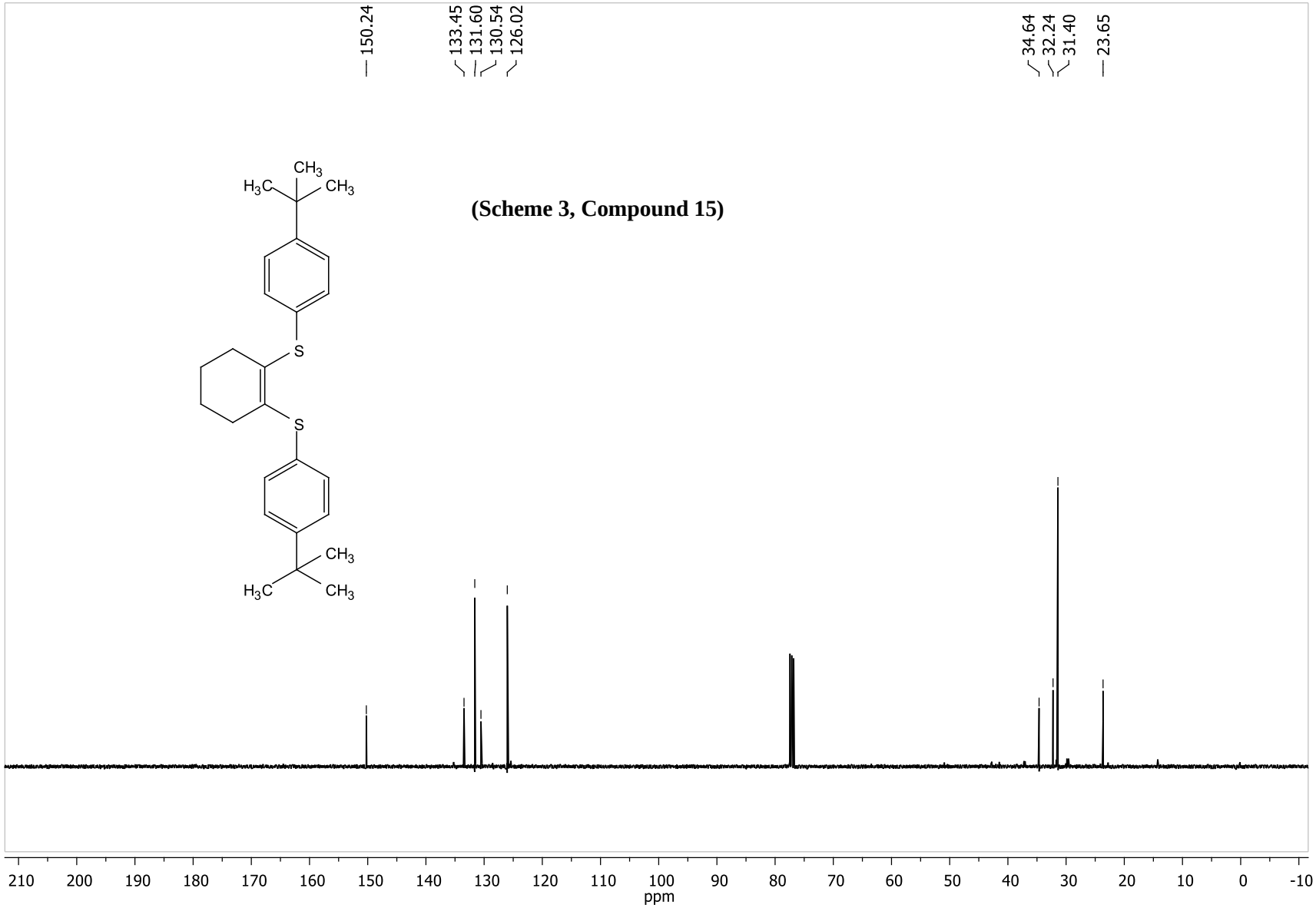

144.52
139.50
138.56
136.16
134.56
132.56
130.76
130.56
129.23
128.66
128.33
128.11
128.00
127.96
127.68
127.20
127.16
127.12
127.08
125.25
123.69
123.65
123.62
123.58
122.54
119.84
21.39
21.32
129
127
125
123
121
f1 (ppm)
Me
CF3
S
S
Me
(Scheme 2, Compound 13)
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

(Scheme 2, Compound 13)

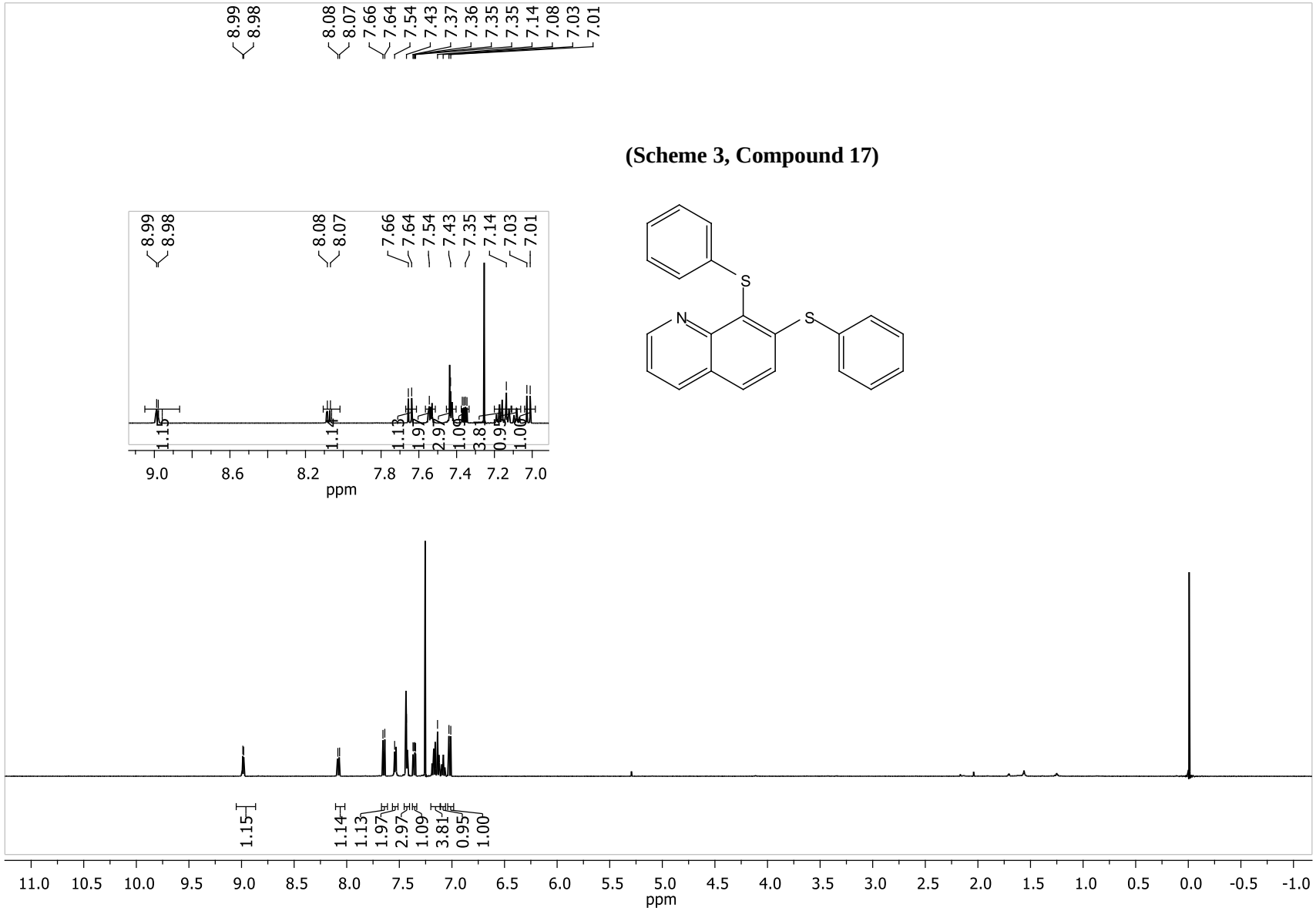


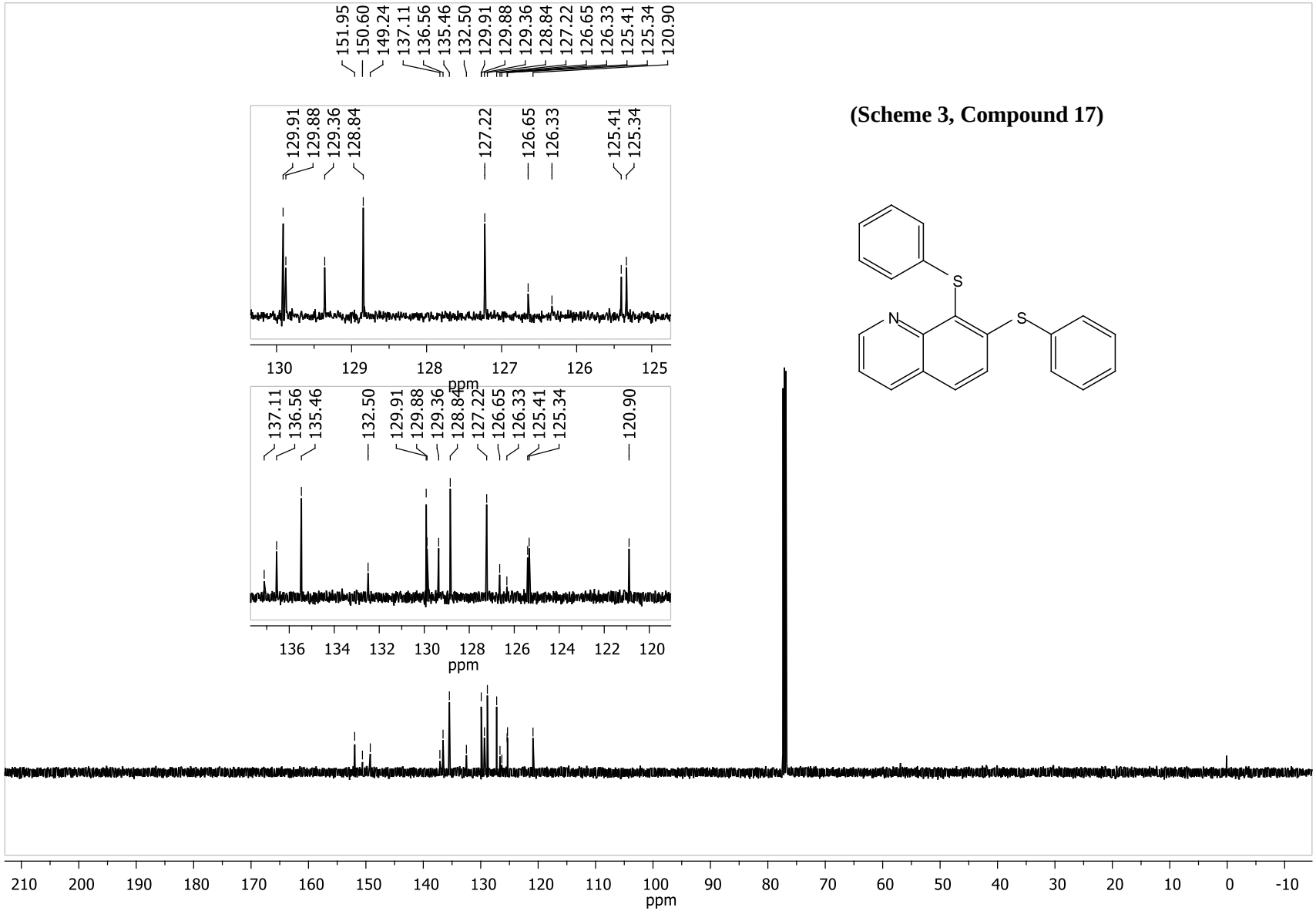
(Scheme 3, Compound 15)

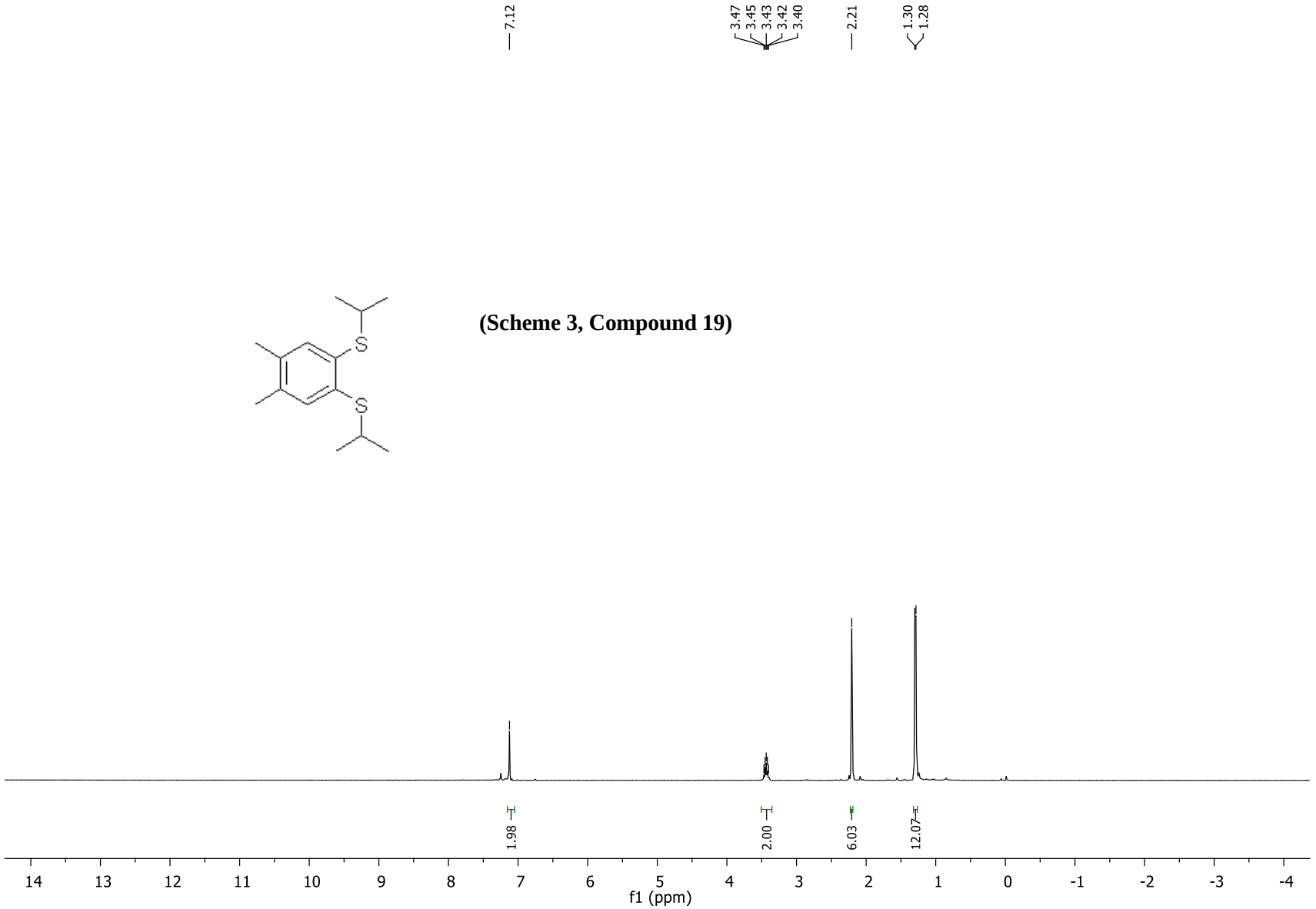



150.24
133.45
131.60
130.54
126.02
34.64
32.24
31.40
23.65
CH3
H3C
CH3
S
S
CH3
H3C
CH3
(Scheme 3, Compound 15)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

(Scheme 3, Compound 17)




151.95
150.60
149.24
137.11
136.56
135.46
132.50
129.91
129.88
129.36
128.84
127.22
126.65
126.33
125.41
125.34
120.90
(Scheme 3, Compound 17)
S
N
S
130
129
128
127
126
125
ppm
137.11
136.56
135.46
132.50
129.91
129.88
129.36
128.84
127.22
126.65
126.33
125.41
125.34
120.90
136
134
132
130
128
126
124
122
120
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



(Scheme 3, Compound 19)

(Scheme 3, Compound 19)