SUPPORTING INFORMATION

New Hindered Amide Base for Aryne Insertion into Si-P, Si-S, Si-N, and C-C Bonds

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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}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.

Materials. The following starting materials were obtained from commercial sources and were used without further purification: 1-bromoadamantane, 1-adamantanamine, 3,5-bis(trifluoromethyl)phenol, 2-naphthol, 2,5-bis(trifluoromethyl)chlorobenzene, 2-trifluoromethyl chlorobenzene, 2-biphenol, 3,4,5-trimethoxyphenol, 3,5-bis(trifluoromethyl)bromobenzene, 2,4-dichlorophenol, 5-hydroxy-1,3-benzodioxole, 4-methoxy-1-naphthol, 5,6,7,8-tetrahydro-2-naphthol, 1-naphthol, 2-chloroanisole, 9-brormophenathrene, 1,4-dimethoxy-2-chlorobenzene, 1,4-bis(trifluoromethyl)-2-chlorobenzene, 1-chloronaphthalene, 3,4,5-trimethoxybromobenzene, 2-chlorostyrene, 9-phenanthrol, 2-bromopyridine, 2-hydroxypyridine, 8-hydroxyquinoline, pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, 1-bromo-2-(trifluoromethoxy)benzene, 4-hydroxybenzaldehyde, 3-hydroxybenzonitrile, 2-(trifluoromethoxy)phenol, 2-chloronapthalene, 2-chlorobenzotrifluoride, (trimethylsilyl)diphenylphosphine, di-p-

tolylphosphine, bis(4-methoxyphenyl)phosphine, trimethyl(ethylthio)silane, isopropyl thiol, tert-butylthiol, trimethyl(phenylthio)silane, *N*,*N*-dimethyltrimethylsilylamine, *N*,*N*-diethyltrimethylsilylamine, *N*-(trimethylsilyl)morpholine, *N*-methylaniline, *N*-tolylaniline, (2-bromophenyl)diphenylphosphine. All aryl triflates were synthesized according to literature methods.[1] Silyldiarylphosphines are either commercially available or were synthesized according to literature procedures.[2] Silyl sulfides and silylamines are either commercially available or were synthesized according to literature methods.[3]

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

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 (Figure S1). 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 (Figure S2). 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.

Figure S1: Example of preparing the ampule to put in the oven

Figure S2: After 72 h in 240 °C

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): δ 1.99 (apparent s, 6H), 1.75 (d, 12H), 1.59 (apparent s, 12H). ^{13}C NMR (100 MHz) δ 52.6, 46.6, 36.6, 30.1. This compound is known.[4]

Lithium di-1-admantylamide (LDAM 1)

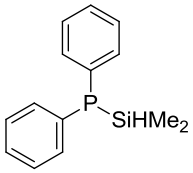
Di-1-adamantylamine (14 g) was placed in oven-dried 500 ml Schlenk flask equipped with a stir bar. Flask was sealed with rubber septum and Teflon tape. Flask was filled with N_2 gas and evacuated at least 5 times (each time 10 minutes). Anhydrous pentane (240 mL) was added to the flask via syringe. n-BuLi (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-d_8. ^{1}H NMR (600 MHz) 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.

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 Adm_2NLi (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 (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 silyl compound (2 - 4 equiv). Subsequently, one third of reaction solvent 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

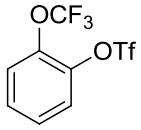
temperature for indicated time, reactions were quenched by adding 2-methyl-2-butanol and then methanol (0.5 mL, unless otherwise stated), followed by dilution with dichloromethane (0.5 mL). To the diluted reaction mixture was added silica gel and then mixture was dried on rotary evaporator, and subjected 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.

Dimethylsilytriphenylphosphine:



Inside the glove box, a Schlenk flask was charged with magnetic stir bar and diphenyl phosphine (20.0 mmol, 3.72 g). Anhydrous THF was added (30.0 mL) and the resulting solution was cooled to - 78 °C. n-BuLi (30.0 mmol, 18.75 mL of 1.6 M in hexane) was then added dropwise, the resulting mixture was allowed to reach - 60 °C, stirred for 20 min and cooled again to - 78 °C. Finally, TMSCl (30.0 mmol, 3.26 g, 3.8 mL) was added dropwise and the crude mixture was allowed to reach room temperature and concentrated to dryness. Dry pentane was added to complete precipitation of LiCl and the crude reaction was filtered via cannula under N_2. This extraction process was repeated twice; the solvents were removed under vacuum and the colorless oil (4.1 g, 84%) was used crude after evaporating the pentane. ^{1}H NMR (400 MHz) δ 7.63 – 7.41 (m, 5H), 7.37 – 7.27 (m, 5H), 4.47 – 4.36 (m, 1H), 0.24 (dd, J = 5.3, 3.9 Hz, 6H). ^{31}P NMR (162 MHz) δ - 62.8.

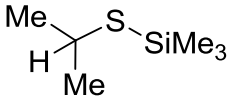
2-Trifluoromethoxyphenyltriflate:



To solution of 2-trifluoromethoxyphenol (10.0 mmol, 1.78 g) in dichloromethane (40 mL) was added pyridine (50.0 mmol, 3.95 g) and the solution was cooled to 0 °C. Trifluoromethanesulfonic anhydride (12.0 mmol, 3.39 g) was added dropwise and the mixture was warmed to room temperature. The reaction was complete within 1 hour as determined by TLC analysis. The mixture was quenched with saturated aqueous $NaHCO_3$, and brine. After drying ($MgSO_4$) the solvent was evaporated

and the residue was purified by column chromatography on silica gel using hexane (R_f = 0.80) to give product as a colorless oil in 61% isolated yield (1.89 g). ^{1}H NMR (500 MHz) δ 7.43 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H). ^{13}C NMR (126 MHz) δ 141.0, 140.8, 129.5, 128.0, 123.7, 122.5, 120.3 (q, J = 261.0 Hz), 118.7 (q, J = 321.0 Hz).

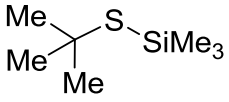
(Isopropylthio)trimethysilane:



Inside the glove box, a Schlenk flask was charged with a magnetic stir bar and isopropylthiol (3.8 g, 50 mmol). Anhydrous THF (50 mL) was added and the resulting solution was cooled to - 78 °C. n-BuLi (57.5 mmol, 36.0 mL of 1.6 M in hexane) was then added dropwise, the resulting mixture was allowed to reach - 70 °C, stirred for 20 min and cooled again to - 78 °C. Finally, TMSCl (10.86 g, 100.0 mmol) was added dropwise and the crude mixture was allowed to reach room temperature and was stirred overnight. The mixture was concentrated to dryness. Dry pentane was added to complete precipitation of LiCl and the crude reaction was filtered via cannula under N_2. This extraction process was repeated twice, the solvents were removed under vacuum and a yellow oil was obtained (5.6 g, 76%).

^{1}H NMR (400 MHz) δ 2.99 (septet, J = 6.7 Hz, 1H), 1.28 (d, J = 6.7 Hz, 6H), 0.26 (s, 9H). ^{13}C NMR (101 MHz) δ 32.5, 27.9, 1.5.

(tert-Butylthio)trimethylsilane:

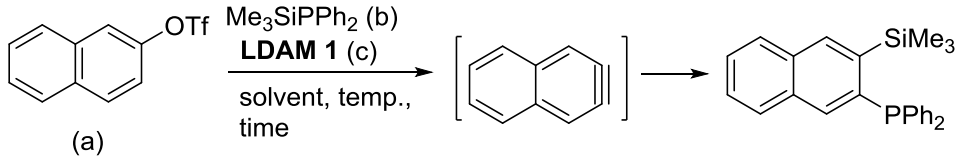


Inside the glove box, a Schlenk flask was charged with magnetic stir bar and tert-butylthiol (4.51 g, 50 mmol). Anhydrous THF (50 mL) was added and the resulting solution was cooled to - 78 °C. n-BuLi (1.15 equiv, 36.0 mL of 1.6 M in hexane) was then added dropwise, the resulting mixture was allowed to reach - 70 °C, stirred for 20 min and cooled again to - 78 °C. Finally, TMSCl (10.9 g, 2.0 equiv) was added dropwise and the crude mixture was allowed to reach room temperature and stirred overnight. The mixture was concentrated to dryness. Dry pentane was added to complete precipitation of LiCl and the crude reaction was filtered via

cannula under N_2. This extraction process was repeated twice, the solvents were removed under vacuum and a colorless oil (7.2 g, 89%) was obtained.

^{1}H NMR (400 MHz) δ 1.42 (s, 9H), 0.31 (s, 9H). ^{13}C NMR (101 MHz) δ 44.6, 35.4, 2.9.

Table S1. Optimization of ArOTf *ortho*-Phosphosilylation[a]

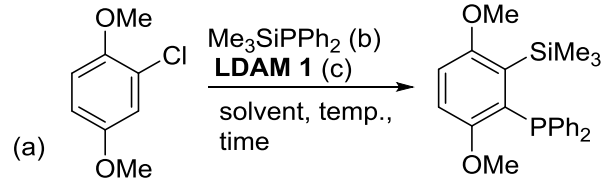


(a)

Entry	(a/b/c)	Solvent	T (°C) ,t (h)	yield (%)[b]
1	1/2/2	THF	0, 30	44
2	1/2/2	Et_2O/THF(20/1)	0, 30	29
3	1/2/2	Et_2O	0, 30	48
4	1/2.5/2	Et_2O	0, 30	40
5	1/1.5/2	Et_2O	0, 30	41
6	**1/2/3**	**Et_2O**	**0, 30**	**67**
7	1/2/3	Et_2O	25, 30	61
8	1/2/3	Et_2O	-78, 30	Trace
9	**1/2/3**	Et_2O + DMPU[d]	0, 30	13[c]

[a] Aryne precursor (0.25 mmol), solvent (1.5 mL). [b] Yields determined by GC with n-decane as an internal standard. [c] Yield determined by ^{31}P NMR with $P(OEt)_3$ as an internal standard. [d] DMPU (15 equiv) was added to the reaction.

Table S2. Optimization of ArCl *ortho*-Phosphosilylation[a]

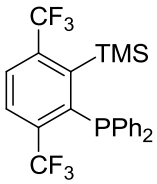


(a)

entry	(a/b/c)	Solvent	T (°C), t (h)	yield (%)[b]
1	1/2/2	Et_2O/C_6H_{12}	0, 30	63
2	1/2/2	Et_2O/THF(20/1)	0, 30	57
3	1/2/2	C_5H_{12}/THF(40/1)	0, 30	68
4	1/2.5/2	C_5H_{12}/THF(40/1)	0, 27	73
5	1/1.5/2	C_5H_{12}/THF(40/1)	0, 27	46
6	1/3/2	C_5H_{12}/THF(40/1)	0, 27	69
7	**1/2.5/1.5**	**C_5H_{12}/THF(40/1)**	**0, 30**	**77**
8	1/2/1.5	C_5H_{12}/THF(40/1)	25, 30	65
9	1/2/1.5	C_5H_{12}/THF(40/1)	-78, 30	Trace

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

3,6-Bis(trifluoromethyl-2-(trimethylsilyl)phenyl)diphenylphosphine (entry 1, Table 2)

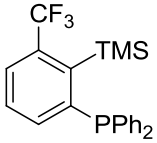


2,5-Bis(trifluoromethyl)chlorobenzene (125 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (323 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 27 hours. After column chromatography (hexanes), 213 mg (91%) of an off-white solid, mp 126-128 °C was obtained (from pentane). R_f = 0.50 (hexanes). ^{1}H NMR (500 MHz) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.32 (s, 6H), 7.26 (s, 4H), 0.55 (s, 9H). Not all ^{13}C-^{19}F and ^{13}C-^{31}P couplings have been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 155.6, 155.1, 144.4, 144.2, 139.7, 138.3, 138.1, 137.8, 137.6, 135.5, 135.4, 132.0, 131.9, 129.3, 129.2, 128.6, 128.21, 128.16, 124.3 (q, *J* = 276 Hz), 123.4 (q, *J* = 277 Hz), 5.4. ^{19}F NMR (471 MHz) δ -54.9, -55.8. ^{31}P NMR (202 MHz) δ -0.9.

FT-IR (neat, cm^{-1}) ν 3082, 3060, 2951, 1585, 1481, 1438, 1343, 1299.

HRMS (CI) calc. For $C_{23}H_{21}F_6PSi$ $[M]^+$: 470.1054; found: 470.1049.

2-(Trimethylsilyl)phenyldiphenylphosphine (entry 2, Table 2)

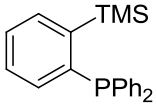


2-(Trifluoromethyl)chlorobenzene (91 mg, 0.5 mmol), diphenyl-(trimethylsilyl)phosphine (323 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 36 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 8/1), 145 mg (72%) of a colorless oil was obtained. R_f = 0.60 (hexanes/dichloromethane: 8/1). ^{1}H NMR (600 MHz) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 7.5, 3.2 Hz, 1H), 7.35 – 7.30 (m, 7H), 7.25 – 7.22 (s, 4H), 0.56 (s, 9H), 0.31. Not all ^{13}C-^{19}F and ^{13}C-^{31}P couplings have not been resolved, list of the peaks given: ^{13}C NMR (151 MHz) δ 148.4, 148.2, 146.7, 146.6, 140.1, 138.3, 138.2, 133.1, 133.0, 128.64, 128.60, 128.5, 128.2, 128.1, 127.0, 126.95, 126.91, 126.87, 124.8 (q, *J* = 275 Hz), 4.85. ^{19}F NMR (565 MHz) δ -55.2. ^{31}P NMR (243 MHz) δ -7.7. Product contains 7% of an isomeric impurity.

FT-IR (neat, cm^{-1}) ν 3055, 2954, 2896, 1585, 1479, 1434, 1396, 1308.

HRMS (CI) calc. For $C_{22}H_{22}F_3PSi$ $[M]^+$: 402.1181; found: 402.1183.

2-(Trimethylsilyl)phenyldiphenylphosphine (entry 3, Table 2)

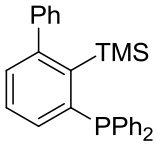


Chlorobenzene (56 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (323 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 27 hours. After column chromatography (pentane), 140 mg (84%) of a colorless oil was obtained. R_f = 0.50 (pentane). ^{1}H NMR (500 MHz) δ 7.65 – 7.62 (m, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 7H), 7.25 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 0.39 (s, 9H). ^{31}P NMR (202 MHz) δ -9.7. This compound is known.[17]

FT-IR (neat, cm^{-1}) ν 3050, 2950, 2894, 1585, 1478, 1434, 1421, 1244.

HRMS (CI) calc. For $C_{21}H_{23}PSi$ $[M]^+$: 334.1307; found: 334.1300.

3- Phenyl-2-(trimethylsilyl)phenyldiphenylphosphine (entry 4, Table 2)

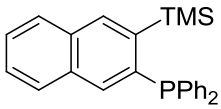


2- Diphenyl triflate[5] (152 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (260 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3.0 mL), 0 °C, 28 hours. After column chromatography (hexanes/dichloromethane: 8/1), 128 mg (62%) of a colorless oil was obtained. R_f = 0.40 (hexanes/dichloromethane: 8/1). ^{1}H NMR (500 MHz) δ 7.43 – 7.23 (m, 18H), 0.13 (s, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (151 MHz) δ 150.4, 150.3, 147.0, 146.7, 145.6, 145.04, 144.95, 139.0, 138.9, 134.9, 133.3, 133.2, 131.1, 129.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.2, 4.2. ^{31}P NMR (243 MHz) δ -8.0.

FT-IR (neat, cm^{-1}) ν 3054, 2927, 1585, 1543, 1478, 1432, 1245, 1184.

HRMS (CI) calc. For $C_{27}H_{27}PSi$ $[M]^+$: 410.1620; found: 410.1620.

2-(Trimethylsilyl)naphthyl-3-diphenylphosphine (entry 5, Table 2)

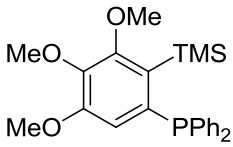


2-Naphthyl triflate[6] (139 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (260 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3 mL), 0 °C, 28 hours. After column chromatography (hexanes), 125 mg (66%) of a colorless oil was obtained. R_f = 0.60 (hexanes). ^{1}H NMR (600 MHz) δ 8.12 (d, *J* = 2.9 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.58 7.60 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.30 (s, 6H), 7.28 – 7.24 (m, 4H), 0.43 (s, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (151 MHz) δ 144.0, 143.8, 139.8, 139.7, 138.24, 138.16, 135.6, 135.5, 135.4, 133.6, 133.5, 132.9, 131.4, 131.3, 128.53, 128.49, 128.42, 127.94, 127.92, 126.9, 126.6, 1.6. ^{31}P NMR (243 MHz) δ - 9.1.

FT-IR (neat, cm^{-1}) ν 3051, 2959, 2924, 2851, 1584, 1480, 1433, 1244, 1102.

HRMS (CI) calc. For $C_{25}H_{25}PSi$ $[M]^+$: 384.1463; found: 384.1447.

3,4,5-Trimethoxy-2-(trimethylsilyl)phenyldiphenylphosphine (entry 6, Table 2)



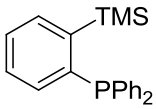
3,4,5-Trimethoxyphenyl triflate[7] (159 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (260 mg, 1.0 mmol), Adm_2NLi (438 mg, 1.5 mmol), Et_2O (3 mL), 0 °C, 28 hours. After column chromatography (hexanes/ethyl acetate: 9/1), 213 mg (47%) of a colorless oil was obtained. R_f = 0.50 (hexanes/ethyl acetate: 9/1).

^{1}H NMR (500 MHz) δ 7.33 – 7.29 (s, 6H), 7.24 – 7.20 (s, 4H), 6.34 (s, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 3.44 (s, 3H), 0.35 (s, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 159.1, 159.0, 153.8, 141.9, 139.0, 138.9, 138.2, 133.6, 133.5, 128.5, 128.4, 115.0, 61.0, 60.6, 55.5, 3.9, 3.8. ^{31}P NMR (202 MHz) δ -5.8.

FT-IR (neat, cm^{-1}) ν 3053, 2935, 2837, 1568, 1547, 1464, 1434, 1343, 1292.

HRMS (CI) calc. For $C_{24}H_{29}O_3PSi$ $[M]^+$: 424.1624; found: 424.1632.

2-(Trimethylsilyl)phenyldiphenylphosphine (entry 7, Table 2)

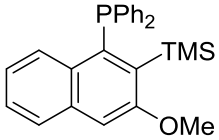


Phenyl triflate[6] (114 mg, 0.5 mmol), diphenyl(trimethylsilyl)phosphine (260 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3 mL), 0 °C, 27 hours. After column chromatography (pentane), 137 mg (82%) of a colorless oil was obtained. R_f = 0.60 (hexanes). ^{1}H NMR (500 MHz) δ 7.65 – 7.62 (m, 1H), 7.36 – 7.32 (m, 1H), 7.32 – 7.27 (m, 7H), 7.25 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 0.39 (s, 9H). ^{31}P NMR (202 MHz) δ -9.7. This compound is known.[17]

FT-IR (neat, cm^{-1}) ν 3050, 2950, 2894, 1585, 1478, 1434, 1421, 1244.

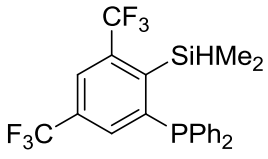
HRMS (CI) calc. For $C_{21}H_{23}PSi$ $[M]^+$: 334.1307; found: 334.1300.

1-Diphenylphosphine-3-methoxy-2-(trimethylsilyl)naphthyl (entry 8, Table 2)



3-Methoxy-2-naphthyl triflate[18] (154 mg, 0.5 mmol), diphenyl-(trimethylsilyl)phosphine (260 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3 mL), start at - 10 °C and then warm to 0 °C, 28 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate: 18/1), 160 mg (77%) of a yellow oil was obtained. R_f = 0.50 (hexanes/ethyl acetate: 18/1). ^{1}H NMR (400 MHz) δ 7.69 (d, *J* = 2.9 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.27 – 7.17 (m, 8H), 6.84 – 6.81 (m, 1H), 3.91 (s, 3H), 0.51 (s, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (100 MHz) δ 161.44, 161.17, 145.8, 145.1, 141.9, 141.8, 137.24, 137.22, 136.3, 131.4, 131.2, 129.4, 128.4, 128.3, 127.4, 127.3, 126.3, 122.9, 107.7, 54.8, 4.9. ^{31}P NMR (162 MHz) δ -9.5.

2-(Dimethylsilyl)phenyldiphenylphosphine (entry 1, Table 3)



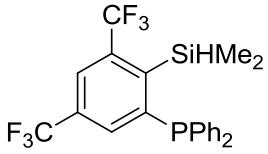
3,5-Bis(trifluoromethyl)phenyltriflate[8] (181 mg, 0.5 mmol), diphenyl(dimethylsilyl)phosphine (245 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3 mL), 0 °C, 36 hours. After column

chromatography (hexanes), 109 mg (48%) of a colorless oil was obtained. R_f = 0.70 (hexanes). ^{1}H NMR (500 MHz) δ 7.89 (s, 1H), 7.48 (s, 1H), 7.38 – 7.35 (m, 5H), 7.24 – 7.20 (m, 4H), 5.02 (septet, J = 3.8 Hz, 1H), 0.44 (d, J = 3.8 Hz, 6H). Not all ^{13}C-^{19}F and ^{13}C-^{31}P couplings are resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 149.2, 149.1, 136.4, 136.3, 133.7, 133.6, 132.1, 132.0, 131.7, 131.4, 130.6, 129.3, 129.01, 128.96, 126.4 (q, J = 274.7 Hz), 123.3 (q, J = 274.7 Hz), 123.2, 122.2, 120.0, -1.70 (d, J = 9.2 Hz). ^{19}F NMR (470 MHz) δ -56.8 (d, J = 5.5 Hz), - 63.4. ^{31}P NMR (202 MHz) δ – 8.0.

FT-IR (neat, cm^{-1}) ν 3068, 2963, 1591, 1438, 1361, 1341, 1278, 1184.

HRMS (APCI) calc. For $C_{22}H_{19}F_6PSi$ $[M+H]^+$: 457.0971; found: 457.0971.

2-(Dimethylsilyl)phenyldiphenylphosphine (entry 1, Table 3)

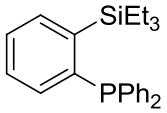


3,5-Bis(trifluoromethyl)bromobenzene (147 mg, 0.5 mmol), diphenyl(dimethylsilyl)phosphine (305 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 36 hours. After column chromatography (hexanes), 146 mg (64%) of a colorless oil was obtained. R_f = 0.70 (hexanes). ^{1}H NMR (500 MHz) δ 7.89 (s, 1H), 7.48 (s, 1H), 7.38 – 7.35 (m, 5H), 7.24 – 7.20 (m, 4H), 5.02 (septet, J = 3.8 Hz, 1H), 0.44 (d, J = 3.8 Hz, 6H). Not all ^{13}C-^{19}F and ^{13}C-^{31}P couplings have been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 149.2, 149.1, 136.4, 136.3, 133.7, 133.6, 132.1, 132.0, 131.7, 131.4, 130.6, 129.3, 129.01, 128.96, 126.4 (q, J = 274.7 Hz), 123.3 (q, J = 274.7 Hz), 123.2, 122.2, 120.0, -1.70 (d, J = 9.2 Hz). ^{19}F NMR (470 MHz) δ -56.8 (d, J = 5.5 Hz), - 63.4. ^{31}P NMR (202 MHz) δ – 8.0.

FT-IR (neat, cm^{-1}) ν 3068, 2963, 1591, 1438, 1361, 1341, 1278, 1184.

HRMS (APCI) calc. For $C_{22}H_{19}F_6PSi$ $[M+H]^+$: 457.0971; found: 457.0971.

2-(Triethylsilyl)phenyldiphenylphosphine (entry 2, Table 3)

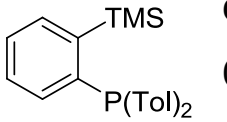


Phenyltriflate (114 mg, 0.5 mmol), diphenyl(triethylsilyl)phosphine[9] (300 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3 mL), 0 °C, 4 7 hours. After column chromatography (hexanes), 118 mg (63%) of a colorless oil was obtained. R_f = 0.60 (hexanes). ^{1}H NMR (500 MHz) δ 7.68 – 7.65 (m, 1H), 7.40 – 7.26 (m, 13H), 1.05 (q, J = 7.5 Hz, 6H), 0.95 (t, J = 7.5 Hz, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 145.6, 145.2, 143.8, 143.7, 138.6, 138.5, 136.2, 136.1, 135.77, 135.76, 133.5, 133.4, 129.1, 128.53, 128.48, 128.33, 128.30, 7.77, 7.75, 5.27, 5.19. ^{31}P NMR (202 MHz) δ – 10.0.

FT-IR (neat, cm^{-1}) ν 3051, 2951, 2871, 1585, 1455, 1435, 1419, 1234.

HRMS (APCI) calc. For $C_{24}H_{29}PSi$ $[M+H]^+$: 377.1849; found: 377.1849.

2-(Trimethylsilyl)phenyl-di-*p*-tolylphosphine (entry 3, Table 3)

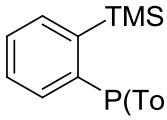


Chlorobenzene (56 mg, 0.5 mmol), di-*p*-tolyl(trimethylsilyl)phosphine[10] (358 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 4 4 hours. After column chromatography (hexanes/dichloromethane: 14/1), 161 mg (89%) of a white solid, mp 106-108 °C was obtained (from pentane). R_f = 0.60 (hexanes/dichloromethane: 14/1). ^{1}H NMR (500 MHz) δ 7.62 – 7.60 (m, 1H), 7.32 (tt, J = 7.4, 1.4 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.16 (m, 1H), 7.12 – 7.08 (m, 8H), 2.33 (s, 6H), 0.37 (d, J = 0.63, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 148.2, 147.8, 143.8, 143.7, 138.1, 135.19, 135.18, 135.07, 134.98, 134.7, 134.6, 133.4, 133.3, 129.22, 129.18, 128.22, 128.20, 21.4, 1.55, 1.47. ^{31}P NMR (202 MHz) δ -11.4.

FT-IR (neat, cm^{-1}) ν 2950, 2922, 1594, 1497, 1446, 1240, 1187, 1114.

HRMS (APCI) calc. For $C_{23}H_{27}PSi$ $[M+H]^+$: 363.1675; found: 363.1692.

2-(Trimethylsilyl)phenyl-di-*p*-tolylphosphine (entry 3, Table 3)

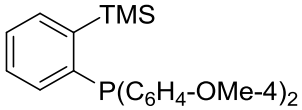


Phenyl triflate (114 mg, 0.5 mmol), di-*p*-tolyl(trimethylsilyl)phosphine[10] (286 mg, 1.0 mmol), LDAM **1** (438 mg, 1.5 mmol), Et_2O (3.0 mL), 0 °C, 4 4 hours. After column chromatography (hexanes/dichloromethane: 14/1), 155 mg (86%) of a white solid, mp 106-108 °C was obtained (from pentane). R_f = 0.60 (hexanes/dichloromethane: 14/1). ^{1}H NMR (500 MHz) δ 7.62 – 7.60 (m, 1H), 7.32 (tt, J = 7.4, 1.4 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.16 (m, 1H), 7.12 – 7.08 (m, 8H), 2.33 (s, 6H), 0.37 (d, J = 0.63, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 148.2, 147.8, 143.8, 143.7, 138.1, 135.19, 135.18, 135.07, 134.98, 134.7, 134.6, 133.4, 133.3, 129.22, 129.18, 128.22, 128.20, 21.4, 1.55, 1.47. ^{31}P NMR (202 MHz) δ -11.4.

FT-IR (neat, cm^{-1}) ν 2950, 2922, 1594, 1497, 1446, 1240, 1187, 1114.

HRMS (APCI) calc. For $C_{23}H_{27}PSi$ $[M+H]^+$: 363.1675; found: 363.1692.

2-(Trimethylsilyl)phenylbis(*p*-methoxyphenyl)phosphine (entry 4, Table 3)

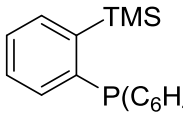


Chlorobenzene (56 mg, 0.5 mmol), bis(p-methoxyphenyl) (trimethylsilyl)phosphine[9] (398 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), pentane (2.94 mL), THF (0.06 mL), 0 °C, 4 4 hours. After column chromatography (hexanes/ethyl acetate: 20/1), 80 mg (41%) of a colorless oil was obtained. R_f = 0.50 (hexanes/ethyl acetate: 20/1). ^{1}H NMR (500 MHz) δ 7.63 – 7.60 (m, 1H), 7.34 – 7.27 (m, 2H), 7.17 – 7.13 (m, 5H), 6.85 (dd, J = 8.8, 1.0 Hz, 4H), 3.79 (s, 6H), 0.37 (d, J = 1.5 Hz, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 159.9, 147.8, 147.5, 144.3, 144.2, 134.9, 134.84, 134.83, 134.80, 134.73, 129.6, 129.5, 129.1, 128.1, 114.2, 114.1, 55.2, 1.54, 1.46. ^{31}P NMR (202 MHz) δ -13.0.

FT-IR (neat, cm^{-1}) ν 2948, 2906, 2836, 1594, 1568, 1497, 1461, 1284, 1245.

HRMS (CI) calc. For $C_{23}H_{27}O_2PSi$ $[M]^+$: 395.1591; found: 395.1583.

2-(Trimethylsilyl)phenylbis(*p*-methoxyphenyl)phosphine (entry 4, Table 3)

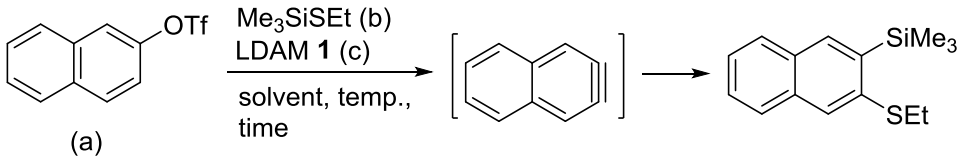


Phenyl triflate (114 mg, 0.5 mmol), bis(p-methoxyphenyl) (trimethylsilyl)phosphine[9] (318 mg, 1.25 mmol), LDAM **1** (220 mg, 0.75 mmol), Et_2O (3.0 mL), 0 °C, 44 hours. After column chromatography (hexanes/ethyl acetate: 20/1), 86 mg (44%) of a colorless oil was obtained. R_f = 0.50 (hexanes/ethyl acetate: 20/1). ^{1}H NMR (500 MHz) δ 7.63 – 7.60 (m, 1H), 7.34 – 7.27 (m, 2H), 7.17 – 7.13 (m, 5H), 6.85 (dd, J = 8.8, 1.0 Hz, 4H), 3.79 (s, 6H), 0.37 (d, J = 1.5 Hz, 9H). ^{13}C-^{31}P Couplings have not been resolved, list of the peaks given: ^{13}C NMR (126 MHz) δ 159.9, 147.8, 147.5, 144.3, 144.2, 134.9, 134.84, 134.83, 134.80, 134.73, 129.6, 129.5, 129.1, 128.1, 114.2, 114.1, 55.2, 1.54, 1.46. ^{31}P NMR (202 MHz) δ -13.0.

FT-IR (neat, cm^{-1}) ν 2948, 2906, 2836, 1594, 1568, 1497, 1461, 1284, 1245.

HRMS (CI) calc. For $C_{23}H_{27}O_2PSi$ $[M]^+$: 395.1591; found: 395.1583.

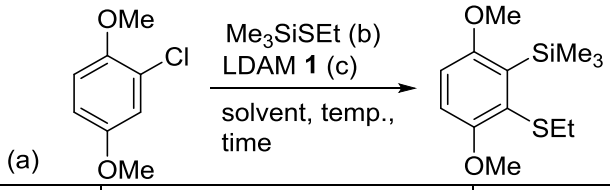
Table S3. Optimization of ArOTf *ortho*-Thiosilylation[a]



entry	(a/b/c)	Solvent	T (°C), t (h)	yield (%)[b]
1	1/2/2	THF	0, 43	28
2	1/2/2	Et_2O	0, 43	51
3	1/2/2	C_5H_{12}/THF (50/1)	0, 43	47
4	1/2/2	Et_2O/C_6H_{12} (1/1)	0, 43	52
5	**1/3/2**	**Et_2O/C_6H_{12} (1/1)**	**0, 43**	**61**
6	1/1/2	Et_2O/C_6H_{12} (1/1)	0, 43	42
7	1/2/1.5	Et_2O/C_6H_{12} (1/1)	0, 43	51
8	1/2/3	Et_2O/C_6H_{12} (1/1)	0, 43	60
9	1/2/2	Et_2O/C_6H_{12} (1/1)	25, 43	51
10	1/2/2	Et_2O/C_6H_{12} (1/1)	-78, 43	35

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

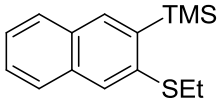
Table S4. Optimization of ArCl ortho-Thiosilylation[a]



entry	(a/b/c)	Solvent	T (°C), t (h)	yield (%)[b]
1	1/2/2	Et_2O/THF (20/1)	25, 38	67
2	1/2/2	C_5H_{12}/THF (50/1)	25, 38	63
3	1/2/2	Et_2O/C_6H_{12} (1/1)	25, 38	62
4	1/2/2	Et_2O	25, 38	68
5	1/3/2	Et_2O	25, 38	76
6	**1/3/1.5**	**Et_2O**	**25, 38**	**78**
8	1/2/2	Et_2O	50, 38	59
9	1/2/2	Et_2O	0, 38	38

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

2-(Ethylthio)-3-(trimethylsilyl)naphthalene (entry 1, Table 4)

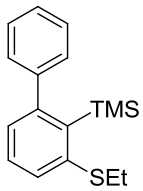


2-Naphthyl triflate[6] (139 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 28 hours. After column chromatography (pentane), 105 mg (81 %) of a colorless oil was obtained. R_f = 0.4 (pentane). ^{1}H NMR (400 MHz) δ 8.00 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.43 (m, 2H), 3.12 (q, *J* = 7.4 Hz, 2H), 1.44 (t, *J* = 7.4 Hz, 3H), 0.54 (s, 9H). ^{13}C NMR (101 MHz) δ 140.4, 139.3, 135.7, 134.3, 131.2, 128.1, 127.0, 126.7, 126.3, 125.6, 29.2, 14.2, 0.5.

FT-IR (neat, cm^{-1}) ν 3051, 2953, 2926, 1620, 1571, 1416, 1244.

HRMS (CI) calc. For $C_{15}H_{20}SiS$ $[M]^+$: 260.1055; found: 260.1057.

1-(Ethylthio)-3-phenyl-2-(trimethylsilyl)benzene (entry 2, Table 4)

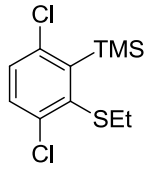


2-Diphenyl triflate[5] (152 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 28 hours. After column chromatography (pentane), 102 mg (71 %) of a colorless oil was obtained. R_f = 0.35 (pentane). ^{1}H NMR (500 MHz) δ 7.46 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.32 – 7.27 (m, 3H), 7.07 (dd, *J* = 7.7, 1.1 Hz, 1H), 3.02 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H), 0.08 (s, 9H). ^{13}C NMR (126 MHz) δ 150.6, 145.2, 144.8, 140.7, 129.8, 129.6, 128.5, 128.4 127.9, 127.2, 30.9, 14.4, 2.8.

FT-IR (neat, cm^{-1}) ν 3054, 2954, 2928, 1578, 1447, 1429, 1310.

HRMS (CI) calc. For $C_{17}H_{22}SiS$ $[M]^+$: 286.1212; found: 286.1220.

1,4-Dichloro-3-(ethylthio)-2-(trimethylsilyl)benzene (entry 3, Table 4)

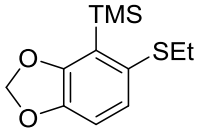


1,4-Dichlorophenyl triflate[11] (148 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 31 hours. After column chromatography (hexanes), 69 mg (52 %) of a colorless oil was obtained. R_f = 0.6 (hexanes). ^{1}H NMR (500 MHz) δ 7.33 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.86 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H), 0.52 (s, 9H). ^{13}C NMR (126 MHz) δ 146.8, 141.9, 139.4, 139.3, 131.5, 131.4 30.9, 13.7, 4.4.

FT-IR (neat, cm^{-1}) ν 2961, 2929, 1399, 1247, 1146, 1099, 1061.

HRMS (CI) calc. For $C_{11}H_{16}SiSCl_2$ $[M]^+$: 278.0119; found: 278.0126.

6-(Ethylthio)-5-(trimethylsilyl)-1,3-benzodioxole (entry 4, Table 4)

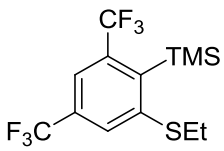


1,3-Benzodioxol-4-yl trifluoromethanesulfonate[12] (135 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 37 hours. After column chromatography (hexanes), 77 mg (61%) of a colorless oil was obtained. R_f = 0.35 (hexanes). ^{1}H NMR (500 MHz) δ 6.95 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 2H), 2.81 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H), 0.40 (s, 9H). ^{13}C NMR (126 MHz) δ 152.9, 145.6, 134.2, 126.9, 122.9, 109.4, 100.3, 31.9, 14.3, 1.7.

FT-IR (neat, cm^{-1}) ν 2959, 2926, 2895, 1575, 1411, 1394, 1318, 1245, 1225, 1142.

HRMS (CI) calc. For $C_{12}H_{18}O_2SiS$ $[M]^+$: 254.0797; found: 254.0797.

1,5-Bis(trifuoromethyl)-3-(ethylthio)-2-(trimethylsilyl)benzene (entry 5, Table 4)



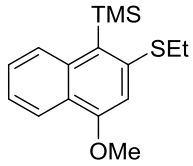
3,5-Bis(trifluoromethyl)phenyl triflate[8] (181 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol),

diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 37 hours. After column chromatography (hexanes), 116 mg (67%) of a colorless oil was obtained. R_f = 0.9 (hexanes). ^{1}H NMR (500 MHz) δ 7.79 (s, 1H), 7.74 (s, 1H), 3.00 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 0.50 (s, 9H). ^{13}C NMR (126 MHz) δ 148.3, 146.5, 136.8 (q, *J* = 31.5 Hz), 131.1 (q, *J* = 31.5 Hz), 129.9, 123.7 (q, *J* = 275 Hz), 123.3 (q, *J* = 273 Hz), 120.4, 31.2, 13.9, 3.0. ^{19}F NMR (470 MHz) δ -56.2, -63.3. Product contains 4% of an isomeric impurity.

FT-IR (neat, cm^{-1}) ν 2973, 2923, 1424, 1334, 1280, 1235, 1190, 1166, 1131.

HRMS (CI) calc. For $C_{13}H_{16}SiSF_6$ $[M]^+$: 346.0646; found: 346.0641.

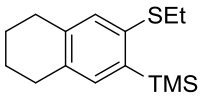
2-(Ethylthio)-4-methoxy-1-(trimethylsilyl)naphthalene (entry 6, Table 4)



4-Methoxy-1-naphthyl triflate[13] (153 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 37 hours. After column chromatography (hexanes), 95 mg (66 %) of a white solid was obtained. Mp 65 – 67 °C (from pentane). ^{1}H-NMR analysis of the crude reaction mixture showed the presence of another isomer of product (4.2:1 ratio). R_f = 0.6 (hexanes). ^{1}H NMR (500 MHz) δ 8.56 (d, *J* = 8.6 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.52 – 7.48 (m, 1H), 6.93 (s, 1H), 4.01 (s, 3H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H), 0.47 (s, 9H). ^{13}C NMR (126 MHz) δ 155.2, 145.8, 135.7, 131.3, 127.2, 126.9, 126.3, 125.8, 122.5, 108.6, 55.4, 32.1, 14.1, 1.0. FT-IR (neat, cm^{-1}) ν 3067, 2998, 2953, 2928, 1578, 1499, 1449, 1406, 1363.

HRMS (CI) calc. For $C_{16}H_{22}OSiS$ $[M]^+$: 290.1161; found: 290.1168.

6-(Ethylthio)-7-(trimethylsilyl)-1,2,3,4-tetrahydronaphthalene (entry 7, Table 4)



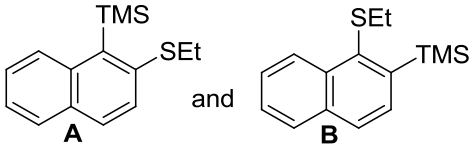
1,2,3,4-Tetrahydro-6-naphthyl triflate[12] (140 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol),

diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 37 hours. After column chromatography (hexanes), 74 mg (56 %) of a colorless oil was obtained. R_f = 0.65 (hexanes). ^{1}H NMR (400 MHz) δ 7.14 (s, 1H), 7.12 (s, 1H), 2.90 (q, *J* = 7.4 Hz, 2H), 2.77 – 2.67 (m, 4H), 1.82 – 1.72 (m, 4H), 1.29 (t, *J* = 7.4 Hz, 3H), 0.34 (s, 9H). ^{13}C NMR (101 MHz) δ 139.4, 139.0, 138.9, 136.1, 134.8, 131.4, 30.2, 29.3, 29.1, 23.3, 23.1, 14.4, 0.3.

FT-IR (neat, cm^{-1}) ν 3001, 2925, 2858, 1585, 1544, 1448, 1372, 1254, 1243.

HRMS (CI) calc. For $C_{15}H_{24}SiS$ $[M]^+$: 264.1368; found: 264.1368.

2-(Ethylthio)-1-(trimethylsilyl)-naphthalene (entry 8, Table 4)



1-Naphthyl triflate[6] (138 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 37 hours. After column chromatography (hexanes), 53.5 mg (41.5 %) of A and 35.5 mg (27.5%) of B as colorless oils was obtained. R_f = 0.40 for A and 0.55 for B (hexanes). Crude isomer ratio was 1.6:1 (analysis by ^{1}H NMR).

For A: ^{1}H NMR (500 MHz) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 15.4, 9.0 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.39 (m, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 0.65 (s, 8H). ^{13}C NMR (126 MHz) δ 142.6, 139.9, 138.1, 132.1, 130.1, 129.3, 128.9, 128.2, 125.7, 125.2, 30.7, 14.5, 4.8. FT-IR (neat, cm^{-1}) ν 3051, 2961, 2926, 1585, 1503, 1440, 1418, 1248.

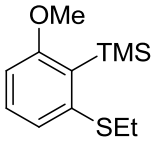
HRMS (CI) calc. For $C_{15}H_{20}SiS$ $[M]^+$: 260.1055; found: 260.1057.

For B: ^{1}H NMR (400 MHz) δ 8.61 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 16.7, 8.1 Hz, 2H), 7.64 – 7.47 (m, 3H), 2.82 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 4H), 0.47 (s, 9H). ^{13}C NMR (101 MHz) δ 145.4, 140.5, 134.8, 134.7, 131.0, 128.7, 128.2, 126.8, 126.50, 126.49, 32.1, 14.2, 1.0.

FT-IR (neat, cm^{-1}) ν 3050, 2952, 2927, 1542, 1447, 1299, 1243, 1148.

HRMS (CI) calc. For $C_{15}H_{20}SiS$ $[M]^+$: 260.1055; found: 260.1057.

1-(Ethylthio)-3-metoxy-2-(trimethylsilyl)benzene (entry 9, Table 4)

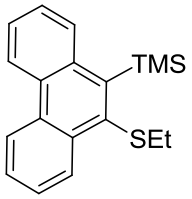


2-Chloroanisole (72 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 39 hours. After column chromatography (hexanes/dichloromethane 6:1), 71 mg (63%) of a colorless oil was obtained. R_f = 0.4 (hexanes/dichloromethane 10:1). ^{1}H NMR (500 MHz) δ 7.24 (t, *J* = 8.0 Hz, *J* = 7.2, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 0.41 (s, 9H). ^{13}C NMR (126 MHz) δ 164.9, 145.0, 130.4, 122.1, 121.0, 107.9, 55.2, 29.4, 14.2, 3.0.

FT-IR (neat, cm^{-1}) ν 3051, 2925, 2853, 1589, 1479, 1422, 1244.

HRMS (CI) calc. For $C_{12}H_{20}OSiS$ $[M]^+$: 240.1004; found: 240.1008.

9-(Ethylthio)-10-(trimethylsilyl)phenanthrene (entry 10, Table 4)

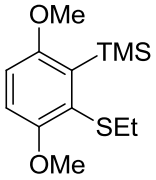


9-Bromophenanthrene (129 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 39 hours. After column chromatography (hexanes), 121 mg (78 %) of a colorless oil was obtained. R_f = 0.6 (pentane). ^{1}H NMR (500 MHz) δ 8.90 – 8.86 (m, 1H), 8.73 – 8.68 (m, 2H), 8.37 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.58 (m, 4H), 2.80 (q, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H), 0.72 (s, 9H). ^{13}C NMR (126 MHz) δ 145.9, 141.6, 135.6, 132.4, 131.8, 130.4, 129.4, 127.6, 127.3, 127.1, 126.6, 125.8, 123.2, 122.9, 32.3, 14.4, 5.4.

FT-IR (neat, cm^{-1}) ν 3064, 2957, 2926, 1551, 1481, 1444, 1373.

HRMS (CI) calc. For $C_{19}H_{22}SiS$ $[M]^+$: 310.1212; found: 310.1205.

1,4-Dimetoxy-3-(ethylthio)-2-(trimethylsilyl)benzene (entry 11, Table 4)

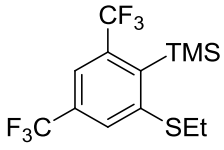


2-Chloro-1,4-dimethoxybenzene (88 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 39 hours. After column chromatography (hexanes/dichloromethane 6:1), 98 mg (74%) of a brown oil was obtained. R_f = 0.3 (hexanes/dichloromethane 6:1). ^{1}H NMR (400 MHz) δ 6.83 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 2.85 (q, *J* = 7.4 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H), 0.41 (s, 9H). ^{13}C NMR (101 MHz) δ 158.4, 154.6, 134.8, 130.6, 112.4, 111.4, 56.3, 55.9, 29.5, 14.2, 3.5.

FT-IR (neat, cm^{-1}) ν 2930, 2831, 1569, 1454, 1418, 1370, 1243, 1180.

HRMS (CI) calc. For $C_{13}H_{22}O_2SiS$ $[M]^+$: 270.1110; found: 270.1105.

1,5-Bis(trifuoromethyl)-3-(ethylthio)-2-(trimethylsilyl)benzene (entry 12, Table 4)

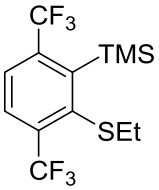


3,5-Bis(trifluoromethyl)bromobenzene (147 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 46 hours. After column chromatography (hexanes), 128 mg (74%) of a colorless oil was obtained. R_f = 0.9 (hexanes).Analysis of crude reaction mixture by ^{1}H-NMR showed isomer ratio of 16:1. ^{1}H NMR (500 MHz) δ 7.79 (s, 1H), 7.74 (s, 1H), 3.00 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 0.50 (s, 9H). ^{13}C NMR (126 MHz) δ 148.3, 146.5, 136.8 (q, *J* = 31.5 Hz), 131.1 (q, *J* = 31.5 Hz), 129.9, 123.7 (q, *J* = 275 Hz), 123.3 (q, *J* = 273 Hz), 120.4, 31.2, 13.9, 3.0. ^{19}F NMR (470 MHz) δ -56.2, -63.3.

FT-IR (neat, cm^{-1}) ν 2973, 2923, 1424, 1334, 1280, 1235, 1190, 1166, 1131.

HRMS (CI) calc. For $C_{13}H_{16}SiSF_6$ $[M]^+$: 346.0646; found: 346.0641.

1,4-Bis(trifuoromethyl)-3-(ethylthio)-2-(trimethylsilyl)benzene (entry 13, Table 4)

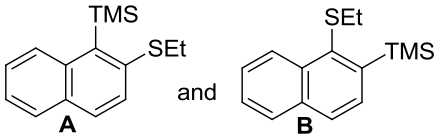


2,5-Bis(trifluoromethyl)chlorobenzene (124 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 46 hours. After column chromatography (hexanes), 127 mg (74%) of a colorless oil was obtained. R_f = 0.9 (hexanes). ^{1}H NMR (500 MHz) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H), 0.48 (s, 9H). ^{13}C NMR (126 MHz) δ 151.8, 144.9, 139.8 (q, *J* = 29 Hz), 137.9 (q, *J* = 28 Hz), 127.7, 126.3, 123.9 (q, *J* = 275 Hz), 123.5 (q, *J* = 275 Hz), 36.0, 13.5, 4.0. ^{19}F NMR (470 MHz) δ -55.9, -59.4.

FT-IR (neat, cm^{-1}) ν 2968, 2917, 2847, 1581, 1444, 1404, 1354, 1303, 1256.

HRMS (CI) calc. For $C_{13}H_{16}SiSF_6$ $[M]^+$: 346.0646; found: 346.0641.

2-(Ethylthio)-1-(trimethylsilyl)naphthalene (entry 14, Table 4)



1-Naphthyl chloride (82 mg, 0.5 mmol), (ethylthio)-trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 46 hours. After column chromatography (hexanes), 60 mg (47 %) of A and 30 mg (23%) of B as a colorless oil was obtained. R_f = 0.40 for A and 0.55 for B (hexanes). Crude isomer ratio was 1.9:1.

For A: ^{1}H NMR (500 MHz) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 15.4, 9.0 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.39 (m, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.4 Hz, 3H), 0.65 (s, 8H). ^{13}C NMR (126 MHz) δ 142.6, 139.9, 138.1, 132.1, 130.1, 129.3, 128.9, 128.2, 125.7, 125.2, 30.7, 14.5, 4.8. FT-IR (neat, cm^{-1}) ν 3051, 2961, 2926, 1585, 1503, 1440, 1418, 1248.

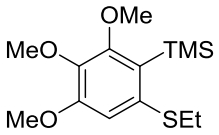
HRMS (CI) calc. For $C_{15}H_{20}SiS$ $[M]^+$: 260.1055; found: 260.1057.

For B: ^{1}H NMR (400 MHz) δ 8.61 (d, *J* = 8.4 Hz, 1H), 7.82 (dd, *J* = 16.7, 8.1 Hz, 2H), 7.64 – 7.47 (m, 3H), 2.82 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 4H), 0.47 (s, 9H). ^{13}C NMR (101 MHz) δ 145.4, 140.5, 134.8, 134.7, 131.0, 128.7, 128.2, 126.8, 126.50, 126.49, 32.1, 14.2, 1.0.

FT-IR (neat, cm^{-1}) ν 3050, 2952, 2927, 1542, 1447, 1299, 1243, 1148.

HRMS (CI) calc. For $C_{15}H_{20}SiS$ [M]$^{+}$: 260.1055; found: 260.1057.

3,4,5-Trimetoxy-2-(trimethylsilyl)ethylthiobenzene (entry 15, Table 4)

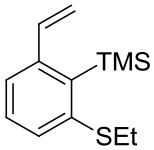


3,4,5-Trimethoxybromobenzene (125 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 46 hours. After column chromatography (hexanes/ethyl acetate 18:1), 101 mg (68%) of a colorless oil was obtained. R_f = 0.35 (hexanes/ethyl acetate 18:1). ^{1}H NMR (400 MHz) δ 6.77 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 2.87 (q, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.4 Hz, 3H), 0.38 (s, 9H). ^{13}C NMR (101 MHz) δ 159.0, 154.2, 140.6, 138.1, 127.0, 111.6, 61.1, 60.6, 56.0, 31.0, 14.3, 3.1.

FT-IR (neat, cm^{-1}) ν 2961, 2932, 2837, 1569, 1465, 1441, 1423, 1354, 1288.

HRMS (CI) calc. For $C_{14}H_{24}O_3SiS$ [M]$^{+}$: 300.1215; found: 300.1221.

1-(Ethylthio)-3-ethenyl-2-(trimethylsilyl)benzene (entry 16, Table 4)



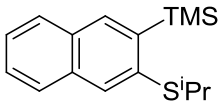
2-Chlorostyrene (71 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 46 hours. After column chromatography (hexanes), 60 mg (52 %) of a colorless oil was obtained. R_f = 0.70 (hexanes). ^{1}H NMR (500 MHz) δ 7.35 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.09 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 11.2 Hz, 1H), 2.92 (q, *J* = 7.4 Hz, 2H), 1.28 (d, *J* = 7.4 Hz, 3H),

0.46 (s, 9H). ^{13}C NMR (126 MHz) δ 146.4, 144.1, 140.5, 140.2, 130.4, 129.3, 125.7, 115.6, 30.8, 14.3, 4.2.

FT-IR (neat, cm^{-1}) ν 3073, 3037, 2963, 2927, 1544, 1433, 1246, 1119, 1051.

HRMS (CI) calc. For $C_{13}H_{20}SiS$ $[M]^+$: 236.1055; found: 236.1052.

2-(Isopropylthio)-3-(trimethylsilyl)naphthalene (Scheme 3, compound 5)

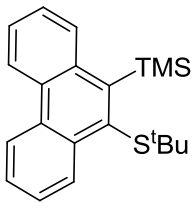


2-Naphthyl triflate[6] (139 mg, 0.5 mmol), (i-propylthio)trimethylsilane (223 mg, 1.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 0 °C, 40 hours. After column chromatography (pentane), 64 mg (47 %) of a yellow oil was obtained. R_f = 0.7 (pentane). ^{1}H NMR (400 MHz) δ 7.95 (s, 1H), 7.84 (s, 1H), 7.76 (dd, J = 28.9, 7.9 Hz, 2H), 7.52 – 7.39 (m, 2H), 3.6 (Septet, J = 6.7 Hz, 1H), 1.37 (d, J = 6.7 Hz, 6H), 0.46 (s, 9H). ^{13}C NMR (101 MHz) δ 140.6, 139.4, 135.6, 134.1, 131.4, 129.2, 128.0, 126.9, 126.8, 125.8, 39.4, 23.1, 0.6.

FT-IR (neat, cm^{-1}) ν 3050, 2958, 2924, 1621, 1572, 1482, 1245.

HRMS (CI) calc. For $C_{15}H_{19}SiS$ $[M\text{-}Me]^+$: 259.0972; found: 259.0971.

9-(*tert*-Butylthio)-10-(trimethylsilyl)phenanthrene (Scheme 3, compound 6)

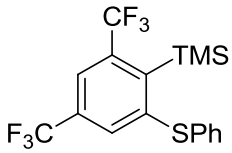


9-Bromophenanthrene (129 mg, 0.5 mmol), (t-butylthio)trimethylsilane (244 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 25 °C, 39 hours. After column chromatography (hexanes), 103 mg (61 %) of a white solid was obtained, mp 94-96 °C (from pentane). R_f = 0.75 (hexanes). ^{1}H NMR (400 MHz) δ 9.08 (dd, J = 8.5, 1.7 Hz, 1H), 8.69 (d, J = 8.7 Hz, 1H), 8.63 (d, J = 8.9 Hz, 2H), 8.28 (d, J = 8.4 Hz, 1H), 7.89 – 7.41 (m, 4H), 1.17 (s, 9H), 0.61 (s, 9H). ^{13}C NMR (101 MHz) δ 149.4, 140.0, 135.6, 135.1, 131.2, 130.4, 129.7, 129.1, 127.2, 126.6, 126.3, 125.6, 123.2, 122.4, 48.6, 31.8, 5.7.

FT-IR (neat, cm^{-1}) ν 3077, 2957, 2923, 2850, 1549, 1479, 1443, 1365, 1249.

For $C_{21}H_{26}SSi$ $[M+H-TMS]^+$: 267.0658; found: 267.0650.

1,5-Bis(trifuoromethyl)-3-(phenylthio)-2-(trimethylsilyl)benzene (Scheme 3, compound 7)

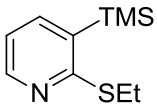


3,5-Bis(trifluoromethyl)phenyltriflate[8] (181 mg, 0.5 mmol), (phenylthio)trimethylsilane (274 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 25 °C, 40 hours. After column chromatography (hexanes), 128 mg (74%) of a colorless oil was obtained. R_f = 0.8 (hexanes). ^{1}H NMR (500 MHz) δ 7.80 (s, 1H), 7.66 (s, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 6.4 Hz, 1H), 7.20 (d, J = 7.9 Hz, 2H), 0.53 (s, 9H). ^{13}C NMR (126 MHz) δ 147.2, 137.1 (q, J = 32.8 Hz), 136.6, 133.9, 133.3, 131.5 (q, J = 32.8 Hz), 130.4, 129.7, 127.6, 123.6 (q, J = 274.7 Hz), 123.0 (q, J = 274.7 Hz), 121.4, 2.93 (q, J = 3.0 Hz). ^{19}F NMR (470 MHz) δ -56.3, -63.3.

FT-IR (neat, cm^{-1}) ν 2903, 1583, 1477, 1441, 1351, 1334, 1277, 1192, 1132.

For $C_{17}H_{16}F_6SSi$ $[M]^+$: 394.0646; found: 394.0638.

2-(Ethylthio)-3-(trimethylsilyl)pyridine (Scheme 3, compound 8)

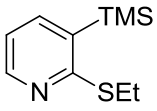


Pyridin-2-yl trifluoromethanesulfonate[6] (114 mg, 0.5 mmol), (ethylthio) trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 25 °C, 28 hours. After column chromatography (hexanes/dichloromethane 3:2), 33 mg (32 %) of a yellow oil was obtained. R_f = 0.35 (hexanes/dichloromethane 3:2). ^{1}H NMR (500 MHz) δ 8.38 (dd, J = 4.9, 1.9 Hz, 3H), 7.58 (dd, J = 7.3, 2.0 Hz, 3H), 6.94 (dd, J = 7.3, 4.9 Hz, 3H), 3.22 (q, J = 7.4 Hz, 6H), 1.35 (t, J = 7.3 Hz, 10H), 0.37 (s, 27H). ^{13}C NMR (126 MHz) δ 164.3, 149.3, 142.3, 133.6, 119.0, 254, 14.8, -0.9.

FT-IR (neat, cm^{-1}) ν 2956, 2923, 2853, 1558, 1547, 1455, 1362, 1249, 1137.

HRMS (APCI) calc. For $C_{10}H_{17}NSSi$ $[M+H]^+$: 212.0924; found: 212.0924.

2-(Ethylthio)-3-(trimethylsilyl)pyridine (Scheme 3, compound 8)

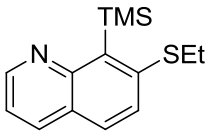


2-Bromopyridine (79 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (3.0 mL), 25 °C, 34 hours. After column chromatography (hexanes/dichloromethane 3:2), 32 mg (31 %) of a yellow oil was obtained. R_f = 0.35 (hexanes/dichloromethane 3:2). ^{1}H NMR (500 MHz) δ 8.38 (dd, J = 4.9, 1.9 Hz, 3H), 7.58 (dd, J = 7.3, 2.0 Hz, 3H), 6.94 (dd, J = 7.3, 4.9 Hz, 3H), 3.22 (q, J = 7.4 Hz, 6H), 1.35 (t, J = 7.3 Hz, 10H), 0.37 (s, 27H). ^{13}C NMR (126 MHz) δ 164.3, 149.3, 142.3, 133.6, 119.0, 254, 14.8, -0.9.

FT-IR (neat, cm^{-1}) ν 2956, 2923, 2853, 1558, 1547, 1455, 1362, 1249, 1137, 839.

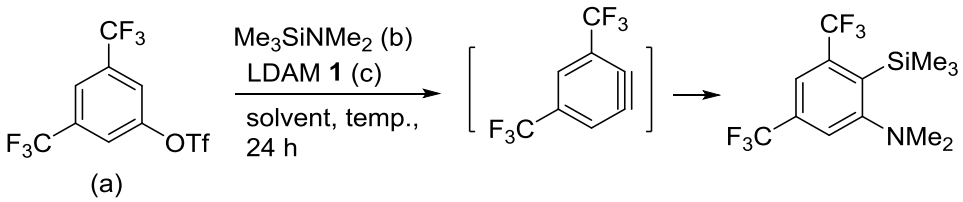
HRMS (APCI) calc. For $C_{10}H_{17}NSSi$ $[M+H]^+$: 212.0924; found: 212.0924.

7-(Ethylthio)-8-(trimethylsilyl)quinoline (Scheme 3, compound 9)



Quinolin-8-yl trifluoromethanesulfonate[6] (139 mg, 0.5 mmol), (ethylthio)trimethylsilane (202 mg, 1.5 mmol), LDAM **1** (220 mg, 0.75 mmol), diethyl ether (1.5 mL), cyclohexane (1.5 mL), 25 °C, 31 hours. After column chromatography (hexanes), 33 mg (26 %) of a yellow oil was obtained. R_f = 0.25 (hexanes). ^{1}H NMR (500 MHz) δ 8.83 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.28 (dd, J = 8.1, 4.1 Hz, 1H), 3.03 (q, J = 7.4 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H), 0.57 (s, 9H). ^{13}C NMR (126 MHz) δ 148.4, 135.8, 134.2, 129.0, 127.8, 125.8, 123.8, 120.2, 118.0, 29.1, 14.5, 4.2.

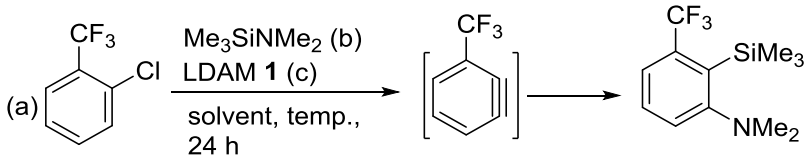
Table S5. Optimization of ArOTf *ortho*-Aminosilylation[a]



entry	(a/b/c)	solvent	T (°C)	yield (%)[b]
1	1/2/2	Et_2O/C_6H_{12} (1/1)	0	48
2	1/2/2	Et_2O/ C_6H_{12} (1/1)	25	50
3	1/4/2	THF	-78	59
4	1/4/2	THF	0	57
5	1/4/2	Et_2O/THF (20/1)	-78	59
6	1/4/2	Et_2O/THF (20/1)	0	64
7	**1/4/2**	**Et_2O/ C_6H_{12} (1/1)**	**25**	**63**
8	1/4/2	Et_2O/THF (20/1)	25	60
9	1/4/2	Et_2O/THF (50/1)	25	40
10	1/4/1.5	Et_2O/ C_6H_{12} (1/1)	25	35

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

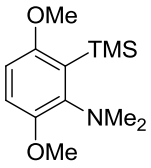
Table S6. Optimization of Aryl Halide *ortho*-Aminosilylation[a]



Entry	Ratio (a/b/c)	Solvent	Temp. (˚C)	Time (h)	yield (%)[a]
1	1/4/2	THF	-78	24	0
2	1/4/2	THF	0	24	47
3	1/4/2	Et_2O/THF (20/1)	0	24	43
4	1/4/2	Et_2O/THF (20/1)	25	24	47
5	1/4/2	Et_2O/ C_6H_{12}(1/1)	25	24	68
6	**1/4/2**	**Et_2O/ C_6H_{12}(1/1)**	**50**	**24**	**81**
7	1/4/1.5	Et_2O/ C_6H_{12}(1/1)	50	24	75
8	1/3/2	Et_2O/ C_6H_{12}(1/1)	50	24	72

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

3,6-Dimethoxy-2-(trimethylsilyl) *N*,*N*-dimethylbenzenamine (entry 1, Table 5)

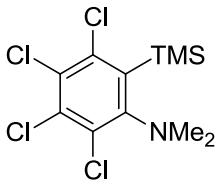


N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 2-chloro-1,4-dimethoxybenzene (88 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 24 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 3/1), 125 mg (99 %) of a white solid, mp 46-48 °C (from pentane) was obtained. R_f = 0.80 (hexanes/dichloromethane: 3/1). ^{1}H NMR (500 MHz) δ 6.87 (d, *J* = 8.8 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 2.76 (s, 6H), 0.37 (s, 9H). ^{13}C NMR (126 MHz) δ 158.7, 154.0, 148.3, 129.3, 113.7, 108.5, 55.8, 55.5, 44.2, 2.3.

FT-IR (neat, cm^{-1}) ν 2974, 2929, 2830, 2781, 1580, 1452, 1429, 1242.

HRMS (ESI) calc. For $C_{13}H_{23}NO_2Si$ $[M+H]^+$: 254.1571; found: 254.1566.

3,4,5,6-Tetrachloro-2-(trimethylsilyl)-*N*,*N*-dimethylbenzenamine (entry 2, Table 5)

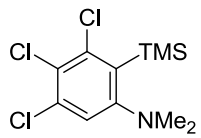


N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 1,2,3,4,5-pentachlorobenzene (126 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 24 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 1/1), 125 mg (76 %) of a colorless oil was obtained. R_f = 0.80 (hexanes/dichloromethane: 1/1). ^{1}H NMR (500 MHz) δ 2.74 (s, 2H), 0.41 (s, 3H). ^{13}C NMR (126 MHz) δ 154.4, 142.1, 137.9, 134.8, 134.6, 131.6, 43.1, 2.7.

FT-IR (neat, cm^{-1}) ν 2901, 2848, 1478, 1448, 1428, 1370, 1344.

HRMS (ESI) calc. For $C_{11}H_{15}Cl_4NSi$ $[M+H]^+$: 329.9801; found: 329.9791.

3,4,5-Trichloro-2-(trimethylsilyl)-*N*,*N*-dimethylbenzenamine (entry 3, Table 5)



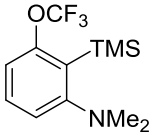
N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 1,2,3,4-tetrachlorobenzene (108 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0

mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 24 hours. After column chromatography (hexanes), 85 mg (57 %) of a light yellow oil was obtained. R_f = 0.80 (hexanes). ^{1}H NMR (500 MHz) δ 7.11 (s, 1H), 2.59 (s, 6H), 0.42 (s, 9H). ^{13}C NMR (126 MHz) δ 160.1, 140.7, 135.6, 134.8, 126.9, 120.7, 46.5, 2.2.

FT-IR (neat, cm^{-1}) ν 2941, 2783, 1552, 1518, 1401, 1333, 1249, 1181.

HRMS (ESI) calc. For $C_{11}H_{16}Cl_3NSi$ $[M+H]^+$: 296.0190; found: 296.0194.

2-(Trimethylsilyl)- 3-trifluoromethoxy-*N*,*N*-dimethylbenzenamine (entry 4, Table 5)

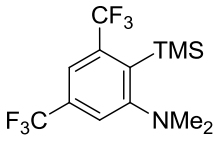


2-Trifluoromethoxybromobenzene (85 mg, 0.35 mmol), *N*,*N*-dimethyltrimethylsilylamine (165 mg, 1.4 mmol), LDAM **1** (204 mg, 0.7 mmol), diethyl ether (1.0 mL), cyclohexane (1.0 mL), 50 °C, 24 hours. After column chromatography (hexanes), 44 mg (46%) of a colorless oil was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (500 MHz) δ 7.33 (t, *J* = 8.1 Hz, 1H), 7.13 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.01 – 6.97 (m, 1H), 2.61 (s, 6H), 0.35 (s, 9H). ^{13}C NMR (126 MHz) δ 162.9, 154.8, 131.0, 129.2, 120.8 (q, *J* = 300 Hz), 119.3, 115.7, 46.9, 1.7.

FT-IR (neat, cm^{-1}) ν 2942, 2826, 2785, 1589, 1563, 1449, 1243, 1155.

HRMS (ESI) calc. For $C_{12}H_{18}F_3NOSi$ $[M+H]^+$: 278.1183; found: 278.1182.

2-(Trimethylsilyl)-3,5-bis-(trifluoromethyl)-*N*,*N*-dimethylbenzenamine (entry 5, Table 5)



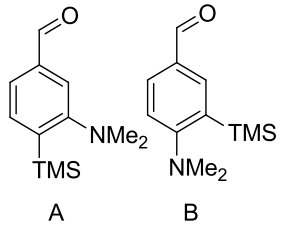
N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 3,5-bis(trifluoromethyl)phenyl triflate[8] (182 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), r.t., 24 hours. After column chromatography (hexanes followed by hexanes), 115 mg (70 %) of a colorless oil was obtained. Rf = 0.80 (hexanes). ^{1}H NMR (400 MHz) δ

7.70 (s, 1H), 7.60 (s, 1H), 2.66 (s, 6H), 0.39 (d, *J* = 1.1 Hz, 9H). ^{13}C NMR (101 MHz) δ 163.3, 141.8, 138.0 (q, J = 31.3 Hz), 132.2 (q, J = 33.3), 124.0 (q, J = 274.7), 123.5 (q, J = 273.7), 120.8, 119.4, 46.8, 2.4 (d, *J* = 2.7 Hz). ^{19}F NMR (470 MHz) δ -56.2, -63.0.

FT-IR (neat, cm^{-1}) ν 2946, 2789, 1457, 1361, 1278, 1257, 1195, 1125.

HRMS (ESI) calc. For $C_{13}H_{17}F_6NSi$ $[M+H]^+$: 330.1107; found: 330.1110.

3-Dimethylamino-4-(trimethylsilyl)benzaldehyde and 4-dimethylamino-3-(trimethylsilyl)benzaldehyde (entry 6, Table 5)



N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 4-formyl-phenyl triflate[14a,b] (128 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 25 °C, 24 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 1/2), 66 mg (60 %) of A as a yellow oil and 30 mg (27 %) of B as a yellow oil was obtained (overall yield = 87 %). Rf = 0.80 for A and 0.60 for B (hexanes/dichloromethane 1:2). Crude isomer ratio was 2:1 (analysis by ^{1}H-NMR).

For A: ^{1}H NMR (400 MHz) δ 9.98 (s, 1H), 7.77 (s, 1H), 7.63 – 7.61 (m, 2H), 2.64 (s, 6H), 0.30 (s, 9H). ^{13}C NMR (100 MHz) δ 192.6, 162.0, 147.2, 138.3, 136.1, 126.6, 121.4, 46.9, - 0.1.

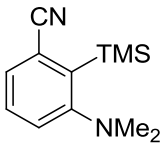
FT-IR (neat, cm^{-1}) ν 2949, 2825, 2782, 1698 (C=O), 1557, 1475, 1455, 1379, 1243, 1192.
HRMS (ESI) calc. For $C_{12}H_{19}NOSi$ $[M+H]^+$: 222.1309; found: 222.1308.

For B: ^{1}H NMR (400 MHz) δ 9.9 (s, 1H), 7.97 (s, 1H), 7.83 – 7.80 (d, J = 8.0 Hz, 1H), 7.21 – 7.19 (d, J = 8.0 Hz, 1H), 2.74 (s, 6H), 0.33 (s, 9H). ^{13}C NMR (100 MHz) δ 191.8, 166.3, 138.7, 135.9, 131.9, 131.2, 119.7, 45.8, 0.3.

FT-IR (neat, cm^{-1}) ν 2905, 2795, 2714, 1659 (C=O), 1588, 1532, 1362, 1279, 1232.

HRMS (ESI) calc. For $C_9H_{11}NO$ $[M+H-TMS]^+$: 150.0913; found: 150.0907.

3-Dimethylamino-2-(trimethylsilyl)benzonitrile (entry 7, Table 5)

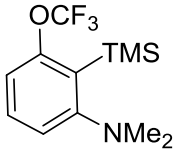


N,*N*-Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 3-cyanophenyl triflate[15] (126 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), r.t., 24 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 1/2), 66 mg (61 %) of a light yellow oil was obtained. R_f = 0.80 (hexanes/dichloromethane: 1/2). ^{1}H NMR (400 MHz) δ 7.45 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.43 - 7.36 (m, 2H), 2.59 (s, 6H), 0.44 (s, 9H). ^{13}C NMR (101 MHz) δ 162.0, 141.4, 131.3, 130.4, 125.7, 120.5, 118.8, 46.8, 1.6.

FT-IR (neat, cm^{-1}) ν 2944, 2827, 2785, 2224 (CN), 1574, 1445.

HRMS (ESI) calc. For $C_{10}H_8O_2F_6S_2$ $[M+H]^+$: 219.1312; found: 219.1316.

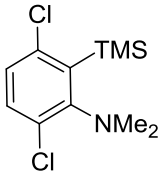
2-(Trimethylsilyl)- 3-trifluoromethoxy-*N*,*N*-dimethylbenzenamine (entry 8, Table 5)



2-Trifluoromethoxyphenyl triflate (109 mg, 0.35 mmol), *N*,*N*-dimethyltrimethylsilylamine (236 mg, 2.0 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.0 mL), cyclohexane (1.0 mL), 25 °C, 24 hours. After column chromatography (hexanes), 56 mg (58%) of a colorless oil was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (500 MHz) δ 7.33 (t, *J* = 8.1 Hz, 1H), 7.13 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.01 – 6.97 (m, 1H), 2.61 (s, 6H), 0.35 (s, 9H). ^{13}C NMR (126 MHz) δ 162.9, 154.8, 131.0, 129.2, 120.8 (q, *J* = 300 Hz), 119.3, 115.7, 46.9, 1.7. FT-IR (neat, cm^{-1}) ν 2942, 2826, 2785, 1589, 1563, 1449, 1243, 1155.

HRMS (ESI) calc. For $C_{12}H_{18}F_3NOSi$ $[M+H]^+$: 278.1183; found: 278.1182.

2-(Trimethylsilyl)- 3,6-dichloro-*N*,*N*-dimethylbenzenamine (entry 9, Table 5)



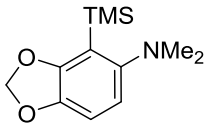
2,5-Dichlorophenyl triflate[11] (104 mg, 0.35 mmol), *N*,*N*-dimethyltrimethylsilylamine (165 mg, 1.4 mmol), LDAM **1** (204 mg, 0.7

mmol), diethyl ether (1.0 mL), cyclohexane (1.0 mL), 25 °C, 24 hours. After column chromatography (hexanes), 50 mg (55%) of a colorless oil was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (600 MHz) δ 7.19 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 2.75 (s, 6H), 0.38 (s, 9H). ^{13}C NMR (151 MHz) δ 155.6, 142.3, 139.3, 134.2, 132.7, 129.2, 43.2, 2.7.

FT-IR (neat, cm^{-1}) ν 2896, 2800, 1552, 1480, 1407, 1363, 1247, 1169.

HRMS (ESI) calc. For $C_{11}H_{17}Cl_2NS_i$ $[M+H]^+$: 262.0580; found: 262.0577.

6-(*N,N*-Dimethylamino)-5-(trimethylsilyl)-1,3-benzodioxole (entry 10, Table 5)

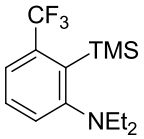


1,3-Benzodioxol-4-yl trifluoromethanesulfonate[12] (96 mg, 0.35 mmol), *N,N*-dimethyltrimethylsilylamine (236 mg, 2.0 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.0 mL), cyclohexane (1.0 mL), 25 °C, 24 hours. After column chromatography (hexanes), 53 mg (64%) of a colorless oil was obtained. R_f = 0.80 (hexanes). ^{1}H NMR (600 MHz) δ 6.77 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 5.87 (s, 2H), 2.55 (s, 6H), 0.32 (s, 9H). ^{13}C NMR (151 MHz) δ 155.4, 152.6, 143.6, 118.6, 114.3, 109.3, 100.2, 47.4, 1.0.

FT-IR (neat, cm^{-1}) ν 2933, 2896, 2821, 2778, 1620, 1446, 1398, 1336, 1242, 1226.

HRMS (ESI) calc. For $C_{10}H_8O_2F_6S_2$ $[M+H]^+$: 238.1258; found: 238.1257.

2-(Trimethylsilyl)-3-(trifluoromethyl)-*N,N*-diethylbenzenamine (Scheme 4, compound 10)



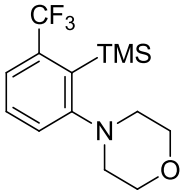
N,N-Diethyltrimethylsilylamine (290 mg, 2.0 mmol), 2-chlorobenzotrifluoride (91 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 28 hours. After column chromatography (hexanes), 44 mg (31 %) of a colorless oil was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (500 MHz) δ 7.43 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H),

7.25 (d, J = 7.8 Hz, 1H), 3.01 (qd, J = 6.8, 4.2 Hz, 4H), 0.98 (td, J = 7.1, 0.7 Hz, 6H), 0.37 (s, 9H). ^{13}C NMR (126 MHz) δ 159.3, 137.4 (q, J = 30.2 Hz), 136.7 (q, J = 4.4 Hz), 129.0, 126.1, 125.1 (q, J = 274.7 Hz), 122.4 (q, J = 6.3 Hz), 48.3, 11.0, 3.2. ^{19}F NMR (470 MHz) δ -55.0.

FT-IR (neat, cm^{-1}) ν 2974, 2924, 2894, 2801, 1609, 1497, 1449, 1421, 1307, 1248.

HRMS (APCI) calc. For $C_{14}H_{22}F_3NSi$ $[M+H]^+$: 290.1546; found: 290.1545.

4-(3-(Trifluoromethyl)-2-(trimethylsilyl)phenyl)morpholine (Scheme 4, compound 11)

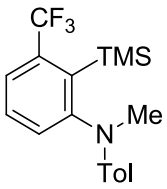


4- (Trimethylsilyl) morpholine (318 mg, 2.0 mmol), 2-chlorobenzotrifluoride (91 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 28 hours. After column chromatography (hexanes followed by hexanes/dichloromethane: 15/1), 122 mg (81 %) of a white solid, mp 82-84 °C (from pentane) was obtained. R_f = 0.50 (hexanes/dichloromethane: 15/1). ^{1}H NMR (500 MHz) δ 7.57 (dd, J = 7.4, 1.2 Hz, 1H), 7.51 – 7.45 (m, 2H), 3.89 (d, J = 10.1 Hz, 2H), 3.81 (t, J = 10.1 Hz, 2H), 2.99 (td, J = 11.8, 3.2 Hz, 2H), 2.74 (d, J = 11.8 Hz, 2H), 0.38 (s, 9H). ^{13}C NMR (126 MHz) δ 161.2, 138.1 (q, J = 1.3 Hz), 136.7 (q, J = 31.5 Hz), 130.1, 126.2, 124.4 (q, J = 274.7 Hz), 124.1 (q, J = 7.6 Hz), 66.9, 54.9, 3.0. ^{19}F NMR (470 MHz) δ -55.8.

FT-IR (neat, cm^{-1}) ν 3058, 2968, 2938, 2918, 2864, 1584, 1549, 1443, 1424, 1364, 1320.

HRMS (APCI) calc. For $C_{14}H_{20}F_3NOSi$ $[M+H]^+$: 304.1339; found: 304.1336.

***N*-Methyl-*N*-(*p*-tolyl)-3-(trifluoromethyl)-2-(trimethylsilyl) aniline (Scheme 4, compound 12)**



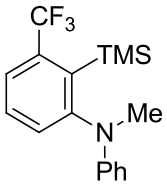
N-Methyl-*N*-(trimethylsilyl)aniline[16] (360 mg, 2.0 mmol), 2-chlorobenzotrifluoride (91 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0

mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 28 hours. After column chromatography (hexanes), 74 mg (44 %) of a colorless oil was obtained. R_f = 0.80 (hexanes). ^{1}H NMR (500 MHz) δ 7.69 – 7.58 (m, 1H), 7.47 (dd, J = 12.5, 7.8 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.00 (dd, J = 7.7, 4.8 Hz, 2H), 6.50 – 6.40 (m, 2H), 3.10 (s, 3H), 2.26 (s, 3H), 0.27 (d, J = 4.1 Hz, 9H). ^{13}C NMR (126 MHz) δ 157.4, 148.3, 139.0, 137.4 (q, J = 30.2 Hz), 132.0, 130.9, 129.4, 127.4, 124.88 (q, J = 274.7 Hz), 124.87 (q, J = 6.3 Hz), 114.91, 42.2, 20.4, 2.4 (q, J = 2.7 Hz). ^{19}F NMR (470 MHz) δ -55.4.

FT-IR (neat, cm^{-1}) ν 2957, 2922, 2862, 2802, 1615, 1512, 1326, 1308, 1251, 1163, 1120.

HRMS (APCI) calc. For $C_{18}H_{22}F_3NSi$ $[M+H]^+$: 338.1546; found: 338.1547.

_N_-Methyl-_N_-phenyl-3-(trifluoromethyl)-2-(trimethylsilyl) aniline (Scheme 4, Compound 13)

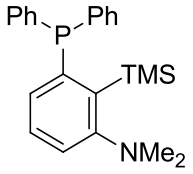


_N_-Methyl-_N_-(trimethylsilyl)aniline[16] (360 mg, 2.0 mmol), 2-chlorobenzotrifluoride (91 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 28 hours. After column chromatography (hexanes), 71 mg (46 %) of a white solid, mp 53-55 °C (from pentane) was obtained. R_f = 0.75 (hexanes). ^{1}H NMR (500 MHz) δ 7.66 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.27 (s, 1H), 7.23 – 7.15 (m, 2H), 6.77 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.9 Hz, 2H), 3.13 (s, 3H), 0.25 (d, J = 1.2 Hz, 9H). ^{13}C NMR (126 MHz) δ 156.8, 150.3, 139.1 (q, J = 1.9 Hz), 137.5 (q, J = 31.5 Hz), 132.2, 131.0, 128.9, 125.0 (q, J = 5.0 Hz), 124.8 (q, J = 274.7 Hz), 118.1, 114.7, 42.0, 2.33 (q, J = 3.1 Hz). ^{19}F NMR (470 MHz) δ -55.4.

FT-IR (neat, cm^{-1}) ν 2991, 2953, 2897, 2807, 1602, 1496, 1473, 1447, 1417, 1329.

HRMS (ESI) calc. For $C_{17}H_{20}F_3NSi$ $[M+H]^+$: 324.1390; found: 324.1389.

3-(Diphenylphosphino)-2-(trimethylsilyl)-*N*,*N*-dimethylaniline (Scheme 5, compound 14)



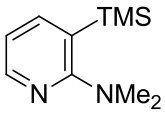
Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), (2-bromophenyl)diphenylphosphine (171 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 50 °C, 25 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate: 19/1), 127 mg (58 %) of a white oil was obtained. R_f = 0.75 (hexanes/ethyl acetate: 19/1). ^{1}H NMR (500 MHz) δ 7.39 – 7.26 (m, 7H), 7.26 – 7.15 (m, 5H), 6.87 – 6.77 (m, 1H), 2.61 (s, 6H), 0.40 (d, J = 2.2 Hz, 9H). ^{13}C NMR (126 MHz) δ 161.8, 161.6, 145.6 145.5, 144.3, 144.2, 139.1, 139.0, 133.7, 133.5, 131.4, 129.65, 129.64, 128.43, 128.38, 128.2, 120.9, 47.0, 4.45, 4.36. ^{31}P NMR (202 MHz) δ -6.8.

FT-IR (neat, cm^{-1}) ν 3051, 2980, 2935, 2820, 2780, 1586, 1551, 1477, 1433, 1243.

HRMS (APCI) calc. For $C_{23}H_{28}NPSi$ $[M+H]^+$: 378.1801; found: 378.1801.

Note: GC/MS shows nearly full conversion of the starting material to the product without formation of any byproducts. However, after column chromatography, partial dehydrosilylation occurred and yield dropped to 58%. Second column on pure product showed 24% dehydrosilylation. Analysis by ^{1}H-NMR of the crude reaction mixture showed 84% yield of product.

***N*,*N*-Dimethyl-3-(trimethylsilyl)pyridin-2-amine (Scheme 5, compound 15)**



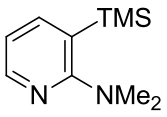
Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), 2-bromopyridine (79 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 25 °C, 24 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate: 5/1), 44 mg (46 %) of a light yellow oil was obtained. R_f = 0.45 (hexanes/ethyl acetate: 5/1). ^{1}H NMR (500 MHz) δ 8.30 (dd, J = 4.8, 2.0 Hz,

1H), 7.72 (dd, J = 7.2, 2.1 Hz, 1H), 6.90 (dd, J = 7.2, 4.8 Hz, 1H), 2.77 (s, 6H), 0.30 (s, 9H). ^{13}C NMR (126 MHz) δ 169.2, 148.6, 145.2, 127.5, 118.2, 44.1, -0.1.

FT-IR (neat, cm^{-1}) ν 3300 (broad peak), 2909, 2852, 1601, 1564, 1453, 1390, 1247.

HRMS (APCI) calc. For $C10H_{18}N_2Si$ $[M+H]^+$: 195.13.12; found: 195.1309.

***N,N*-Dimethyl-3-(trimethylsilyl)pyridin-2-amine (Scheme 5, compound 15)**



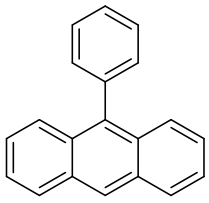
Dimethyltrimethylsilylamine (236 mg, 2.0 mmol), pyridin-2-yl trifluoromethanesulfonate (114 mg, 0.5 mmol), LDAM **1** (292 mg, 1.0 mmol), diethyl ether (1.25 mL), cyclohexane (1.25 mL), 25 °C, 28 hours. After column chromatography (hexanes followed by hexanes/ethyl acetate: 5/1), 30 mg (31 %) of a light yellow oil was obtained. R_f = 0.45 (hexanes/ethyl acetate: 5/1). ^{1}H NMR (500 MHz) δ 8.30 (dd, J = 4.8, 2.0 Hz, 1H), 7.72 (dd, J = 7.2, 2.1 Hz, 1H), 6.90 (dd, J = 7.2, 4.8 Hz, 1H), 2.77 (s, 6H), 0.30 (s, 9H). ^{13}C NMR (126 MHz) δ 169.2, 148.6, 145.2, 127.5, 118.2, 44.1, -0.1.

FT-IR (neat, cm^{-1}) ν 3300 (broad peak), 2909, 2852, 1601, 1564, 1453, 1390, 1247.

HRMS (APCI) calc. For $C10H_{18}N_2Si$ $[M+H]^+$: 195.13.12; found: 195.1309.

Insertion of Arynes into C-C bonds (Scheme 6):

9-Phenylanthracene (Scheme 6, compound 16)

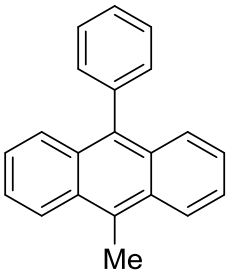


Inside the glovebox a 2-dram vial was charged with a stir bar and LDAM **1** (205 mg, 0.7 mmol). The vial was taken out and to the vial pentane/THF (15:1, 1.0 mL) was added via syringe. In another 1-dram vial, chlorobenzene (50 mg, 0.44 mmol), acetophenone (24 mg, 0.2 mmol), and 0.5 mL of pentane/THF (15:1, 0.5 mL) were mixed. The content of 1-dram vial was dropwise added to base solution. The reaction was stirred at room temperature for 30 hours. Quench with aqueous citric acid and extraction with dichloromethane,

followed by column chromatography (hexanes) gave 38 mg (75 %) of a white solid. R_f = 0.50 (hexanes). This compound is known.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.03 – 8.06 (m, 2H), 7.65 – 7.68 (m, 2H), 7.54 – 7.59 (m, 3H), 7.42 – 7.48 (m, 4H), 7.34 – 7.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.8, 137.1, 131.4, 130.3, 130.3, 128.5, 128.4, 127.6, 126.9, 126.6, 125.4, 125.2.

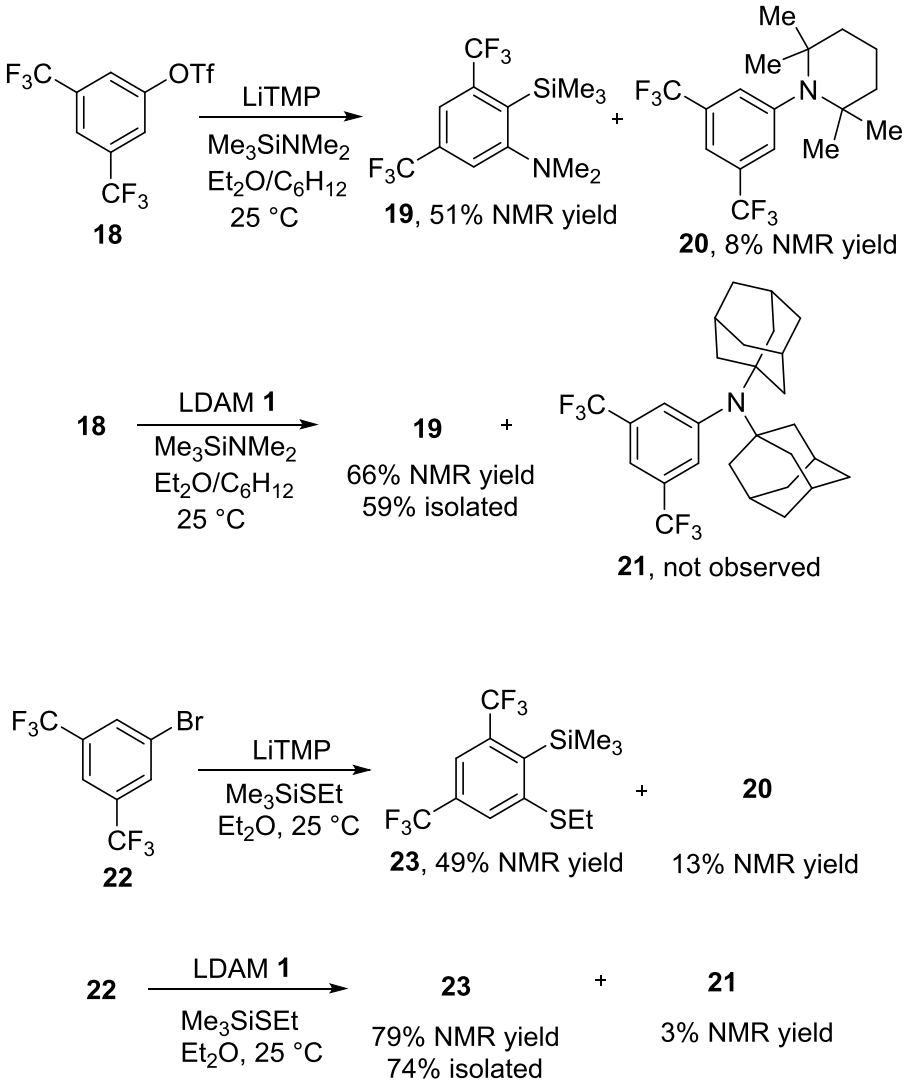
10- Methyl-9-phenylanthracene (Scheme 6, compound 17)



Inside the glovebox a 2-dram vial was charged with LDAM **1** (205 mg, 0.7 mmol). The vial was taken out and to the vial, and pentane/THF (15:1, 1.0 mL) was added via syringe. In another 1-dram vial, chlorobenzene (50 mg, 0.44 mmol), propiophenone (27 mg, 0.2 mmol), (15:1, 0.5 mL) were mixed. The content of 1-dram vial was dropwise added to base solution. The reaction was stirred at room temperature for 30 hours. Quench with aqueous citric acid and extraction with dichloromethane, followed by column chromatography (hexanes) gave 35 mg (66 %) of a yellow solid. R_f = 0.50 (hexanes). This compound is known.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, 2H), 7.68 (d, 2H), 7.50 – 7.57 (m, 5H), 7.41 (m, 2H), 7.33 – 7.37 (m, 2H), 3.17 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.5, 135.8, 131.7, 130.3, 130.1, 128.4, 127.8, 127.4, 125.0, 124.74, 124.69, 14.0. Signal for one carbon atom could not be located.

Comparison of LiTMP and LDAM (Scheme 7):



Compounds 19, 20, and 21: 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 LiTMP (0.147 g, 1.0 mmol). The sealed vial was then taken out of the glovebox. Two thirds of solvent mixture (Et_2O/C_6H_{12}: 1/1, 2.0 mL) was added via syringe to the reaction vial. Vial was stirred for 5-10 minutes at room temperature. In another vial, 3,5-bis(trifluoromethyl)phenyl triflate[8] (0.181 g, 0.5 mmol) was mixed with dimethyltrimethylsilylamine (236 mg, 2.0 mmol). Subsequently, one third of reaction solvent was added to this vial. The solution of

reactants was added to the reaction vial containing base in 1 minute by syringe. After stirring at room temperature for 24 h, reactions were quenched by adding 2-methyl-2-butanol and then methanol (0.5 mL), followed by dilution with dichloromethane (0.5 mL). After passing the crude mixture through a short pad of silica and evaporating the solvent, the mixture was subjected to the ^{1}H-NMR analysis in chloroform-d. The NMR yields for compounds **19** and **20** were 51% and 8%, respectively. After column chromatography (hexanes), 83 mg of a colorless oil which was a mixture of compounds **19** and **20** was obtained. R_f = 0.85 (hexanes). ^{1}H NMR (400 MHz) for compound **20**: δ 7.72 (s, 1H), 7.65 (s, 2H), 1.77 – 1.70 (m, 2H), 1.61 – 1.56 (m, 4H), 1.01 (s, 9H). ^{1}H NMR (400 MHz) for compound **19**: δ 7.70 (s, 1H), 7.60 (s, 1H), 2.66 (s, 6H), 0.39 (d, *J* = 1.1 Hz, 9H).

Same reaction was run with LDAM and the crude mixture analysis by ^{19}F-NMR with trifluorotoluene as an internal standard showed 66% yield for **19**. Compound **21** was not detected. After column chromatography (hexanes), 97 mg (59 %) of **19** as a colorless oil was obtained. R_f = 0.85 (hexanes). ^{1}H NMR (400 MHz) δ 7.70 (s, 1H), 7.60 (s, 1H), 2.66 (s, 6H), 0.39 (d, *J* = 1.1 Hz, 9H).

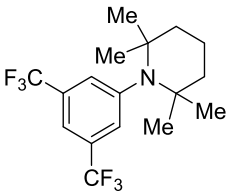
Compounds 23, 20, and 21: outside the glovebox a 2-dram vial was equipped with two magnetic stirring bars (size: 5x1x1 mm). The vial was placed inside the glovebox. To the vial was added solid LiTMP (0.147 g, 1.0 mmol). The sealed vial was then taken out of the glovebox. Two thirds of solvent (Et_2O, 2.0 mL) was added via syringe to the reaction vial. Vial was stirred for 5-10 minutes at room temperature. In another vial, 3,5-bis(trifluoromethyl)bromobenzene (0.147 g, 0.5 mmol) was mixed with (ethylthio)trimethylsilane (202 mg, 1.5 mmol). Subsequently, one third of reaction solvent was added to this vial. The solution of reactants was added to the reaction vial containing base in 1 minute by syringe. After stirring at room temperature for 46 h, reactions were quenched by adding 2-methyl-2-butanol and then methanol (0.5 mL), followed by dilution with dichloromethane (0.5 mL). After passing the crude mixture through a short pad of silica and evaporating the solvent, the mixture was subjected

to ^{19}F-NMR analysis in chloroform-d with trifluorotoluene internal standard. The NMR yields for compounds **23** and **20** were 49% and 13%, respectively. After column chromatography (hexanes), 86 mg of a colorless oil which was a mixture of compounds **23** and **20** was obtained, R_f = 0.9 (hexanes).

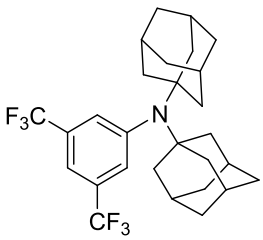
Same reaction was run with LDAM and the crude mixture NMR with trifluorotoluene as an internal standard showed 79% yield for compound **23**. About 3% of compound **21** was detected by ^{19}F-NMR with trifluorotoluene internal standard. After column chromatography (hexanes), 128 mg (74 %) **23** as a colorless oil was obtained. R_f = 0.9 (hexanes).

Isolation of 20 and 21

Compounds **20** and **21** were prepared in the following reactions:



20: 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 LiTMP (0.147 g, 1.0 mmol). The sealed vial was then taken out of the glovebox. Two thirds of solvent (Et_2O/THF:10/1, 2.0 mL) was added via syringe to the reaction vial. Vial was stirred for 5-10 minutes at room temperature. In another vial, to the 3,5-bis(trifluoromethyl)bromobenzene (0.147 g, 0.5 mmol) was added one third of reaction solvent. The solution was added to the reaction vial containing base in 1 minute by syringe. After stirring at room temperature for 24 h, reactions were quenched by adding 2-methyl-2-butanol and then methanol (0.5 mL), followed by dilution with dichloromethane (0.5 mL). After column chromatography (hexanes), 80 mg (45%) of **20** as a colorless oil was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (400 MHz) δ 7.72 (s, 1H), 7.65 (s, 2H), 1.76 – 1.72 (m, 2H), 1.61 – 1.57 (m, 4H), 1.01 (s, 12H). ^{13}C NMR (101 MHz) δ 148.7, 134.2, 131.2 (q, J = 32 Hz), 123.5 (q, J = 275 Hz), 119.5, 54.6, 42.0, 29.6, 18.1. ^{19}F NMR (376 MHz) δ -62.7.



21: 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 **1** (0.292 g, 1.0 mmol). The sealed vial was then taken out of the glovebox. Two thirds of solvent (Et_2O/THF 10/1, 2.0 mL) was added via syringe to the reaction vial. Vial was stirred for 5-10 minutes at room temperature. In another vial, to the 3,5-bis(trifluoromethyl)bromobenzene (0.147 g, 0.5 mmol) was added in one third of reaction solvent. The solution was added to the reaction vial containing base in 1 minute by syringe. After stirring at room temperature for 24 h, reaction was quenched by adding 2-methyl-2-butanol and then methanol (0.5 mL), followed by dilution with dichloromethane (0.5 mL). After column chromatography (hexanes), 20 mg (8%) of a white solid, **21**, was obtained. R_f = 0.90 (hexanes). ^{1}H NMR (400 MHz) δ 7.66 (s, 1H), 7.50 (s, 2H), 2.00 (apparent s, 6H), 1.83 (apparent s, 12H), 1.55 (apparent s, 12H). ^{13}C NMR (101 MHz) δ 148.9, 135.1, 130.0 (q, J = 33 Hz), 123.8 (q, J = 274 Hz), 119.0, 58.3, 46.1, 36.4, 30.5. ^{19}F NMR (376 MHz) δ -62.4.

X-ray Crystallographic Data

Procedure for crystal growth:

Di-1-adamantylamine (600 mg, 2.1 mmol) and a magnetic stirrer bar were placed in a 50 mL Schlenk flask. Flask was sealed by rubber septum and Teflon tape and attached to the N_2 line. Flask was filled with N_2 gas and evacuated 5 times. Anhydrous pentane (35 mL) was added to the flask via syringe. The suspension was stirred for at least one hour at 25 ˚C to dissolve the amine. The stirring was stopped and n-BuLi (1.6M in hexane, 1.6 mL) was injected dropwise via syringe into the solution. The color changed to light brown and solution was transparent. After 48 hours, crystals were formed on the stirrer bar and wall of flask. Then, the solvent was removed quickly by syringe and washed one time with 30 mL anhydrous pentane. The solvent was removed and to the flask was added heavy mineral oil (30 mL) by syringe. The mixture was shaken and was laid out on the glass sheet (1 X 1 ft) to pick a suitable crystal. The selected crystal was immediately placed to the machine for measurement to avoid decomposition.

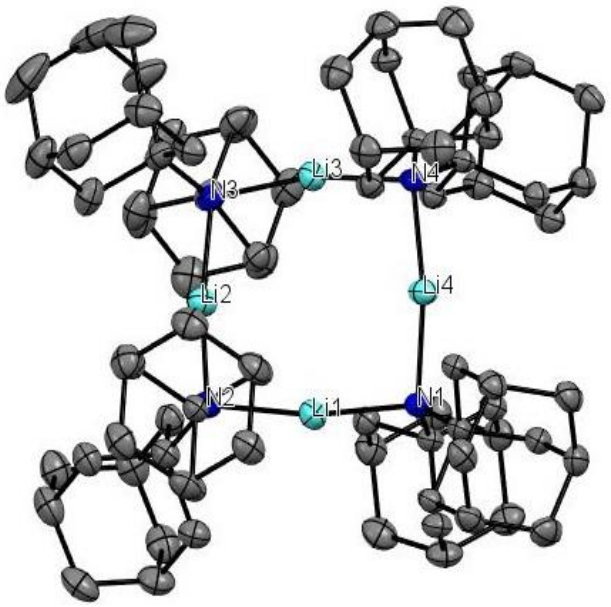


Figure S3: X-ray crystal structure for lithium di-1-adamantylamide. Hydrogen atoms are omitted for clarity. Atoms are drawn at 50% probability level.

Space-filled crystal structure for LiTMP and LDAM to compare the accessibility of nitrogen on amide for hydrogen abstraction.

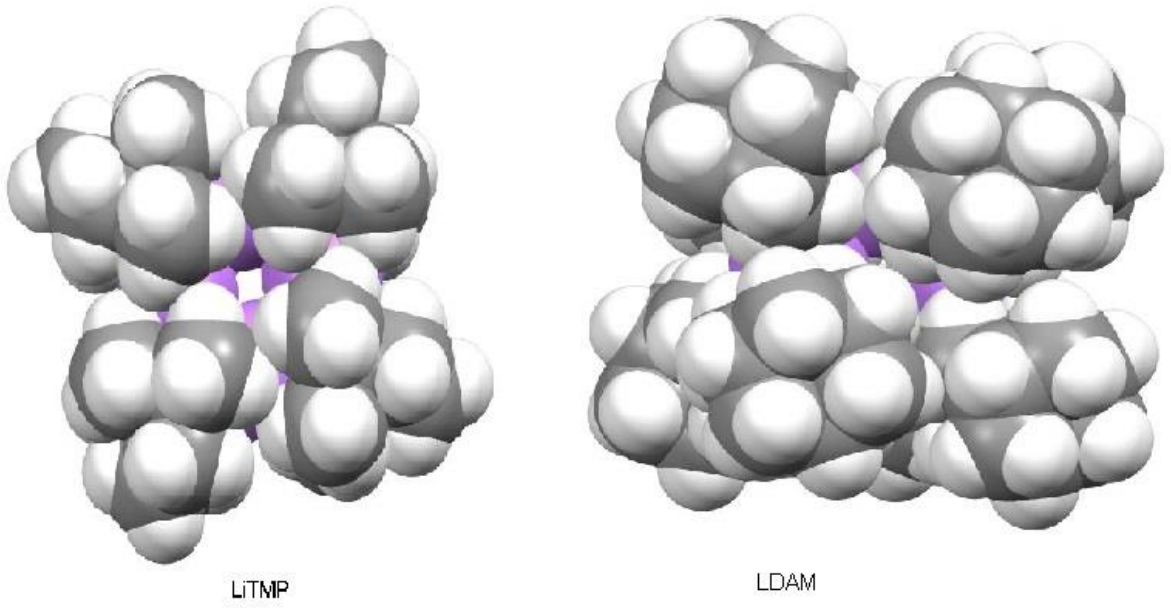


Figure S4: Space-filled crystal structure for LiTMP and LDAM.

The measurements were made with a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector using CuK\a radiation at 123 K. The reflections were collected using a narrow-frame algorithm with scan widths of 0.50\% in omega and an exposure time of 20 s/frame. The data were integrated using the Bruker Apex-II program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and an absorption correction was applied using SADABS. Redundant reflections were averaged. The structure was solved by direct method and refined with the program SHELXL 2014. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically with riding displacement parameters. Data collection and refinement details are listed in Table S7.

XW114_Adm2NLi

Table S7 Crystal data and structure refinement for XW114_Adm2NLi.

Identification code	XW114_Adm2NLi
Empirical formula	$C_{165}H_{252}Li_8N_8$
Formula weight	2403.25
Temperature/K	123(2)
Crystal system	Triclinic
Space group	P-1
a/Å	11.8908(3)
b/Å	15.5218(3)
c/Å	19.7689(5)
α/°	95.344(1)
β/°	90.555(1)
γ/°	108.045(1)
Volume/Å^3	3451.27(14)
Z	1
ρ_{calc}g/cm^3	1.156
μ/mm^{-1}	0.476
F(000)	1322.0
Crystal size/mm^3	0.340 × 0.220 × 0.020
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.492 to 133.464
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -19 ≤ l ≤ 22
Reflections collected	38423
Independent reflections	11892 [R_{int} = 0.0328, R_{sigma} = 0.0365]
Data/restraints/parameters	11892/54/840
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0591, wR_2 = 0.1575
Final R indexes [all data]	R_1 = 0.0668, wR_2 = 0.1674
Largest diff. peak/hole / e Å^{-3}	0.38/-0.24

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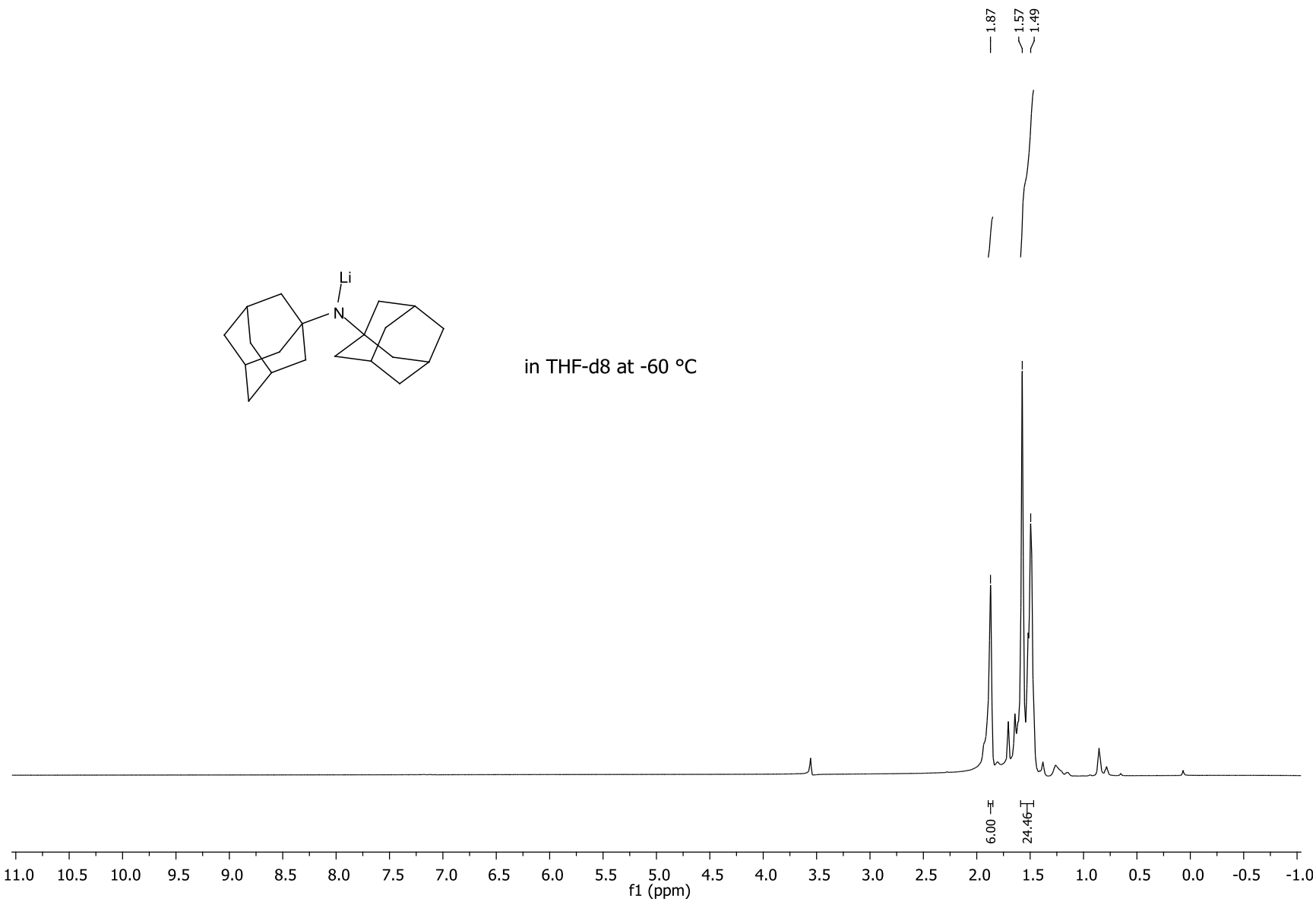
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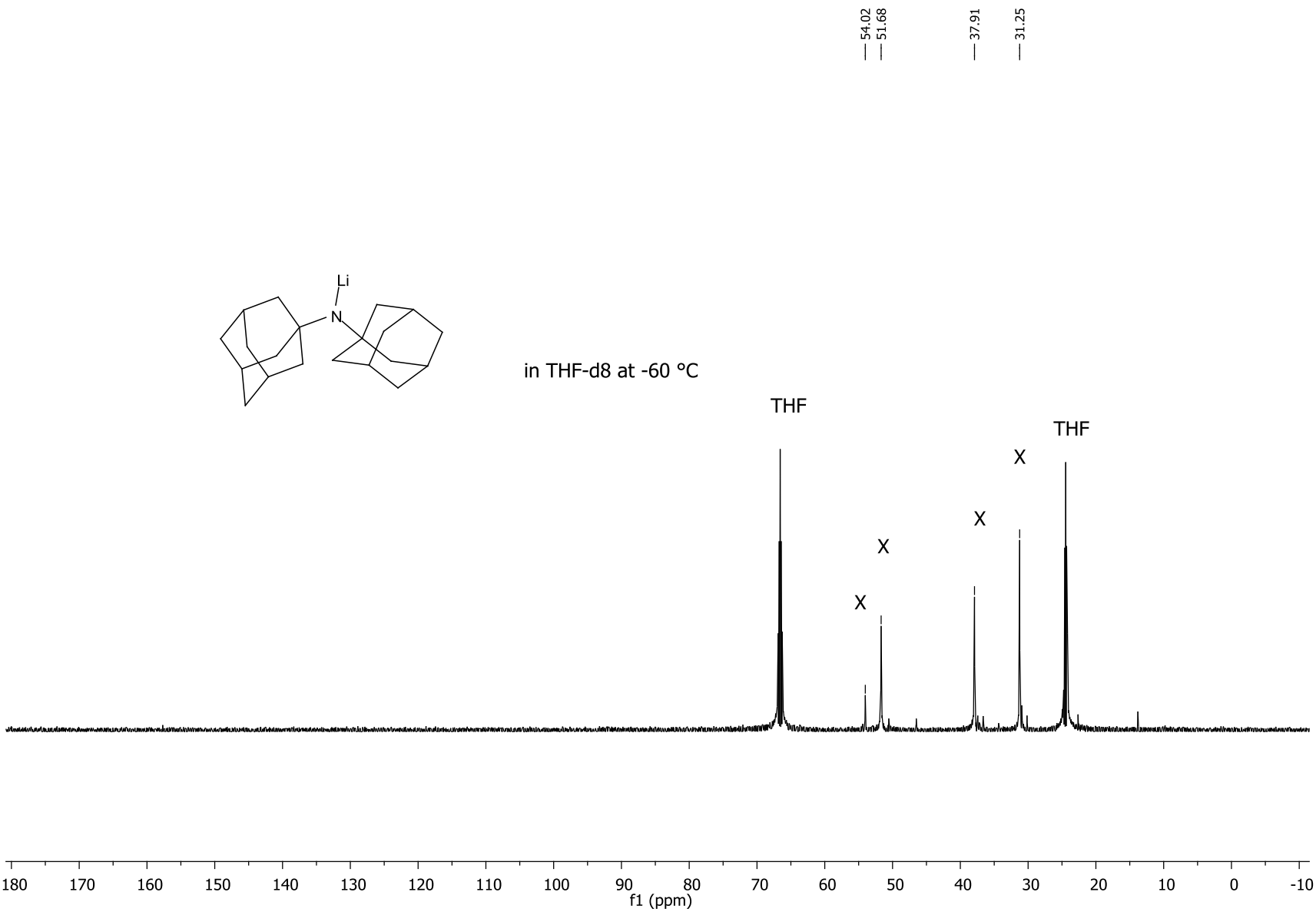
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Li
N
in THF-d8 at -60 °C
THF
THF
X
X
X
X
180
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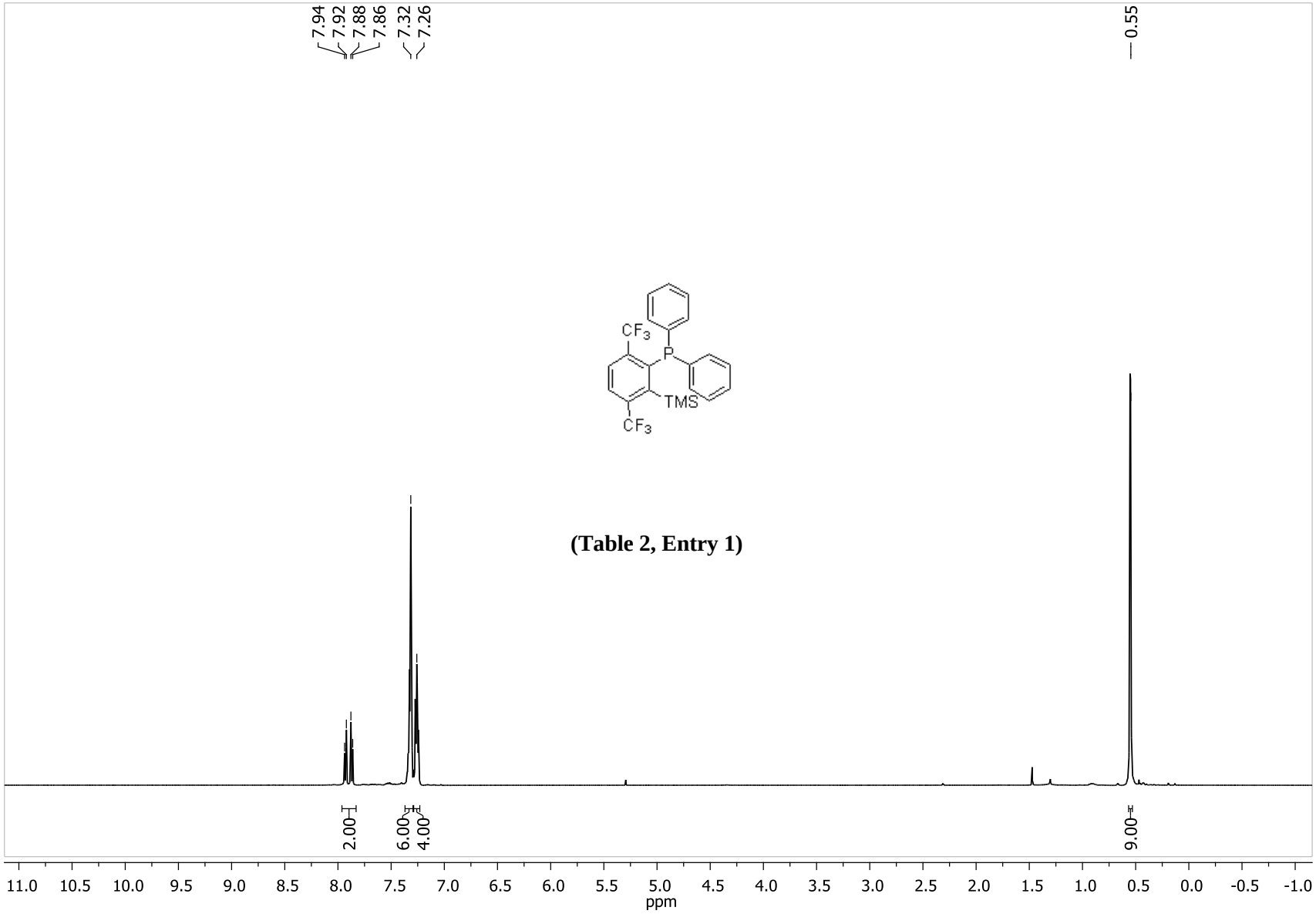
f1 (ppm)



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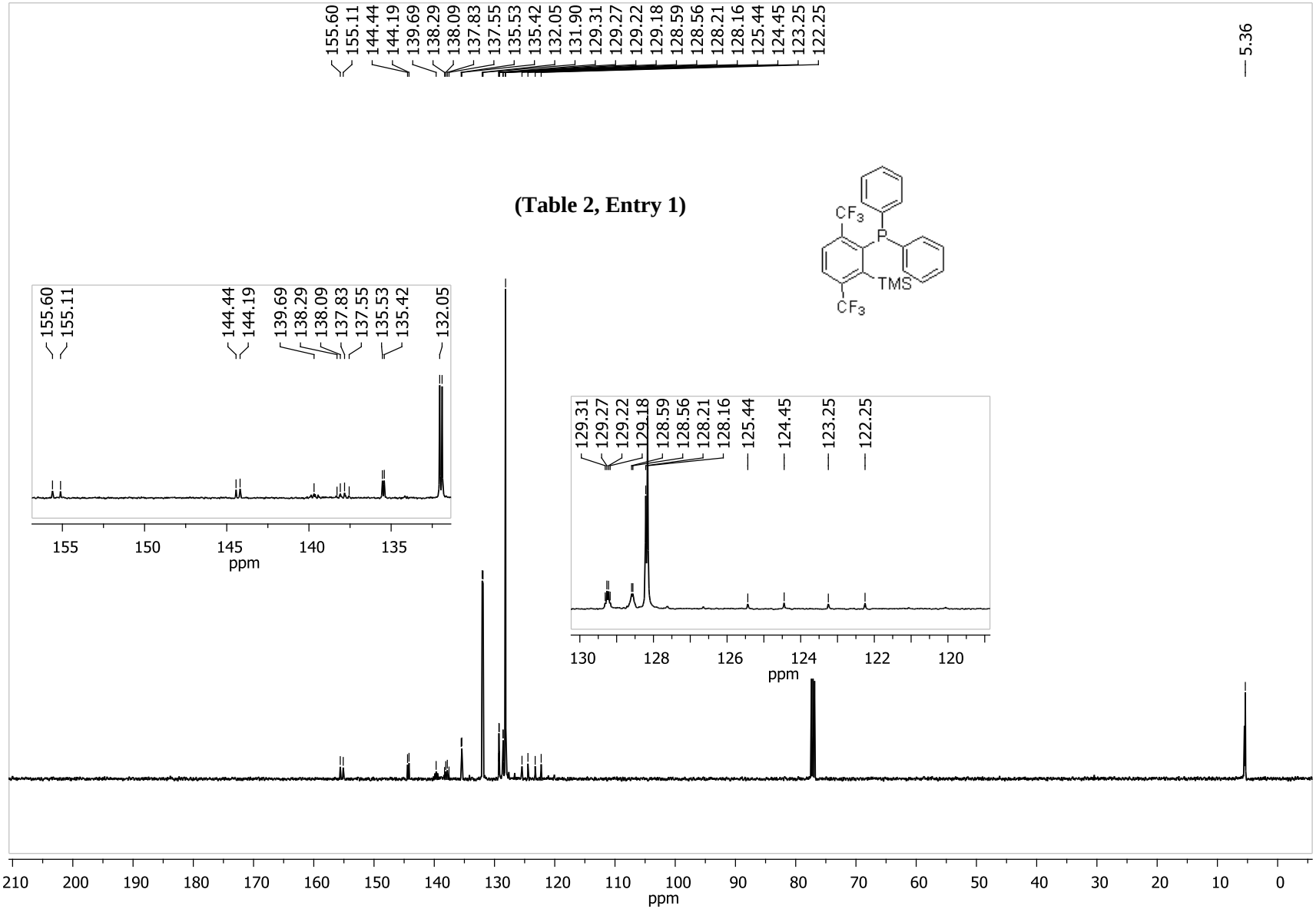
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ppm
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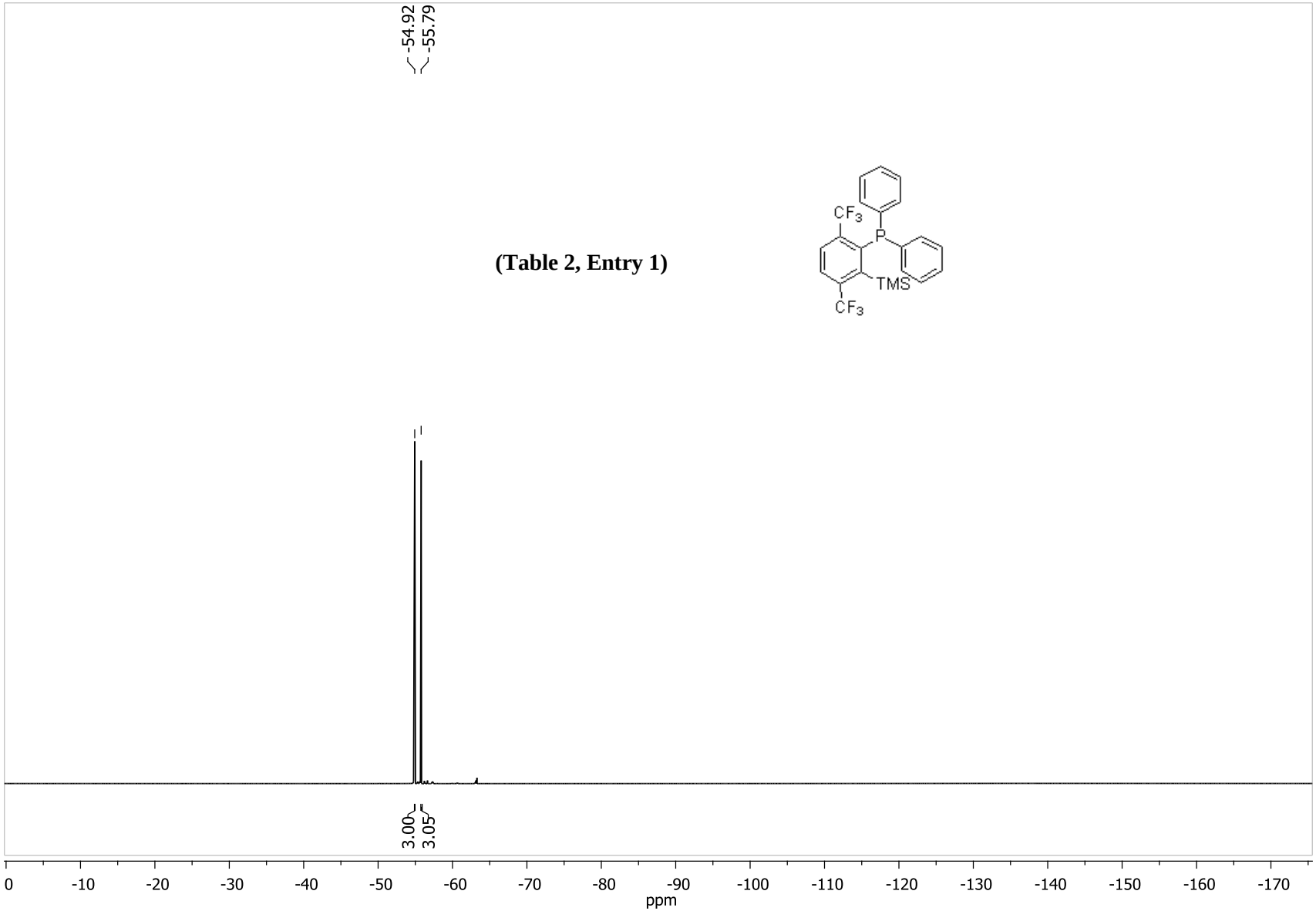

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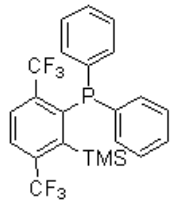

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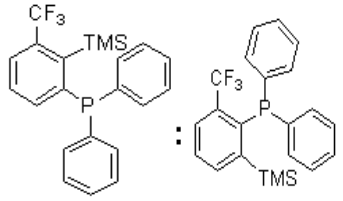

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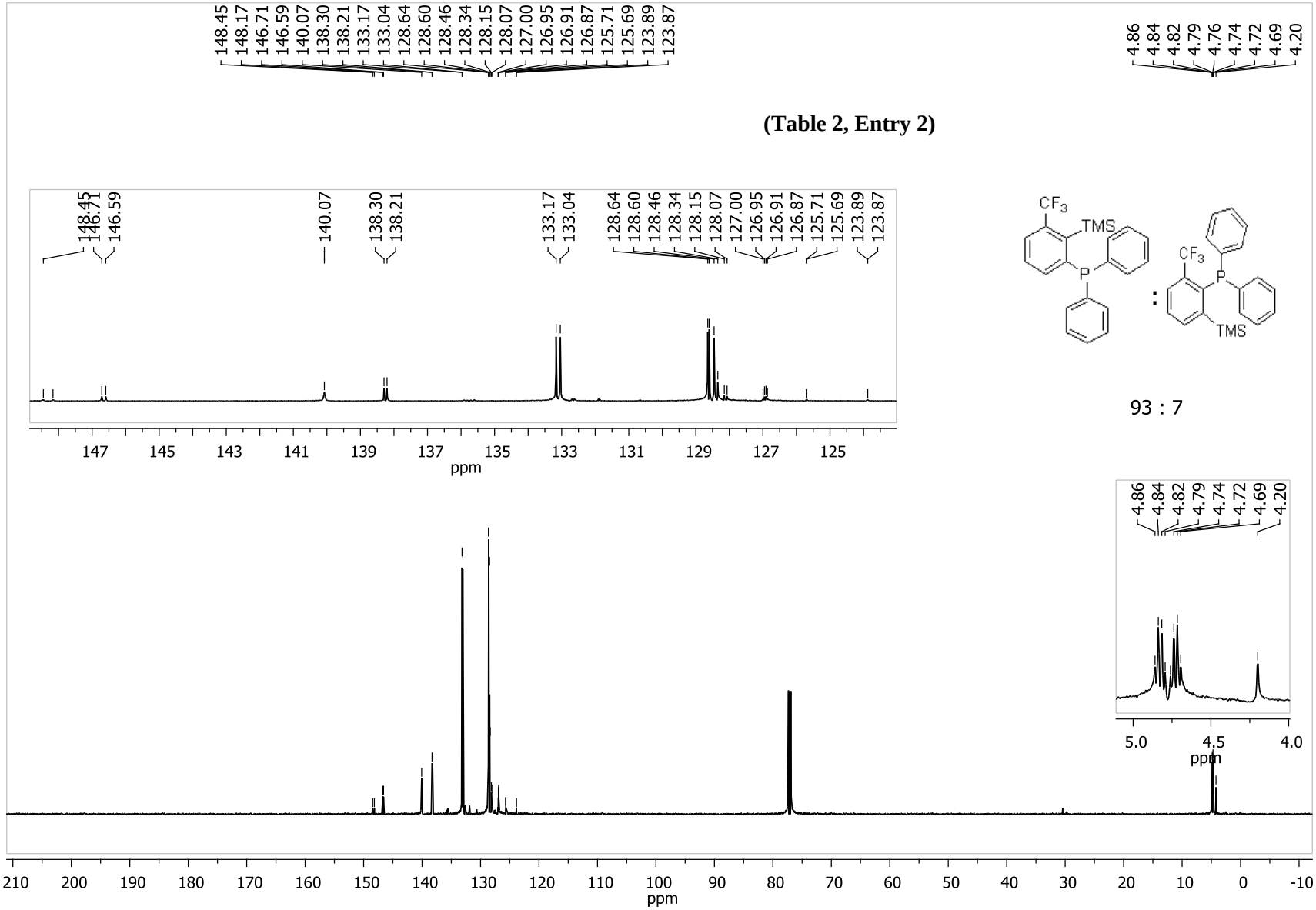
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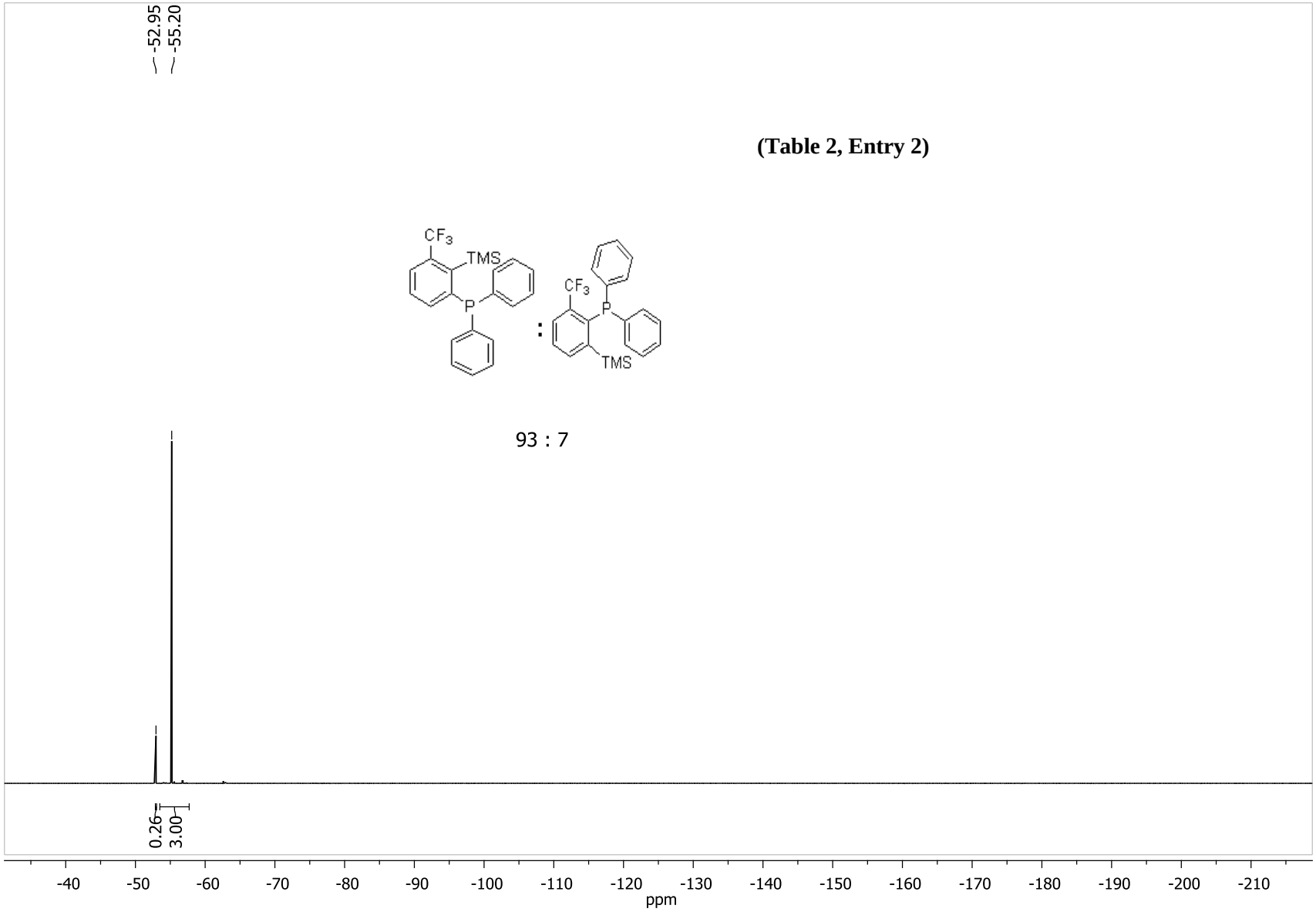
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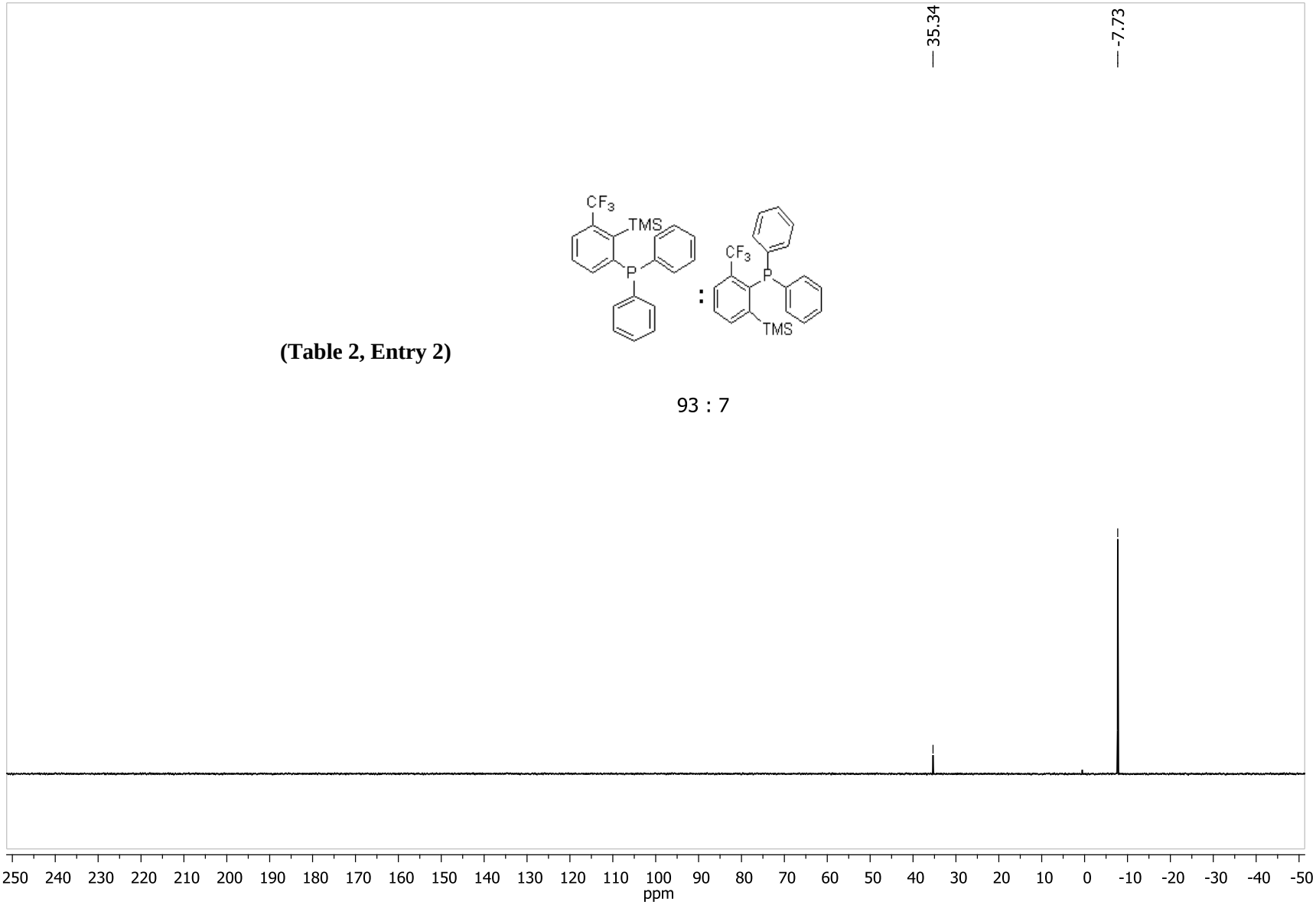

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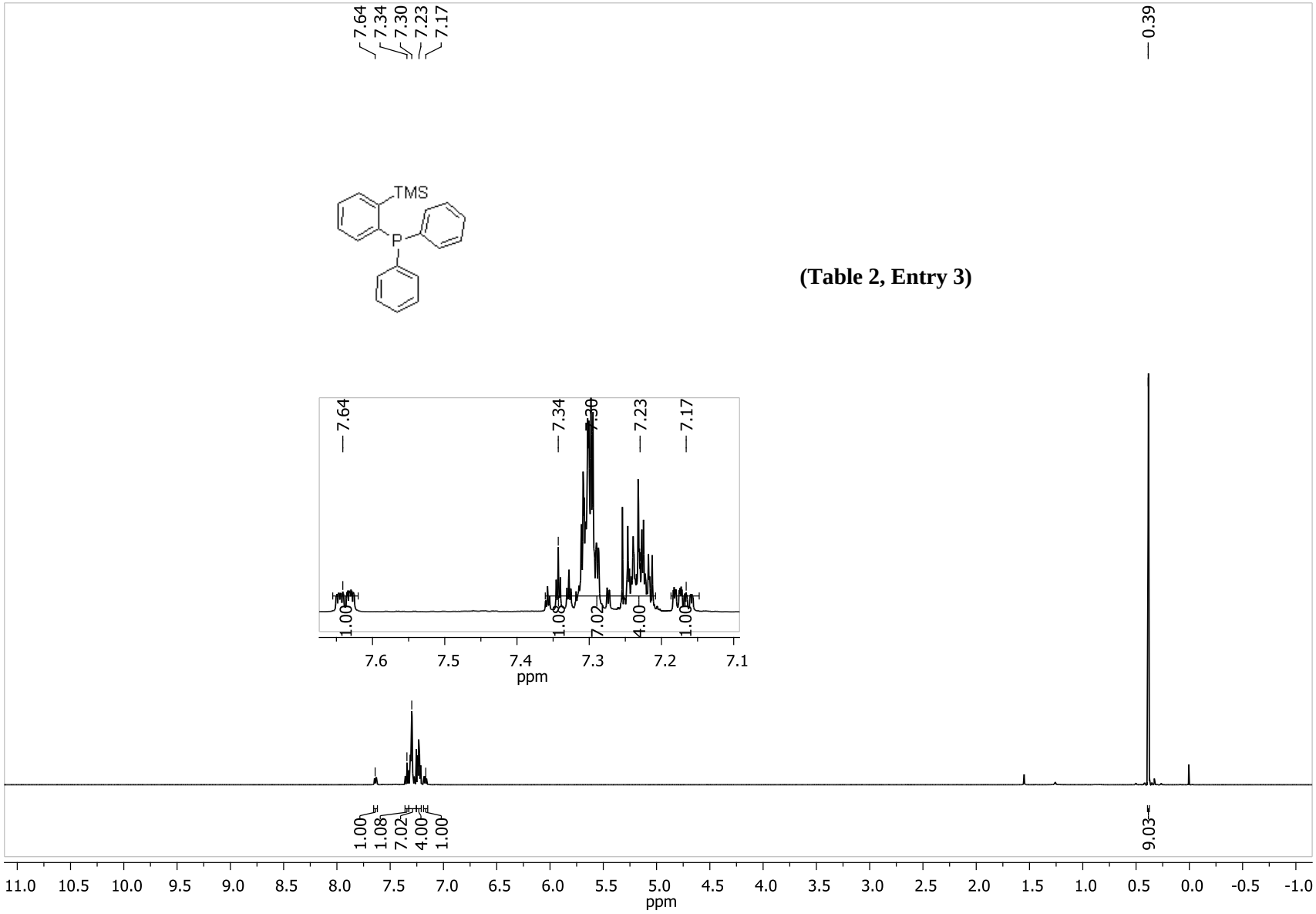

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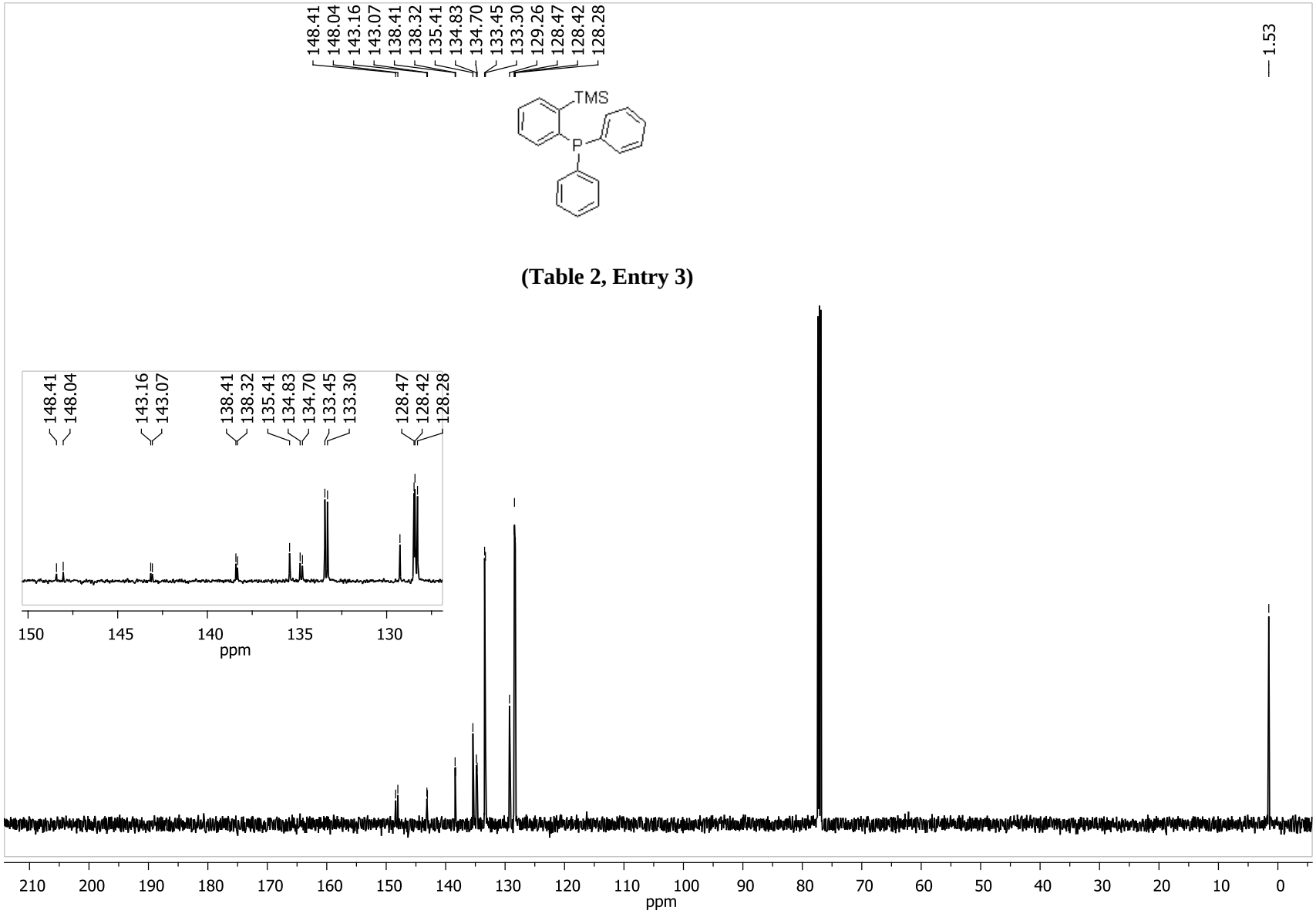

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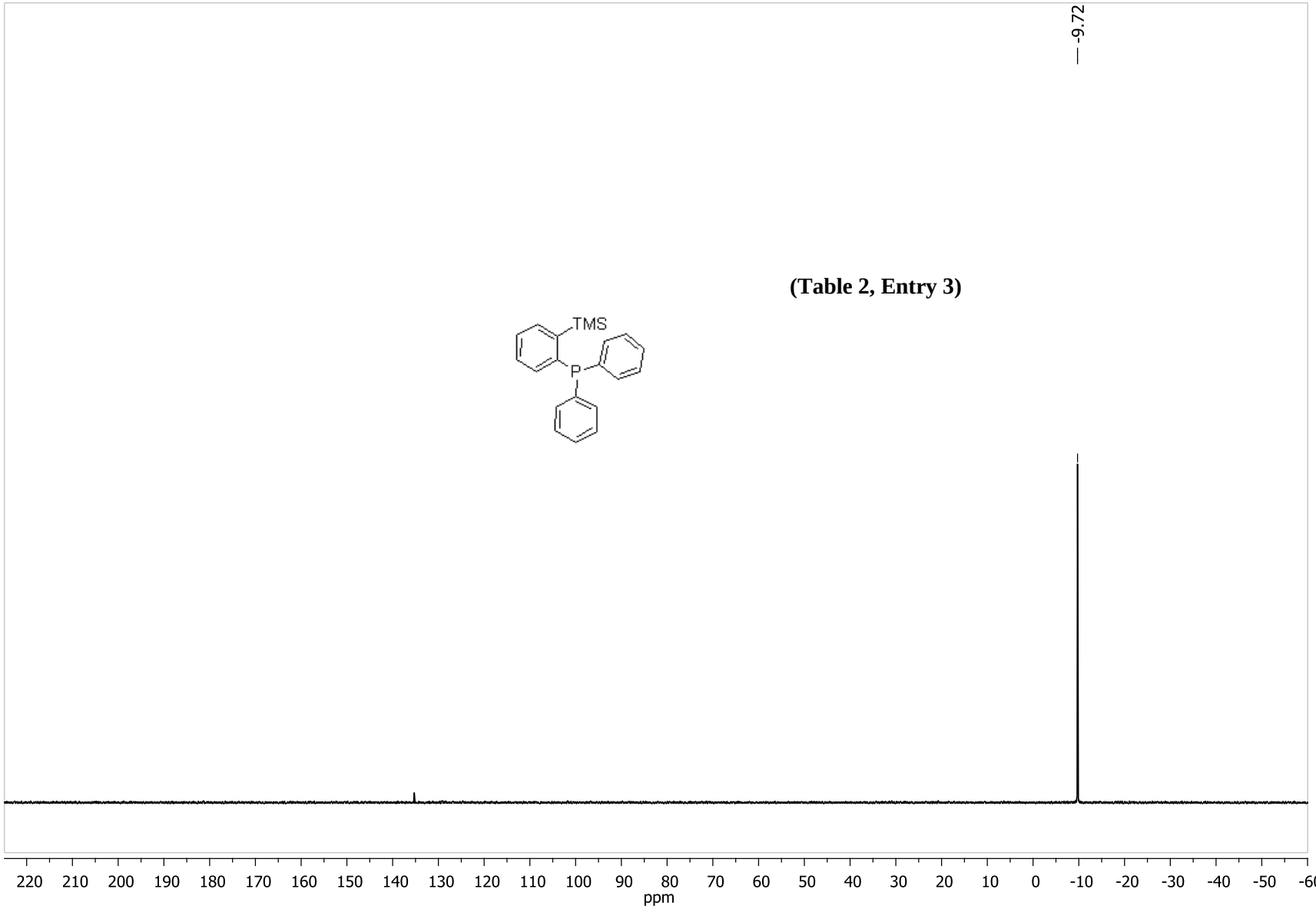

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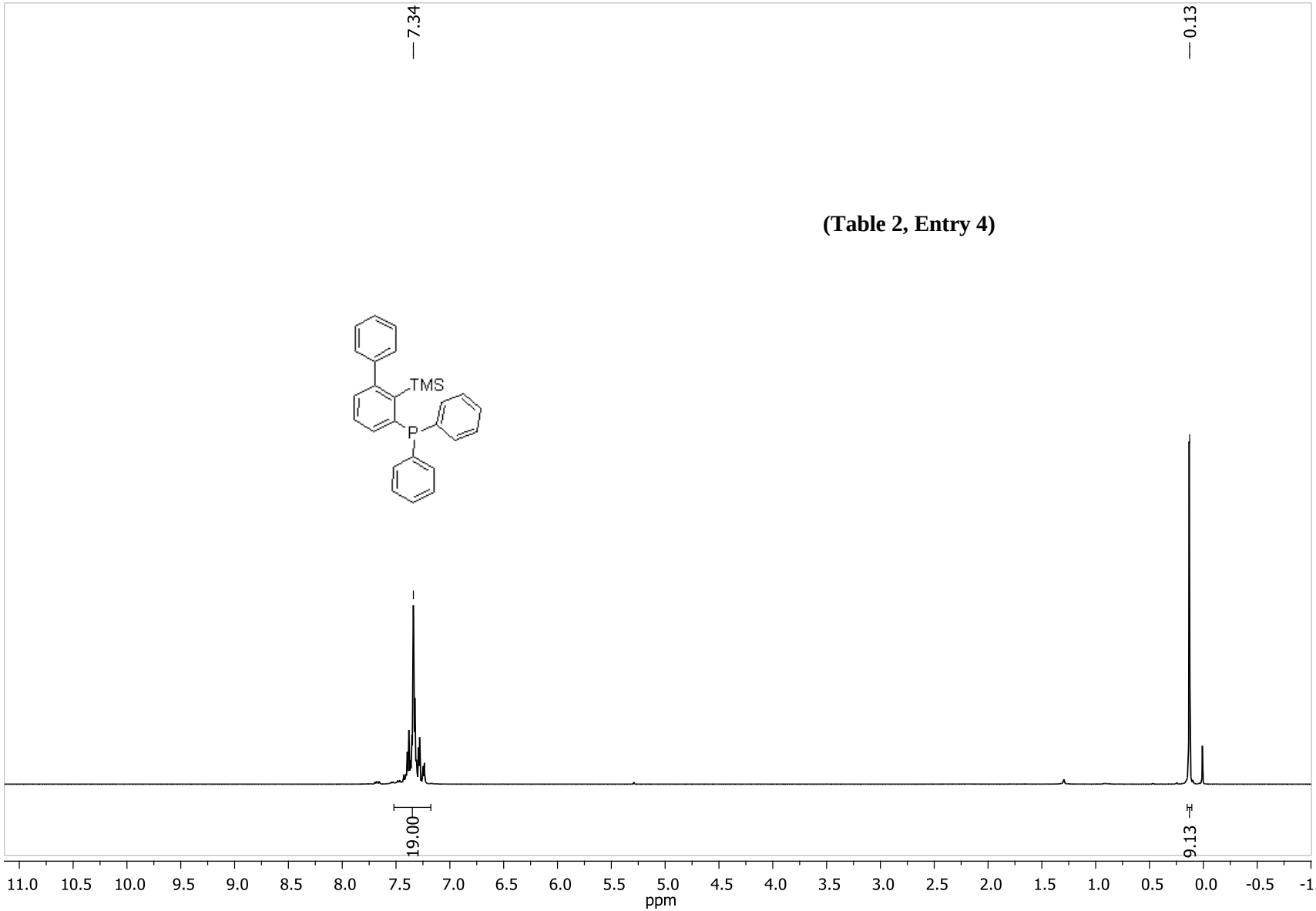

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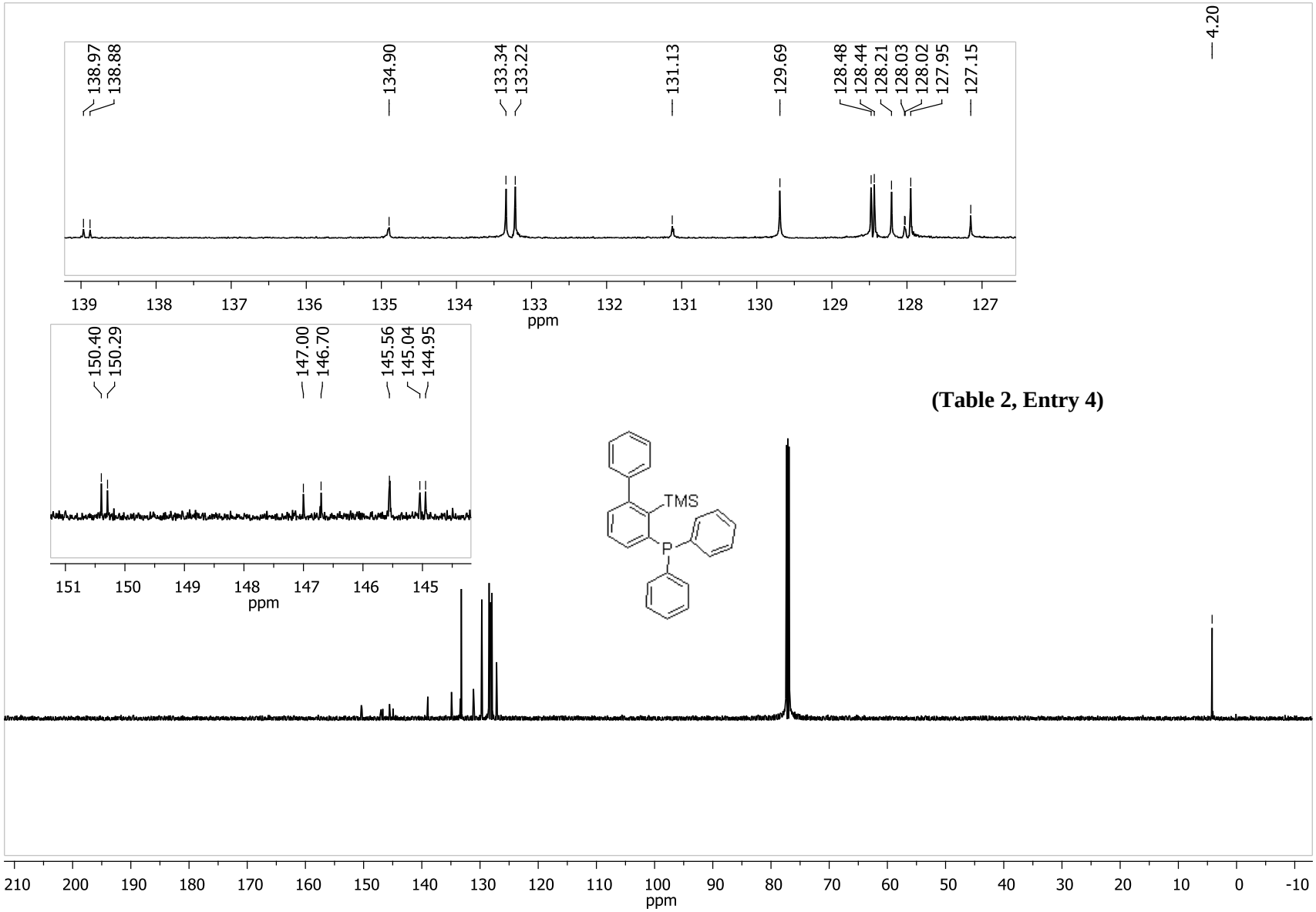

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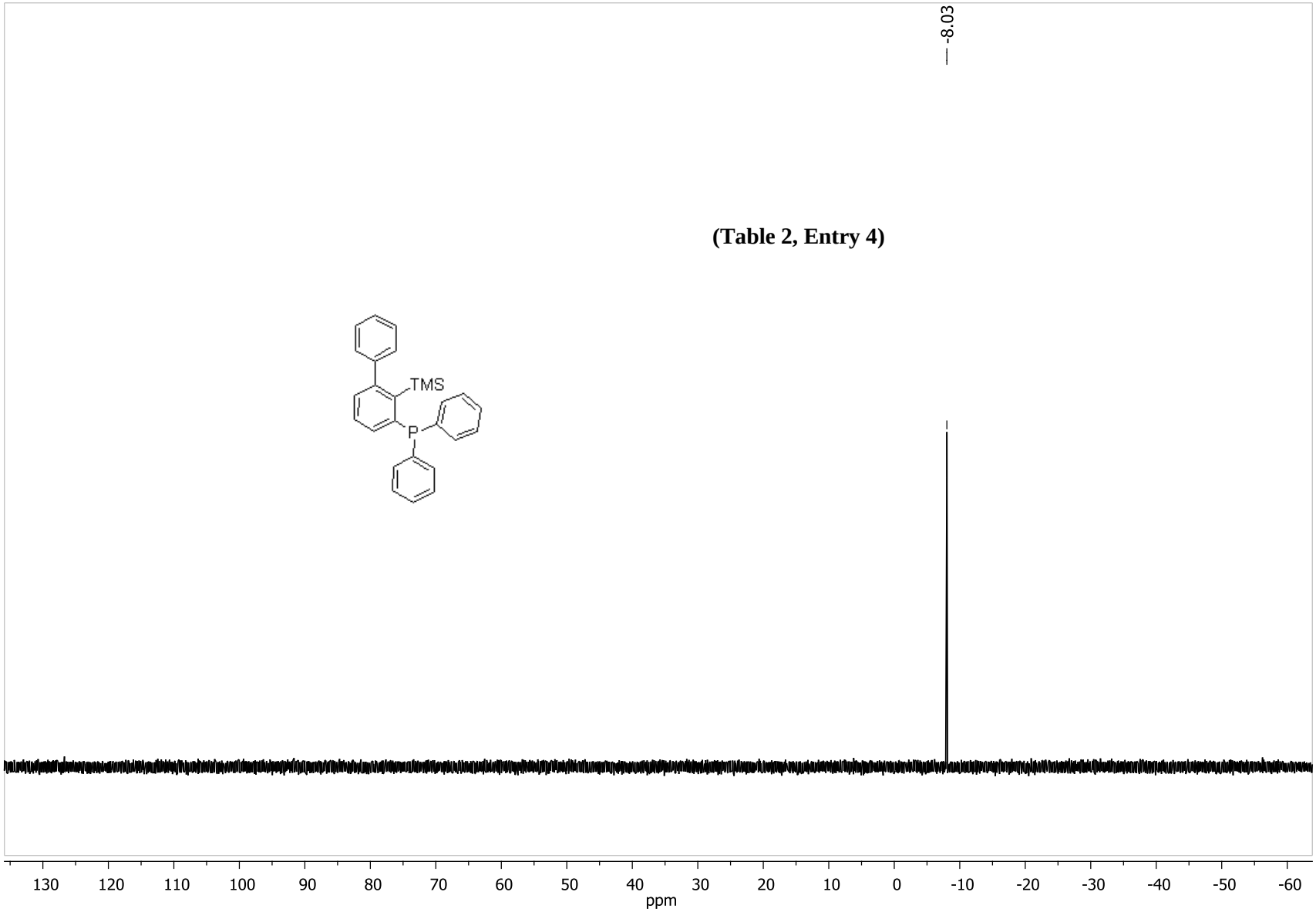

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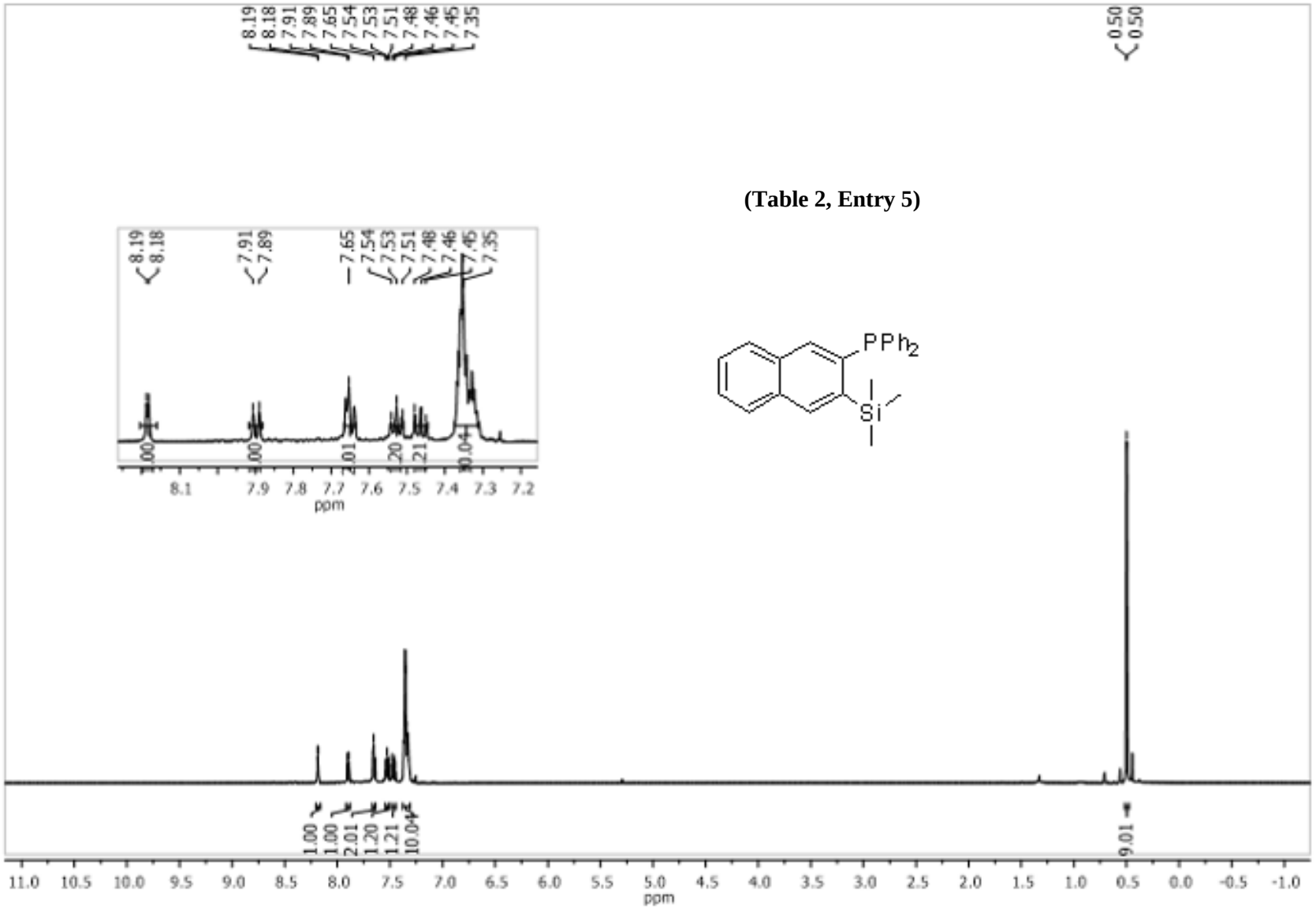

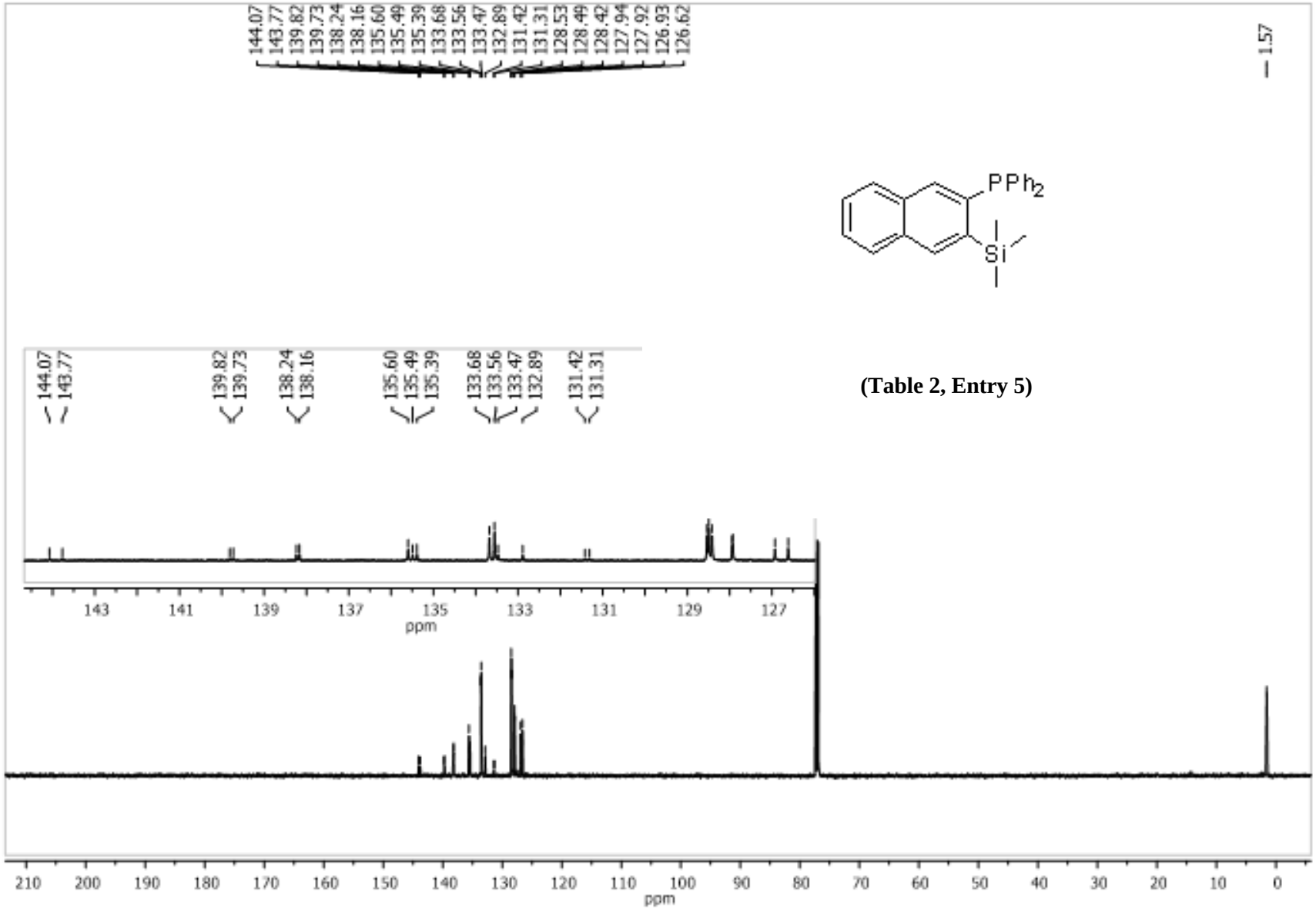
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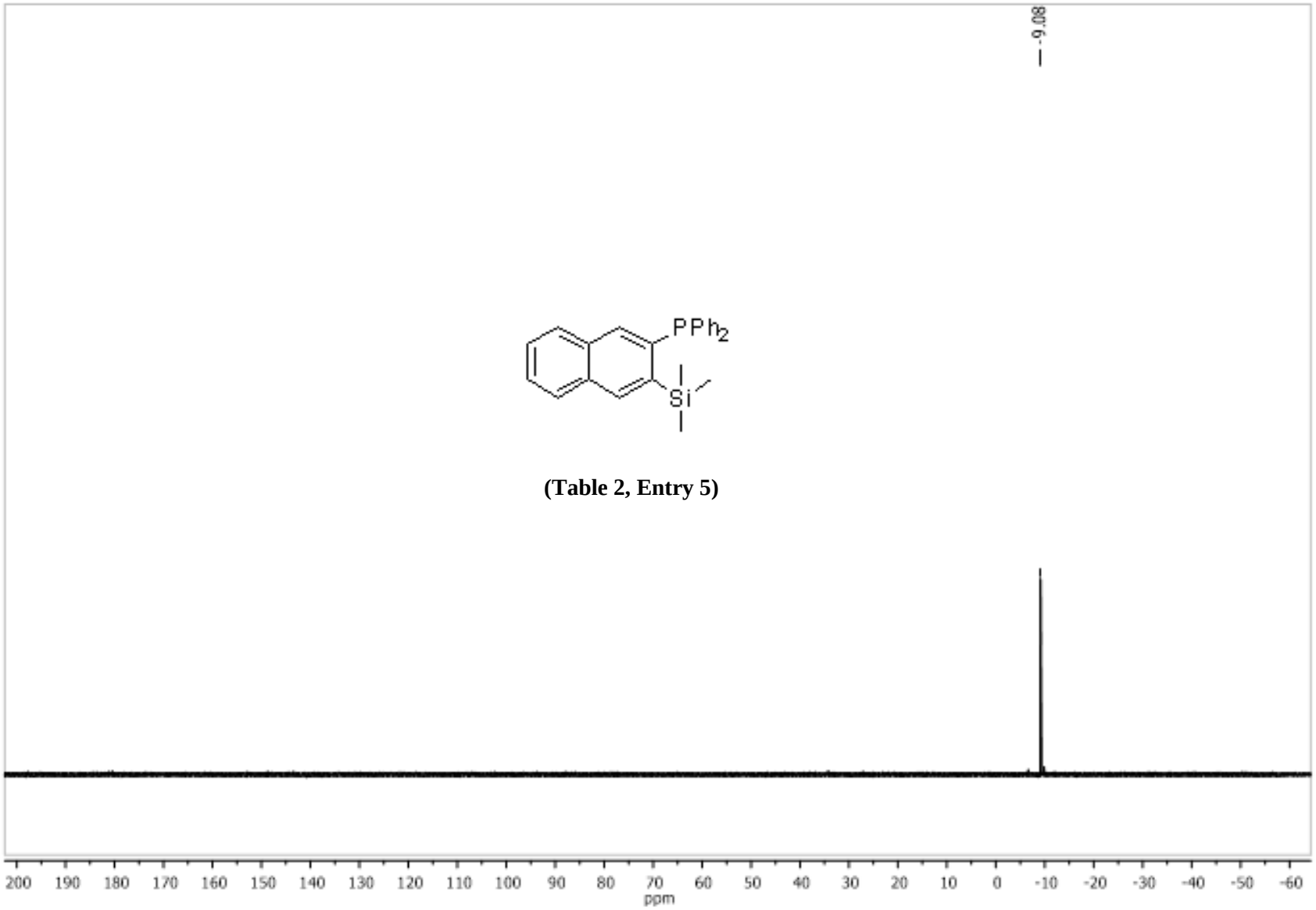
ppm
ppm



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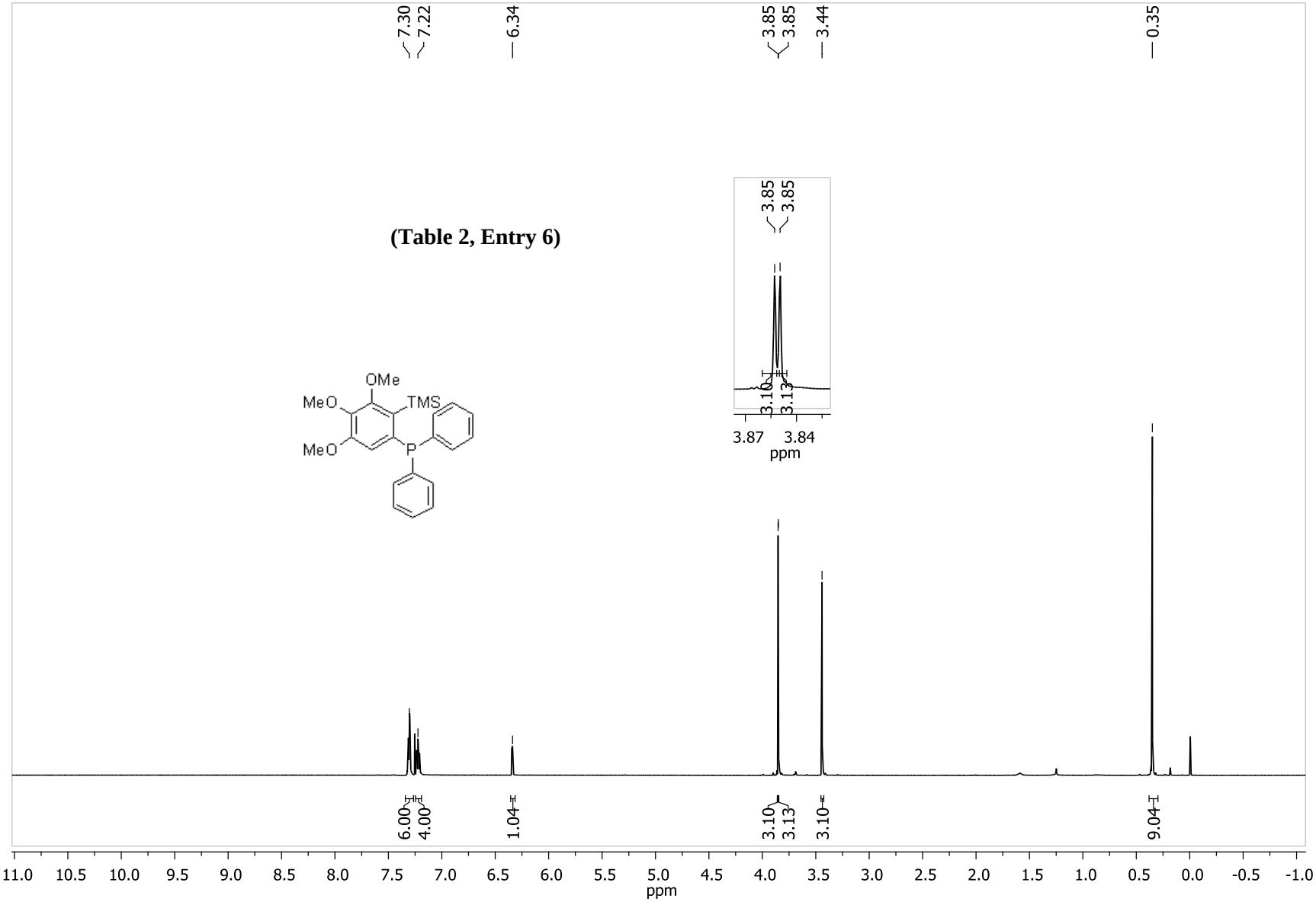
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ppm
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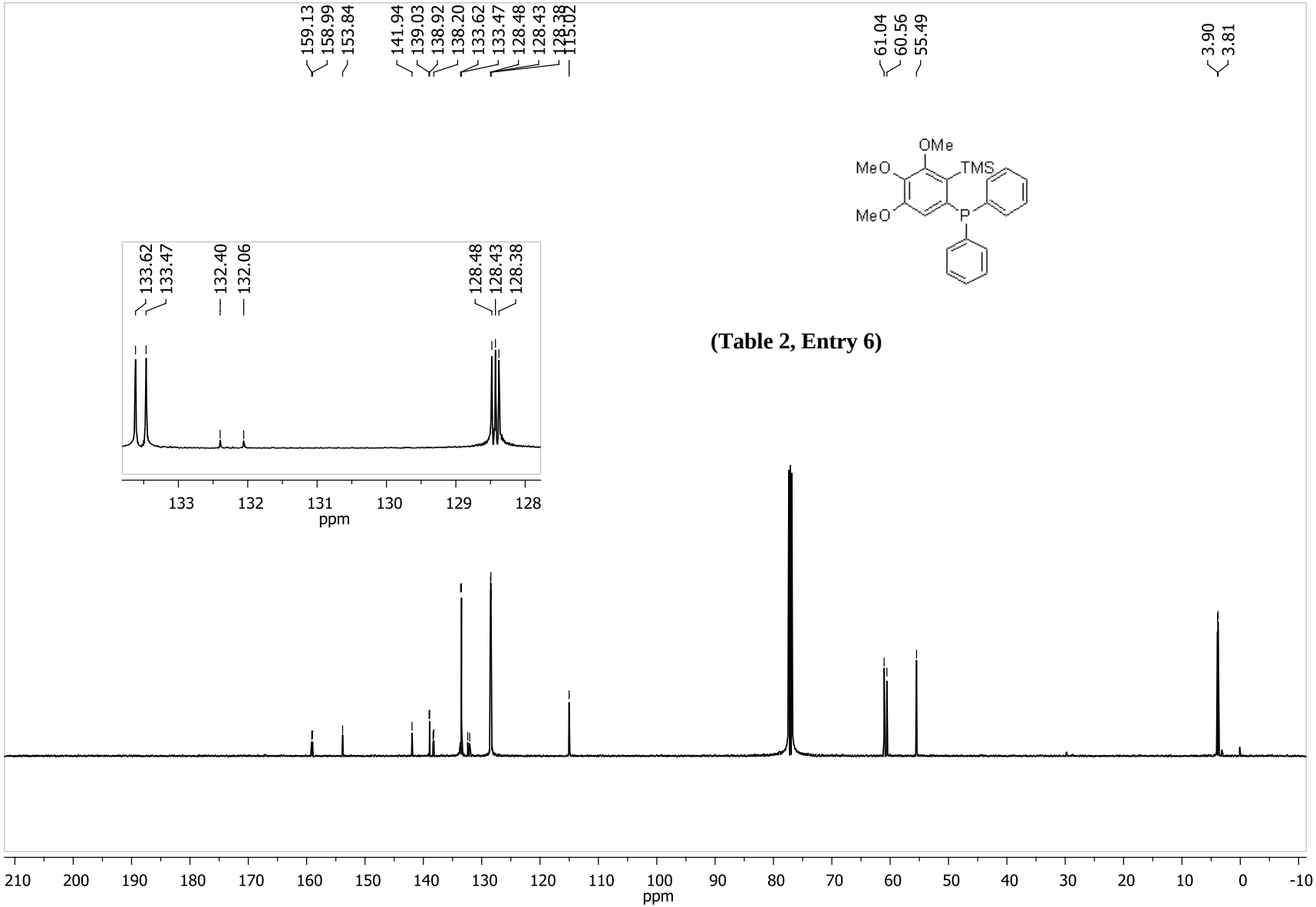

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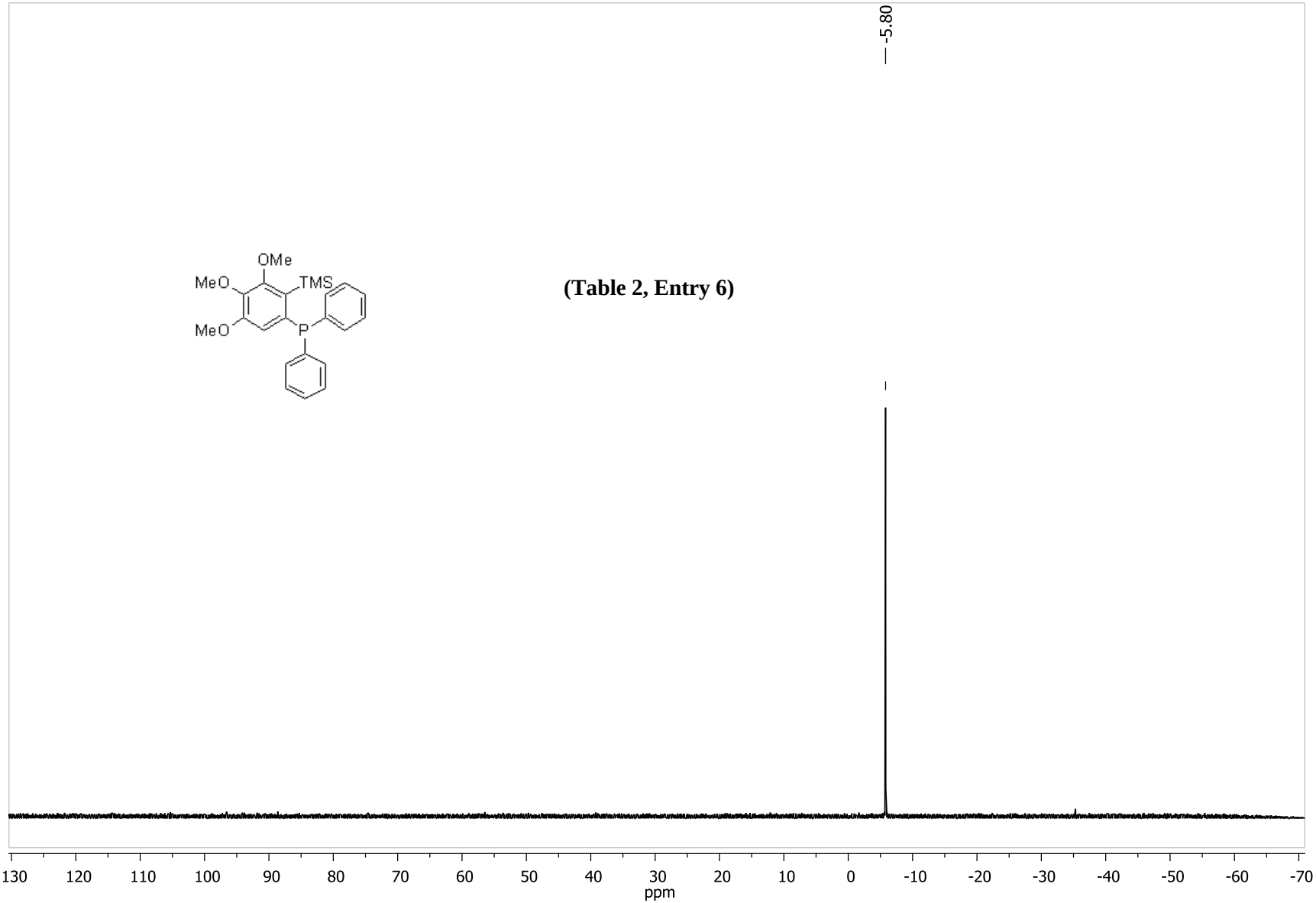
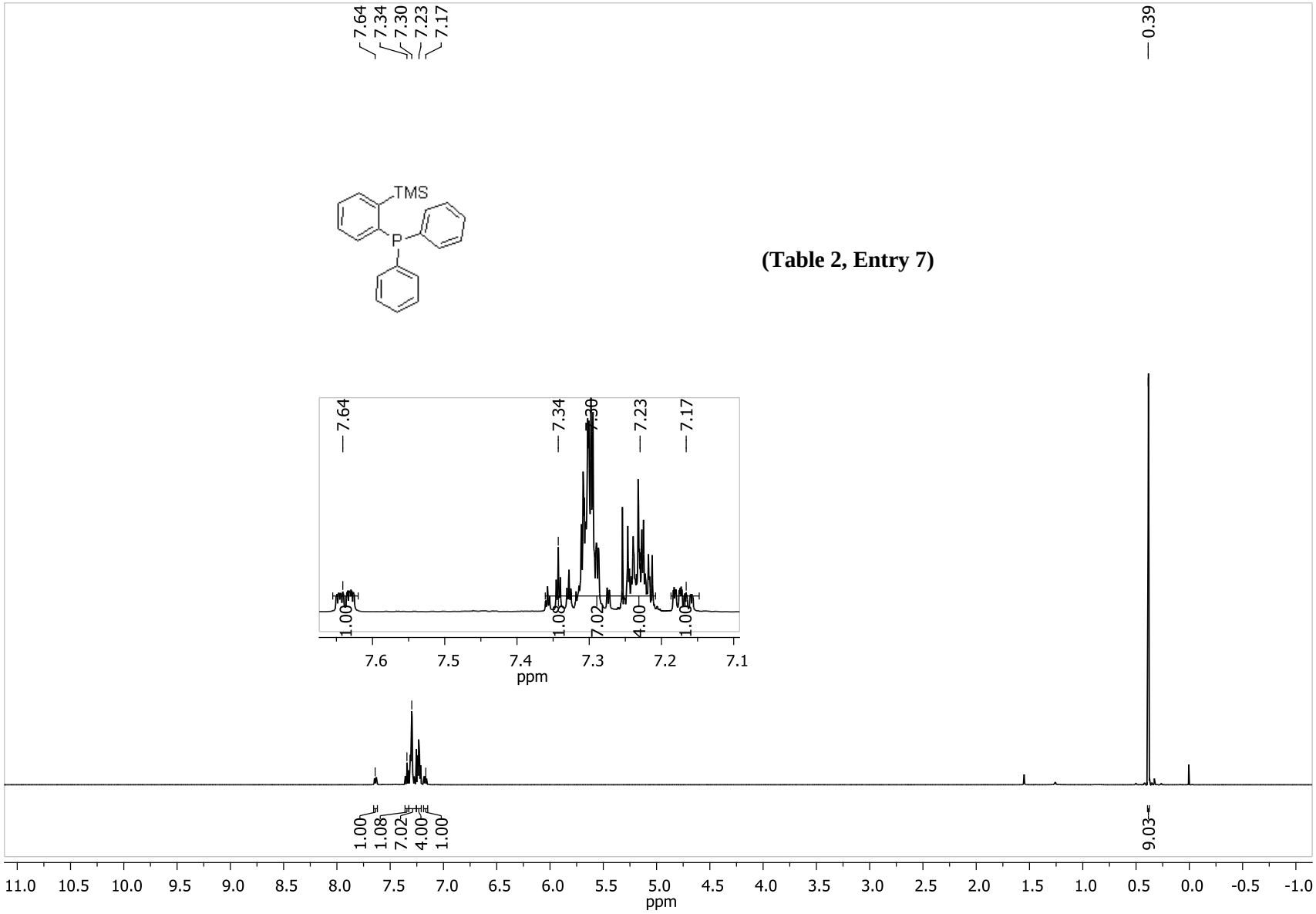
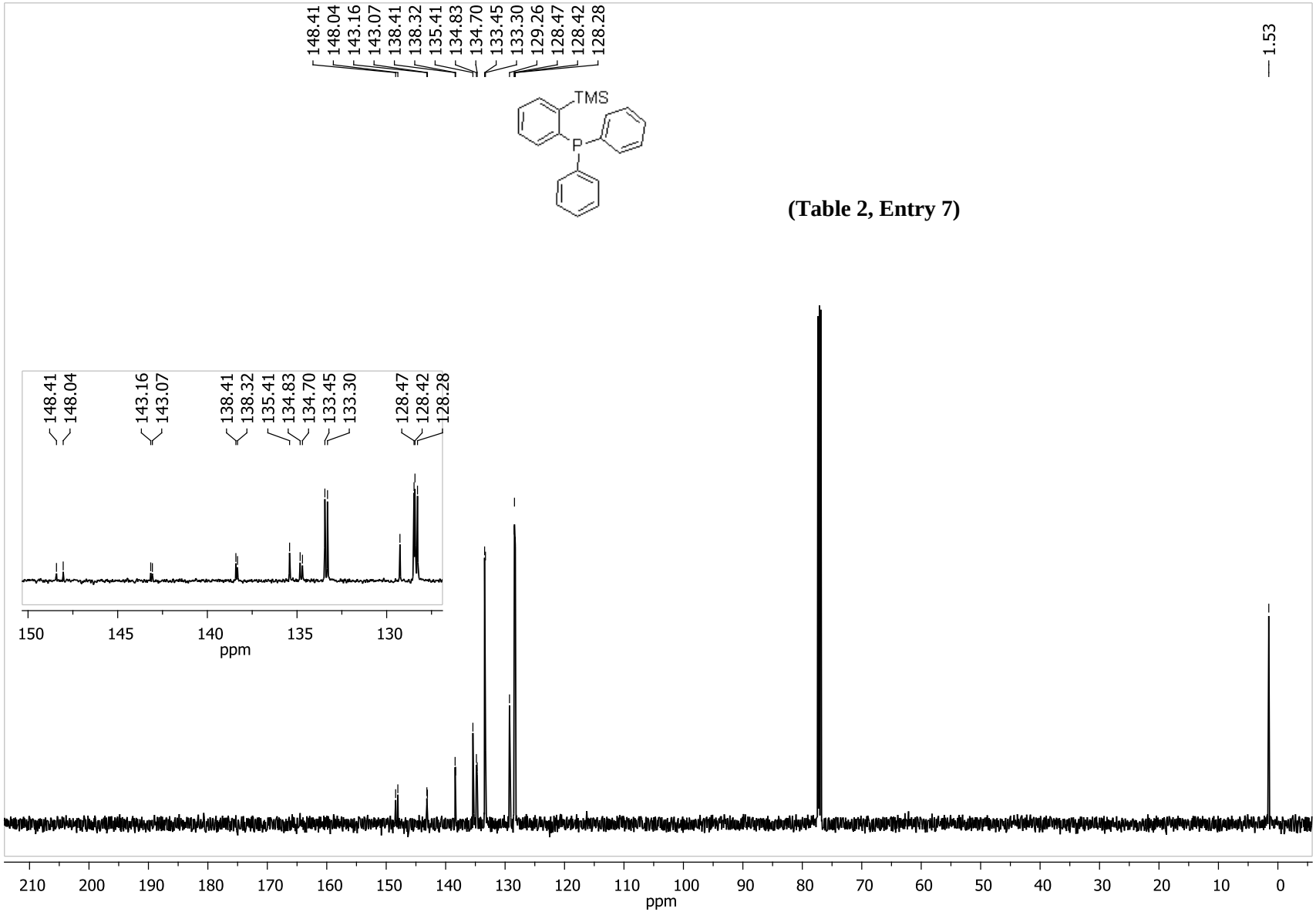


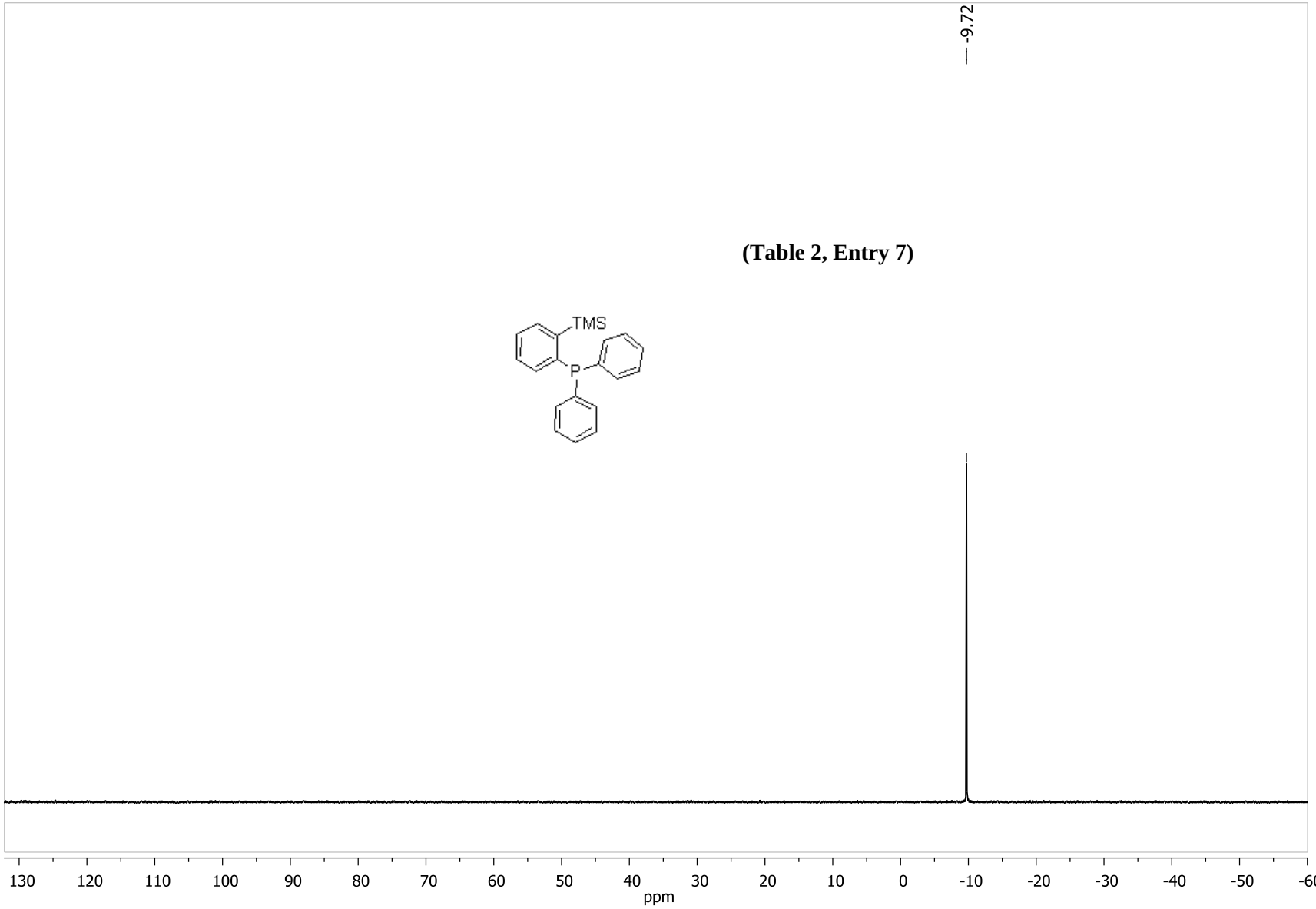
(Table 2, Entry 6)


7.64
7.34
7.30
7.23
7.17
0.39
TMS
P
(Table 2, Entry 7)
1.00
1.08
7.02
4.00
1.00
9.03
ppm



(Table 2, Entry 7)

(Table 2, Entry 7)



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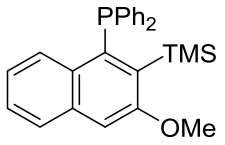

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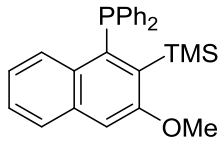

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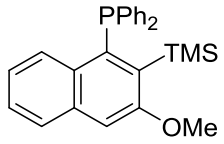

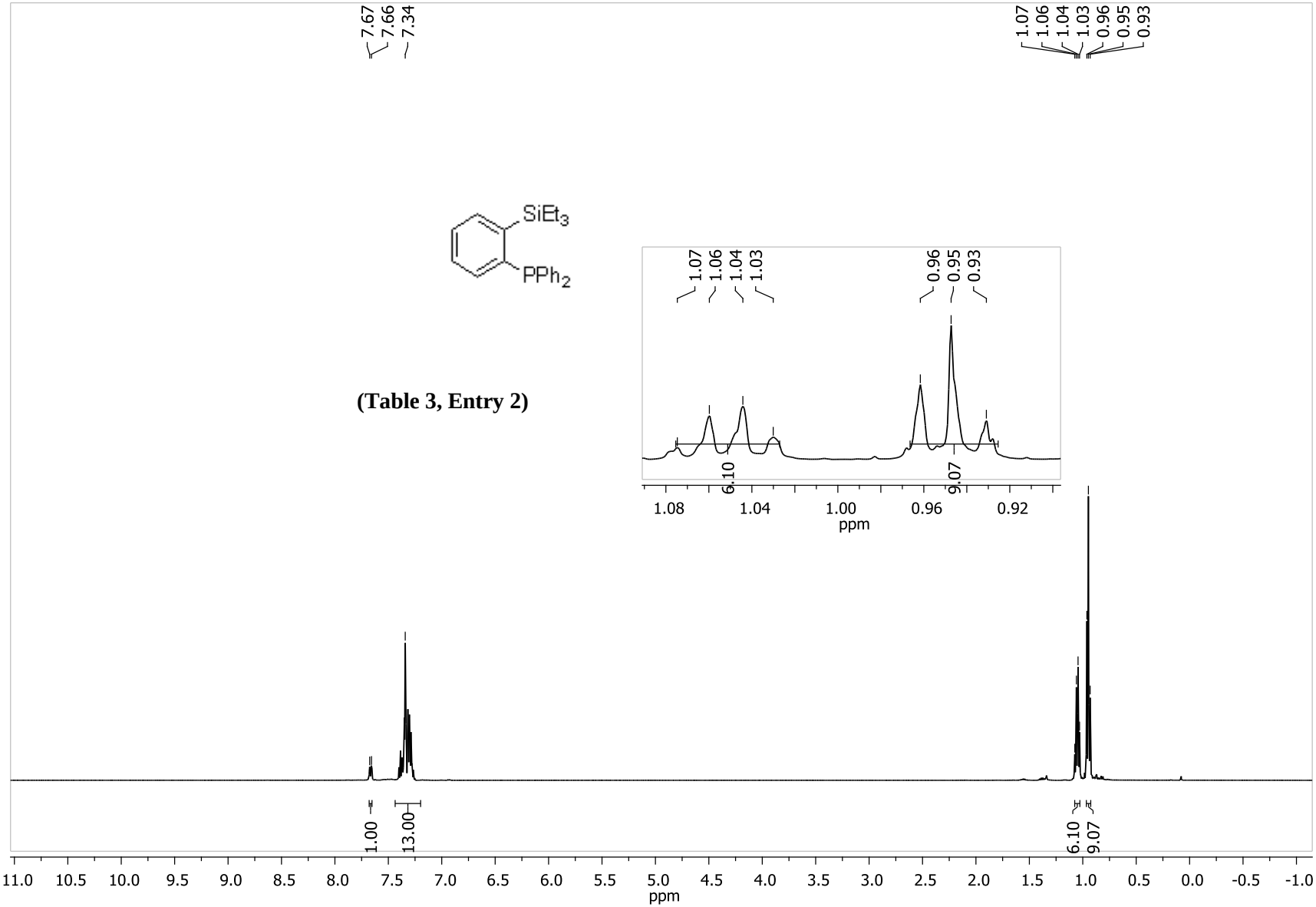

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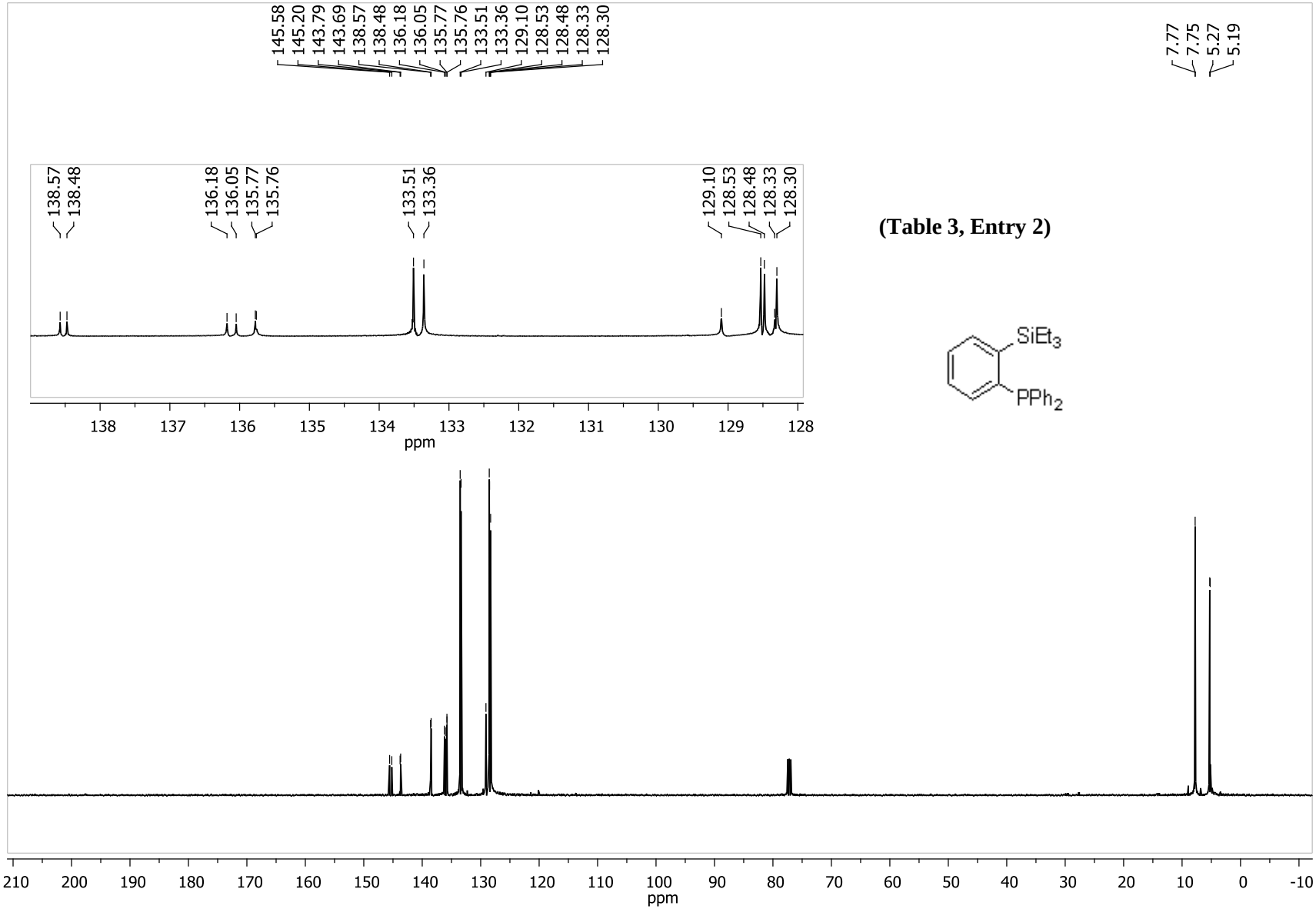
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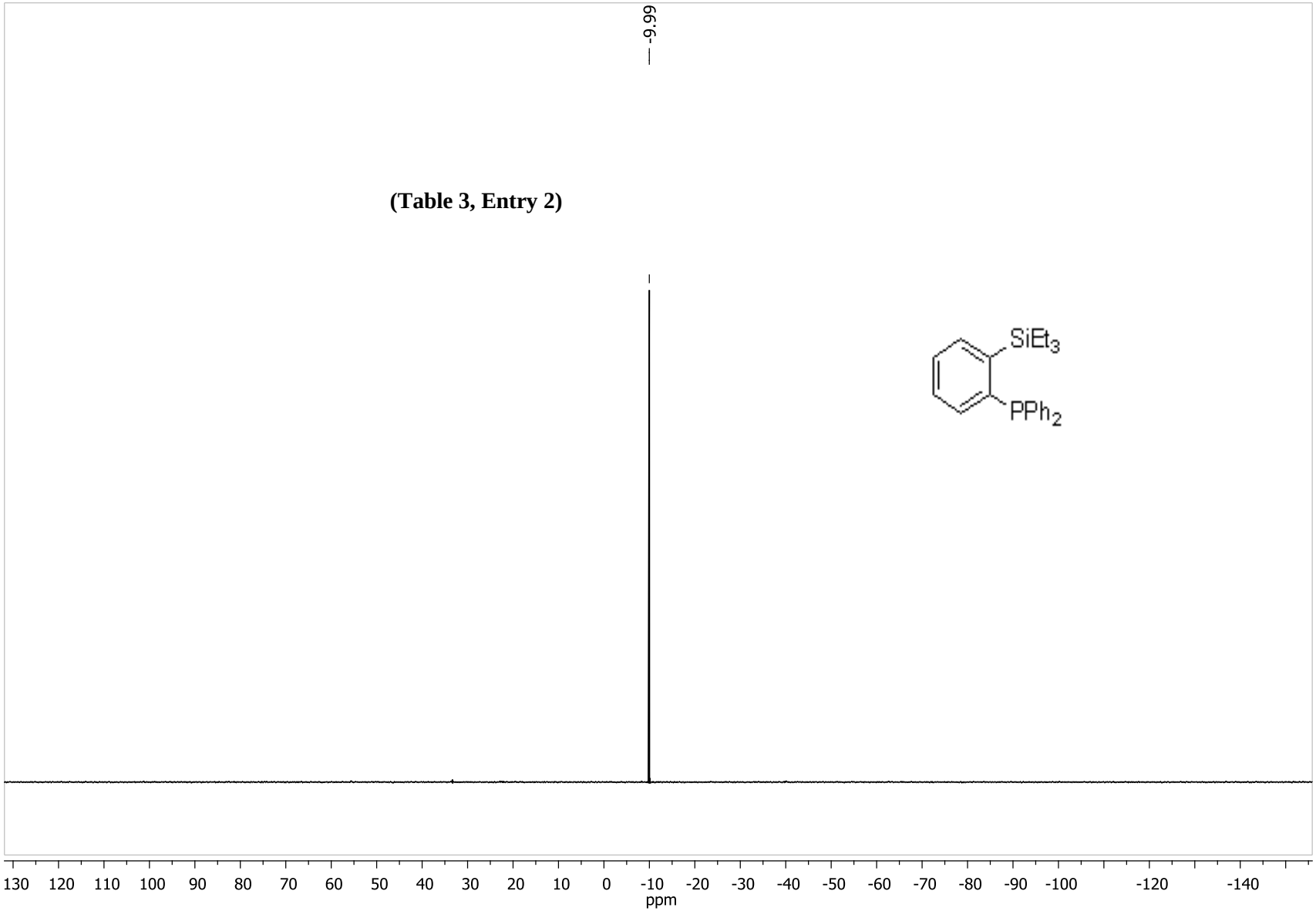
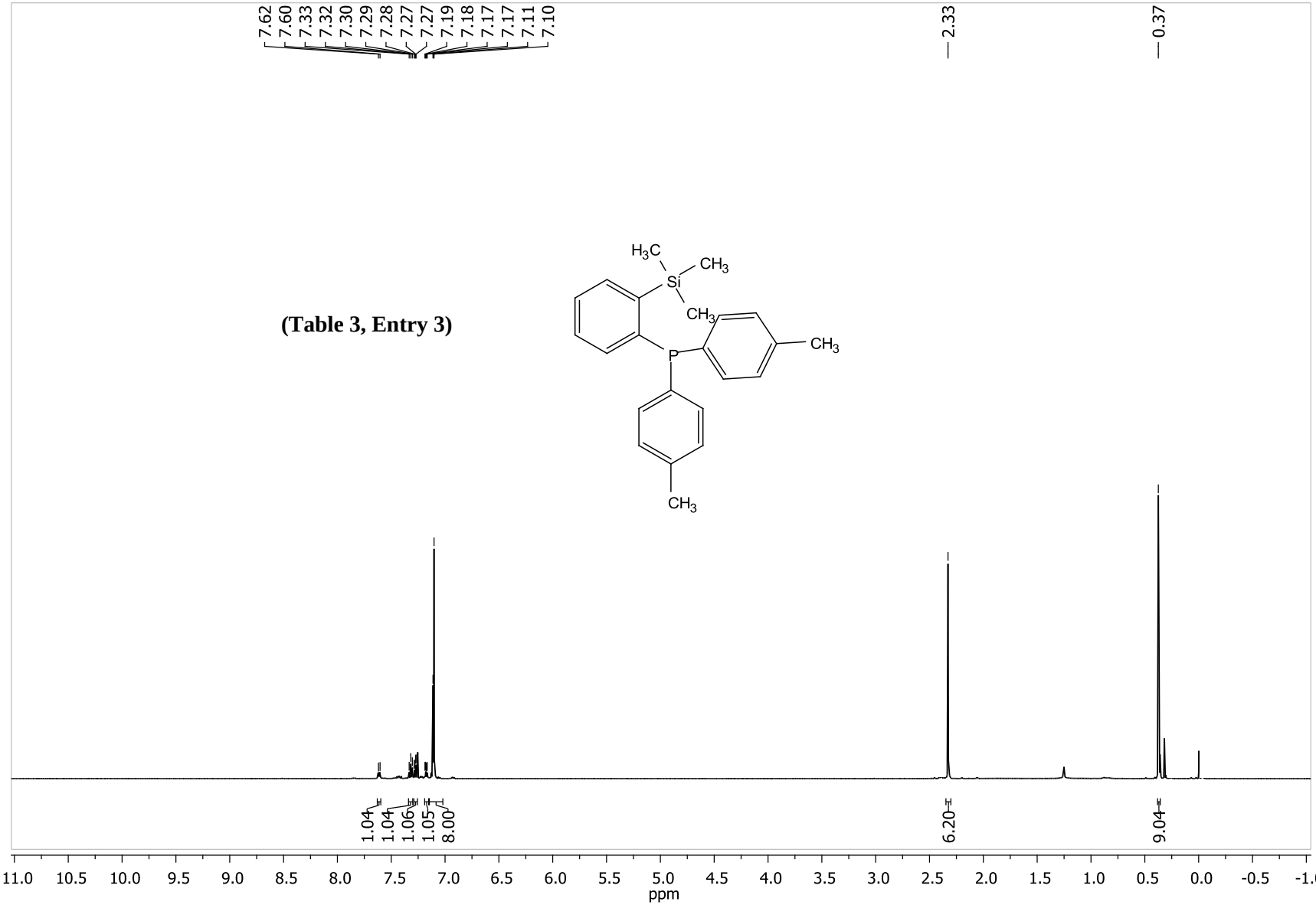
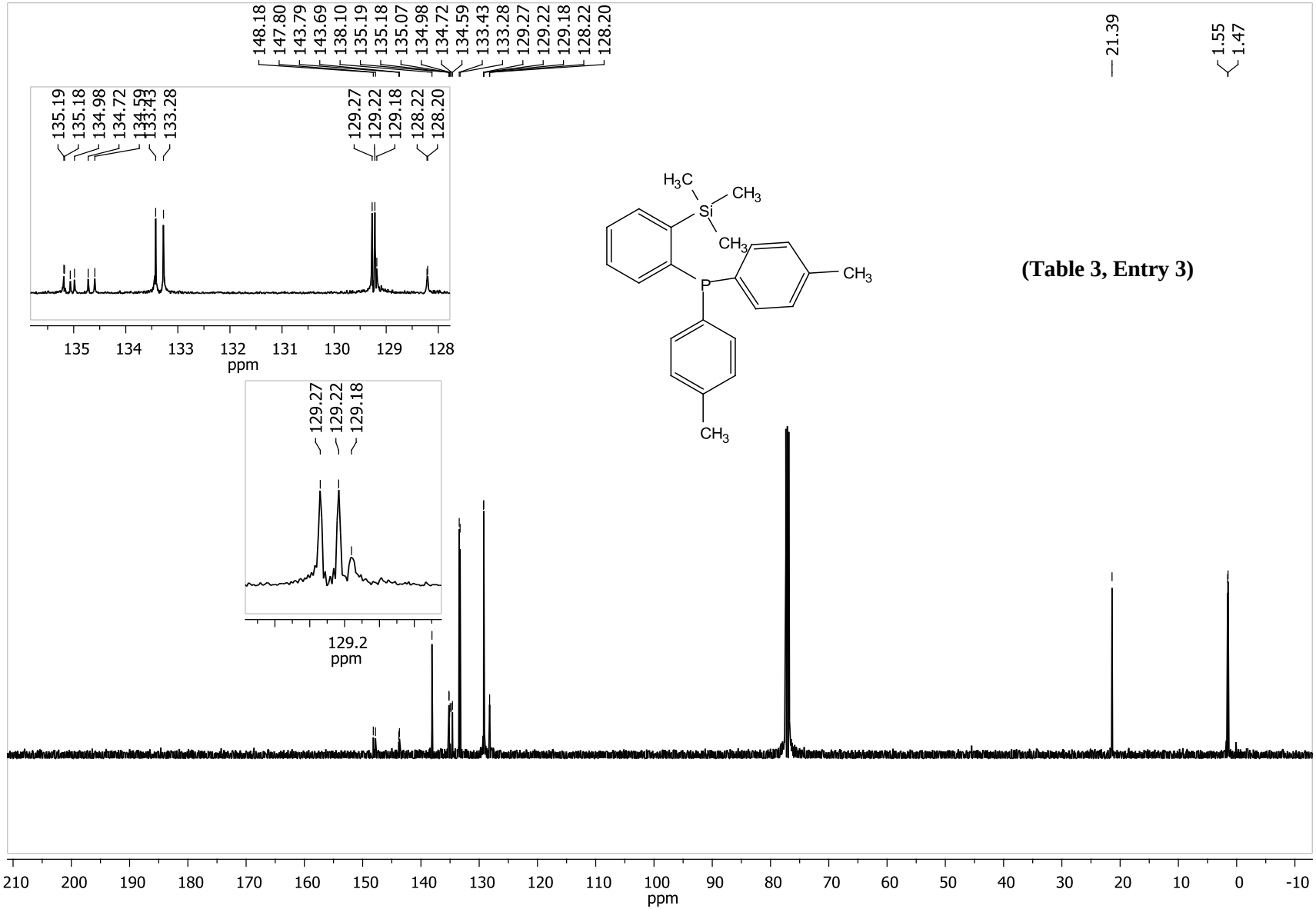
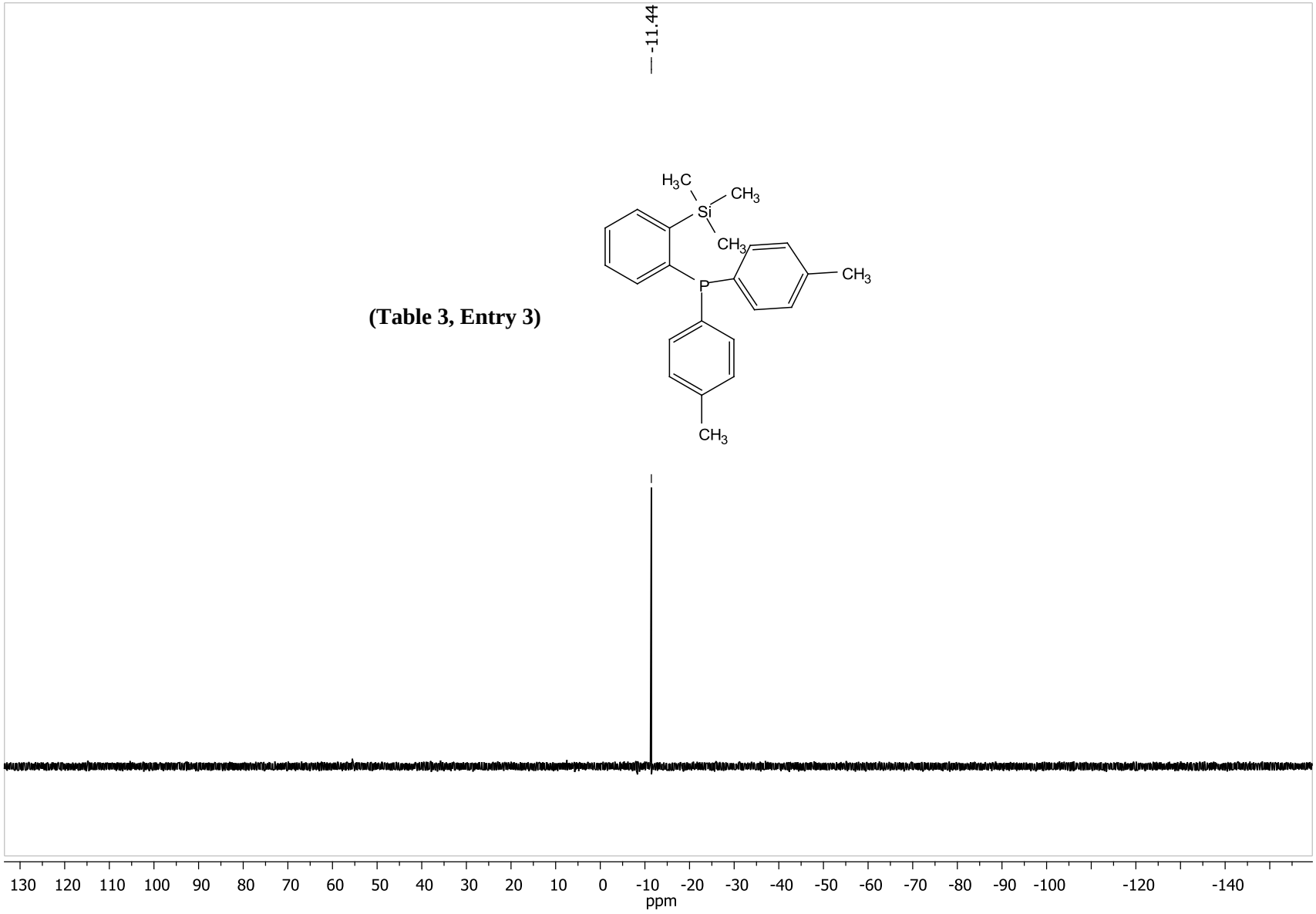
145.20
143.79
143.69
138.57
138.48
136.18
136.05
135.77
135.76
133.51
133.36
129.10
128.53
128.48
128.33
128.30
7.77
7.75
5.27
5.19
138.57
138.48
136.18
136.05
135.77
135.76
133.51
133.36
129.10
128.53
128.48
128.33
128.30
138
137
136
135
134
133
132
131
130
129
128
ppm
(Table 3, Entry 2)
SiEt3
PPh2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

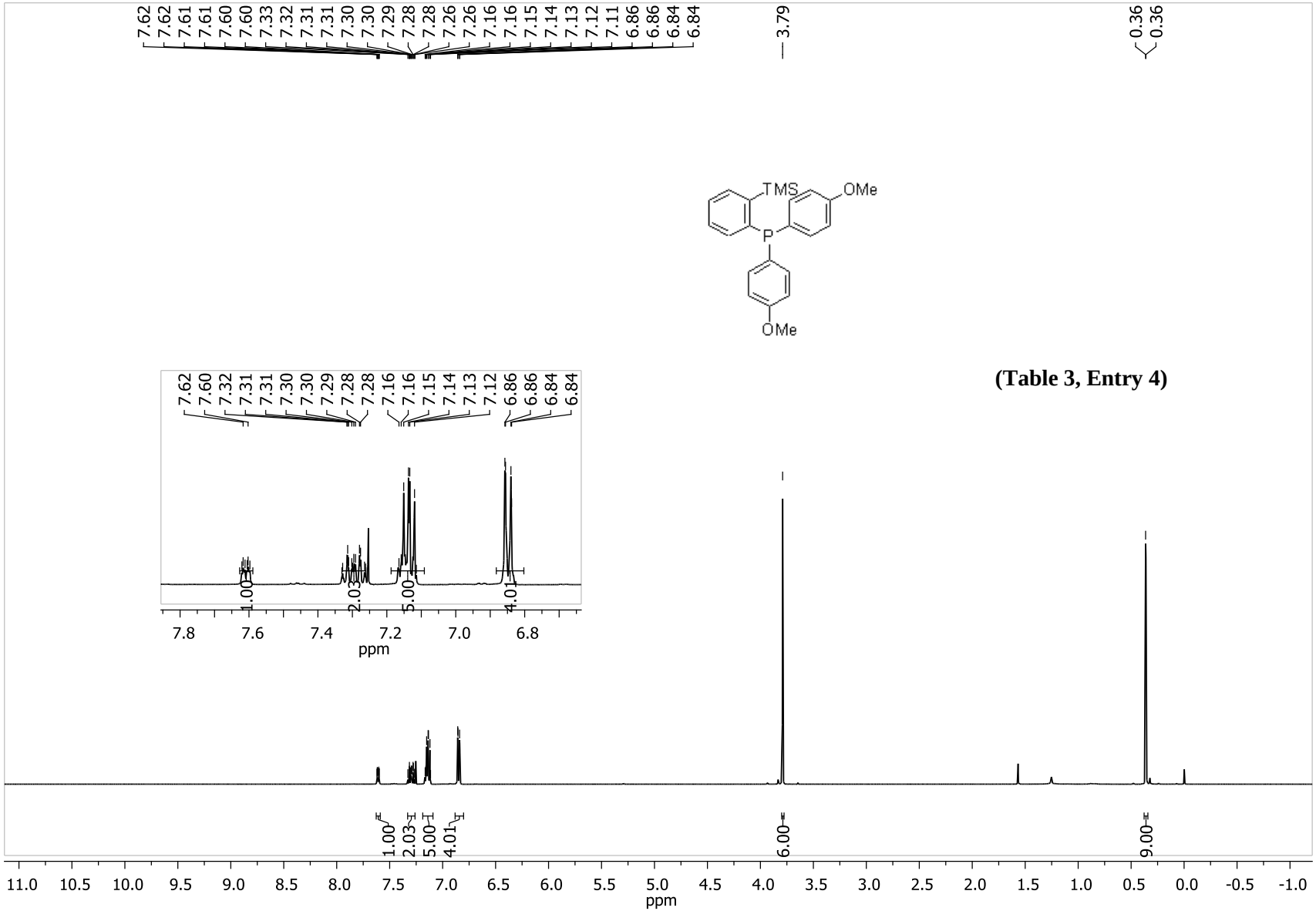

-9.99
(Table 3, Entry 2)
SiEt3
PPh2
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
ppm

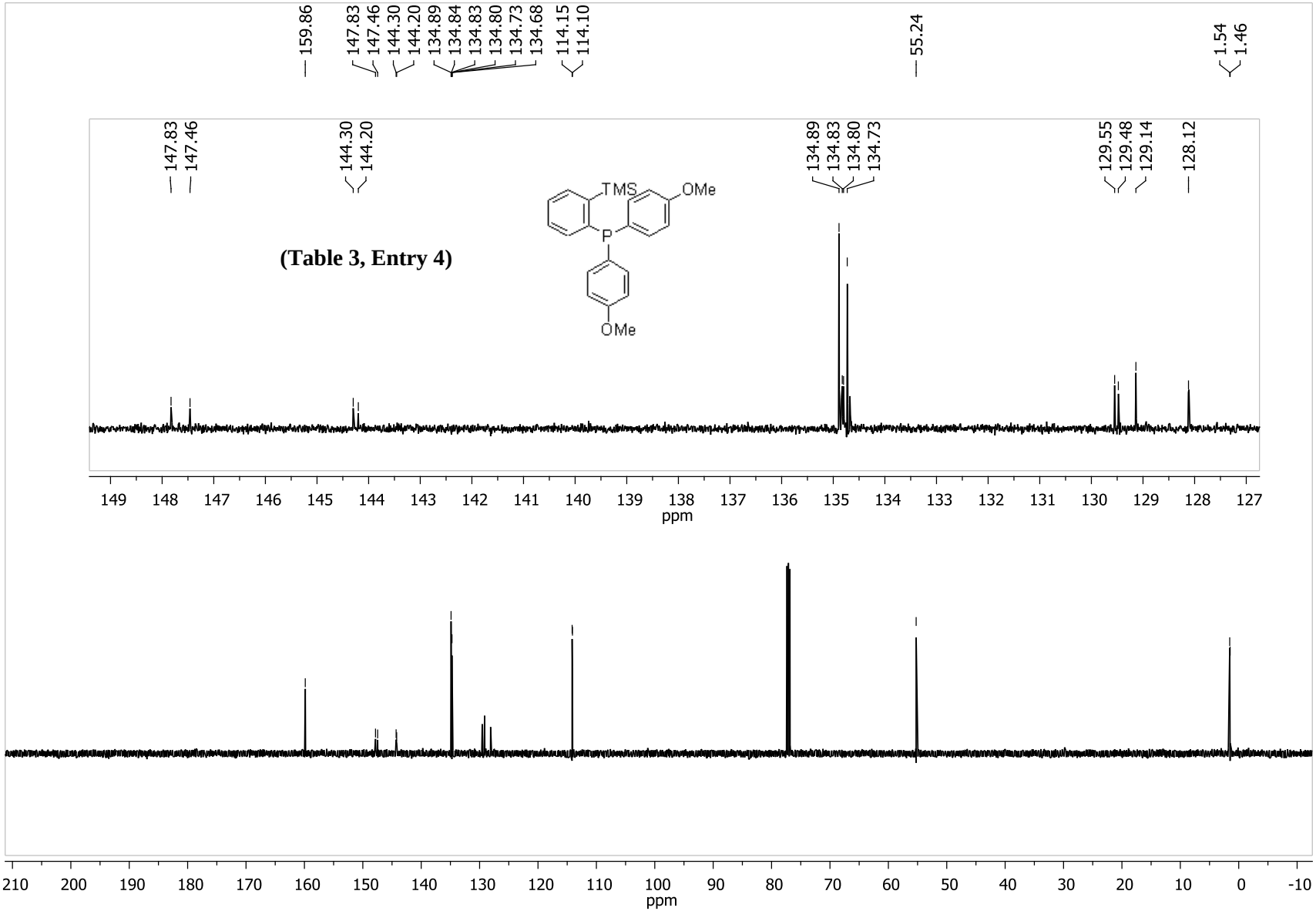

7.62
7.60
7.33
7.32
7.30
7.29
7.28
7.27
7.27
7.19
7.18
7.17
7.17
7.11
7.10
2.33
0.37
(Table 3, Entry 3)
H3C
CH3
Si
CH3
CH3
P
CH3
1.04
1.04
1.06
1.05
8.00
6.20
9.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


148.18
147.80
143.79
143.69
138.10
135.19
135.18
135.07
134.98
134.72
134.59
133.43
133.28
129.27
129.22
129.18
128.22
128.20
21.39
1.55
1.47
(Table 3, Entry 3)
ppm
129.2
ppm

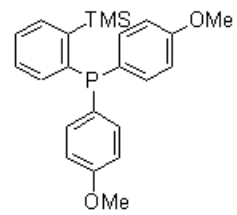
(Table 3, Entry 3)




7.62
7.62
7.61
7.61
7.60
7.60
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.26
7.16
7.16
7.15
7.14
7.13
7.12
7.11
6.86
6.86
6.84
6.84
3.79
0.36
0.36
TMS
OMe
P
OMe
(Table 3, Entry 4)
1.00
2.03
5.00
4.01
6.00
9.00
ppm


159.86
147.83
147.46
144.30
144.20
134.89
134.84
134.83
134.80
134.73
134.68
114.15
114.10
55.24
1.54
1.46
147.83
147.46
144.30
144.20
134.89
134.83
134.80
134.73
129.55
129.48
129.14
128.12
TMS
OMe
P
OMe
(Table 3, Entry 4)
149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127
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 3, Entry 4)



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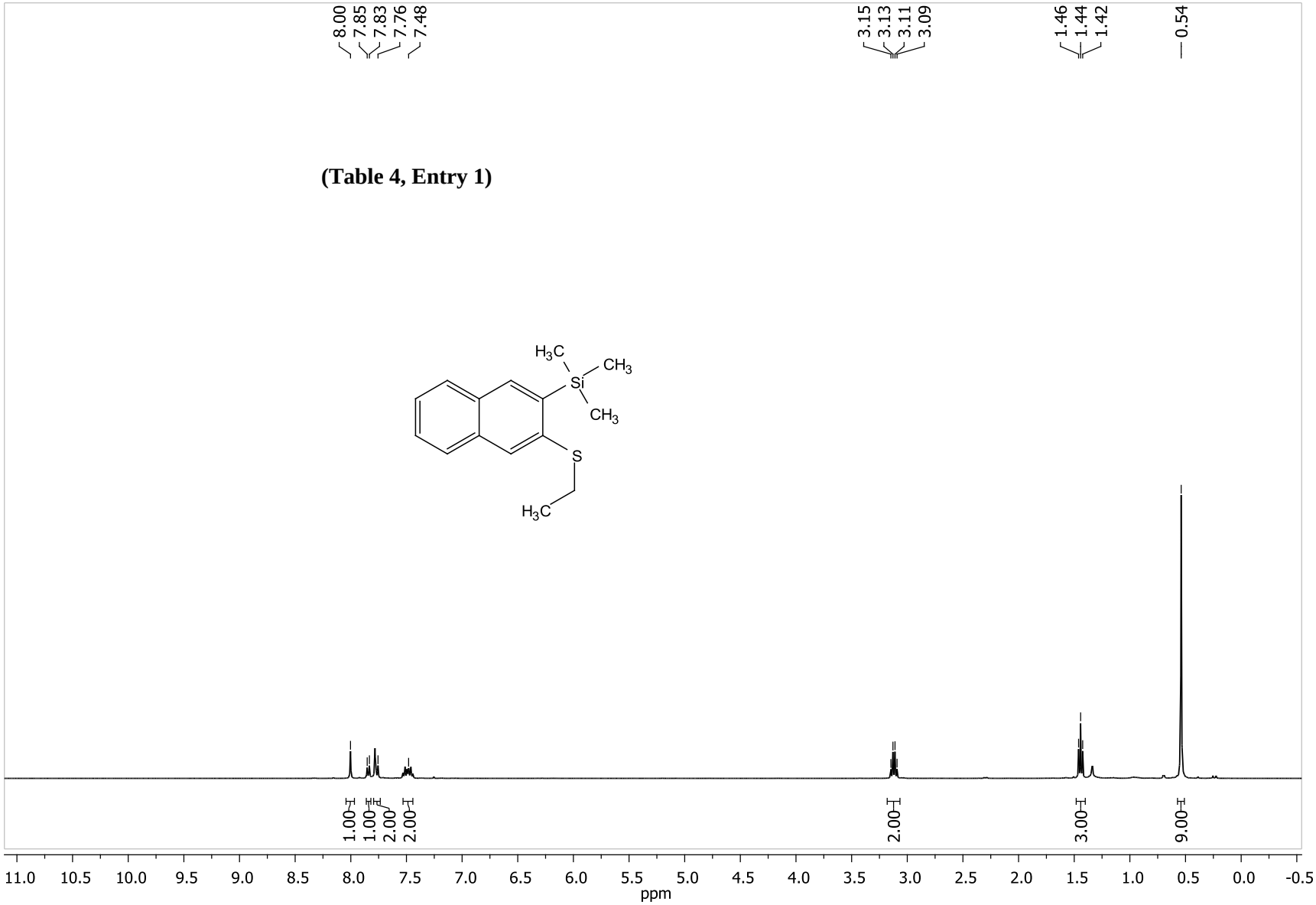
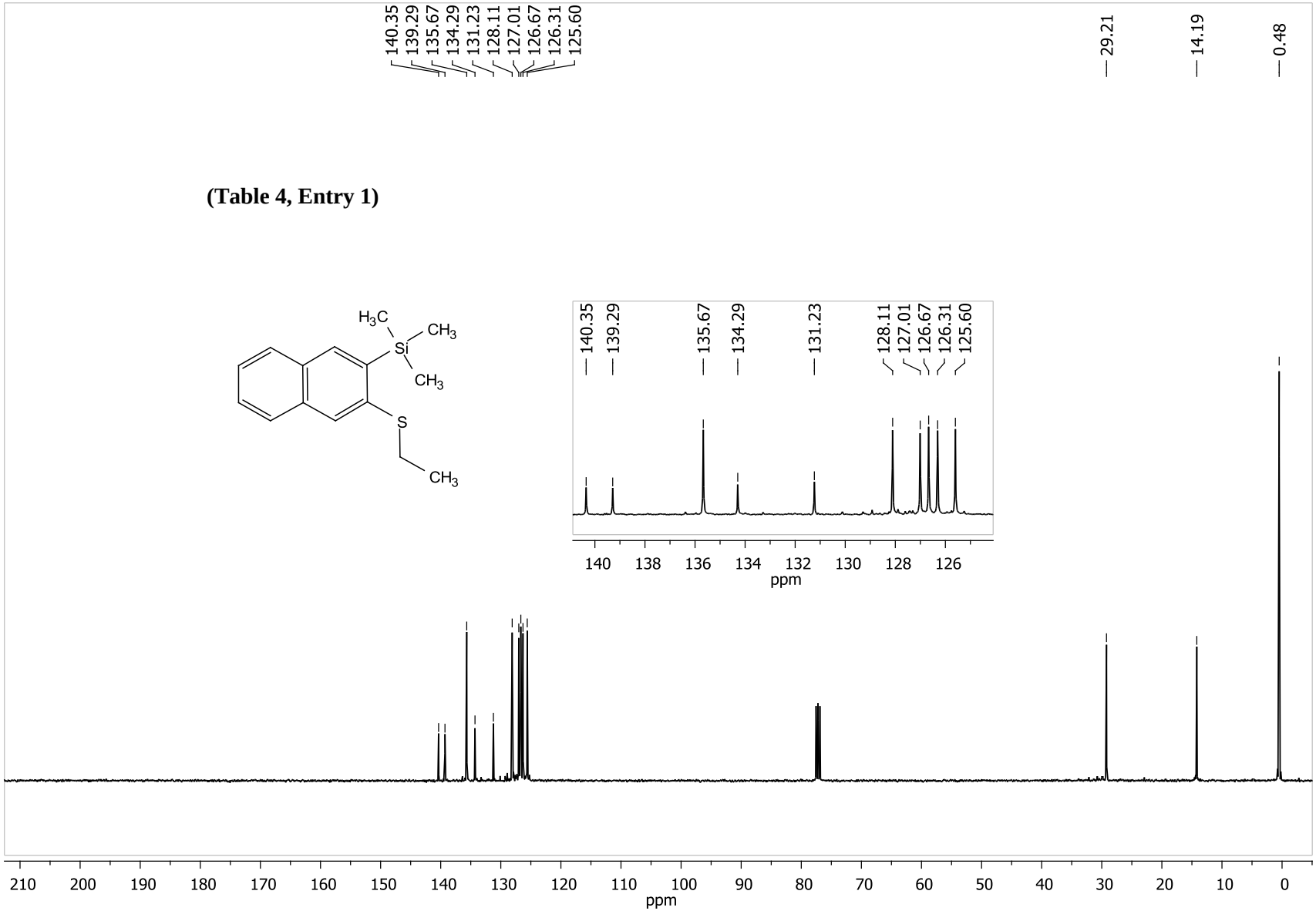
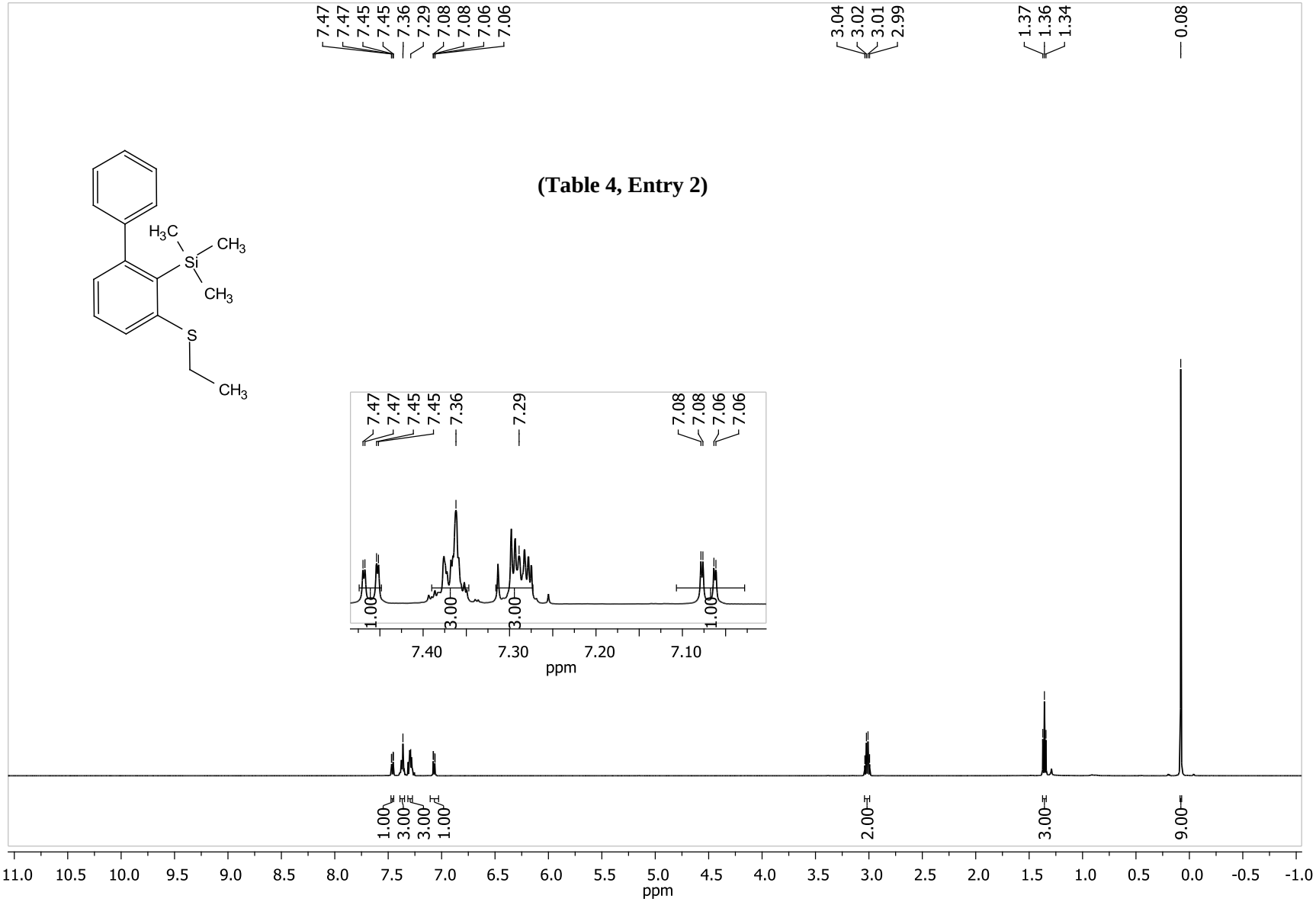
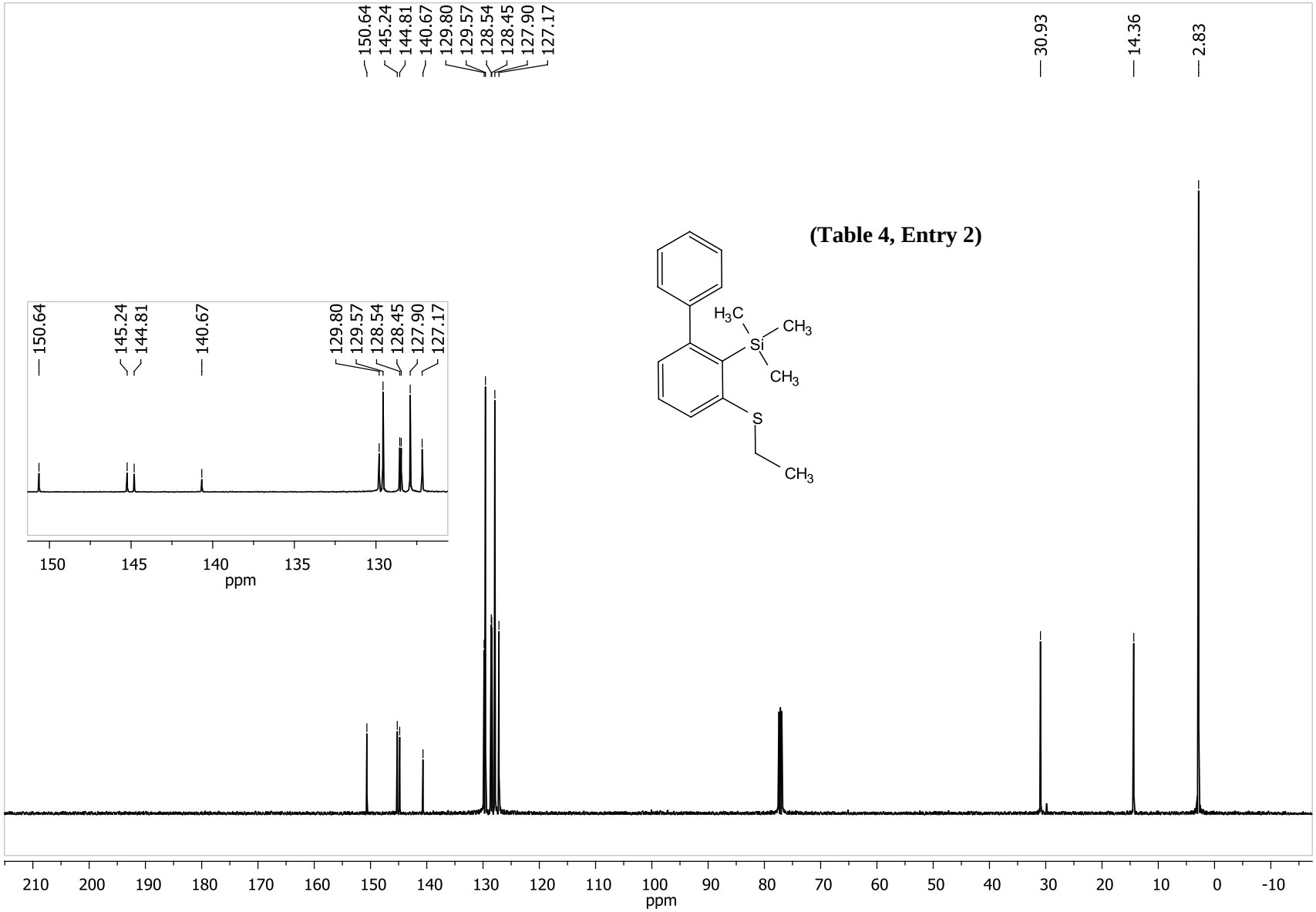


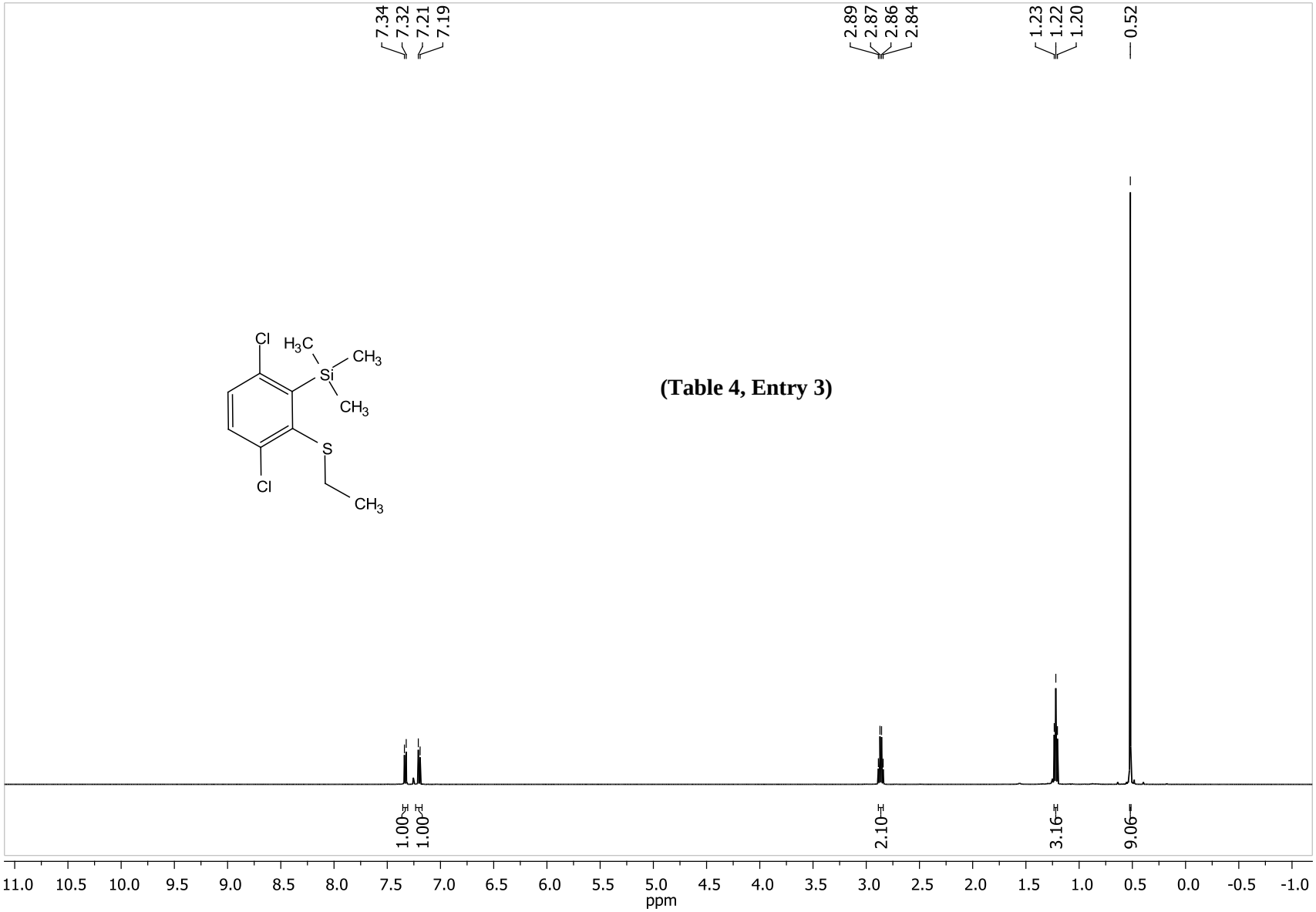
(Table 4, Entry 1)

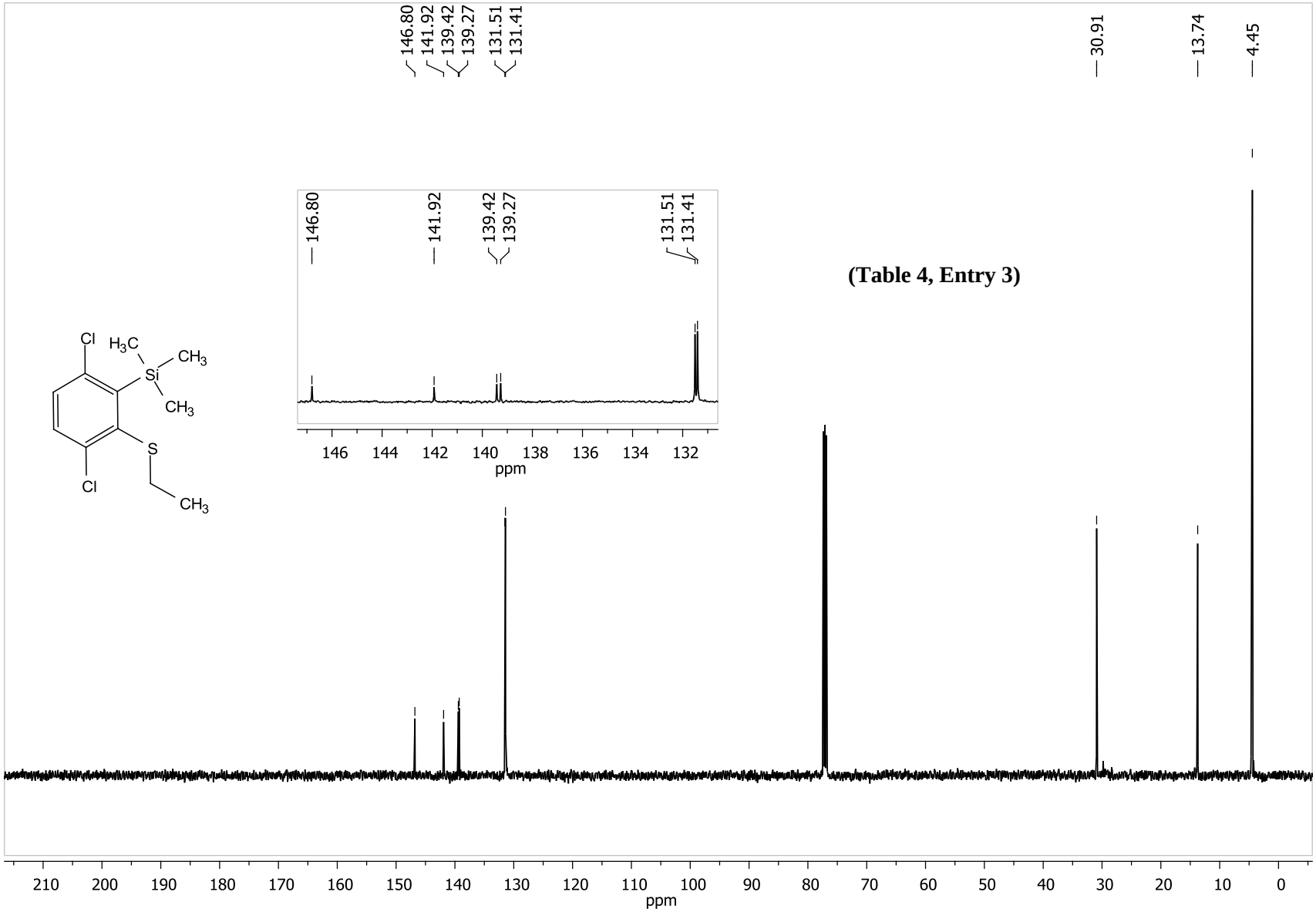


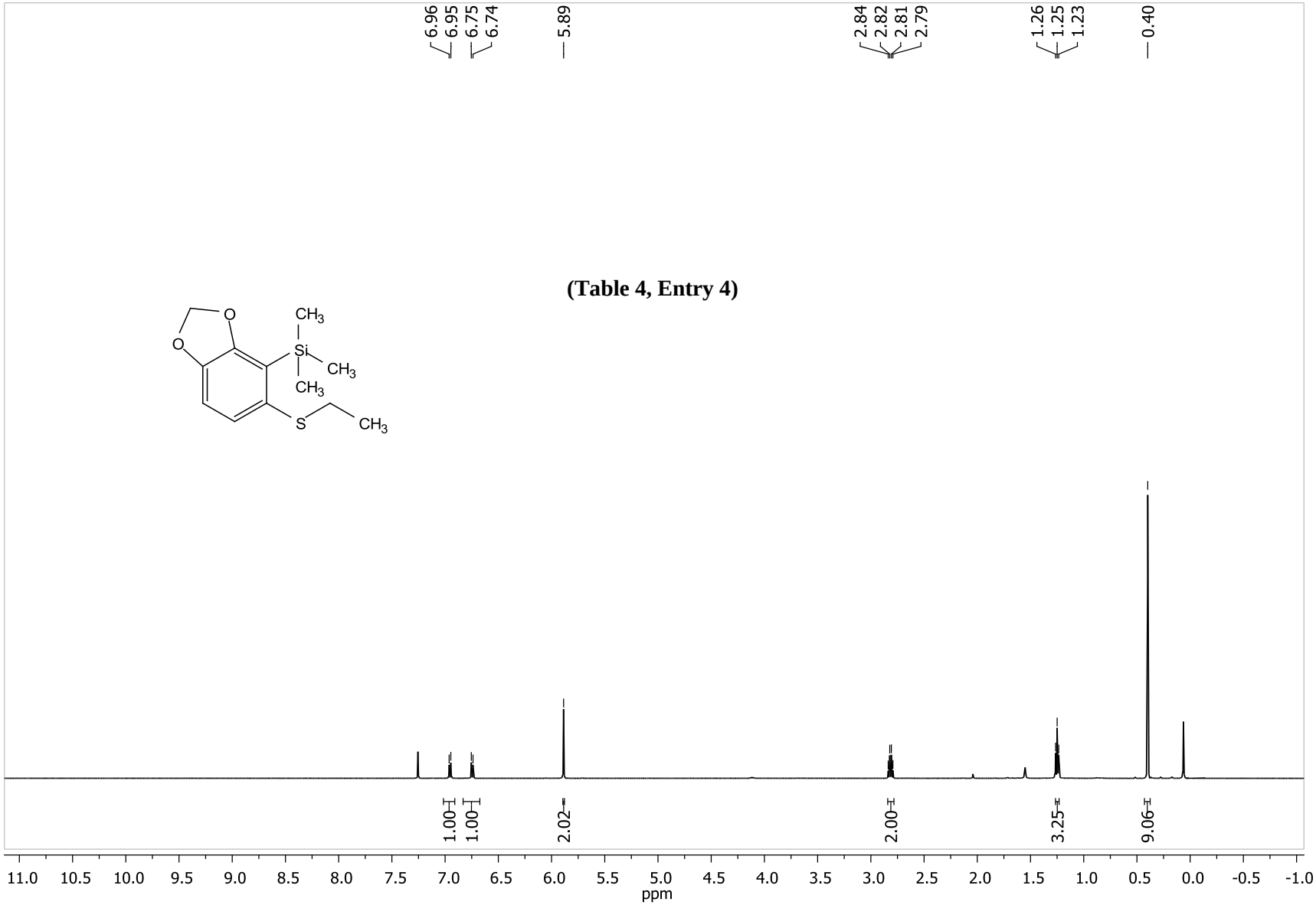


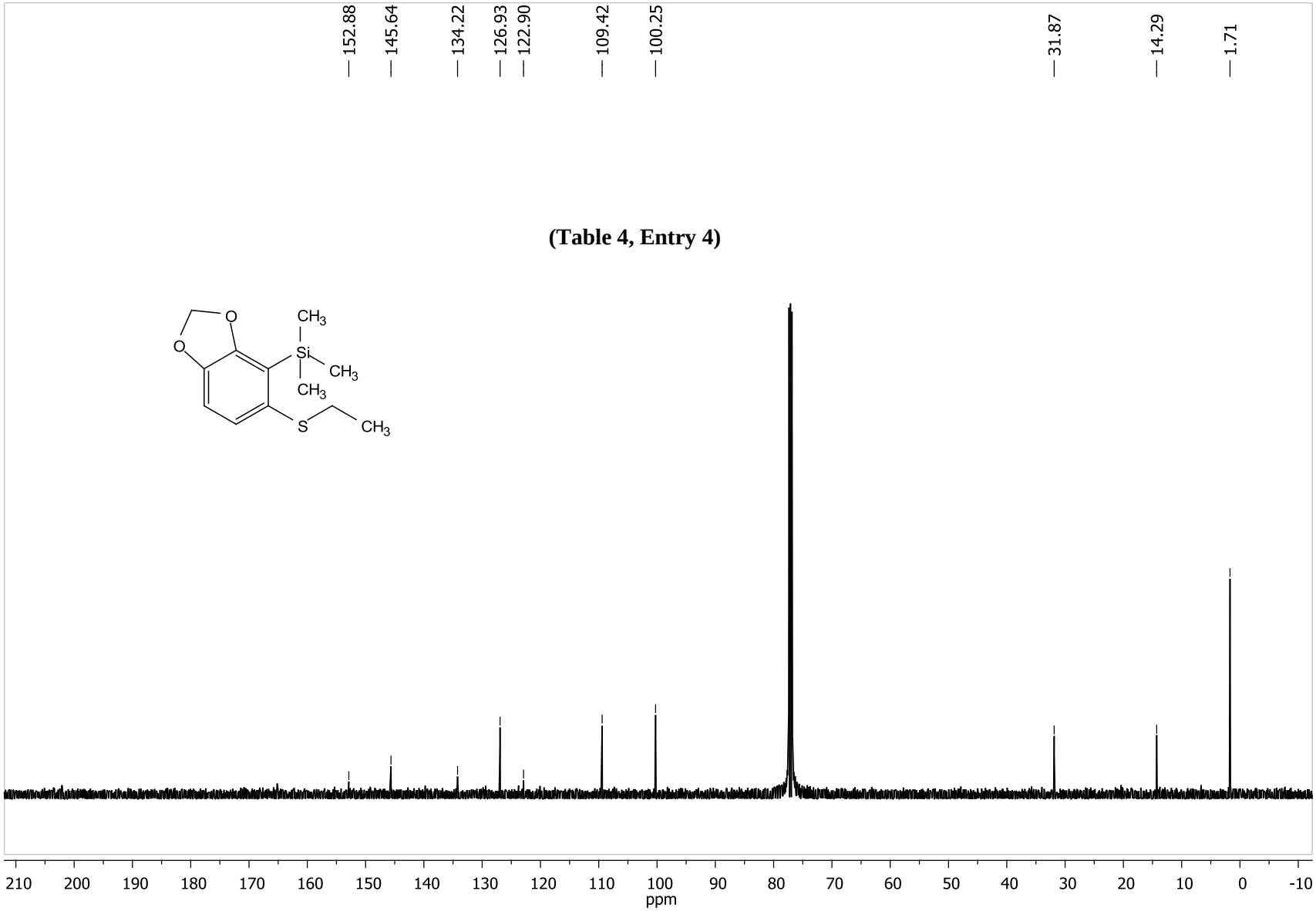
(Table 4, Entry 2)


150.64
145.24
144.81
140.67
129.80
129.57
128.54
128.45
127.90
127.17
30.93
14.36
2.83
(Table 4, Entry 2)
H3C
CH3
Si
CH3
S
CH3
ppm
ppm


7.34
7.32
7.21
7.19
2.89
2.87
2.86
2.84
1.23
1.22
1.20
0.52
Cl
H3C
CH3
Si
CH3
S
Cl
CH3
(Table 4, Entry 3)
1.00
1.00
2.10
3.16
9.06
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


146.80
141.92
139.42
139.27
131.51
131.41
30.91
13.74
4.45
(Table 4, Entry 3)
Cl
H3C
CH3
Si
CH3
S
Cl
CH3
ppm
ppm


6.96
6.95
6.75
6.74
5.89
2.84
2.82
2.81
2.79
1.26
1.25
1.23
0.40
(Table 4, Entry 4)
O
O
CH3
Si
CH3
CH3
S
CH3
1.00
1.00
2.02
2.00
3.25
9.06
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



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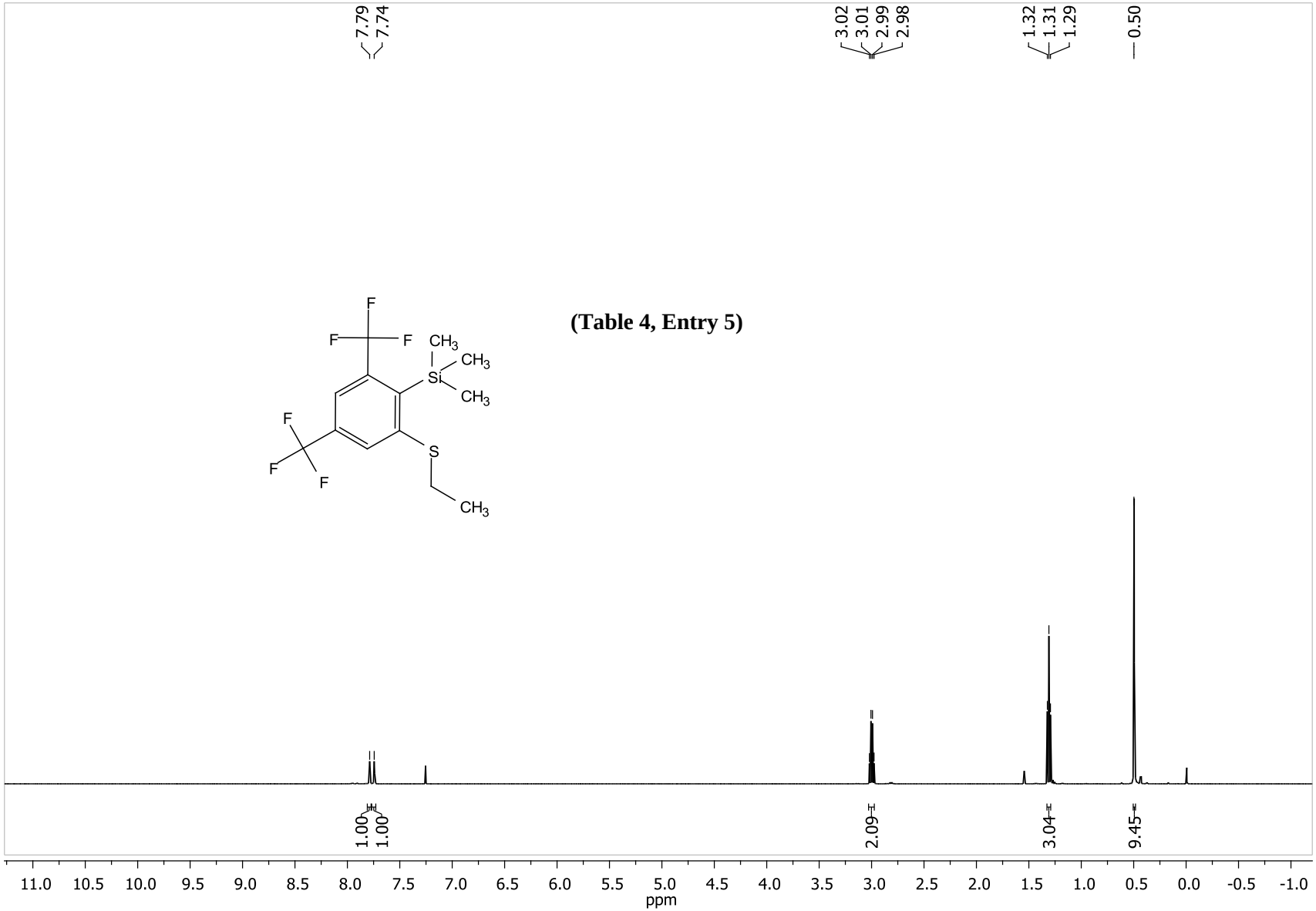

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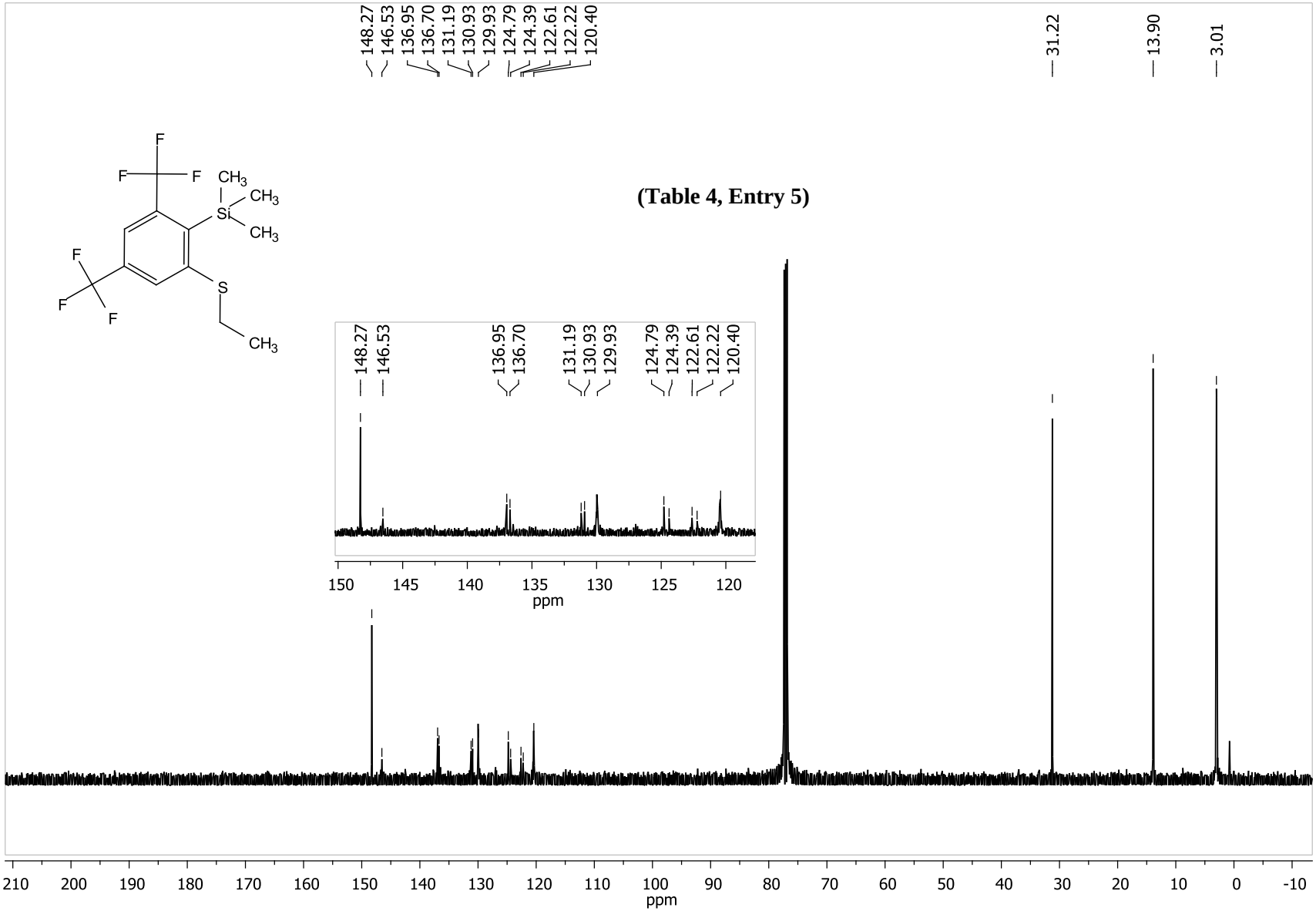
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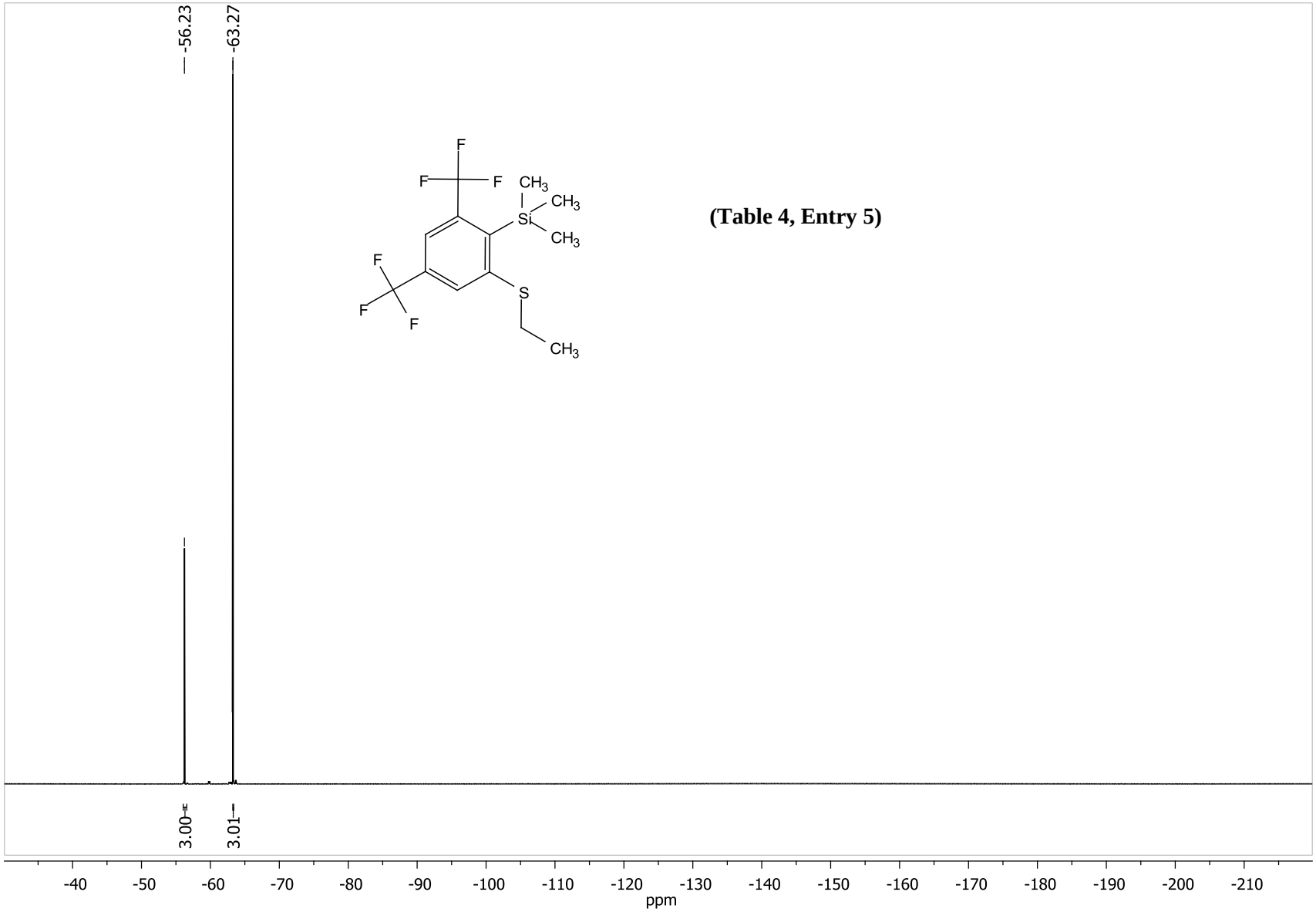
146.53
136.95
136.70
131.19
130.93
129.93
124.79
124.39
122.61
122.22
120.40
31.22
13.90
3.01
F
F
F
CH3
CH3
Si
CH3
F
F
F
S
CH3
(Table 4, Entry 5)
150
145
140
135
130
125
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



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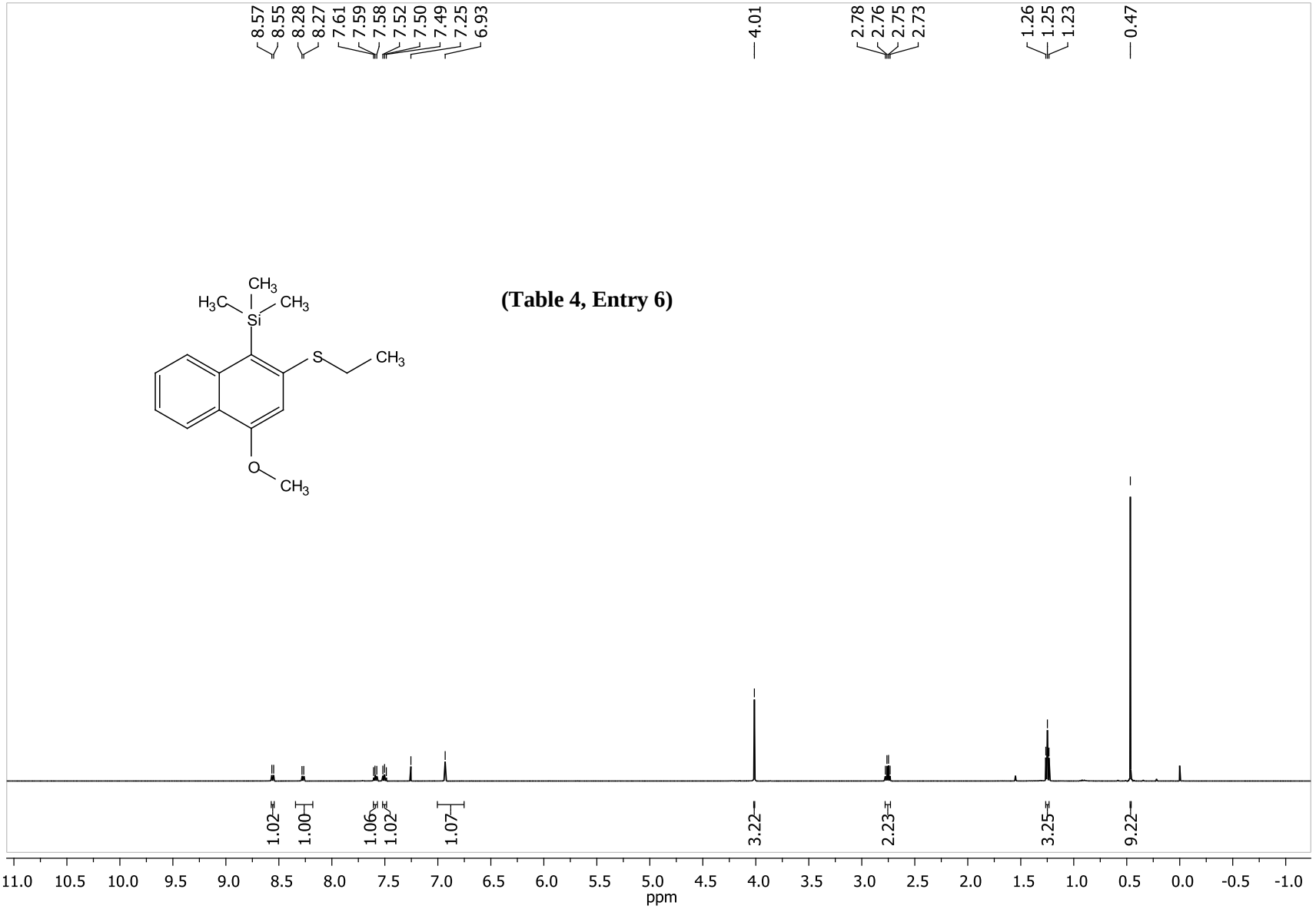

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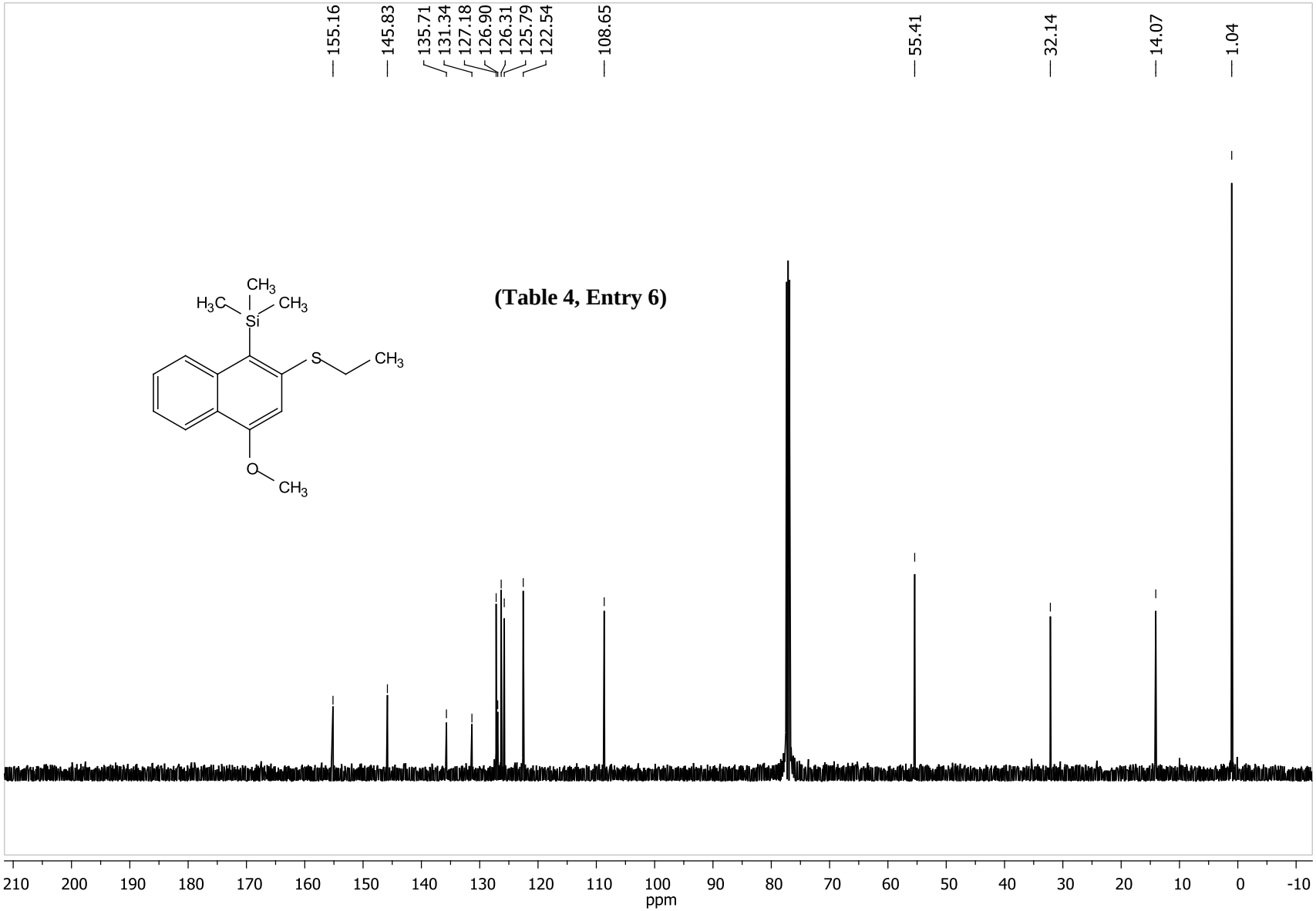
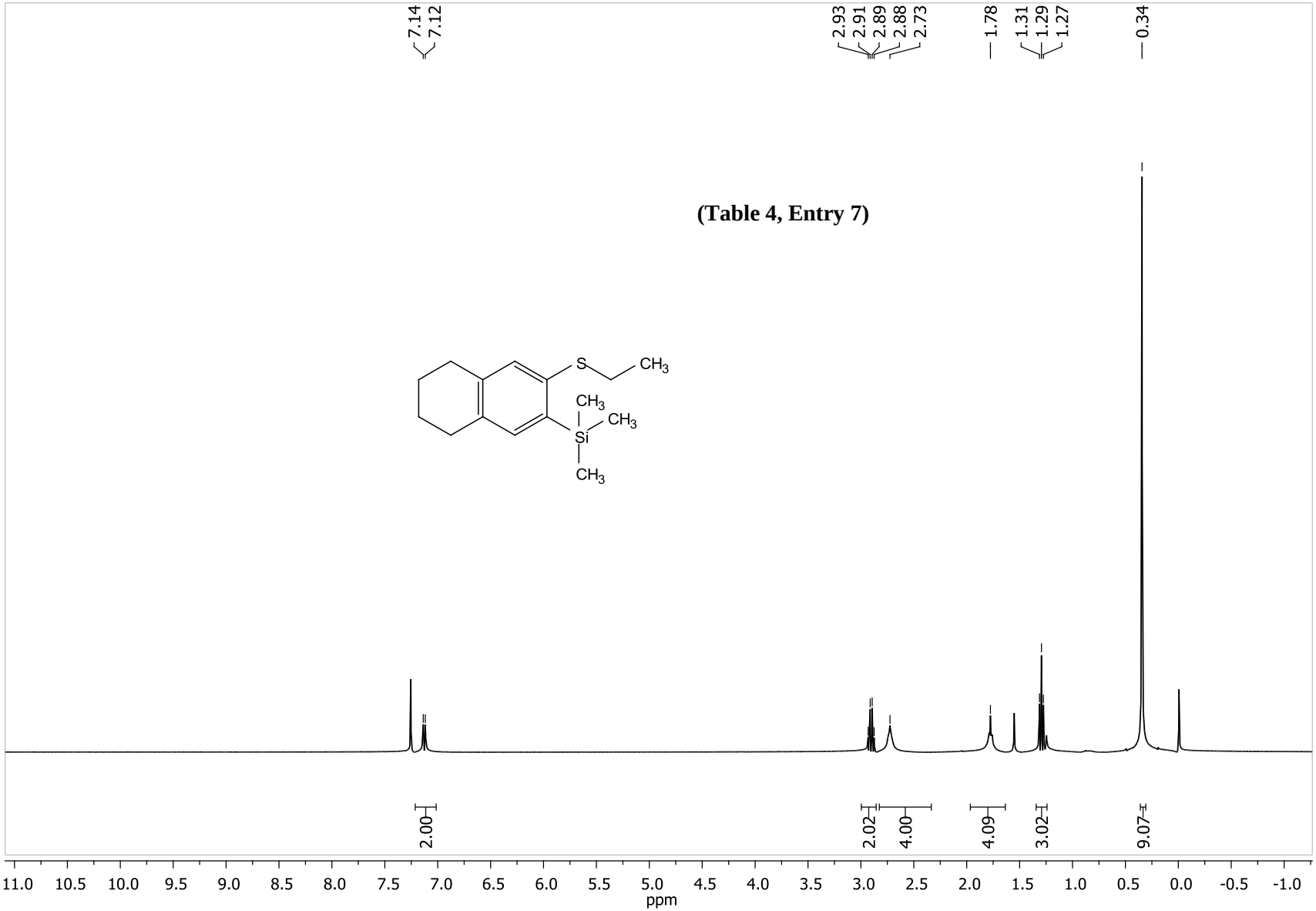
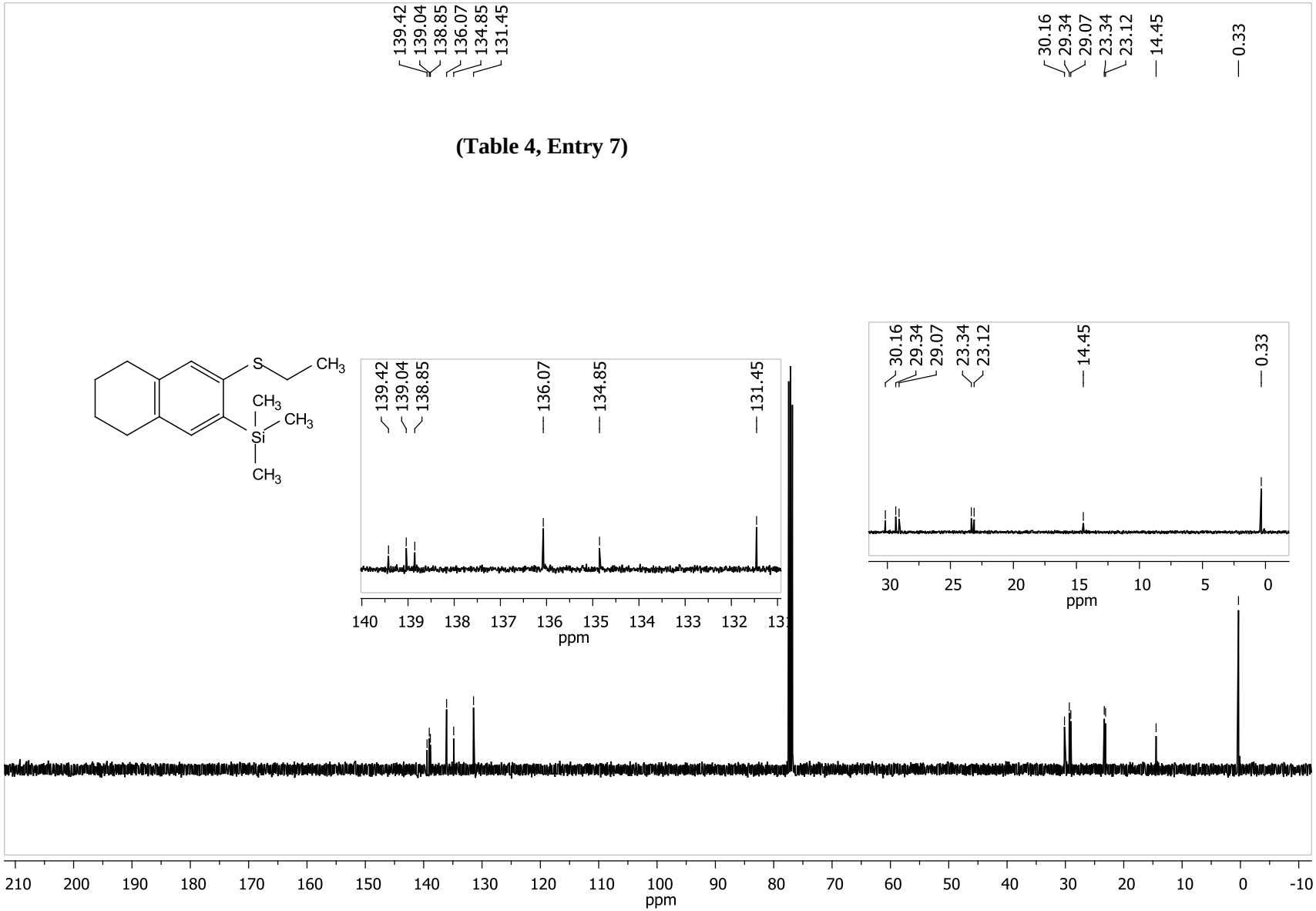
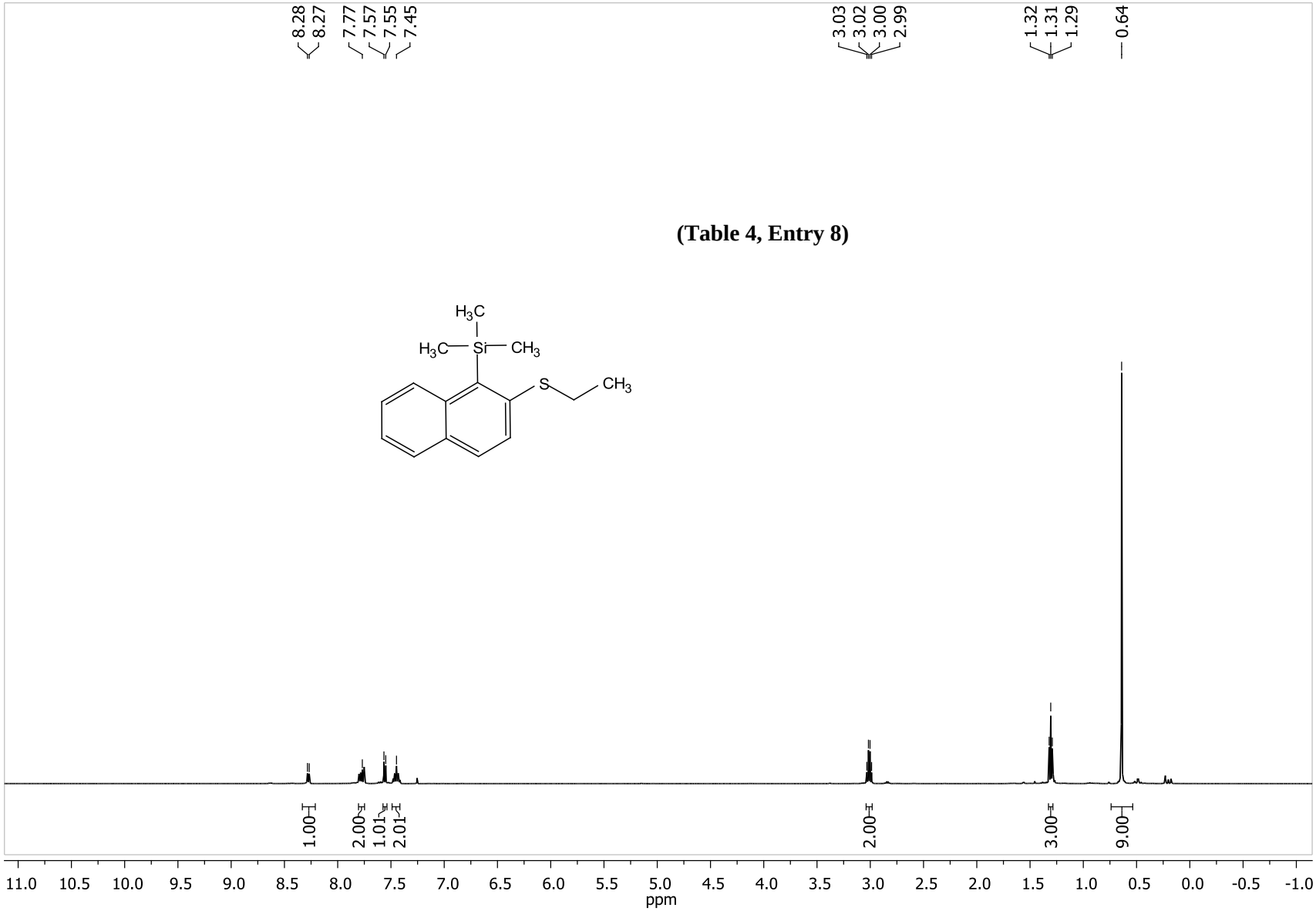

155.16
145.83
135.71
131.34
127.18
126.90
126.31
125.79
122.54
108.65
55.41
32.14
14.07
1.04
CH3
H3C
CH3
Si
S
CH3
O
CH3
(Table 4, Entry 6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

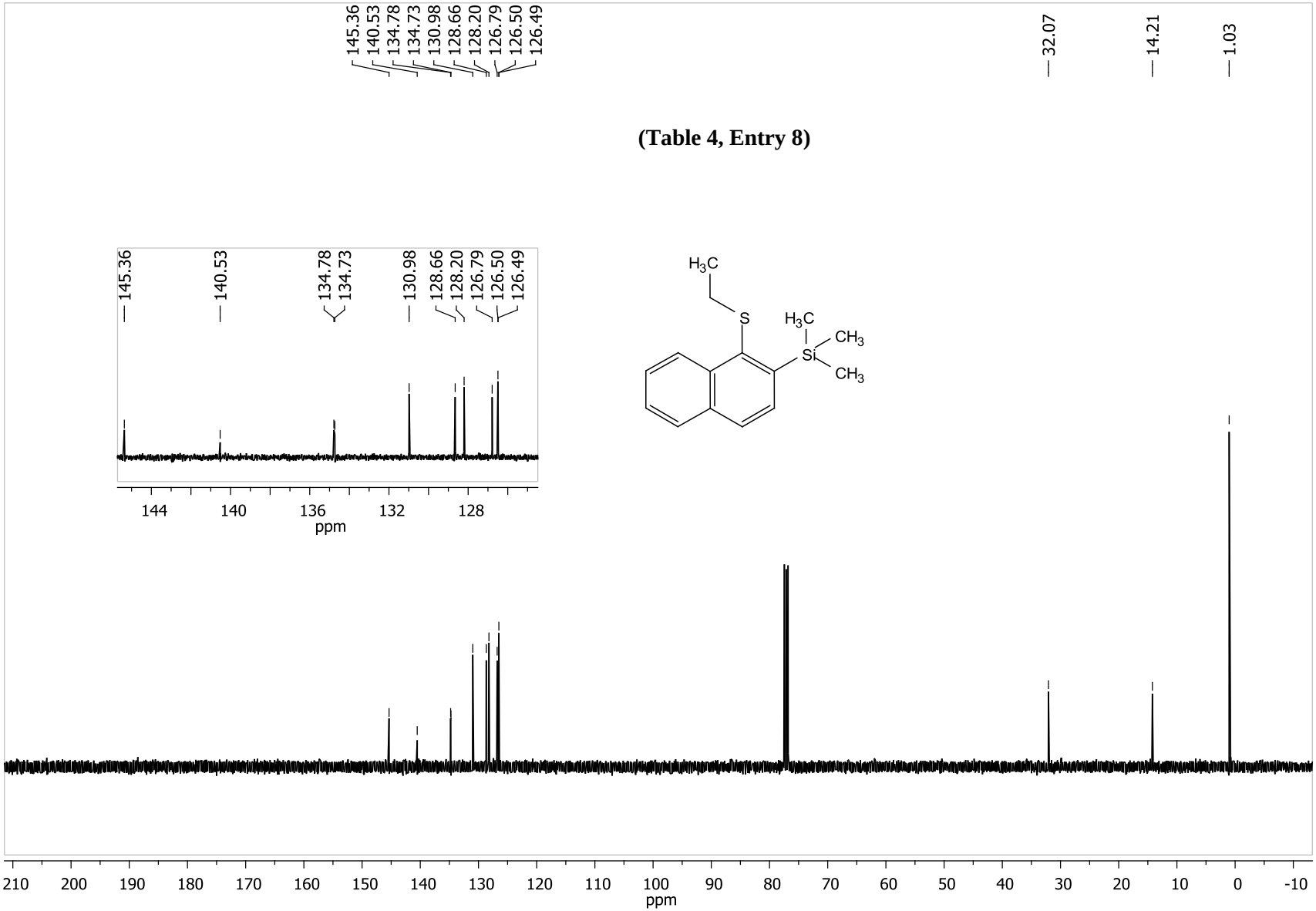

7.14
7.12
2.93
2.91
2.89
2.88
2.73
1.78
1.31
1.29
1.27
0.34
(Table 4, Entry 7)
S
CH3
CH3
CH3
Si
CH3
2.00
2.02
4.00
4.09
3.02
9.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

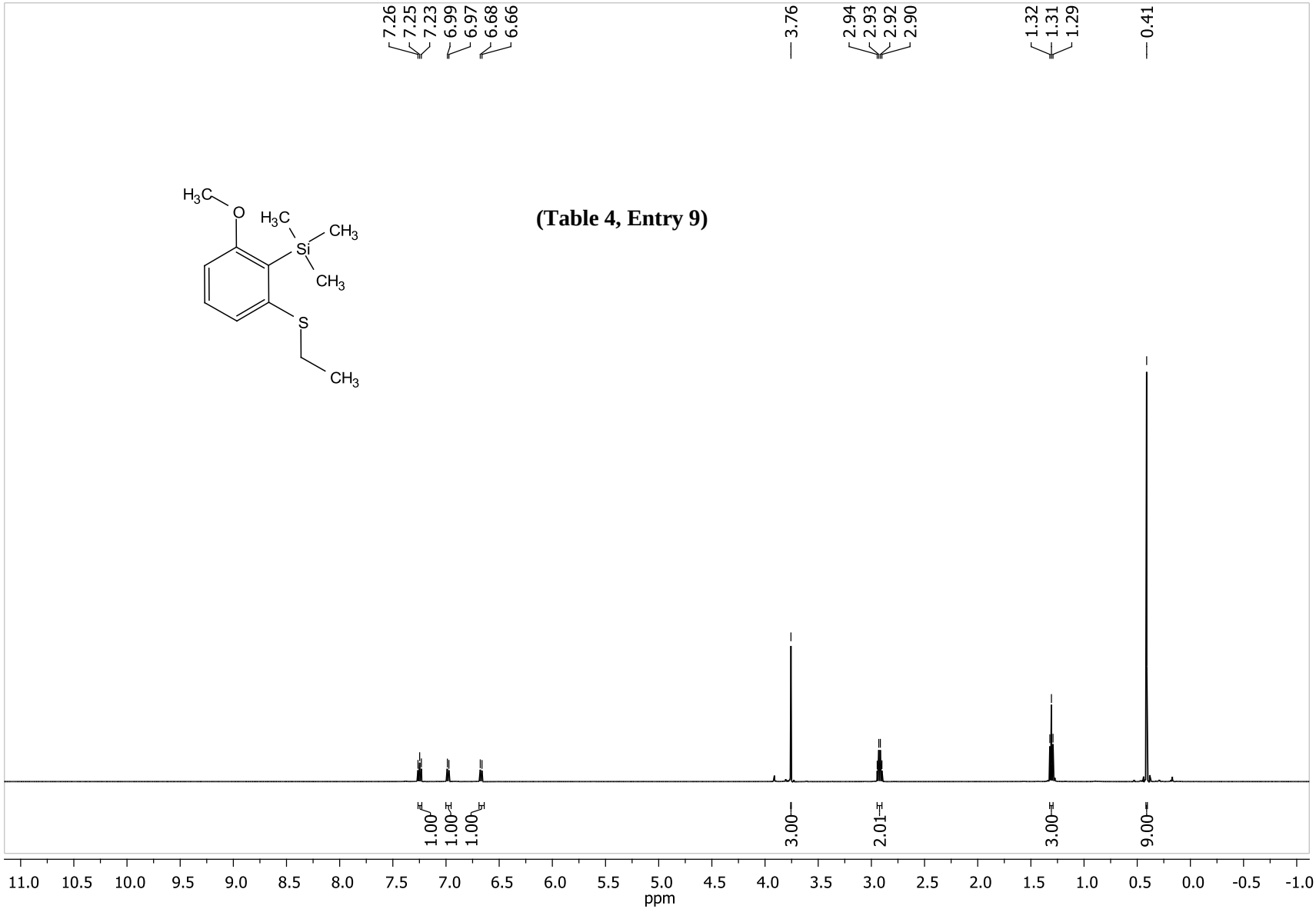


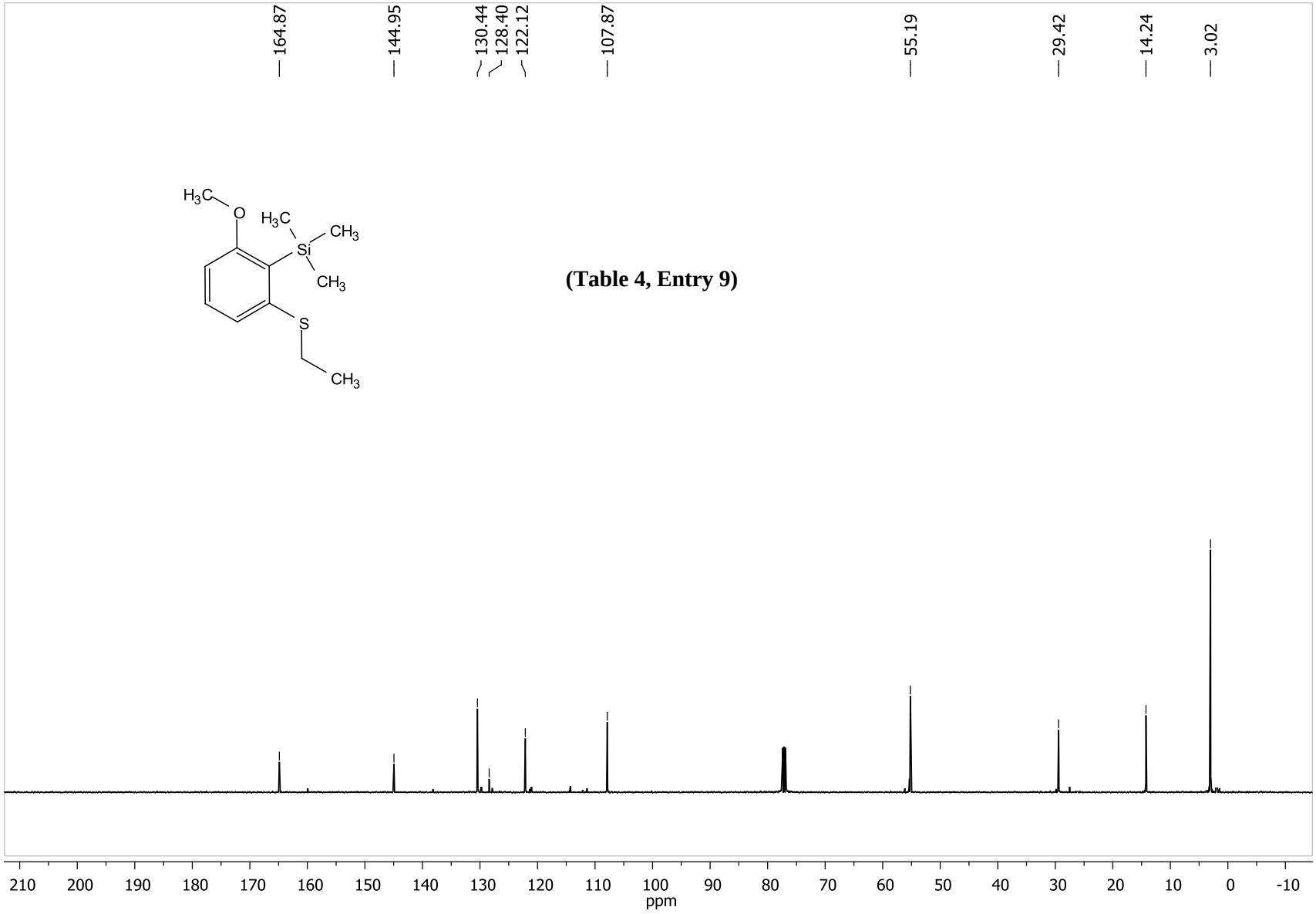
(Table 4, Entry 7)

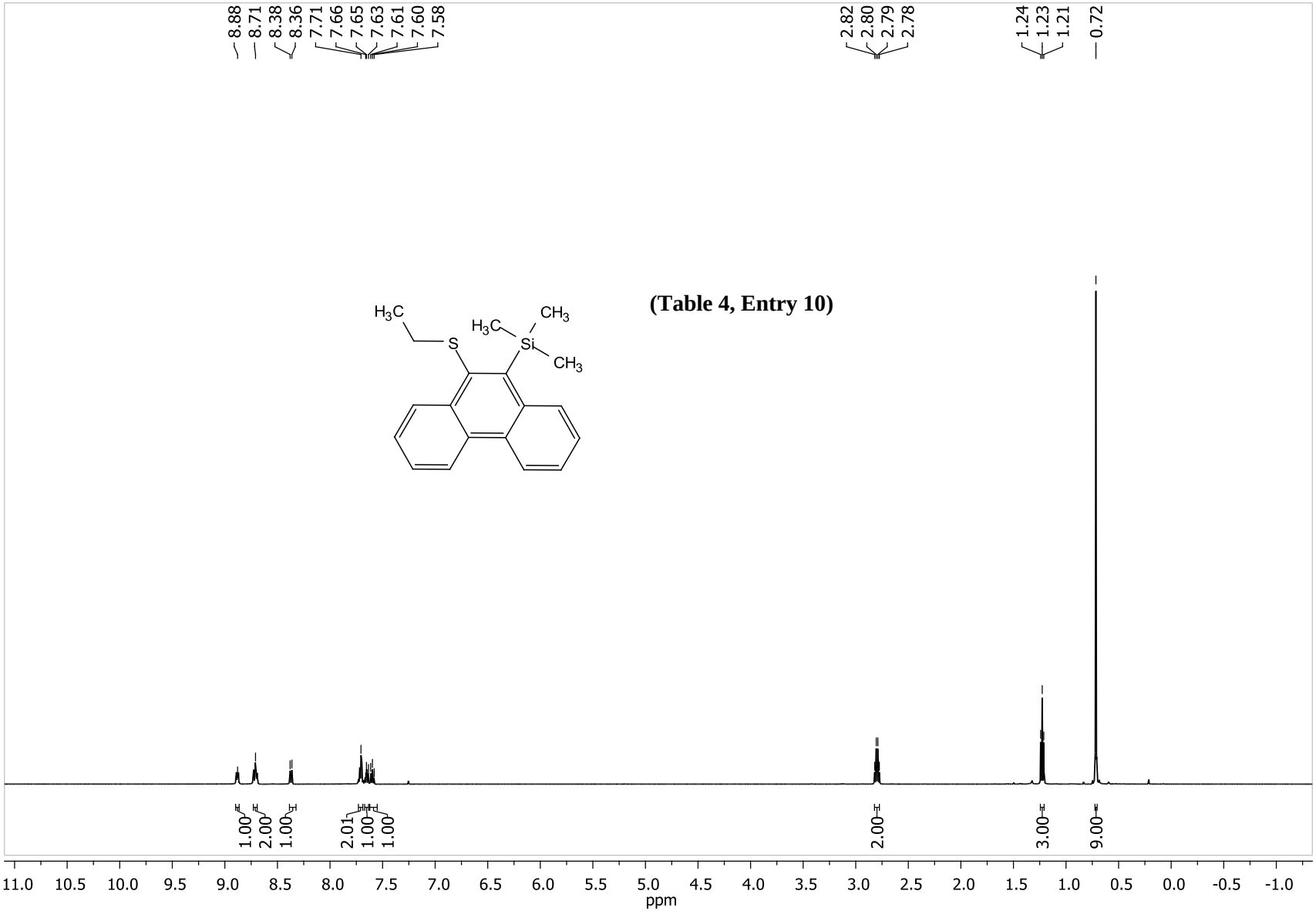
(Table 4, Entry 8)




145.36
140.53
134.78
134.73
130.98
128.66
128.20
126.79
126.50
126.49
32.07
14.21
1.03
(Table 4, Entry 8)
H3C
S
H3C
CH3
Si
CH3
144
140
136
132
128
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

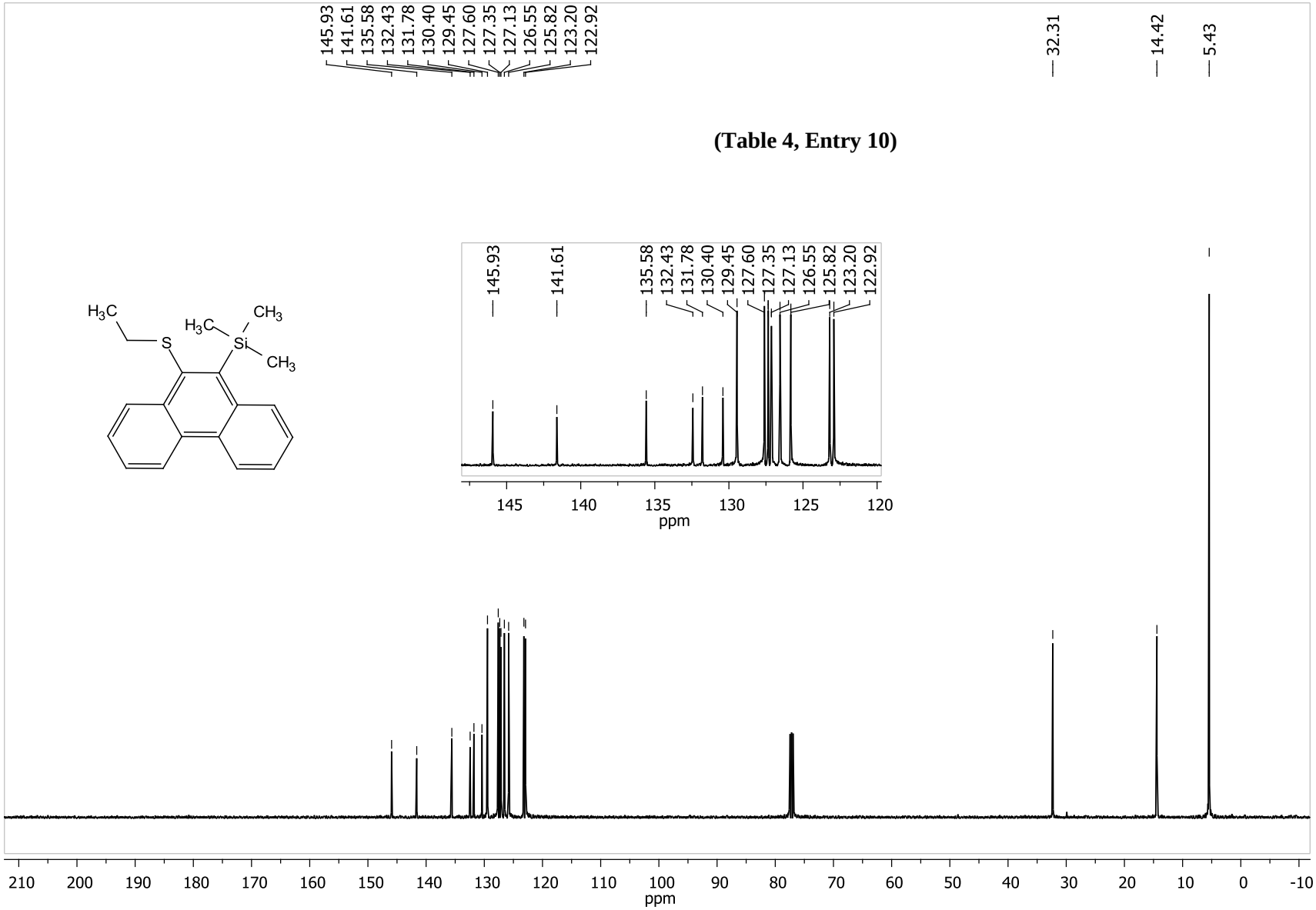

7.26
7.25
7.23
6.99
6.97
6.68
6.66
3.76
2.94
2.93
2.92
2.90
1.32
1.31
1.29
0.41
H3C
O
H3C
CH3
Si
CH3
S
CH3
(Table 4, Entry 9)
1.00
1.00
1.00
3.00
2.01
3.00
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

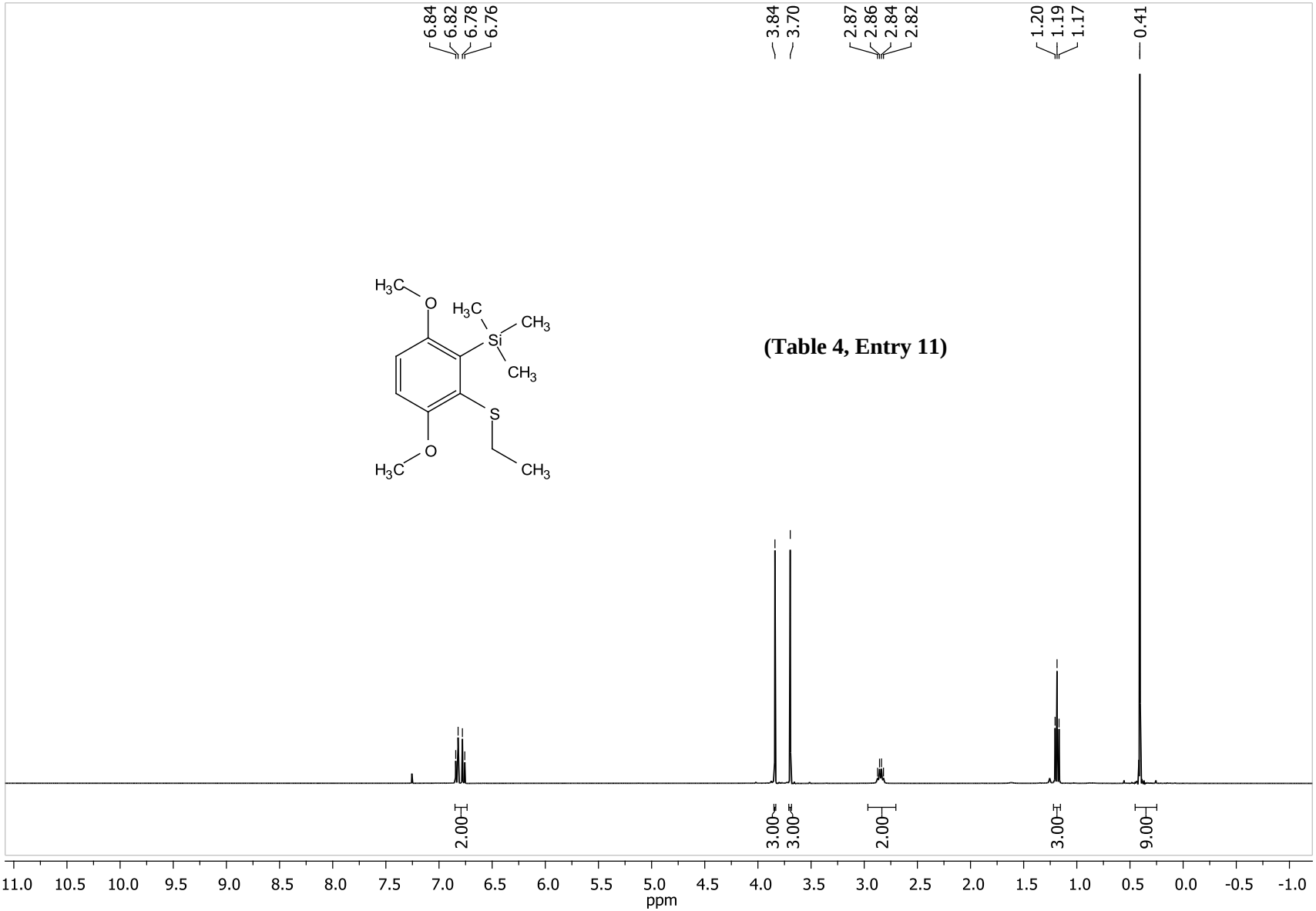

164.87
144.95
130.44
128.40
122.12
107.87
55.19
29.42
14.24
3.02
H3C
O
H3C
CH3
Si
CH3
S
CH3
(Table 4, Entry 9)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

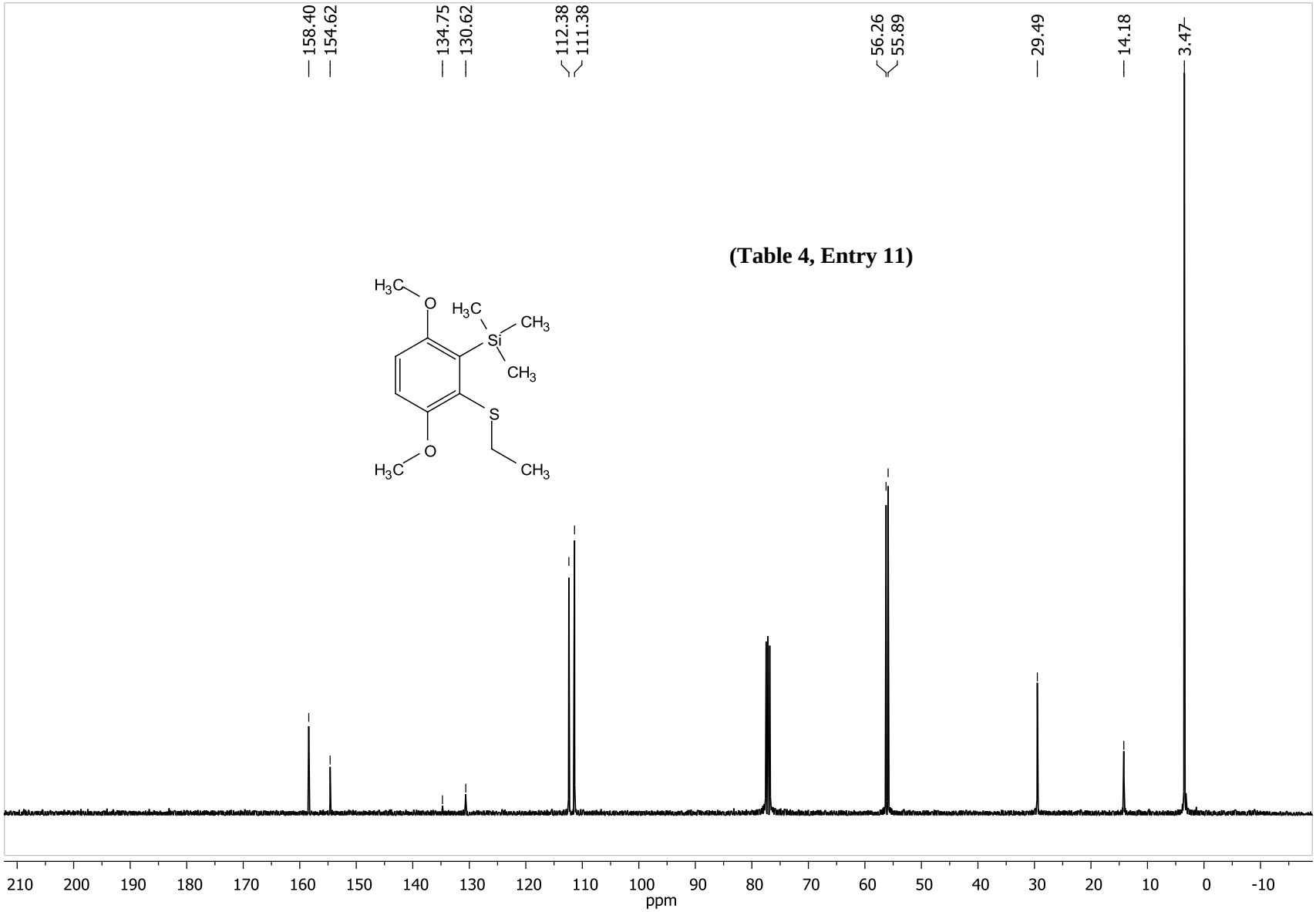


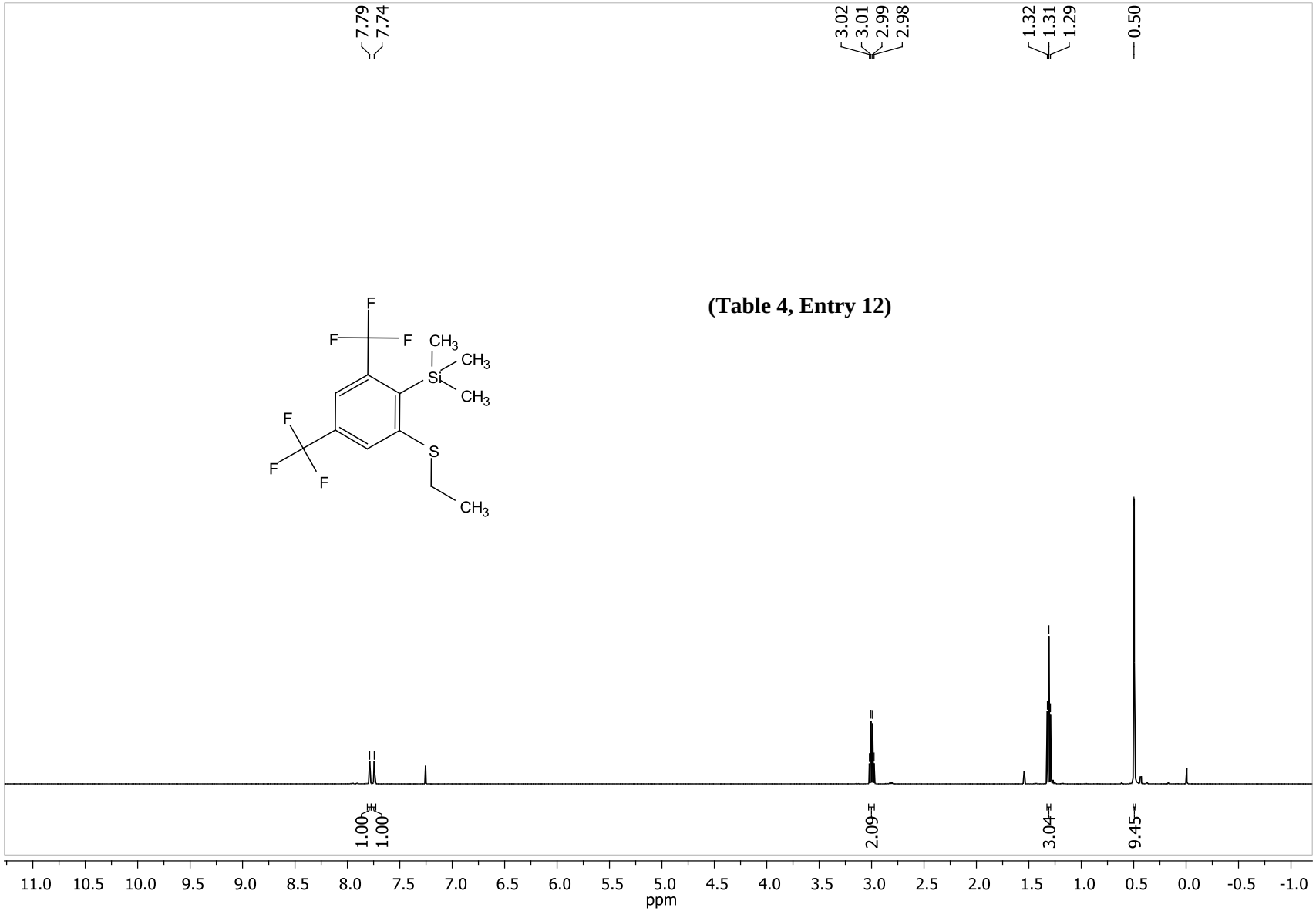
(Table 4, Entry 10)

(Table 4, Entry 10)

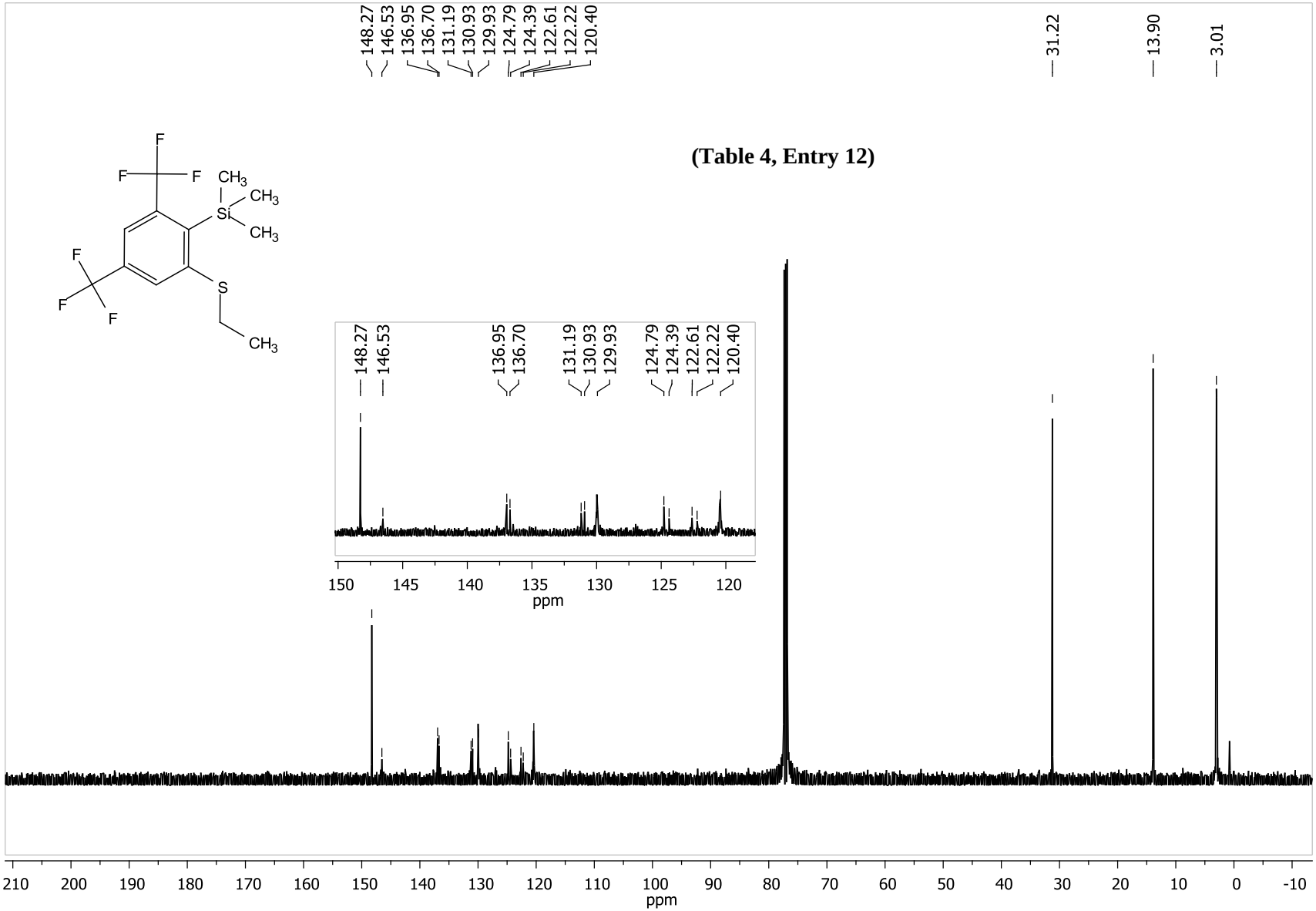


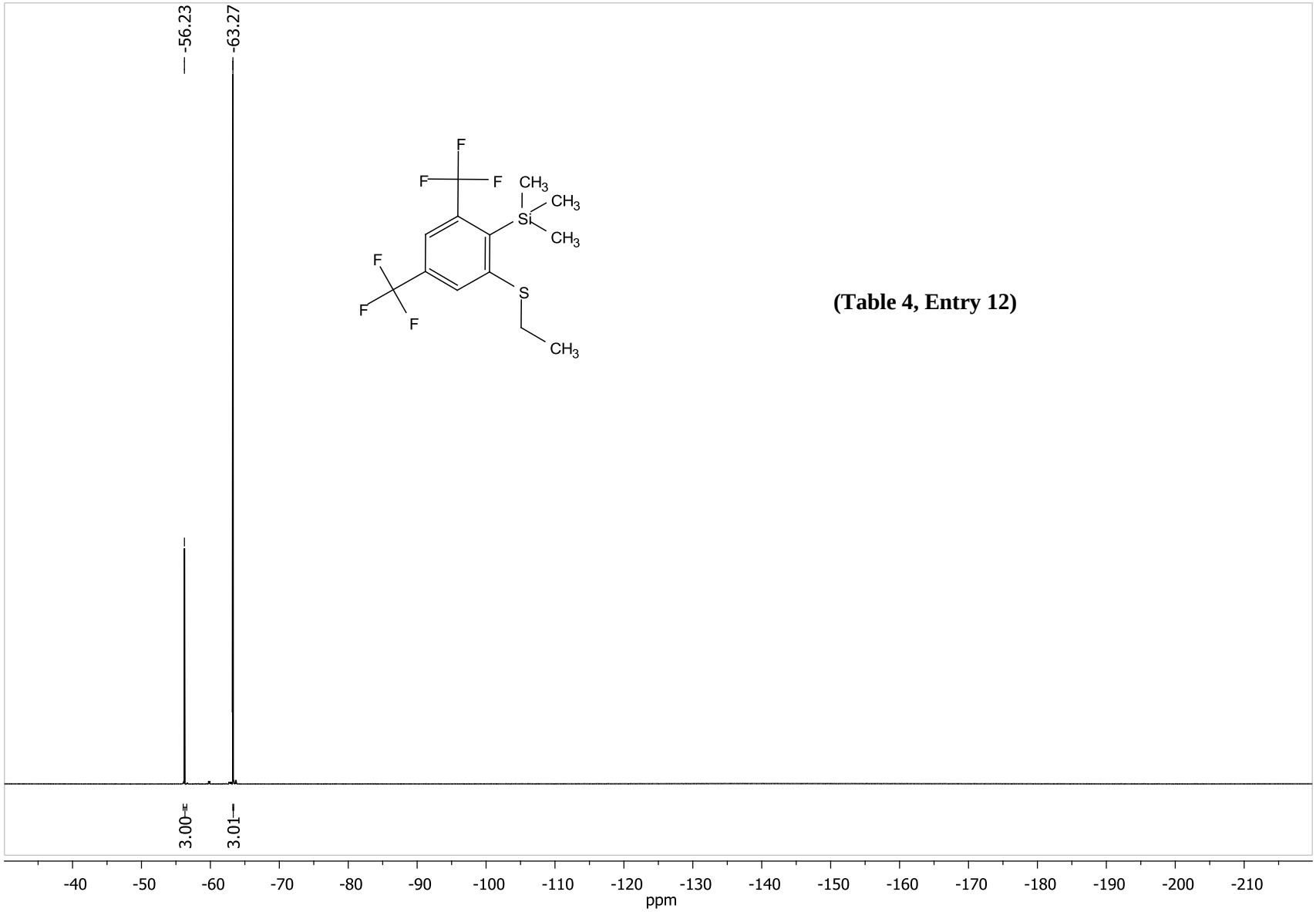

6.84
6.82
6.78
6.76
3.84
3.70
2.87
2.86
2.84
2.82
1.20
1.19
1.17
0.41
H3C
O
H3C
Si
CH3
CH3
S
O
H3C
CH3
(Table 4, Entry 11)
2.00
3.00
3.00
2.00
3.00
9.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


158.40
154.62
134.75
130.62
112.38
111.38
56.26
55.89
29.49
14.18
3.47
(Table 4, Entry 11)
H3C
O
H3C
Si
CH3
CH3
S
O
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

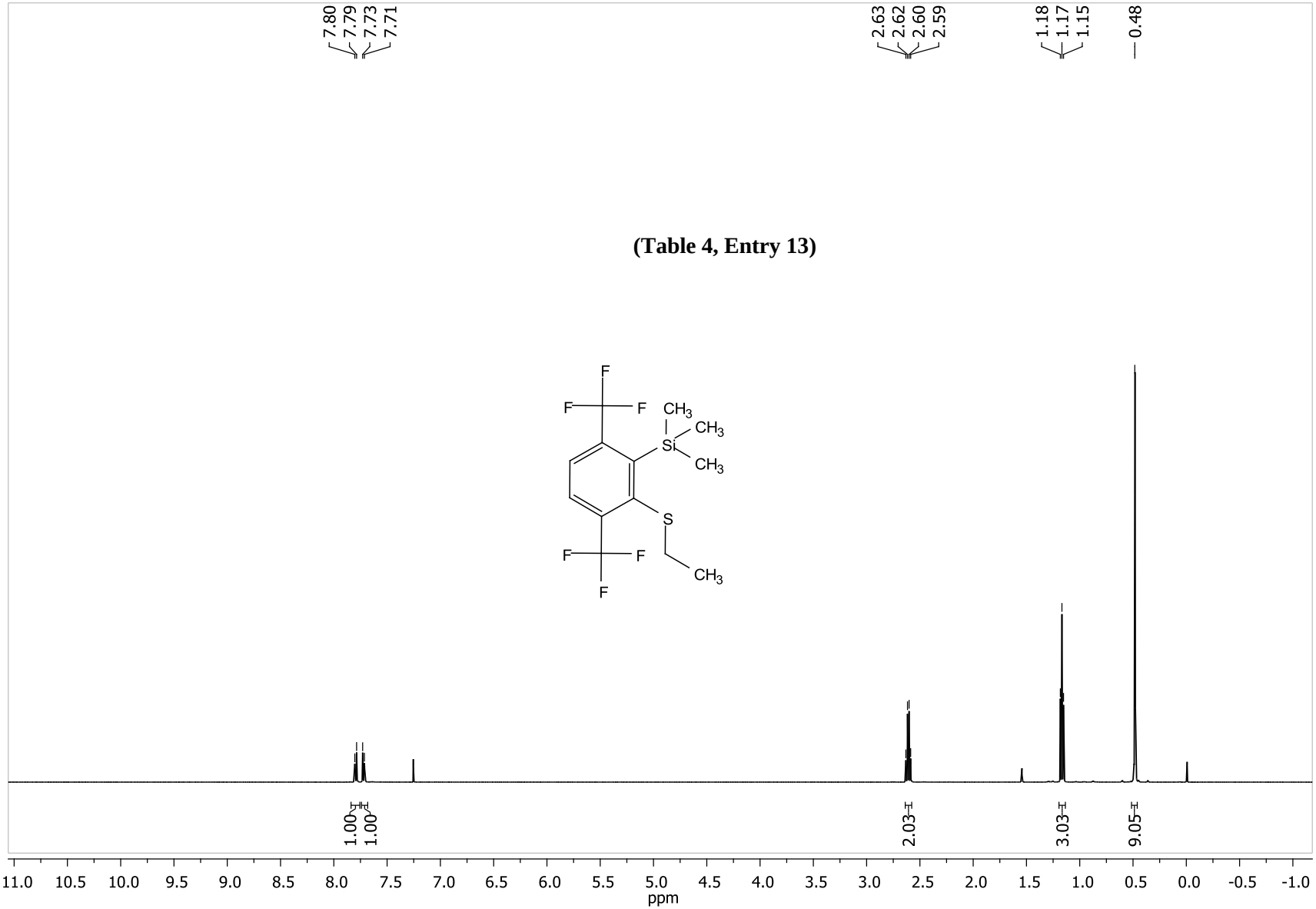


(Table 4, Entry 12)

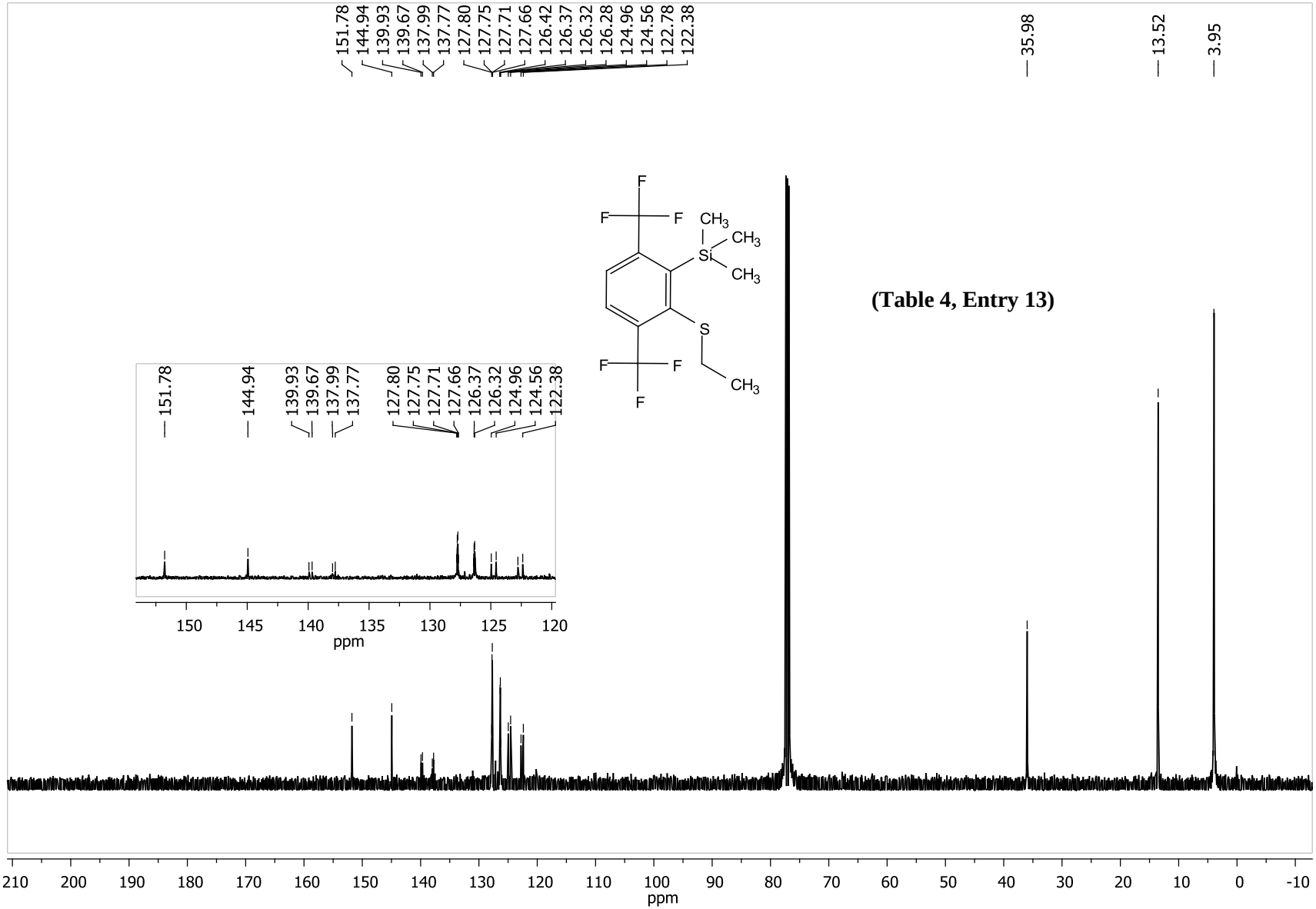

148.27
146.53
136.95
136.70
131.19
130.93
129.93
124.79
124.39
122.61
122.22
120.40
31.22
13.90
3.01
(Table 4, Entry 12)
F
F
F
CH3
CH3
Si
CH3
F
F
F
S
CH3
148.27
146.53
136.95
136.70
131.19
130.93
129.93
124.79
124.39
122.61
122.22
120.40
150
145
140
135
130
125
120
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

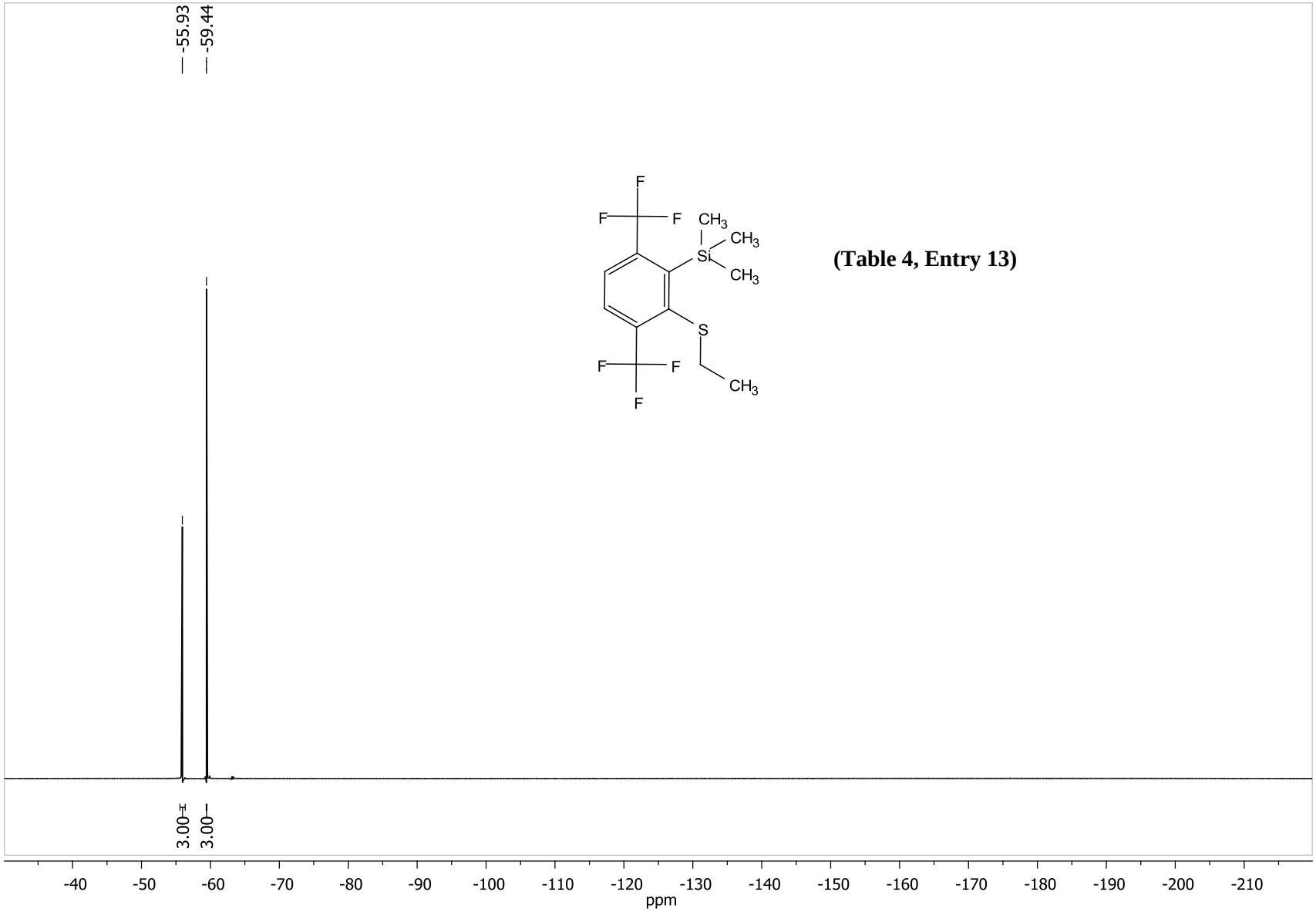


(Table 4, Entry 12)

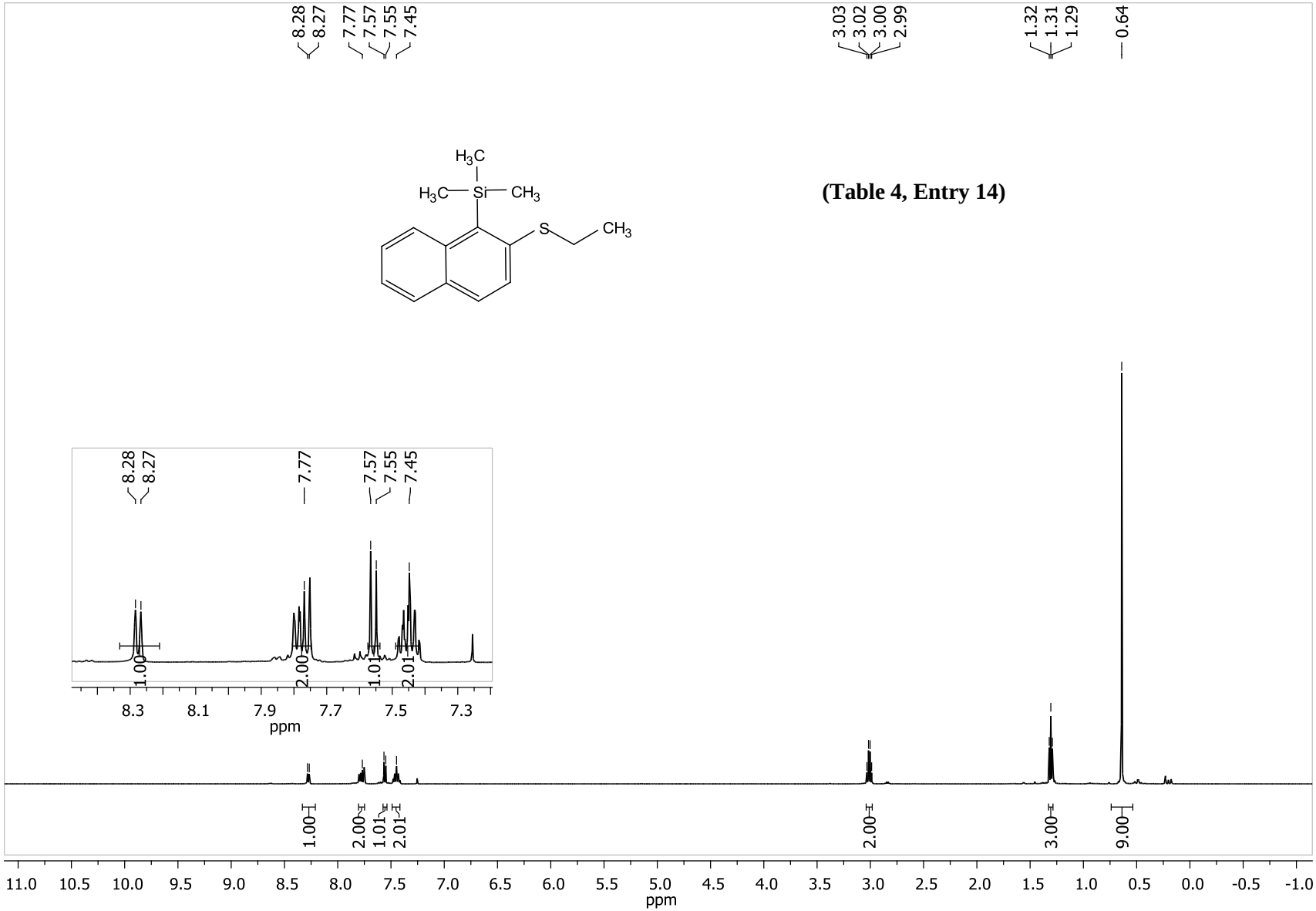


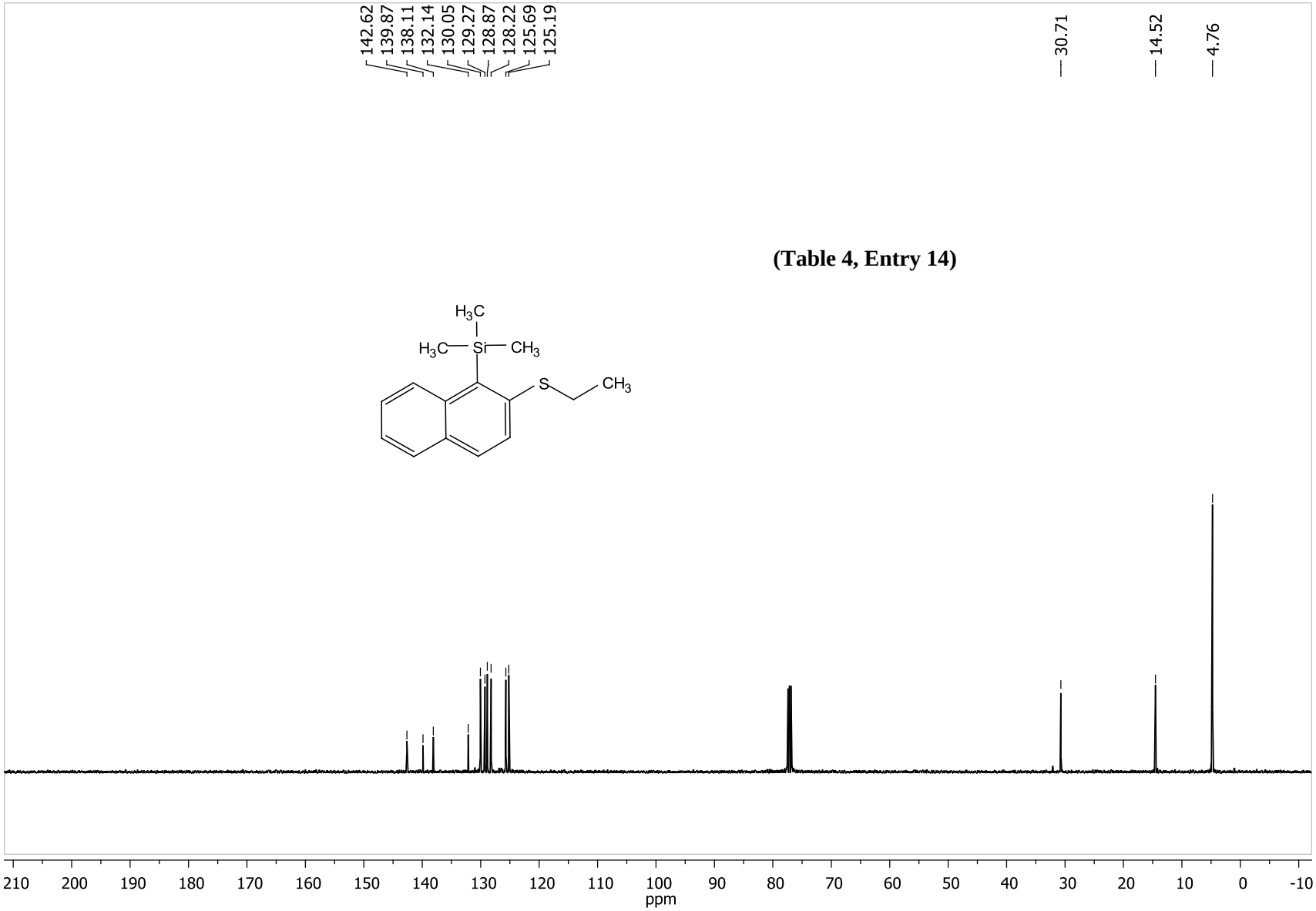
(Table 4, Entry 13)


151.78
144.94
139.93
139.67
137.99
137.77
127.80
127.75
127.71
127.66
126.42
126.37
126.32
126.28
124.96
124.56
122.78
122.38
35.98
13.52
3.95
F
F
F
CH3
CH3
Si
CH3
S
F
F
F
CH3
(Table 4, Entry 13)
150
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
-10
ppm



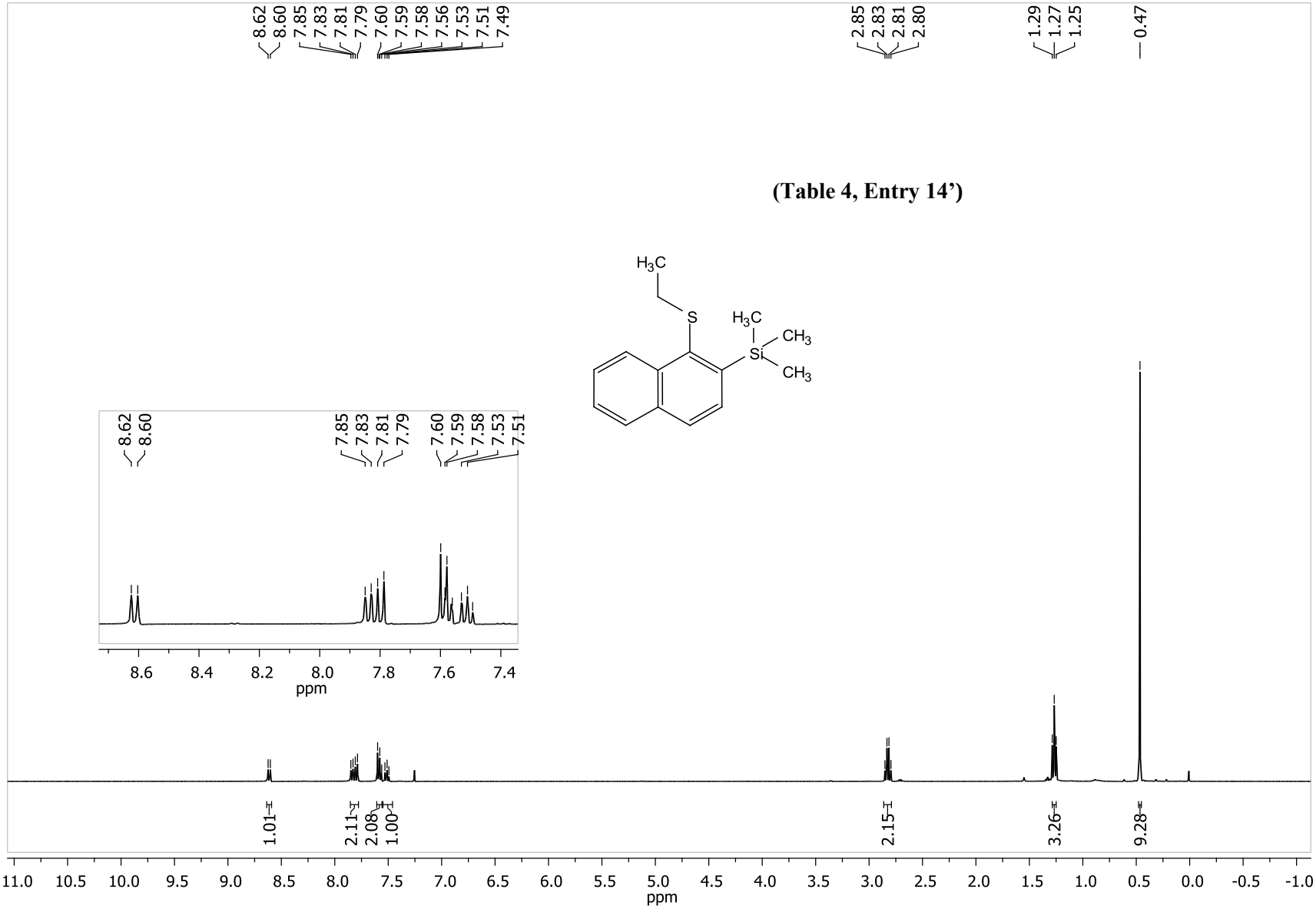
(Table 4, Entry 13)

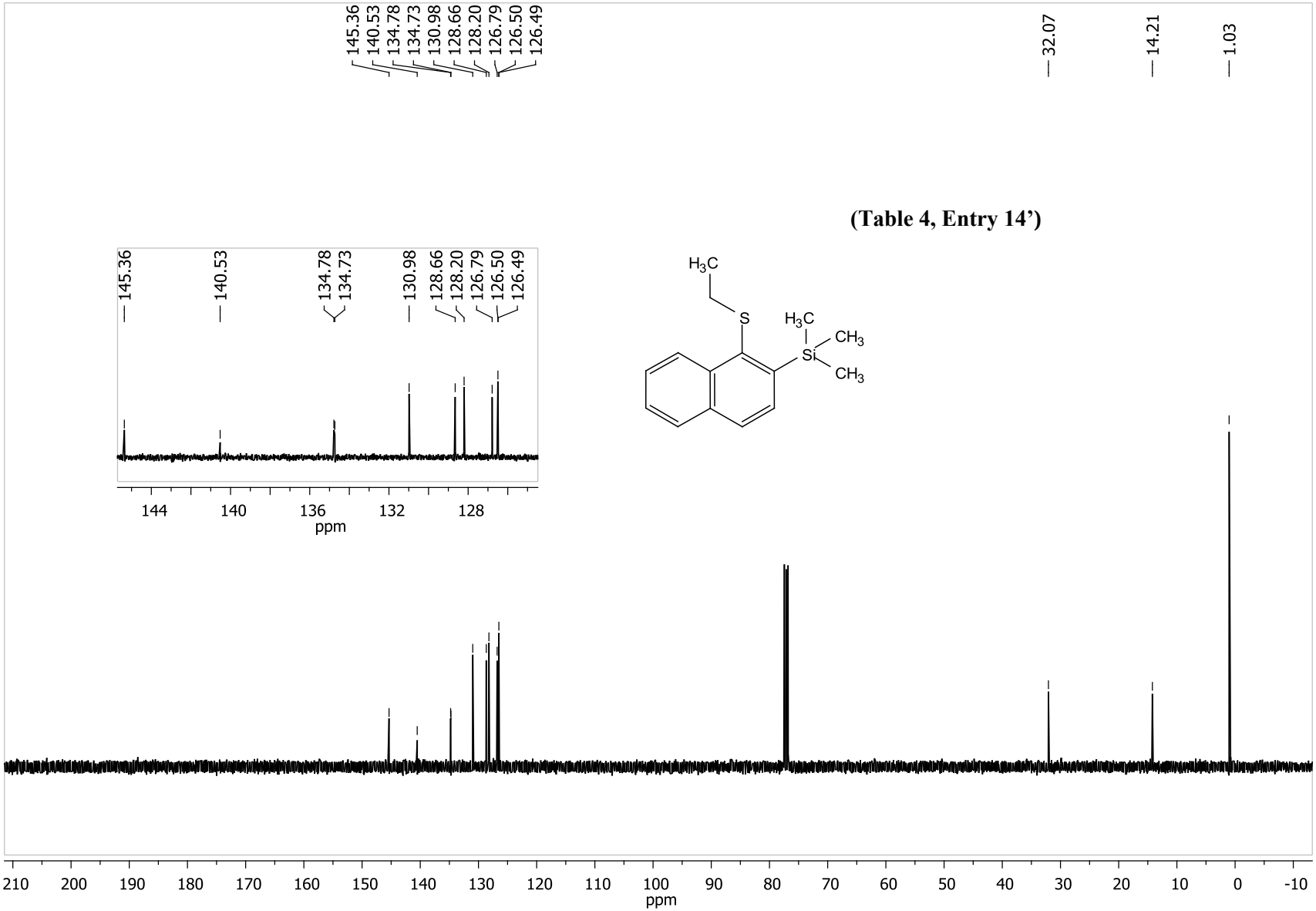

8.28
8.27
7.77
7.57
7.55
7.45
3.03
3.02
3.00
2.99
1.32
1.31
1.29
0.64
H3C
H3C Si CH3
S
CH3
(Table 4, Entry 14)
1.00
2.00
1.01
2.01
2.00
3.00
9.00
ppm



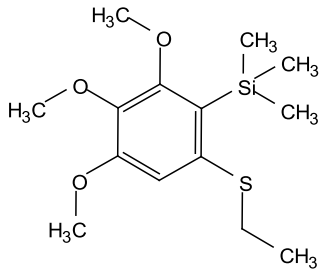
(Table 4, Entry 14)

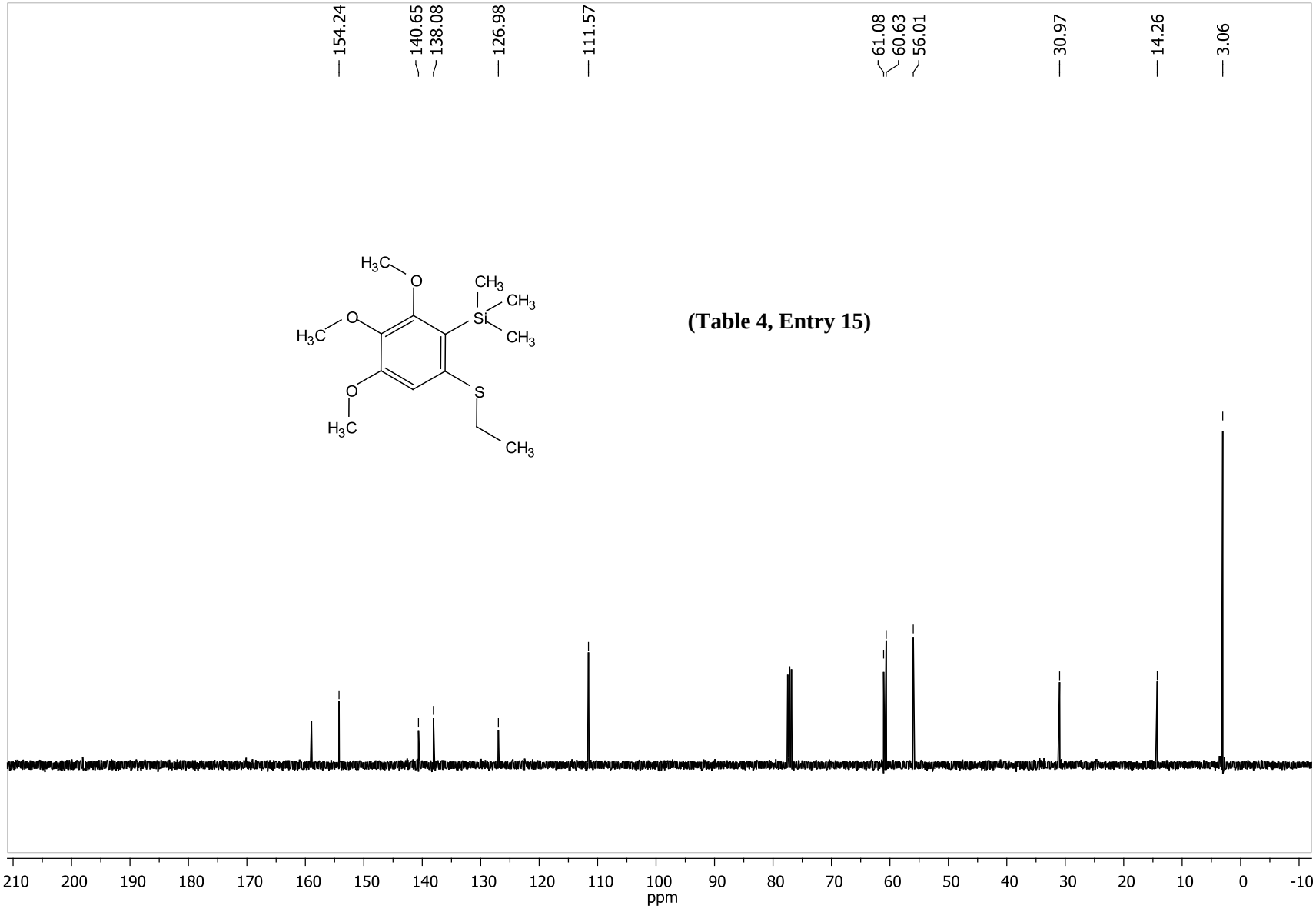
(Table 4, Entry 14')

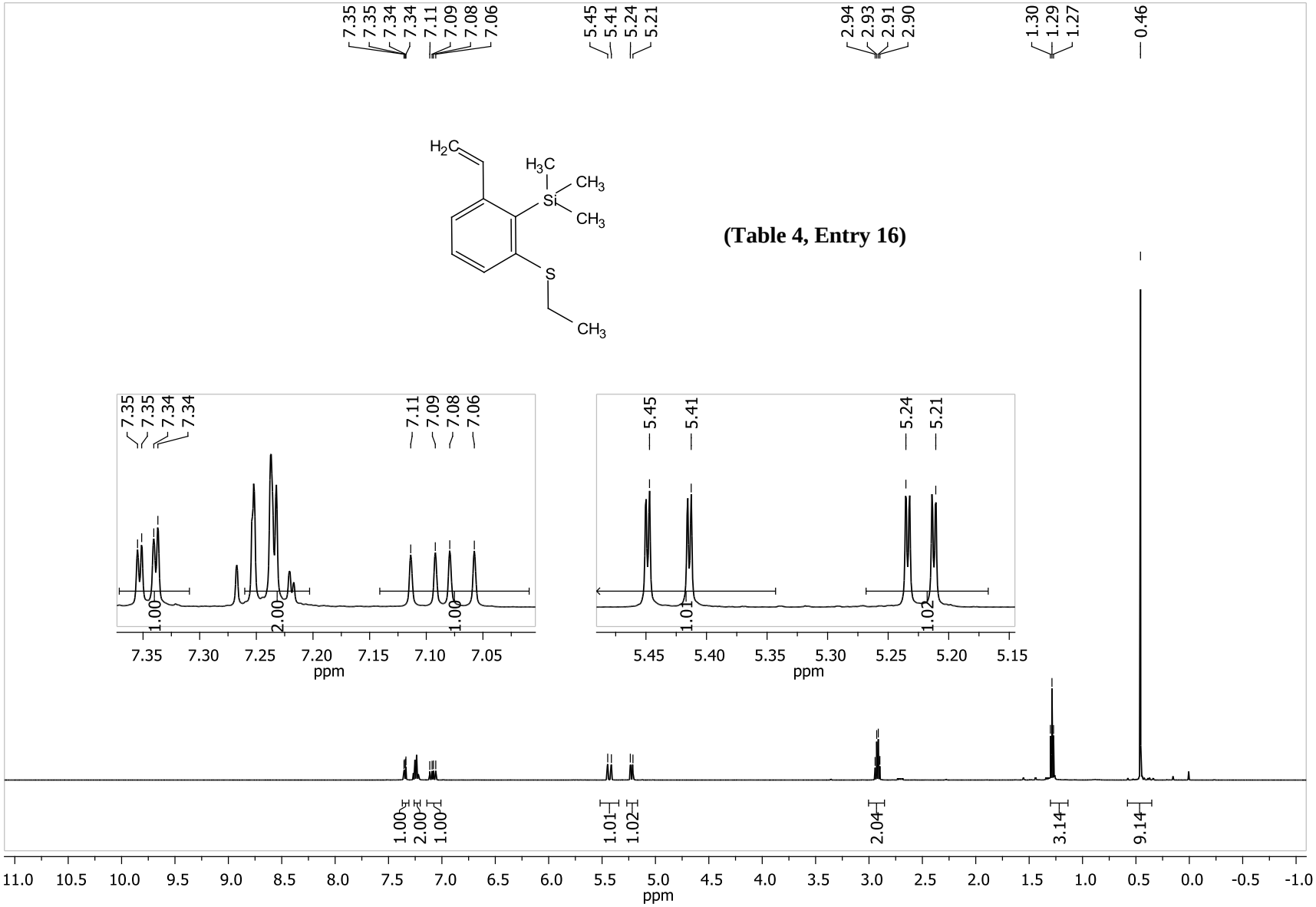


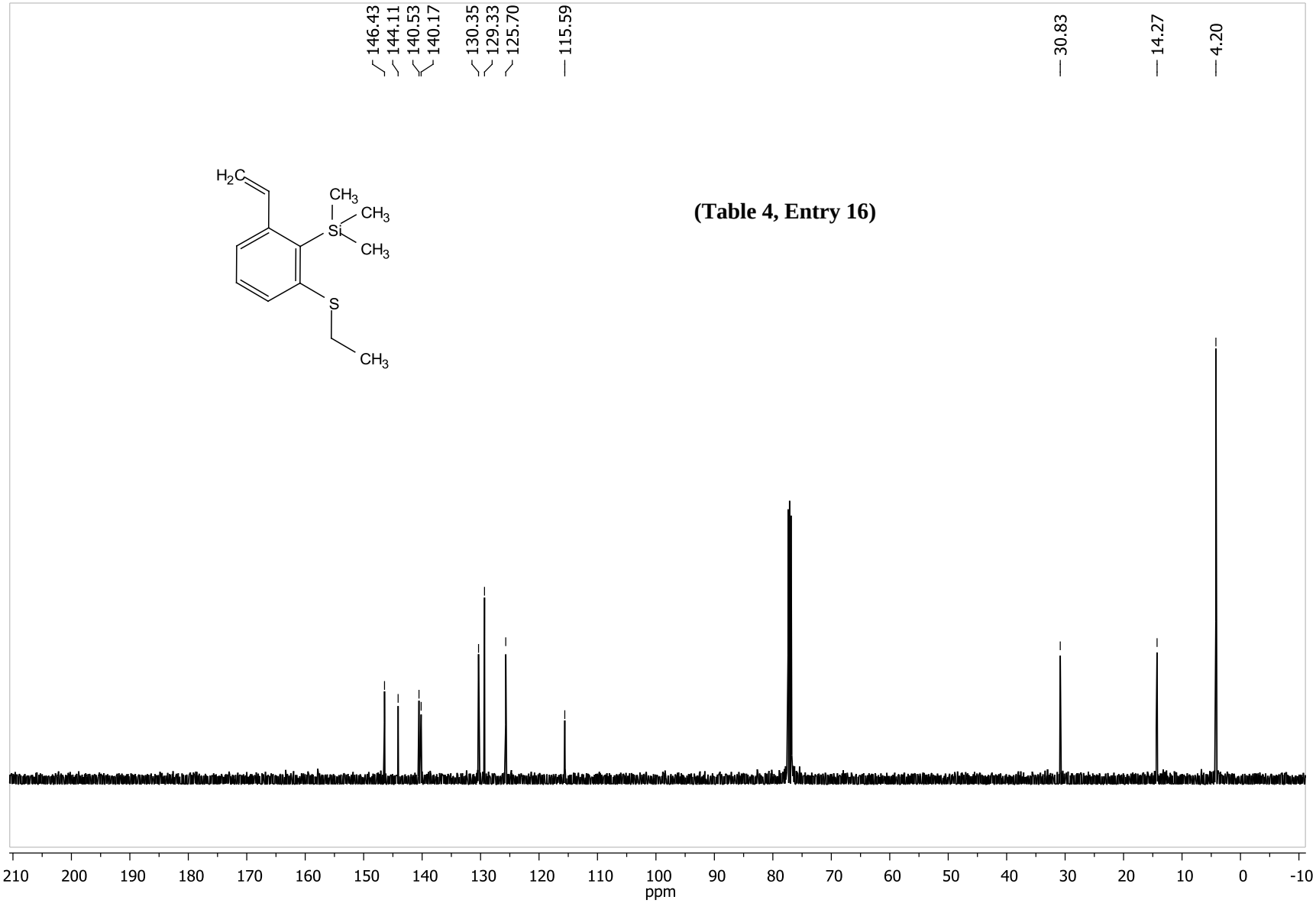

145.36
140.53
134.78
134.73
130.98
128.66
128.20
126.79
126.50
126.49
32.07
14.21
1.03
(Table 4, Entry 14')
H3C
S
H3C
CH3
Si
CH3
144
140
136
132
128
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

(Table 4, Entry 15)

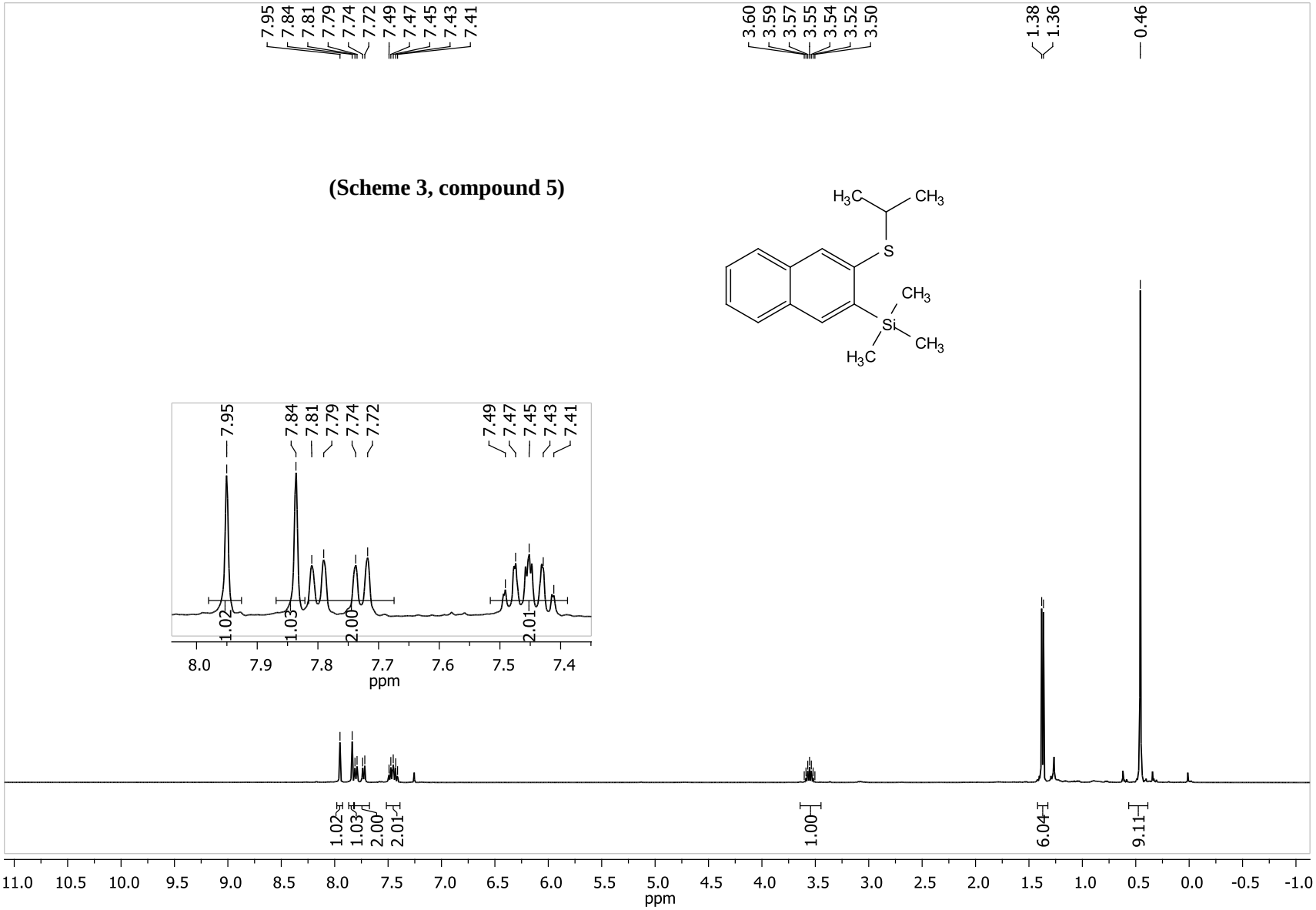



154.24
140.65
138.08
126.98
111.57
61.08
60.63
56.01
30.97
14.26
3.06
H3C
O
CH3
CH3
Si
CH3
H3C
O
O
H3C
S
CH3
(Table 4, Entry 15)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

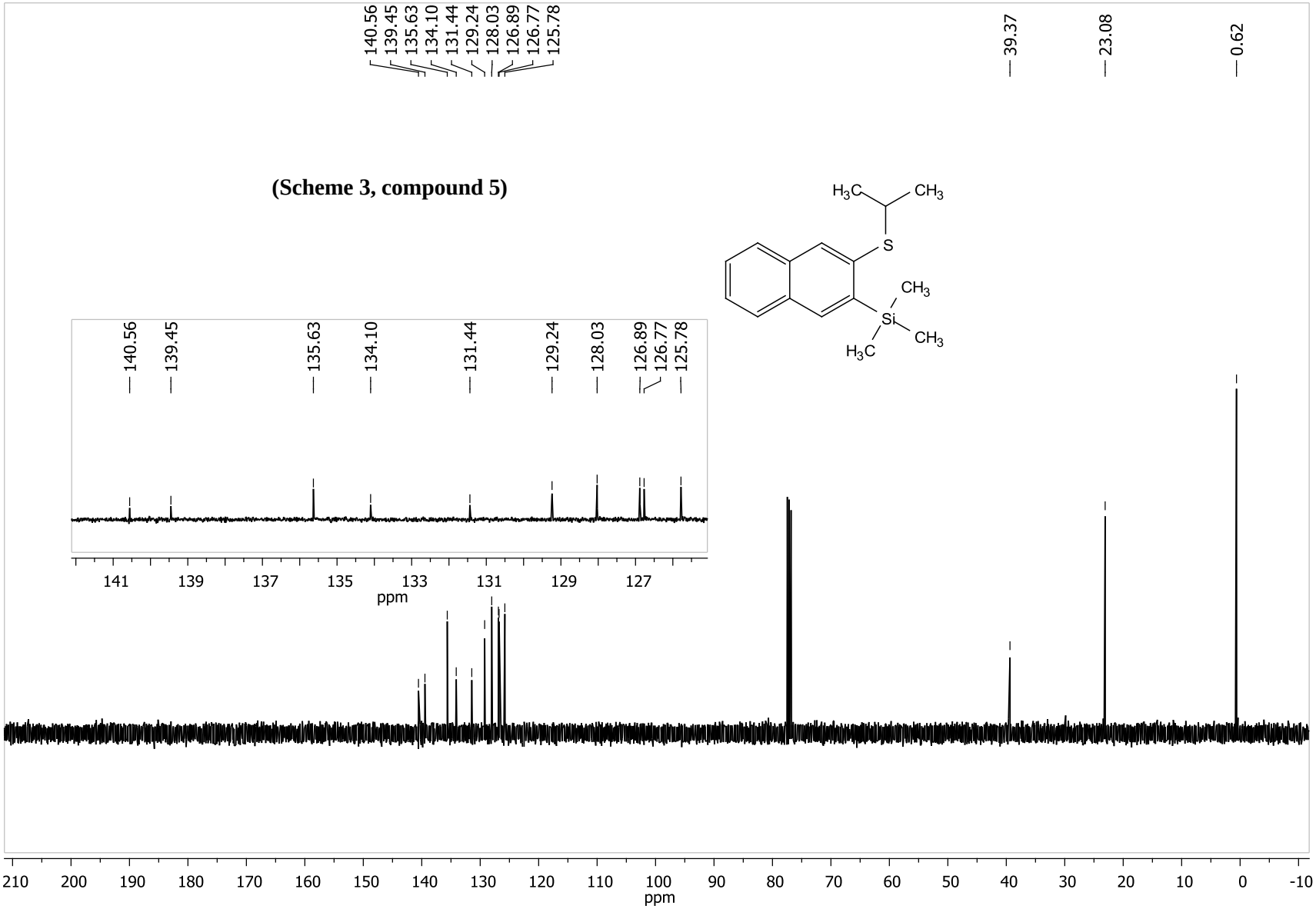

7.35
7.35
7.34
7.34
7.11
7.09
7.08
7.06
5.45
5.41
5.24
5.21
2.94
2.93
2.91
2.90
1.30
1.29
1.27
0.46
H2C
H3C
CH3
Si
CH3
S
CH3
(Table 4, Entry 16)
1.00
2.00
1.00
7.35 7.30 7.25 7.20 7.15 7.10 7.05
ppm
1.01
1.02
5.45 5.40 5.35 5.30 5.25 5.20 5.15
ppm
1.00
2.00
1.00
1.01
1.02
2.04
3.14
9.14
11.0 10.5 10.0 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


146.43
144.11
140.53
140.17
130.35
129.33
125.70
115.59
30.83
14.27
4.20
H2C
CH3
CH3
Si
CH3
S
CH3
(Table 4, Entry 16)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

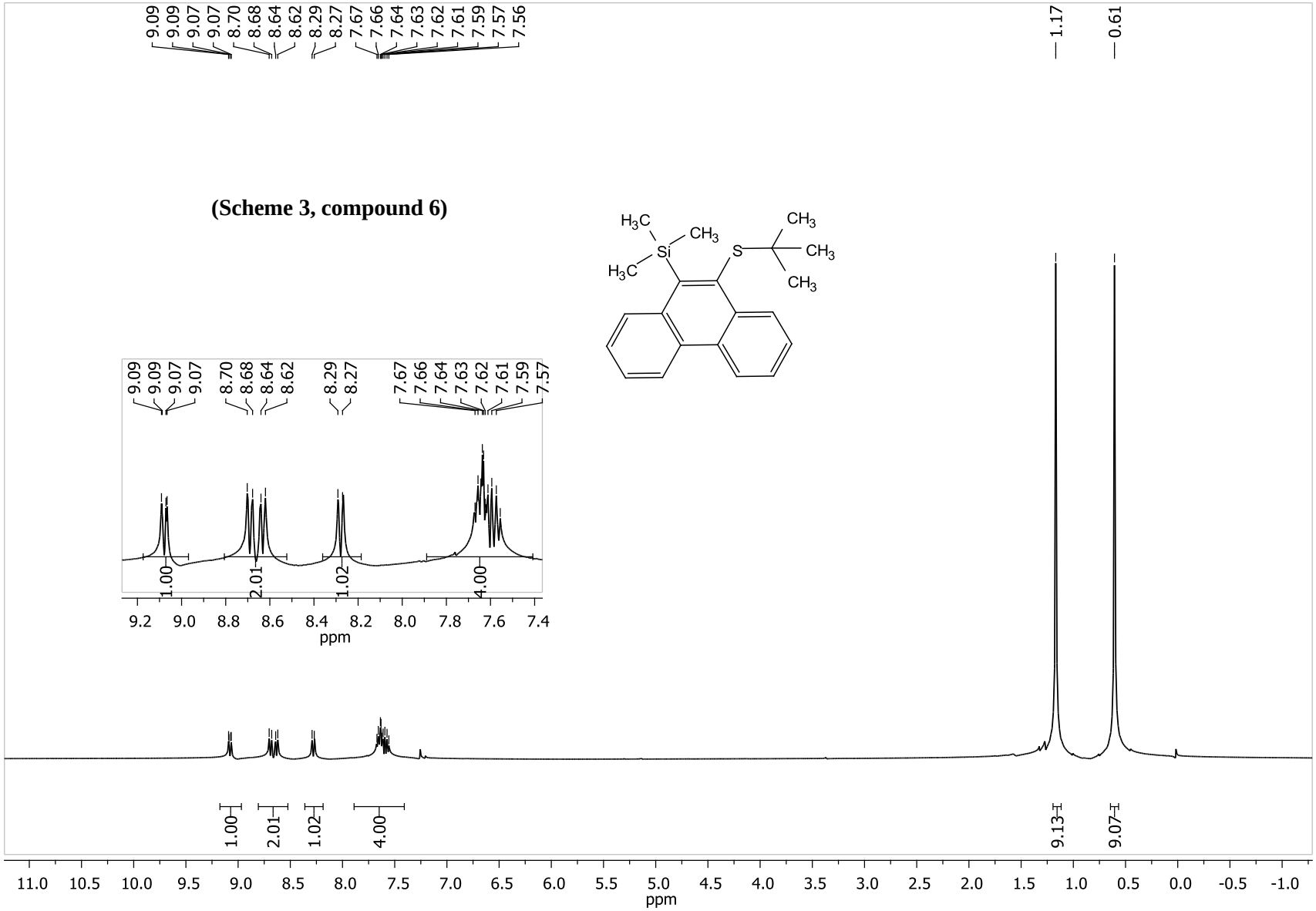
(Scheme 3, compound 5)



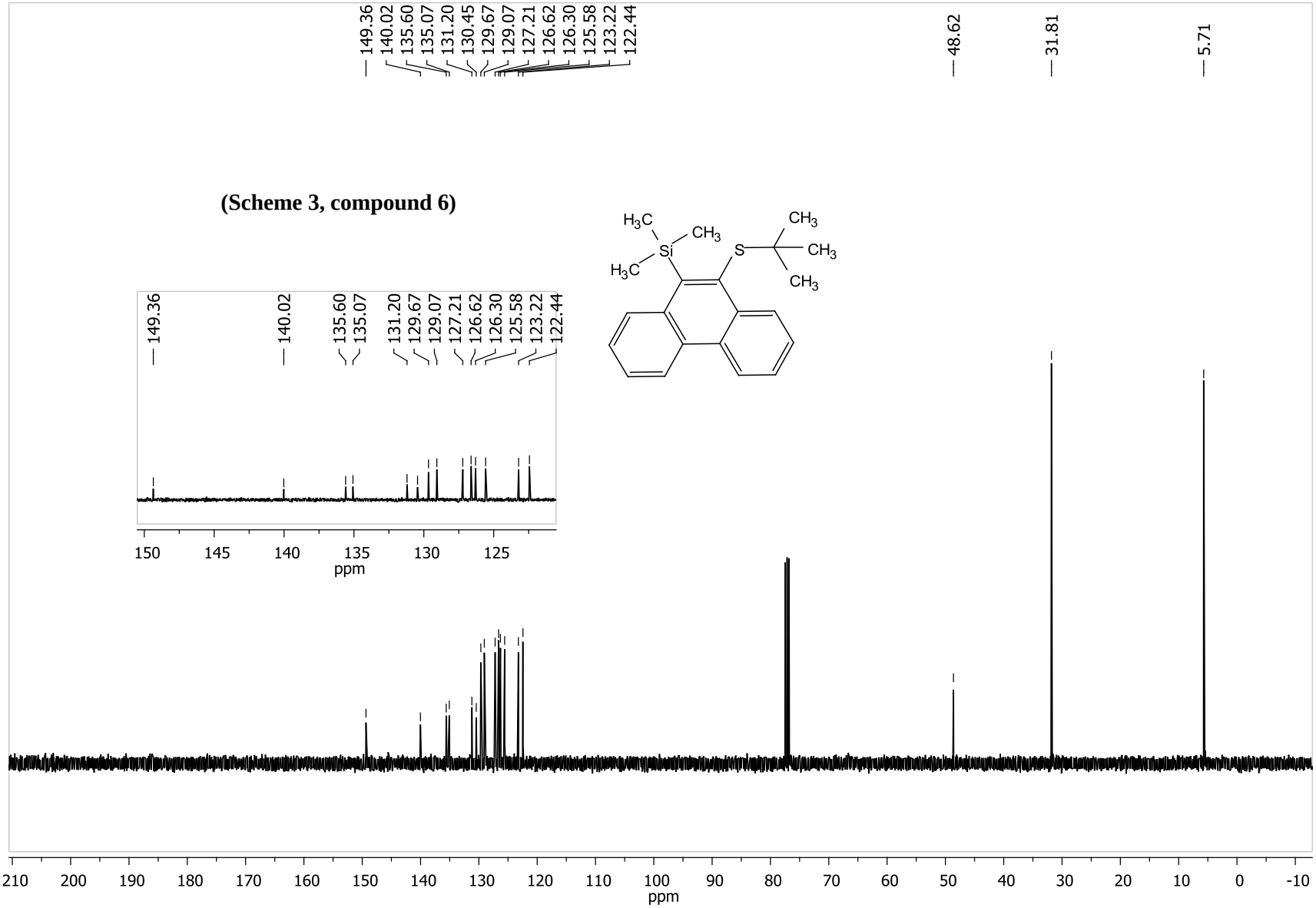
(Scheme 3, compound 5)



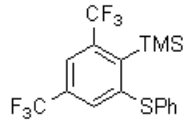
(Scheme 3, compound 6)

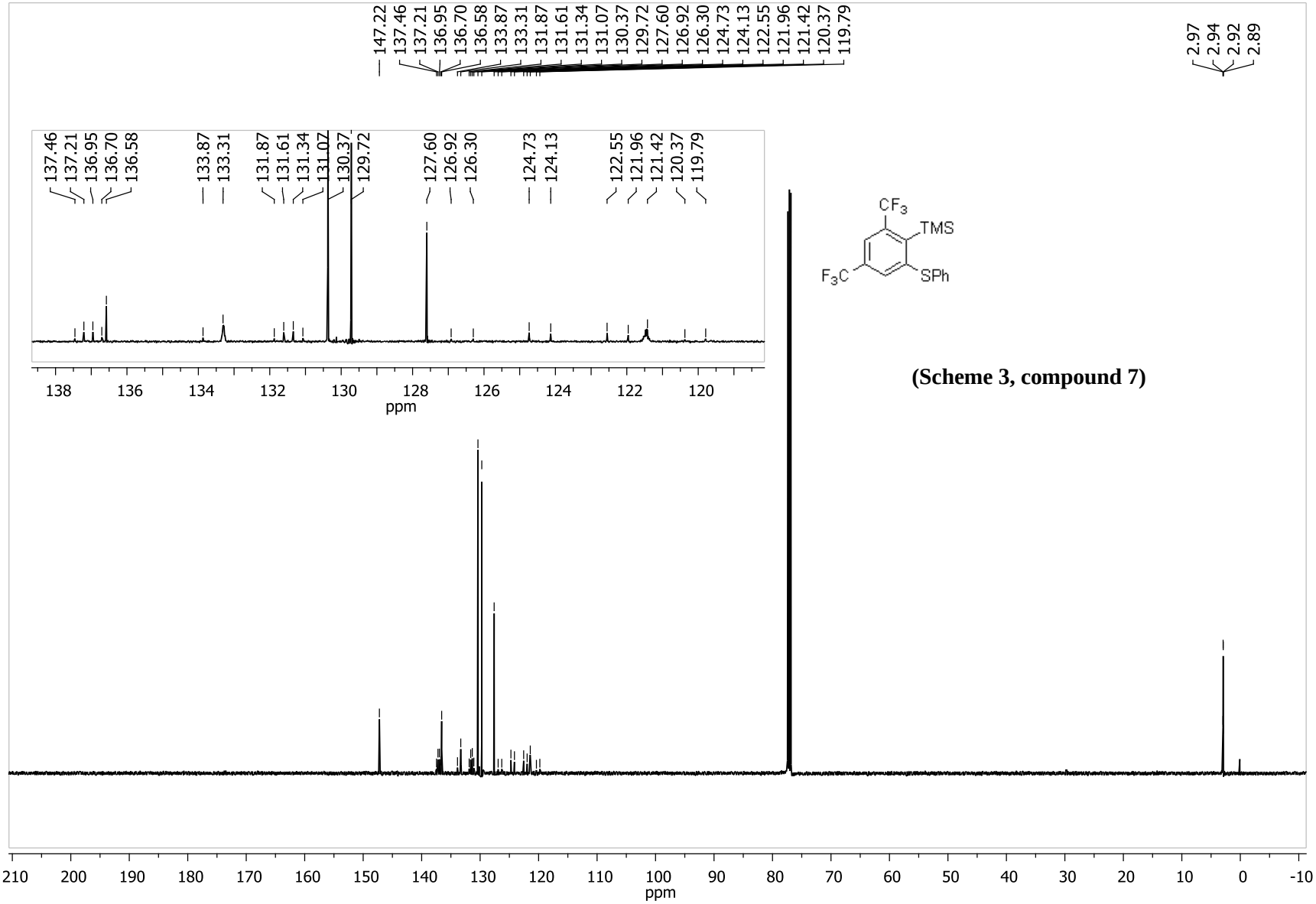


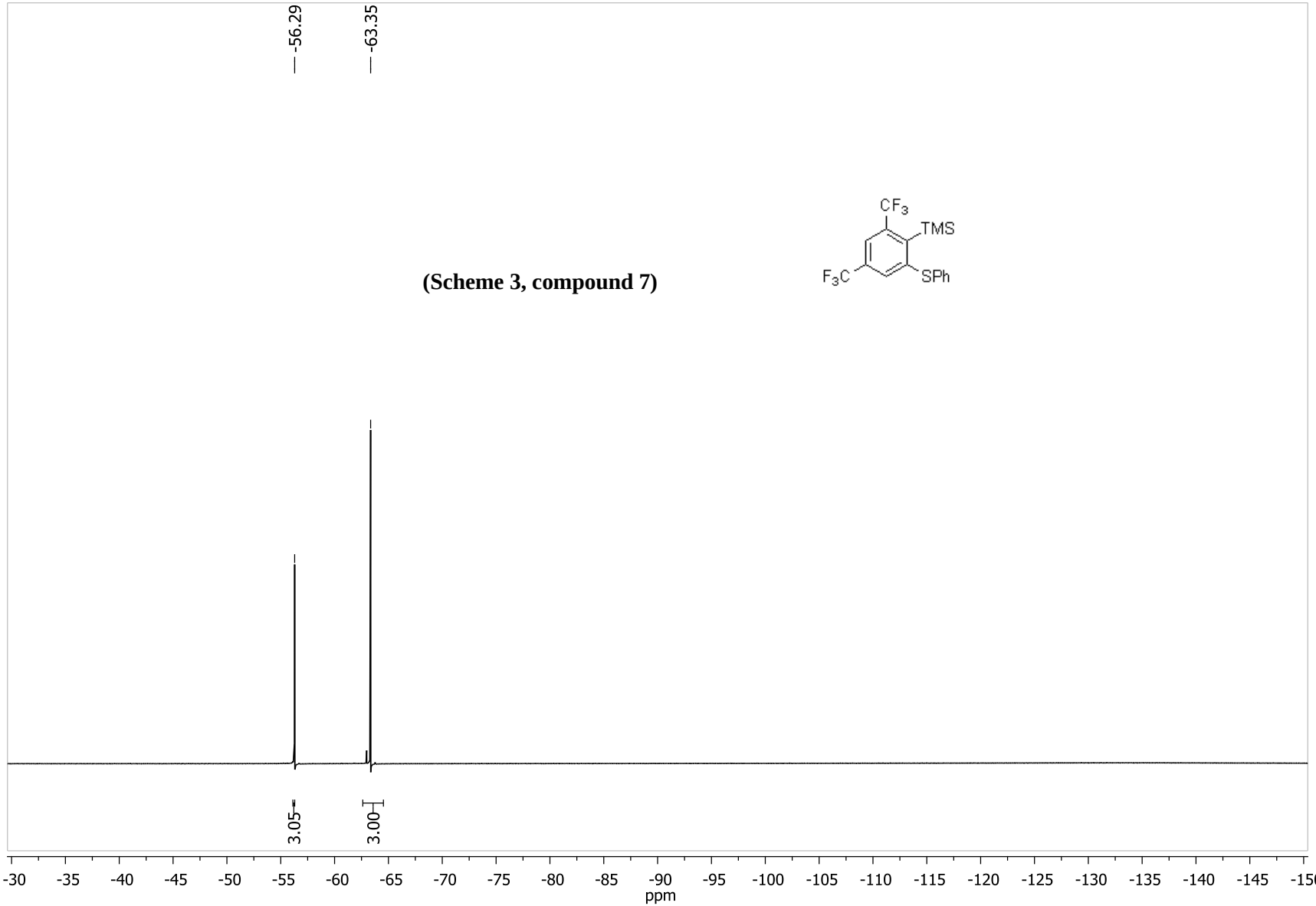
(Scheme 3, compound 6)



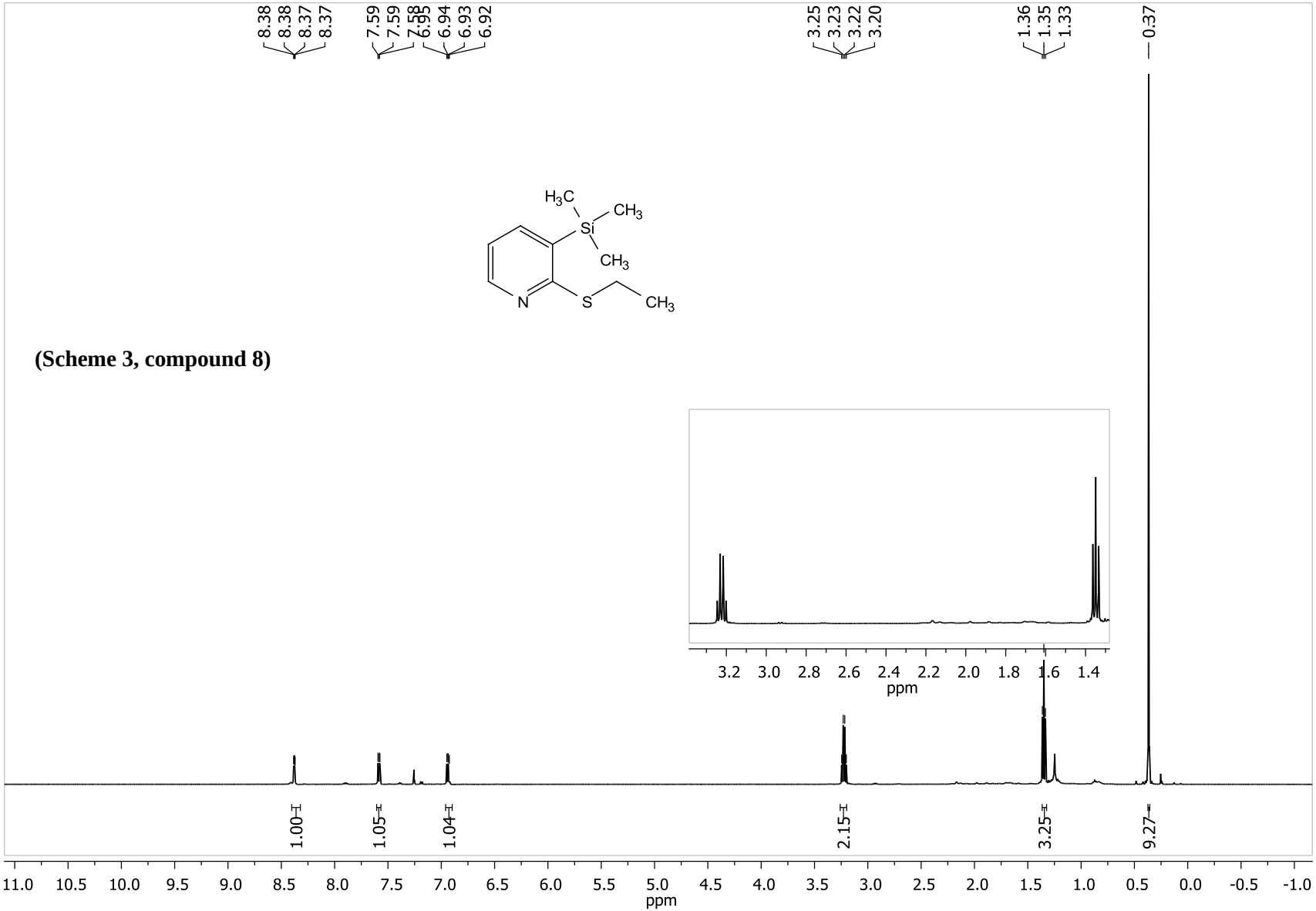
(Scheme 3, compound 7)



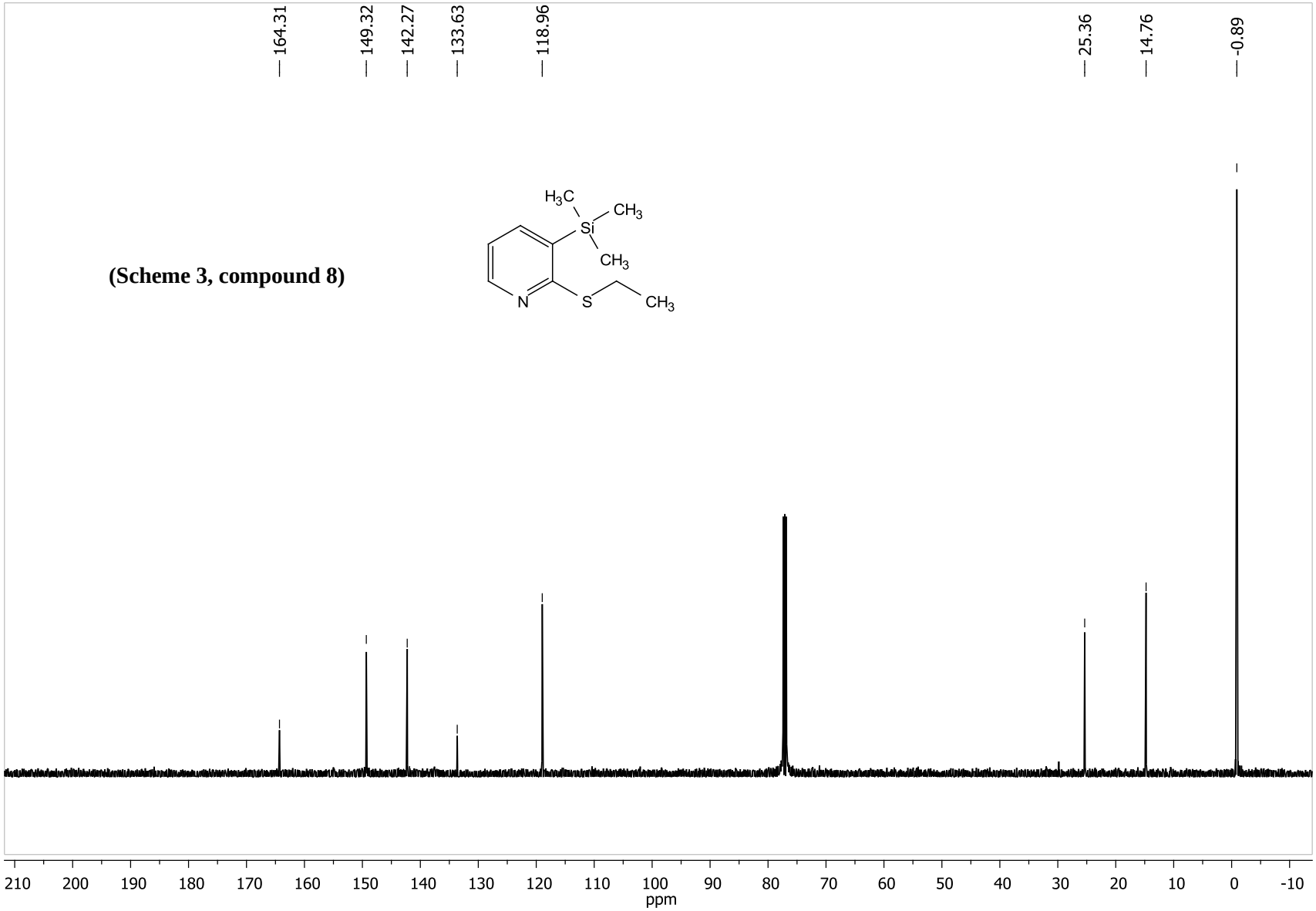

147.22
137.46
137.21
136.95
136.70
136.58
133.87
133.31
131.87
131.61
131.34
131.07
130.37
129.72
127.60
126.92
126.30
124.73
124.13
122.55
121.96
121.42
120.37
119.79
2.97
2.94
2.92
2.89
CF3
TMS
F3C
SPh
(Scheme 3, compound 7)
ppm
ppm

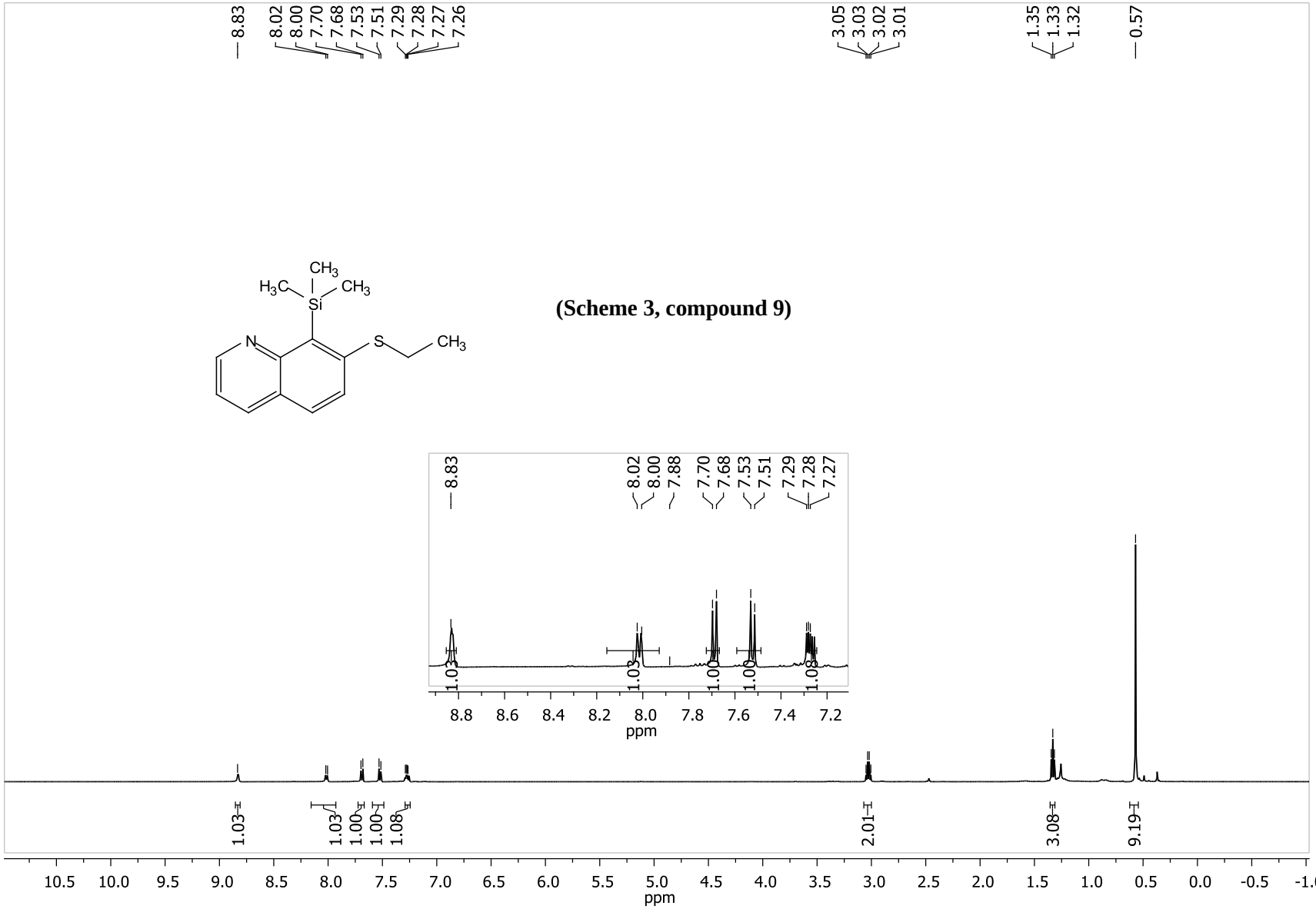


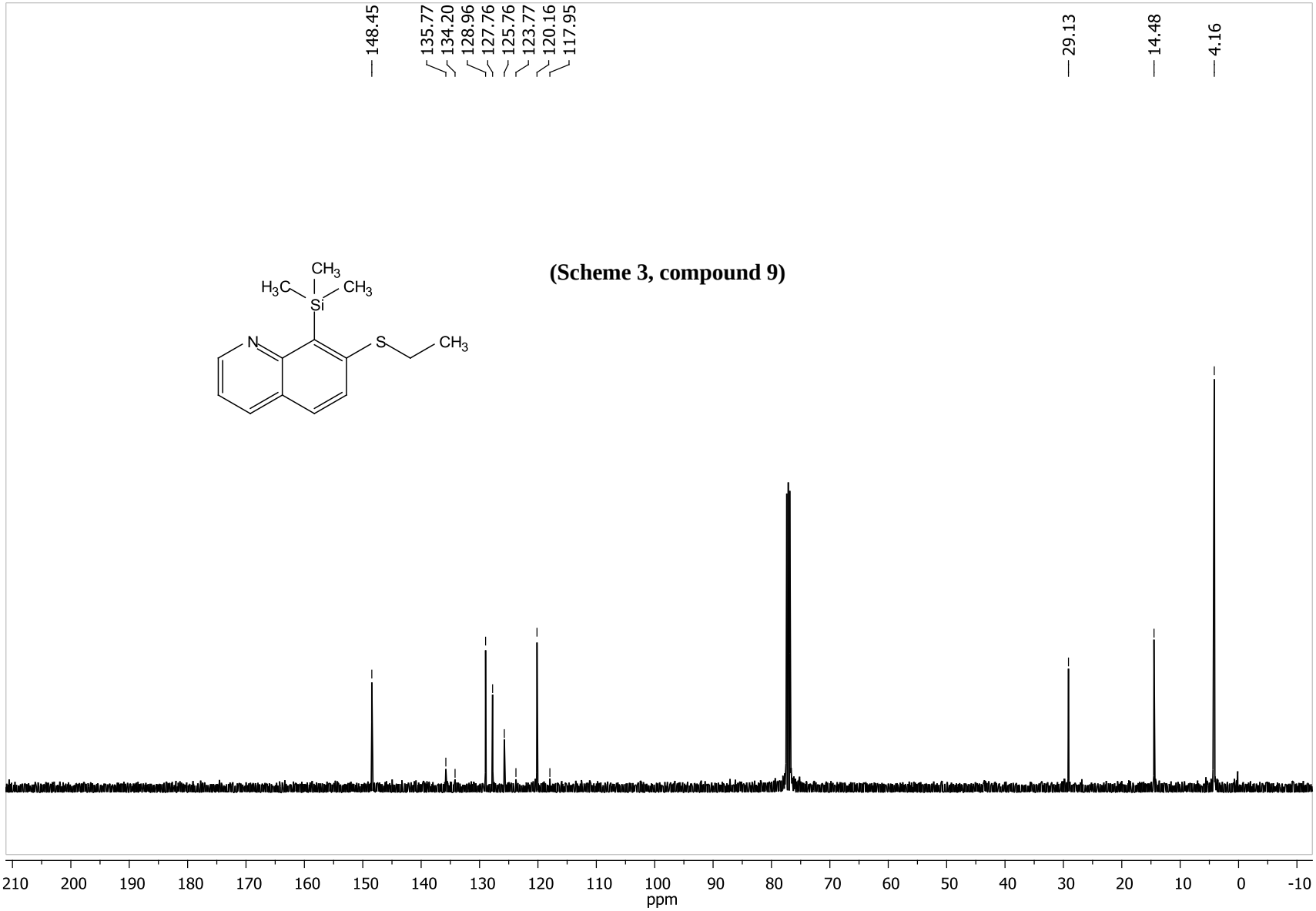
(Scheme 3, compound 7)

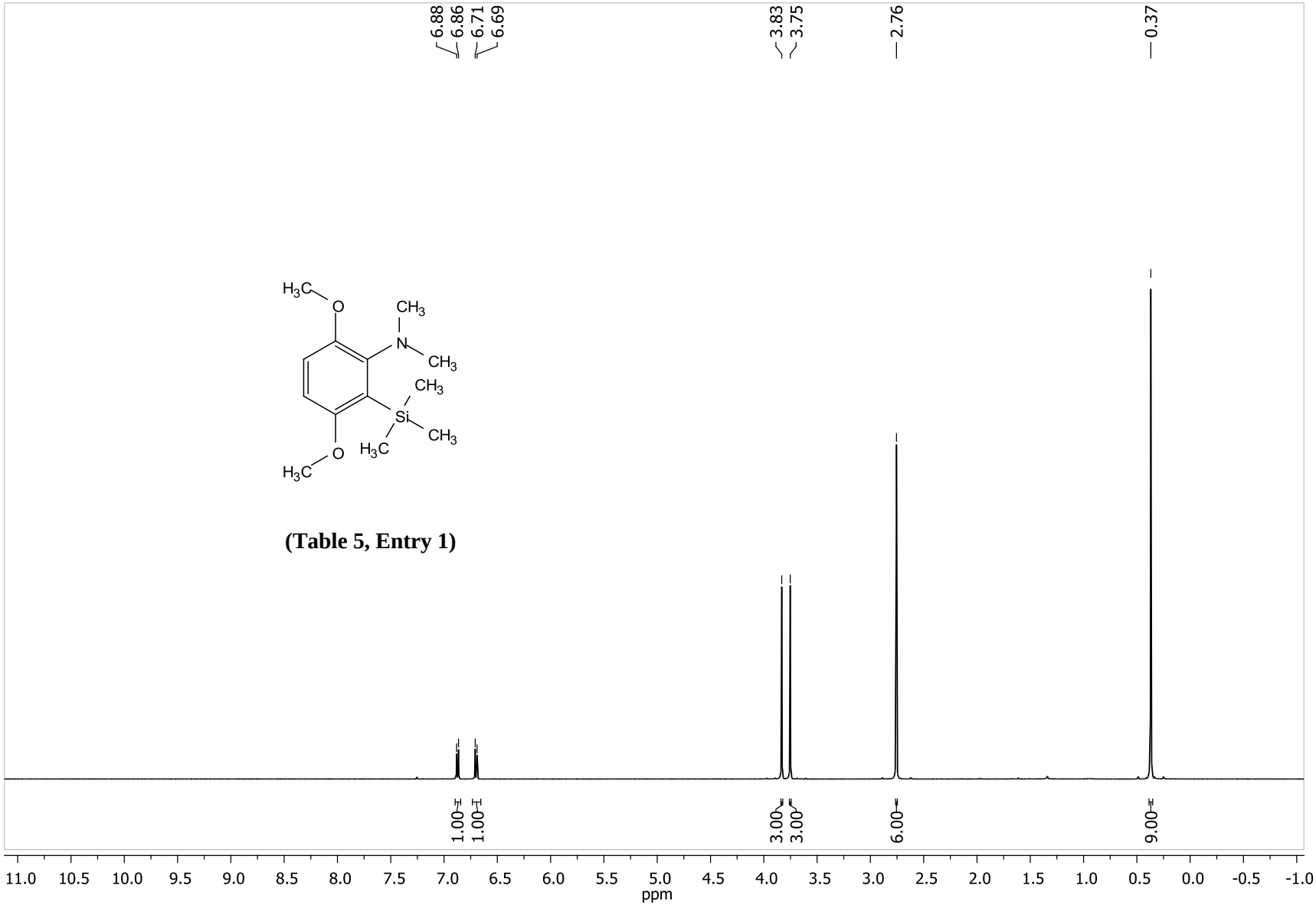


(Scheme 3, compound 8)

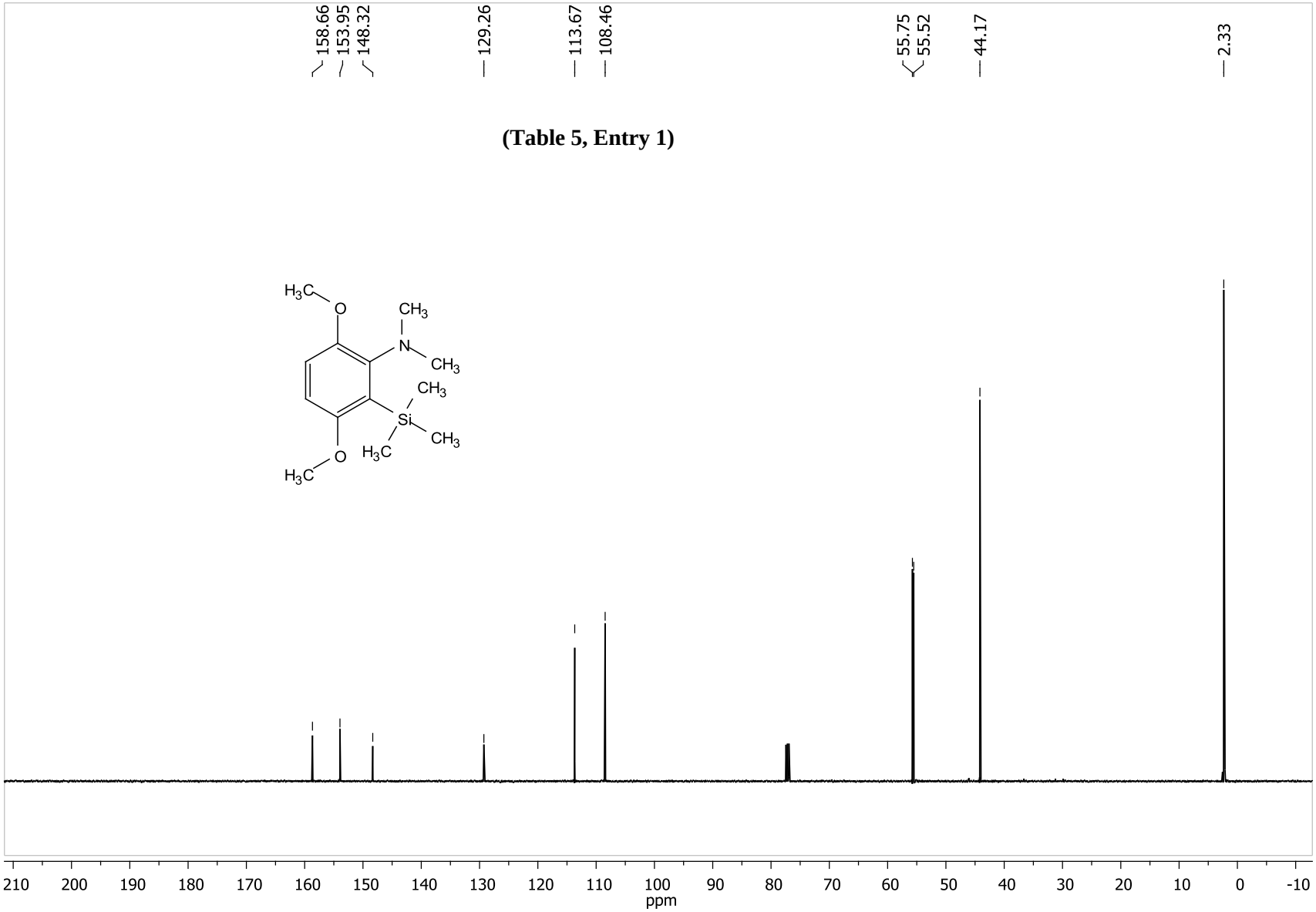

164.31
149.32
142.27
133.63
118.96
25.36
14.76
-0.89
H3C
CH3
Si
CH3
N
S
CH3
(Scheme 3, compound 8)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


8.83
8.02
8.00
7.70
7.68
7.53
7.51
7.29
7.28
7.27
7.26
3.05
3.03
3.02
3.01
1.35
1.33
1.32
0.57
CH3
H3C
CH3
Si
N
S
CH3
(Scheme 3, compound 9)
8.83
8.02
8.00
7.88
7.70
7.68
7.53
7.51
7.29
7.28
7.27
1.03
1.03
1.00
1.00
1.08
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.03
1.03
1.00
1.00
1.08
2.01
3.08
9.19
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

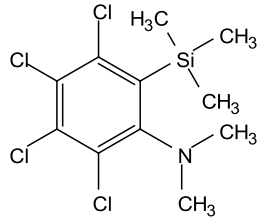

148.45
135.77
134.20
128.96
127.76
125.76
123.77
120.16
117.95
29.13
14.48
4.16
CH3
H3C
CH3
Si
N
S
CH3
(Scheme 3, compound 9)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

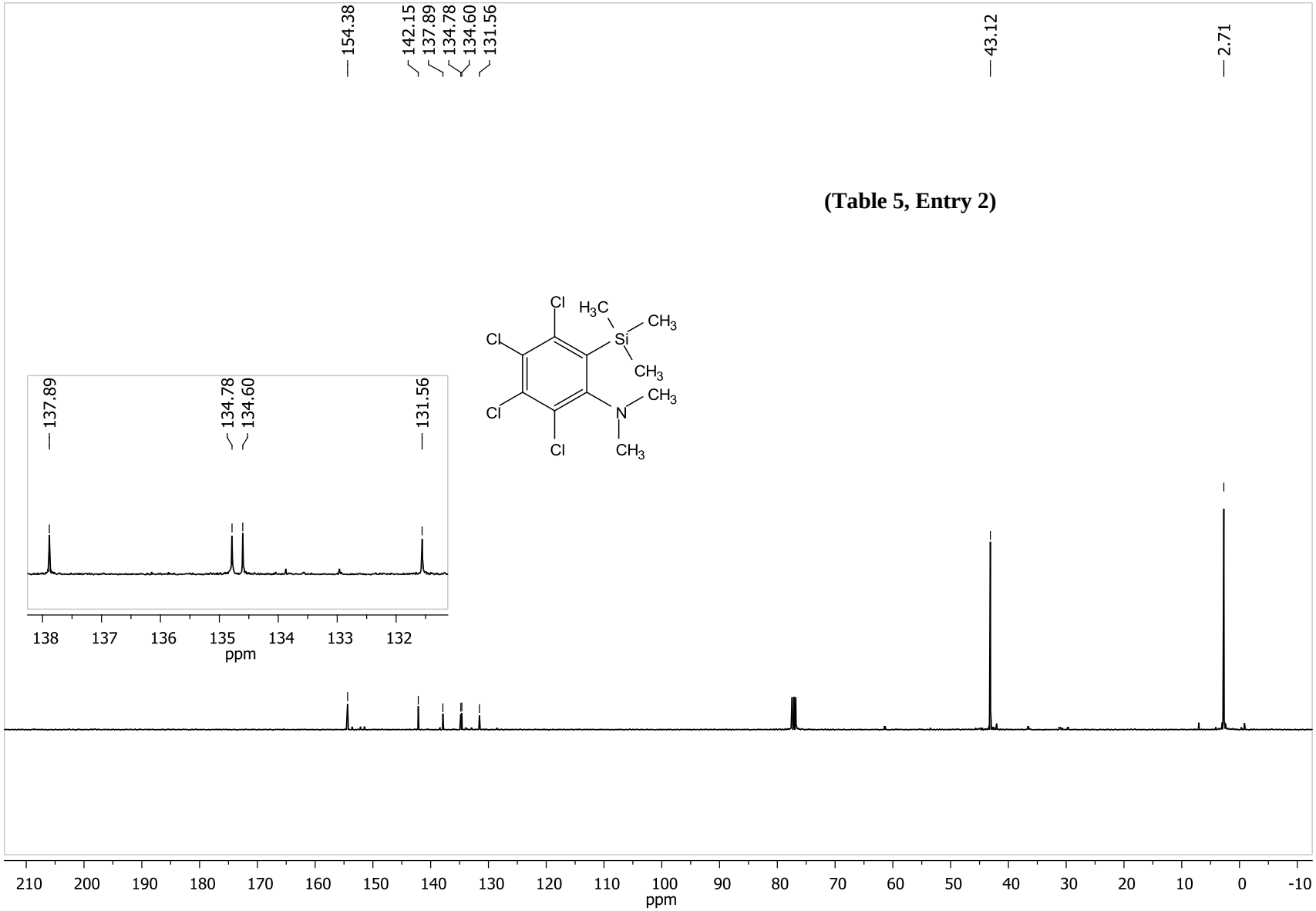


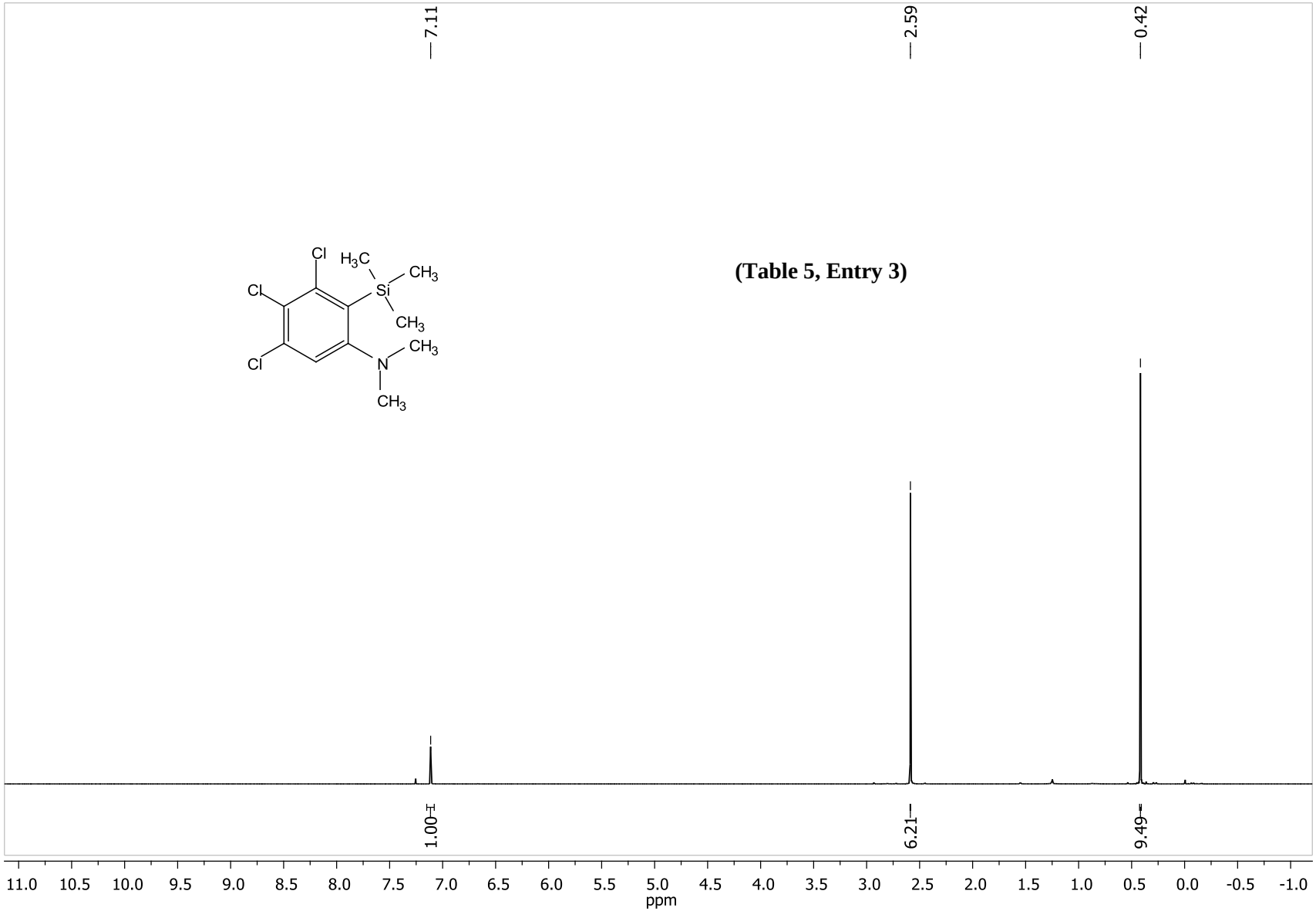
(Table 5, Entry 1)

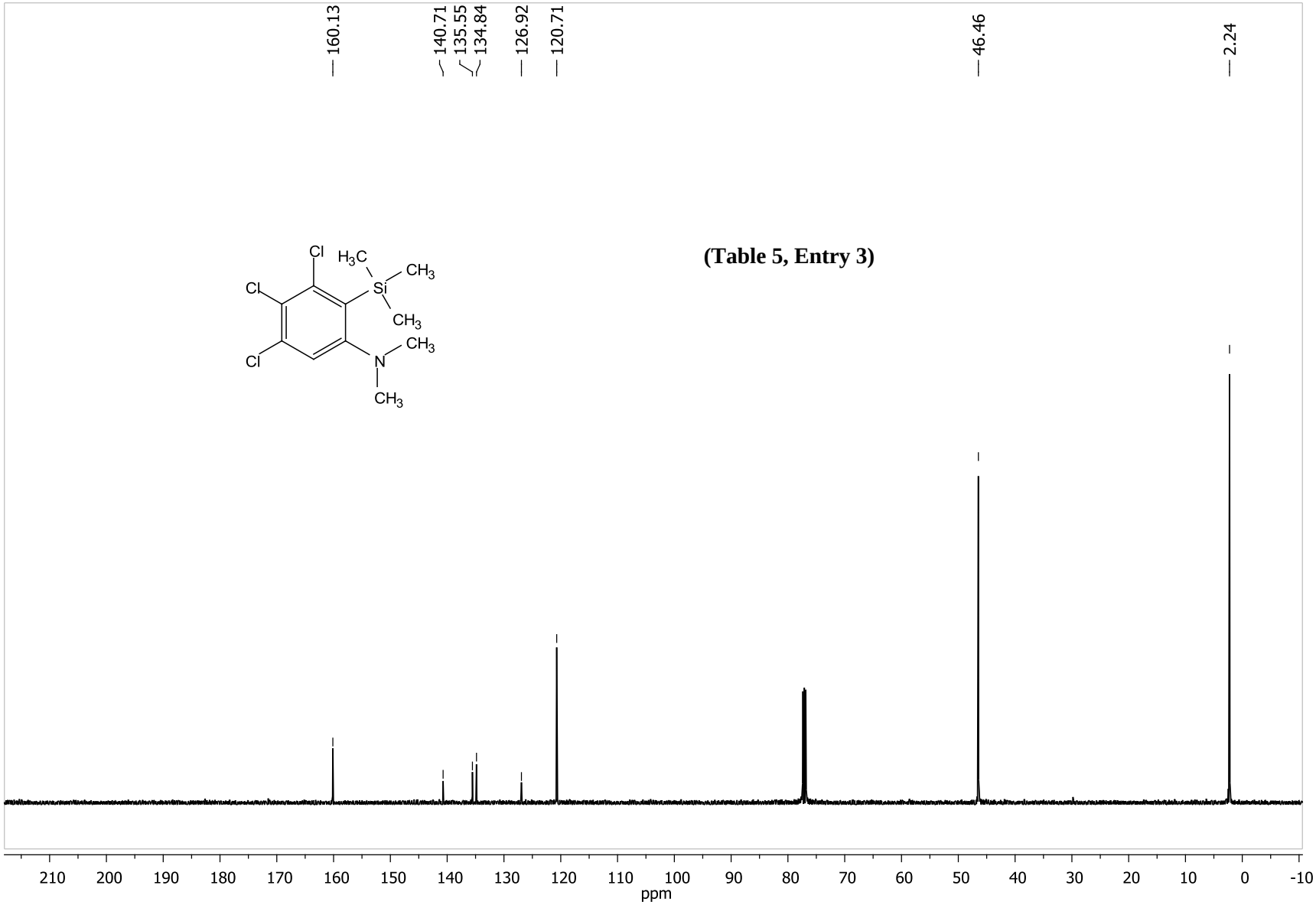

158.66
153.95
148.32
129.26
113.67
108.46
55.75
55.52
44.17
2.33
(Table 5, Entry 1)
H3C
O
CH3
N
CH3
CH3
Si
CH3
H3C
O
H3C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

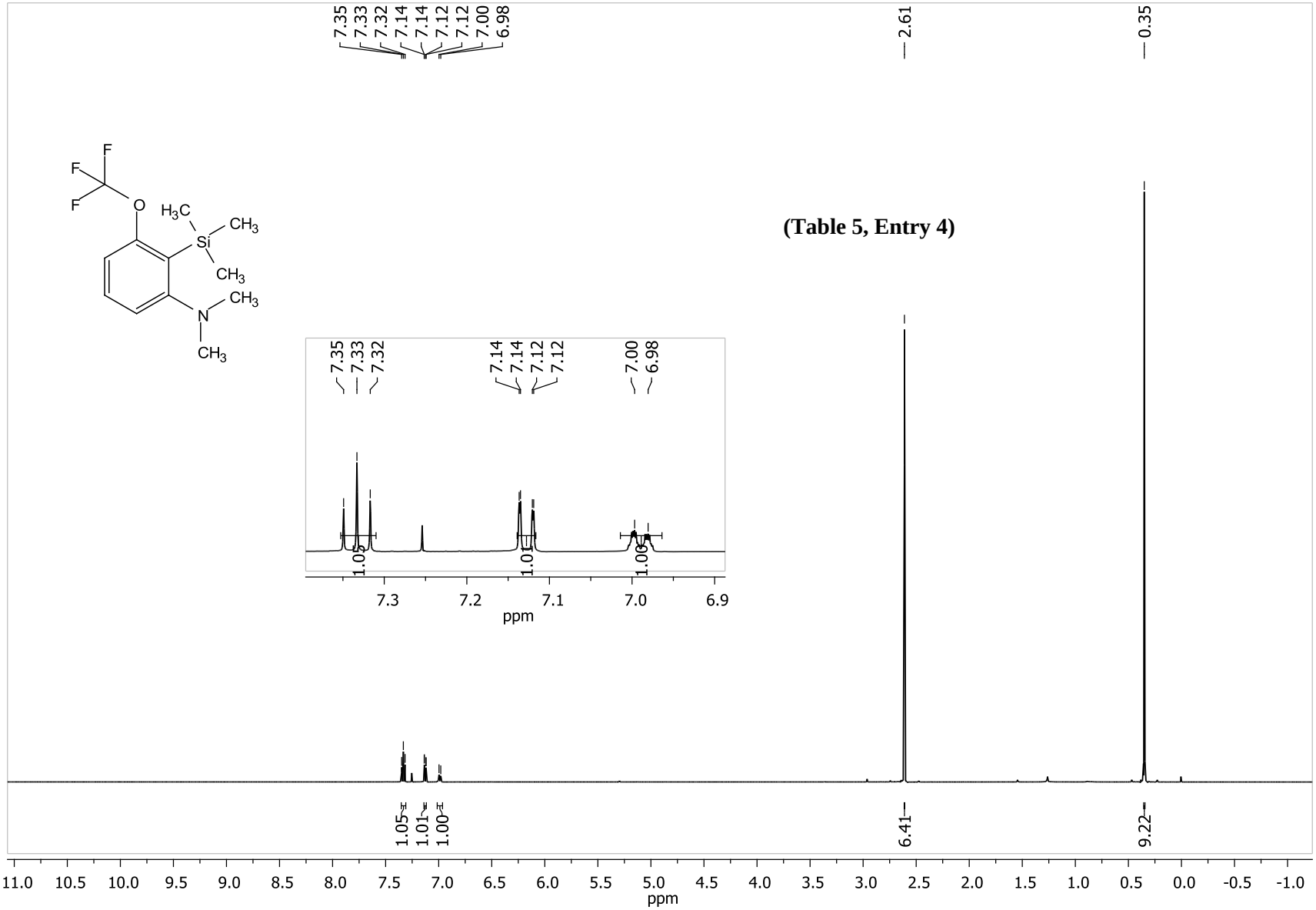
(Table 5, Entry 2)



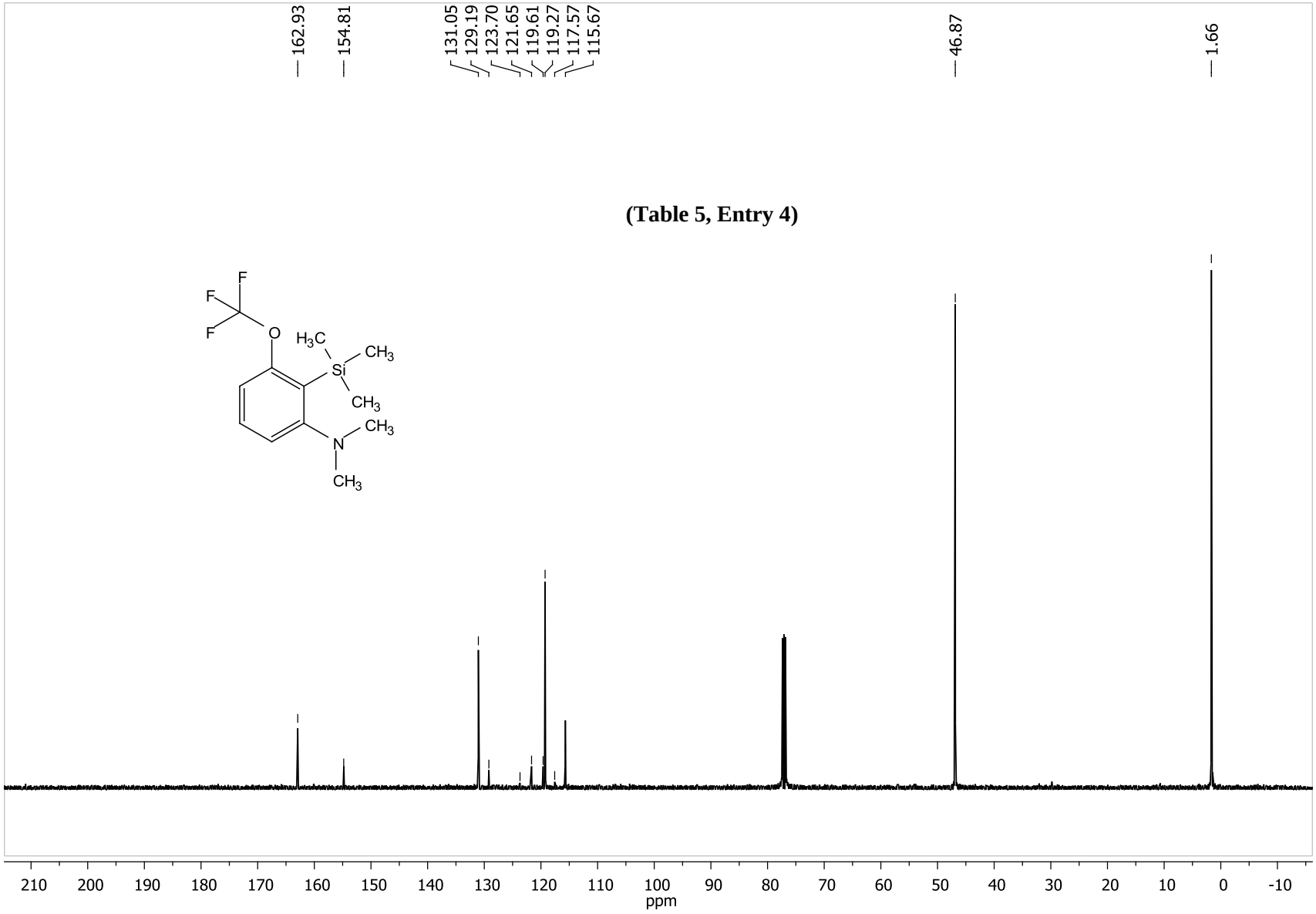

154.38
142.15
137.89
134.78
134.60
131.56
43.12
2.71
(Table 5, Entry 2)
Cl
H3C
CH3
Si
CH3
Cl
CH3
Cl
N
Cl
CH3
137.89
134.78
134.60
131.56
138
137
136
135
134
133
132
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.11
2.59
0.42
Cl
H3C
CH3
Si
CH3
Cl
CH3
N
Cl
CH3
(Table 5, Entry 3)
1.00
6.21
9.49
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm

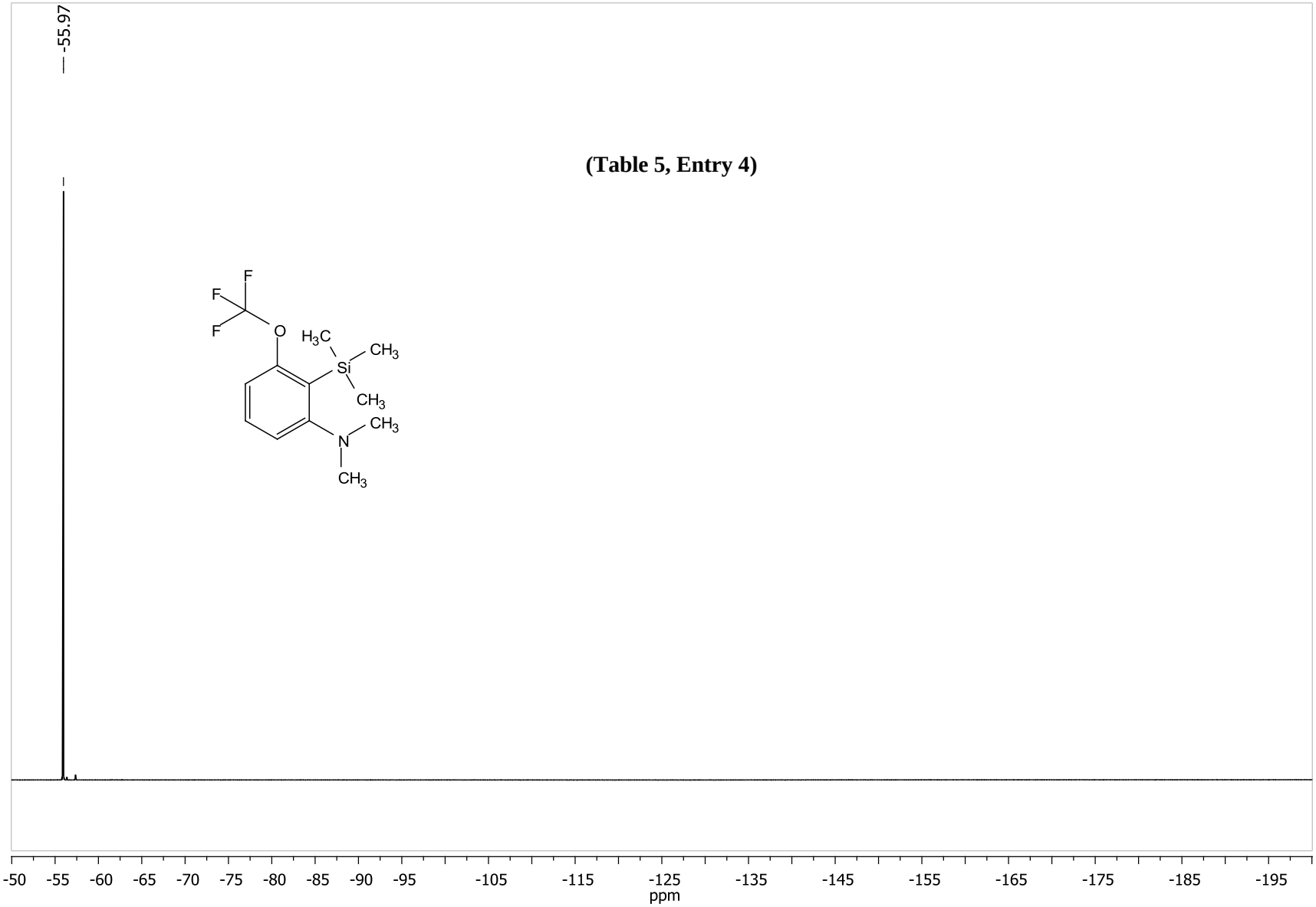

160.13
140.71
135.55
134.84
126.92
120.71
46.46
2.24
Cl
H3C
CH3
Si
CH3
Cl
CH3
Cl
N
CH3
(Table 5, Entry 3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


7.35
7.33
7.32
7.14
7.14
7.12
7.12
7.00
6.98
2.61
0.35
F
F
F
O
H3C
CH3
Si
CH3
CH3
N
CH3
(Table 5, Entry 4)
1.05
1.01
1.00
7.3
7.2
7.1
7.0
6.9
ppm
6.41
9.22
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

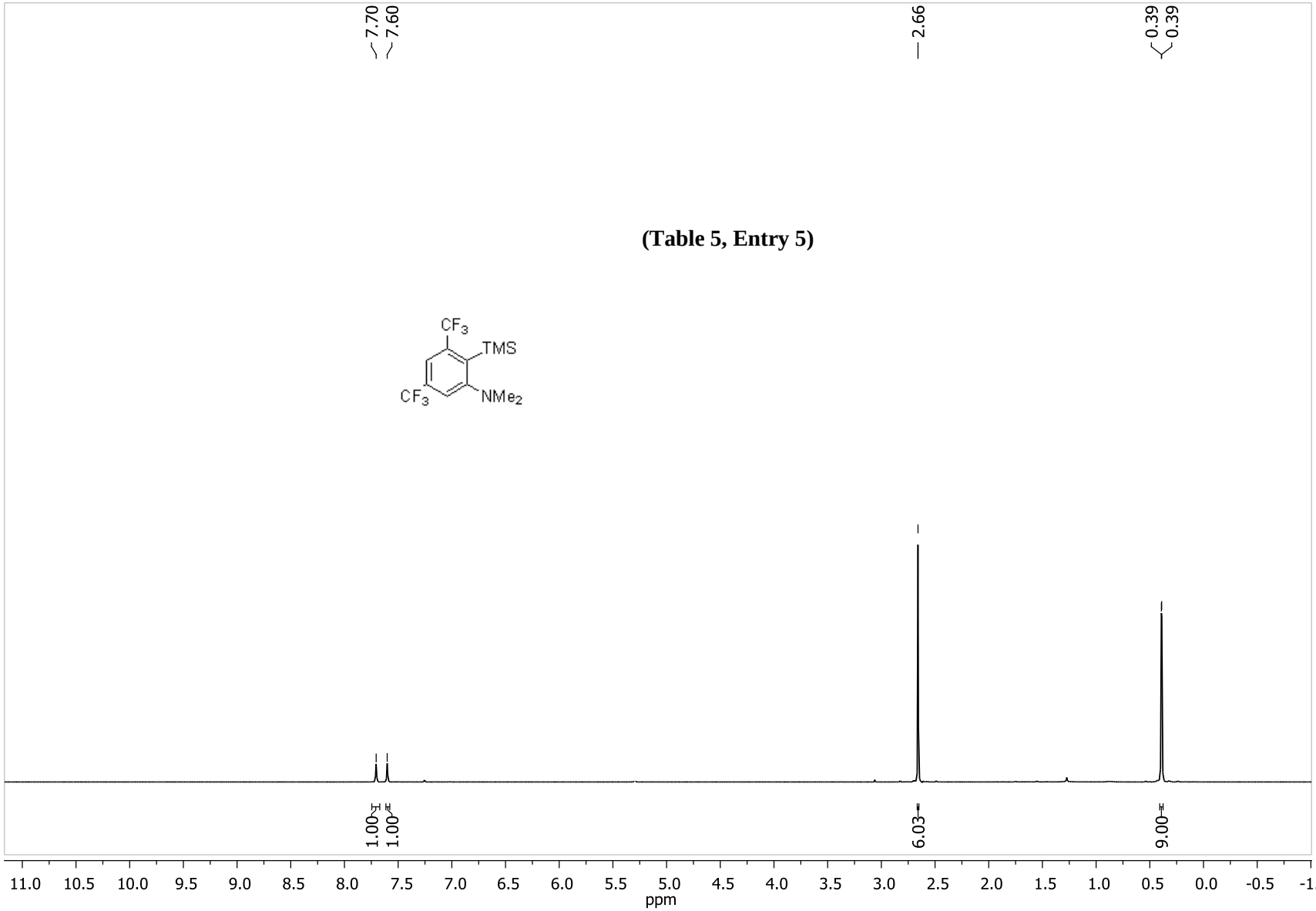
(Table 5, Entry 4)

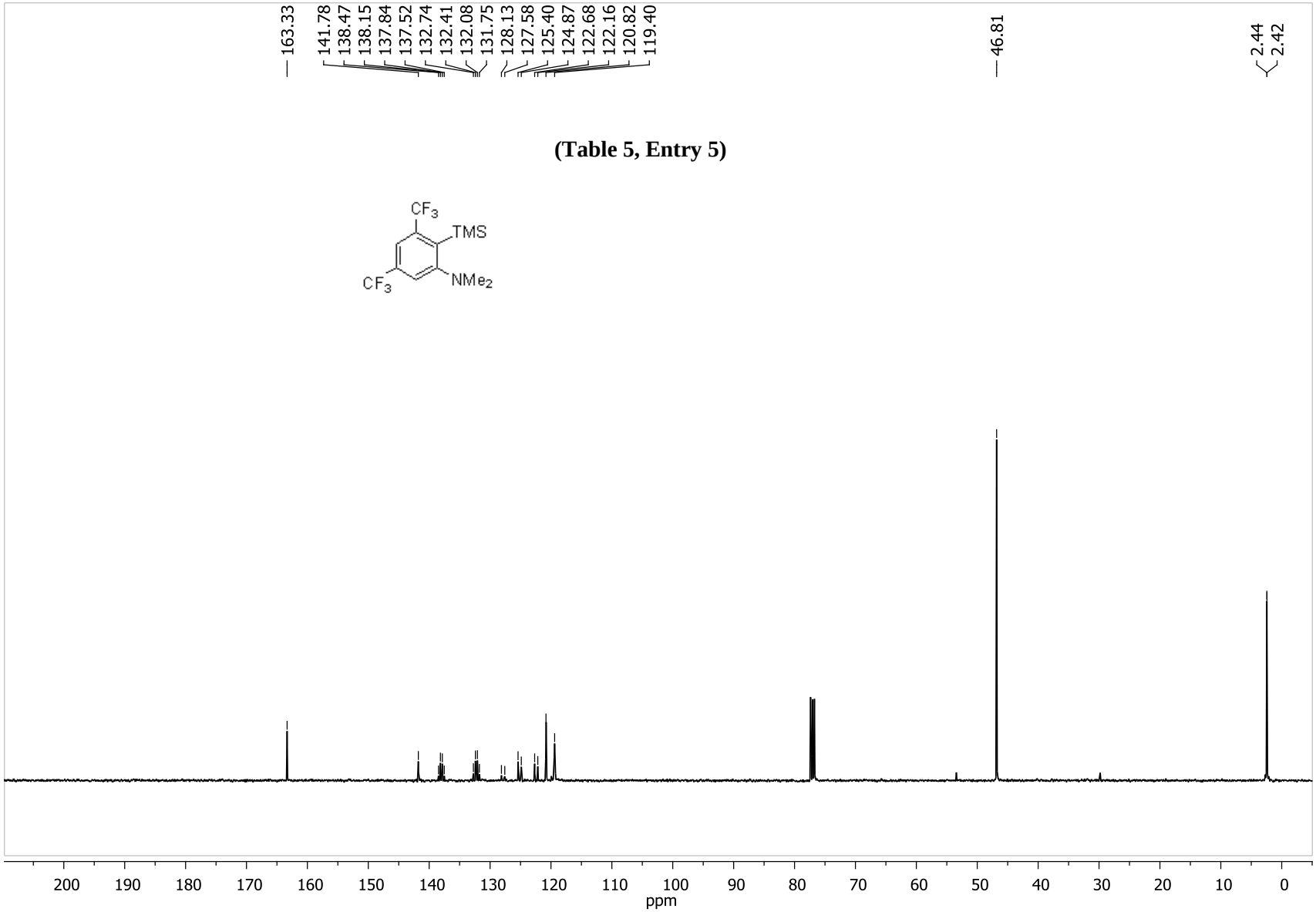


(Table 5, Entry 4)

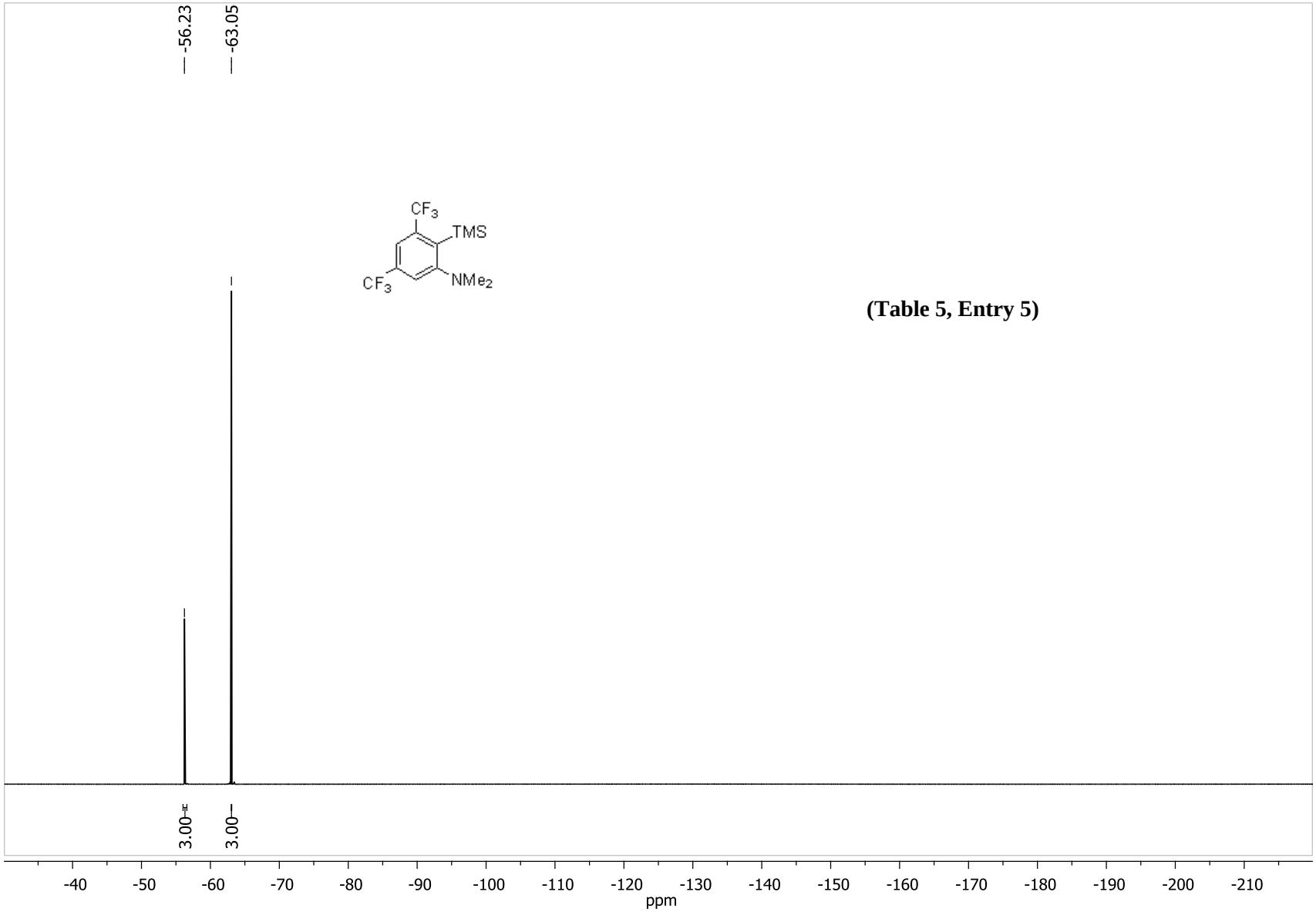


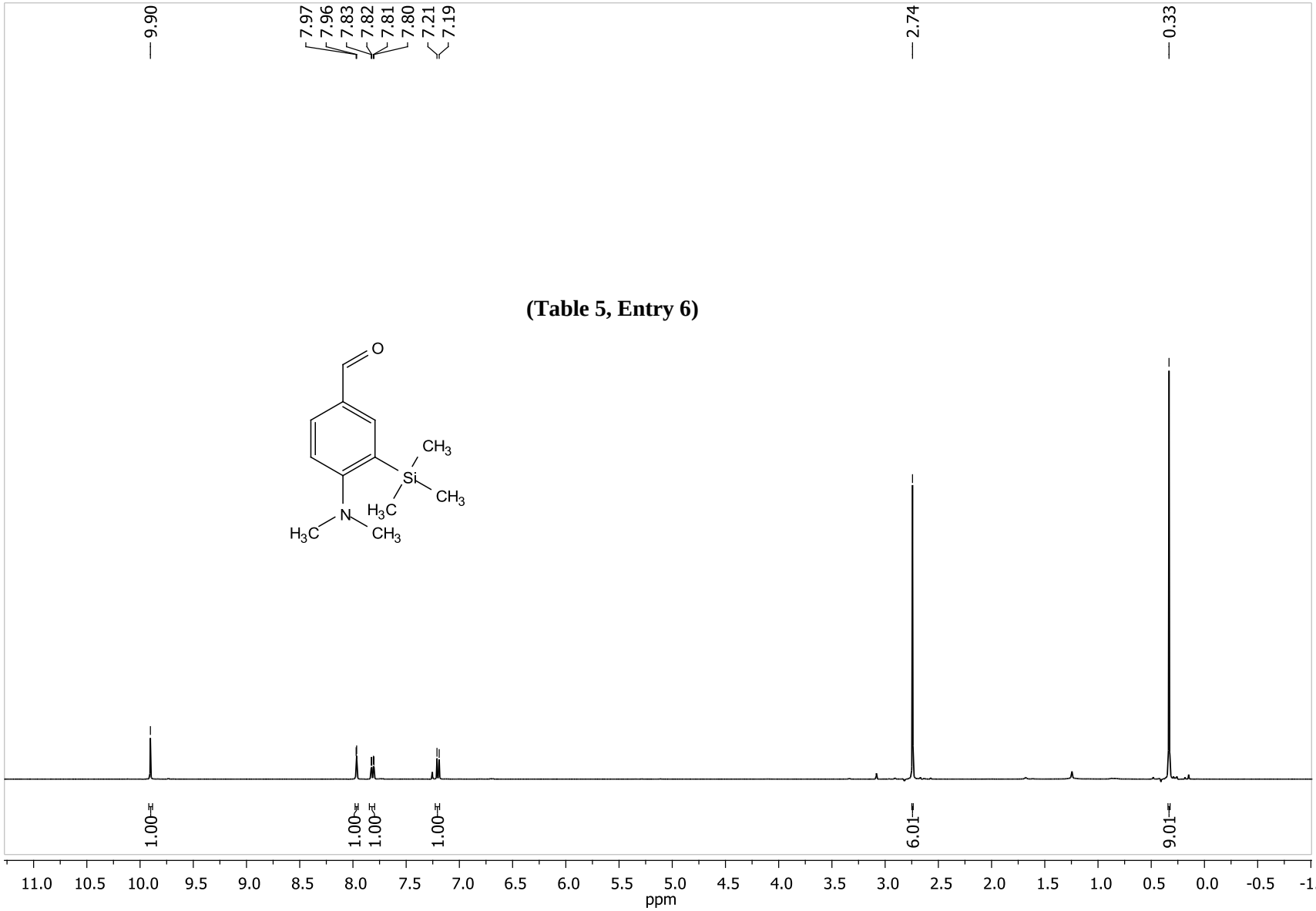
(Table 5, Entry 5)

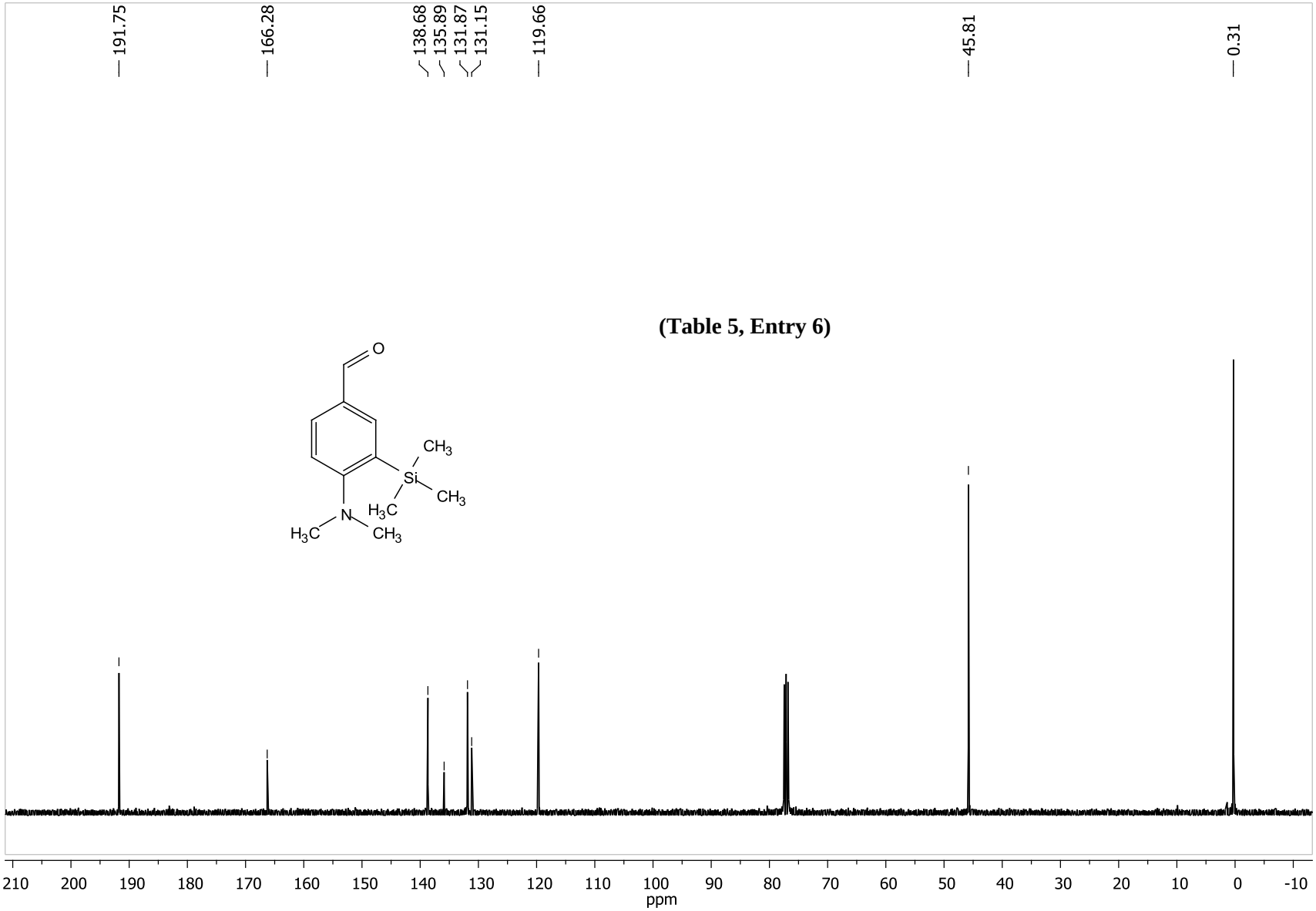


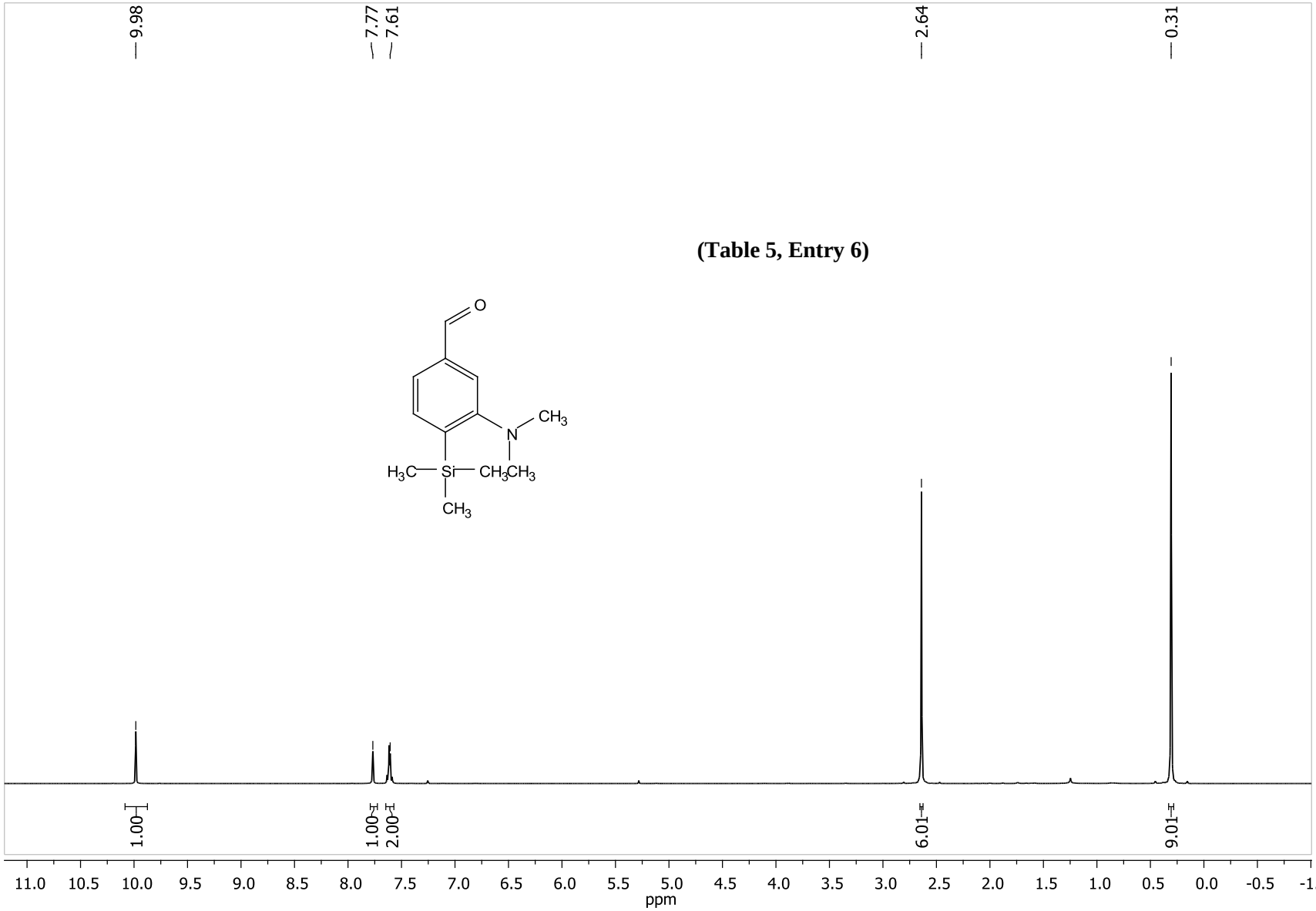


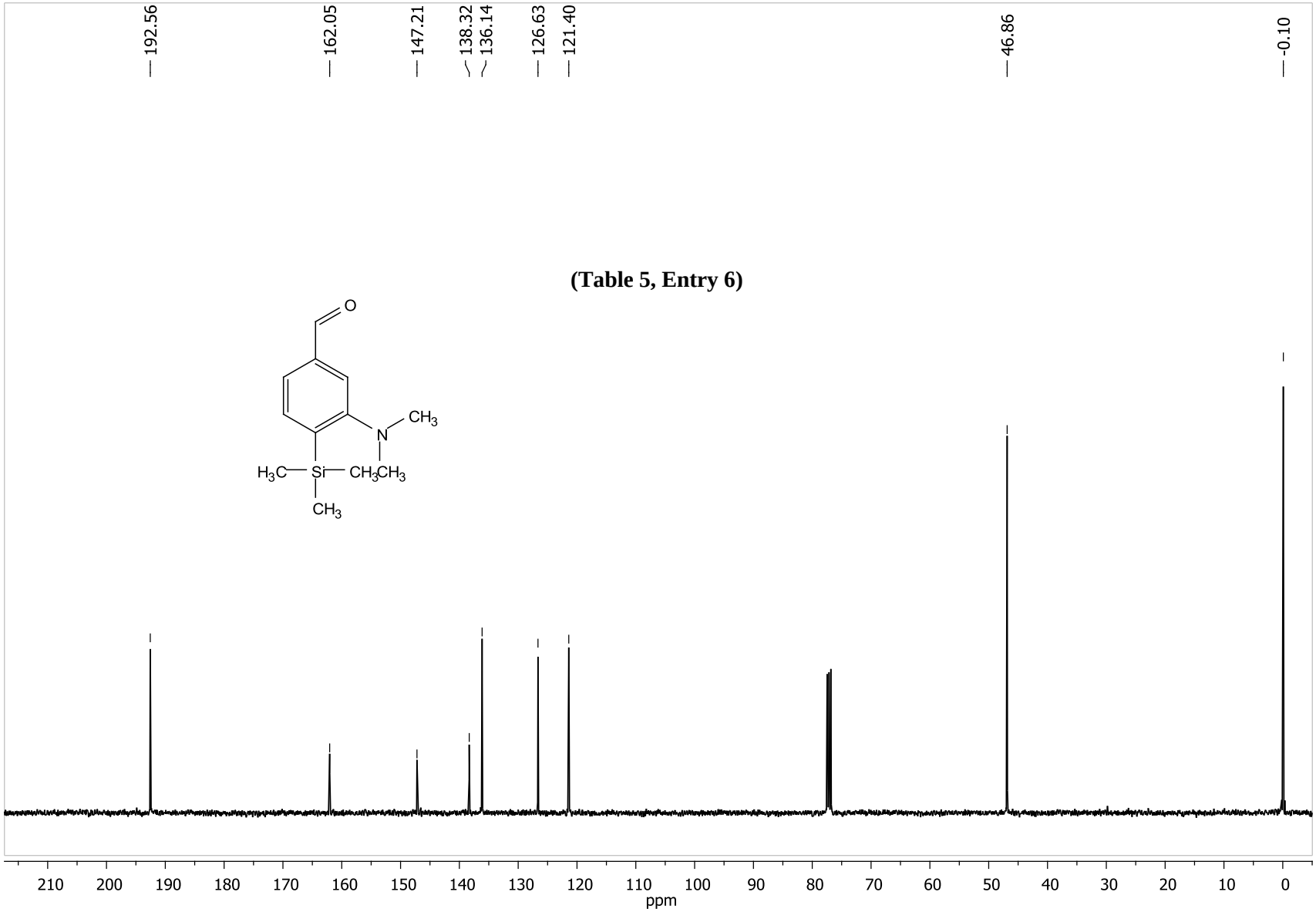
(Table 5, Entry 5)


-56.23
-63.05
CF3
TMS
NMe2
CF3
(Table 5, Entry 5)
3.00
3.00
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

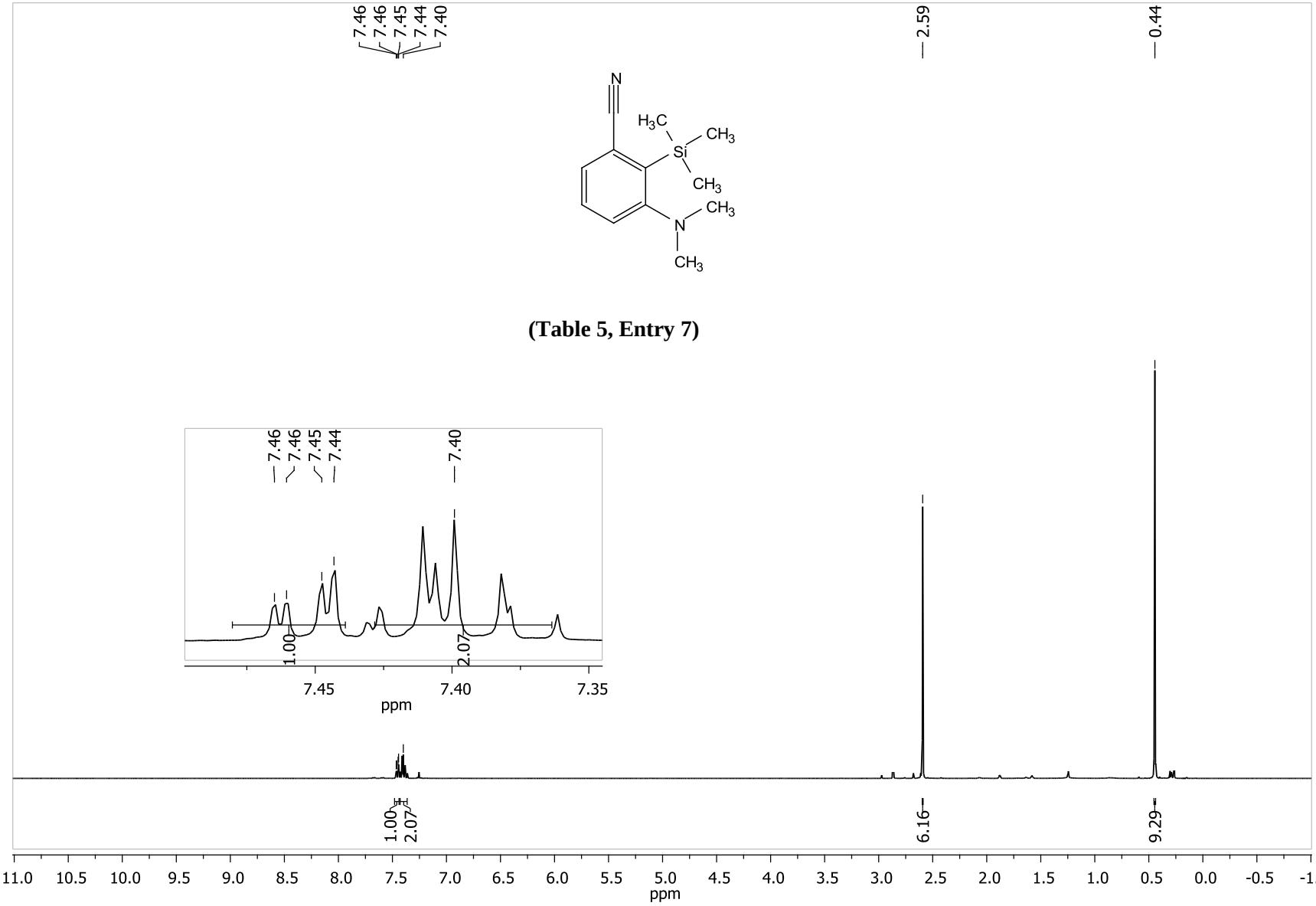

9.90
7.97
7.96
7.83
7.82
7.81
7.80
7.21
7.19
2.74
0.33
(Table 5, Entry 6)
O
CH3
Si
CH3
H3C
N
H3C
CH3
1.00
1.00
1.00
1.00
6.01
9.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


191.75
166.28
138.68
135.89
131.87
131.15
119.66
45.81
0.31
(Table 5, Entry 6)
O
CH3
Si
CH3
H3C
N
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

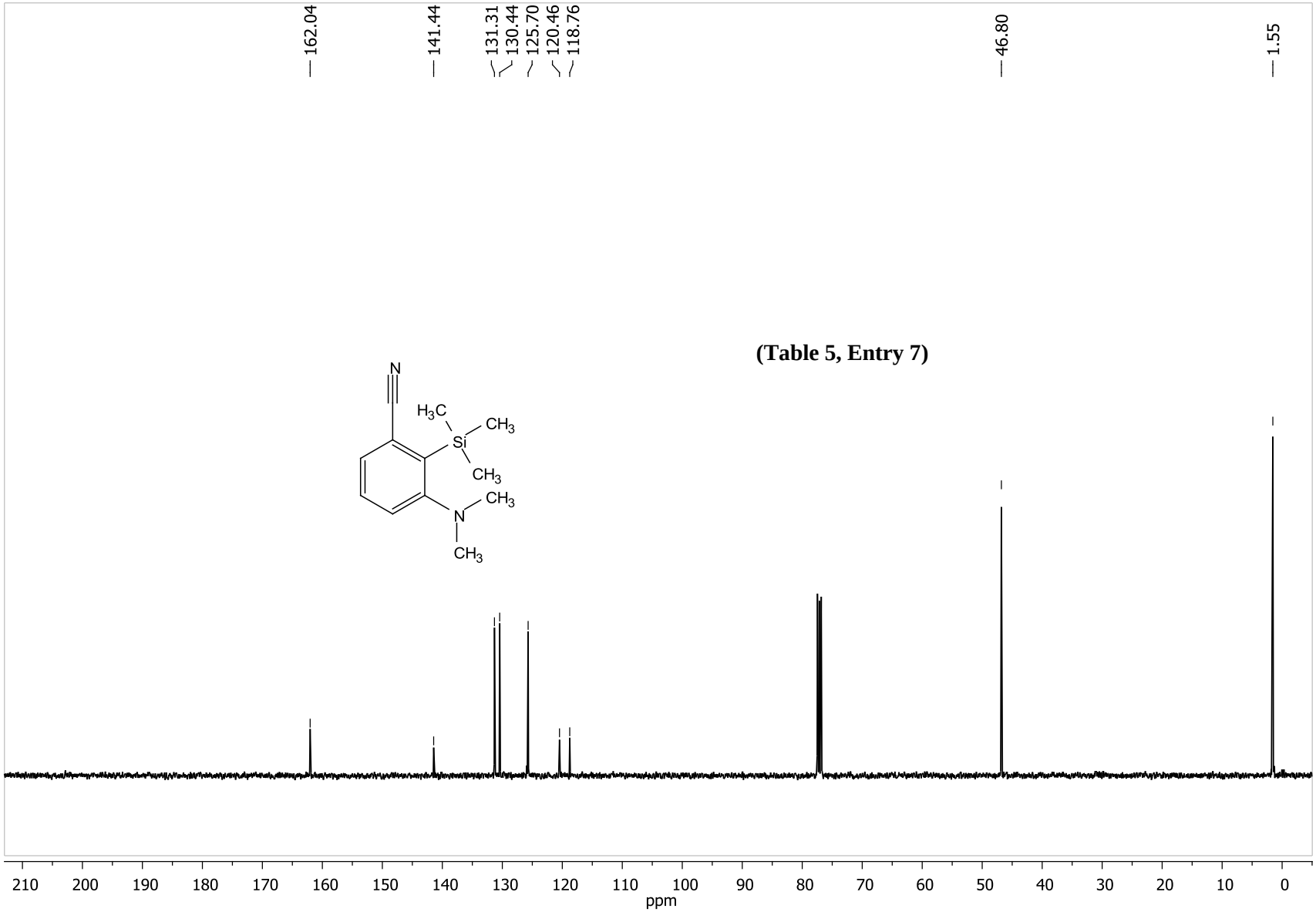

9.98
7.77
7.61
2.64
0.31
(Table 5, Entry 6)
O
CH3
N
H3C
Si
CH3CH3
CH3
1.00
1.00
2.00
6.01
9.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

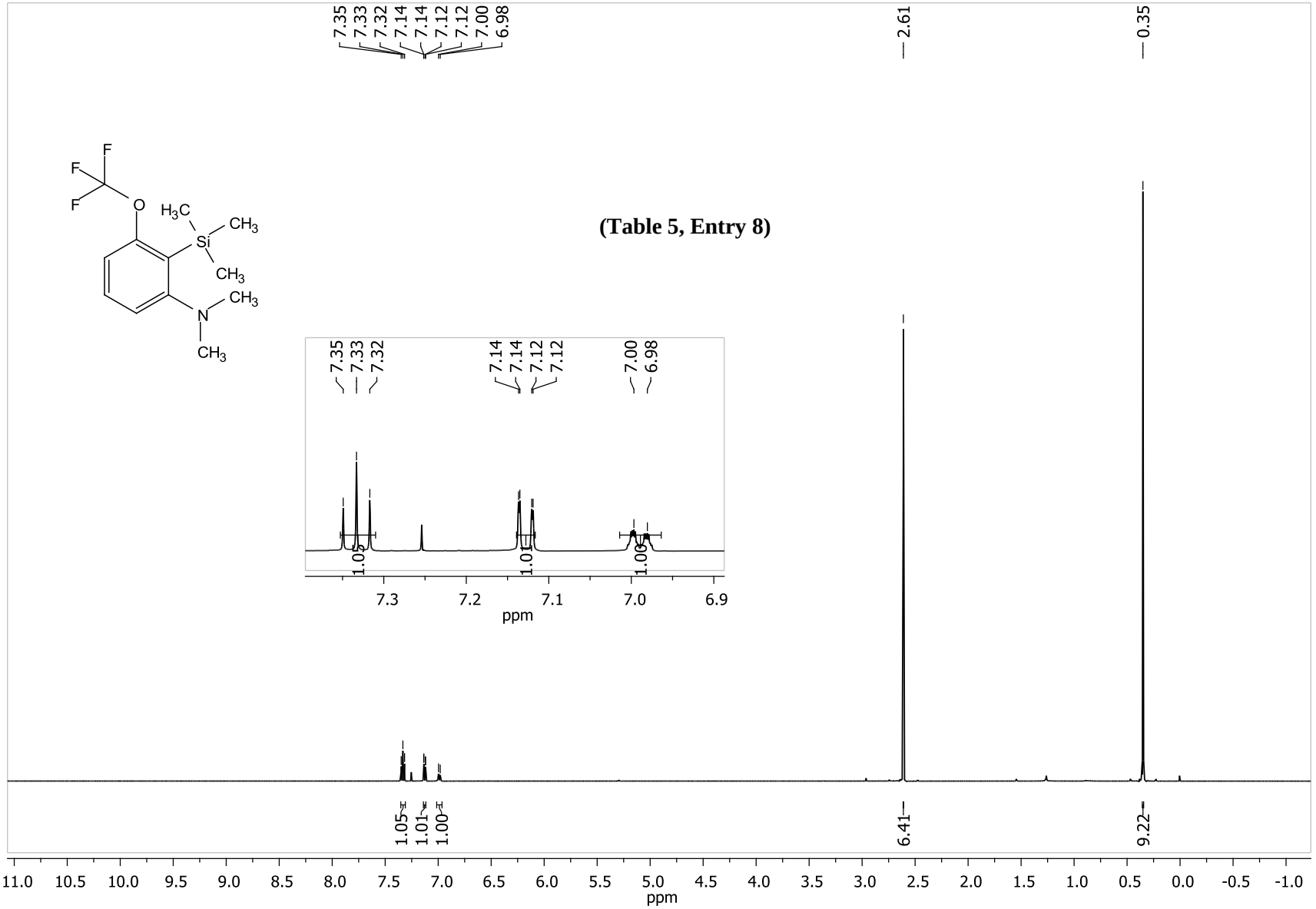


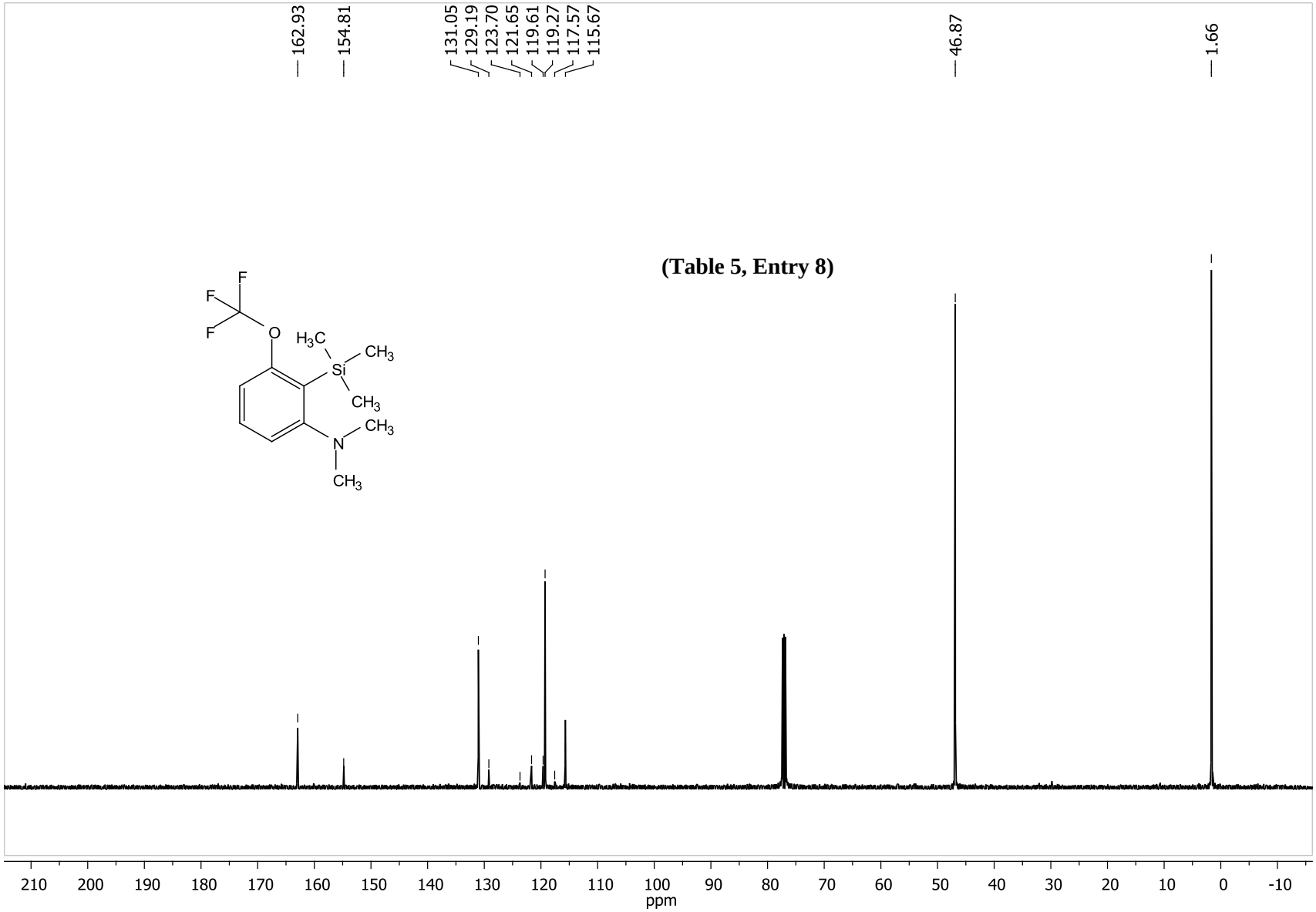
(Table 5, Entry 6)

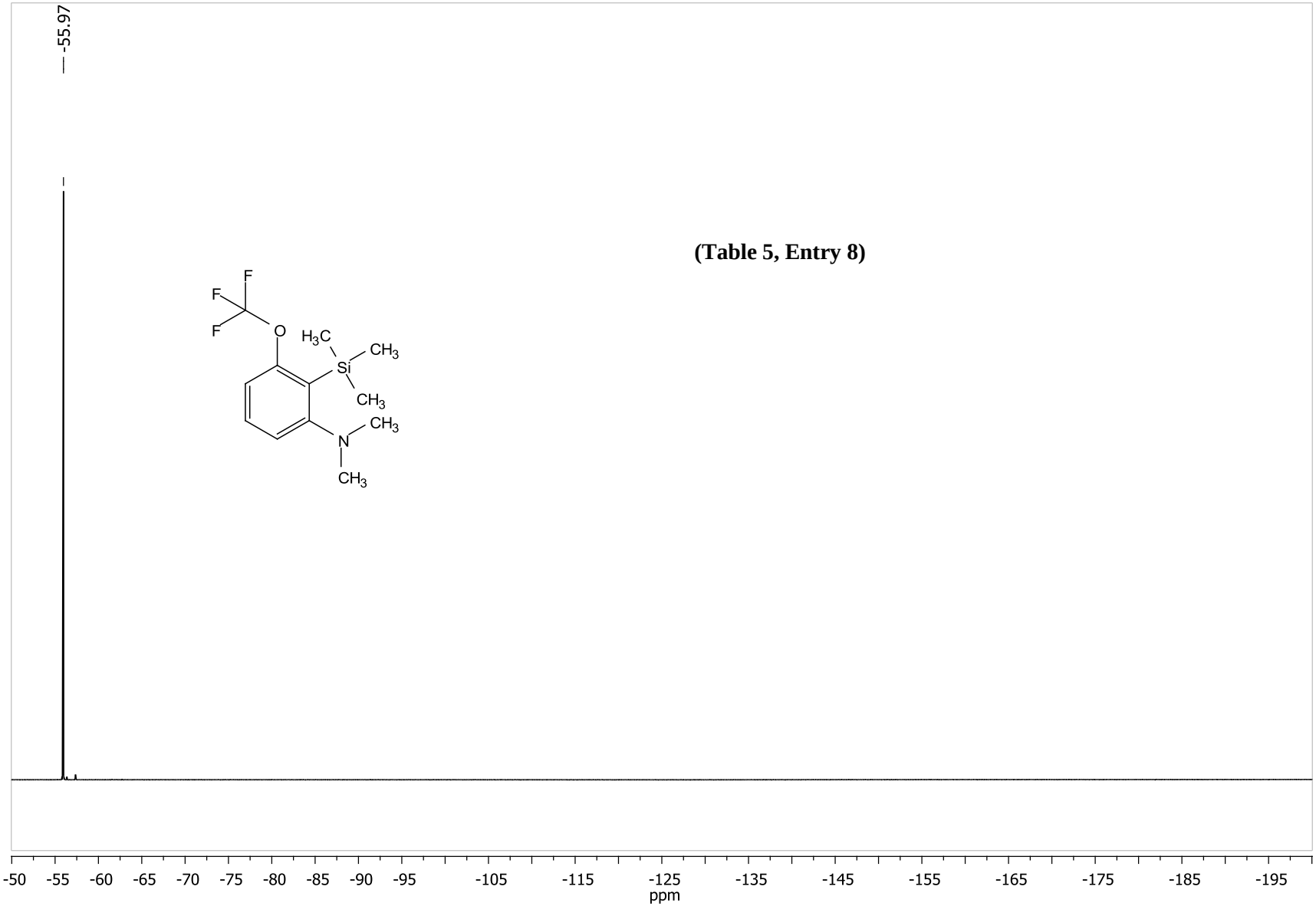


(Table 5, Entry 7)


162.04
141.44
131.31
130.44
125.70
120.46
118.76
46.80
1.55
(Table 5, Entry 7)
N
H3C
CH3
Si
CH3
CH3
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

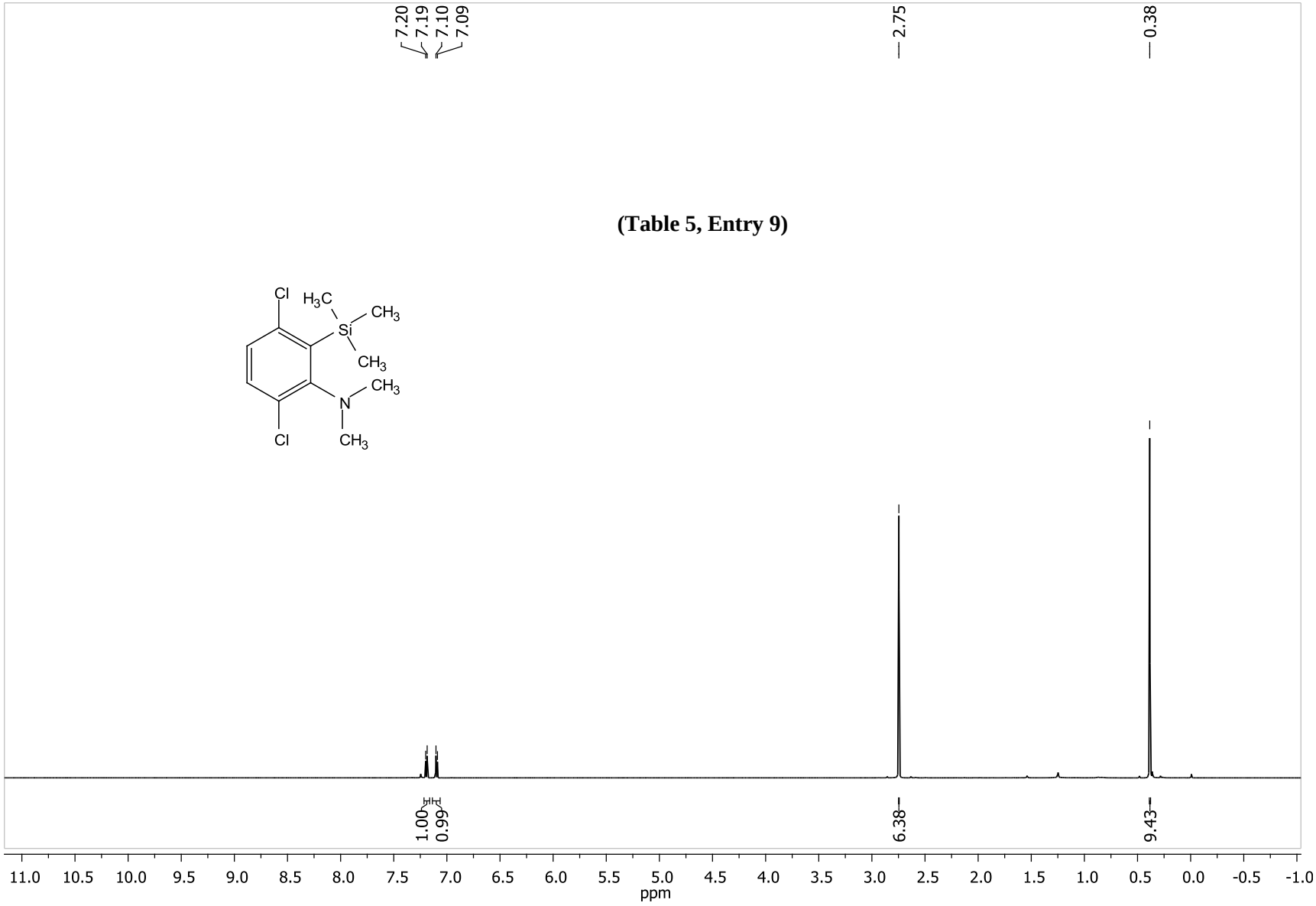

7.35
7.33
7.32
7.14
7.14
7.12
7.12
7.00
6.98
2.61
0.35
F
F
F
O
H3C
Si
CH3
CH3
N
CH3
CH3
(Table 5, Entry 8)
1.05
1.01
1.00
7.3
7.2
7.1
7.0
6.9
ppm
6.41
9.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm

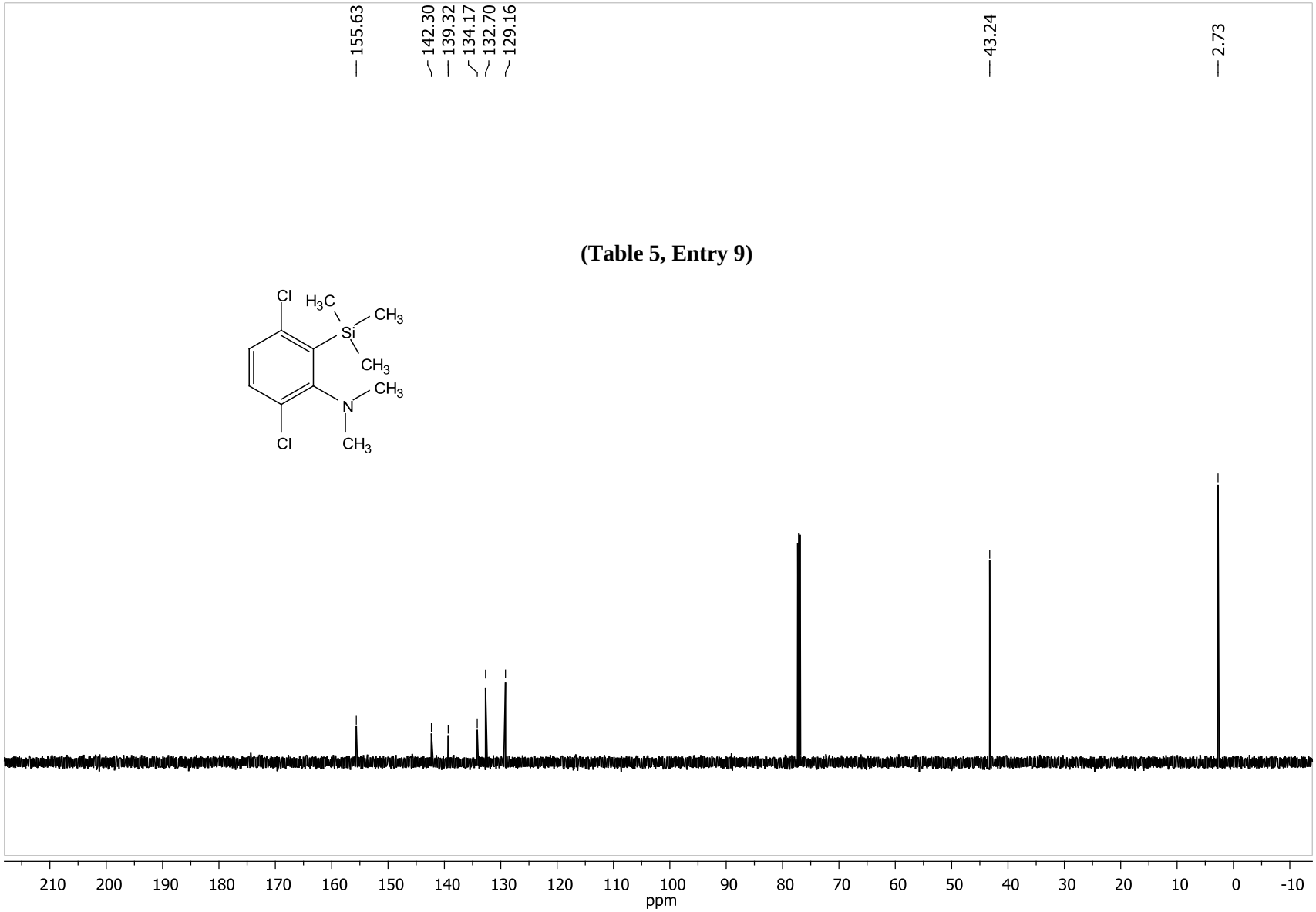

162.93
154.81
131.05
129.19
123.70
121.65
119.61
119.27
117.57
115.67
46.87
1.66
(Table 5, Entry 8)
F
F
F
O
H3C
CH3
Si
CH3
CH3
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



(Table 5, Entry 8)

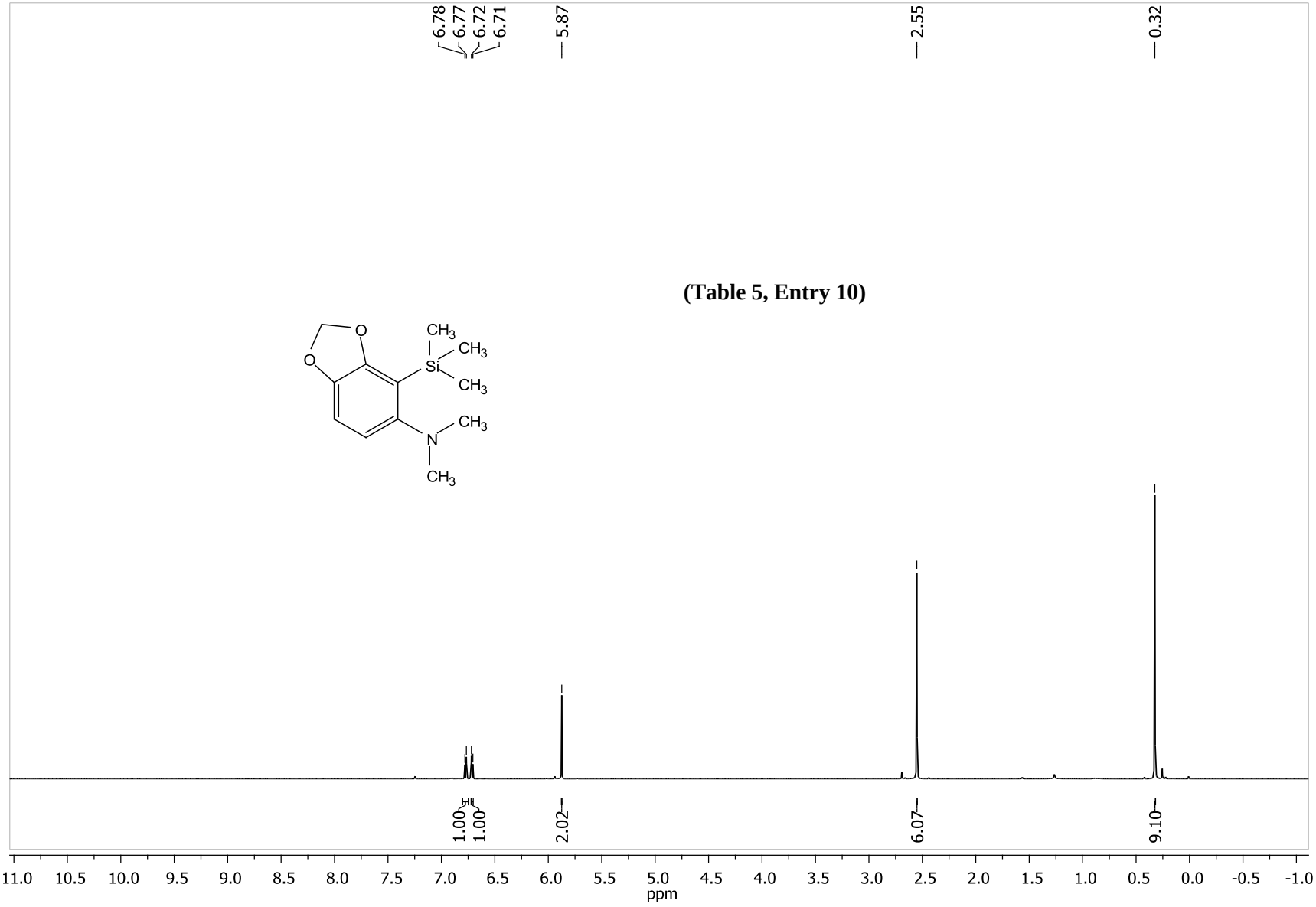
(Table 5, Entry 9)

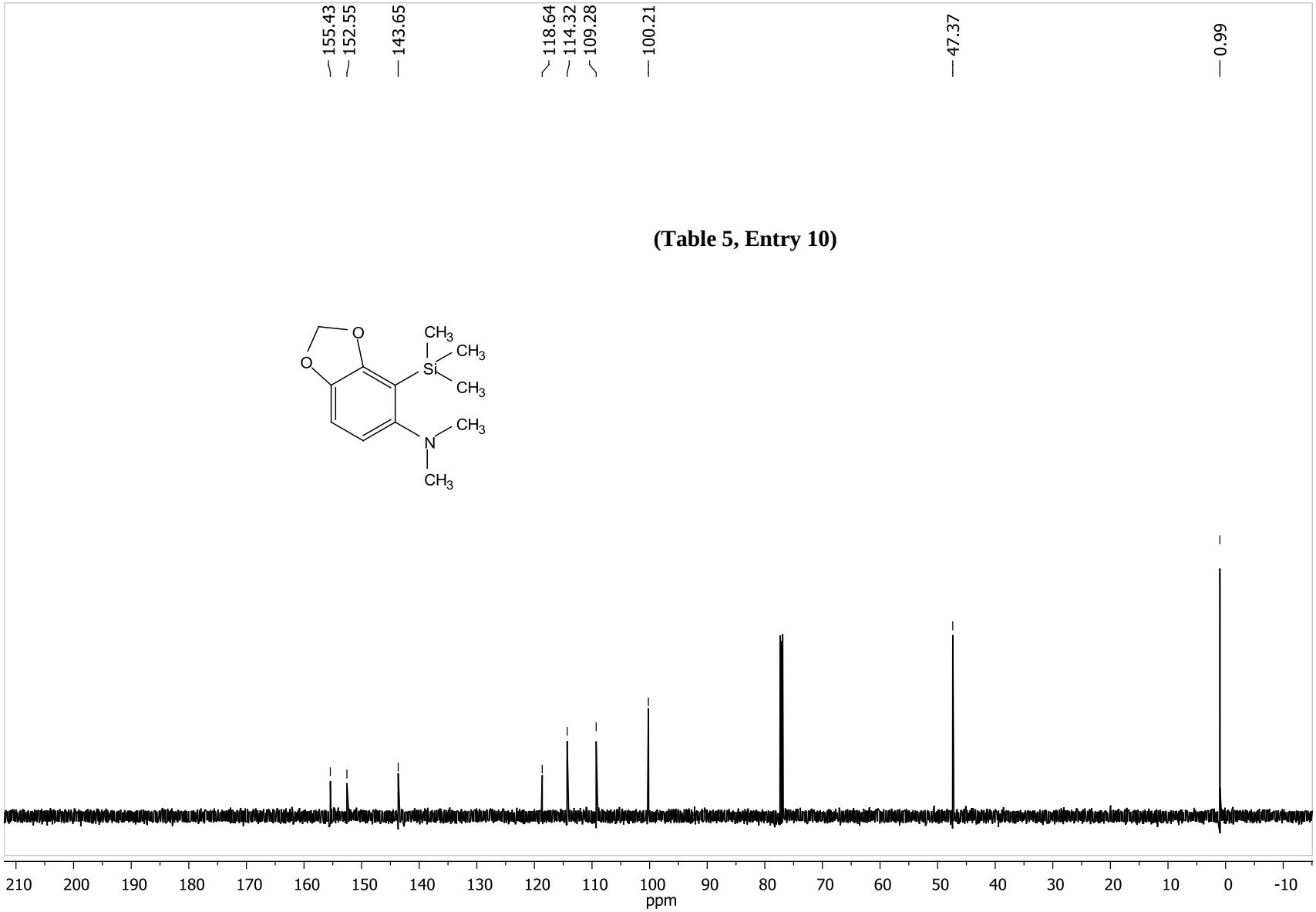




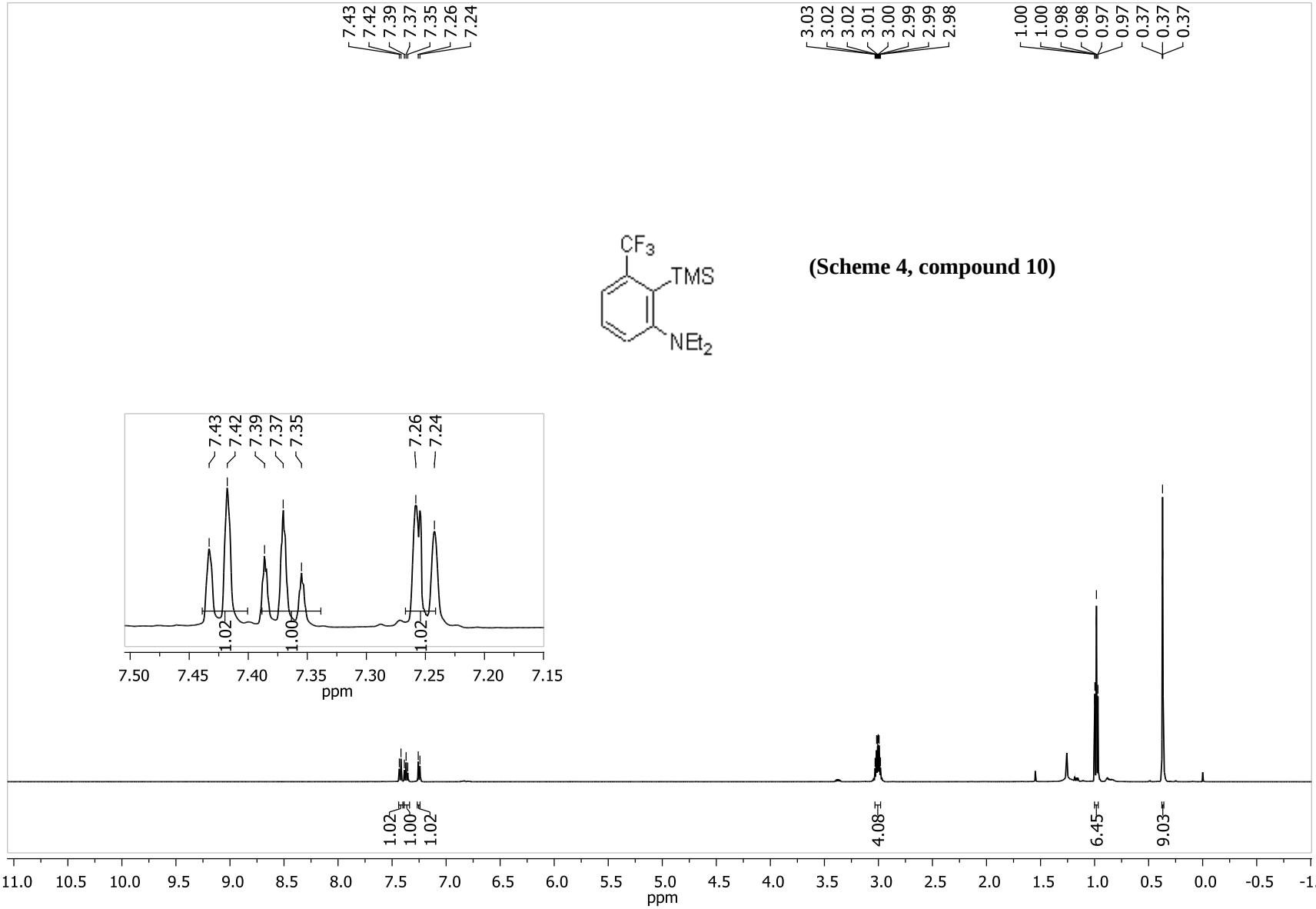
(Table 5, Entry 9)

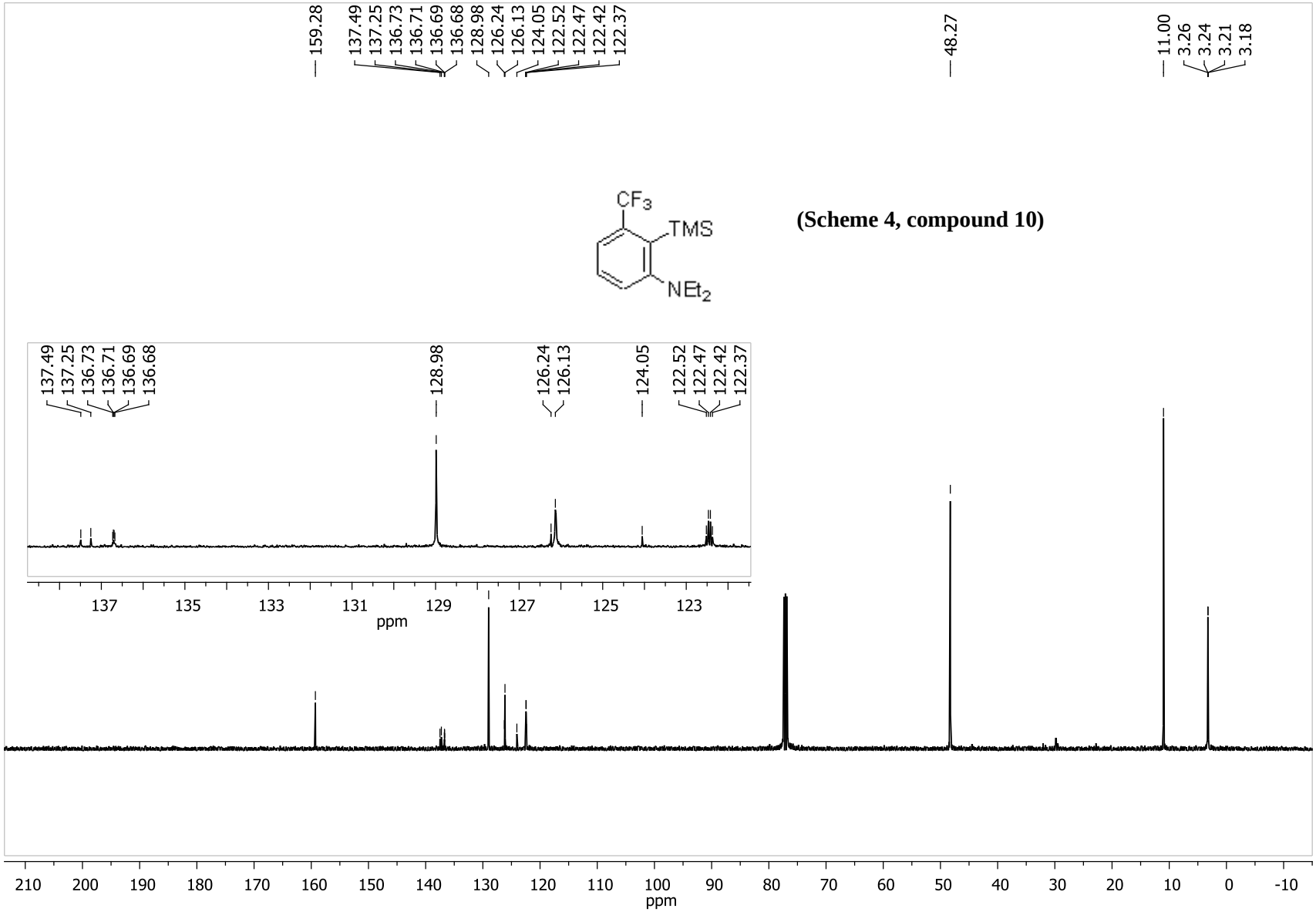
(Table 5, Entry 10)



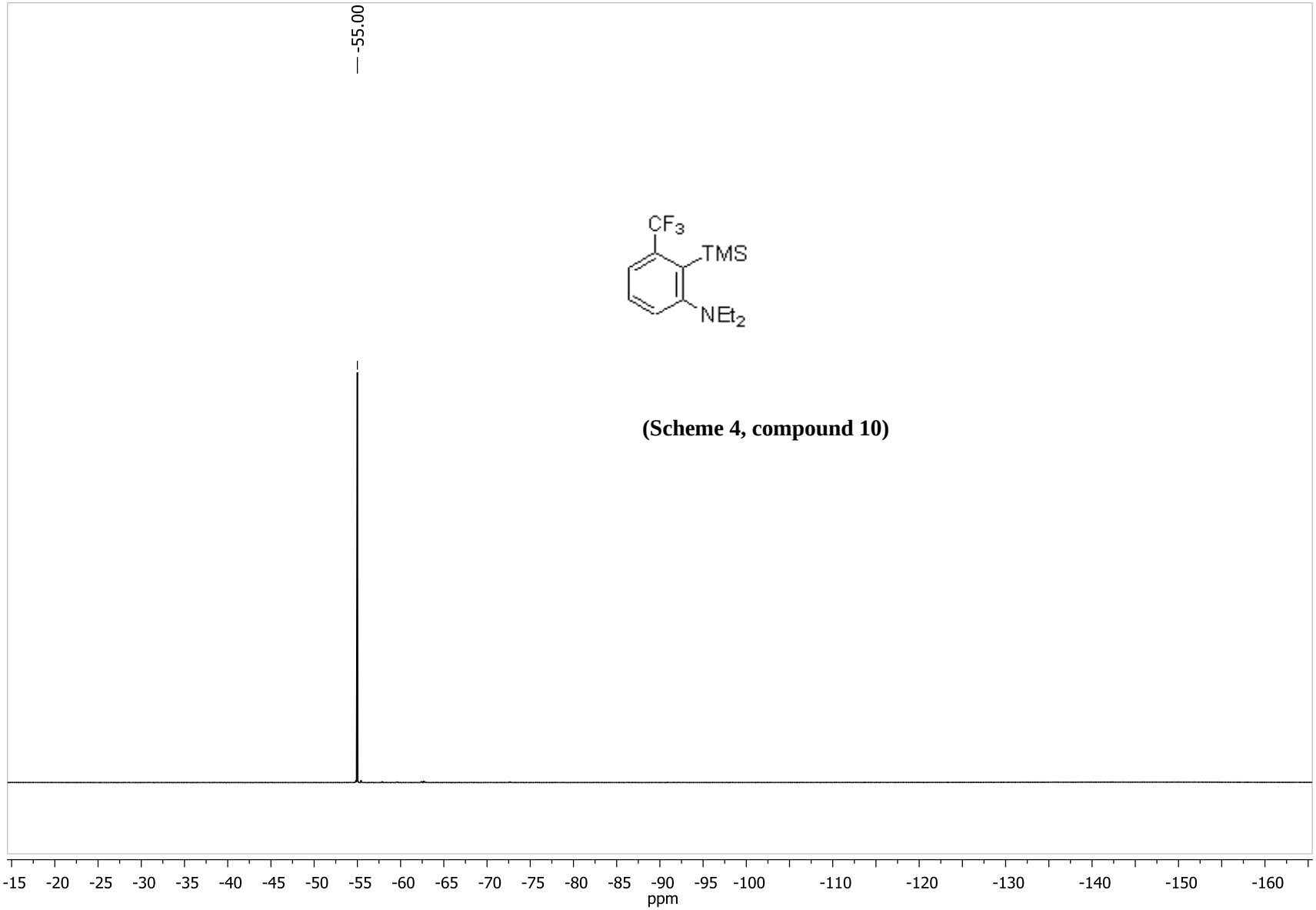


(Table 5, Entry 10)

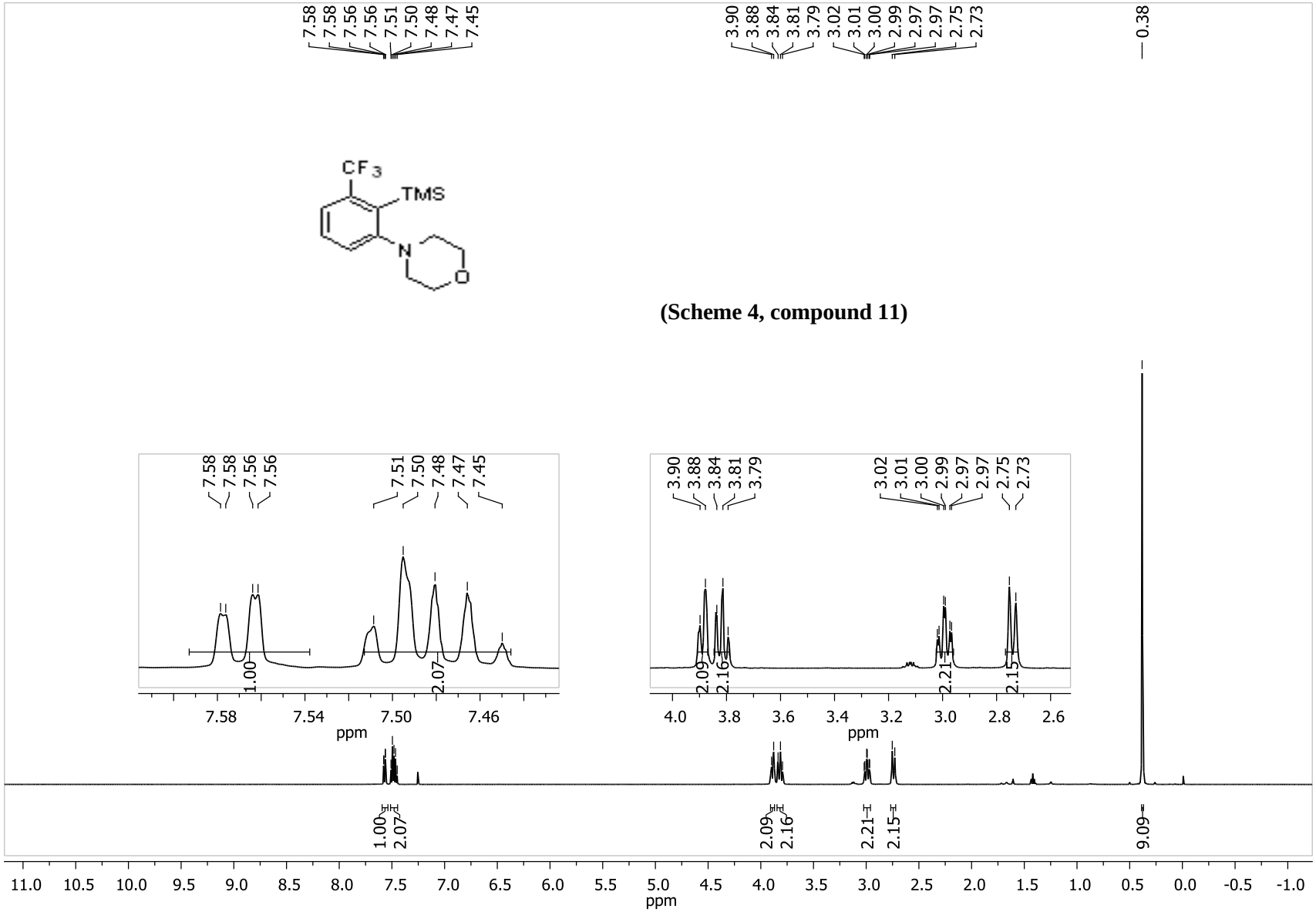

7.43
7.42
7.39
7.37
7.35
7.26
7.24
3.03
3.02
3.02
3.01
3.00
2.99
2.99
2.98
1.00
1.00
0.98
0.98
0.97
0.97
0.37
0.37
0.37
CF3
TMS
NEt2
(Scheme 4, compound 10)
1.02
1.00
1.02
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
ppm
1.02
1.00
1.02
4.08
6.45
9.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm



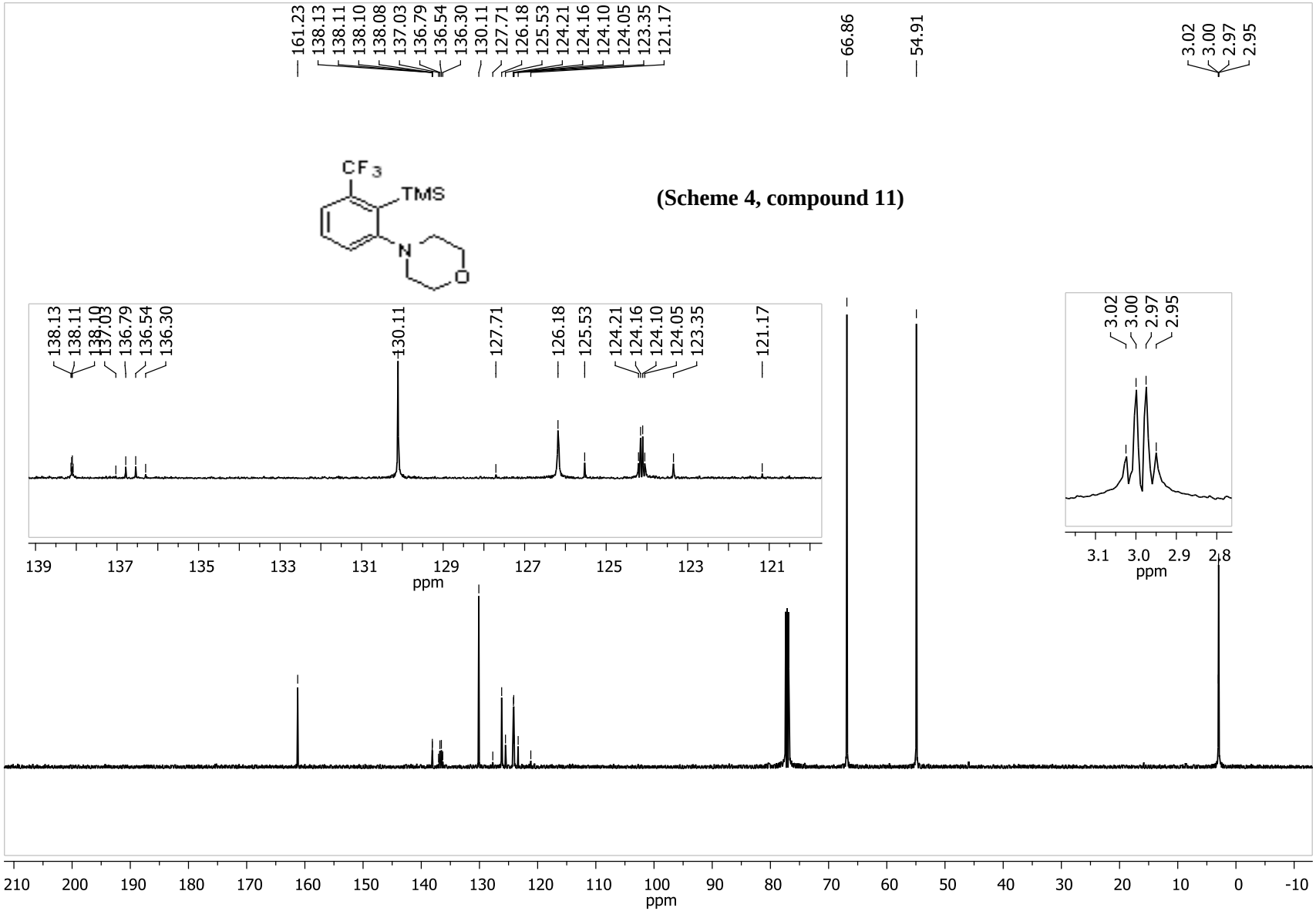
(Scheme 4, compound 10)



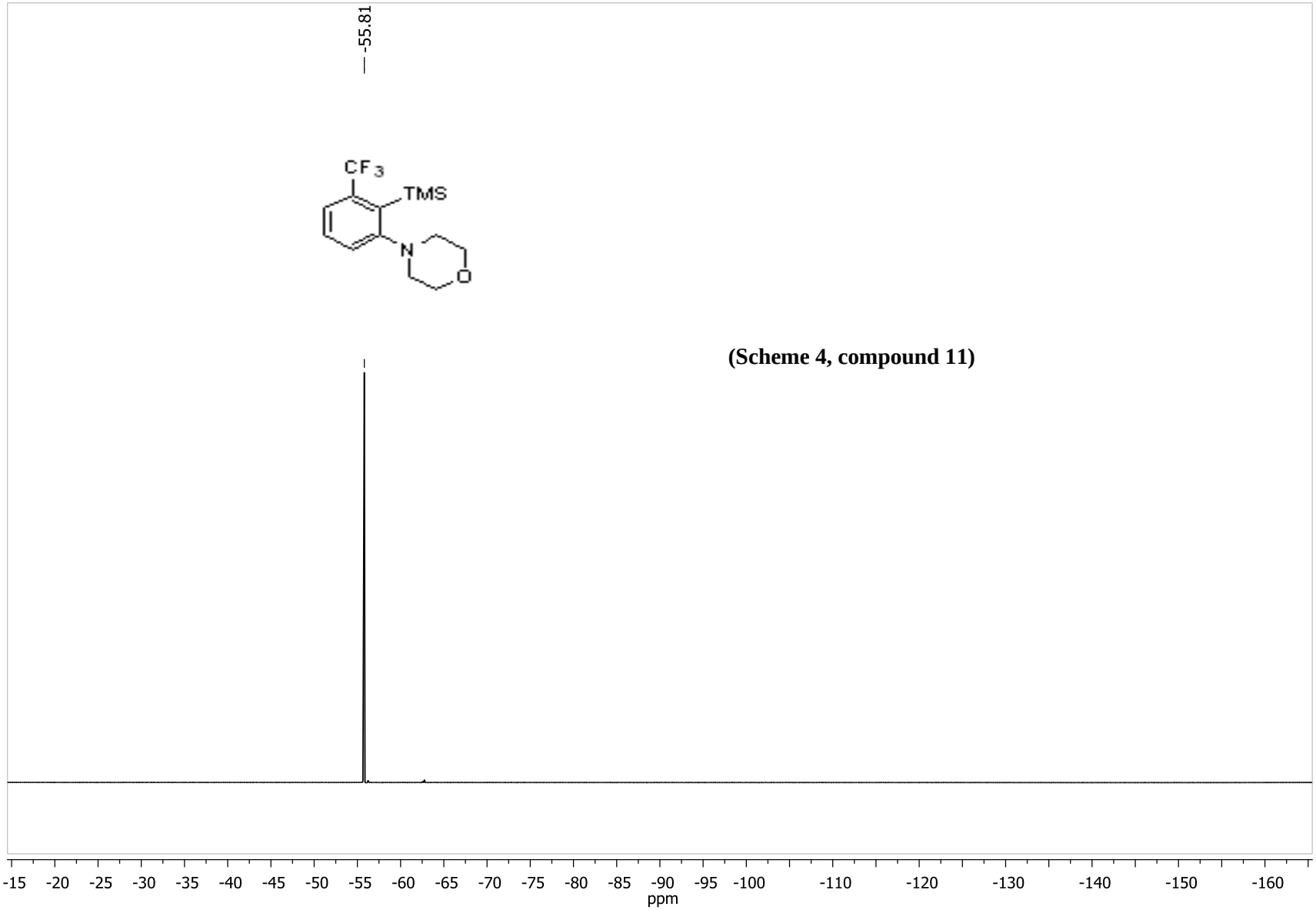
(Scheme 4, compound 10)



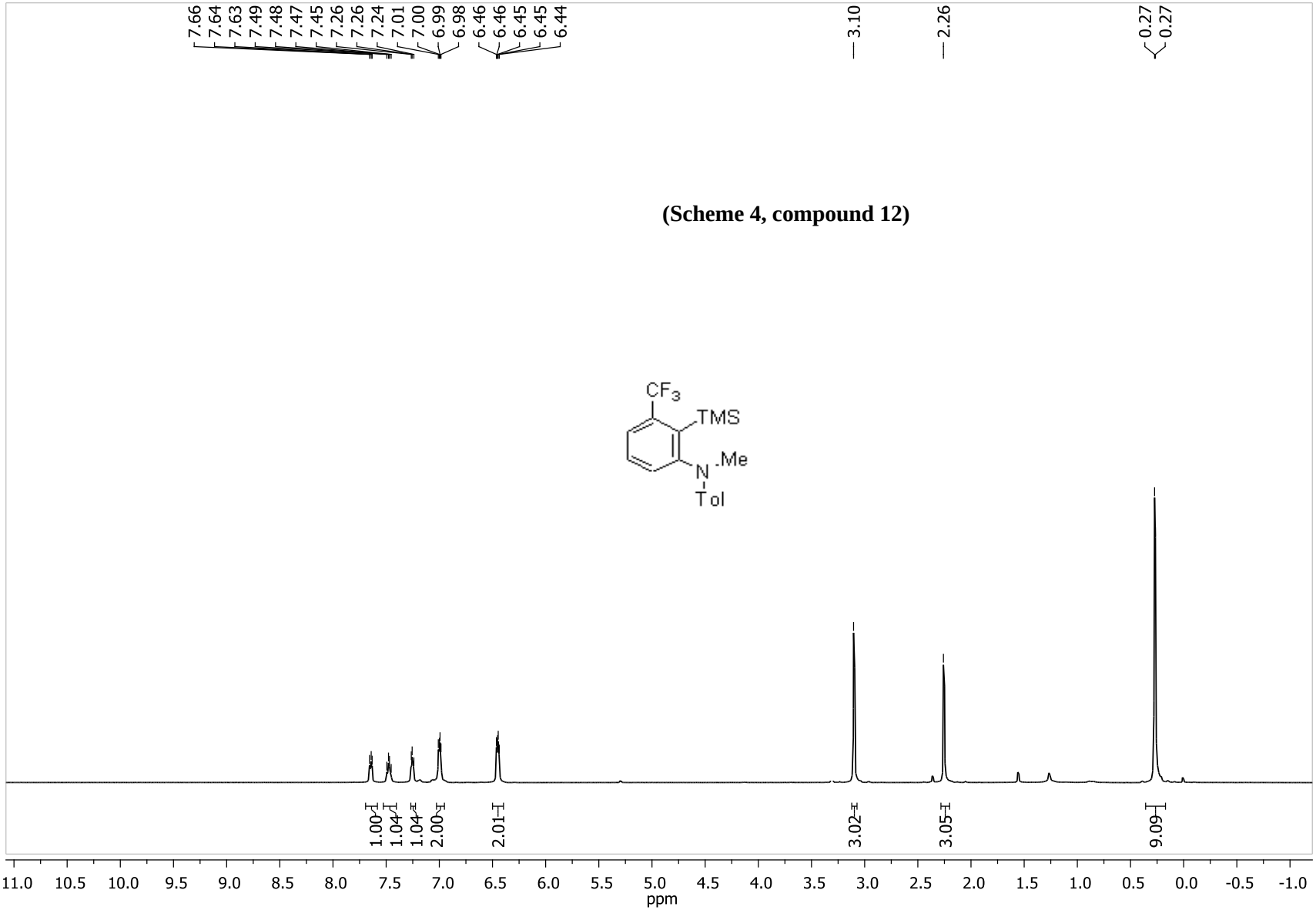
(Scheme 4, compound 11)



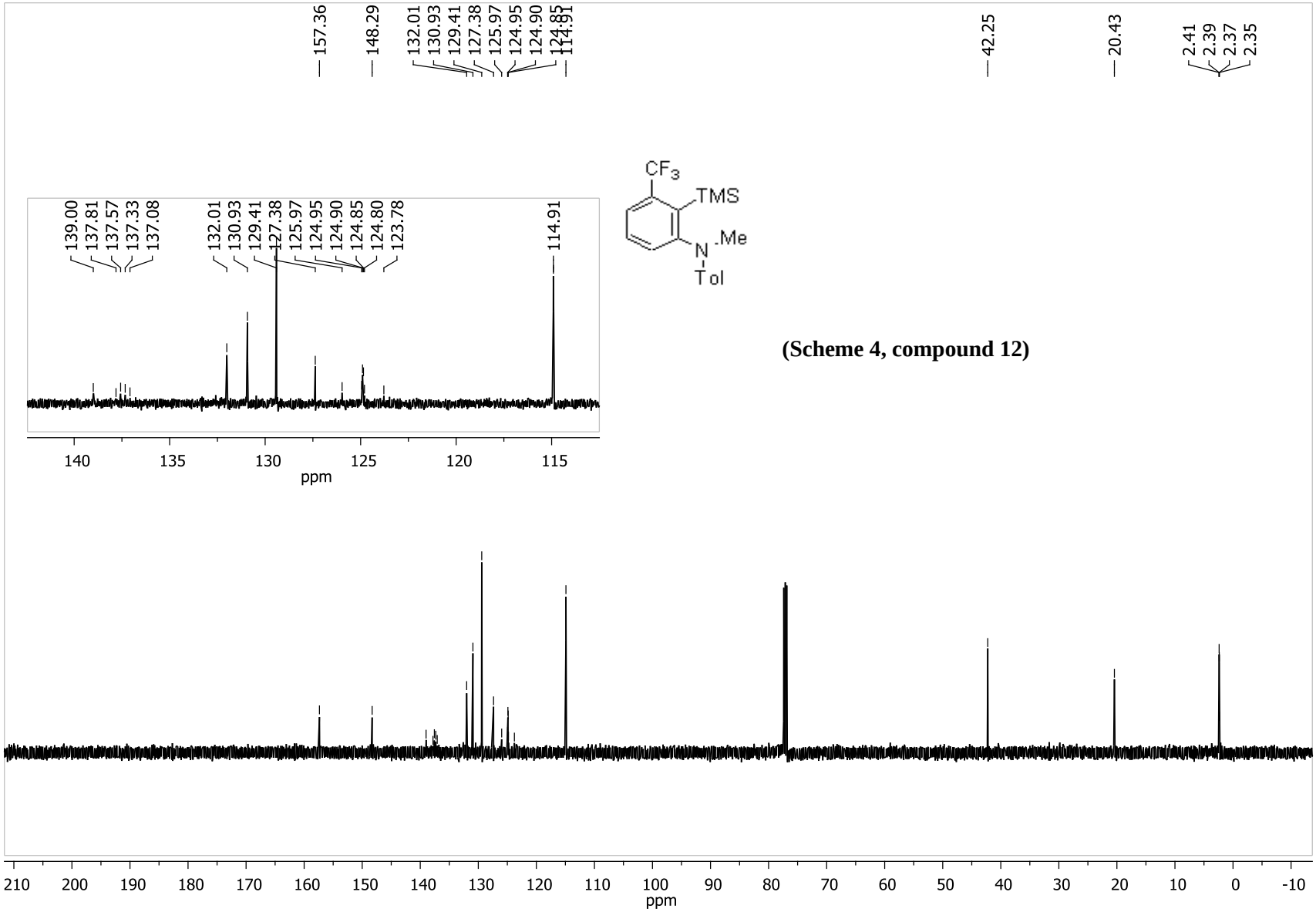
(Scheme 4, compound 11)



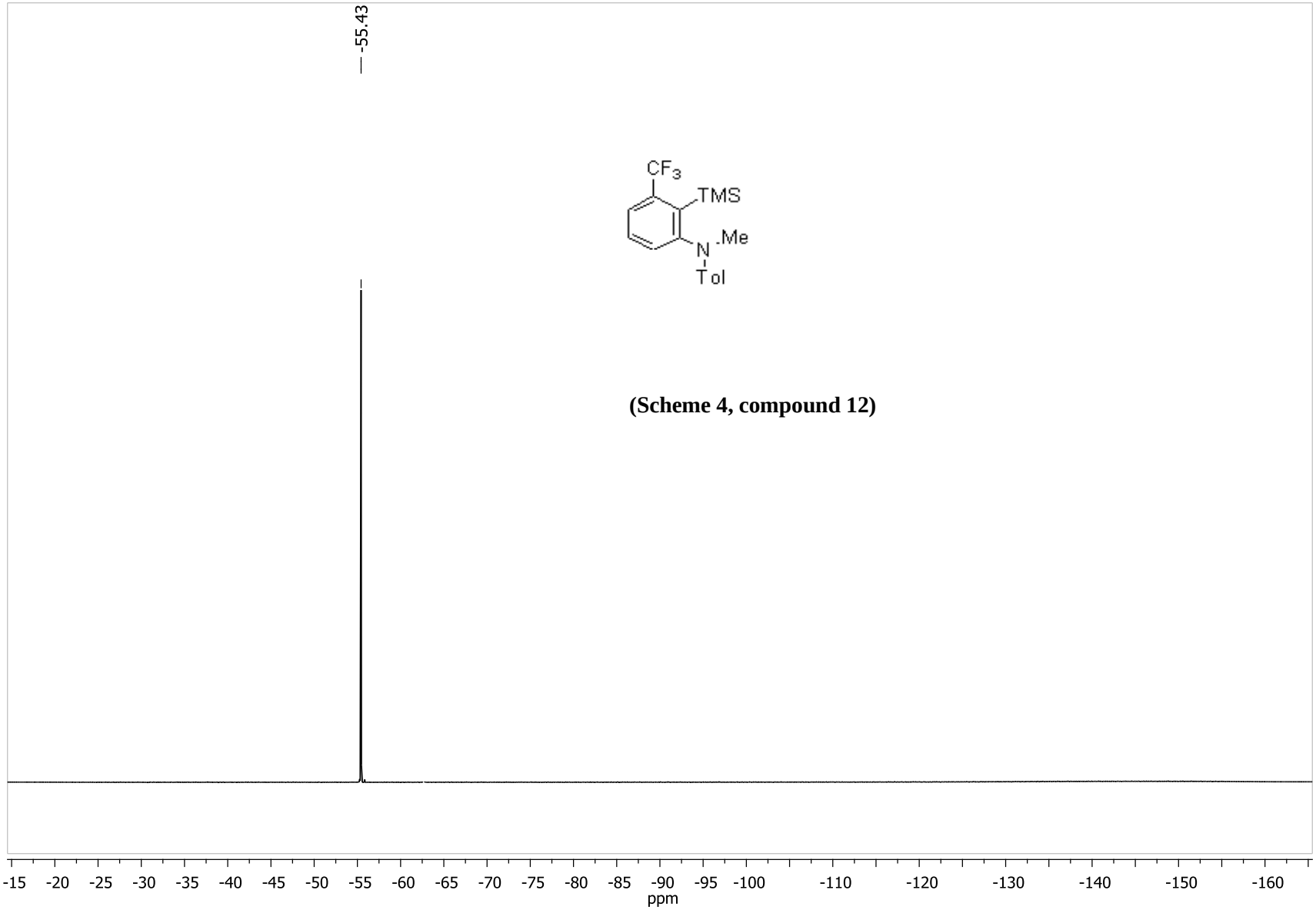
(Scheme 4, compound 11)



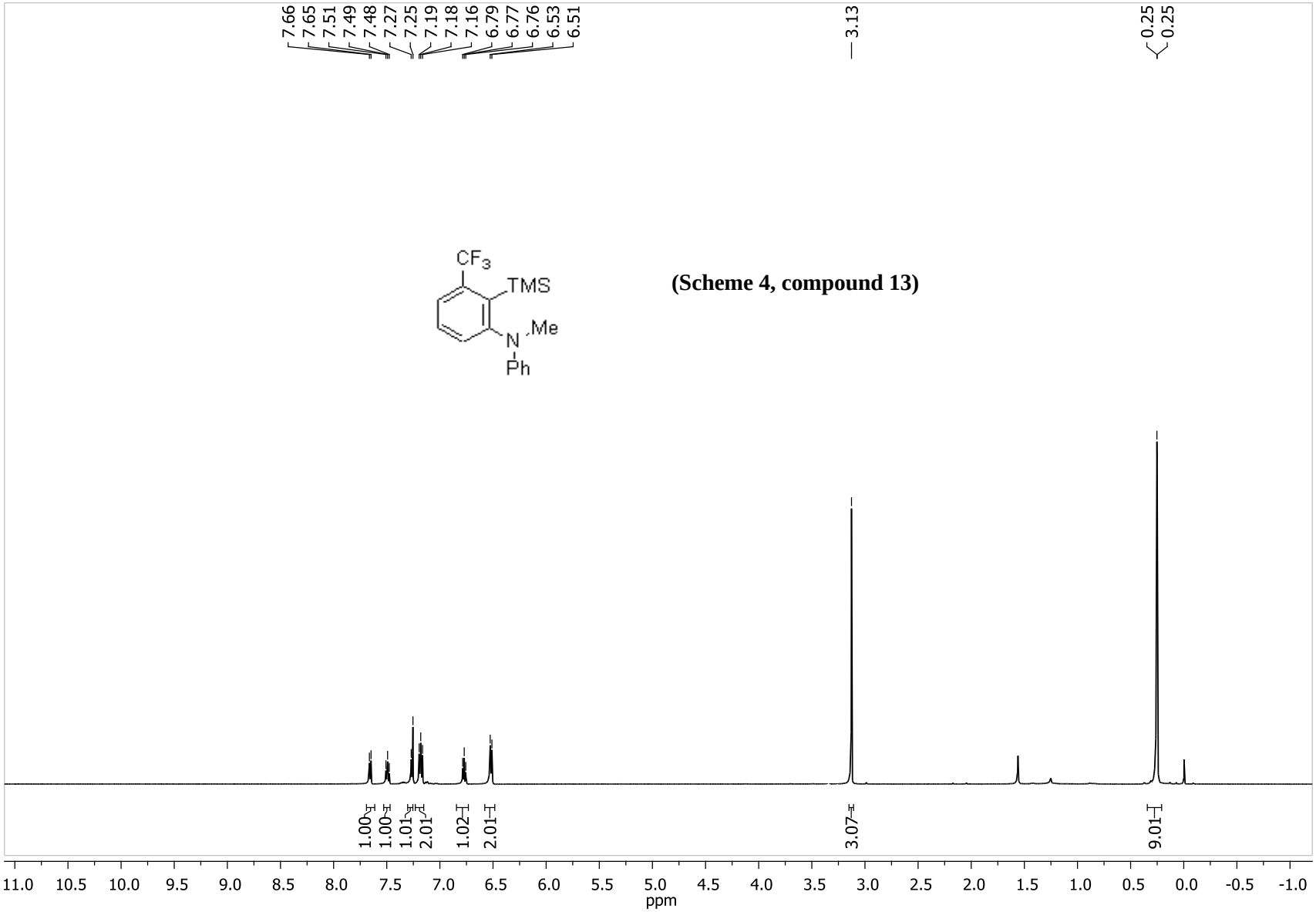
(Scheme 4, compound 12)



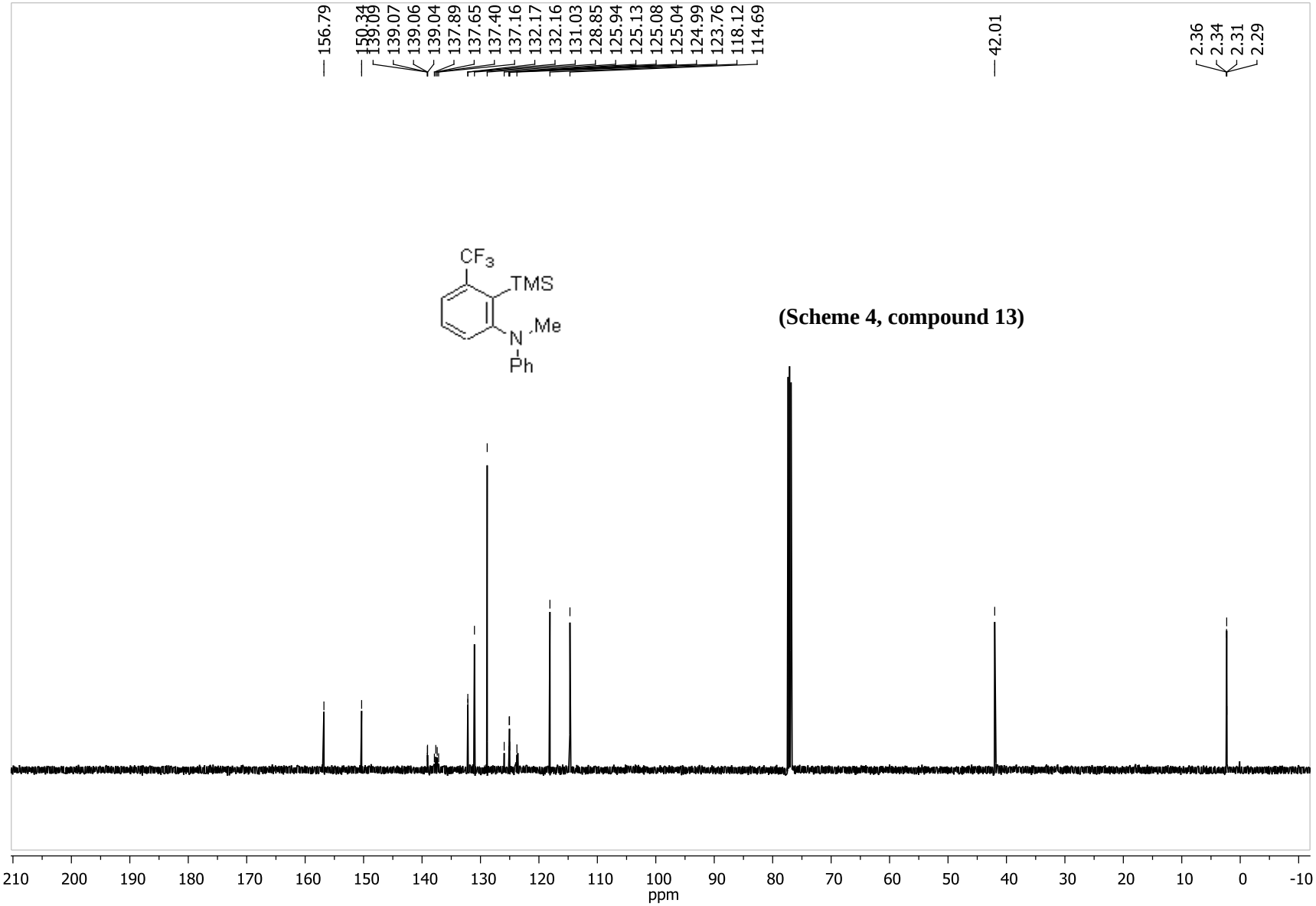
(Scheme 4, compound 12)

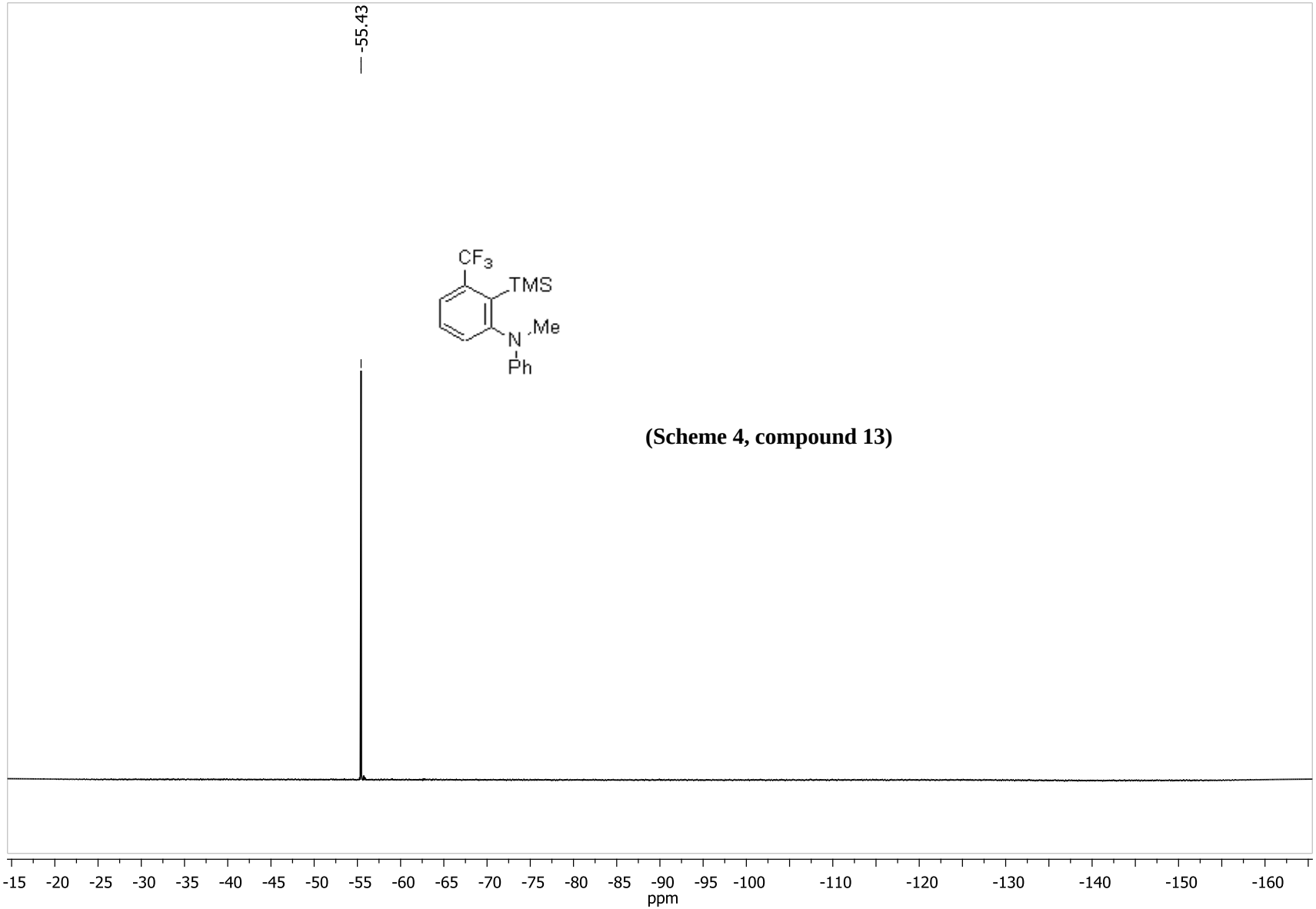


(Scheme 4, compound 12)

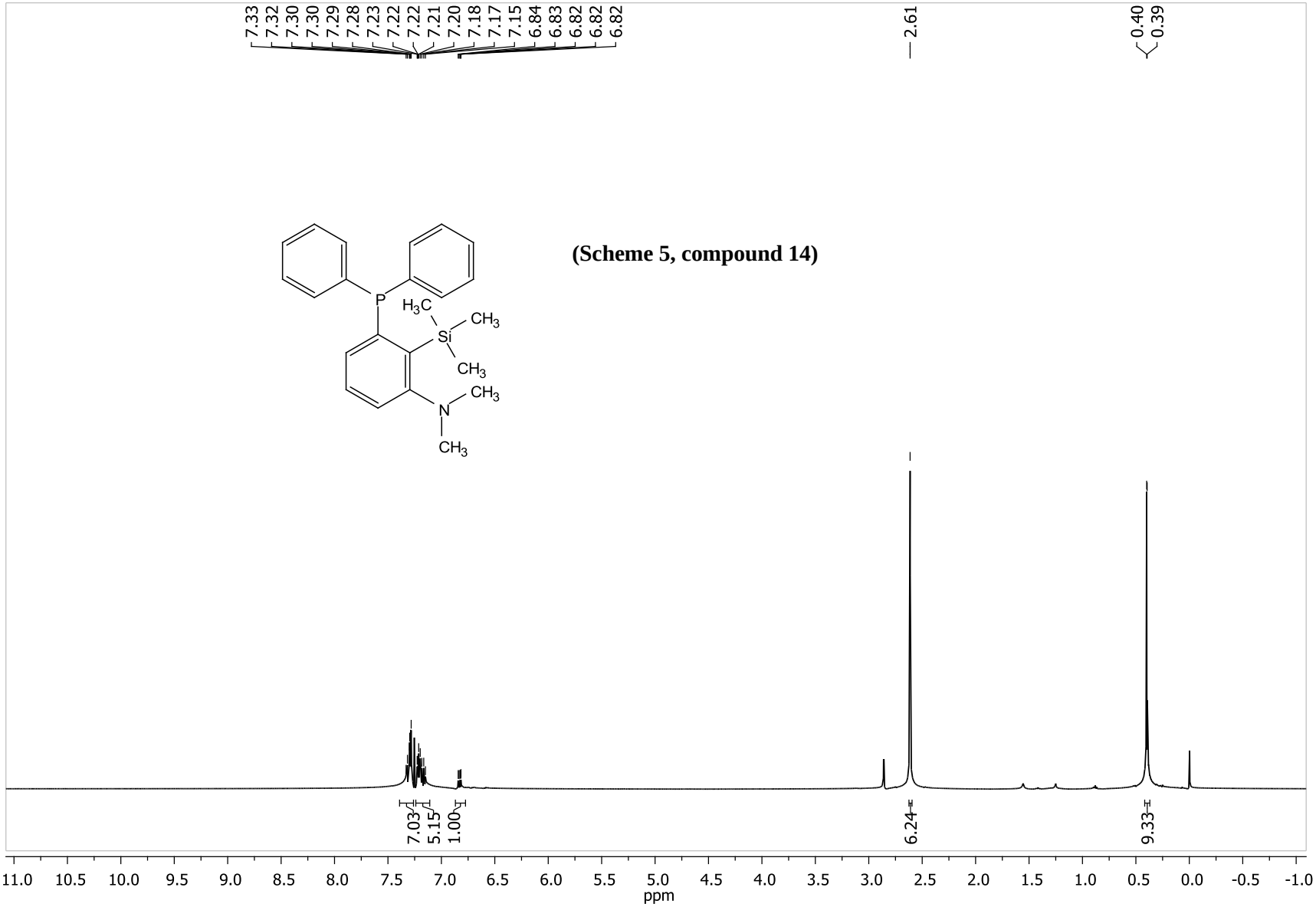


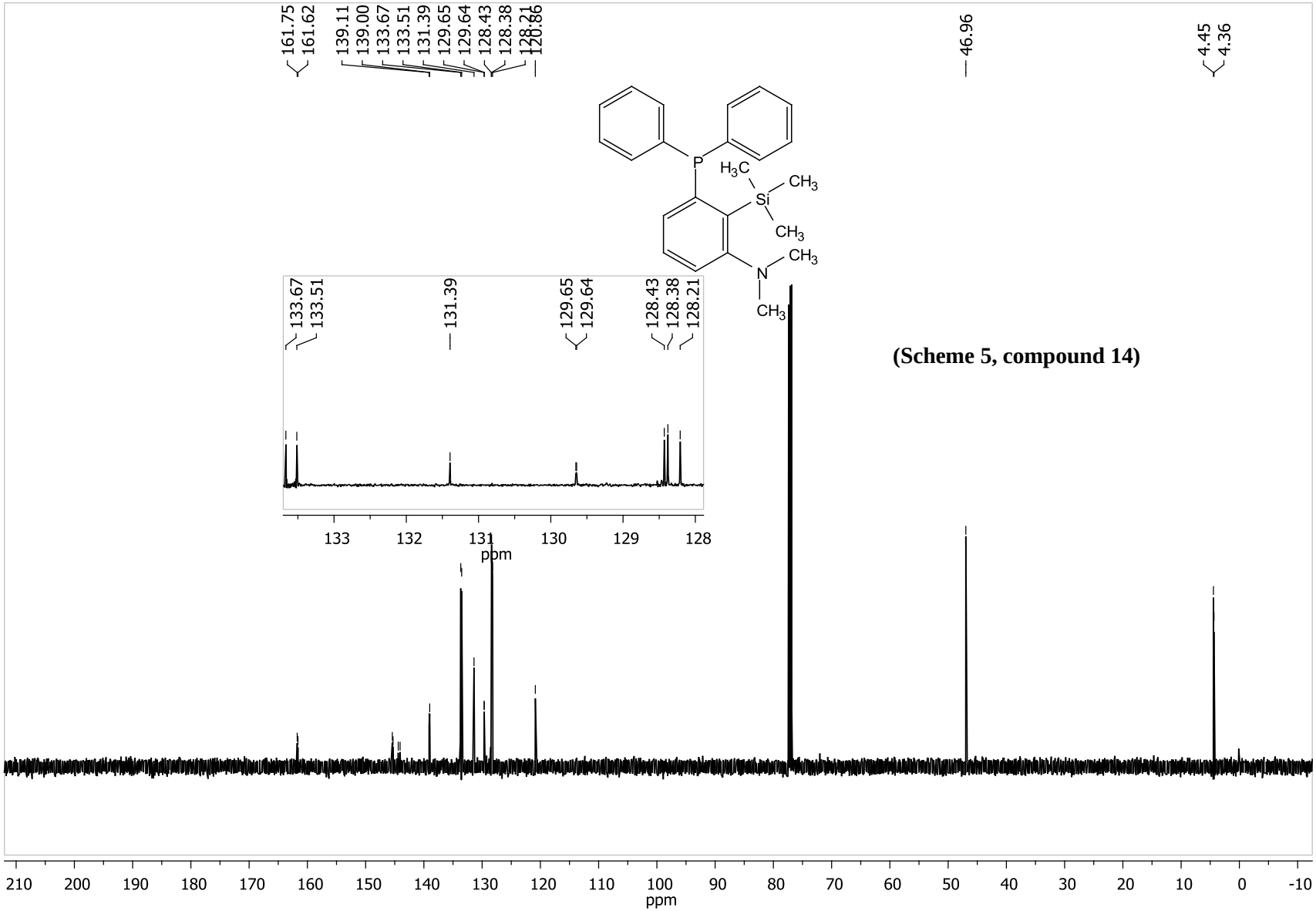
(Scheme 4, compound 13)

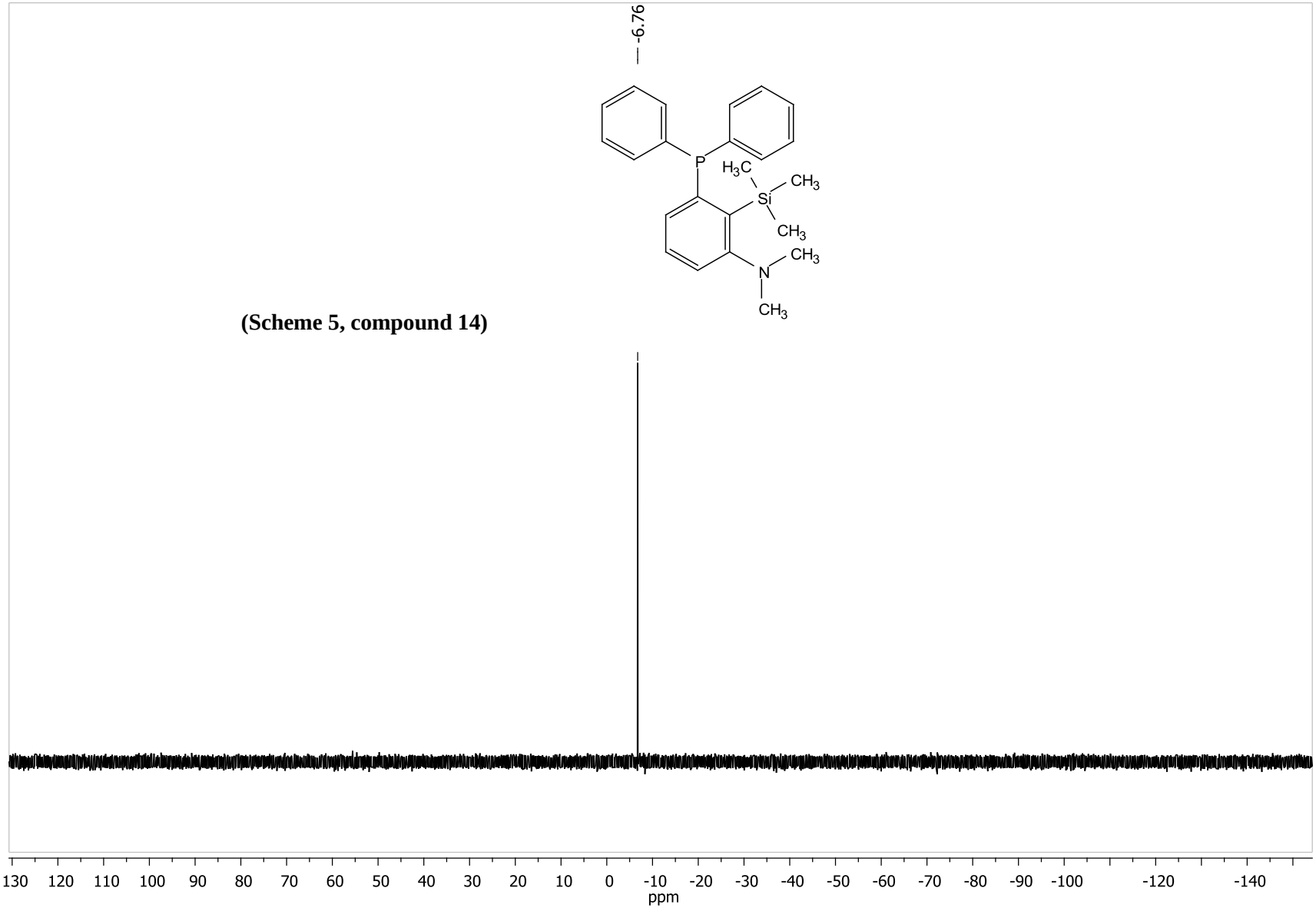

156.79
150.34
139.09
139.07
139.06
139.04
137.89
137.65
137.40
137.16
132.17
132.16
131.03
128.85
125.94
125.13
125.08
125.04
124.99
123.76
118.12
114.69
42.01
2.36
2.34
2.31
2.29
CF3
TMS
N
Me
Ph
(Scheme 4, compound 13)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm



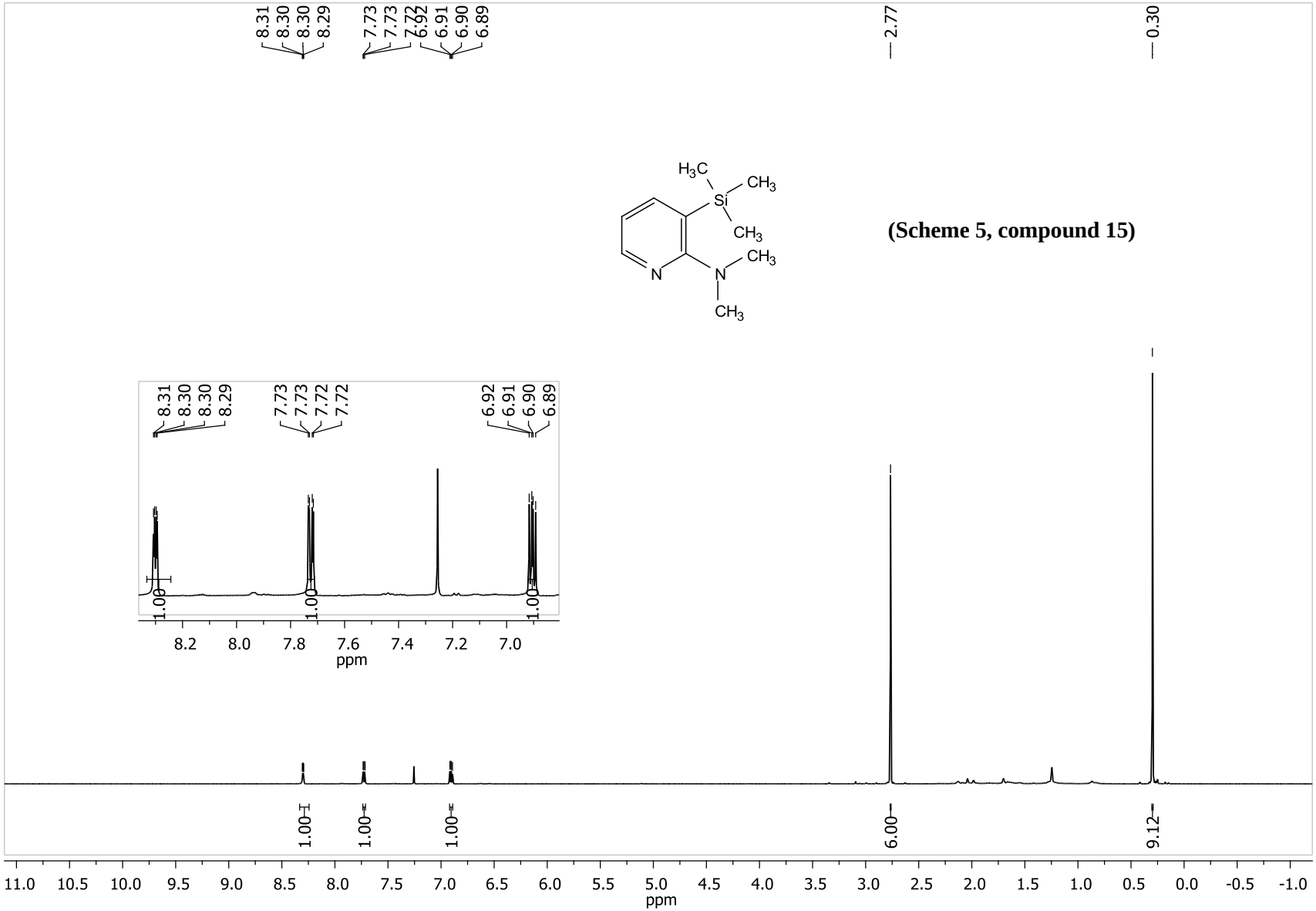
(Scheme 4, compound 13)

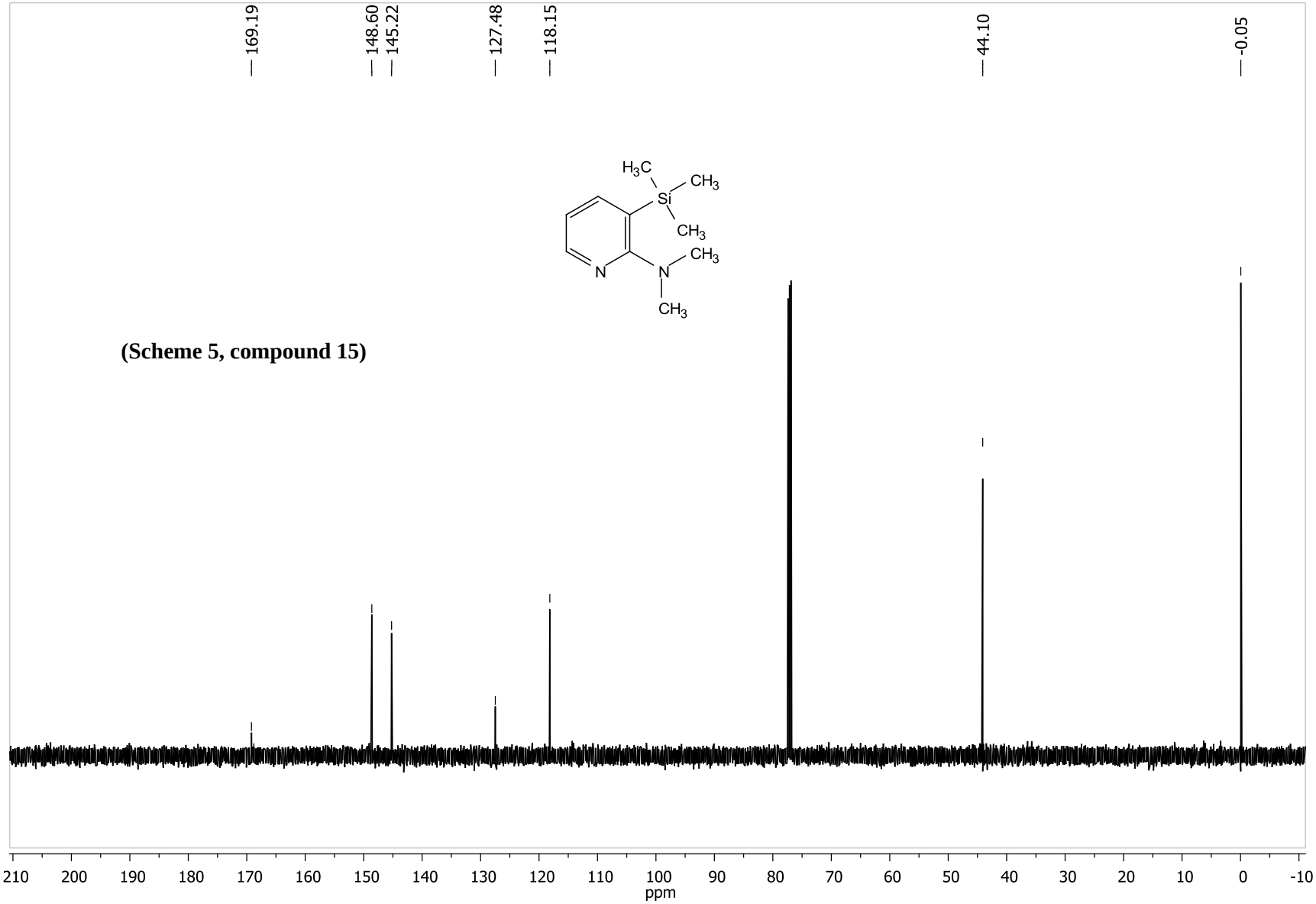

7.33
7.32
7.30
7.30
7.29
7.28
7.23
7.22
7.22
7.21
7.20
7.18
7.17
7.15
6.84
6.83
6.82
6.82
6.82
2.61
0.40
0.39
P
H3C
CH3
Si
CH3
CH3
N
CH3
(Scheme 5, compound 14)
7.03
5.15
1.00
6.24
9.33
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


161.75
161.62
139.11
139.00
133.67
133.51
131.39
129.65
129.64
128.43
128.38
128.21
120.86
46.96
4.45
4.36
P
H3C
CH3
Si
CH3
CH3
N
CH3
133.67
133.51
131.39
129.65
129.64
128.43
128.38
128.21
133
132
131
130
129
128
ppm
(Scheme 5, compound 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

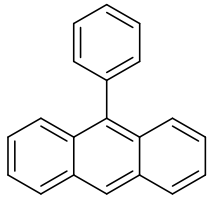


(Scheme 5, compound 14)

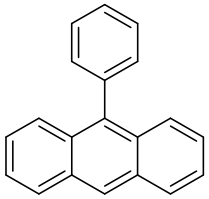

8.31
8.30
8.30
8.29
7.73
7.73
7.72
7.72
6.92
6.91
6.90
6.89
2.77
0.30
H3C
CH3
Si
CH3
CH3
N
N
CH3
(Scheme 5, compound 15)
1.00
1.00
1.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm
1.00
1.00
1.00
6.00
9.12
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm


169.19
148.60
145.22
127.48
118.15
44.10
-0.05
H3C
CH3
Si
CH3
CH3
N
N
CH3
(Scheme 5, 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

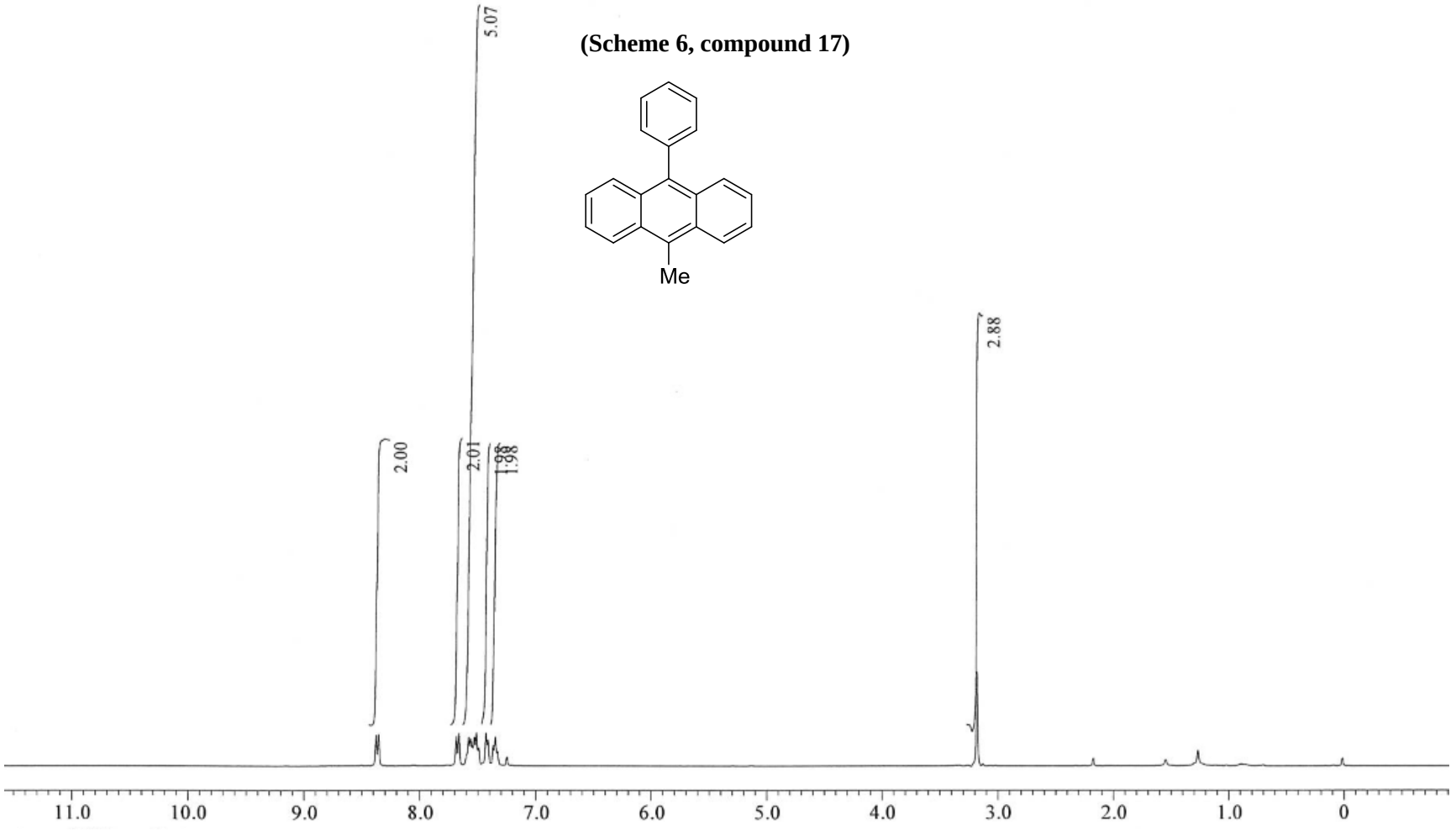
(Scheme 6, compound 16)



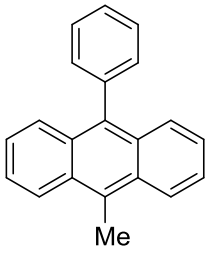
(Scheme 6, compound 16)

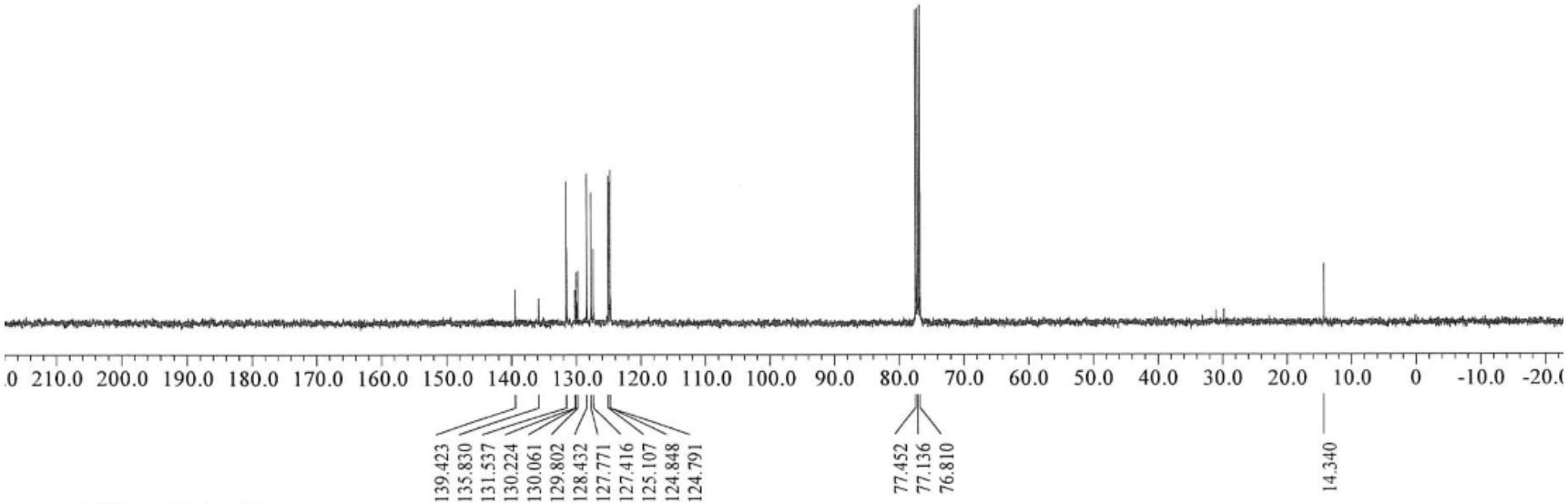


(Scheme 6, compound 17)

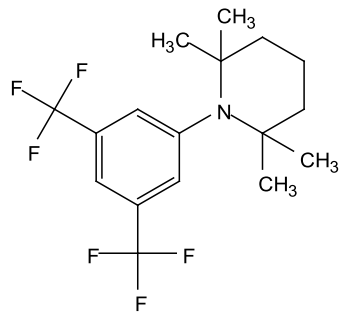


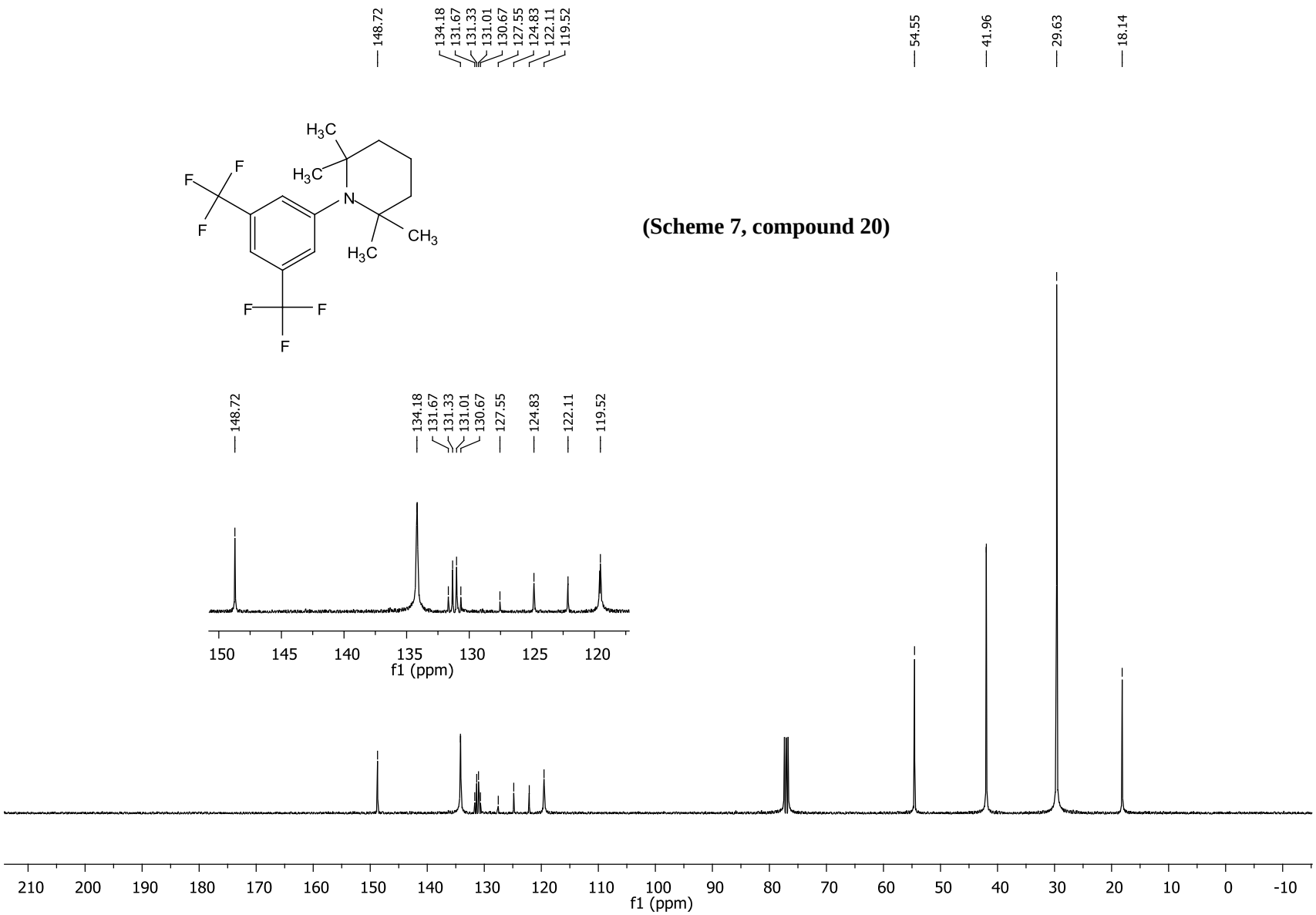
(Scheme 6, compound 17)



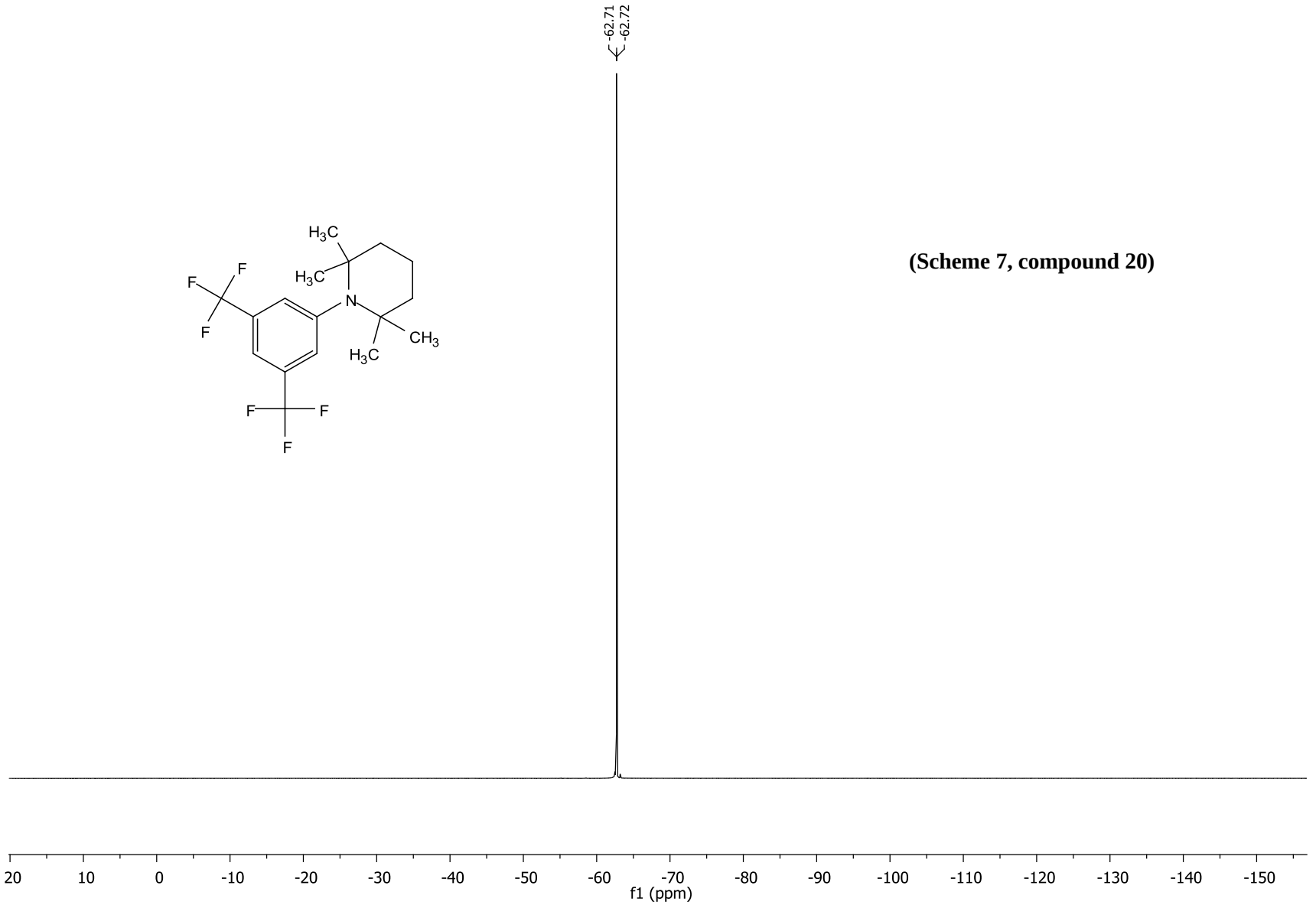


(Scheme 7, compound 20)



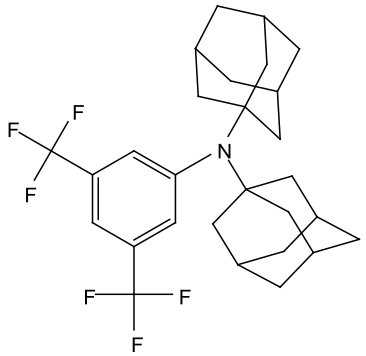


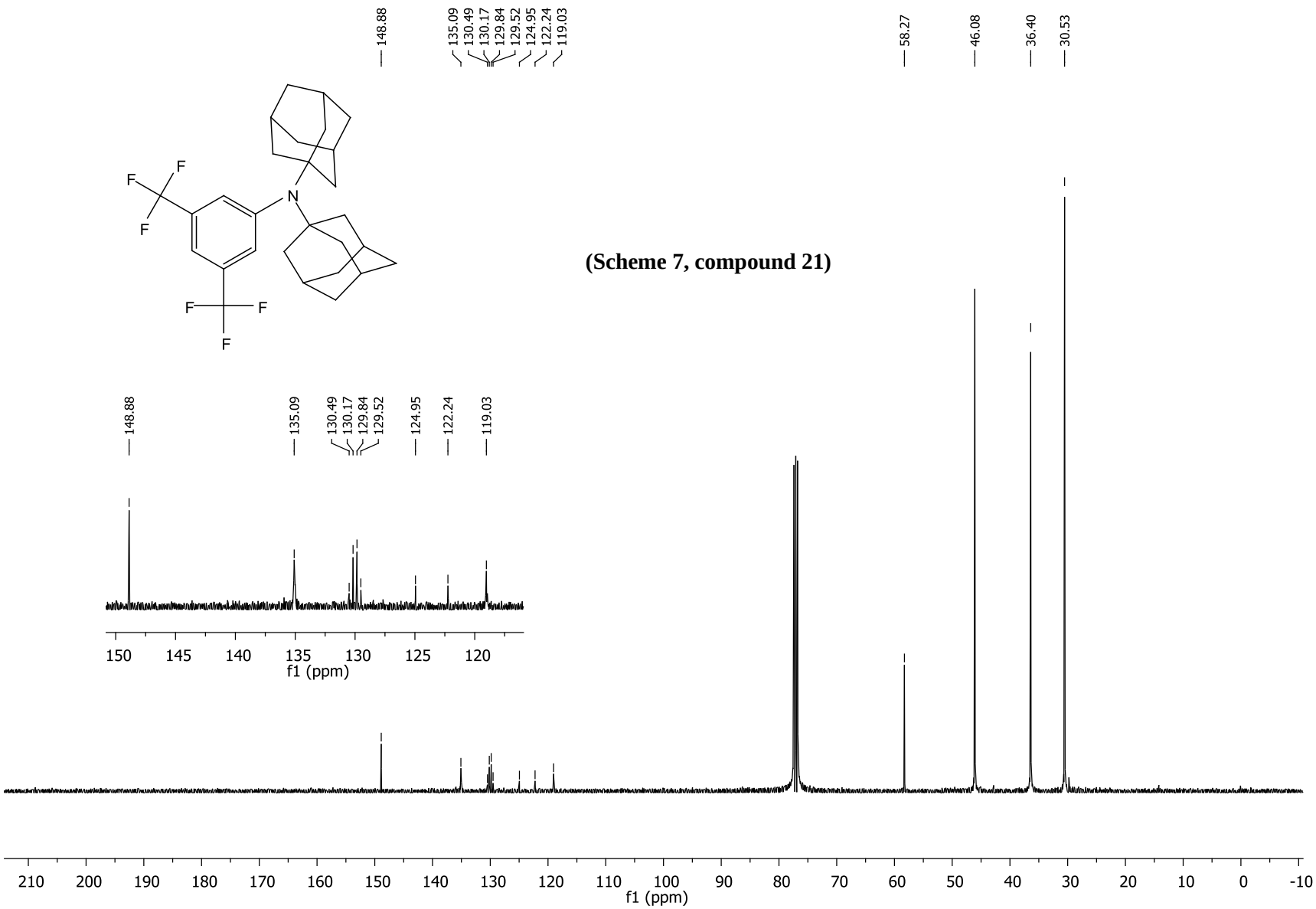
(Scheme 7, compound 20)

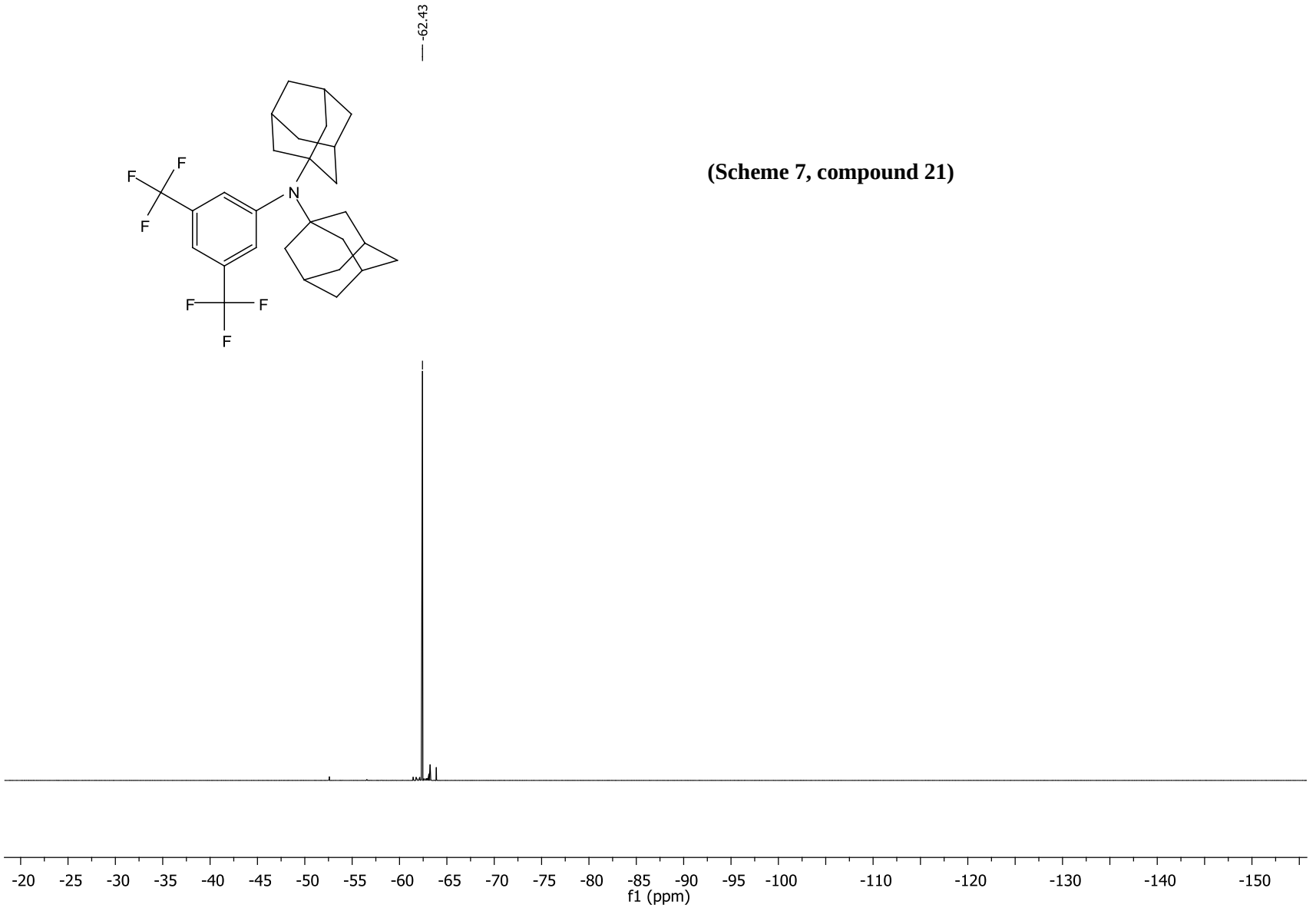


(Scheme 7, compound 20)

(Scheme 7, compound 21)




148.88
135.09
130.49
130.17
129.84
129.52
124.95
122.24
119.03
58.27
46.08
36.40
30.53
F
F
F
N
F
F
F
(Scheme 7, compound 21)
f1 (ppm)
f1 (ppm)



(Scheme 7, compound 21)