Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Aminoquinoline-Directed, Cobalt-Catalyzed Carbonylation of Sulfonamide sp^2 C-H Bonds

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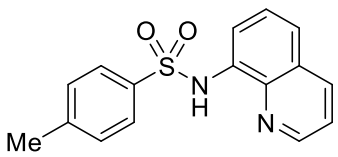
I. General considerations

Reactions were run in either 20 mL or 40 mL vials with PTFE/Liner screw caps. Column chromatography was performed on 60Å silica gel (Dynamic Adsorbents Inc.). The ^{1}H, ^{13}C, and ^{19}F spectra were recorded on JEOL EC-400, JEOL EC-500, or JEOL EC-600 spectrometers using residual solvent peak as a reference. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent QTOF mass spectrometer at the Mass Spectrometry Facility (MSF) of the Department of Chemistry and Biochemistry, University of Texas-Austin. IR spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. All procedures were performed under ambient air unless otherwise noted. Reagents and solvents were obtained from commercial sources and used without further purification. Potassium pivalate was synthesized following the literature procedure.[1] Products were visualized under $KMnO_4$ stain unless otherwise noted.

II. Synthesis of starting sulfonamides[2,3]

4-Methyl-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 1, entry 1, Table 2)

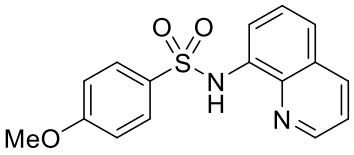


In a 40 mL vial, 8-aminoquinoline (1.44 g, 10 mmol, 1 equiv) was dissolved in pyridine (7 mL). Under air, 4-toluenesulfonyl chloride (1.91 g, 10 mmol, 1 equiv) was added to the stirred solution in one portion. The vial was capped and placed in a pre-heated oil bath at 130 °C (oil temperature). After 30 min, the solution was cooled to 70 °C followed by rapidly pouring the solution into cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 50 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Recrystallization from toluene afforded 1.89 g (63%) of 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide as an off-white solid. This compound is known.[2]

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.21 (s, 1H), 8.74 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.07 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.50 – 7.36 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H).

[1] A. P. Breen, J. A. Murphy, C. W. Patterson and N. F. Wooster, *Tetrahedron*, 1993, **49**, 10643.
[2] M. Rouffet, M. C. A. F. de Oliveira, Y. Udi, A. Agrawal, I. Sagi, J. A. McCammon and S. M. Cohen, *J. Am. Chem. Soc.*, 2010, **132**, 8232.

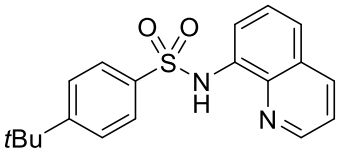
4-Methoxy-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 2, entry 2, Table 2)



In a 40 mL vial, 8-aminoquinoline (505 mg, 3.5 mmol, 1 equiv) was dissolved in pyridine (7 mL). Under air, 4-methoxybenzenesulfonyl chloride (723 mg, 3.5 mmol, 1 equiv) was added to the stirred solution in one portion. The vial was capped and placed in a pre-heated oil bath set at 130 °C (oil temperature). After 30 min, the solution was cooled to room temperature and then diluted with cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (hexanes/EtOAc from 3:1 to 1:1) followed by trituration with hexanes/EtOAc 4:1 afforded 0.675 g (61%) of 4-methoxy-*N*-(quinolin-8-yl)benzenesulfonamide as a white solid. This compound is known.[2]

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.19 (s, 1H), 8.75 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.13 – 8.02 (m, 1H), 7.89 – 7.77 (m, 3H), 7.47 – 7.36 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H).

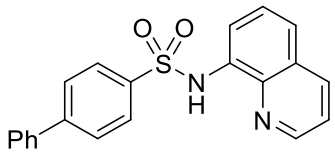
4-*tert*-Butyl-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 3, entry 3, Table 2)



In a 100 mL round-bottom flask, 8-aminoquinoline (1.51 g, 10.5 mmol, 1.05 equiv) and triethylamine (1.67 mL, 12 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (20 mL). To this solution was slowly added solid 4-*tert*-butyl-benzenesulfonyl chloride (2.33 g, 10 mmol, 1 equiv) at 0 °C. Resulting solution was stirred at room temperature overnight. Subsequently, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Trituration from hexanes/EtOAc 3:1 afforded 1.59 g (47%) of 4-*tert*-butyl-*N*-(quinolin-8-yl)benzenesulfonamide as an off-white solid. This compound is known.[2]

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.24 (s, 1H), 8.74 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.88 – 7.76 (m, 3H), 7.46 – 7.32 (m, 5H), 1.22 (s, 10H).

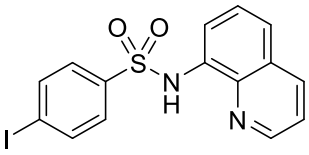
***N*-(Quinolin-8-yl)-[1,1'-biphenyl]-4-sulfonamide (starting material 4, entry 4, Table 2)**



In a 100 mL round-bottom flask, 8-aminoquinoline (1.51 g, 10.5 mmol, 1.05 equiv), triethylamine (1.67 mL, 12 mmol, 1.2 equiv), and 4-dimethylaminopyridine (61 mg, 0.5 mmol, 5 mol%) were dissolved in CH_2Cl_2 (20 mL). To this solution solid biphenyl-4-sulfonyl chloride (2.53 g, 10 mmol, 1 equiv) was slowly added at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient toluene/EtOAc from 100:1 to 50:1) afforded 2.03 g (56%) of *N*-(quinolin-8-yl)-[1,1'-biphenyl]-4-sulfonamide as a white solid. This compound is known.[2]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.29 (s, 1H), 8.76 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.87 (dd, J = 5.7, 3.3 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.55 – 7.54 (m, 1H), 7.48 – 7.45 (m, 4H), 7.43 – 7.38 (m, 3H), 7.37 – 7.33 (m, 1H).

4-Iodo-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 5, entry 5, Table 2)



In a 100 mL round-bottom flask, 8-aminoquinoline (757 mg, 5.25 mmol, 1.05 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution solid 4-iodobenzenesulfonyl chloride (1.51 g, 5 mmol, 1 equiv) was slowly added at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by recrystallization from hexanes/EtOAc 2:1 afforded 1.46 g (71%) of 4-iodo-*N*-(quinolin-8-yl)benzenesulfonamide as an off-white solid.

R_f = 0.43 (hexanes/EtOAc 10:1), mp = 186 – 187 ^{o}C (hexanes/EtOAc 2:1)

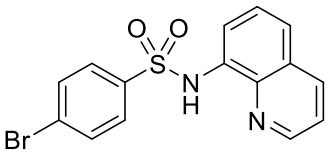
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.23 (s, 1H), 8.75 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.82 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.72 – 7.68 (m, 2H), 7.63 – 7.58 (m, 2H), 7.51 – 7.39 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 149.0, 139.1, 138.6, 138.2, 136.4, 133.4, 128.7, 128.3, 126.9, 122.6, 122.2, 115.3, 100.6.

FT-IR (neat, cm^{-1}) ν 1566, 1468, 1409, 1335, 1304.

HR-MS calcd. for $C_{15}H_{11}IN_2O_2S$ $[M+H]^+$: 410.9659; found: 410.9661.

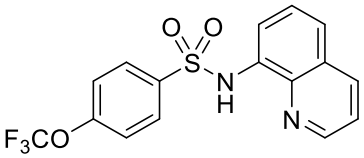
4-Bromo-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 6, entry 6, Table 2)



In a 100 mL round-bottom flask, 8-aminoquinoline (757 mg, 5.25 mmol, 1.05 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution solid 4-bromobenzenesulfonyl chloride (1.28 g, 5 mmol, 1 equiv) was slowly added at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel using CH_2Cl_2 eluent and recrystallization from hexanes/Et_2O 2:1 afforded 1.29 g (71%) of 4-bromo-*N*-(quinolin-8-yl)benzenesulfonamide as a white solid. This compound is known.[3]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.23 (s, 1H), 8.75 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.82 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.54 – 7.40 (m, 5H).

4-Trifluoromethoxy-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 7, entry 7, Table 2)



In a 100 mL round-bottom flask, 8-aminoquinoline (757 mg, 5.25 mmol, 1.05 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution was slowly added 4-trifluoromethoxybenzenesulfonyl chloride (0.85 mL, 1.3 g, 5 mmol, 1 equiv) at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase

[3] T. Lan, L. Wang and Y. Rao, *Org. Lett.*, 2017, **19**, 972.

was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel using CH_2Cl_2 eluent afforded 1.49 g (81%) of 4-trifluoromethoxy-*N*-(quinolin-8-yl)benzenesulfonamide as an off-white solid.

R_f = 0.47 (hexanes/EtOAc 3:1), mp = 64 – 66 ^oC (Et_2O)

^1H NMR (500 MHz, $CDCl_3$, ppm) δ 9.24 (s, 1H), 8.74 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.84 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 2H).

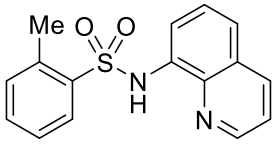
^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 152.3, 149.0, 138.6, 137.7, 136.4, 133.4, 129.4, 128.3, 126.9, 122.8, 122.2, 120.7, 120.2 (q, J_{C-F} = 260 Hz, 2 signals of the quartet could not be assigned), 115.6.

^{19}F NMR (471 MHz, $CDCl_3$, ppm) δ -57.64.

FT-IR (neat, cm^{-1}) ν 1504, 1377, 1260, 1215, 1085.

HR-MS calcd. for $C_{16}H_{11}F_3N_2O_3S$ $[M+H]^+$: 369.0515; found: 369.0523.

2-Methyl-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 8, entry 8, Table 2)

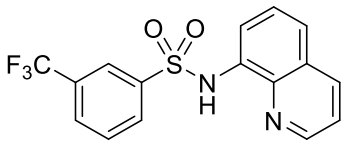


In a 200 mL round-bottom flask, 8-aminoquinoline (1.59 g, 11 mmol, 1.1 equiv) and triethylamine (1.7 mL, 12 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (50 mL). To this solution was slowly added 2-toluenesulfonyl chloride (1.4 mL, 1.91 g, 10 mmol, 1 equiv) at 0 ^oC. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 25 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 4:1 to 1:1) following by recrystallization from hexanes/EtOAc 8:1 afforded 2.08 g (70%) of 2-methyl-*N*-(quinolin-8-yl)benzenesulfonamide as a white solid. This compound is known.[4]

[4] O. Planas, C. Whiteoak, A. Company and X. Ribas, *Adv. Synth. Catal.*, 2015, **357**, 4003.

^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.34 (s, 1H), 8.78 (d, *J* = 1.9 Hz, 1H), 8.08 (t, *J* = 7.0 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.46 – 7.30 (m, 4H), 7.23 (t, *J* = 7.7 Hz, 1H, overlapping with $CHCl_3$ signal), 7.15 (d, *J* = 7.4 Hz, 1H).

3-Trifluoromethyl-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 9, entry 9, Table 2)

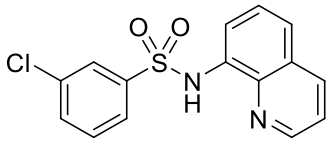


In a 100 mL round-bottom flask, 8-aminoquinoline (721 mg, 5 mmol, 1 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution at 0 °C was slowly added 3-trifluoromethylbenzenesulfonyl chloride (1 mL, 1.47 g, 6 mmol, 1.2 equiv). Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 10:1 to 5:1) afforded 1.25 g (71%) of 3-trifluoromethyl-*N*-(quinolin-8-yl)benzenesulfonamide as a light yellow oil which slowly solidifiesd. This compound is known.[2]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.24 (s, 1H), 8.75 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.15 (s, 1H), 8.10 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.86 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -62.9.

3-Chloromethyl-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 10, entry 10, Table 2)



In a 40 mL vial, 8-aminoquinoline (721 mg, 5 mmol, 1.43 equiv) was dissolved in pyridine (5 mL). Under air, 3-chlorobenzenesulfonyl chloride (739 mg, 3.5 mmol, 1 equiv) was added to the stirring solution in one portion. The vial was then capped and placed in a pre-heated oil bath at 130 °C (oil temperature). After 30 min, the solution was cooled to room temperature and diluted with cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column

chromatography on silica gel using toluene/EtOAc 50:1 eluent afforded 0.911 g (82%) of an off-white solid.

R_f = 0.29 (hexanes/EtOAc 3:1), mp = 97 – 98 ^oC (toluene)

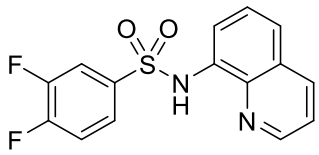
^1H NMR (400 MHz, $CDCl_3$, ppm) δ 9.25 (s, 1H), 8.75 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.90 (t, *J* = 1.9 Hz, 1H), 7.82 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.50 – 7.39 (m, 4H), 7.39 – 7.36 (m, 1H), 7.27 (t, *J* = 8 Hz, 1H, overlapping with $CHCl_3$ signal).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 149.0, 141.0, 138.6, 136.4, 135.1, 133.3, 133.2, 130.3, 128.3, 127.4, 126.9, 125.4, 122.8, 122.2, 115.4.

FT-IR (neat, cm^{-1}) ν 1500, 1369, 1309, 1166, 1084.

HR-MS calcd. for $C_{15}H_{11}ClN_2O_2S$ $[M+H]^+$: 319.0303; found: 319.0302.

3,4-Difluoro-*N*-(quinolin-8-yl)benzenesulfonamide (starting material 11, entry 11, Table 2)



In a 100 mL round-bottom flask, 8-aminoquinoline (721 mg, 5 mmol, 1 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution was slowly added 3,4-difluorobenzenesulfonyl chloride (0.8 mL, 1.3 g, 6 mmol, 1.2 equiv) at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel using CH_2Cl_2 eluent afforded 1.11 g (69%) of 3,4-difluoro-*N*-(quinolin-8-yl)benzenesulfonamide as a white solid.

R_f = 0.34 (hexanes/EtOAc 3:1), mp = 86 – 88 ^oC (hexanes/EtOAc 10:1).

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 9.23 (s, 1H), 8.76 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.83 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.73 (ddd, *J* = 9.4, 7.2, 2.2 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.51 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.13 (td, *J* = 9.0, 7.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 153.3 (dd, J_{C-F} = 257.8, 12.6 Hz), 149.9 (dd, J_{C-F} = 254.6, 13.5 Hz, one signal of doublet could not be assigned), 149.1, 138.7, 136.48, 136.1 (t, J_{C-F} = 3.8

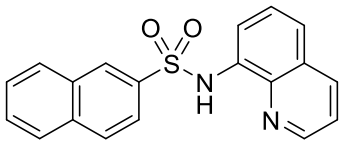
Hz), 133.2, 128.3, 126.9, 124.5, 123.0, 122.3, 118.1 (d, J_{C-F} = 18.5 Hz), 117.3 (d, J_{C-F} = 19.8 Hz), 115.7.

^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ -128.81 (dddd, *J* = 20.6, 9.6, 7.2, 4.1 Hz, 1F), -133.65 (dddd, *J* = 20.5, 9.1, 7.5, 1.2 Hz, 1F).

FT-IR (neat, cm^{-1}) ν 1505, 1363, 1277, 1166.

HR-MS calcd. for $C_{15}H_{10}F_2N_2O_2S$ $[M+H]^+$: 321.0504; found: 321.0506.

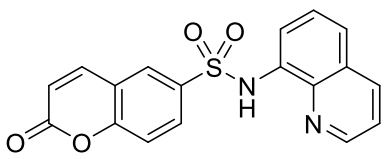
***N*-(Quinolin-8-yl)naphthalene-2-sulfonamide (starting material 12, entry 12, Table 2)**



In a 100 mL round-bottom flask, 8-aminoquinoline (757 mg, 5.25 mmol, 1.05 equiv) and triethylamine (0.83 mL, 6 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (25 mL). To this solution was slowly added 2-naphthalenesulfonyl chloride (1.13 g, 5 mmol, 1 equiv) at 0 °C. Resulting solution was stirred at room temperature overnight. After completion, reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by recrystallization from hexanes/EtOAc 2:1 afforded 1.29 g (77%) of *N*-(quinolin-8-yl)naphthalene-2-sulfonamide as an off-white solid. This compound is known.[2]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.35 (s, 1H), 8.75 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.52 (d, *J* = 1.4 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.81 – 7.74 (m, 2H), 7.58 – 7.49 (m, 2H), 7.43 – 7.35 (m, 3H).

2-Oxo-*N*-(quinolin-8-yl)-2*H*-chromene-6-sulfonamide (starting material 13, entry 13, Table 2)



In a 40 mL vial, 8-aminoquinoline (505 mg, 3.5 mmol, 1 equiv) was dissolved in pyridine (7 mL). Under air, coumarin 6-sulfonyl chloride (856 mg, 3.5 mmol, 1 equiv) was added to the stirred solution in one portion. The vial was then capped and placed in a pre-heated oil bath at 130 °C (oil temperature). After 30 min, the solution was cooled to room temperature and diluted with cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Recrystallization from toluene afforded 0.687 g (56%) of 2-oxo-*N*-(quinolin-8-yl)-2*H*-chromene-6-sulfonamide as a gray solid.

R_f = 0.7 (hexanes/EtOAc 1:1), mp = 167 – 169 ^oC (toluene).

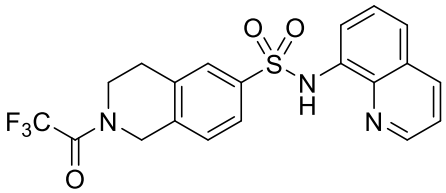
^1H NMR (400 MHz, $CDCl_3$, ppm) δ 9.26 (s, 1H), 8.75 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.08 (d, *J* = 2.2 Hz, 1H), 7.99 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.85 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.64 (d, *J* = 9.7 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.25 (d, *J* = 8.8 Hz, 1H, overlapping with $CHCl_3$ signal), 6.44 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.3, 156.5, 149.1, 142.5, 138.7, 136.5, 135.7, 133.3, 130.2, 128.3, 127.7, 126.9, 122.9, 122.3, 118.8, 118.3, 117.9, 115.7.

FT-IR (neat, cm^{-1}) ν 1720, 1503, 1374, 1163, 1108.

HR-MS calcd. for $C_{18}H_{12}N_2O_4S$ $[M+H]^+$: 353.0591; found: 353.0595.

_N_-(quinolin-8-yl)-2-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroisoquinoline-6-sulfonamide (starting material 14, entry 14, Table 2)



In a 40 mL vial, 8-aminoquinoline (505 mg, 3.5 mmol, 1.15 equiv) was dissolved in pyridine (5 mL). Under air, 2-trifluoroacetyl-1,2,3,4-tetrahydroisoquinoline-7-sulfonyl chloride (1.00 g, 3.05 mmol, 1 equiv) was added to the stirred solution in one portion. The vial was then capped and placed in a pre-heated oil bath at 130 °C (oil temperature). After 30 min, the solution was cooled to 70 °C followed by rapidly pouring the solution into cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 20 mL).

Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) afforded 0.635 g (48%) of *N*-(quinolin-8-yl)-2-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydro-isoquinoline-6-sulfonamide as a light yellow oil that slowly solidifies. Product exists as a 2:1 mixture of rotamers at room temperature. Coalescence of their ^{1}H NMR signals is observed above 80 °C.

R_f = 0.11 (hexanes/EtOAc 3:1).

At 80 °C: ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 9.61 (bs, 1H), 8.82 (bs, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.83 (bs, 1H), 7.78 – 7.63 (m, 2H), 7.62 (d, J = 8.1 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 4.69 (bs, 3H), 3.72 (bs, 3H), 2.87 (bs, 3H).

At 80 °C: List of peaks is given due to mixture of two rotamers: ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 155.6 (d, J_{C-F} = 33.3 Hz), 155.0 (d, J_{C-F} = 32.3 Hz), 149.8, 140.5, 140.1, 139.3, 138.4, 137.0, 134.1, 133.6, 129.9, 128.7, 127.2, 126.0, 125.8, 125.7, 125.5, 123.5, 122.8, 121.1, 118.3, 117.1, 117.0, 115.4, 112.5, 46.7, 45.5, 42.9, 41.6, 29.1, 27.6.

At 80 °C: ^{19}F NMR (470 MHz, DMSO-d_6, ppm) δ -68.6.

FT-IR (neat, cm^{-1}) ν 1688, 1504, 1371, 1197, 1138, 1085.

HR-MS calcd. for $C_{20}H_{16}F_3N_3O_3S$ $[M+H]^+$: 436.0937; found: 436.0944.

III. Cobalt-catalyzed carbonylation of aminoquinoline sulfonamides

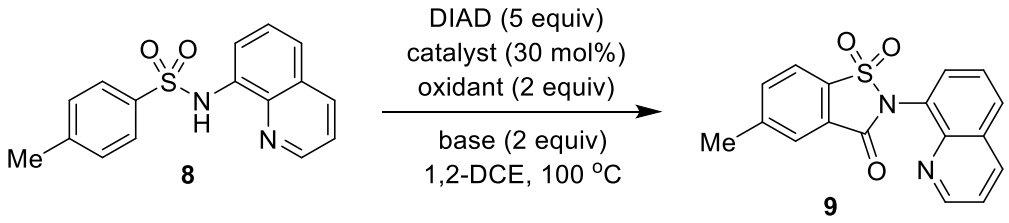
1. Optimization

Optimization conditions

Procedure for optimization reactions: A 20 mL vial equipped with a magnetic stir bar was charged with 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (0.5 mmol, 149 mg), CO source (0.625 mmol, 1.25 equiv), catalyst (0.15 mmol, 30 mol%), cooxidant (1.0 mmol, 2 equiv), base (1.0 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Reaction mixture was heated at 100 °C. After 2 h, 8 h, and 20 h, the vial was opened and reaction was charged with additional CO source (0.625 mmol, 1.25 equiv, total 4 times = 5 equiv). After 24 h, reaction was cooled to room

temperature. Crude mixture was diluted with saturated aqueous potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) yielded the product. *Please note that vial opening while adding CO source allows oxygen from air to enter the vial; the headspace volume is important for reproducibility of the reactions.*

Table S1. Optimization of Sulfonamide Carbonylation

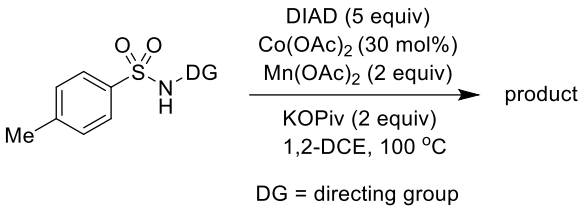


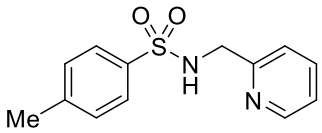
Entry	catalyst	cooxidant	base	Yield of **9**[a], %
1	$Co(OAc)_2$	$Mn(OAc)_2$	KOAc	48
2	$Co(OAc)_2$	$Mn(OAc)_2$	NaOPiv	67
3	$Co(OAc)_2$	$Mn(OAc)_2$	KOPiv	71
4	$Co(OAc)_2$	$Mn(OAc)_2$	KOPiv	38[b]
5	$CoCl_2$	$Mn(OAc)_2$	KOPiv	64
6	$Co(acac)_2$	$Mn(OAc)_2$	KOPiv	31
7	$Co(acac)_3$	$Mn(OAc)_2$	KOPiv	25
8	$Co(OAc)_2$	$Mn(OAc)_3*H_2O$	KOPiv	18
9	$Co(OAc)_2$	$Mn(OAc)_2$	KOPiv	62[c]
10	$Co(OAc)_2$	$Mn(OAc)_2$	KOPiv	0[d]

11	$Co(OAc)_2$	$Mn(OAc)_2$	KOPiv	0[e]
12	none	$Mn(OAc)_2$	KOPiv	0
13	$Co(OAc)_2$	none	KOPiv	<5

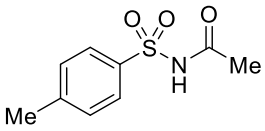
[a] Isolated yields.[b] DIAD (2.5 mmol, 5 equiv) added at once at the beginning of the reaction.[c] di-*tert*-butyl azodicarboxylate (2.5 mmol, 5 equiv) was used.[d] $Mo(CO)_6$ (1.5 mmol, 3 equiv) was used.[e] HCOONa (5 mmol, 5 equiv) was used. Abbreviations: DIAD = diisopropyl azodicarboxylate, DCE = 1,2-dichloroethane, acac = acetylacetonate.

Screening of other directing groups

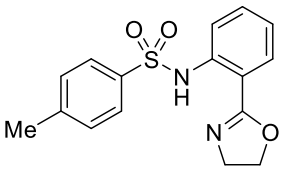




Decomposition of starting sulfonamide



Decomposition of starting sulfonamide



Recovery of starting sulfonamide

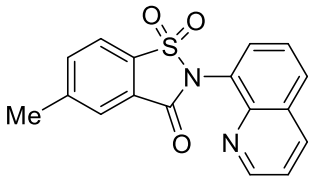
2. Characterization of products

General procedure for sulfonamide carbonylation (except entry 12, Table 2): A 20 mL vial equipped with a magnetic stir bar was charged with sulfonamide (0.5 mmol), DIAD (0.123 mL, 0.625 mmol, 1.25 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1 mmol, 2 equiv), KOPiv (140 mg, 1 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Reaction mixture was heated at 100 °C (entries 1-11 and 13, Table 2) or 85 °C (entry 14, Table 2). After 2 h, 8 h, and 20 h, the vial was opened and reaction was charged with additional DIAD (0.123 mL, 0.625 mmol, 1.25 equiv, total of 4 times = 5 equiv). After 24 h (entries 2-11 and 13, Table 2) or

30 h (large scale of entry 1, Table 2 and entry 14, Table 2), reaction was cooled to room temperature. Crude mixture was diluted with saturated potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel using appropriate eluent followed by concentrating the fraction of product and drying the residue under vacuum yielded pure product.

5-Methyl-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 1, Entry 3 and Table 2, Entry 1)

4-Methyl-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc from 3:1 to 1:1), 115 mg (71%) of a tan solid was obtained.



Large scale: A 150-mL pressure tube was charged with 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (746 mg, 2.5 mmol), DIAD (0.62 mL, 3.125 mmol, 1.25 equiv), $Co(OAc)_2$ (133 mg, 0.75 mmol, 30 mol%), $Mn(OAc)_2$ (865 mg, 5.0 mmol, 2 equiv), KOPiv (701 mg, 5.0 mmol, 2 equiv), and 1,2-dichloroethane (50 mL). The reaction was heated at 100 °C. After 3 h, 12 h, and 24 h, the vial was opened and reaction was charged with additional DIAD (0.62 mL each time, 3.125 mmol, 1.25 equiv, total 4 times = 5 equiv). After 30 h, reaction was cooled to room temperature. Crude mixture was diluted with saturated aqueous potassium sodium tartrate solution (100 mL) followed by extraction with CH_2Cl_2 (3 x 50 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) yielded 551 mg (68%) of a tan solid.

R_f = 0.53 (hexanes/EtOAc 1:1), mp 239 – 241 °C (hexanes/EtOAc 3:1).

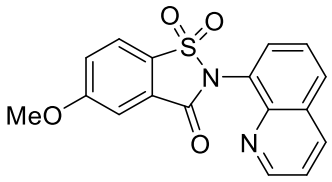
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.89 (d, *J* = 3.3 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.95 (m, 3H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 8.3, 4.1 Hz, 1H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.3, 151.6, 146.0, 144.8, 136.4, 135.6, 135.6, 131.8, 131.2, 129.7, 127.9, 126.6, 126.3, 126.1, 122.3, 121.3, 22.0.

FT-IR (neat, cm^{-1}) ν 1744, 1332, 1297, 1185, 1162.

HR-MS calcd. for $C_{17}H_{12}N_2O_3S$ $[M+H]^+$: 325.0641; found: 325.0643.

5-Methoxy-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 2)



4-Methoxy-*N*-(quinolin-8-yl)benzenesulfonamide (157 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc from 3:1 to 1:1), 100 mg (59%) of a white solid was obtained.

R_f = 0.47 (hexanes/EtOAc 1:1), mp 244 – 246 °C (hexanes/EtOAc 3:1).

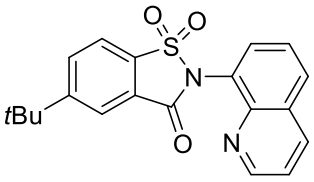
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 2.4 Hz, 1H), 7.46 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 164.6, 159.1, 151.6, 144.8, 136.4, 131.8, 131.2, 130.3, 129.9, 129.8, 126.7, 126.4, 123.1, 122.3, 122.0, 109.0, 56.5.

FT-IR (neat, cm^{-1}) ν 1738, 1597, 1483, 1328, 1295, 1245, 1184, 1137, 1123, 1074, 1046.

HR-MS calcd. for $C_{17}H_{12}N_2O_4S$ $[M+H]^+$: 341.0591; found: 341.0593.

5-(*tert*-Butyl)-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 3)



4-*tert*-Butyl-*N*-(quinolin-8-yl)benzenesulfonamide (170 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc from 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 132 mg (72%) of a white solid was obtained.

R_f = 0.78 (hexanes/EtOAc 1:1), decomposes at 290 – 292 °C (hexanes/EtOAc 10:1).

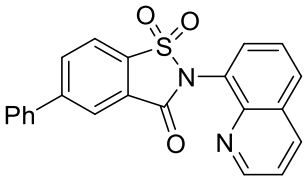
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.27 – 8.19 (m, 2H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.95 (s, 2H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.5, 159.2, 151.6, 144.9, 136.4, 135.4, 132.2, 131.8, 131.2, 129.8, 127.8, 126.7, 126.4, 122.9, 122.3, 121.3, 36.0, 31.2.

FT-IR (neat, cm^{-1}) ν 1731, 1335, 1325, 1299, 1157, 1142.

HR-MS calcd. for $C_{20}H_{18}N_2O_3S$ $[M+H]^+$: 367.1111; found: 367.1113.

5-Phenyl-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 4)



N-(Quinolin-8-yl)-[1,1'-biphenyl]-4-sulfonamide (180 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 110 mg (57%) of a white solid was obtained.

R_f = 0.2 (hexanes/EtOAc 3:1), mp 257 – 259 °C (hexanes/EtOAc 10:1).

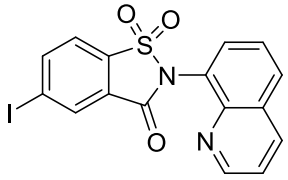
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 2.6 Hz, 1H), 8.38 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.12 – 8.02 (m, 3H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.65 (m, 3H), 7.53 – 7.46 (m, 3H), 7.43 (dd, *J* = 8.0, 3.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 159.1, 151.6, 148.0, 144.8, 138.2, 136.6, 136.4, 133.5, 131.8, 131.3, 129.8, 129.5, 129.4, 128.5, 127.6, 126.6, 126.4, 124.2, 122.4, 122.0.

FT-IR (neat, cm^{-1}) ν 1738, 1342, 1326, 1307, 1184.

HR-MS calcd. for $C_{22}H_{14}N_2O_3S$ $[M+H]^+$: 387.0798; found: 387.0804.

5-Iodo-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 5)



4-Iodo-*N*-(quinolin-8-yl)benzenesulfonamide (205 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 160 mg (73%) of a white solid was obtained.

R_f = 0.2 (hexanes/EtOAc 3:1), mp 270 – 272 °C (hexanes/EtOAc 3:1).

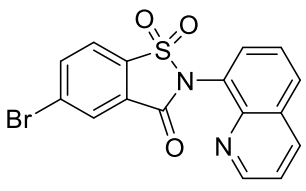
^{1}H NMR (600 MHz, DMSO-d_6, ppm) δ 8.86 (d, *J* = 3.2 Hz, 1H), 8.56 – 8.47 (m, 3H), 8.29 – 8.24 (m, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.62 (dd, *J* = 8.2, 4.1 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6, ppm) δ 157.9, 152.2, 145.2, 144.2, 137.3, 137.1, 134.5, 132.3, 132.1, 129.70, 128.2, 127.1, 126.3, 124.0, 123.2, 104.2.

FT-IR (neat, cm^{-1}) ν 1752, 1318, 1286, 1177, 1136.

HR-MS calcd. for $C_{16}H_9IN_2O_3S$ $[M+H]^+$: 436.9451; found: 436.9455.

5-Bromo-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 6)



4-Bromo-*N*-(quinolin-8-yl)benzenesulfonamide (182 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24

h. After column chromatography (gradient hexanes/EtOAc 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 119 mg (61%) of a tan solid was obtained.

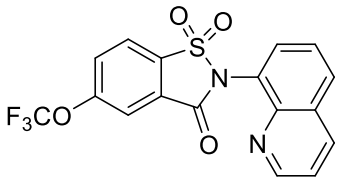
R_f = 0.28 (hexanes/EtOAc 3:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (dd, *J* = 4.0, 1.3 Hz, 1H), 8.35 (d, *J* = 1.3 Hz, 1H), 8.25 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.12 – 7.94 (m, 3H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.8, 151.6, 144.6, 138.0, 136.9, 136.4, 131.7, 131.4, 129.8, 129.5, 129.4, 129.1, 126.4, 126.3, 122.8, 122.4.

2-(Quinolin-8-yl)-5-(trifluoromethoxy)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 7)

4-Trifluoromethoxy-*N*-(quinolin-8-yl)benzenesulfonamide (184 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc from 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 125 mg (63%) of a white solid was obtained.



R_f = 0.27 (hexanes/EtOAc 3:1), mp 193 – 195 °C (hexanes/EtOAc 10:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (d, *J* = 2.9 Hz, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.12 – 7.96 (m, 4H), 7.78 – 7.63 (m, 2H), 7.47 (dd, *J* = 8.2, 4.1 Hz, 1H).

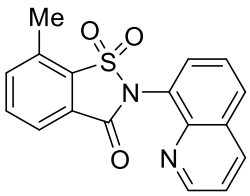
^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 157.6, 153.6, 151.7, 144.6, 136.4, 136.0, 131.7, 131.5, 130.4, 129.8, 127.0, 126.4, 126.2, 123.7, 122.5, 120.3 (q, J_{C-F} = 262 Hz), 117.6.

^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -57.66.

FT-IR (neat, cm^{-1}) ν 1752, 1337, 1256, 1071, 1047.

HR-MS calcd. for $C_{17}H_9F_3N_2O_4S$ $[M+H]^+$: 395.0308; found: 395.0313.

7-Methyl-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 8)



2-Methyl-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 3:1 to 1:1), 89 mg (55%) of a tan solid was obtained.

R_f = 0.52 (hexanes/EtOAc 1:1), mp 232 – 234 °C (hexanes/EtOAc 3:1).

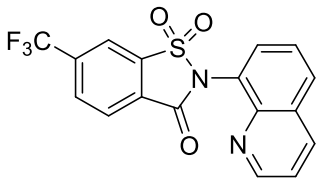
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.92 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.23 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.04 – 8.02 (m, 1H), 8.01 – 7.99 (m, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.67 (dd, *J* = 14.8, 7.3 Hz, 2H), 7.45 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.2, 151.6, 144.9, 136.6, 136.4, 134.9, 134.3, 131.9, 131.2, 129.8, 127.9, 126.6, 126.4, 123.3, 122.3, 17.9. One signal could not be located.

FT-IR (neat, cm^{-1}) ν 1741, 1321, 1299, 1180, 1141.

HR-MS calcd. for $C_{17}H_{12}N_2O_3S$ $[M+H]^+$: 325.0641; found: 325.0645.

2-(Quinolin-8-yl)-6-(trifluoromethyl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 9)



3-Trifluoromethyl-*N*-(quinolin-8-yl)benzenesulfonamide (176 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 10:1 to 3:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 88 mg (47%) of a white solid was obtained.

R_f = 0.17 (hexanes/EtOAc 3:1), mp 232 – 234 °C (hexanes/EtOAc 10:1)

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.90 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 8.25 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.04 (ddd, *J* = 13.6, 7.8, 1.0 Hz, 2H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H).

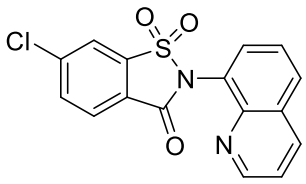
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.7, 151.7, 144.5, 139.0, 137.0 (q, J_{C-F} = 34 Hz, 1 signal of the quartet could not be assigned), 136.4, 131.7, 131.6, 130.6, 129.8, 126.8, 126.4, 126.08, 122.6 (q, J_{C-F} = 275 Hz), 122.5, 119.24, 119.21.

^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -62.8.

FT-IR (neat, cm^{-1}) ν 1735, 1347, 1321, 1304, 1183, 1146, 1131, 1076, 1056, 1047.

HR-MS calcd. for $C_{17}H_9F_3N_2O_3S$ $[M+H]^+$: 379.0359; found: 379.0360.

6-Chloro-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 10)



3-Chloro-*N*-(quinolin-8-yl)benzenesulfonamide (159 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 4:1 to 2:1), 83 mg (48%) of a tan solid was obtained.

R_f = 0.24 (hexanes/EtOAc 2:1), mp 260 – 262 °C (hexanes/EtOAc 3:1).

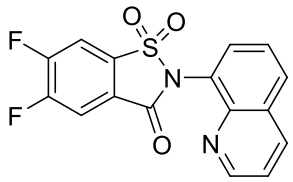
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.24 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.06 – 7.97 (m, 3H), 7.85 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 158.2, 151.6, 144.6, 141.9, 139.6, 136.4, 134.8, 131.8, 131.4, 129.8, 127.2, 126.4, 126.3, 126.0, 122.4, 121.9.

FT-IR (neat, cm^{-1}) ν 1744, 1321, 1296, 1173, 1140, 1127, 1054.

HR-MS calcd. for $C_{16}H_9ClN_2O_3S$ $[M+H]^+$: 345.0095; found: 345.0099.

5,6-Difluoro-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 11)



3,4-Difluoro-*N*-(quinolin-8-yl)benzenesulfonamide (160 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 10:1 to 3:1), a colorless oil was obtained. Recrystallization from hexanes/EtOAc 20:1 afforded 119 mg (69%) of a white solid. Structural assignment was verified by by ^{13}C DEPT-135.

R_f = 0.23 (hexanes/EtOAc 3:1), mp 194 – 196 °C (hexanes/EtOAc 20:1).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.90 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.24 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.09 – 7.97 (m, 3H), 7.91 – 7.84 (m, 1H), 7.73 – 7.65 (m, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H).

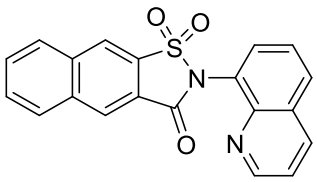
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 157.1, 154.8 (dd, J_{C-F} = 265.6, 22.2 Hz), 154.7 (dd, J_{C-F} = 265.6, 21.2 Hz), 151.7, 144.5, 136.4, 134.8 (dd, J_{C-F} = 7.0, 4.0 Hz), 131.8, 131.6, 129.8, 126.4, 126.2, 125.2 (dd, J_{C-F} = 7.2, 3.5 Hz), 122.5, 115.5 (d, J_{C-F} = 20.4 Hz), 111.8 (d, J_{C-F} = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -121.9 (dt, *J* = 18.7, 7.1 Hz, 1F), -123.6 (ddd, *J* = 18.7, 8.2, 6.3 Hz, 1F).

FT-IR (neat, cm^{-1}) ν 1737, 1337, 1323, 1305, 1171.

HR-MS calcd. for $C_{16}H_8F_2N_2O_3S$ $[M+H]^+$: 347.0296; found: 347.0298.

2-(Quinolin-8-yl)naphtho[2,3-*d*]isothiazol-3(2*H*)-one 1,1-dioxide (Table 2, Entry 12)



A 20 mL vial equipped with a magnetic stir bar was charged with *N*-(quinolin-8-yl)naphthalene-2-sulfonamide (167 mg, 0.5 mmol), DIAD (0.3 mL, 1.5 mmol, 3 equiv), $CoCl_2$ (13 mg, 0.1 mmol, 20 mol%), $Mn(OAc)_2$ (173 mg, 1 mmol, 2 equiv), KOPiv (140 mg, 1 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Reaction mixture was heated at 120 °C for 24 h. Alfter cooling to room temperature, crude mixture was diluted with saturated potassium sodium tartrate

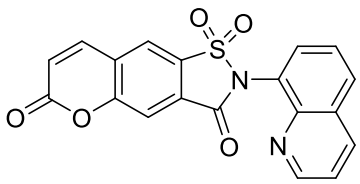
solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 4:1 to 1:1) followed by titutration with hexanes/$CHCl_3$ (1:1, 4 mL) yielded 92 mg (51%) of a white solid.

R_f = 0.13 (hexanes/EtOAc 3:1).

^{1}H NMR (600 MHz, DMSO-*d*$_6$, ppm) δ 9.10 (s, 1H), 8.95 (s, 1H), 8.89 – 8.85 (m, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.82 (dd, *J* = 11.1, 4.5 Hz, 1H), 7.66 – 7.61 (m, 1H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$, ppm) δ 159.2, 152.1, 144.6, 137.2, 135.4, 135.2, 133.7, 132.1, 131.9, 131.2, 131.0, 130.8, 130.4, 129.7, 128.1, 127.0, 126.9, 123.9, 123.1, 122.9.

2-(Quinolin-8-yl)-2*H*-chromeno[7,6-*d*]isothiazole-3,6-dione 1,1-dioxide (Table 2, Entry 13)



2-Oxo-*N*-(quinolin-8-yl)-2*H*-chromene-6-sulfonamide (176 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 100 °C, 24 h. After column chromatography (gradient hexanes/EtOAc 4:1 to 1:1) and trituration with hexanes/EtOAc 20:1 (2 x 10 mL), 122 mg (65%) of a white solid was obtained. Product is visualized under UV lamp.

R_f = 0.23 (hexanes/EtOAc 1:1), decomposes at 271 – 273 °C (hexanes/EtOAc 1:1).

^{1}H NMR (400 MHz, DMSO-*d*$_6$, ppm) δ 8.89 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.84 (s, 1H), 8.54 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.29 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.22 – 8.19 (m, 2H), 8.03 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.82 (dd, *J* = 8.1, 7.5 Hz, 1H), 7.64 (dd, *J* = 8.3, 4.2 Hz, 1H), 6.86 (d, *J* = 9.6 Hz, 1H).

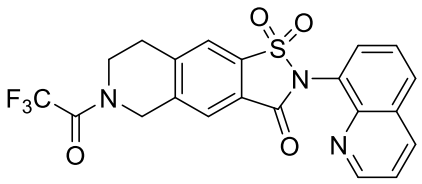
^{13}C NMR (101 MHz, DMSO-*d*$_6$, ppm) δ 159.2, 158.0, 152.2, 144.2, 143.2, 137.3, 132.8, 132.25, 132.20, 129.7, 129.1, 127.01, 126.3, 125.1, 123.5, 123.2, 120.8, 114.6. One carbon signal could not be located.

FT-IR (neat, cm^{-1}) ν 1732, 1169.

HR-MS calcd. for $C_{19}H_{10}N_2O_5S$ [M+H]$^+$: 379.0383; found: 379.0386.

2-(Quinolin-8-yl)-6-(2,2,2-trifluoroacetyl)-5,6,7,8-tetrahydroisothiazolo[5,4-*g*]isoquinolin-3(2*H*)-one 1,1-dioxide (Table 2, Entry 14)

N-(Quinolin-8-yl)-2-(2,2,2-trifluoroacetyl)-1,2,3,4-tetrahydroisoquinoline-6-sulfonamide (218 mg, 0.5 mmol), DIAD (0.123 mL x 4 times, 2.5 mmol, 5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1 mmol, 2 equiv), KOPiv (140 mg, 1 mmol, 2 equiv), 1,2-dichloroethane (10 mL), 85 °C, 30 h. After column chromatography (gradient hexanes/EtOAc 3:1 to 1:1), 114 mg (50%) of a tan solid was obtained. Product exists as a 2:1 mixture of rotamers at room temperature. Coalescence of their ^{1}H NMR signals is observed above 80 °C.



R_f = 0.44 (hexanes/EtOAc 1:1).

At 80 °C: ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.84 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.32 (bs, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.08 (bs, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.60 (dd, J = 8.2, 4.1 Hz, 1H), 5.01 (bs, 2H), 3.90 (bs, 2H), 3.20 (bs, 2H).

At 80 °C: Due to presence of amide rotamers, list of peaks is given: ^{13}C NMR (101 MHz, DMSO-d_6, ppm) 158.9, 155.5 (d, J_{C-F} = 36.4 Hz), 151.9, 144.5, 143.4, 142.9, 141.4, 137.1, 136.3, 132.0, 131.8, 129.8, 127.0, 126.9, 126.1, 125.6, 123.0, 120.8, 120.6, 118.3, 115.4, 114.7, 47.2, 46.1, 42.8, 41.4, 29.7, 28.3.

At 80 ºC: ^{19}F NMR (376 MHz, DMSO-d_6, ppm) δ -68.5.

FT-IR (neat, cm^{-1}) ν 1736, 1688, 1366, 1294, 1170, 1136, 1055.

HR-MS calcd. for $C_{21}H_{14}F_3N_3O_4S$ [M+H]$^+$: 462.0730; found: 462.0735.

3. Control experiments

Reaction with CO gas (Table 1, entry 1): A 20 mL vial equipped with a magnetic stir bar was charged with 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.5 mmol), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol,

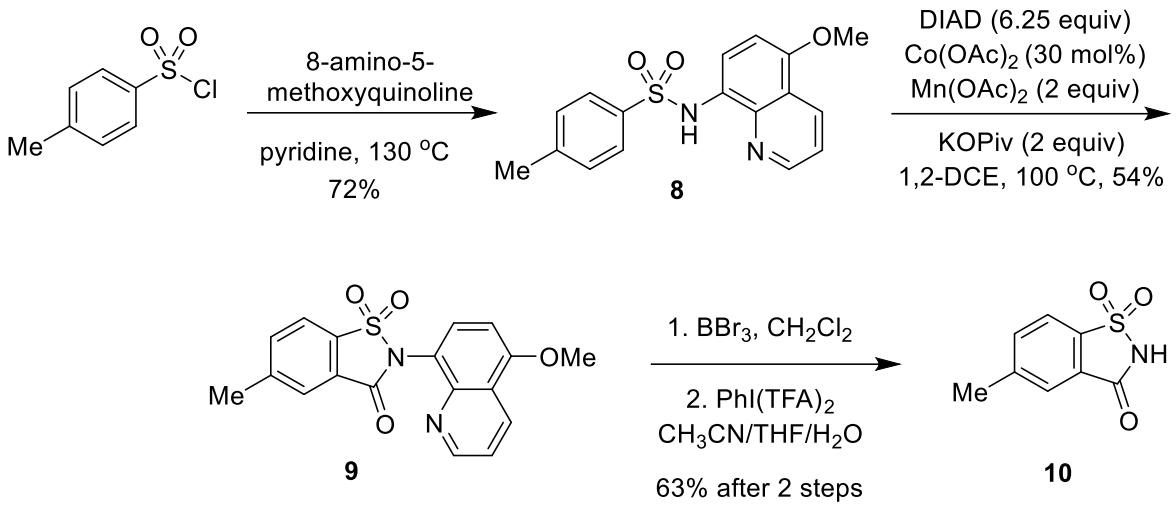
2 equiv), and 1,2-dichloroethane (10 mL). Carbon monoxide was bubbled through the mixture for 5 min at room temperature. The vial was capped and heated at 100 °C. After 24 h, reaction was cooled to room temperature. Crude mixture was diluted with saturated aqueous potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) gave 140 mg (94%) of starting material. Less than 5% of 5-methyl-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide was isolated after column chromatography.

Reaction with DIAD, reaction vessel periodically opened to air: A 20 mL vial equipped with a magnetic stir bar was charged with 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.5 mmol), DIAD (0.123 mL, 0.625 mmol, 1.25 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Reaction mixture was heated at 100 °C. After 2 h, the vial was opened and reaction was charged with additional DIAD (0.123 mL, 0.625 mL, 1.25 equiv). After 12 h, reaction was cooled to room temperature. Crude mixture was diluted with saturated aqueous potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) gave 52 mg (32%) of 5-methyl-2-(quinolin-8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide.

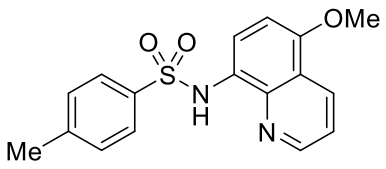
Reaction with DIAD under nitrogen: A 20 mL vial equipped with a magnetic stir bar was charged with 4-methyl-*N*-(quinolin-8-yl)benzenesulfonamide (149 mg, 0.5 mmol), DIAD (0.25 mL, 1.25 mmol, 2.5 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Nitrogen was bubbled through the mixture for 15 min at room temperature. Reaction vessel was then purged with nitrogen, capped, and heated at 100 °C. After 12 h, reaction was cooled to room temperature. Crude mixture was diluted with saturated potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 3:1 to 1:1) gave 19 mg (12%) of 5-methyl-2-(quinolin-

8-yl)benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide. The latter two experiments show that oxygen from air is the terminal oxidant.

III. Removal of directing group (Scheme 1)



***N*-(5-Methoxyquinolin-8-yl)-4-methylbenzenesulfonamide (8, Scheme 1)**



In a 40 mL vial, 8-amino-5-methoxyquinoline (1 g, 5.74 mmol, 1.05 equiv) was dissolved in pyridine (5 mL). Under air, 4-toluenesulfonyl chloride (1.04 g, 5.47 mmol, 1 equiv) was added to the stirred solution in one portion. The vial was capped and placed in a pre-heated oil bath at 130 °C (oil temperature). After 30 min, the reaction was cooled to 70 °C followed by rapidly pouring the solution into cold water (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 50 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography (gradient toluene/EtOAc from 100:1 to 50:1) afforded 1.3 g (72%) of *N*-(5-methoxyquinolin-8-yl)-4-methylbenzenesulfonamide as a light yellow solid.

R_f = 0.37 (hexanes/EtOAc 3:1), mp = 113 – 115 °C (Et_2O).

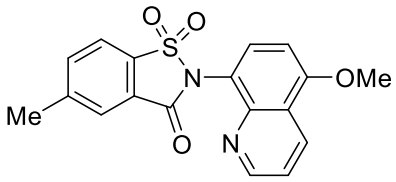
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.83 (s, 1H), 8.71 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 8.4, 4.3 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 151.25, 149.23, 143.52, 139.69, 136.39, 131.27, 129.41, 127.31, 126.84, 121.01, 120.71, 116.77, 104.08, 55.80, 21.53.

FT-IR (neat, cm^{-1}) ν 1479, 1424, 1327, 1308, 1271, 1161, 1145, 1087, 1067.

HR-MS calcd. for $C_{17}H_{16}N_2O_3S$ $[M+H]^+$: 329.0954; found: 329.0957.

2-(5-Methoxyquinolin-8-yl)-5-methylbenzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (9, Scheme 1)



A 20 mL vial was charged with *N*-(5-methoxyquinolin-8-yl)-4-methylbenzenesulfonamide (164 mg, 0.5 mmol), DIAD (0.123 mL, 0.625 mmol, 1.25 equiv), $Co(OAc)_2$ (27 mg, 0.15 mmol, 30 mol%), $Mn(OAc)_2$ (173 mg, 1.0 mmol, 2 equiv), KOPiv (140 mg, 1.0 mmol, 2 equiv), and 1,2-dichloroethane (10 mL). Reaction mixture was heated at 100 °C. After 2 h, 8 h, 20 h, and 24 h, the vial was opened and reaction was charged with additional DIAD (0.123 mL, 0.625 mmol, 1.25 equiv, total 5 times = 6.25 equiv). After 30 h, reaction was cooled to room temperature. Crude mixture was diluted with saturated aqueous potassium sodium tartrate solution (20 mL) followed by extraction with CH_2Cl_2 (3 x 30 mL). Combined organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification by column chromatography on silica gel (gradient hexanes/EtOAc from 4:1 to 1:1) afforded 96 mg (54%) of 2-(5-methoxyquinolin-8-yl)-5-methylbenzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide as a tan solid.

R_f = 0.1 (hexanes/EtOAc 3:1), mp = 248 – 250 °C (hexanes/EtOAc 1:1).

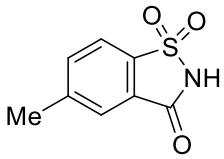
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.89 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.60 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.97 (s, 1H), 7.89 (dd, *J* = 12.8, 8.1 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 4.03 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 159.5, 157.5, 151.7, 145.8, 145.4, 135.5, 132.4, 131.3, 128.0, 126.1, 122.1, 121.4, 118.5, 103.9, 56.2, 22.0. Two carbon signals could not be assigned.

FT-IR (neat, cm^{-1}) ν 1726, 1588, 1399, 1341, 1299, 1182, 1165, 1148, 1119, 1089, 1064.

HR-MS calcd. for $C_{18}H_{14}N_2O_4S$ $[M+H]^+$: 355.0747; found: 355.0749.

5-Methylbenzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (10, Scheme 1)



An adaptation of a known procedure was used.[5] An oven-dried 20 mL vial was charged with 2-(5-methoxyquinolin-8-yl)-5-methylbenzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (177 mg, 0.5 mmol). The vial was evacuated and backfilled with nitrogen three times. Under N_2, CH_2Cl_2 (5 mL) was added via syringe. The flask was placed in an ice/water bath, followed by adding dropwise a CH_2Cl_2 solution of BBr_3 (1 M, 2 mL, 2 mmol, 4 equiv) under vigorous stirring. Resulting solution was then stirred at room temperature for 16 h. The flask was placed in an ice/water bath and the reaction was slowly quenched with H_2O (10 mL) under air. The crude mixture was then extracted with ethyl acetate (3 x 20 mL). Combined organic phase was dried over Na_2SO_4, filtered, concentrated, and used for next step without further purification.

The orange residue was suspended in mixture of CH_3CN, THF, and H_2O (4:1:2 v/v, 10 mL). The flask containing the suspension was placed in ice/water bath, followed by slow addition of [bis(trifluoroacetoxy)iodo]benzene (322 mg, 0.75 mmol, 1.5 equiv; 5 min). The solution was kept at 0 °C and vigorously stirred for 6 h. Reaction was then quenched by adding H_2O (5 mL) at 0 °C and was extracted with $CHCl_3$/*iso*-propanol 3:1 (3 x 15 mL). Combined organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was placed in crushed ice (around 5 g) and the crude product was obtained. Washing with cold water (20 mL) and mixture of hexanes/EtOAc 9:1 (10 mL x 2) followed by drying under vacuum at 60 °C overnight afforded 66 mg (63%) of 5-methylbenzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide as a brown solid. This compound is known.[6]

mp = 200 – 202 °C (hexanes/EtOAc 3:1).

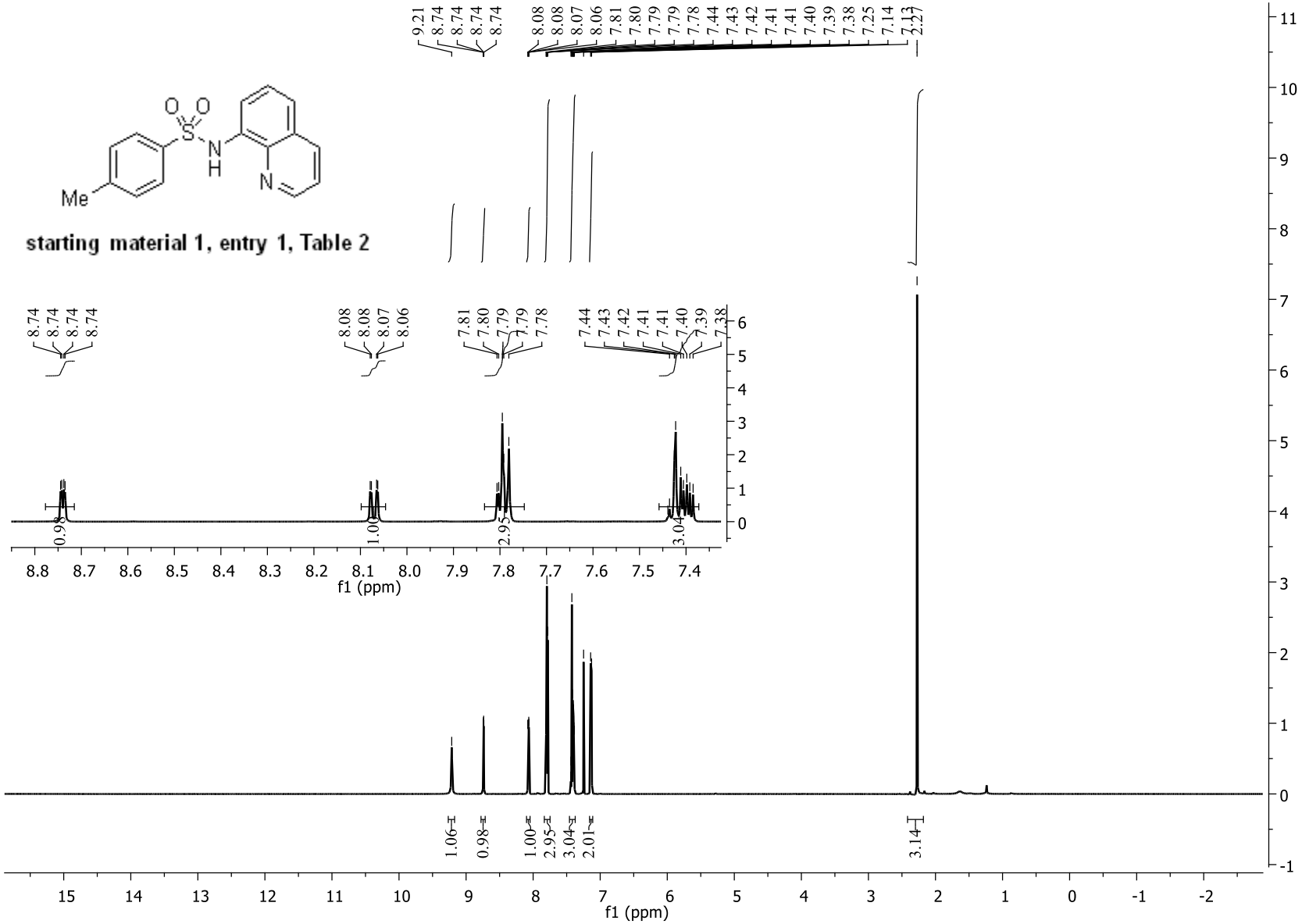
^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 10.41 (bs, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.90 – 7.75 (m, 2H), 2.46 (s, 3H, overlapping with DMSO signal).

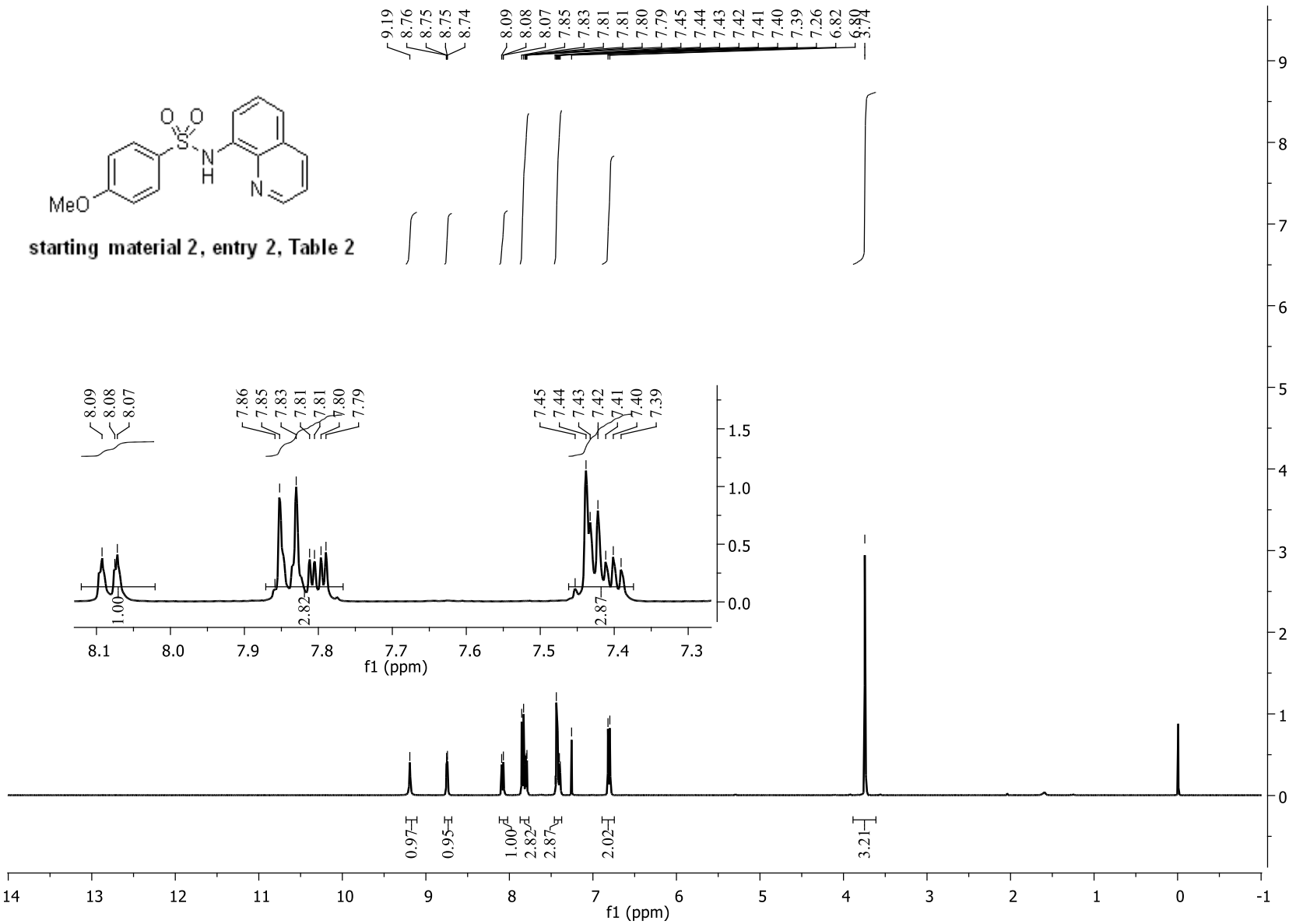
[5] This procedure is slightly modified from known procedure: (a) Nakazaki, A.; Mori, A.; Kobayashi, S.; Nishikawa, T. *Tetrahedron Lett.* **2012**, *53*, 7131. (b) Deng, Y.; Gong, W.; He, J.; Yu, J.-Q. *Angew. Chem. Int. Ed.* **2014**, *53*, 6692.

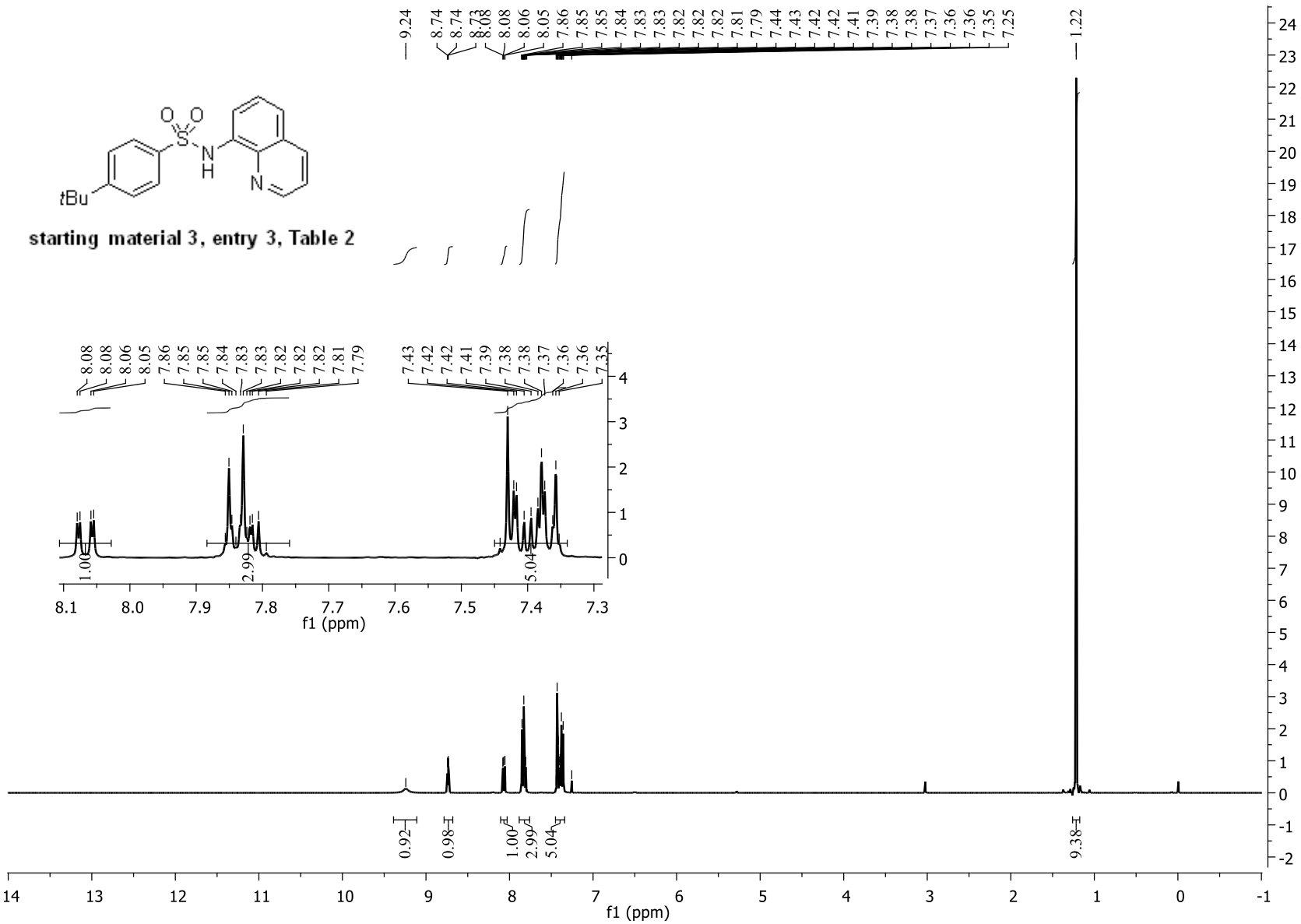
[6] Lombardino, J. G. *J. Org. Chem.* **1971**, *36*, 1843.

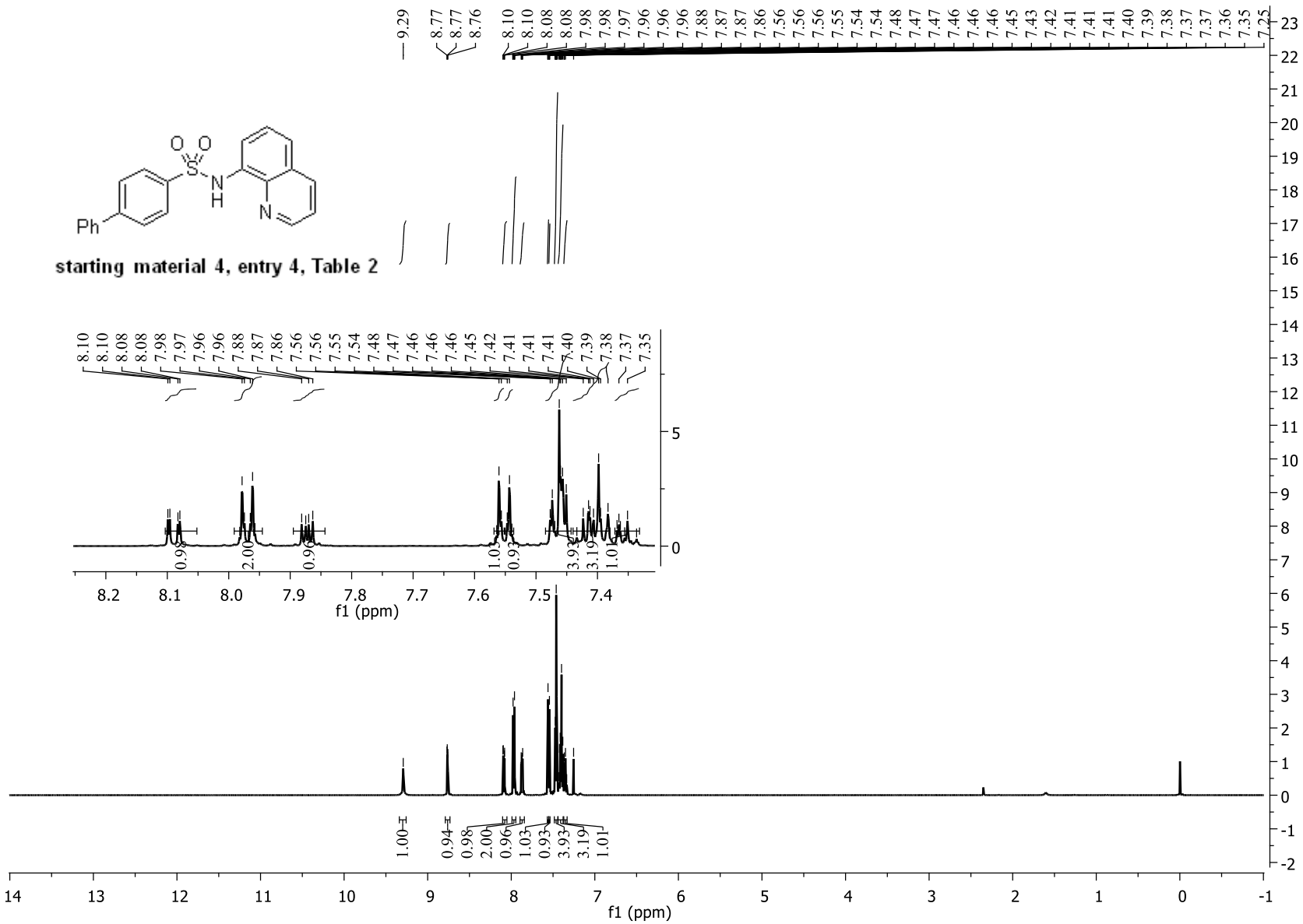
^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 161.28, 146.37, 137.06, 136.55, 128.16, 125.47, 121.54, 21.61.

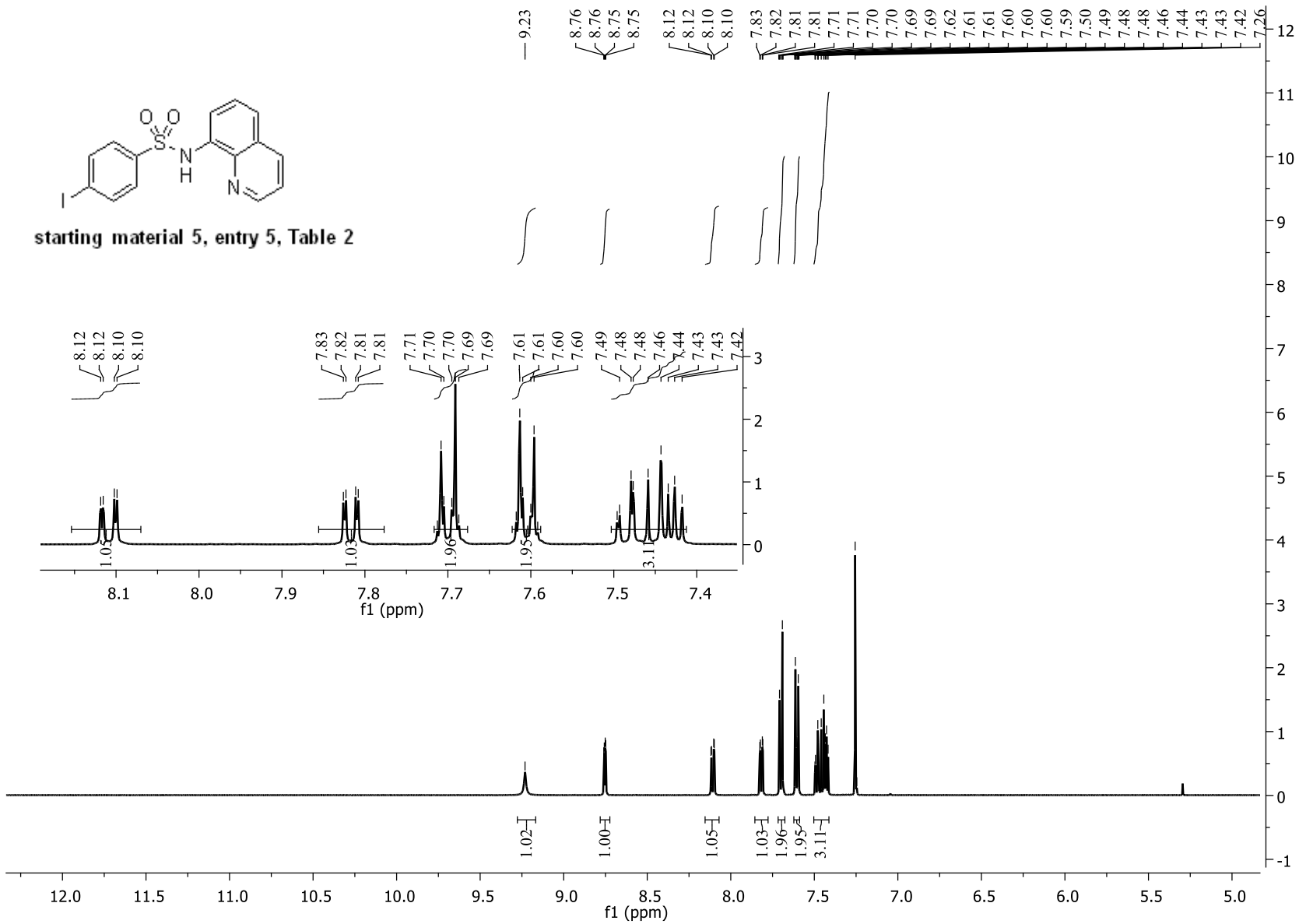
FT-IR (neat, cm^{-1}) ν 1714, 1336, 1296, 1257, 1175, 1138, 1116.

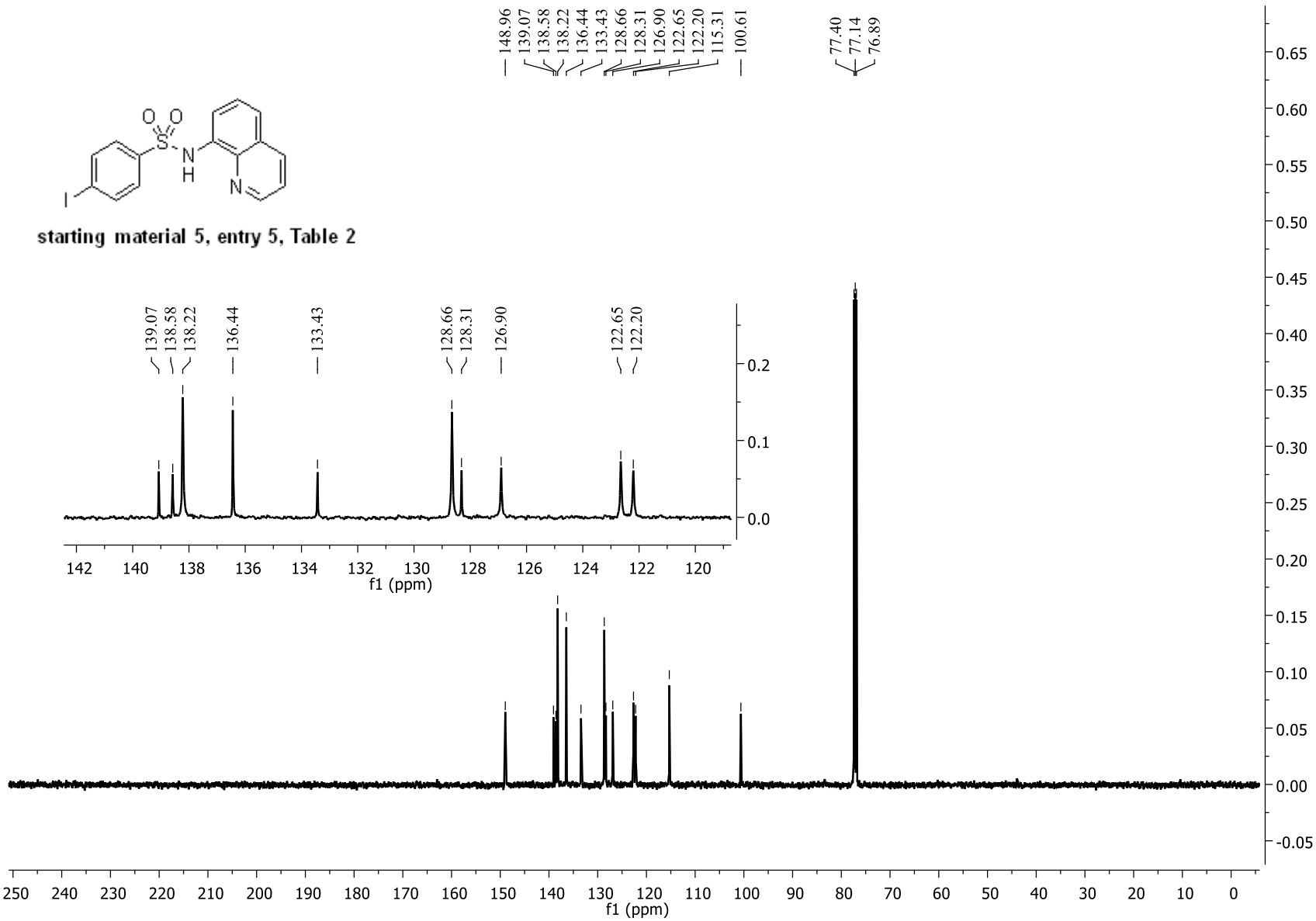

starting material 1, entry 1, Table 2
f1 (ppm)
f1 (ppm)

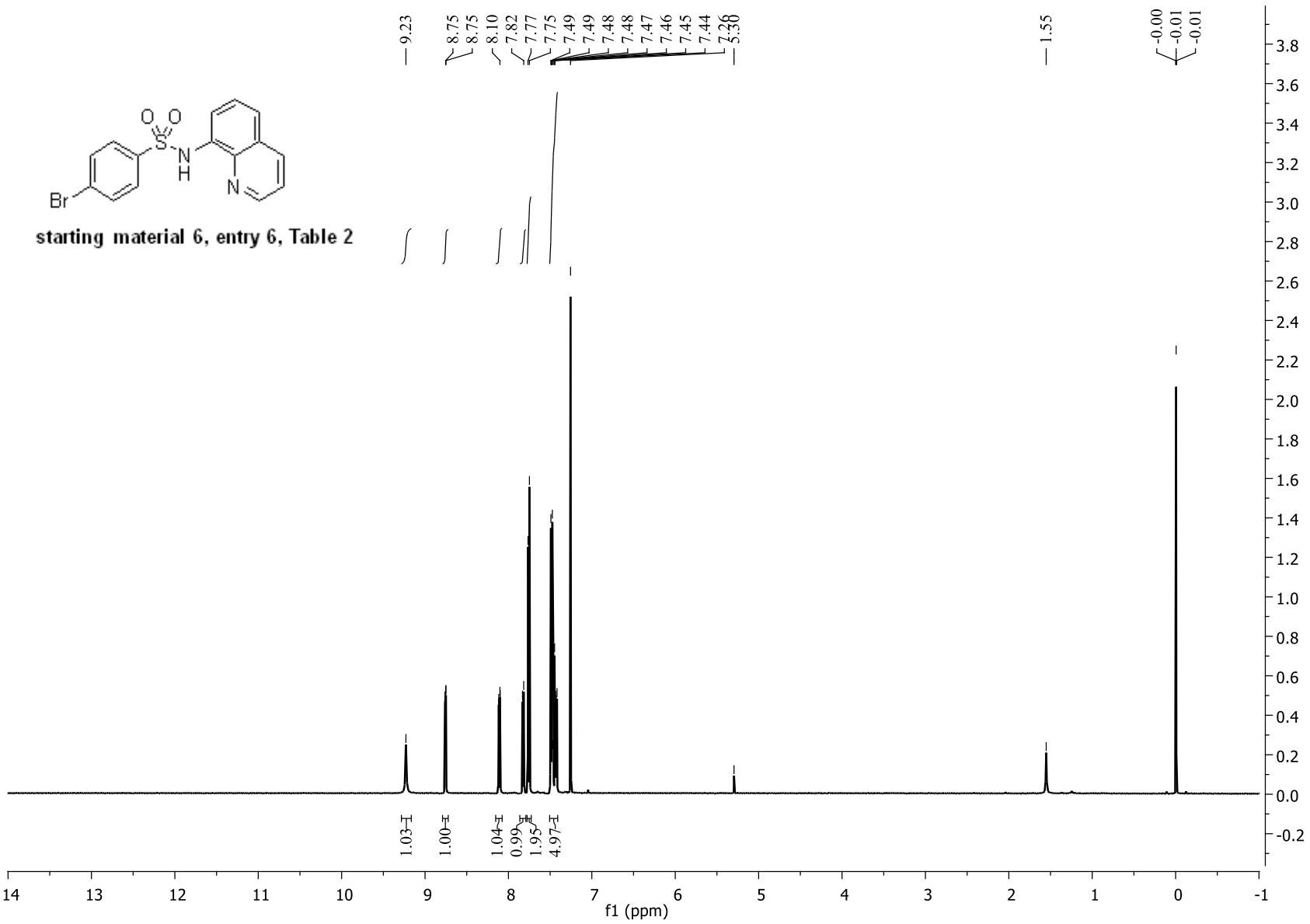

9.19
8.76
8.75
8.75
8.74
8.09
8.08
8.07
7.85
7.83
7.81
7.81
7.80
7.79
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.26
6.82
6.80
3.74
MeO
starting material 2, entry 2, Table 2
f1 (ppm)
0.97
0.95
1.00
2.82
2.87
2.02
3.21

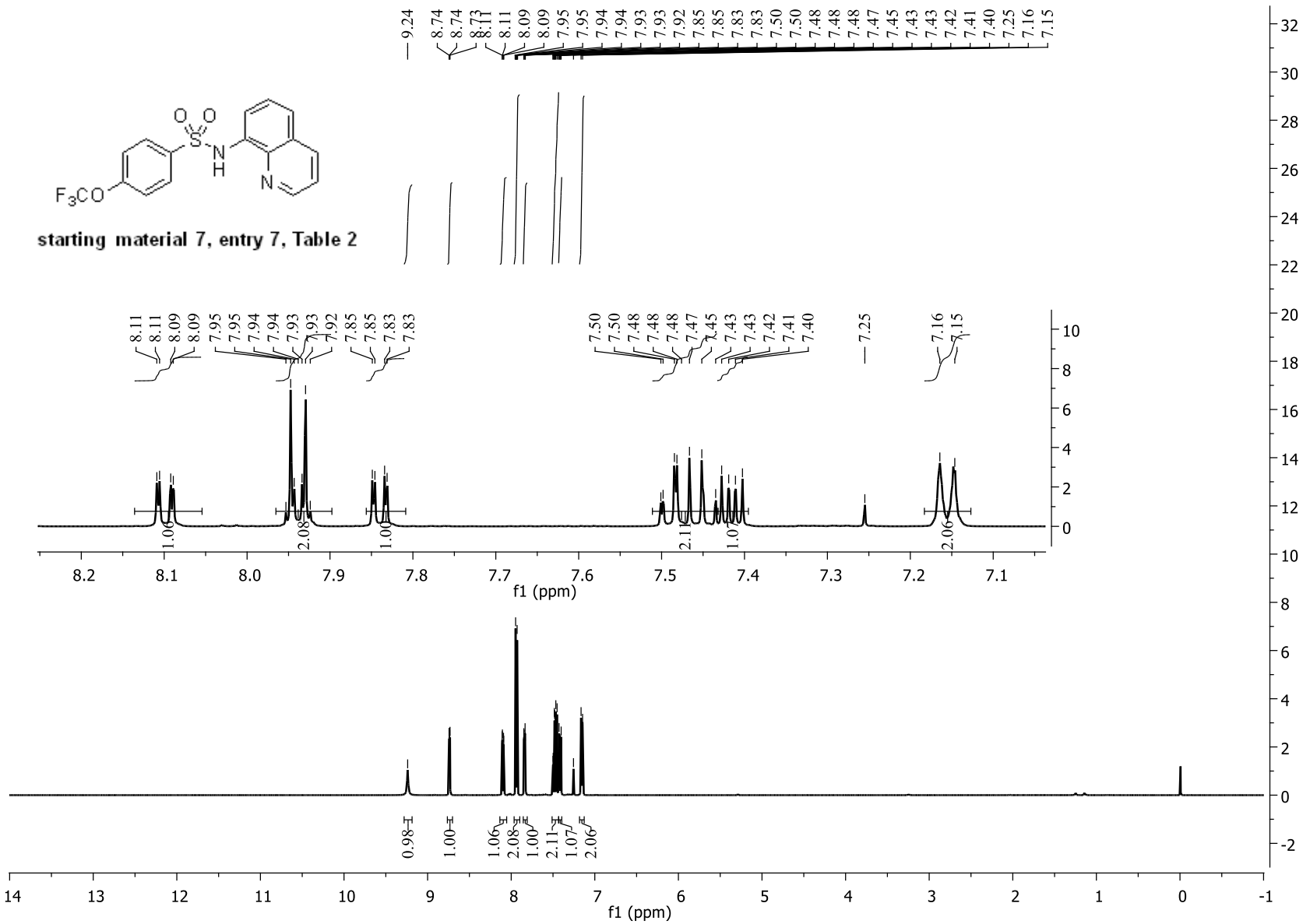

starting material 3, entry 3, Table 2
f1 (ppm)

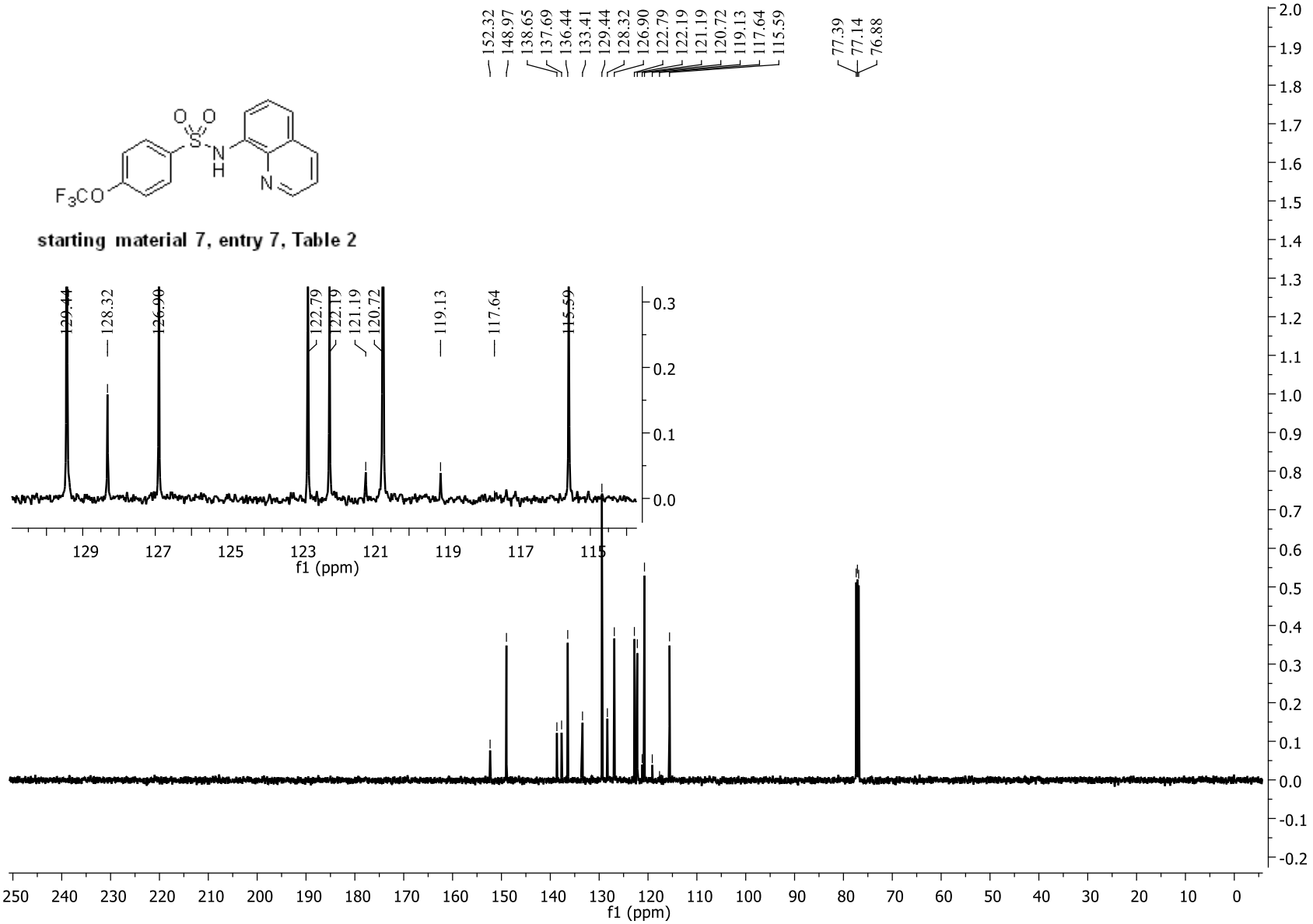

starting material 4, entry 4, Table 2
f1 (ppm)
f1 (ppm)

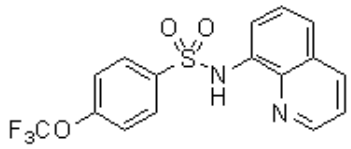

starting material 5, entry 5, Table 2
f1 (ppm)
f1 (ppm)


148.96
139.07
138.58
138.22
136.44
133.43
128.66
128.31
126.90
122.65
122.20
115.31
100.61
77.40
77.14
76.89
O
O
S
N
H
I
N
starting material 5, entry 5, Table 2
f1 (ppm)
f1 (ppm)

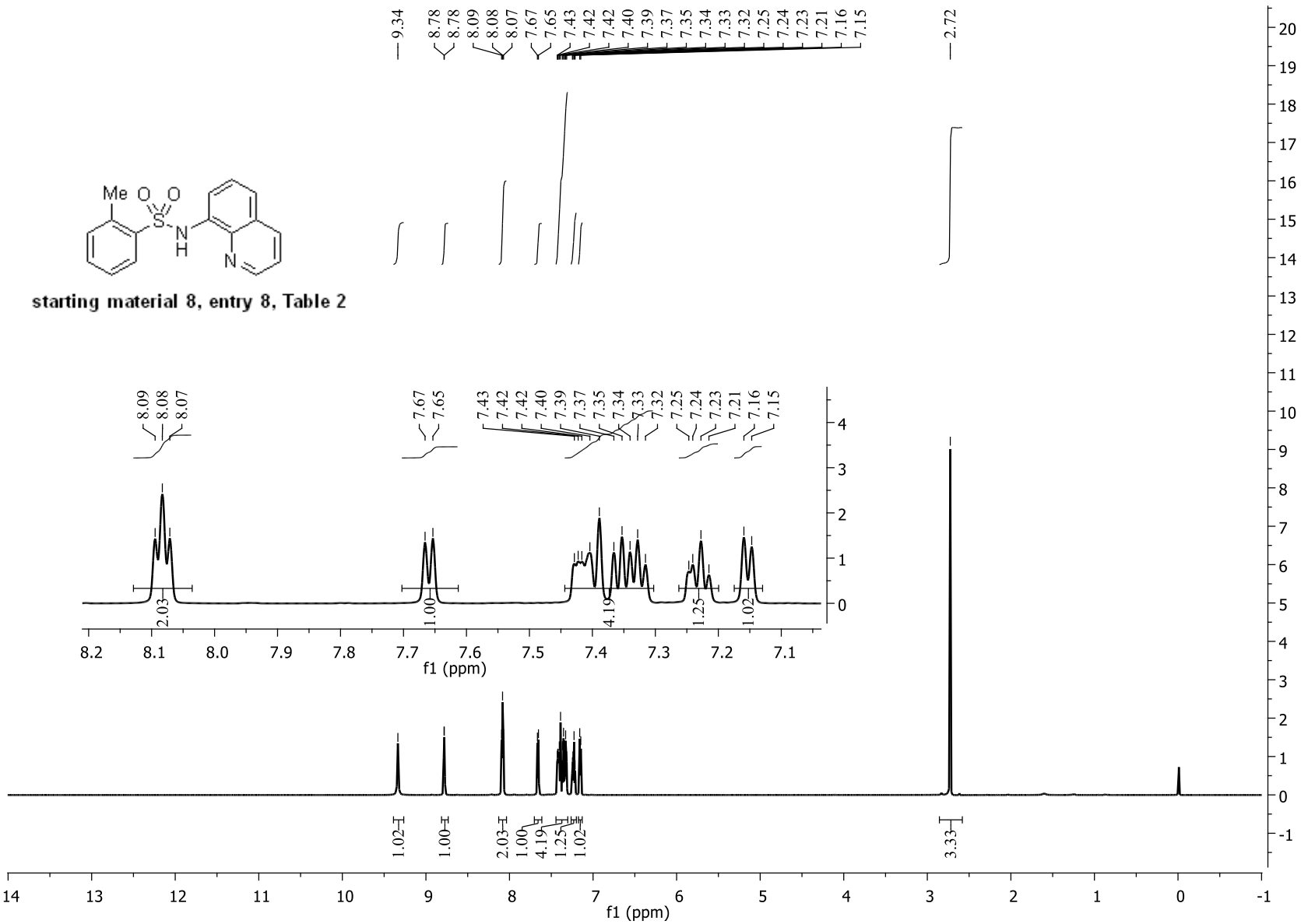

9.23
8.75
8.75
8.10
7.82
7.77
7.75
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.26
5.30
1.55
-0.00
-0.01
-0.01
Br
O
O
S
N
H
N
starting material 6, entry 6, Table 2
1.03
1.00
1.04
0.99
1.95
4.97
f1 (ppm)

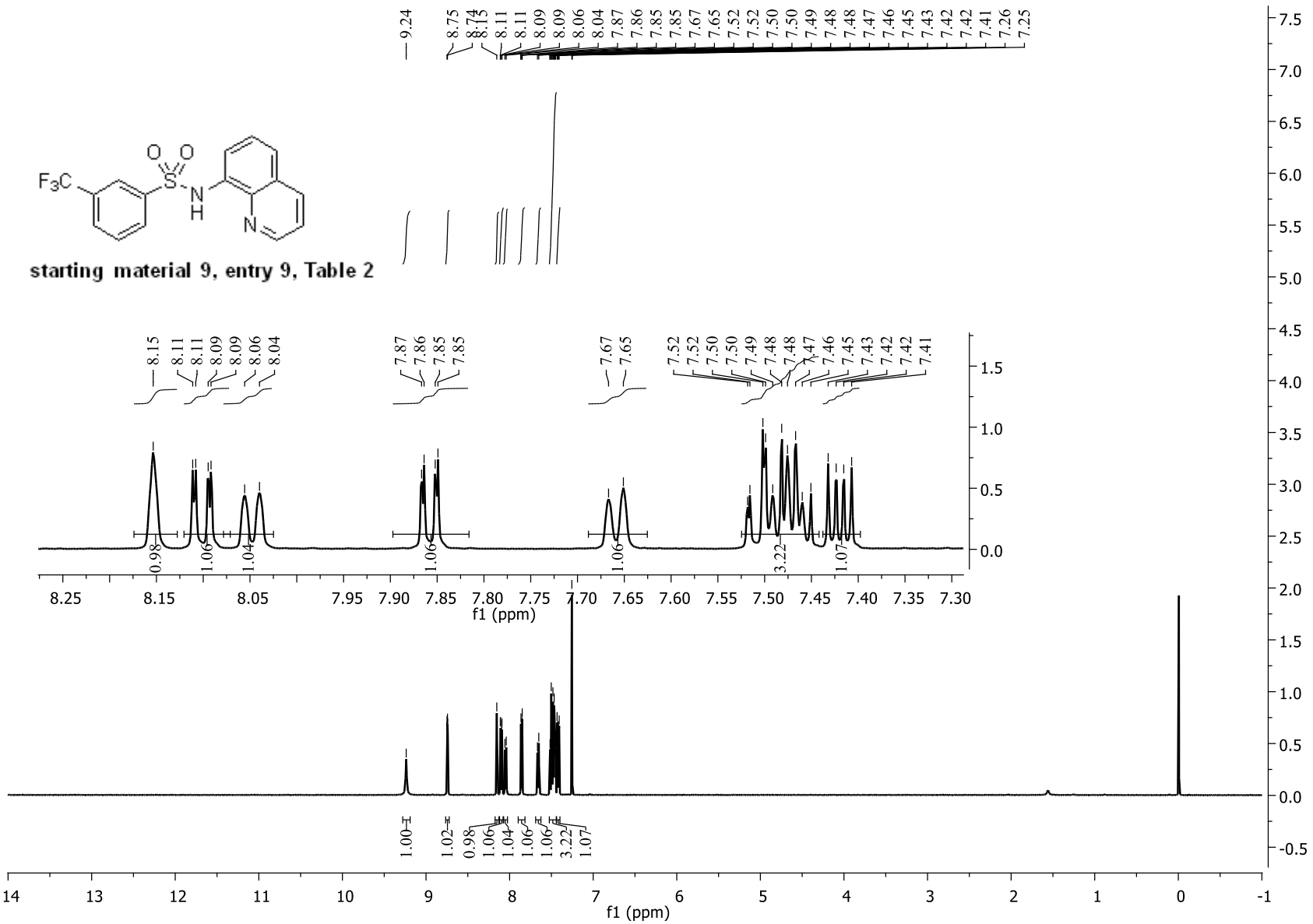

starting material 7, entry 7, Table 2
f1 (ppm)
f1 (ppm)

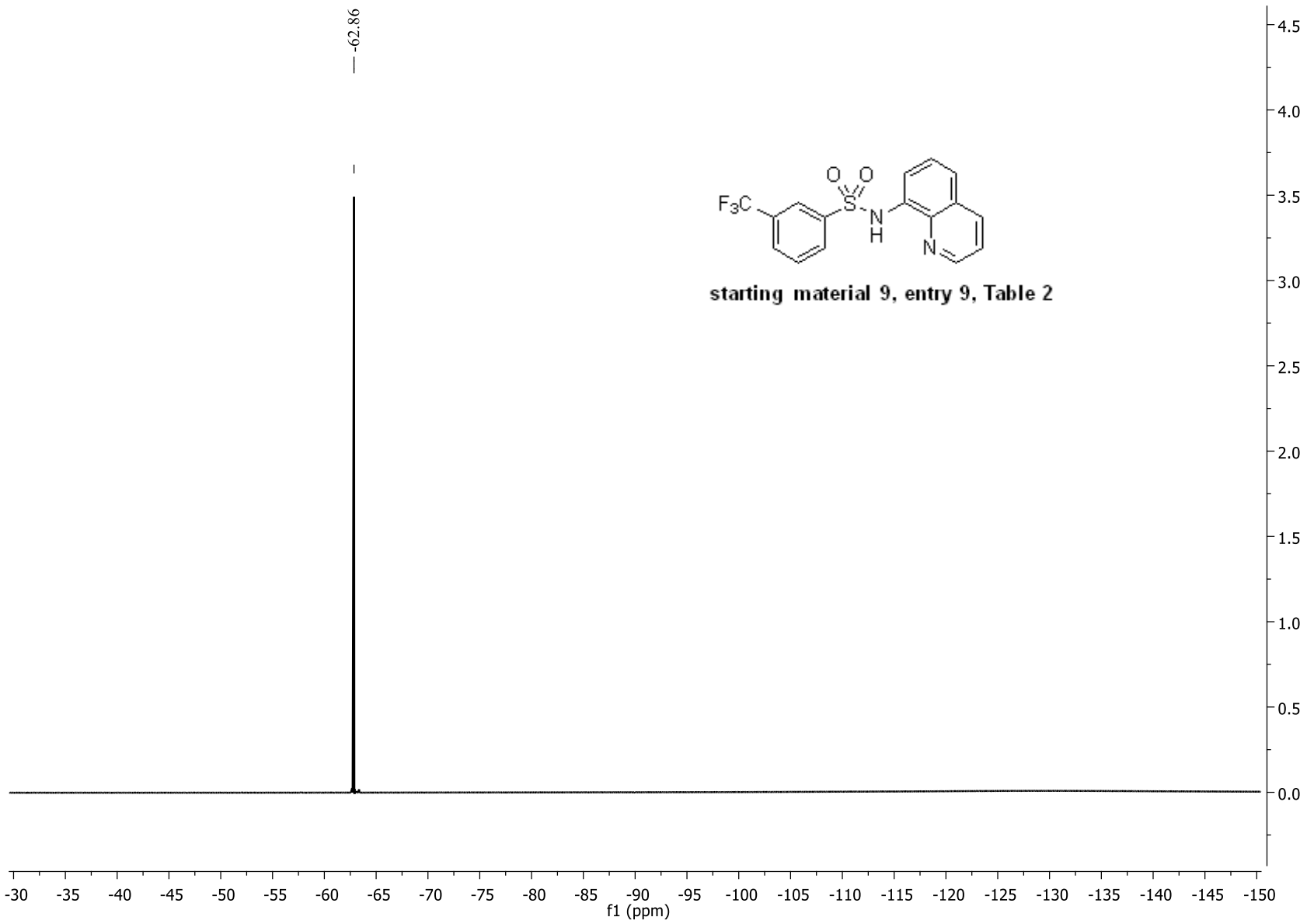

152.32
148.97
138.65
137.69
136.44
133.41
129.44
128.32
126.90
122.79
122.19
121.19
120.72
119.13
117.64
115.59
77.39
77.14
76.88
O
O
S
N
H
N
F3CO
starting material 7, entry 7, Table 2
f1 (ppm)
f1 (ppm)

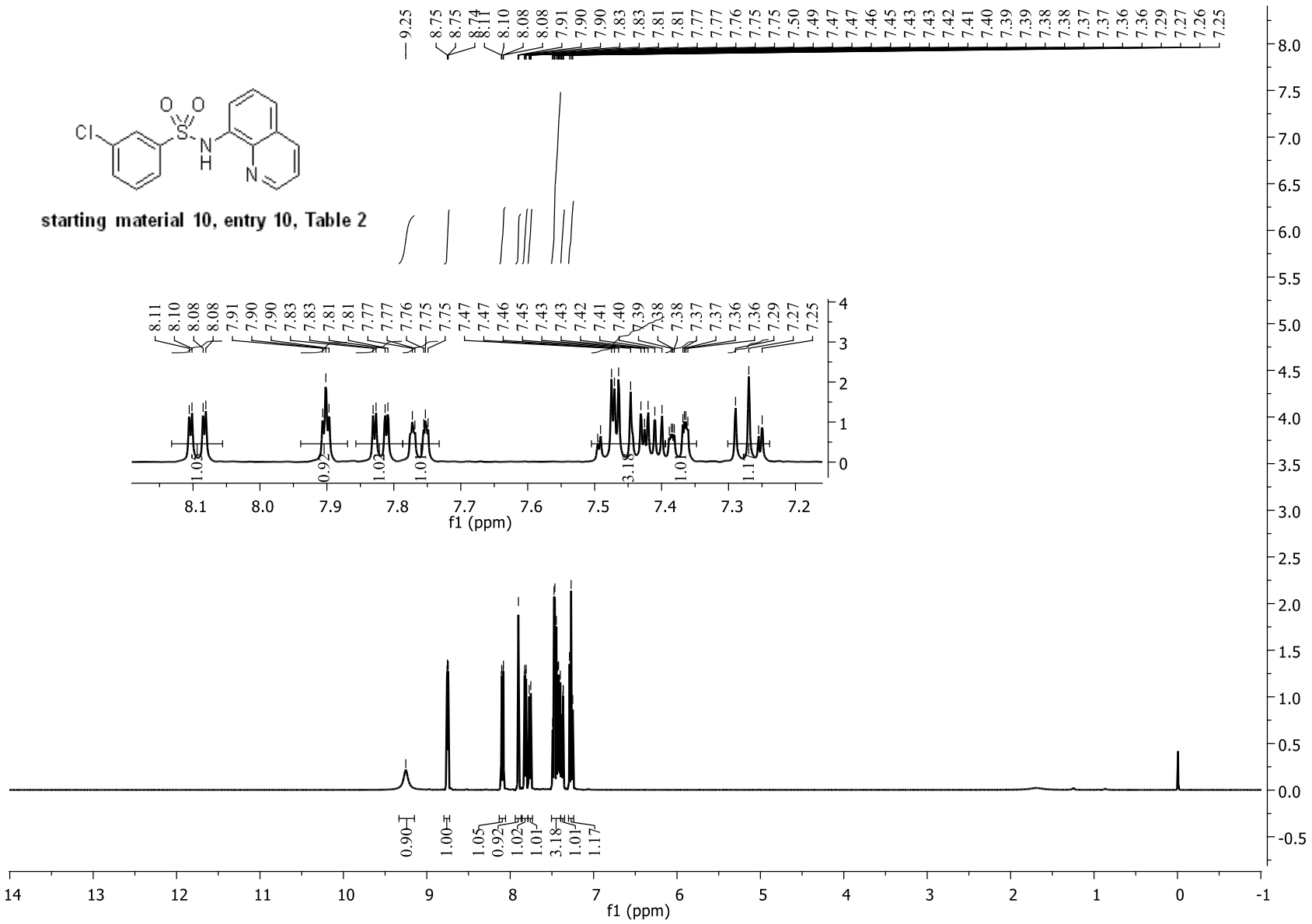


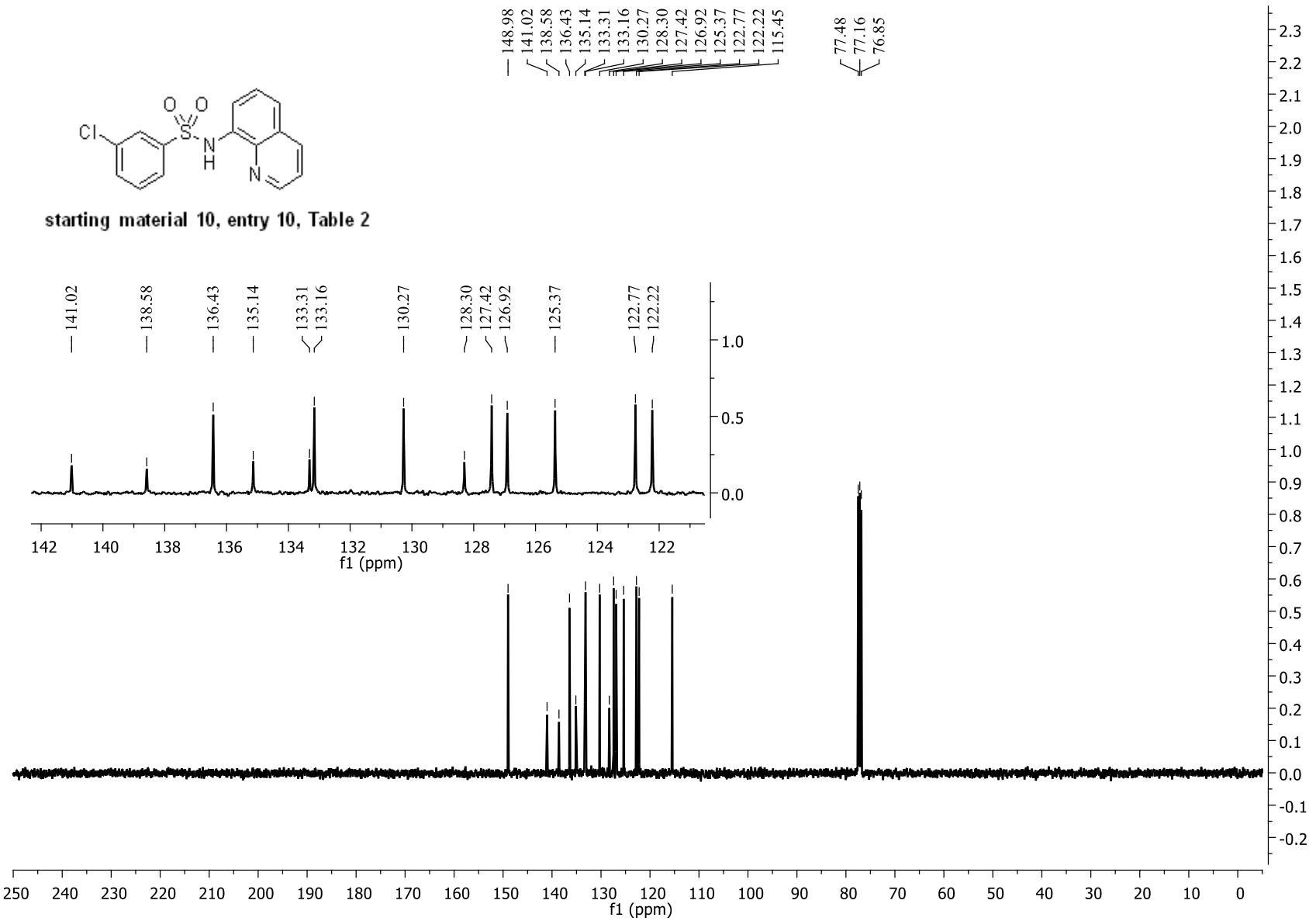
starting material 7, entry 7, Table 2

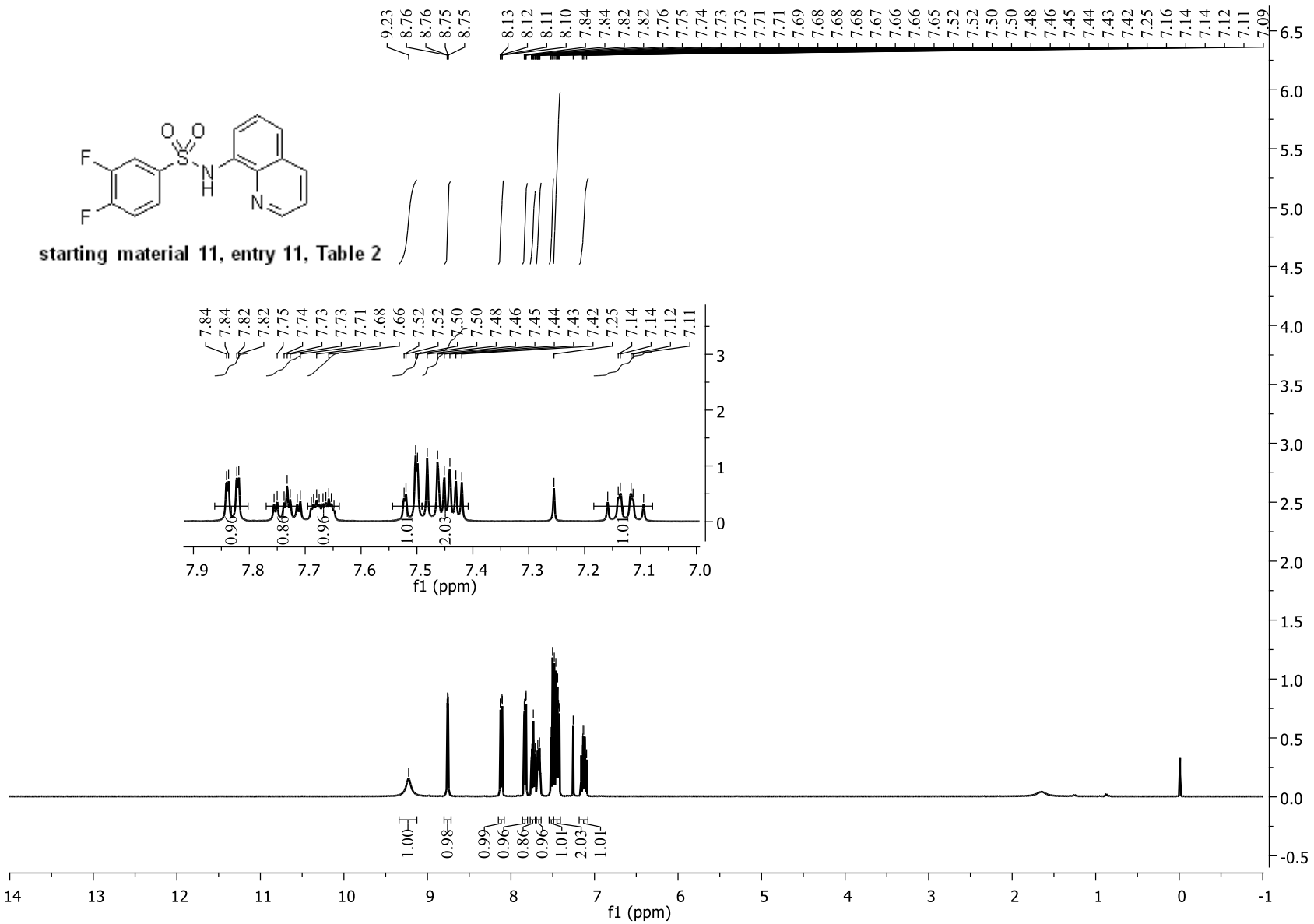

9.34
8.78
8.78
8.09
8.08
8.07
7.67
7.65
7.43
7.42
7.42
7.40
7.39
7.37
7.35
7.34
7.33
7.32
7.25
7.24
7.23
7.21
7.16
7.15
2.72
Me
O
O
S
N
H
N
starting material 8, entry 8, Table 2
2.03
1.00
4.19
1.25
1.02
f1 (ppm)
1.02
1.00
2.03
1.00
4.19
1.25
1.02
3.33
f1 (ppm)

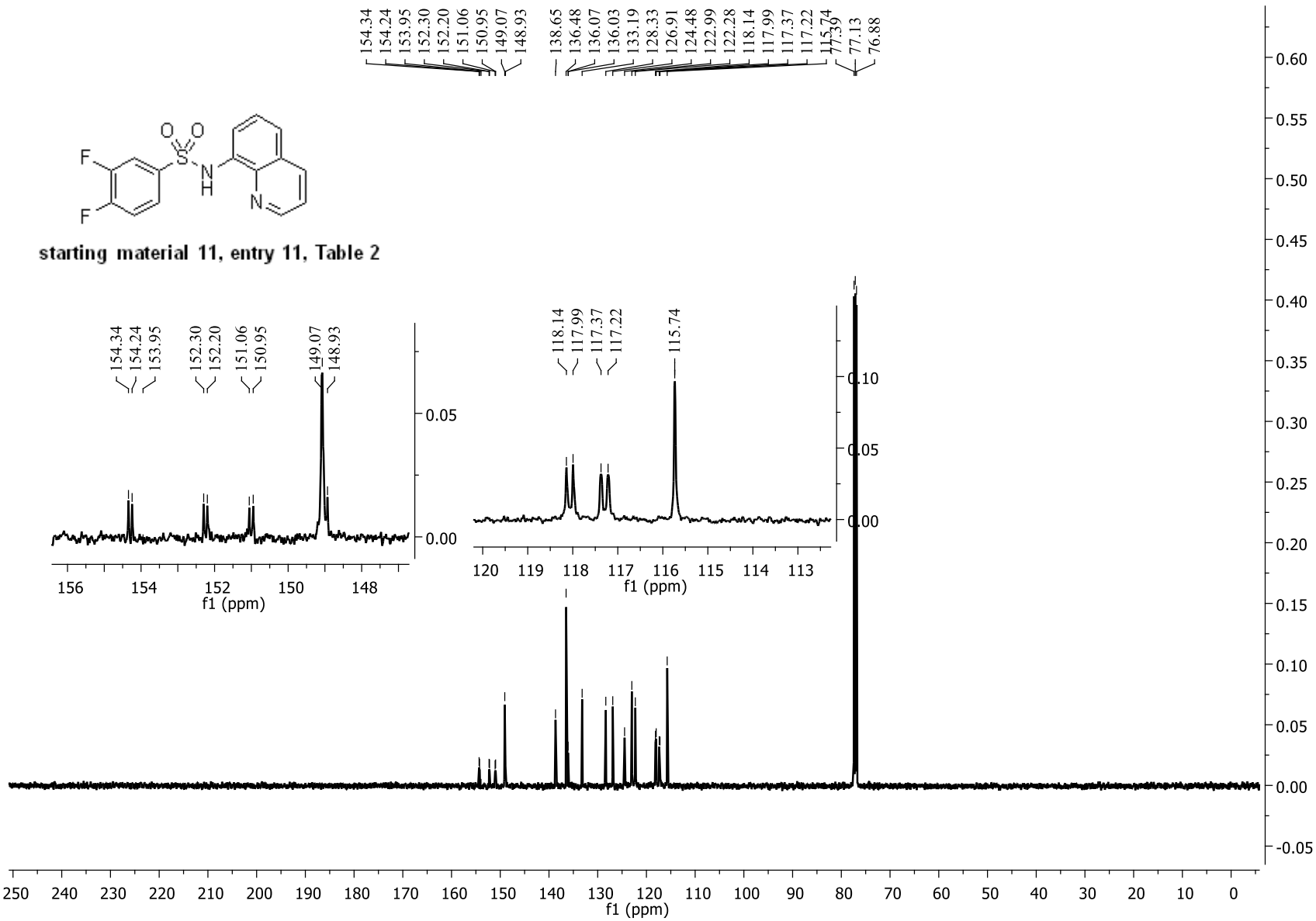

9.24
8.75
8.74
8.15
8.11
8.11
8.09
8.09
8.06
8.04
7.87
7.86
7.85
7.85
7.67
7.65
7.52
7.52
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.43
7.42
7.42
7.41
7.26
7.25
F3C
O
O
S
N
H
N
starting material 9, entry 9, Table 2
0.98
1.06
1.04
1.06
1.06
3.22
1.07
f1 (ppm)
1.00
1.02
0.98
1.06
1.04
1.06
1.06
3.22
1.07
f1 (ppm)

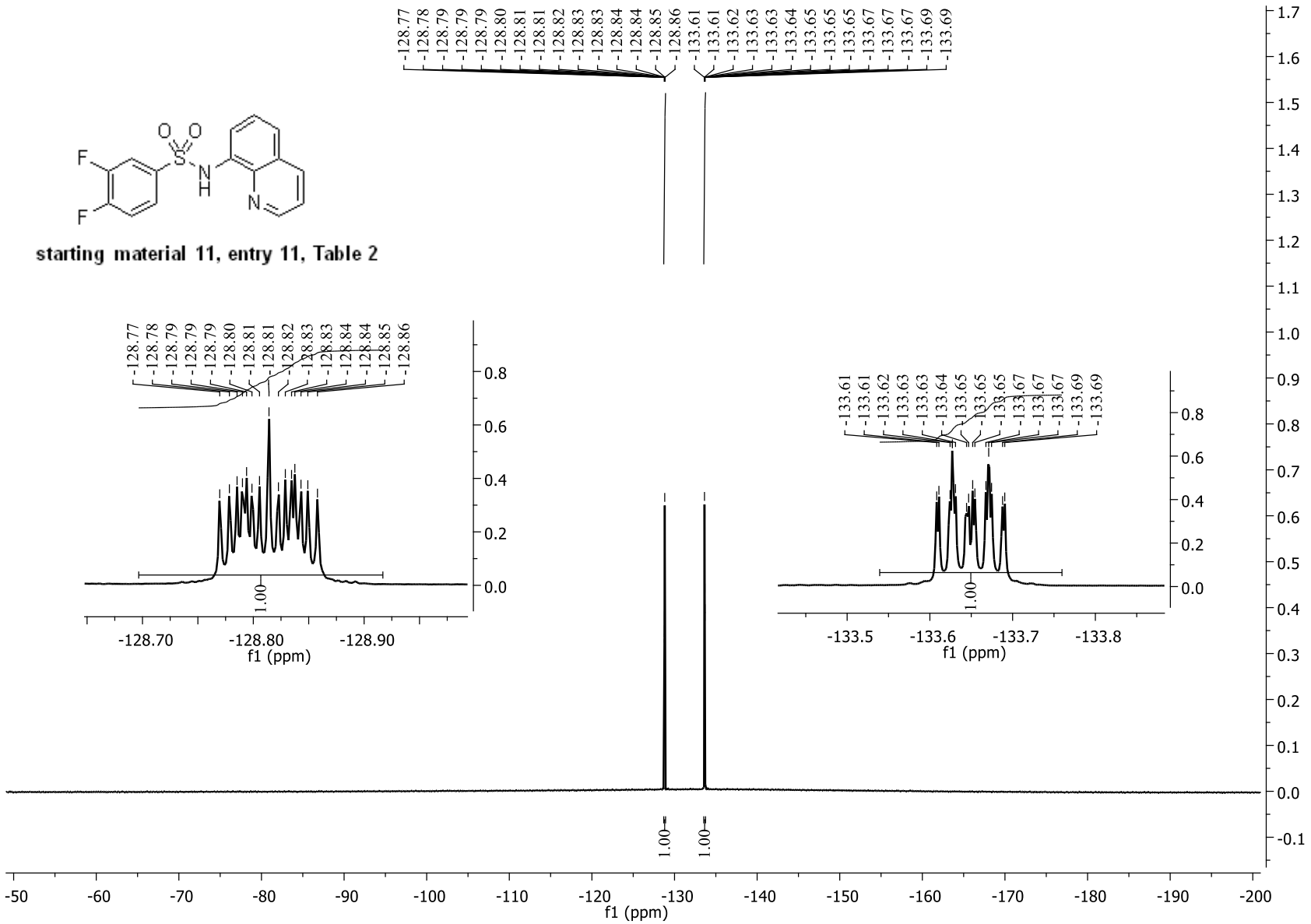

-62.86
starting material 9, entry 9, Table 2
f1 (ppm)

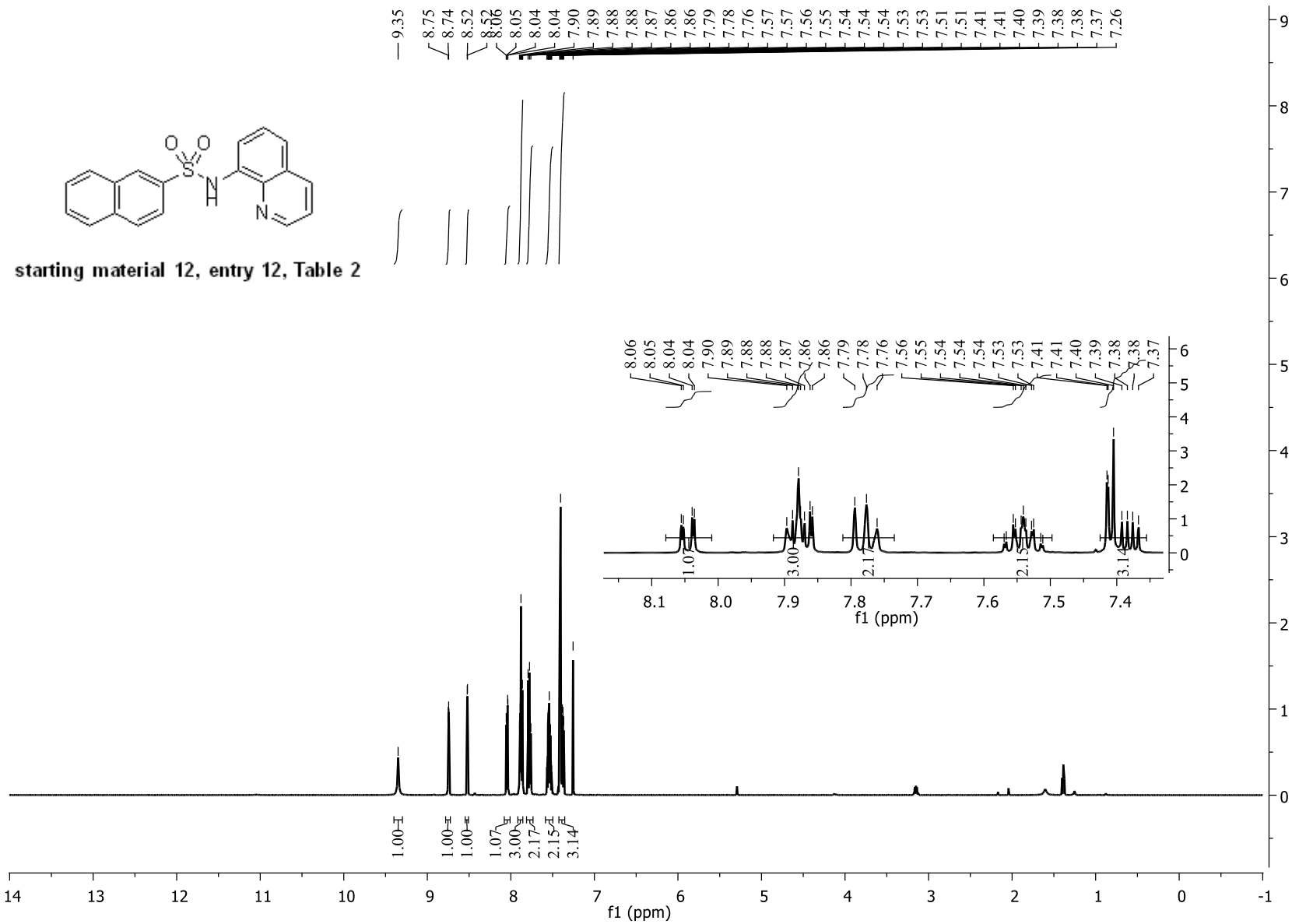

starting material 10, entry 10, Table 2
f1 (ppm)
f1 (ppm)

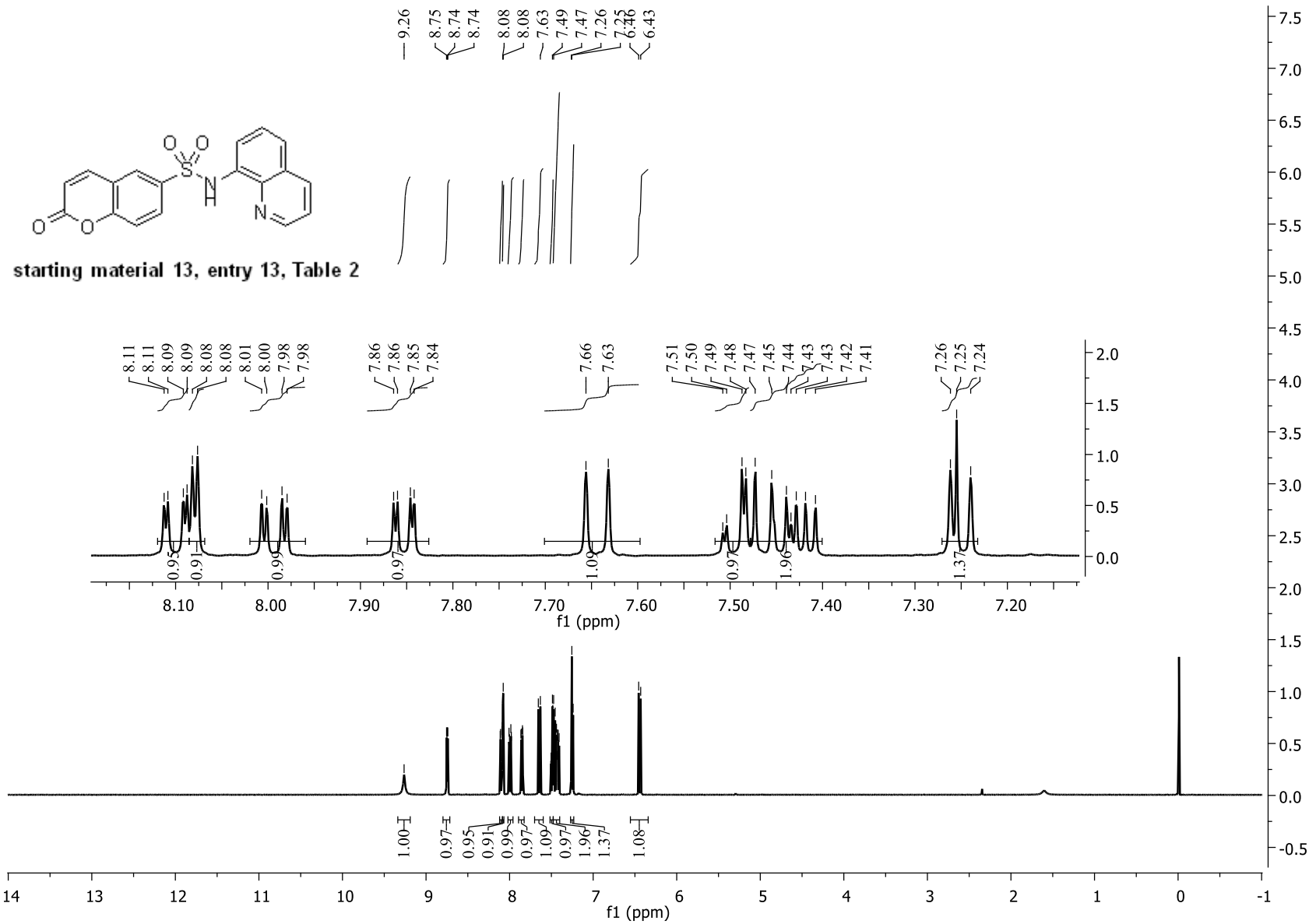

148.98
141.02
138.58
136.43
135.14
133.31
133.16
130.27
128.30
127.42
126.92
125.37
122.77
122.22
115.45
77.48
77.16
76.85
Cl
O
O
S
N
H
N
starting material 10, entry 10, Table 2
f1 (ppm)
f1 (ppm)

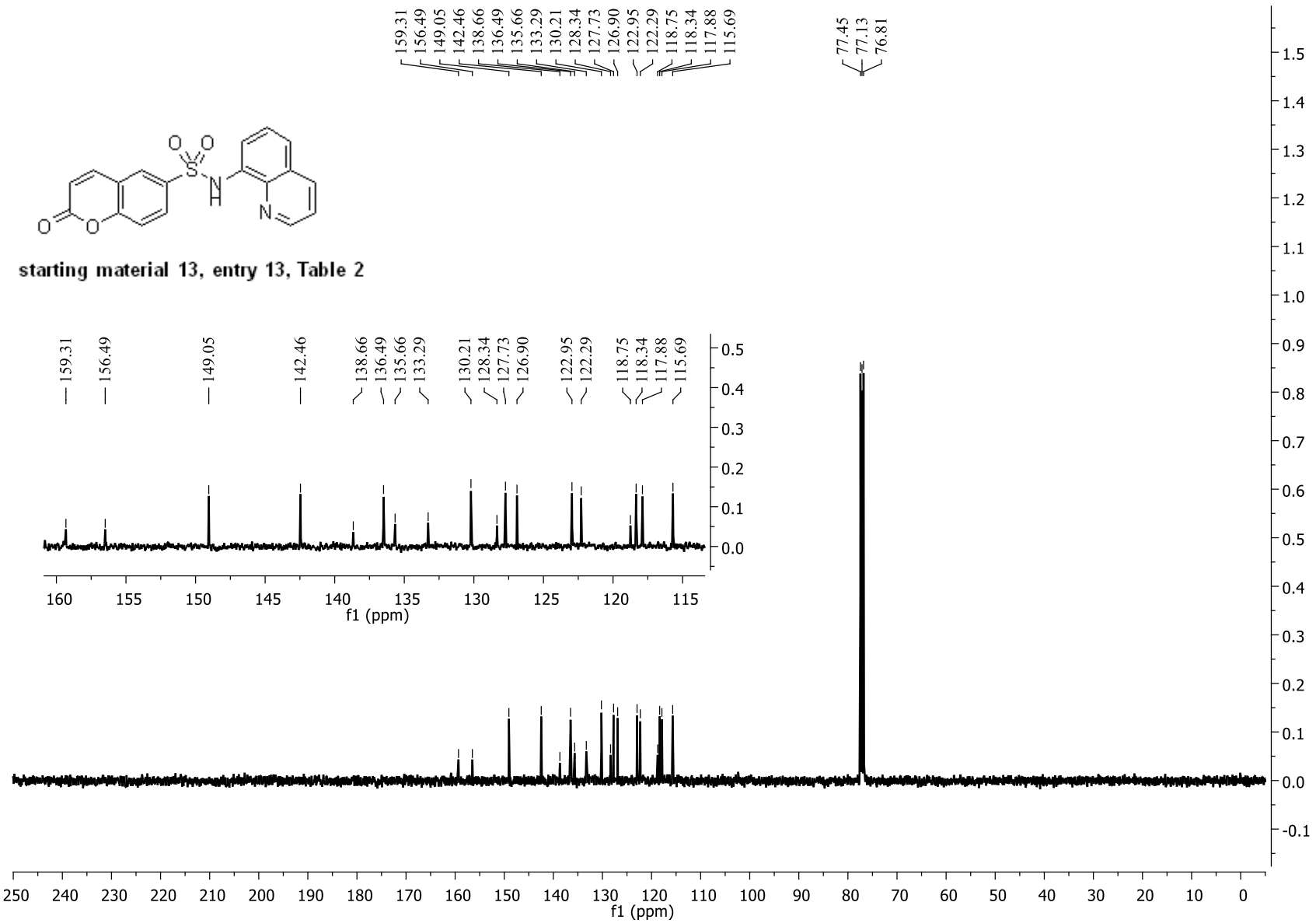

starting material 11, entry 11, Table 2
f1 (ppm)
f1 (ppm)

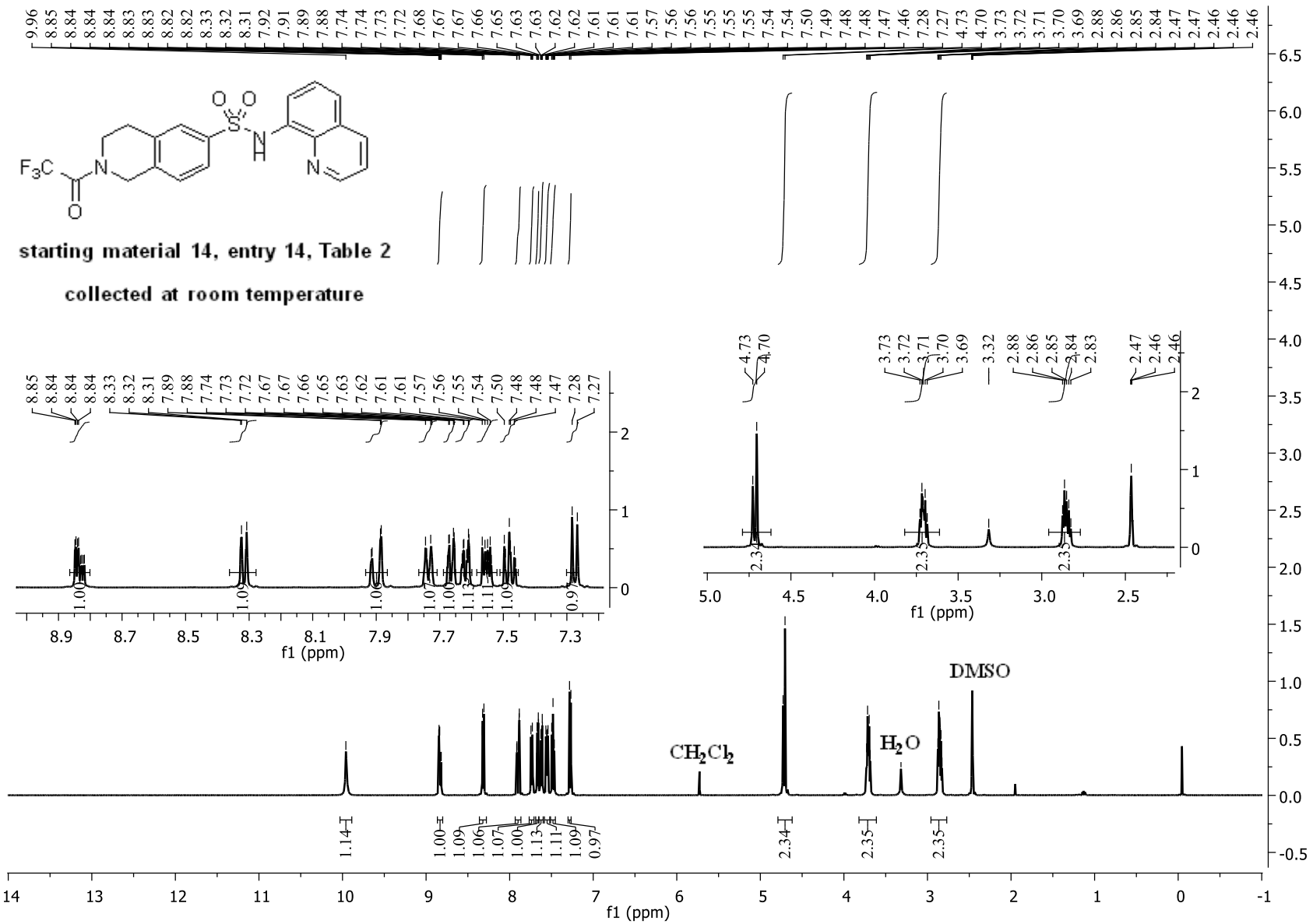

154.34
154.24
153.95
152.30
152.20
151.06
150.95
149.07
148.93
138.65
136.48
136.07
136.03
133.19
128.33
126.91
124.48
122.99
122.28
118.14
117.99
117.37
117.22
115.74
77.39
77.13
76.88
O
O
S
N
H
F
F
N
starting material 11, entry 11, Table 2
f1 (ppm)
f1 (ppm)
f1 (ppm)

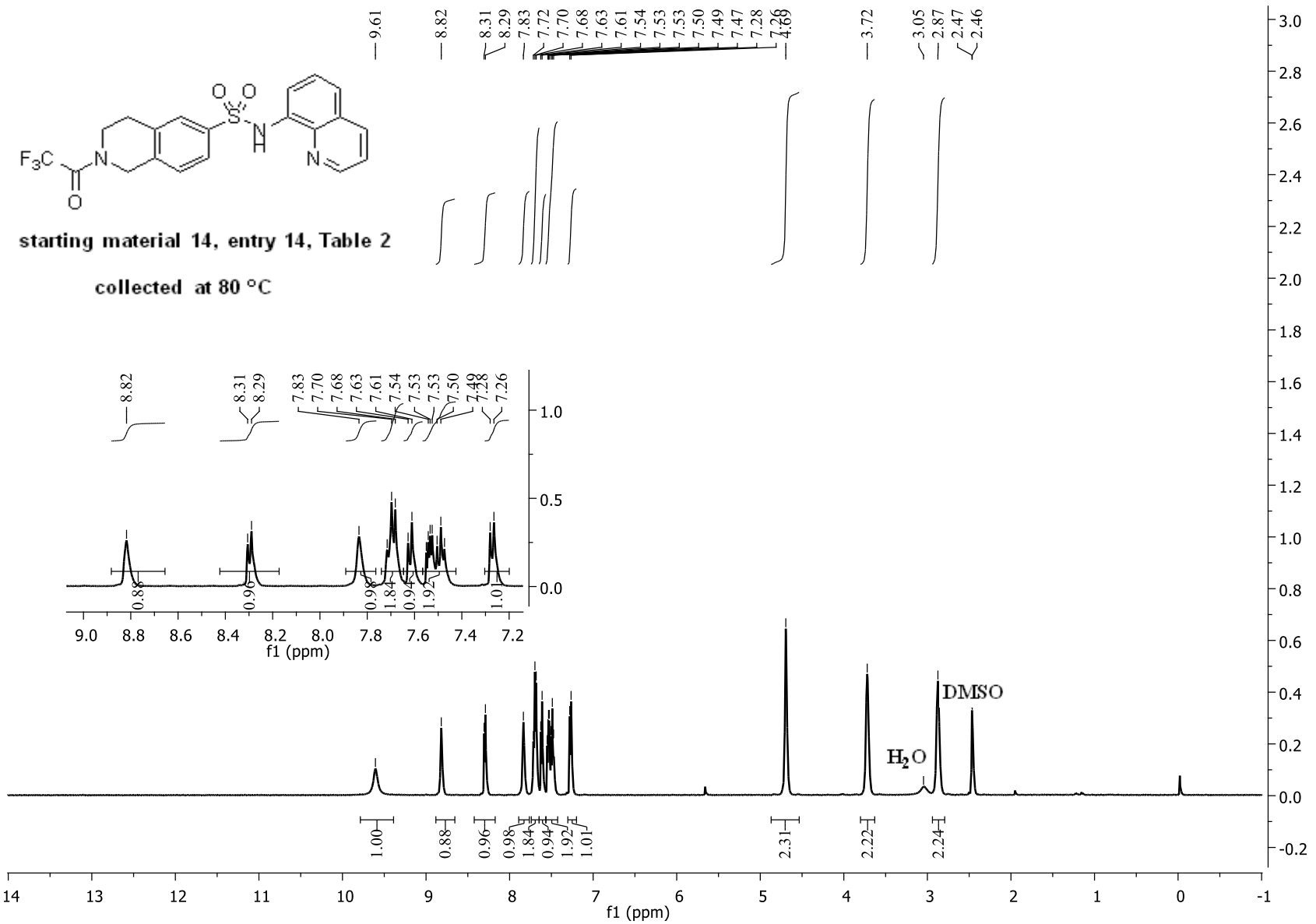

starting material 11, entry 11, Table 2
f1 (ppm)

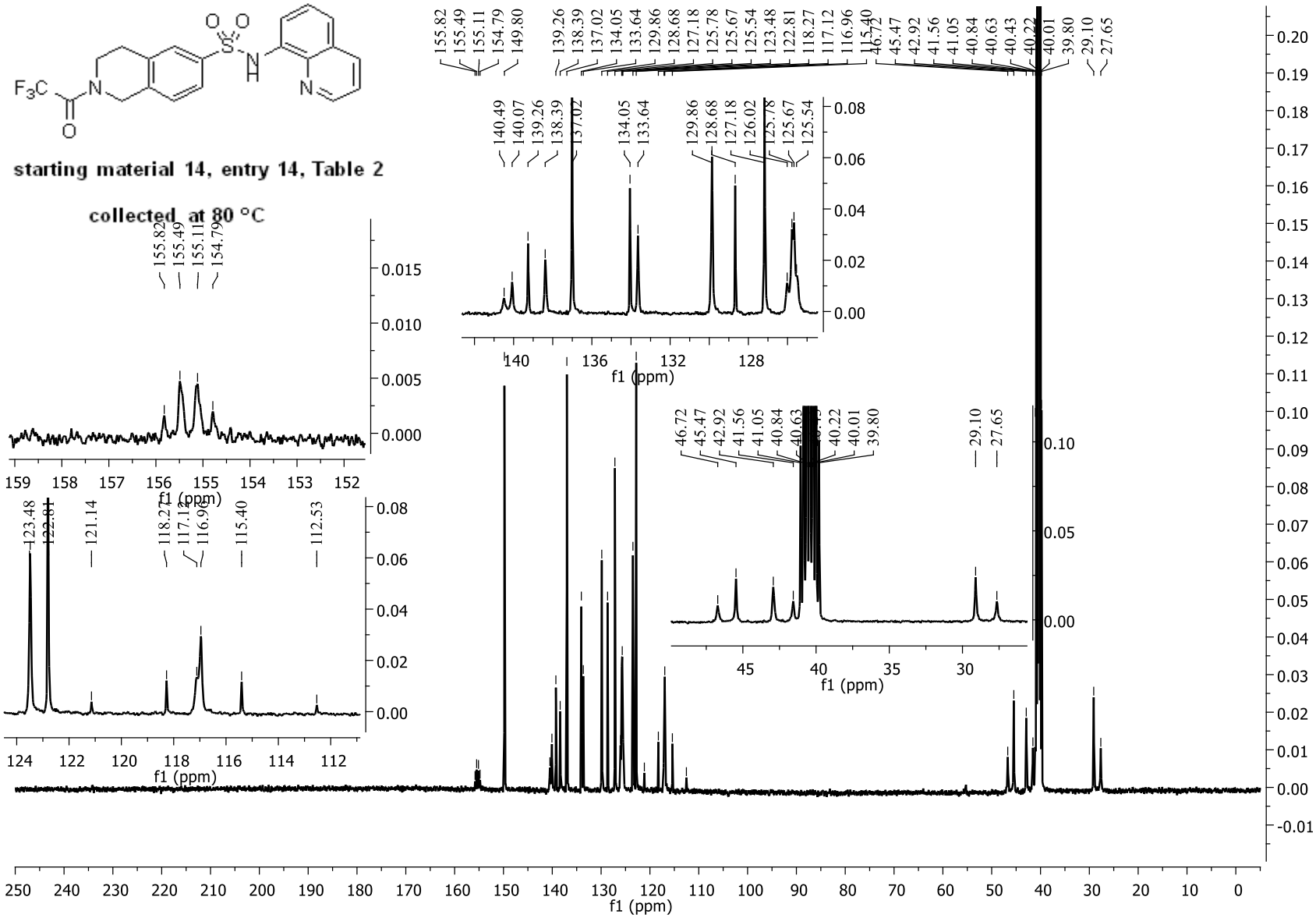

starting material 12, entry 12, Table 2
f1 (ppm)


starting material 13, entry 13, Table 2
f1 (ppm)
f1 (ppm)


159.31
156.49
149.05
142.46
138.66
136.49
135.66
133.29
130.21
128.34
127.73
126.90
122.95
122.29
118.75
118.34
117.88
115.69
77.45
77.13
76.81
O
O
S
O
N
H
N
O
starting material 13, entry 13, Table 2
f1 (ppm)
f1 (ppm)


starting material 14, entry 14, Table 2
collected at room temperature
CH2Cl2
H2O
DMSO
f1 (ppm)


starting material 14, entry 14, Table 2
collected at 80 °C
DMSO
H2O
f1 (ppm)


starting material 14, entry 14, Table 2
collected at 80 °C
155.82
155.49
155.11
154.79
149.80
139.26
138.39
137.02
134.05
133.64
129.86
128.68
127.18
125.78
125.67
125.54
123.48
122.81
118.27
117.12
116.96
115.40
46.72
45.47
42.92
41.56
41.05
40.84
40.63
40.43
40.22
40.01
39.80
29.10
27.65
140.49
140.07
139.26
138.39
137.02
134.05
133.64
129.86
128.68
127.18
126.02
125.78
125.67
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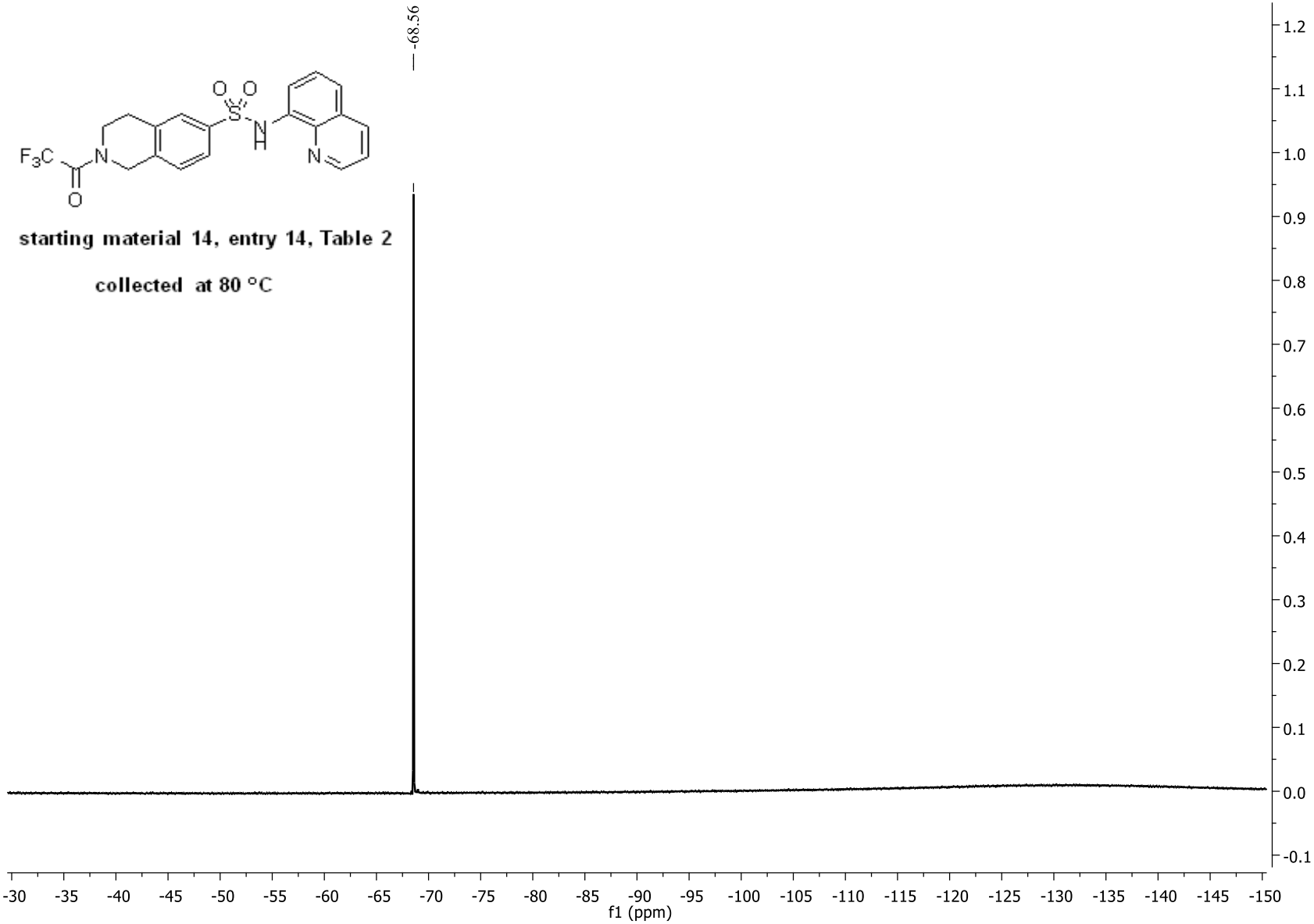
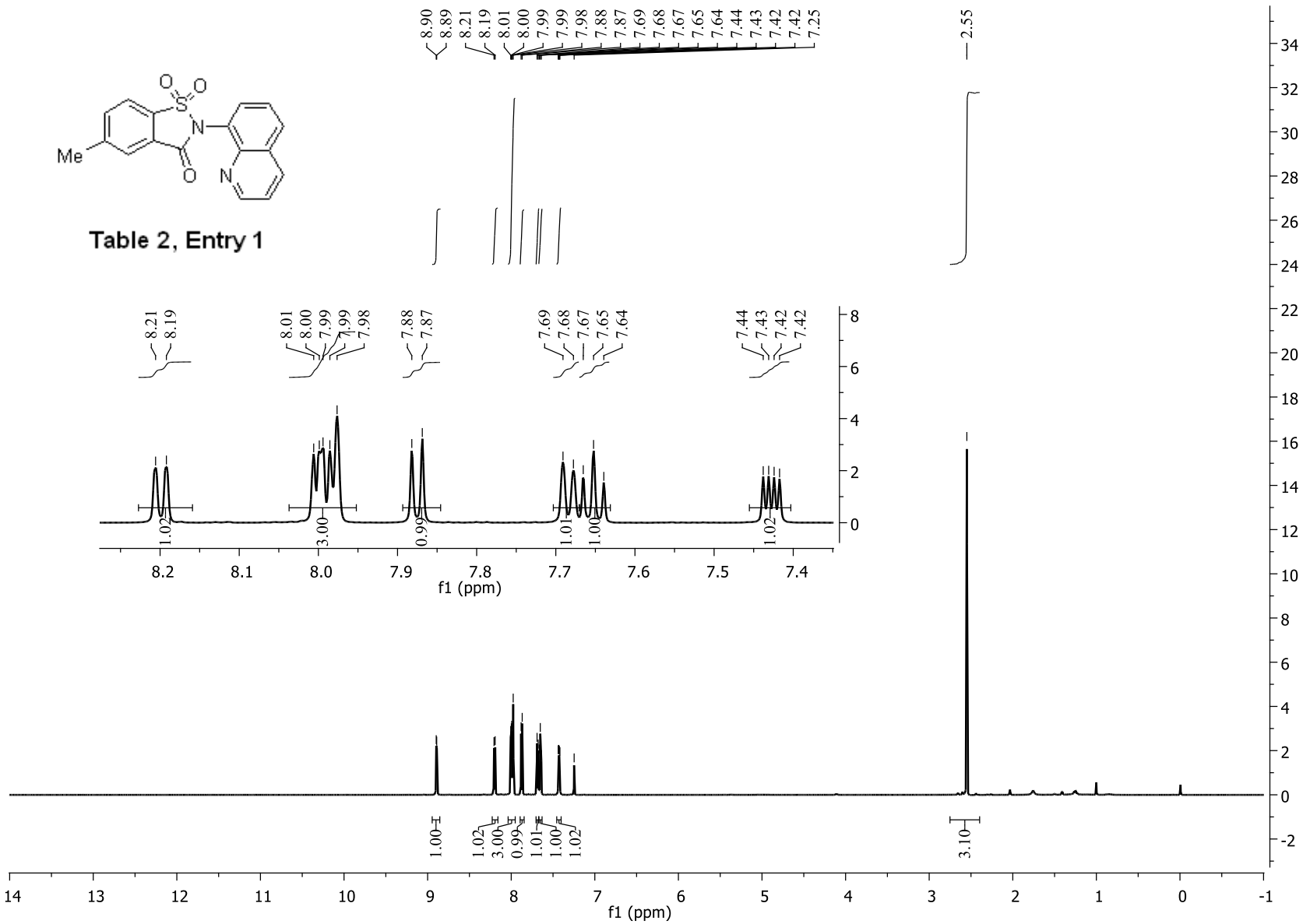
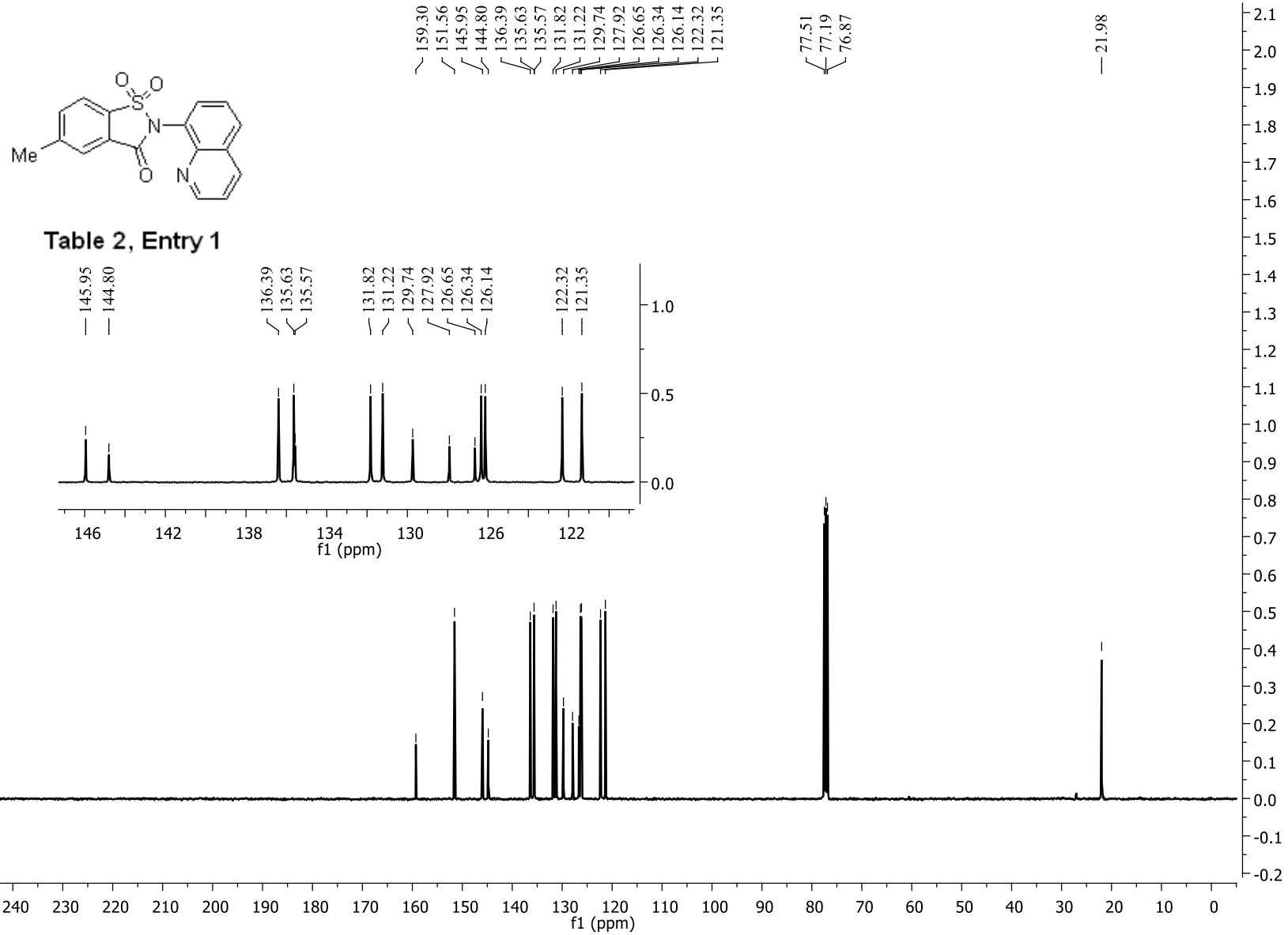
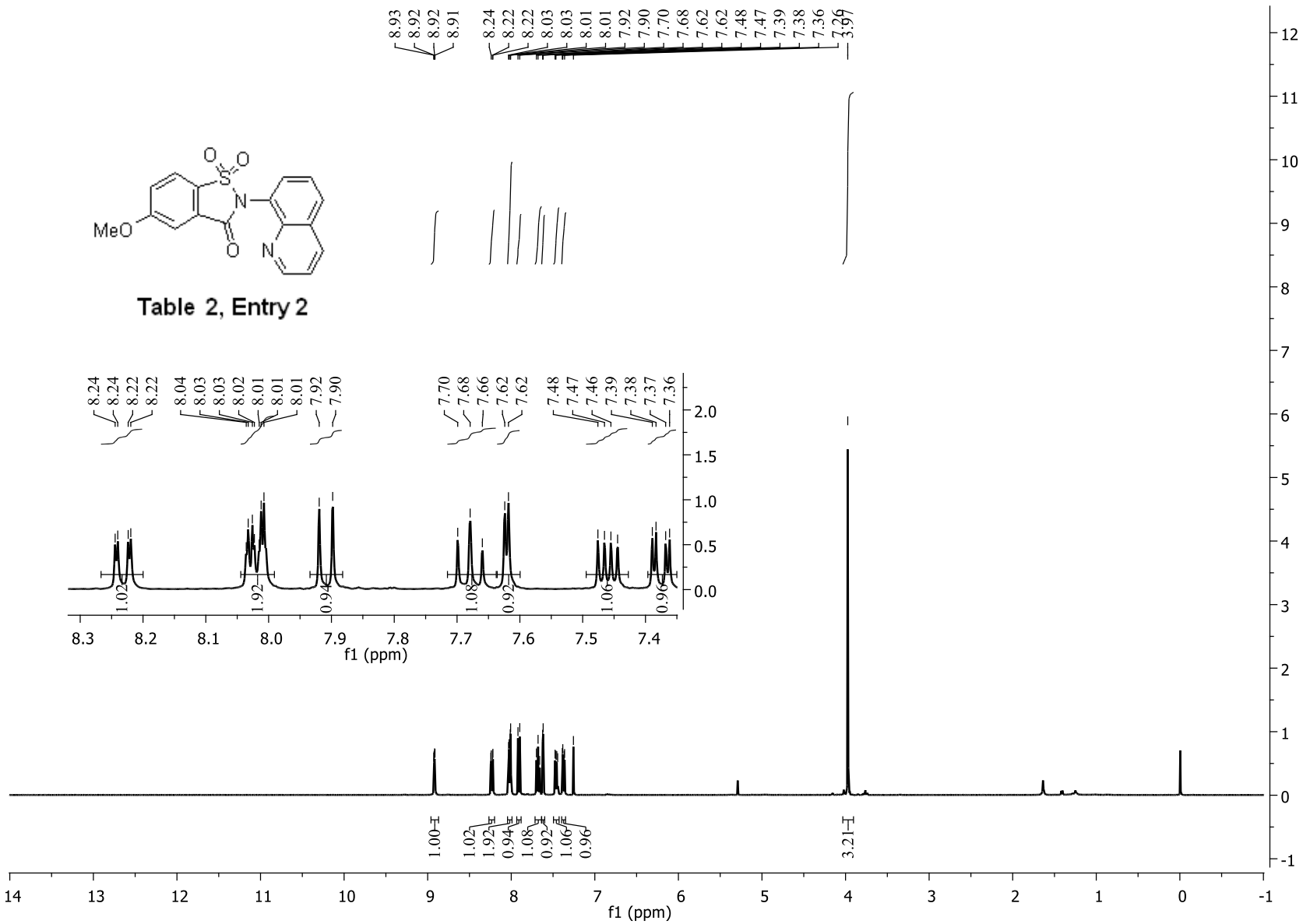
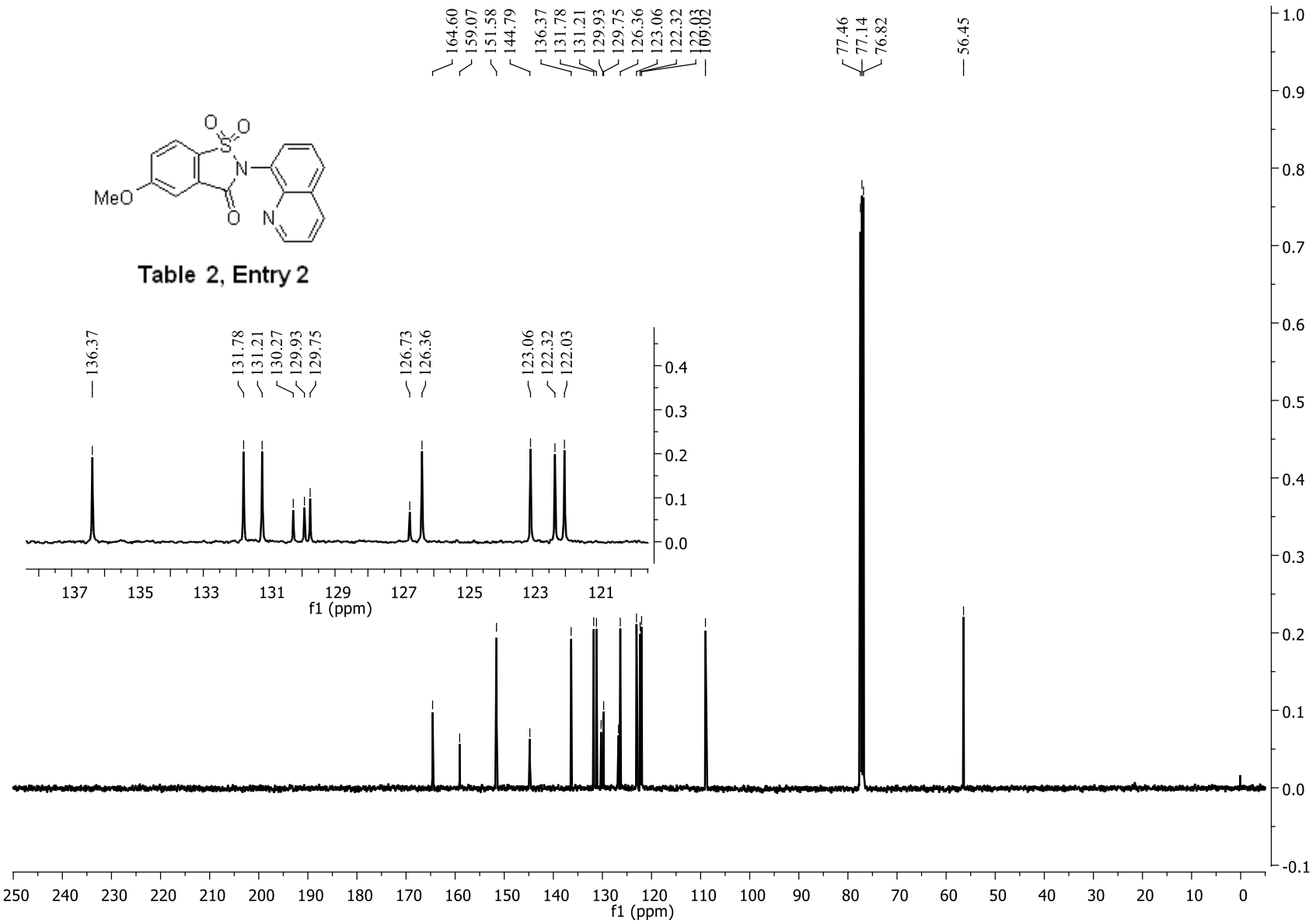
123.48
122.81
121.14
118.27
117.12
116.96
115.40
112.53
f1 (ppm)

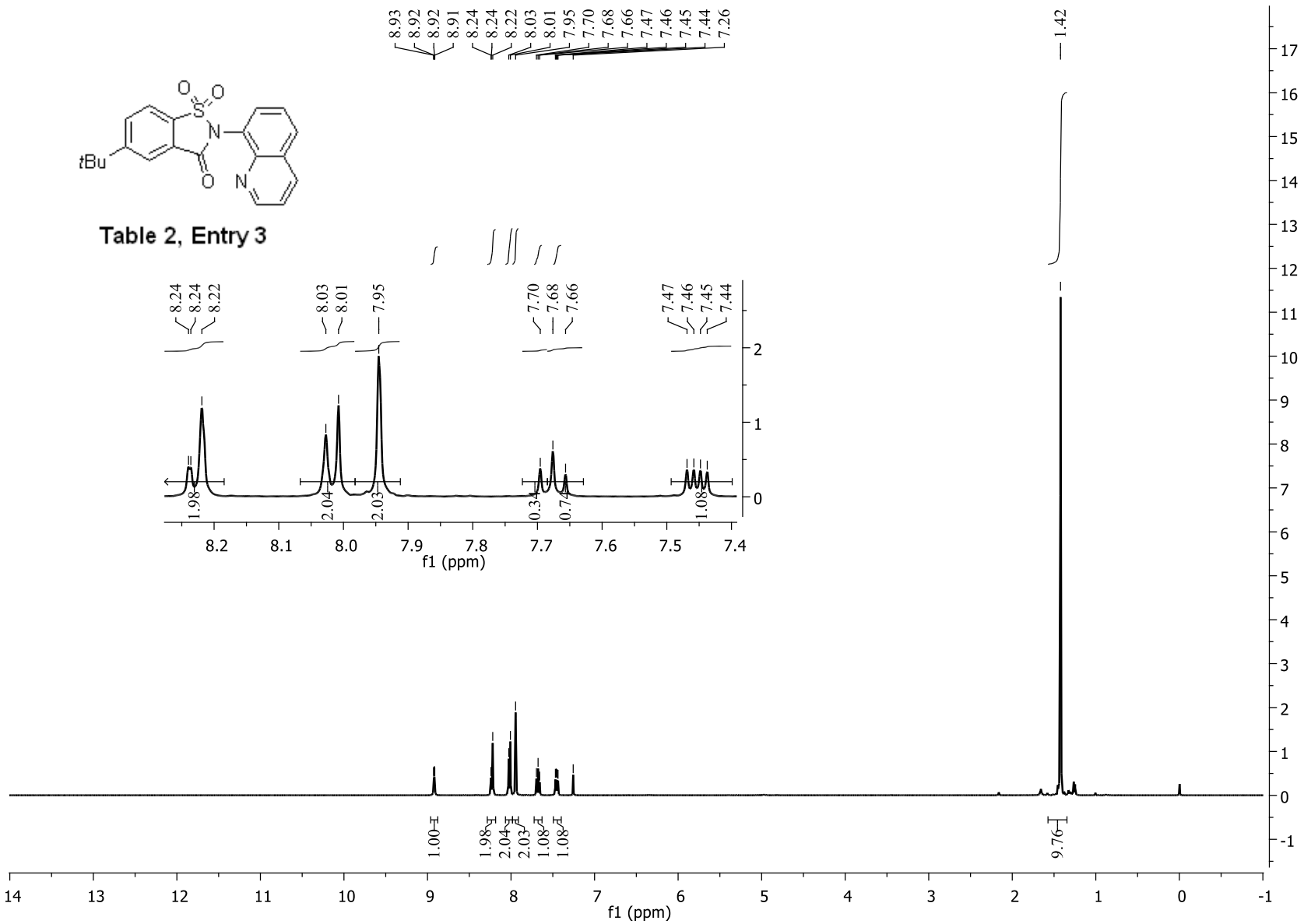

-68.56
starting material 14, entry 14, Table 2
collected at 80 °C
f1 (ppm)


Me
Table 2, Entry 1
f1 (ppm)


Me
O
O
S
N
O
N
Table 2, Entry 1
159.30
151.56
145.95
144.80
136.39
135.63
135.57
131.82
131.22
129.74
127.92
126.65
126.34
126.14
122.32
121.35
77.51
77.19
76.87
21.98
f1 (ppm)


MeO
Table 2, Entry 2
f1 (ppm)


MeO
O
O
S
N
O
N
Table 2, Entry 2
164.60
159.07
151.58
144.79
136.37
131.78
131.21
129.93
129.75
126.36
123.06
122.32
122.03
109.02
77.46
77.14
76.82
56.45
f1 (ppm)
136.37
131.78
131.21
130.27
129.93
129.75
126.73
126.36
123.06
122.32
122.03
f1 (ppm)


tBu
Table 2, Entry 3
f1 (ppm)

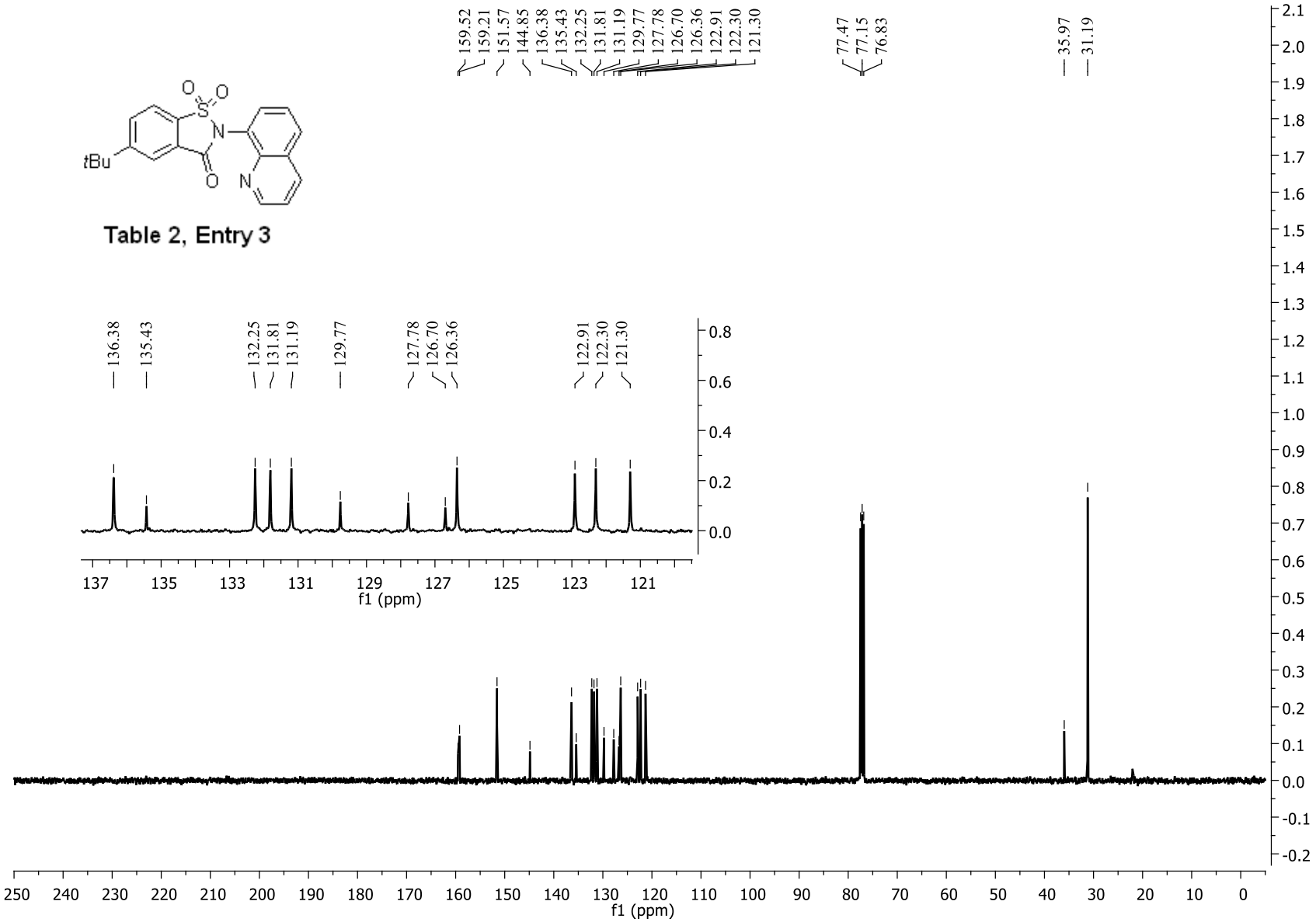
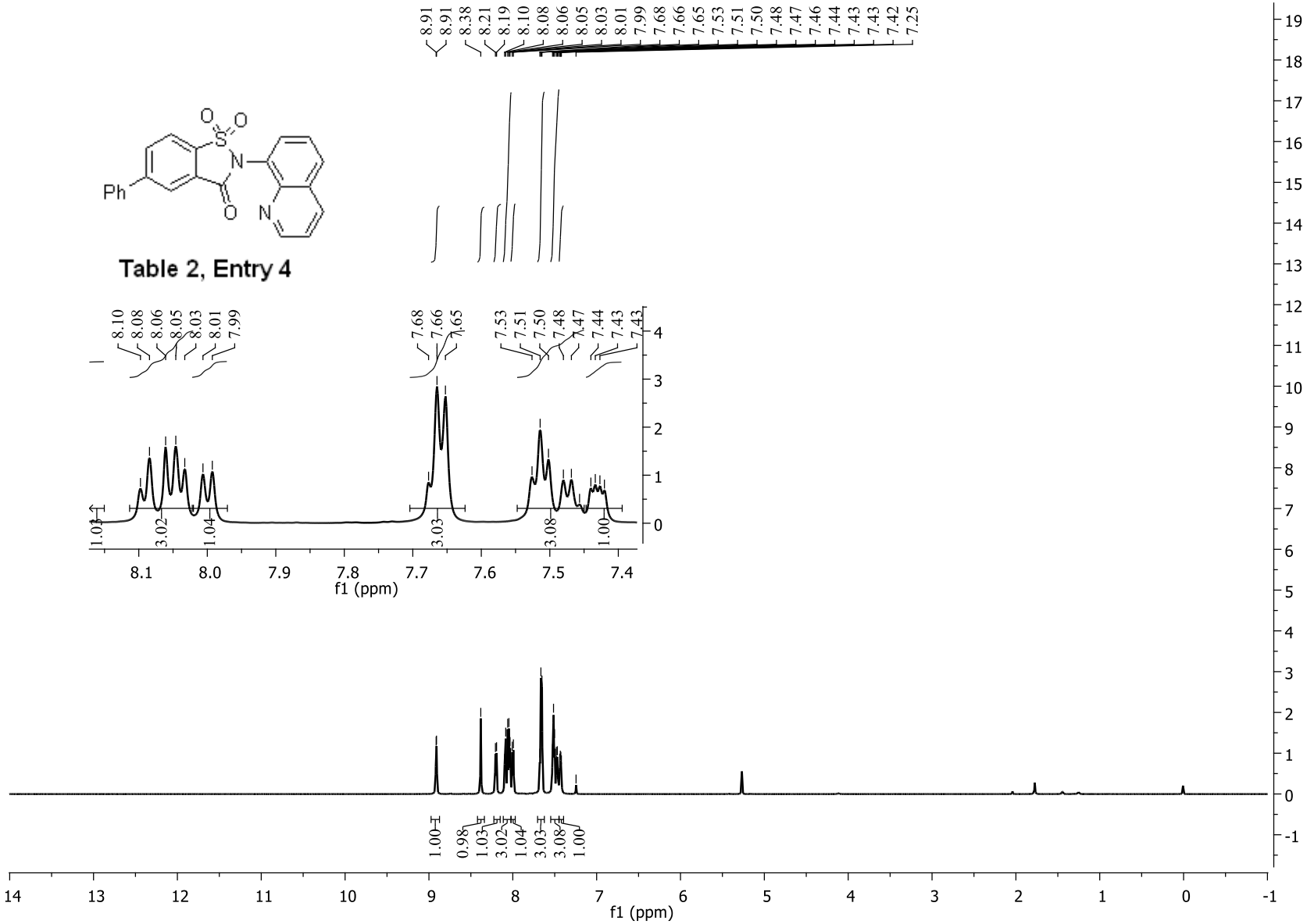
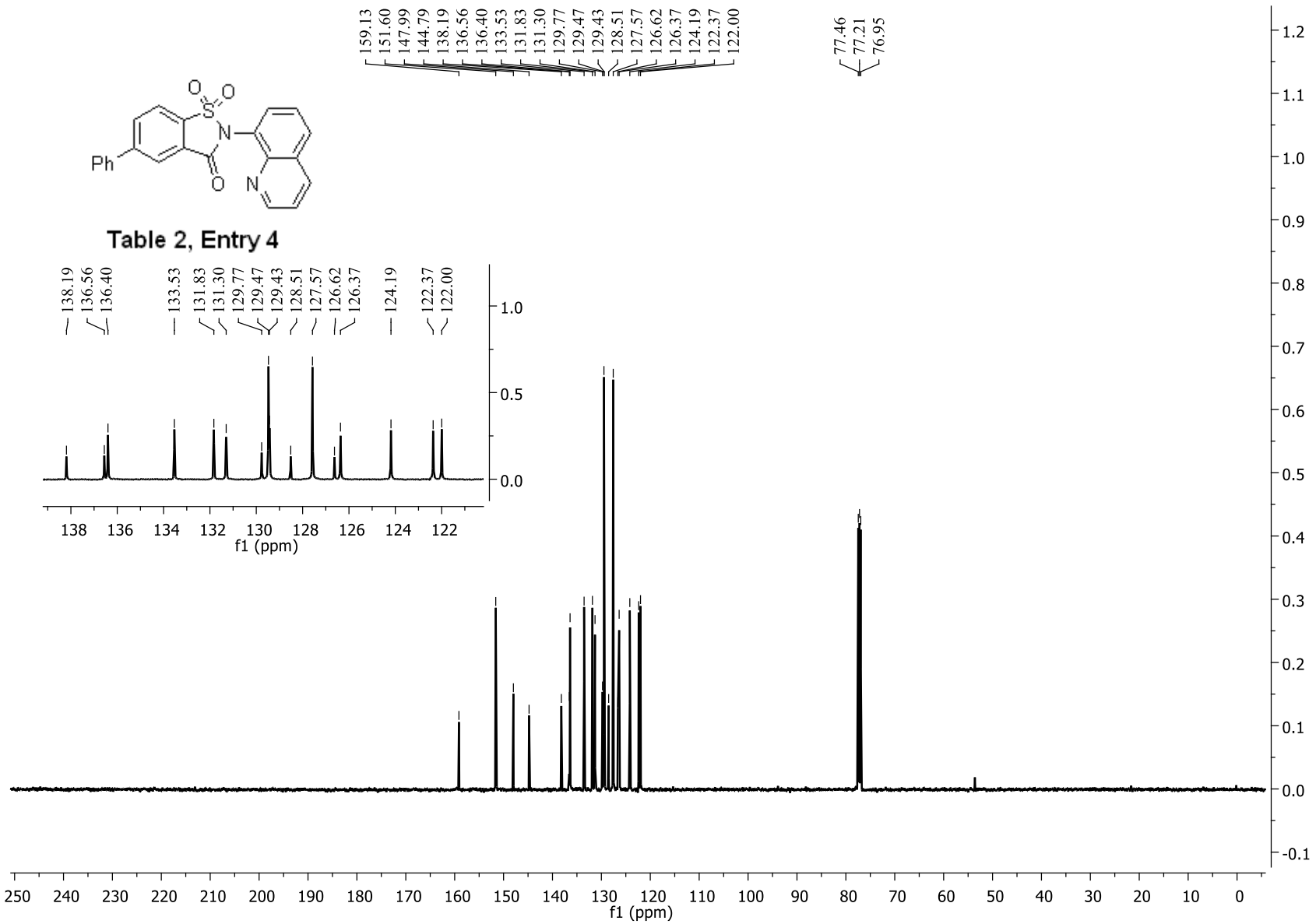
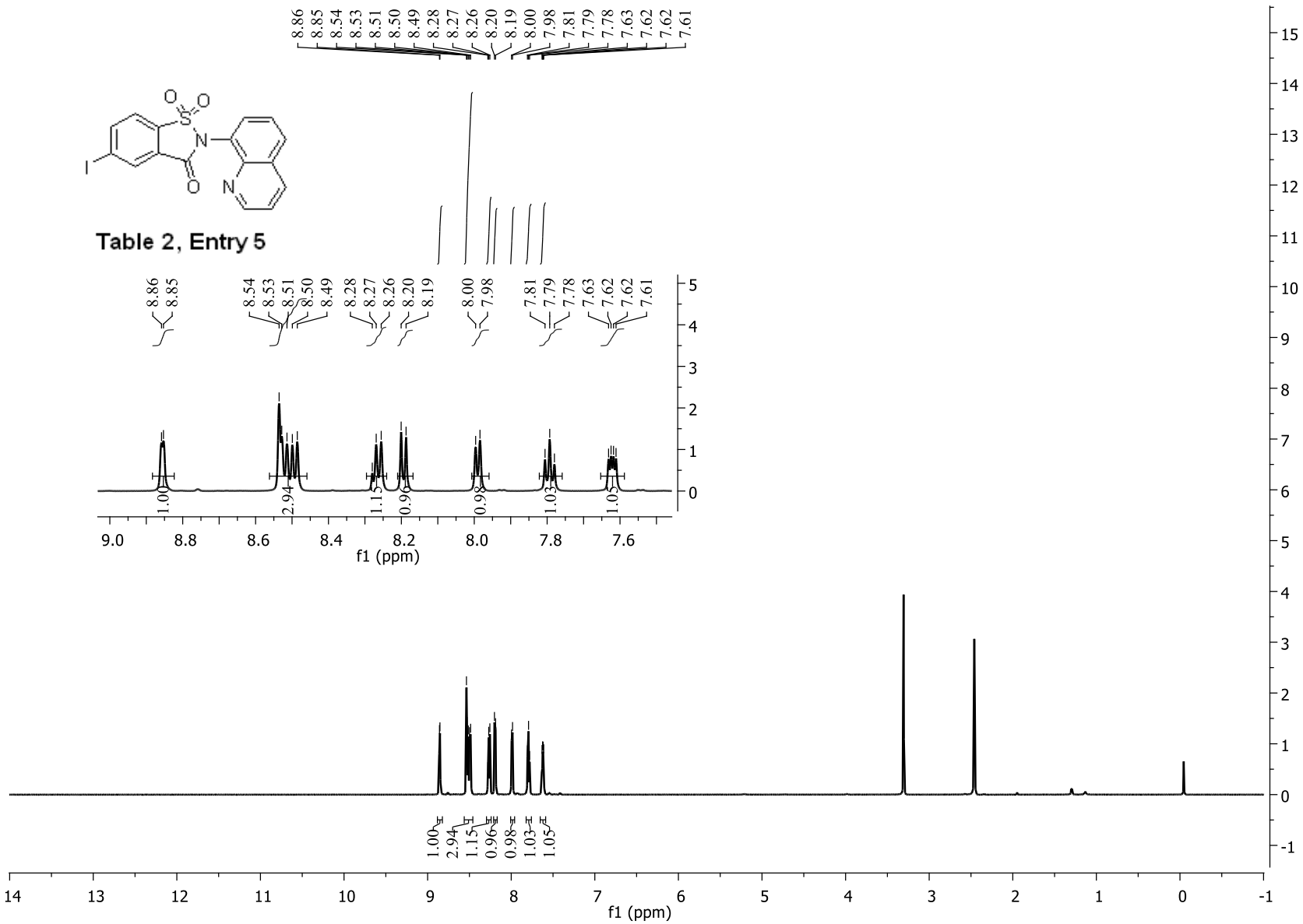


Table 2, Entry 3


8.91
8.91
8.38
8.21
8.19
8.10
8.08
8.06
8.05
8.03
8.01
7.99
7.68
7.66
7.65
7.53
7.51
7.50
7.48
7.47
7.46
7.44
7.43
7.43
7.42
7.25
O
O
S
N
Ph
O
N
Table 2, Entry 4
8.10
8.08
8.06
8.05
8.03
8.01
7.99
7.68
7.66
7.65
7.53
7.51
7.50
7.48
7.47
7.44
7.43
7.43
1.01
3.02
1.04
3.03
3.08
1.00
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
f1 (ppm)
1.00
0.98
1.03
3.02
1.04
3.03
3.08
1.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


159.13
151.60
147.99
144.79
138.19
136.56
136.40
133.53
131.83
131.30
129.77
129.47
129.43
128.51
127.57
126.62
126.37
124.19
122.37
122.00
77.46
77.21
76.95
O
O
S
N
Ph
O
N
Table 2, Entry 4
f1 (ppm)
f1 (ppm)


8.86
8.85
8.54
8.53
8.51
8.50
8.49
8.28
8.27
8.26
8.20
8.19
8.00
7.98
7.81
7.79
7.78
7.63
7.62
7.62
7.61
O
O
S
N
I
O
N
Table 2, Entry 5
1.00
2.94
1.15
0.96
0.98
1.03
1.05
f1 (ppm)

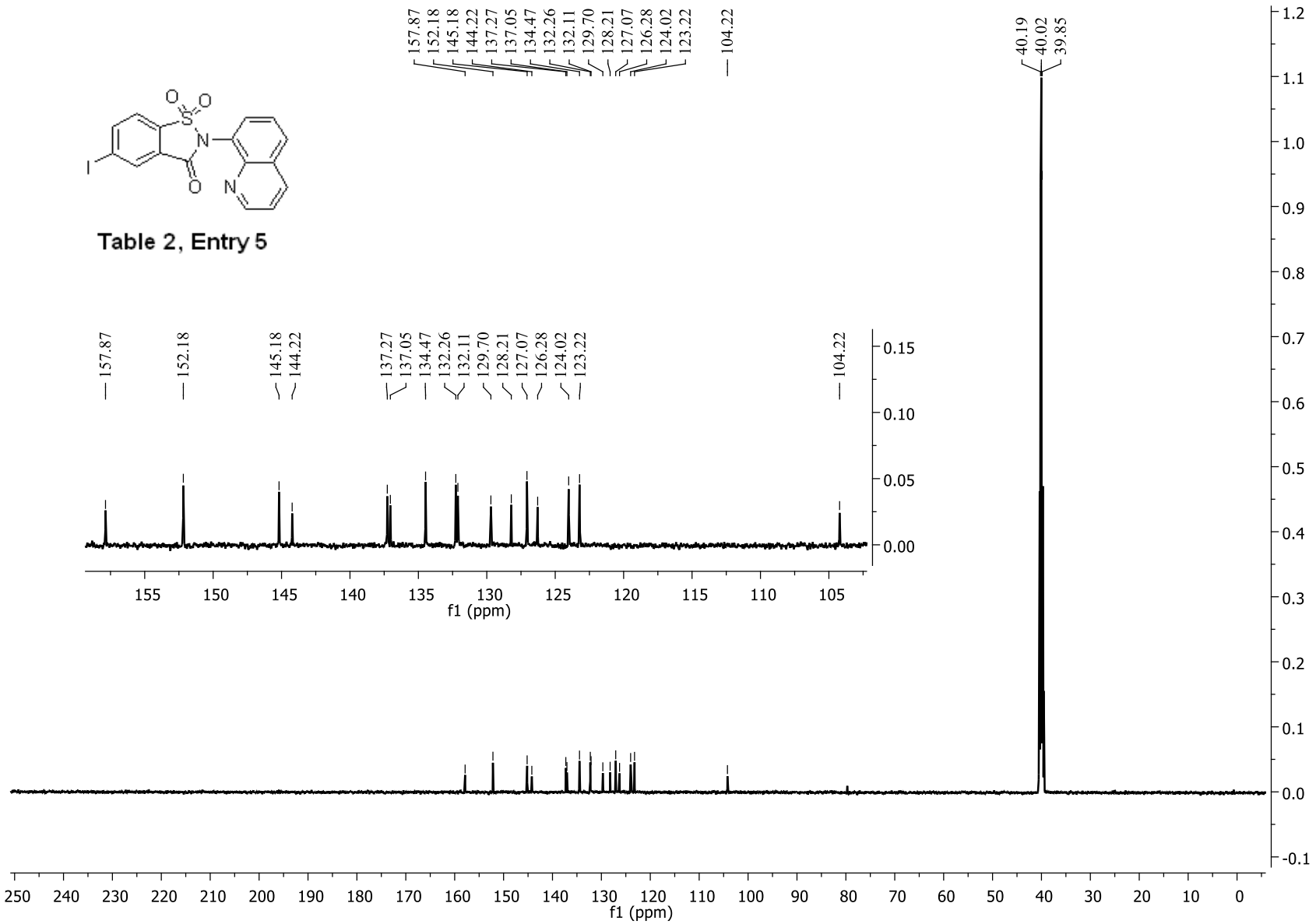


Table 2, Entry 5
157.87
152.18
145.18
144.22
137.27
137.05
134.47
132.26
132.11
129.70
128.21
127.07
126.28
124.02
123.22
104.22
40.19
40.02
39.85
f1 (ppm)

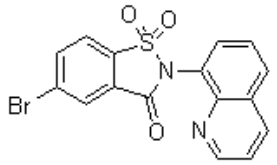
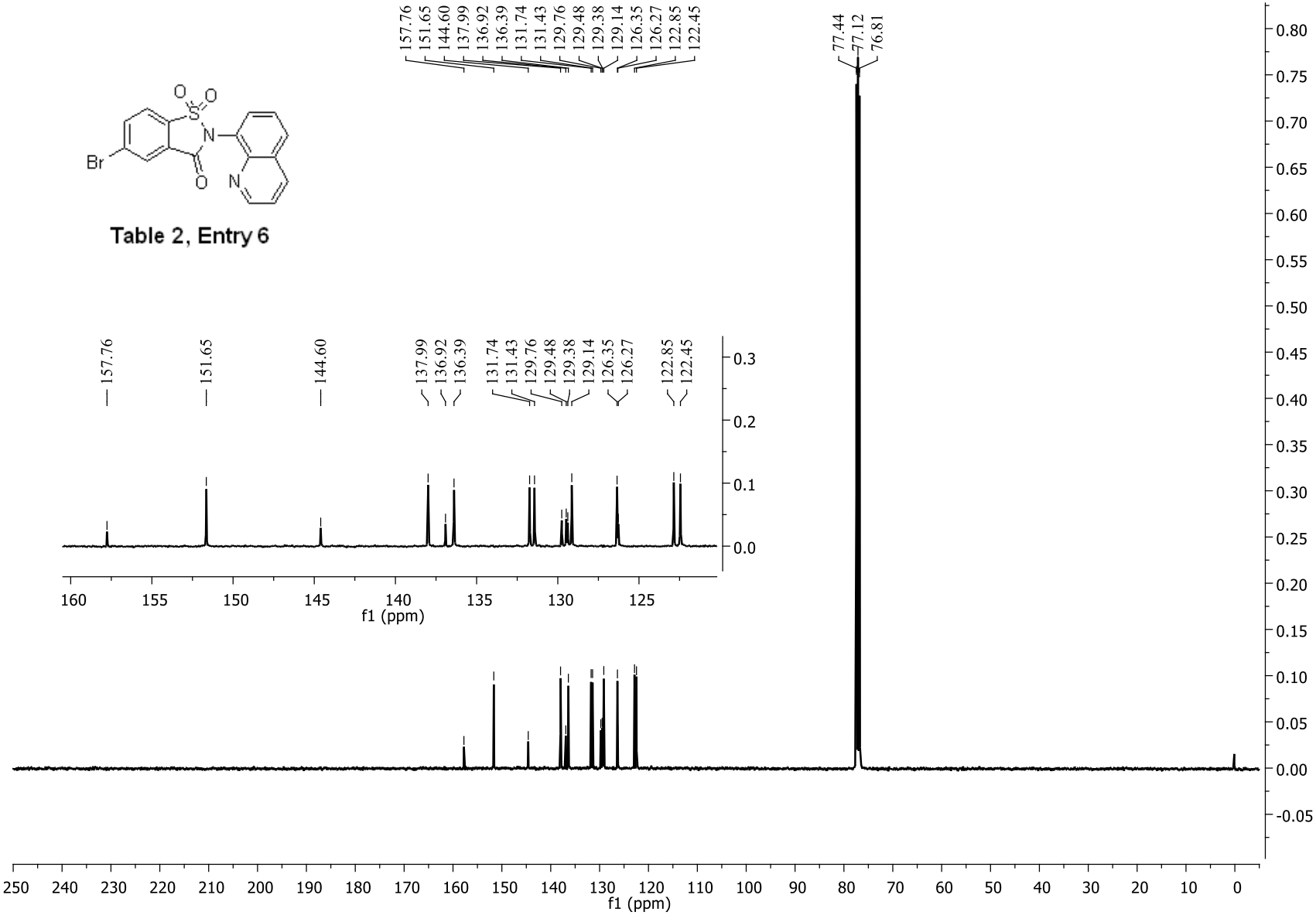
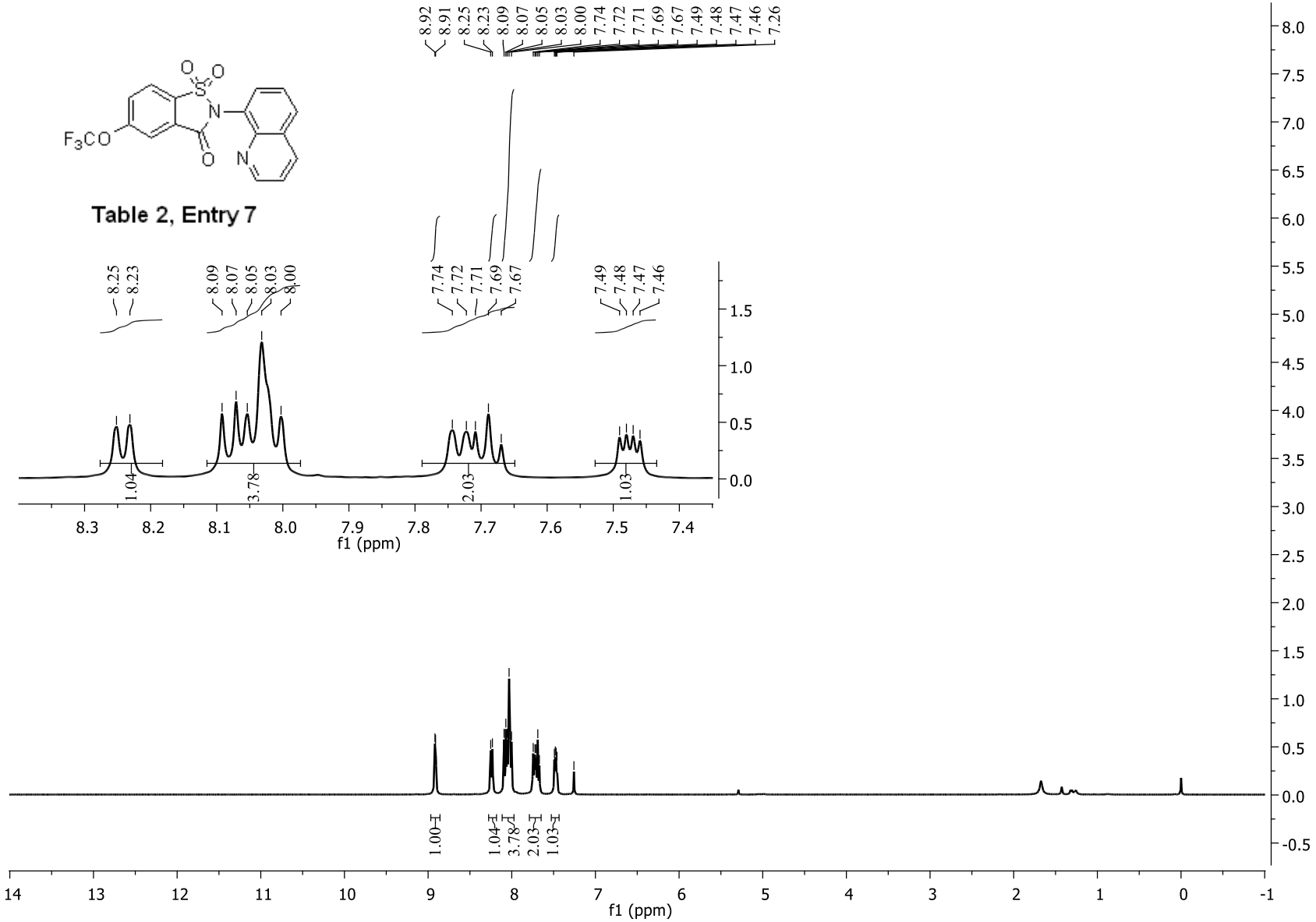


Table 2, Entry 6


157.76
151.65
144.60
137.99
136.92
136.39
131.74
131.43
129.76
129.48
129.38
129.14
126.35
126.27
122.85
122.45
77.44
77.12
76.81
Br
O
O
S
N
O
N
Table 2, Entry 6
f1 (ppm)
f1 (ppm)


F3CO
O
O
S
N
O
N
Table 2, Entry 7
8.92
8.91
8.25
8.23
8.09
8.07
8.05
8.03
8.00
7.74
7.72
7.71
7.69
7.67
7.49
7.48
7.47
7.46
7.26
1.04
3.78
2.03
1.03
f1 (ppm)
1.00
1.04
3.78
2.03
1.03
f1 (ppm)

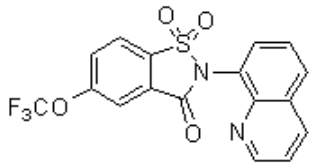


Table 2, Entry 7

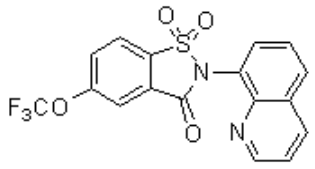
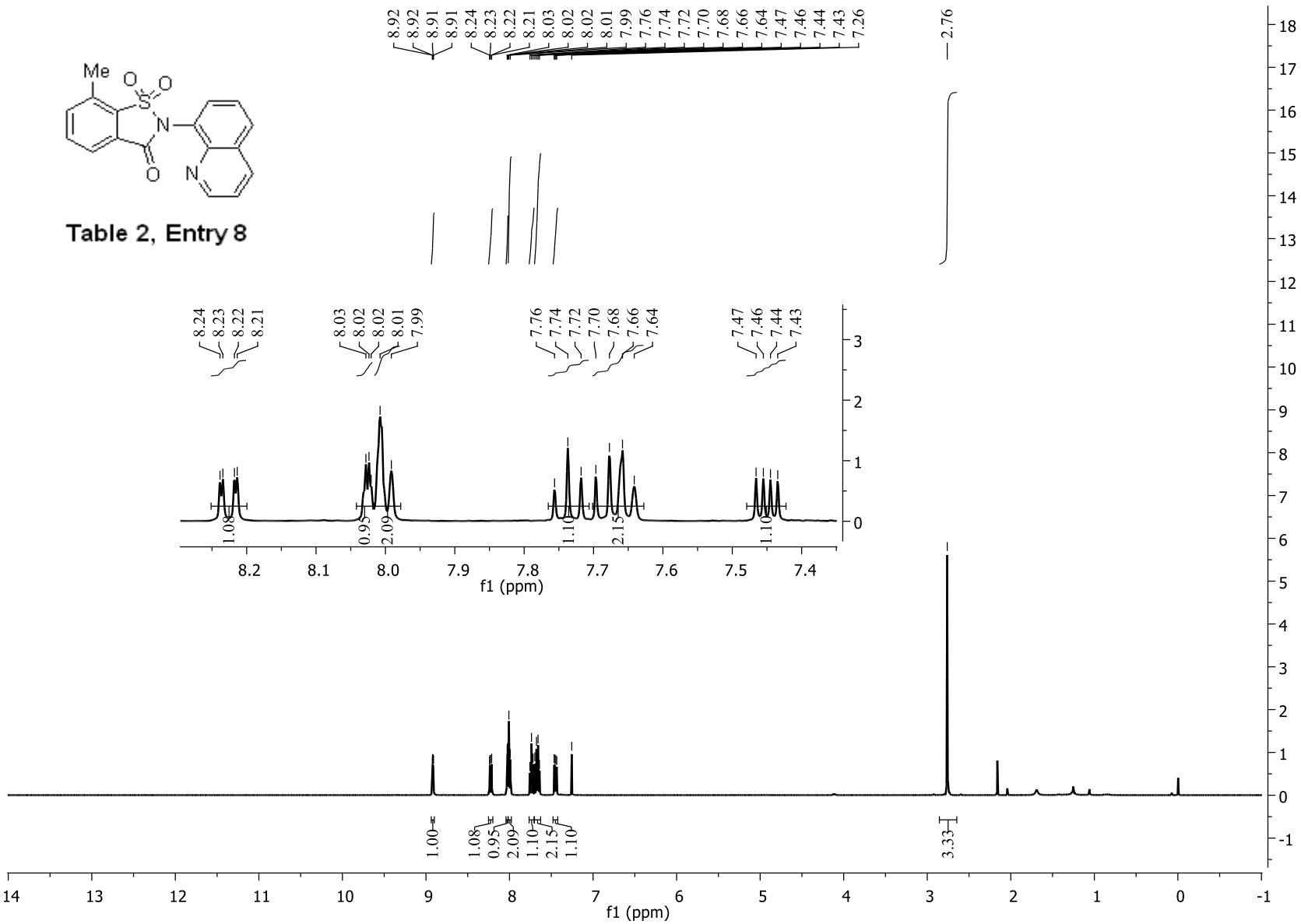
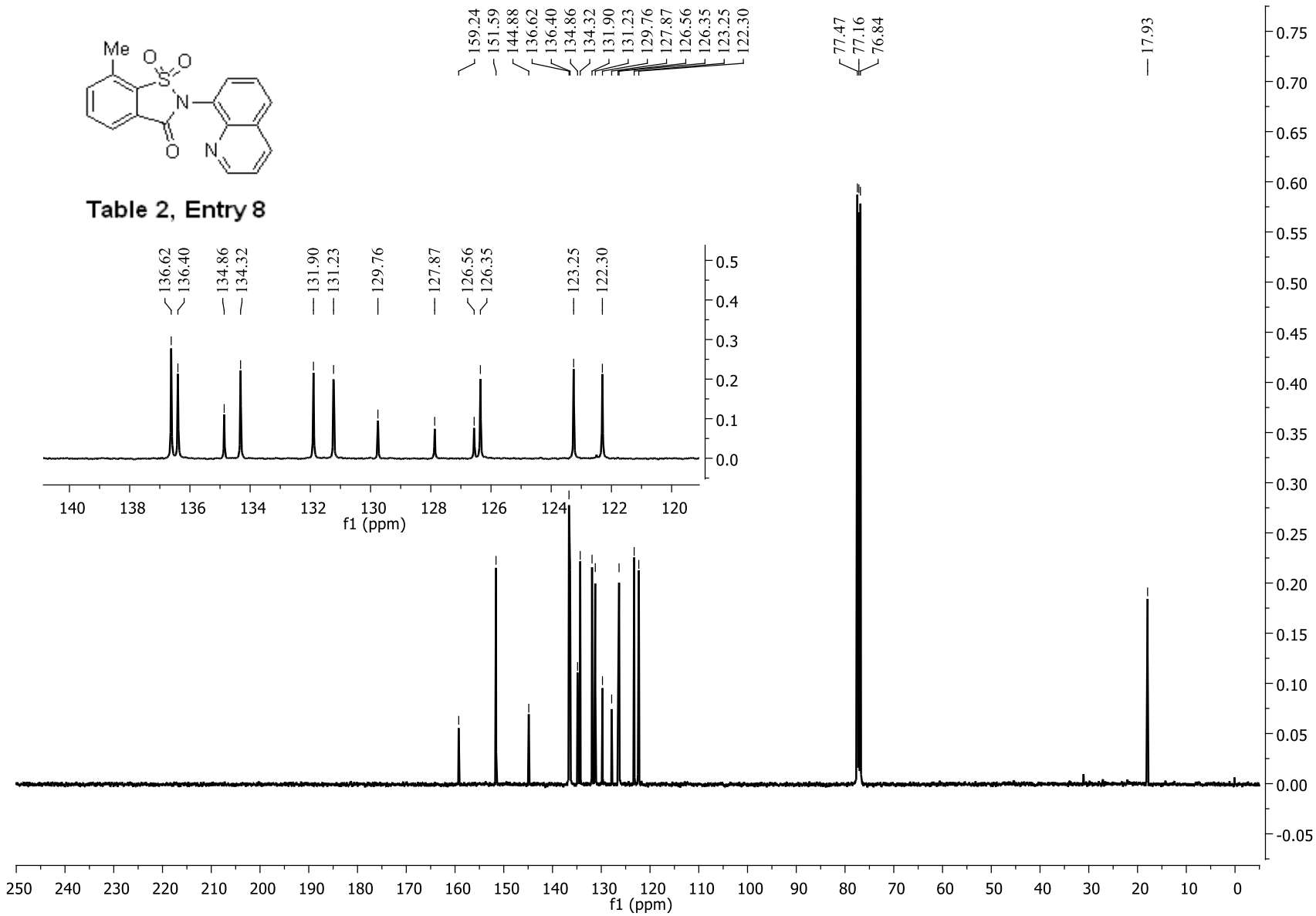
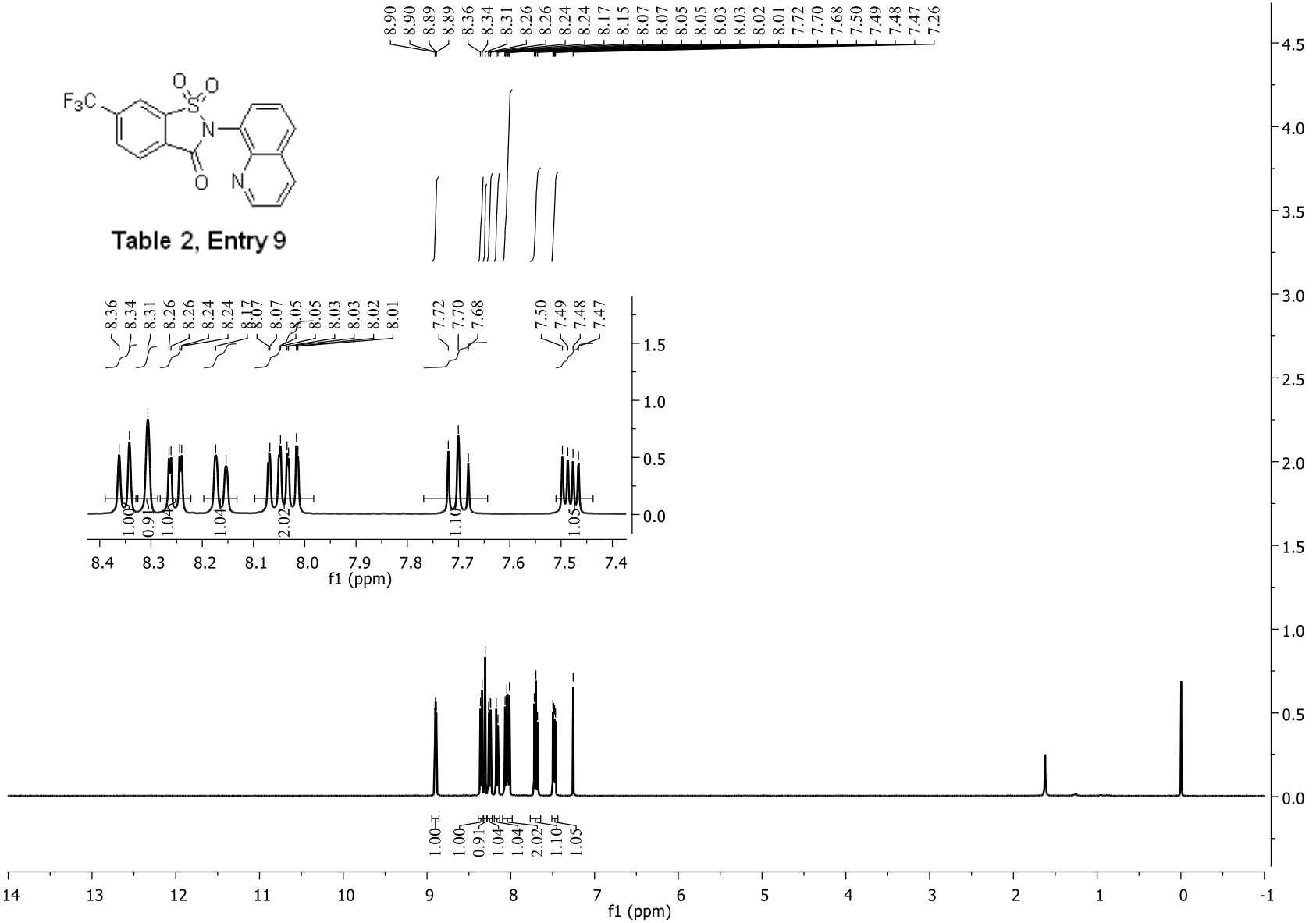
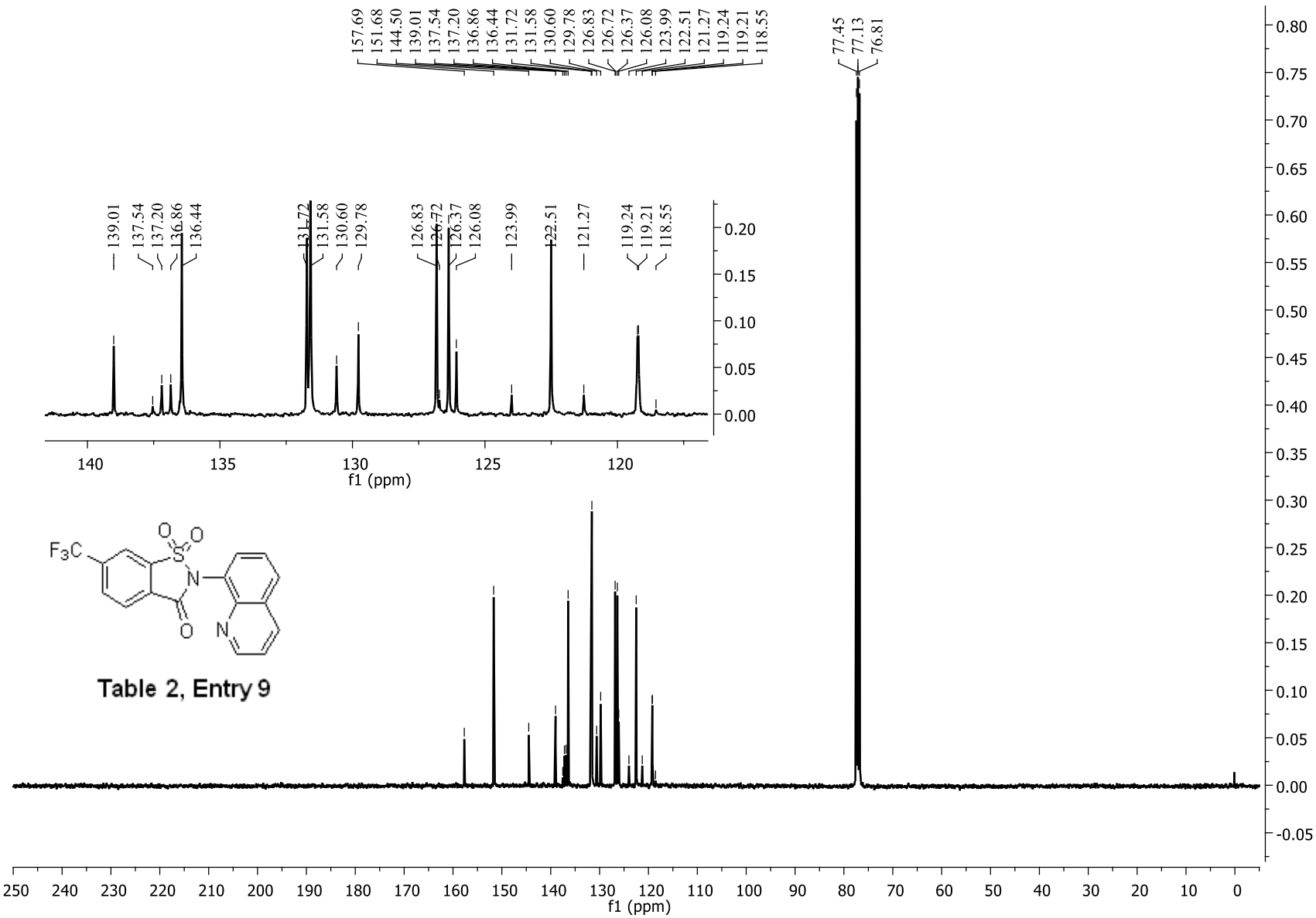


Table 2, Entry 7


Me
O
O
S
N
O
N
Table 2, Entry 8
8.92
8.92
8.91
8.91
8.24
8.23
8.22
8.21
8.03
8.02
8.02
8.01
7.99
7.76
7.74
7.72
7.70
7.68
7.66
7.64
7.47
7.46
7.44
7.43
7.26
2.76
1.08
0.95
2.09
1.10
2.15
1.10
3.33
f1 (ppm)


Me
O
O
S
N
O
N
Table 2, Entry 8
159.24
151.59
144.88
136.62
136.40
134.86
134.32
131.90
131.23
129.76
127.87
126.56
126.35
123.25
122.30
77.47
77.16
76.84
17.93
f1 (ppm)
f1 (ppm)


F3C
O
O
S
N
O
N
Table 2, Entry 9
8.90
8.90
8.89
8.89
8.36
8.34
8.31
8.26
8.26
8.24
8.24
8.17
8.15
8.07
8.07
8.05
8.05
8.03
8.03
8.02
8.01
7.72
7.70
7.68
7.50
7.49
7.48
7.47
7.26
1.00
0.91
1.04
1.04
2.02
1.10
1.05
f1 (ppm)
f1 (ppm)


157.69
151.68
144.50
139.01
137.54
137.20
136.86
136.44
131.72
131.58
130.60
129.78
126.83
126.72
126.37
126.08
123.99
122.51
121.27
119.24
119.21
118.55
77.45
77.13
76.81
f1 (ppm)
F3C
O
O
S
N
O
N
Table 2, Entry 9

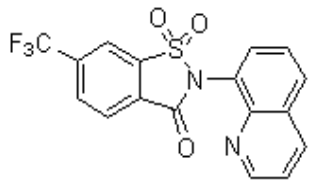
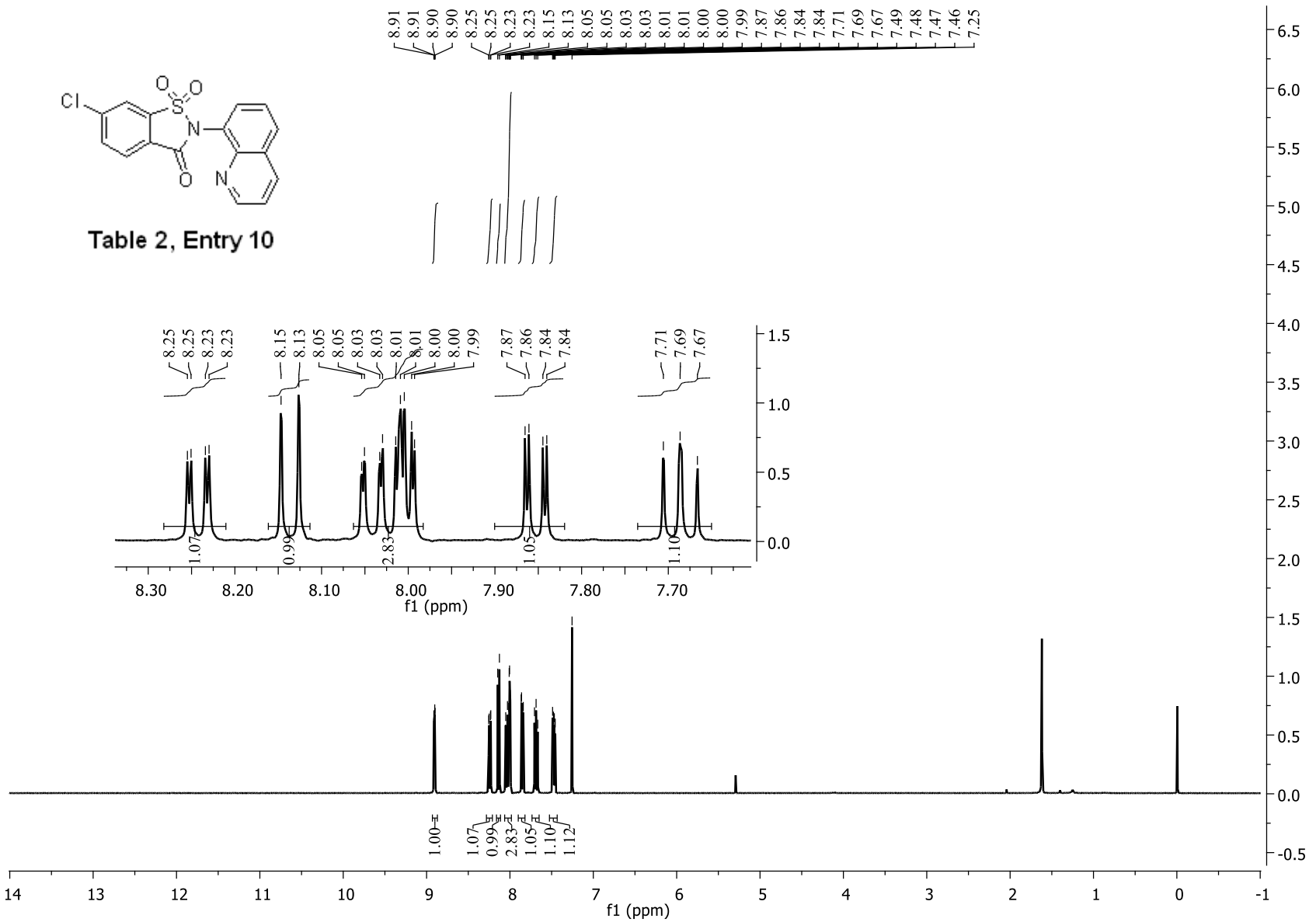
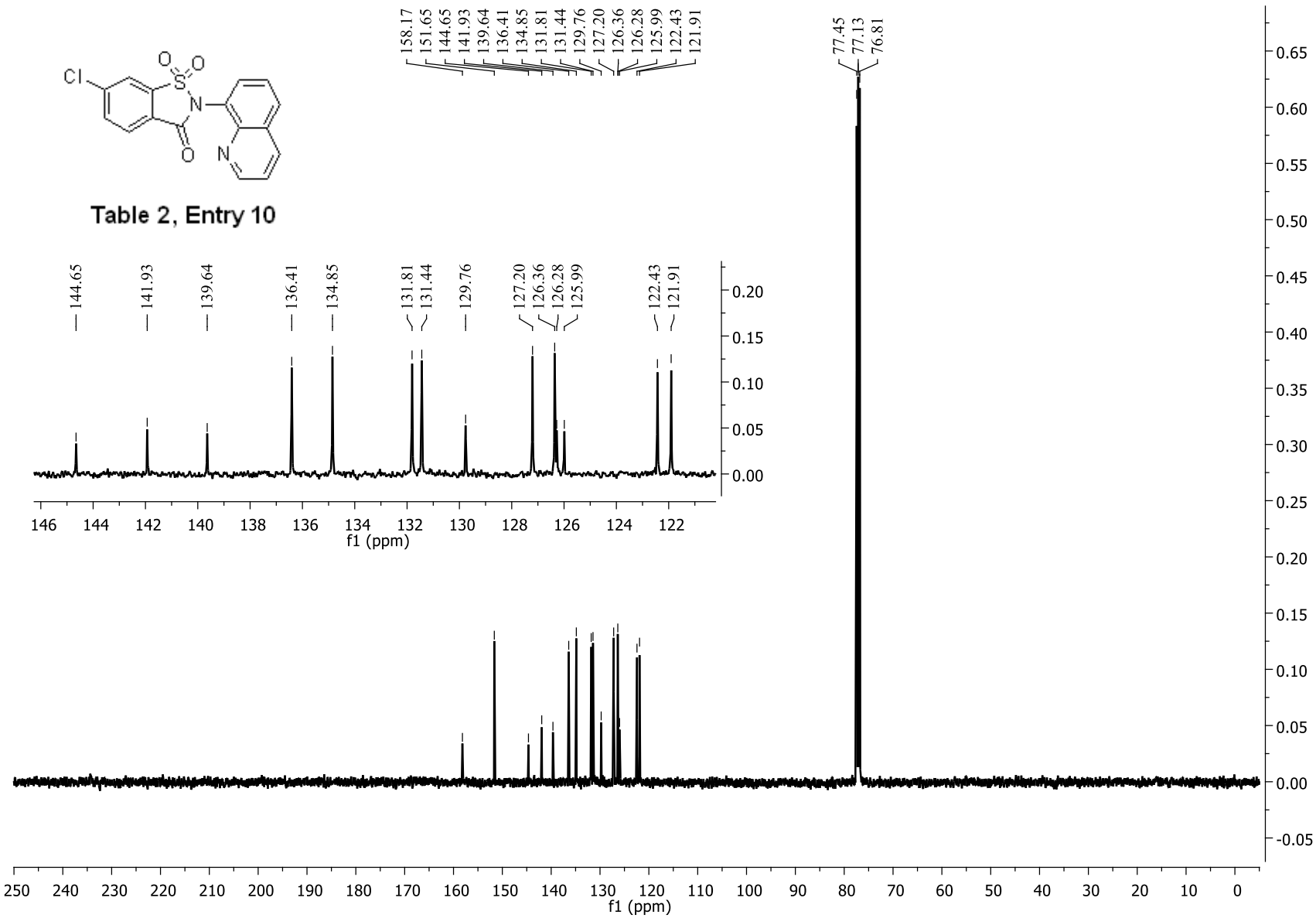
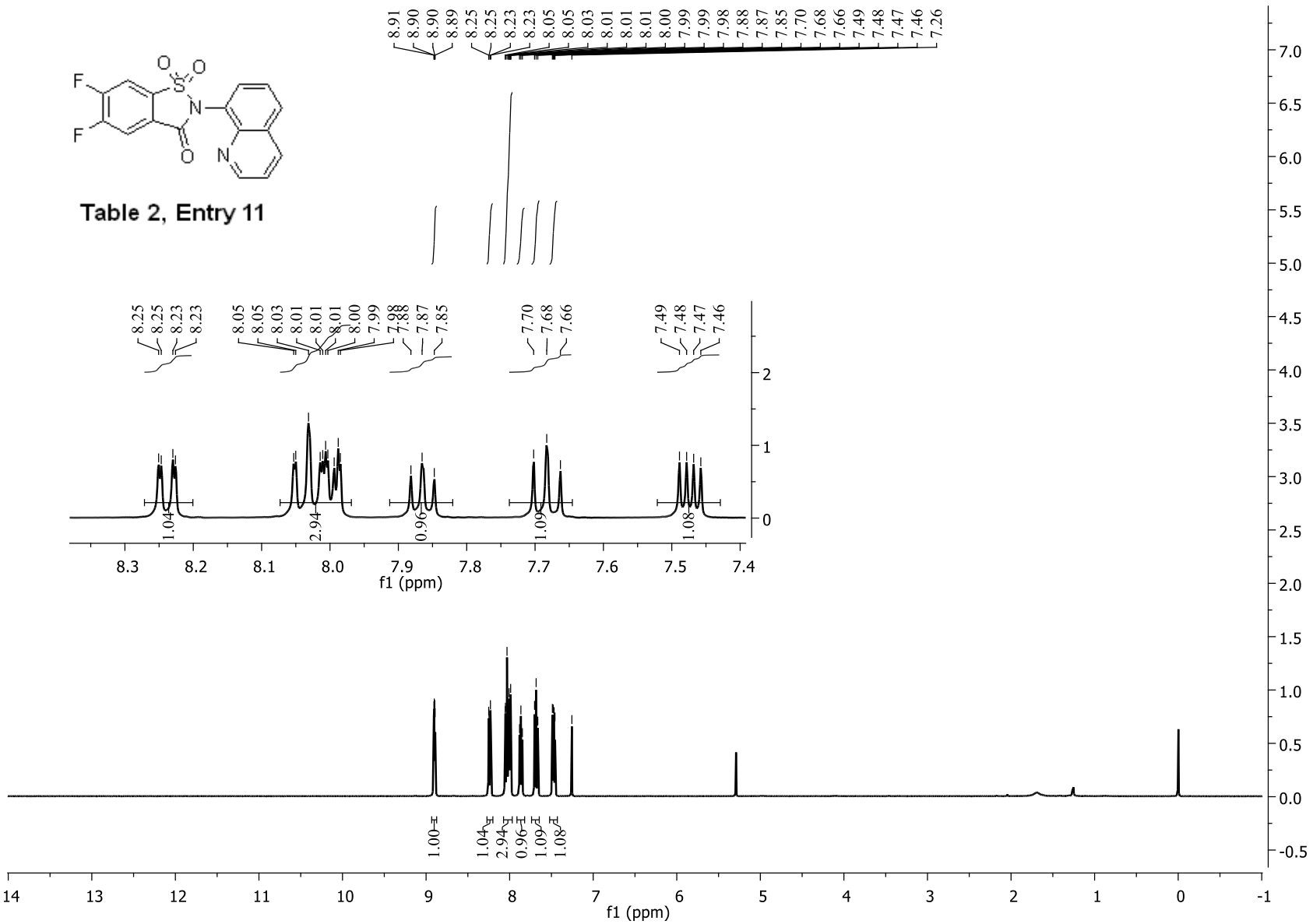


Table 2, Entry 9


Cl
O
O
S
N
O
N
Table 2, Entry 10
8.91
8.91
8.90
8.90
8.25
8.25
8.23
8.23
8.15
8.13
8.05
8.05
8.03
8.03
8.01
8.01
8.00
8.00
7.99
7.87
7.86
7.84
7.84
7.71
7.69
7.67
7.49
7.48
7.47
7.46
7.25
1.07
0.99
2.83
1.05
1.10
1.12
f1 (ppm)


Cl
O
O
S
N
O
N
Table 2, Entry 10
158.17
151.65
144.65
141.93
139.64
136.41
134.85
131.81
131.44
129.76
127.20
126.36
126.28
125.99
122.43
121.91
77.45
77.13
76.81
f1 (ppm)


F
F
O
O
S
N
O
N
Table 2, Entry 11
8.91
8.90
8.90
8.89
8.25
8.25
8.23
8.23
8.05
8.05
8.03
8.01
8.01
8.01
8.00
7.99
7.99
7.98
7.88
7.87
7.85
7.70
7.68
7.66
7.49
7.48
7.47
7.46
7.26
1.04
2.94
0.96
1.09
1.08
1.00
f1 (ppm)
f1 (ppm)

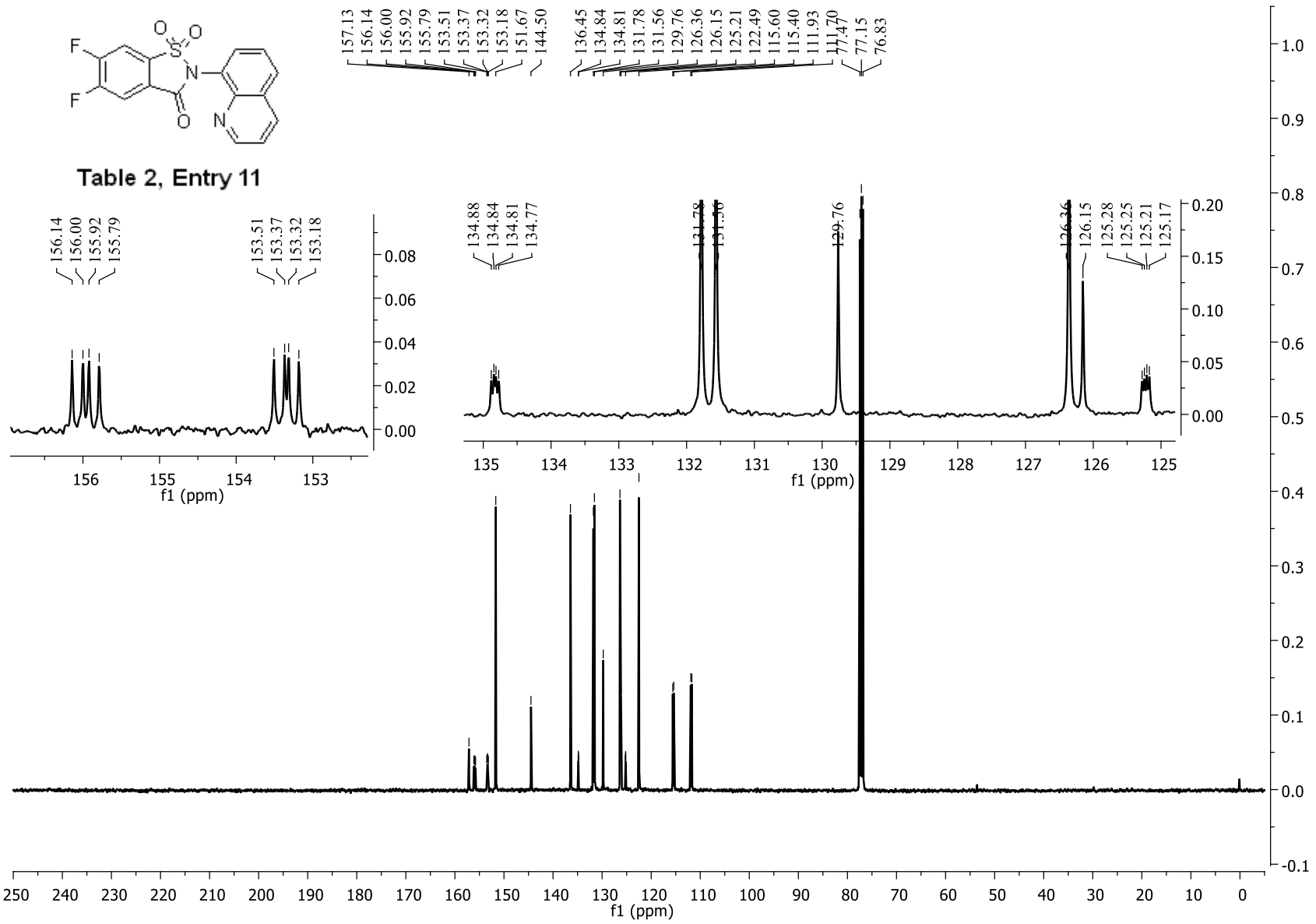


Table 2, Entry 11
157.13
156.14
156.00
155.92
155.79
153.51
153.37
153.32
153.18
151.67
144.50
136.45
134.84
134.81
131.78
131.56
129.76
126.36
126.15
125.21
122.49
115.60
115.40
111.93
111.70
77.47
77.15
76.83
f1 (ppm)

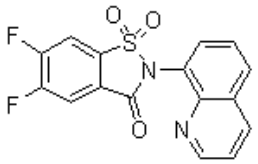
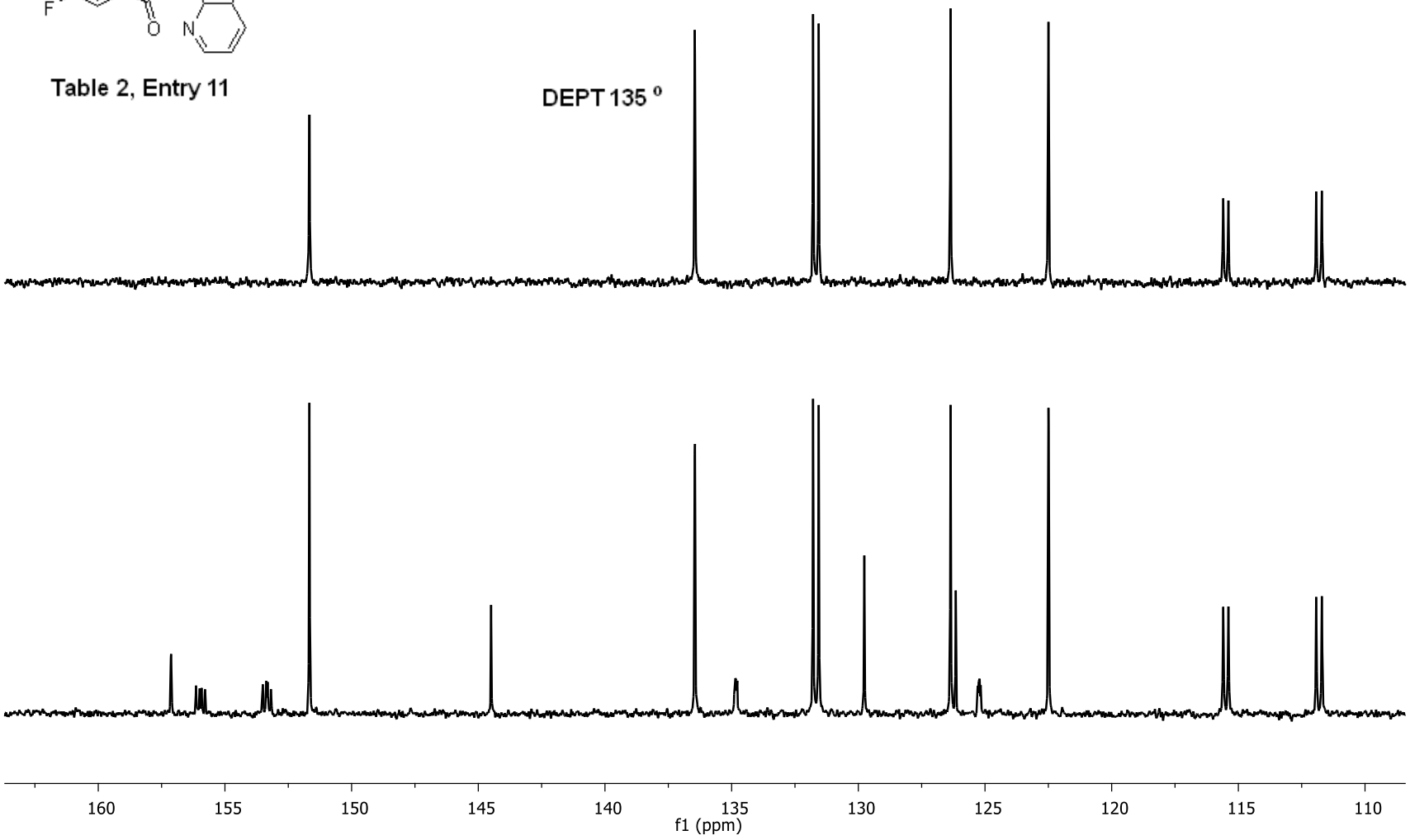


Table 2, Entry 11

DEPT 135 °



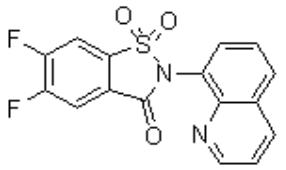
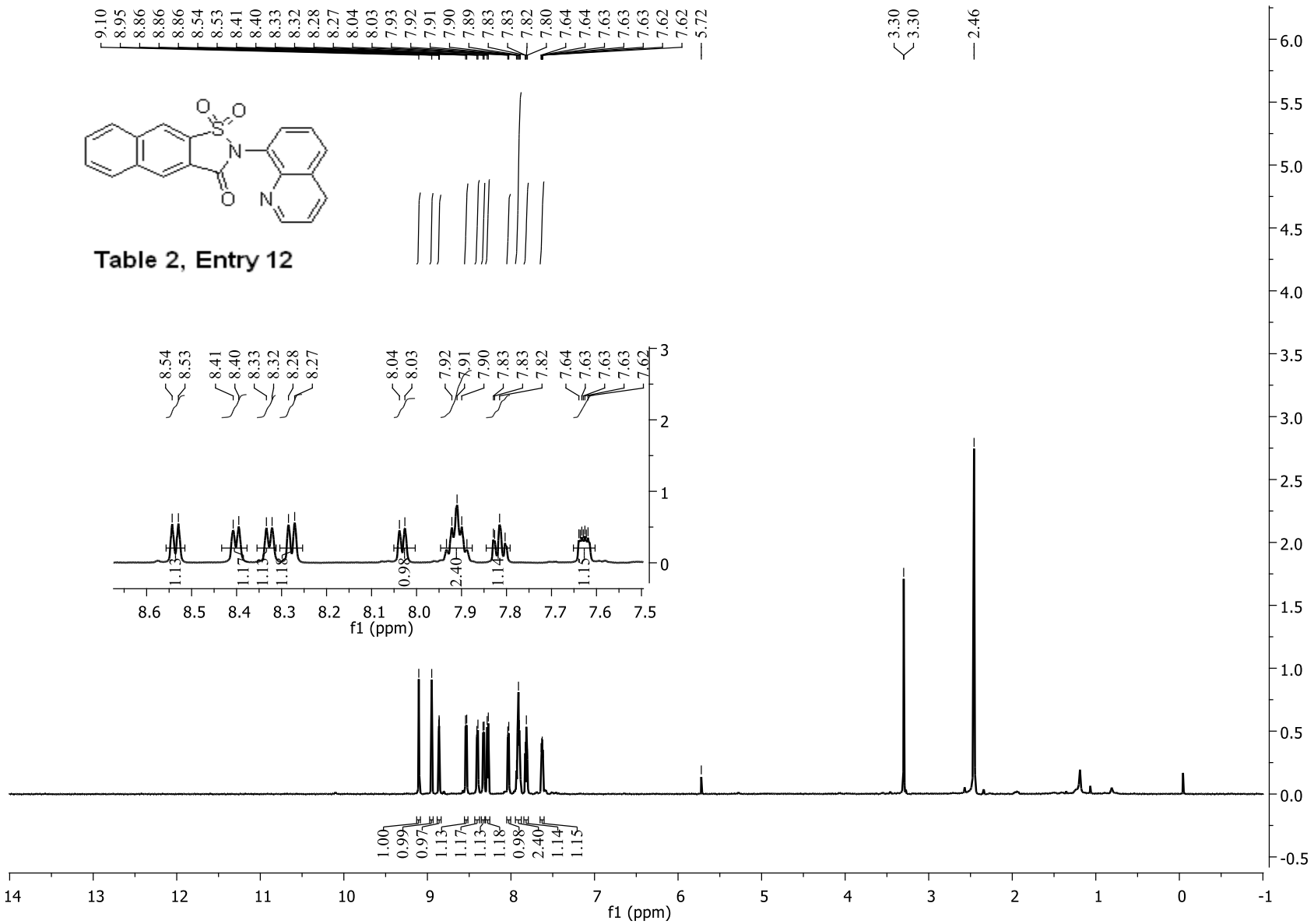
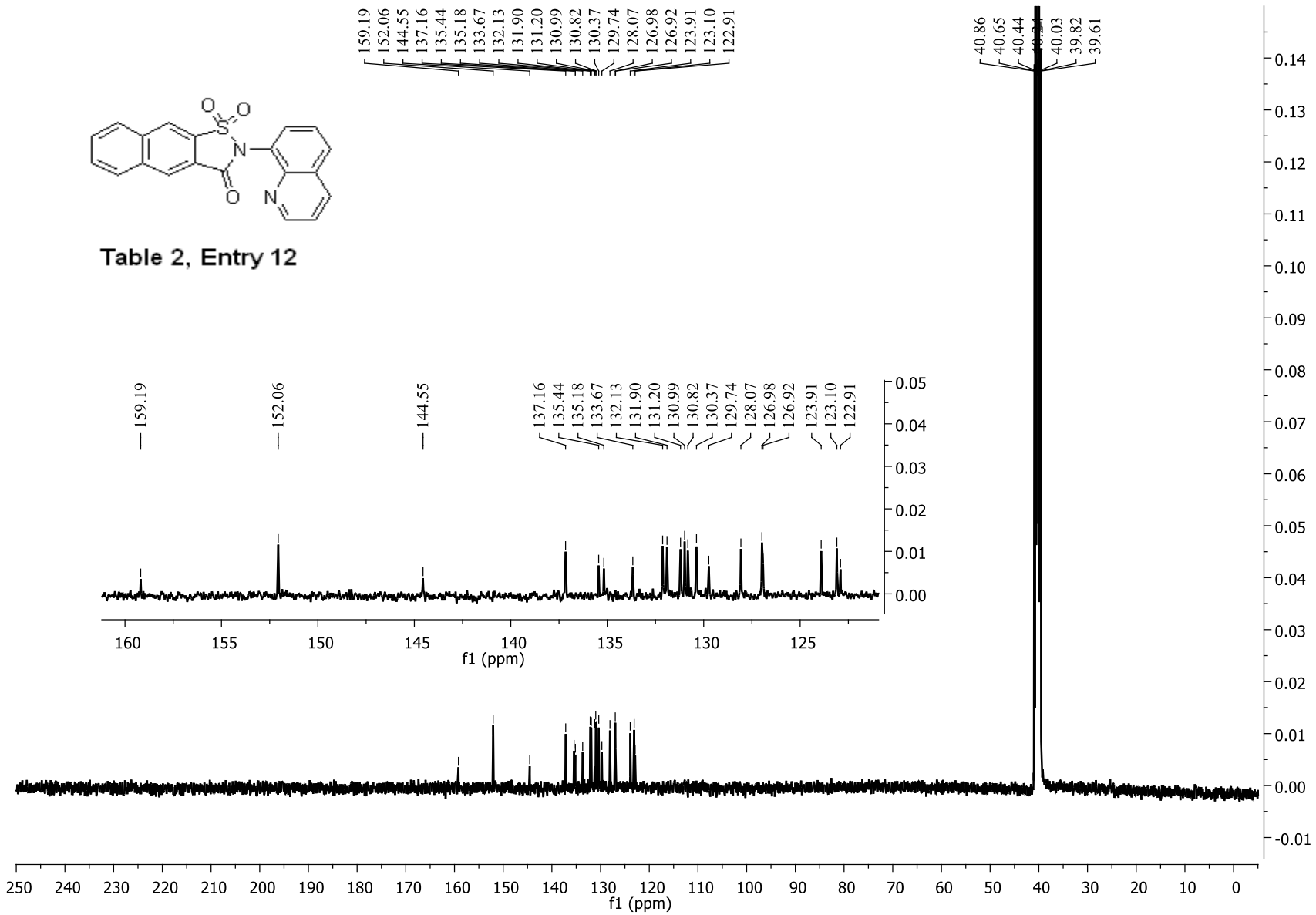
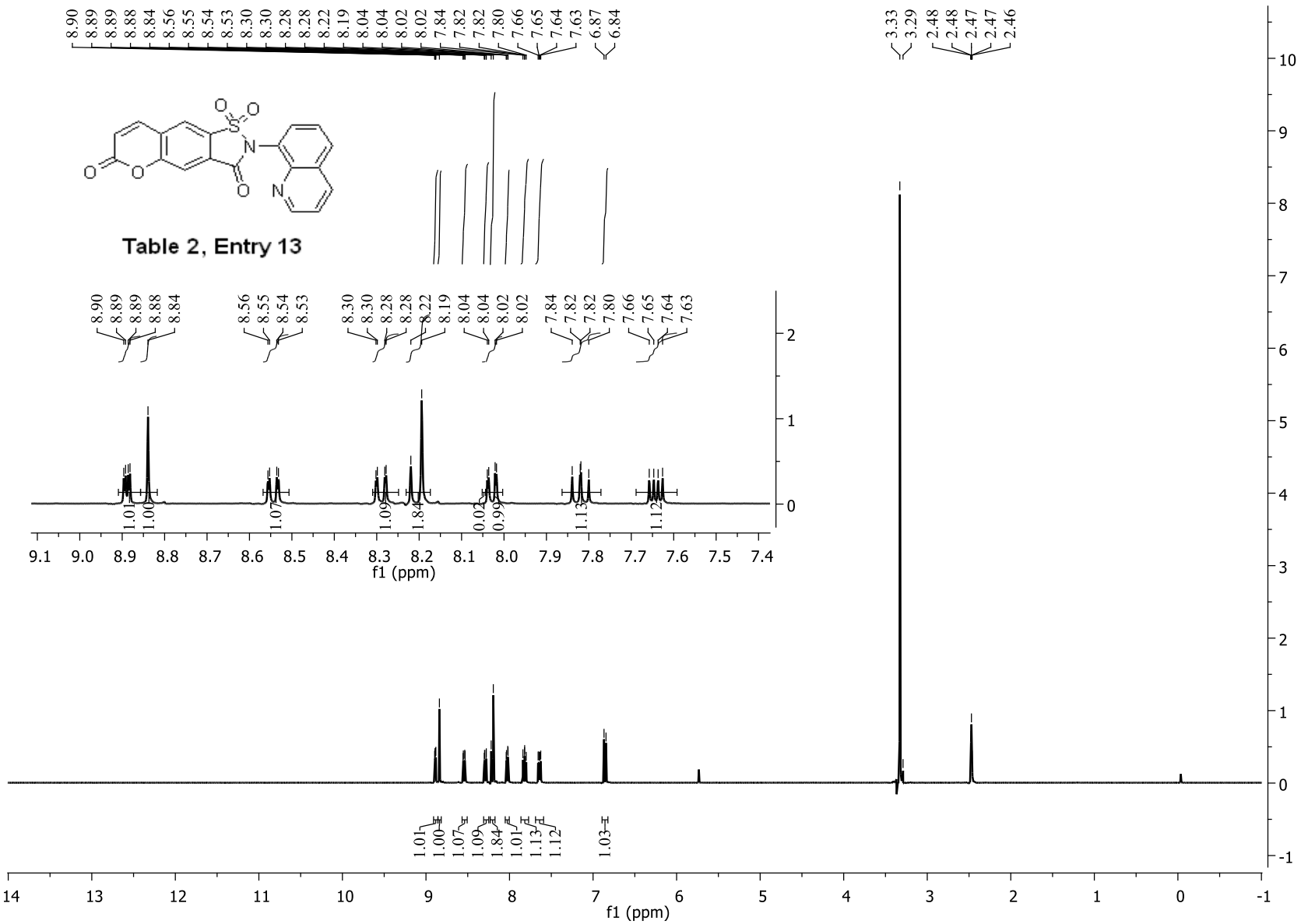


Table 2, Entry 11


9.10
8.95
8.86
8.86
8.86
8.54
8.53
8.41
8.40
8.33
8.32
8.28
8.27
8.04
8.03
7.93
7.92
7.91
7.90
7.89
7.83
7.82
7.80
7.64
7.64
7.63
7.63
7.63
7.62
7.62
5.72
3.30
3.30
2.46
O
O
S
N
O
N
Table 2, Entry 12
8.54
8.53
8.41
8.40
8.33
8.32
8.28
8.27
8.04
8.03
7.92
7.91
7.90
7.83
7.83
7.82
7.64
7.63
7.63
7.63
7.62
1.13
1.17
1.13
1.18
0.98
2.40
1.14
1.15
f1 (ppm)
1.00
0.99
0.97
1.13
1.17
1.13
1.18
0.98
2.40
1.14
1.15
f1 (ppm)


159.19
152.06
144.55
137.16
135.44
135.18
133.67
132.13
131.90
131.20
130.99
130.82
130.37
129.74
128.07
126.98
126.92
123.91
123.10
122.91
40.86
40.65
40.44
40.03
39.82
39.61
Table 2, Entry 12
f1 (ppm)
f1 (ppm)


8.90 8.89 8.89 8.88 8.84 8.56 8.55 8.54 8.53 8.30 8.30 8.28 8.28 8.22 8.19 8.04 8.04 8.02 8.02 7.84 7.82 7.82 7.80 7.66 7.65 7.64 7.63 6.87 6.84
3.33 3.29 2.48 2.48 2.47 2.47 2.46
Table 2, Entry 13
f1 (ppm)
f1 (ppm)

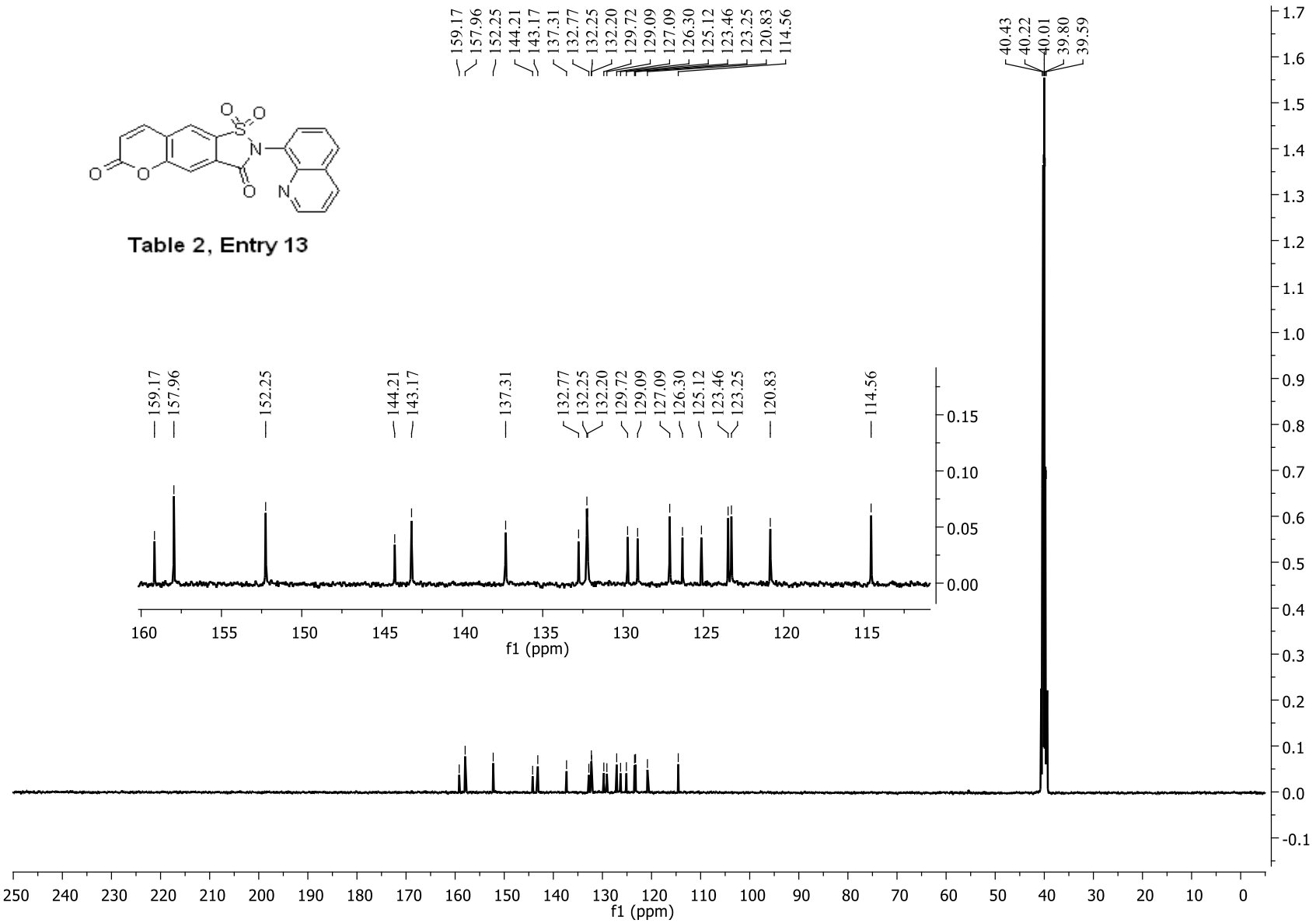


Table 2, Entry 13
159.17
157.96
152.25
144.21
143.17
137.31
132.77
132.25
132.20
129.72
129.09
127.09
126.30
125.12
123.46
123.25
120.83
114.56
40.43
40.22
40.01
39.80
39.59
f1 (ppm)
f1 (ppm)

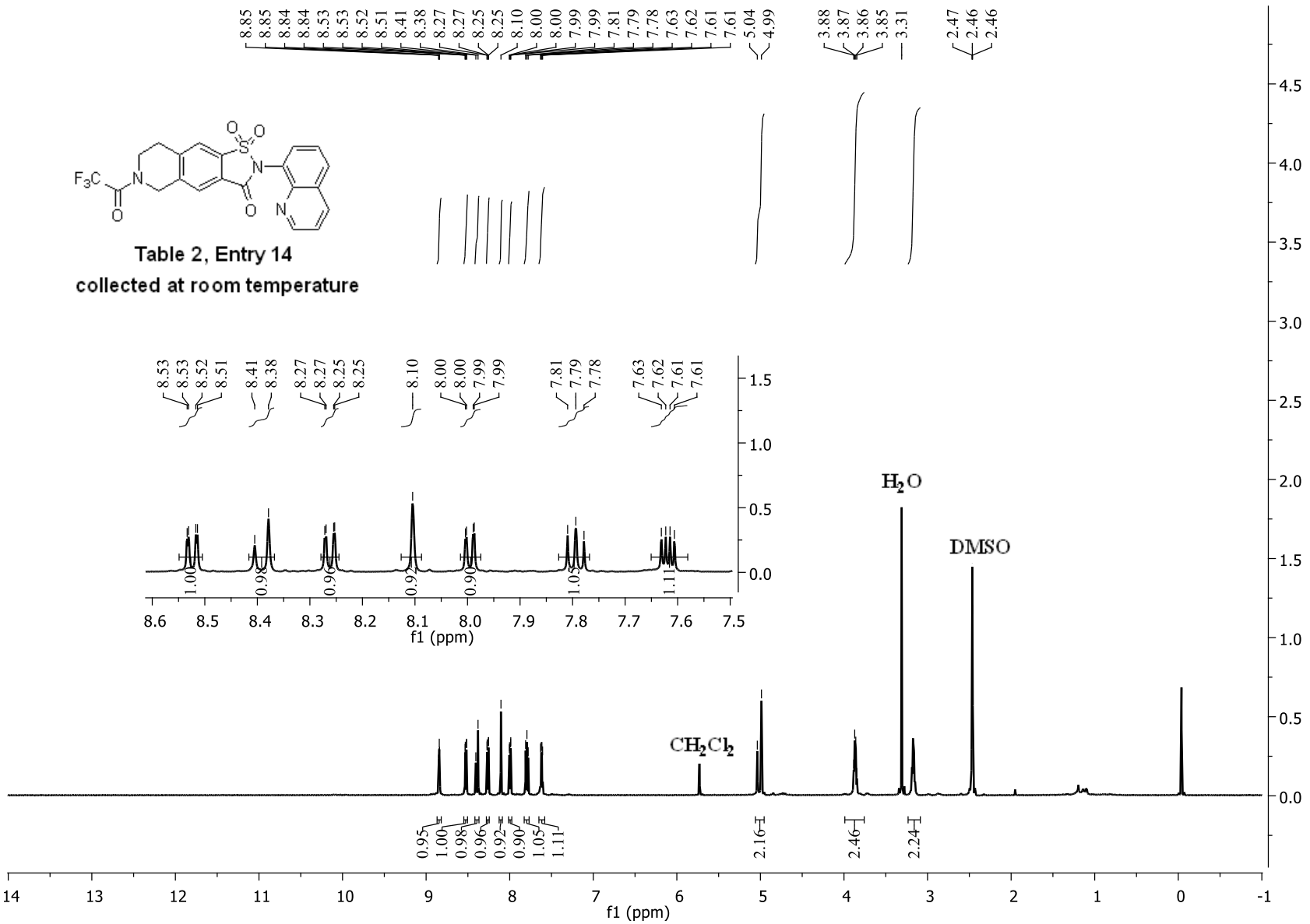


Table 2, Entry 14
collected at room temperature
H2O
DMSO
CH2Cl2
f1 (ppm)

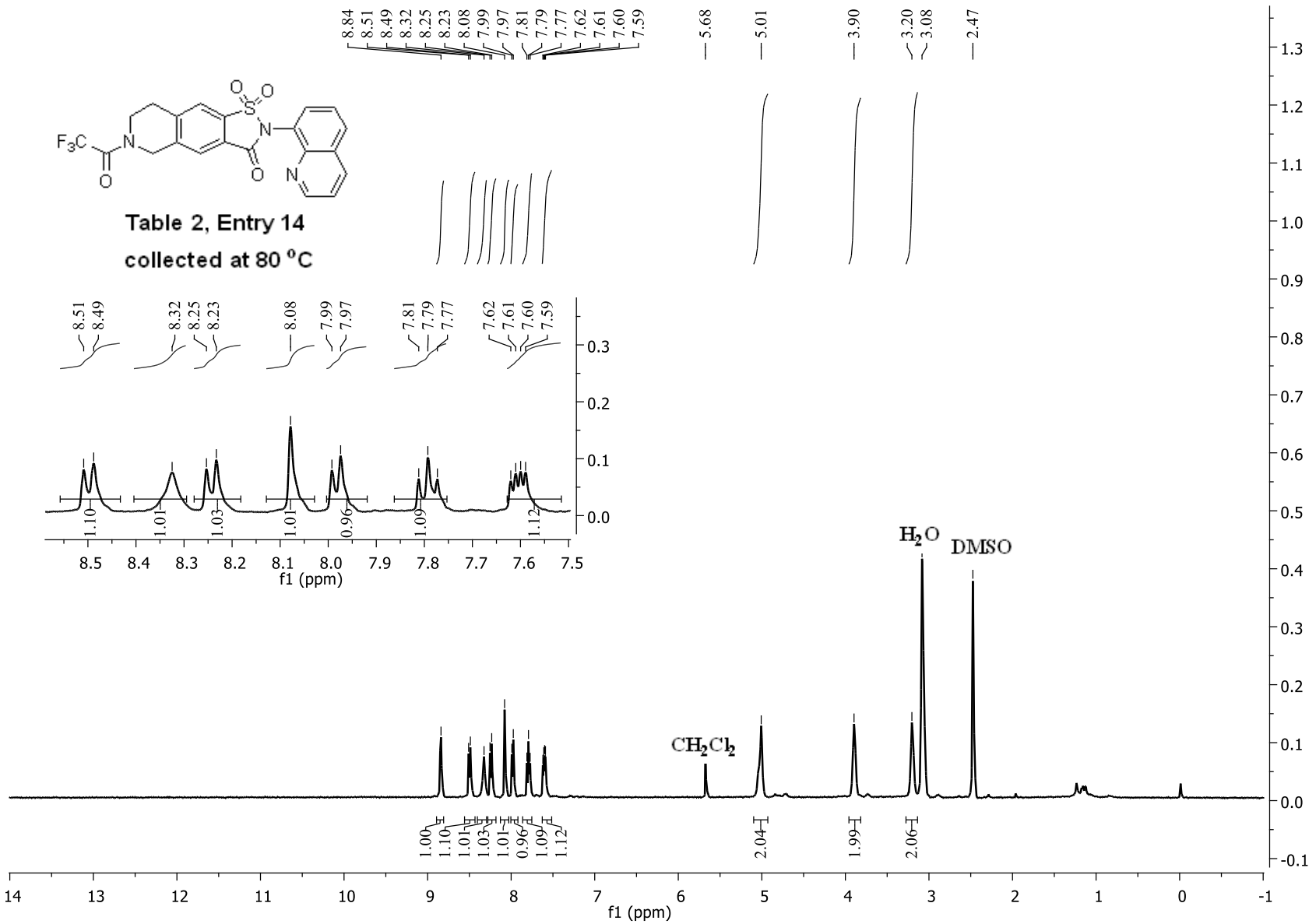


Table 2, Entry 14
collected at 80 °C
f1 (ppm)
CH2Cl2
H2O
DMSO

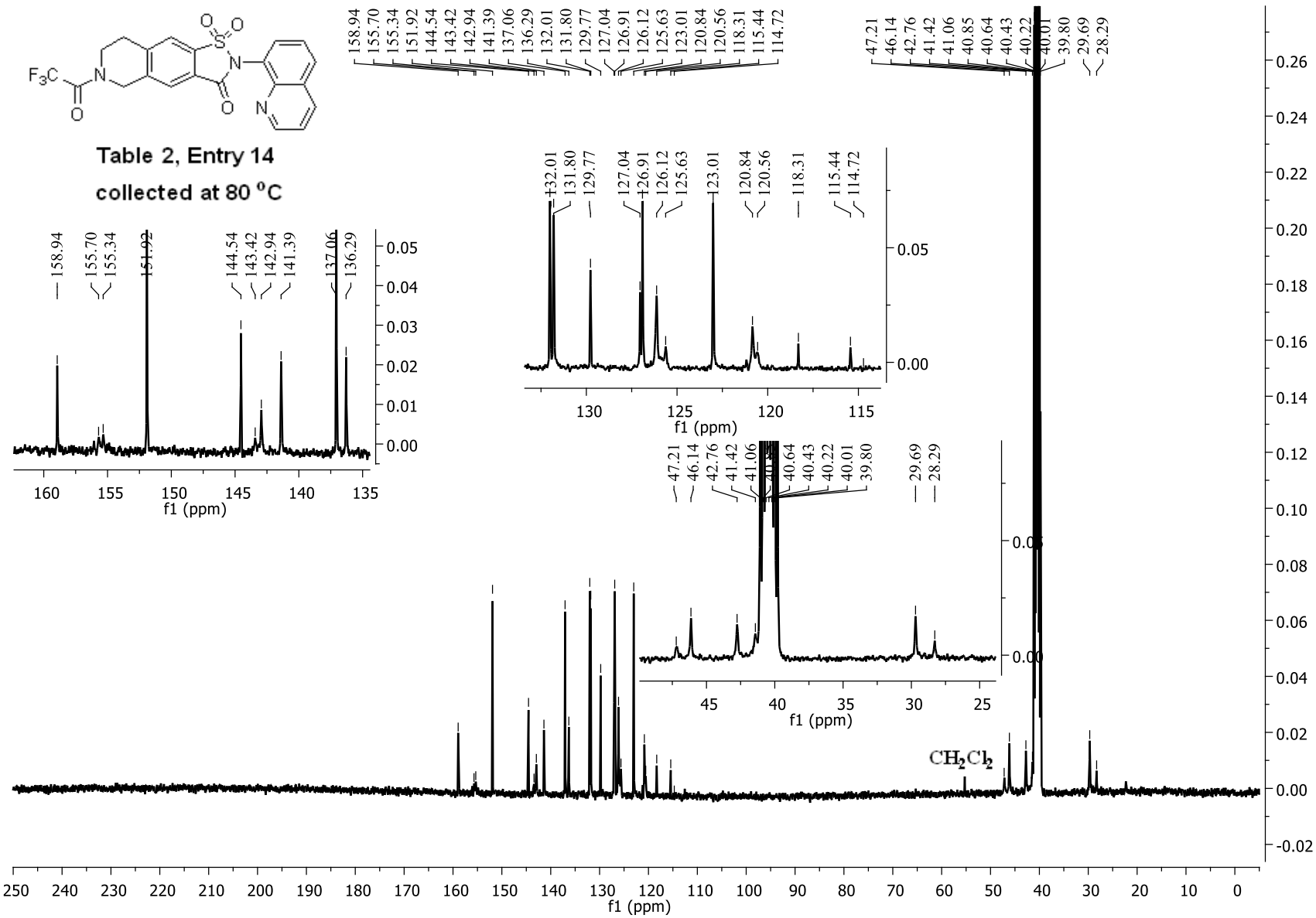


Table 2, Entry 14
collected at 80 °C
158.94
155.70
155.34
151.92
144.54
143.42
142.94
141.39
137.06
136.29
132.01
131.80
129.77
127.04
126.91
126.12
125.63
123.01
120.84
120.56
118.31
115.44
114.72
47.21
46.14
42.76
41.42
41.06
40.85
40.64
40.43
40.22
40.01
39.80
29.69
28.29
CH2Cl2
f1 (ppm)

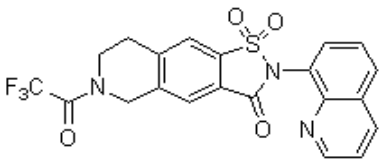
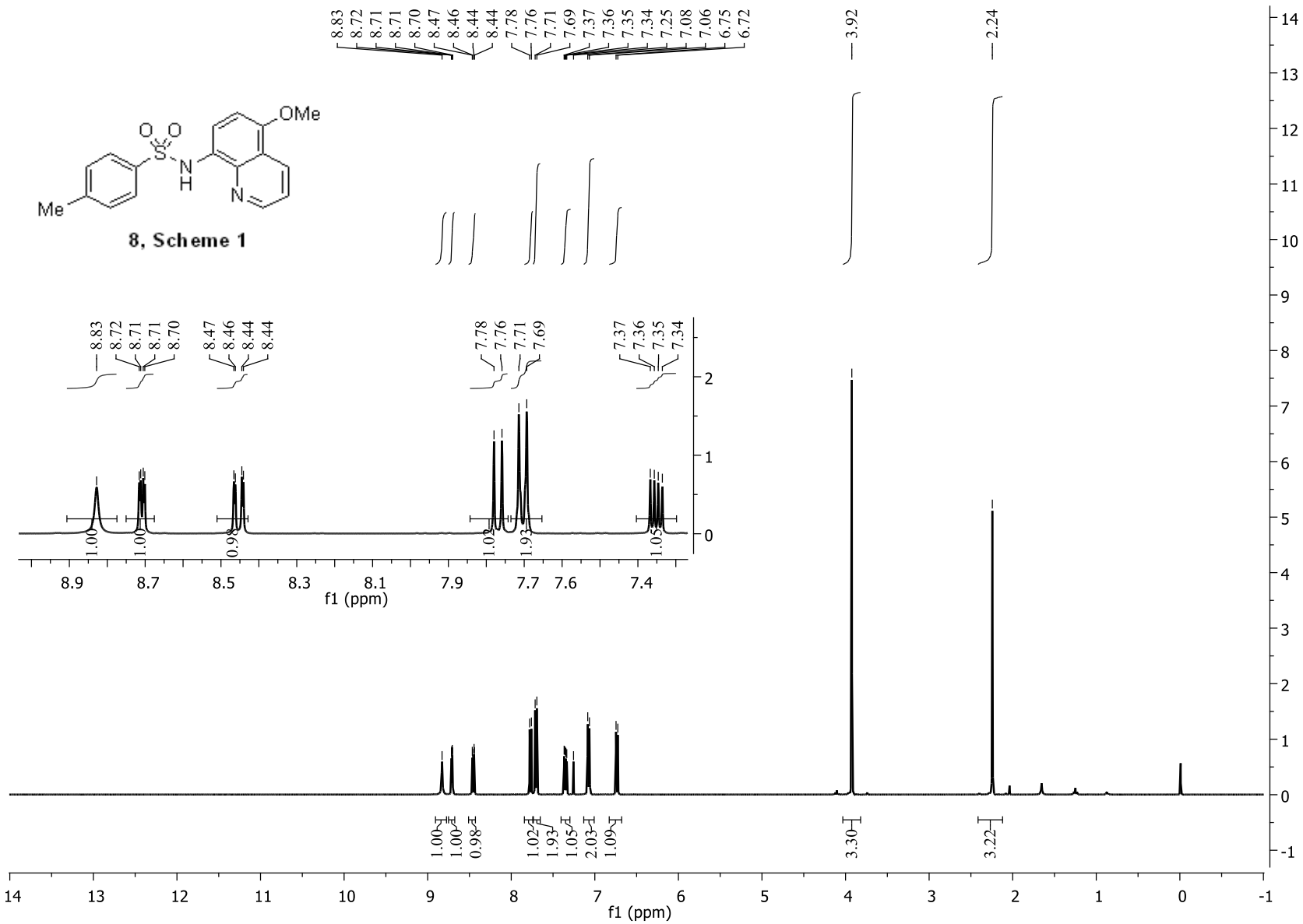
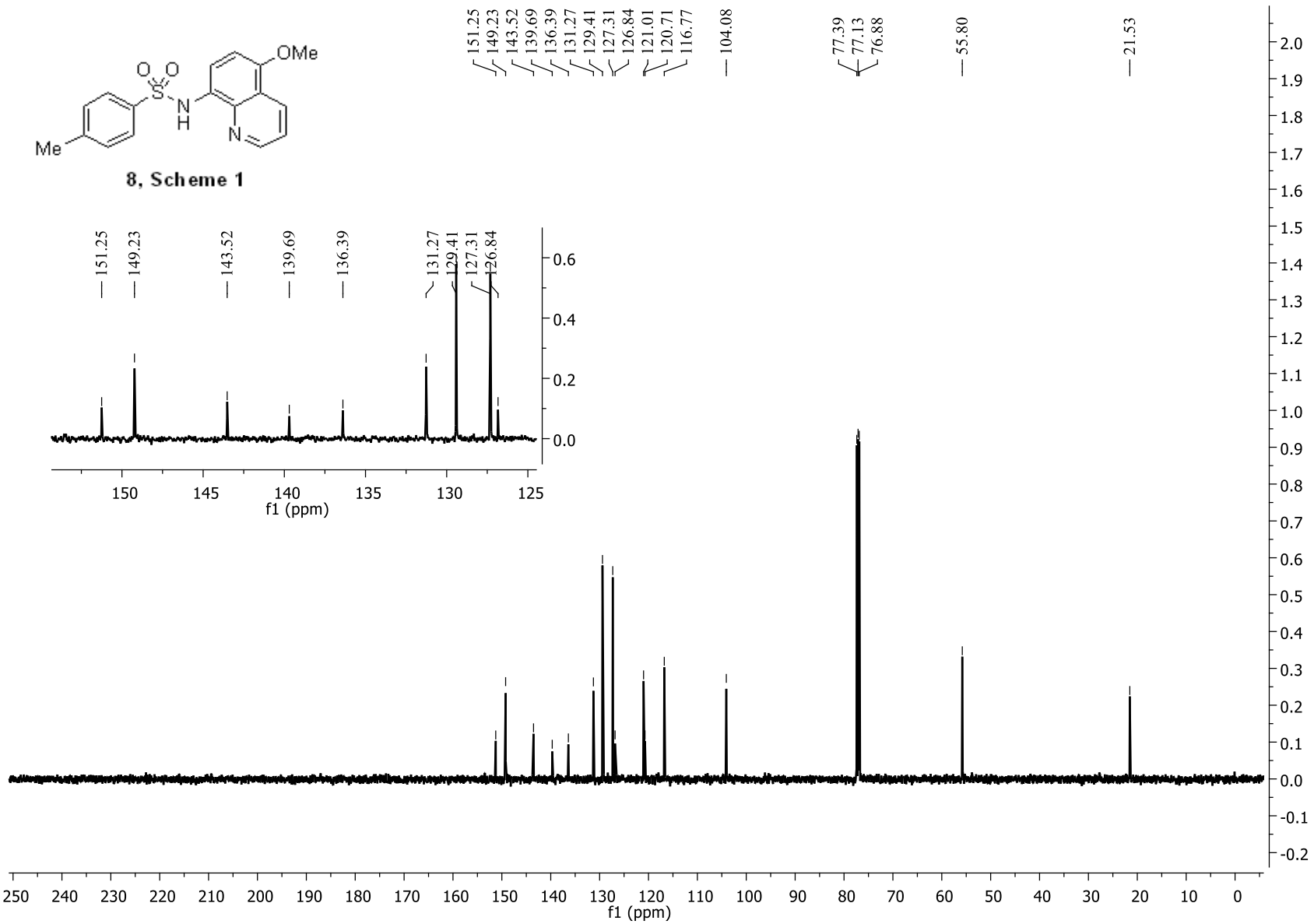
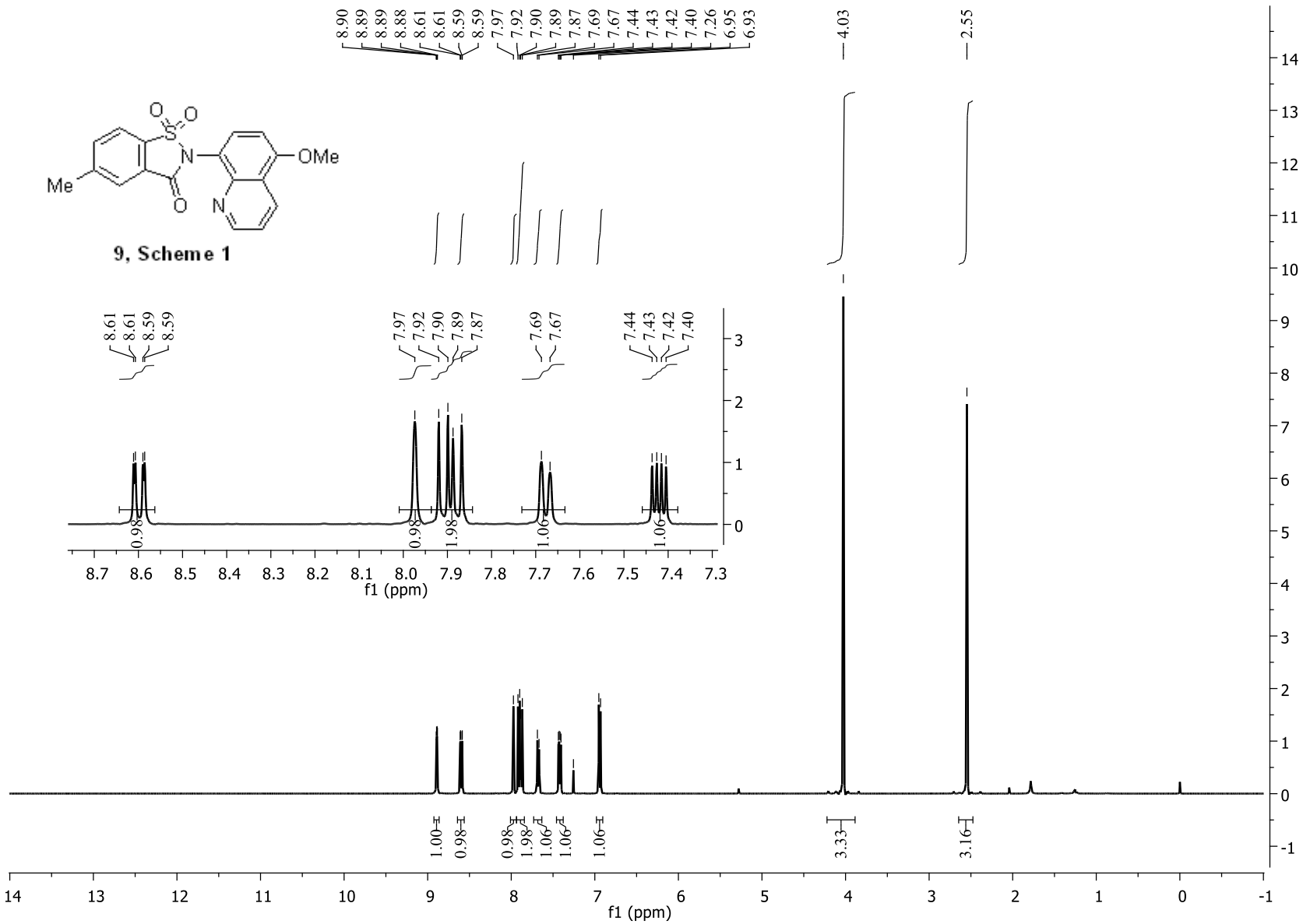


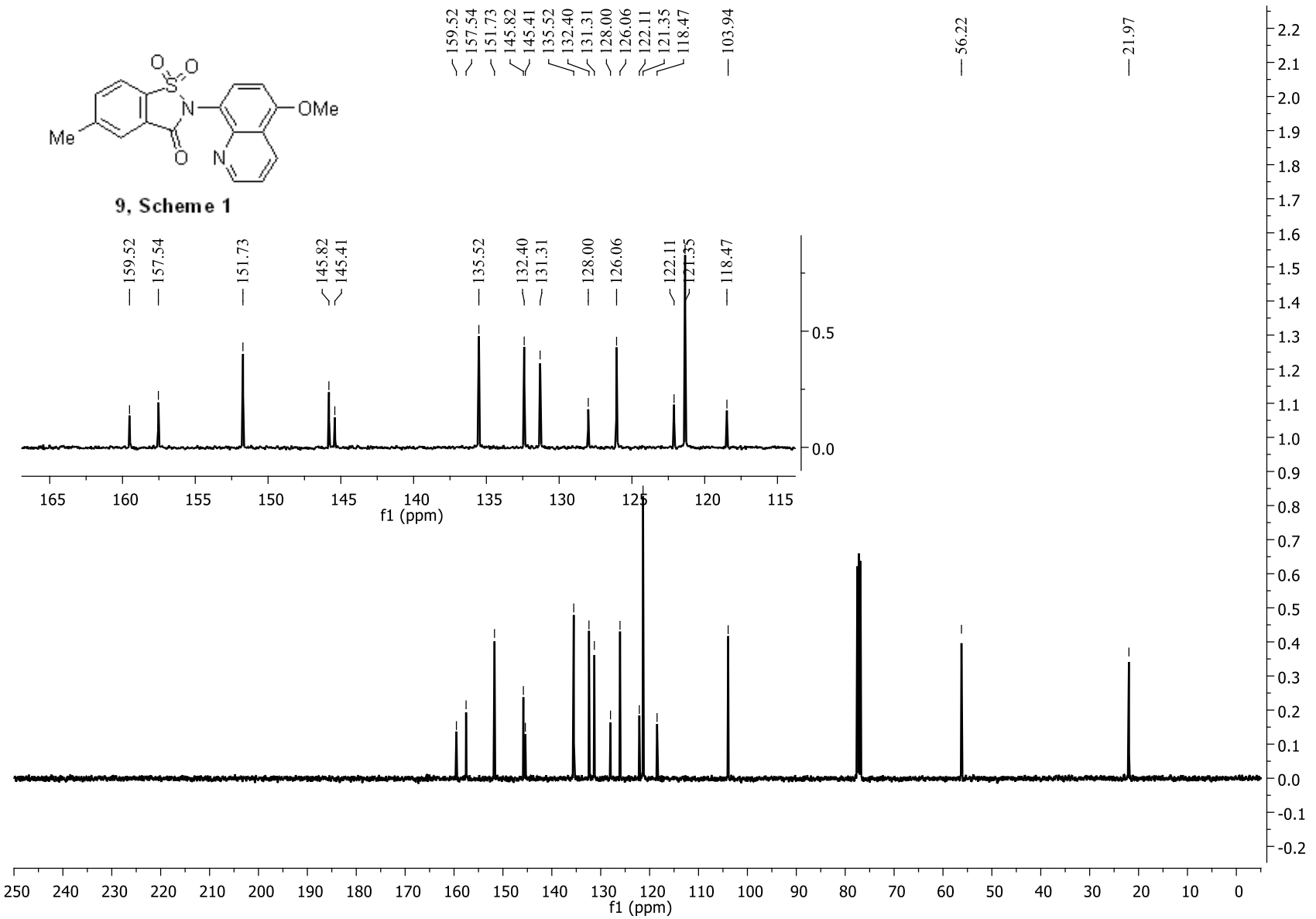
Table 2, Entry 14

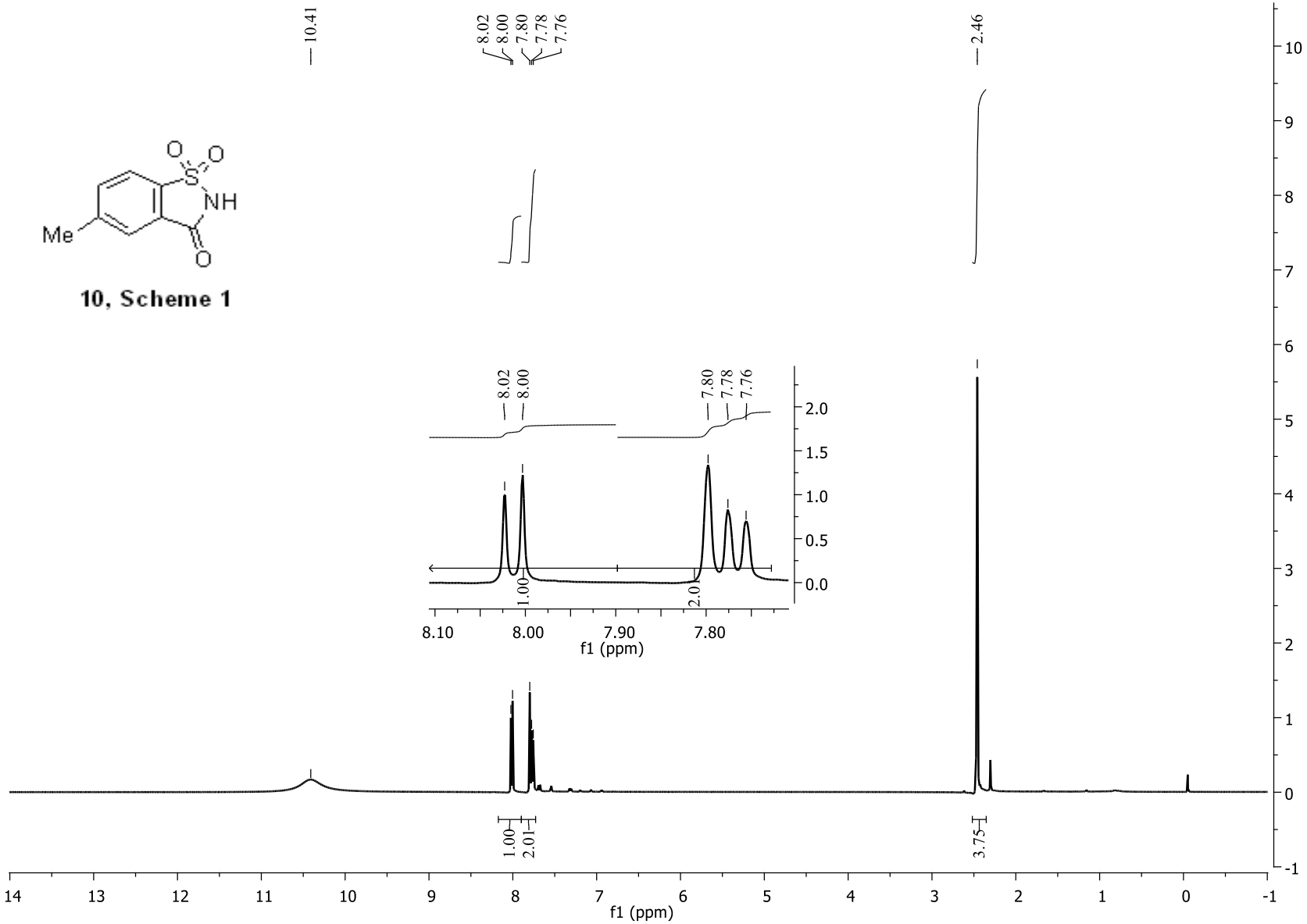
collected at 80 °C

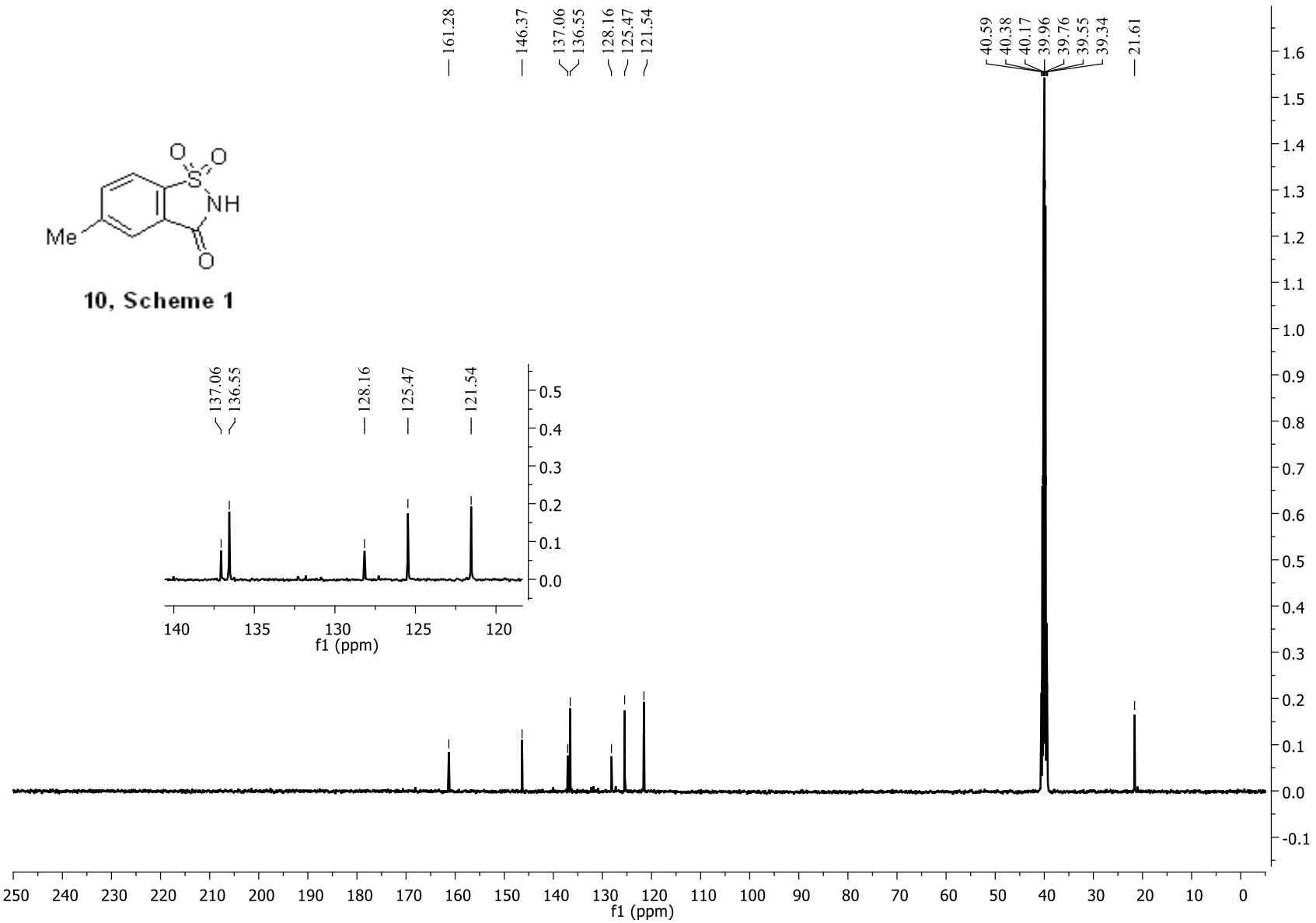

8.83
8.72
8.71
8.71
8.70
8.47
8.46
8.44
8.44
7.78
7.76
7.71
7.69
7.37
7.36
7.35
7.34
7.25
7.08
7.06
6.75
6.72
3.92
2.24
OMe
Me
O
O
S
N
H
N
8, Scheme 1
1.00
1.00
0.98
1.02
1.93
1.05
2.03
1.09
3.30
3.22
f1 (ppm)


OMe
O
O
S
N
H
N
Me
8, Scheme 1
151.25
149.23
143.52
139.69
136.39
131.27
129.41
127.31
126.84
121.01
120.71
116.77
104.08
77.39
77.13
76.88
55.80
21.53
f1 (ppm)


8.90
8.89
8.89
8.88
8.61
8.61
8.59
8.59
7.97
7.92
7.90
7.89
7.87
7.69
7.67
7.44
7.43
7.42
7.40
7.26
6.95
6.93
4.03
2.55
Me
OMe
9, Scheme 1
f1 (ppm)
1.00
0.98
0.98
1.98
1.06
1.06
1.06
3.33
3.16


159.52
157.54
151.73
145.82
145.41
135.52
132.40
131.31
128.00
126.06
122.11
121.35
118.47
103.94
56.22
21.97
Me
OMe
O
O
S
N
O
N
9, Scheme 1
f1 (ppm)
f1 (ppm)


10.41
8.02
8.00
7.80
7.78
7.76
2.46
Me
NH
O
O
O
10, Scheme 1
1.00
2.01
3.75
f1 (ppm)


161.28
146.37
137.06
136.55
128.16
125.47
121.54
40.59
40.38
40.17
39.96
39.76
39.55
39.34
21.61
O
O
S
NH
Me
O
10, Scheme 1
f1 (ppm)
f1 (ppm)