— SUPPORTING INFORMATION —

Copper-Catalyzed Amination of Primary Benzylic C—H Bonds with Primary and Secondary Sulfonamides

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I. TABLE S1. Previously reported C–H aminations of primary benzylic hydrocarbons

Reference	Hydrocarbon Substrate	Catalyst	Hydrocarbon Equivalents	Yield
Au, S.-Z.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120-9132.	Toluene	$Ru^{VI}(TPP)(NTs)_2$ (Stoichiometric)	solvent	9-11%
Yamawaki, M.; Tsutsui, H.; Kitagaki, S.; Anada, M.; Hashimoto, S. *Tetrahedron Lett.* **2002**, *43*, 9561-9564	Toluene	Rh_2(S-TCPTTL)$_4$/PhI=NNs	solvent	30%
Leung, S. K.-Y.; Tsui, W.-M.; Huang, J.-S.; Che, C.-M.; Liang, J.-L.; Zhu, N. *J. Am. Chem. Soc.* **2005**, *127*, 16629-16640.	Toluene	Ru(VI)[Por]$(NSO_2Ns)_2$ (stoichiometric)	20-40 equiv	22%
Li, Z.; Capretto, D. A.; Rahaman, R. He, C. *Angew. Chem. Int. Ed.* **2007**, *46*, 5184-5186.	Mesitylene	$[Ag(BPA)OTf]_2$•xH_2O / PhI=NNs	10 equiv	25%
Fructos, M. R.; Trofimenko, S.; Díaz-Requejo, M. M.; Pérez P. J. *J. Am. Chem. Soc.* **2006**, *128*, 11784-11791.	Toluene Mesitylene	Tp^{Br3}Cu(NCMe)/PhI=NTs or Chloramine-T, 25 °C	solvent solvent	65-95% (GC) 65-95% (GC)
Bhuyan, R.; Nicholas, K. M. *Org. Lett.* **2007**, *9*, 3957-3959.	Toluene	$[MeCN]_4CuPF_6$/ anh. Chloramine-T, 60 °C	1 equiv	54%
Liang, C.; Collet, F.; Robert-Peillard, F.; Müller, P.; Dodd, R. H.; Dauban, P. *J. Am. Chem. Soc.* **2008**, *130*, 343-350.	4-methoxytoluene	$Rh_2\{(S)$-nta$\}_4$/sulfonimidamide PhI(OCO*t*-Bu)$_2$	1 equiv 5 equiv	46% 85%
Huard, K.; Lebel, H. *Chem. Eur. J.* **2008**, *14*, 6222-6230.	Toluene Mesitylene	$Rh_2(tpa)_4$/TrocNH-OTs	15 equiv 15 equiv	50% 67%
Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 9961-9964.	Toluene	$[\{(Cl_2NN)Cu\}_2$(μ-benzene)]/Adam-N_3, 110 °C	solvent	92%
Fan, R.; Li, W.; Pu, D.; Zhang, L. *Org. Lett.* **2009**, *11*, 1425-1428.	Toluene	$PhI(OAc)_2/I_2$ 50 °C	10 equiv	45%

II. General Methods

IIa. General experimental procedures

All reactions were run under a nitrogen atmosphere with exclusion of moisture from reagents and glassware using standard techniques.[1] Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ninhydrin or aqueous potassium permanganate. For purification, column chromatography was performed using 230-400 mesh ultra pure silica gel.

^{1}H and ^{13}C NMR spectra were recorded at 23 °C using a 400 MHz NMR. Chemical shifts (δ) are represented in parts per million from tetramethylsilane and referenced to residual protons in the NMR solvent [$CDCl_3$: ^{1}H NMR δ = 7.26 ppm (singlet); ^{13}C NMR δ = 77.0 ppm (triplet)]. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sx = sextet, sept = septet, m = multiplet and br = broad), and coupling constant (*J*) are in Hz. All ^{13}C NMR spectra were obtained with complete proton decoupling. High-resolution mass spectra (HRMS) were performed using an LC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system. Infrared spectra were obtained as a thin film on NaCl plates or as a KBr pellet. Absorption maxima (ν) are reported in wave numbers (cm^{-1}). Melting points are uncorrected. Differential scanning calorimetry (DSC) was carried out using a TAI Q1000 (10°C/min, 50mL/min nitrogen) with high pressure capsules and seals (part no. 900815.901, 900814.901). Sample(s) were heated from 30 to 300°C. The DSC was calibrated for temperature and heat flow with indium (Goodfellow, 99.999% Pure).

[1] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-sensitive Compounds*, 2nd Edition, Wiley: New York, **1986**.

IIb. Materials and reagents

Commercial reagents were purchased from standard suppliers and used without further purification unless otherwise noted. Anhydrous tetrakis(acetonitrile)copper(I) hexafluorophosphate (Sigma-Aldrich or Strem, 98+%) and copper(II) trifluoromethansulfonate (Strem, 98%) were purchased as a free flowing white solids and used as received. The copper-catalysts were typically weighted into smaller vials containing about 500 mg of reagent in a glovebox and sealed. The smaller containers were transferred outside the glovebox, stored in a desiccator while being utilized and kept for no more than 2 weeks outside the glovebox. *Tert*-butylperoxybenzoate and *tert*-butylperoxyacetate (75 wt% in aliphatic hydrocarbons) were stored refrigerated.

III. Experimental Procedures and Characterization

[CAUTION: CARE SHOULD BE TAKEN WHEN MIXING A METAL WITH A PEROXIDE OXIDANT. USE OF A BLAST SHIELD IN A WELL VENTILATED FUMEHOOD IS RECOMMENDED. HOWEVER, NO ISSUES WERE REPORTED BY THE AUTHORS DURING THE COURSE OF THESE EXPERIMENTS.][2]

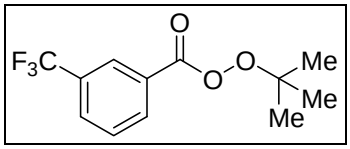
IIIa. General procedure for the copper-catalyzed amination of primary benzylic C–H bonds with sulfonamides. Into a 20 mL vial equipped with a magnetic stir bar was weighted $[MeCN]_4CuPF_6$ (74 mg, 0.2 mmol, 10 mol%), 1,3-indanedione (44 mg, 0.3 mmol, 15 mol%) and the sulfonamide (2.0 mmol, 1.0 equiv). The mixture was diluted with the benzylic hydrocarbon (50 mmol, 25 equiv) and stirred at room temperature for 15 minutes. After this time, the 3-$CF_3C_6H_4CO_3$*t*-Bu oxidant (1.05 g, 4.0 mmol, 2.0 equiv) was added in a single addition via syringe. The vial was placed under an atmosphere of nitrogen and fitted with a septum or Teflon coated-cap. The mixture was stirred at room temperature and a colour change to a dark green solution was typically noted after stirring for 1-2 h. After 3 days of stirring at room temperature, the resulting mixture was poured into a 125 mL separatory funnel containing aqueous sodium carbonate (75 mL) and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The desired products were purified by column chromatography through silica gel, eluting with a mixture of hexanes and ethyl acetate.

IIIb. Procedure for the exploration of reaction parameters for the amination of toluene with *N*-methyl toluenesulfonamide (Table 1). Into a 4 mL reaction vial equipped with a magnetic stir bar was weighted the copper catalyst (10 mol%, 0.10 mmol), ligand (15 mol%, 0.15 mmol) and *N*-methyl toluenesulfonamide (185 mg, 1.0 mmol). The solids were suspended in toluene (2.6 mL, 25.0 mmol) and the suspension was stirred at room temperature for 10 minutes and then oxidant (2 equiv, 2.0 mmol) was added. The suspension was stirred at room temperature for 3 days and then

[2] (a) *Bretherick's Handbook of Reactive Chemical Hazards*, *7th Edition*; Urben, P. G. Ed; Elsevier: Oxford, 2007; pp288-290. (b) Churchill, D. G. *J. Chem. Ed.* **2006**, *83*, 1798-1803.

concentrated under reduced pressure. The unpurified reaction mixture was treated with 1.0 mL of a 0.33 M solution of internal standard (1,3,5-trimethoxybenzene) in $CDCl_3$. The reaction was further diluted with $CDCl_3$ (3 mL) and filtered through a 25 mm syringe filter equipped with a 1 μM glass fiber membrane to remove the copper residues. An aliquot of the filtered solution was analyzed by ^{1}H NMR spectroscopy. Integration of the product peaks at 4.2 ppm (2H, s) was compared to the internal standard peaks at 6.1 ppm (1H, s, calibrated to 100%) and 3.8 ppm (3H, s).

IIIc. Preparation of *tert*-butyl 3-(trifluoromethyl)benzenecarboperoxoate (oxidant C, Table 1).



[Analysis by differential scanning calorimetry (DSC) using a high pressure capsule demonstrated exothermic decomposition of this compound begins at 110 °C and reached a maximum at 165 °C].

Into a flame-dried, 500 mL round-bottom flask fitted with a rubber septum and under an atmosphere of nitrogen were added anhydrous dichloromethane (200 mL) and 3-trifluoromethylbenzoyl chloride (6.0 mL, 40 mmol, 1.0 equiv). The solution was cooled to 0 °C in an ice bath and pyridine (9.4 mL, 116 mmol, 3.0 equiv) was added followed by drop wise addition of *tert*-butyl hydrogen peroxide (7.7 mL, 56 mmol, 1.4 equiv, 70 wt% in water). The mixture was stirred at 0 °C for 1 h and then stirred at room temperature for 16 h. The reaction mixture was diluted with 1 M aqueous HCl solution (200 mL), stirred vigorously for 20 minutes and poured into a 500 mL separatory funnel. The organic layer was further washed with 1 M aqueous HCl solution (100 mL), water (200 mL), saturated aqueous $NaHCO_3$ (200 mL), water (200 mL) and brine (150 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield a colourless oil. Purification by column chromatography through silica gel, eluting with 100% hexanes to 10% EtOAc in hexanes as a gradient afforded the title compound as a colourless liquid (6.7 g, 64% yield). This compound was stored in a vial under nitrogen at 4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (1H, s), 8.16, (1H, d, J = 8.0 Hz), 7.87 (1H ,d, J = 8.0 Hz), 7.64 (1H, t, J = 8.0 Hz), 1.44 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 132.3, 131.4 (q, J = 33 Hz, J_{C-F}), 129.9 (q, J = 4 Hz, J_{C-F}), 129.4, 128.6, 126.0 (q, J = 4 Hz, J_{C-F}), 123.4 (q, J = 273 Hz, J_{C-F}), 84.4, 26.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.89.

IR (neat film) ν 2985, 2938, 1756, 1368, 1125, 922, 848, 695 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{12}H_{13}F_3O_3Na$ $[M+Na]^+$: 285.0709, found: 285.0715.

IIId. Preparation of Secondary Sulfonamides. The following secondary sulfonamides were prepared from the commercially available sulfonyl chloride (1.0 equiv), *N*-alkylamine (2.0 equiv) and pyridine (2.0 equiv) in CH_2Cl_2 (0.2 M) at room temperature for 4-16 h under standard conditions: *N*-methyl-4-methoxybenzenesulfonamide, *N*-methyl-4-*tert*-butylbenzenesulfonamide, *N*-methyl-2-naphthylsulfonamide, *N*-cyclopropyl-4-methylbenzenesulfonamide.

The preparation of *N*-cyclopropyl-4-methylbenzenesulfonamide is representative. Into a 500 mL round-bottom flask equipped with a magnetic stir bar and under nitrogen was weighted *p*-toluenesulfonyl chloride (7.63 g, 40.0 mmol) and dichloromethane (200 mL). The suspension was cooled to 0 °C and then *N*-cyclopropylamine (4.57 g, 80.0 mmol) was added, followed by the addition of pyridine (6.47 mL, 80.0 mmol). The resulting suspension was stirred at room temperature for 16 h. The reaction mixture was poured into a 500 mL separatory funnel and washed with 1 M aqueous HCl solution (3 × 100 mL), water (100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography through silica gel, eluting with 100% hexanes to 25% EtOAc in hexanes as a gradient afforded the title compound as a white solid (7.31 g, 87% yield).

^{1}H NMR spectra is identical to those previously reported.[3]

mp = 79-80 °C (lit = 74-76 °C).[3]

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.6, 129.6, 127.4, 24.2, 21.5, 6.0.

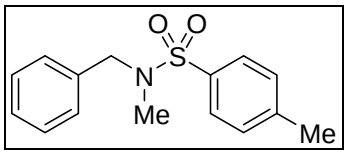
IR (KBr) ν 3255, 2995, 1911, 1796, 1644, 1496, 1321, 1164, 1094, 699 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{10}H_{14}NO_2S$ $[M+H]^+$: 212.0740, found: 212.0737.

[3] Bridge, A. J.; Sanchez, J. P. *J. Heterocyclic Chem.* **1990**, *27*, 1527-1536.

IIIe. Characterization Data (Substrates in Table 2 and 3).

***N*-Benzyl-*N*,4-dimethylbenzenesulfonamide (Table 2, entry 1).**



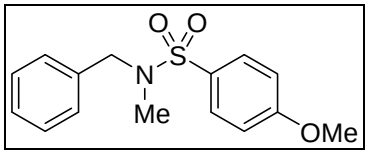
The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 40% ethyl acetate in hexanes afforded the title compound as an off-white solid (397 mg, 72% yield).

^{1}H NMR, ^{13}C NMR and IR spectra were identical to those previously reported.[4]

mp 94-95 °C

HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}NO_2SNa$ $[M+Na]^+$: 298.0872, found: 298.0888.

***N*-Benzyl-4-methoxy-*N*-methylbenzenesulfonamide (Table 2, entry 2).**



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-methoxybenzenesulfonamide (402 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as an off-white solid (417 mg, 72% yield).

mp 117-118 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (2H, d, *J* = 9.0 Hz), 7.38-7.31 (5H, m), 7.05 (2H, d, *J* = 9.0 Hz), 4.14 (2H, s), 3.92 (3H, s), 2.60 (3H, s).

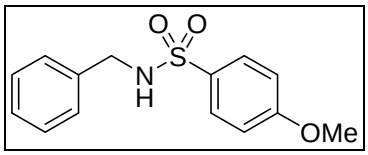
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 135.7, 129.6, 129.0, 128.6, 128.4, 127.9, 114.3, 55.6, 54.1, 34.3.

IR (KBr) ν 3002, 2846, 1595, 1455, 1339, 1305, 1261, 1153, 736, 560 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}NO_3SNa$ $[M+Na]^+$: 314.0821, found: 314.0824.

[4] Powell, D. A.; Pelletier, G. *Tetrahedron Lett.* **2008**, *49*, 2495-2498.

N-Benzyl-4-methoxybenzenesulfonamide (Table 2, entry 3).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and 4-methoxybenzenesulfonamide (374 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (176 mg, 32% yield).

The ^{1}H NMR spectra is similar, with small differences in the chemical shifts to those previously reported, and is included for completeness.[5]

mp 108-109 °C (lit = 107.5-108 °C, ref 3b)

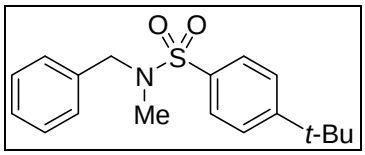
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (2H, m), 7.33-7.21 (5H, m), 6.99 (2H, d, *J* = 9.0 Hz), 4.73 (1H, t, *J* = 6.0 Hz), 4.13 (2H, d, *J* = 6.0 Hz), 3.90 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 136.3, 131.4, 129.3, 128.7, 127.9, 127.8, 114.2, 55.6, 47.2.

IR (KBr) ν 3256, 3068, 2839, 1597, 1303, 1254, 1148, 1024, 831, 730, 565 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{16}NO_3S$ $[M+H]^+$: 278.0845, found: 278.0848.

N-Benzyl-4-*tert*-butyl-N-methylbenzenesulfonamide (Table 2, entry 4).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-*tert*-butylbenzenesulfonamide (454 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow solid (453 mg, 71% yield).

mp 116-118 °C

[5] (a) MacPherson, L. J.; Bayburt, E. K.; Capparelli, M. P.; Carroll, B. J.; Goldstein, R.; Justice, M. R.; Zhu, L.; Hu, S.-i.; Melton, R. A.; Fryer, L.; Goldberg, R. L.; Doughty, J. R.; Spirito, S.; Blancuzzi, V.; Wilson, D.; O'Byrne, E. M.; Ganu, V.; Parker, D. T. *J. Med. Chem.* **1997**, *40*, 2525-2532. (b) Nyasse, B.; Grehn, L.; Ragnarsson, U.; Maia, H. L. S.; Monteiro, L. S.; Leito, I.; Koppel, I.; Koppel, J. *J. Chem. Soc. Perkin Trans. 1* **1995**, 2025-2031.

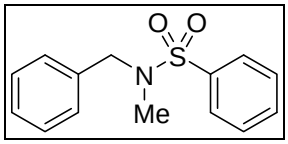
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, *J* = 8.5 Hz), 7.59 (2H, d, *J* = 8.5 Hz), 7.36-7.32 (5H, m), 4.18 (2H, s), 2.63 (3H, s), 1.39 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 135.7, 134.4, 128.6, 128.4, 127.8, 127.3, 126.1, 54.1, 35.1, 34.3, 31.1.

IR (KBr) ν 2963, 1594, 1334, 943, 835, 723 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{18}H_{23}NO_2SNa$ $[M+Na]^+$: 340.1342, found: 340.1343.

_N_-Benzyl-_N_-methylbenzenesulfonamide (Table 2, entry 5).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-benzenesulfonamide (342 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as slight-yellow coloured solid (271 mg, 52% yield).

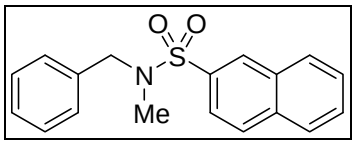
^{1}H NMR and ^{13}C NMR spectra were identical to those previously reported.[6]

mp 85-87 °C (lit 92-93 °C)[6]

IR (KBr) ν 3036, 2947, 1449, 1337, 1163, 1126, 740, 695, 580 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{16}NO_2S$ $[M+H]^+$: 262.0896, found: 262.0907.

_N_-Benzyl-_N_-methylnaphthalene-2-sulfonamide (Table 2, entry 6).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-naphthalene-2-sulfonamide (442 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to

[6] Katritzky, A. R.; Zhang, G.; Wu, J. *Synthetic Comm.*. **1994**, *24*, 205-216.

20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (348 mg, 56% yield).

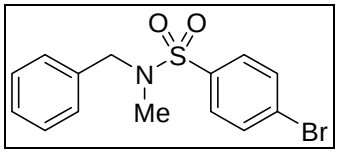
The ^{1}H and ^{13}C NMR spectra are identical to those previously reported.[7]

mp 95-96 °C

IR (KBr) ν 3057, 1496, 1361, 1334, 1163, 932, 728, 698, 651 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{18}H_{18}NO_2S$ $[M+H]^+$: 312.1053, found: 312.1053.

N-Benzyl-4-bromo-N-methylbenzenesulfonamide (Table 2, entry 7).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-bromobenzenesulfonamide (500 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow solid (382 mg, 56% yield).

mp 96-97 °C

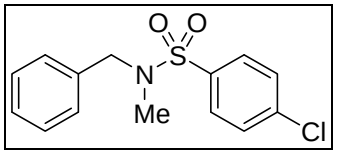
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.72 (4H, m), 7.38-7.31 (5H, m), 4.17 (2H, s), 2.63 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.3, 132.4, 128.9, 128.7, 128.3, 128.0, 127.7, 54.1, 34.3.

IR (KBr) ν 3091, 2971, 1574, 1464, 1333, 1160, 923, 909, 778, 745 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{15}BrNO_2S$ $[M+H]^+$: 340.0001, found: 340.0000.

N-Benzyl-4-chloro-N-methylbenzenesulfonamide (Table 2, entry 8).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-chlorobenzenesulfonamide (411 mg, 2.0 mmol).

[7] Nyasse, B.; Grehn, L.; Maia, H. L. S.; Monteiro, L. S.; Ragnarsson, U. *J. Org. Chem.* **1999**, *64*, 7135-7139.

Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (271 mg, 46% yield).

mp 85-86 °C

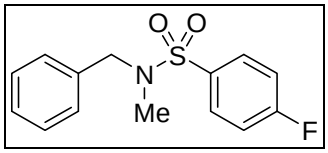
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (2H, d, *J* = 8.5 Hz), 7.56 (2H, d, *J* = 8.5 Hz), 7.39-7.31 (5H, m), 4.17 (2H, s), 2.64 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 136.0, 135.3, 129.4, 128.8, 128.7, 128.3, 128.0, 54.1, 34.3.

IR (KBr) ν 3088, 3073, 2964, 1587, 1459, 1335, 1160, 1090, 906, 779, 752, 718 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{15}ClNO_2S$ $[M+H]^+$: 296.0507, found: 296.0516.

_N_-Benzyl-4-fluoro-_N_-methylbenzenesulfonamide (Table 2, entry 9).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-4-fluorobenzenesulfonamide (378 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (250 mg, 45% yield).

mp 70-71 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (2H, m), 7.39-7.24 (7H, m), 4.17 (2H, s), 2.63 (3H, s).

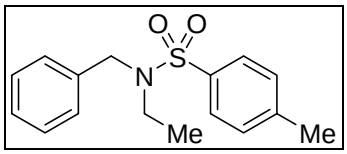
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 255 Hz, $J_{C\text{-}F}$), 135.3, 133.6, 130.1 (d, *J* = 9 Hz, $J_{C\text{-}F}$), 128.7, 128.3, 128.0, 116.4 (d, *J* = 22 Hz, $J_{C\text{-}F}$), 54.1, 34.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -105.3.

IR (KBr) ν 3068, 2966, 1591, 1493, 1376, 1333, 1297, 1128, 1187, 1156, 845, 770, 727 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{14}H_{15}FNO_2S$ $[M+H]^+$: 280.0802, found: 280.0806.

N-Benzyl-N-ethyl-4-methylbenzenesulfonamide (Table 2, entry 10).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-ethyl-4-toluenesulfonamide (400 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow oil (200 mg, 35% yield).

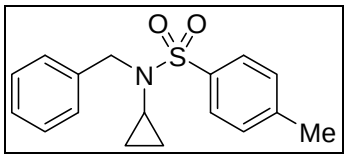
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J* = 8.0 Hz), 7.35-7.28 (7H, m), 4.36 (2H, s), 3.21 (2H, q, *J* = 7.0 Hz), 2.46 (3H, s), 0.95 (3H, t, *J* = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.3, 136.5, 129.7, 128.5, 128.2, 127.6, 127.1, 51.0, 42.3, 21.5, 13.2.

IR (neat film) ν 3031, 2977, 1721, 1687, 1598, 1495, 1454, 1382, 1336, 1155, 1091, 723, 652 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{16}H_{20}NO_2S$ $[M+H]^+$: 290.1209, found: 290.1216.

N-Benzyl-N-cyclopropyl-4-methylbenzenesulfonamide (Table 2, entry 11).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-cyclopropyl-4-toluenesulfonamide (422 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (287 mg, 48% yield).

mp 60-61 °C

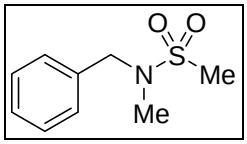
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J* = 8.0 Hz), 7.37-7.27 (7H, m), 4.36 (2H, s), 2.46 (3H, s), 2.02 (1H, tt, *J* = 7.0, 3.5 Hz), 0.69-0.62 (2H, m), 0.58-0.53 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 137.0, 135.5, 129.5, 128.6, 128.3, 127.6, 127.5, 54.7, 30.8, 21.5, 7.0.

IR (KBr) ν 3030, 2977, 2919, 1598, 1455, 1343, 1304, 1168, 1091, 1073, 814, 711, 600 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{17}H_{20}NO_2S$ $[M+H]^+$: 302.1209, found: 302.1210.

N-Benzyl-N-methylmethanesulfonamide (Table 2, entry 12).

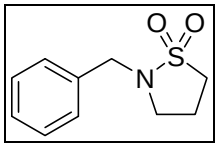


The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and *N*-methyl-methanesulfonamide (220 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow oil (165 mg, 41% yield).

The ^{1}H NMR, ^{13}C NMR and IR spectra are identical to those previously reported.[8]

HRMS (ESI+) *m*/*z* calcd for $C_9H_{14}NO_2S$ $[M+H]^+$: 200.0740, found: 200.0742.

2-Benzylisothiazolidine 1,1-dioxide (Table 2, entry 13).

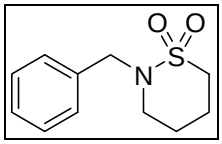


The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and 1,3-propanesultam (243 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 40% ethyl acetate in hexanes afforded the title compound as a light yellow oil (227 mg, 54% yield).

The ^{1}H NMR, ^{13}C NMR and IR spectra are identical to those previously reported.[9]

HRMS (ESI+) *m*/*z* calcd for $C_{10}H_{14}NO_2S$ $[M+H]^+$: 212.0740, found: 212.0731.

2-Benzyl-1,2-thiazinane 1,1-dioxide (Table 2, entry 14).



[8] Alonso, E.; Ramon, D. J.; Yus, M. *Tetrahedron* **1997**, *53*, 14355-14368.
[9] Cooper, G. F. *Synthesis* **1991**, 859-860.

The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and 1,3-butanesultam (270 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a yellow-orange oil (337 mg, 75% yield).

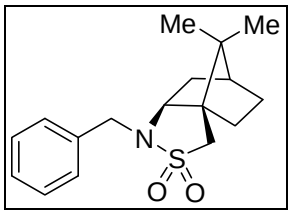
The ^{1}H NMR spectra is identical to those previously reported.[10]

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 128.6, 128.4, 127.8, 49.9, 48.7, 48.2, 23.9, 21.6.

IR (neat film) ν 2950, 2865, 1727, 1496, 1455, 1355, 1329, 1292, 1193, 1140, 1159, 896, 766 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{11}H_{16}NO_2S$ [M+H]$^+$: 226.0896, found: 226.0898.

(3a*R*, 7a*S*)-1-Benzyl-8,8-dimethylhexahydro-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (Table 2, entry 15).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using toluene (5.3 mL, 50.0 mmol) and (1*R*)-(+)-2,10-camphorsultam (430 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as an off-white solid (376 mg, 62% yield).

mp 54-55 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (5H, m), 4.46 (1H, d, *J* = 14.5 Hz), 3.78 (1H, d, *J* = 14.5 Hz), 3.18 (2H, s), 3.14-3.10 (1H, m), 1.89-1.78 (2H, m), 1.74-1.72 (1H, m), 1.53-1.42 (2H, m), 1.40-1.33 (1H, m), 1.27-1.20 (1H, m), 1.08 (3H, s), 0.90 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 129.2, 128.4, 127.8, 67.8, 49.7, 49.0, 47.7, 47.6, 44.5, 35.4, 32.2, 26.7, 20.2, 19.9.

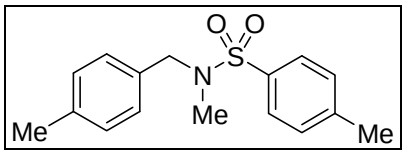
$[\alpha]_D^{23}$ +23.8 (*c* = 1.2, CH_2Cl_2).

IR (KBr) ν 3030, 2955, 2880, 1455, 1302, 1098, 1051, 742, 711 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{17}H_{24}NO_2S$ [M+H]$^+$: 306.1522, found: 306.1524.

[10] Lee, J.; Askin, D.; Jensen, M. S.; Zhong, Y.-L. **WO 2003/016294** A1

N,4-Dimethyl-N-(4-methylbenzyl)benzenesulfonamide (Table 3, entry 1).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using *para*-xylene (6.2 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as an off-white solid (350 mg, 61% yield).

mp 76-77 °C

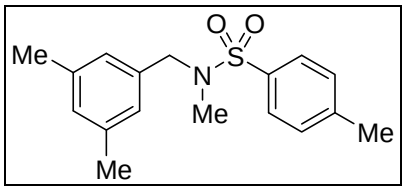
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz), 7.28-7.15 (4H, m), 4.10 (2H, s), 2.59 (3H, s), 2.48 (3H, s), 2.36 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.6, 134.3, 132.6, 129.7, 129.3, 128.4, 127.5, 53.9, 34.2, 21.5, 21.1.

IR (KBr) ν 2923, 1452, 1336, 1159, 1086, 925, 811, 759 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{16}H_{20}NO_2S$ $[M+H]^+$: 290.1209, found: 290.1209.

N-(3,5-Dimethylbenzyl)-N,4-dimethylbenzenesulfonamide (Table 3, entry 2).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using mesitylene (7.0 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as a light yellow solid (338 mg, 56% yield).

mp 96-98 °C

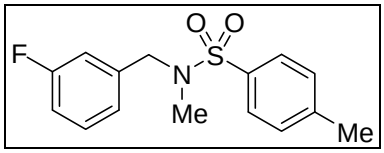
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz), 6.94-6.91 (3H, m), 4.07 (2H, s), 2.60 (3H, s), 2.48 (3H, s), 2.31 (6H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.2, 135.5, 134.3, 129.7, 129.4, 127.5, 126.2, 54.1, 34.3, 21.5, 21.2.

IR (KBr) ν 2918, 2854, 1596, 1452, 1344, 1192, 1163, 1088, 927, 760 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{17}H_{22}NO_2S$ $[M+H]^+$: 304.1366, found: 304.1370.

_N_-(3-Fluorobenzyl)-_N_,4-dimethylbenzenesulfonamide (Table 3, entry 3).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 3-fluorotoluene (5.5 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as an tan-yellow solid (371 mg, 63% yield).

mp 55-56 °C

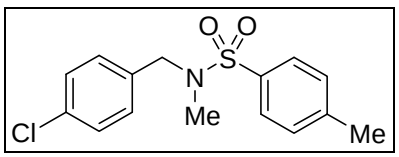
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, d, *J* = 7.0 Hz), 7.38 (2H, d, *J* = 7.0 Hz), 7.32 (1H, d, *J* = 6.0 Hz), 7.12-7.01 (3H, m), 4.15 (2H, s), 2.63 (3H, s), 2.48 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 247 Hz, J_{C-F}), 143.6, 138.4 (d, *J* = 7 Hz, J_{C-F}), 134.2, 130.2 (d, *J* = 8 Hz, J_{C-F}), 129.8, 127.5, 123.8 (d, *J* = 3 Hz, J_{C-F}), 115.1 (d, *J* = 22 Hz, J_{C-F}), 114.8 (d, *J* = 21 Hz, J_{C-F}), 53.7, 34.5, 21.5.

IR (KBr) ν 2925, 1614, 1588, 1487, 1452, 1339, 1254, 1154, 951, 801, 743 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}FNO_2S$ $[M+H]^+$: 294.0959, found: 294.0963.

_N_-(4-Chlorobenzyl)-_N_,4-dimethylbenzenesulfonamide (Table 3, entry 4).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 4-chlorotoluene (6.3 g, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol).

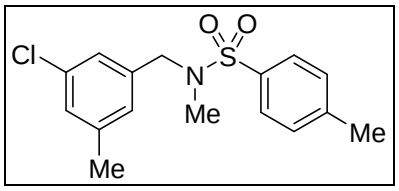
Purification by column chromatography through silica gel using a gradient of 100% hexanes to 20% ethyl acetate in hexanes afforded the title compound as an off-white solid (388 mg, 63% yield). The ^{1}H NMR spectra is similar, with small differences in the chemical shifts to those previously reported, and is included for completeness.[11] The ^{13}C NMR and IR spectra are identical to those previously reported.

mp 82-83 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, *J* = 8.0 Hz), 7.38 (2H, d, *J* = 8.0 Hz), 7.33 (2H, d, *J* = 8.5 Hz), 7.26 (2H, d, *J* = 8.5 Hz), 4.11 (2H, s), 2.60 (3H, s), 2.48 (3H, s).

HRMS (ESI+) *m*/*z* calcd for $C_{15}H_{17}ClNO_2S$ $[M+H]^+$: 310.0663, found: 310.0664.

_N_-(3-Chloro-5-methylbenzyl)-_N_,4-dimethylbenzenesulfonamide (Table 3, entry 5).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 5-chloro-*m*-xylene (6.8 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow solid (3796 mg, 61% yield).

mp 94-96 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz), 7.11-7.03 (3H, m), 4.08 (2H, s), 2.62 (3H, s), 2.48 (3H, s), 2.33 (3H, s).

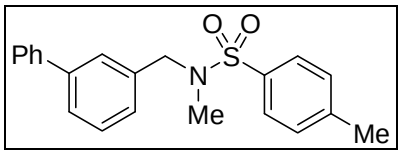
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.2, 137.6, 134.3, 134.2, 129.8, 128.7, 127.4, 127.2, 125.4, 53.6, 34.5, 21.5, 21.1.

IR (KBr) ν 2922, 2855, 1578, 1450, 1344, 1164, 1087, 934, 756 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{16}H_{19}ClNO_2S$ $[M+H]^+$: 324.0820, found: 324.0816.

[11] Sreedhar, B.; Reddy, P. S.; Reddy, M. A.; Neelima, B.; Arundhathi, R. *Tetrahedron Lett.* **2007**, *48*, 8174-8177.

N-(Biphenyl-3-ylmethyl)-N,4-dimethylbenzenesulfonamide (Table 3, entry 6).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 3-phenyltoluene (8.3 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as an off-white solid (498 mg, 71% yield).

mp 90-91 °C

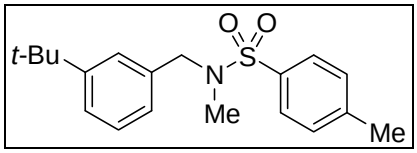
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (2H, d, *J* = 8.0 Hz), 7.60-7.52 (4H, m), 7.48-7.30 (7H, m), 4.23 (2H, s), 2.66 (3H, s), 2.48 (3H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.6, 140.6, 136.2, 134.4, 129.8, 129.1, 128.8, 127.52, 127.45, 127.3, 127.1, 127.0, 126.7, 54.2, 34.4, 21.5.

IR (KBr) ν 3064, 2855, 1596, 1455, 1362, 1340, 1303, 1118, 1162, 1087, 936, 742 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{21}H_{21}NO_2SNa$ $[M+Na]^+$: 374.1185, found: 374.1191.

N-(3-*tert*-Butylbenzyl)-N,4-dimethylbenzenesulfonamide (Table 3, entry 7).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 1-*tert*-butyl-3-methylbenzene (7.41 g, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow oil (440 mg, 66% yield).

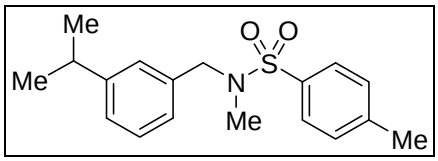
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J* = 8.0 Hz), 7.39-7.27 (5H, m), 7.14 (1H, d, *J* = 7.5 Hz), 4.16 (2H, s), 2.62 (3H, s), 2.48 (3H, s), 1.32 (9H, s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 143.4, 135.2, 134.3, 129.7, 128.3, 127.5, 125.5, 125.2, 124.8, 54.3, 34.6, 34.2, 31.3, 21.5.

IR (neat film) ν 2963, 2867, 1599, 1458, 1341, 1305, 1207, 1163, 1090, 939, 750 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{19}H_{25}NO_2SNa$ $[M+Na]^+$: 354.1498, found: 354.1499.

_N_,4-Dimethyl-_N_-[3-(propan-2-yl)benzyl]benzenesulfonamide (Table 3, entry 8).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using 3-*iso*-propyltoluene (7.8 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow solid (247 mg, 39% yield).

mp 73-75 °C

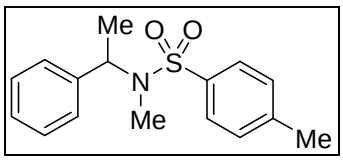
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz), 7.28-7.20 (4H, m), 4.11 (2H, s), 2.92 (1H, sept, *J* = 7.0 Hz), 2.60 (3H, s), 2.48 (3H, s), 1.26 (6H, d, *J* = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.3, 134.4, 132.9, 129.7, 128.4, 127.5, 126.6, 53.9, 34.3, 33.8, 23.9, 21.5.

IR (KBr) ν 2958, 2934, 1598, 1466, 1337, 1187, 1160, 1086, 980, 918, 725 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{18}H_{24}NO_2S$ $[M+H]^+$: 318.1522, found: 318.1534.

_N_,4-Dimethyl-_N_-(1-phenylethyl)benzenesulfonamide (Table 3, entry 9).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using ethylbenzene (6.1 mL, 50.0 mmol) and *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol). Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded the title compound as a light yellow solid (370 mg, 64% yield).

mp 69-70 °C (lit: 77-78 °C)[12]

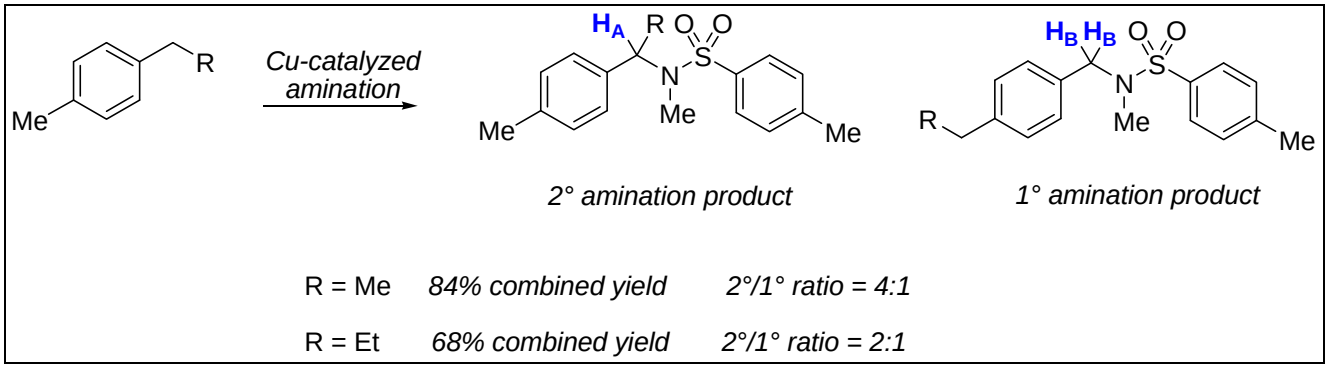
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J* = 8.0 Hz), 7.35-7.27 (7H, m), 5.31 (1H, q, *J* = 7.0 Hz), 2.60 (3H, s), 2.46 (3H, s), 1.31 (3H, d, *J* = 7.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 139.9, 137.2, 129.6, 128.3, 127.5, 127.2, 127.1, 54.7, 28.3, 21.5, 15.1.

IR (KBr) ν 2925, 1450, 1333, 1168, 1144, 1084, 921, 722, 654 cm^{-1}.

HRMS (ESI+) *m*/*z* calcd for $C_{16}H_{20}NO_2S$ $[M+H]^+$: 290.1209, found: 290.1205.

IIIf. Exploration of C–H amination selectivity between primary and secondary benzylic sites (Scheme 1).



The general procedure for the copper-catalyzed amination was employed (2.0 mmol scale), using either 4-ethyltoluene (6.98 mL, 50.0 mmol) or 4-*n*-propyltoluene (7.81 mL, 50.0 mmol) with *N*-methyl-4-toluenesulfonamide (370 mg, 2.0 mmol).

4-Ethyltoluene: Analysis of the unpurified reaction mixture by ^{1}H NMR spectroscopy revealed a 4:1 ratio of 2°/1° amination products (2° amination product: H_A = 5.27 ppm, q, 1H versus 1° amination product: H_B = 4.11 ppm, s, 2H).

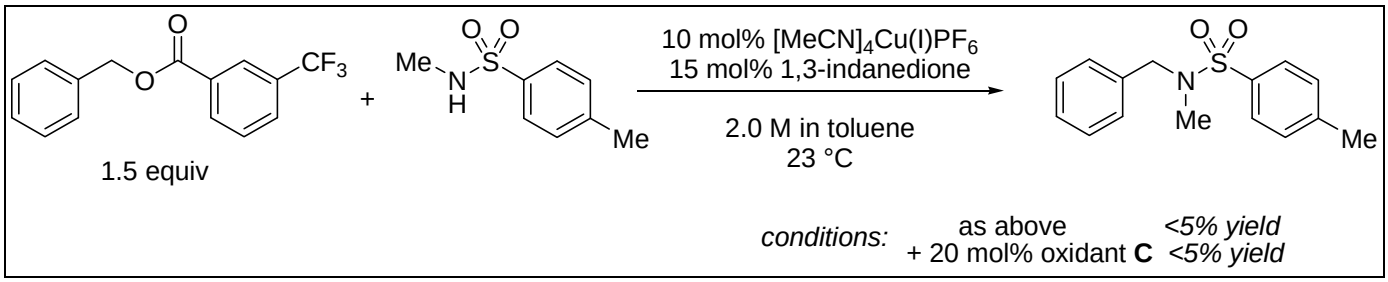
Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded a 4:1 mixture of the above regioisomeric products as a light yellow oil which could not readily be separated by column chromatography (509 mg, 84% combined yield).

[12] Catt, J. D.; Matier, W. L. *J. Org. Chem.* **1974**, *39*, 566-568.

4-*n*-Propyltoluene: Analysis of the unpurified reaction mixture by ^{1}H NMR spectroscopy revealed a 2:1 ratio of 2°/1° amination products (2° amination product: H_A = 5.00 ppm, t, 1H versus 1° amination product: H_B = 4.11 ppm, s, 2H).

Purification by column chromatography through silica gel using a gradient of 100% hexanes to 10% ethyl acetate in hexanes afforded a 2:1 mixture of the above regioisomeric products as a light yellow oil which could not readily be separated by column chromatography (431 mg, 68% combined yield).

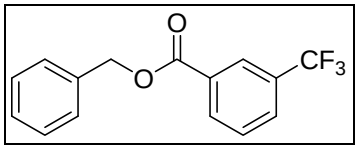
IIIg. Reaction of benzyl 3-(trifluoromethyl)benzoate with *N*-methyl 4-toluenesulfonamide (Scheme 2).



Into a 5 mL vial equipped with a magnetic stir bar was weighted $[MeCN]_4CuPF_6$ (37 mg, 0.1 mmol), 1,3-indanedione (22 mg, 0.15 mmol) and *N*-methyl-4-toluenesulfonamide (185 mg, 1.0 mmol). The mixture was diluted with toluene (0.5 mL, 2.0 M) and stirred at room temperature for 5 minutes. To the mixture was added benzyl 3-(trifluoromethyl)benzoate (420 mg, 1.5 mmol). The vial was placed under an atmosphere of nitrogen and fitted with a teflon coated cap and the mixture was stirred at room temperature for 3 days. The resulting mixture was concentrated under reduced pressure and treated with 1.0 mL of a 0.33 M solution of internal standard (1,3,5-trimethoxybenzene) in $CDCl_3$. The reaction was further diluted with $CDCl_3$ (3 mL) and filtered through a 25 mm syringe filter equipped with a 1 μM glass fiber membrane to remove the copper residues. An aliquot of the filtered solution was analyzed by ^{1}H NMR analysis. Integration of the product peaks at 4.2 ppm (2H, s) was compared to the internal standard peaks at 6.1 ppm (1H, s, calibrated to 100%) and 3.8 ppm (3H, s). Less than 5% of the amination product was detected by ^{1}H NMR analysis of the unpurified reaction mixture, with the majority of the reaction mixture consisting of unreacted starting materials.

A similar reaction in the presence of 20 mol% 3-$CF_3C_6H_4CO_3$*t*-Bu oxidant (52 mg, 0.2 mmol) also afforded <5% of the amination product as determined by ^{1}H NMR analysis versus an internal standard.

Preparation of benzyl 3-(trifluoromethyl)benzoate.



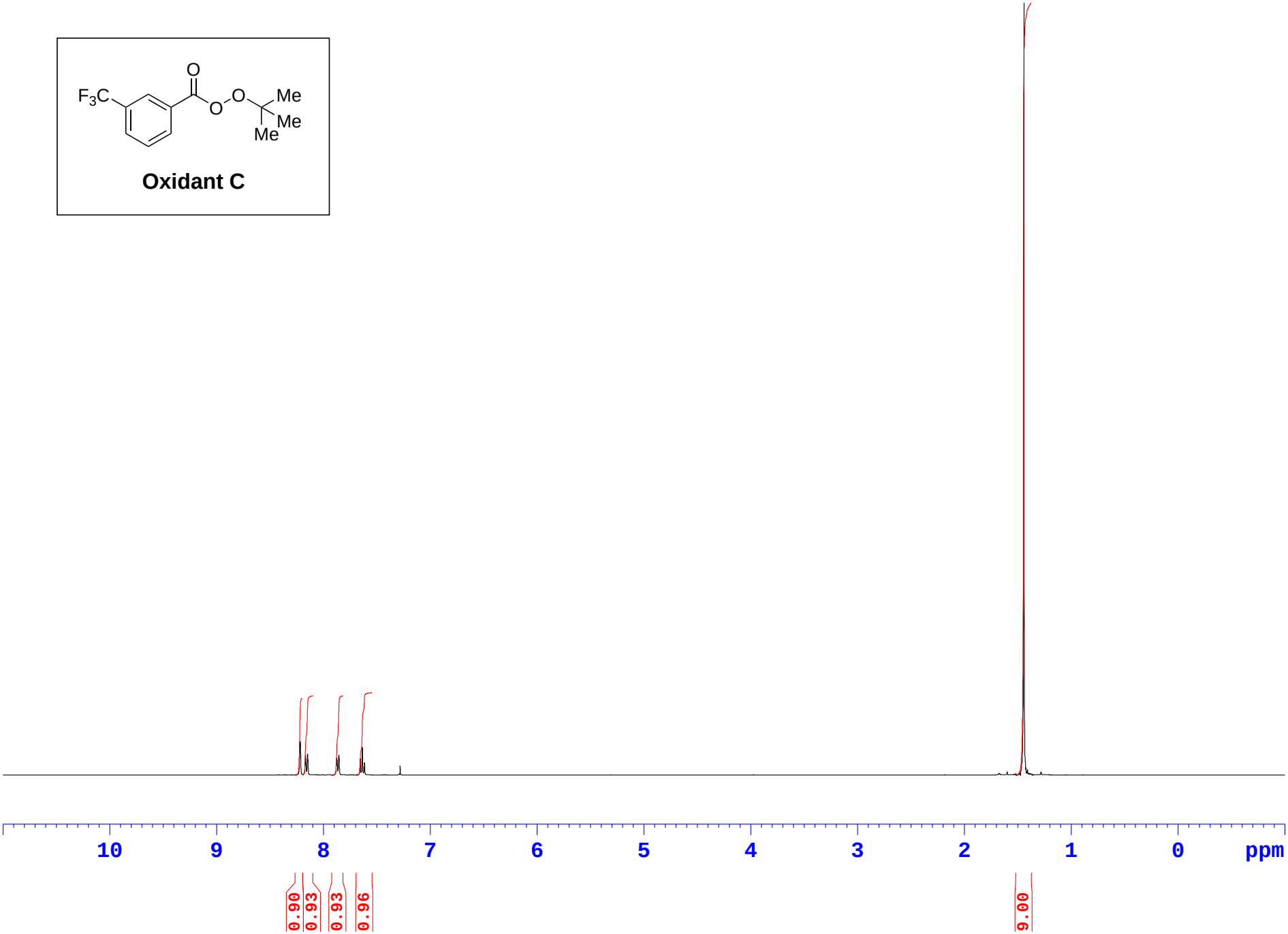
Into a 250 mL flame-dried round-bottom flask equipped with a magnetic stir bar and under a nitrogen atmosphere was added benzyl alcohol (4.8 mL, 46.2 mmol, 1.0 equiv), pyridine (5.6 mL, 69.3 mmol, 1.5 equiv) and CH_2Cl_2 (200 mL). The solution was treated with 3-trifluoromethylbenzoyl chloride (7.7 mL, 50.8 mmol, 1.1 equiv) and the resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched with 1 M HCl aqueous solution (200 mL), poured into a 500 mL separatory funnel and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated to an oil. Purification by column chromatography through silica gel, eluting with 100% hexanes to 10% EtOAc in hexanes as a gradient afforded the title compound as a clear liquid (7.97 g, 62% yield).

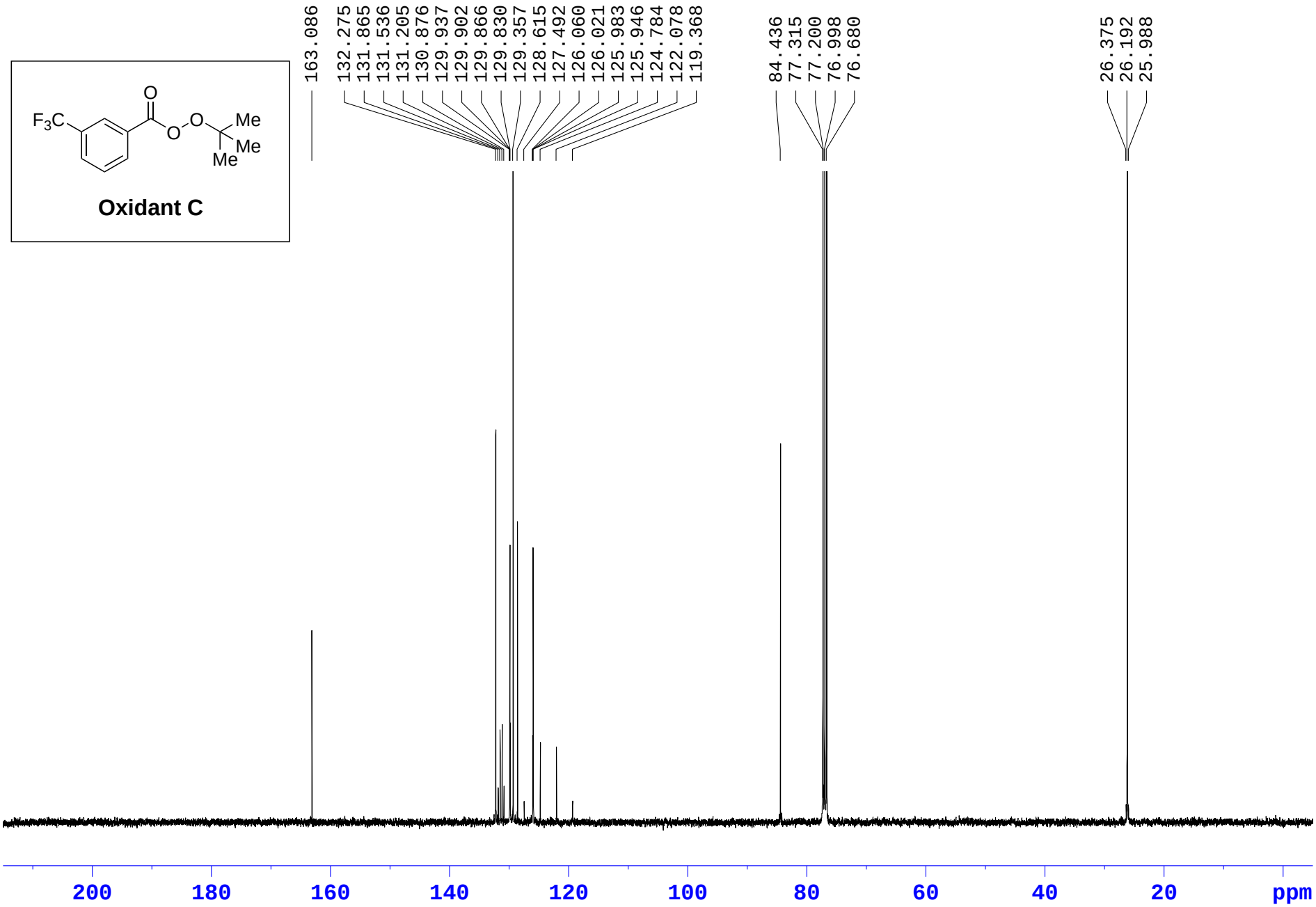
^{1}H and ^{13}C NMR were identical to those previously reported.[13]

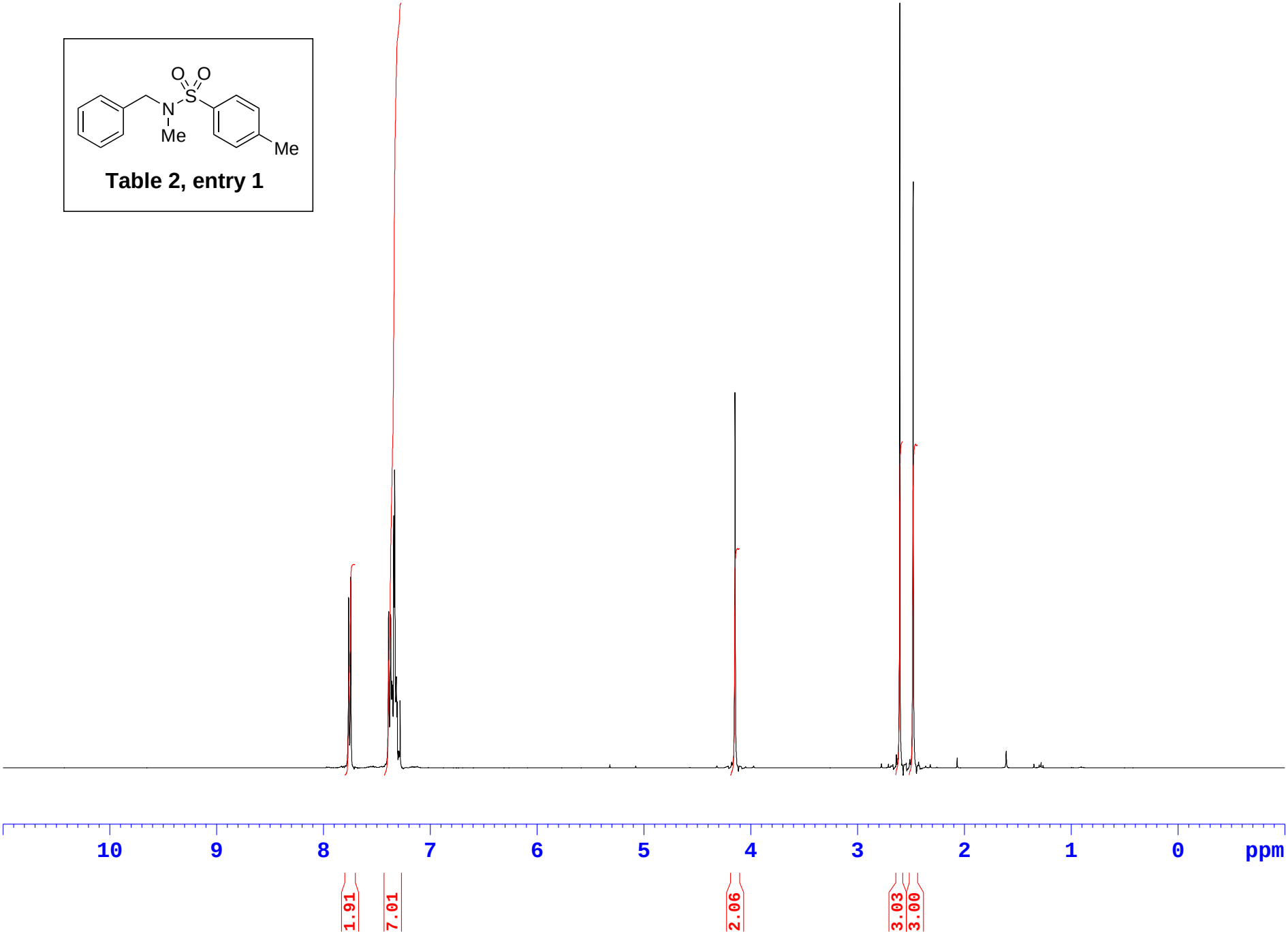
[13] Tummatorn, J.; Albiniak, P. A.; Dudley, G. B. *J. Org. Chem.* **2007**, *72*, 8962-8964.

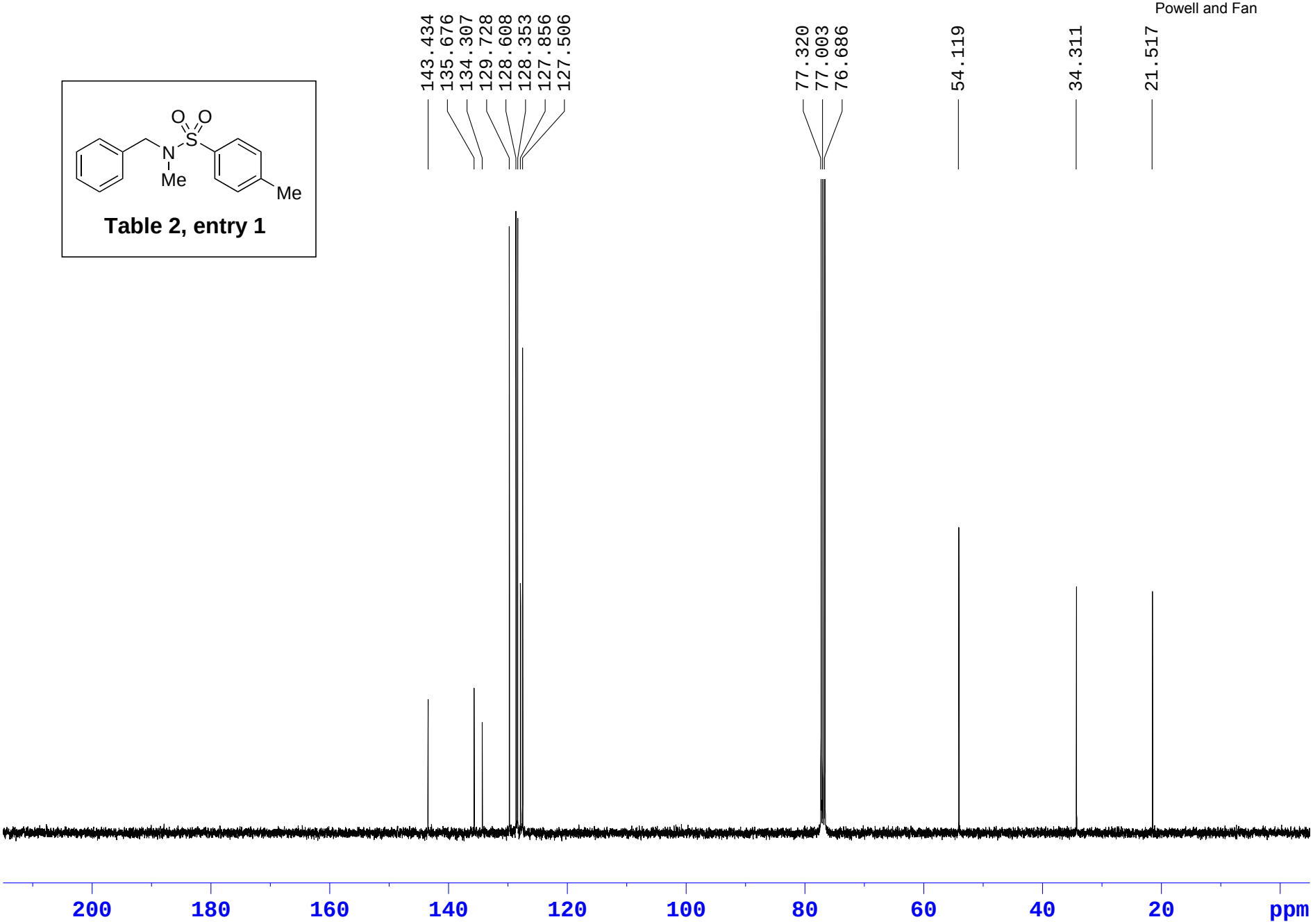
IV. ^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds

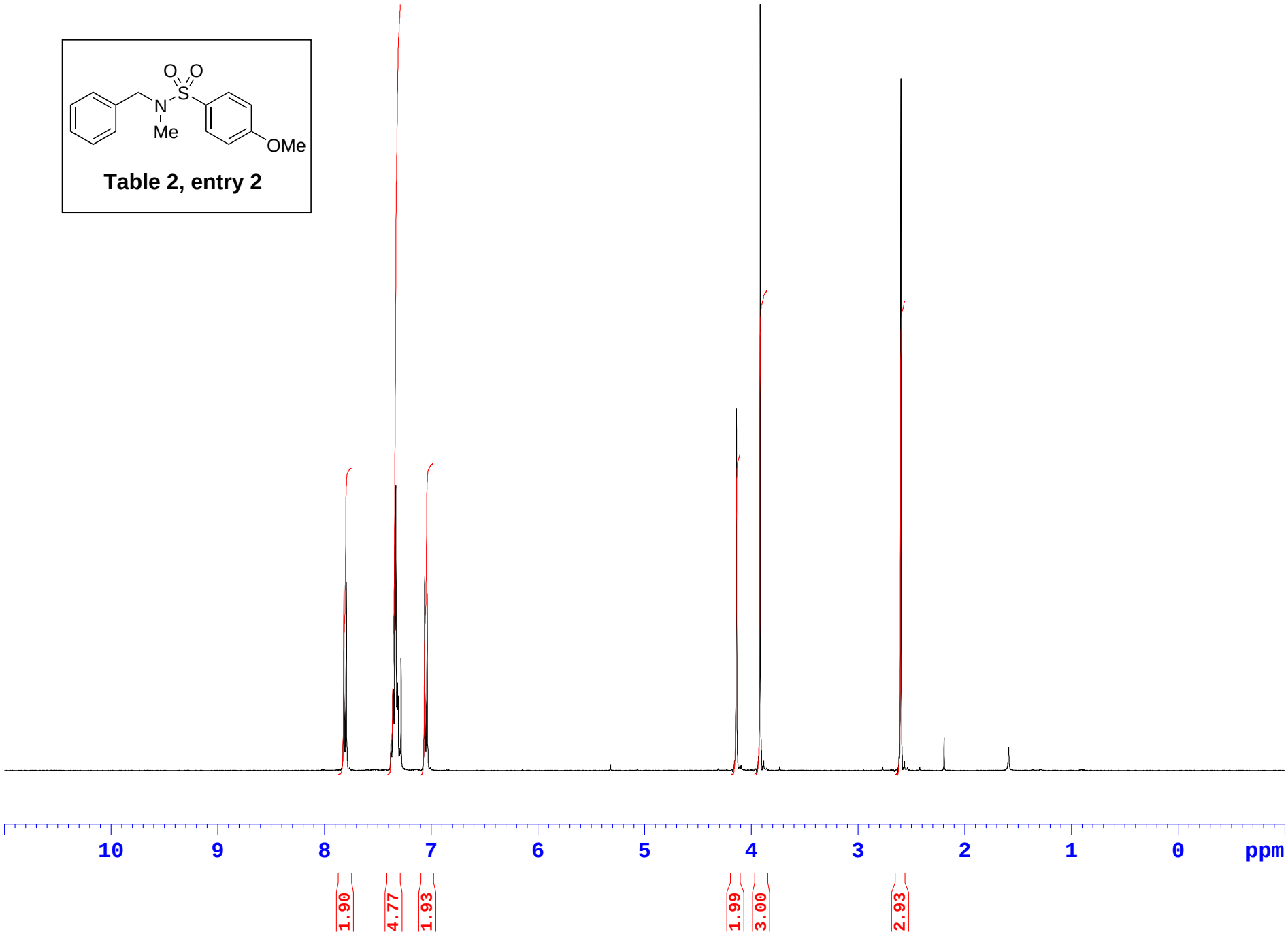
Oxidant C

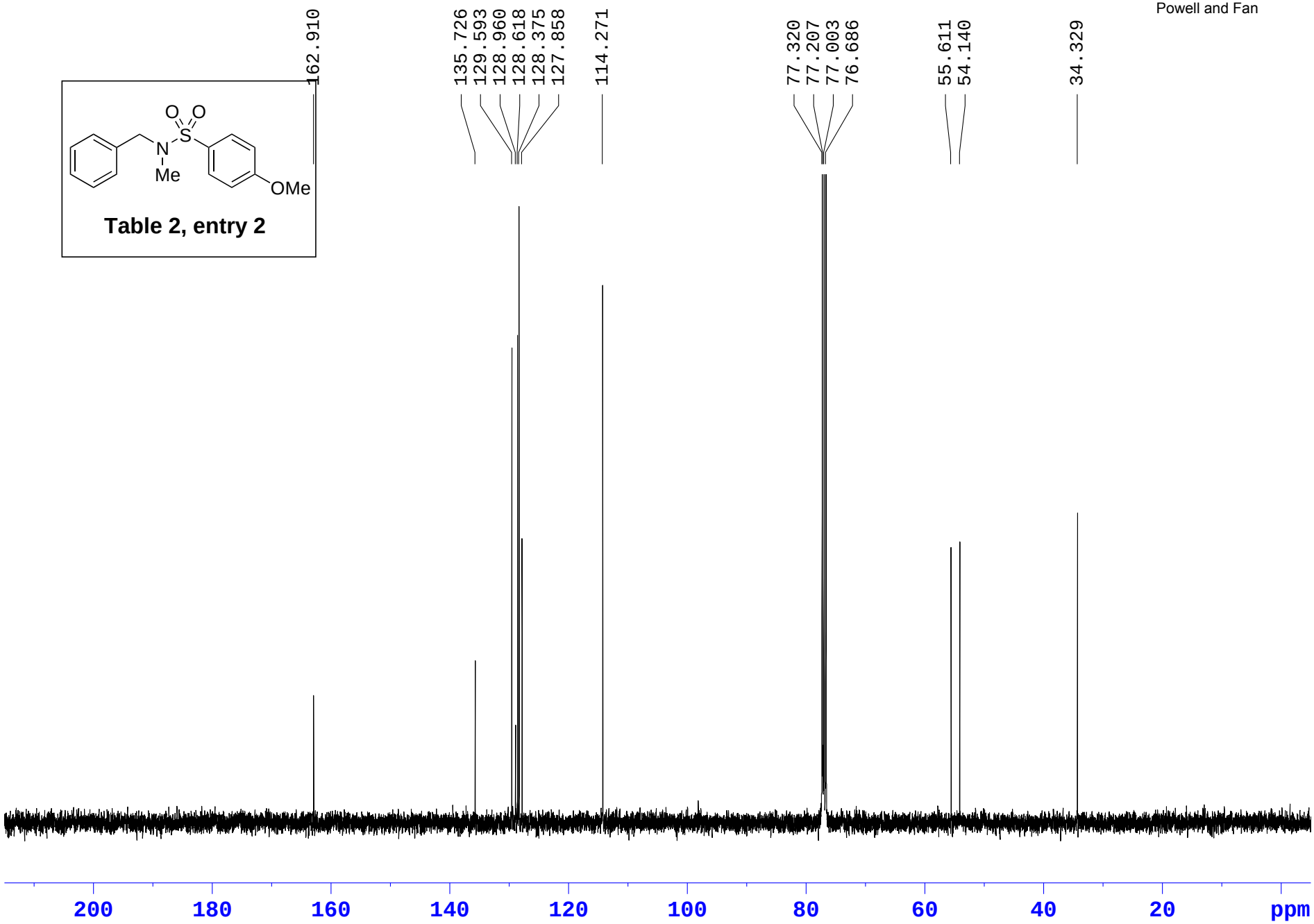


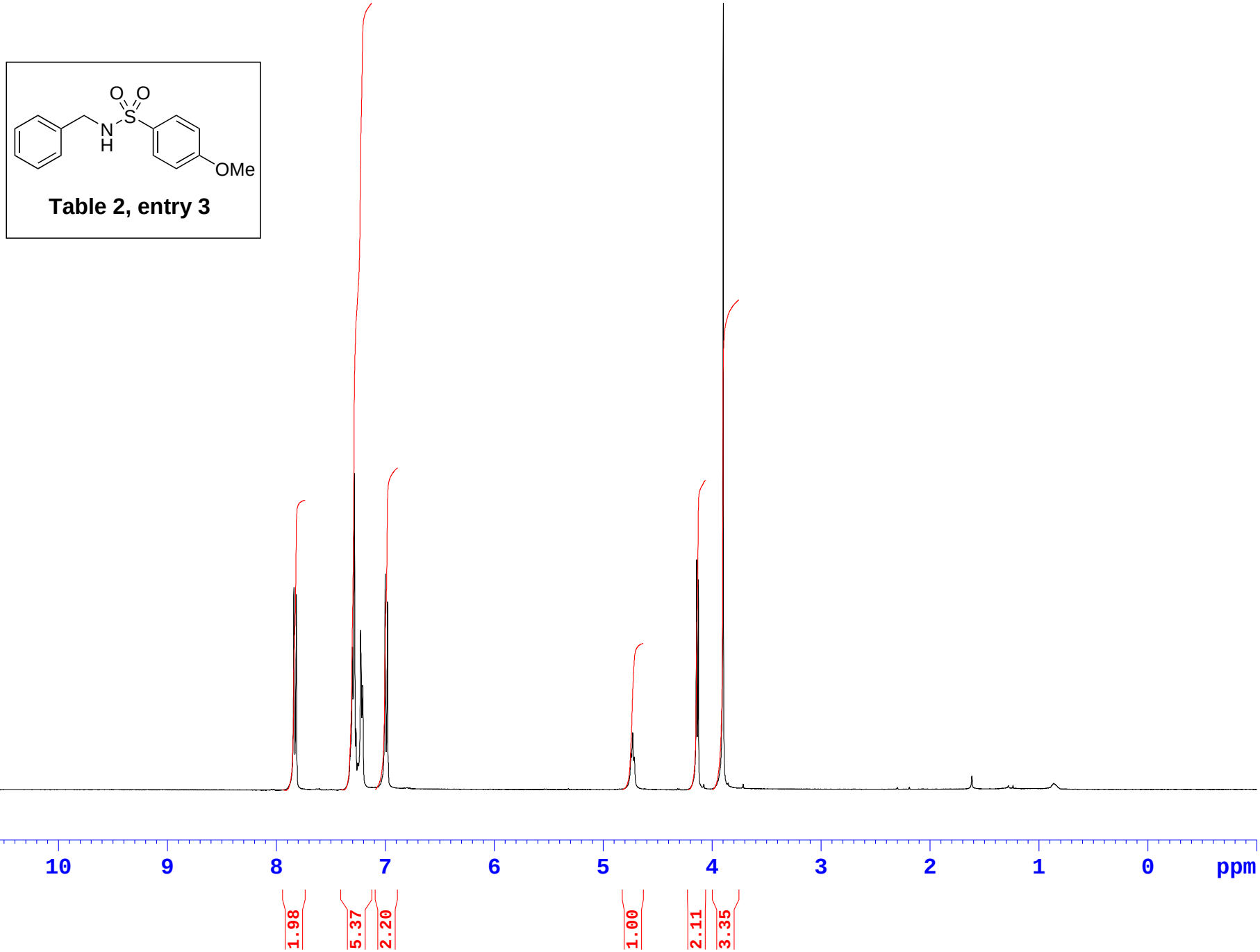

163.086
132.275
131.865
131.536
131.205
130.876
129.937
129.902
129.866
129.830
129.357
128.615
127.492
126.060
126.021
125.983
125.946
124.784
122.078
119.368
84.436
77.315
77.200
76.998
76.680
26.375
26.192
25.988
F3C
O
O
O
Me
Me
Me
Oxidant C
200
180
160
140
120
100
80
60
40
20
ppm


O O
S
N
Me
Me
Table 2, entry 1
10
9
8
7
6
5
4
3
2
1
0
ppm
1.91
7.01
2.06
3.03
3.00


143.434
135.676
134.307
129.728
128.608
128.353
127.856
127.506
77.320
77.003
76.686
54.119
34.311
21.517
O
O
S
N
Me
Me
Table 2, entry 1
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
OMe
Table 2, entry 2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.90
4.77
1.93
1.99
3.00
2.93


162.910
135.726
129.593
128.960
128.618
128.375
127.858
114.271
77.320
77.207
77.003
76.686
55.611
54.140
34.329
O
O
S
N
Me
OMe
Table 2, entry 2
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
H
OMe
Table 2, entry 3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
5.37
2.20
1.00
2.11
3.35

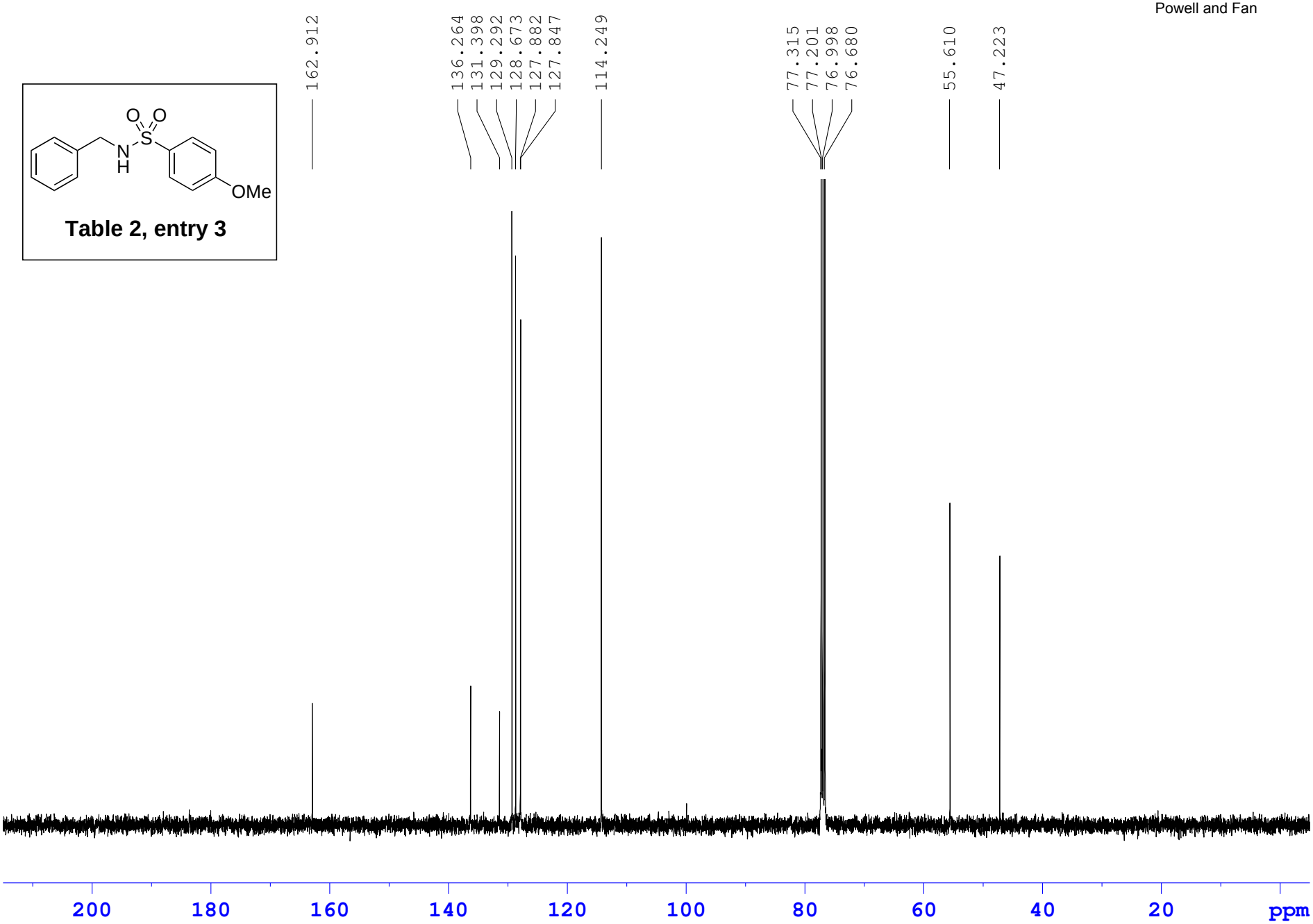
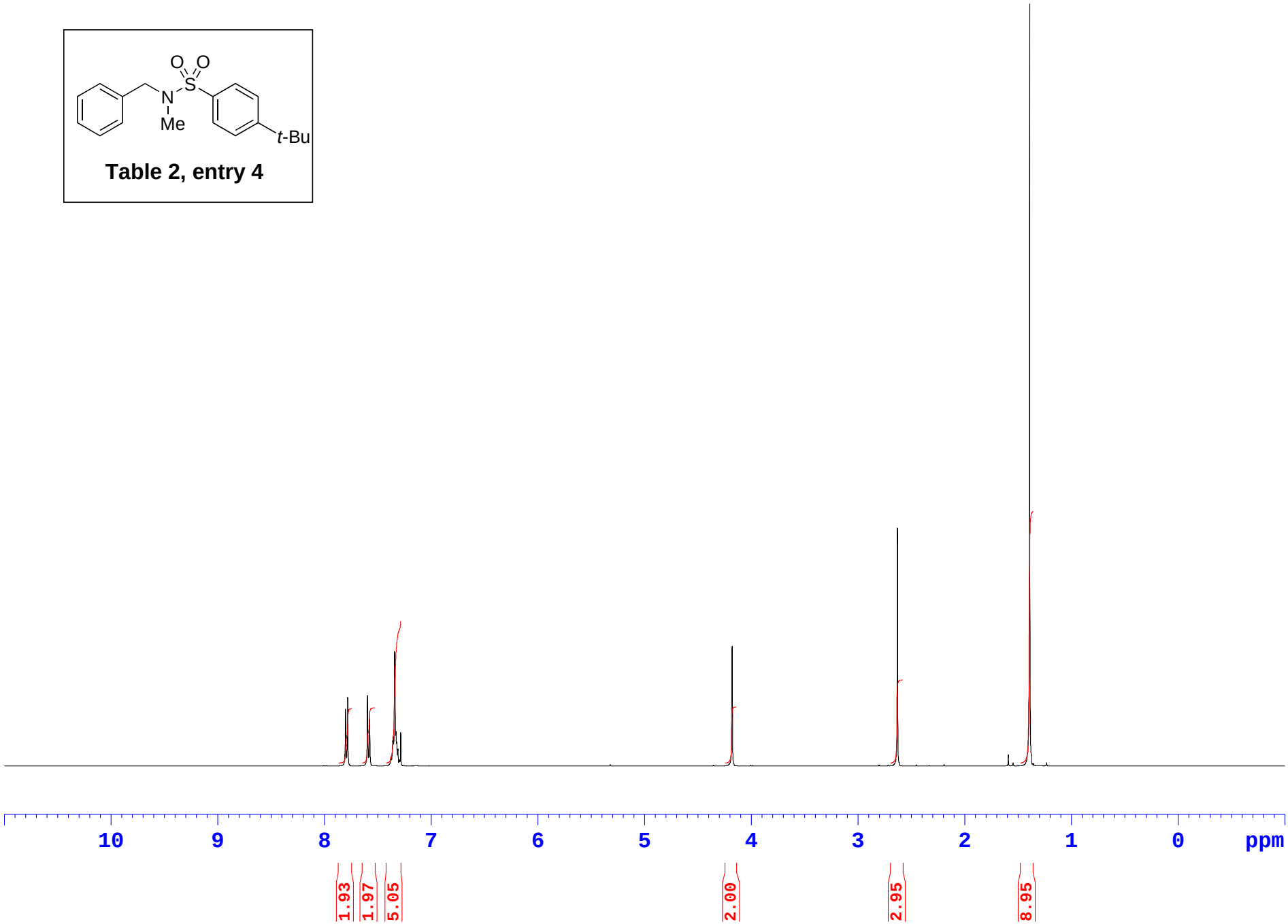
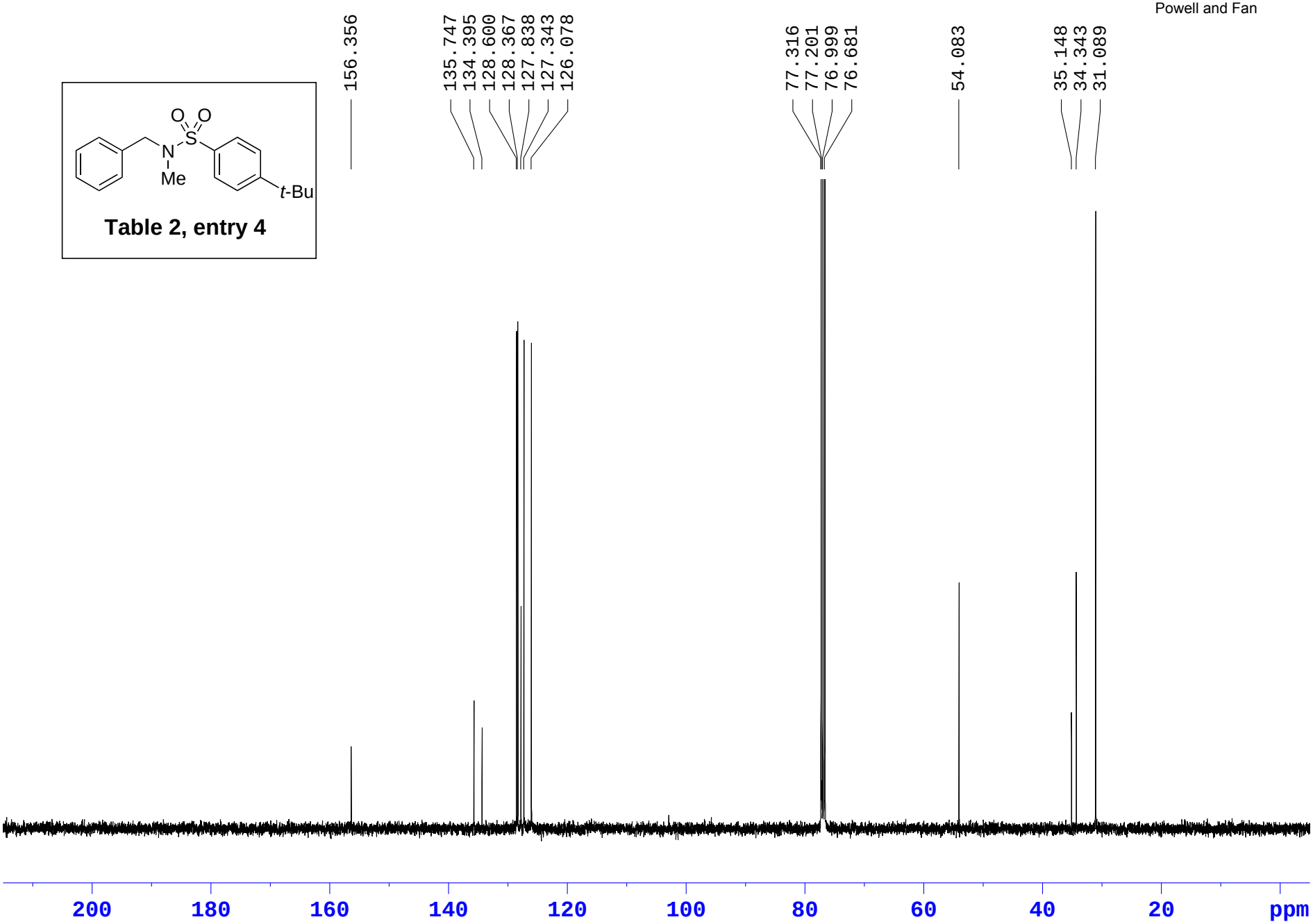

162.912
136.264
131.398
129.292
128.673
127.882
127.847
114.249
77.315
77.201
76.998
76.680
55.610
47.223
O
O
S
N
H
OMe
Table 2, entry 3
200
180
160
140
120
100
80
60
40
20
ppm

Table 2, entry 4




156.356
135.747
134.395
128.600
128.367
127.838
127.343
126.078
77.316
77.201
76.999
76.681
54.083
35.148
34.343
31.089
O
O
S
N
Me
t-Bu
Table 2, entry 4
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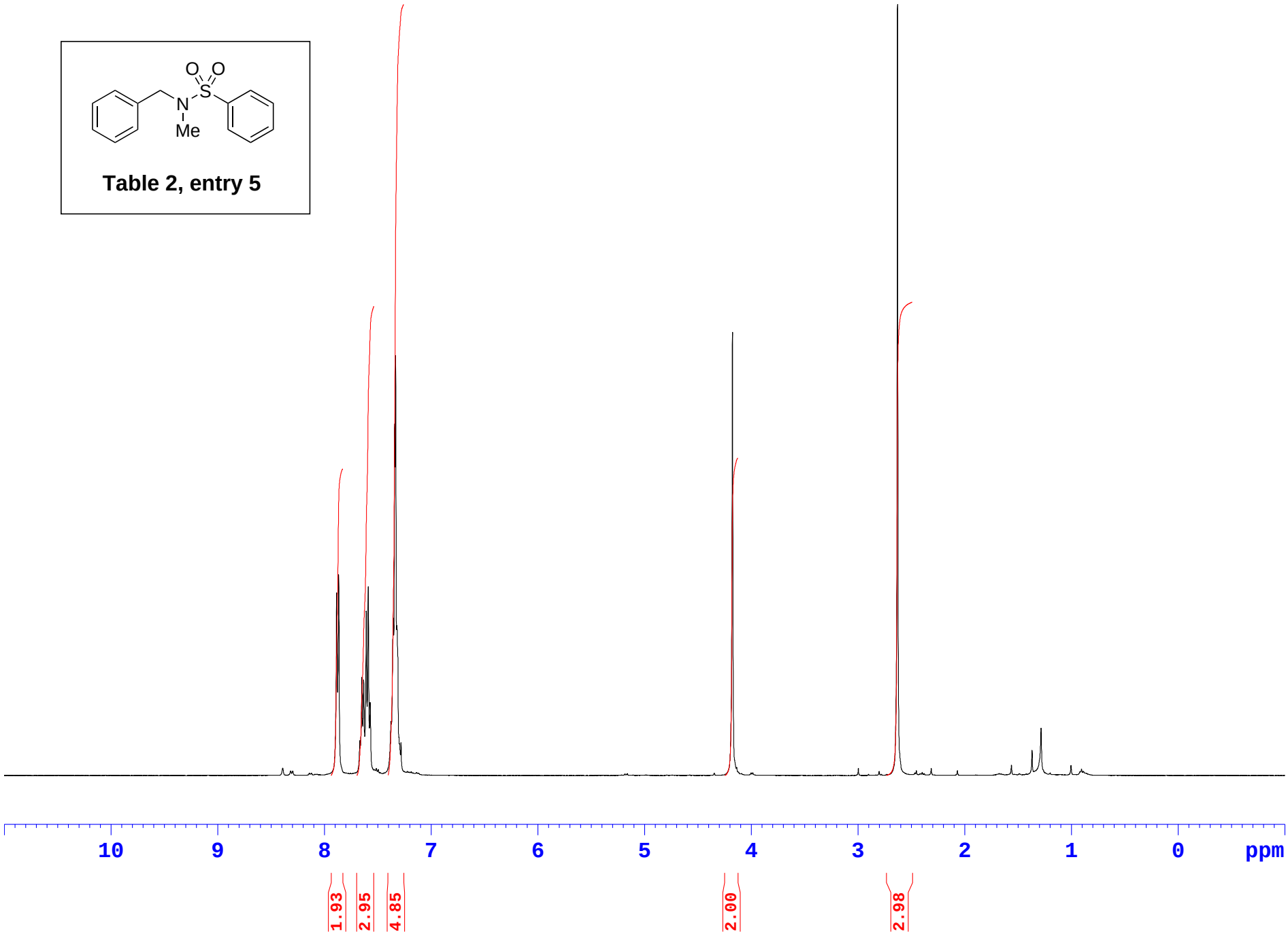
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
Table 2, entry 5
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
2.95
4.85
2.00
2.98

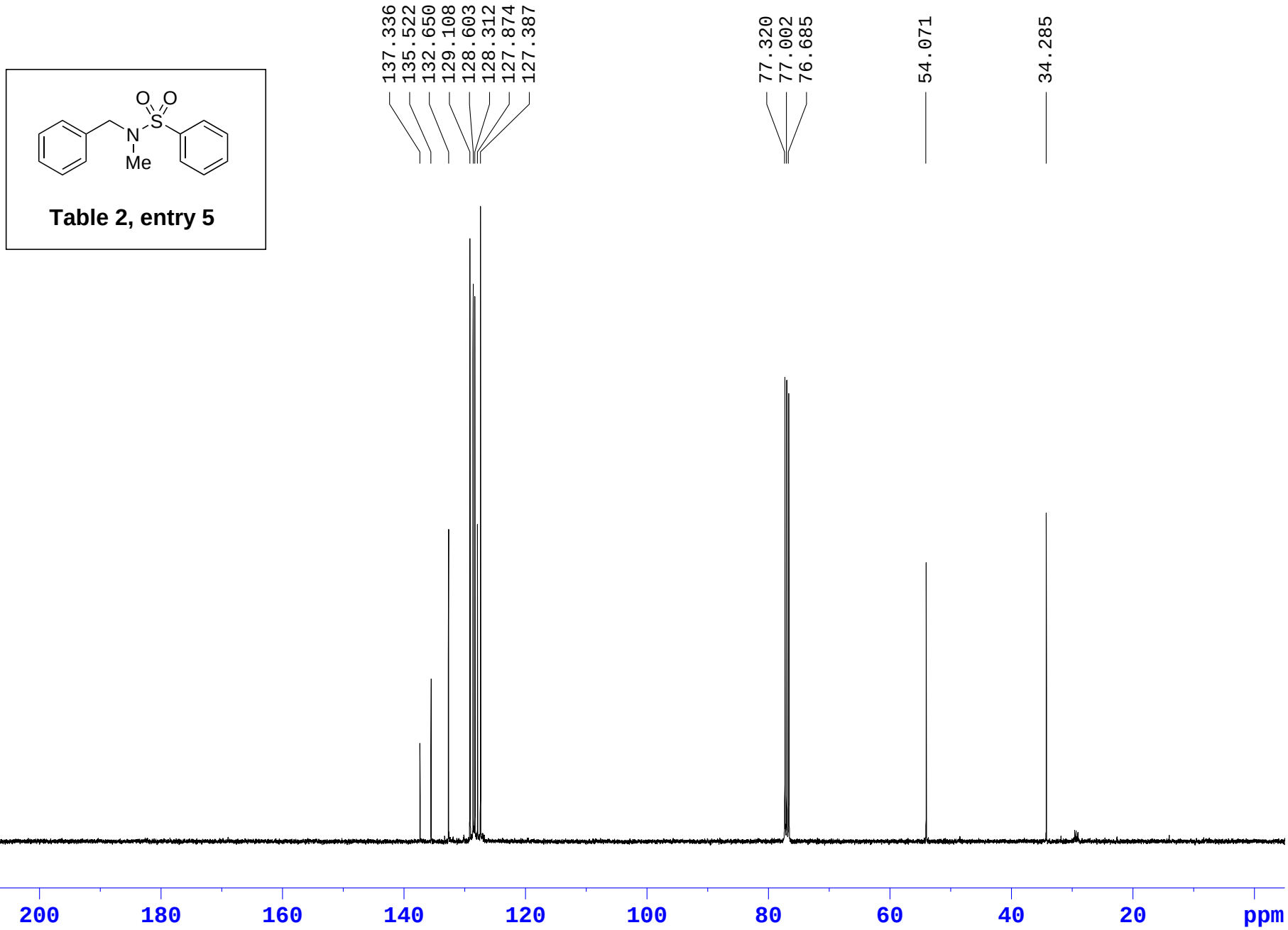
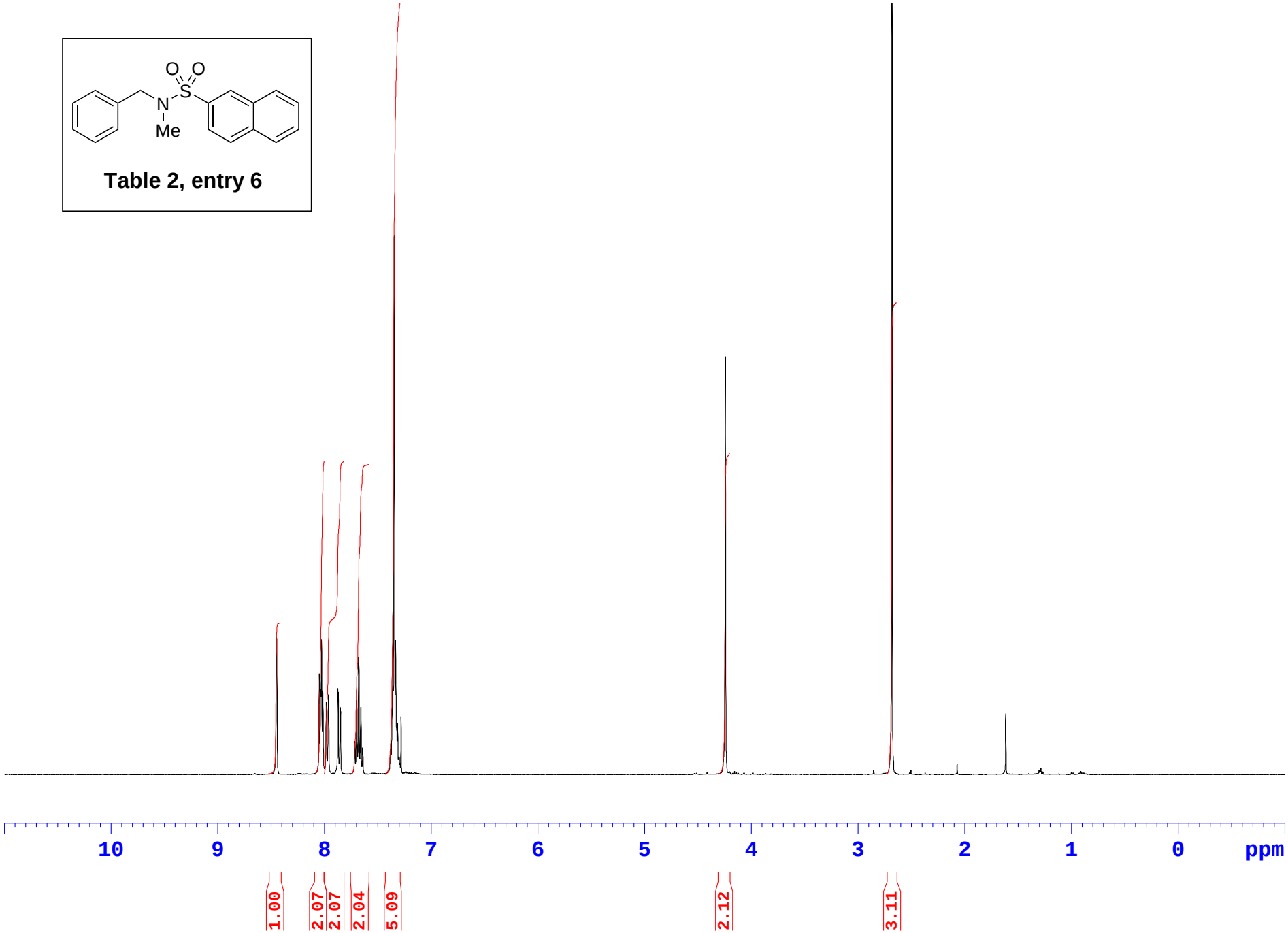


Table 2, entry 5


O O
S
N
Me
Table 2, entry 6
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
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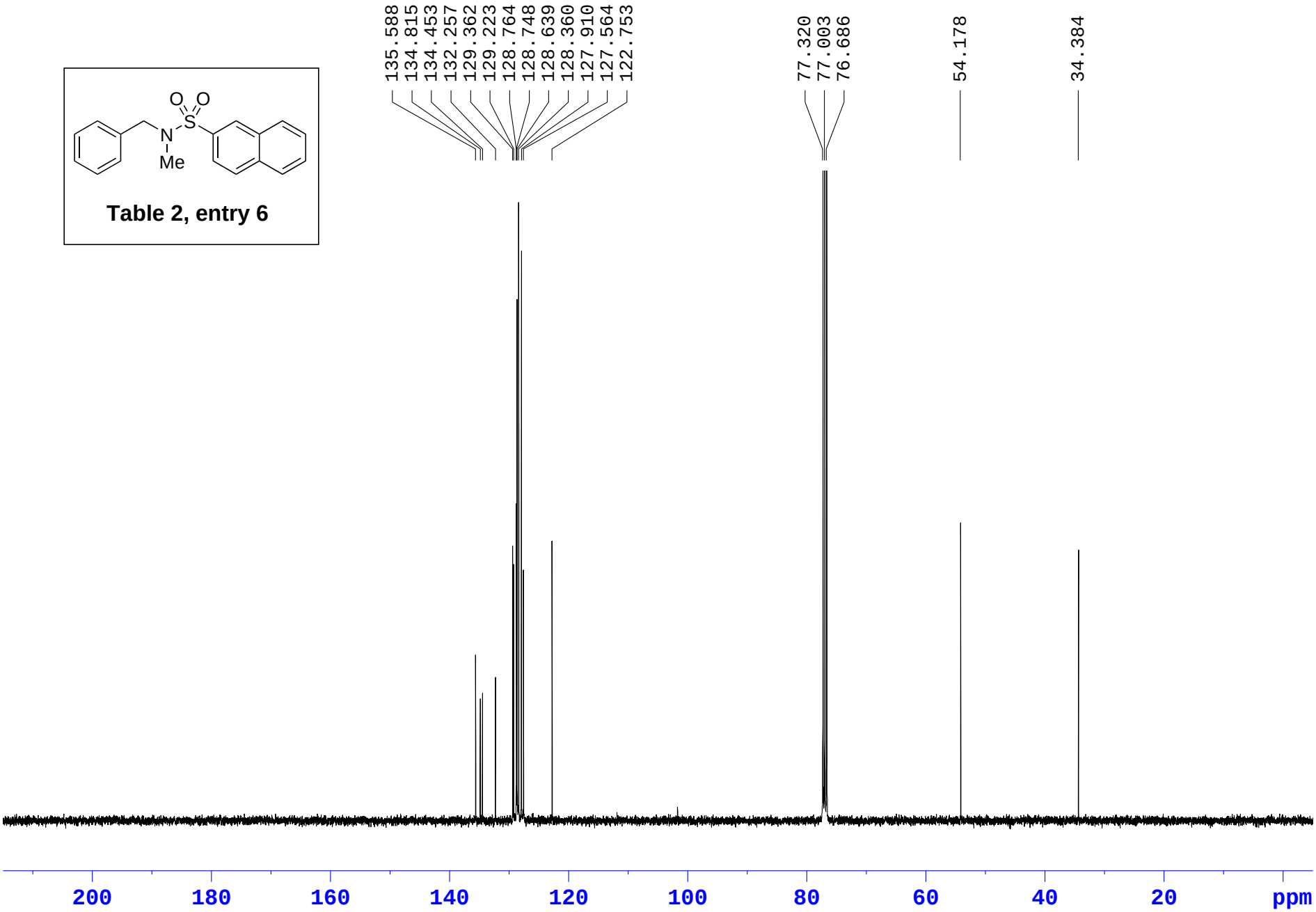
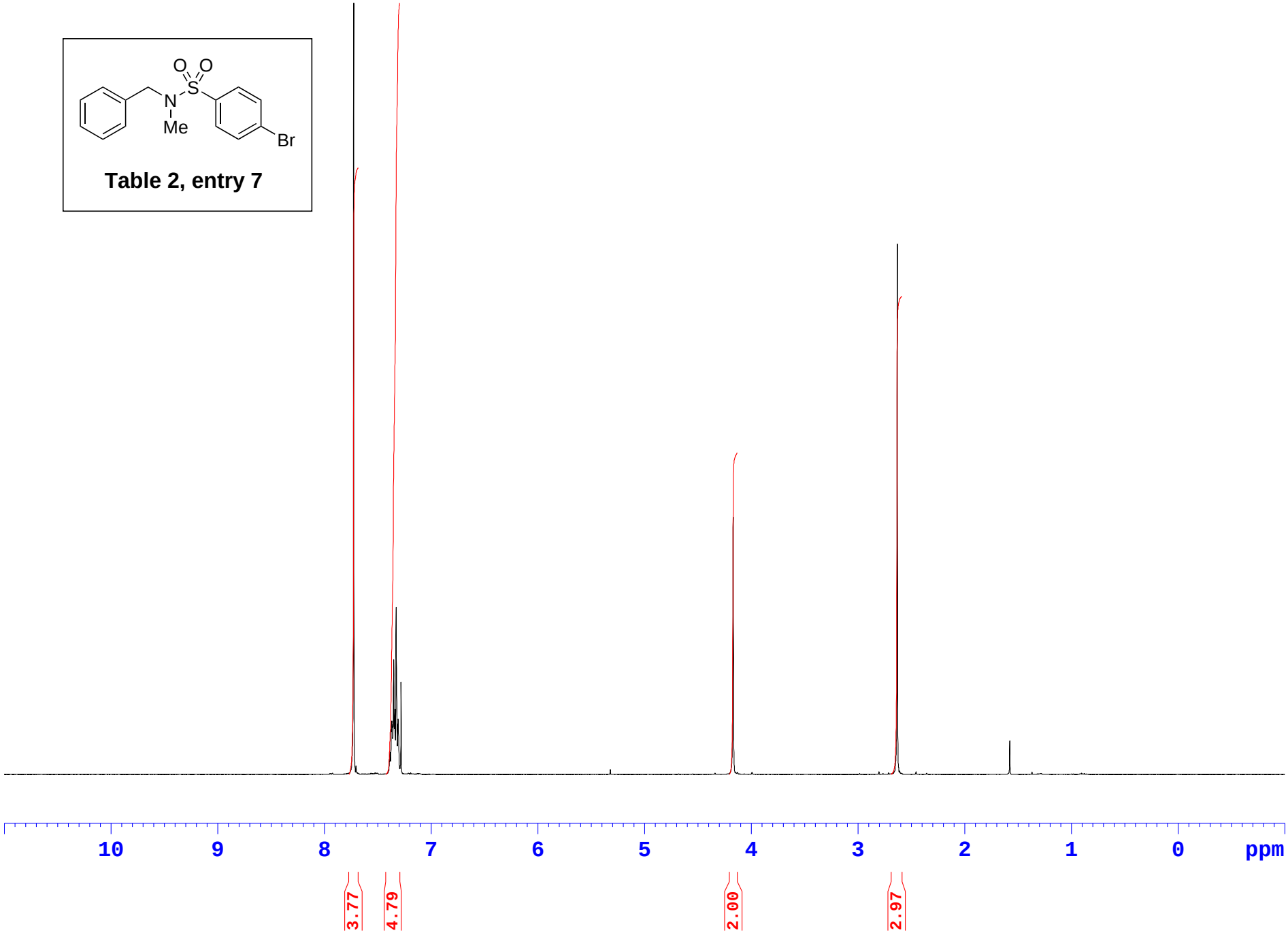
2.07
2.04
5.09
2.12
3.11


135.588
134.815
134.453
132.257
129.362
129.223
128.764
128.748
128.639
128.360
127.910
127.564
122.753
77.320
77.003
76.686
54.178
34.384
O
O
S
N
Me
Table 2, entry 6
200
180
160
140
120
100
80
60
40
20
ppm


O O
S
N
Me
Br
Table 2, entry 7
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8
7
6
5
4
3
2
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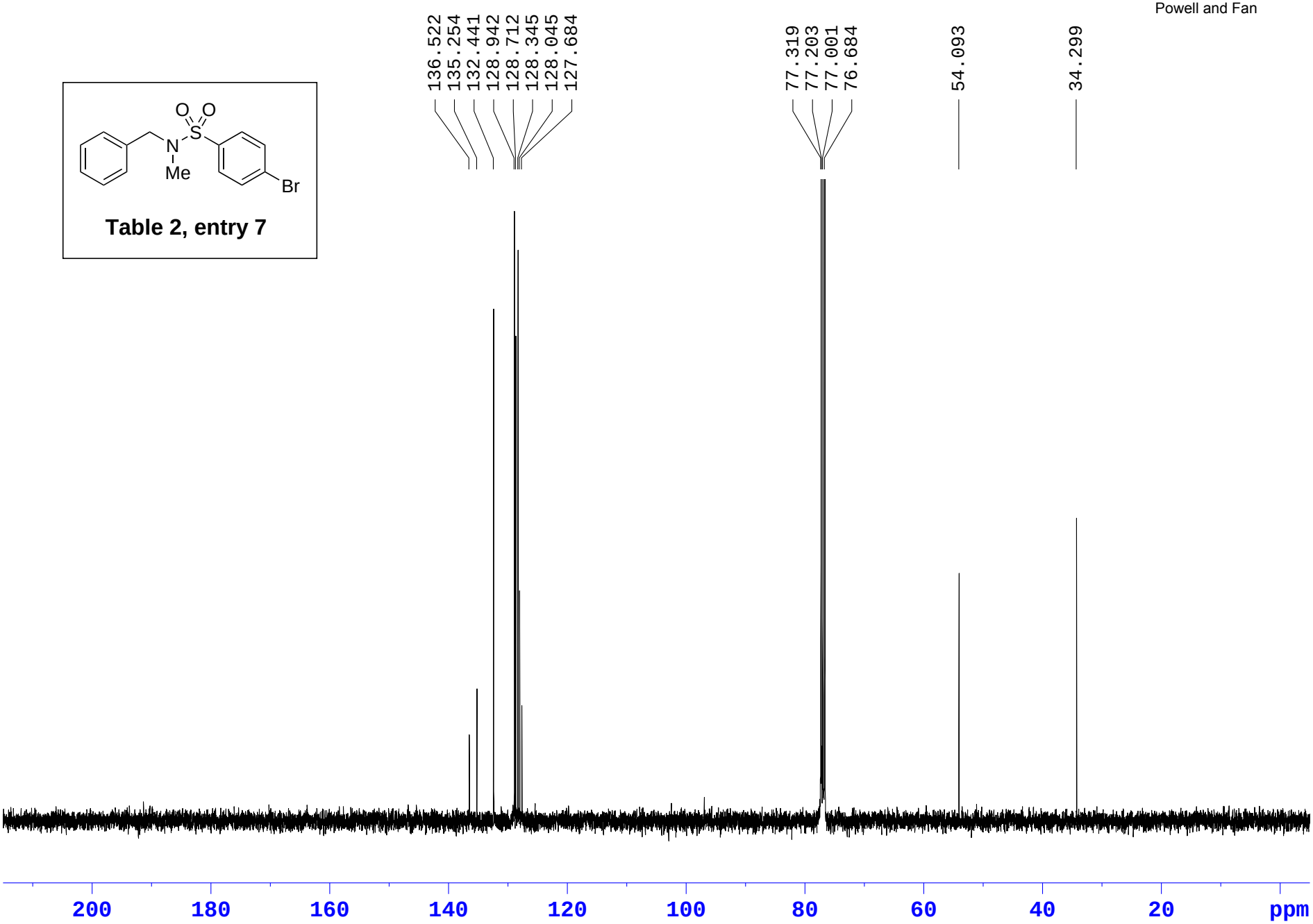
2.97


136.522
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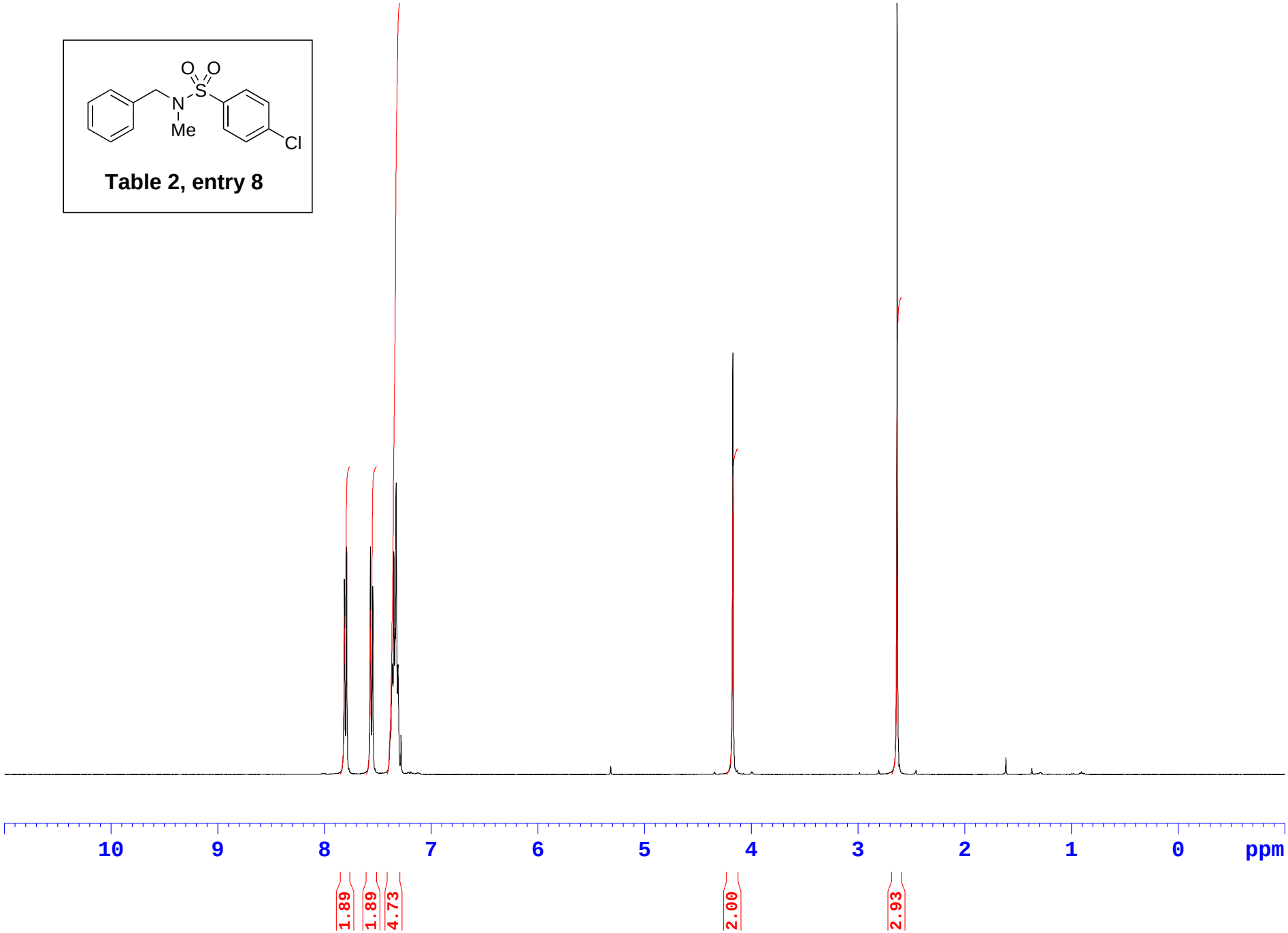
132.441
128.942
128.712
128.345
128.045
127.684
77.319
77.203
77.001
76.684
54.093
34.299
O
O
S
N
Me
Br
Table 2, entry 7
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
Cl
Table 2, entry 8
10
9
8
7
6
5
4
3
2
1
0
ppm
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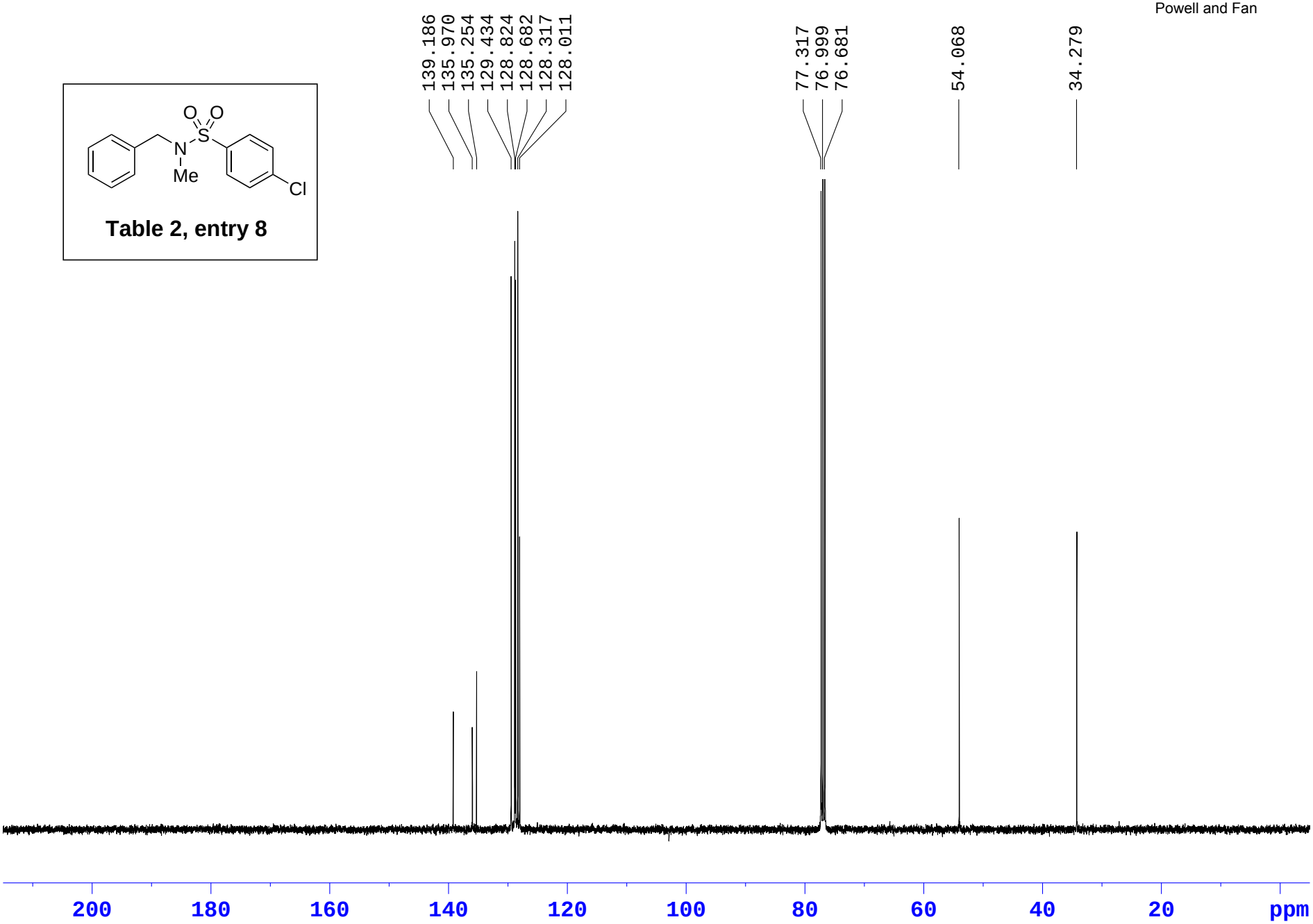
1.89
4.73
2.00
2.93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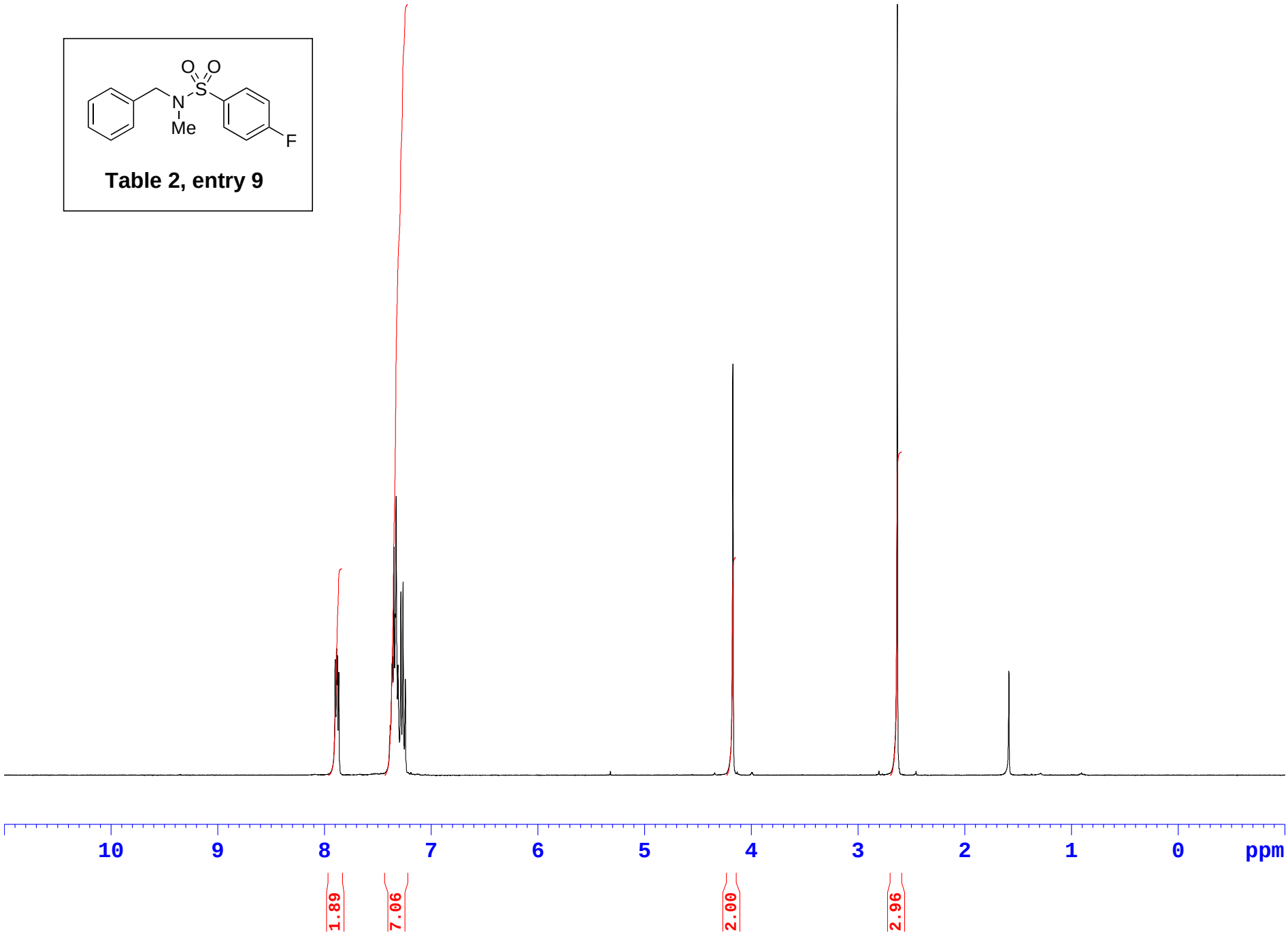
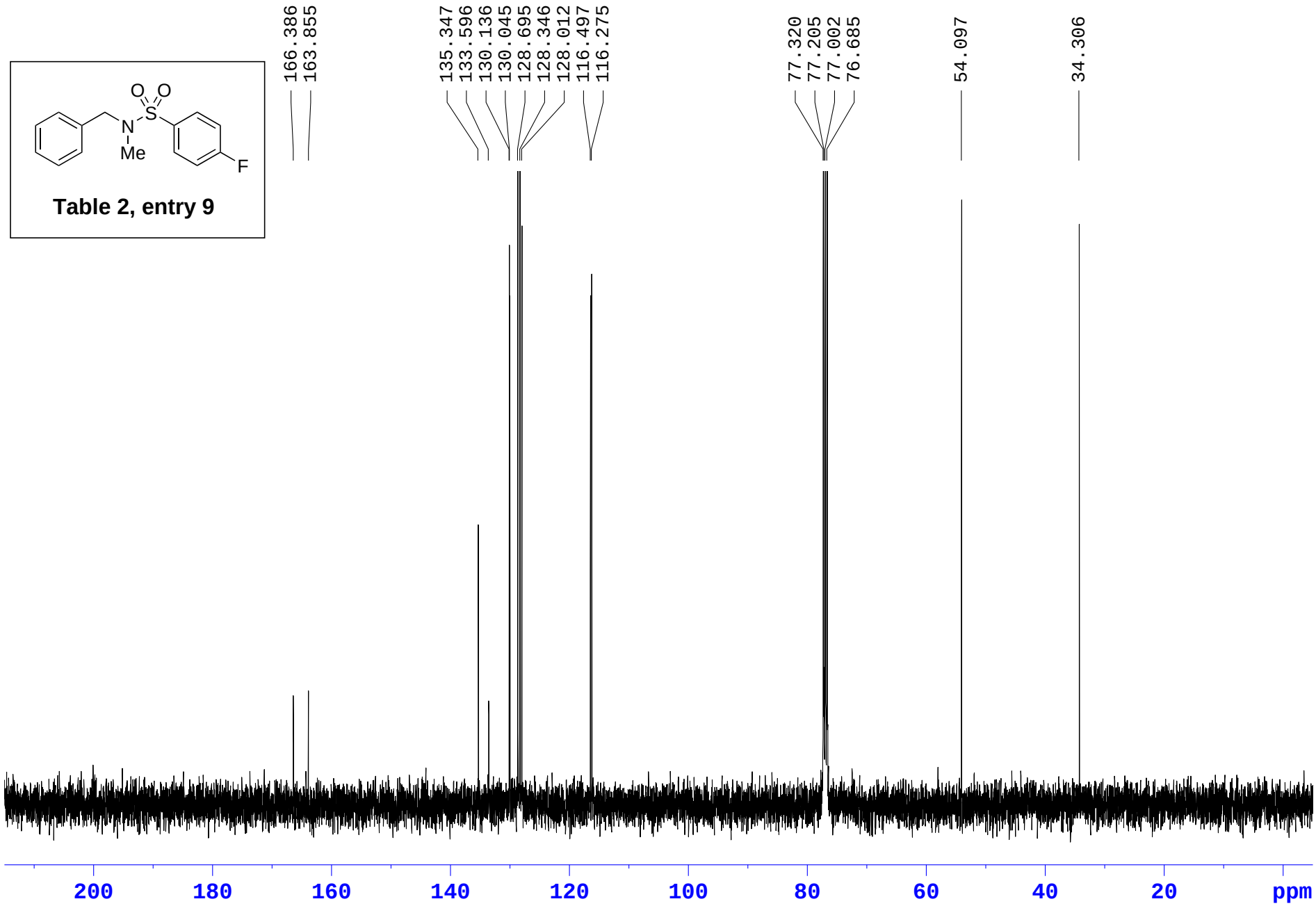
129.434
128.824
128.682
128.317
128.011
77.317
76.999
76.681
54.068
34.279
O
O
S
N
Me
Cl
Table 2, entry 8
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
F
Table 2, entry 9
10
9
8
7
6
5
4
3
2
1
0
ppm
1.89
7.06
2.00
2.96


166.386
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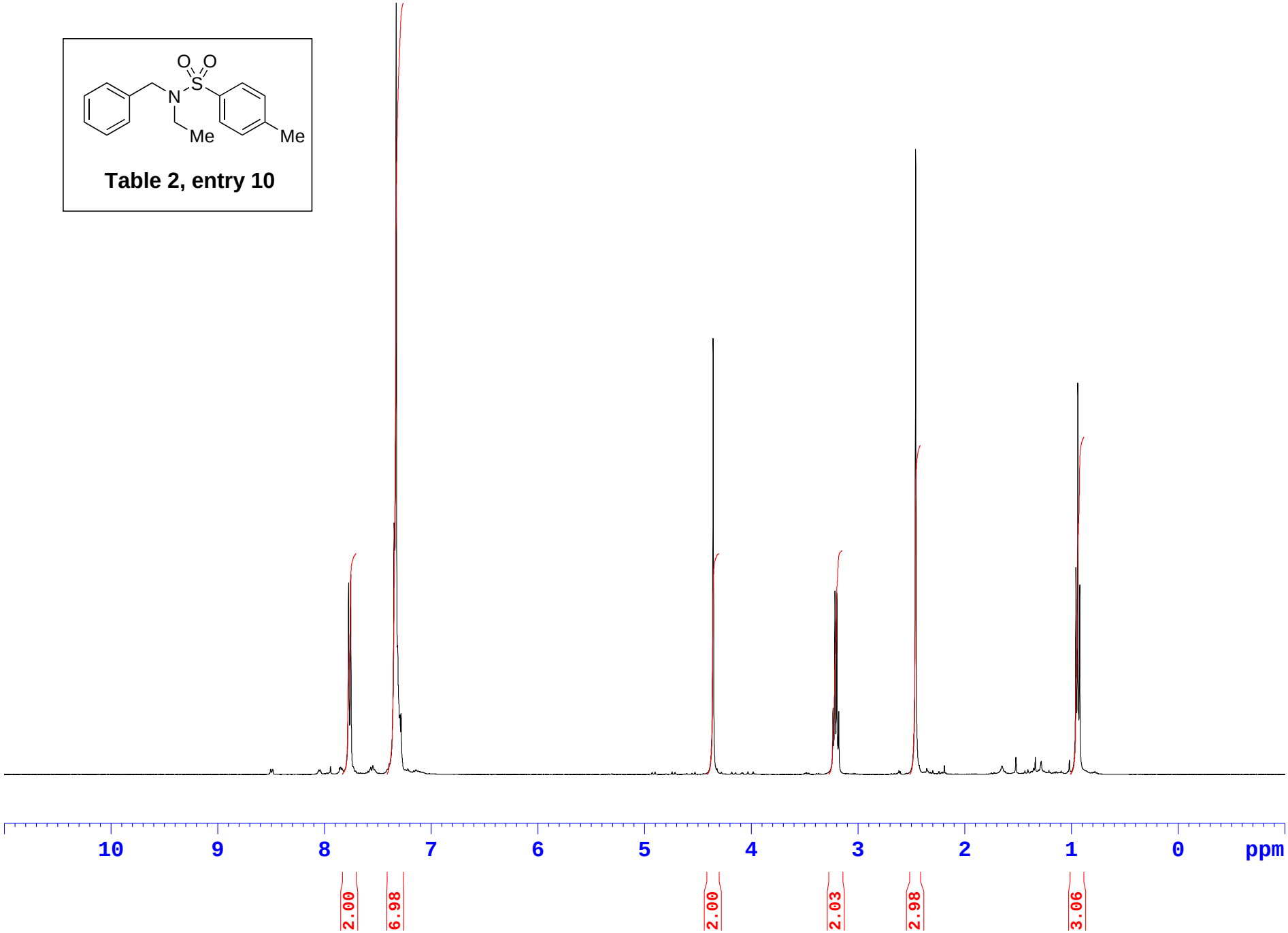
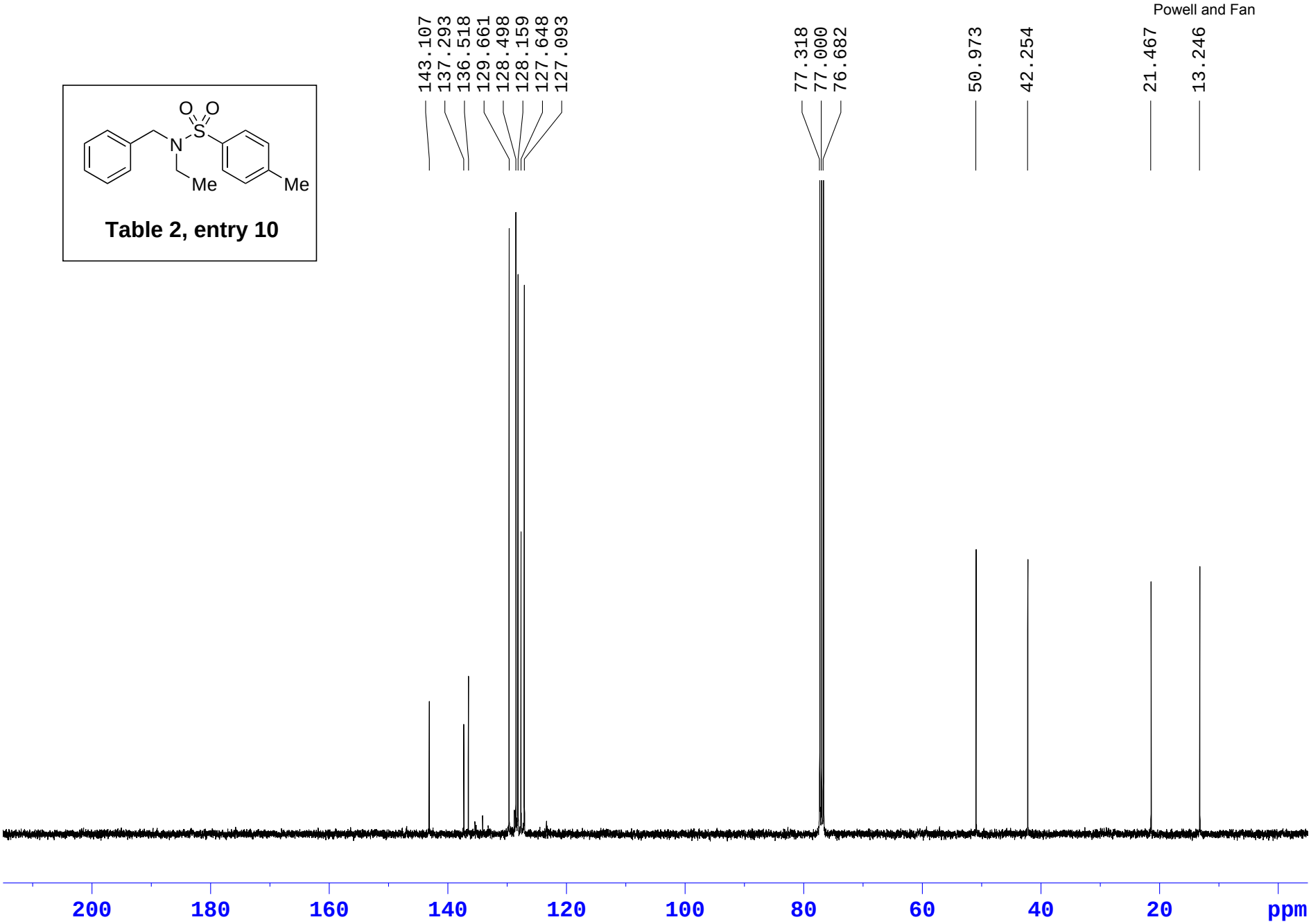
133.596
130.136
130.045
128.695
128.346
128.012
116.497
116.275
77.320
77.205
77.002
76.685
54.097
34.306
O
O
S
N
Me
F
Table 2, entry 9
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
Me
Table 2, entry 10
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
6.98
2.00
2.03
2.98
3.06


Powell and Fan
143.107
137.293
136.518
129.661
128.498
128.159
127.648
127.093
77.318
77.000
76.682
50.973
42.254
21.467
13.246
O
O
S
N
Me
Me
Table 2, entry 10
200
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160
140
120
100
80
60
40
20
ppm

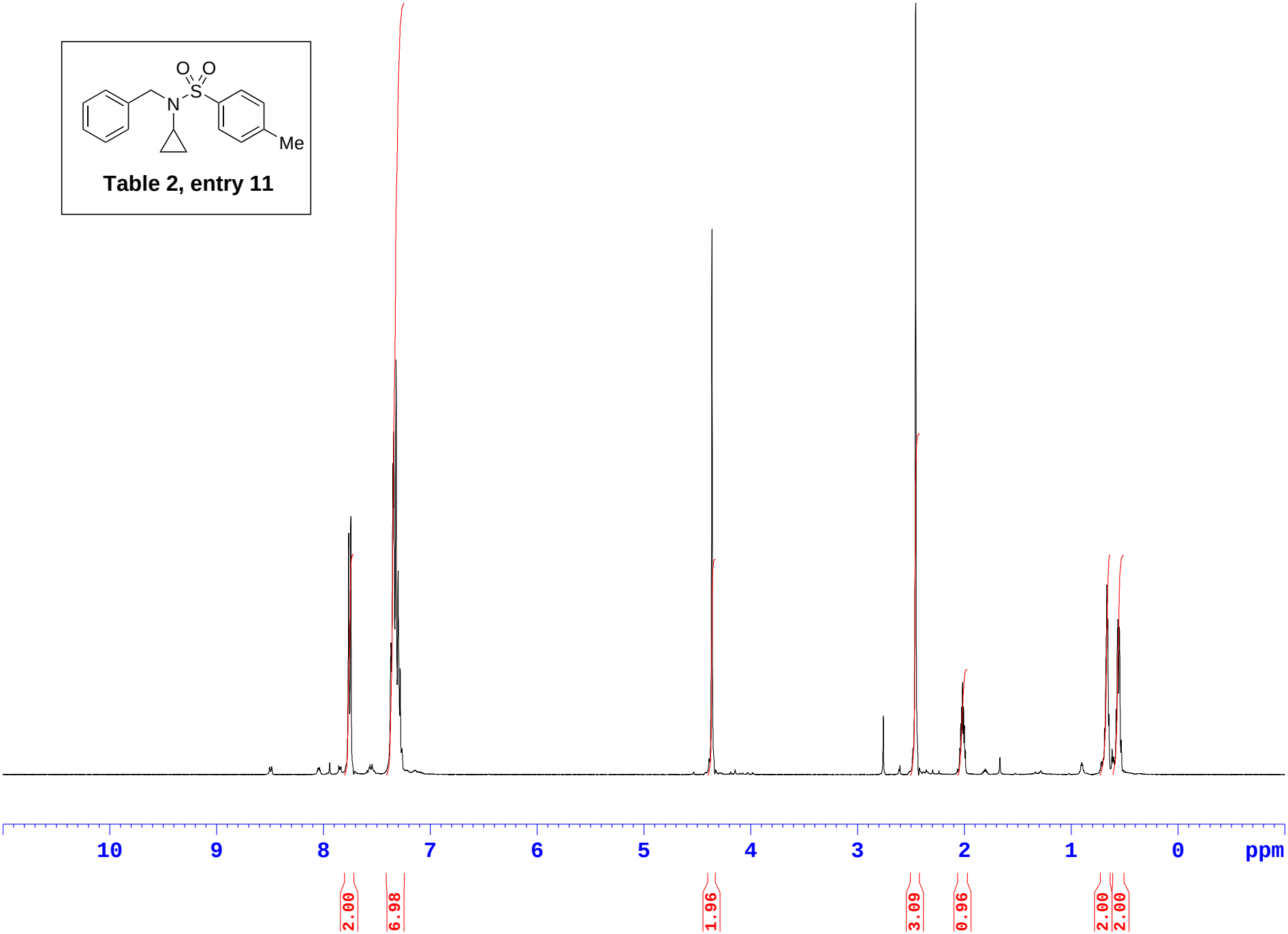
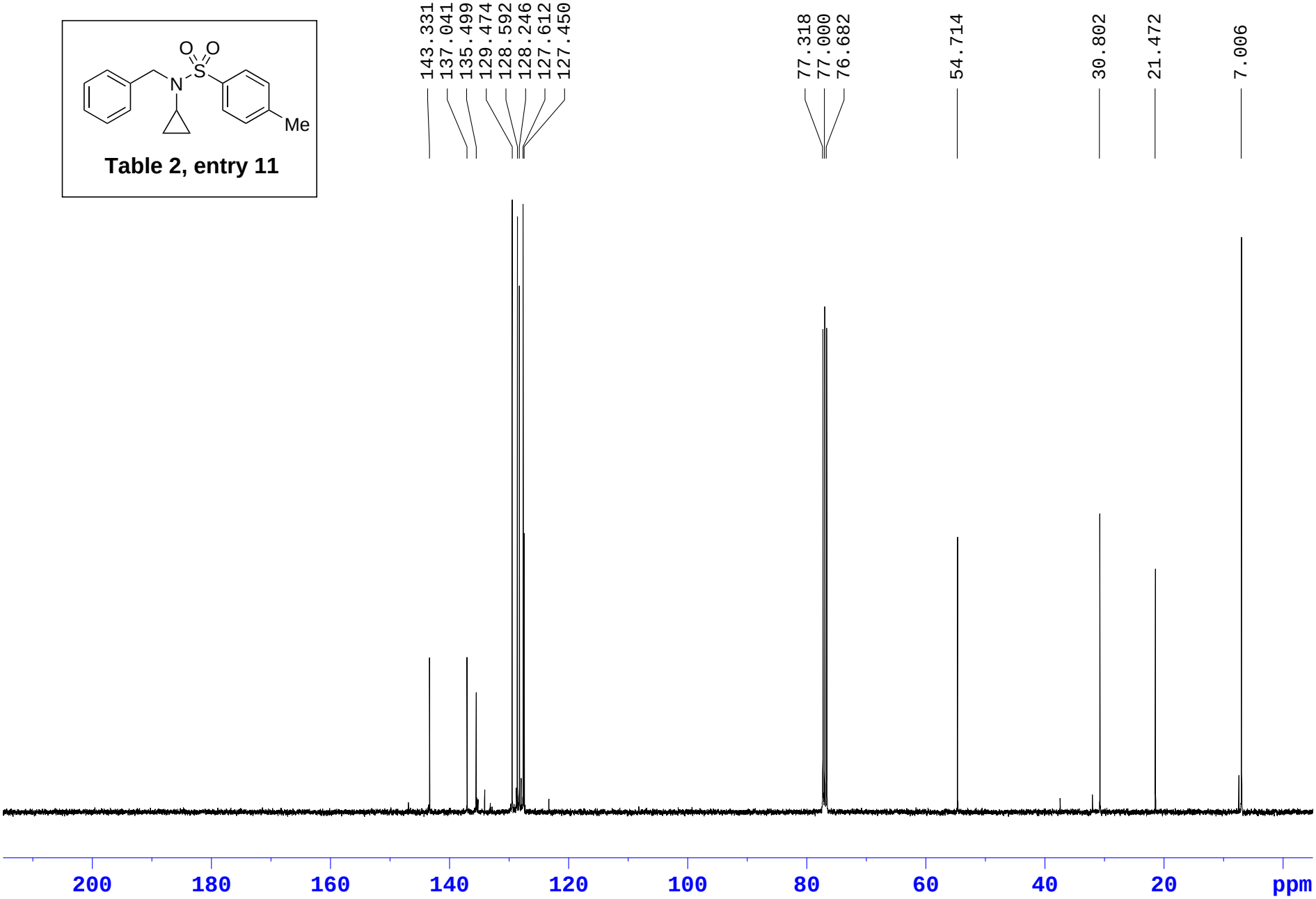

O
O
S
N
Me
Table 2, entry 11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
6.98
1.96
3.09
0.96
2.00
2.00

Table 2, entry 11



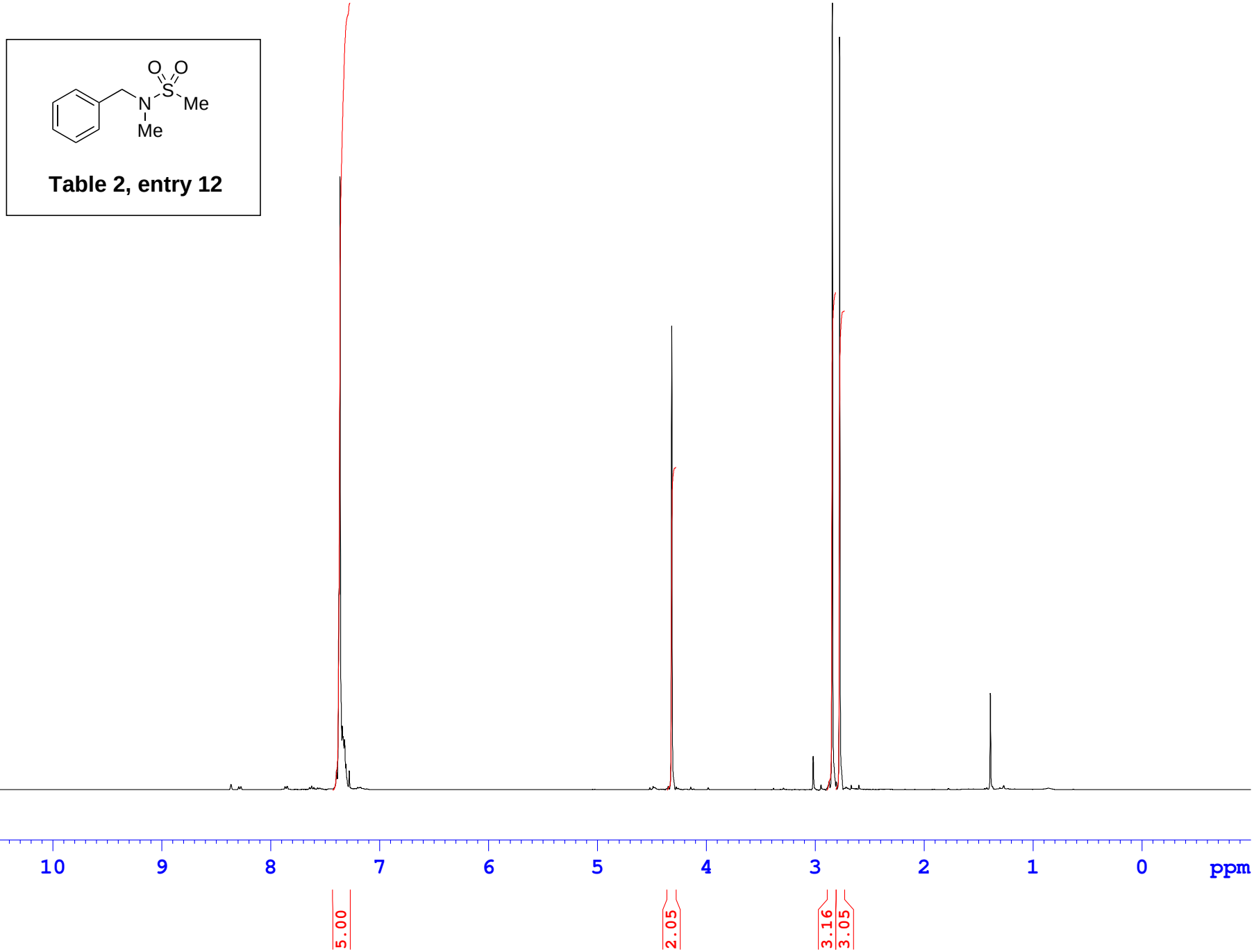

O O
S
N
Me
Me
Table 2, entry 12
10
9
8
7
6
5
4
3
2
1
0
ppm
5.00
2.05
3.16
3.05

Table 2, entry 12

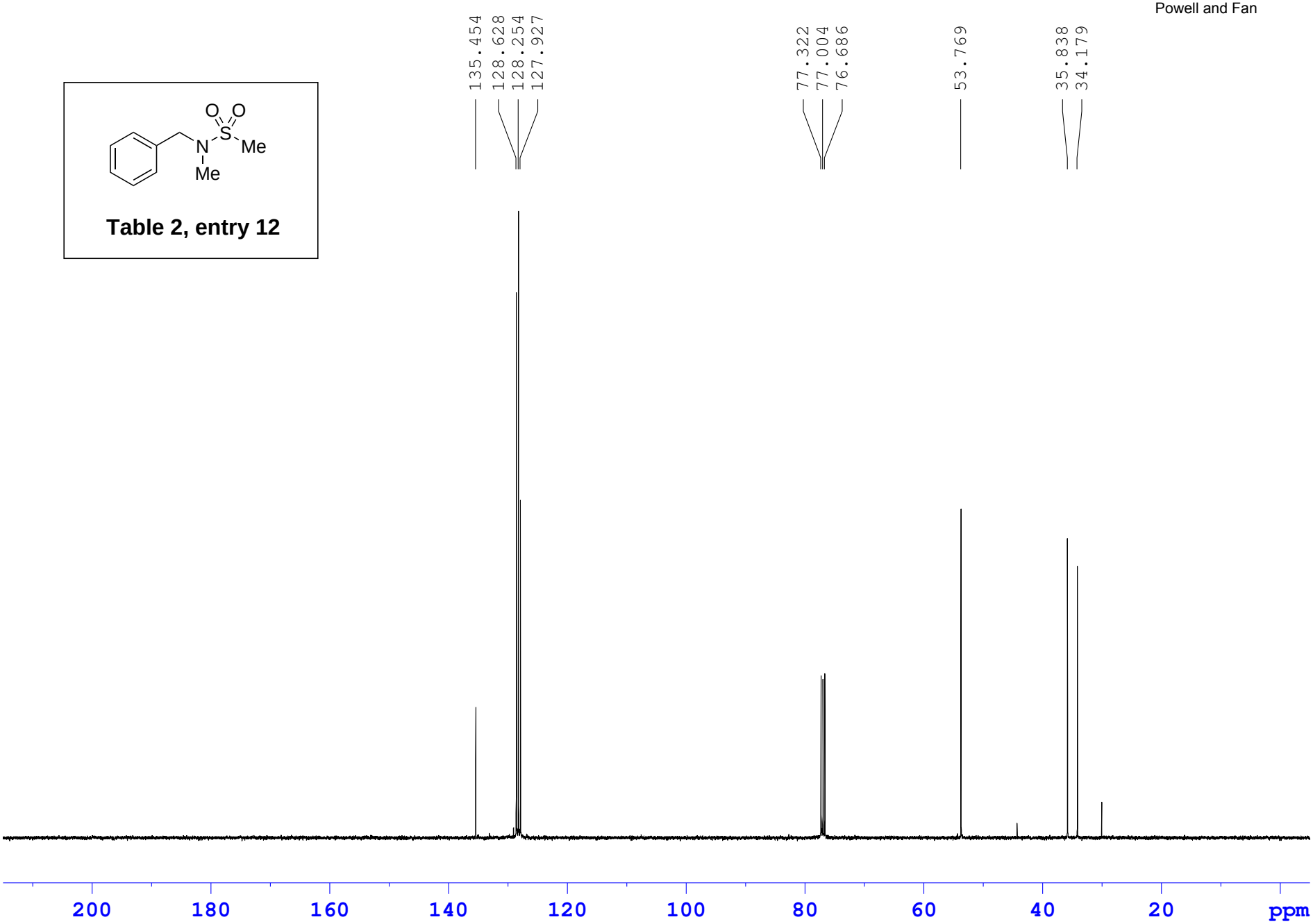
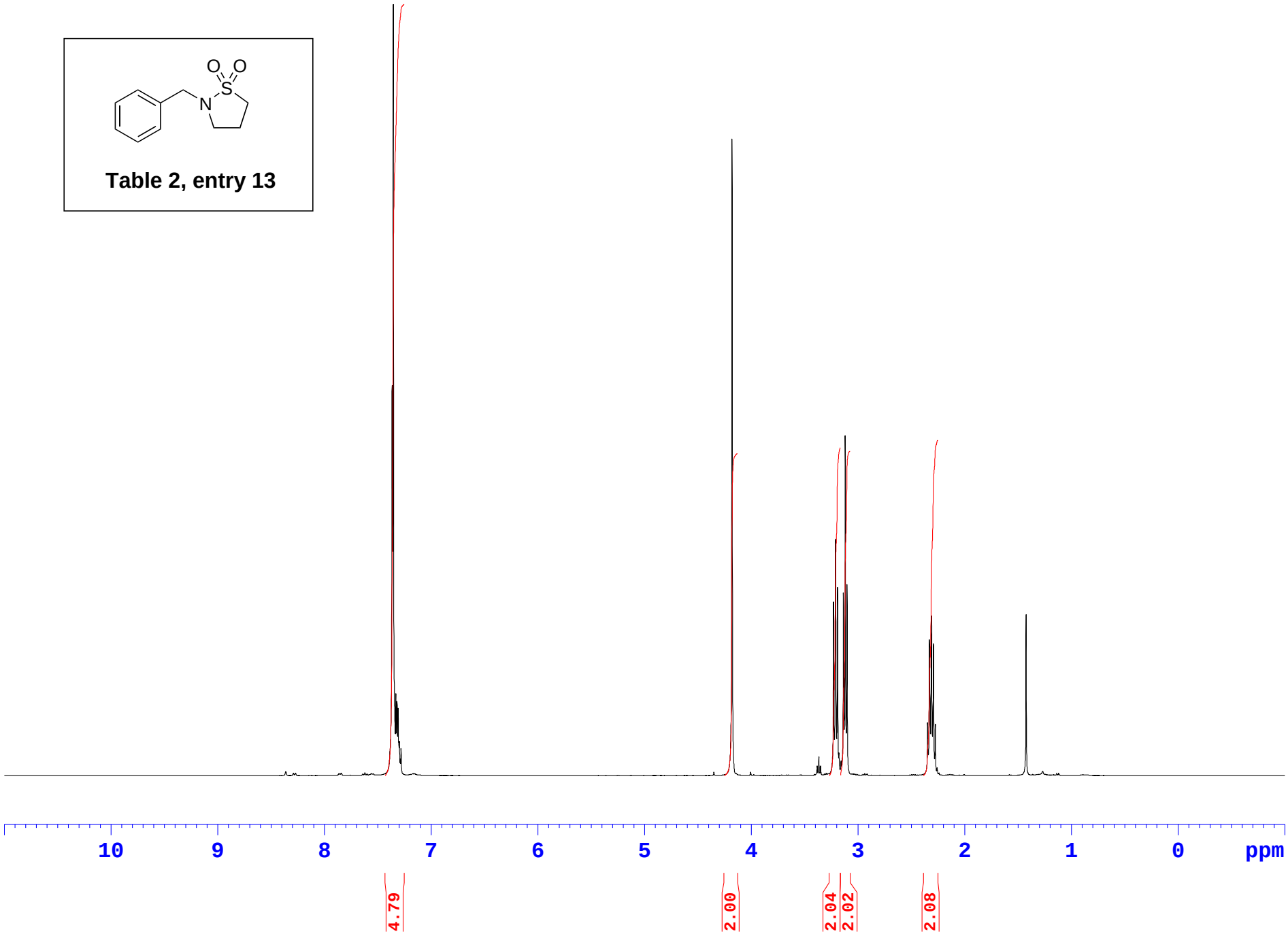


Table 2, entry 13



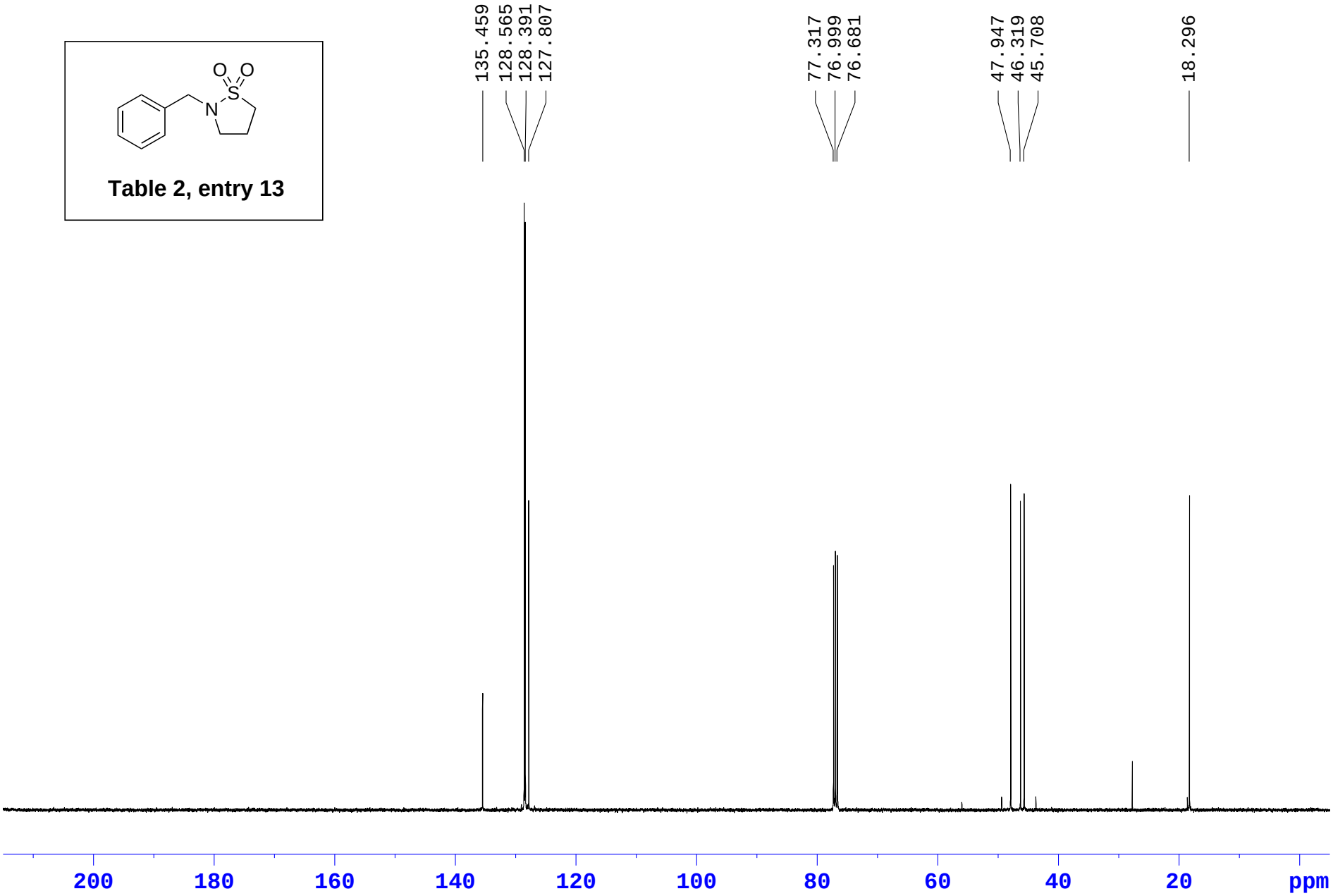


Table 2, entry 13
135.459
128.565
128.391
127.807
77.317
76.999
76.681
47.947
46.319
45.708
18.296
200
180
160
140
120
100
80
60
40
20
ppm

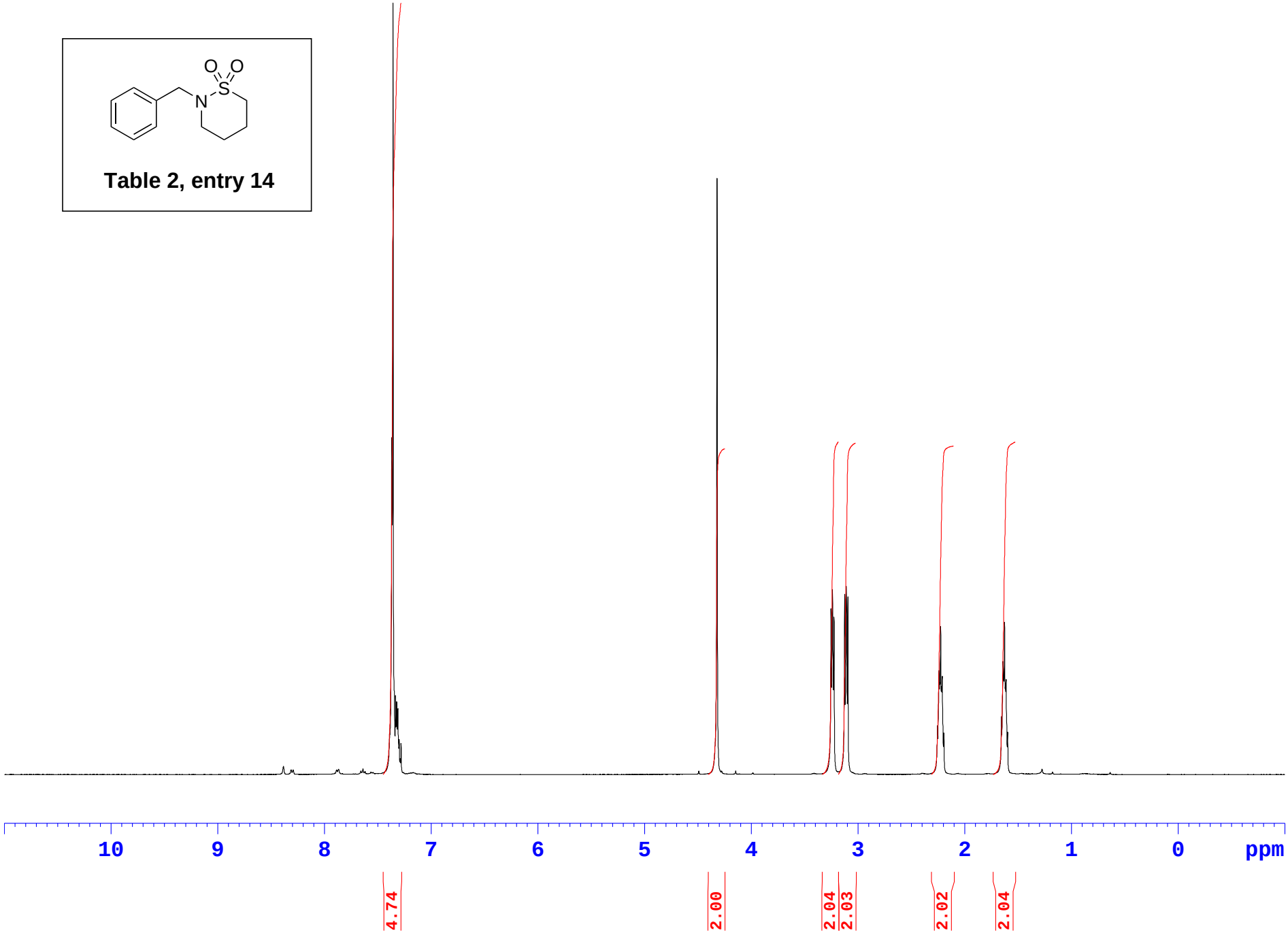


Table 2, entry 14
10
9
8
7
6
5
4
3
2
1
0
ppm
4.74
2.00
2.04
2.03
2.02
2.04

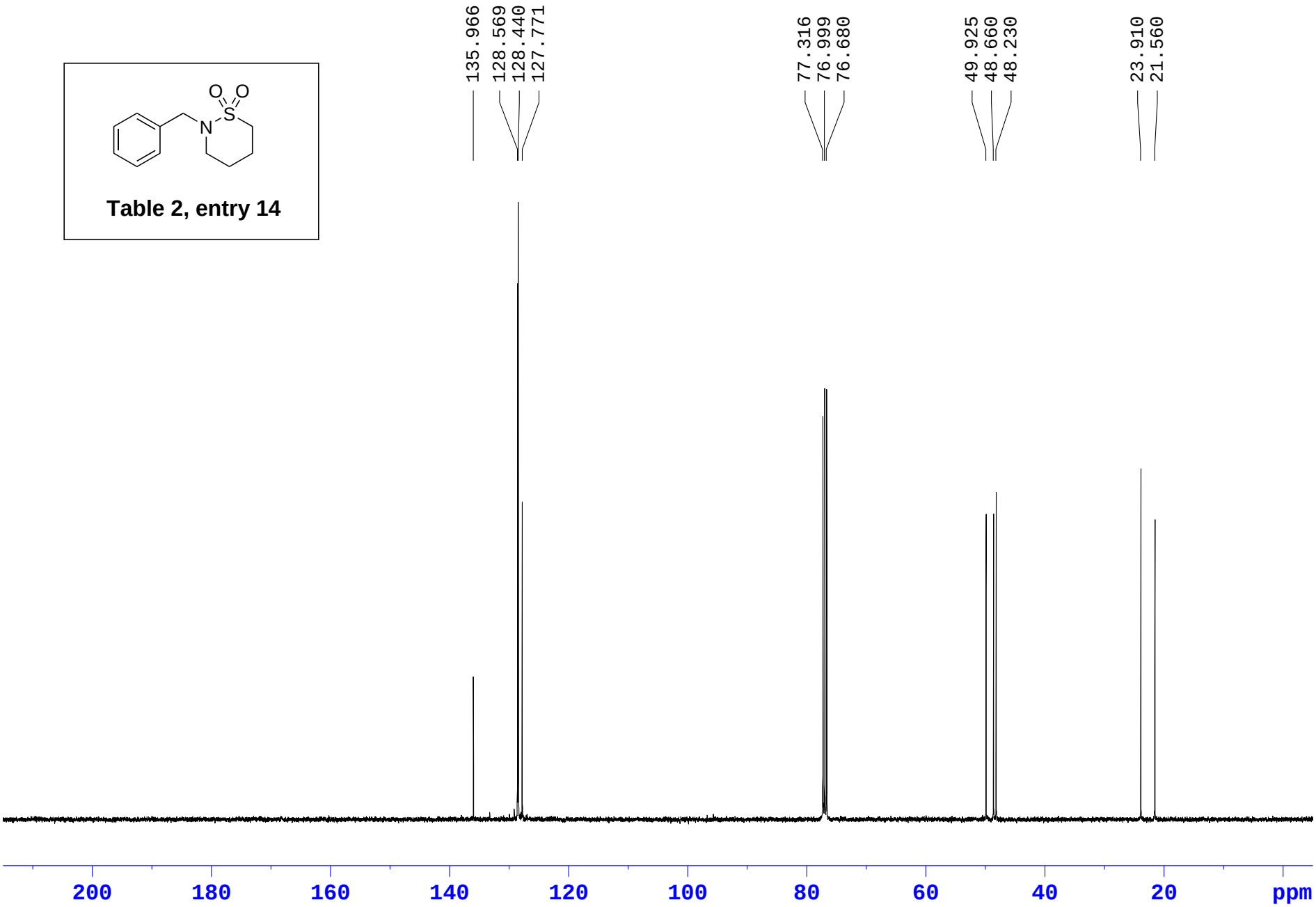
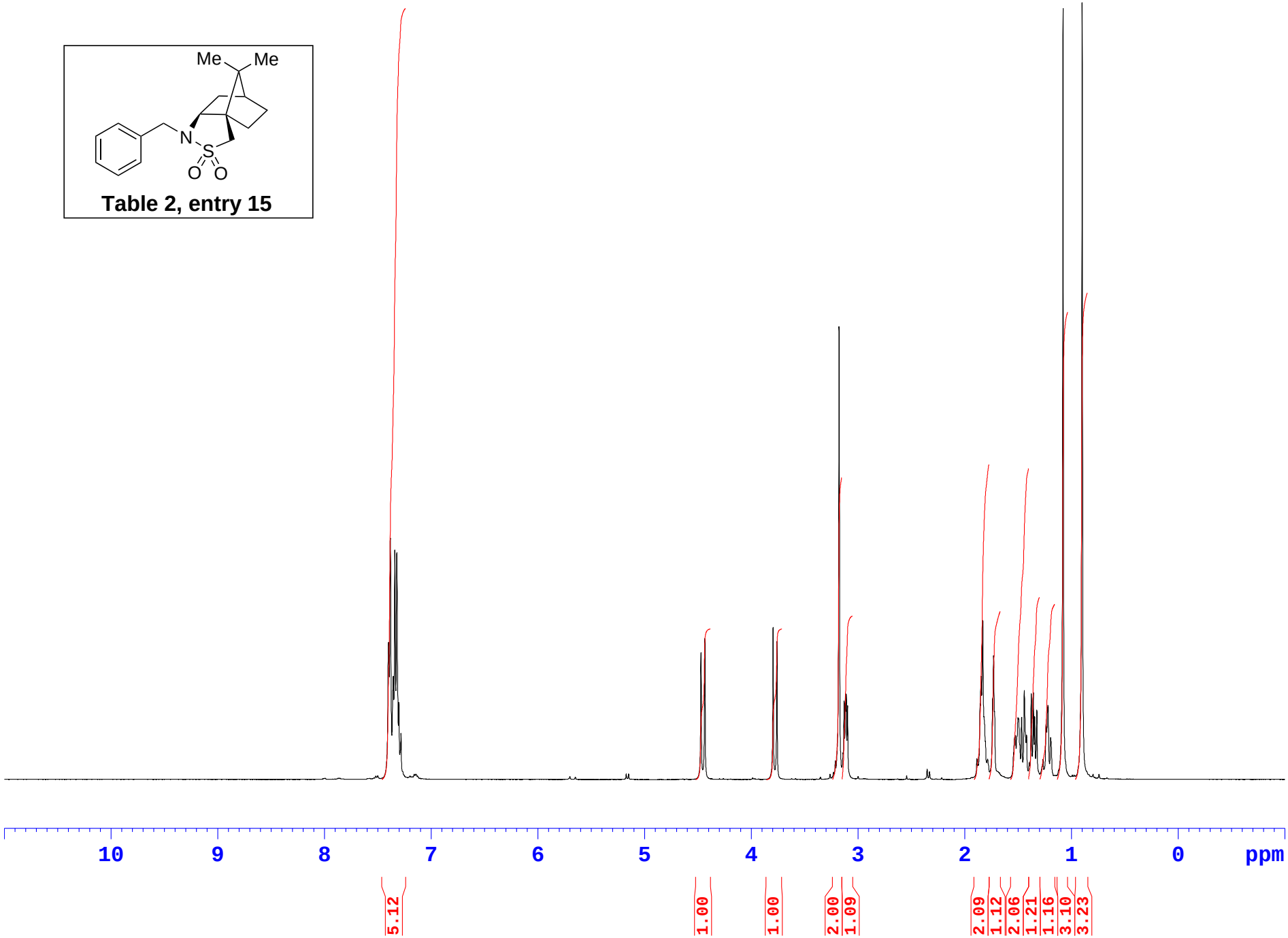
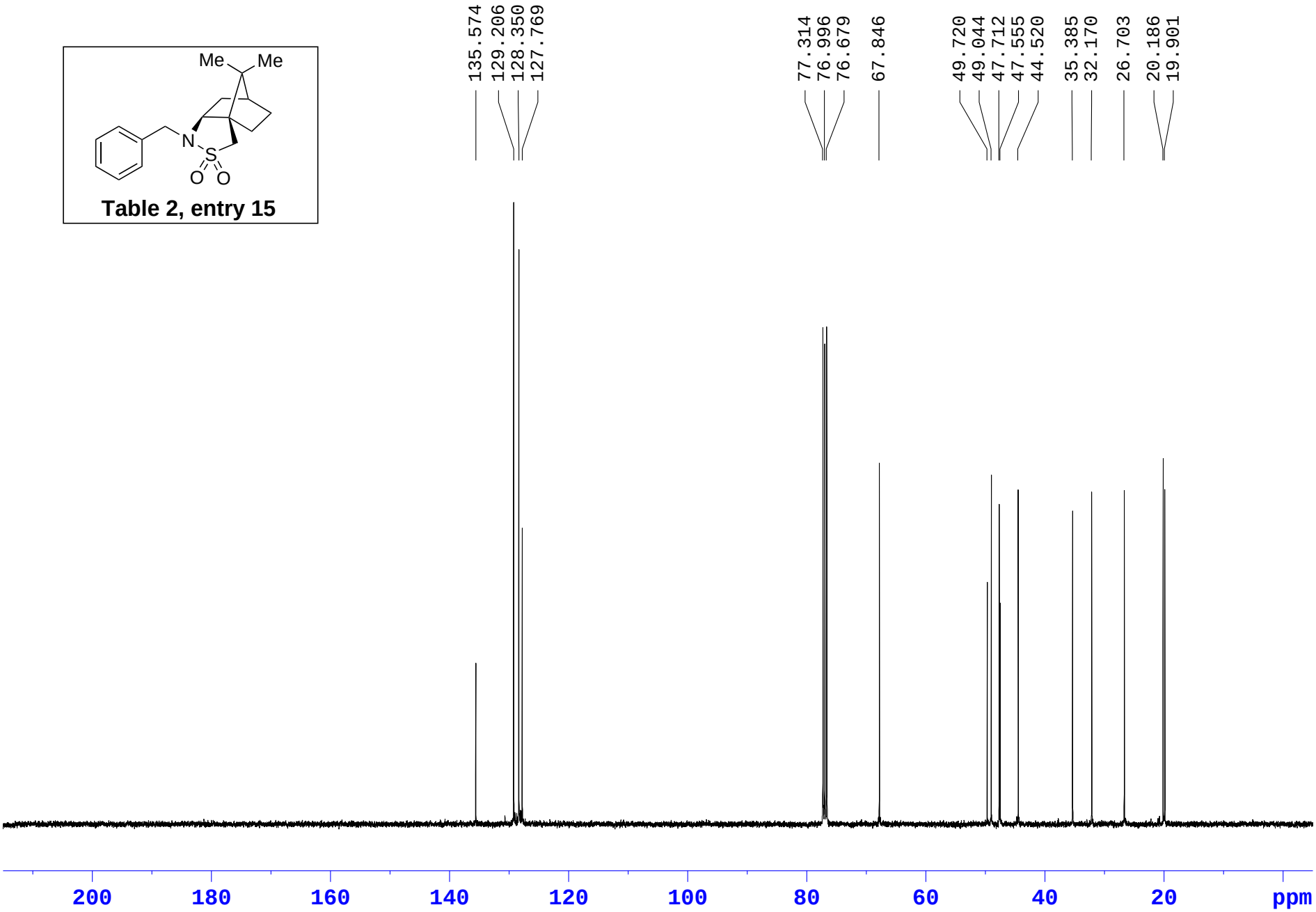
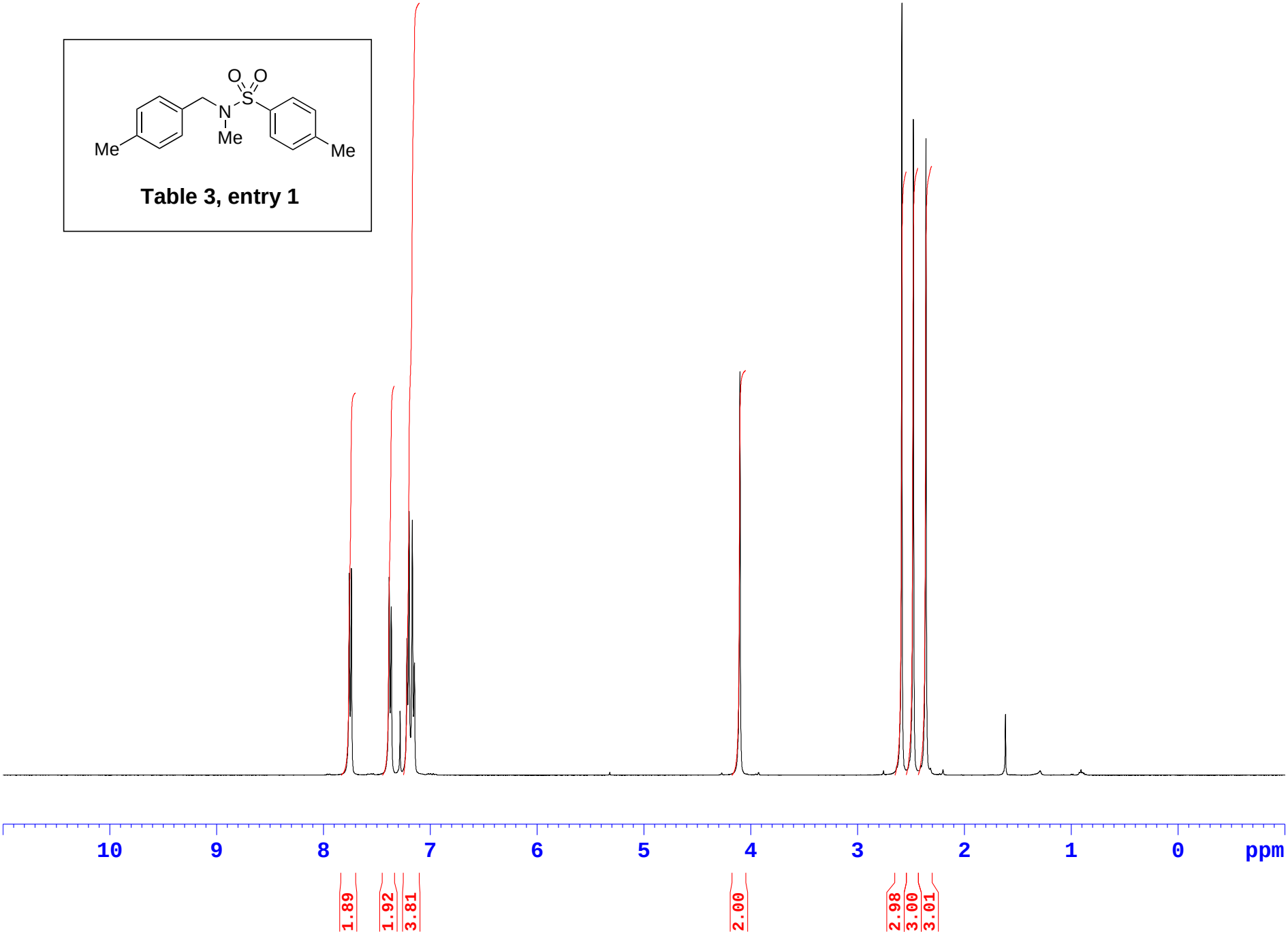
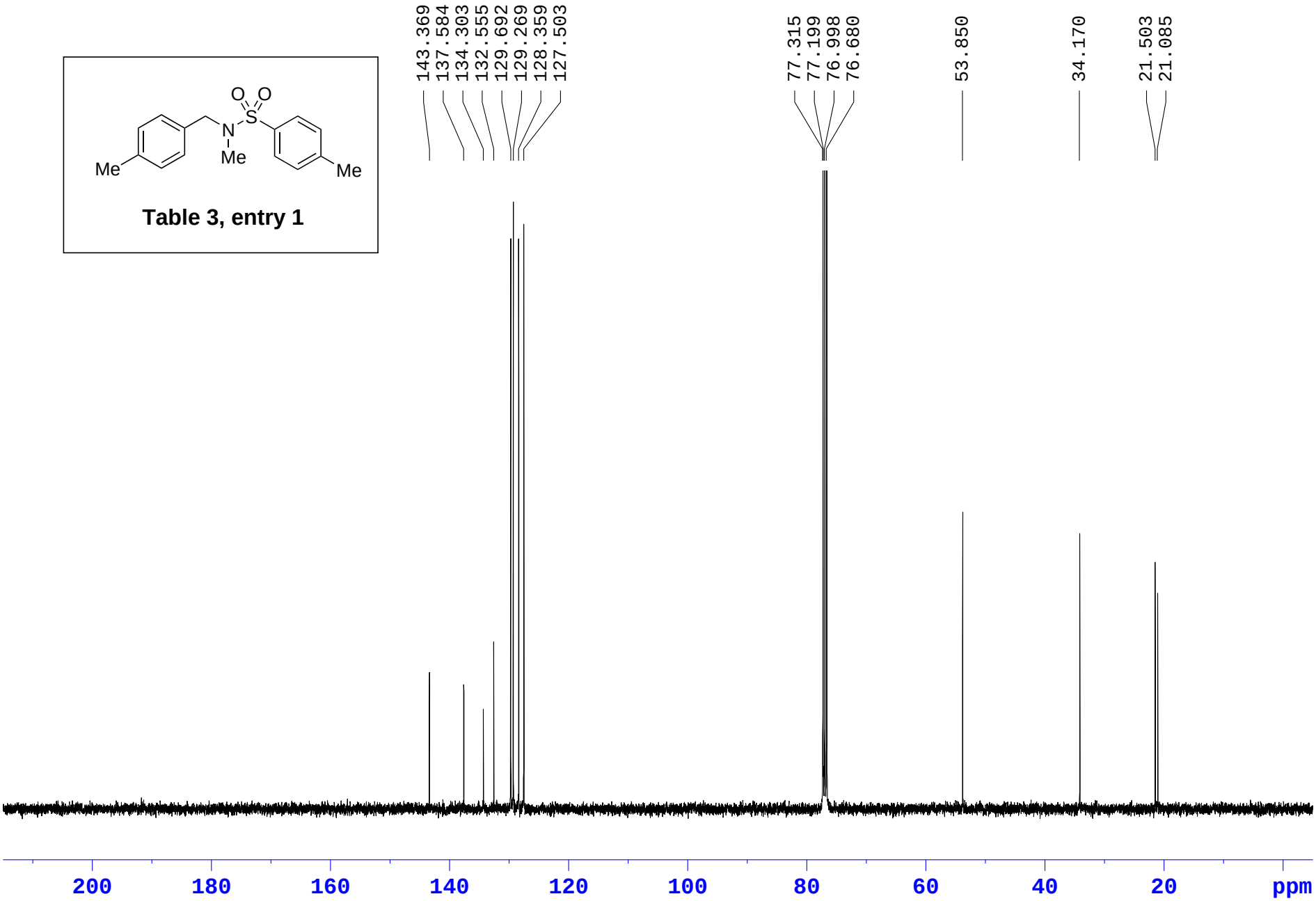

135.966
128.569
128.440
127.771
77.316
76.999
76.680
49.925
48.660
48.230
23.910
21.560
O
O
S
N
Table 2, entry 14
200
180
160
140
120
100
80
60
40
20
ppm

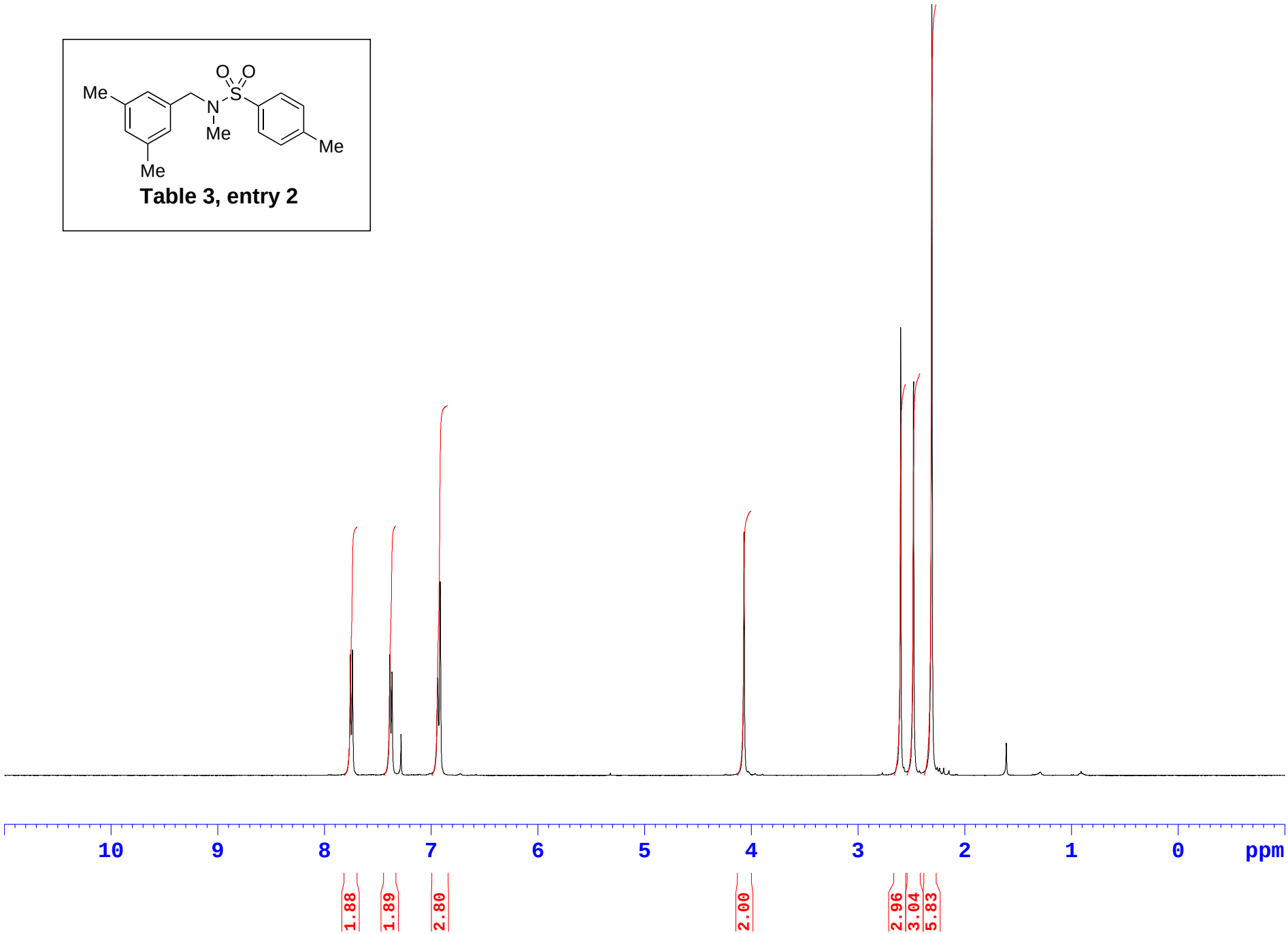
Table 2, entry 15

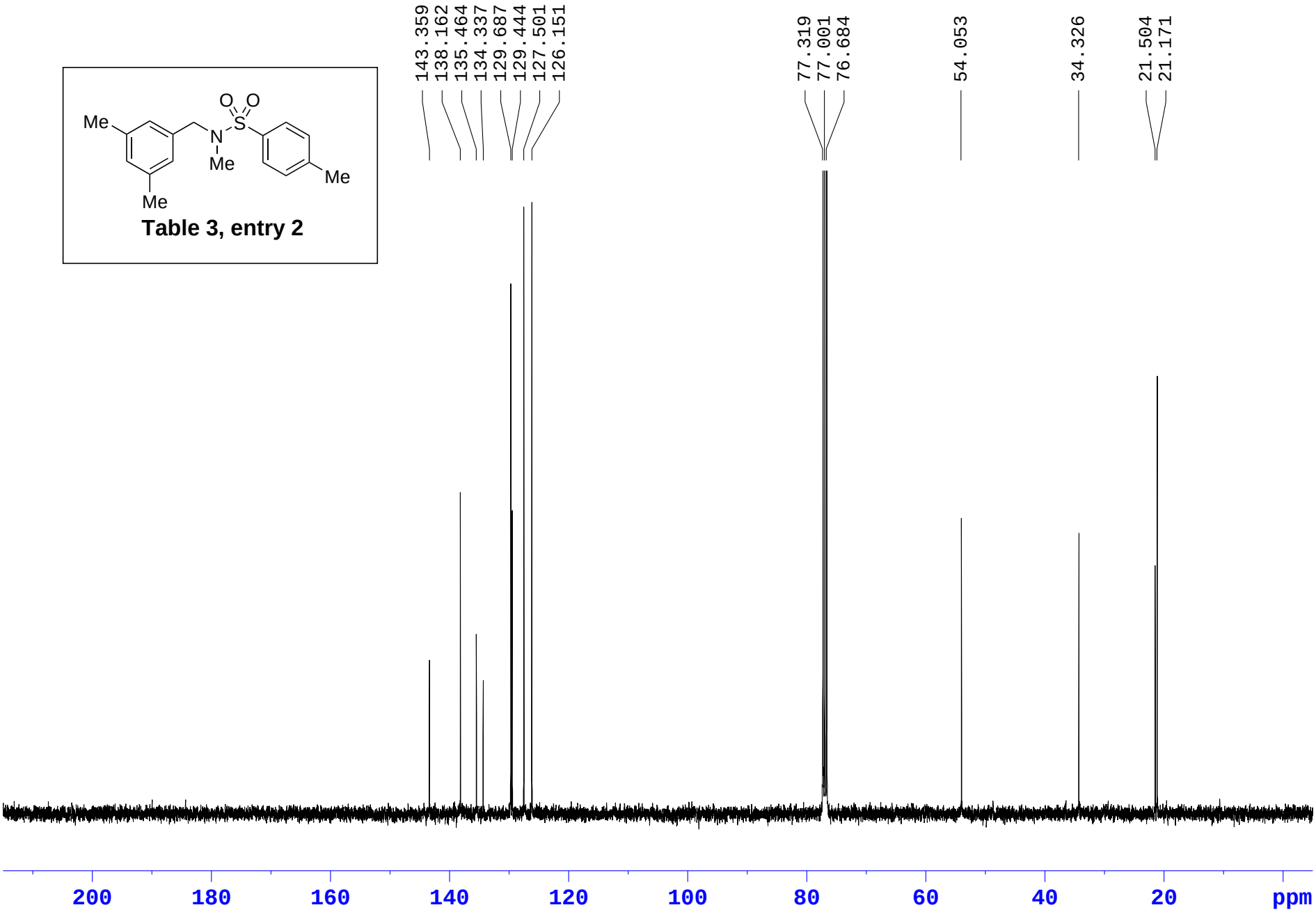


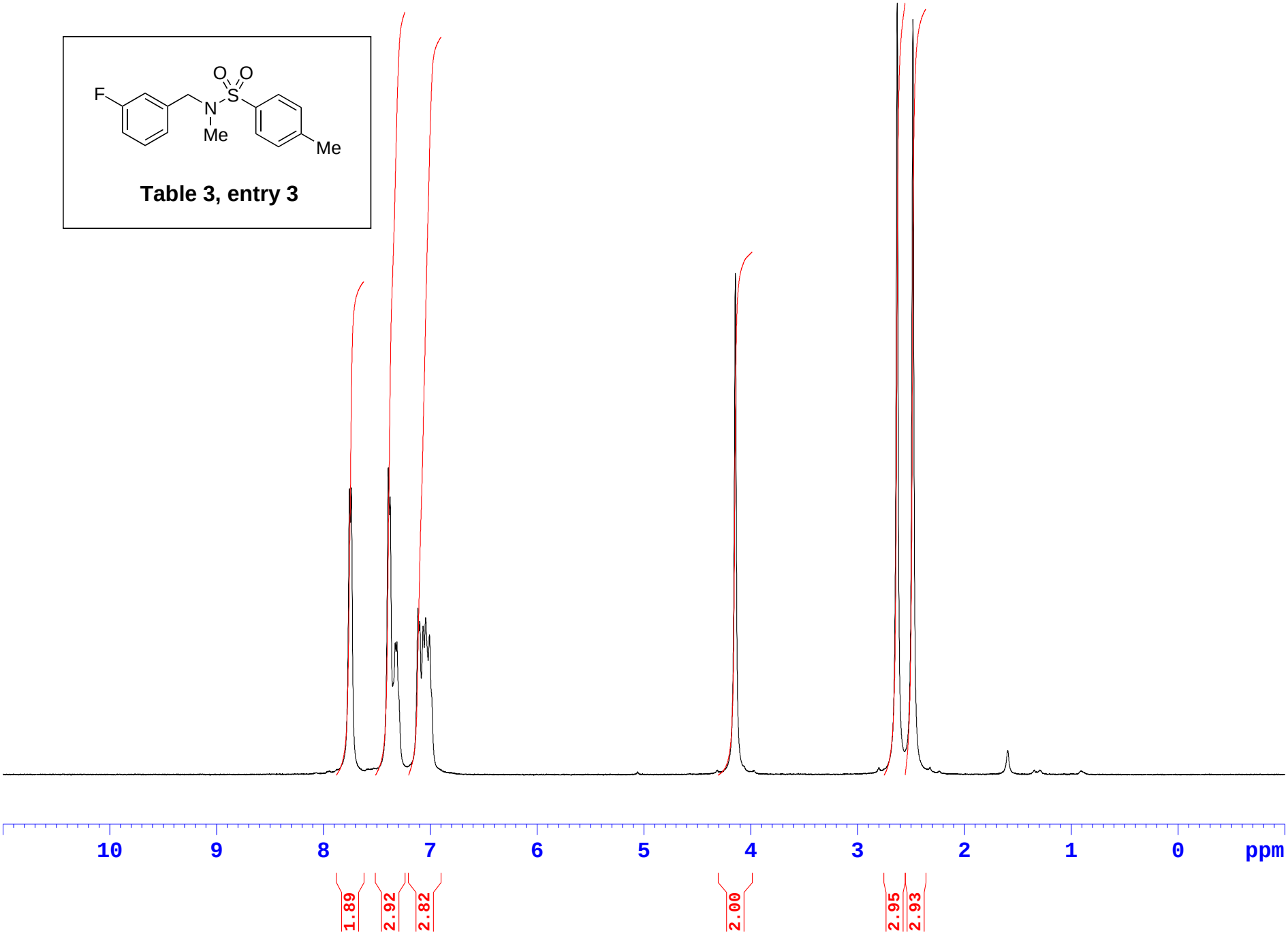

Me
Me
N
S
O
O
Table 2, entry 15
135.574
129.206
128.350
127.769
77.314
76.996
76.679
67.846
49.720
49.044
47.712
47.555
44.520
35.385
32.170
26.703
20.186
19.901
200
180
160
140
120
100
80
60
40
20
ppm


O
O
S
N
Me
Me
Me
Table 3, entry 1
10
9
8
7
6
5
4
3
2
1
0
ppm
1.89
1.92
3.81
2.00
2.98
3.00
3.01


143.369
137.584
134.303
132.555
129.692
129.269
128.359
127.503
77.315
77.199
76.998
76.680
53.850
34.170
21.503
21.085
O
O
S
N
Me
Me
Me
Table 3, entry 1
200
180
160
140
120
100
80
60
40
20
ppm


Me
O
O
S
N
Me
Me
Me
Table 3, entry 2
10
9
8
7
6
5
4
3
2
1
0
ppm
1.88
1.89
2.80
2.00
2.96
3.04
5.83


Me
O
O
S
N
Me
Me
Me
Table 3, entry 2
143.359
138.162
135.464
134.337
129.687
129.444
127.501
126.151
77.319
77.001
76.684
54.053
34.326
21.504
21.171
200
180
160
140
120
100
80
60
40
20
ppm


F
O
O
S
N
Me
Me
Table 3, entry 3
10
9
8
7
6
5
4
3
2
1
0
ppm
1.89
2.92
2.82
2.00
2.95
2.93

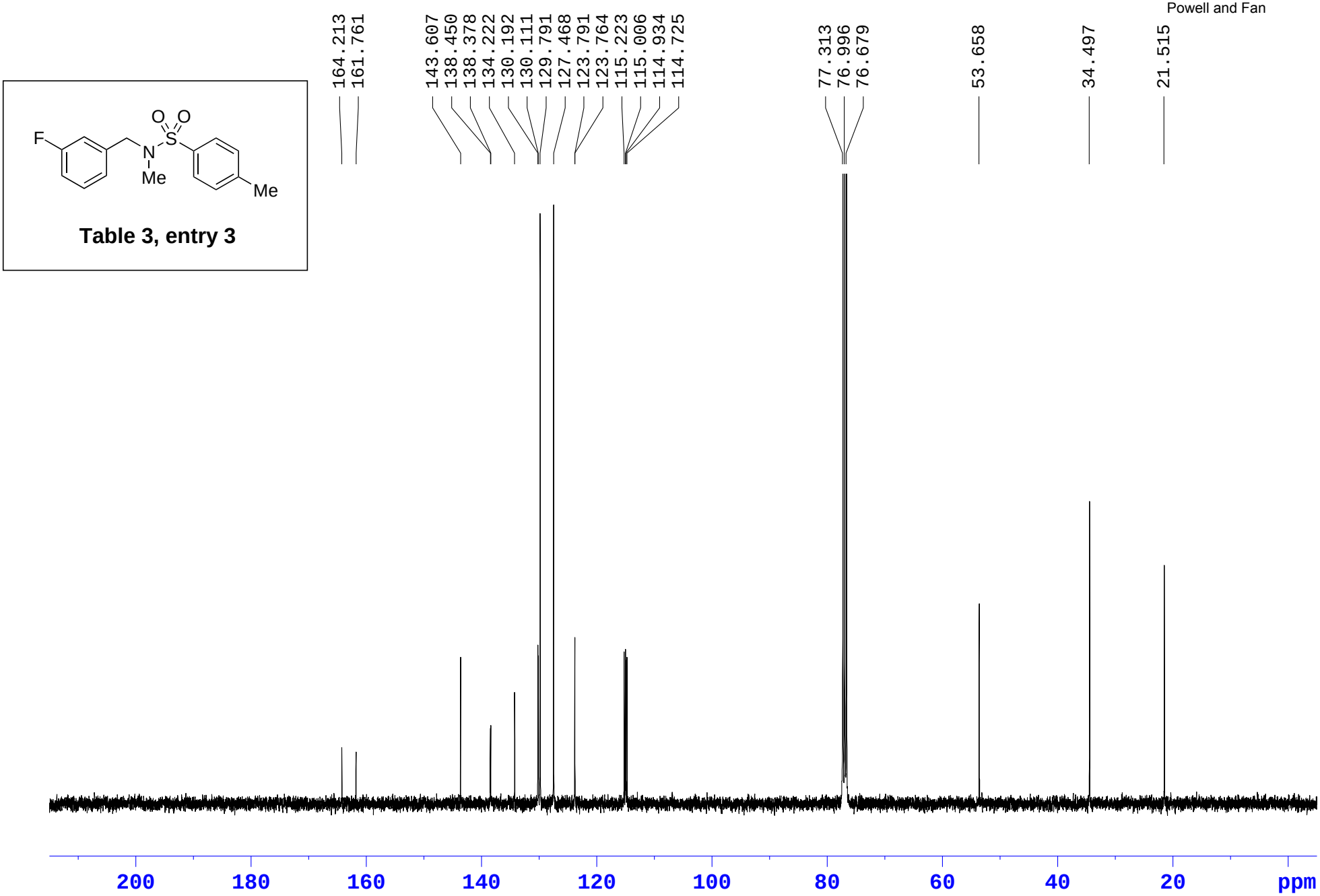
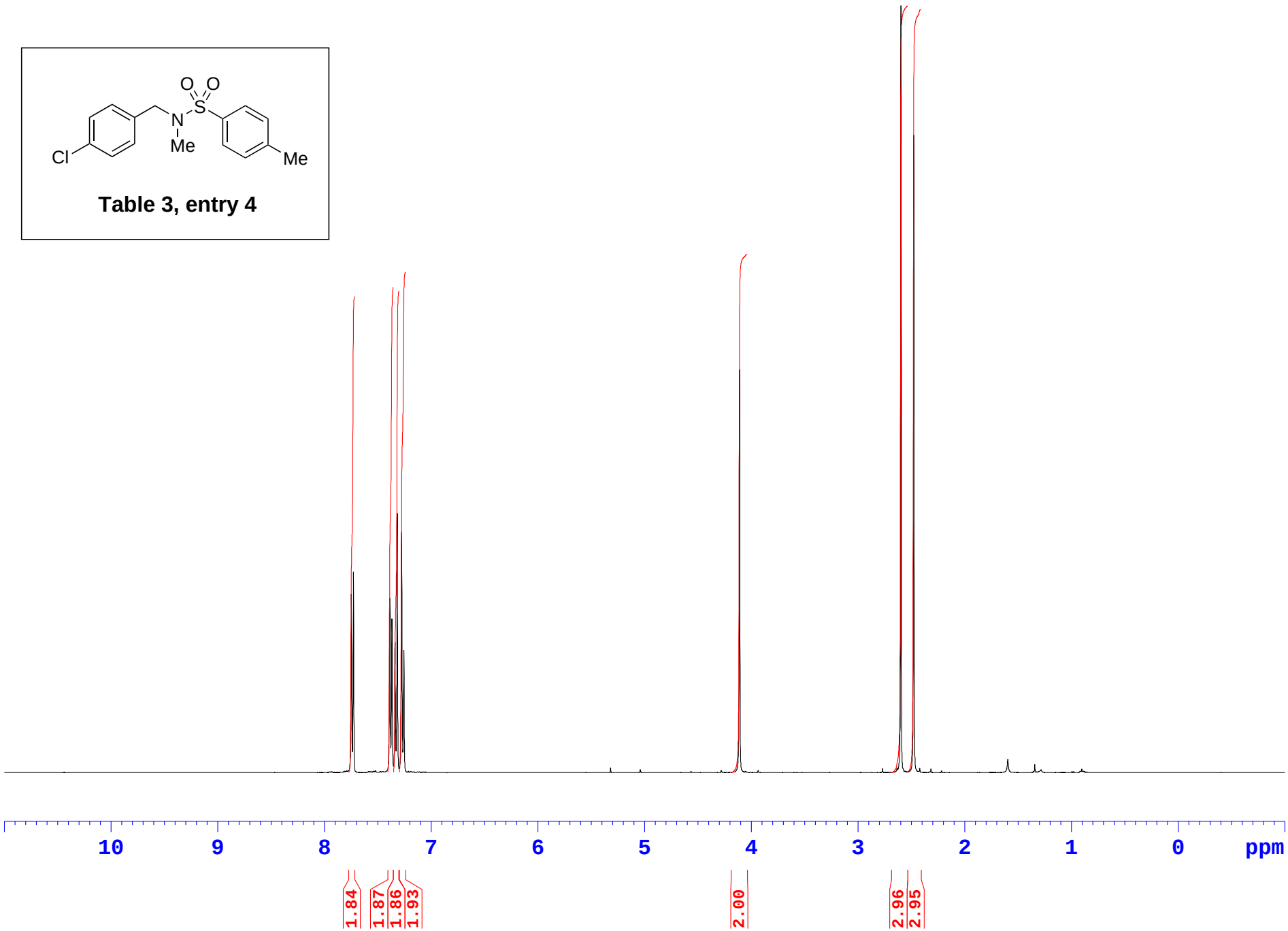

F
O
O
S
N
Me
Me
Table 3, entry 3
164.213
161.761
143.607
138.450
138.378
134.222
130.192
130.111
129.791
127.468
123.791
123.764
115.223
115.006
114.934
114.725
77.313
76.996
76.679
53.658
34.497
21.515
200
180
160
140
120
100
80
60
40
20
ppm

Table 3, entry 4



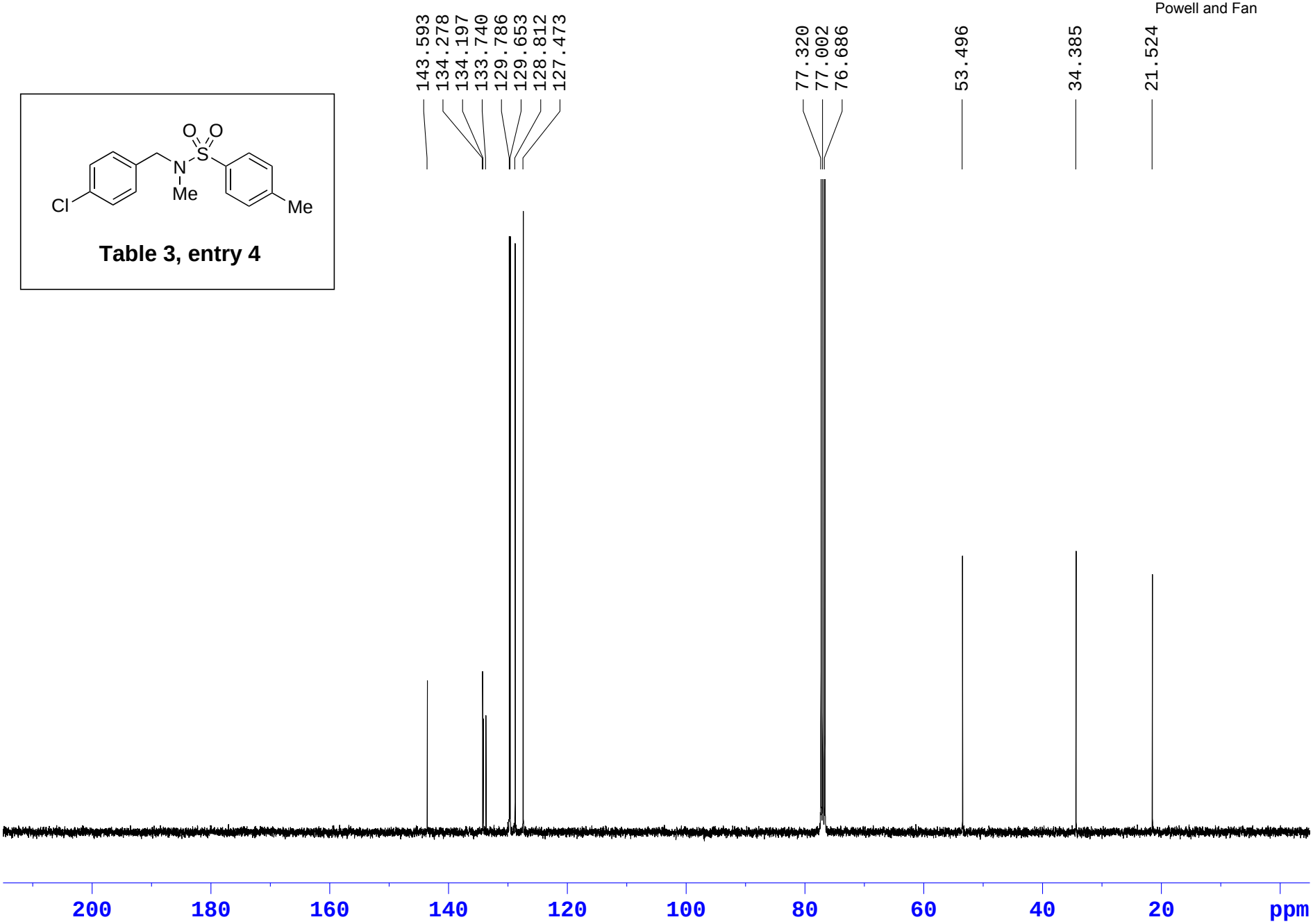
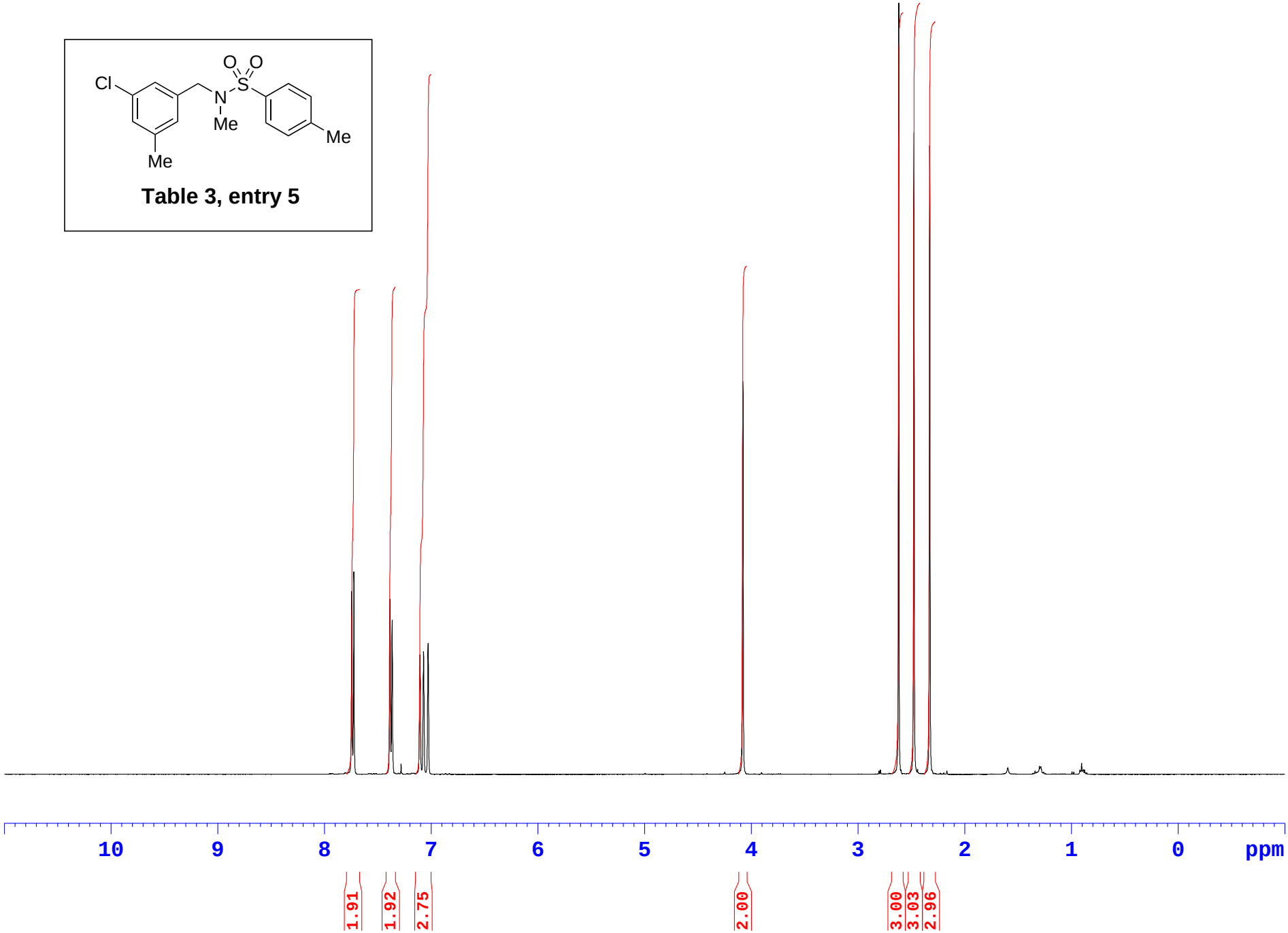


Table 3, entry 4

Table 3, entry 5



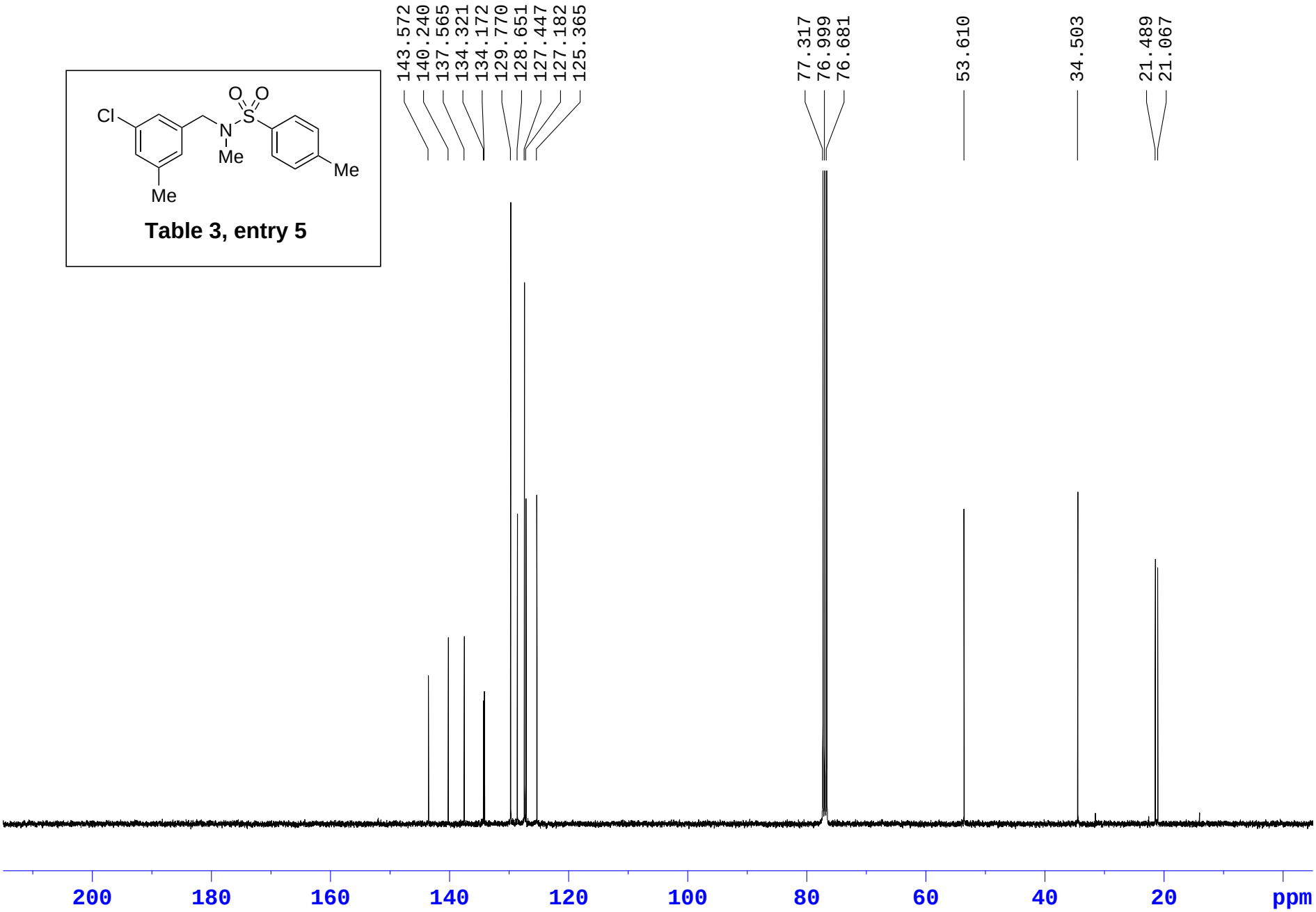
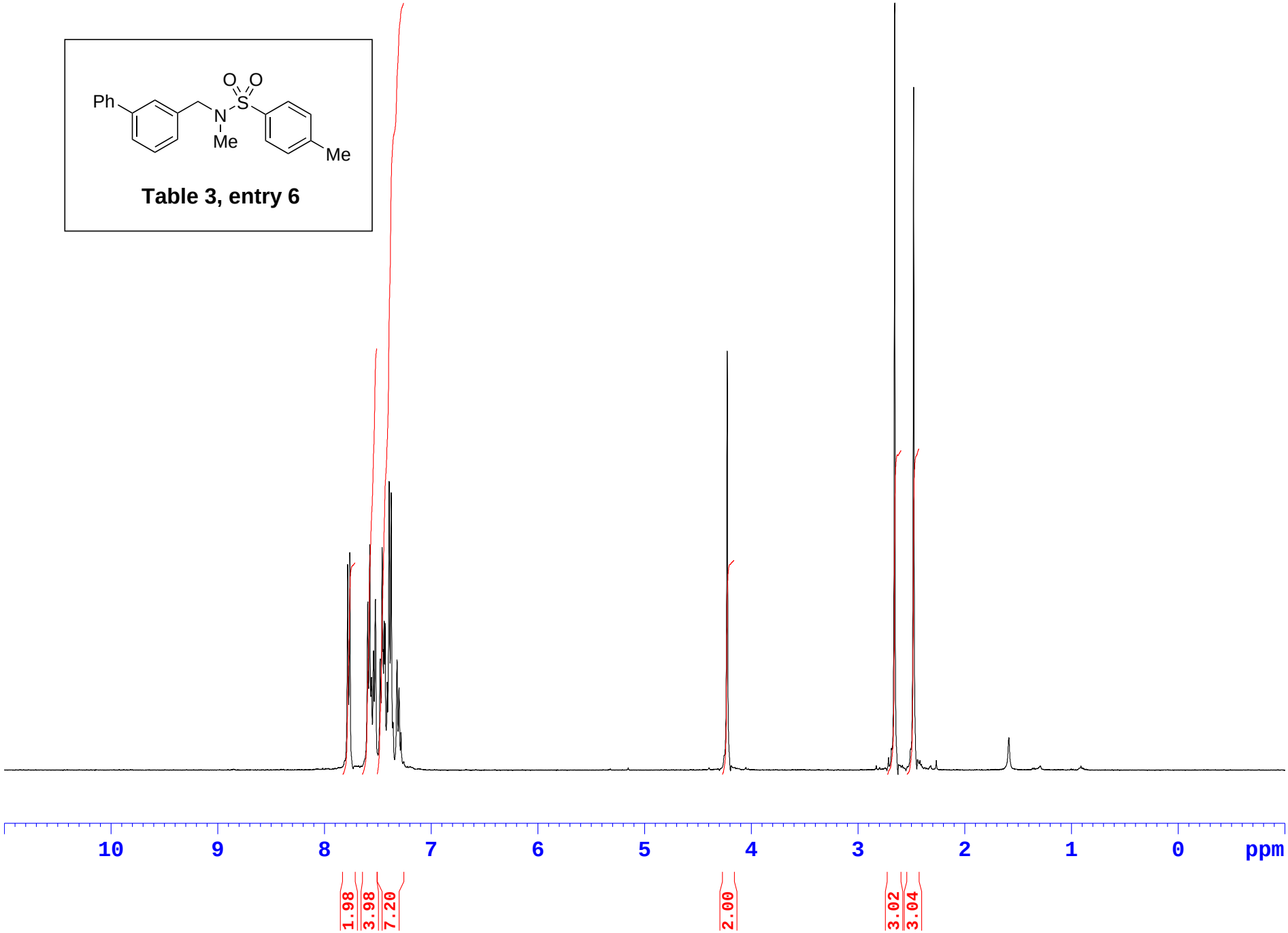

143.572
140.240
137.565
134.321
134.172
129.770
128.651
127.447
127.182
125.365
77.317
76.999
76.681
53.610
34.503
21.489
21.067
Cl
O
O
S
N
Me
Me
Me
Table 3, entry 5
200
180
160
140
120
100
80
60
40
20
ppm

Table 3, entry 6



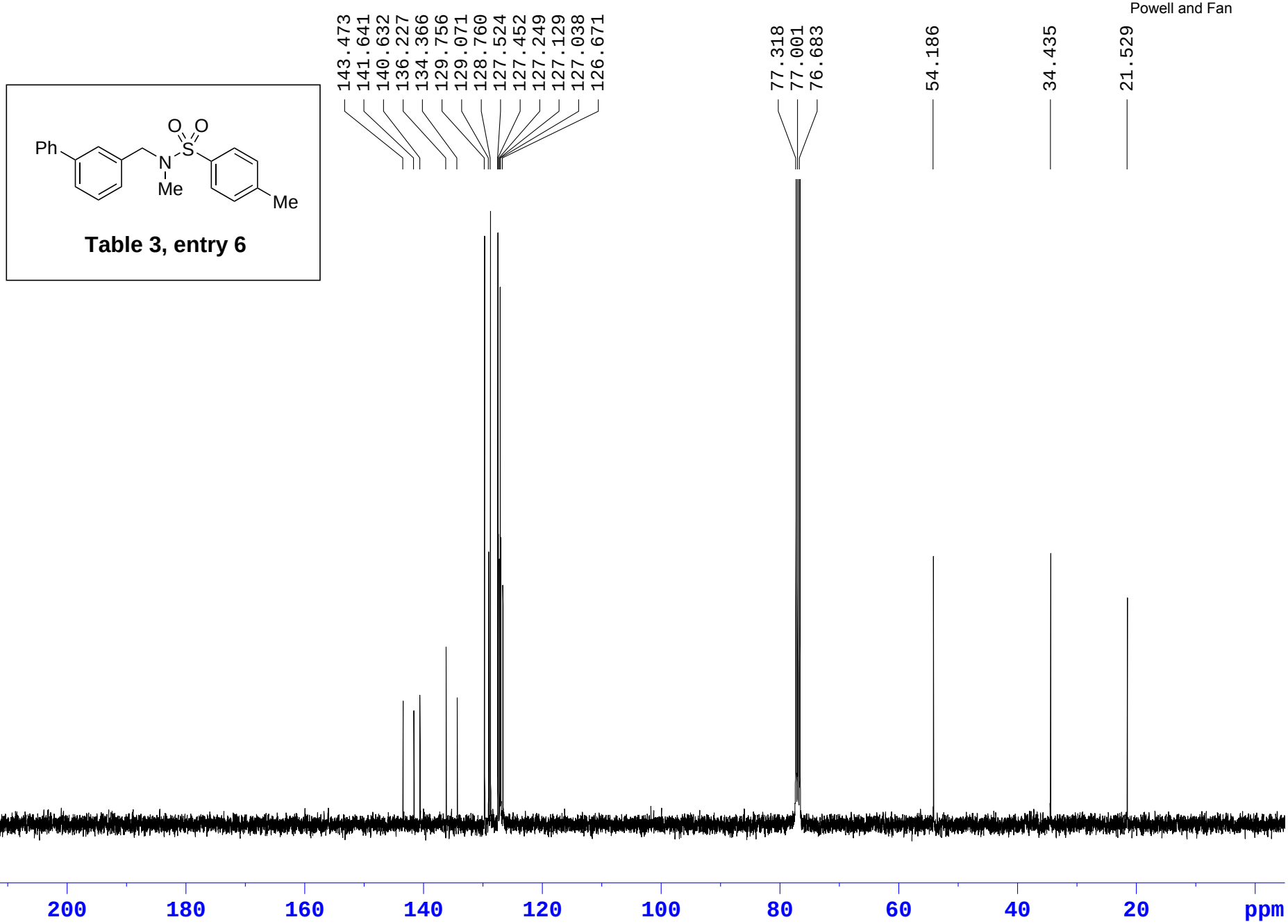


Table 3, entry 6

Table 3, entry 7

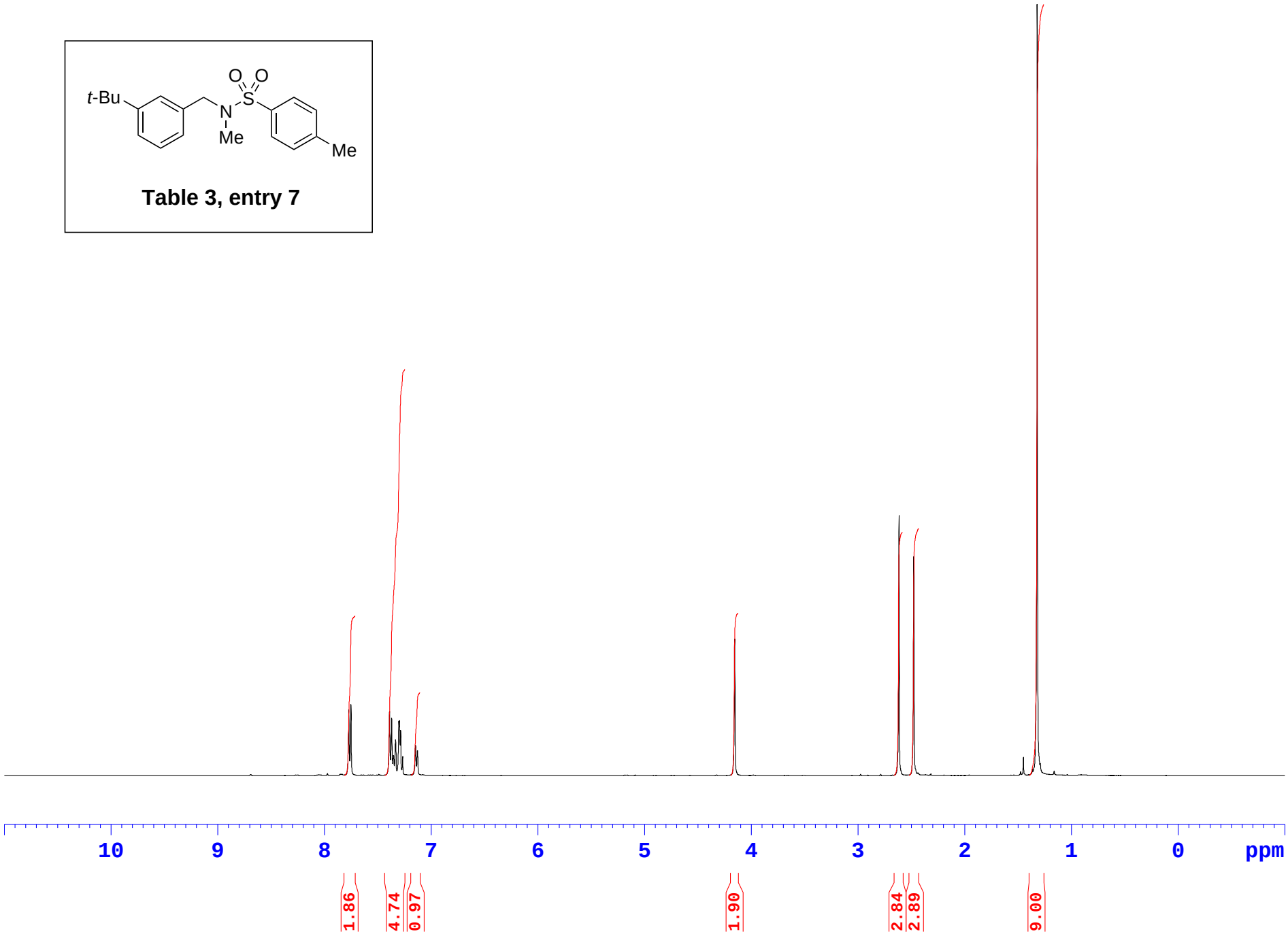
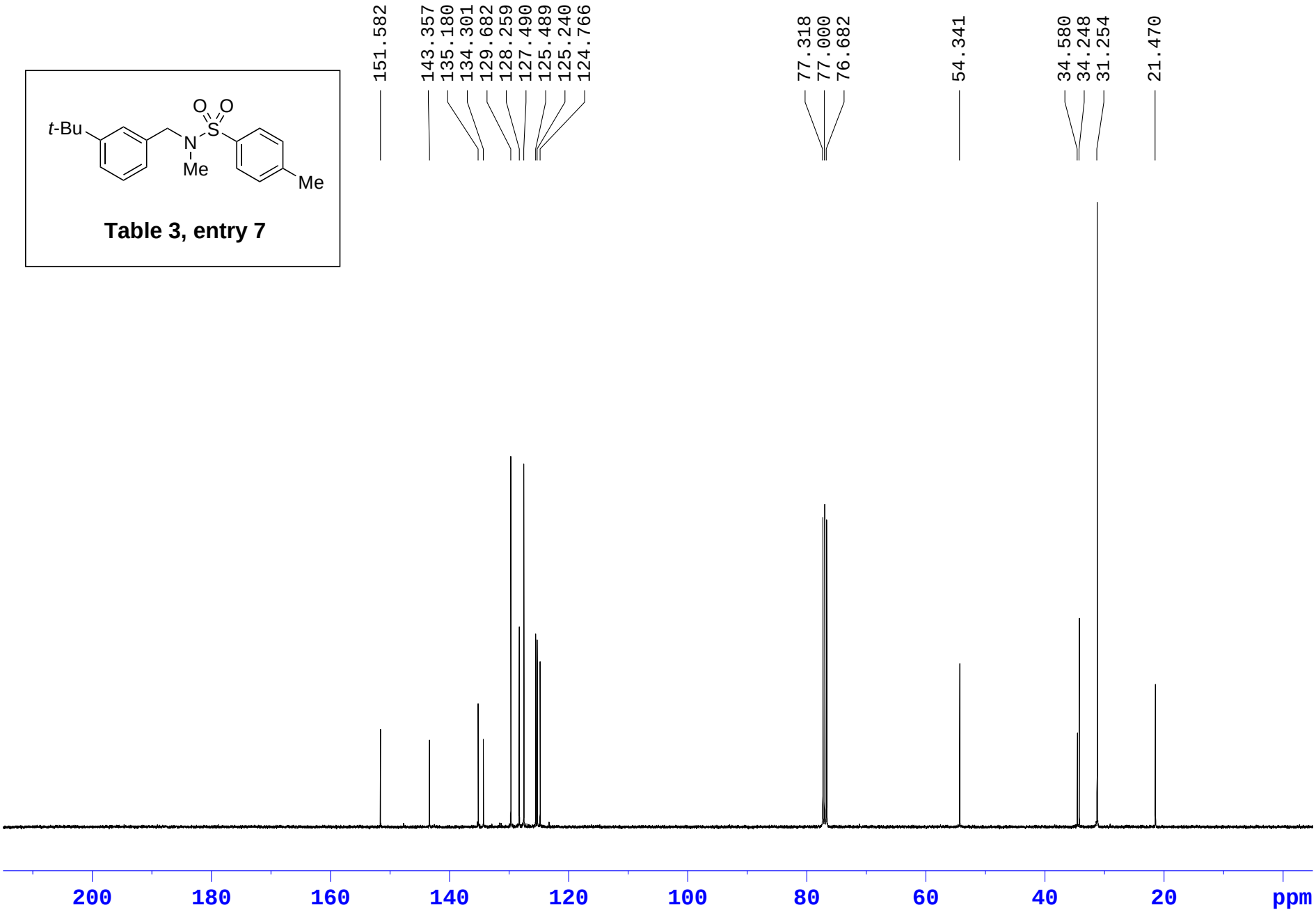
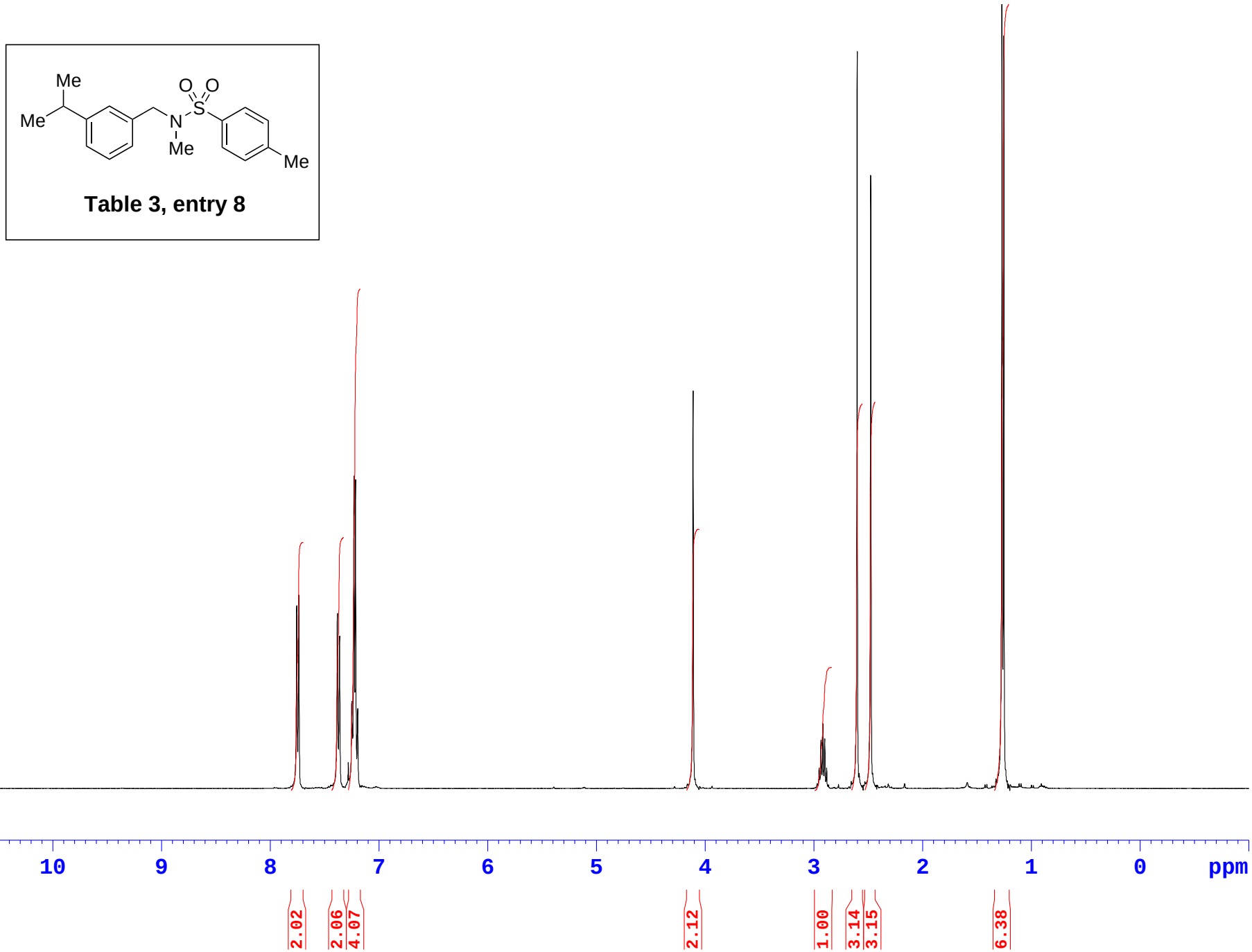


Table 3, entry 7




Me
Me
O O
S
N
Me
Me
Table 3, entry 8
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.06
4.07
2.12
1.00
3.14
3.15
6.38

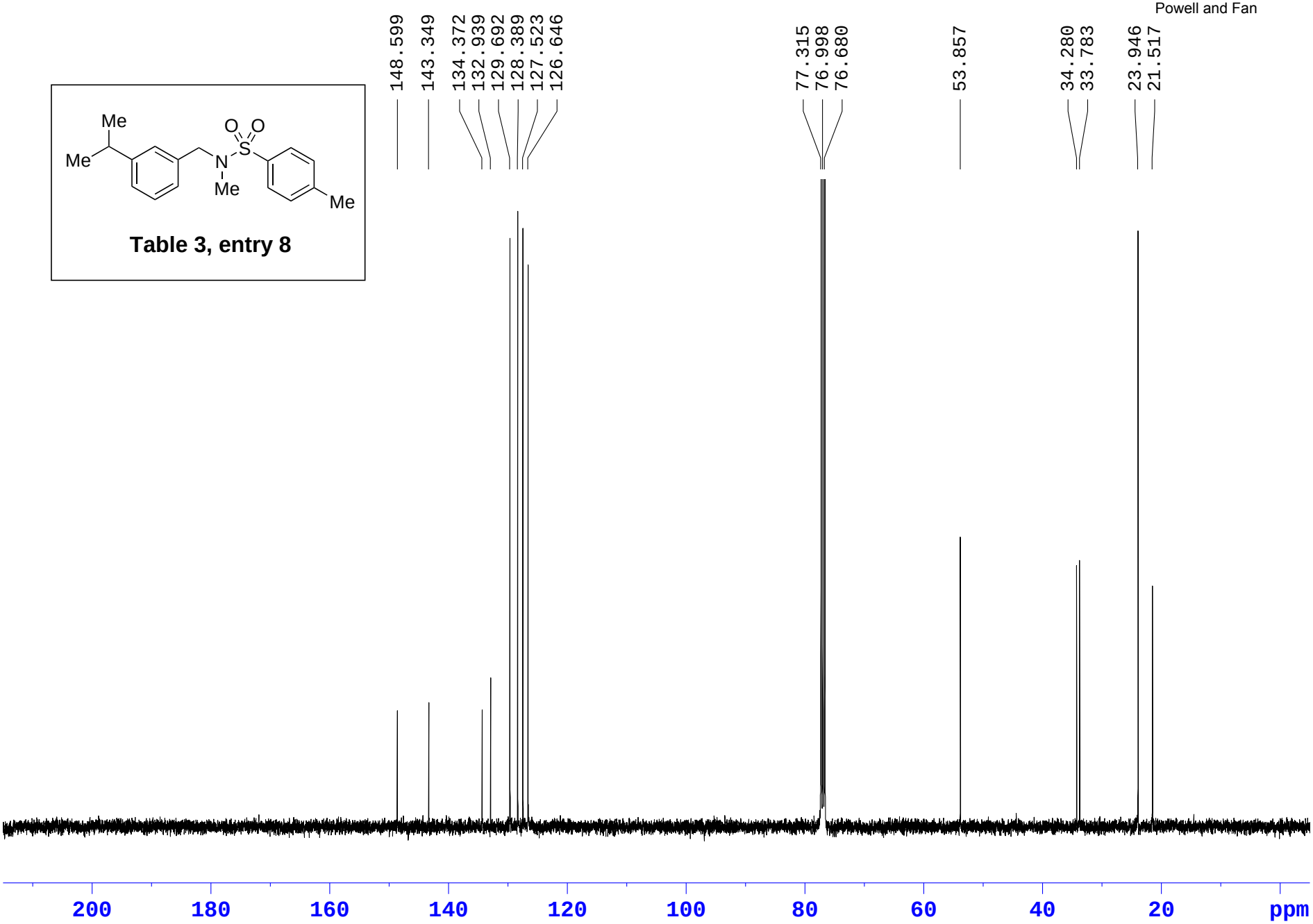
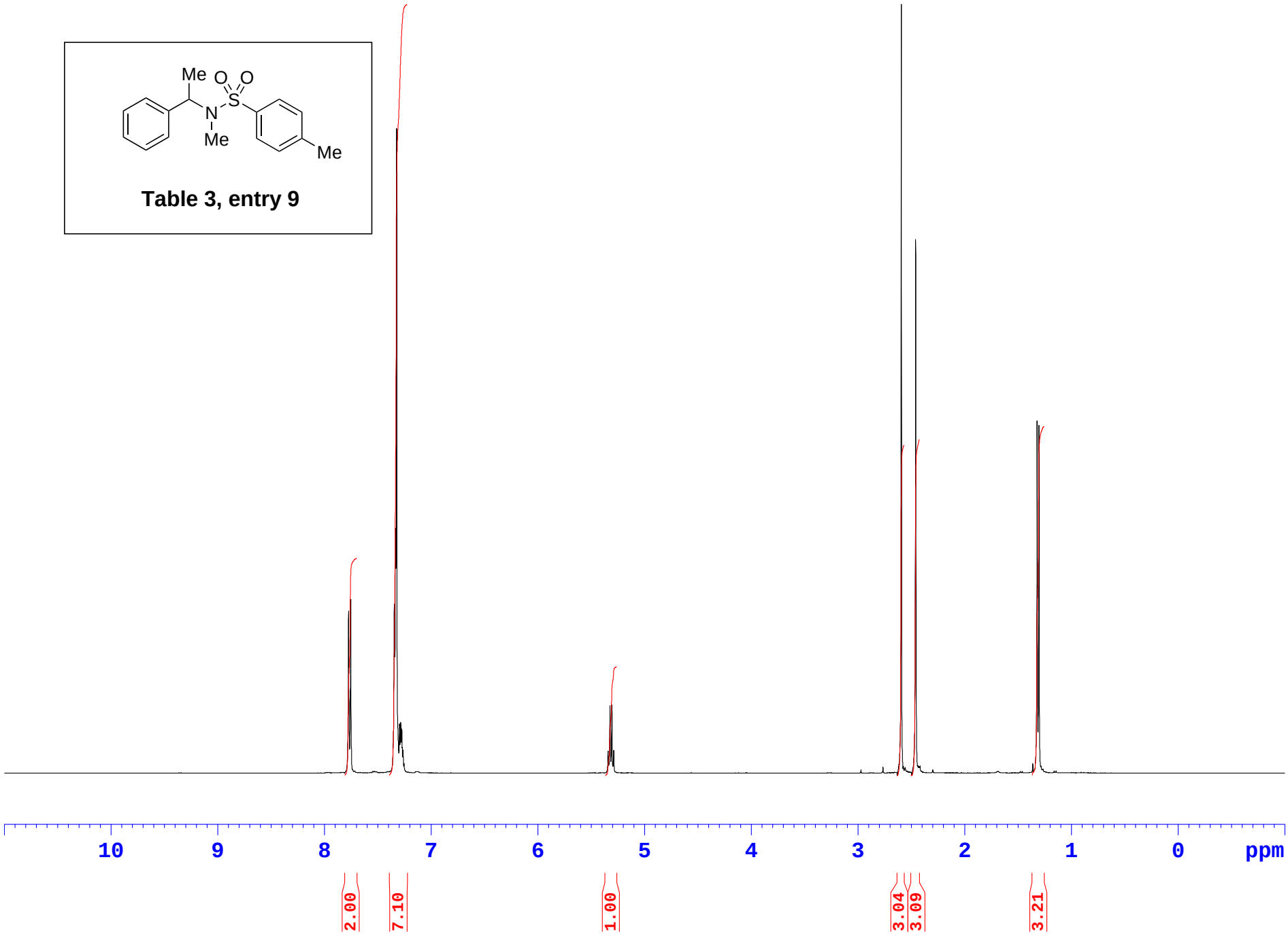
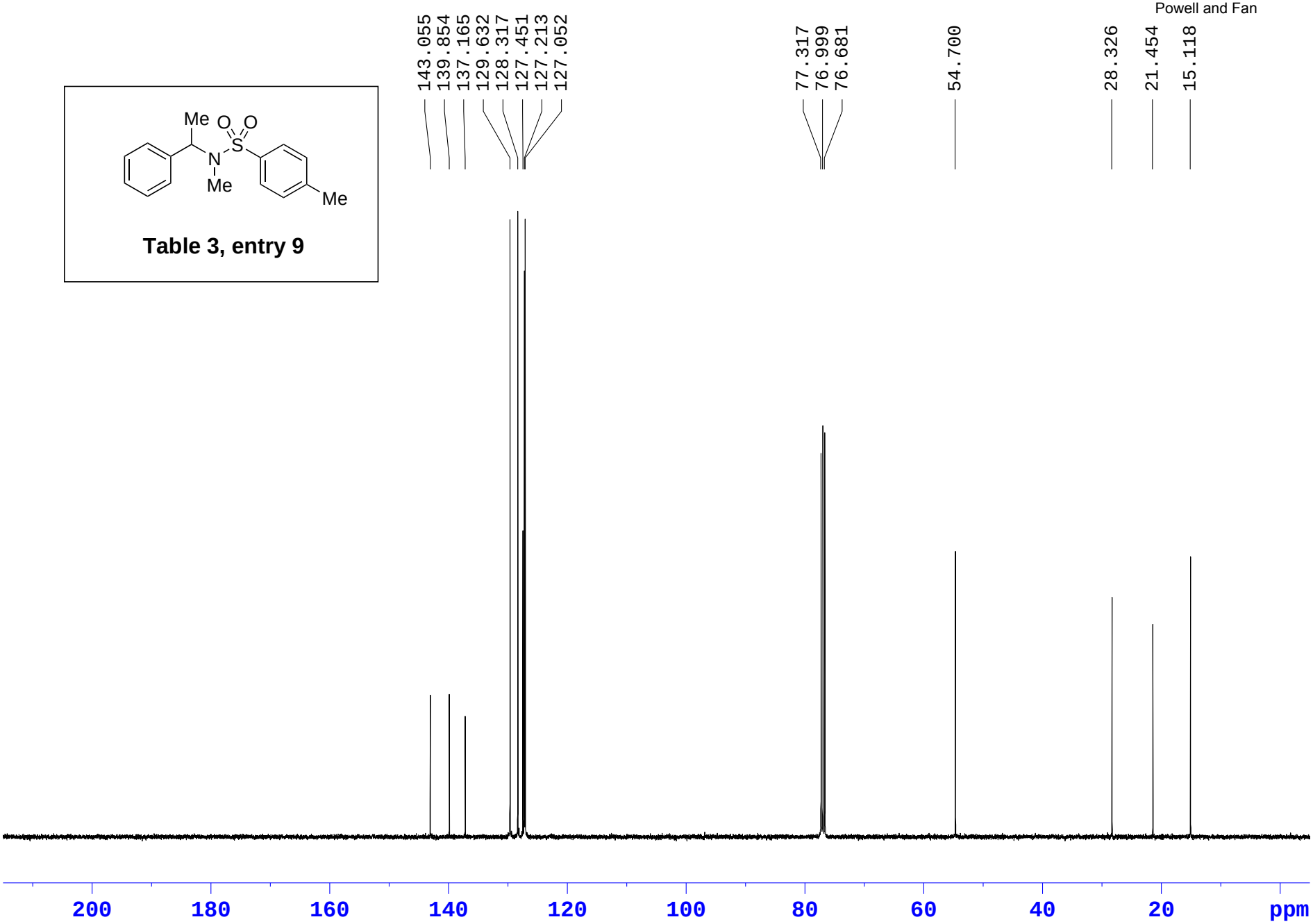
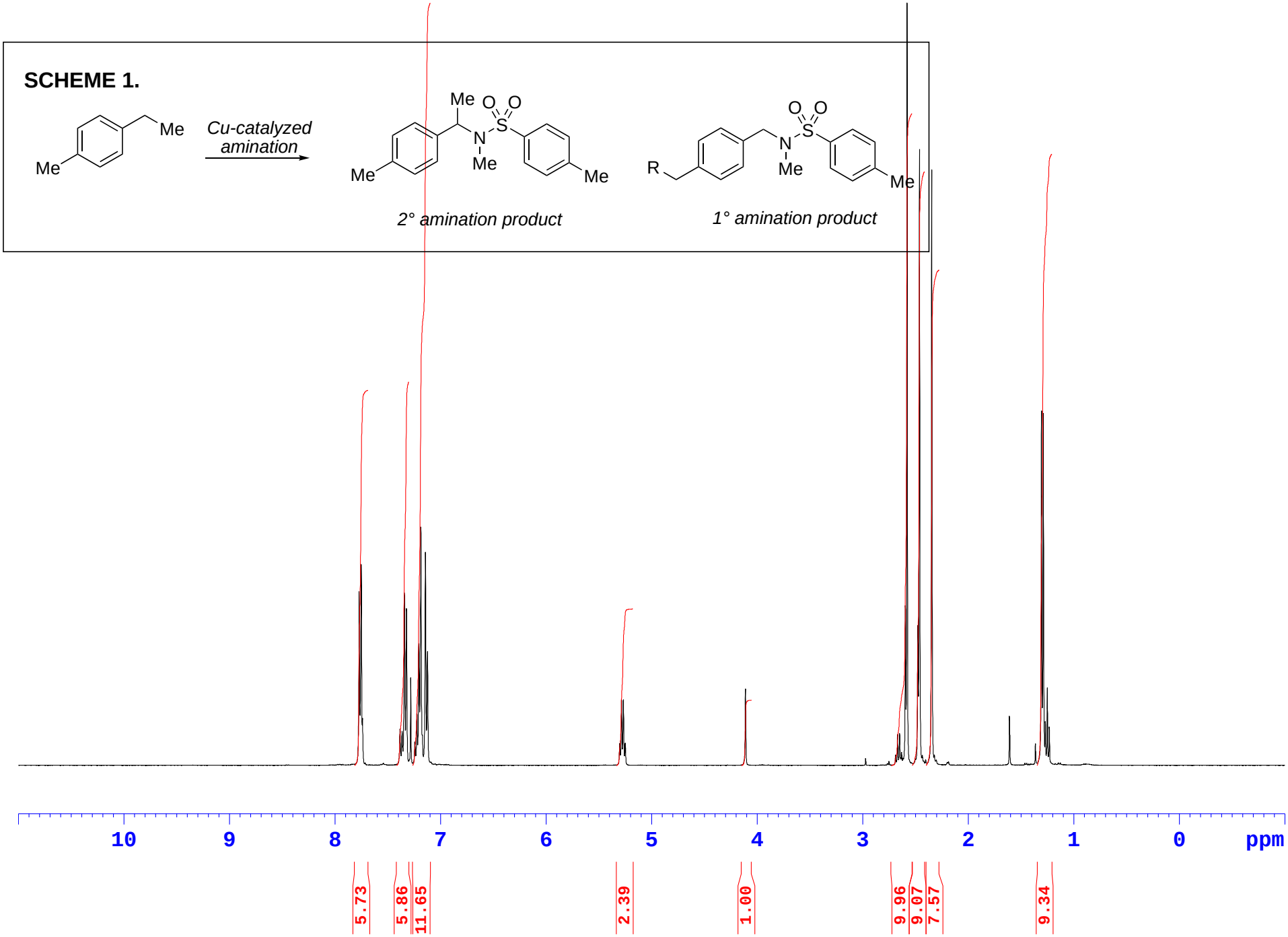
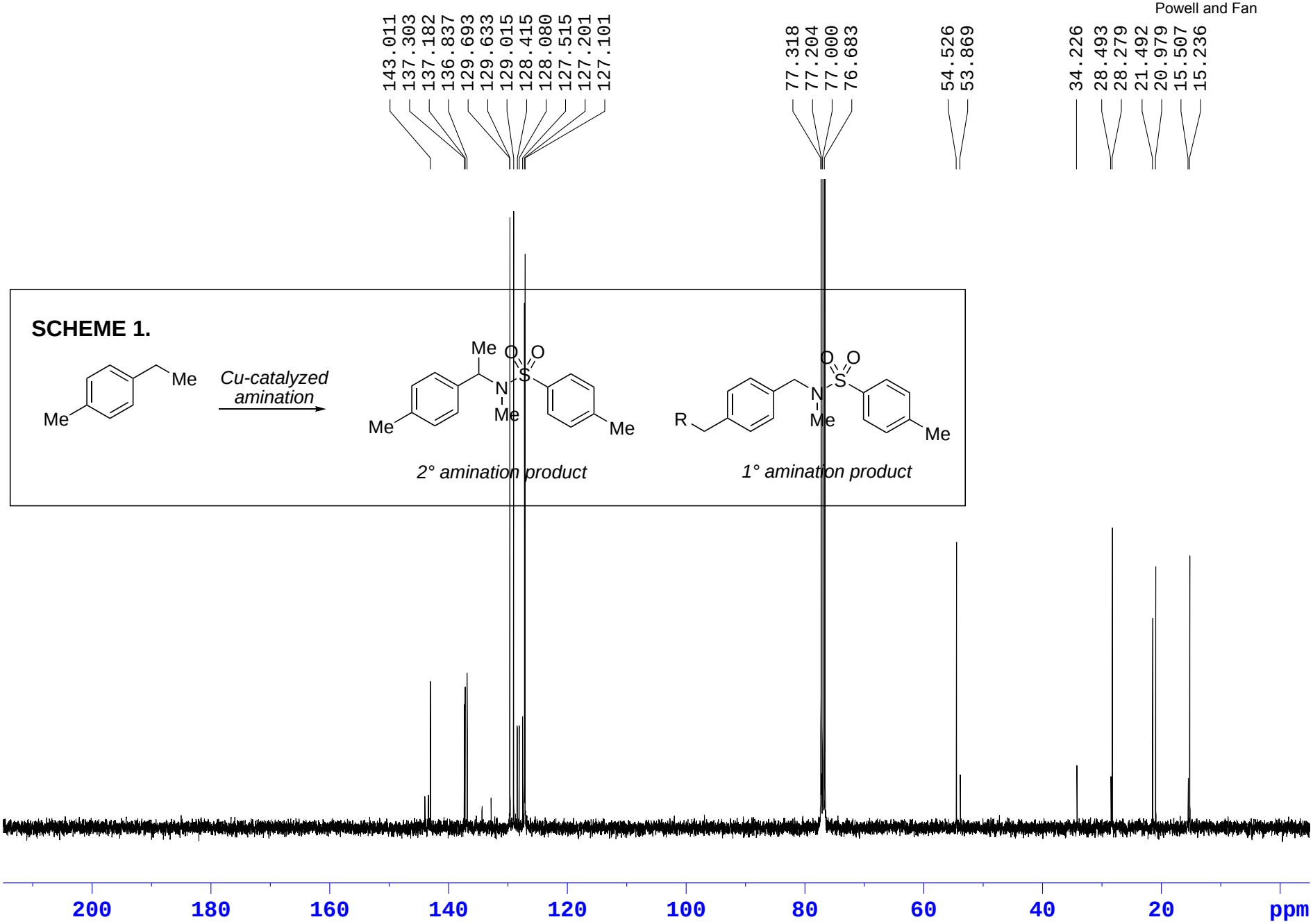

Me
Me
O O
S
N
Me
Me
Table 3, entry 8
148.599
143.349
134.372
132.939
129.692
128.389
127.523
126.646
77.315
76.998
76.680
53.857
34.280
33.783
23.946
21.517
200
180
160
140
120
100
80
60
40
20
ppm

Table 3, entry 9



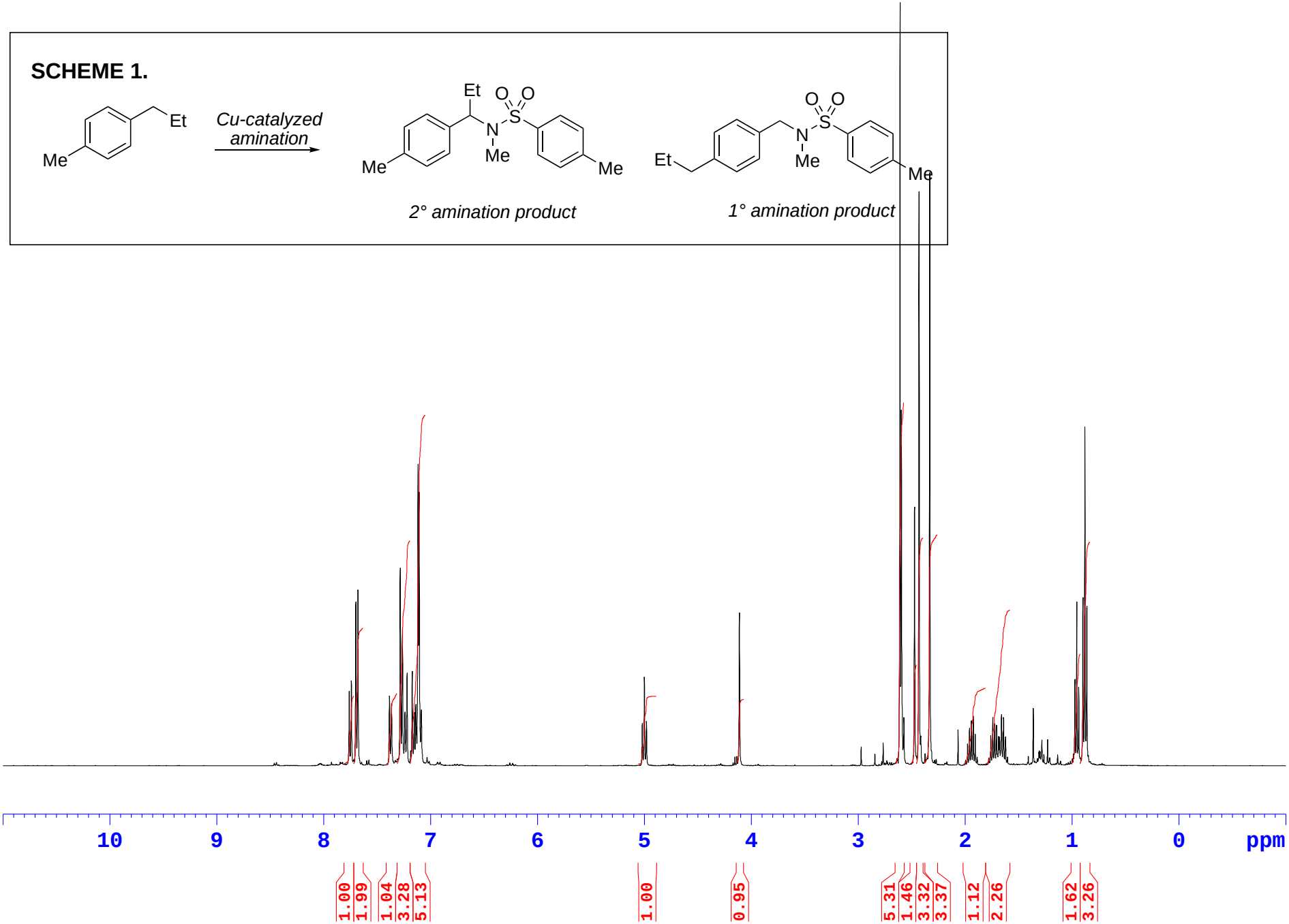

143.055
139.854
137.165
129.632
128.317
127.451
127.213
127.052
77.317
76.999
76.681
54.700
28.326
21.454
15.118
Me
O
O
S
N
Me
Me
Table 3, entry 9
200
180
160
140
120
100
80
60
40
20
ppm

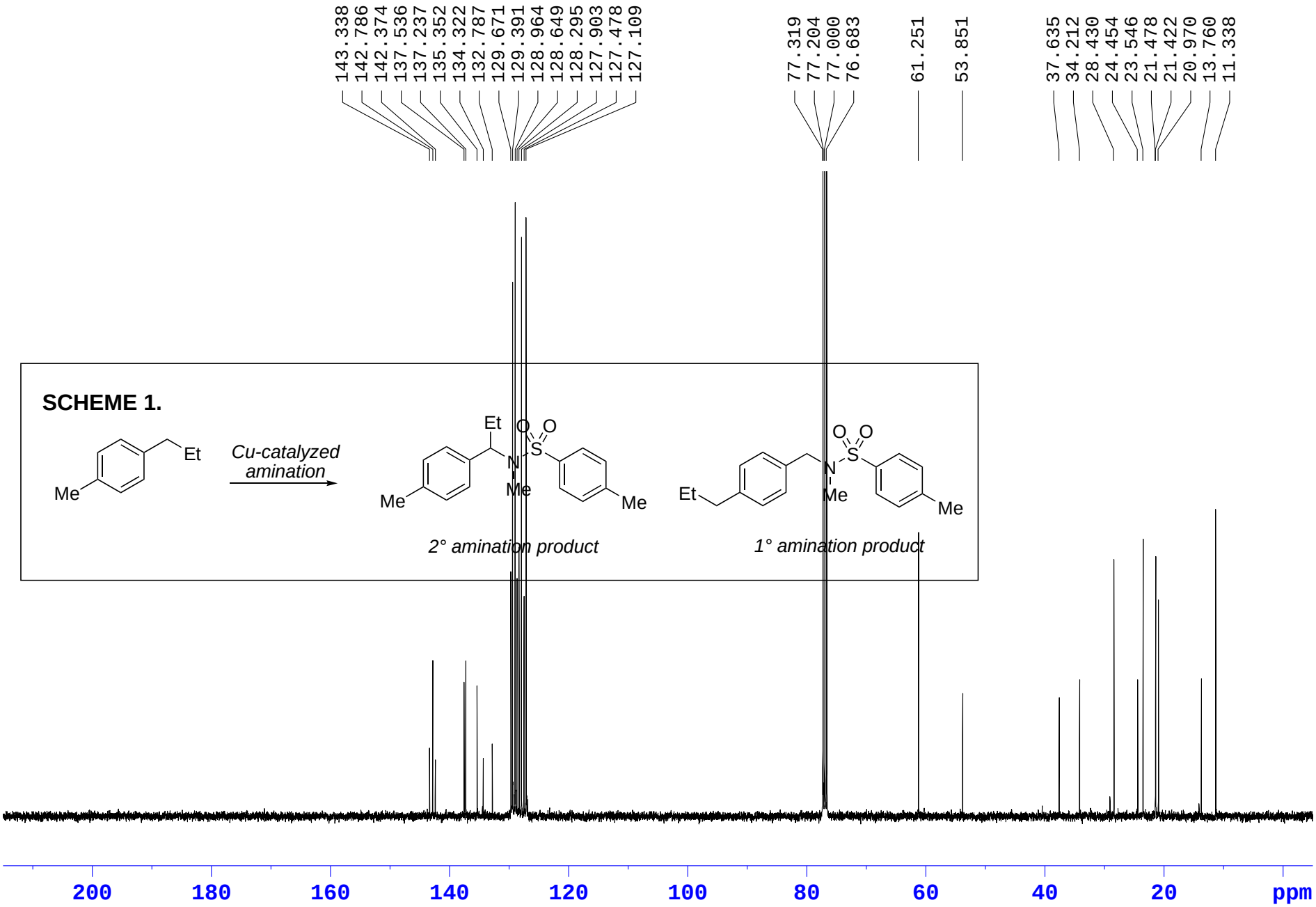

SCHEME 1.
Me
Me
Cu-catalyzed amination
Me
O O
S
N
Me
Me
Me
2° amination product
O O
S
N
Me
R
Me
1° amination product
10
9
8
7
6
5
4
3
2
1
0
ppm
5.73
5.86
11.65
2.39
1.00
9.96
9.07
7.57
9.34

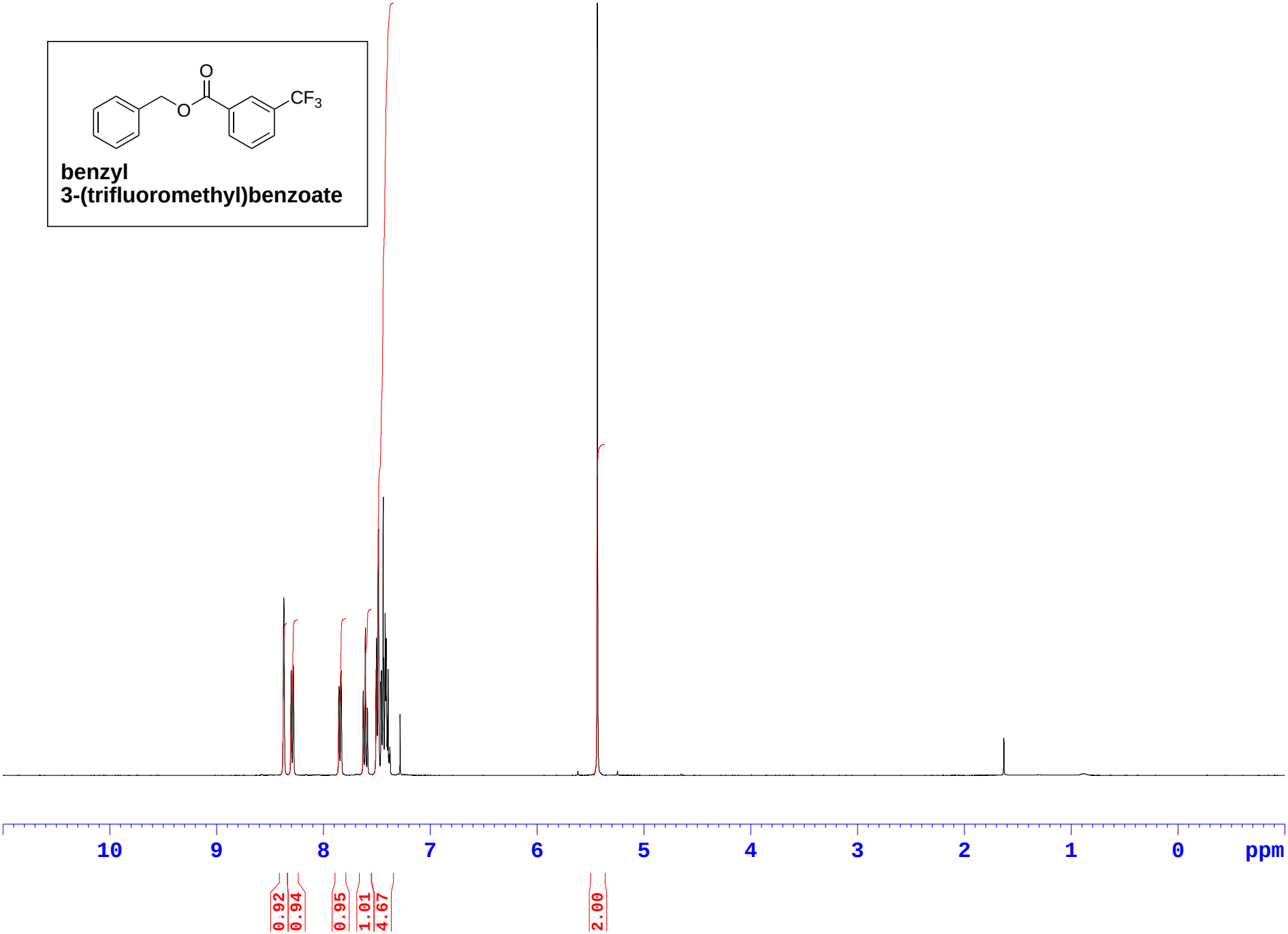

143.011
137.303
137.182
136.837
129.693
129.633
129.015
128.415
128.080
127.515
127.201
127.101
77.318
77.204
77.000
76.683
54.526
53.869
34.226
28.493
28.279
21.492
20.979
15.507
15.236
SCHEME 1.
Me
Me
Cu-catalyzed amination
Me
O
O
S
N
Me
Me
Me
2° amination product
O
O
S
N
Me
R
Me
1° amination product
200
180
160
140
120
100
80
60
40
20
ppm

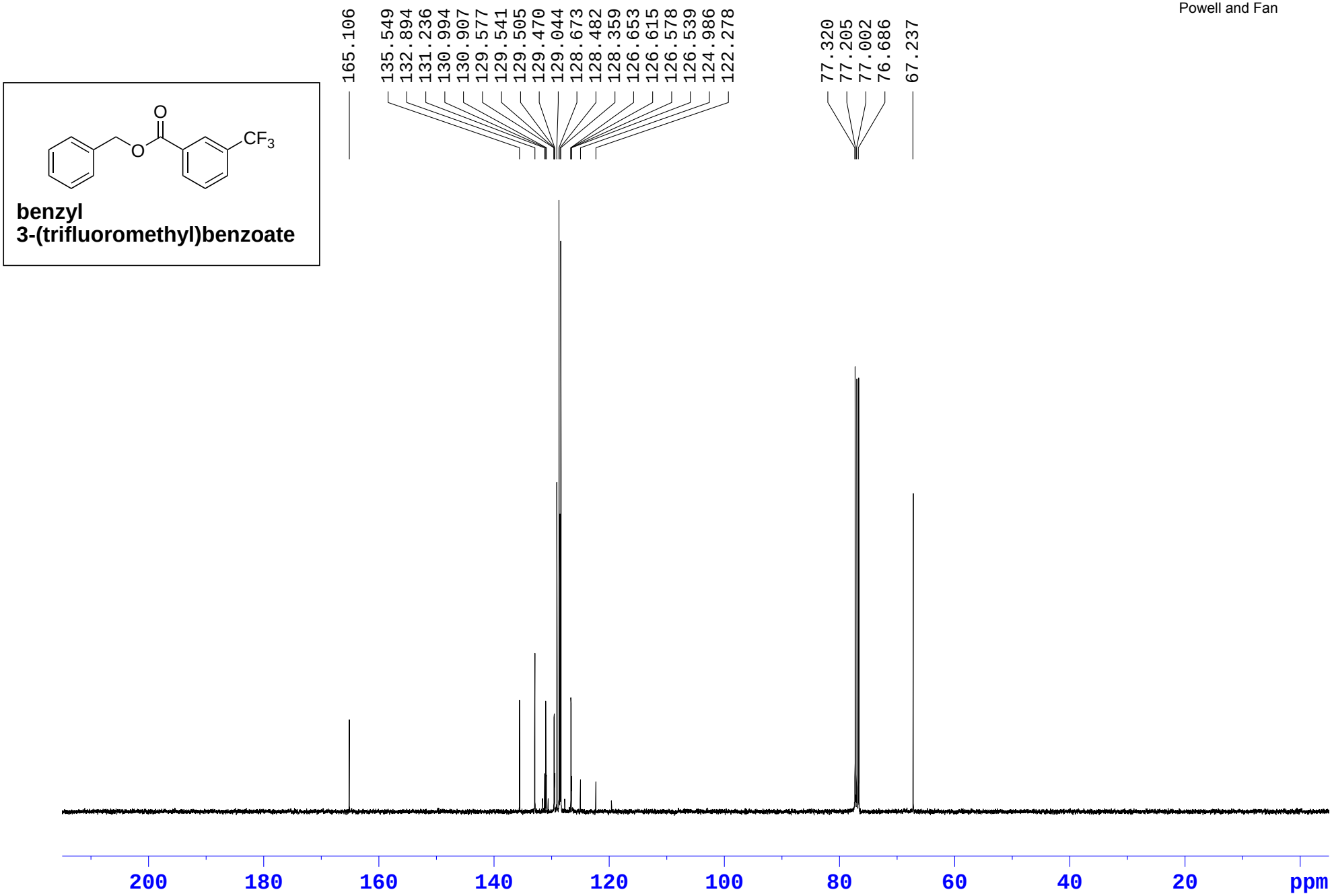
SCHEME 1.

2° amination product *1° amination product*




143.338
142.786
142.374
137.536
137.237
135.352
134.322
132.787
129.671
129.391
128.964
128.649
128.295
127.903
127.478
127.109
77.319
77.204
77.000
76.683
61.251
53.851
37.635
34.212
28.430
24.454
23.546
21.478
21.422
20.970
13.760
11.338
SCHEME 1.
Et
Me
Cu-catalyzed amination
Et
O
O
S
N
Me
Me
Me
2° amination product
O
O
S
N
Me
Et
Me
1° amination product
200
180
160
140
120
100
80
60
40
20
ppm


O
O
CF3
benzyl
3-(trifluoromethyl)benzoate
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.94
0.95
1.01
4.67
2.00


165.106
135.549
132.894
131.236
130.994
130.907
129.577
129.541
129.505
129.470
129.044
128.673
128.482
128.359
126.653
126.615
126.578
126.539
124.986
122.278
77.320
77.205
77.002
76.686
67.237
O
O
CF3
benzyl
3-(trifluoromethyl)benzoate
200
180
160
140
120
100
80
60
40
20
ppm