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An Atom-economic Approach to Carboxylic Acids via Pd-Catalyzed Direct Addition of Formic Acid to Olefins with Acetic Anhydride as Co-catalyst

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Supporting Information

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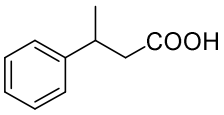
General Methods. All commercially available reagents were used without further purification. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. Olefins **1a**, **1d-f**, and **1h-p** were purchased from commercial suppliers. Olefins **1b**, **1c**, and **1g** were prepared from the corresponding ketone via Wittig reaction.

Representative procedure for hydrocarboxylation (Table 2, entry 1). To a stirred mixture of $Pd(OAc)_2$ (0.0034 g, 0.015 mmol), Xantphos (0.0087 g, 0.015 mmol), and toluene (0.10 mL) in a vial (4.0 mL) were added α-methylstyrene (**1a**) (0.0591 g, 0.50 mmol), HCOOH (0.046 g, 1.00 mmol), and Ac_2O (0.0102 g, 0.10 mmol) successively via syringe. The vial was purged with Ar to remove the air and tightly sealed with a septum cap. The reaction mixture was stirred at 70 ^{o}C for 24 h, cooled to rt, diluted with CH_2Cl_2 (3.0 mL), and poured into saturated aqueous $NaHCO_3$ (40 mL) in a separatory funnel. Upon vigorous shaking, the mixture was washed with CH_2Cl_2 (3 x 40 mL). The aqueous layer was acidified with 2N HCl (40 mL), extracted with CH_2Cl_2 (3 x 30 mL), dried over Na_2SO_4, filtered, and concentrated to give carboxylic acid **2a** as a light yellow oil (0.0758 g, 93% yield) [for Table 2, entry 8, the product was purified by flash chromatography [(silica gel, eluent: hexane/ethyl acetate = 20/1)].

Procedures for gram scale hydrocarboxylation reaction (Scheme 3). To a stirred mixture of $Pd(OAc)_2$ (0.0674 g, 0.30 mmol), Xantphos (0.1736 g, 0.30 mmol), and toluene (2.0 mL) in a flask (25.0 mL) were added α-methylstyrene (**1a**) (1.180 g, 10.0 mmol), HCOOH (0.920 g, 20.0 mmol), and Ac_2O (0.204 g, 2.0 mmol) successively via syringe. The flask was purged with Ar to remove the air and connected with a condenser having a balloon on the top. The reaction mixture was stirred at 70 ^{o}C for 48 h, cooled to rt, diluted with CH_2Cl_2 (3.0 mL), and poured into 1N NaOH (40 mL) in a separatory funnel. Upon

vigorous shaking, the mixture was washed with CH_2Cl_2 (3 x 100 mL). The aqueous layer was acidified with 2N HCl (40 mL), extracted with CH_2Cl_2 (3 x 80 mL), dried over Na_2SO_4, filtered, and concentrated to give carboxylic acid **2a** as a light yellow oil (1.477 g, 90 % yield).

Table 2, entry 1



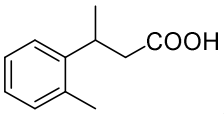
2a

Light yellow oil; IR (film) 2966, 1707, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 2H), 7.25-7.16 (m, 3H), 3.33-3.20 (m, 1H), 2.65 (dd, *J* = 15.5, 6.8 Hz, 1H), 2.56 (dd, *J* = 15.5, 8.2 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 145.6, 128.7, 126.9, 126.7, 42.8, 36.3, 22.0.

Sabbani, S.; Hedenström, E.; Andersson, J. *Tetrahedron: Asymmetry* **2007**, *18*, 1712.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

Table 2, entry 2



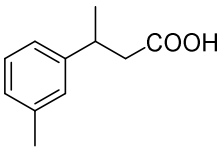
2b

White soild; mp. 47-50 ^oC; IR (film) 2967, 1708, 1412 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.08 (m, 4H), 3.61-3.48 (m, 1H), 2.70 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.58 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.39 (s, 3H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 143.8, 135.5, 130.7, 126.6, 126.4, 125.2, 42.0, 31.4, 21.5, 19.6.

Sun, X. F.; Zhou, L.; Wang, C. J.; Zhang, X. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2623.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

Table 2, entry 3



2c

Light yellow oil; IR (film) 2965, 1708, 1298 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.14 (m, 1H), 7.07-6.96 (m, 3H), 3.30-3.16 (m, 1H), 2.66 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.53 (dd, *J* = 15.5, 8.4 Hz, 1H), 2.33 (s, 3H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 145.6, 138.3, 128.7, 127.7, 127.5, 123.9, 42.8, 36.2, 22.1, 21.7.

Sun, X. F.; Zhou, L.; Wang, C. J.; Zhang, X. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2623.
Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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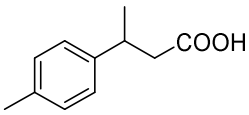

2d

White soild; mp. 89-92 °C; IR (film) 2965, 1702, 1315 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 4H), 3.34-3.16 (m, 1H), 2.66 (dd, *J* = 15.5, 6.8 Hz, 1H), 2.57 (dd, *J* = 15.5, 8.2 Hz, 1H), 2.33 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 142.6, 136.2, 129.5, 126.8, 42.9, 36.0, 22.2, 21.2.

Davisson, V. J.; Poulter, C. D.; *J. Am. Chem. Soc.* **1993**, *115*, 1245.
Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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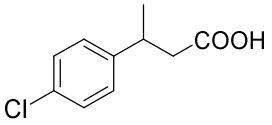

2e

White solid; mp. 92-94 °C; IR (film) 2962, 1706, 1316 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.31-3.18 (m, 1H), 2.63 (dd, *J* = 15.6, 7.3 Hz, 1H), 2.56 (dd, *J* = 15.6, 7.8 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 178.5, 144.0, 132.4, 128.9, 128.3, 42.6, 35.8, 22.1.

Sun, X. F.; Zhou, L.; Wang, C. J.; Zhang, X. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2623.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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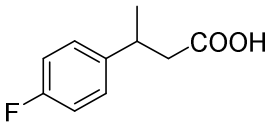
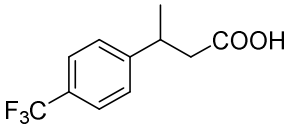


2f

White solid; mp. 63-66 °C; IR (film) 2976, 1705, 1511 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.13 (m, 2H), 7.03-6.93 (m, 2H), 3.30-3.22 (m, 1H), 2.63 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.57 (dd, *J* = 15.6, 7.8 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 161.6 (d, *J* = 243 Hz), 141.2 (d, *J* = 3 Hz), 128.3 (d, *J* = 8 Hz), 115.5 (d, *J* = 22 Hz), 42.9, 35.7, 22.2; HRMS (EI) Calcd for $C_{10}H_{11}FO_2$ (M): 182.0743; Found: 182.0747.

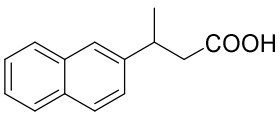
Table 2, entry 7



2g

White solid; mp. 90-92 °C; IR (film) 2972, 1709, 1328 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.38-3.30 (m, 1H), 2.68 (dd, *J* = 15.8, 7.3 Hz, 1H), 2.61 (dd, *J* = 15.8, 7.7 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 149.6, 129.1 (q, *J* = 32 Hz), 127.4, 125.8, 124.4 (q, *J* = 270 Hz), 42.4, 36.2, 21.9; HRMS (EI) Calcd for $C_{11}H_{11}F_3O_2$ (M): 232.0711; Found: 232.0706.

Table 2, entry 8



2h

Light yellow solid; mp. 111-114 °C; IR (film) 2972, 1697, 1295 cm^{-1}; ^1H NMR (400

MHz, $CDCl_3$) δ 7.89-7.78 (m, 3H), 7.69 (s, 1H), 7.53-7.43 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 3.54-3.41 (m, 1H), 2.81 (dd, *J* = 15.5, 6.8 Hz, 1H), 2.69 (dd, *J* = 15.6, 8.2 Hz, 1H), 1.43 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 143.1, 133.7, 132.6, 128.5, 127.9, 127.8, 126.2, 125.7, 125.6, 125.1, 42.7, 36.4, 22.1.

Sun, X. F.; Zhou, L.; Wang, C. J.; Zhang, X. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2623.
Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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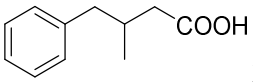

2i

Light yellow oil; IR (film) 2961, 1707, 1292 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.23-7.11 (m, 3H), 2.63 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.51 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.37 (dd, *J* = 14.8, 5.5 Hz, 1H), 2.33-2.21 (m, 1H), 2.16 (dd, *J* = 14.7, 7.8 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 140.2, 129.4, 128.5, 126.3, 43.1, 41.0, 32.3, 19.8.

Sun, X. F.; Zhou, L.; Wang, C. J.; Zhang, X. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 2623.
Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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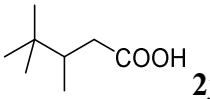
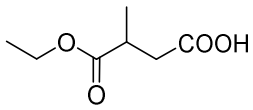


2j

Light yellow oil; IR (film) 2964, 1709, 1413 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.54 (dd, *J* = 15.0, 3.2 Hz, 1H), 1.98 (dd, *J* = 14.9, 10.8 Hz, 1H), 1.86-1.73 (m, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 40.0, 37.6, 32.9, 27.3, 15.2.

Aurell M. J.; Domingo, L. R.; Mestres, R.; Munoz, E.; Zaragoza, R. J. *Tetrahedron* **1999**, *55*, 815.

Table 2, entry 11

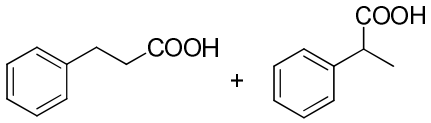


2k

Light yellow oil; IR (film) 2983, 1732, 1712, 1181 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.09 (q, *J* = 7.1 Hz, 2H), 2.89-2.77 (m, 1H), 2.72 (dd, *J* = 16.8, 8.2 Hz, 1H), 2.39 (dd, *J* = 16.8, 5.8 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 175.4, 61.0, 37.5, 35.8, 17.1, 14.2.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

Table 2, entry 12



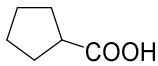
2l

Light yellow oil; IR (film) 3029, 1709, 1454 cm^{-1}; linear isomer:[1] ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 5H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 140.3, 128.7, 128.4, 126.6, 35.8, 30.7. branched isomer:[2] ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 5H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 140.0, 128.9, 127.8, 127.6, 45.6, 18.3.

1) Tanaka, H.; Chou, J.; Mine, M.; Kuroboshi, M. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1745.

2) Milne, J. E.; Storz, T.; Colyer, J. T.; Thiel, O. R.; Seran, M. D.; Larsen, R. D.; Murry, J. A. *J. Org. Chem.* **2011**, *76*, 9519.

Table 2, entry 13



2m

Light yellow oil; IR (film) 2960, 1703, 1233 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.84-2.70 (m, 1H), 1.99-1.77 (m, 4H), 1.77-1.65 (m, 2H), 1.65-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 43.9, 30.2, 26.0.

Zhao, J. F.; Christian, M. L.; Armido, S. *Adv. Synth. Catal.* **2013**, *355*, 1098.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

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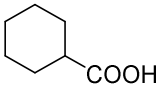


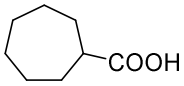
2n

Light yellow oil; IR (film) 2932, 1705, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.01-1.86 (m, 2H), 1.86-1.69 (m, 2H), 1.69-1.55 (m, 1H), 1.55-1.37 (m, 2H), 1.37-1.15 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 43.2, 28.9, 25.9, 25.5.

Zhao, J. F.; Christian, M. L.; Armido, S. *Adv. Synth. Catal.* **2013**, *355*, 1098.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

Table 2, entry 15

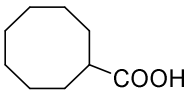


2o

Light yellow oil; IR (film) 2927, 1702, 1226 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57-2.44 (m, 1H), 2.03-1.90 (m, 2H), 1.80-1.63 (m, 4H), 1.63-1.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.1, 45.0, 30.8, 28.5, 26.4.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.

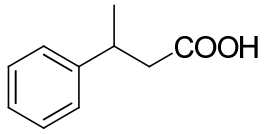
Table 2, entry 16



2p

Light yellow oil; IR (film) 2923, 1702, 1230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60-2.48 (m, 1H), 1.99-1.84 (m, 2H), 1.81-1.64 (m, 4H), 1.64-1.42 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 43.7, 28.6, 27.0, 26.3, 25.4.

Wang, Y.; Ren, W.; Li, J.; Wang, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 5960.



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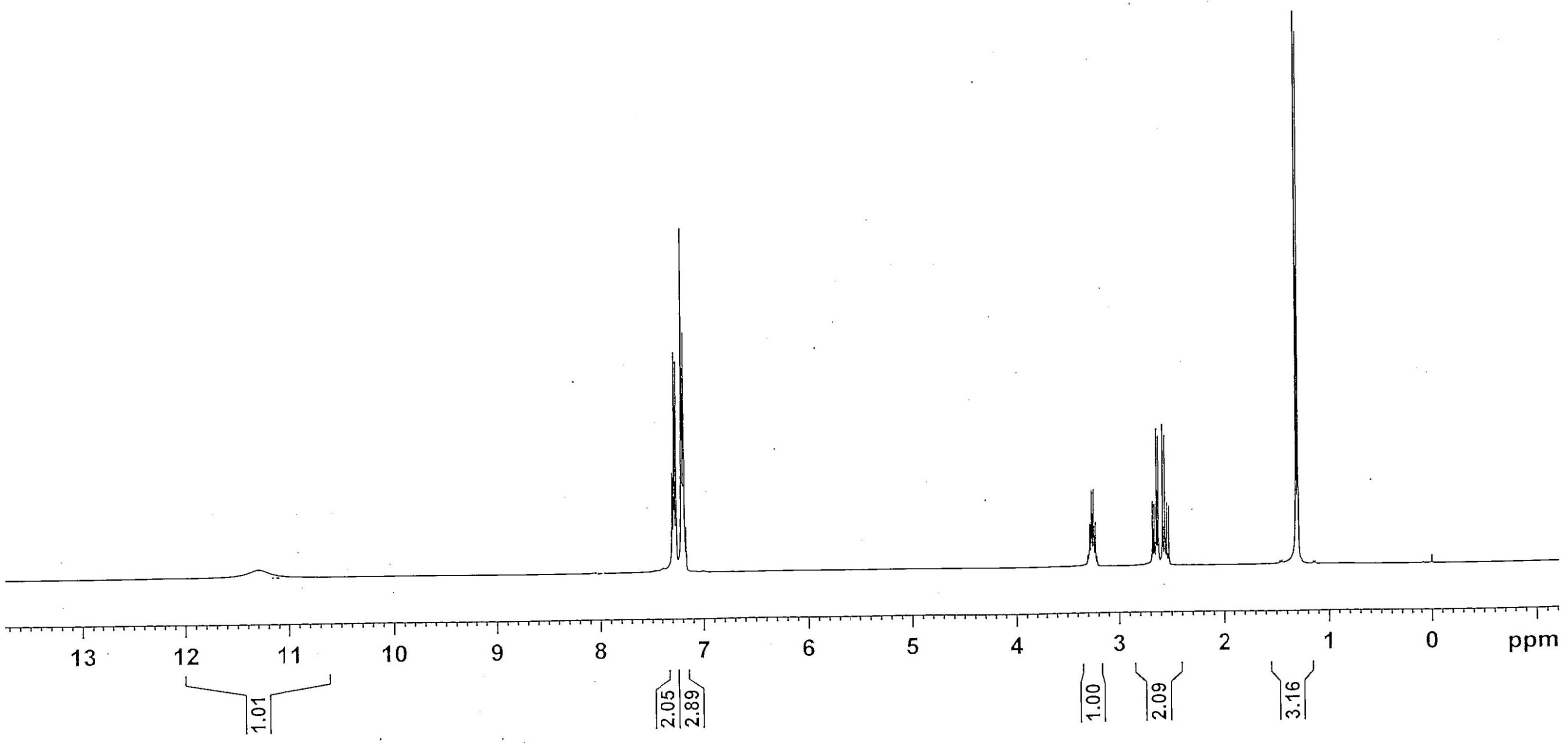

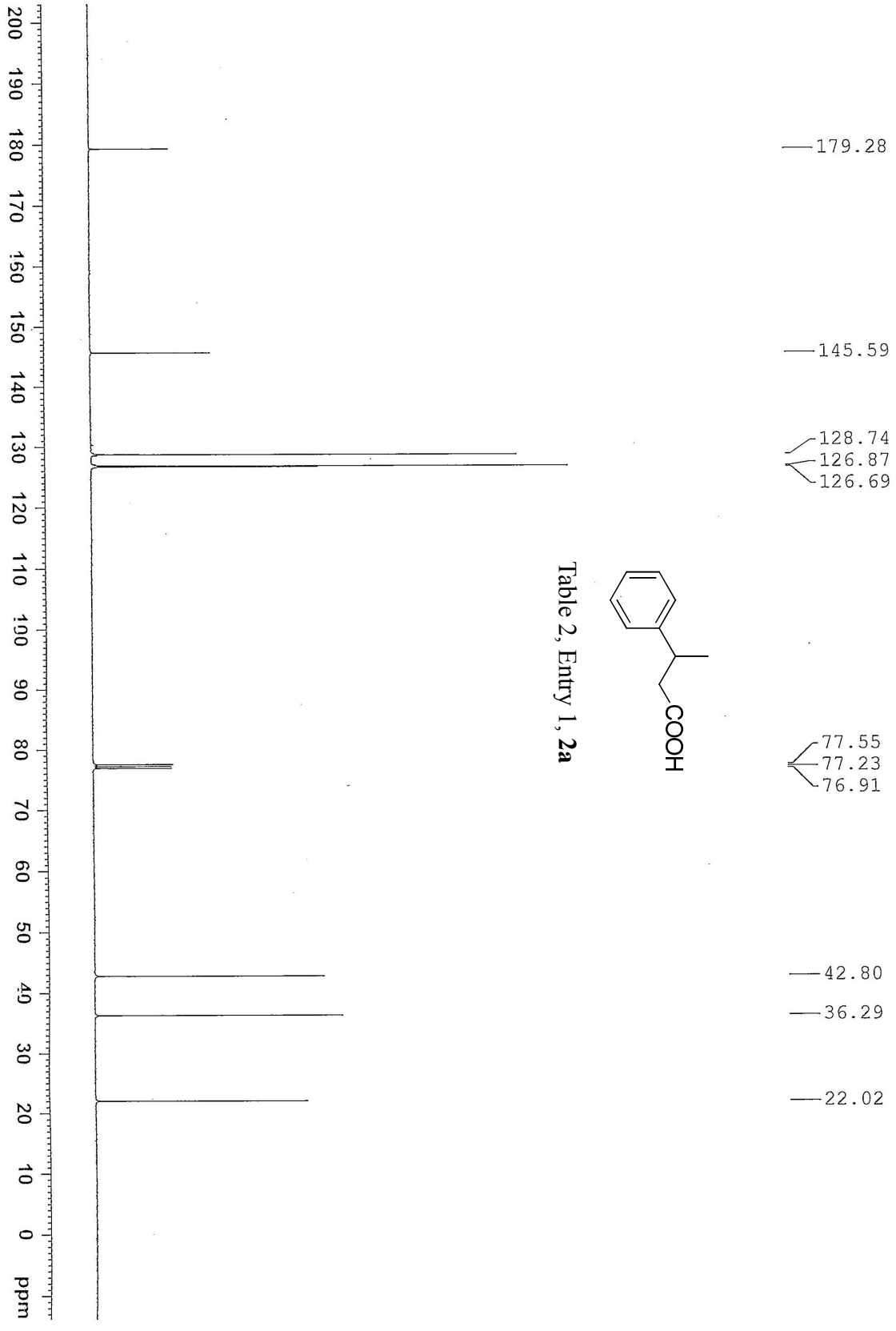

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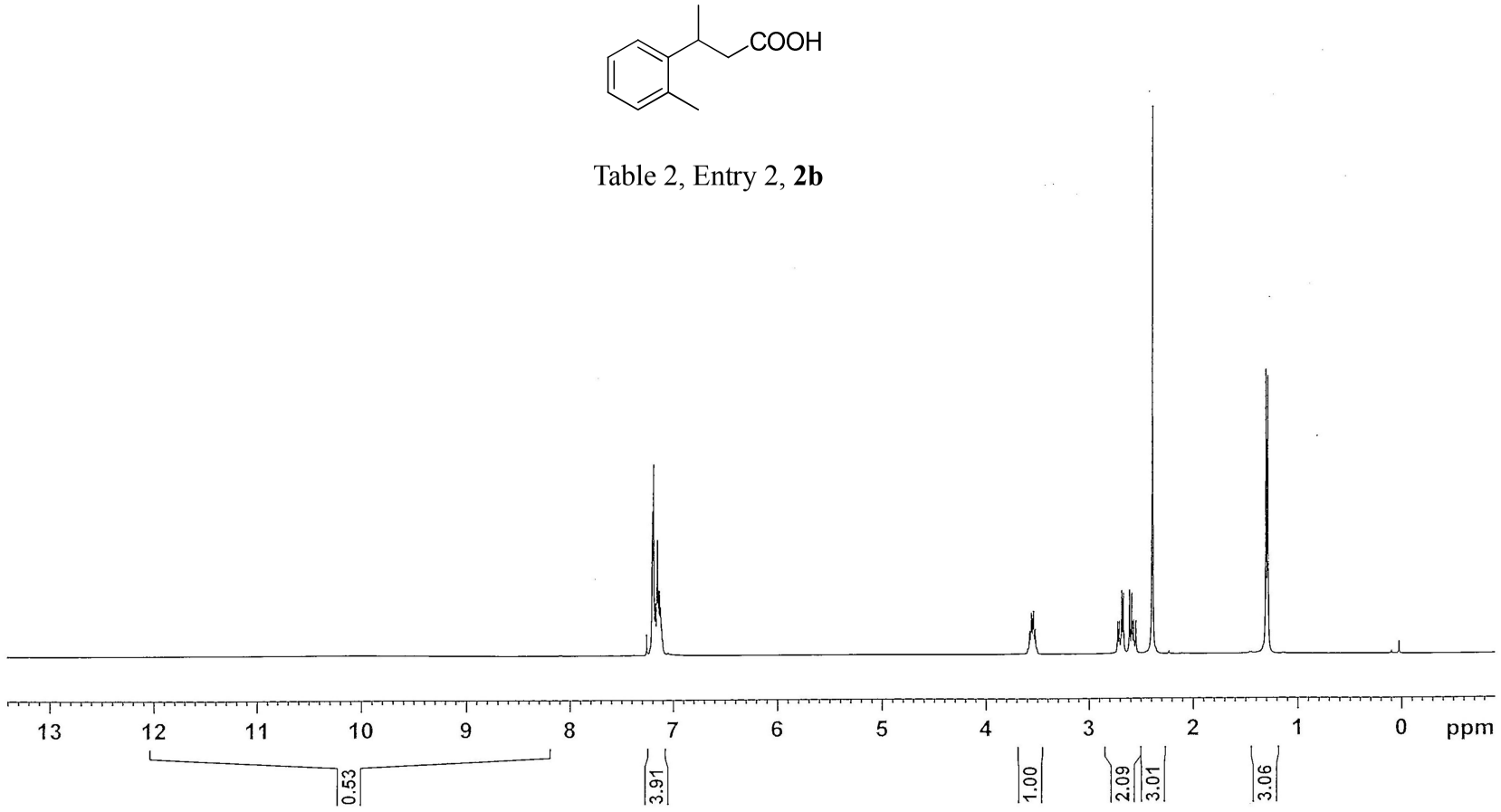

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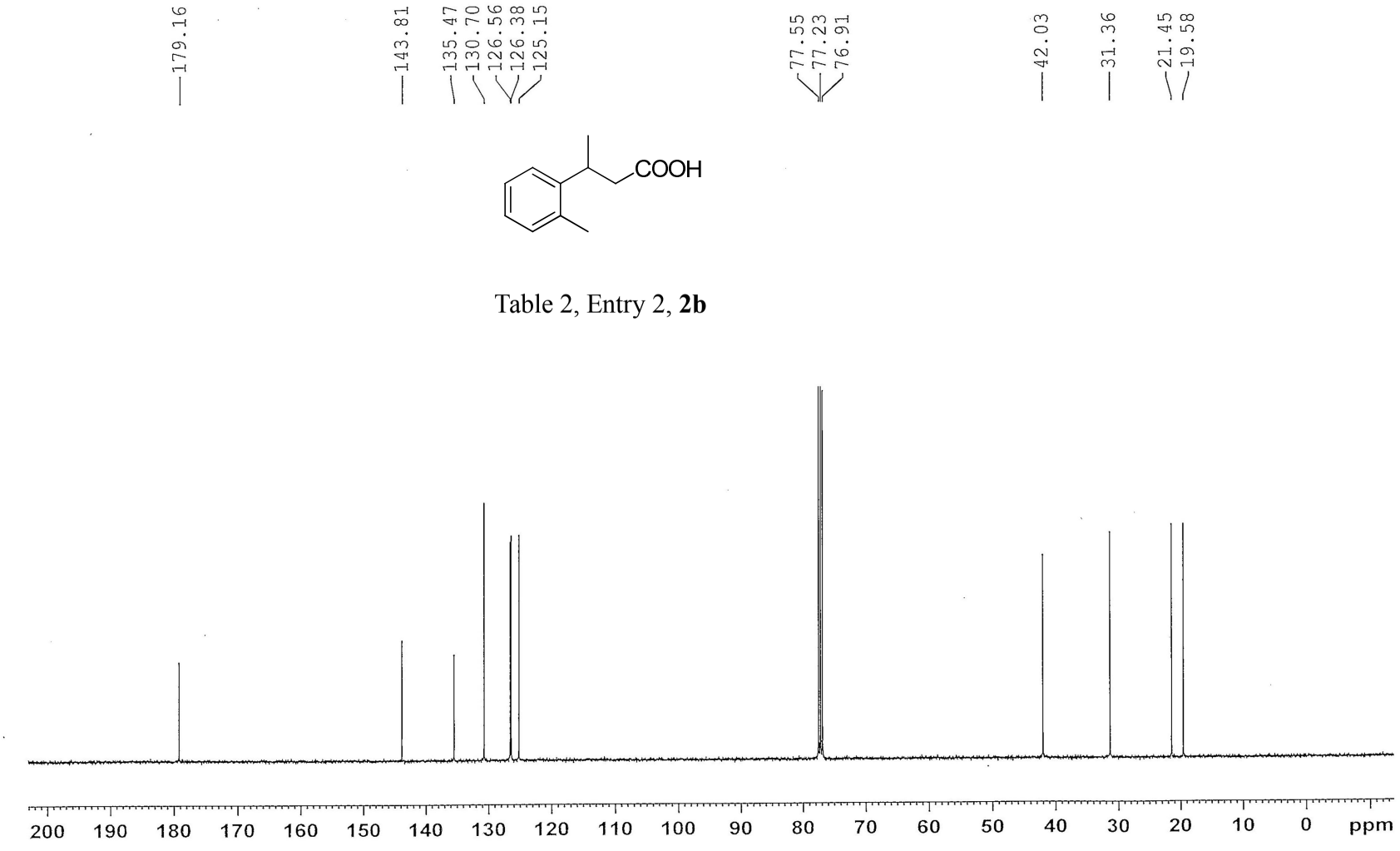


Table 2, Entry 2, **2b**

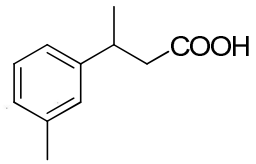
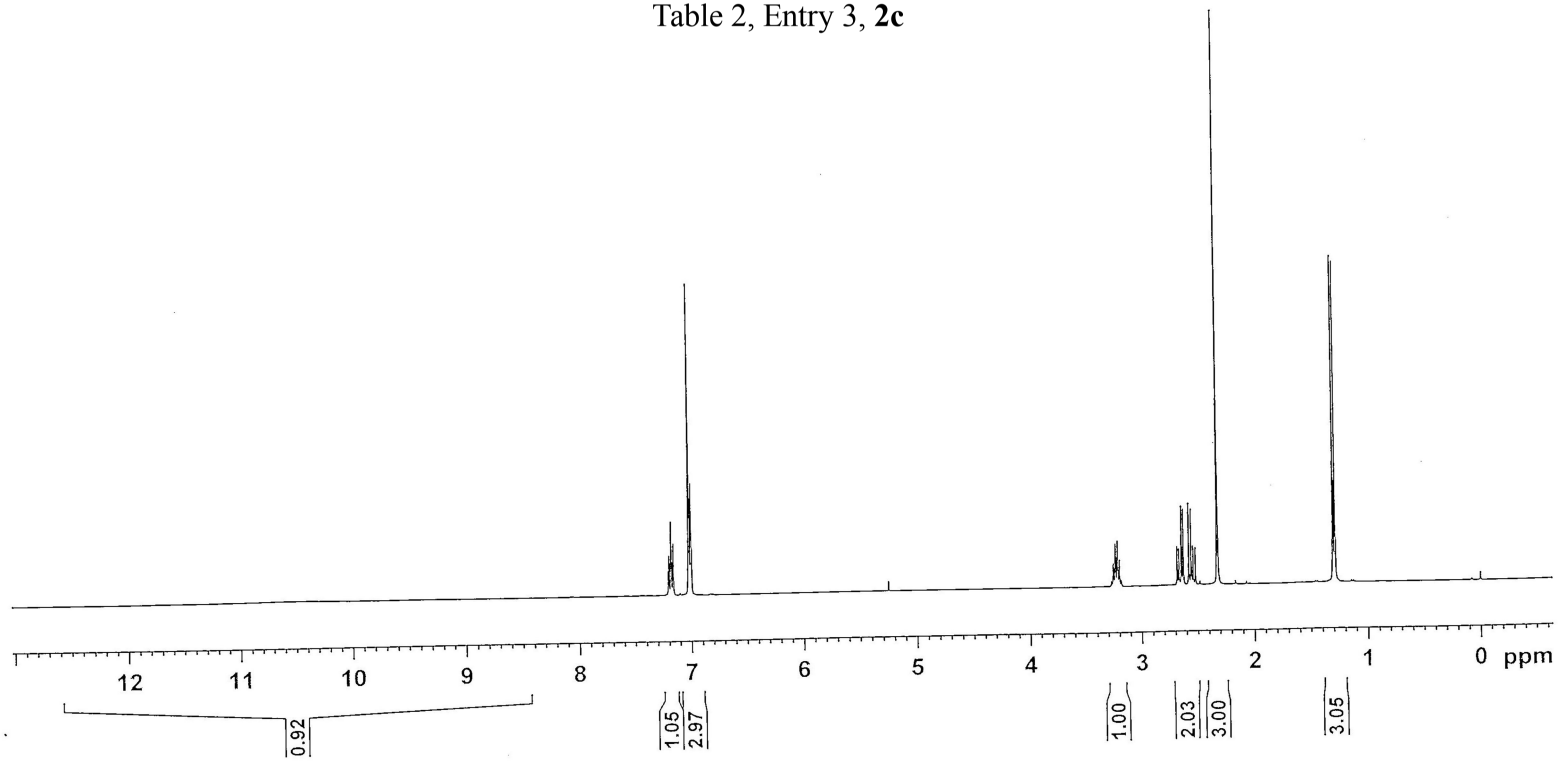


Table 2, Entry 3, **2c**



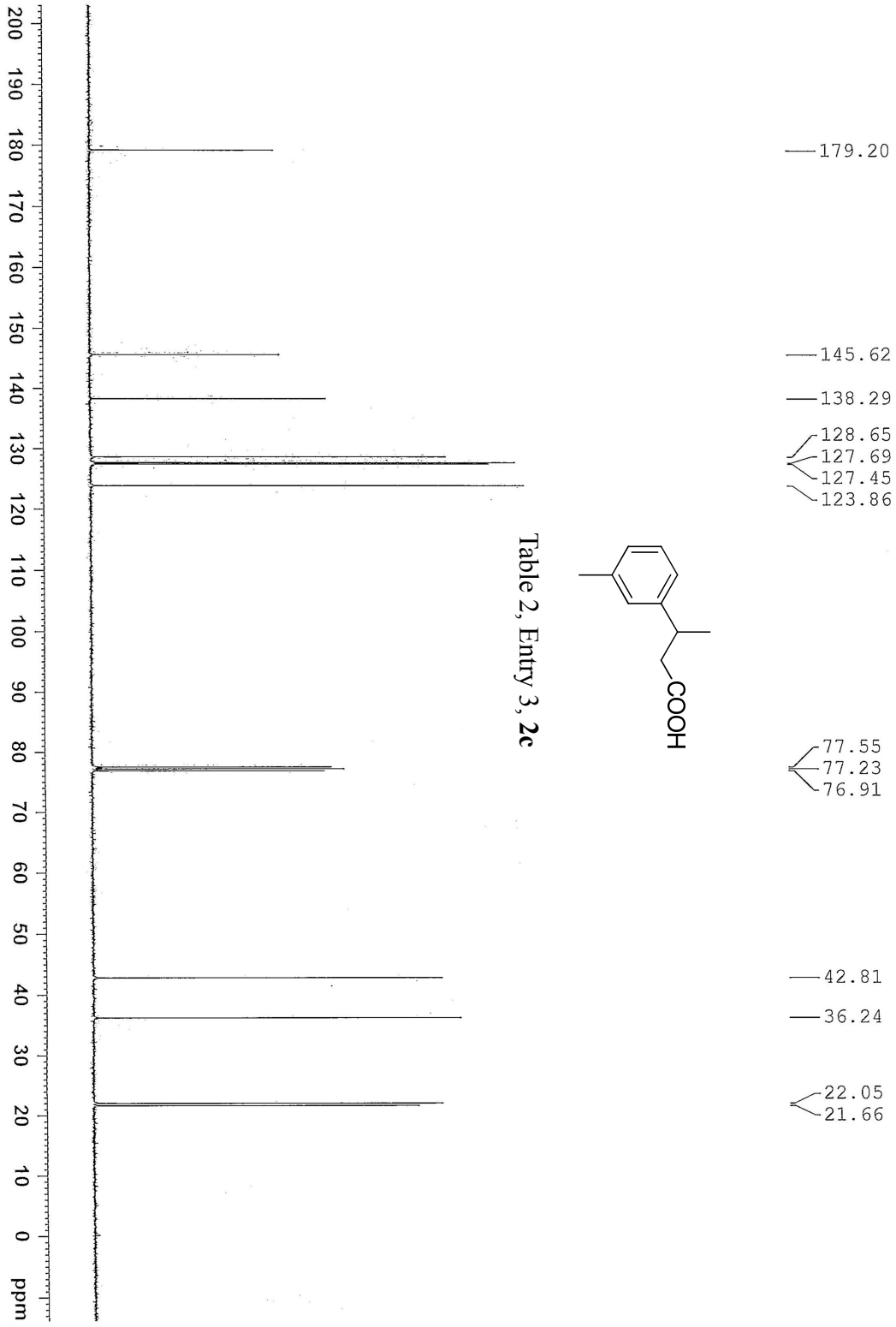


Table 2, Entry 3, **2c**

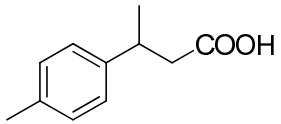
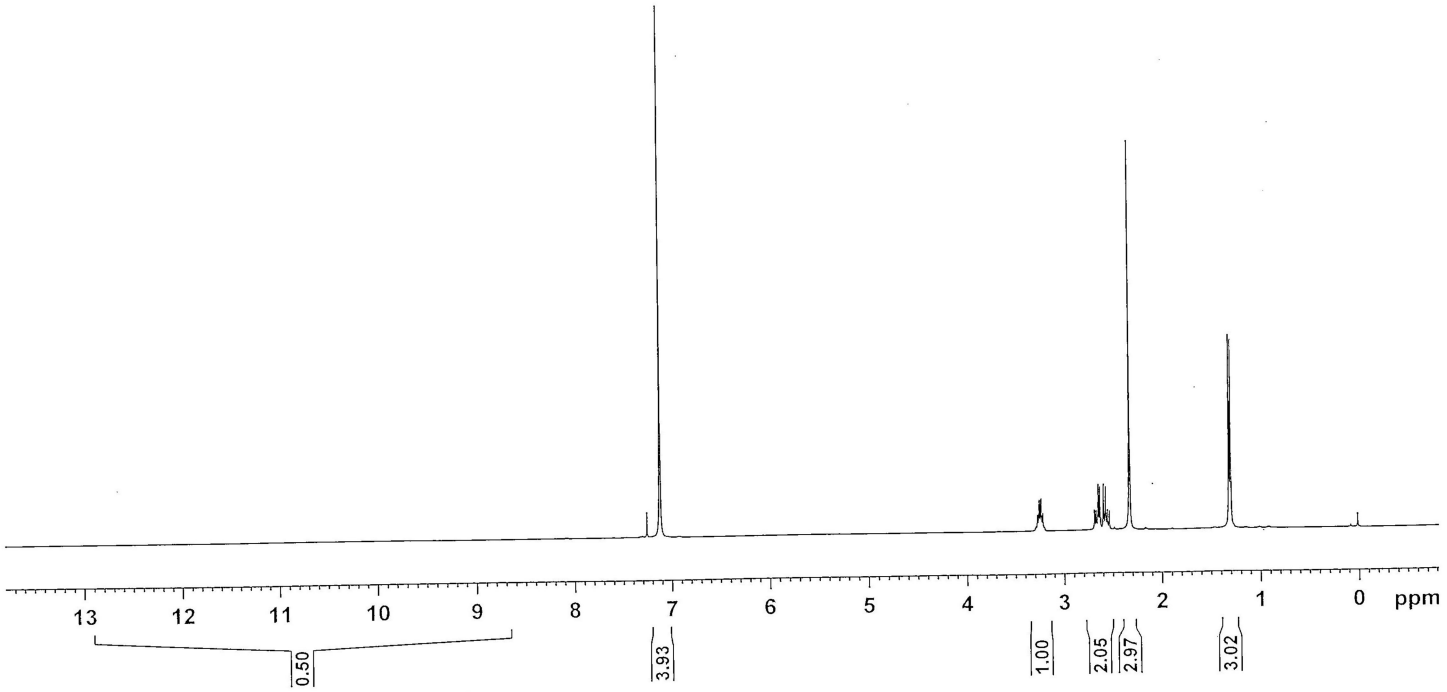


Table 2, Entry 4, **2d**



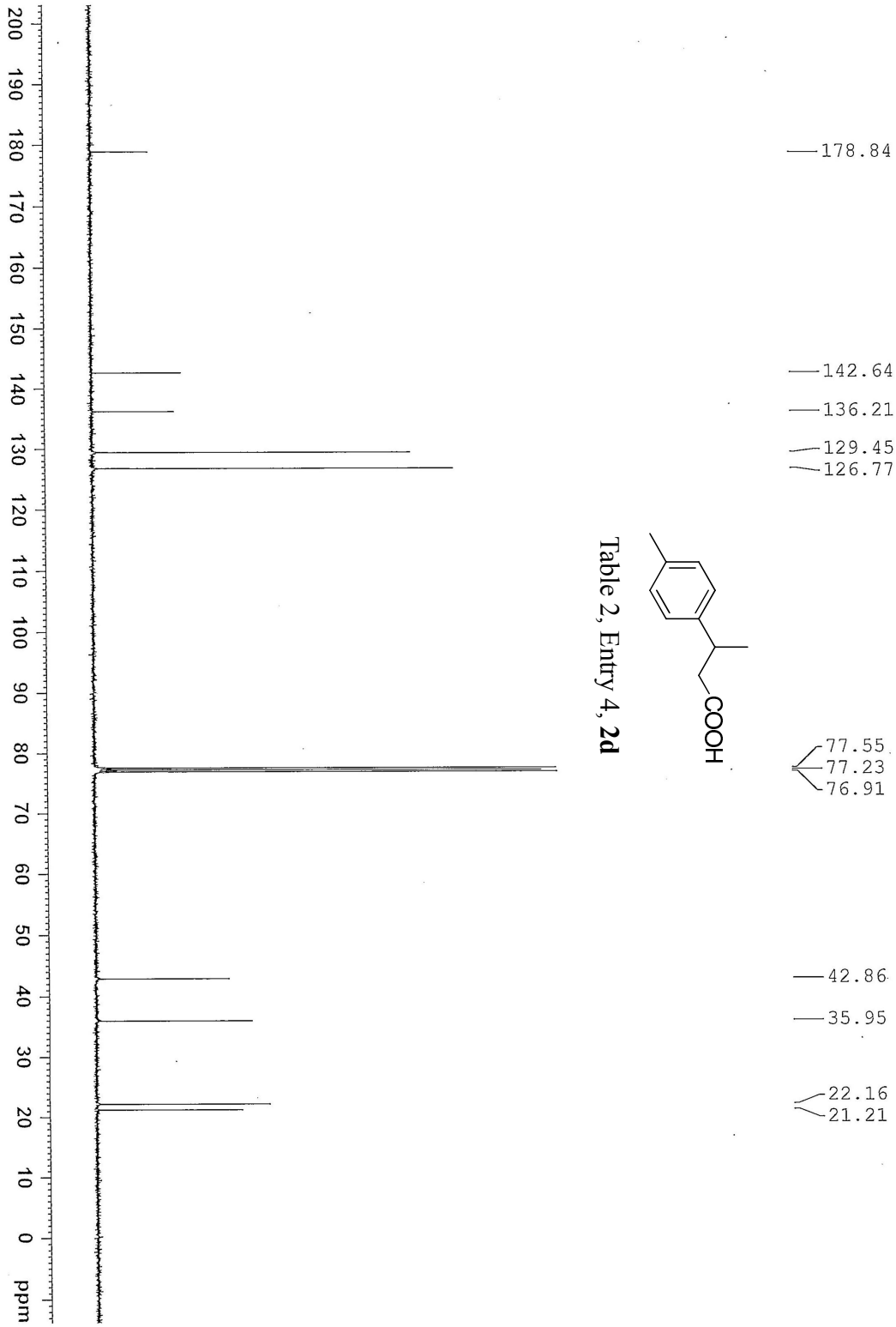


Table 2, Entry 4, **2d**

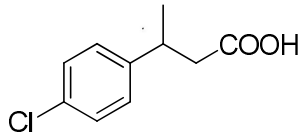
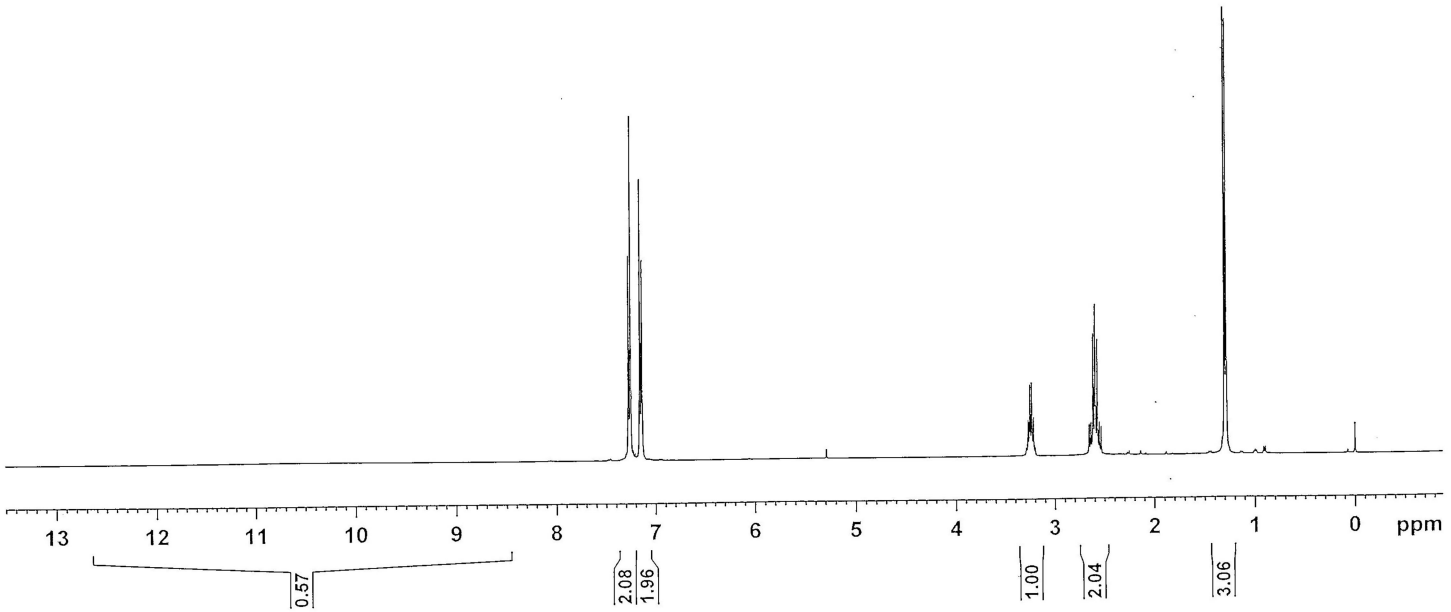


Table 2, Entry 5, **2e**



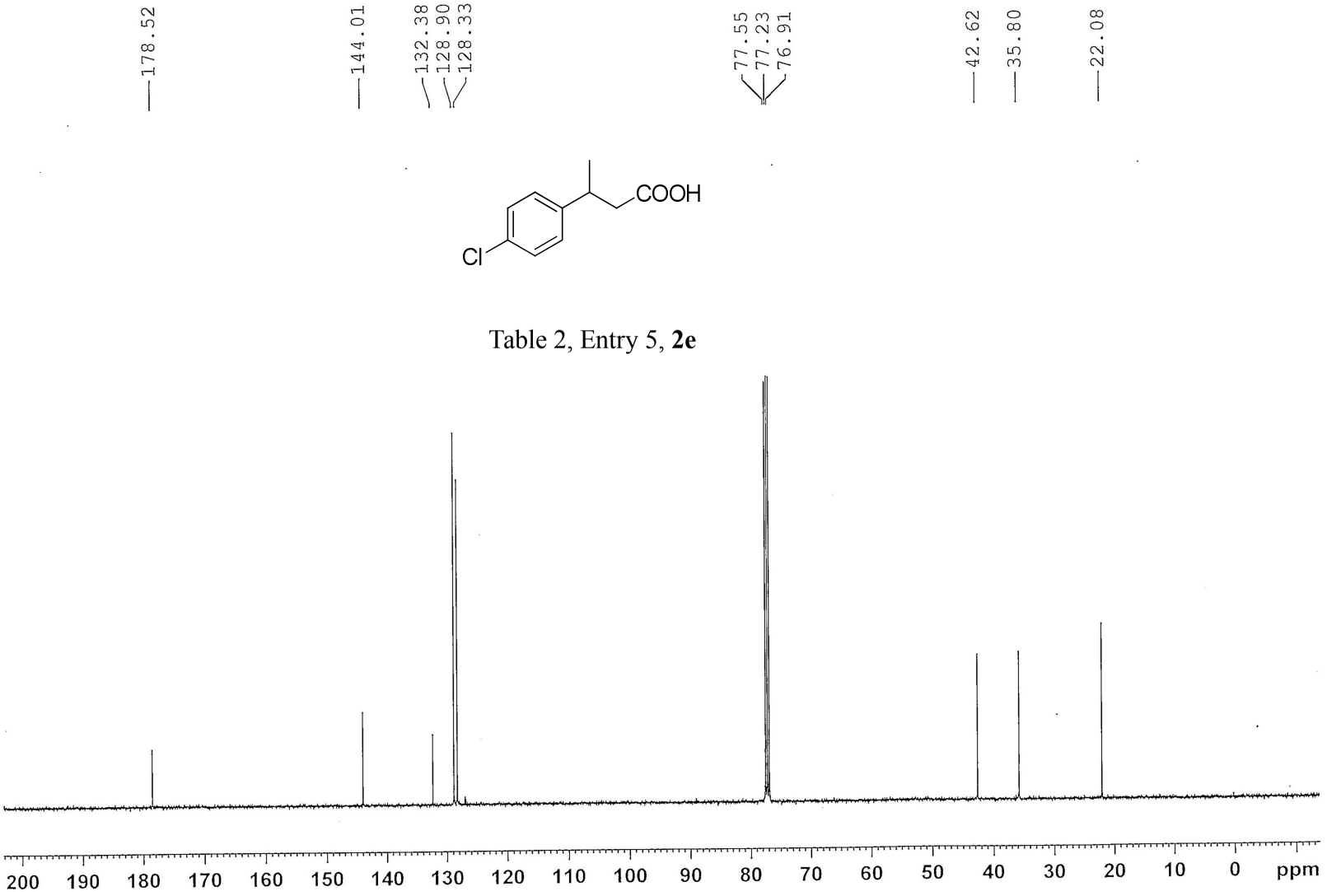


Table 2, Entry 5, **2e**

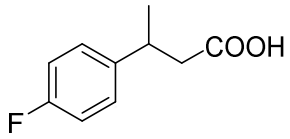
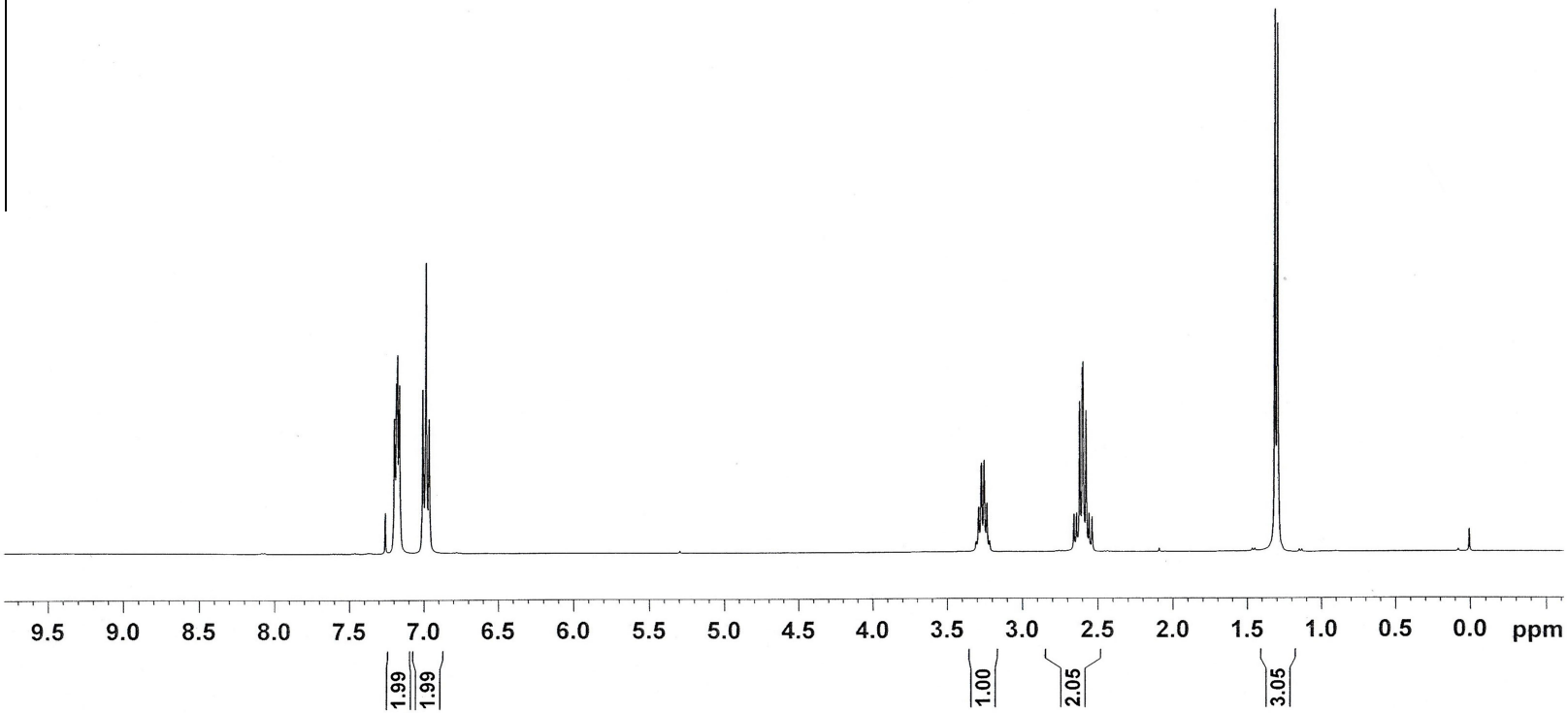


Table 2, Entry 6, **2f**



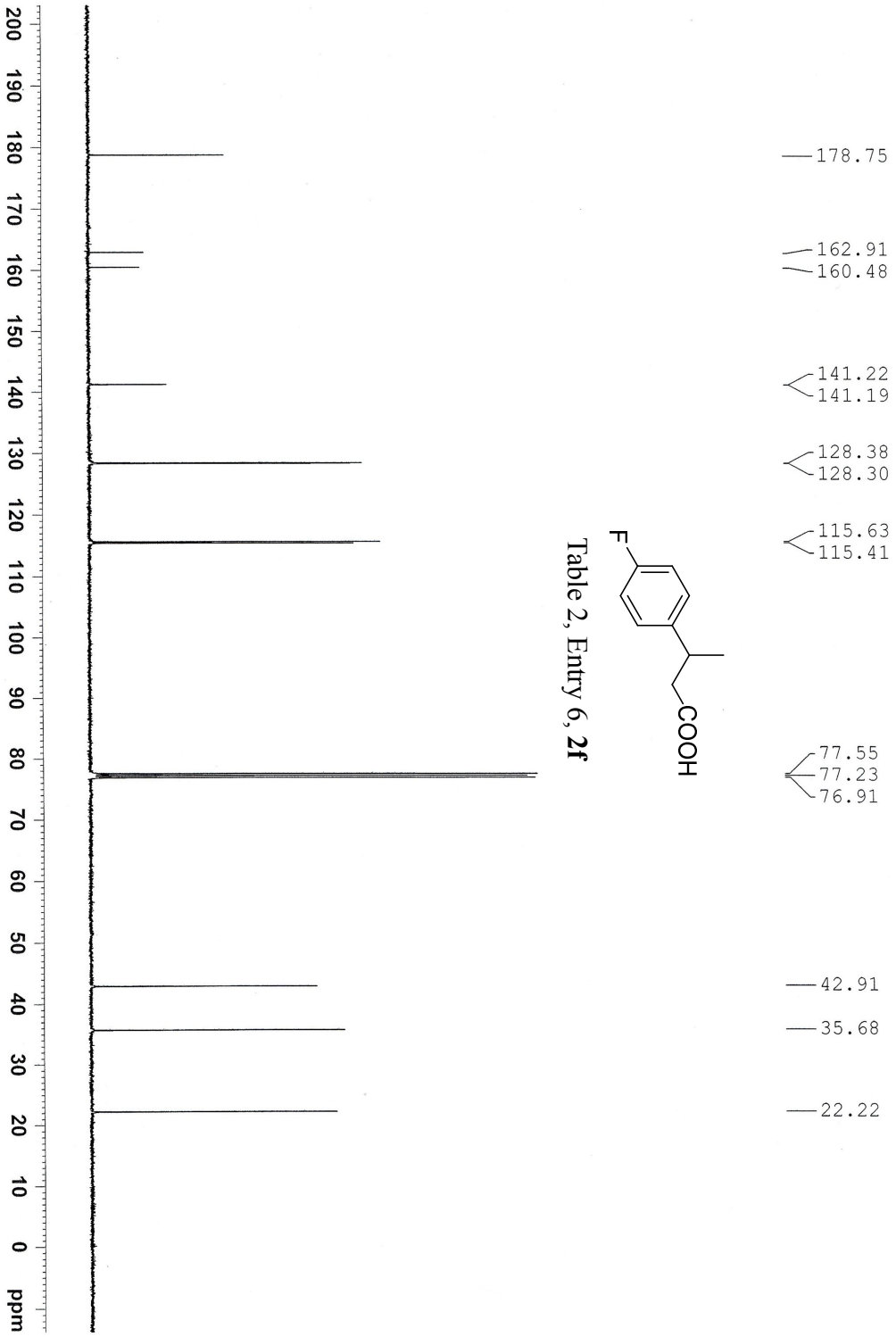


Table 2, Entry 6, **2f**

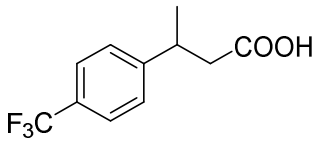
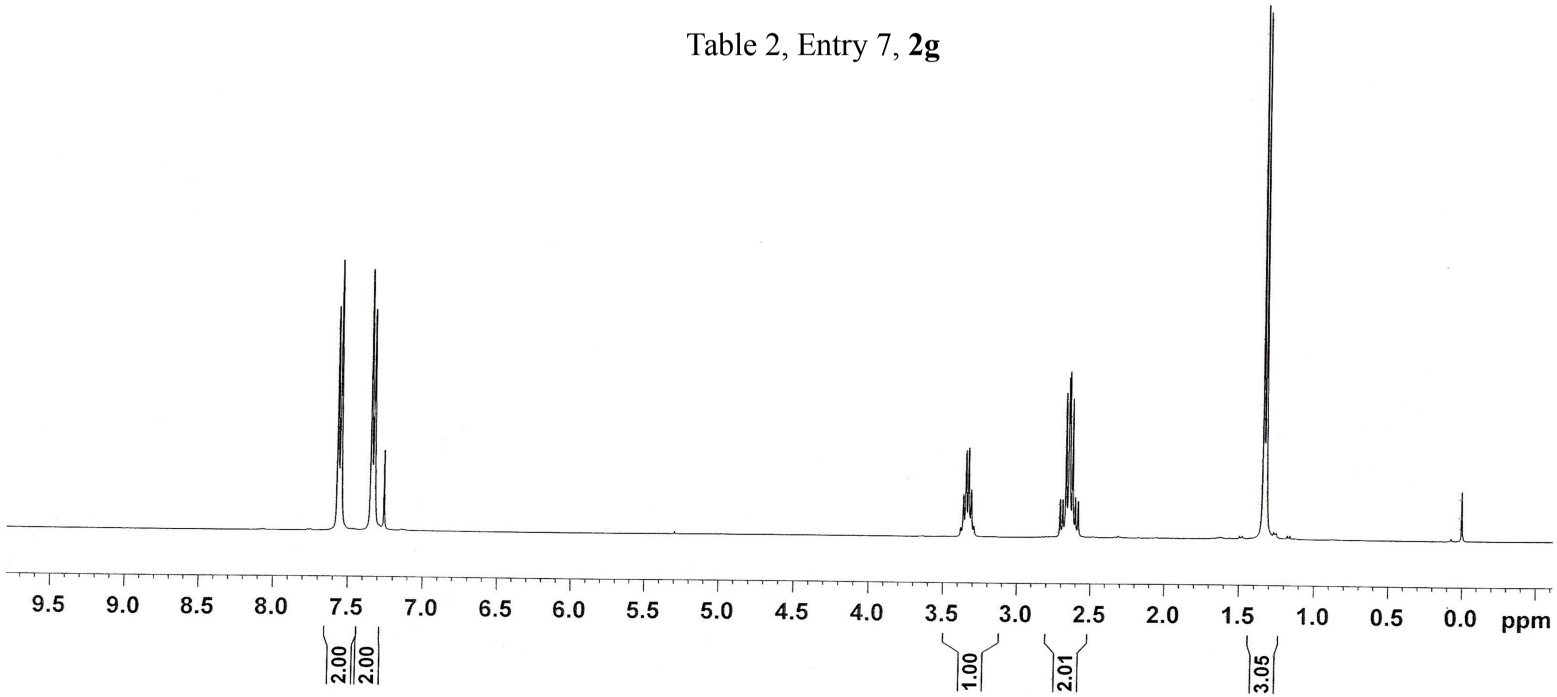
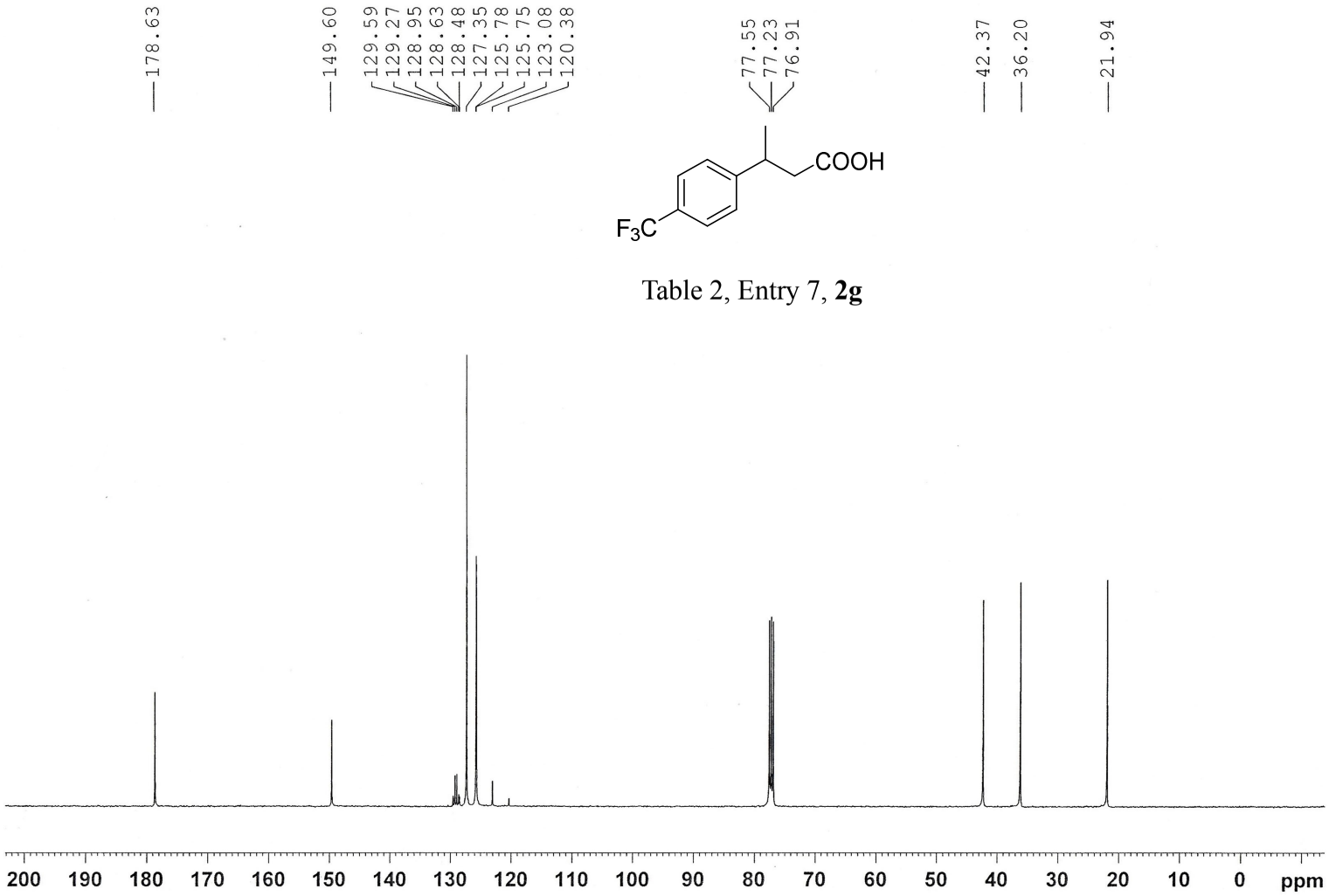


Table 2, Entry 7, **2g**





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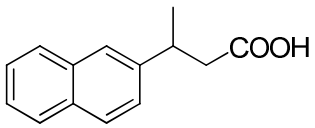
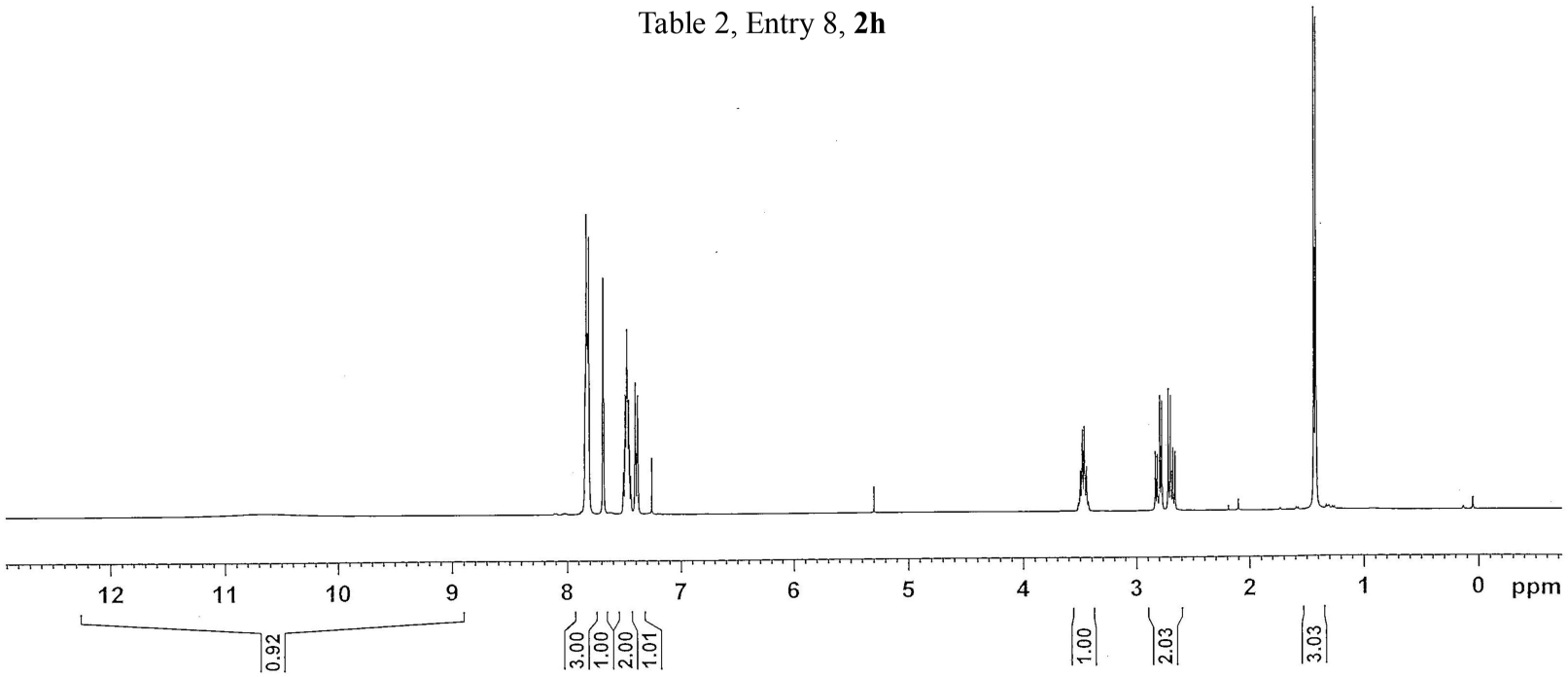


Table 2, Entry 8, **2h**



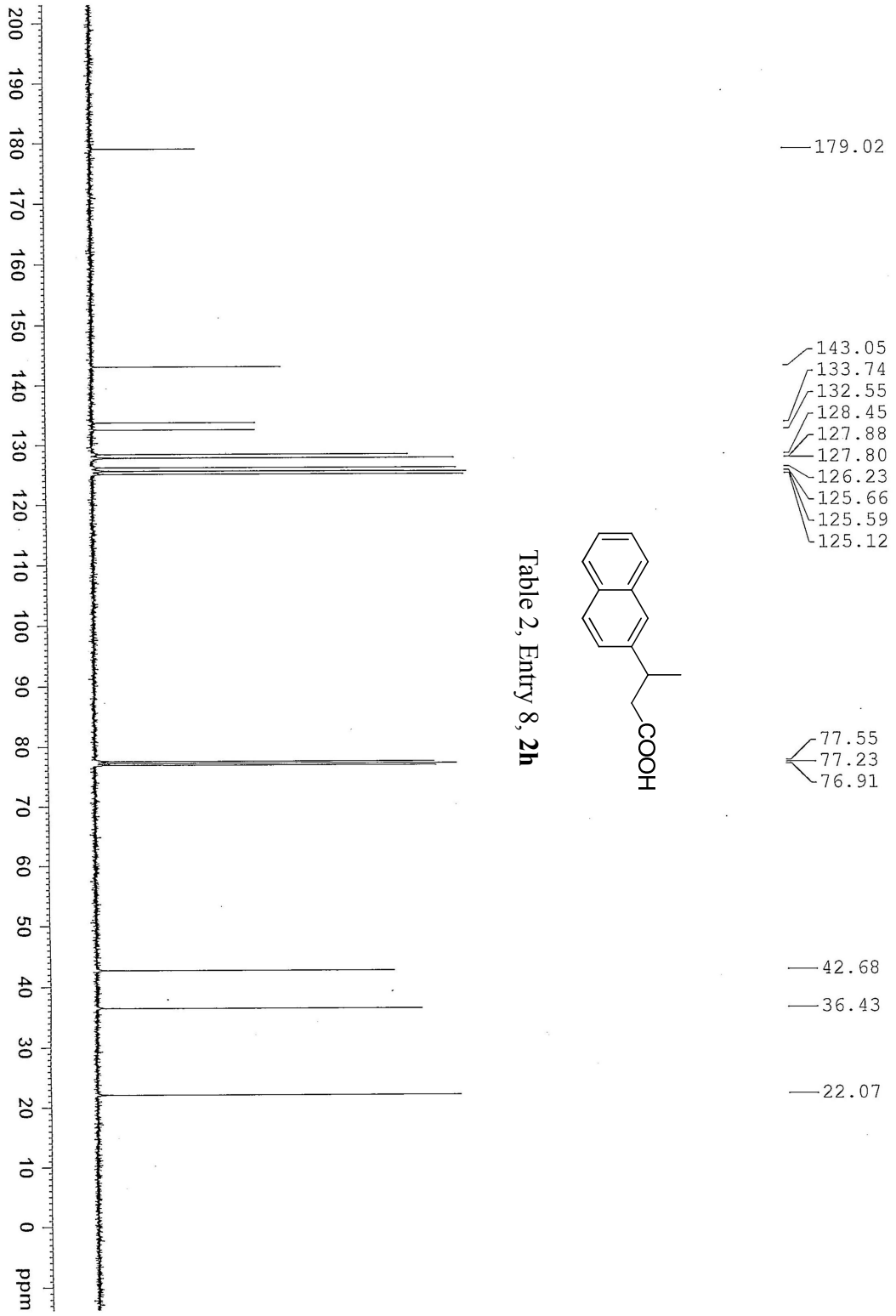


Table 2, Entry 8, **2h**

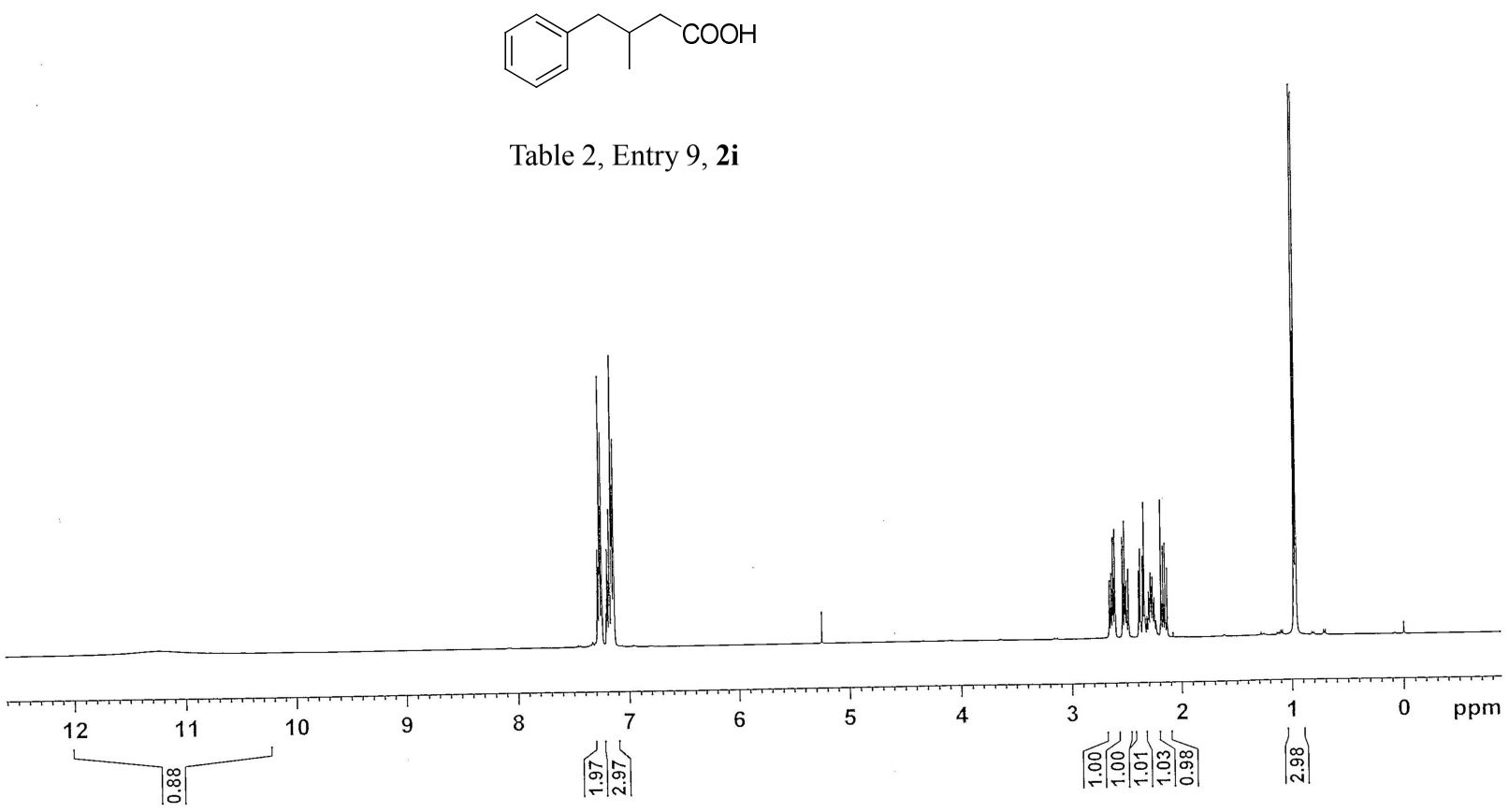


Table 2, Entry 9, **2i**

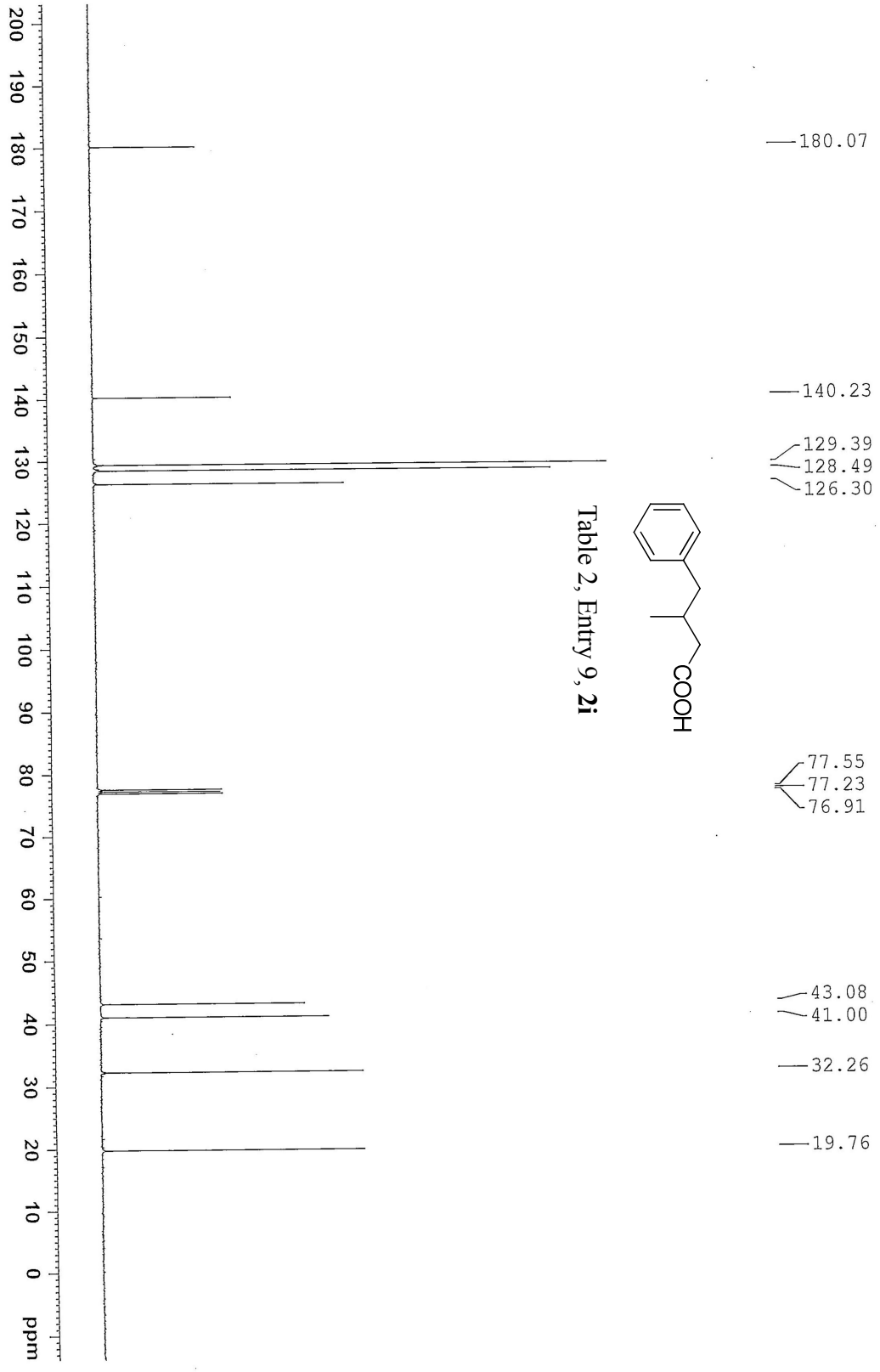


Table 2, Entry 9, **2i**

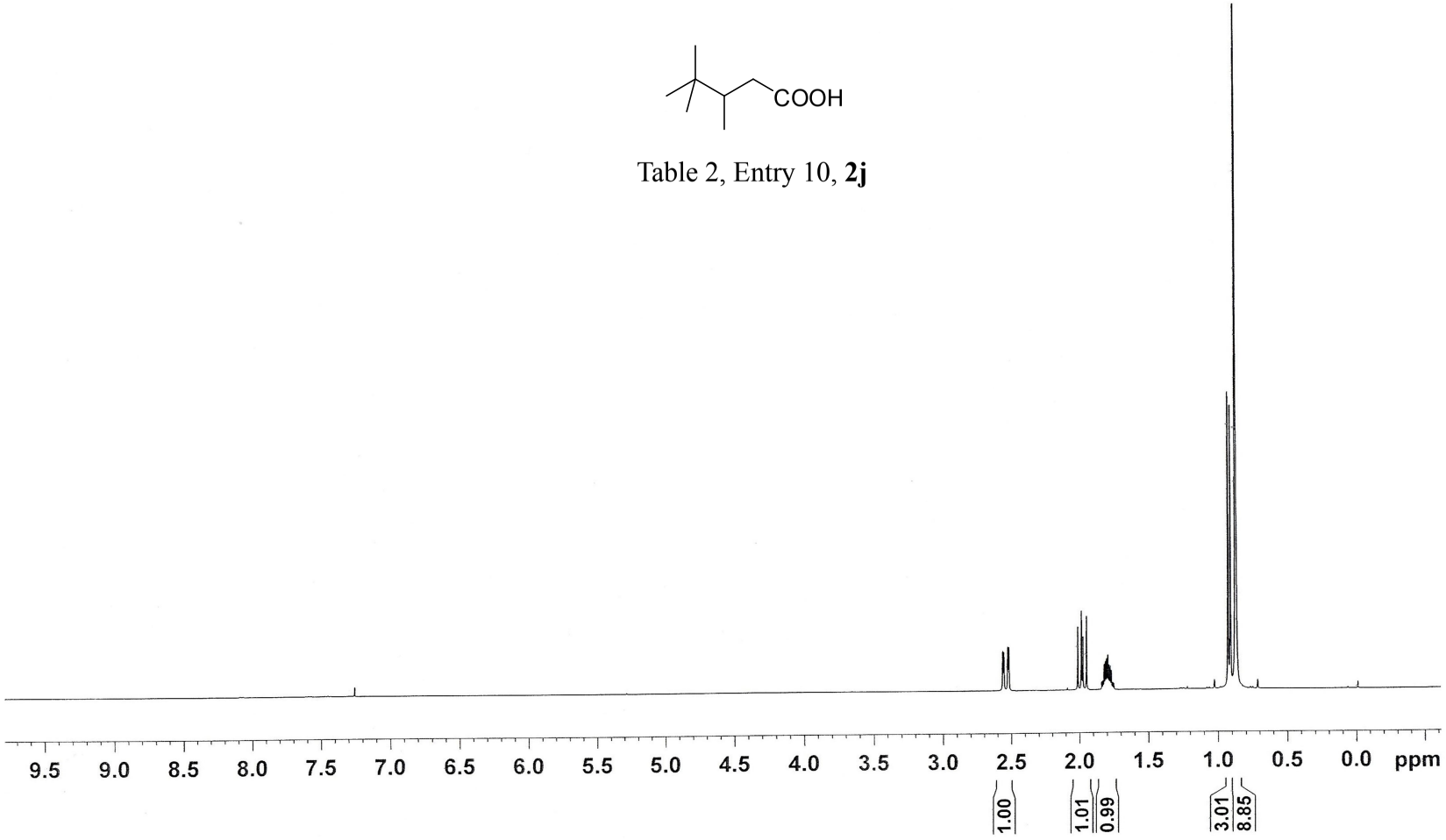


Table 2, Entry 10, **2j**

Table 2, Entry 10, **2j**

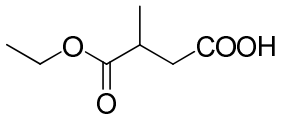
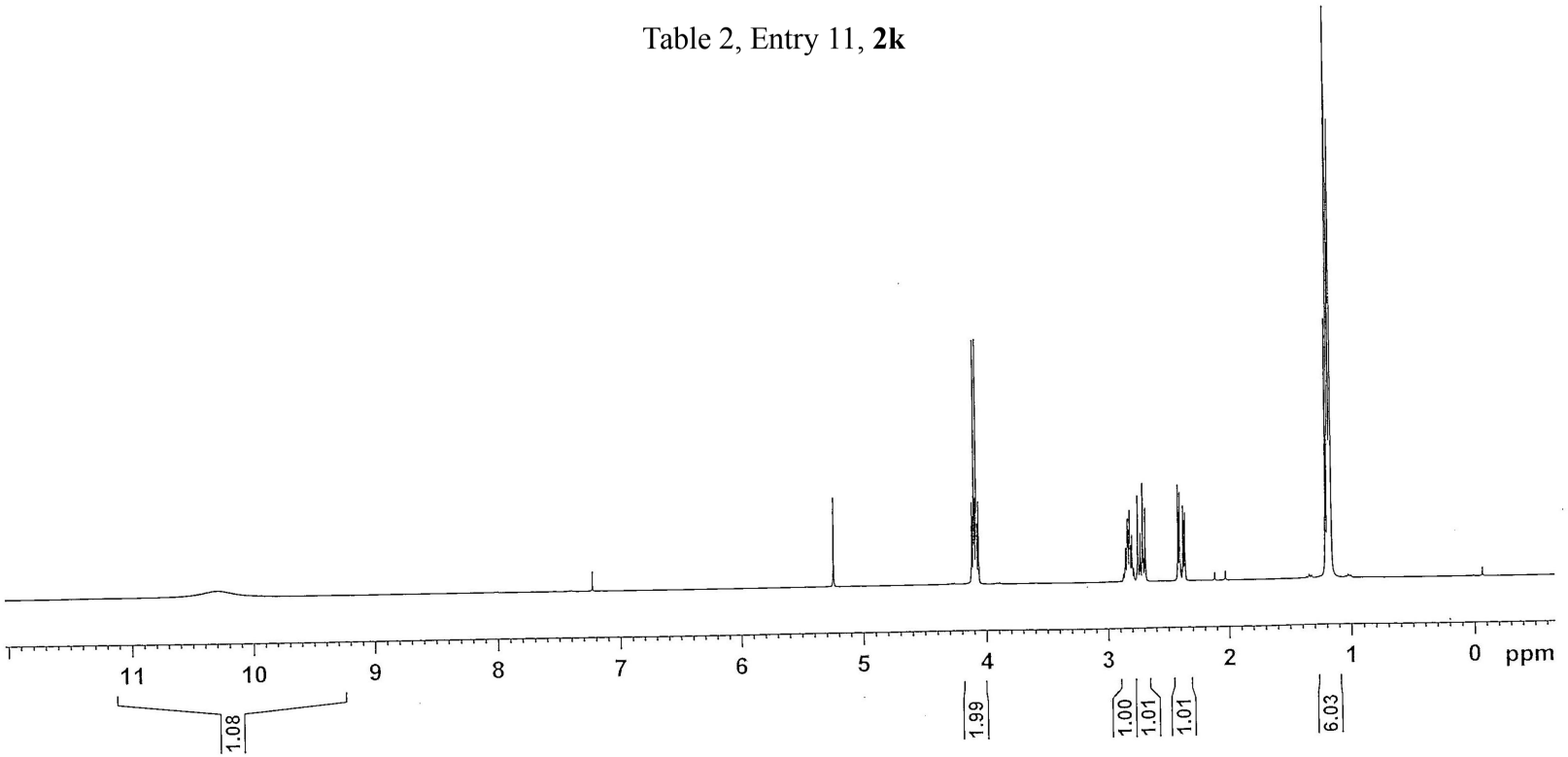


Table 2, Entry 11, **2k**



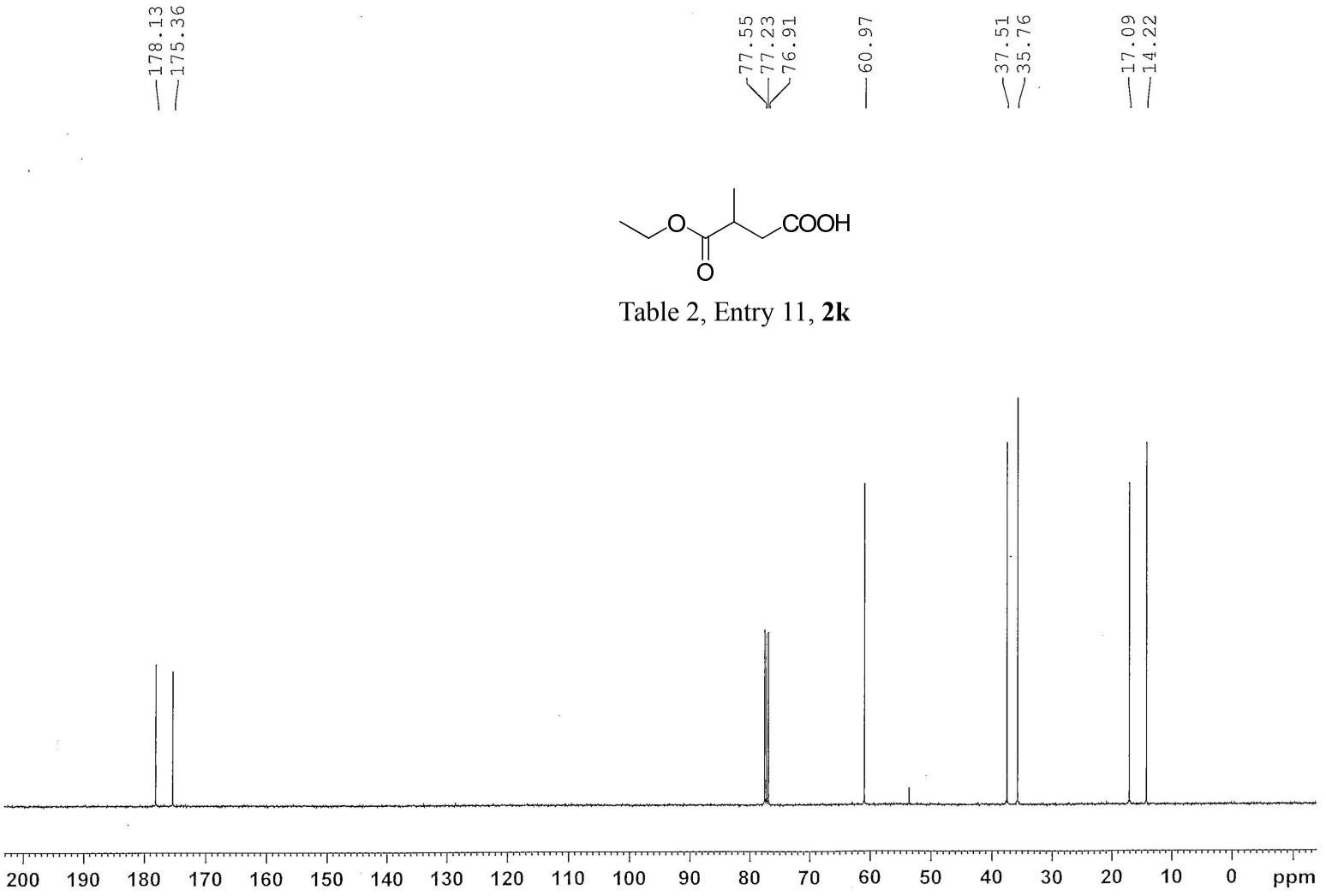


Table 2, Entry 11, **2k**

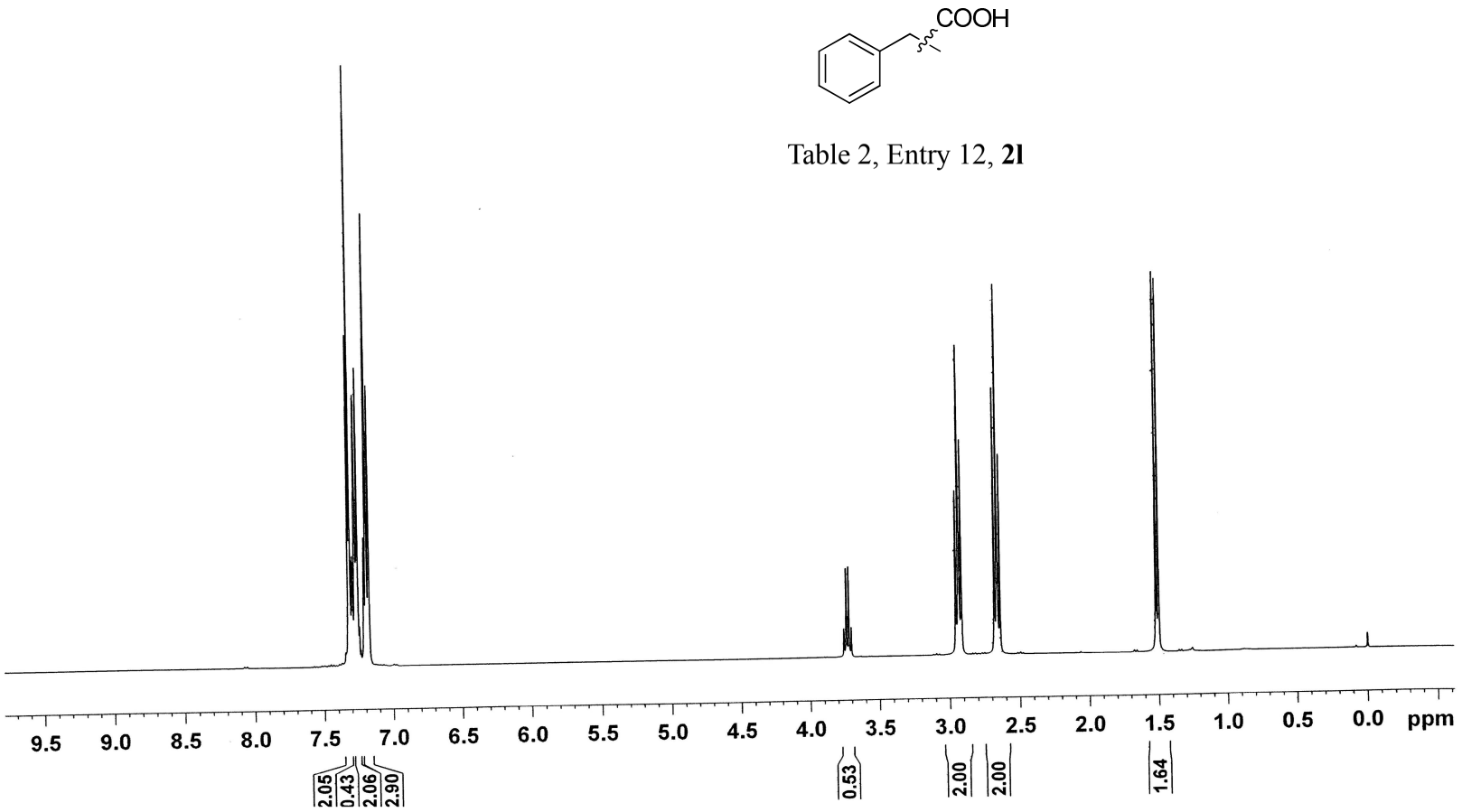
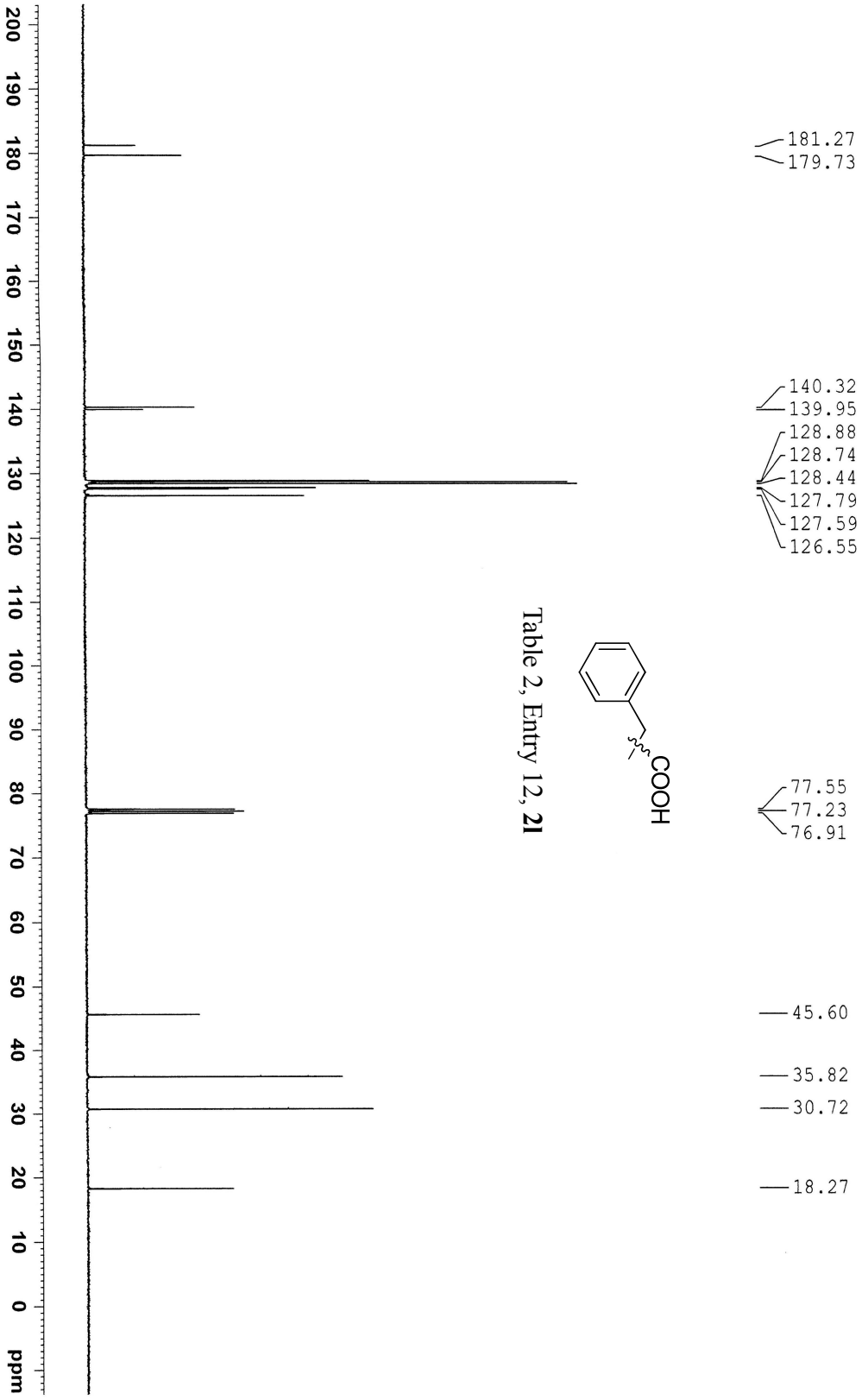


Table 2, Entry 12, **2l**


181.27
179.73
140.32
139.95
128.88
128.74
128.44
127.79
127.59
126.55
77.55
77.23
76.91
45.60
35.82
30.72
18.27
COOH
Table 2, Entry 12, 2l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

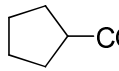
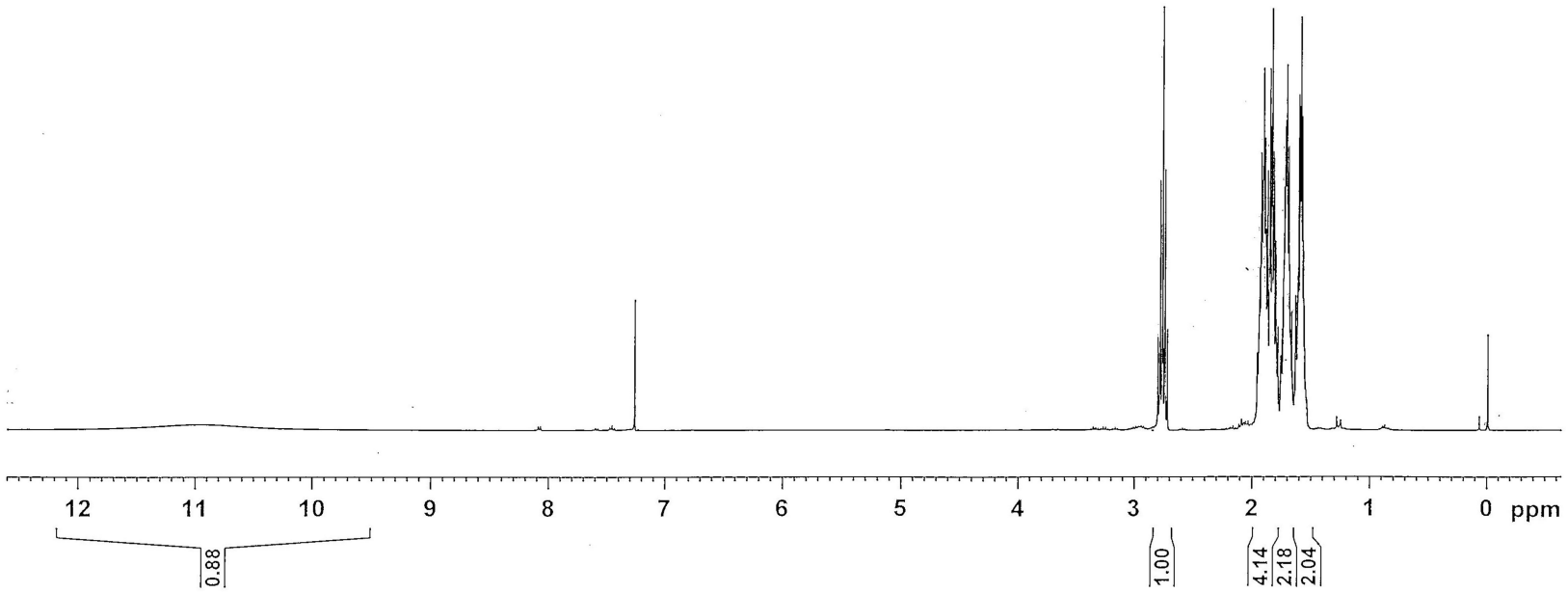


Table 2, Entry 13, **2m**



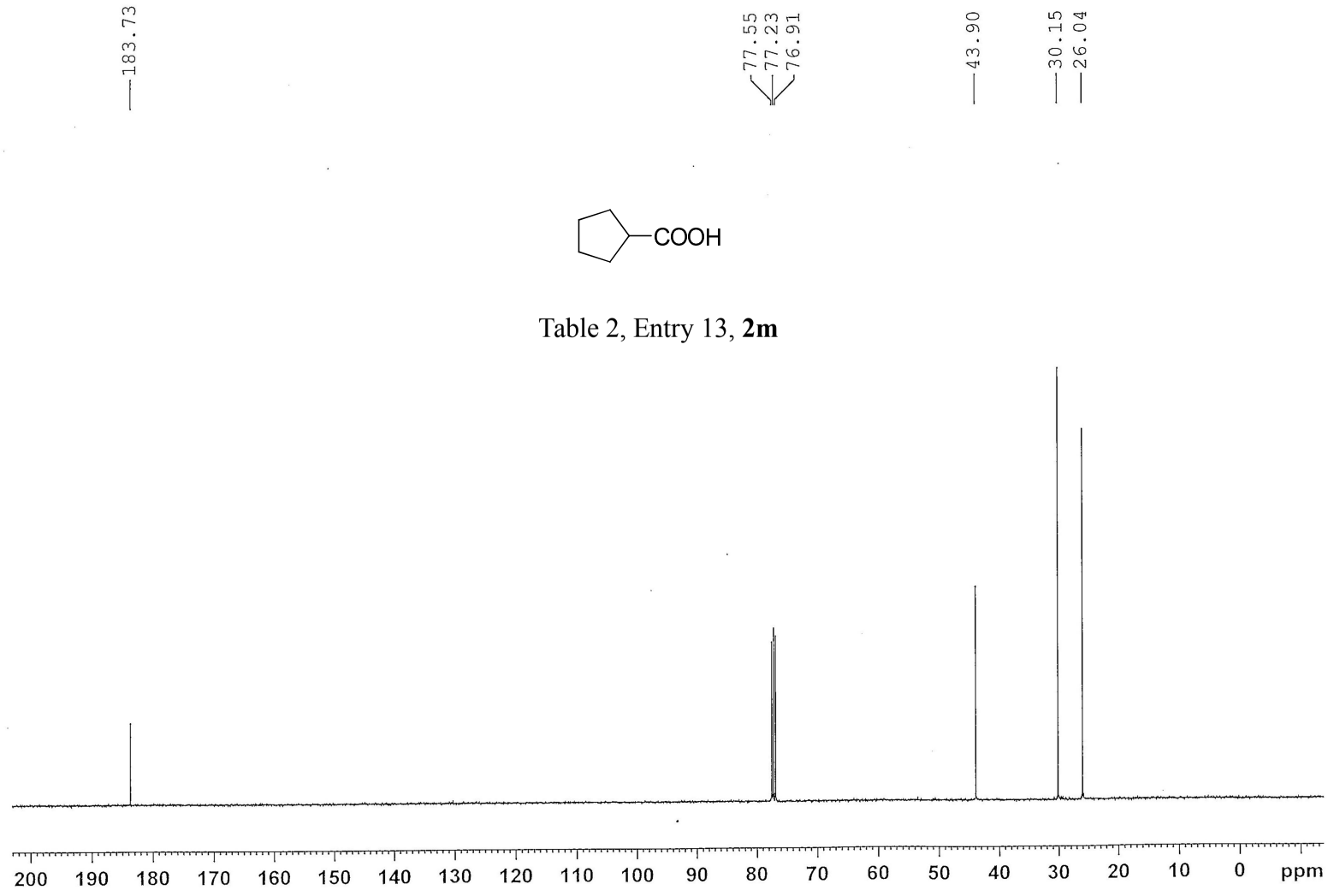


Table 2, Entry 13, **2m**

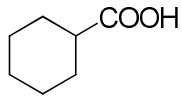
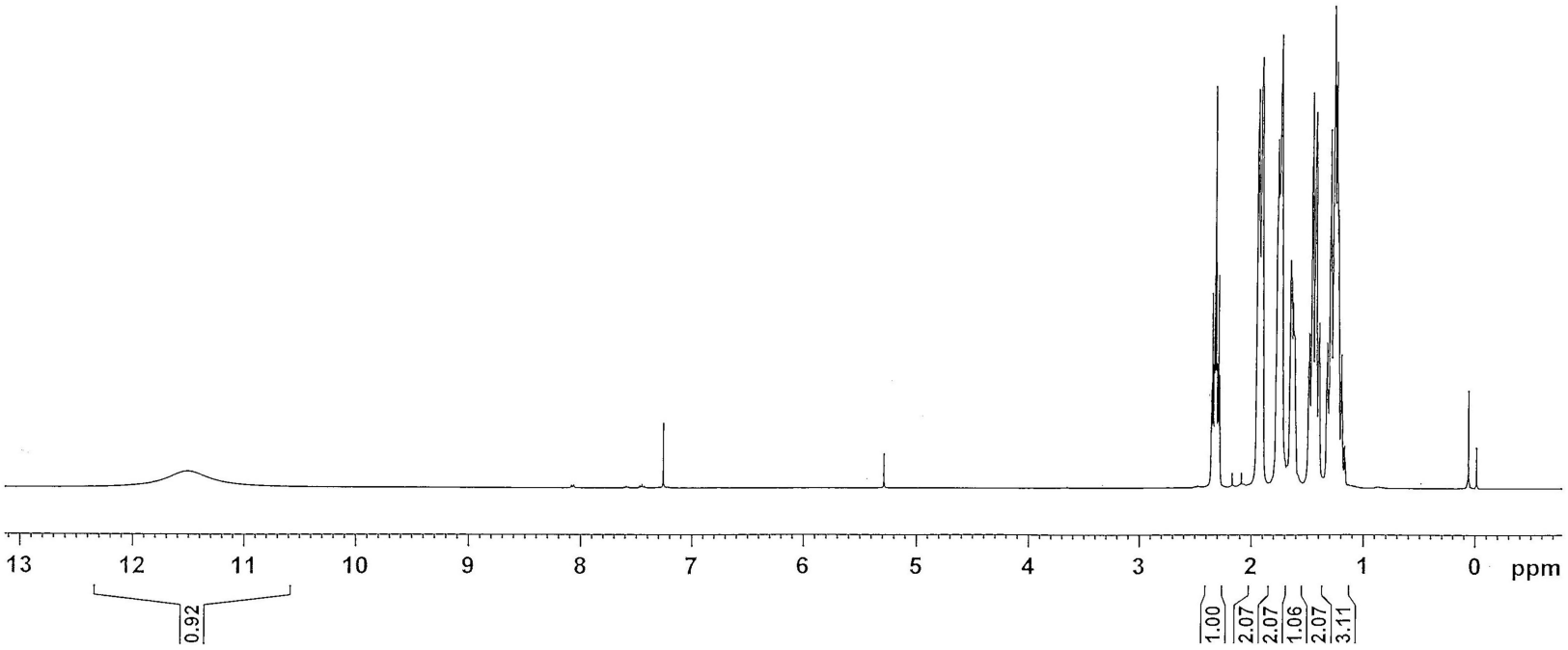


Table 2, Entry 14, **2n**



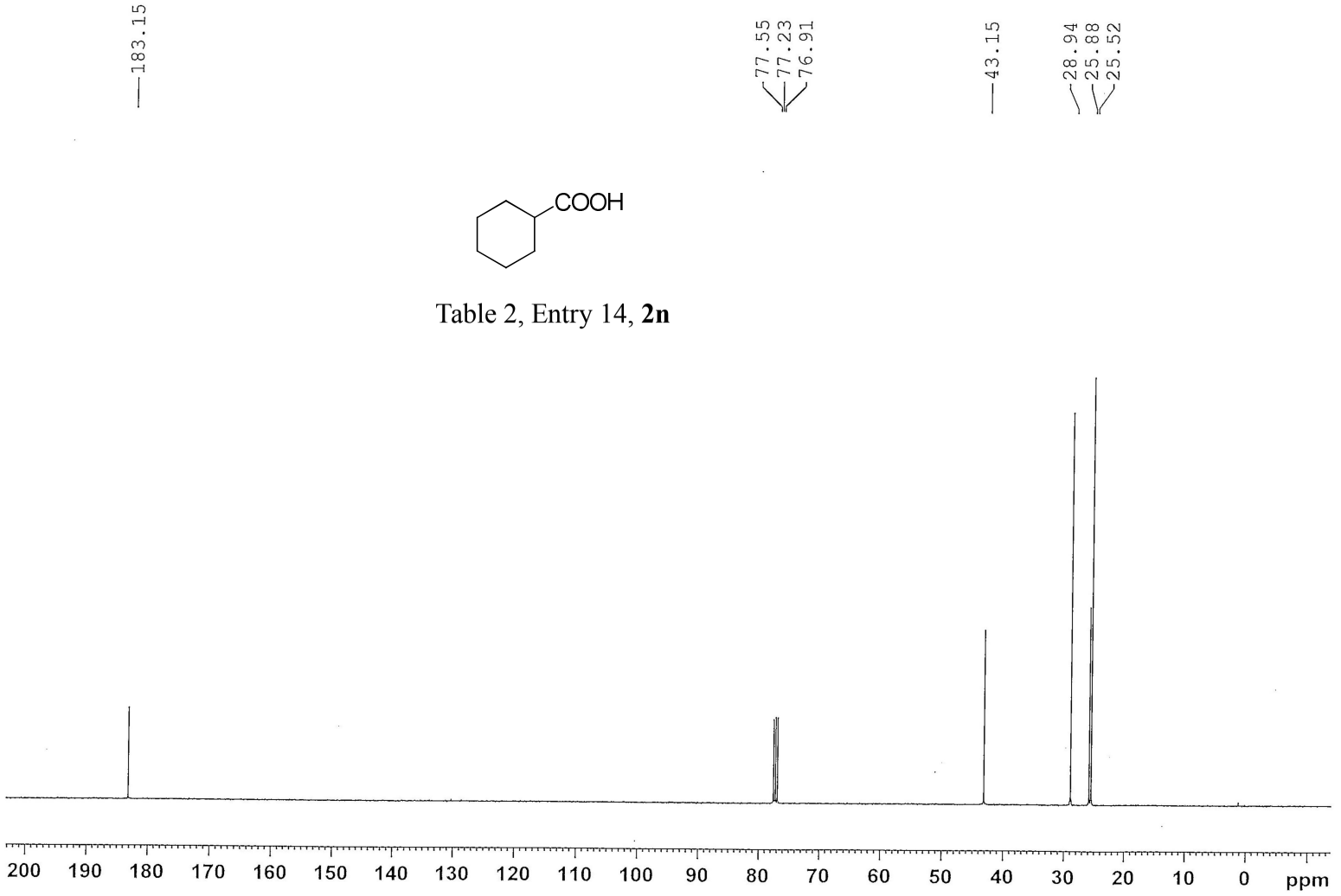


Table 2, Entry 14, **2n**

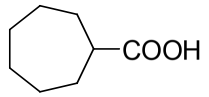
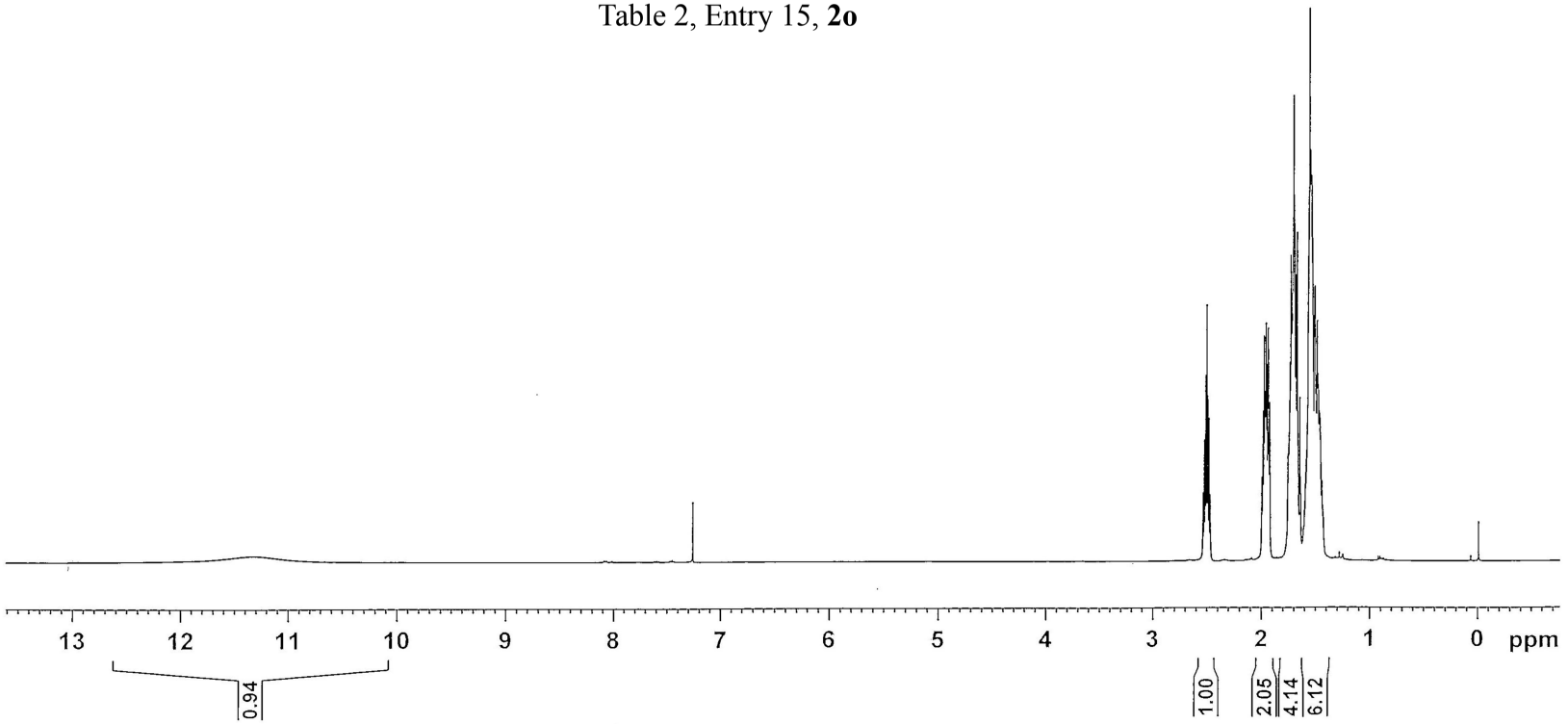


Table 2, Entry 15, **2o**



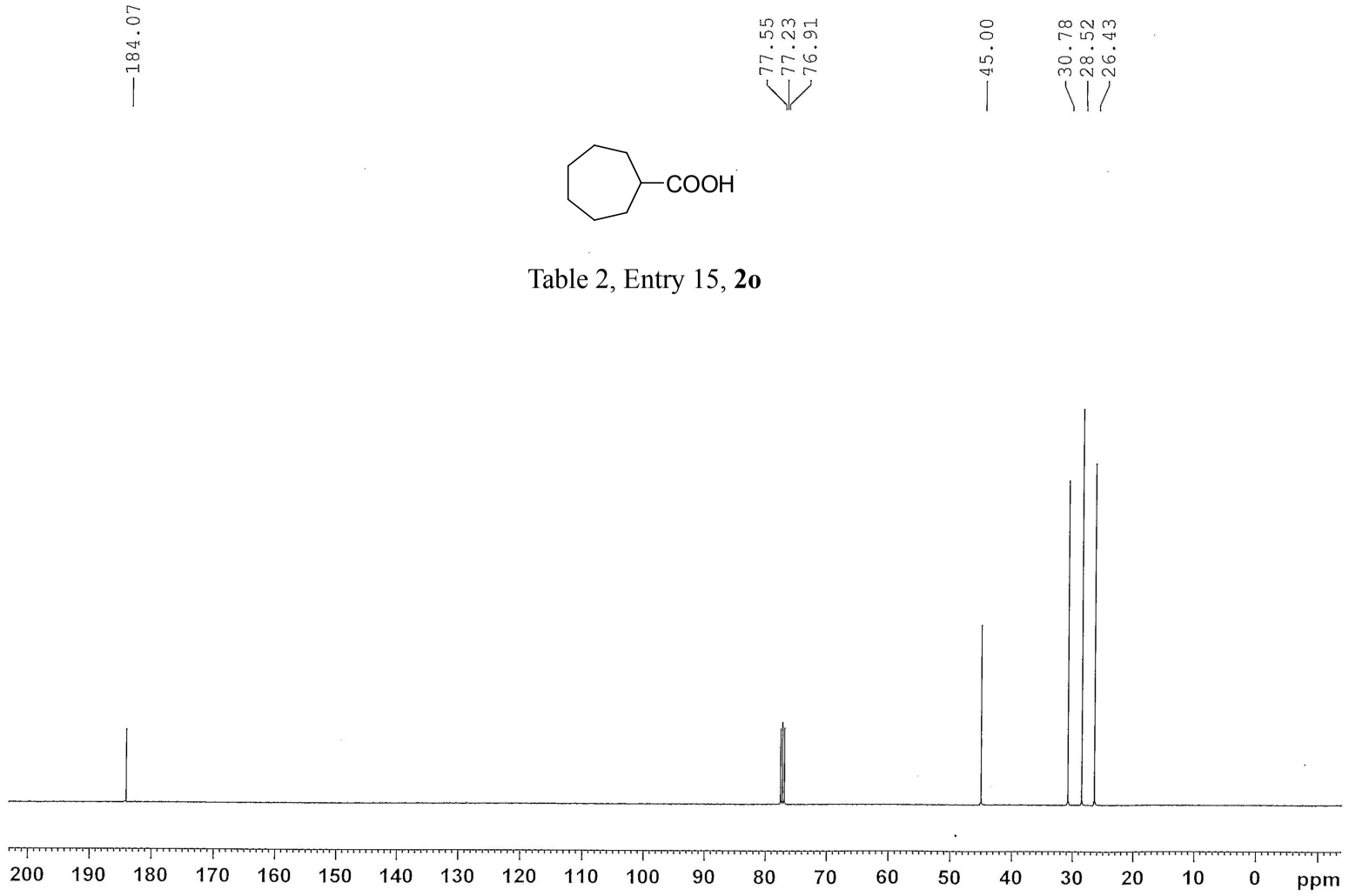


Table 2, Entry 15, **2o**

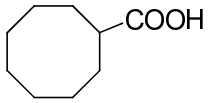
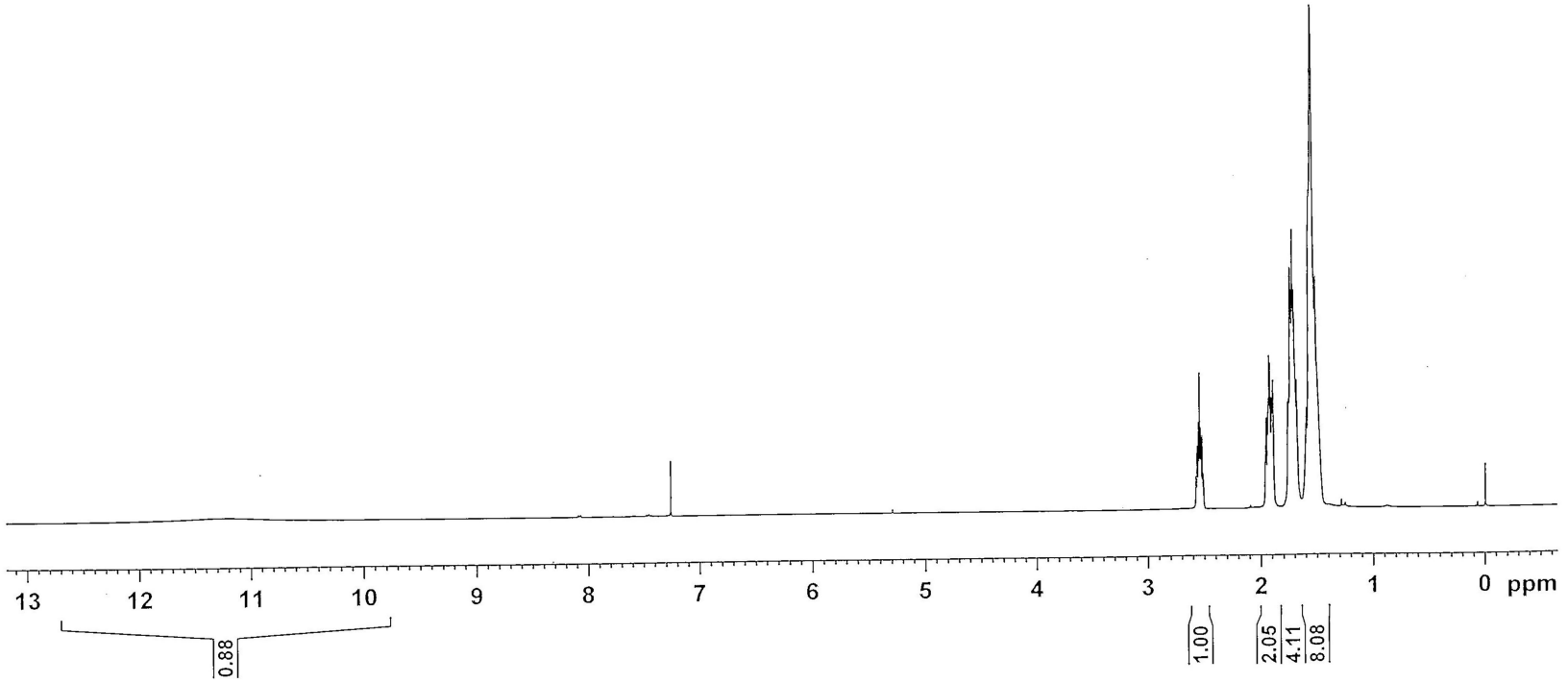


Table 2, Entry 16, **2p**



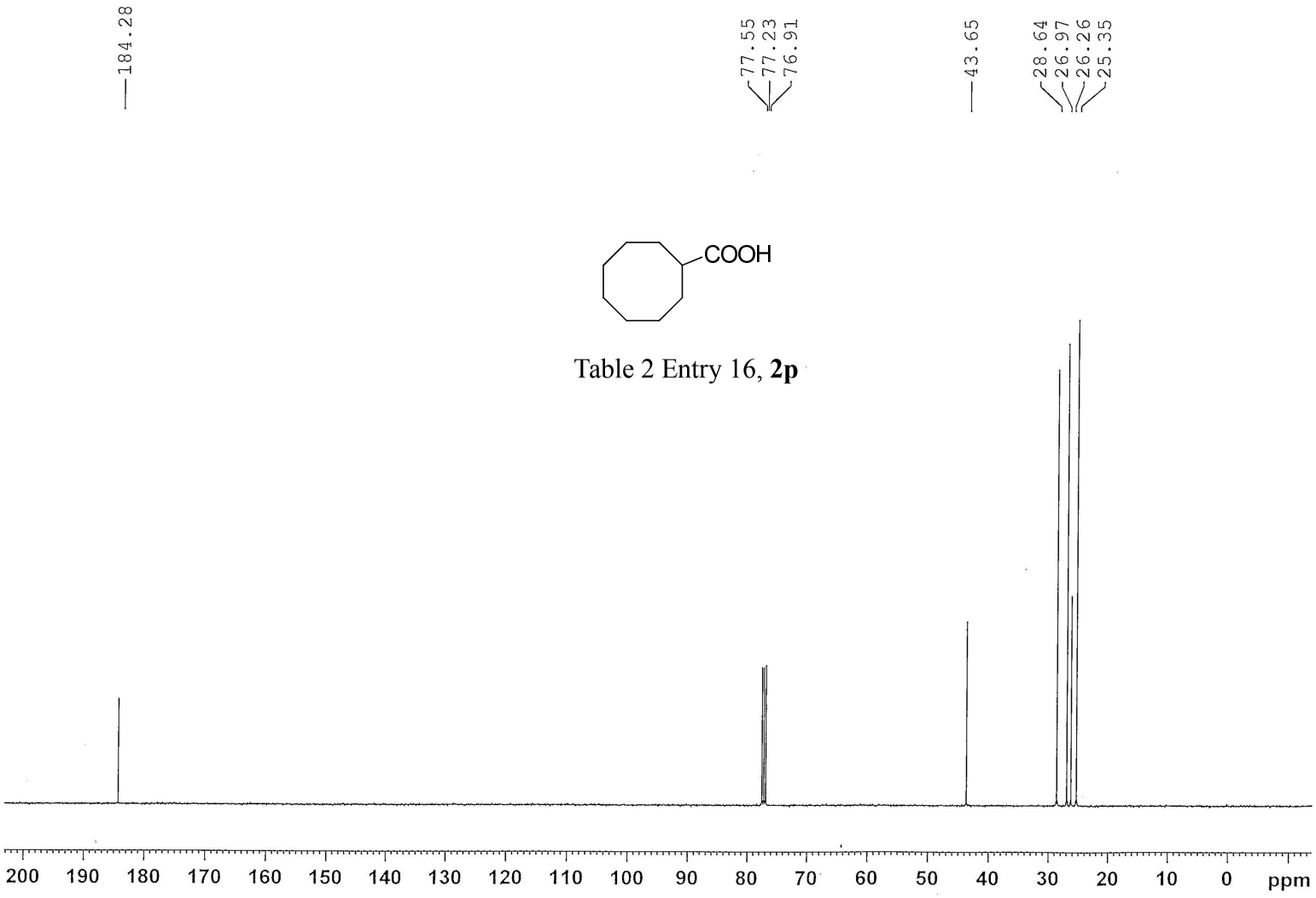


Table 2 Entry 16, **2p**