Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

An Effective Route to β^2-Amino Acid Derivatives via Pd-Catalyzed Regioselective Hydrocarboxylation of 1,2-Disubstituted Enimides

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Supporting Information

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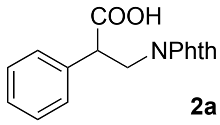
General Methods. All commercially available reagents were used without further purification. All solvents used for the reaction were purified with solvent purification system. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer 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. (*E*)-1,2-Disubstituted enimides were synthesized from *N*-vinylphthalimide and the corresponding aryl iodides via Heck reaction according to the reported procedure.[1] (*Z*)-1,2-Disubstituted enimides were synthesized via Ru-catalyzed addition of *o*-phthalimide to the corresponding alkynes based on the reported method.[2]

1) Nanteuil, de F.; Waser, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 9009
2) Goossen, L. J.; Blanchot, M.; Brinkmann, C.; Goossen, K.; Karch, R.; Rivas-Nass, A. *J. Org. Chem.* **2006**, *71*, 9506

Representative procedure for hydrocarboxylation (Table 2, 2a). To a mixture of $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$ (0.00457 g, 0.0125 mmol), PPh_3 (0.02623 g, 0.10 mmol), and toluene (0.250 mL) in a vial (1.5 mL) were added enimide **1a** (0.1246 g, 0.50 mmol), HCOOPh (0.0733 g, 0.60 mmol), and HCOOH (0.046 g, 1.00 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 80 °C for 48 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: DCM/MeOH = 80/1) to give compound **2a** as a light yellow solid (0.1462 g, 99% yield).

Table 2, 2a



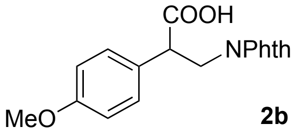
2a

Yellow solid; mp. 167-168 °C; IR (film) 1777, 1707, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 2H), 7.71-7.64 (m, 2H), 7.36-7.24 (m, 5H), 4.35 (dd, *J* = 8.8, 7.1 Hz, 1H), 4.24 (dd, *J* = 13.8, 7.1 Hz, 1H), 4.24 (dd, *J* = 13.8, 8.9 Hz, 1H);

^{13}C NMR (100 MHz, DMSO-d_6) δ 172.7, 167.4, 136.3, 134.5, 131.2, 128.5, 128.1, 127.6, 123.1, 48.7, 40.0; HRMS (ESI) Calcd for $C_{17}H_{14}NO_4$ (M+H): 296.0917; Found: 296.0917.

Calmès, M.; Escale, F. *Tetrahedron: Asymmetry* **1998**, *9*, 2845

Table 2, 2b



2b

Yellow solid; mp. 201-203 °C; IR (film) 1771, 1707, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.71-7.64 (m, 2H), 7.28-7.23 (m, 2H), 6.84-6.78 (m, 2H), 4.31 (dd, *J* = 9.0, 7.2 Hz, 1H), 4.23-4.12 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 167.5, 158.6, 134.5, 131.2, 129.2, 128.1, 123.1, 113.9, 55.0, 47.9, 40.1; HRMS (ESI) Calcd for $C_{18}H_{16}NO_5$ (M+H): 326.1023; Found: 326.1021.

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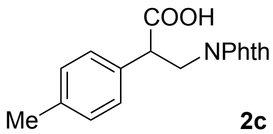
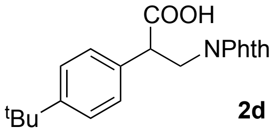
Table 2, 2c



2c

Yellow solid; mp. 181-182 °C; IR (film) 1771, 1707, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.71-7.64 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.31 (dd, *J* = 8.7, 7.2 Hz, 1H), 4.22 (dd, *J* = 13.8, 7.1 Hz, 1H), 4.16 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 167.9, 137.2, 135.0, 133.7, 131.7, 129.6, 128.4, 123.5, 48.8, 40.5, 21.1; HRMS (ESI) Calcd for $C_{18}H_{16}NO_4$ (M+H): 310.1074; Found: 310.1066.

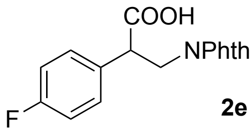
Table 2, 2d



2d

Yellow solid; mp. 220-222 °C; IR (film) 1774, 1718, 720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H), 7.71-7.64 (m, 2H), 7.33-7.25 (m, 4H), 4.37-4.22 (m, 2H), 4.11 (dd, *J* = 13.4, 7.6 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.8, 167.5, 149.9, 134.5, 133.2, 131.3, 127.7, 125.3, 123.1, 48.3, 40.0, 34.2, 31.0; HRMS (ESI) Calcd for $C_{21}H_{22}NO_4$ (M+H): 352.1543; Found: 352.1544.

Table 2, 2e

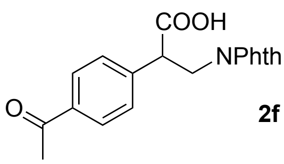


2e

Yellow solid; mp. 182-183 °C; IR (film) 1774, 1704, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.74 (m, 2H), 7.72-7.65 (m, 2H), 7.34-7.28 (m, 2H), 7.01-6.94 (m, 2H), 4.33 (t, *J* = 8.4 Hz, 1H), 4.19 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.6, 167.4, 161.5 (d, *J* = 242.1 Hz), 134.6, 132.5 (d, *J* = 3.0 Hz), 131.2, 130.2 (d, *J* = 8.1 Hz), 123.1, 115.3 (d, *J* = 21.2 Hz), 48.0, 40.0; HRMS (ESI) Calcd for $C_{17}H_{13}FNO_4$ (M+H): 314.0823; Found: 314.0826.

Calmès, M.; Escale, F.; Glot, C.; Rolland, M.; Martinez, J. *Eur. J. Org. Chem.* **2000**, 2459

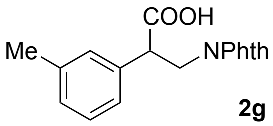
Table 2, 2f



2f

Yellow solid; mp. 205-207 °C; IR (film) 1771, 1709, 1681, 717 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (br s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.84-7.78 (m, 4H), 7.42 (d, J = 8.2 Hz, 2H), 4.21 (dd, J = 9.2, 6.5 Hz, 1H), 4.13 (dd, J = 13.8, 6.5 Hz, 1H), 4.05 (dd, J = 13.8, 9.4 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.6, 172.2, 167.5, 141.7, 136.1, 134.6, 131.2, 128.6, 128.5, 123.2, 48.9, 39.8, 26.7; HRMS (ESI) Calcd for $C_{19}H_{16}NO_5$ (M+H): 338.1023; Found: 338.1020.

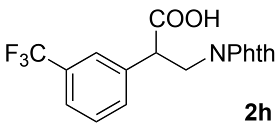
Table 2, 2g



2g

Yellow solid; mp. 146-148 °C; IR (film) 1774, 1707, 1693, 717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.71-7.65 (m, 2H), 7.21-7.11 (m, 3H), 7.09-7.05 (m, 1H), 4.36-4.20 (m, 2H), 4.13 (dd, J = 13.6, 8.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.7, 167.5, 137.7, 136.2, 134.5, 131.2, 128.6, 128.4, 128.2, 125.1, 123.1, 48.6, 40.0, 20.9; HRMS (ESI) Calcd for $C_{18}H_{16}NO_4$ (M+H): 310.1074; Found: 310.1072.

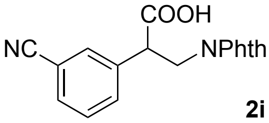
Table 2, 2h



2h

Yellow solid; mp. 129-130 °C; IR (film) 1776, 1704, 708 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84-7.77 (m, 4H), 7.64-7.56 (m, 3H), 7.55-7.47 (m, 1H), 4.23 (dd, J = 9.3, 6.4 Hz, 1H), 4.14 (dd, J = 13.8, 6.4 Hz, 1H), 4.05 (dd, J = 13.8, 9.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.2, 167.4, 137.8, 134.6, 132.6, 131.2, 129.6, 129.1 (q, J = 31.4 Hz), 124.9 (q, J = 3.7 Hz), 124.4 (q, J = 3.6 Hz), 124.0 (q, J = 270.8 Hz), 123.1, 48.6, 39.8; HRMS (ESI) Calcd for $C_{18}H_{13}F_3NO_4$ (M+H): 364.0791; Found: 364.0787.

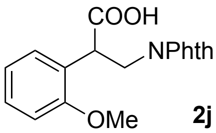
Table 2, 2i



2i

Yellow solid; mp. 202-204 °C; IR (film) 2225, 1777, 1707, 708 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.04 (br s, 1H), 7.86-7.76 (m, 5H), 7.72 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 4.21-4.11 (m, 2H), 4.04 (dd, J = 15.2, 11.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.1, 167.4, 138.1, 134.6, 133.5, 132.2, 131.4, 131.2, 129.7, 123.2, 118.6, 111.4, 48.6, 39.8; HRMS (ESI) Calcd for $C_{18}H_{13}N_2O_4$ (M+H): 321.0870; Found: 321.0877.

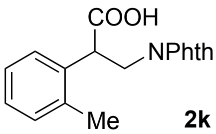
Table 2, 2j



2j

Yellow solid; mp. 179-181 °C; IR (film) 1770, 1709, 716 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (br s, 1H), 7.79 (br s, 4H), 7.17 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.90-6.76 (m, 2H), 4.30 (t, J = 8.0 Hz, 1H), 4.03 (d, J = 7.8 Hz, 2H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 167.3, 157.0, 134.4, 131.3, 129.1, 128.8, 125.0, 122.9, 120.4, 111.0, 55.3, 42.9, 38.9; HRMS (ESI) Calcd for $C_{18}H_{16}NO_5$ (M+H): 326.1023; Found: 326.1022.

Table 2, 2k

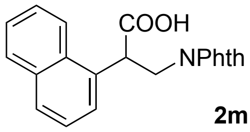


2k

Yellow solid; mp. 173-175 °C; IR (film) 1773, 1706, 716 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (br s, 1H), 7.85-7.78 (m, 4H), 7.27 (d, J = 7.0 Hz, 1H), 7.19-7.08 (m, 3H), 4.42 (t, J = 8.0 Hz, 1H), 4.13 (dd, J = 13.8, 7.6 Hz, 1H), 3.96 (dd, J = 13.8, 8.2 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 167.6, 136.3, 134.8, 134.6, 131.2, 130.4, 127.4, 127.1, 126.2, 123.1, 44.5, 39.4, 19.0;

HRMS (ESI) Calcd for $C_{18}H_{16}NO_4$ (M+H): 310.1074; Found: 310.1076.

Table 2, 2m



2m

Yellow solid; mp. 175-177 °C; IR (film) 1767, 1744, 1718, 722 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (br s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.82-7.74 (m, 4H), 7.59-7.44 (m, 4H), 4.95 (t, J = 7.6 Hz, 1H), 4.35 (dd, J = 13.8, 7.9 Hz, 1H), 4.06 (dd, J = 13.8, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 167.6, 134.5, 133.5, 132.8, 131.3, 131.2, 128.9, 128.1, 126.6, 125.8, 125.5, 125.4, 123.0, 122.8, 44.5, 40.0; HRMS (ESI) Calcd for $C_{21}H_{16}NO_4$ (M+H): 346.1074; Found: 346.1073.

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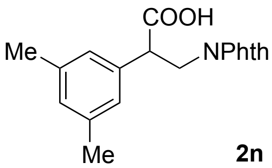
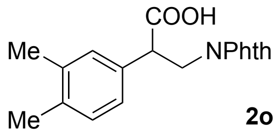
Table 2, 2n



2n

Yellow solid; mp. 187-189 °C; IR (film) 1774, 1719, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 2H), 7.71-7.65 (m, 2H), 6.95 (s, 2H), 6.89 (s, 1H), 4.31-4.21 (m, 2H), 4.12-4.01 (m, 1H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.7, 167.5, 137.5, 136.1, 134.5, 131.2, 129.0, 125.7, 123.1, 48.5, 40.0, 20.8; HRMS (ESI) Calcd for $C_{19}H_{18}NO_4$ (M+H): 324.1230; Found: 324.1234.

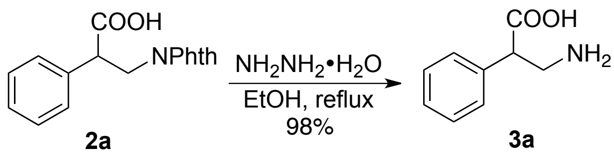
Table 2, 2o



2o

Yellow solid; mp. 181-183 °C; IR (film) 1768, 1718, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.71-7.65 (m, 2H), 7.12-7.02 (m, 3H), 4.32-4.19 (m, 2H), 4.11 (dd, *J* = 13.3, 8.0 Hz, 1H), 2.19 (s, 3H), 2.189 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 167.5, 136.3, 135.5, 134.5, 133.6, 131.2, 129.6, 129.1, 125.3, 123.1, 48.3, 40.0, 19.3, 19.0; HRMS (ESI) Calcd for $C_{19}H_{18}NO_4$ (M+H): 324.1230; Found: 324.1236.

Procedure for the hydrolysis in Scheme 5

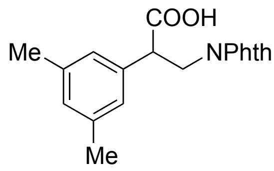


2a **3a**

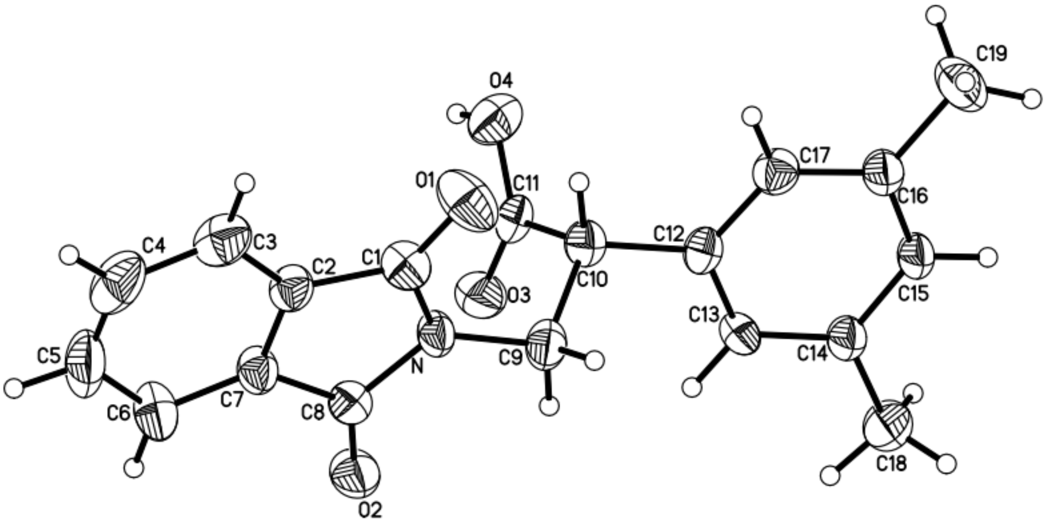
To a solution of compound **2a** (0.1476 g, 0.50 mmol) in EtOH (14 mL) was added hydrazine hydrate (0.41 g, 8.3 mmol) dropwise. The reaction mixture was stirred at reflux for 10 h, cooled to rt, filtered, and washed with ether (3x). The filter cake was dissolved in water (15 mL) and was washed with AcOEt. The aqueous layer was lyophilized to give amino acid **3a** as a white solid (0.0811 g, 98%); mp. 212-213 °C; IR (film) 3449, 1649, 1621, 1564, 693 cm^{-1}; ^{1}H NMR (400 MHz, D_2O) δ 7.48-7.30 (m, 5H), 3.79 (t, *J* = 7.5 Hz, 1H), 3.47 (dd, *J* = 12.8, 7.8 Hz, 1H), 3.28 (dd, *J* = 12.8, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 178.3, 137.2, 129.2, 128.1, 127.9, 51.4, 42.3; HRMS (ESI) Calcd for $C_9H_{12}NO_2$ (M+H): 166.0863; Found: 166.0860.

1) Calmès, M.; Escale, F.; Glot, C.; Rolland, M.; Martinez, J. *Eur. J. Org. Chem.* **2000**, 2459
2) Weiner, B.; Baeza, A.; Jerphagnon, T. B.; Feringa, L. *J. Am. Chem. Soc.* **2009**, *131*, 9473
3) Stefani, H. A.; Amaral, M. F. Z. J.; Reyes-Rangel, G.; Vargas-Caporali, J.; Juaristi, E. *Eur. J. Org. Chem.* **2010**, 6393

The X-ray structure of compound **2n**



2n



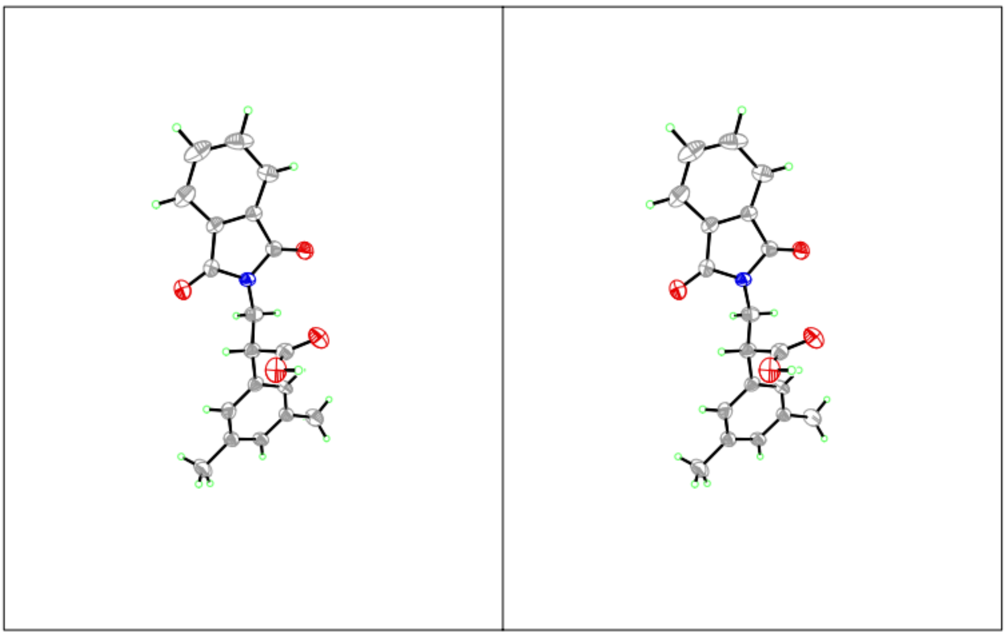


Table 1. Crystal data and structure refinement for **2n**.

Identification code	**2n**	
Empirical formula	$C_{19}H_{17}NO_4$	
Formula weight	323.34	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1250(16) Å	alpha = 90.91(3)°.
	b = 9.3280(19) Å	beta = 96.19(3)°.
	c = 11.408(2) Å	gamma = 107.69(3)°.
Volume	817.8(3) Å^3	
Z	2	
Calculated density	1.313 Mg/m^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	340	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.80 to 25.37°	
Limiting indices	0<=h<=9, -11<=k<=10, -13<=l<=13	
Reflections collected / unique	3234 / 3007 [R(int) = 0.0378]	
Completeness to theta = 25.37°	99.9 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.9908 and 0.9817	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3007 / 0 / 217	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0691, wR2 = 0.1238	
R indices (all data)	R1 = 0.1599, wR2 = 0.1481	
Largest diff. peak and hole	0.174 and -0.164 e. Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2n**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N	7101(4)	5661(3)	6651(3)	51(1)
O(1)	10037(4)	6857(3)	7012(3)	90(1)
C(1)	8836(5)	5725(5)	6703(4)	59(1)
O(2)	4444(3)	3880(3)	6031(2)	70(1)
C(2)	8852(5)	4215(4)	6342(3)	54(1)
O(3)	4539(4)	5570(3)	8629(2)	73(1)
C(3)	10256(6)	3680(6)	6272(4)	76(1)
O(4)	6927(3)	6395(3)	9914(3)	73(1)
C(4)	9848(8)	2188(7)	5849(4)	92(2)
C(5)	8175(8)	1311(5)	5564(4)	93(2)
C(6)	6766(6)	1868(5)	5643(4)	76(1)
C(7)	7177(5)	3323(4)	6043(3)	54(1)
C(8)	6007(5)	4236(4)	6218(3)	52(1)
C(9)	6502(5)	6957(4)	6834(3)	62(1)
C(10)	6929(5)	7588(4)	8103(3)	53(1)
C(11)	6055(5)	6416(4)	8927(4)	52(1)
C(12)	6430(5)	9010(4)	8288(3)	50(1)
C(13)	4744(5)	9050(4)	7992(3)	54(1)
C(14)	4302(5)	10341(4)	8185(3)	52(1)
C(15)	5605(5)	11602(4)	8698(3)	55(1)
C(16)	7301(5)	11622(4)	8995(3)	56(1)
C(17)	7682(5)	10308(4)	8781(3)	56(1)
C(18)	2468(5)	10396(4)	7905(4)	81(1)
C(19)	8669(6)	13015(4)	9563(4)	90(2)

Table 3. Bond lengths [Å] and angles [°] for **2n**.

N-C(1)	1.387(4)
N-C(8)	1.402(4)
N-C(9)	1.454(4)
O(1)-C(1)	1.216(4)
C(1)-C(2)	1.465(5)
O(2)-C(8)	1.205(4)
C(2)-C(7)	1.365(5)
C(2)-C(3)	1.386(5)
O(3)-C(11)	1.251(4)
C(3)-C(4)	1.394(6)
C(3)-H(3A)	0.9300
O(4)-C(11)	1.268(4)
O(4)-H(4B)	0.8200
C(4)-C(5)	1.358(6)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.404(6)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.354(5)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.482(5)
C(9)-C(10)	1.517(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.513(5)
C(10)-C(12)	1.518(4)
C(10)-H(10A)	0.9800
C(12)-C(17)	1.387(5)
C(12)-C(13)	1.387(5)
C(13)-C(14)	1.378(4)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.391(5)
C(14)-C(18)	1.506(5)
C(15)-C(16)	1.378(5)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.376(5)
C(16)-C(19)	1.512(5)

C(17)-H(17A)	0.9300
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(1)-N-C(8)	110.9(3)
C(1)-N-C(9)	124.4(3)
C(8)-N-C(9)	124.0(3)
O(1)-C(1)-N	123.4(4)
O(1)-C(1)-C(2)	130.2(4)
N-C(1)-C(2)	106.5(3)
C(7)-C(2)-C(3)	121.9(4)
C(7)-C(2)-C(1)	108.8(3)
C(3)-C(2)-C(1)	129.3(4)
C(2)-C(3)-C(4)	115.7(4)
C(2)-C(3)-H(3A)	122.1
C(4)-C(3)-H(3A)	122.1
C(11)-O(4)-H(4B)	109.5
C(5)-C(4)-C(3)	121.6(4)
C(5)-C(4)-H(4A)	119.2
C(3)-C(4)-H(4A)	119.2
C(4)-C(5)-C(6)	122.0(4)
C(4)-C(5)-H(5A)	119.0
C(6)-C(5)-H(5A)	119.0
C(7)-C(6)-C(5)	115.9(4)
C(7)-C(6)-H(6A)	122.0
C(5)-C(6)-H(6A)	122.0
C(6)-C(7)-C(2)	122.8(4)
C(6)-C(7)-C(8)	129.1(4)
C(2)-C(7)-C(8)	108.1(3)
O(2)-C(8)-N	125.4(3)
O(2)-C(8)-C(7)	129.0(4)
N-C(8)-C(7)	105.6(3)
N-C(9)-C(10)	112.5(3)
N-C(9)-H(9A)	109.1
C(10)-C(9)-H(9A)	109.1

N-C(9)-H(9B)	109.1
C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
C(11)-C(10)-C(9)	110.5(3)
C(11)-C(10)-C(12)	109.6(3)
C(9)-C(10)-C(12)	113.1(3)
C(11)-C(10)-H(10A)	107.8
C(9)-C(10)-H(10A)	107.8
C(12)-C(10)-H(10A)	107.8
O(3)-C(11)-O(4)	124.1(4)
O(3)-C(11)-C(10)	119.8(4)
O(4)-C(11)-C(10)	116.1(4)
C(17)-C(12)-C(13)	118.5(3)
C(17)-C(12)-C(10)	119.5(3)
C(13)-C(12)-C(10)	121.9(3)
C(14)-C(13)-C(12)	121.3(3)
C(14)-C(13)-H(13A)	119.3
C(12)-C(13)-H(13A)	119.3
C(13)-C(14)-C(15)	117.6(3)
C(13)-C(14)-C(18)	122.2(4)
C(15)-C(14)-C(18)	120.1(3)
C(16)-C(15)-C(14)	123.2(3)
C(16)-C(15)-H(15A)	118.4
C(14)-C(15)-H(15A)	118.4
C(17)-C(16)-C(15)	117.1(4)
C(17)-C(16)-C(19)	121.6(4)
C(15)-C(16)-C(19)	121.3(3)
C(16)-C(17)-C(12)	122.2(4)
C(16)-C(17)-H(17A)	118.9
C(12)-C(17)-H(17A)	118.9
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5

H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2n**. The anisotropic displacement factor exponent takes the form: $-2 pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N	49(2)	41(2)	66(2)	-6(2)	5(2)	20(2)
O(1)	61(2)	82(2)	112(3)	-25(2)	22(2)	-4(2)
C(1)	49(3)	62(3)	64(3)	-1(2)	14(2)	13(2)
O(2)	49(2)	66(2)	91(2)	-10(2)	-3(2)	17(1)
C(2)	53(3)	57(3)	58(3)	1(2)	9(2)	26(2)
O(3)	72(2)	63(2)	72(2)	2(2)	-9(2)	8(2)
C(3)	71(3)	103(4)	69(3)	3(3)	13(3)	48(3)
O(4)	67(2)	80(2)	75(2)	22(2)	6(2)	25(2)
C(4)	110(5)	112(5)	87(4)	15(3)	24(4)	80(4)
C(5)	138(5)	58(3)	99(4)	3(3)	23(4)	53(3)
C(6)	84(3)	51(3)	92(4)	-5(2)	14(3)	21(3)
C(7)	50(2)	47(2)	68(3)	-2(2)	9(2)	18(2)
C(8)	54(3)	51(2)	51(3)	0(2)	4(2)	17(2)
C(9)	77(3)	50(2)	65(3)	4(2)	7(2)	29(2)
C(10)	56(3)	49(2)	56(3)	1(2)	9(2)	20(2)
C(11)	58(3)	46(2)	61(3)	8(2)	9(2)	29(2)
C(12)	52(2)	47(2)	56(3)	4(2)	11(2)	24(2)
C(13)	59(3)	39(2)	55(3)	-6(2)	-4(2)	7(2)
C(14)	51(2)	45(2)	63(3)	-4(2)	1(2)	20(2)
C(15)	57(3)	42(2)	68(3)	-8(2)	0(2)	24(2)
C(16)	55(3)	47(2)	66(3)	-3(2)	2(2)	18(2)
C(17)	47(2)	58(3)	64(3)	5(2)	6(2)	18(2)
C(18)	65(3)	74(3)	107(4)	-9(3)	-14(3)	34(2)
C(19)	73(3)	66(3)	118(4)	-31(3)	-13(3)	12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2n**.

	x	y	z	U(eq)
H(3A)	11397	4278	6493	91
H(4B)	6354	5736	10305	110
H(4A)	10745	1783	5760	110
H(5A)	7956	311	5309	111
H(6A)	5620	1274	5434	91
H(9A)	5253	6665	6619	75
H(9B)	7039	7737	6320	75
H(10A)	8189	7840	8312	63
H(13A)	3895	8188	7657	65
H(15A)	5317	12474	8847	65
H(17A)	8817	10290	8974	67
H(18A)	1737	9439	7558	121
H(18B)	2454	11167	7360	121
H(18C)	2044	10617	8618	121
H(19A)	8163	13814	9633	135
H(19B)	9605	13319	9083	135
H(19C)	9108	12798	10332	135

Table 6. Torsion angles [°] for **2n**.

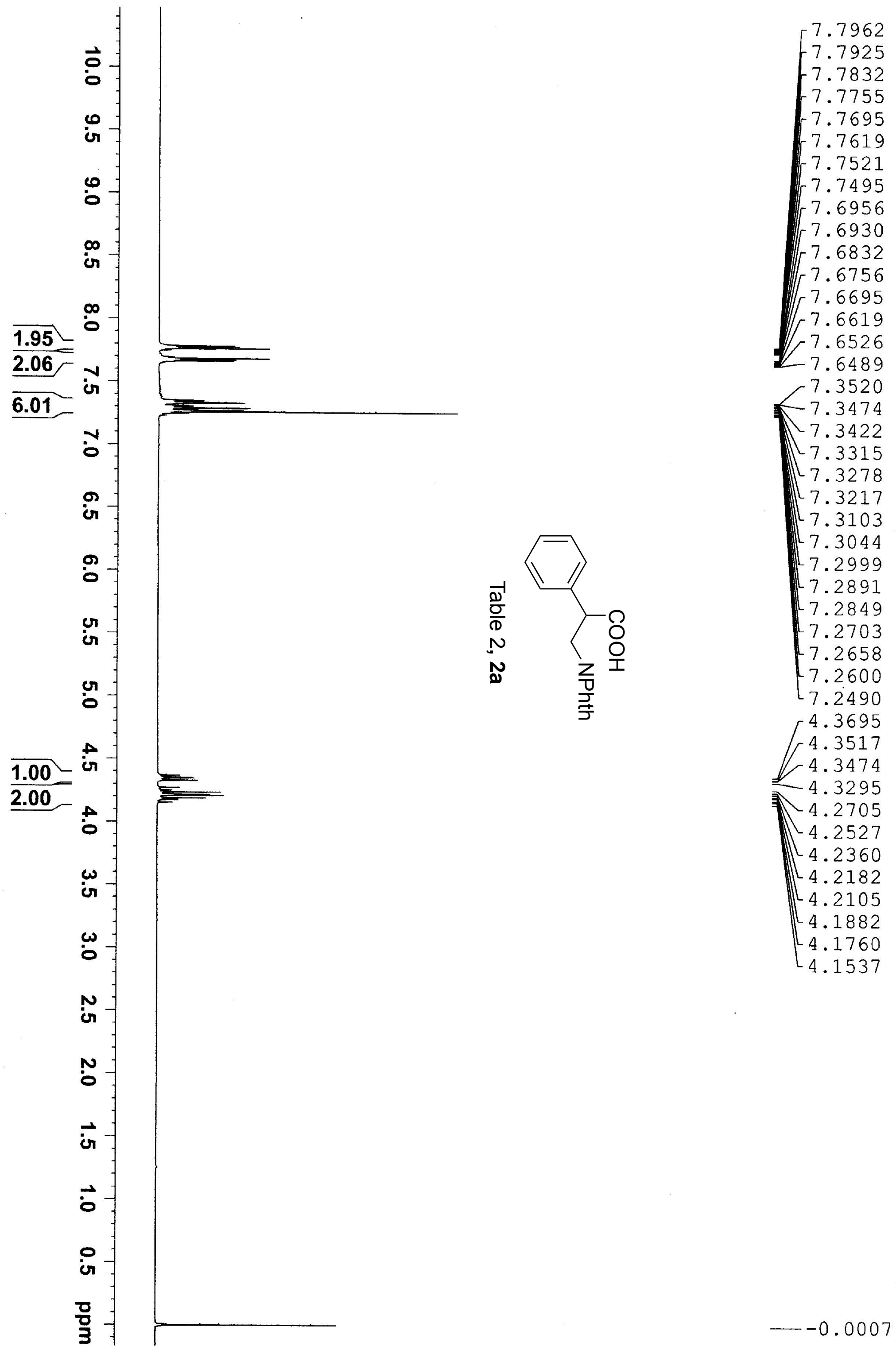
C(8)-N-C(1)-O(1)	177.5(4)
C(9)-N-C(1)-O(1)	6.8(6)
C(8)-N-C(1)-C(2)	-3.3(4)
C(9)-N-C(1)-C(2)	-174.0(3)
O(1)-C(1)-C(2)-C(7)	-178.4(5)
N-C(1)-C(2)-C(7)	2.4(4)
O(1)-C(1)-C(2)-C(3)	0.8(8)
N-C(1)-C(2)-C(3)	-178.3(4)
C(7)-C(2)-C(3)-C(4)	1.6(6)
C(1)-C(2)-C(3)-C(4)	-177.6(4)
C(2)-C(3)-C(4)-C(5)	-2.1(7)
C(3)-C(4)-C(5)-C(6)	2.0(8)
C(4)-C(5)-C(6)-C(7)	-1.3(7)
C(5)-C(6)-C(7)-C(2)	0.8(6)
C(5)-C(6)-C(7)-C(8)	179.5(4)
C(3)-C(2)-C(7)-C(6)	-1.0(7)
C(1)-C(2)-C(7)-C(6)	178.3(4)
C(3)-C(2)-C(7)-C(8)	180.0(4)
C(1)-C(2)-C(7)-C(8)	-0.7(4)
C(1)-N-C(8)-O(2)	-176.6(4)
C(9)-N-C(8)-O(2)	-5.9(6)
C(1)-N-C(8)-C(7)	2.9(4)
C(9)-N-C(8)-C(7)	173.6(3)
C(6)-C(7)-C(8)-O(2)	-0.8(7)
C(2)-C(7)-C(8)-O(2)	178.2(4)
C(6)-C(7)-C(8)-N	179.8(4)
C(2)-C(7)-C(8)-N	-1.3(4)
C(1)-N-C(9)-C(10)	-68.7(5)
C(8)-N-C(9)-C(10)	121.8(4)
N-C(9)-C(10)-C(11)	-60.9(4)
N-C(9)-C(10)-C(12)	175.8(3)
C(9)-C(10)-C(11)-O(3)	-39.7(5)
C(12)-C(10)-C(11)-O(3)	85.6(4)
C(9)-C(10)-C(11)-O(4)	142.2(3)
C(12)-C(10)-C(11)-O(4)	-92.5(4)
C(11)-C(10)-C(12)-C(17)	111.8(4)

C(9)-C(10)-C(12)-C(17)	-124.4(4)
C(11)-C(10)-C(12)-C(13)	-67.3(4)
C(9)-C(10)-C(12)-C(13)	56.5(5)
C(17)-C(12)-C(13)-C(14)	-0.3(6)
C(10)-C(12)-C(13)-C(14)	178.8(3)
C(12)-C(13)-C(14)-C(15)	-0.6(5)
C(12)-C(13)-C(14)-C(18)	-178.1(4)
C(13)-C(14)-C(15)-C(16)	1.3(6)
C(18)-C(14)-C(15)-C(16)	178.9(4)
C(14)-C(15)-C(16)-C(17)	-1.0(6)
C(14)-C(15)-C(16)-C(19)	-179.3(4)
C(15)-C(16)-C(17)-C(12)	0.0(6)
C(19)-C(16)-C(17)-C(12)	178.3(4)
C(13)-C(12)-C(17)-C(16)	0.6(6)
C(10)-C(12)-C(17)-C(16)	-178.6(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **2n** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)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7.7755
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7.6695
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7.6526
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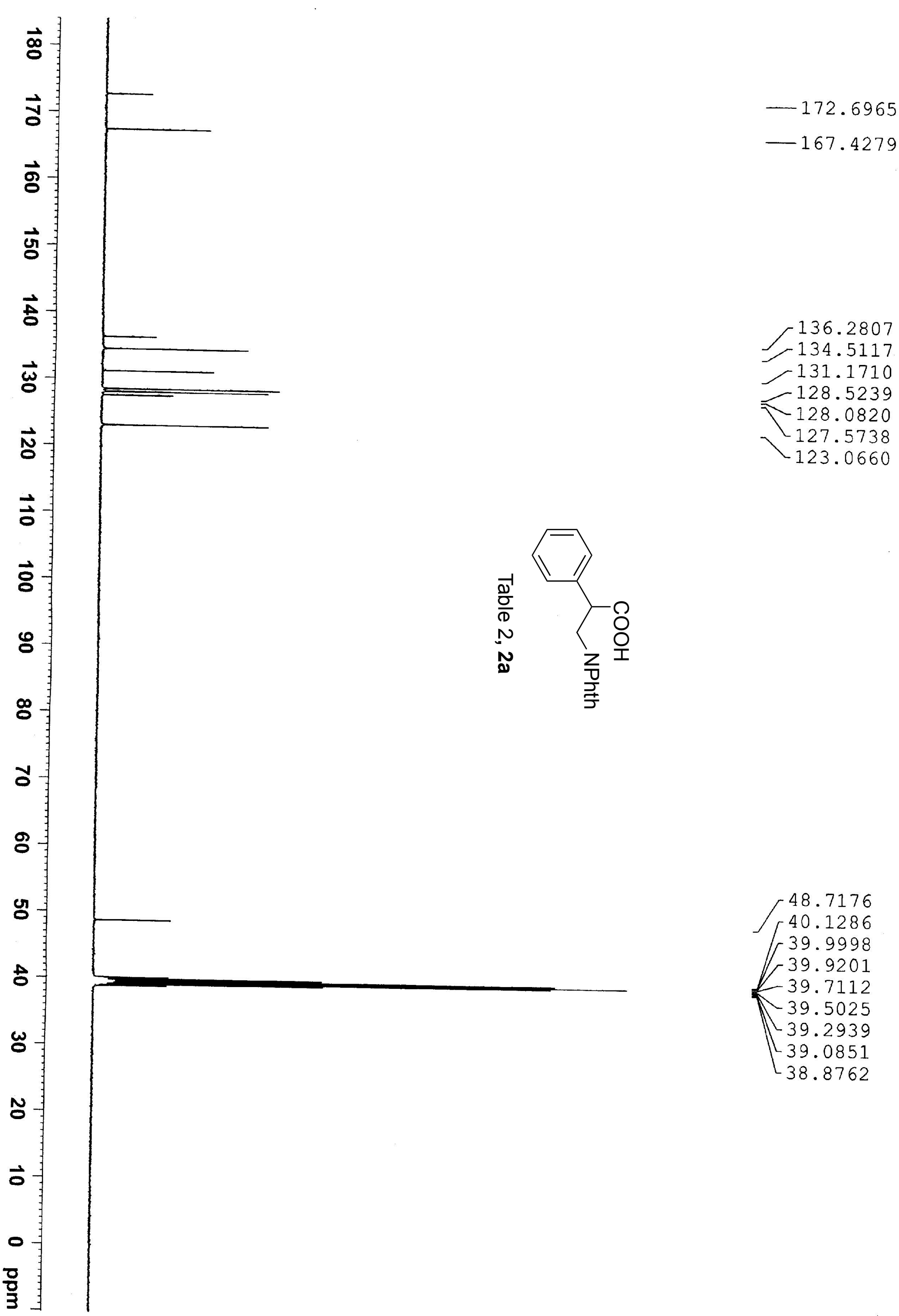
7.3474
7.3422
7.3315
7.3278
7.3217
7.3103
7.3044
7.2999
7.2891
7.2849
7.2703
7.2658
7.2600
7.2490
4.3695
4.3517
4.3474
4.3295
4.2705
4.2527
4.2360
4.2182
4.2105
4.1882
4.1760
4.1537
-0.0007
COOH
NPhth
Table 2, 2a
1.95
2.06
6.01
1.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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127.5738
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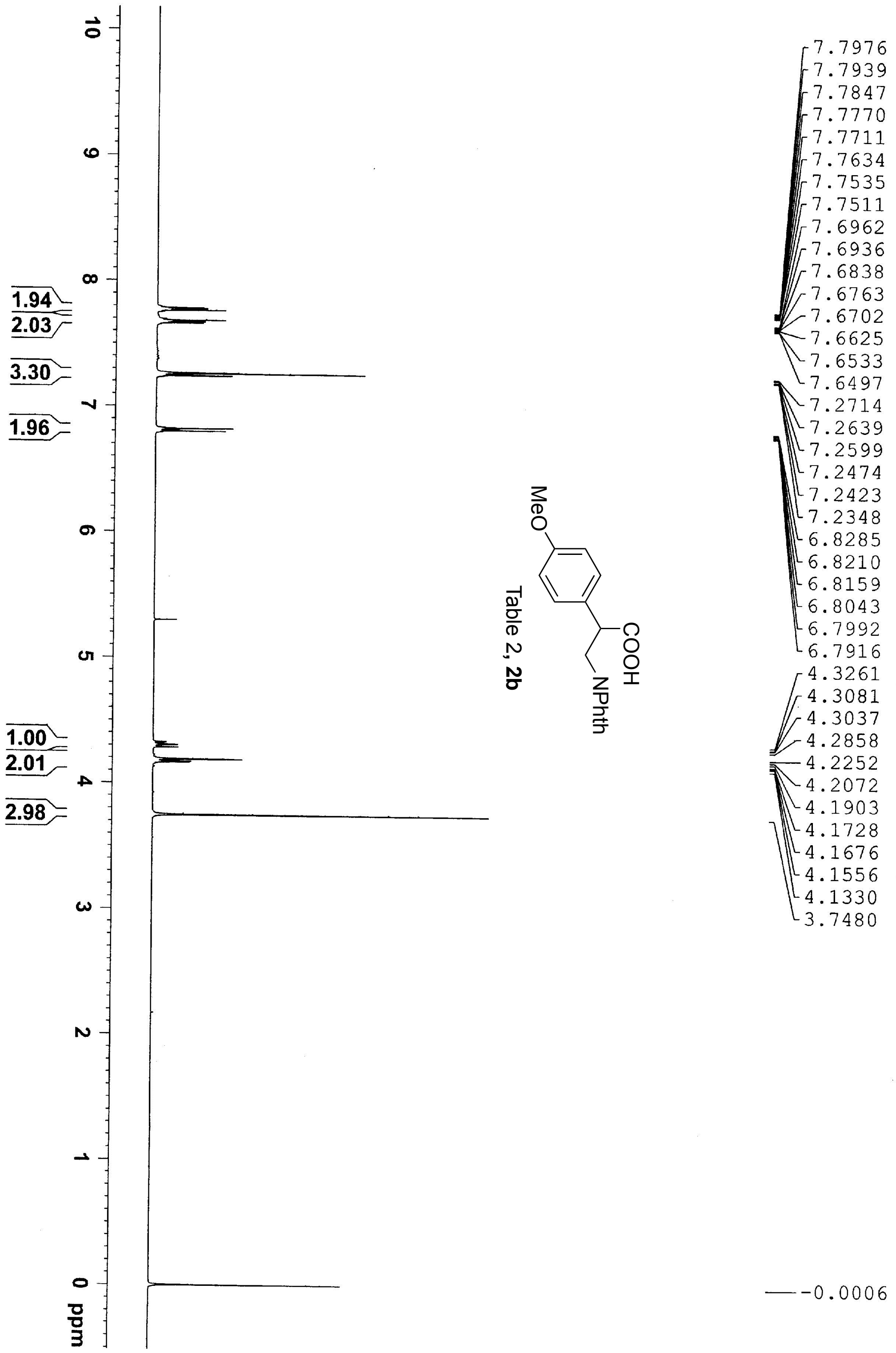
40.1286
39.9998
39.9201
39.7112
39.5025
39.2939
39.0851
38.8762
COOH
NPhth
Table 2, 2a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


MeO
COOH
NPhth
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7.7711
7.7634
7.7535
7.7511
7.6962
7.6936
7.6838
7.6763
7.6702
7.6625
7.6533
7.6497
7.2714
7.2639
7.2599
7.2474
7.2423
7.2348
6.8285
6.8210
6.8159
6.8043
6.7992
6.7916
4.3261
4.3081
4.3037
4.2858
4.2252
4.2072
4.1903
4.1728
4.1676
4.1556
4.1330
3.7480
-0.0006
1.94
2.03
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1.00
2.01
2.98
10
9
8
7
6
5
4
3
2
1
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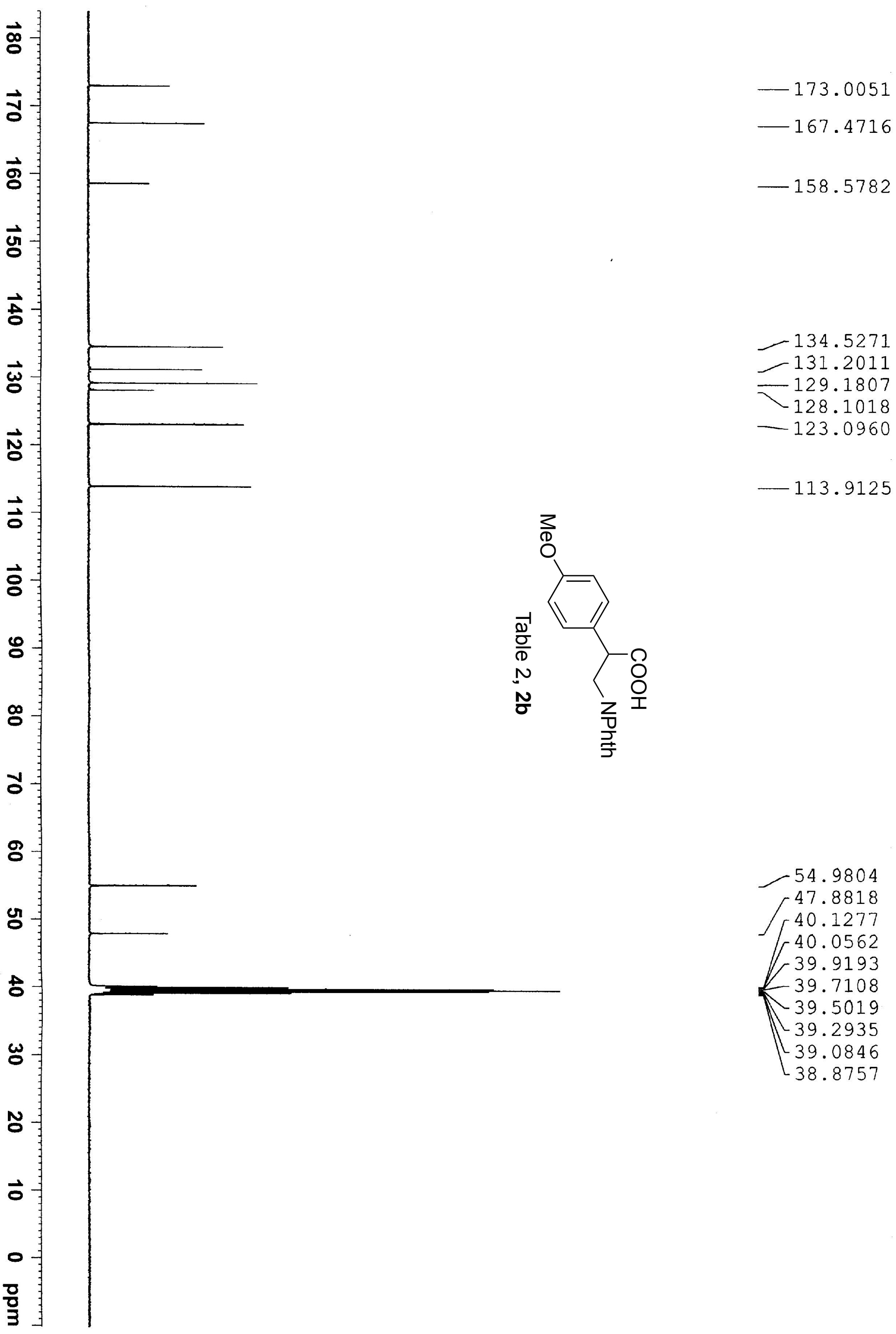
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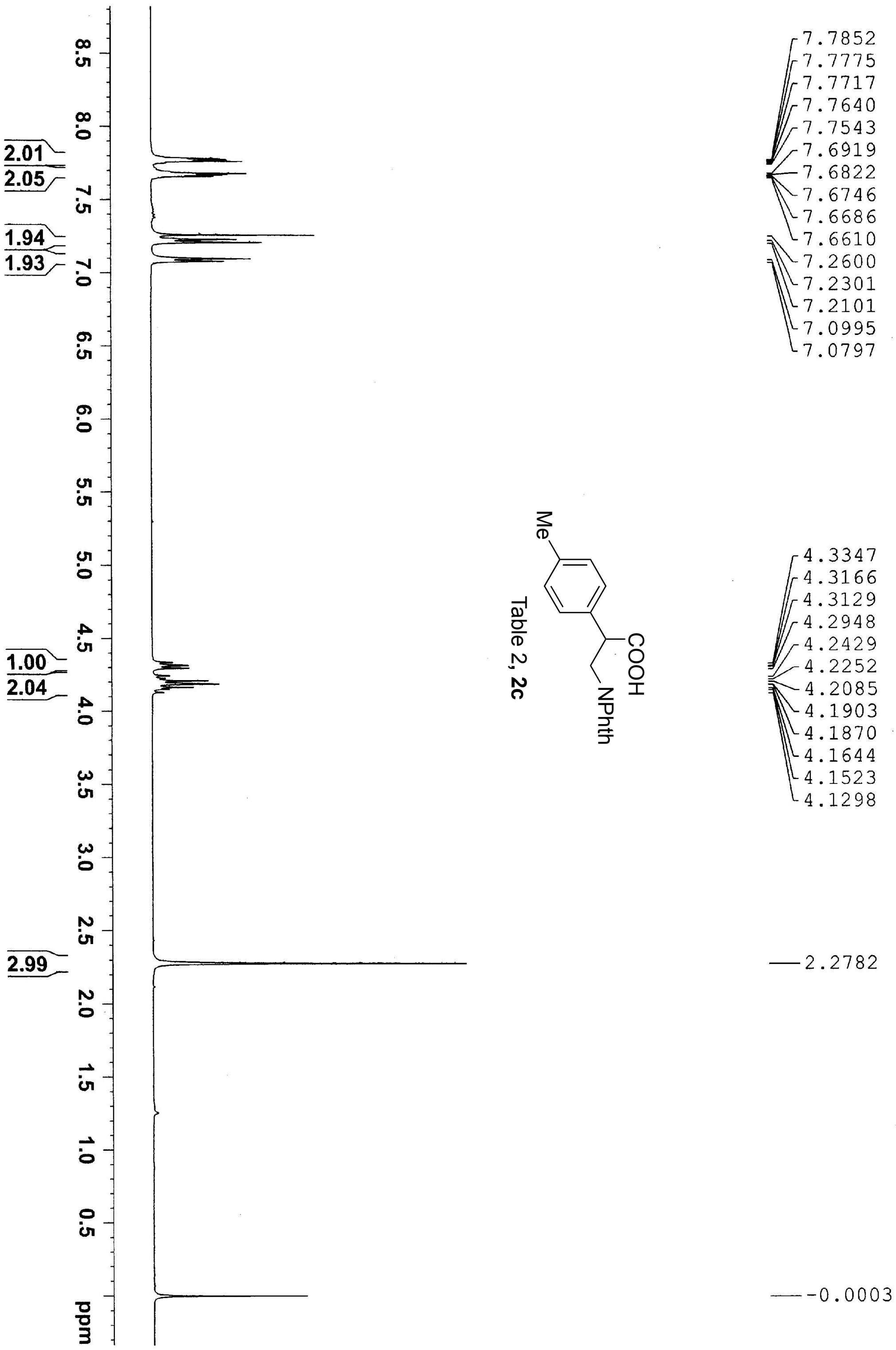
47.8818
40.1277
40.0562
39.9193
39.7108
39.5019
39.2935
39.0846
38.8757
MeO
COOH
NPhth
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Table 2, **2b**



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7.7640
7.7543
7.6919
7.6822
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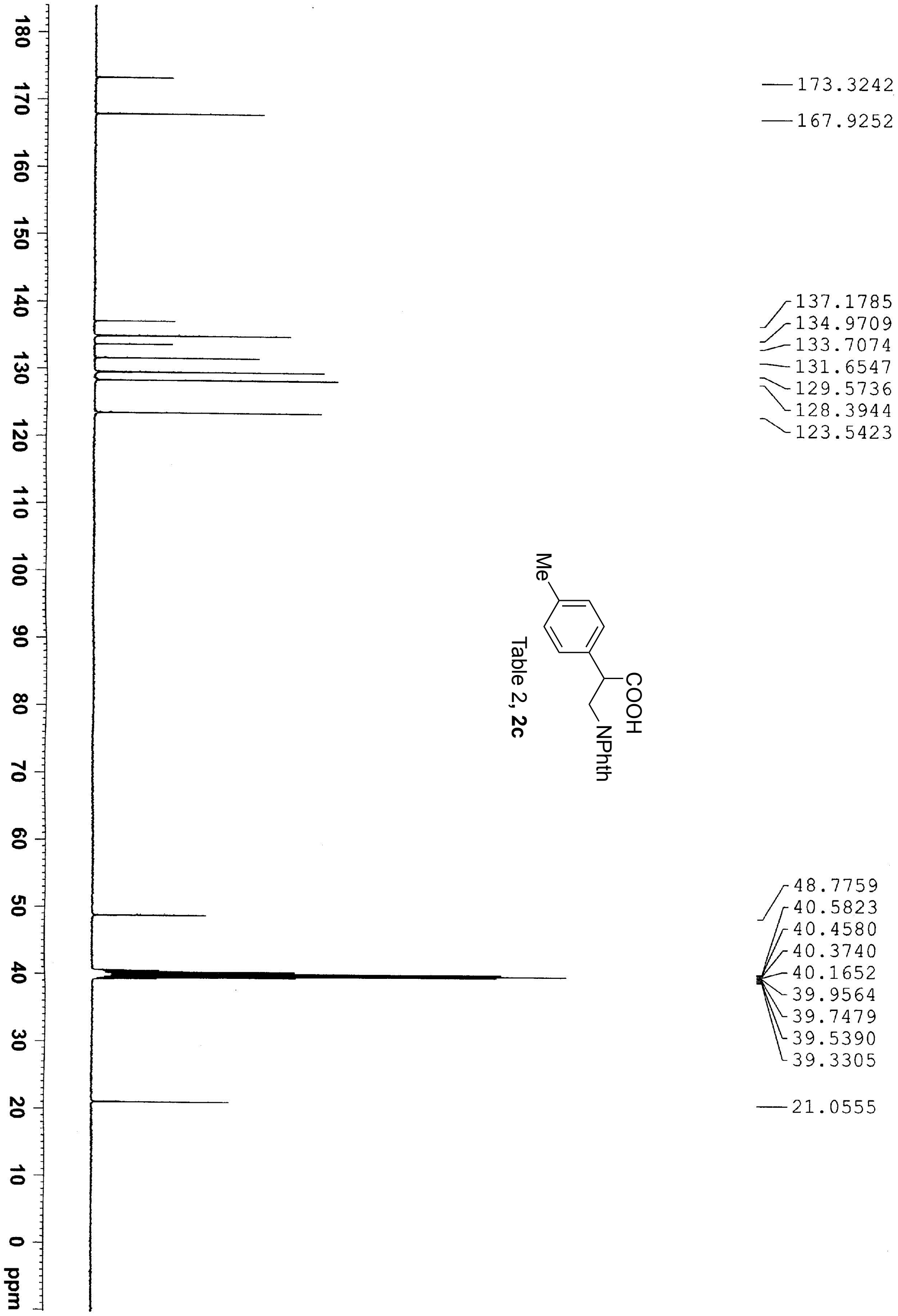
7.2301
7.2101
7.0995
7.0797
4.3347
4.3166
4.3129
4.2948
4.2429
4.2252
4.2085
4.1903
4.1870
4.1644
4.1523
4.1298
2.2782
-0.0003
2.01
2.05
1.94
1.93
1.00
2.04
2.99
Me
COOH
NPhth
Table 2, **2c**
ppm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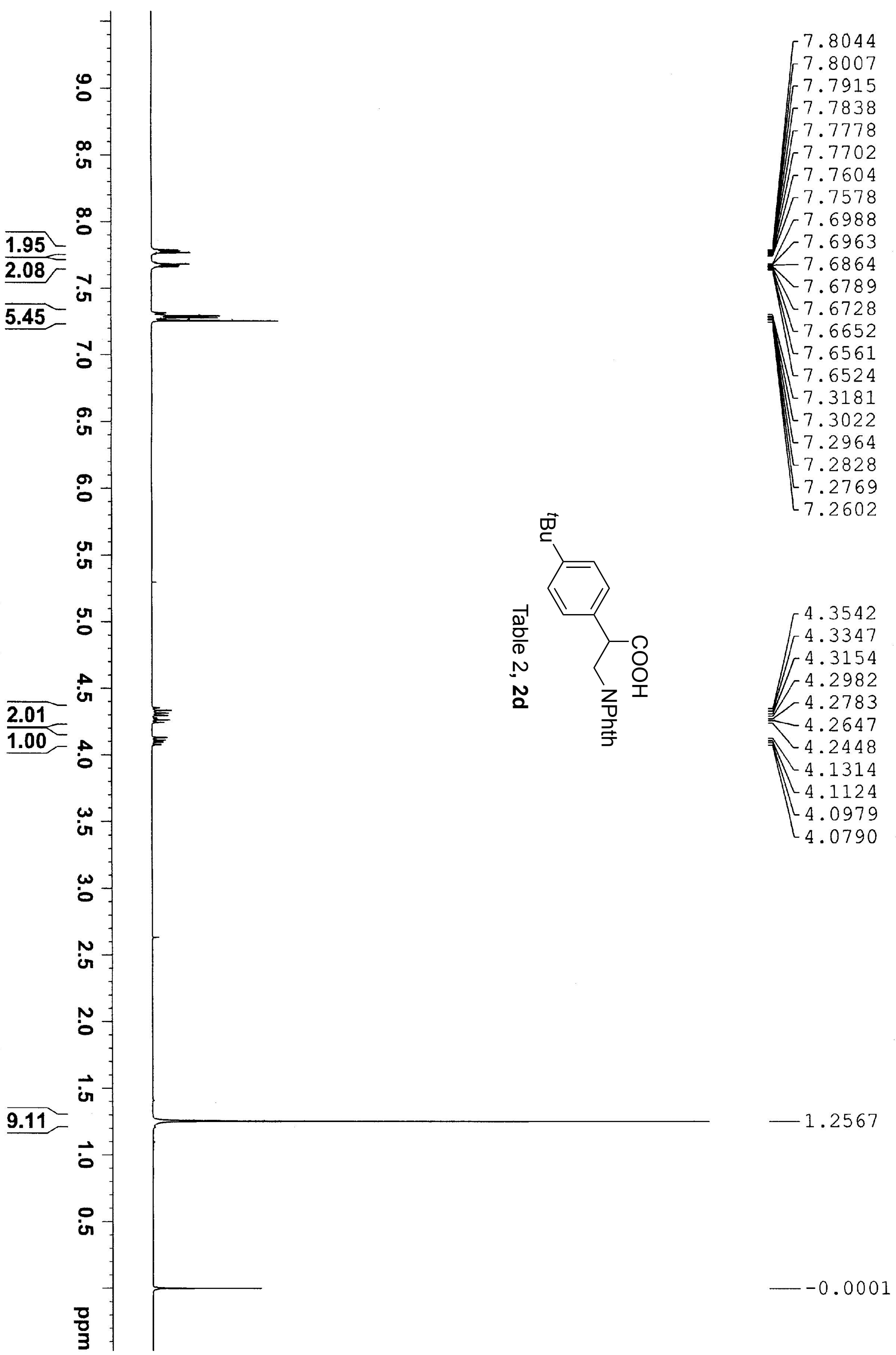
40.4580
40.3740
40.1652
39.9564
39.7479
39.5390
39.3305
21.0555
Me
COOH
NPhth
Table 2, 2c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.6789
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7.6652
7.6561
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7.3181
7.3022
7.2964
7.2828
7.2769
7.2602
4.3542
4.3347
4.3154
4.2982
4.2783
4.2647
4.2448
4.1314
4.1124
4.0979
4.0790
1.2567
-0.0001
1.95
2.08
5.45
2.01
1.00
9.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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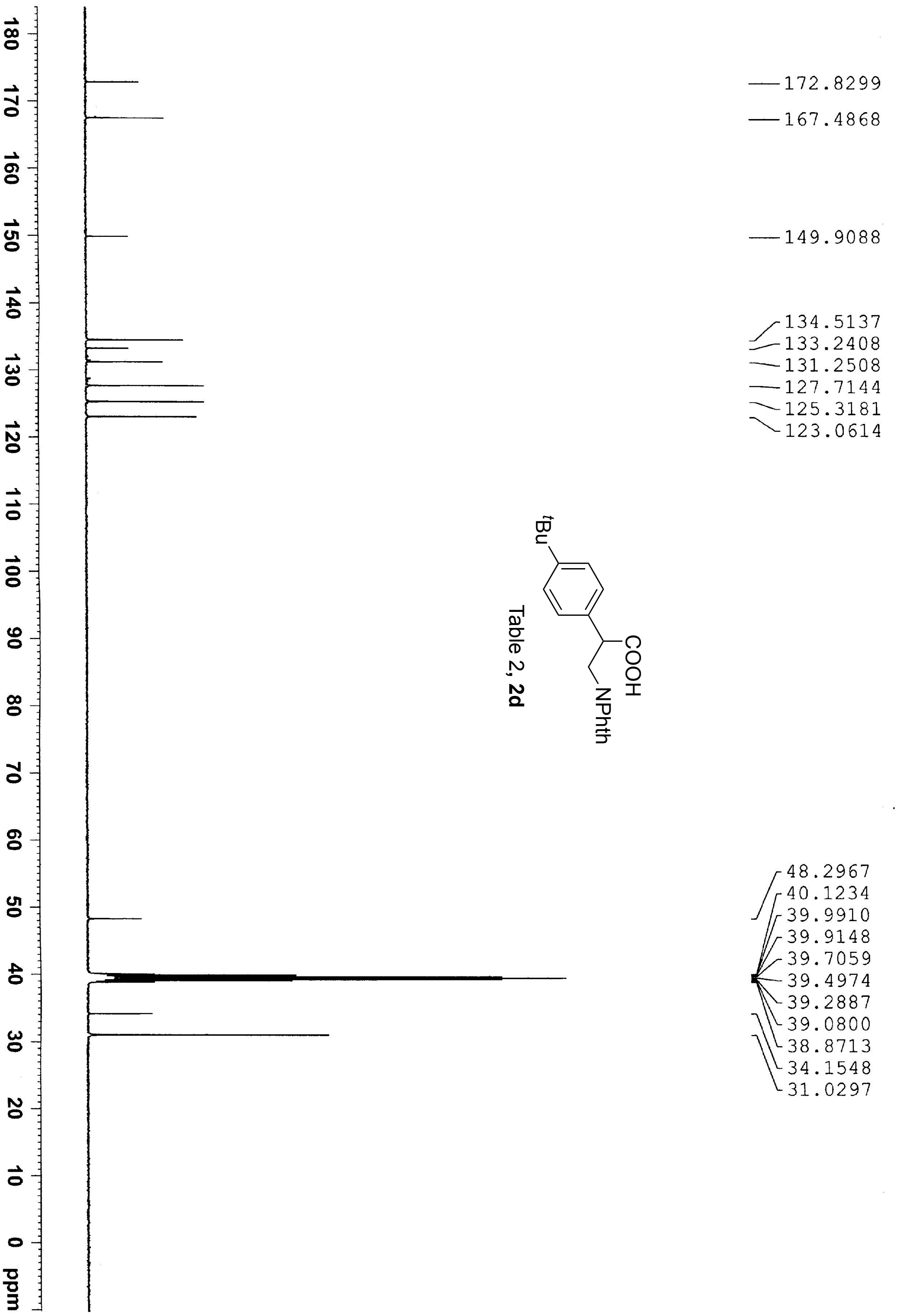
3.0
2.5
2.0
1.5
1.0
0.5
ppm
tBu
COOH
NPhth
Table 2, 2d



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149.9088
134.5137
133.2408
131.2508
127.7144
125.3181
123.0614
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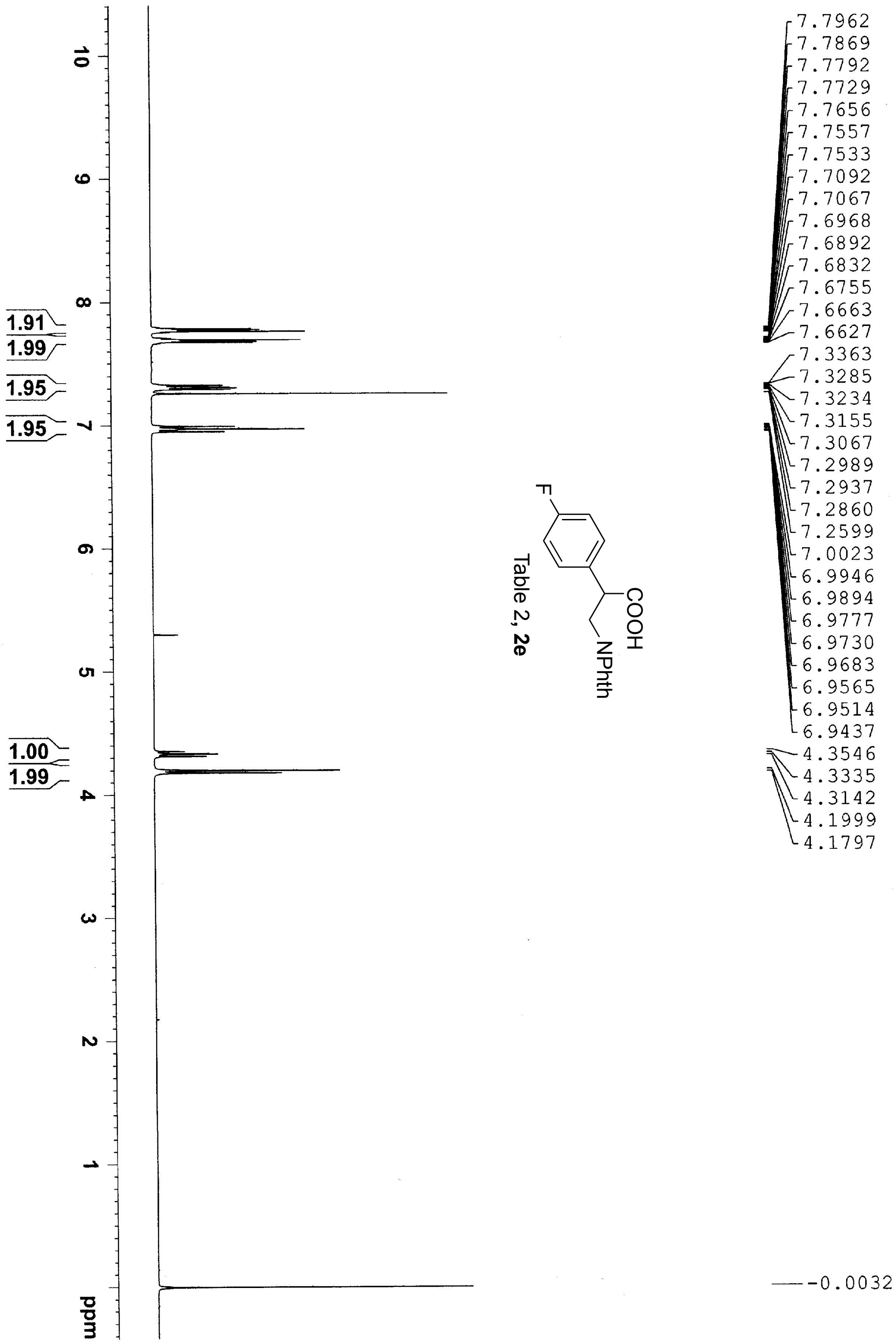
40.1234
39.9910
39.9148
39.7059
39.4974
39.2887
39.0800
38.8713
34.1548
31.0297
tBu
COOH
NPhth
Table 2, 2d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F
COOH
NPhth
Table 2, **2e**
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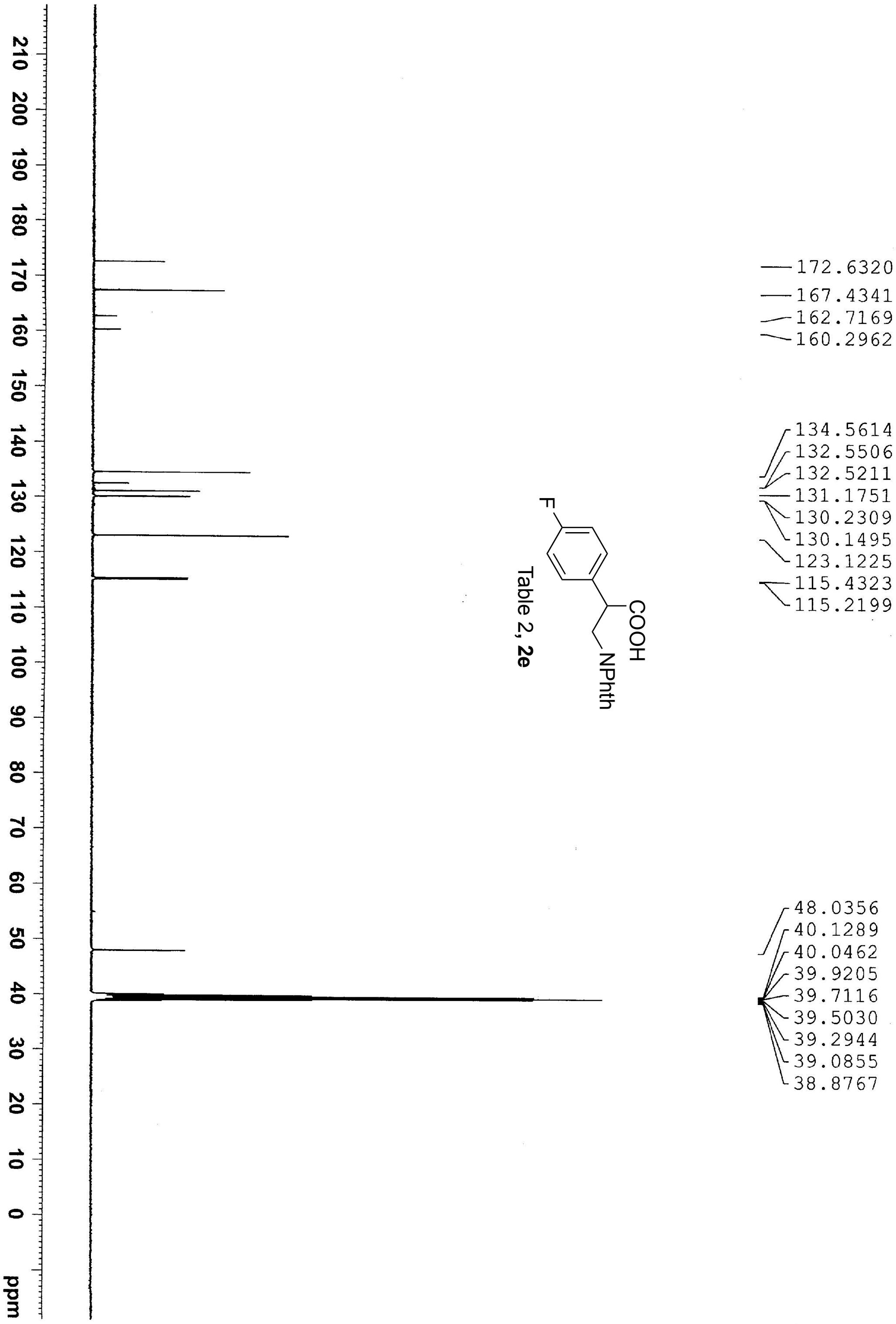
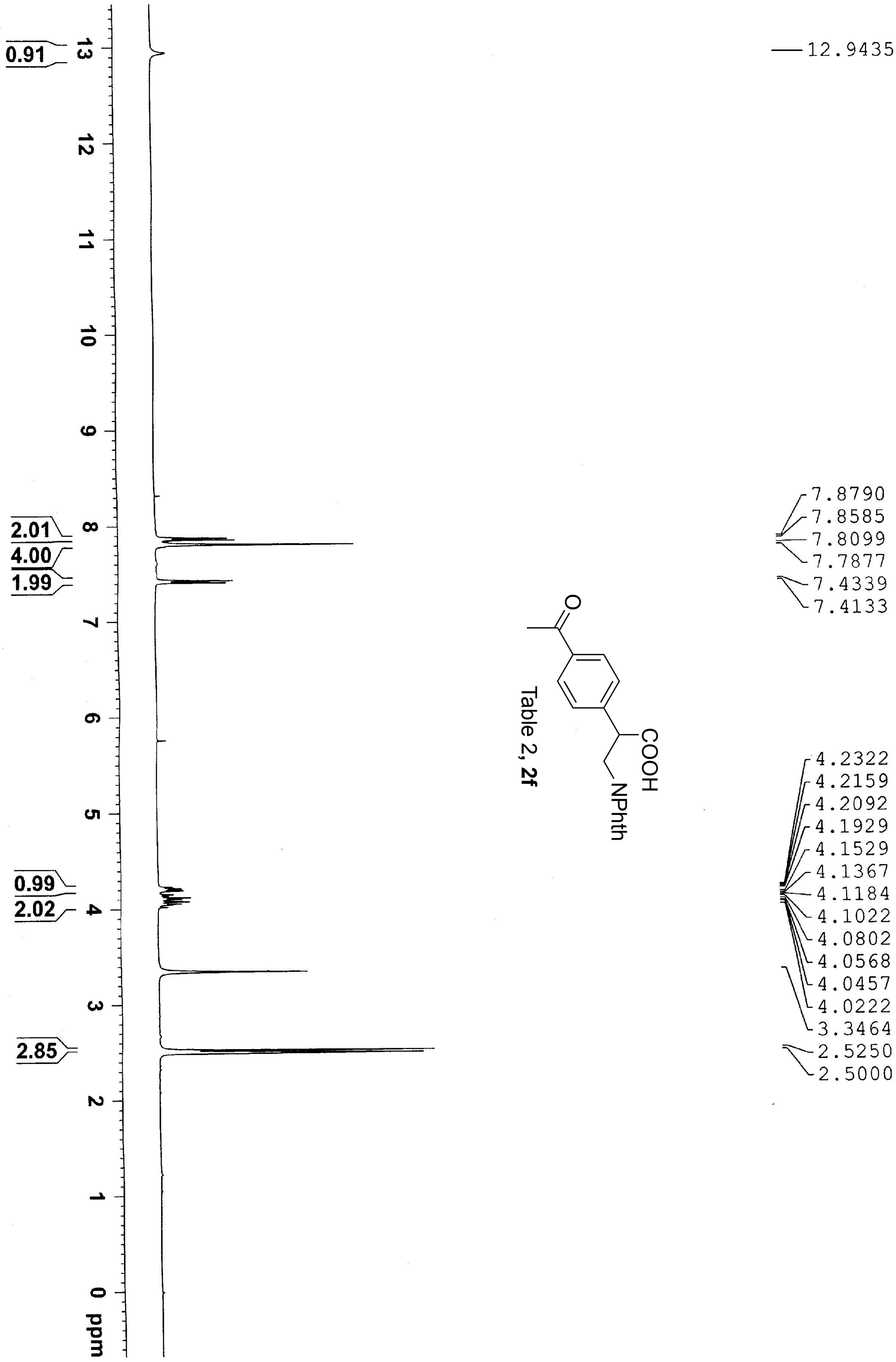
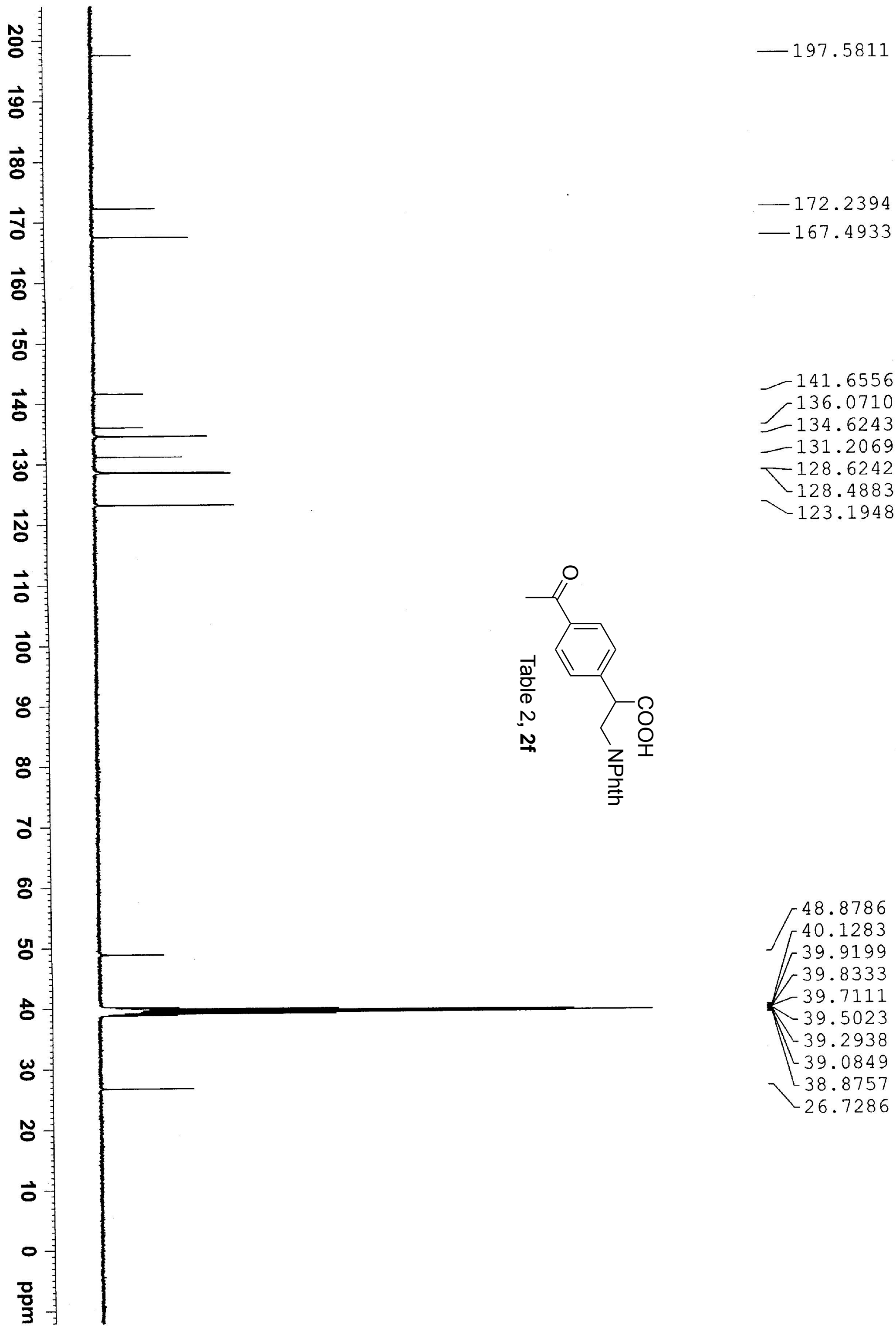
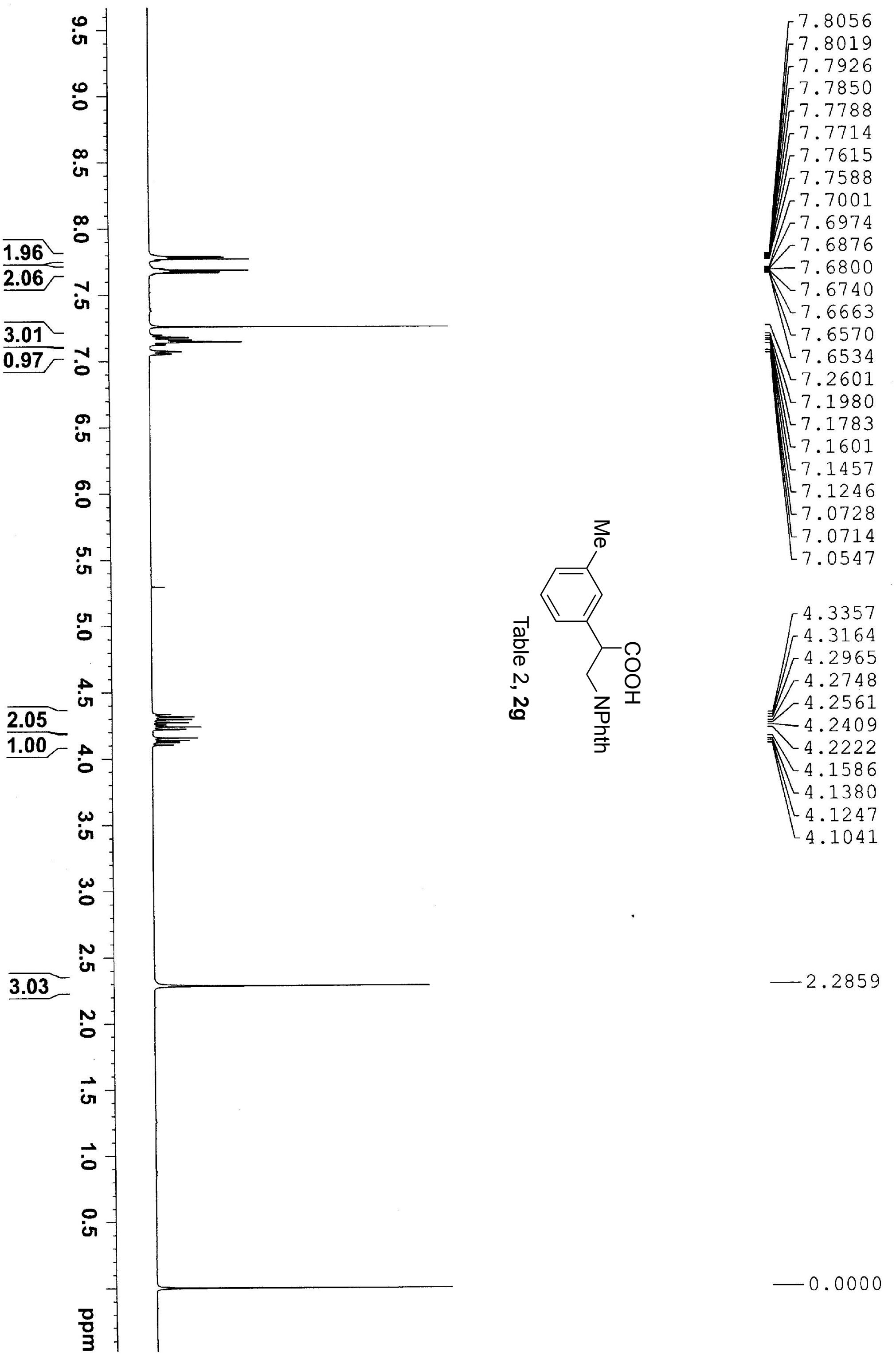
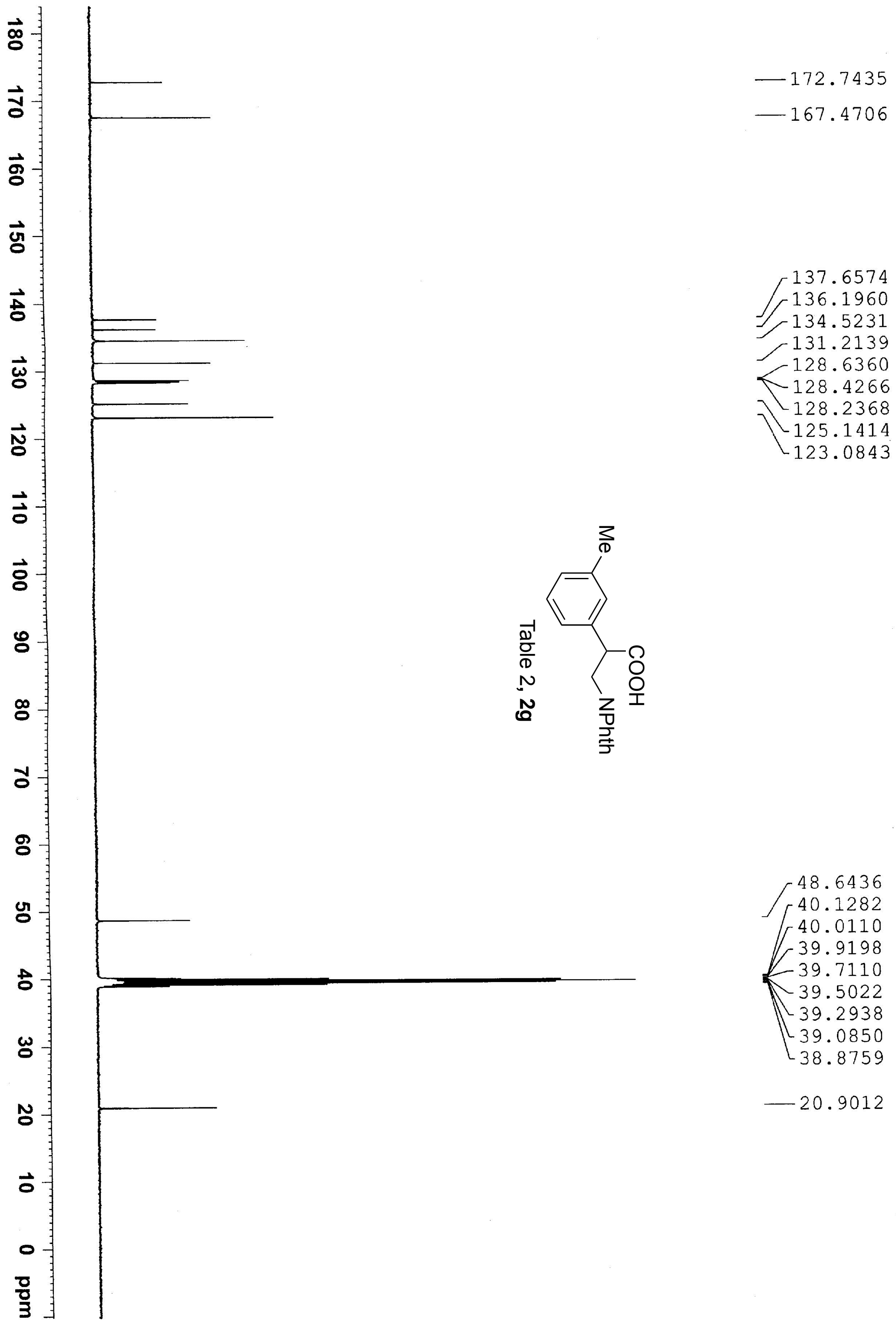
7.7656
7.7557
7.7533
7.7092
7.7067
7.6968
7.6892
7.6832
7.6755
7.6663
7.6627
7.3363
7.3285
7.3234
7.3155
7.3067
7.2989
7.2937
7.2860
7.2599
7.0023
6.9946
6.9894
6.9777
6.9730
6.9683
6.9565
6.9514
6.9437
4.3546
4.3335
4.3142
4.1999
4.1797
-0.0032
1.91
1.99
1.95
1.95
1.00
1.99
ppm


172.6320
167.4341
162.7169
160.2962
134.5614
132.5506
132.5211
131.1751
130.2309
130.1495
123.1225
115.4323
115.2199
48.0356
40.1289
40.0462
39.9205
39.7116
39.5030
39.2944
39.0855
38.8767
F
COOH
NPhth
Table 2, 2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


12.9435
7.8790
7.8585
7.8099
7.7877
7.4339
7.4133
4.2322
4.2159
4.2092
4.1929
4.1529
4.1367
4.1184
4.1022
4.0802
4.0568
4.0457
4.0222
3.3464
2.5250
2.5000
0.91
2.01
4.00
1.99
0.99
2.02
2.85
ppm
COOH
NPhth
O
Table 2, 2f


197.5811
172.2394
167.4933
141.6556
136.0710
134.6243
131.2069
128.6242
128.4883
123.1948
48.8786
40.1283
39.9199
39.8333
39.7111
39.5023
39.2938
39.0849
38.8757
26.7286
COOH
NPhth
O
Table 2, 2f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.8056
7.8019
7.7926
7.7850
7.7788
7.7714
7.7615
7.7588
7.7001
7.6974
7.6876
7.6800
7.6740
7.6663
7.6570
7.6534
7.2601
7.1980
7.1783
7.1601
7.1457
7.1246
7.0728
7.0714
7.0547
4.3357
4.3164
4.2965
4.2748
4.2561
4.2409
4.2222
4.1586
4.1380
4.1247
4.1041
2.2859
0.0000
Me
COOH
NPhth
Table 2, 2g
1.96
2.06
3.01
0.97
2.05
1.00
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


172.7435
167.4706
137.6574
136.1960
134.5231
131.2139
128.6360
128.4266
128.2368
125.1414
123.0843
48.6436
40.1282
40.0110
39.9198
39.7110
39.5022
39.2938
39.0850
38.8759
20.9012
Me
COOH
NPhth
Table 2, 2g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

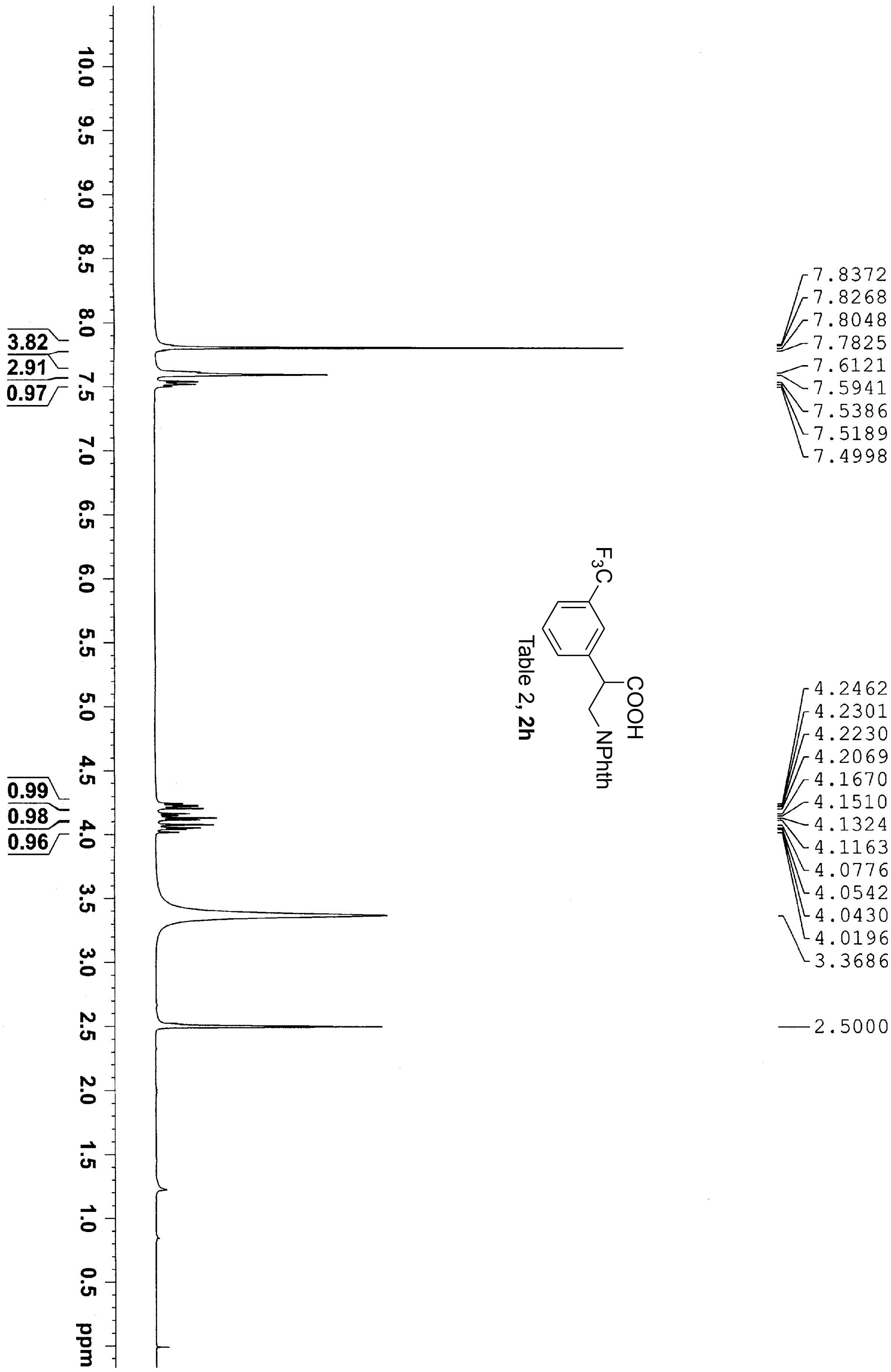
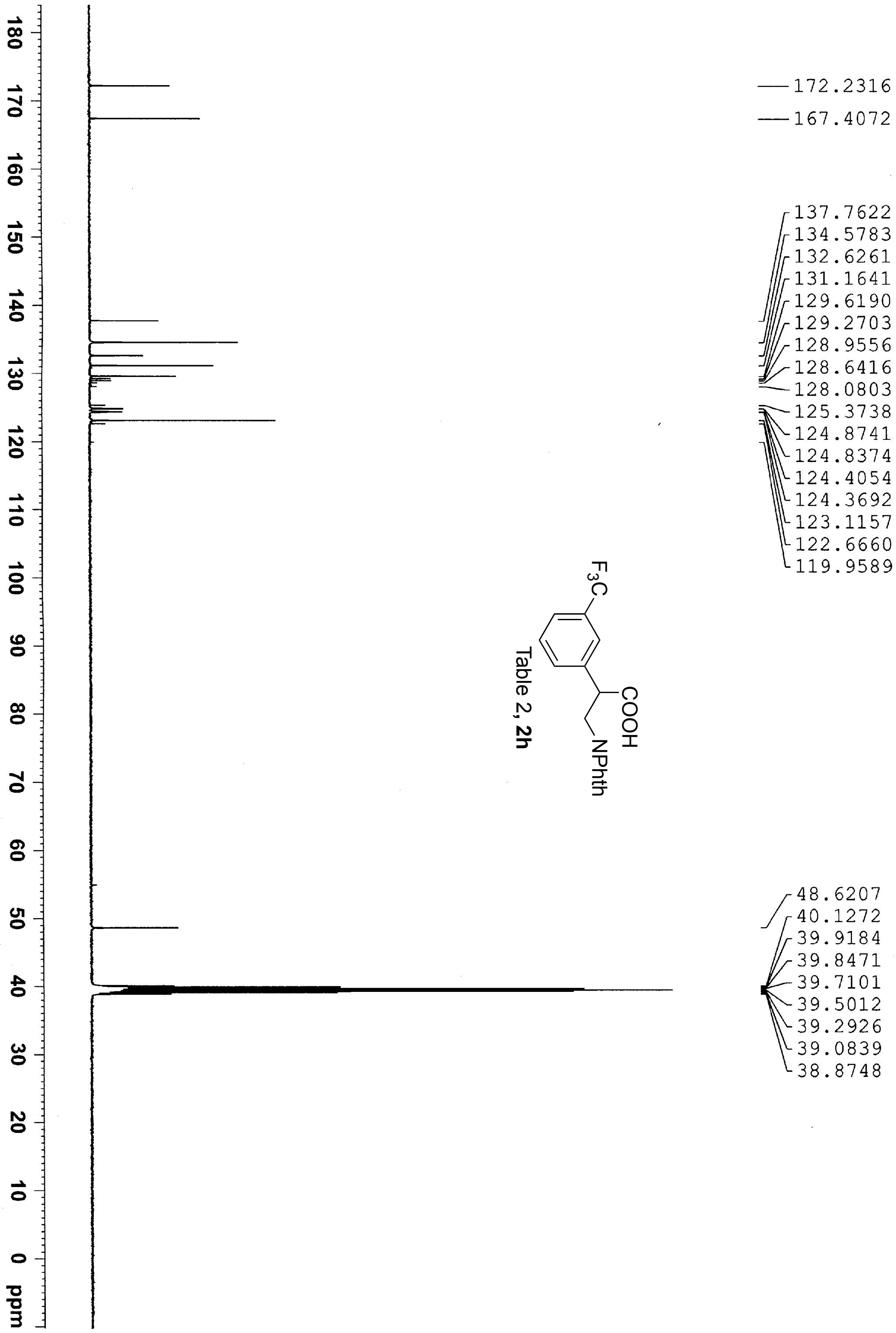

7.8372
7.8268
7.8048
7.7825
7.6121
7.5941
7.5386
7.5189
7.4998
4.2462
4.2301
4.2230
4.2069
4.1670
4.1510
4.1324
4.1163
4.0776
4.0542
4.0430
4.0196
3.3686
2.5000
F3C
COOH
NPhth
3.82
2.91
0.97
0.99
0.98
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

Table 2, **2h**


172.2316
167.4072
137.7622
134.5783
132.6261
131.1641
129.6190
129.2703
128.9556
128.6416
128.0803
125.3738
124.8741
124.8374
124.4054
124.3692
123.1157
122.6660
119.9589
48.6207
40.1272
39.9184
39.8471
39.7101
39.5012
39.2926
39.0839
38.8748
F3C
COOH
NPhth
Table 2, 2h
ppm

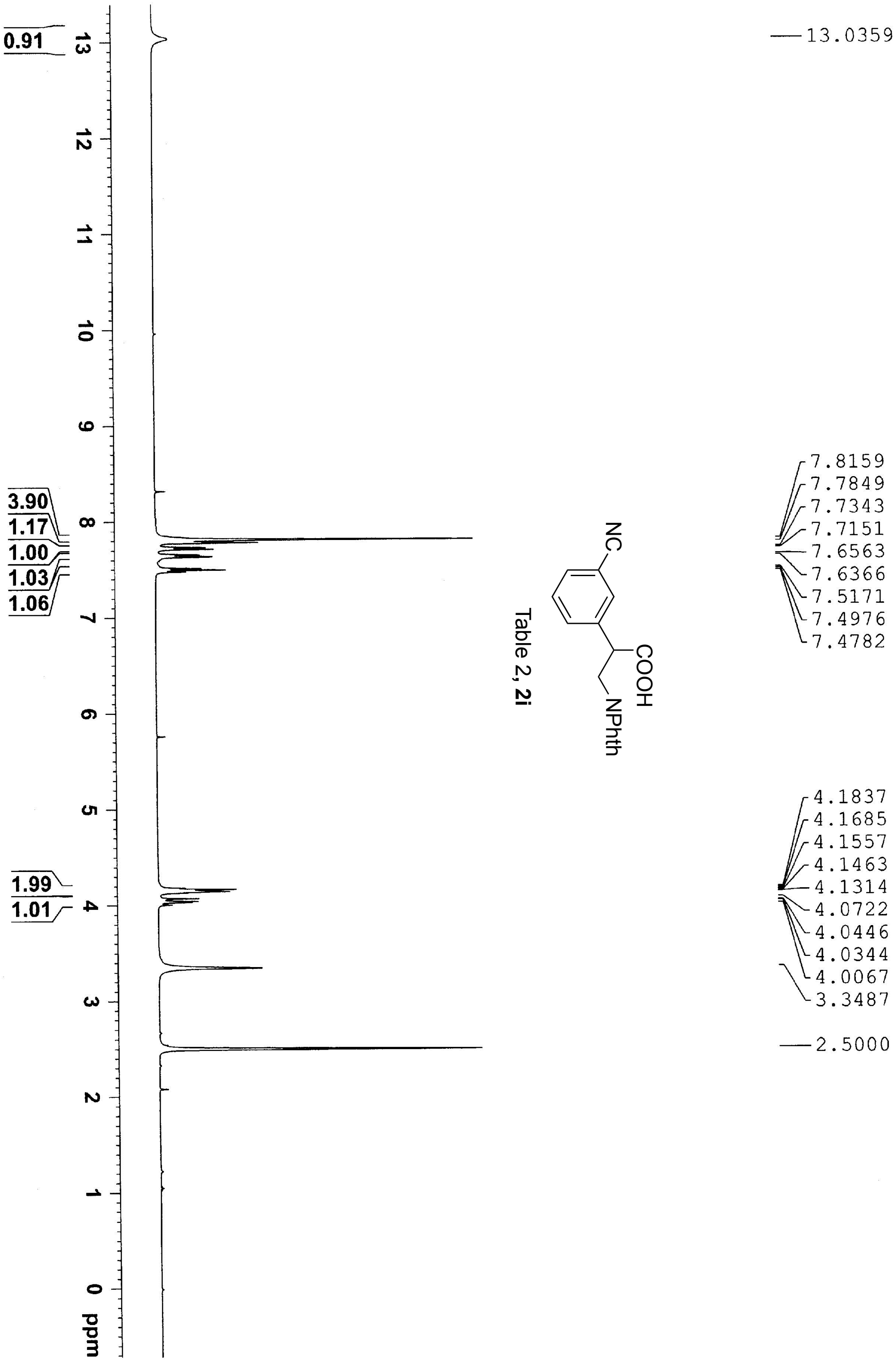
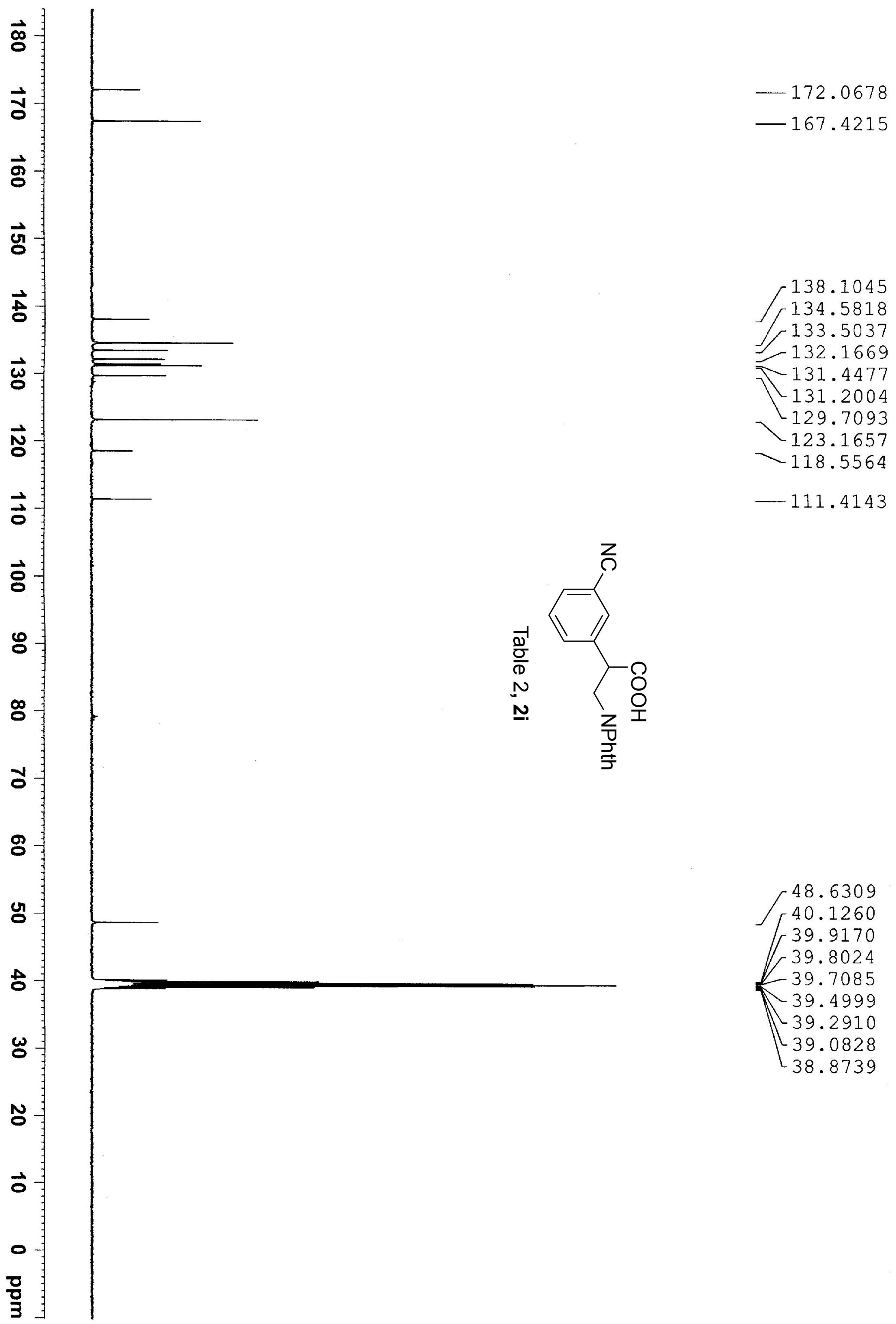
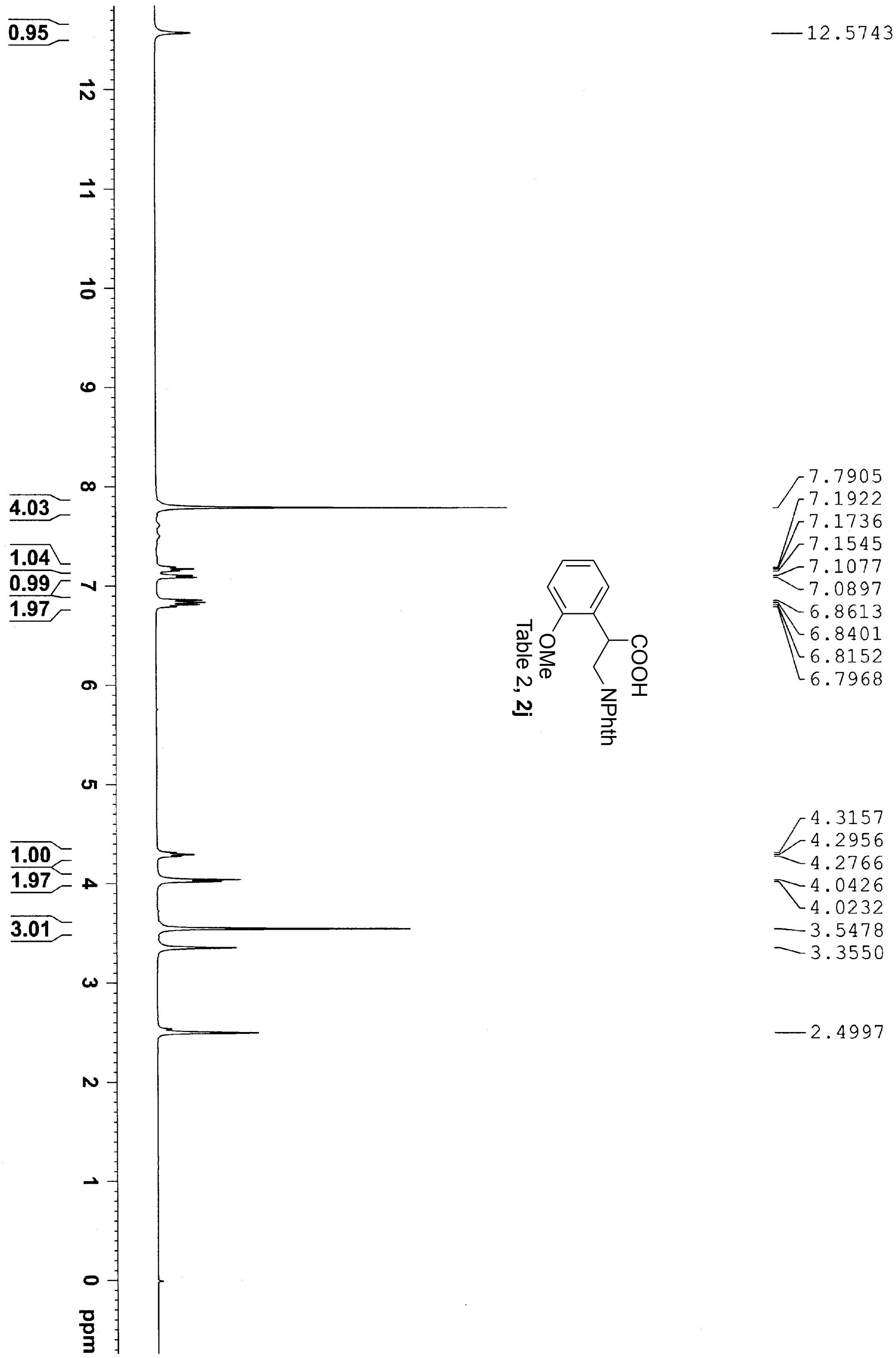
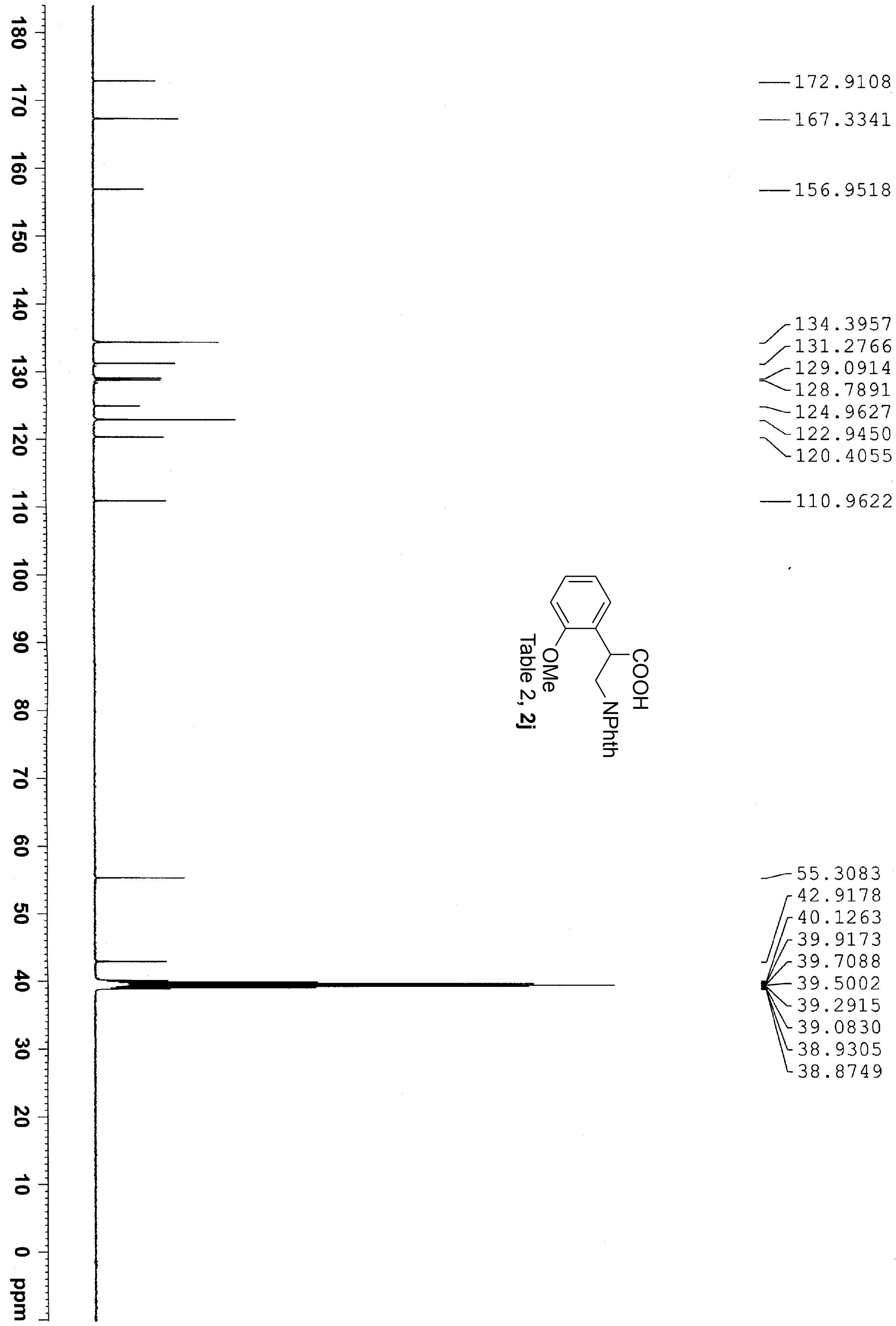


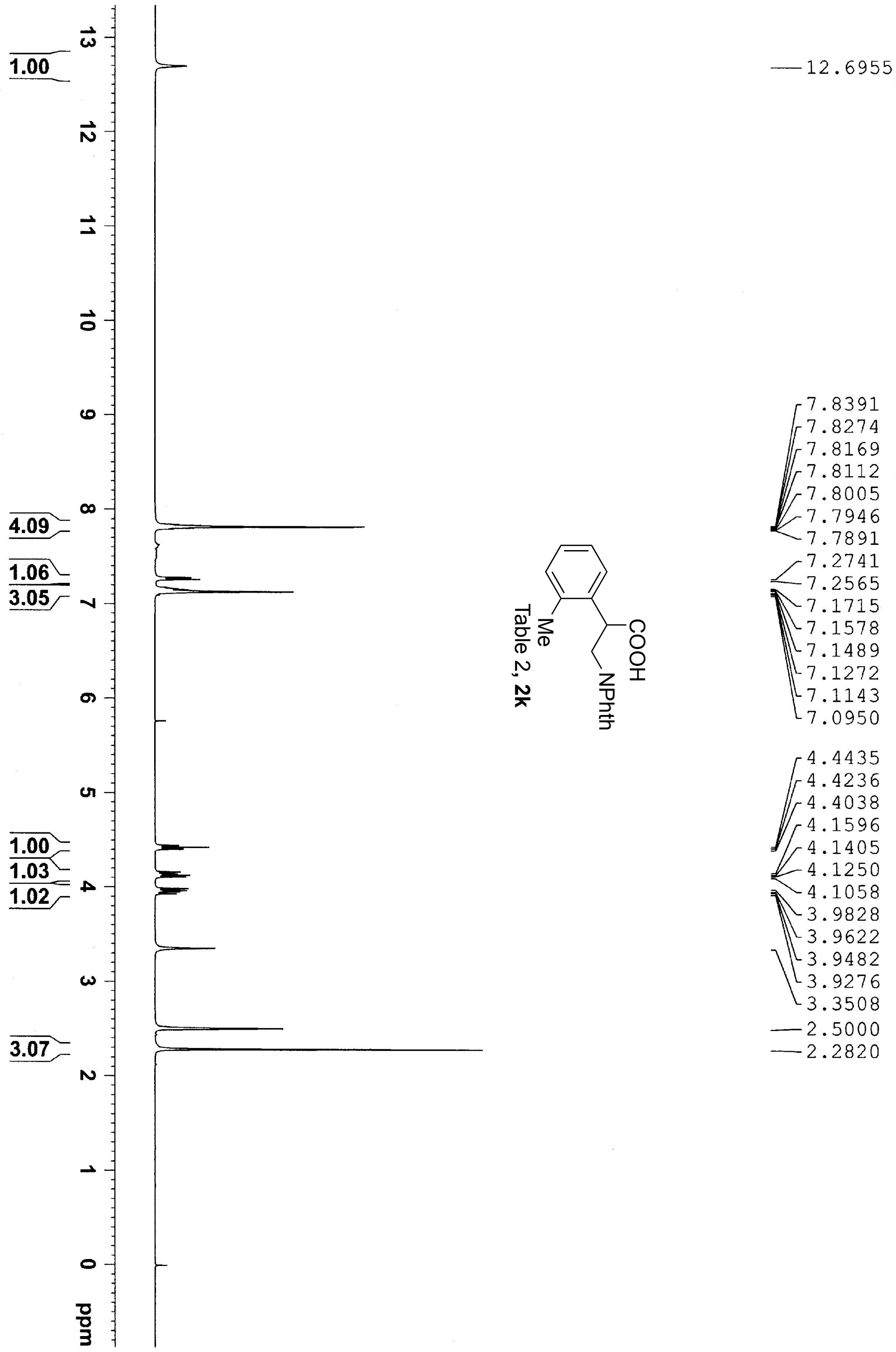
Table 2, 2i
NC
COOH
NPhth
13.0359
7.8159
7.7849
7.7343
7.7151
7.6563
7.6366
7.5171
7.4976
7.4782
4.1837
4.1685
4.1557
4.1463
4.1314
4.0722
4.0446
4.0344
4.0067
3.3487
2.5000
0.91
3.90
1.17
1.00
1.03
1.06
1.99
1.01
ppm

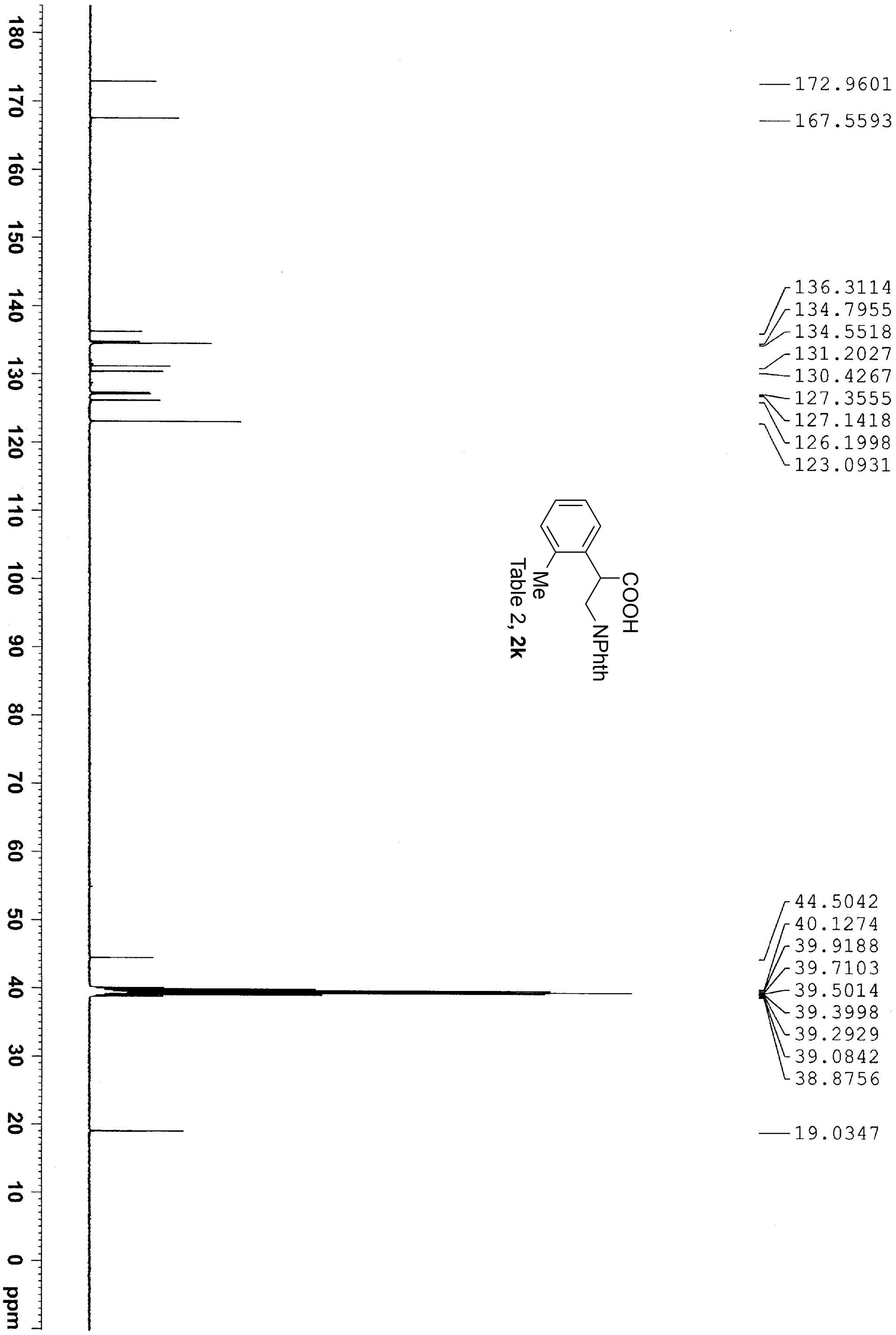

172.0678
167.4215
138.1045
134.5818
133.5037
132.1669
131.4477
131.2004
129.7093
123.1657
118.5564
111.4143
NC
COOH
NPhth
Table 2, 2i
48.6309
40.1260
39.9170
39.8024
39.7085
39.4999
39.2910
39.0828
38.8739
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



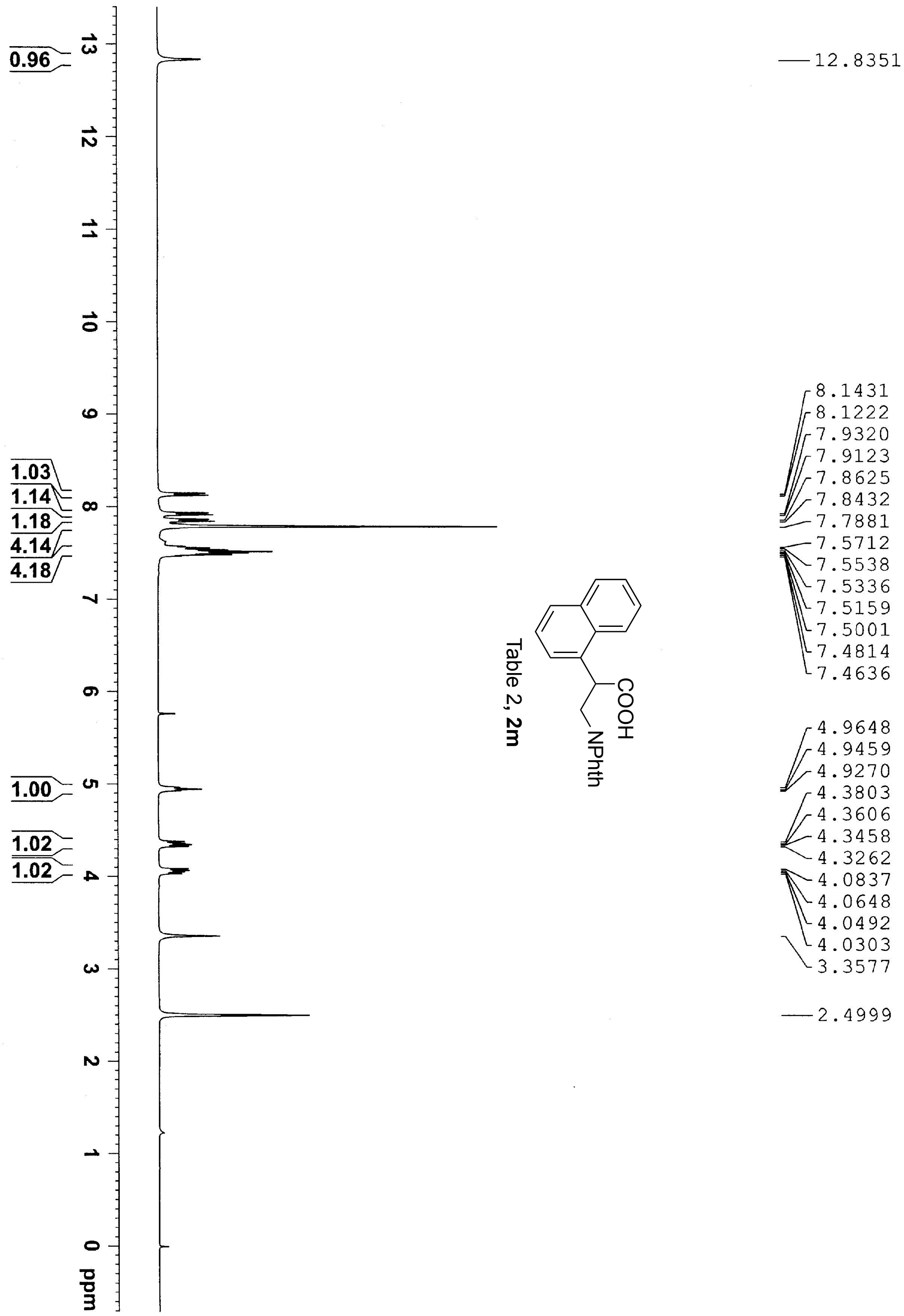
12.5743
7.7905
7.1922
7.1736
7.1545
7.1077
7.0897
6.8613
6.8401
6.8152
6.7968
4.3157
4.2956
4.2766
4.0426
4.0232
3.5478
3.3550
2.4997
COOH
NPhth
OMe
Table 2, 2j
0.95
4.03
1.04
0.99
1.97
1.00
1.97
3.01
ppm

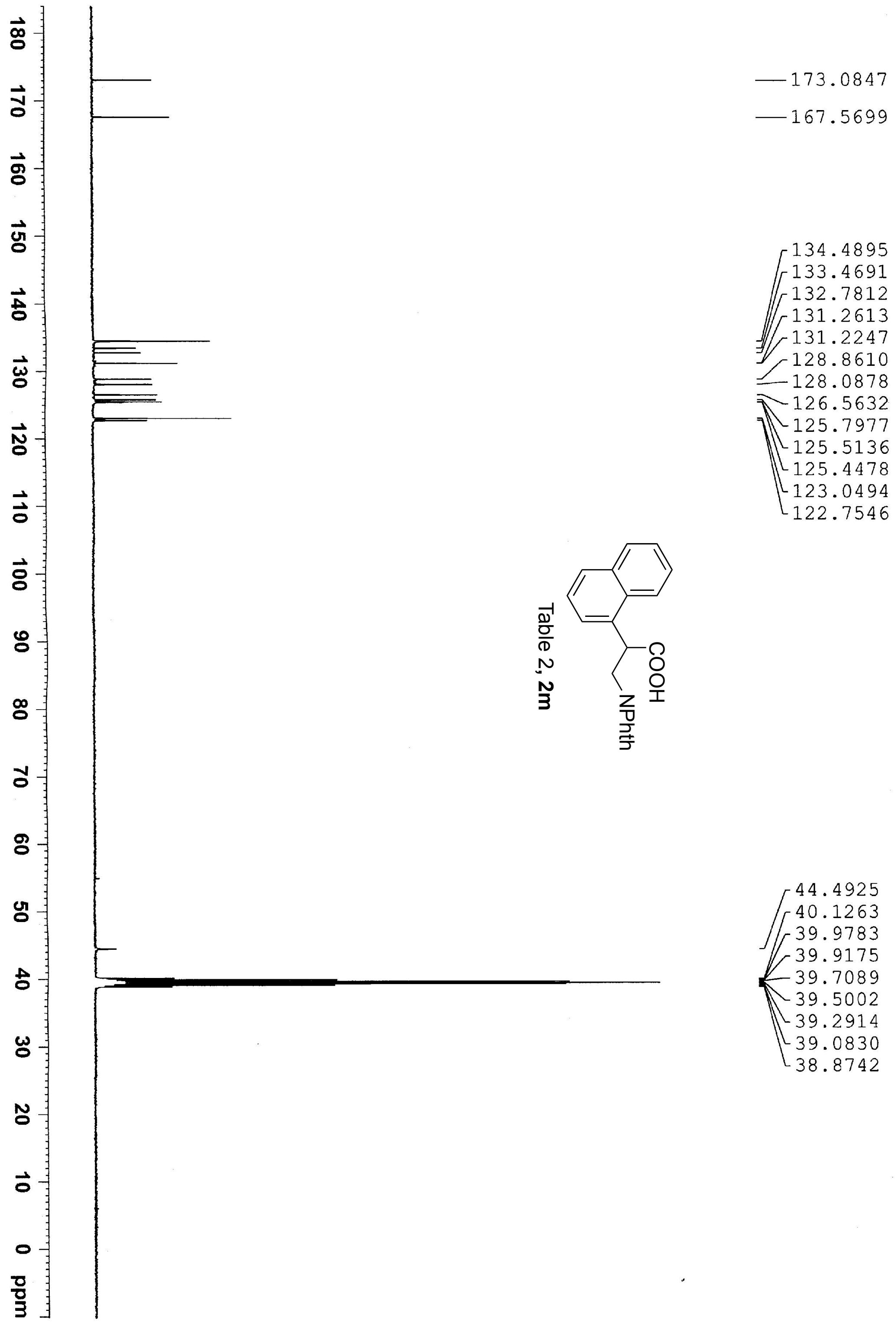

172.9108
167.3341
156.9518
134.3957
131.2766
129.0914
128.7891
124.9627
122.9450
120.4055
110.9622
55.3083
42.9178
40.1263
39.9173
39.7088
39.5002
39.2915
39.0830
38.9305
38.8749
COOH
NPhth
OMe
Table 2, 2j
ppm

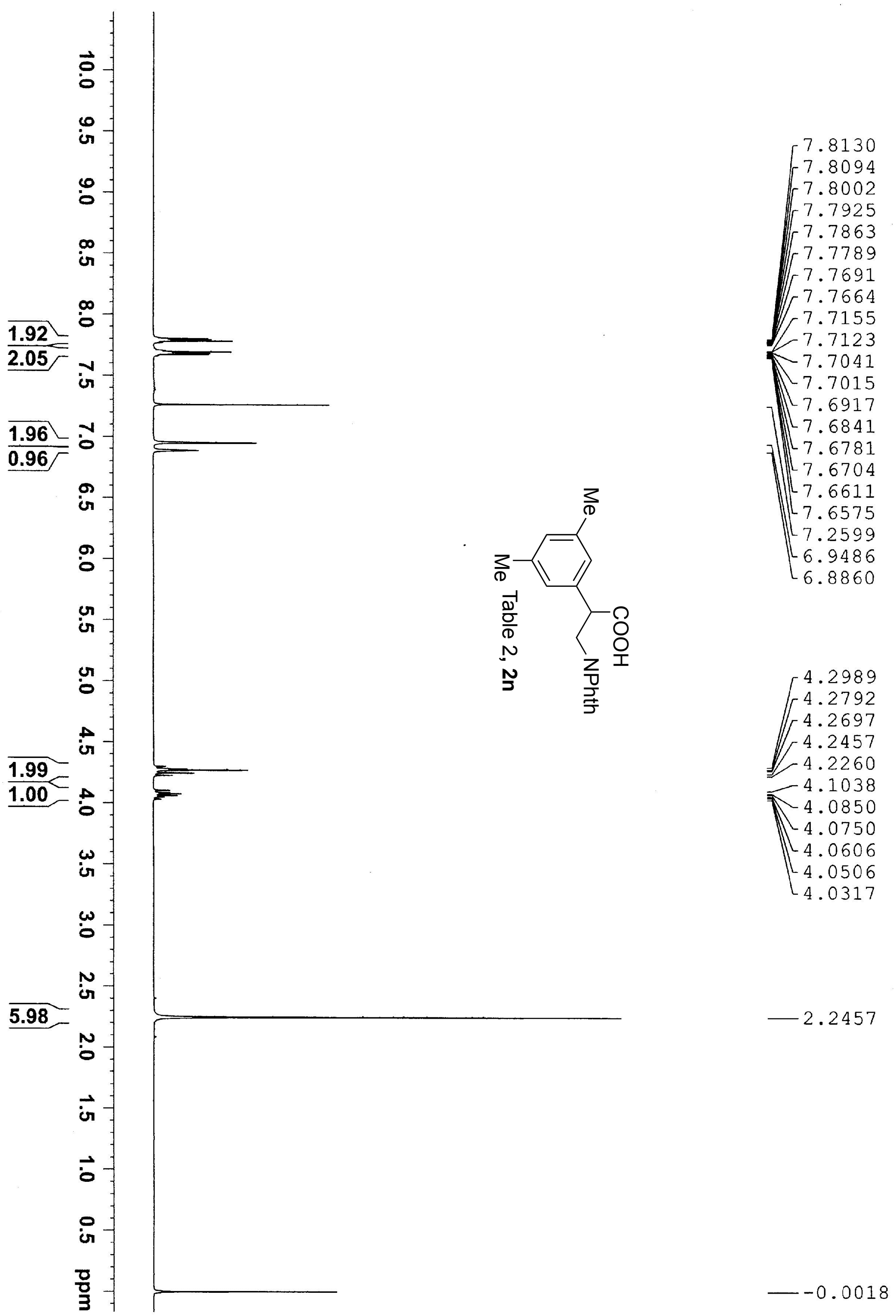

COOH
NPhth
Me
Table 2, 2k
12.6955
7.8391
7.8274
7.8169
7.8112
7.8005
7.7946
7.7891
7.2741
7.2565
7.1715
7.1578
7.1489
7.1272
7.1143
7.0950
4.4435
4.4236
4.4038
4.1596
4.1405
4.1250
4.1058
3.9828
3.9622
3.9482
3.9276
3.3508
2.5000
2.2820
1.00
4.09
1.06
3.05
1.00
1.03
1.02
3.07
ppm



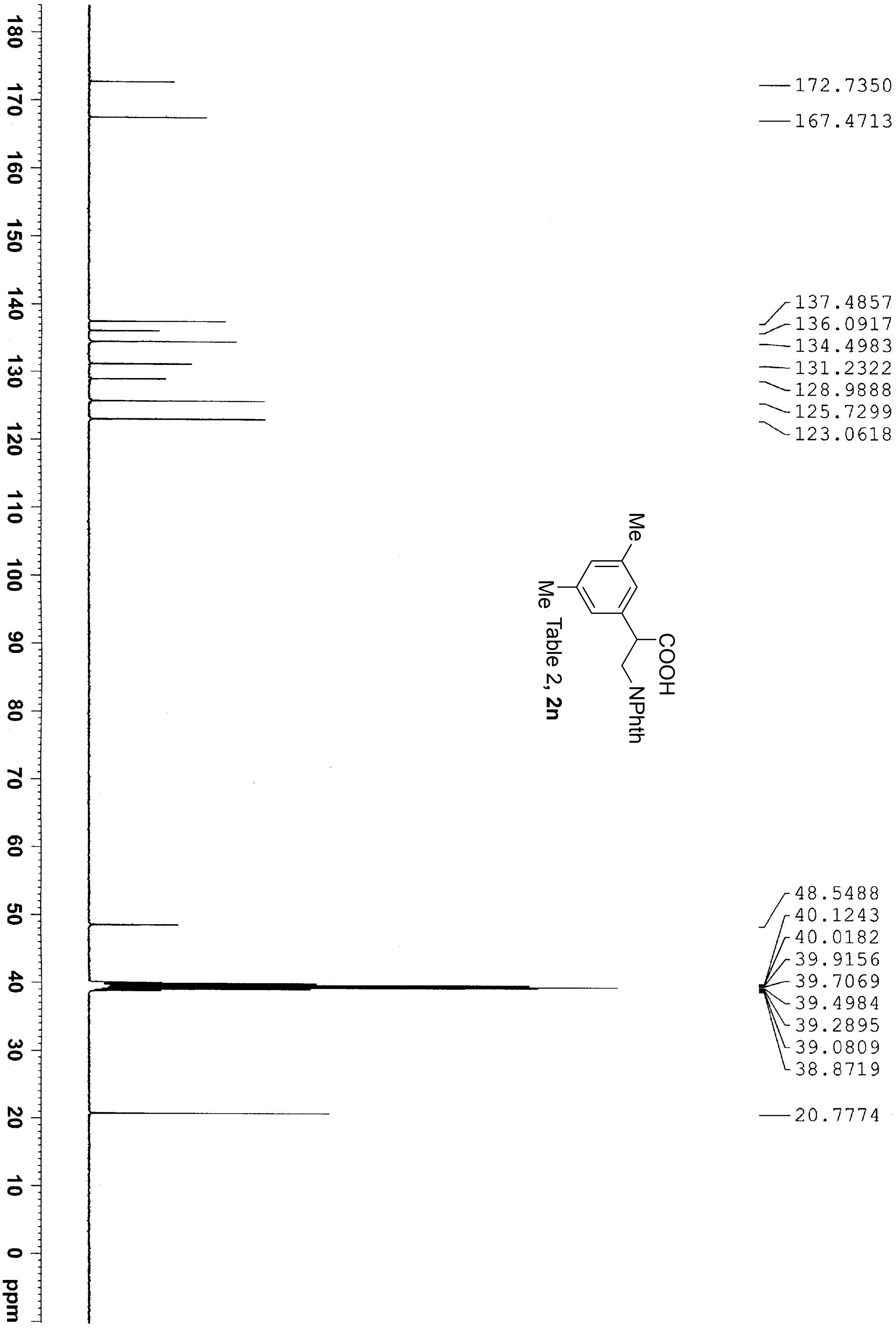
172.9601
167.5593
136.3114
134.7955
134.5518
131.2027
130.4267
127.3555
127.1418
126.1998
123.0931
44.5042
40.1274
39.9188
39.7103
39.5014
39.3998
39.2929
39.0842
38.8756
19.0347
COOH
NPhth
Me
Table 2, 2k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


12.8351
8.1431
8.1222
7.9320
7.9123
7.8625
7.8432
7.7881
7.5712
7.5538
7.5336
7.5159
7.5001
7.4814
7.4636
4.9648
4.9459
4.9270
4.3803
4.3606
4.3458
4.3262
4.0837
4.0648
4.0492
4.0303
3.3577
2.4999
COOH
NPhth
Table 2, **2m**
0.96
1.03
1.14
1.18
4.14
4.18
1.00
1.02
1.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm


173.0847
167.5699
134.4895
133.4691
132.7812
131.2613
131.2247
128.8610
128.0878
126.5632
125.7977
125.5136
125.4478
123.0494
122.7546
44.4925
40.1263
39.9783
39.9175
39.7089
39.5002
39.2914
39.0830
38.8742
COOH
NPhth
Table 2, 2m
ppm



7.8130
7.8094
7.8002
7.7925
7.7863
7.7789
7.7691
7.7664
7.7155
7.7123
7.7041
7.7015
7.6917
7.6841
7.6781
7.6704
7.6611
7.6575
7.2599
6.9486
6.8860
4.2989
4.2792
4.2697
4.2457
4.2260
4.1038
4.0850
4.0750
4.0606
4.0506
4.0317
2.2457
-0.0018
Me
Me
COOH
NPhth
Table 2, **2n**
1.92
2.05
1.96
0.96
1.99
1.00
5.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



172.7350
167.4713
137.4857
136.0917
134.4983
131.2322
128.9888
125.7299
123.0618
48.5488
40.1243
40.0182
39.9156
39.7069
39.4984
39.2895
39.0809
38.8719
20.7774
Me
Me
COOH
NPhth
Table 2, 2n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

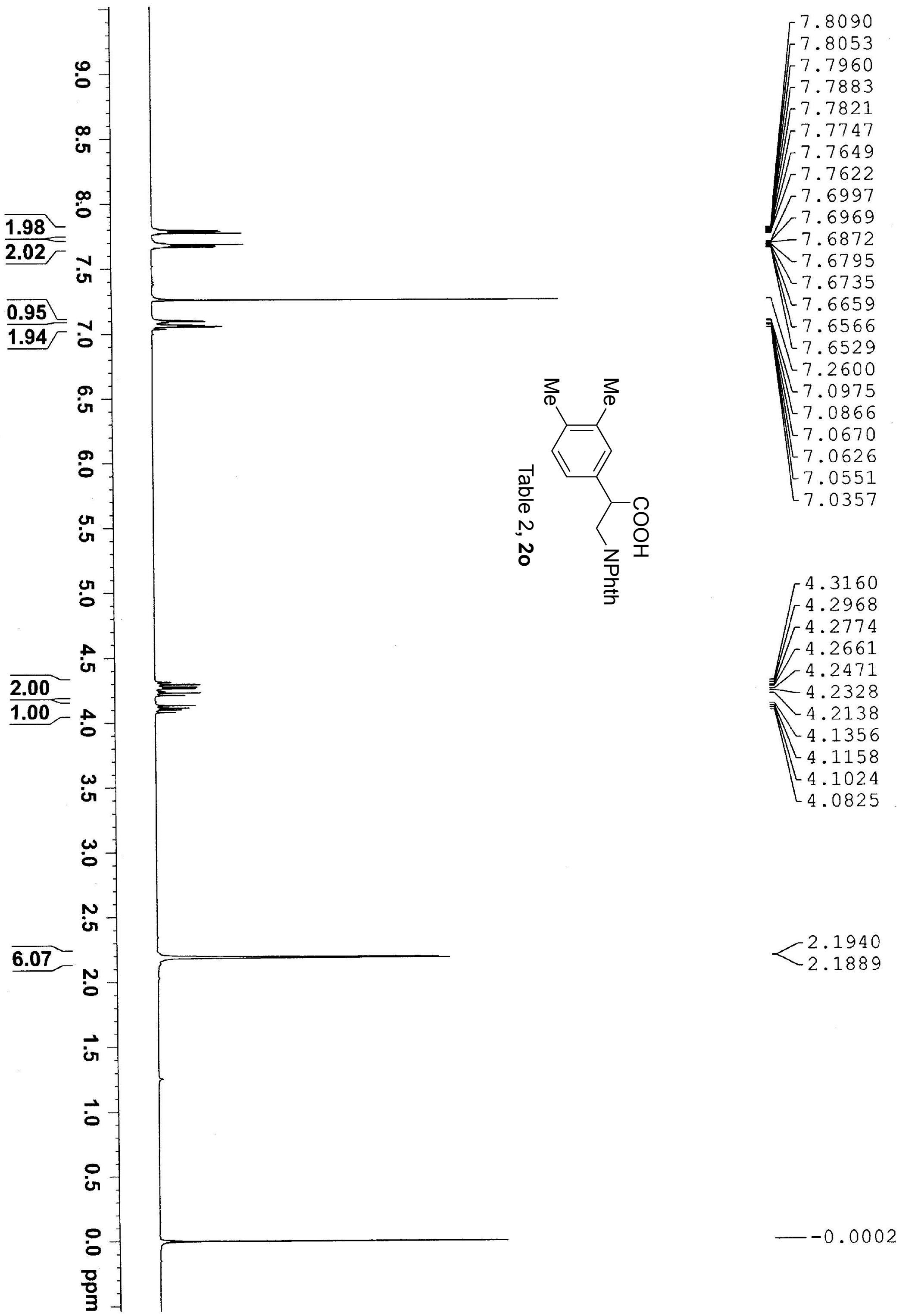


Table 2, **2o**
COOH
NPhth
Me
Me
7.8090
7.8053
7.7960
7.7883
7.7821
7.7747
7.7649
7.7622
7.6997
7.6969
7.6872
7.6795
7.6735
7.6659
7.6566
7.6529
7.2600
7.0975
7.0866
7.0670
7.0626
7.0551
7.0357
4.3160
4.2968
4.2774
4.2661
4.2471
4.2328
4.2138
4.1356
4.1158
4.1024
4.0825
2.1940
2.1889
-0.0002
1.98
2.02
0.95
1.94
2.00
1.00
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

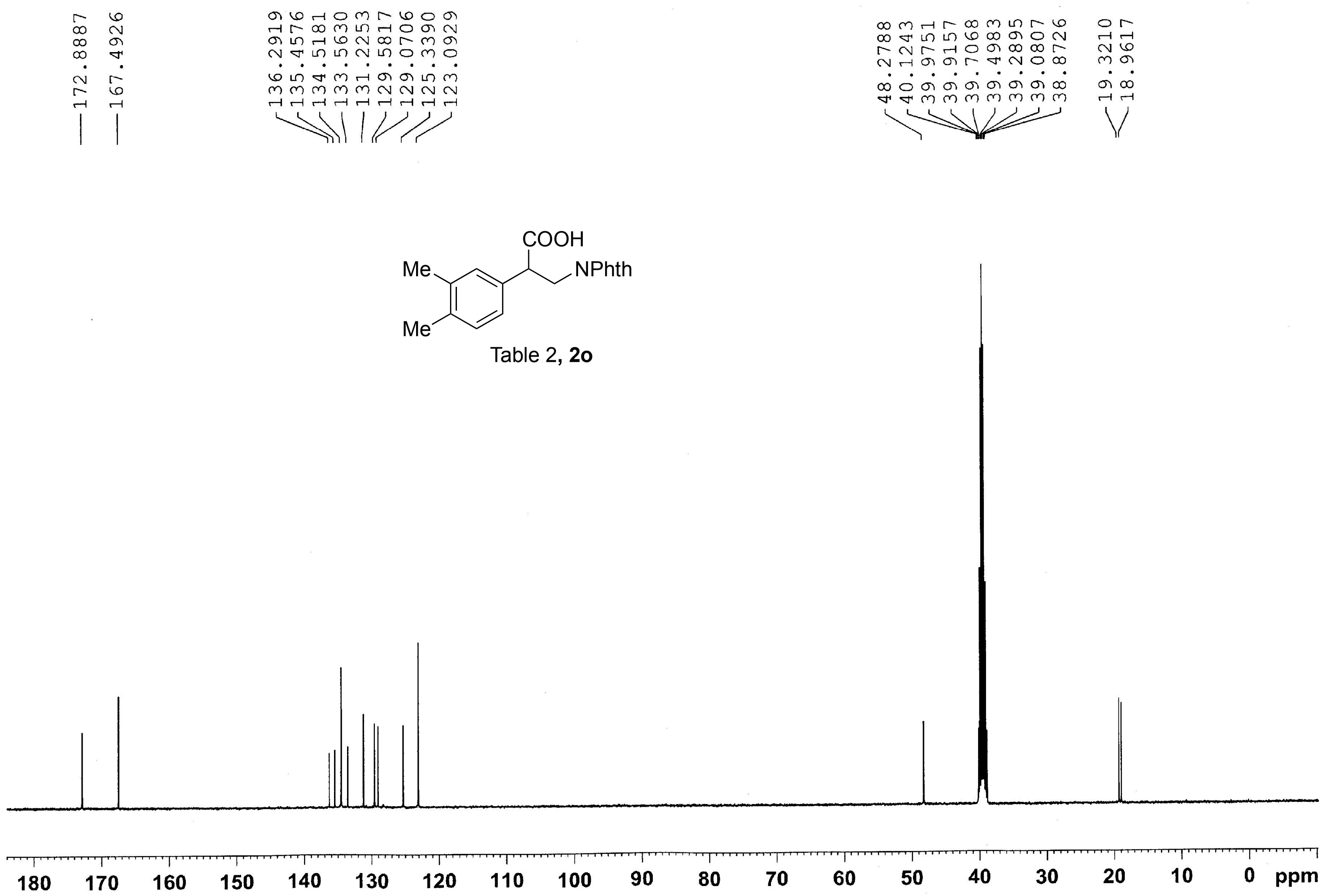
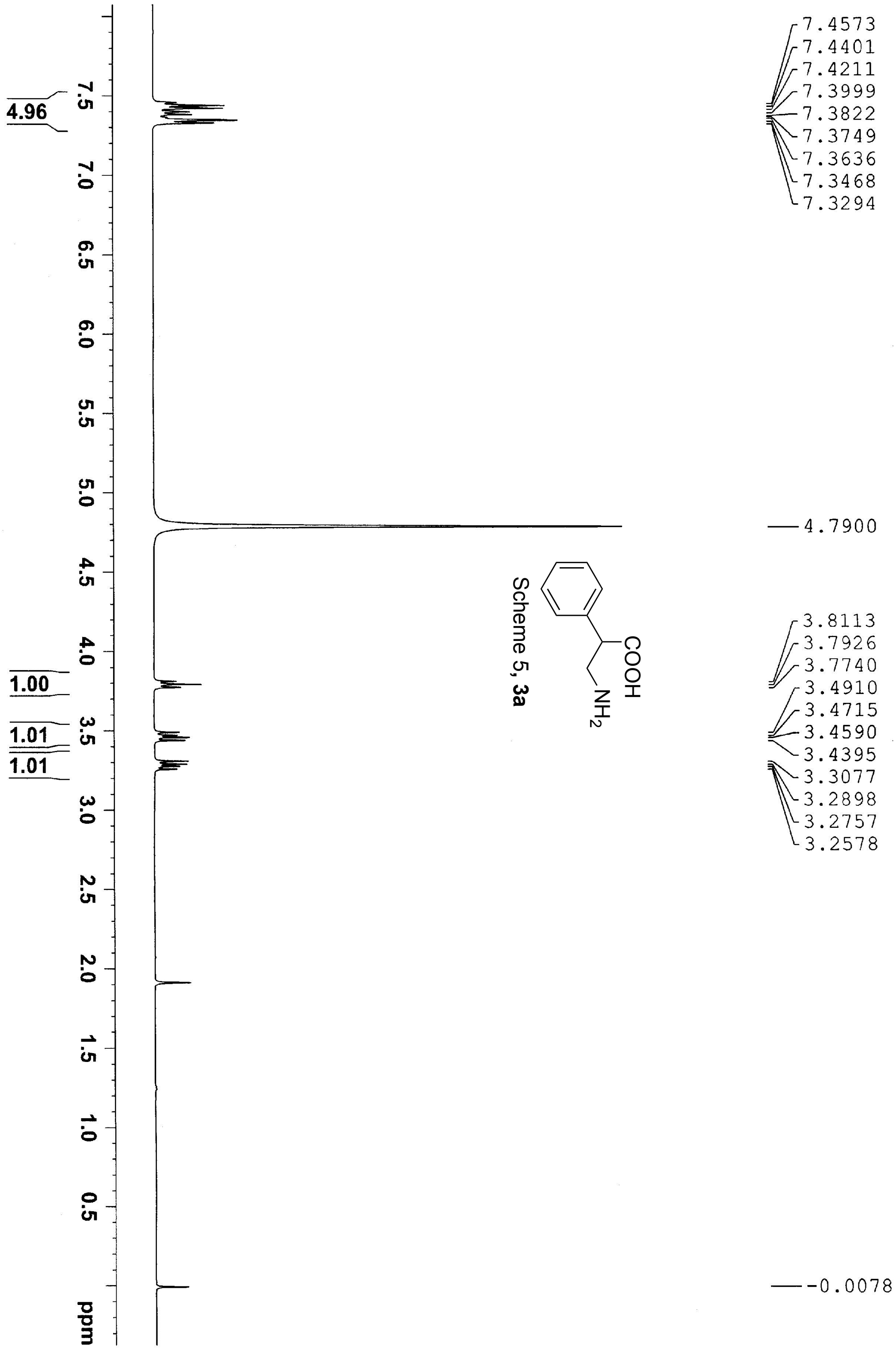
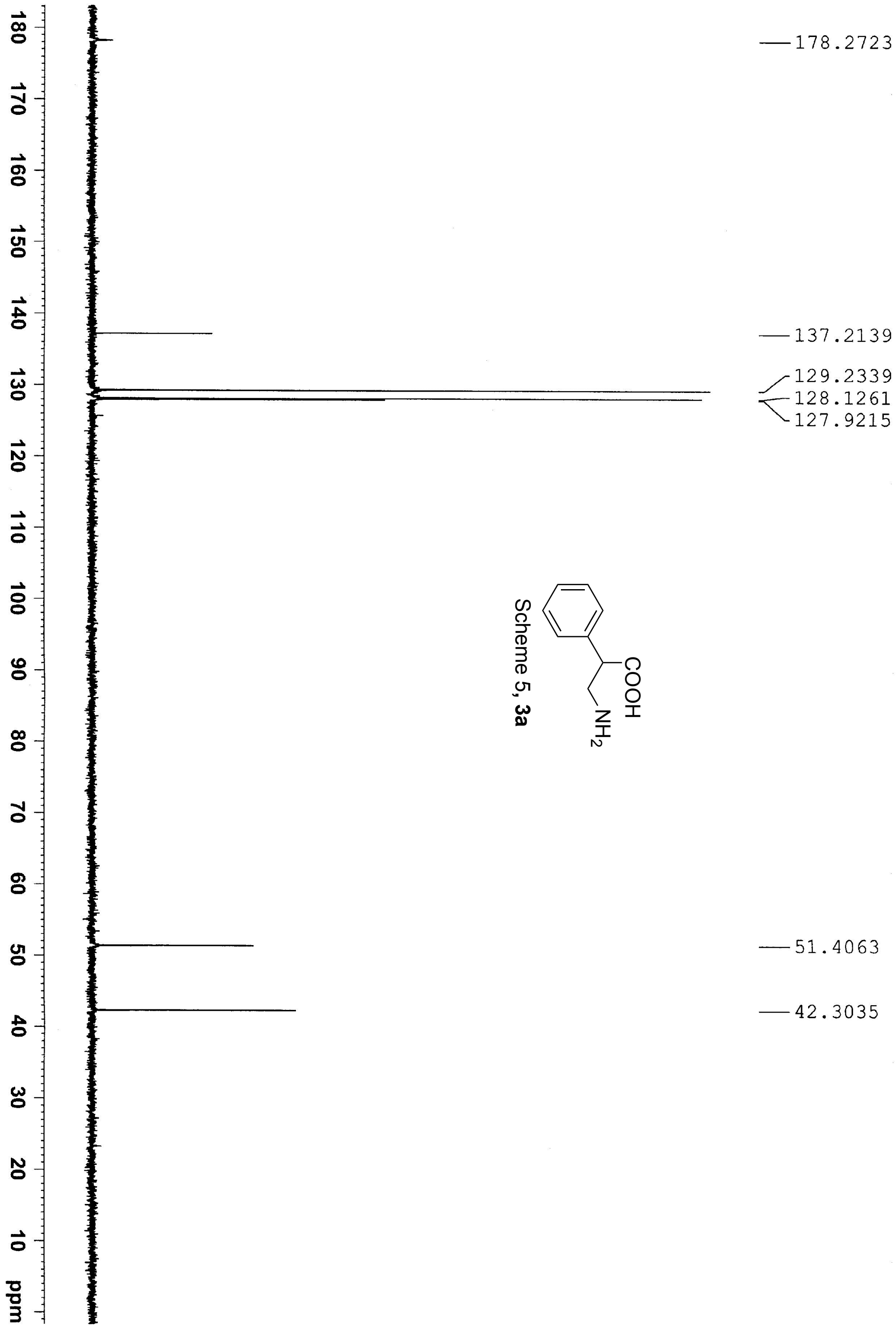

172.8887
167.4926
136.2919
135.4576
134.5181
133.5630
131.2253
129.5817
129.0706
125.3390
123.0929
48.2788
40.1243
39.9751
39.9157
39.7068
39.4983
39.2895
39.0807
38.8726
19.3210
18.9617
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
COOH
NPhth
Me
Me

Table 2, **2o**


7.4573
7.4401
7.4211
7.3999
7.3822
7.3749
7.3636
7.3468
7.3294
4.7900
3.8113
3.7926
3.7740
3.4910
3.4715
3.4590
3.4395
3.3077
3.2898
3.2757
3.2578
-0.0078
COOH
NH2
Scheme 5, 3a
4.96
1.00
1.01
1.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


178.2723
137.2139
129.2339
128.1261
127.9215
51.4063
42.3035
COOH
NH2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Scheme 5, **3a**