Pd-Catalyzed Hydroesterification of 1,1-Disubstituted Terminal Olefins with Aryl Formates

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Supporting Information

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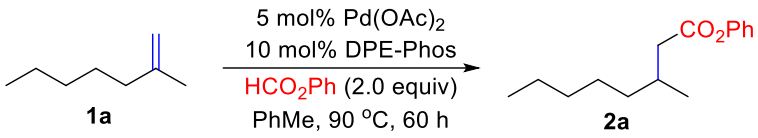
General Methods. All commercially available reagents were used without further purification unless otherwise noted. All dry solvents were purified with solvent purification system before use. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz 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. High resolution mass spectra (HRMS, ESI) were recorded using ion trap. Olefins **1a**-**1d**, **1j**-**1q**, **1s**-**1y**, and **1aa** were purchased from commercial suppliers. Olefin **1e** was prepared from 3-methylbut-3-en-1-ol by protection with TBSCl.[1] Olefin **1f** and **1g** were prepared from 3-methylbut-3-en-1-ol via Mitsunobu reaction with estrone[2] and phthalimide,[3] respectively. Olefin **1h** was prepared from the corresponding indole via deprotonation with NaH and nucleophilic substitution reaction with 3-methylbut-3-en-1-yl 4-methylbenzenesulfonate.[1,4] Olefins **1i** and **1r** were prepared from the corresponding ketones via Wittig reaction with methyltriphenylphosphonium bromide.[5] Olefin **1z** was prepared via the coupling of 3-chloro-2-methylprop-1-ene and (*E*)-styrylboronic acid.[6]

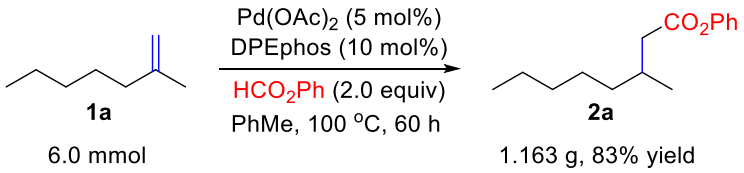
1) J. C. Siu, J. B. Parry, and S. Lin, *J. Am. Chem. Soc.*, 2019, **141**, 2825.
2) X. Ma, H. Dang, J. A. Rose, P. Rablen and S. B. Herzon, *J. Am. Chem. Soc.*, 2017, **139**, 5998.
3) X. Zheng, B. Cao, T.-L. Liu and X. Zhang, *Adv. Synth. Catal.*, 2013, **355**, 679.
4) A. Banerjee, S. Sarkar, J. A. Shah, N. C. Frederiks, E. A. Bazan-Bergamino, C. J. Johnson and M.-Y. Ngai, *Angew. Chem. Int. Ed.*, 2022, **61**, e202113841.
5) W. Chen, Y. Chen, X. Gu, Z. Chen and C.-Y. Ho, *Nat. Commun.*, 2022, **13**, 5507.
6) C. Dong, L. Zhang, X. Xue, H. Li, Z. Yu, W. Tang and L. Xu, *RSC Adv.*, 2014, **4**, 11152.

Representative procedure for hydroesterification (Table 2, entry 1).



To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), ligand DPEphos (0.0269 g, 0.050 mmol), and PhMe (0.25 mL) in a pressure tube (2.0 mL) were added 2-methyl-1-heptene (**1a**) (0.0561 g, 0.50 mmol) and HCO_2Ph (0.1221 g, 1.0 mmol) successively via syringe. The tube was purged with N_2 to remove the air and tightly sealed with a Teflon cap. The reaction mixture was stirred at 90 ℃ for 60 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50:1) to give ester **2a** as a colorless oil (0.0992 g, 85% yield).

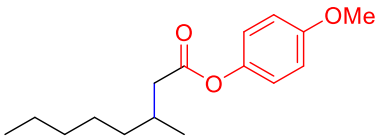
Procedure for gram scale hydroesterification (Scheme 4).



To a mixture of $Pd(OAc)_2$ (0.0674 g, 0.30 mmol), ligand DPEphos (0.3231 g, 0.60 mmol), and PhMe (2.0 mL) in a pressure tube (15.0 mL) were added 2-methyl-1-heptene (**1a**) (0.6733 g, 6.0 mmol) and HCO_2Ph (1.4654 g, 12.0 mmol) successively via syringe. The tube was purged with N_2 to remove the air and tightly sealed with a Teflon cap. The reaction mixture was stirred at 100 ℃ for 60 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 50:1) to give ester **2a** as a colorless oil (1.163 g, 83% yield).

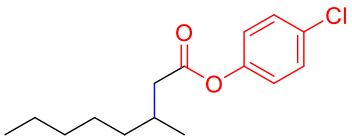
Characterization data of esters 2

Scheme 3, 2a-1



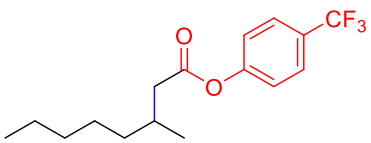
Colorless oil; 0.0680 g (51% yield), eluent: petroleum ether/ethyl acetate = 30:1; IR (film) 1755, 1506, 1194 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-6.97 (m, 2H), 6.92-6.86 (m, 2H), 3.80 (s, 3H), 2.53 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.34 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.17-2.01 (m, 1H), 1.45-1.24 (m, 8H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 157.3, 144.4, 122.5, 114.6, 55.7, 42.0, 36.9, 32.2, 30.7, 26.8, 22.8, 20.0, 14.3. HRMS (ESI) calcd for $C_{16}H_{25}O_3$ $(M+H)^+$: 265.1798; found: 265.1800.

Scheme 3, 2a-2



Colorless oil; 0.1181 g (88% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1759, 1487, 1202, 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.61 (m, 2H), 7.35-7.30 (m, 2H), 2.85 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.65 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.44-2.31 (m, 1H), 1.73-1.53 (m, 8H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.20 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 149.4, 131.2, 129.6, 123.2, 41.9, 36.9, 32.1, 30.7, 26.8, 22.8, 20.0, 14.3. HRMS (ESI) calcd for $C_{15}H_{22}ClO_2$ $(M+H)^+$: 269.1303; found: 269.1303.

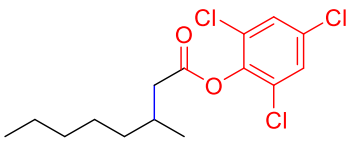
Scheme 3, 2a-3



Colorless oil; 0.1367 g (90% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1763, 1325, 1064 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 2.58 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.38 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.16-2.03 (m, 1H), 1.45-1.24 (m, 8H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H);

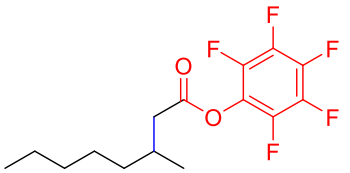
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 153.4, 128.2 (q, *J* = 32.6 Hz), 127.0 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.2 Hz), 122.3, 41.9, 36.9, 32.1, 30.7, 26.8, 22.8, 20.0, 14.3. HRMS (ESI) calcd for $C_{16}H_{22}F_3O_2$ $(M+H)^+$: 303.1566; found: 303.1568.

Scheme 3, 2a-4



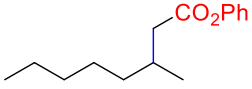
Colorless oil; 0.1204 g (71% yield), eluent: petroleum ether; IR (film) 1776, 1447, 1089 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 2.65 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.45 (dd, *J* = 15.2, 8.0, 1H), 2.20-2.06 (m, 1H), 1.49-1.22 (m, 8H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 143.3, 132.0, 129.8, 128.8, 41.2, 36.8, 32.1, 30.5, 26.8, 22.8, 20.0, 14.3. HRMS (ESI) calcd for $C_{15}H_{20}Cl_3O_2$ $(M+H)^+$: 337.0523; found: 337.0524.

Scheme 3, 2a-5



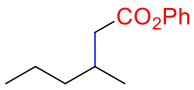
Colorless oil; 0.1368 g (84% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1790, 1520, 1000 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (dd, *J* = 15.2, 6.4 Hz, 1H), 2.46 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.16-2.02 (m, 1H), 1.46-1.23 (m, 8H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 141.4 (dm, *J* = 250.3 Hz, 1C), 139.6 (dm, *J* = 255.5 Hz, 1C), 138.1 (dm, *J* = 252.7 Hz, 1C), 125.5-125.2 (m, 1C), 41.0, 36.7, 32.1, 30.8, 26.8, 22.8, 19.7, 14.2. HRMS (ESI) calcd for $C_{15}H_{17}F_5O_2Na$ $(M+Na)^+$: 347.1041; found: 347.1043.

Table 2, 2a



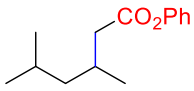
Colorless oil; 0.0992 g (85% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1758, 1492, 1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.13-7.07 (m, 2H), 2.58 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.38 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.18-2.06 (m, 1H), 1.50-1.25 (m, 8H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.93 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 150.9, 129.5, 125.8, 121.8, 42.0, 36.8, 32.1, 30.7, 26.8, 22.8, 19.9, 14.2. HRMS (ESI) calcd for $C_{15}H_{23}O_2$ $(M+H)^+$: 235.1693; found: 235.1694.

Table 2, 2b



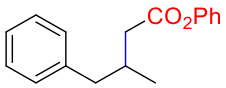
Colorless oil; 0.0746 g (72% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1759, 1260, 1101 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.25-7.20 (m, 1H), 7.11-7.06 (m, 2H), 2.56 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.36 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.17-2.05 (m, 1H), 1.45-1.24 (m, 4H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 150.9, 129.6, 125.9, 121.8, 42.0, 39.2, 30.5, 20.2, 19.9, 14.4; HRMS (ESI) calcd for $C_{13}H_{19}O_2$ $(M+H)^+$: 207.1380; found: 207.1381.

Table 2, 2c



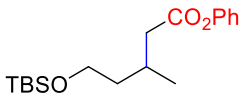
Colorless oil; 0.0900 g (82% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1757, 1492, 1197 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.26-7.21 (m, 1H), 7.12-7.07 (m, 2H), 2.55 (dd, *J* = 14.8, 6.0 Hz, 1H), 2.36 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.26-2.13 (m, 1H), 1.77-1.66 (m, 1H), 1.31-1.15 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 150.9, 129.6, 125.9, 121.8, 46.4, 42.3, 28.4, 25.4, 23.4, 22.3, 20.0; HRMS (ESI) calcd for $C_{14}H_{21}O_2$ $(M+H)^+$: 221.1536; found: 221.1537.

Table 2, 2d



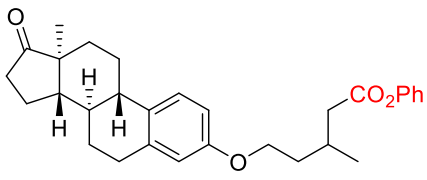
Colorless oil; 0.1164 g (92% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1756, 1492, 1194 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.19 (m, 4H), 7.16-7.10 (m, 4H), 7.00-6.95 (m, 2H), 2.64 (dd, *J* = 13.2, 6.4 Hz, 1H), 2.54-2.45 (m, 2H), 2.39-2.25 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 150.8, 140.2, 129.5, 129.4, 128.5, 126.3, 125.9, 121.7, 43.1, 41.1, 32.6, 19.8. HRMS (ESI) calcd for $C_{17}H_{19}O_2$ $(M+H)^+$: 255.1380; found: 255.1381.

Table 2, 2e



Colorless oil; 0.1300 g (81% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1759, 1493, 1197, 1096 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.26-7.21 (m, 1H), 7.12-7.08 (m, 2H), 3.79-3.68 (m, 2H), 2.64 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.41 (dd, *J* = 14.8, 8.4 Hz, 1H), 2.36-2.23 (m, 1H), 1.75-1.65 (m, 1H), 1.59-1.49 (m, 1H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 150.9, 129.5, 125.8, 121.8, 61.1, 41.9, 39.5, 27.7, 26.1, 19.9, 18.5, -5.1, -5.2; HRMS (ESI) calcd for $C_{18}H_{31}O_3Si$ $(M+H)^+$: 323.2037; found: 323.2039.

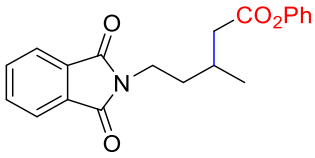
Table 2, 2f



White solid; 0.200 g (87% yield), eluent: petroleum ether/ethyl acetate = 20:1; mp. 84.9-86.0 °C; IR (film) 1738, 1494, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.23-7.15 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.72 (dd, *J* = 8.4, 2.4 Hz,

1H), 6.65 (d, *J* = 2.4 Hz, 1H), 4.07-3.96 (m, 2H), 2.95-2.81 (m, 2H), 2.64 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.52-2.33 (m, 4H), 2.27-2.18 (m, 1H), 2.17-1.87 (m, 5H), 1.81-1.70 (m, 1H), 1.65-1.35 (m, 6H), 1.12 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 171.4, 156.9, 150.7, 137.8, 132.1, 129.4, 126.4, 125.8, 121.7, 114.6, 112.2, 65.6, 50.4, 48.0, 44.0, 41.6, 38.4, 35.9, 35.8, 31.7, 29.7, 27.9, 26.6, 26.0, 21.6, 19.9, 13.9; HRMS (ESI) calcd for $C_{30}H_{37}O_4$ $(M+H)^+$: 461.2686; found: 461.2690.

Table 2, 2g

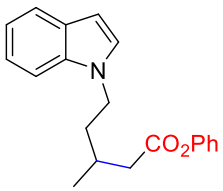


White solid; 0.1260 g (75% yield), eluent: petroleum ether/ethyl acetate = 15:1; mp. 96.1-98.2 °C; IR (film) 1755, 1711, 1397 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 2H), 7.72-7.66 (m, 2H), 7.39-7.32 (m, 2H), 7.23-7.18 (m, 1H), 7.09-7.04 (m, 2H), 3.78 (t, *J* = 7.2 Hz, 2H), 2.64 (dd, *J* = 15.2, 6.0 Hz, 1H), 2.45 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.23-2.07 (m, 1H), 1.92-1.81 (m, 1H), 1.71-1.61 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.5, 150.8, 134.1, 132.3, 129.6, 125.9, 123.4, 121.8, 41.5, 36.0, 35.2, 28.3, 19.6;

1) L. K. G. Ackerman, J. I. M. Alvarado and A. G. Doyle, *J. Am. Chem. Soc.*, 2018, **140**, 14059.

2) J. Li, T. Shen, Y. Yang and Y. Shi, *Chin. J. Chem.*, 2024, **42**, 1381.

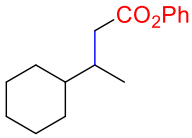
Table 2, 2h



Colorless oil; 0.1181 g (77% yield), eluent: petroleum ether/ethyl acetate = 15:1; IR (film) 1753, 1492, 1194 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.41-7.35 (m, 3H), 7.26-7.20 (m, 2H), 7.16-7.10 (m, 2H), 7.04-6.99 (m, 2H), 6.52 (d, *J* =

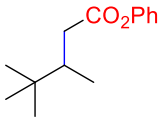
3.2 Hz, 1H), 4.30-4.11 (m, 2H), 2.57 (dd, *J* = 15.2, 6.4 Hz, 1H), 2.48 (dd, *J* = 15.2, 7.2 Hz, 1H), 2.25-2.13 (m, 1H), 2.11-2.01 (m, 1H), 1.87-1.76 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 150.7, 136.0, 129.6, 128.8, 127.7, 126.0, 121.70, 121.67, 121.2, 119.5, 109.4, 101.4, 44.3, 41.6, 36.8, 28.4, 19.8; HRMS (ESI) calcd for $C_{20}H_{22}NO_2$ $(M+H)^+$: 308.1645; found: 308.1642.

Table 2, 2i



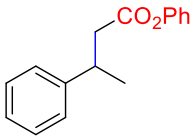
Colorless oil; 0.0860 g (70% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1757, 1492, 1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.25-7.20 (m, 1H), 7.11-7.05 (m, 2H), 2.63 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.34 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.07-1.96 (m, 1H), 1.82-1.64 (m, 5H), 1.35-1.04 (m, 6H), 1.02 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 150.9, 129.6, 125.9, 121.8, 42.8, 39.5, 35.8, 30.5, 29.2, 26.9, 26.84, 26.82, 16.8. HRMS (ESI) calcd for $C_{16}H_{23}O_2$ $(M+H)^+$: 247.1693; found: 247.1694.

Table 2, 2j



Colorless oil; 0.0720 g (65% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1758, 1194, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.26-7.21 (m, 1H), 7.11-7.07 (m, 2H), 2.76 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.22 (dd, *J* = 14.8, 10.8 Hz, 1H), 2.01-1.91 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 151.0, 129.6, 125.9, 121.8, 40.3, 37.8, 33.0, 27.3, 15.2; HRMS (ESI) calcd for $C_{14}H_{21}O_2$ $(M+H)^+$: 221.1536; found: 221.1538.

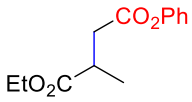
Table 2, 2k



Colorless oil; 0.0980 g (82% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1753, 1492, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 6H), 7.24-7.19 (m, 1H), 7.18-7.13 (m, 1H), 6.90-6.85 (m, 2H), 3.44-3.33 (m, 1H), 2.83 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.78 (dd, *J* = 14.8, 7.6 Hz, 1H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 150.7, 145.3, 129.5, 128.7, 127.0, 126.8, 125.9, 121.7, 43.1, 36.9, 22.1.

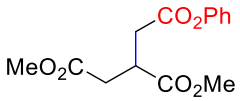
P. Yuan, J. Chen, J. Zhao and Y. Huang, *Angew. Chem. Int. Ed.*, 2018, **57**, 8503.

Table 2, 2l



Colorless oil; 0.0945 g (80% yield), eluent: petroleum ether/ethyl acetate = 20:1; IR (film) 1760, 1732, 1493, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 7.24-7.18 (m, 1H), 7.11-7.06 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.07-2.93 (m, 2H), 2.71-2.60 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 170.5, 150.7, 129.5, 125.9, 121.6, 60.9, 37.8, 36.0, 17.1, 14.3; HRMS (ESI) calcd for $C_{13}H_{17}O_4$ $(M+H)^+$: 237.1121; found: 237.1120.

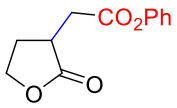
Table 2, 2m



Yellow oil; 0.0850 g (61% yield), eluent: petroleum ether/ethyl acetate = 20:1 to 10:1; IR (film) 1737, 1194, 1140 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 2H), 7.25-7.19 (m, 1H), 7.11-7.05 (m, 2H), 3.73 (s, 3H), 3.70 (s, 3H), 3.42-3.34 (m, 1H), 3.02 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.86 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.85 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.70 (dd, *J* = 16.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 171.8, 170.1,

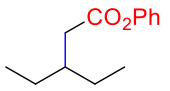
150.6, 129.6, 126.1, 121.6, 52.5, 52.1, 37.5, 35.5, 35.2; HRMS (ESI) calcd for $C_{14}H_{16}O_6Na$ $(M+Na)^+$: 303.0839; found: 303.0832.

Table 2, 2n



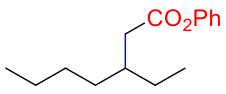
Colorless oil; 0.0692 g (63% yield), eluent: petroleum ether/ethyl acetate = 20:1 to 3:1; IR (film) 1760, 1196, 1143 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 2H), 7.31-7.25 (m, 1H), 7.17-7.11 (m, 2H), 4.47 (td, *J* = 9.2, 2.0 Hz, 1H), 4.34-4.25 (m, 1H), 3.19 (dd, *J* = 16.8, 4.4 Hz, 1H), 3.15-3.06 (m, 1H), 2.84 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.68-2.59 (m, 1H), 2.26-2.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 170.0, 150.6, 129.7, 126.3, 121.6, 66.8, 36.2, 34.9, 28.8; HRMS (ESI) calcd for $C_{12}H_{12}O_4Na$ $(M+Na)^+$: 243.0628; found: 243.0629.

Table 2, 2o



Colorless oil; 0.0598 g (58% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1756, 1492, 1197 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.26-7.20 (m, 1H), 7.12-7.07 (m, 2H), 2.50 (d, *J* = 6.8 Hz, 2H), 1.97-1.85 (m, 1H), 1.55-1.38 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.9, 129.6, 125.9, 121.8, 38.7, 38.3, 26.1, 11.1. HRMS (ESI) calcd for $C_{13}H_{19}O_2$ $(M+H)^+$: 207.1380; found: 207.1381.

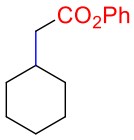
Table 2, 2p



Colorless oil; 0.0762 g (65% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1758, 1492, 1196 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H),

7.26-7.20 (m, 1H), 7.11-7.06 (m, 2H), 2.50 (d, *J* = 7.2 Hz, 2H), 2.01-1.90 (m, 1H), 1.54-1.29 (m, 8H), 0.98-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 150.9, 129.6, 125.9, 121.8, 39.0, 36.8, 33.3, 29.0, 26.6, 23.1, 14.3, 11.0; HRMS (ESI) calcd for $C_{15}H_{23}O_2$ $(M+H)^+$: 235.1693; found: 235.1694.

Scheme 2, 2q



Colorless oil; 0.0789 g (72% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1756, 1492, 1197 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.26-7.20 (m, 1H), 7.12-7.07 (m, 2H), 2.45 (d, *J* = 7.2 Hz, 2H), 2.01-1.90 (m, 1H), 1.90-1.81 (m, 2H), 1.81-1.66 (m, 3H), 1.40-1.27 (m, 2H), 1.27-1.17 (m, 1H), 1.16-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 150.9, 129.5, 125.8, 121.8, 42.3, 35.2, 33.2, 26.3, 26.2.

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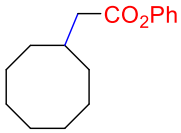
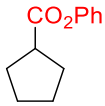
Table 2, 2r



Colorless oil; 0.0710 g (58% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1756, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.26-7.20 (m, 1H), 7.12-7.06 (m, 2H), 2.48 (d, *J* = 7.6 Hz, 2H), 2.30-2.17 (m, 1H), 1.80-1.38 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 150.9, 129.5, 125.9, 121.8, 43.0, 34.9, 32.4, 27.2, 26.4, 25.4; HRMS (ESI) calcd for $C_{16}H_{23}O_2$ $(M+H)^+$: 247.1693; found: 247.1693.

Table 2, 2s



Colorless oil; 0.0734 g (77% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1754, 1492, 1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.25-7.19 (m, 1H), 7.10-7.06 (m, 2H), 3.04-2.95 (m, 1H), 2.09-1.91 (m, 4H), 1.84-1.73 (m, 2H), 1.71-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 151.1, 129.5, 125.8, 121.7, 44.0, 30.3, 26.1;

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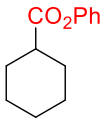
Table 2, 2t

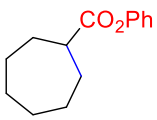


Colorless oil; 0.0985 g (96% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1754, 1492, 1151 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 7.25-7.19 (m, 1H), 7.10-7.05 (m, 2H), 2.57 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.12-2.04 (m, 2H), 1.88-1.79 (m, 2H), 1.73-1.55 (m, 3H), 1.43-1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 151.1, 129.5, 125.8, 121.7, 43.4, 29.1, 25.9, 25.6;

1) L. K. G. Ackerman, J. I. M. Alvarado and A. G. Doyle, *J. Am. Chem. Soc*., 2018, **140**, 14059-14063.

2) J. Li, T. Shen, Y. Yang and Y. Shi, *Chin. J. Chem*., 2024, **42**, 1381.

Table 2, 2u

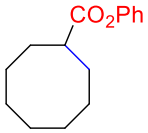


Colorless oil; 0.0700 g (64% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1755, 1197 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.10-7.05 (m, 2H), 2.80-2.70 (m, 1H), 2.15-2.05 (m, 2H), 1.90-1.76 (m, 4H),

1.68-1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 151.1, 129.5, 125.8, 121.7, 45.1, 30.9, 28.5, 26.5;

L. K. G. Ackerman, J. I. M. Alvarado and A. G. Doyle, *J. Am. Chem. Soc.*, 2018, **140**, 14059-14063.

Table 2, 2v

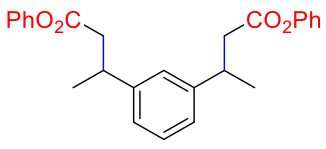


Colorless oil; 0.0650 g (56% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1755, 1196 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.25-7.19 (m, 1H), 7.10-7.05 (m, 2H), 2.83-2.74 (m, 1H), 2.11-2.02 (m, 2H), 1.92-1.76 (m, 4H), 1.68-1.52 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 151.1, 129.5, 125.8, 121.7, 43.8, 28.9, 27.0, 26.3, 25.4;

1) L. K. G. Ackerman, J. I. M. Alvarado and A. G. Doyle, *J. Am. Chem. Soc.*, 2018, **140**, 14059-14063.

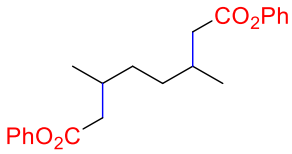
2) J. Li, T. Shen, Y. Yang and Y. Shi, *Chin. J. Chem.*, 2024, **42**, 1381.

Table 2, 2w



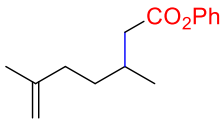
Colorless oil; 0.1600 g (80% yield), eluent: petroleum ether/DCM = 3:1; IR (film) 1755, 1493, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 7.23-7.16 (m, 5H), 6.93-6.88 (m, 4H), 3.48-3.36 (m, 2H), 2.87 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.81 (dd, *J* = 14.8, 8.0 Hz, 2H), 1.42 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 150.8, 145.81, 145.79, 129.6, 129.1, 126.0, 125.8, 125.3, 125.2, 121.7, 43.2, 43.1, 37.0, 22.2, 22.1; HRMS (ESI) calcd for $C_{26}H_{27}O_4$ $(M+H)^+$: 403.1904; found: 403.1906..

Table 2, 2x



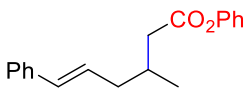
Colorless oil; 0.1360 g (77% yield), eluent: petroleum ether/DCM = 3:1; IR (film) 1755, 1493, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 4H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 4H), 2.64-2.55 (m, 2H), 2.46-2.37 (m, 2H), 2.20-2.07 (m, 2H), 1.60-1.48 (m, 2H), 1.44-1.32 (m, 2H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.7, 150.8, 129.6, 125.9, 121.7, 42.0, 41.8, 34.1, 34.0, 30.8, 30.7, 20.0, 19.8; HRMS (ESI) calcd for $C_{22}H_{27}O_4$ $(M+H)^+$: 355.1904; found: 355.1906.

Table 2, 2y



Colorless oil; 0.0520 g (45% yield), eluent: petroleum ether/ethyl acetate = 50:1 to 3:1; IR (film) 1757, 1492, 1195 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.26-7.20 (m, 1H), 7.11-7.06 (m, 2H), 4.75-4.71 (m, 2H), 2.58 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.40 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.18-2.01 (m, 3H), 1.75 (s, 3H), 1.66-1.56 (m, 1H), 1.48-1.38 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 150.9, 145.8, 129.6, 125.9, 121.8, 110.2, 41.9, 35.3, 34.7, 30.4, 22.6, 19.8; HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $(M+H)^+$: 233.1536; found: 233.1537.

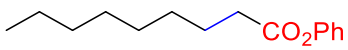
Table 2, 2z



Colorless oil; 0.1175 g (84% yield), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1755, 1492, 1194 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 6H), 7.14-7.07 (m, 2H), 6.97-6.91 (m, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.12 (dt, *J* = 16.0, 6.8 Hz,

1H), 2.52 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.30 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.24-2.11 (m, 3H), 1.01 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 150.8, 137.6, 132.3, 129.5, 128.7, 128.2, 127.3, 126.2, 125.9, 121.7, 41.2, 40.3, 30.9, 20.0; HRMS (ESI) calcd for $C_{19}H_{20}O_2Na$ $(M+Na)^+$: 303.1356; found: 303.1352.

Scheme 5, 2aa



Colorless oil; 0.1043 g (89% yield, l/b = 3:1), eluent: petroleum ether/ethyl acetate = 50:1; IR (film) 1761, 1197 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.11-7.06 (m, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.81-1.72 (m, 2H), 1.43-1.28 (m, 10H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 151.0, 129.6, 125.9, 121.8, 34.6, 32.0, 29.4, 29.34, 29.32, 25.2, 22.9, 14.3.

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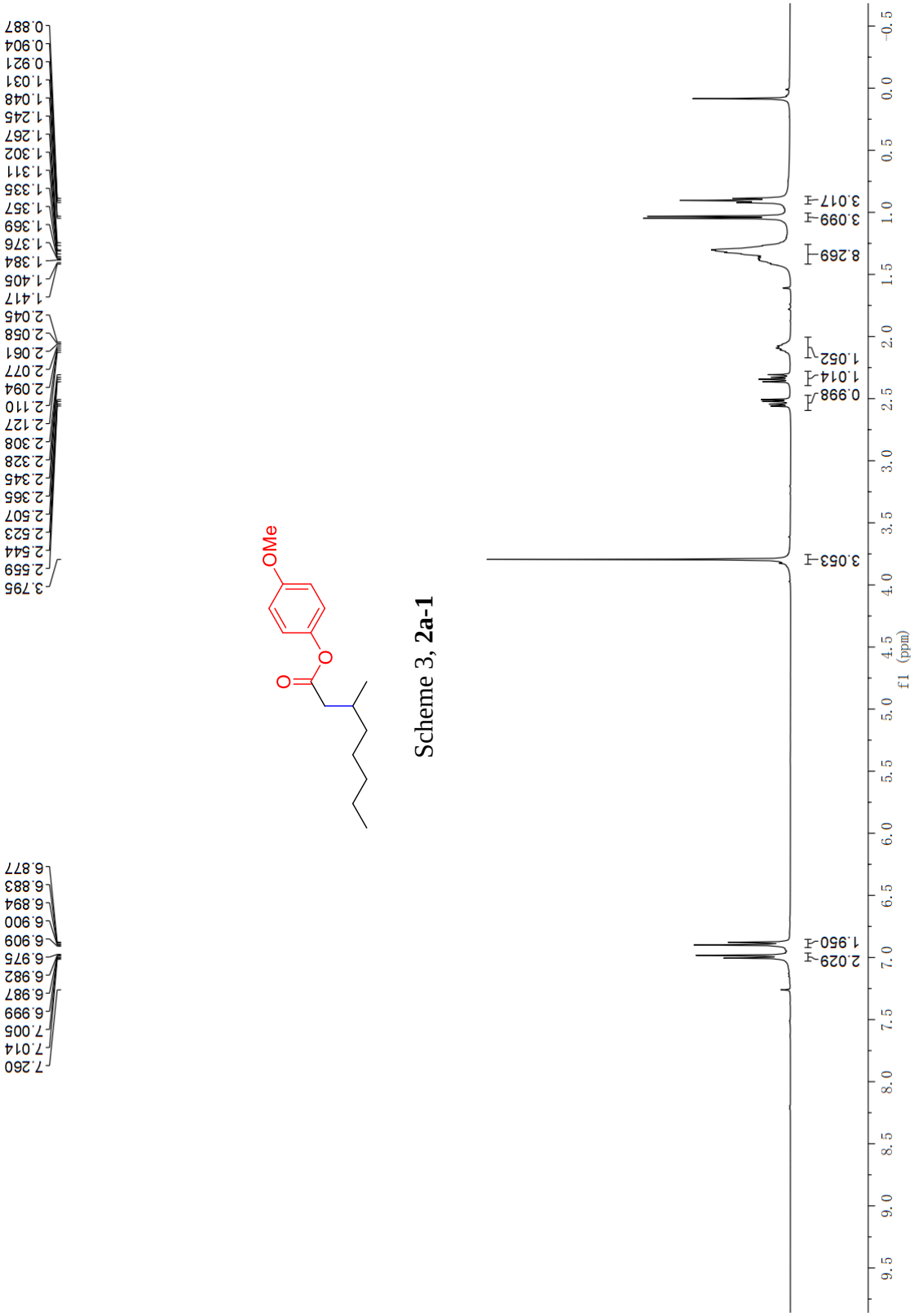
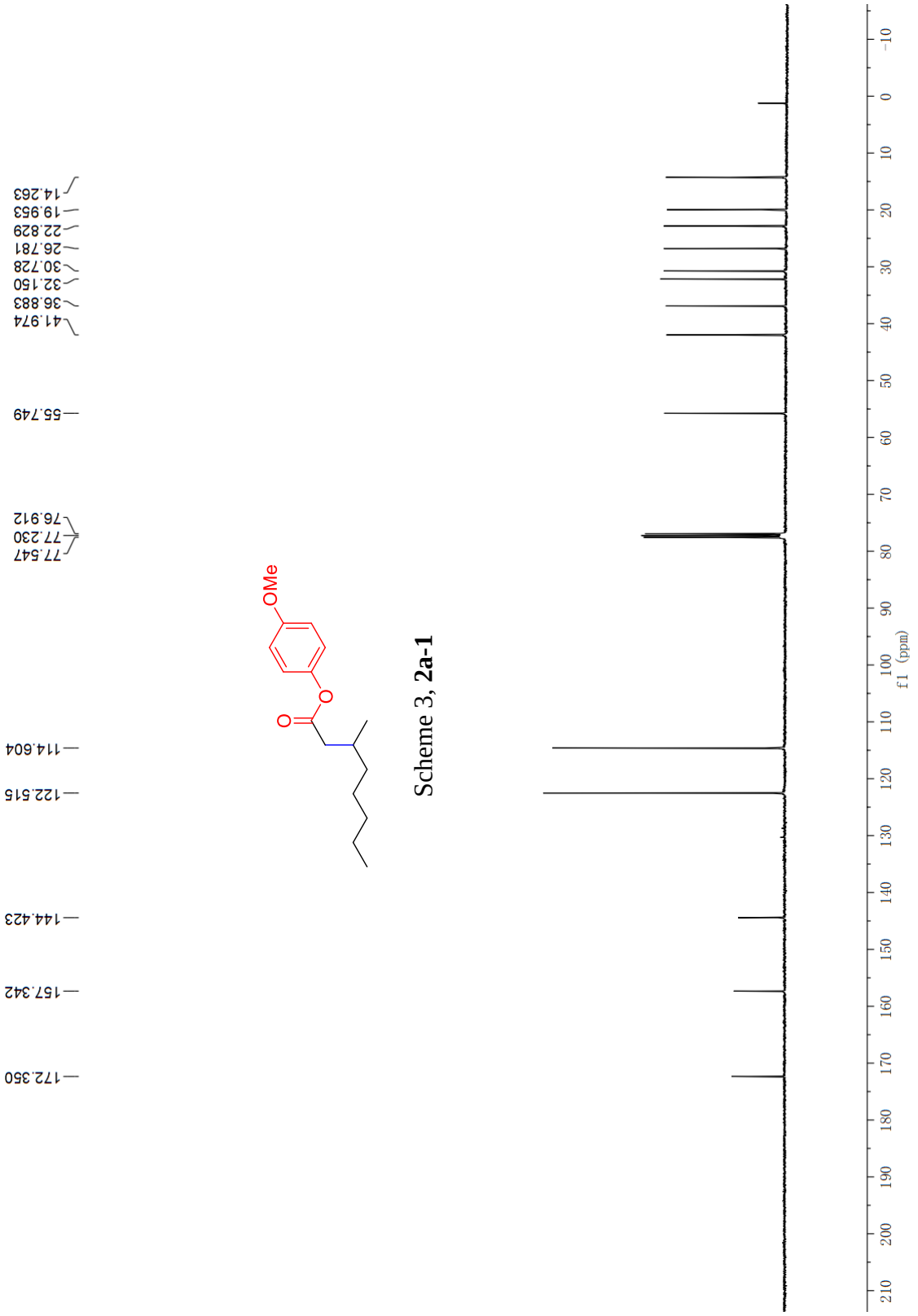
NMR spectra

^{1}H NMR Spectrum of **2a-1** ($CDCl_3$, 400 MHz)



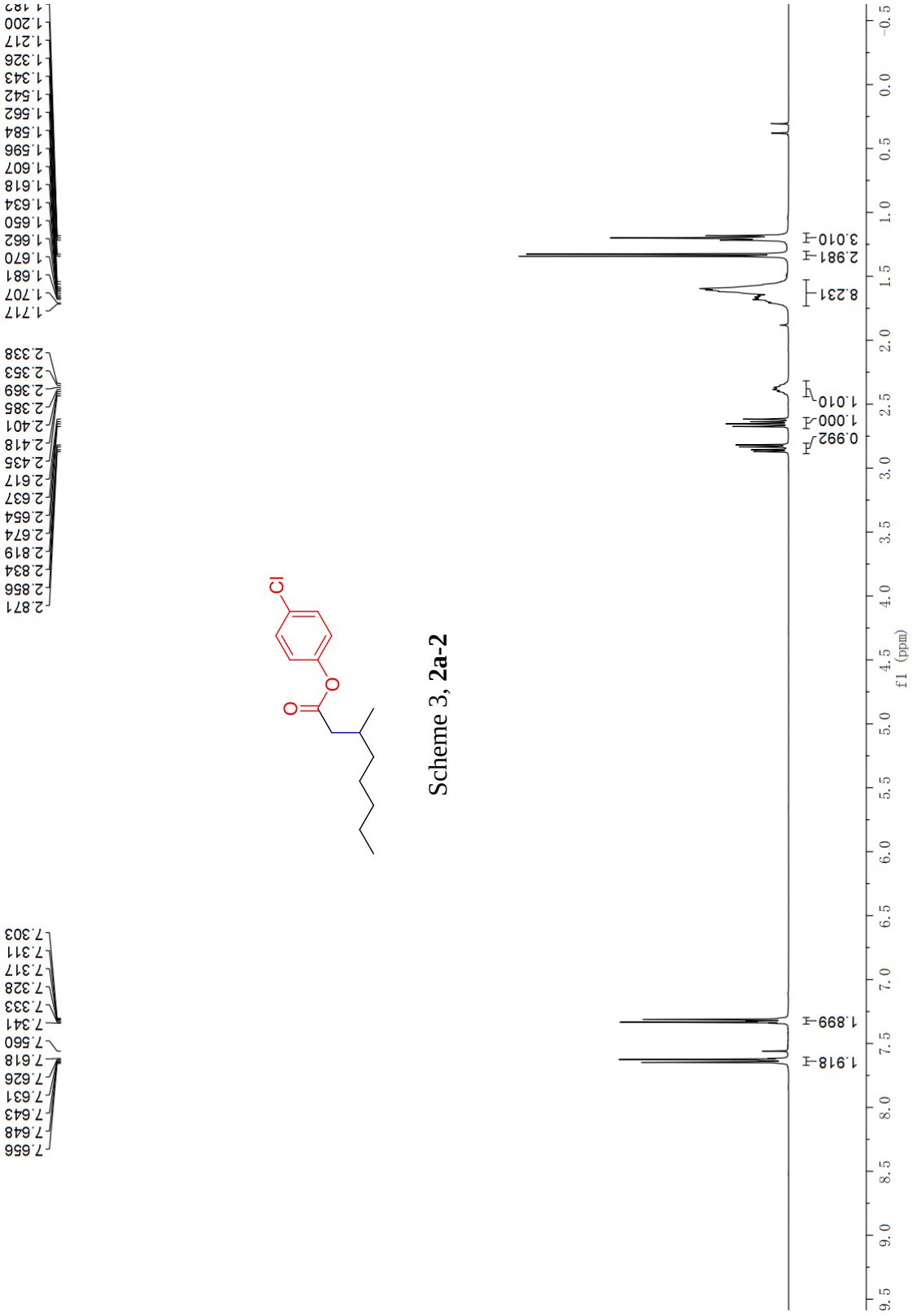
Scheme 3, **2a-1**

^{13}C NMR Spectrum of **2a-1** ($CDCl_3$, 100 MHz)



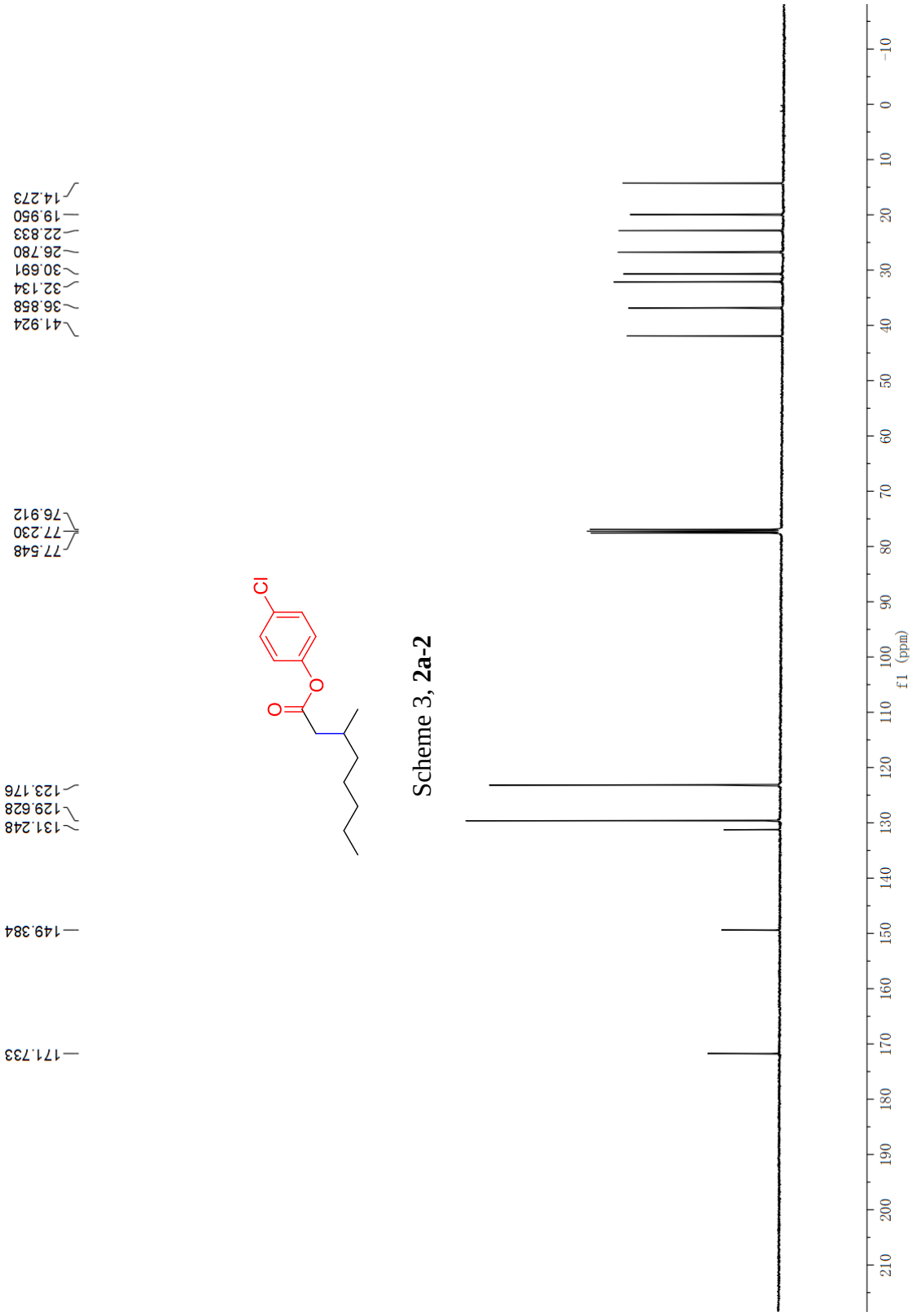
Scheme 3, **2a-1**

^{1}H NMR Spectrum of **2a-2** ($CDCl_3$, 400 MHz)



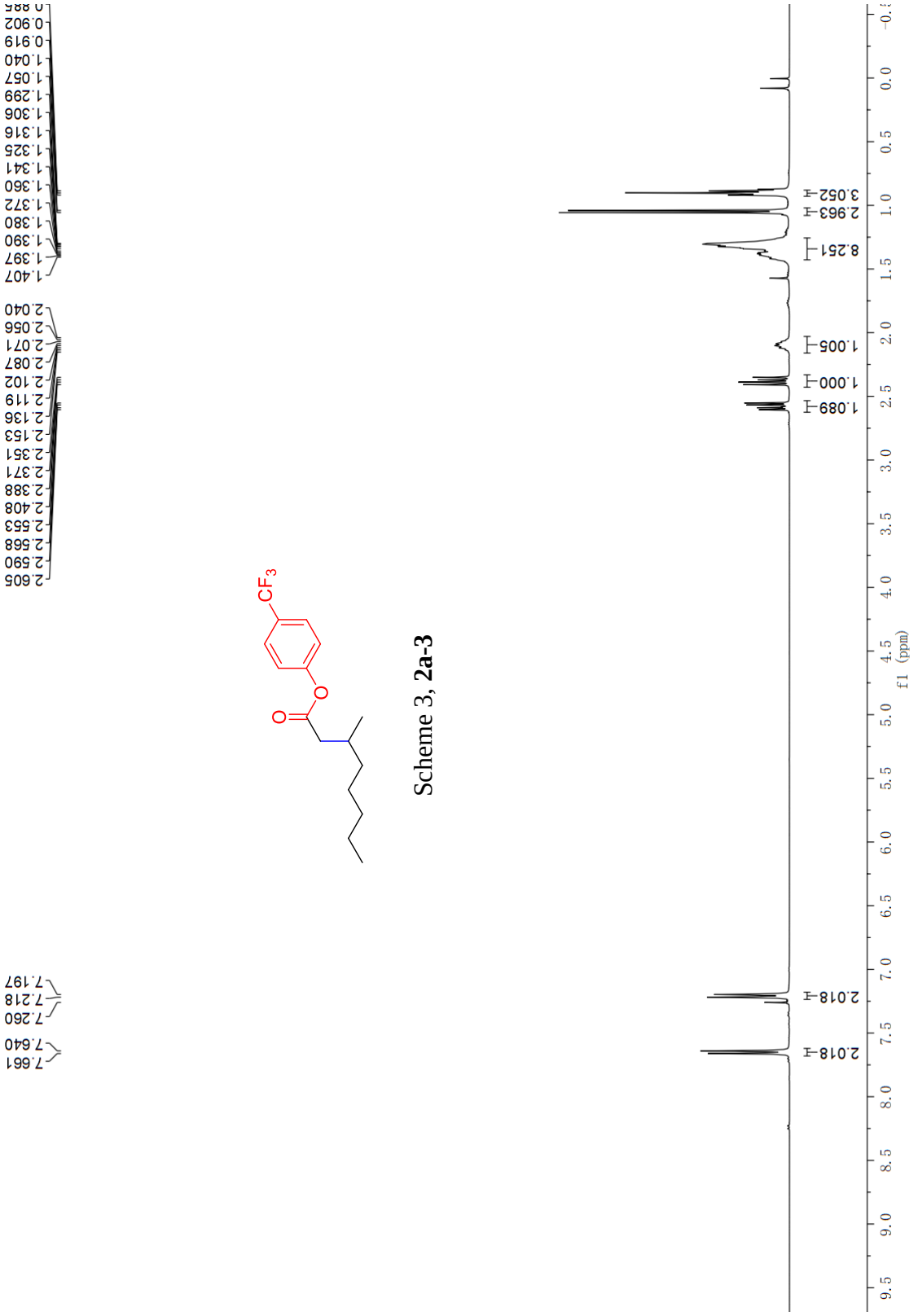
Scheme 3, **2a-2**

^{13}C NMR Spectrum of **2a-2** ($CDCl_3$, 100 MHz)



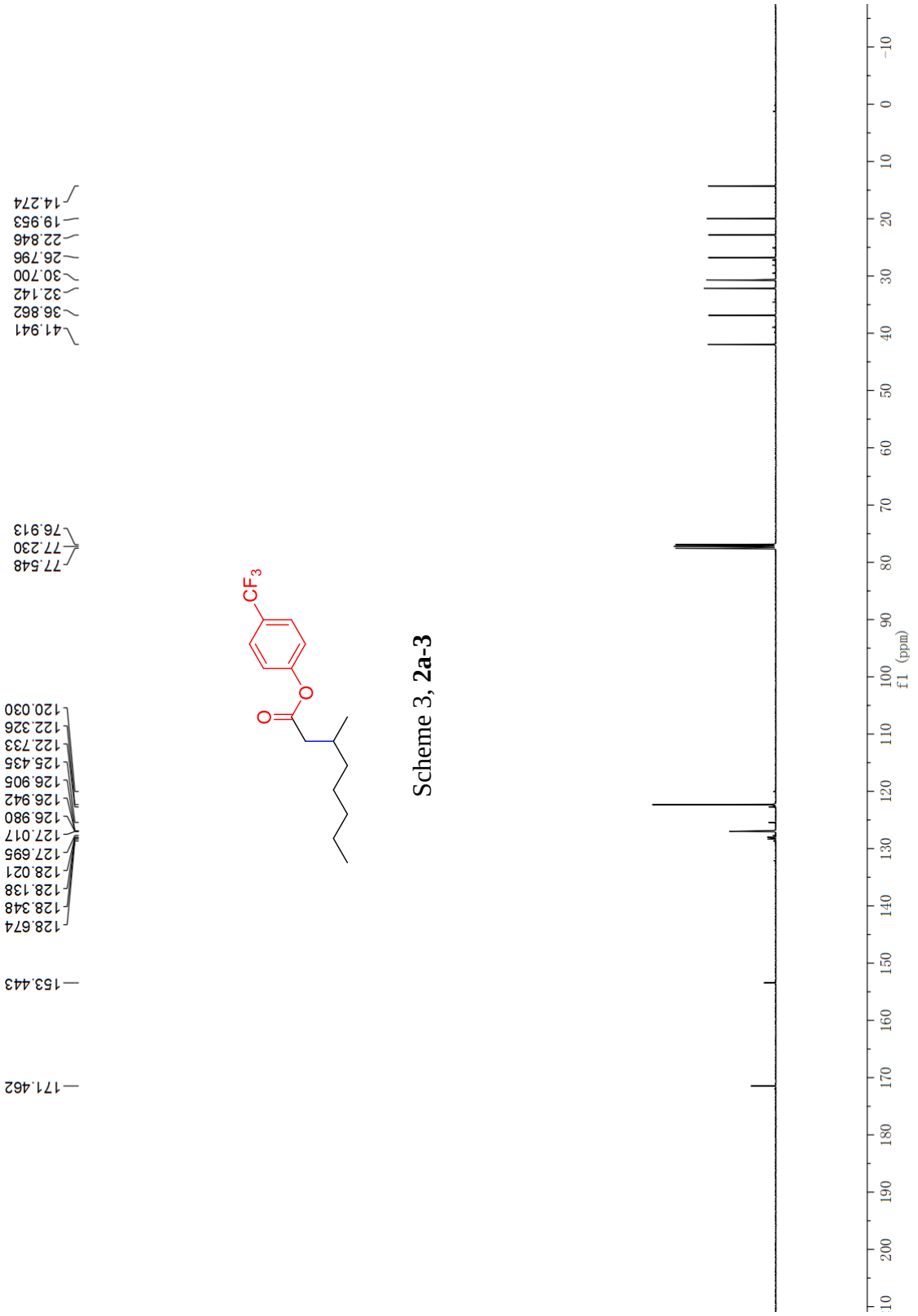
Scheme 3, **2a-2**

^{1}H NMR Spectrum of **2a-3** ($CDCl_3$, 400 MHz)



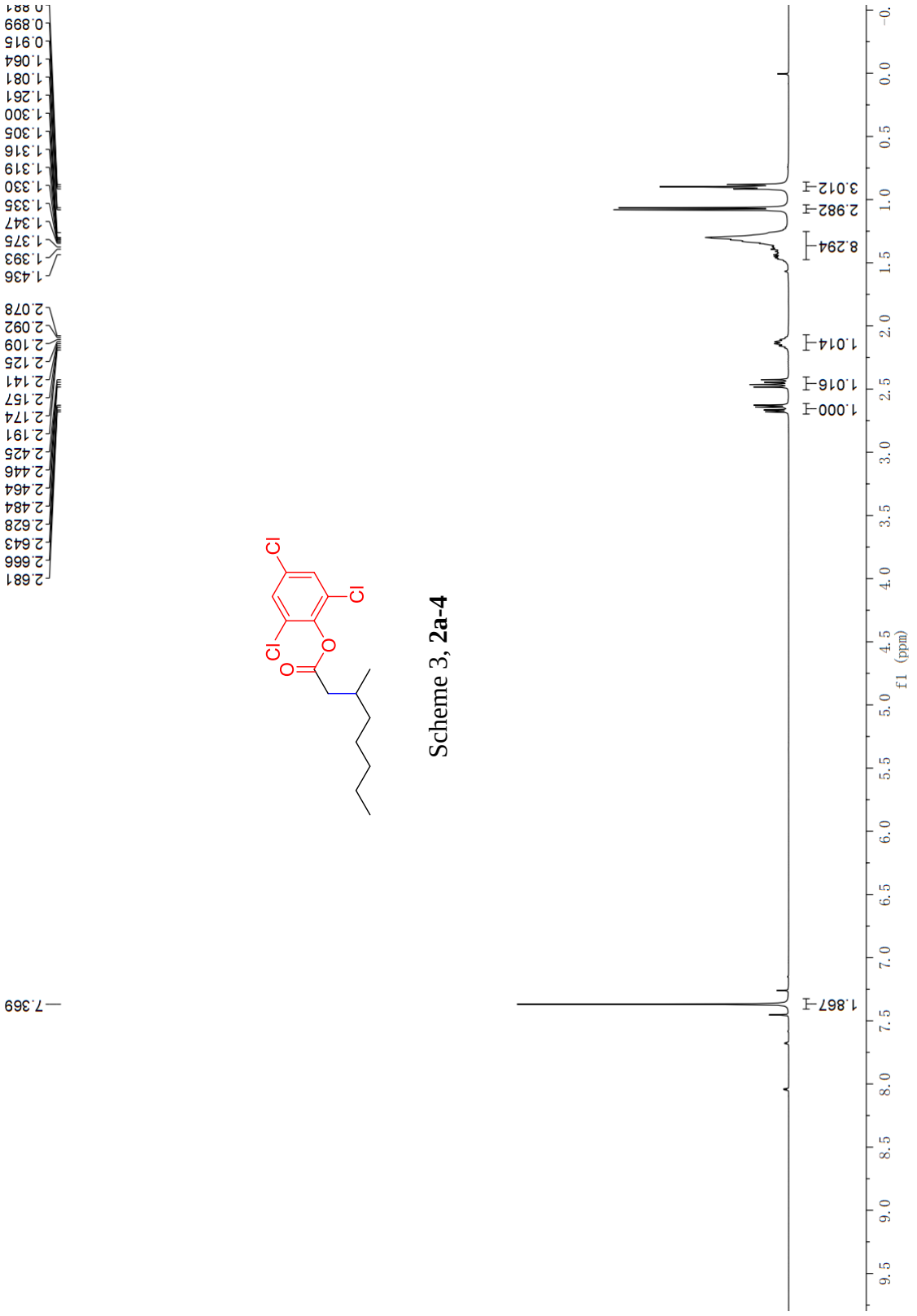
Scheme 3, **2a-3**

^{13}C NMR Spectrum of **2a-3** ($CDCl_3$, 100 MHz)



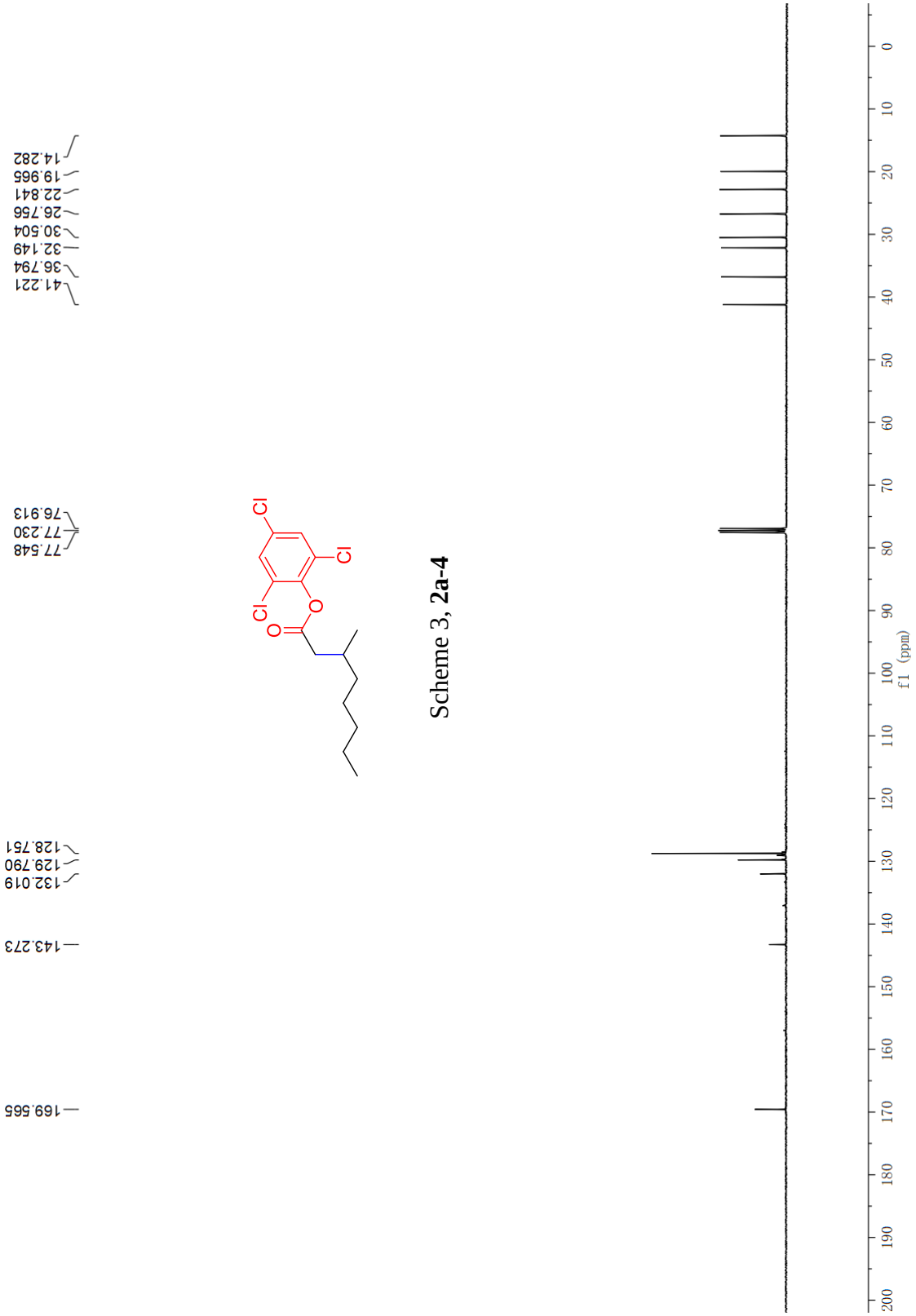
Scheme 3, **2a-3**

^{1}H NMR Spectrum of **2a-4** ($CDCl_3$, 400 MHz)



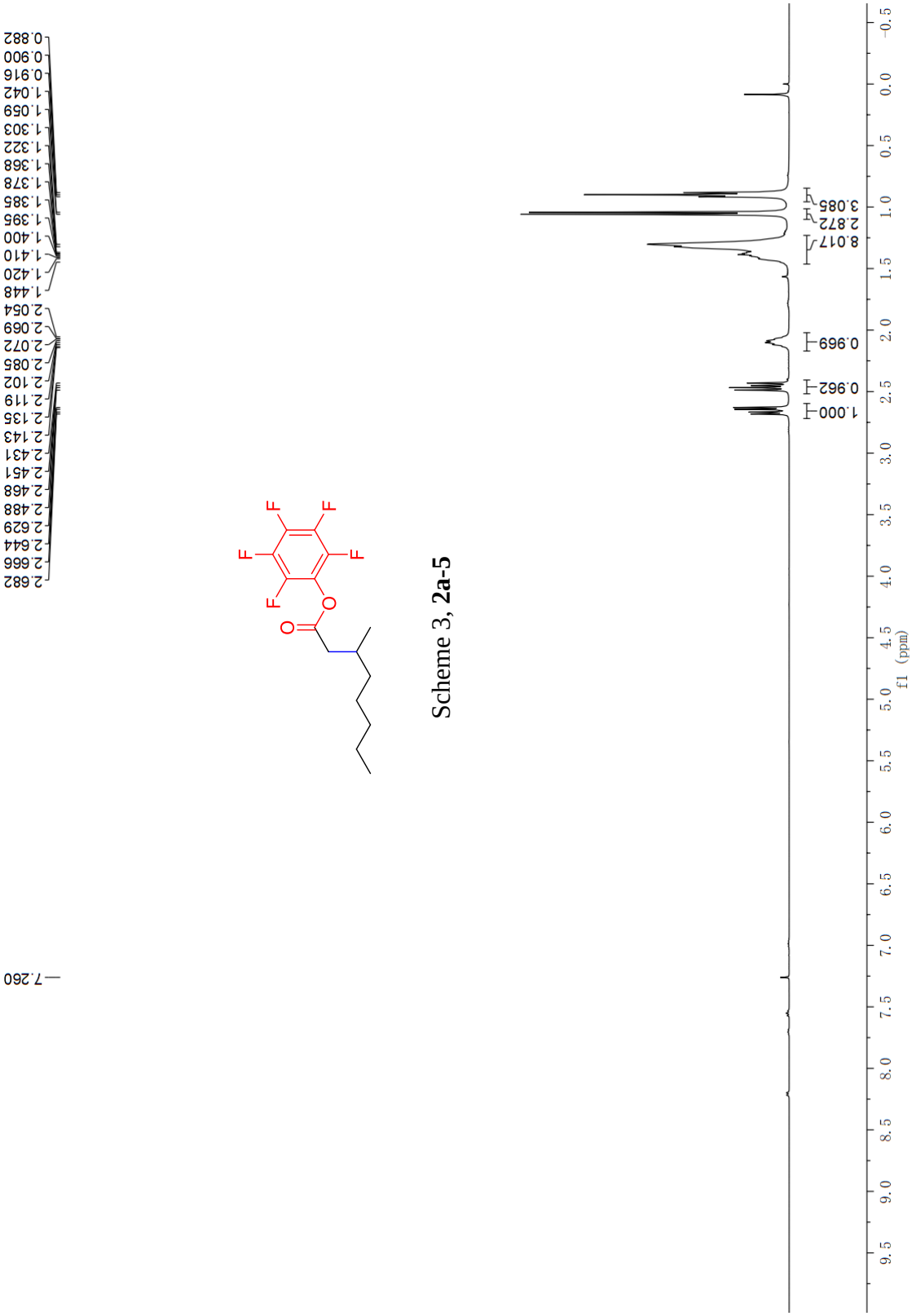
Scheme 3, **2a-4**

^{13}C NMR Spectrum of **2a-4** ($CDCl_3$, 100 MHz)



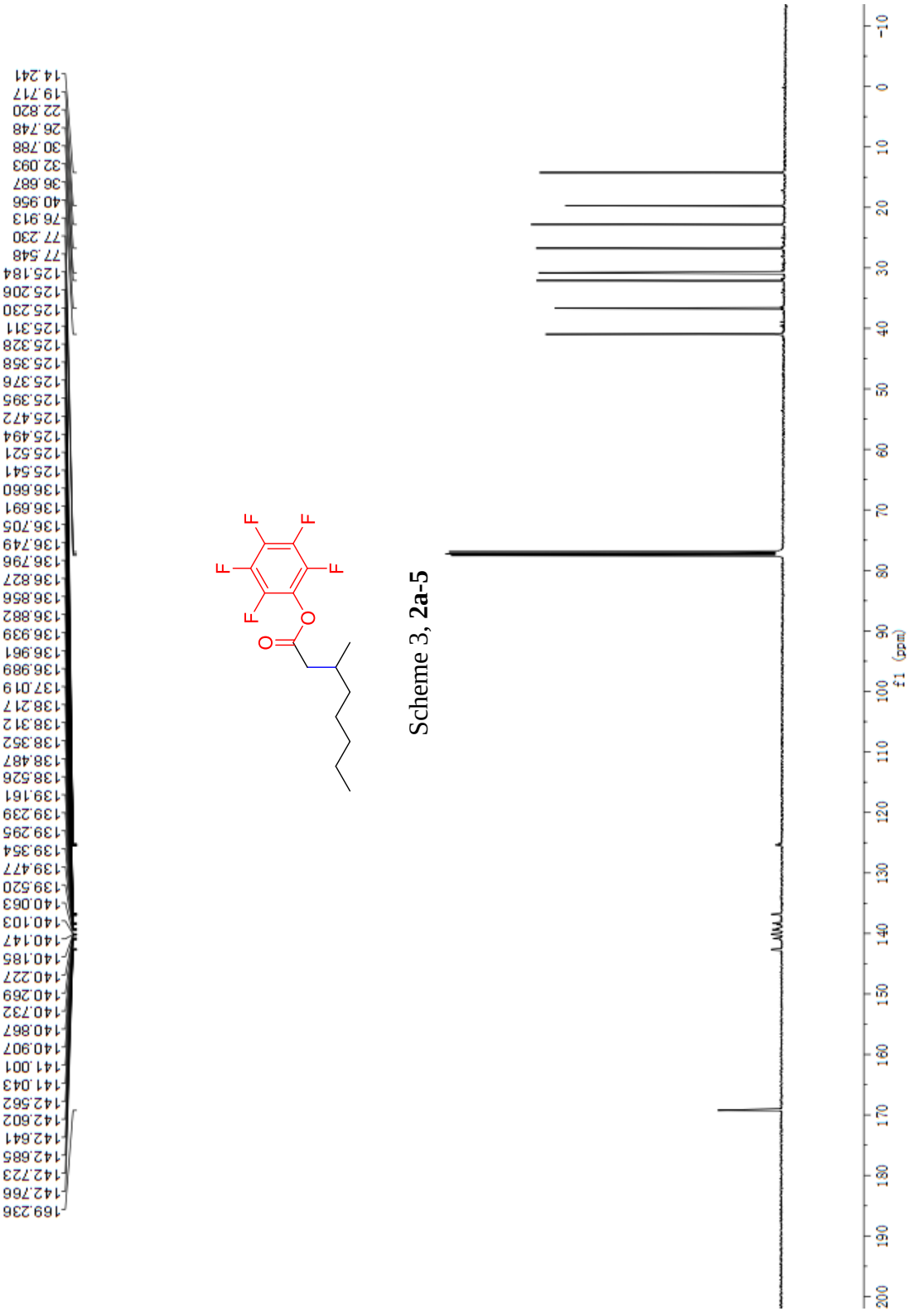
Scheme 3, **2a-4**

^{1}H NMR Spectrum of **2a-5** ($CDCl_3$, 400 MHz)

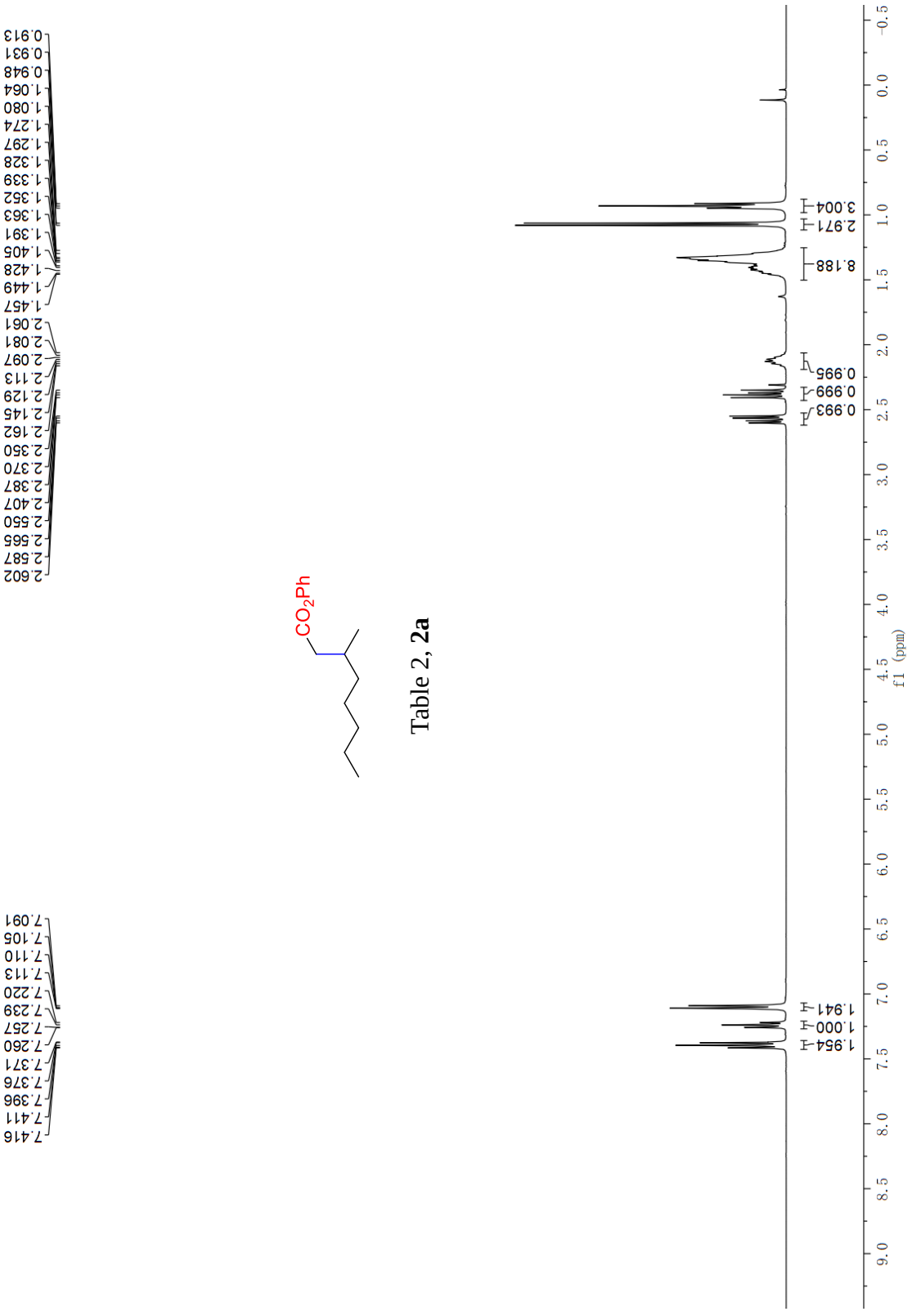


Scheme 3, **2a-5**

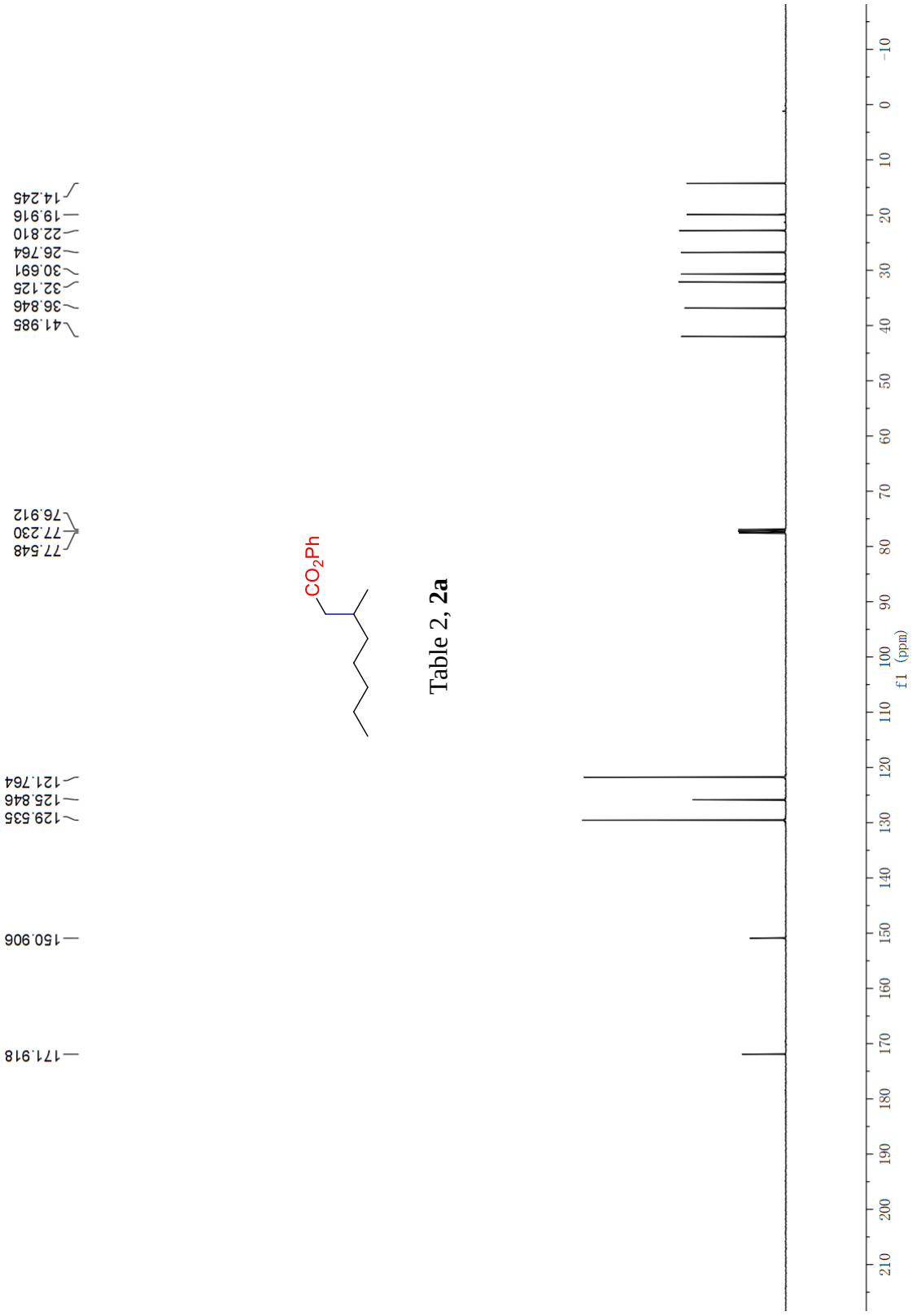
^{13}C NMR Spectrum of **2a-5** ($CDCl_3$, 100 MHz)



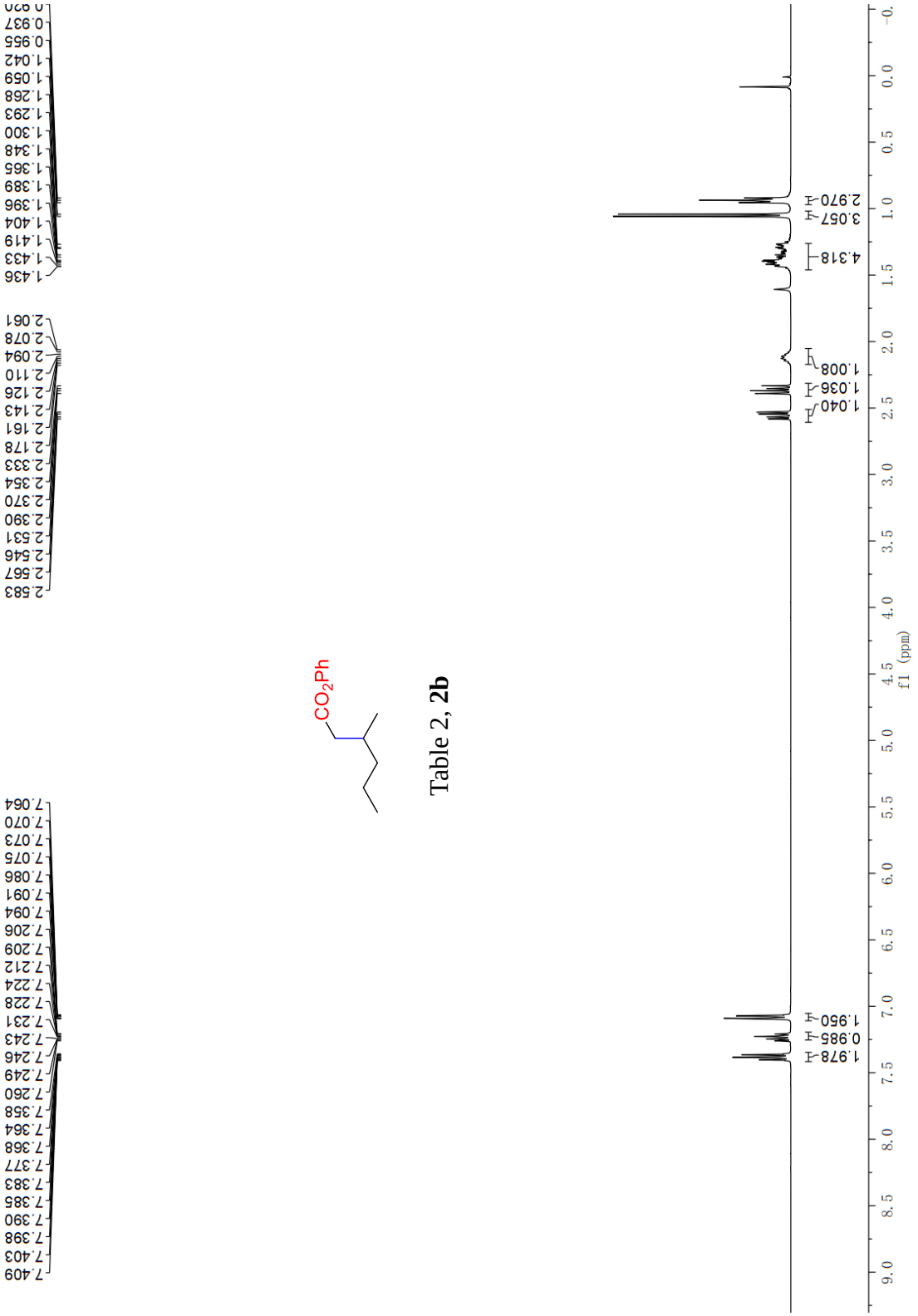
^{1}H NMR Spectrum of **2a** ($CDCl_3$, 400 MHz)



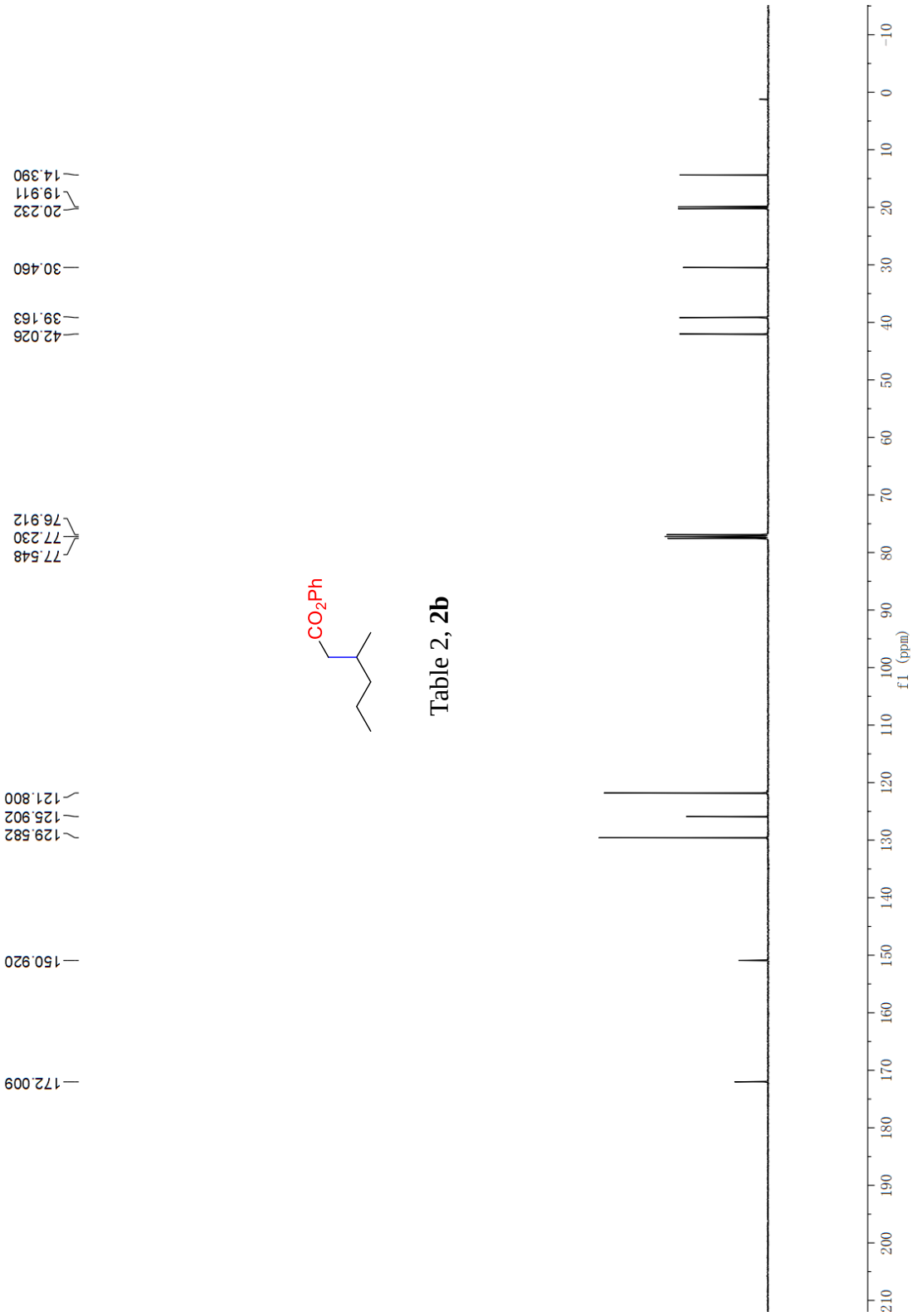
^{13}C NMR Spectrum of **2a** ($CDCl_3$, 100 MHz)



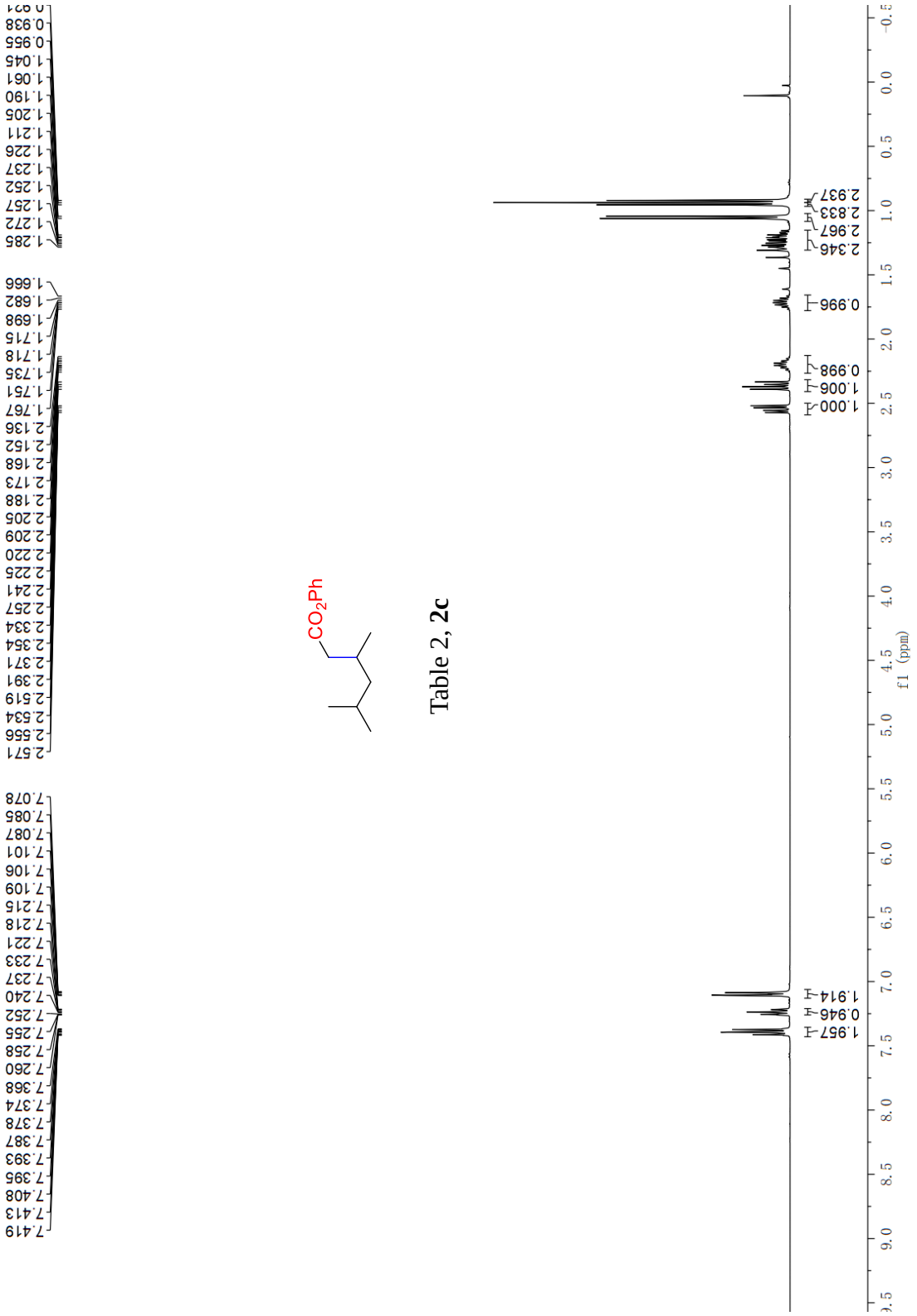
^{1}H NMR Spectrum of **2b** ($CDCl_3$, 400 MHz)



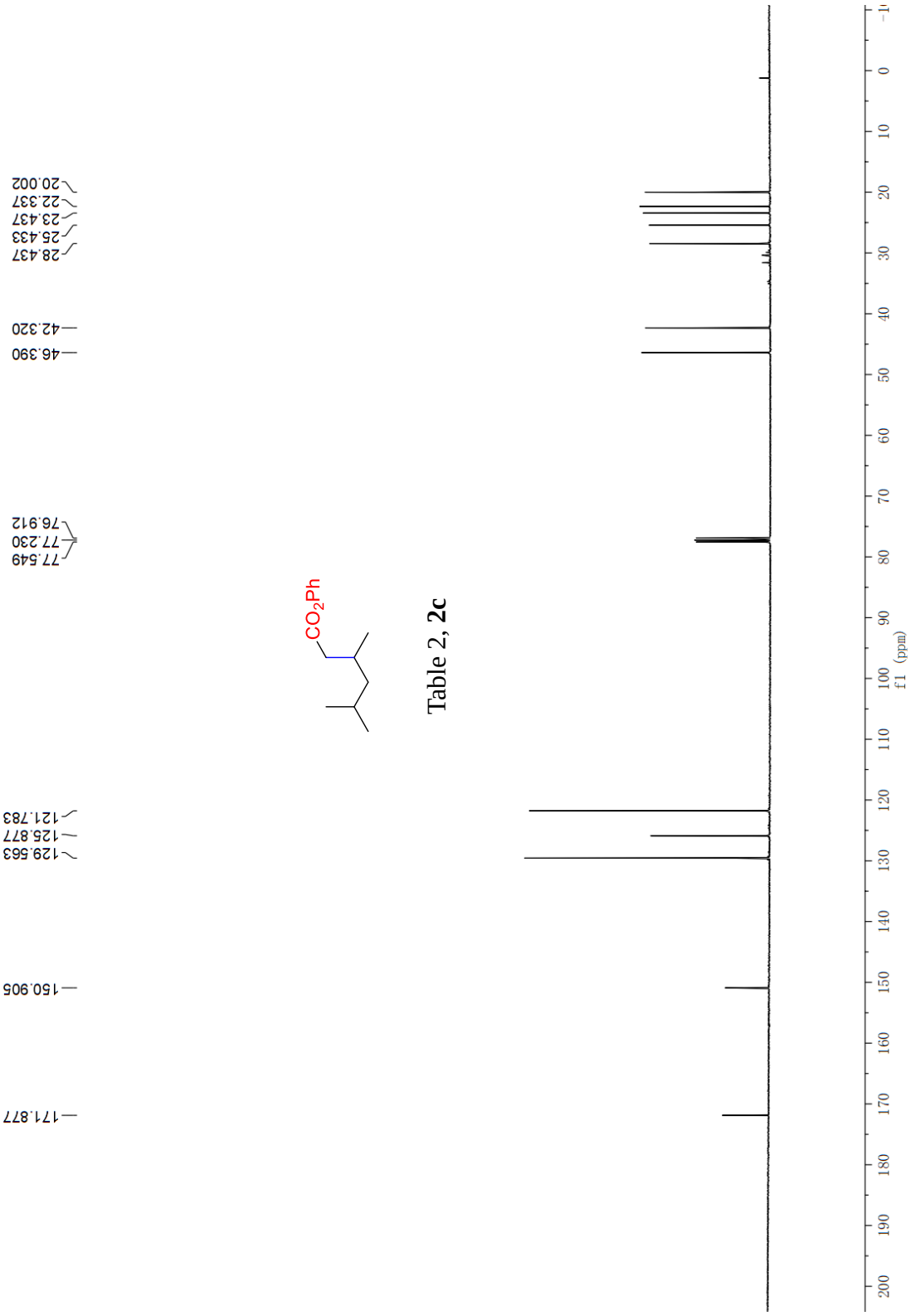
^{13}C NMR Spectrum of **2b** ($CDCl_3$, 100 MHz)



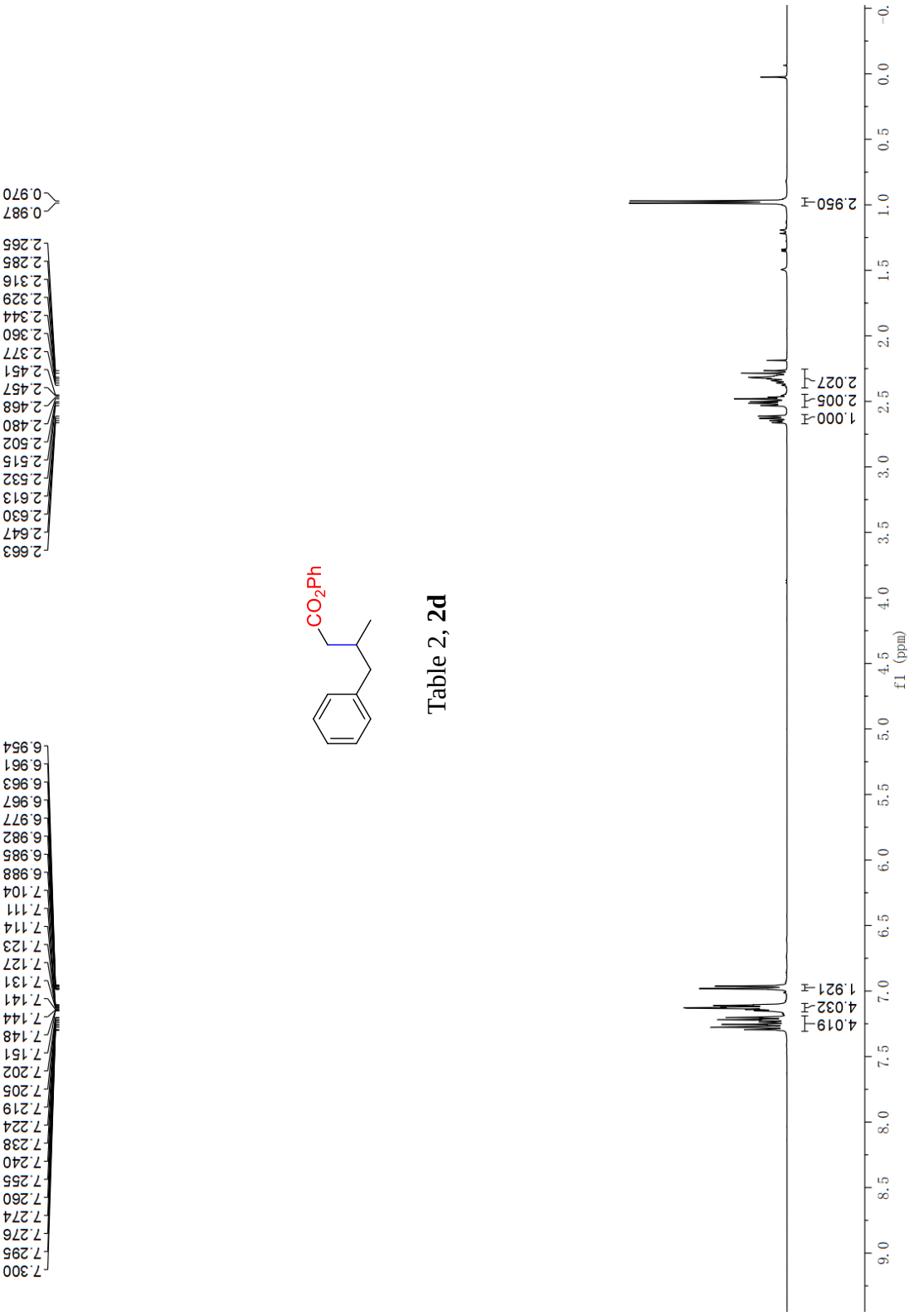
^{1}H NMR Spectrum of **2c** ($CDCl_3$, 400 MHz)



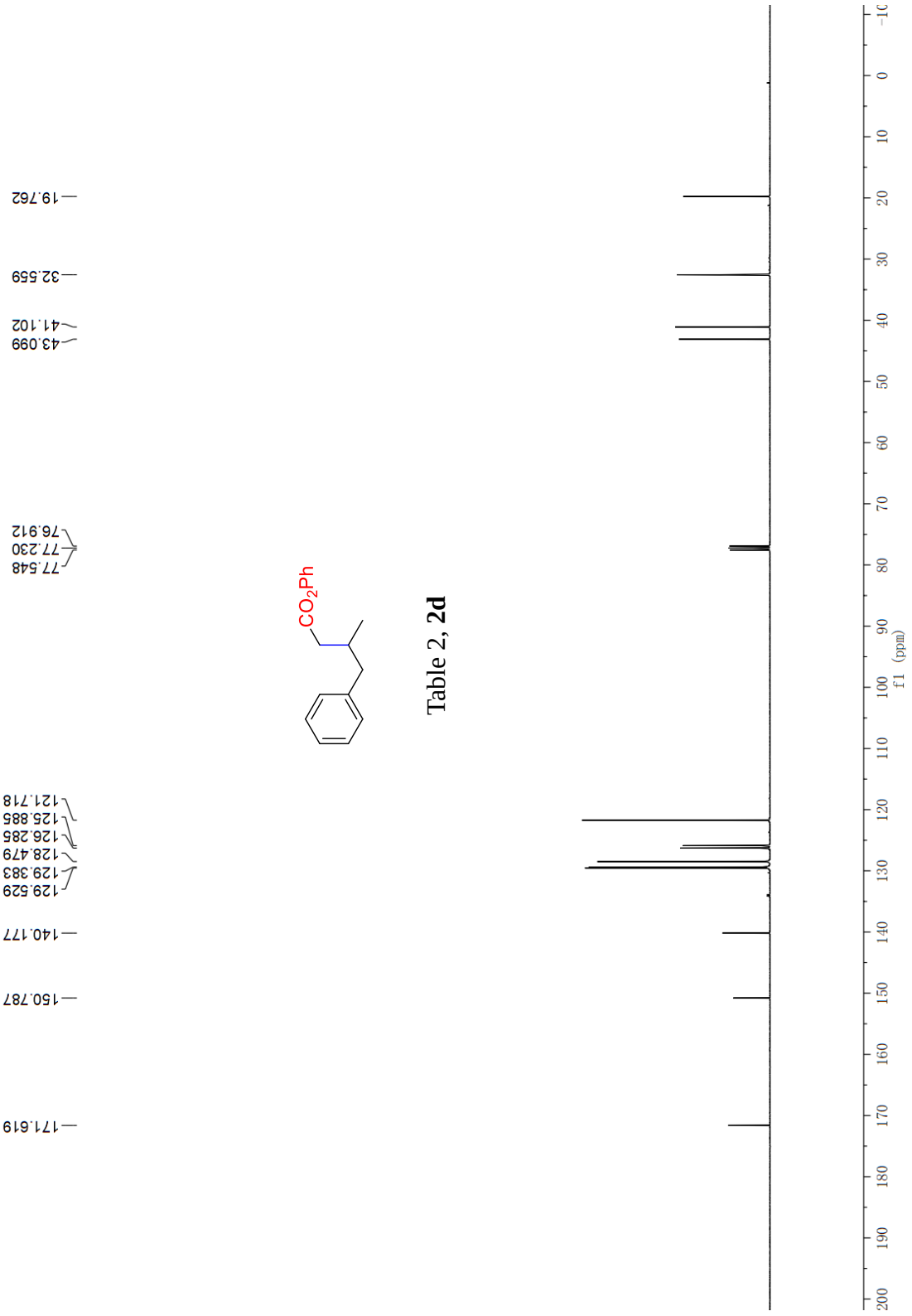
^{13}C NMR Spectrum of **2c** ($CDCl_3$, 100 MHz)



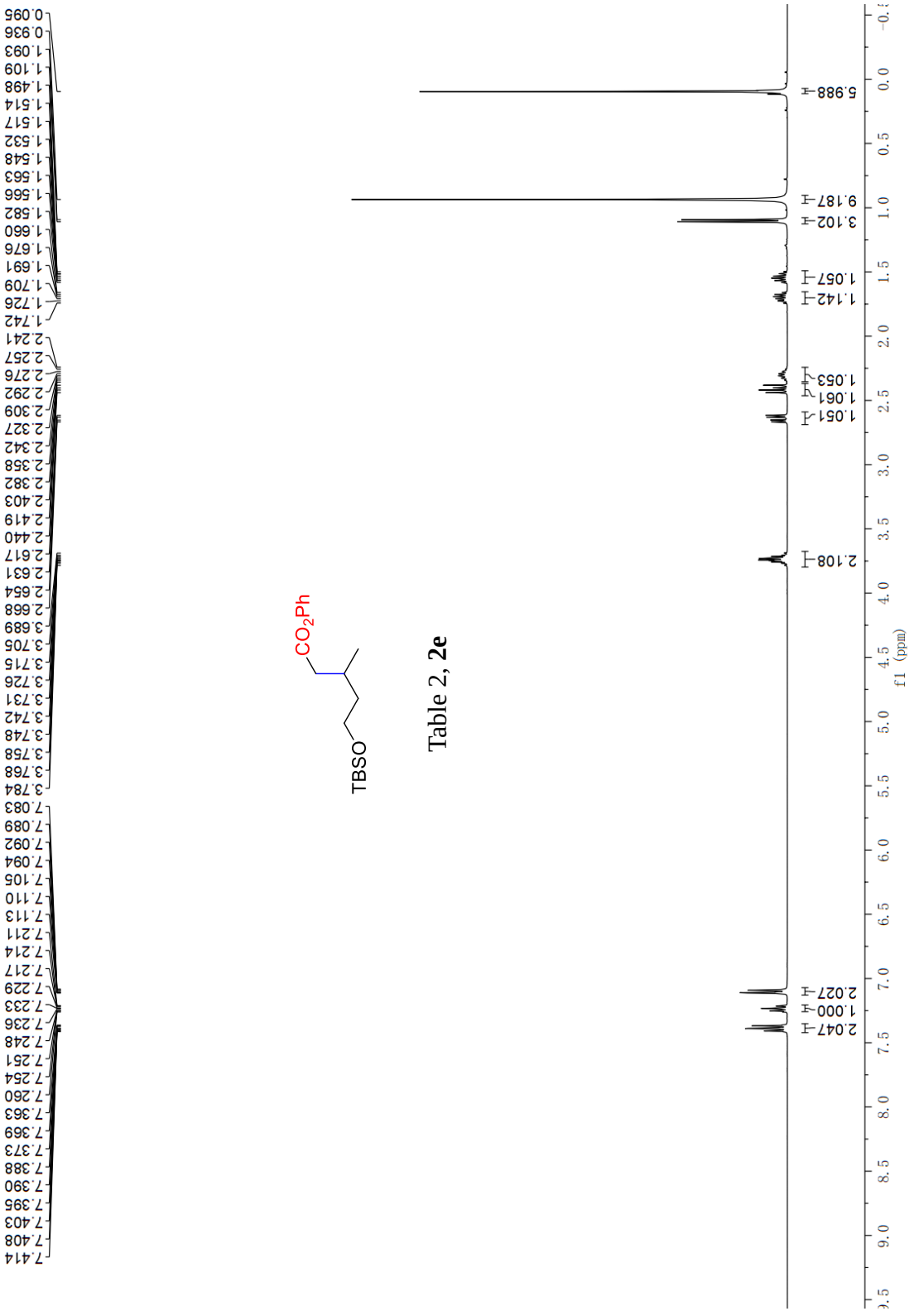
^{1}H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz)



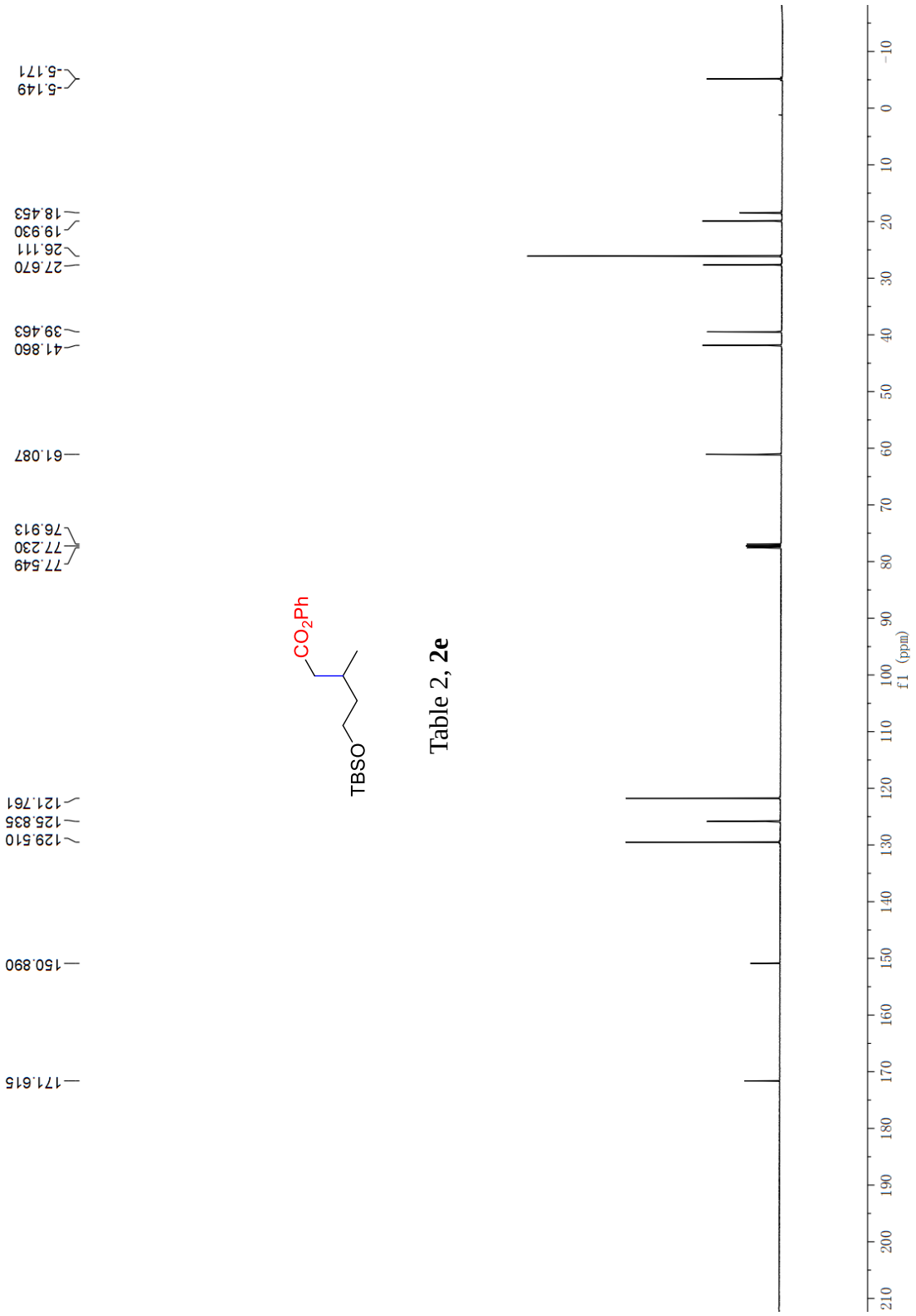
^{13}C NMR Spectrum of **2d** ($CDCl_3$, 100 MHz)



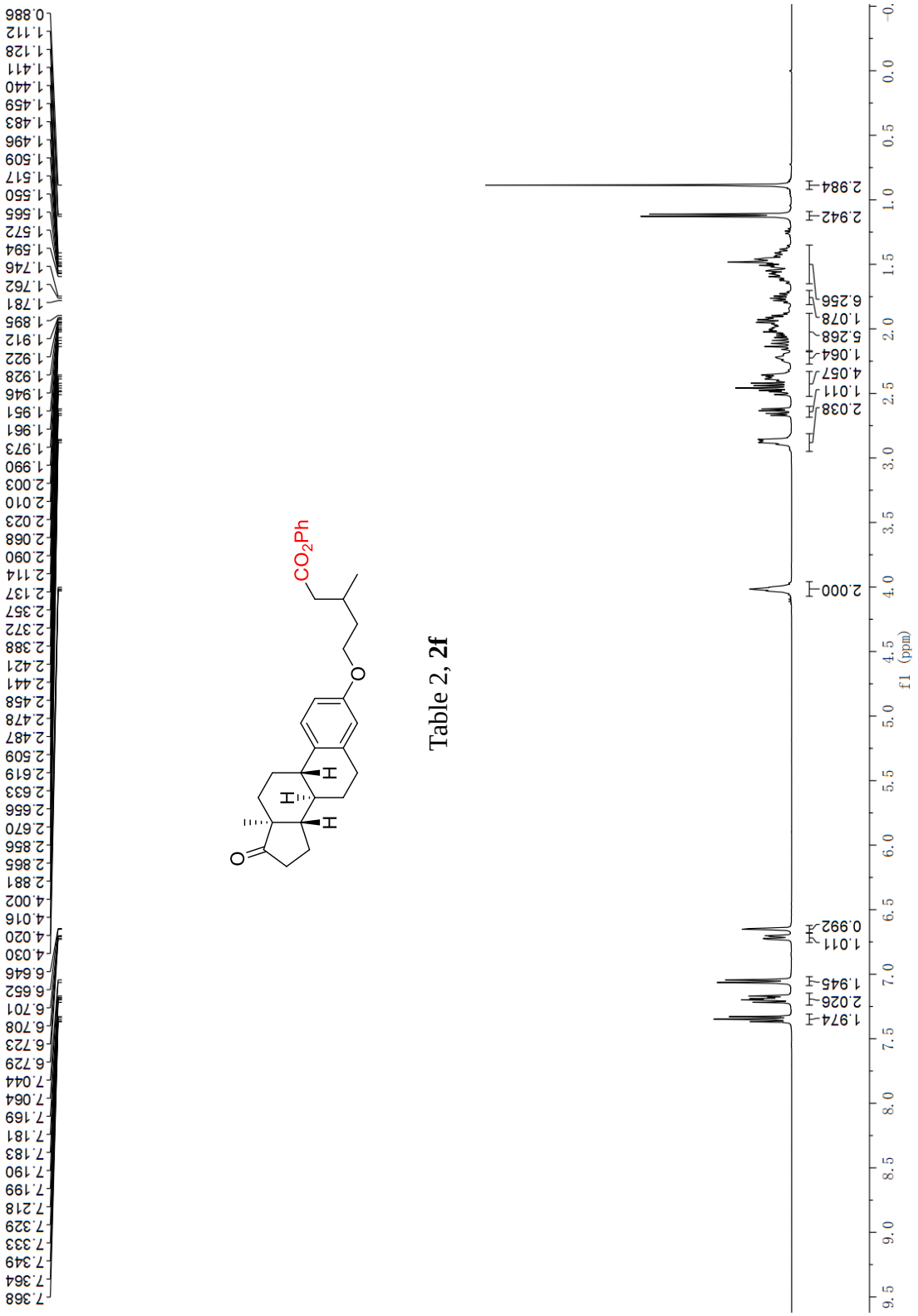
^{1}H NMR Spectrum of **2e** ($CDCl_3$, 400 MHz)



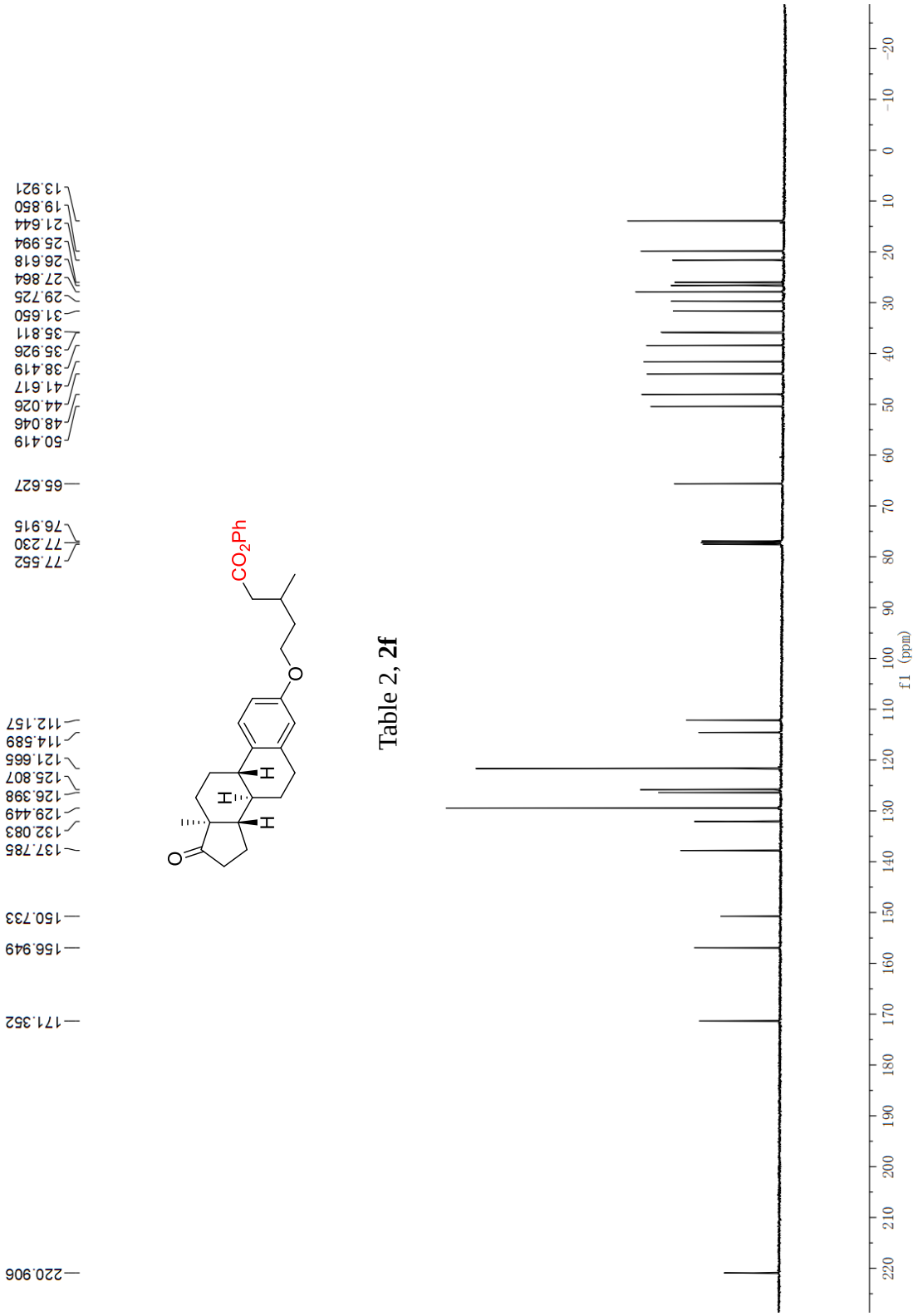
^{13}C NMR Spectrum of **2e** ($CDCl_3$, 100 MHz)



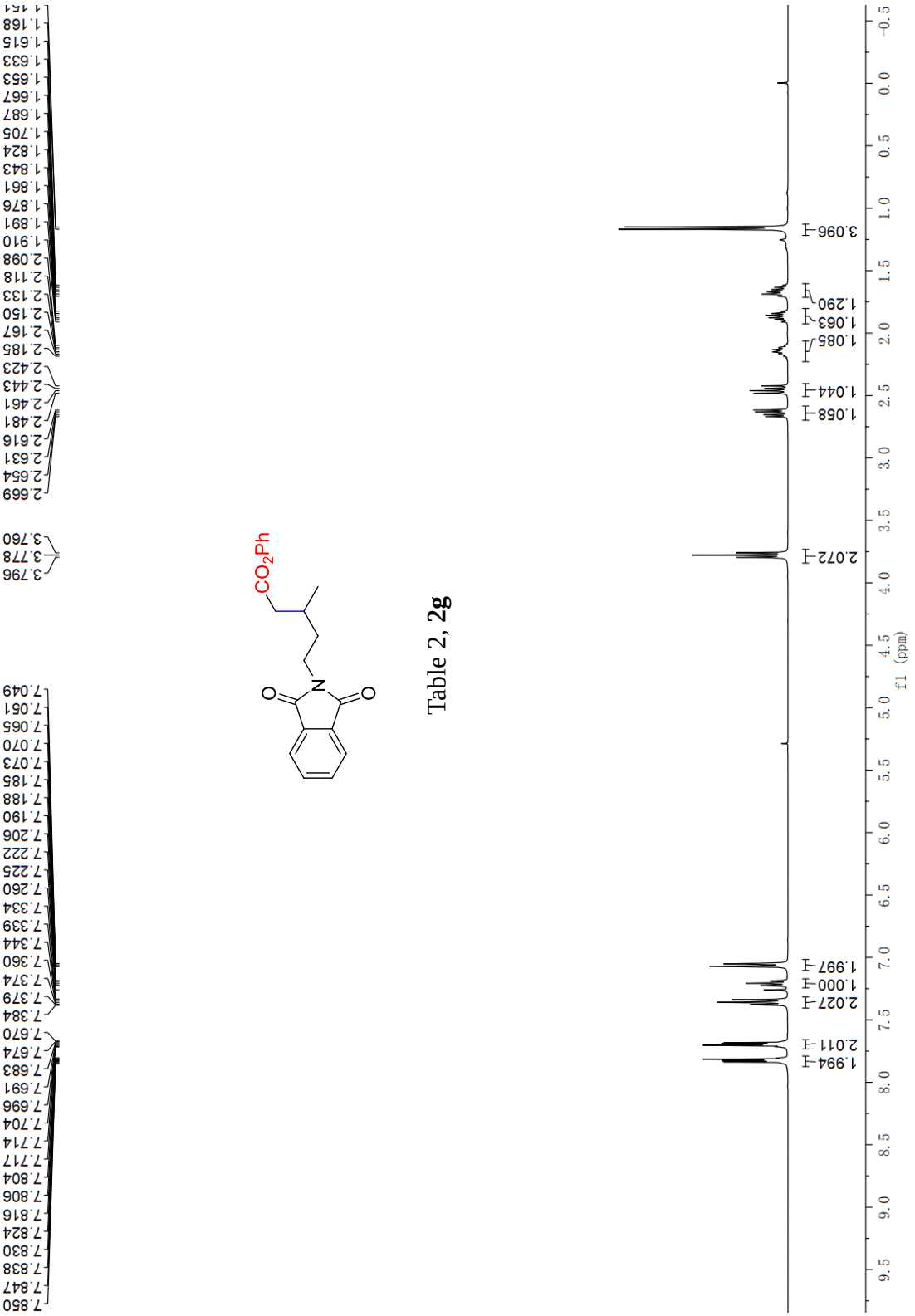
^{1}H NMR Spectrum of **2f** ($CDCl_3$, 400 MHz)



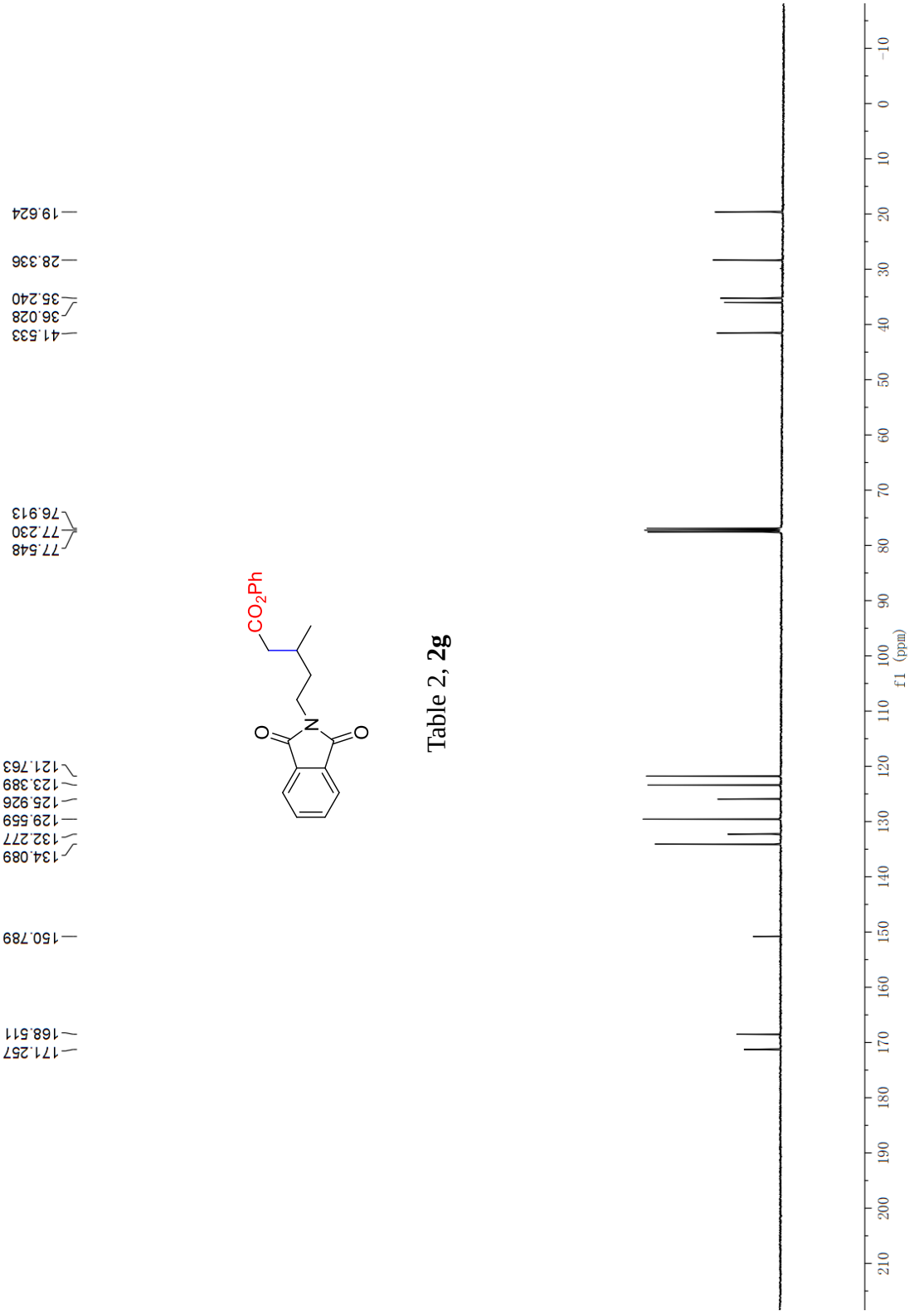
^{13}C NMR Spectrum of **2f** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2g** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2g** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2h** ($CDCl_3$, 400 MHz)

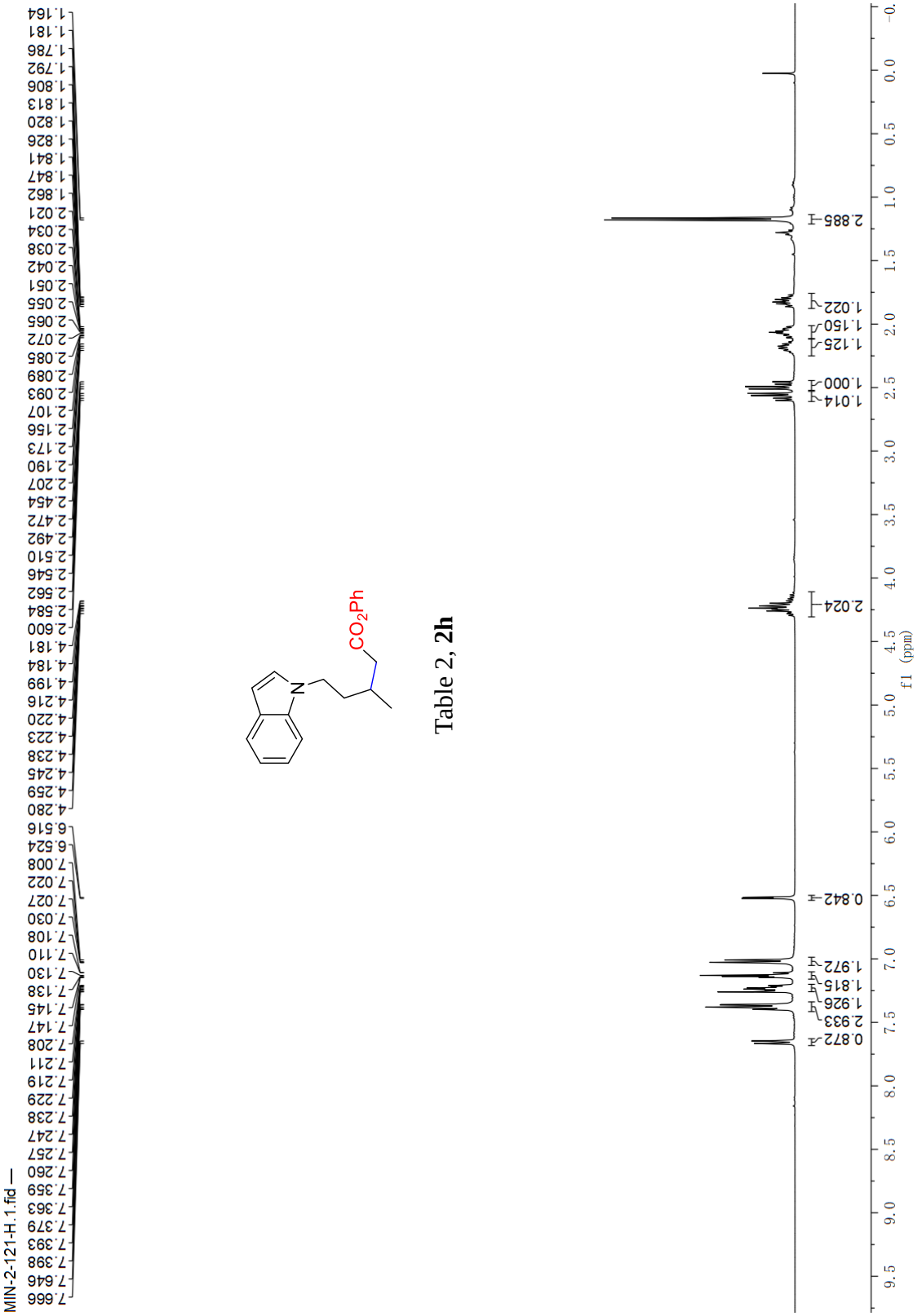
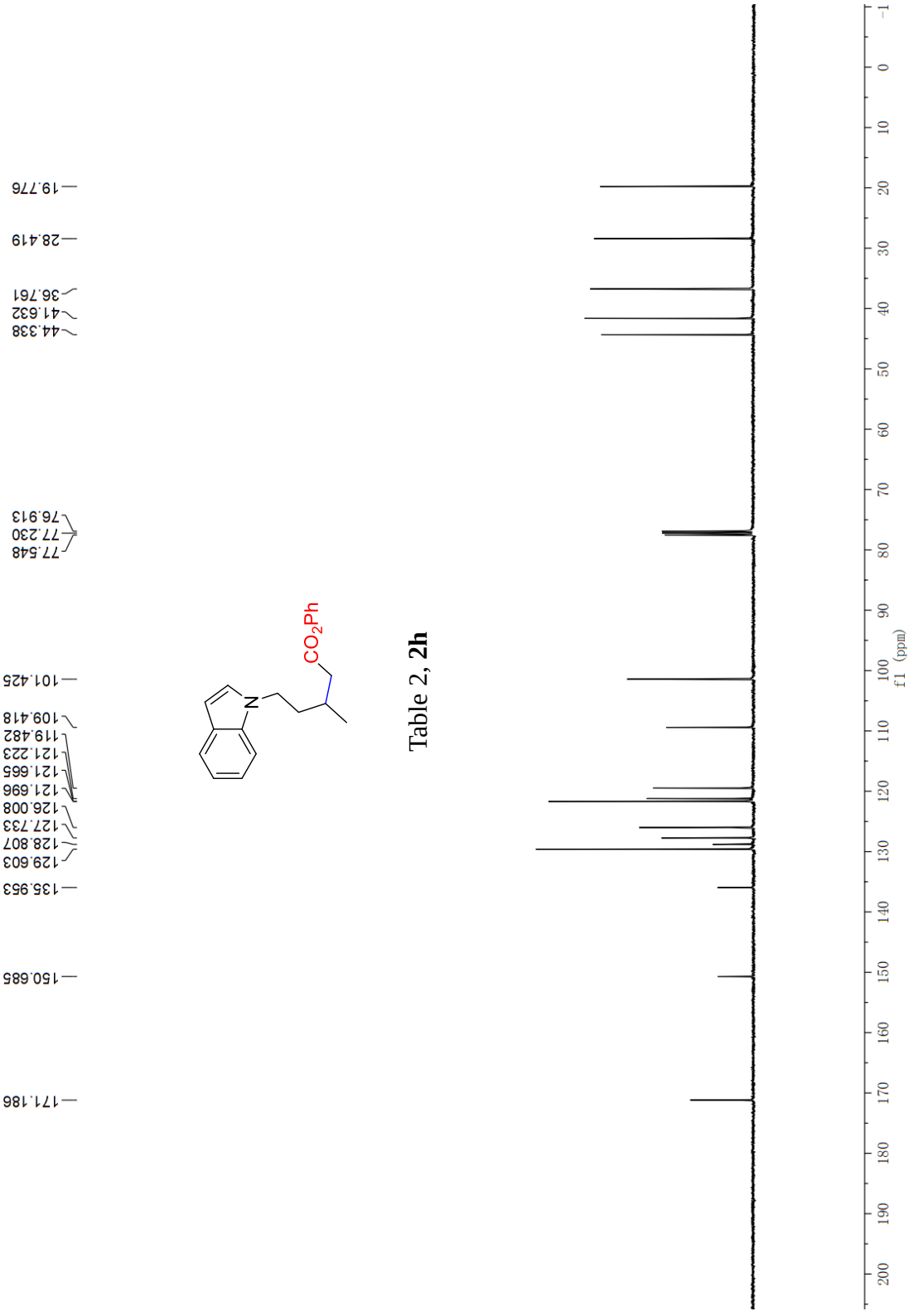
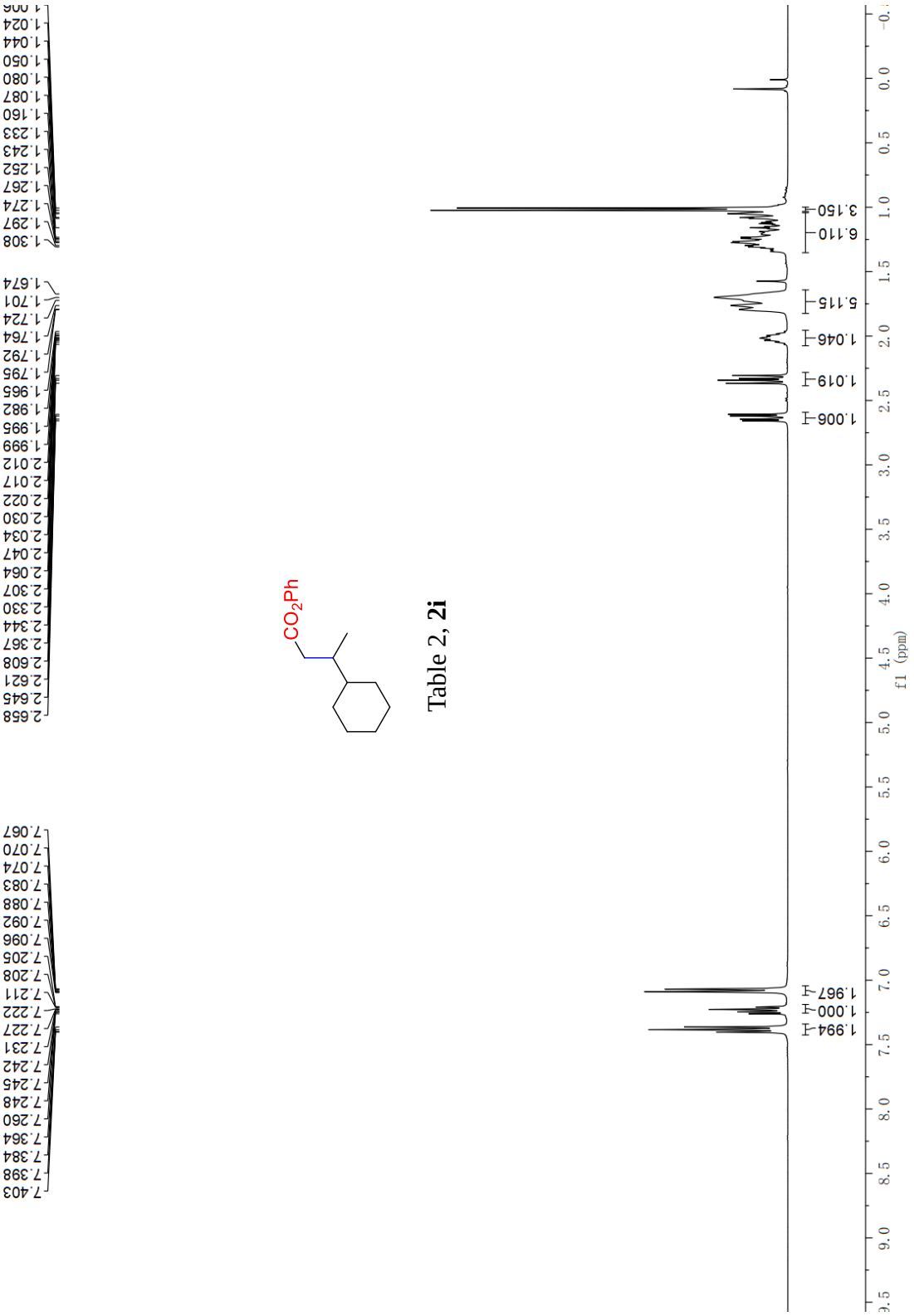


Table 2, **2h**

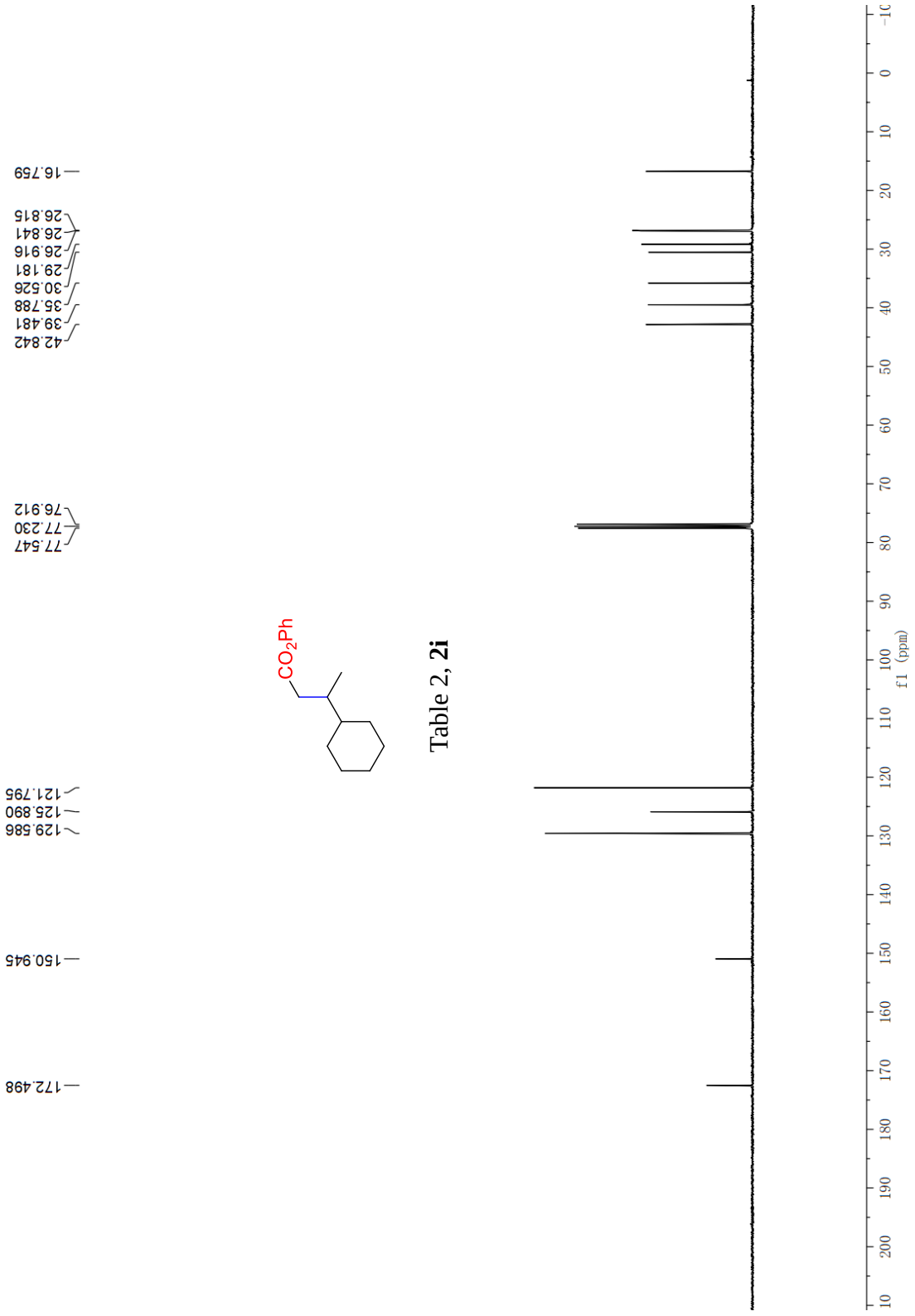
^{13}C NMR Spectrum of **2h** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2i** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2i** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2j** ($CDCl_3$, 400 MHz)

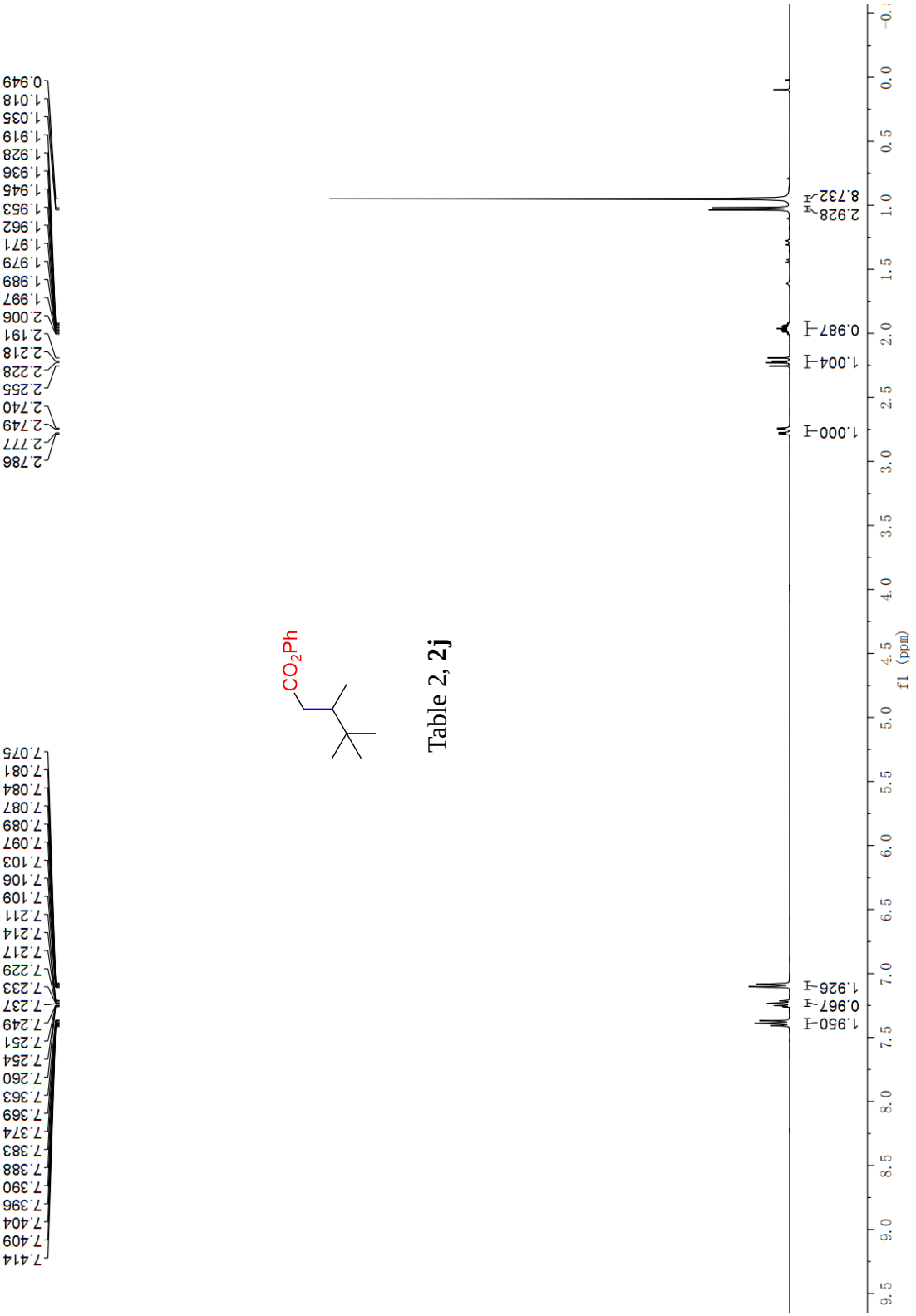
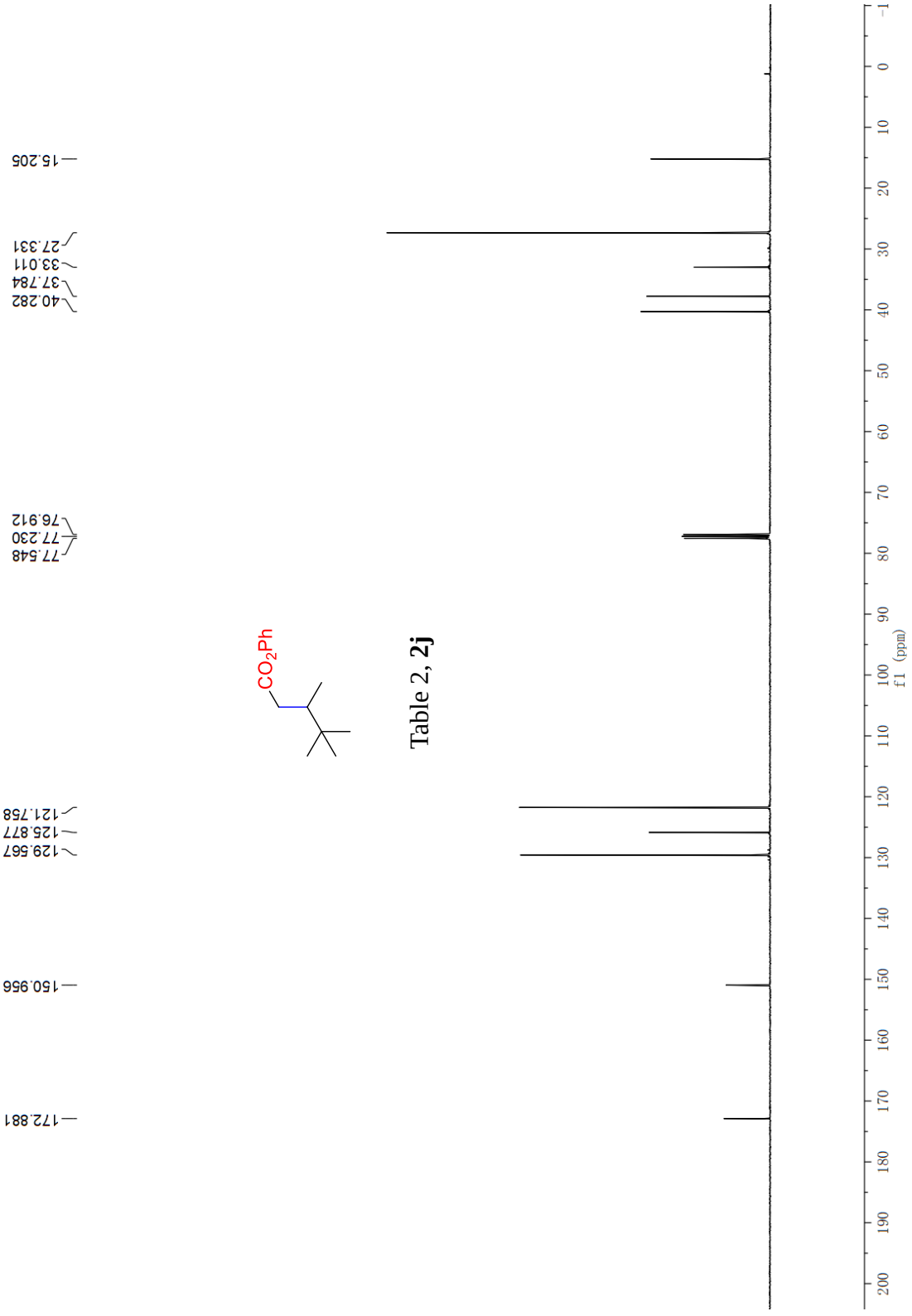
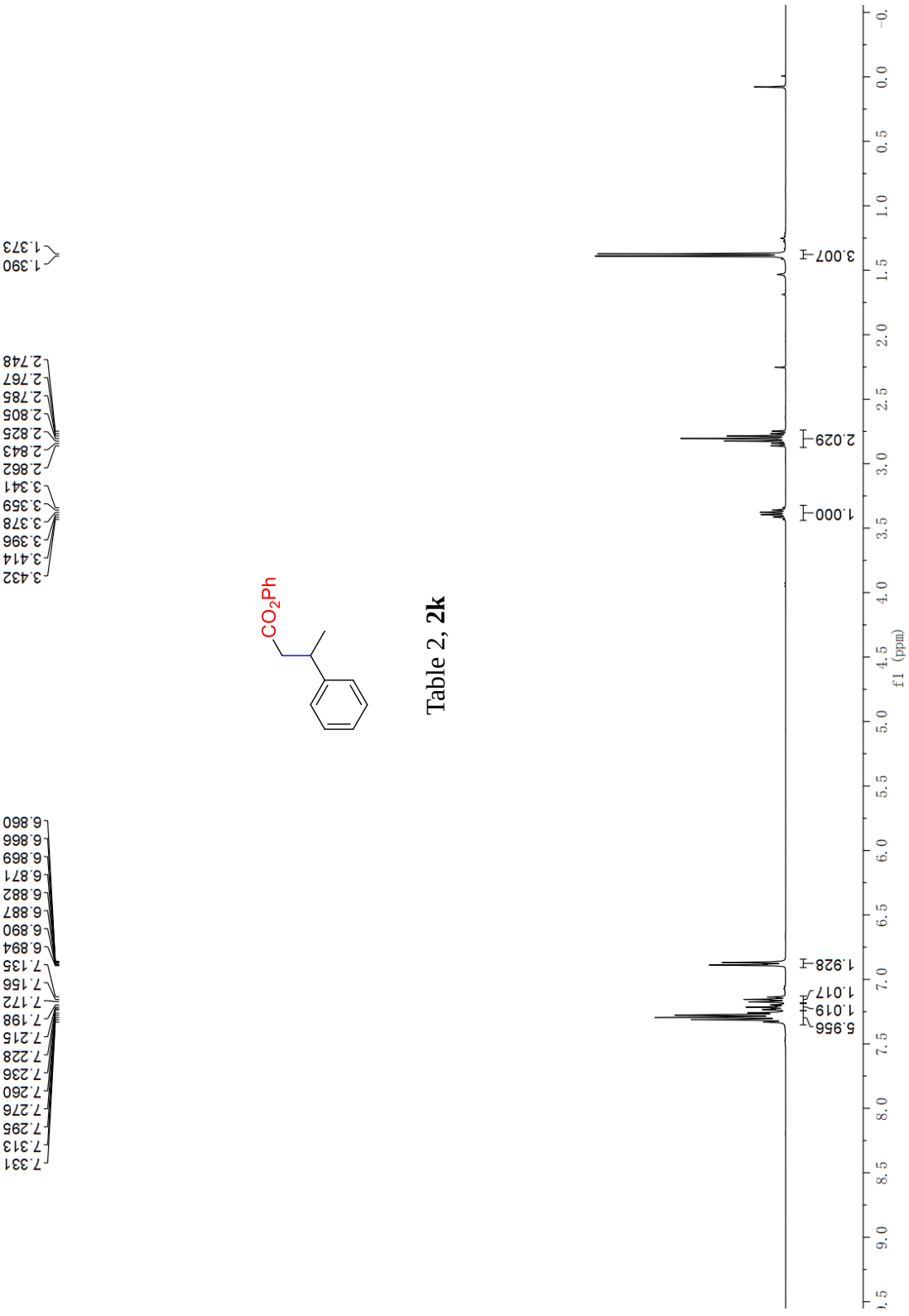


Table 2, **2j**

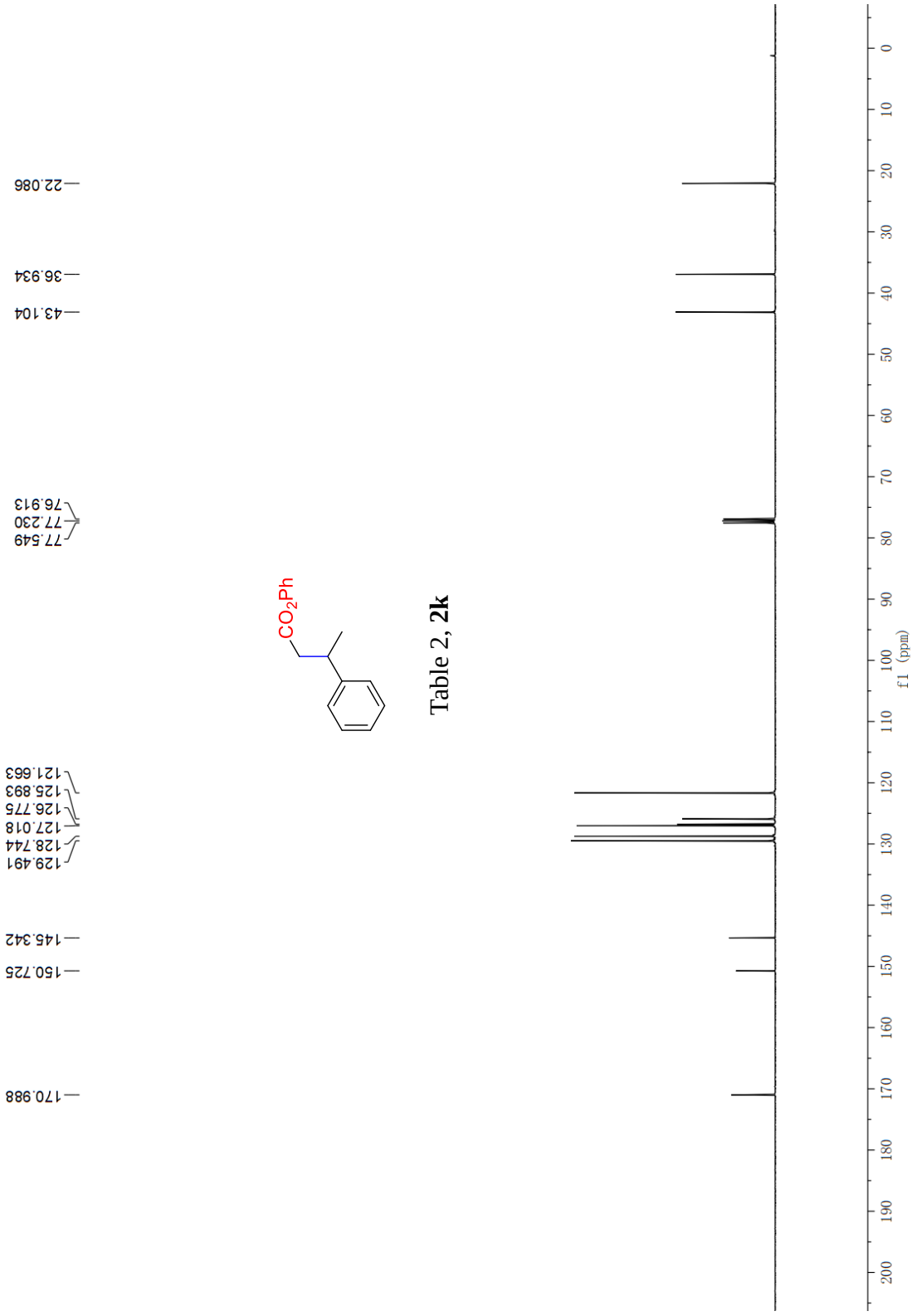
^{13}C NMR Spectrum of **2j** ($CDCl_3$, 100 MHz)



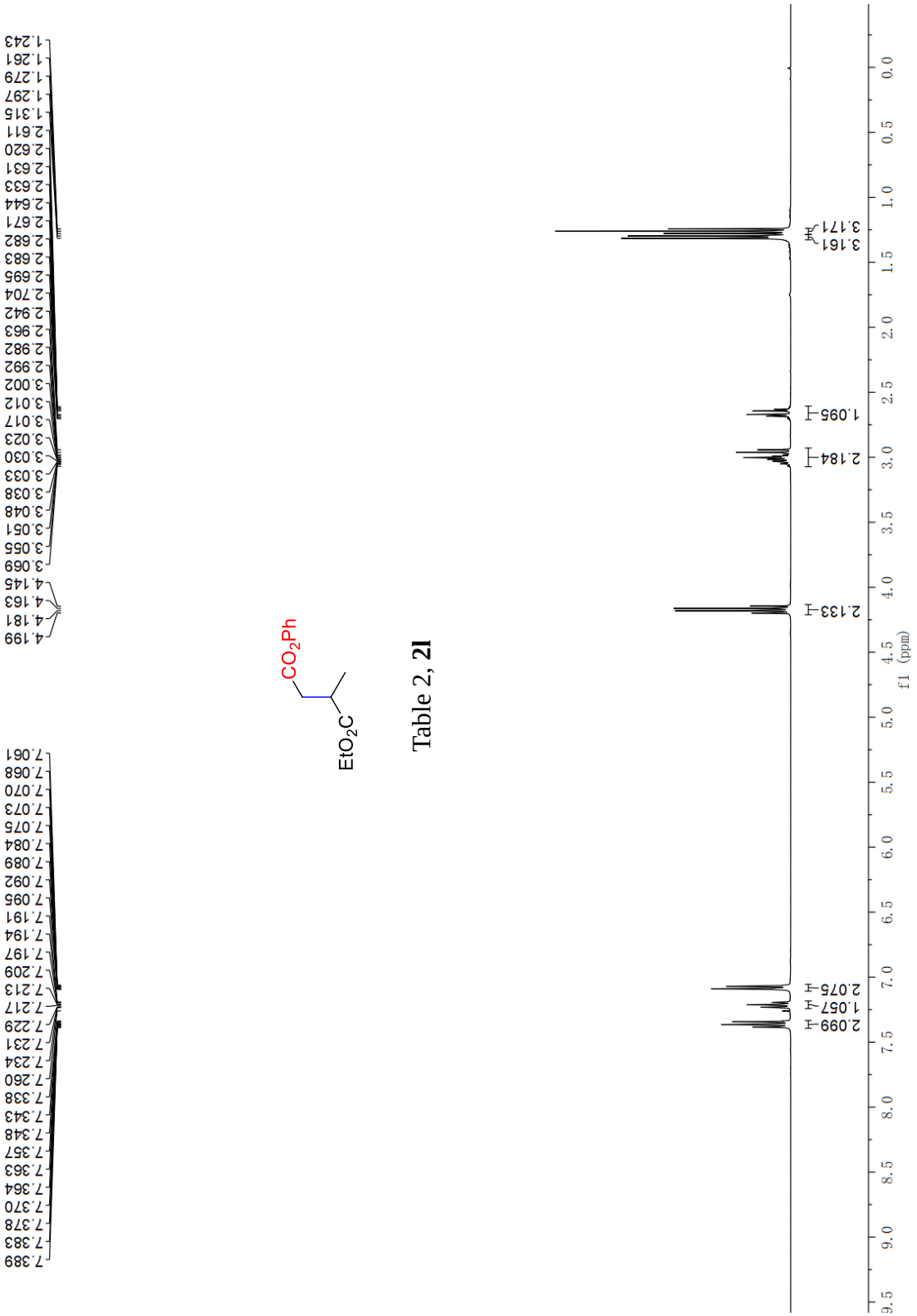
^{1}H NMR Spectrum of **2k** ($CDCl_3$, 400 MHz)



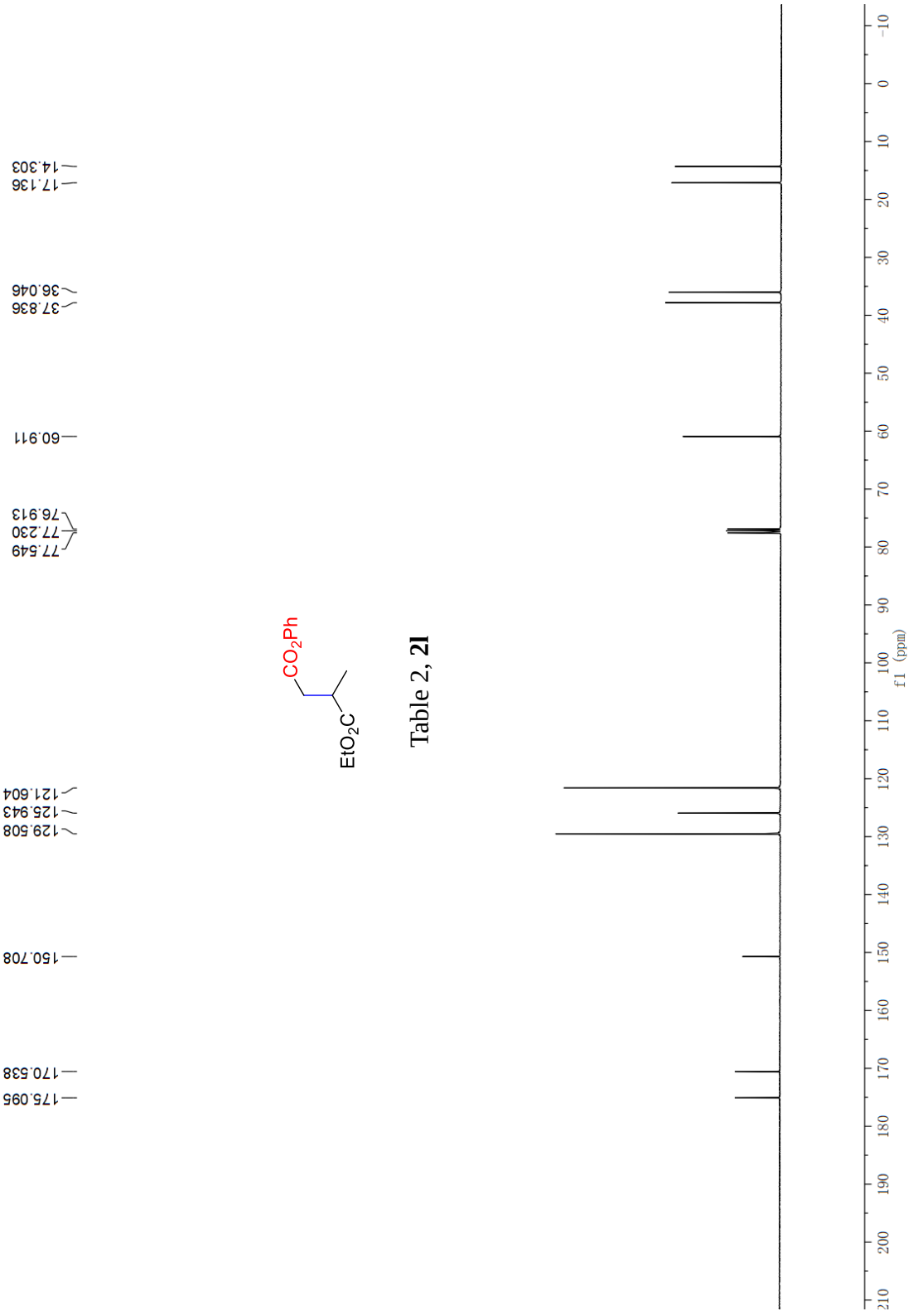
^{13}C NMR Spectrum of **2k** ($CDCl_3$, 100 MHz)



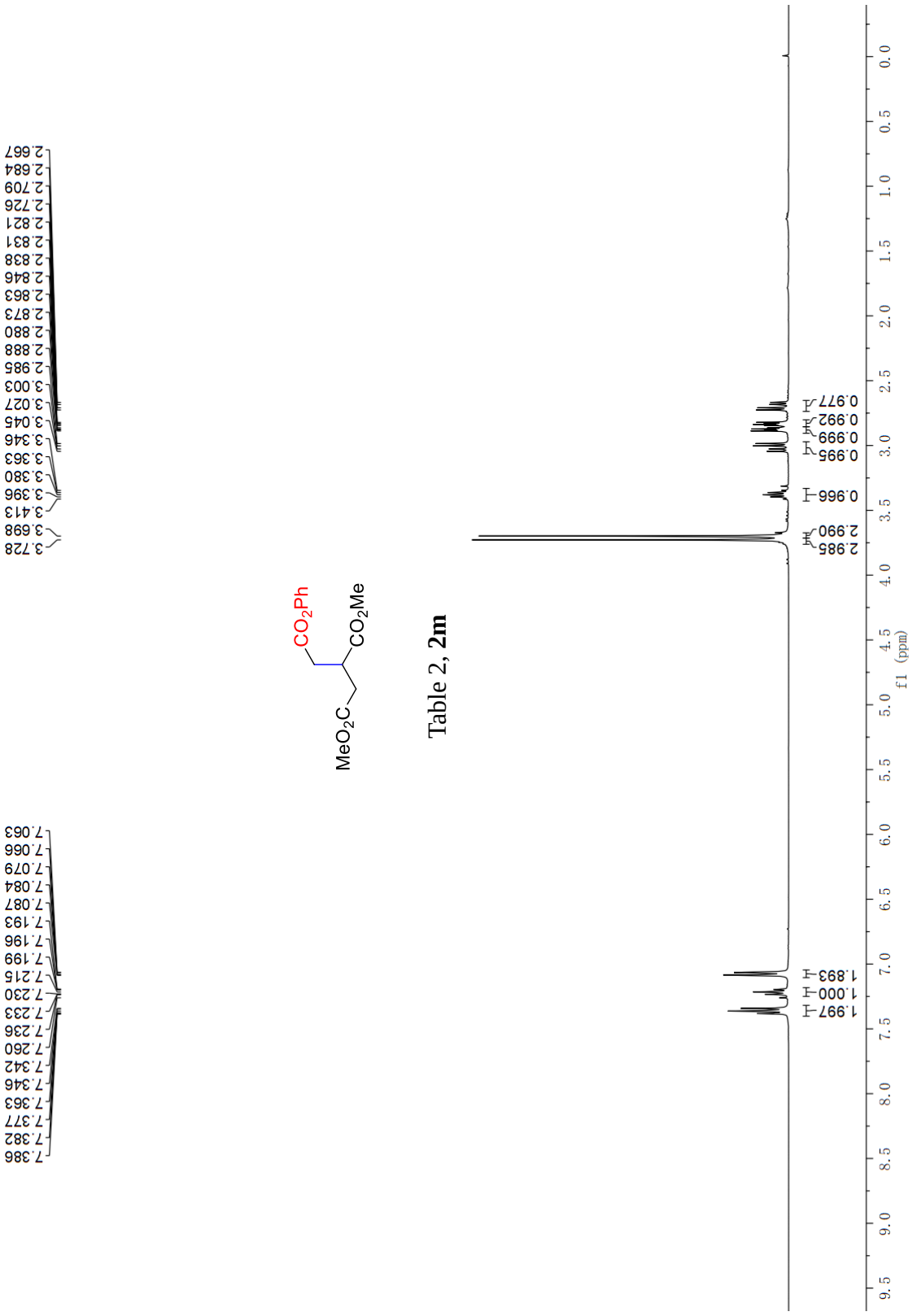
^{1}H NMR Spectrum of **2l** ($CDCl_3$, 400 MHz)



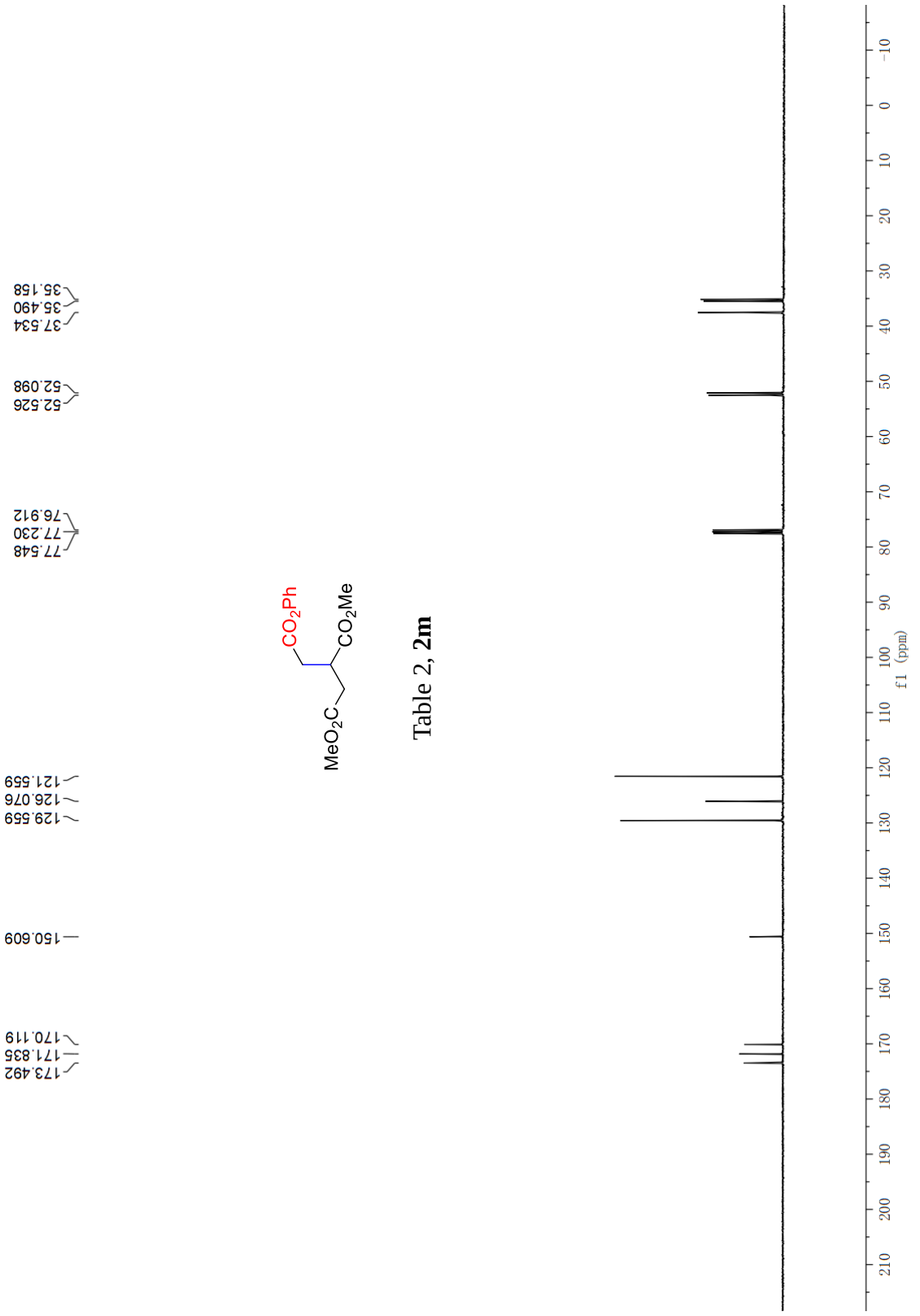
^{13}C NMR Spectrum of **2l** ($CDCl_3$, 100 MHz)



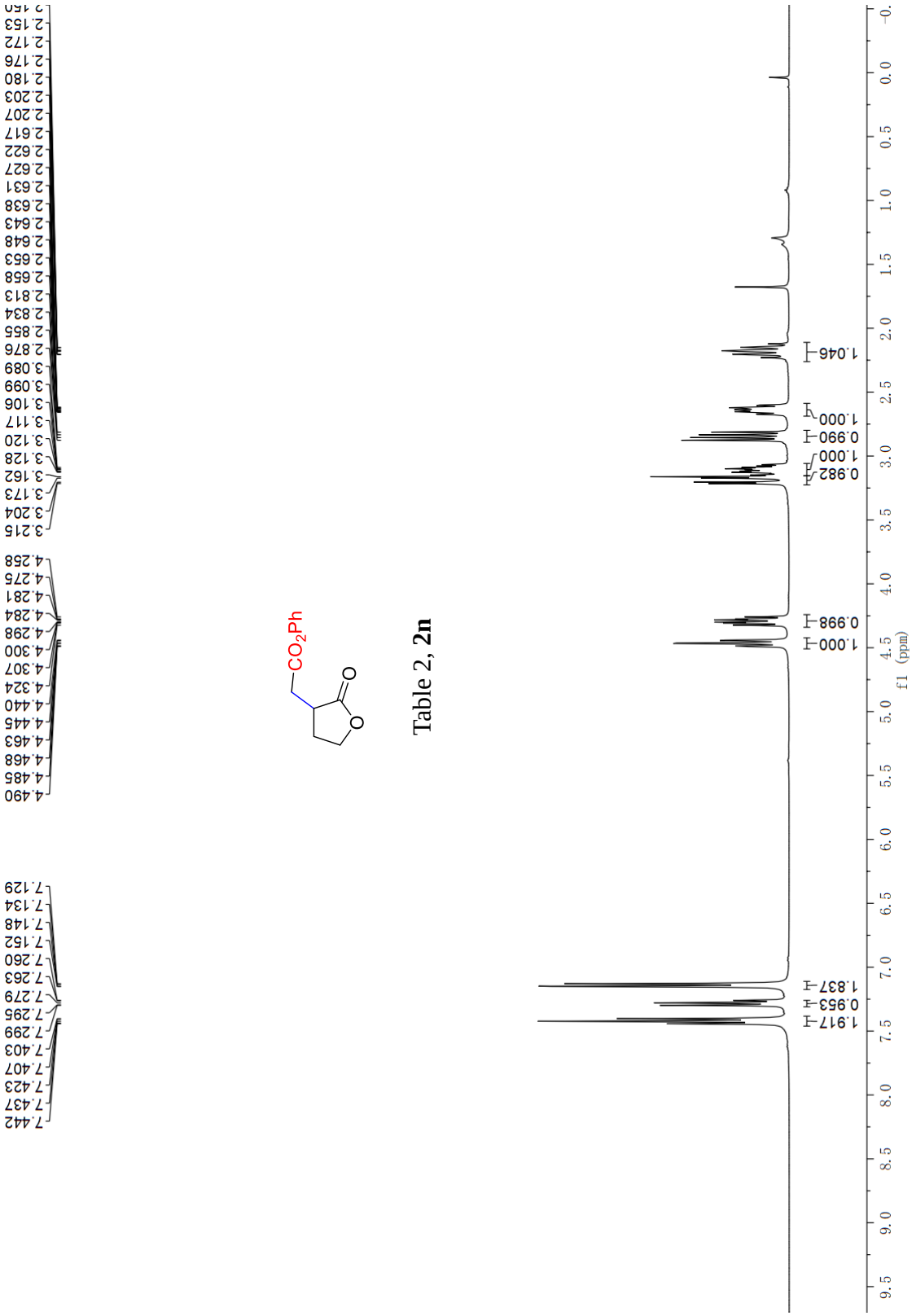
^{1}H NMR Spectrum of **2m** ($CDCl_3$, 400 MHz)



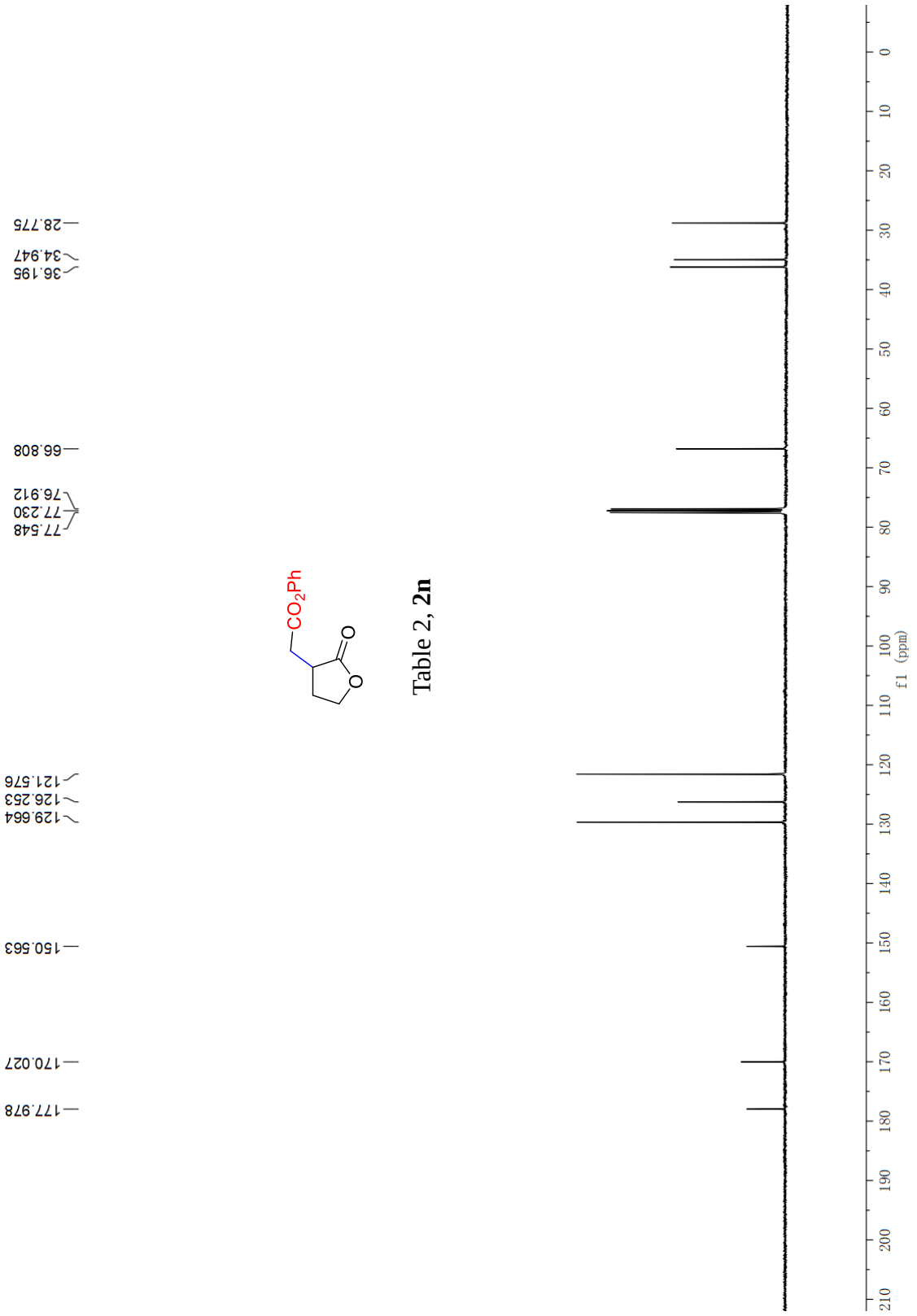
^{13}C NMR Spectrum of **2m** ($CDCl_3$, 100 MHz)



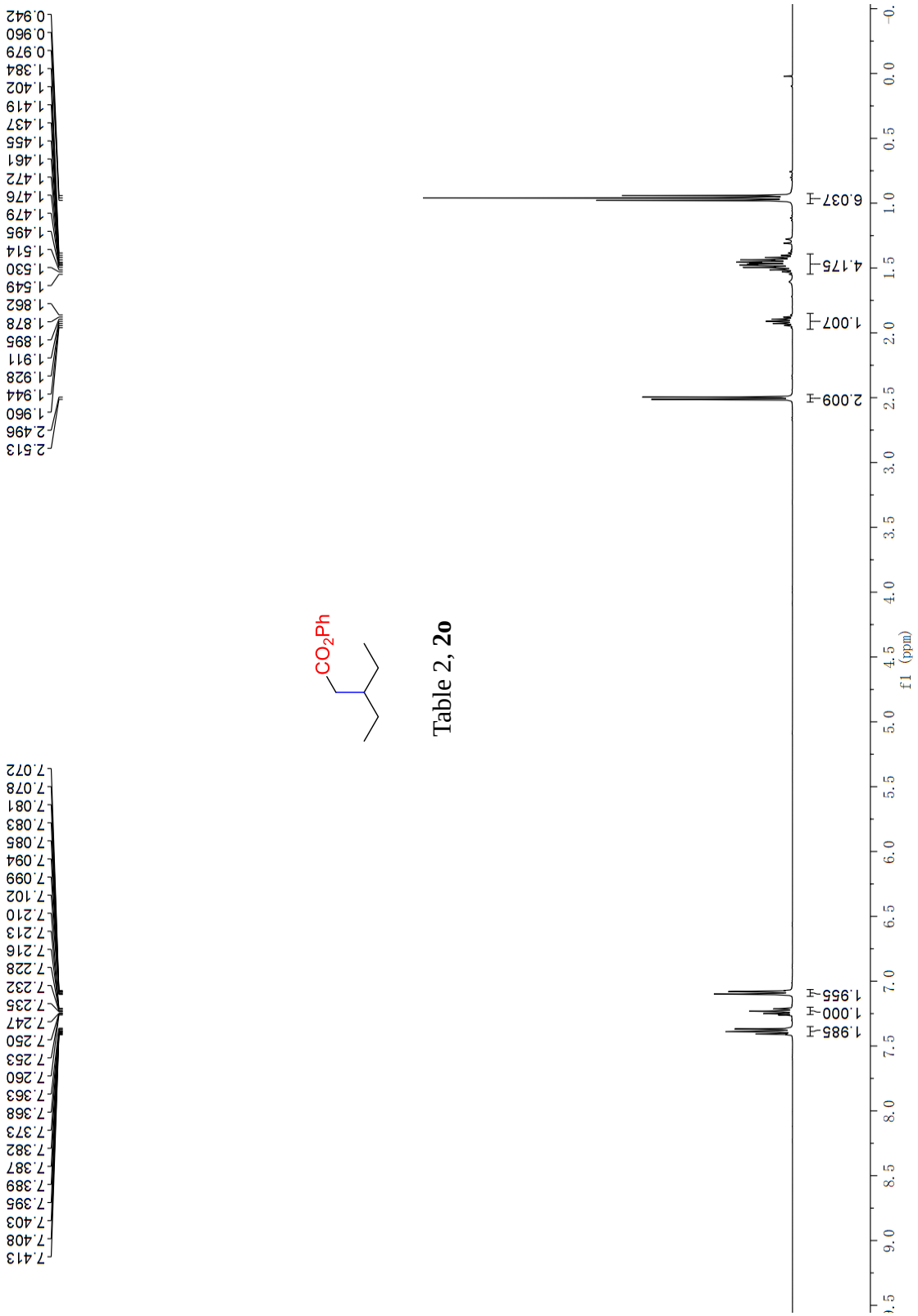
^{1}H NMR Spectrum of **2n** ($CDCl_3$, 400 MHz)



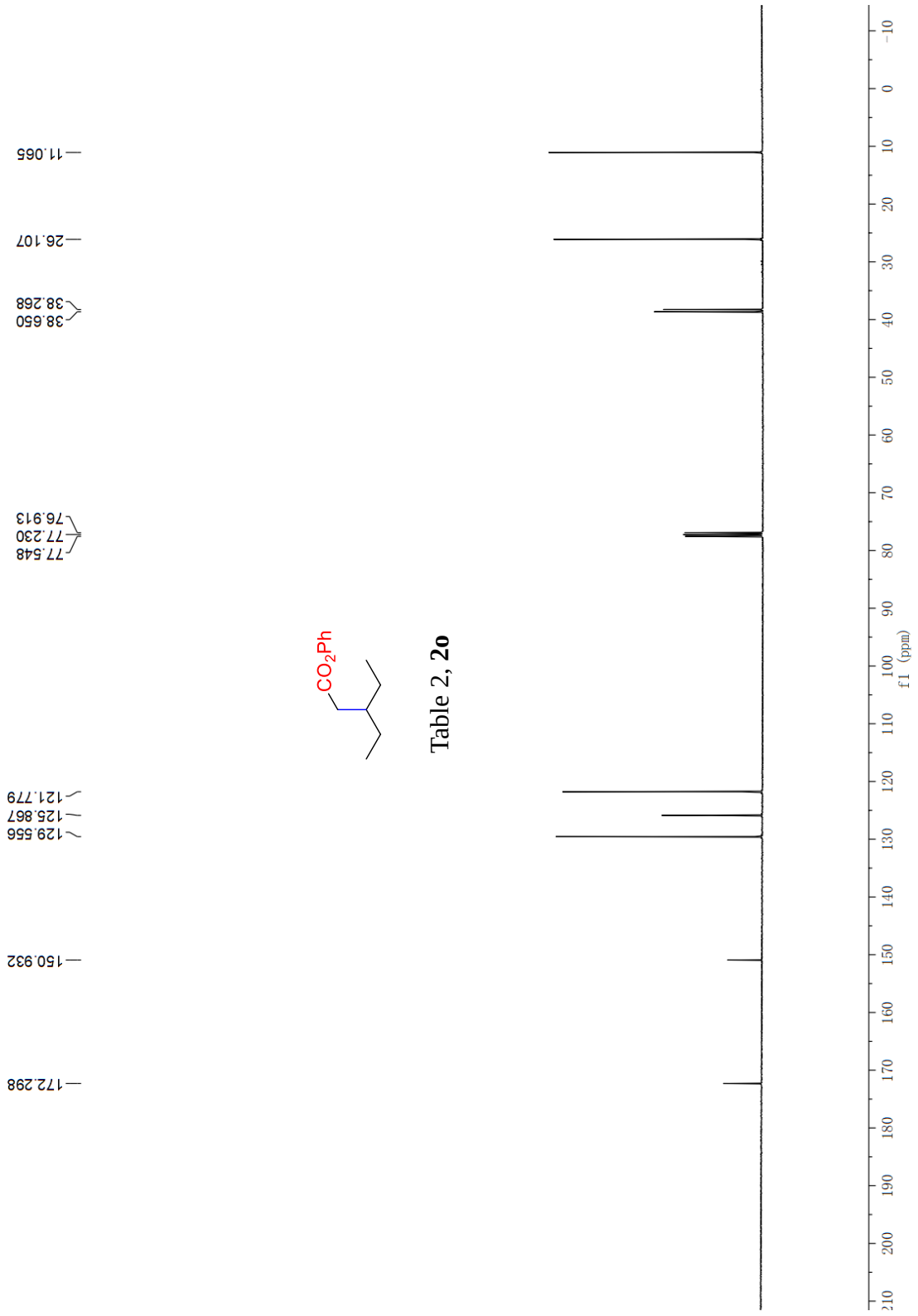
^{13}C NMR Spectrum of **2n** ($CDCl_3$, 100 MHz)



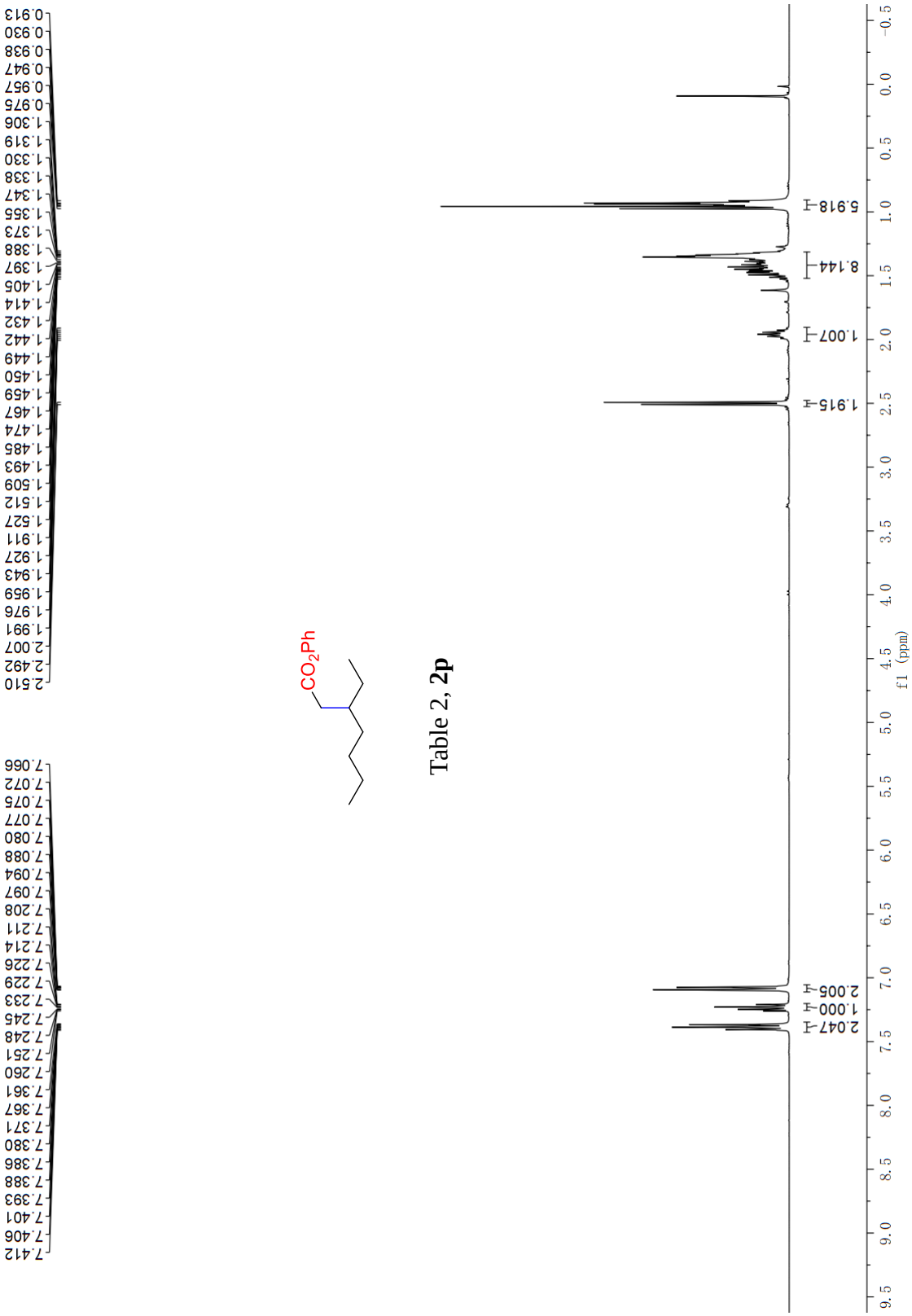
^{1}H NMR Spectrum of **2o** ($CDCl_3$, 400 MHz)



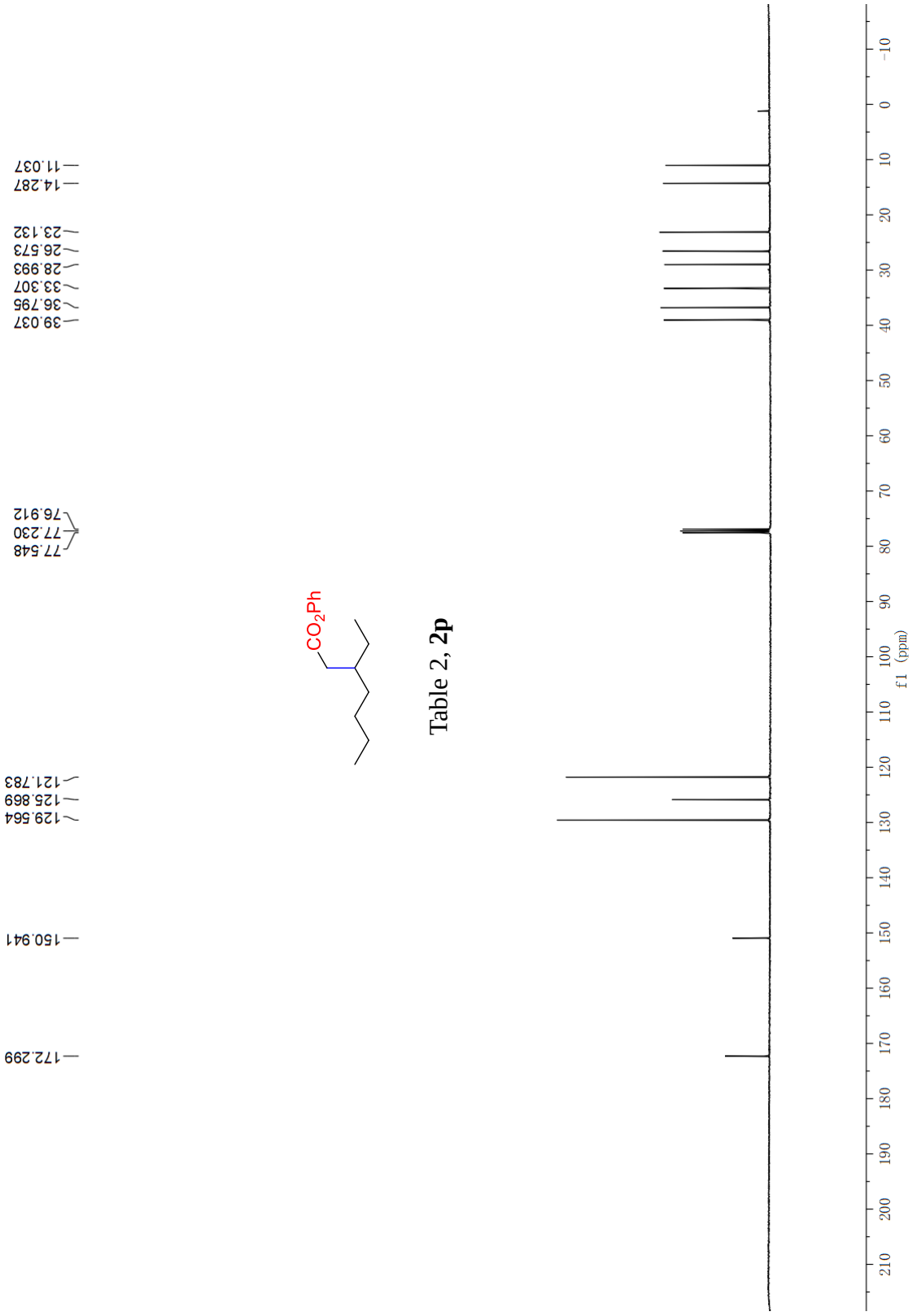
^{13}C NMR Spectrum of **2o** ($CDCl_3$, 100 MHz)



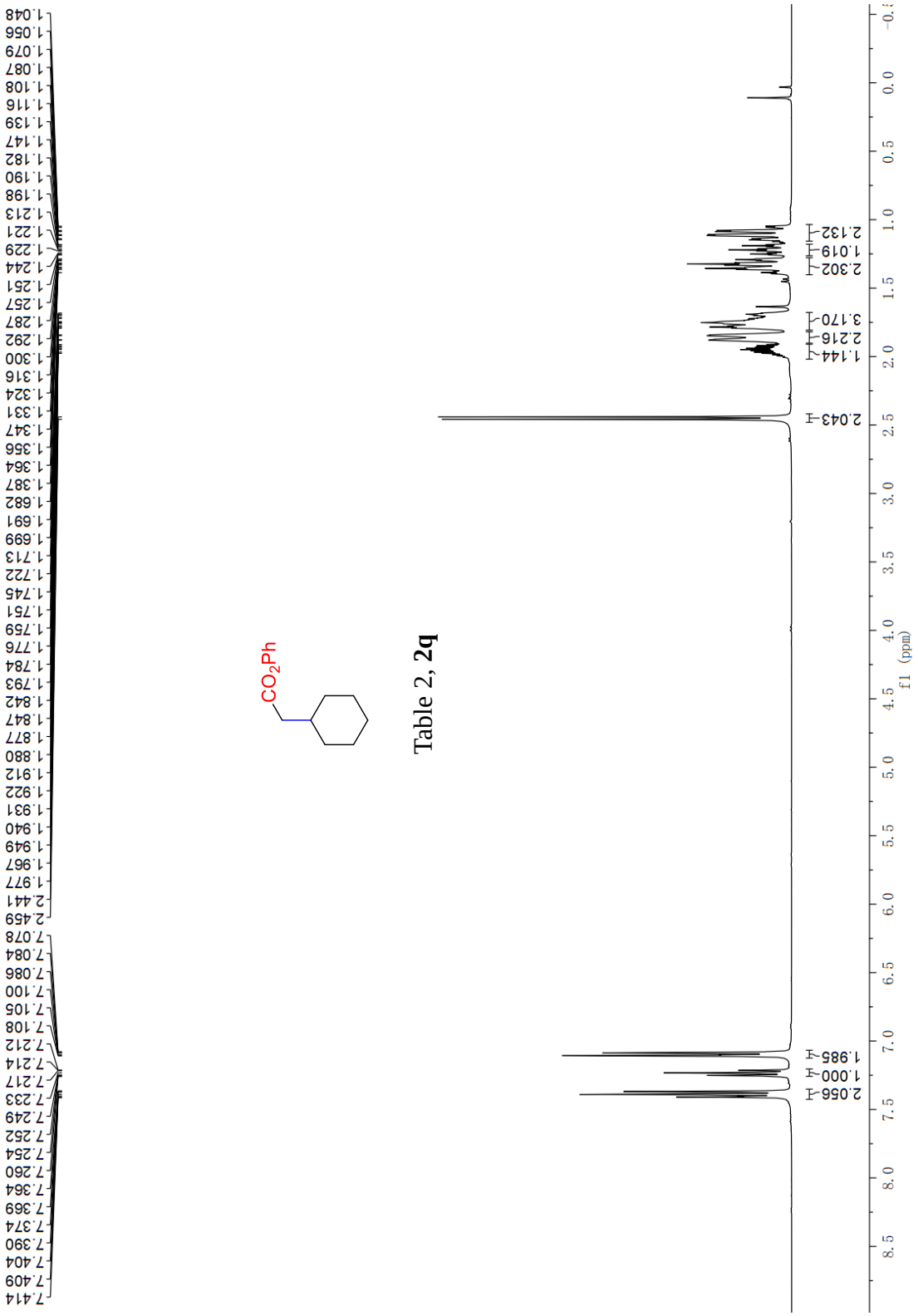
^{1}H NMR Spectrum of **2p** ($CDCl_3$, 400 MHz)



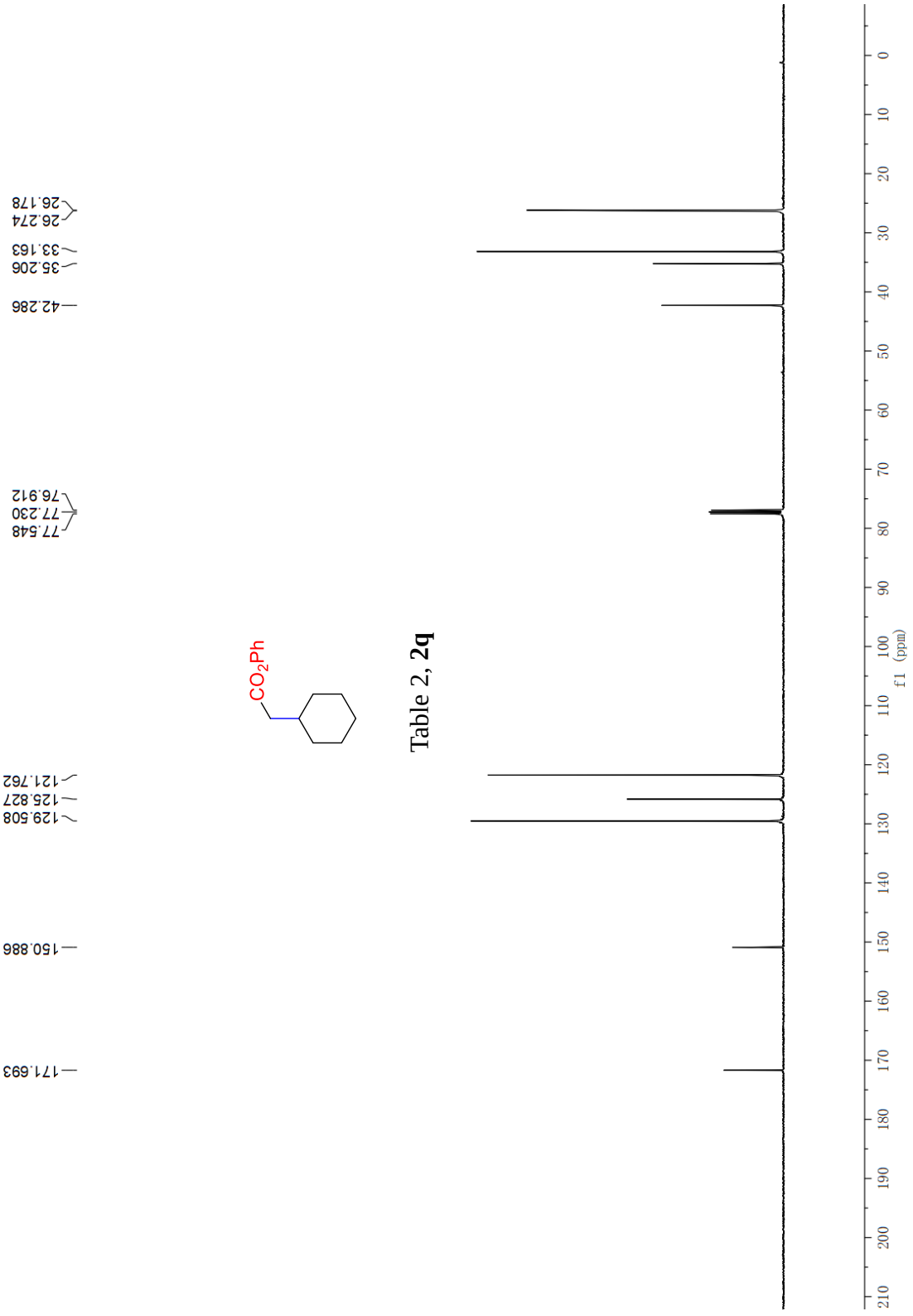
^{13}C NMR Spectrum of **2p** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2q** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2q** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2r** ($CDCl_3$, 400 MHz)

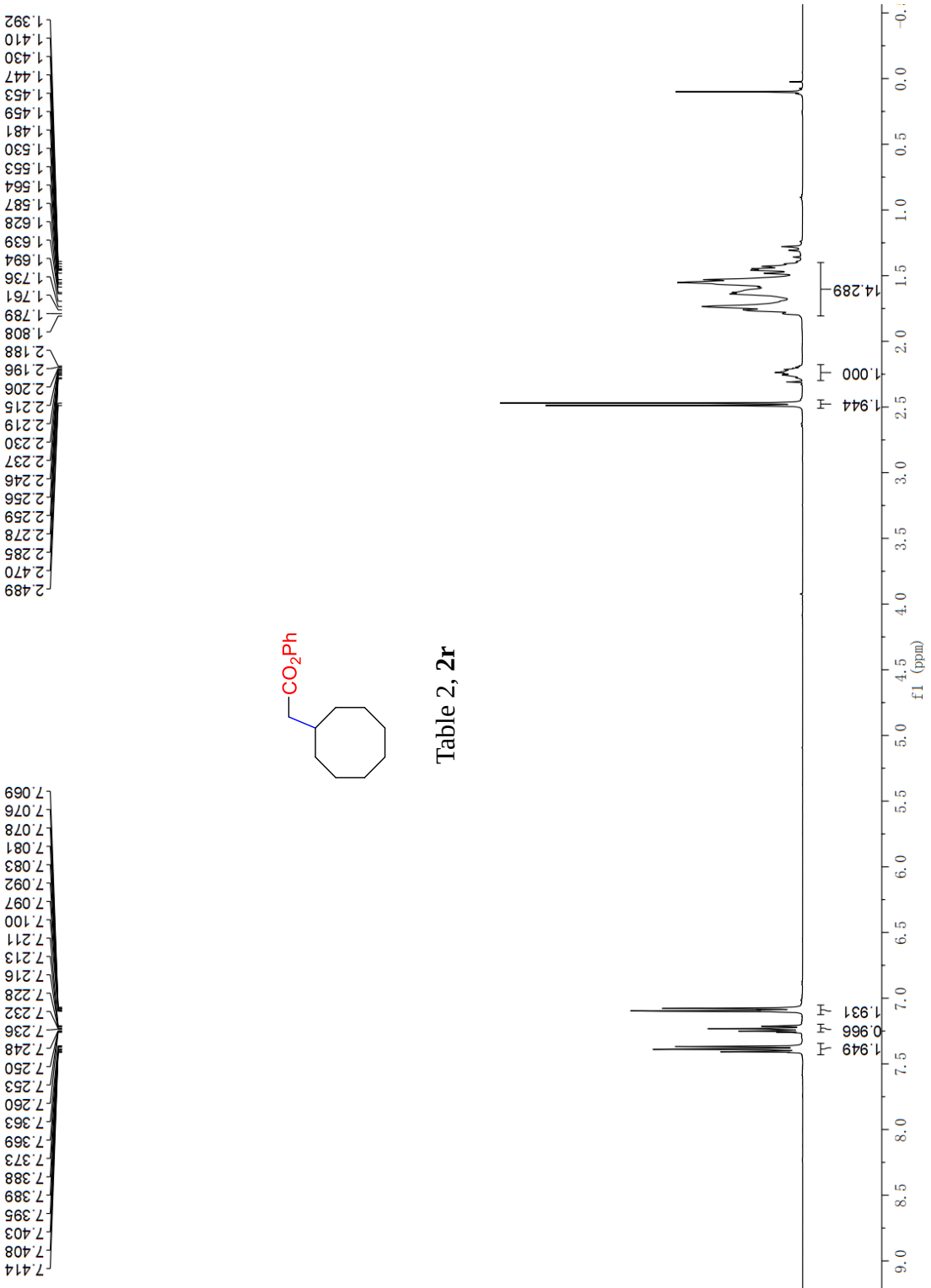
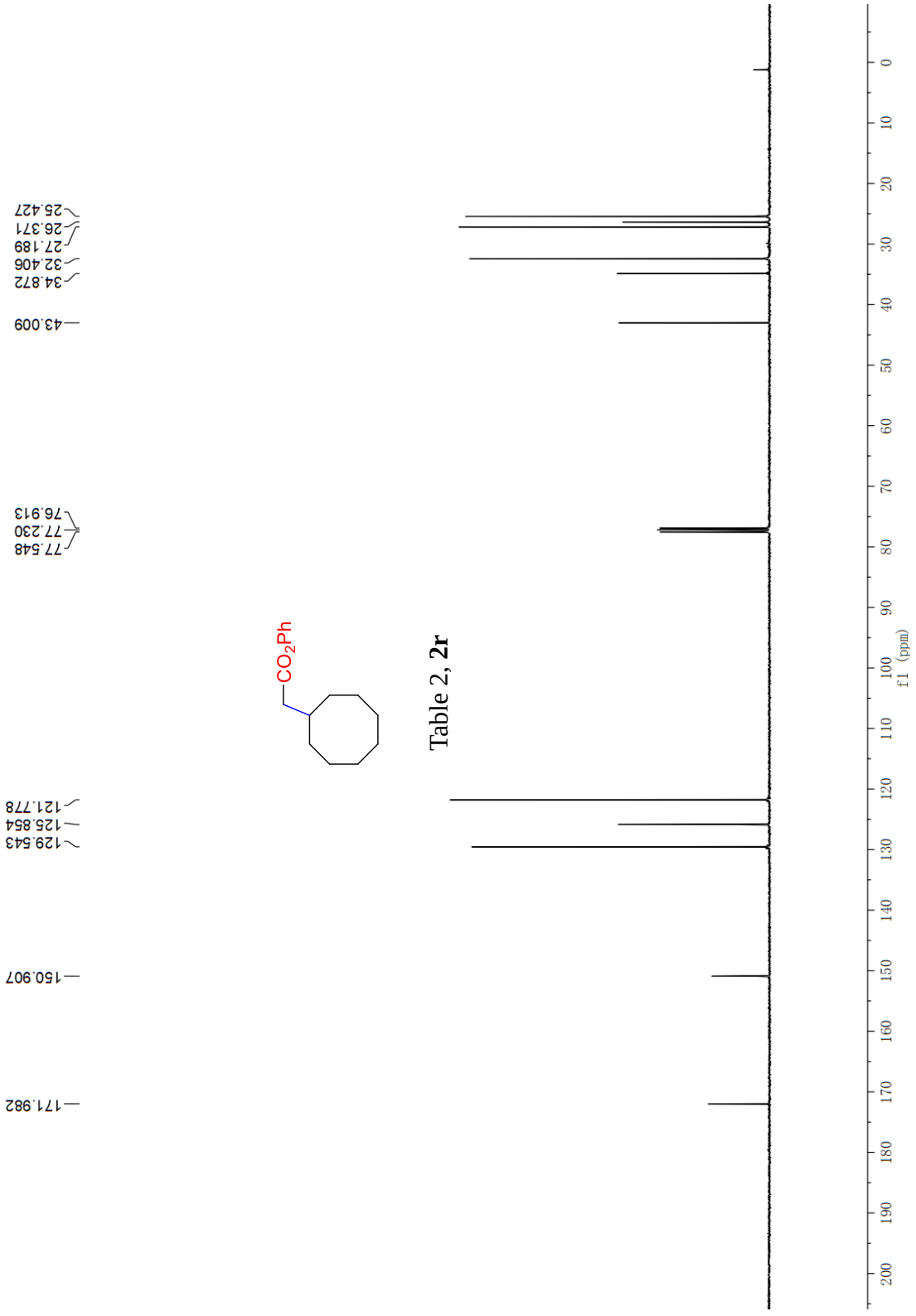
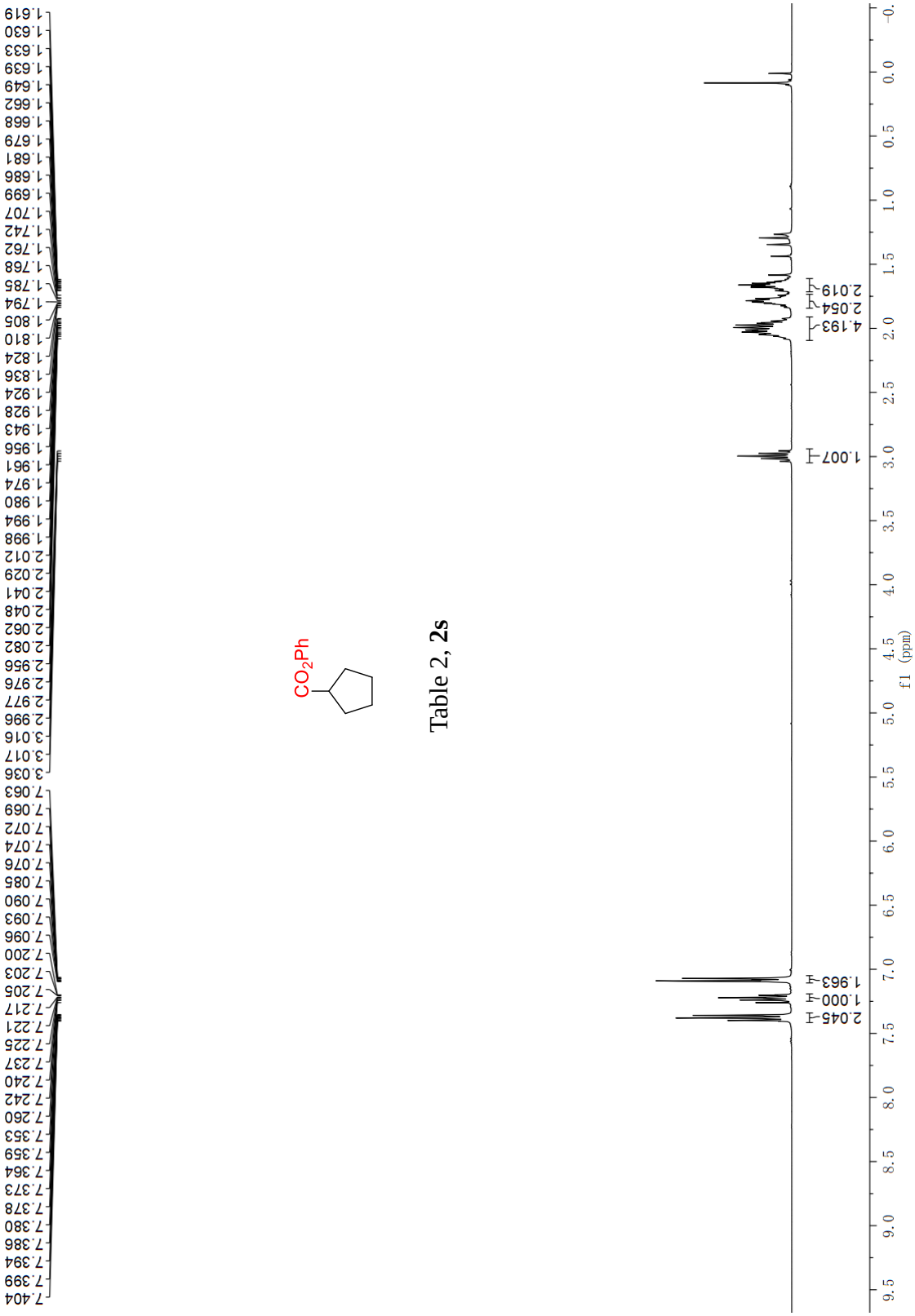


Table 2, **2r**

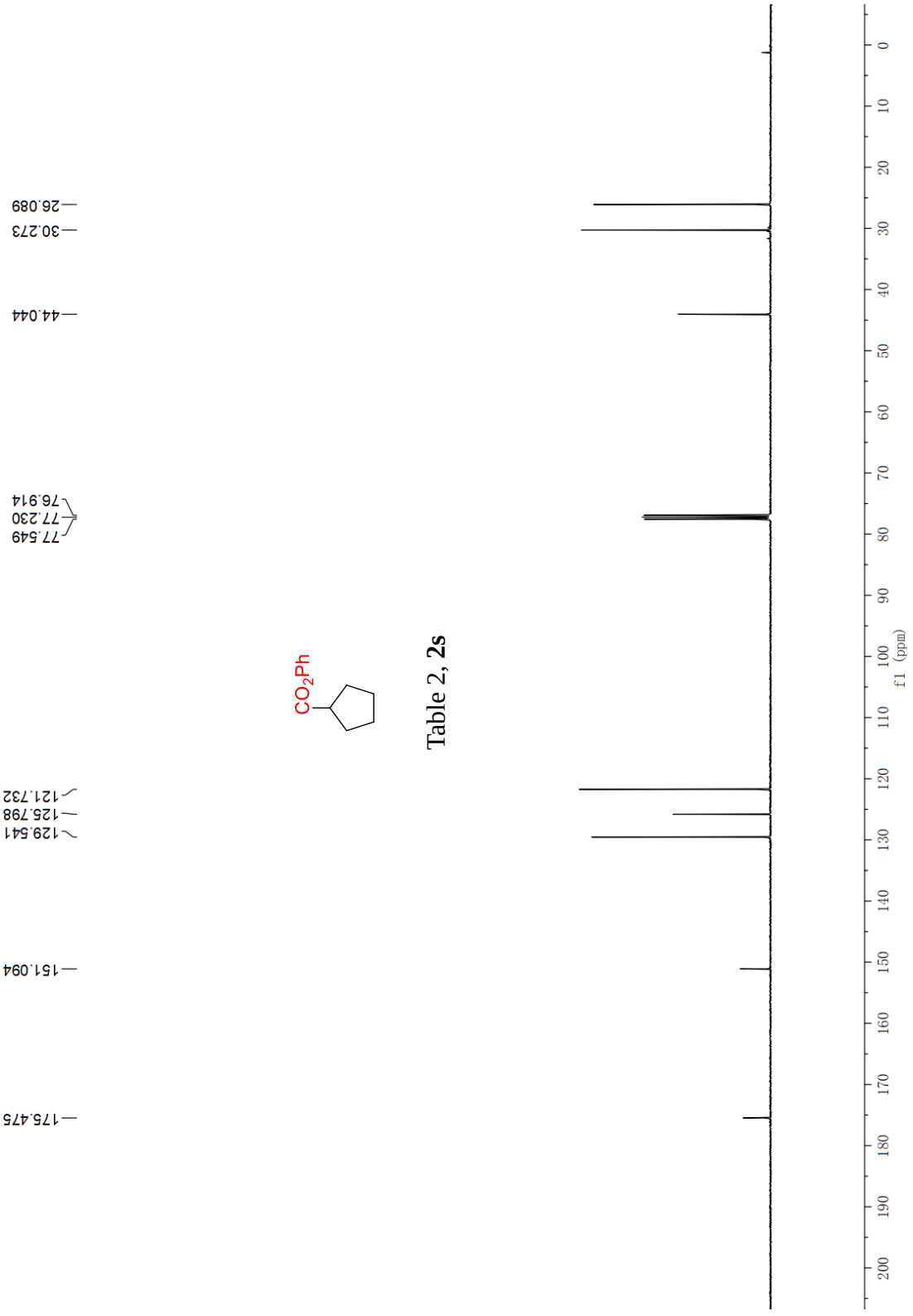
^{13}C NMR Spectrum of **2r** ($CDCl_3$, 100 MHz)



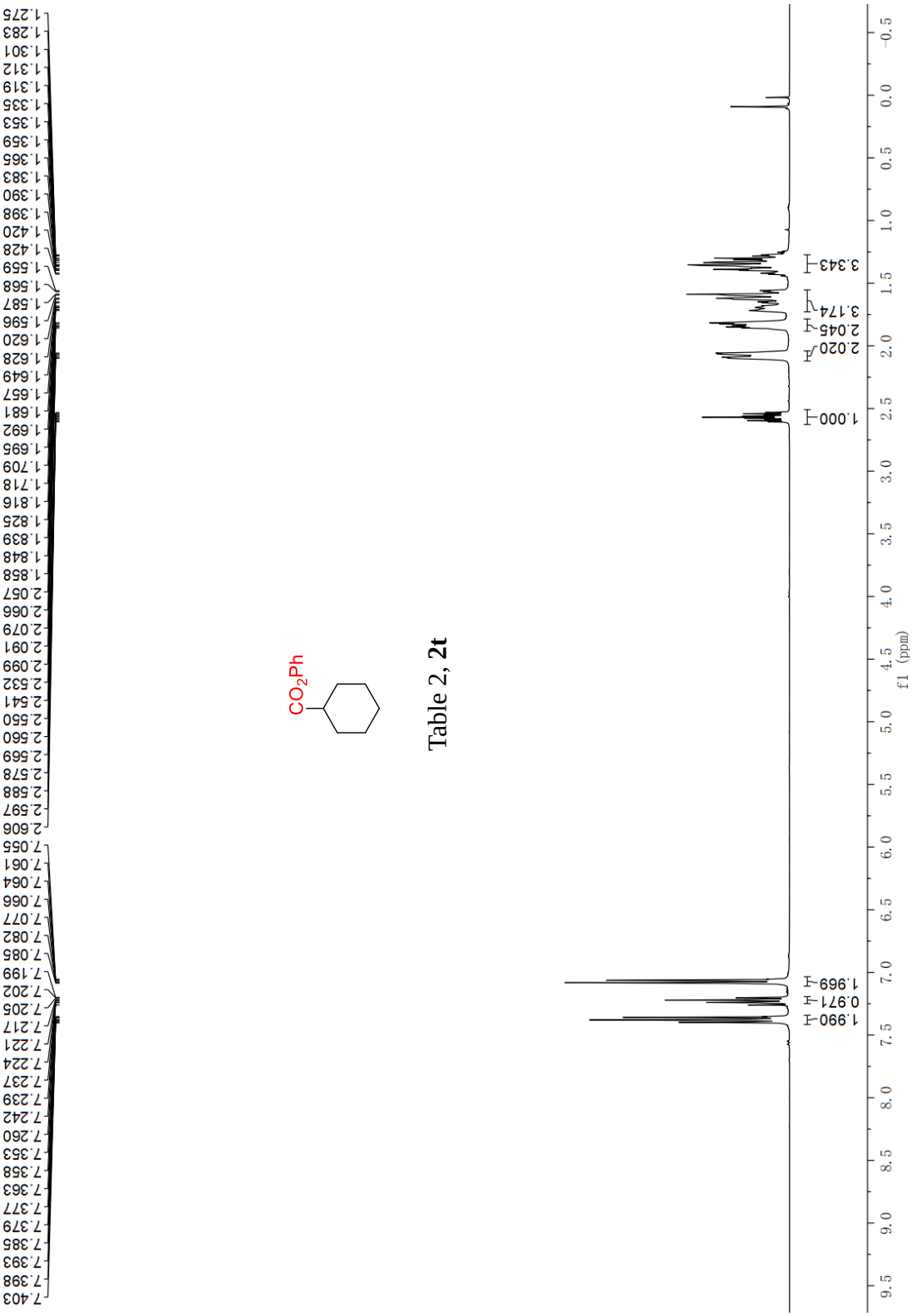
^{1}H NMR Spectrum of **2s** ($CDCl_3$, 400 MHz)



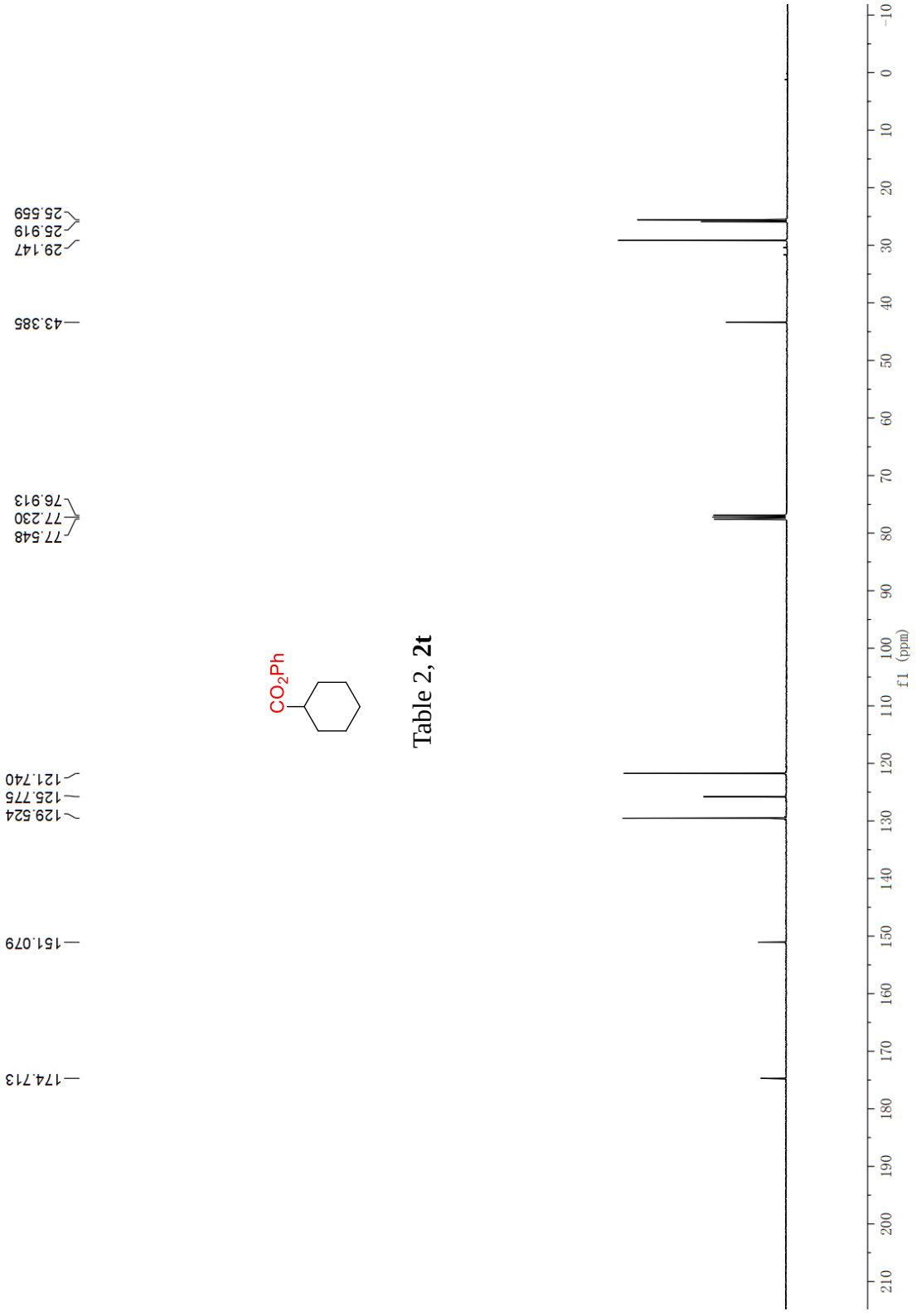
^{13}C NMR Spectrum of **2s** ($CDCl_3$, 100 MHz)



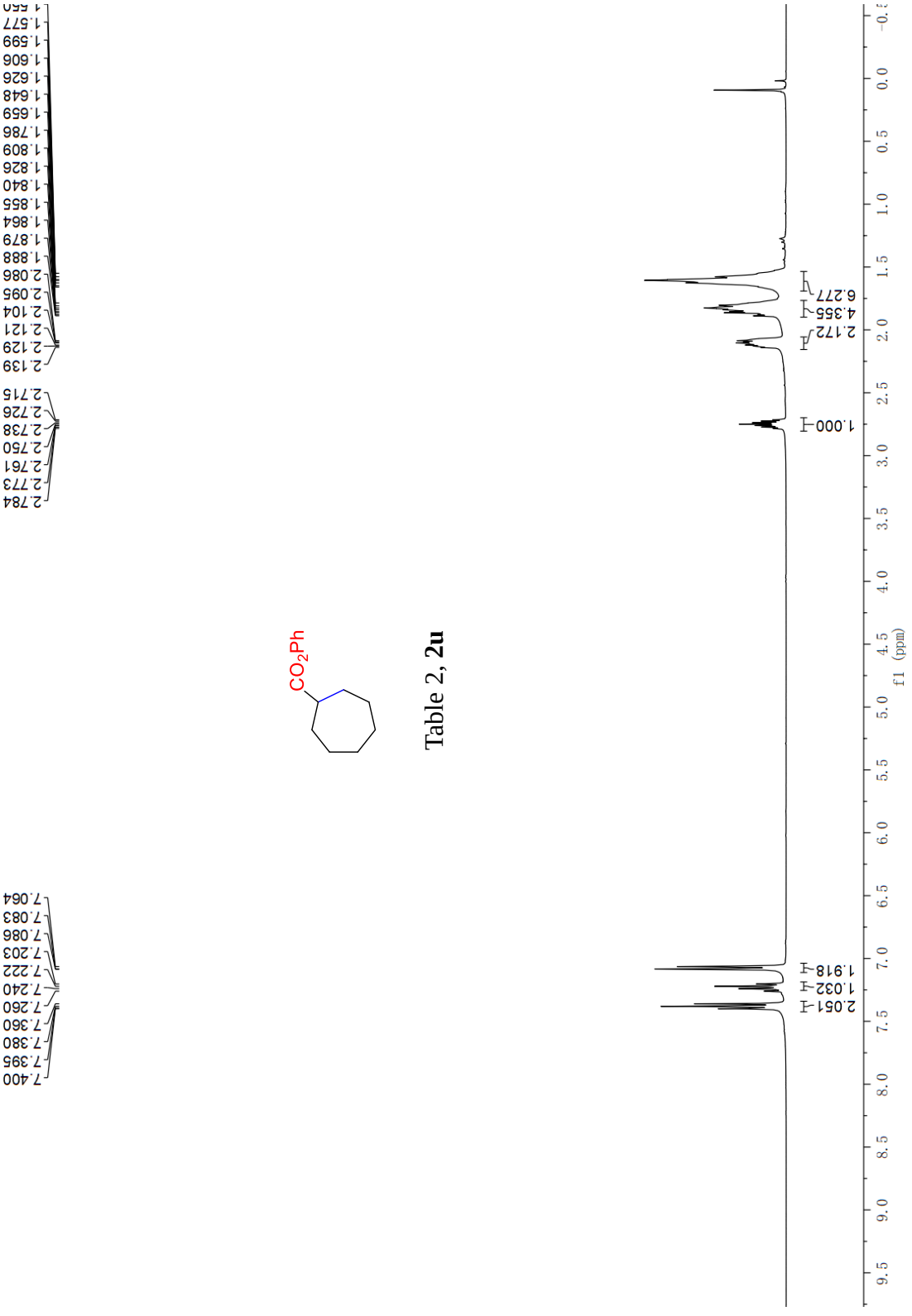
^{1}H NMR Spectrum of **2t** ($CDCl_3$, 400 MHz)



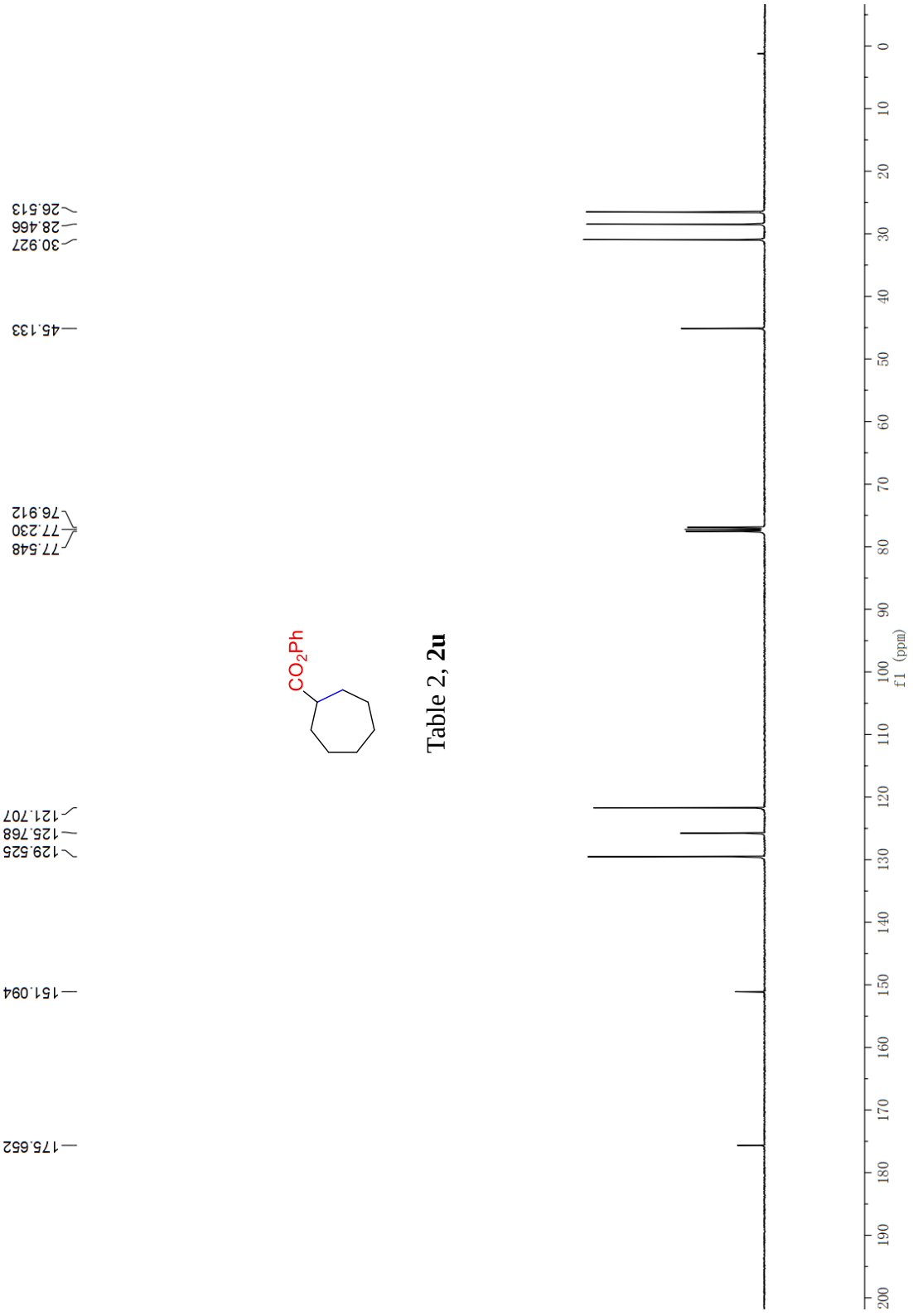
^{13}C NMR Spectrum of **2t** ($CDCl_3$, 100 MHz)



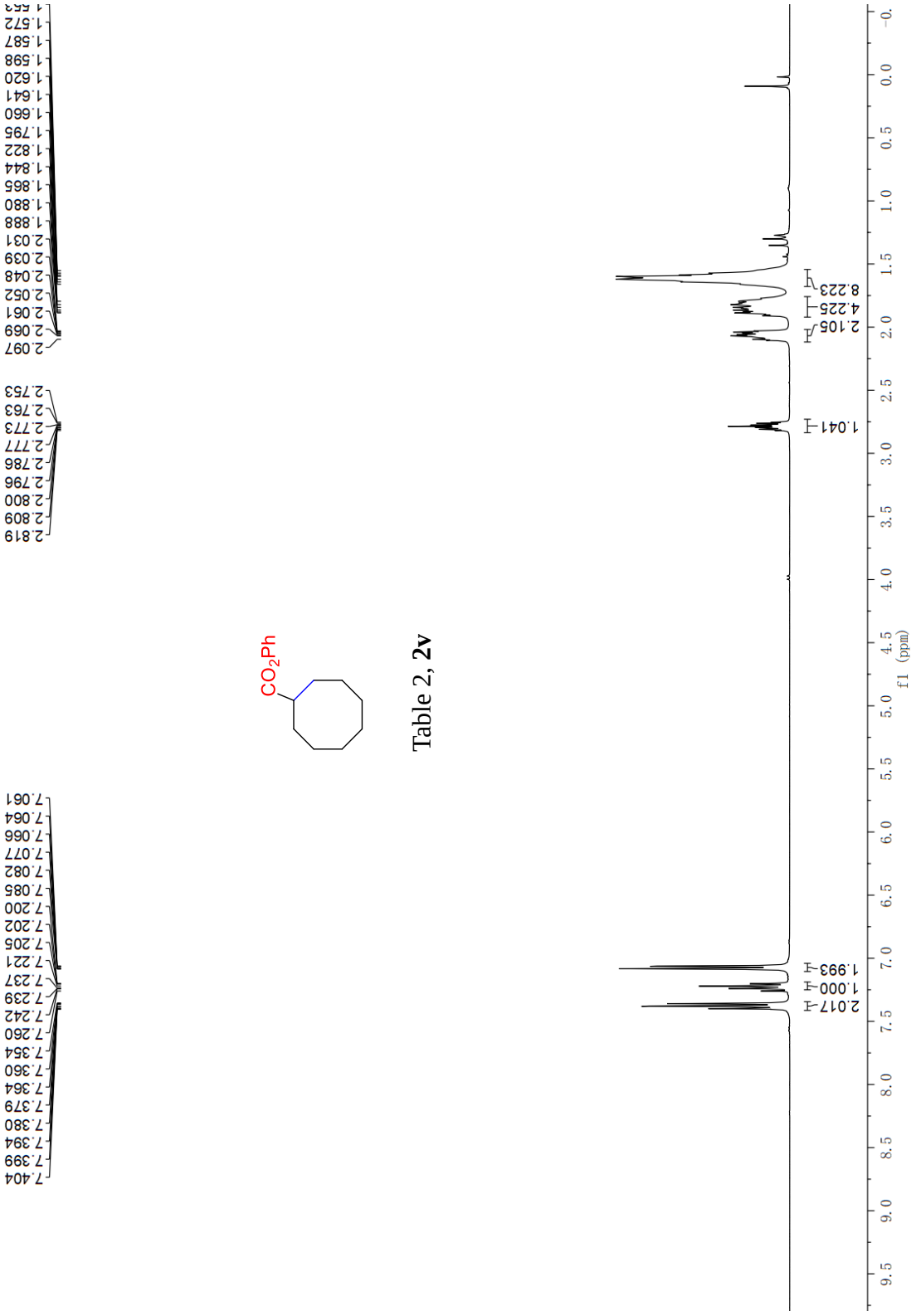
^{1}H NMR Spectrum of **2u** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2u** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2v** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2v** ($CDCl_3$, 100 MHz)

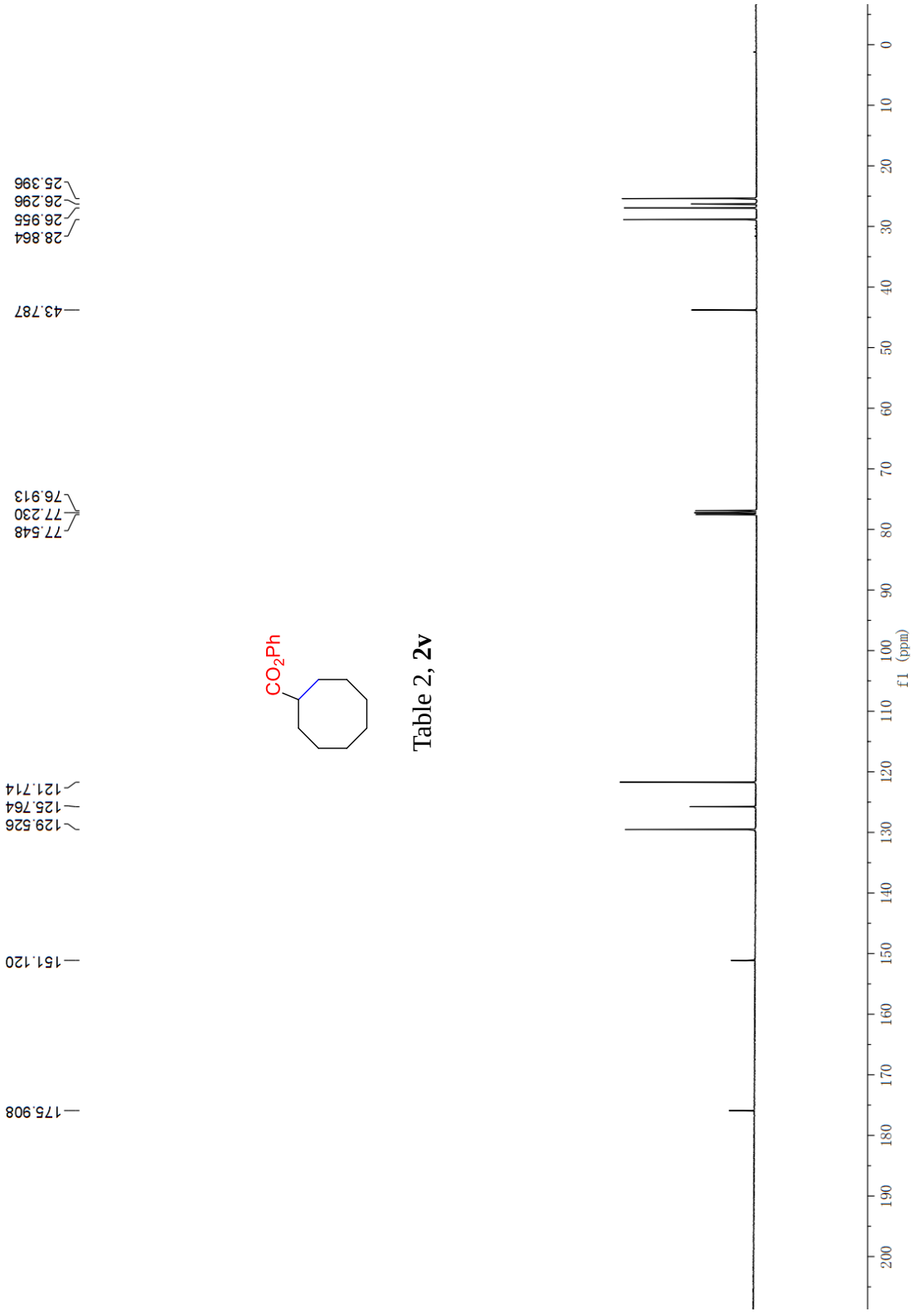
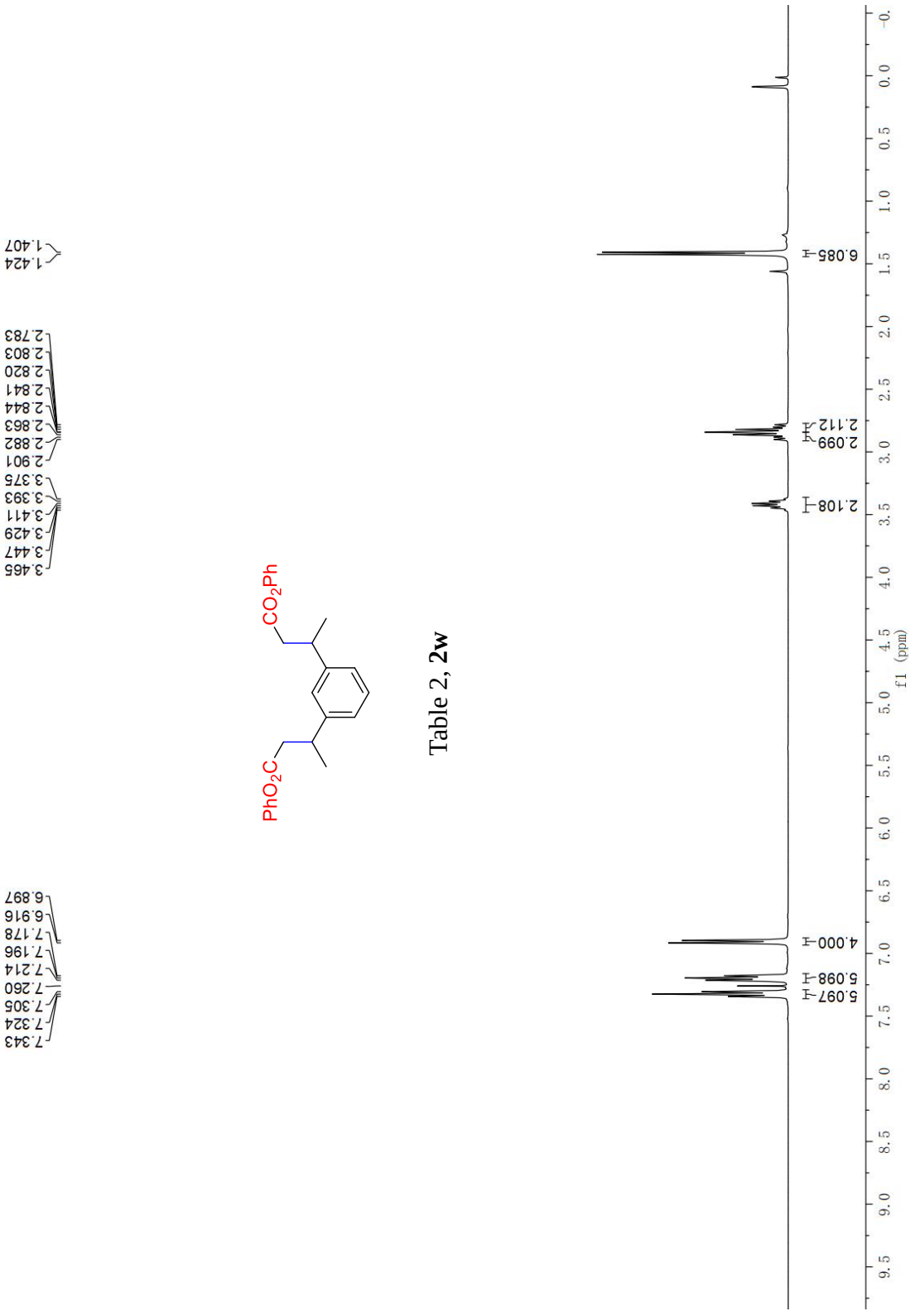
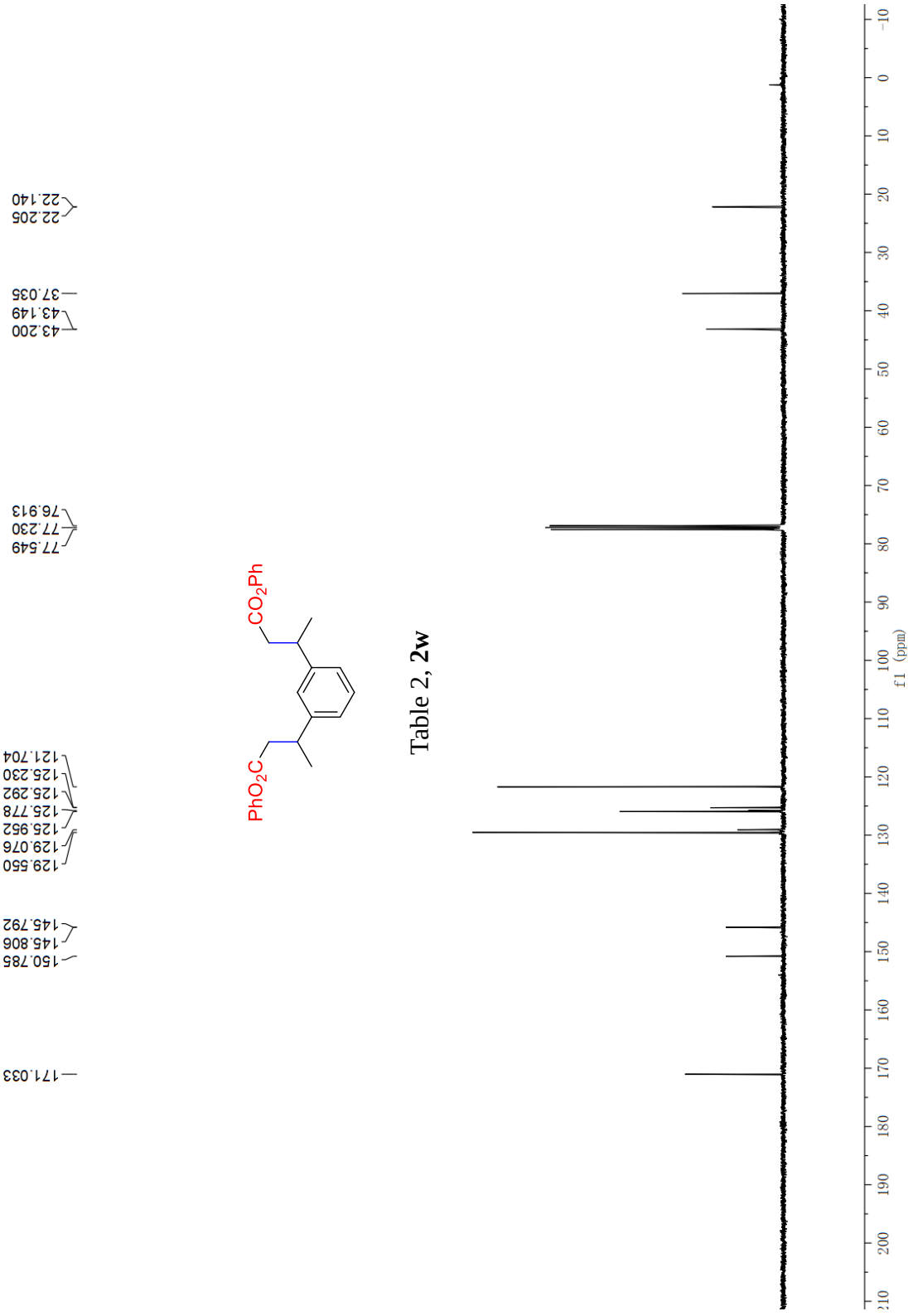


Table 2, **2v**

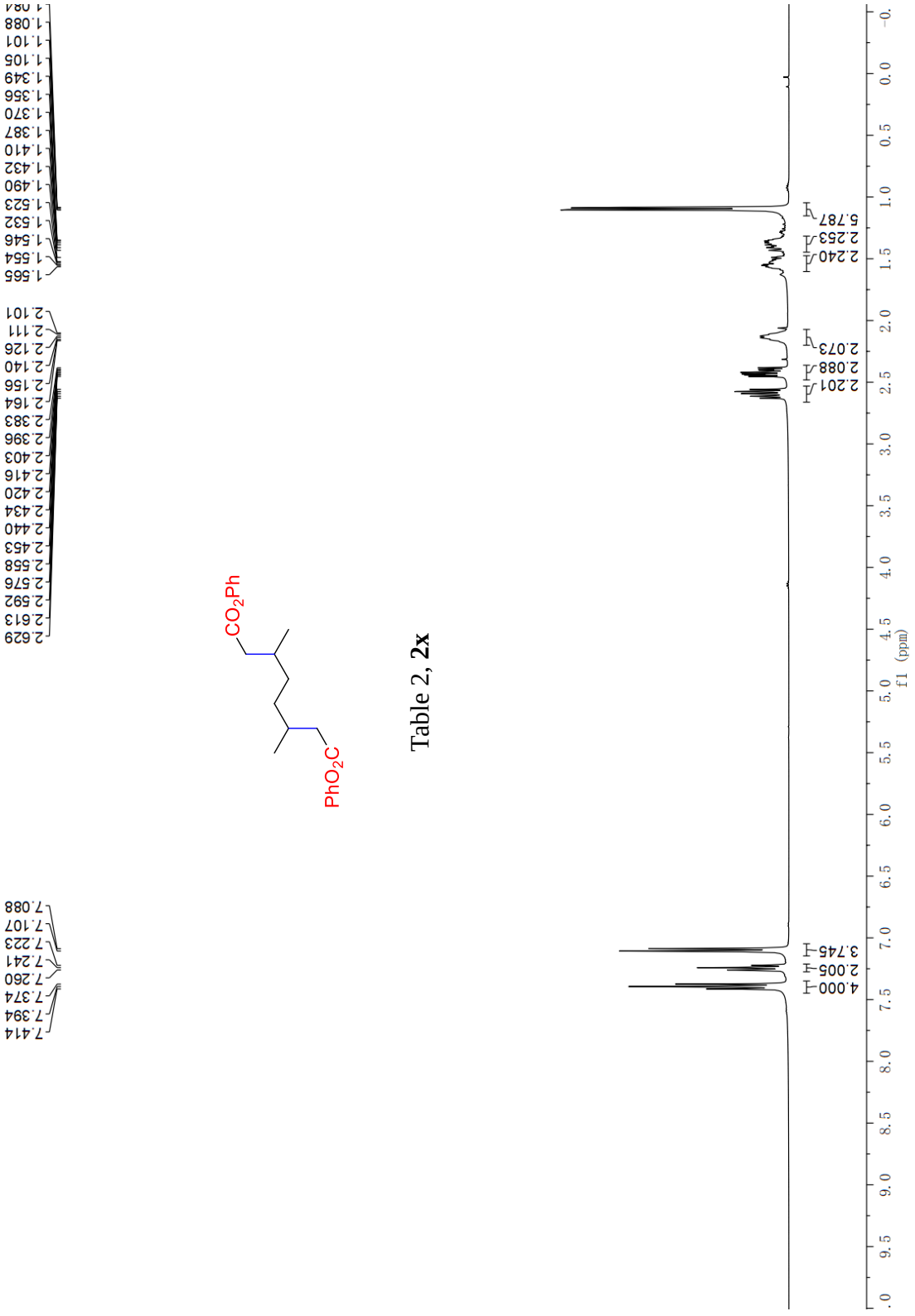
^{1}H NMR Spectrum of **2w** ($CDCl_3$, 400 MHz)



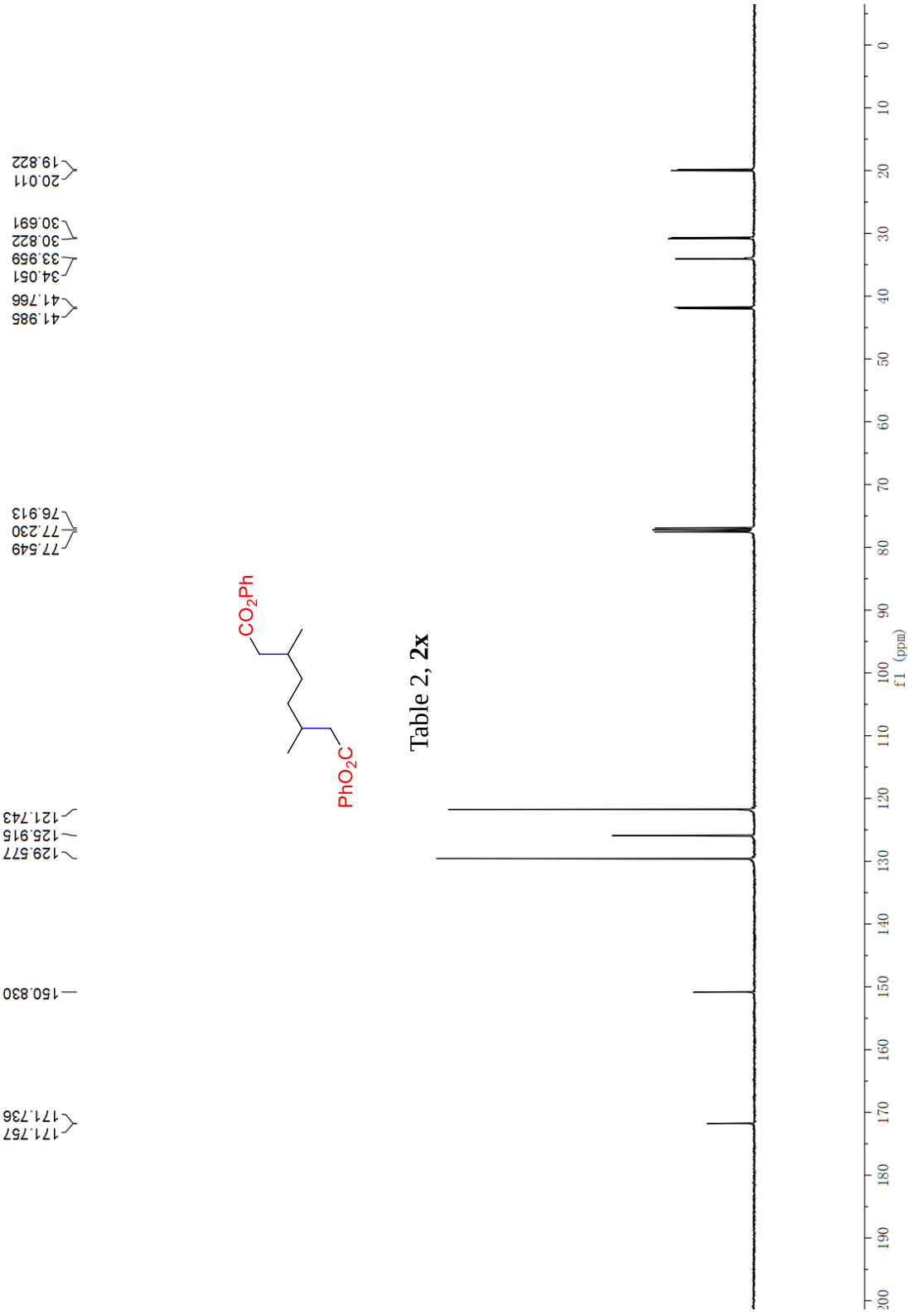
^{13}C NMR Spectrum of **2w** ($CDCl_3$, 100 MHz)



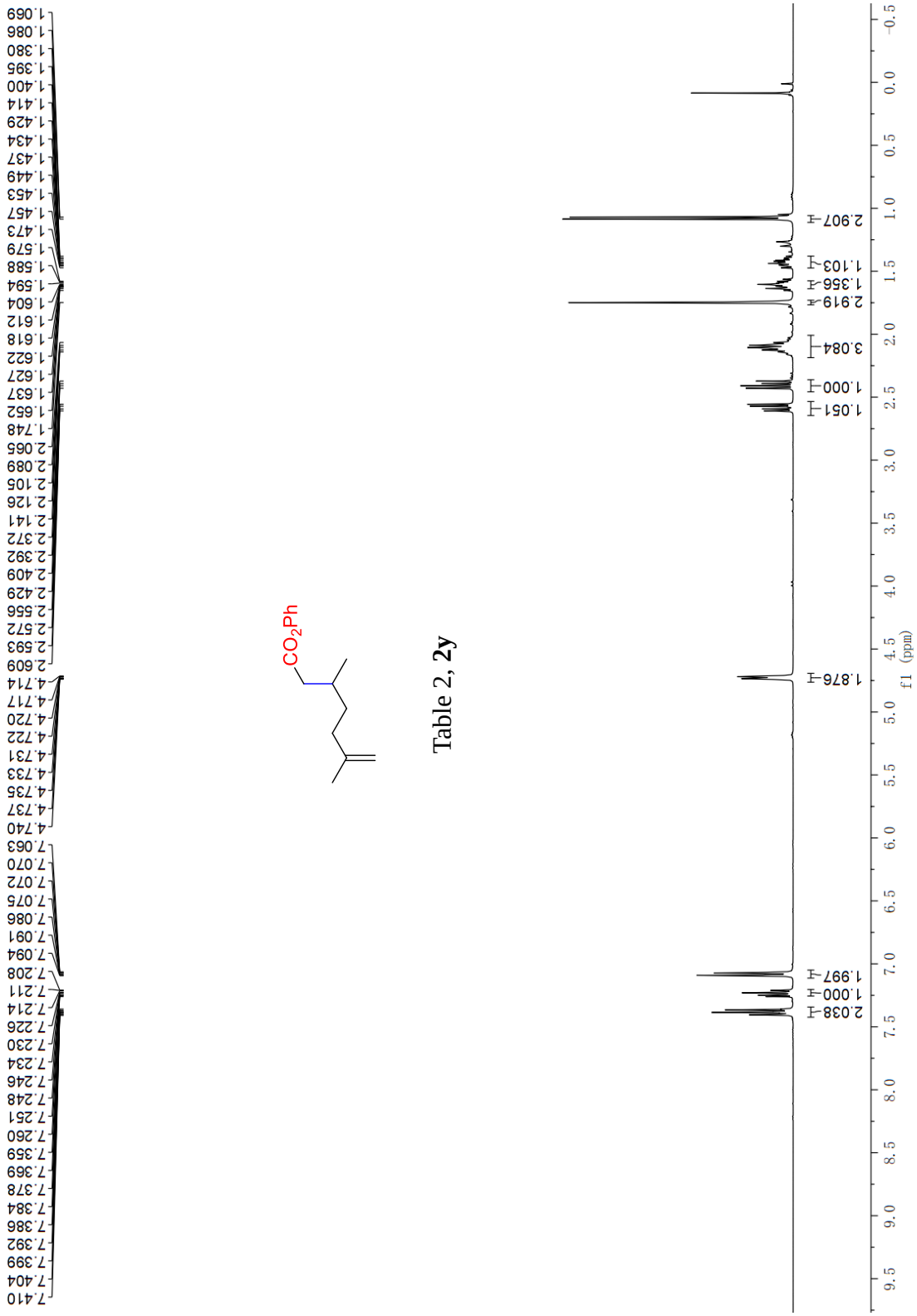
^{1}H NMR Spectrum of **2x** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2x** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2y** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2y** ($CDCl_3$, 100 MHz)

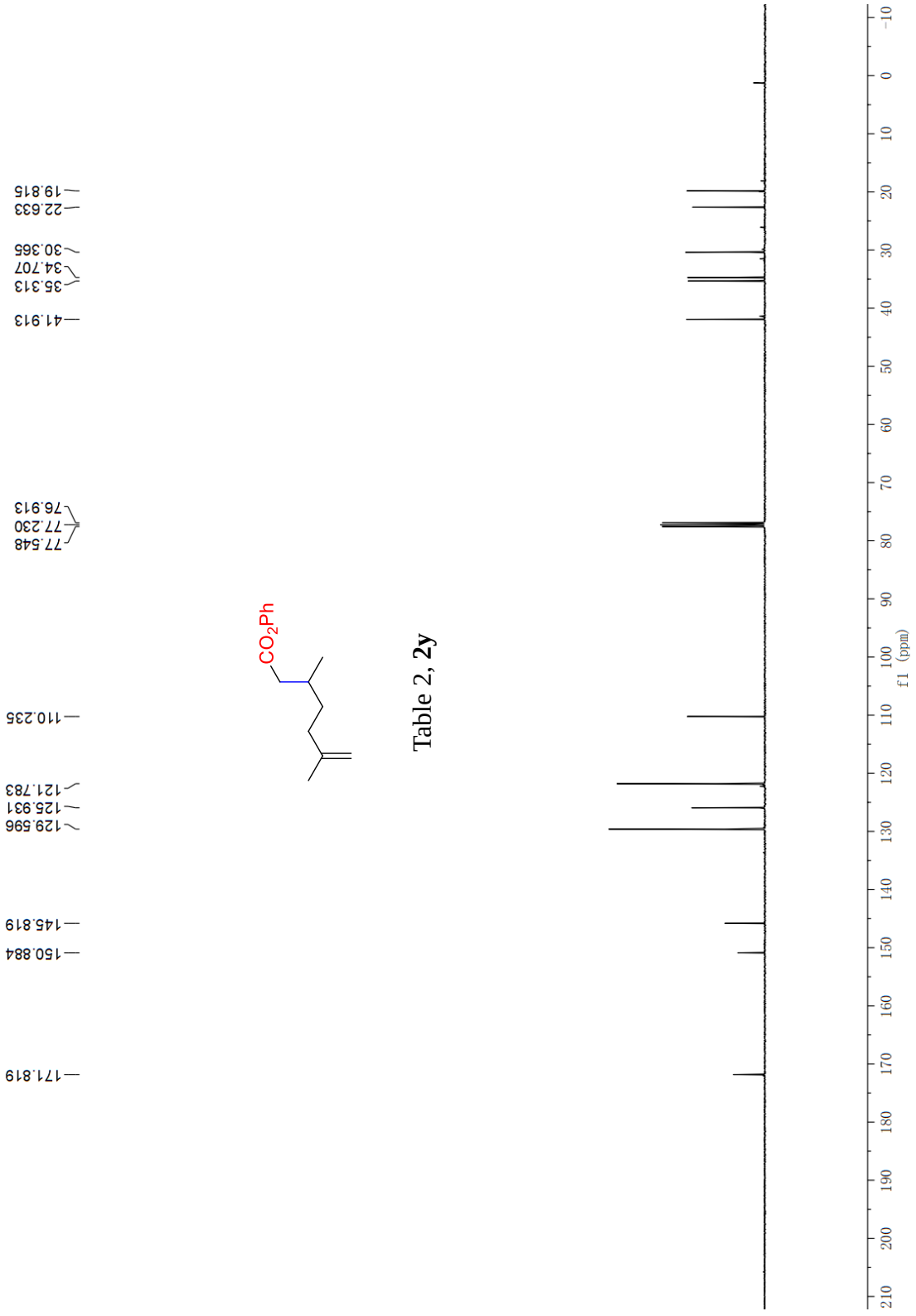
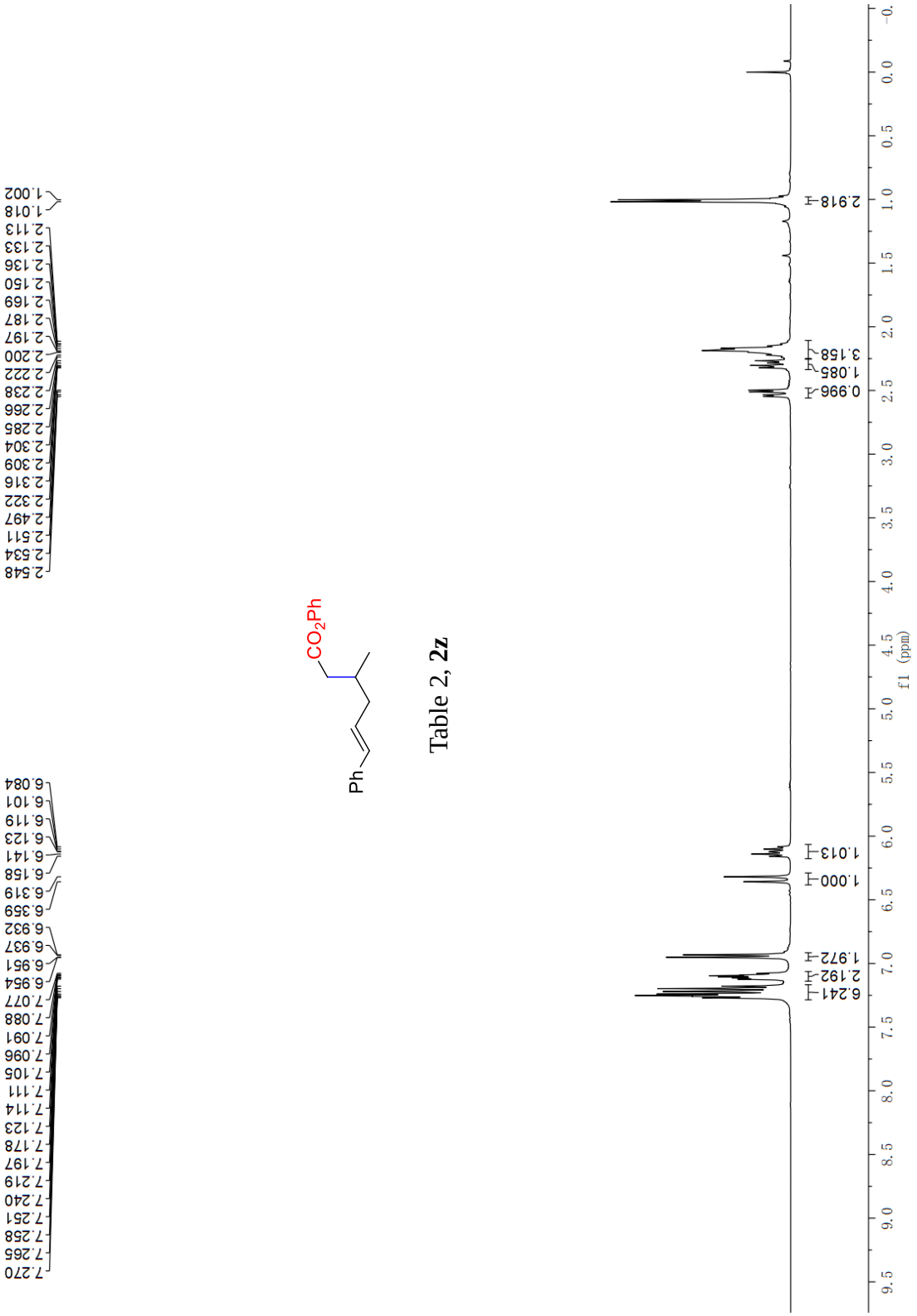


Table 2, **2y**

^{1}H NMR Spectrum of **2z** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2z** ($CDCl_3$, 100 MHz)

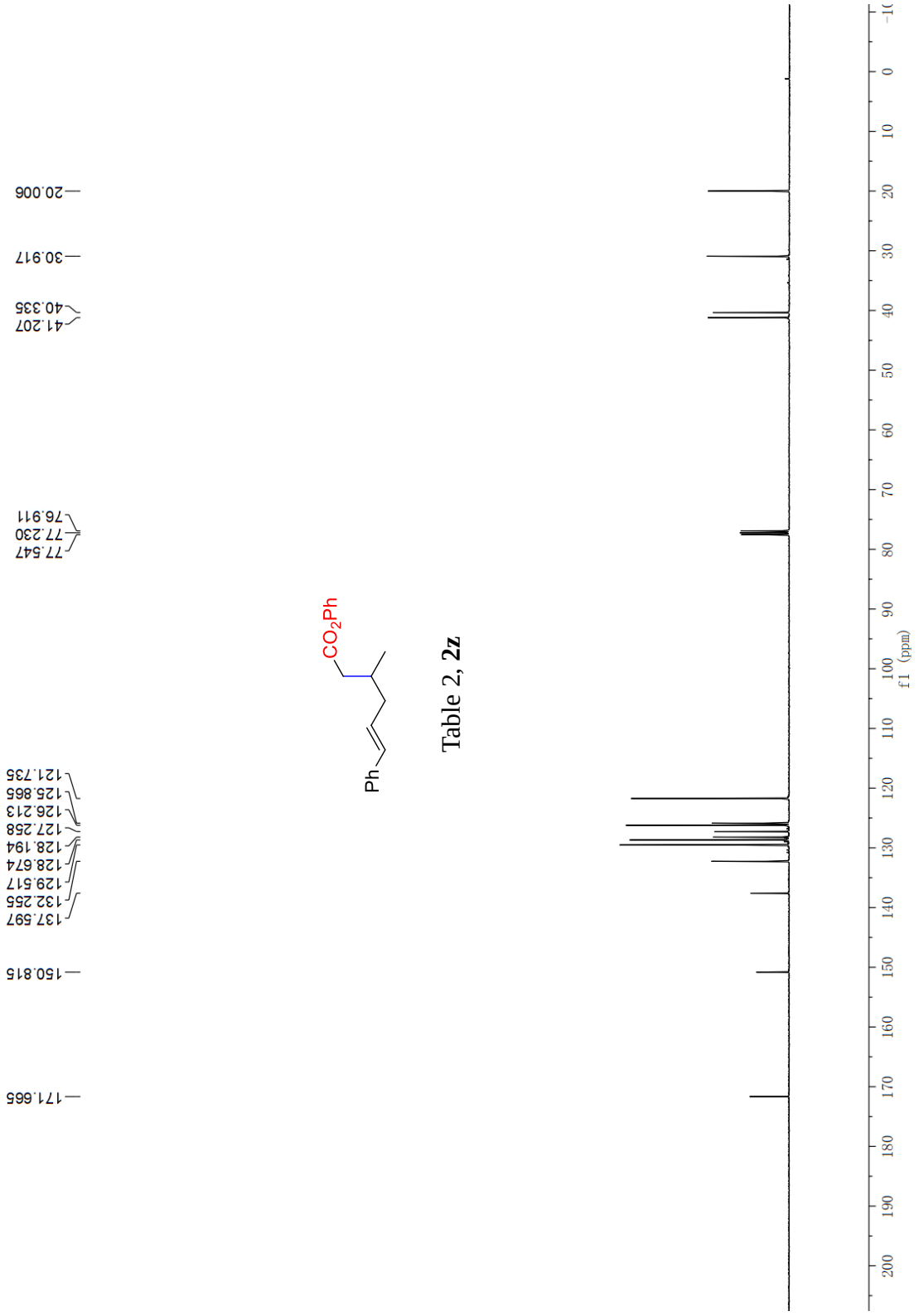
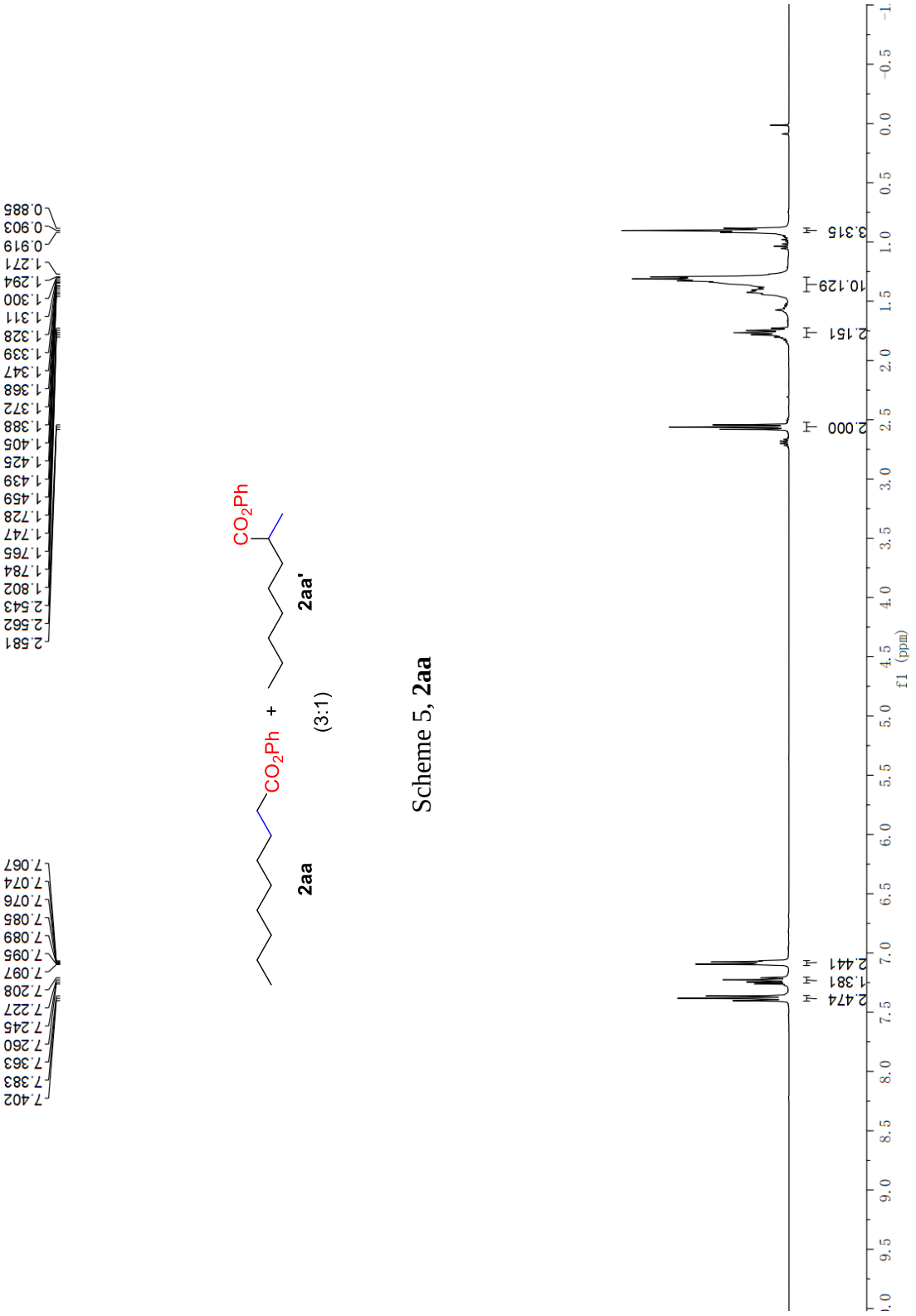


Table 2, **2z**

^{1}H NMR Spectrum of **2aa** ($CDCl_3$, 400 MHz)



Scheme 5, **2aa**

^{13}C NMR Spectrum of **2aa** ($CDCl_3$, 100 MHz)