Pd-Catalyzed Highly Regioselective Olefin Isomerization -Hydrocarboxylation with Formic Acid. A Facile Approach to Linear Carboxylic Acids from Internal Olefins

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Supporting Information

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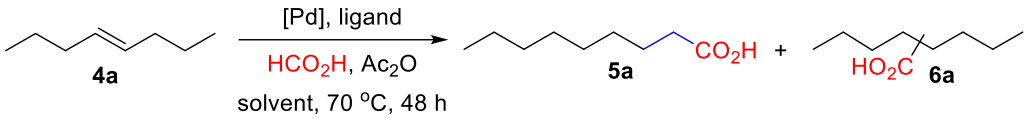
General Methods. All commercially available reagents were used without further purification unless otherwise noted. All dry solvents were purified with solvent purification system before use. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz 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.

Table S1. Studies of hydrocarboxylation conditions[a]

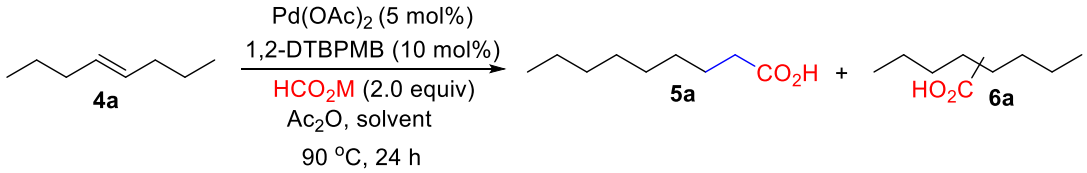


entry	catalyst	ligand	solvent	yield (%)[b] (**5a**:**6a**)[c]
1	$Pd(OAc)_2$	PPh_3	DCE	99 (1:1)
2	$Pd(OAc)_2$	(*o*-tolyl)$_3$P	DCE	NP
3	$Pd(OAc)_2$	(*p*-tolyl)$_3$P	DCE	99 (1:1)
4	$Pd(OAc)_2$	(*p*-OMe-Ph)$_3$P	DCE	99 (2:1)
5	$Pd(OAc)_2$	(*p*-F-Ph)$_3$P	DCE	66 (2:1)
6	$Pd(OAc)_2$	(*p*-CF_3-Ph)$_3$P	DCE	trace
7	$Pd(OAc)_2$	PPh_2Cy	DCE	76 (2:1)
8	$Pd(OAc)_2$	$PPhCy_2$	DCE	71 (5:1)
9	$Pd(OAc)_2$	PCy_3	DCE	trace
10	$Pd(OAc)_2$	dppe	DCE	NP
11	$Pd(OAc)_2$	dppp	DCE	NP
12	$Pd(OAc)_2$	dppb	DCE	64 (1:2)
13	$Pd(OAc)_2$	dppf	DCE	84 (1:1)
14	$Pd(OAc)_2$	BINAP	DCE	NP
15	$Pd(OAc)_2$	Xantphos	DCE	88 (1:1)
16	$Pd(OAc)_2$	DPEPhos	DCE	99 (2:1)
17	$Pd(OAc)_2$	1,2-DTBPMB	DCE	79 (15:1)
18	$Pd(acac)_2$	1,2-DTBPMB	DCE	92 (9:1)
19	$Pd(OH)_2$	1,2-DTBPMB	DCE	99 (9:1)
20	$Pd(TFA)_2$	1,2-DTBPMB	DCE	trace
21	$PdCl_2$	1,2-DTBPMB	DCE	trace
22	$[allylPdCl]_2$	1,2-DTBPMB	DCE	10 (2:1)
23	$Pd(dba)_2$	1,2-DTBPMB	DCE	95 (13:1)
24	$Pd(PPh_3)_4$	1,2-DTBPMB	DCE	81 (2:1)
25	$Pd(OAc)_2$	1,2-DTBPMB	acetone	99 (>20:1)
26	$Pd(OAc)_2$	1,2-DTBPMB	EA	99 (>20:1)

27	$Pd(OAc)_2$	1,2-DTBPMB	DCM	97 (14:1)
28	$Pd(OAc)_2$	1,2-DTBPMB	MeCN	91 (10:1)
29	$Pd(OAc)_2$	1,2-DTBPMB	DME	99 (13:1)
30	$Pd(OAc)_2$	1,2-DTBPMB	THF	86 (14:1)
31	$Pd(OAc)_2$	1,2-DTBPMB	dioxane	84 (16:1)
32	$Pd(OAc)_2$	1,2-DTBPMB	DMF	75 (13:1)
33	$Pd(OAc)_2$	1,2-DTBPMB	$CHCl_3$	trace
34	$Pd(OAc)_2$	1,2-DTBPMB	*n*-hexane	trace
35	$Pd(OAc)_2$	1,2-DTBPMB	neat	91 (16:1)
36	$Pd(OAc)_2$	1,2-DTBPMB	acetone (110 °C)	74 (12:1)
37	$Pd(OAc)_2$	1,2-DTBPMB	acetone (90 °C)	98 (16:1)
38	$Pd(OAc)_2$	1,2-DTBPMB	acetone (50 °C)	98 (>20:1)
39	$Pd(OAc)_2$	1,2-DTBPMB	acetone (40 °C)	99 (>20:1)
40	$Pd(OAc)_2$	1,2-DTBPMB	acetone (25 °C)	92 (>20:1)
41[d]	$Pd(OAc)_2$	1,2-DTBPMB	acetone (40 °C)	99 (92)[e] (>20:1)

[a] All reactions were carried out with substrate **4a** (0.50 mmol), Pd (0.025 mmol), ligand (0.050 or 0.10 mmol, Pd/P = 1/4), HCO_2H (1.0 mmol), and Ac_2O (0.10 mmol) in solvent (0.10 mL) under N_2 at 70 °C for 48 h unless otherwise noted. [b] The yield was determined by the ^1H NMR analysis of the crude reaction mixture with 1,1,2,2-tetrachloroethane as internal standard. [c] The ratio of **5a**/**6a** was determined by ^1H NMR analysis of the crude reaction mixture. [d] For 24 h. [e] Isolated yield. NP = no product.

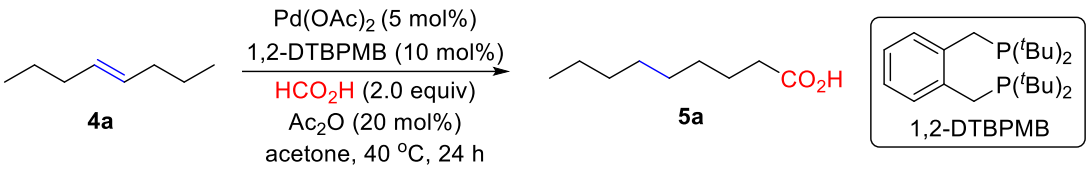
Table S2. Studies of hydrocarboxylation with formate salts[a]



entry	HCO_2M	solvent	temperature (°C)	yield (%)[b] (**5a**:**6a**)[c]
1	$HCO_2Li·H_2O$	DCE	90	89 (88)[d] (>20:1)
2	$(HCO_2)_2Mg·H_2O$	DCE	90	66 (16:1)
3	HCO_2Na	DCE	90	trace
4	$HCO_2Cs·H_2O$	DCE	90	NP
5	HCO_2NH_4	DCE	90	NP
6	$HCO_2Li·H_2O$	1.4-dioxane	90	trace
7	$HCO_2Li·H_2O$	CH_3CN	90	37 (17:1)
8	$HCO_2Li·H_2O$	EtOAc	90	8 (4:1)
9	$HCO_2Li·H_2O$	acetone	90	18 (>20:1)
10	$HCO_2Li·H_2O$	DCE	70	71 (>20:1)
11	$HCO_2Li·H_2O$	DCE	40	29 (>20:1)
12[e]	$HCO_2Li·H_2O$	DCE	90	trace

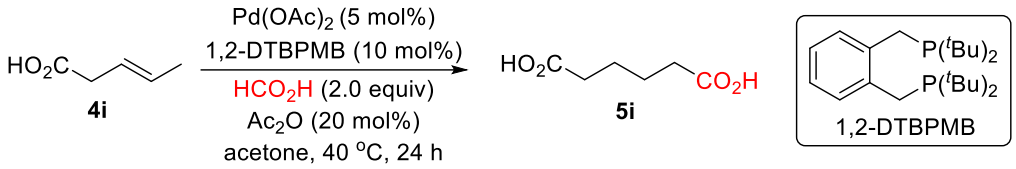
[a] All reactions were carried out with substrate **4a** (0.50 mmol), $Pd(OAc)_2$ (0.025 mmol), 1,2-DTBPMB (0.050 mmol), HCO_2M (1.0 mmol), and Ac_2O (0.50 mmol) in solvent (0.10 mL) under N_2 for 24 h. [b] The yield was determined by the ^1H NMR analysis of the crude reaction mixture with 1,1,2,2-tetrachloroethane as internal standard. [c] The ratio of **5a**/**6a** was determined by ^1H NMR analysis of the crude reaction mixture. [d] Isolated yield. [e] With Ac_2O (0.10 mmol). NP = no product.

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



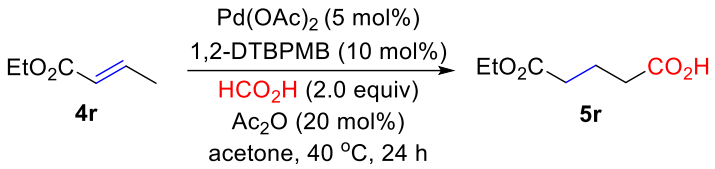
To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), ligand 1,2-DTBPMB (0.0197 g, 0.050 mmol), and acetone (0.1 mL) in a sealed tube (2.0 mL) were added *trans*-4-octene (**4a**) (0.0561 g, 0.50 mmol), HCO_2H (0.0460 g, 1.0 mmol), and Ac_2O (0.0102 g, 0.10 mmol) successively via syringe. The tube was purged with N_2 to remove the air and tightly sealed with a Teflon cap. The reaction mixture was stirred in oil bath (40 °C) for 24 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 5:1) to give acid **5a** as a colorless oil (0.0727 g, 92% yield, l/b > 20:1).

Representative procedure for hydrocarboxylation (Table 2, entry 9).



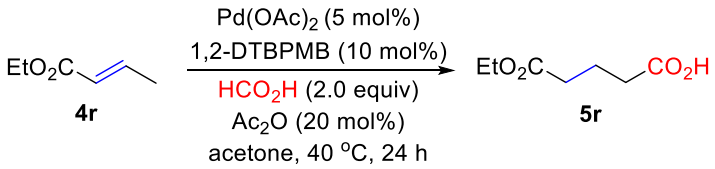
To a mixture of $Pd(OAc)_2$ (0.0056 g, 0.025 mmol), ligand 1,2-DTBPMB (0.0197 g, 0.050 mmol), and acetone (0.1 mL) in a sealed tube (2.0 mL) were added 3-pentenoic acid (**4i**) (0.0501 g, 0.50 mmol), HCO_2H (0.0460 g, 1.0 mmol), and Ac_2O (0.0102 g, 0.10 mmol) successively via syringe. The tube was purged with N_2 to remove the air and tightly sealed with a Teflon cap. The reaction mixture was stirred in oil bath (40 °C) for 24 h and lots of solid appeared. The reaction mixture was cooled to rt and diluted DCM (2 mL) to dissolve the solid. Upon addition of petroleum ether (20 mL), the mixture was stood at rt to precipitate the product. After the mother liquid was decanted, the resulting solid was rinsed with petroleum ether and dried to give adipic acid (**5i**) as a white solid (0.0716 g, 98% yield, l/b > 20:1).

Procedure for gram scale hydrocarboxylation in a sealed tube (Scheme 5)



To a mixture of $Pd(OAc)_2$ (0.1011 g, 0.45 mmol), ligand 1,2-DTBPMB (0.3551 g, 0.90 mmol), and acetone (1.8 mL) in a sealed tube (15.0 mL) were added ethyl crotonate (**4r**) (1.0273 g, 9.0 mmol), HCO_2H (0.8285 g, 18.0 mmol), and Ac_2O (0.1838 g, 1.80 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 in oil bath (40 ℃) for 24 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 5:1) to give acid **5r** as a light yellow oil (1.4012 g, 97% yield, l/b > 20:1).

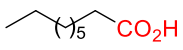
Procedure for gram scale hydrocarboxylation with a balloon (Scheme 6)



To a mixture of $Pd(OAc)_2$ (0.1011 g, 0.45 mmol), ligand 1,2-DTBPMB (0.3551 g, 0.90 mmol), and acetone (1.8 mL) in a reaction tube (10.0 mL) were added ethyl crotonate (**4r**) (1.0273 g, 9.0 mmol), HCO_2H (0.8285 g, 18.0 mmol), and Ac_2O (0.1838 g, 1.80 mmol) successively via syringe. The tube was purged with N_2 to remove the air and connected with a balloon on the top of the tube. The reaction mixture was stirred in oil bath (40 ℃) for 24 h, cooled to rt, and purified by flash chromatography (silica gel, eluent: petroleum ether/ethyl acetate = 5:1) to give acid **5r** as a light yellow oil (1.3759 g, 95% yield, l/b > 20:1).

Characterization data of carboxylic acids 5

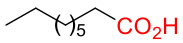
Table 2, entry 1



5a

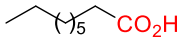
Light yellow oil; 0.0727 g (92% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1; IR (film) 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.2 (br s, 1H), 2.34 (t, *J* = 7.2 Hz, 2H), 1.67-1.58 (m, 2H), 1.36-1.22 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 34.3, 32.0, 29.4, 29.25, 29.21, 24.8, 22.8, 14.2; HRMS (ESI) calcd for $C_9H_{17}O_2$ $(M-H)^+$: 157.1223; found: 157.1220.[1]

Table 2, entry 2

 **5a**

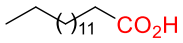
Light yellow oil; 0.0619 g (78% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1.

Table 2, entry 3

 **5a**

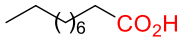
Light yellow oil; 0.0631 g (80% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1.

Table 2, entry 4

 **5d**

White solid; 0.0804 g (66% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1; mp. 40.9-42.8 ℃; IR (film) 1703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.1 (br s, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.68-1.58 (m, 2H), 1.37-1.20 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 34.3, 32.1, 29.9, 29.83, 29.81, 29.75, 29.6, 29.5, 29.4, 29.2, 24.8, 22.9, 14.3; HRMS (ESI) calcd for $C_{15}H_{29}O_2$ $(M-H)^+$: 241.2162; found: 241.2168.[2]

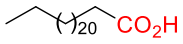
Table 2, entry 5

 **5e**

Light yellow oil; 0.0742 g (86% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate

= 5:1; IR (film) 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.3 (br s, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.68-1.58 (m, 2H), 1.37-1.22 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 34.3, 32.0, 29.5, 29.4, 29.2, 24.8, 22.8, 14.2; HRMS (ESI) calcd for $C_{10}H_{19}O_2$ $(M-H)^+$: 171.1380; found: 171.1378.[3]

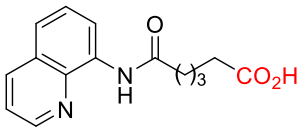
Table 2, entry 6



5f

White solid; 0.1144 g (62% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1; mp. 75.9-77.3 ℃; IR (film) 1694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.3 (br s, 1H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.68-1.59 (m, 2H), 1.37-1.19 (m, 40H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 34.1, 32.1, 29.9, 29.83, 29.80, 29.75, 29.6, 29.5, 29.4, 29.2, 24.8, 22.9, 14.3; HRMS (ESI) calcd for $C_{24}H_{48}O_2Na$ $(M+Na)^+$: 391.3547; found: 391.3540.

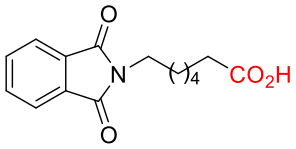
Table 2, entry 7



5g

White solid; 0.0843 g (62% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1, mp. 112.3-114.1 ℃; IR (film) 1690, 1528, 1487 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.0 (br s, 1H), 9.79 (s, 1H), 8.78 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.75 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55-7.45 (m, 2H), 7.42 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 1.93-1.82 (m, 2H), 1.82-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 171.6, 148.2, 138.3, 136.6, 134.3, 128.0, 127.5, 121.72, 121.66, 116.9, 37.7, 33.9, 25.0, 24.3; HRMS (ESI) calcd for $C_{15}H_{15}N_2O_3$ $(M-H)^+$: 271.1077; found: 271.1087.[4]

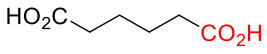
Table 2, entry 8



5h

White solid; 0.1280 g (93% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1, mp. 104.3-106.6 ℃; IR (film) 1770, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.3 (br s, 1H), 7.86-7.79 (m, 2H), 7.73-7.66 (m, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.72-1.56 (m, 4H), 1.43-1.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 168.6, 134.0, 132.2, 123.3, 38.0, 34.0, 28.7, 28.5, 26.6, 24.6; HRMS (ESI) calcd for $C_{15}H_{16}NO_4$ $(M-H)^+$: 274.1074; found: 274.1085.[5]

Table 2, entry 9



5i

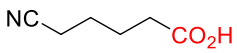
White solid; 0.0716 g (98% yield, l/b > 20:1), mp. 149.3-151.6 ℃; IR (film) 1711 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.99 (br s, 2H), 2.25-2.15 (m, 4H), 1.55-1.43 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.5, 33.5, 24.1; HRMS (ESI) calcd for $C_6H_9O_4$ $(M-H)^+$: 145.0495; found: 145.0493.[6]

Table 2, entry 10

5j

White solid; 0.1284 g (75% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1 to 3:1, mp. 59.0-61.2 ℃; IR (film) 1741, 1707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.0 (br s, 1H), 3.65 (s, 3H), 2.33 (t, *J* = 7.6 Hz, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.68-1.55 (m, 4H), 1.36-1.20 (m, 26H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 174.6, 51.6, 34.2, 29.79, 29.76, 29.72, 29.58, 29.56, 29.4, 29.3, 29.2, 25.1, 24.8; HRMS (ESI) calcd for $C_{20}H_{38}O_4Na$ $(M+Na)^+$: 365.2662; found: 365.2661.

Table 2, entry 11

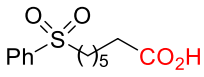


5k

Colorless oil; 0.0440 g (69% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate =

2:1; IR (film) 2247, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (br s, 1H), 2.41 (t, *J* = 6.4 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 1.83-1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 119.4, 33.1, 24.8, 23.7, 17.1; HRMS (ESI) calcd for $C_6H_8NO_2$ $(M-H)^+$: 126.0550; found: 126.0546.[7]

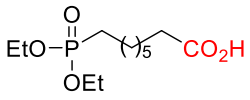
Table 2, entry 12



5l

White solid; 0.0969 g (72% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1, mp. 98.6-99.8 °C; IR (film) 1704, 1292, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.2 (br s, 1H), 7.93-7.86 (m, 2H), 7.68-7.62 (m, 1H), 7.59-7.53 (m, 2H), 3.12-3.03 (m, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.77-1.65 (m, 2H), 1.64-1.52 (m, 2H), 1.42-1.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 139.1, 133.8, 129.4, 128.1, 56.2, 33.8, 28.4, 27.9, 24.3, 22.5; HRMS (ESI) calcd for $C_{13}H_{17}O_4S$ $(M-H)^+$: 269.0842; found: 269.0850.[8]

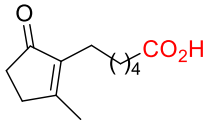
Table 2, entry 13



5m

Light yellow oil; 0.0783 g (56% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1 to 0:1; IR (film) 1723, 1189, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (br s, 1H), 4.15-4.00 (m, 4H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.77-1.65 (m, 2H), 1.64-1.50 (m, 4H), 1.39-1.25 (m, 6H), 1.29 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 61.8 (d, *J* = 6.6 Hz), 34.2, 30.4 (d, *J* = 16.9 Hz), 28.9, 28.8 (d, *J* = 0.2 Hz), 25.6 (d, *J* = 139.7 Hz), 24.8, 22.3 (d, *J* = 5.2 Hz), 16.5 (d, *J* = 6.0 Hz); HRMS (ESI) calcd for $C_{12}H_{25}O_5PNa$ $(M+Na)^+$: 303.1332; found: 303.1332.

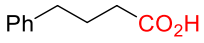
Table 2, entry 14



5n

Colorless oil; 0.0662 g (63% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 2:1; IR (film) 1732, 1697, 1632, 1387 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.89 (br s, 1H), 2.50-2.42 (m, 2H), 2.36-2.32 (m, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.14 (t, *J* = 7.2 Hz, 2H), 2.02 (s, 3H), 1.65-1.55 (m, 2H), 1.41-1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 179.4, 171.0, 140.5, 34.4, 34.0, 31.7, 29.0, 28.0, 24.6, 22.9, 17.4; HRMS (ESI) calcd for $C_{12}H_{19}O_3$ $(M+H)^+$: 211.1329; found: 211.1329.

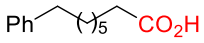
Table 2, entry 15



5o

White solid; 0.0617 g (75% yield for **5o** and **5o'**), eluent: petroleum ether/ethyl acetate = 5:1, mp. 49.6-52.0 °C; IR (film) 1706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.86 (br s, 1H), 7.33-7.28 (m, 2H), 7.24-7.18 (m, 3H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.04-1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 141.3, 128.6, 128.5, 126.2, 35.1, 33.5, 26.3; HRMS (ESI) calcd for $C_{10}H_{11}O_2$ $(M-H)^+$: 163.0754; found: 163.0751.[9,10]

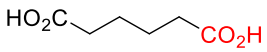
Table 2, entry 16



5p

Colorless oil; 0.0615 g (56% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1; IR (film) 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.9 (br s, 1H), 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.69-1.57 (m, 4H), 1.40-1.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 142.9, 128.5, 128.4, 125.7, 36.1, 34.2, 31.6, 29.24, 29.21, 29.1, 24.8; HRMS (ESI) calcd for $C_{14}H_{19}O_2$ $(M-H)^+$: 219.1380; found: 219.1382.[3]

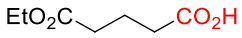
Table 2, entry 17



5i

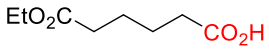
White solid; 0.0658 g (90% yield, l/b > 20:1).

Table 2, entry 18

 **5r**

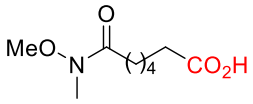
Colorless oil; 0.0622 g (78% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 2:1; IR (film) 1732, 1709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.0 (br s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 7.6 Hz, 2H), 2.37 (t, *J* = 7.2 Hz, 2H), 1.98-1.88 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 173.1, 60.6, 33.3, 33.1, 19.9, 14.3; HRMS (ESI) calcd for $C_7H_{11}O_4$ $(M-H)^+$: 159.0652; found: 159.0651.[11]

Table 2, entry 19

 **5s**

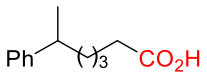
Colorless oil; 0.0721 g (83% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 2:1; IR (film) 1734, 1707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.0 (br s, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.39-2.25 (m, 4H), 1.70-1.59 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 173.5, 60.5, 34.0, 33.7, 24.4, 24.1, 14.3; HRMS (ESI) calcd for $C_8H_{13}O_4$ $(M-H)^+$: 173.0808; found: 173.0808.[12]

Table 2, entry 20

 **5t**

Yellow oil; 0.0766 g (75% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1; IR (film) 1730,1709, 1661, 1624, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.6 (br s, 1H), 3.64 (s, 3H), 3.14 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 1.68-1.56 (m, 4H), 1.40-1.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 174.7, 61.3, 33.9, 32.2, 31.6, 28.8, 24.5, 24.3; HRMS (ESI) calcd for $C_9H_{18}NO_4$ $(M+H)^+$: 204.1230; found: 204.1229.

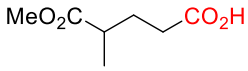
Table 2, entry 21

 **5u**

Colorless oil; 0.0715 g (69% yield), eluent: petroleum ether/ethyl acetate = 5:1; IR

(film) 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.5 (br s, 1H), 7.35-7.28 (m, 2H), 7.24-7.17 (m, 3H), 2.76-2.66 (m, 1H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.72-1.56 (m, 4H), 1.38-1.19 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 147.6, 128.4, 127.1, 126.0, 39.9, 38.1, 34.1, 27.3, 24.8, 22.5; HRMS (ESI) calcd for $C_{13}H_{17}O_2$ $(M-H)^+$: 205.1223; found: 205.1223.[13]

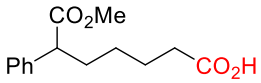
Table 2, entry 22



5v

Colorless oil; 0.0556 g (69% yield), eluent: petroleum ether/ethyl acetate = 2:1; IR (film) 1737, 1715, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.4 (br s, 1H), 3.67 (s, 3H), 2.57-2.46 (m, 1H), 2.42-2.34 (m, 2H), 2.01-1.90 (m, 1H), 1.82-1.71 (m, 1H), 1.17 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 176.6, 51.9, 38.6, 31.7, 28.3, 17.2; HRMS (ESI) calcd for $C_7H_{11}O_4$ $(M-H)^+$: 159.0652; found: 159.0650.[14]

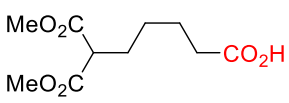
Table 2, entry 23



5w

Light yellow oil; 0.0764 g (61% yield), eluent: petroleum ether/ethyl acetate = 2:1 to 1:1; IR (film) 1735, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.9 (br s, 1H), 7.35-7.23 (m, 5H), 3.65 (s, 3H), 3.55 (t, *J* = 7.6 Hz, 1H), 2.32 (t, *J* = 7.6 Hz, 2H), 2.15-2.04 (m, 1H), 1.85-1.74 (m, 1H), 1.71-1.58 (m, 2H), 1.38-1.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 174.5, 139.0, 128.8, 128.0, 127.4, 52.1, 51.5, 33.9, 33.2, 27.0, 24.4; HRMS (ESI) calcd for $C_{14}H_{18}O_4Na$ $(M+Na)^+$: 273.1097; found: 273.1098.

Table 2, entry 24

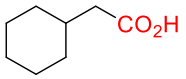


5x

Light yellow oil; 0.050 g (43% yield), eluent: petroleum ether/ethyl acetate = 2:1 to 1:1; IR (film) 1736, 1709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.23 (br s, 1H), 3.72 (s, 6H),

3.36 (t, *J* = 7.6 Hz, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.96-1.86 (m, 2H), 1.69-1.59 (m, 2H), 1.41-1.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 169.9, 52.6, 51.5, 33.7, 28.5, 26.8, 24.3; HRMS (ESI) calcd for $C_{10}H_{16}O_6Na$ $(M+Na)^+$: 255.0839; found: 255.0839.

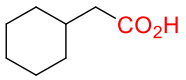
Table 2, entry 25



5y

Light yellow oil; 0.0207 g (29% yield), eluent: petroleum ether/ethyl acetate = 5:1; IR (film) 1708 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.0 (br s, 1H), 2.22 (d, *J* = 6.4 Hz, 2H), 1.83-1.62 (m, 6H), 1.33-1.21 (m, 2H), 1.19-1.11 (m, 1H), 1.03-0.89 (m, 2H), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.9, 42.1, 34.8, 33.1, 26.2, 26.1; HRMS (ESI) calcd for $C_8H_{13}O_2$ $(M-H)^+$: 141.0910; found: 141.0906.[15]

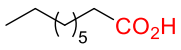
Table 2, entry 26



5y

Light yellow oil; 0.0183 g (26% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1.

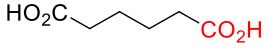
Table 3, entry 1



5a

Light yellow oil; 0.0654 g (83% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1.

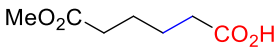
Table 3, entry 2



5i

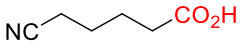
White solid; 0.0669 g (92% yield, l/b > 20:1).

Table 3, entry 3

 **5ac**

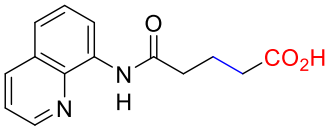
Light yellow oil; 0.0686 g (86% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 2:1; IR (film) 1737, 1715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (br s, 1H), 3.64 (s, 3H), 2.41-2.26 (m, 4H), 1.74-1.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 174.0, 51.7, 33.7, 24.3, 24.1; HRMS (ESI) calcd for $C_7H_{11}O_4$ $(M-H)^+$: 159.0652; found: 159.0650.[16]

Table 3, entry 4

 **5k**

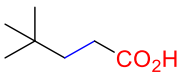
Colorless oil; 0.0495 g (78% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1 to 0:1.

Table 3, entry 5

 **5ae**

White solid; 0.0986 g (76% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 1:1 to 0:1; mp. 96.3-98.2 ℃; IR (film) 1712, 1688, 1529, 1487 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.1 (br s, 1H), 9.8 (br s, 1H), 8.76 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.72 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53-7.44 (m, 2H), 7.40 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.21-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 171.3, 148.3, 138.3, 136.6, 134.2, 128.0, 127.4, 121.9, 121.6, 117.1, 36.7, 33.2, 20.6; HRMS (ESI) calcd for $C_{14}H_{13}N_2O_3$ $(M-H)^-$: 257.0932; found: 257.0928.

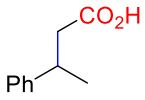
Table 3, entry 6

 **5af**

Colorless oil; 0.0349 g (54% yield, l/b > 20:1), eluent: petroleum ether/ethyl acetate = 5:1; IR (film) 1711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.2 (br s, 1H), 2.33 (t, *J* = 8.0 Hz, 2H), 1.56 (t, *J* = 8.4 Hz, 2H), 0.90 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2,

38.4, 30.2, 30.1, 29.1; HRMS (ESI) calcd for $C_7H_{13}O_2$ $(M-H)^+$: 129.0910; found: 129.0906.[1]

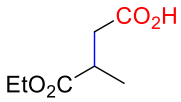
Table 3, entry 7



5ag

Colorless oil; 0.0375 g (46% yield), eluent: petroleum ether/ethyl acetate = 5:1; IR (film) 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.25-7.18 (m, 3H), 3.34-3.21 (m, 1H), 2.67 (dd, *J* = 15.6, 6.8 Hz, 1H), 2.57 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.32 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 145.5, 128.7, 126.8, 126.6, 42.7, 36.3, 22.0; HRMS (ESI) calcd for $C_{10}H_{11}O_2$ $(M-H)^+$: 163.0754; found: 163.0752.[1]

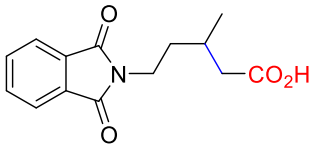
Table 3, entry 8



5ah

Colorless oil; 0.0603 g (75% yield), eluent: petroleum ether/ethyl acetate = 5:1 to 1:1; IR (film) 1733, 1715, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.71 (br s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.92-2.82 (m, 1H), 2.76 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.43 (dd, *J* = 16.8, 5.6 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.22 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 175.3, 60.9, 37.5, 35.7, 17.0, 14.2; HRMS (ESI) calcd for $C_7H_{11}O_4$ $(M-H)^+$: 159.0652; found: 159.0650.[17]

Table 3, entry 9

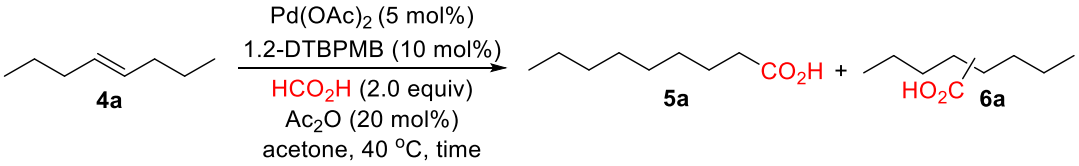


5ai

White solid; 0.0759 g (58% yield), eluent: petroleum ether/ethyl acetate = 5:1 to 1:1; mp. 101.1-103.8; IR (film) 1771, 1711, 1400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.4 (br s, 1H), 7.88-7.75 (m, 2H), 7.73-7.62 (m, 2H); 3.71 (t, *J* = 7.2 Hz, 2H), 2.44 (dd, *J* = 15.2, 5.6 Hz, 1H), 2.21 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.05-1.91 (m, 1H), 1.81-1.69 (m, 1H),

1.63-1.51 (m, 1H), 1.06 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 168.5, 134.0, 132.2, 123.3, 41.2, 36.0, 35.1, 27.8, 19.5. HRMS (ESI) calcd for $C_{14}H_{15}NO_4Na$ $(M+Na)^+$: 284.0893; found: 284.0894.

Plot of the yield for hydrocarboxylation of *trans*-4-octene (4a) vs time



Time (h)	1	2	3	4	5	6	8	16	24	36	48
Yield (%)	25	58	79	84	86	87	90	94	99	99	99
l/b	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1	>20:1

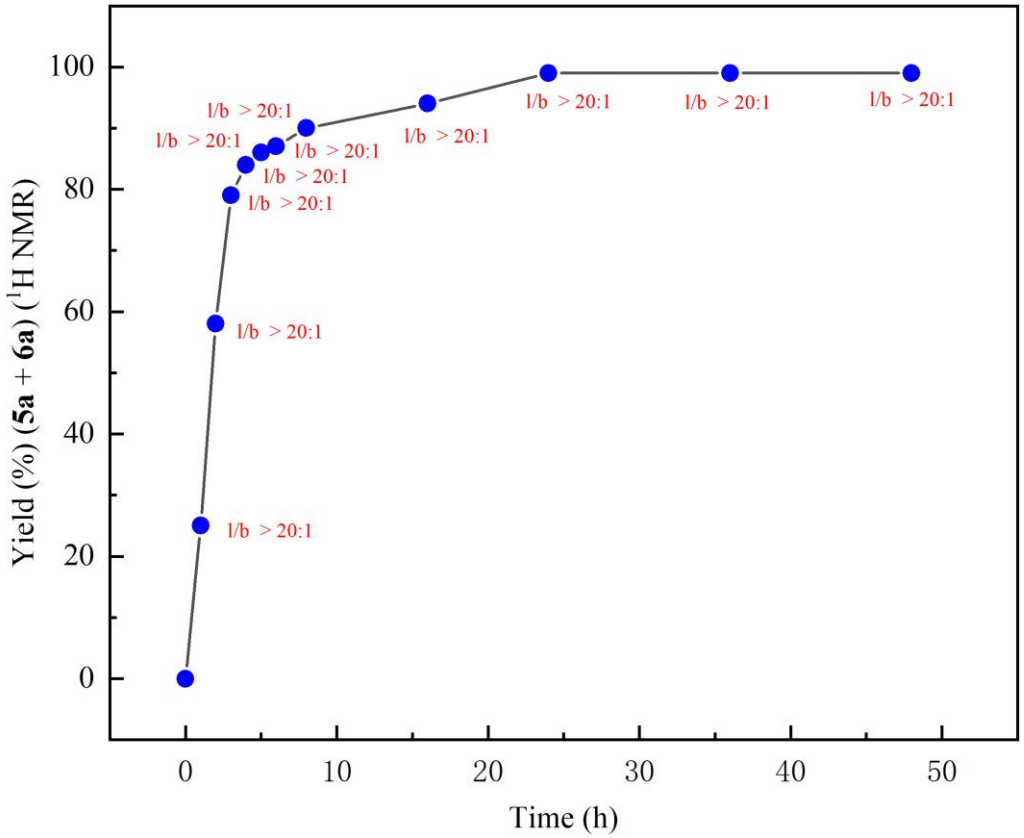


Figure S1. Plot of the yield for hydrocarboxylation of *trans*-4-octene (**4a**) vs time.

Note: The hydrocarboxylation reactions were carried out as described in representative procedure. The sample was taken from the reaction mixture at indicated reaction time (one reaction tube for one reaction time) and dissolved in $CDCl_3$. The yields and l/b ratios of **5a** and **6a** were determined by ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

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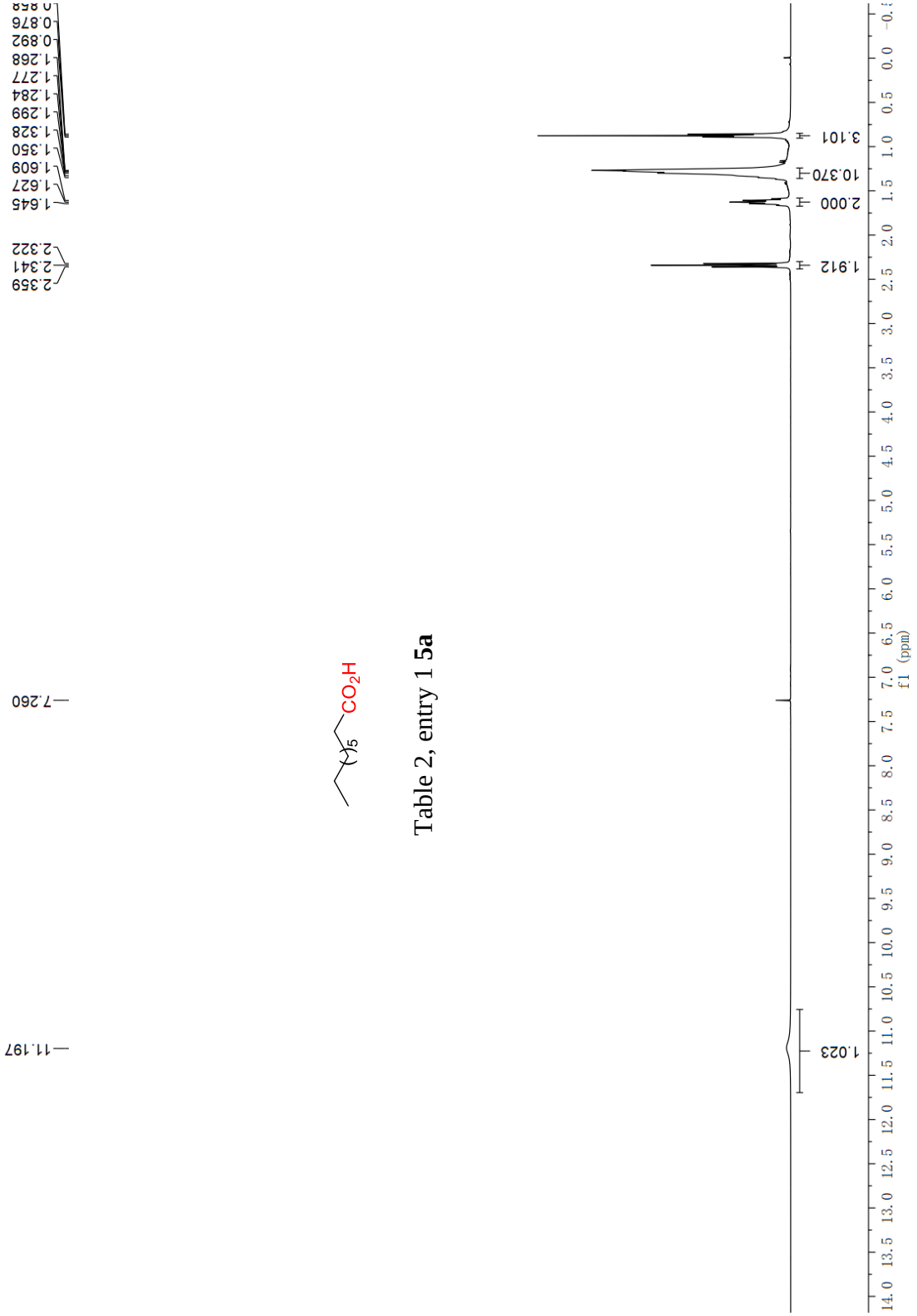
^{1}H NMR Spectrum of **5a** ($CDCl_3$, 400 MHz)



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

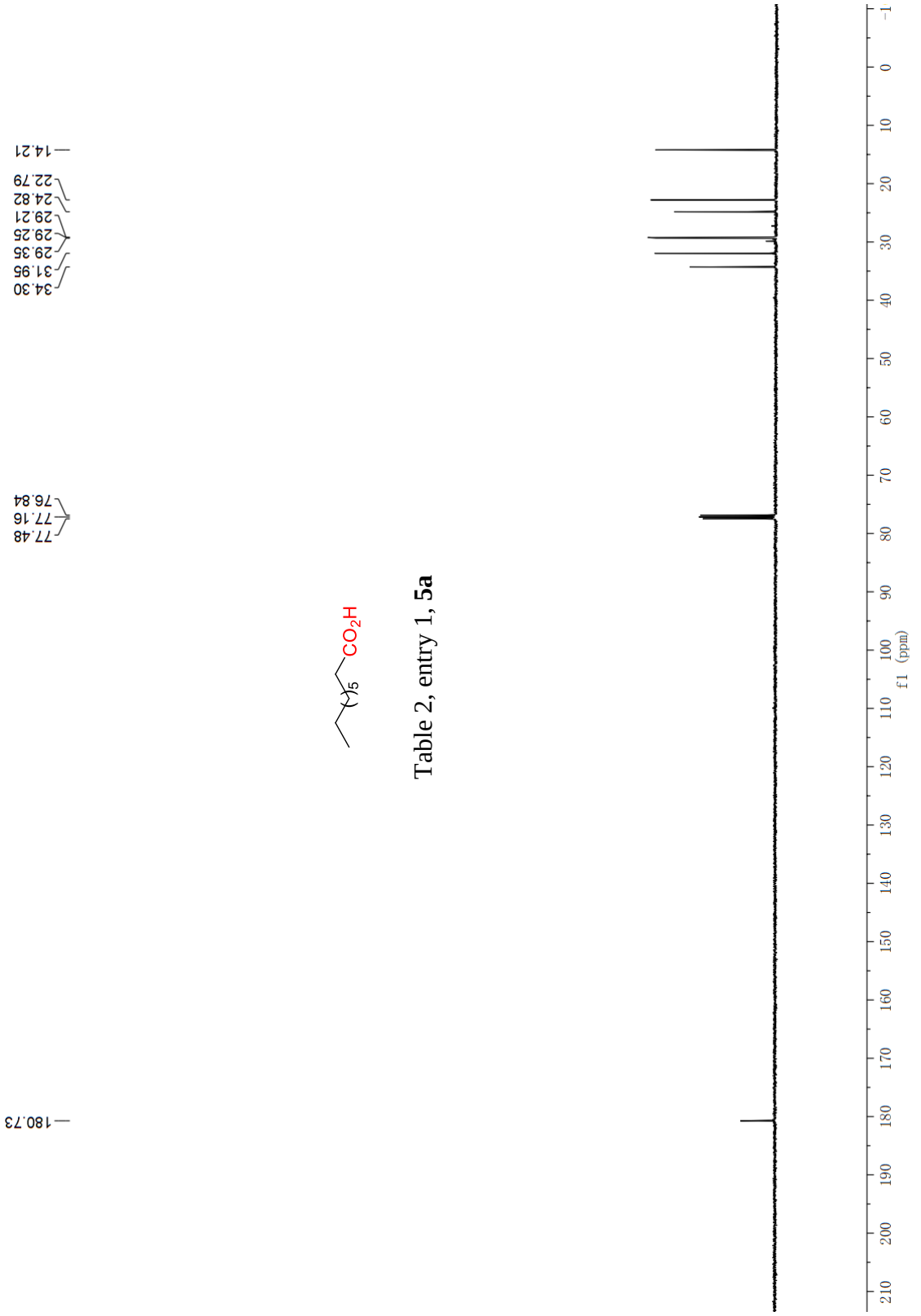


Table 2, entry 1, **5a**

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

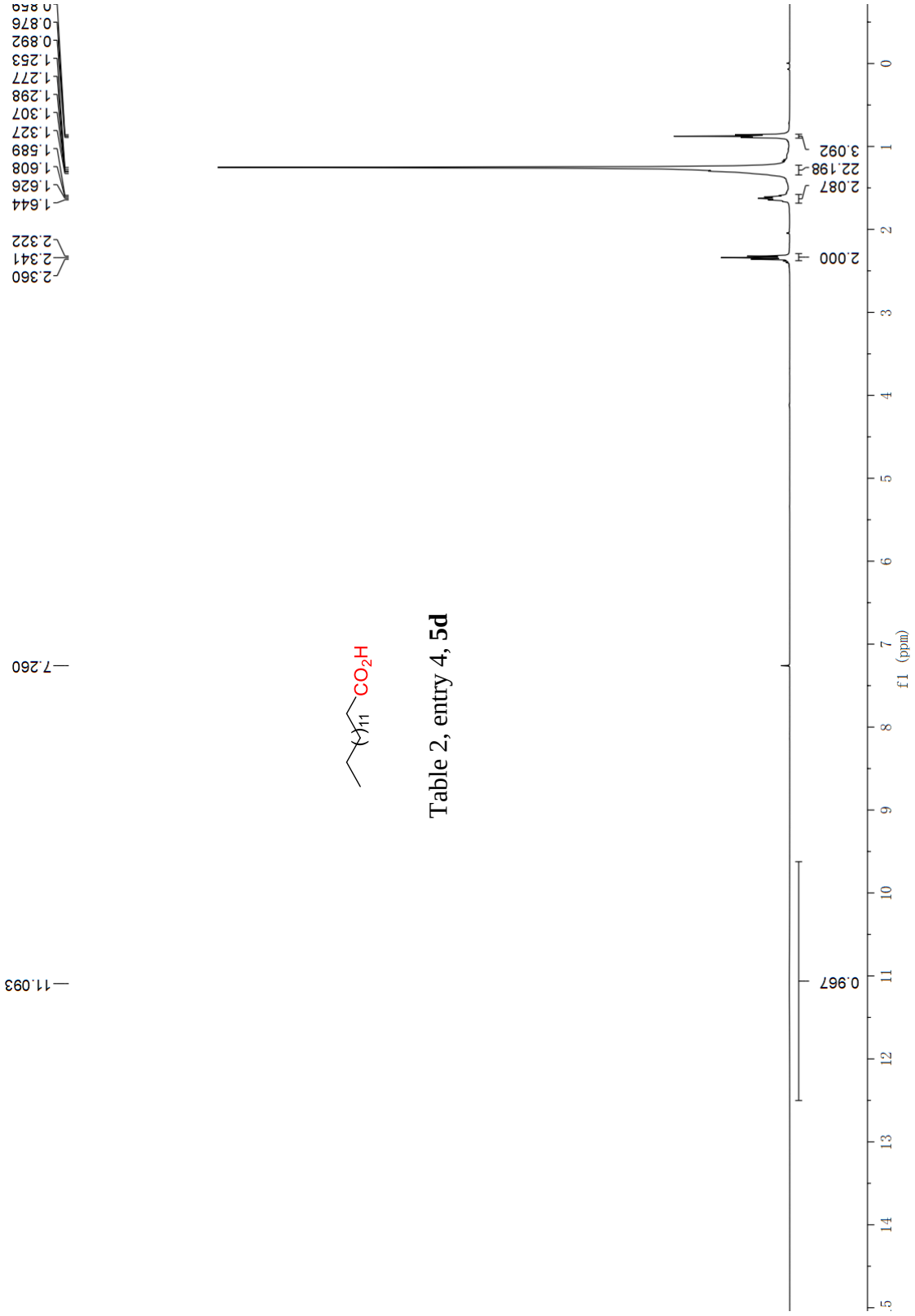


Table 2, entry 4, **5d**

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

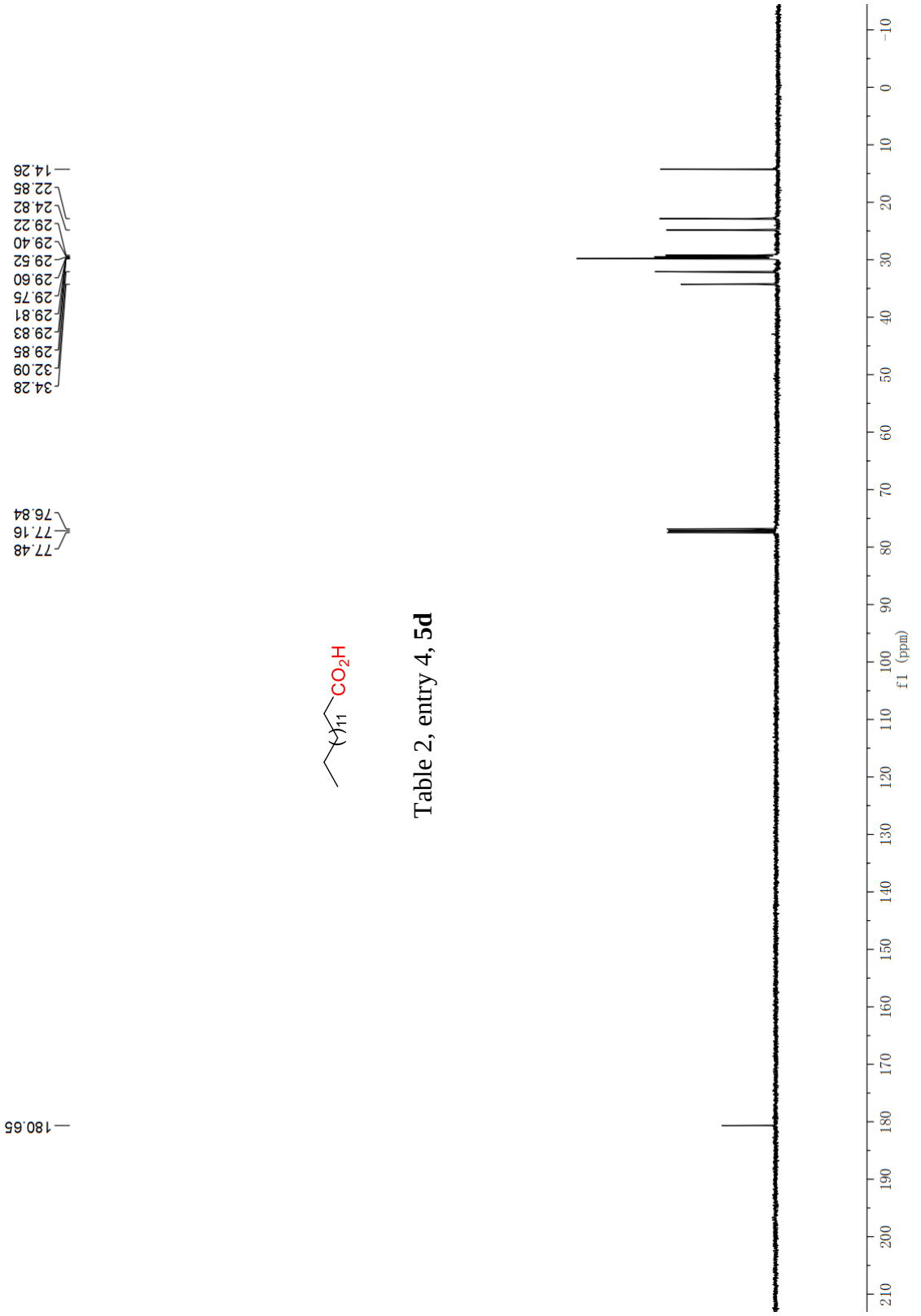


Table 2, entry 4, **5d**

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

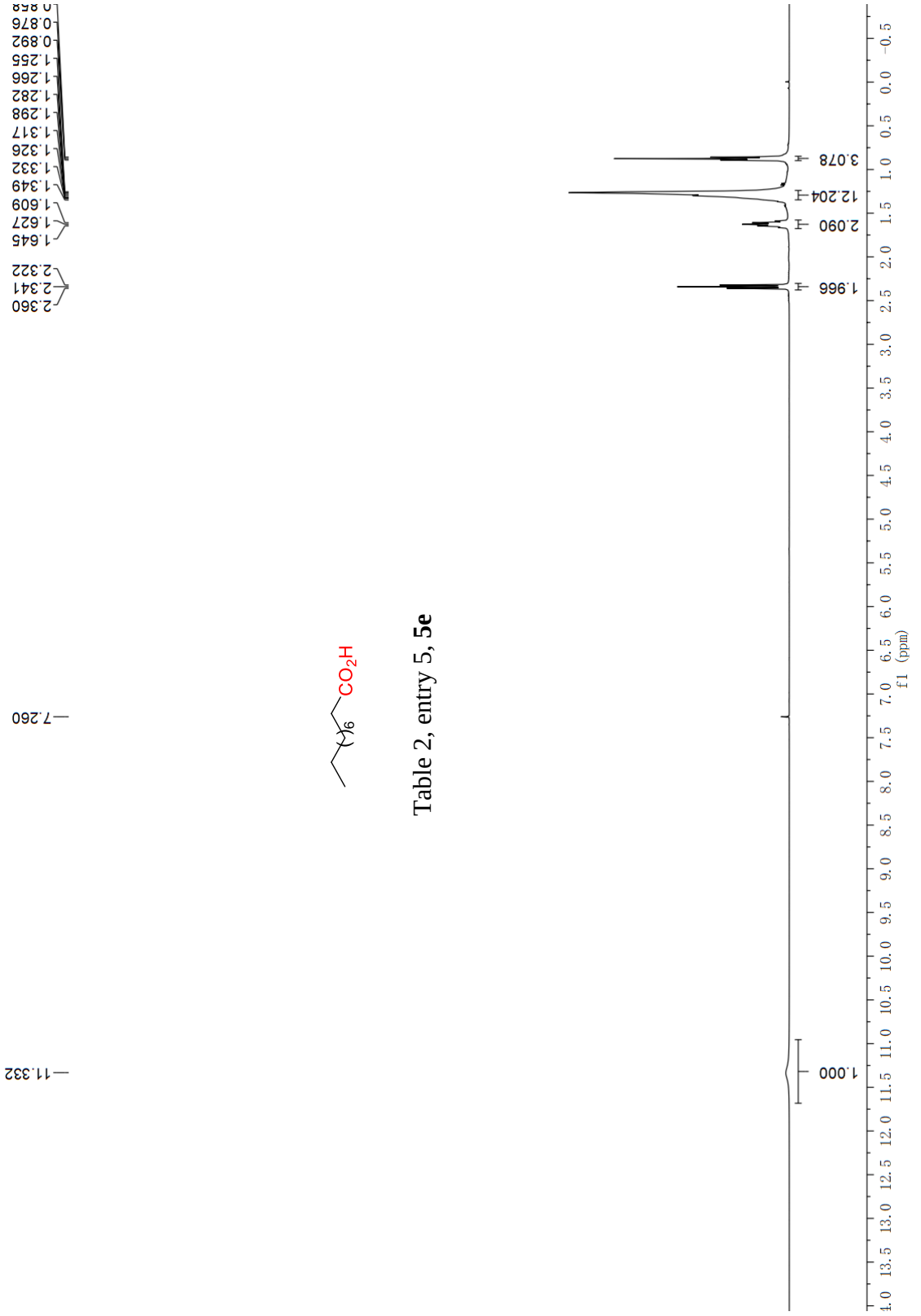


Table 2, entry 5, **5e**

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

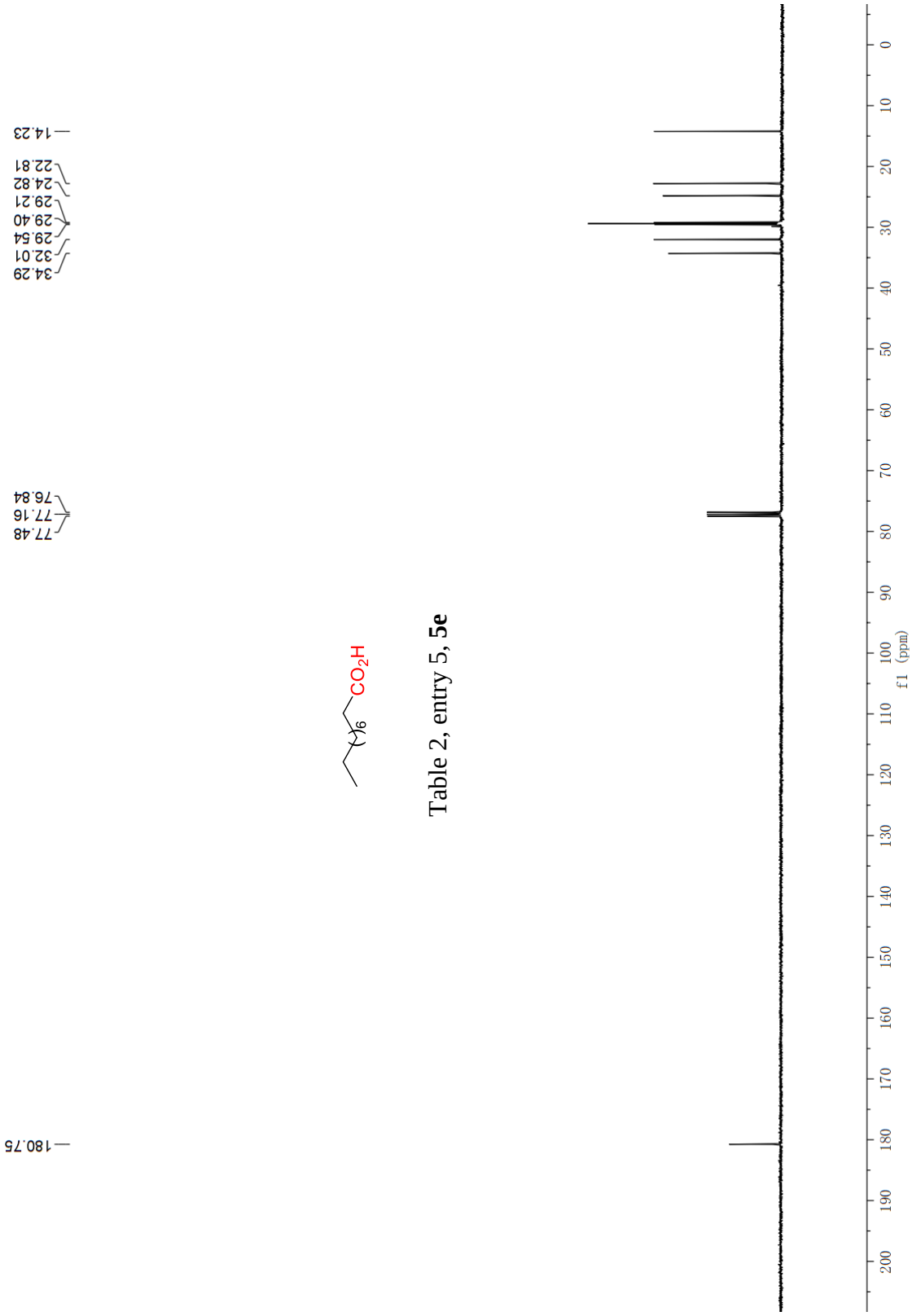
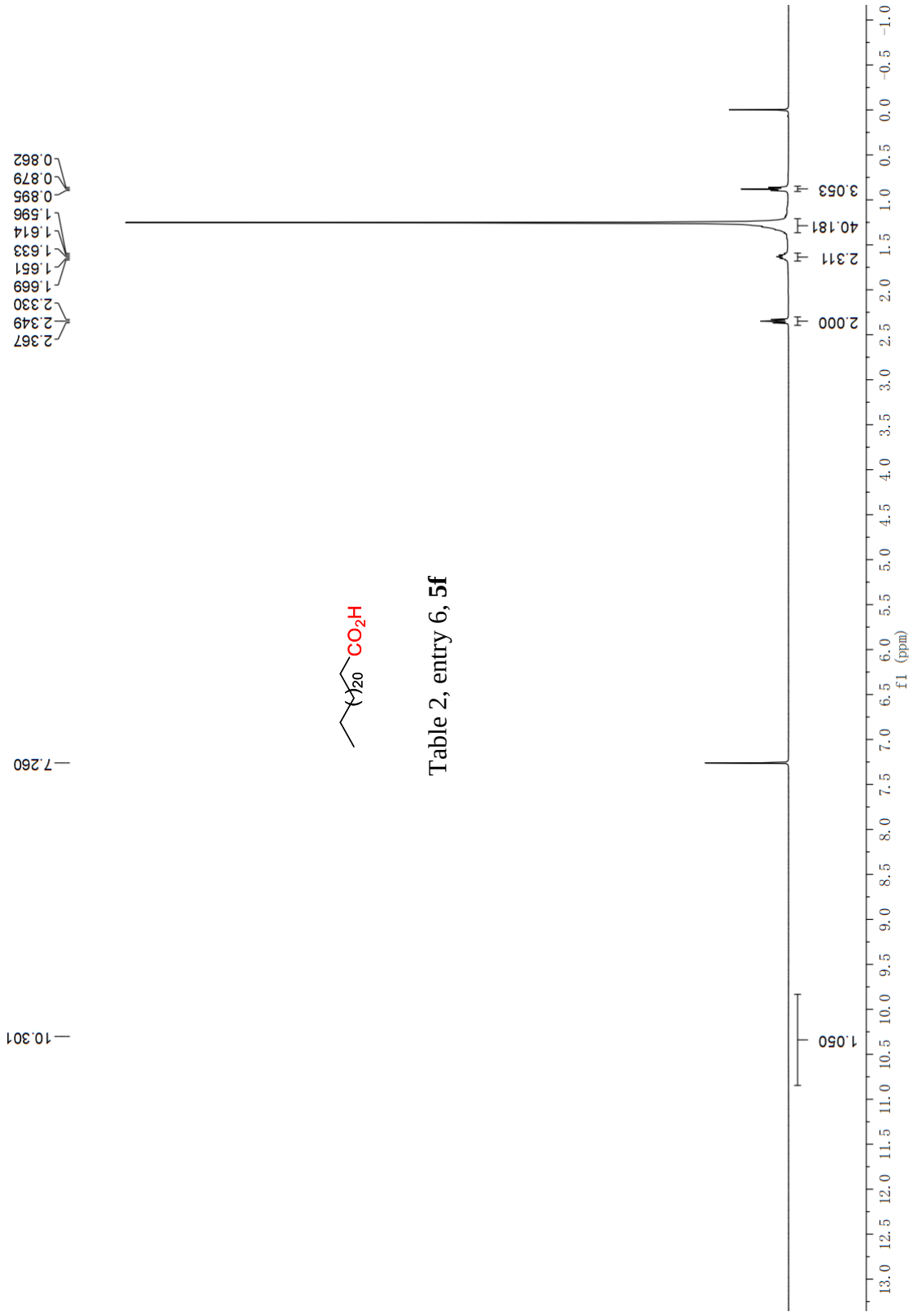


Table 2, entry 5, **5e**

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



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

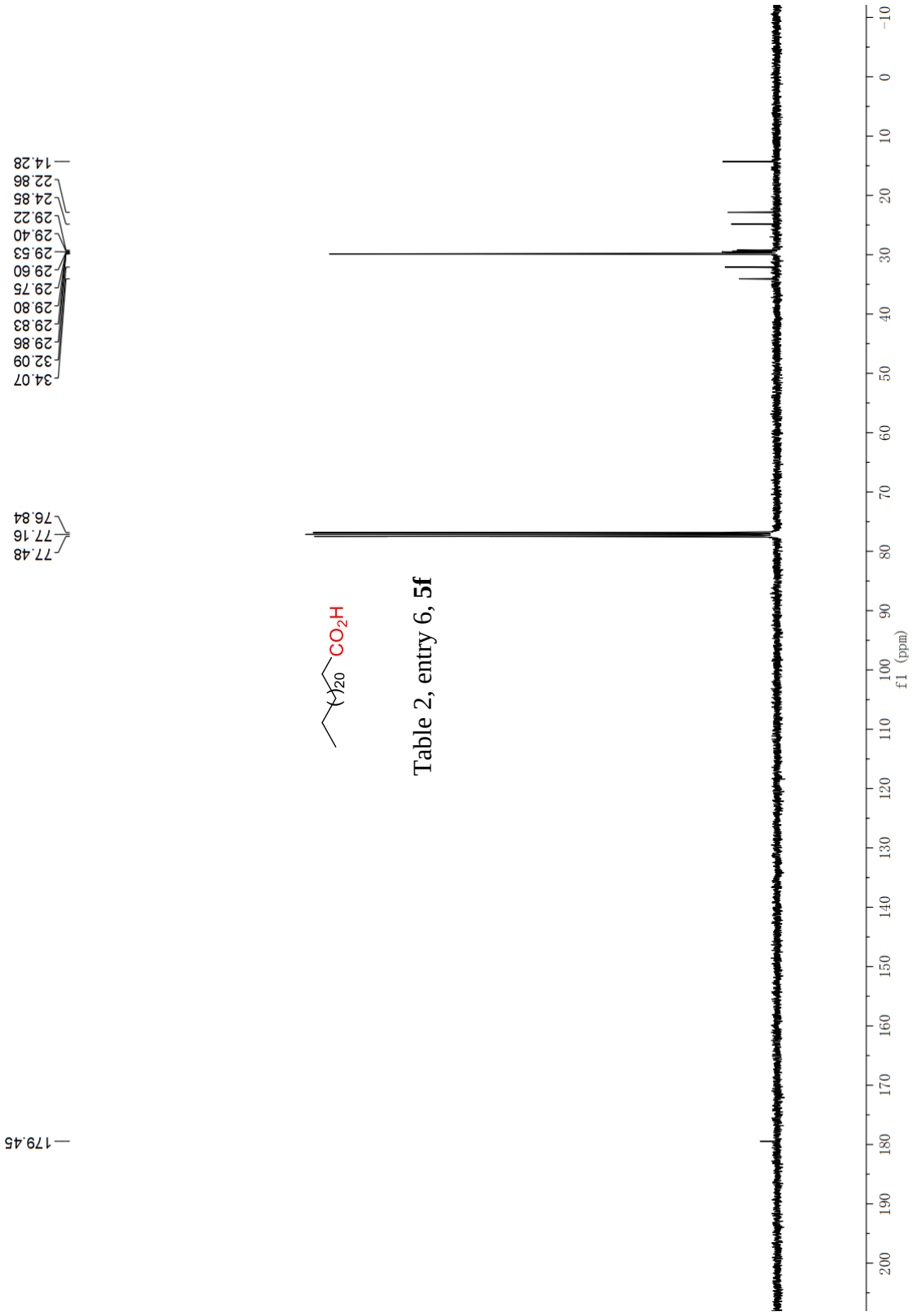
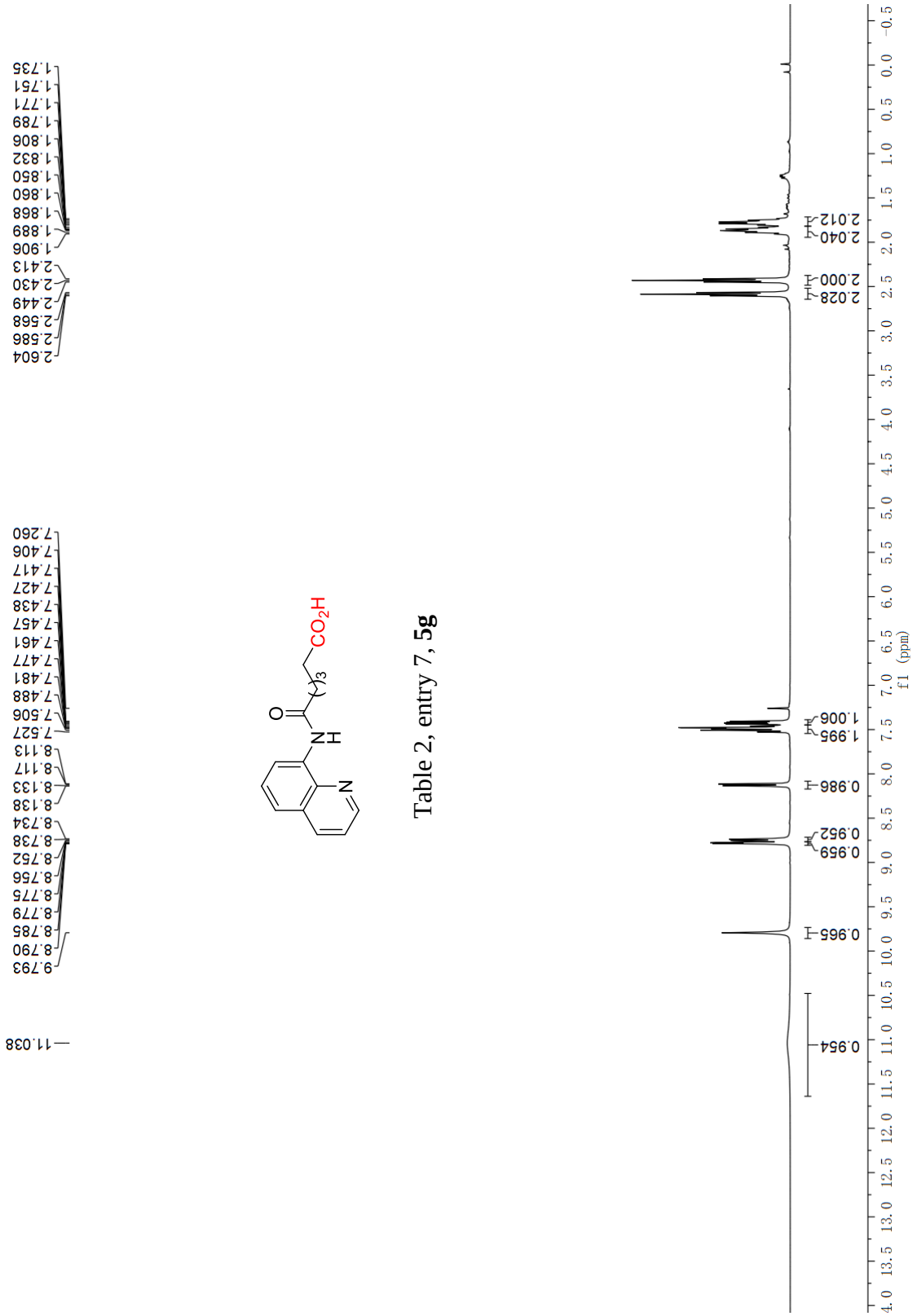
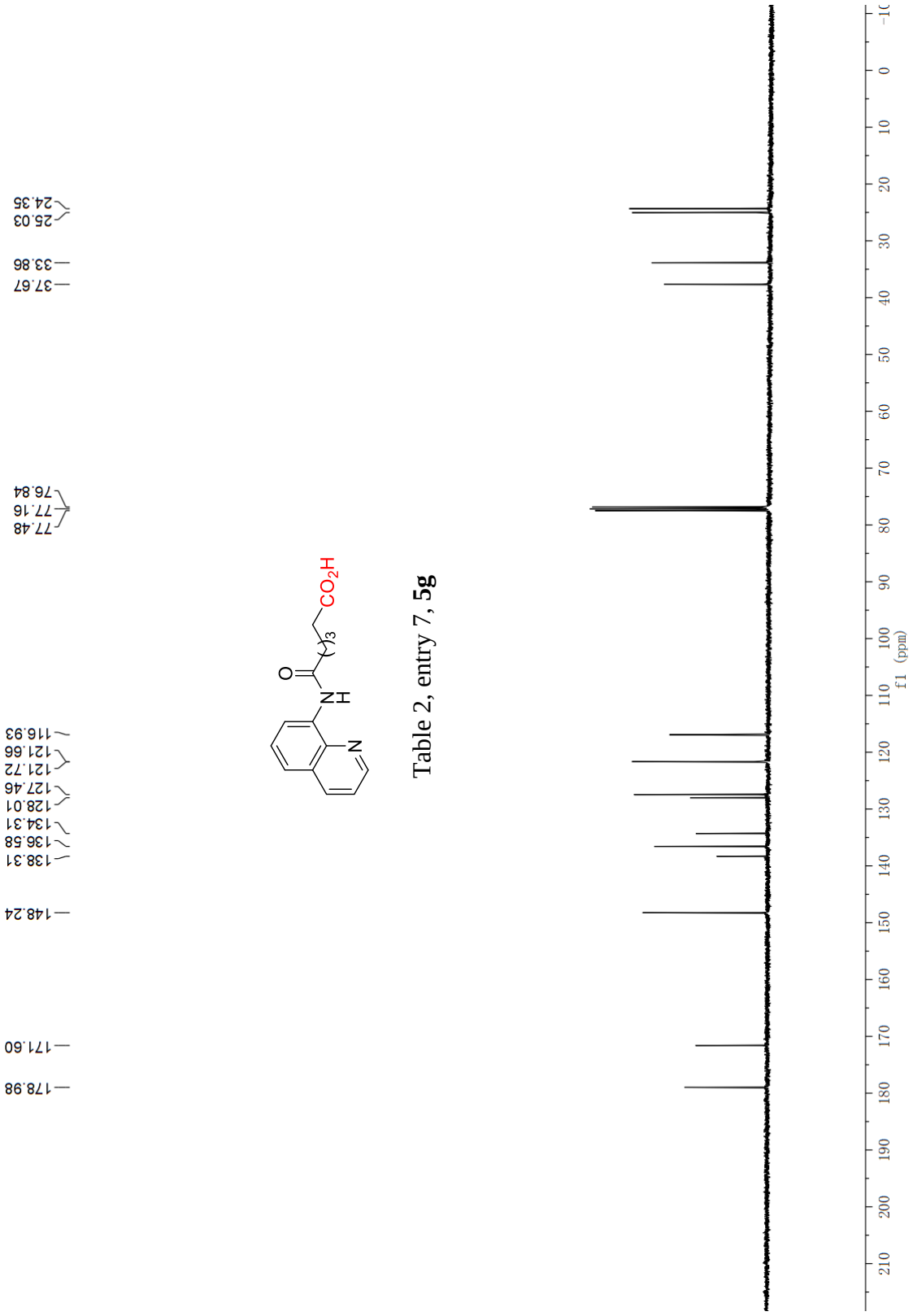


Table 2, entry 6, **5f**

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



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



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

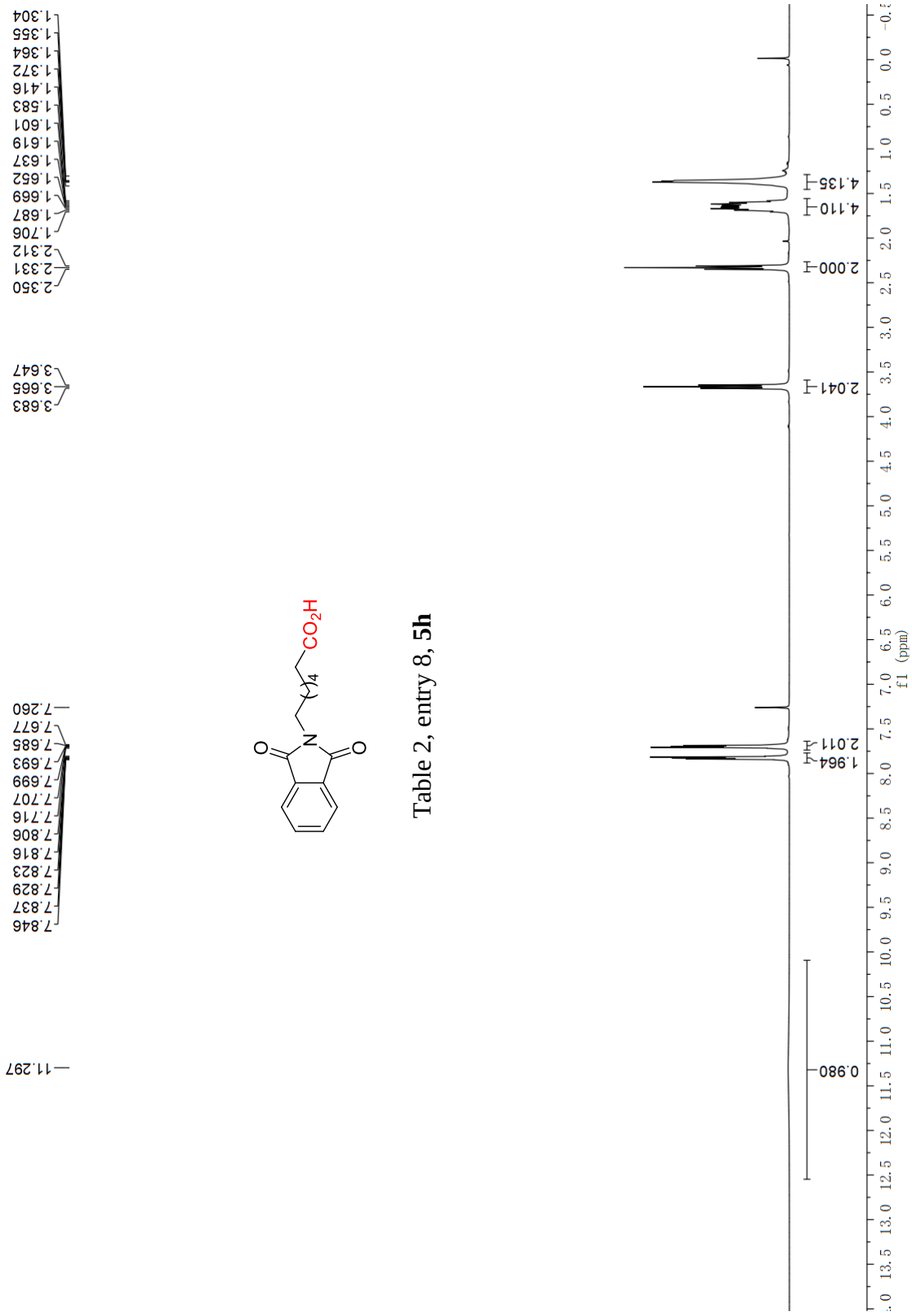


Table 2, entry 8, **5h**

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

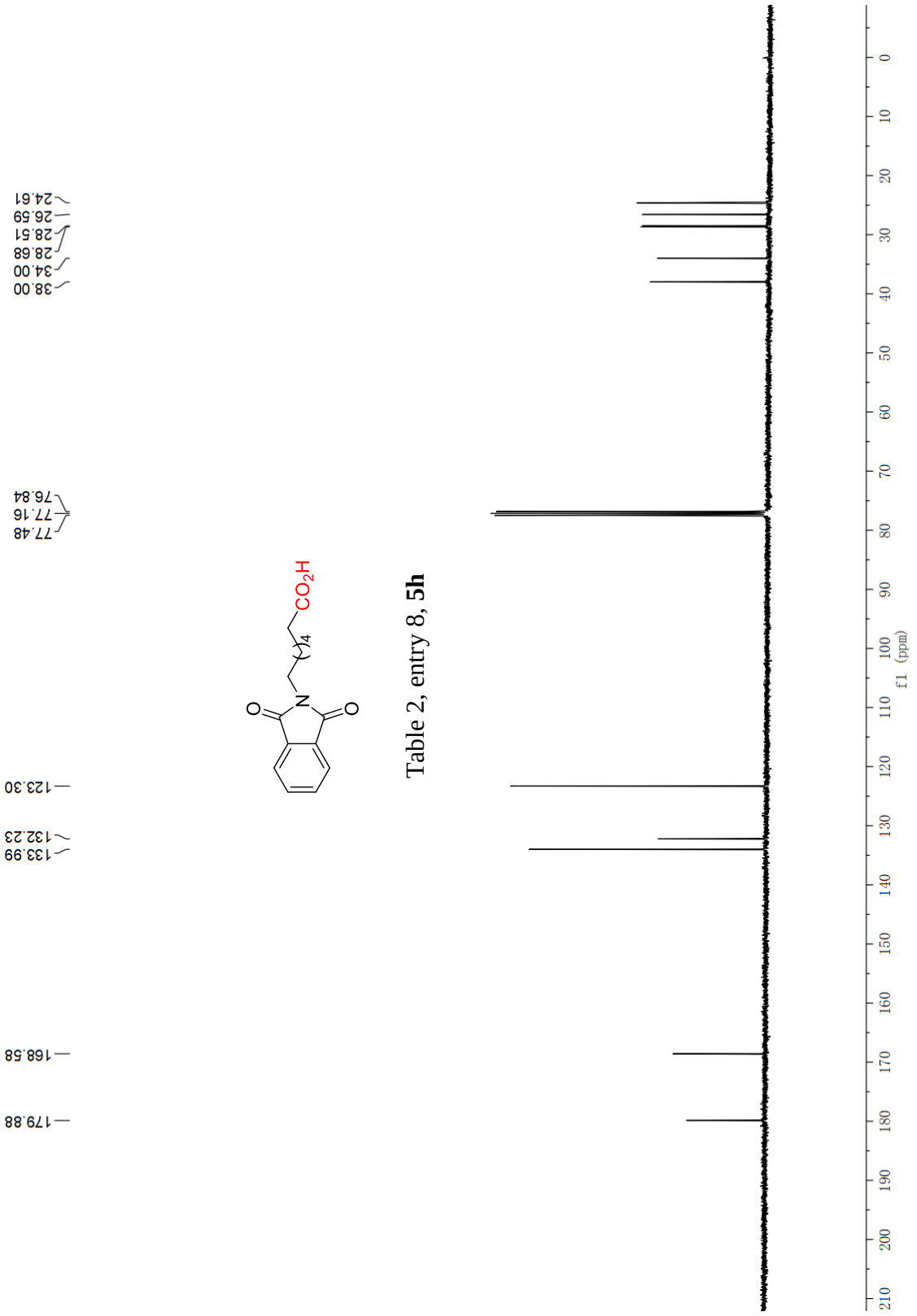
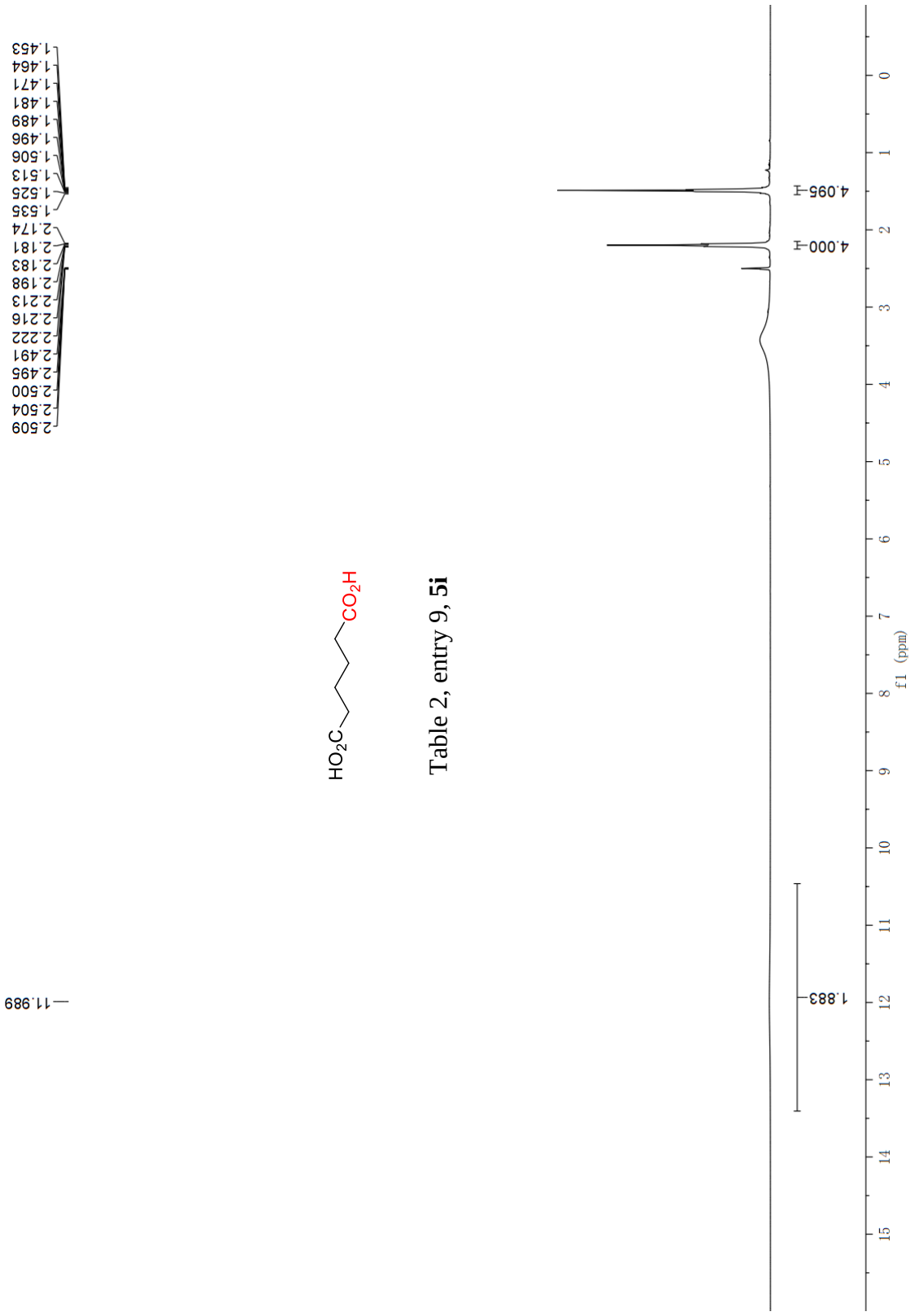
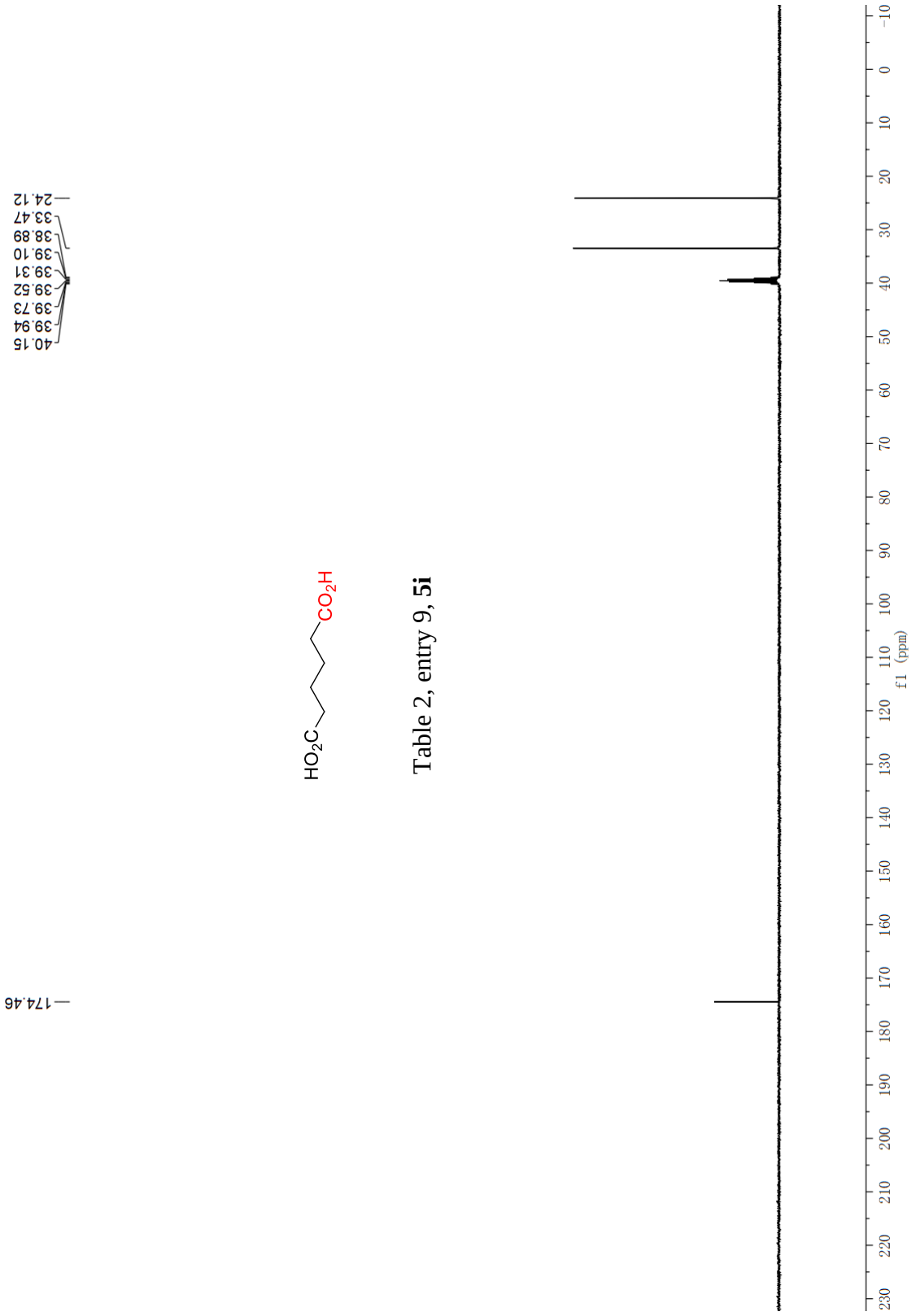


Table 2, entry 8, **5h**

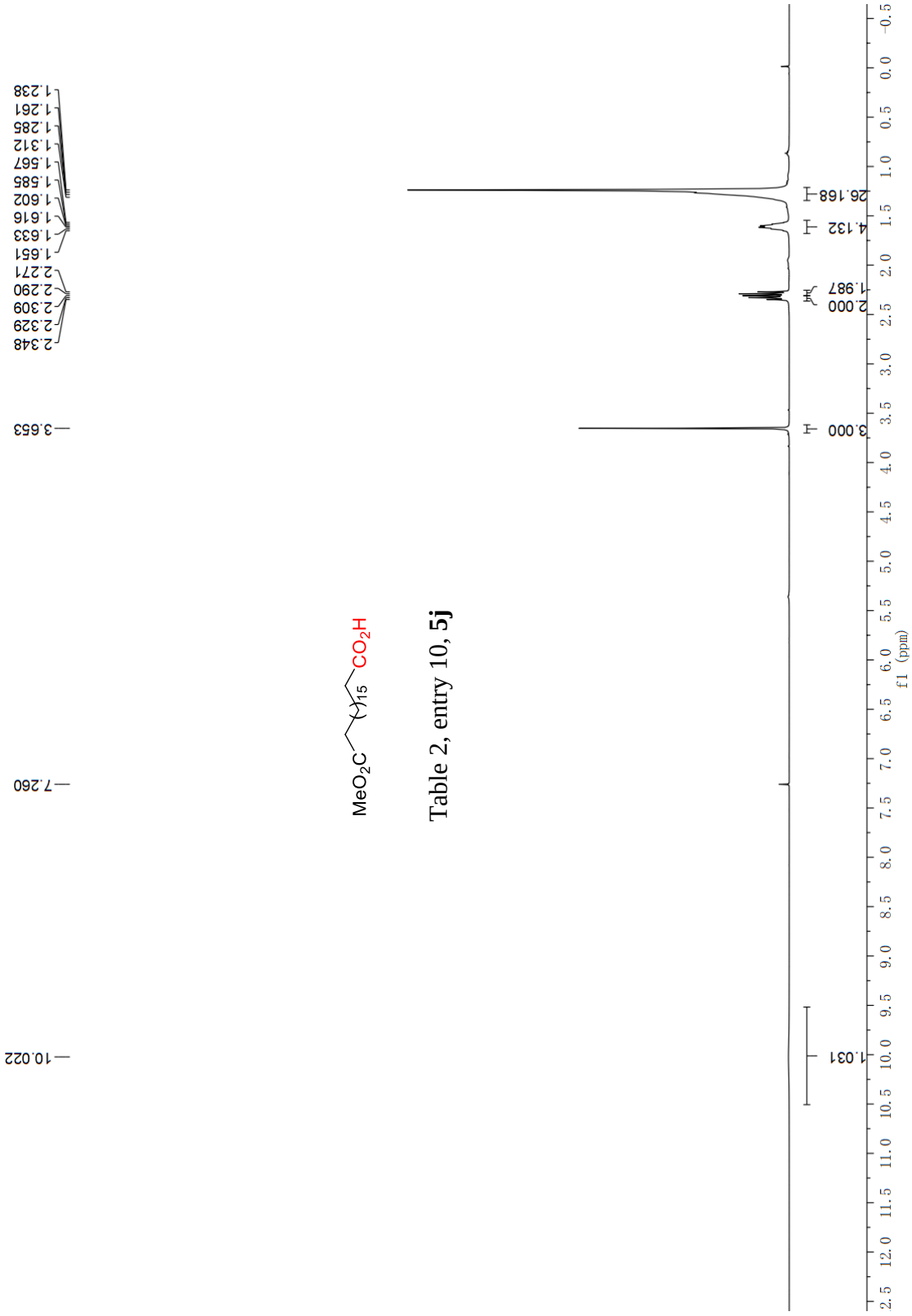
^{1}H NMR Spectrum of **5i** (DMSO-d_6, 400 MHz)



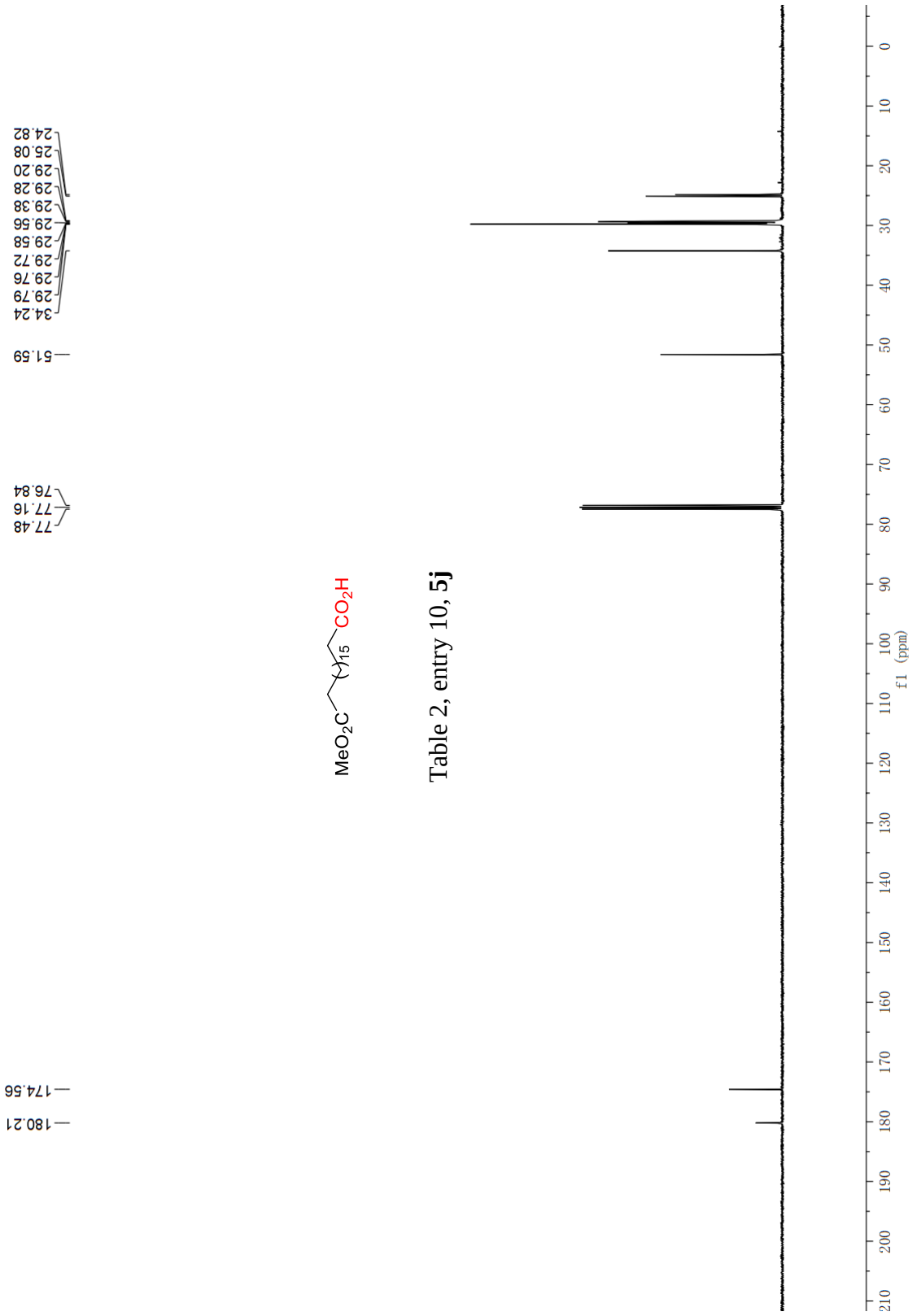
^{13}C NMR Spectrum of **5i** (DMSO-d_6, 100 MHz)



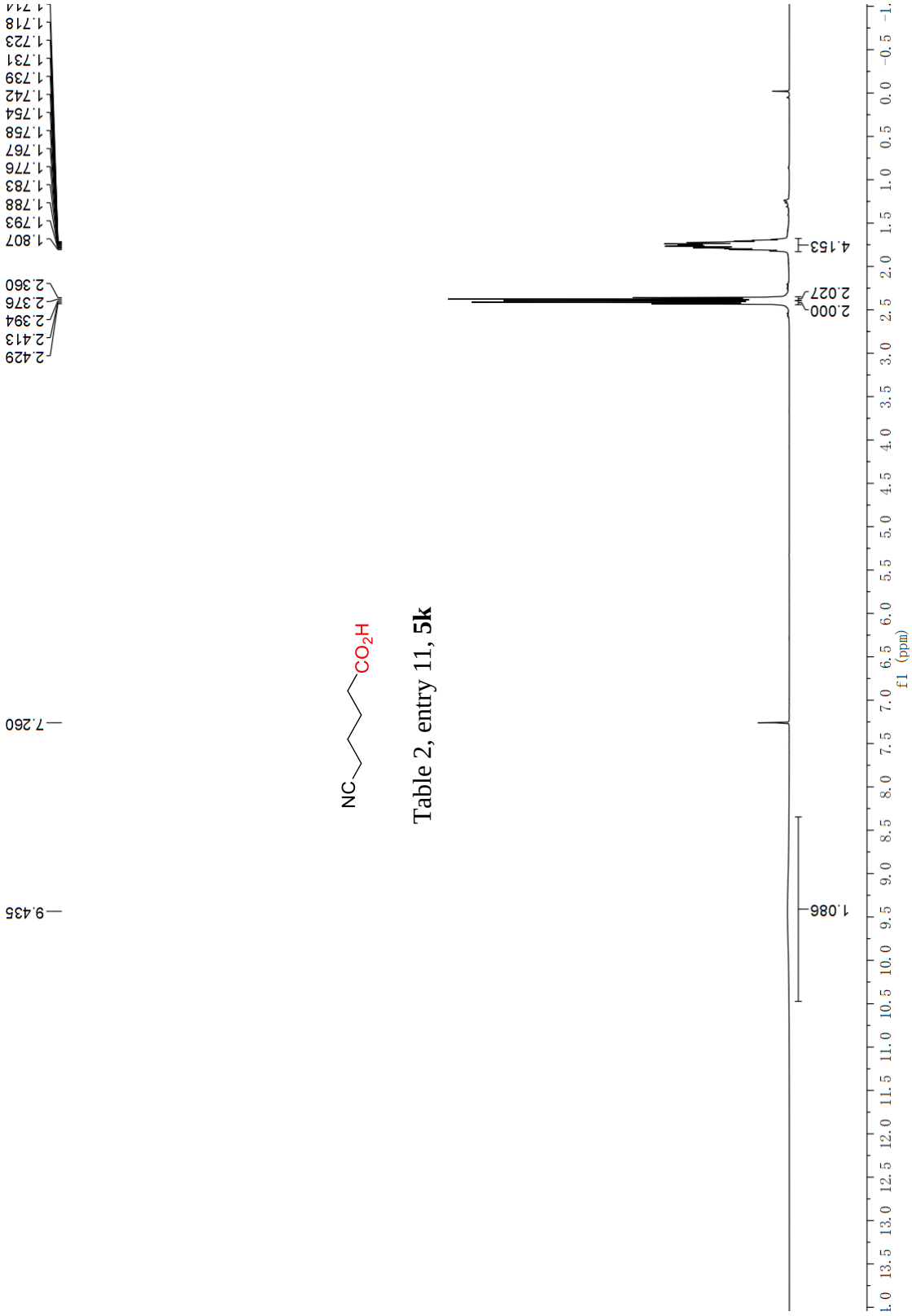
^{1}H NMR Spectrum of **5j** ($CDCl_3$, 400 MHz)



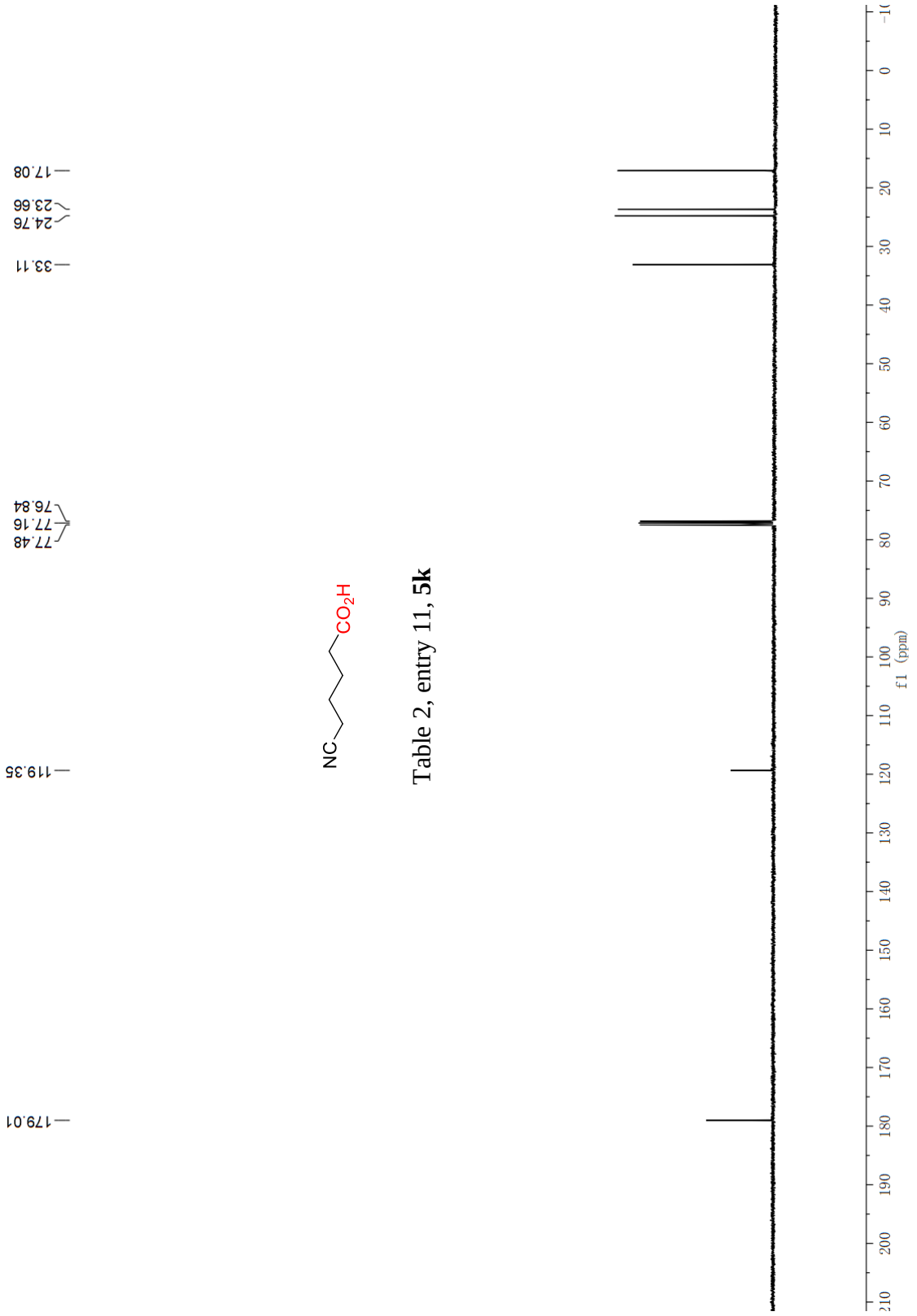
^{13}C NMR Spectrum of **5j** ($CDCl_3$, 100 MHz)



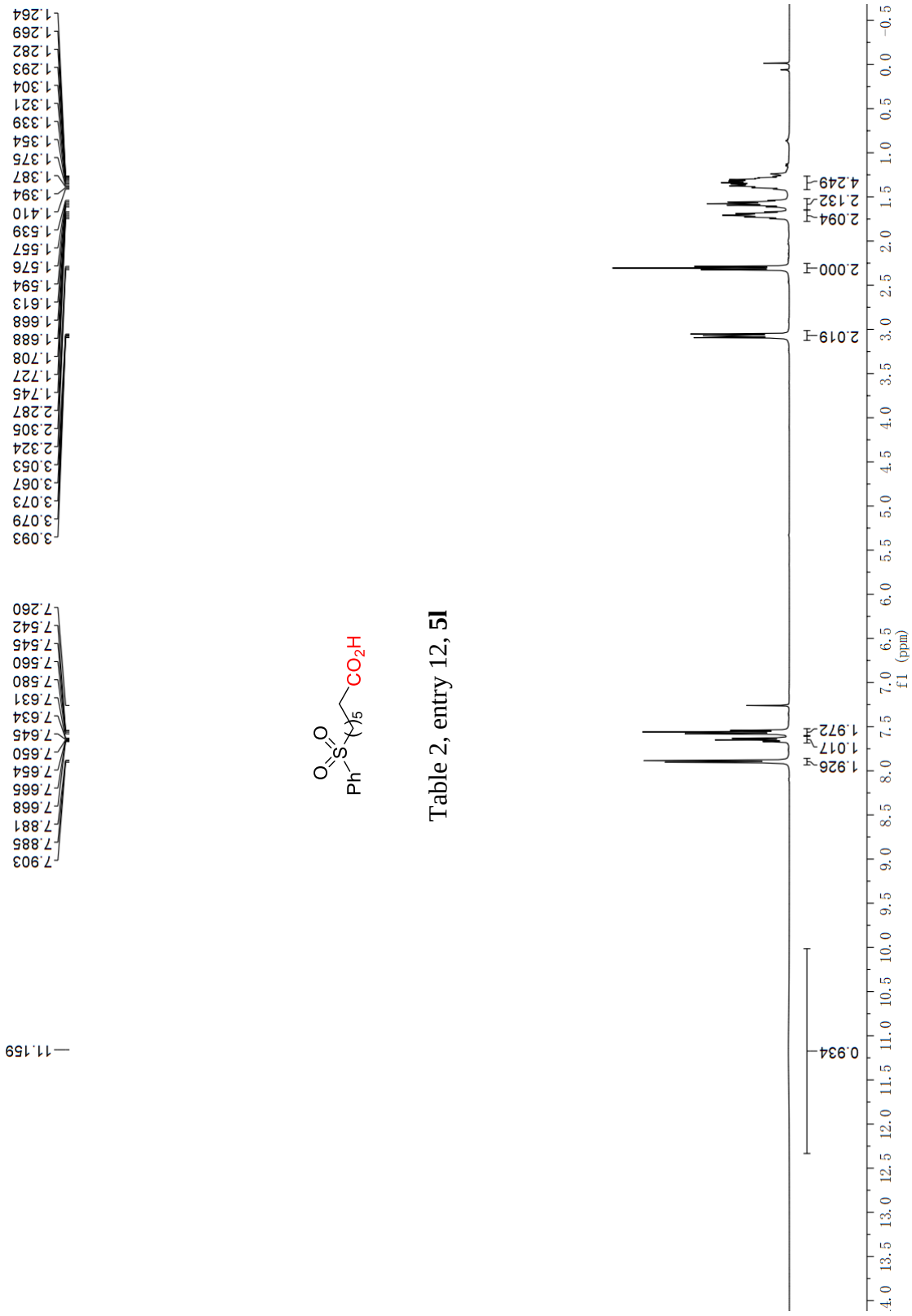
^{1}H NMR Spectrum of **5k** ($CDCl_3$, 400 MHz)



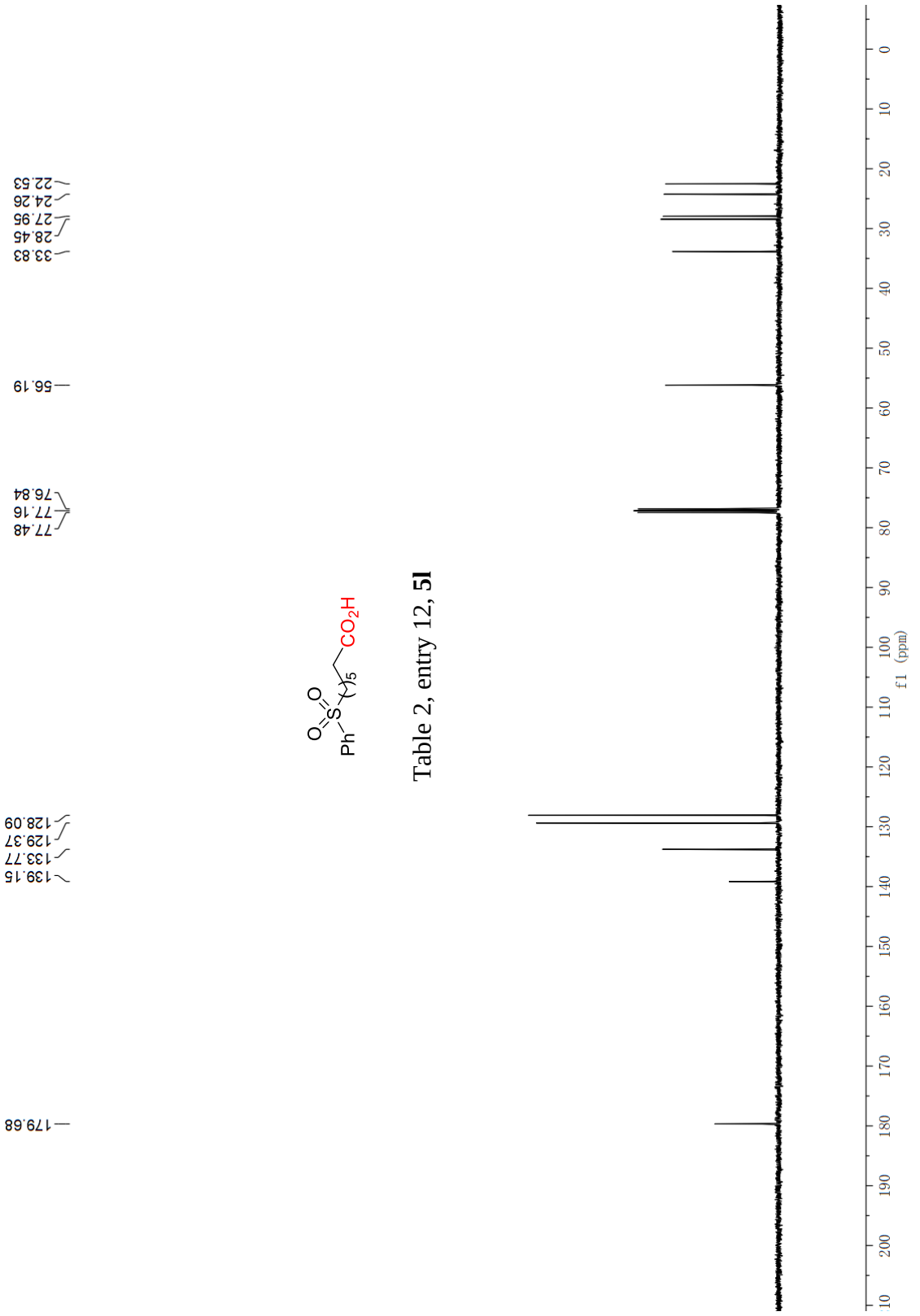
^{13}C NMR Spectrum of **5k** ($CDCl_3$, 100 MHz)



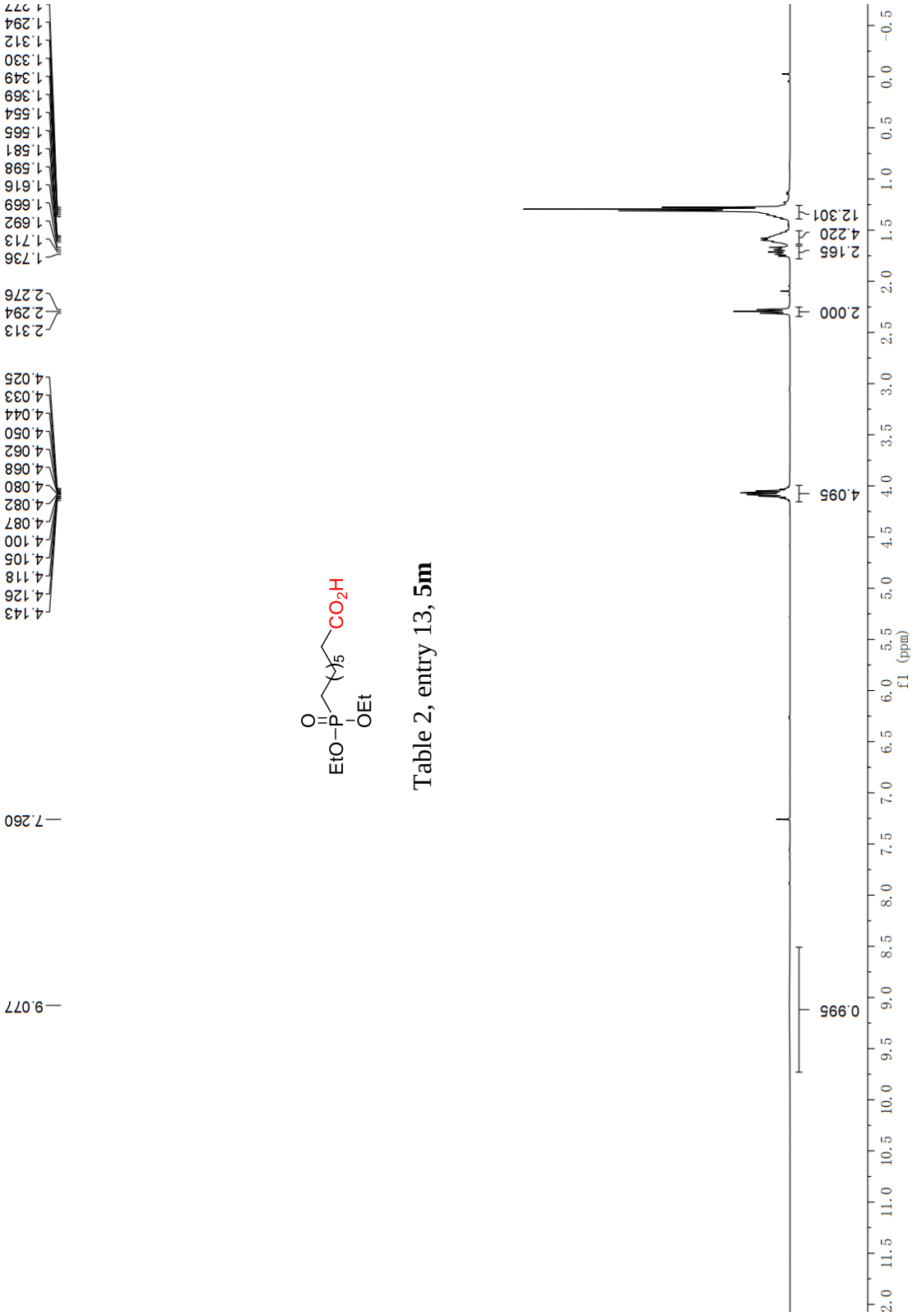
^{1}H NMR Spectrum of **5l** ($CDCl_3$, 400 MHz)



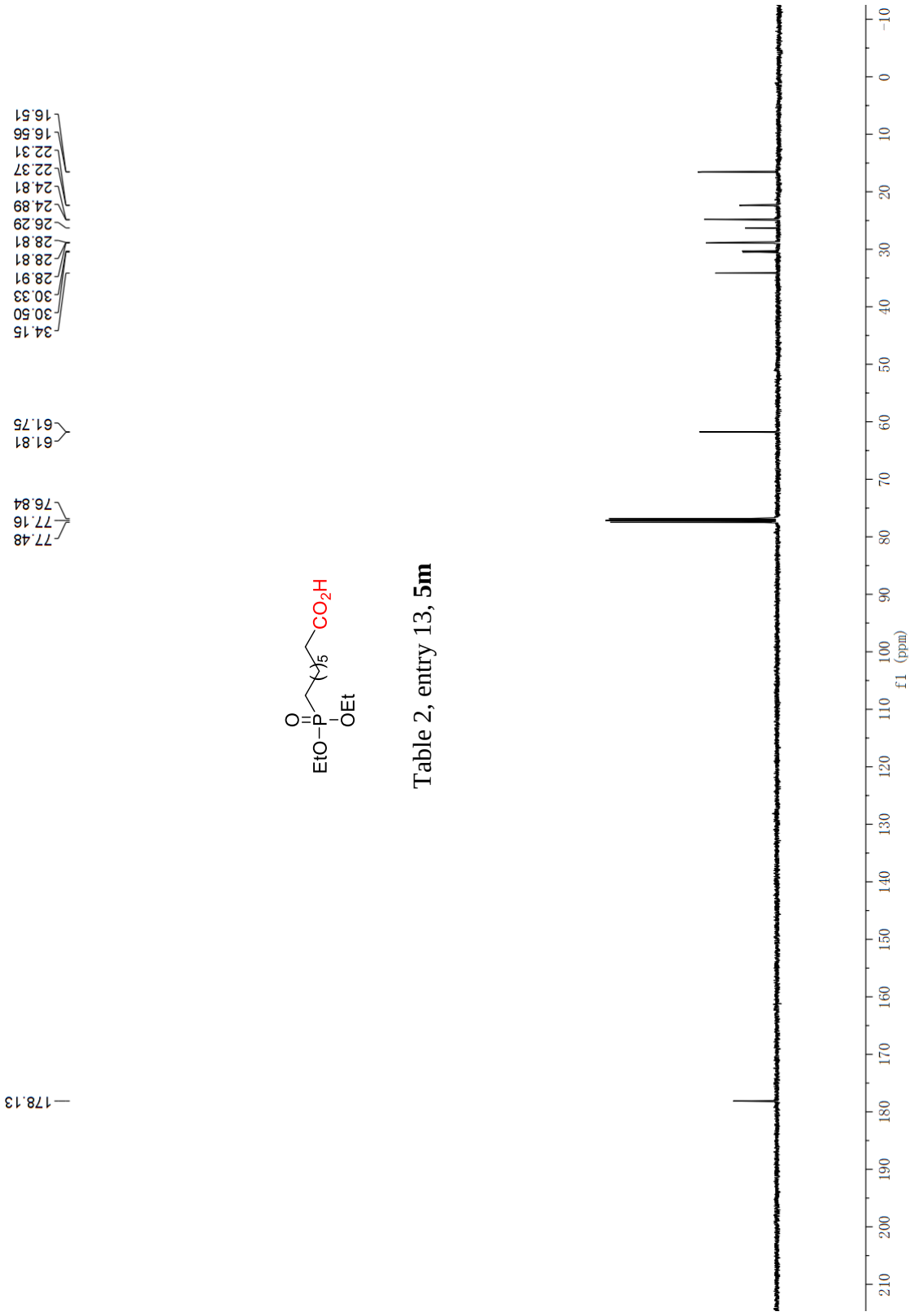
^{13}C NMR Spectrum of **5l** ($CDCl_3$, 100 MHz)



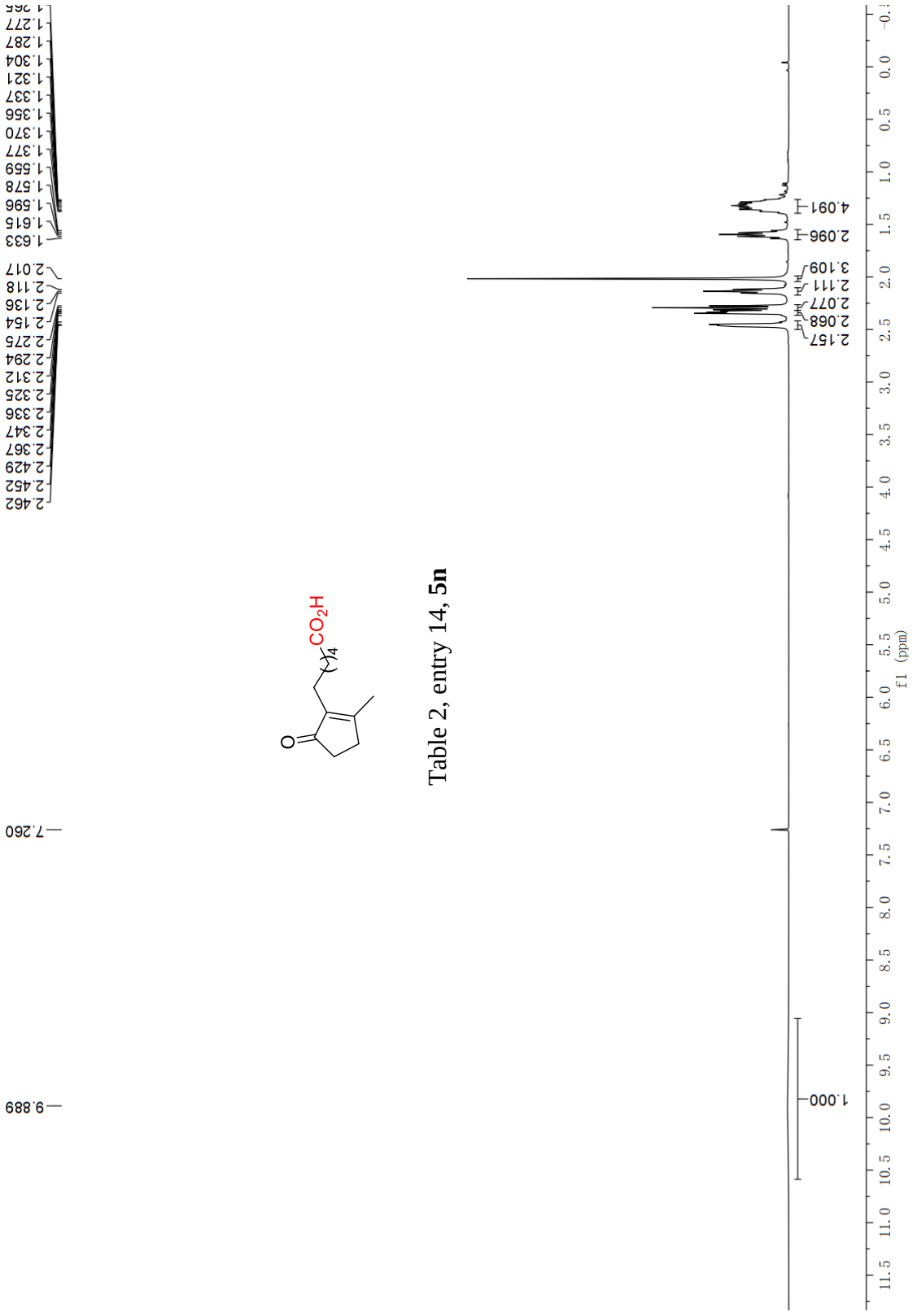
^{1}H NMR Spectrum of **5m** ($CDCl_3$, 400 MHz)



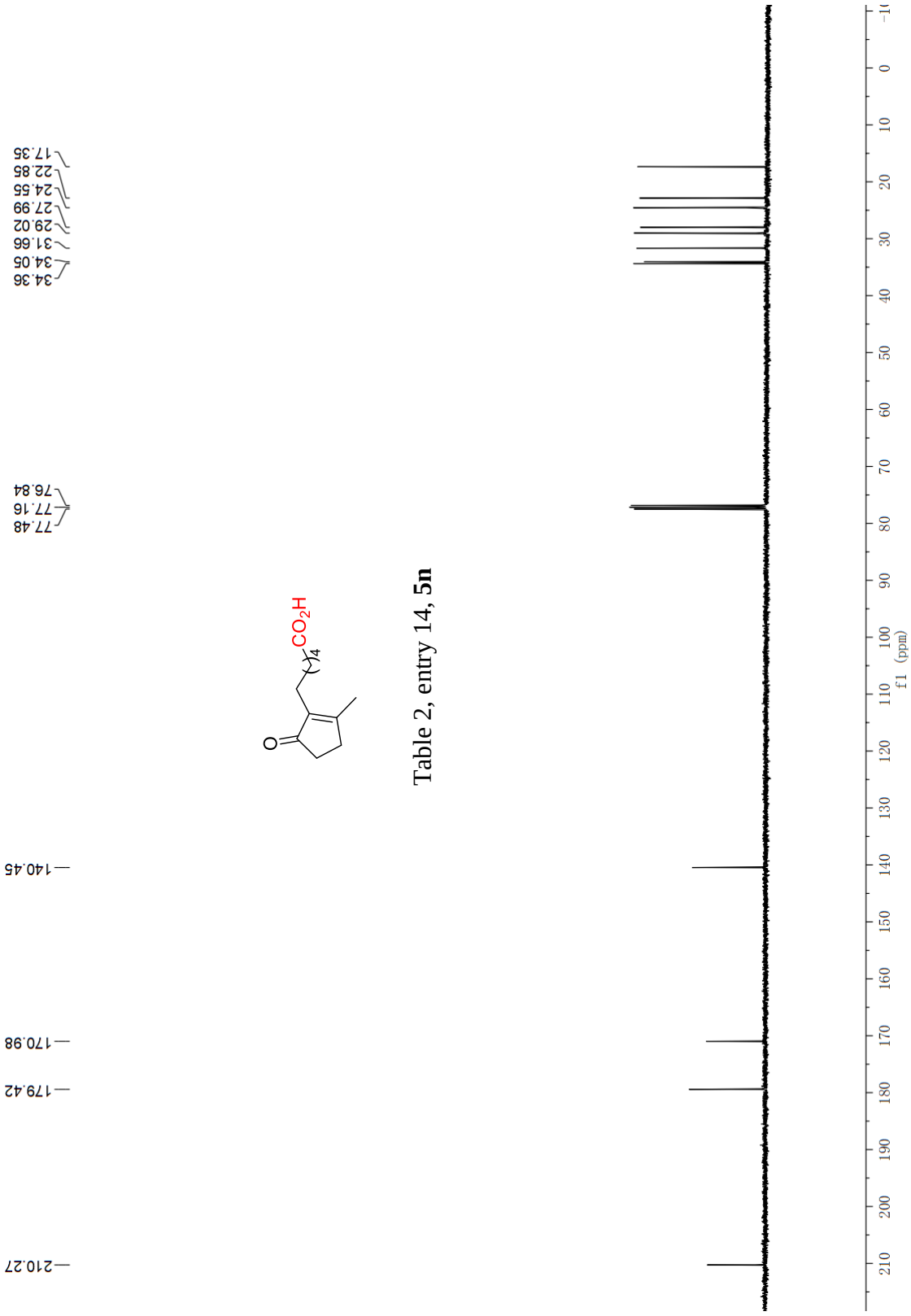
^{13}C NMR Spectrum of **5m** ($CDCl_3$, 100 MHz)



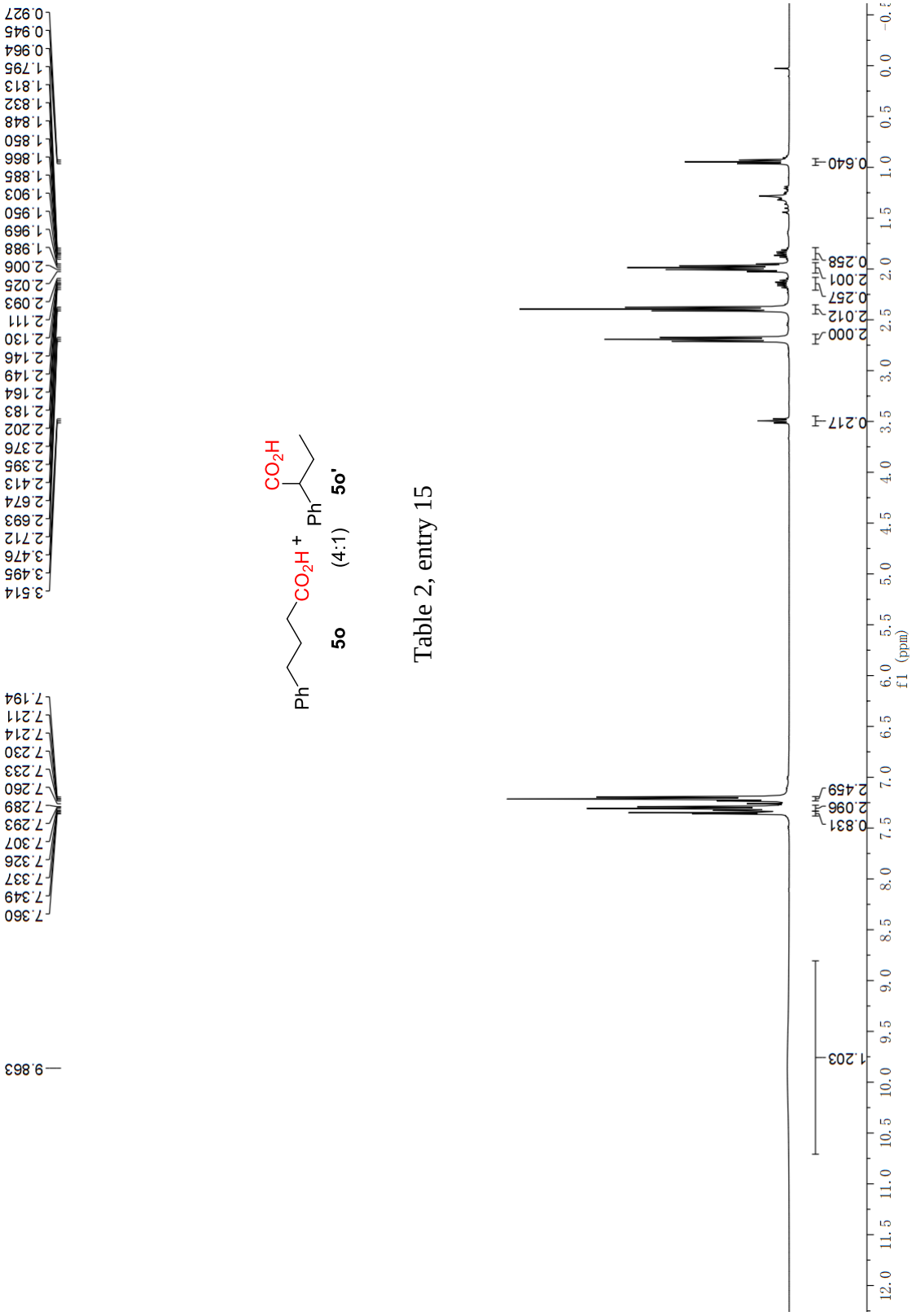
^{1}H NMR Spectrum of **5n** ($CDCl_3$, 400 MHz)



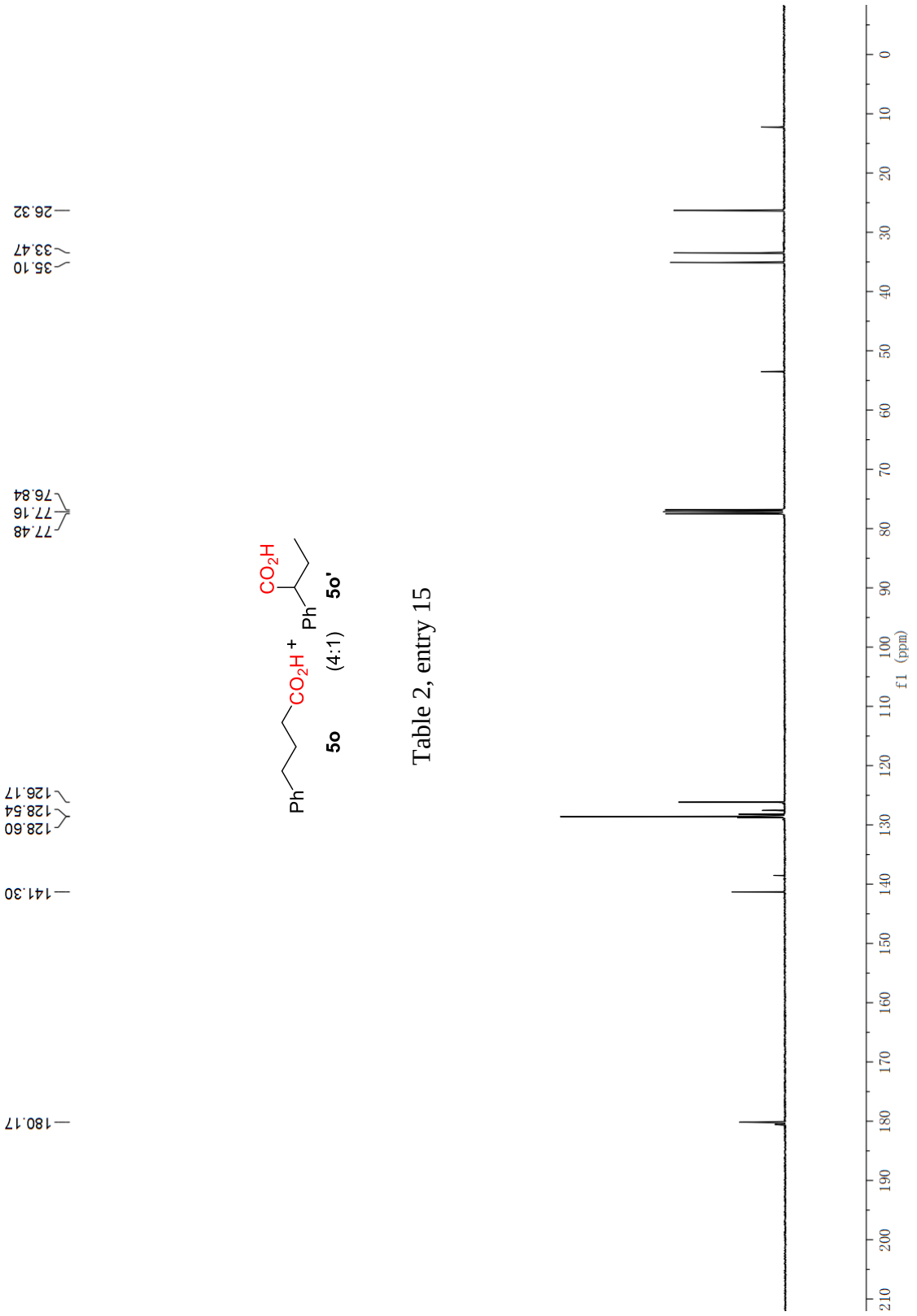
^{13}C NMR Spectrum of **5n** ($CDCl_3$, 100 MHz)



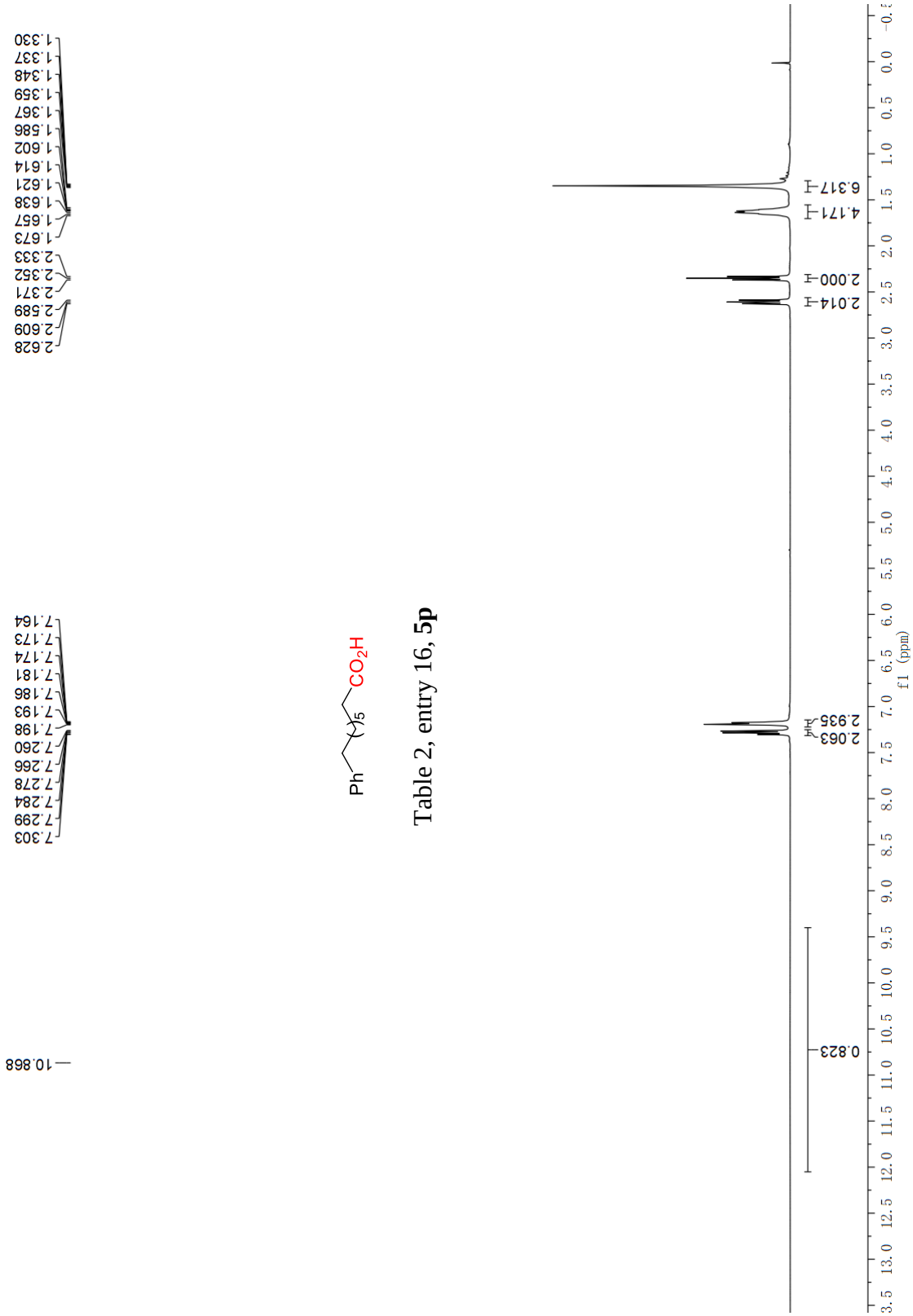
^{1}H NMR Spectrum of **5o + 5o'** ($CDCl_3$, 400 MHz)



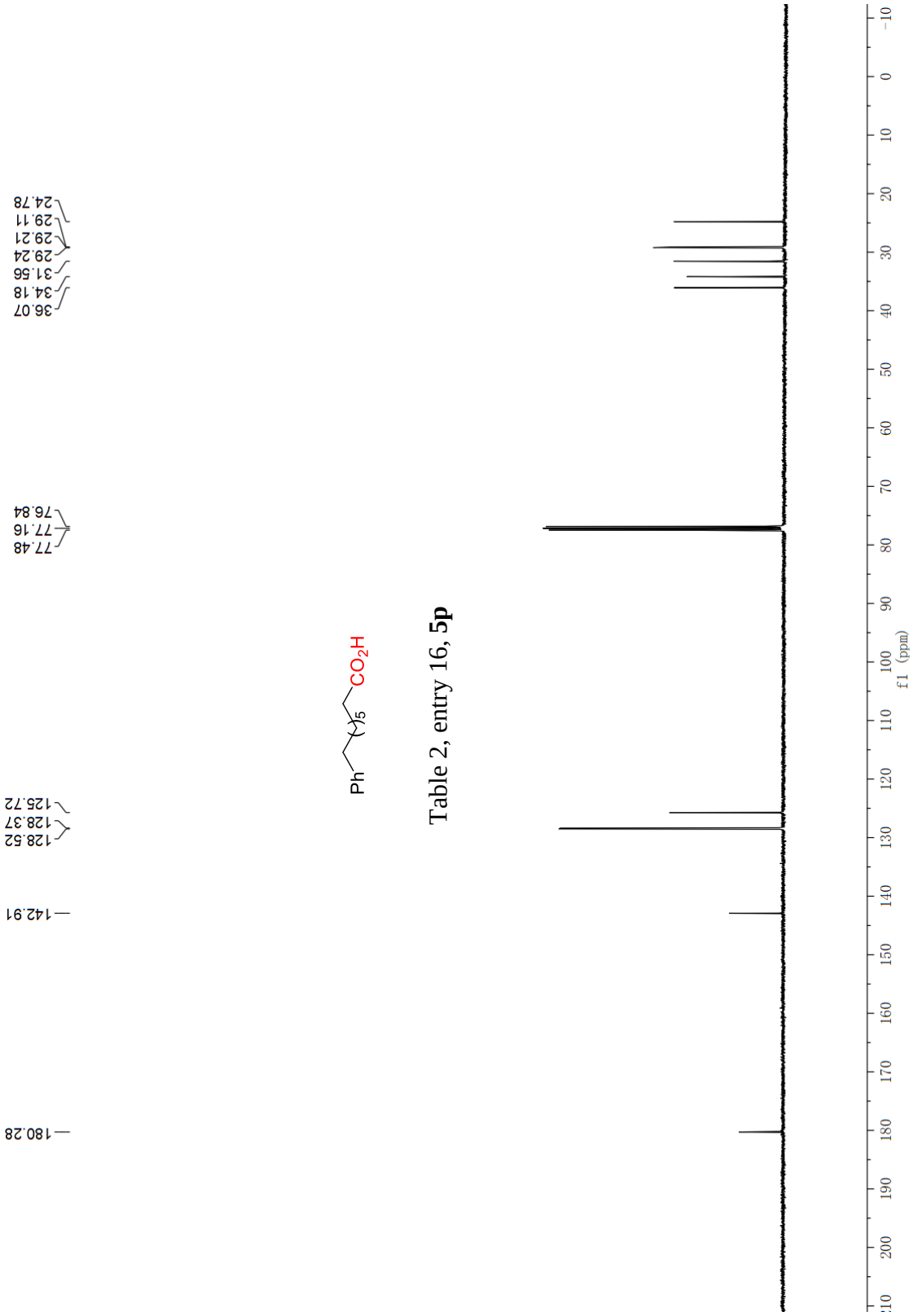
^{13}C NMR Spectrum of **5o + 5o'** ($CDCl_3$, 100 MHz)



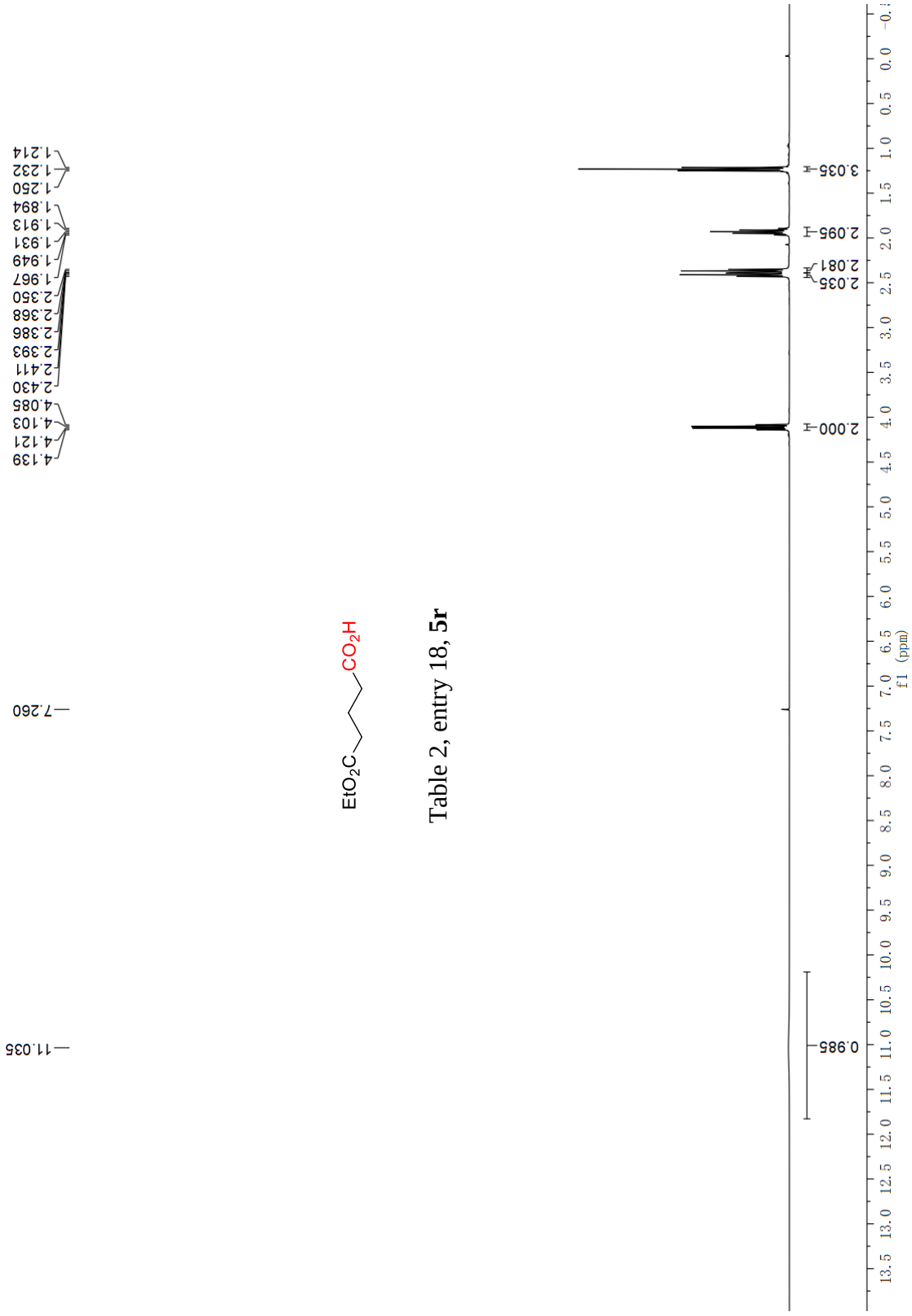
^{1}H NMR Spectrum of **5p** ($CDCl_3$, 400 MHz)



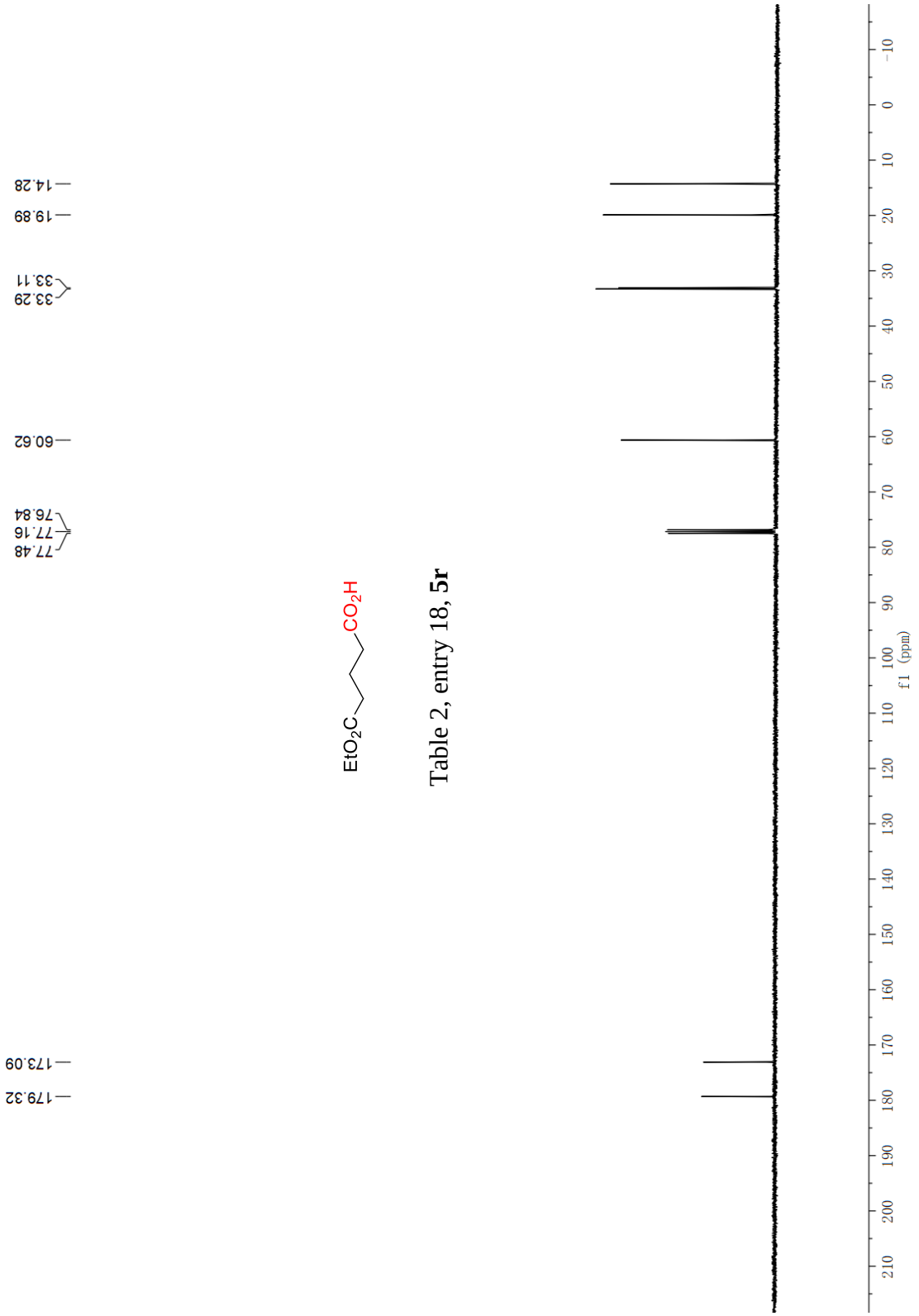
^{13}C NMR Spectrum of **5p** ($CDCl_3$, 100 MHz)



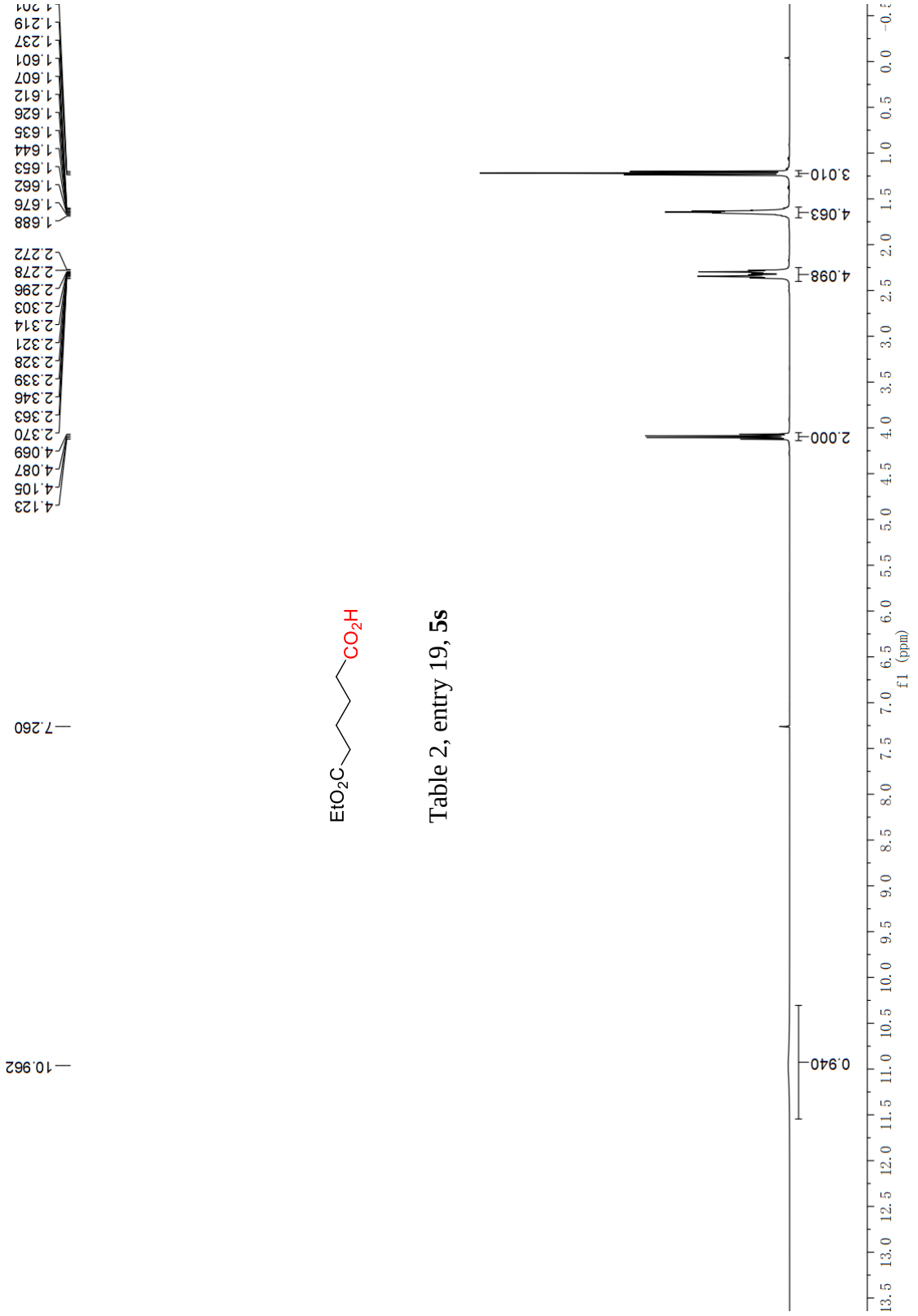
^{1}H NMR Spectrum of **5r** ($CDCl_3$, 400 MHz)



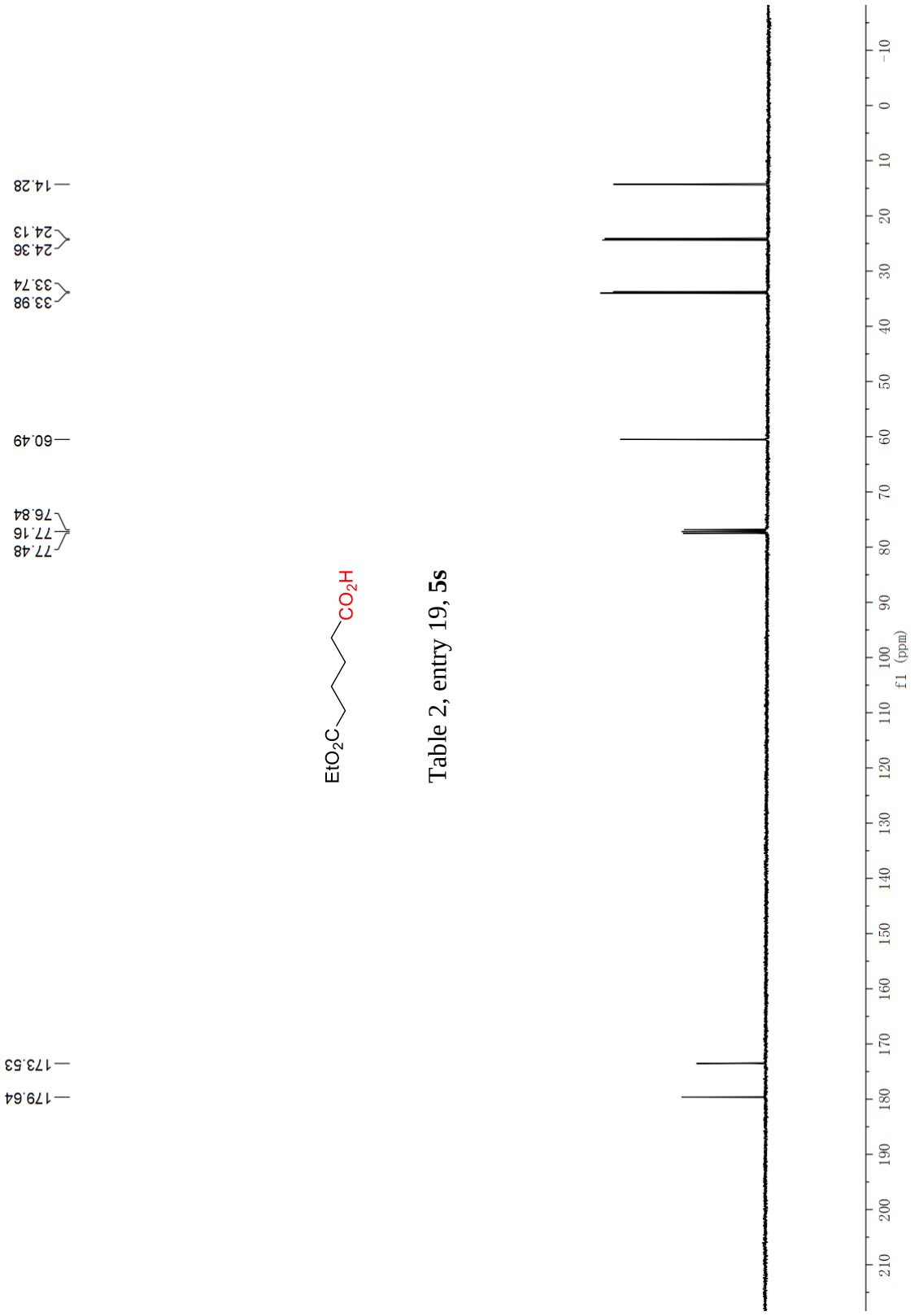
^{13}C NMR Spectrum of **5r** ($CDCl_3$, 100 MHz)



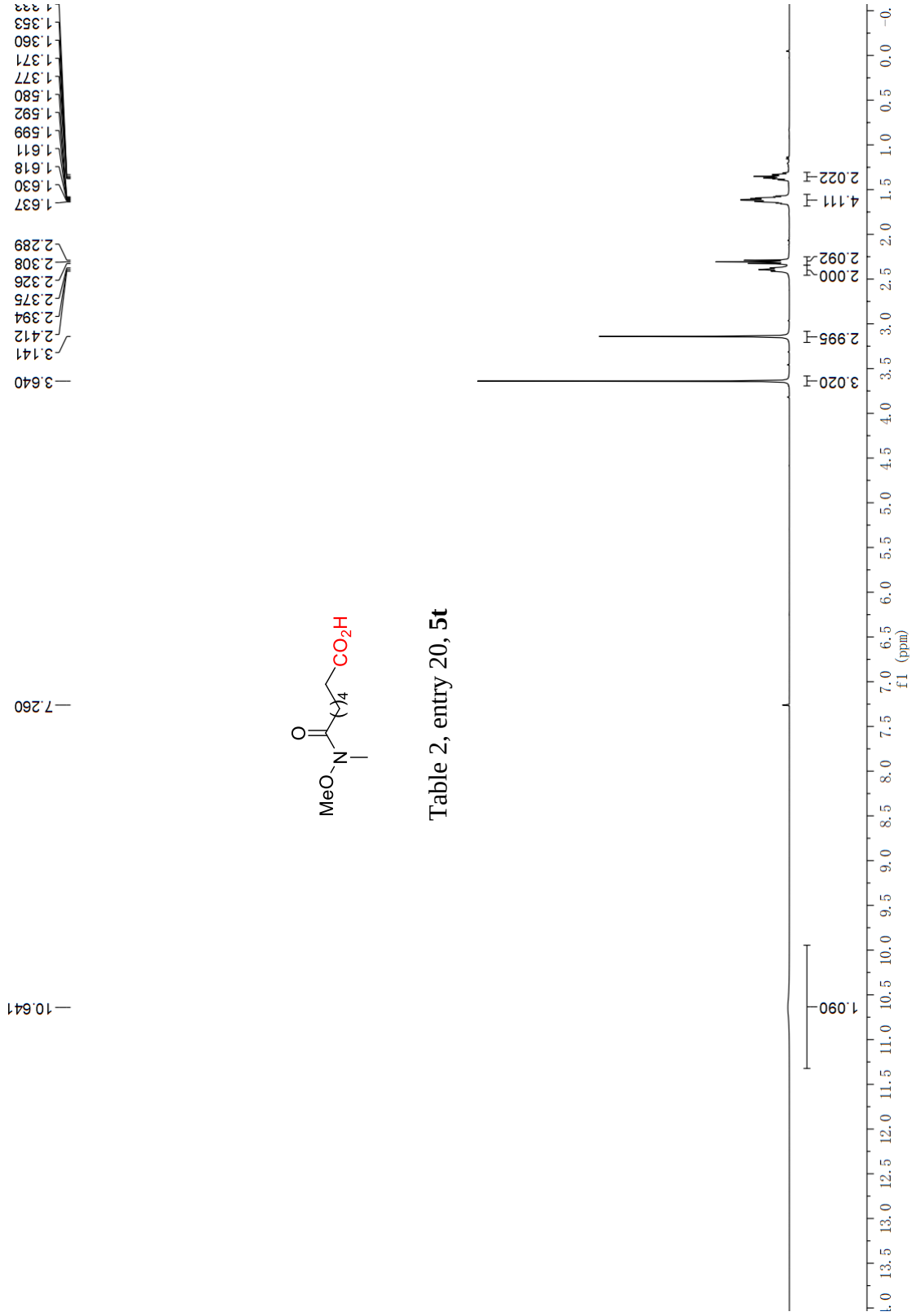
^{1}H NMR Spectrum of **5s** ($CDCl_3$, 400 MHz)



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



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



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

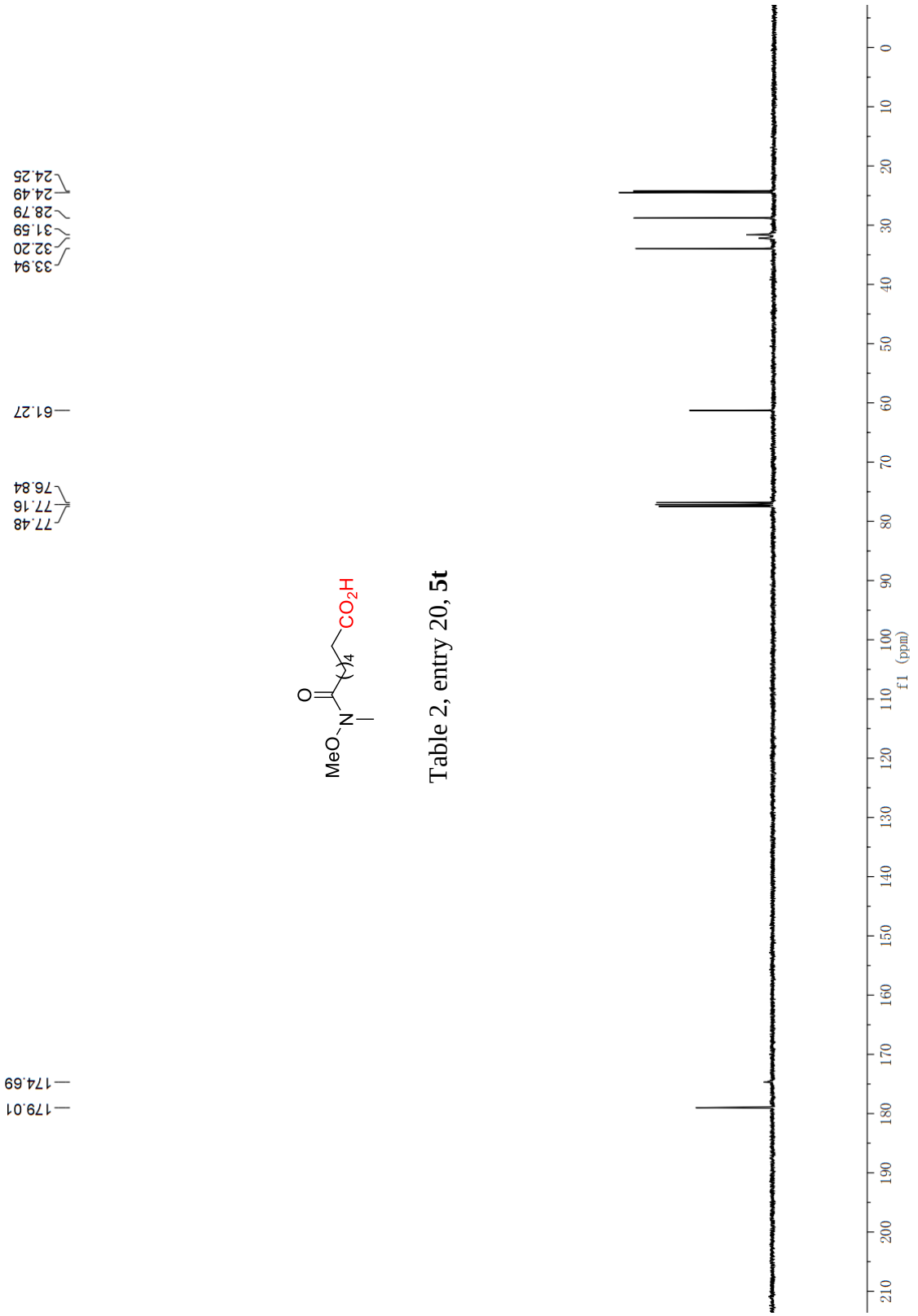
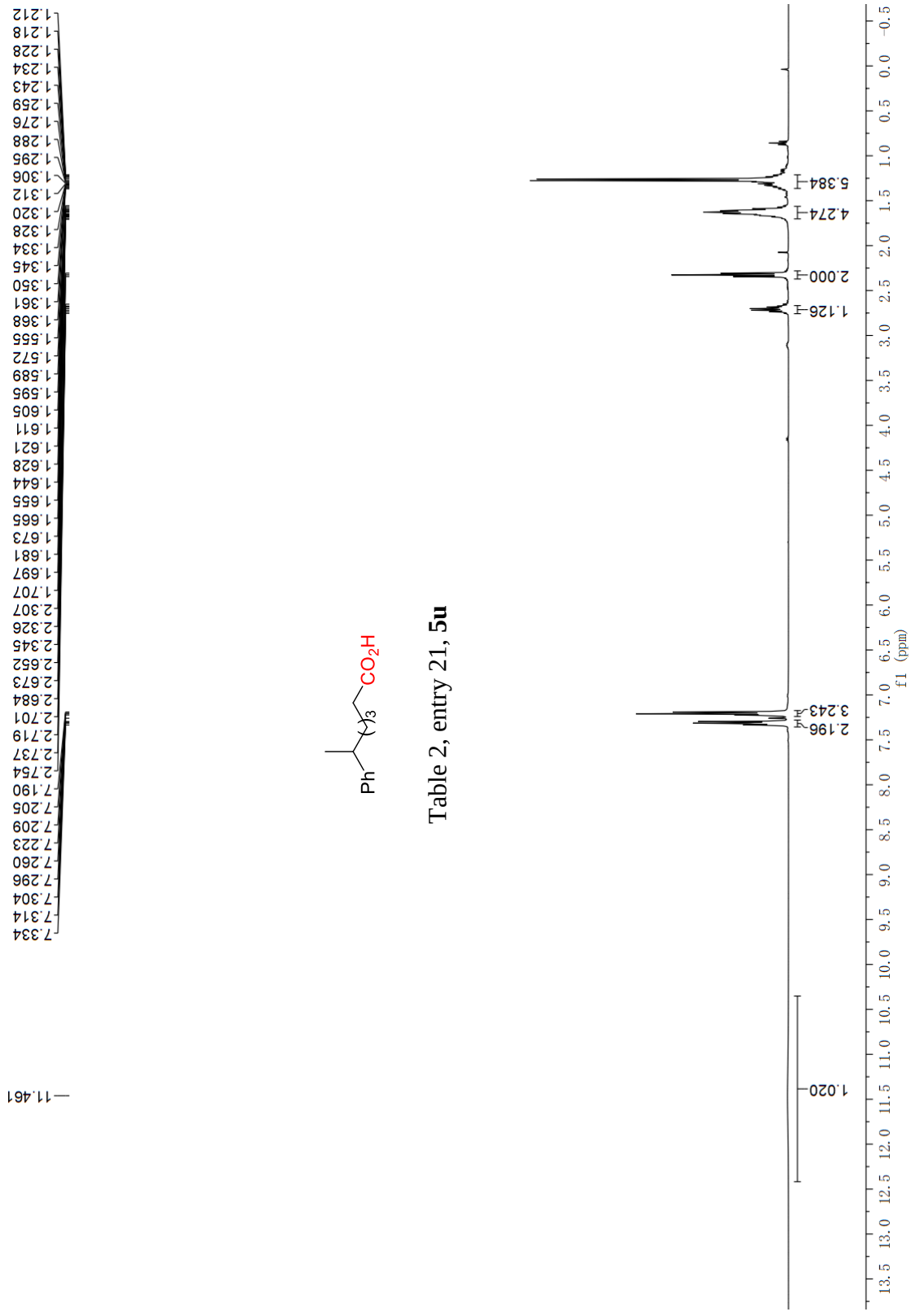
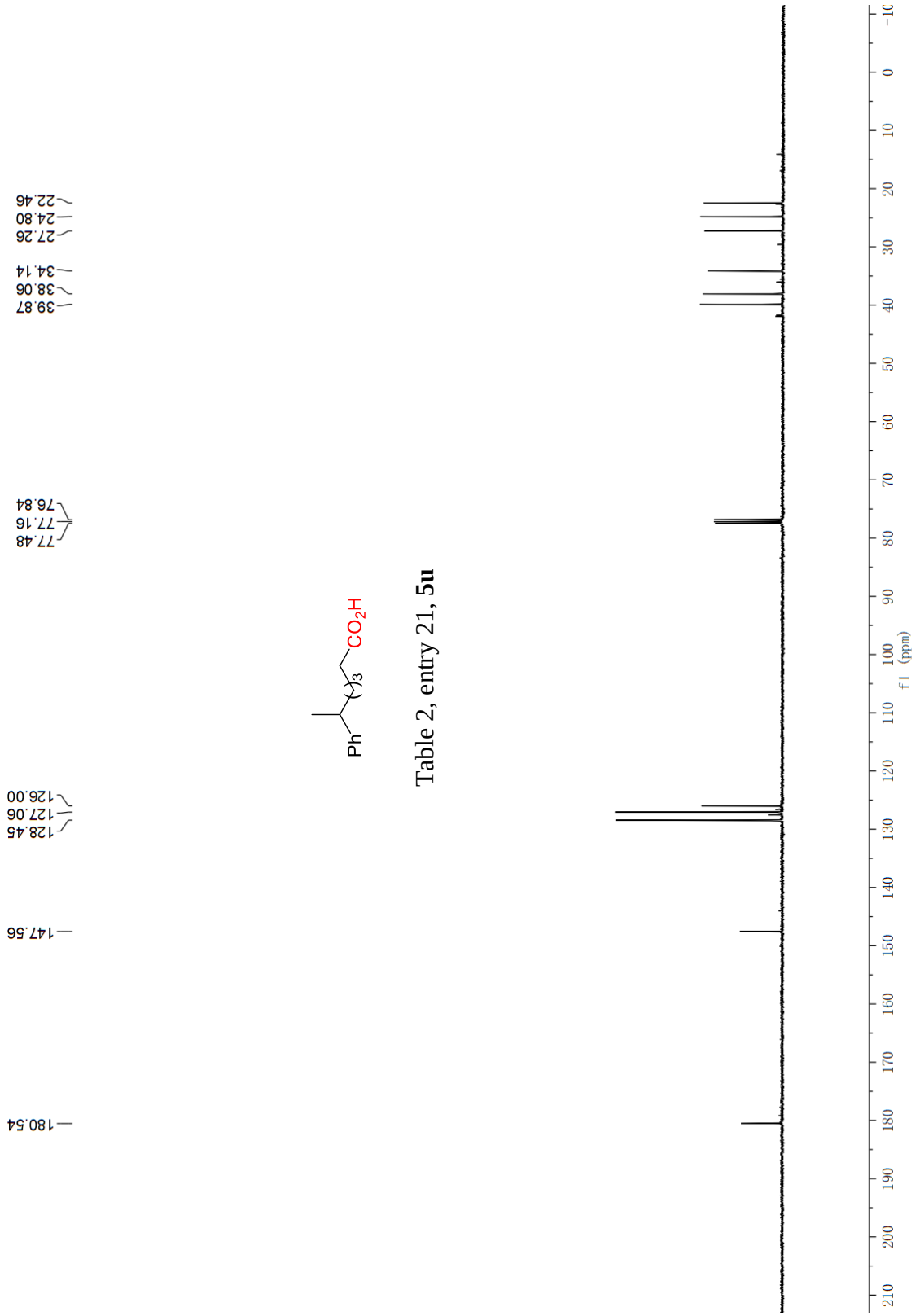


Table 2, entry 20, **5t**

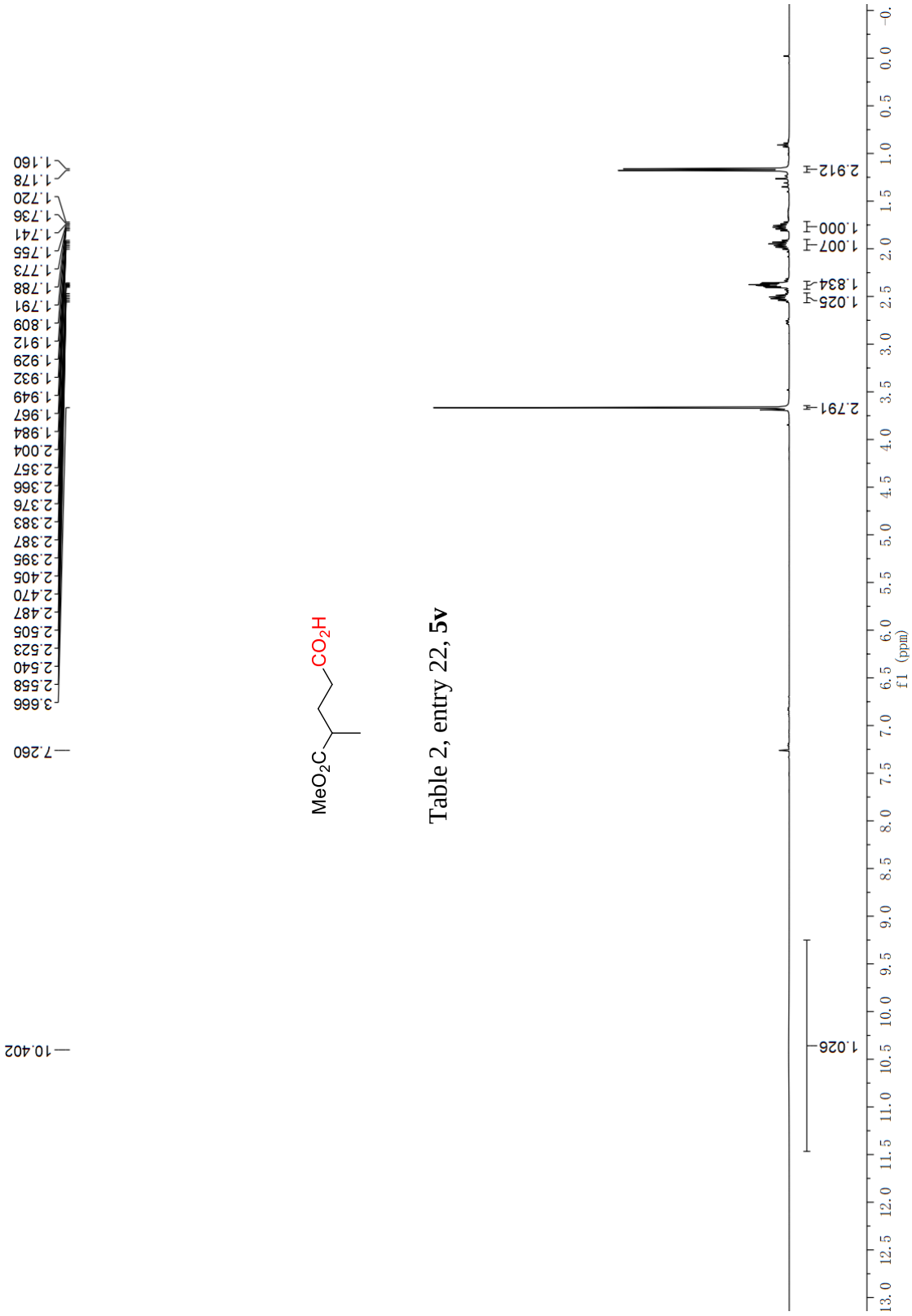
^{1}H NMR Spectrum of **5u** ($CDCl_3$, 400 MHz)



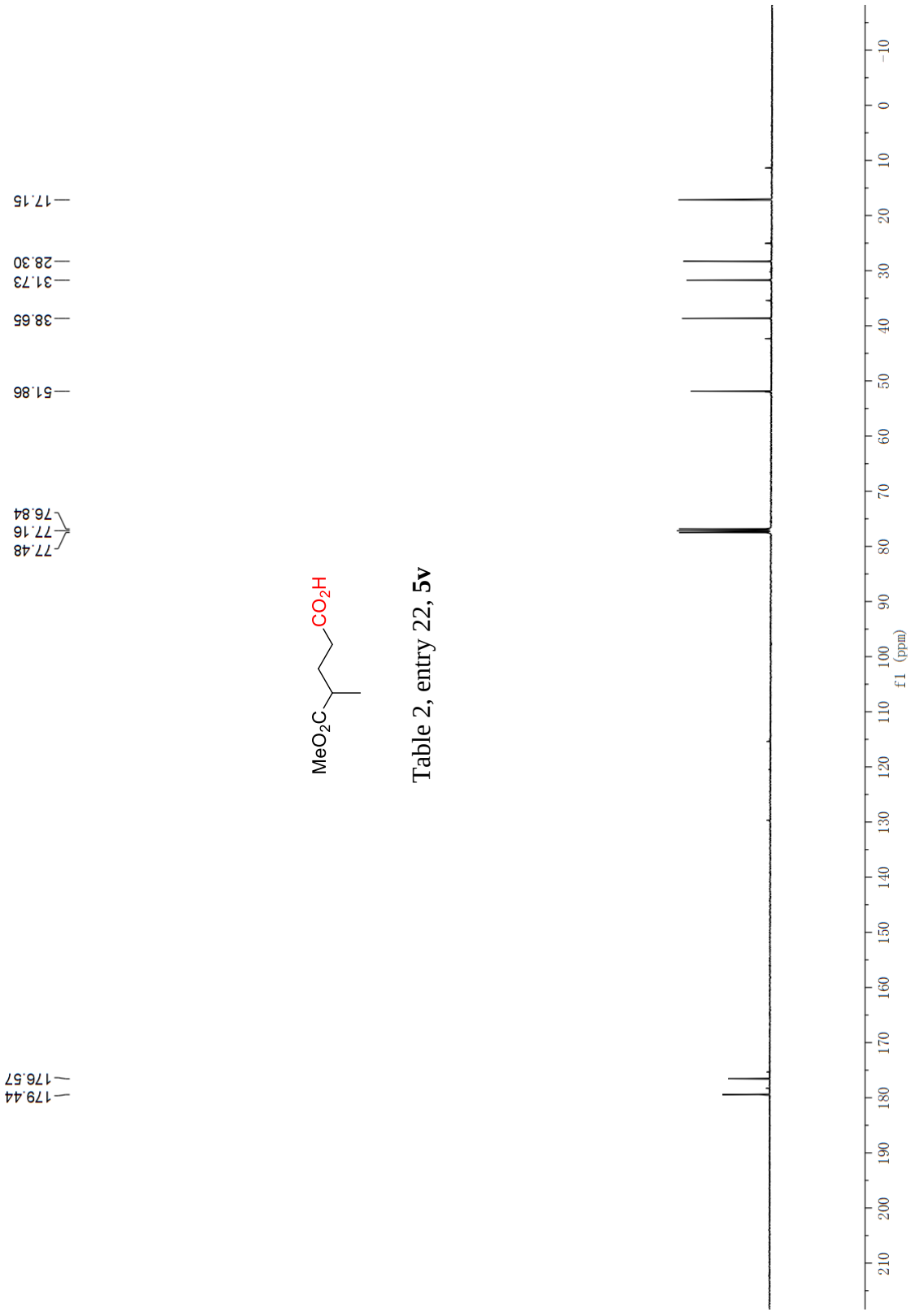
^{13}C NMR Spectrum of **5u** ($CDCl_3$, 100 MHz)



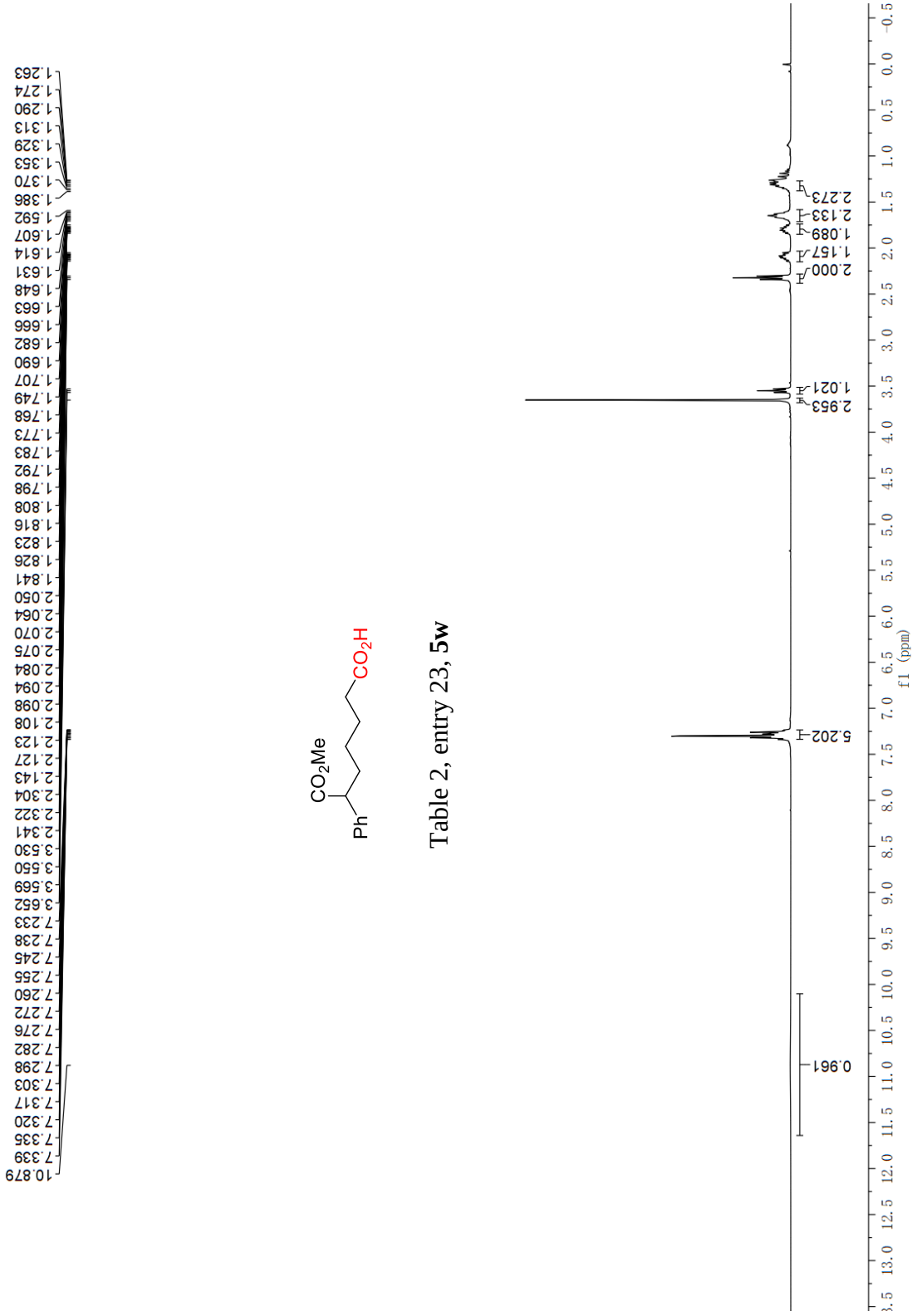
^{1}H NMR Spectrum of **5v** ($CDCl_3$, 400 MHz)



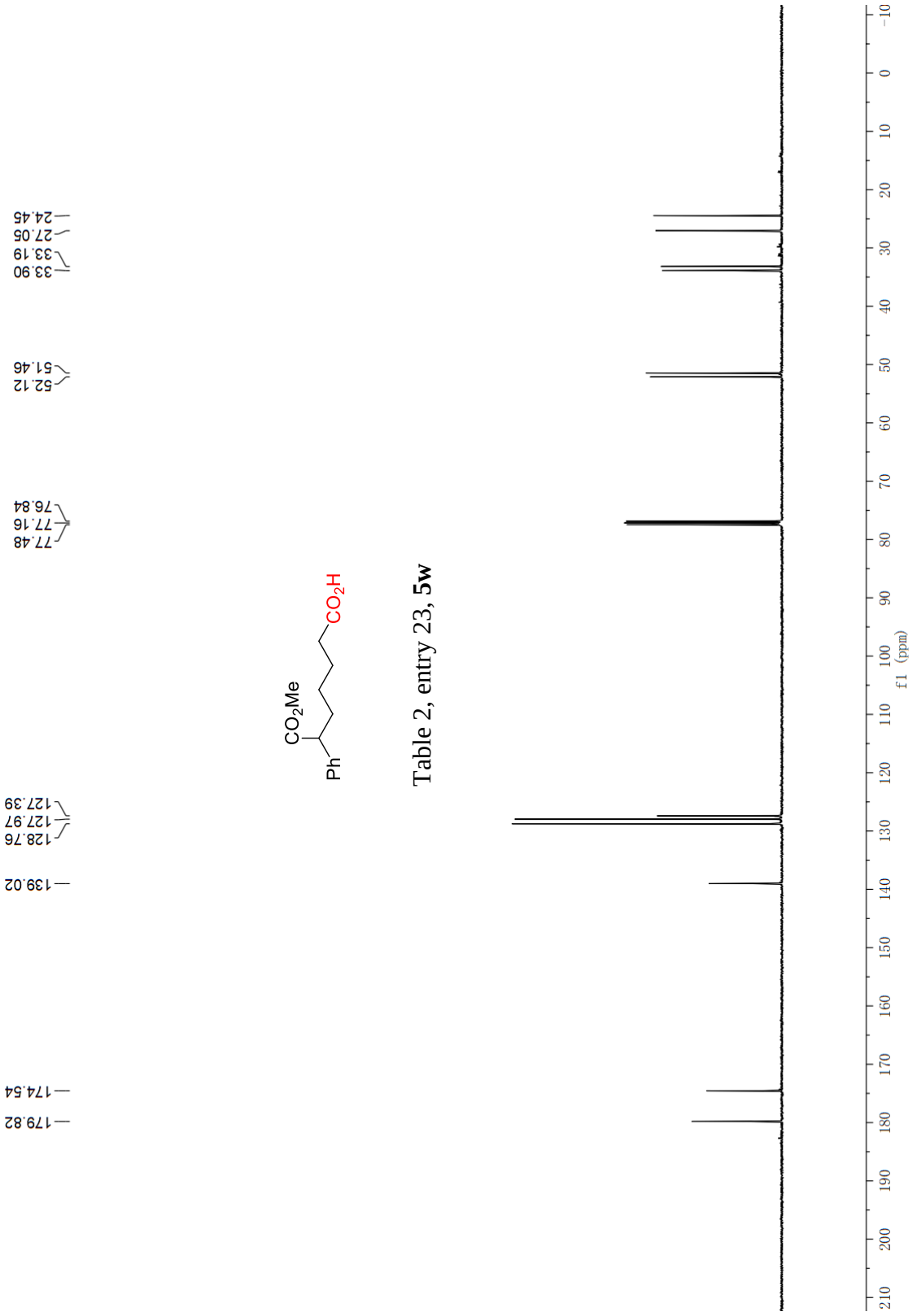
^{13}C NMR Spectrum of **5v** ($CDCl_3$, 100 MHz)



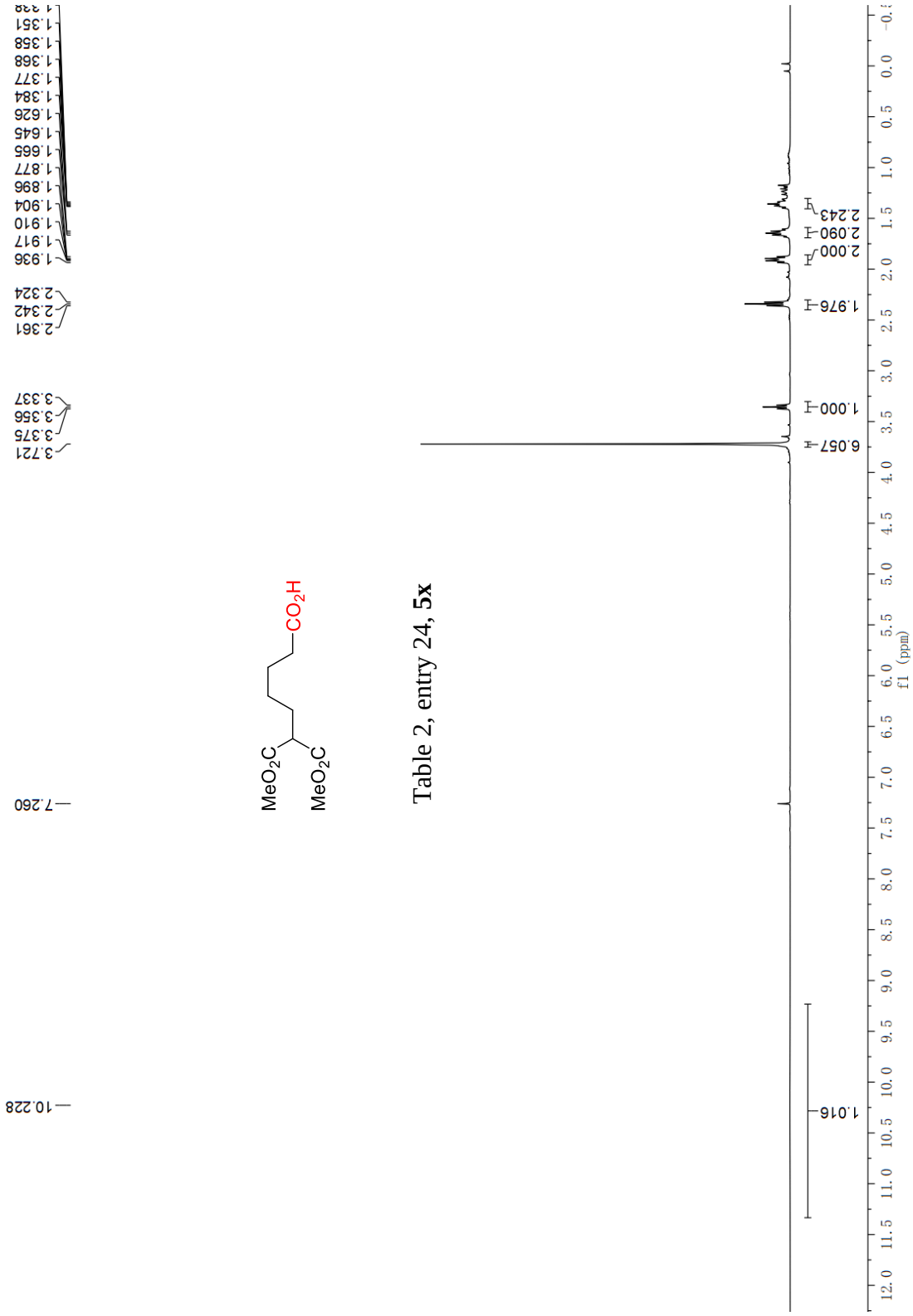
^{1}H NMR Spectrum of **5w** ($CDCl_3$, 400 MHz)



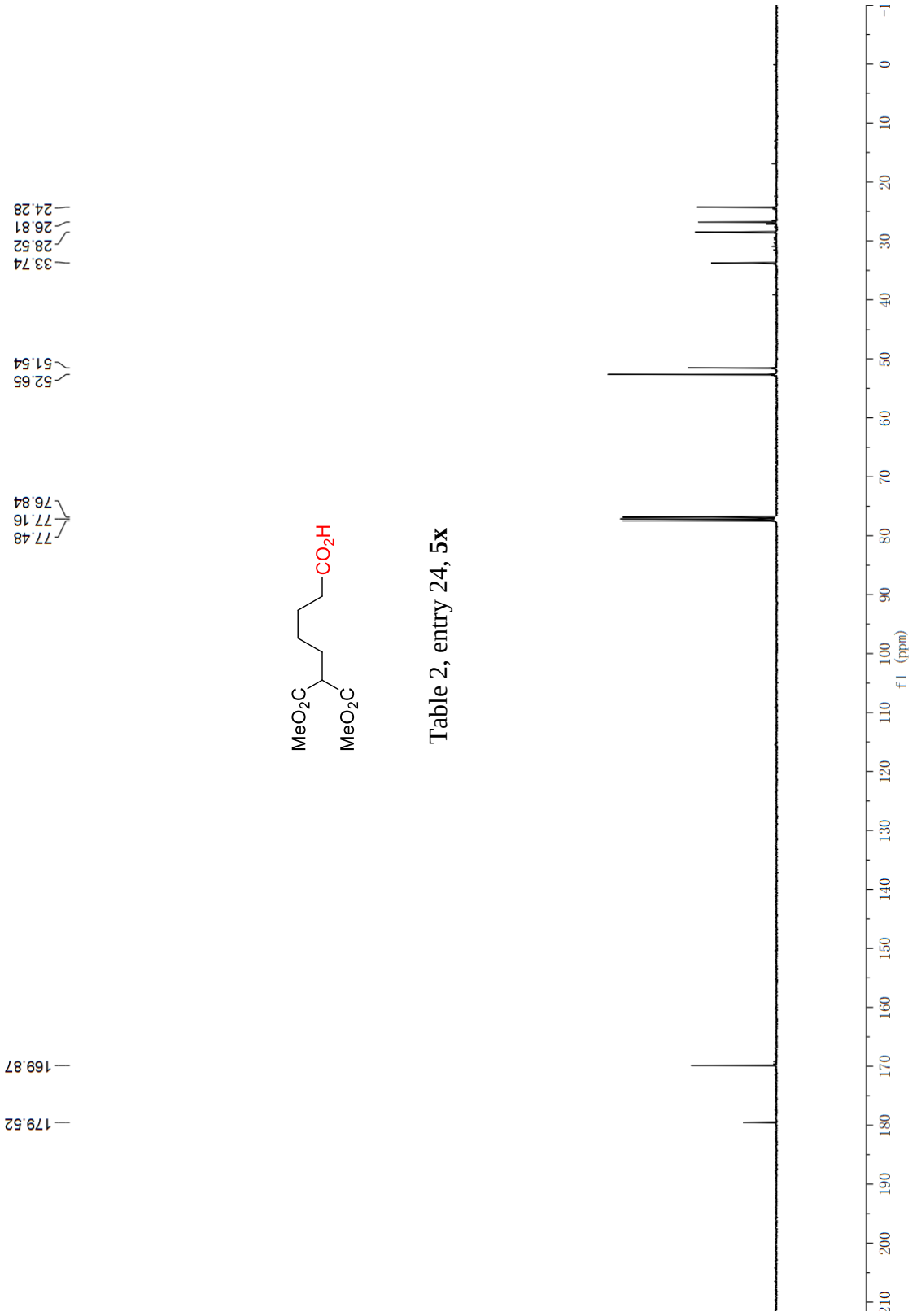
^{13}C NMR Spectrum of **5w** ($CDCl_3$, 100 MHz)



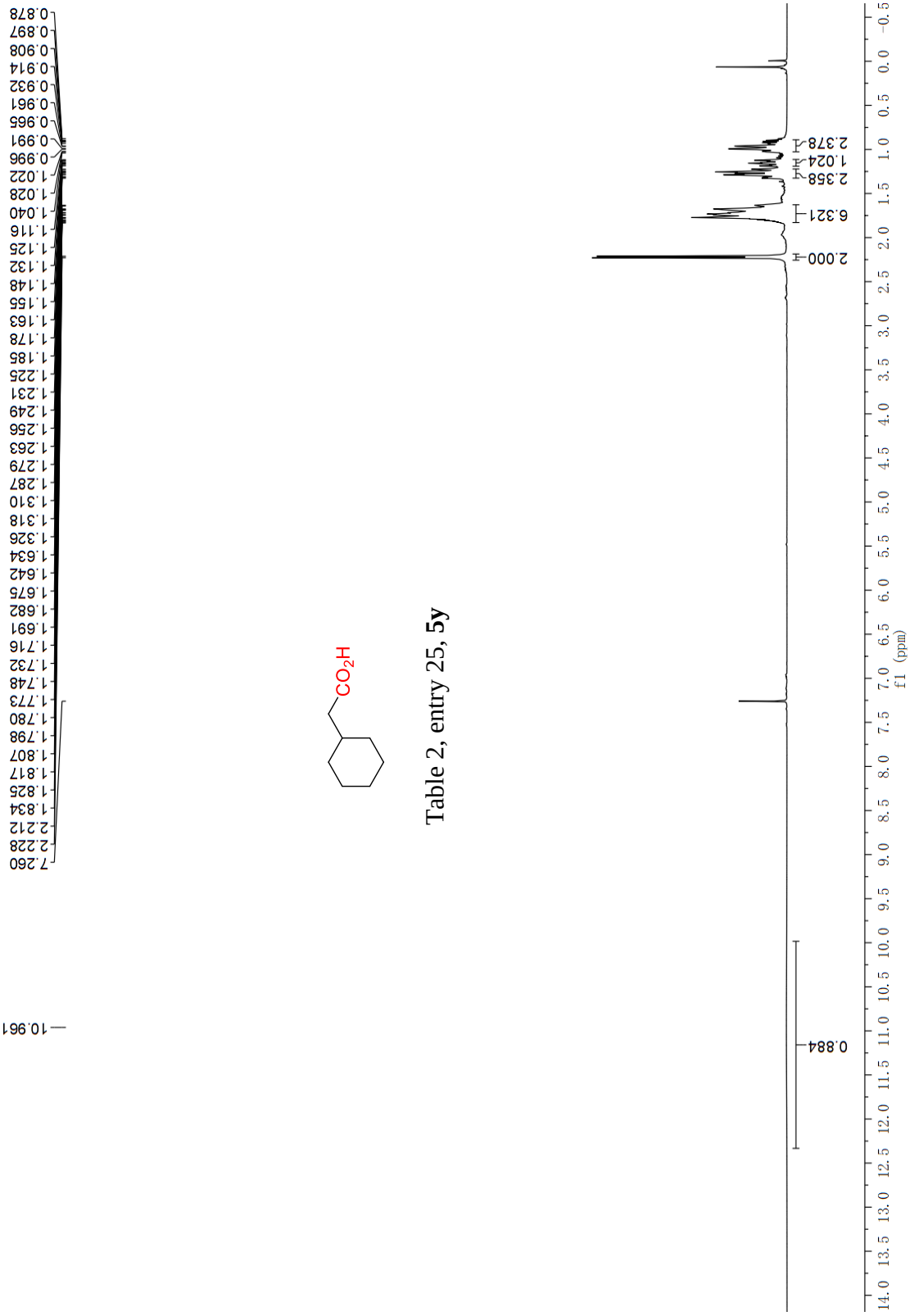
^{1}H NMR Spectrum of **5x** ($CDCl_3$, 400 MHz)



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



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



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

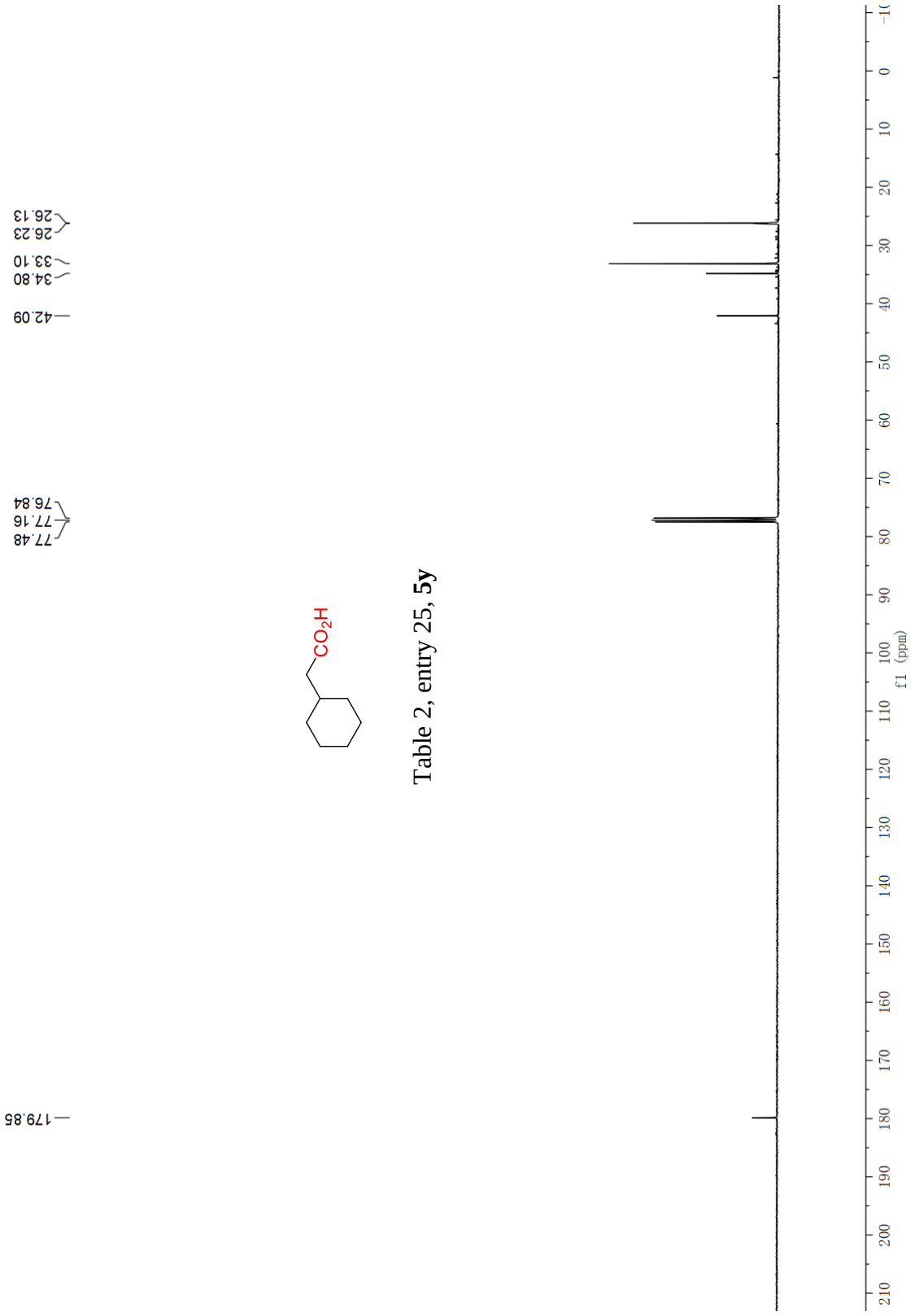
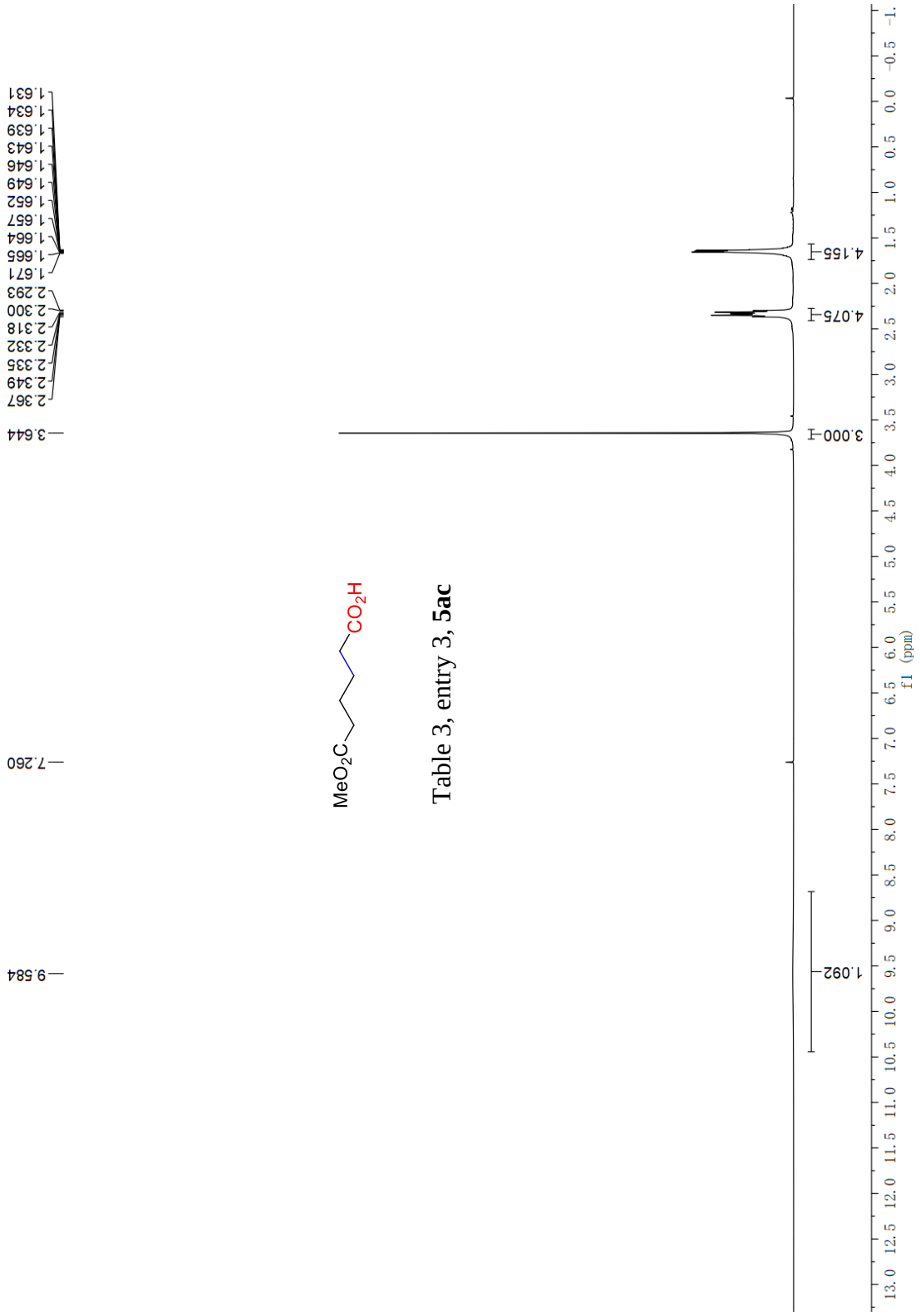
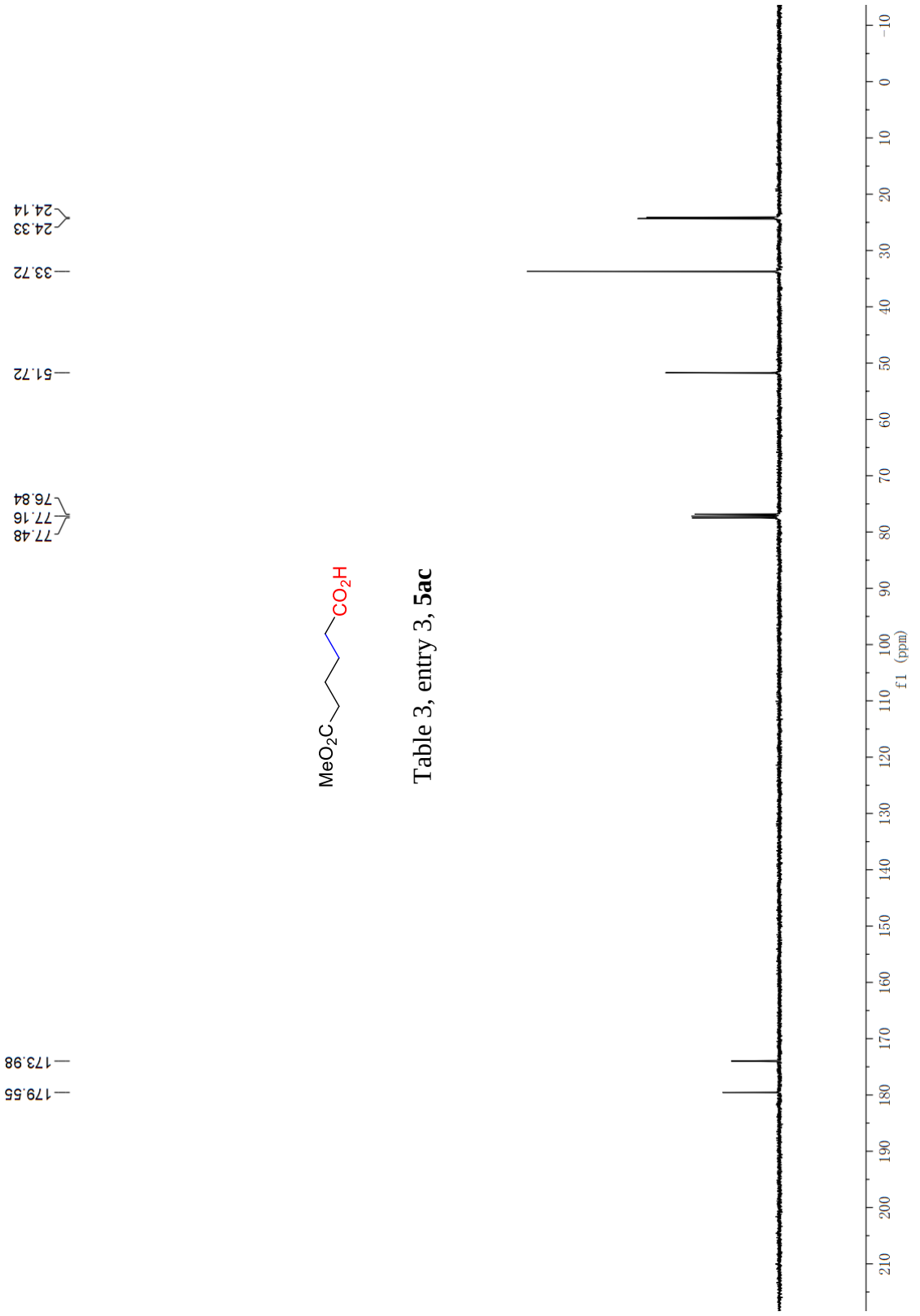


Table 2, entry 25, **5y**

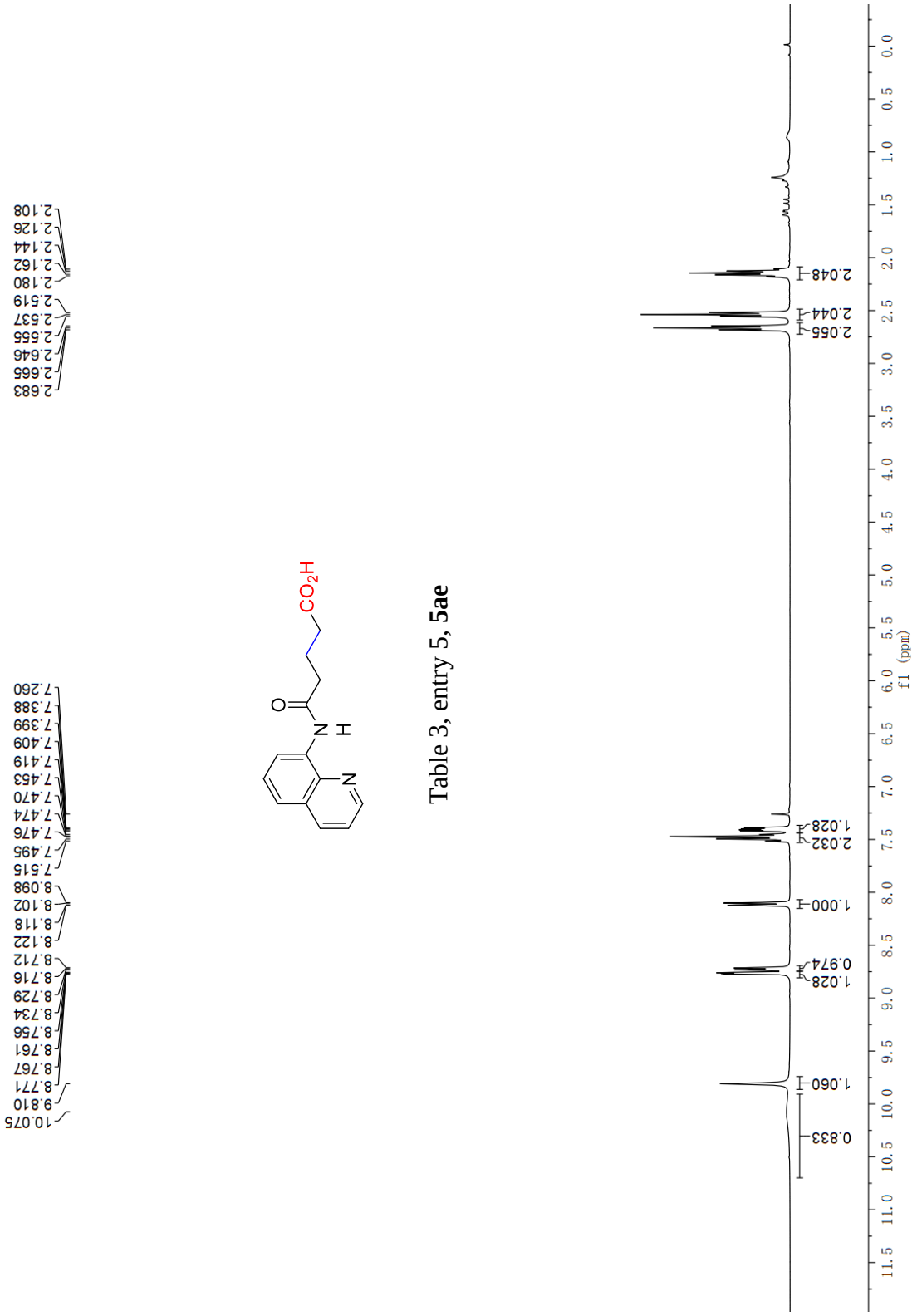
^{1}H NMR Spectrum of **5ac** ($CDCl_3$, 400 MHz)



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



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



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

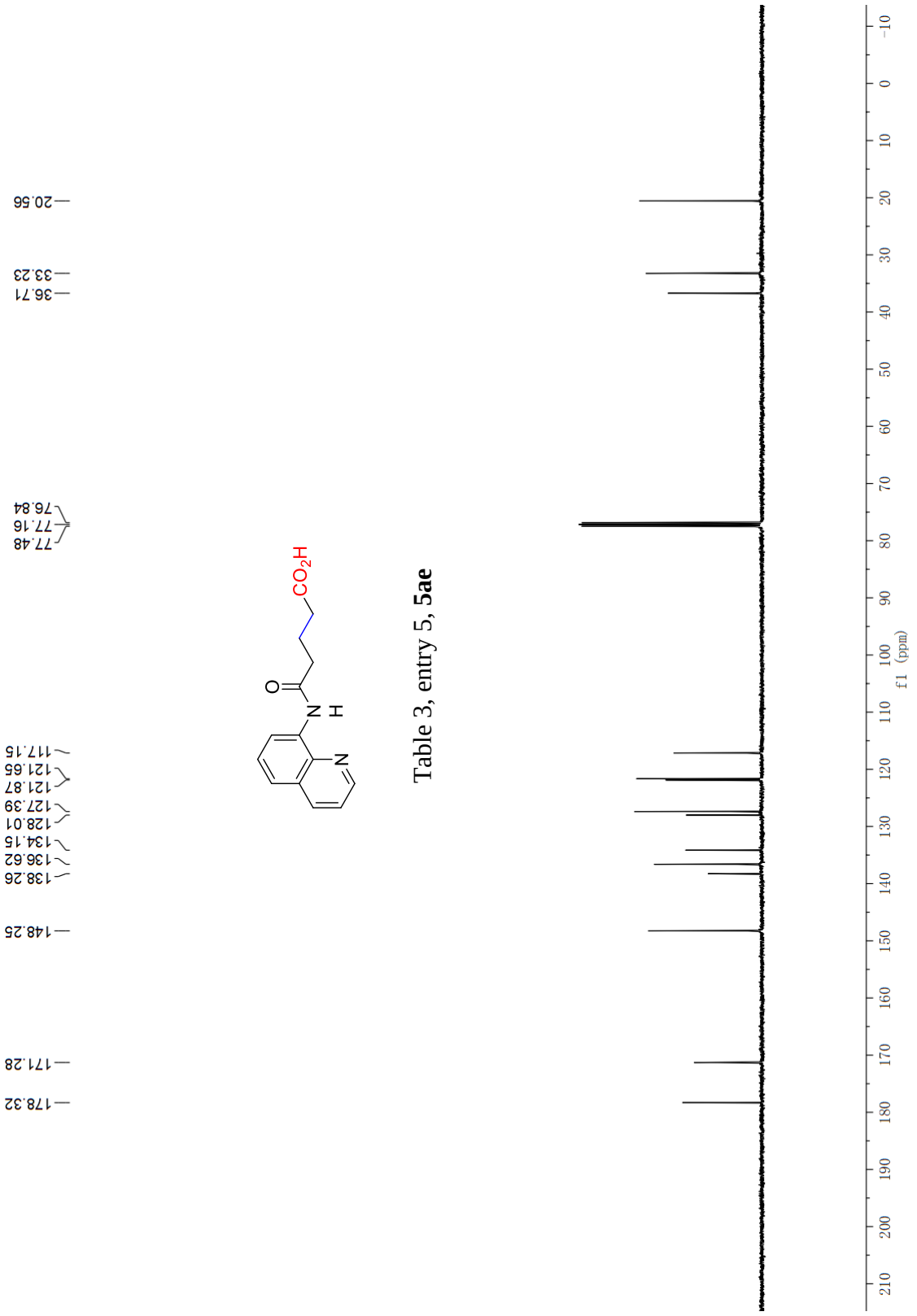
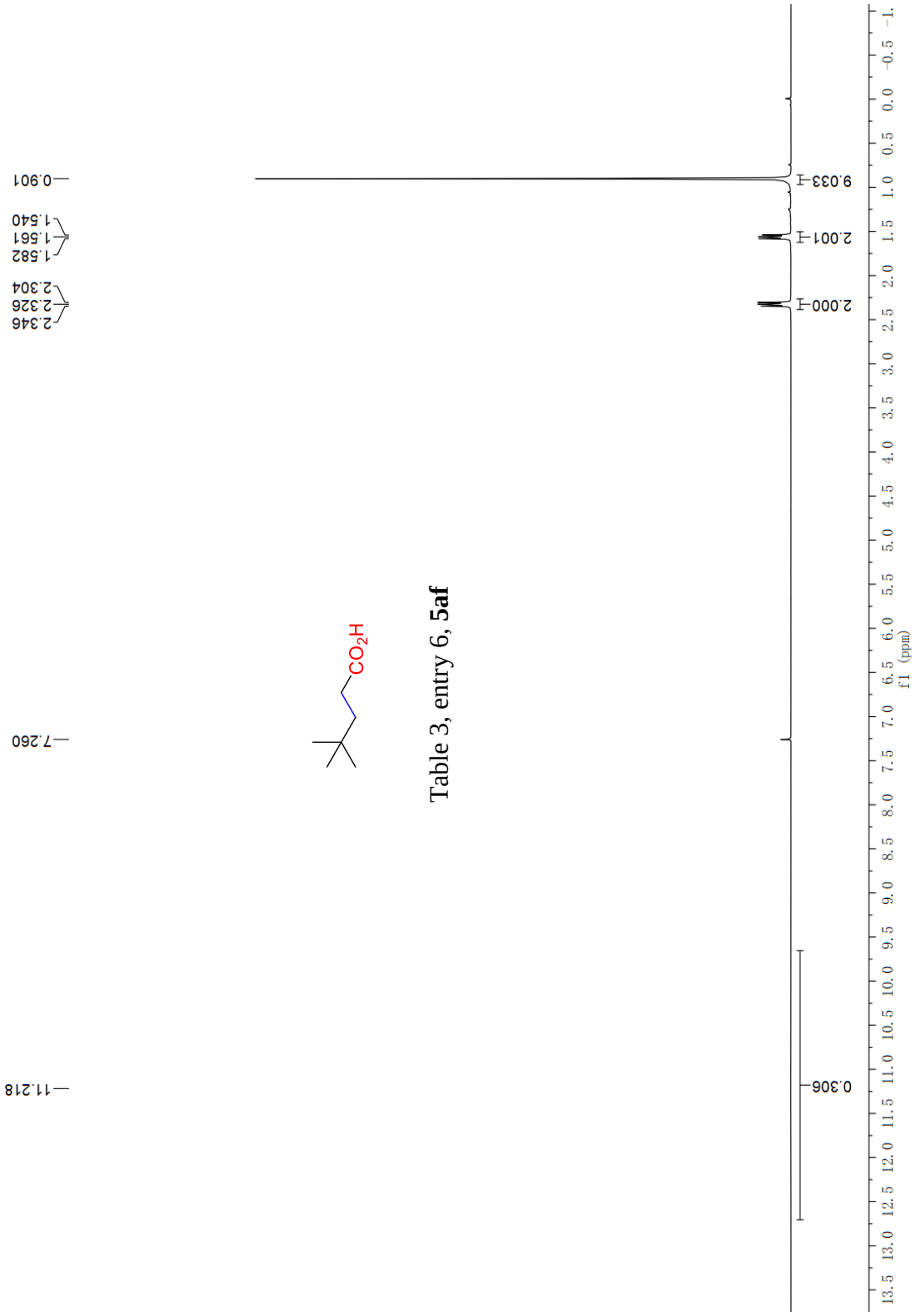


Table 3, entry 5, **5ae**

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



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

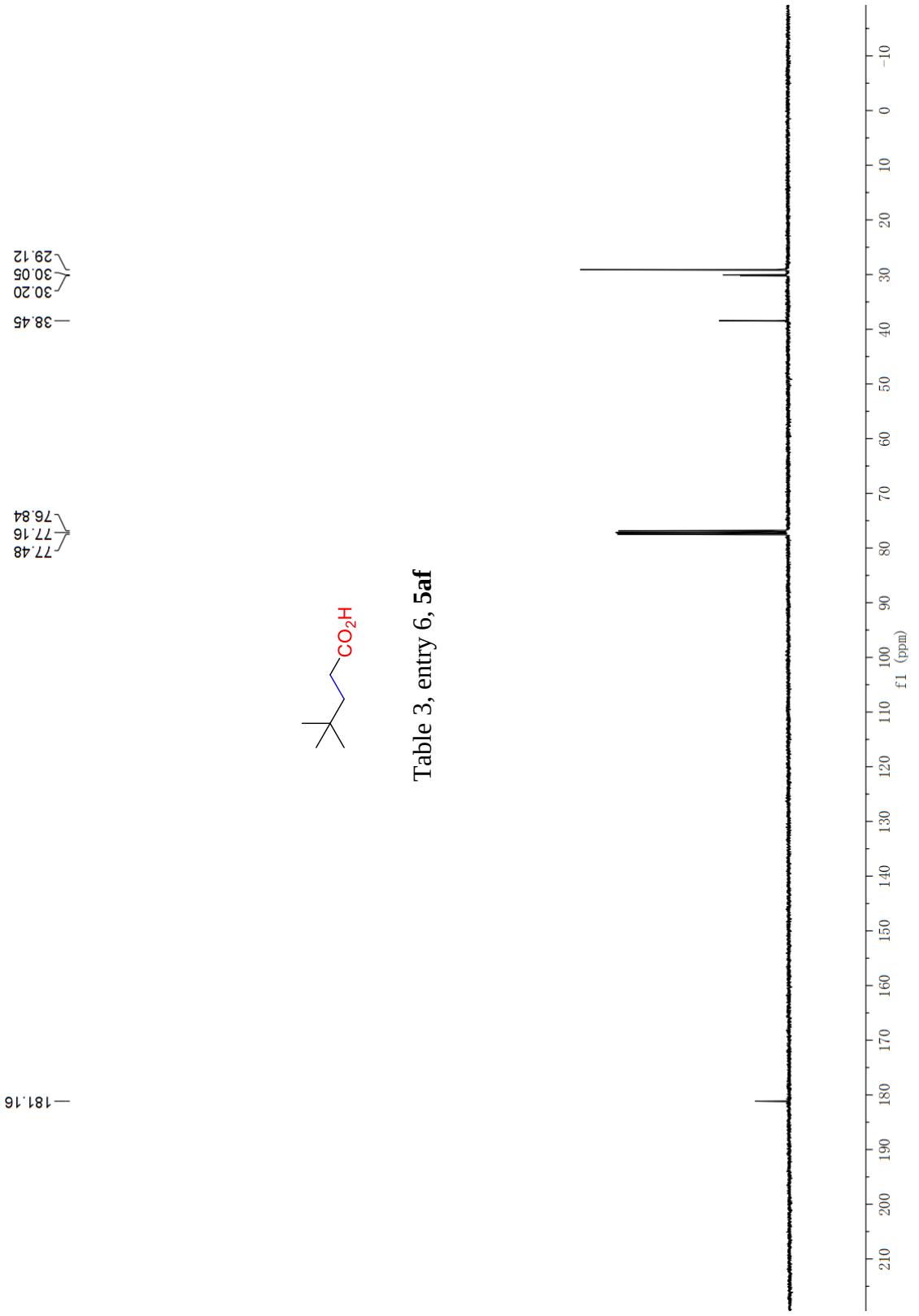
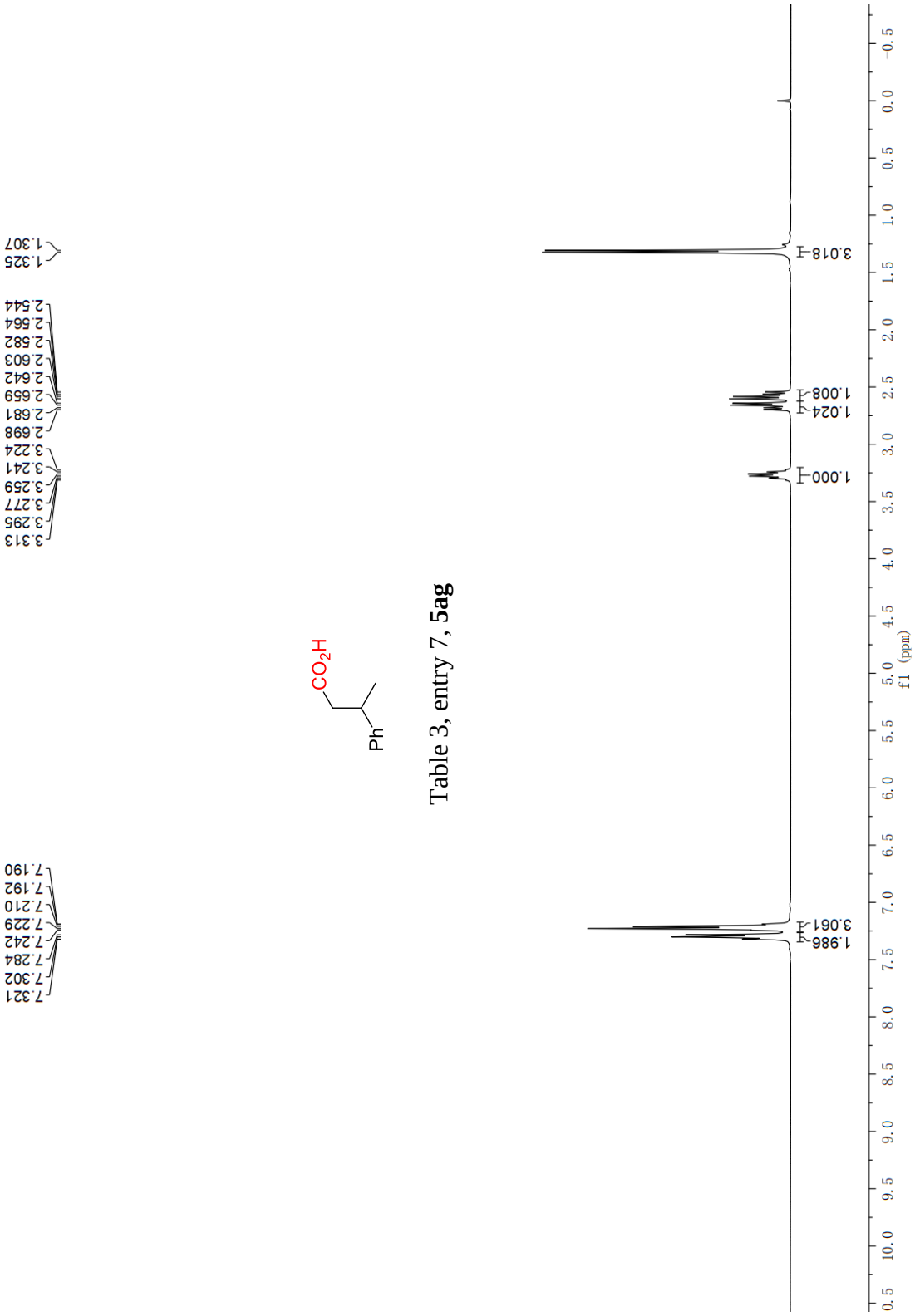
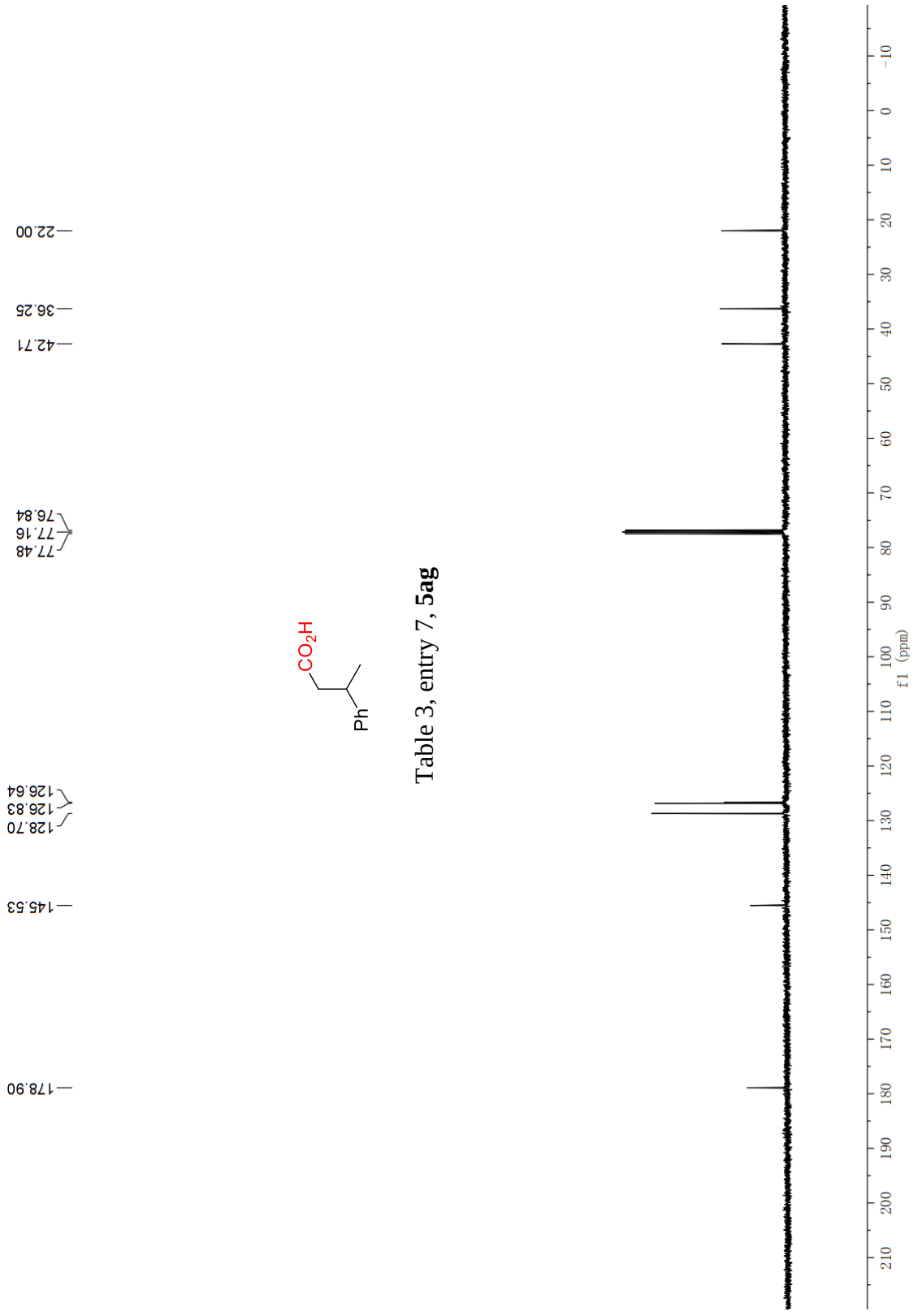


Table 3, entry 6, **5af**

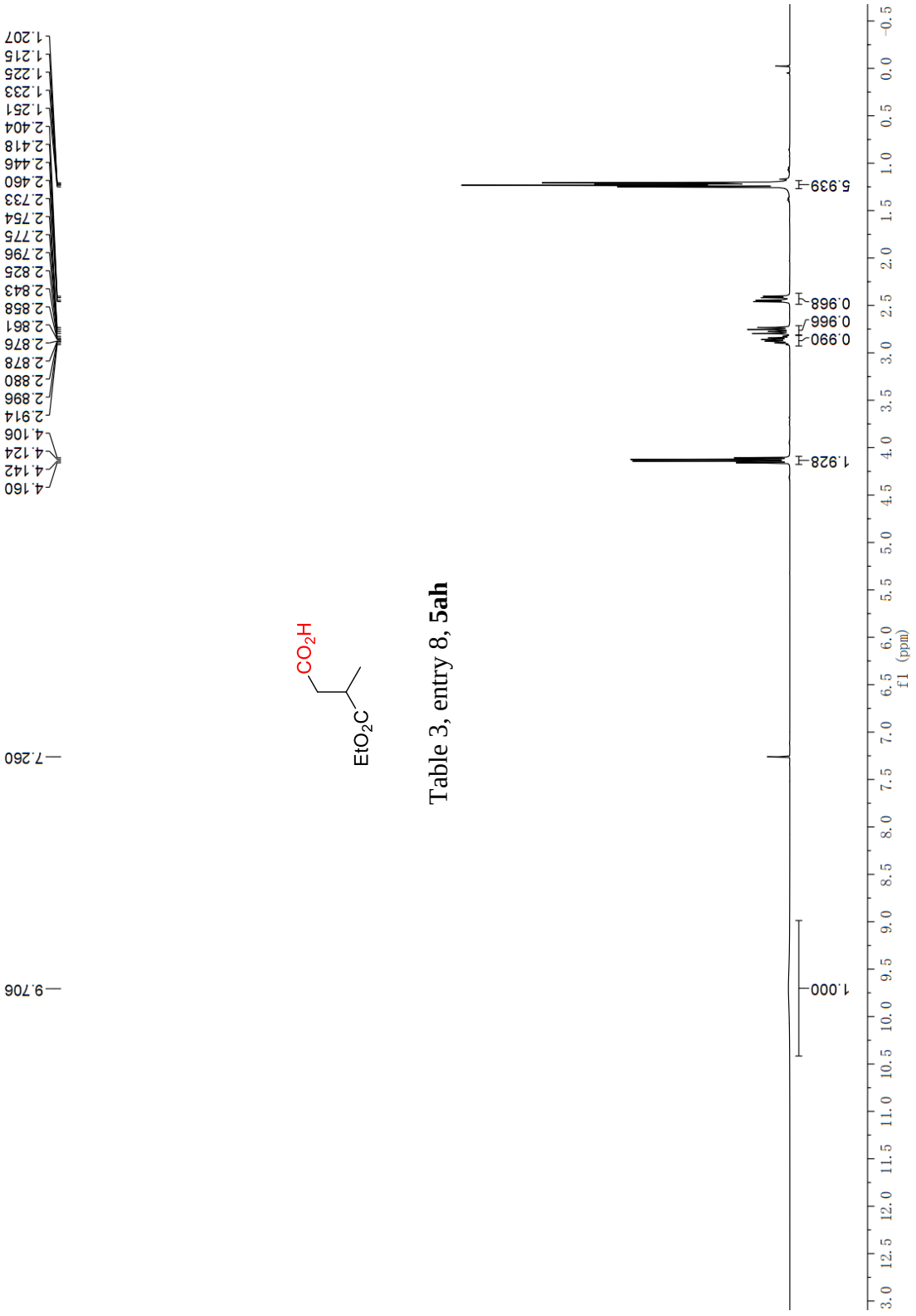
^{1}H NMR Spectrum of **5ag** ($CDCl_3$, 400 MHz)



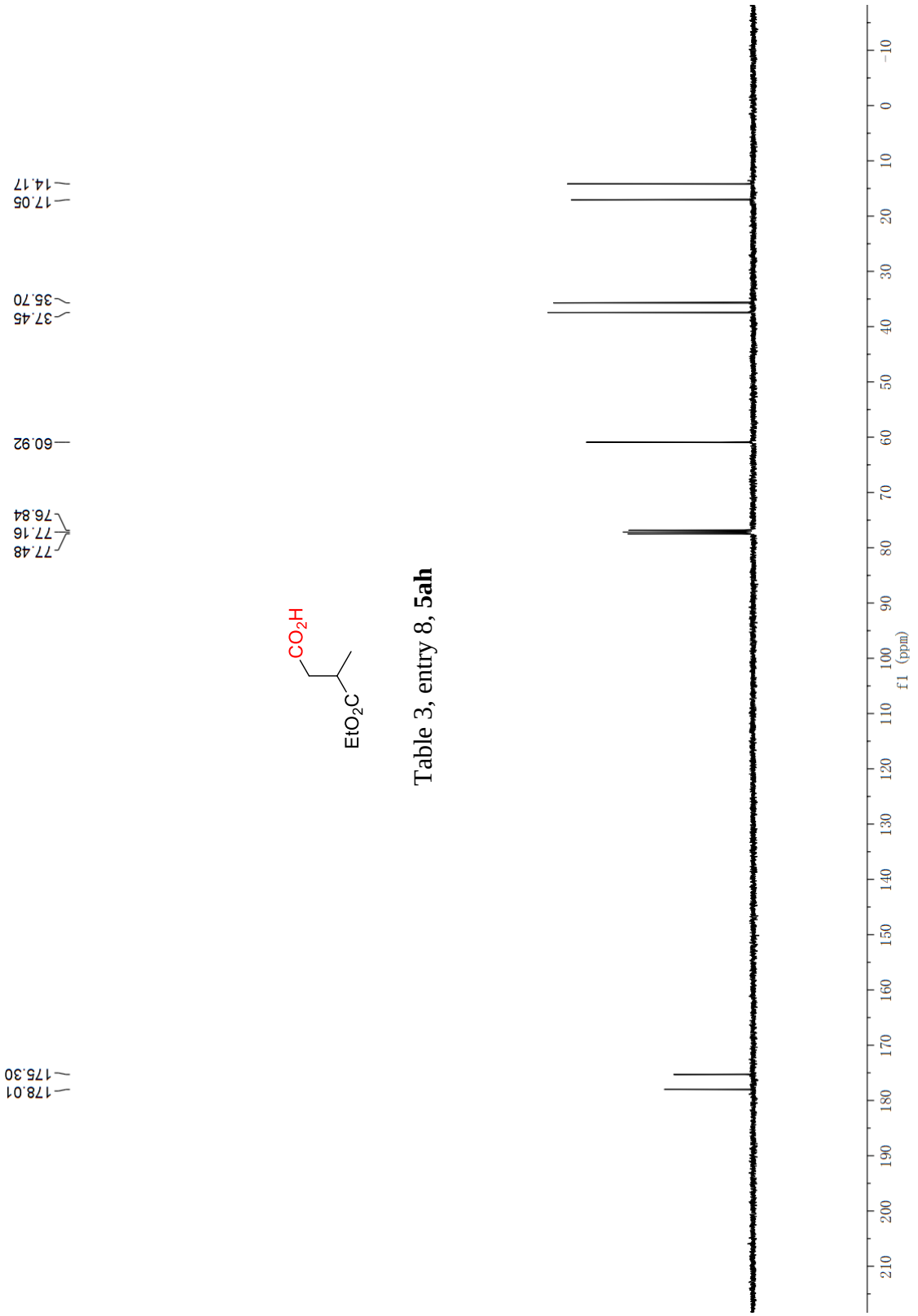
^{13}C NMR Spectrum of **5ag** ($CDCl_3$, 100 MHz)



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



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



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

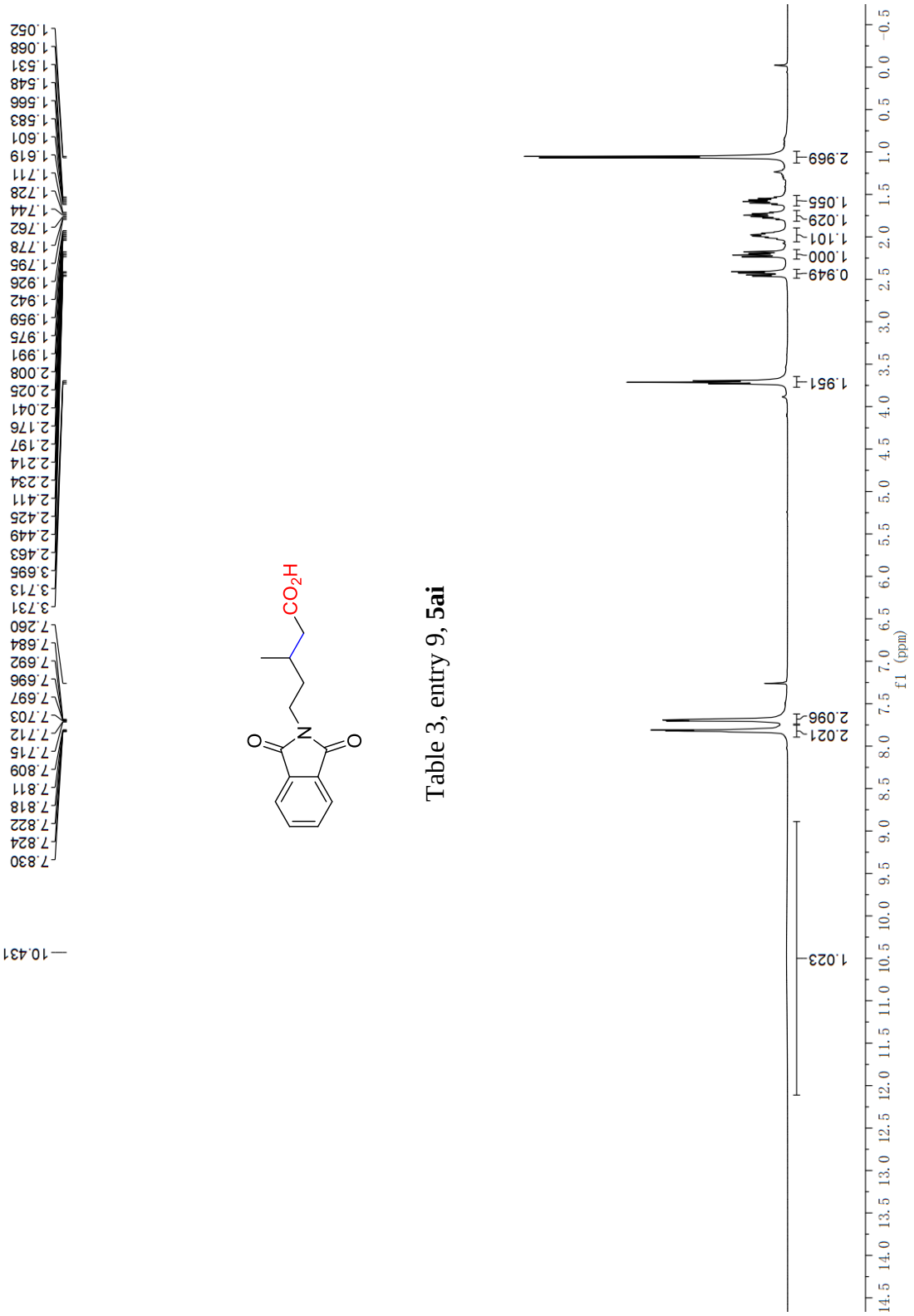
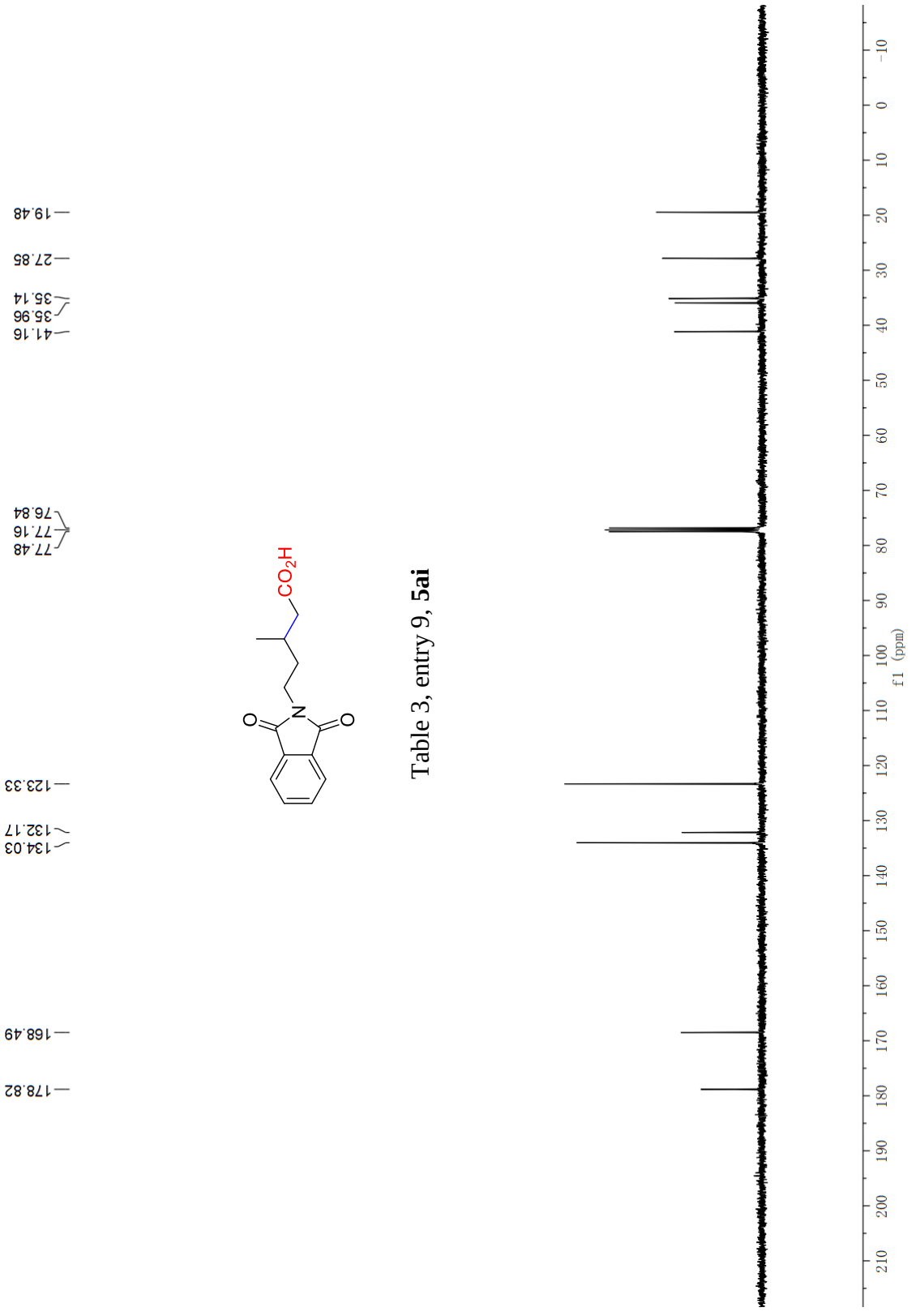
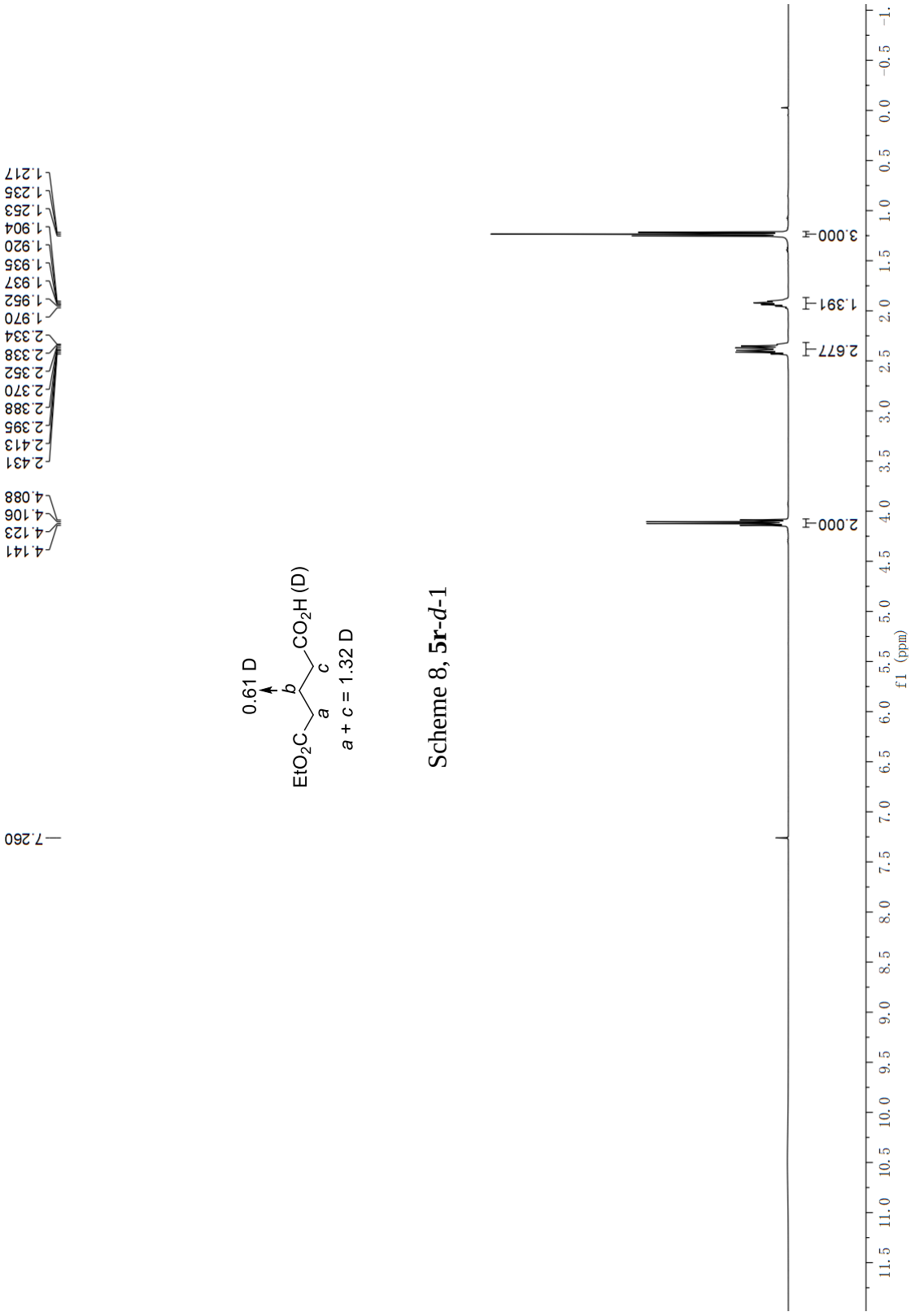


Table 3, entry 9, **5ai**

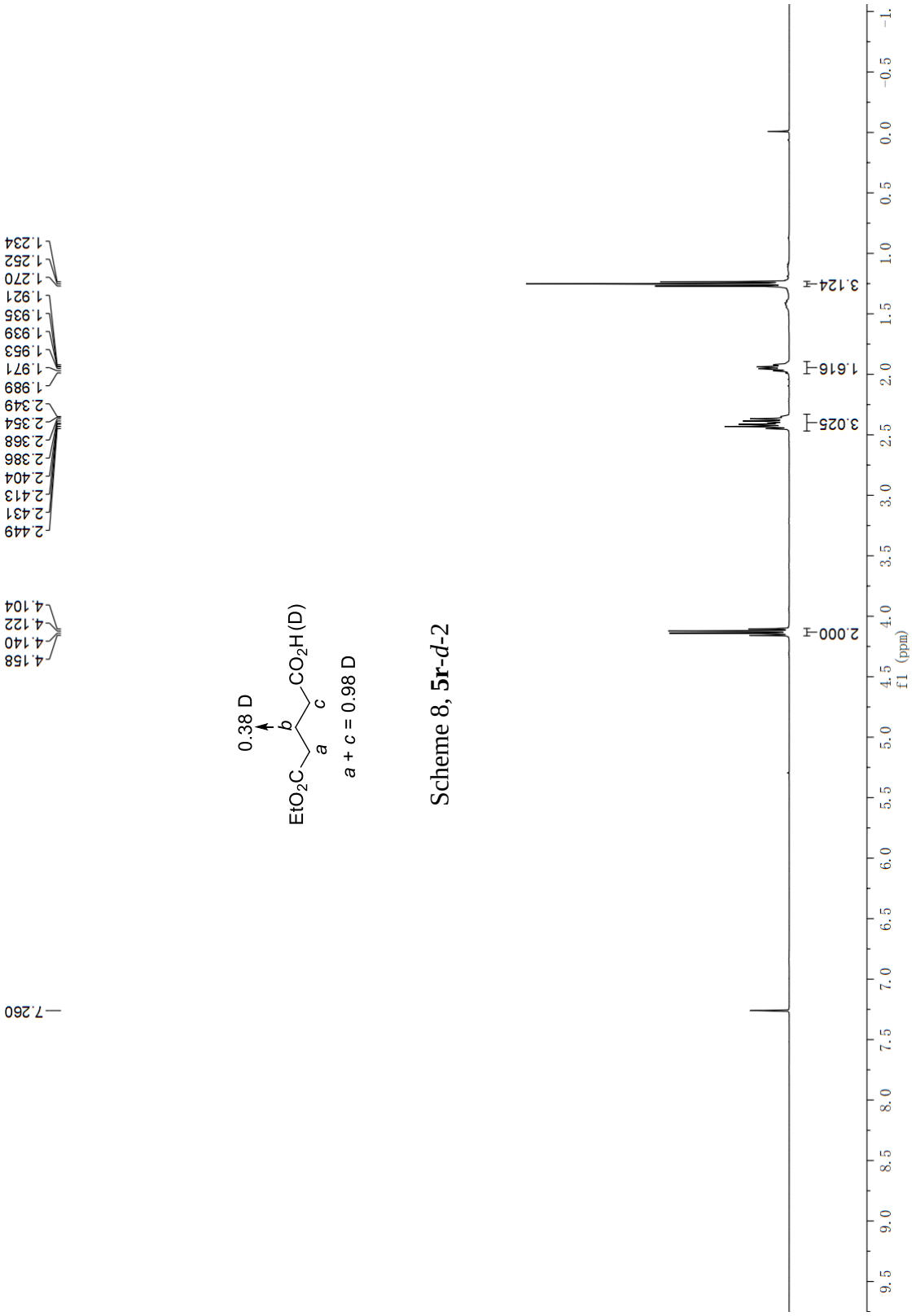
^{13}C NMR Spectrum of **5ai** ($CDCl_3$, 100 MHz)



[1]H NMR Spectrum of **5r**-*d*-1 ($CDCl_3$, 400 MHz)



[1]H NMR Spectrum of **5r**-*d*-2 ($CDCl_3$, 400 MHz)



Scheme 8, **5r**-*d*-2

[1]H NMR Spectrum of recovered **4r** ($CDCl_3$, 400 MHz)