Supporting information

Iron-Anthraquinone Cooperative Catalysis Enables Mild C–C Bond Cleavage of Cyclohexanones via Oxygen-Centered Radicals

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Table of Contents

1. Reagents.

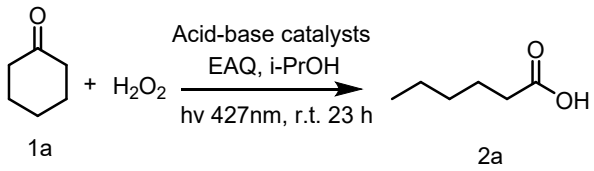
Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel.

2. Instruments.

Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014 system equipped with an FFAP capillary column (30 m × 0.32 mm × 0.5 μm). High-Resolution Mass Spectrometry (HRMS) data were acquired using a Thermo Fisher Scientific Q Exactive Plus Orbitrap LC-MS system with heated electrospray ionization (HESI) source. NMR spectra ($^{1}H/^{13}C$) were recorded on either a Varian DLG400 (400 MHz) or Bruker AVANCE III 500 (500 MHz) spectrometer using $CDCl_3$ or *d*-DMSO as solvent with tetramethylsilane (TMS) as internal standard.

3. Reaction Condition Optimization.

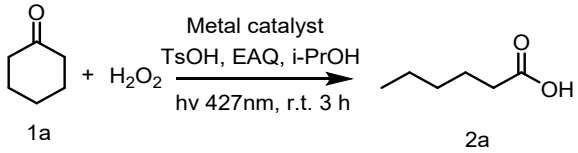
Table S1. Influence of the Acid-base catalysts[a]



Entry	Acid-base catalysts	Yield (%)
1	TfOH	18
2	**TsOH**	**36**
3	H_2SO_4	27
4	AcOH	6
5	HCOOH	5
6	TFA	25
7	HNO_3	21
8	NaOH	0

[a]Reaction conditions: **1a** (1.9 mmol), H_2O_2 (1.75 equiv), EAQ (3 mol%), under 427 nm lamp irradiation, Acid-base catalysts (12 mol%), Solvent (2.8 mL), and r.t. for 23 h under Air atmosphere.

Table S2. Influence of the Acid-base catalysts[a]

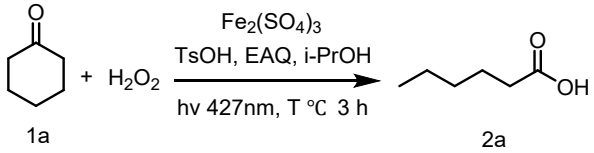


1a 2a

Entry	Metal catalysts	Yield (%)
1	$CoSO_4$	6
2	**$Fe_2(SO_4)_3$**	**44**
3	$CuSO_4$	18
4	$MnSO_4$	7
5	$VOSO_4$	5
6	$Cr_2(SO4)_3$	5

[a]Reaction conditions: **1a** (1.9 mmol), H_2O_2 (1.75 equiv), EAQ (3 mol%), under 427 nm lamp irradiation, TsOH (12 mol%), Solvent (2.8 mL), metal catalyst (M^{n+}, 0.05 mol%) and r.t. for 3 h under Air atmosphere.

Table S3. Influence of the Temperature[a]

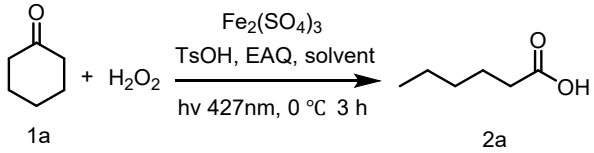


1a 2a

Entry	Temperature(℃)	Yield (%)
1	**0**	**54**
2	10	49
3	20	44
4	30	32

[a]Reaction conditions: **1a** (1.9 mmol), H_2O_2 (1.75 equiv), EAQ (3 mol%), under 427 nm lamp irradiation, TsOH (12 mol%), Solvent (2.8 mL), $Fe_2(SO_4)_3$ (0.025 mol%) and T ℃ for 3 h under Air atmosphere.

Table S4. Influence of the Photocatalyst equivalent and solvent[a]

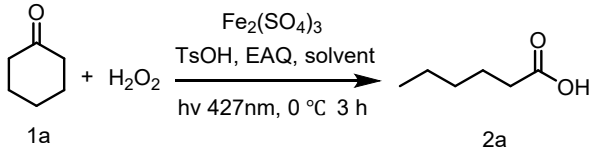


1a 2a

Entry	Equiv. EAQ (mol%)	Solvent	Yield (%)
1	3	i-PrOH	54
2	6	i-PrOH	62
3	9	i-PrOH	61
4	9	i-PrOH: acetone=4:1	55
5	9	i-PrOH: toluene =4:1	33
6	9	i-PrOH: THF=1:1	44
7	9	IPA:EA=1:1	55
8	10	i-PrOH: 1-Phenylethanol =2:1	80
9	**10**	**i-PrOH: 1-Phenylethanol =4:1**	**82**

[a]Reaction conditions: **1a** (1.9 mmol), H_2O_2 (1.75 equiv), EAQ (n mol%), under 427 nm lamp irradiation, TsOH (12 mol%), Solvent (2.8 mL), $Fe_2(SO_4)_3$ (0.025 mol%) and 0 ℃ for 3 h under Air atmosphere.

Table S5. iron ion equivalent on the reaction[a]



1a 2a

Entry	n(Fe^{3+}) (mmol)	Eq. (Fe^{3+}) (%)	Yield (%)
1	0.000475	0.025	76
2	**0.00095**	**0.05**	**82**
3	0.0019	0.1	74
4	0.0057	0.3	62
5	0.0114	0.6	52
6	0.0228	1.2	44
7	0.0456	2.4	37

[a]Reaction conditions: **1a** (1.9 mmol), H_2O_2 (1.75 equiv), EAQ (10 mol%), under 427 nm lamp irradiation, TsOH (12 mol%), Solvent (2.8 mL), $Fe_2(SO_4)_3$ (n mol%) and 0 ℃ for 3 h under Air atmosphere.

4. General procedure.

A jacketed quartz reactor was charged with cyclohexanone (0.1864 g, 1.9 mmol), 2-ethylanthraquinone (EAQ, 0.0449 g, 0.19 mmol), p-toluenesulfonic acid monohydrate ($TsOH \cdot H_2O$, 0.0437 g, 0.23 mmol), isopropanol (1.569 g, 26.1 mmol), and 1-phenylethanol (0.798 g, 6.53 mmol). A $Fe_2(SO_4)_3$ stock solution was prepared by dissolving 0.09497 g of iron(III) sulfate in deionized water and diluting to 10 mL in a volumetric flask. The reaction mixture received 20 µL of this solution via micropipette. After circulating coolant through the jacket and inserting a stirring bar, the system equilibrated thermally. A 30 wt% aqueous H_2O_2 solution (0.377 g) was added via syringe pump over 1 min. Photolysis proceeded under 427 nm LED irradiation (top-mounted) with vigorous stirring (800 rpm).

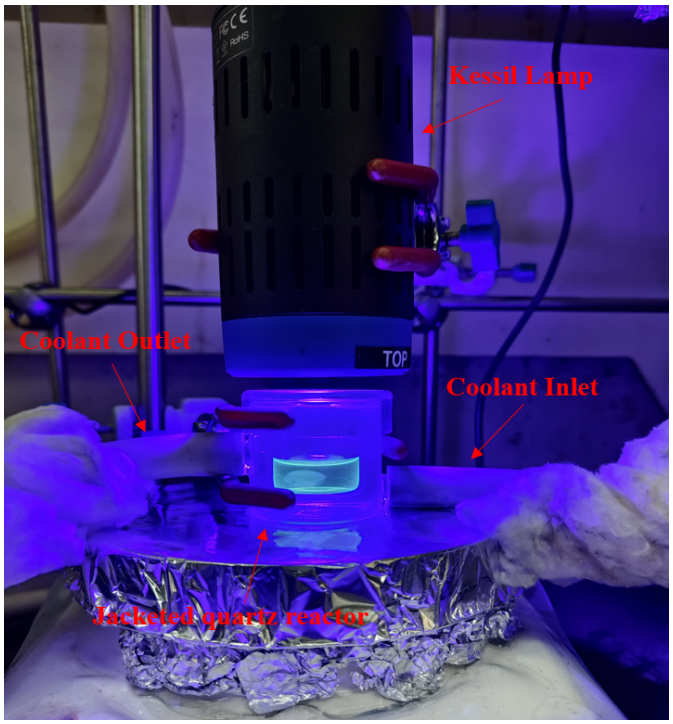


Figure S1. Schematic of the Reaction Setup

5. Control and light-on/off experiments.

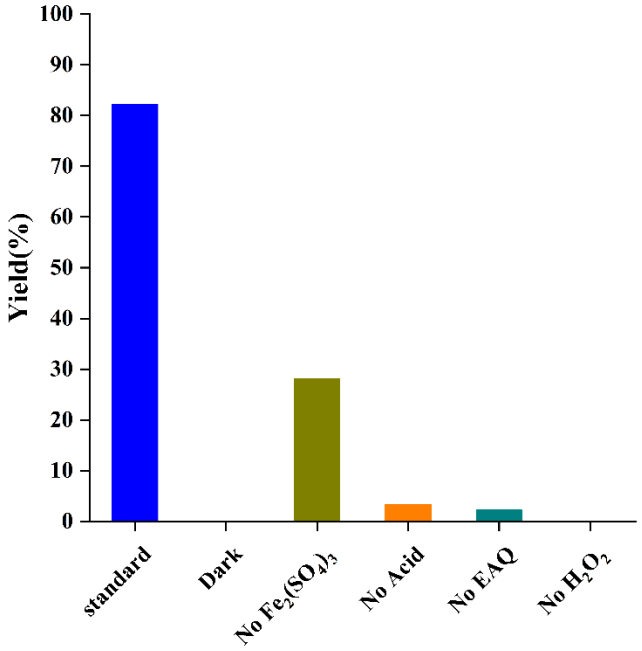


Figure S2. Control experiments

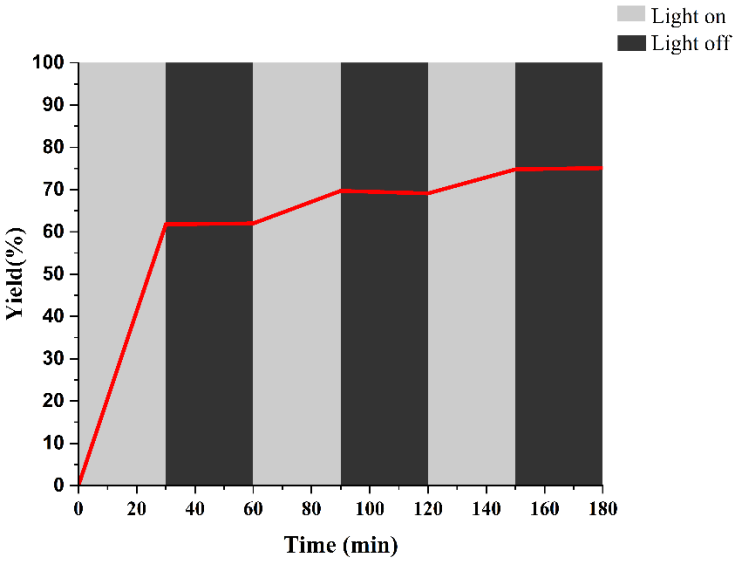


Figure S3. Light-on/off experiment

6. High-Resolution Mass Spectrometry Spectrum.

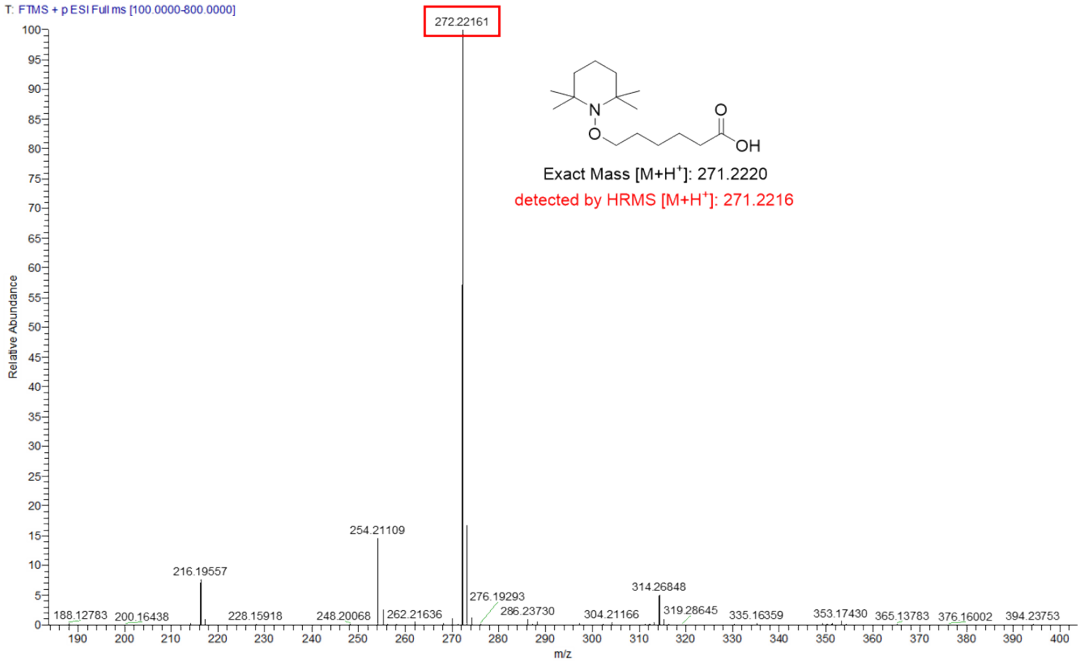


Figure S4.

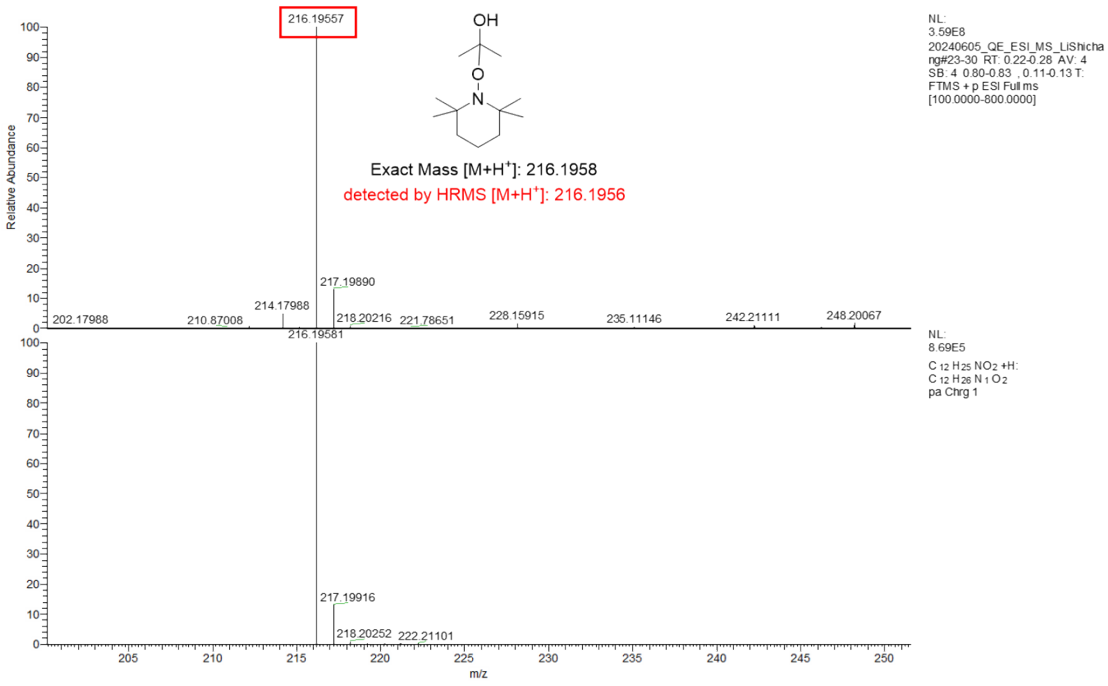


Figure S5.

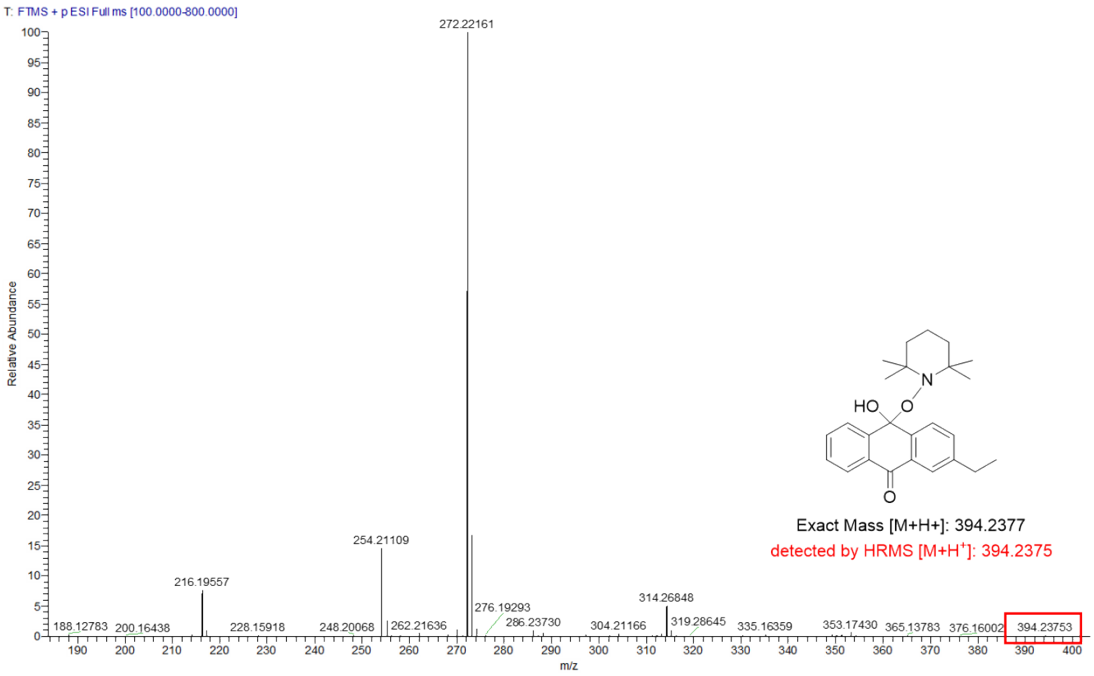


Figure S6.

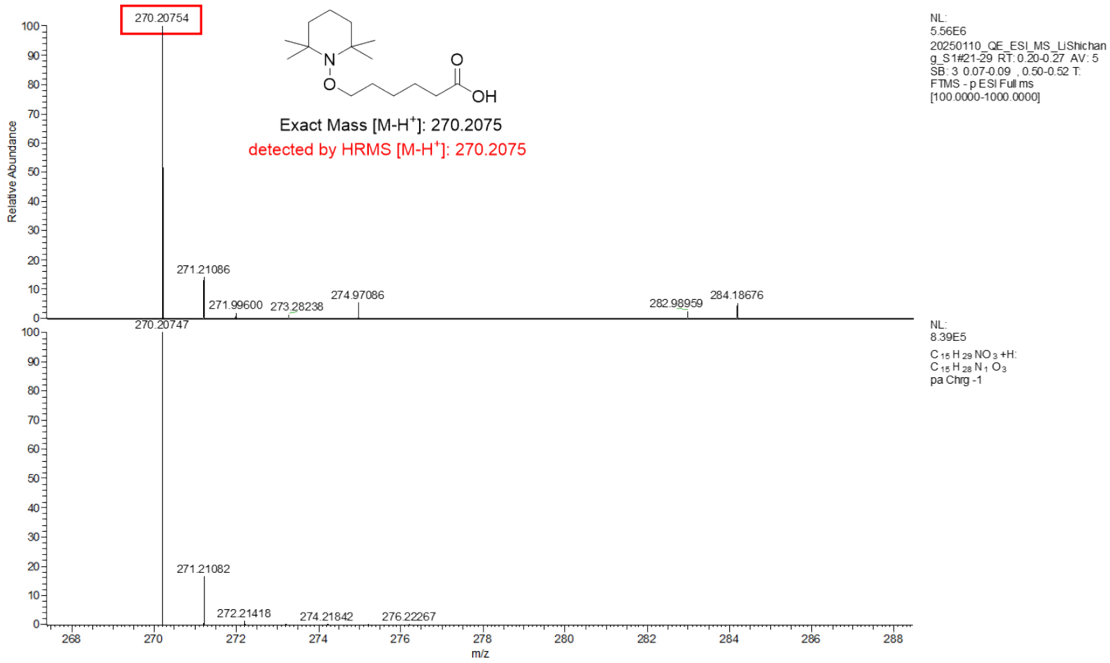


Figure S7.

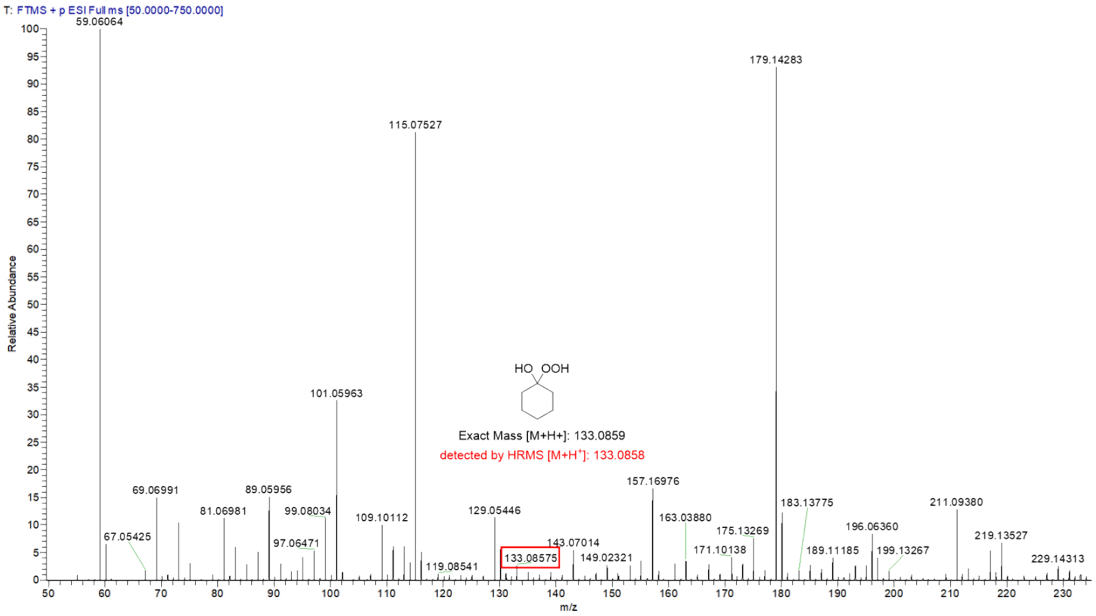
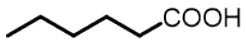

T: FTMS + p ESI Full ms [50.0000-750.0000]
Relative Abundance
m/z
59.06064
115.07527
179.14283
101.05963
69.06991
89.05956
81.06981
99.08034
109.10112
129.05446
157.16976
67.05425
97.06471
119.08541
133.08575
143.07014
149.02321
163.03880
175.13269
171.10138
183.13775
211.09380
196.06360
189.11185
199.13267
219.13527
229.14313
HO
OOH
Exact Mass [M+H+]: 133.0859
detected by HRMS [M+H+]: 133.0858

Figure S8.

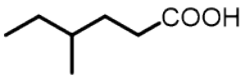
7. Characterization of Products.

Hexanoic acid (2a)



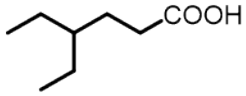
Colorless oil, Isolated yield: 177.0 mg, 80%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.92 – 1.48 (m, 2H), 1.48 – 1.14 (m, 4H), 1.07 – 0.67 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.49, 34.08, 31.21, 24.36, 22.30, 13.87.

4-methylhexanoic acid (2b)



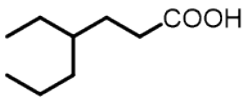
Colorless oil, Isolated yield: 135.2 mg, 55%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.57 – 2.09 (m, 2H), 1.69 (dddd, J = 13.6, 9.1, 6.5, 4.8 Hz, 1H), 1.56 – 1.07 (m, 4H), 0.99 – 0.70 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.26, 33.92, 31.83, 31.22, 29.10, 18.76, 11.25. **HRMS (ESI)** m/z: [M-H^+]$^-$ Calcd for $C_7H_{14}O_2$ 129.0921; Found: 129.0920.

4-ethylhexanoic acid (2c)



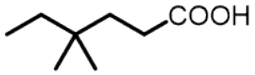
Colorless oil, Isolated yield: 132.8 mg, 49%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.58 – 2.06 (m, 2H), 1.96 – 1.50 (m, 2H), 1.49 – 0.97 (m, 5H), 0.87 (dt, J = 12.3, 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.04, 39.82, 31.50, 27.56, 25.05, 10.73. **HRMS (ESI)** m/z: [M-H^+]$^-$ Calcd for $C_8H_{16}O_2$ 143.1077; Found: 143.1075

4-ethylheptanoic acid (2d)



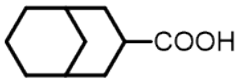
Colorless oil, Isolated yield: 135.2 mg, 45%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.51 – 2.16 (m, 2H), 1.90 – 1.50 (m, 2H), 1.47 – 1.06 (m, 7H), 0.87 (dt, J = 12.2, 6.9 Hz, 6H)**. ^{13}C NMR** (101 MHz, Chloroform-d) δ 179.90, 38.10, 35.11, 31.41, 27.95, 25.51, 19.69, 14.43, 10.69. **HRMS (ESI)** m/z: [M-H^+]$^-$ Calcd for $C_9H_{18}O_2$ 157.1234; Found: 157.1231.

4,4-dimethylhexanoic acid (2e)



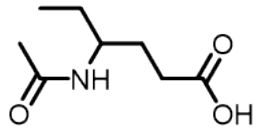
Colorless oil, Isolated yield: 129.5 mg, 47%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 11.18 (s, 1H), 2.48 – 2.09 (m, 2H), 1.81 – 1.40 (m, 2H), 1.23 (q, J = 7.4 Hz, 2H), 1.06 – 0.53 (m, 9H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.41, 35.78, 33.85, 32.43, 29.32, 26.23, 8.30. **HRMS (ESI)** m/z: [M-H^+]$^-$ Calcd for $C_8H_{16}O_2$ 143.1077; Found: 143.1075.

bicyclo[3.3.1]nonane-3-carboxylic acid (2f)



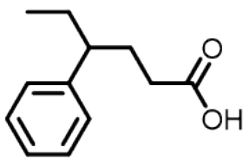
White solid, Isolated yield: 131.6 mg, 41%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 10.70 (s, 1H), 2.56 (tt, J = 12.7, 5.8 Hz, 1H), 2.42 – 2.05 (m, 4H), 1.95 – 0.93 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 182.23, 35.74, 32.89, 29.13, 28.90, 24.83, 15.94. **HRMS (ESI)** m/z: [M-H^+]$^-$ Calcd for $C_{10}H_{16}O_2$ 167.1077; Found: 167.1075.

4-acetamidohexanoic acid (2g)



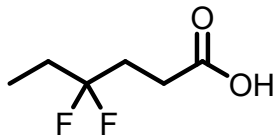
White solid, Isolated yield: 211.1 mg, 64%.(Eluent: V_{DCM} : V_{MeOH} = 50:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 5.40 (d, J = 9.1 Hz, 1H), 3.99 – 3.80 (m, 1H), 2.41 (t, J = 7.0 Hz, 2H), 2.02 (s, 3H), 1.92 – 1.40 (m, 4H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 180.49, 34.08, 31.21, 24.36, 22.30, 13.87. **HRMS (ESI)** m/z: $[M-H^+]^-$ Calcd for $C_8H_{15}NO_3$ 172.0979; Found: 172.0977.

4-phenylhexanoic acid (2h)



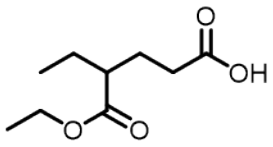
White solid, Isolated yield: 263.5 mg, 72%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 10.94 (s, 1H), 7.39 – 7.02 (m, 5H), 2.44 (tt, J = 9.9, 5.1 Hz, 1H), 2.18 (t, J = 7.5 Hz, 2H), 2.08 – 1.79 (m, 2H), 1.74 – 1.54 (m, 2H), 0.78 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 179.38, 144.24, 128.45, 127.73, 126.31, 47.17, 32.08, 31.16, 29.62, 12.11. **HRMS (ESI)** m/z: $[M-H^+]^-$ Calcd for $C_{12}H_{16}O_2$ 191.1077; Found:191.1075.

4,4-difluorohexanoic acid (2i)



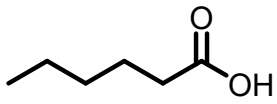
White solid, Isolated yield: 172.2 mg, 60%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.68 – 2.48 (m, 2H), 2.18 (tdd, J = 17.0, 8.6, 7.0 Hz, 2H), 1.88 (ddt, J = 23.9, 16.4, 7.5 Hz, 2H), 1.03 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 178.78, 124.32 (t, J = 240.8 Hz), 30.88 (t, J = 26.0 Hz), 29.93 (t, J = 25.9 Hz), 26.97 (t, J = 4.9 Hz), 6.55 (t, J = 5.7 Hz). **^{19}F NMR** (377 MHz, Chloroform-d) δ -102.24 (p, J = 16.7 Hz). **HRMS (ESI)** m/z: $[M-H^+]^-$ Calcd for $C_6H_{10}F_2O_2$ 151.0576; Found: 151.0573.

4-(ethoxycarbonyl)hexanoic acid (2j)



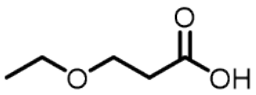
White solid, Isolated yield: 222.3 mg, 62%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 4.15 (q, J = 7.1 Hz, 2H), 2.81 – 2.21 (m, 3H), 2.04 – 1.34 (m, 4H), 1.26 (td, J = 7.1, 1.5 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 178.50, 175.45, 60.35, 46.21, 31.64, 26.45, 25.36, 14.31, 11.58. **HRMS (ESI)** m/z: $[M\text{-}H^{+}]^{-}$ Calcd for $C_9H_{16}O_4$ 187.0976; Found: 187.0973.

2-ethylpentanedioic acid (2k)



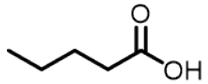
Colorless oil, Isolated yield: 163.2 mg, 74%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 11.48 (s, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.64 (dq, J = 10.0, 7.4 Hz, 2H), 1.33 (dq, J = 7.2, 4.0, 3.3 Hz, 4H), 1.08 – 0.72 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 179.98, 33.99, 31.21, 24.37, 22.30, 13.88.

3-ethoxypropanoic acid (2l)



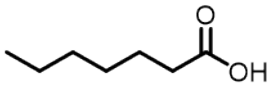
Colorless oil, Isolated yield: 152.1 mg, 68%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 3.71 (t, J = 6.3 Hz, 2H), 3.53 (q, J = 7.0 Hz, 2H), 2.63 (t, J = 6.3 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 177.05, 66.56, 65.44, 34.91, 15.01. **HRMS (ESI)** m/z: $[M\text{-}H^{+}]^{-}$ Calcd for $C_5H_{10}O_3$ 117.0557; Found: 117.0555.

pentanoic acid (2m)



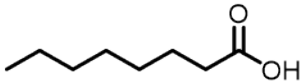
Colorless oil, Isolated yield: 60.3 mg, 31%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, Chloroform-d) δ 2.35 (t, J = 7.5 Hz, 2H), 1.62 (p, J = 7.5 Hz, 2H), 1.46 – 1.31 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.31, 33.79, 26.73, 22.18, 13.68.

heptanoic acid (2n)



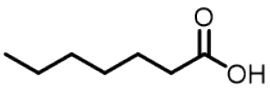
Colorless oil, Isolated yield: 35.1 mg, 14%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.35 (t, J = 7.5 Hz, 2H), 1.75 – 1.54 (m, 2H), 1.47 – 1.05 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 179.30, 33.91, 31.43, 28.73, 24.65, 22.47, 14.02.

octanoic acid (2o)



Colorless oil, Isolated yield: 40.8 mg, 15%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 2.35 (t, J = 7.5 Hz, 2H), 1.92 – 1.48 (m, 2H), 1.48 – 1.14 (m, 4H), 1.07 – 0.67 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 180.49, 34.08, 31.21, 24.36, 22.30, 13.87.

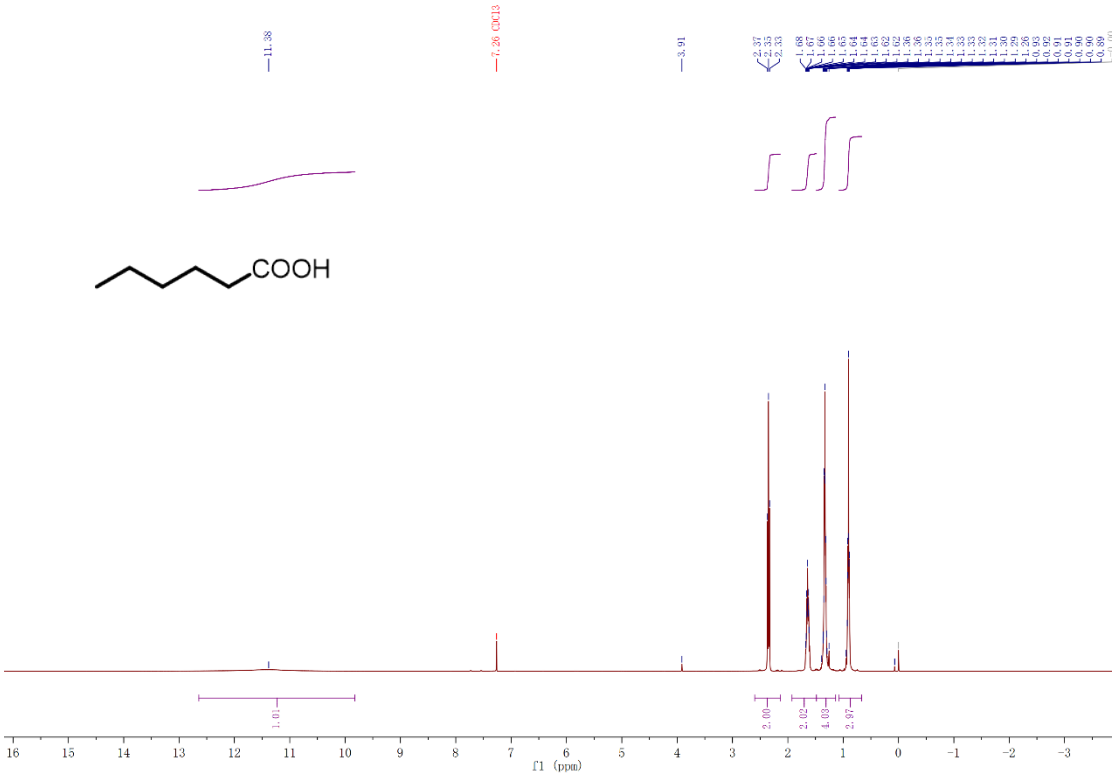
heptanoic acid (2p)



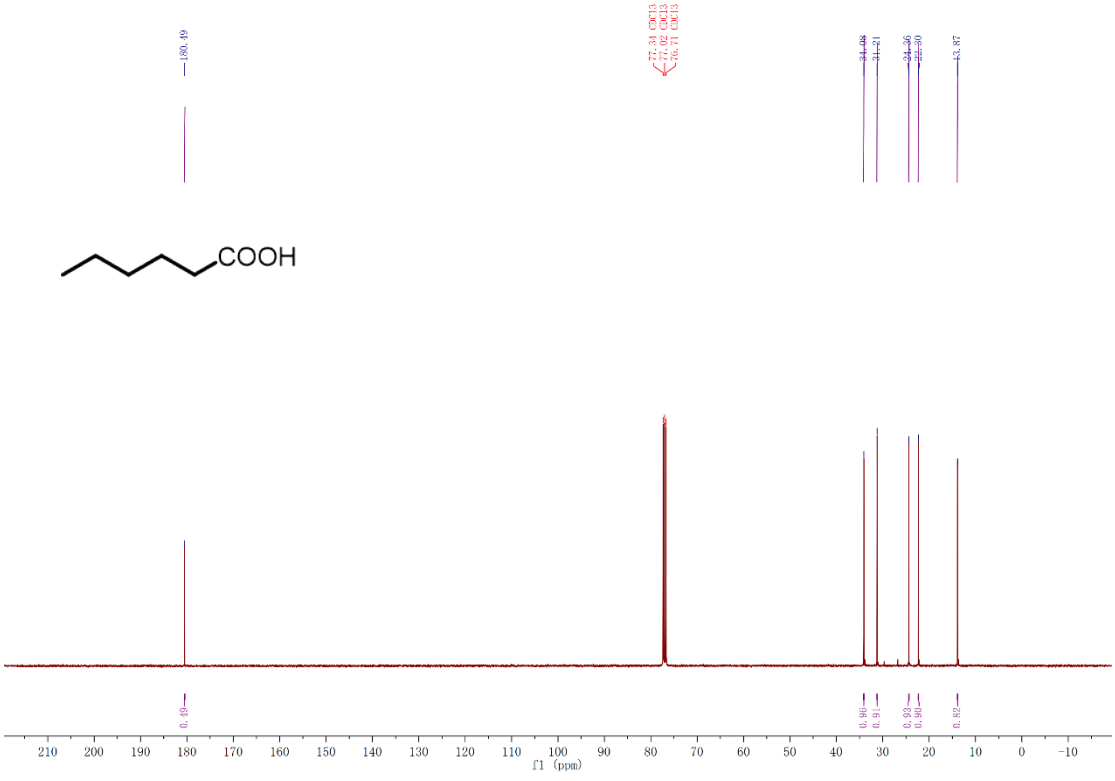
Colorless oil, Isolated yield: 67.0 mg, 27%.(Eluent: V_{PE} : V_{EA} = 10:1 with 1% formic acid), **^{1}H NMR** (500 MHz, Chloroform-d) δ 2.53 – 2.22 (m, 2H), 1.78 – 1.54 (m, 2H), 1.40 – 1.15 (m, 6H), 0.89 (q, J = 7.1, 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 179.59, 33.96, 31.43, 28.73, 24.65, 22.47, 14.02.

8. NMR Spectra of Products.

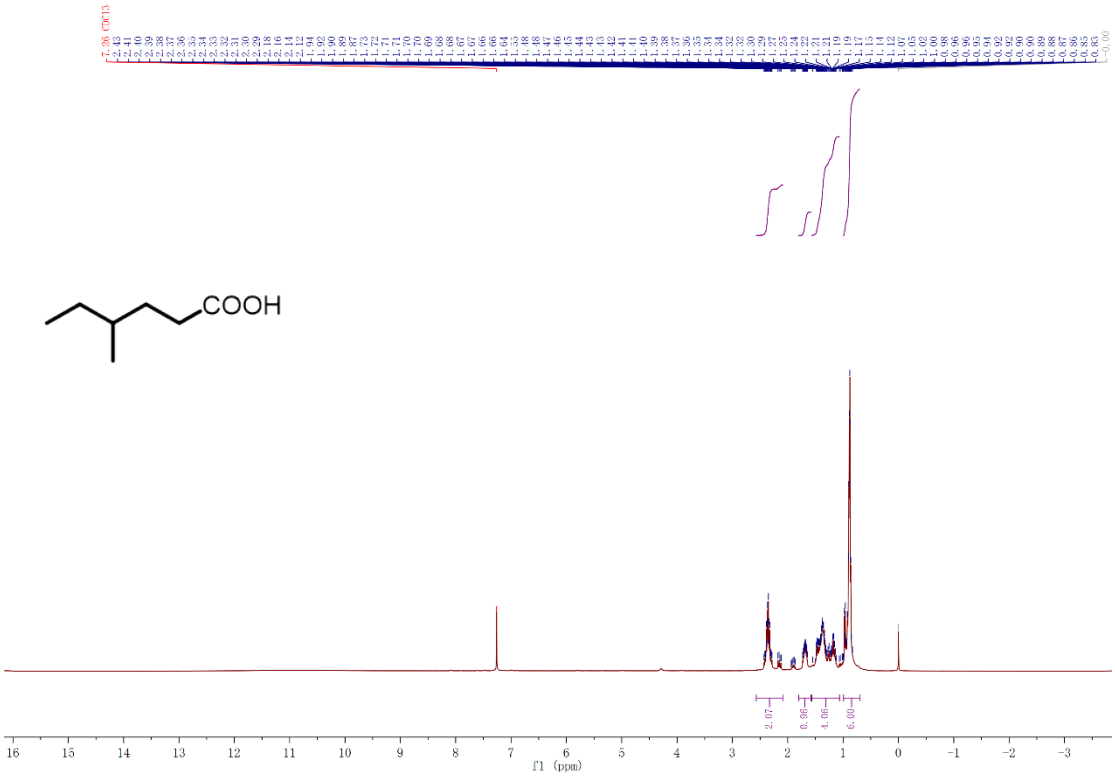
^{1}H NMR of compound 2a (400 MHz, $CDCl_3$)



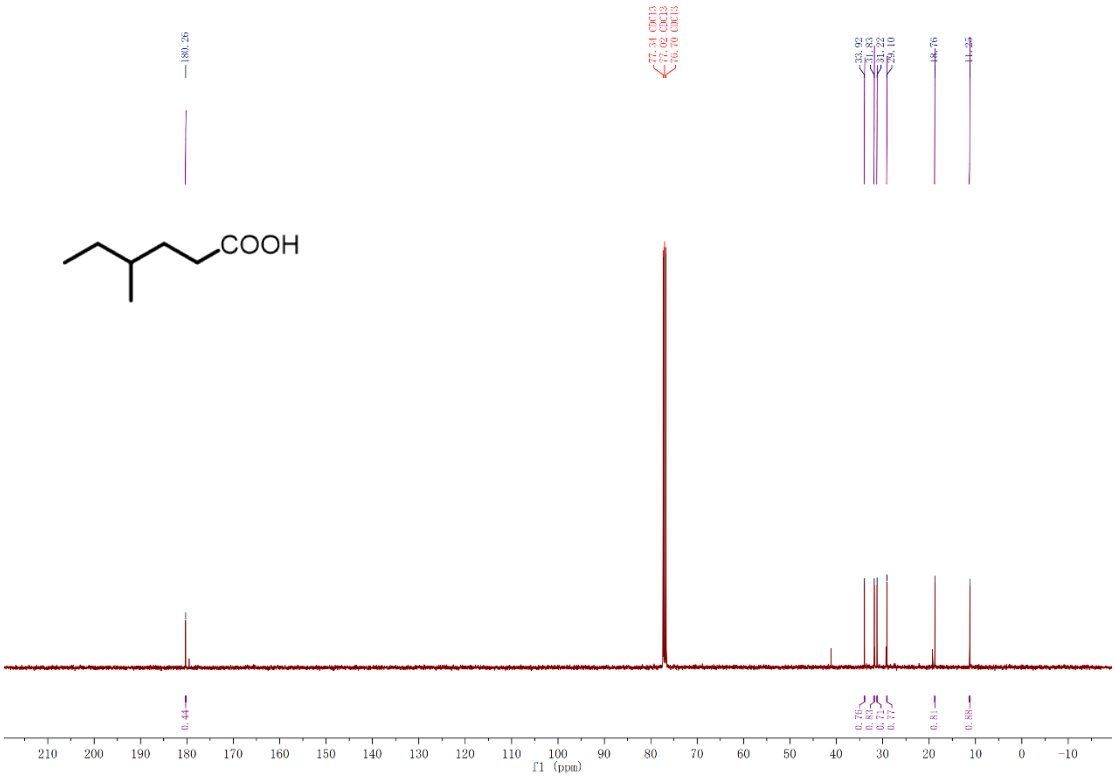
^{13}C NMR of compound 2a (101 MHz, $CDCl_3$)



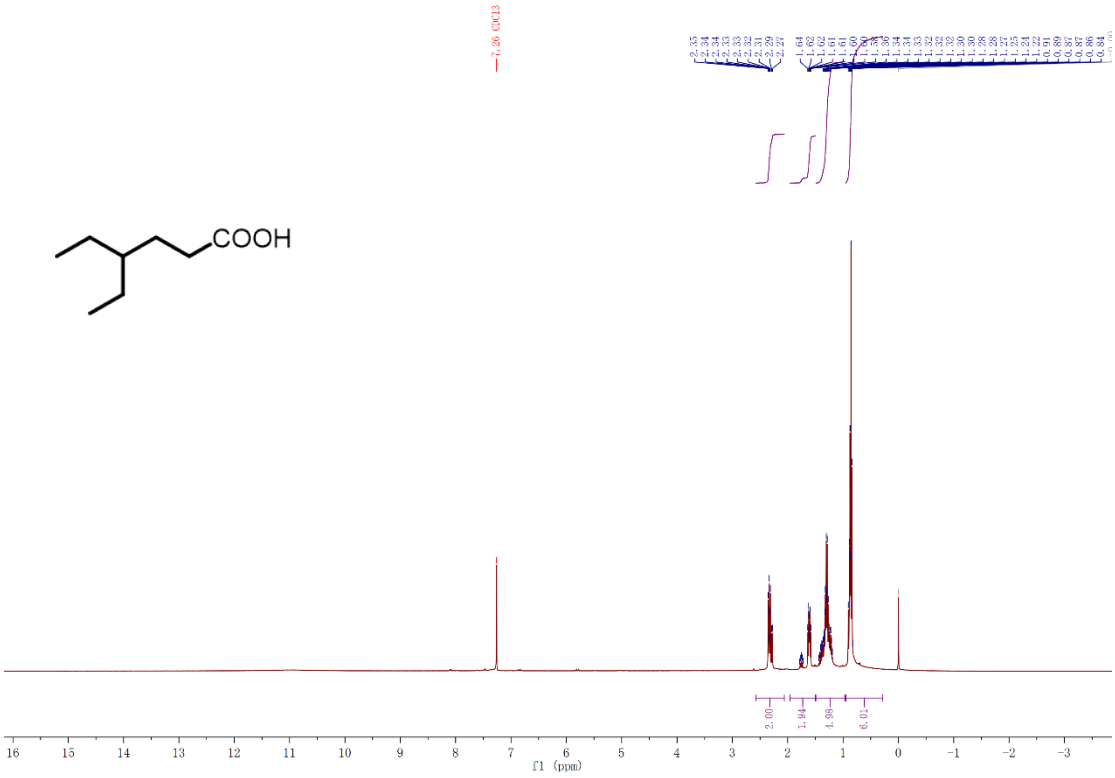
^{1}H NMR of compound 2b (400 MHz, $CDCl_3$)



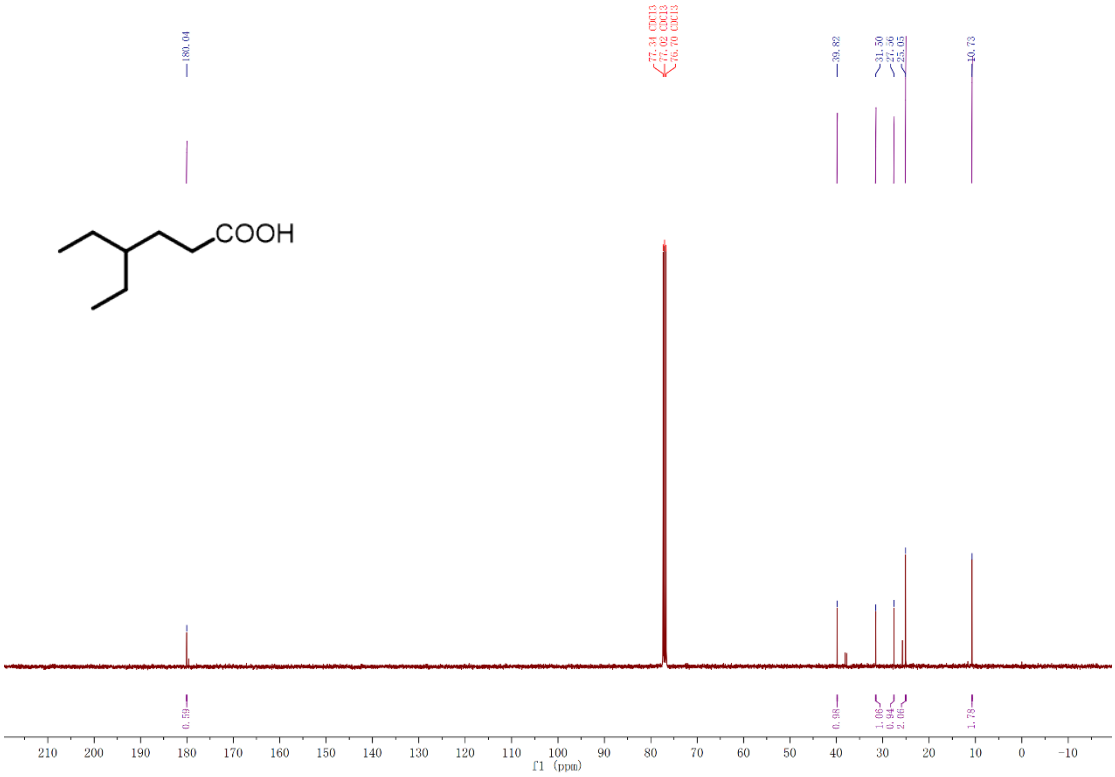
^{13}C NMR of compound 2b (101 MHz, $CDCl_3$)



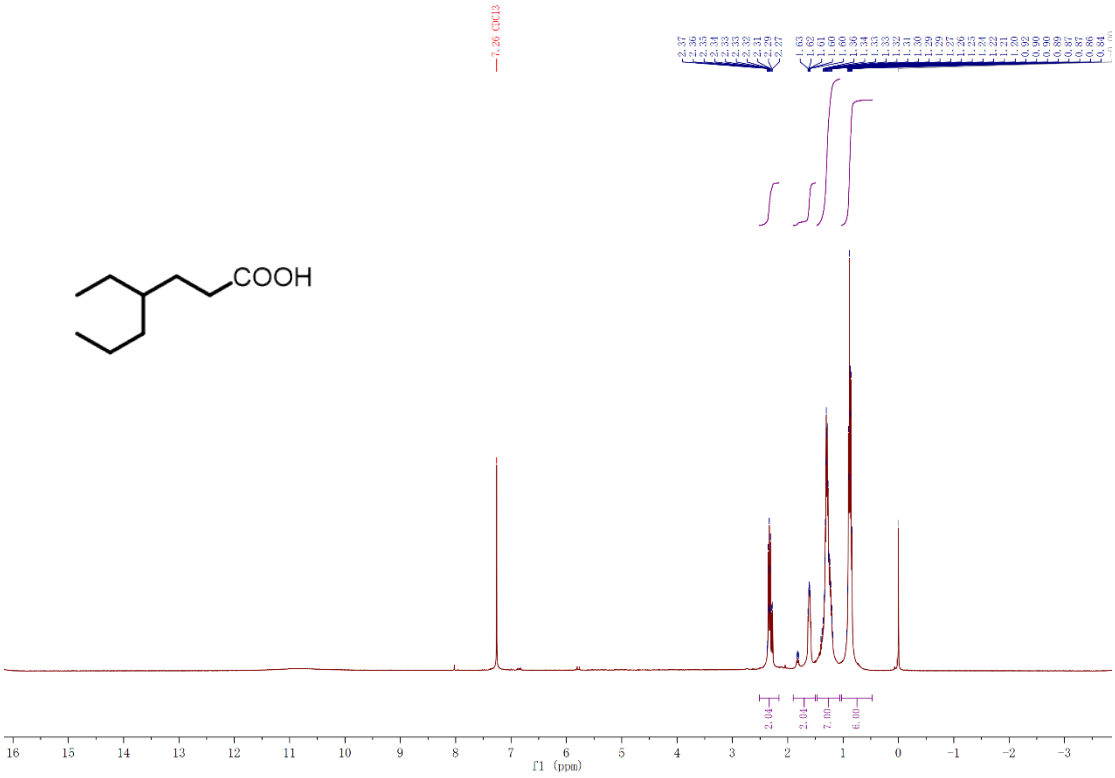
^{1}H NMR of compound 2c (400 MHz, $CDCl_3$)



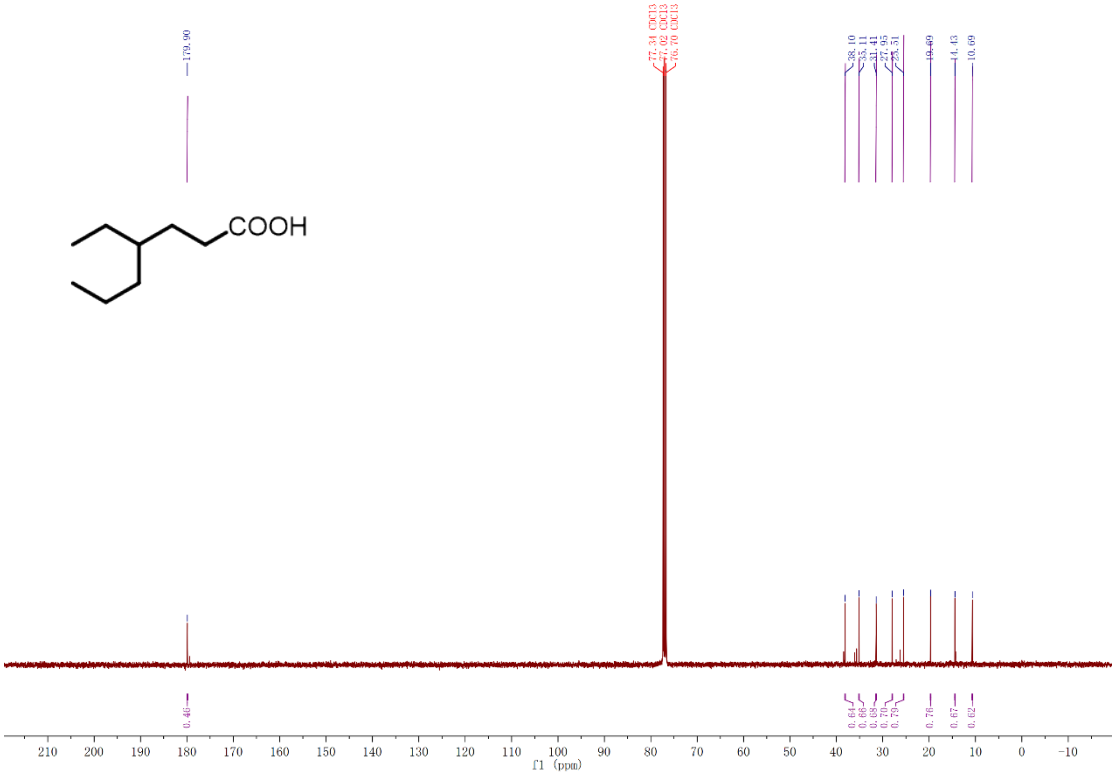
^{13}C NMR of compound 2c (101 MHz, $CDCl_3$)



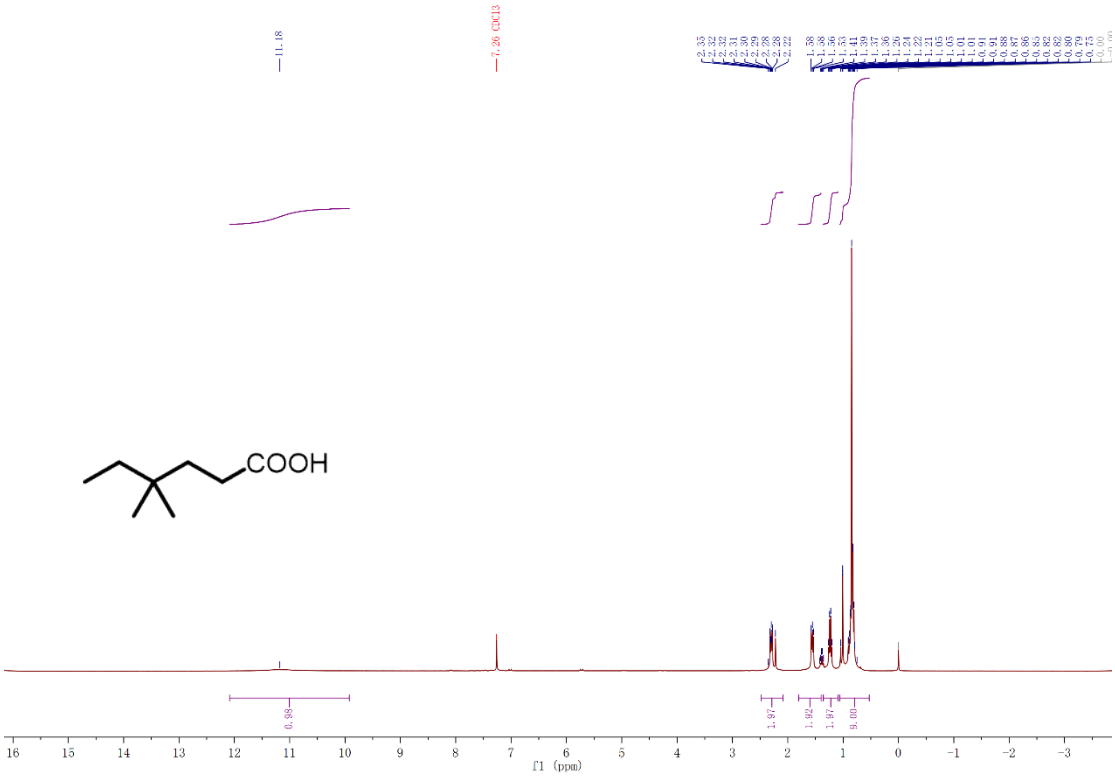
^{1}H NMR of compound 2d (400 MHz, $CDCl_3$)



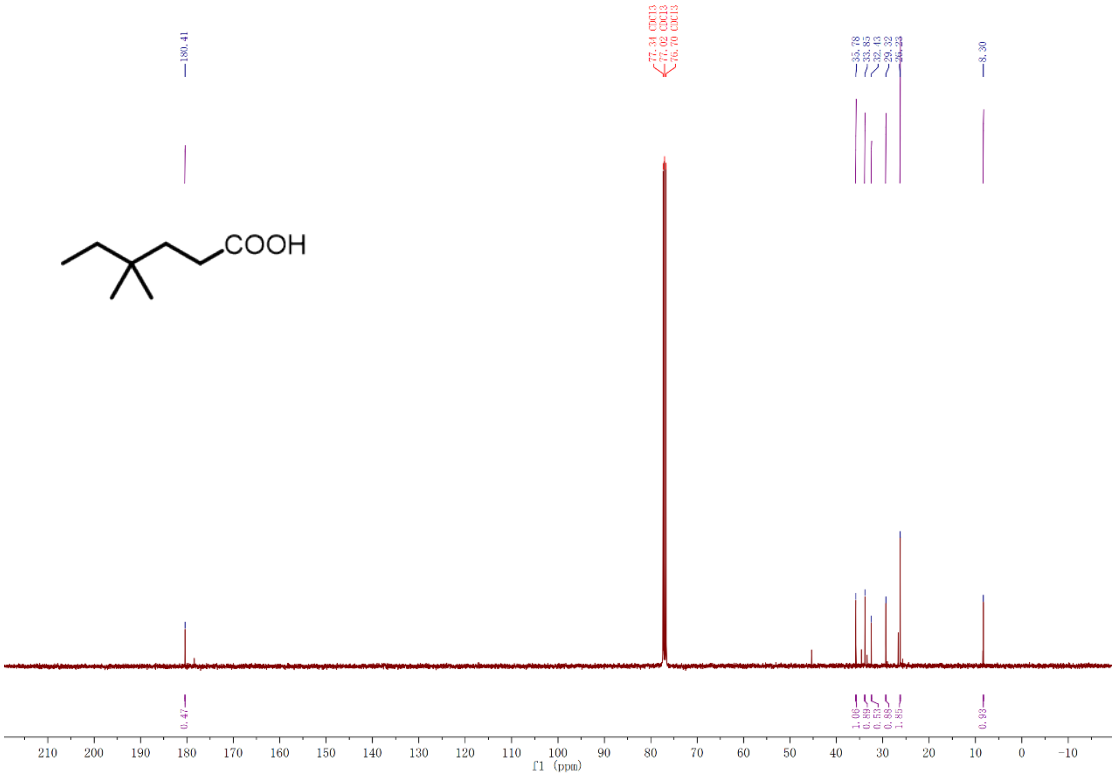
^{13}C NMR of compound 2d (101 MHz, $CDCl_3$)



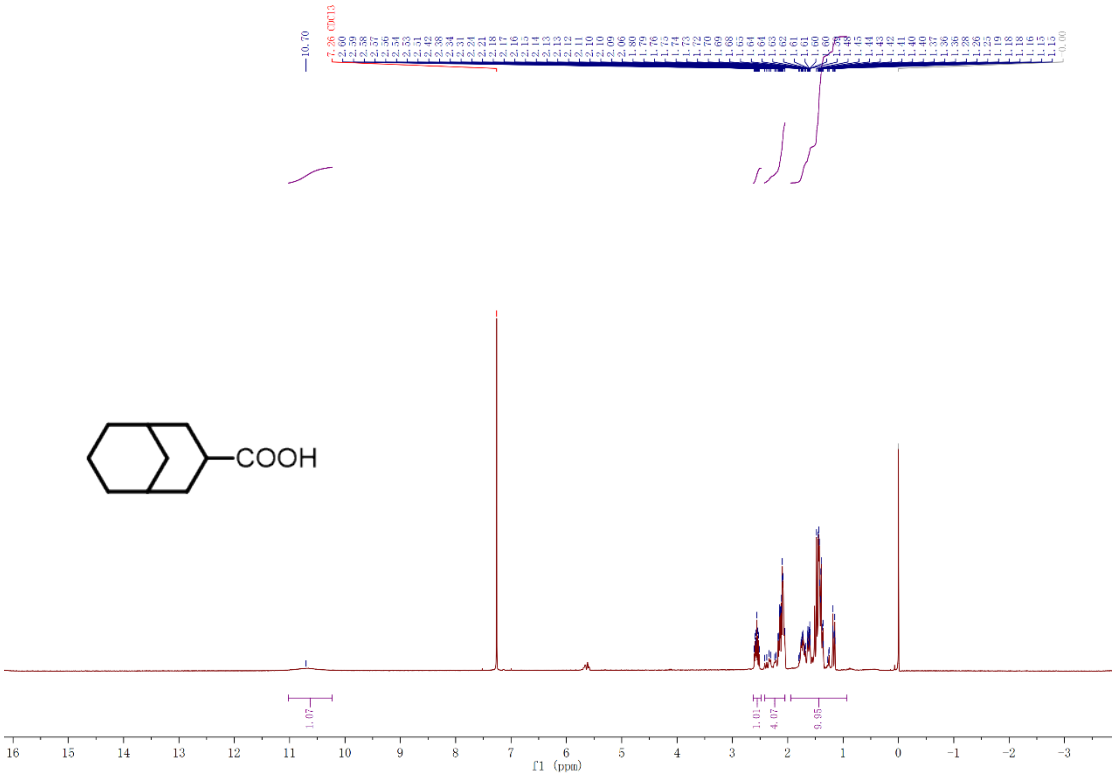
^{1}H NMR of compound 2e (400 MHz, $CDCl_3$)



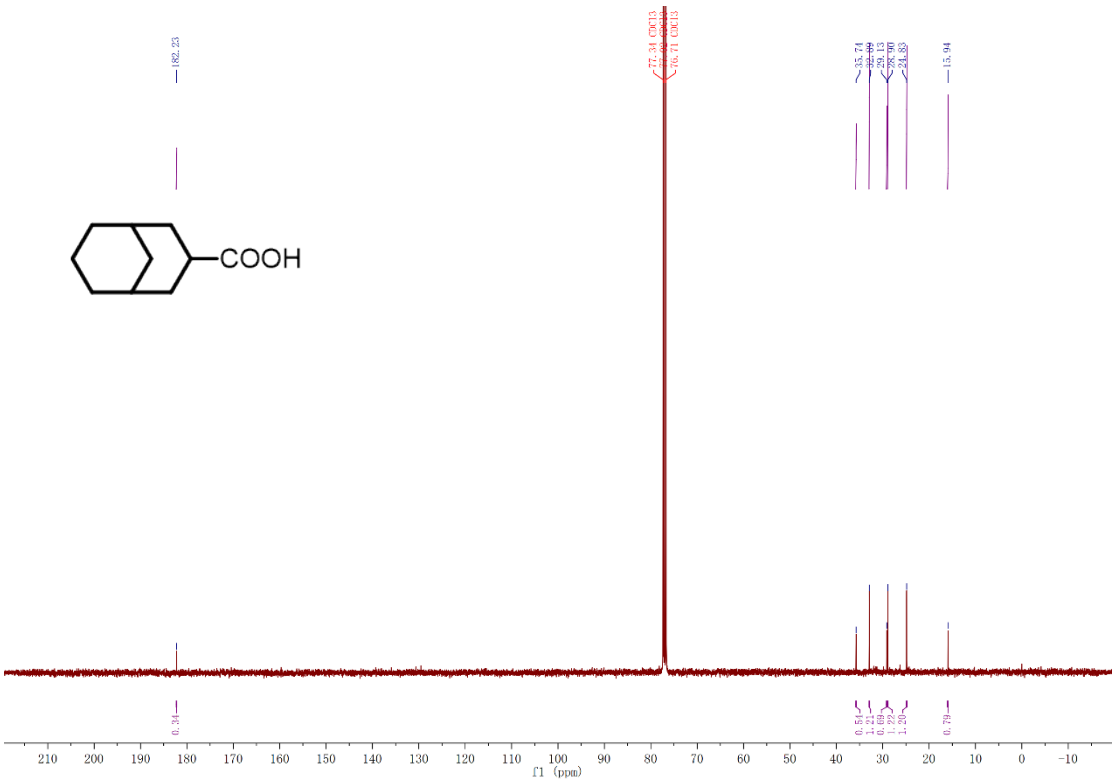
^{13}C NMR of compound 2e (101 MHz, $CDCl_3$)



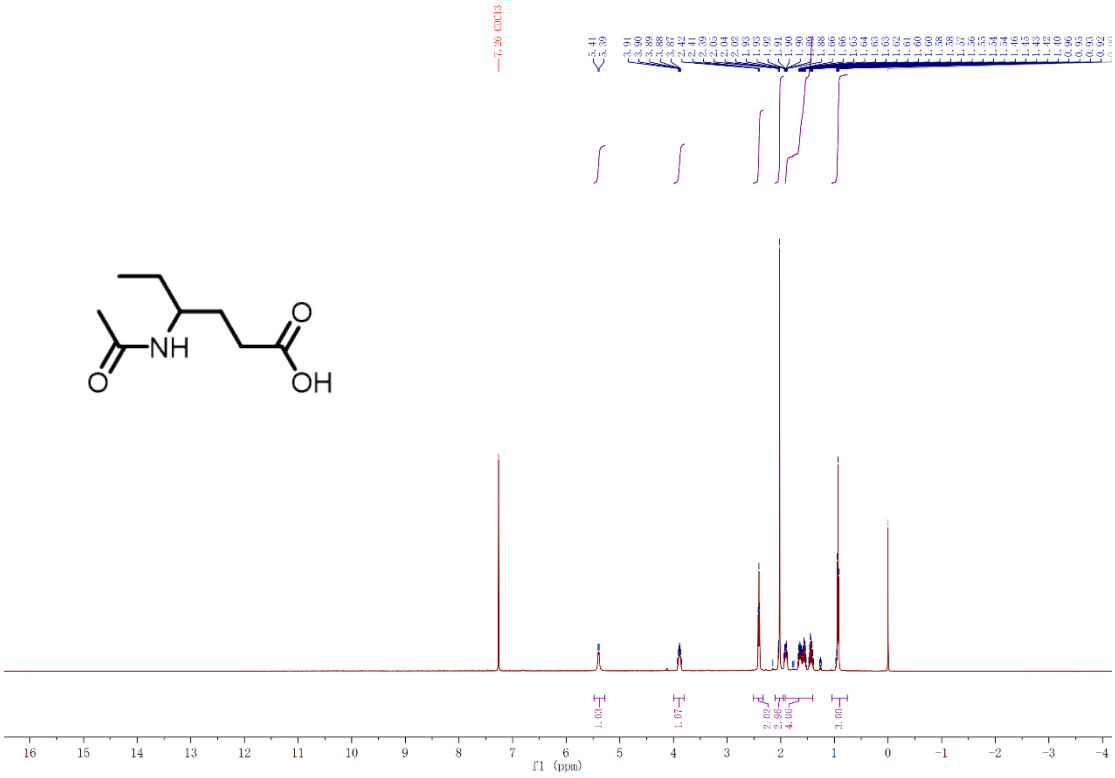
^{1}H NMR of compound 2f (400 MHz, $CDCl_3$)



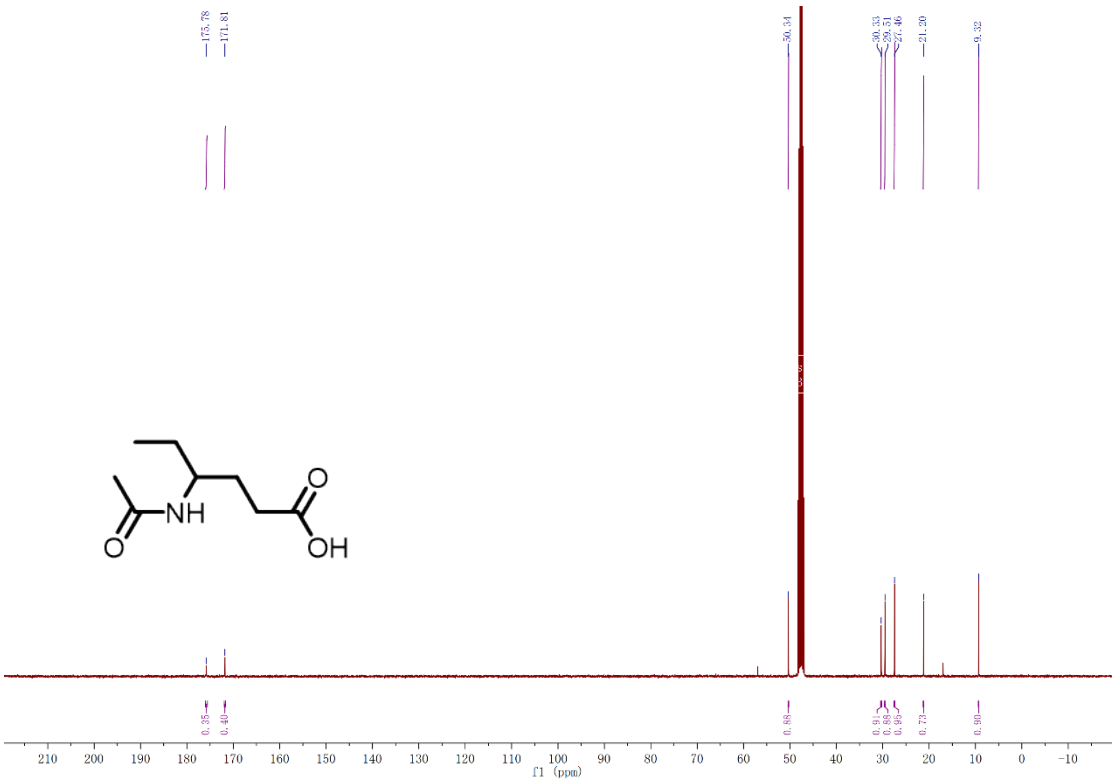
^{13}C NMR of compound 2f (101 MHz, $CDCl_3$)



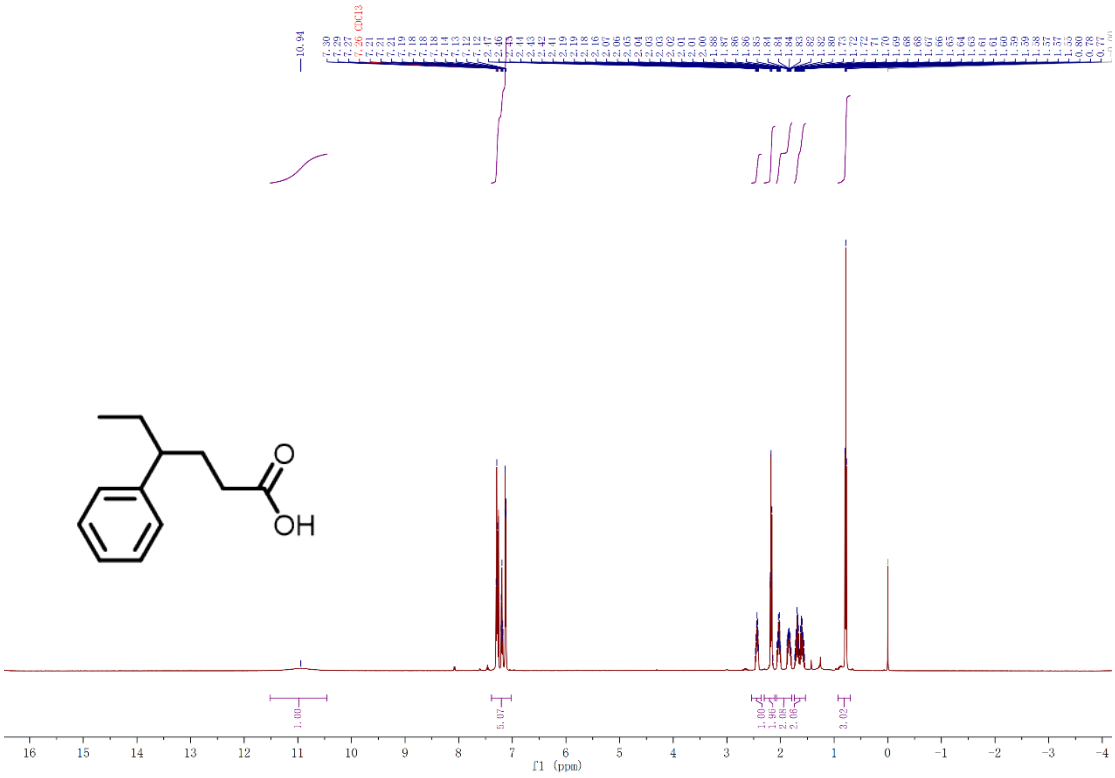
^{1}H NMR of compound 2g (500 MHz, $CDCl_3$)



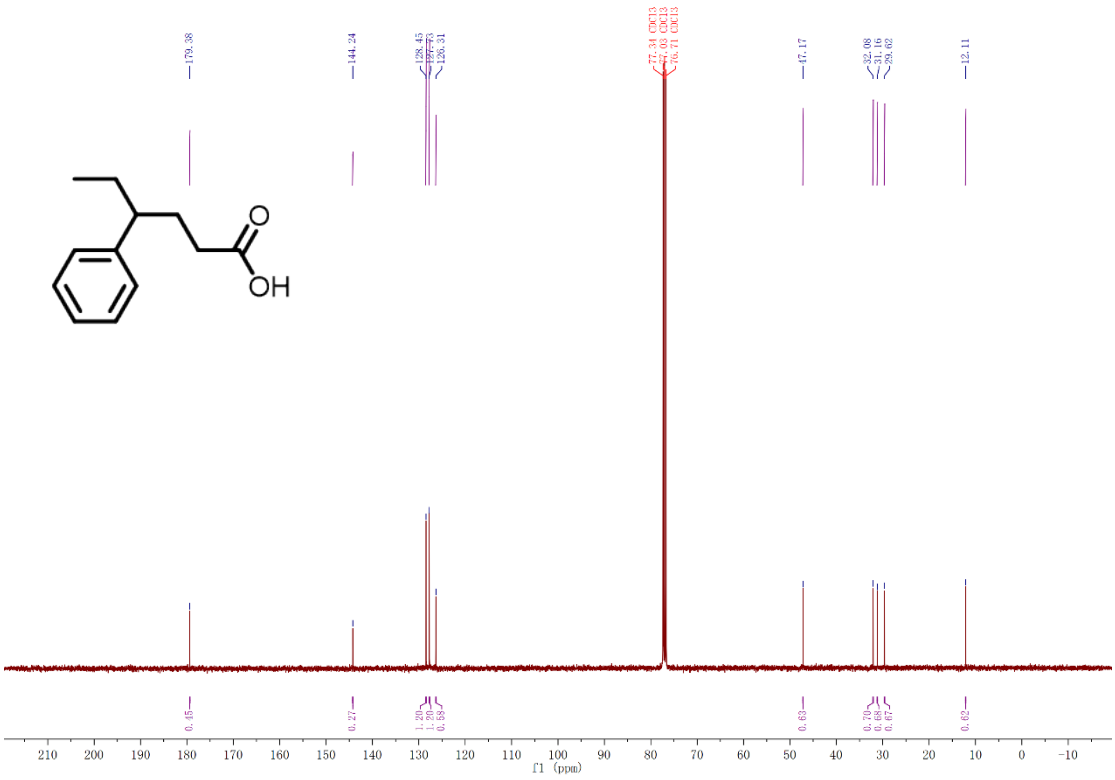
^{13}C NMR of compound 2g (101 MHz, CD_3OD)



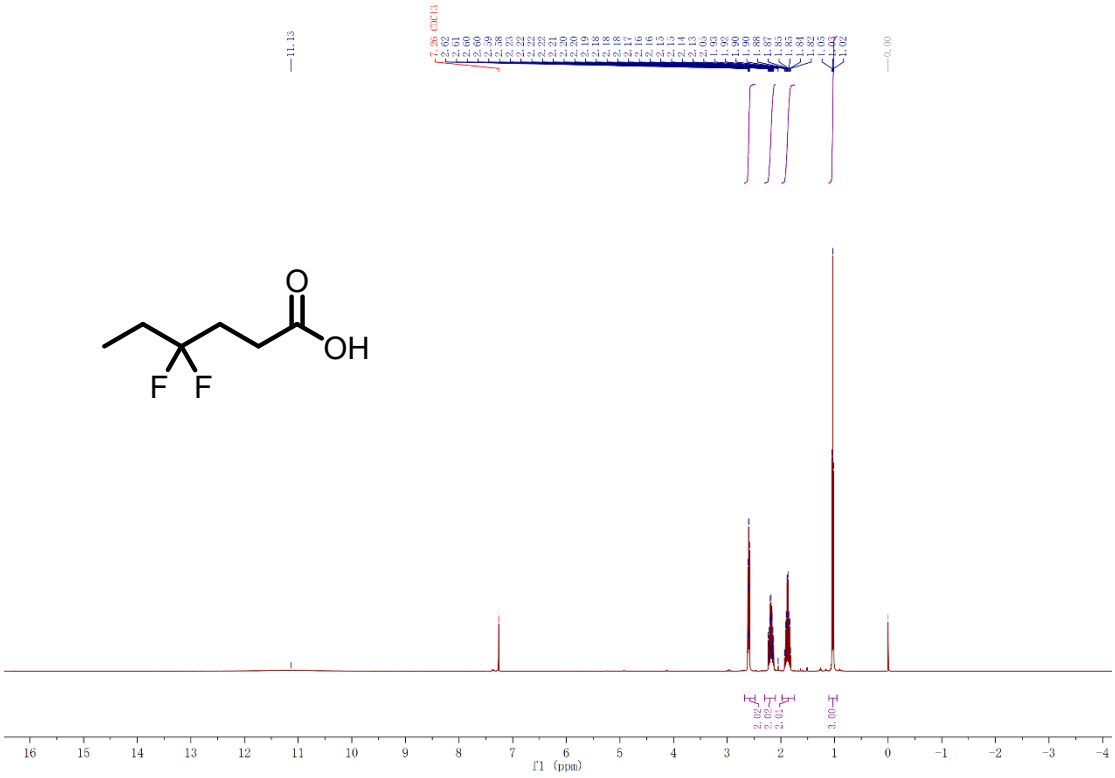
^{1}H NMR of compound 2h (500 MHz, $CDCl_3$)



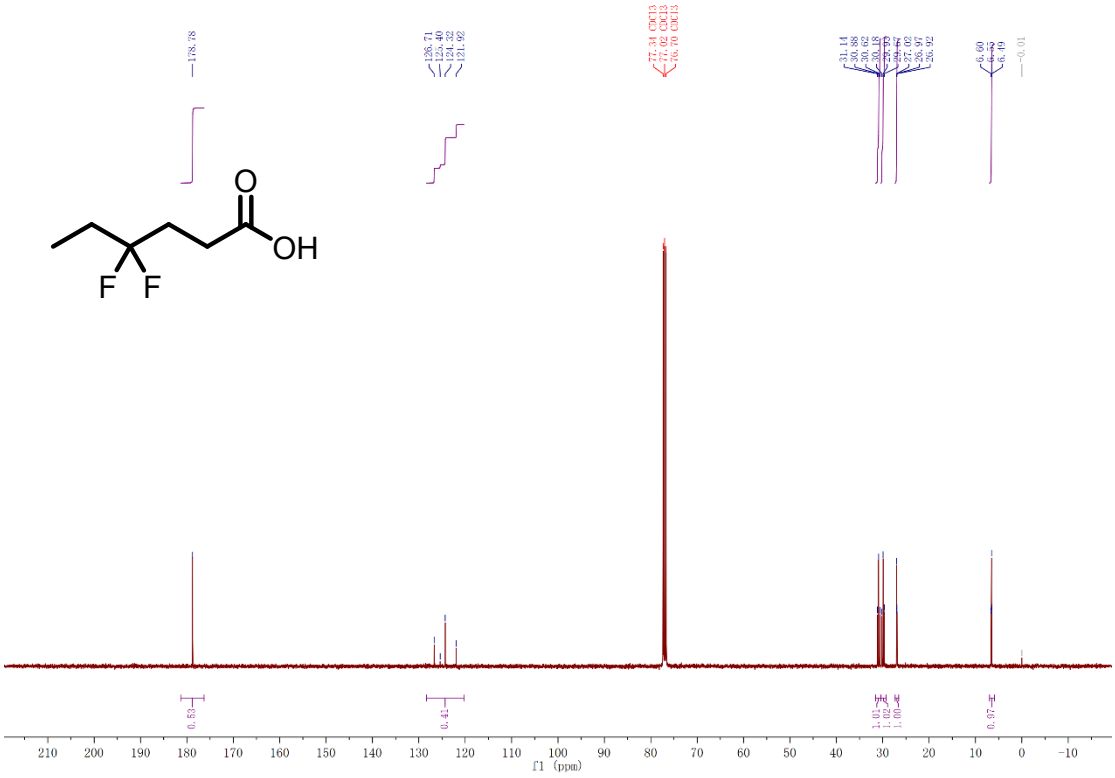
^{13}C NMR of compound 2h (101 MHz, $CDCl_3$)



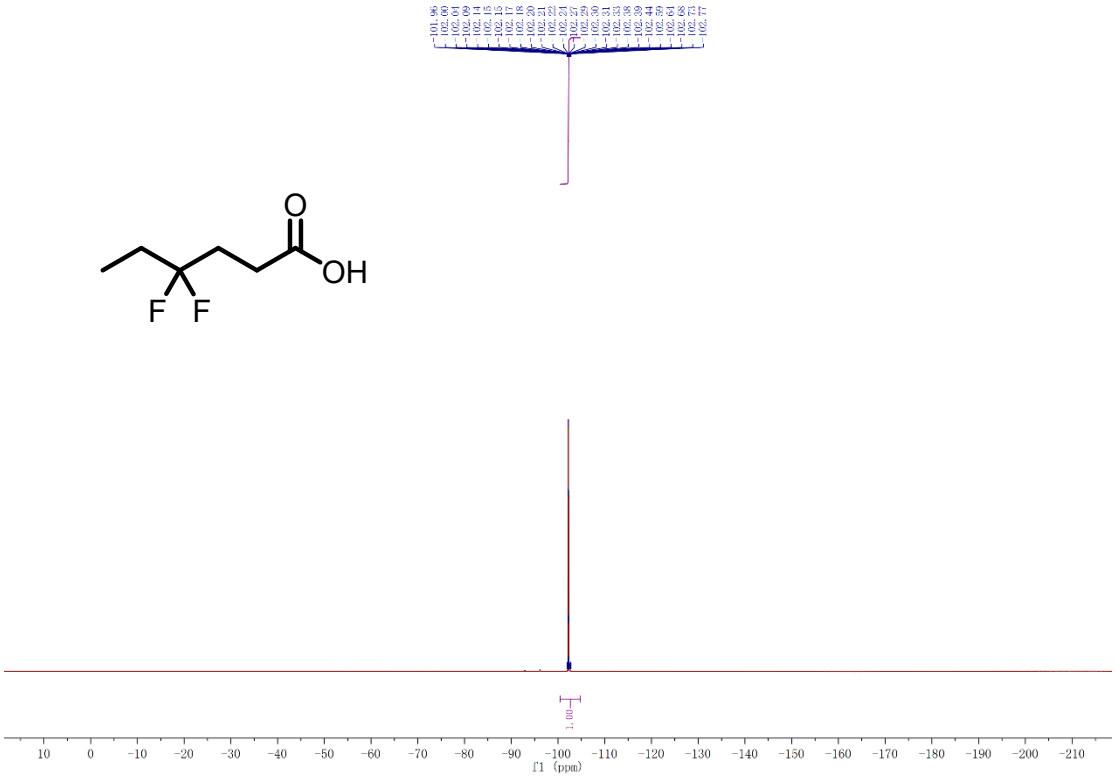
^{1}H NMR of compound 2i (500 MHz, $CDCl_3$)



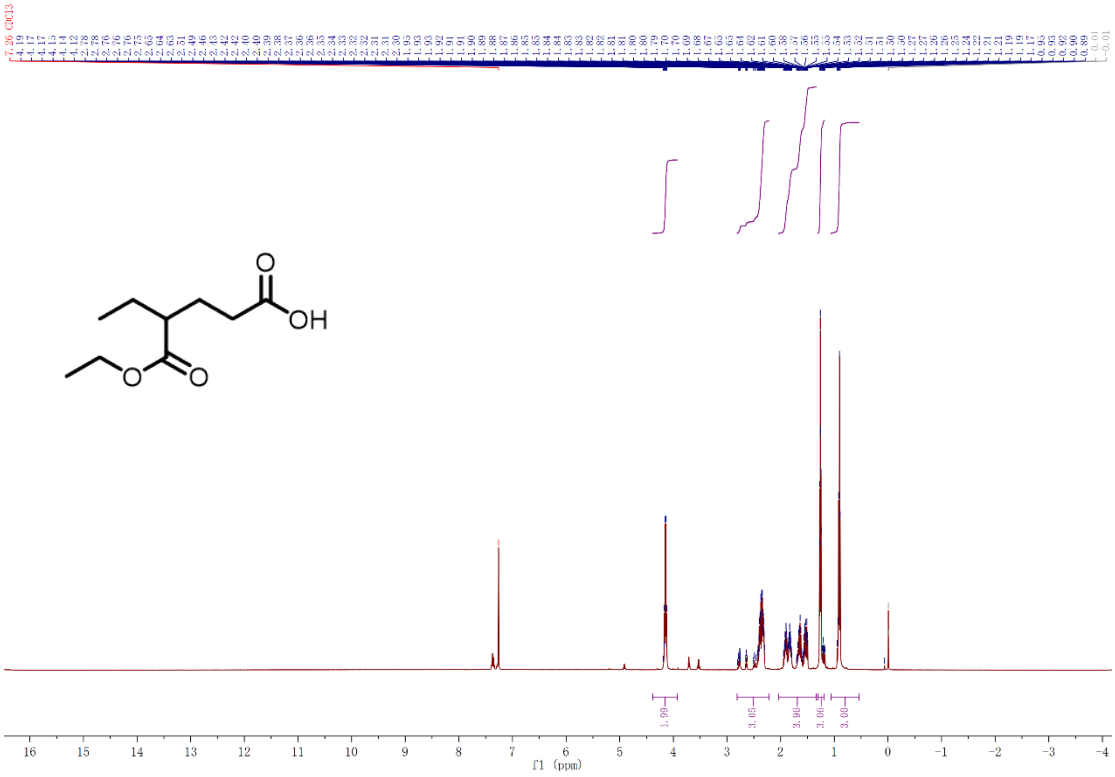
^{13}C NMR of compound 2i (101 MHz, $CDCl_3$)



^{19}F NMR of compound 2i (377 MHz, $CDCl_3$)

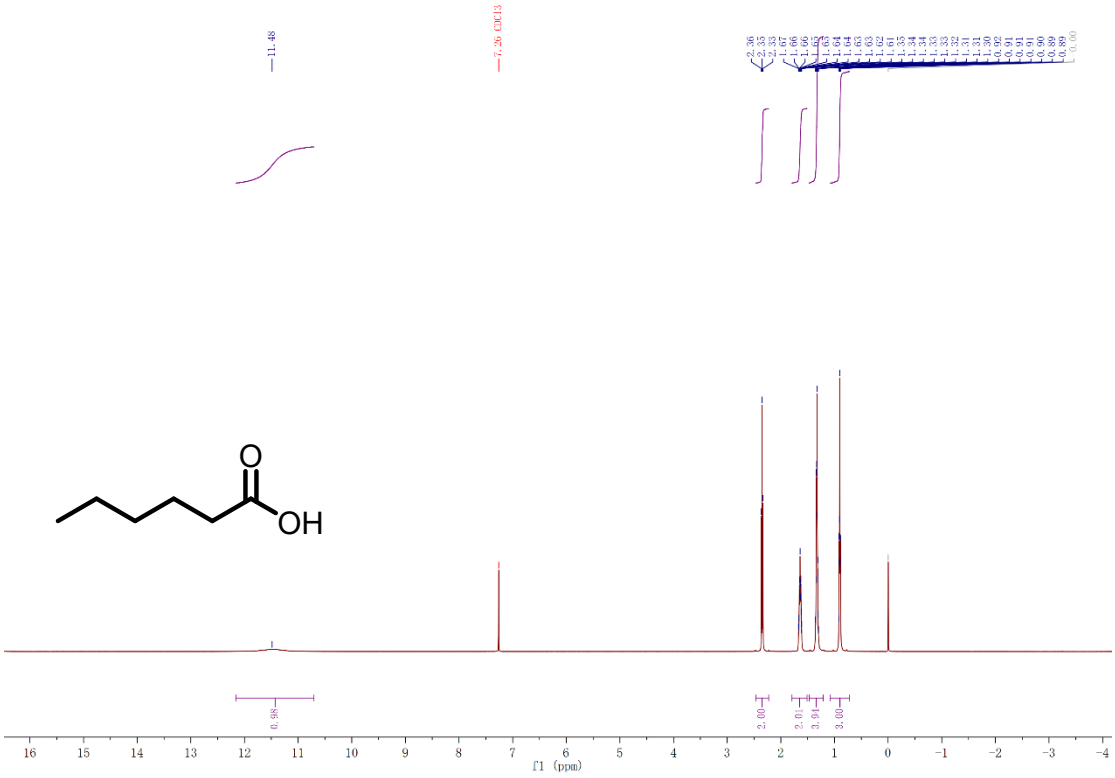


^{1}H NMR of compound 2j (500 MHz, $CDCl_3$)

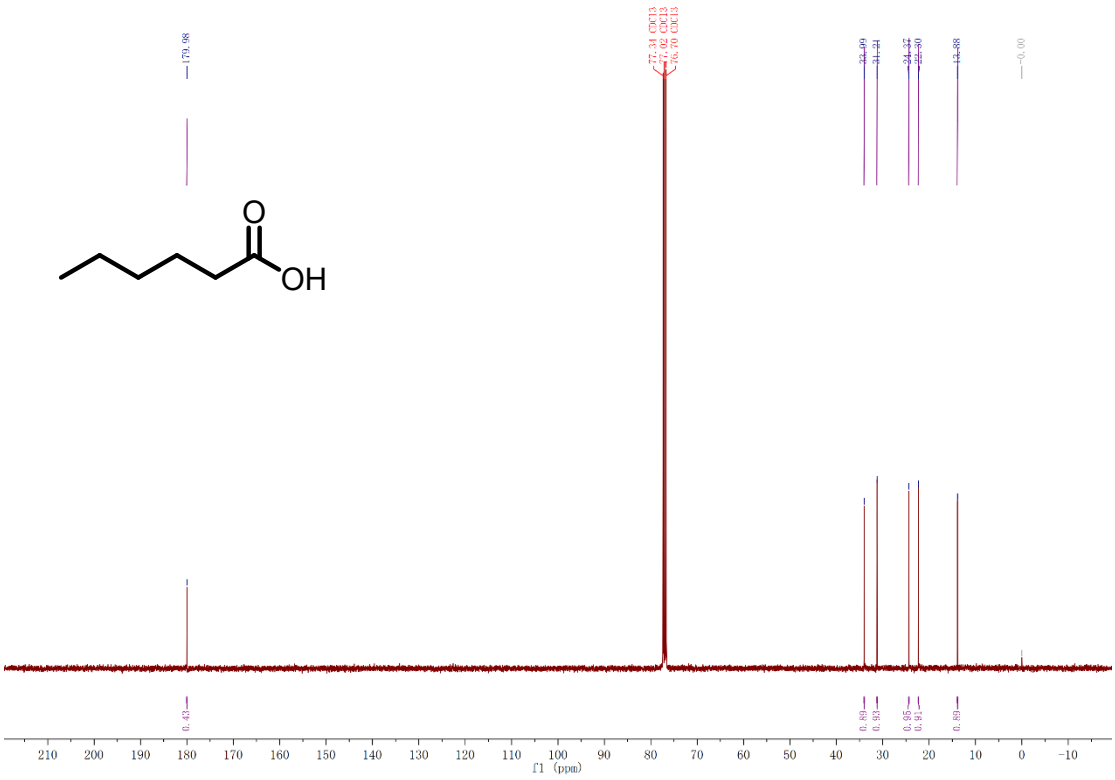


^{13}C NMR of compound 2j (101 MHz, $CDCl_3$)

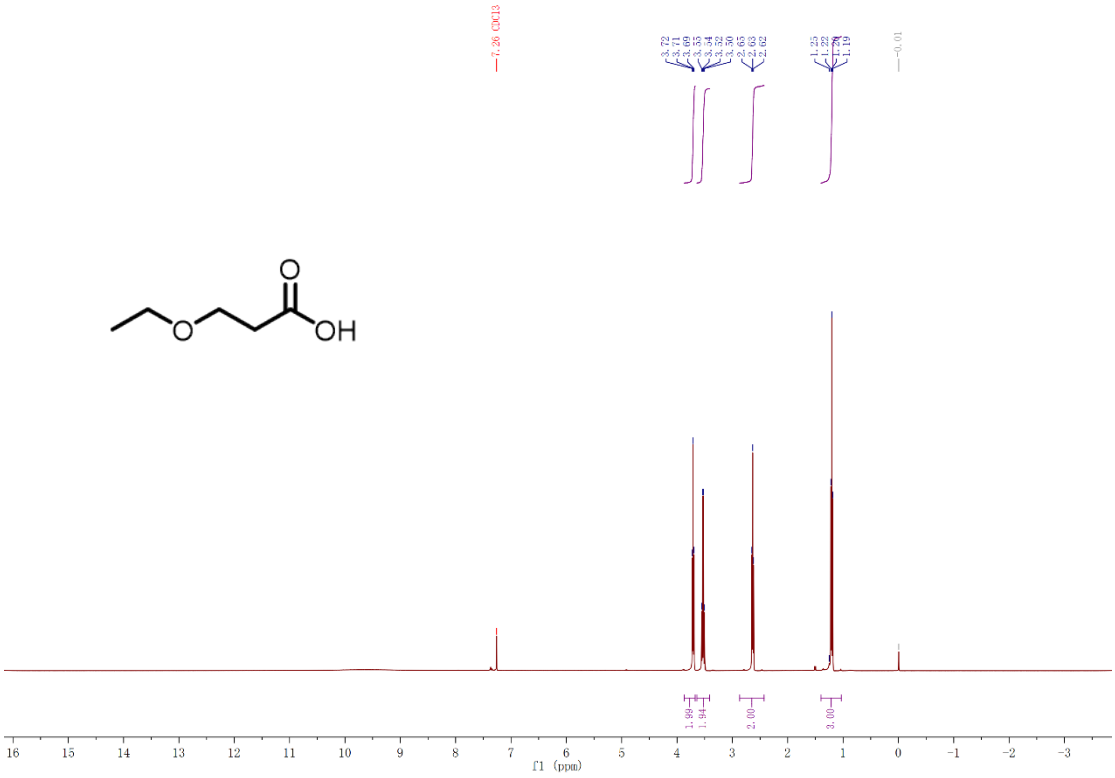
^{1}H NMR of compound 2k (500 MHz, $CDCl_3$)



^{13}C NMR of compound 2k (101 MHz, $CDCl_3$)

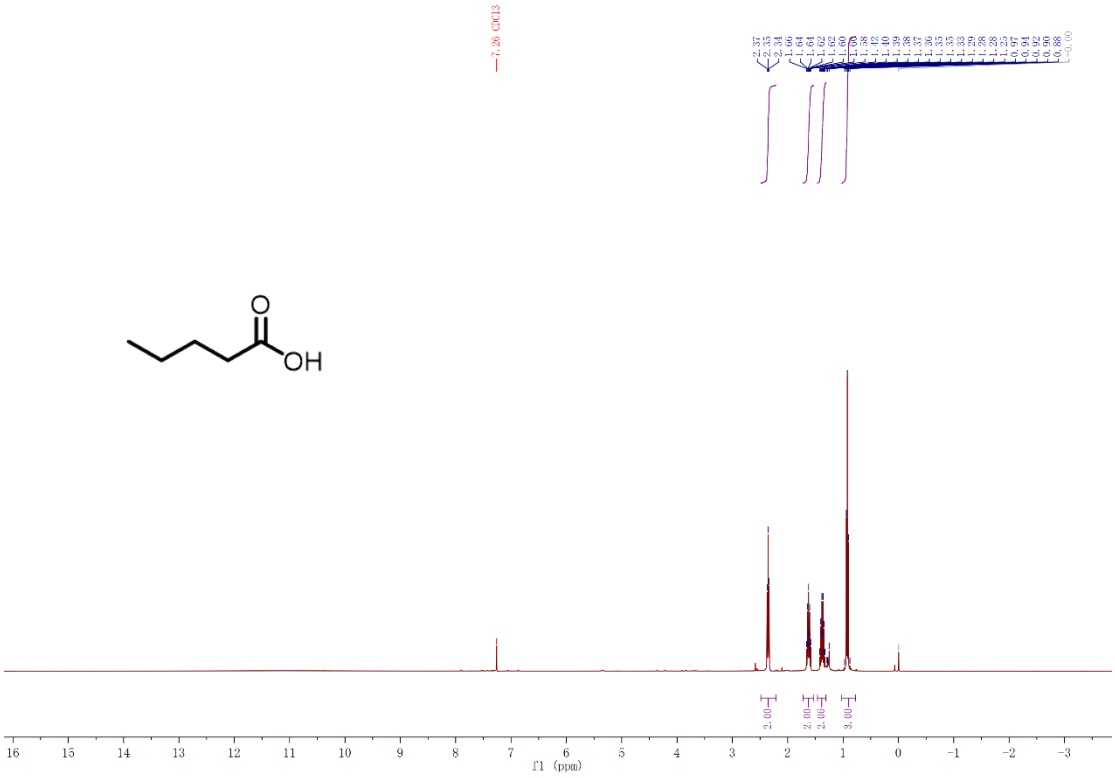


^{1}H NMR of compound 2l (400 MHz, $CDCl_3$)

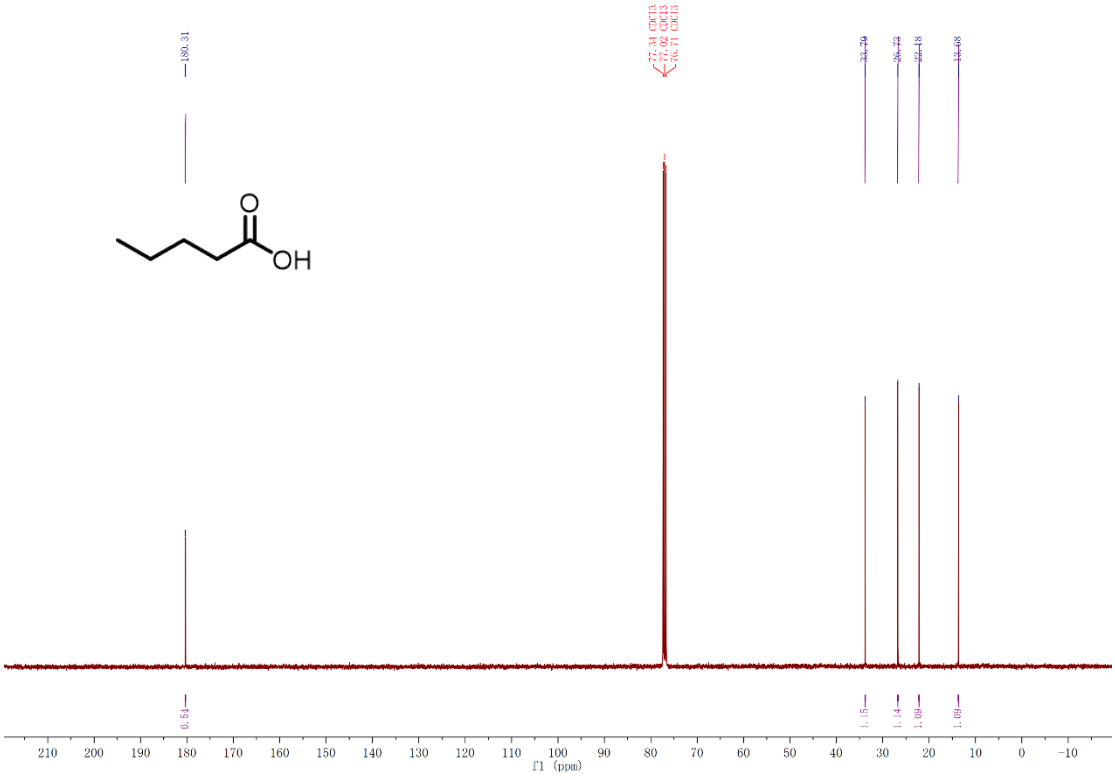


^{13}C NMR of compound 2l (101 MHz, $CDCl_3$)

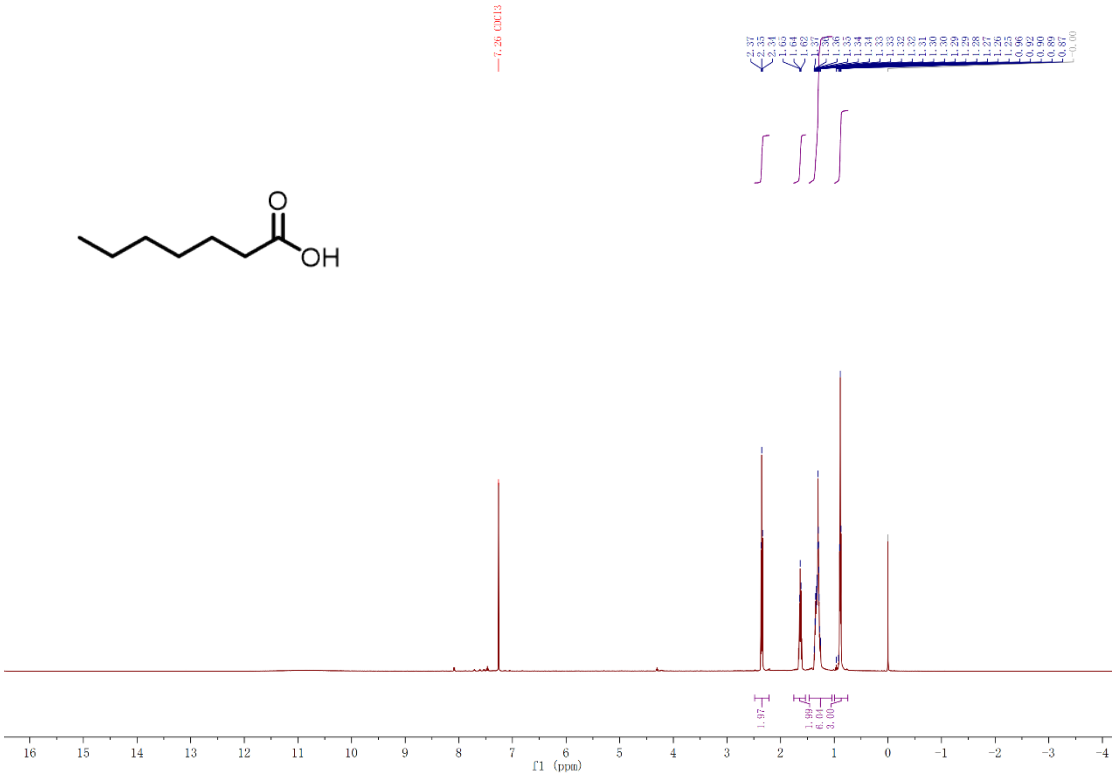
^{1}H NMR of compound 2m (400 MHz, $CDCl_3$)



^{13}C NMR of compound 2m (101 MHz, $CDCl_3$)

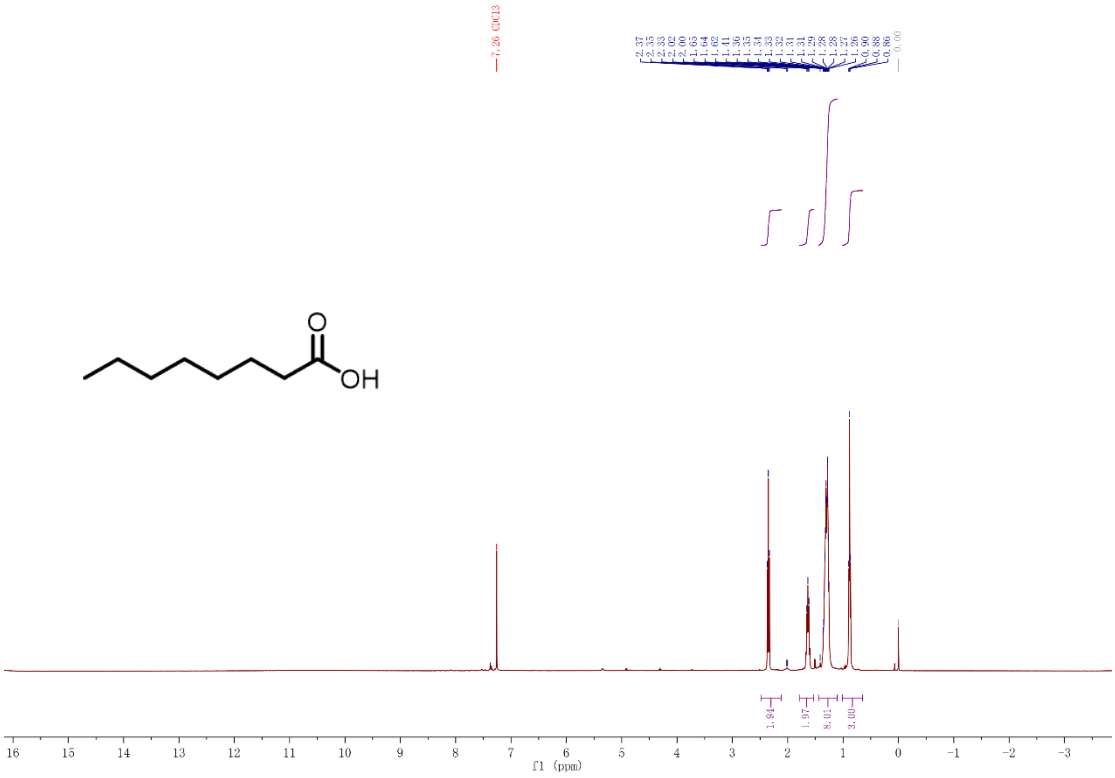


^{1}H NMR of compound 2n (500 MHz, $CDCl_3$)

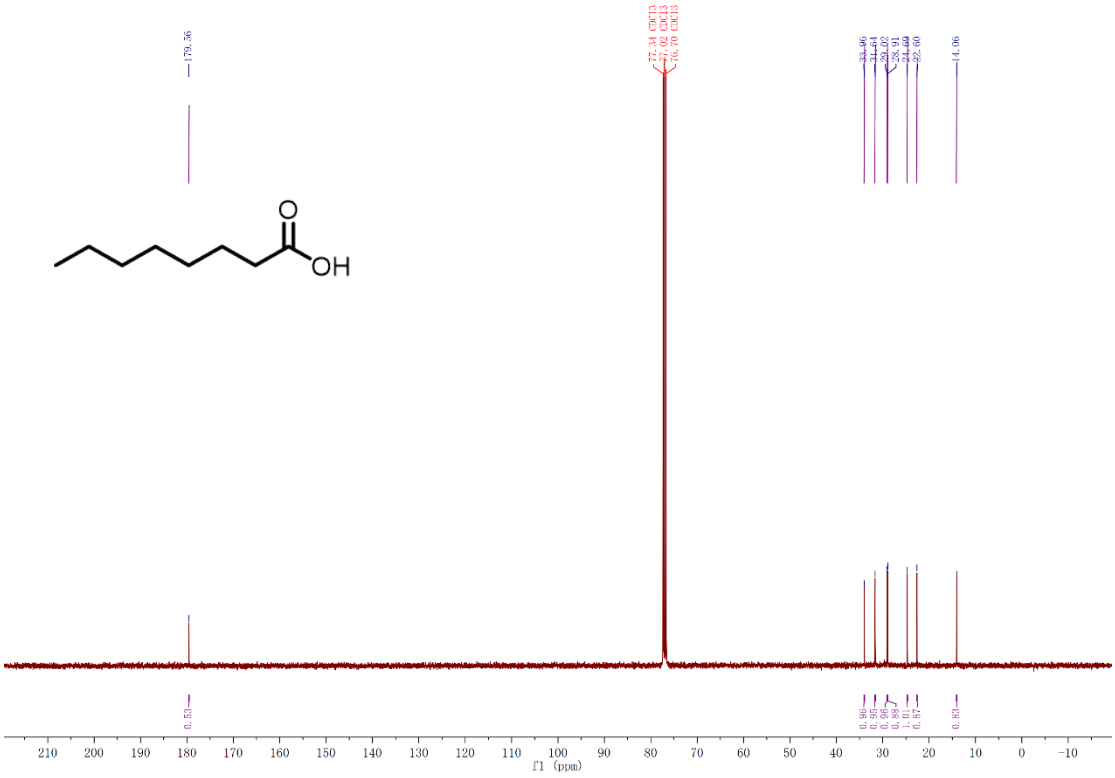


^{13}C NMR of compound 2n (101 MHz, $CDCl_3$)

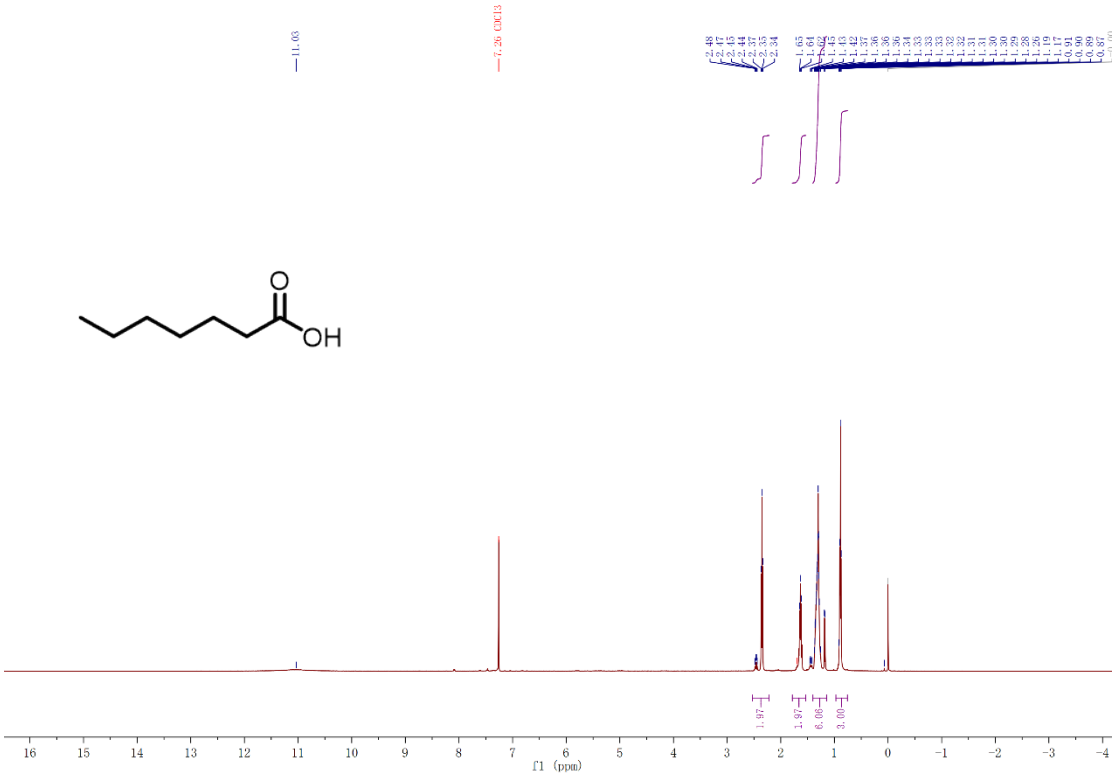
^{1}H NMR of compound 2o (400 MHz, $CDCl_3$)



^{13}C NMR of compound 2o (101 MHz, $CDCl_3$)



^{1}H NMR of compound 2p (500 MHz, $CDCl_3$)



^{13}C NMR of compound 2p (101 MHz, $CDCl_3$)