Supporting Information

Decarboxylative Giese Additions through Electron Donor-Acceptor Complex under Catalyst-free Thermal Condition

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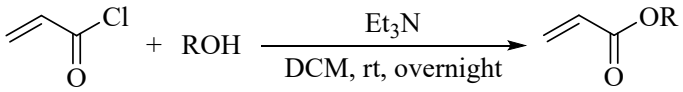
1. General Information

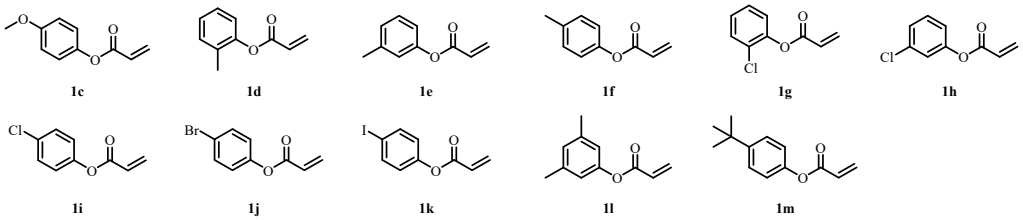
All commercially available reagents were used without further purification unless otherwise stated. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 500 (or 300/600) Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS).

2. Preparation of Substrates.

2.1 Preparation of acrylate(**1c**-**1m**).

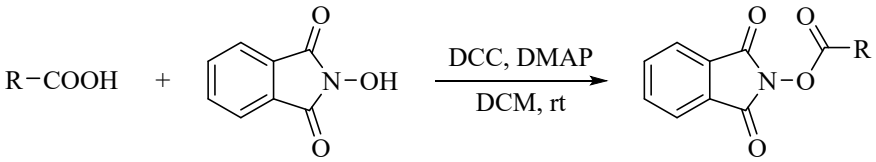


The **1c-1m** can be synthesized by the methods with yields of 40%-90% :

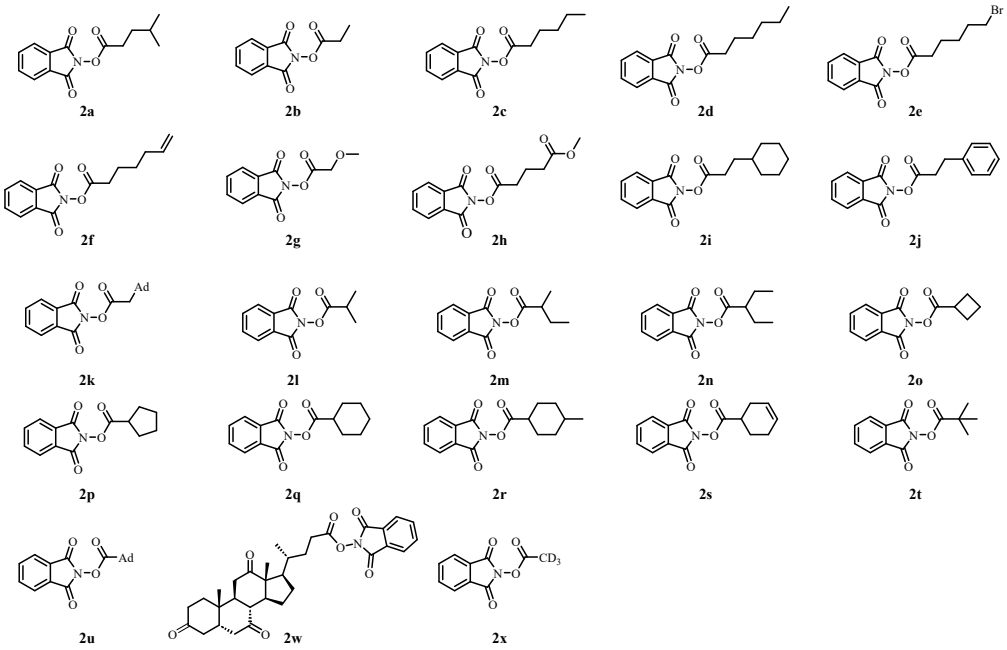


Derivative of alcohol or phenol (10 mmol) was mixed with Et_3N (15 mmol) in 30 mL DCM and cooled to 0 ℃ in an ice-water bath. Then acryloyl chloride (12 mmol) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA= 20:1 to 10:1) to get the desired product.

2.2 Preparation of N-Hydroxyphthalimide Esters(**2a-2w**).



The **2a-2w** can be synthesized by the methods with yields of 65%-90%:



To a 100 mL round-bottom flask, N-Hydroxyphthalimide (10 mmol) and carboxylic acid (10 mmol) were dissolved in 30 mL DCM, DCC (11 mmol) DMAP (1 mmol) and were added. The reaction mixture was stirred at room temperature. The residue was purified by silica gel column chromatography (PE/EA = 10:1 to 1:1) to get the desired product.

1c, colorless oil[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 – 7.02 (m, 2H), 6.92 – 6.88 (m, 2H), 6.59 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.99 (dd, *J* = 10.5, 1.3 Hz, 1H), 3.81 (s, 3H).

1d, colorless oil[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.16 (td, *J* = 7.4, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.63 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.36 (dd, *J* = 17.3, 10.5 Hz, 1H), 6.03 (dd, *J* = 10.5, 1.3 Hz, 1H), 2.20 (s, 3H).

1e, colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.63 – 6.58 (m, 1H), 6.33 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.01 (dd, *J* = 10.4, 1.3 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.6, 139.7, 132.4, 129.2, 128.1, 126.7, 122.1, 118.5, 21.3.

1f, colorless oil[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.05 – 6.98 (m, 2H), 6.60 (dd, *J* = 17.2, 1.3 Hz, 1H), 6.32 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.00 (dd, *J* = 10.4, 1.4 Hz, 1H), 2.35 (s, 3H).

1g, colorless oil[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.30 (td, *J* = 7.7, 1.6 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.67 (dd, *J* = 17.3, 1.1 Hz, 1H), 6.37 (dd, *J* = 17.3, 10.5 Hz, 1H), 6.07 (dd, *J* = 10.4, 1.1 Hz, 1H).

1h, colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.19 (t, *J* = 2.1 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.61 (dd, *J* = 17.3, 1.1 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.03 (dd, *J* = 10.4, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 151.1, 134.7, 133.1, 130.2, 127.6, 126.2, 122.3, 120.0.

1i, colorless oil[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.12 – 7.06 (m, 2H), 6.61 (dd, *J* = 17.3, 1.2 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.03 (dd, *J* = 10.5, 1.2 Hz, 1H).

1j, colorless oil[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.06 – 7.00 (m, 2H), 6.61 (dd, *J* = 17.3, 1.1 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.03 (dd, *J* = 10.5, 1.2 Hz, 1H).

1k, yellow oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 6.95 – 6.88 (m, 2H), 6.60 (dd, *J* = 17.3, 1.2 Hz, 1H), 6.30 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.02 (dd, *J* = 10.5, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 150.5, 138.5, 133.1, 127.7, 123.8, 89.9.

1l, colorless oil

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 – 6.87 (m, 1H), 6.76 (d, *J* = 1.5 Hz, 2H), 6.59 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.32 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.99 (dd, *J* = 10.4, 1.3 Hz, 1H), 2.33 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 150.5, 139.3, 132.3, 128.1, 127.6, 119.1, 21.3.

1m, colorless oil[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.08 – 7.03 (m, 2H), 6.60 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.32 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.00 (dd, *J* = 10.4, 1.3 Hz, 1H), 1.33 (s, 9H).

2a, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 2.69 – 2.65 (m, 2H), 1.72 – 1.66 (m, 3H), 0.96 (d, *J* = 6.5 Hz, 6H).

2b, white solid[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.77 (m, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

2c, colorless solid[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.79 (q, *J* = 7.5 Hz, 3H), 1.44 – 1.35 (m, 3H), 0.93 (t, *J* = 7.1 Hz, 4H).

2d, white solid[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.80 – 7.76 (m, 2H), 2.65 (t, *J* = 7.4 Hz, 3H), 1.81 – 1.75 (m, 2H), 1.47 – 1.41 (m, 2H), 1.34 – 1.31 (m, 5H), 0.90 (t, *J* = 7.0 Hz, 2H).

2e, white solid[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.82 – 7.77 (m, 2H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.86 – 1.80 (m, 2H), 1.65 – 1.58 (m, 2H).

2f, colorless solid[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 5.86 – 5.76 (m, 1H), 5.07 – 4.94 (m, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.84 – 1.78 (m, 2H), 1.59 – 1.52 (m, 2H).

2g, white solid[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.45 (s, 2H), 3.55 (s, 3H).

2h, white solid[11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 3.71 (s, 3H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 3H), 2.15 – 2.09 (m, 2H).

2i, white solid[6]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.69 – 2.64 (m, 2H), 1.78 – 1.66 (m, 8H), 1.28 – 1.20 (m, 3H), 0.98 – 0.90 (m, 2H).

2j, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.84 – 7.79 (m, 2H), 7.38 – 7.33 (m, 2H), 7.30 – 7.27 (m, 3H), 3.13 (t, *J* = 7.8 Hz, 2H), 3.03 – 2.99 (m, 2H).

2k, white solid[12]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 2.40 (s, 2H), 2.04 (s, 1H), 1.76 – 1.69 (m, 14H).

2l, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 2.99 – 2.90 (m, 1H), 1.37 (d, *J* = 6.9 Hz, 6H).

2m, white solid[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 2.78 (p, *J* = 6.9 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.74 – 1.65 (m, 1H), 1.35 (d, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H).

2n, white solid[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.63 – 2.56 (m, 1H), 1.83 – 1.78 (m, 2H), 1.74 – 1.69 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 6H).

2o, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.83 – 7.79 (m, 2H), 3.58 – 3.50 (m, 1H), 2.58 – 2.50 (m, 2H), 2.47 – 2.37 (m, 2H), 2.17 – 2.05 (m, 2H).

2p, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.80 – 7.76 (m, 2H), 3.15 – 3.07 (m, 1H), 2.10 – 2.01 (m, 4H), 1.84 – 1.76 (m, 2H), 1.71 – 1.64 (m, 2H).

2q, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 2.77 – 2.70 (m, 1H), 2.13 – 2.07 (m, 2H), 1.86 – 1.81 (m, 2H), 1.70 – 1.63 (m, 3H), 1.40 – 1.32 (m, 3H).

2r, white solid[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 2.67 – 2.59 (m, 1H), 2.20 – 2.15 (m, 2H), 1.86 – 1.81 (m, 2H), 1.66 – 1.58 (m, 2H), 1.45 – 1.39 (m, 1H), 1.06 – 0.98 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H).

2s, white solid[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 5.77 – 5.69 (m, 2H), 3.03 – 2.97 (m, 1H), 2.48 – 2.41 (m, 2H), 2.27 – 2.15 (m, 3H), 1.95 – 1.87 (m, 1H).

2t, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 1.43 (s, 9H).

2u, white solid[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.80 – 7.75 (m, 2H), 2.16 – 2.09 (m, 9H), 1.80 – 1.76 (m, 6H).

2w, white solid[5]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 2H), 2.94 – 2.73 (m, 5H), 2.37 – 2.20 (m, 8H), 2.17 – 1.92 (m, 11H), 1.40 (s, 3H), 1.12 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H).

2x, white solid[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.82 – 7.78 (m, 3H).

All NMR data of materials were compared with the following literature:

(1) J. Ye, P. Li, R. Jin, H. Feng, F. Cai, J. Wang, B. Li, *Org. Lett.*, 2026, **28**, 208-212

(2) S. Maity, S. Agasti, A. M. Earsad, A. Hazra, D. Maiti, *Chemistry*, 2015, **21**, 11320-11324

(3) A. Petti, M. J. Karrasch, P. Chahar, F. H. Wessels, N. Hölter, F. Boser, C. G. Daniliuc, F. Glorius, *J. Am. Chem. Soc.*, 2025, **147**, 13276-13285

(4) J. C. Hsieh, Y. H. Chu, K. Muralirajan, C. H. Cheng, *Chem. Commun.*, 2017, **53**, 11584-11587

(5) He S H, Chen G L, Gong X Y, Ao G Z, Liu F, J. Org. Chem. 2023, 88, 6671-6681

(6) Bisoyi A, Tripathy A R, Yedase G S, P S S, Choudhury U, Yatham V R, J. Org. Chem. 2023, 88, 2631-2641

(7) Zhang M, Liu L, Tan Y, Jing Y, Liu Y, Wang Z, Wang Q, Angew. Chem. Int. Ed. 2024, 63, e202318344

(8) Dai P F, Wang Y P, Qu J P, Kang Y B, Org. Lett. 2021, 23, 9360-9364

(9) Chan C M, Xing Q, Chow Y C, Hung S F, Yu W Y, Org. Lett. 2019, 21, 8037-8043

(10) Zhou Z, Sales Z S, Pippel D J, Qian M, Martin C L, J. Org. Chem. 2022, 87, 14948-14952

(11) Li F, Dong J, Liao H et al., Sci. China Chem. 2024, 67, 3389-3396

(12) Tortajada A, Duan Y Y, Sahoo B, Cong F, Toupalas G, Sallustrau A, Loreau O, Audisio D, Martin R, ACS Catal. 2019, 9, 5897-5901

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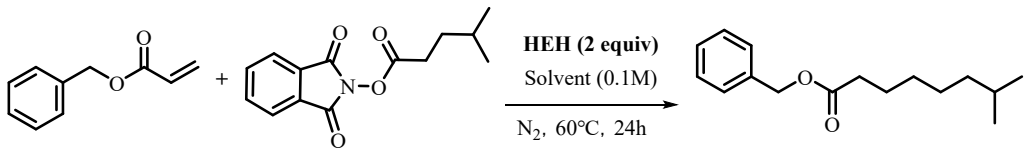
3. Investigation of the Key Reaction Parameters.

Table S1. Screening of solvent.[a]



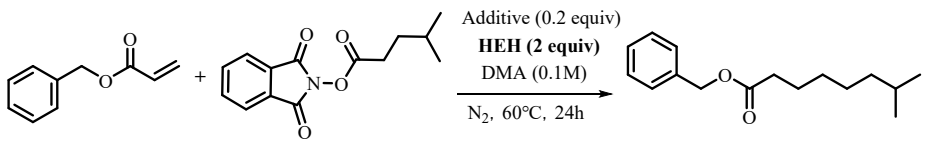
1a **2a** **3aa**

entry	solvent	yield[b] (%)
1	MeOH	30%
2	MTBE	15%

3	chloroform	trace
4	THF	95%(76%)[c]
5	Heptane	trace
6	acetone	32%
7	DCE	26%
8	DCM	trace
9	EA	22%
10	MeCN	34%
11	PhMe	N.R.
12	EtOH	N.R.
13	TBA	45%
14	ethylene glycol	trace
15	Isopropyl alcohol	53%
16	Carbon tetrachloride	trace
17	Naphthene	trace
18	DMSO	76%
19	DMF	100% (80%)[c]
20	DMA	100% (84%)[c]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and HEH (0.4 mmol) in solvent (2 mL) were stirred in an 8 mL vial at 60 °C under N_2 for 24 h. [b]Yields were determined by ^{1}H NMR using 1,3,5-Trimethoxybenzene as the internal standard. [c]Isolated yields are given.

Table S2. Screening of additive.[a]



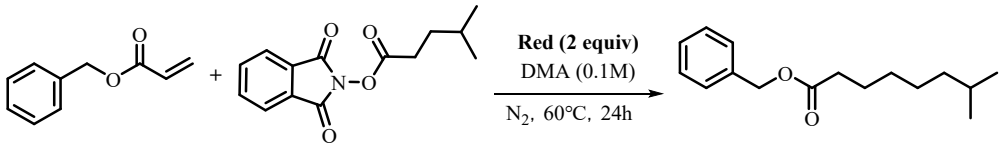
1a **2a** **3aa**

entry	Additive	yield[b] (%)
1	TBAI	83%
2	NaI	77%
3	KI	67%

4	CuI	36%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), HEH (0.4 mmol) and additive (0.04 mmol) in DMA (2 mL) were stirred in an 8 mL vial at 60 ℃ under N_2 for 24 h. [b]Isolated yields of **3aa** are given.

Table S3. Screening of reductant.[a]

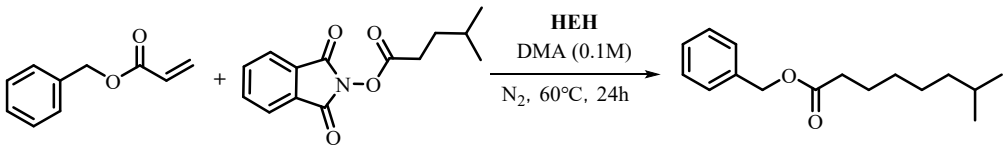


1a **2a** **3aa**

entry	Reductant	yield[b] (%)
1	$NaBH_4$	N.R.
2	$AlLiH_4$	N.R.
3	NaH	N.R.
4	TTMS	N.R.
5	Ph_2SiH_2	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and reductant (0.4 mmol) in DMA (2 mL) were stirred in an 8 mL vial at 60 ℃ under N_2 for 24 h. [b]Isolated yields are given.

Table S4. Screening of ratio of **1a:2a:HEH**.[a]



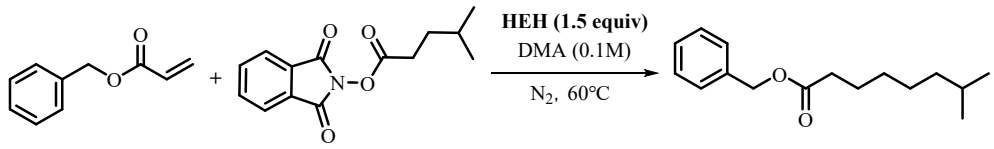
1a **2a** **3aa**

entry	ratio (x:y**:z**)	yield[b] (%)
1	1:1.2:1.5	94%
2	1:1.5:1.5	88%
3	1:2:1.5	79%
4	1:1.2:1.2	78%
5	1:1.2:2	84%

[a]Reaction conditions: **1a** (x mmol), **2a** (y mmol) and HEH (z mmol) in DMA (2 ml) were stirred

in an 8 mL vial at 60 ℃ under N_2 for 24 h. [b]Isolated yields are given.

Table S5. Screening of reaction time.[a]

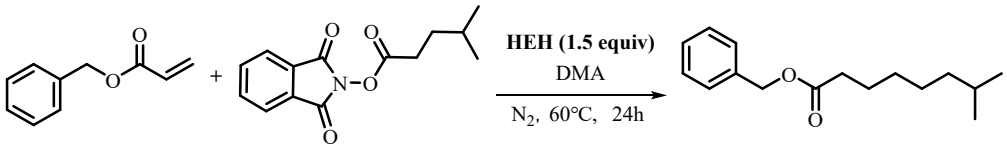


1a **2a** **3aa**

entry	time	yield[b] (%)
1	3h	57%
2	6h	63%
3	9h	69%
4	24h	94%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and HEH (0.3 mmol) in DMA (2 ml) were stirred in an 8 mL vial at 60 ℃ under N_2 for x h. [b]Isolated yields are given.

Table S6. Screening of concentration.[a]

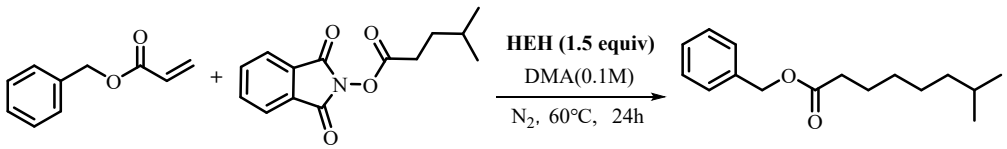


1a **2a** **3aa**

entry	concentration	yield[b] (%)
1	0.5 M	44%
2	0.2 M	74%
3	0.1 M	94%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol) and HEH (0.3 mmol) in DMA (x mL) were stirred in an 8 mL vial at 60 ℃ under N_2 for 24 h. [b]Isolated yields are given.

Table S7. Control experiments.[a]



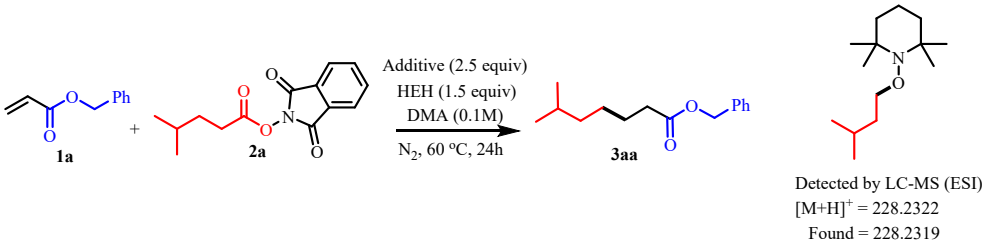
1a **2a** **3aa**

entry	deviation from the standard conditions	yield[b] (%)
1	Standard conditions	94%
2	r.t. instead of 60 ℃	29%
3	40 ℃ instead of 60 ℃	46%
4	80 ℃ instead of 60 ℃	80%
5	No HEH	N.R.
6	Air instead of N_2	63%
7	under dark	91%

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (0.24 mmol) in DMA (2 mL) were stirred in an 8 mL vial for 24 h. [b]Isolated yields are given.

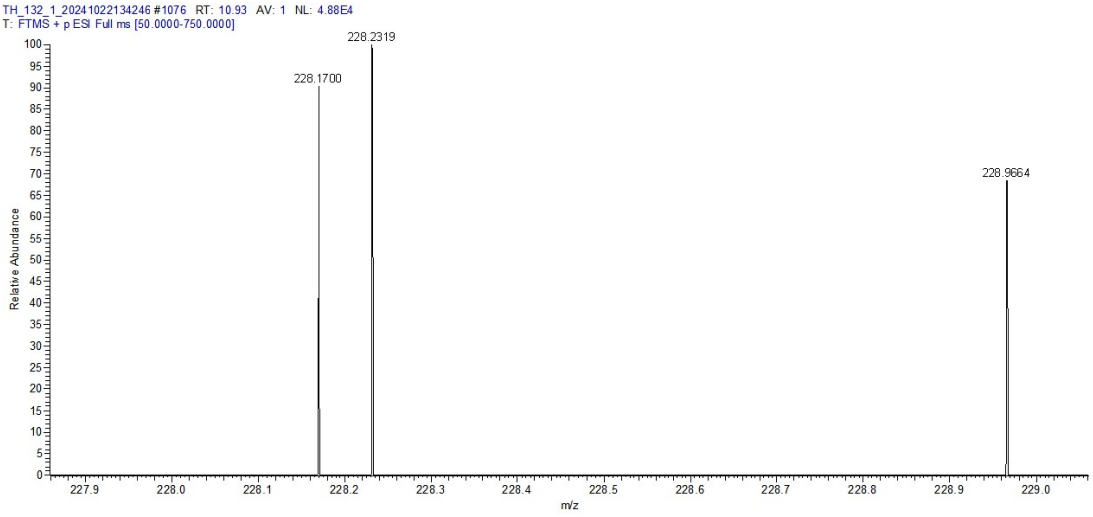
4. Investigation of the mechamism.

4.1 Radical inhibition experiment

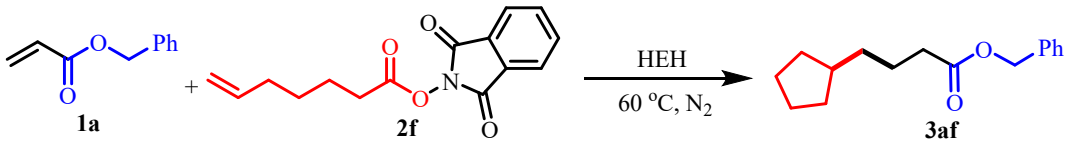


entry	Additive	yield[b] (%)
1	TEMPO	trace
2	BHT	trace
3	1,1-Diphenylethylene	29%

To a 8 mL glass vial was added **1a** (0.2 mmol), **2a** (0.24 mmol), DMA (2 ml) and Additive (0.5 mmol). The reaction mixture was degassed by bubbling with nitrogen for 15-20 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred at at 60 ℃ temperature for 24 h. [b]Isolated yields of **3aa** are given.



4.2 Radical clock experiment



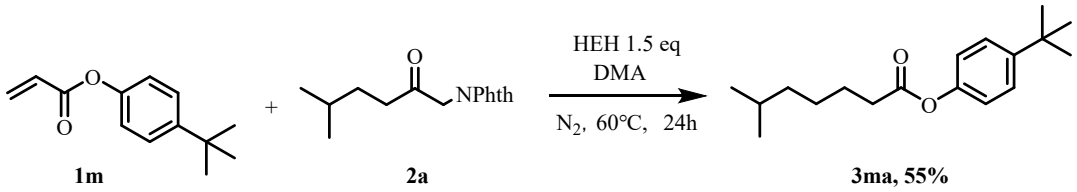
To a 8 mL glass vial was added **1a** (0.2 mmol), **2f** (0.24 mmol), HEH (0.3 mmol) and DMA (2 ml). The reaction mixture was degassed by bubbling with nitrogen for 15-20 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred at 60 °C temperature for 24 h. [b]Isolated yield of 3af are given.

5. Experimental Procedures and Product Characterization.

5.1 General Procedure for the α–aminoalkylation of ethyl 2-(phenylamino) acetate (1a):

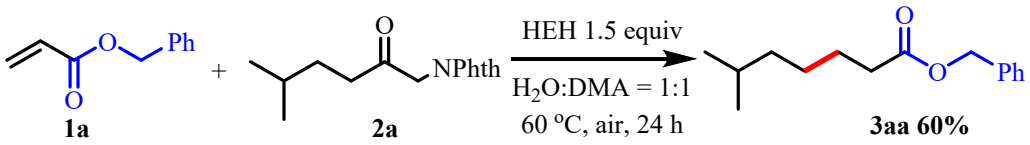
To a 8 mL glass vial was added **1a** (0.2 mmol), **2a** (0.24 mmol), **HEH** (0.3 mmol) and DMA (2 ml). The reaction mixtures were degassed by bubbling with nitrogen for 15-20 s with an outlet needle and the vials were sealed with PTFE caps. The mixtures were then stirred at 60 °C for 24 h. The resulting mixture was diluted with 10 mL EtOAc and washed with saturated NaCl (2 x 10 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was then purified by column chromatography on silica gel to give the desired products (petroleum ether/ethyl acetate from 1/1 to 20/1).

5.2 Scale-up experiment



1m **2a** **3ma, 55%**

To a 100 mL round-bottom flask, 1m (5 mmol), 2a (6 mmol) and HEH (7.5 mmol) were dissolved in 30 mL DMA under an atmosphere of N_2. The reaction mixture was stirred at 60 °C for 24 h. The resulting mixture was diluted with 50 mL EtOAc and washed with saturated NaCl (2 x 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was then purified by column chromatography on silica gel to give the desired products. (petroleum ether/ethyl acetate = 20/1).

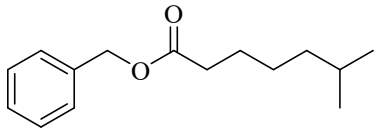


1a **2a** **3aa 60%**

To a 8 mL glass vial was added **1a** (0.2 mmol), **2a** (0.24 mmol), DMA/H_2O = 1:1 (2 ml). The mixture was then stirred at at 60 °C temperature for 24 h under air condition. The reaction mixture was concentrated in vacuum to remove the solvent and the residue was purified by silica gel column chromatography (PE/EA= 20:1) to get the desired product.

5.2 Product Characterization.

benzyl 6-methylheptanoate(Colorless oil, 44 mg, 94% Yield)**(3aa)**

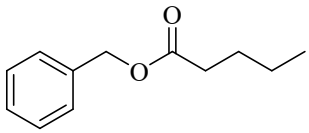


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 5H), 5.12 (s, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.55 – 1.48 (m, 1H), 1.33 – 1.29 (m, 2H), 1.20 – 1.15 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.7, 136.2, 128.6, 128.2, 128.2, 66.1, 38.6, 34.4, 27.8, 26.9, 25.2, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1622.

benzyl pentanoate(Colorless oil, 27 mg, 70% Yield)**(3ab)**

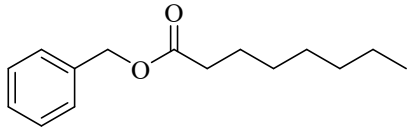


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 5H), 5.14 (s, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.64 (m, 2H), 1.40 – 1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.7, 136.2, 128.6, 128.2, 66.1, 34.1, 27.0, 22.3, 13.7.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1145.

benzyl heptanoate(Colorless oil, 28 mg, 63% Yield)**(3ac)**

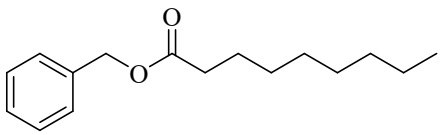


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 5H), 5.14 (s, 2H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.66 (q, *J* = 7.3 Hz, 2H), 1.34 – 1.27 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8, 136.2, 128.3, 128.2, 128.2, 66.1, 34.4, 31.7, 29.1, 28.9, 25.0, 22.6, 14.1.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{20}O_2$ 234.1620, found 234.1622.

benzyl nonanoate(Colorless oil, 32 mg, 64% Yield)**(3ad)**

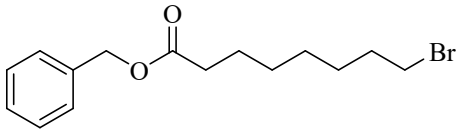


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 5.11 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.32 – 1.23 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.7, 136.2, 128.5, 128.2, 66.1, 34.4, 31.8, 29.2, 29.1, 29.1, 25.0, 22.6, 14.1.

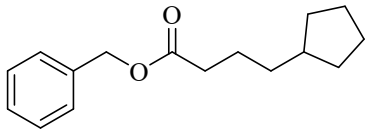
HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1779.

benzyl 8-bromooctanoate(Colorless oil, 36 mg, 57% Yield)**(3ae)**



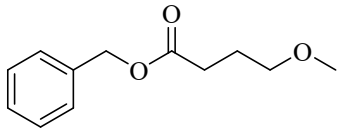
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.86 – 1.81 (m, 2H), 1.68 – 1.62 (m, 2H), 1.45 – 1.39 (m, 2H), 1.35 – 1.30 (m, 4H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.6, 136.1, 128.6, 128.2, 66.1, 34.2, 33.9, 32.7, 28.9, 28.4, 28.0, 24.8.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{21}O_2Br$ 312.0725, found 312.0720.

benzyl 4-cyclopentylbutanoate(Colorless oil, 21 mg, 43% Yield)**(3af)**



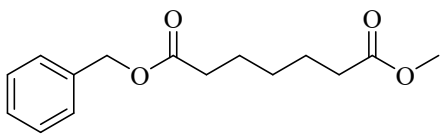
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 5.12 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.70 (m, 3H), 1.69 – 1.63 (m, 2H), 1.62 – 1.55 (m, 2H), 1.54 – 1.44 (m, 2H), 1.34 – 1.29 (m, 2H), 1.14 – 0.99 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*)) δ 173.7, 136.2, 128.6, 128.2, 128.2, 66.1, 39.8, 35.6, 34.6, 32.6, 25.2, 24.2.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1620.

benzyl 4-methoxybutanoate(Colorless oil, 36 mg, 95% Yield)**(3ag)**



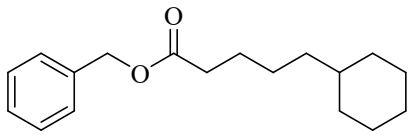
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 5H), 5.12 (s, 2H), 3.40 (t, *J* = 6.2 Hz, 2H), 3.31 (s, 3H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.94 – 1.89 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.3, 136.1, 128.6, 128.2, 128.2, 71.5, 66.2, 58.6, 31.0, 24.9.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{12}H_{16}O_3$ 208.1099, found 208.1092.

1-benzyl 7-methyl heptanedioate(Colorless oil, 37 mg, 70% Yield)**(3ah)**



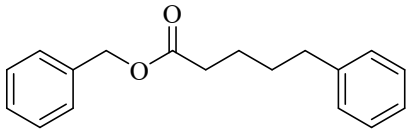
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 5.11 (s, 2H), 3.66 (d, *J* = 1.5 Hz, 3H), 2.36 (t, *J* = 7.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.69 – 1.62 (m, 4H), 1.37 – 1.33 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 173.4, 136.1, 128.6, 128.2, 66.2, 51.5, 34.1, 33.9, 28.6, 24.6.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1360.

benzyl 5-cyclohexylpentanoate(Colorless oil, 36 mg, 65% Yield)**(3ai)**



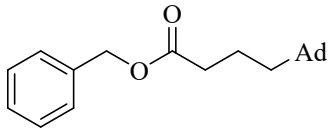
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 5H), 5.12 (s, 2H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.60 (m, 8H), 1.33 – 1.29 (m, 2H), 1.21 – 1.14 (m, 5H), 0.87 – 0.81 (m, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.7, 136.2, 128.6, 128.2, 128.2, 66.1, 37.5, 37.1, 34.4, 33.4, 26.7, 26.4, 26.4, 25.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{26}O_2$ 274.1933, found 274.1937.

benzyl 5-phenylpentanoate(Colorless oil, 50 mg, 94% Yield)**(3aj)**



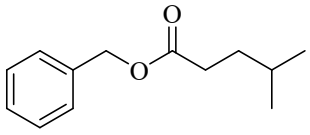
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 5H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.16 (m, 3H), 5.13 (s, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.76 – 1.64 (m, 4H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.5, 142.1, 136.1, 128.6, 128.4, 128.4, 128.2, 125.8, 66.2, 35.6, 34.2, 30.9, 24.6.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1466.

benzyl 4-((3r,5r,7r)-adamantan-1-yl)butanoate(Colorless oil, 34 mg, 54% Yield)**(3ak)**



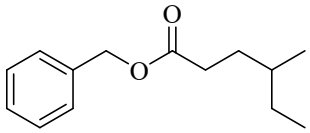
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.93 (s, 3H), 1.68 (s, 2H), 1.63 – 1.56 (m, 6H), 1.45 (d, *J* = 2.9 Hz, 6H), 1.07 – 1.02 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8, 136.2, 128.6, 128.3, 128.2, 66.1, 44.1, 42.4, 37.2, 35.2, 32.2, 28.7, 18.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{28}O_2$ 312.2089, found 312.2084.

benzyl 4-methylpentanoate(Colorless oil, 39 mg, 95% Yield)**(3al)**



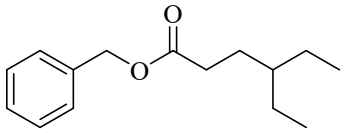
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 5.12 (s, 2H), 2.39 – 2.35 (m, 2H), 1.59 – 1.52 (m, 3H), 0.90 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.9, 136.1, 128.6, 128.2, 66.1, 33.7, 32.4, 27.7, 22.2.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1307.

benzyl 4-methylhexanoate(Colorless oil, 29 mg, 65% Yield)**(3am)**



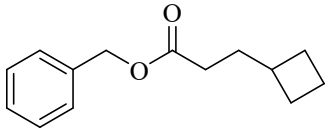
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 5H), 5.11 (s, 2H), 2.42 – 2.30 (m, 2H), 1.73 – 1.66 (m, 1H), 1.50 – 1.42 (m, 1H), 1.38 – 1.30 (m, 3H), 1.19 – 1.12 (m, 1H), 0.89 – 0.84 (m, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.0, 136.1, 128.6, 128.2, 128.2, 66.1, 34.0, 32.2, 31.5, 29.1, 18.8, 11.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1464.

benzyl 4-ethylhexanoate(Colorless oil, 26 mg, 55% Yield)**(3an)**



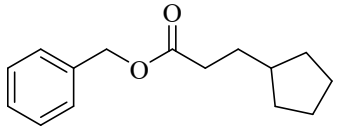
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 – 7.32 (m, 5H), 5.14 (s, 2H), 2.39 – 2.34 (m, 2H), 1.67 – 1.61 (m, 3H), 1.33 – 1.29 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.1, 136.2, 128.6, 128.2, 128.2, 66.1, 39.9, 31.9, 27.8, 25.1, 10.8.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1623.

benzyl 3-cyclobutylpropanoate(Colorless oil, 21 mg, 48% Yield)**(3ao)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 5.11 (s, 2H), 2.26 (q, *J* = 9.0, 8.3 Hz, 3H), 2.06 – 2.00 (m, 2H), 1.89 – 1.77 (m, 2H), 1.74 (q, *J* = 7.6 Hz, 2H), 1.63 – 1.56 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.7, 136.1, 128.6, 128.2, 66.1, 35.5, 32.2, 32.0, 27.9, 18.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1302.

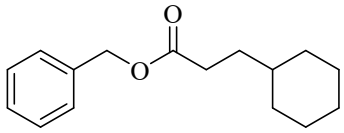
benzyl 3-cyclopentylpropanoate(Colorless oil, 23 mg, 49% Yield)**(3ap)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 5.12 (s, 2H), 2.39 – 2.36 (m, 2H), 1.79 – 1.72 (m, 3H), 1.69 – 1.64 (m, 2H), 1.62 – 1.56 (m, 2H), 1.55 – 1.46 (m, 2H), 1.13 – 1.05 (m, 2H).

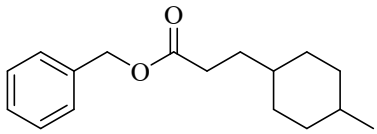
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.9, 136.2, 128.6, 128.2, 128.2, 66.1, 39.7, 33.7, 32.4, 31.1, 25.1.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{20}O_2$ 232.1463, found 232.1462.

benzyl 3-cyclohexylpropanoate(Colorless oil, 32 mg, 64% Yield)**(3aq)**



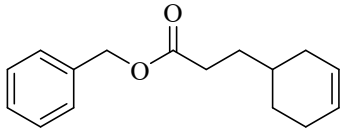
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.11 (s, 2H), 2.39 – 2.35 (m, 2H), 1.72 – 1.66 (m, 4H), 1.66 – 1.60 (m, 1H with H_2O), 1.57 – 1.52 (m, 2H), 1.24 – 1.11 (m, 4H), 0.92 – 0.84 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.0, 136.2, 128.6, 128.2, 128.2, 66.1, 37.2, 33.0, 32.3, 31.9, 26.5, 26.2.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{22}O_2$ 246.1420, found 246.1422.

benzyl 3-(4-methylcyclohexyl)propanoate(Colorless oil, 15 mg, 26% Yield)**(3ar)**



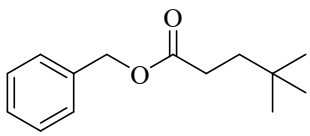
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.11 (d, *J* = 2.3 Hz, 2H), 2.36 (q, *J* = 8.1 Hz, 3H), 1.73 – 1.60 (m, 4H), 1.54 (q, *J* = 7.4 Hz, 1H), 1.48 – 1.39 (m, 3H with High boiling solvent), 1.36 – 1.10 (m, 3H with), 0.90 – 0.85 (m, 4H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.0, 174.0, 136.2, 136.2, 128.6, 128.2, 128.2, 128.2, 66.1, 66.1, 37.0, 35.1, 32.9, 32.7, 32.4, 32.3, 32.1, 30.6, 28.4, 22.7.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1771.

benzyl 3-(cyclohex-3-en-1-yl)propanoate(Colorless oil, 34 mg, 70% Yield)**(3as)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 5H), 5.70 – 5.58 (m, 2H), 5.12 (s, 2H), 2.41 (t, *J* = 7.8 Hz, 2H), 2.12 – 2.00 (m, 3H), 1.75 – 1.61 (m, 4H), 1.26 – 1.18 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8, 136.1, 128.6, 128.2, 127.0, 126.2, 66.2, 33.1, 32.0, 31.5, 31.5, 28.6, 25.1.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1466.

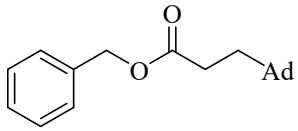
benzyl 4,4-dimethylpentanoate (Colorless oil, 33 mg, 75% Yield)**(3at)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 5.12 (s, 2H), 2.39 – 2.29 (m, 2H), 1.61 – 1.55 (m, 2H), 0.89 (s, 9H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 174.3, 136.1, 128.6, 128.3, 128.2, 66.2, 38.6, 30.2, 29.0.

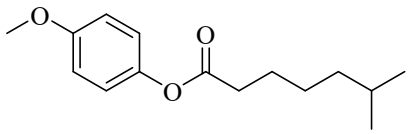
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1466.

benzyl 3-((3r,5r,7r)-adamantan-1-yl)propanoate(Colorless oil, 45 mg, 75% Yield)**(3au)**



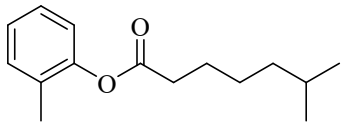
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.93 (s, 3H), 1.74 – 1.65 (m, 3H), 1.64 – 1.54 (m, 6H), 1.45 (d, *J* = 2.9 Hz, 6H), 1.09 – 0.99 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.8, 136.2, 128.6, 128.3, 128.2, 66.1, 44.1, 42.4, 37.2, 35.2, 32.2, 28.7, 18.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{20}H_{26}O_2$ 298.1933, found 298.1935.

4-methoxyphenyl 6-methylheptanoate(Colorless oil, 48 mg, 95% Yield)**(3ba)**



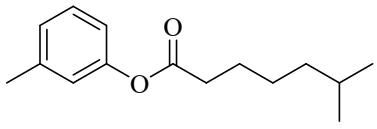
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.02 – 6.97 (m, 2H), 6.91 – 6.86 (m, 2H), 3.79 (s, 3H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.76 – 1.70 (m, 2H), 1.59 – 1.53 (m, 1H), 1.44 – 1.38 (m, 2H), 1.26 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.7, 157.2, 144.3, 122.3, 114.4, 55.6, 38.6, 34.4, 27.8, 26.9, 25.2, 22.6.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1569.

o-tolyl 6-methylheptanoate(Colorless oil, 26 mg, 55% Yield)**(3ca)**



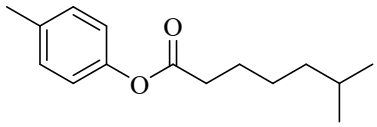
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 2H), 7.14 (m, 1H), 6.99 (dd, *J* = 8.0, 1.3 Hz, 1H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.60 – 1.55 (m, 2H), 1.46 – 1.41 (m, 1H with H_2O), 1.27 – 1.23 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.1, 149.4, 131.1, 130.1, 126.9, 125.9, 121.9, 38.6, 34.3, 27.9, 27.0, 25.3, 22.6, 16.2.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1617.

m-tolyl 6-methylheptanoate(Colorless oil, 22 mg, 48% Yield)**(3da)**



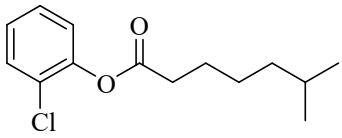
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.27 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.92 – 6.88 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 2H), 1.76 (p, *J* = 7.6 Hz, 2H), 1.63 – 1.56 (m, 1H with H_2O), 1.46 – 1.41 (m, 2H), 1.28 – 1.24 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 150.7, 139.6, 129.1, 126.5, 122.2, 118.5, 38.6, 34.5, 27.8, 26.9, 25.2, 22.6, 22.6, 21.3.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1615.

p-tolyl 6-methylheptanoate(Colorless oil, 38 mg, 82% Yield **(3ea)**



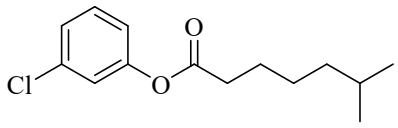
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 8.1 Hz, 2H), 6.97 – 6.94 (m, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 1.74 (p, *J* = 7.6 Hz, 2H), 1.58 – 1.53 (m, 1H), 1.44 – 1.39 (m, 2H), 1.26 – 1.22 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.6, 148.5, 135.3, 129.9, 121.3, 38.6, 34.5, 27.8, 26.9, 25.2, 22.6, 20.9.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1622.

3-chlorophenyl 6-methylheptanoate(Colorless oil, 37 mg, 72% Yield)**(3fa)**



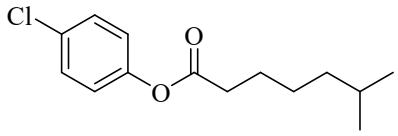
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (td, *J* = 7.8, 1.6 Hz, 1H), 7.18 (td, *J* = 7.7, 1.6 Hz, 1H), 7.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.60 – 1.53 (m, 1H with H_2O), 1.46 – 1.41 (m, 2H), 1.26 – 1.23 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 147.1, 130.3, 127.7, 126.9, 123.8, 38.6, 34.1, 27.9, 26.9, 25.2, 22.6.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_2Cl$ 254.1074, found 254.1077.

4-chlorophenyl 6-methylheptanoate(Colorless oil, 34 mg, 67% Yield)**(3ga)**



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 8.1 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.12 (t, *J* = 2.1 Hz, 1H), 7.00 – 6.97 (m, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.59 – 1.54 (m, 1H with H_2O), 1.43 – 1.38 (m, 2H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.9, 151.3, 134.7, 130.1, 126.0, 122.3, 120.0, 38.5, 34.3, 27.8, 26.9, 25.1, 22.6.
HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_2Cl$ 254.1074, found 254.1075.

4-chlorophenyl 6-methylheptanoate(Colorless oil, 37 mg, 72% Yield)**(3ha)**

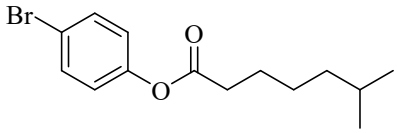


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.35 – 7.32 (m, 2H), 7.04 – 7.01 (m, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.60 – 1.53 (m, 1H with H_2O), 1.43 – 1.38 (m, 2H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.1, 149.2, 131.1, 129.5, 123.0, 38.5, 34.4, 27.8, 26.9, 25.1, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_2Cl$ 254.1074, found 254.1077.

4-bromophenyl 6-methylheptanoate(Colorless oil, 55 mg, 92% Yield)**(3ia)**

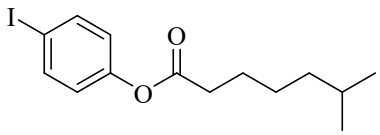


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 6.99 – 6.94 (m, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.58 – 1.54 (m, 1H with H_2O), 1.43 – 1.37 (m, 2H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.0, 149.8, 132.4, 123.4, 118.8, 38.5, 34.4, 27.8, 26.9, 25.1, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_2Br$ 298.0568, found 298.0563.

4-iodophenyl 6-methylheptanoate(Colorless oil, 66 mg, 95% Yield)**(3ja)**

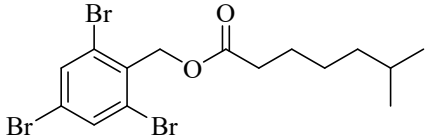


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 – 7.66 (m, 2H), 6.87 – 6.83 (m, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.72 (p, *J* = 7.6 Hz, 2H), 1.58 – 1.53 (m, 1H), 1.43 – 1.37 (m, 2H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.0, 150.6, 138.5, 123.8, 89.7, 38.5, 34.4, 27.8, 26.9, 25.1, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{19}O_2I$ 346.0430, found 346.0434.

2,4,6-tribromobenzyl 6-methylheptanoate(Colorless oil, 69 mg, 74% Yield)**(3ka)**

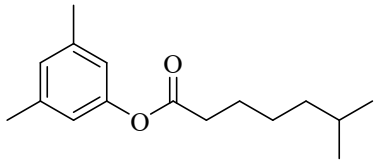


^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.67 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.48 – 1.42 (m, 2H), 1.28 – 1.22 (m, 3H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.8, 145.8, 134.8, 119.7, 118.5, 38.5, 33.9, 27.9, 26.9, 25.0, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{17}O_2Br_3$ 453.8779, found 453.8784.

3,5-dimethylphenyl 6-methylheptanoate(Colorless oil, 46 mg, 92% Yield)**(3la)**

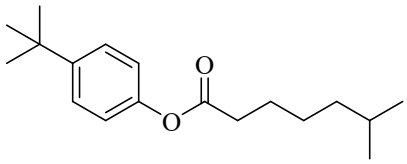


^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.85 (s, 1H), 6.68 (s, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 6H), 1.73 (p, *J* = 7.6 Hz, 2H), 1.59 – 1.54 (m, 1H), 1.44 – 1.38 (m, 2H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.6, 150.7, 139.2, 127.45, 119.2, 38.6, 34.5, 27.8, 26.9, 25.3, 22.6, 21.2.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1771.

4-(tert-butyl)phenyl 6-methylheptanoate(Colorless oil, 44 mg, 79% Yield)**(3ma)**

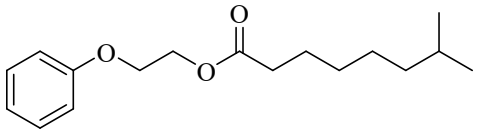


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.36 (m, 2H), 7.01 – 6.97 (m, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.74 (p, *J* = 7.6 Hz, 2H), 1.60 – 1.53 (m, 1H with H_2O), 1.44 – 1.39 (m, 2H), 1.32 (s, 9H), 1.25 – 1.21 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.6, 148.5, 148.4, 126.3, 120.9, 38.6, 34.5, 31.4, 27.8, 26.9, 25.2, 22.6.

HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{28}O_2$ 276.2089, found 276.2083.

2-phenoxyethyl 7-methyloctanoate(Colorless oil, 38 mg, 69% Yield)**(3na)**

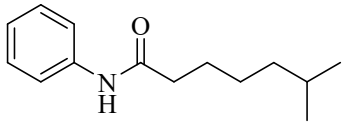


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 4.45 – 4.41 (m, 2H), 4.17 (t, *J* = 5.9, 3.7 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.64 – 1.60 (m, 2H), 1.51 (m, 1H), 1.31 (m, 2H), 1.19 – 1.14 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 173.9, 158.5, 129.5, 121.2, 114.6, 65.9, 62.6, 38.5, 34.2, 27.8, 26.9, 25.2, 22.6.

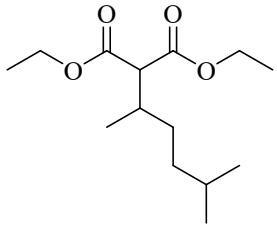
HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{24}O_3$ 264.1725, found 264.1723.

6-methyl-N-phenylheptanamide(3pa)(Colorless oil, 40 mg, 84% Yield)**(3oa)**



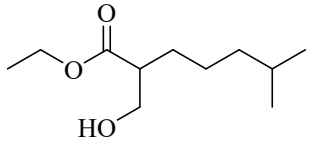
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.17 – 7.06 (m, 2H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.71 (p, *J* = 7.6 Hz, 2H), 1.57 – 1.50 (m, 1H), 1.41 – 1.33 (m, 2H), 1.26 – 1.19 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.4, 138.0, 129.0, 124.2, 119.8, 38.7, 37.9, 27.9, 27.1, 25.9, 22.6.

diethyl 2-(5-methylhexan-2-yl)malonate(3oa)(Colorless oil, 40 mg, 77% Yield)**(3pa)**



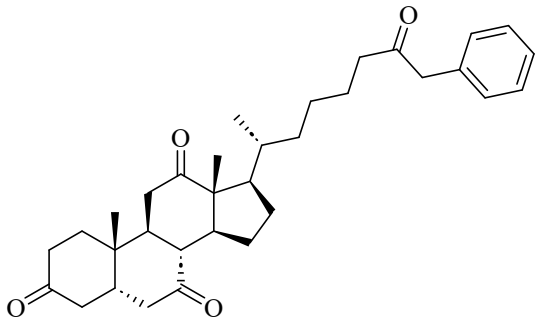
^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.19 (q, *J* = 7.1 Hz, 4H), 3.22 (d, *J* = 8.1 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.52 – 1.37 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 1.23 – 1.14 (m, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.86 (dd, *J* = 6.6, 4.1 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.1, 168.9, 61.1, 61.1, 57.8, 36.0, 33.6, 32.1, 28.0, 22.8, 22.3, 17.0, 14.1, 14.1.

ethyl 2-(hydroxymethyl)-6-methylheptanoate(3qa)(Colorless oil, 28 mg, 70% Yield)**(3qa)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.23 – 4.12 (m, 2H), 3.78 – 3.70 (m, 2H), 2.59 – 2.53 (m, 1H), 1.65 – 1.58 (m, 1H), 1.55 – 1.46 (m, 2H), 1.35 – 1.29 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 – 1.14 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.6, 168.1, 134.3, 132.7, 123.6, 63.2, 60.6, 47.6, 38.8, 28.7, 27.8, 25.0, 22.6, 22.5, 14.3.

(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-7-oxo-8-phenyloctan-2-yl)dodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione(Colorless oil, 44 mg, 44% Yield) **(3aw)**



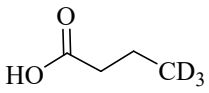
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 5H), 5.10 (d, *J* = 10.9 Hz, 2H), 2.98 – 2.77 (m, 3H), 2.40 – 2.30 (m, 4H), 2.30 – 2.25 (m, 2H), 2.25 – 2.18 (m, 2H), 2.04 – 1.82 (m, 6H), 1.73 – 1.54

(m, 4H), 1.40 (s, 3H), 1.31 – 1.18 (m, 4H), 1.18 – 1.09 (m, 2H), 1.08 – 1.02 (m, 3H), 0.87 – 0.76 (m, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 212.0, 209.1, 208.8, 173.7, 136.1, 128.6, 128.3, 128.2, 128.2, 66.1, 56.9, 51.8, 49.0, 46.9, 45.8, 45.6, 45.0, 42.8, 38.7, 36.6, 36.1, 35.9, 35.3, 35.0, 34.4, 33.8, 27.8, 26.1, 25.6, 25.3, 25.2, 24.9, 21.9, 19.0, 11.9.

Due to the high boiling point, HRMS (EI) data could not be obtained.

butanoic-4,4,4-d3 acid (Colorless oil, 10 mg, 60% Yield) **(3ax)**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.36 (t, J = 7.4 Hz, 2H), 1.68 (t, J = 7.4 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.0, 35.7, 17.9.

HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_4H_4D_3O_2$ 90.0640, found 90.0644.

For NMR Spectra: The presence of esters with high boiling points in organic solvents results in the appearance of impurity peaks in the high field region of the ^{1}H NMR spectrum, as well as three three minor peaks around 30 ppm in the ^{13}C NMR spectrum.

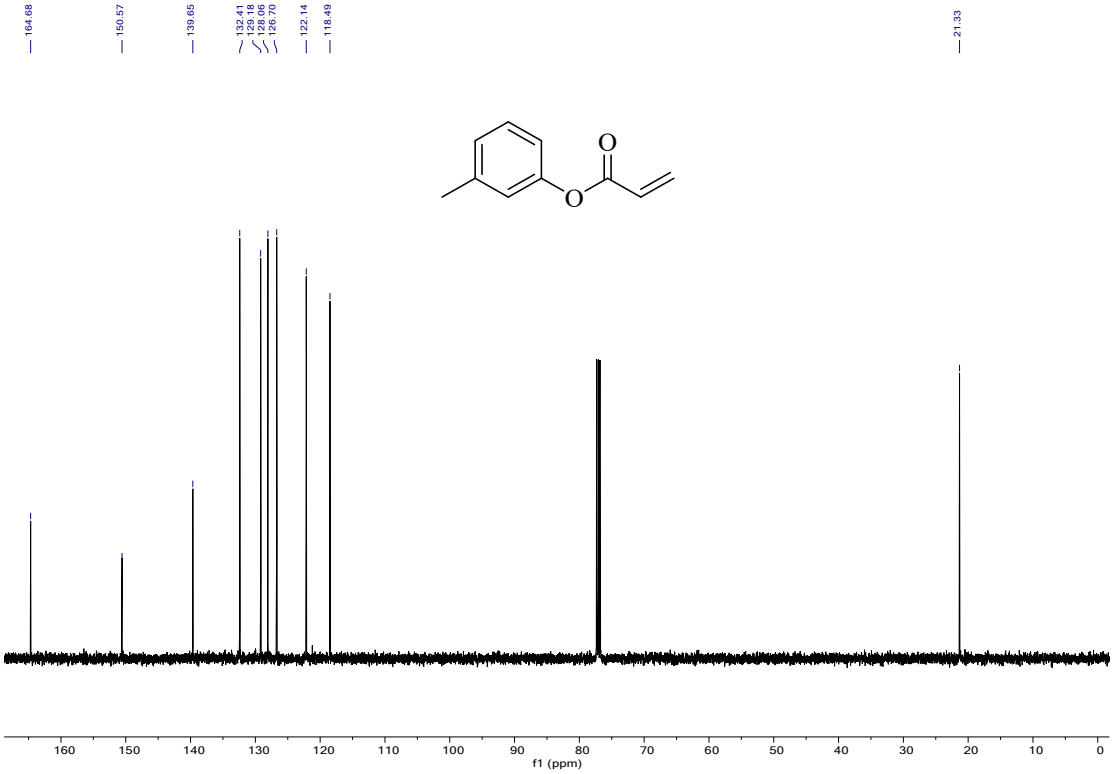
6. NMR Spectra

^{1}H NMR spectrum of compound **1c**

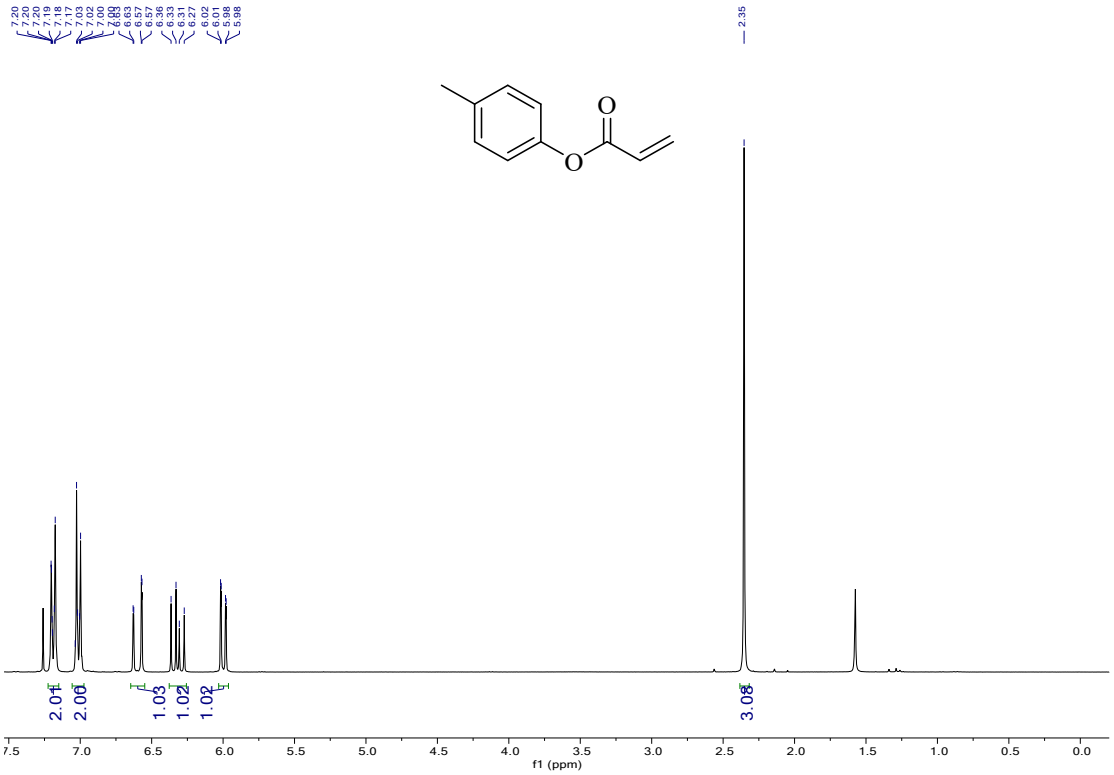
^{1}H NMR spectrum of compound **1d**

^{1}H NMR spectrum of compound **1e**

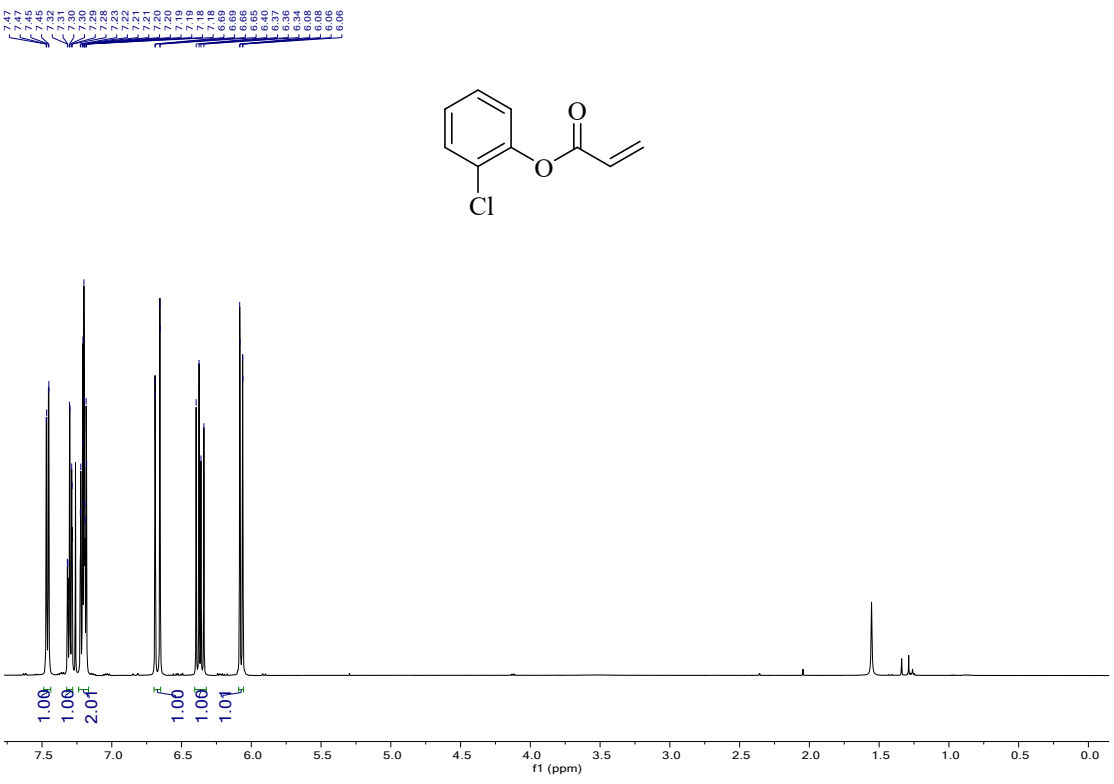
^{13}C NMR spectrum of compound **1e**



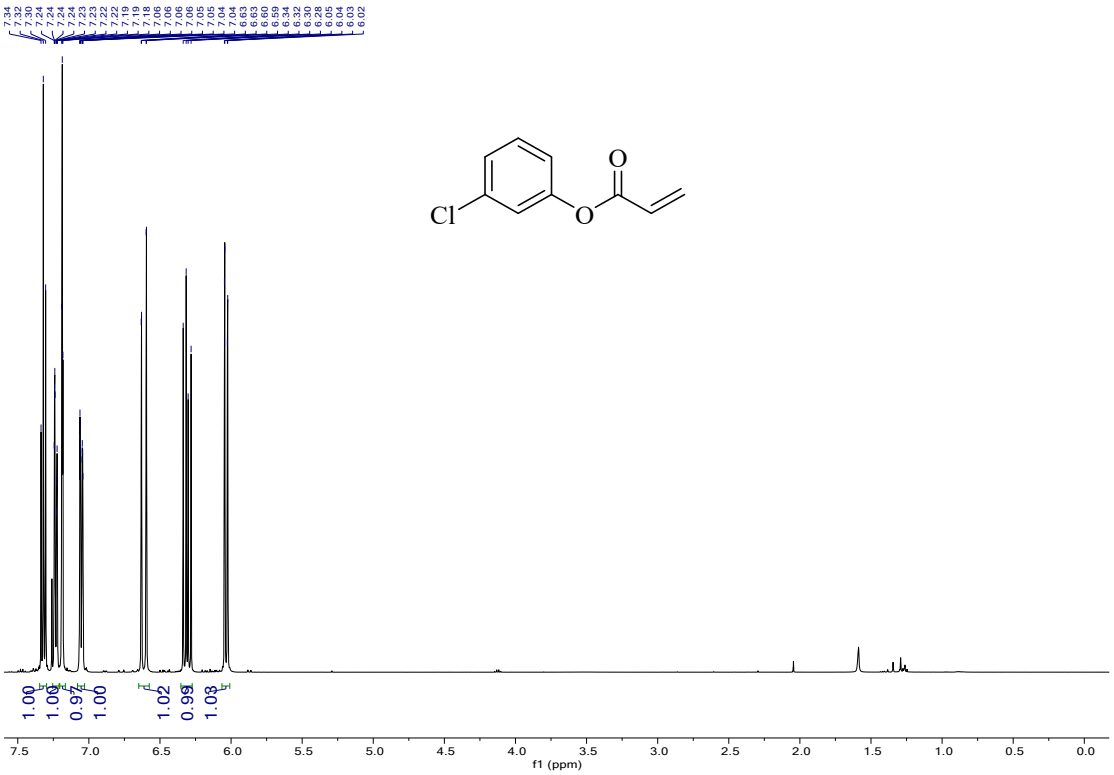
^{1}H NMR spectrum of compound **1f**



^{1}H NMR spectrum of compound **1g**

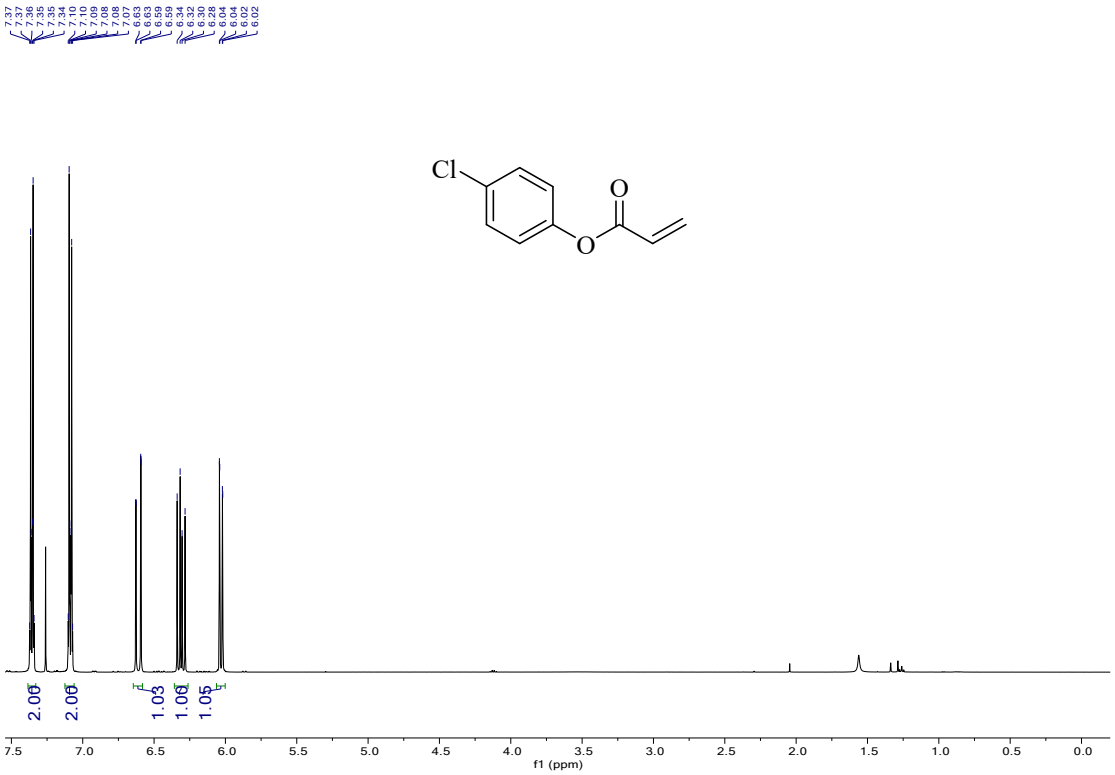


^{1}H NMR spectrum of compound **1h**

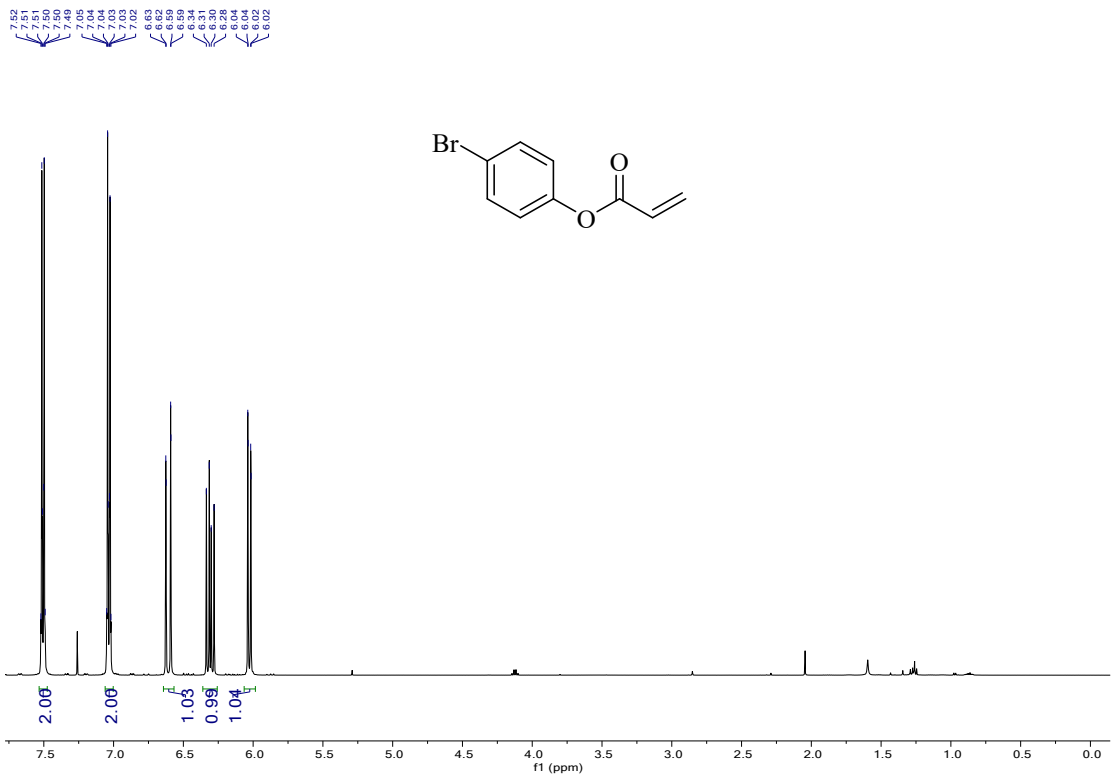


^{13}C NMR spectrum of compound **1h**

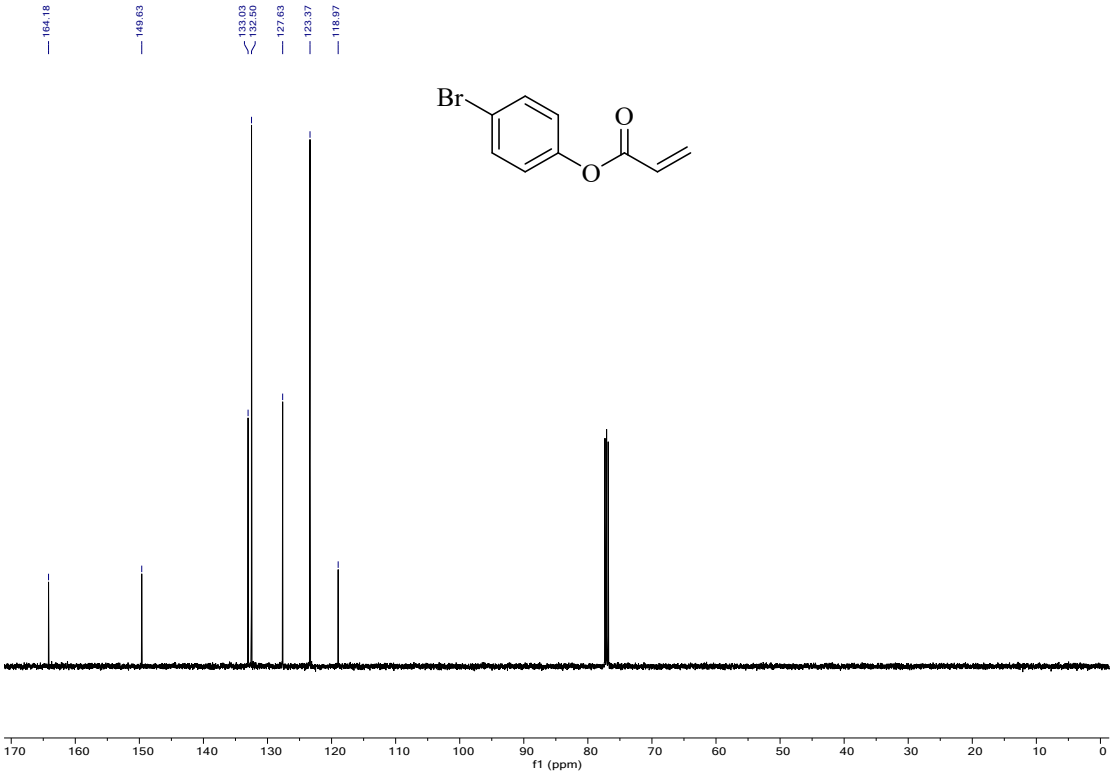
^{1}H NMR spectrum of compound **1i**



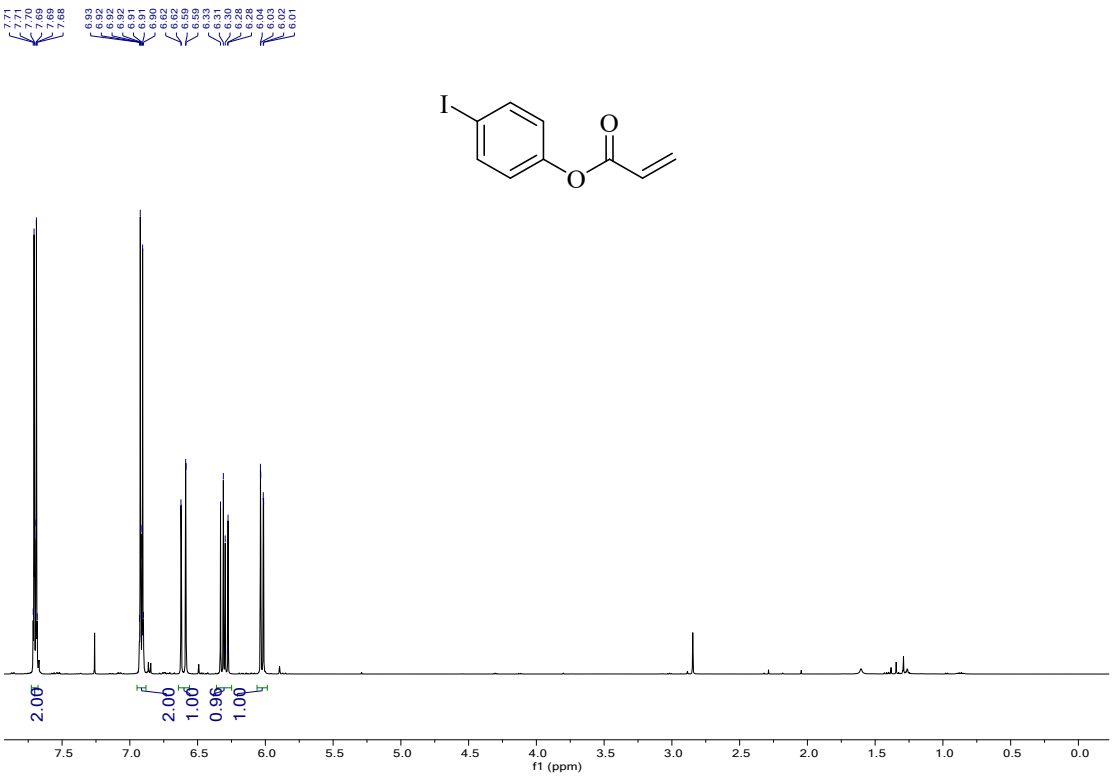
^{1}H NMR spectrum of compound **1j**



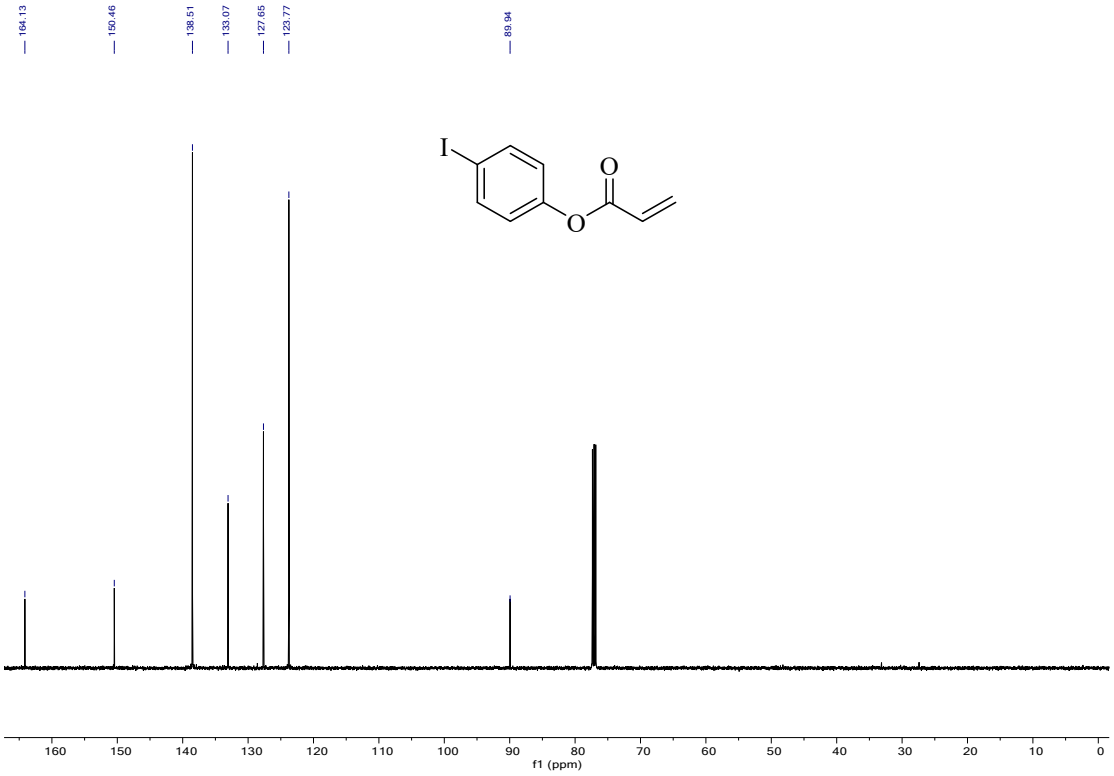
^{13}C NMR spectrum of compound **1j**



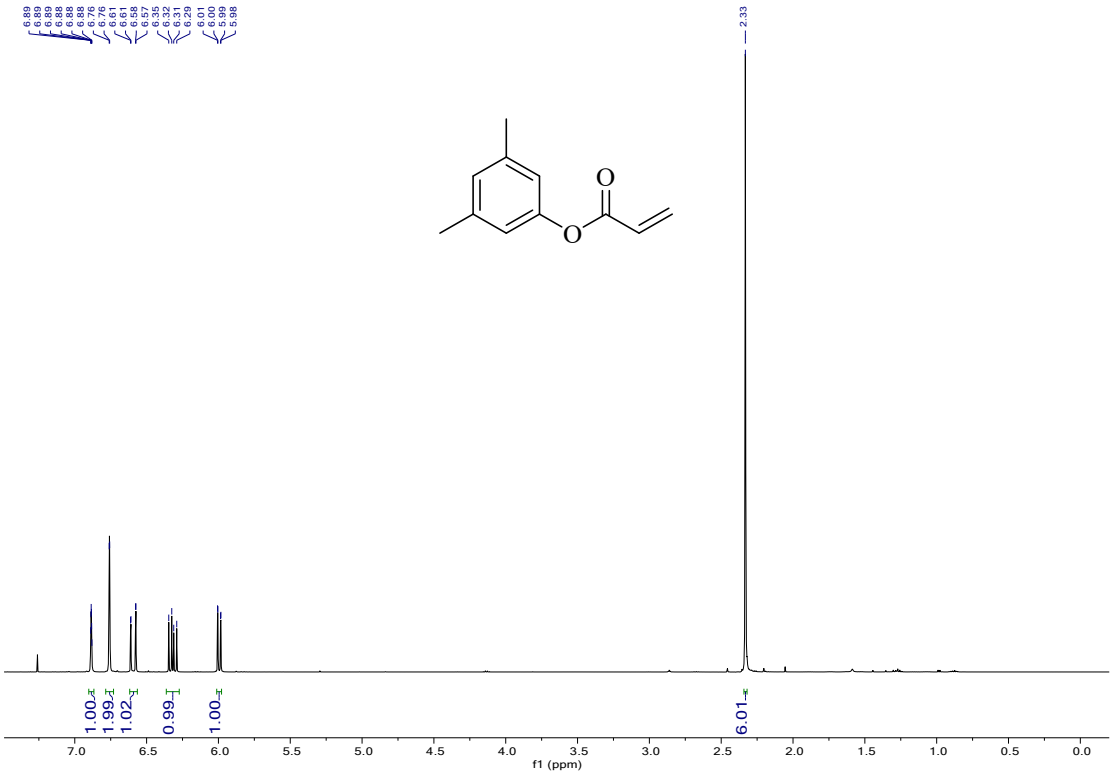
^{1}H NMR spectrum of compound **1k**



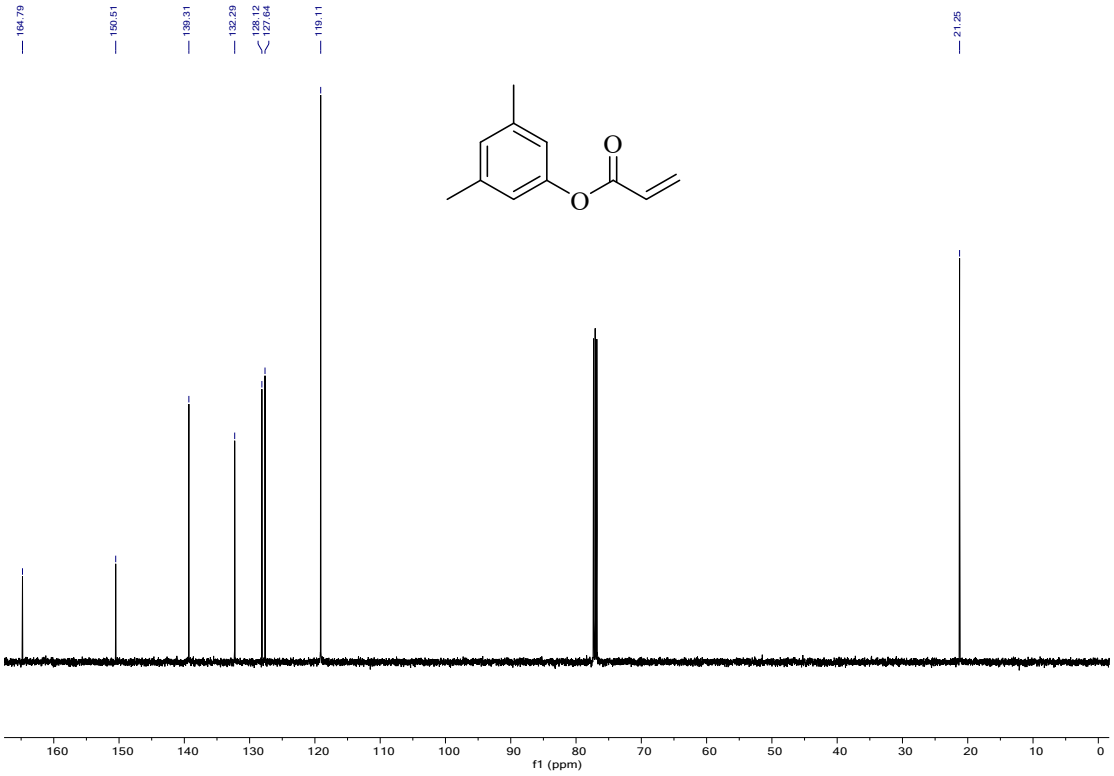
^{13}C NMR spectrum of compound **1k**



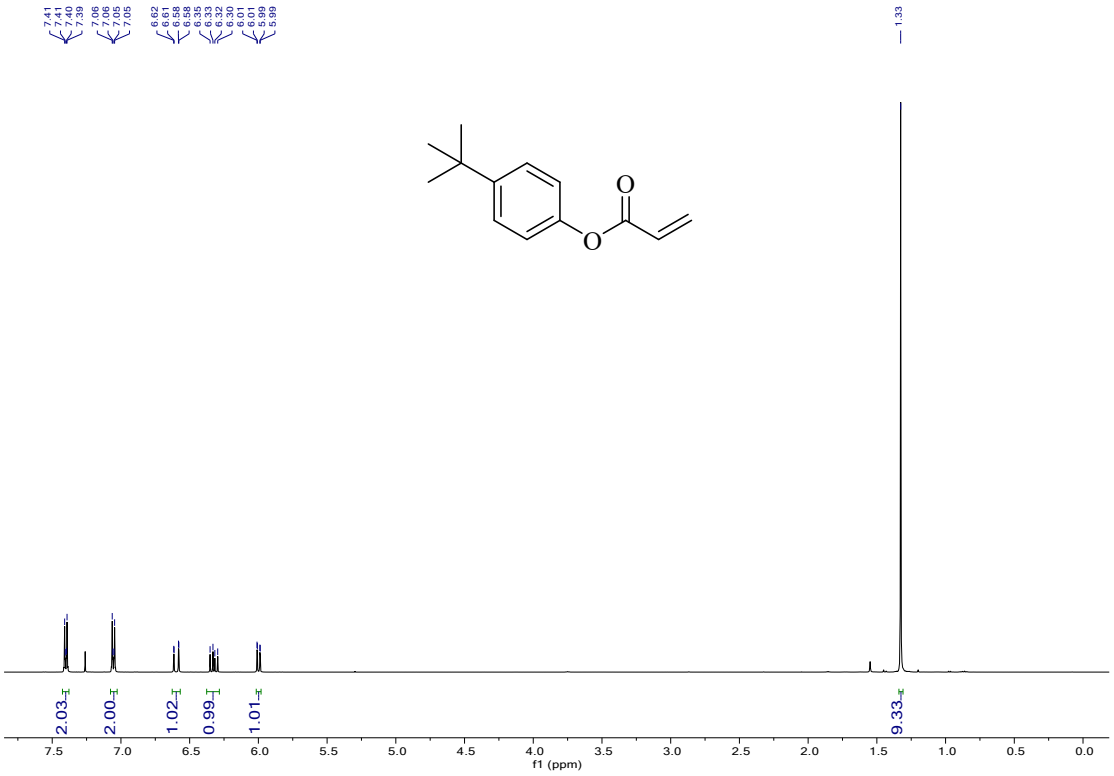
^{1}H NMR spectrum of compound **1l**



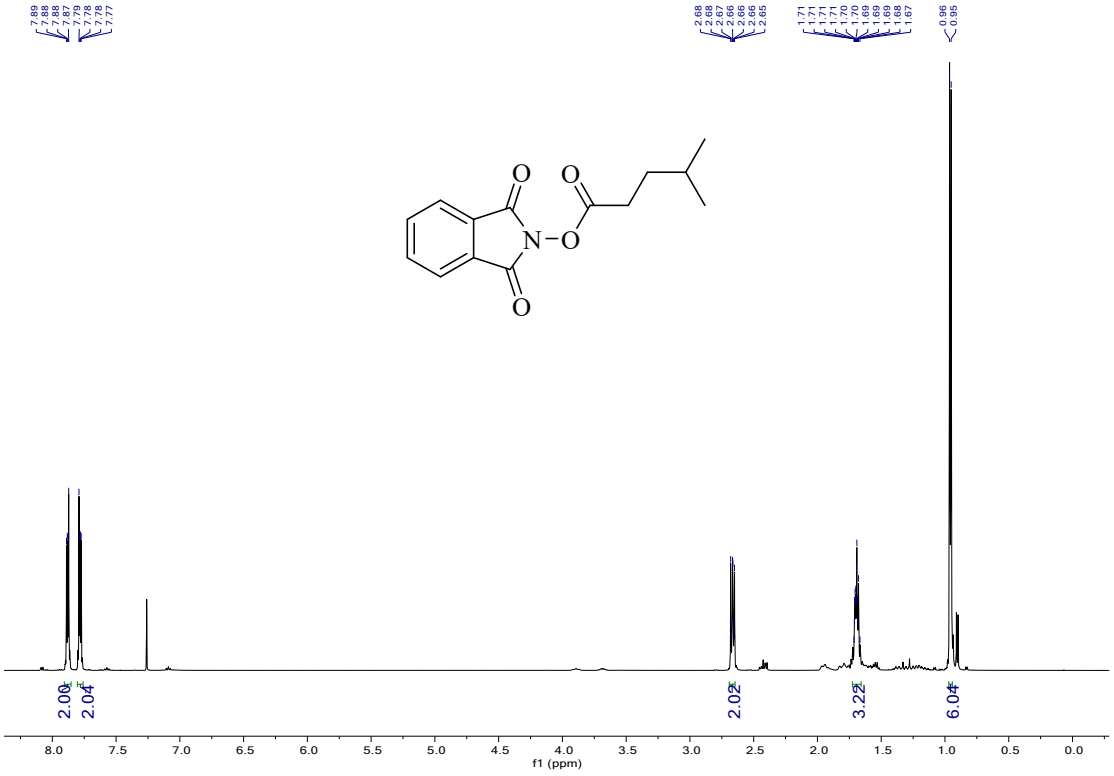
^{13}C NMR spectrum of compound **1l**



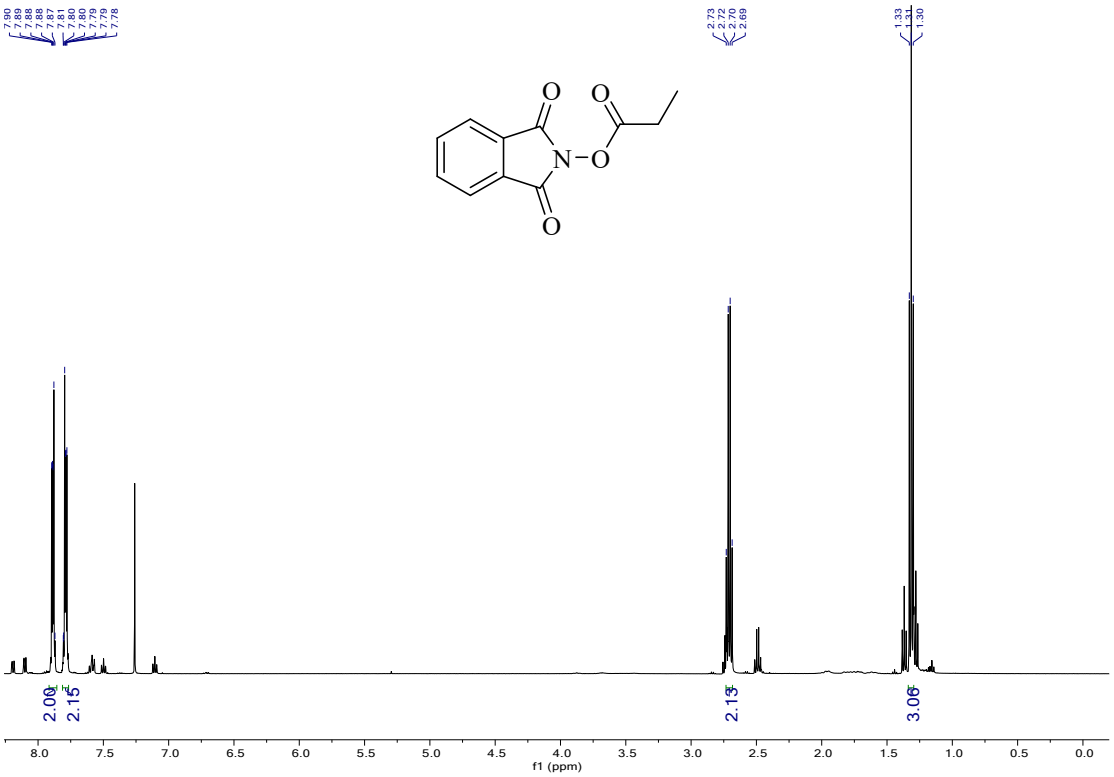
^{1}H NMR spectrum of compound **1m**



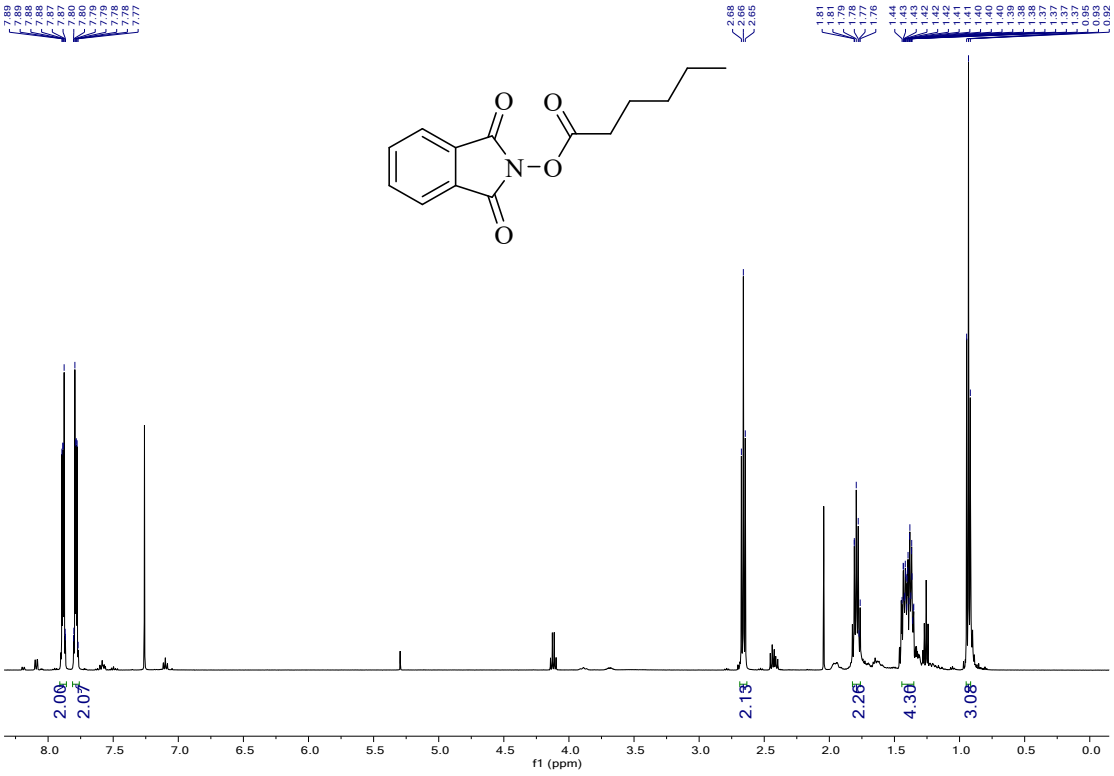
^{1}H NMR spectrum of compound **2a**



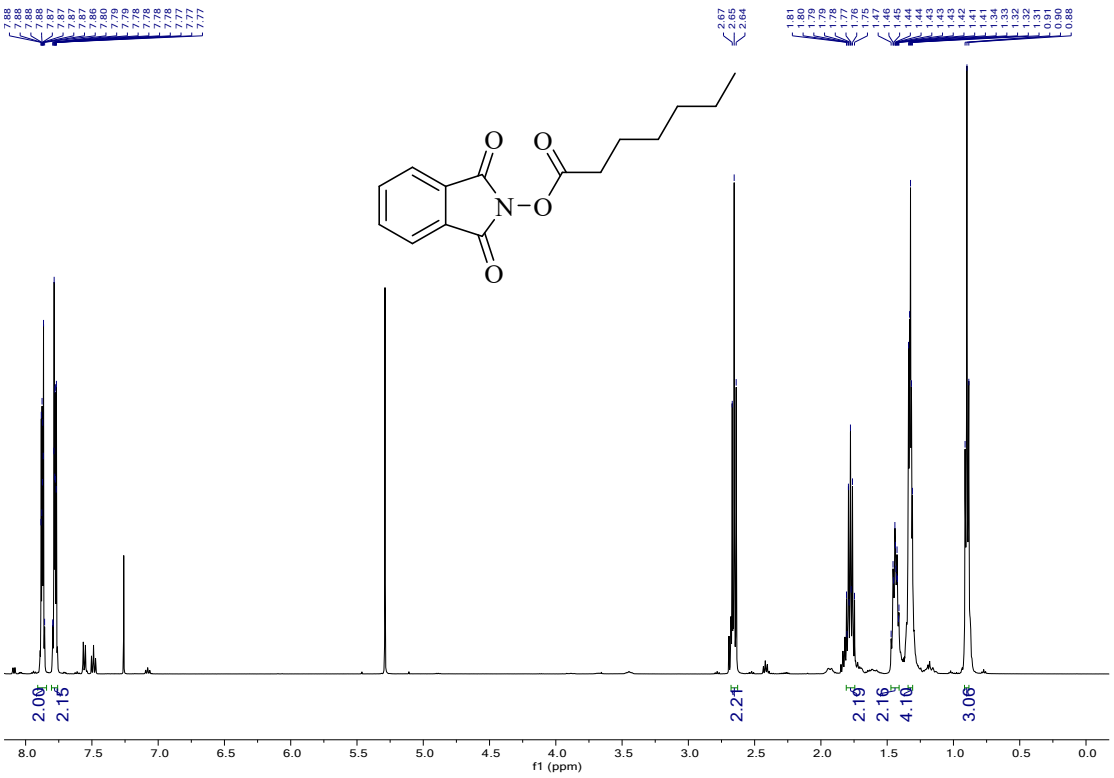
^{1}H NMR spectrum of compound **2b**



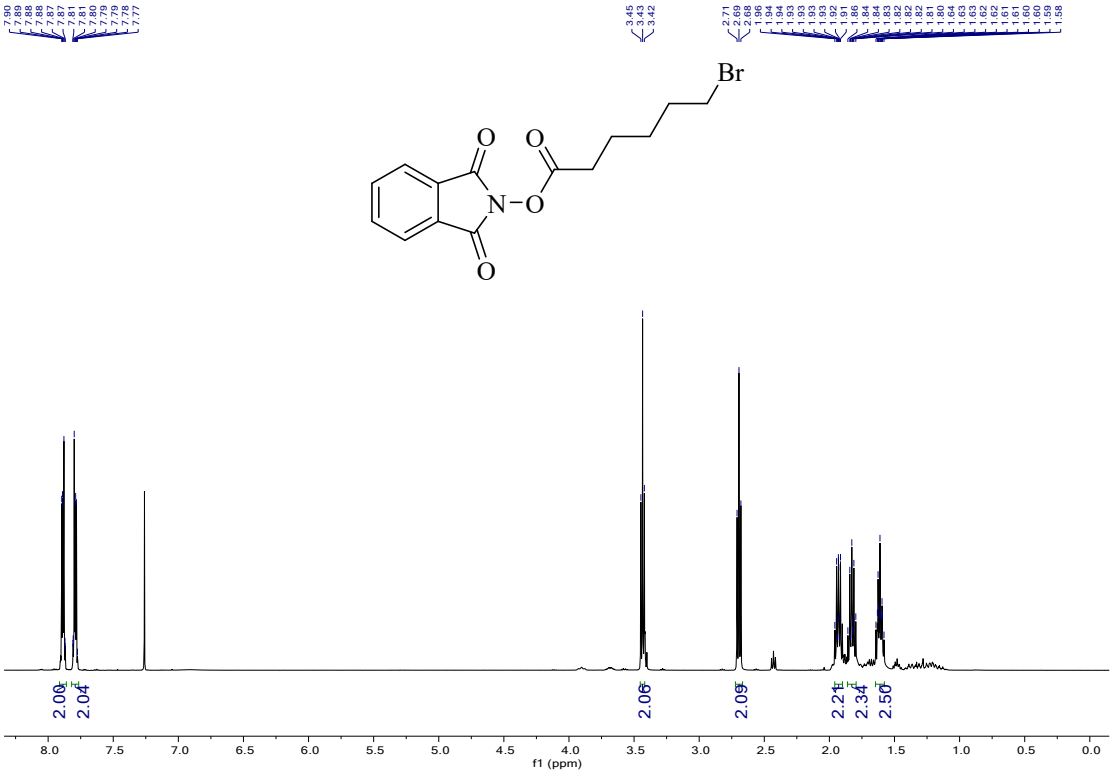
^{1}H NMR spectrum of compound **2c**



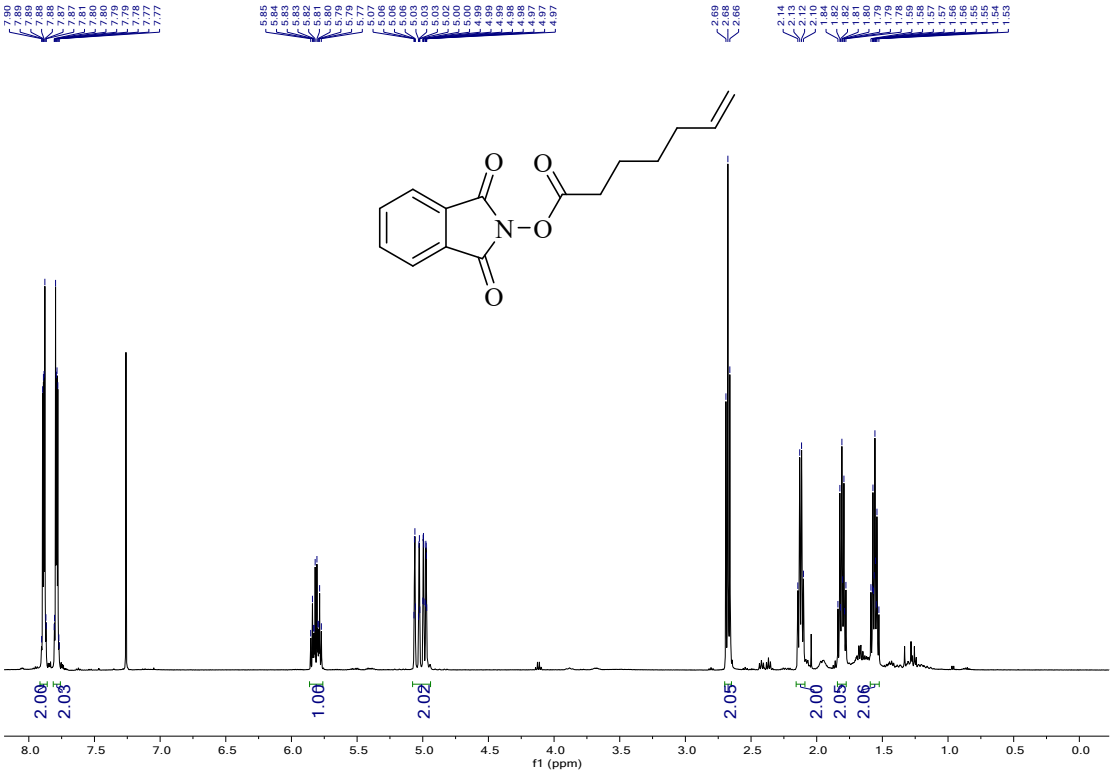
^{1}H NMR spectrum of compound **2d**



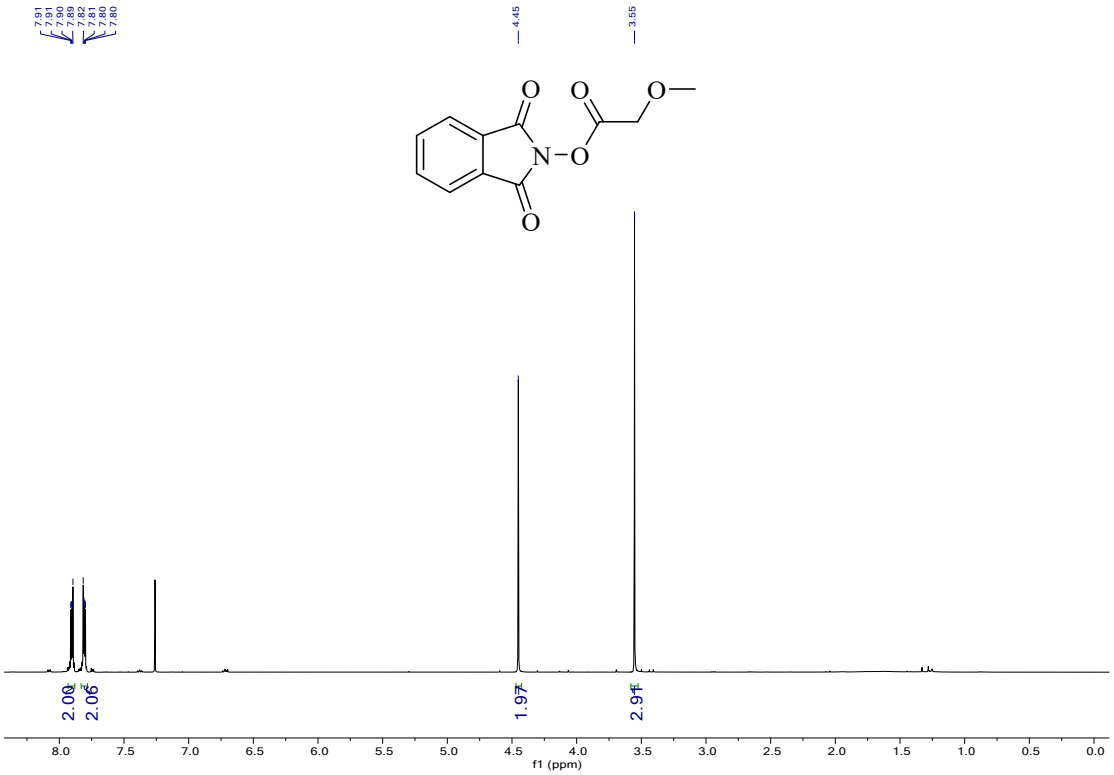
^{1}H NMR spectrum of compound **2e**



^{1}H NMR spectrum of compound **2f**

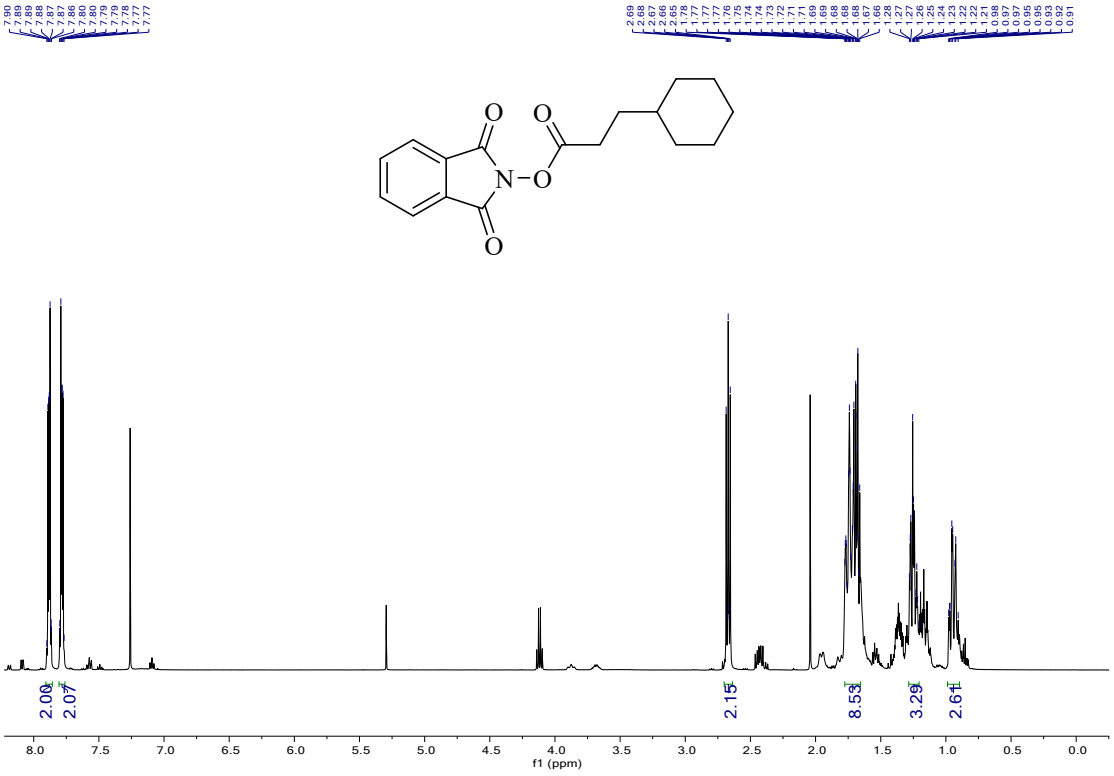


^{1}H NMR spectrum of compound **2g**

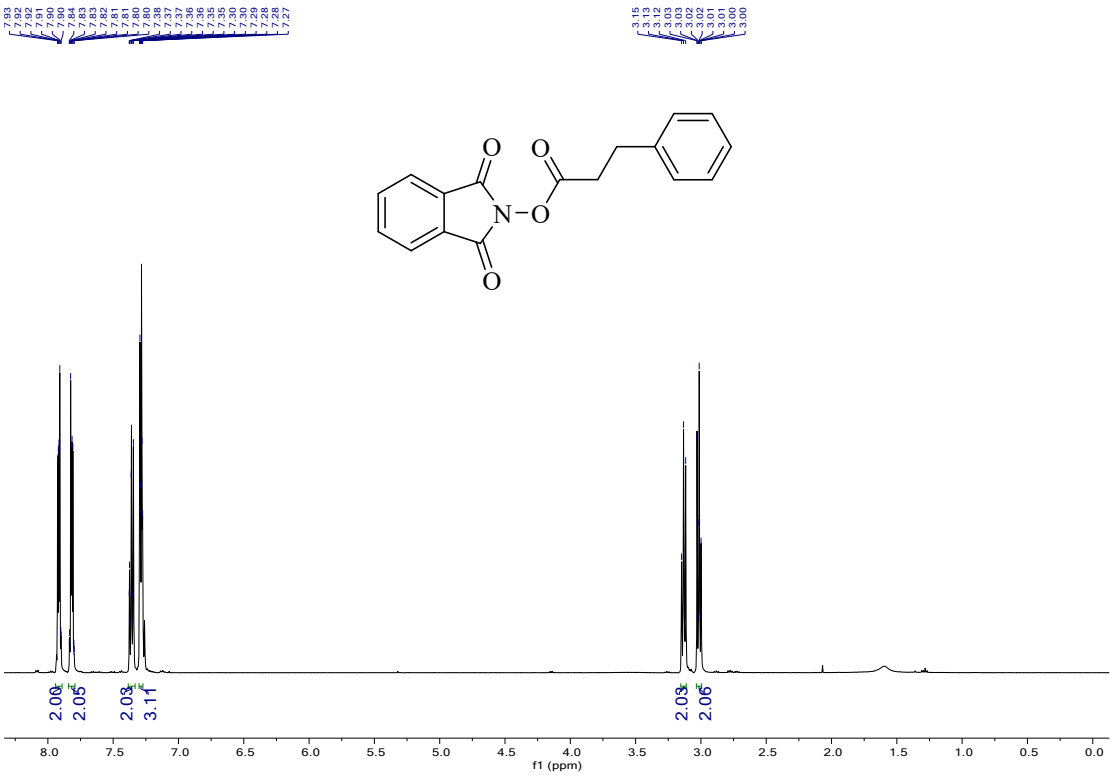


^{1}H NMR spectrum of compound **2h**

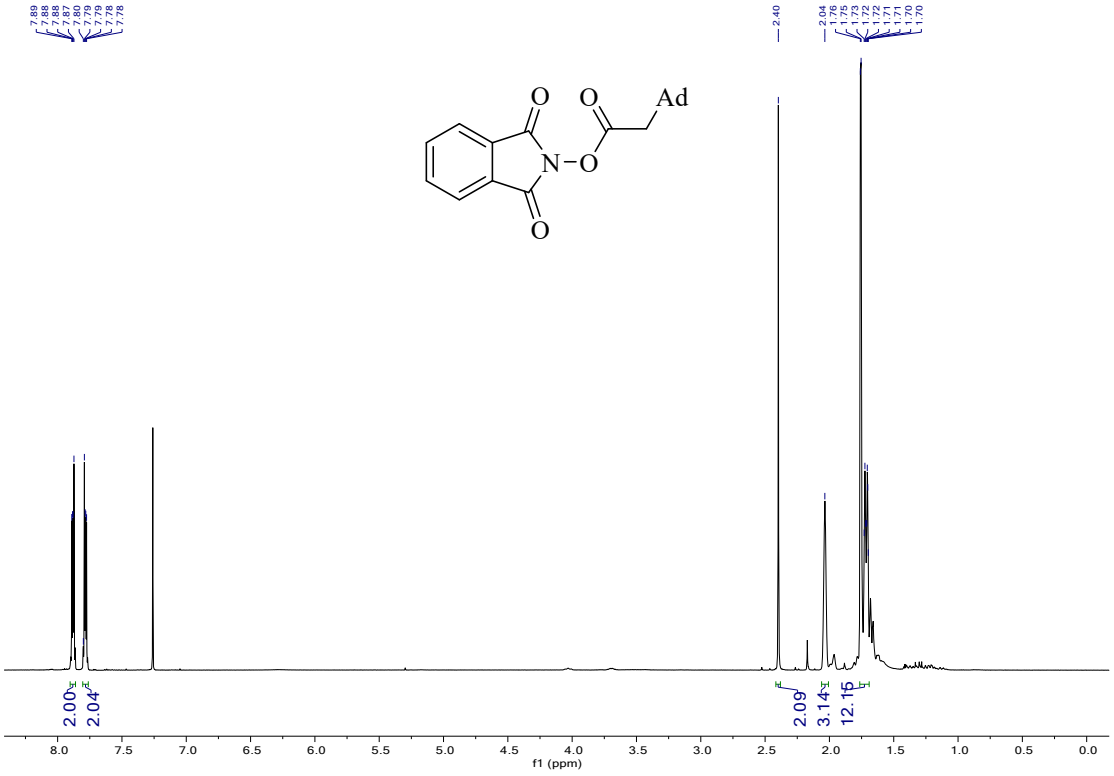
^{1}H NMR spectrum of compound **2i**



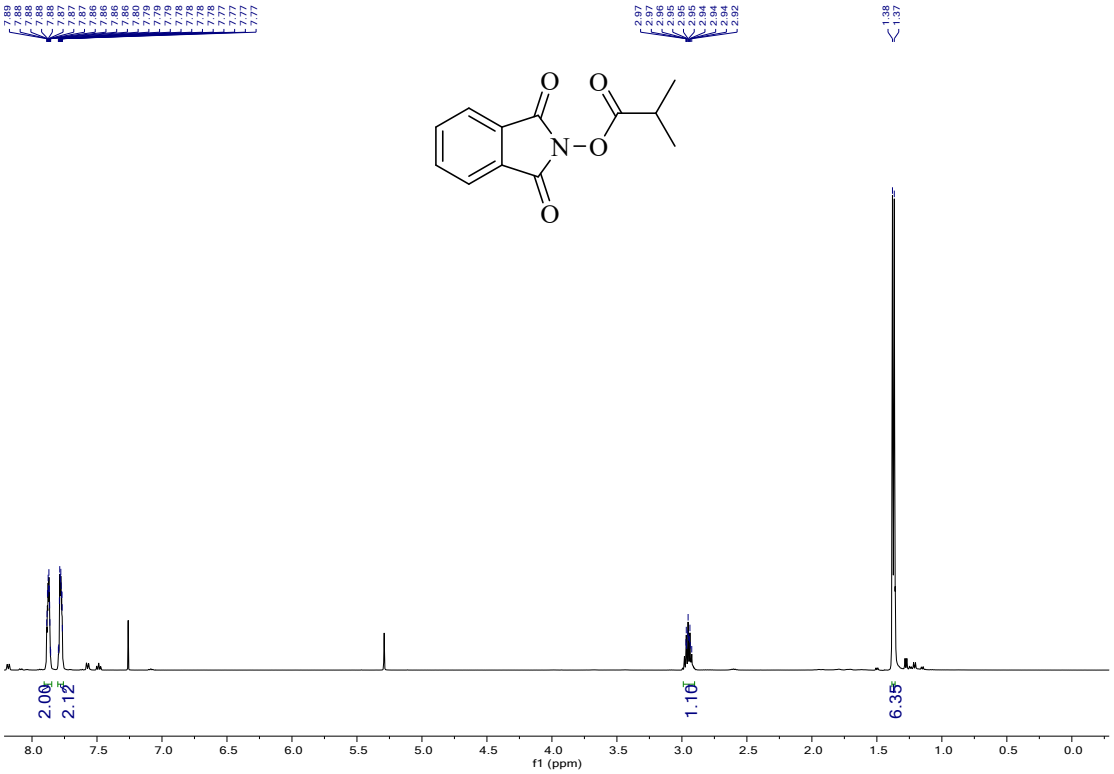
^{1}H NMR spectrum of compound **2j**



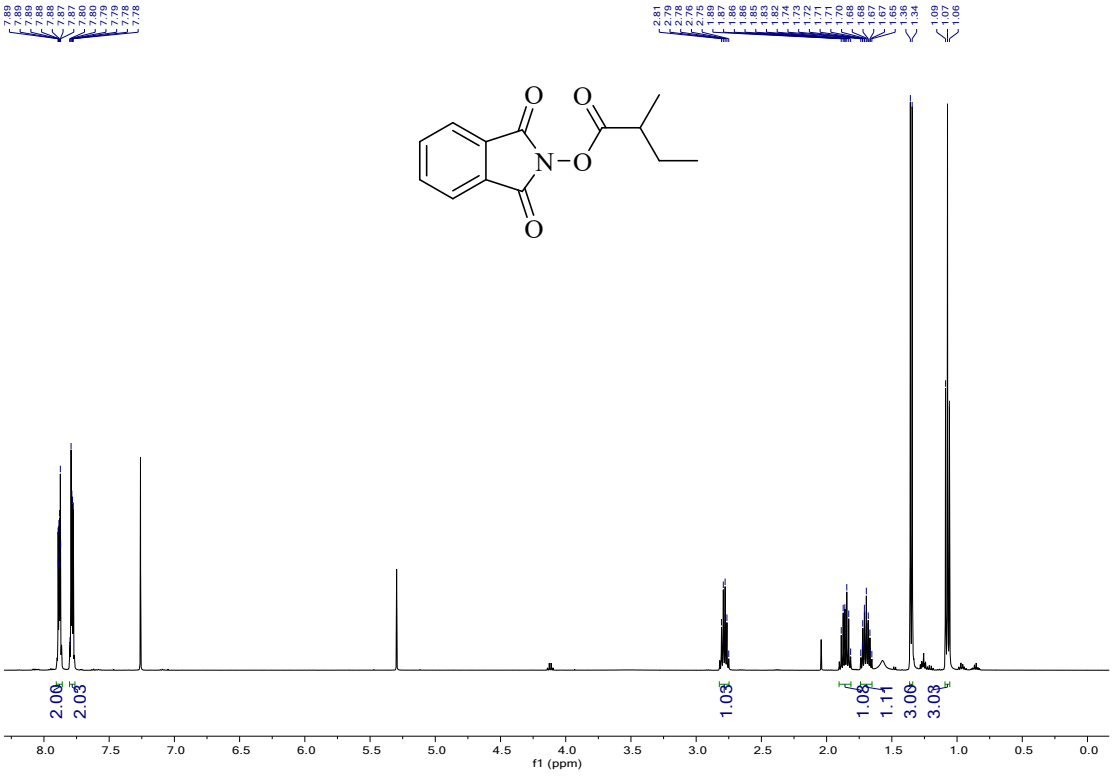
^{1}H NMR spectrum of compound **2k**



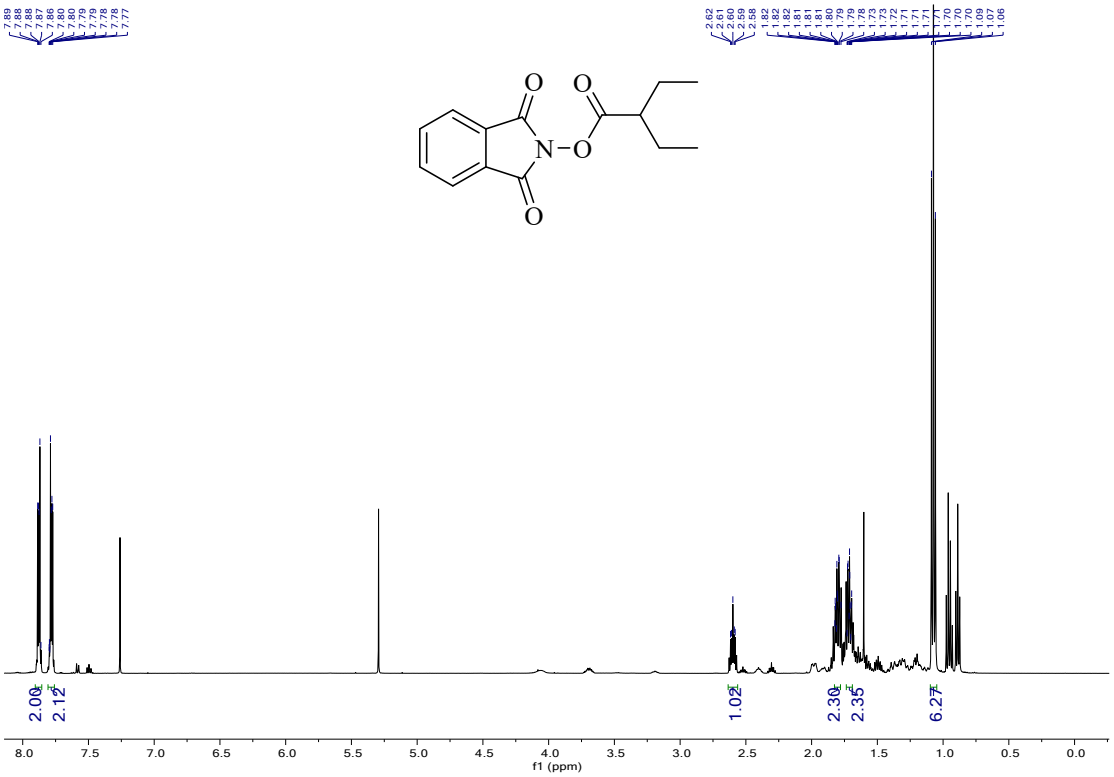
^{1}H NMR spectrum of compound **2l**



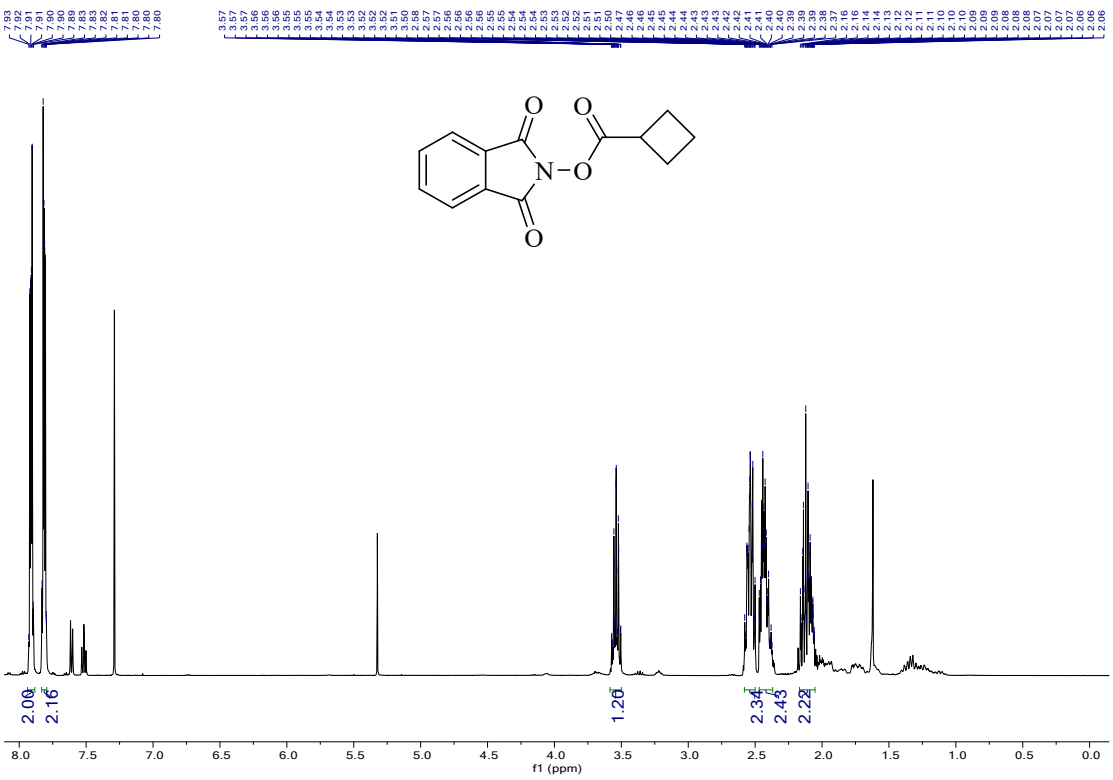
^{1}H NMR spectrum of compound **2m**



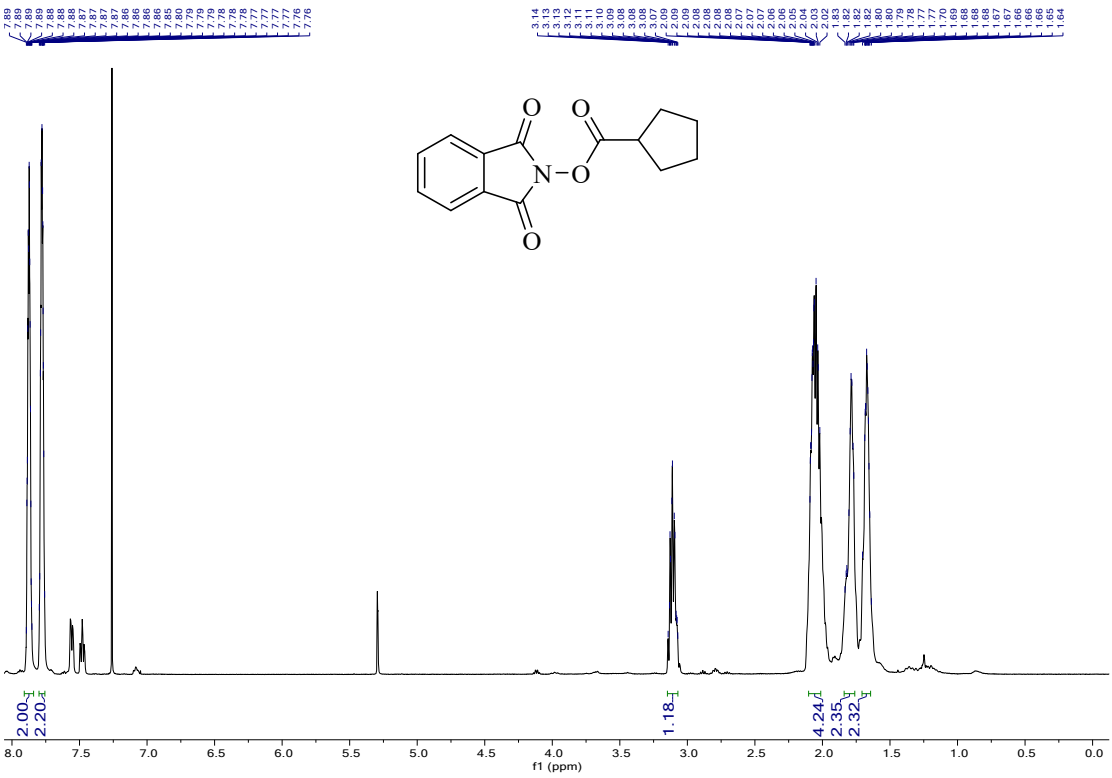
^{1}H NMR spectrum of compound **2n**



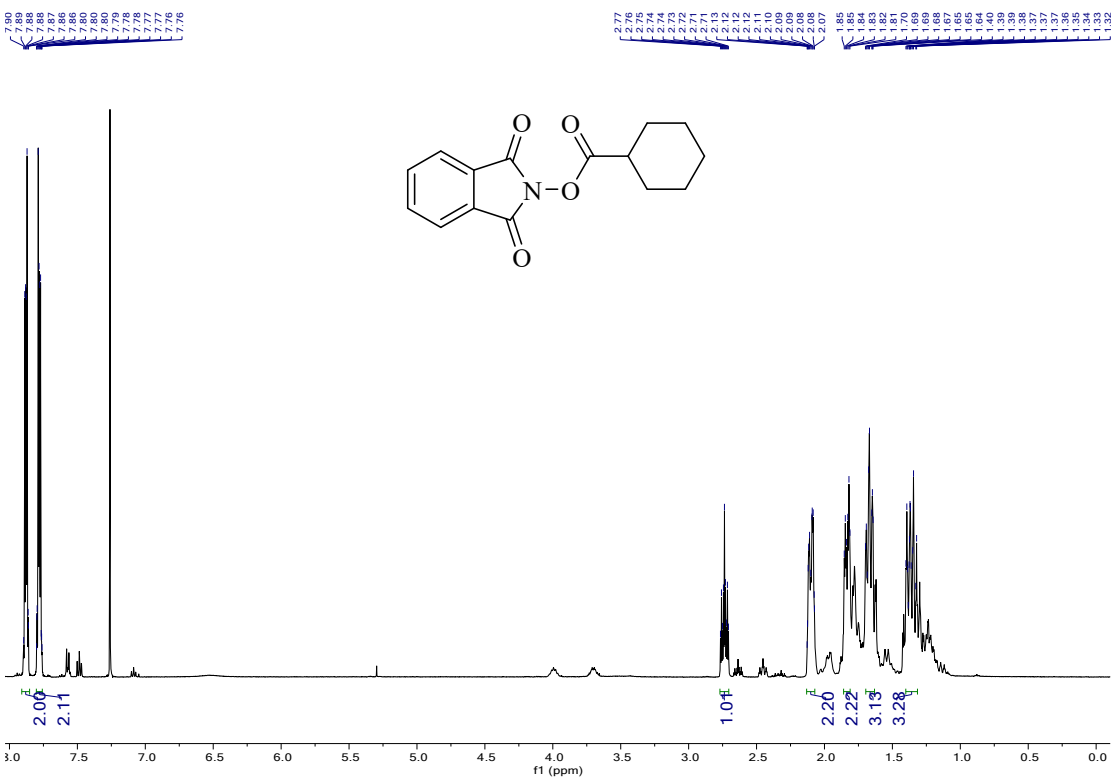
^{1}H NMR spectrum of compound **2o**



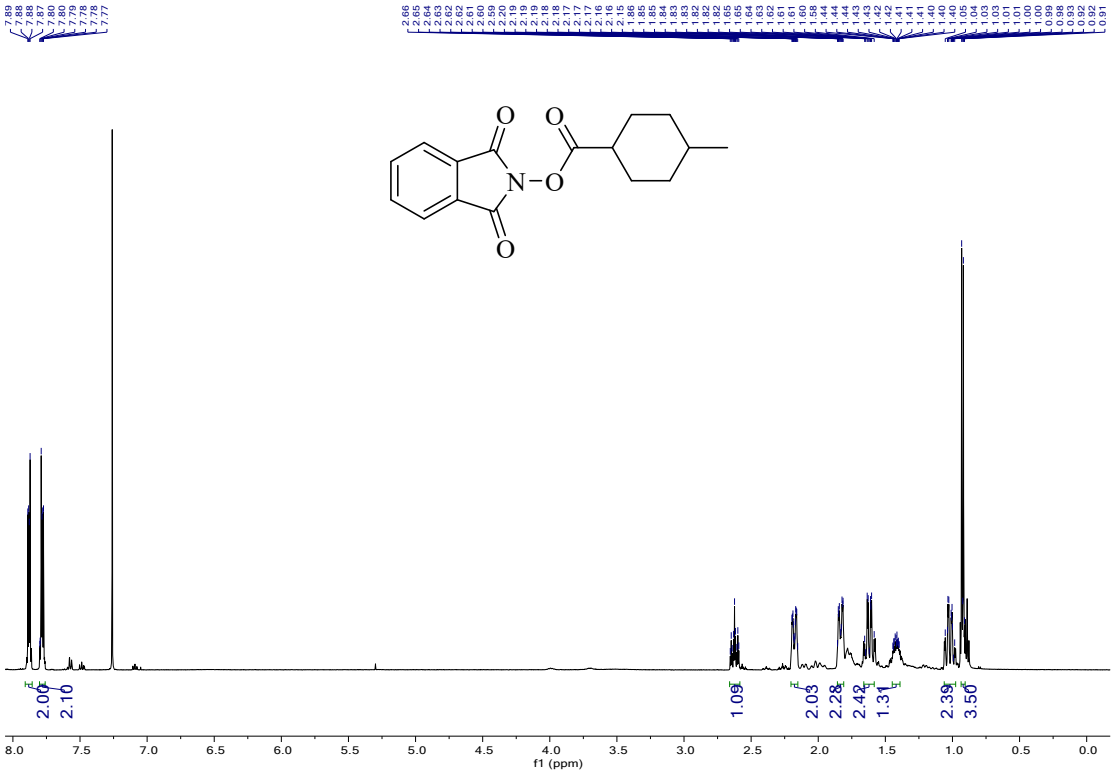
^{1}H NMR spectrum of compound **2p**



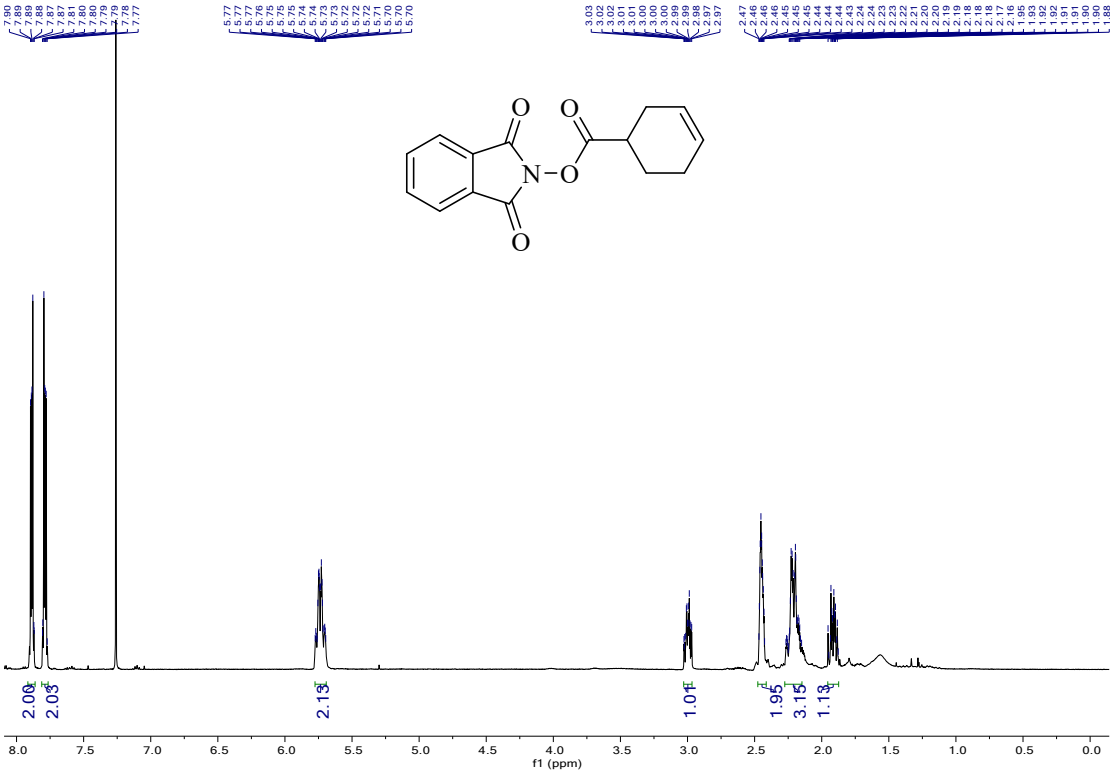
^{1}H NMR spectrum of compound **2q**



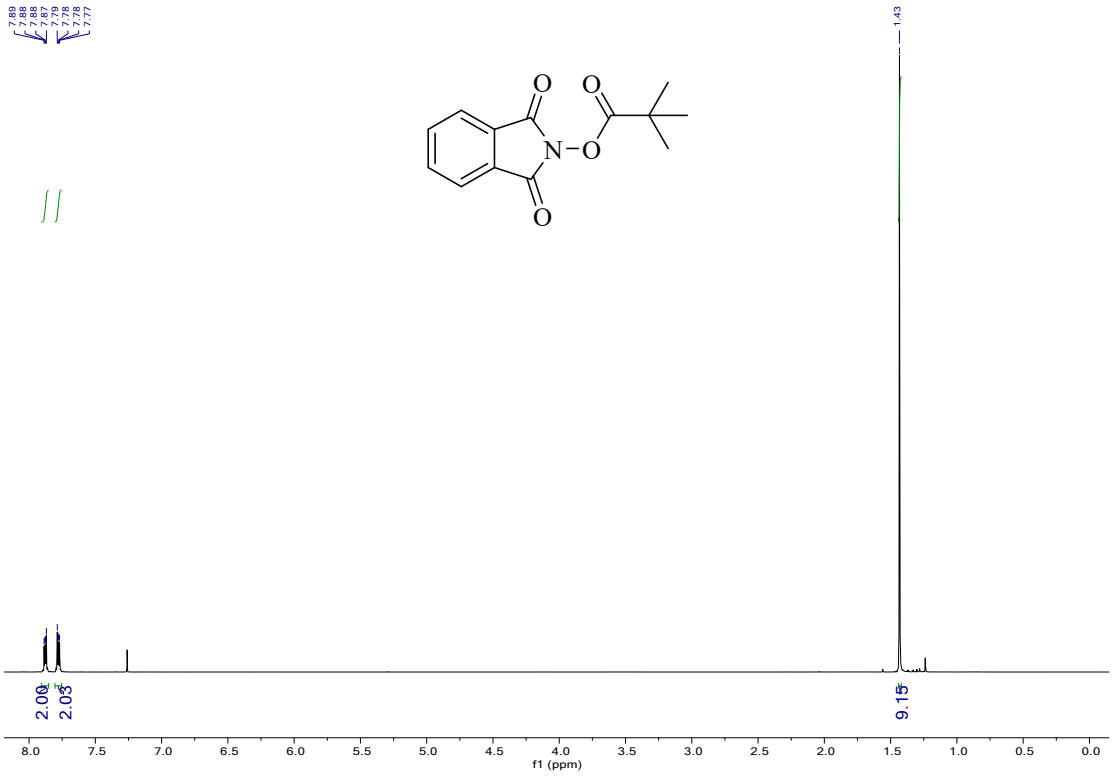
^{1}H NMR spectrum of compound **2r**



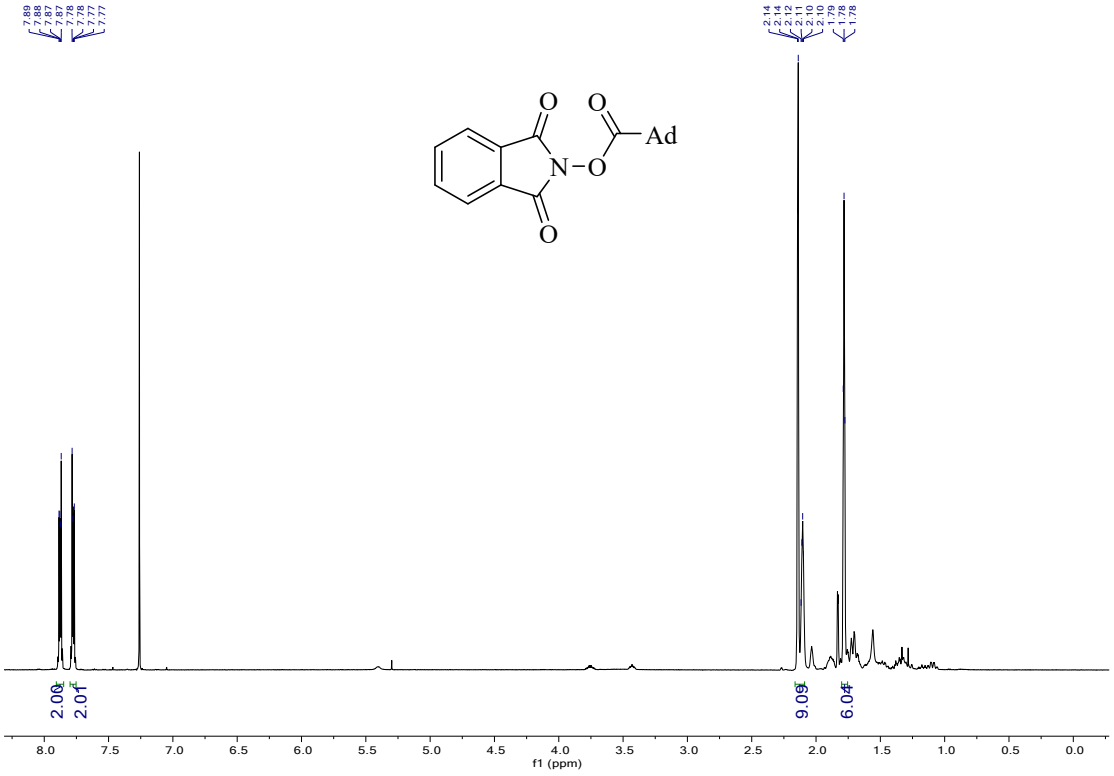
^{1}H NMR spectrum of compound **2s**



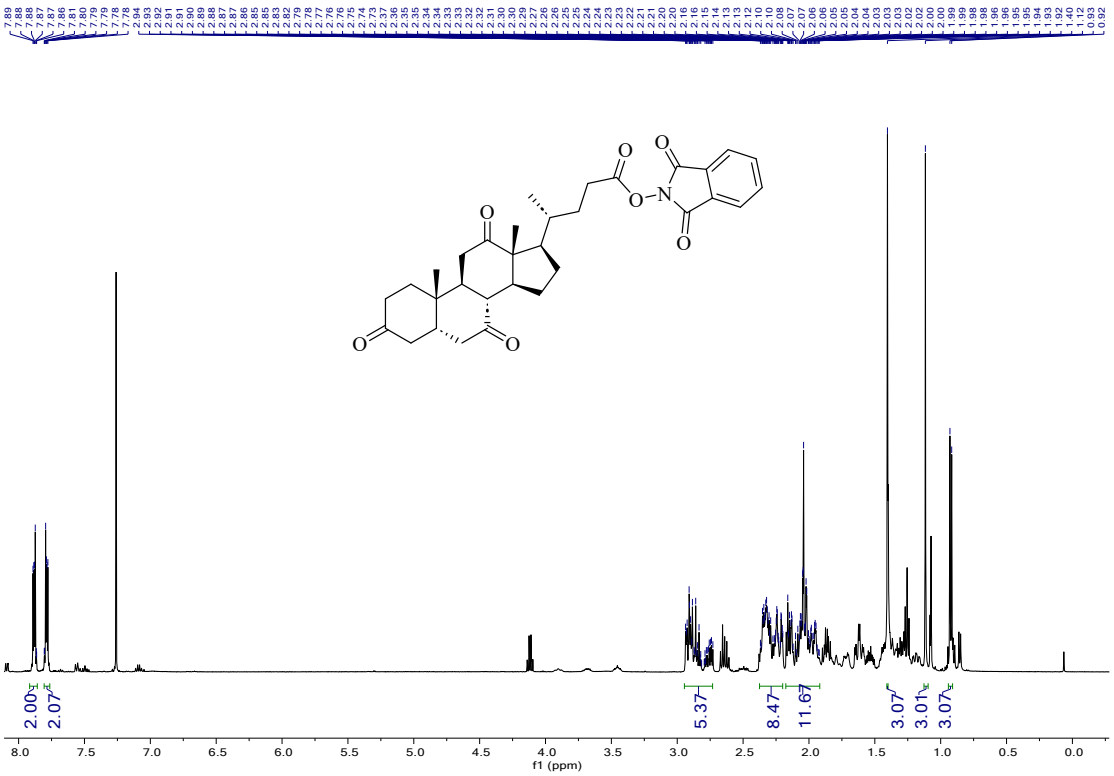
^{1}H NMR spectrum of compound **2t**



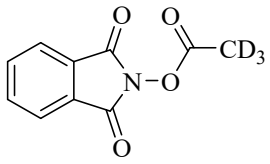
^{1}H NMR spectrum of compound **2u**

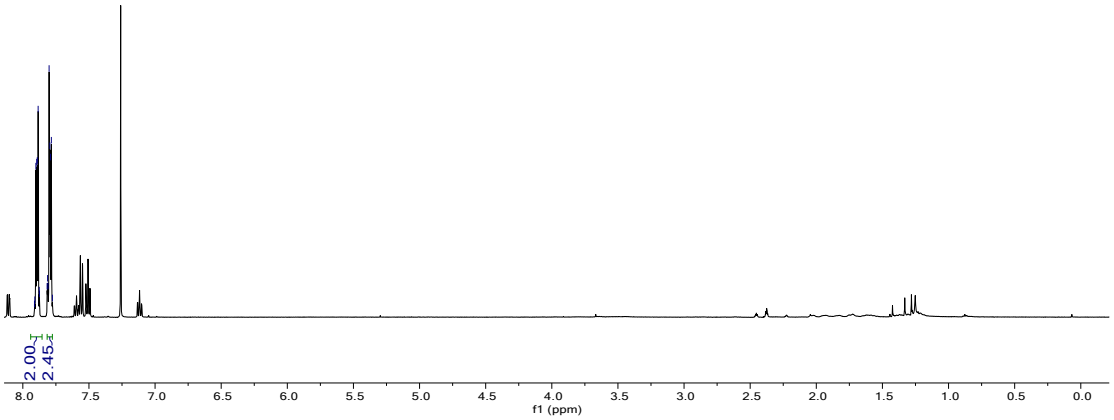


^{1}H NMR spectrum of compound **2w**

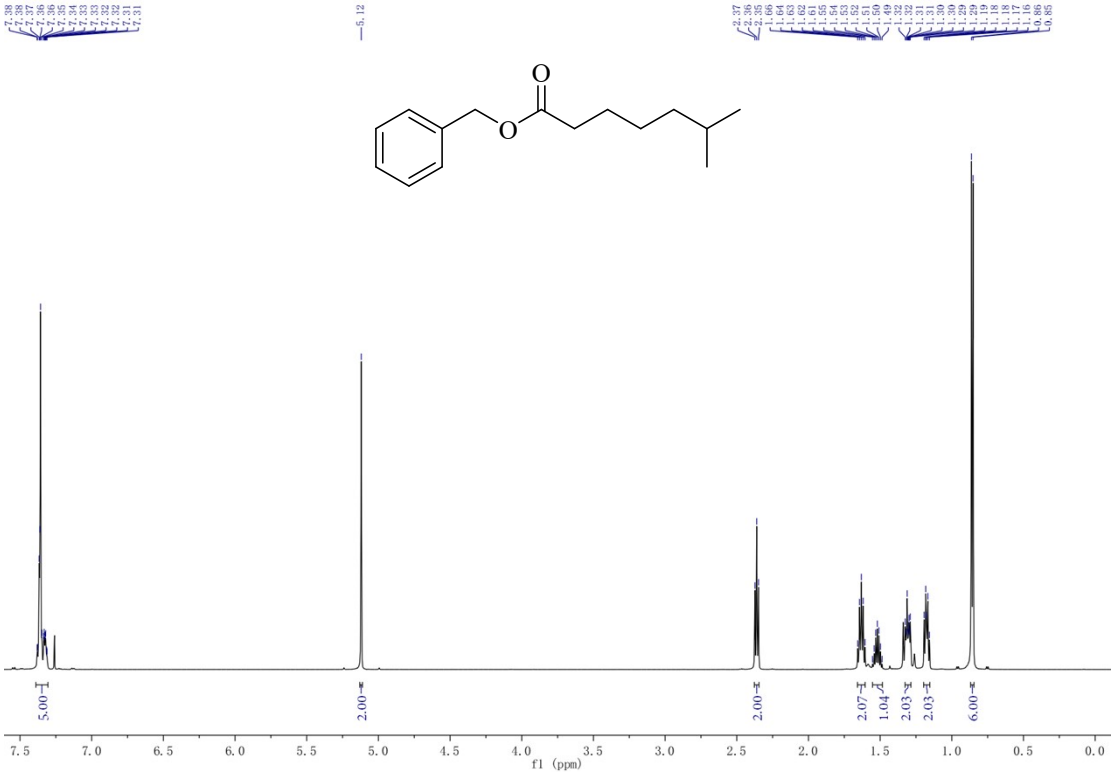


^{1}H NMR spectrum of compound **2x**





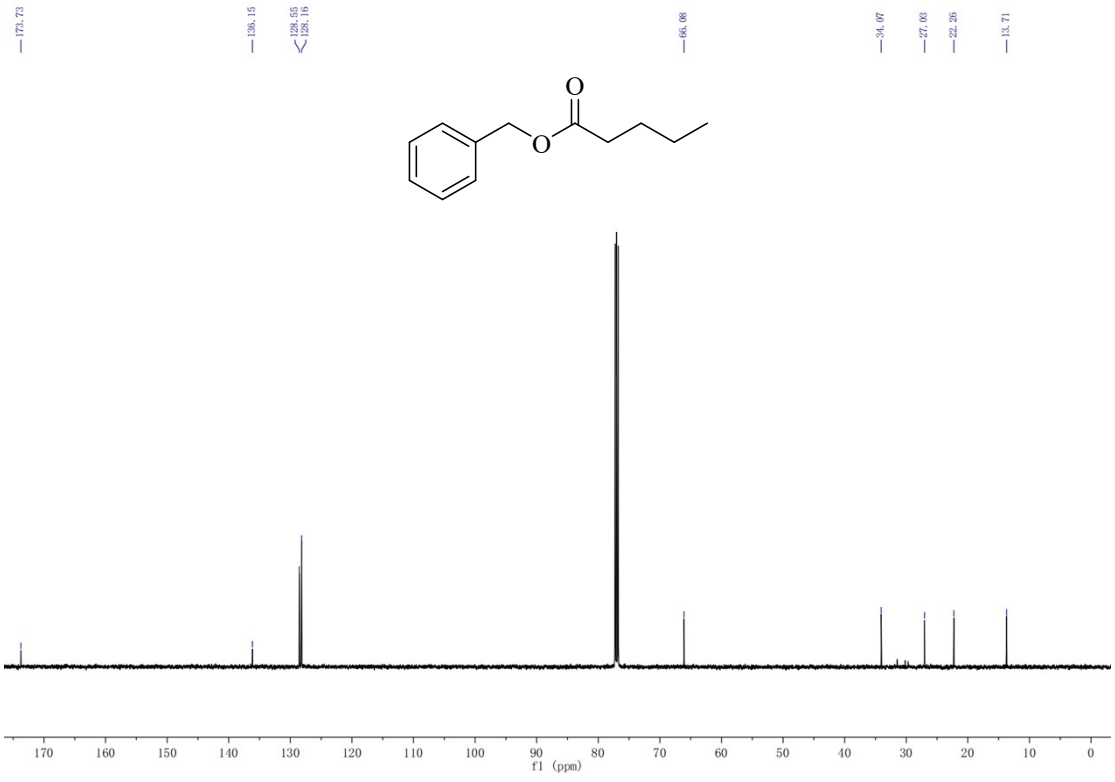
^{1}H NMR spectrum of compound **3aa**



^{13}C NMR spectrum of compound **3aa**

^{1}H NMR spectrum of compound **3ab**

^{13}C NMR spectrum of compound **3ab**



^{1}H NMR spectrum of compound **3ac**

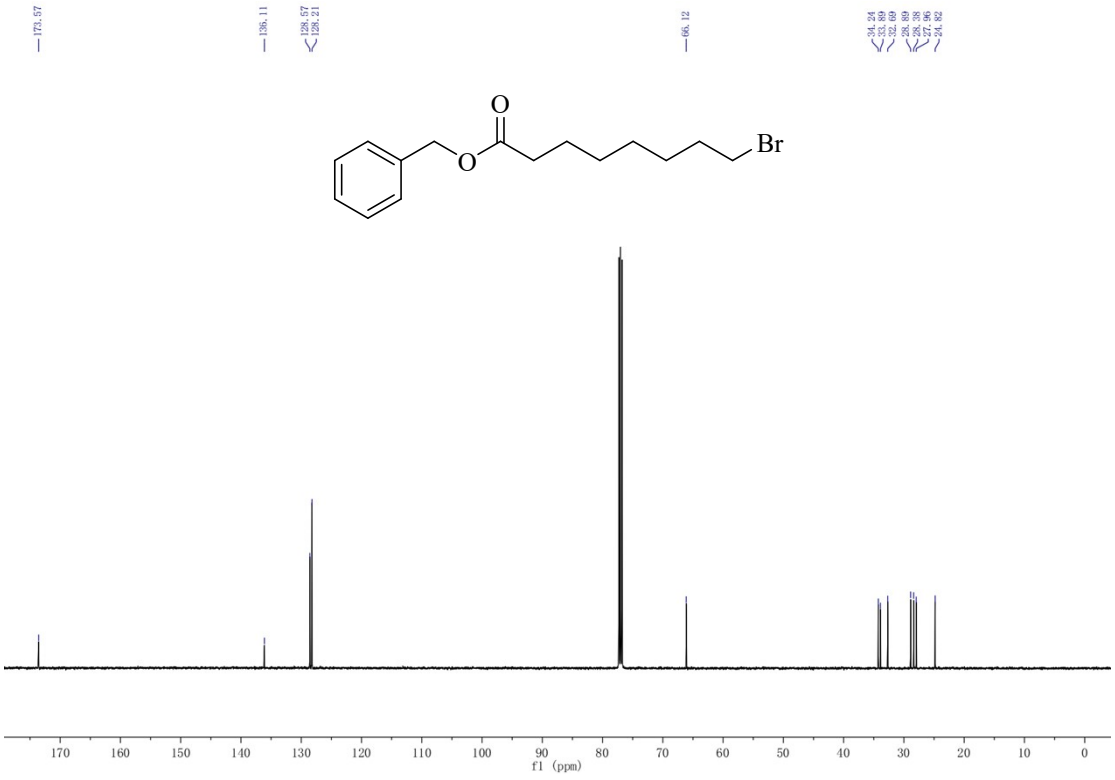
^{13}C NMR spectrum of compound **3ac**

^{1}H NMR spectrum of compound **3ad**

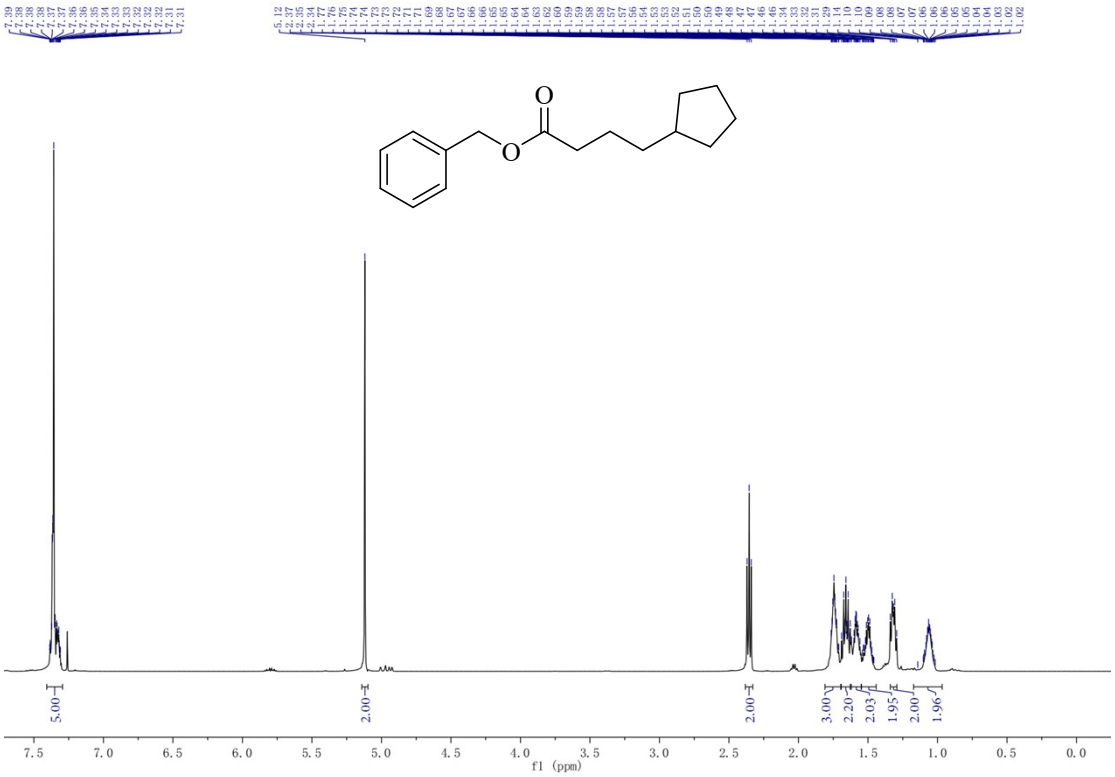
^{13}C NMR spectrum of compound **3ad**

^{1}H NMR spectrum of compound **3ae**

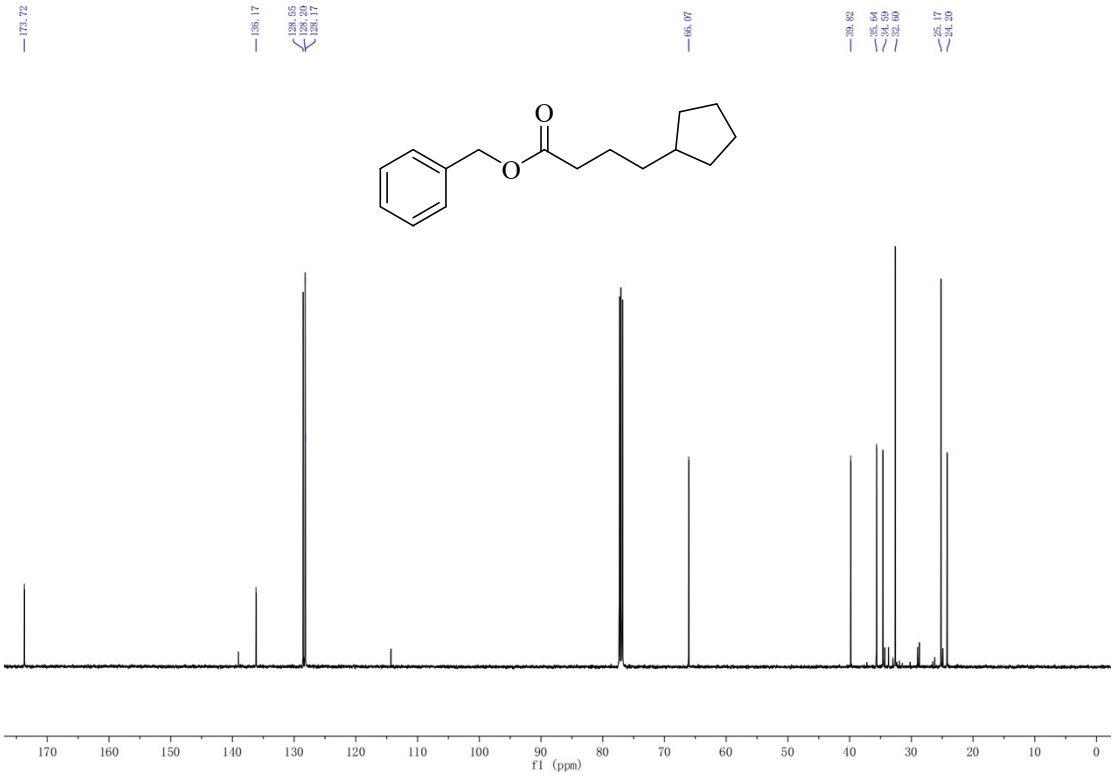
^{13}C NMR spectrum of compound **3ae**



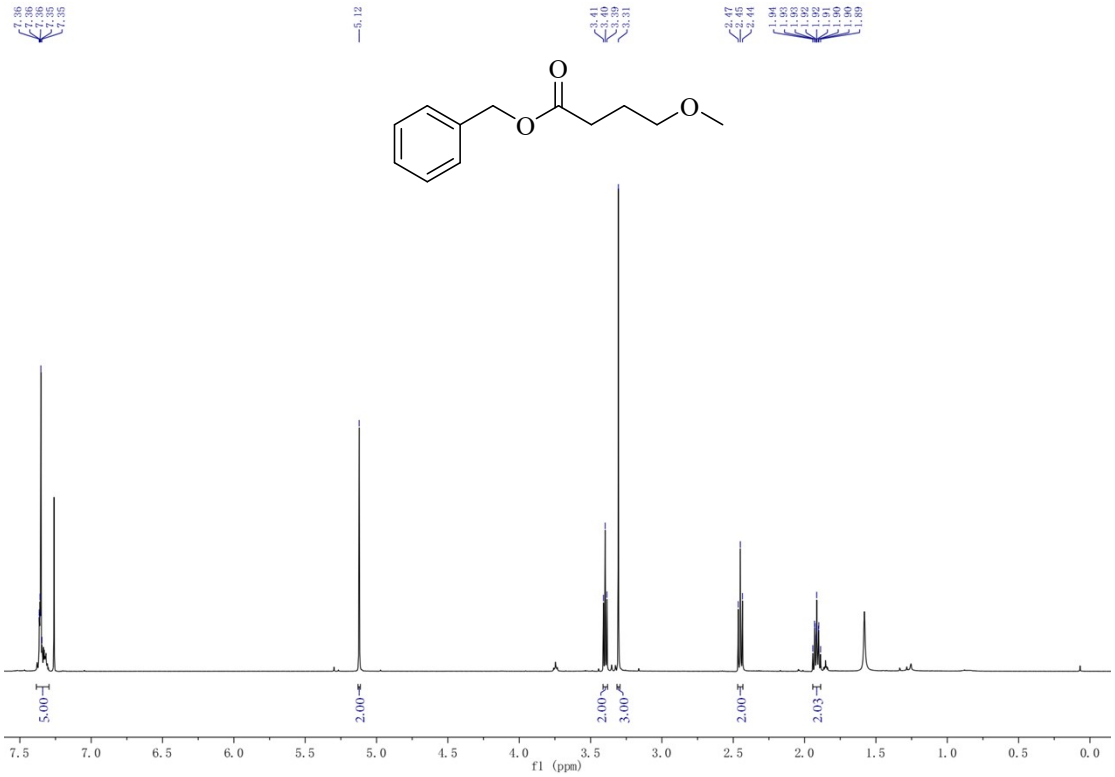
^{1}H NMR spectrum of compound **3af**



^{13}C NMR spectrum of compound **3af**

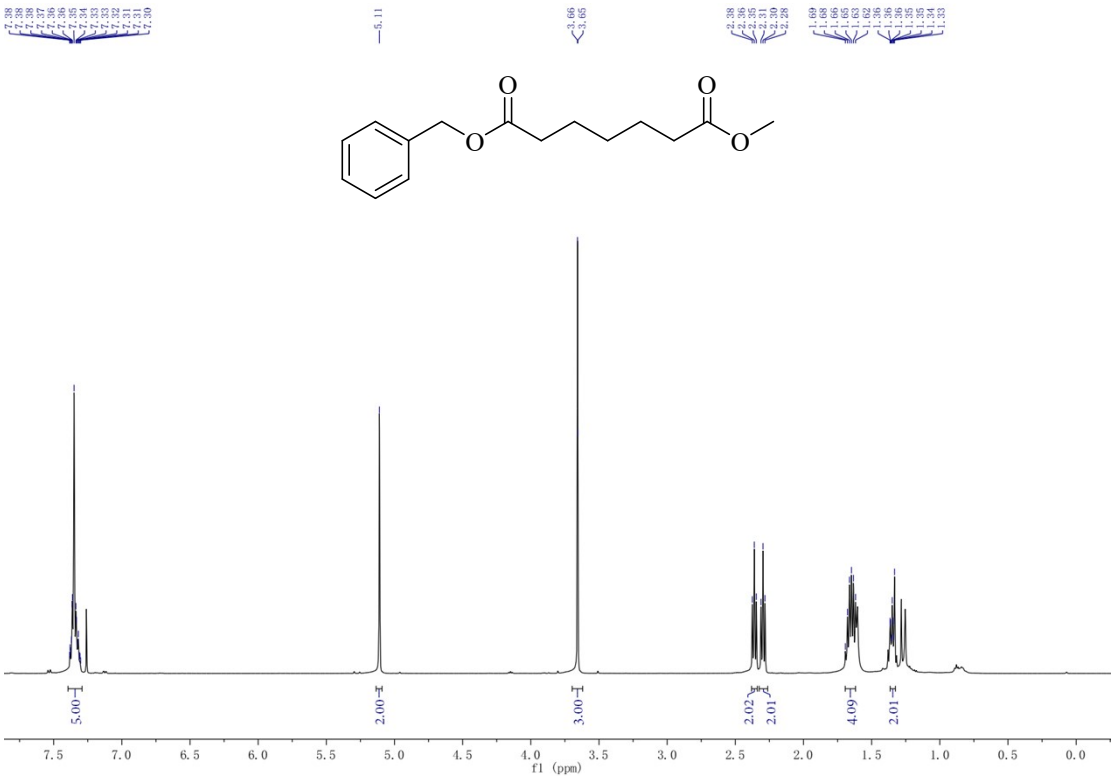


^{1}H NMR spectrum of compound **3ag**



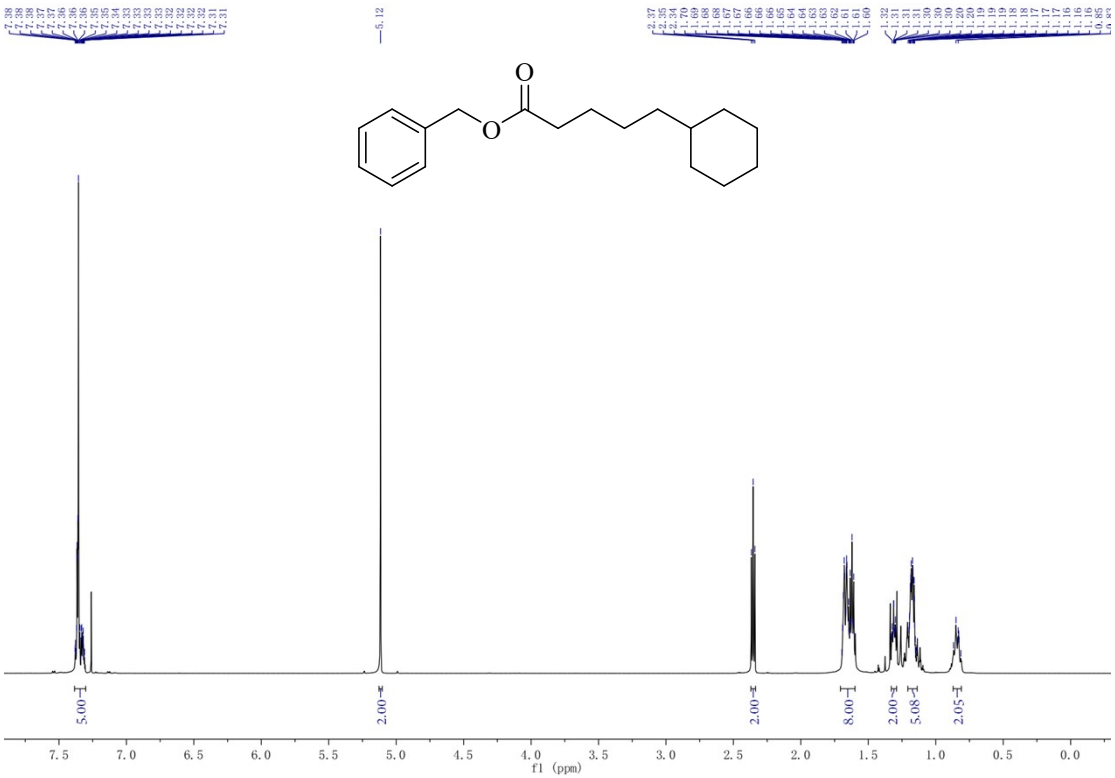
^{13}C NMR spectrum of compound **3ag**

^{1}H NMR spectrum of compound **3ah**

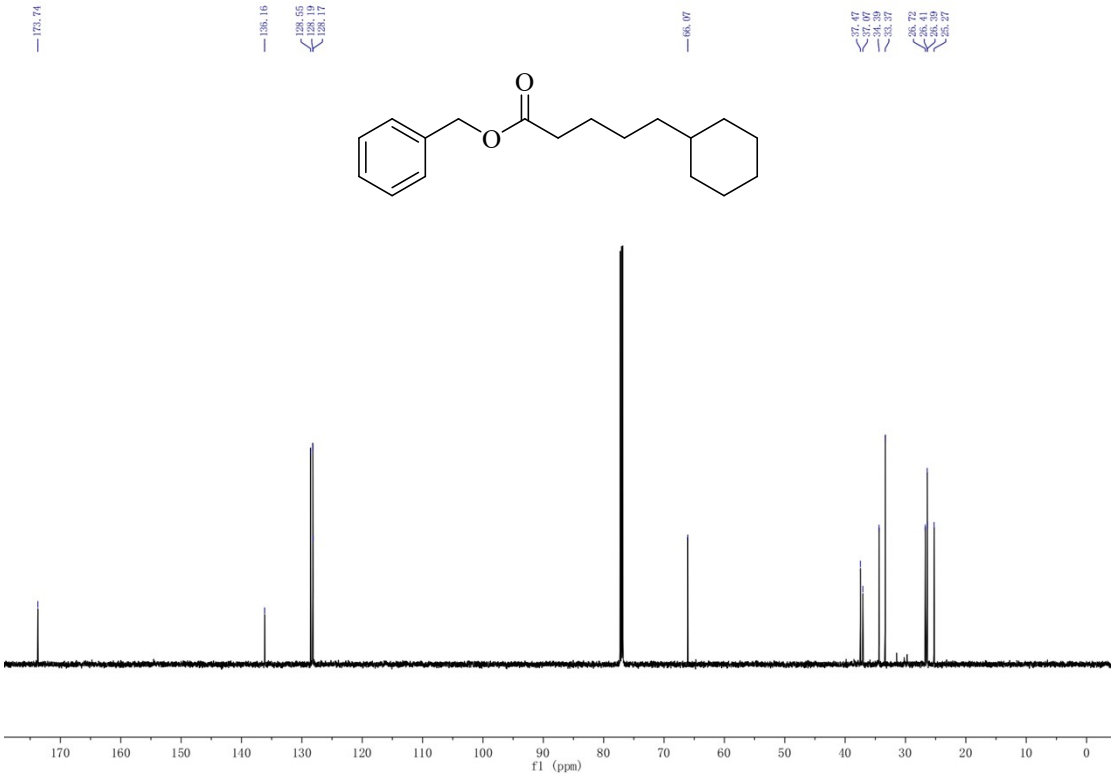


^{13}C NMR spectrum of compound **3ah**

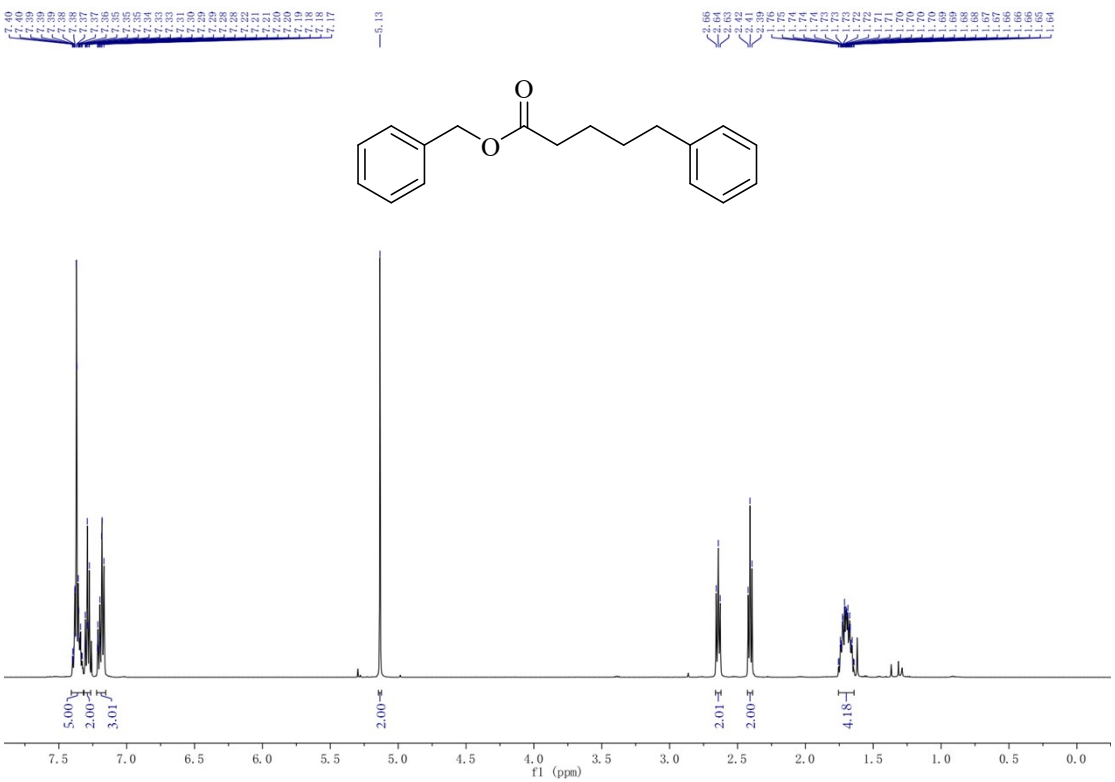
^{1}H NMR spectrum of compound **3ai**



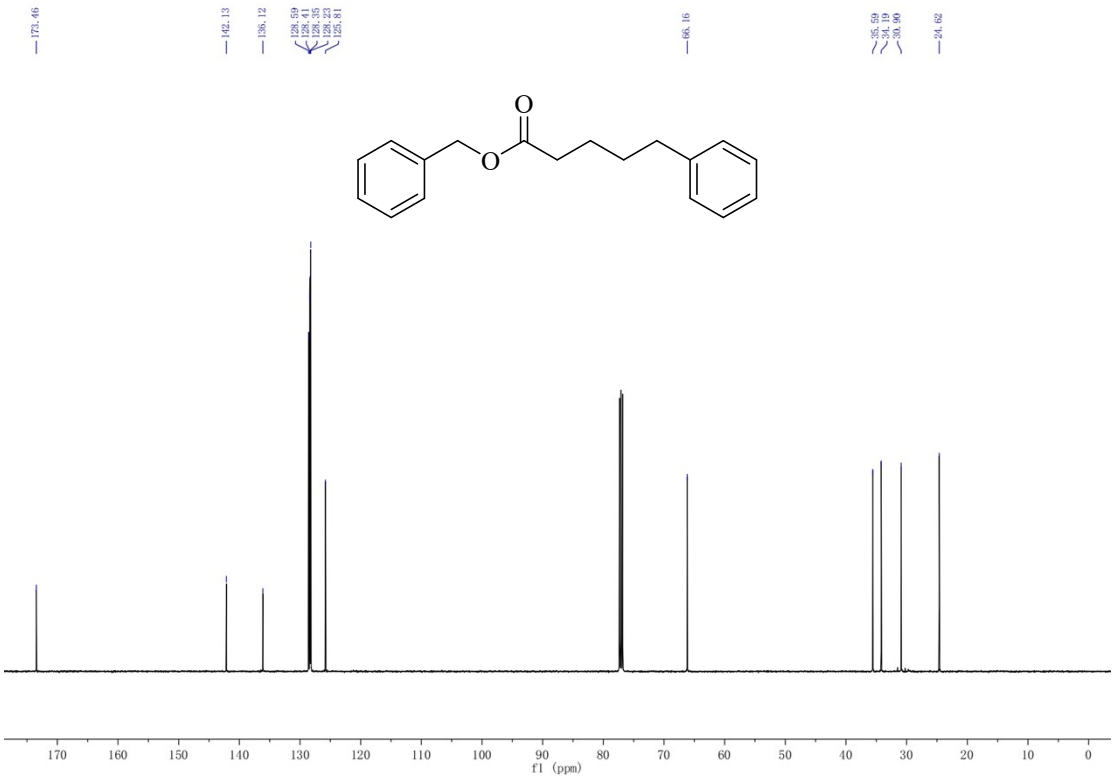
^{13}C NMR spectrum of compound **3ai**



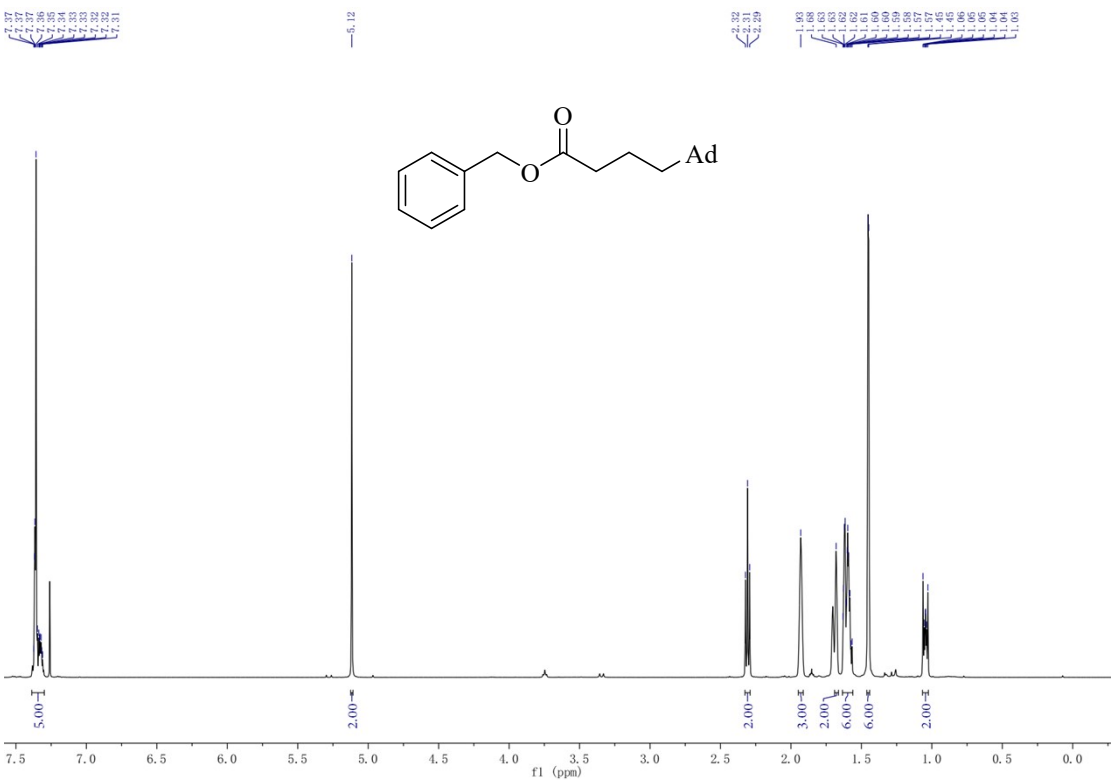
^{1}H NMR spectrum of compound **3aj**



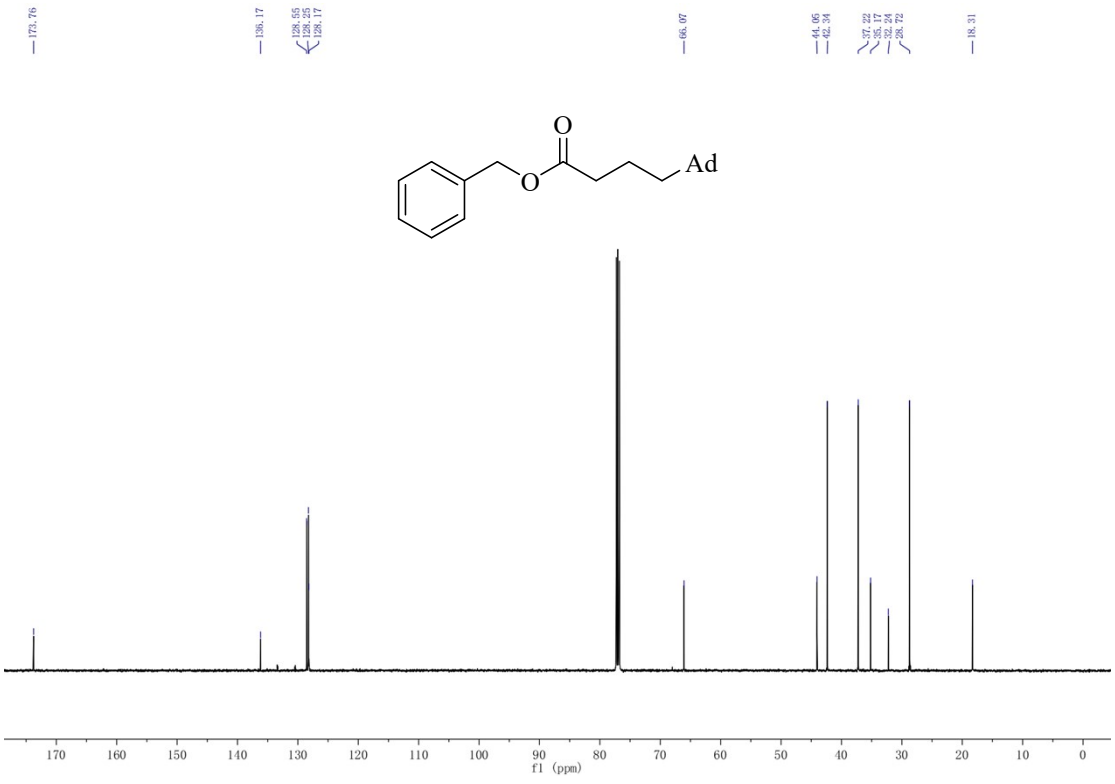
^{13}C NMR spectrum of compound **3aj**



^{1}H NMR spectrum of compound **3ak**

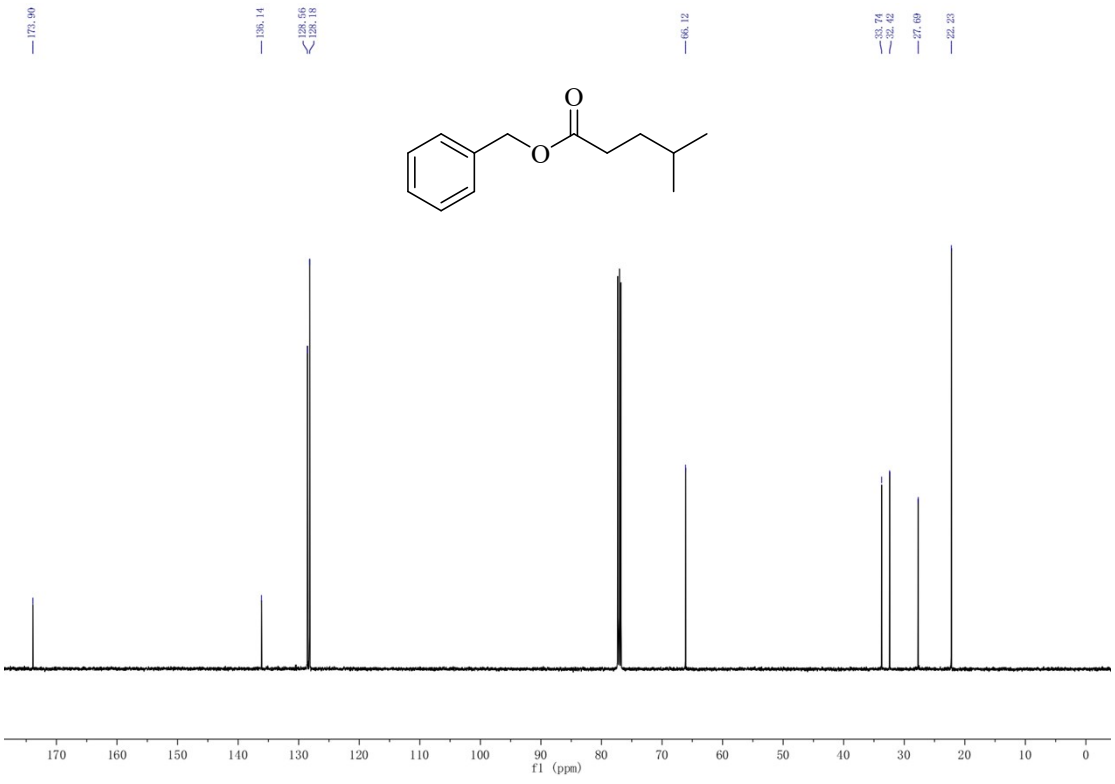


^{13}C NMR spectrum of compound **3ak**

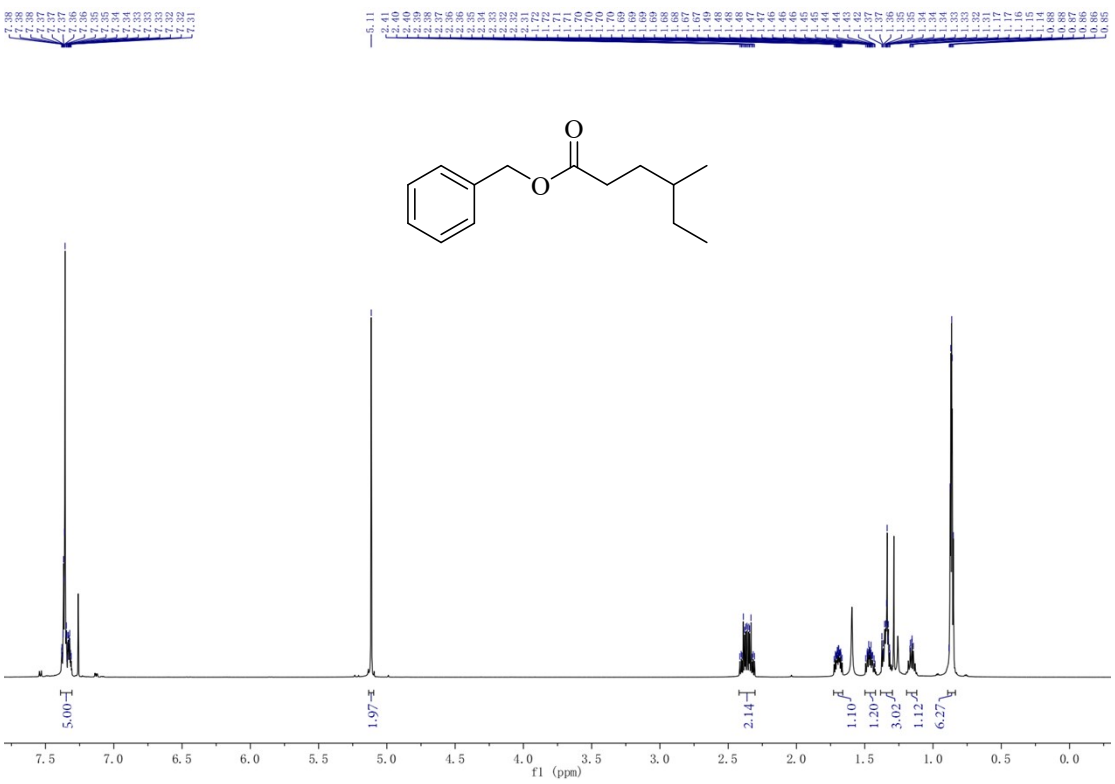


^{1}H NMR spectrum of compound **3al**

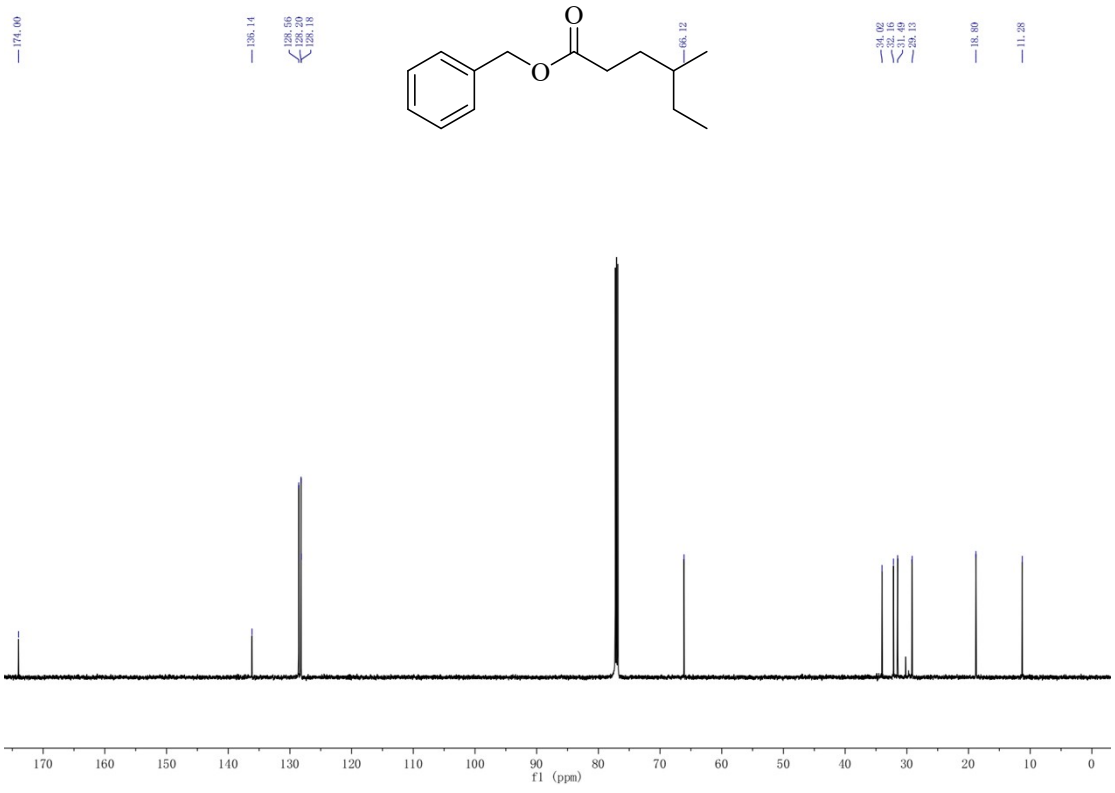
^{13}C NMR spectrum of compound **3al**



^{1}H NMR spectrum of compound **3am**



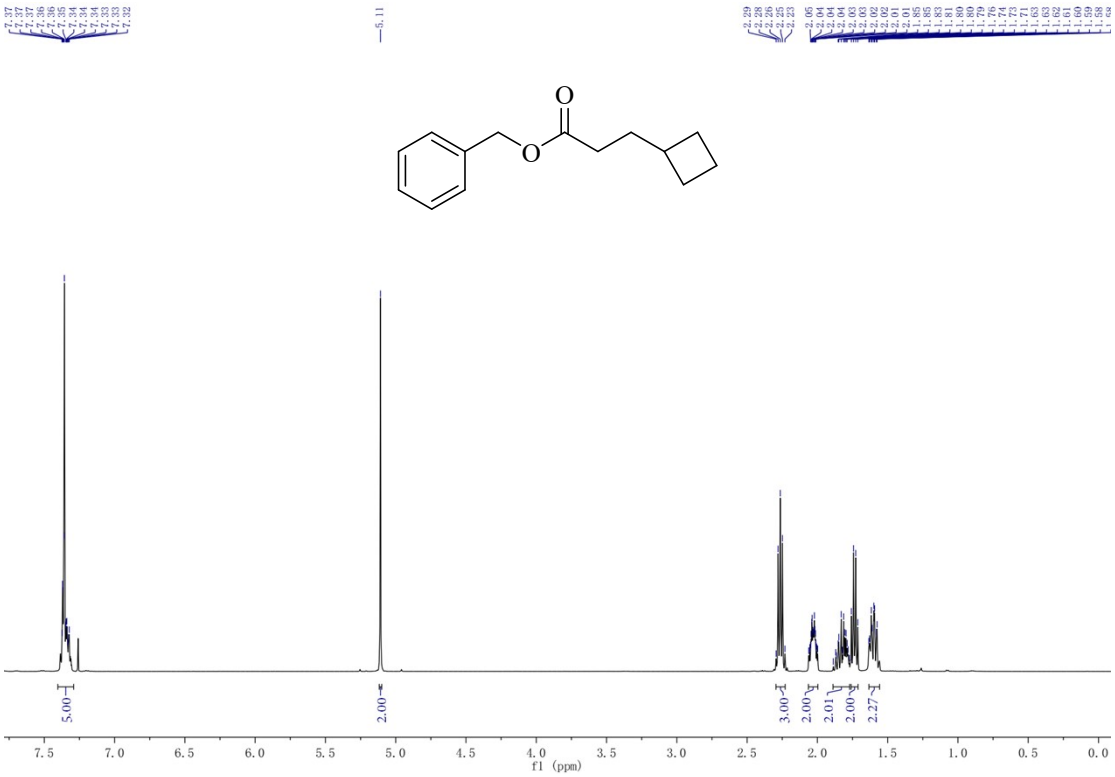
^{13}C NMR spectrum of compound **3am**



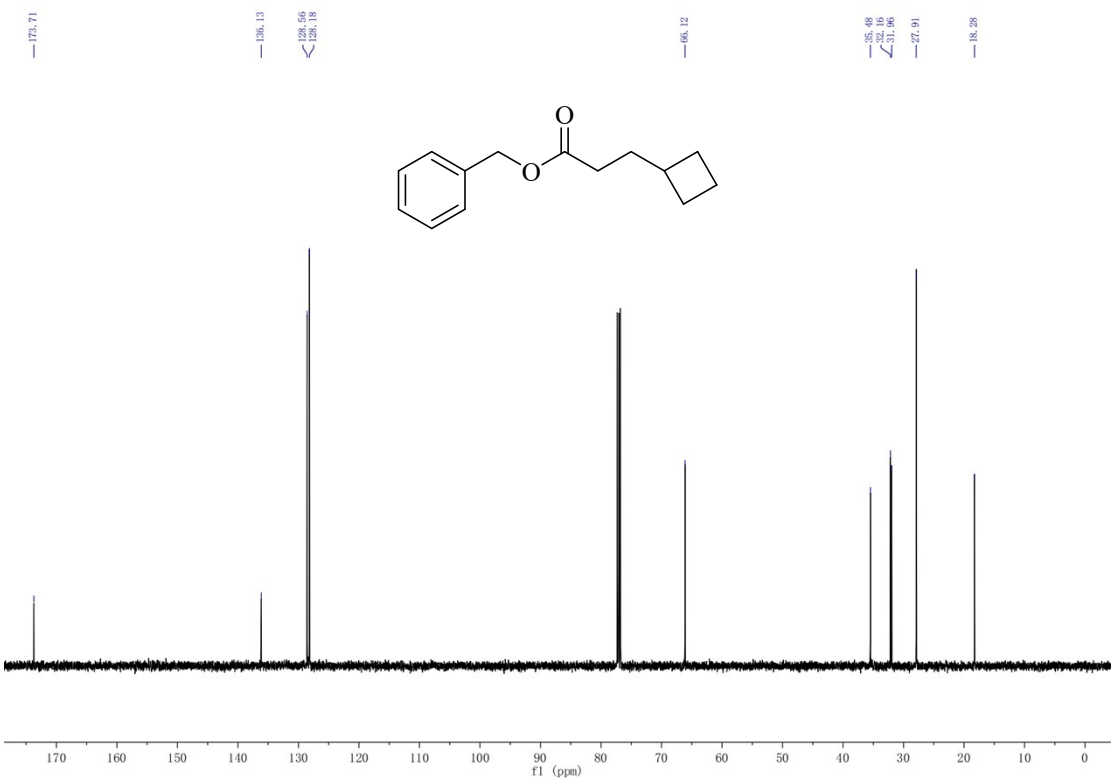
^{1}H NMR spectrum of compound **3an**

^{13}C NMR spectrum of compound **3an**

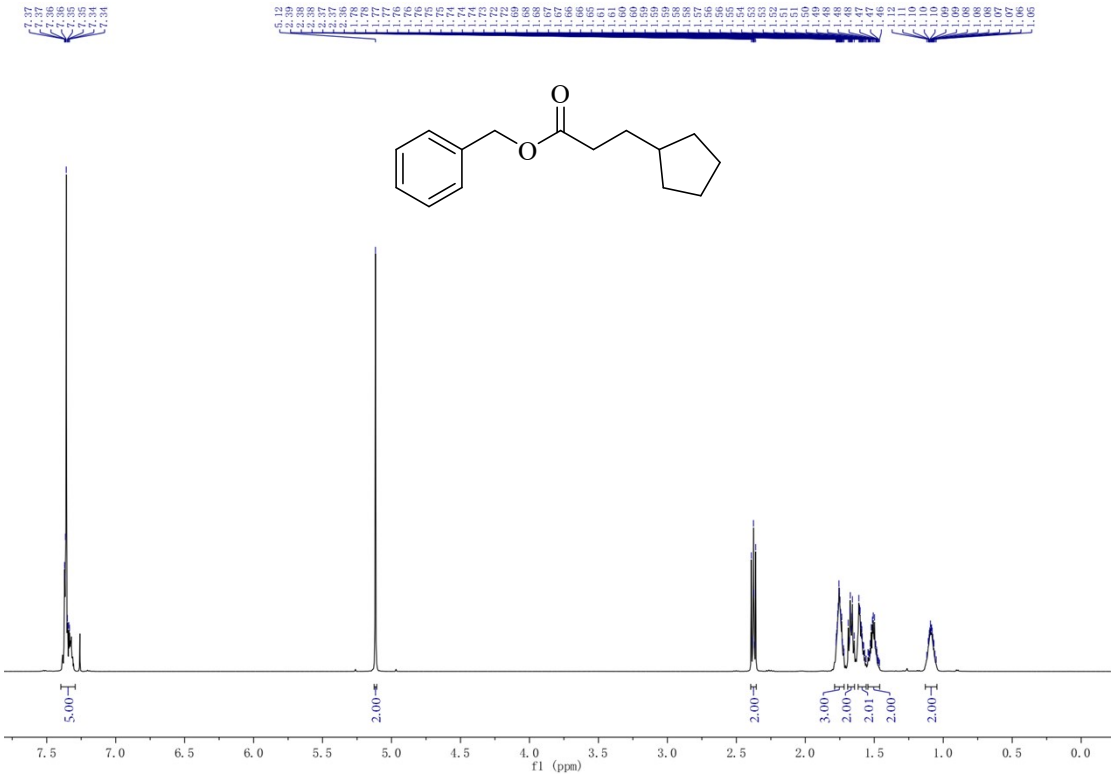
^{1}H NMR spectrum of compound **3ao**



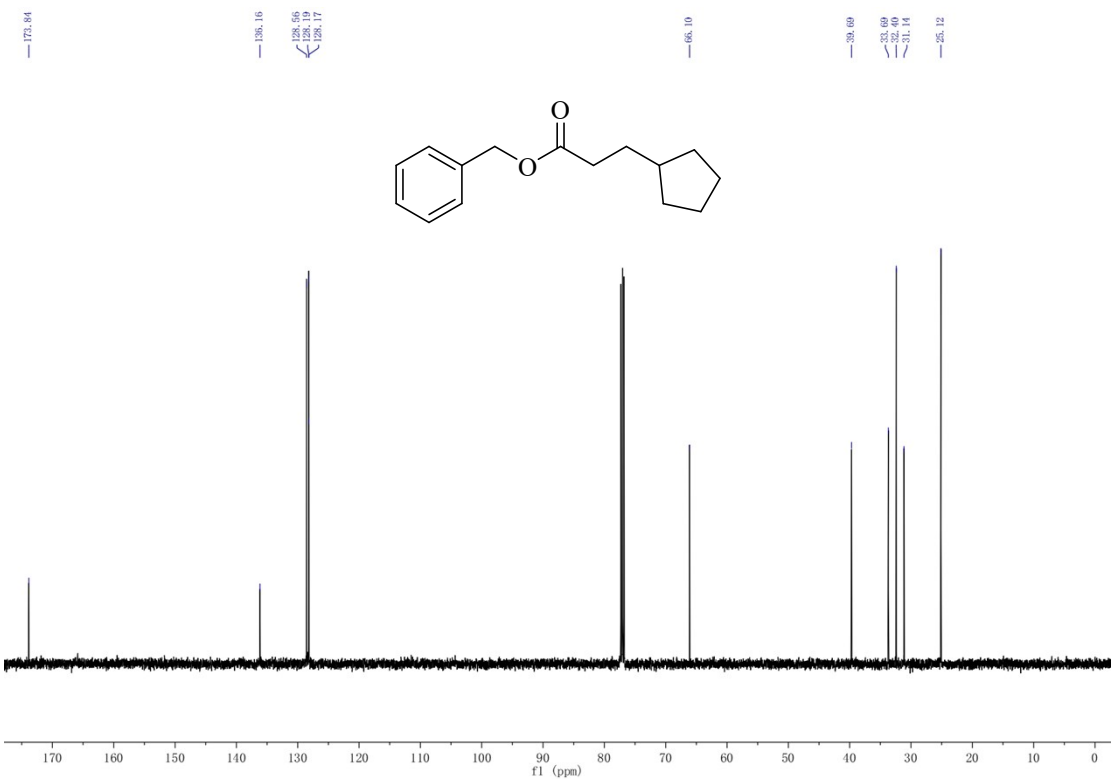
^{13}C NMR spectrum of compound **3ao**



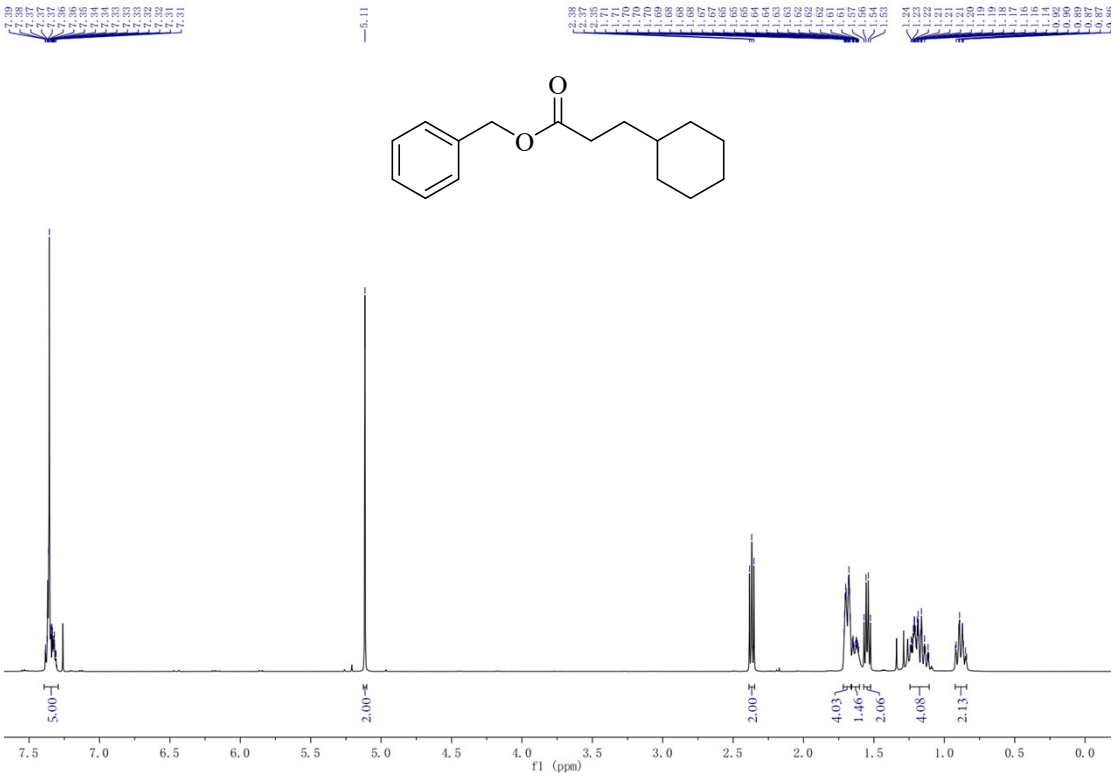
^{1}H NMR spectrum of compound **3ap**



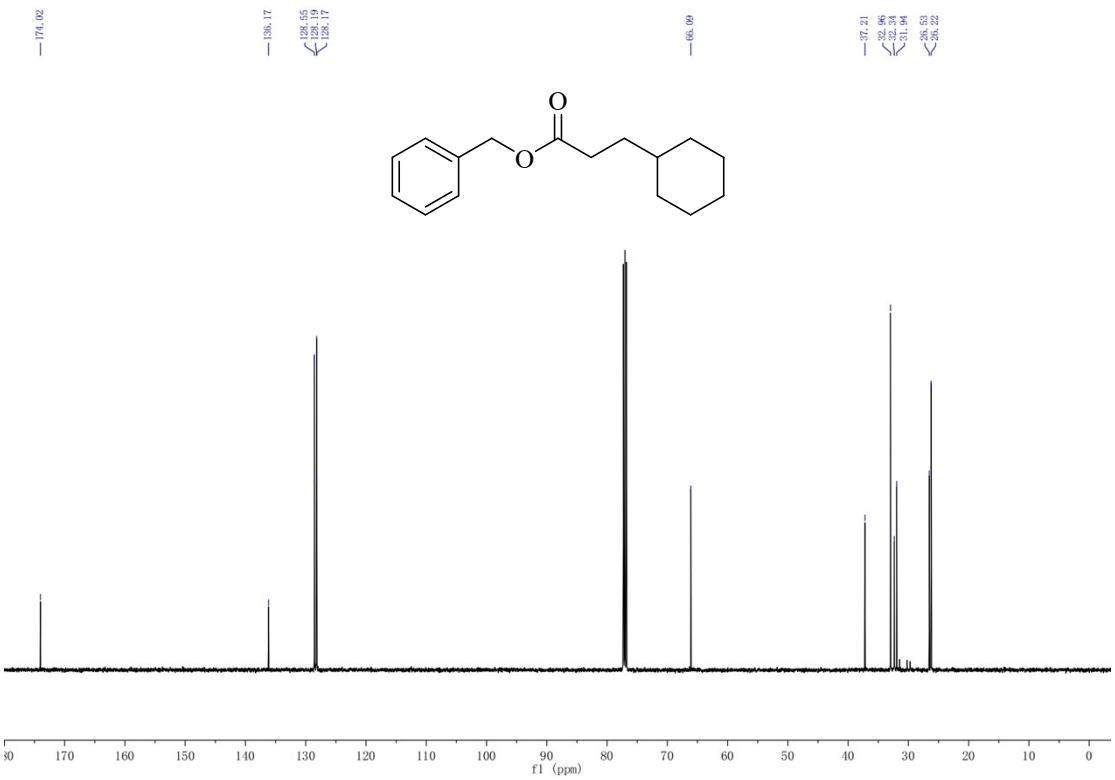
^{13}C NMR spectrum of compound **3ap**



^{1}H NMR spectrum of compound **3aq**

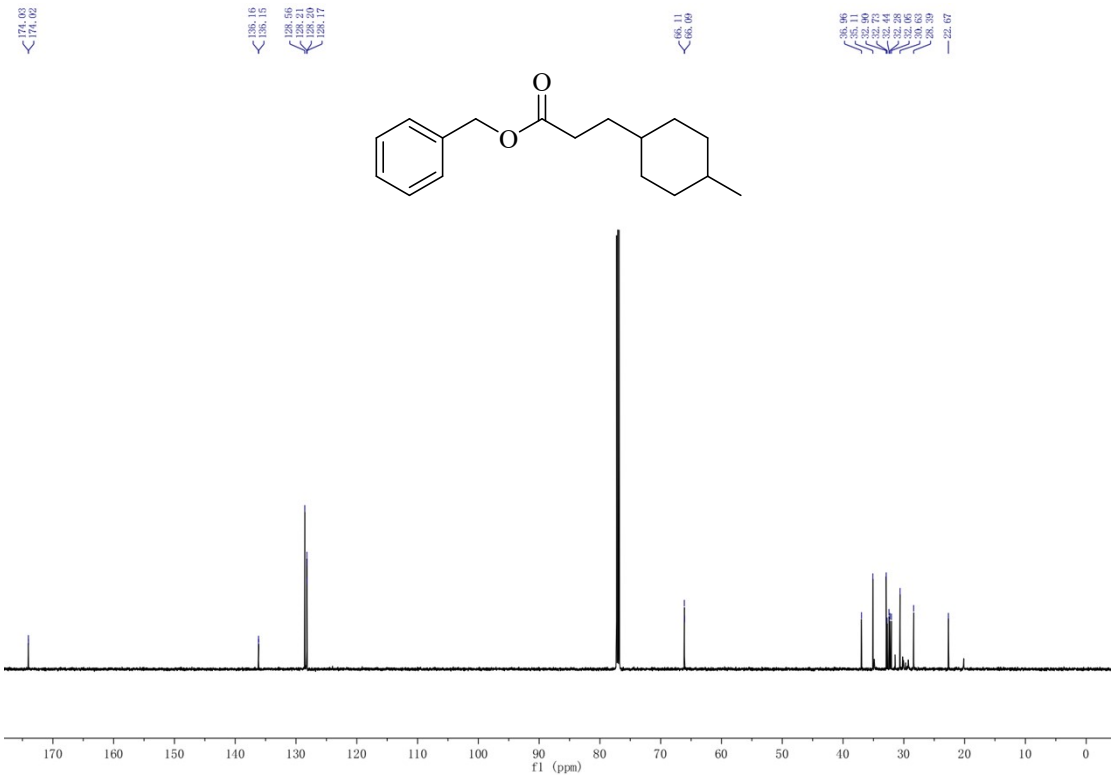


^{13}C NMR spectrum of compound **3aq**

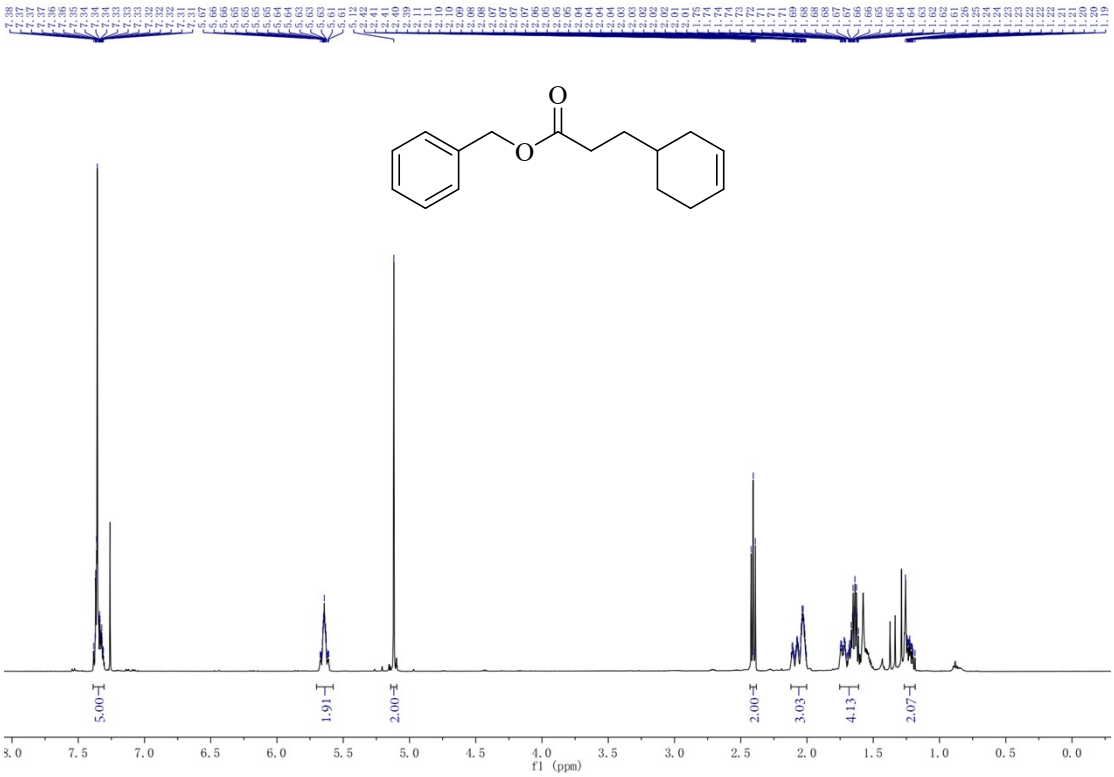


^{1}H NMR spectrum of compound **3ar**

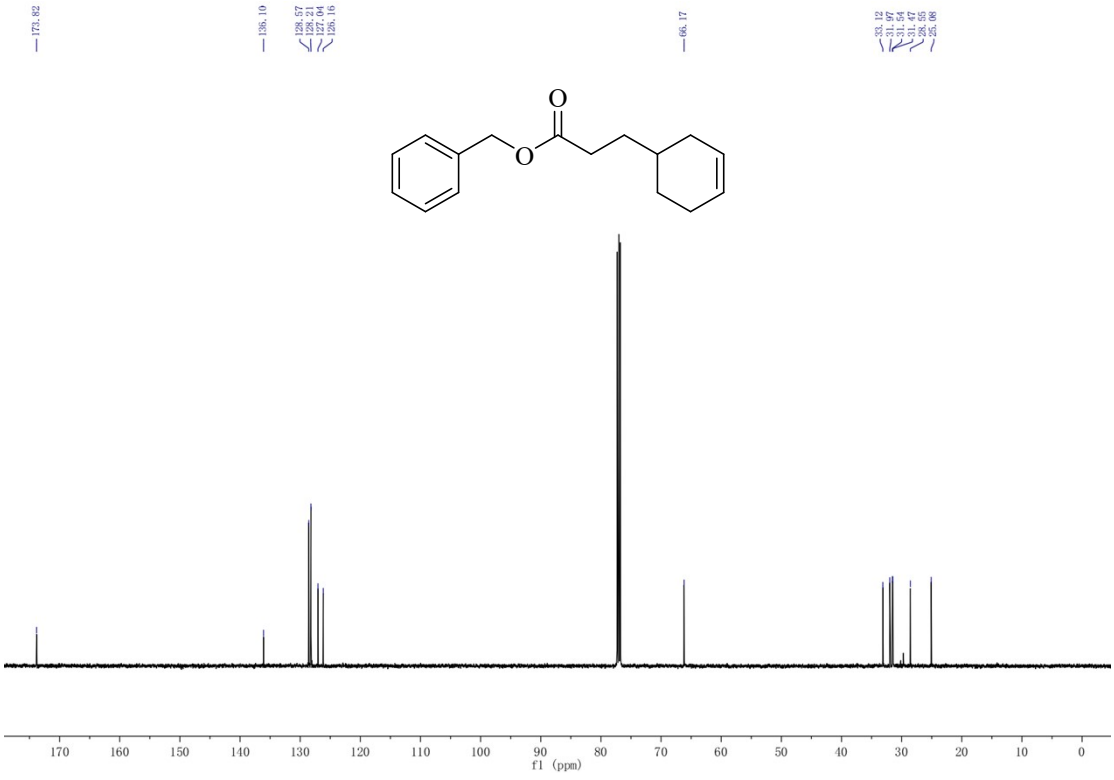
^{13}C NMR spectrum of compound **3ar**



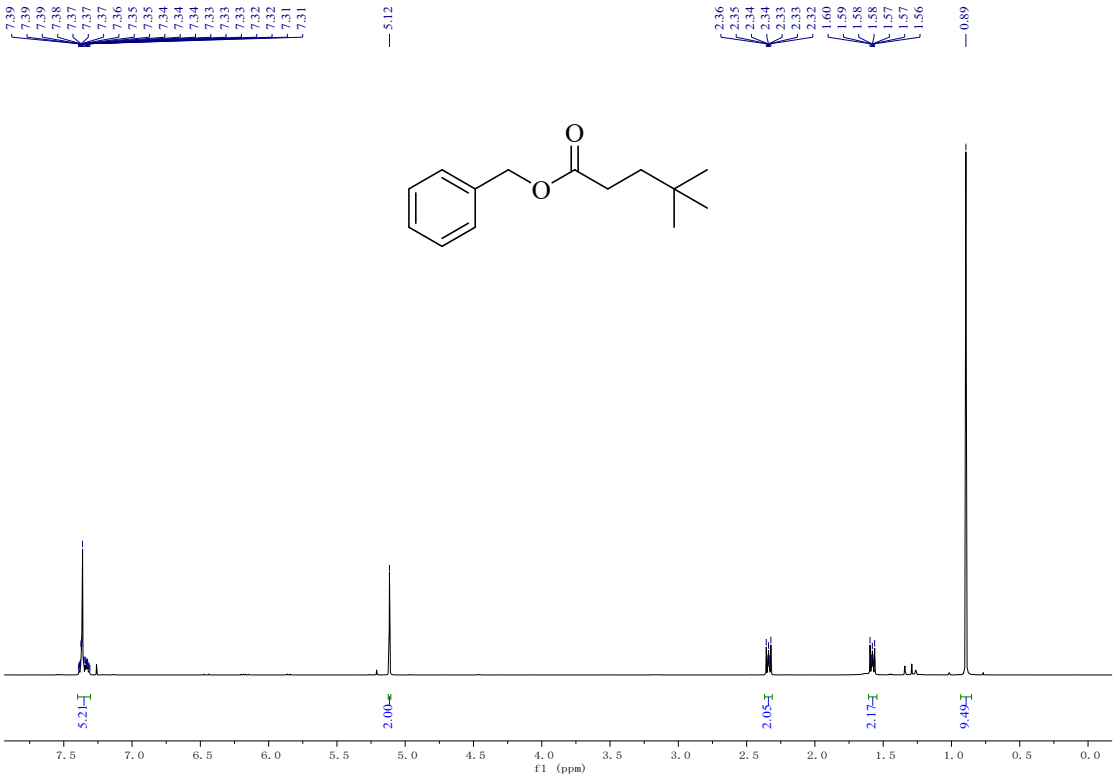
^{1}H NMR spectrum of compound **3as**



^{13}C NMR spectrum of compound **3as**

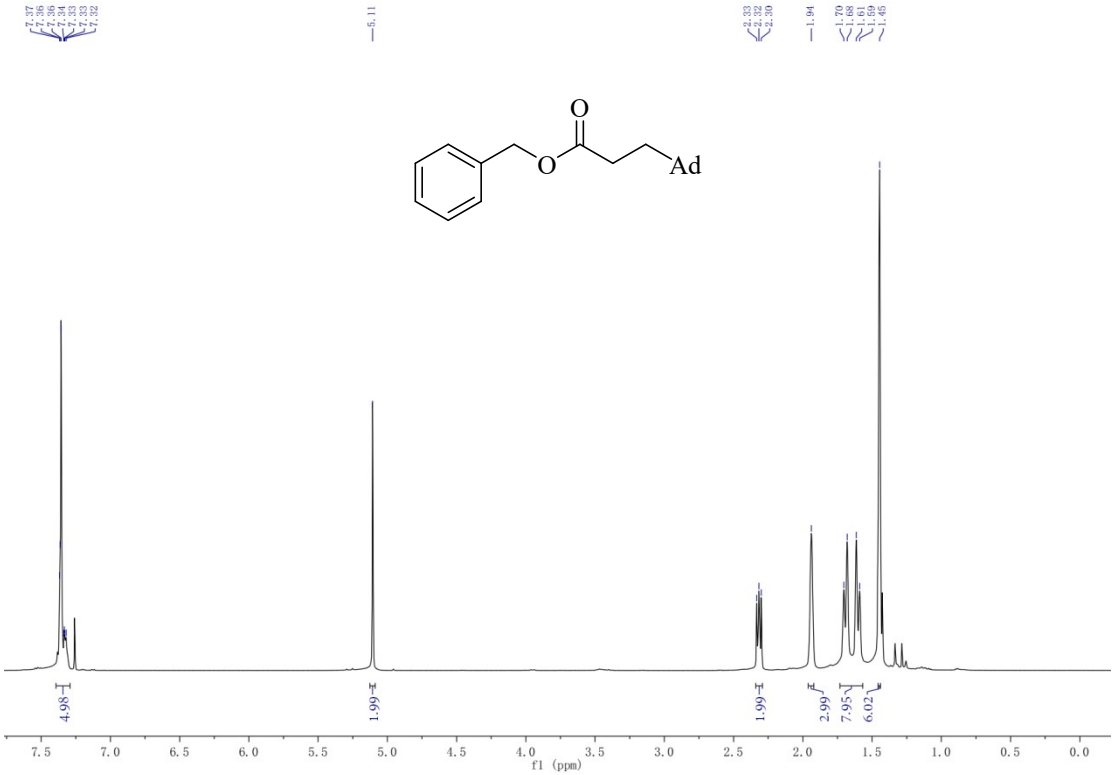


^{1}H NMR spectrum of compound **3at**

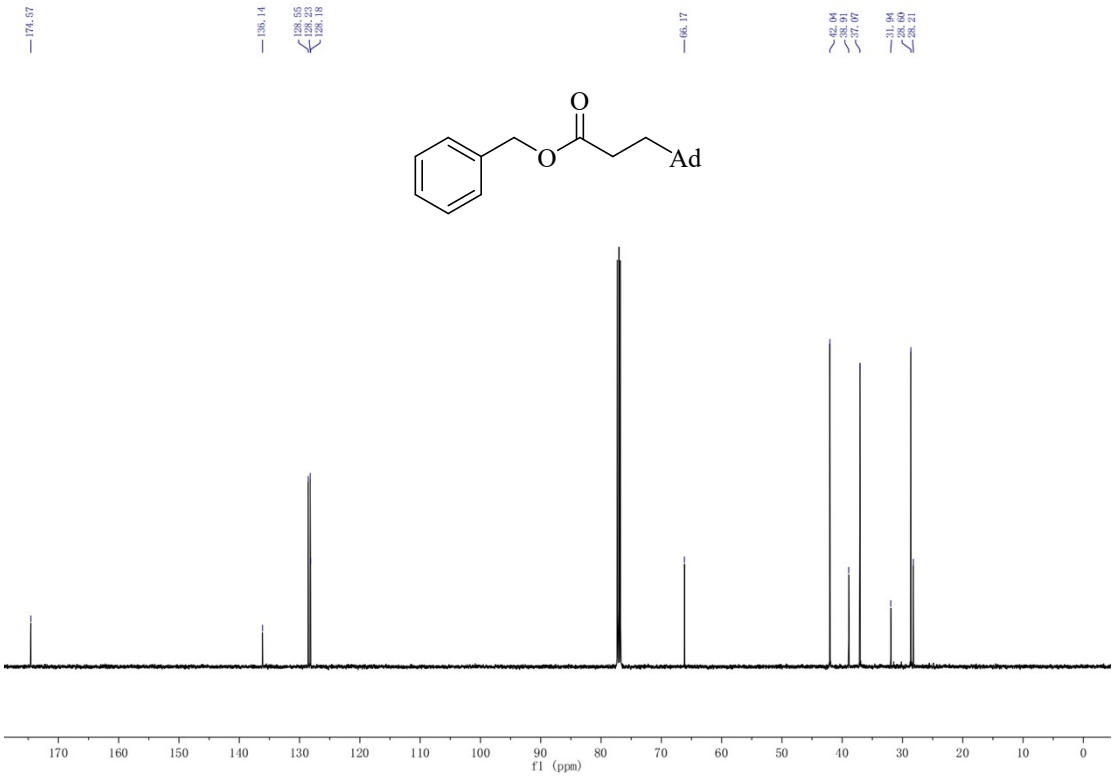


^{13}C NMR spectrum of compound **3at**

^{1}H NMR spectrum of compound **3au**

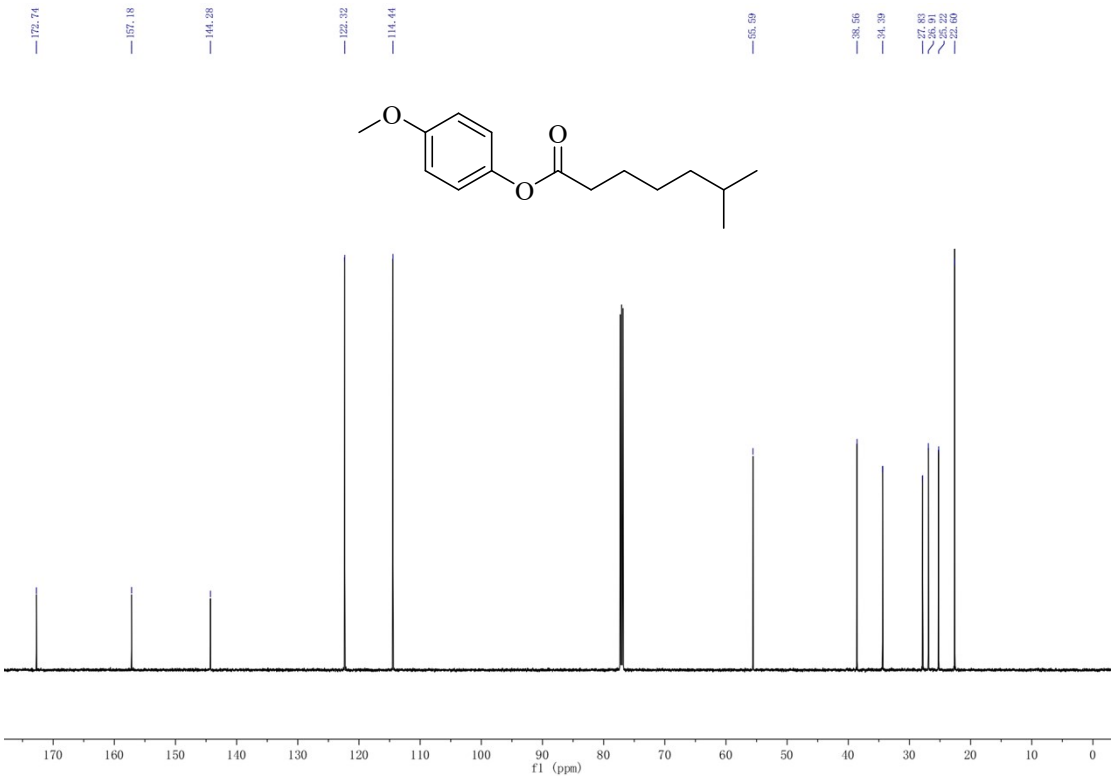


^{13}C NMR spectrum of compound **3au**

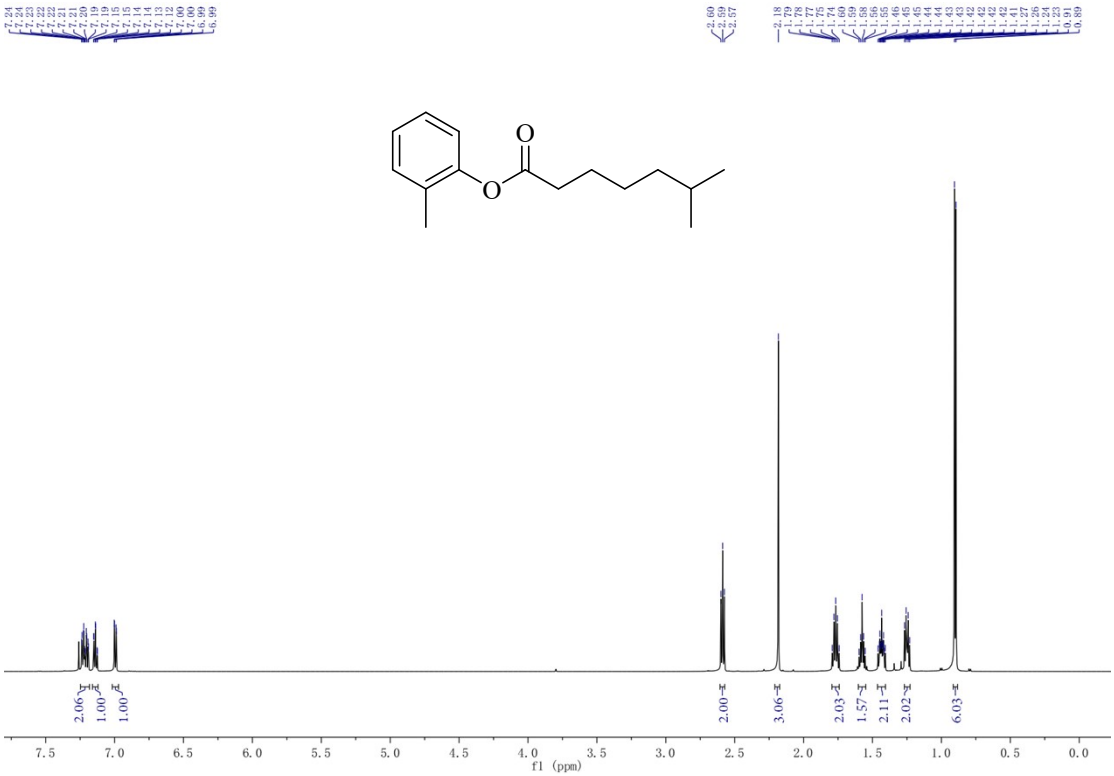


^{1}H NMR spectrum of compound **3ba**

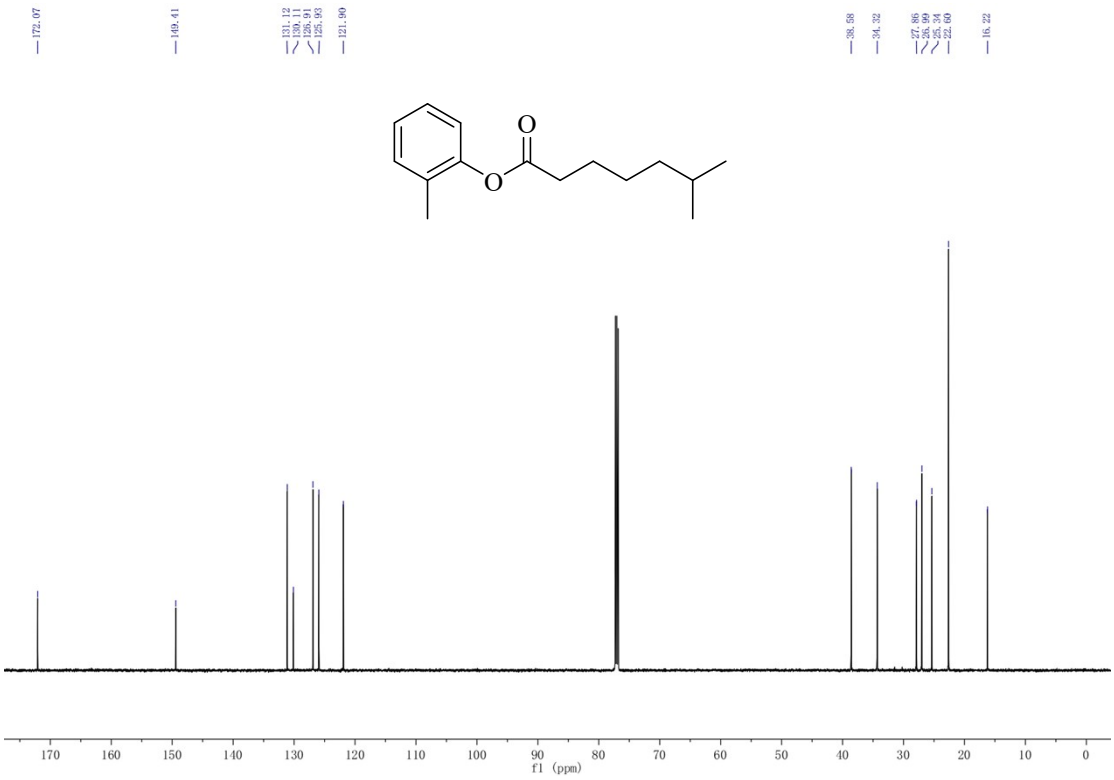
^{13}C NMR spectrum of compound **3ba**



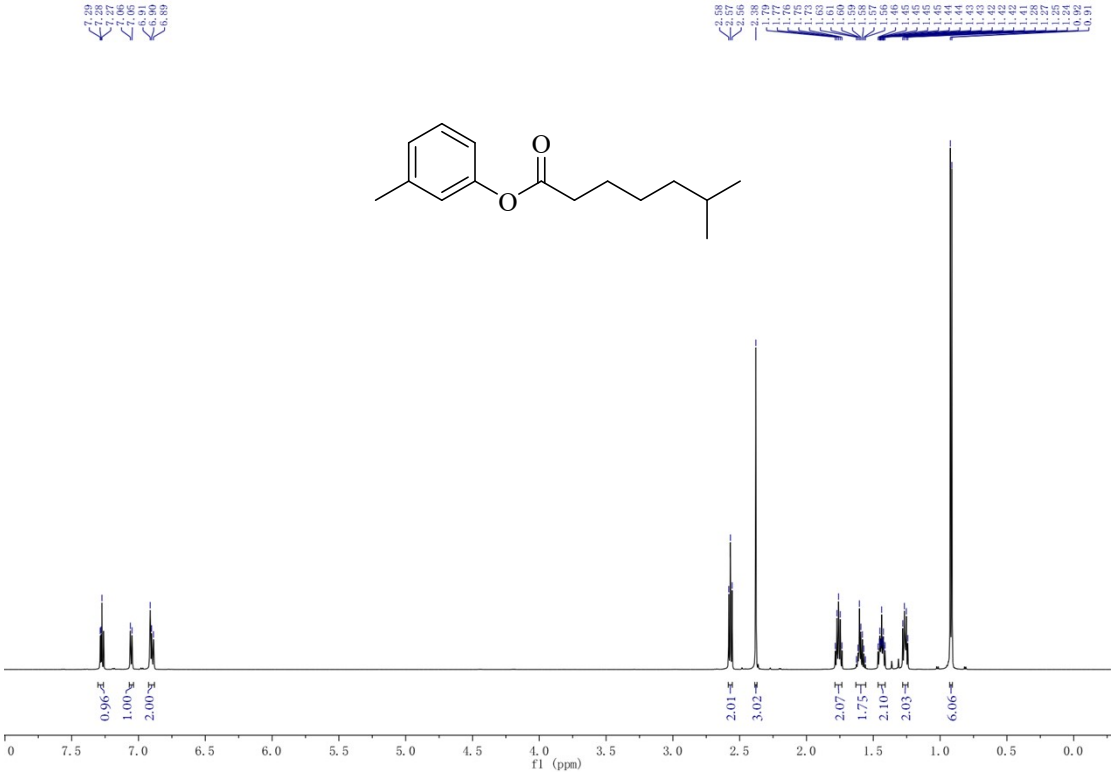
^{1}H NMR spectrum of compound **3ca**



^{13}C NMR spectrum of compound **3ca**

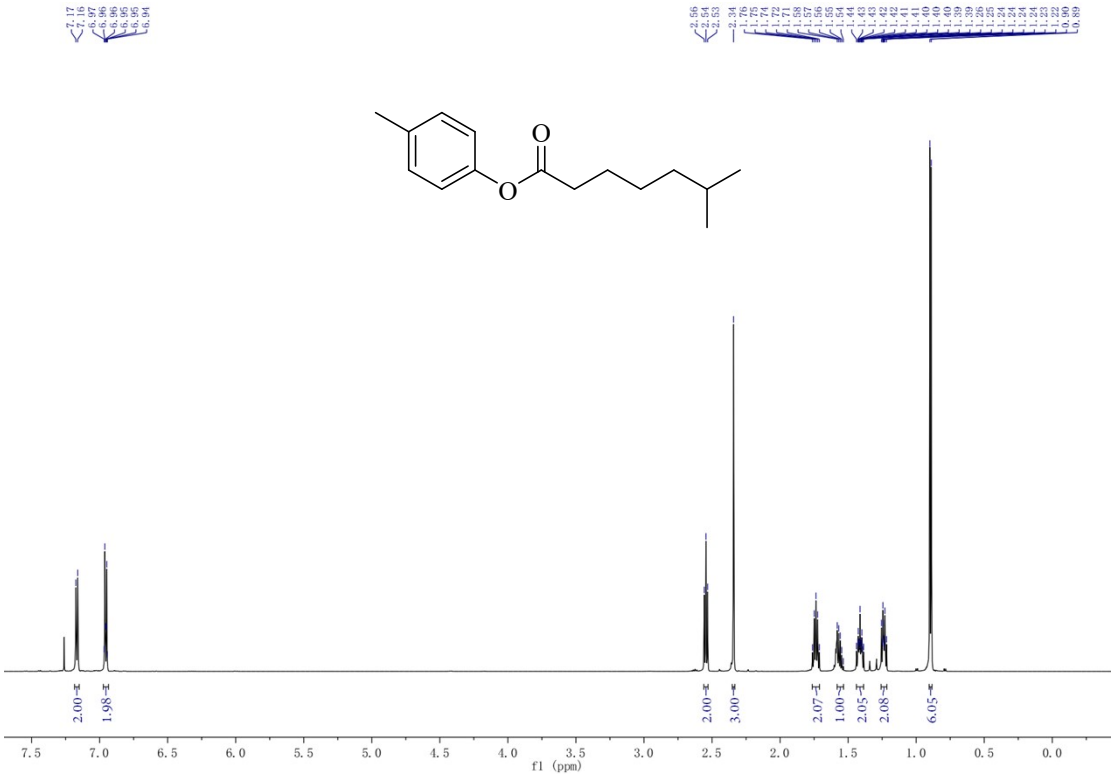


^{1}H NMR spectrum of compound **3da**

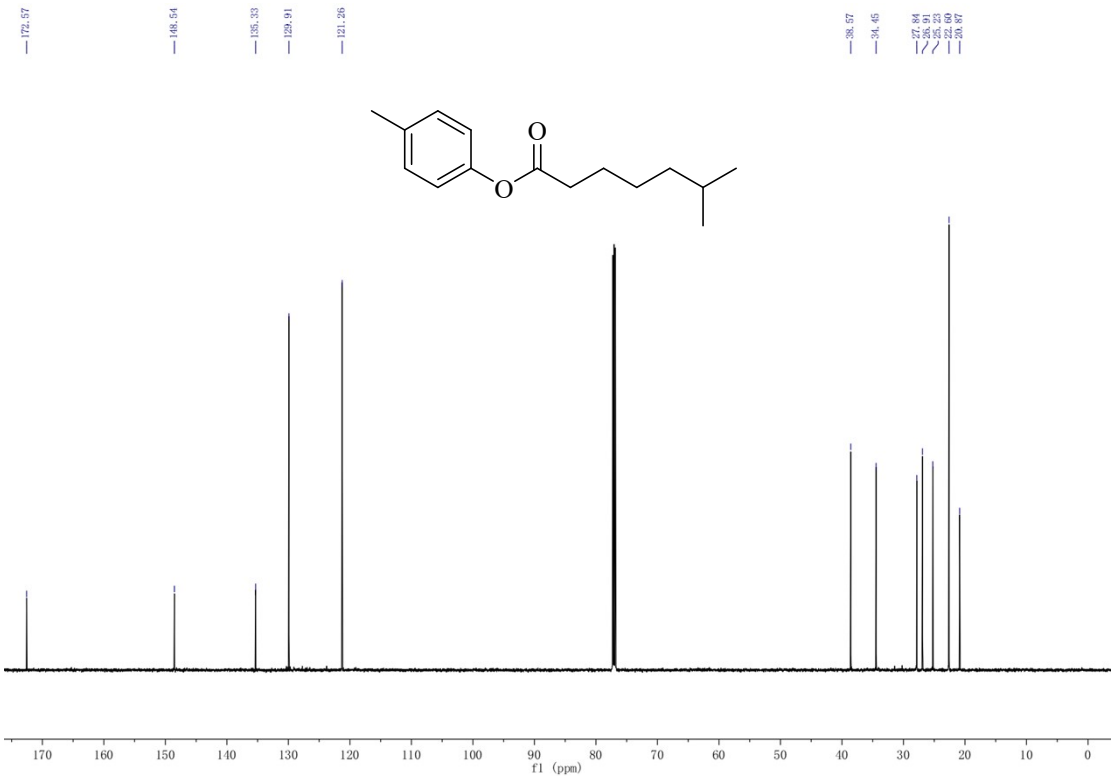


^{13}C NMR spectrum of compound **3da**

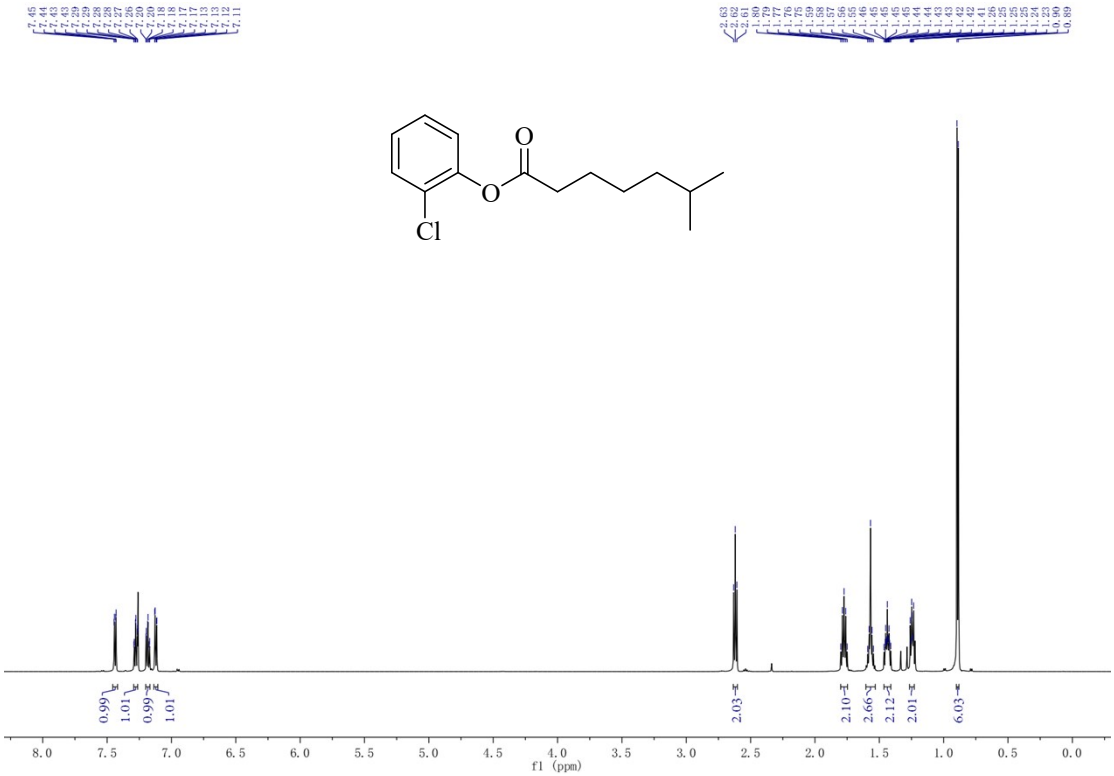
^{1}H NMR spectrum of compound **3ea**



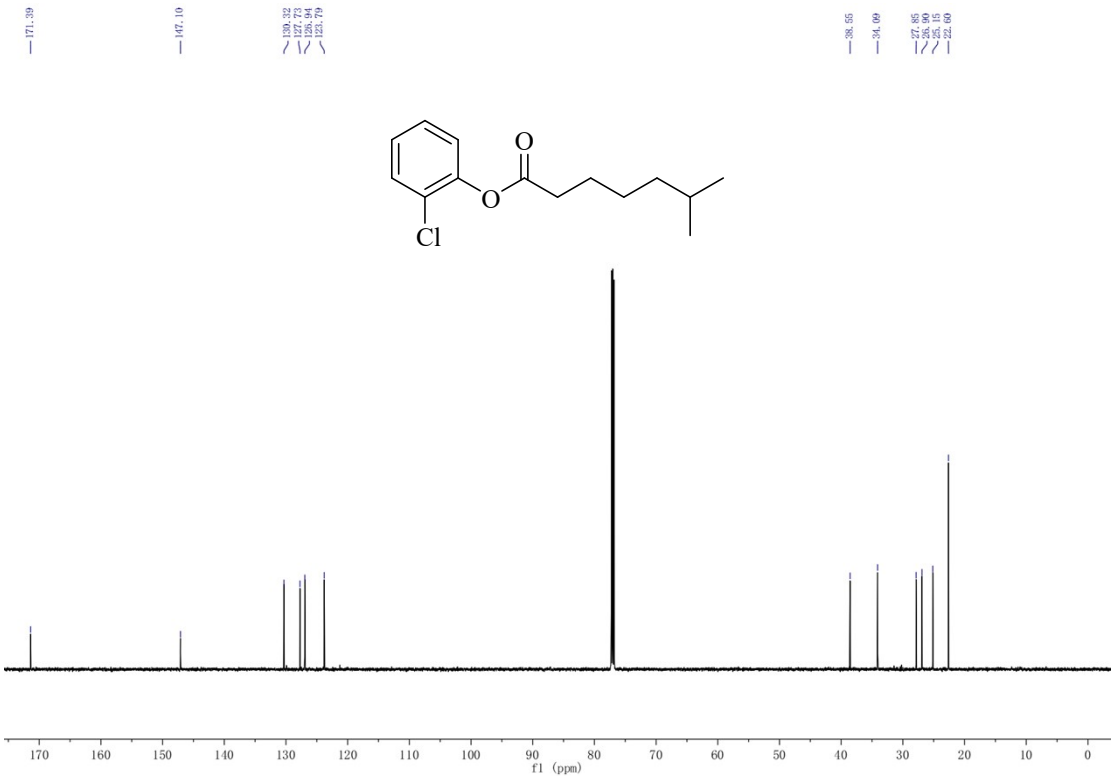
^{13}C NMR spectrum of compound **3ea**



^{1}H NMR spectrum of compound **3fa**



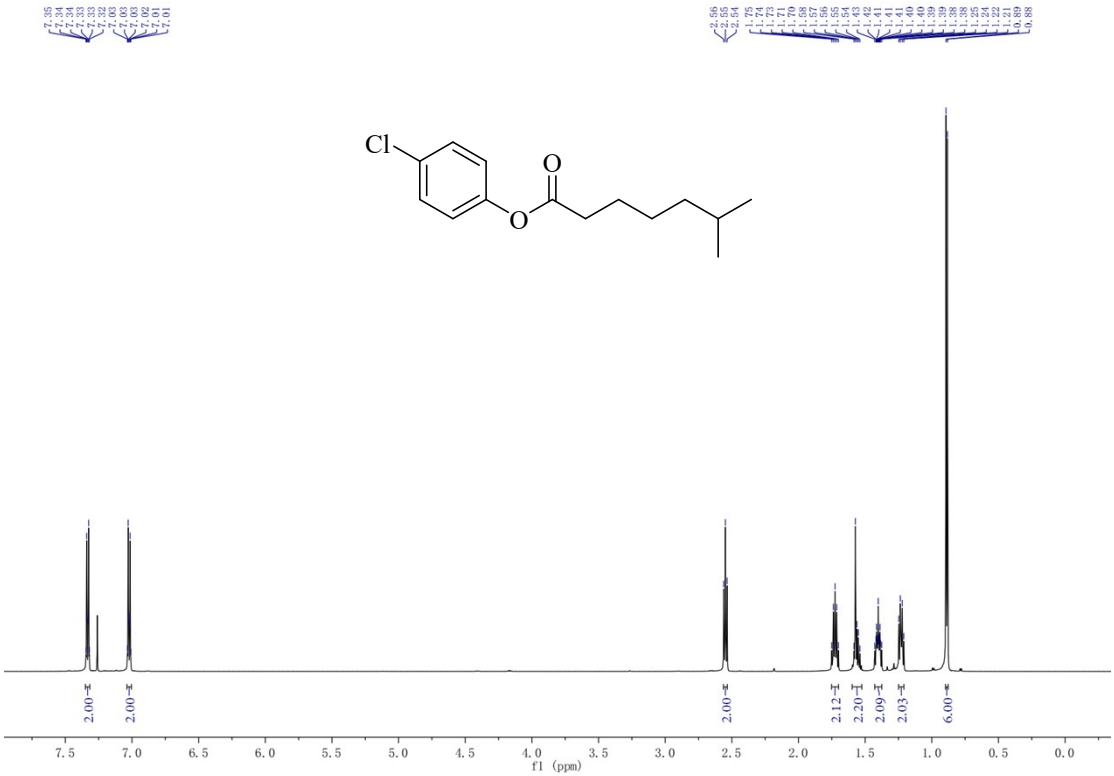
^{13}C NMR spectrum of compound **3fa**



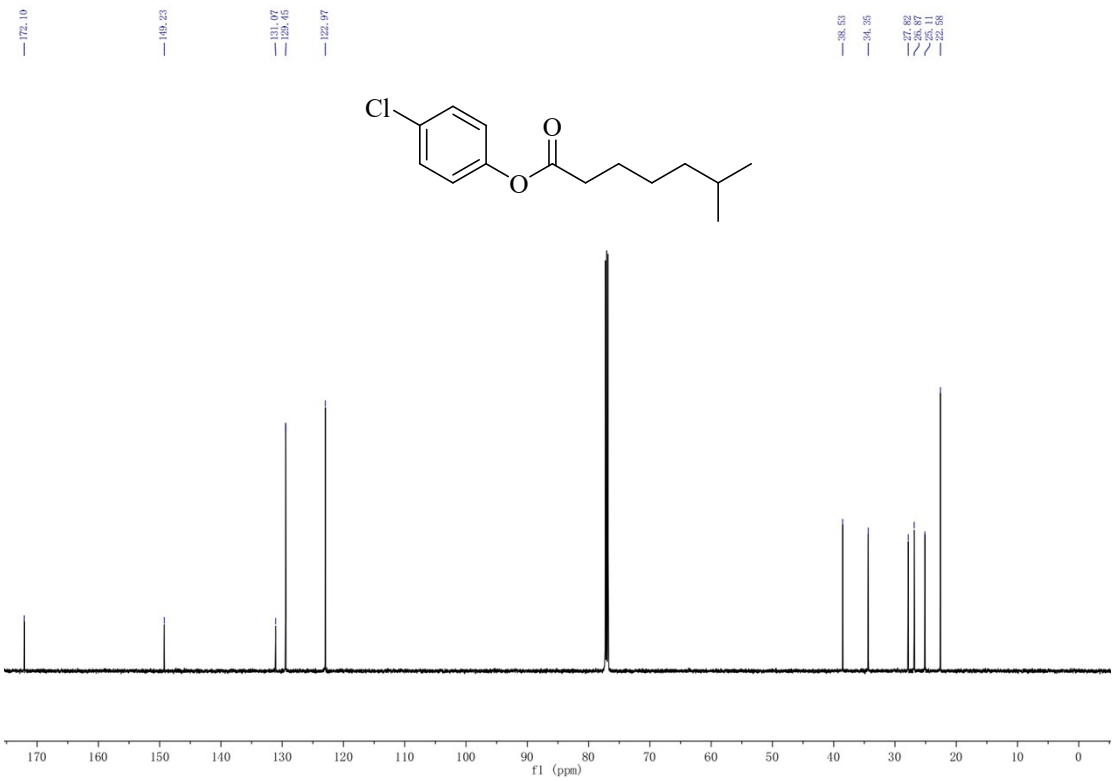
^{1}H NMR spectrum of compound **3ga**

^{13}C NMR spectrum of compound **3ga**

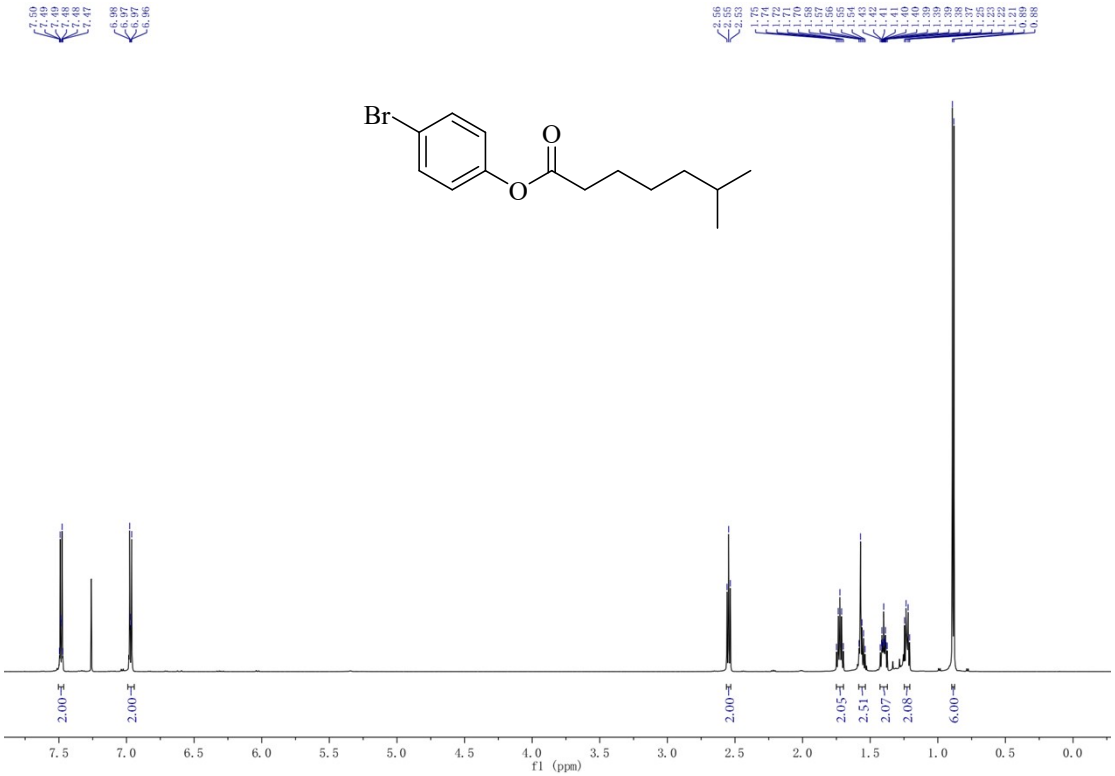
^{1}H NMR spectrum of compound **3ha**



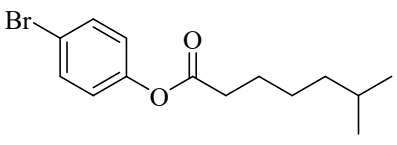
^{13}C NMR spectrum of compound **3ha**

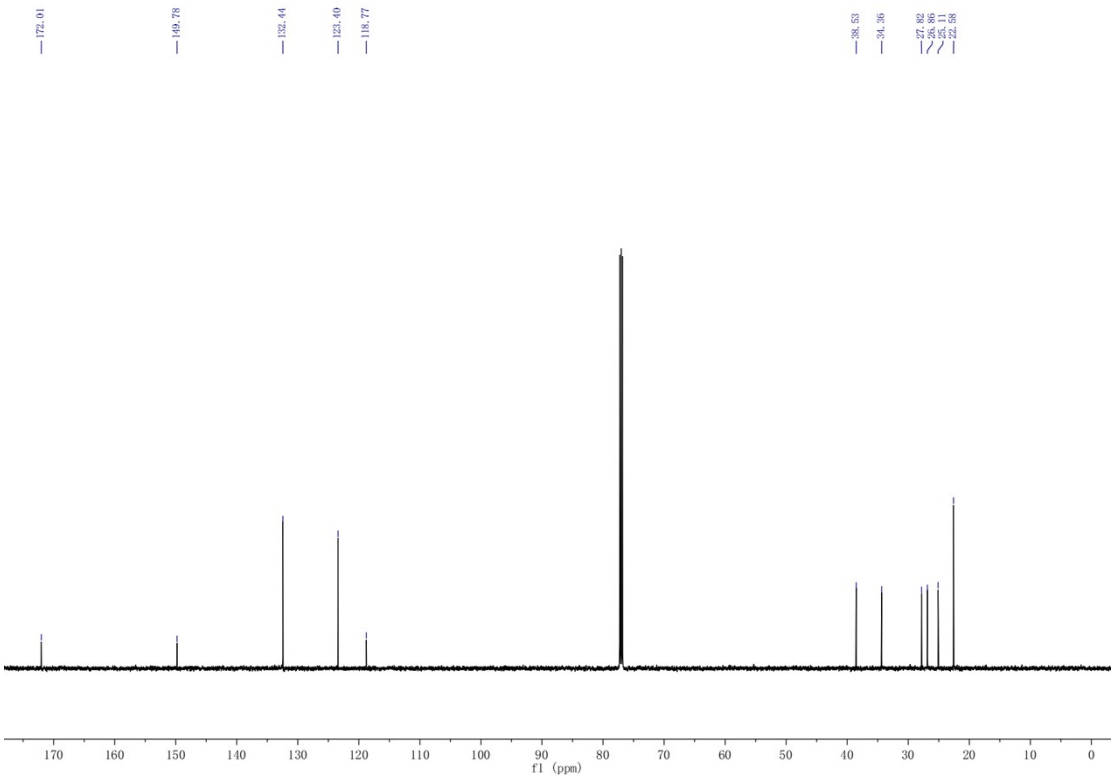


^{1}H NMR spectrum of compound **3ia**



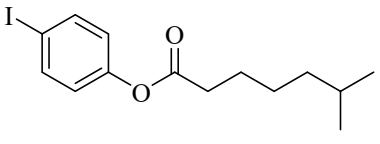
^{13}C NMR spectrum of compound **3ia**

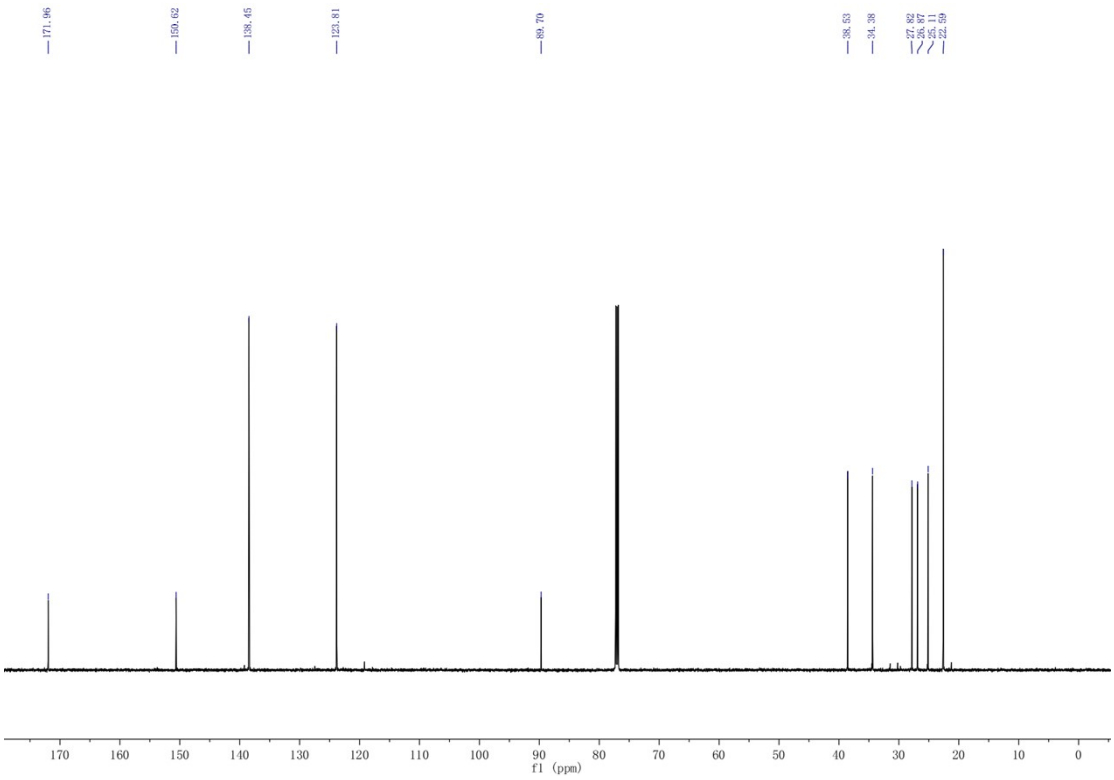




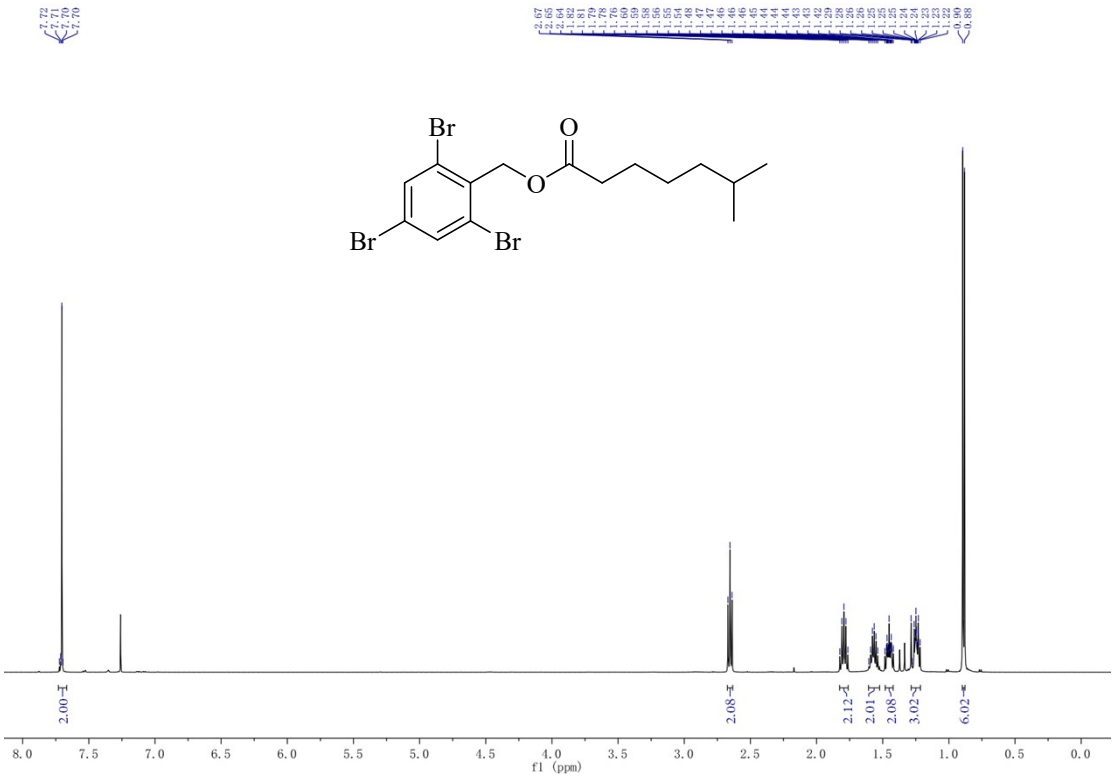
^{1}H NMR spectrum of compound **3ja**

^{13}C NMR spectrum of compound **3ja**

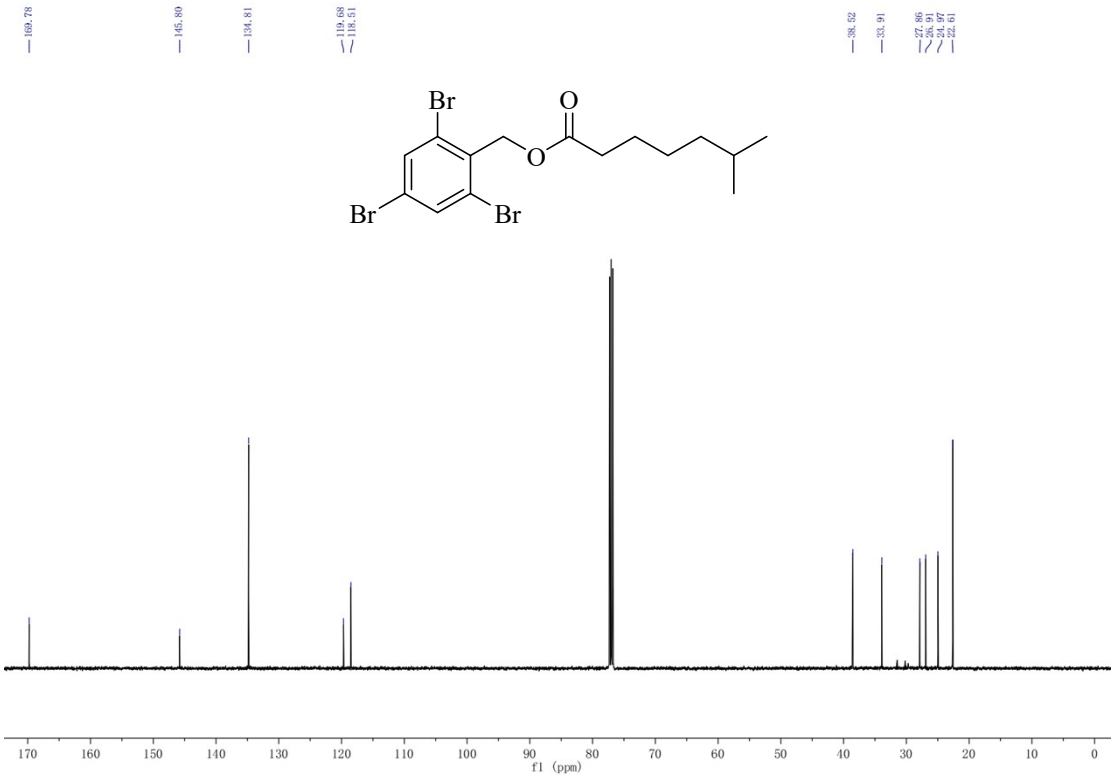




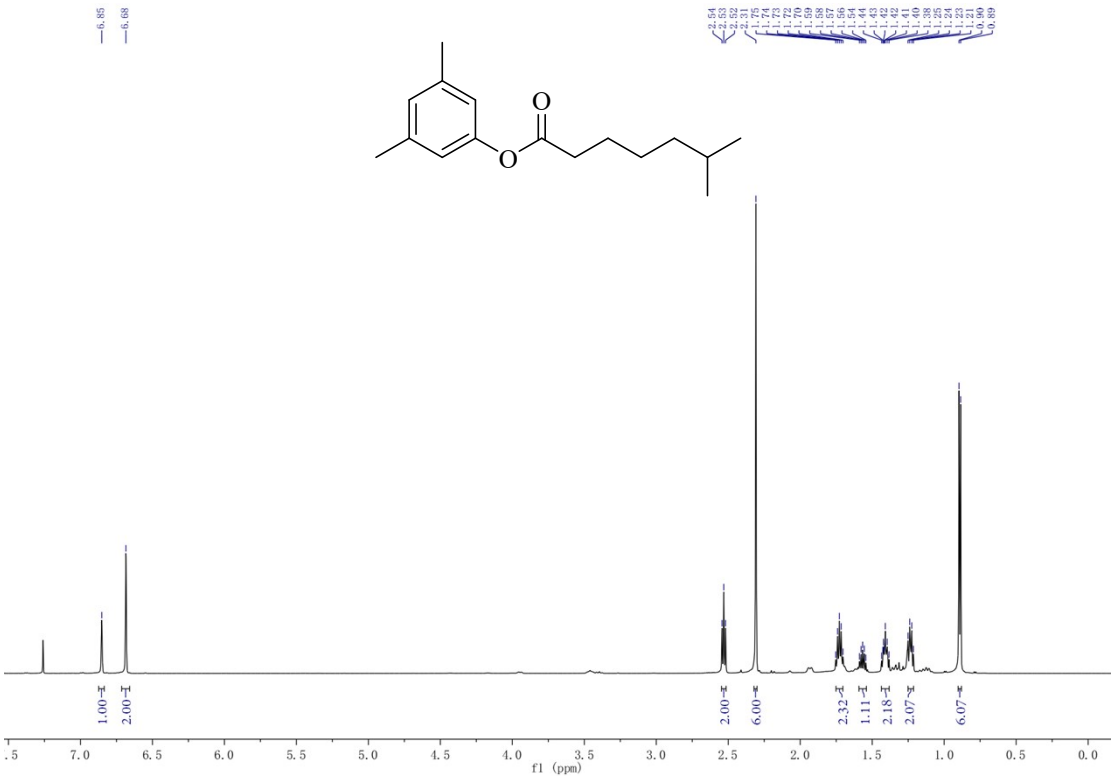
^{1}H NMR spectrum of compound **3na**



^{13}C NMR spectrum of compound **3na**

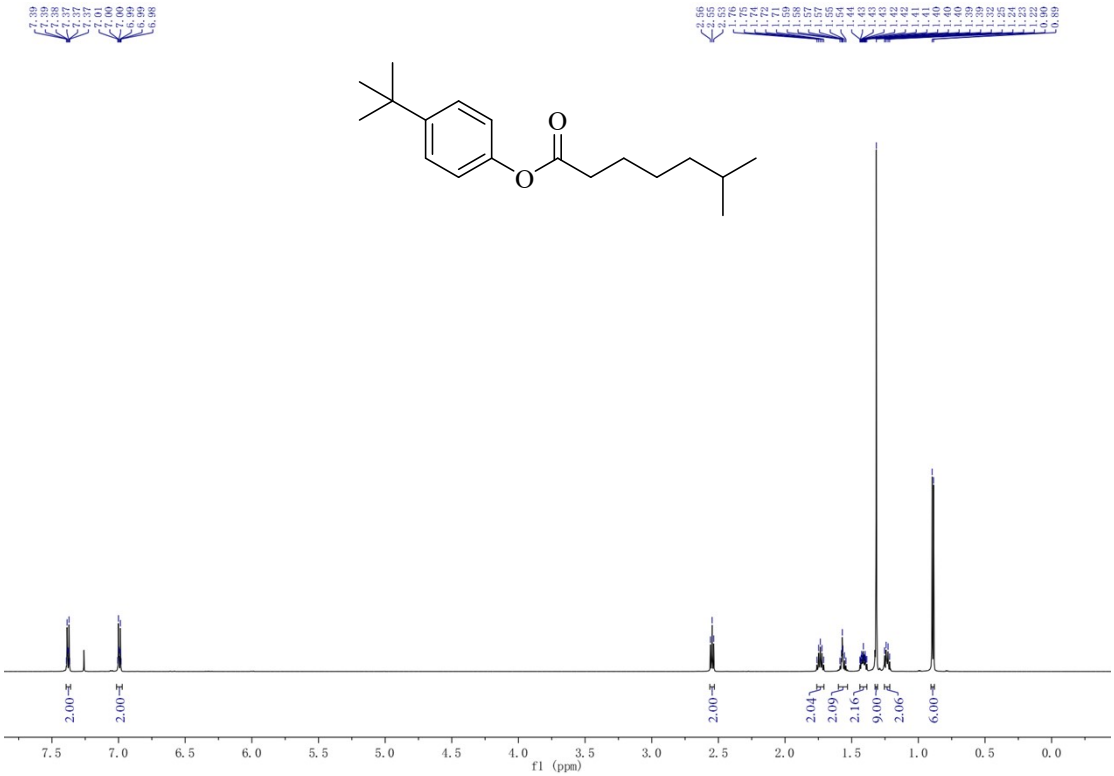


^{1}H NMR spectrum of compound **3la**

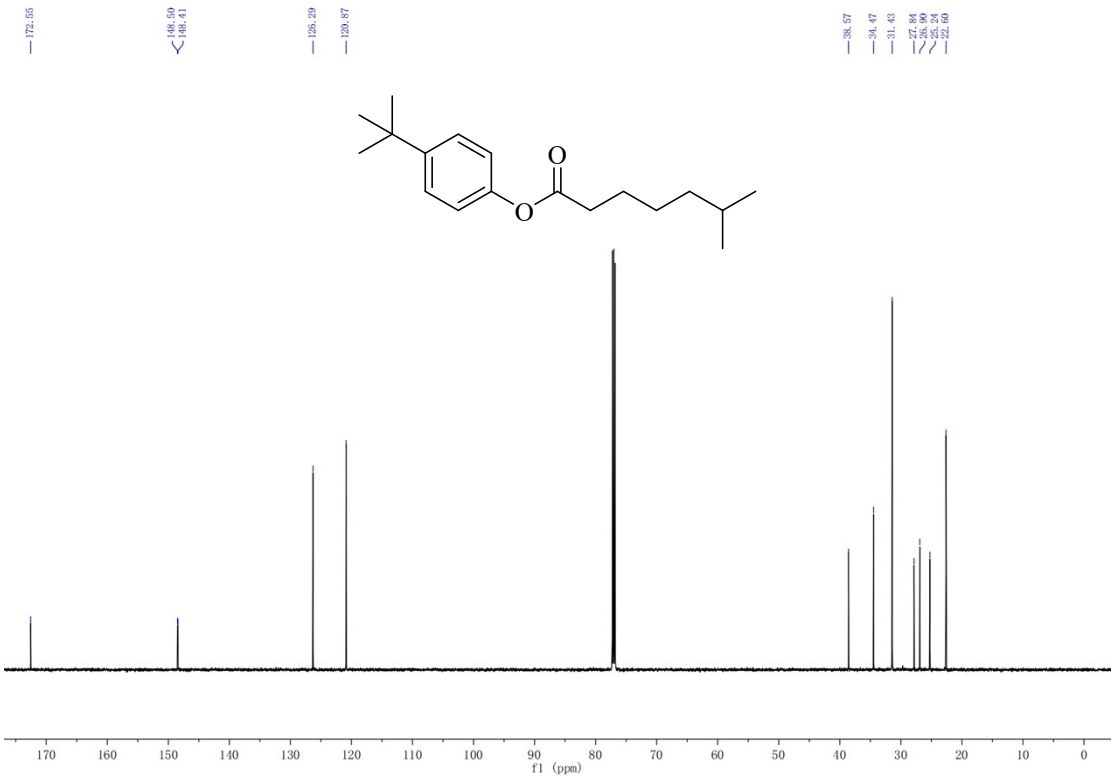


^{13}C NMR spectrum of compound **3la**

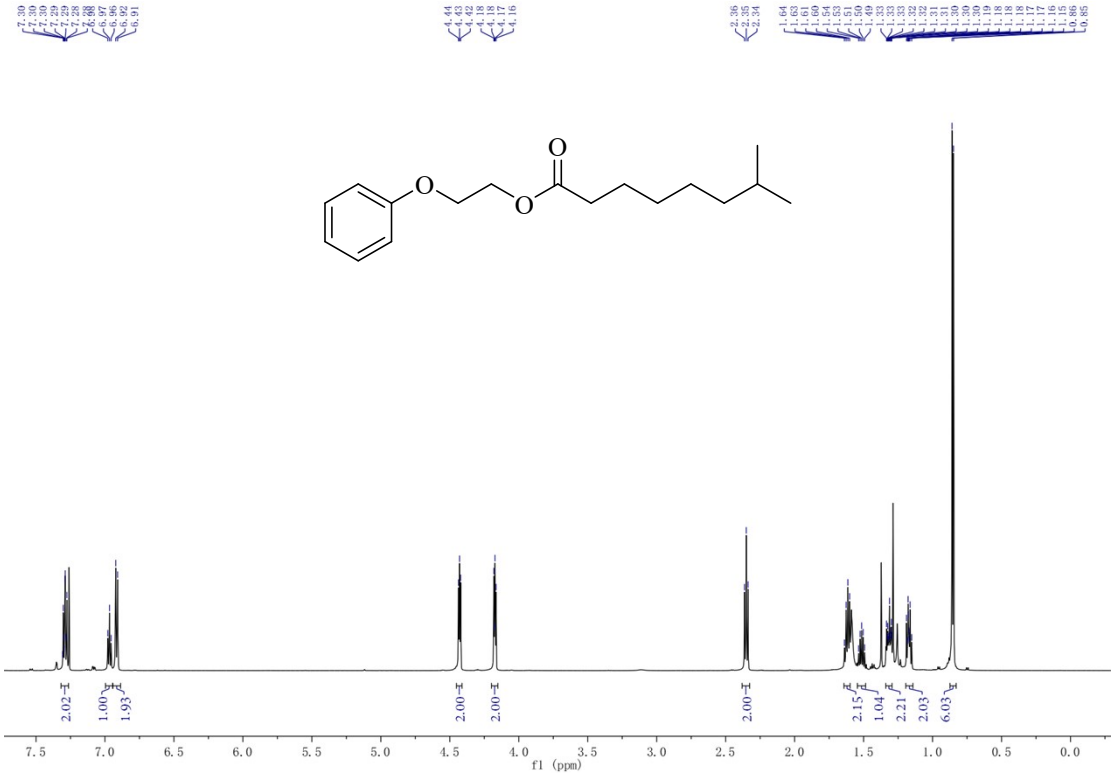
^{1}H NMR spectrum of compound **3ma**



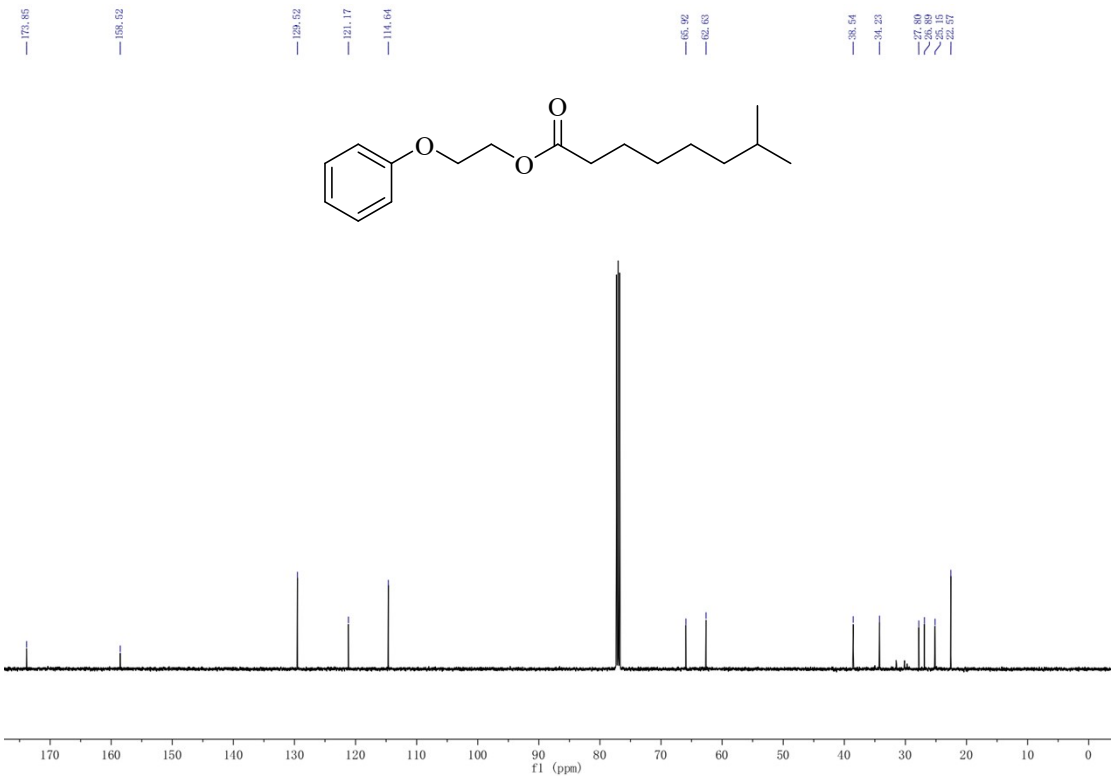
^{13}C NMR spectrum of compound **3ma**



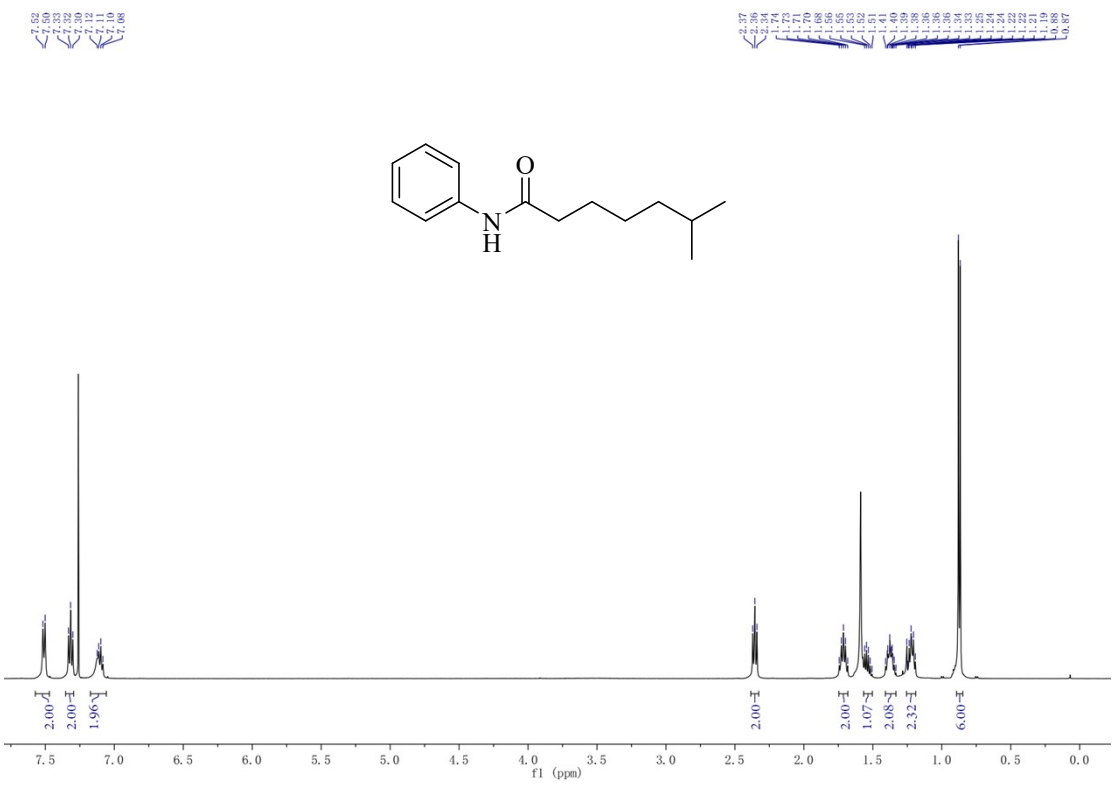
^{1}H NMR spectrum of compound **3na**



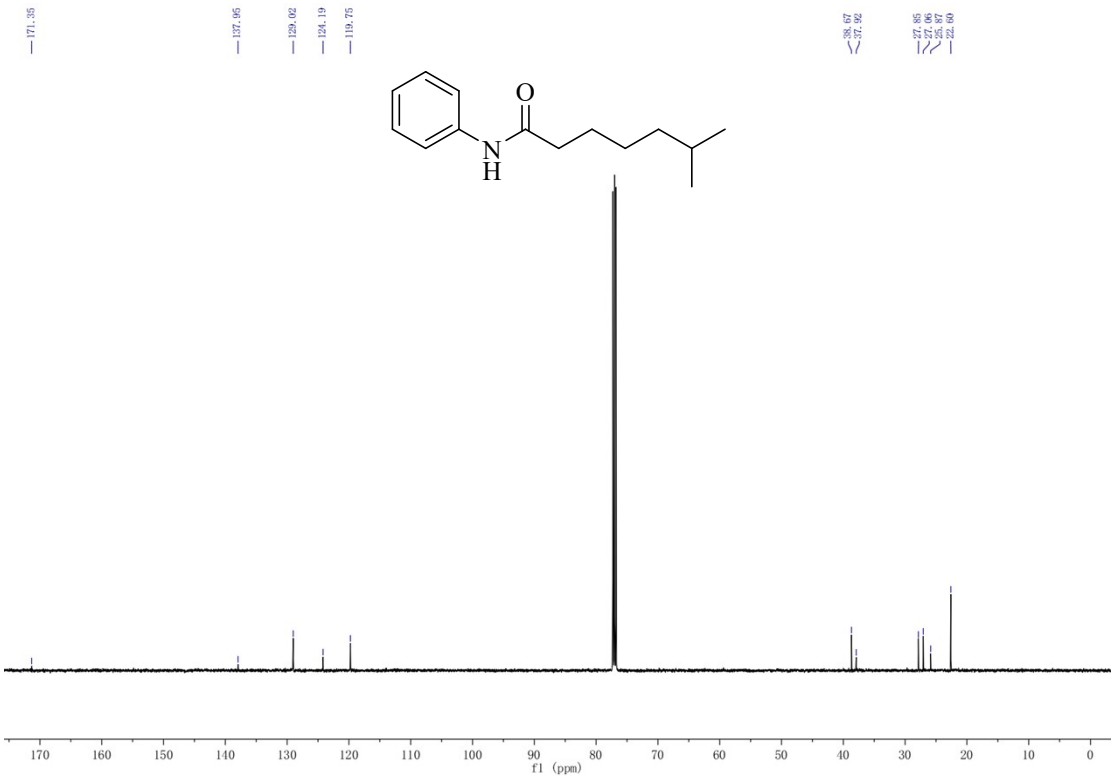
^{13}C NMR spectrum of compound **3na**



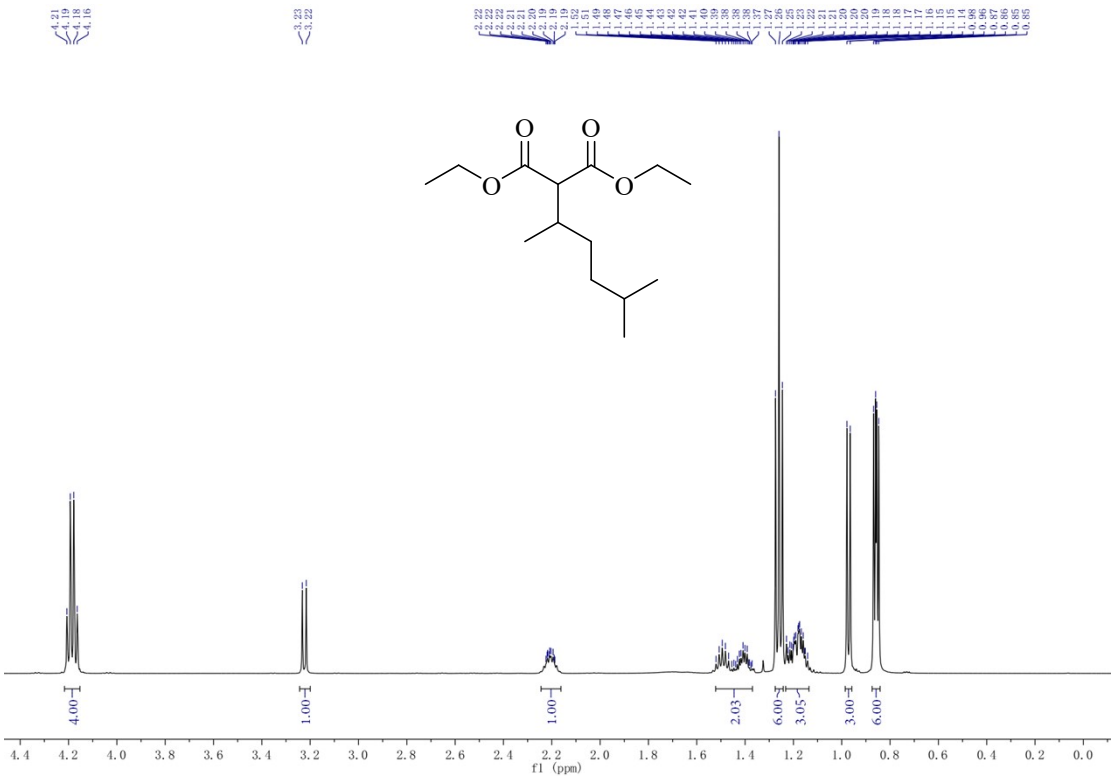
^{1}H NMR spectrum of compound **3oa**



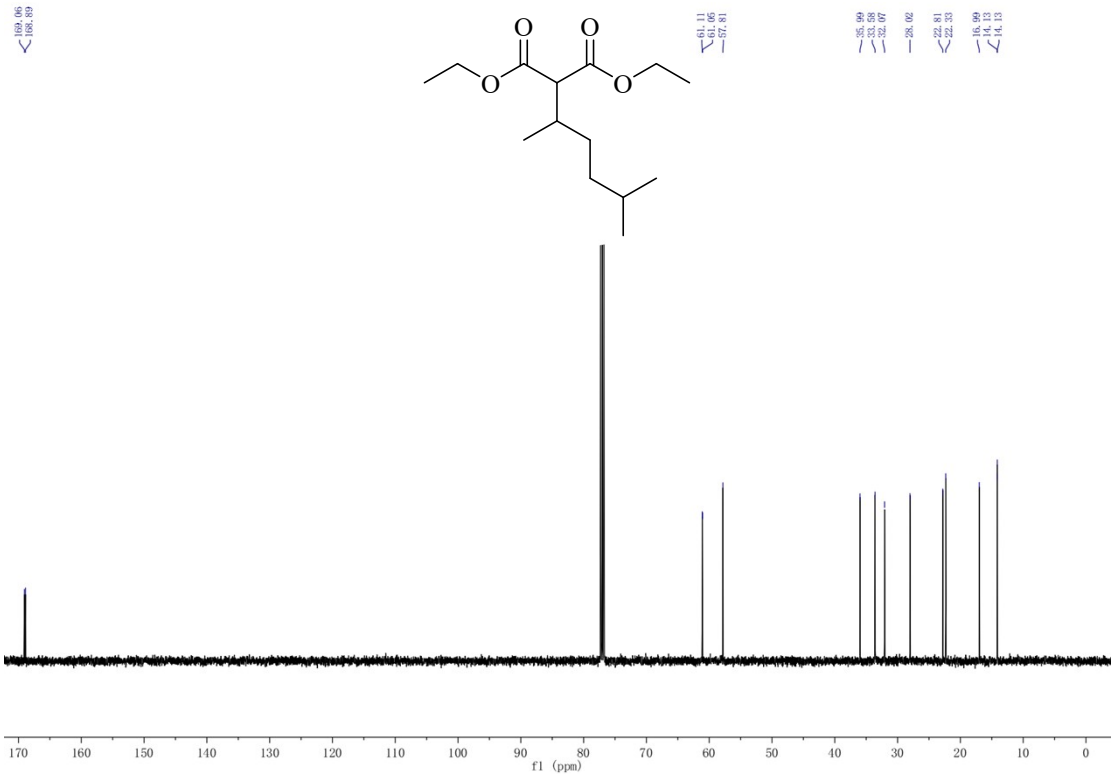
^{13}C NMR spectrum of compound **3oa**



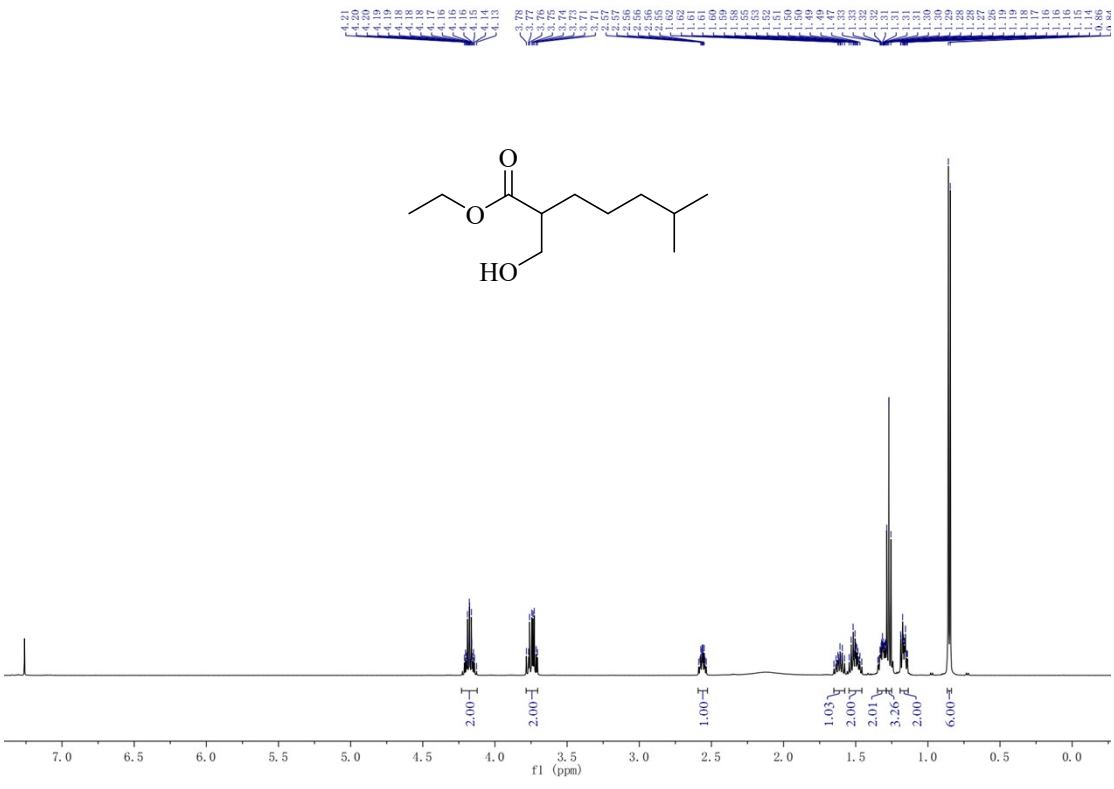
^{1}H NMR spectrum of compound **3pa**



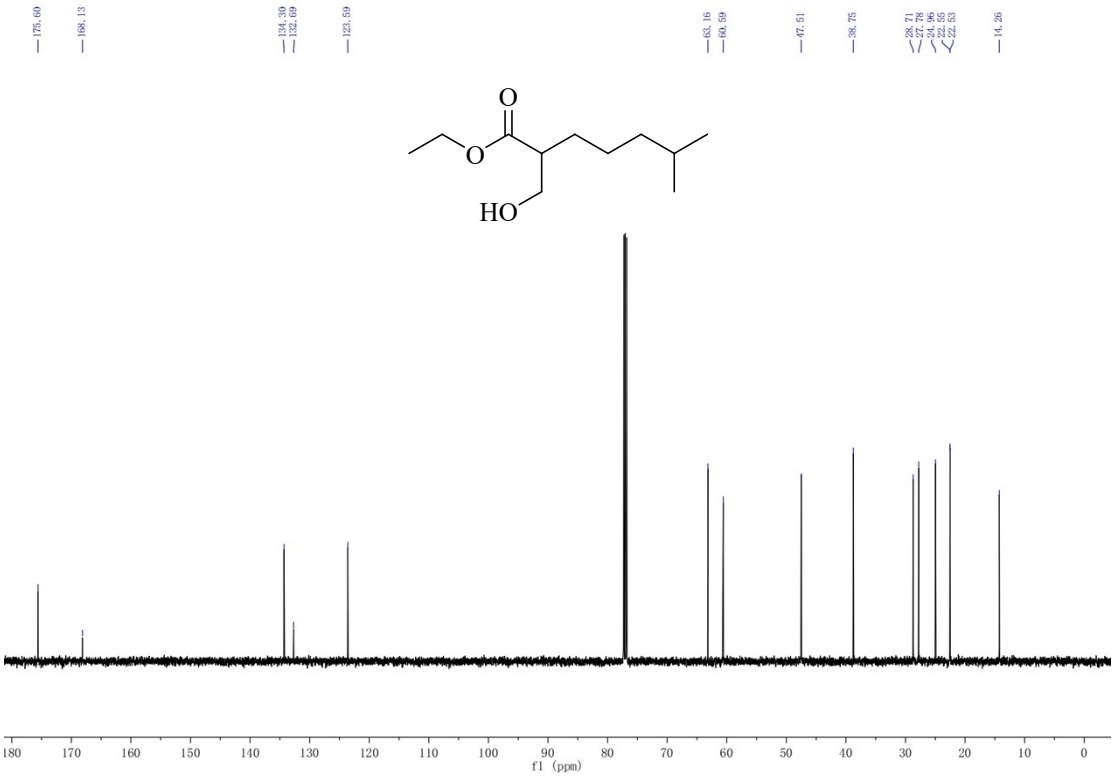
^{13}C NMR spectrum of compound **3pa**



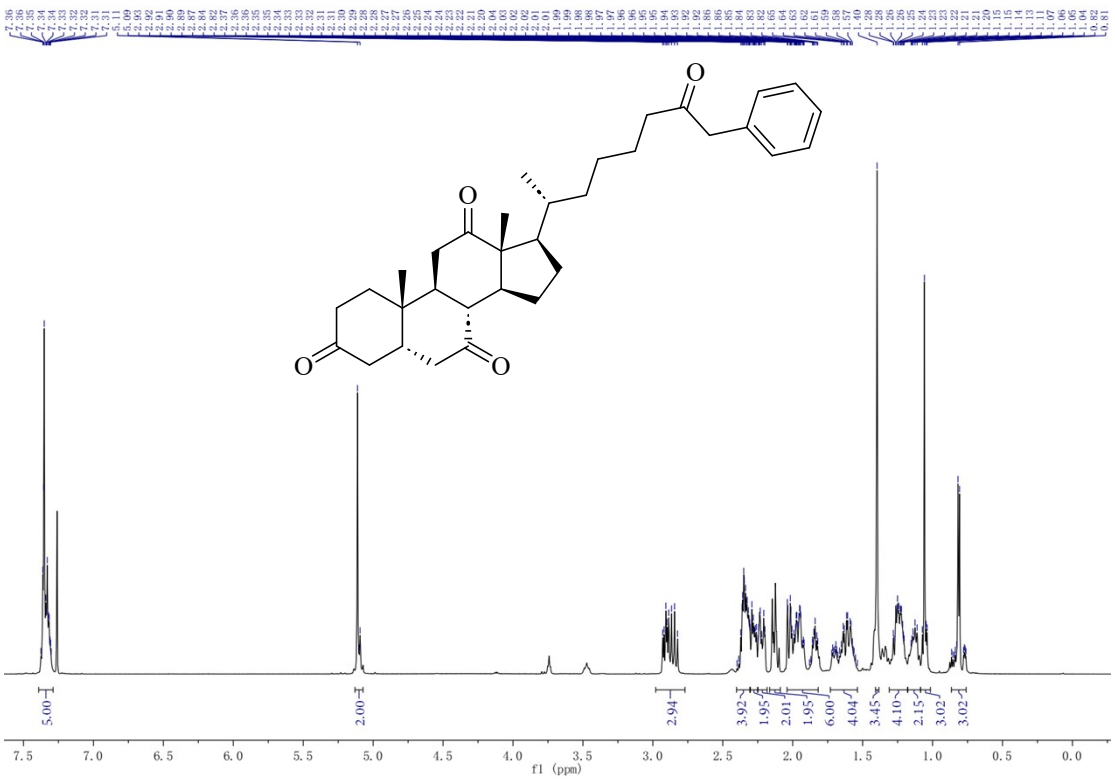
^{1}H NMR spectrum of compound **3qa**

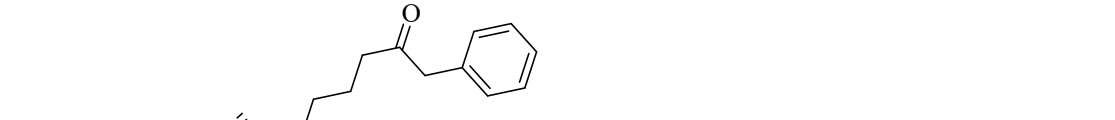


^{13}C NMR spectrum of compound **3qa**

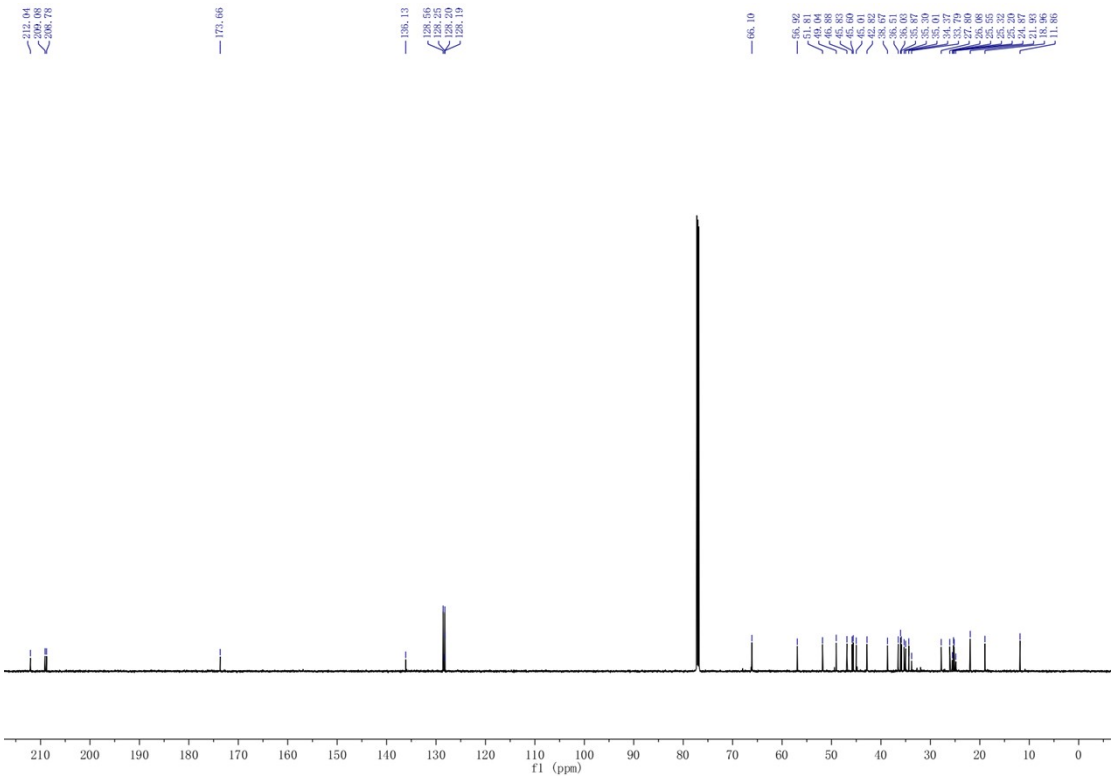


^{1}H NMR spectrum of compound **3aw**

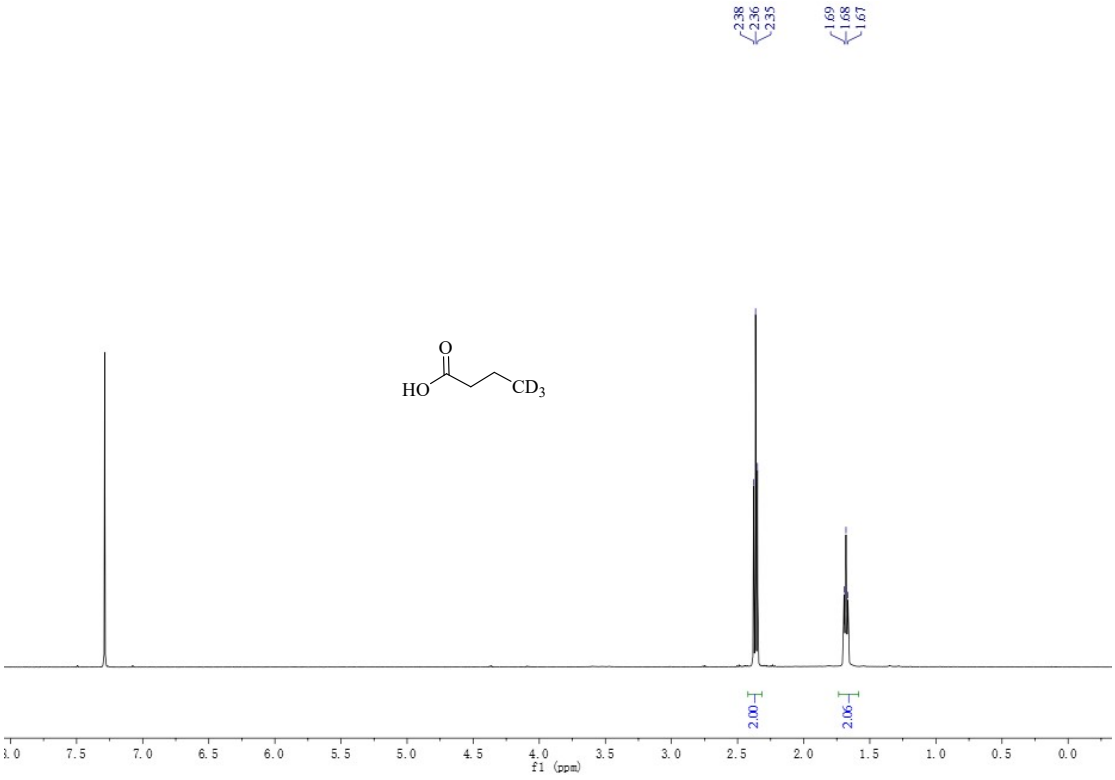




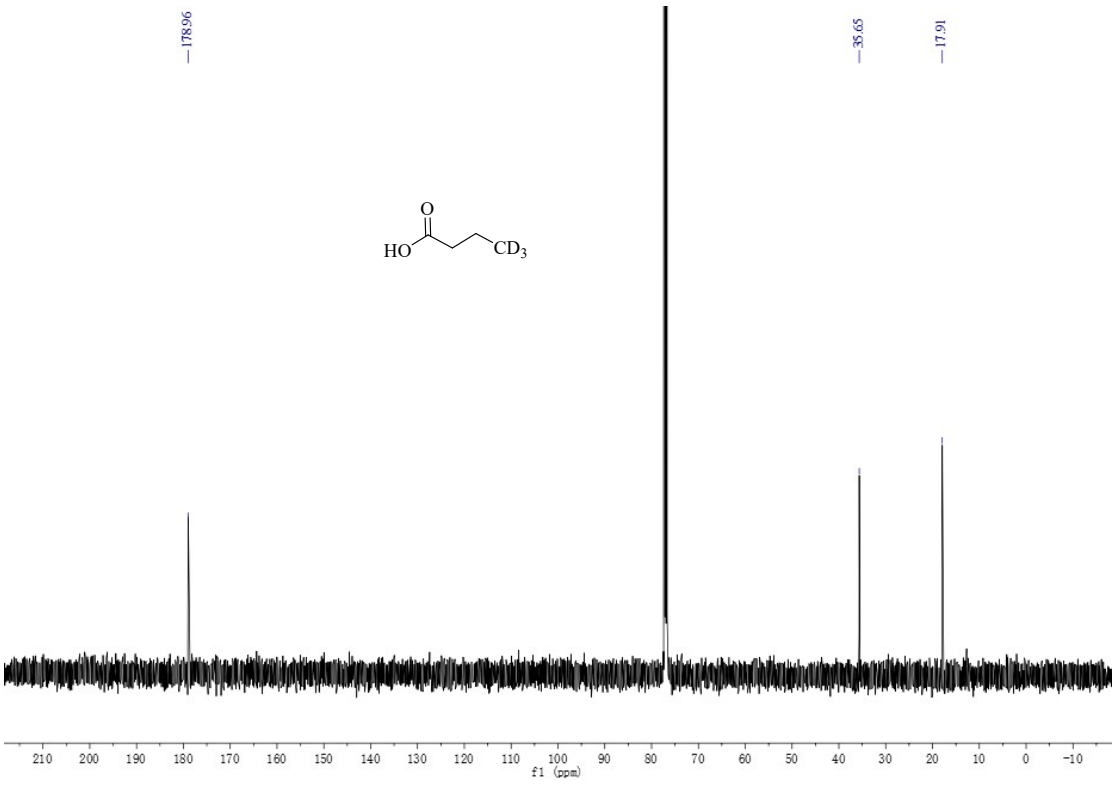
^{13}C NMR spectrum of compound **3aw**



^{1}H NMR spectrum of compound **3ax**



^{13}C NMR spectrum of compound **3ax**

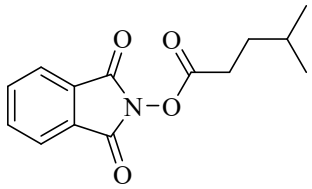


7. DFT calculation

In our calculations, Gaussian 16 program was used to carry out total density functional theory (DFT) calculations. Geometry optimizations were performed by B3LYP functional with dispersion correction of D3(BJ). The vibrational frequencies calculations were conducted at the same level of theory to be sure whether every optimized stationary point is an energy minimum or a transition state and evaluate the zero-point vibrational energy and thermal corrections at 298 K.

Cartesian coordinates of the optimized structure

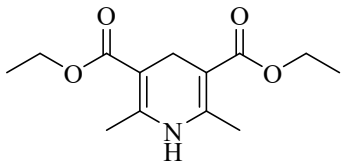
2a



O	-1.41491	-0.54419	-0.17802
C	-3.84873	1.14812	1.16453
C	-4.47132	-0.00785	0.80205
C	-4.527	2.35992	1.24728
C	-5.82646	-0.05281	0.4907
C	-5.90294	2.36116	0.93435
H	-4.02363	3.25835	1.53771
C	-6.55229	1.15551	0.55628
H	-6.30111	-0.97028	0.2117
H	-6.45952	3.27374	0.98238
H	-7.596	1.16363	0.32069
C	-0.14732	0.0952	-0.0068
O	0.44322	0.03455	1.10277
C	0.49508	0.858	-1.18028
H	0.17789	1.87966	-1.15788
H	0.19302	0.41095	-2.1043
C	2.02872	0.79379	-1.05612
H	2.3459	-0.22787	-1.07853
H	2.33078	1.24084	-0.13211
C	4.20476	1.49237	-2.10545
H	4.65111	2.02237	-2.92079
H	4.50682	1.93942	-1.18143
H	4.52195	0.47071	-2.12786
C	2.67112	1.55658	-2.22961
H	2.35394	2.57825	-2.2072
C	2.23639	0.91316	-3.5595
H	2.55357	-0.1085	-3.58191
H	1.1708	0.95778	-3.64577
H	2.68273	1.44316	-4.37484
C	-2.37712	0.82734	1.45406

C	-3.43619	-1.13905	0.83744
N	-2.07945	-0.55833	1.00848
O	-1.55301	1.61251	1.99063
O	-3.69614	-2.36667	0.74284

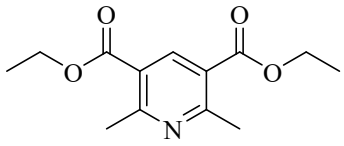
HEH



C	3.073	1.354	-0.0199
C	2.4345	2.3311	-0.6816
N	1.2501	2.1056	-1.3332
C	0.6506	0.8732	-1.3469
C	1.1931	-0.1823	-0.7209
C	2.4997	-0.0452	0.0294
C	0.5667	-1.3786	-0.7609
C	-0.6434	0.7002	-2.0795
C	3.0315	3.7037	-0.7088
C	4.2386	1.6221	0.6082
O	4.8805	0.6524	1.2698
C	6.0578	1.1602	1.8371
O	1.1022	-2.4353	-0.1389
C	0.2828	-3.5591	-0.316
O	4.7014	2.7374	0.5724
C	6.7807	0.0495	2.5876
C	0.9005	-4.7558	0.3953
O	-0.4768	-1.4944	-1.3584
H	0.7875	2.9019	-1.8377
H	2.3256	-0.3181	1.0943
H	3.2351	-0.7209	-0.4619
H	-0.9447	1.6698	-2.5355
H	-0.5167	-0.0623	-2.8803
H	-1.4306	0.3647	-1.3677
H	3.9845	3.7058	-0.1339
H	3.234	3.9987	-1.7627
H	2.3202	4.4266	-0.2504
H	6.7175	1.5534	1.0316
H	5.8043	1.9815	2.5442
H	-0.7245	-3.354	0.1106
H	0.1884	-3.7816	-1.4024
H	7.7153	0.4527	3.0379
H	6.121	-0.3436	3.3931

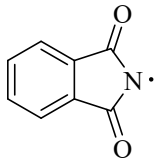
H	7.0342	-0.7718	1.8805
H	0.25	-5.6479	0.2547
H	1.9079	-4.9608	-0.0312
H	0.9949	-4.5332	1.4817

diethyl 2,6-dimethylpyridine-3,5-dicarboxylate



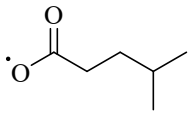
C	0.8158	0.5948	0.6978
C	0.1563	1.604	0.0144
N	-0.8364	1.3847	-0.8752
C	-1.1837	0.0969	-1.0894
C	-0.5837	-0.9791	-0.4549
C	0.4355	-0.7212	0.4558
C	-0.9783	-2.245	-0.714
C	-2.2803	-0.1841	-2.0689
C	0.5678	3.0191	0.2771
C	1.8018	0.8815	1.5758
O	2.1533	2.1537	1.795
C	3.1897	2.2068	2.7377
O	-1.9606	-2.4728	-1.5934
C	-2.1967	-3.8508	-1.6987
O	2.366	-0.0108	2.1628
C	3.5824	3.6581	2.9804
C	-3.3158	-4.0996	-2.7013
O	-0.4441	-3.1712	-0.1517
H	0.9357	-1.5493	0.9792
H	-2.6571	0.7748	-2.49
H	-1.8872	-0.8213	-2.8924
H	-3.1116	-0.7145	-1.5528
H	1.39	3.0338	1.0272
H	0.9222	3.4838	-0.6701
H	-0.3023	3.5916	0.6694
H	2.8451	1.7516	3.6932
H	4.0696	1.6437	2.3536
H	-1.2695	-4.3601	-2.0444
H	-2.4934	-4.2532	-0.7043
H	4.4052	3.7002	3.7287
H	3.9271	4.1133	2.0249
H	2.7026	4.2212	3.3645
H	-3.5032	-5.1935	-2.7849
H	-4.243	-3.5902	-2.3556
H	-3.0191	-3.6972	-3.6957

Radical intermediate I



C	-3.85322	1.1457	1.14555
C	-4.46743	0.00527	0.78795
C	-4.529	2.35894	1.23626
C	-5.82417	-0.04587	0.4822
C	-5.90493	2.36415	0.92605
H	-4.02339	3.25482	1.53061
C	-6.55376	1.15944	0.5483
H	-6.29648	-0.96575	0.20718
H	-6.46053	3.27722	0.97626
H	-7.5978	1.16558	0.31412
C	-2.37767	0.81365	1.44622
C	-3.42395	-1.12904	0.83705
N	-2.1175	-0.46849	0.78743
O	-1.57168	1.49374	2.13283
O	-3.6494	-2.36408	0.92314

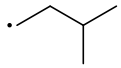
Radical intermediate II



O	-1.41491	-0.54419	-0.17802
C	-0.14732	0.0952	-0.0068
O	0.44322	0.03455	1.10277
C	0.49508	0.858	-1.18028
H	0.17789	1.87966	-1.15788
H	0.19302	0.41095	-2.1043
C	2.02872	0.79379	-1.05612
H	2.3459	-0.22787	-1.07853
H	2.33078	1.24084	-0.13211
C	4.20476	1.49237	-2.10545
H	4.65111	2.02237	-2.92079
H	4.50682	1.93942	-1.18143
H	4.52195	0.47071	-2.12786
C	2.67112	1.55658	-2.22961
H	2.35394	2.57825	-2.2072
C	2.23639	0.91316	-3.5595
H	2.55357	-0.1085	-3.58191
H	1.1708	0.95778	-3.64577

H	2.68273	1.44316	-4.37484

Radical intermediate III

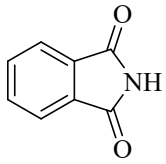


C	0.4885	0.95481	-1.28997
H	-0.04234	1.77505	-0.85371
H	-0.04128	0.20976	-1.84596
C	2.01499	0.84661	-1.11762
H	2.30239	-0.18406	-1.12319
H	2.30138	1.29171	-0.18769
C	4.24218	1.47296	-2.10332
H	4.72902	1.98334	-2.90793
H	4.52856	1.91807	-1.17339
H	4.52957	0.44229	-2.10889
C	2.71568	1.58117	-2.27566
H	2.42829	2.61184	-2.27009
C	2.30351	0.94055	-3.61406
H	2.5909	-0.09012	-3.61963
H	1.24289	1.01574	-3.7338
H	2.79035	1.45093	-4.41867

CO_2

O	-1.35751	-0.42743	-0.42246
C	-0.373	-0.13815	0.30599
O	0.6115	0.15114	1.03443

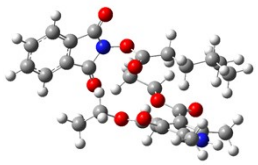
isoindoline-1,3-dione



C	-3.85322	1.1457	1.14555
C	-4.46743	0.00527	0.78795
C	-4.529	2.35894	1.23626
C	-5.82417	-0.04587	0.4822
C	-5.90493	2.36415	0.92605
H	-4.02339	3.25482	1.53061
C	-6.55376	1.15944	0.5483
H	-6.29648	-0.96575	0.20718
H	-6.46053	3.27722	0.97626
H	-7.5978	1.16558	0.31412
C	-2.37767	0.81365	1.44622

C	-3.42395	-1.12904	0.83705
O	-1.57168	1.49374	2.13283
O	-3.6494	-2.36408	0.92314
N	-2.1175	-0.46849	0.78743
H	-1.8184	-0.33584	-0.15753

EDA complex (**2a** and **HEH**)



C	3.073	1.354	-0.0199
C	2.4345	2.3311	-0.6816
N	1.2501	2.1056	-1.3332
C	0.6506	0.8732	-1.3469
C	1.1931	-0.1823	-0.7209
C	2.4997	-0.0452	0.0294
C	0.5667	-1.3786	-0.7609
C	-0.6434	0.7002	-2.0795
C	3.0315	3.7037	-0.7088
C	4.2386	1.6221	0.6082
O	4.8805	0.6524	1.2698
C	6.0578	1.1602	1.8371
O	1.1022	-2.4353	-0.1389
C	0.2828	-3.5591	-0.316
O	4.7014	2.7374	0.5724
C	6.7807	0.0495	2.5876
C	0.9005	-4.7558	0.3953
O	-0.4768	-1.4944	-1.3584
H	0.7875	2.9019	-1.8377
H	2.3256	-0.3181	1.0943
H	3.2351	-0.7209	-0.4619
H	-0.9447	1.6698	-2.5355
H	-0.5167	-0.0623	-2.8803
H	-1.4306	0.3647	-1.3677
H	3.9845	3.7058	-0.1339
H	3.234	3.9987	-1.7627
H	2.3202	4.4266	-0.2504
H	6.7175	1.5534	1.0316
H	5.8043	1.9815	2.5442
H	-0.7245	-3.354	0.1106
H	0.1884	-3.7816	-1.4024

H	7.7153	0.4527	3.0379
H	6.121	-0.3436	3.3931
H	7.0342	-0.7718	1.8805
H	0.25	-5.6479	0.2547
H	1.9079	-4.9608	-0.0312
H	0.9949	-4.5332	1.4817
O	-5.82193	3.08387	-0.08434
C	-8.25576	4.77617	1.25821
C	-8.87835	3.62021	0.89573
C	-8.93402	5.98797	1.34096
C	-10.23348	3.57525	0.58438
C	-10.30997	5.98921	1.02803
H	-8.43066	6.8864	1.63139
C	-10.95932	4.78356	0.64996
H	-10.70814	2.65777	0.30538
H	-10.86655	6.90179	1.07606
H	-12.00303	4.79169	0.41437
C	-4.55435	3.72325	0.08688
O	-3.96381	3.6626	1.19645
C	-3.91195	4.48605	-1.0866
H	-4.22913	5.50771	-1.0642
H	-4.21401	4.039	-2.01062
C	-2.37831	4.42184	-0.96244
H	-2.06112	3.40018	-0.98485
H	-2.07625	4.86889	-0.03843
C	-0.20226	5.12042	-2.01177
H	0.24408	5.65042	-2.82711
H	0.09979	5.56748	-1.08775
H	0.11492	4.09876	-2.03417
C	-1.73591	5.18464	-2.13593
H	-2.05309	6.2063	-2.11352
C	-2.17064	4.54122	-3.46582
H	-1.85346	3.51955	-3.48823
H	-3.23622	4.58583	-3.55209
H	-1.7243	5.07121	-4.28116
C	-6.78415	4.45539	1.54774
C	-7.84322	2.489	0.93112
N	-6.48648	3.06972	1.10216
O	-5.96003	5.24056	2.08431
O	-8.10316	1.26138	0.83652