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Visible-Light-Initiated Manganese-Catalyzed Giese Addition of Unactivated Alkyl Iodides to Electron-Poor Olefins

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Supporting Information

1. General Information

Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 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 FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). Blue LED (36 W, λ_{max} = 470 nm) purchased from JIADENG (LS) was used for blue light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature.

Figure S1. Photograph of the photocatalytic reactor used for reactions conducted under blue LED irradiation.

2. Preparation of (1*R*,4*S*)-2-iodo-1-isopropyl-4-methylcyclohexane and (8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-iodo-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthrene.

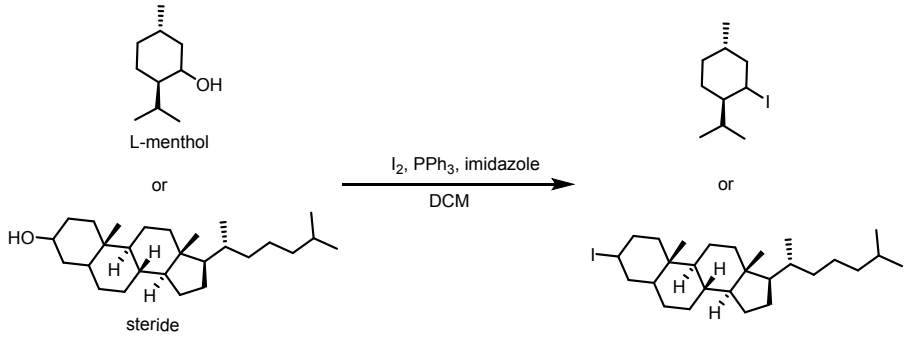
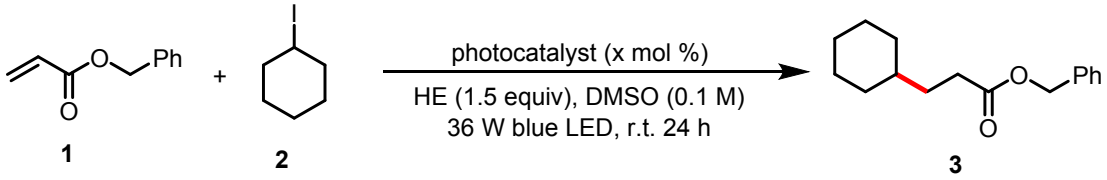


Figure S2

The alkyl iodides were synthesized according to literature report.[1] The spectral data of the alkyl iodides are consistent with the literature data.[1]

3. Investigation of the key reaction parameters.

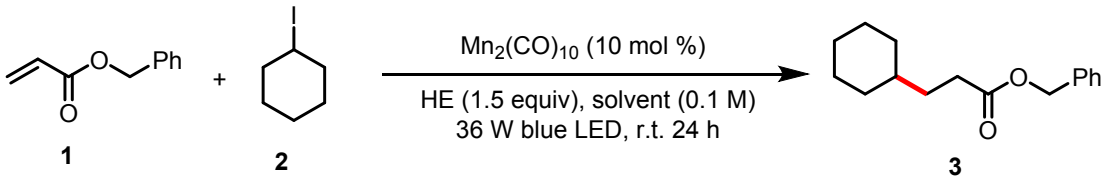
Table S1. Screening of photocatalysts[a]



entry	photocatalyst	x	yield (%)[b]
1	**$Mn_2(CO)_{10}$**	**10**	**96 (92)[c]**
2[d]	$Mn(CO)_5I$	10	82
3	$Fe_2(CO)_9$	10	NR
4	$Co_2(CO)_8$	10	NR
5[e]	$[Ru(bpy)_3](PF_6)_2$	1	NR
6[e]	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	1	NR
7[e]	$Ir(ppy)_3$	1	NR
8[e]	$[Ir(dtbbpy)(ppy)_2][PF_6]$	1	NR

[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), photocatalyst (0.003x mmol), HEH (0.45 mmol), and DMSO (3 mL) under Ar atmosphere. [b]Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [c]Isolated yields are given. [d]Catalyst loading increased to 0.06 mmol. NR = no reaction. [e]Catalyst loading reduced to 0.003 mmol.

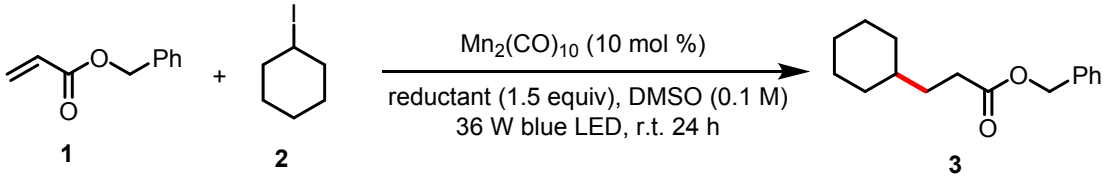
Table S2. Screening of different solvents[a]



entry	solvent	yield (%)[b]
1	acetone	84
2	MeOH	87
3	DMF	90
4	DMA	34
5	CH_3CN	83
6	**DMSO**	**96 (92)[c]**

[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), $Mn_2(CO)_{10}$ (0.03 mmol), HEH (0.45 mmol), and solvent (3 mL) under Ar atmosphere. [b]Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [c]Isolated yields are given.

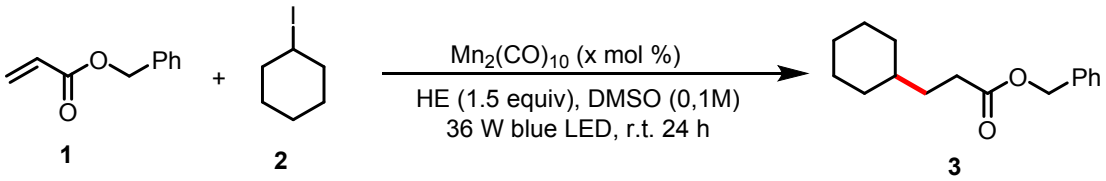
Table S3. Screening of different reductants[a]



entry	reductant	yield (%)[b]
1	TTMS	NR
2	Et_3SiH	NR
3	$PhSiH_3$	NR
4	$NaBH_4$	NR
5	**HE**	**96 (92)[c]**

[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), $Mn_2(CO)_{10}$ (0.03 mmol), reductant (0.45 mmol), and DMSO (3 mL) under Ar atmosphere. [b]Determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [c]Isolated yields are given.

Table S4. Screening of the amount of $Mn_2(CO)_{10}$[a]

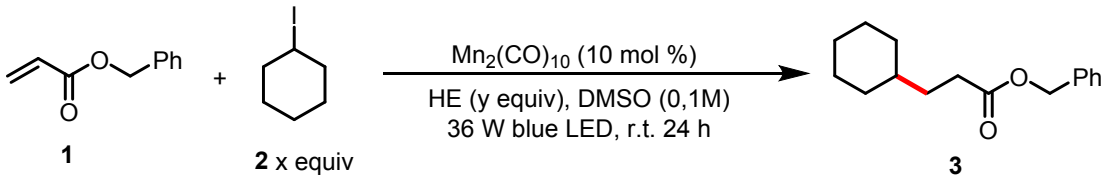


entry	x mmol%. $Mn_2(CO)_{10}$	yield (%)[b]
1	0	NR
2	2	44
3	5	82
4	**10**	**96 (92)[c]**
5	15	96

6	20	96

[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.6 mmol), $Mn_2(CO)_{10}$ (0.003x mmol), HEH (0.45 mmol), and DMSO (3 mL) under Ar atmosphere. [b]Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. [c]Isolated yields are given. NR = no reaction.

Table S5. Screening of the amount of iodocyclohexane and HEH[a]



entry	x eq. iodocyclohexane	y eq. HEH	yield (%)[b]
1	**2**	**1.5**	**96 (92)[c]**
2	1.5	1.5	88
3	1.2	1.5	73
6	2	1.2	87

[a]General conditions, unless otherwise noted: **1** (0.3 mmol), **2** (0.3x mmol), $Mn_2(CO)_{10}$ (0.03 mmol), HEH (0.3y mmol), and DMSO (3 mL) under Ar atmosphere. [b]Determined by ^{1}H NMR spectroscopy using dibromomethane as an internal standard. [c]Isolated yields are given.

4. Investigation of the mechamism.

4.1 TEMPO and 1,1-diphenylethylene were used as radical scavengers.

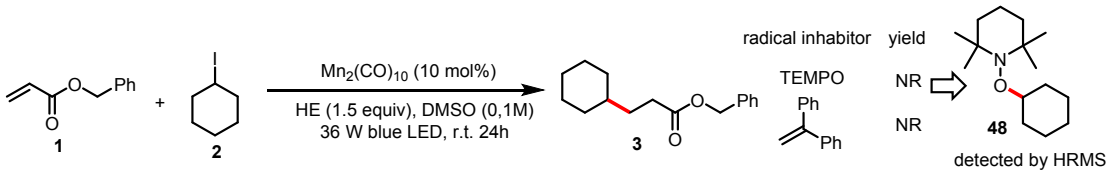
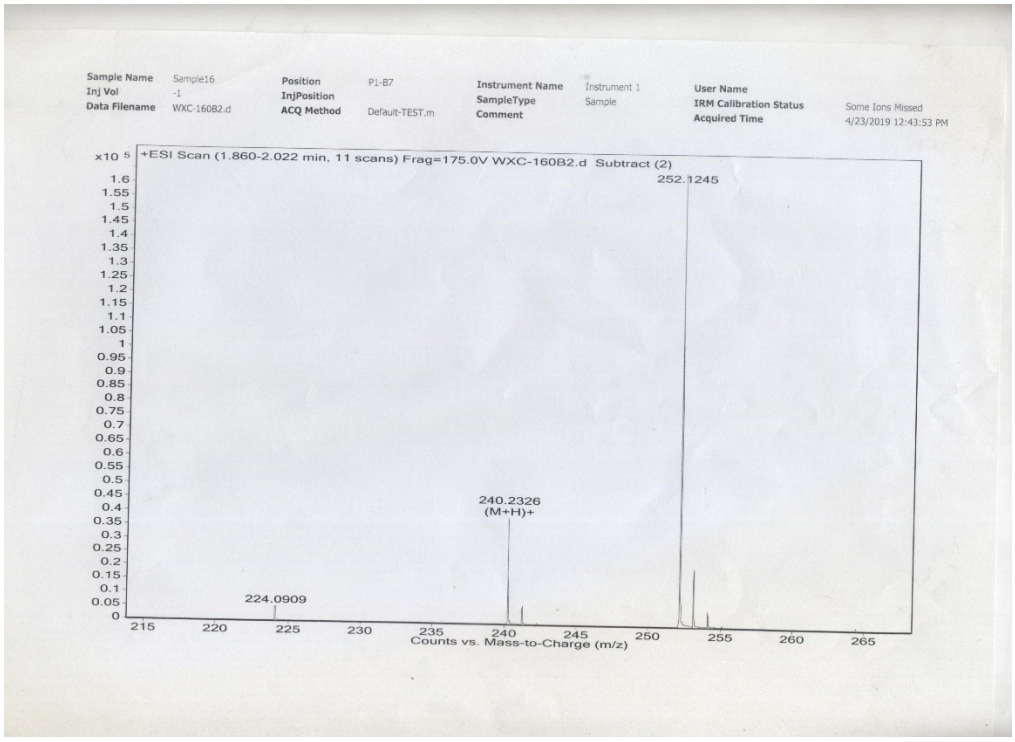


Figure S3

To a 10 mL glass vial was added $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol, 1 mol %), **1** (0.3 mmol, 1.0 equiv), **2** (78 μL, 0.6 mmol, 2.0 equiv), TEMPO (117 mg, 0.75 mmol, 2.5 equiv) or 1,1-diphenylethylene (135 mg, 0.75 mmol, 2.5 equiv), HEH (114 mg, 0.45 mmol, 2.0 equiv) and 3.0 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The corresponding alkylated product **3** was not observed based on ^{1}H NMR analysis, and the corresponding product of radical trapping, 1-(cyclohexyloxy)-2,2,6,6-tetrame-thylpiperidine (**49**), was observed by mass spectrometry.


Sample Name Sample16
Inj Vol -1
Data Filename WXC-160B2.d
Position P1-B7
InjPosition
ACQ Method Default-TEST.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Some Ions Missed
Acquired Time 4/23/2019 12:43:53 PM
x10 5
+ESI Scan (1.860-2.022 min, 11 scans) Frag=175.0V WXC-160B2.d Subtract (2)
252.1245
240.2326
(M+H)+
224.0909
Counts vs. Mass-to-Charge (m/z)

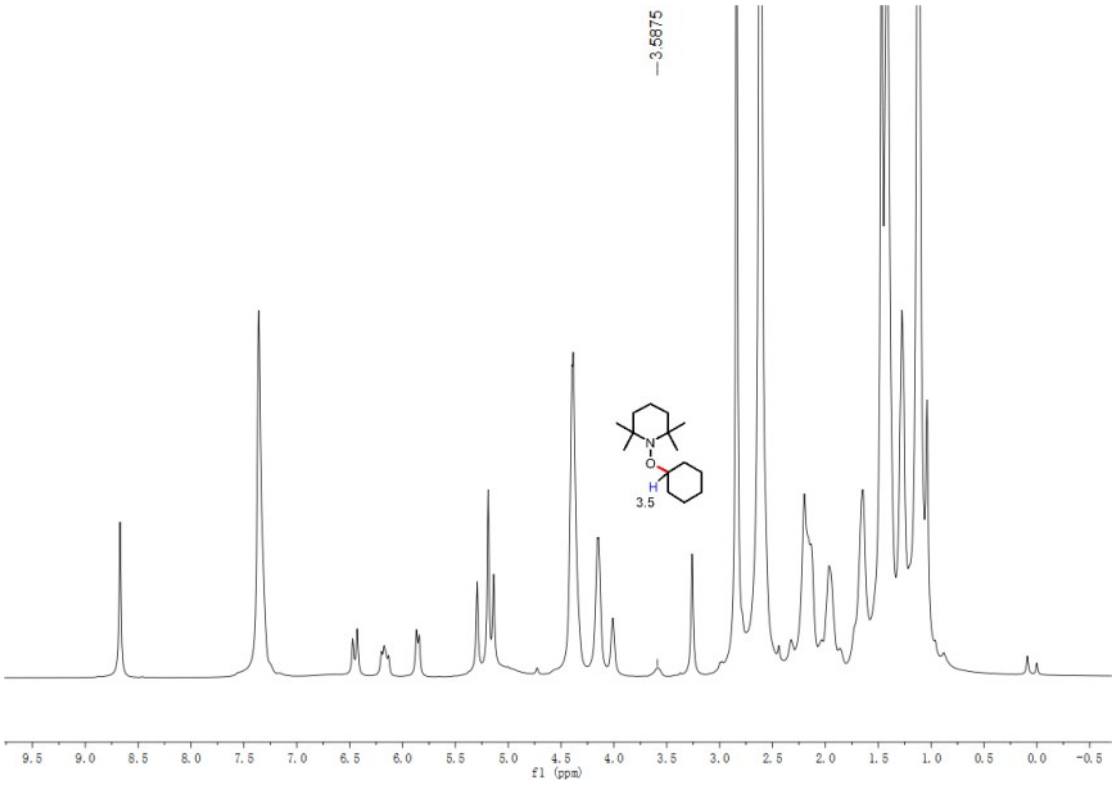

3.5875
3.5
f1 (ppm)

Figure S4. The crude ^{1}H NMR spectra of the reaction in Figure S3.

4.2 Radical clock experiment.

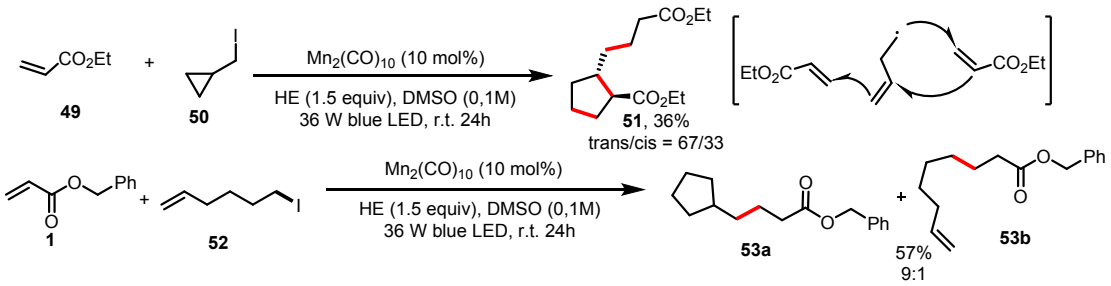
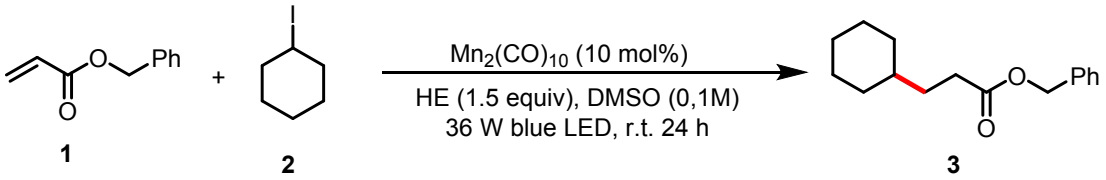


Figure S5

To a 10 mL glass vial was added $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol, 1 mol %), **1** (0.3 mmol, 1.0 equiv), iodoalkanes (0.6 mmol, 2.0 equiv), HEH (114 mg, 0.45 mmol, 2.0 equiv) and 3.0 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The mixture was diluted with 10 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

4.3 Light/dark experiment.

Table S6



entry	light on and off conditions	yield (%)
1	on 5 minutes	56
2	on 5 minutes, off 24 h	80
3	on 24 h	96

The yield was determined by 1H NMR spectroscopy using dibromomethane as the internal standard.

4.4 Deuterium labelling experiment

In order to confirm the source of hydrogen atom of product, we performed two different deuterium-labeling experiments (Figure S6). While the reaction in d_6-DMSO resulted no deuterated coupled product, the experiments with d_2-HE led to incorporation of deuterium into the desired product (>99% D incorporation).

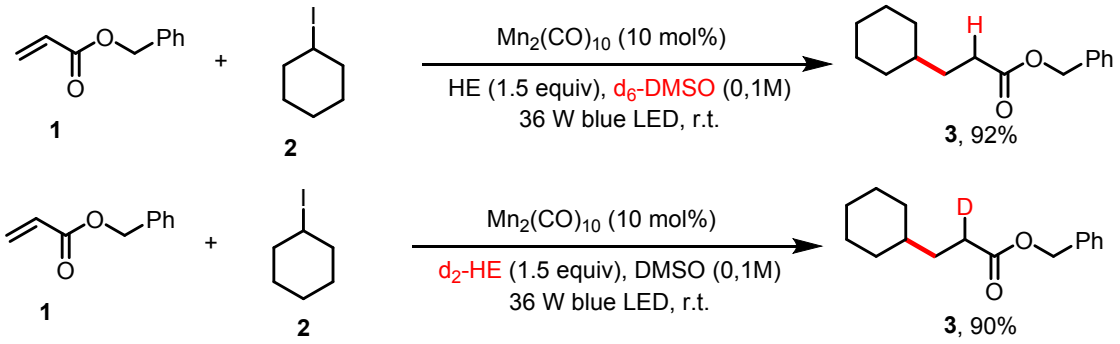


Figure S6

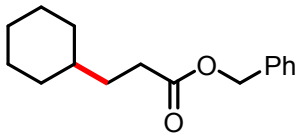
5. Experimental procedures and product characterization.

5.1 General procedure for the Giese reaction with unactivated alkyl iodides:

To a 10 mL glass vial was added $Mn_2(CO)_{10}$ (11.7 mg, 0.03 mmol, 1 mol %), Michael acceptors (0.3 mmol, 1.0 equiv), iodoalkanes (0.6 mmol, 2.0 equiv), HEH (114 mg, 0.45 mmol, 2.0 equiv) and 3.0 mL of DMSO. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 36 W Blue LED (approximately 2 cm away from the light source) at room temperature for 24 h. The mixture was diluted with 10 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

5.2. Product characterization

benzyl 3-cyclohexylpropanoate (3).



According to the *general procedure*.

Colorless oil (67.9 mg, 92%).

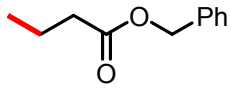
R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.24 (m, 5H), 5.11 (s, 2H), 2.42 – 2.30 (m, 2H), 1.65 (dd, J = 24.4, 6.8 Hz, 5H), 1.58 – 1.47 (m, 2H), 1.28 – 1.08 (m, 4H), 0.87 (dd, J = 21.2, 11.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 136.3, 128.6, 128.3, 128.2, 66.2, 37.3, 33.0, 32.4, 32.0, 26.6, 26.3.

HRMS (ESI) calcd for $C_{16}H_{23}O_2$ $[M + H]^+$ 247.1693, found 247.1696.

benzyl butyrate (4).



According to the *general procedure*.

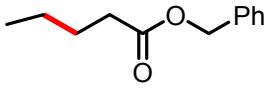
Yellow oil (37.4 mg, 70%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 5.12 (s, 2H), 2.34 (t, J = 7.2 Hz, 2H), 1.76 – 1.59 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 136.3, 131.2, 128.7, 128.3, 66.2, 36.3, 18.6, 13.8.

HRMS (ESI) calcd for $C_{11}H_{15}O_2$ $[M + H]^+$ 179.1067, found 179.1068.

benzyl pentanoate (5).



According to the *general procedure*.

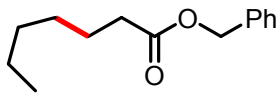
Yellow oil (42.0 mg, 73%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 5H), 5.11 (s, 2H), 2.36 (t, J = 7.6 Hz, 2H), 1.63 (dt, J = 15.2, 7.6 Hz, 2H), 1.34 (dq, J = 14.8, 7.2 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 136.2, 128.6, 128.3, 66.2, 34.1, 27.1, 22.4, 13.8.

HRMS (ESI) calcd for $C_{12}H_{17}O_2$ $[M + H]^+$ 193.1223, found 193.1226.

benzyl heptanoate (6).



According to the *general procedure*.

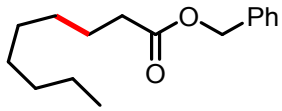
Yellow oil (41.6 mg, 63%).

R_f 0.50 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 5.11 (s, 2H), 2.42 – 2.28 (m, 2H), 1.64 (dt, J = 14.0, 7.2 Hz, 2H), 1.39 – 1.20 (m, 6H), 0.87 (dd, J = 6.8, 5.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 136.2, 128.6, 128.3, 128.2, 66.2, 34.4, 31.5, 28.9, 25.0, 22.6, 14.1.

HRMS (ESI) calcd for $C_{14}H_{21}O_2$ $[M + H]^+$ 221.1536, found 221.1538.

benzyl nonanoate (7).



According to the *general procedure*.

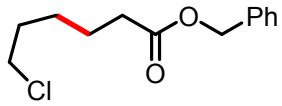
Yellow oil (54.3 mg, 73%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 5H), 5.11 (s, 2H), 2.42 – 2.29 (m, 2H), 1.74 – 1.56 (m, 2H), 1.27 (d, J = 8.0 Hz, 10H), 0.96 – 0.80 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 136.2, 128.6, 128.3, 128.2, 66.2, 34.4, 31.9, 29.3, 29.2, 25.1, 22.8, 14.2.

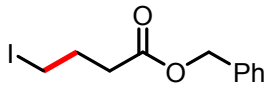
HRMS (ESI) calcd for $C_{16}H_{25}O_2$ $[M + H]^+$ 249.1849, found 249.1854.

benzyl 6-chlorohexanoate (8).



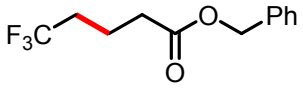
According to the *general procedure*.
Yellow oil (36.7 mg, 51%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.15 (m, 5H), 5.00 (s, 2H), 3.40 (t, J = 6.8 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 1.74 – 1.60 (m, 2H), 1.56 (dt, J = 15.2, 7.6 Hz, 2H), 1.41 – 1.28 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 136.1, 128.6, 128.3, 66.3, 44.8, 34.1, 32.3, 26.4, 24.3.
HRMS (ESI) calcd for $C_{13}H_{21}ClNO_2$ $[M + NH_4]^+$ 258.1255, found 258.1259.

benzyl 4-iodobutanoate (9).



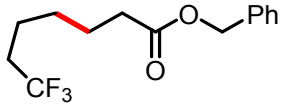
According to the *general procedure*.
Yellow oil (29.2 mg, 32%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.10 (m, 5H), 5.10 (d, J = 18.4 Hz, 2H), 3.36 – 3.04 (m, 2H), 2.63 – 2.30 (m, 2H), 2.28 – 1.93 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 135.9, 128.7, 128.5, 128.4, 66.6, 34.9, 28.5, 5.6.
HRMS (ESI) calcd for $C_{11}H_{14}IO_2$ $[M + H]^+$ 305.0533, found 305.0536.

benzyl 5,5,5-trifluoropentanoate (10).



According to the *general procedure*.
Colorless oil (38.4 mg, 52%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.13 (s, 2H), 2.46 (t, J = 7.2 Hz, 2H), 2.24 – 2.02 (m, 2H), 2.02 – 1.82 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 129.4 (q, J = 275 Hz), 128.8, 128.5, 128.4, 66.6, 33.0 (q, J = 28.7 Hz), 32.9, 17.5 (q, J = 3.1 Hz).
HRMS (ESI) calcd for $C_{12}H_{14}F_3O_2$ $[M + H]^+$ 247.0940, found 247.0943.

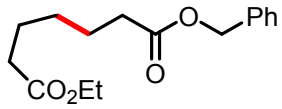
benzyl 7,7,7-trifluoroheptanoate (11).



According to the *general procedure*.
Yellow oil (60.0 mg, 73%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 5.11 (s, 2H), 2.37 (t, J = 7.6 Hz, 2H), 2.12 – 1.96 (m, 2H), 1.73 – 1.61 (m, 2H), 1.55 (dt, J = 11.6, 7.6 Hz, 2H), 1.46 – 1.32 (m, 2H). **^{13}C NMR**

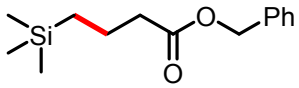
(100 MHz, $CDCl_3$) δ 173.3, 136.1, 128.7, 128.6, 128.3, 127.2 (q, J = 275 Hz), 66.3, 34.0, 33.6(q, J = 28.3 Hz), 28.2, 24.6, 21.7 (q, J = 2.7 Hz).
HRMS (ESI) calcd for $C_{14}H_{21}F_3NO_2$ $[M + NH_4]^+$ 292.1519, found 292.1521.

1-benzyl 7-ethyl heptanedioate (12).



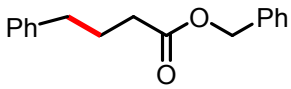
According to the *general procedure*.
Yellow oil (48.4 mg, 58%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 5H), 5.11 (s, 2H), 4.19 – 4.05 (m, 2H), 2.36 (dd, J = 10.4, 4.4 Hz, 2H), 2.28 (dd, J = 10.4, 4.4 Hz, 2H), 1.66 (dt, J = 13.2, 7.2 Hz, 4H), 1.43 – 1.30 (m, 2H), 1.29 – 1.18 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7, 173.5, 136.2, 128.7, 128.3, 66.2, 60.3, 34.2, 34.2, 28.7, 24.7, 14.3.
HRMS (ESI) calcd for $C_{16}H_{23}O_4$ $[M + H]^+$ 279.1591, found 279.1593.

benzyl 4-(trimethylsilyl)butanoate (13).



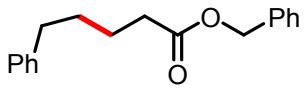
According to the *general procedure*.
Yellow oil (46.5 mg, 62%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 5H), 5.13 (s, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.77 – 1.58 (m, 2H), 0.59 – 0.41 (m, 2H), -0.01 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 136.3, 128.7, 128.3, 128.3, 66.1, 38.1, 19.9, 16.6, -1.7.
HRMS (ESI) calcd for $C_{14}H_{26}NO_2Si$ $[M + NH_4]^+$ 268.1727, found 268.1731.

benzyl 4-phenylbutanoate (14).



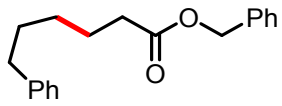
According to the *general procedure*.
Colorless oil (22.1 mg, 29%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.29 – 7.23 (m, 2H), 7.17 (dd, J = 15.2, 7.6 Hz, 3H), 5.11 (s, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.37 (t, J = 7.6 Hz, 2H), 2.07 – 1.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.4, 141.4, 136.1, 128.7, 128.6, 128.5, 128.4, 126.1, 66.3, 35.2, 33.7, 26.6.
HRMS (ESI) calcd for $C_{17}H_{19}O_2$ $[M + H]^+$ 255.1380, found 255.1378.

benzyl 5-phenylpentanoate (15).



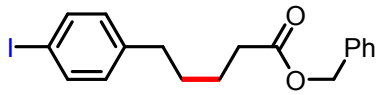
According to the *general procedure*.
Colorless oil (61.9 mg, 77%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 7.26 (dd, J = 13.6, 6.4 Hz, 2H), 7.15 (dd, J = 12.4, 7.2 Hz, 3H), 5.10 (s, 2H), 2.60 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 1.77 – 1.56 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 142.2, 136.2, 128.6, 128.5, 128.4, 128.3, 128.2, 125.9, 66.2, 35.6, 34.2, 30.9, 24.7.
HRMS (ESI) calcd for $C_{18}H_{24}NO_2$ $[M + NH_4]^+$ 286.1802, found 286.1799.

benzyl 6-phenylhexanoate (16).



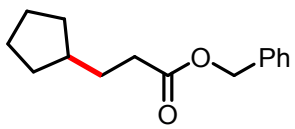
According to the *general procedure*.
Yellow oil (60.1 mg, 71%).
R_f 0.40 (Petroleum ether/EtOAc, 40/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 13.6 Hz, 5H), 7.25 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 3H), 5.09 (s, 2H), 2.58 (t, J = 7.6 Hz, 2H), 2.33 (t, J = 7.6 Hz, 2H), 1.79 – 1.54 (m, 4H), 1.43 – 1.28 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 142.5, 136.2, 128.6, 128.5, 128.4, 128.3, 128.2, 125.7, 66.2, 35.8, 34.3, 31.1, 28.8, 24.9.
HRMS (ESI) calcd for $C_{19}H_{26}NO_2$ $[M + NH_4]^+$ 300.1958, found 300.1956.

benzyl 5-(4-iodophenyl)pentanoate (17).



According to the *general procedure*.
Yellow oil (80.4 mg, 68%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.49 (m, 2H), 7.34 (d, J = 5.6 Hz, 5H), 6.96 – 6.82 (m, 2H), 5.10 (s, 2H), 2.54 (t, J = 7.2 Hz, 2H), 2.36 (t, J = 6.4 Hz, 2H), 1.71 – 1.52 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 141.7, 137.4, 136.1, 130.6, 128.6, 128.3, 90.9, 66.2, 35.1, 34.1, 30.7, 24.5.
HRMS (ESI) calcd for $C_{18}H_{23}INO_2$ $[M + NH_4]^+$ 412.0768, found 412.0759.

benzyl 3-cyclopentylpropanoate (18).



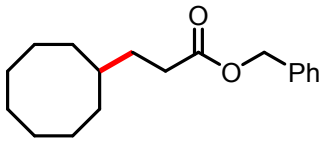
According to the *general procedure*.
Yellow oil (55.7 mg, 80%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 5H), 5.11 (s, 2H), 2.36 (s, 2H), 1.87 – 1.40 (m, 9H), 1.08 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 136.2, 128.6, 128.2, 66.2, 39.8, 33.8, 32.5, 31.2, 25.2.

HRMS (ESI) calcd for $C_{15}H_{24}NO_2$ $[M + NH_4]^+$ 250.1802, found 250.1803.

benzyl 3-cyclooctylpropanoate (19).



According to the *general procedure*.

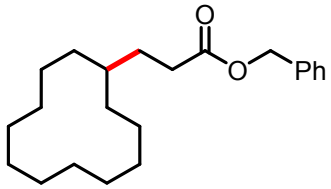
Yellow oil (61.6 mg, 75%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.26 (m, 5H), 5.11 (s, 2H), 2.45 – 2.29 (m, 2H), 1.72 – 1.51 (m, 9H), 1.50 – 1.35 (m, 6H), 1.32 – 1.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 136.2, 128.6, 128.3, 128.2, 66.2, 36.9, 33.1, 32.6, 32.1, 27.3, 26.4, 25.5.

HRMS (ESI) calcd for $C_{18}H_{30}NO_2$ $[M + NH_4]^+$ 292.2271, found 292.2270.

benzyl 3-cyclododecylpropanoate (20).



According to the *general procedure*.

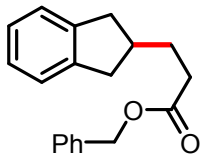
Yellow oil (60.4 mg, 61%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.11 (s, 2H), 2.44 – 2.29 (m, 2H), 1.57 (dd, J = 15.2, 7.2 Hz, 2H), 1.43 – 1.19 (m, 23H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 136.2, 128.6, 128.3, 128.2, 66.2, 33.6, 32.5, 30.1, 28.8, 24.8, 24.2, 23.4, 23.3, 21.7.

HRMS (ESI) calcd for $C_{22}H_{38}NO_2$ $[M + NH_4]^+$ 348.2897, found 348.2896.

benzyl 3-(2,3-dihydro-1H-inden-2-yl)propanoate (21).



According to the *general procedure*.

Yellow oil (61.3 mg, 73%).

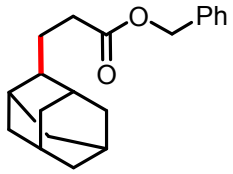
R_f 0.30 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 7.15 (dt, J = 7.2, 3.6 Hz, 2H), 7.13 – 7.06 (m, 2H), 5.11 (s, 2H), 3.02 (dd, J = 15.2, 8.0 Hz, 2H), 2.57 (dd, J = 15.2, 8.0 Hz, 2H), 2.48 – 2.37 (m, 3H), 1.86 (dd, J = 15.2, 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 143.1, 136.1, 128.7,

128.3, 126.2, 124.5, 66.3, 39.7, 39.0, 33.3, 30.8.

HRMS (ESI) calcd for $C_{19}H_{24}NO_2$ $[M + NH_4]^+$ 298.1802, found 298.1802.

benzyl 3-(adamantan-2-yl)propanoate (22).



According to the *general procedure*.

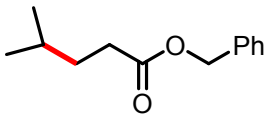
Colorless oil (66.2 mg, 74%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.11 (s, 2H), 2.39 – 2.28 (m, 2H), 1.93 – 1.75 (m, 8H), 1.69 (d, J = 13.2 Hz, 6H), 1.60 (t, J = 7.2 Hz, 1H), 1.49 (d, J = 12.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 136.2, 128.6, 128.3, 128.2, 66.2, 44.1, 39.2, 38.4, 32.7, 31.7, 31.6, 28.3, 28.1, 27.9.

HRMS (ESI) calcd for $C_{20}H_{30}NO_2$ $[M + NH_4]^+$ 316.2271, found 316.2270.

benzyl 4-methylpentanoate (23).



According to the *general procedure*.

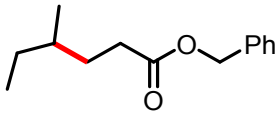
Yellow oil (46.4 mg, 75%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.26 (m, 5H), 5.11 (s, 2H), 2.44 – 2.28 (m, 2H), 1.64 – 1.48 (m, 3H), 0.89 (d, J = 6.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 136.2, 128.6, 128.3, 66.2, 33.8, 32.5, 27.8, 22.3.

HRMS (ESI) calcd for $C_{13}H_{22}NO_2$ $[M + NH_4]^+$ 224.1645, found 224.1639.

benzyl (R)-4-methylhexanoate (24).



According to the *general procedure*.

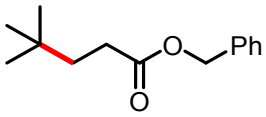
Yellow oil (48.8 mg, 74%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.26 (m, 5H), 5.11 (s, 2H), 2.47 – 2.22 (m, 2H), 1.79 – 1.61 (m, 1H), 1.46 (ddd, J = 17.2, 10.8, 4.0 Hz, 1H), 1.39 – 1.26 (m, 2H), 1.21 – 1.07 (m, 1H), 0.97 – 0.76 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 136.2, 128.6, 128.3, 128.2, 66.2, 34.1, 32.2, 31.6, 29.2, 18.9, 11.4.

HRMS (ESI) calcd for $C_{14}H_{24}NO_2$ $[M + NH_4]^+$ 238.1802, found 238.1809.

benzyl 4,4-dimethylpentanoate (25).



According to the *general procedure*.

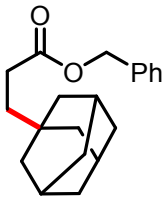
Yellow oil (54.1 mg, 82%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.26 (m, 5H), 5.10 (d, J = 2.0 Hz, 2H), 2.43 – 2.24 (m, 2H), 1.68 – 1.49 (m, 2H), 0.88 (d, J = 2.0 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.3, 136.2, 128.6, 128.3, 128.2, 66.3, 38.6, 30.2, 30.1, 29.1.

HRMS (ESI) calcd for $C_{14}H_{24}NO_2$ $[M + NH_4]^+$ 238.1802, found 238.1802.

benzyl 3-(adamantan-1-yl)propanoate (26).



According to the *general procedure*.

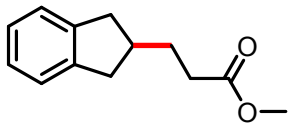
Colorless oil (71.5 mg, 80%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.26 (m, 5H), 5.10 (d, J = 2.4 Hz, 2H), 2.41 – 2.25 (m, 2H), 1.94 (s, 3H), 1.69 (d, J = 11.6 Hz, 3H), 1.60 (d, J = 11.6 Hz, 3H), 1.45 (s, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6, 136.2, 128.6, 128.3, 128.2, 66.2, 42.1, 39.0, 37.1, 32.0, 28.7, 28.3.

HRMS (ESI) calcd for $C_{20}H_{30}NO_2$ $[M + NH_4]^+$ 316.2271, found 316.2269.

methyl 3-(2,3-dihydro-1H-inden-2-yl)propanoate (27).



According to the *general procedure*.

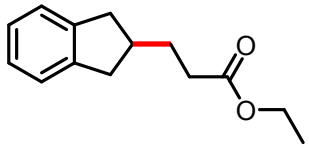
Yellow oil (58.1 mg, 95%).

R_f 0.40 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 2H), 3.68 (d, J = 2.4 Hz, 3H), 3.12 – 2.97 (m, 2H), 2.59 (dd, J = 15.2, 8.0 Hz, 2H), 2.52 – 2.33 (m, 3H), 1.85 (qd, J = 8.0, 2.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2, 143.2, 126.2, 124.5, 51.7, 39.7, 39.0, 33.1, 30.8.

HRMS (ESI) calcd for $C_{13}H_{20}NO_2$ $[M + NH_4]^+$ 222.1489, found 222.1493.

ethyl 3-(2,3-dihydro-1H-inden-2-yl)propanoate (28).



According to the *general procedure*.

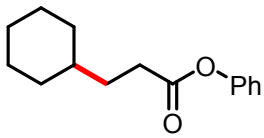
Colorless oil (62.1 mg, 95%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 4.13 (tt, J = 7.2, 3.6 Hz, 2H), 3.04 (dd, J = 15.6, 7.6 Hz, 2H), 2.59 (dd, J = 15.6, 8.0 Hz, 2H), 2.41 (ddd, J = 15.6, 11.6, 4.4 Hz, 3H), 1.84 (dt, J = 8.4, 4.0 Hz, 2H), 1.26 (td, J = 7.2, 1.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7, 143.2, 126.2, 124.5, 60.4, 39.7, 39.0, 33.3, 30.8, 14.3.

HRMS (ESI) calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1380.

phenyl 3-cyclohexylpropanoate (29).



According to the *general procedure*.

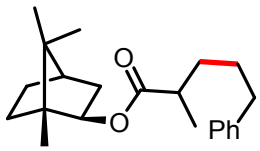
Yellow oil (58.5 mg, 84%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (t, J = 8.0 Hz, 2H), 7.22 (dd, J = 13.2, 5.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 1.82 – 1.60 (m, 7H), 1.41 – 1.09 (m, 4H), 0.94 (dd, J = 22.4, 10.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 150.9, 129.5, 125.8, 121.7, 37.3, 33.1, 32.4, 32.1, 26.6, 26.3.

HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $[M + H]^+$ 233.1536, found 233.1533.

(1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-methyl-5-phenylpentanoate (30).



According to the *general procedure*.

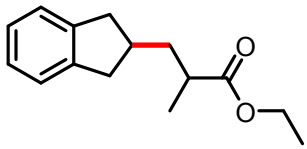
Yellow oil (33.5 mg, 34%).

R_f 0.35 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.64 (dd, J = 7.6, 2.8 Hz, 1H), 2.71 – 2.53 (m, 2H), 2.51 – 2.35 (m, 1H), 1.88 – 1.35 (m, 10H), 1.22 – 1.03 (m, 5H), 1.01 – 0.92 (m, 3H), 0.90 – 0.78 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 142.3, 128.5, 128.41, 125.8, 80.7, 48.8, 48.7, 47.0, 45.1, 40.0, 39.9, 39.0, 36.0, 35.9, 33.9, 33.4, 33.3, 29.2, 27.2, 20.2, 20.0, 17.3, 17.2, 11.6, 11.5.

HRMS (ESI) calcd for $C_{22}H_{36}NO_2$ $[M + NH_4]^+$ 346.2741, found 346.2735.

ethyl 3-(2,3-dihydro-1H-inden-2-yl)-2-methylpropanoate (31).



According to the *general procedure*.

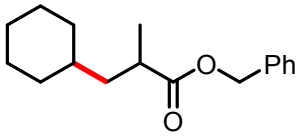
Yellow oil (51.5 mg, 74%).

R_f 0.40 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 2H), 7.14 – 7.07 (m, 2H), 4.14 (qd, J = 7.2, 2.4 Hz, 2H), 3.04 (ddd, J = 22.4, 15.6, 7.2 Hz, 2H), 2.71 – 2.36 (m, 4H), 2.00 – 1.84 (m, 1H), 1.58 (ddd, J = 13.6, 8.0, 2.4 Hz, 1H), 1.26 (td, J = 7.2, 2.4 Hz, 3H), 1.19 (dd, J = 6.8, 2.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 143.3, 126.2, 124.5, 60.3, 39.9, 39.3, 39.3, 38.7, 38.3, 17.7, 14.4.

HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $[M + H]^+$ 233.1536, found 233.1533.

benzyl 3-cyclohexyl-2-methylpropanoate (32).



According to the *general procedure*.

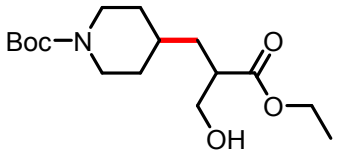
Yellow oil (45.2 mg, 58%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 5.17 – 5.06 (m, 2H), 2.60 (dd, J = 12.4, 6.4 Hz, 1H), 1.78 – 1.59 (m, 6H), 1.29 – 1.11 (m, 8H), 0.94 – 0.73 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.2, 136.4, 128.6, 128.2, 66.0, 41.7, 37.0, 35.5, 33.3, 33.2, 26.6, 26.3, 17.7.

HRMS (ESI) calcd for $C_{17}H_{25}O_2$ $[M + H]^+$ 261.1849, found 261.1844.

tert-butyl 4-(3-ethoxy-2-(hydroxymethyl)-3-oxopropyl)piperidine-1-carboxylate (33).



According to the *general procedure*.

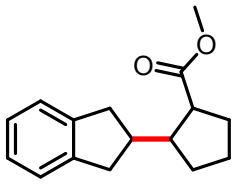
Yellow oil (48.2 mg, 51%).

R_f 0.30 (Petroleum ether/EtOAc, 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 4.32 – 4.13 (m, 4H), 4.02 (t, J = 11.6 Hz, 2H), 2.61 – 2.41 (m, 2H), 2.31 (s, 5H), 1.44 (s, 9H), 1.30 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 155.0, 145.3, 79.3, 59.9, 44.1, 37.7, 28.6, 27.9, 19.7, 14.5.

HRMS (ESI) calcd for $C_{16}H_{30}NO_5$ $[M + H]^+$ 316.2118, found 316.2119.

methyl (2S)-2-(2,3-dihydro-1H-inden-2-yl)cyclopentane-1-carboxylate (34).



According to the *general procedure*. Obtained as a trans/cis mixture in a 4/1 ratio.

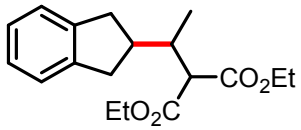
Colorless oil (30.3 mg, 41%).

R_f 0.50 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 4H), 3.78 – 3.64 (m, 3H), 3.11 – 2.90 (m, 2H), 2.64 (dt, J = 15.6, 7.6 Hz, 2H), 2.57 – 2.27 (m, 3H), 2.03 – 1.79 (m, 3H), 1.79 – 1.62 (m, 2H),

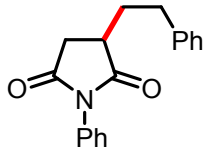
1.38 (dt, J = 14.8, 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.5, 143.5, 143.3, 126.1, 126.0, 124.3, 124.2, 51.7, 49.2, 49.1, 45.5, 37.8, 31.5, 31.3, 25.2.
HRMS (ESI) calcd for $C_{16}H_{21}O_2$ $[M + H]^+$ 245.1536, found 245.1536.

diethyl (R)-2-(1-(2,3-dihydro-1H-inden-2-yl)ethyl)malonate (35).



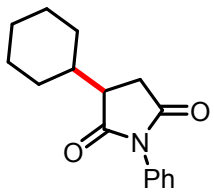
According to the *general procedure*.
Yellow oil (50.2 mg, 55%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 2H), 7.15 – 7.09 (m, 2H), 4.32 – 4.14 (m, 4H), 3.51 (dd, J = 6.0, 1.2 Hz, 1H), 3.15 – 2.90 (m, 2H), 2.78 – 2.58 (m, 2H), 2.54 – 2.34 (m, 2H), 1.28 (t, J = 7.2 Hz, 6H), 1.13 – 1.03 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 168.7, 143.1, 143.0, 126.3, 124.4, 124.3, 61.4, 61.2, 56.0, 43.9, 38.3, 37.8, 36.5, 14.6, 14.3, 14.2.
HRMS (ESI) calcd for $C_{18}H_{25}O_4$ $[M + H]^+$ 305.1747, found 305.1751.

(R)-3-phenethyl-1-phenylpyrrolidine-2,5-dione (36).



According to the *general procedure*.
Yellow solid (32.6 mg, 39%). M.p. = 87 – 88 °C.
R_f 0.40 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.24 (dd, J = 16.4, 8.0 Hz, 5H), 3.06 – 2.88 (m, 2H), 2.87 – 2.68 (m, 2H), 2.65 – 2.48 (m, 1H), 2.42 – 2.26 (m, 1H), 1.94 (td, J = 14.4, 8.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 175.5, 140.3, 131.9, 129.3, 128.8, 128.7, 128.6, 126.6, 126.5, 39.3, 34.7, 33.2, 33.1.
HRMS (ESI) calcd for $C_{18}H_{18}NO_2$ $[M + H]^+$ 280.1332, found 280.1333.

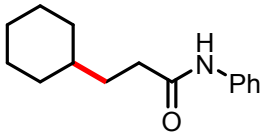
(R)-3-cyclohexyl-1-phenylpyrrolidine-2,5-dione (37).



According to the *general procedure*.
White solid (43.2 mg, 56%). M.p. = 103 – 104 °C.
R_f 0.60 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 2H), 2.98 – 2.74 (m, 2H), 2.63 (dd, J = 18.0, 3.6 Hz, 1H), 2.02 (dd, J = 11.6, 8.8 Hz, 1H), 1.83 – 1.63 (m, 4H), 1.56 (d, J = 13.2 Hz, 1H), 1.35 – 1.02 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

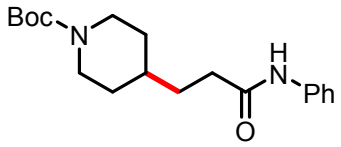
178.6, 176.1, 132.0, 129.3, 128.7, 126.6, 45.6, 39.3, 31.4, 30.5, 27.7, 26.3, 26.1, 25.9.
HRMS (ESI) calcd for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1489, found 258.1488.

3-cyclohexyl-N-phenylpropanamide (38).



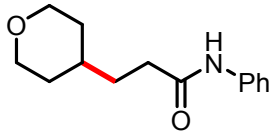
According to the *general procedure*.
Yellow solid (47.8 mg, 69%). M.p. = 88 – 89 °C.
R_f 0.40 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 2.44 – 2.27 (m, 2H), 1.79 – 1.56 (m, 7H), 1.37 – 1.10 (m, 4H), 1.01 – 0.82 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 138.2, 129.0, 124.2, 119.9, 37.4, 35.4, 33.2, 33.1, 26.6, 26.3.
HRMS (ESI) calcd for $C_{15}H_{22}NO$ $[M + H]^+$ 232.1696, found 232.1697.

tert-butyl 4-(3-oxo-3-(phenylamino)propyl)piperidine-1-carboxylate (39).



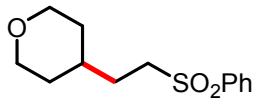
According to the *general procedure*.
Yellow solid (46.8 mg, 47%). M.p. = 120 – 121 °C.
R_f 0.30 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 4.06 (s, 2H), 2.64 (s, 2H), 2.37 (t, J = 7.6 Hz, 2H), 1.63 (d, J = 13.2 Hz, 4H), 1.49 – 1.37 (m, 10H), 1.06 (qd, J = 12.6, 4.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 154.9, 138.3, 128.9, 124.1, 119.9, 79.5, 44.6, 43.5, 35.5, 34.5, 32.0, 28.5.
HRMS (ESI) calcd for $C_{19}H_{28}NaN_2O_3$ $[M + Na]^+$ 355.1992, found 355.1989.

N-phenyl-3-(tetrahydro-2H-pyran-4-yl)propanamide (40).



According to the *general procedure*.
Yellow oil (37.0 mg, 53%).
R_f 0.30 (Petroleum ether/EtOAc, 4/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 3.93 (dd, J = 11.2, 4.0 Hz, 2H), 3.35 (dd, J = 17.2, 6.2 Hz, 2H), 2.44 – 2.29 (m, 2H), 1.66 (dd, J = 14.8, 7.2 Hz, 2H), 1.62 – 1.46 (m, 3H), 1.35 – 1.13 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 138.1, 128.9, 124.3, 120.0, 67.9, 34.5, 34.4, 32.8, 32.4.
HRMS (ESI) calcd for $C_{14}H_{20}NO_2$ $[M + H]^+$ 234.1489, found 234.1489.

4-(2-(phenylsulfonyl)ethyl)tetrahydro-2H-pyran (41).



According to the *general procedure*.

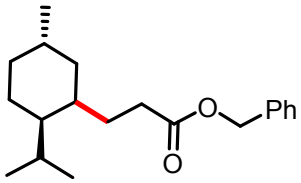
Yellow oil (54.9 mg, 72%).

R_f 0.40 (Petroleum ether/EtOAc, 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 3.92 (dd, J = 11.2, 4.0 Hz, 2H), 3.32 (dd, J = 17.6, 6.0 Hz, 2H), 3.20 – 3.04 (m, 2H), 1.72 – 1.62 (m, 2H), 1.62 – 1.48 (m, 3H), 1.24 (ddd, J = 24.8, 12.8, 3.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.0, 133.8, 129.3, 127.9, 67.6, 53.6, 33.8, 32.4, 29.2.

HRMS (ESI) calcd for $C_{13}H_{19}O_3S$ $[M + H]^+$ 255.1049, found 255.1053.

benzyl 3-((1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)propanoate (42).



According to the *general procedure*.

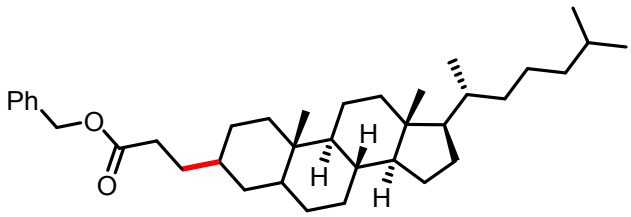
Yellow oil (60.7 mg, 67%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 5H), 5.06 – 4.95 (m, 2H), 2.41 – 2.04 (m, 2H), 1.93 – 1.65 (m, 2H), 1.53 (ddt, J = 30.8, 24.0, 13.2 Hz, 4H), 1.42 – 1.06 (m, 3H), 0.82 – 0.69 (m, 9H), 0.60 (d, J = 6.8 Hz, 2H), 0.51 (dd, J = 24.0, 12.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2, 174.0, 155.9, 136.2, 136.1, 135.1, 128.6, 128.3, 128.2, 128.1, 66.2, 66.1, 62.9, 48.2, 46.9, 46.5, 42.6, 40.8, 40.4, 38.2, 37.8, 37.5, 35.8, 35.6, 35.3, 34.6, 32.8, 32.7, 31.9, 31.0, 30.3, 29.2, 27.8, 26.4, 25.9, 25.3, 25.1, 24.8, 24.2, 23.7, 22.8, 22.5, 21.7, 21.6, 20.7, 20.5, 18.5, 15.2.

HRMS (ESI) calcd for $C_{20}H_{31}O_2$ $[M + H]^+$ 303.2319, found 303.2318.

benzyl 3-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl)propanoate (43).



According to the *general procedure*.

Yellow solid (64.1 mg, 40%). M.p. = 45 – 46 °C.

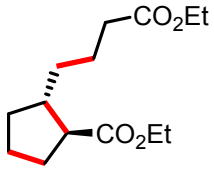
R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.27 (m, 5H), 5.11 (s, 2H), 2.34 (dd, J = 16.8, 10.0 Hz, 2H), 1.95 (d, J = 12.0 Hz, 1H), 1.84 – 1.41 (m, 10H), 1.33 (m, 5H), 1.27 – 0.94 (m, 16H), 0.88 (m, 10H), 0.75 (d, J = 17.2 Hz, 3H), 0.66 (d, J = 17.2 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1,

174.0, 136.2, 128.7, 128.4, 128.3, 128.2, 66.2, 66.1, 56.7, 56.4, 56.3, 54.8, 54.7, 46.6, 42.7, 40.4, 40.2, 39.6, 38.6, 37.7, 36.5, 36.3, 36.2, 35.9, 35.6, 35.4, 33.3, 33.2, 32.9, 32.7, 32.4, 32.3, 32.2, 32.1, 29.1, 29.0, 28.7, 28.4, 28.1, 27.2, 25.4, 24.3, 23.9, 22.9, 22.7, 21.1, 20.9, 18.8, 12.4, 12.2, 11.8.

HRMS (ESI) calcd for $C_{37}H_{59}O_2$ $[M + H]^+$ 535.4510, found 535.4518.

ethyl (1S)-2-(4-ethoxy-4-oxobutyl)cyclopentane-1-carboxylate (51).



According to the *general procedure*. Obtained as a trans/cis mixture in a 58/42 ratio.[2] The spectral data of the alkyl iodides are consistent with the literature data.[2]

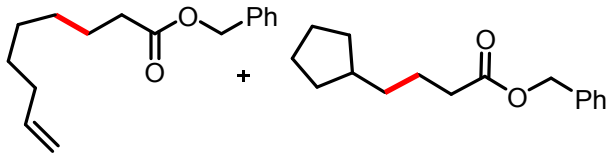
Yellow oil (33.1 mg, 36%).

R_f 0.40 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 – 4.00 (m, 4H), 2.90 – 2.74 (m, 1H), 2.38 – 2.21 (m, 2H), 2.07 (dd, J = 16.0, 7.6 Hz, 1H), 1.92 – 1.75 (m, 3H), 1.72 – 1.18 (m, 13H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 175.5, 173.7, 60.3, 59.9, 50.5, 47.6, 44.1, 43.6, 34.9, 34.6, 34.5, 32.6, 31.1, 30.7, 30.4, 28.5, 24.8, 24.1, 23.9, 23.7, 14.4, 14.3.

HRMS (ESI) calcd for $C_{14}H_{25}O_4$ $[M + H]^+$ 257.1747, found 257.1749.

benzyl non-8-enoate and benzyl 4-cyclopentylbutanoate (53).



According to the *general procedure*.

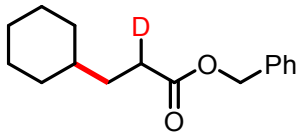
Yellow oil (42.1 mg, 57%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 5H), 5.86 – 5.70 (m, 0.2H), 5.11 (s, 2H), 5.04 – 4.88 (m, 0.4H), 2.35 (t, J = 7.6 Hz, 2H), 2.02 (dd, J = 14.0, 6.8 Hz, 1H), 1.81 – 1.42 (m, 8H), 1.40 – 1.23 (m, 3H), 1.05 (dd, J = 5.6, 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 139.1, 136.2, 128.6, 128.3, 128.2, 114.4, 66.2, 39.9, 35.7, 34.7, 34.4, 33.8, 32.7, 29.0, 28.8, 25.3, 25.0, 24.3.

HRMS (ESI) calcd for $C_{16}H_{23}O_2$ $[M + H]^+$ 247.1693, found 247.1696.

benzyl 3-cyclohexylpropanoate-2-d (d-3).



According to the *general procedure*.

Yellow oil (66.7 mg, 90%).

R_f 0.40 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 5H), 5.11 (s, 2H), 2.41 – 2.29 (m, 1H), 1.66 (t, J = 15.2 Hz, 5H), 1.54 (t, J = 7.2 Hz, 2H), 1.27 – 1.08 (m, 4H), 0.87 (dd, J = 21.4, 11.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 136.2, 128.6, 128.3, 128.2, 66.2, 37.3, 33.1, 32.4, 31.7 (t, J = 19.4 Hz), 26.6, 26.3.

HRMS (ESI) calcd for $C_{16}H_{22}DO_2$ $[M + H]^+$ 248.1755, found 248.1752.

6. General procedure for Suzuki coupling reaction

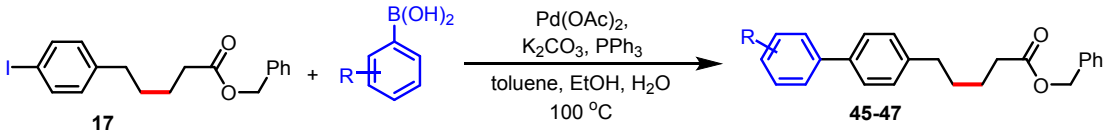
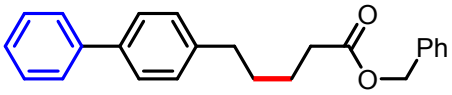


Figure S7

Synthesized pure compound **17** (0.3 mmol, 1.0 equiv), corresponding boronic acid (0.33 mmol, 1.1 equiv), K_2CO_3 (0.6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.015 mmol, 5.0 mol %), PPh_3 (0.045 mmol, 0.15 equiv), toluene (3.3 mL, 0.113M), equal mixture of ethanol/water (0.34 mL, 0.565 M) were taken into a re-sealable pressure tube (13 x 100 mm) and was allowed it to stir at 100 °C for 24h. After finishing the reaction, the solvent mixture was evaporated and again diluted with dicholomethane (20 mL). This diluted mixture was then passed through a celite bed followed by the washing of this bed with additional amount of dicholomethane (20 mL). This combined organic layer was washed with water (1 x 20 mL) using a separating funnel. The collected organic layer was dried over $MgSO_4$ and solvent was evaporated under reduced pressure. This crude product was then subjected to purification using flash column chromatography to get pure product.

benzyl 5-([1,1'-biphenyl]-4-yl)pentanoate (45).



According to the *general procedure*.

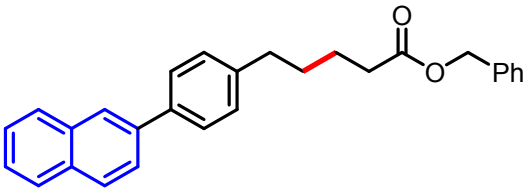
White solid (71.2 mg, 69%). M.p. = 45 – 46 °C.

R_f 0.25 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.47 – 7.28 (m, 8H), 7.23 (t, J = 5.6 Hz, 2H), 5.11 (s, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.40 (t, J = 7.2 Hz, 2H), 1.80 – 1.62 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 141.4, 141.2, 138.9, 136.2, 128.9, 128.8, 128.7, 128.3, 127.2, 127.1, 66.3, 35.3, 34.3, 30.9, 24.7.

HRMS (ESI) calcd for $C_{24}H_{28}NO_2$ $[M + NH_4]^+$ 362.2115, found 362.2108.

benzyl 5-(4-(naphthalen-2-yl)phenyl)pentanoate (46).



According to the *general procedure*.

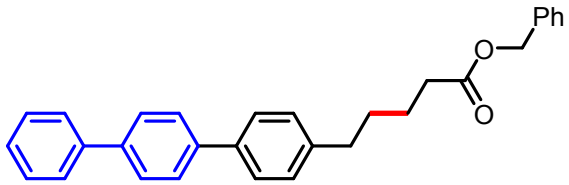
White solid (76.8 mg, 65%). M.p. = 43 – 44 °C.

R_f 0.25 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 – 7.79 (m, 3H), 7.72 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.52 – 7.40 (m, 2H), 7.31 (dt, J = 10.4, 4.4 Hz, 5H), 7.25 (d, J = 8.0 Hz, 2H), 5.11 (s, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.39 (t, J = 6.8 Hz, 2H), 1.80 – 1.61 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 141.4, 138.7, 138.5, 136.1, 133.8, 132.6, 129.0, 128.7, 128.4, 128.3, 128.2, 127.7, 127.4, 126.3, 125.9, 125.6, 125.6, 66.2, 35.3, 34.2, 30.9, 24.7.

HRMS (ESI) calcd for $C_{28}H_{30}NO_2$ $[M + NH_4]^+$ 412.2271, found 412.2268.

benzyl 5-([1,1':4',1''-terphenyl]-4-yl)pentanoate (47).



According to the *general procedure*. Synthesized pure compound **17** (3 mmol, 1.0 equiv), corresponding boronic acid (3.3 mmol, 1.1 equiv), K_2CO_3 (6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.15 mmol, 5.0 mol %), PPh_3 (0.45 mmol, 0.15 equiv), toluene (33 mL, 0.113M), equal mixture of ethanol/water (3.4 mL, 0.565 M) were taken into a re-sealable pressure tube (100 mL) and was allowed it to stir at 100 ^{o}C for 24h.

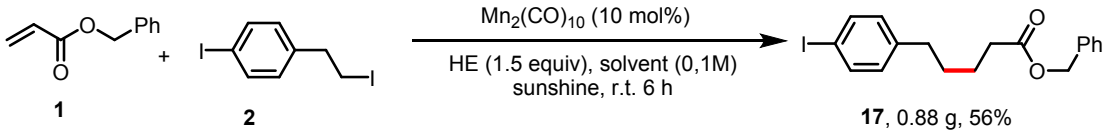
Yellow solid (0.76 g, 60%). M.p. = 105 – 106 °C.

R_f 0.25 (Petroleum ether/EtOAc, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 6H), 7.55 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.24 (d, J = 8.0 Hz, 2H), 5.12 (s, 2H), 2.67 (t, J = 7.2 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.71 (dd, J = 8.0, 4.4 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 141.5, 140.9, 140.1, 139.9, 138.3, 136.2, 129.0, 128.9, 128.7, 128.3, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 66.3, 35.3, 34.3, 30.9, 24.7.

HRMS (ESI) calcd for $C_{30}H_{30}NO_2$ $[M + NH_4]^+$ 438.2428, found 438.2427.

7. Gram-scale reaction



1 **2** **17**, 0.88 g, 56%

Figure S8

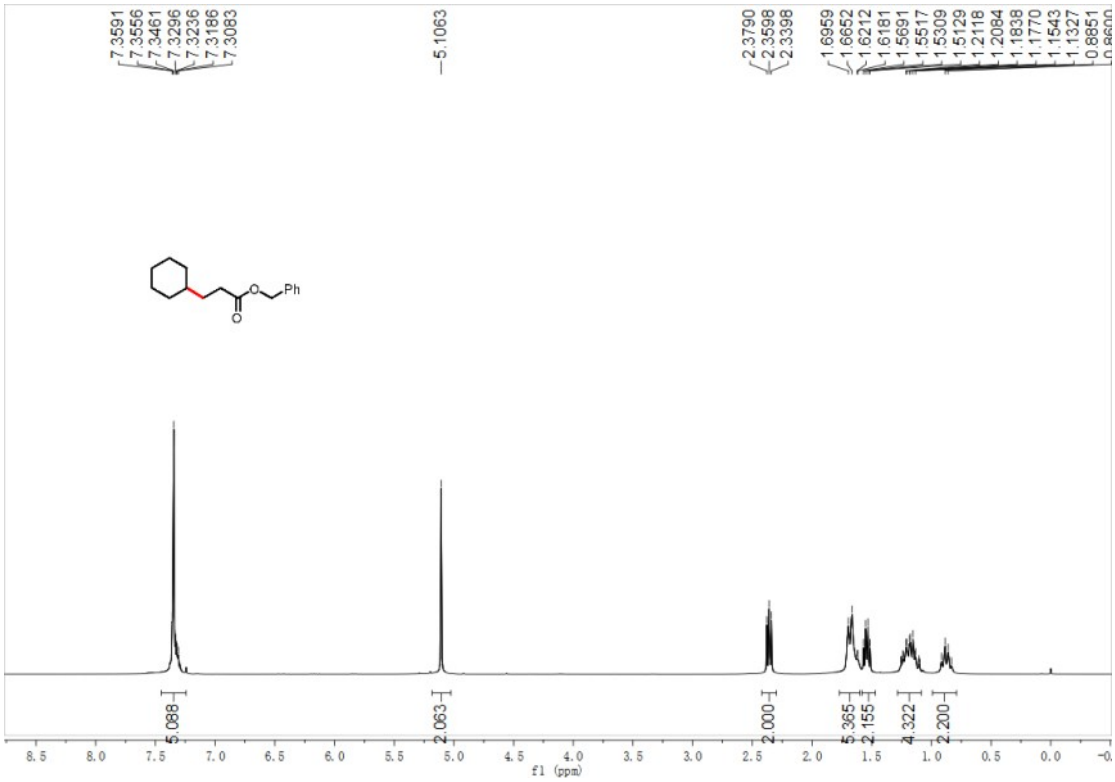
To an oven dried Schlenk tube was added $Mn_2(CO)_{10}$ (156 mg, 0.4 mmol, 10 mol %), Michael acceptors (4.0 mmol, 1.0 equiv), iodoalkanes (8.0 mmol, 2.0 equiv), HEH (6.0 mmol, 1.5 equiv) and 40 mL of DMSO. The tube was evacuated and backfilled with Ar (this process was repeated three times). The mixture was then stirred rapidly and irradiated under shushine at room temperature for 6 h. The mixture was diluted with 50 mL of aqueous 1 M $NaHCO_3$ solution, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na_2SO_4, and concentrated in vacuum. After purification by flash column chromatography on silica gel, the product was obtained in 56%.

References

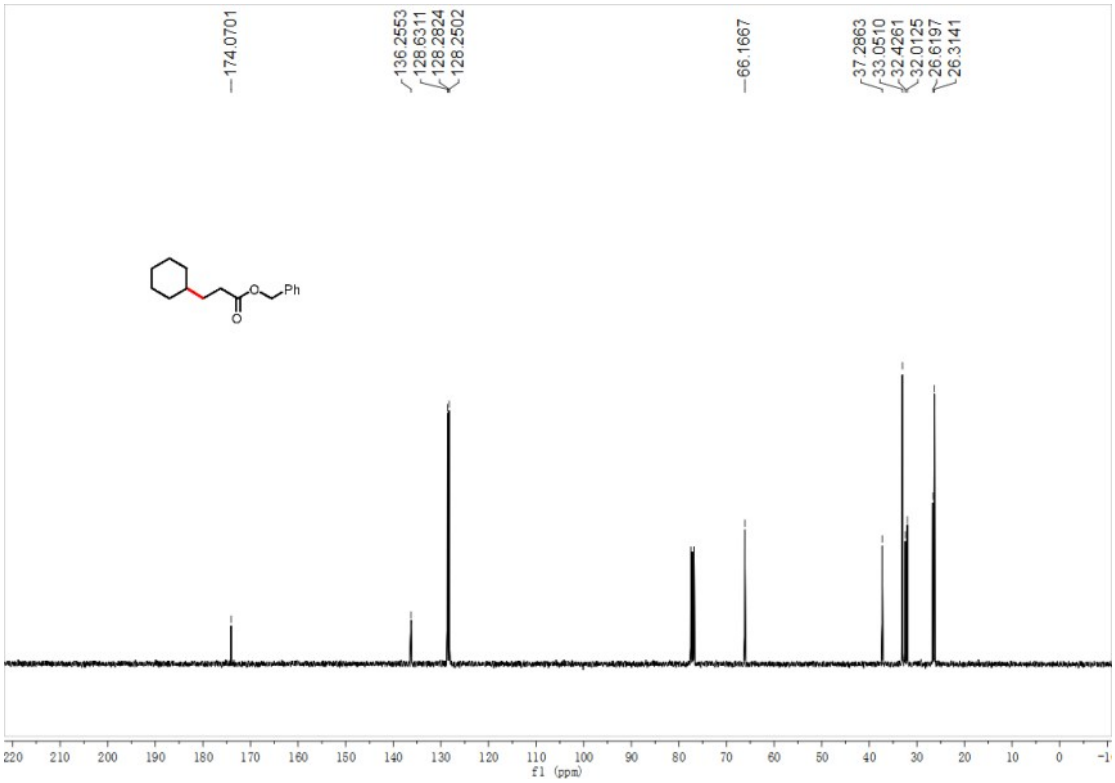
[1] S. Rezazadeh, V. Devannah, D. A. Watson, *J. Am. Chem. Soc*. 2017, **139**, 8110.
[2] S. Sumino, I. Ryu, *Org. Lett*. 2016, **18**, 52.

NMR Spectra

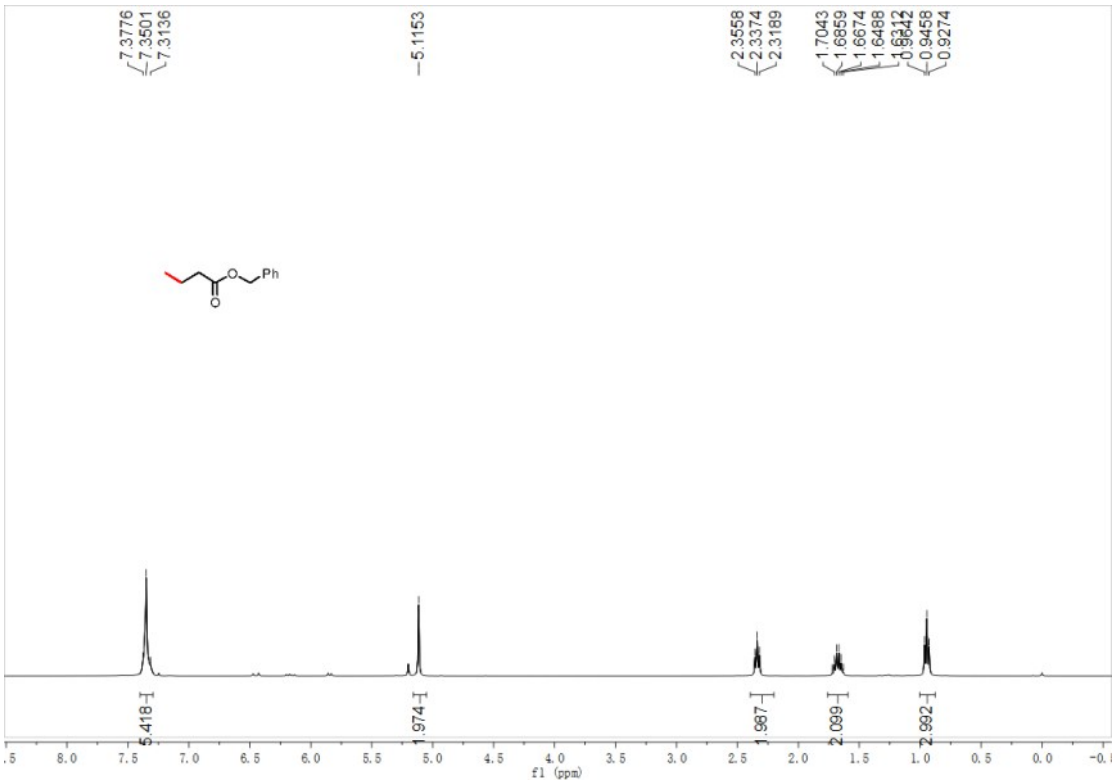
^{1}H NMR spectrum of compound **3**



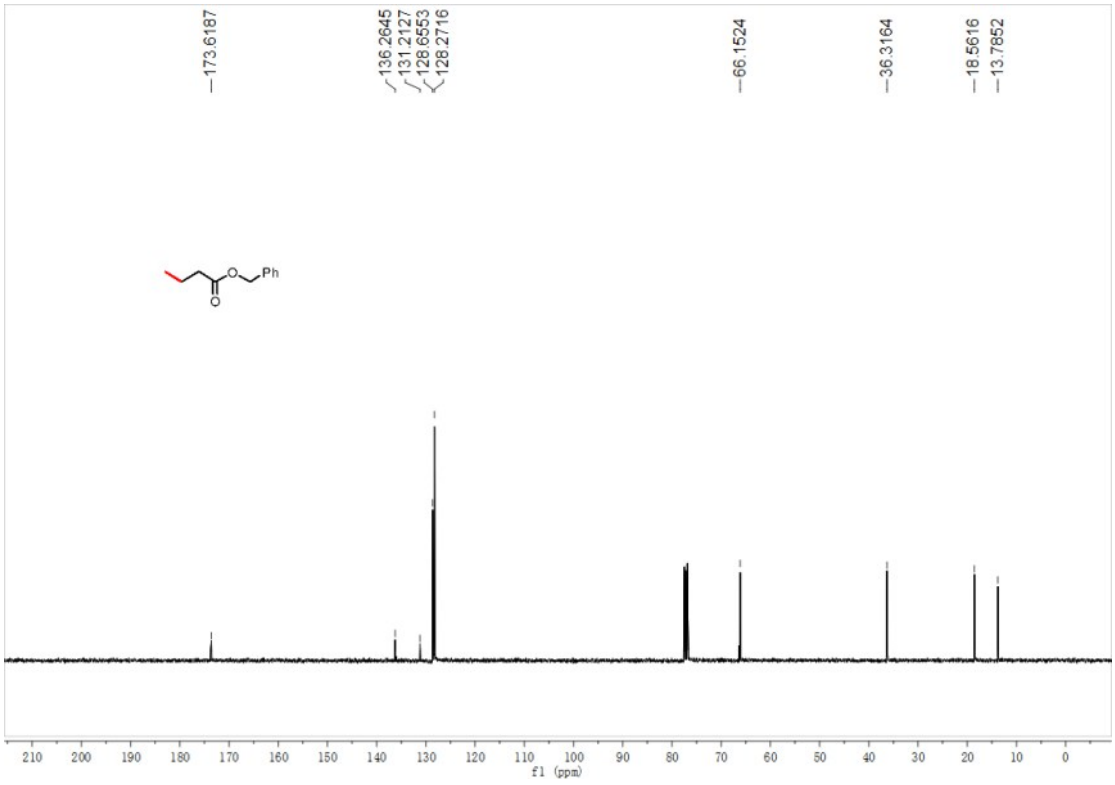
^{13}C NMR spectrum of compound **3**



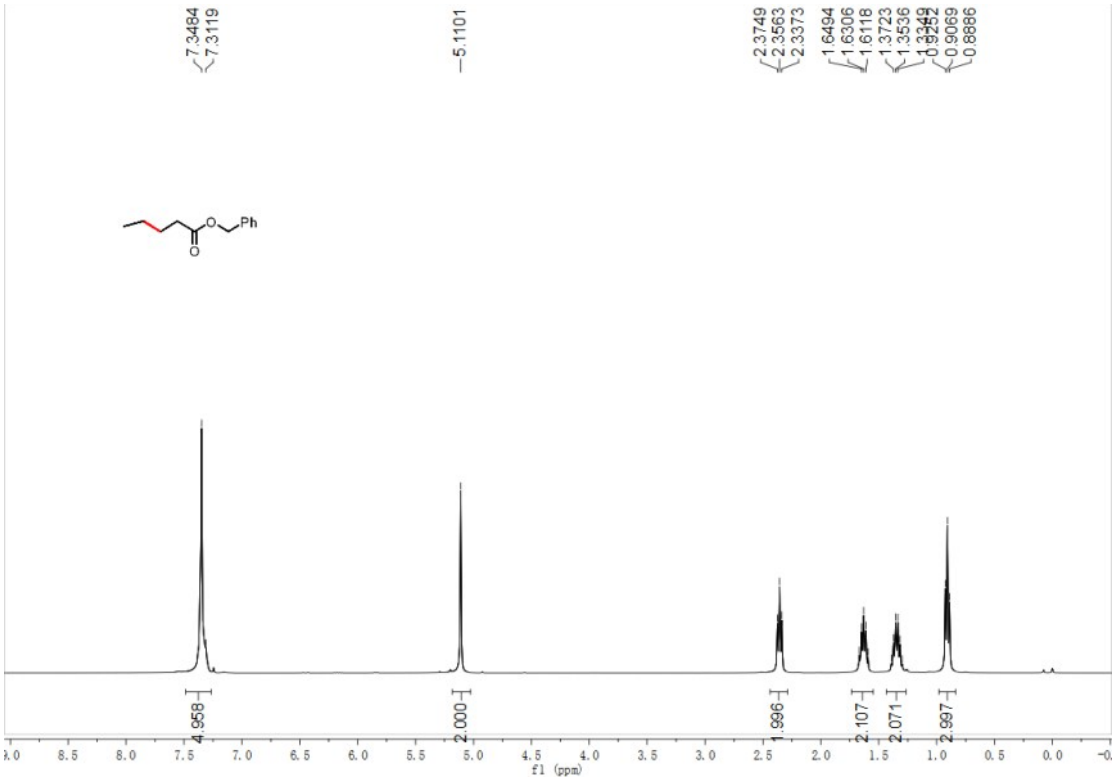
^{1}H NMR spectrum of compound **4**



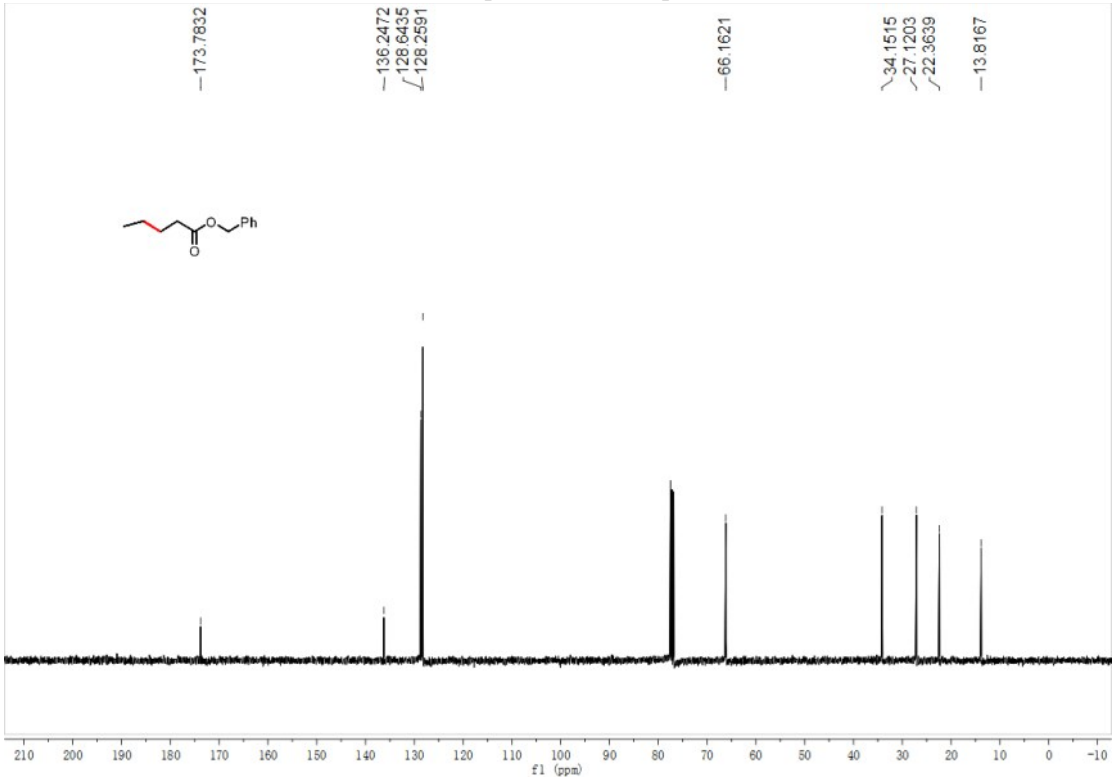
^{13}C NMR spectrum of compound **4**



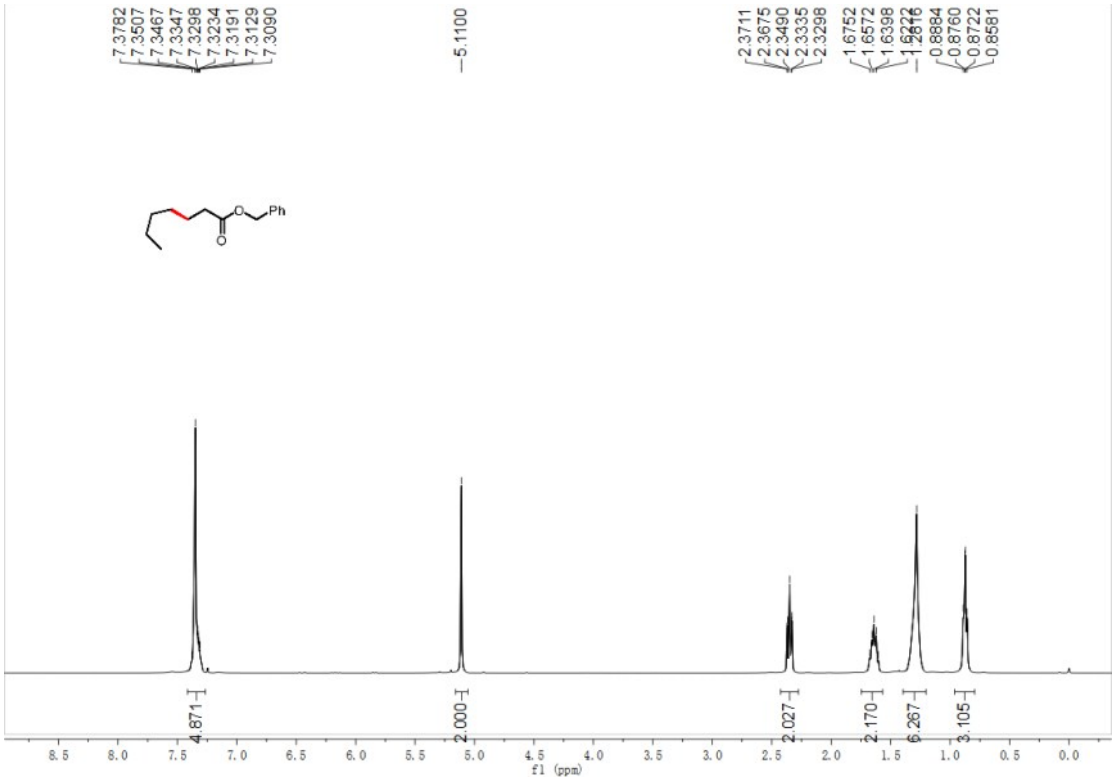
^{1}H NMR spectrum of compound **5**



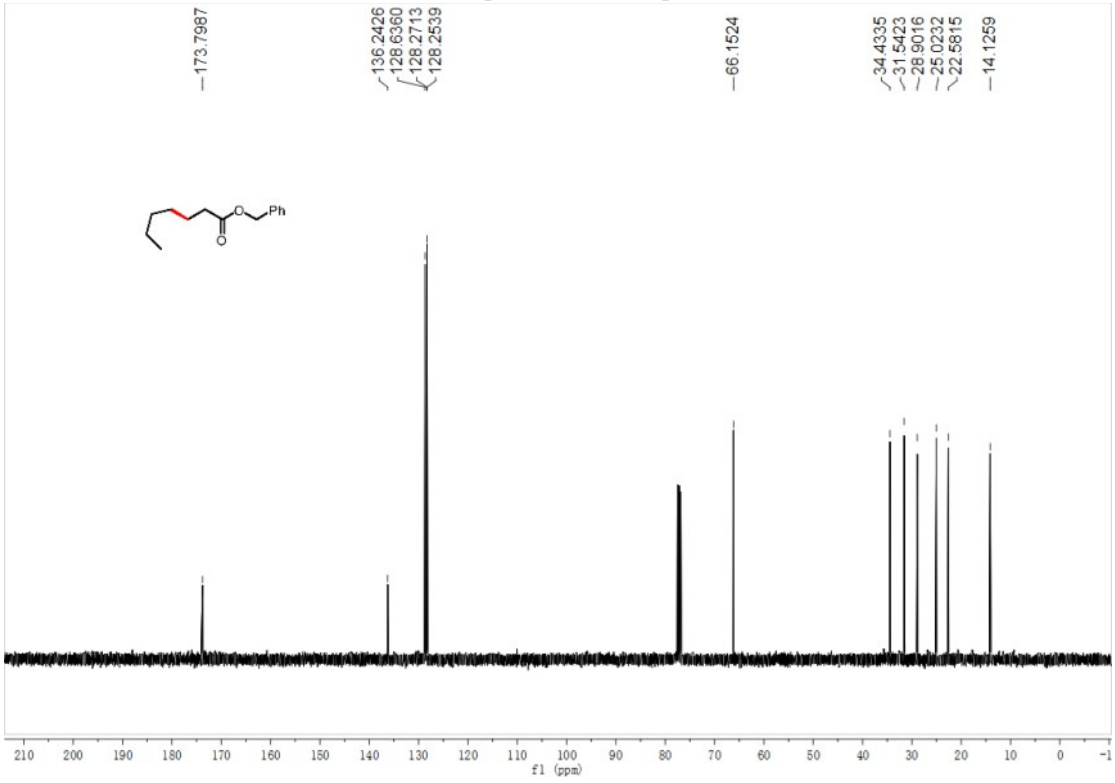
^{13}C NMR spectrum of compound **5**



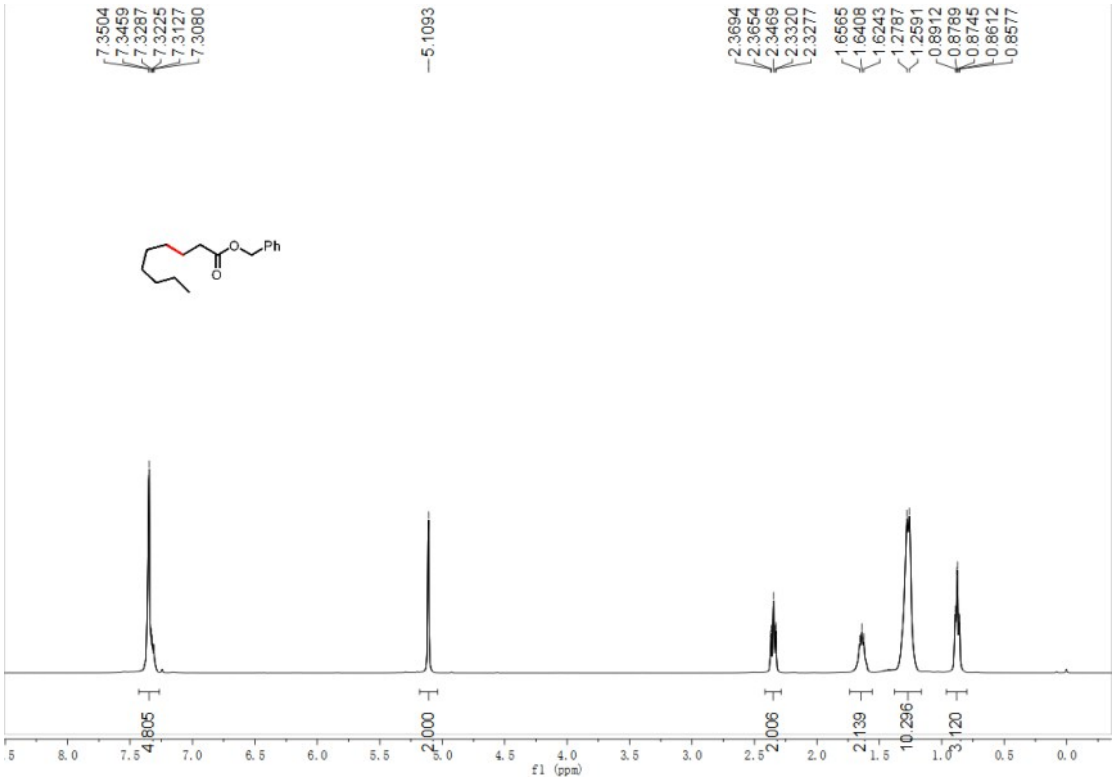
^{1}H NMR spectrum of compound **of 6**



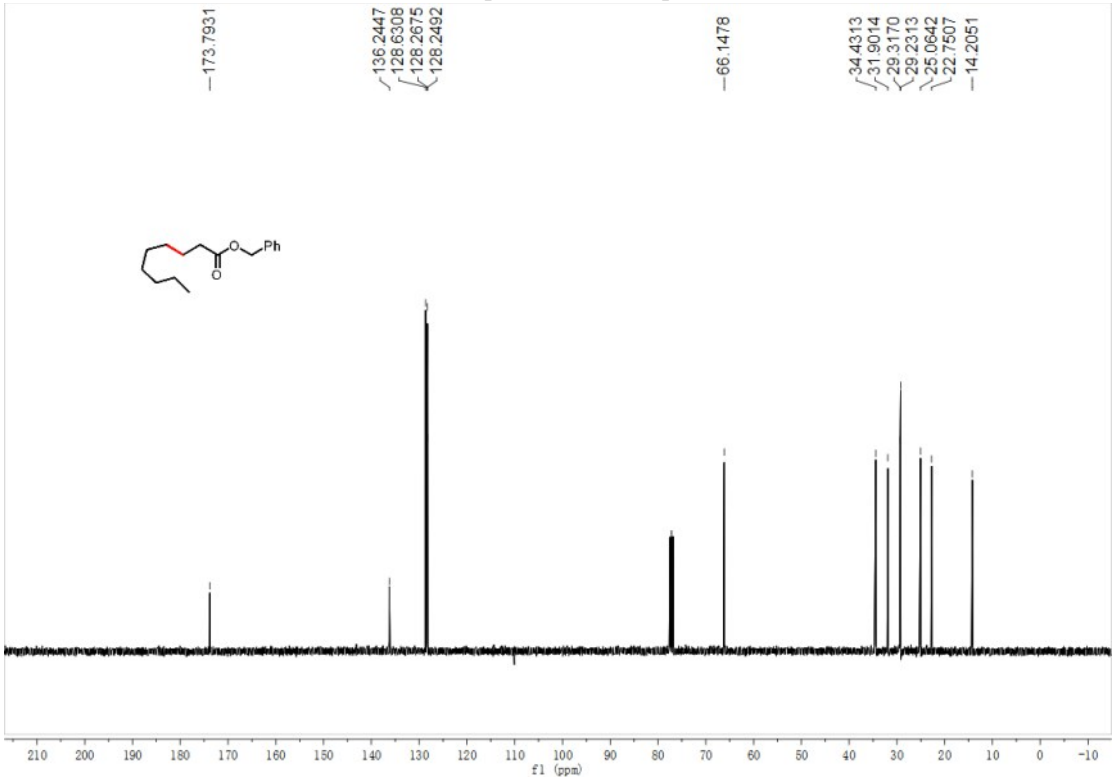
^{13}C NMR spectrum of compound **6**



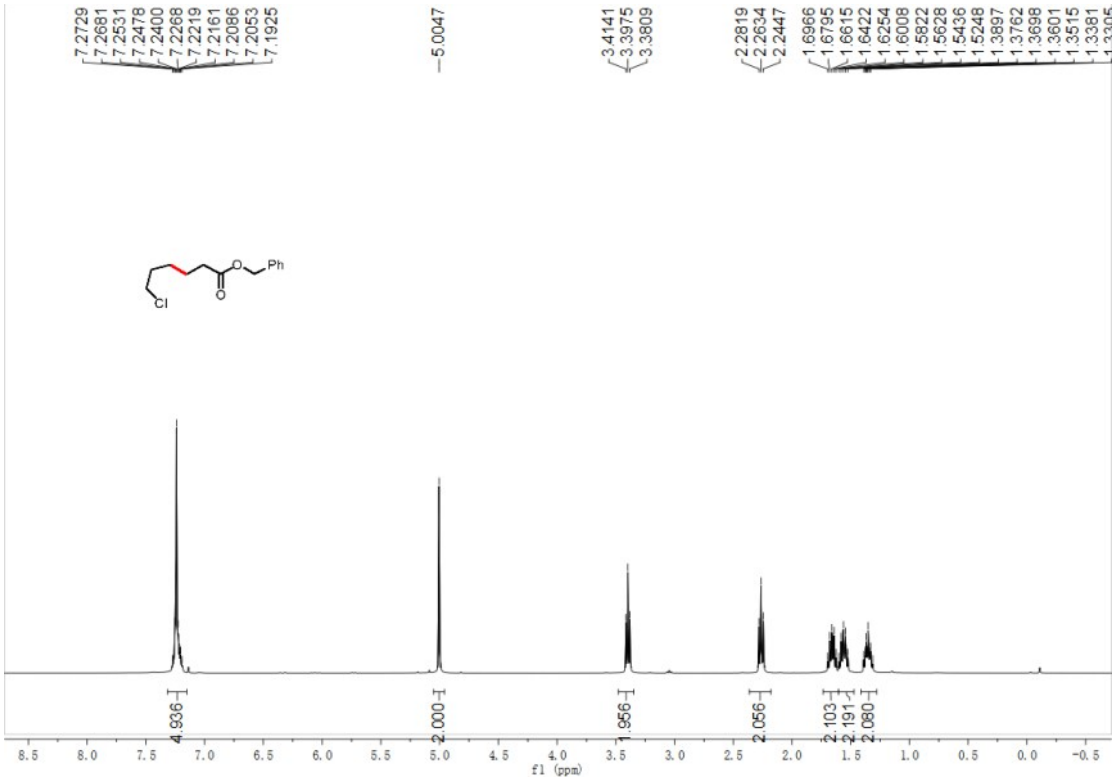
^{1}H NMR spectrum of compound **7**



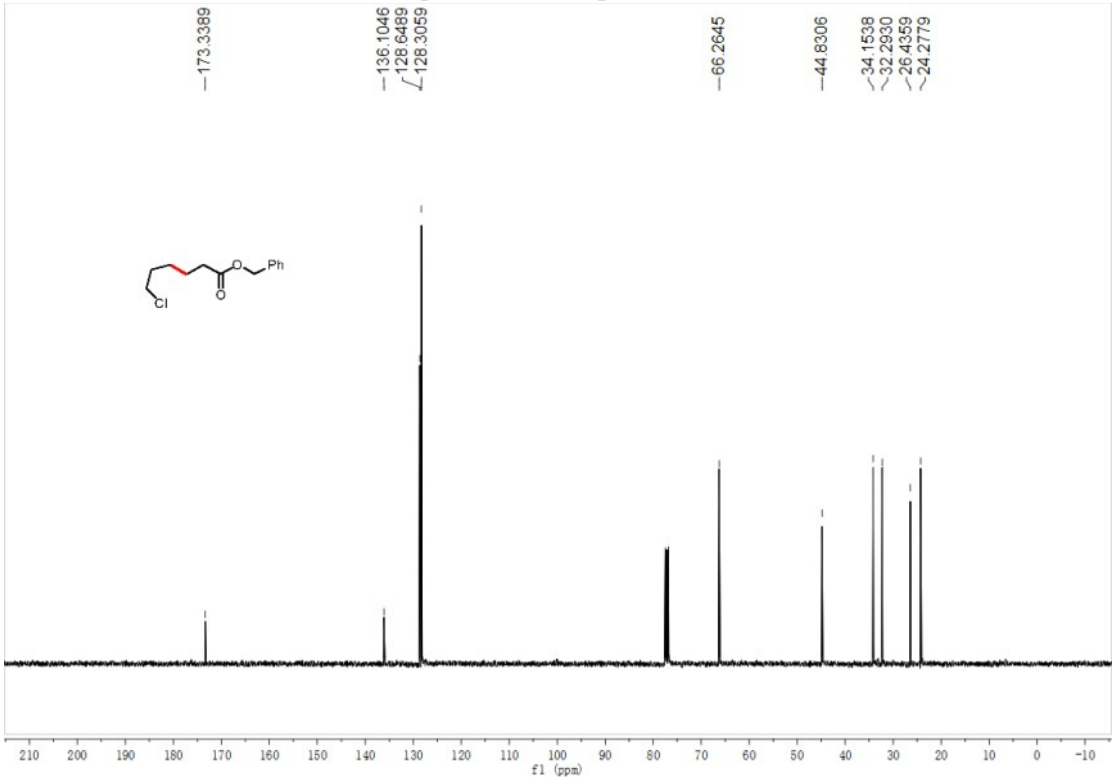
^{13}C NMR spectrum of compound **7**



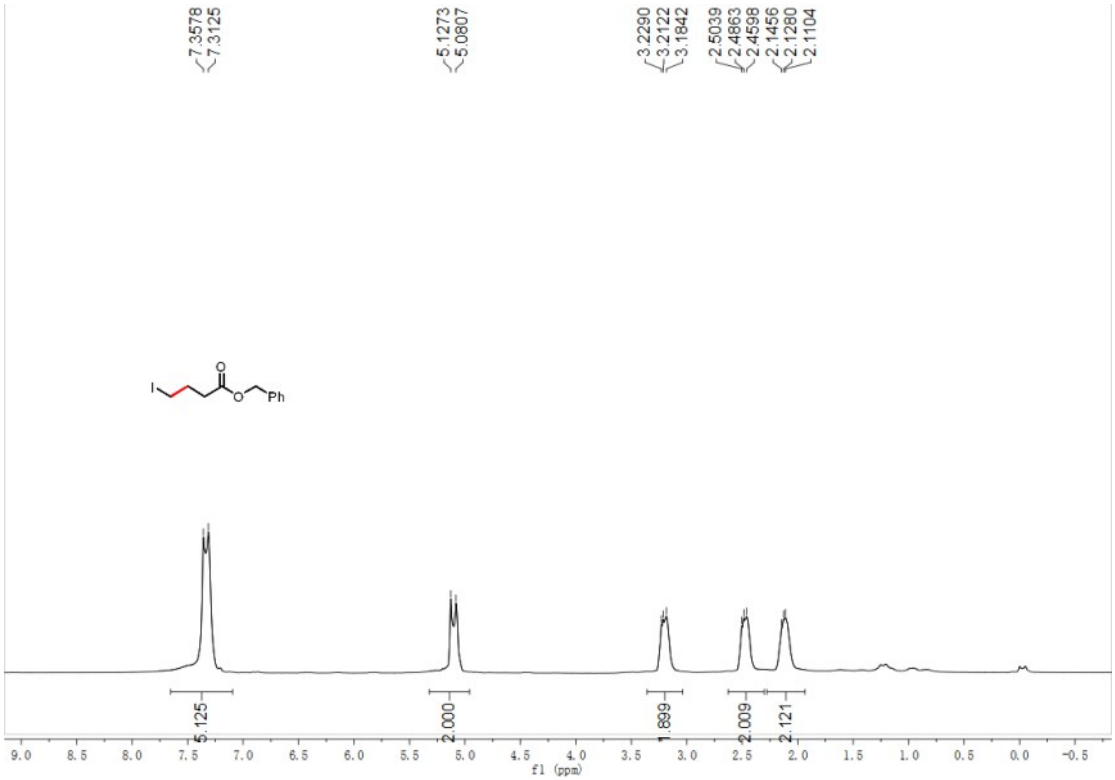
^{1}H NMR spectrum of compound **8**



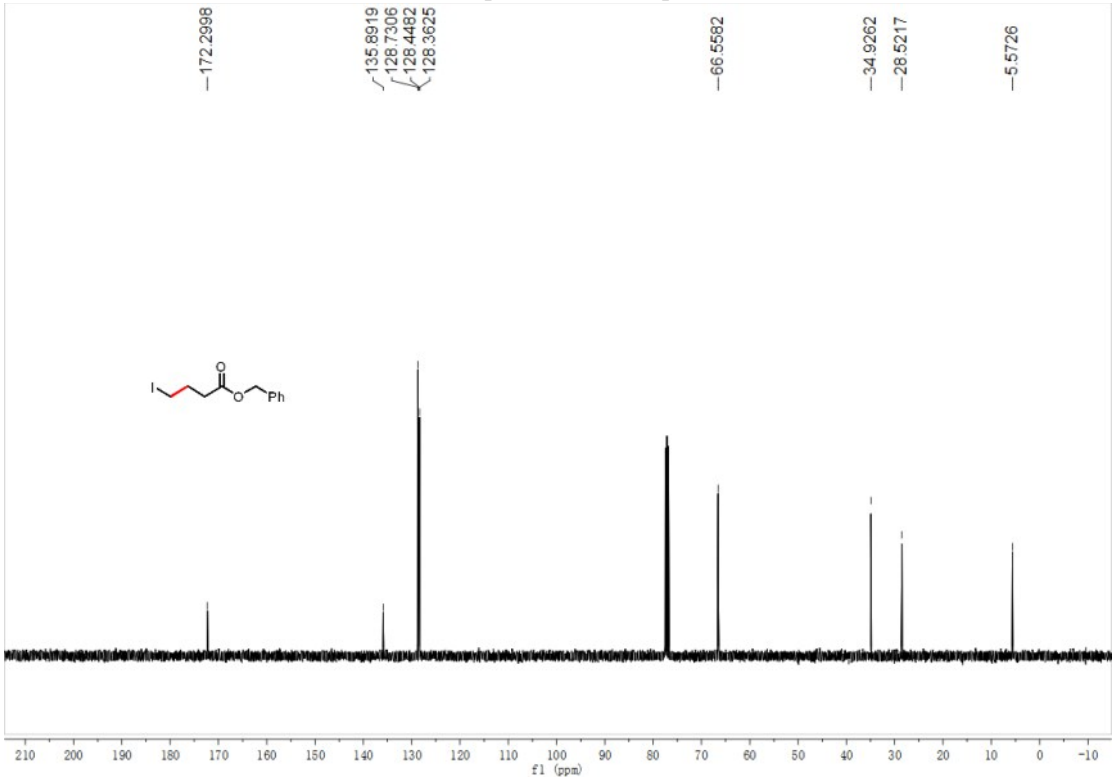
^{13}C NMR spectrum of compound **8**



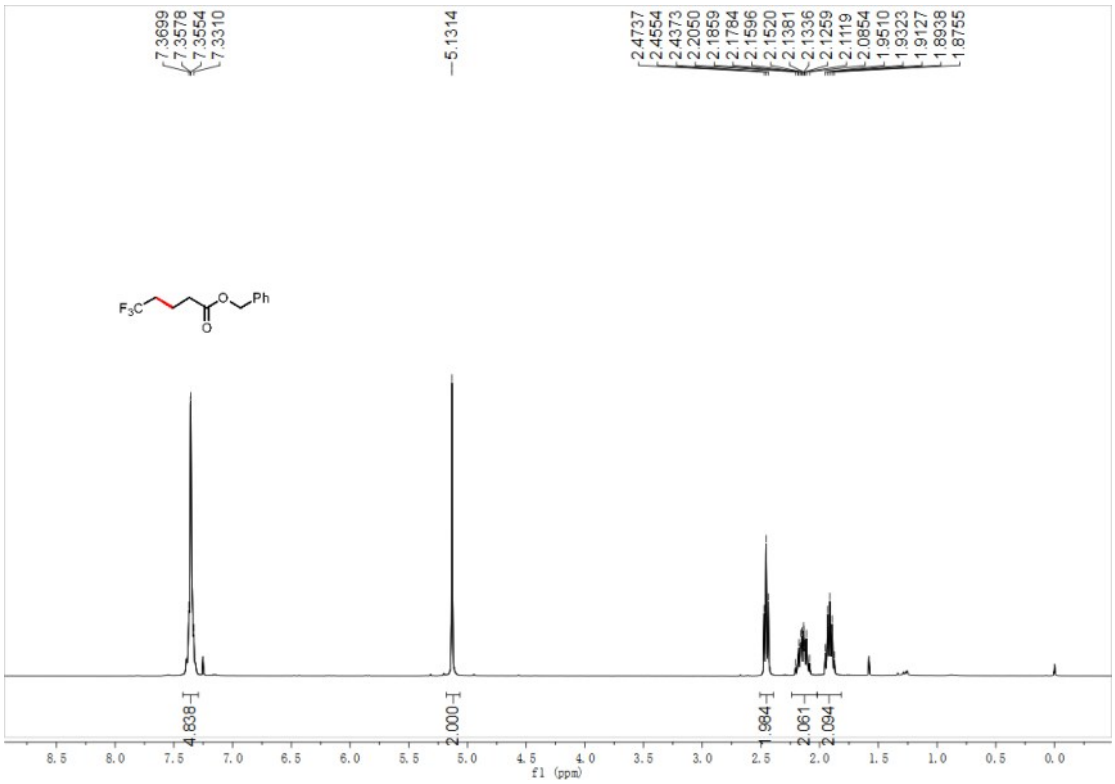
^{1}H NMR spectrum of compound **9**



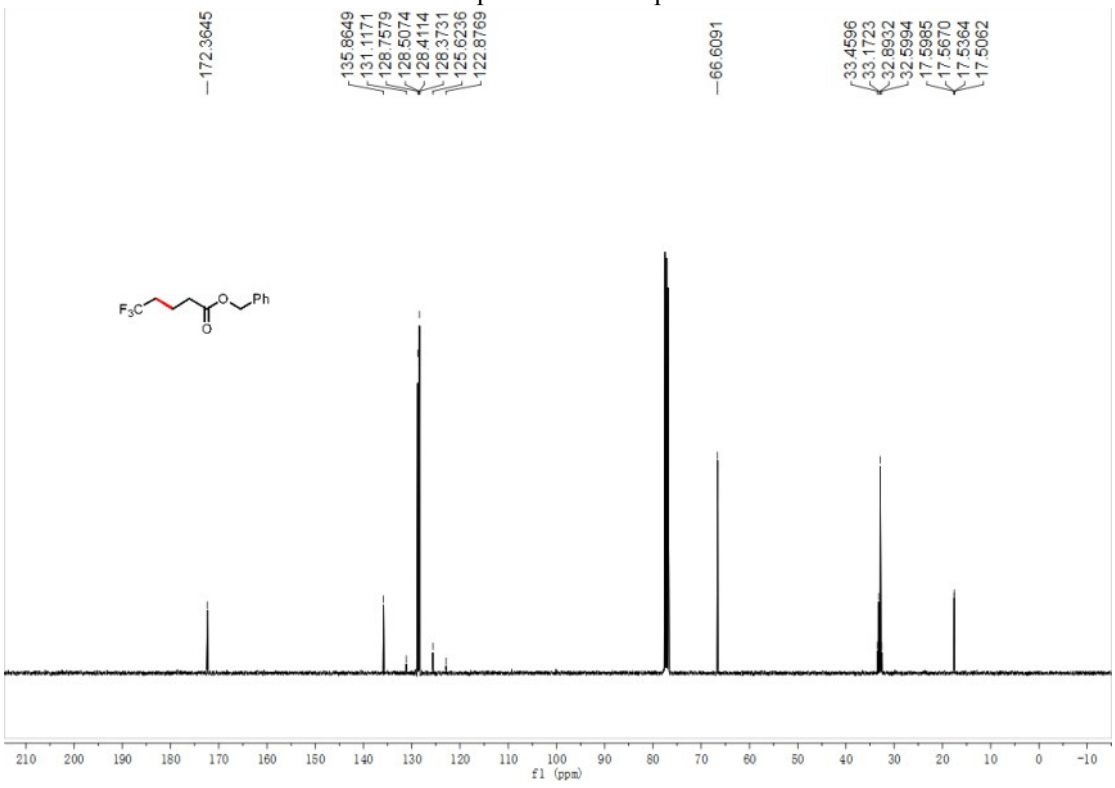
^{13}C NMR spectrum of compound **9**



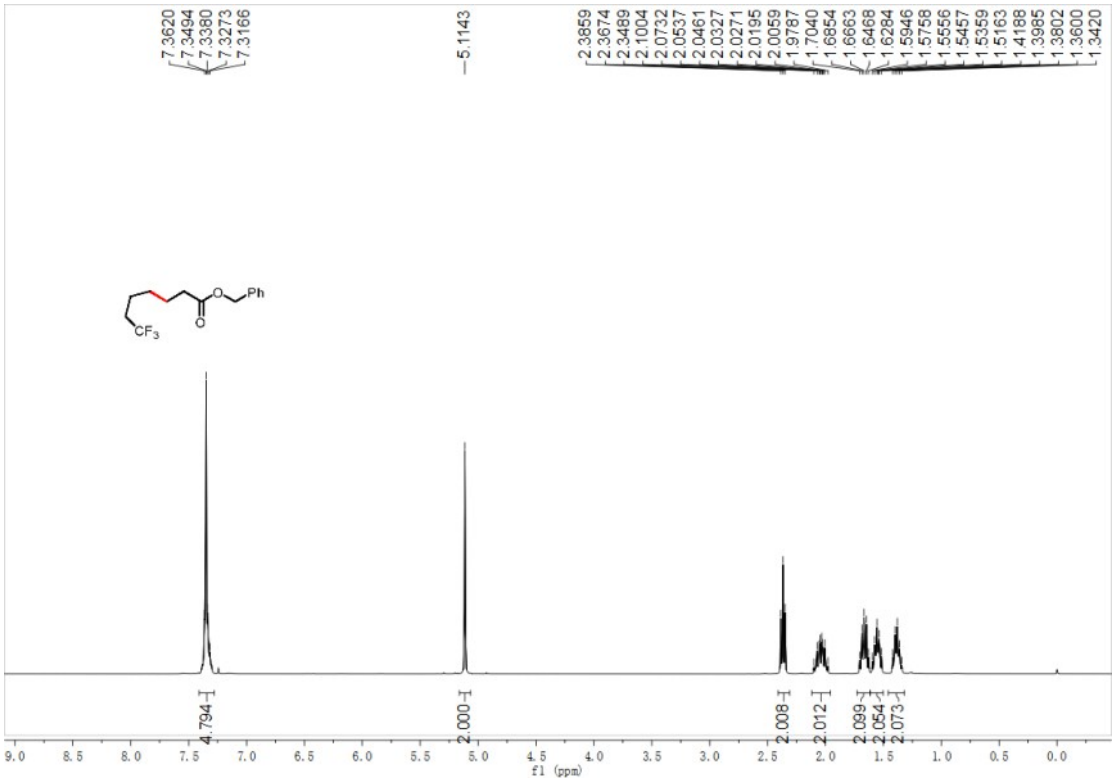
^{1}H NMR spectrum of compound **10**



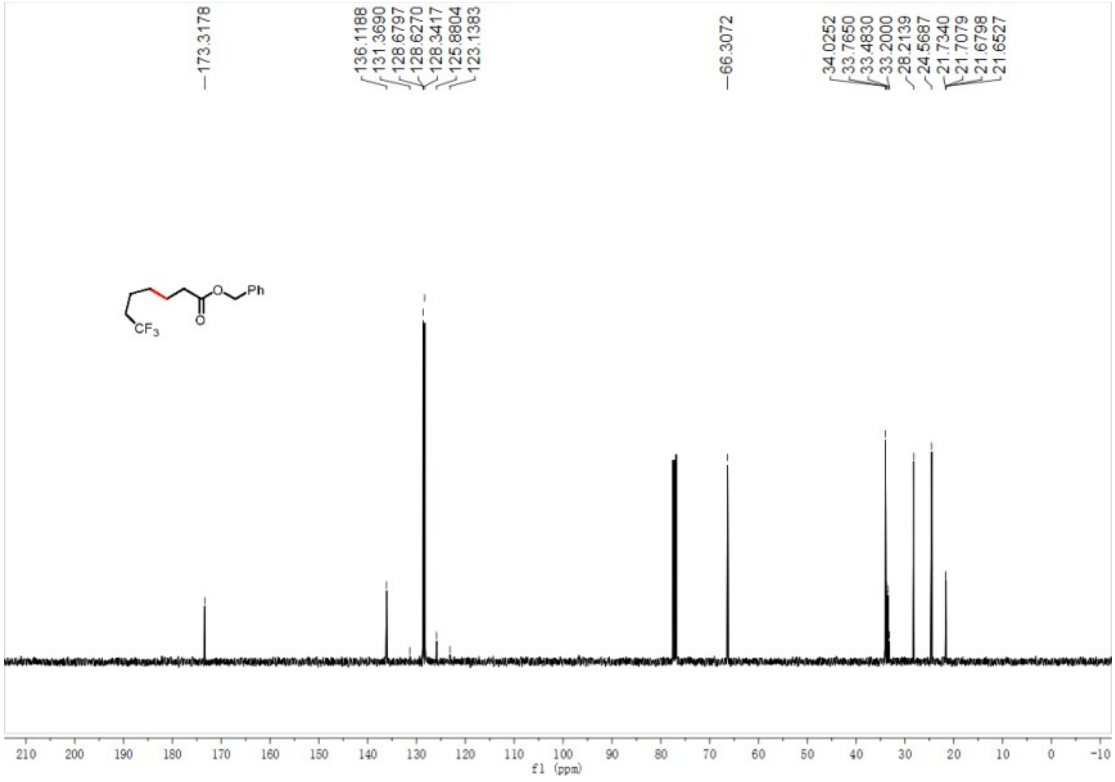
^{13}C NMR spectrum of compound **10**



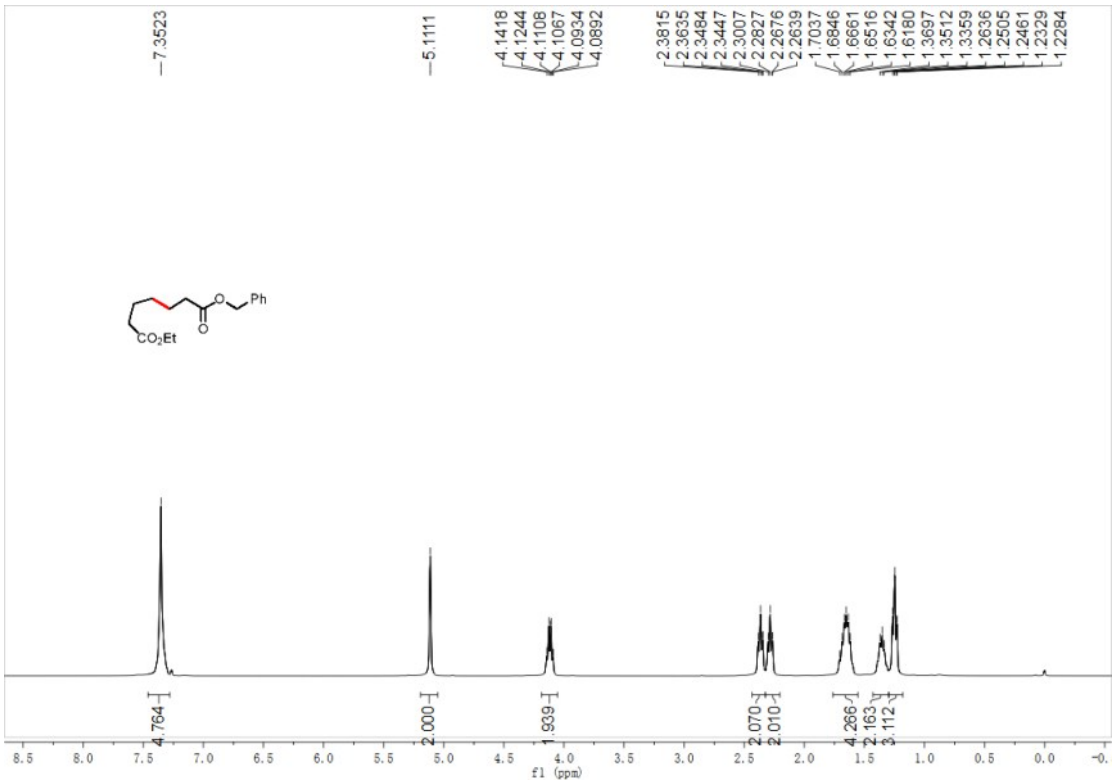
^{1}H NMR spectrum of compound **11**



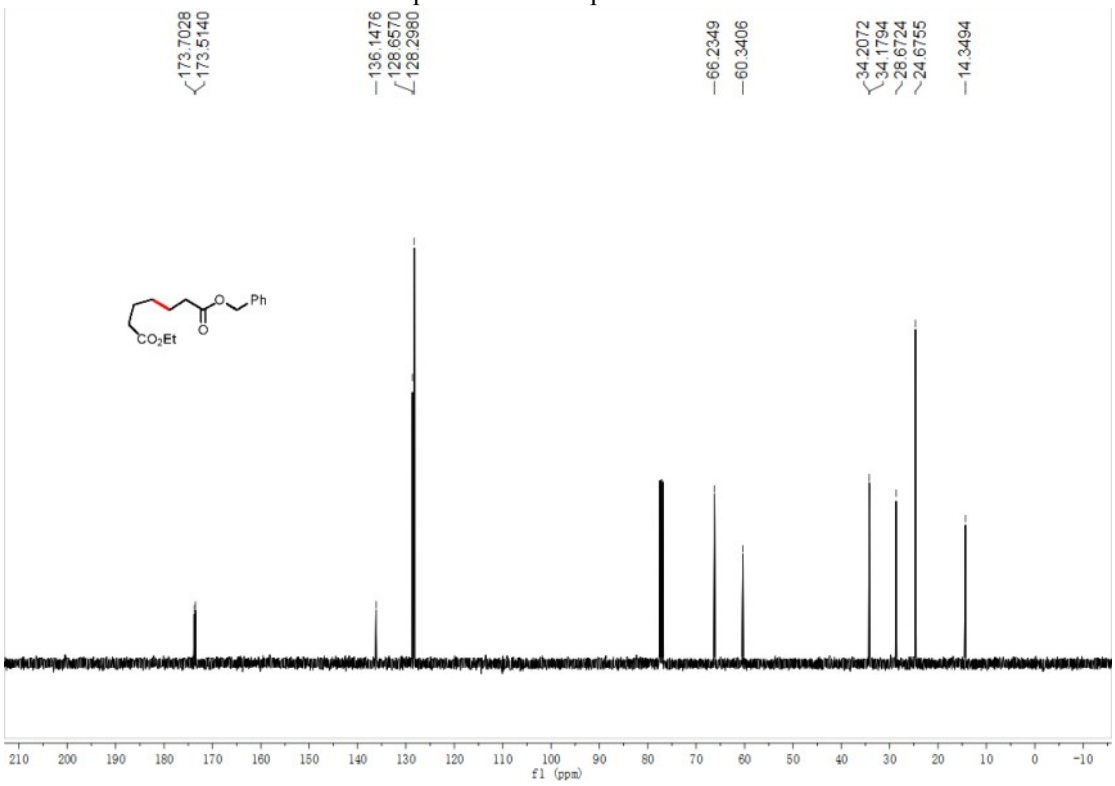
^{13}C NMR spectrum of compound **11**



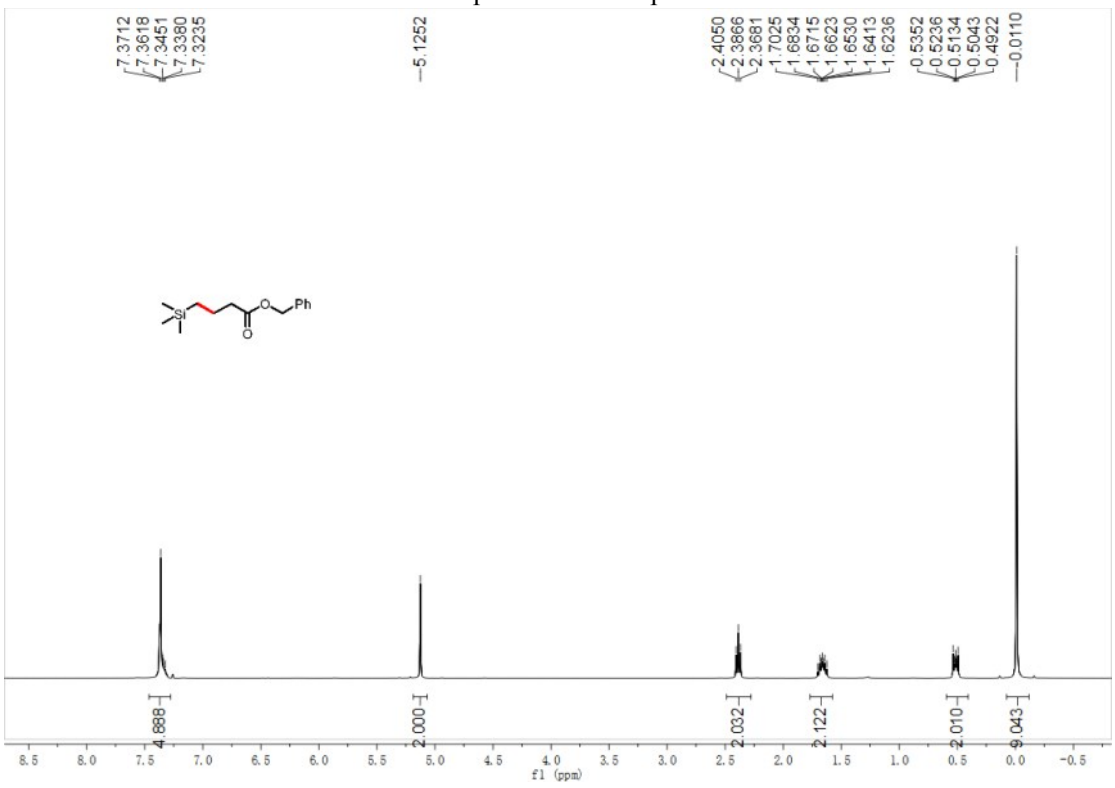
^{1}H NMR spectrum of compound **12**



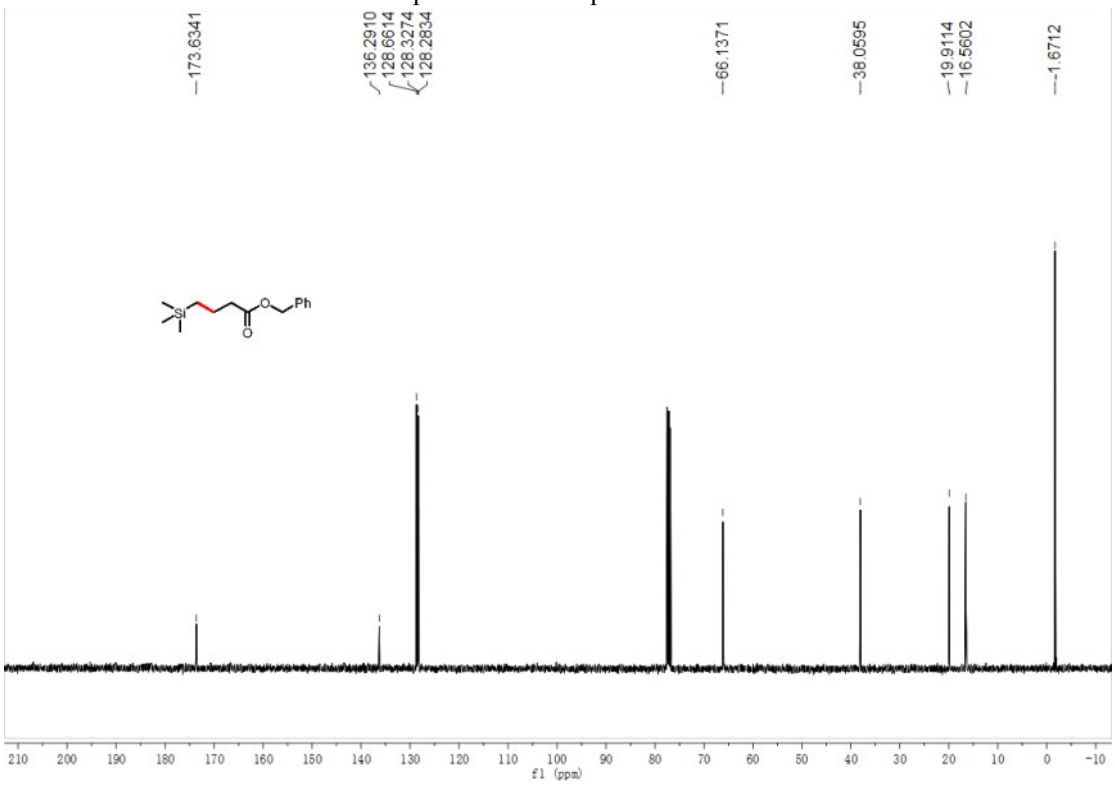
^{13}C NMR spectrum of compound **12**



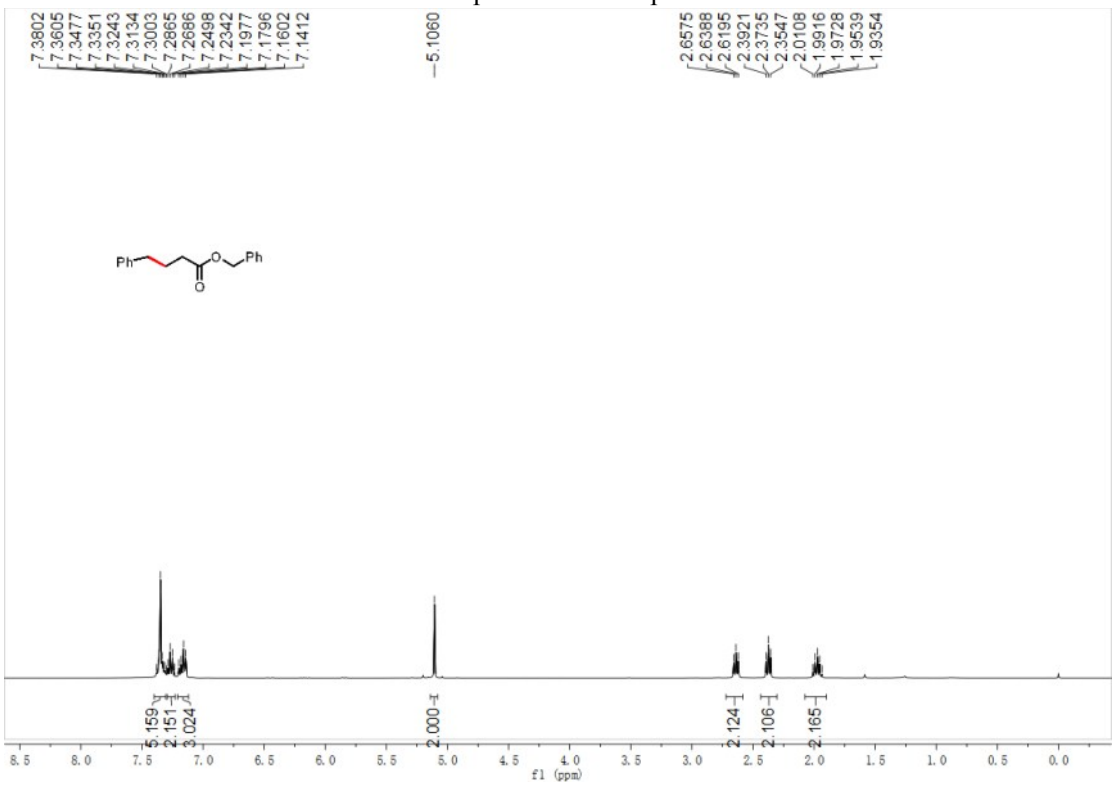
^{1}H NMR spectrum of compound **13**



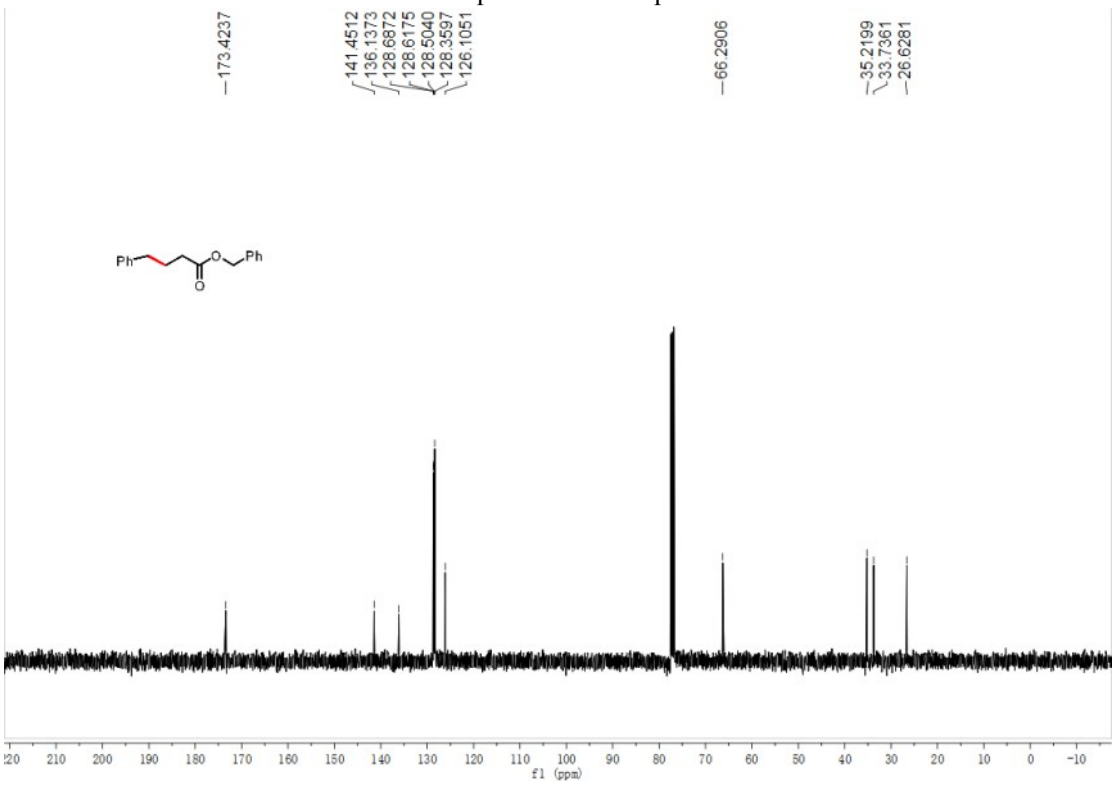
^{13}C NMR spectrum of compound **13**



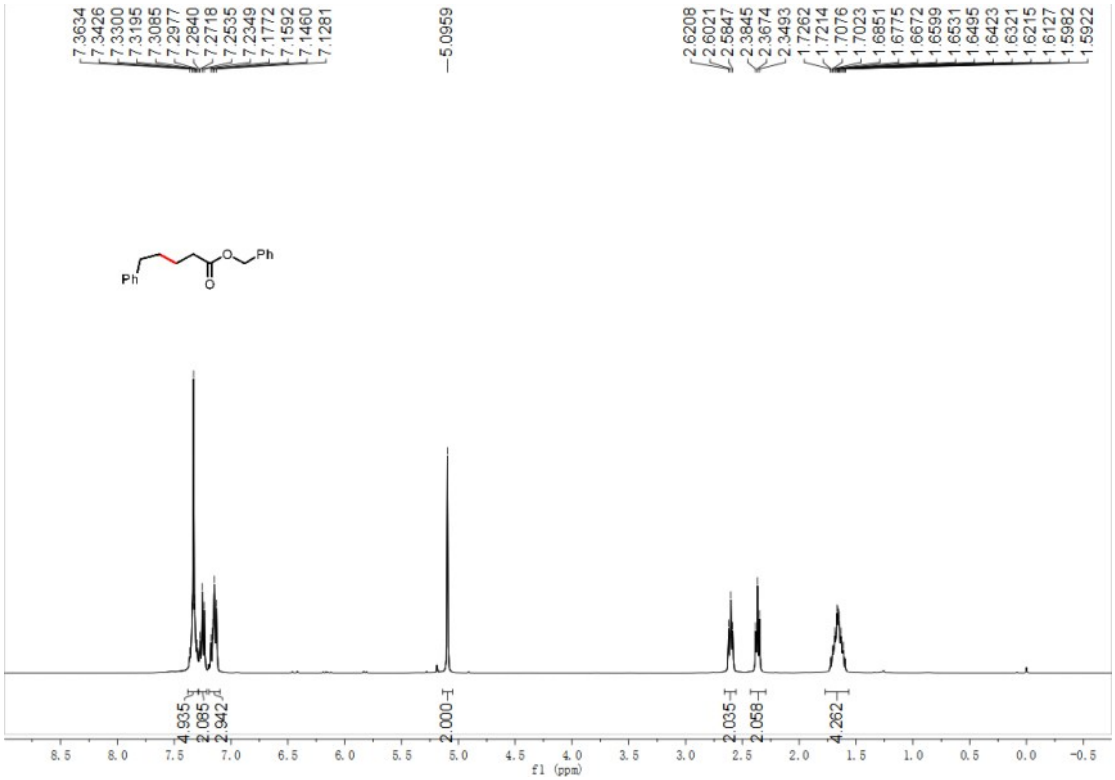
^{1}H NMR spectrum of compound **14**



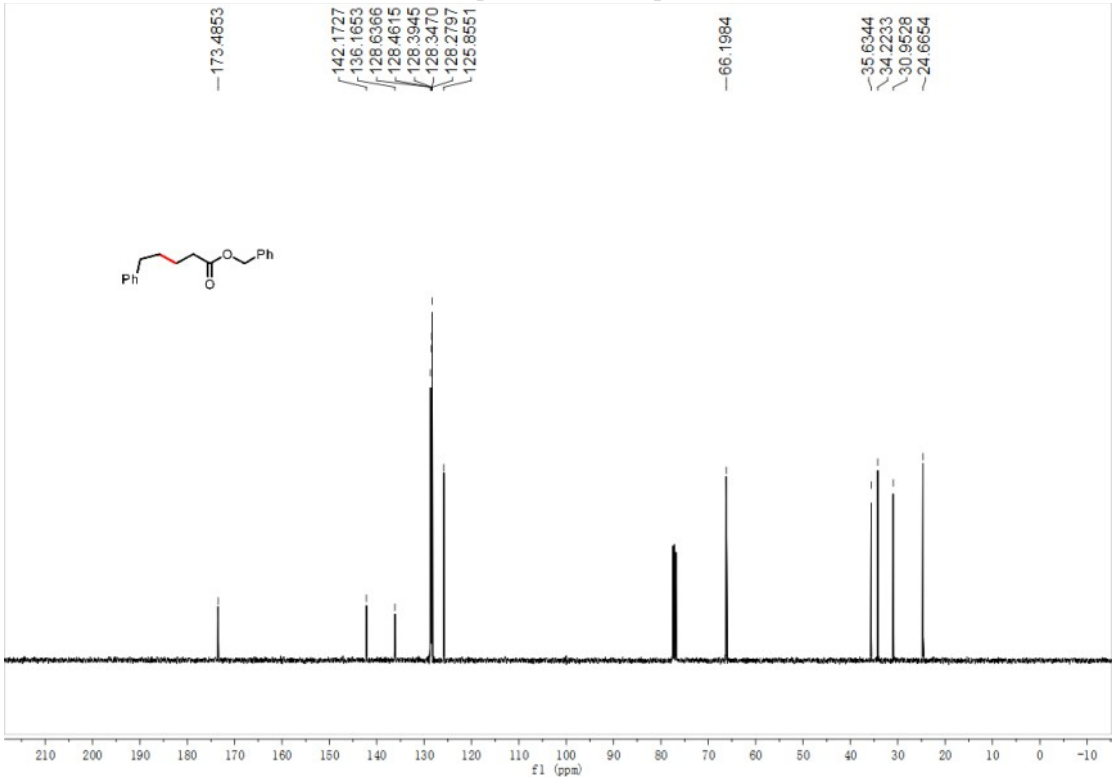
^{13}C NMR spectrum of compound **14**



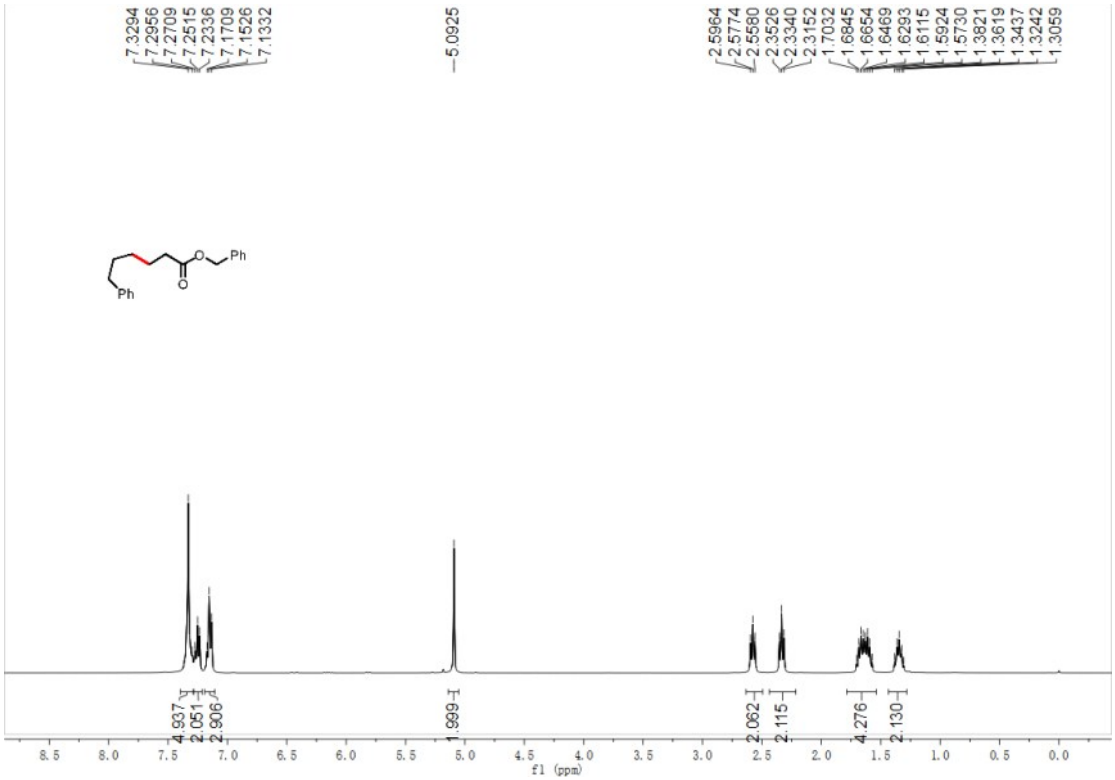
^{1}H NMR spectrum of compound **15**



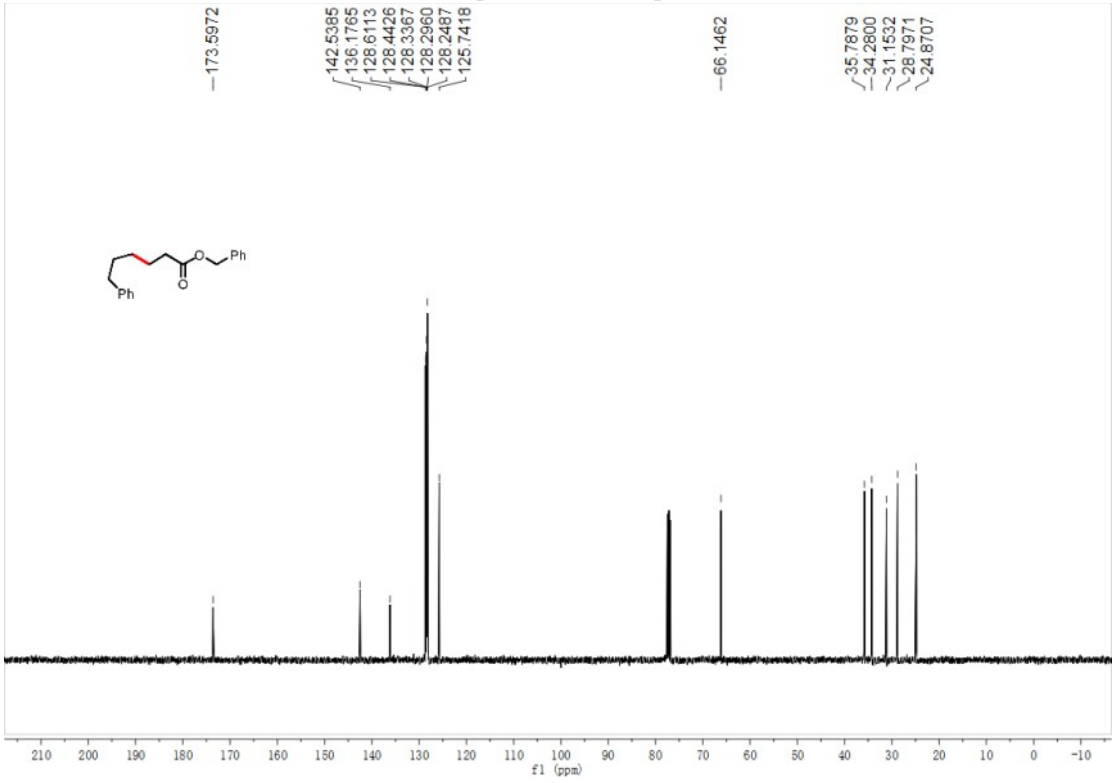
^{13}C NMR spectrum of compound **15**



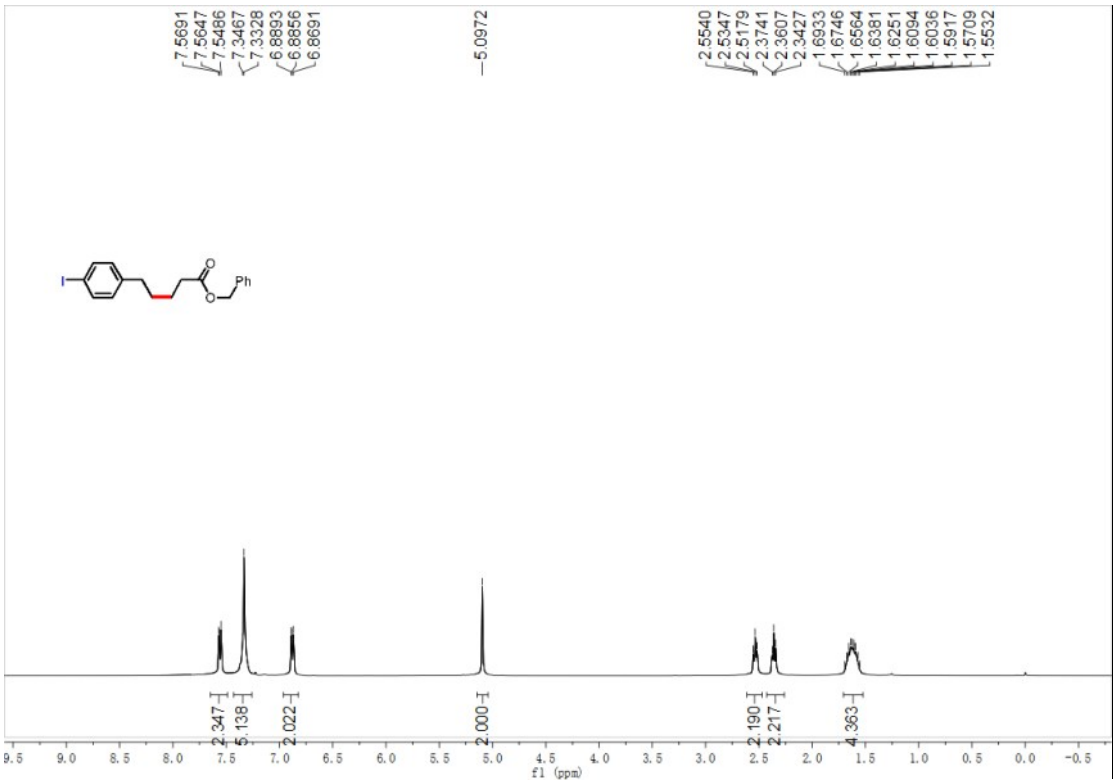
^{1}H NMR spectrum of compound **16**



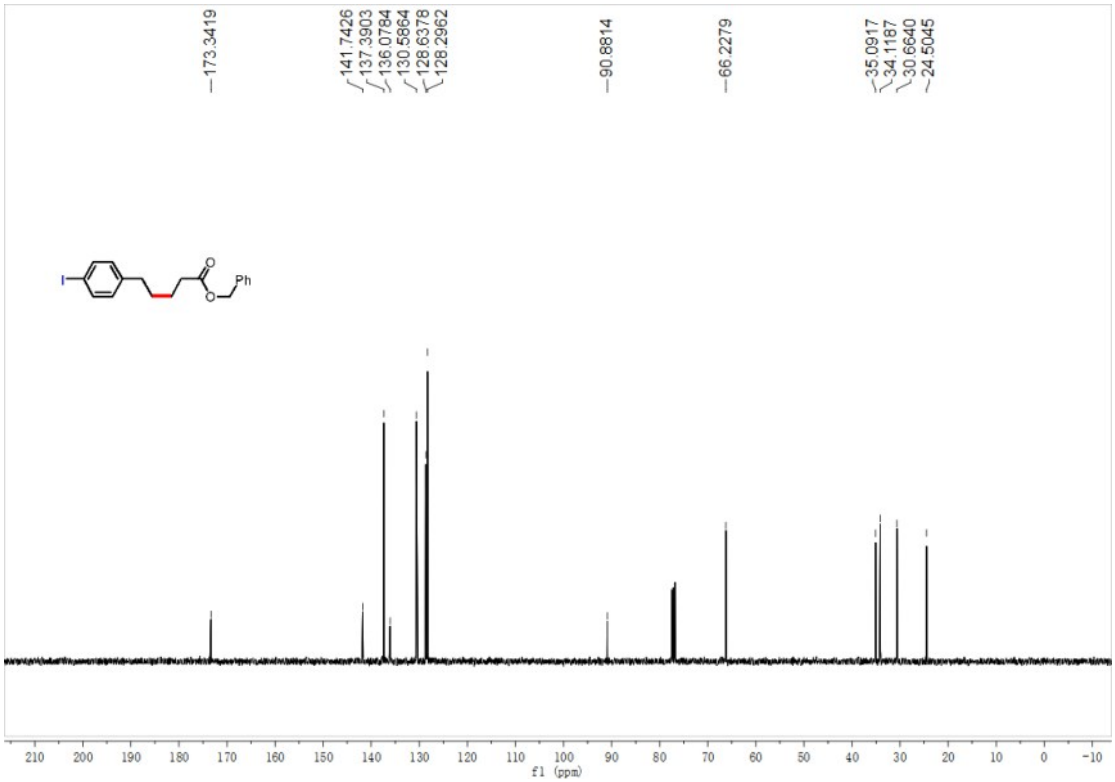
^{13}C NMR spectrum of compound **16**



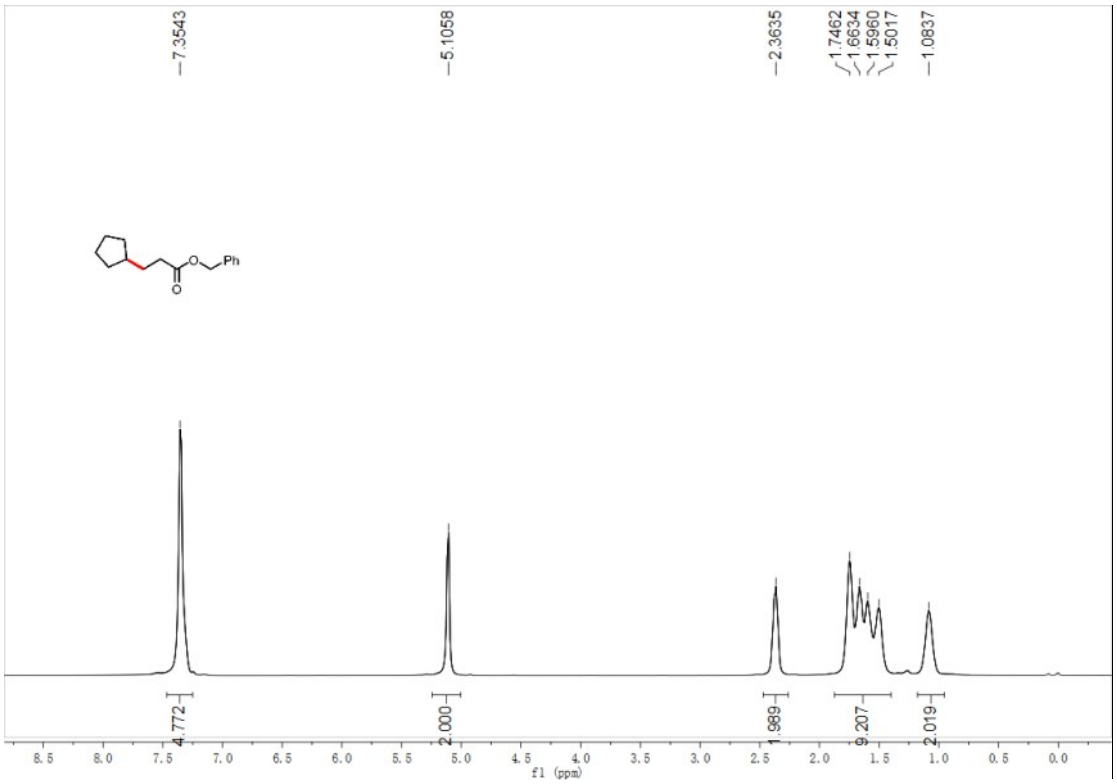
^{1}H NMR spectrum of compound **17**



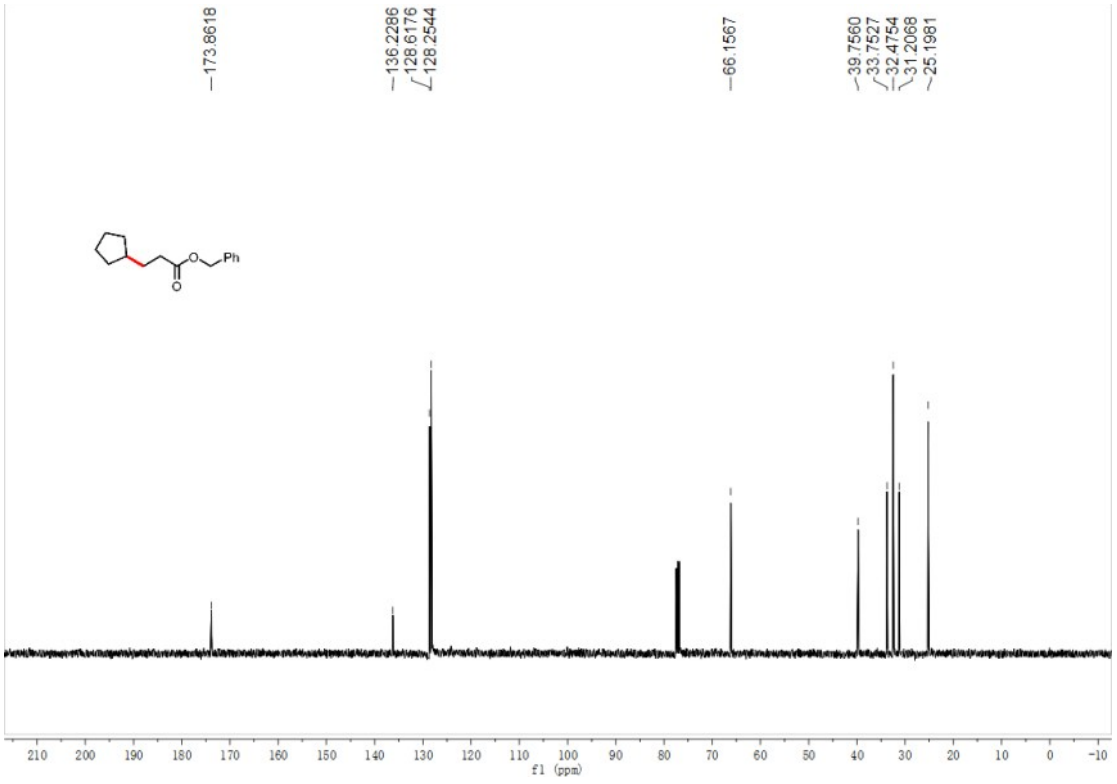
^{13}C NMR spectrum of compound **17**



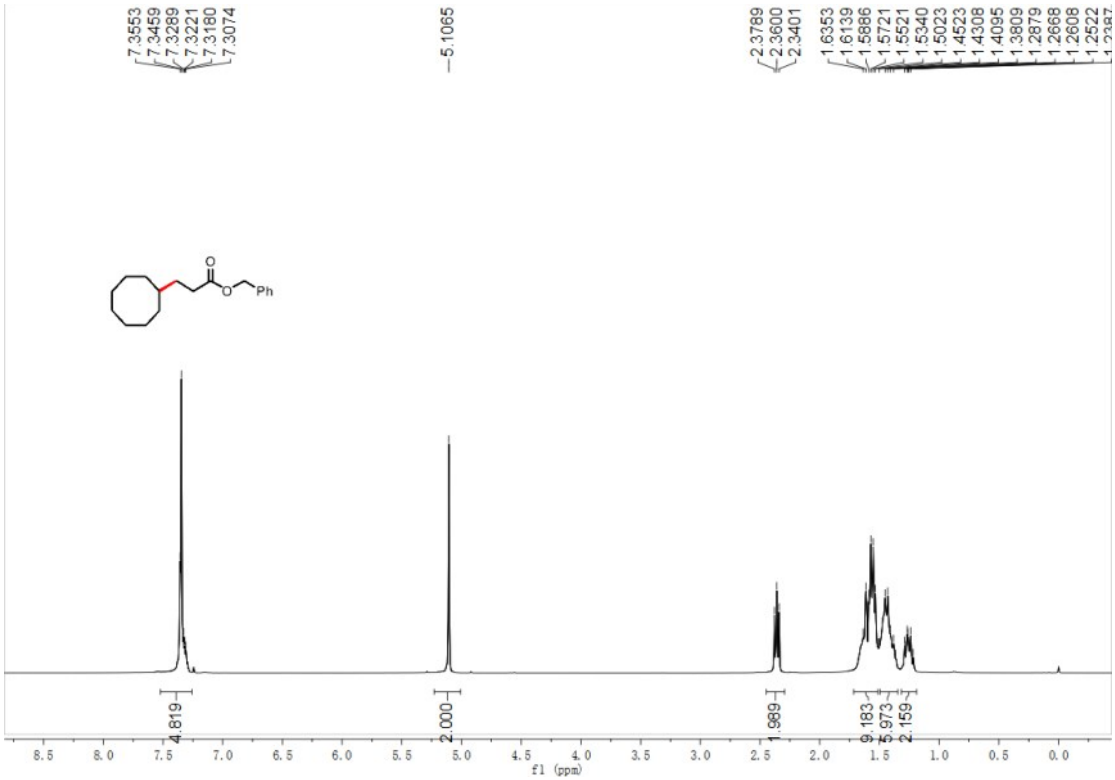
^{1}H NMR spectrum of compound **18**



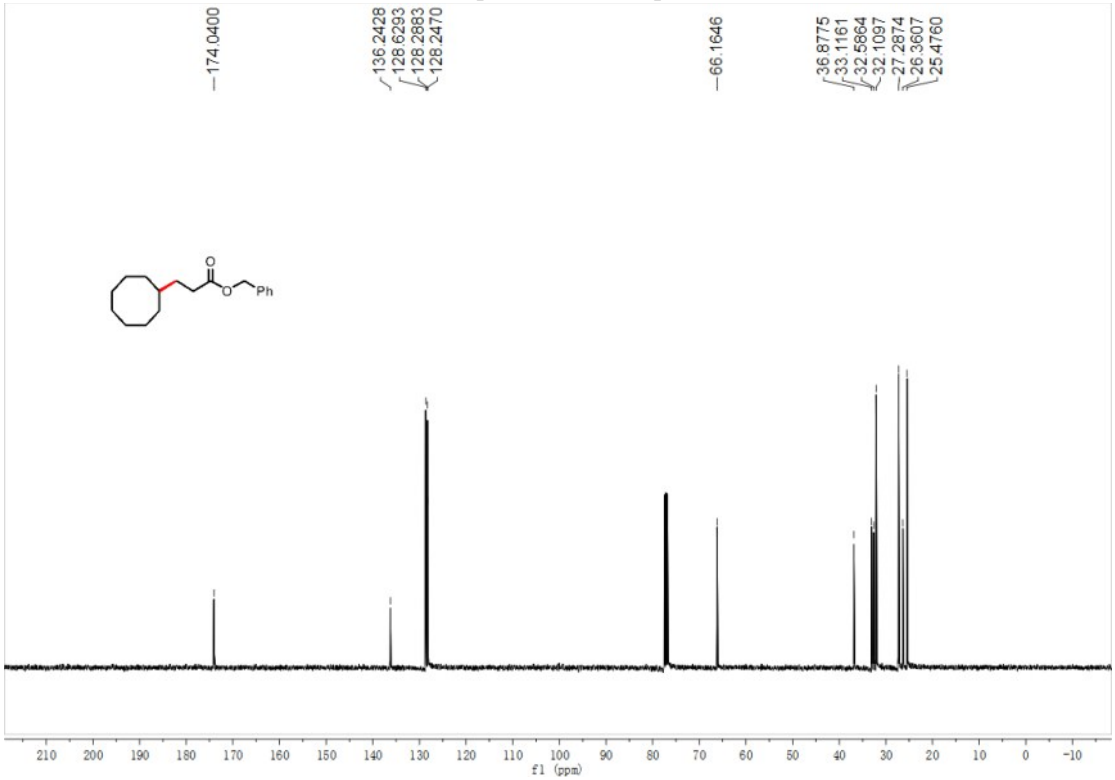
^{13}C NMR spectrum of compound **18**



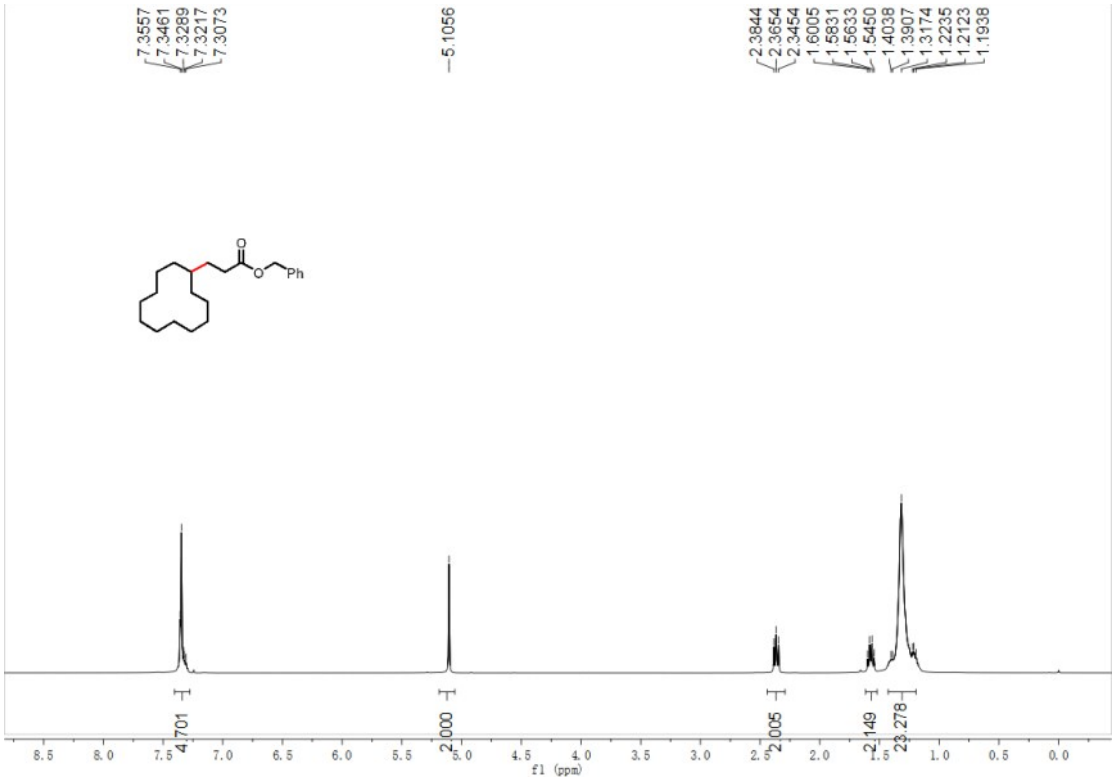
^{1}H NMR spectrum of compound **19**



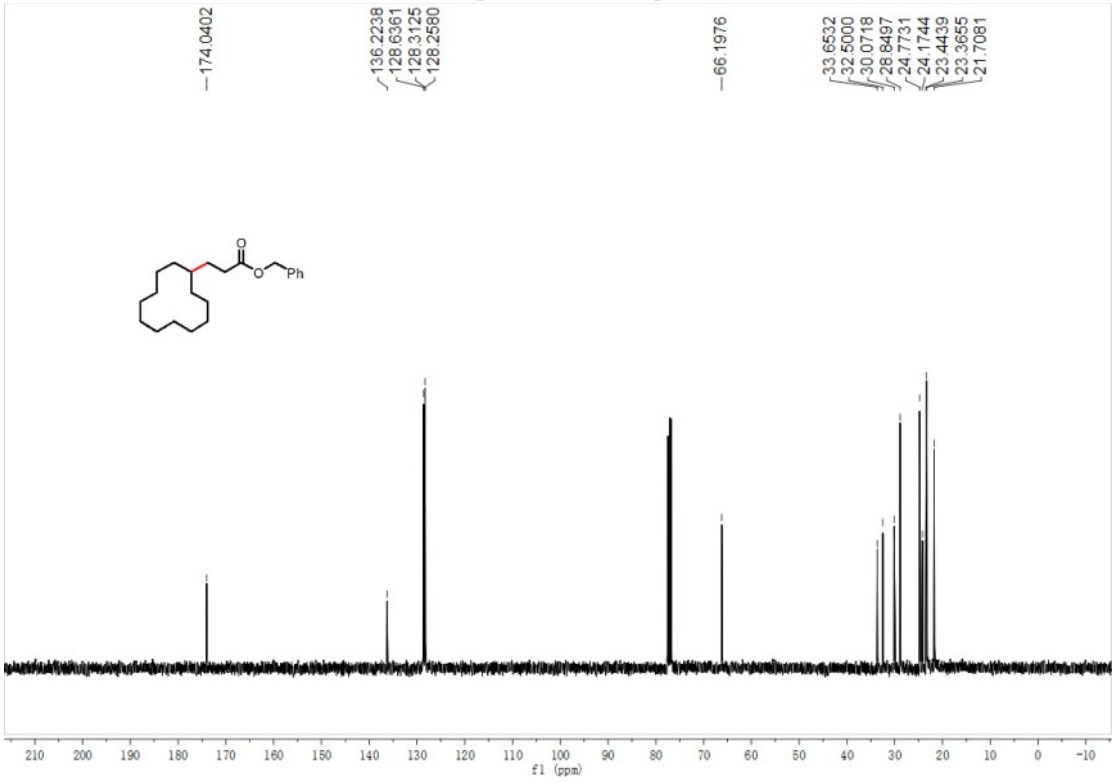
^{13}C NMR spectrum of compound **19**



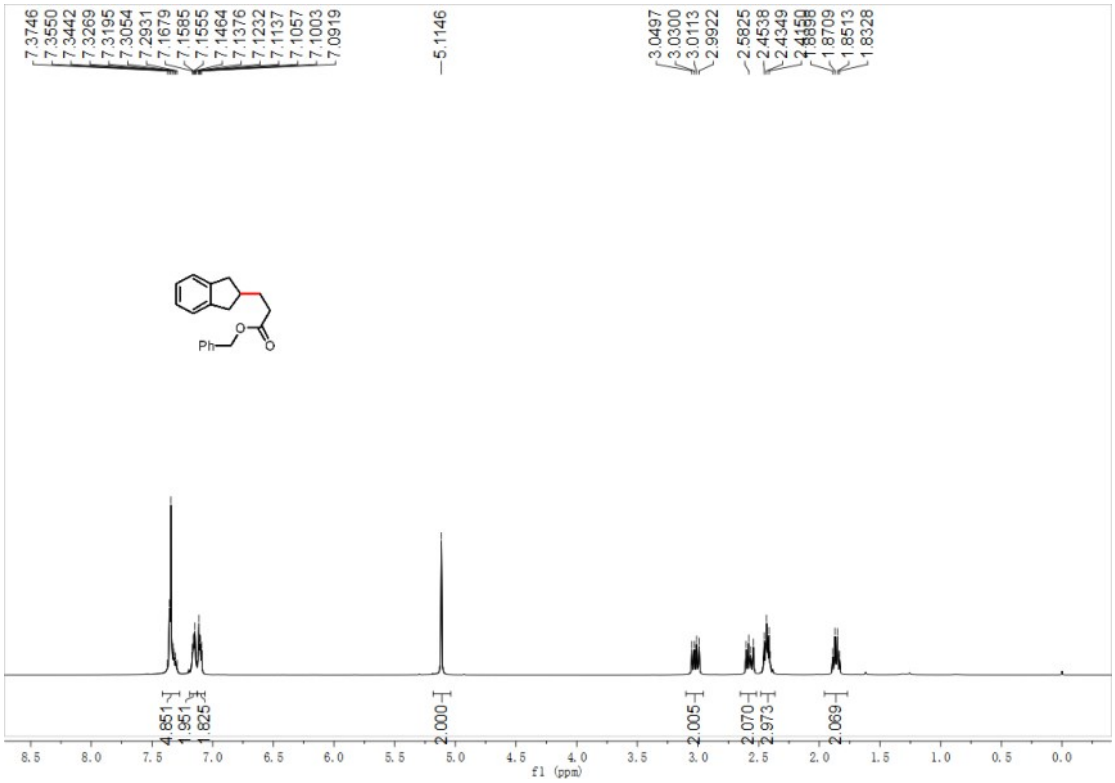
^{1}H NMR spectrum of compound **20**



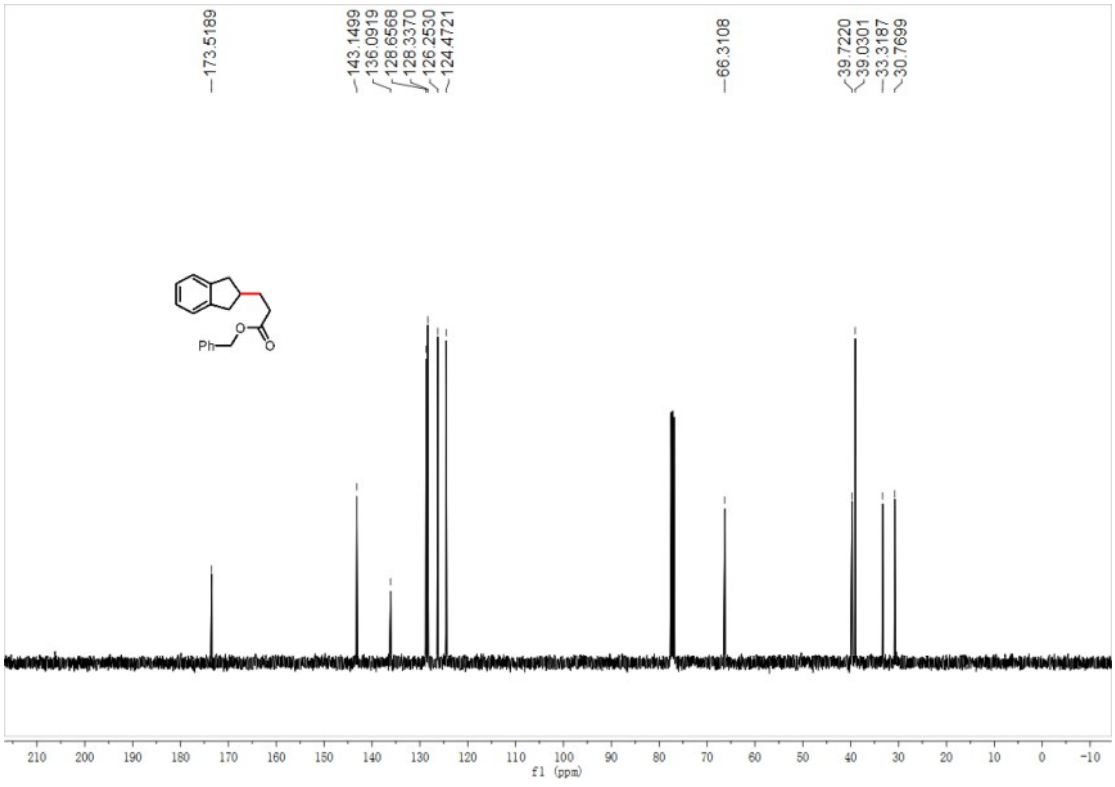
^{13}C NMR spectrum of compound **20**



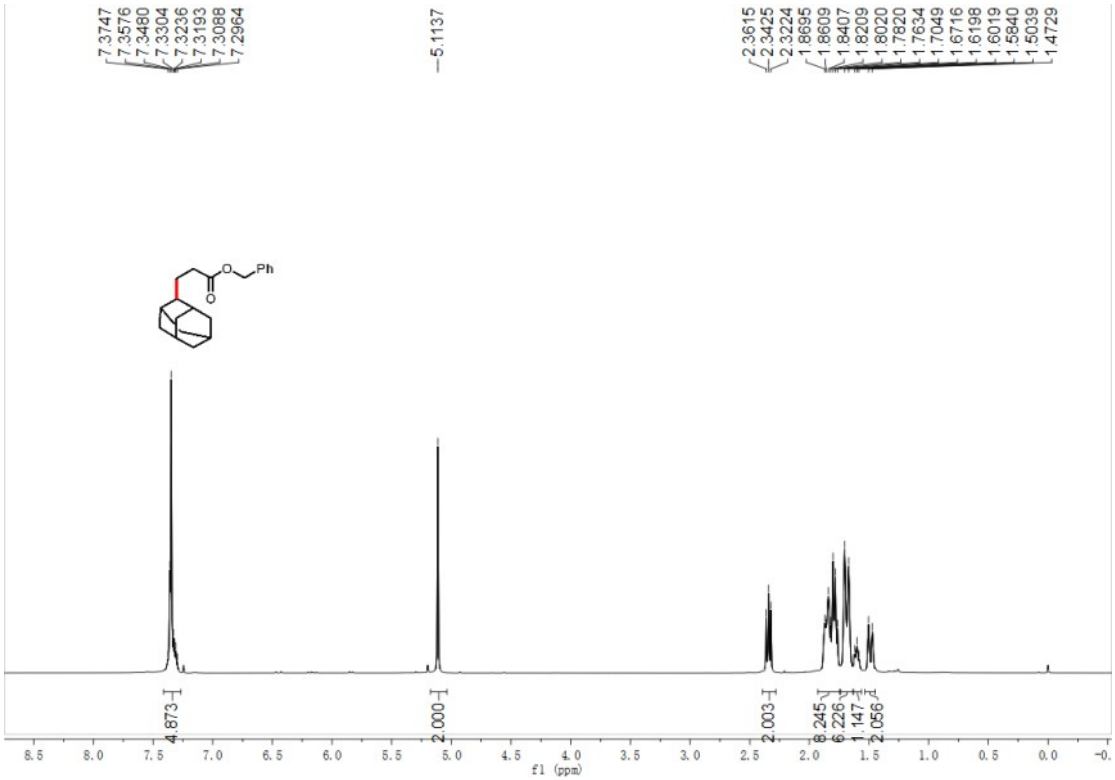
^{1}H NMR spectrum of compound **21**



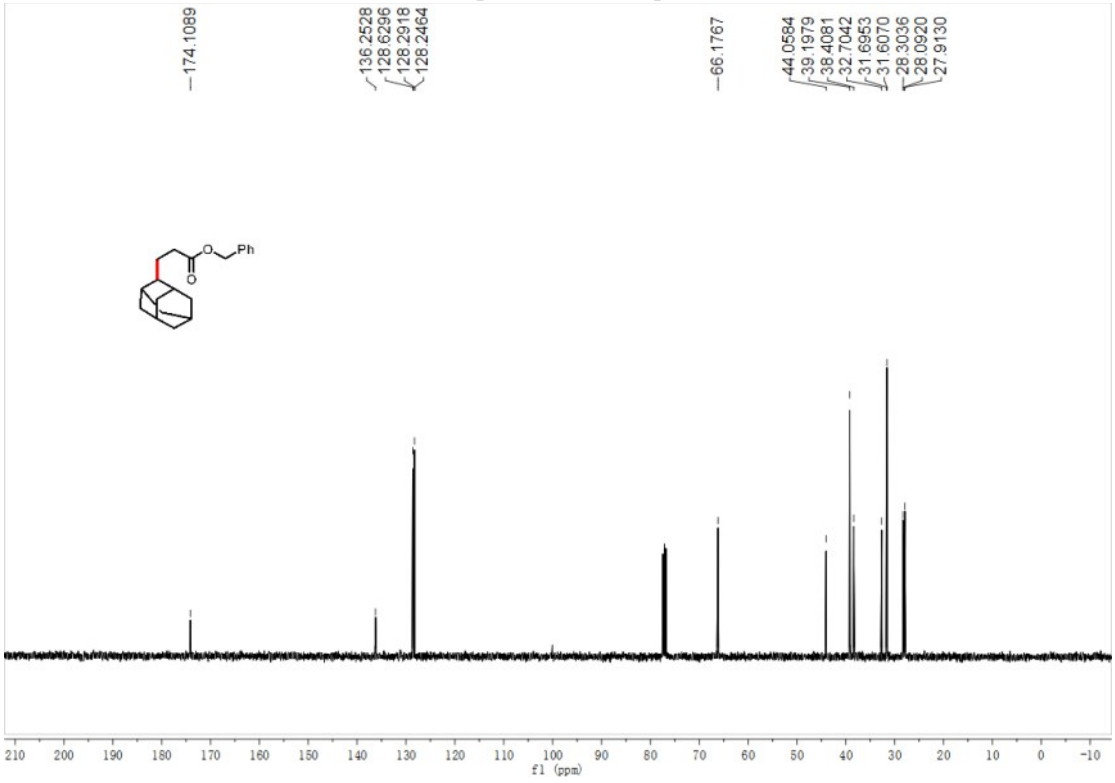
^{13}C NMR spectrum of compound **21**



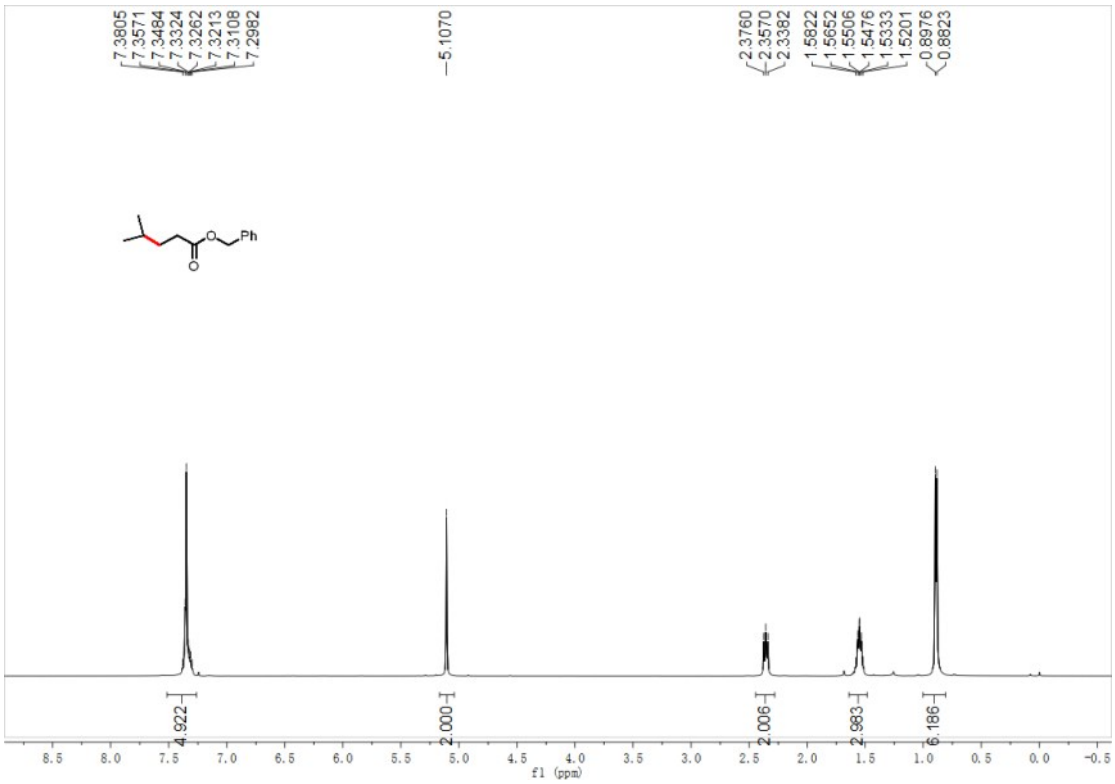
^{1}H NMR spectrum of compound **22**



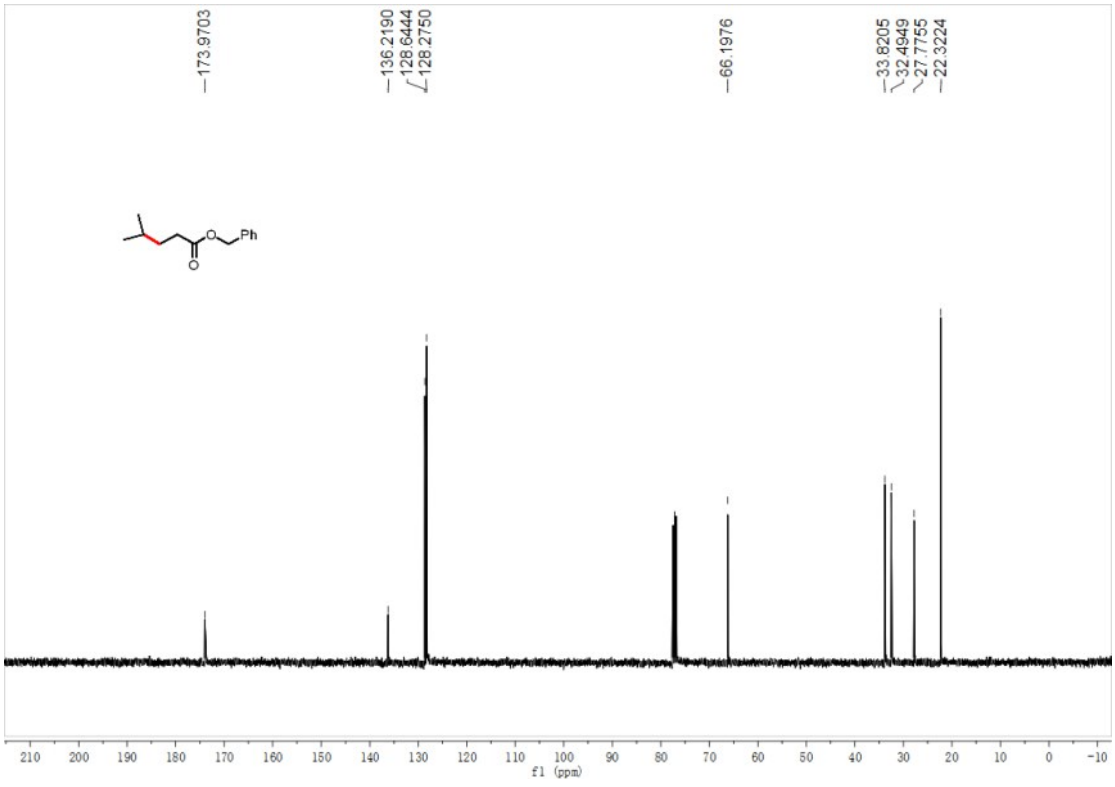
^{13}C NMR spectrum of compound **22**



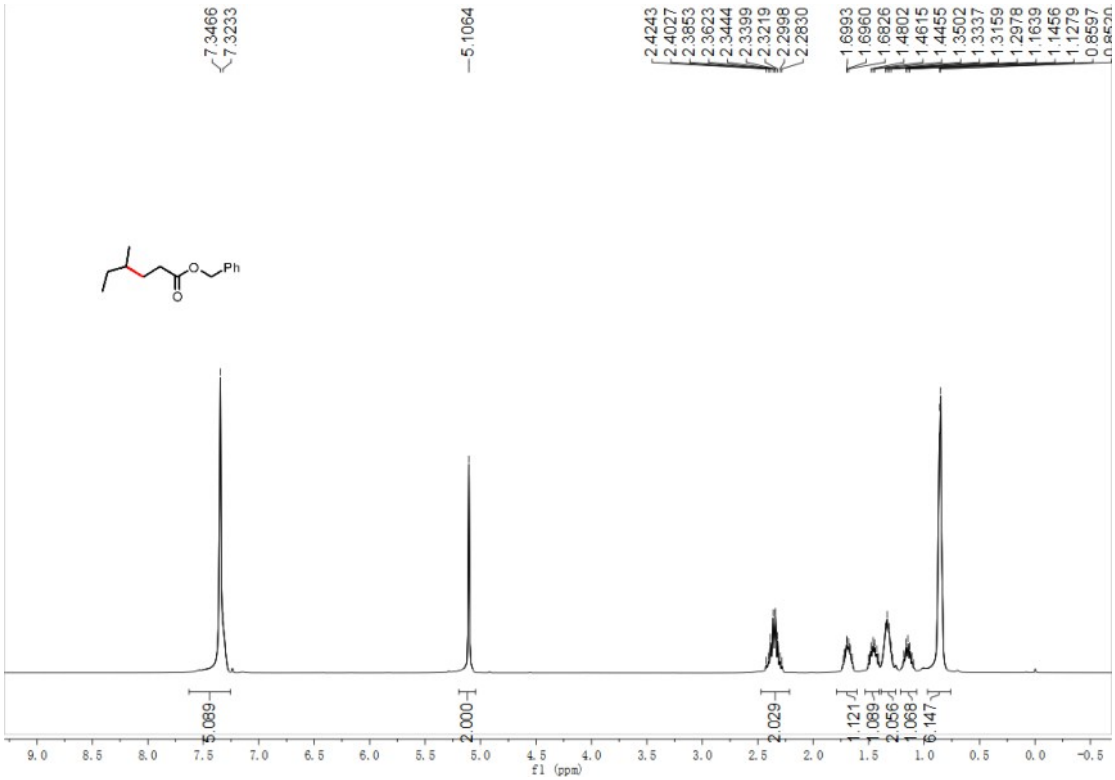
^{1}H NMR spectrum of compound **23**



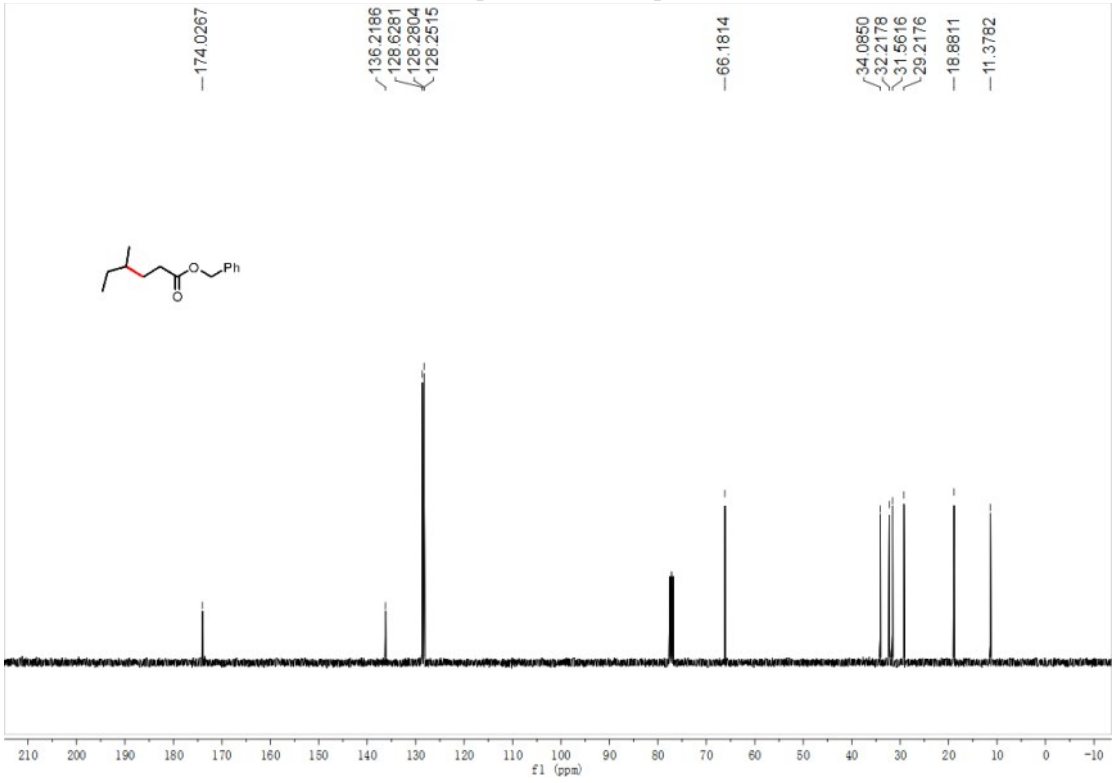
^{13}C NMR spectrum of compound **23**



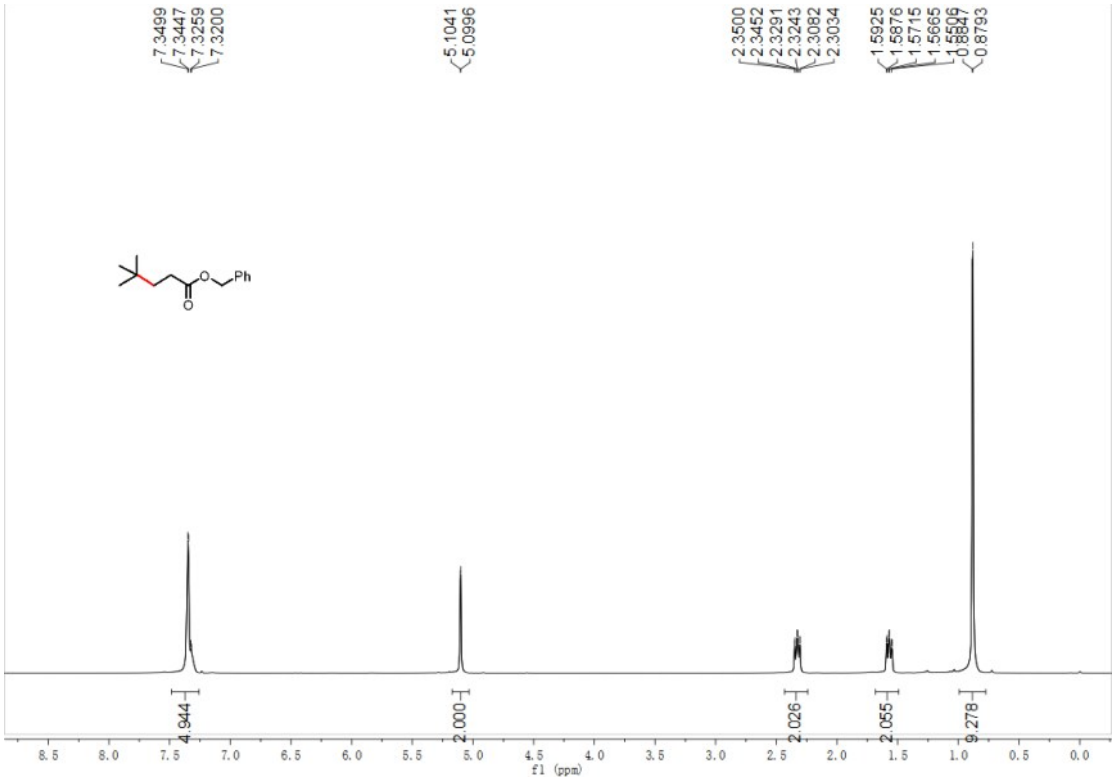
^{1}H NMR spectrum of compound **24**



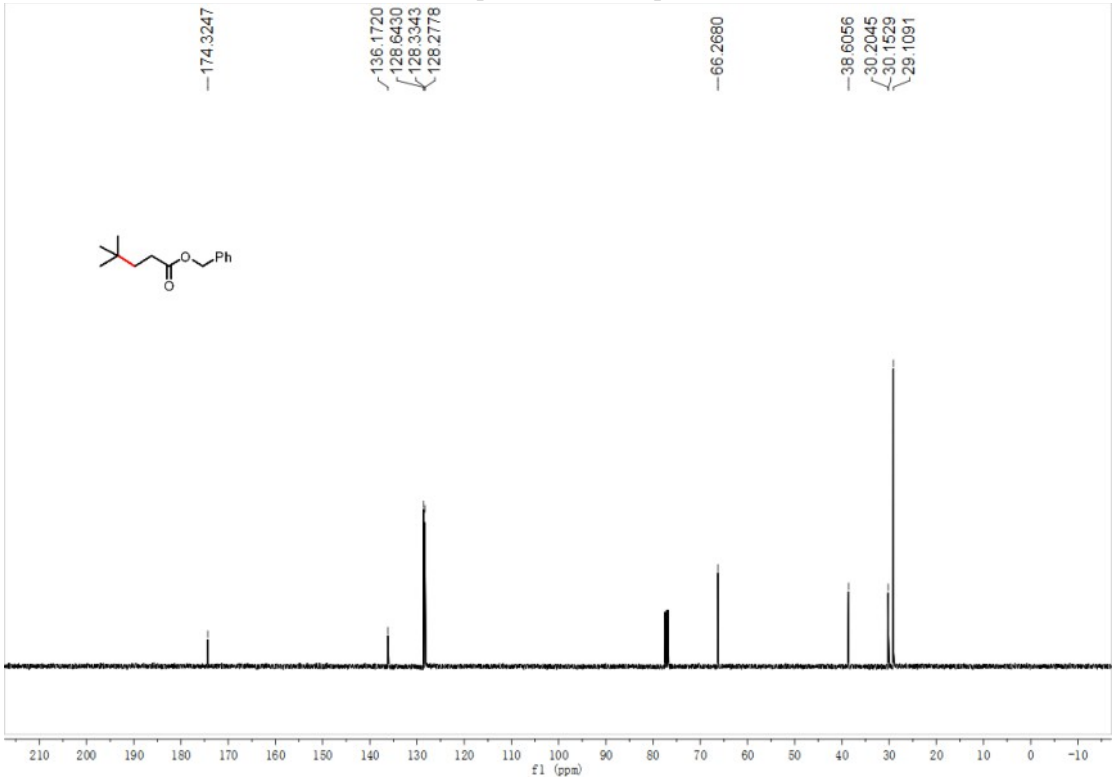
^{13}C NMR spectrum of compound **24**



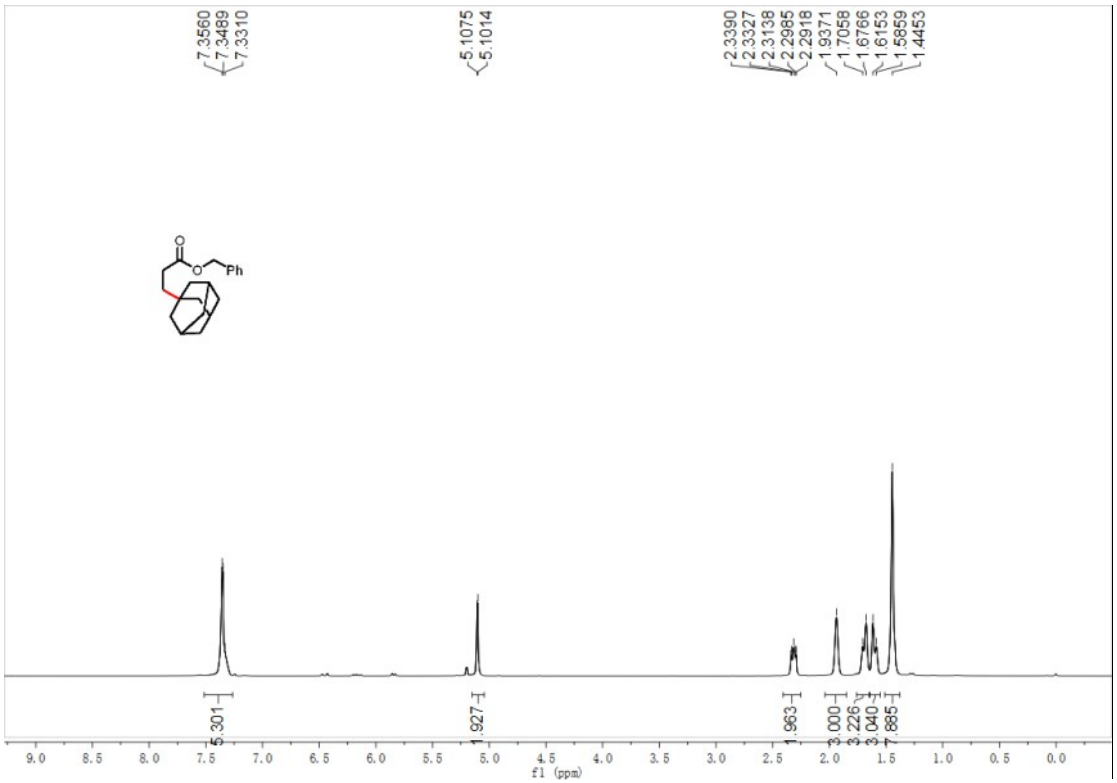
^{1}H NMR spectrum of compound **25**



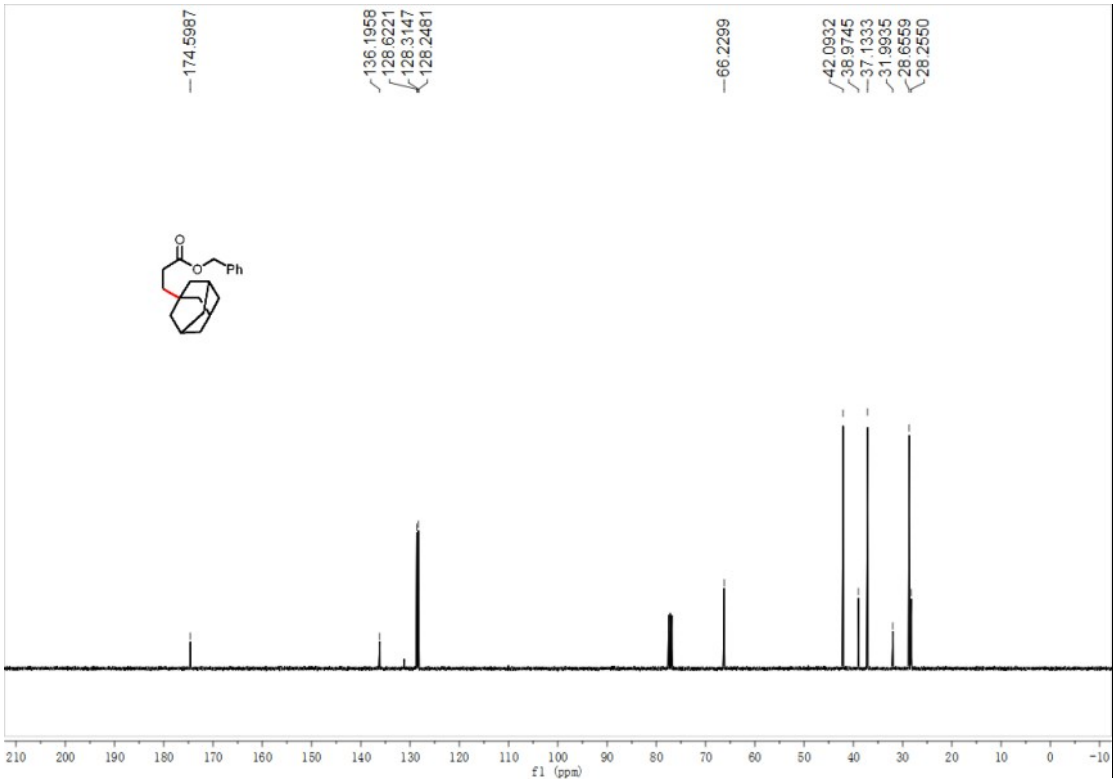
^{13}C NMR spectrum of compound **25**



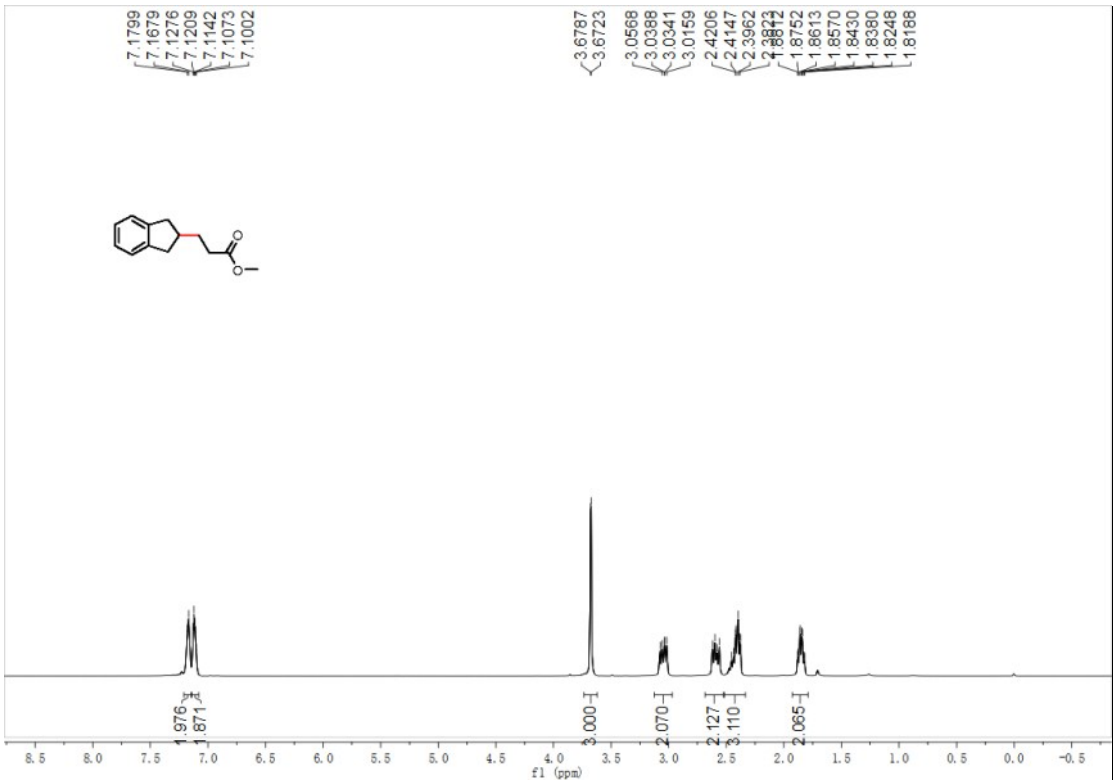
^{1}H NMR spectrum of compound **26**



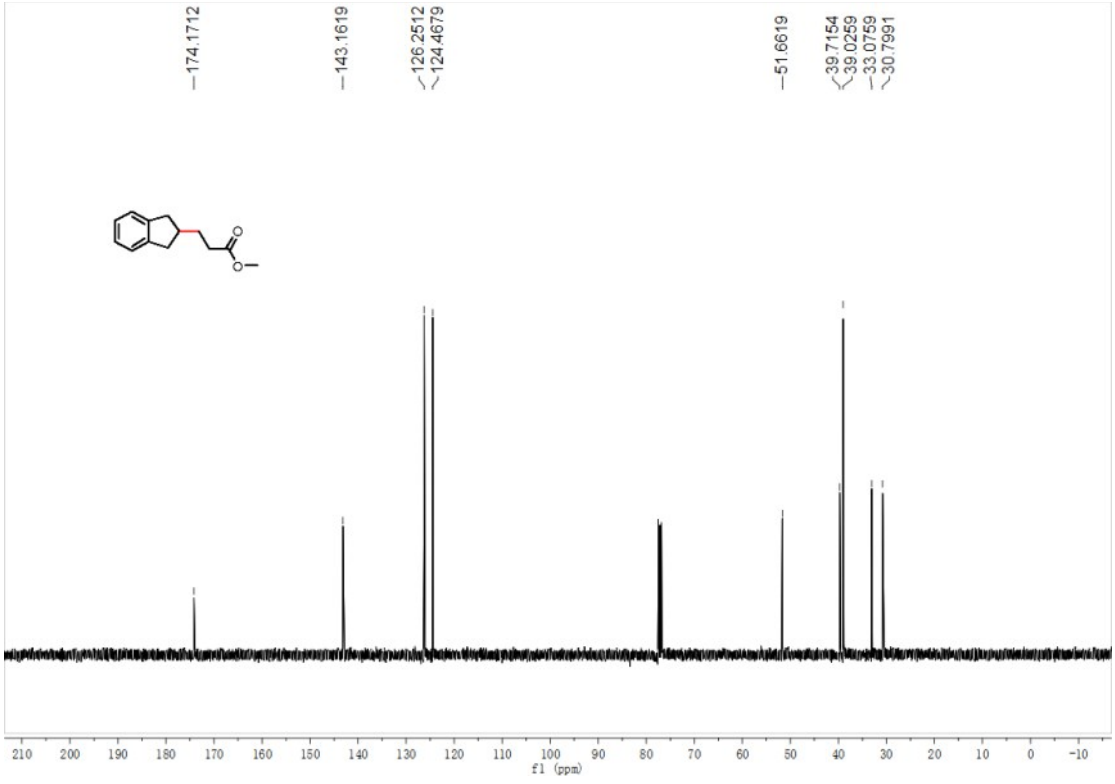
^{13}C NMR spectrum of compound **26**



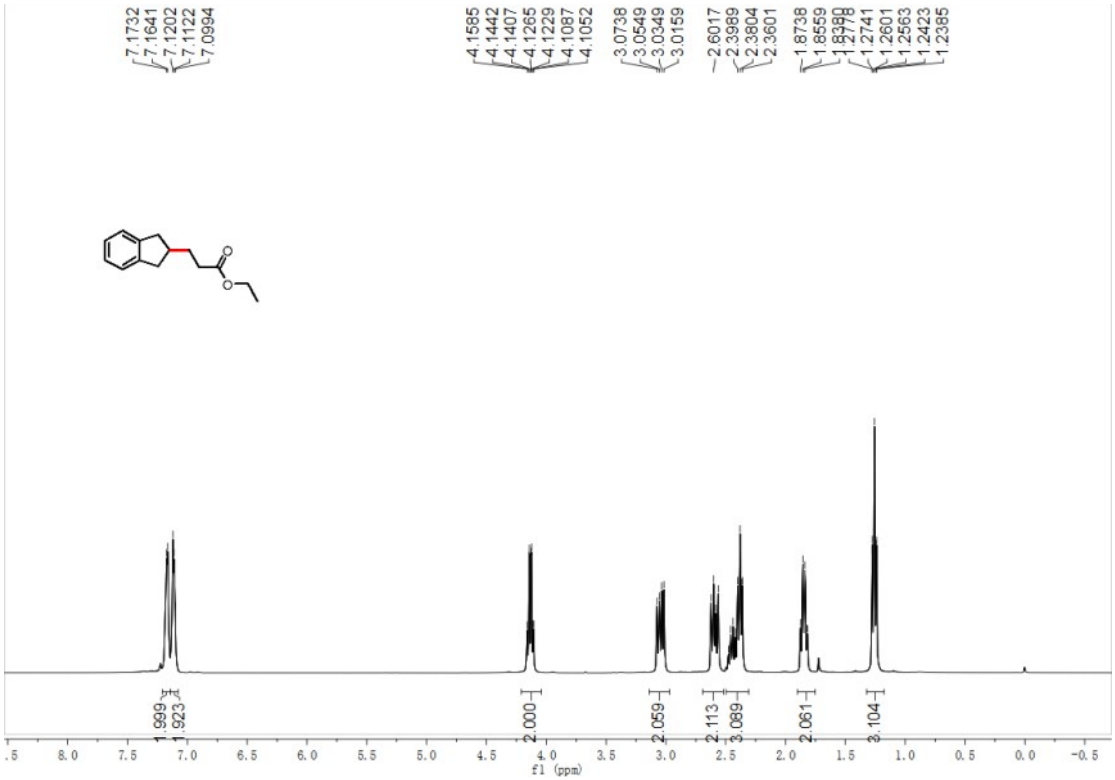
^{1}H NMR spectrum of compound **27**



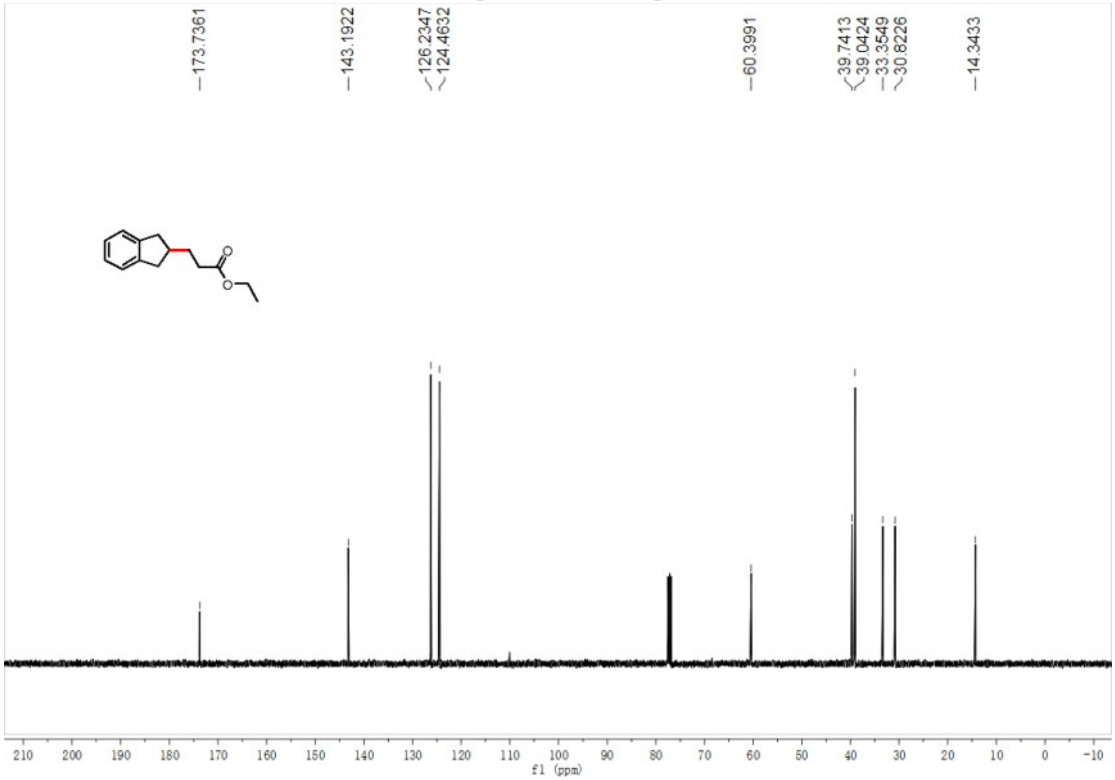
^{13}C NMR spectrum of compound **27**



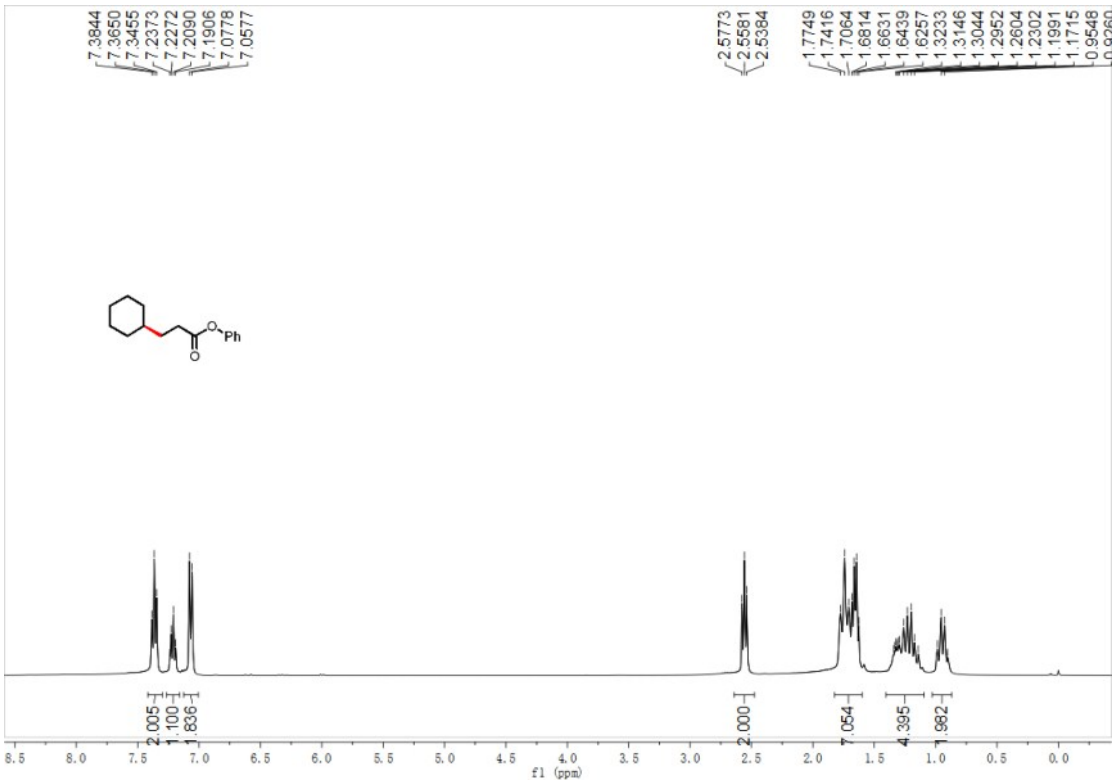
^{1}H NMR spectrum of compound **28**



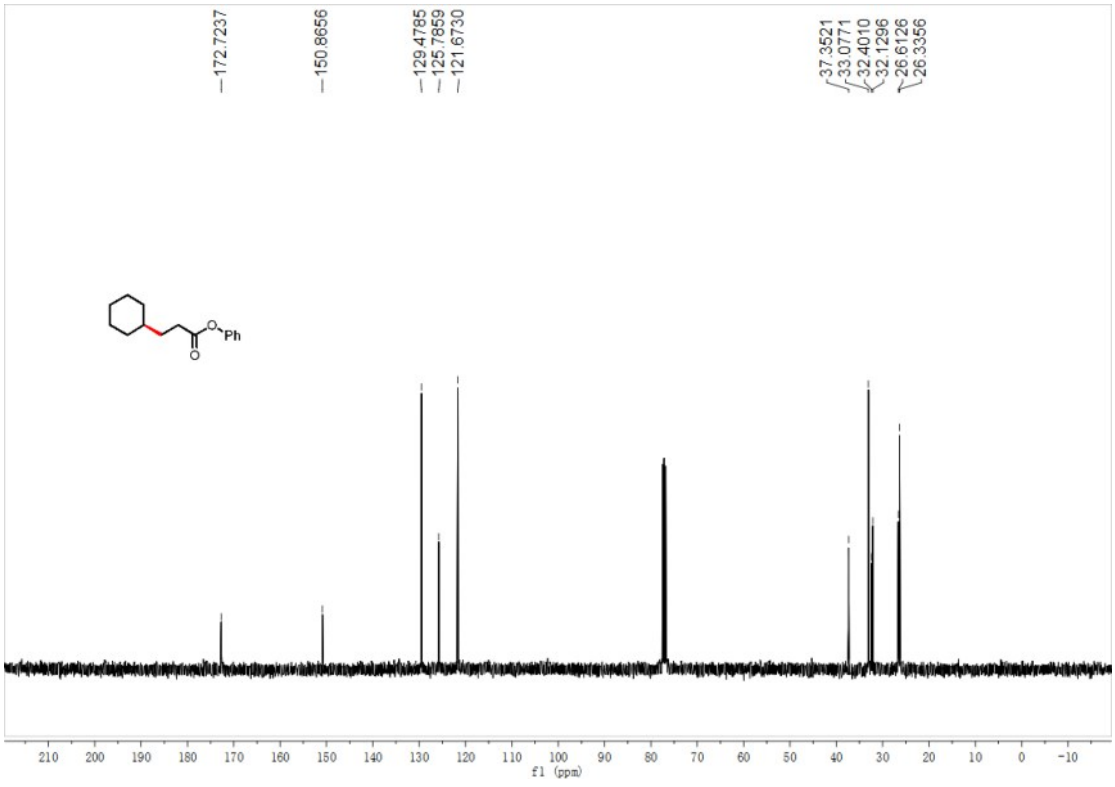
^{13}C NMR spectrum of compound **28**



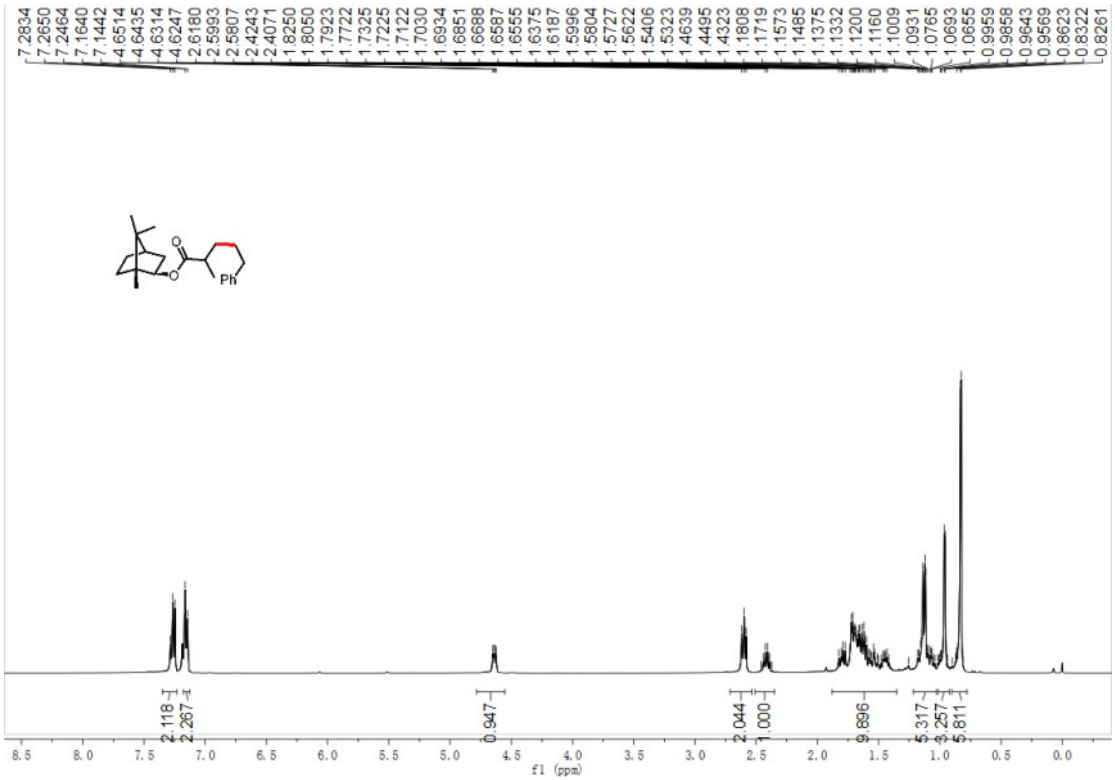
^{1}H NMR spectrum of compound **29**



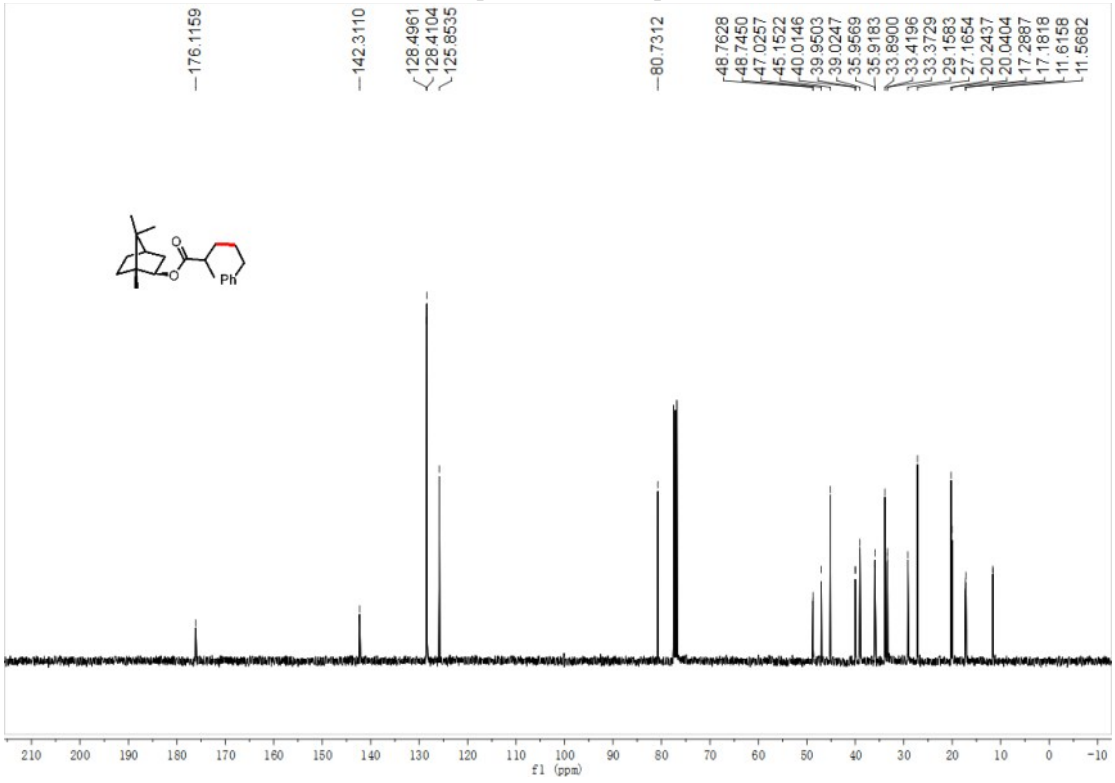
^{13}C NMR spectrum of compound **29**



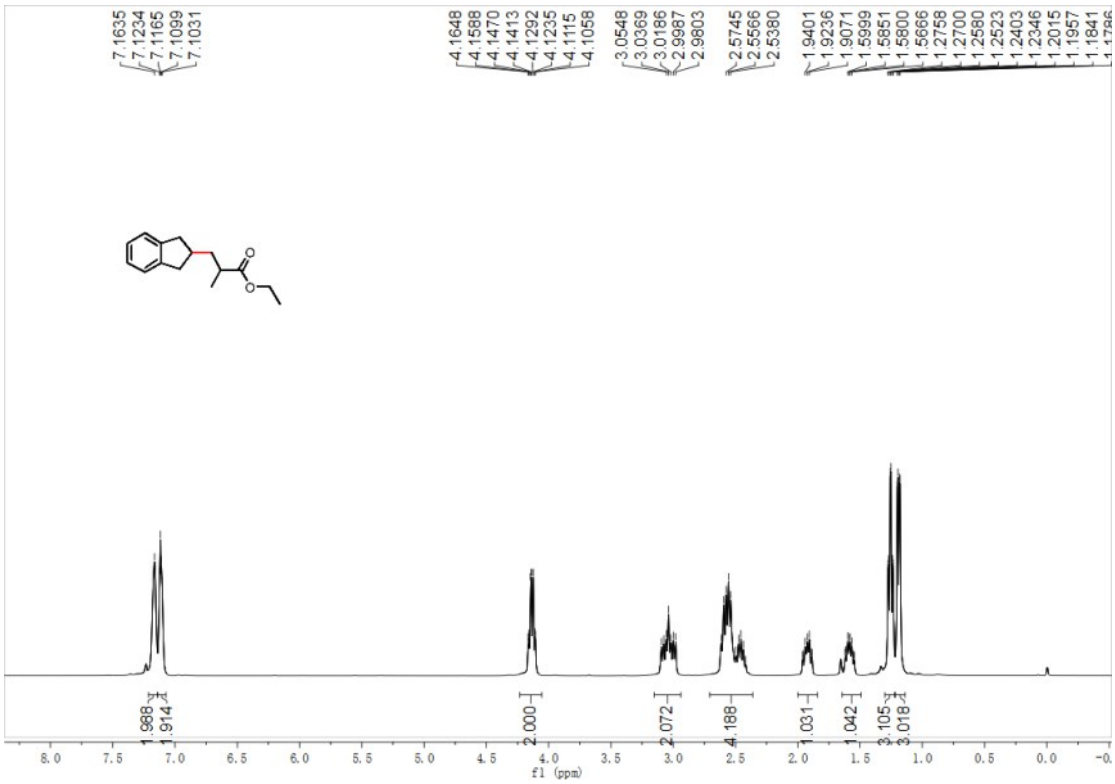
^{1}H NMR spectrum of compound **30**



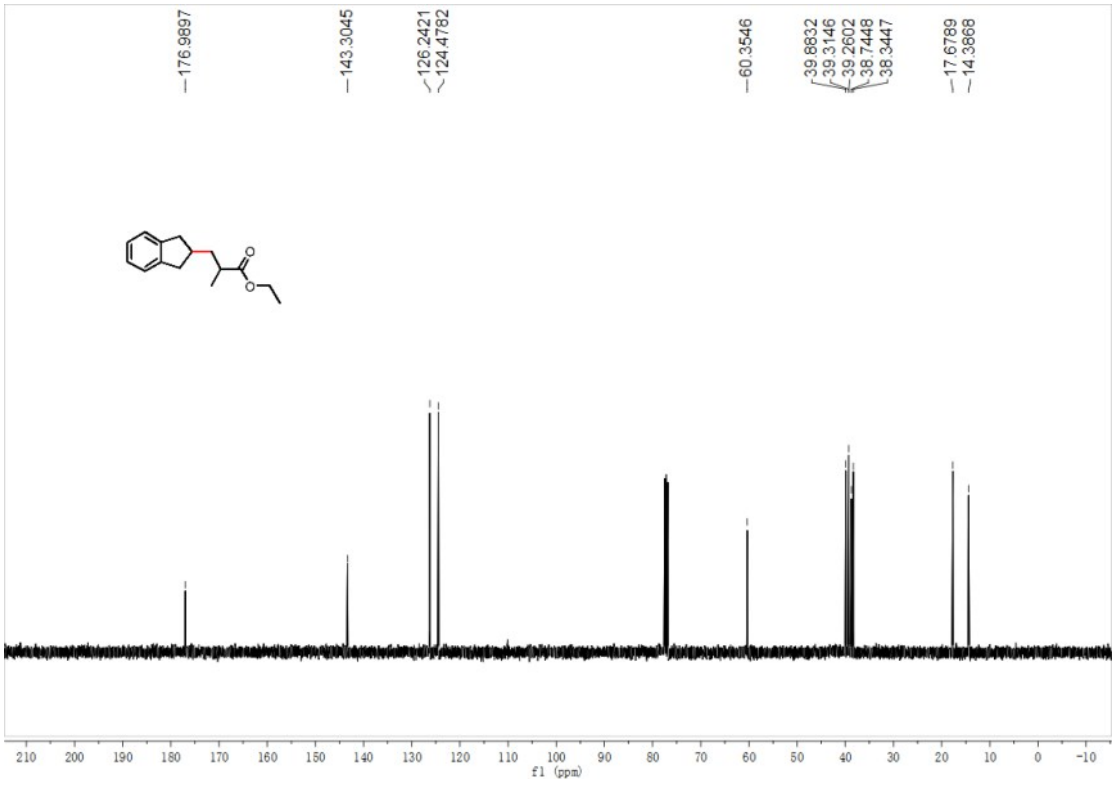
^{13}C NMR spectrum of compound **30**



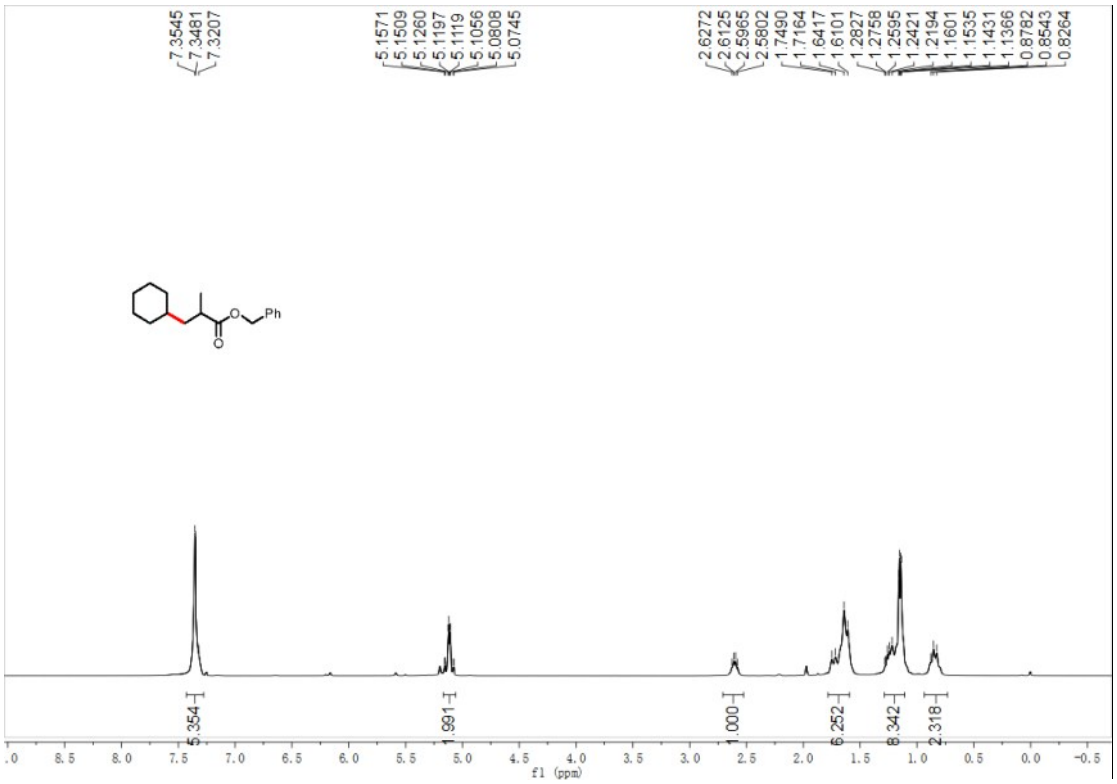
^{1}H NMR spectrum of compound **31**



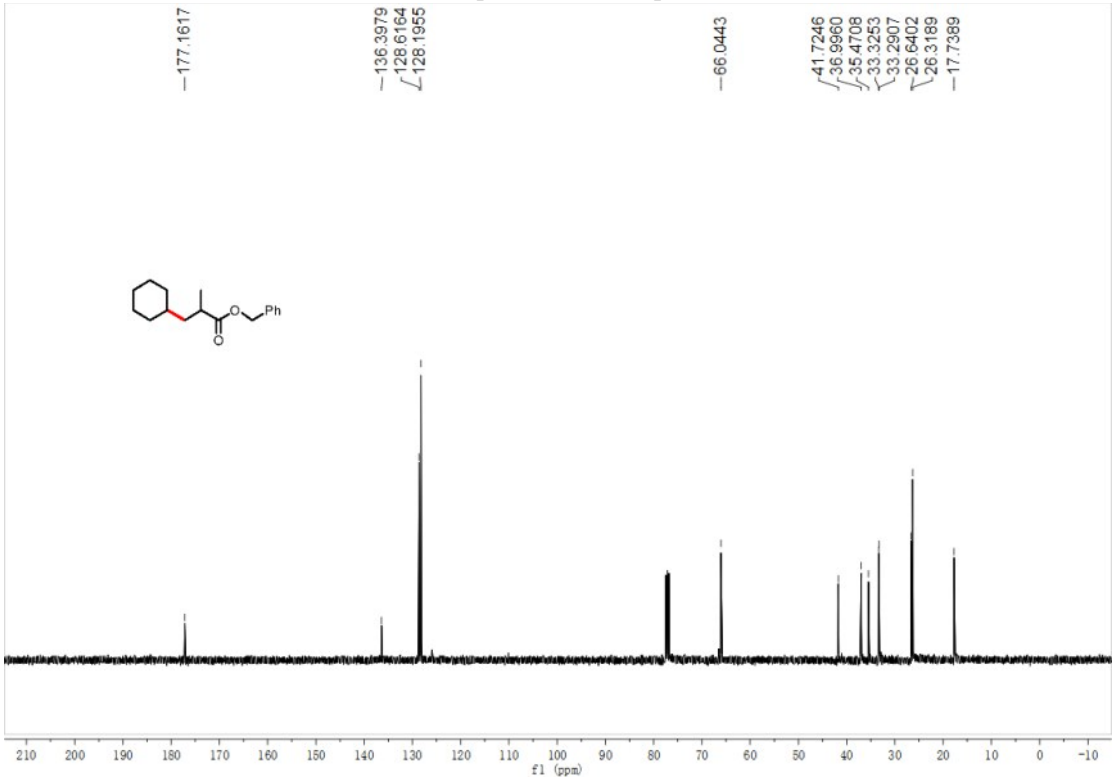
^{13}C NMR spectrum of compound **31**



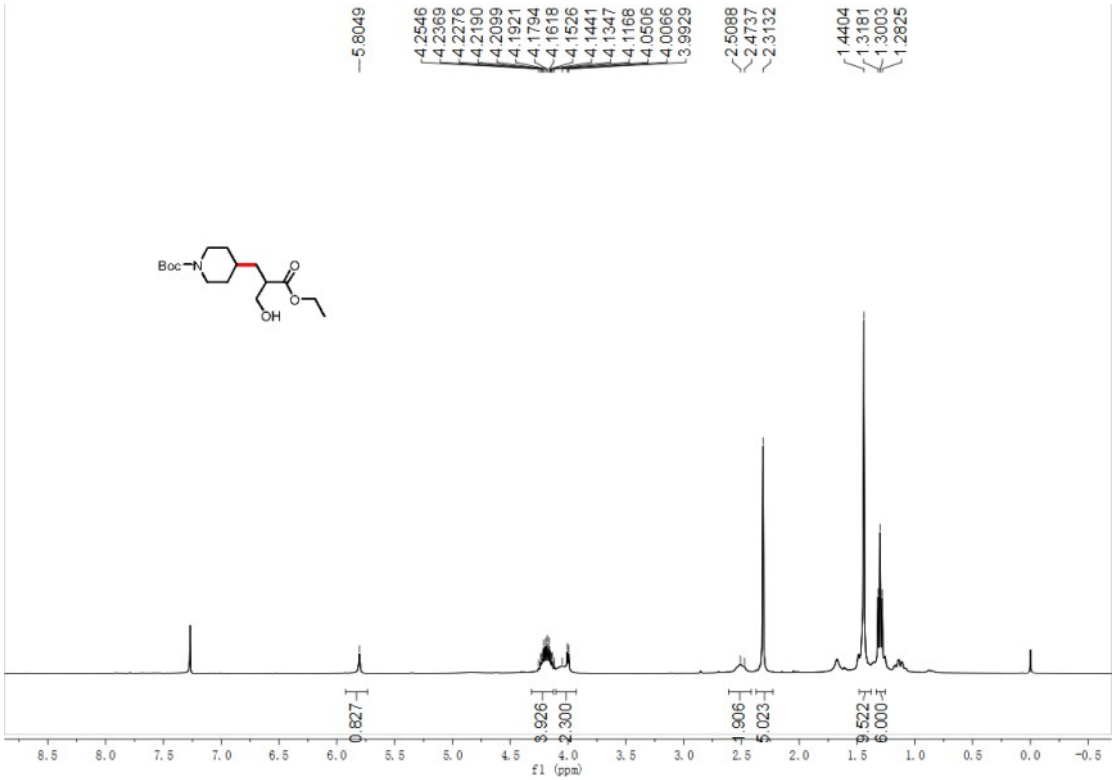
^{1}H NMR spectrum of compound **32**



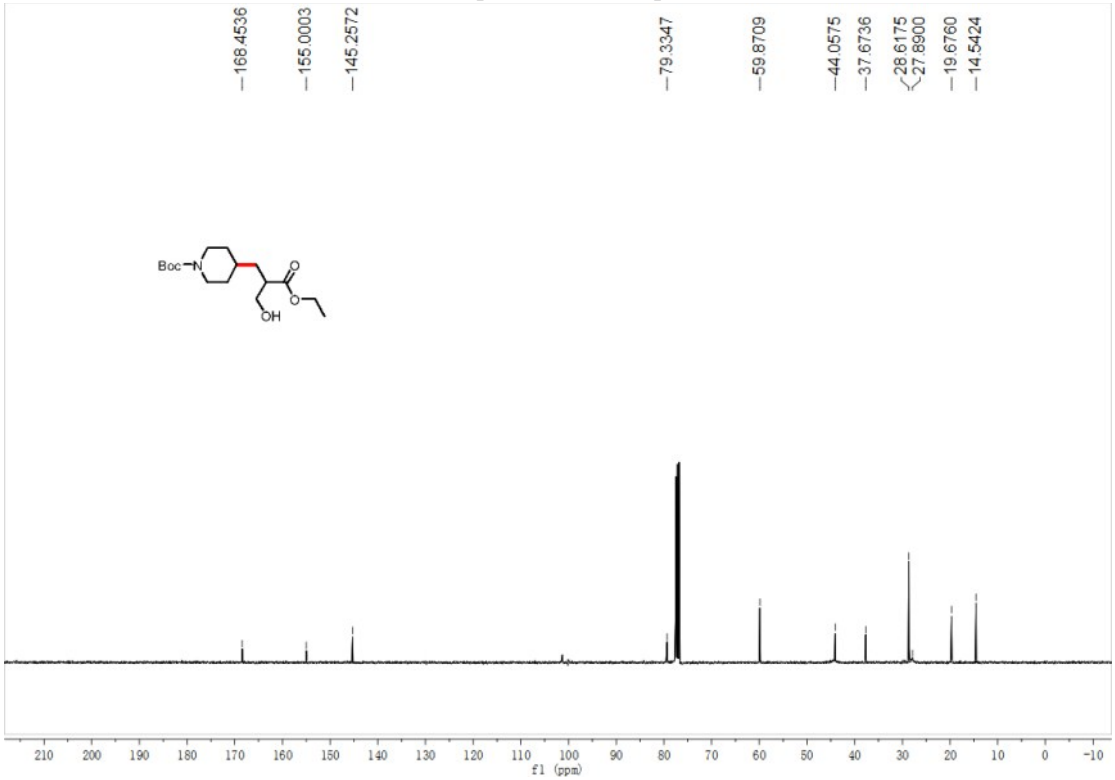
^{13}C NMR spectrum of compound **32**



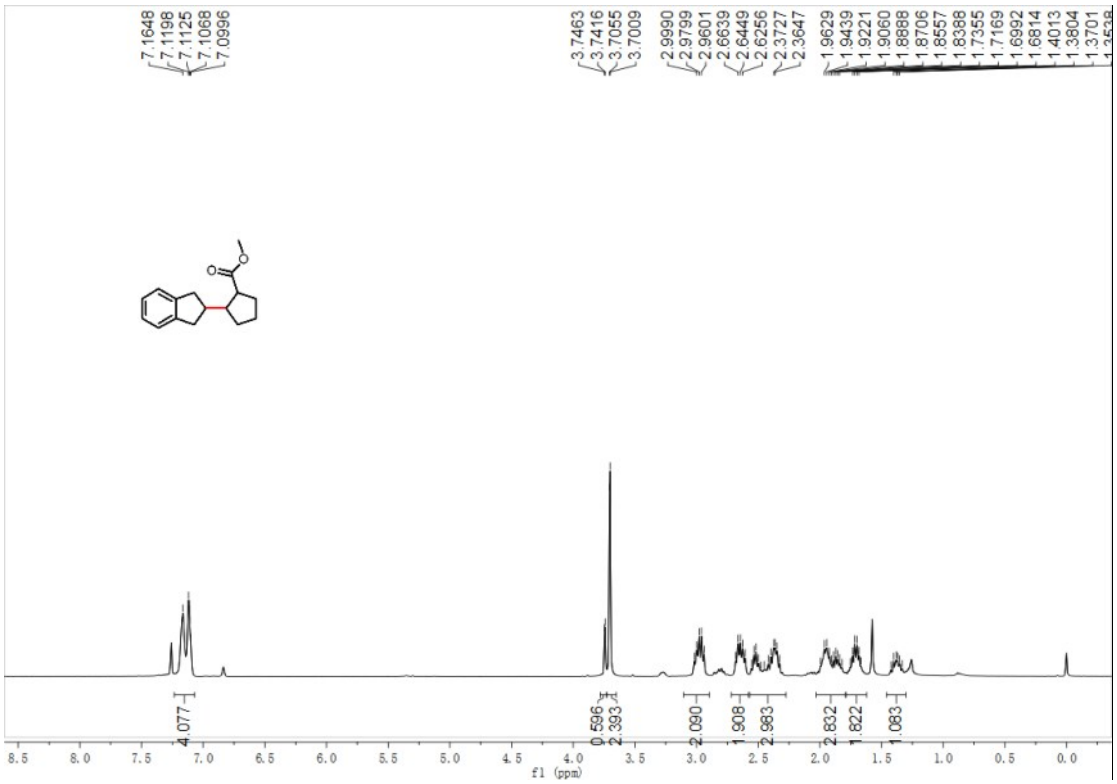
^{1}H NMR spectrum of compound **33**



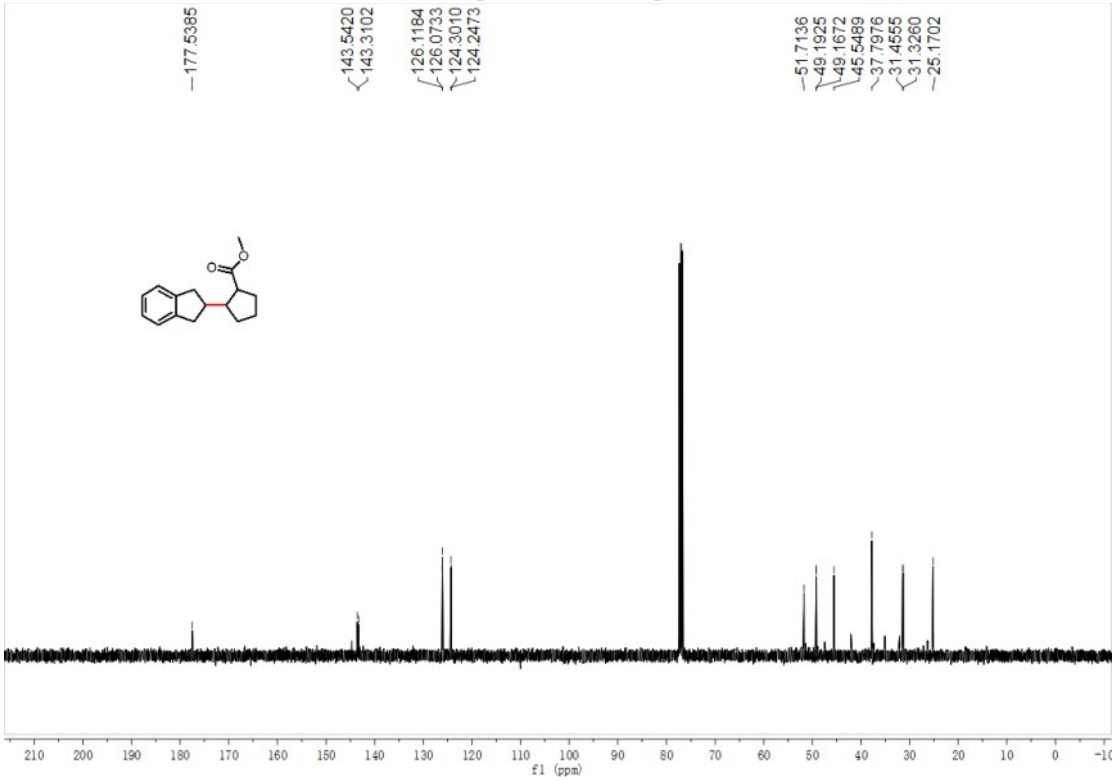
^{13}C NMR spectrum of compound **33**



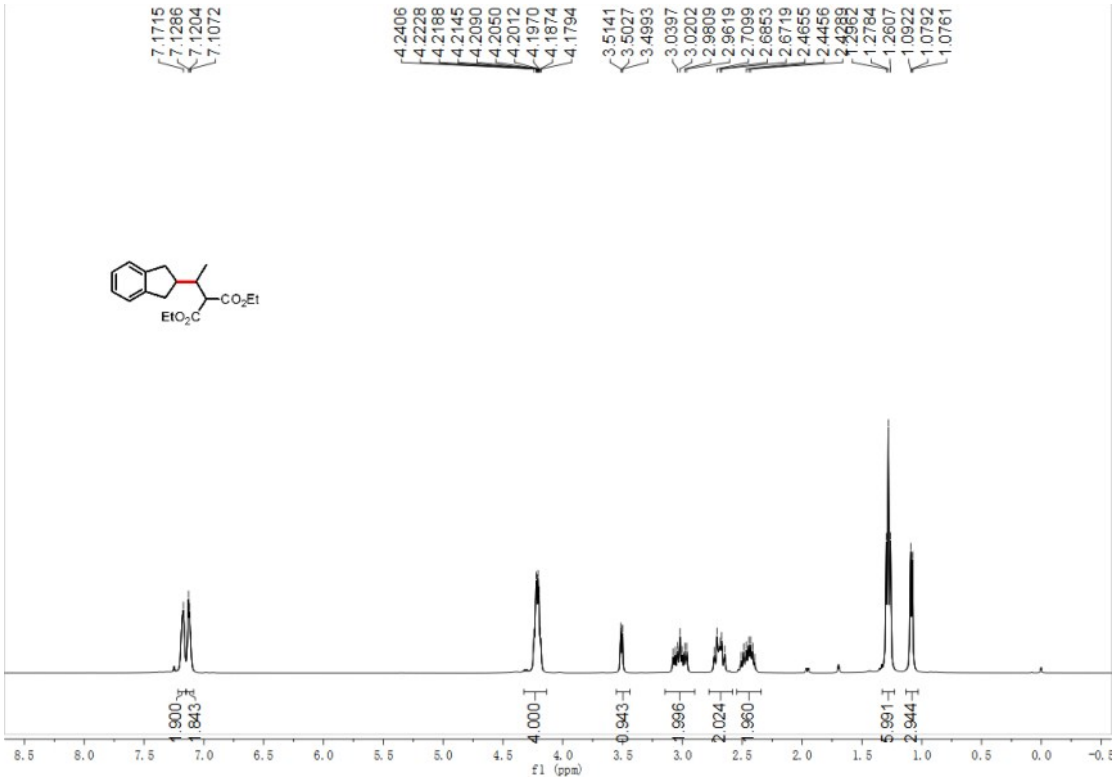
^{1}H NMR spectrum of compound **34**



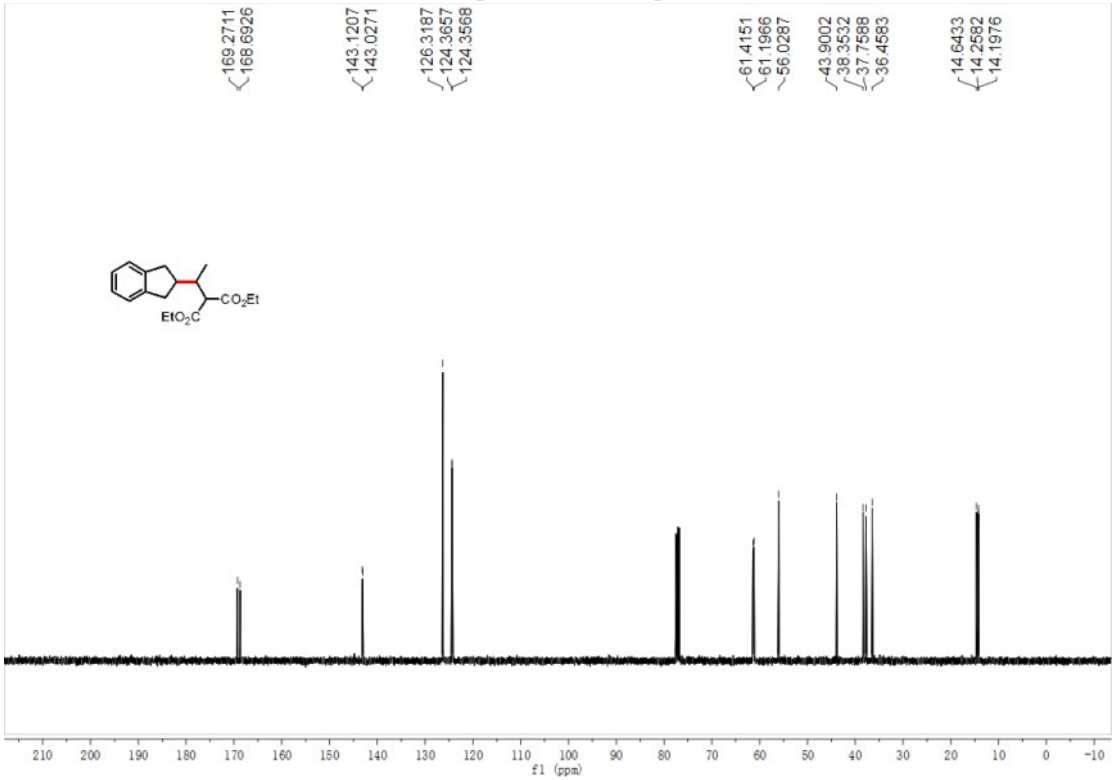
^{13}C NMR spectrum of compound **34**



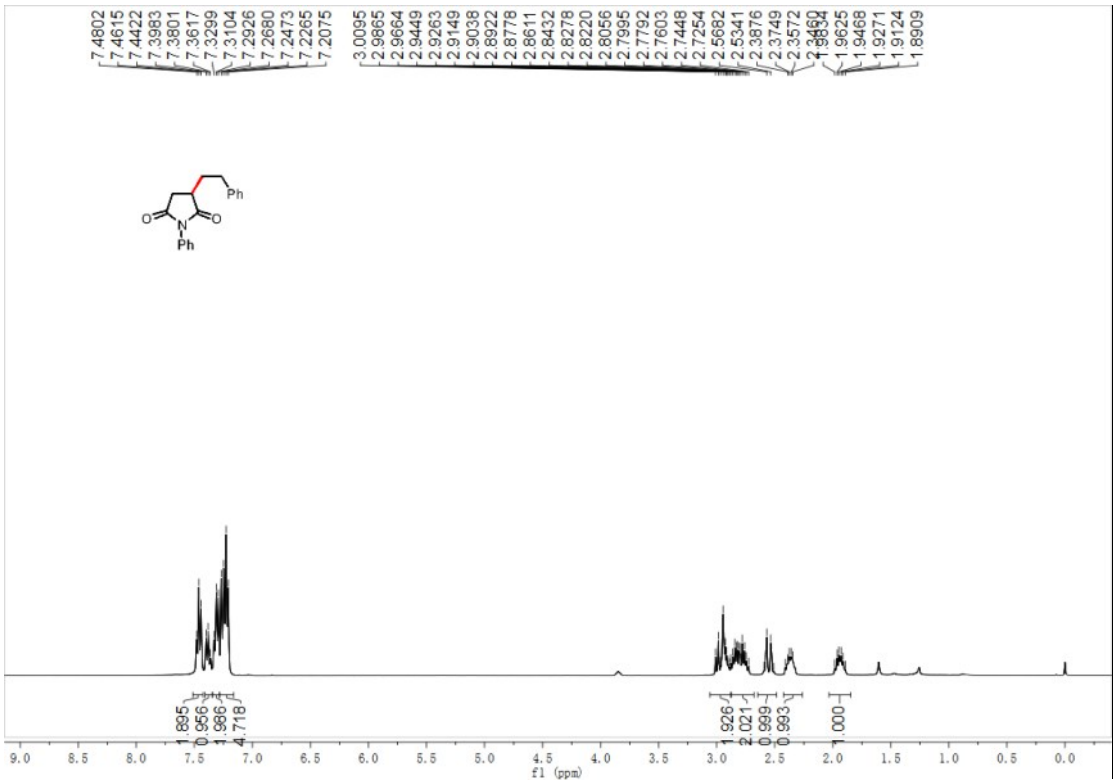
^{1}H NMR spectrum of compound **35**



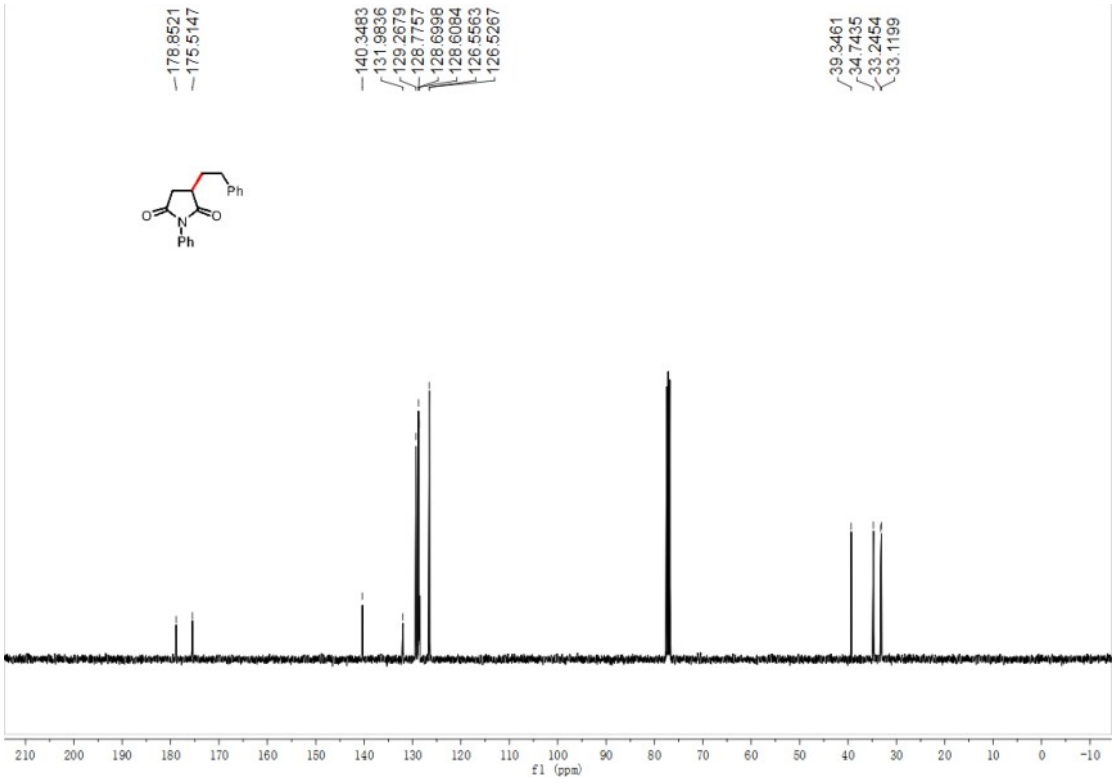
^{13}C NMR spectrum of compound **35**



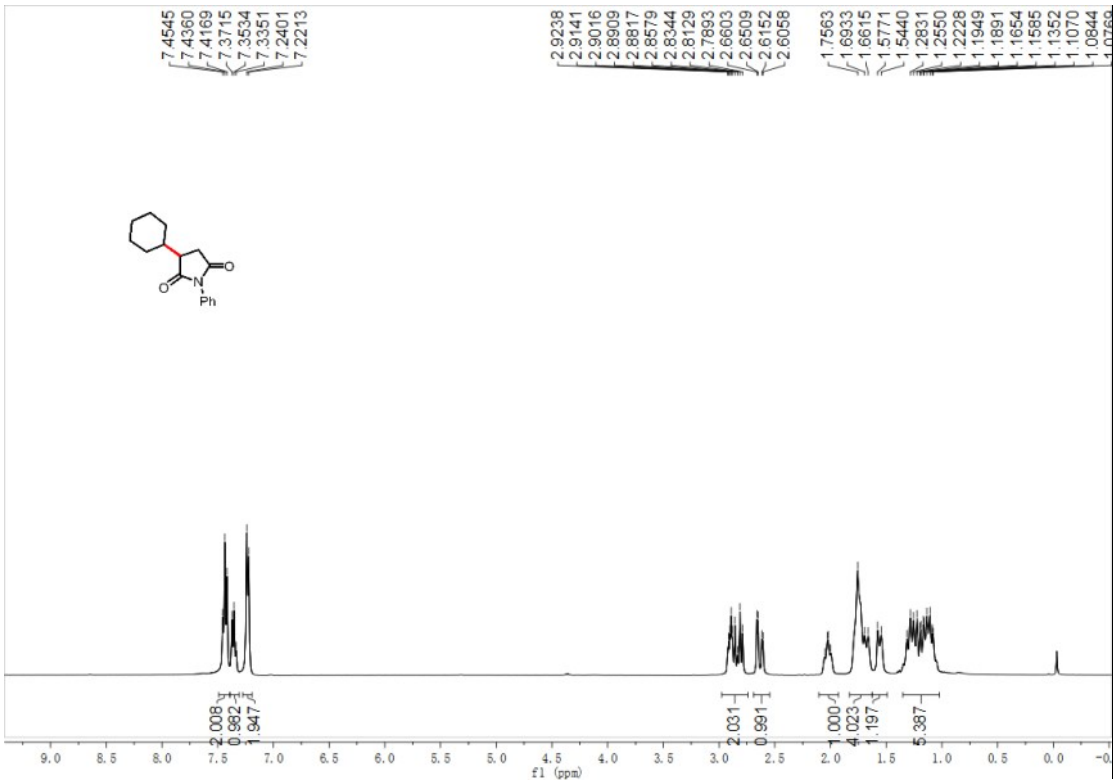
^{1}H NMR spectrum of compound **36**



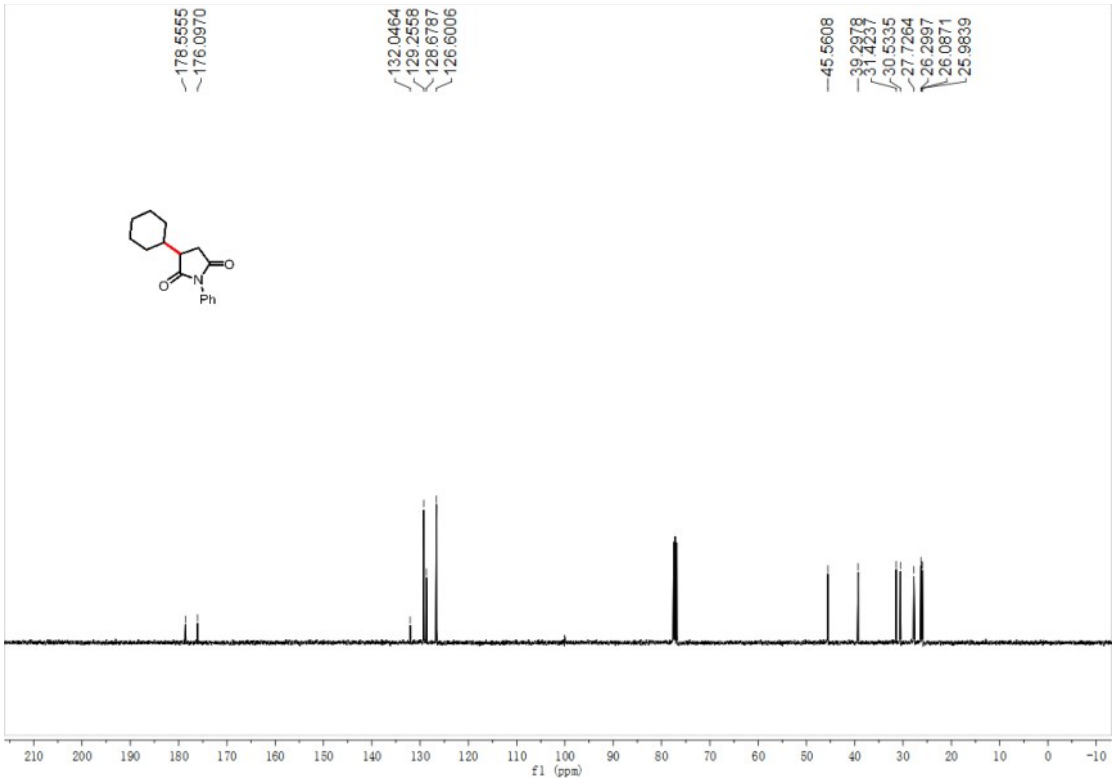
^{13}C NMR spectrum of compound **36**



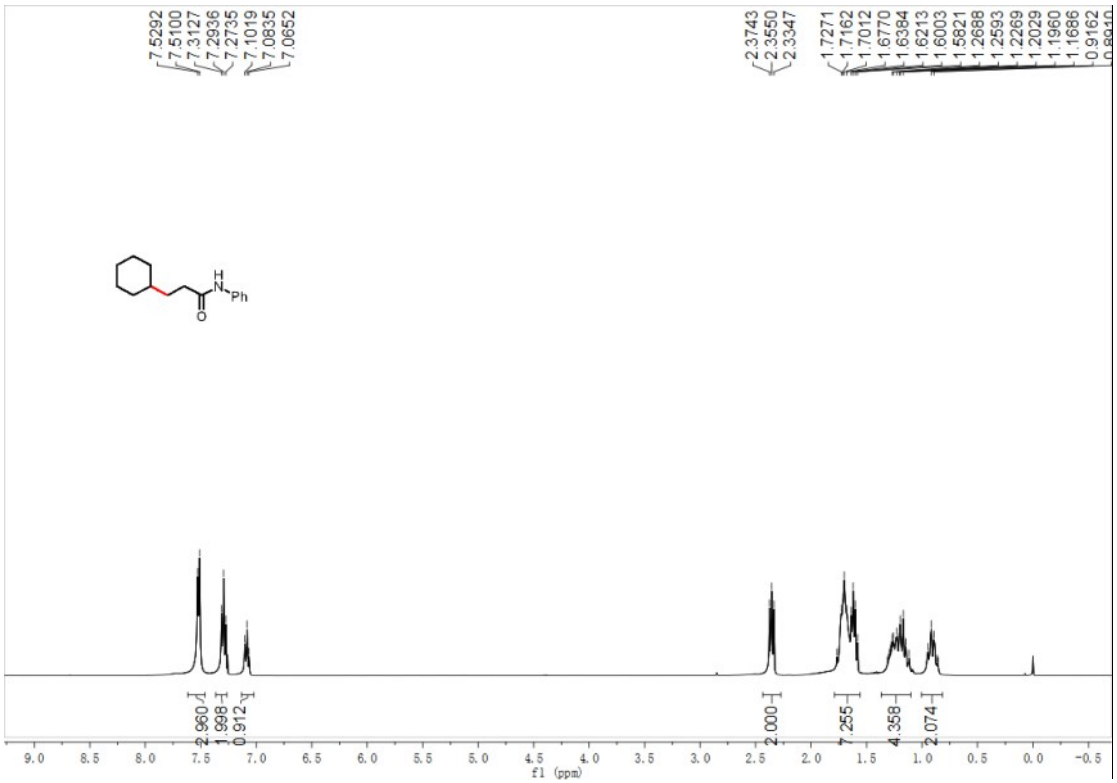
^{1}H NMR spectrum of compound **37**



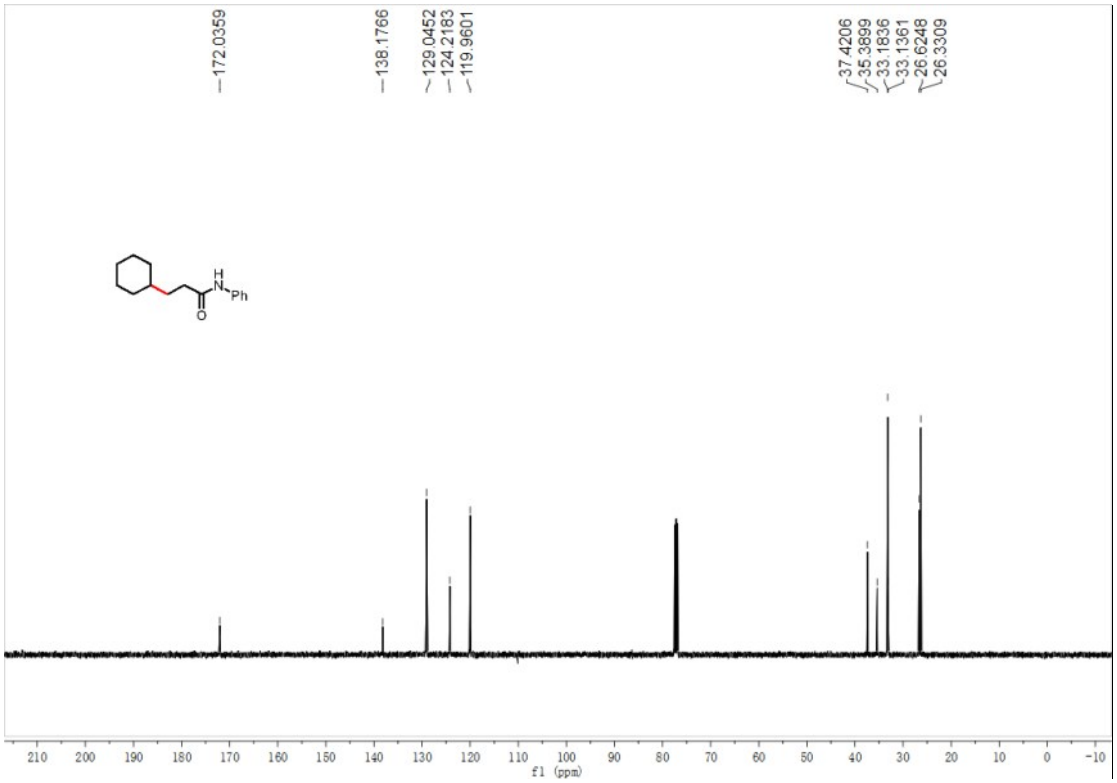
^{13}C NMR spectrum of compound **37**



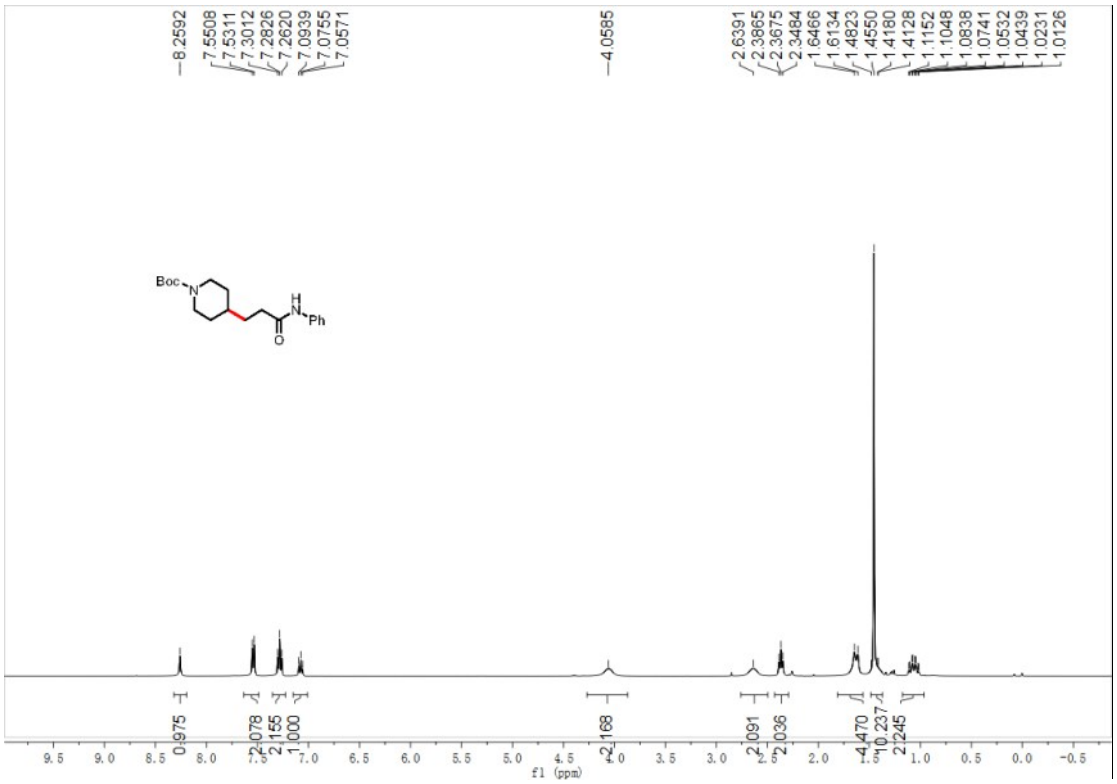
^{1}H NMR spectrum of compound **38**



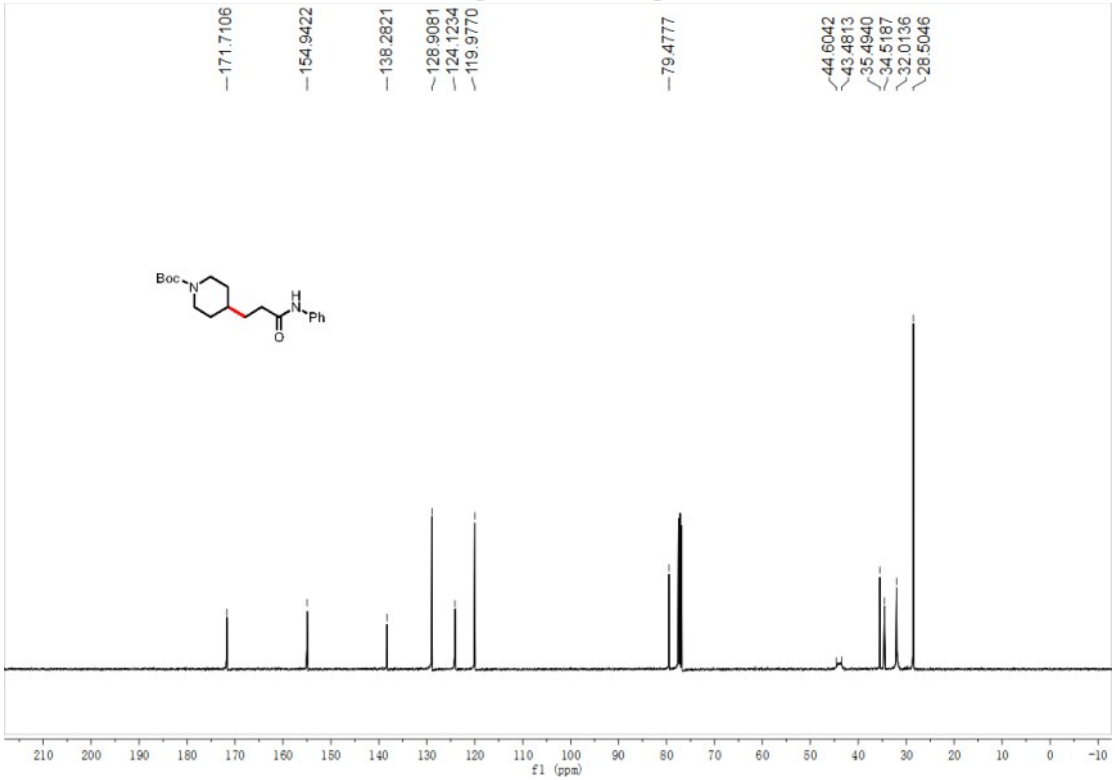
^{13}C NMR spectrum of compound **38**



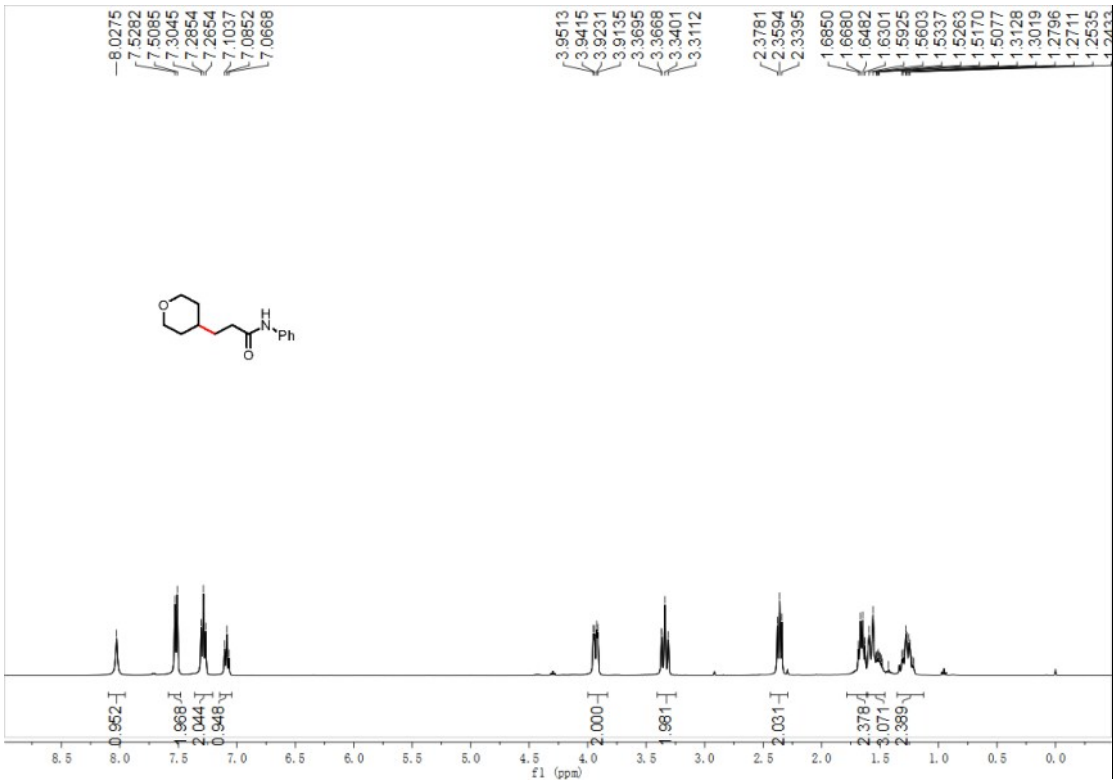
^{1}H NMR spectrum of compound **39**



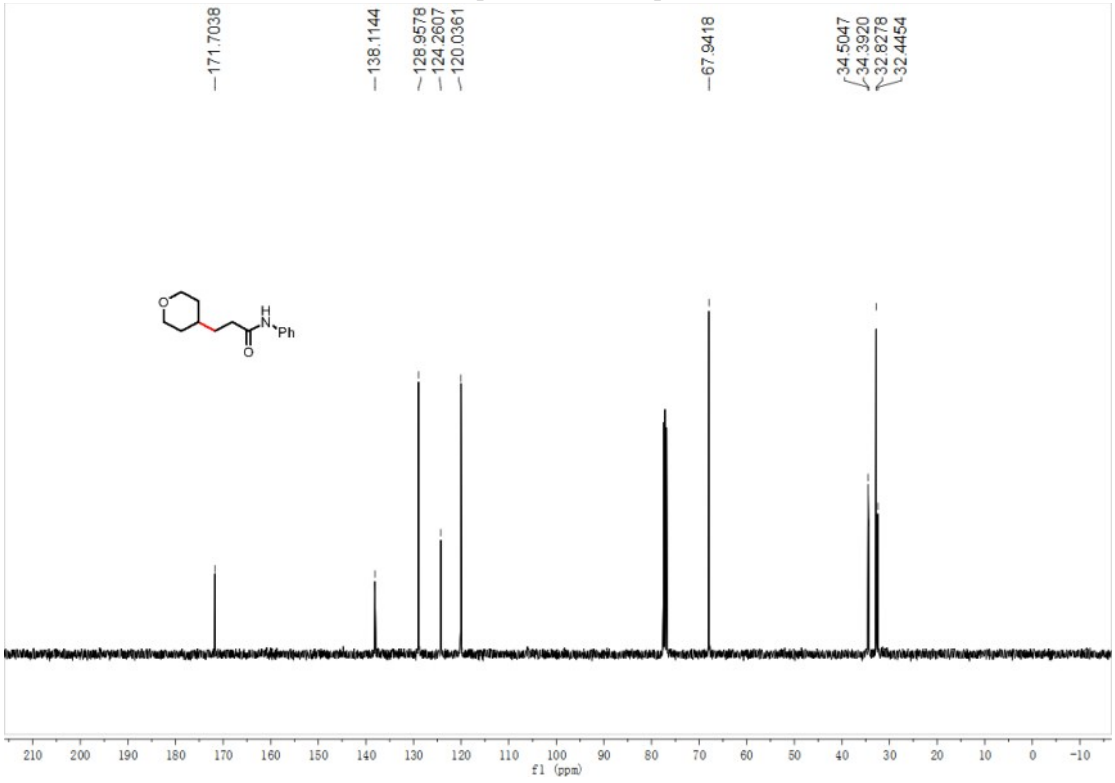
^{13}C NMR spectrum of compound **39**



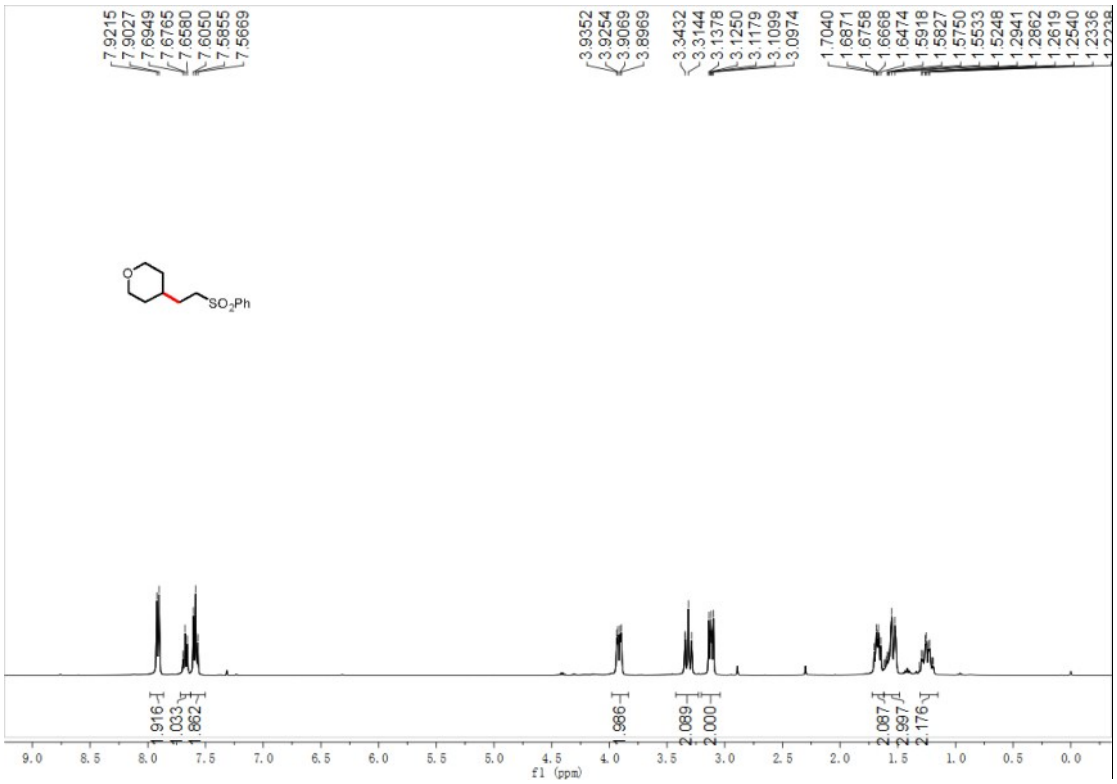
^{1}H NMR spectrum of compound **40**



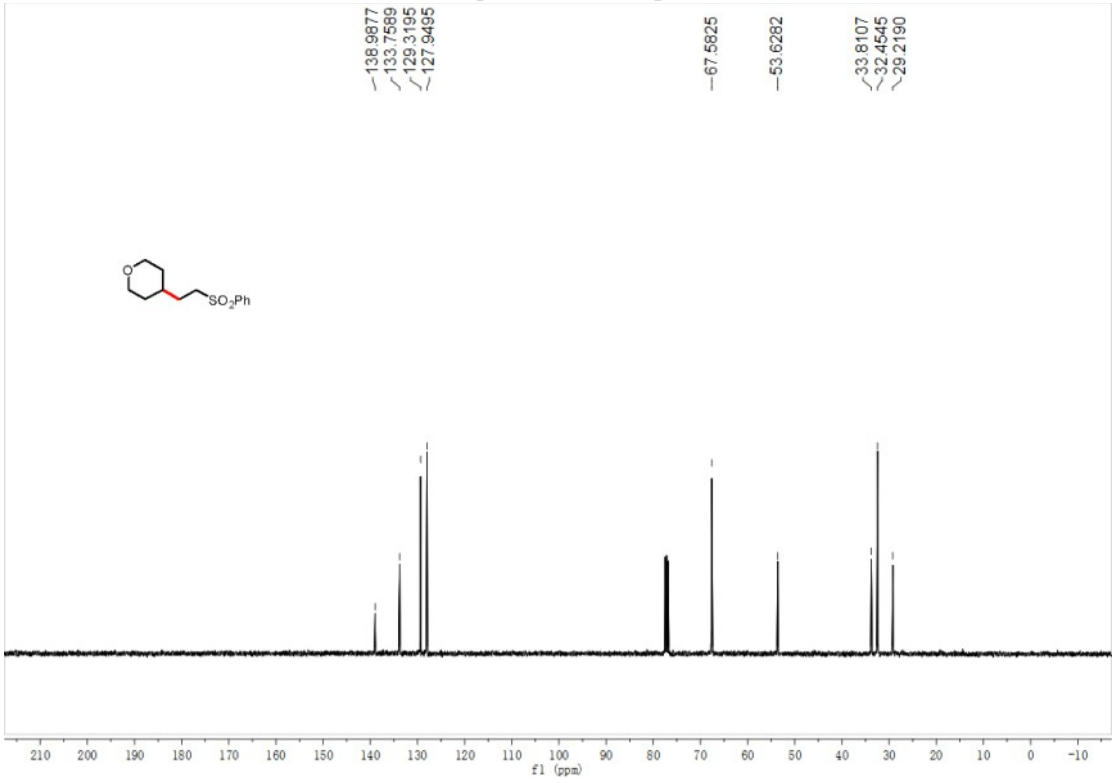
^{13}C NMR spectrum of compound **40**



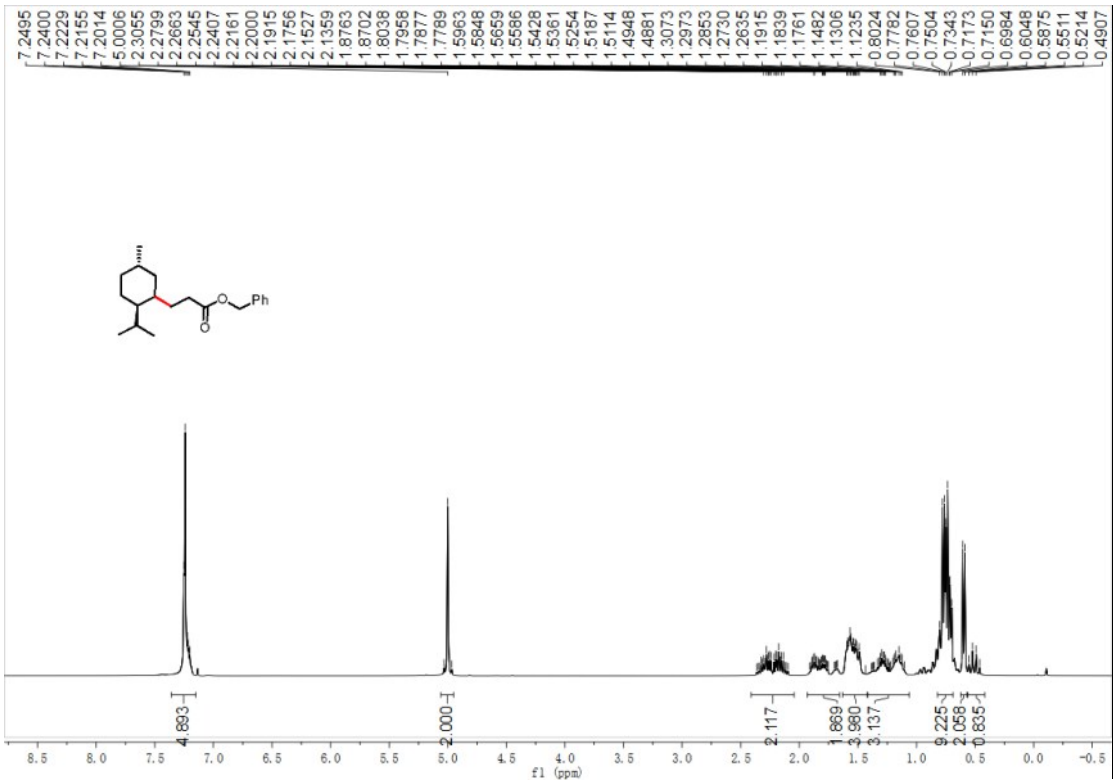
^{1}H NMR spectrum of compound **41**



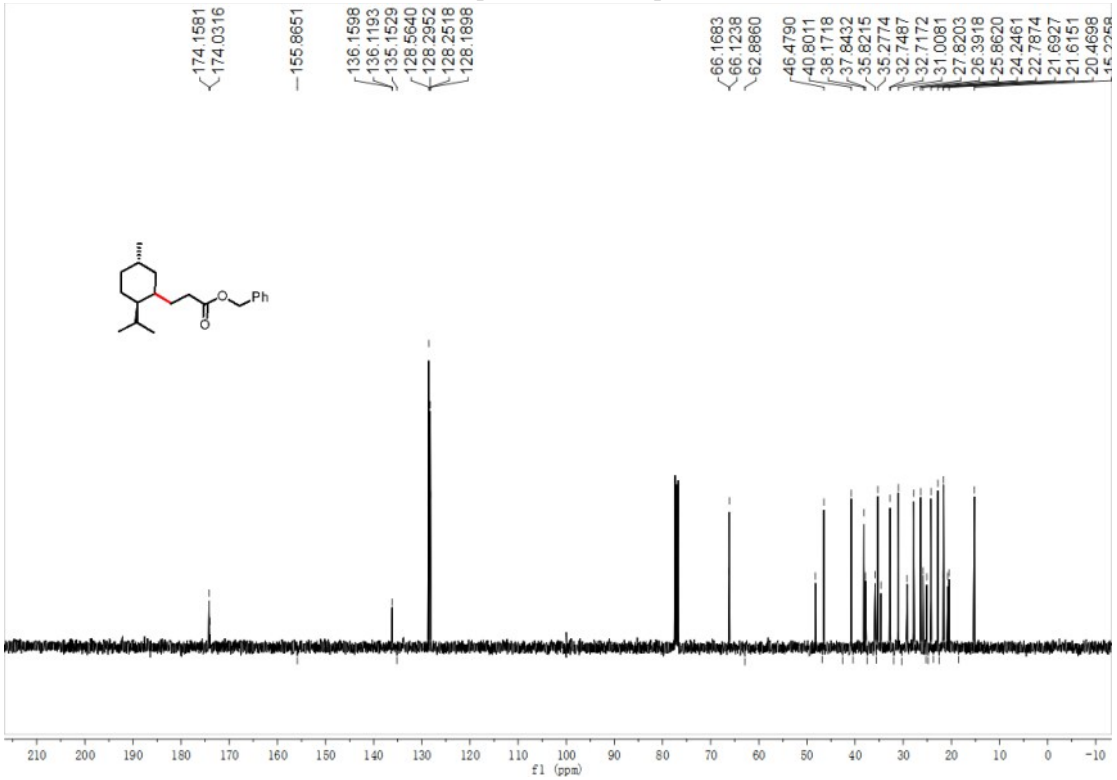
^{13}C NMR spectrum of compound **41**



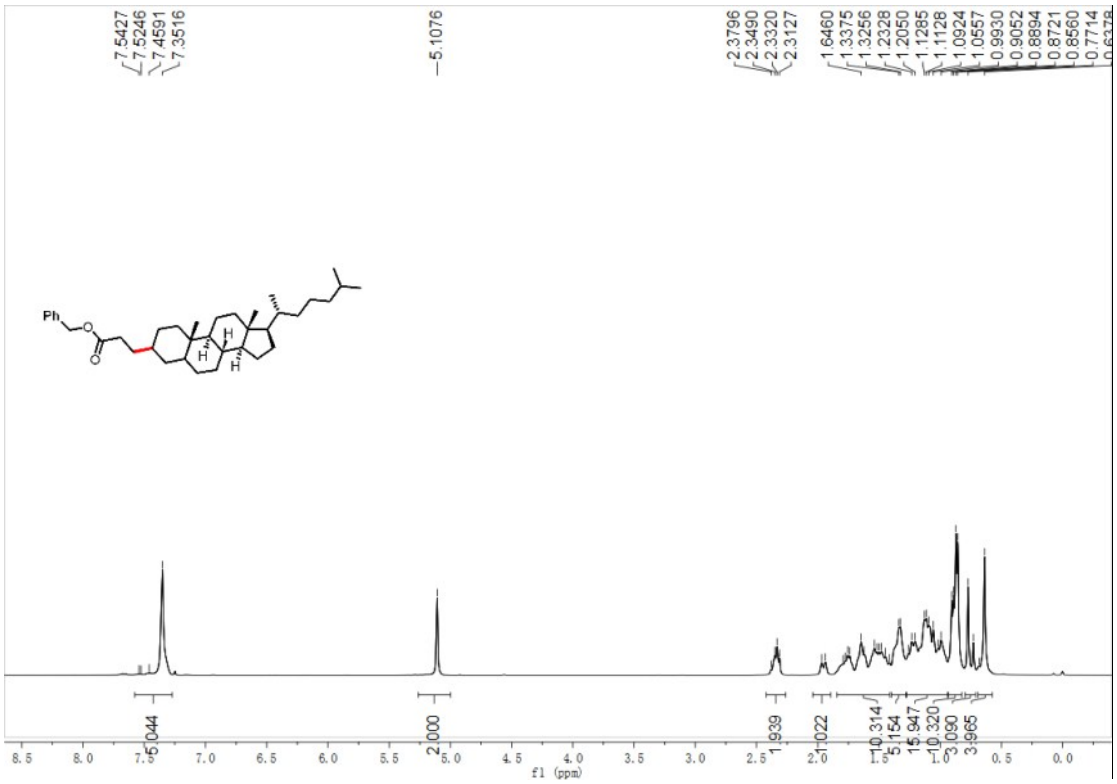
^{1}H NMR spectrum of compound **42**



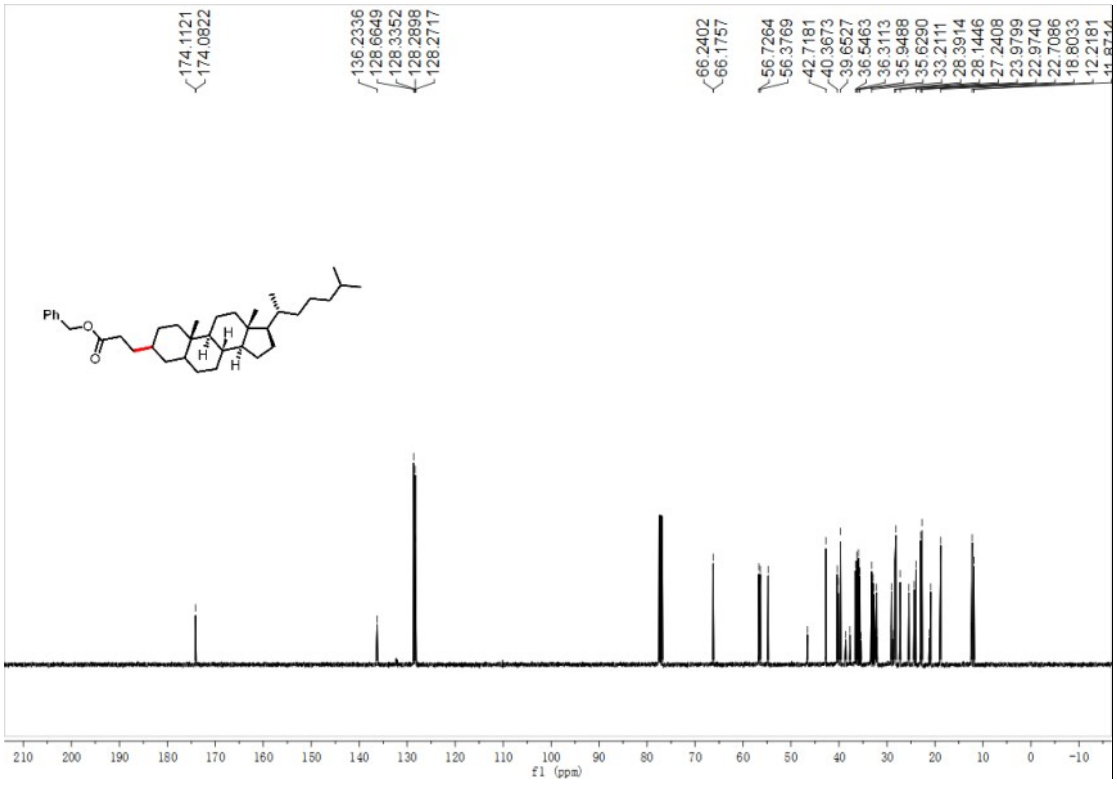
^{13}C NMR spectrum of compound **42**



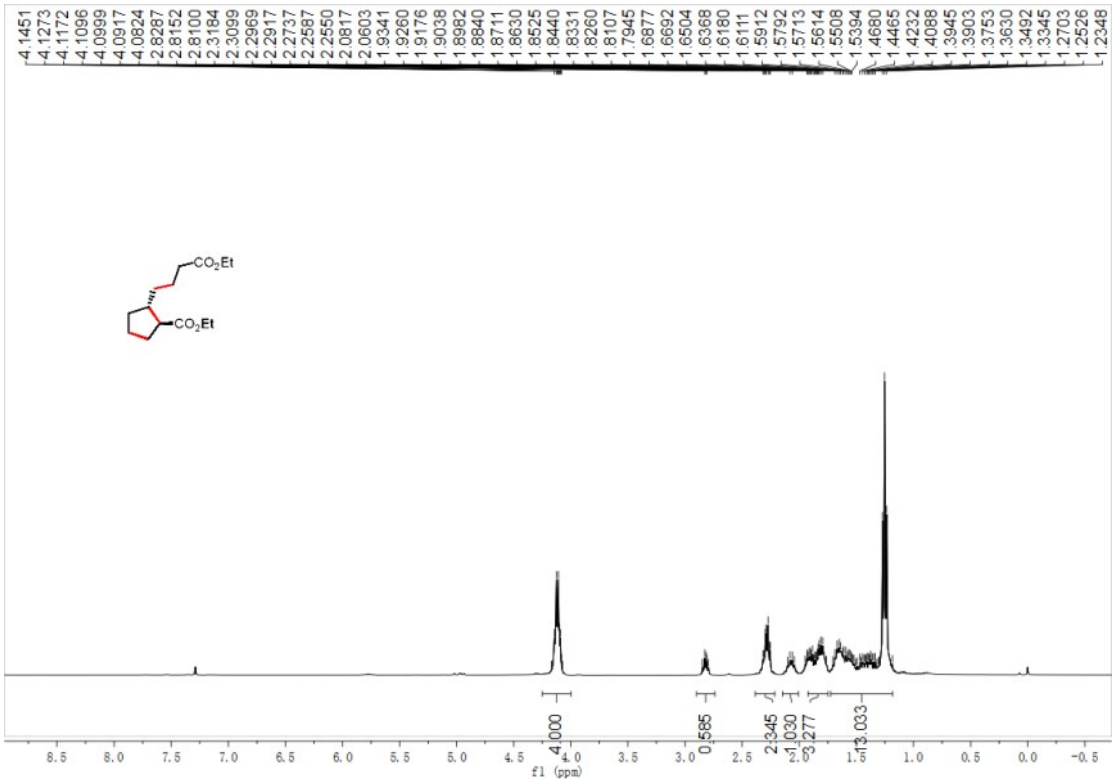
^{1}H NMR spectrum of compound **43**



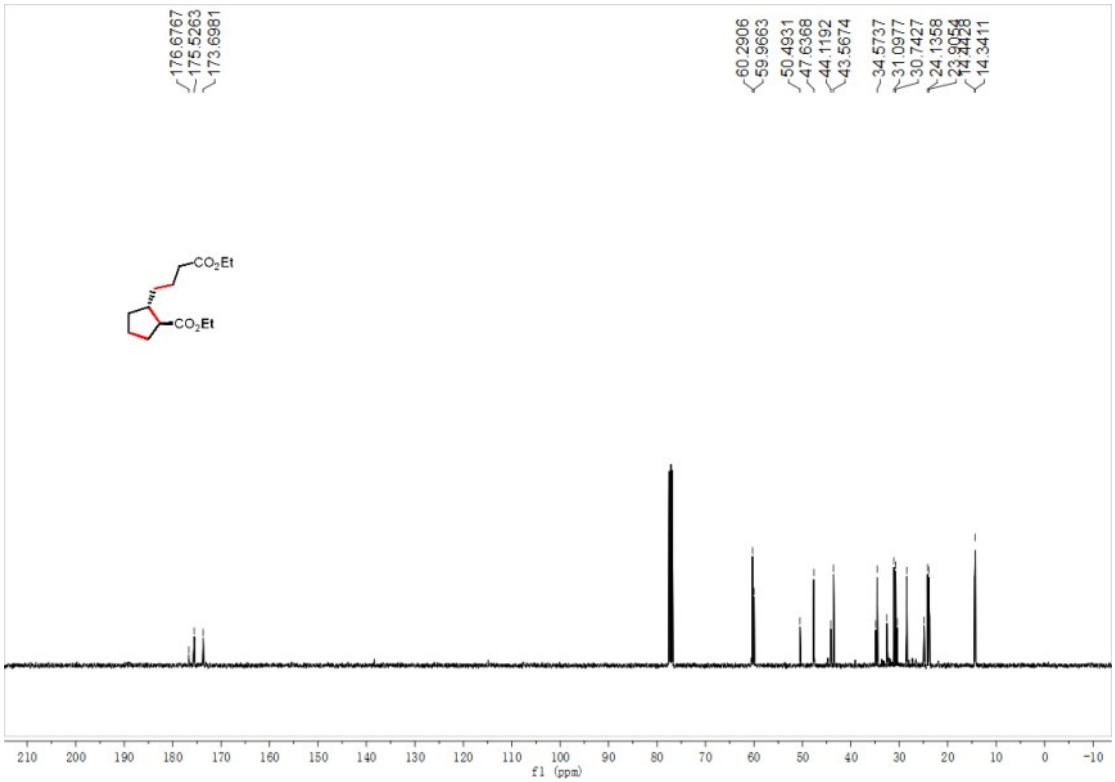
^{13}C NMR spectrum of compound **43**



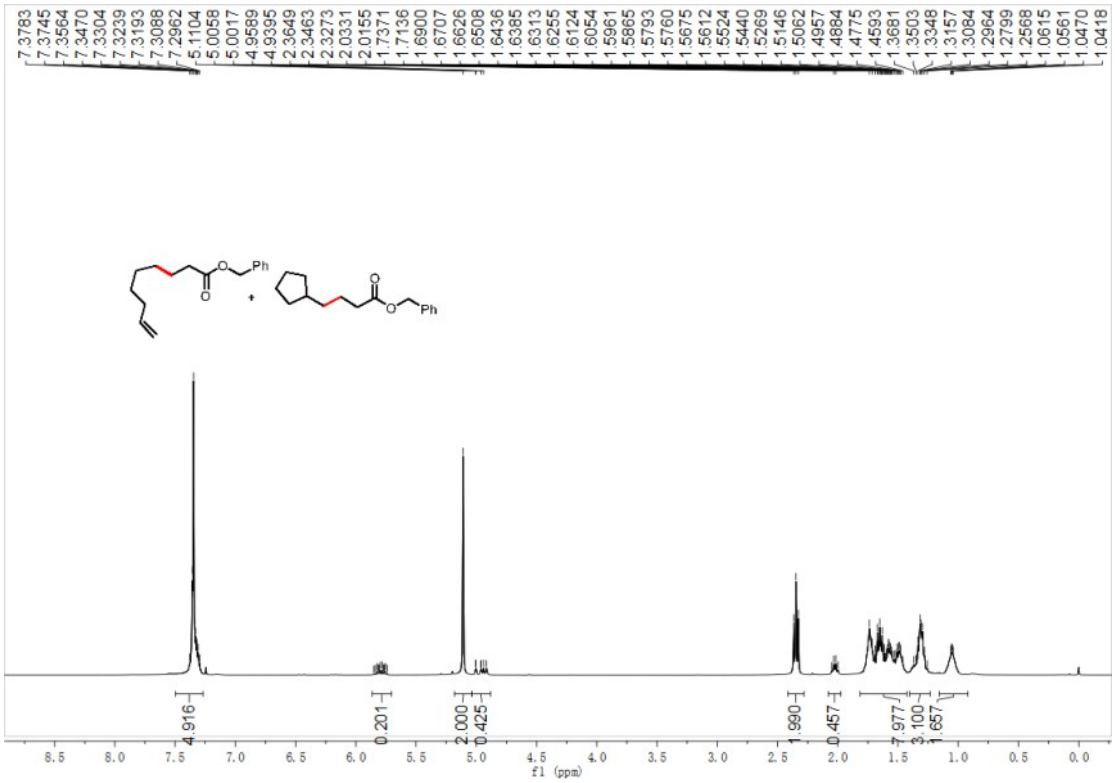
^{1}H NMR spectrum of compound **51**



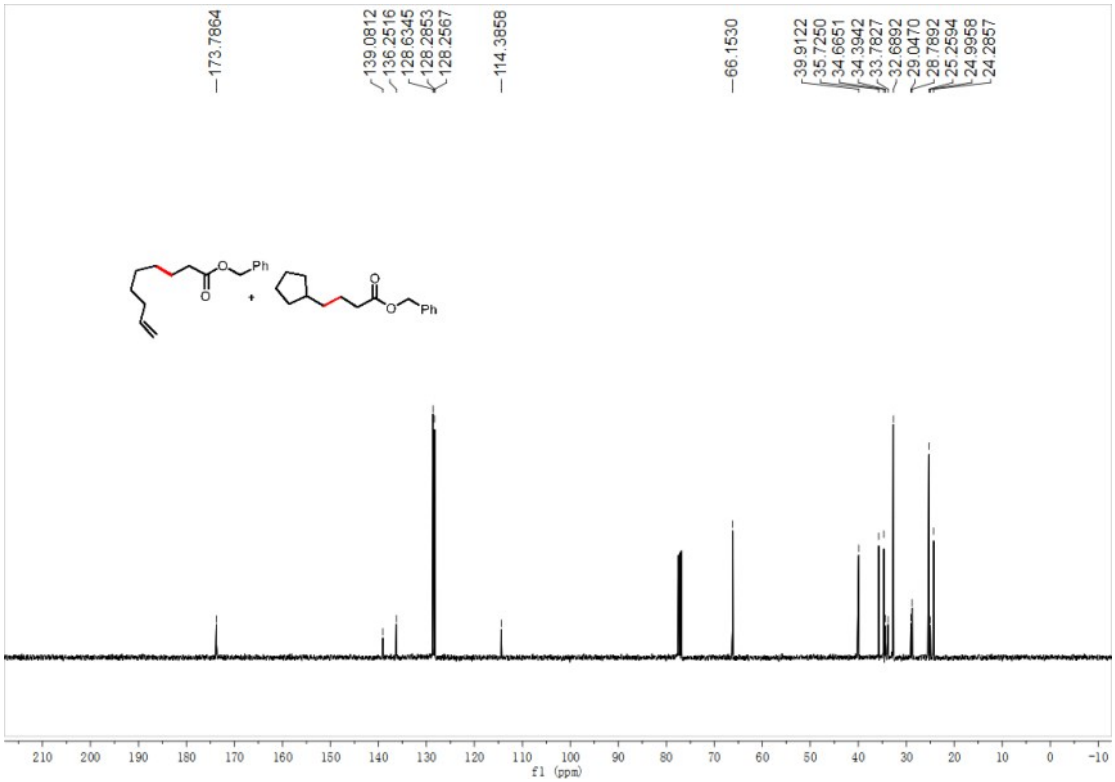
^{13}C NMR spectrum of compound **51**



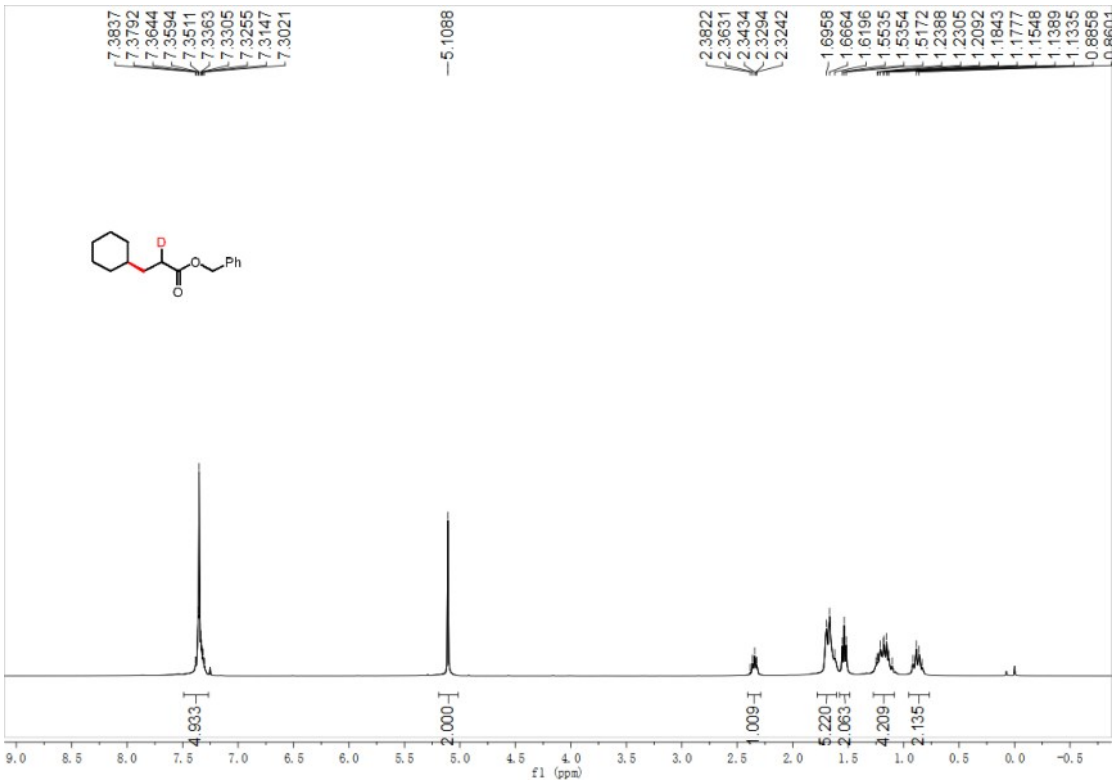
^{1}H NMR spectrum of compound **53**



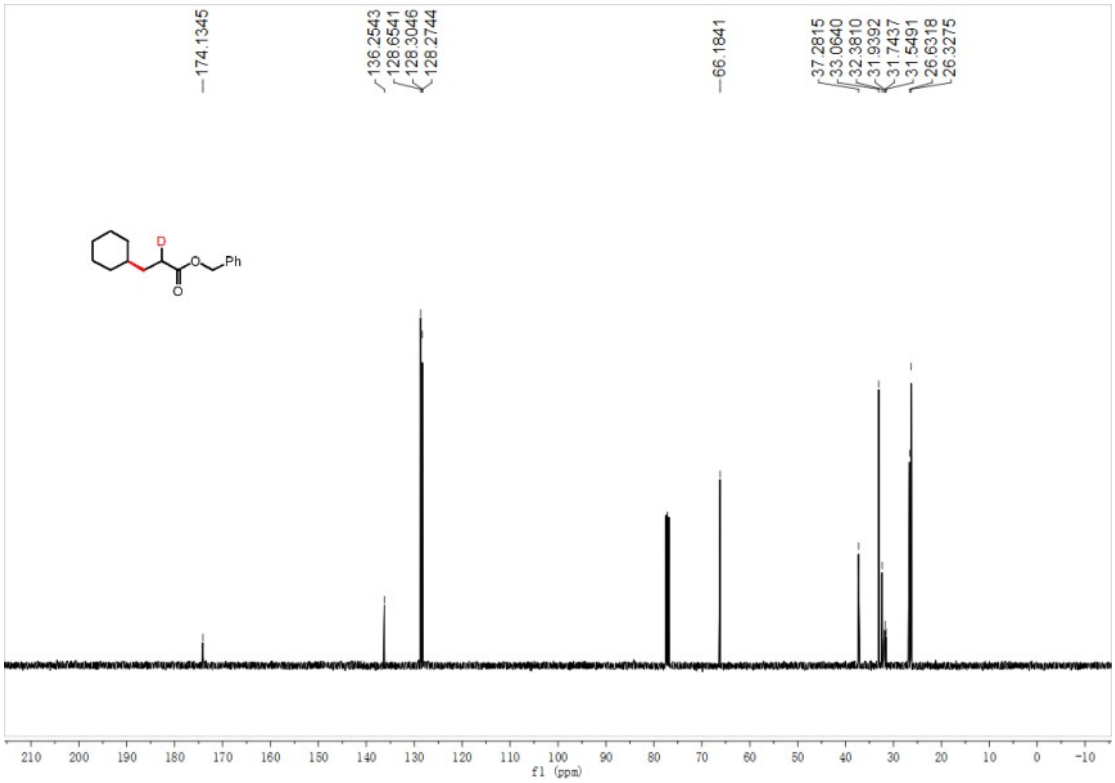
^{13}C NMR spectrum of compound **53**



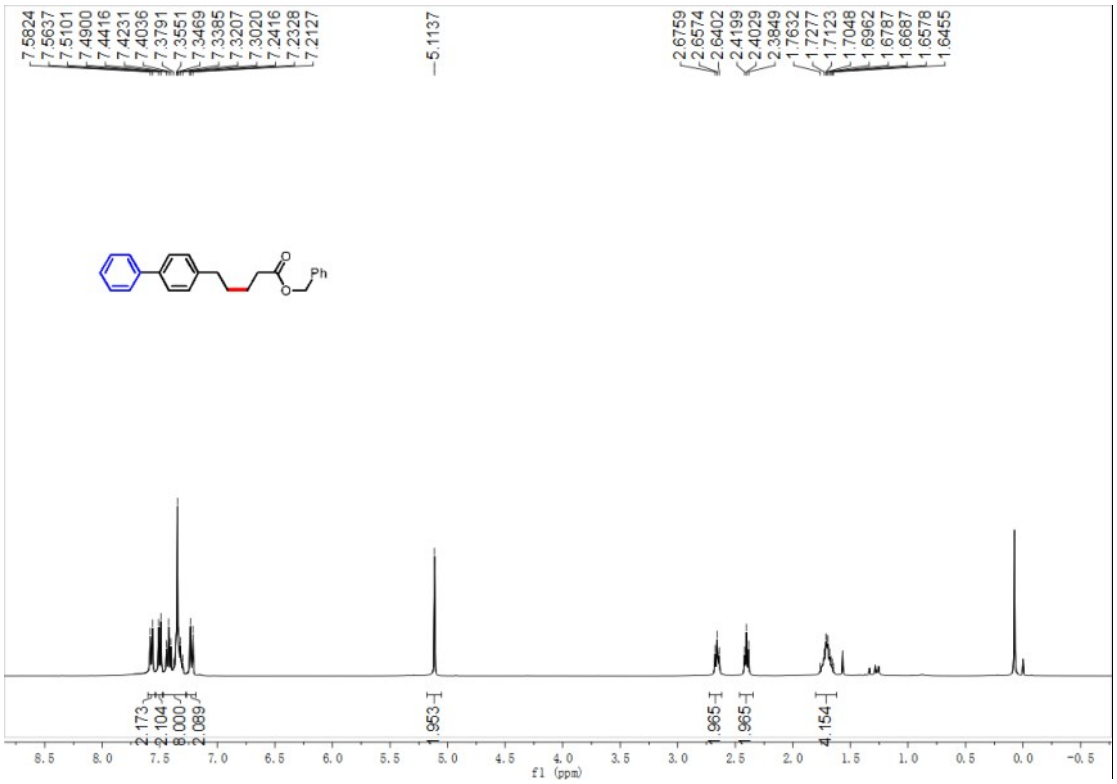
^{1}H NMR spectrum of compound **d-3**



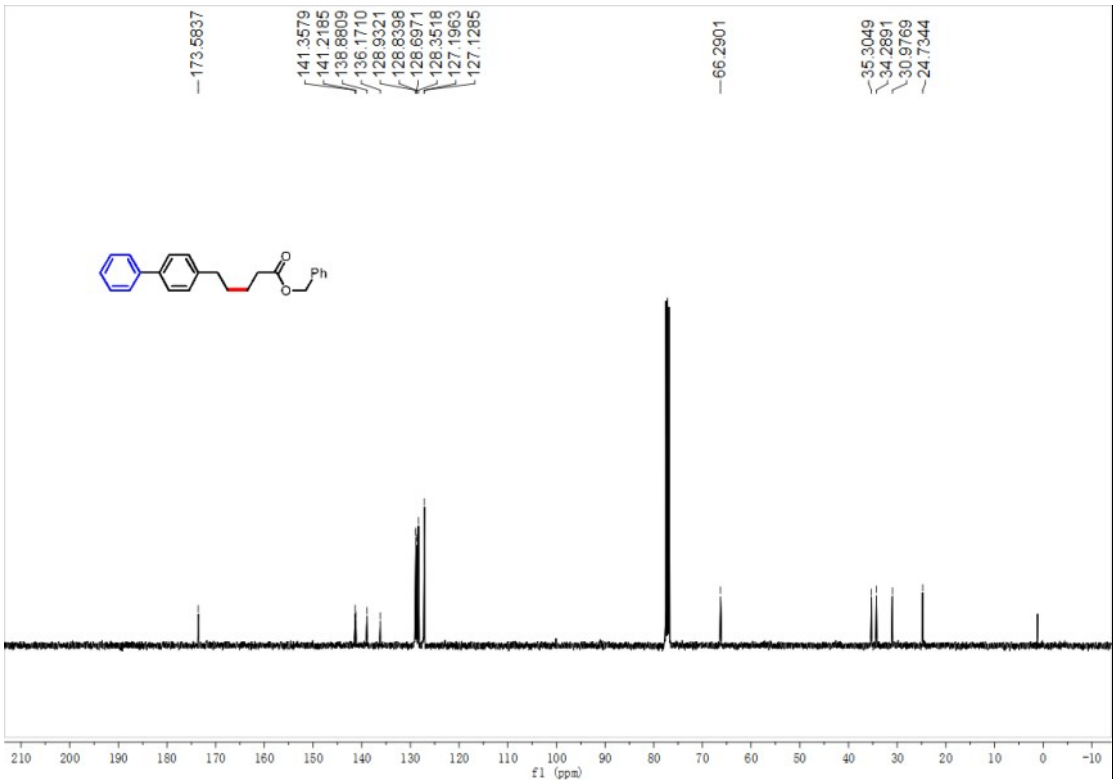
^{13}C NMR spectrum of compound **d-3**



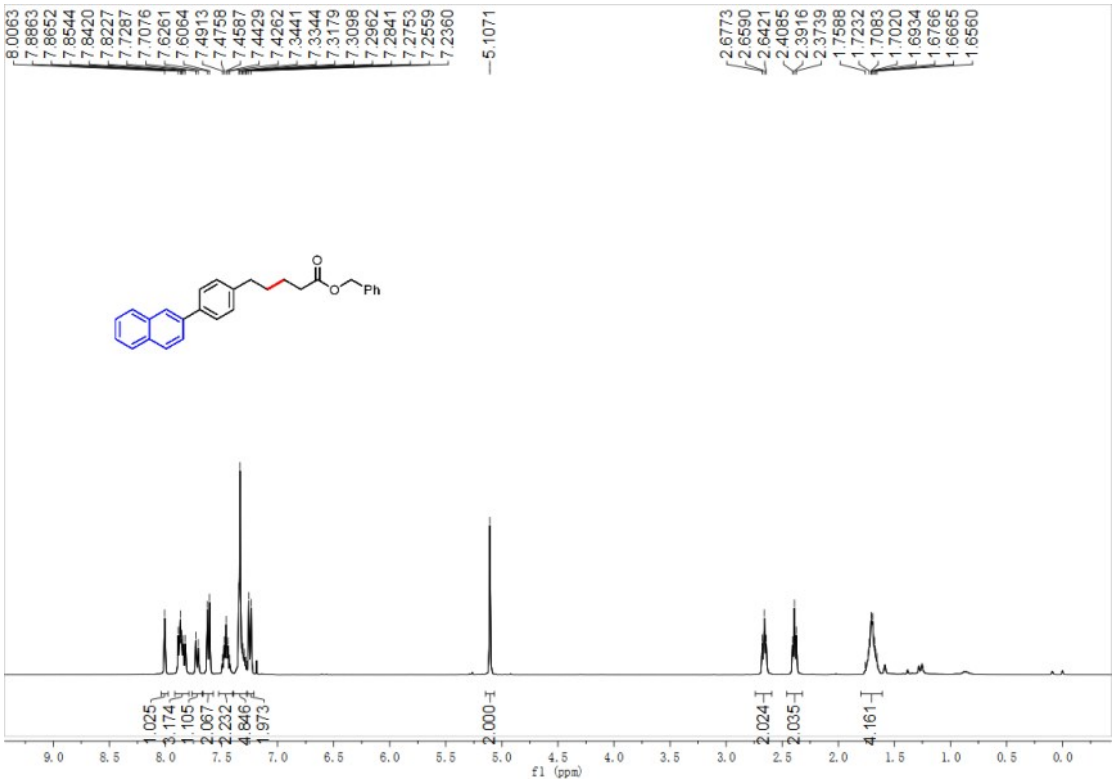
^{1}H NMR spectrum of compound **45**



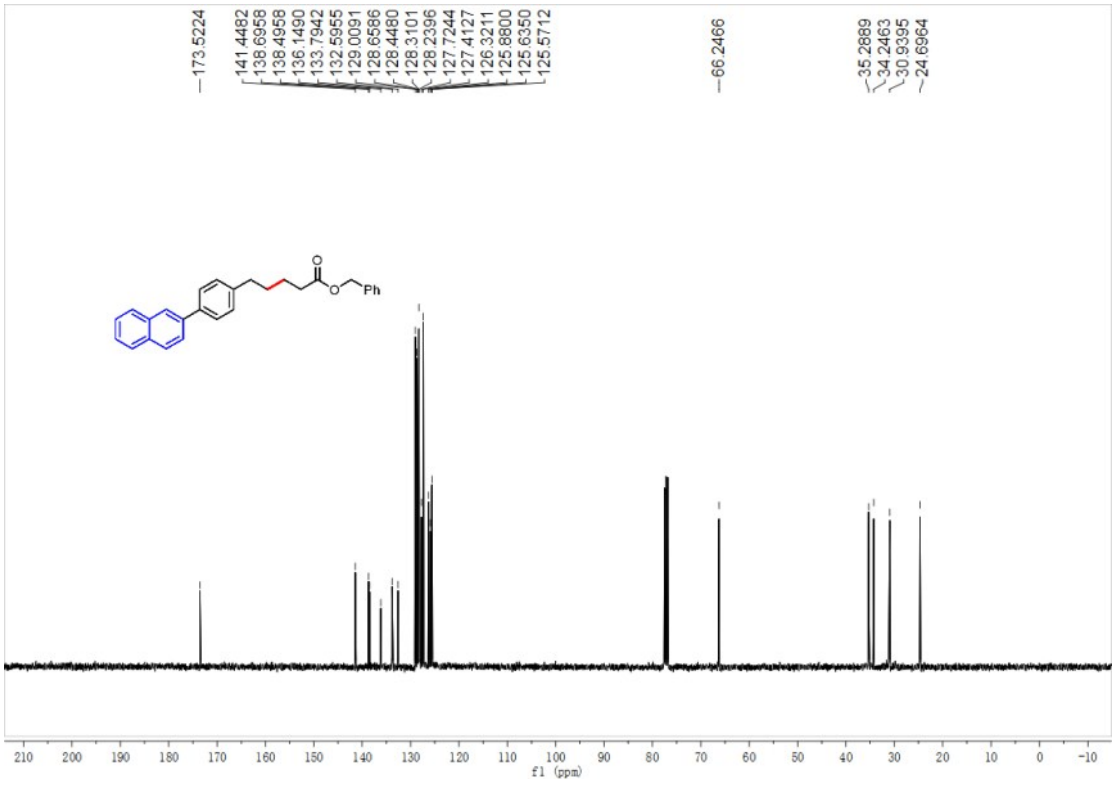
^{13}C NMR spectrum of compound **45**



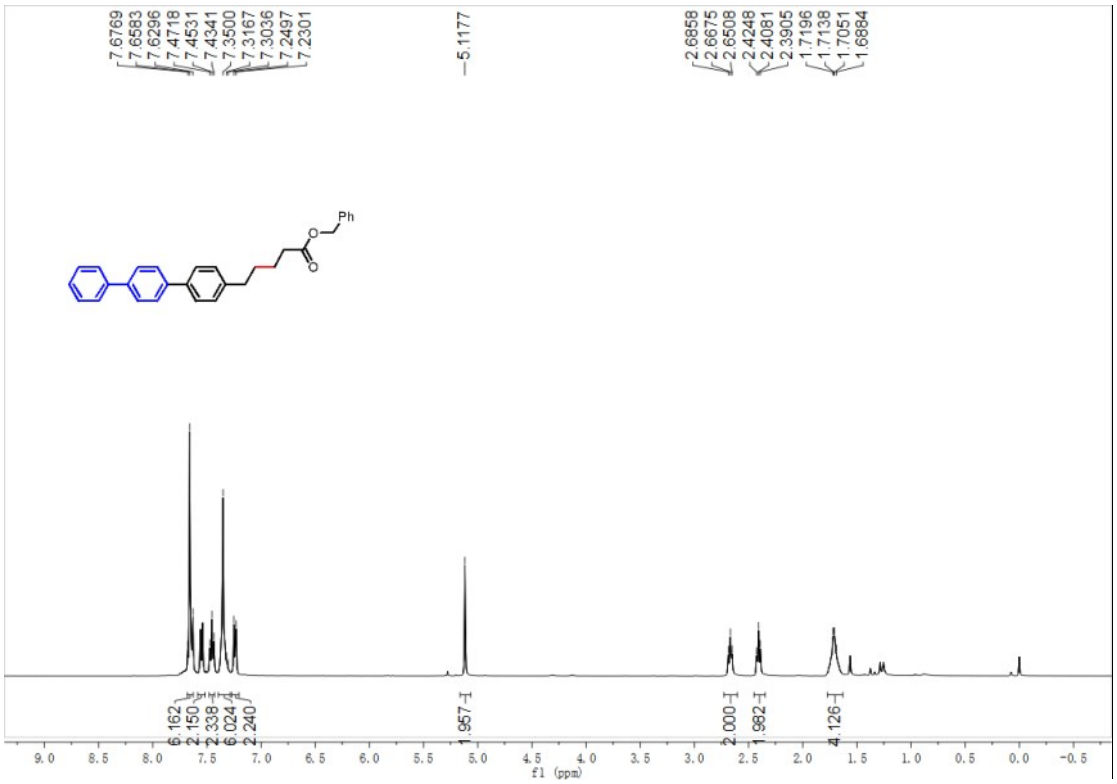
^{1}H NMR spectrum of compound **46**



^{13}C NMR spectrum of compound **46**



^{1}H NMR spectrum of compound **47**



^{13}C NMR spectrum of compound **47**