Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

H-Bonding-Promoted Radical Addition of Simple Alcohols to Unactivated Alkenes

Yunfei Tian[†] and Zhong-Quan Liu* [†‡]

[†] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

[‡] State Key Laboratory Cultivation Base for TCM Quality and Efficacy, College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023, China

E-mail: liuzhq@lzu.edu.cn and liuzq@njucm.edu.cn

General Information

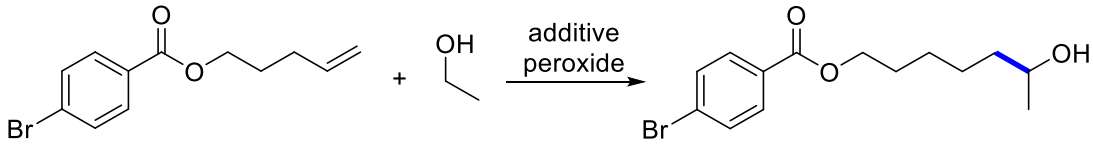
^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by ^{1}H and ^{13}C NMR, ^{31}P NMR, MS, and HRMS. The starting materials were purchased from Energy Chemicals, Alfa Aesar, Acros Organics, J&K Chemicals, Adamas, or Aldrich and used without further purification.

Typical procedure

Reaction of alcohols with alkenes: A mixture of alkenes (1 equiv., 0.10 mmol), alcohols (10 mL), KF (50 mol%, 0.05 mmol), and TBPA (5 equiv., 0.50 mmol) was heated at 140 ^{o}C (the measured temperature of the oil bath) for 18 h in a sealed tube (35 mL). After the reaction completed (detected by TLC), the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.

Modification of the typical conditions

(1) Optimization of the reaction conditions. [a]

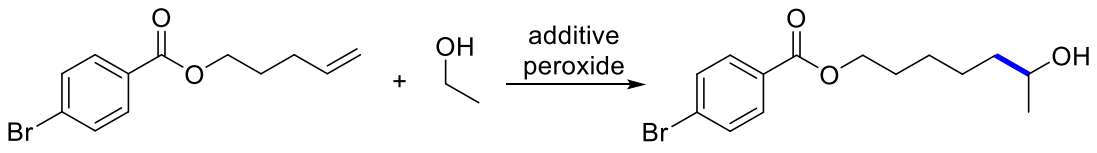


entry	EtOH (mL)	additive (mol %)	peroxide (equiv)	T (^{o}C)	t (h)	yield (%)[b]
1	10	KF(20)	TBPA(5)	140	2	65
2	10	KF(20)	TBPA(5)	140	4	68
3	10	KF(20)	TBPA(5)	140	6	69
4	10	KF(20)	TBPA(5)	140	8	75
5	10	KF(20)	TBPA(5)	140	10	76
6	10	KF(20)	TBPA(5)	140	12	78
7	10	KF(20)	TBPA(5)	140	15	76
8	10	KF(20)	TBPA(5)	140	18	82
9	10	KF(20)	TBPA(5)	140	24	82
10	10	KF(20)	TBPA(5)	100	18	31
11	10	KF(20)	TBPA(5)	110	18	47
12	10	KF(20)	TBPA(5)	120	18	54
13	10	KF(20)	TBPA(5)	130	18	70
14	10	KF(20)	TBPA(2)	140	18	67
15	10	KF(20)	TBPA(3)	140	18	70
16	10	KF(20)	TBPA(4)	140	18	72
17	10	KF(20)	TBPA(6)	140	18	79
18	10	KF(20)	TBPA(7)	140	18	76
19	10	KF(0)	TBPA(5)	140	18	25
20	10	KF(5)	TBPA(5)	140	18	39
21	10	KF(10)	TBPA(5)	140	18	56
22	10	KF(30)	TBPA(5)	140	18	81
23	10	KF(40)	TBPA(5)	140	18	85
24	10	KF(50)	TBPA(5)	140	18	87
25	10	KF(60)	TBPA(5)	140	18	85
26	10	KF(80)	TBPA(5)	140	18	76
27	10	KF(100)	TBPA(5)	140	18	81
28	1	KF (50)	TBPA(5)	140	18	34
29	3	KF (50)	TBPA(5)	140	18	47
30	5	KF (50)	TBPA(5)	140	18	73
31	7	KF (50)	TBPA(5)	140	18	77
32	12	KF (50)	TBPA(5)	140	18	86
33	15	KF (50)	TBPA(5)	140	18	81
34	10	KF (50)	TBHP (in	140	18	24

			decane, 5)			
35	10	KF (50)	TBHP (in water, 5)	140	18	26
36	10	KF (50)	TBPB(5)	140	18	49
37	10	KF (50)	BPO(5)	140	18	N.R
38	10	KF (50)	AIBN (5)	140	18	N.R
39	10	CuF_2 (50)	TBPA(5)	140	18	N.R
40	10	AgF (50)	TBPA(5)	140	18	28
41	10	NaF (50)	TBPA(5)	140	18	71
42	10	CsF (50)	TBPA(5)	140	18	59
43	10	KCl (50)	TBPA(5)	140	18	19
44	10	KBr (50)	TBPA(5)	140	18	20
45	10	KI (50)	TBPA(5)	140	18	23
46	10	TBAB (50)	TBPA(5)	140	18	17
47	10	TBAI (50)	TBPA(5)	140	18	10
48	10	TBAF (50)	TBPA(5)	140	18	58
49	10	TBAF (50)	DCP (5)	140	18	81
50	10	K_2CO_3(50)	TBPA(5)	140	18	37
51	10	$ZnF_2.4H_2O$(50)	TBPA(5)	140	18	71
52	10	MnF_2(50)	TBPA(5)	140	18	18
53	10	CoF_2(50)	TBPA(5)	140	18	N.R
54	10	FeF_3(50)	TBPA(5)	140	18	N.R
55	10	-	TBPB(5)	140	18	N.R
56	10	KF(50)	DCP(5)	140	18	85

[a] Reaction conditions: Alkenes (1 equiv, 0.10 mmol), peroxide (5 equiv, 0.50 mmol), ethanol as solvent, 140 ^{o}C (measured temperature of the oil bath), sealed tube, unless otherwise noted. [b] Isolated yield. TBPA = *tert*-butyl peroxyacetate; DCP = dicumyl peroxide; TBHP = *tert*-butyl hydroperoxide.

(2) Optimization of the H-Bond Acceptors. [a]

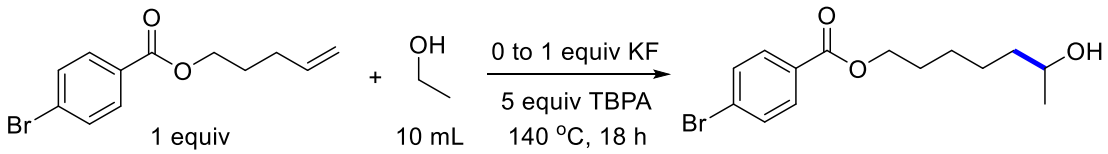


entry	additive (50 mol%)	peroxide	yield (%)[b]
1	-	TBPA	25
2	FeF_3	TBPA	NR
3	CoF_2	TBPA	NR
4	CuF_2	TBPA	NR
5	MnF_2	TBPA	18

6	$ZnF_2.4H_2O$	TBPA	71
7	CsF	TBPA	59
8	CsF	DCP	75
9	NaF	TBPA	71
10	**NaF**	**DCP**	**85**
11	**KF**	**TBPA**	**87**
12	**KF**	**DCP**	**85**
13	TBAF	TBPA	58
14	TBAF	DCP	81
15	KBF_4	TBPA	80
16	KBF_4	DCP	79
17	KPF_6	TBPA	81
18	KPF_6	DCP	77
19	KH_2PO_4	TBPA	64
20	K_2HPO_4	TBPA	74
21	K_2CO_3	TBPA	37
22	KCl	TBPA	19
23	KBr	TBPA	20
24	KI	TBPA	23
25	TBAB	TBPA	17
26	TBAI	TBPA	10

[a] Reaction conditions: Alkenes (1 equiv, 0.10 mmol), additive (50 mol%, 0.05mmol), peroxide (5 equiv, 0.50 mmol), 10 mL of ethanol as solvent, 140 °C (measured temperature of the oil bath), sealed tube, 18 hrs, unless otherwise noted. [b] Isolated yield. TBPA = *tert*-butyl peroxyacetate; DCP = dicumyl peroxide.

(3) Optimization of the amounts of KF. [a]

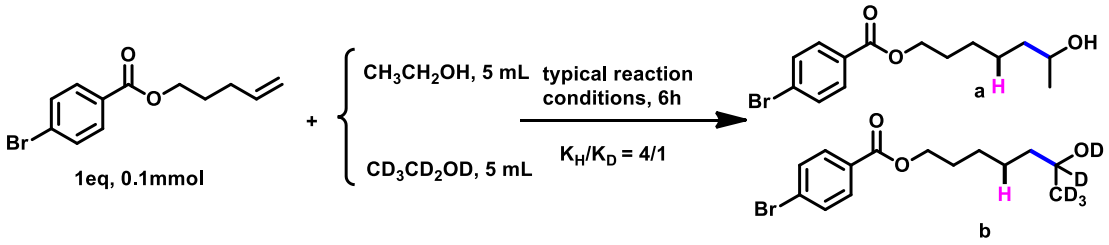


entry	additive	peroxide	yield (%)[b]
1	-	TBPA	25
2	KF (5 mol%)	TBPA	39
3	KF (10 mol%)	TBPA	56
4	**KF (20 mol%)**	**TBPA**	**82**
5	KF (30 mol%)	TBPA	81
6	KF (40 mol%)	TBPA	85
7	**KF (50 mol%)**	**TBPA**	**87**
8	KF (60 mol%)	TBPA	85

9	KF (80 mol%)	TBPA	76
10	KF (100 mol%)	TBPA	81

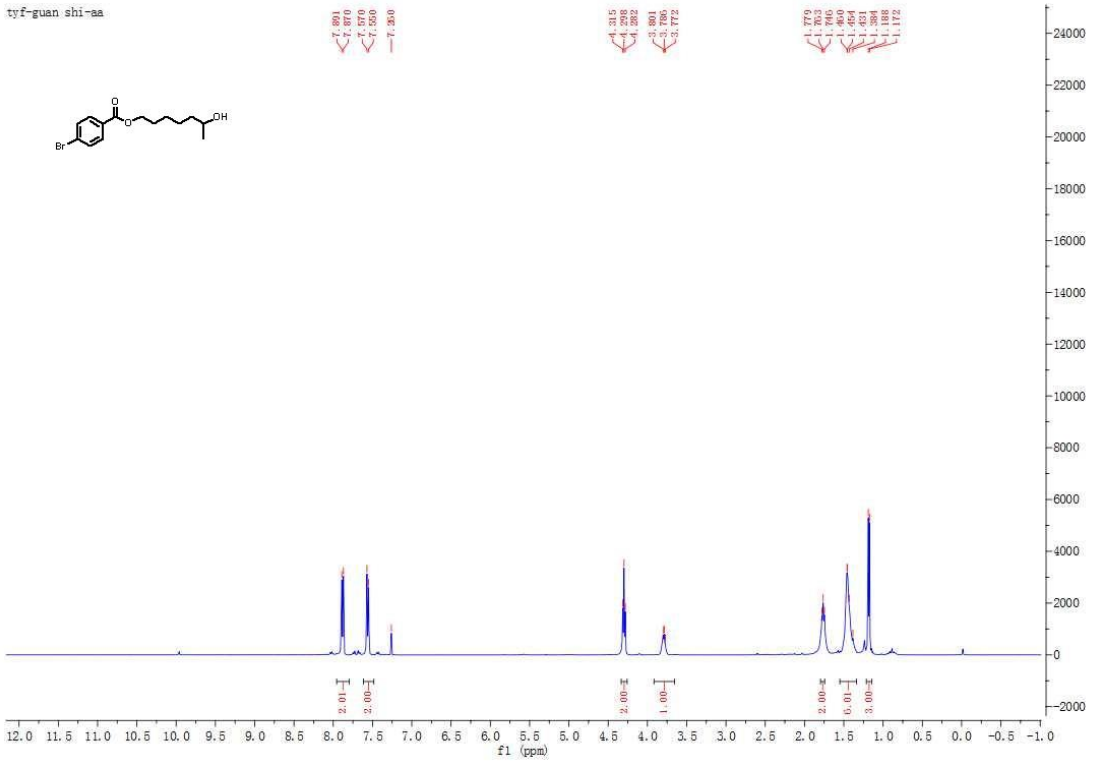
[a] Reaction conditions: Alkenes (1 equiv, 0.10 mmol), peroxide (5 equiv, 0.50 mmol), 10 mL of ethanol as solvent, 140 ^{o}C (measured temperature of the oil bath), sealed tube, 18 hrs, unless otherwise noted. [b] Isolated yield. TBPA = *tert*-butyl peroxyacetate.

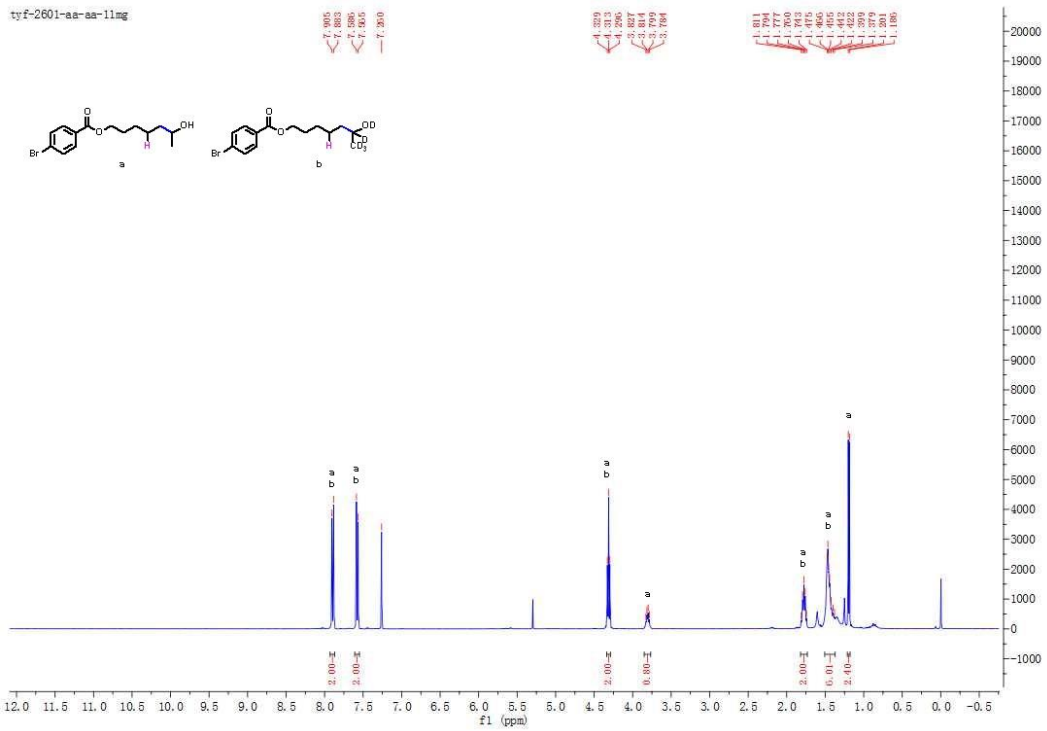
Competing Kinetic Isotope Effect (KIE) Experiment:



Conversion 33%, a(yield, 26.4%), b(yield, 6.6%)

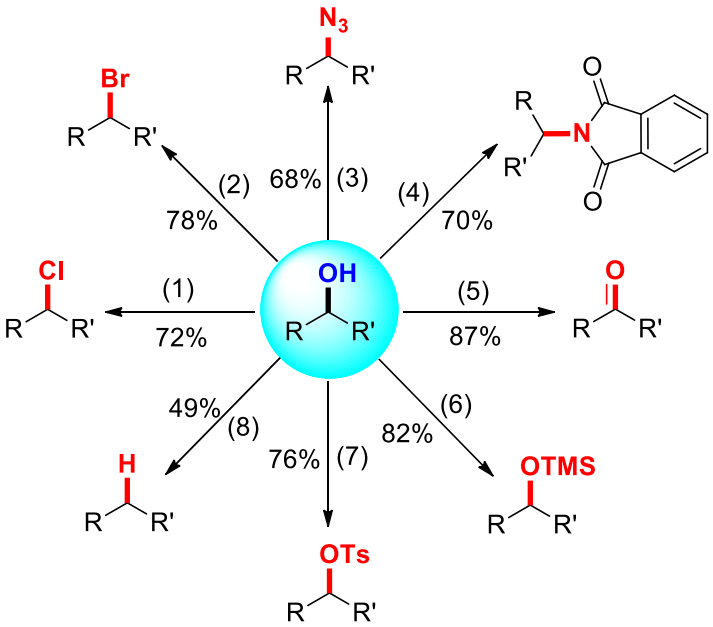
^{1}H NMR





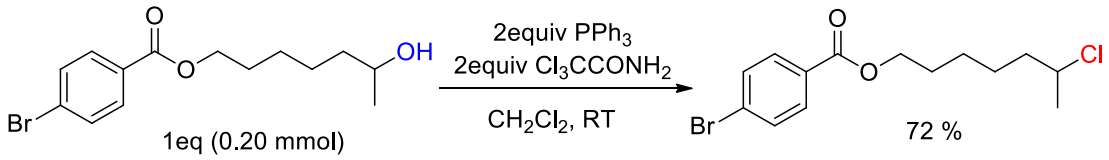
Note: The value of k_H/k_D was calculated from the ^{1}H NMR spectra above which should be the mixture of compound **a** and **b** (the KIE scheme). The sum of the integral of **a** and **b** at chemical shift 4.30 – 4.33 was integrated as 2.00 (both **a** and **b** keep the same double bond hydrogen). Compound **a** has one hydrogen atoms at chemical shift 3.78 – 3.83, while **b** has no H atoms here. The amount of **a** could be defined as 0.80, on the other hand, the sum of **a** and **b** is 1.00, so the amount of **b** is 0.2 (1.00 – 0.80 = 0.2). As a result, k_H / k_D=0.80 / 0.2 = 4.

Versatile transformations of alcohols:



Transformation of product.

(1).



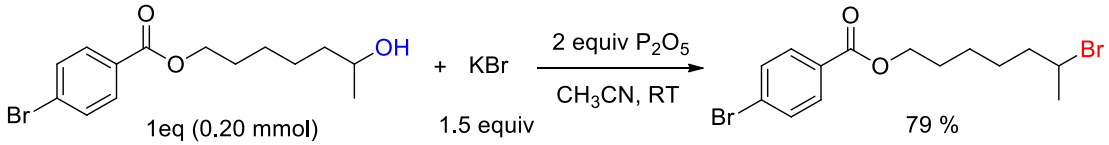
To a stirred solution of alcohol (0.20 mmol, 62.8 mg) and PPh_3 (0.40 mmol, 104.8 mg) in dry CH_2Cl_2 (0.5 mL) was added Cl_3CCONH_2 (0.40 mmol, 64.8 mg) at room temperature under an N_2 atmosphere. After reaction completion (TLC), the reaction was quenched with cold water and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated in vacuum. Purification by silica-gel chromatography (hexane/AcOEt = 60/1) gave the corresponding product (48.0 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 4.07 – 3.99 (m, 1H), 1.63 – 1.55 (m, 1H), 1.82 – 1.71 (m, 4H), 1.61 – 1.54 (m, 1H), 1.51 (d, *J* = 6.8 Hz, 3H), 1.51 – 1.43 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.3, 127.9, 65.2, 58.6, 40.2, 28.6, 26.3, 25.6, 25.4.

HRMS (ESI, m/z): Calculated for $C_{14}H_{18}BrClNaO_2$ $(M+Na)^+$ 355.0071, found 355.0078.

(2).



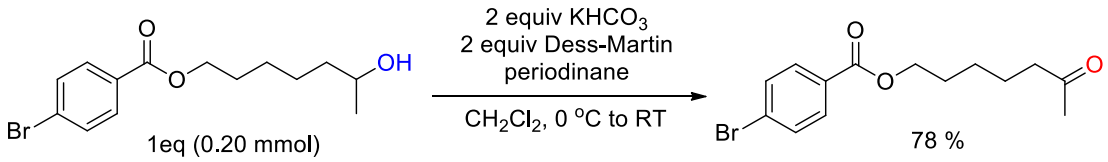
To a mixture of alcohol (0.20 mmol, 62.8 mg) and KBr (0.30 mmol, 35.7mg) in acetonitrile (1 mL), P_2O_5 (0.40 mmol, 56.8 mg) was added and the reaction was stirred at room temperature. After reaction completion (TLC), the reaction mixture was filtered and the residue washed with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the corresponding product. Further purification by silicagel chromatography (hexane/AcOEt = 60/1) gave the corresponding product (59.7 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 4.32 (t, J = 6.4 Hz, 2H), 4.18 – 4.09 (m, 1H), 1.89 – 1.75 (m, 4H), 1.71 (d, J = 6.4 Hz, 3H), 1.64 – 1.56 (m, 1H), 1.53 – 1.41 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.3, 128.0, 65.2, 51.6, 41.0, 28.5, 27.5, 26.5, 25.5.

HRMS (ESI, m/z): Calculated for $C_{14}H_{19}Br_2O_2$ $(M+H)^+$ 378.9726, found 378.9721.

(3).



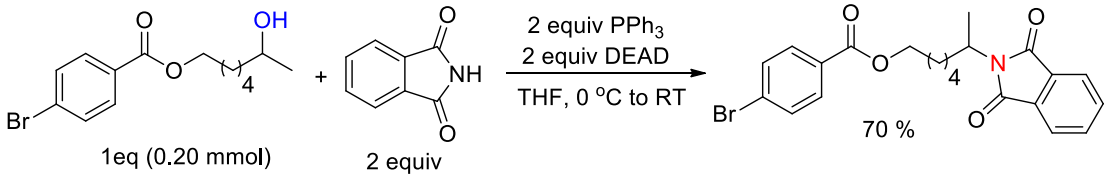
To a solution of alcohol (0.20 mmol, 62.8 mg) in dry DCM (2 ml) was added Sodium bicarbonate (33.6 mg, 0.40 mmol) at 0 °C. After addition of Dess-Martin periodinane (169.6 mg, 0.40 mmol), the solution was stiired at 0 °C. After reaction completion (TLC), the mixture was purified by silica gel chromatography (hexane/ EtOAc = 20/1) to afford the corresponding product (49.0 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.80 – 1.73 (m, 2H), 1.67 – 1.60 (m, 2H), 1.46 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 208.7, 165.8, 131.6, 131.0, 129.2, 127.9, 65.0, 43.4, 29.9, 28.5, 25.6, 23.3.

HRMS (ESI, m/z): Calculated for $C_{14}H_{21}BrNO_3$ $(M+NH_4)^+$ 330.0699, found 330.0698.

(4).



To a solution of PPh_3 (0.40 mmol, 104.8 mg) and O-Phthalimide (0.40 mmol, 58.8 mg) in THF (0.3 M), alcohol (0.20 mmol, 62.8 mg) was added slowly under N_2 atmosphere. The reaction mixture was cooled to 0 °C and DEAD (0.40 mmol, 69.6 mg) in THF (0.5 M) was added slowly. The reaction mixture was allowed to warm to room temperature and was stirred for 6 h. After completion of reaction, the solvent was removed in a rotary evaporator and the crude product was directly subjected to column chromatography using ethyl acetate and hexane as eluents to give corresponding product (62 mg, 70% yield).

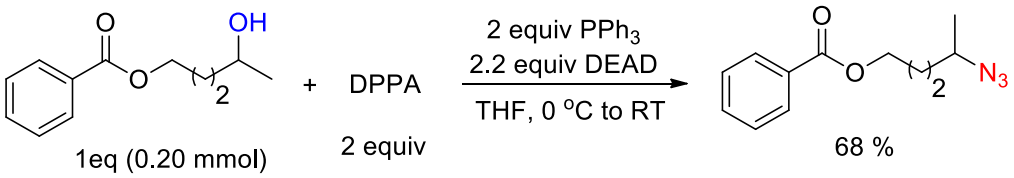
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.8 Hz, 2H), 7.80 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.69 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.40 – 4.31 (m, 1H), 4.26 (t, *J* = 6.4 Hz,

2H), 2.16 – 2.07 (m, 1H), 1.79 – 1.68 (m, 3H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.52 – 1.25 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.5, 165.8, 133.8, 131.9, 131.6, 131.0, 129.3, 127.9, 123.0, 65.2, 47.3, 33.6, 28.5, 26.5, 25.7, 18.7.

HRMS (ESI, m/z): Calculated for $C_{22}H_{22}BrNNaO_4$ $(M+Na)^+$ 466.0624, found 466.0623.

(5).



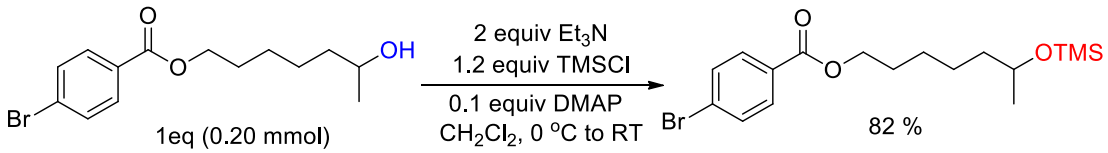
To a solution of PPh_3 (0.40 mmol, 104.8 mg) in THF (2 mL), DEAD (0.44 mmol, 76.6 mg) was added dropwise at -20 °C. After stirring for 15 min, a solution of alcohol (0.20 mmol, 41.6 mg) in THF (1 mL) and DPPA (0.4 mmol, 110 mg) was added. Reaction mixture was allowed to warm up to room temperature and was stirred for 24 h. After completion of reaction, the solvent was removed in a rotary evaporator and the crude product was directly subjected to column chromatography using ethyl acetate and hexane as eluents to give the corresponding product (31.6 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.55 – 3.50 (m, 1H), 1.94 – 1.79 (m, 2H), 1.66 – 1.61 (m, 2H), 1.30 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 132.9, 130.2, 129.5, 128.3, 64.4, 57.5, 32.7, 25.4, 19.4.

HRMS (ESI, m/z): Calculated for $C_{12}H_{15}N_3NaO_2(M+Na)^+$ 256.1056, found 256.1058.

(6).



Et_3N (0.4 mmol, 56 µL) and TMSCl (0.24 mmol, 21 µL) were added sequentially to a solution of alcohol (0.20 mmol, 62.8 mg) in dry CH_2Cl_2 (5 mL) at 0 °C. After being stirred for 5 min at the same temperature, DMAP (0.02 mmol, 2.4 mg) was added and stirring was continued for 10 min with slowly warming to room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with DCM. The

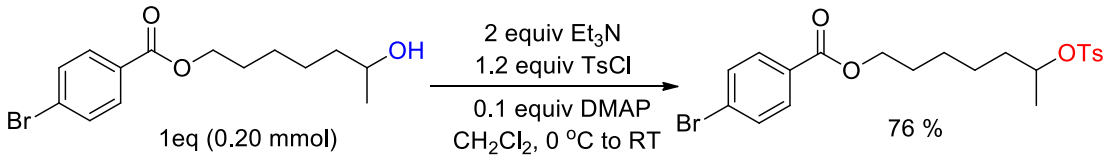
combined organic extracts were dried (Na_2SO_4), filtered and concentrated in vacuum. Purification of the residue by column chromatography provided corresponding product (63.5 mg, 82 % yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.80 – 3.73 (m, 1H), 1.80 – 1.73 (m, 2H), 1.50 – 1.28 (m, 6H), 1.13 (d, *J* = 6.4 Hz, 3H), 0.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.4, 127.9, 68.4, 65.3, 39.5, 28.7, 26.1, 25.6, 23.9, 0.3.

HRMS (ESI, m/z): Calculated for $C_{17}H_{28}BrO_3Si$ $(M+H)^+$ 387.0986, found 387.0981.

(7).



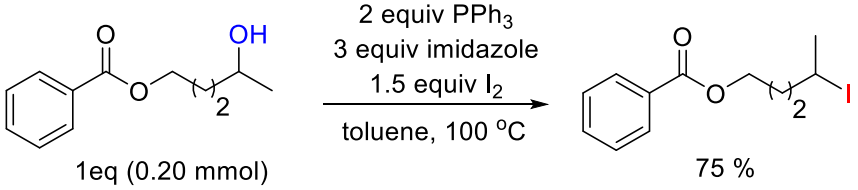
Et_3N (0.4mmol, 56 µL) and TsCl (0.24 mmol, 45.8mg) were added sequentially to a solution of alcohol (0.20 mmol, 62.8mg) in dry CH_2Cl_2 (5 mL) at 0 °C. After being stirred for 5 min at the same temperature, DMAP (0.02 mmol, 2.4mg) was added and stirring was continued for 10 min with slow warming to room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with DCM. The combined organic extracts were dried (Na_2SO_4), filtered and concentrated in vacuum. Purification of the residue by column chromatography provided pure product (71.1 mg, 76 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.65 – 4.58 (m, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.70 – 1.58 (m, 3H), 1.56 – 1.48 (m, 1H), 1.36 – 1.28 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 144.4, 134.5, 131.7, 131.0, 129.7, 129.2, 127.9, 127.7, 80.2, 65.0, 36.4, 28.4, 25.6, 24.5, 21.6, 20.8.

HRMS (ESI, m/z): Calculated for $C_{21}H_{29}BrNO_5S$ $(M+NH_4)^+$ 486.0944, found 486.0947.

(8).

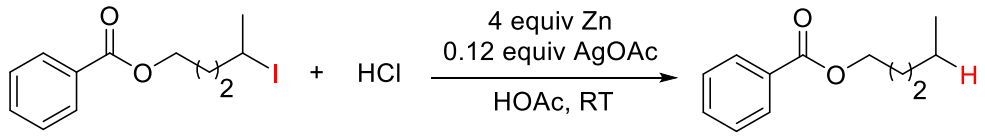


A solution of alcohol (0.20 mmol, 41.6 mg) in toluene (5 mL) was treated with triphenylphosphine (0.40 mmol, 104.8 mg), imidazole (0.60 mmol, 40.8 mg), and iodine (0.30 mmol, 76 mg). The mixture was heated at 100 °C for 1 h under blanket of argon. After reaching room temperature, the mixture was poured into a saturated solution of $NaHCO_3$. Excess triphenylphosphine was destroyed by the addition of iodine until the iodine coloration persisted in the organic layer. The organic layer was washed twice with 5% (wt.) $Na_2S_2O_3$ and brine, dried over ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified on silica gel (hexanes/ethyl acetate, 8/1) to give corresponding product (48 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.80 – 3.73 (m, 1H), 1.80 – 1.73 (m, 2H), 1.50 – 1.28 (m, 6H), 1.13 (d, *J* = 6.4 Hz, 3H), 0.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.4, 127.9, 68.4, 65.3, 39.5, 28.7, 26.1, 25.6, 23.9, 0.3.

HRMS (ESI, m/z): Calculated for $C_{12}H_{19}INO_2$ $(M+NH_4)^+$ 336.0455, found 336.0459.



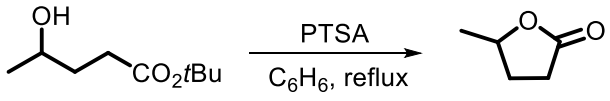
The alkyl iodides (1eq, 0.25 mmol), Zn (4eq, 65 mg), and AgOAc (0.03 mmol, 5 mg) were mixed together in HOAc (0.5 mL), under vigorous stirring. 0.05mL of concentrated HCl (37%) was added dropise over a 1 min period. The mixture was further stirred for 5 min. and then filtered. The reaction mixture was then diluted with DCM, filtered through silica gel with copious washings (DCM), concentrated, and purified by column chromatography (hexane/AcOEt = 20/1) gave the corresponding product (32 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 8.04 (m, 2H), 7.55 – 7.50 (m, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.46 – 1.33 (m, 4H), 0.93 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.5, 132.6, 130.4, 129.4, 128.2, 64.9, 28.3, 28.1, 22.2, 13.8.

HRMS (ESI, m/z): Calculated for $C_{12}H_{17}O_2$ $(M+H)^+$ 193.1223, found 193.1218.

(9).



70 %

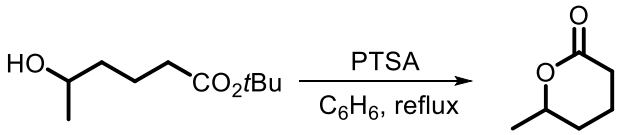
To a 50-mL round-bottomed flask equipped with a reflux condenser were added alcohol (0.20 mmol, 34.8 mg), benzene (14 mL) and *p*-toluenesulfonic acid monohydrate (4 mg, 0.022 mmol), The reaction mixture was refluxed at around 85 ^{o}C for 4 h, and then cooled to room temperature. The solvent was removed under reduced pressure, and the residue was directly subjected to the flash column chromatography on silica gel eluting with cyclohexane/AcOEt (80:16) to afford the corresponding product (14mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67 – 4.59 (m, 1H), 2.56 – 2.52 (m, 2H), 2.39 – 2.31 (m, 1H), 1.87 – 1.77 (m, 1H), 1.41 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 177.1, 77.2, 29.7, 29.1, 21.0.

MS(EI): *m/z*(%): 100(12.0), 85(73.0), 56(100), 43(23.9), 41(29.7), 39(7.9).

(10).



66 %

To a 50-mL round-bottomed flask equipped with a reflux condenser were added alcohol (0.20 mmol, 37.6 mg), benzene (14 mL) and *p*-toluenesulfonic acid monohydrate (4 mg, 0.022 mmol), The reaction mixture was refluxed at around 85 ^{o}C for 4 h, and then cooled to room temperature. The solvent was removed under reduced pressure, and the residue was directly subjected to the flash column chromatography on silica gel eluting with cyclohexane/AcOEt (80:16) to afford the corresponding product (15mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.47 – 4.39 (m, 1H), 2.60 – 2.52 (m, 1H), 2.47 – 2.38 (m, 1H), 1.94 – 1.79 (m, 3H), 1.56 – 1.46 (m, 1H), 1.36 (d, *J* = 6.4 Hz, 3H).

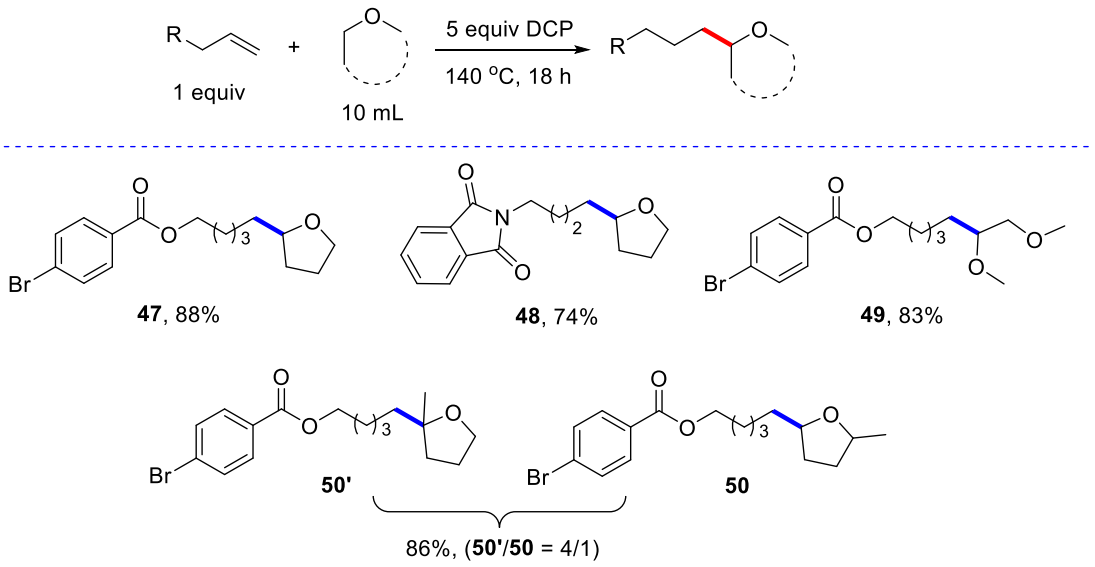
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 76.9, 29.5, 29.2, 21.6, 18.5.

MS(EI): *m/z*(%): 114(10.6), 99(10.9), 70(88.1), 55(31.9), 42(100), 39(11.8).

Reactions of ethers with alkenes:

Typical procedure for reaction of ethers with alkenes: A mixture of alkenes (1 equiv., 0.10 mmol), ethers (10 mL), and DCP (5 equiv., 0.50 mmol) was heated at 140 ^{o}C (the measured temperature of the oil bath) for 18 h in a sealed tube (35 mL). After the reaction

completed (detected by TLC), the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product.



All known compounds are determined by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS analysis.

References:

1. W. Pluempanupat and W. Chavasiri, *Tetrahedron Lett*. **2006***, 47*, 6821–6823.
2. L. Khazdooz, A. Zarei, H. Aghaei. G. Azizi, M. M. Gheisari, *Tetrahedron Lett*. **2016**, *57*, 168–171.
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5. P. Niedziejko, M. Szewczyk, P. Kalicki, Z. Kałuza, *Tetrahedron: Asymm.* **2015**, *26*, 1083–1094.
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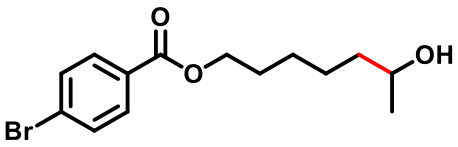
8. A. Gansauer, C.-A. Fan, F. Keller, and J. Keil, *J. Am. Chem. Soc.* **2007**, *129*, 3484-3485.

Physical data for the following products:

1. 6-hydroxyheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



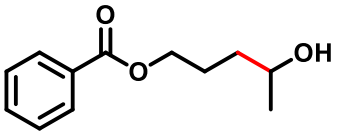
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.76 (m, 1H), 1.81 – 1.74 (m, 2H), 1.51 – 1.40 (m, 6H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.3, 127.9, 68.0, 65.2, 39.1, 28.7, 26.0, 25.4, 23.6.

HRMS (ESI, m/z): Calculated for $C_{14}H_{19}Br_1NaO_3$ $(M+Na)^+$ 337.0410, found 377.0413.

2. 4-hydroxypentyl benzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



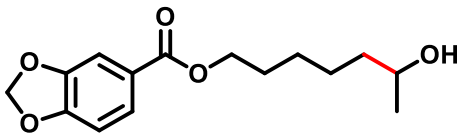
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.89 – 3.81 (m, 1H), 2.07 (s, 1H), 1.90 – 1.75 (m, 2H), 1.58 (dd, *J* = 14.8, 7.6 Hz, 2H), 1.21 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 132.8, 130.3, 129.5, 128.3, 67.5, 64.9, 35.5, 25.1, 23.5.

HRMS (ESI, m/z): Calculated for $C_{12}H_{17}O_3$ $(M+ H)^+$ 209.1172, found 209.1171.

3. 6-hydroxyheptyl benzo[d][1,3]dioxole-5-carboxylate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.02 (s, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.82 – 3.75 (m, 1H), 1.78 – 1.71 (m, 2H), 1.52 – 1.33 (m, 6H), 1.18 (d, *J* = 6.0 Hz, 3H).

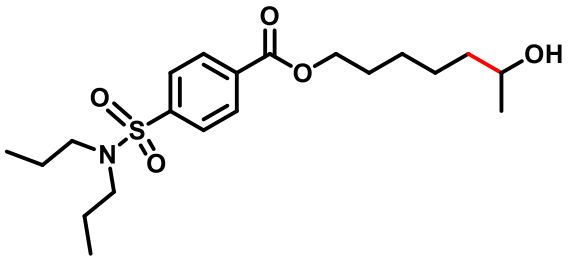
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 151.4, 147.6, 125.2, 124.4, 109.4, 107.9, 101.7, 67.9, 64.9, 39.1, 28.7, 26.0, 25.4, 23.5.

HRMS (ESI, m/z): Calculated for $C_{15}H_{20}NaO_5$ $(M+ Na)^+$ 303.1203, found 303.1200.

4. 6-hydroxyheptyl 4-(N,N-dipropylsulfamoyl)benzoate

A light yellow liquid after purification by flash column chromatography (petroleum

ether/ethyl acetate = 5/1)



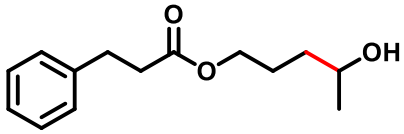
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 3.86 – 3.77 (m, 1H), 3.12 – 3.08 (m, 4H), 1.83 – 1.76 (m, 2H), 1.59 – 1.39 (m, 10 H), 1.20 (d, *J* = 6.0 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 144.2, 133.7, 130.2, 127.0, 68.0, 65.6, 49.9, 39.1, 28.6, 26.0, 25.4, 23.6, 21.9, 11.2.

HRMS (ESI, m/z): Calculated for $C_{20}H_{33}NNaO_5S$ $(M+Na)^+$ 422.1972, found 422.1978.

5. 4-hydroxypentyl 3-phenylpropanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



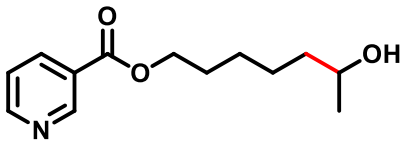
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 2H), 7.23 – 7.21 (m, 3H), 4.11 (t, *J* = 6.4 Hz, 2H), 3.84 – 3.76 (m, 1H), 2.97 (t, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.94 (s, 1H), 1.81 – 1.61 (m, 2H), 1.46 (dd, *J* = 14.4, 7.6 Hz, 2H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 140.4, 128.4, 128.2, 126.1, 67.4, 64.4, 35.8, 35.3, 30.9, 24.9, 23.4.

HRMS (ESI, m/z): Calculated for $C_{14}H_{20}NaO_3$ $(M+ Na)^+$ 259.1305, found 259.1303.

6. 6-hydroxyheptyl nicotinate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1).



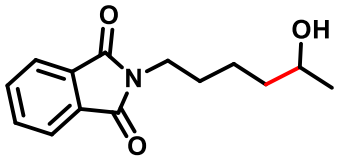
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.76 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.37 (m, 1H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.74 (m, 1H), 1.83 – 1.71 (m, 2H), 1.55 – 1.33 (m, 6H), 1.18 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.3, 153.2, 150.8, 137.0, 126.3, 123.3, 67.8, 65.4, 39.1, 28.6, 26.0, 25.4, 23.6.

HRMS (ESI, m/z): Calculated for $C_{13}H_{20}NO_3$ $(M+H)^+$ 238.1438, found 238.1437.

7. 2-(5-hydroxyhexyl)isoindoline-1,3-dione

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1)



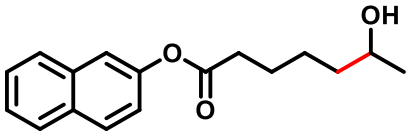
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (dd, *J* = 5.2, 2.8 Hz, 2H), 7.70 (dd, *J* = 5.2, 2.8 Hz, 2H), 3.82 – 3.74 (m, 1H), 3.69 (t, *J* = 7.2 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.54 – 1.34 (m, 4H), 1.17 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.5, 133.7, 132.1, 123.2, 67.8, 38.6, 37.8, 28.5, 23.5, 22.9.

HRMS (ESI, m/z): Calculated for $C_{14}H_{17}NNaO_3$ $(M+Na)^+$ 270.1101, found 270.1104.

8. naphthalen-2-yl 6-hydroxyheptanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



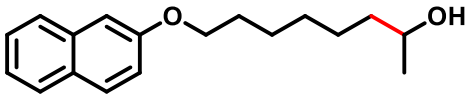
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.55 (s, 1H), 7.51 – 7.44 (m, 2H), 7.26 – 7.21 (m, 1H), 3.90 – 3.80 (m, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.88 – 1.75 (m, 2H), 1.63 – 1.42 (m, 4H), 1.22 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.3, 148.3, 133.7, 131.4, 129.4, 127.7, 127.6, 126.5, 125.6, 121.1, 118.5, 67.8, 38.8, 34.4, 25.3, 24.9, 23.6.

HRMS (ESI, m/z): Calculated for $C_{17}H_{24}NO_3$ $(M+NH_4)^+$ 290.1751, found 290.1750.

9. 8-(naphthalen-2-yloxy)octan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1)



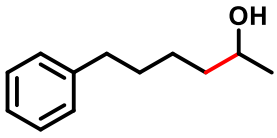
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 11.2, 2.0 Hz, 2H), 4.08 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.77 (m, 1H), 1.90 – 1.83 (m, 2H), 1.57 – 1.37 (m, 8H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.0, 134.6, 129.3, 128.8, 127.6, 126.6, 126.3, 123.4, 119.0, 106.5, 68.1, 67.9, 39.2, 29.4, 29.2, 26.1, 25.7, 23.5.

HRMS (ESI, m/z): Calculated for $C_{18}H_{24}NaO_2$ $(M+ Na)^+$ 295.1669, found 295.1665.

10. 6-phenylhexan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



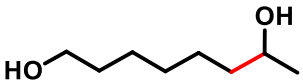
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 6.8 Hz, 3H), 3.85 – 3.75 (m, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.03 (s, 1H), , 1.75 – 1.63 (m, 2H), 1.59 – 1.34 (m, 4H), 1.21 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.5, 128.3, 128.2, 125.5, 67.9, 39.0, 35.8, 31.4, 25.4, 23.4.

HRMS (ESI, m/z): Calculated for $C_{12}H_{22}NO$ $(M+NH_4)^+$ 196.1696, found 196.1695.

11. octane-1,7-diol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1).



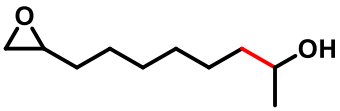
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 – 3.71 (m, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.04 (s, 2H), 1.59 – 1.50 (m, 2H), 1.48 – 1.26 (m, 8H), 1.16 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 68.0, 62.7, 39.1, 32.6, 29.3, 25.6, 25.6, 23.4.

HRMS (ESI, m/z): Calculated for $C_8H_{18}NaO_2$ $(M+ Na)^+$ 169.1199, found 169.1202.

12. 8-(oxiran-2-yl)octan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



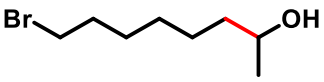
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 – 3.73 (m, 1H), 2.92 – 2.85 (m, 1H), 2.73 (t, *J* = 4.4 Hz, 1H), 2.45 (dd, *J* = 5.2, 2.8 Hz, 1H), 1.55 – 1.27 (m, 12H), 1.17 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 68.1, 52.4, 47.1, 39.3, 32.5, 29.5, 29.4, 25.9, 25.7, 23.5.

HRMS (ESI, m/z): Calculated for $C_{10}H_{20}NaO_2$ $(M+ Na)^+$ 195.1356, found 195.1359.

13. 8-bromooctan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



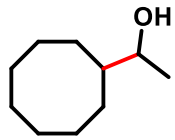
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 – 3.77 (m, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.46 – 1.32 (m, 8H), 1.18 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 68.1, 39.2, 33.9, 32.7, 28.7, 28.1, 25.6, 23.5.

HRMS (ESI, m/z): Calculated for $C_8H_{17}BrNaO$ $(M+Na)^+$ 231.0355, found 231.0359.

14. 1-cyclooctylethanol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1)



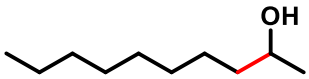
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 – 3.60 (m, 1H), 1.74 – 1.43 (m, 17H), 1.34 – 1.27 (m, 3H), 1.13 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 73.0, 44.3, 28.8, 28.4, 26.9, 26.7, 26.7, 26.3, 26.1, 19.9.

MS(EI): *m/z*(%): 155(0.1), 141(0.8), 111(41.1), 110(40.1), 95(10.7), 82(35.2), 81(23.7), 69(100).

15. decan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



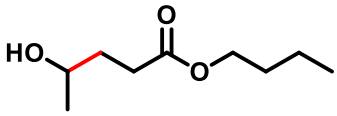
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 – 3.71 (m, 1H), 1.89 (s, 1H), 1.43 – 1.36 (m, 2H), 1.31 – 1.20 (m, 12H), 1.15 (d, *J* = 6.4 Hz, 3H), 0.85 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 68.0, 39.3, 31.8, 29.6, 29.5, 29.2, 25.7, 23.4, 22.6, 14.0.

MS(EI): *m/z*(%): 158(0.1),157(1.0),143(9.3), 112(21.7), 97(17.6), 83(29.6), 69(44.5), 55(27.3), 45(100).

16. butyl 4-hydroxypentanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



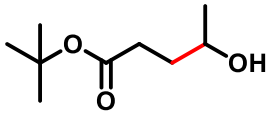
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.06 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.77 (m, 1H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.08 (s, 1H), 1.82 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 1.40 – 1.31 (m, 2H), 1.19 (d, *J* = 6.4 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 67.3, 64.4, 33.8, 30.7, 30.6, 23.4, 19.1, 13.6.

HRMS (ESI, m/z): Calculated for $C_9H_{19}O_3$ $(M+H)^+$ 175.1329, found 175.1326.

17 . tert-butyl 4-hydroxypentanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



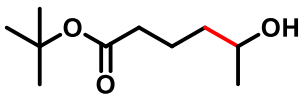
^{1}H NMR (400 MHz, $CDCl_3$): δ3.86 – 3.79 (m, 1H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.01 – 1.88 (m, 1H), 1.80 – 1.64 (m, 3H), 1.44 (s, 9H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 80.5, 67.5, 34.0, 32.1, 28.1, 23.5.

HRMS (ESI, m/z): Calculated for $C_9H_{18}NaO_3$ $(M+Na)^+$ 197.1148, found 197.1150.

18 . tert-butyl 5-hydroxyhexanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



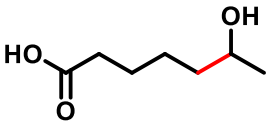
^{1}H NMR (400 MHz, $CDCl_3$): δ3.77– 3.71 (m, 1H), 2.32 (s, 1H), 2.19 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.46 – 1.33 (m, 2H), 1.39 (s, 9H), 1.14 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.2, 80.1, 67.3, 38.4, 35.2, 28.0, 23.3, 21.0.

HRMS (ESI, m/z): Calculated for $C_{10}H_{20}KO_3$ $(M+K)^+$ 227.0469, found 227.0468.

19 . 6-hydroxyheptanoic acid

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 2/1).



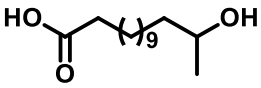
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (s, 1H), 3.84 – 3.76 (m, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.68 – 1.57 (m, 2H), 1.51 – 1.30 (m, 4H), 1.17 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.9, 67.9, 38.6, 33.9, 25.1, 24.6, 23.2.

HRMS (ESI, m/z): Calculated for $C_7H_{15}O_3$ $(M+H)^+$ 147.1380, found 147.1378.

20 . 13-hydroxytetradecanoic acid

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 2/1).



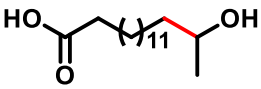
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 1H), 3.82 – 3.76 (m, 1H), 2.32 (t, *J* = 7.2 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.45 – 1.25 (m, 18H), 1.17 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.4, 68.3, 39.2, 34.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 25.7, 24.7, 23.3.

HRMS (ESI, m/z): Calculated for $C_{14}H_{28}O_3$ $(M+Na)^+$ 267.1931, found 267.1930.

21. 15-hydroxyhexadecanoic acid

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 2/1).



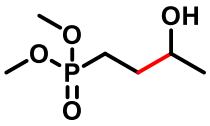
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (s, 1H), 3.85 – 3.75 (m, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.51 – 1.22 (m, 22H), 1.18 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.4, 68.3, 39.3, 34.0, 29.6, 29.6, 29.5, 29.5, 29.5, 29.5, 29.4, 29.2, 29.0, 25.7, 24.7, 23.3.

HRMS (ESI, m/z): Calculated for $C_{16}H_{32}NaO_3$ $(M+Na)^+$ 295.2244, found 295.2243.

22. dimethyl (3-hydroxybutyl)phosphonate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 – 3.69 (m, 1H), 3.64 (s, 3H), 3.61 (s, 3H), 3.47 (s, 1H), 1.93 – 1.52 (m, 4H), 1.08 (d, *J* = 6.4 Hz, 3H).

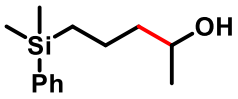
^{13}C NMR (101 MHz, $CDCl_3$): δ 66.9, 52.2, 31.2, 22.9, 21.3, 19.9.

^{31}P NMR (162 MHz, $CDCl_3$): δ 37.78 – 33.85 (m, 1P).

HRMS (ESI, m/z): Calculated for $C_6H_{16}O_4P$ $(M+H)^+$ 183.0781, found 183.0779.

23. 5-(dimethyl(phenyl)silyl)pentan-2-ol

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



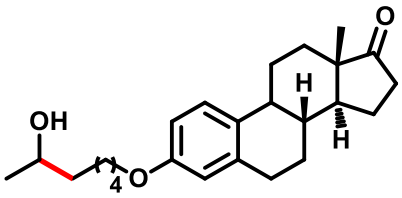
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 2.0 Hz, 2H), 7.38 (t, *J* = 2.0 Hz, 3H), 3.81 – 3.75 (m, 1H), 1.58 – 1.36 (m, 4H), 1.17 (d, *J* = 6.4 Hz, 3H), 0.85 – 0.73 (m, 2H), 0.30 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 133.5, 128.8, 127.7, 67.7, 43.1, 23.4, 20.1, 15.7, -3.1.

HRMS (ESI, m/z): Calculated for $C_{13}H_{22}KOSi$ $(M+K)^+$ 261.1072, found 261.1069.

24. (8R,9S,13S,14S)-3-((6-hydroxyheptyl)oxy)-13-methyl-7,8,9,11,12,13,15,16 –octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



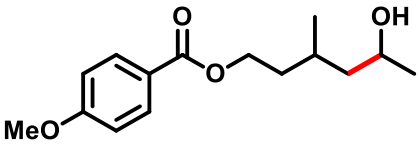
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.8 Hz, 1H), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.64 (s, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.77 (m, 1H), 2.91 – 2.87 (m, 2H), 2.50 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.41 – 2.37 (m, 1H), 2.27 – 2.18 (m, 1H), 2.18 – 1.93 (m, 5H), 1.81 – 1.74 (m, 3H), 1.67 – 1.36 (m, 10H), 1.19 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 220.9, 157.1, 137.6, 131.8, 126.2, 114.5, 112.1, 68.0, 67.7, 50.4, 48.0, 43.9, 39.2, 38.4, 35.8, 31.6, 29.6, 29.3, 26.5, 26.1, 25.9, 25.5, 23.5, 21.5, 13.8.

HRMS (ESI, m/z): Calculated for $C_{25}H_{37}O_3$ $(M+H)^+$ 385.2737, found 385.2743.

25. 5-hydroxy-3-methylhexyl 4-methoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



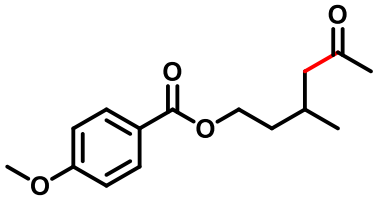
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H), 4.33 – 4.20 (m, 2H), 3.88 – 3.80 (m, 1H), 3.74 (s, 3H), 2.60 (s, 1H), 1.83 – 1.66 (m, 2H), 1.57 – 1.46 (m, 1H), 1.40 – 1.31 (m, 1H), 1.19 – 1.10 (m, 4H), 0.91 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 163.0, 131.3, 122.5, 113.3, 65.1, 62.8, 55.1, 46.3, 36.0, 26.5, 24.1, 19.1.

HRMS (ESI, m/z): Calculated for $C_{15}H_{26}NO_4$ $(M+NH_4)^+$ 284.1048, found 284.1047.

25'. 3-methyl-5-oxohexyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1).



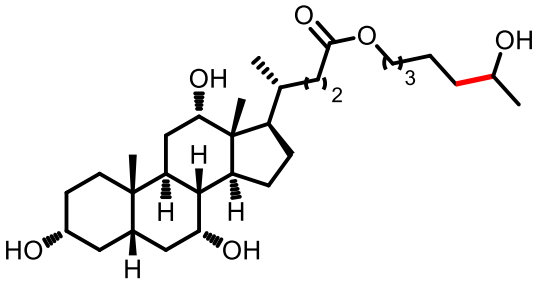
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.37 – 4.26 (m, 2H), 3.85 (s, 3H), 2.50 (dd, J = 16.4, 5.6 Hz, 1H), 2.33 (dd, J = 16.2, 7.8 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.13 (s, 3H), 1.82 – 1.74 (m, 1H), 1.66 – 1.57 (m, 1H), 0.99 (d, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 208.2, 166.3, 163.3, 131.5, 122.7, 113.6, 62.6, 55.4, 50.8, 35.4, 30.4, 26.3, 19.7.

HRMS (ESI, m/z): Calculated for $C_{15}H_{20}KO_4$ $(M+K)^+$ 303.0993, found 303.0994.

26. (4R)-6-hydroxyheptyl 4-((3R,5S,7R,8R,9S,10S,12S,13R,14S)-3,7,12-trihydroxy -10,13- dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 1/3).



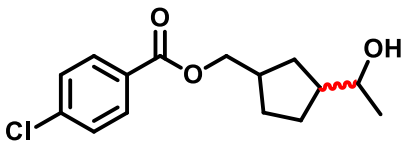
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (t, *J* = 6.4 Hz, 2H), 3.92 (s, 1H), 3.80 (s, 1H), 3.78 – 3.74 (m, 1H), 3.70 – 3.55 (m, 1H), 3.40 (d, *J* = 6.0 Hz, 3H), 3.16 (s, 2H), 2.37 – 2.31 (m, 1H), 2.24 – 2.13 (m, 3H), 1.90 – 1.11 (m, 27H), 0.96 (d, *J* = 5.2 Hz, 3H), 0.90 (d, *J* = 12 Hz, 3H), 0.85 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 73.0, 71.8, 68.5, 67.8, 64.2, 46.9, 46.3, 41.4, 40.4, 39.4, 39.1, 35.2, 34.7, 31.3, 30.9, 30.2, 29.5, 28.6, 28.1, 27.4, 26.5, 26.3, 25.9, 25.8, 25.3, 23.4, 23.2, 22.4, 17.2, 12.4.

HRMS (ESI, m/z): Calculated for $C_{31}H_{54}NaO_6$ $(M+ Na)^+$ 545.3813, found 545.3818.

27. (3-(1-hydroxyethyl)cyclopentyl)methyl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



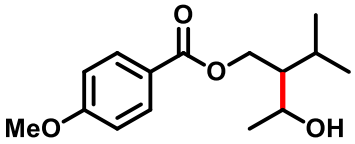
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 4.23 – 4.18 (m, 2H), 3.63 – 3.58 (m, 1H), 2.45 – 2.40 (m, 1H), 1.98 – 1.91 (m, 2H), 1.86 – 1.62 (m, 2H), 1.56 – 1.27 (m, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 139.3, 130.9, 128.8, 128.6, 71.9, 68.9, 46.8, 38.1, 31.4, 29.7, 28.7, 22.3.

HRMS (ESI, m/z): Calculated for $C_{15}H_{19}ClNaO_3$ $(M+Na)^+$ 305.0915, found 305.0914.

28. 3-hydroxy-2-isopropylbutyl 4-methoxybenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



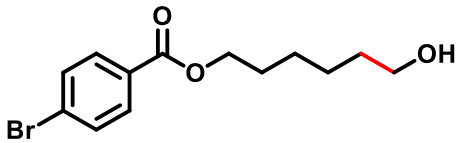
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 4.60 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.47 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.03 – 3.97 (m, 1H), 3.85 (s, 3H), 2.03 – 1.94 (m, 1H), 1.83 (s, 1H), 1.54 – 1.49 (m, 1H), 1.30 (d, *J* = 6.4 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6, 163.4, 131.6, 122.5, 113.7, 67.3, 62.7, 55.4, 50.6, 27.5, 22.1, 21.5, 19.2.

HRMS (ESI, m/z): Calculated for $C_{15}H_{22}NaO_4$ $(M+Na)^+$ 289.1410, found 289.1411.

29. 6-hydroxyhexyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



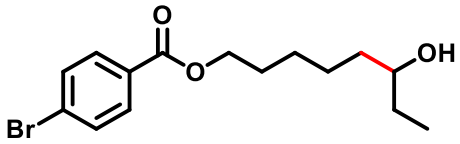
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.63 – 1.56 (m, 2H), 1.50 – 1.42 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.0, 129.3, 127.9, 65.2, 62.8, 32.5, 28.6, 25.8, 25.4.

HRMS (ESI, m/z): Calculated for $C_{13}H_{21}BrNO_3$ $(M+NH_4)^+$ 318.0699, found 318.0698.

30. 6-hydroxyoctyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



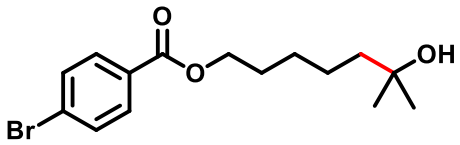
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.57 – 3.48 (m, 1H), 1.80 – 1.72 (m, 2H), 1.54 – 1.39 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.0, 129.3, 127.9, 73.1, 65.2, 36.7, 30.2, 28.6, 26.1, 25.3, 9.9.

HRMS (ESI, m/z): Calculated for $C_{15}H_{25}BrNO_3$ $(M+NH_4)^+$ 346.1012, found 346.1013.

31. 6-hydroxy-6-methylheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



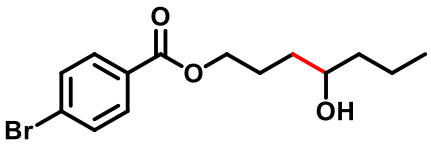
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.52 – 1.37 (m, 6H), 1.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9 131.6, 131.0, 129.3, 127.9 70.8, 65.3 43.7, 29.2, 28.7, 26.5, 24.0.

HRMS (ESI, m/z): Calculated for $C_{15}H_{21}BrNaO_3$ $(M+Na)^+$ 351.0566, found 351.0574.

32. 4-hydroxyheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



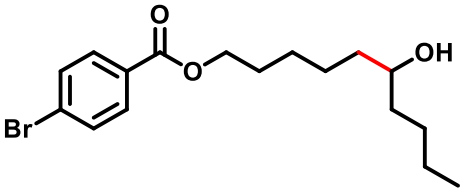
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4Hz, 2H), 7.57 (d, *J* = 8.4Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 3.71 – 3.62 (m, 1H), 1.99 – 1.71 (m, 2H), 1.66 – 1.30 (m, 6H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.0, 129.3, 127.9, 71.2, 65.3, 39.8, 33.7, 25.0, 18.8, 14.0.

HRMS (ESI, m/z): Calculated for $C_{14}H_{19}BrNaO_3$ $(M+Na)^+$ 337.0410, found 337.0417.

33. 6-hydroxydecyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



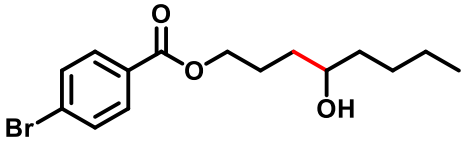
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.64 – 3.55 (m, 1H), 1.81 – 1.74 (m, 2H), 1.51 – 1.29 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.1, 129.3, 127.9, 71.8, 65.3, 37.3, 37.2, 28.7, 27.8, 26.1, 25.3, 22.7, 14.1.

HRMS (ESI, m/z): Calculated for $C_{17}H_{29}BrNO_3$ $(M+NH_4)^+$ 374.1325, found 374.1327.

34. 4-hydroxyoctyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



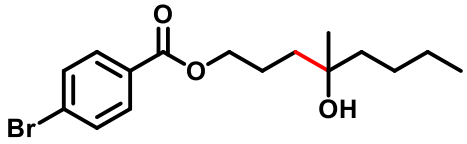
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.69 – 3.63 (m, 1H), 1.99 – 1.77 (m, 2H), 1.63 – 1.28 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.2, 128.0, 71.5, 65.3, 37.3, 33.7, 27.8, 25.0, 22.7, 14.0.

HRMS (ESI, m/z): Calculated for $C_{15}H_{21}BrNaO_3$ $(M+Na)^+$ 351.0566, found 351.0572.

35. 4-hydroxy-4-methylheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



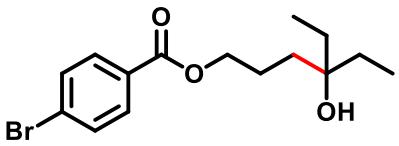
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.59 – 1.55 (m, 2H), 1.50 – 1.46 (m, 2H), 1.33 – 1.30 (m, 4H), 1.19 (s, 3H), 0.91 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.3, 128.0, 72.4, 65.7, 41.7, 37.9, 26.9, 26.1, 23.4, 23.2, 14.1.

HRMS (ESI, m/z): Calculated for $C_{16}H_{23}BrNaO_3$ $(M+Na)^+$ 365.0723, found 365.0726.

36. 4-ethyl-4-hydroxyhexyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1)



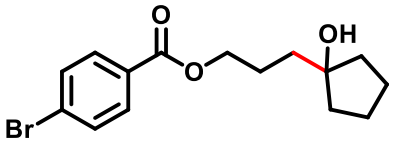
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.83 – 1.78 (m, 2H), 1.56 – 1.47 (m, 6H), 1.16 (s, 1H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.0, 129.3, 127.9, 74.3, 65.7, 34.4, 31.0, 23.0, 7.8.

HRMS (ESI, m/z): Calculated for $C_{15}H_{21}BrNaO_3$ $(M+Na)^+$ 351.0566, found 351.0572.

37. 3-(1-hydroxycyclopentyl)propyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



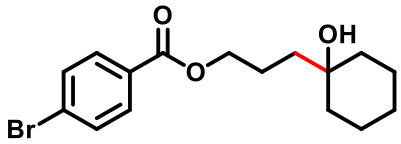
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.85 – 1.77 (m, 2H), 1.70 – 1.54 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.0, 129.3, 127.9, 82.1, 65.7, 39.8, 37.6, 24.3, 23.7.

HRMS (ESI, m/z): Calculated for $C_{15}H_{19}BrNaO_3$ $(M+Na)^+$ 349.0410, found 349.0415.

38. 3-(1-hydroxycyclohexyl)propyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



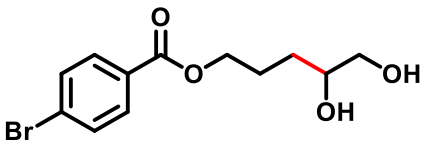
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.62 – 1.36 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.0, 129.3, 127.9, 71.0, 65.8, 38.5, 37.4, 25.7, 22.5, 22.2.

HRMS (ESI, m/z): Calculated for $C_{16}H_{21}BrNaO_3$ $(M+ Na)^+$ 363.0566, found 363.0567.

39. 4,5-dihydroxypentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1).



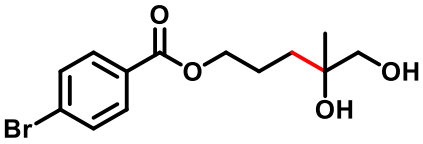
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.78 – 3.74 (m, 1H), 3.67 (d, *J* = 10.8 Hz, 1H), 3.48 – 3.44 (m, 1H), 2.74 (s, 1H), 2.48 (s, 1H), 2.01 – 1.78 (m, 2H), 1.60 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 131.7, 131.1, 129.1, 128.1, 71.7, 66.7, 65.1, 29.4, 25.0.

HRMS (ESI, m/z): Calculated for $C_{12}H_{16}BrO_4$ $(M+H)^+$ 303.0226, found 303.0224.

40. 4,5-dihydroxy-4-methylpentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1)



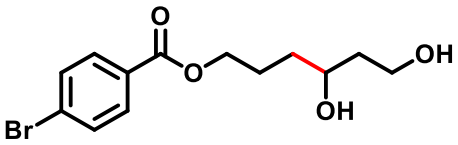
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.8 Hz, 2H), 3.47 (q, *J* = 10.8 Hz, 2H), 2.21 (s, 2H), 1.90 – 1.80 (m, 2H), 1.67 – 1.54 (m, 2H), 1.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.2, 128.0, 72.5, 69.8, 65.6, 34.7, 23.3, 23.2.

HRMS (ESI, m/z): Calculated for $C_{13}H_{18}BrO_4$ $(M+H)^+$ 317.0383, found 317.0384.

41. 6,8-dihydroxyoctyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1)



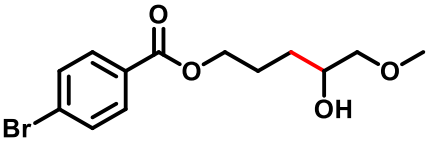
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.98 – 3.85 (m, 2H), 3.85 – 3.77 (m, 1H), 3.07 (s, 1H), 2.72 (s, 1H), 1.98 – 1.77 (m, 2H), 1.80 – 1.74 (m, 2H), 1.73 – 1.68 (m, 2H), 1.64 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.0, 129.2, 128.0, 71.4, 65.2, 61.6, 38.3, 34.0, 24.9.

HRMS (ESI, m/z): Calculated for $C_{13}H_{17}BrNaO_4$ $(M+Na)^+$ 339.0202, found 339.0199.

42[1]. 4-hydroxy-5-methoxypentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



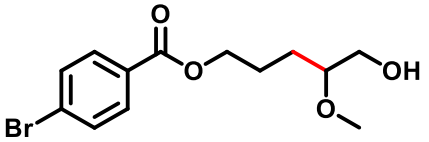
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 6.4 Hz, 2H), 3.87 – 3.81 (m, 1H), 3.42 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.39 (s, 3H), 3.26 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.03 – 1.92 (m, 1H), 1.90 – 1.79 (m, 1H), 1.60 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.2, 128.0, 76.8, 70.0, 65.1, 59.0, 29.5, 24.9.

HRMS (ESI, m/z): Calculated for $C_{13}H_{18}BrO_4$ $(M+H)^+$ 317.0383, found 317.0384.

42[2]. 5-hydroxy-4-methoxypentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



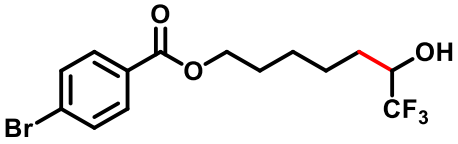
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.72 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.55 – 3.52 (m, 1H), 3.41 (s, 3H) , 3.35 – 3.29 (m, 1H), 1.89 – 1.79 (m, 2H), 1.77 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 131.7, 131.0, 129.2, 128.0, 80.9, 65.1, 63.5, 57.2, 27.0, 24.6.

HRMS (ESI, m/z): Calculated for $C_{13}H_{18}BrO_4$ $(M+H)^+$ 317.0383, found 317.0383.

43. 7,7,7-trifluoro-6-hydroxyheptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.98 – 3.87 (m, 1H), 2.20 (s, 1H), 1.83 – 1.76 (m, 2H), 1.74 – 1.61 (m, 4H), 1.54 – 1.47 (m, 2H).

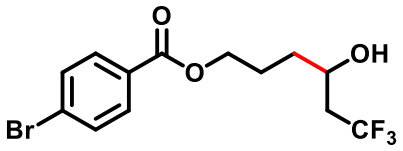
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 131.7, 131.1, 129.2, 128.0, 125.1 (q, *J* = 282.8 Hz), 70.4 (q, *J* = 30.9 Hz), 65.0, 29.4, 28.5, 25.7, 24.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -80.02 (d, *J* = 6.7 Hz, 3F).

HRMS (ESI, m/z): Calculated for $C_{14}H_{20}BrF_3NO_3$ $(M+NH_4)^+$ 386.0573, found 386.0574.

44. 6,6,6-trifluoro-4-hydroxyhexyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 4.15 – 4.05 (m, 1H), 2.38 – 2.23 (m, 2H), 2.03 (d, *J* = 3.6 Hz, 1H), 2.00 – 1.81(m, 2H), 1.70 – 1.65(m, 2H).

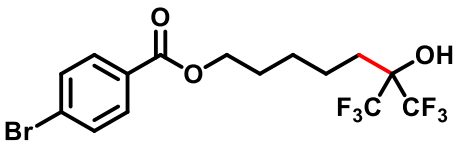
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.1, 128.1, 126.3 (q, *J* = 278.2 Hz), 65.8 (q, *J* = 3.0 Hz), 64.8, 41.34 (q, *J* = 26.6 Hz), 33.5, 24.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.51 (t, *J* = 10.9 Hz, 3F).

HRMS (ESI, m/z): Calculated for $C_{13}H_{15}BrF_3O_3$ $(M+H)^+$ 355.0151, found 355.0152.

45. 7,7,7-trifluoro-6-hydroxy-6-(trifluoromethyl)heptyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 4.32 (t, *J* =

6.8 Hz, 2H), 3.38 (s, 1H), 1.97 – 1.93 (m, 2H), 1.84 – 1.77 (m, 2H), 1.67 – 1.59 (m, 2H), 1.52 – 1.44 (m, 2H).

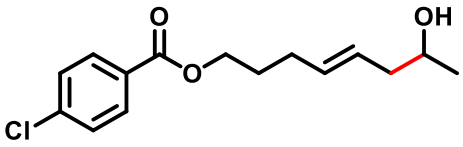
^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 131.7, 131.1, 129.1, 128.1, 123.16 (q, *J* = 285.7 Hz), 76.7 – 75.6 (m), 65.0, 30.3, 28.3, 26.4, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -76.6 (s, 6F).

HRMS (ESI, m/z): Calculated for $C_{15}H_{16}BrF_6O_3$ $(M+H)^+$ 437.0182, found 437.0168.

46. (E)-7-hydroxyoct-4-en-1-yl 4-chlorobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



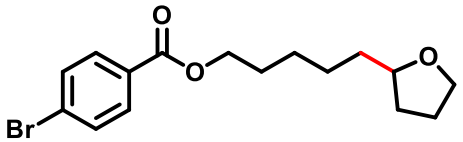
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.62 – 5.43 (m, 2H), 4.33 (td, *J* = 6.4, 1.2 Hz, 2H), 3.85 – 3.76 (m, 1H), 2.26 – 2.07 (m, 4H), 1.89 – 1.82 (m, 2H), 1.61 (s, 1H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.7, 139.3, 132.6, 130.9, 128.8, 128.7, 127.3, 67.2, 64.5, 42.5, 29.0, 28.4, 22.7.

HRMS (ESI, m/z): Calculated for $C_{15}H_{19}ClNaO_3$ $(M+Na)^+$ 305.0915, found 305.0918.

47. 5-(tetrahydrofuran-2-yl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



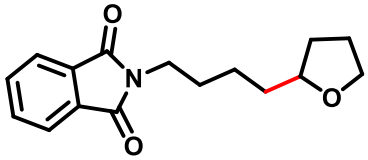
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.85 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.81 – 3.75 (m, 1H), 3.70 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.90 – 1.82 (m, 2H), 1.80 – 1.73 (m, 2H), 1.62 – 1.56 (m, 1H), 1.52 – 1.38 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.4, 127.9, 79.2, 67.6, 65.3, 35.6, 31.4, 28.7, 26.2, 26.1, 25.7.

HRMS (ESI, m/z): Calculated for $C_{16}H_{21}BrNaO_3$ $(M+Na)^+$ 363.0566, found 363.0572.

48. 2-(4-(tetrahydrofuran-2-yl)butyl)isoindoline-1,3-dione

A colorless solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1).



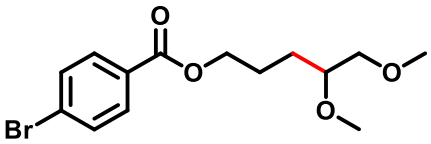
^{1}H NMR (400 MHz, $CDCl_3$): δ7.80 – 7.76 (m, 2H), 7.67 – 7.65 (m, 2H), 3.81 – 3.71 (m, 2H), 3.65 – 3.62 (m, 3H), 1.92 – 1.78 (m, 3H), 1.68 – 1.65 (m, 2H), 1.54 – 1.31 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 133.7, 132.0, 123.0, 78.9, 67.5, 37.8, 35.1, 31.2, 28.5, 25.6, 23.6.

HRMS (ESI, m/z): Calculated for $C_{16}H_{19}NNaO_3$ $(M+Na)^+$ 296.1257, found 296.1262.

49. 4,5-dimethoxypentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



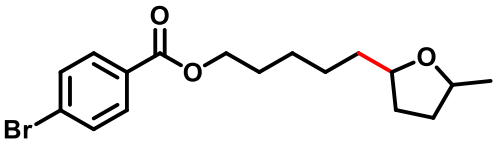
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 6.4 Hz, 2H), 3.44 – 3.42 (m, 1H), 3.42 (s, 3H), 3.40 – 3.33 (m, 5H), 1.95 – 1.76 (m, 2H), 1.71 – 1.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.3, 127.9, 79.5, 74.3, 65.3, 59.2, 57.5, 27.9, 24.7.

HRMS (ESI, m/z): Calculated for $C_{14}H_{23}BrNO_4$ $(M+NH_4)^+$ 348.0805, found 348.0808.

50. 5-(5-methyltetrahydrofuran-2-yl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



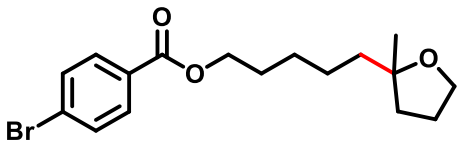
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.95 – 3.72 (m, 2H), 1.97 – 1.85 (m, 2H), 1.81 – 1.60 (m, 4H), 1.53 – 1.39 (m, 5H), 1.23 (d, *J* = 6.0 Hz, 3H), 0.92 – 0.85 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.7, 131.1, 129.4, 127.9, 79.4, 75.2, 65.3, 36.1, 32.8, 31.3, 28.6, 26.2, 25.9, 21.4.

HRMS (ESI, m/z): Calculated for $C_{17}H_{24}BrO_3$ $(M+H)^+$ 355.0903, found 355.0906.

50'. 5-(2-methyltetrahydrofuran-2-yl)pentyl 4-bromobenzoate

A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



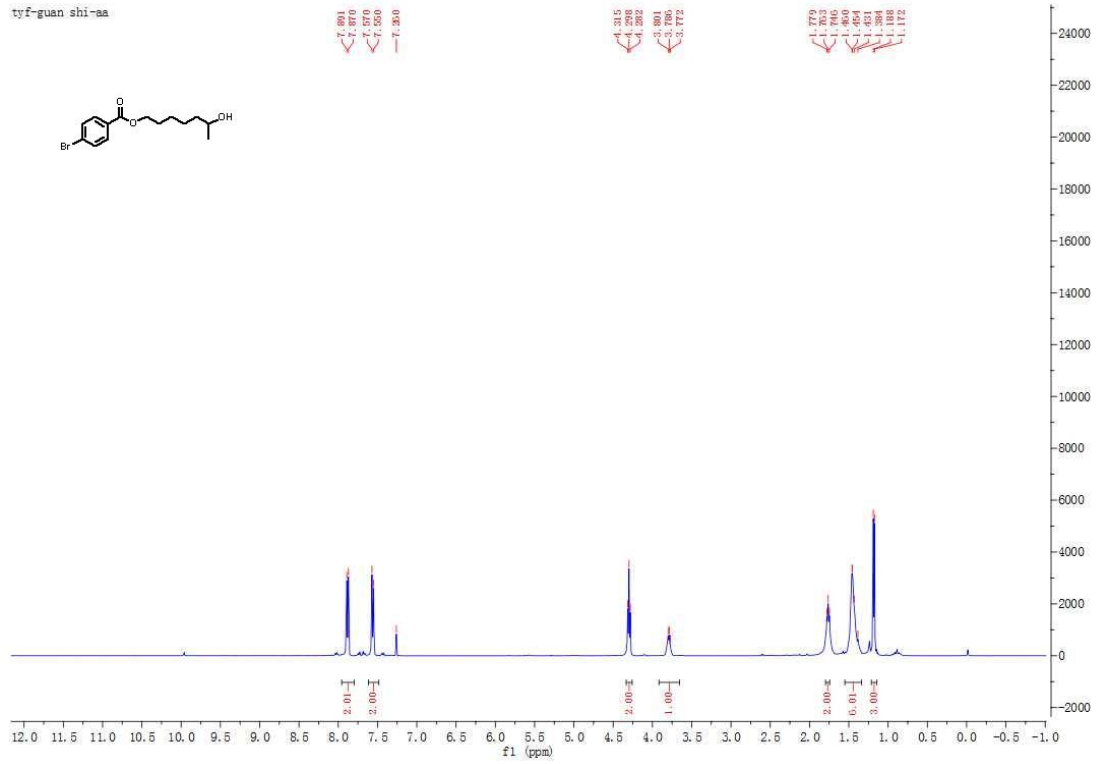
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.85 – 3.75 (m, 2H), 1.98 – 1.84 (m, 2H), 1.77 – 1.59 (m, 4H), 1.54 – 1.39 (m, 5H), 1.24 – 1.19 (m, 1H), 1.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 131.6, 131.0, 129.3, 127.9, 82.4, 67.1, 65.3, 41.1, 36.7, 28.7, 26.6, 26.1, 25.6, 24.4.

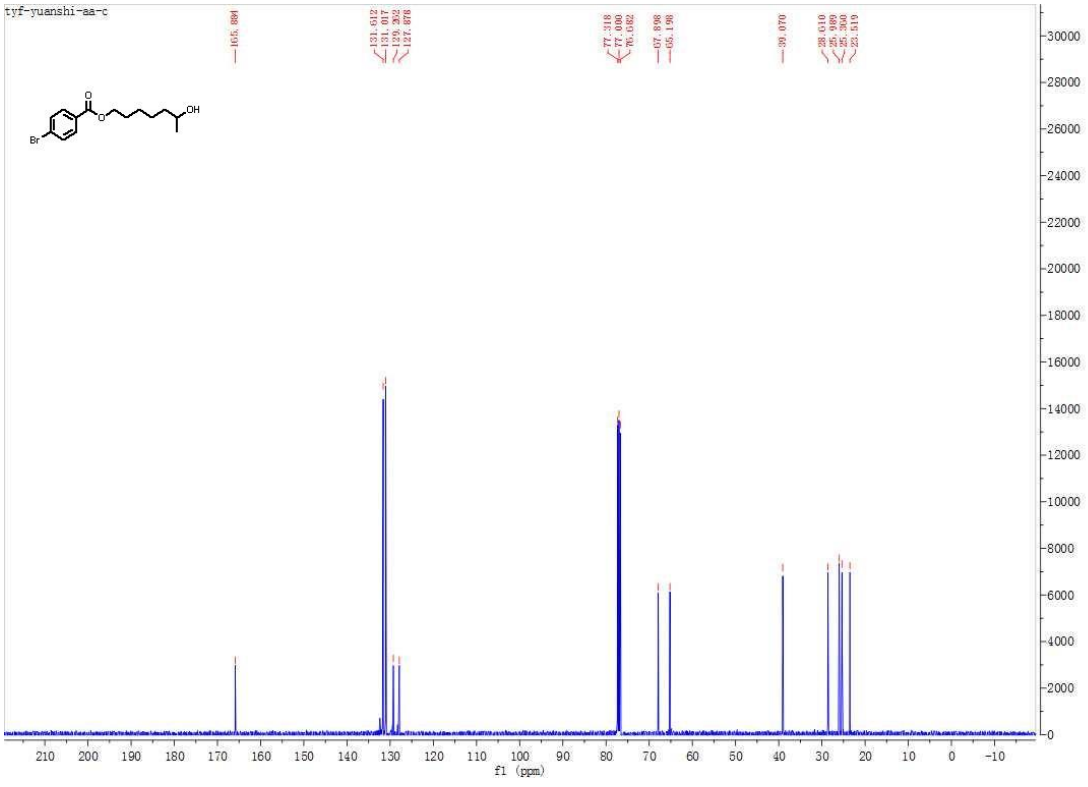
HRMS (ESI, m/z): Calculated for $C_{17}H_{24}BrO_3$ $(M+H)^+$ 355.0903, found 355.0905.

Copies of the ^{1}H NMR, ^{13}C NMR, ^{135}DEPT spectra

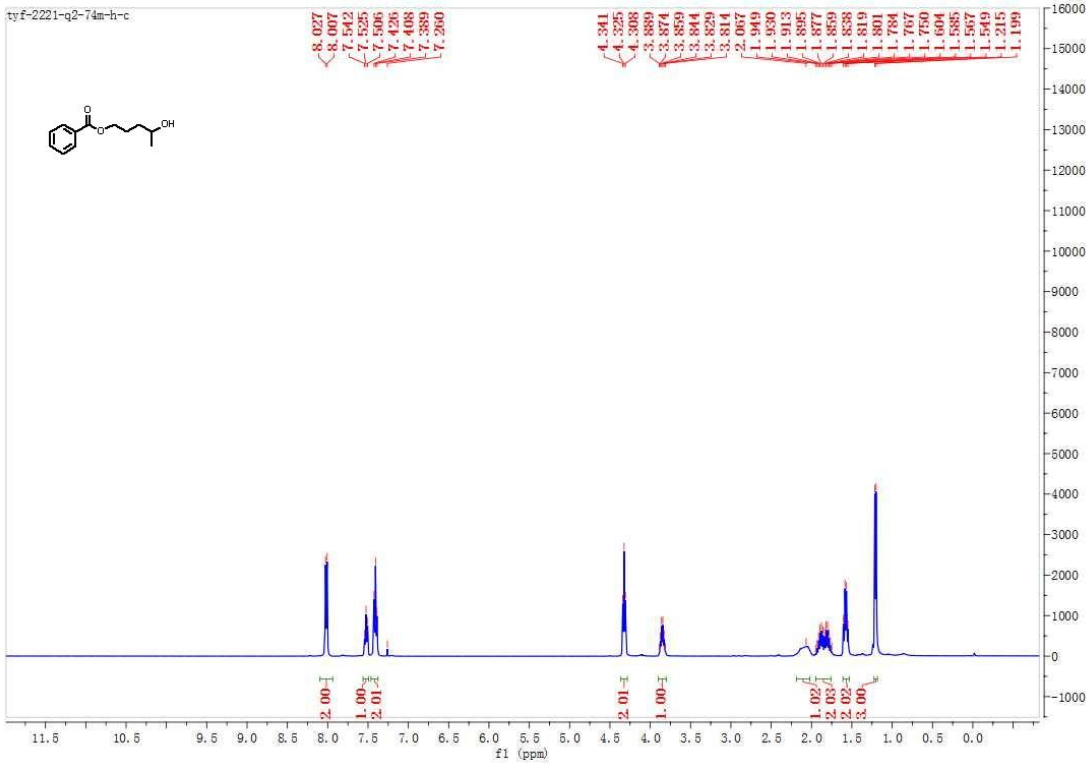
1-^{1}H NMR



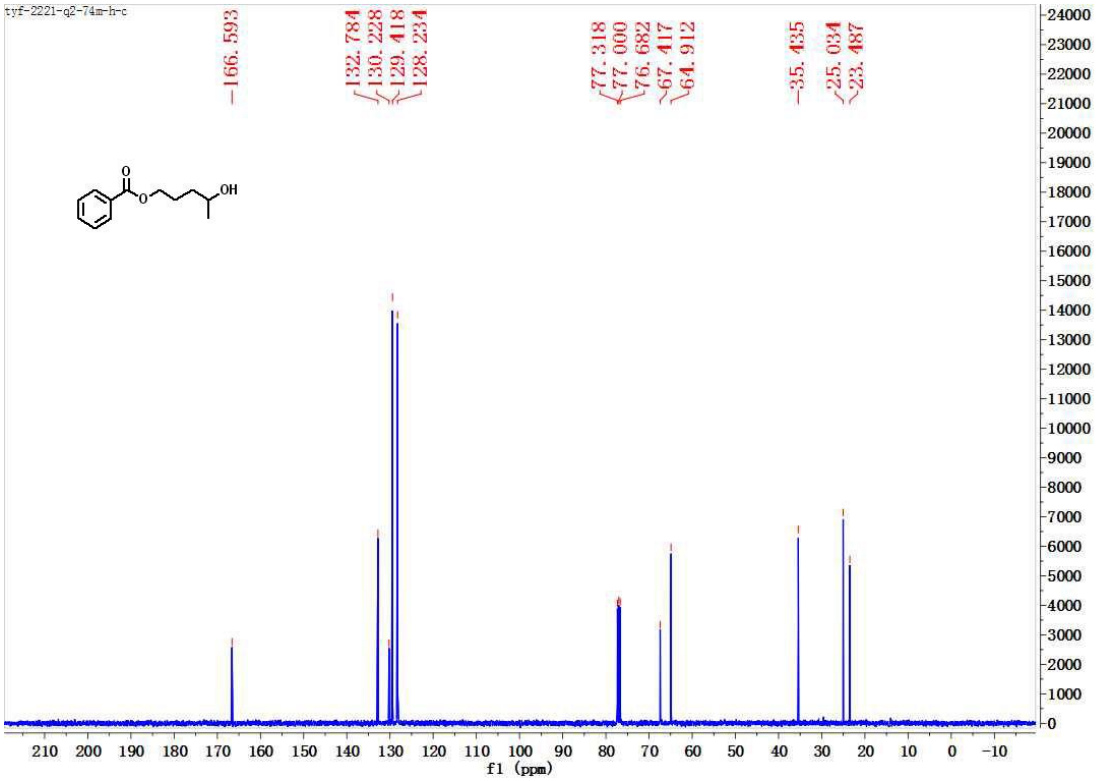
1-^{13}C NMR



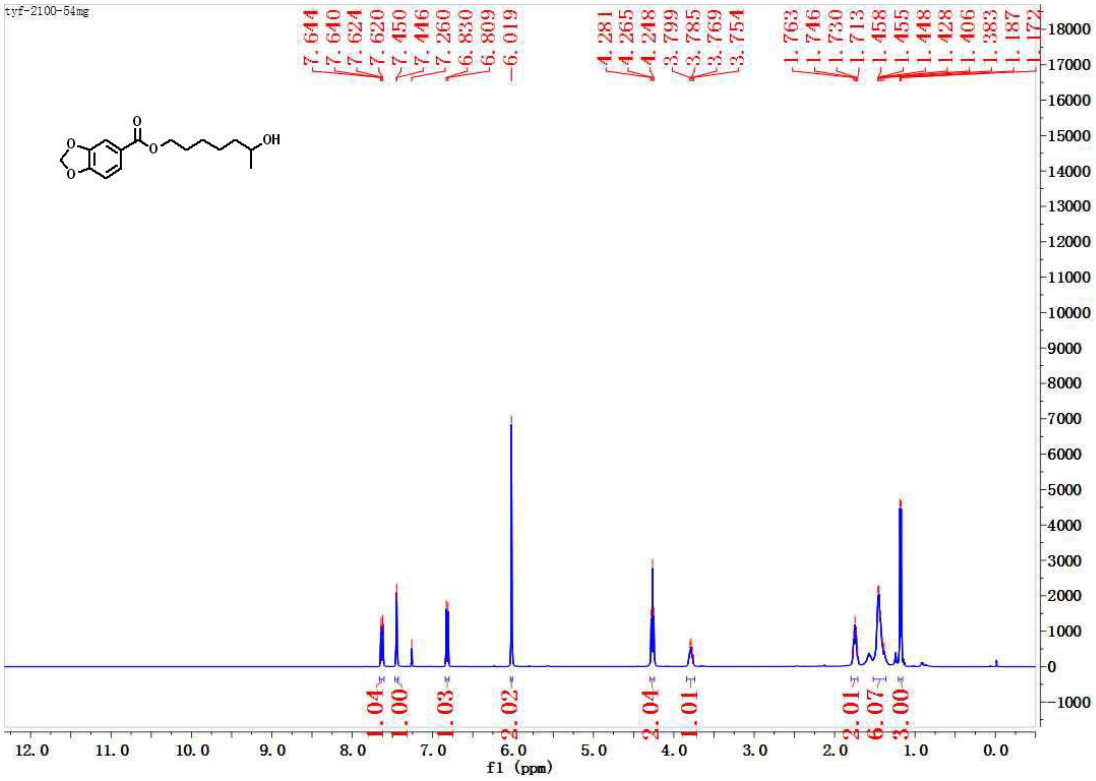
2-^{1}H NMR



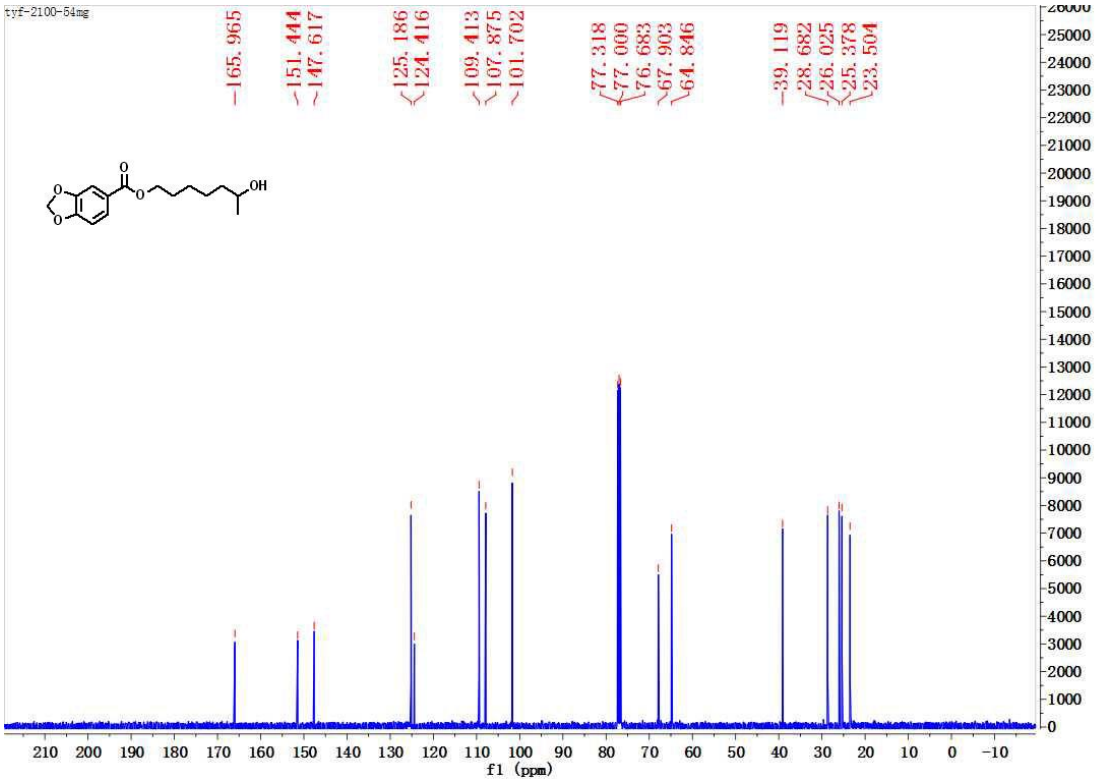
2-^{13}C NMR



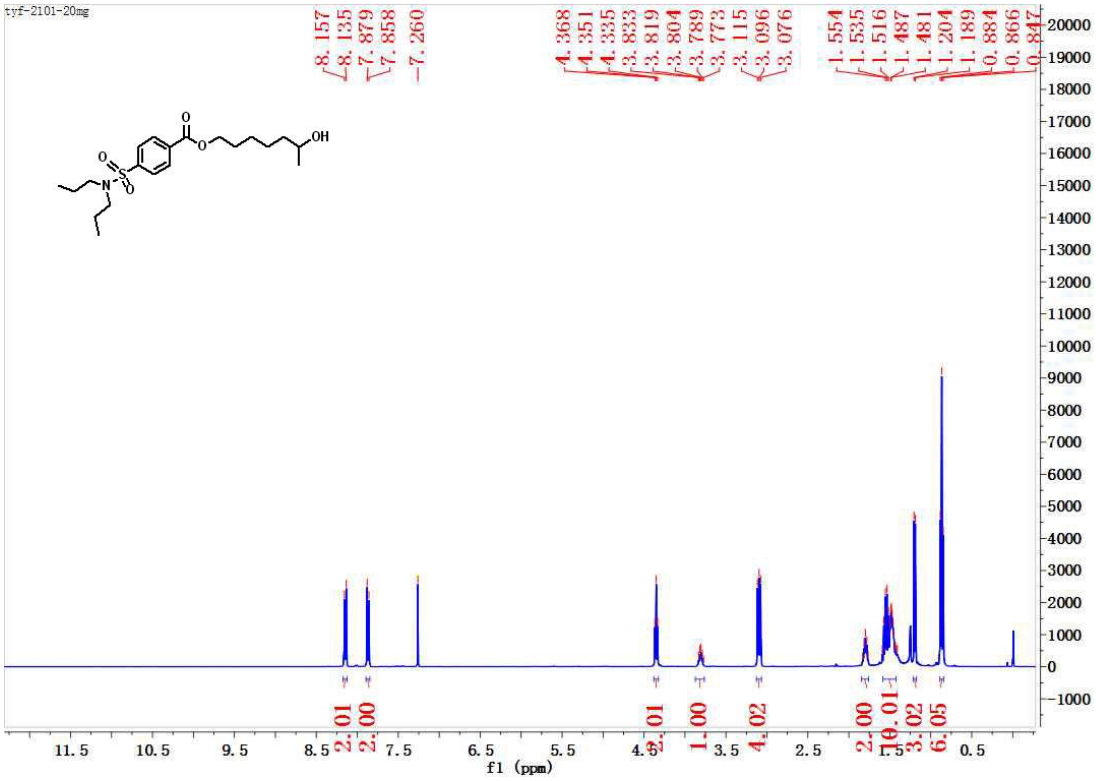
3-^{1}H NMR



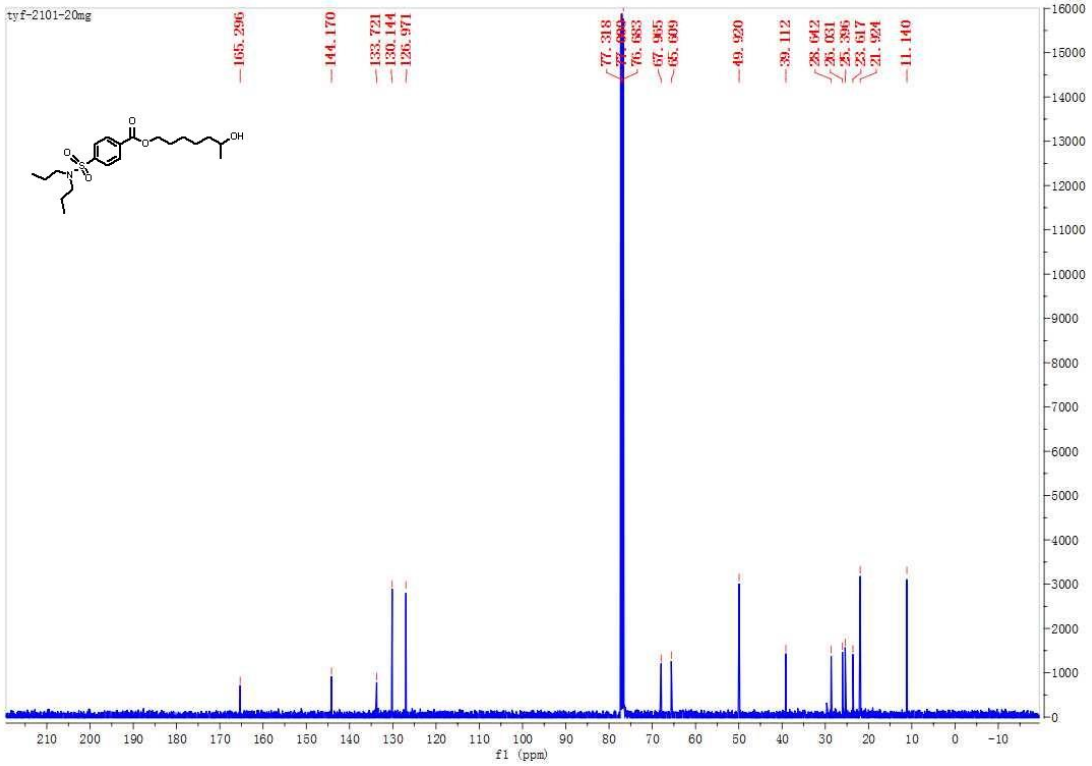
3-^{13}C NMR



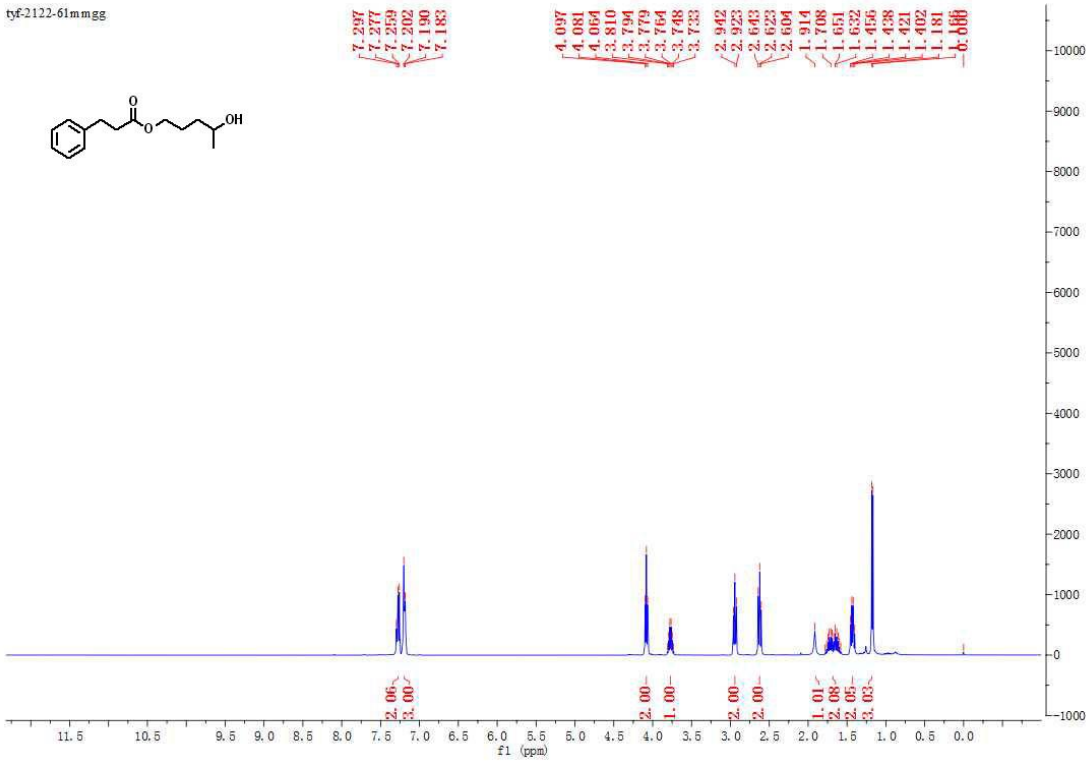
4-^{1}H NMR



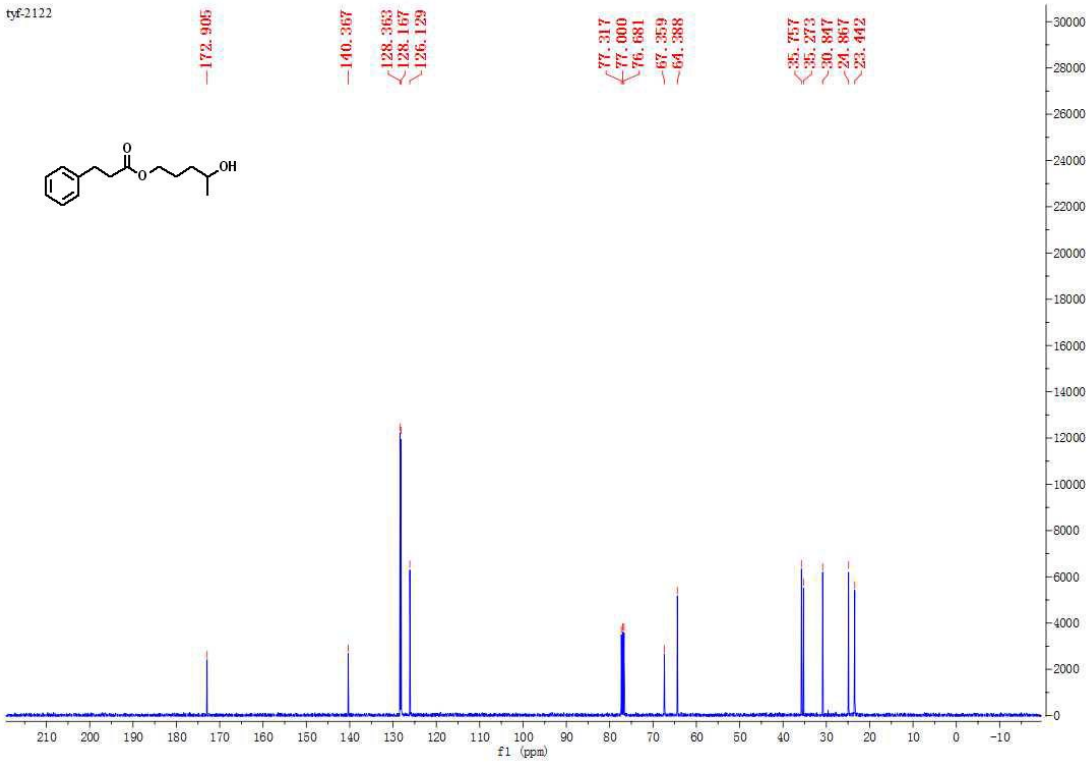
4-^{13}C NMR



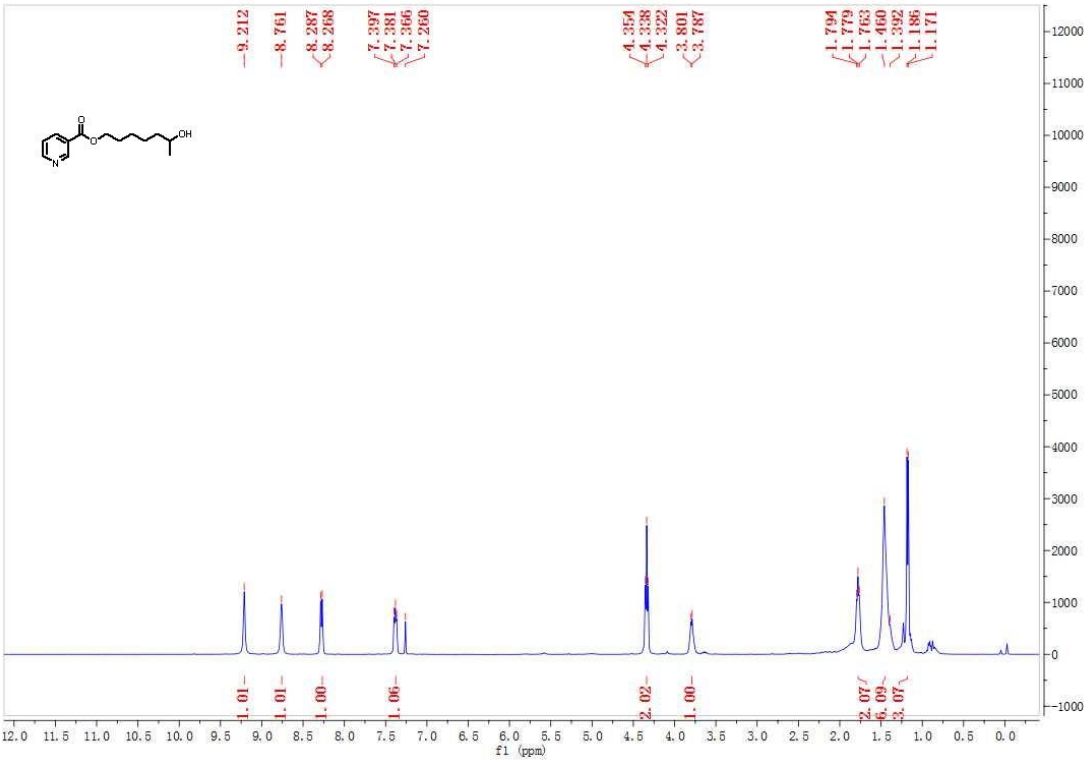
5-^{1}H NMR



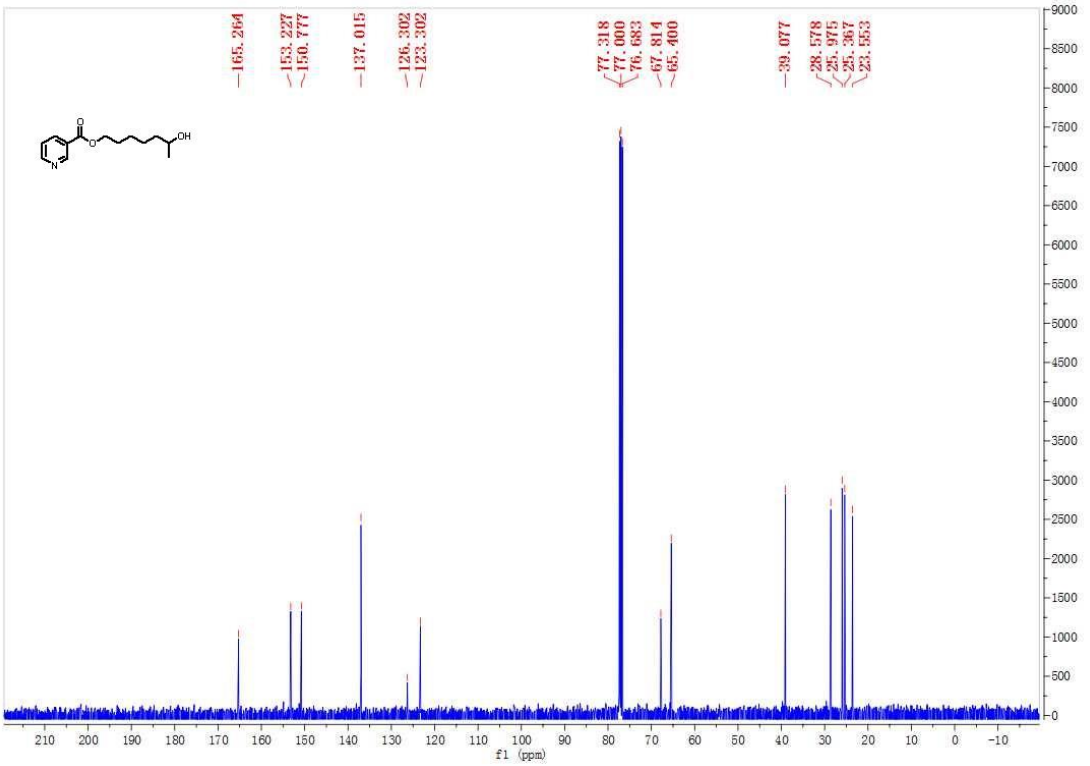
5-^{13}C NMR



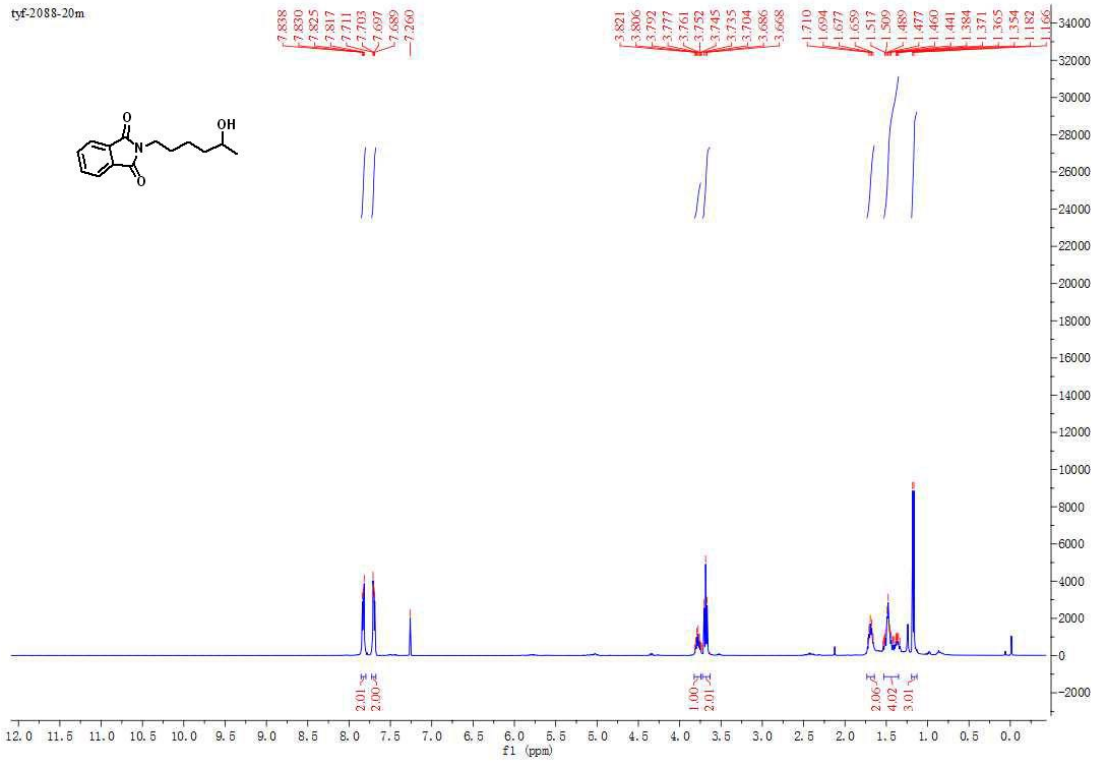
6-^{1}H NMR



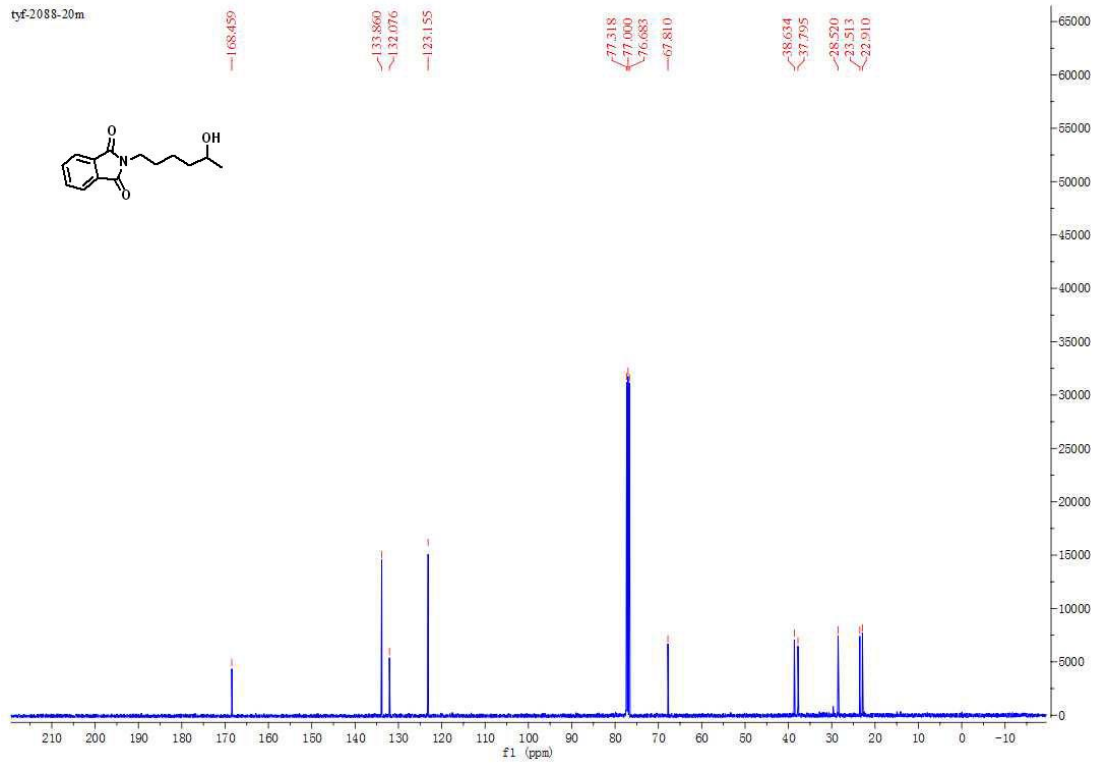
6-^{13}C NMR



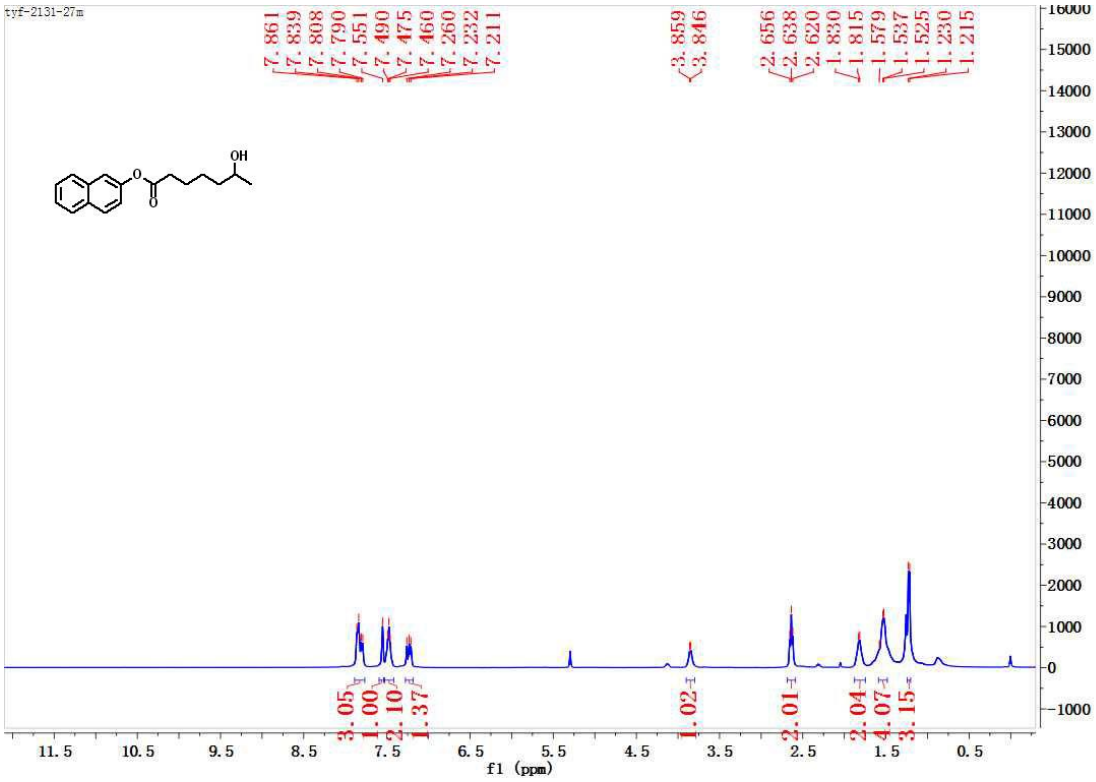
7-^{1}H NMR



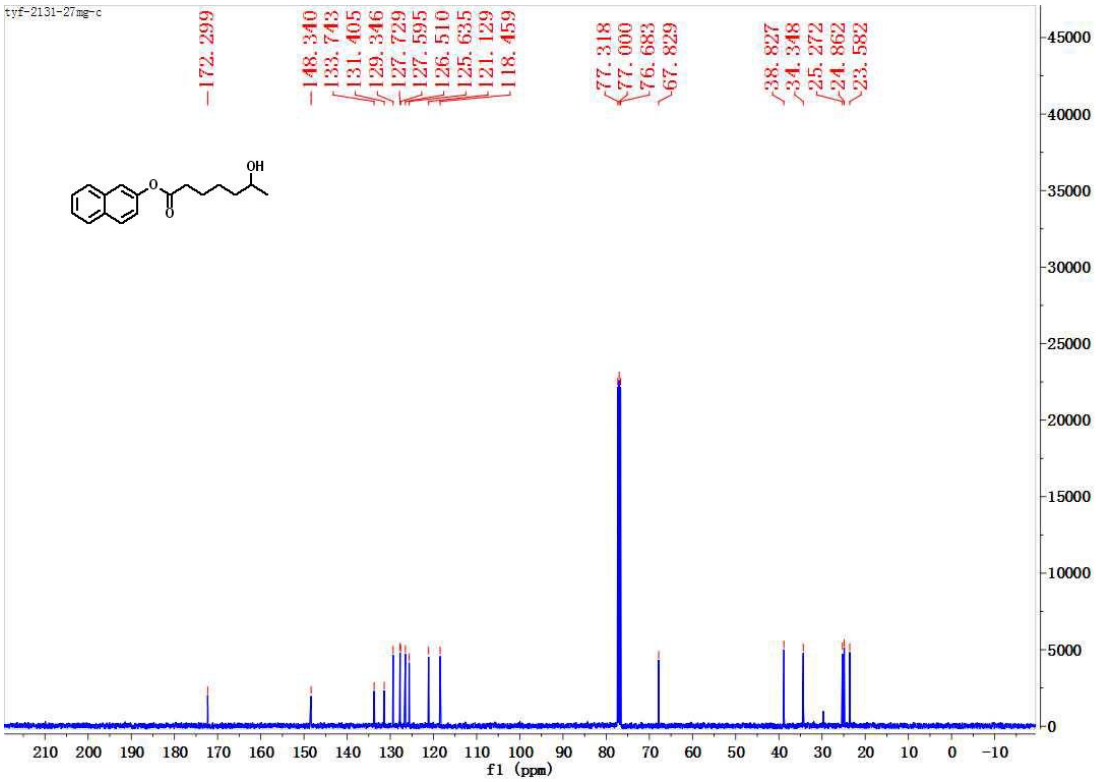
7-^{13}C NMR



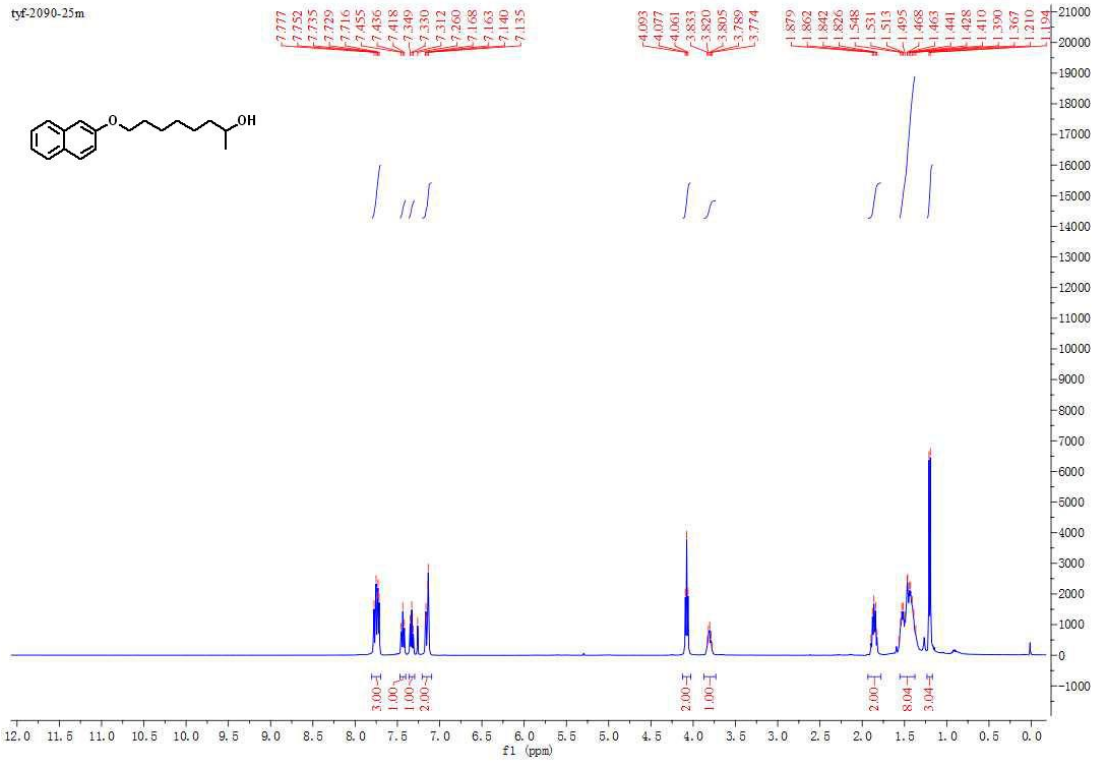
8-^{1}H NMR



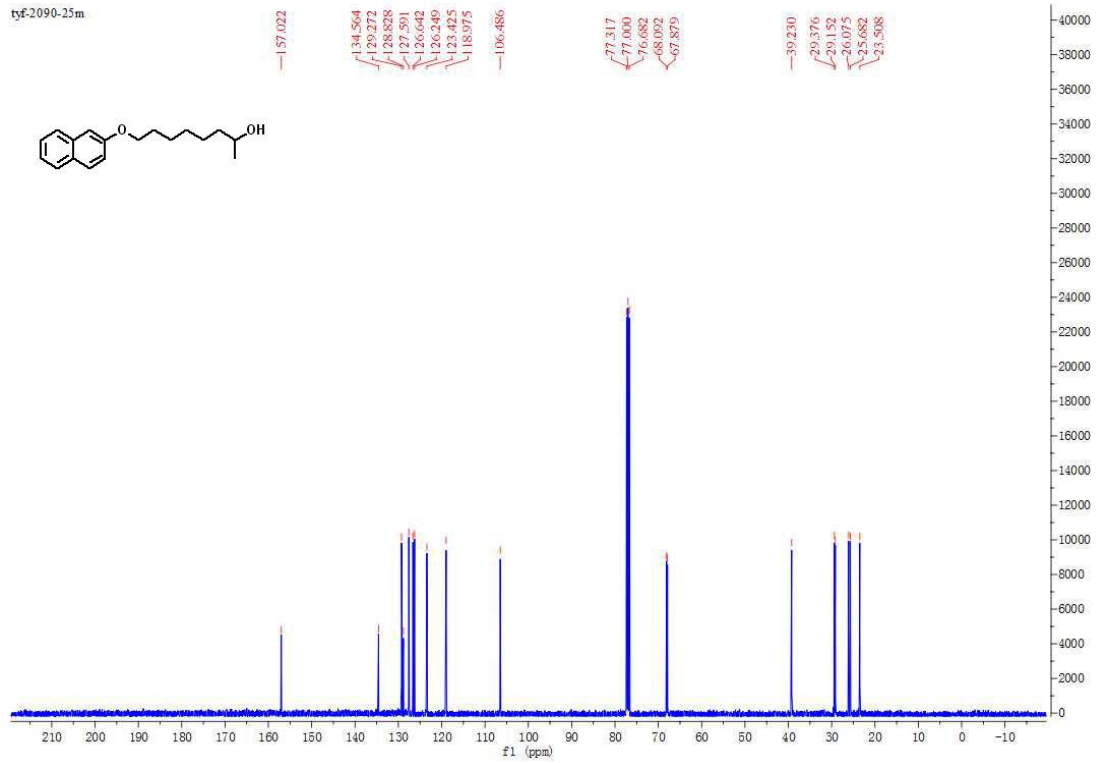
8-^{13}C NMR



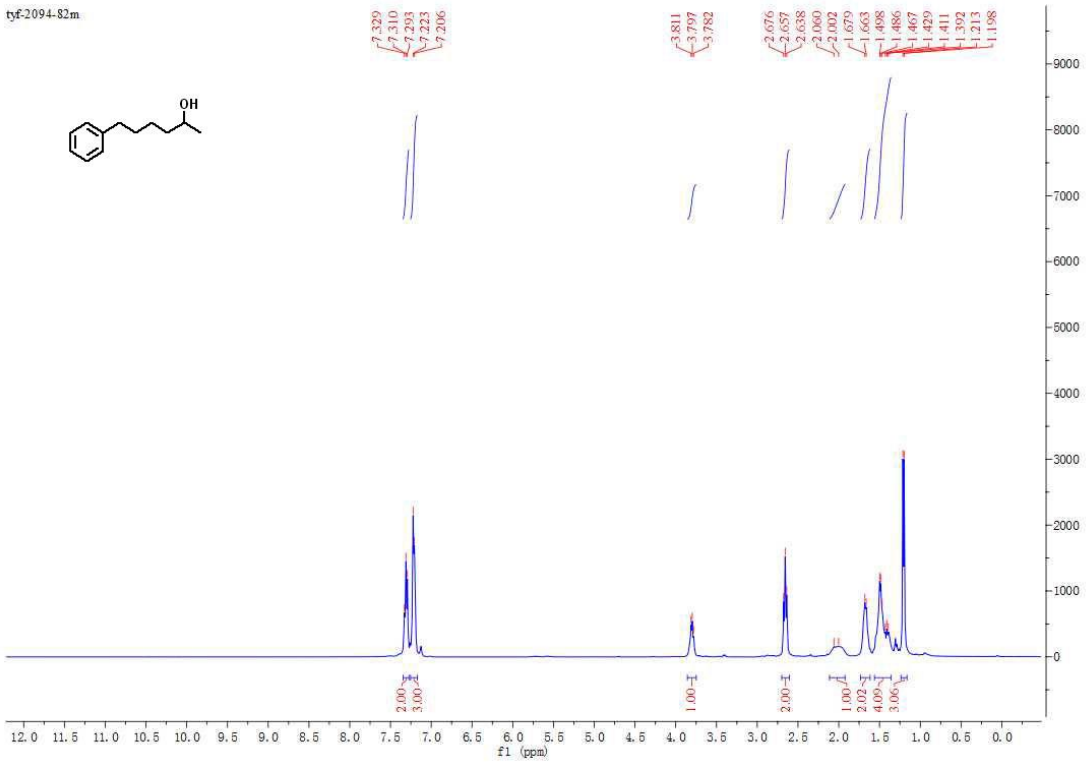
9-^{1}H NMR



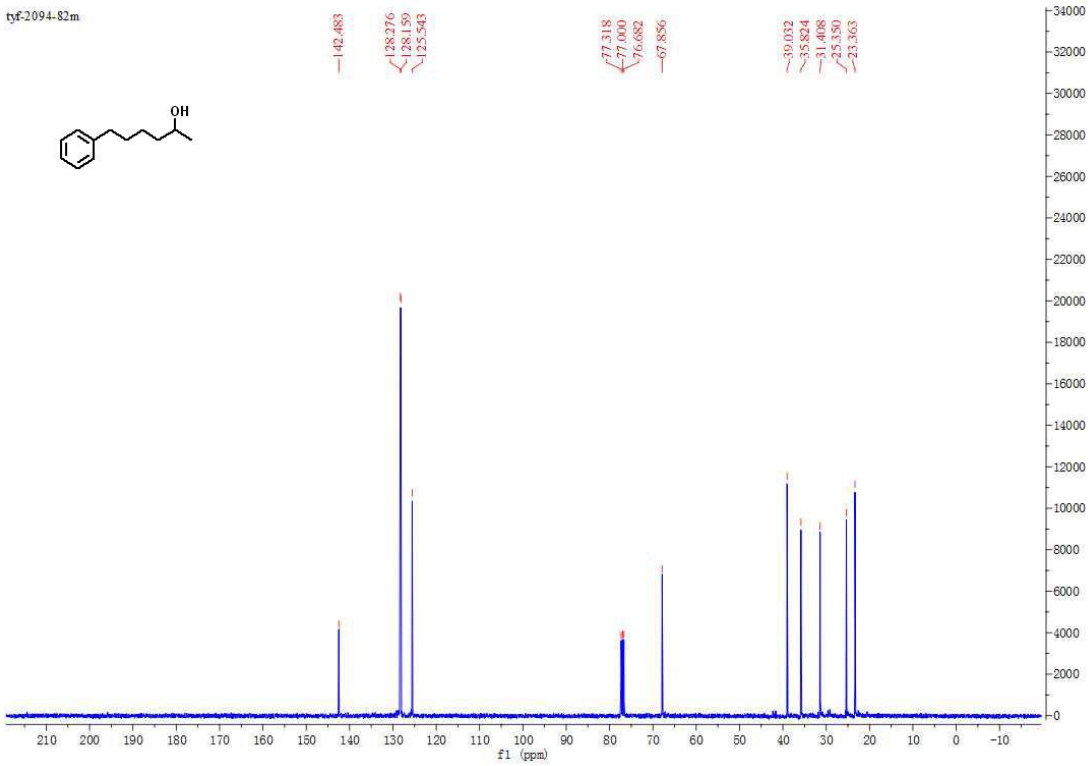
9-^{13}C NMR



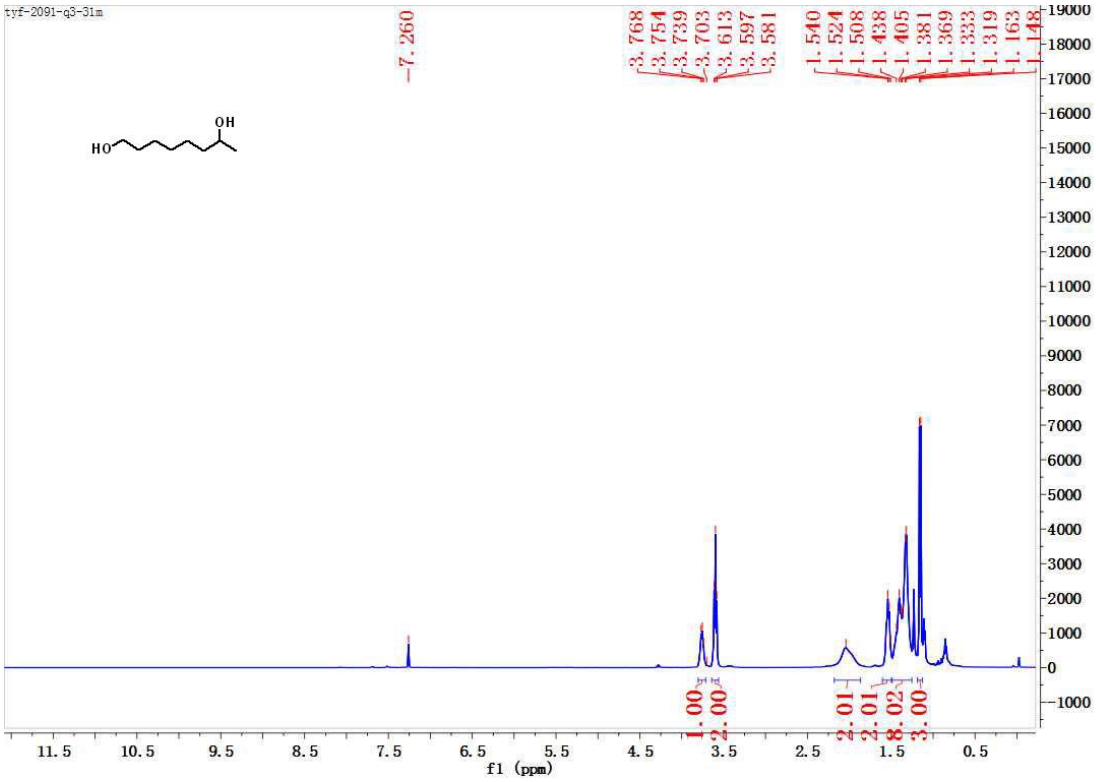
10-^{1}H NMR



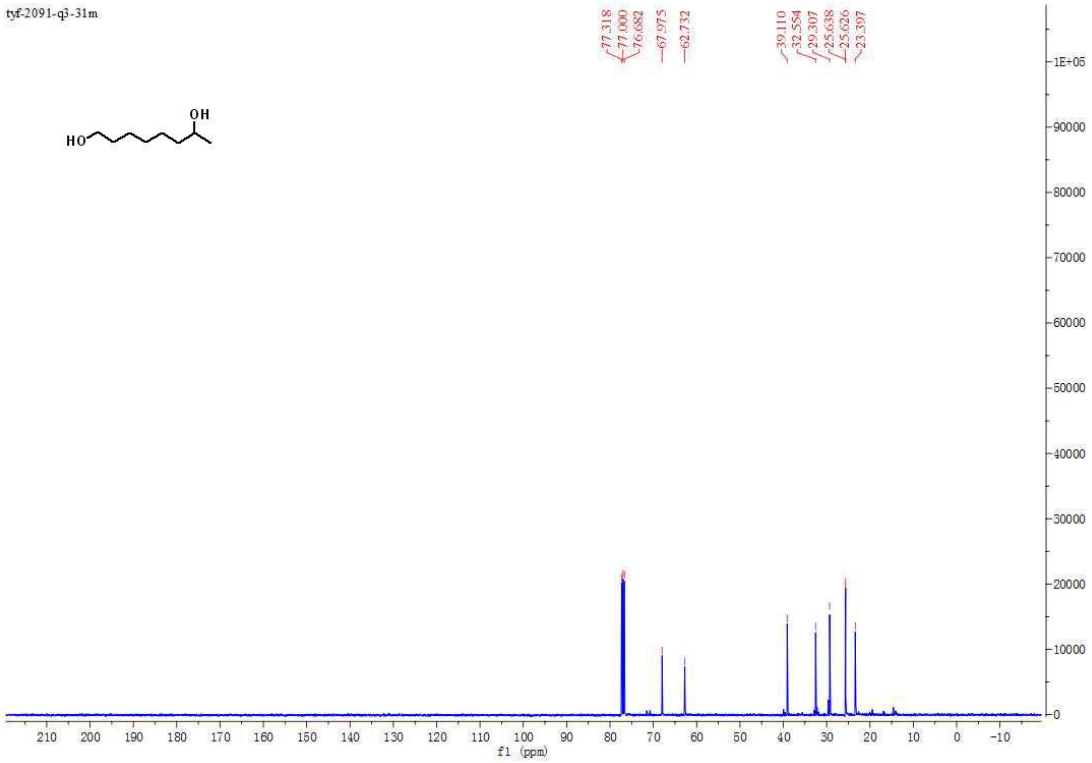
10-^{13}C NMR



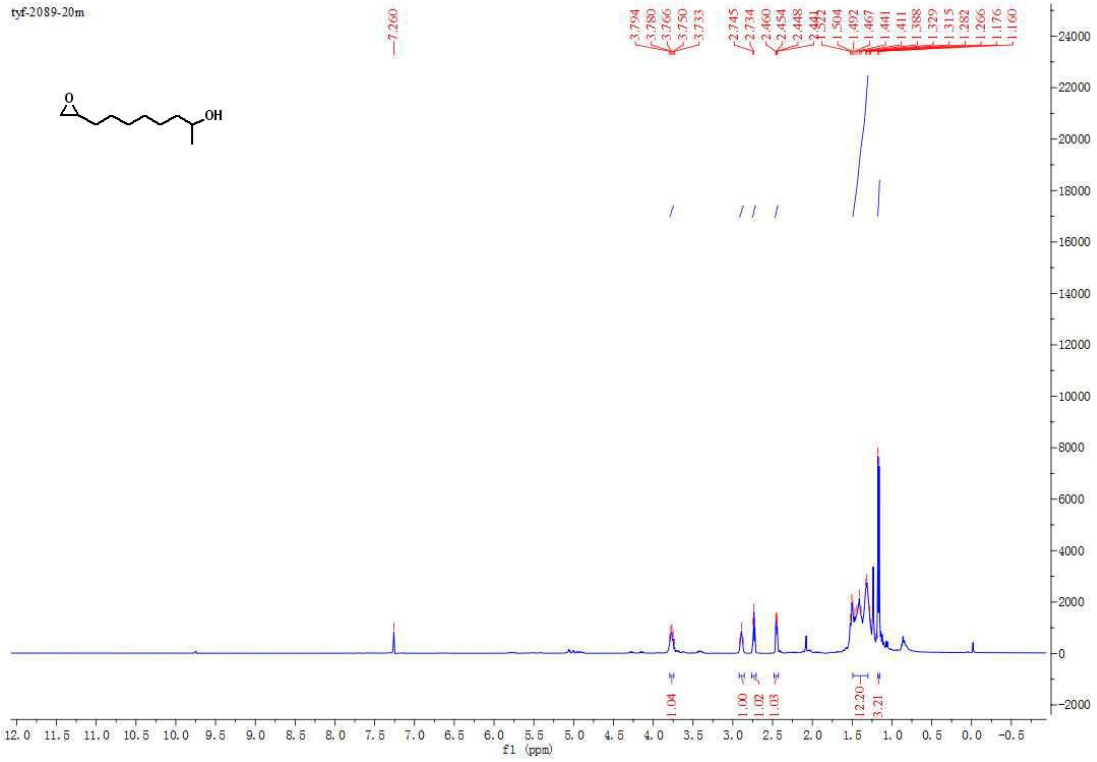
11-^{1}H NMR



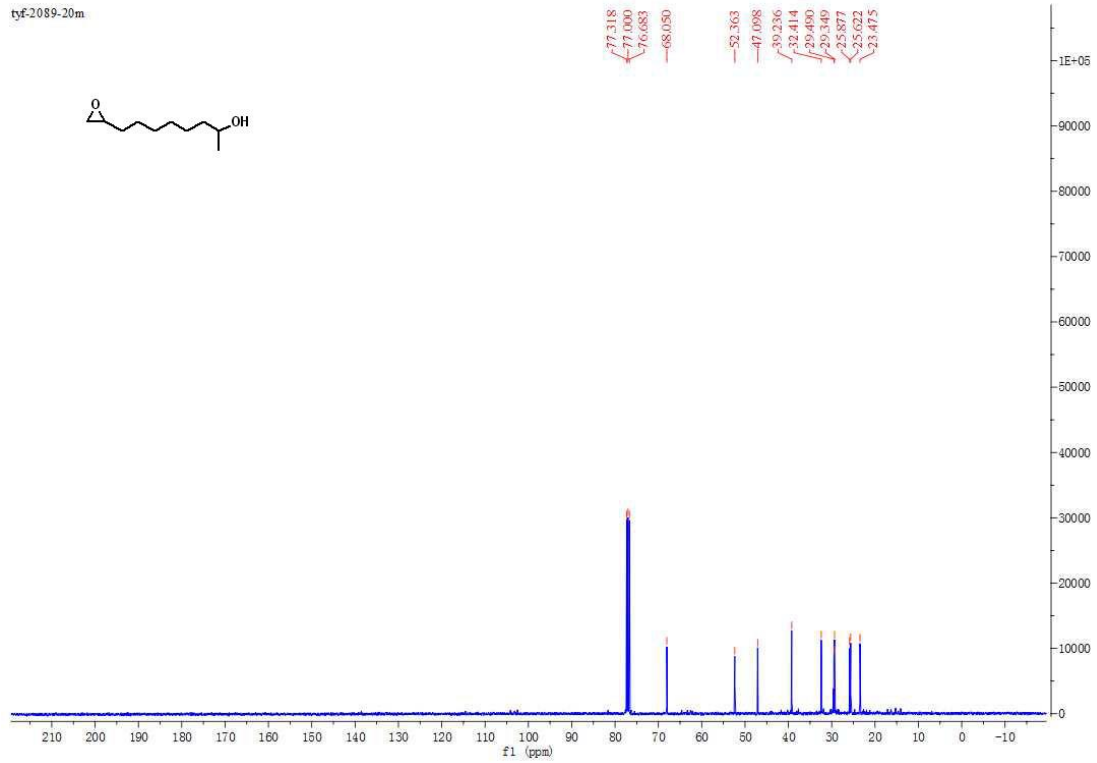
11-^{13}C NMR



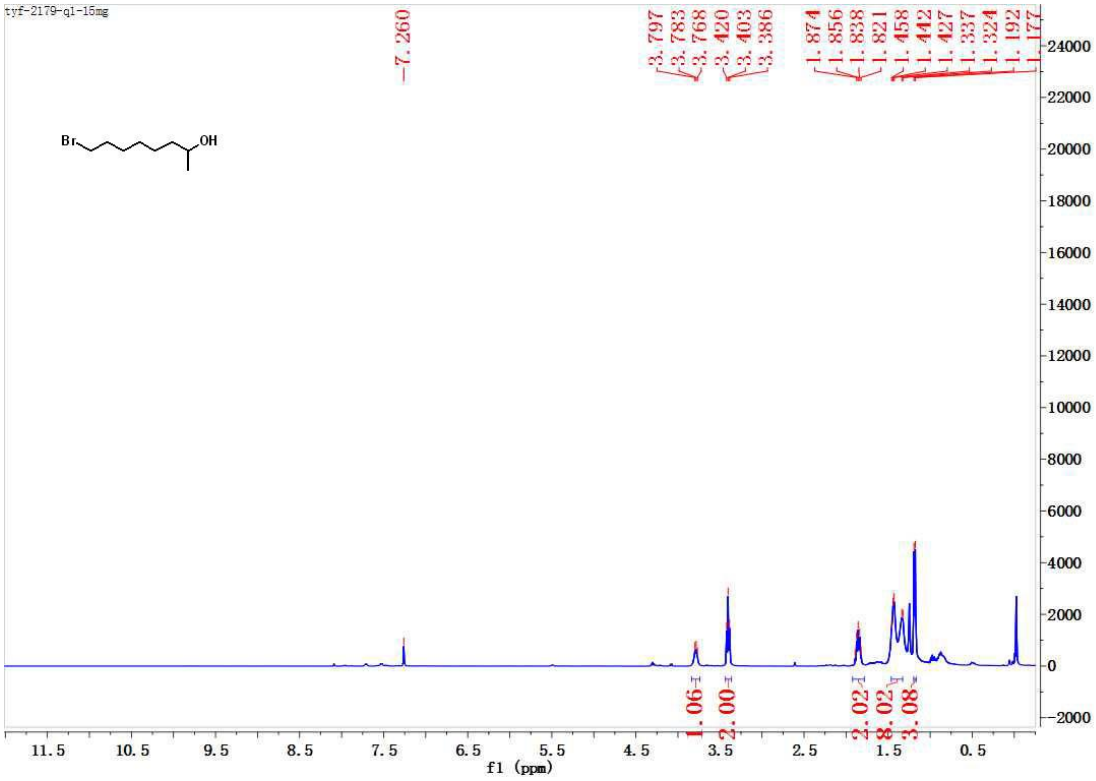
12-^{1}H NMR



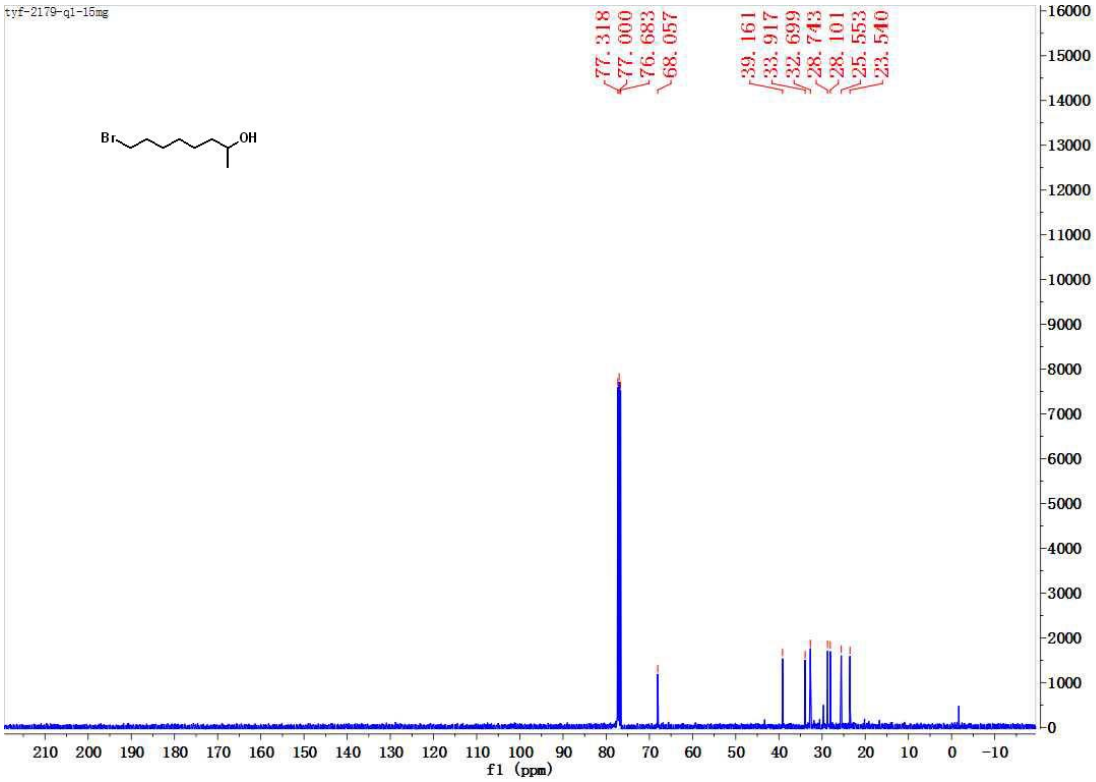
12-^{13}C NMR



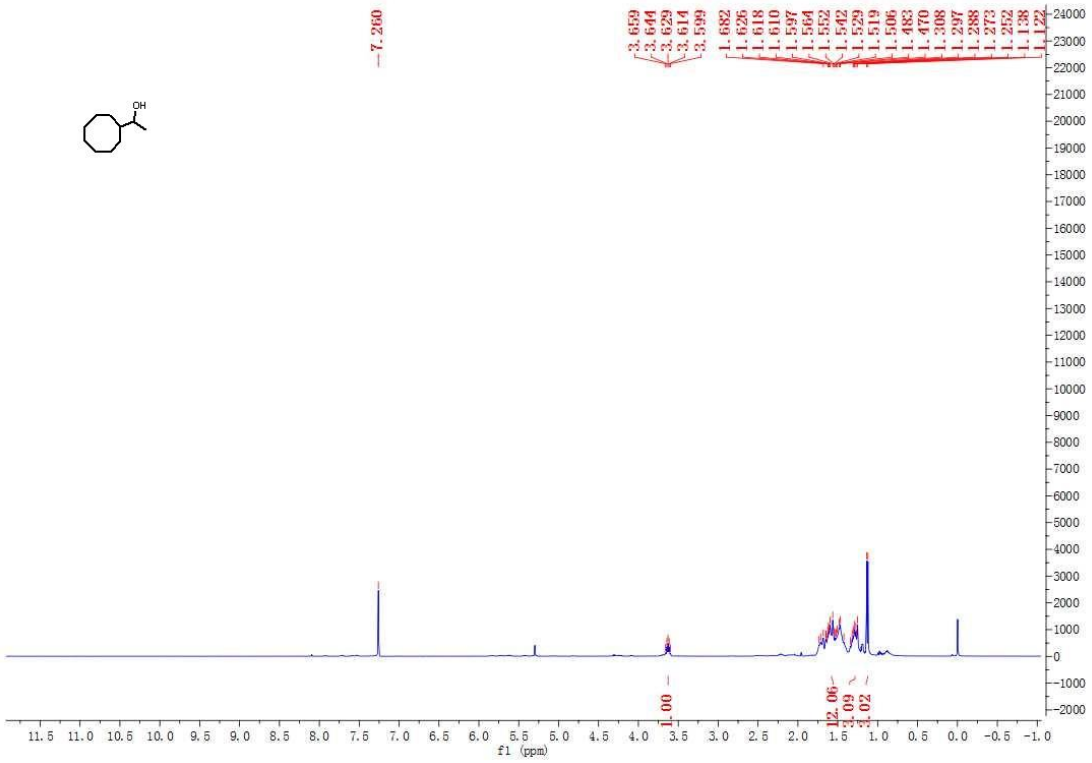
13-^{1}H NMR



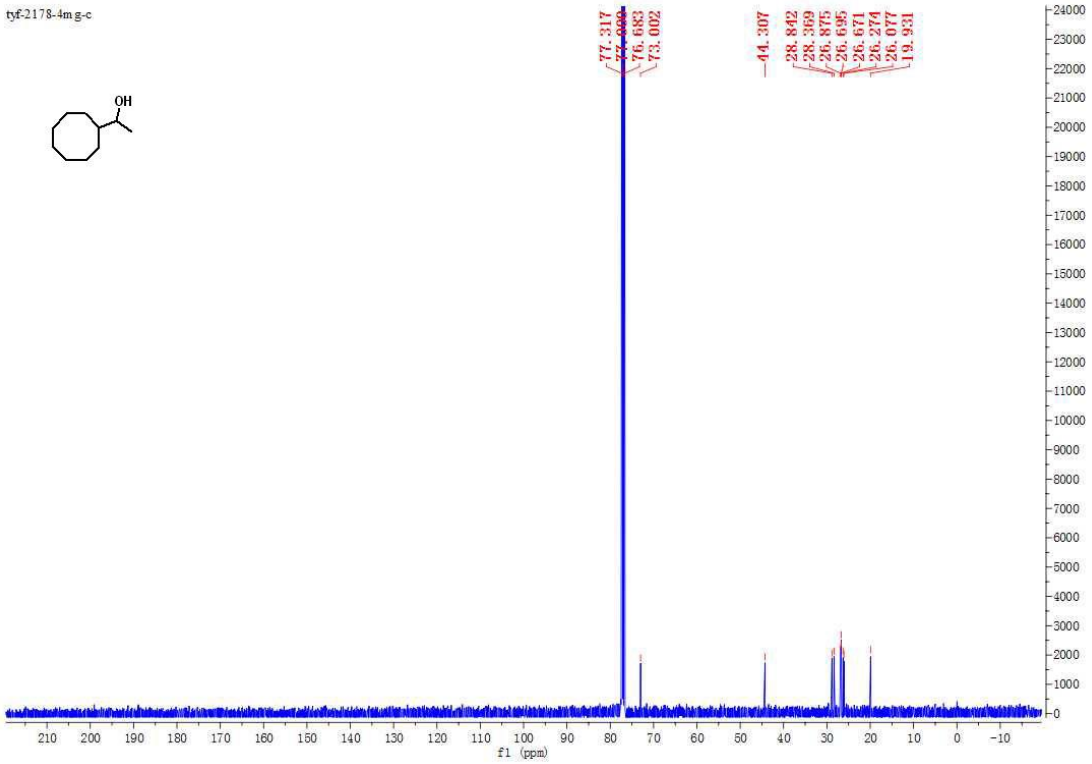
13-^{13}C NMR



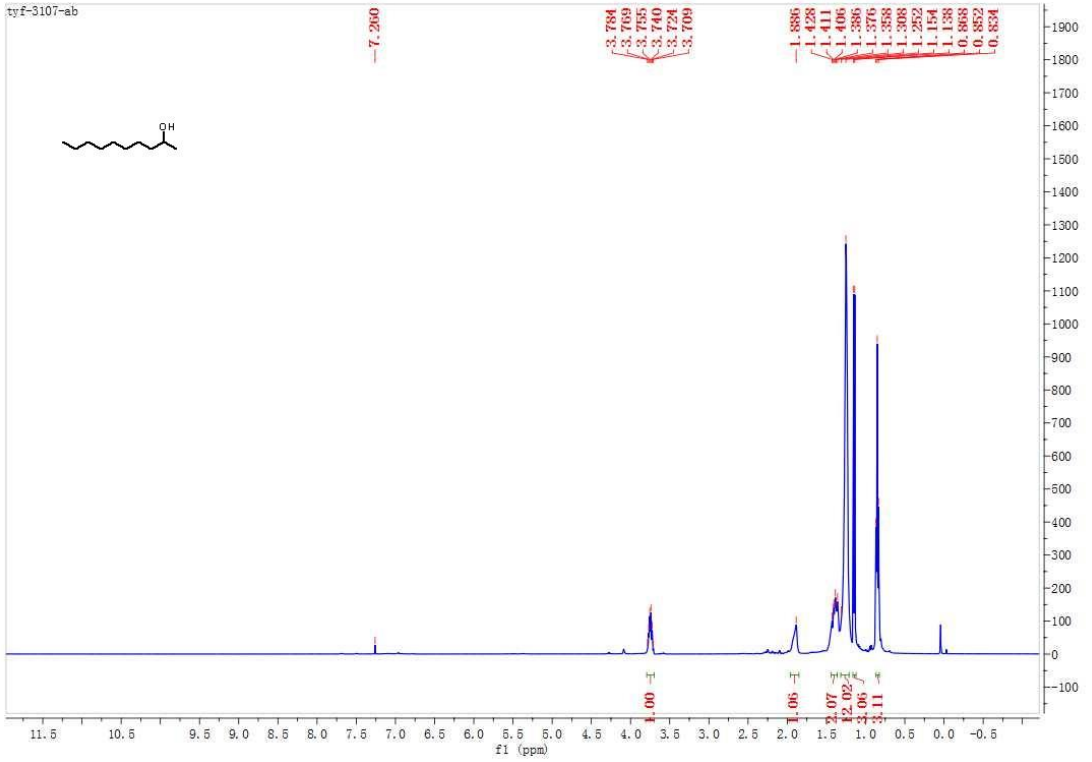
14-^{1}H NMR



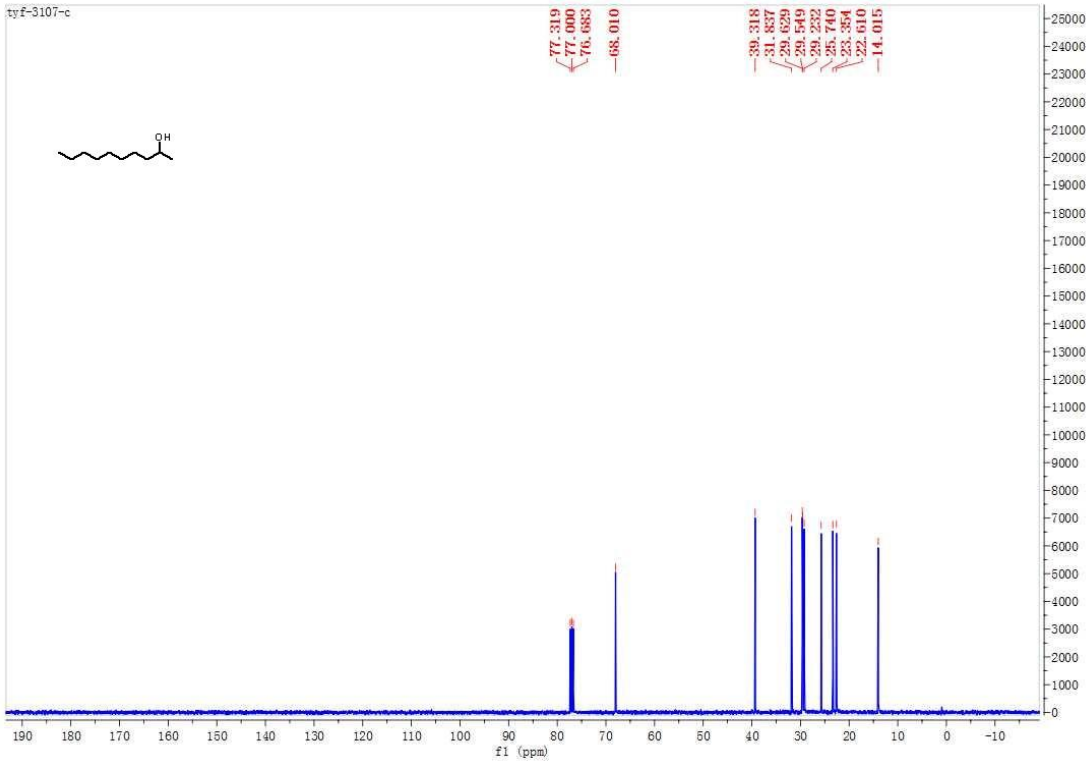
14-^{13}C NMR



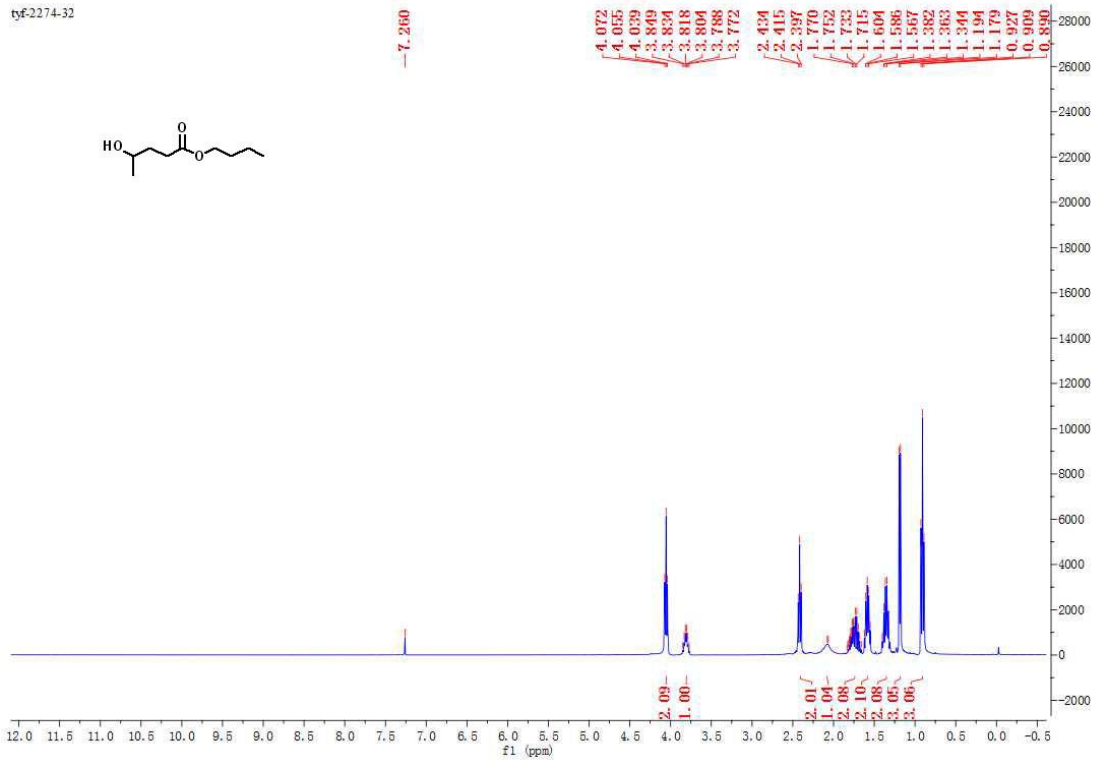
15-^{1}H NMR



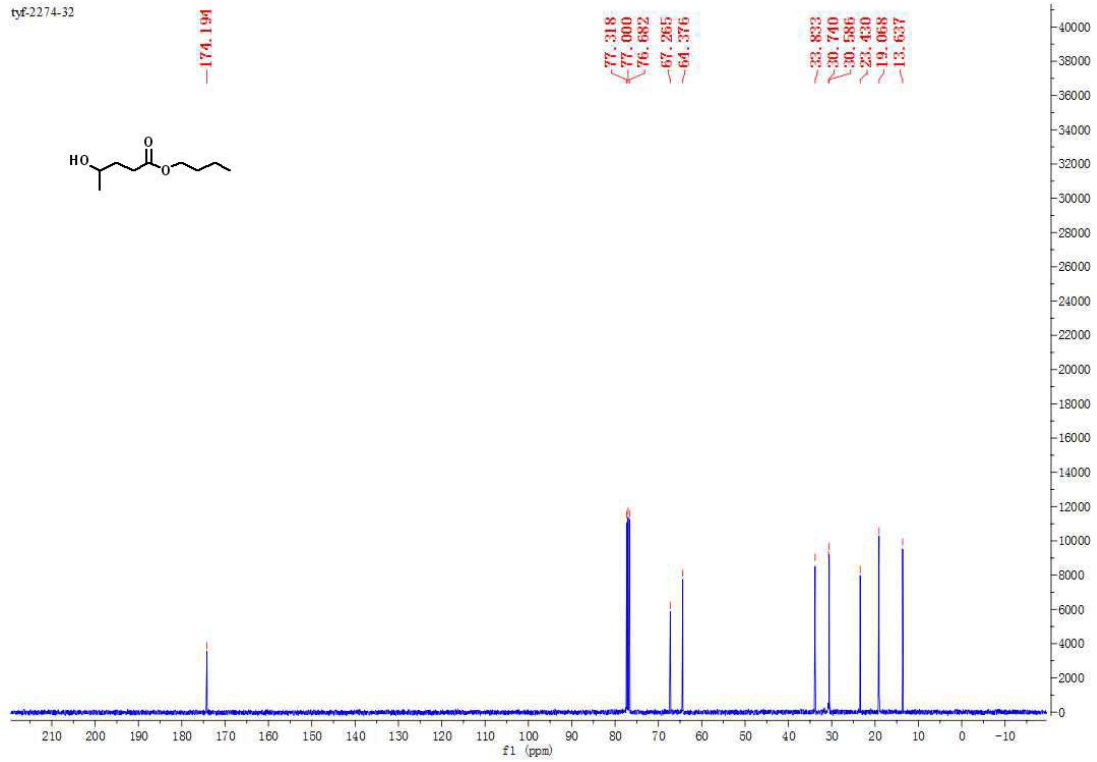
15-^{13}C NMR



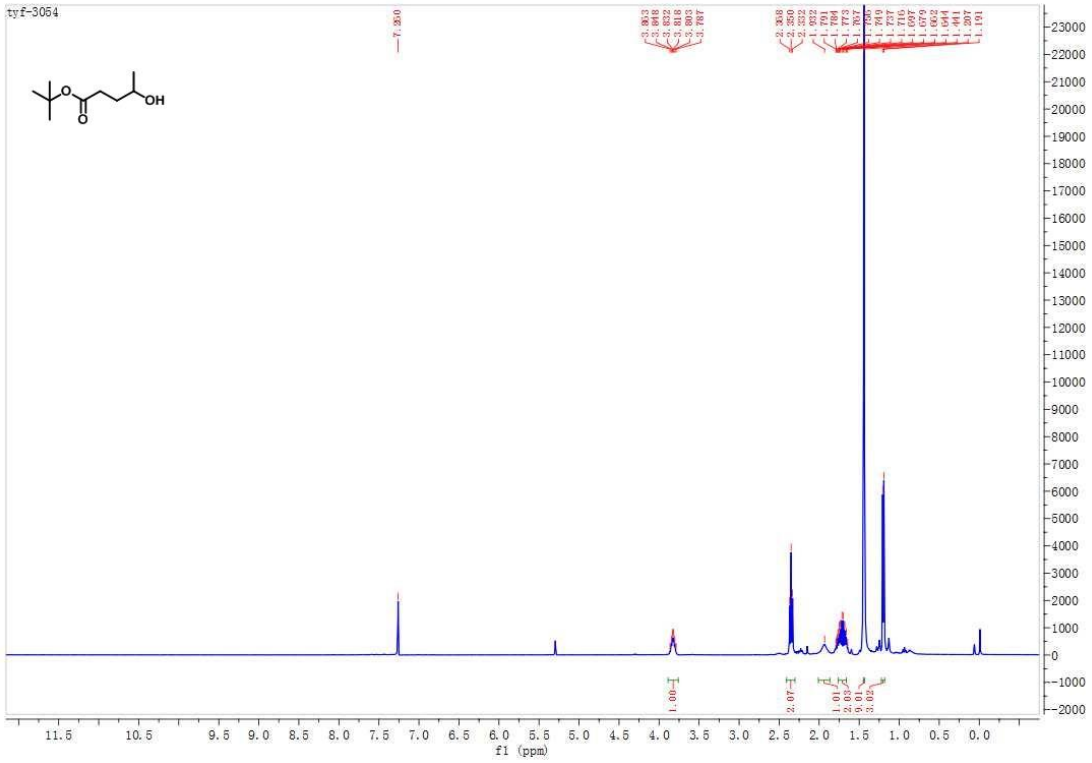
16-^{1}H NMR



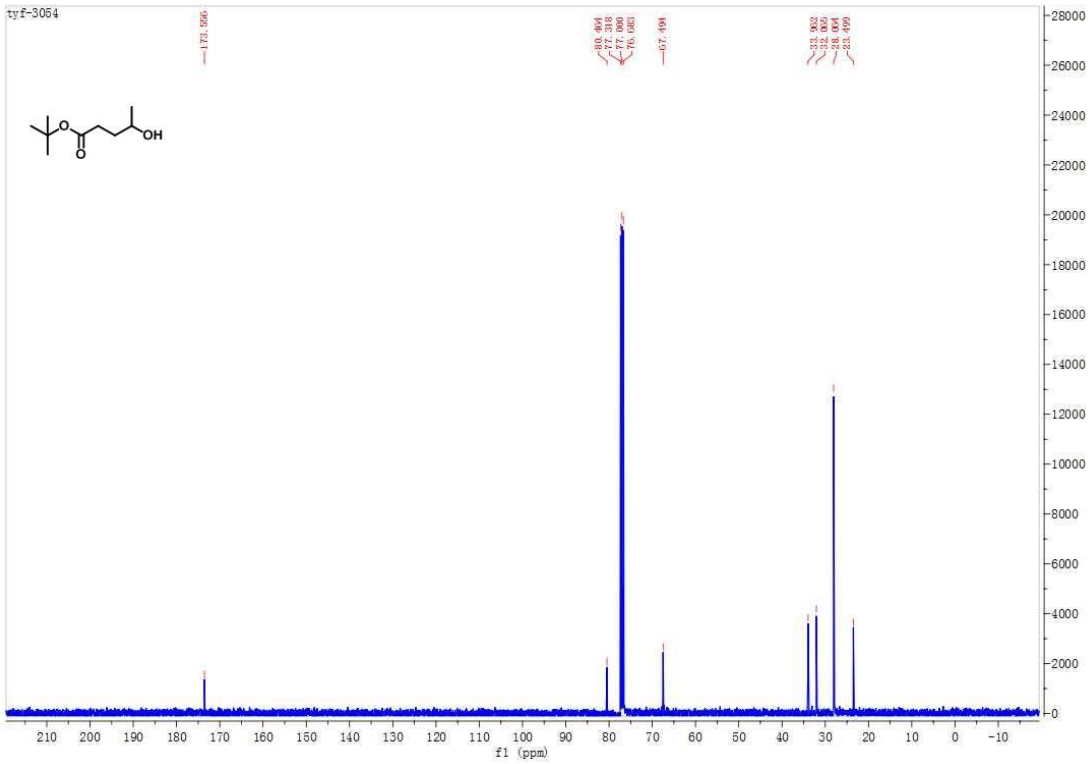
16-^{13}C NMR



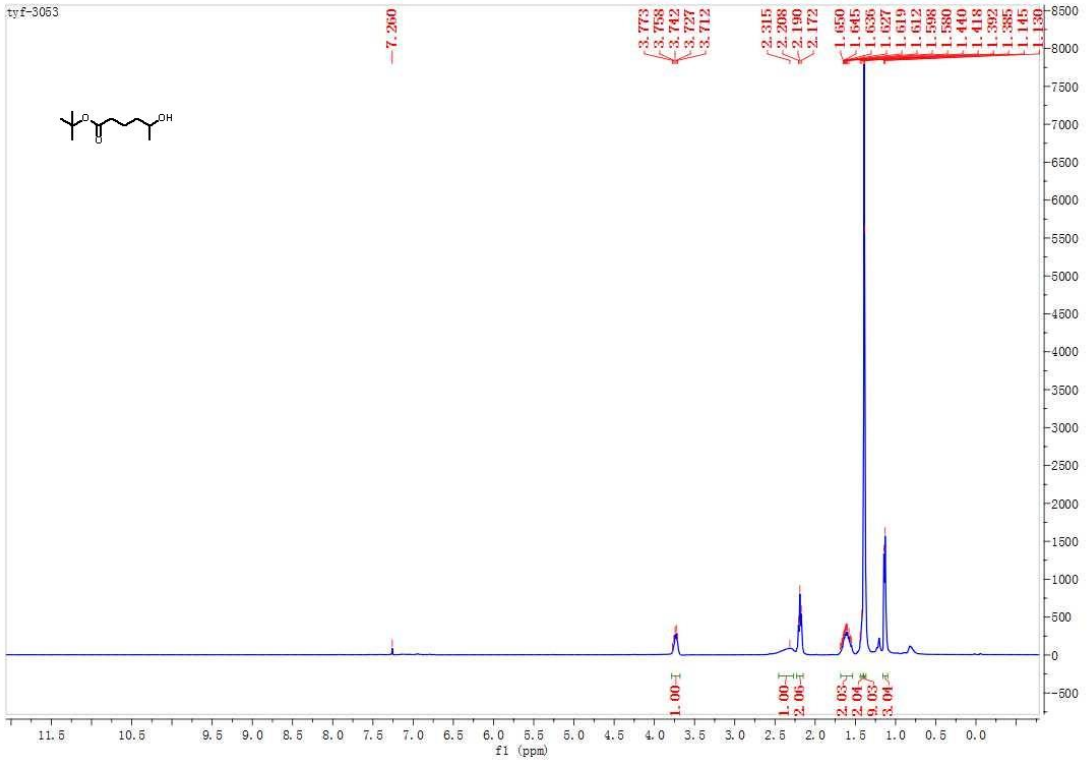
17-^{1}H NMR



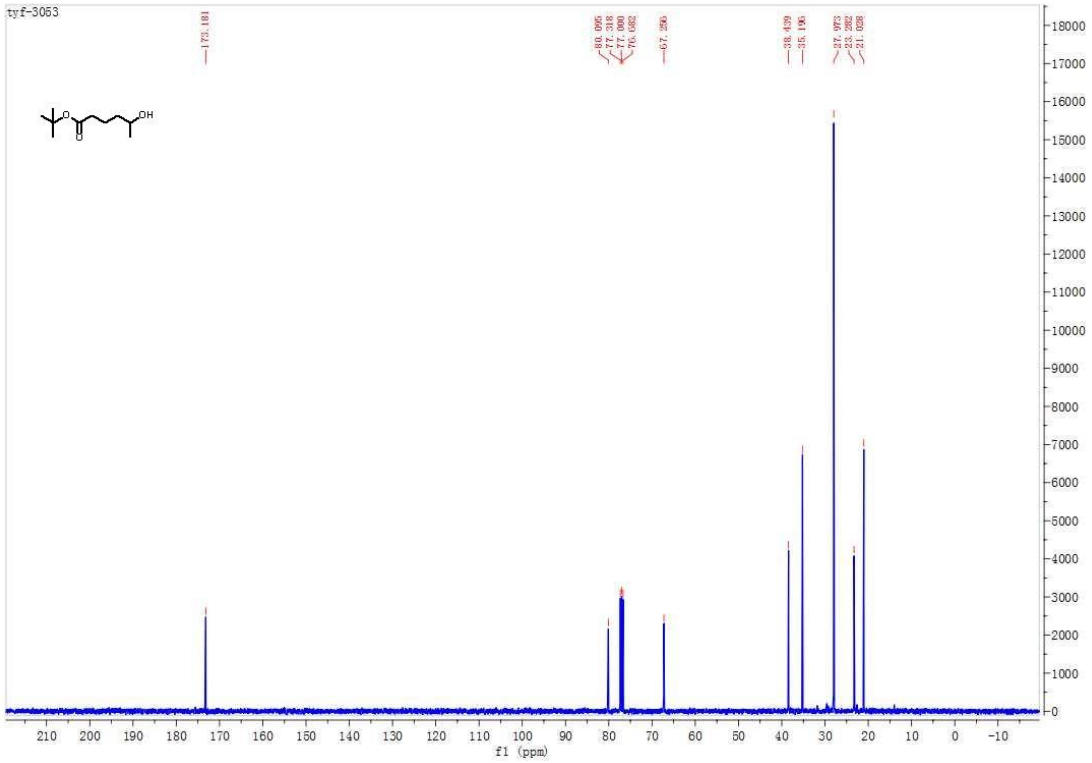
17-^{13}C NMR



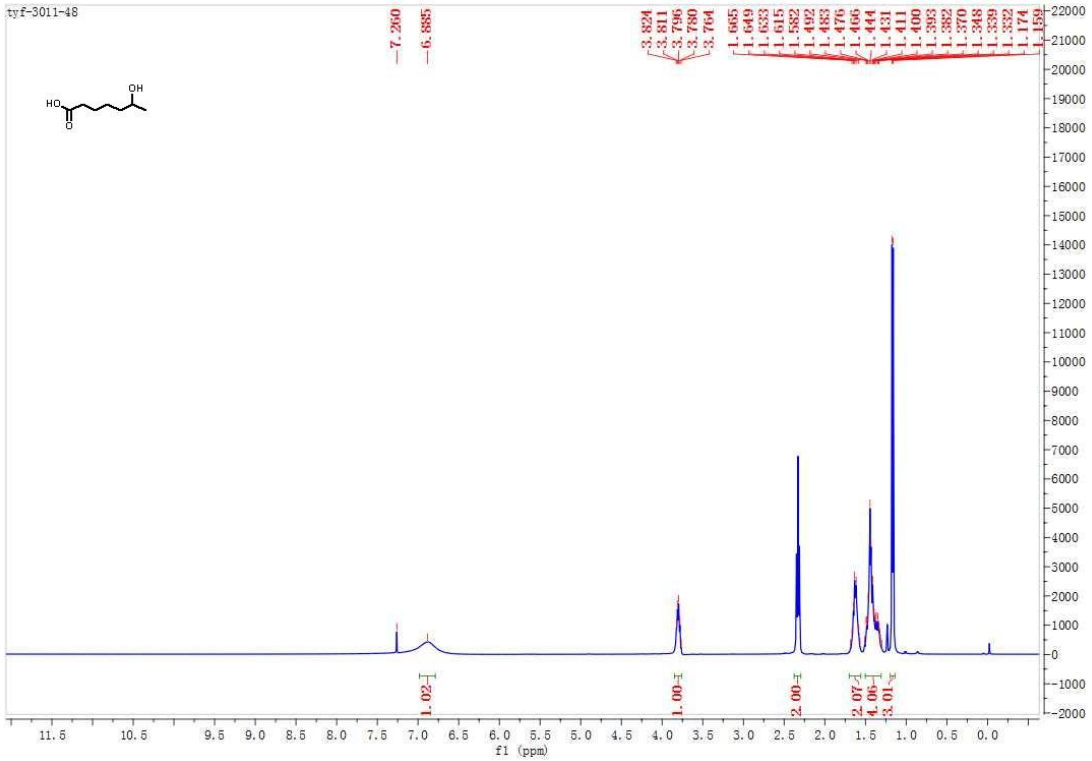
18-^{1}H NMR



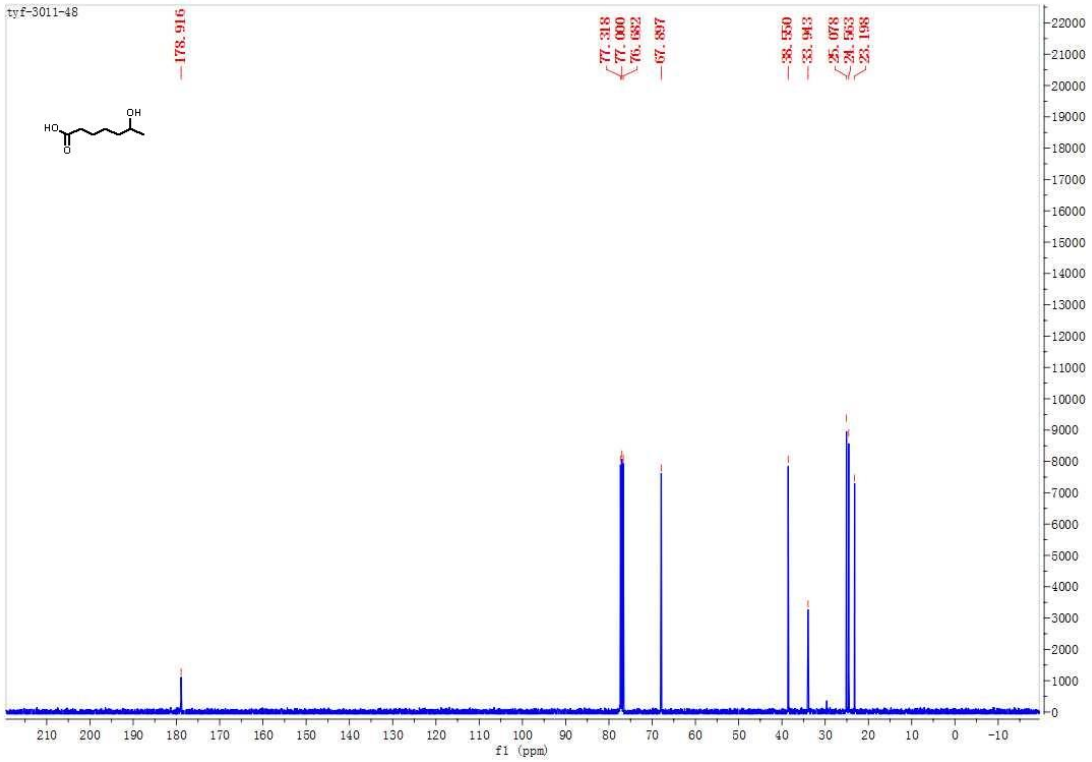
18-^{13}C NMR



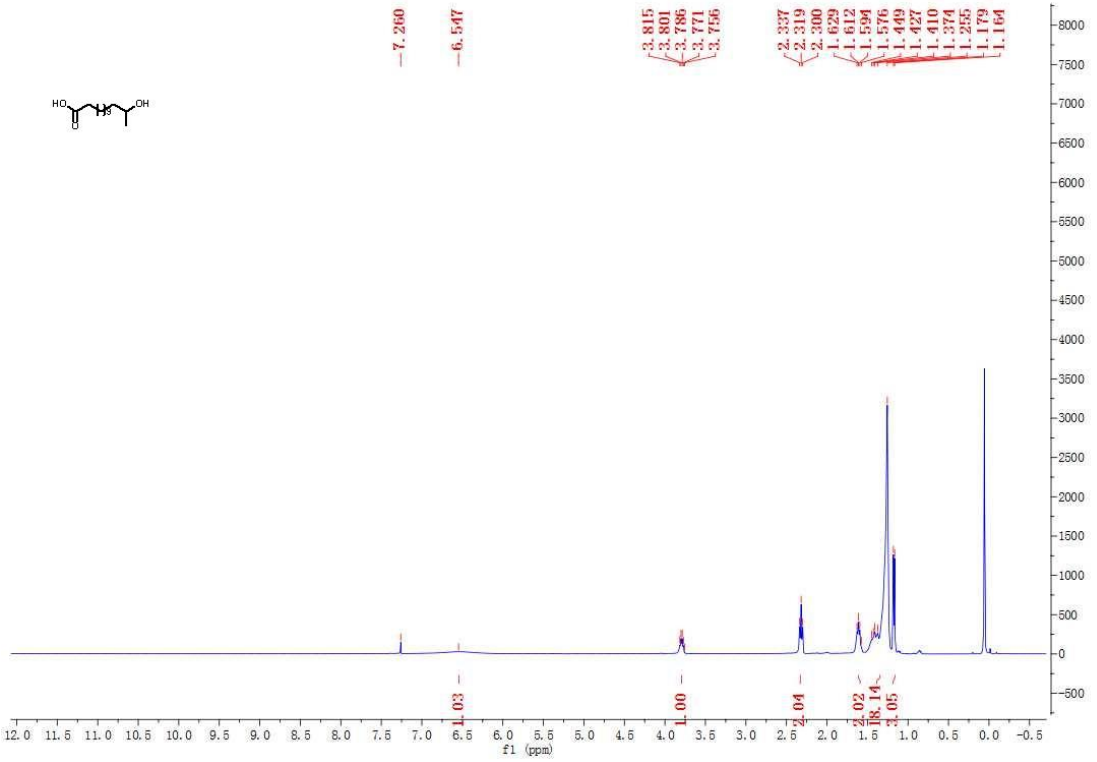
19-^{1}H NMR



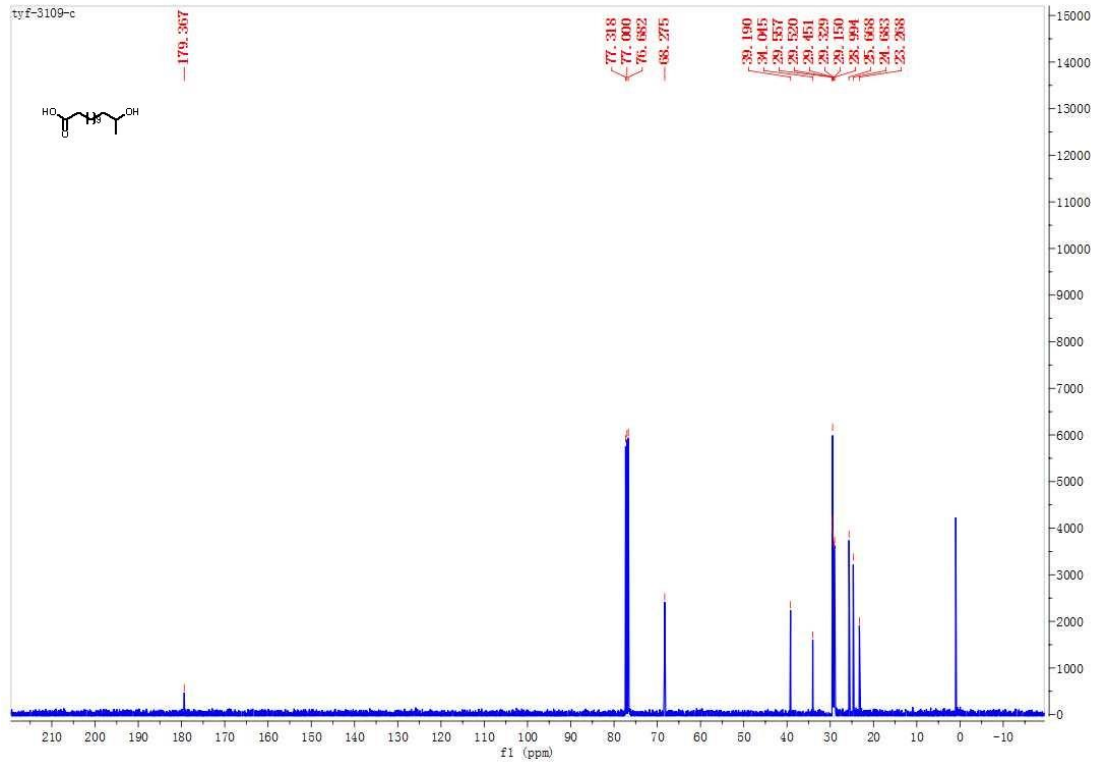
19-^{13}C NMR



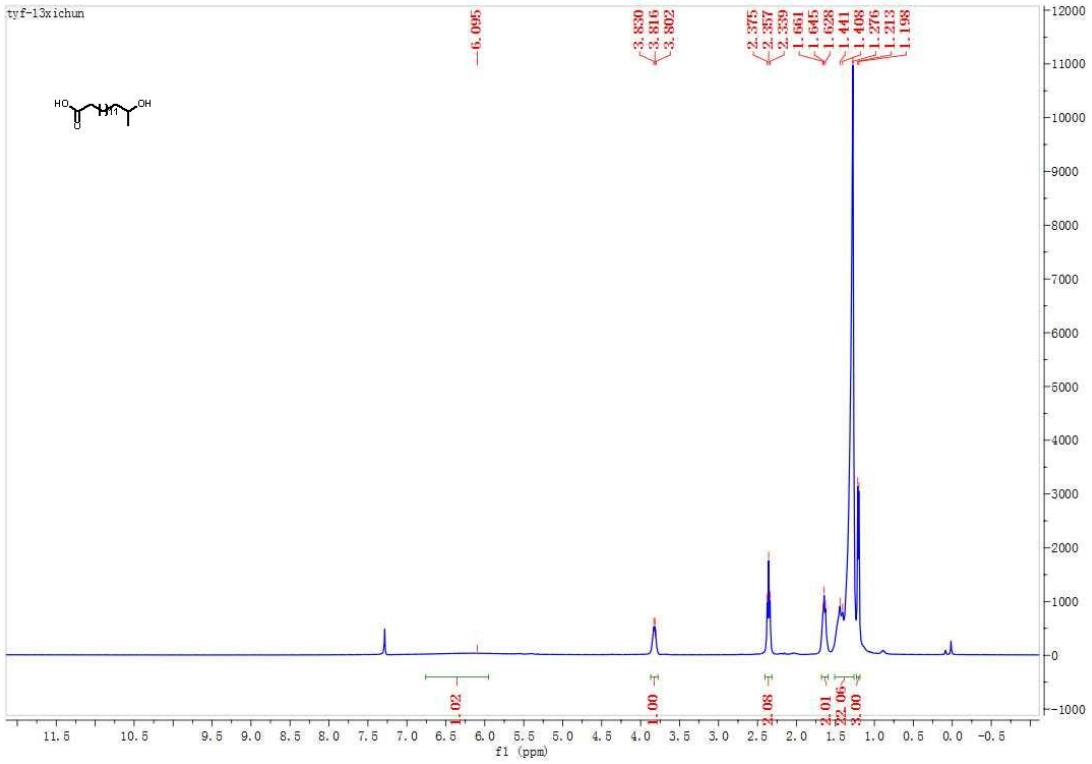
20-^{1}H NMR



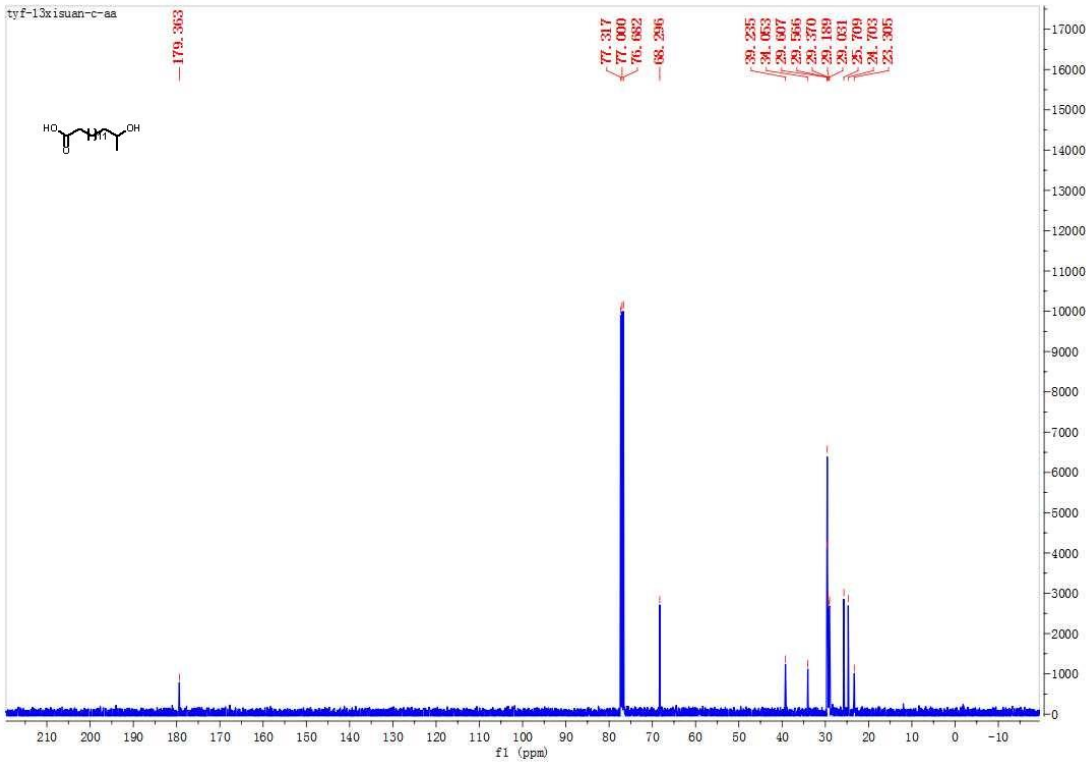
20-^{13}C NMR



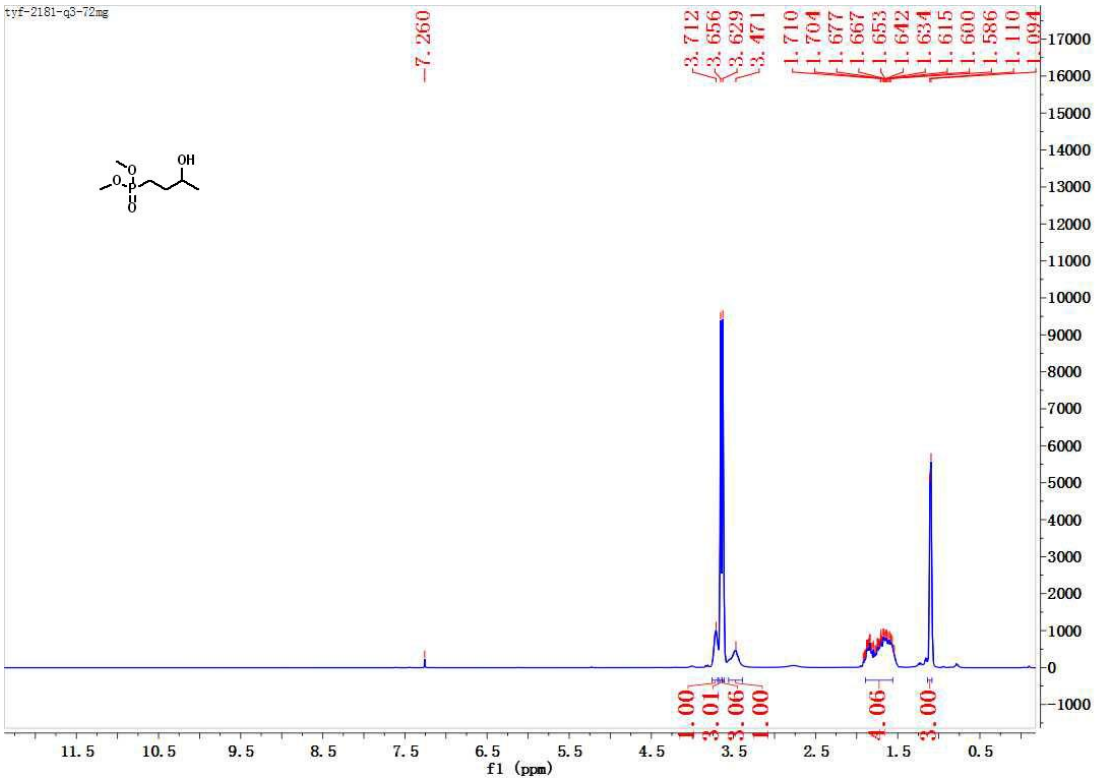
21-^{1}H NMR



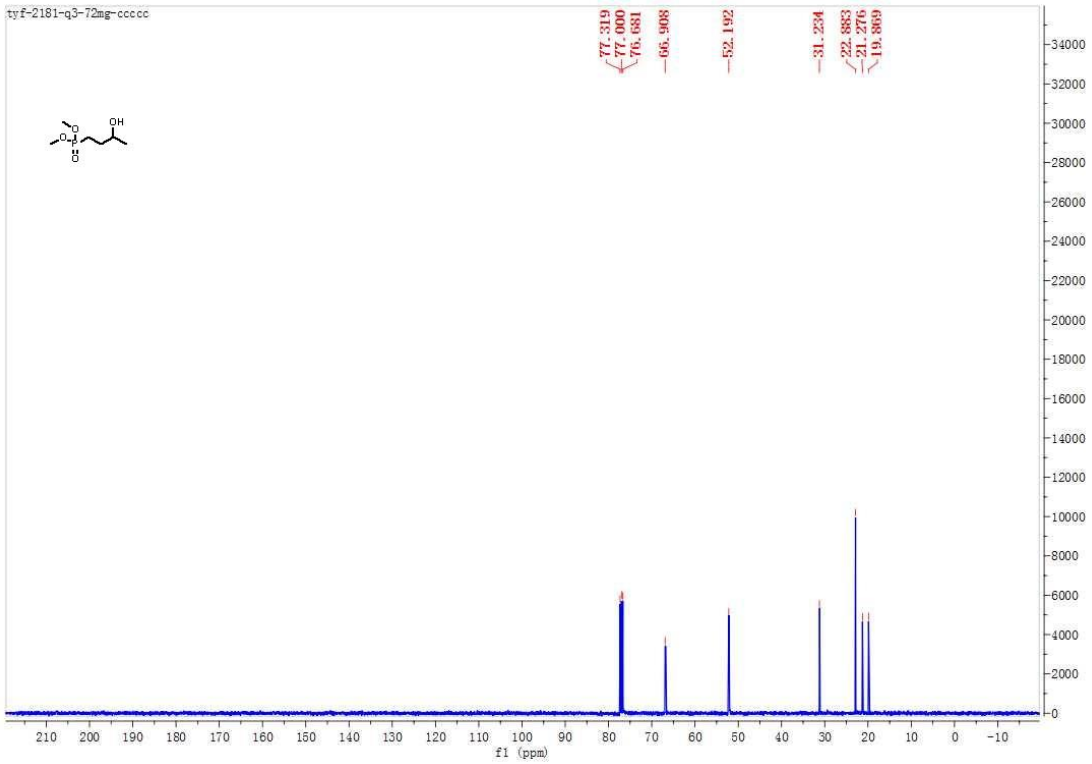
21-^{13}C NMR



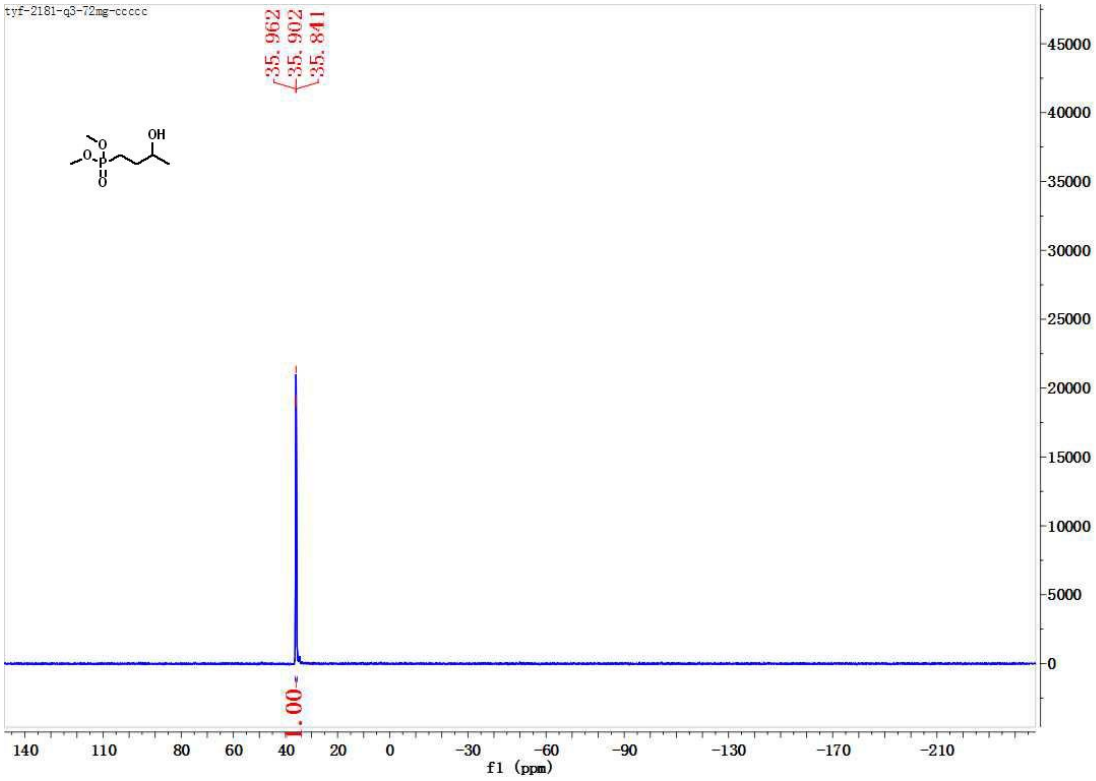
22-^{1}H NMR



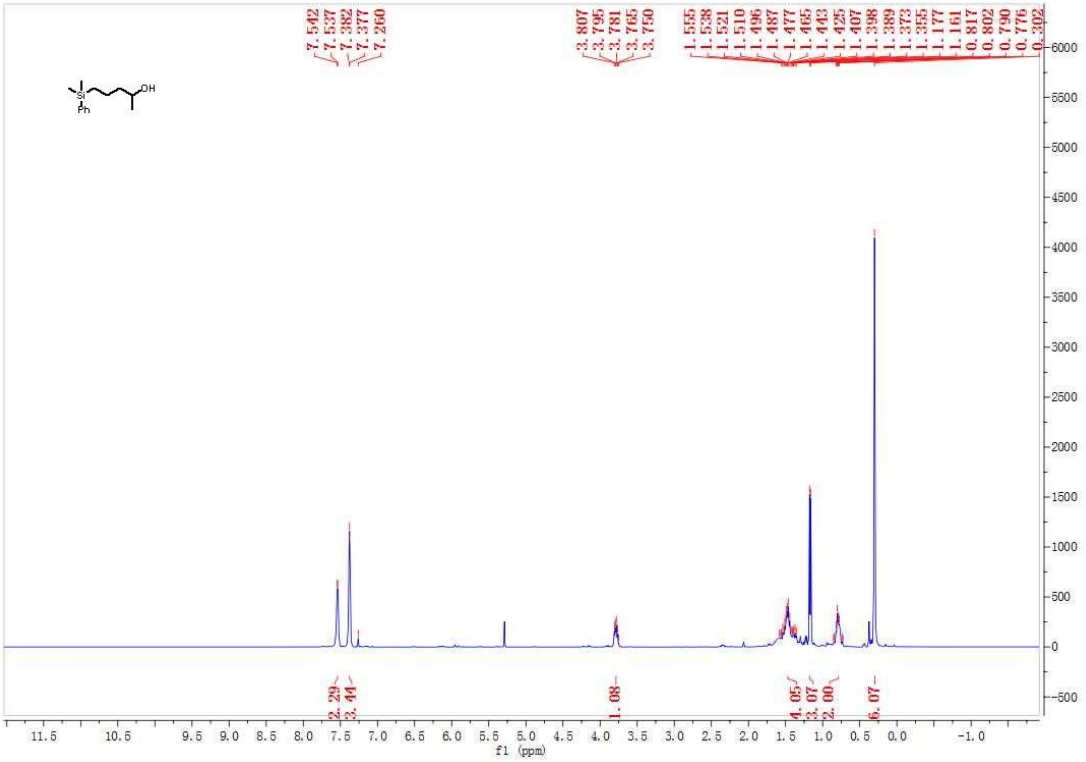
22-^{13}C NMR



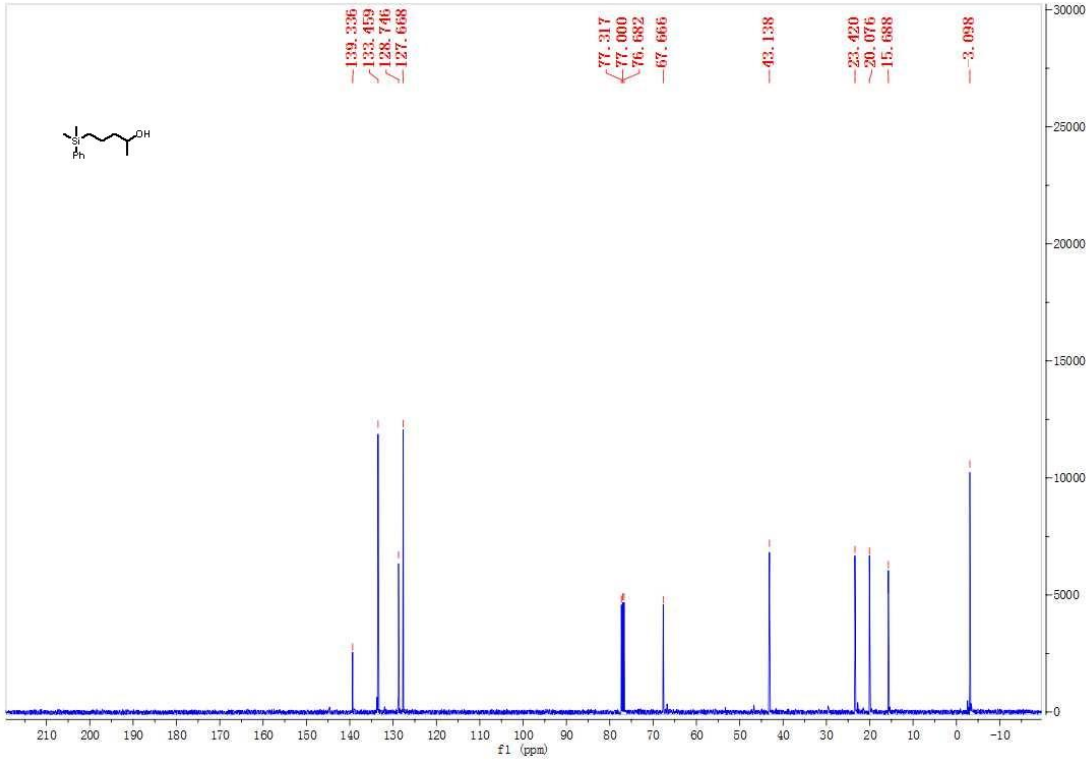
22-^{31}PNMR NMR



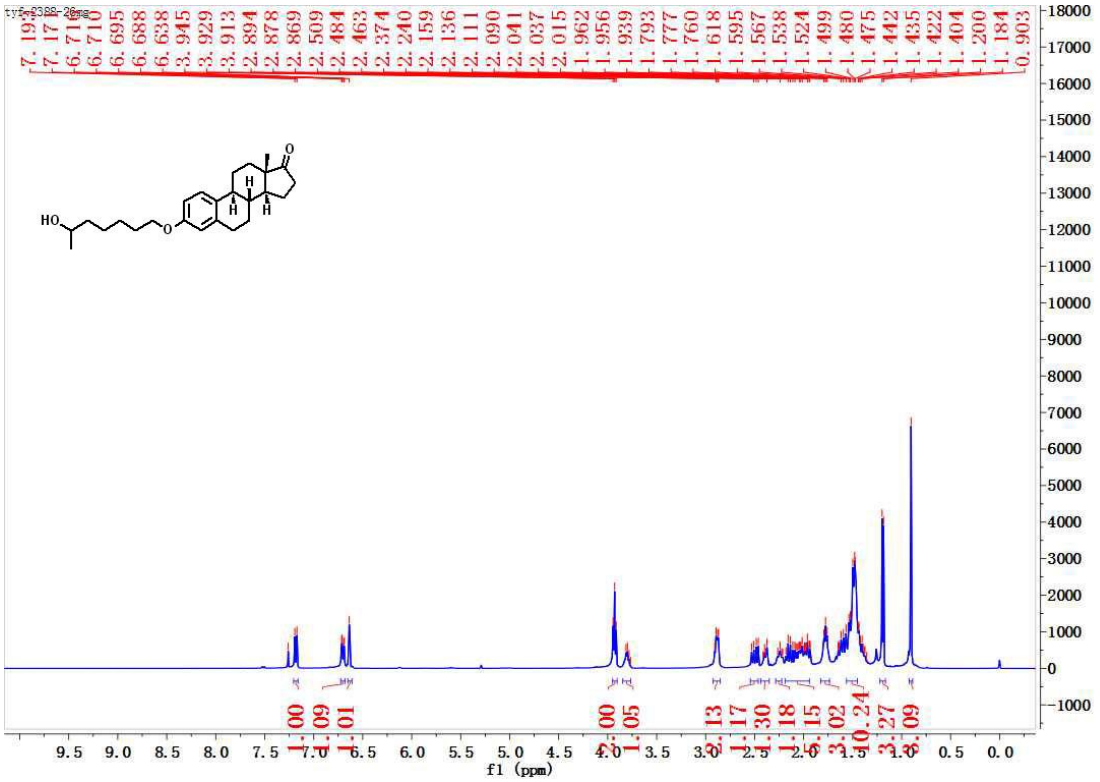
23-^{1}H NMR



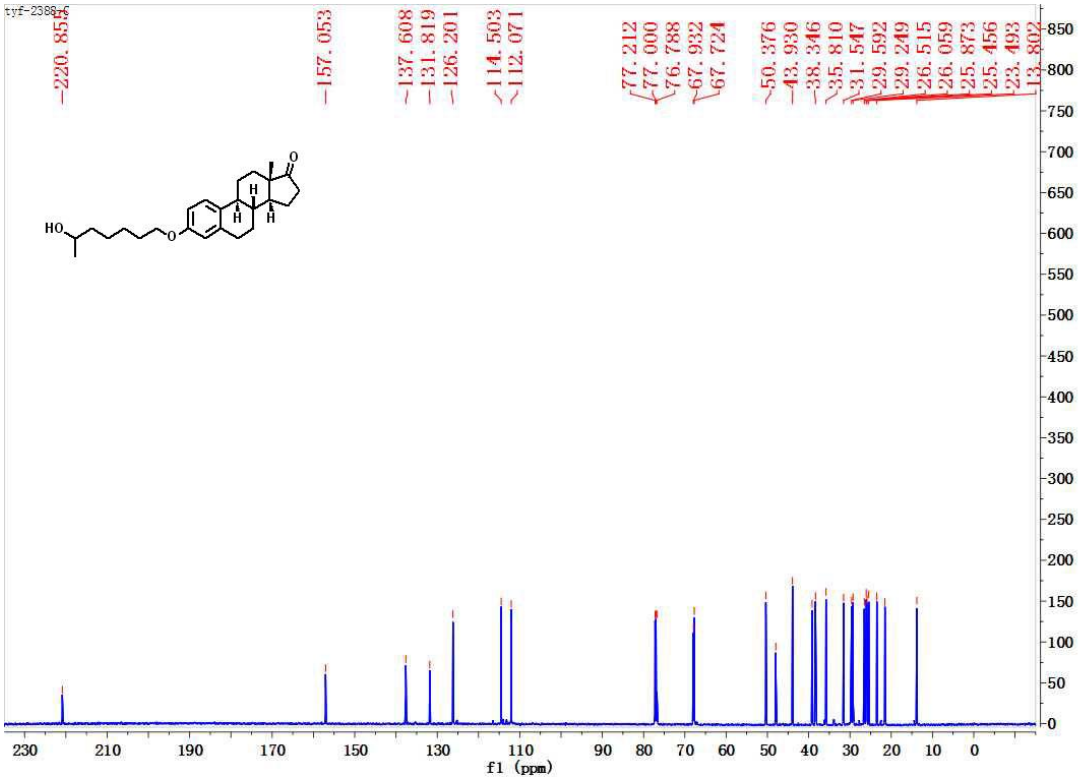
23-^{13}C NMR



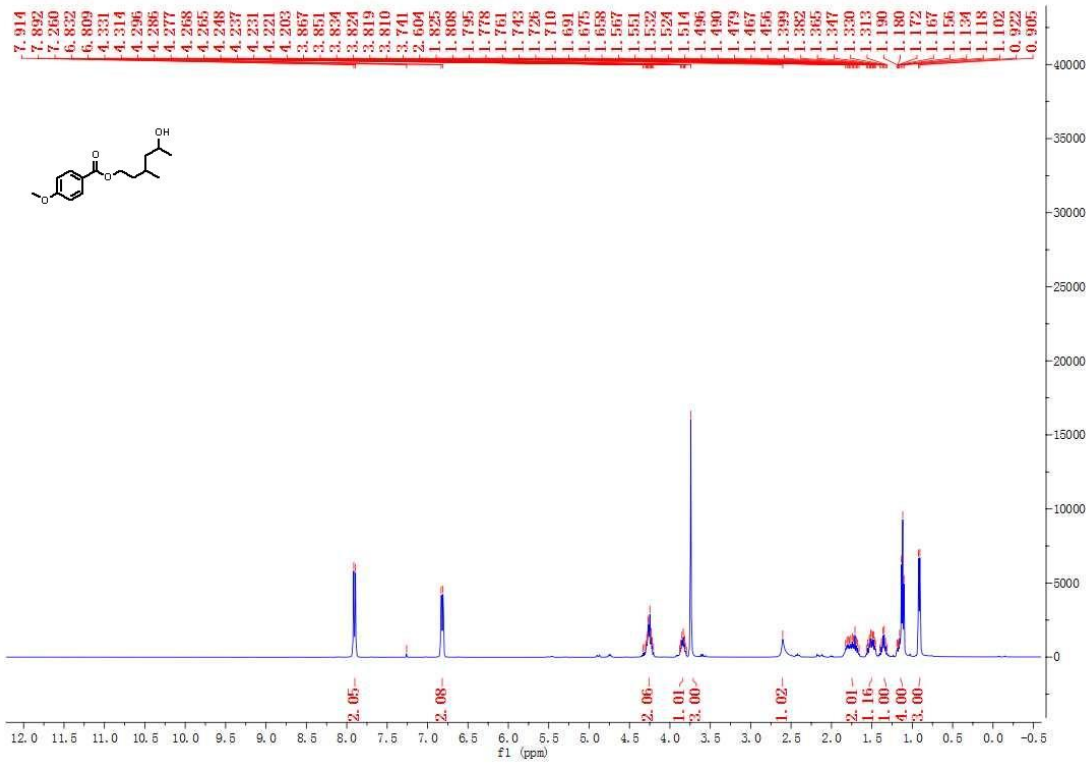
24-^{1}H NMR



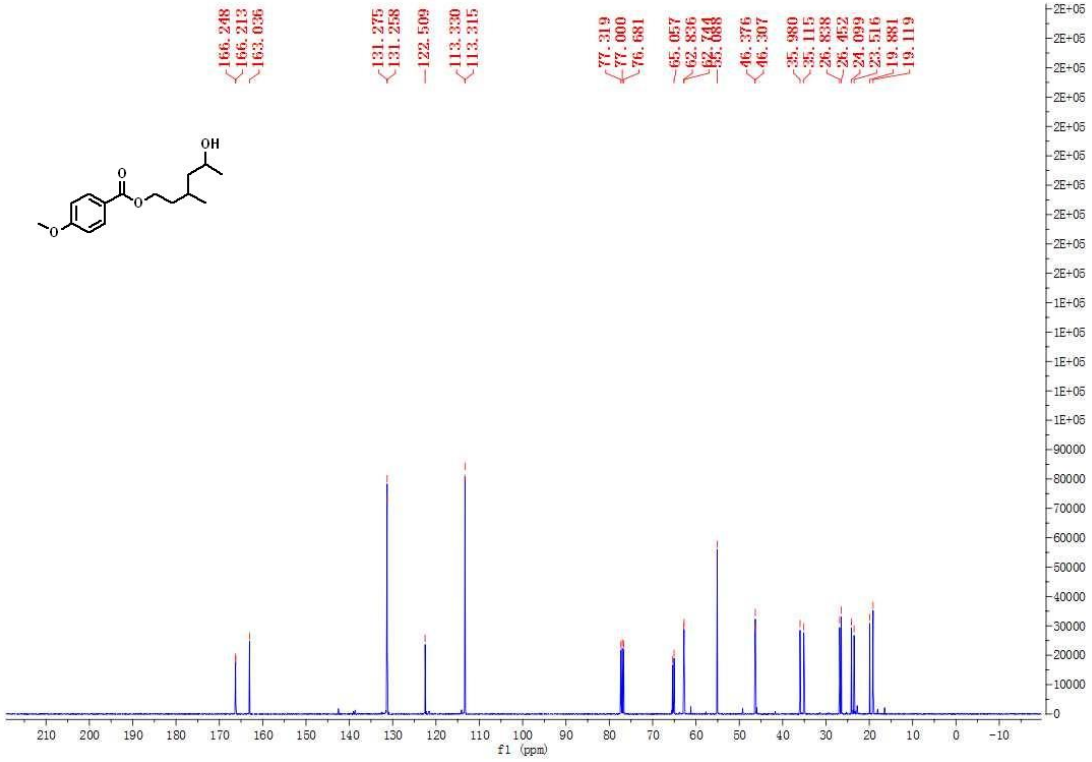
24-^{13}C NMR



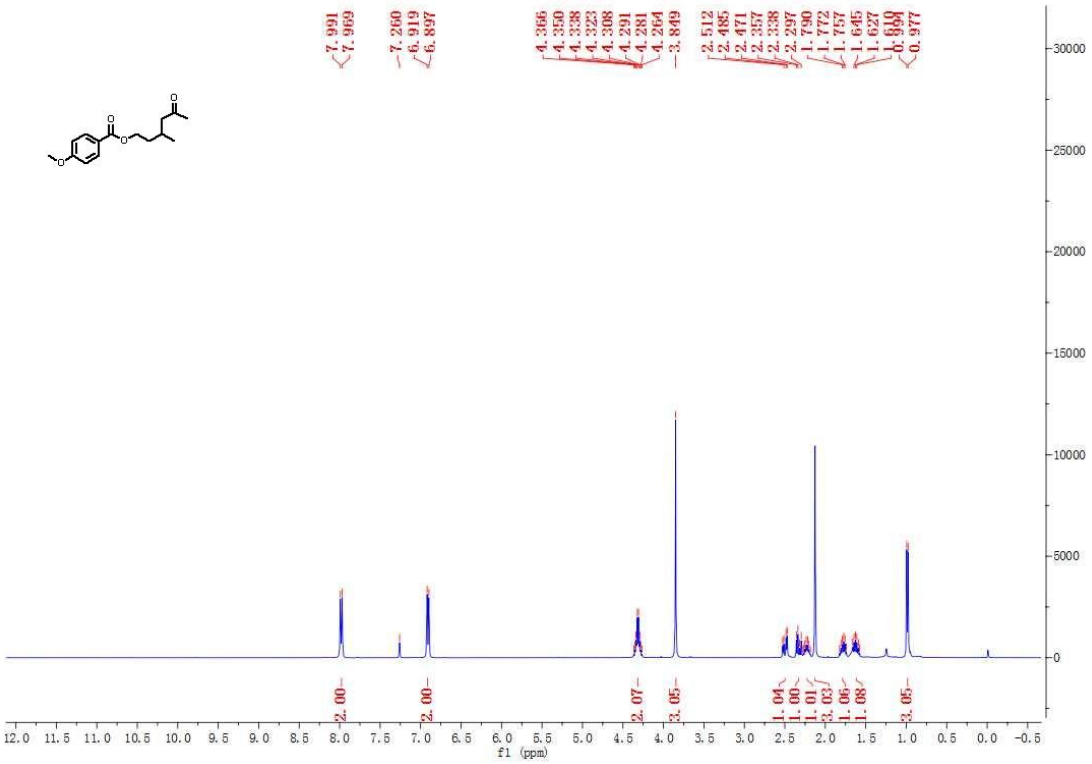
25-^{1}H NMR



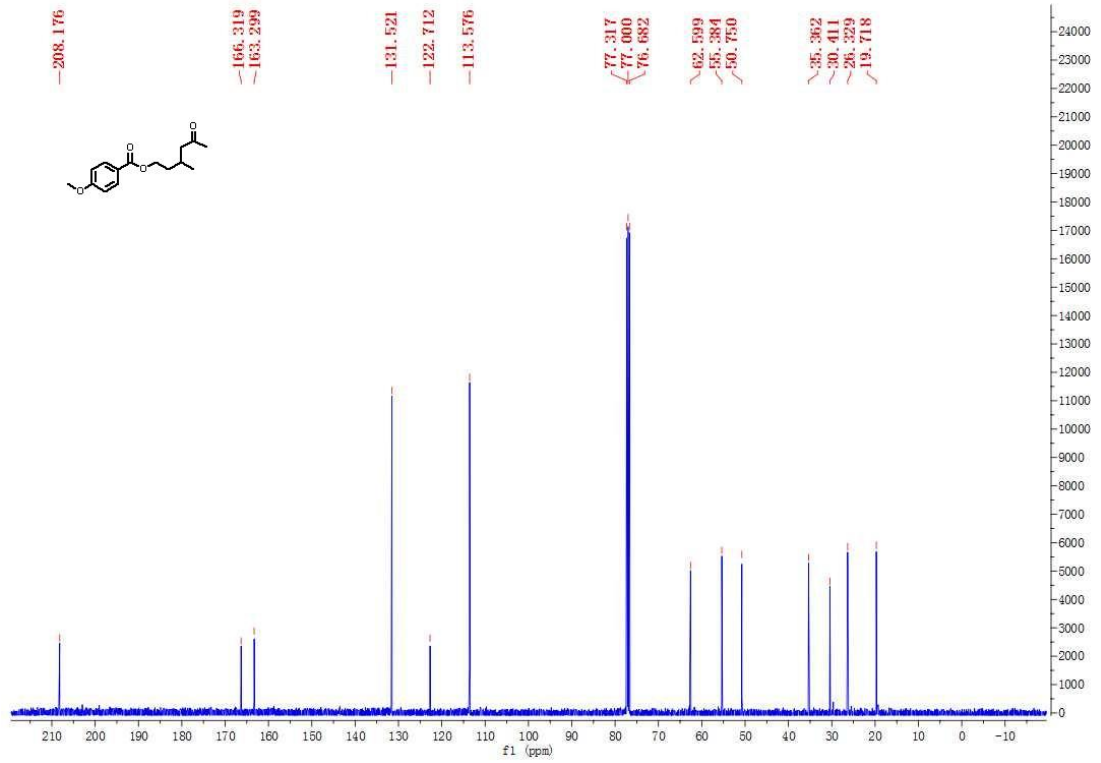
25-^{13}C NMR



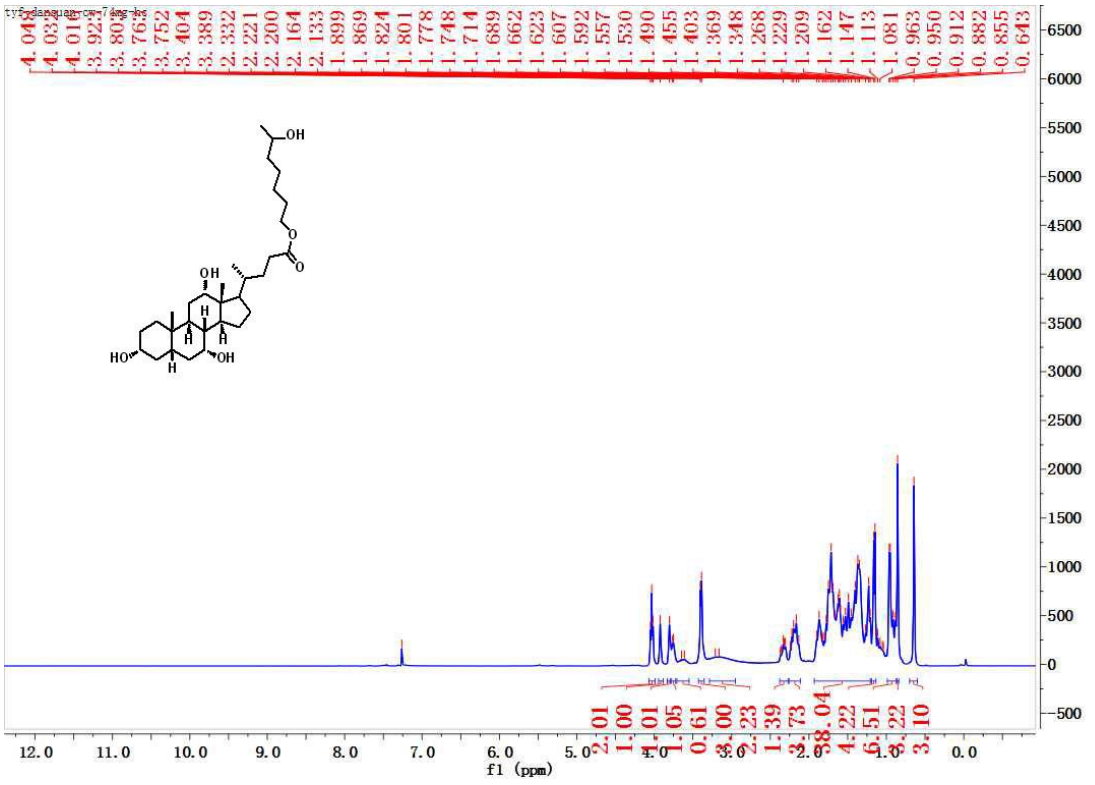
25'-^{1}H NMR



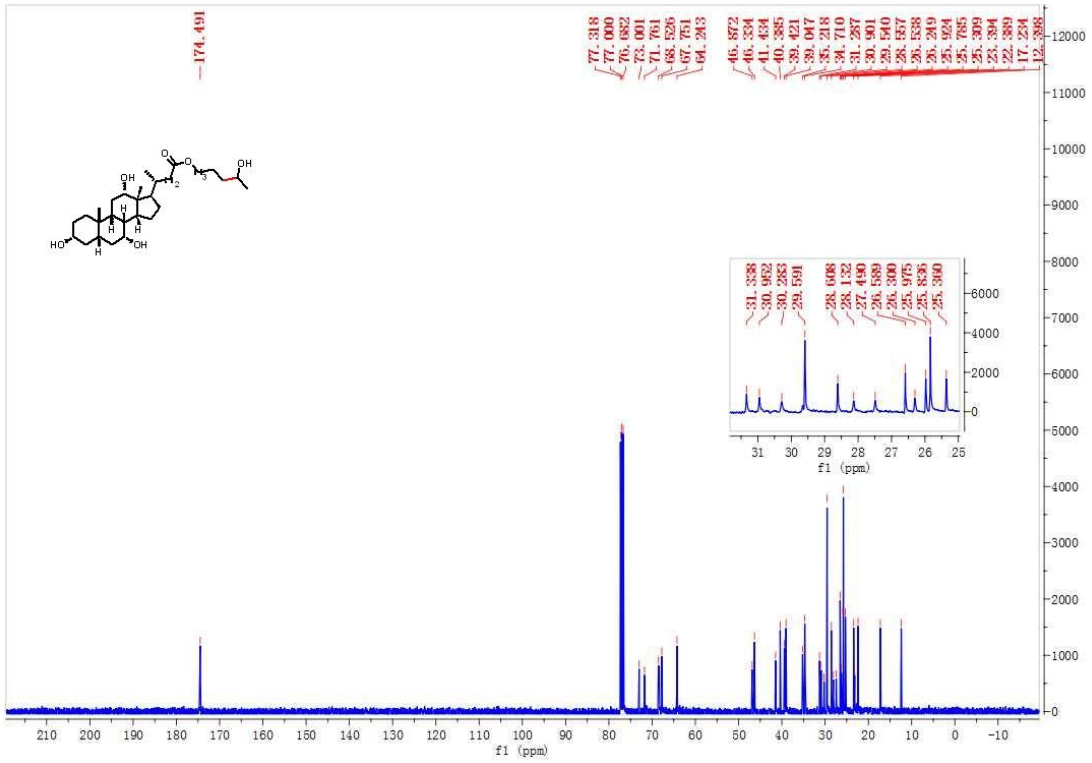
25'-^{13}C NMR



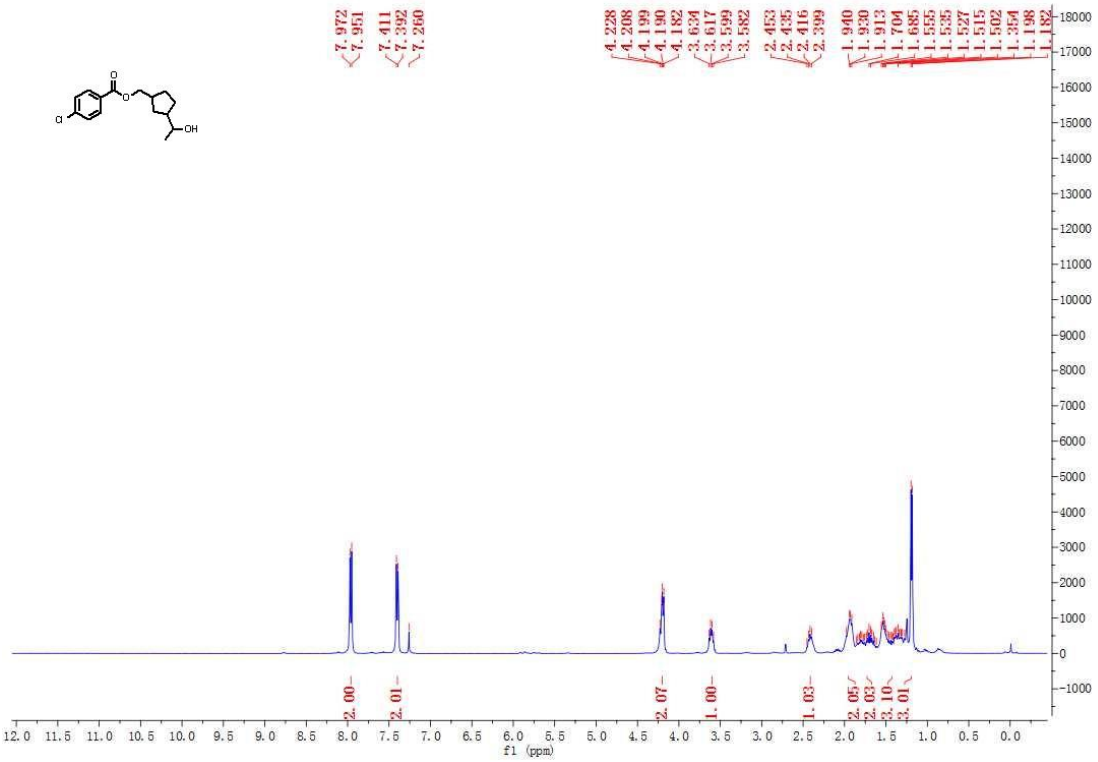
26-^{1}H NMR



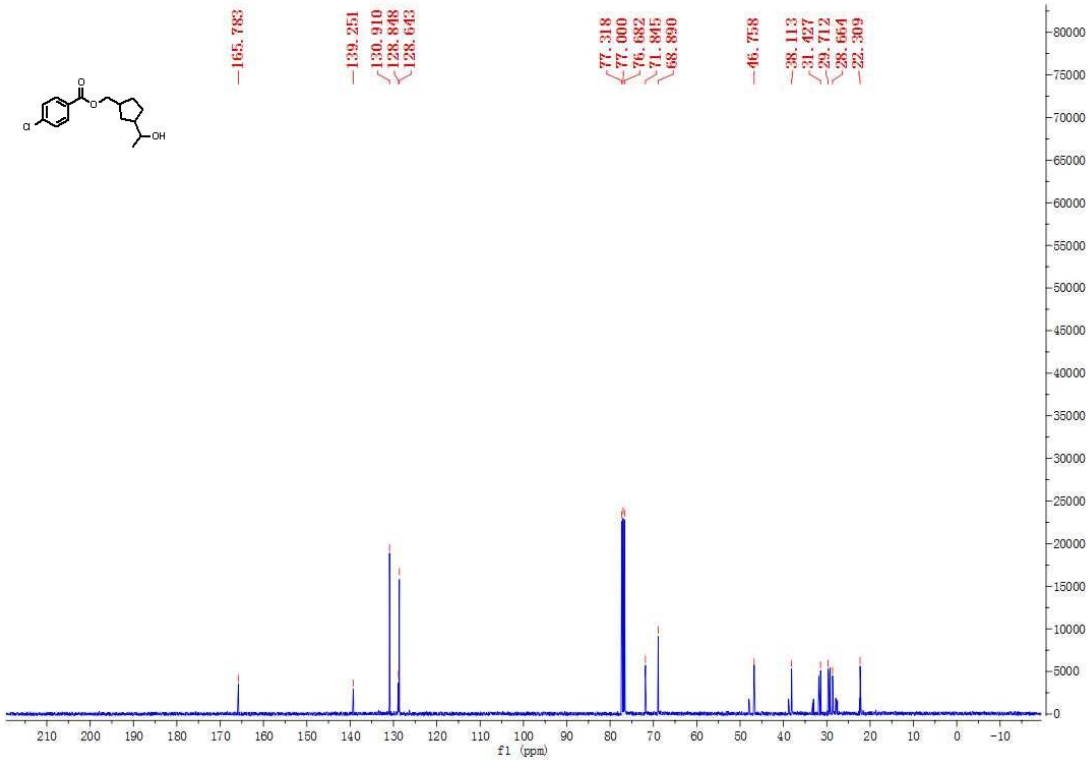
26-^{13}C NMR



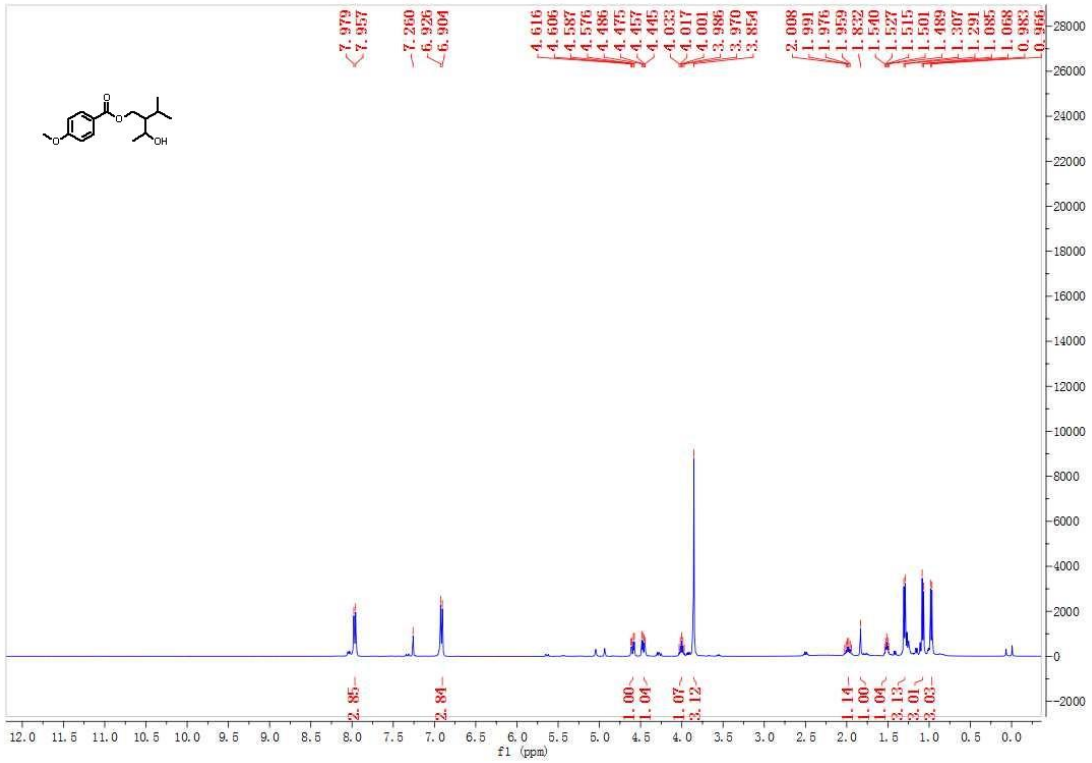
27-^{1}H NMR



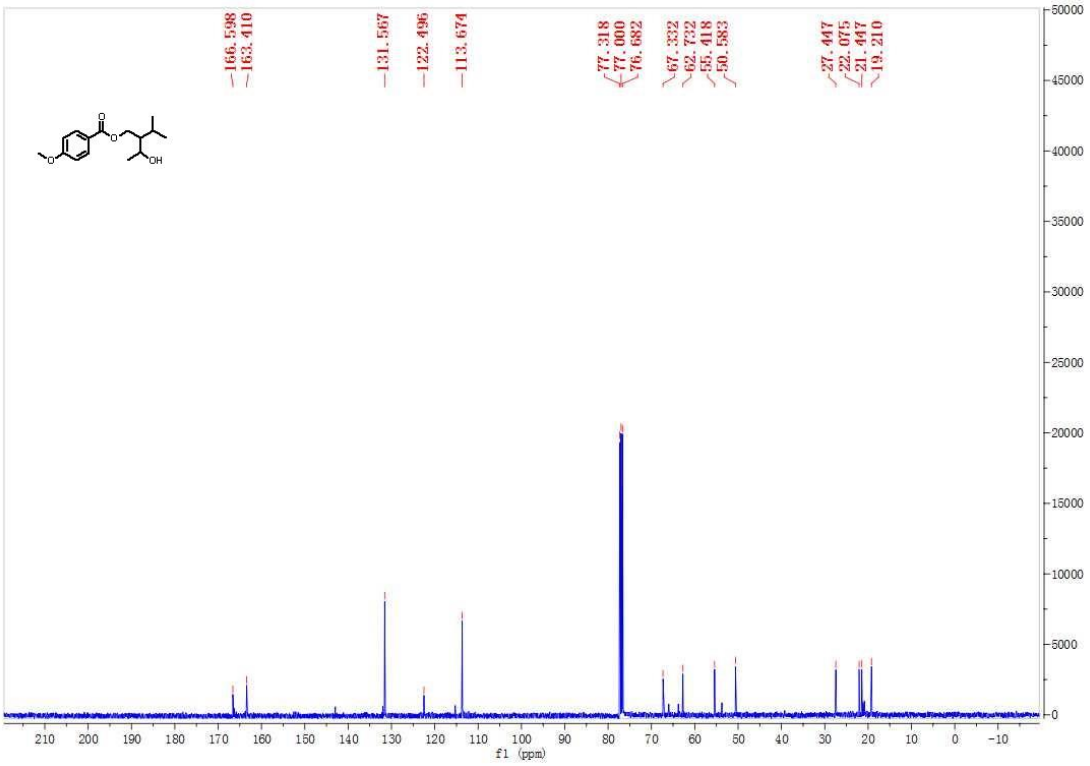
27-^{13}C NMR



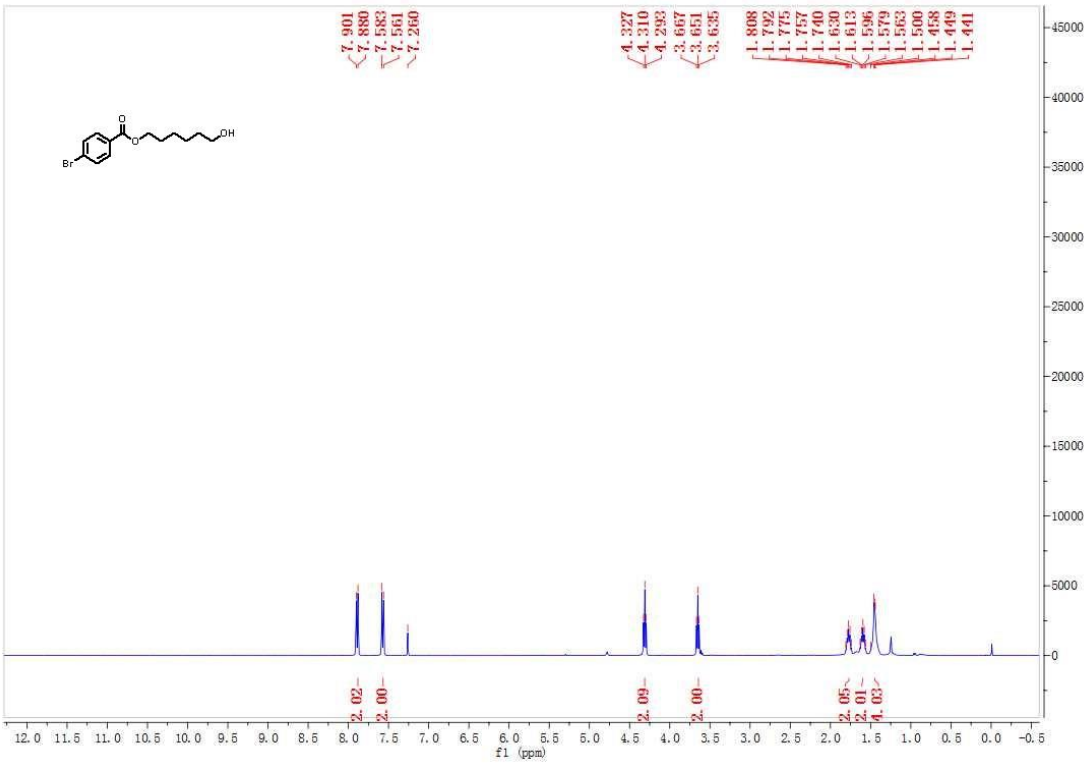
28-^{1}H NMR



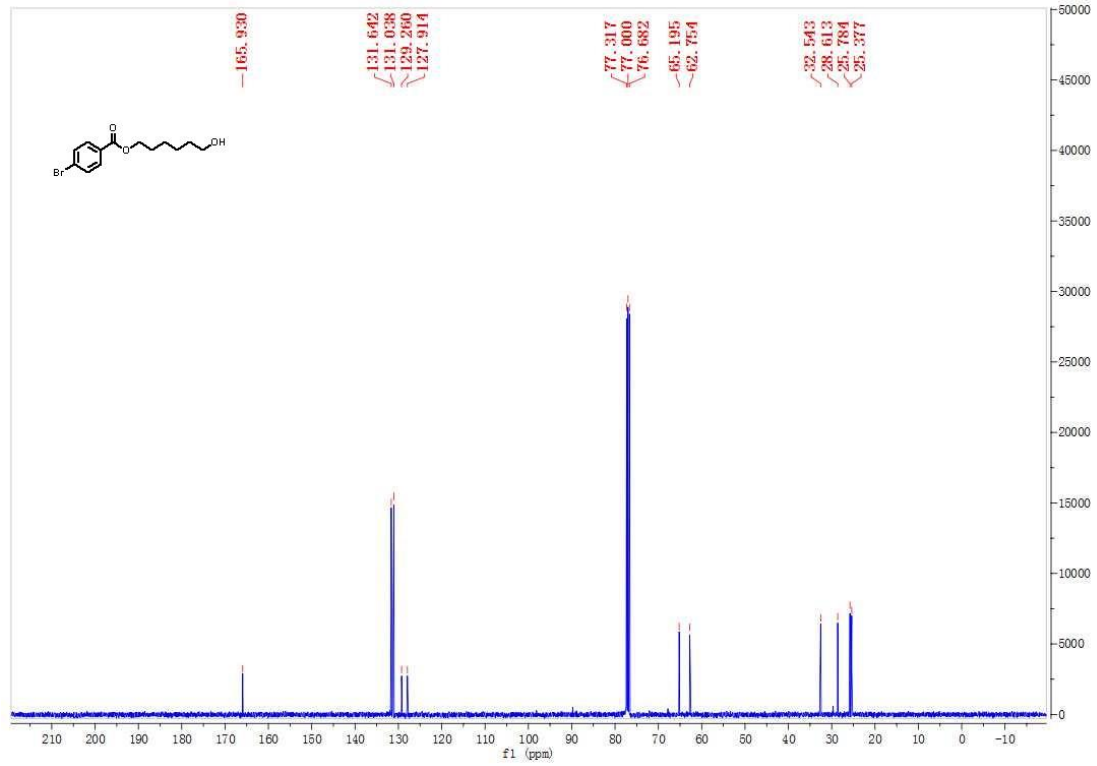
28-^{13}C NMR



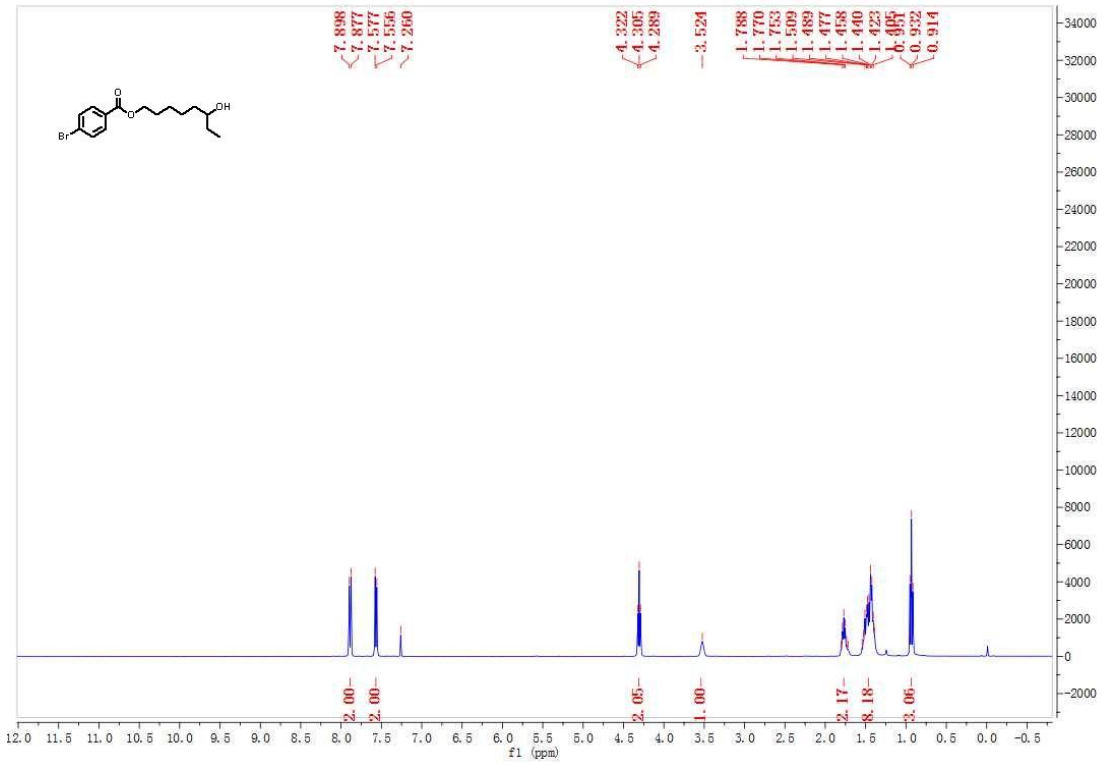
29-^{1}H NMR



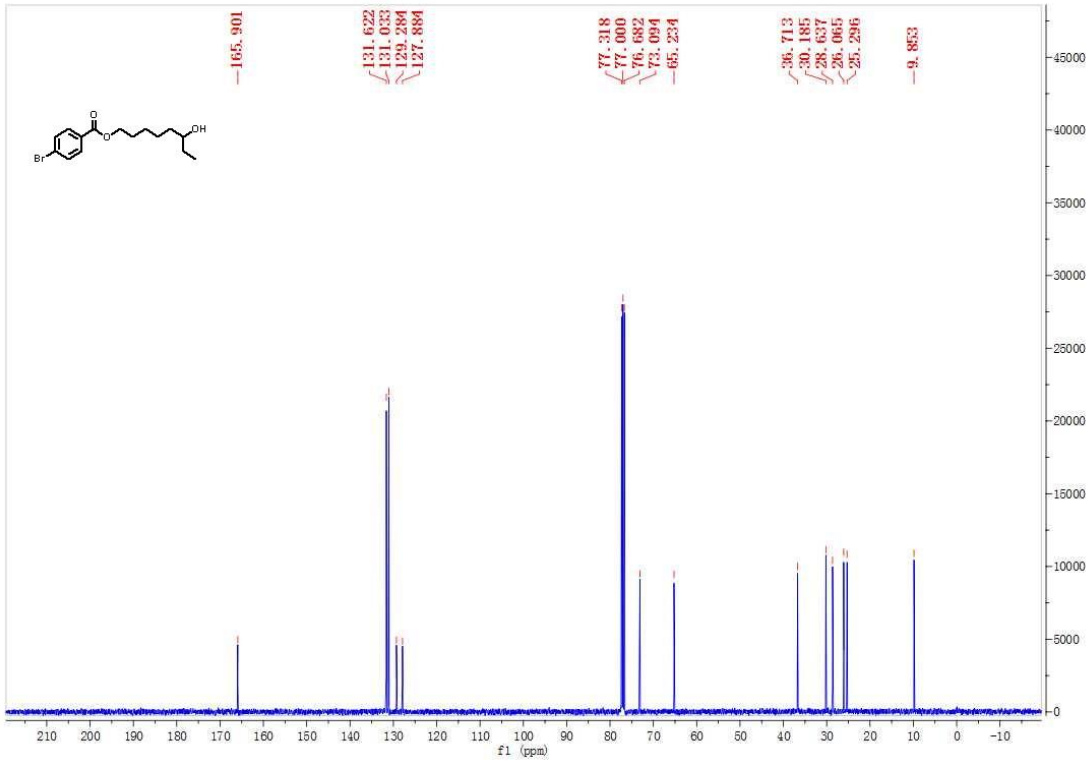
29-^{13}C NMR



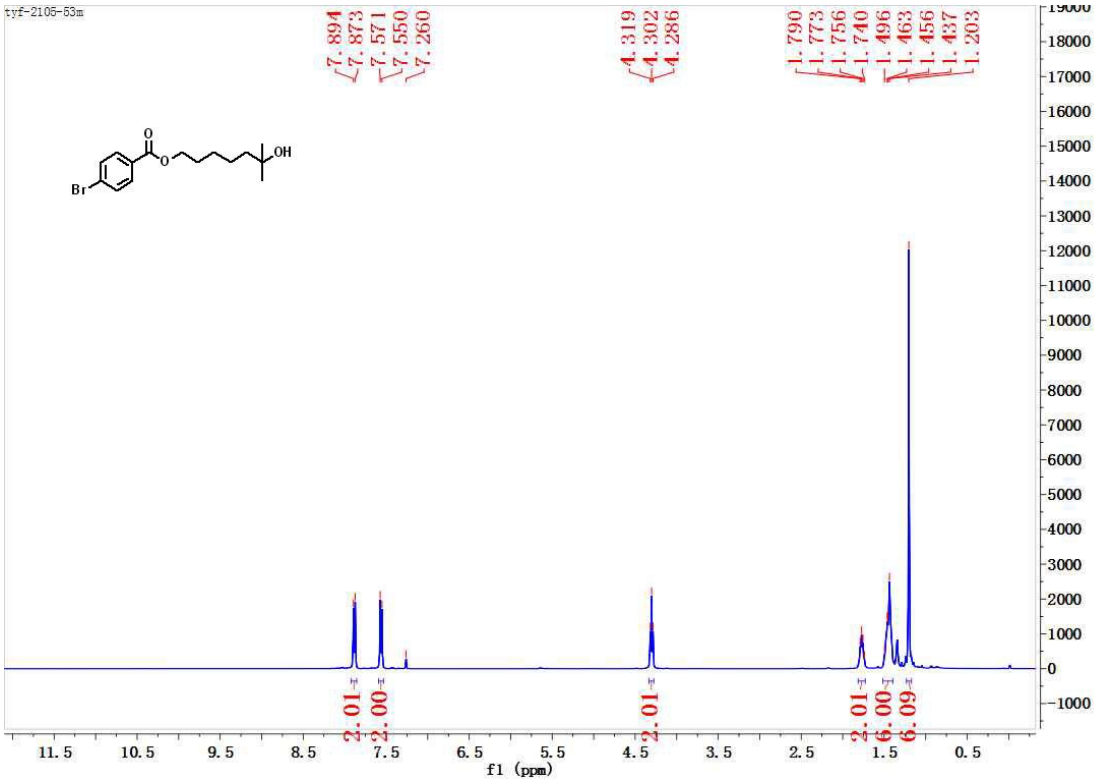
30-^{1}H NMR



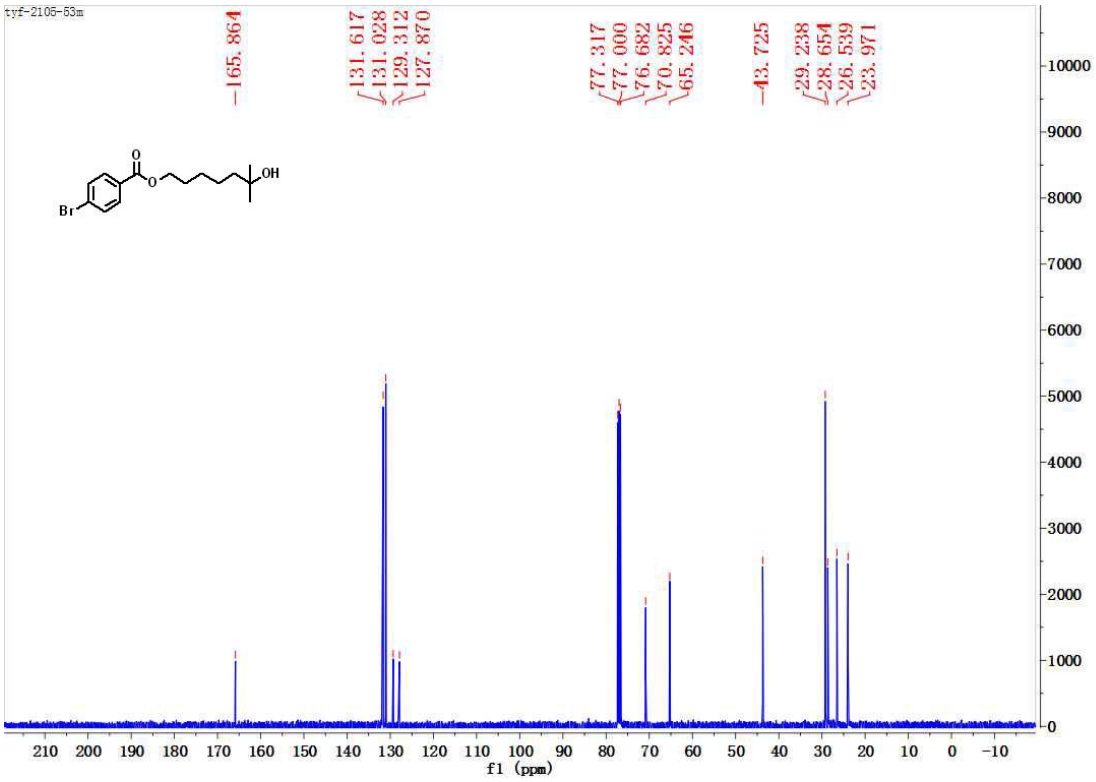
30-^{13}C NMR



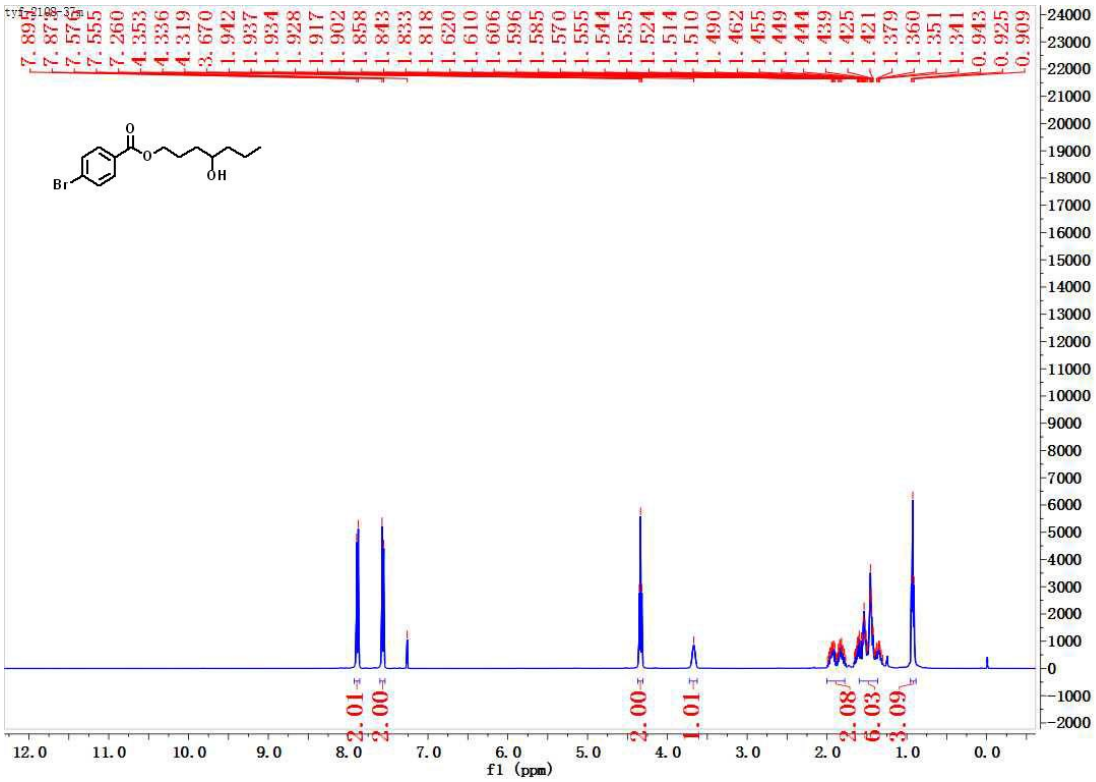
31-^{1}H NMR



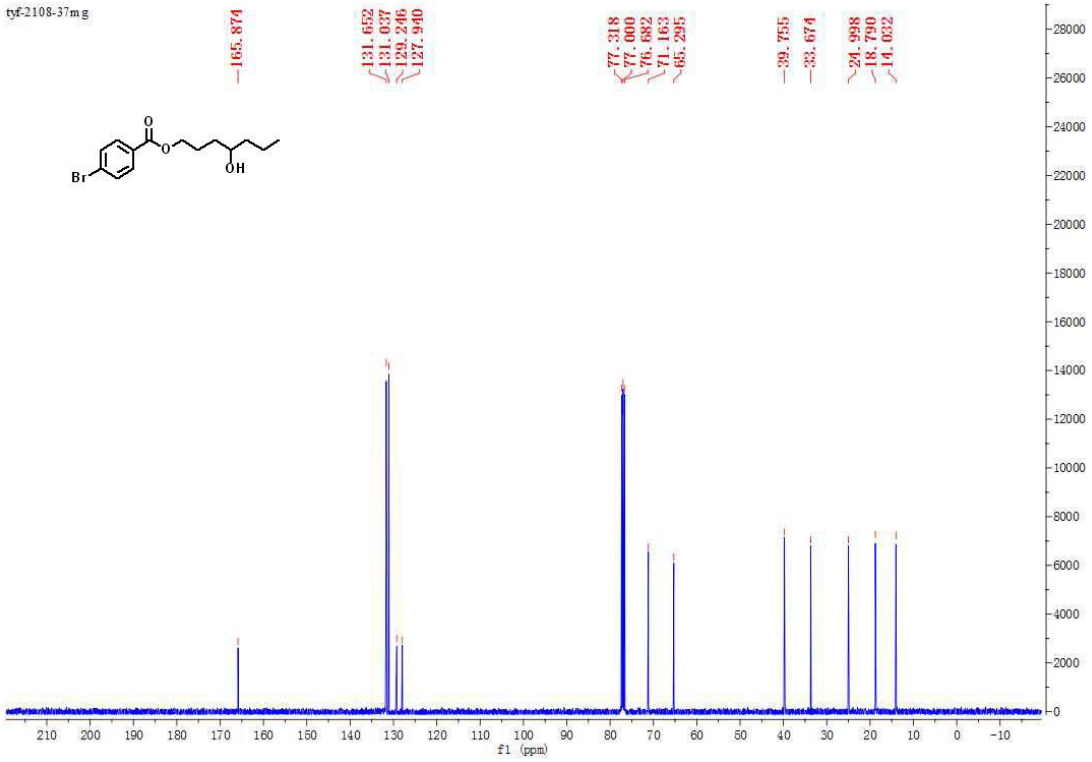
31-^{13}C NMR



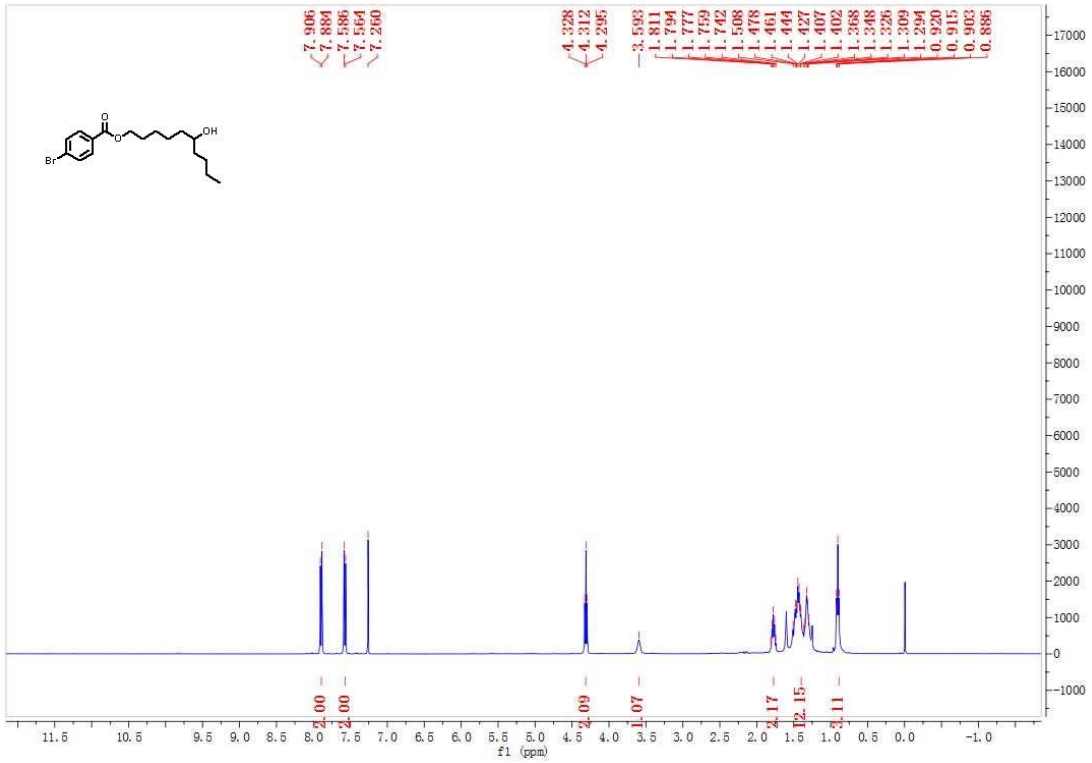
32-^{1}H NMR



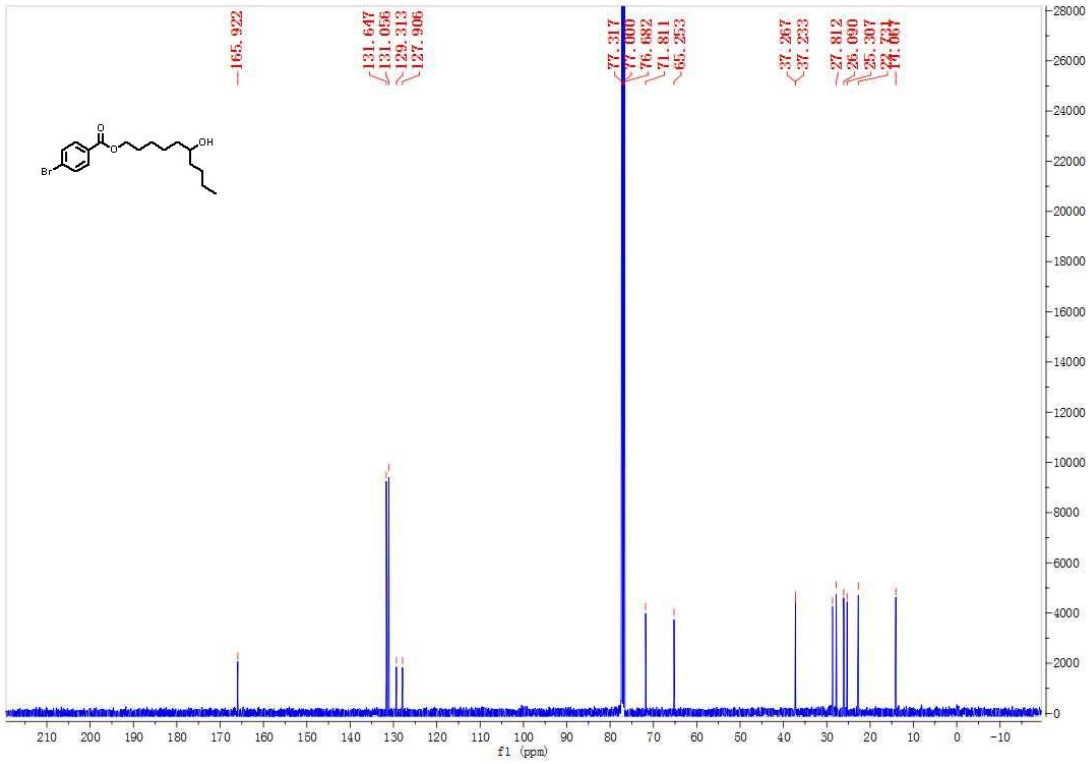
32-^{13}C NMR



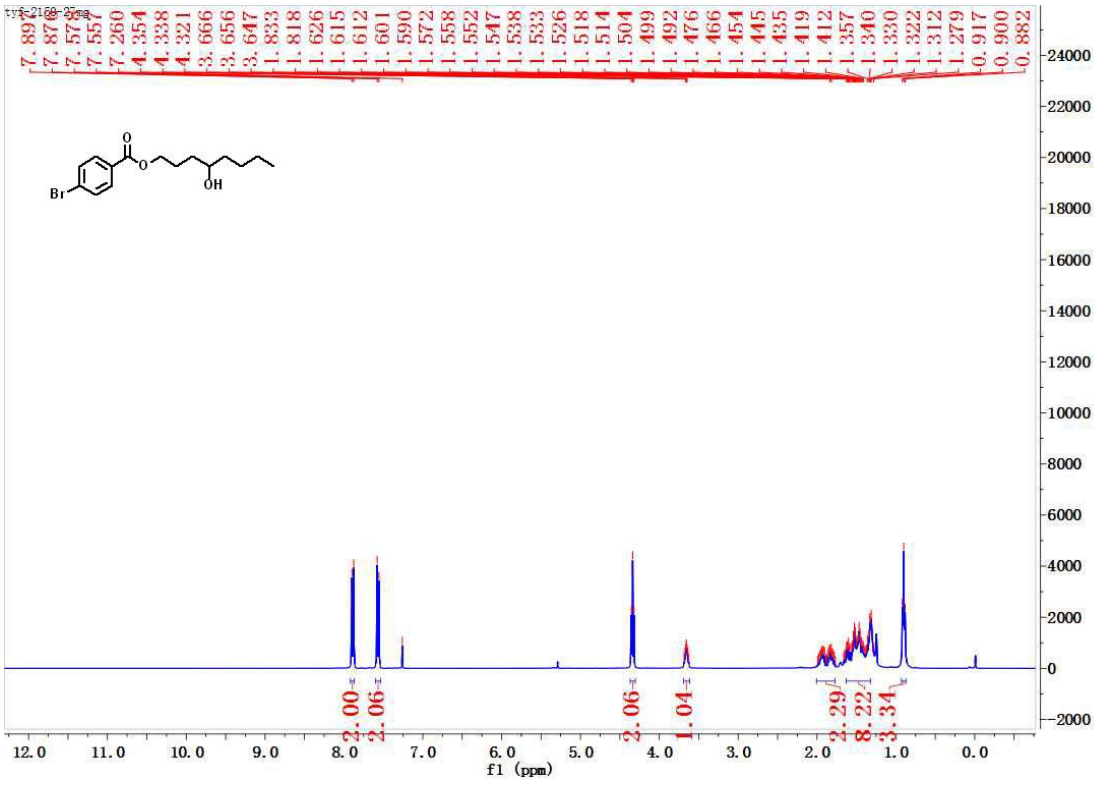
33-^{1}H NMR



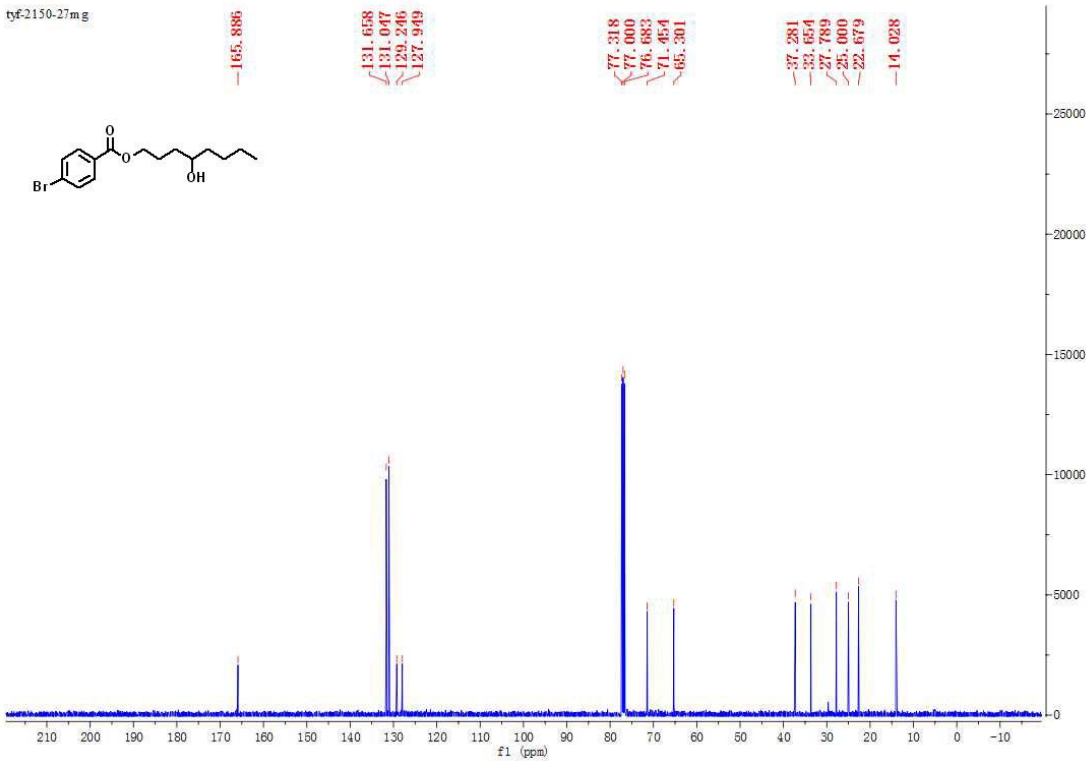
33-^{13}C NMR



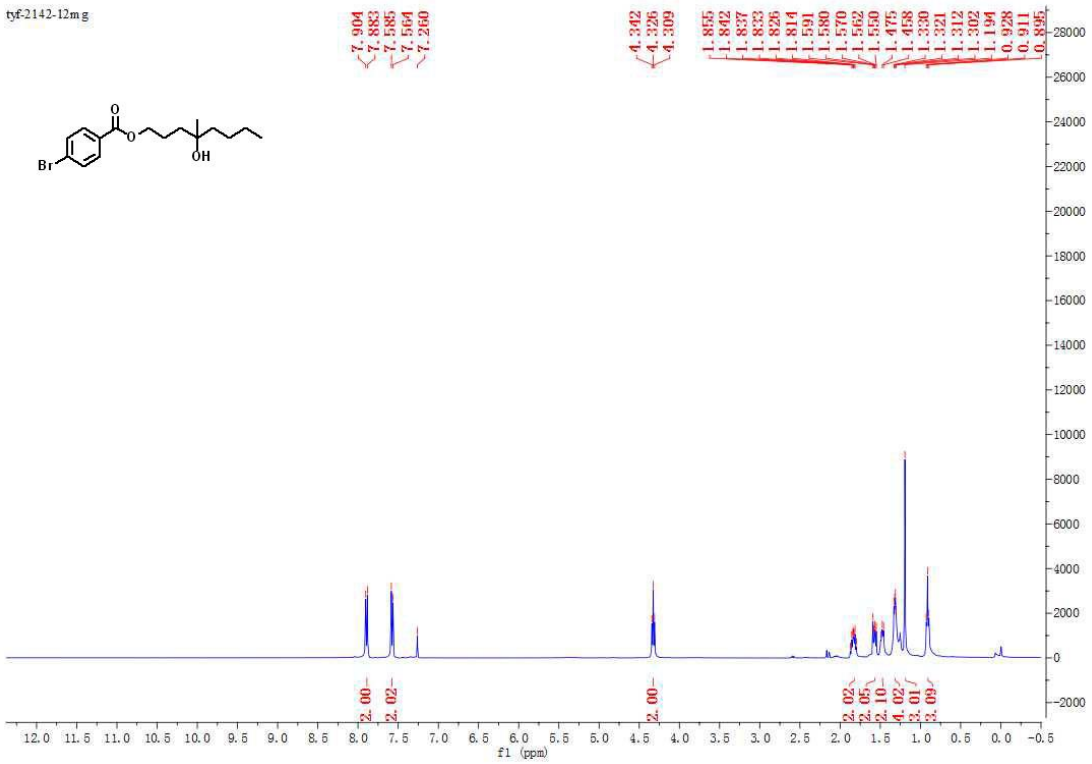
34-^{1}H NMR



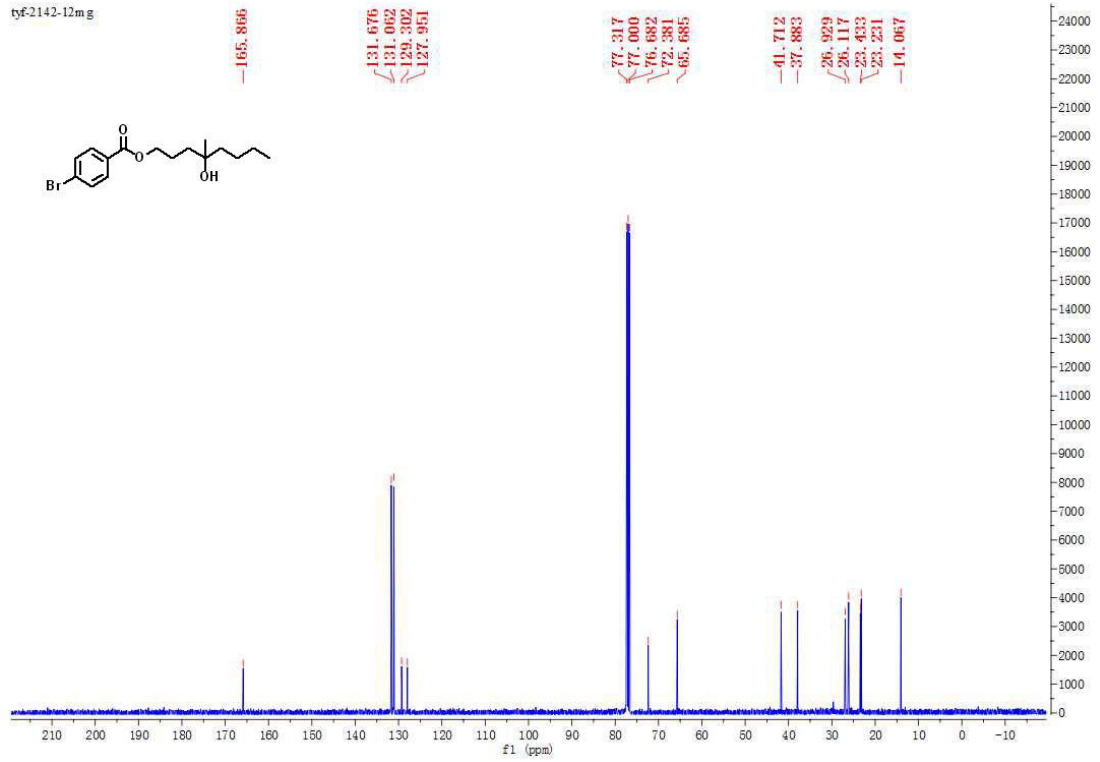
34-^{13}C NMR



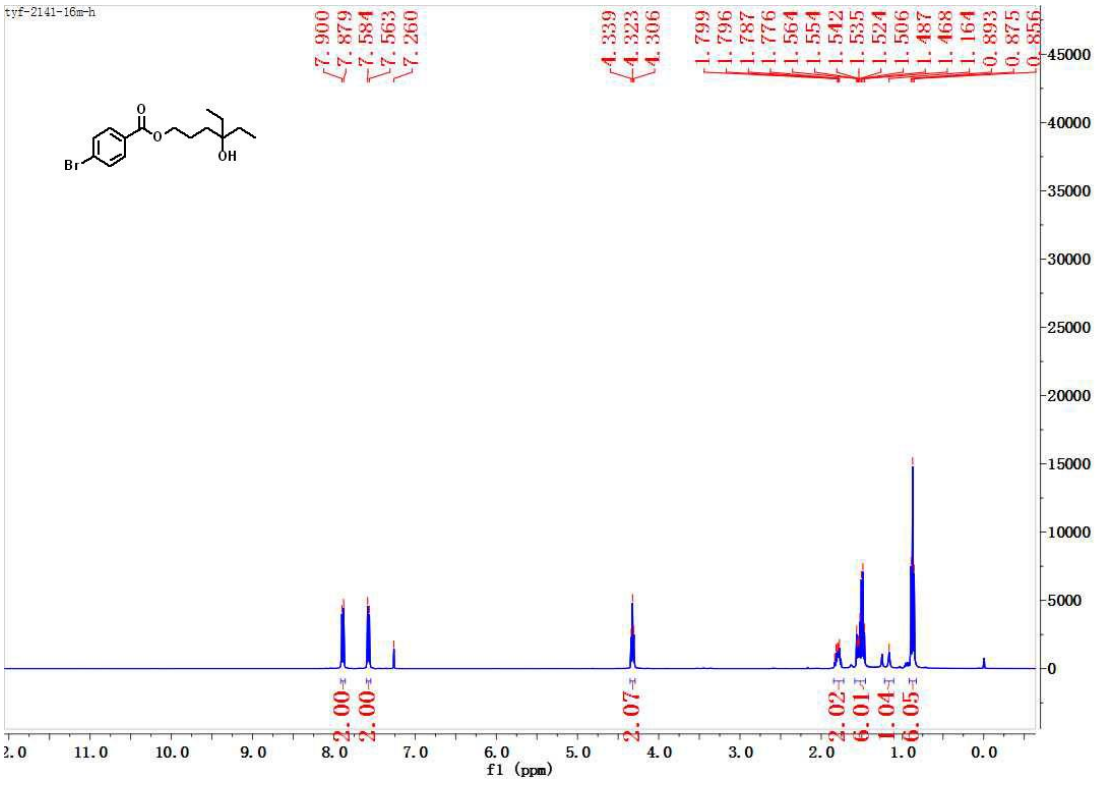
35-^{1}H NMR



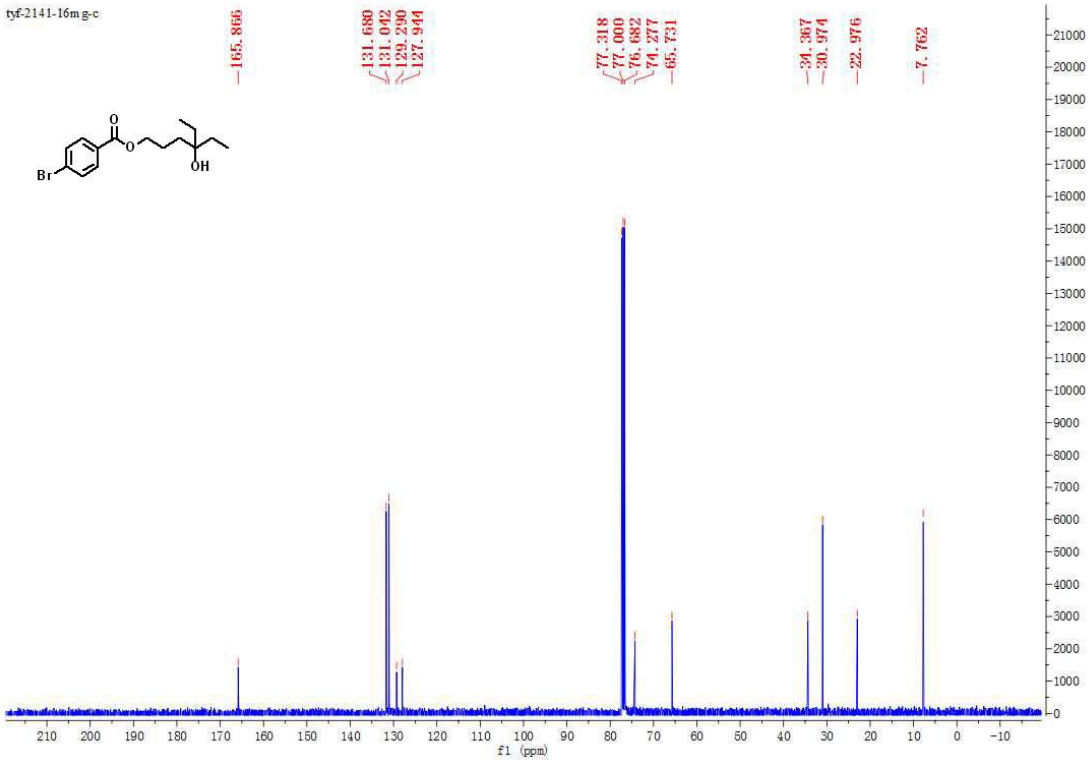
35-^{13}C NMR



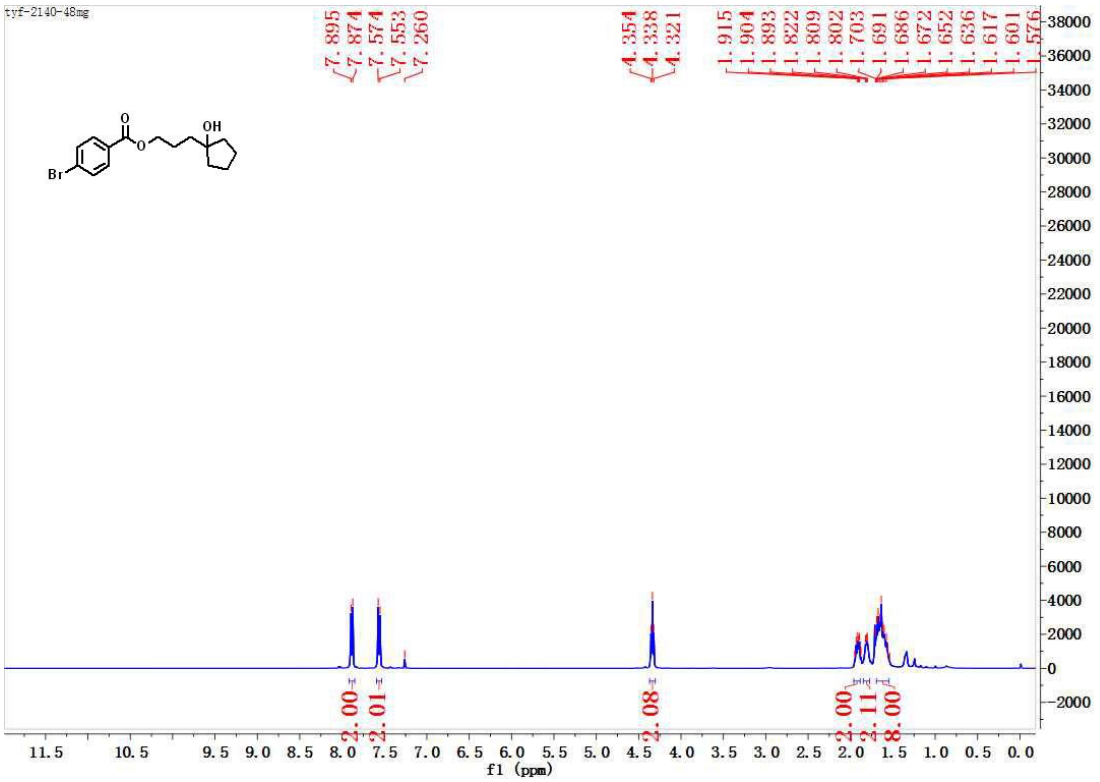
36-^{1}H NMR



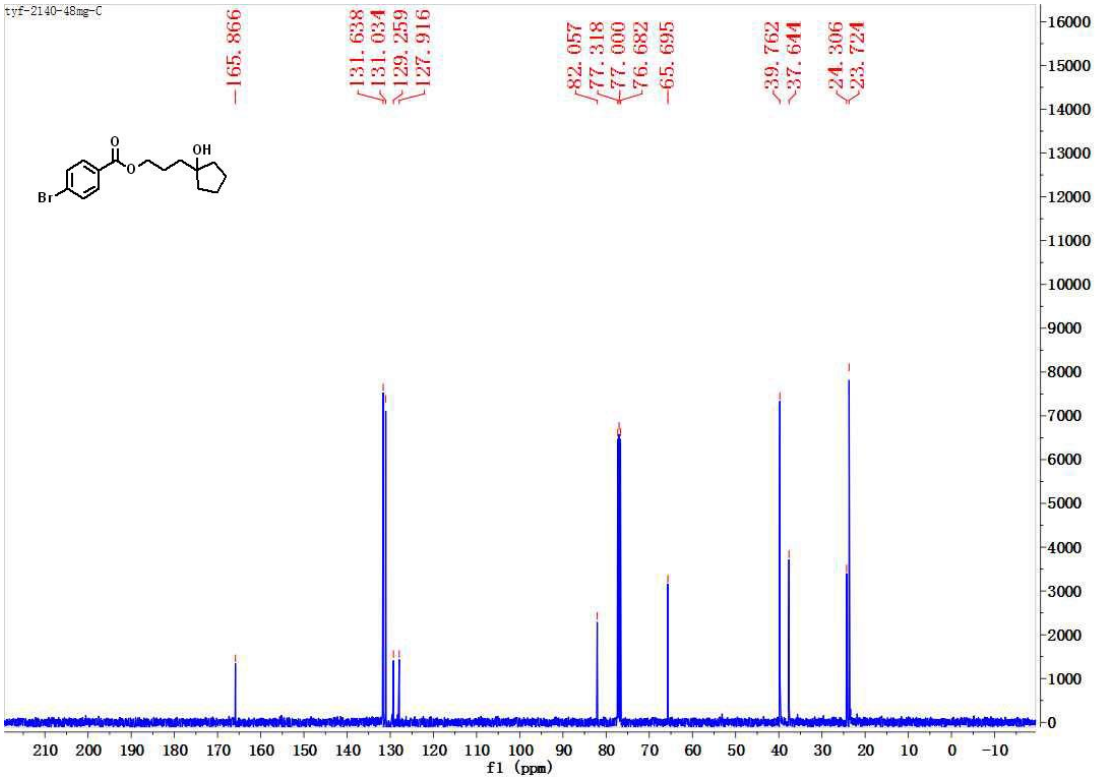
36-^{13}C NMR



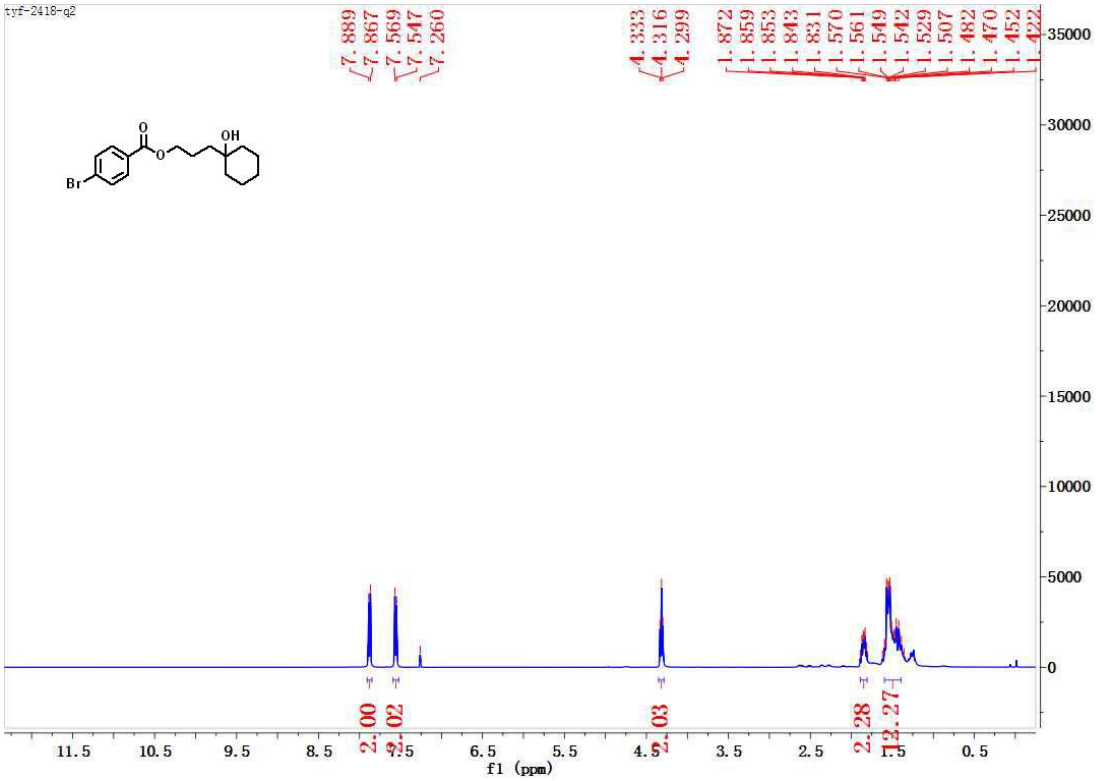
37-^{1}H NMR



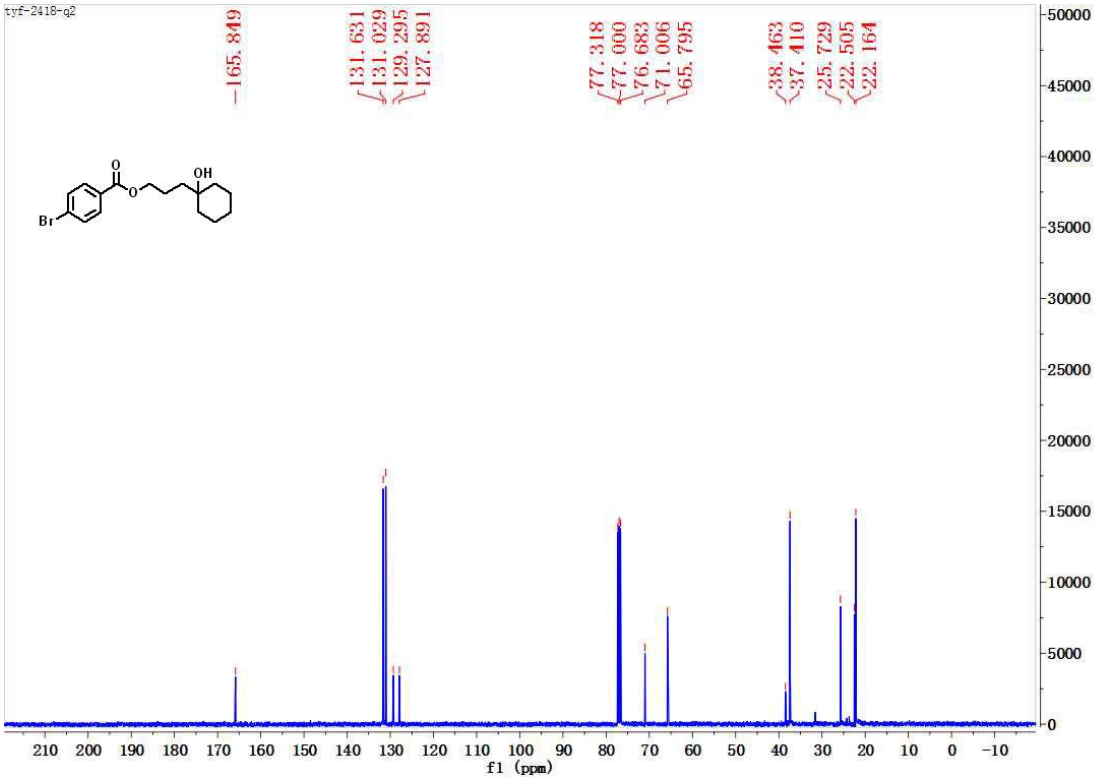
37-^{13}C NMR



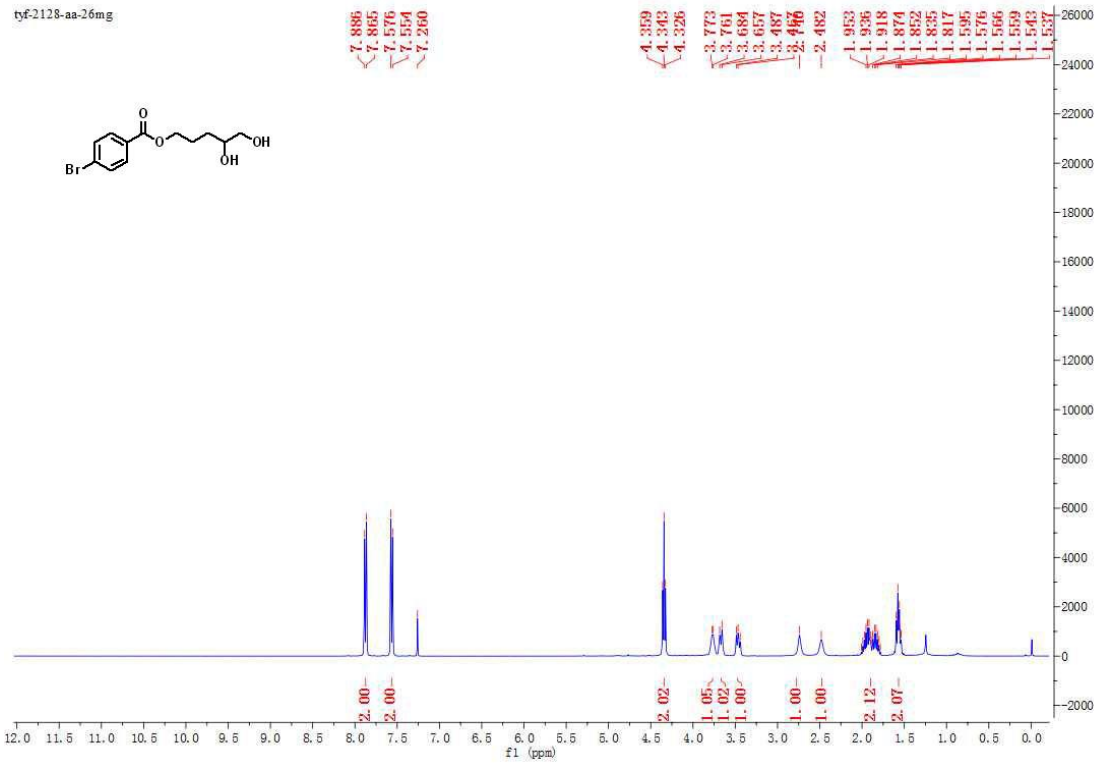
38-^{1}H NMR



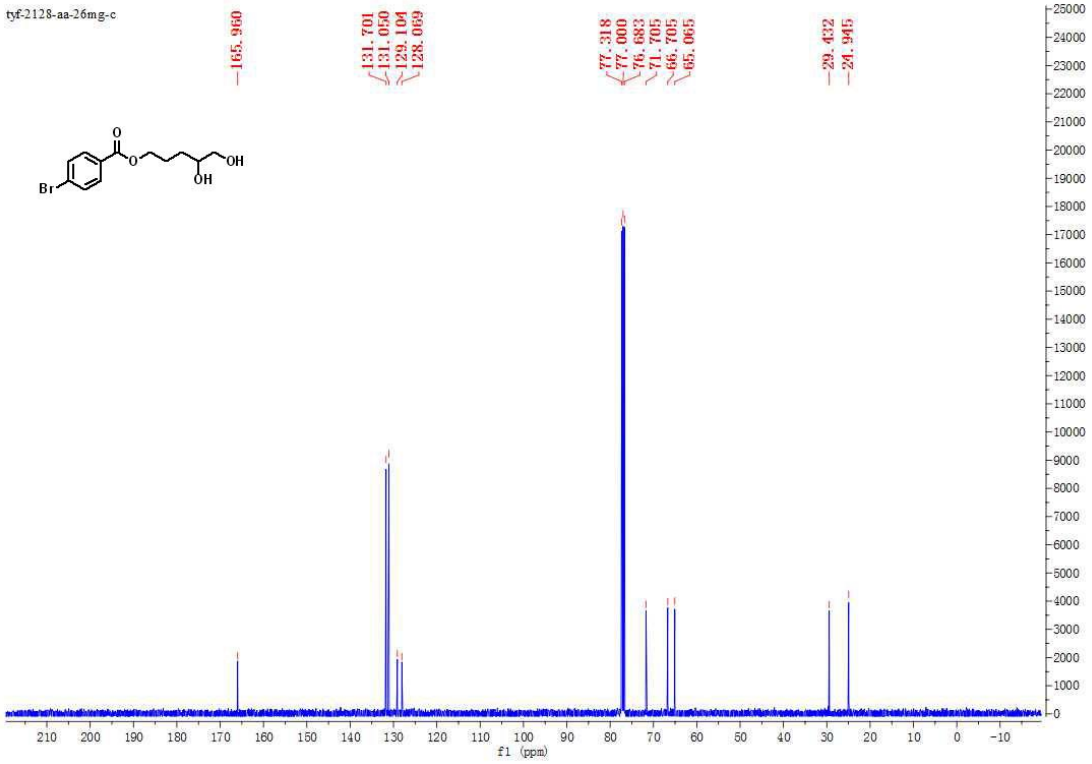
38-^{13}C NMR



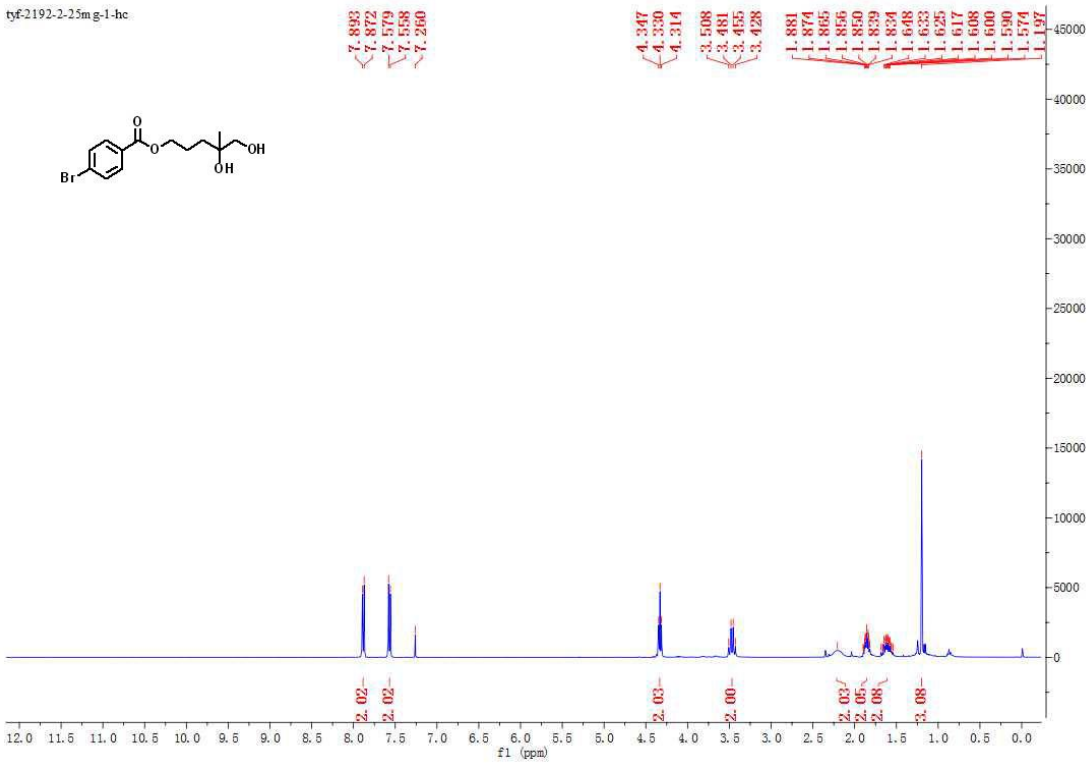
39-^{1}H NMR



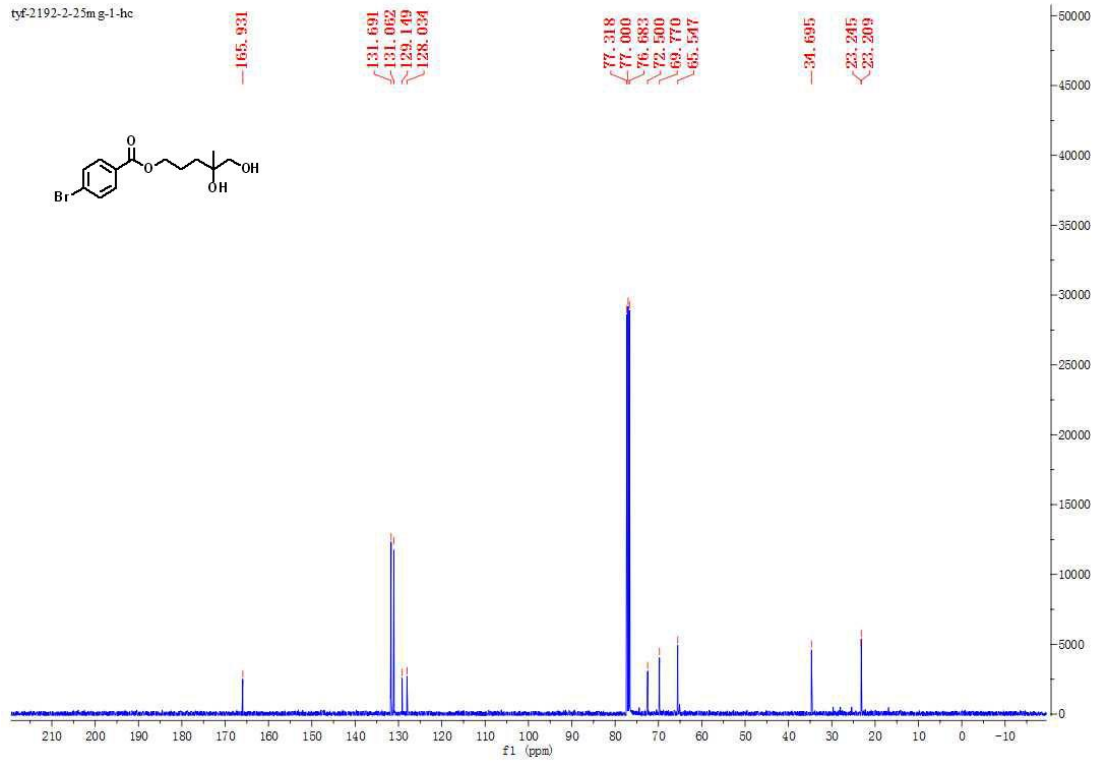
39-^{13}C NMR



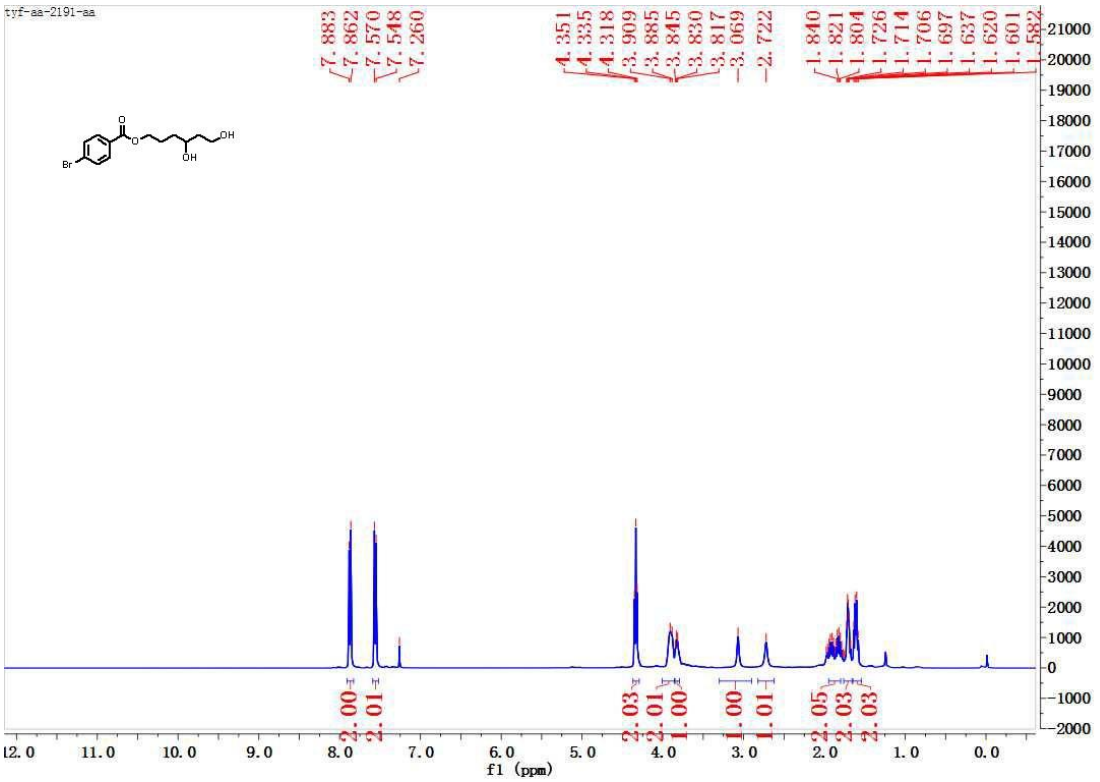
40-^{1}H NMR



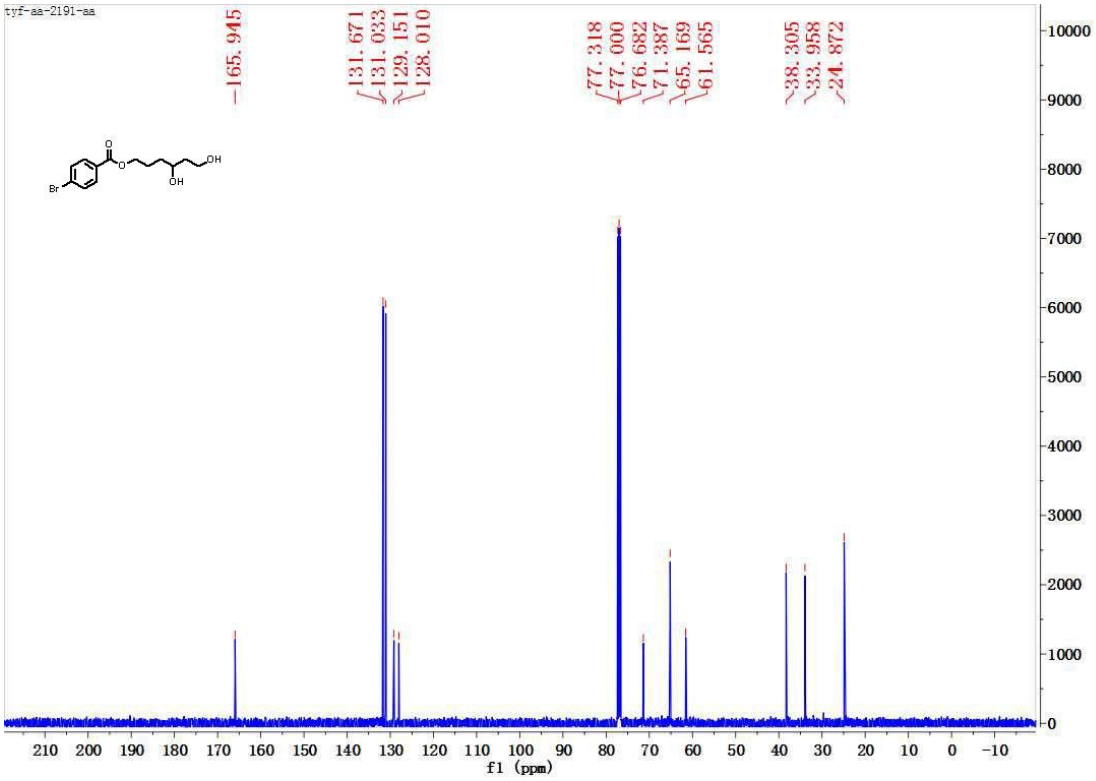
40-^{13}C NMR



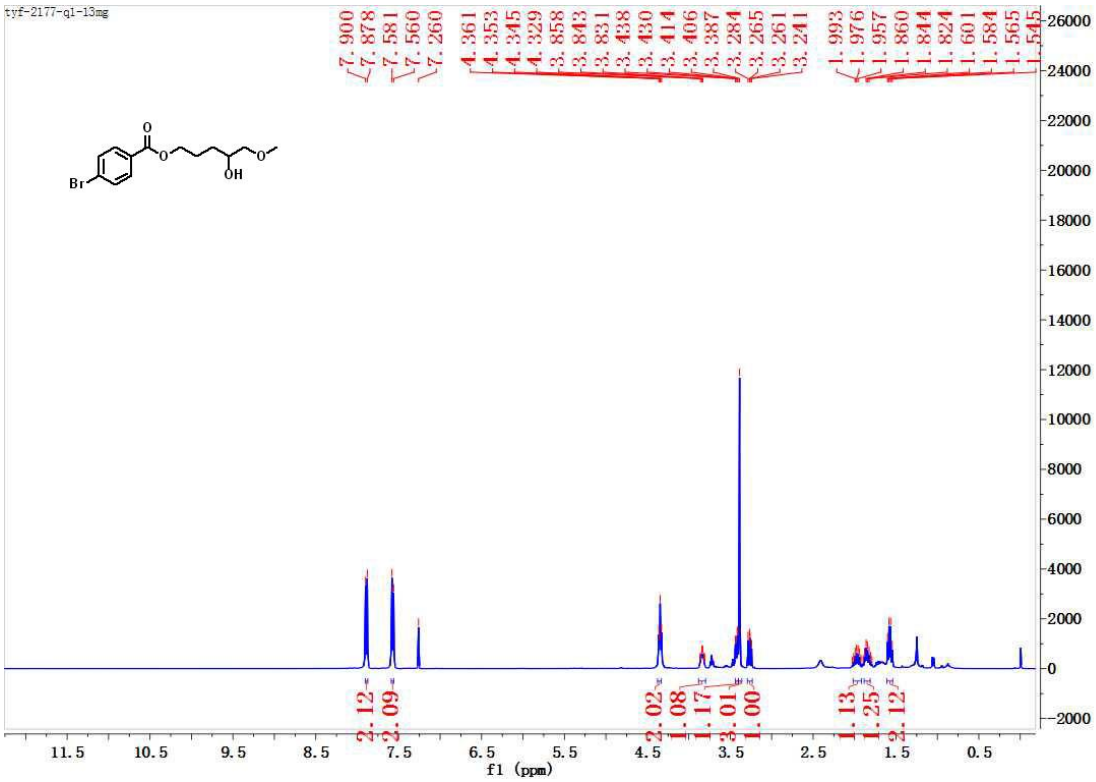
41-^{1}H NMR



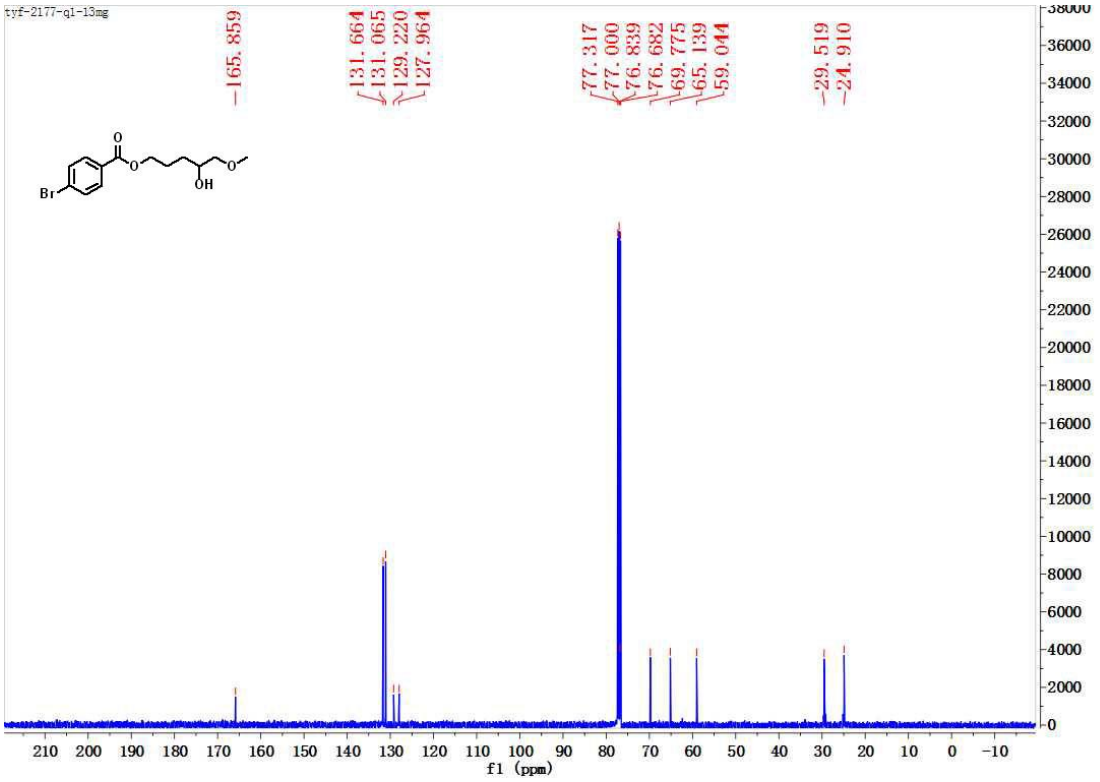
41-^{13}C NMR



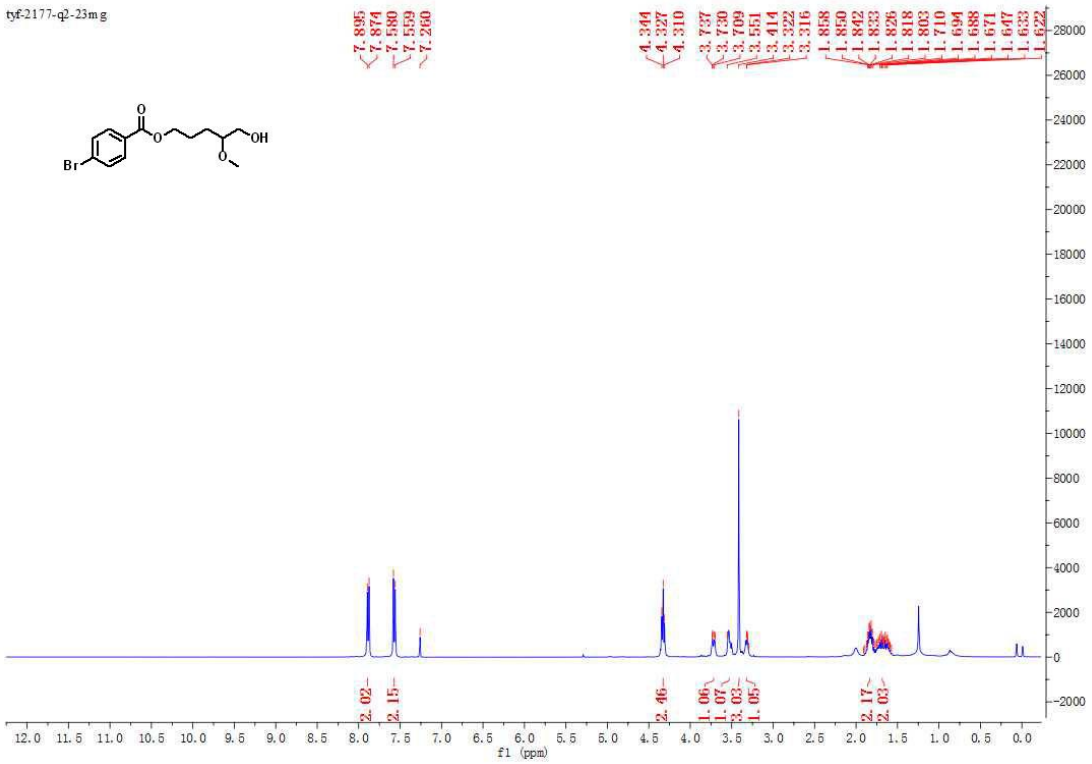
42^{1}-^{1}H NMR



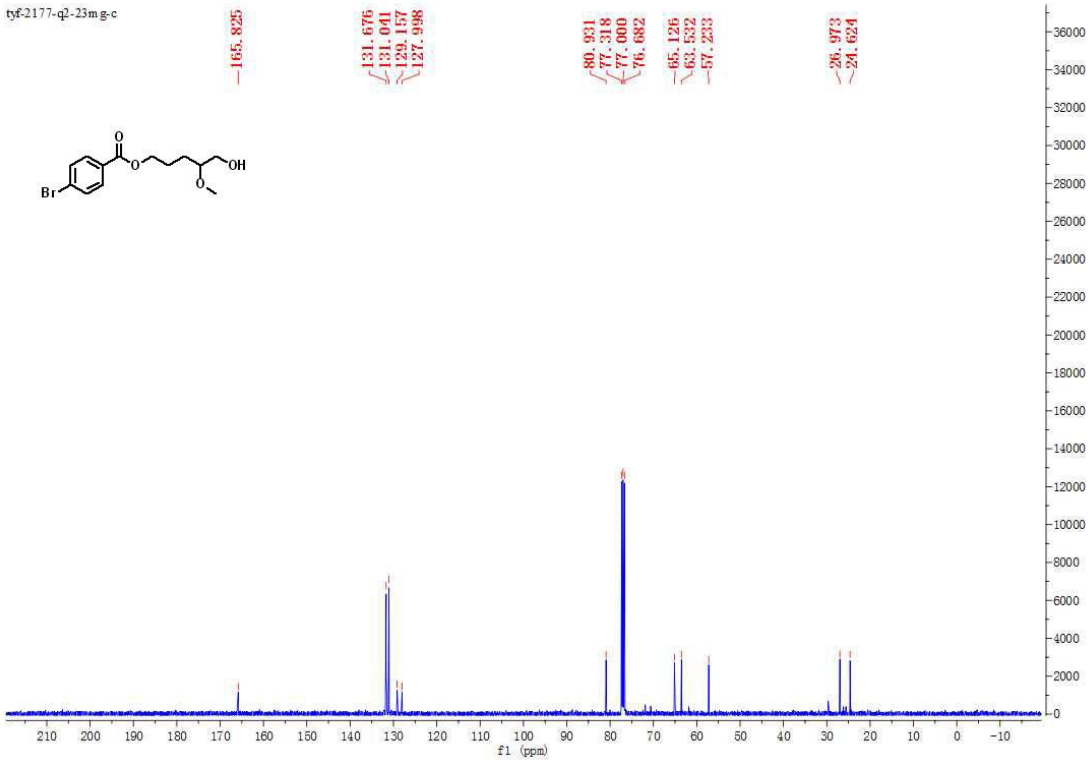
42[1]-^{13}C NMR



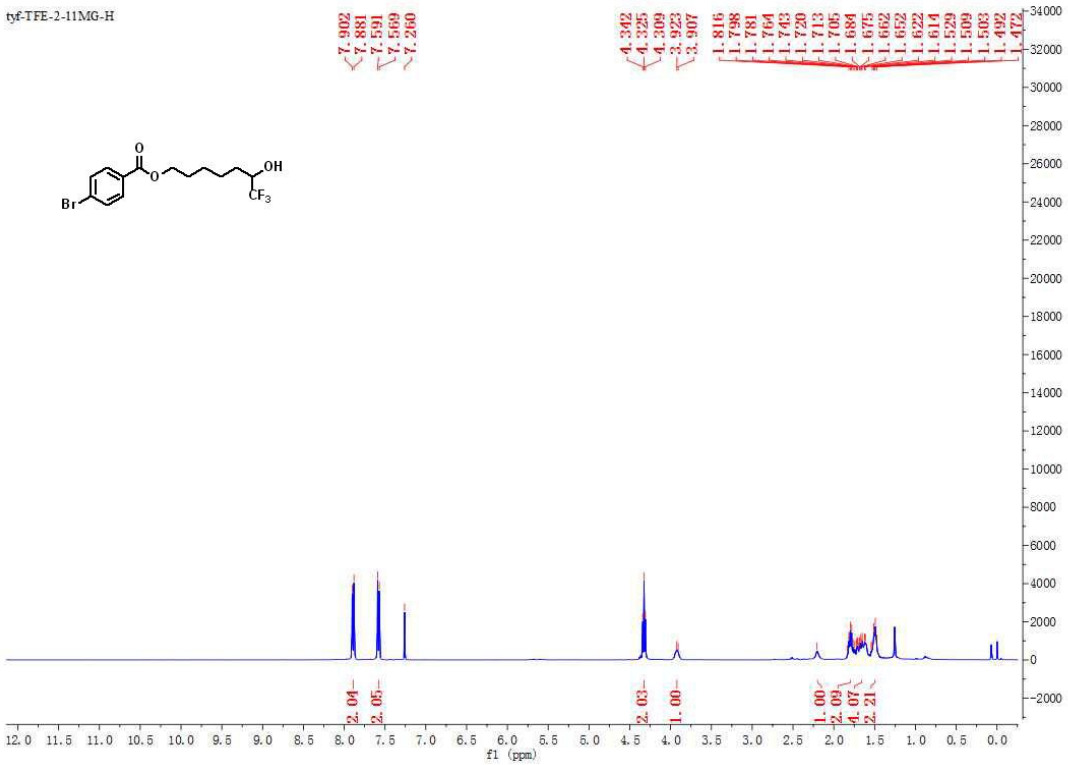
42[2]-^{1}H NMR



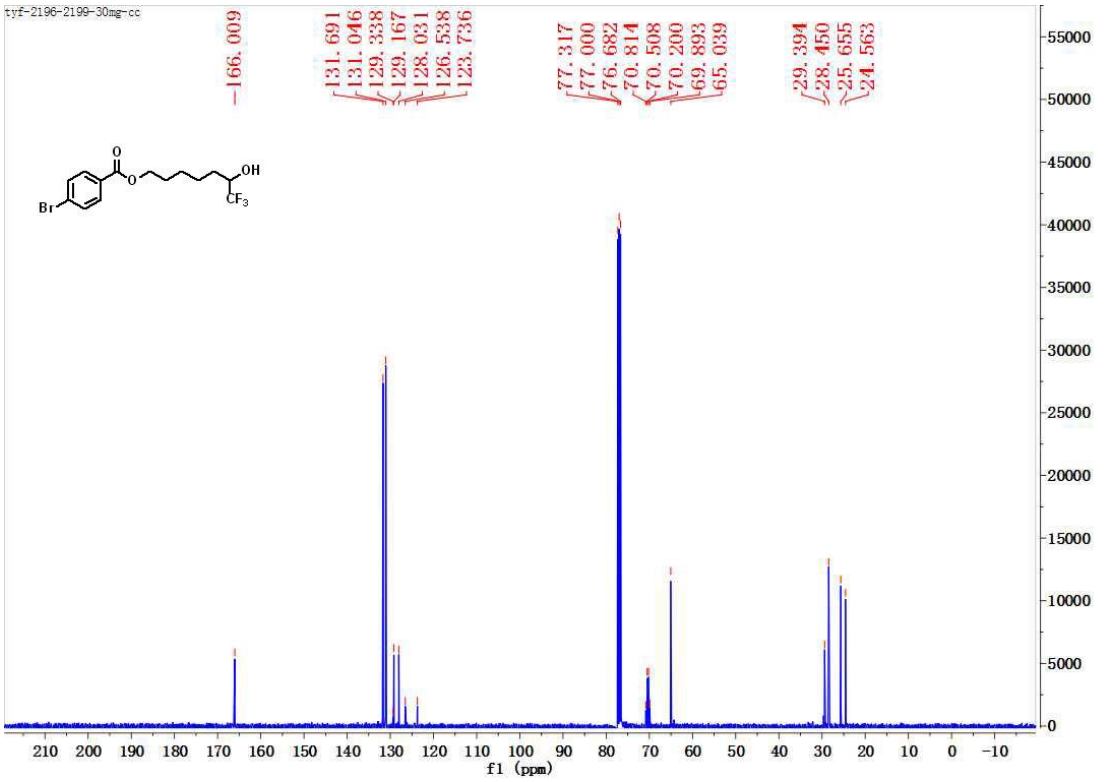
42^{2}-^{13}C NMR



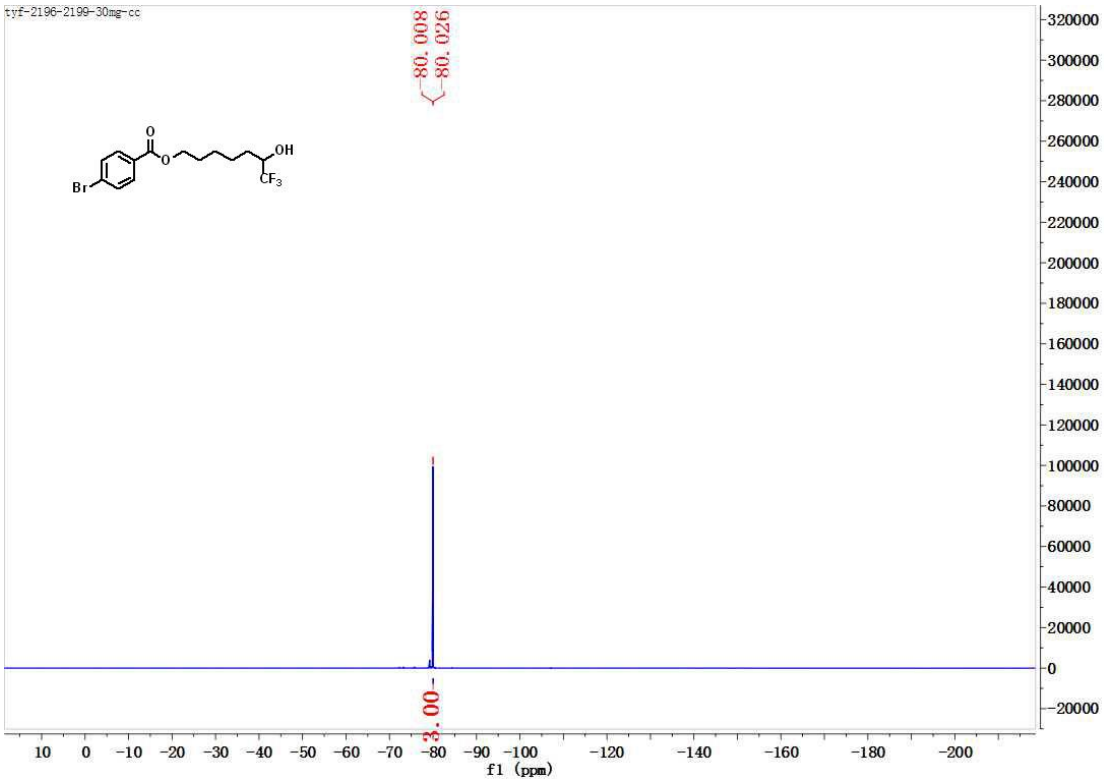
43-^{1}H NMR



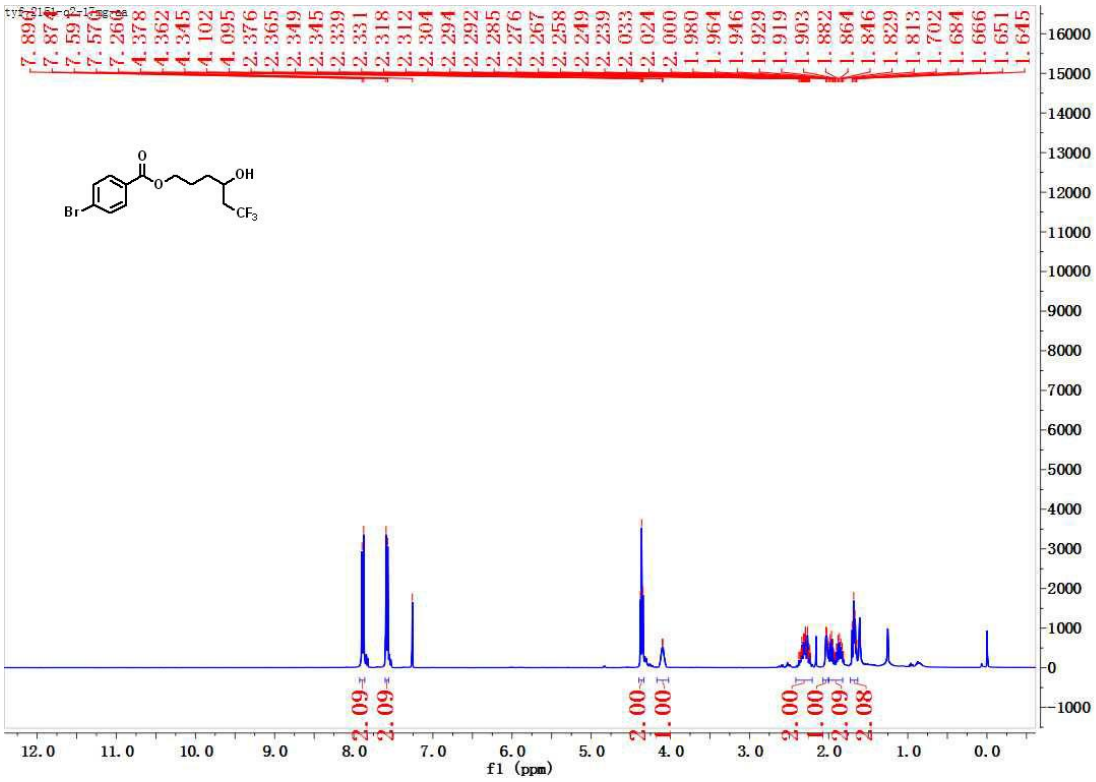
43-^{13}C NMR



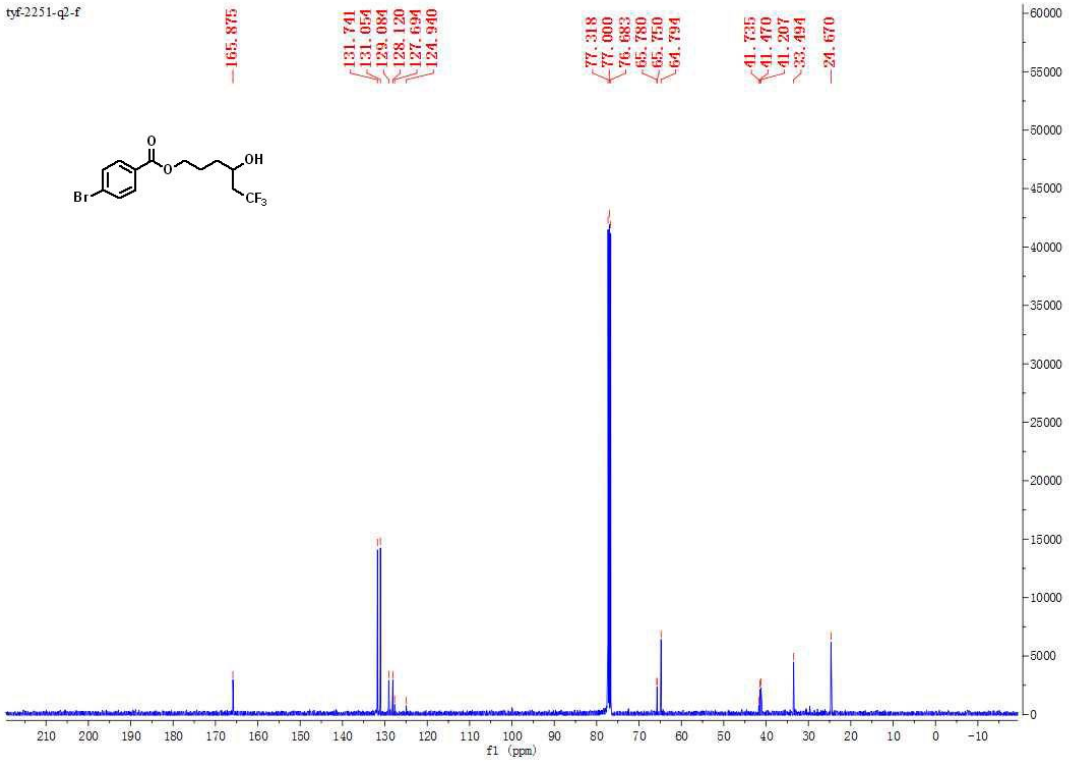
43-^{19}F NMR



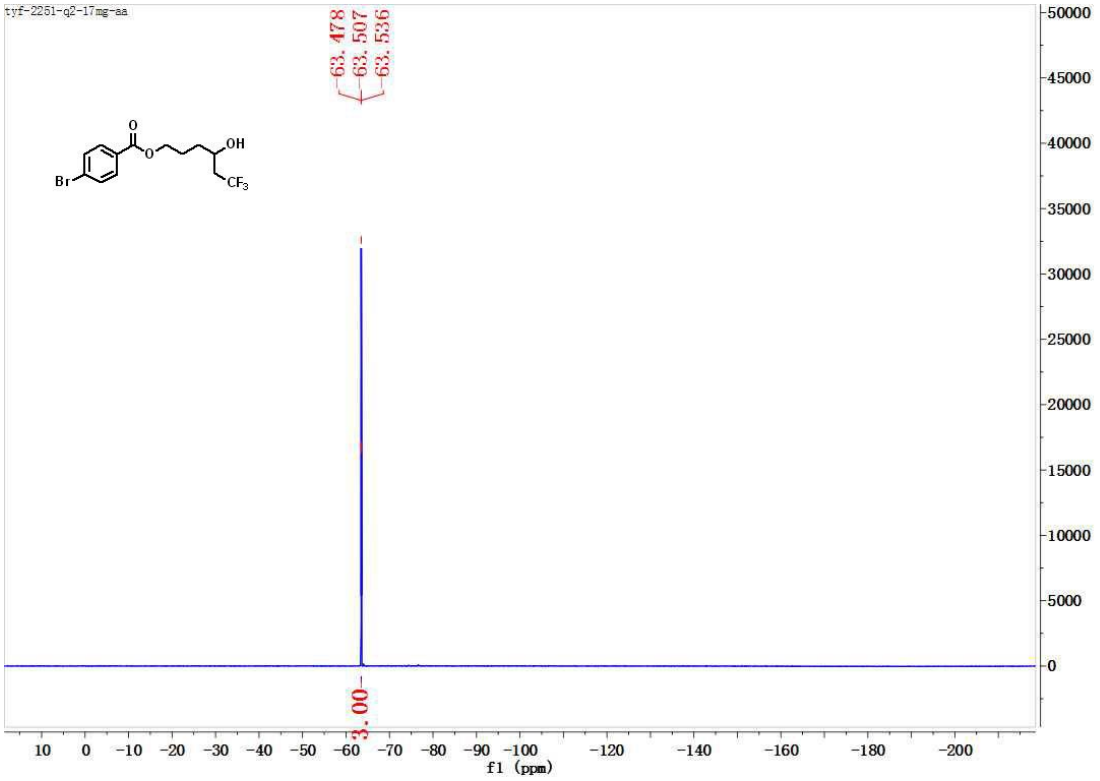
44-^{1}H NMR



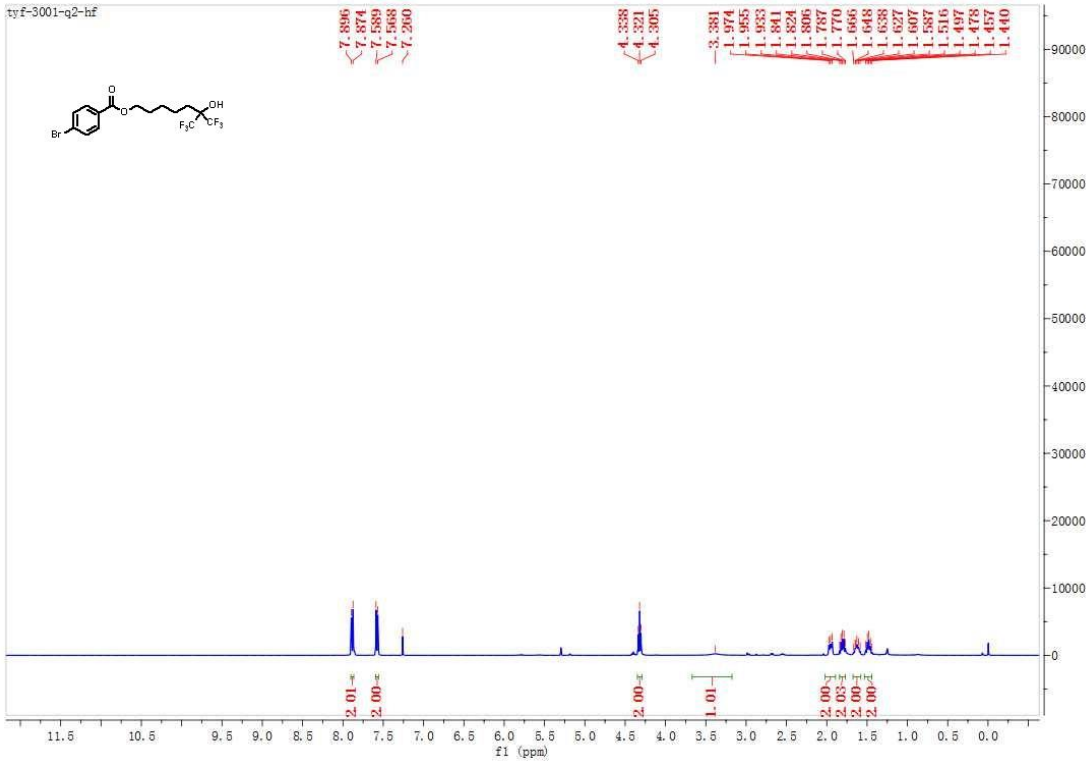
44-^{13}C NMR



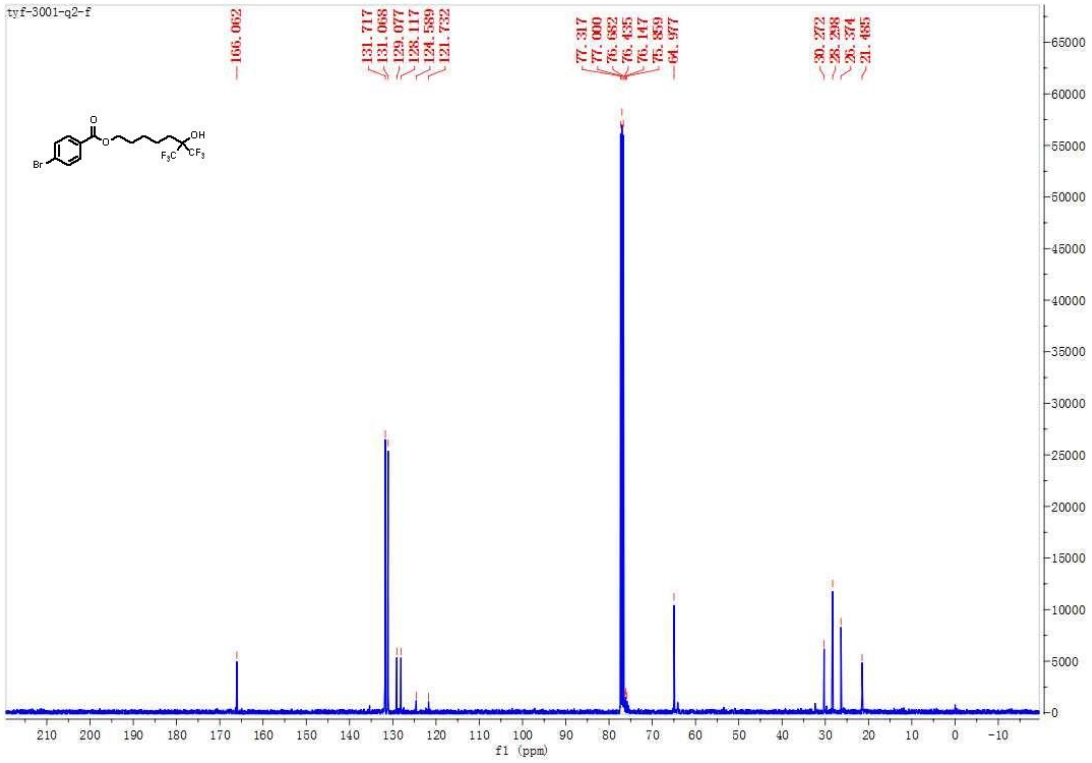
44-^{19}F NMR



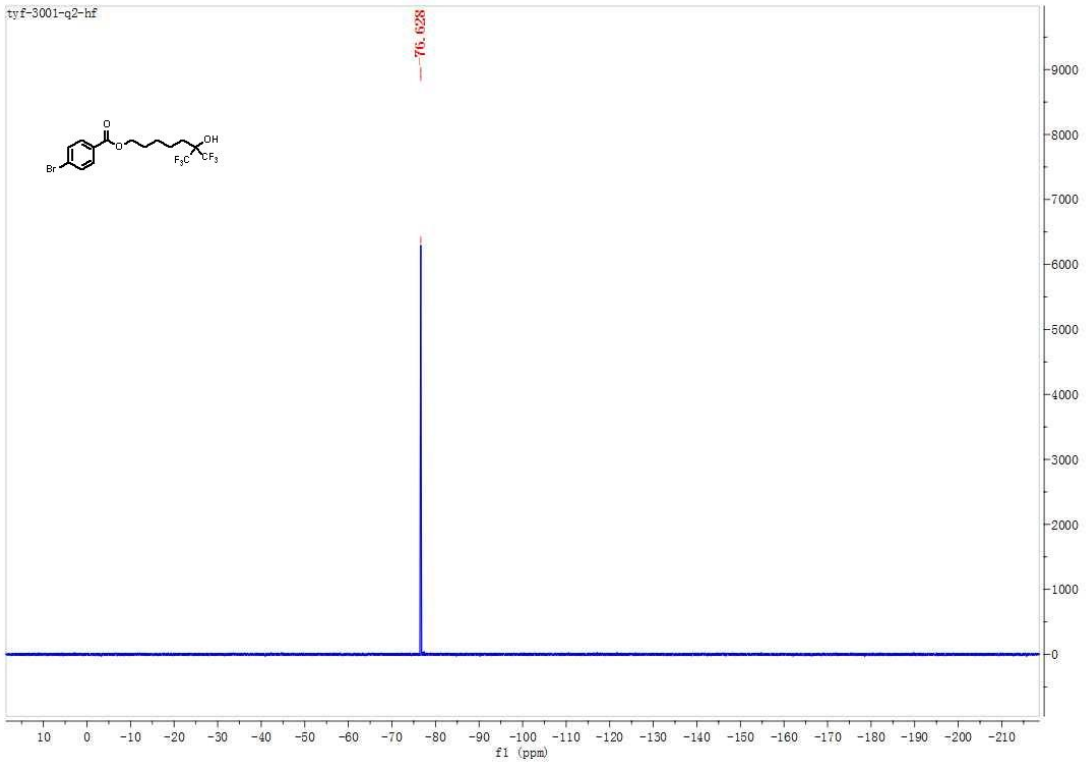
45-^{1}H NMR



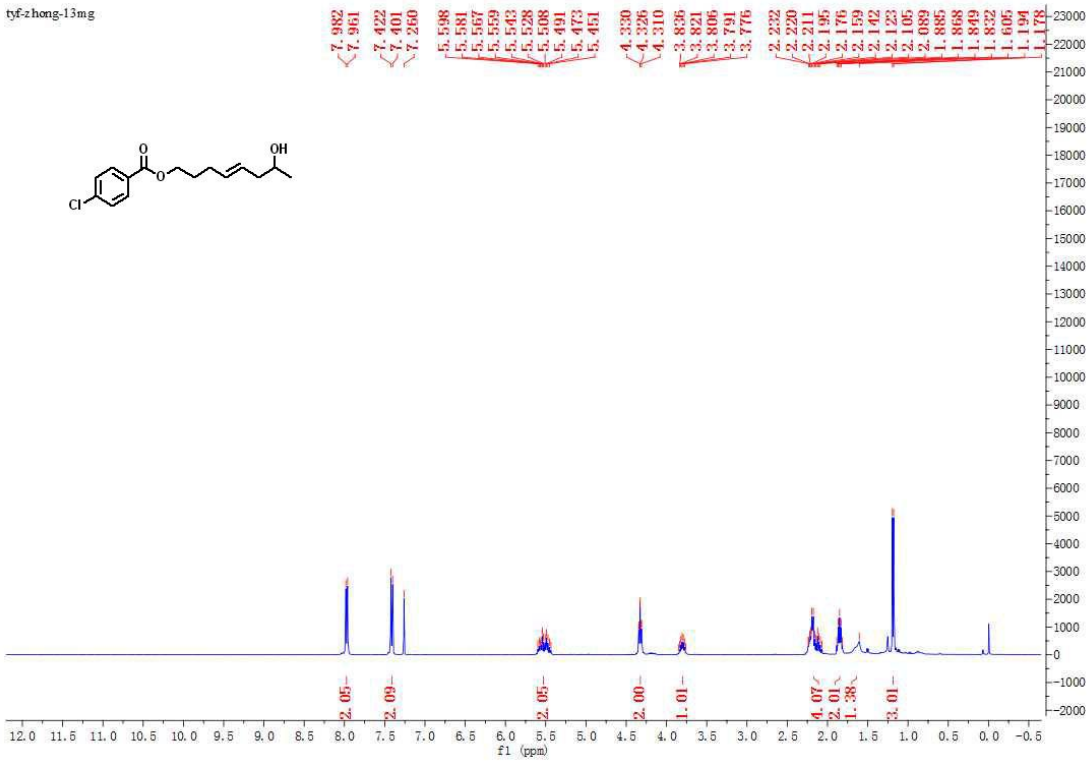
45-^{13}C NMR



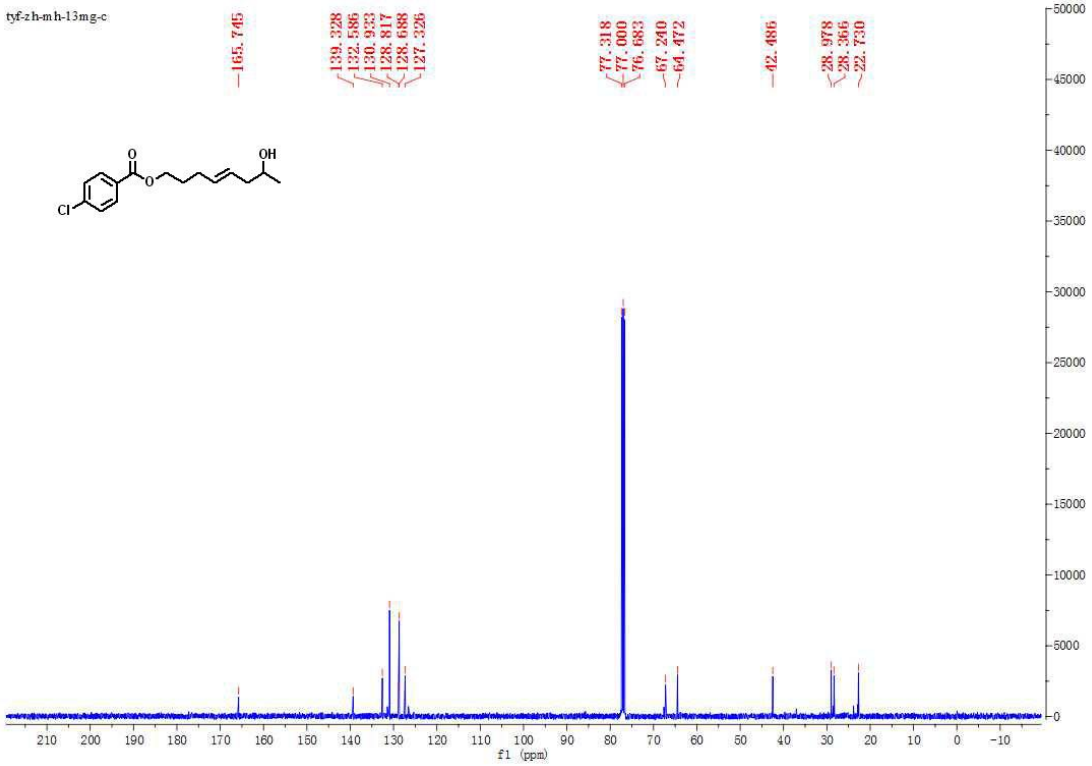
45-^{19}F NMR



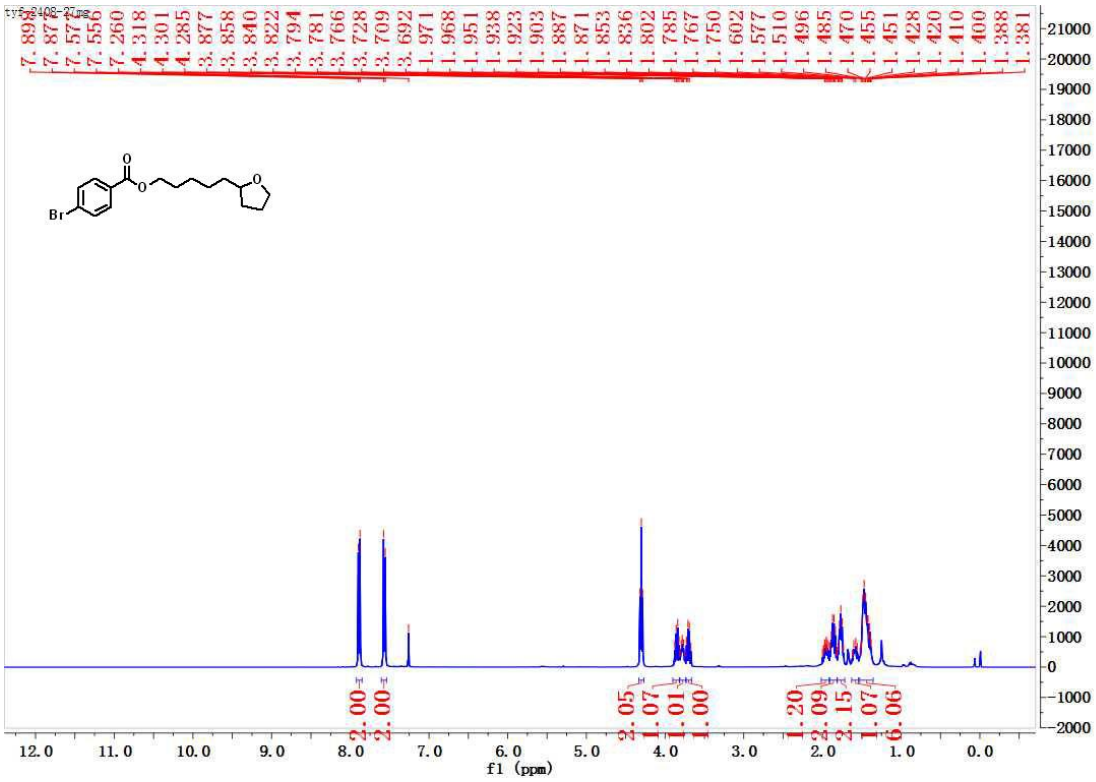
46-^{1}H NMR



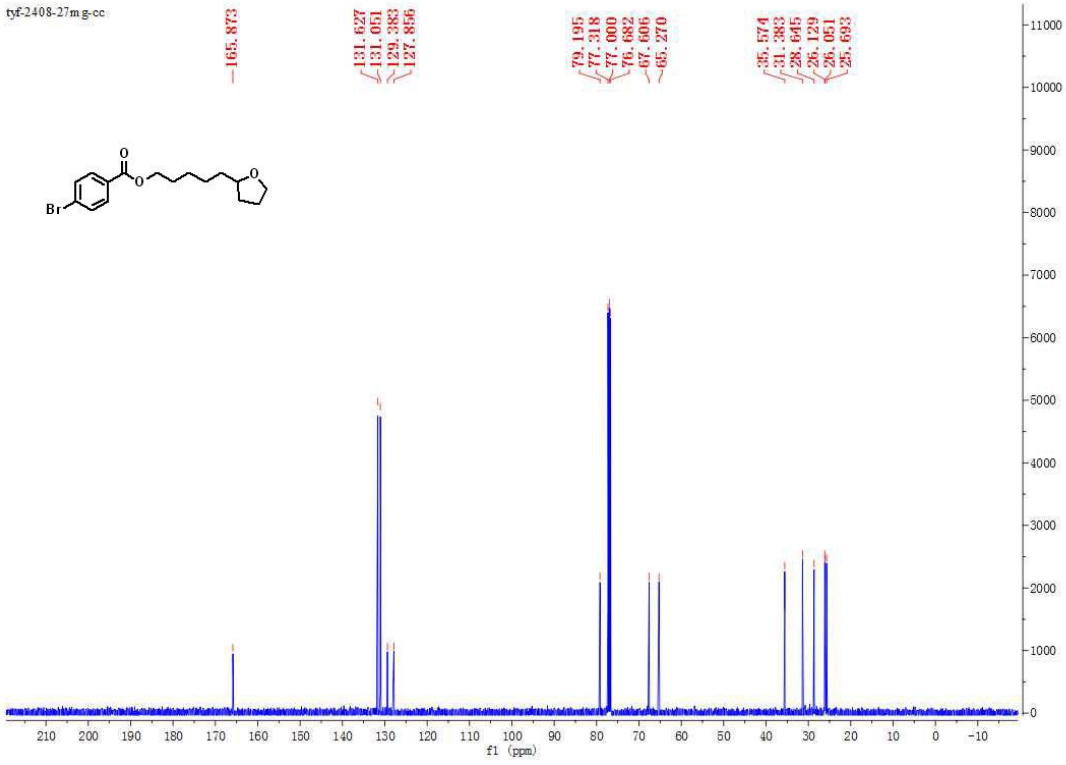
46-^{13}C NMR



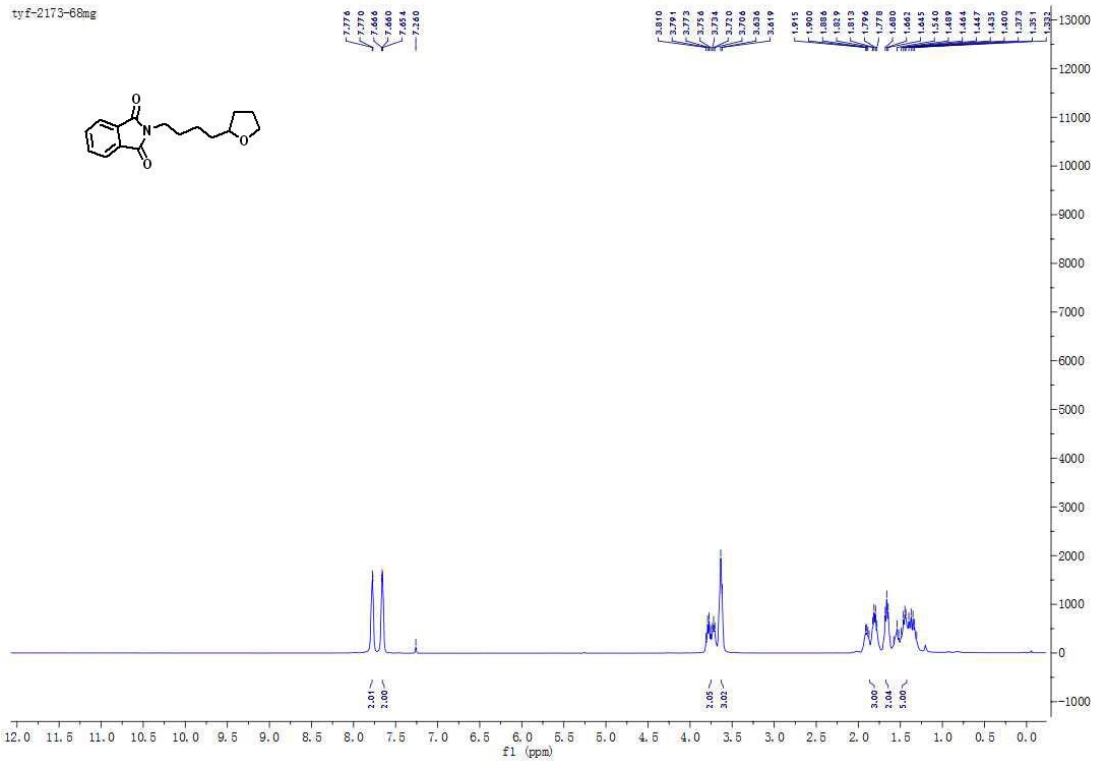
47-^{1}H NMR



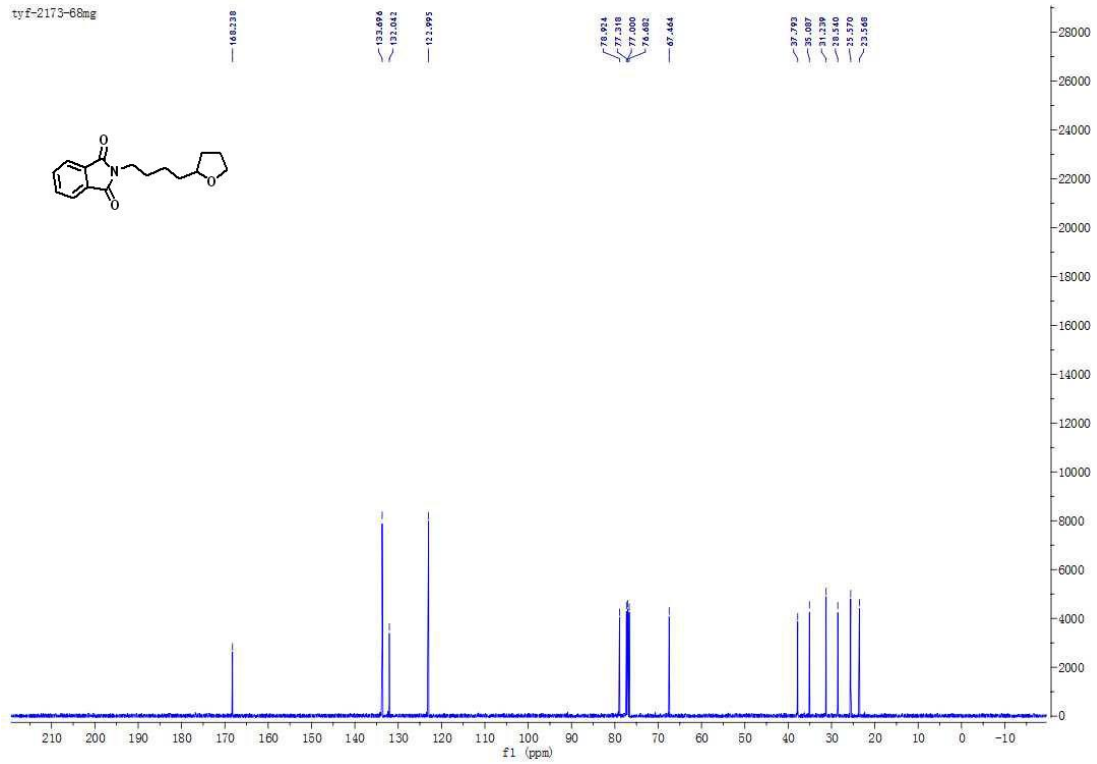
47-^{13}C NMR



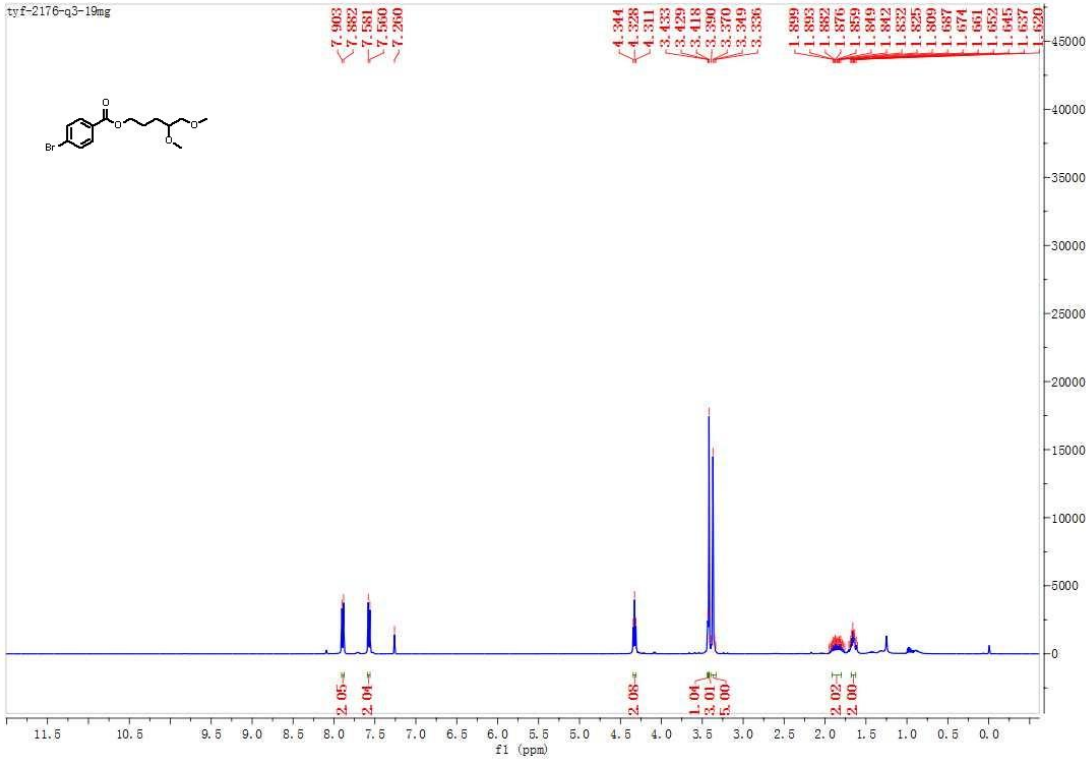
48-^{1}H NMR



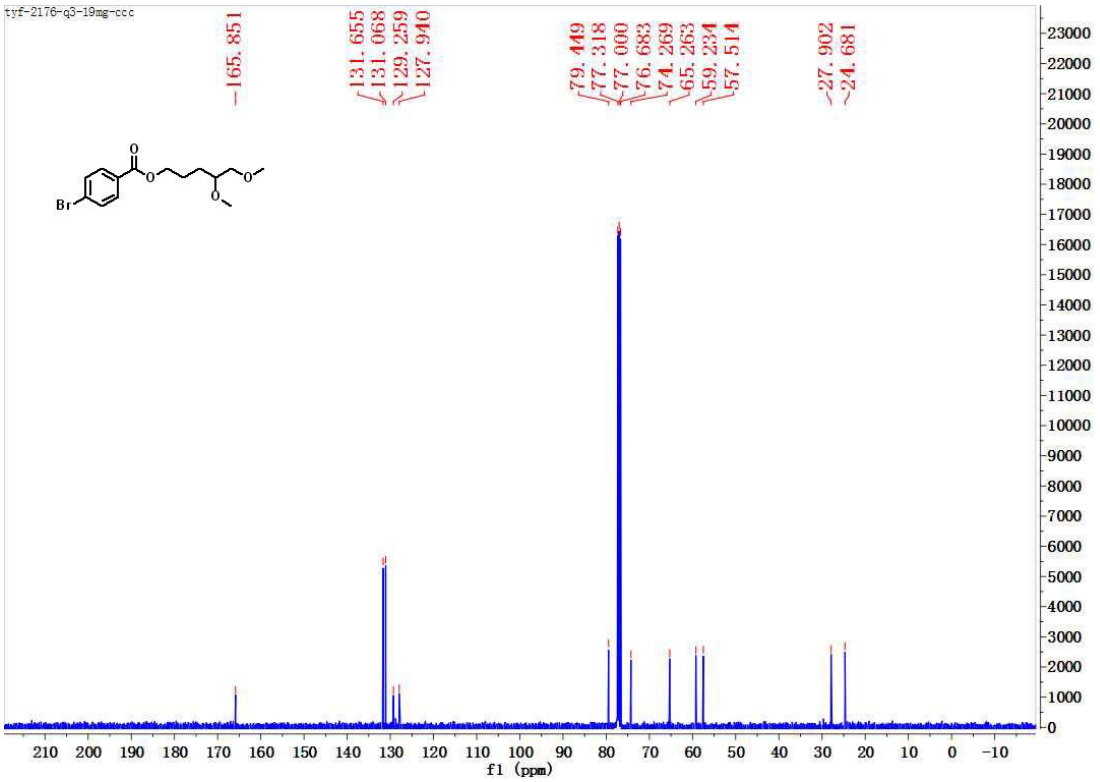
48-^{13}C NMR



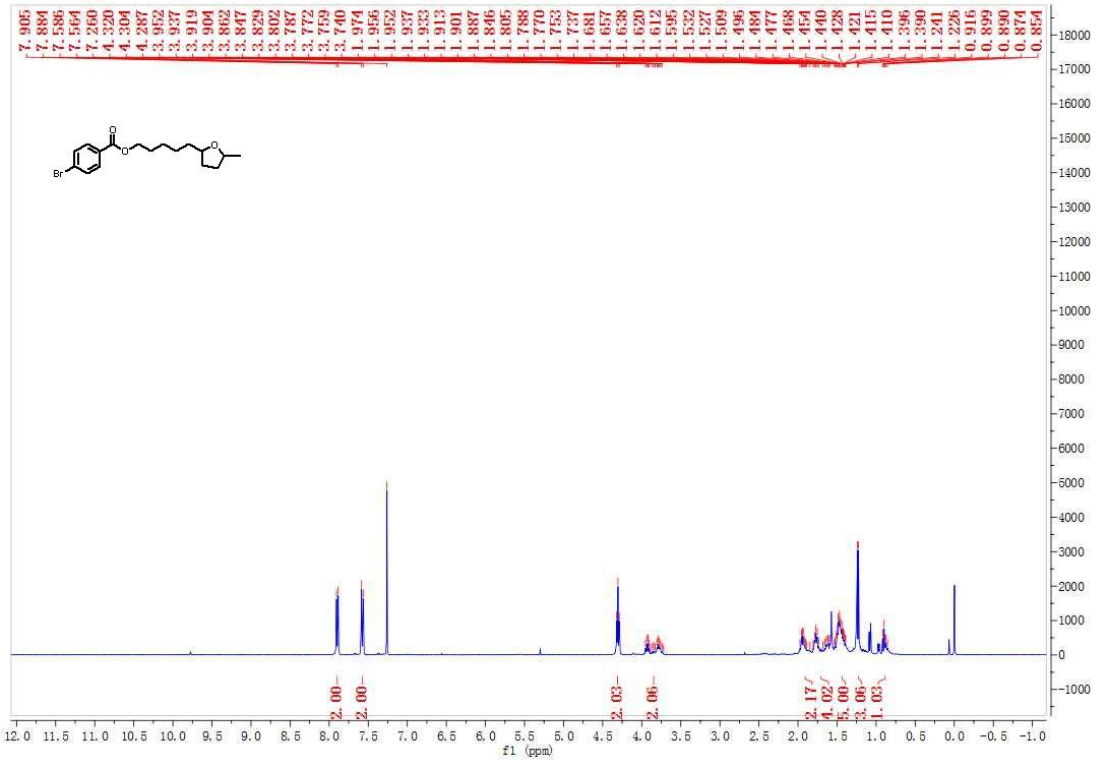
49-^{1}H NMR



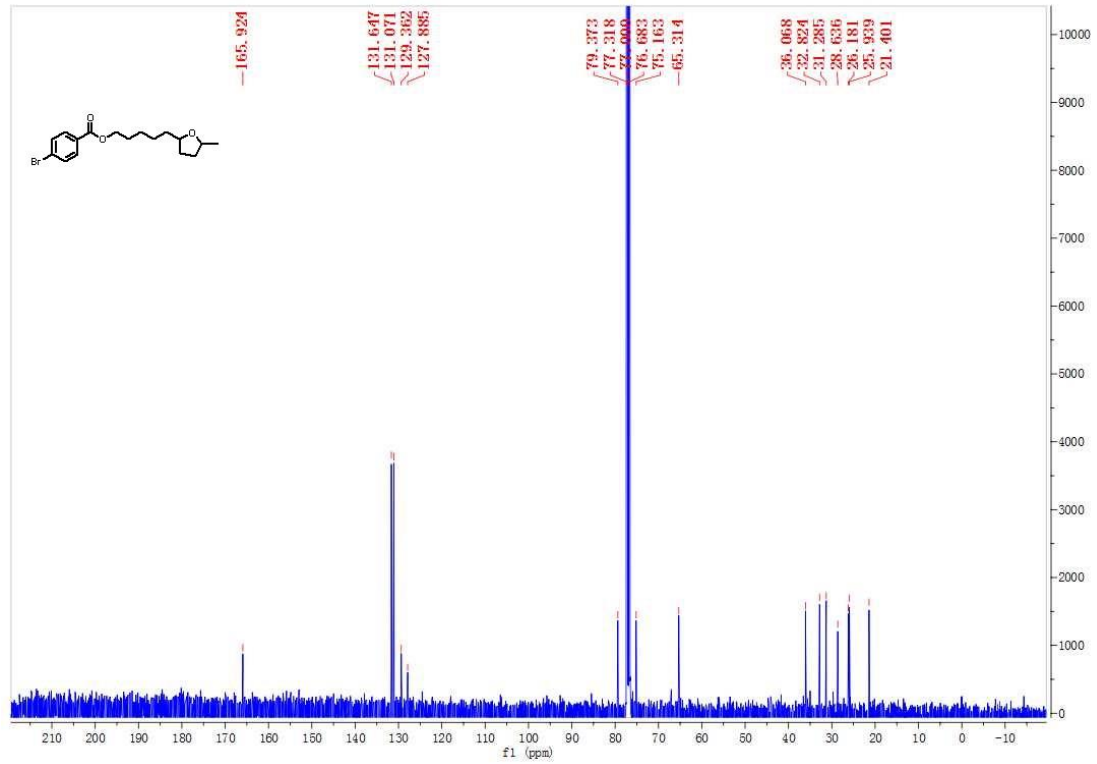
49-^{13}C NMR



50-^{1}H NMR



50-^{13}C NMR



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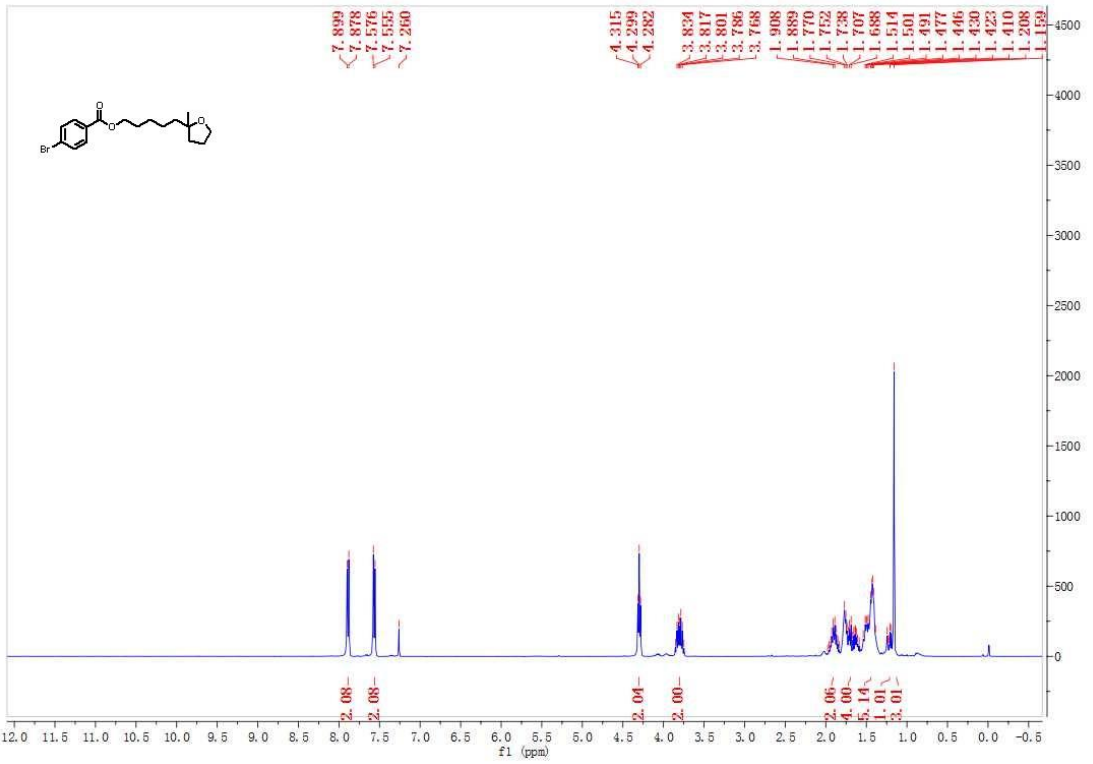
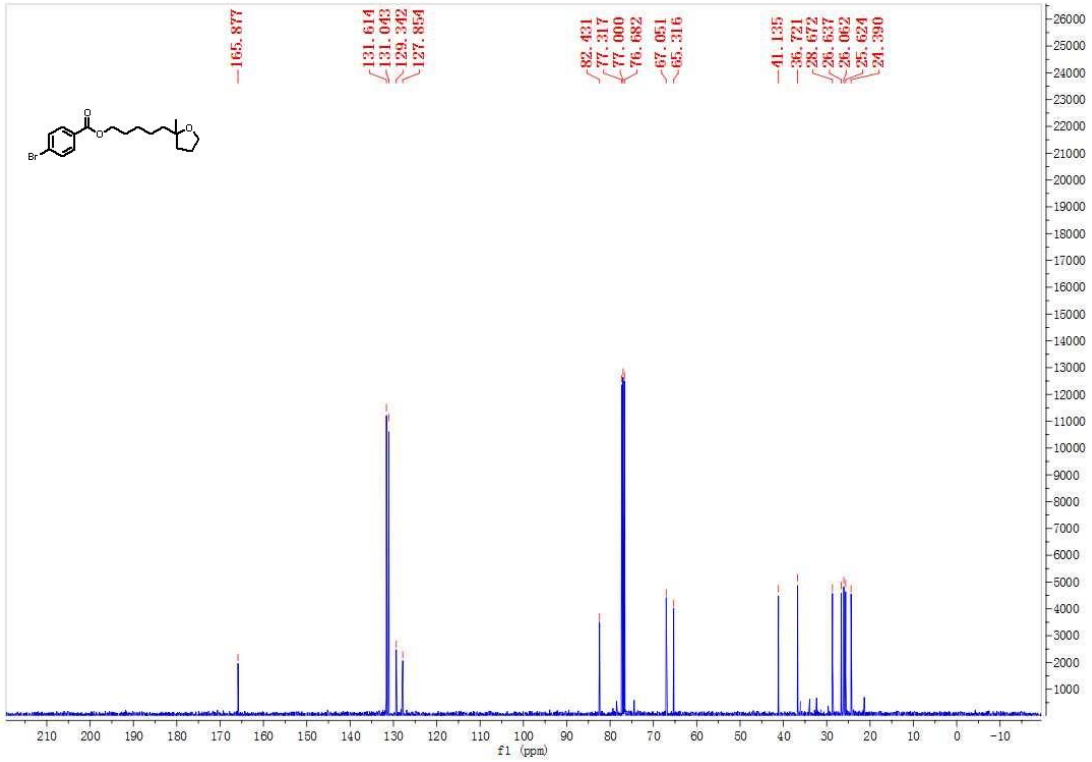
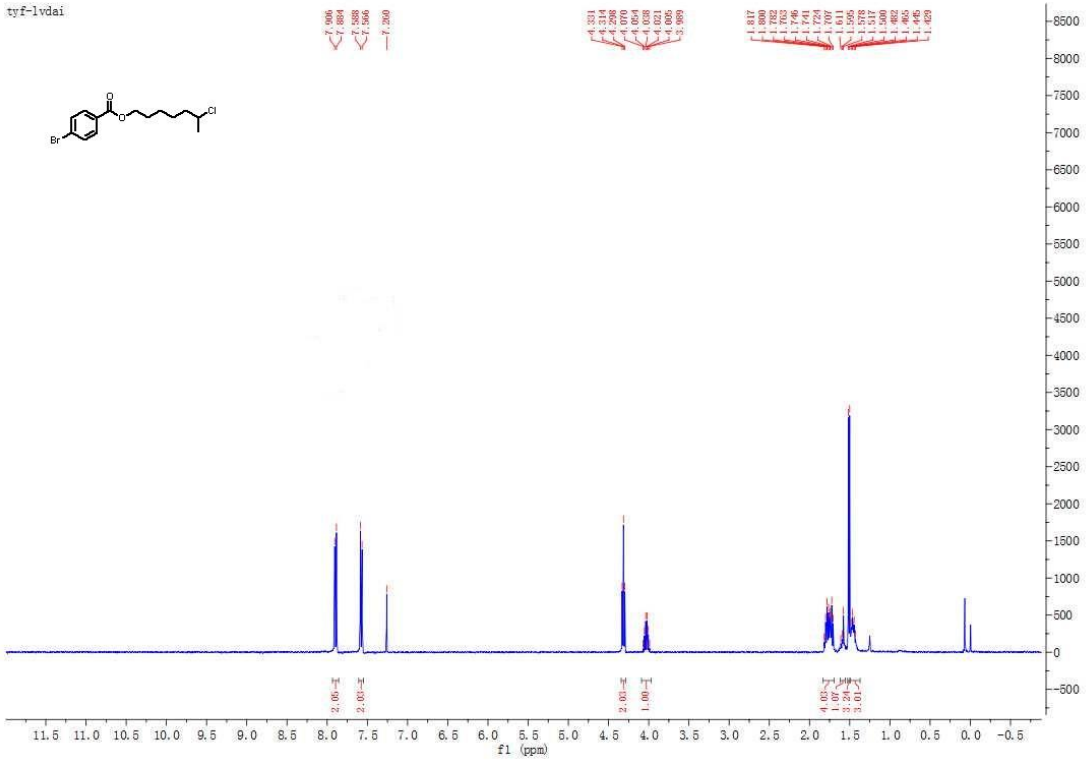


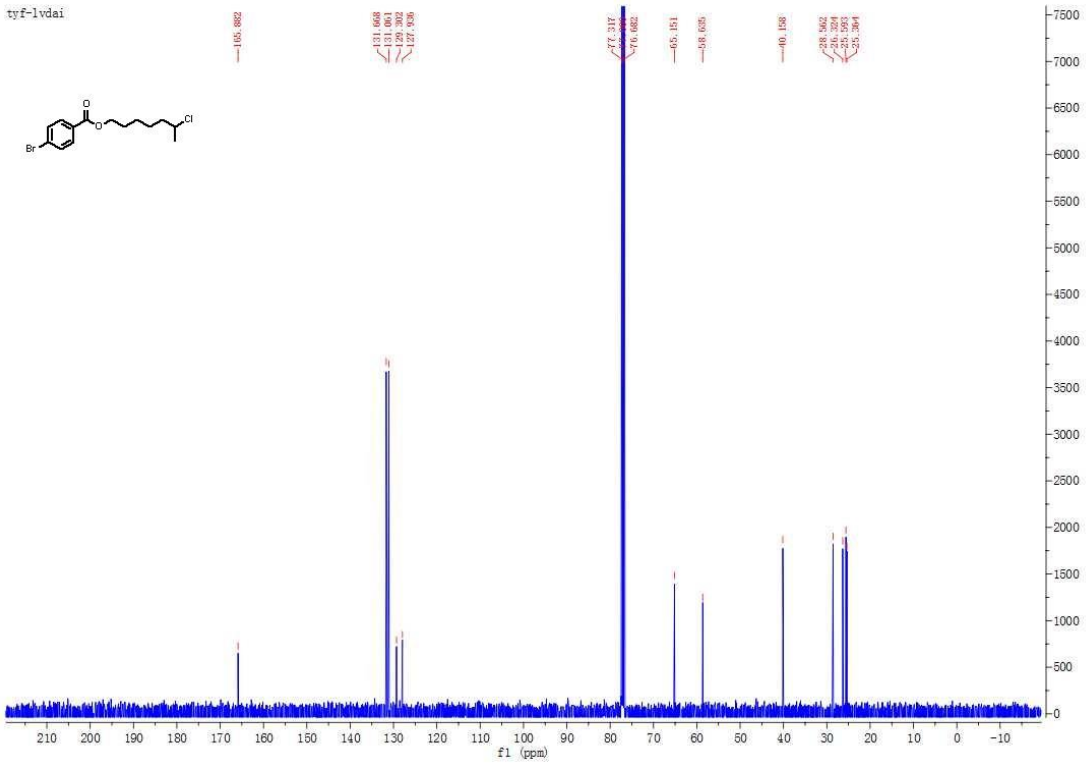
50'-^{13}C NMR



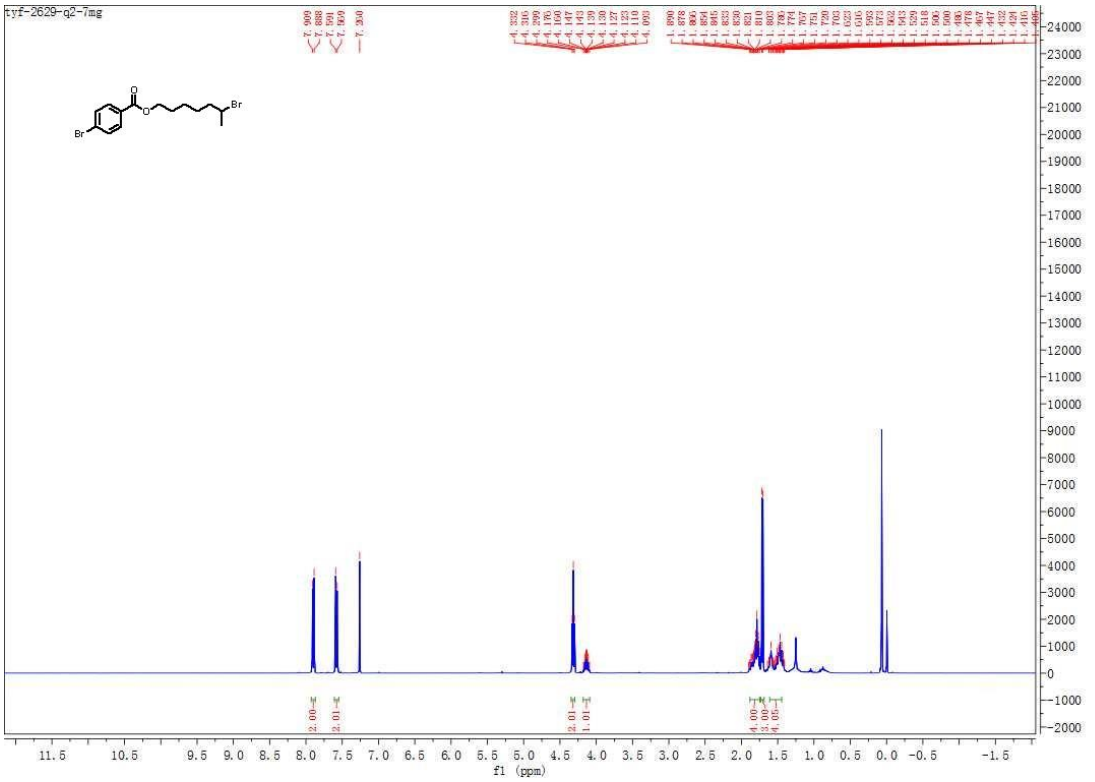
51-^{1}H NMR



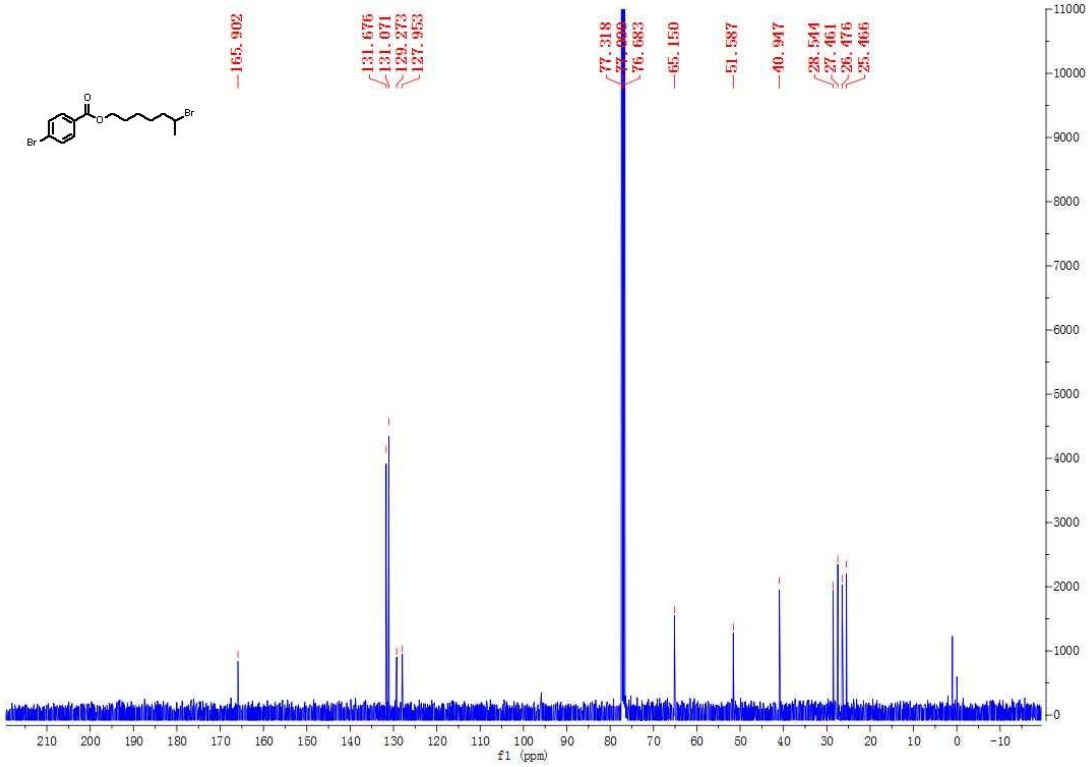
51-^{13}C NMR



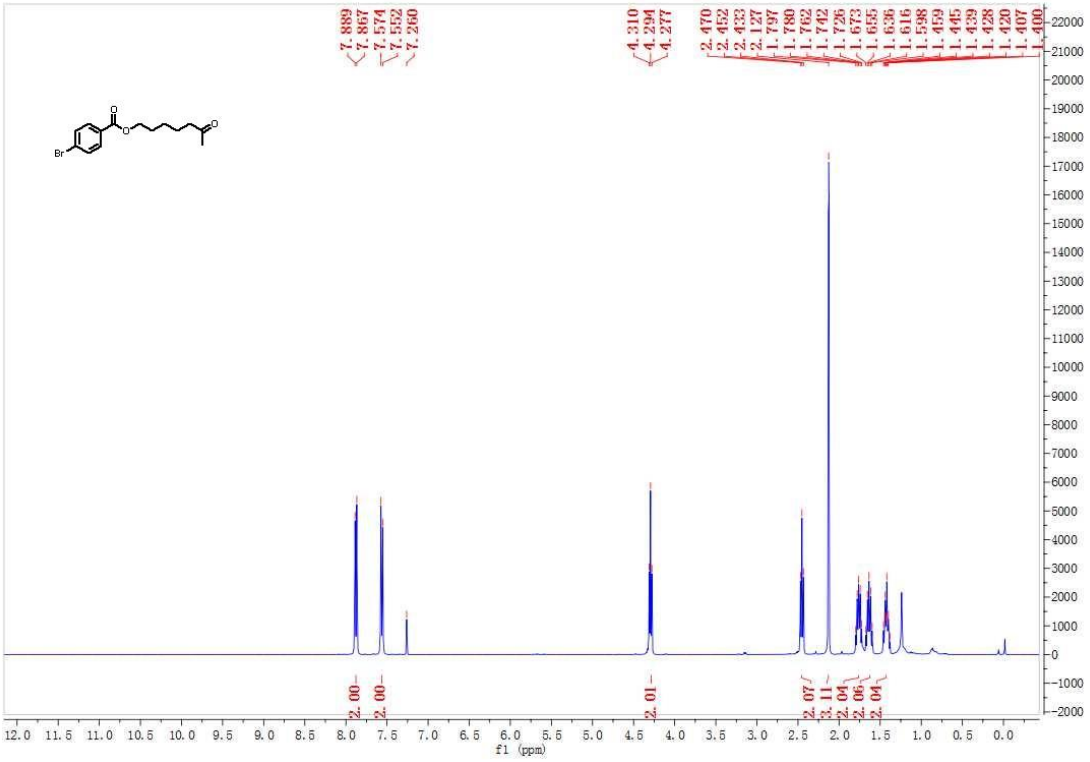
52-^{1}H NMR



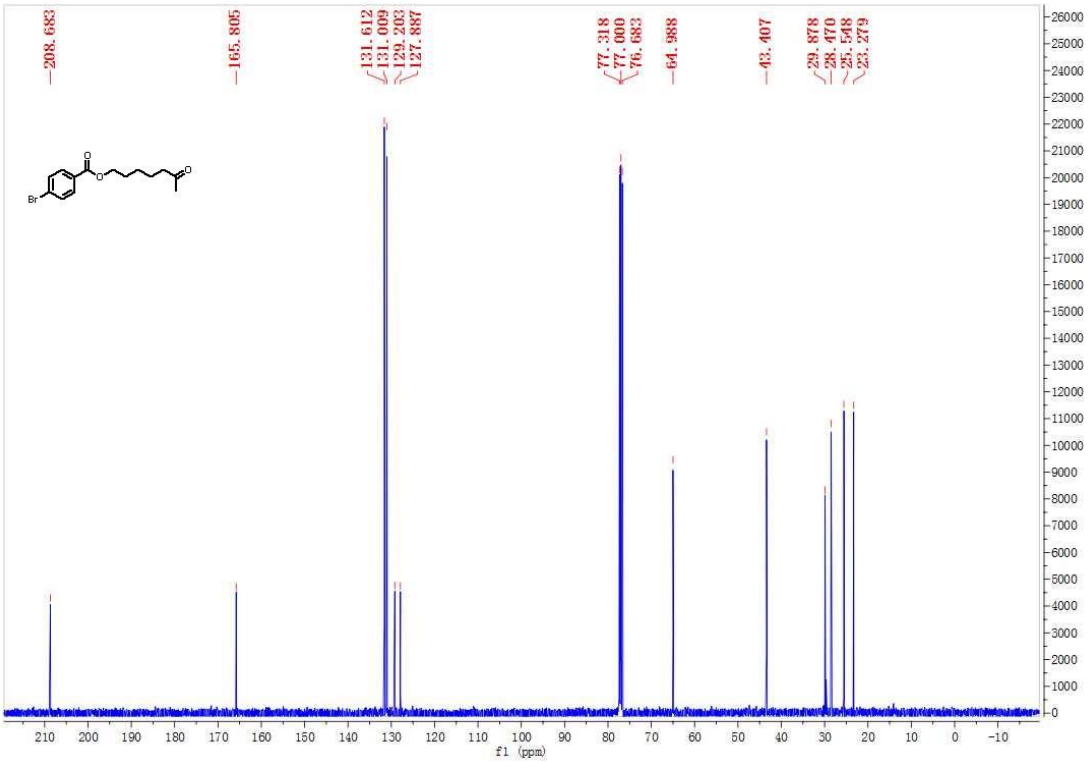
52-^{13}C NMR



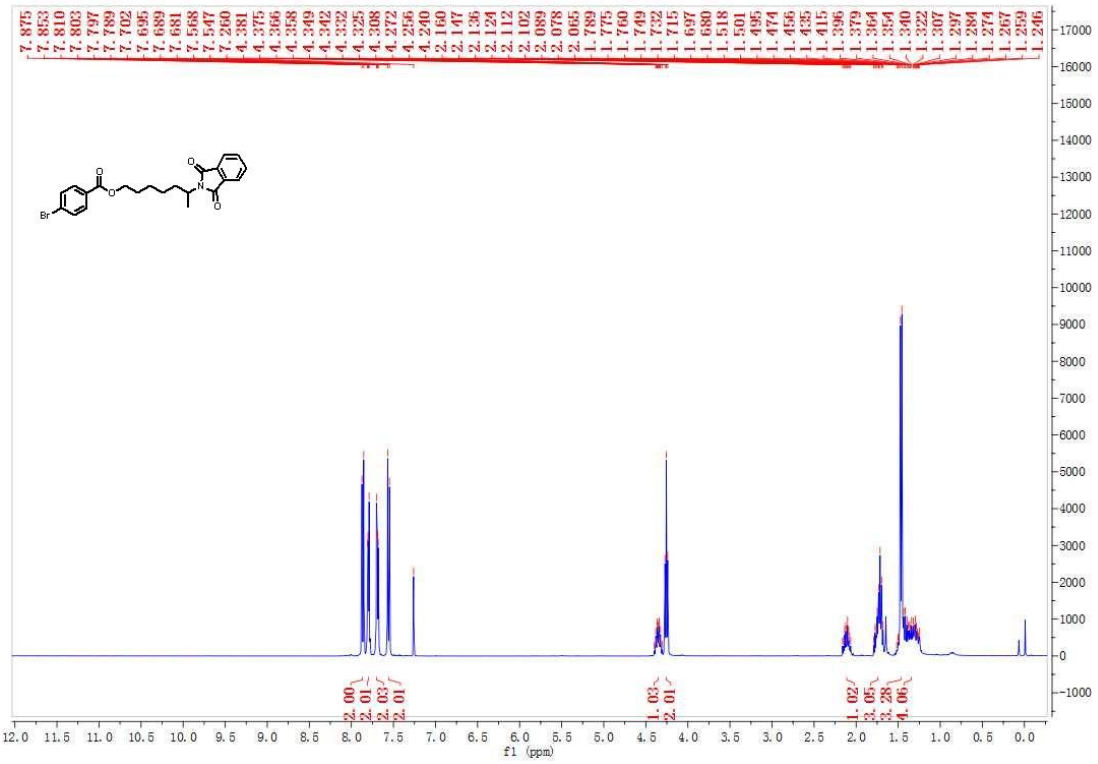
53-^{1}H NMR



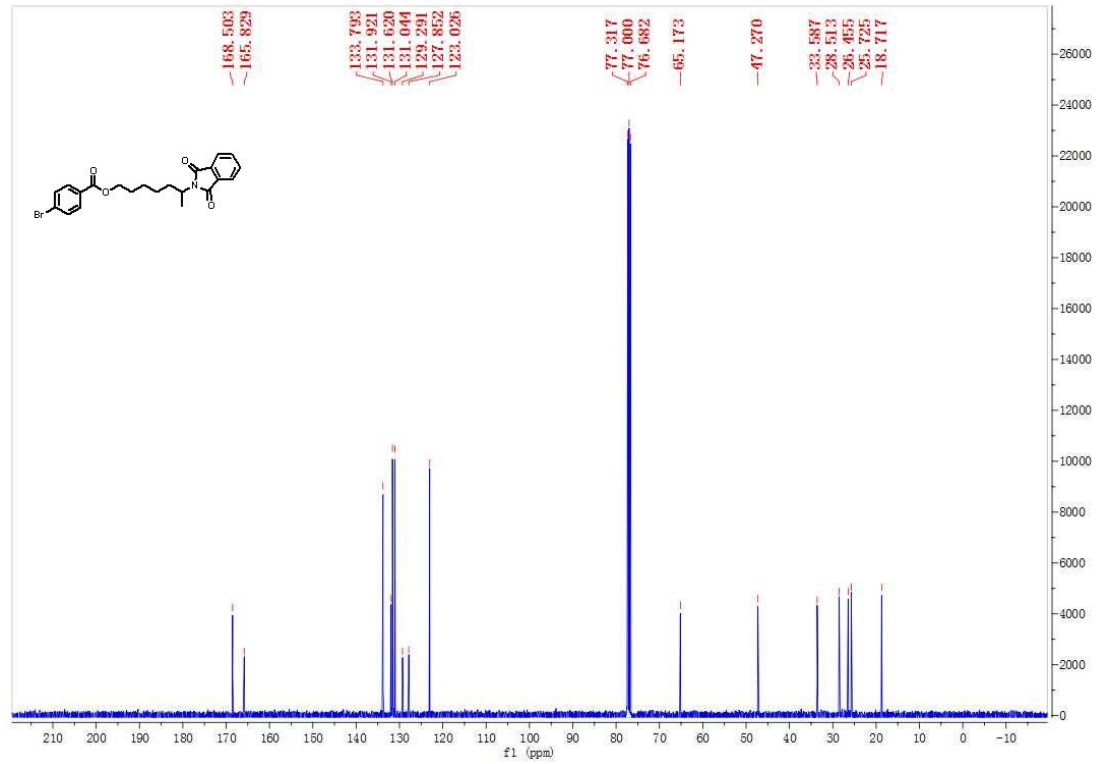
53-^{13}C NMR



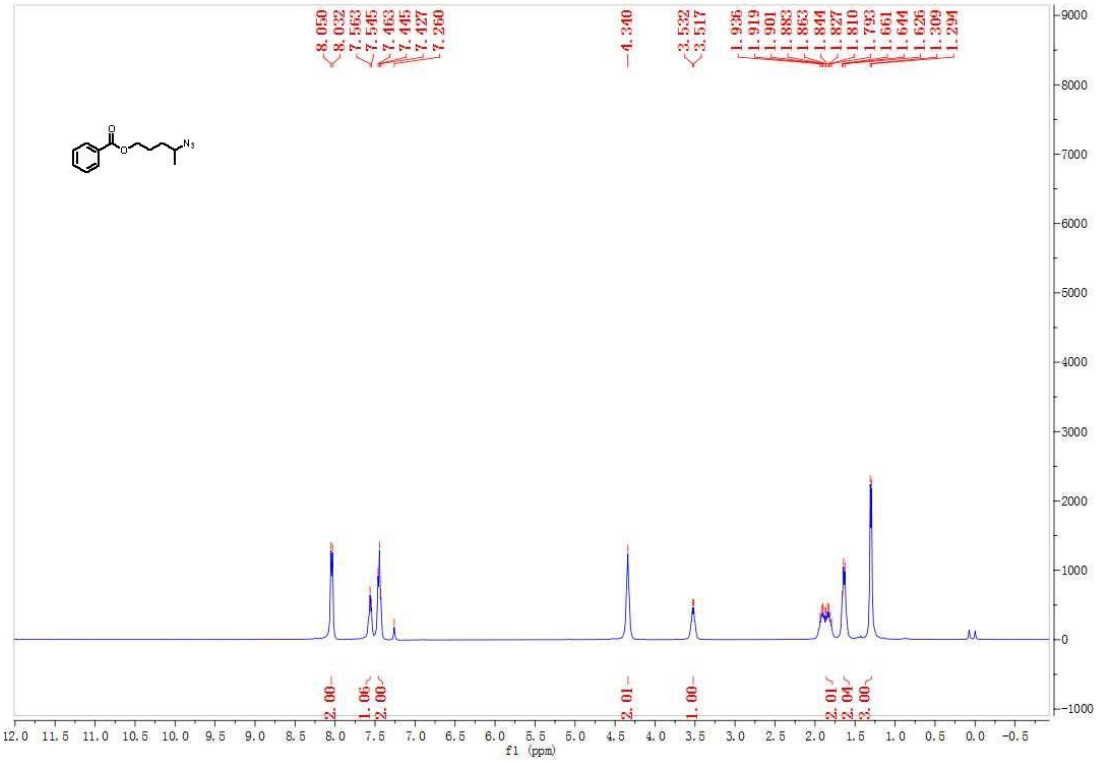
54-^{1}H NMR



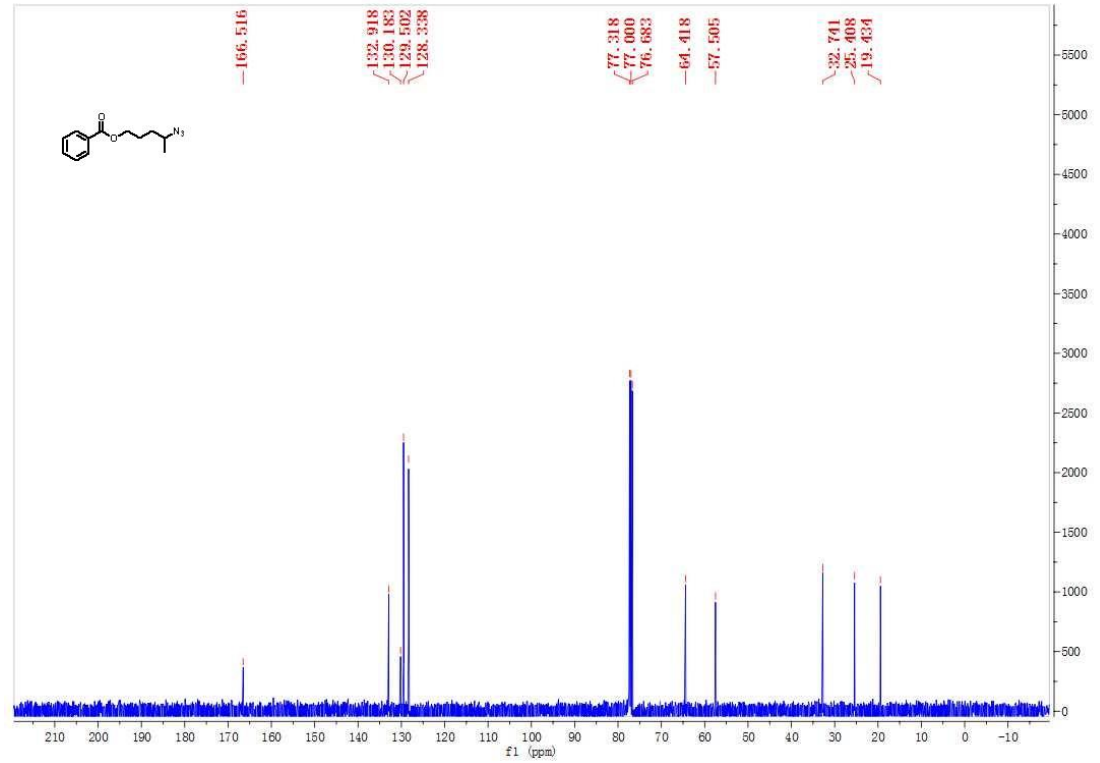
54-^{13}C NMR



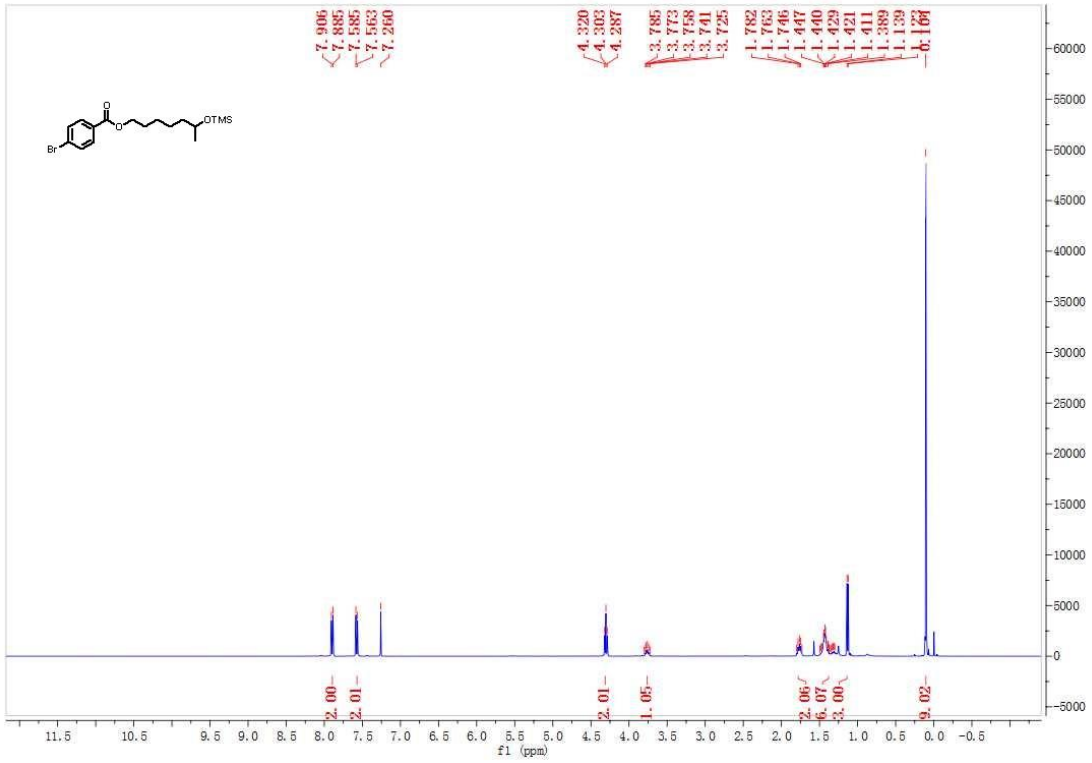
55-^{1}H NMR



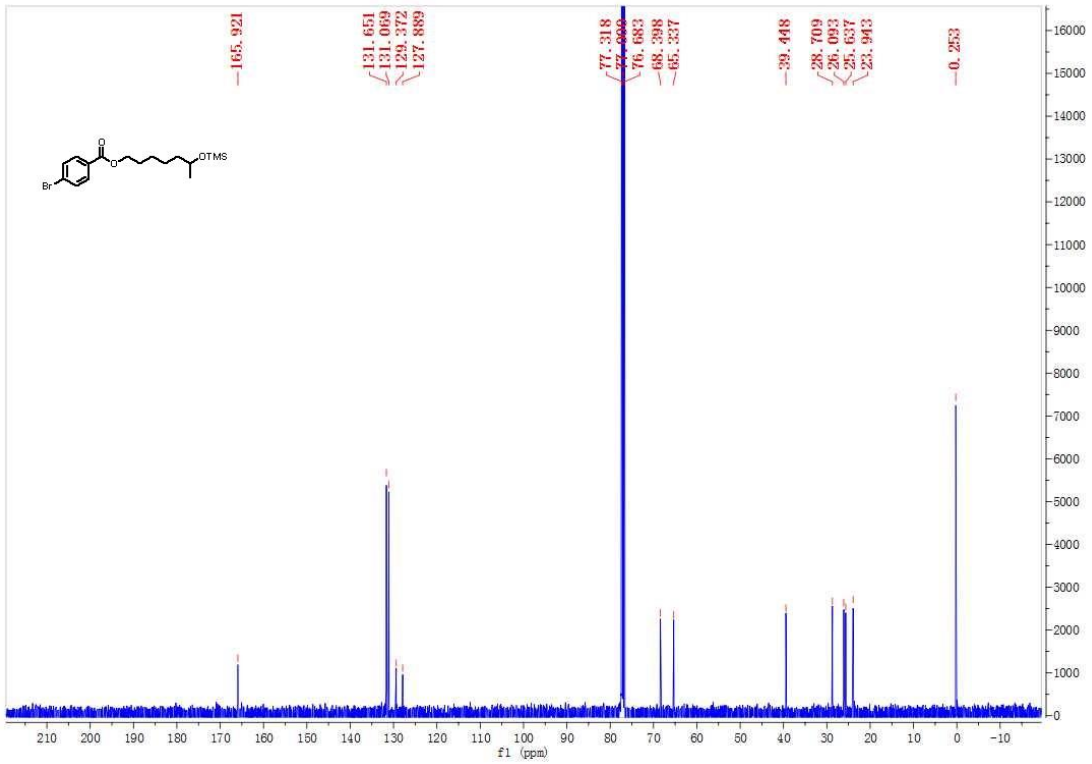
55-^{13}C NMR



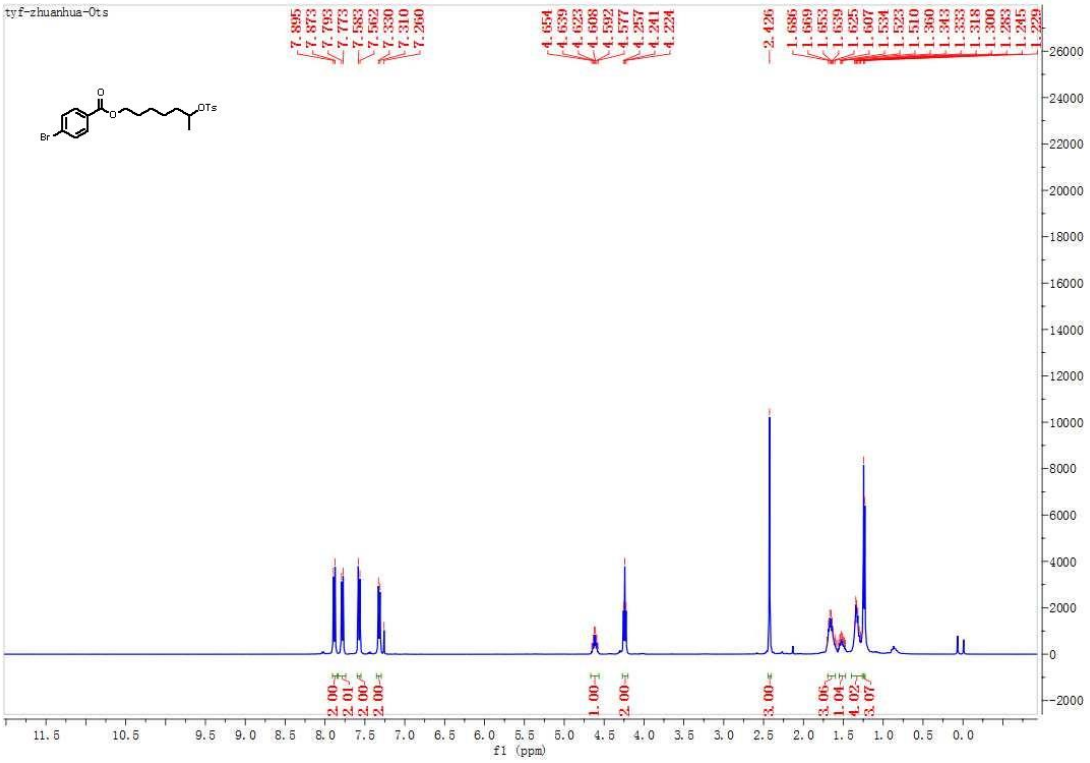
56-^{1}H NMR



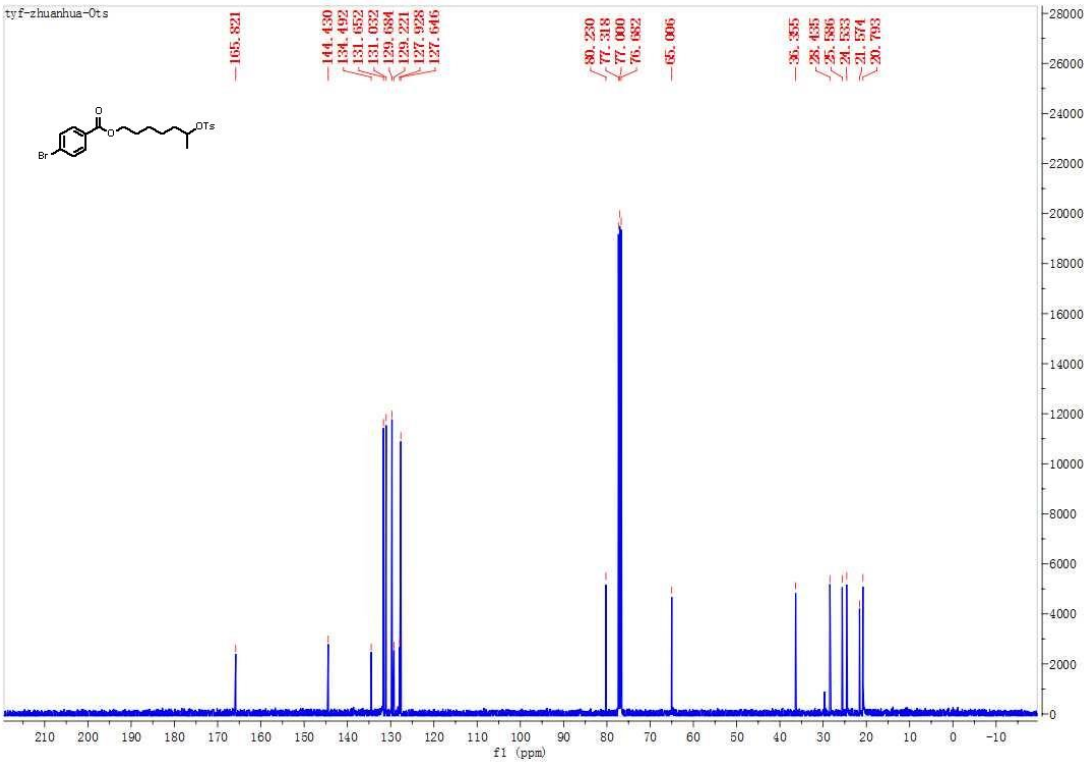
56-^{13}C NMR



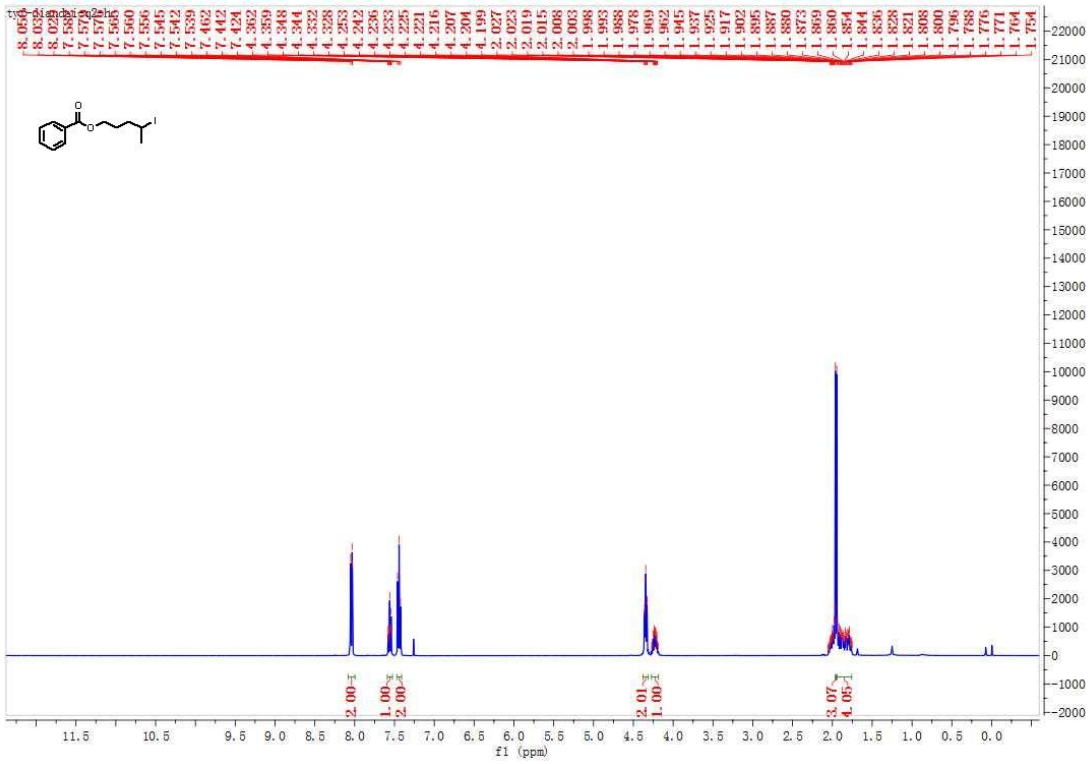
57-^{1}H NMR



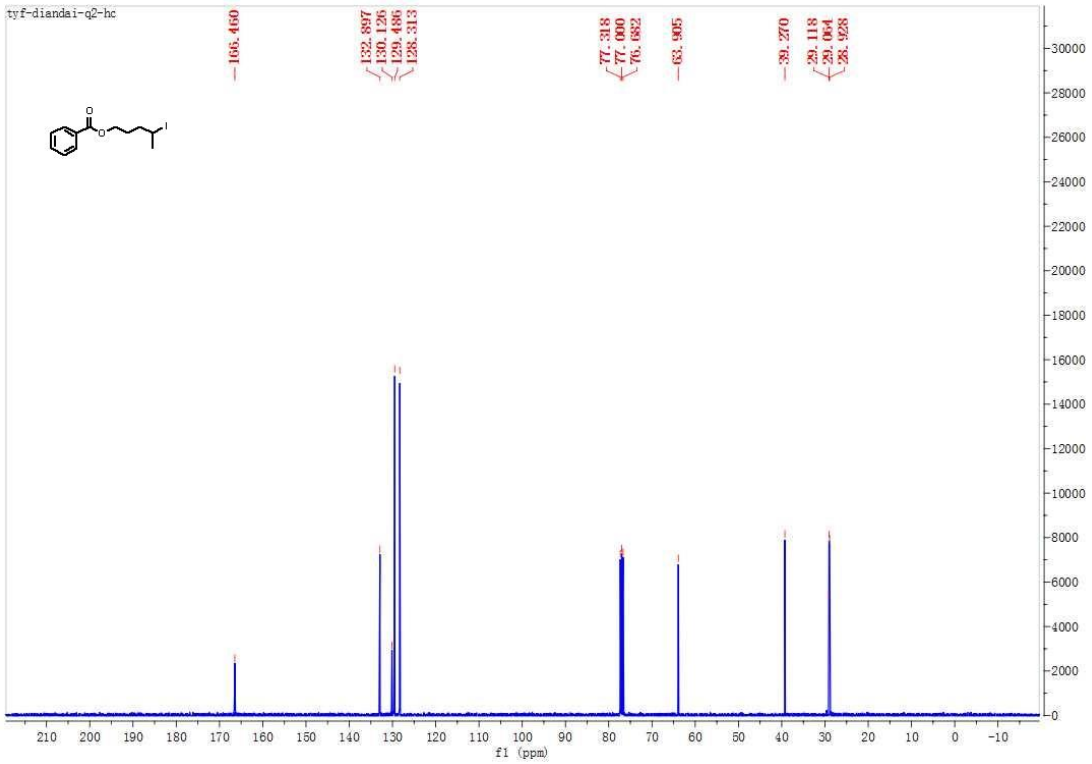
57-^{13}C NMR



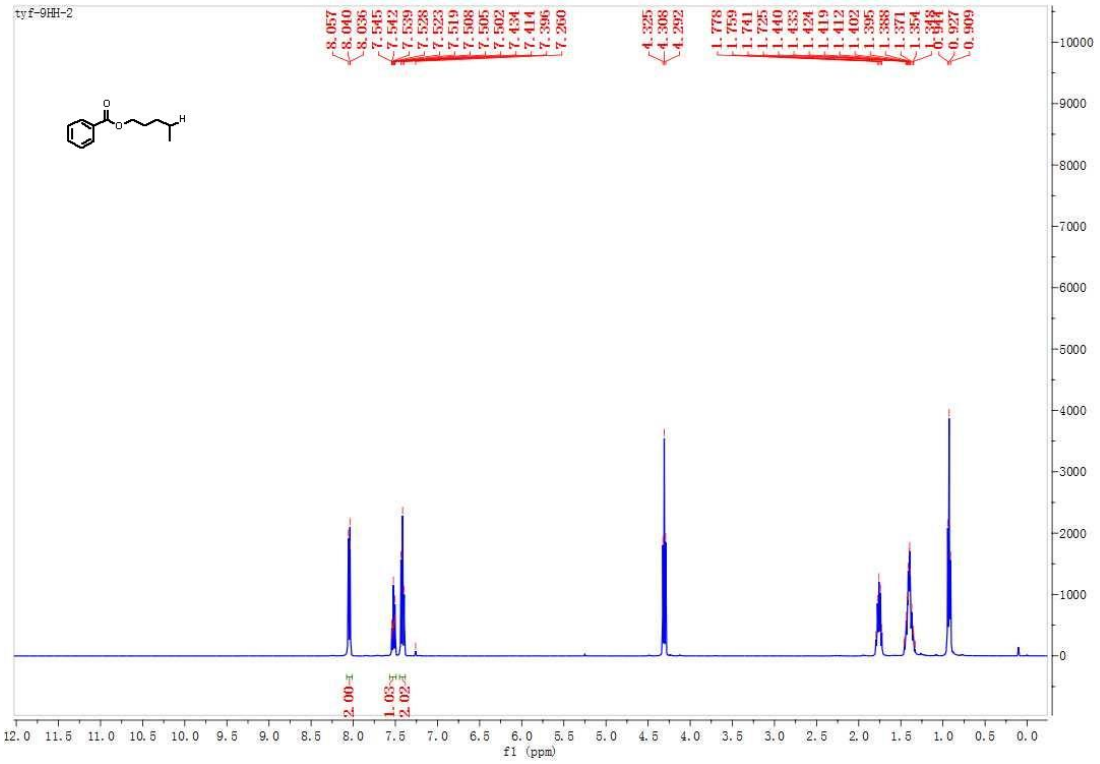
58-^{1}H NMR



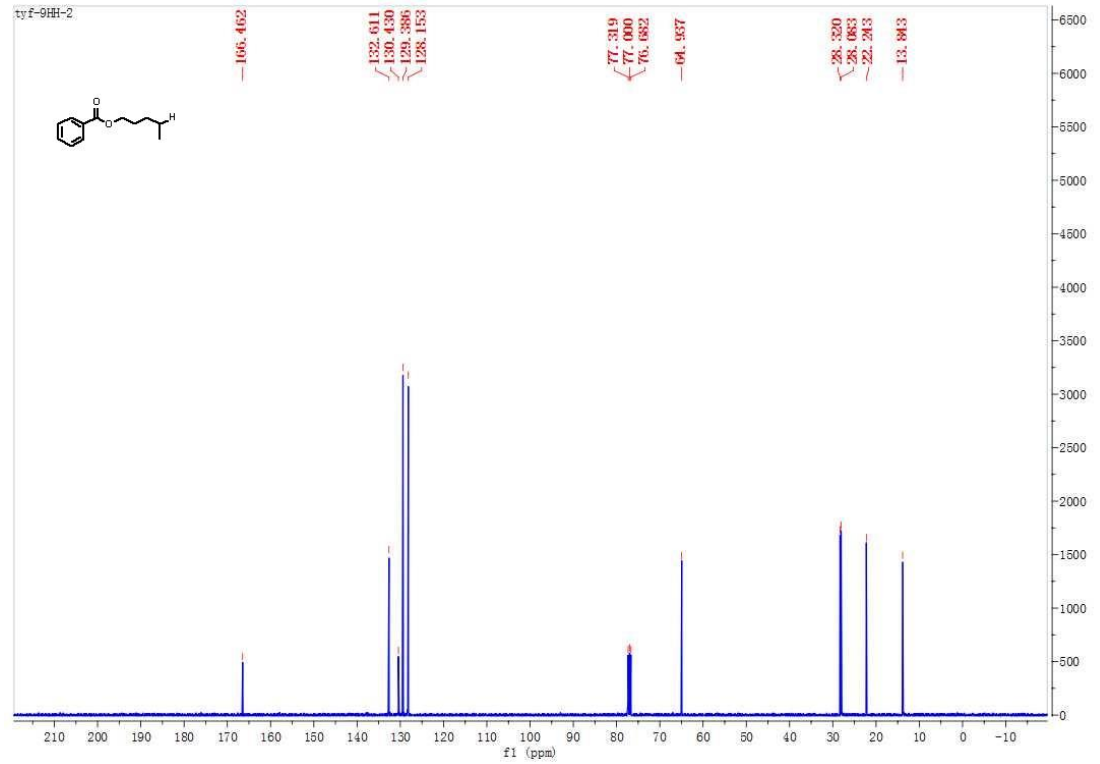
58-^{13}C NMR



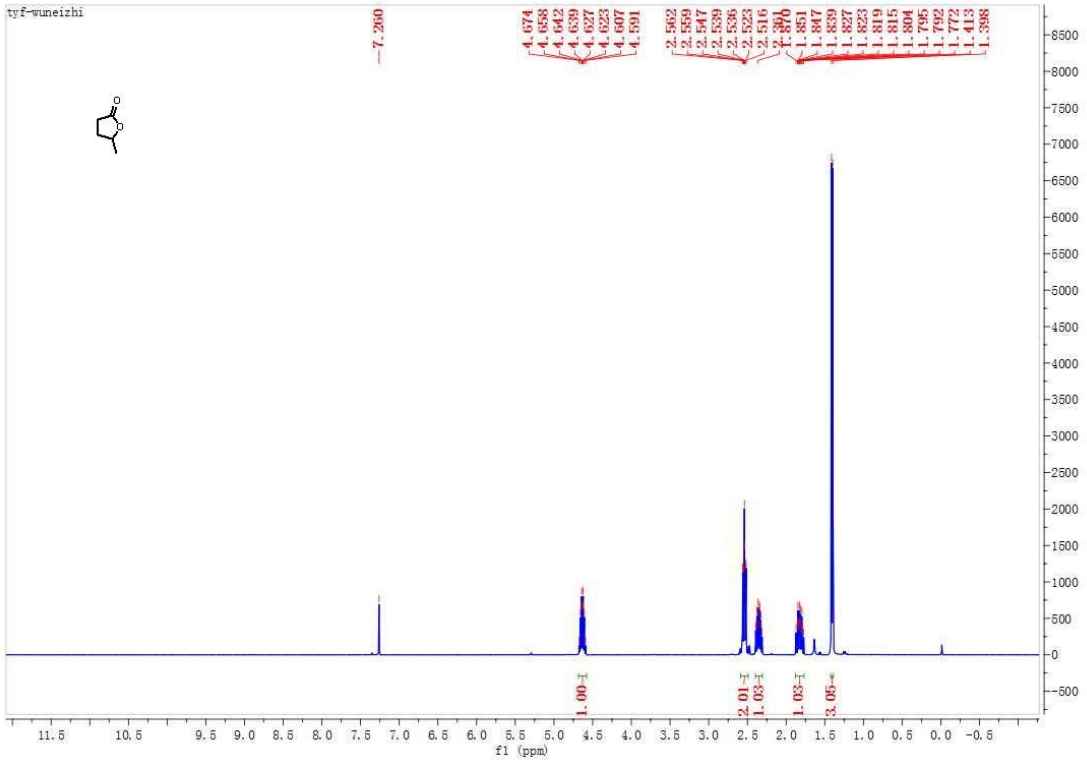
59-^{1}H NMR



59-^{13}C NMR



60-^{1}H NMR



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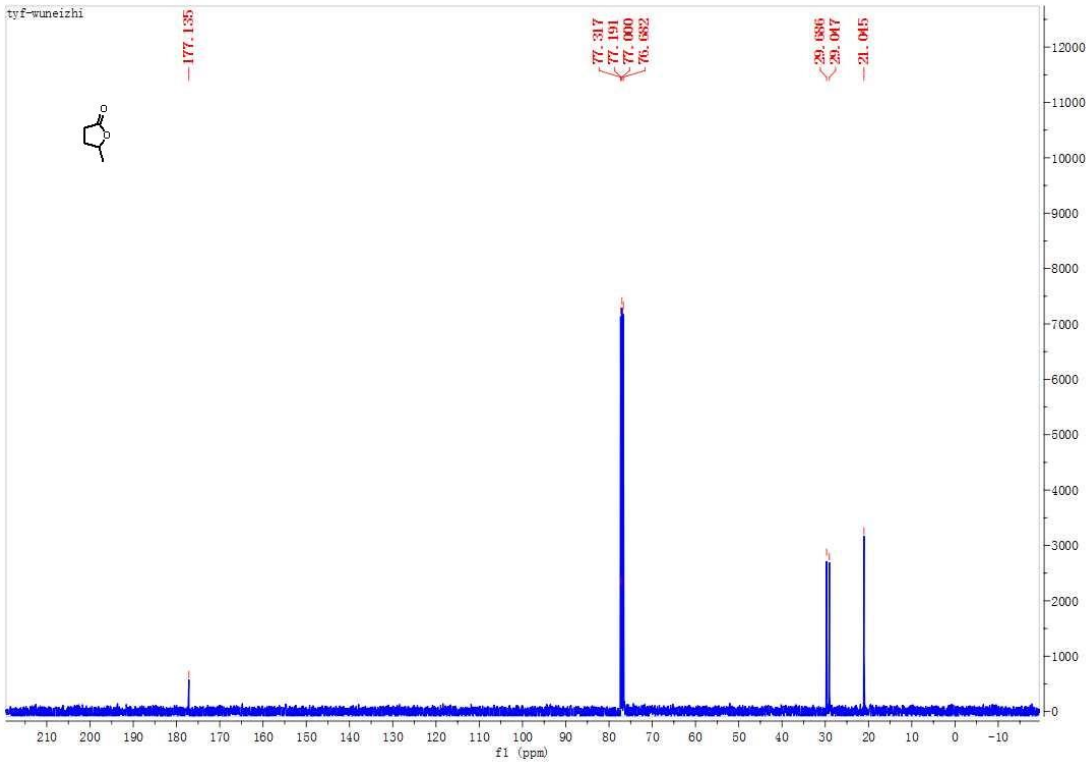
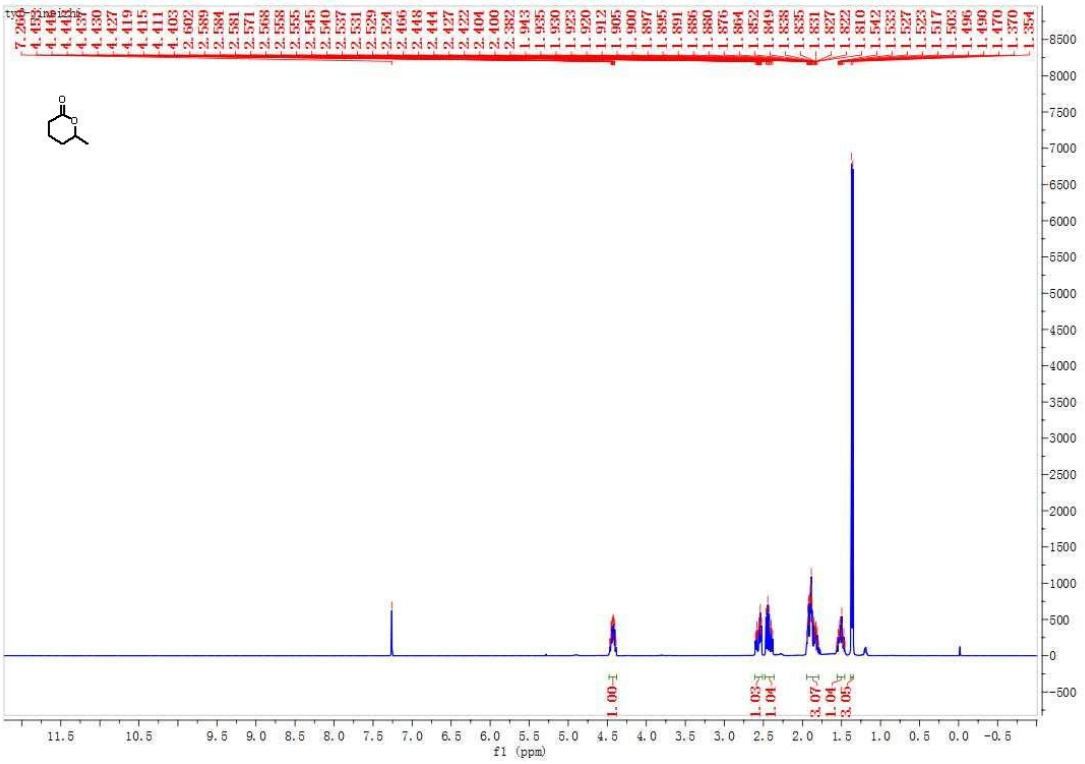


61-^{1}H NMR



61-^{13}C NMR