Supporting Information

Site-selective 2º C-H chlorination of alkane by metal-free electrochemistry

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Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Superdry solvents and deuterated solvents were purchased from Energy Chemical. Starting materials for this study were purchased from Leyan or were synthesized according to reported procedures.

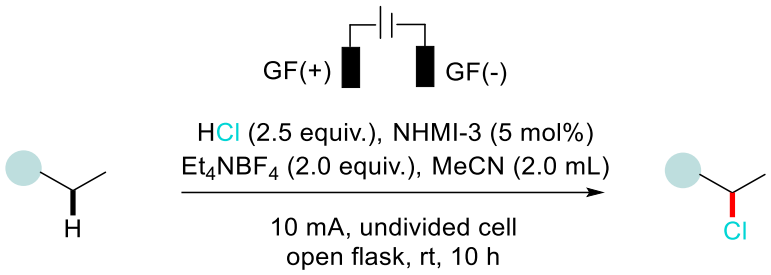
TLC were performed on silica gel Leyan HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λmax = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Shanghai Haohong Scientific Co., Ltd.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectrometry (HRMS) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS). GC analysis was performed on 7890A-7000C/Agilent. HPLC analysis was performed on 1260 Infinity II/Agilent with ZORBAX SB-C18 columns. All reactions were carried out in a 10.0 mL of Glass bottles.

3. General procedure

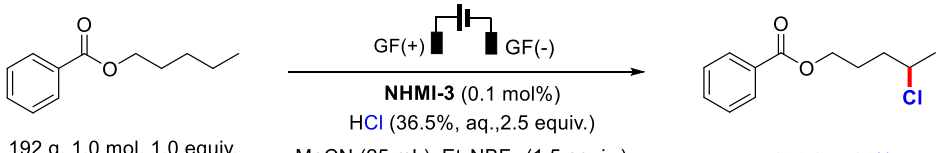
3.1 Electrochemical chlorination of C(sp^3)-H bond



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. Substrate (1.0 mmol, 1.0 equiv.) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5%, aqueous, 2.5 mmol, 2.5 equiv.) was added in batches, first added one portion of HCl (1.5 equiv.) to react for about 5 hours, and then added another portion of HCl (1.0 equiv.). The reaction mixture was electrolyzed with a constant current of 10 mA at room temperature. After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired product. It is worth noting that the reaction mixture always opened to air during C(sp^3)-H bonds chlorination reactions.

4. Gram-scale experiment:

4.1 Hectogram-scale experiment 1a



Put two graphite felts ($5^2\pi$ cm^2 x 0.5 cm) as both cathode and anode in a 500 mL of beaker. The graphite felt electrode attached to a platinum wire. Et_4NBF_4 (1.5 equiv.) was first dissolved in MeCN (25.0 mL) and stirred for 30 min at room temperature. Substrate **1a** (1.0 mol, 1.0 equiv.) and **NHMI-3** (0.1 mol%) then were added. Finally,

HCl (concentrated, 36.5%, aqueous, 2.5 mol, 2.5 equiv.) was added in batches, first add 60.0 mL, then add 30.0 mL every 6 hours, for a total of 210.0 mL HCl. The reaction mixture was stirred and electrolyzed with a constant current of 1.5 A at room temperature for 36 h. After the reaction completed as monitored with TLC, the solvents were removed in *vacuo* and the residue was purified by silica gel flash chromatography to give the desired products **1b** (144.6 g, 64 %). It is worth noting that the recovery rate of **NHMI-3** is 71 %. The site-selectivity is 97:3, which was determined by GC-MS. Faraday efficiency η = 64% (The calculation method is shown on page S32).

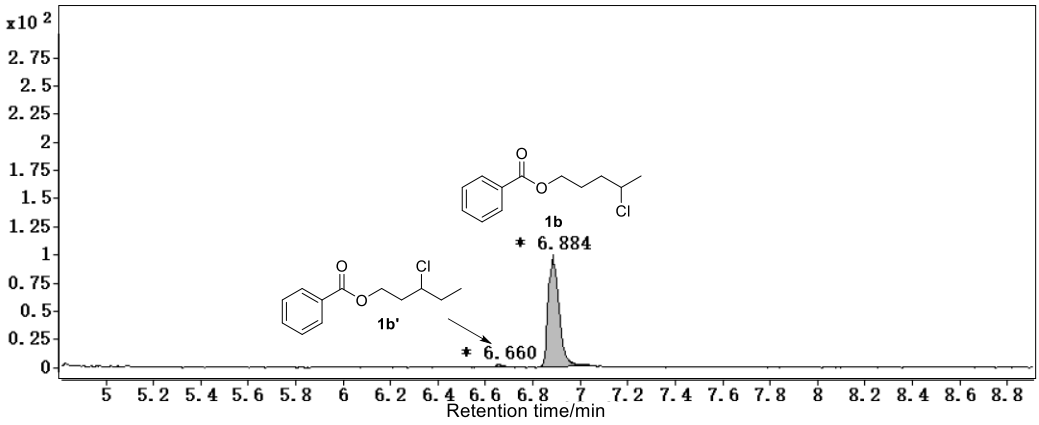
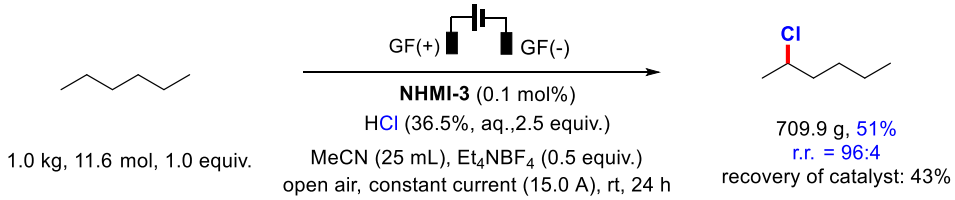


Figure S1. Chromatogram of hectogram-scale **1a**

Chromatogram of hectogram **1a**: Selectivity		
Product	Retention Time	Percent Area
1b	6.884	97.16
1b'	6.660	2.84

Table S1. Site-selectivity of hectogram-scale **1a**

4.1 Kilogram-scale experiment - hexane



Put two graphite felts ($10^2\pi$ cm^2 x 0.5 cm) as both cathode and anode in a 4000 mL of beaker. The graphite felt electrode attached to a platinum wire. Et_4NBF_4 (0.5 equiv.) was first dissolved in MeCN (25.0 mL) and stirred for 30 min at room temperature. Substrate hexane (11.6 mol, 1.0 kg, 1.0 equiv.) and **NHMI-3** (0.1 mol%, 9.5g) then were added. Finally, HCl (concentrated, 36.5%, aqueous, 29.0 mol, 2.5 equiv.) was

added in batches, first add 900.0 mL, then add 500.0 mL every 6 hours, for a total of 2400.0 mL HCl. The reaction mixture was stirred and electrolyzed with a constant current of 15.0 A at room temperature for 24 h. We analyzed 2.0 μL of sample by GC-MS every 1 h. After the reaction is completed, it is distilled at 69 ℃ under atmospheric pressure carefully. Purify the residue by column chromatography on silica gel with ethyl acetate and petroleum ether (1: 100) as eluent to obtain pure product 2-chlorohexane (709.9 g, 51% yield). It is worth noting that the recovery rate of **NHMI-3** is 43 %. The site-selectivity is 96:4, which was determined by GC-MS. Faraday efficiency η = 88% (The calculation method is shown on page S32).

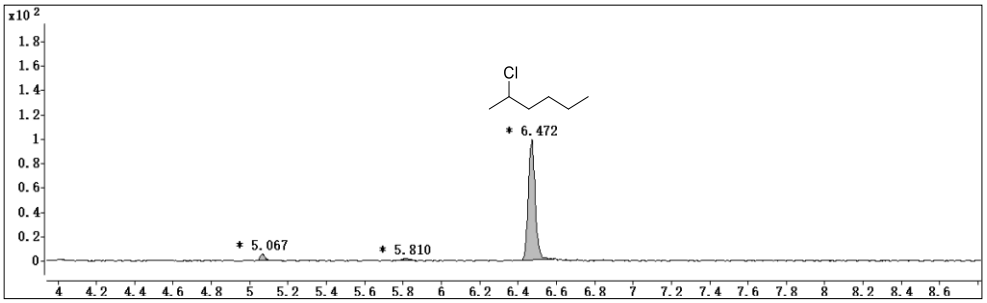
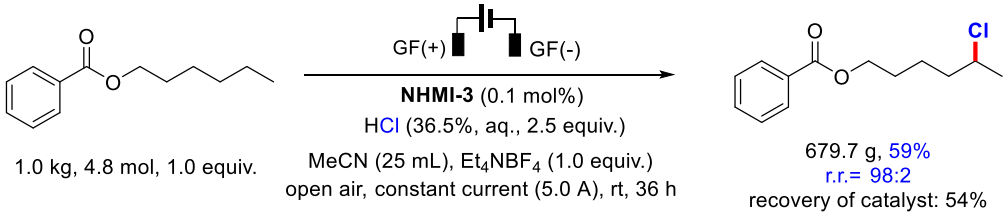


Figure S2. Chromatogram of kilogram-scale **hexane**

Chromatogram of kilogram-scale **hexane**: Selectivity		
Product	Retention Time	Percent Area
2-chlorohexane	6.472	96.27
unknow	5.810	3.73
hexane	5.067	--

Table S2. Site-selectivity of kilogram-scale **hexane**

4.3 Kilogram-scale experiment - 3a



Put two graphite felts ($10^2\pi$ cm^2 x 0.5 cm) as both cathode and anode in a 1000 mL of beaker. The graphite felt electrodes attached to a platinum wire. Et_4NBF_4 (1.0 equiv.) was first dissolved in MeCN (25.0 mL) and stirred for 30 min at room temperature. Substrate **3a** (4.8 mol, 1.0 equiv.) and **NHMI-3** (0.1 mol%, 3.9g) then were added. Finally, HCl (concentrated, 36.5, aqueous, 12.0 mol, 2.5 equiv.) was added in batches,

first add 400.0 mL, then add 120.0 mL every 6 hours, for a total of 1L HCl. The reaction mixture was stirred and electrolyzed with a constant current of 5.0 A at room temperature for 36 h. After the reaction completed as monitored with TLC, the solvents were removed in vacuo and the residue was purified by silica gel flash chromatography to give the desired products **3b** (679.7 g, 59 %). It is worth noting that the recovery rate of **NHMI-3** is 54%. The site-selectivity is 98:2, which was determined by GC-MS. Faraday efficiency η = 84% (The calculation method is shown on page S32).

Note: The two graphite felts should be avoided direct contact during the reaction. We use PTFE to separate the electrodes.

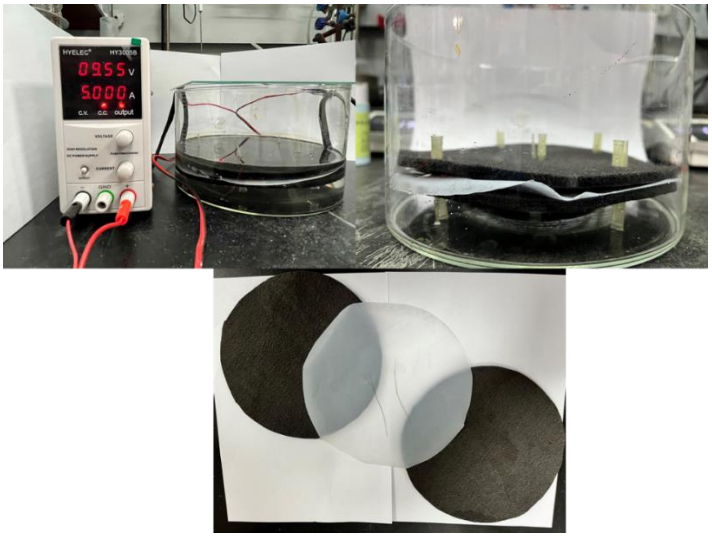


Figure S3. Reaction setup for Kilogram-scale experiments.

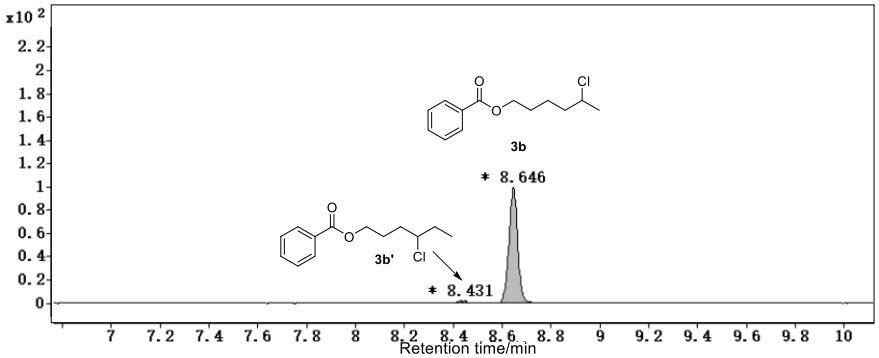


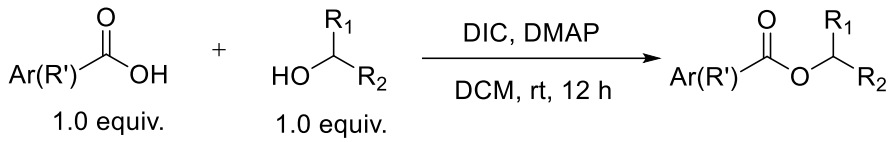
Figure S4. Chromatogram of kilogram-scale **3a**

Chromatogram of kilogram-scale **3a**: Selectivity		
Product	Retention Time	Percent Area
3b	8.646	97.83
3b'	8.431	2.17

Table S3. Site-selectivity of kilogram-scale **3a**

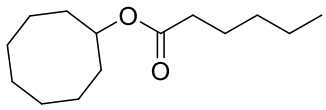
5. Synthesis of substrates

5.1 General procedure for synthesis of Esters:



Carboxylic acid (10.0 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (1.0 mmol, 0.1 equiv.) were added to a flask. DCM (30.0 mL) and corresponding alcohol (10.0 mmol, 1.0 equiv.) were then added, followed by *N,N'*-diisopropylcarbodiimide (DIC) (10.0 mmol, 1.0 equiv.). The reaction mixture was allowed to stir at room temperature overnight, before quenched with H_2O (10.0 mL) and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography to yield pure substrate.

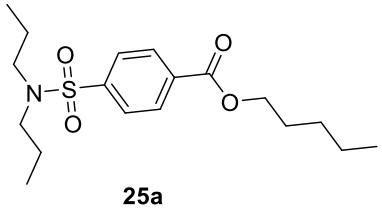
Cyclooctyl hexanoate



20a

R_f = 0.6, 5% acetone in hexane, yellowish oil (1.87 g, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.93 (tt, J = 8.3, 3.9 Hz, 1H), 2.25 (t, J = 7.5 Hz, 2H), 1.78 (ddt, J = 11.7, 5.8, 2.8 Hz, 2H), 1.71 (ddd, J = 14.8, 10.1, 6.9 Hz, 4H), 1.61 (q, J = 7.5 Hz, 4H), 1.55 – 1.48 (m, 6H), 1.33 – 1.27 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.44, 74.88, 34.94, 31.70, 31.45, 27.25, 25.53, 24.93, 23.08, 22.47, 14.05. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{27}O_2^+$ 227.2006; Found: 227.2008.

Pentyl 4-(N,N-dipropylsulfamoyl)benzoate

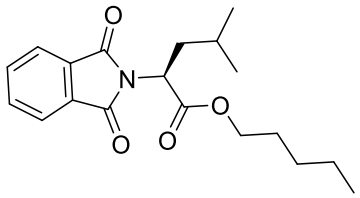


25a

R_f = 0.5, 10% acetone in hexane, yellowish oil (2.91 g, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 3.19 – 2.93 (m, 4H), 1.76 (p, J = 6.9 Hz, 2H), 1.52

(h, J = 7.4 Hz, 4H), 1.44 – 1.31 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H), 0.84 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.38, 144.14, 133.85, 130.23, 127.03, 65.84, 49.99, 28.40, 28.20, 22.40, 22.00, 14.05, 11.22. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{30}NO_4S^+$ 356.1890 ; Found: 356.1892.

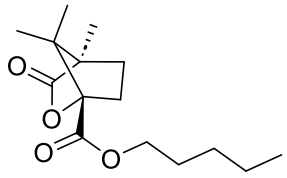
Pentyl (S)-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate



28a

R_f = 0.6, 5% acetone in hexane, white oil (2.33 g, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 5.1, 2.8 Hz, 2H), 7.73 (dd, J = 5.2, 2.8 Hz, 2H), 4.92 (dd, J = 11.5, 4.2 Hz, 1H), 4.17 – 4.03 (m, 2H), 2.37 – 2.27 (m, 1H), 1.95 (ddd, J = 14.3, 10.3, 4.3 Hz, 1H), 1.60 – 1.45 (m, 3H), 1.26 – 1.17 (m, 4H), 0.92 (dd, J = 13.5, 6.6 Hz, 6H), 0.79 (t, J = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.74, 167.73, 134.11, 131.83, 123.41, 65.82, 50.76, 37.22, 28.05, 27.88, 25.08, 23.13, 22.12, 21.01, 13.83. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{26}NO_4^+$ 332.1856 ; Found: 332.1857.

Pentyl (1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate

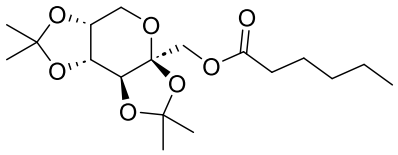


29a

R_f = 0.8, 5% acetone in hexane, white oil (2.09 g, 78% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.21 (td, J = 6.7, 2.0 Hz, 2H), 2.45 – 2.34 (m, 1H), 2.02 (ddd, J = 13.7, 9.3, 4.5 Hz, 1H), 1.91 (ddd, J = 13.5, 10.7, 4.5 Hz, 1H), 1.70 – 1.64 (m, 3H), 1.33 (p, J = 3.7 Hz, 4H), 1.10 (s, 3H), 1.04 (s, 3H), 0.95 (s, 3H), 0.92 – 0.85 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.33, 167.67, 91.30, 77.36, 65.86, 54.88, 54.21, 30.73, 29.07, 28.35, 28.06, 22.33, 16.90, 16.85, 14.04, 9.83. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{25}O_4^+$ 269.1747 ; Found: 269.1747.

((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-

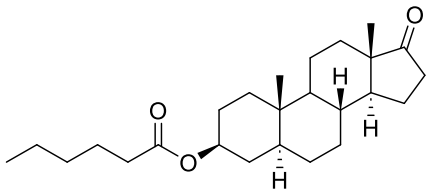
b:4',5'-d]pyran-3a-yl)methyl hexanoate



30a

R_f = 0.6, 5% acetone in hexane, white oil (2.33 g, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.59 (t, *J* = 7.4 Hz, 1H), 4.38 (t, *J* = 10.1 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 1H), 4.23 (t, *J* = 7.4 Hz, 1H), 4.02 (t, *J* = 9.8 Hz, 1H), 3.89 (t, *J* = 10.2 Hz, 1H), 3.75 (dd, *J* = 13.2, 7.9 Hz, 1H), 2.44 – 2.26 (m, 2H), 1.71 – 1.54 (m, 3H), 1.52 (dd, *J* = 14.4, 6.8 Hz, 3H), 1.47 (d, *J* = 7.8 Hz, 3H), 1.42 – 1.37 (m, 3H), 1.34 – 1.28 (m, 6H), 0.88 (dd, *J* = 13.3, 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.22, 109.28, 108.84, 101.74, 77.36, 70.93, 70.66, 70.22, 65.25, 61.37, 34.23, 31.42, 26.63, 26.03, 25.37, 24.60, 24.21, 22.44, 14.03. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{31}O_7^+$ 359.2064 ; Found: 359.2066.

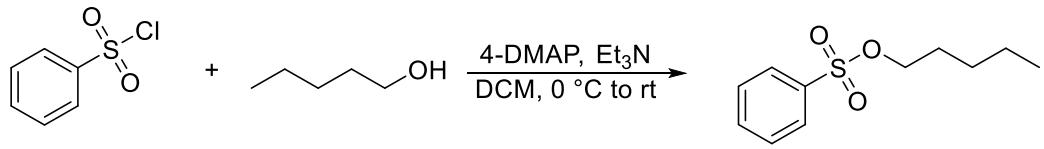
(3*S*,5*S*,8*R*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl hexanoate



31a

R_f = 0.6, 20% acetone in hexane, white solid (2.76 g, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.69 (td, *J* = 11.0, 5.3 Hz, 1H), 2.42 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.25 (d, *J* = 7.4 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.95 – 1.89 (m, 1H), 1.82 – 1.72 (m, 4H), 1.66 – 1.58 (m, 4H), 1.56 – 1.45 (m, 4H), 1.36 – 1.24 (m, 10H), 1.08 – 0.94 (m, 3H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.85 (s, 6H), 0.72 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.35, 73.14, 54.32, 51.36, 47.74, 44.66, 36.71, 35.81, 35.64, 35.03, 34.67, 33.98, 31.53, 31.27, 30.80, 28.27, 27.44, 24.73, 22.29, 21.76, 20.45, 13.89, 13.80, 12.20. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{41}O_3^+$ 389.3050 ; Found: 389.3053.

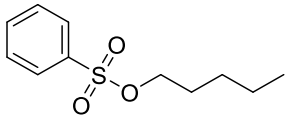
5.2 Synthesis of compound 10a



9a

Benzenesulfonyl chloride (8.0 mmol, 1.0 equiv.) was dissolved in DCM (50 mL). A solution of pentan-1-ol (8.0 mmol, 1.0 equiv.), 4-DMAP (0.8 mmol, 10 mol%) and triethylamine (9.6 mmol, 1.2 equiv.) in DCM (20.0 mL) was added to the sulfonyl chloride solution slowly at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then poured into water (50.0 mL). The water layer was extracted with DCM. The organic layers were combined and washed with 3M HCl (50.0 mL), sodium bicarbonate (50.0 mL), and water (50.0 mL). The organic phase was dried over Na_2SO_4. The solvent was removed in *vacuo* and the resulting residue was purified by silica gel flash chromatography to give the desired product. Spectra data are consistent with those reported in the literature.

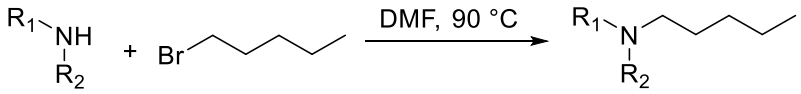
Pentyl 4-methylbenzenesulfonate



10a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.34 g, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.2, 0.9 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 4.05 (t, J = 6.5 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.32 – 1.24 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.25, 133.65, 129.20, 127.79, 70.95, 28.50, 27.41, 21.99, 13.79.[1]

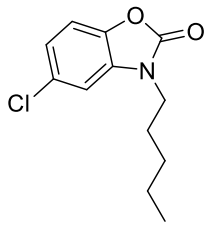
5.3 Synthesis of compound 23a and 24a



The secondary amine (22.0 mmol, 1.1 equiv.) was added to a solution of 1-bromopentane (20.0 mmol, 1.0 equiv.) in 25 mL of anhydrous DMF. The mixture was heated to 90 °C for 16 h. After cooled to room temperature, the reaction mixture was poured into water (75.0 mL) and extracted with DCM (3 x 50.0 mL). The combined organic phase was washed with 100 mL of 0.2 M KOH (aq.) and water. The organic

phase was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The resulting crude yellow oil was purified by silica gel column chromatography (eluted with hexane/acetone (v/v 20:1)) to afford the products, spectra data are consistent with those reported in the literature.

5-chloro-3-pentylbenzo[d]oxazol-2(3*H*)-one

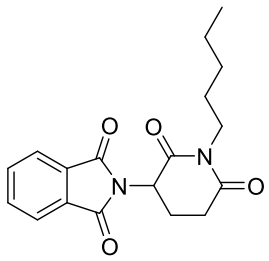


23a

R_f = 0.7, 5% acetone in hexane, yellowish oil (3.68 g, 70% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.4 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 1.9 Hz, 1H), 3.77 (t, J = 7.4 Hz, 2H), 1.75 (t, J = 7.4 Hz, 2H), 1.35 (q, J = 4.5, 4.0 Hz, 4H), 0.89 (t, J = 6.7 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.43, 141.21, 132.32, 129.35, 122.19, 110.86, 108.84, 42.60, 28.78, 27.44, 22.30, 13.96. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{15}ClNO_2^+$ 240.0786 ; Found: 240.0790.

2-(2,6-dioxo-1-pentylpiperidin-3-yl)isoindoline-1,3-dione

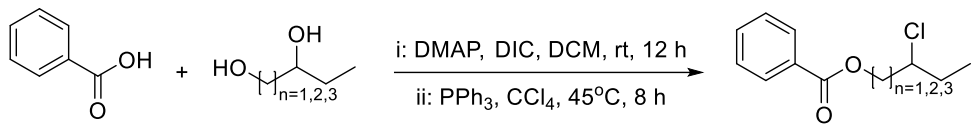


24a

R_f = 0.5, 5% acetone in hexane, yellowish oil (5.34 g, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.74 (dd, J = 5.6, 3.1 Hz, 2H), 4.97 (dd, J = 12.4, 5.3 Hz, 1H), 3.77 (q, J = 6.8 Hz, 2H), 2.94 (ddd, J = 11.6, 7.8, 4.0 Hz, 1H), 2.77 (td, J = 13.4, 4.1 Hz, 2H), 2.10 (dd, J = 11.5, 4.8 Hz, 1H), 1.52 (p, J = 7.5 Hz, 2H), 1.33 – 1.23 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.94, 168.53, 167.53, 134.49, 131.87, 123.80, 77.36, 50.26, 40.82, 32.14, 29.06, 27.54, 22.36, 22.11, 14.05. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{21}N_2O_4^+$ 329.1496 ; Found: 329.1496.

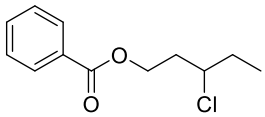
5.4 Synthesis of 1-3b'



1-3b'

Benzoic acid (1.0 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (0.1 mmol, 0.1 equiv.) were added to a flask. DCM (3.0 mL) and corresponding alcohol (1.0 mmol, 1.0 equiv.) were then added, followed by *N,N'*-diisopropylcarbodiimide (DIC) (1.5 mmol, 1.5 equiv.). The reaction mixture was allowed to stir at room temperature overnight, before quenched with H_2O (10.0 mL) and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated in *vacuo*. After simple purification, the crude product was obtained. The crude product and PPh_3 (3.0 equiv.) were added in CCl_4 (2.0 mL), the reaction was heated to 90°C and stirred 8 h. When the reaction was complete, remove the solvent in *vacuo*, the residue was purified by silica gel column chromatography, affording **1-3b'**.

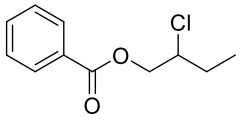
3-chloropentyl benzoate



1b'

R_f = 0.7, 5% acetone in hexane, yellowish oil (142 mg, Total yield of two steps: 54%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 4.53 (tdd, J = 11.2, 9.8, 5.7 Hz, 2H), 4.07 (ddd, J = 12.7, 8.4, 4.0 Hz, 1H), 2.31 – 2.24 (m, 1H), 2.12 (qd, J = 10.0, 5.2 Hz, 1H), 1.87 (tdt, J = 38.0, 14.7, 7.4 Hz, 2H), 1.10 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.42, 133.00, 130.15, 129.57, 128.38, 62.12, 61.58, 37.06, 31.64, 10.83.[2]

2-chlorobutyl benzoate

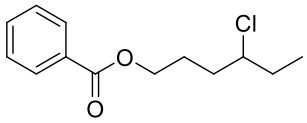


2b'

R_f = 0.7, 5% acetone in hexane, yellowish oil (114 mg, Total yield of two steps: 53%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.60 (ddd, J = 7.1, 2.5, 1.3 Hz, 1H), 7.48 (dd, J = 10.7, 4.8 Hz, 2H), 4.55 – 4.46 (m, 2H), 4.17 (dtd, J = 8.6, 5.9, 4.5 Hz, 1H), 1.99 (dqd, J = 14.6, 7.4, 4.4 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.13

(t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.11, 133.25, 129.73, 128.46, 67.66, 60.78, 28.00, 10.65.[3]

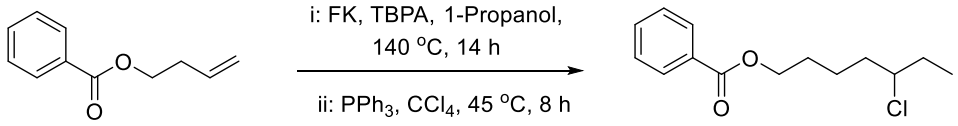
4-chlorohexyl benzoate



3b'

R_f = 0.7, 5% acetone in hexane, yellowish oil (131 mg, Total yield of two steps: 55%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 4.41 – 4.34 (m, 2H), 3.93 (dq, J = 12.0, 4.1 Hz, 1H), 2.07 (dd, J = 12.6, 7.0 Hz, 1H), 1.93 (dd, J = 10.6, 6.4 Hz, 2H), 1.85 – 1.77 (m, 4H), 1.36 – 1.30 (m, 1H), 1.06 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.55, 132.93, 130.27, 129.54, 128.37, 65.02, 64.40, 34.64, 31.59, 25.94, 10.98. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}ClO_2^+$ 241.0990 ; Found: 241.0990.

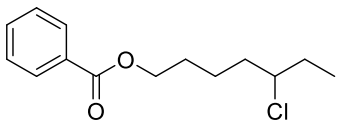
5.5 Synthesis of 4b'



4b'

A mixture of alkenes (1.0 mmol, 1 equiv.), ethers (5.0 mL), FK (0.5 mmol, 0.5 equiv.), and TBPA (5.0 mmol, 5 equiv.) was heated at 140°C for 14 h in a sealed tube. After the reaction completed (detected by TLC), the mixture was evaporated under vacuum and purified by column chromatography to afford the desired product. The crude product and PPh_3 (3.0 equiv.) were added in CCl_4 (2.0 mL), the reaction was heated to 90° C and stirred 8 h. When the reaction was complete, remove the solvent in *vacuo*, the residue was purified by silica gel column chromatography, affording **4b'**.

5-chloroheptyl benzoate

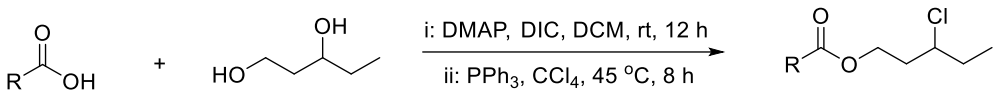


4b'

R_f = 0.6, 5% acetone in hexane, yellowish oil (117 mg, Total yield of two steps: 47%).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.2, 1.0 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.36 (ddd, J = 6.4, 3.8, 1.3 Hz, 2H), 3.94

– 3.82 (m, 1H), 1.96 – 1.66 (m, 8H), 1.64 – 1.57 (m, 1H), 1.05 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 132.88, 130.38, 129.54, 128.35, 65.43, 64.74, 37.65, 31.55, 28.29, 23.15, 10.97. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{20}ClO_2^+$ 255.1146; Found: 255.1146.

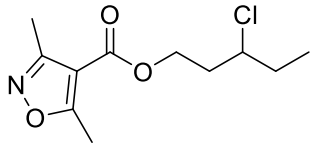
5.6 Synthesis of 8b', 26b', 27b',29b'



8b', 26b', 27b',29b'

Carboxylic acid (1.0 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (0.1 mmol, 0.1 equiv.) were added to a flask. DCM (3.0 mL) and pentane-1,3-diol (1.0 mmol, 1.0 equiv.) were then added, followed by *N,N'*-diisopropylcarbodiimide (DIC) (1.5 mmol, 1.5 equiv.). The reaction mixture was allowed to stir at room temperature overnight, before quenched with H_2O (10.0 mL) and the mixture was extracted with DCM (3 x 20.0 mL). The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated in *vacuo*. After simple purification, the crude product was obtained. The crude product and PPh_3 (3.0 equiv.) were added in CCl_4 (2.0 mL), the reaction was heated to 90°C and stirred 8 h. When the reaction was complete, remove the solvent in *vacuo*, the residue was purified by silica gel column chromatography, affording **8b', 26b', 27b',29b'**.

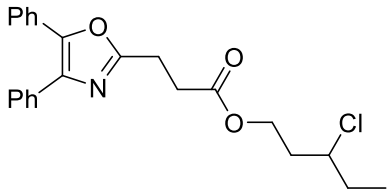
3-chloropentyl 3,5-dimethylisoxazole-4-carboxylate



8b'

R_f = 0.6, 10% acetone in hexane, yellowish oil (124 mg, Total yield of two steps: 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.54 – 4.40 (m, 2H), 4.01 – 3.93 (m, 1H), 2.66 (s, 3H), 2.43 (s, 3H), 2.22 (dddd, J = 14.8, 8.4, 6.5, 3.5 Hz, 1H), 2.07 (ddd, J = 14.8, 10.2, 5.3 Hz, 1H), 1.92 – 1.75 (m, 2H), 1.07 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.32, 162.23, 159.77, 108.57, 61.81, 61.37, 36.87, 31.69, 13.39, 11.87, 10.86. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{17}ClNO_3^+$ 246.0891; Found: 246.0892.

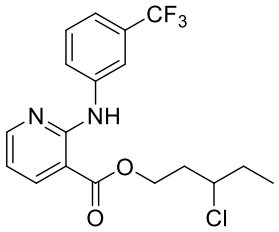
3-chloropentyl 3-(4,5-diphenyloxazol-2-yl)propanoate



26b'

R_f = 0.6, 15% acetone in hexane, yellowish oil (187 mg, Total yield of two steps: 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.62 – 7.57 (m, 2H), 7.41 – 7.31 (m, 6H), 5.12 – 5.04 (m, 1H), 3.53 (ddd, *J* = 8.0, 6.3, 1.9 Hz, 2H), 3.22 (dd, *J* = 11.1, 4.2 Hz, 2H), 2.95 (dd, *J* = 11.1, 4.1 Hz, 2H), 2.09 – 1.97 (m, 2H), 1.68 – 1.61 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.63, 161.75, 145.44, 135.15, 132.45, 128.96, 128.66, 128.55, 128.48, 128.06, 127.89, 126.51, 73.16, 40.89, 36.69, 31.20, 27.06, 23.54, 9.42. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{23}H_{25}ClNO_3^+$ 398.1517; Found: 398.1518.

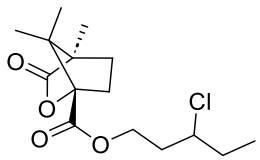
3-chloropentyl 2-((3-(trifluoromethyl)phenyl)amino)nicotinate



27b'

R_f = 0.6, 25% acetone in hexane, yellowish oil (187 mg, Total yield of two steps: 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.44 (dd, *J* = 4.7, 2.0 Hz, 1H), 8.27 (dd, *J* = 7.8, 2.0 Hz, 1H), 8.13 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 6.81 (dd, *J* = 7.8, 4.7 Hz, 1H), 4.66 – 4.48 (m, 2H), 4.12 – 4.01 (m, 1H), 2.29 (dddd, *J* = 14.7, 8.3, 6.4, 3.5 Hz, 1H), 2.14 (qd, *J* = 10.2, 5.3 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.11 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.30, 155.78, 153.18, 140.29, 140.13, 129.20, 123.49, 119.04, 119.01, 117.12, 117.08, 114.06, 107.32, 62.61, 61.43, 36.87, 31.72, 10.87. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.60. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{19}ClF_3N_2O_2^+$ 387.1082; Found: 387.1081.

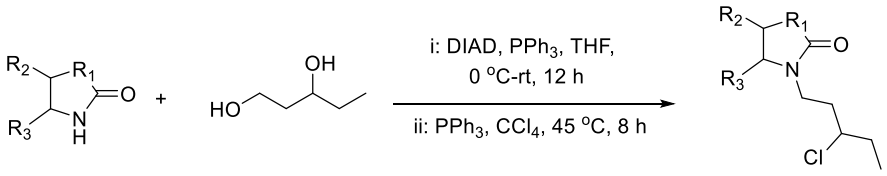
3-chloropentyl(1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-carboxylate



29b'

R_f = 0.7, 15% acetone in hexane, yellowish oil (172 mg, Total yield of two steps: 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.48 – 4.36 (m, 2H), 4.00 – 3.91 (m, 1H), 2.48 – 2.39 (m, 1H), 2.17 (ttd, *J* = 8.2, 6.8, 3.4 Hz, 1H), 2.07 – 1.98 (m, 2H), 1.94 (ddd, *J* = 13.3, 10.8, 4.5 Hz, 1H), 1.84 (dtd, *J* = 14.3, 7.2, 2.5 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.73 – 1.68 (m, 1H), 1.12 (s, 3H), 1.06 (dd, *J* = 8.5, 5.3 Hz, 6H), 0.97 (d, *J* = 4.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.17, 178.12, 167.44, 167.40, 91.09, 91.02, 62.81, 61.19, 54.79, 54.75, 54.25, 54.20, 36.66, 36.56, 31.63, 30.68, 30.63, 28.93, 28.91, 16.76, 16.72, 16.71, 10.80, 9.71, 9.70. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{24}ClO_4^+$ 303.1358; Found: 303.1358.

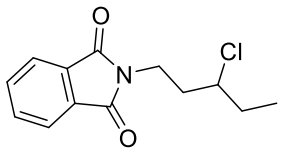
5.7 Synthesis of 11b', 23b', 24b'



11b', 23b', 24b'

Pentane-1,3-diol (1.0 mmol, 1.0 equiv.), amide (1.5 mmol, 1.5 equiv.), and PPh_3 (1.5 mmol, 1.5 equiv.) were then added and the reaction was cooled to 0°C. Diisopropyl azodicarboxylate (1.5 mmol, 1.5 equiv.) was then added dropwise over 5 min. The reaction was allowed to warm to room temperature and stir overnight. When the reaction was complete by TLC the reaction was concentrated under reduced pressure and purified directly via column chromatography to give the product. The crude product and PPh_3 (3.0 equiv.) were added in CCl_4 (2.0 mL), the reaction was heated to 90° C and stirred 8 h. When the reaction was complete, remove the solvent in *vacuo*, the residue was purified by silica gel column chromatography, affording **11b', 23b', 24b'**.

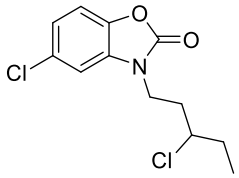
2-(3-chloropentyl)isoindoline-1,3-dione



11b'

R_f = 0.7, 25% acetone in hexane, yellowish oil (110 mg, Total yield of two steps: 44%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.72 (dd, J = 5.4, 3.0 Hz, 2H), 3.96 – 3.79 (m, 3H), 2.20 – 2.00 (m, 2H), 1.81 (dddd, J = 29.5, 22.0, 11.0, 6.0 Hz, 2H), 1.03 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.18, 133.97, 132.06, 123.23, 62.32, 36.54, 35.66, 31.47, 10.74. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{15}ClNO_2^+$ 252.0786; Found: 252.0785.

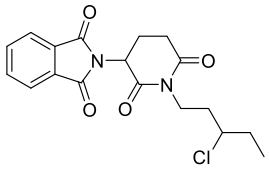
5-chloro-3-(3-chloropentyl)benzo[d]oxazol-2(3*H*)-one



23b'

R_f = 0.6, 25% acetone in hexane, yellowish oil (117 mg, Total yield of two steps: 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (dd, J = 15.7, 7.1 Hz, 3H), 4.08 – 3.97 (m, 2H), 3.87 (ddd, J = 10.8, 7.6, 3.7 Hz, 1H), 2.31 (dtd, J = 10.5, 7.9, 2.6 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.90 – 1.74 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.22, 141.10, 132.14, 129.54, 122.43, 110.92, 108.90, 62.01, 40.09, 35.82, 31.65, 10.80. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{14}Cl_2NO_2^+$ 274.0396; Found: 274.0395.

2-(1-(3-chloropentyl)-2,6-dioxopiperidin-3-yl)isoindoline-1,3-dione



24b'

R_f = 0.6, 30% acetone in hexane, yellowish oil (136 mg, Total yield of two steps: 38%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 – 7.72 (m, 4H), 5.08 – 4.91 (m, 1H), 4.17 – 4.01 (m, 1H), 4.00 – 3.84 (m, 2H), 3.07 – 2.94 (m, 1H), 2.89 – 2.73 (m, 2H), 2.14 (s, 1H), 2.05 – 1.95 (m, 2H), 1.86 – 1.71 (m, 2H), 1.04 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.80, 168.47, 167.39, 134.44, 131.77, 123.75, 62.86, 62.74, 50.12, 38.53, 38.44, 35.84, 35.72, 31.99, 31.58, 31.46, 22.01,

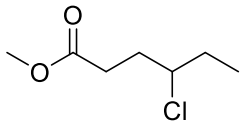
10.78. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{20}Cl_2NO_4^+$ 363.1106; Found: 363.1101.

5.8 Synthesis of 14b', 19b',20b', 30b', 31b'

14b', 19b',20b', 30b', 31b'

Carboxylic acid (1.0 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (0.1 mmol, 0.1 equiv.) were added to a flask. DCM (3.0 mL) and corresponding alcohol (1.0 mmol, 1.0 equiv.) were then added, followed by *N,N'*-diisopropylcarbodiimide (DIC) (1.2 mmol, 1.2 equiv.). The reaction mixture was allowed to stir at room temperature overnight, before quenched with H_2O (5.0 mL) and the mixture was extracted with DCM (3 x 5.0 mL). The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography, affording **14b', 19b',20b', 30b', 31b'**.

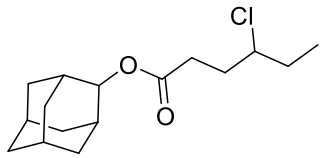
methyl 4-chlorohexanoate



14b'

R_f = 0.6, hexane, yellowish oil (116 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.88 (td, J = 8.3, 3.9 Hz, 1H), 3.69 (s, 3H), 2.61 – 2.50 (m, 2H), 2.18 – 2.10 (m, 1H), 1.98 – 1.90 (m, 1H), 1.84 – 1.72 (m, 2H), 1.04 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.43, 64.54, 51.68, 33.00, 31.62, 31.00, 10.94. [4]

adamantan-2-yl 4-chlorohexanoate

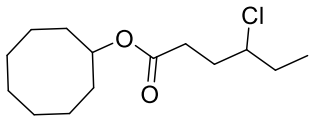


19b'

R_f = 0.6, 10% acetone in hexane, yellowish oil (198mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.95 (s, 1H), 3.92 (ddd, J = 12.8, 8.2, 4.3 Hz, 1H), 2.64 – 2.51 (m, 2H), 2.20 – 2.12 (m, 1H), 2.02 (d, J = 14.2 Hz, 4H), 1.86 (t, J = 9.6 Hz, 5H), 1.82 – 1.73 (m, 6H), 1.58 (d, J = 12.3 Hz, 2H), 1.06 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.37, 64.70, 37.37, 36.32, 33.19, 31.87, 31.86, 31.78,

31.63, 27.21, 26.98, 10.98. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{26}ClO_2^+$ 285.1616; Found: 285.1615.

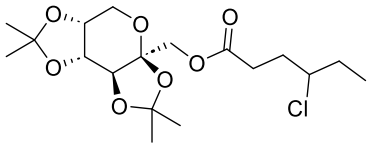
cyclooctyl 4-chlorohexanoate



20b'

R_f = 0.6, 5% acetone in hexane, yellowish oil (173mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.02 – 4.91 (m, 1H), 3.96 – 3.85 (m, 1H), 2.62 – 2.43 (m, 2H), 2.13 (dddd, *J* = 15.5, 8.4, 7.2, 3.5 Hz, 1H), 1.98 – 1.89 (m, 1H), 1.77 (dddd, *J* = 14.5, 10.2, 6.1, 2.5 Hz, 8H), 1.60 – 1.48 (m, 8H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.36, 75.24, 64.68, 33.12, 31.73, 31.63, 31.51, 27.07, 25.37, 22.92, 10.97. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{26}ClO_2^+$ 261.1616; Found: 261.1619.

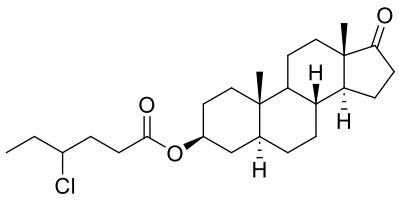
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-d]pyran-3a-yl)methyl 4-chlorohexanoate



30b'

R_f = 0.6, 20% acetone in hexane, yellowish oil (237mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.62 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.44 (dd, *J* = 11.7, 4.0 Hz, 1H), 4.32 (d, *J* = 2.6 Hz, 1H), 4.25 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.05 (dd, *J* = 11.7, 2.5 Hz, 1H), 3.95 – 3.86 (m, 2H), 3.78 (d, *J* = 13.0 Hz, 1H), 2.70 – 2.53 (m, 2H), 2.23 – 2.12 (m, 1H), 2.02 – 1.89 (m, 1H), 1.86 – 1.71 (m, 2H), 1.56 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.29, 172.27, 109.12, 108.77, 108.75, 101.47, 70.75, 70.52, 70.50, 70.03, 65.30, 65.25, 64.47, 61.24, 32.88, 31.66, 31.64, 31.05, 31.04, 26.48, 25.89, 25.26, 25.23, 24.05, 10.94. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{30}ClO_7^+$ 393.1675; Found: 393.1671.

(3*S*,5*S*,8*R*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-chlorohexanoate

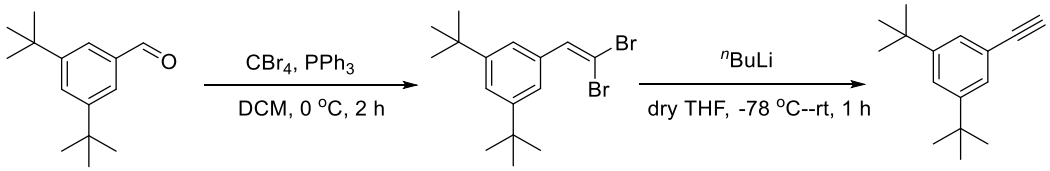


31b'

R_f = 0.6, 20% acetone in hexane, yellowish oil (248mg, 52% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.73 – 4.66 (m, 1H), 3.94 – 3.81 (m, 1H), 2.56 – 2.39 (m, 3H), 2.13 – 2.02 (m, 2H), 1.92 (tt, *J* = 9.5, 5.0 Hz, 2H), 1.83 – 1.72 (m, 6H), 1.64 (dd, *J* = 22.0, 8.8 Hz, 2H), 1.51 (ddd, *J* = 24.6, 11.5, 5.3 Hz, 3H), 1.42 – 1.31 (m, 3H), 1.30 – 1.22 (m, 4H), 1.06 – 0.96 (m, 5H), 0.85 (s, 6H), 0.71 (td, *J* = 11.3, 3.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.48, 73.60, 64.63, 54.27, 51.33, 47.75, 44.62, 36.67, 35.83, 35.63, 35.00, 33.93, 33.92, 33.06, 31.63, 31.61, 31.59, 31.50, 30.79, 28.25, 27.41, 27.39, 21.76, 20.45, 13.81, 12.21, 10.96. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{40}ClO_3^+$ 423.2660; Found: 423.2658.

6. Synthesis of catalysts

6.1 Synthesis of S3

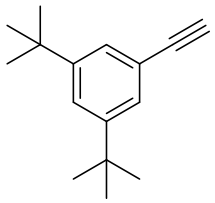


S1 **S2** **S3**

Dissolve triphenylphosphine (10.5 g, 40.0 mmol, 4.00 equiv.) and carbon tetrabromide (6.7 g, 20.0 mmol, 2.00 equiv.) in anhydrous DCM (10.0 mL) and stir at 0 °C for 30 minutes. Dissolve 3, 5-tert-butylbenzaldehyde **S1** (2.18 g, 10 mmol) separately in DCM (10 mL) and add dropwise to the chilled reaction over 5 minutes. Stir the mixture at 0 °C for 1 h. Separate the react with 5 M $CuSO_4$ (30 mL). Separate the aqueous and organic layers. Back-extract the aqueous layer with chloroform (20.0 mL). Wash the combined organics with brine (20.0 mL) and dry with anhydrous $MgSO_4$. Remove the solvent and purify by a short silica plug. Dissolve the 1, 1-dibromoalkene **S2** intermediate in anhydrous THF (18.0 mL) and chill to -78 °C in a dry ice/acetone bath under nitrogen. Add *n*-butyllithium (2.5 M in hexanes) (10.0 mL, 25 mmol) dropwise

to the vigorously-stirred reaction. Keep the mixture for 30 minutes, warm up to ambient temperature and stir for an hour. Quench the reaction by the slow addition of water (10.0 mL) under nitrogen. Separate the aqueous and organic layers. Extract the aqueous layer with diethyl ether (4 x 15.0 mL) and dry the combine organics with $MgSO_4$. Remove the solvent in *vacuo*, the residue was purified by silica gel column chromatography, affording **S3**.

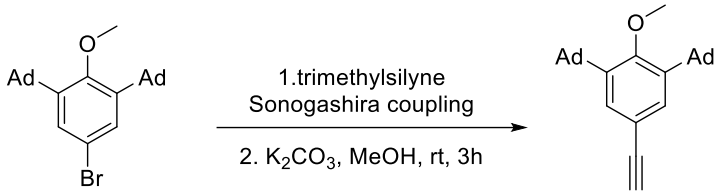
1,3-di-tert-butyl-5-ethynylbenzene



S3

R_f = 0.9, 5% acetone in hexane, white solid (1.6 g, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.41 (s, 2H), 3.07 (s, 1H), 1.36 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.87, 126.40, 123.26, 121.07, 84.87, 75.83, 34.81, 31.33.[5]

6.2 Synthesis of S5

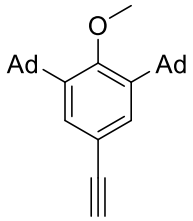


S4 **S5**

S4 was synthesized according to reported procedure.[6]

Under nitrogen conditions, **S4** (624 mg, 1.5 mmol), palladium dichloride (0.5 mmol%), cuprous iodide (0.01 equiv.), triethylamine (2.0 equiv.), and trimethylsilyne (2.0 equiv.) were dissolved in 10.0 mL anhydrous THF, and then reacted at 60 ºC for 12 h. Extract the aqueous layer with EtOAc (3 x 20.0 mL). The intermediate was obtained by column chromatography separation. Next, dissolve the intermediate in a mixed solvent of methanol and DCM (5.0 mL), then add potassium carbonate (2.0 equiv.) and react at room temperature for 3 h. Extract the aqueous layer with DCM (3 x 20.0 mL). The target product **S5** was obtained by concentration column chromatography separation.

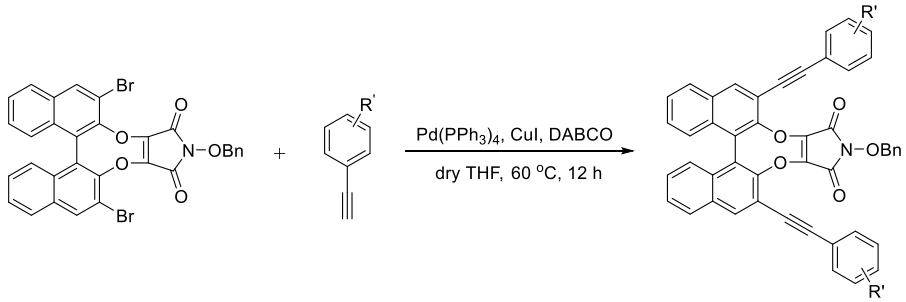
1,1'-(5-ethynyl-2-methoxy-1,3-phenylene)bis(adamantane)



S5

R_f = 0.9, hexane, yellow solid (350 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (s, 2H), 3.66 (s, 3H), 2.99 (s, 1H), 2.09 (d, J = 12.9 Hz, 18H), 1.77 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.43, 144.08, 130.33, 116.40, 84.72, 65.94, 42.61, 38.56, 36.91, 29.27. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{29}H_{37}O^+$ 401.2839; Found: 401.2839.

6.3 Synthesis of S7-10

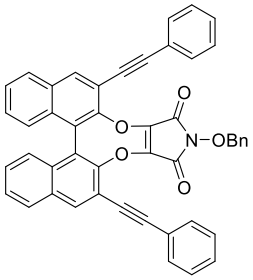


S6 **S7-10**

S6 was synthesized according to reported procedure.[7]

(±)-2-(Benzyloxy)-5,16-diiodo-1*H*-dinaphtho[2',1':5,6;1",2":7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione (435 mg; 0.68 mmol), phenylacetylene derivatives (2.0 mmol), $Pd(PPh_3)_4$ (18 mg, 0.015 mmol), CuI (30 mg, 0. 15 mmol), DABCO (170 mg, 1.5 mmol) were dissolved in dry THF 5.0 mL. The resulting dark red solution was stirred at room temperature for 15 min and turned yellow; the solution was stirred at 60 °C for 12 h. The mixture was then washed with water (10.0 mL) and the aqueous phase was extracted with ethyl acetate (3 x 10.0 mL), dried over Na_2SO_4, filtered and evaporated to give a brown solid which was purified over silica (20 g; cyclohexane:ethyl acetate 9:1) to give an off yellow solid.

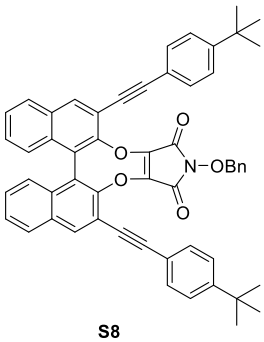
2-(benzyloxy)-5,16-bis(phenylethynyl)-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione



S7

R_f = 0.5, 5% acetone in hexane, yellow solid (330 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 4H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.40 (dt, *J* = 14.1, 6.5 Hz, 9H), 7.34 – 7.31 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 5.04 (dd, *J* = 28.1, 10.4 Hz, 2H).. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.06, 149.14, 135.44, 135.34, 133.70, 132.21, 132.10, 131.60, 129.66, 129.18, 128.80, 128.43, 128.37, 128.11, 128.05, 127.08, 126.54, 124.03, 122.80, 116.38, 95.83, 83.50, 80.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{47}H_{28}NO_5^+$ 686.1962; Found: 686.1966.

2-(benzyloxy)-5,16-bis((4-(tert-butyl)phenyl)ethynyl)-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione

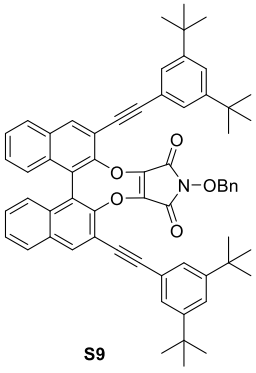


S8

R_f = 0.5, 5% acetone in hexane, yellow solid (352 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 4H), 7.38 (d, *J* = 6.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 15.3, 7.8 Hz, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 5.05 (dd, *J* = 34.2, 10.4 Hz, 2H), 1.36 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.03, 152.07, 149.18, 135.39, 135.25, 133.77, 131.99, 131.95, 131.62, 129.63, 129.12, 128.41, 128.06, 127.91, 127.01, 126.55, 125.38, 124.04, 119.77, 116.62, 96.13, 82.90, 80.01, 34.90, 31.23. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{55}H_{44}NO_5^+$ 798.3214; Found: 798.3213.

2-(benzyloxy)-5,16-bis((3,5-di-tert-butylphenyl)ethynyl)-1*H*-

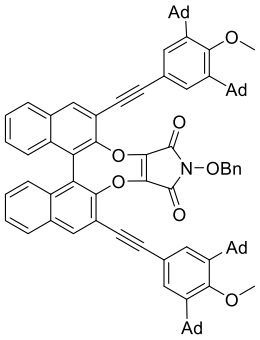
dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione



S9

R_f = 0.5, 5% acetone in hexane, yellow solid (426 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.72 (s, 4H), 7.55 (t, J = 7.5 Hz, 2H), 7.49 (s, 2H), 7.34 (t, J = 7.3 Hz, 4H), 7.24 (dt, J = 14.1, 7.0 Hz, 3H), 7.16 (d, J = 8.5 Hz, 2H), 5.04 (q, J = 10.1 Hz, 2H), 1.43 (s, 36H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.99, 150.76, 149.26, 135.44, 135.20, 133.78, 132.00, 131.62, 129.57, 129.02, 128.33, 128.03, 127.86, 126.98, 126.67, 126.57, 124.06, 123.15, 121.73, 116.66, 97.07, 82.30, 79.93, 34.95, 31.43. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{63}H_{60}NO_5^+$ 910.4466; Found: 910.4468.

2-(benzyloxy)-5,16-bis(3,5-di-adamantan-1-yl)-4-methoxyphenyl)ethynyl)-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione

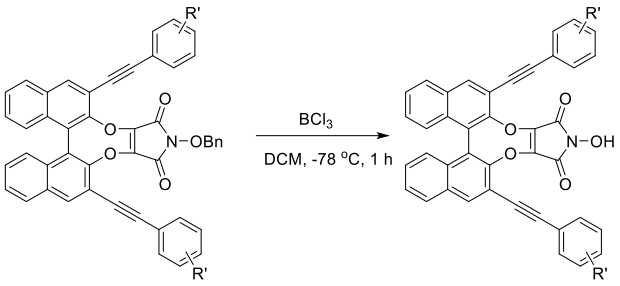


S10

R_f = 0.5, 3% acetone in hexane, yellow solid (549 mg, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (s, 2H), 7.92 (d, J = 8.2 Hz, 2H), 7.71 (s, 4H), 7.51 (t, J = 7.5 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.19 (dd, J = 15.8, 7.2 Hz, 3H), 7.13 (d, J = 8.5 Hz, 2H), 5.03 (s, 2H), 3.69 (s, 6H), 2.20 (s, 24H), 2.09 (s, 12H), 1.79 (d, J = 12.5 Hz, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.52, 160.90, 149.23, 144.05, 135.39, 134.90, 133.80, 131.89, 131.64, 130.66, 129.29, 129.01, 128.34, 127.97, 127.73, 126.92, 126.56, 124.04, 117.18, 116.81, 97.04, 82.09, 79.59, 65.94, 42.68, 38.73, 36.99,

29.36. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{89}H_{88}NO_7^+$ 1282.6555; Found: 1282.6556.

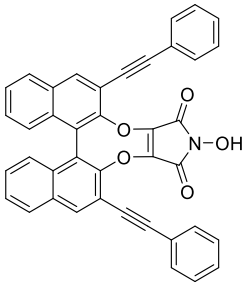
6.5 Synthesis of NHMI-1-4



S7-10 NHMI-1-4

S7-10 (0.24 mmol) was dissolved in DCM (15.0 mL). Boron trichloride (67 µL, 0.96 mmol) diluted in DCM (5.0 mL) was dropewisely added at -78 °C. The mixture was stirred over 1h at -78 °C. Water (5.0 mL) was then dropewisely added at 0 °C and the mixture was stirred over 1h at room temperature. The aqueous phase was extracted with DCM (3 x 10.0 mL), the organic phases were gathered and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was dissolved in a minimum amount of chloroform, crashed out by addition of pentane and filtered to give the desired product as a yellow solid which was used without any further purification.

2-hydroxy-5,16-bis(phenylethynyl)-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione

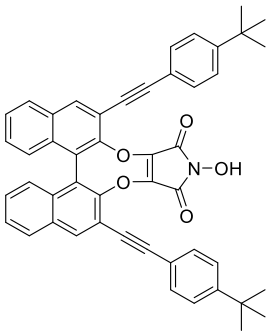


NHMI-1

R_f = 0.5, 10% acetone in hexane, yellow solid (95 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.20 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 7.0 Hz, 4H), 7.55 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.19 (dq, J = 14.4, 7.1 Hz, 6H), 7.12 (d, J = 8.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.29, 149.02, 135.49, 135.35, 132.06, 132.04, 131.59, 128.75, 128.31, 128.12, 128.10, 127.15, 126.54, 123.89, 122.52, 116.45, 96.00, 83.37. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd

for $C_{40}H_{22}NO_5^+$ 596.1492; Found: 596.1494.

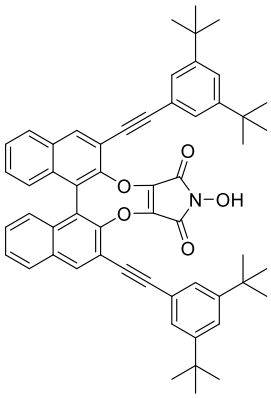
5,16-bis((4-(tert-butyl)phenyl)ethynyl)-2-hydroxy-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione



NHMI-2

R_f = 0.5, 10% acetone in hexane, yellow solid (107 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (s, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.83 (s, 1H), 7.61 (d, J = 8.3 Hz, 4H), 7.54 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 8.5 Hz, 2H), 1.26 (s, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.03, 152.05, 149.02, 135.53, 135.18, 132.00, 131.73, 131.63, 128.02, 127.87, 127.02, 126.55, 125.38, 123.86, 119.55, 116.66, 96.19, 82.86, 34.80, 31.09. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{48}H_{38}NO_5^+$ 708.2744; Found: 708.2745.

5,16-bis((3,5-di-tert-butylphenyl)ethynyl)-2-hydroxy-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione

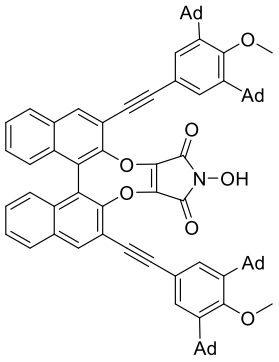


NHMI-3

R_f = 0.5, 10% acetone in hexane, yellow solid (136 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 1.2 Hz, 4H), 7.55 (t, J = 7.5 Hz, 2H), 7.47 (s, 2H), 7.35 (t, J = 7.7 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.57 (s, 1H), 1.40 (s, 36H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.36, 150.84, 149.24, 135.83, 135.24, 132.02, 131.63, 128.03, 127.89, 127.00, 126.57,

124.03, 123.25, 121.66, 116.59, 97.06, 82.34, 34.91, 31.37. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{56}H_{54}NO_5^+$ 820.3997; Found: 820.3997.

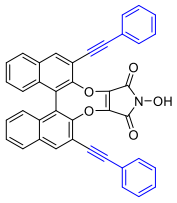
5,16-bis((3,5-di(-adamantan-1-yl)-4-methoxyphenyl)ethynyl)-2-hydroxy-1*H*-dinaphtho[2',1':5,6;1'',2'':7,8][1,4]dioxocino[2,3-c]pyrrole-1,3(2*H*)-dione



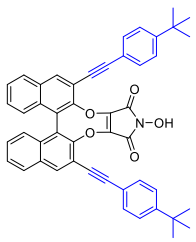
NHMI-4

R_f = 0.5, 5% acetone in hexane, yellow solid (191 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 4H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.46 (s, 1H), 3.66 (s, 6H), 2.17 (s, 24H), 2.08 (s, 12H), 1.78 (q, *J* = 12.0 Hz, 24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.46, 161.29, 149.21, 144.08, 135.81, 134.94, 131.91, 131.64, 130.63, 127.99, 127.78, 126.96, 126.58, 124.00, 117.09, 116.79, 97.06, 82.12, 65.92, 42.65, 38.72, 36.96, 29.36. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{82}H_{82}NO_7^+$ 1192.6086; Found: 1192.6088.

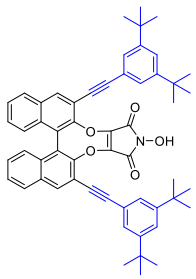
7. Optimization of Reaction Conditions



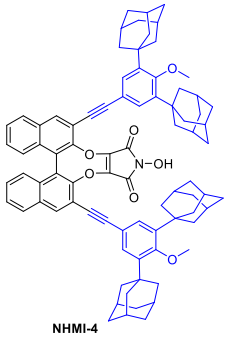
NHMI-1



NHMI-2

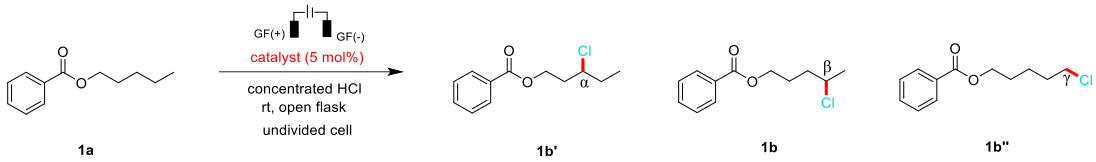


NHMI-3



NHMI-4

7.1 Optimization of N-Hydroxyimido Derivative[a]



Entry	Catalyst	Yield (%) [b]	Ratio (**a**:**b**:**c**)[c]
1	**NHMI-1**	70	$C_\alpha : C_\beta : C_\gamma$ = 51:44:5
2	**NHMI-2**	69	$C_\alpha : C_\beta : C_\gamma$ = 26:74:0
3	**NHMI-3**	72	$C_\alpha : C_\beta : C_\gamma$ = 3:97:0
4	**NHMI-4**	68	$C_\alpha : C_\beta : C_\gamma$ = 0:89:11

[a]Reaction conditions: Reaction conditions: substrate (1.0 mmol, 1.0 equiv.), **NHMI-X** (5.0 mol%), Et_4NBF_4 (2.0 equiv.), HCl (aqueous, 36.5%, 2.5 equiv.), MeCN (2.0 mL), graphite felts as both anode and cathode (2.0 cm × 2.0 cm × 0.5 cm), constant current (10.0 mA), room temperature, open air, 10 h. [b]The yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c]The ratio were determined by GC-MS.

7.2 GC data of optimization of catalysts

We first separated the three products from the system as pure products, standard chromatograms of the three products were obtained. Then, the same GC method was used for catalyst screening. The specific GC data is as follows.

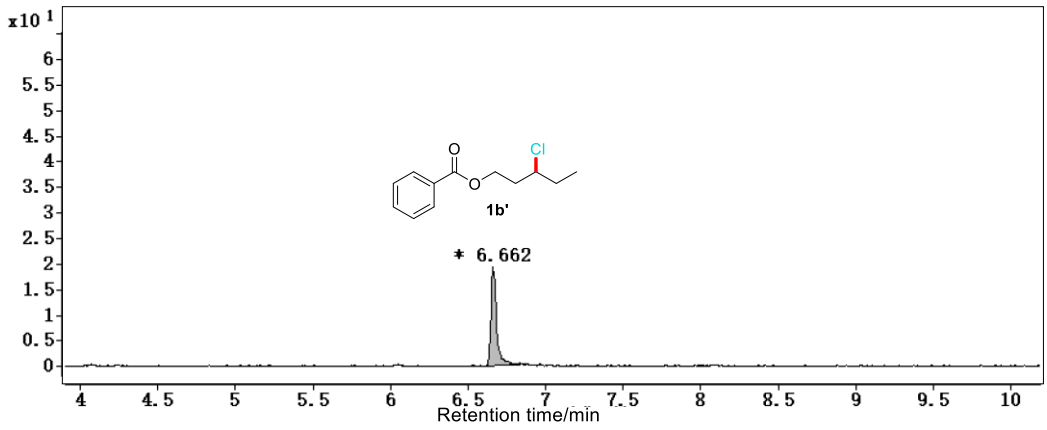


Figure S5. Chromatogram of **1b'**

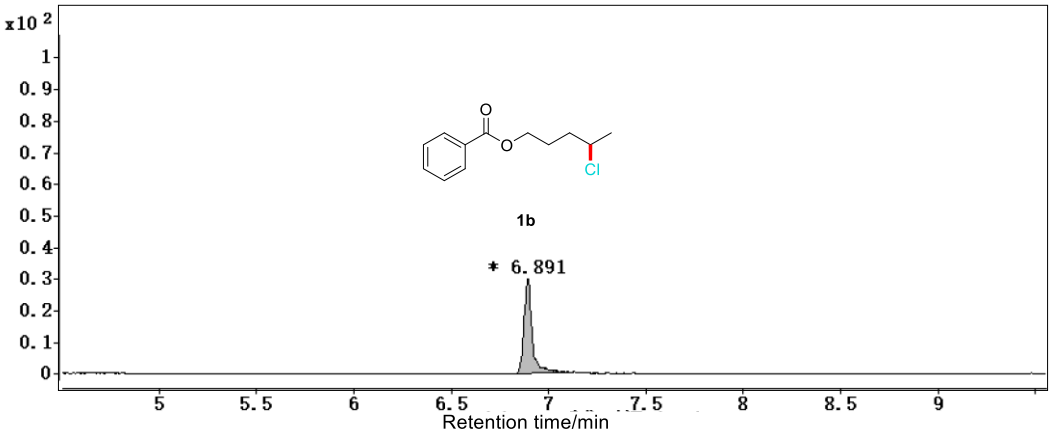


Figure S6. Chromatogram of **1b**

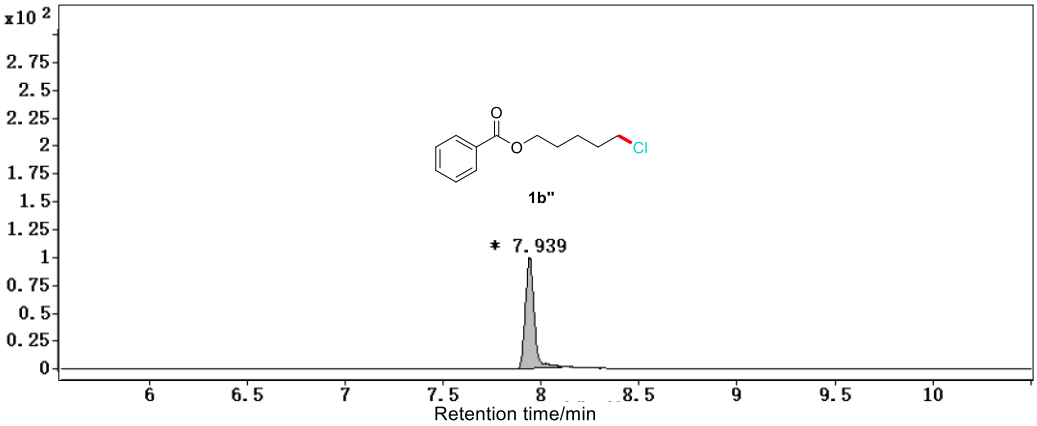


Figure S7. Chromatogram of **1b”**

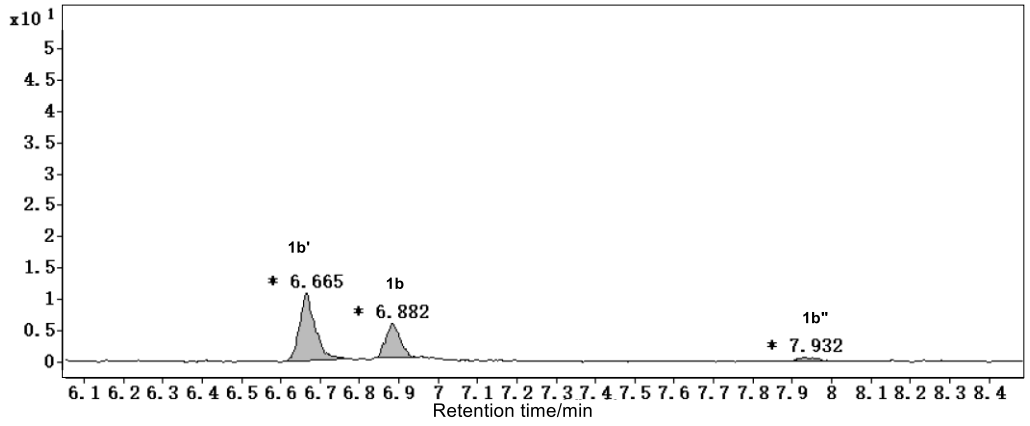


Figure S8. Chromatogram of optimization of **NHMI-1**

Chromatogram of **NHMI-1**: Selectivity		
Product	Retention Time	Percent Area
1b’	6.665	51.24
1b	6.882	43.83
1b”	7.932	4.93

Table S4. Date of optimization of **NHMI-1**

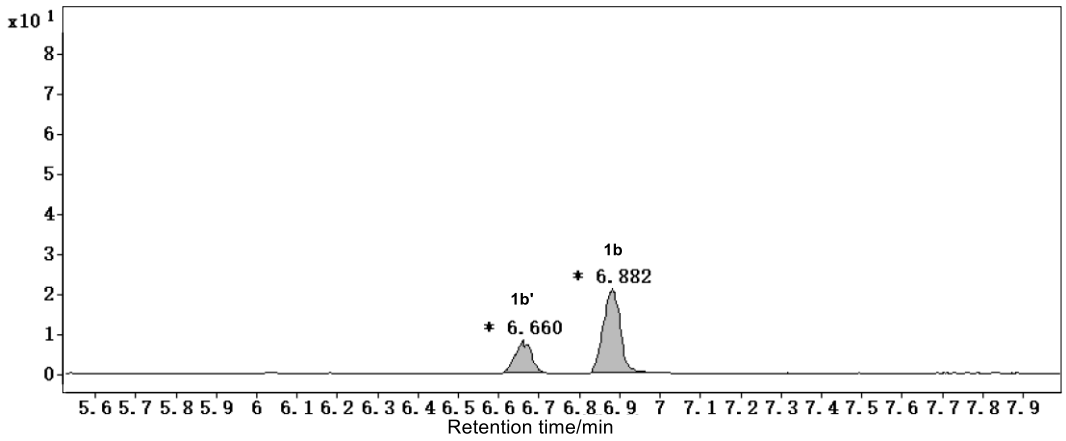


Figure S9. Chromatogram of optimization of **NHMI-2**

Chromatogram of **NHMI-2**: Selectivity		
Product	Retention Time	Percent Area
1b'	6.665	25.80
1b	6.882	74.20
1b"	---	---

Table S5. Date of optimization of **NHMI-2**

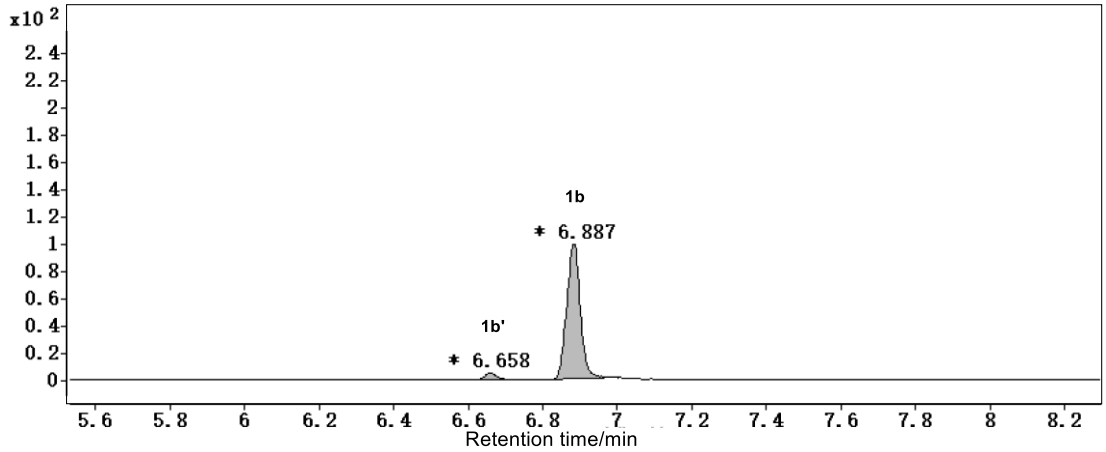


Figure S10. Chromatogram of optimization of **NHMI-3**

Chromatogram of **NHMI-3**: Selectivity		
Product	Retention Time	Percent Area
1b'	6.658	3.42
1b	6.887	96.58
1b"	---	---

Table S6. Date of optimization of **NHMI-3**

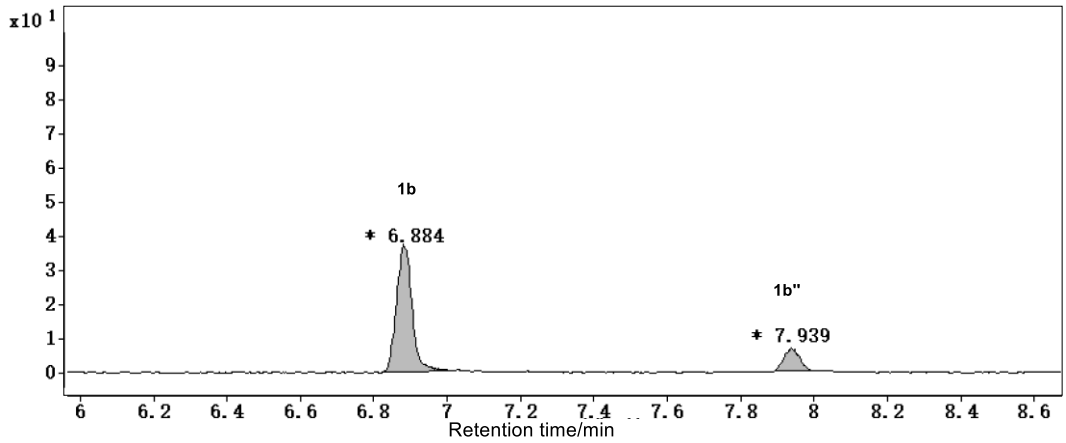


Figure S11. Chromatogram of optimization of **NHMI-4**

Chromatogram of **NHMI-4**: Selectivity		
Product	Retention Time	Percent Area
1b'	---	---
1b	6.884	88.79
1b"	7.932	11.21

Table S7. Date of optimization of **NHMI-4**

7.3 Optimization of Reaction Conditions of C(sp^3)-H bonds chlorination

All screening reactions were carried out at a 0.5 mmol scale in a 10 mL glass bottles. **1a** (96.1 mg, 0.5 mmol, 1.0 equiv.), other specified reagents were added to a 10 mL Glass bottles. Graphite felt (2 cm x 2 cm x 0.5 cm) are used as both anode and cathode respectively. The graphite felt (GF) anode and cathode attached to a platinum wire. The constant current electrolysis was carried out at room temperature. After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desired product.

Reuse of the electrodes A: After the reaction is completed in the electrolytic cell, remove the graphite felt and wash it in the order of acetone, 1M HCl, and water. Finally, clean the electrode with acetone to ensure that the electrode surface is thoroughly washed. Then vacuum dry the graphite felt electrode. It can continue to be used for the next reaction.

Note: The graphite felt (GF) differs from graphite rod dramatically in the aspects of original material, manufacture process, structure, and properties.[8]

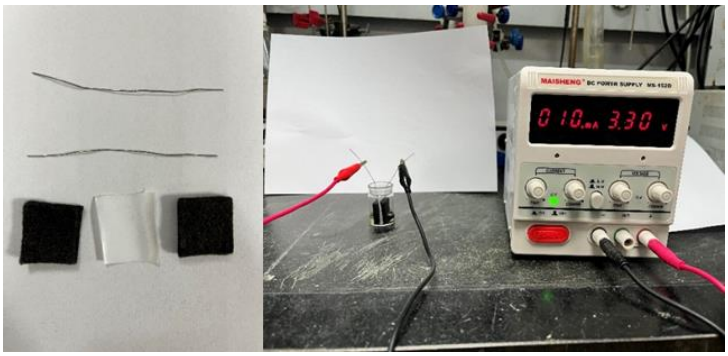
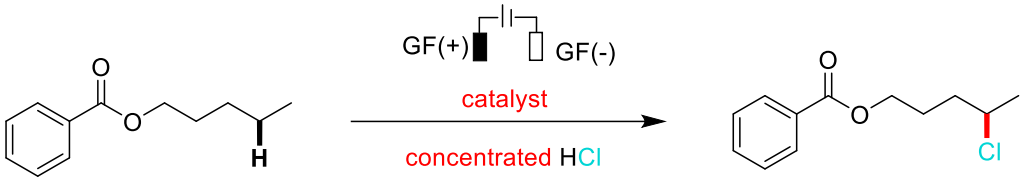


Figure S12. Reaction setup for template experiments.



1a **1b**

entry	reagents (equiv.)/ Cl source (equiv.)/ electrolyte (equiv.)/ current(mA/V)/ electrode/ atmosphere/ time (h)	Yield of **1b** (%) [a]	RSM (%)[b]
1	**NHMI-3** (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	70	< 10
2	**NHMI-3** (10 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	67	< 10
3	**NHMI-3** (5 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	68	< 10
4	**NHMI-3** (5 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 20/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	43	< 10
5	**NHMI-3** (5 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/3.0 V/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	57	< 10
6	**NHMI-3** (5 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 2.5 V/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	32	18
7	**NHMI-3** (5 mol%)/ HCl (1.5+1.0) [c] / Et_4NBF_4 (2.0)/ 10 mA/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	66	< 10
8	**NHMI-3** (5 mol%)/ HCl (1.5+2.5) [c] / Et_4NBF_4 (2.0)/ 10 mA/ GF (+) | GF (-)/ MeCN (2)/ open air/ 10	68	< 10

[a]The yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [b]RSM is short for the recovery of starting material. [c]Add in batches, first add 1.5 equiv. of HCl, react for about 5 hours, and then add 1.0/2.5 equiv. of HCl.

7.3 Calculation of Faradaic efficiency

The faradaic efficiency of the reaction was calculated using the follow formula.[9]

$$\eta = \frac{\text{Qtheo}}{\text{Qexp}}$$

Where,

$$Q_{theo} = Z_p . N_p . F$$

$$Q_{exp} = I.t = Z . N . F . equiv$$

$$\eta = \frac{Z.N.Y.F}{Z.N.F.equiv} = \frac{Y}{equiv}$$

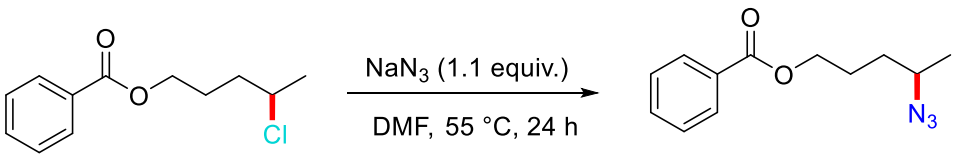
η: Faradaic efficiency in percent [%], $Qtheo$: theoretical charge in Coulomb[C], $Qexp$: experimental charge in Coulomb [C], equiv.: electron equivalents (F mol-1 or equiv.), Zp: Number of electrons per product [-], Np: Number of moles of the product [mol], Y: yield in percent [%].

Here, Y=68%, equiv. =2.24 Fmol^{-1}

$$\eta = \frac{68\%}{2.24} = \mathbf{30.4\%}$$

8. Conversion of introduced chlorine atom

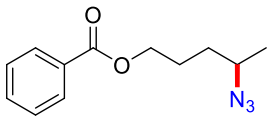
8.1 Converted to compound 32



1b **32**

To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv.) in DMF (2.0 mL) was added NaN_3 (72 mg, 1.1 mmol, 1.1 equiv.) and the reaction mixture was stirred at 55 ^oC for 24 h. The reaction mixture was extracted with EtOAc. The combined organic layers were washed with bine, dried over Na_2SO_4 and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **32**.

4-azidopentyl benzoate

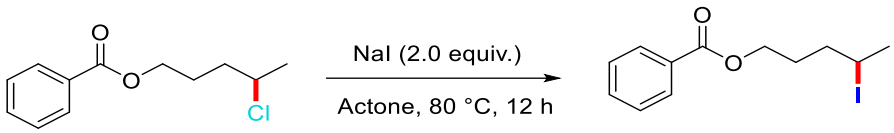


32

R_f = 0.4, 5% acetone in hexane, yellowish oil (188 m g, 81%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 – 7.96 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.39 – 4.28 (m, 2H), 3.53 (dd, J = 13.1, 6.6 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.67 – 1.61 (m, 2H), 1.30 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.57, 132.94, 130.24, 129.54, 128.37, 64.46, 57.55, 32.79, 25.45, 19.46.[10]

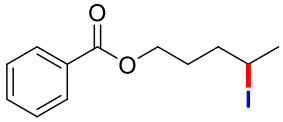
8.2 Converted to compound 33



1b **33**

In a 15 mL resealable pressure tube, **1b** (339 mg, 1.5 mmol, 1.0 equiv.) and NaI (3.0 mmol, 2.0 equiv.) were dissolved in acetone (5.0 mL). The solution was stirred and heated at 80 ºC for 12 h. After cooling to room temperature, DCM was added until the complete precipitation of salts. The mixture was filtered and the solvent was evaporated under vacuum. Then, the mixture was extracted with EtOAc and 0.1 M aqueous $Na_2S_2O_3$ solution. The combined organic phases were washed with saturated brine and dried over anhydrous Na_2SO_4, then filtered and concentrated by rotary evaporation. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **33**.

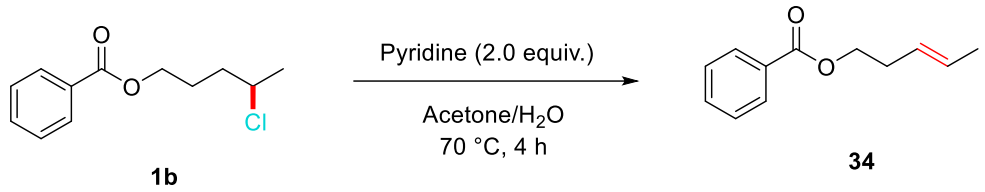
4-iodopentyl benzoate



33

R_f = 0.7, 5% acetone in hexane, yellowish oil (271 mg, 55% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 4.42 – 4.28 (m, 2H), 4.15 – 4.06 (m, 1H), 2.06 – 1.82 (m, 4H), 1.54 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.54, 132.94, 130.28, 129.55, 128.38, 64.34, 58.12, 36.86, 26.06, 25.42.[10]

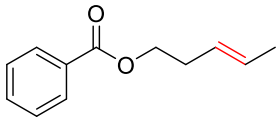
8.3 Converted to compound 34



1b **34**

To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv.) in 20.0 mL of 3:1 acetone/water was added Pyridine (2.0 mmol, 2.0 equiv.) in a 48.0 mL resealable pressure tube under nitrogen. The solution was stirred and heated at 70 °C for 4 h. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure to remove most of the acetone. The product was extracted with EtOAc (3 x 10.0 mL). The combined EtOAc extracts were washed with 3 M HCl (8.0 mL) and 10% $NaHCO_3$ (3 x 5.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **34**.

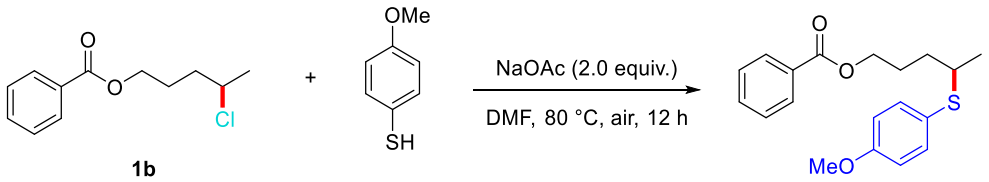
(*E*)-pent-3-en-1-yl benzoate



34

R_f = 0.7, 5% acetone in hexane, yellowish oil (219 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 5.65 – 5.44 (m, 2H), 4.32 (t, J = 6.8 Hz, 2H), 2.45 (q, J = 6.7 Hz, 2H), 1.68 (d, J = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.58, 132.80, 130.48, 129.54, 128.31, 128.02, 126.33, 64.62, 32.08, 18.00.[11]

8.4 Converted to compound 35

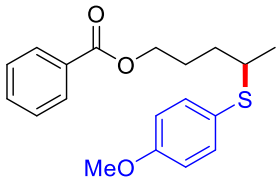


1b 2.0 equiv. **35**

In a 15 mL resealable pressure tube, **1b** (339 mg, 1.5 mmol, 1.0 equiv.) and 4-methoxybenzenethiol (3.0 mmol, 2.0 equiv.) and NaOAc (3.0 mmol, 2.0 equiv.) were dissolved in DMF (5.0 mL). The reaction mixture was heated to 80 °C for 12 h under

air. After the reaction equilibrium, the mixture was extracted with DCM. The combined organic phases were washed with saturated brine and dried over anhydrous Na_2SO_4, then filtered and concentrated by rotary evaporation. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **35**.

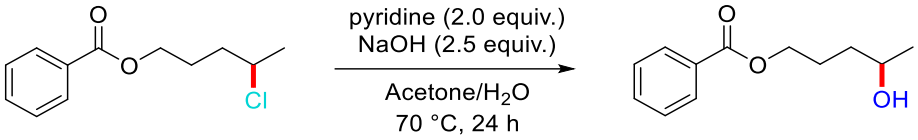
4-((4-methoxyphenyl)thio)pentyl benzoate



35

R_f = 0.7, 5% acetone in hexane, yellowish oil (198 mg, 46% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 4.32 (t, J = 6.5 Hz, 2H), 3.76 (s, 3H), 3.07 (dd, J = 13.4, 6.7 Hz, 1H), 1.98 – 1.91 (m, 2H), 1.75 – 1.66 (m, 1H), 1.60 (tt, J = 14.4, 7.4 Hz, 1H), 1.26 (d, J = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.56, 159.50, 135.89, 134.41, 132.87, 130.37, 129.55, 128.34, 124.57, 114.40, 64.70, 55.26, 44.19, 32.80, 26.20, 21.09. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{23}O_3S^+$ 331.1362; Found: 331.1363.

8.5 Converted to compound 36

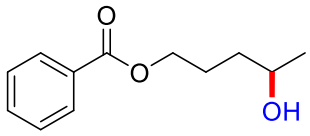


1b **36**

To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv.) in 20.0 mL of 3:1 acetone/water was added Pyridine (2.0 mmol, 2.0 equiv.) and NaOH (2.5 mmol, 2.5 equiv.) in a 48.0 mL resealable pressure tube under nitrogen. The solution was stirred and heated at 70 ºC for 24 h. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure remove most of the acetone. The product was extracted with EtOAc (3 x 10.0 mL). The combined EtOAc extracts were washed with 3 M HCl (8.0 mL) and 10% $NaHCO_3$ (3 x 5.0 mL). The combined organic

layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **36**.

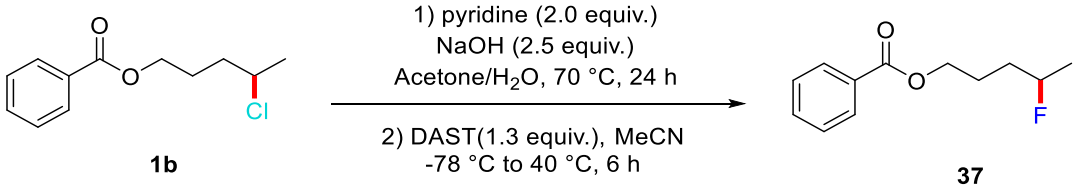
4-hydroxypentyl benzoate



36

R_f = 0.3, 10% acetone in hexane, yellowish oil (134 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J= 7.5 Hz, 2H), 7.57 (m, 1H), 7.45 (m, 2H), 4.62 (m, 1H), 4.39 (m, 1H), 3.98 (m, 1H), 2.05 (bs, 1H), 1.97 (m, 1H), 1.86 (m, 1H), 1.27 (d, J= 6.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.69, 132.88, 130.35, 129.53, 128.34, 67.60, 64.99, 35.56, 25.14, 23.61.[12]

8.6 Converted to compound 37



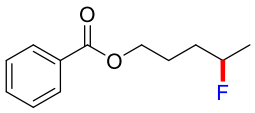
1b **37**

To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv.) in 20.0 mL of 3:1 acetone/water was added Pyridine (2.0 mmol, 2.0 equiv.) and NaOH (2.5 mmol, 2.5 equiv.) in a 48.0 mL resealable pressure tube under nitrogen. The solution was stirred and heated at 70 °C for 24 h. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure to remove most of the acetone. The product was extracted with EtOAc (3 x 10.0 mL). The combined EtOAc extracts were washed with 3 M HCl (8.0 mL) and saturated aqueous $NaHCO_3$ (3 x 5.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure.

To a solution of the crude residue in MeCN (5.0 mL) was added a solution of DAST (209 mg, 1.3 mmol,1.3 equiv.) in MeCN (5.0 mL) at -78 °C under nitrogen. The reaction mixture was warmed to 40 °C and stirred for 6 h. The reaction mixture was extracted with DCM (3 x 10.0 mL), washed with saturated aqueous $NaHCO_3$ (3 x 5.0 mL) and

brine (3 x 5.0 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **37**.

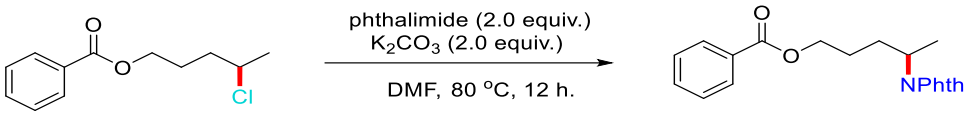
4-fluoropentyl benzoate



37

R_f = 0.6, 5% acetone in hexane, yellowish oil (112 mg, 56% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.84 – 4.63 (m, 1H), 4.41 – 4.32 (m, 2H), 2.03 – 1.92 (m, 1H), 1.90 – 1.69 (m, 3H), 1.36 (dd, J = 23.8, 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.51, 132.89, 130.34, 129.52, 128.35, 90.99, 89.67, 64.58, 33.56, 33.39, 24.59, 24.55, 21.07, 20.88. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -173.20, -173.23, -173.25, -173.28, -173.30, -173.31, -173.34, -173.35, -173.36, -173.39, -173.40, -173.40, -173.42, -173.44, -173.45, -173.47, -173.49, -173.50, -173.52, -173.55.[13]

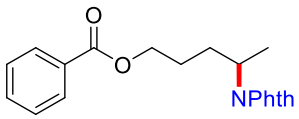
8.7 Converted to compound 38



1b **38**

In a 15 mL resealable pressure tube, **1b** (226 mg, 1.0 mmol, 1.0 equiv.) and phthalimide (2.0 mmol, 2.0 equiv.) and K_2CO_3 (2.0 mmol, 2.0 equiv.) were dissolved in DMF (5.0 mL). The reaction mixture was heated to 80 °C for 12 h under air. After the reaction equilibrium, the mixture was extracted with DCM. The combined organic phases were washed with saturated brine and dried over anhydrous Na_2SO_4, then filtered and concentrated by rotary evaporation. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **38**

4-(1,3-dioxoisoindolin-2-yl)pentyl benzoate



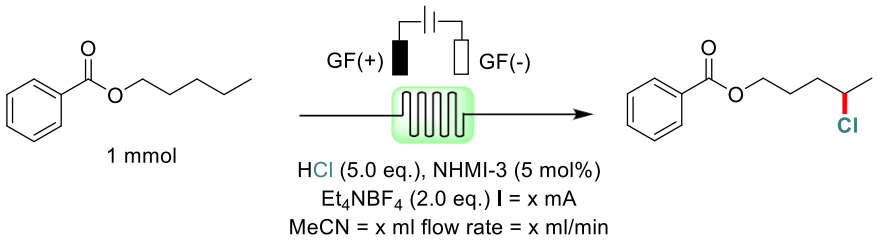
38

R_f = 0.6, 10% acetone in hexane, yellowish oil (279 mg, 83%

yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.81 (dt, J = 6.9, 3.5 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 4.42 (ddd, J = 12.8, 6.7, 2.8 Hz, 1H), 4.31 (t, J = 6.5 Hz, 2H), 2.30 – 2.19 (m, 1H), 1.91 (ddt, J = 13.7, 11.1, 5.7 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.51 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46, 166.51, 133.89, 132.85, 131.93, 130.27, 129.55, 128.31, 123.12, 64.38, 47.13, 30.24, 26.17, 18.75. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{20}H_{20}NO_4^+$ 338.1387; Found: 338.1390.

9. Flow electrochemistry

9.1 Optimization of flow electrochemistry conditions[a]



Entry	Deviation from standard conditions	Yield of **1b** (%) [b, c]
1[d]	0.2 mL min^{-1}/MeCN (2.0 mL) / 10mA	23
2	0.4 mL min^{-1}/MeCN (2.0 mL) / 10mA	45
3	0.6 mL min^{-1}/MeCN (2.0 mL) / 10mA	48
4	0.4 mL min^{-1}/MeCN (4.0 mL) / 10mA	52
5	0.4 mLmin^{-1}/MeCN (6.0 mL) / 10mA	41
6	0.4 mL min^{-1}/MeCN (4.0 mL) / 20mA	53
7	**0.4 mL min^{-1}/MeCN (4.0 mL) / 25mA**	**69**
8	0.4 mL min^{-1}/MeCN (4.0 mL) / 30mA	52
9	0.4 mL min^{-1}/MeCN (4.0 mL) / 35mA	47

[a] Reaction conditions: **1a** (1.0 mmol, 1 equiv.), graphite felts as electrodes (2.0 cm × 6.0 cm × 0.2 cm), constant current, **NHMI-3** (5 mol%), Et_4NBF_4 (2.0 equiv.). HCl (5.0 equiv.), 4h. room temperature. [b] Isolated yield. [c] RSM is short for the recovery of starting material. Faraday efficiency η = 38% (The calculation method is shown on page S32).

9.2 Detailed steps for the continuous flow electrolysis

Note: The screws of the assembled plate were screwed applying a torque of 5.5 N · m.

For all procedures in flow, the reactor should be fully filled before starting the electrolysis to reach the steady state.

General procedure of the electrochemical chlorination reactions in flow: The electrolysis was conducted using a flow electrolytic cell equipped with a graphite anode and a graphite cathode with the exposed surface area of 12 cm^2. The solution containing substrate (1 mmol, 1.0 equiv.), Et_4NBF_4 (2.0 equiv.), HCl (5.0 equiv.) **NHMI-3** (5 mmol%) in MeCN (4.0 mL) was pushed using a syringe pump to pass through the flow cell operated with a flow rate of 0.40 mL min^{-1} and a constant current in the range of 25 mA. Stay for a total of 4 hours. The solution was then electrolyzed as specified for each entry. After 1.5 residence times when the reactor reached steady state. Upon completion the solution was dissolved in DCM (10.0 mL) and washed with water (3x10.0 mL) to remove the remaining catalyst. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure to afford the crude product. The reaction mixture was purified by column chromatography on silica gel.

Flow Reactor Compartments: A: slot for graphite felt (Teflon base) B and B': graphite cathode (2 cm × 6 cm × 0.2 cm); C: turbulence promoter; D: gasket.

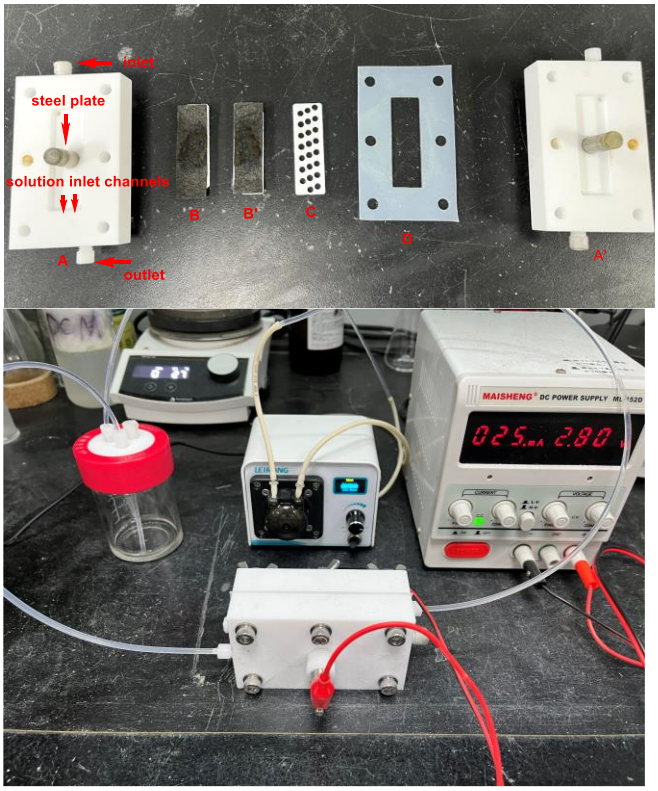
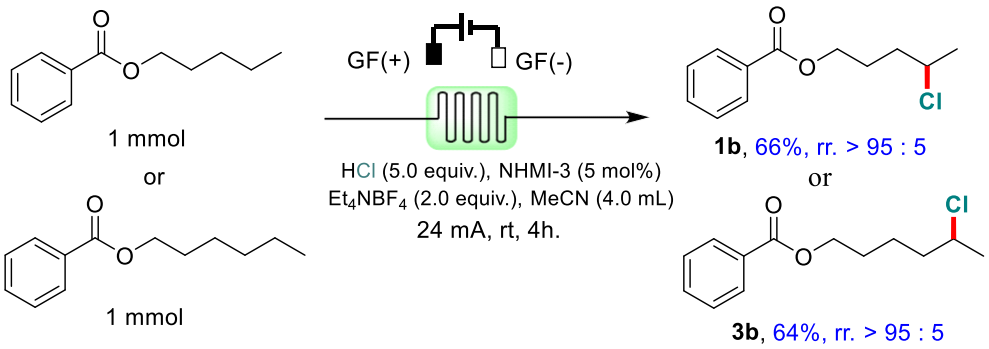


Figure S13. Flow electrochemical cell assembly

Reuse of the electrodes for the flow electrolysis B:

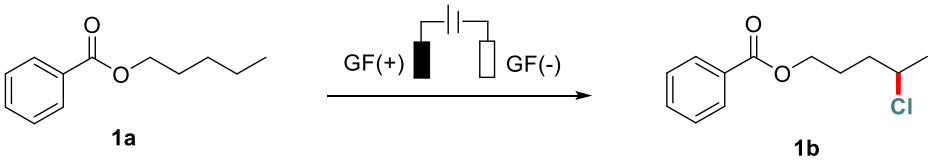
After reaction according to GP of flow electrolysis the reactor was flushed of its remaining working solution with air and then purged with acetone. The reactor was disassembled, and the electrodes were submitted to a sequential cleaning using acetone, 1 M HCl, water and finally acetone to flush the surface of the electrode. Then vacuum dry the graphite felt electrode. It can continue to be used for the next reaction.



The reaction proceeds according to the flow electrochemical program described earlier, and the yield and regioselectivity are determined using crude ^{1}H NMR. Product characterization can be found in the following text.

9.3 Electrodes Recycling Experiments

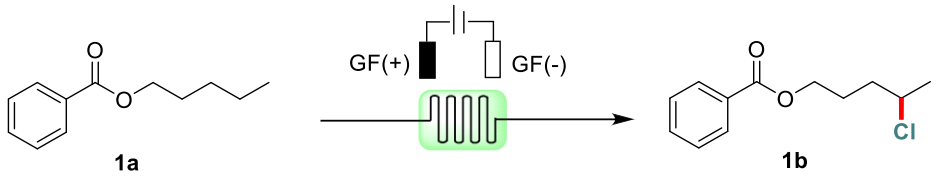
According to the GP-A program for reaction, After the reaction is complete, process the graphite felt electrode according to the cleaning procedure A, use the same electrode for the next reaction, and calculate the yield obtained by reusing the graphite felt electrode.



Number of repeated uses	Yield of **1b** (%) [b]
1	69
2	67
3	71
4	66
5	63

[a] Reaction conditions: **1a** (1.0 mmol, 1 equiv.), graphite felts as electrodes (2.0 cm × 2.0 cm × 0.2 cm), constant current, **NHMI-3** (5 mol%), Et_4NBF_4 (2.0 equiv.). HCl (2.5 equiv.), 10mA, MeCN (2.0 mL), room temperature. [b] Isolated yield.

According to the GP program for flow electrolysis, After the reaction is complete, process the graphite felt electrode according to the cleaning procedure B, use the same electrode for the next reaction, and calculate the yield obtained by reusing the graphite felt electrode.



Number of repeated uses	Yield of **1b** (%) [b]
1	71
2	68
3	70
4	64
5	60

[a] Reaction conditions: **1a** (1.0 mmol, 1 equiv.), graphite felts as electrodes (2.0 cm × 6.0 cm × 0.2 cm), constant current, **NHMI-3** (5 mol%), Et_4NBF_4 (2.0 equiv.), HCl (5.0 equiv.), 25 mA, MeCN (4.0 mL), 0.4 mL/min, room temperature. [b] Isolated yield. [c] RSM is short for the recovery of starting material.

10. Cyclic voltammetry (CV) experiment

Cyclic voltammograms were measured using a CHI 730E bipotentiostat equipped with electrochemical analysis software. A reaction was set up using General Procedure with three electrodes: Sn as working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter as electrode, the electrodes were polished with 0.05 μm aluminum oxide, ultrasonically rinsed with ethanol and ultrapure water before measurements. The solvent deoxygenated by nitrogen bubbling for 0.5 h. The CV plotting convention was IUPAC. The starting point was 0.0 V.

10.1 Blank experiment

cyclic voltammetry experiment of **blank** sample using **glassy carbon** working electrode at 100 mV/S. A solution of Et_4NBF_4 (0.1 mmol) in 10.0 mL anhydrous MeCN was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

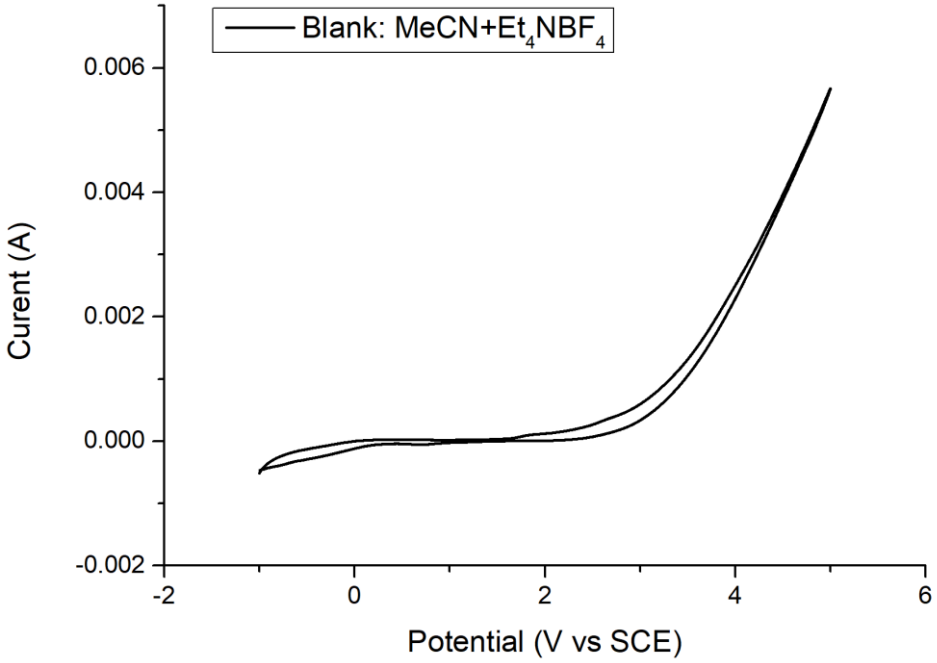


Figure S14. CV curve of blank

10.2 Cyclic voltammetry experiment of NHMI-3 using glassy carbon working electrode at 100 mV/S.

A solution of **NHMI-3** (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10.0 mL anhydrous MeCN was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

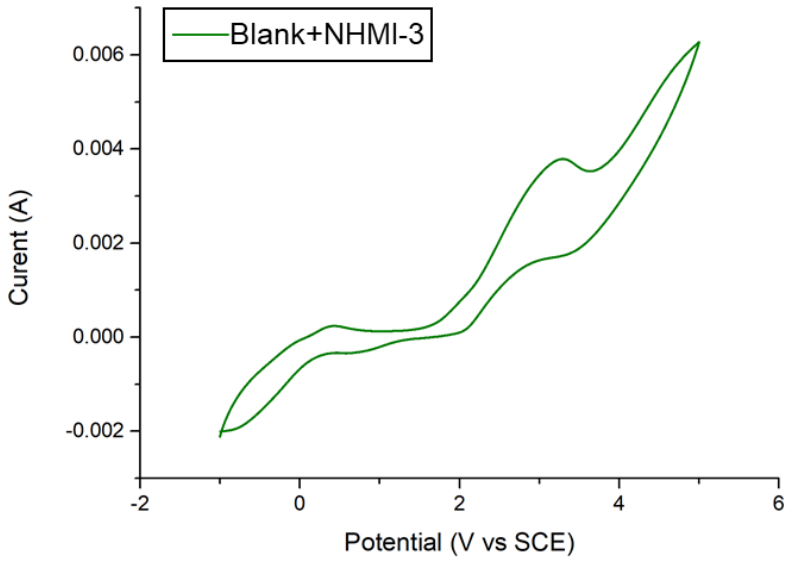


Figure S15. CV curve of **NHMI-3**

10.3 Cyclic voltammetry experiment of HCl (aq. 36.5) using glassy carbon working electrode at 100 mV/S.

A solution of HCl (aq. 36.5, 0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10.0 mL anhydrous MeCN was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

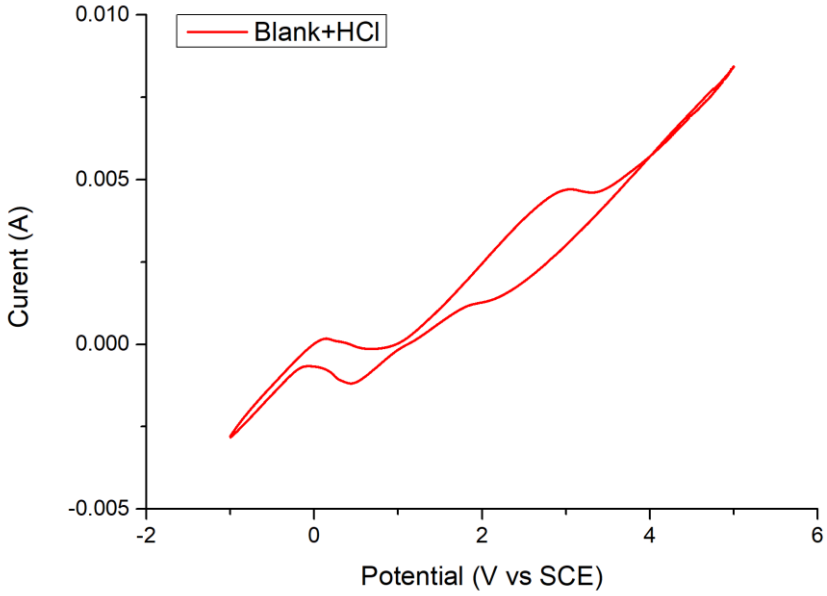


Figure S16. CV curve of HCl (aq. 36.5)

10.4 Cyclic voltammetry experiment of NHMI-3 and HCl (aq. 36.5) using glassy carbon working electrode at 100 mV/S.

A solution of **NHMI-3** (0.1 mmol) and HCl (aq. 36.5, 0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10.0 mL anhydrous MeCN was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a Pt counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.

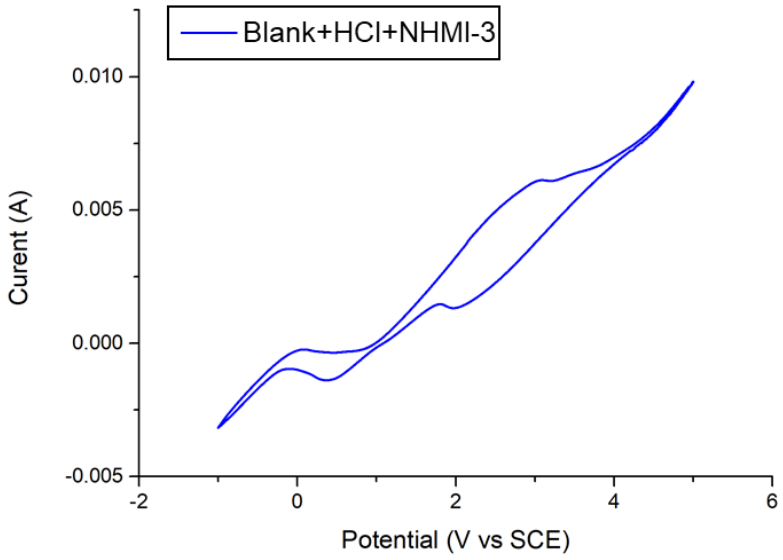


Figure S17. CV curve of **NHMI-3** and HCl (aq. 36.5%)

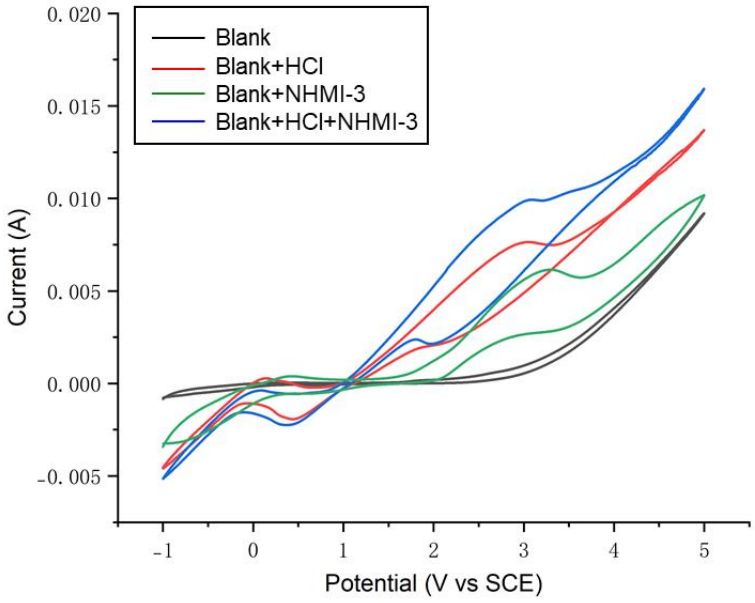


Figure S18. CV curve

Results:

A peak for oxidation of **NHMI-3** was observed at 3.42 V in MeCN (*vs.* SCE).

A peak for oxidation of **HCl** (aq. 36.5%) was observed at 2.97 V in MeCN (*vs.* SCE).

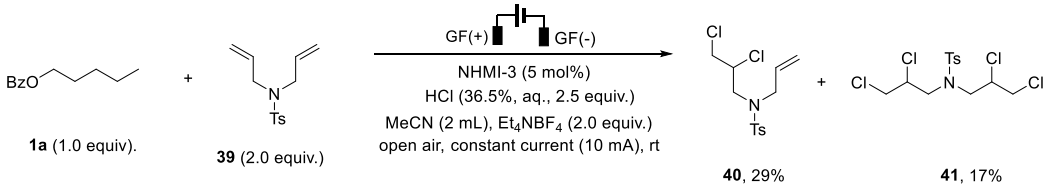
A peak for oxidation of **NHMI-3** was observed at 3.04 V in MeCN with **HCl** (aq. 36.5).

A peak for oxidation of **HCl** (aq. 36.5%) was observed at 3.05 V in MeCN with **NHMI-3**.

Cyclic voltammetry (CV) of a mixture of **NHMI-3** and **HCl** (aq. 36.5%) revealed that the oxidation potential of **NHMI-3** could be effectively lowered under acid conditions.

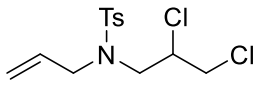
11. Mechanistic Study

11.1 Radical clock experiments



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. *N,N*-diallyl-4-methylbenzenesulfonamide (2.0 mmol, 2.0 equiv.), **1a** (1.0 mmol, 1.0 equiv.) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5%, aqueous, 2.5 mmol, 2.5 equiv.) was added dropwise. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature. After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the products **40** and **41**. It is important to note that we did not observe the product **1b.**

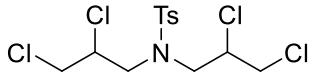
***N*-allyl-*N*-(2,3-dichloropropyl)-4-methylbenzenesulfonamide**



40 R_f = 0.7, 5% acetone in hexane, white solid (93 mg, 29% yield)

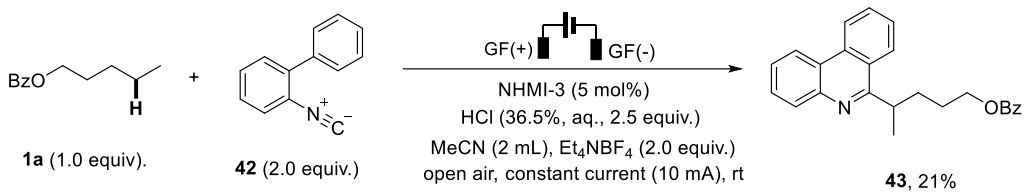
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.62 – 5.49 (m, 1H), 5.23 – 5.14 (m, 2H), 4.44 (ddd, J = 9.8, 7.0, 5.0 Hz, 1H), 3.93 (d, J = 6.5 Hz, 1H), 3.88 – 3.80 (m, 3H), 3.57 (dd, J = 15.0, 7.3 Hz, 1H), 3.27 (dd, J = 15.0, 6.6 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.11, 136.00, 132.34, 130.06, 127.56, 120.46, 58.96, 52.95, 51.03, 46.73, 21.69.[14]

***N,N*-bis(2,3-dichloropropyl)-4-methylbenzenesulfonamide**



41 R_f = 0.8, 5% acetone in hexane, colourless oil (55 mg, 17% yield)**^{1}H NMR** (500 MHz, $CDCl_3$)δ 7.69 – 7.63 (m, 2H), 7.26 (d, J = 8.0 Hz, 2H), 5.57 (ddt, J = 16.6, 10.2, 6.3 Hz, 2H), 5.10 (ddd, J = 6.0, 3.8, 1.3 Hz, 4H), 3.76 (d, J = 6.3 Hz, 4H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.24, 137.33, 132.63, 129.68, 127.09, 118.91, 49.34, 21.45.[14]

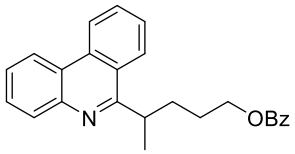
11.2 The capture of carbon radicals



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. 2-isocyano-1,1'-biphenyl (2.0mmol, 2.0 equiv.), **1a** (1.0 mmol, 1.0 equiv.) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5, aqueous, 2.5 mmol, 2.5 equiv.) was added in batches, first added HCl (1.5 equiv.), react for about 5 hours, and then added HCl (1.0 equiv.). The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature. After

the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the product **43**.

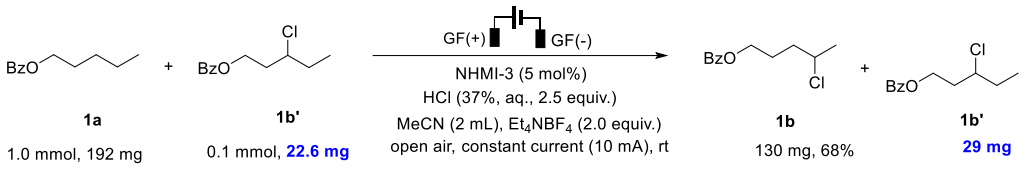
4-(phenanthridin-6-yl)pentyl benzoate



43

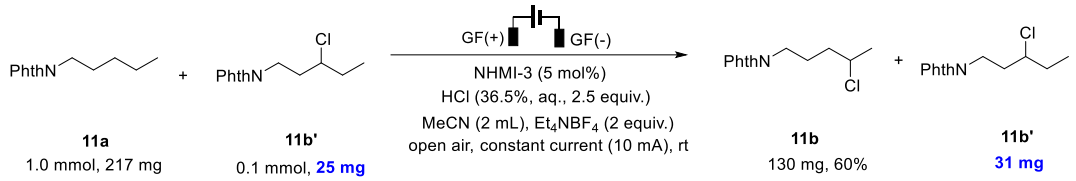
R_f = 0.7, 8% acetone in hexane, pale-yellow oil (77 mg, 21% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.58 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.68 (ddd, *J* = 24.2, 16.5, 7.3 Hz, 3H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.37 (t, *J* = 6.4 Hz, 2H), 3.95 (dd, *J* = 13.5, 6.8 Hz, 1H), 2.42 (dd, *J* = 21.1, 14.9 Hz, 1H), 2.00 – 1.84 (m, 3H), 1.53 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.77, 130.47, 130.04, 129.97, 129.56, 128.43, 128.29, 127.22, 126.28, 125.44, 125.08, 123.35, 122.65, 121.84, 65.20, 36.24, 32.15, 29.71, 27.02, 20.58. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{24}NO_2^+$ 370.1802; Found: 370.1805.

11.3 Control experiments



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. **1b'** (0.1 mmol, 22.6 mg), **1a** (1 mmol, 192mg) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5, aqueous, 2.5 mmol, 2.5 equiv.) was added in batches, first added HCl (1.5 equiv.), react for about 5 hours, and then added HCl (1.0 equiv.). The reaction mixture was stirred and electrolyzed with

a constant current of 10 mA at room temperature. After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the product **1b** (130mg, 68% yield) and **1b'** (29mg).

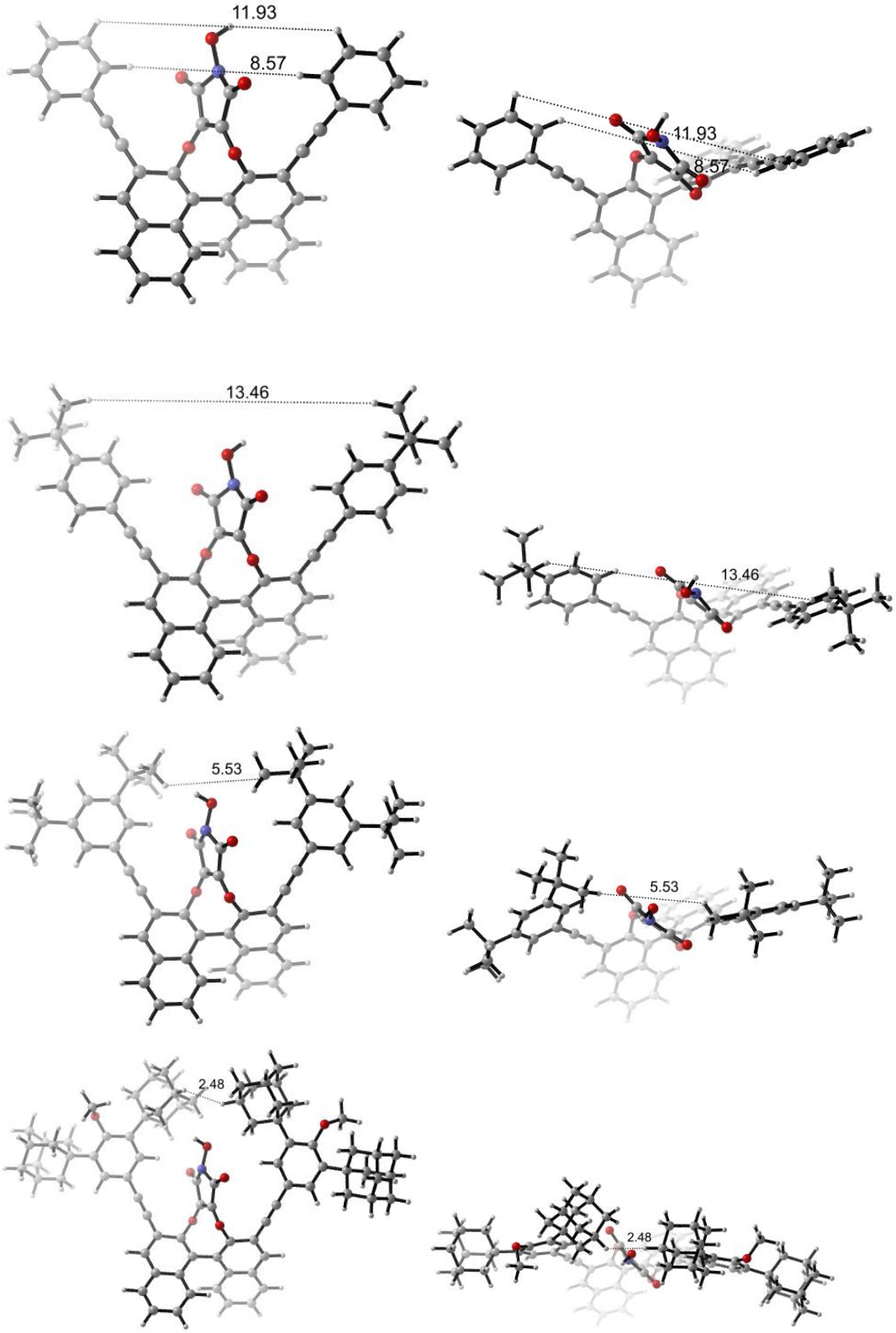


Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. **11b'** (0.1 mmol, 22.6 mg), **11a** (1 mmol, 192mg) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5%, aqueous, 2.5 mmol, 2.5 equiv.) was added in batches, first added HCl (1.5 equiv.), react for about 5 hours, and then added HCl (1.0 equiv.). The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature. After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the product **11b** (130mg, 60% yield) and **11b'** (31mg).

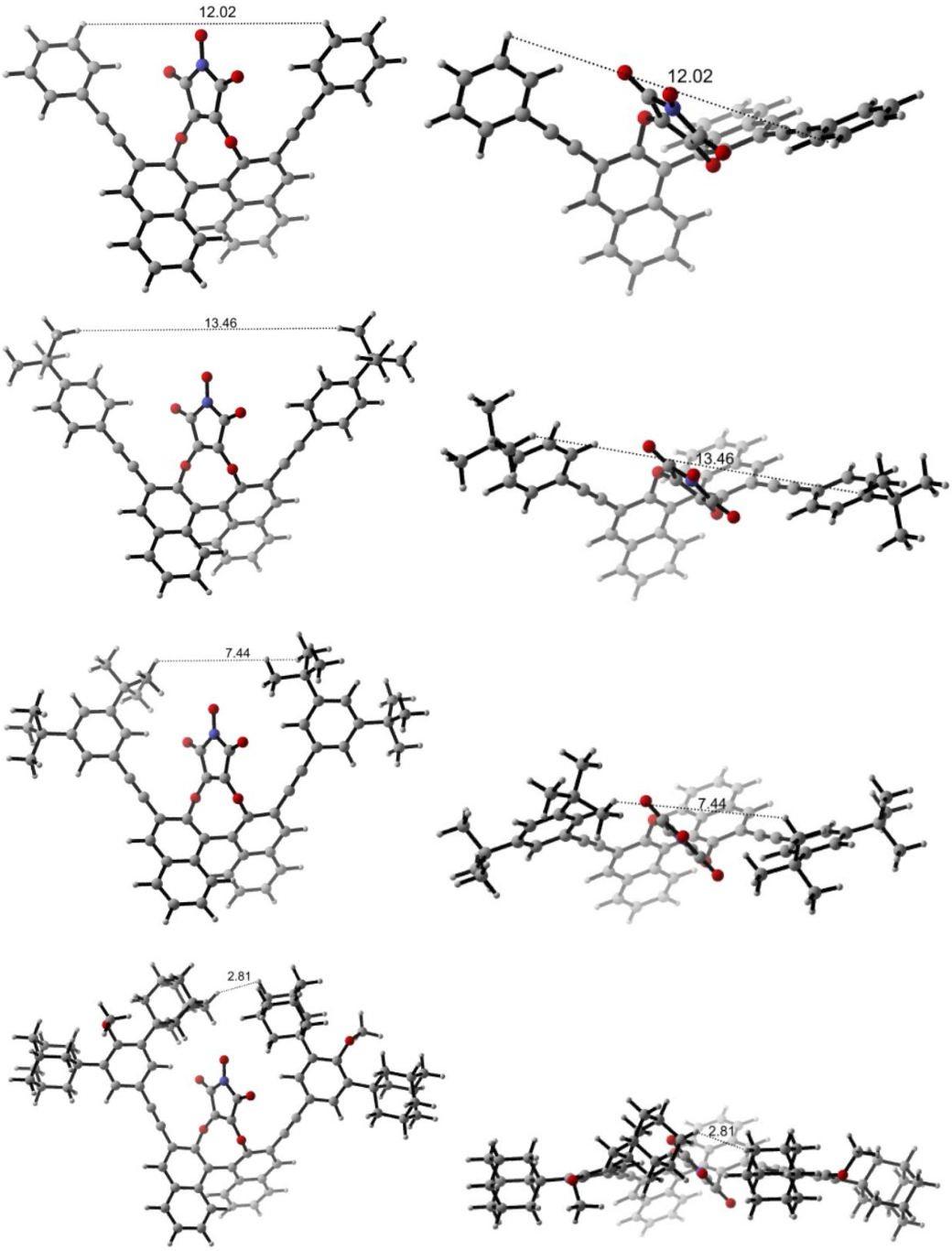
11.4 Computational details

All calculations were performed using the Gaussian 16 package.[15] The geometry optimizations were carried out with the density functional theory B3LYP[16] at the standard 6-31G (d, p)[17] basis set. Solvent (acetonitrile) effects were considered with the SCRF method using the PCM[18] model. The vibrational frequency calculations were performed at the same computational level for each optimized structure to confirm it as a minimum structure.

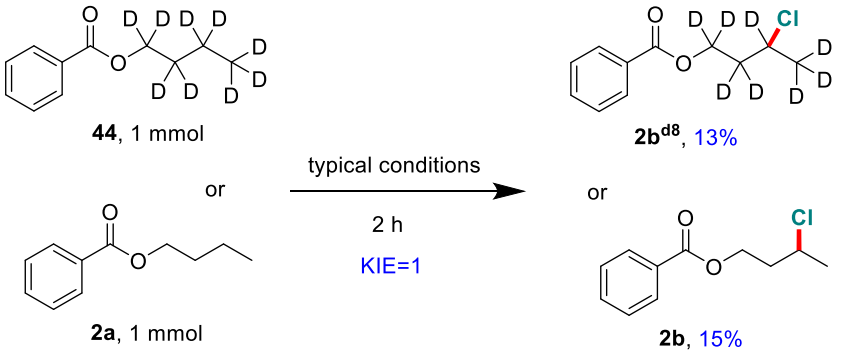
The calculation structure of catalysts



The calculation structure of the corresponding N-O radicals



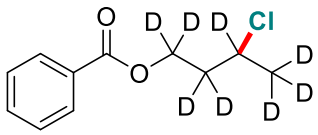
11.5 Deuterated KIE experiments



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively.

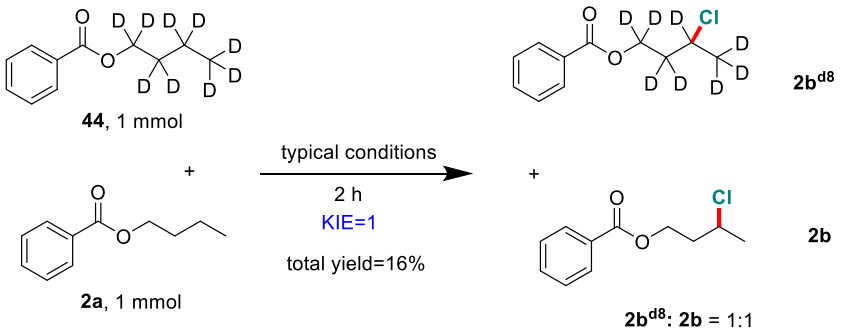
The graphite felt anode attached to a platinum wire. **44** (1 mmol), and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5%, aqueous, 2.5 mmol, 2.5 equiv.) was added dropwise. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature (23 °C). After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the product **2b^{d8}** in 13% yield. Under the same conditions led to the product **2b** in 15% yield. Comparing the yield of **2b^{d8}** and **2b**, we found the KIE value was 1.0.

3-chlorobutyl-1,1,2,2,3,4,4,4-*d*$_8$ benzoate



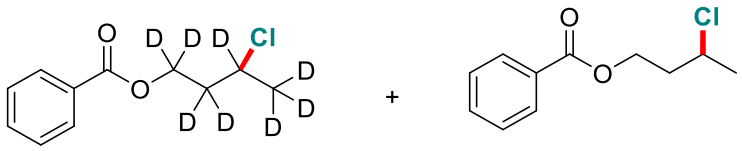
2b^{d8}

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.71, 132.76, 130.57, 129.52, 128.30.



Two graphite felts (2 cm x 2 cm x 0.5 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. **44** (1.0 mmol), **2a** (1.0 mmol) and **NHMI-3** (0.05 mmol, 5 mol%) were first dissolved in MeCN (2.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.0 mmol, 2.0 equiv.). Finally, HCl (concentrated, 36.5%, aqueous, 2.5 mmol, 2.5 equiv.) was added

dropwise. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature (23 °C). After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2.0 mL). Then the mixture was extracted with DCM (3 x 5.0 mL), the combined organic phase was washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by chromatography on silica gel to afford the product **2b^{d8}** and **2b** in combined 16% yield. Comparing the ^{1}H NMR spectra, we found the ratio of **2b**: **2b^{d8}** was 1:1, so the intermolecular KIE value was 1.0.

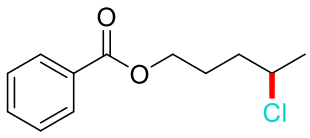


2b^{d8} **2b**

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 4H), 7.58 (dd, J = 15.9, 7.5 Hz, 2H), 7.46 (td, J = 7.6, 5.1 Hz, 4H), 4.57 – 4.47 (m, 2H), 4.30 – 4.23 (m, 1H), 2.28 – 2.21 (m, 2H), 2.17 – 2.10 (m, 2H), 1.62 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.70, 166.39, 133.02, 132.76, 130.57, 130.12, 129.57, 129.52, 128.39, 128.30, 62.10, 54.86, 39.16, 25.47.

12. Characterization data of products

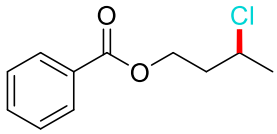
4-chloropentyl benzoate



1b

R_f = 0.7, 5% acetone in hexane, yellowish oil (154 mg, 68% yield). Followed the general procedure (r.r.=96:4). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.7 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.42 – 4.32 (m, 2H), 4.12 (dd, J = 11.4, 7.0 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.97 – 1.84 (m, 3H), 1.56 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.41, 132.98, 130.18, 129.56, 128.37, 62.11, 61.56, 37.07, 31.63, 10.80.[19]

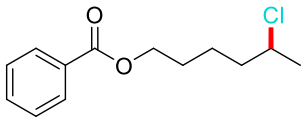
3-chlorobutyl benzoate



2b

R_f = 0.7, 5% acetone in hexane, yellowish oil (110 mg, 52% yield). Followed the general procedure (r.r.=100:0). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 4.49 (tdd, J = 11.3, 9.7, 5.6 Hz, 2H), 4.30 – 4.20 (m, 1H), 2.27 – 2.08 (m, 2H), 1.60 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.41, 133.04, 130.09, 129.58, 128.40, 62.10, 54.89, 39.14, 25.49.[19]

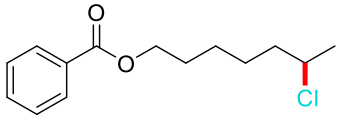
5-chlorohexyl benzoate



3b

R_f = 0.7, 5% acetone in hexane, yellowish oil (148 mg, 66% yield). Followed the general procedure (r.r.=95:5). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 4.33 (t, J = 6.4 Hz, 2H), 4.05 (dd, J = 12.9, 6.5 Hz, 1H), 1.83 – 1.76 (m, 4H), 1.69 (dt, J = 15.1, 7.4 Hz, 1H), 1.60 – 1.55 (m, 1H), 1.52 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 132.88, 130.38, 129.54, 128.35, 64.70, 58.47, 39.87, 28.24, 25.37, 23.25.[20]

6-chloroheptyl benzoate

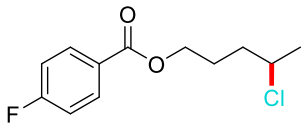


4b

R_f = 0.7, 5% acetone in hexane, yellowish oil (154 mg, 61% yield). Followed the general procedure (r.r.=92:8). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 2H), 7.57 (d, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.35 (t, J = 6.6 Hz, 2H), 4.06 (dd, J = 13.0, 6.5 Hz, 1H), 1.79 (ddd, J = 12.3, 11.7, 6.6 Hz, 5H), 1.63 – 1.58 (m, 1H), 1.52 (dd, J = 12.8, 6.3 Hz, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.57, 133.01, 132.92, 130.30, 129.54, 128.36, 64.42, 63.13, 40.63, 35.07, 25.90, 19.71, 13.54. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for

$C_{14}H_{20}ClO_2^+$ 255.1146; Found: 255.1147.

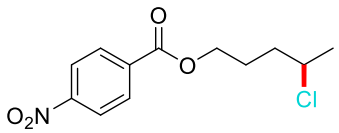
4-chloropentyl 4-fluorobenzoate



5b

R_f = 0.7, 5% acetone in hexane, yellowish oil (151 mg, 62% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 – 8.00 (m, 2H), 7.10 (t, J = 8.6 Hz, 2H), 4.39 – 4.28 (m, 2H), 4.15 – 4.02 (m, 1H), 2.02 (qd, J = 9.8, 3.8 Hz, 1H), 1.87 (qdd, J = 16.2, 6.4, 3.6 Hz, 3H), 1.54 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.72, 165.49, 164.70, 132.10, 132.02, 126.51, 126.49, 115.56, 115.38, 64.46, 58.06, 36.80, 26.01, 25.36. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.73, -105.74, -105.75, -105.76, -105.76, -105.77. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{15}ClFO_2^+$ 245.0739; Found: 245.0740.

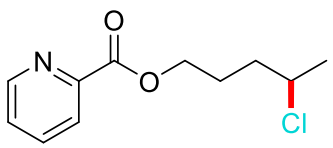
4-chloropentyl 4-nitrobenzoate



6b

R_f = 0.7, 5% acetone in hexane, yellowish oil (160 mg, 59% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 8.22 (d, J = 8.8 Hz, 2H), 4.50 – 4.39 (m, 2H), 4.17 – 4.06 (m, 1H), 2.12 – 2.03 (m, 1H), 1.99 – 1.83 (m, 3H), 1.57 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.63, 150.56, 135.60, 130.68, 123.56, 65.35, 57.98, 36.74, 25.93, 25.41. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{15}ClNO_4^+$ 272.0684; Found: 272.0685.

4-chloropentyl picolinate

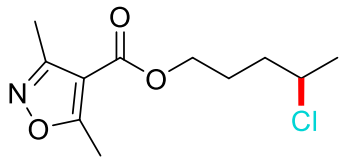


7b

R_f = 0.5, 7% acetone in hexane, yellowish oil (107 mg, 47%

yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 – 8.65 (m, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.82 (td, J = 7.7, 1.7 Hz, 1H), 7.45 (ddd, J = 7.6, 4.7, 1.1 Hz, 1H), 4.46 – 4.38 (m, 2H), 4.10 – 4.02 (m, 1H), 2.08 – 2.01 (m, 1H), 1.95 – 1.80 (m, 3H), 1.50 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.15, 149.89, 148.07, 136.97, 126.86, 125.11, 65.24, 58.05, 36.65, 26.02, 25.35. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{15}ClNO_2^+$ 228.0786; Found: 228.0783.

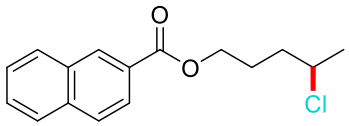
4-chloropentyl 3,5-dimethylisoxazole-4-carboxylate



8b

R_f = 0.7, 6% acetone in hexane, yellowish oil (125 mg, 51% yield). Followed the general procedure (r.r.=97:3). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.31 (t, J = 6.1 Hz, 2H), 4.09 (dd, J = 11.4, 6.8 Hz, 1H), 2.66 (s, 3H), 2.44 (s, 3H), 2.02 (dt, J = 14.4, 8.3 Hz, 1H), 1.93 – 1.81 (m, 3H), 1.56 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.23, 162.38, 159.80, 108.64, 63.92, 57.87, 36.80, 25.88, 25.37, 13.36, 11.84. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{17}ClNO_3^+$ 246.0891; Found: 246.0890.

4-chloropentyl 2-naphthoate

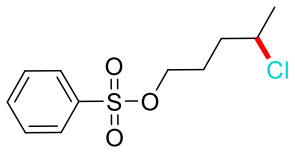


9b

R_f = 0.7, 5% acetone in hexane, yellowish oil (196 mg, 71% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.94 (d, J = 8.7 Hz, 1H), 8.19 (dd, J = 7.3, 1.1 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.63 (ddd, J = 8.5, 6.8, 1.3 Hz, 1H), 7.53 (ddd, J = 17.3, 11.7, 4.4 Hz, 2H), 4.48 – 4.41 (m, 2H), 4.11 (dtd, J = 11.0, 6.5, 4.6 Hz, 1H), 2.14 – 2.05 (m, 1H), 2.01 – 1.86 (m, 3H), 1.56 (d, J = 6.6 Hz, 3H), 1.13 (d, J = 6.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.50, 133.88,

133.39, 131.39, 130.13, 128.58, 127.78, 127.21, 126.24, 125.80, 124.51, 64.44, 58.16, 36.94, 26.12, 25.43. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{18}ClO_2^+$ 277.0990; Found: 277.0990.

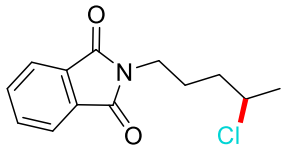
4-chloropentyl benzenesulfonate



10b

R_f = 0.7, 5% acetone in hexane, yellowish oil (173 mg, 66% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.8 Hz, 2H), 4.12 – 4.04 (m, 2H), 4.00 – 3.91 (m, 1H), 1.94 – 1.86 (m, 1H), 1.78 (tdd, J = 13.0, 10.2, 4.9 Hz, 2H), 1.72 – 1.64 (m, 1H), 1.48 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.10, 133.78, 129.27, 127.83, 70.07, 57.65, 35.99, 26.16, 25.34. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{16}ClO_3S^+$ 263.0503; Found: 263.0504.

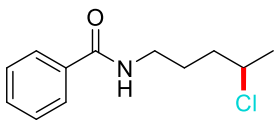
2-(4-chloropentyl)isoindoline-1,3-dione



11b

R_f = 0.5, 12% acetone in hexane, yellowish oil (153 mg, 61% yield). Followed the general procedure (r.r.=97:3). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd, J = 5.4, 3.0 Hz, 2H), 4.10 – 3.96 (m, 1H), 3.68 (dd, J = 13.5, 6.8 Hz, 2H), 1.93 – 1.86 (m, 1H), 1.81 – 1.68 (m, 3H), 1.46 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.30, 133.93, 132.04, 123.19, 57.89, 37.29, 25.86, 25.32.[19]

***N*-(4-chloropentyl)benzamide**

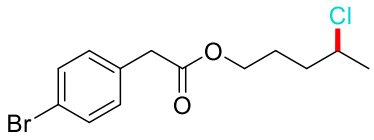


12b

R_f = 0.7, 6% acetone in hexane, yellowish oil (133 mg, 59%

yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.4 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.38 (br, 1H), 4.09 (dd, J = 10.0, 6.5 Hz, 1H), 3.54 – 3.45 (m, 2H), 1.88 – 1.75 (m, 4H), 1.53 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.80, 134.73, 131.56, 128.69, 126.99, 58.48, 39.59, 37.66, 27.03, 25.52.[21]

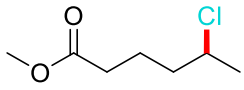
4-chloropentyl 2-(4-bromophenyl)acetate



13b

R_f = 0.7, 5% acetone in hexane, yellowish oil (169 mg, 53% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H), 4.14 – 4.08 (m, 2H), 4.02 – 3.95 (m, 1H), 3.56 (s, 2H), 1.90 – 1.81 (m, 1H), 1.76 – 1.66 (m, 3H), 1.48 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.95, 133.02, 131.67, 131.01, 121.15, 64.37, 58.02, 40.76, 36.61, 25.84, 25.37. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{17}BrClO_2^+$ 319.0095; Found: 319.0094.

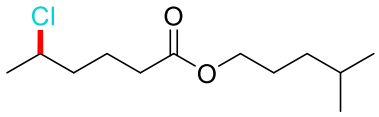
methyl 5-chlorohexanoate



14b

R_f = 0.4, hexane, yellowish oil (103 mg, 63% yield). Followed the general procedure (r.r.=96:4). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.15 - 4.01 (m, 3 H), 2.06 (s, 3 H), 1.94 - 1.70 (m, 4 H), 1.54 (d, J = 6.6 Hz, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.49, 58.00, 51.42, 39.44, 33.27, 25.21, 21.99.[22]

4-methylpentyl 5-chlorohexanoate

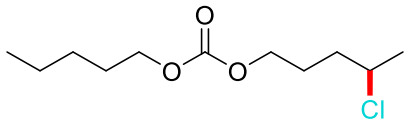


15b

R_f = 0.5, 3% acetone in hexane, yellowish oil (119 mg,

51% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.10 – 3.99 (m, 3H), 2.33 (t, J = 6.8 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.78 – 1.70 (m, 3H), 1.65 – 1.60 (m, 2H), 1.56 (d, J = 6.7 Hz, 1H), 1.51 (d, J = 6.5 Hz, 3H), 1.22 (dt, J = 11.1, 7.0 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.83, 63.54, 58.07, 36.74, 34.27, 31.30, 25.95, 25.35, 24.65, 22.30, 13.88. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{24}ClO_2^+$ 235.1459; Found: 235.1455.

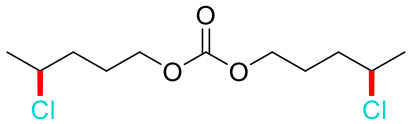
4-chloropentyl pentyl carbonate



16b

R_f = 0.7, 5% acetone in hexane, yellowish oil (156 mg, 66% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.17 – 4.11 (m, 4H), 4.04 (dd, *J* = 11.9, 5.6 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.88 – 1.76 (m, 3H), 1.69 – 1.65 (m, 2H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.37 – 1.33 (m, 4H), 0.91 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.31, 68.17, 67.19, 58.05, 36.47, 28.36, 27.82, 26.02, 25.37, 22.29, 13.91. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{22}ClO_3^+$ 237.1252; Found: 237.1250.

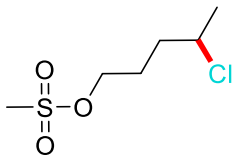
bis(4-chloropentyl) carbonate



17b

R_f = 0.6, 5% acetone in hexane, yellowish oil (143 mg, 53% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.17 (td, *J* = 6.1, 3.7 Hz, 4H), 4.04 (dt, *J* = 6.4, 5.1 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.81 (dddd, *J* = 16.1, 11.9, 5.6, 2.7 Hz, 6H), 1.53 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.19, 67.34, 57.99, 36.46, 25.99, 25.36. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{21}Cl_2O_3^+$ 271.0862; Found: 271.0861.

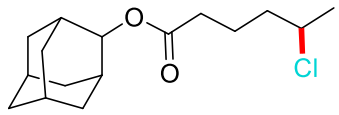
4-chloropentyl methanesulfonate



18b

R_f = 0.7, 5% acetone in hexane, yellowish oil (114 mg, 57% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.33 – 4.26 (m, 2H), 4.11 – 4.05 (m, 1H), 3.04 (s, 3H), 2.08 – 2.01 (m, 1H), 1.96 – 1.88 (m, 2H), 1.85 – 1.78 (m, 1H), 1.17 (d, J = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 69.23, 57.71, 37.47, 36.09, 26.46, 25.40. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_6H_{14}ClO_3S^+$ 201.0347; Found: 201.0350.

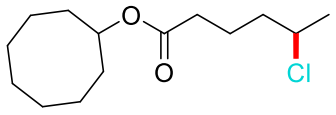
(1*r*,3*r*,5*r*,7*r*)-adamantan-2-yl 5-chlorohexanoate



19b

R_f = 0.6, 10% acetone in hexane, yellowish oil (130 mg, 46% yield). Followed the general procedure (r.r.=96:4). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.94 (s, 1H), 4.09 – 3.97 (m, 1H), 2.37 (t, J = 6.6 Hz, 2H), 2.01 (d, J = 15.9 Hz, 4H), 1.87 (dd, J = 17.1, 6.4 Hz, 5H), 1.80 – 1.73 (m, 7H), 1.56 (d, J = 11.7 Hz, 2H), 1.52 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.56, 76.95, 58.11, 39.54, 37.38, 36.33, 34.11, 31.90, 31.79, 27.23, 27.00, 25.30, 22.25. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{16}H_{26}ClO_2^+$ 285.1616; Found: 285.1618.

cyclooctyl 5-chlorohexanoate

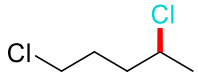


20b

R_f = 0.6, 5% acetone in hexane, yellowish oil (127 mg, 49% yield). Followed the general procedure (r.r.=96:4). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.90 (ddd, J = 12.2, 8.2, 3.8 Hz, 1H), 3.98 (dd, J = 11.7, 6.7 Hz, 1H), 2.25 (td, J = 6.7, 3.3 Hz, 2H), 1.80 – 1.62 (m, 11H), 1.56 – 1.45 (m, 10H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.50, 74.96, 58.07, 39.49, 34.01, 31.51, 27.05, 25.36, 25.26, 22.90, 22.14. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for

$C_{14}H_{26}ClO_2^+$ 261.1616; Found: 261.1616.

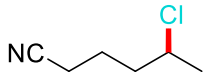
1,4-dichloropentane



21b

R_f = 0.6, hexane, yellowish oil (89 mg, 64% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.24 – 4.06 (m, 1H), 3.46 (dd, J = 11.3, 5.3 Hz, 2H), 2.20 – 2.06 (m, 1H), 2.07 – 1.89 (m, 3H), 1.77 – 1.69 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 50.21, 39.33, 32.85, 30.83, 26.54.[22]

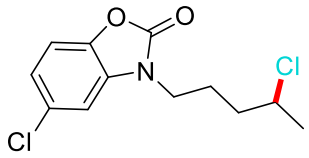
5-chlorohexanenitrile



22b

R_f = 0.6, 5% acetone in hexane, yellowish oil (69 mg, 53% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.04 (ddd, J = 9.9, 4.9, 2.7 Hz, 1H), 2.44 – 2.37 (m, 2H), 1.92 (ddd, J = 12.1, 7.5, 3.2 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.54 (dd, J = 6.5, 2.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 119.25, 57.32, 38.78, 25.34, 22.59, 16.73.[22]

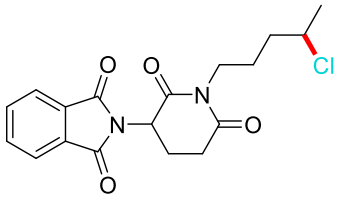
5-chloro-3-(4-chloropentyl)benzo[*d*]oxazol-2(3*H*)-one



23b

R_f = 0.5, 12% acetone in hexane, yellowish oil (172 mg, 63% yield). Followed the general procedure (r.r.=96:4). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (dt, J = 8.5, 5.2 Hz, 2H), 6.98 (d, J = 1.9 Hz, 1H), 4.06 (dqd, J = 8.5, 6.5, 4.6 Hz, 1H), 3.88 – 3.77 (m, 2H), 2.06 – 1.97 (m, 1H), 1.89 (tdd, J = 13.5, 10.2, 6.5 Hz, 1H), 1.83 – 1.72 (m, 2H), 1.50 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.33, 141.12, 131.97, 129.40, 122.33, 110.89, 108.76, 57.74, 41.87, 36.87, 25.41, 24.93. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{14}Cl_2NO_2^+$ 274.0396; Found: 274.0397.

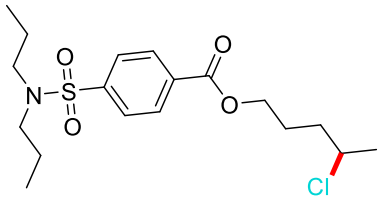
2-(1-(4-chloropentyl)-2,6-dioxopiperidin-3-yl)isoindoline-1,3-dione



24b

R_f = 0.5, 15% acetone in hexane, yellowish oil (214 mg, 59% yield). Followed the general procedure A (r.r.=97:3). The r.r. was determined by HPLC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 5.5, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.0 Hz, 2H), 4.97 (ddd, J = 14.9, 7.6, 4.4 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.87 – 3.77 (m, 2H), 3.01 – 2.91 (m, 1H), 2.82 – 2.71 (m, 2H), 2.17 – 2.07 (m, 1H), 1.82 – 1.74 (m, 1H), 1.73 – 1.66 (m, 3H), 1.48 (dd, J = 6.5, 1.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.83, 168.56, 168.53, 167.37, 134.42, 131.77, 123.73, 58.14, 58.05, 50.13, 40.01, 39.84, 37.37, 37.17, 31.99, 25.29, 25.12, 24.97, 22.02. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{20}Cl_2NO_4^+$ 363.1106; Found: 363.1108.

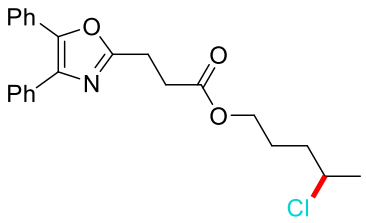
4-chloropentyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate



25b

R_f = 0.5, 20% acetone in hexane, yellowish oil (249 mg, 64% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 4.40 – 4.29 (m, 2H), 4.11 – 4.02 (m, 1H), 3.06 (dd, J = 8.5, 6.9 Hz, 4H), 2.00 (dddd, J = 16.3, 12.5, 8.0, 4.3 Hz, 1H), 1.92 – 1.79 (m, 3H), 1.54 – 1.48 (m, 7H), 0.83 (t, J = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.14, 144.28, 133.50, 130.15, 126.98, 64.98, 58.01, 49.92, 36.74, 25.93, 25.37, 21.91, 11.12. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{29}ClNO_4S^+$ 390.1500; Found: 390.1497.

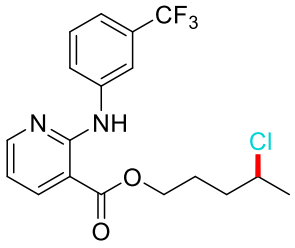
4-chloropentyl 3-(4,5-diphenyloxazol-2-yl)propanoate



26b

R_f = 0.5, 15% acetone in hexane, yellowish oil (242 mg, 61% yield). Followed the general procedure A (r.r.=97:3). The r.r. was determined by HPLC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 7.41 – 7.32 (m, 6H), 4.26 – 4.13 (m, 2H), 4.08 – 3.97 (m, 1H), 3.21 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.5 Hz, 2H), 1.96 – 1.86 (m, 1H), 1.84 – 1.71 (m, 3H), 1.49 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.96, 161.72, 145.43, 135.14, 132.45, 128.98, 128.65, 128.54, 128.47, 128.07, 127.89, 126.48, 64.18, 58.08, 36.65, 31.12, 25.91, 25.34, 23.55. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{23}H_{25}ClNO_3^+$ 398.1517; Found: 398.1514.

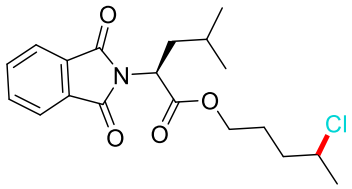
4-chloropentyl 2-((3-(trifluoromethyl)phenyl)amino)nicotinate



27b

R_f = 0.5, 25% acetone in hexane, yellowish oil (228 mg, 59% yield). Followed the general procedure A (r.r.=96:4). The r.r. was determined by HPLC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.40 (s, 1H), 8.46 – 8.40 (m, 1H), 8.32 – 8.25 (m, 1H), 8.13 (s, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.44 (t, J = 7.9 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 6.81 (dd, J = 7.8, 4.8 Hz, 1H), 4.44 – 4.33 (m, 2H), 4.11 (dt, J = 13.0, 6.5 Hz, 1H), 2.12 – 2.01 (m, 1H), 1.97 – 1.85 (m, 3H), 1.58 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.40, 155.77, 153.06, 140.37, 140.10, 129.17, 123.43, 118.95, 118.92, 117.05, 117.02, 114.06, 107.46, 64.83, 58.00, 36.78, 25.93, 25.39. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.57. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{19}ClF_3N_2O_2^+$ 387.1082; Found: 387.1082.

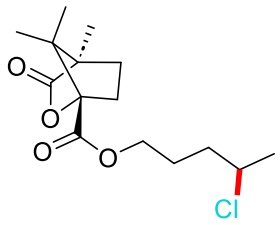
4-chloropentyl (2*S*)-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate



28b

R_f = 0.5, 15% acetone in hexane, yellowish oil (208 mg, 57% yield). Followed the general procedure (r.r.>95:5). The r.r. was determined by crude ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dt, J = 4.7, 3.1 Hz, 2H), 7.73 – 7.69 (m, 2H), 4.91 (dt, J = 11.4, 3.8 Hz, 1H), 4.27 – 4.00 (m, 2H), 3.99 – 3.82 (m, 1H), 2.32 – 2.24 (m, 1H), 1.93 (ddd, J = 14.2, 10.2, 4.1 Hz, 1H), 1.83 – 1.73 (m, 1H), 1.71 – 1.55 (m, 3H), 1.47 (ddd, J = 10.0, 8.5, 5.2 Hz, 1H), 1.39 (dt, J = 6.3, 4.1 Hz, 3H), 0.91 (ddd, J = 13.5, 6.4, 3.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.67, 167.69, 134.19, 131.79, 123.47, 65.02, 64.97, 57.83, 57.79, 50.69, 50.67, 37.27, 36.45, 36.41, 25.67, 25.64, 25.27, 25.22, 25.06, 23.12, 21.03. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{25}ClNO_4^+$ 366.1467; Found: 366.1464.

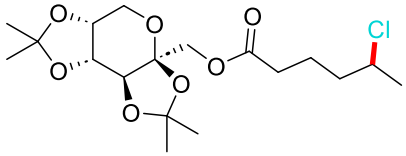
4-chloropentyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate



29b

R_f = 0.5, 10% acetone in hexane, yellowish oil (178 mg, 59% yield). Followed the general procedure (r.r.=97:3). The r.r. was determined by GC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.24 – 4.15 (m, 2H), 4.03 – 3.94 (m, 1H), 2.36 (ddd, J = 13.5, 10.8, 4.2 Hz, 1H), 1.96 (ddd, J = 13.6, 9.3, 4.6 Hz, 1H), 1.88 (tdd, J = 13.1, 7.2, 3.6 Hz, 2H), 1.81 – 1.67 (m, 3H), 1.62 (ddd, J = 13.3, 9.3, 4.2 Hz, 1H), 1.46 (d, J = 6.6 Hz, 3H), 1.05 (s, 3H), 1.00 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.03, 167.38, 91.05, 64.92, 64.88, 57.90, 57.88, 54.71, 54.07, 36.55, 36.51, 30.63, 28.90, 25.81, 25.81, 25.34, 25.32, 16.74, 16.71, 16.70, 9.66. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{24}ClO_4^+$ 303.1358; Found: 303.1355.

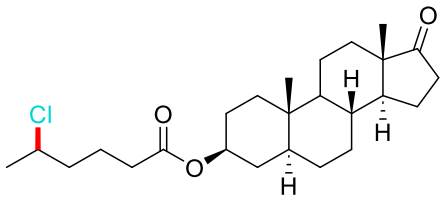
((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 5-chlorohexanoate



30b

R_f = 0.5, 20% acetone in hexane, yellowish oil (220 mg, 56% yield). Followed the general procedure A (r.r.=98:2). The r.r. was determined by HPLC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.58 (dd, J = 7.9, 2.4 Hz, 1H), 4.38 (d, J = 11.7 Hz, 1H), 4.27 (d, J = 1.9 Hz, 1H), 4.21 (d, J = 7.9 Hz, 1H), 4.04 – 3.97 (m, 2H), 3.87 (dd, J = 13.0, 1.6 Hz, 1H), 3.73 (d, J = 13.0 Hz, 1H), 2.37 (t, J = 6.4 Hz, 2H), 1.84 (ddd, J = 11.1, 9.1, 6.6 Hz, 1H), 1.77 – 1.69 (m, 3H), 1.51 (s, 3H), 1.48 (d, J = 6.5 Hz, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.42, 109.10, 108.69, 101.50, 70.74, 70.55, 70.04, 65.28, 61.22, 58.05, 39.40, 33.37, 26.45, 25.87, 25.27, 25.22, 24.05, 21.87. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{30}ClO_7^+$ 393.1675; Found: 393.1677.

(3*S*,5*S*,8*R*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 5-chlorohexanoate



31b

R_f = 0.5, 15% acetone in hexane, white solid (228 mg, 54% yield). Followed the general procedure A (r.r.=96:4). The r.r. was determined by HPLC analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.75 – 4.61 (m, 1H), 3.99 (dt, J = 12.7, 6.5 Hz, 1H), 2.40 (dd, J = 19.2, 8.8 Hz, 1H), 2.26 (t, J = 6.7 Hz, 2H), 2.08 – 1.99 (m, 1H), 1.93 – 1.87 (m, 1H), 1.75 (ddd, J = 28.7, 11.8, 5.4 Hz, 8H), 1.61 (dd, J = 23.1, 9.7 Hz, 2H), 1.53 – 1.43 (m, 6H), 1.38 – 1.28 (m, 3H), 1.27 – 1.19 (m, 4H), 1.04 – 0.93 (m, 2H), 0.82 (s, 6H), 0.72 – 0.66 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.07, 172.70, 73.44, 58.10, 54.30, 51.35, 47.74, 44.65, 39.49, 36.69, 35.81, 35.63, 35.02, 33.96, 31.52, 30.79, 28.26, 27.43, 25.28, 22.12, 21.75, 20.45, 13.80, 12.20. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{40}ClO_3^+$ 423.2660; Found: 423.2661.

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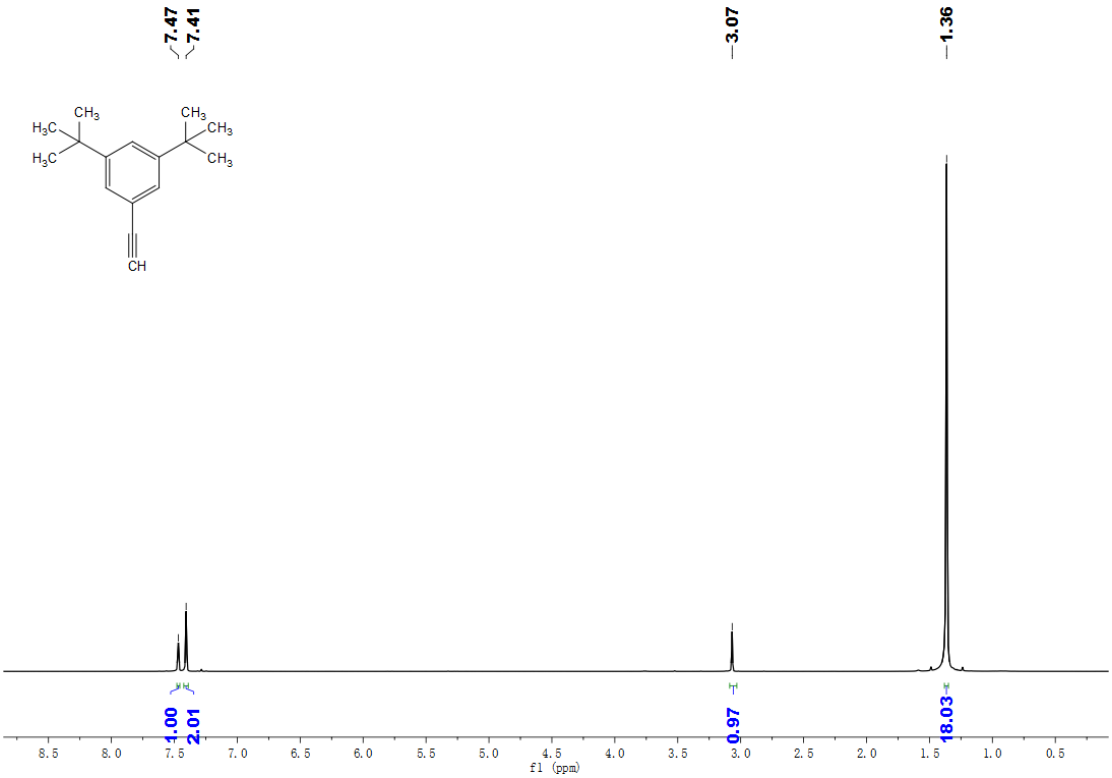
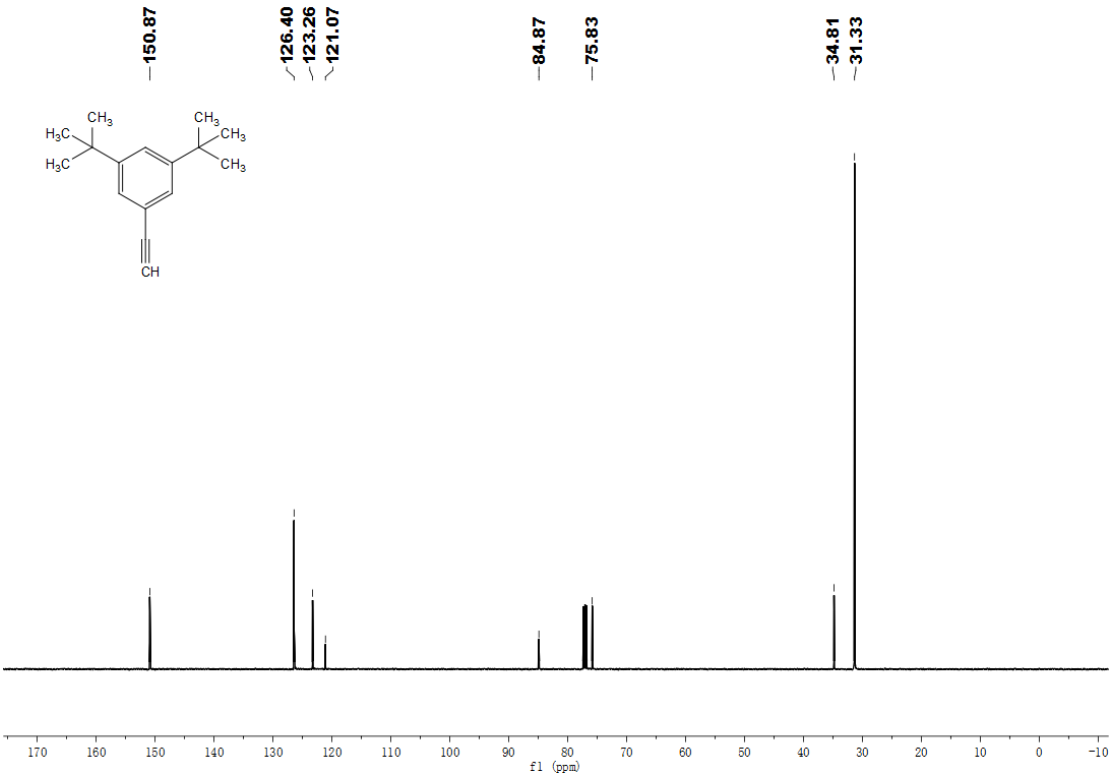
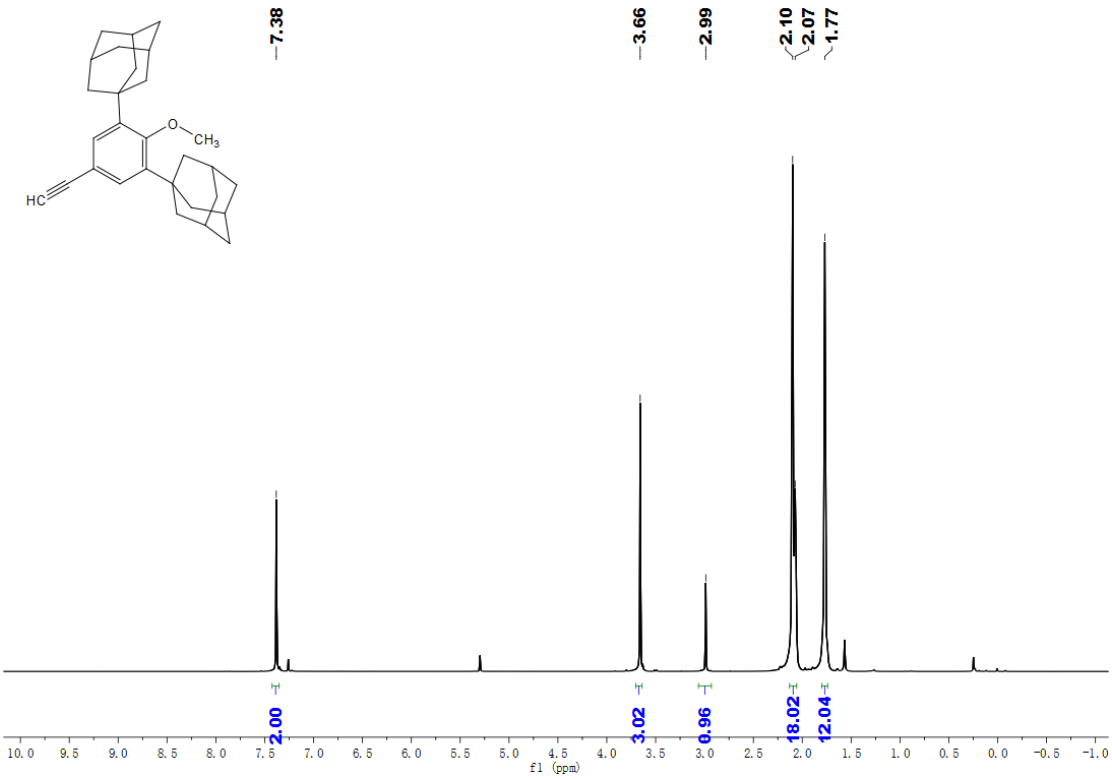
14. ^{1}H-NMR and ^{13}C-NMR spectra



^{1}H NMR of compound **S3** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **S3** (126 MHz, $CDCl_3$)



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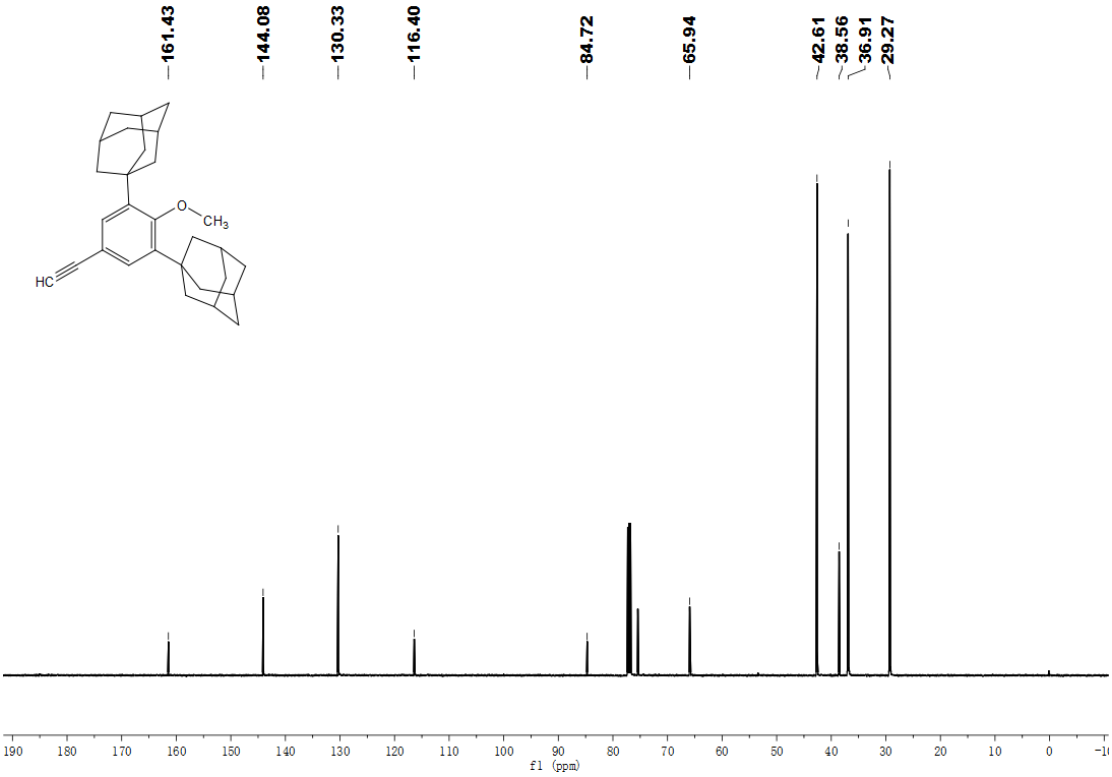
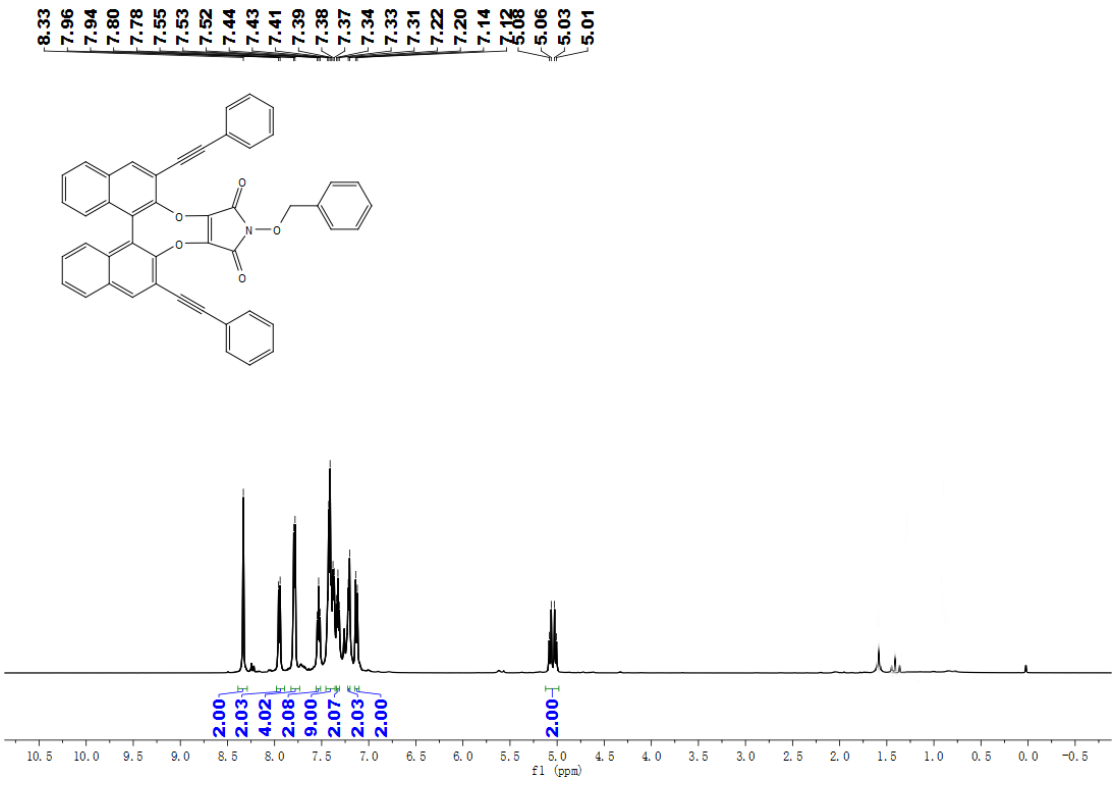


^{13}C NMR of compound **S5** (126 MHz, $CDCl_3$)



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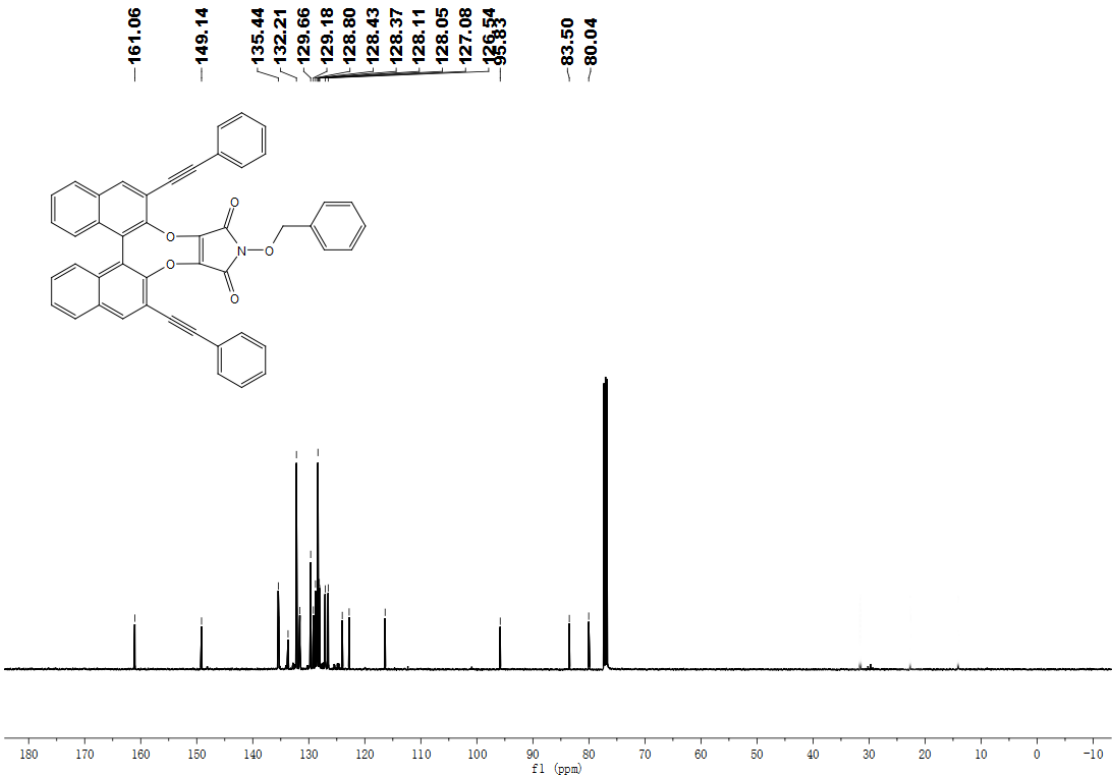
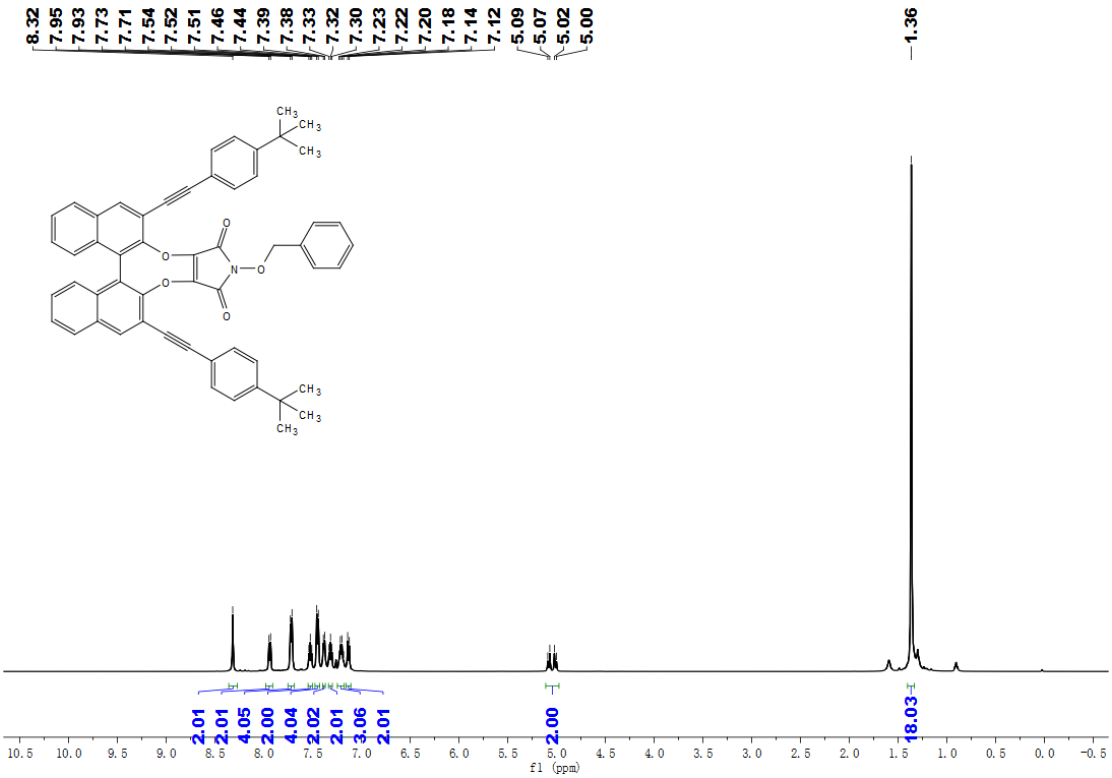
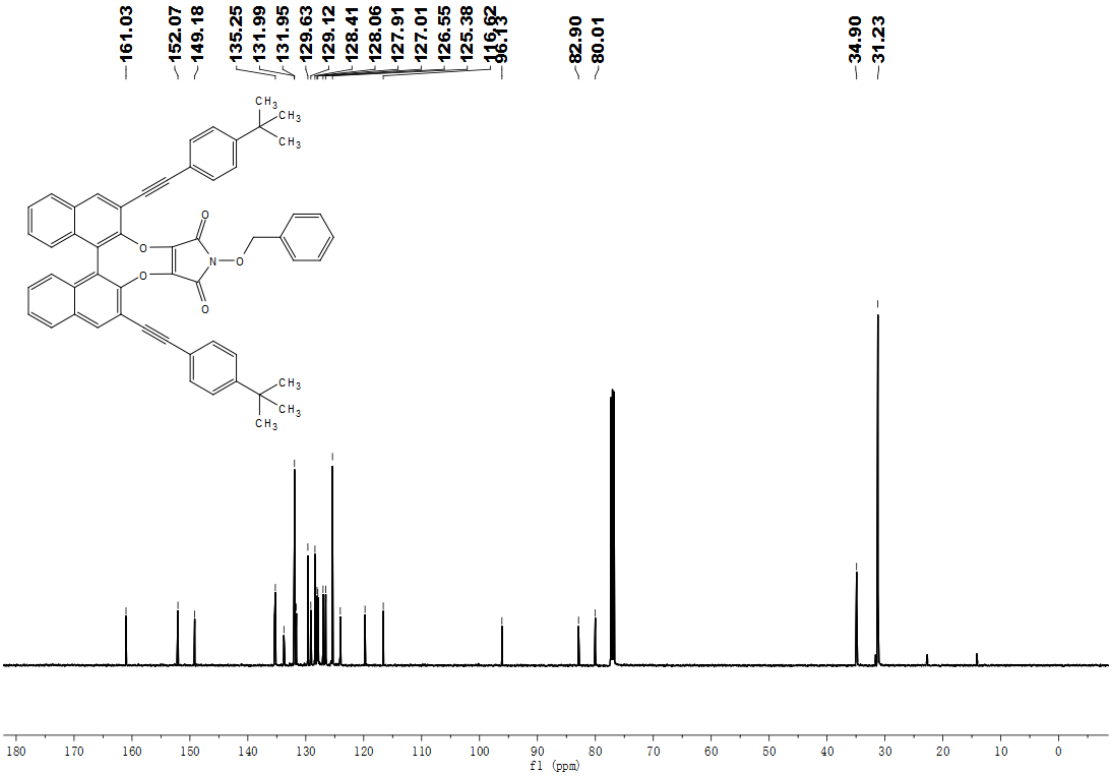


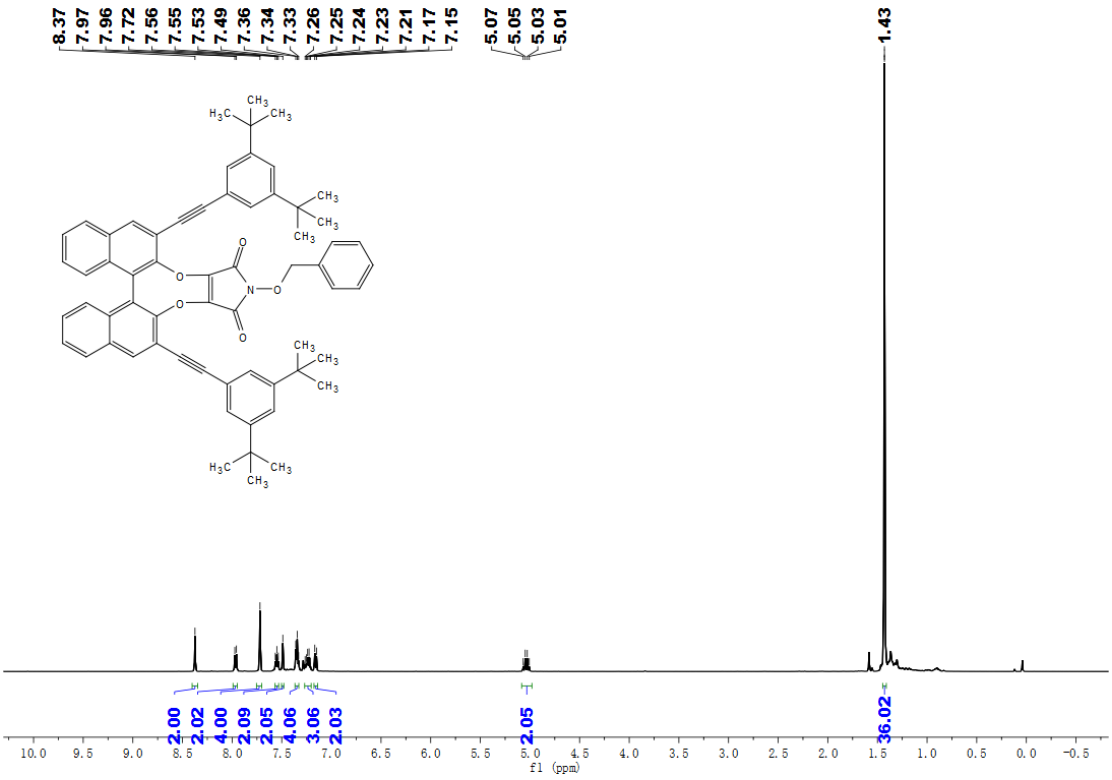
^{13}C NMR of compound **S7** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **S8** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **S8** (126 MHz, $CDCl_3$)



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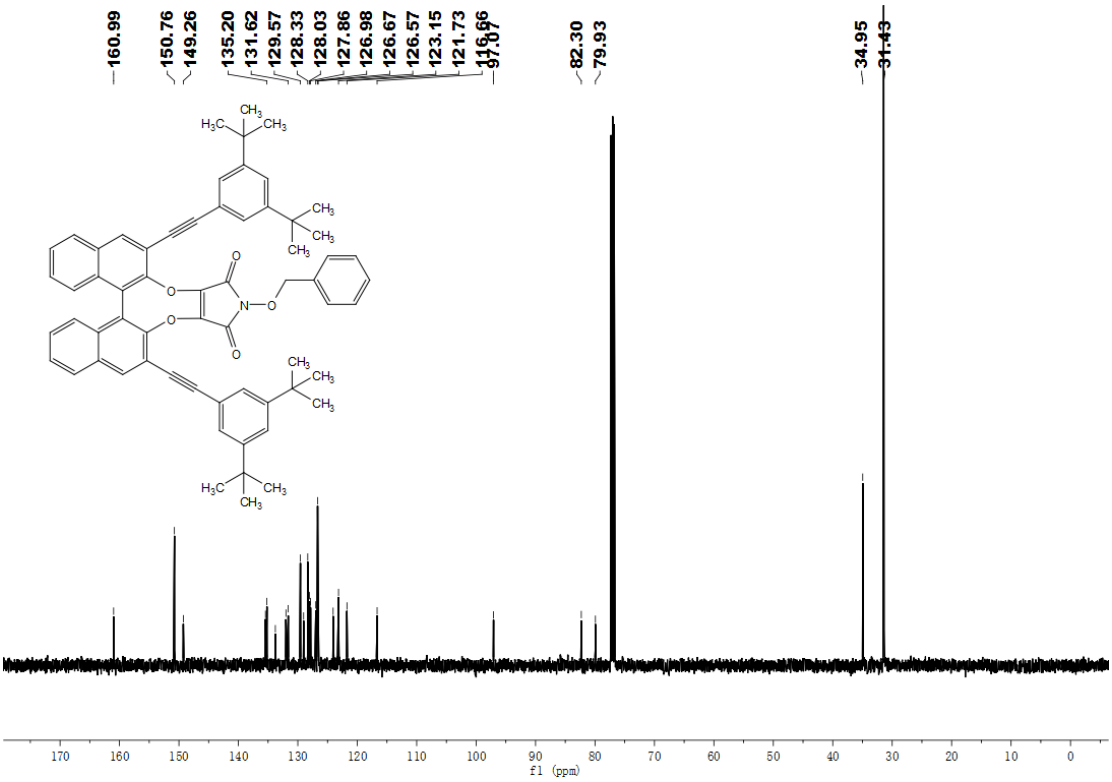
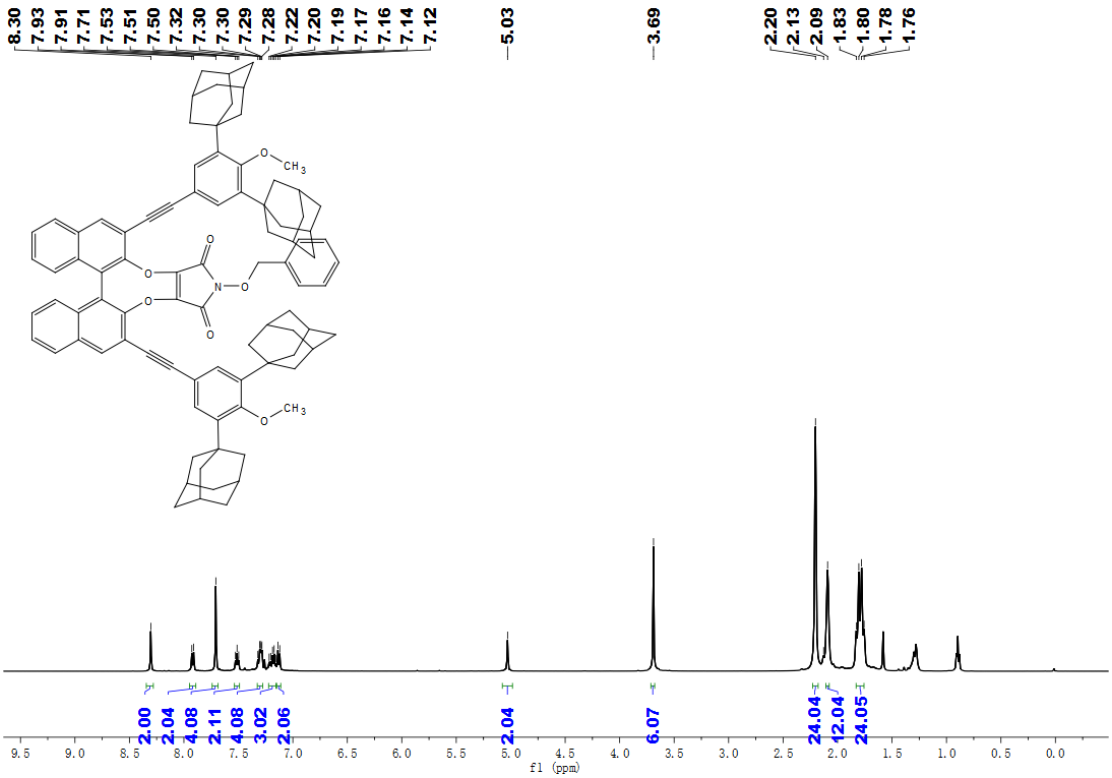


^{13}C NMR of compound **S9** (126 MHz, $CDCl_3$)



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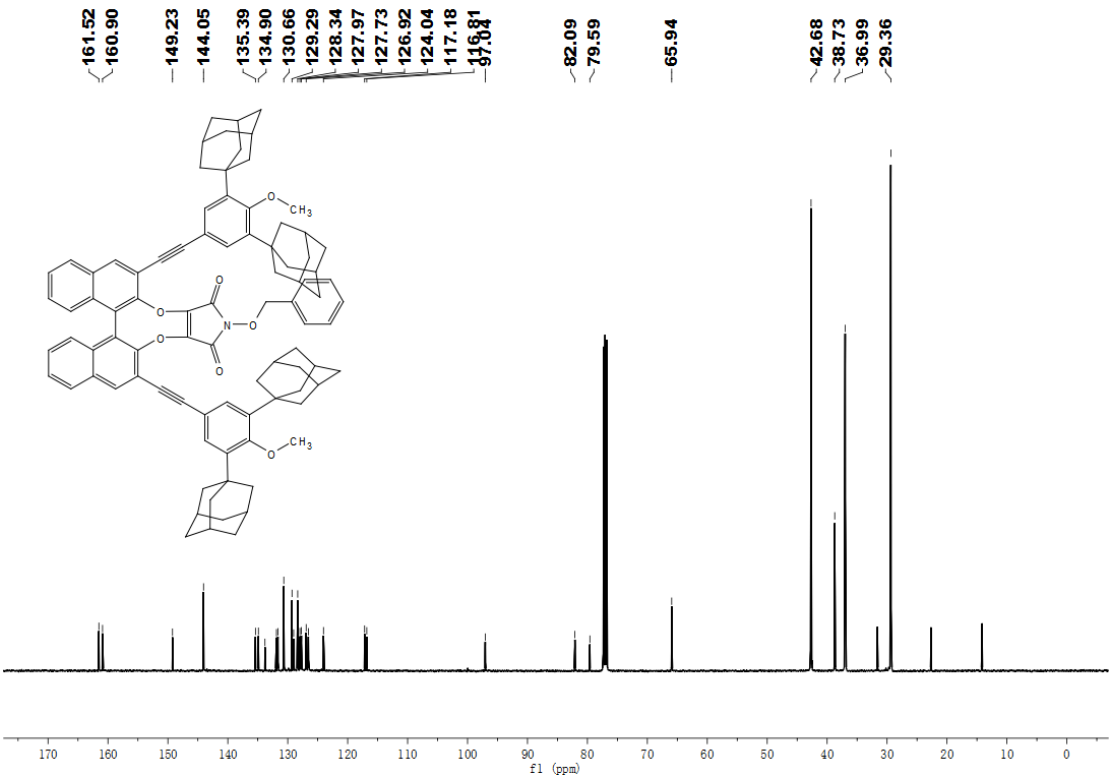

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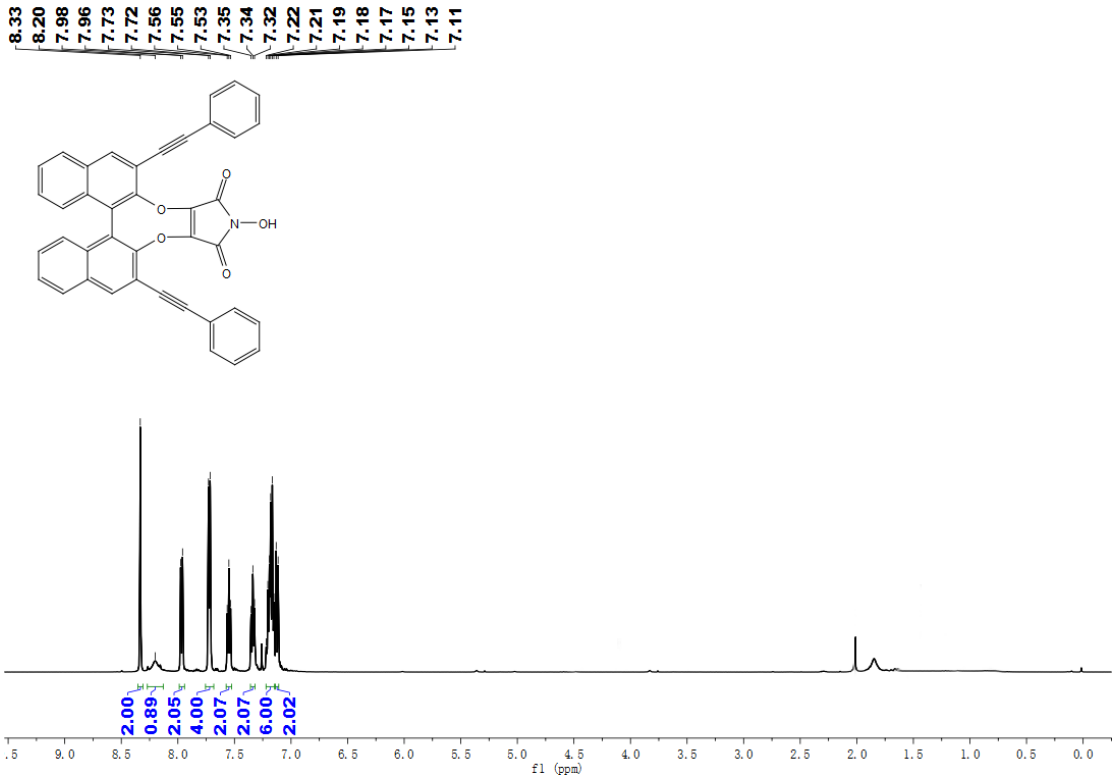
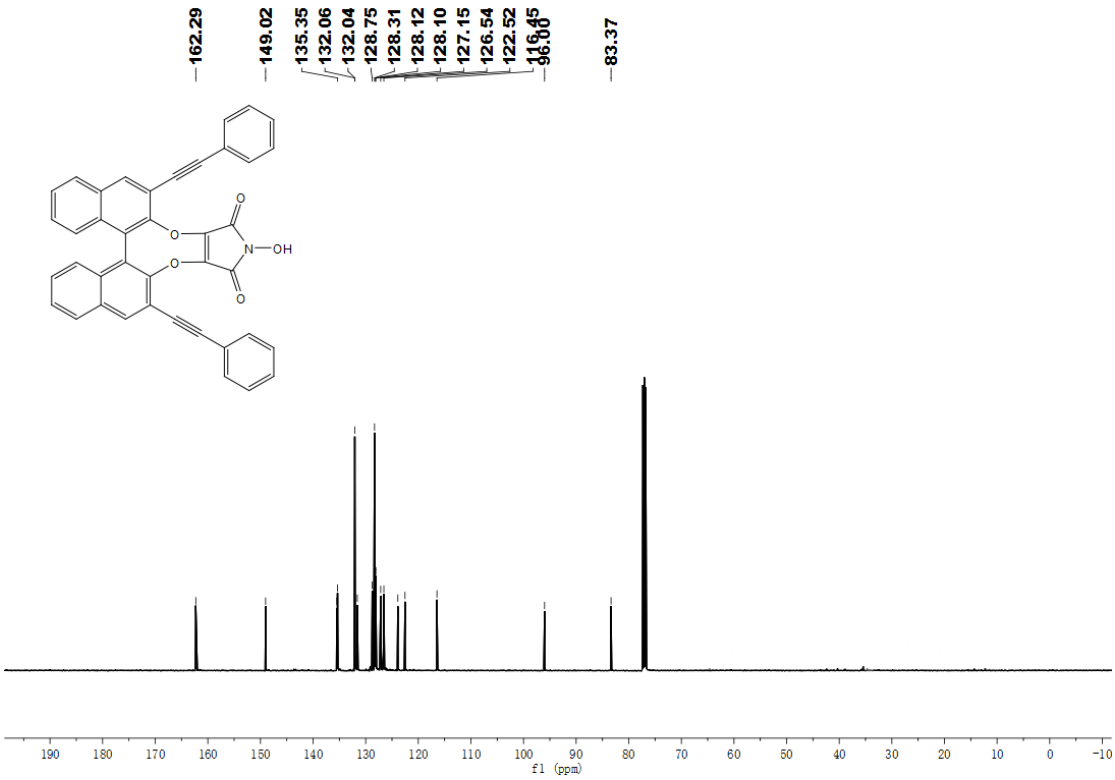
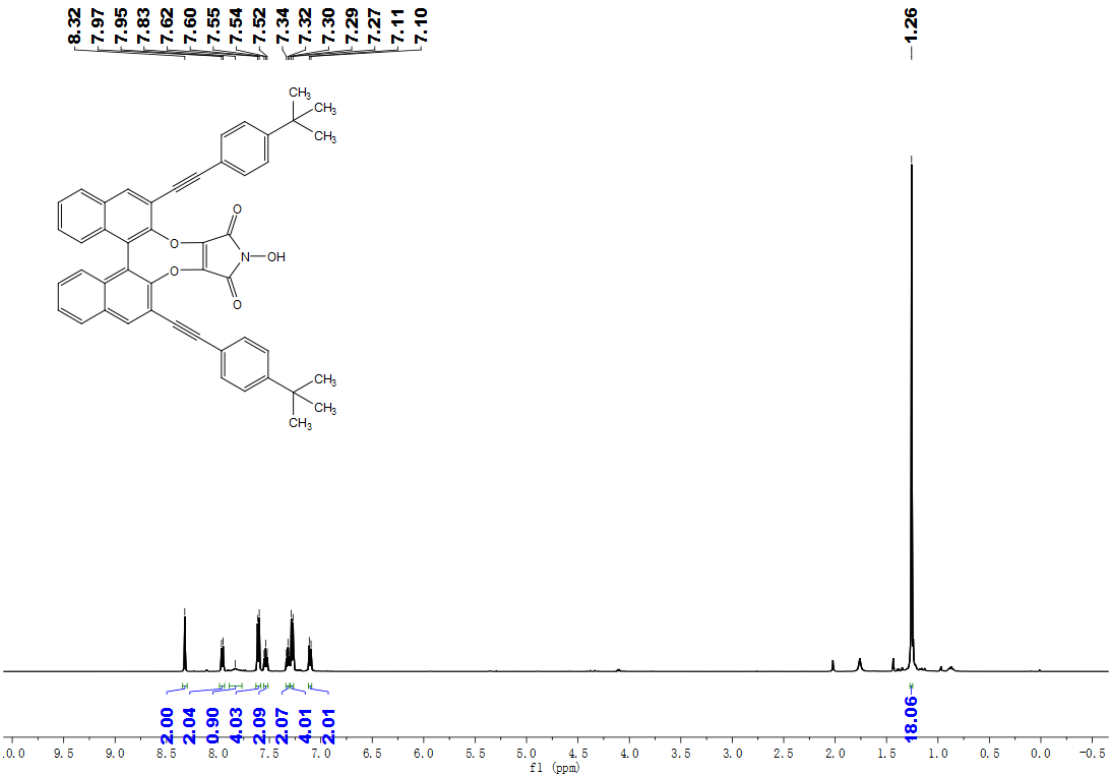


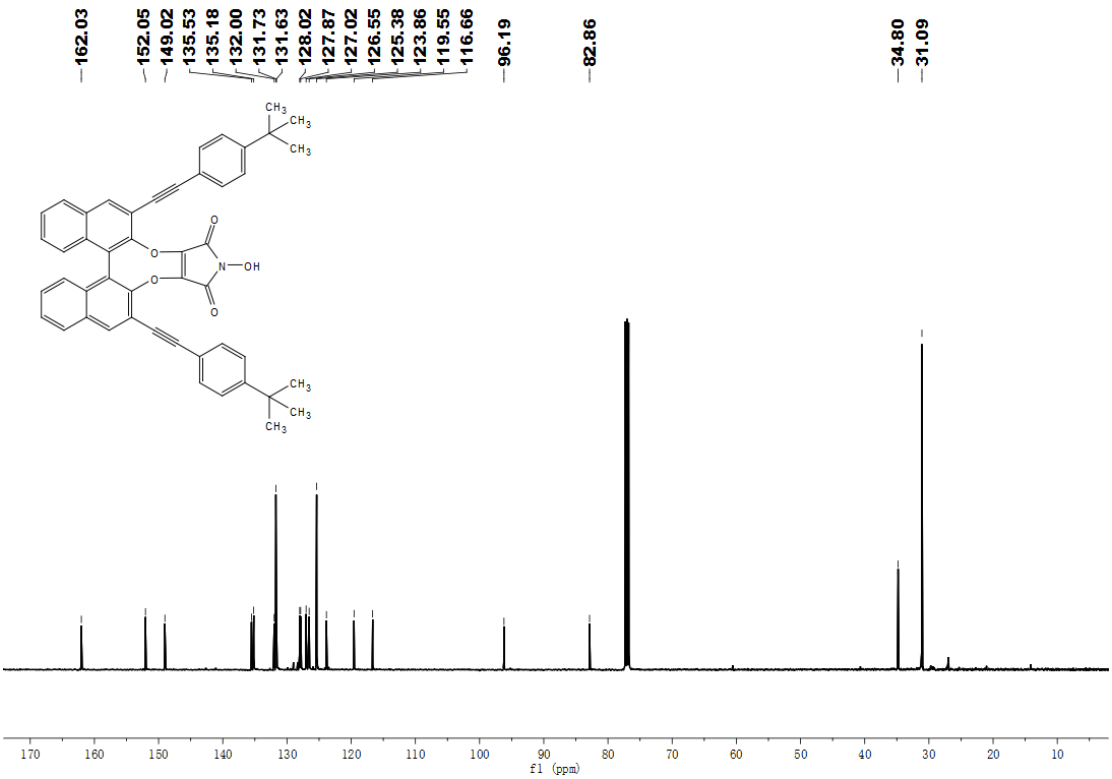
^{1}H NMR of compound **NHMI-1** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **NHMI-1** (126 MHz, $CDCl_3$)



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



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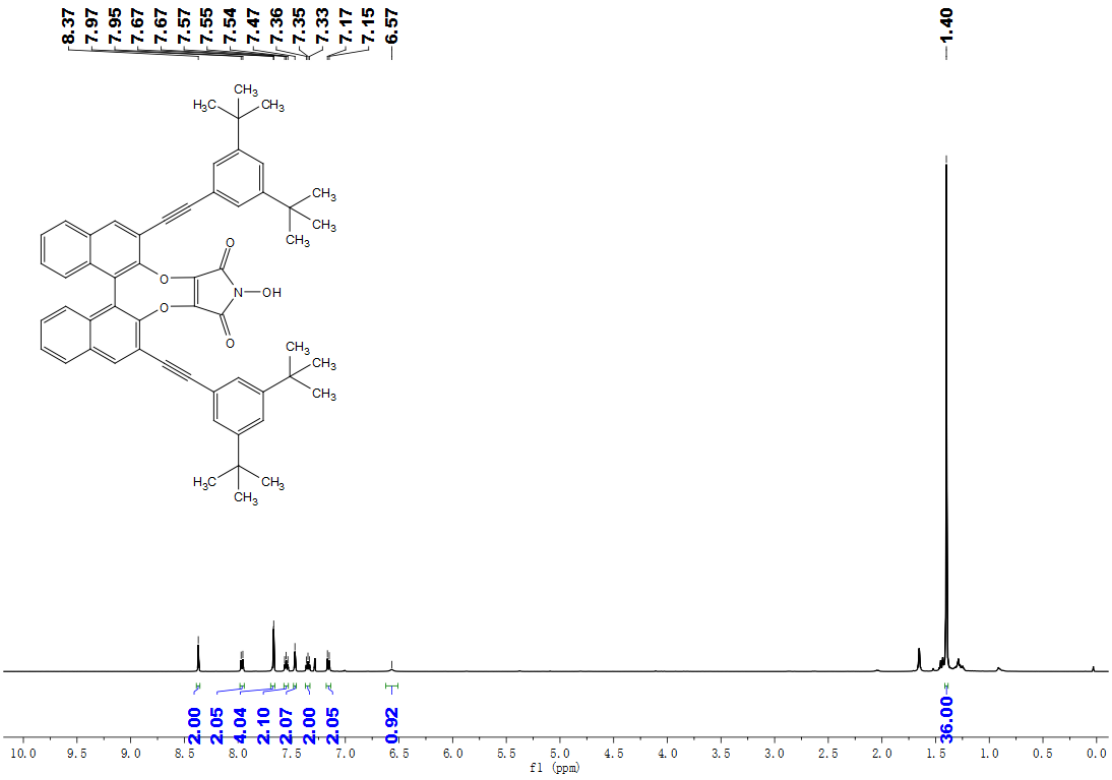

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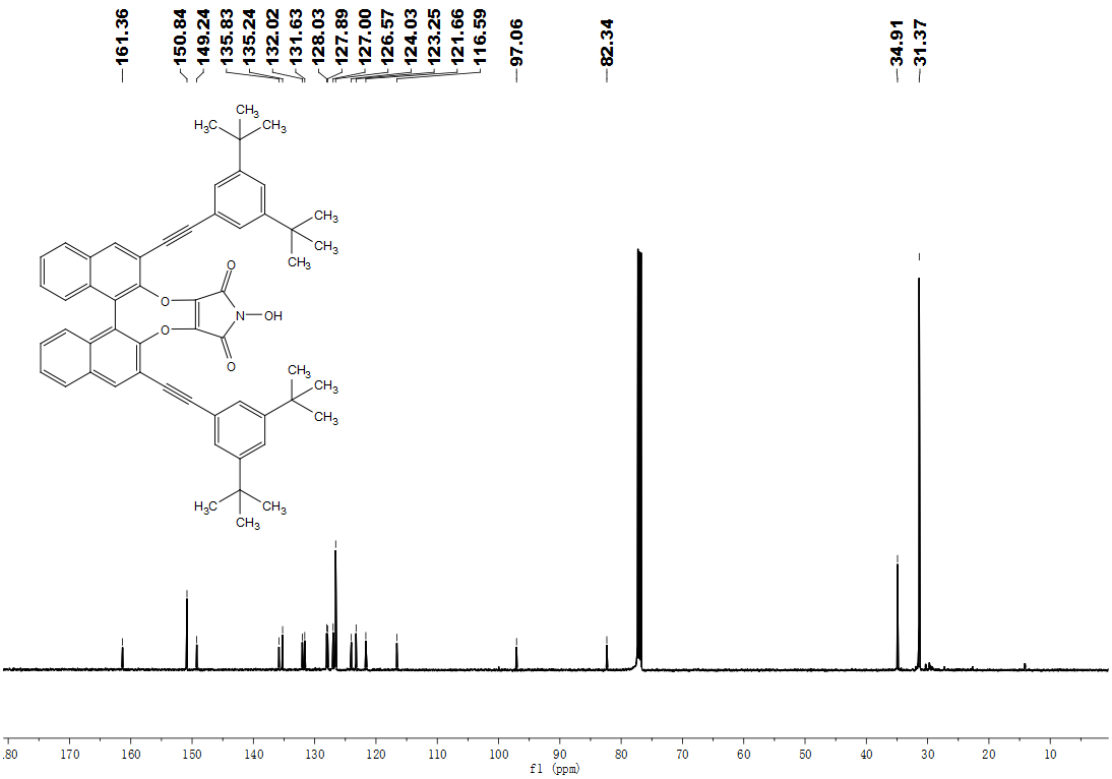
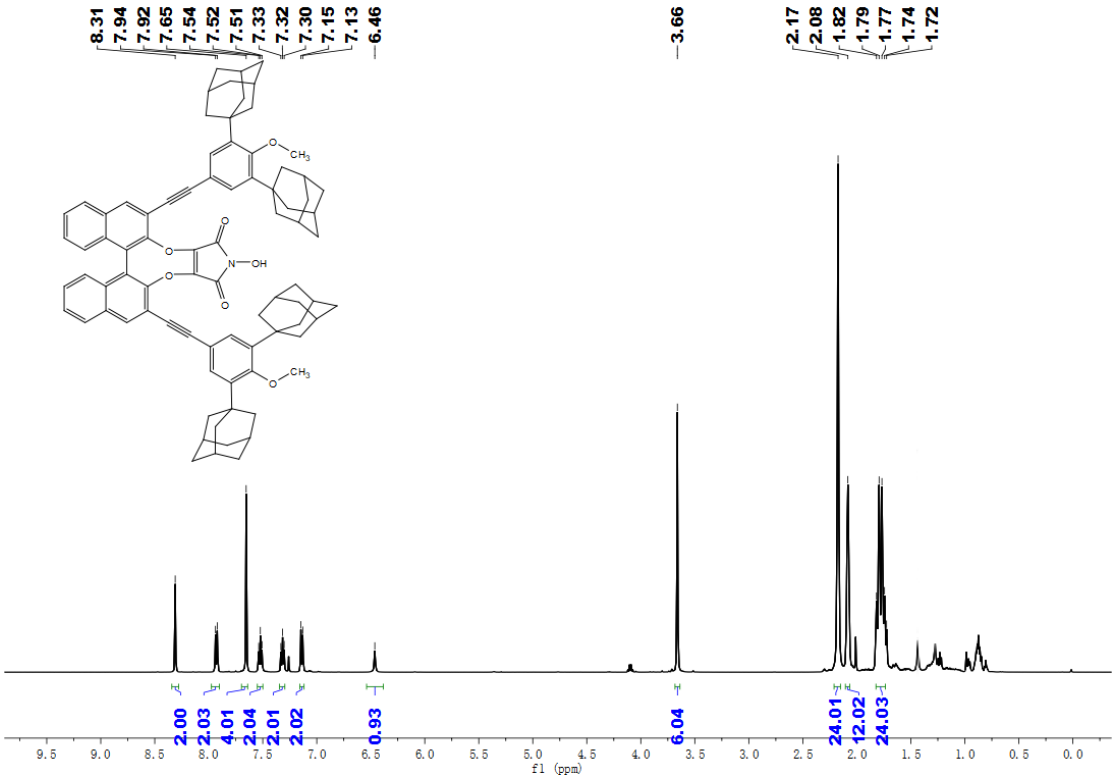
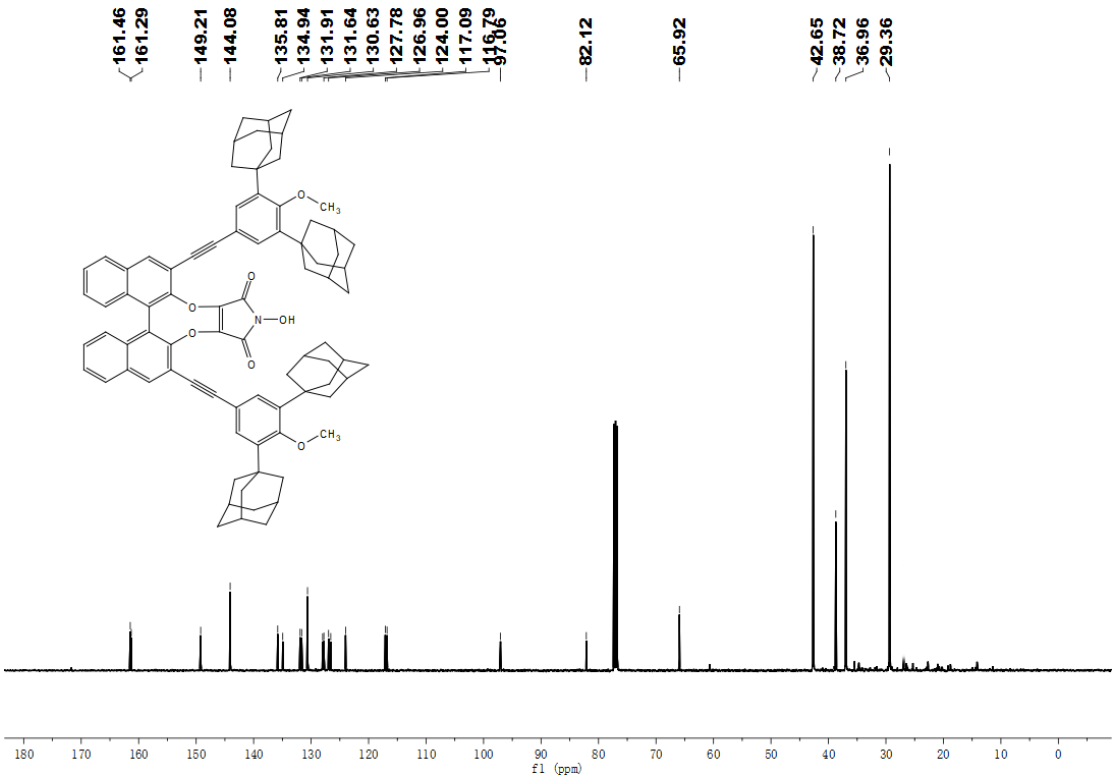


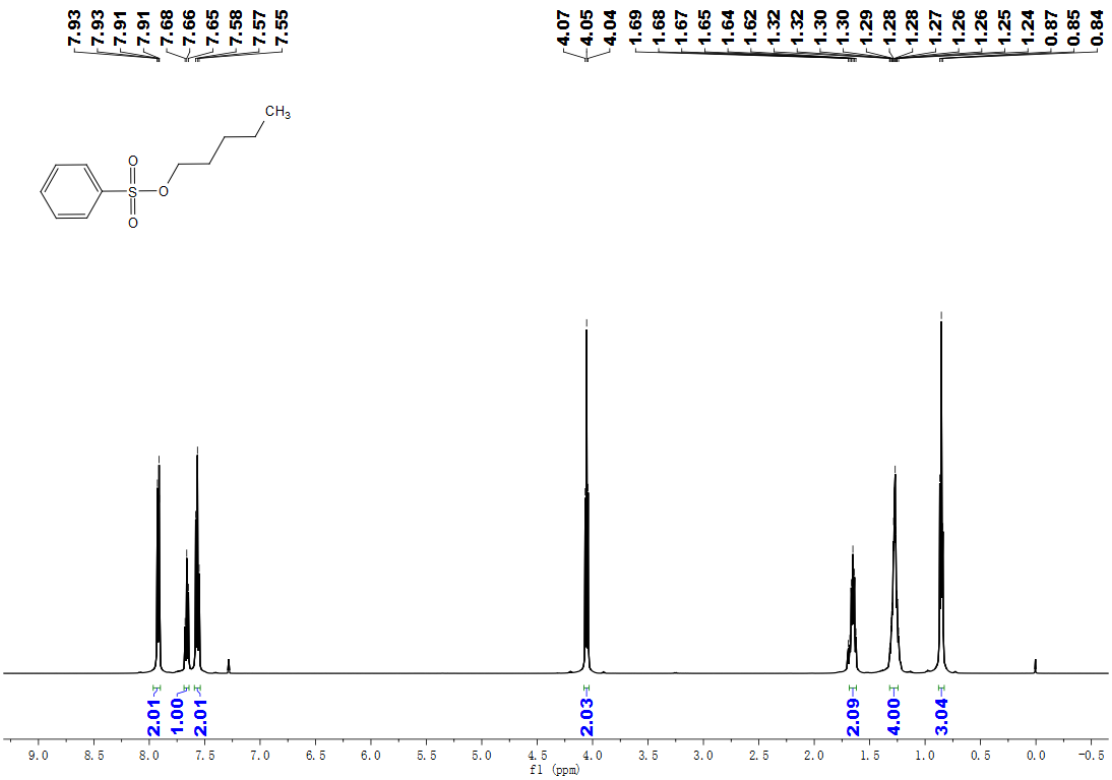
^{13}C NMR of compound **NHMI-3** (126 MHz, $CDCl_3$)



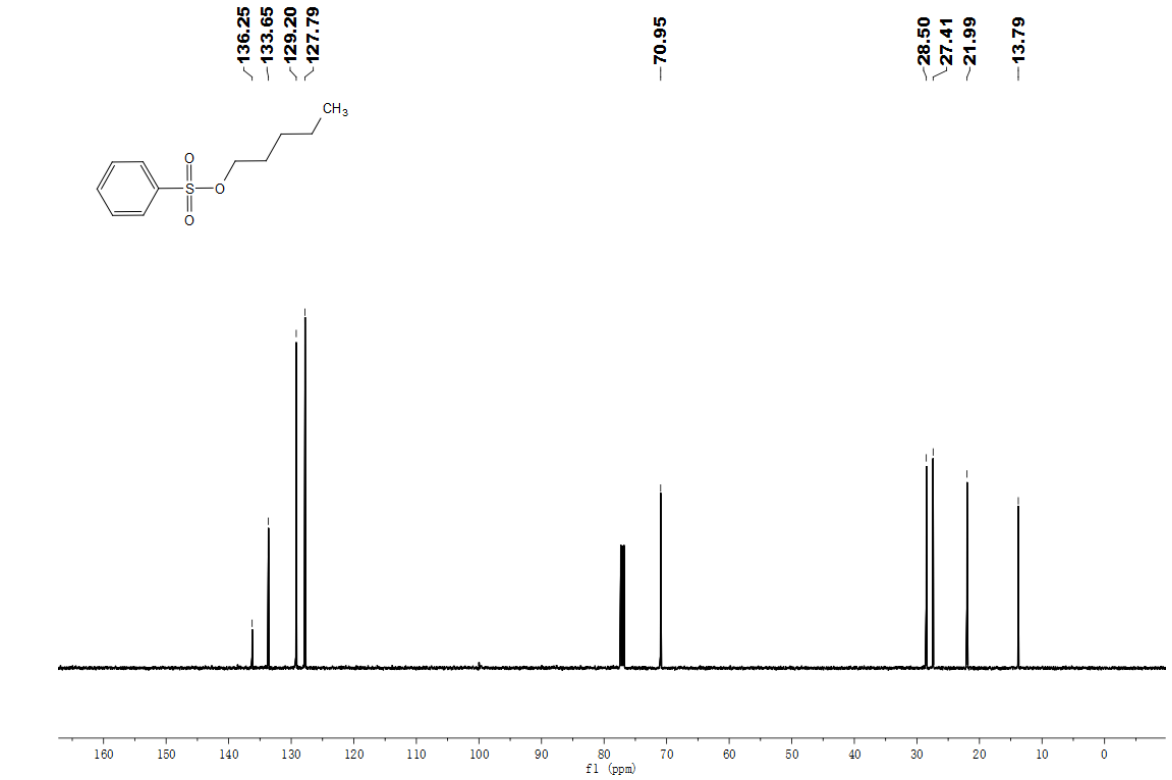
^{1}H NMR of compound **NHMI-4** (500 MHz, $CDCl_3$)



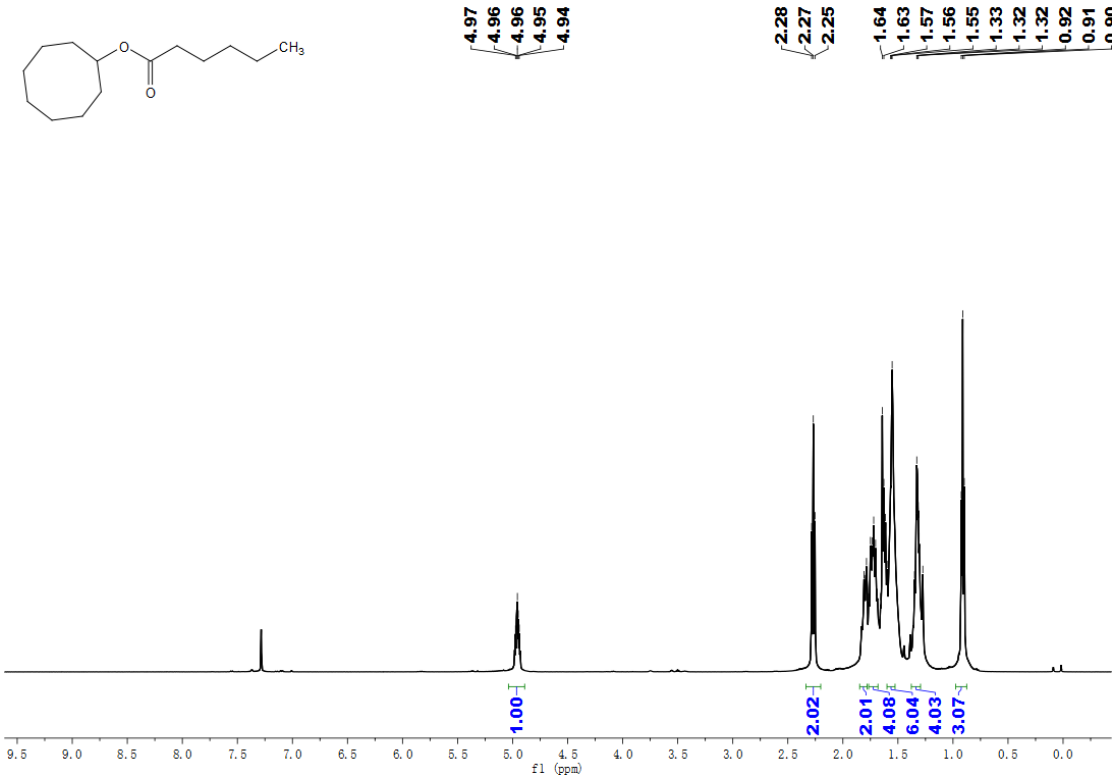
^{13}C NMR of compound **NHMI-4** (126 MHz, $CDCl_3$)



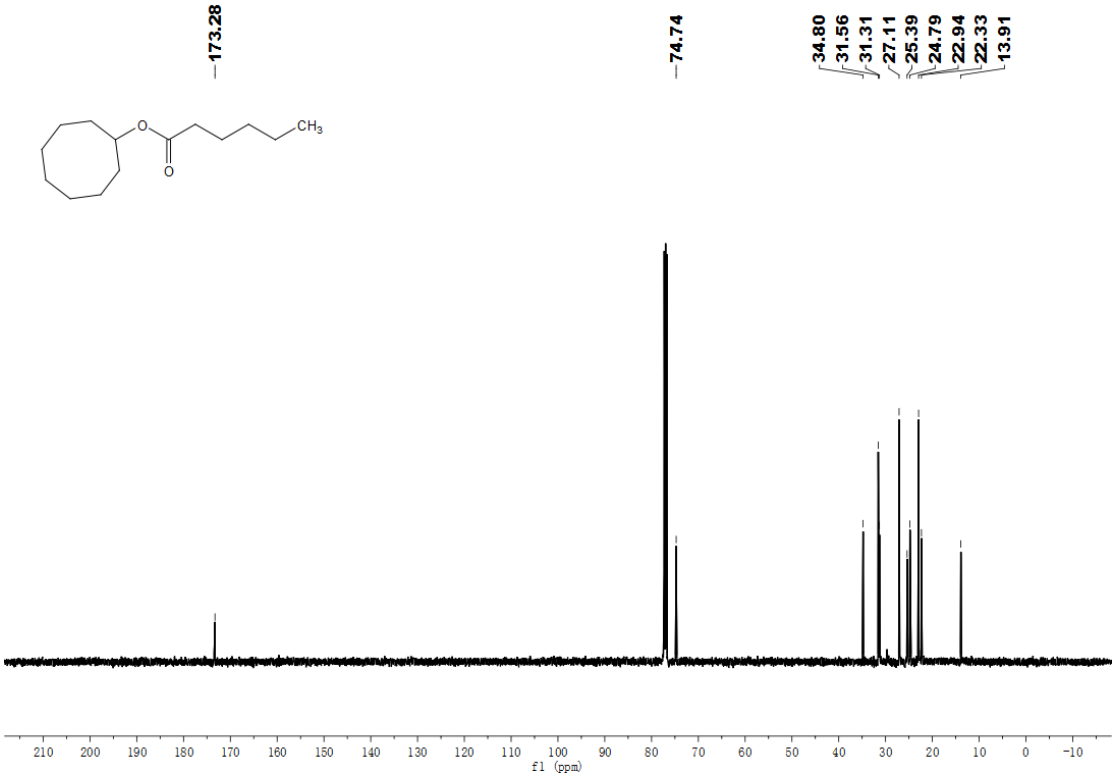
^{1}H NMR of compound **10a** (500 MHz, $CDCl_3$)



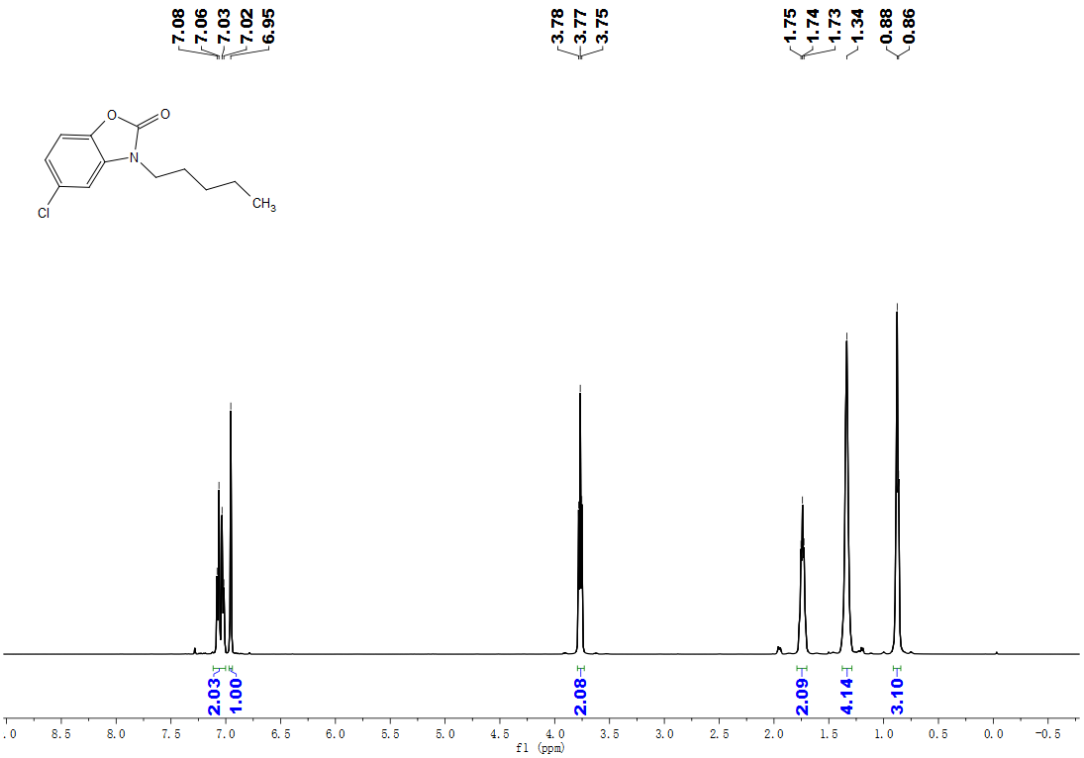
^{13}C NMR of compound **10a** (126 MHz, $CDCl_3$)



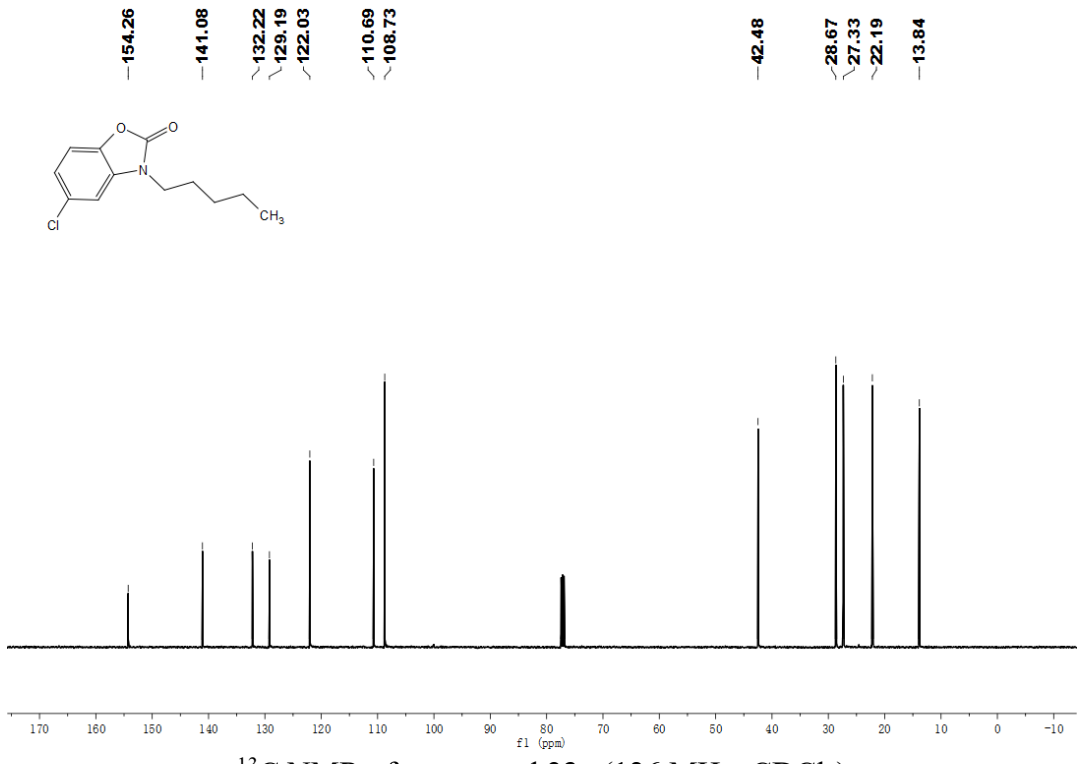
^{1}H NMR of compound **20a** (500 MHz, $CDCl_3$)



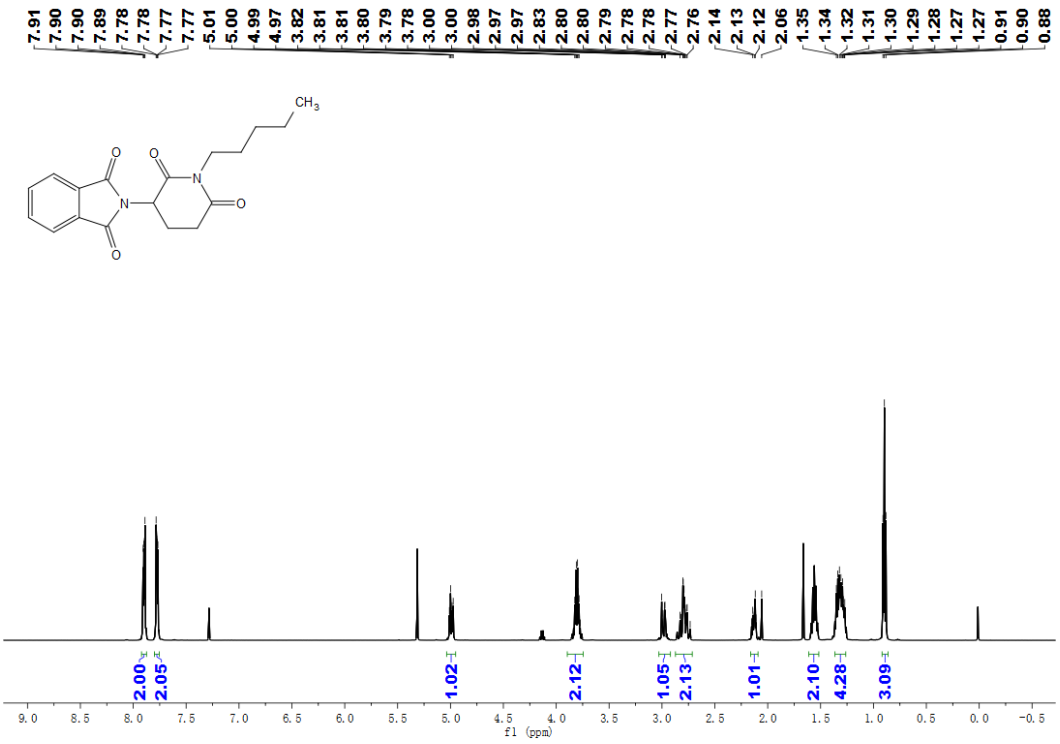
^{13}C NMR of compound **20a** (126 MHz, $CDCl_3$)



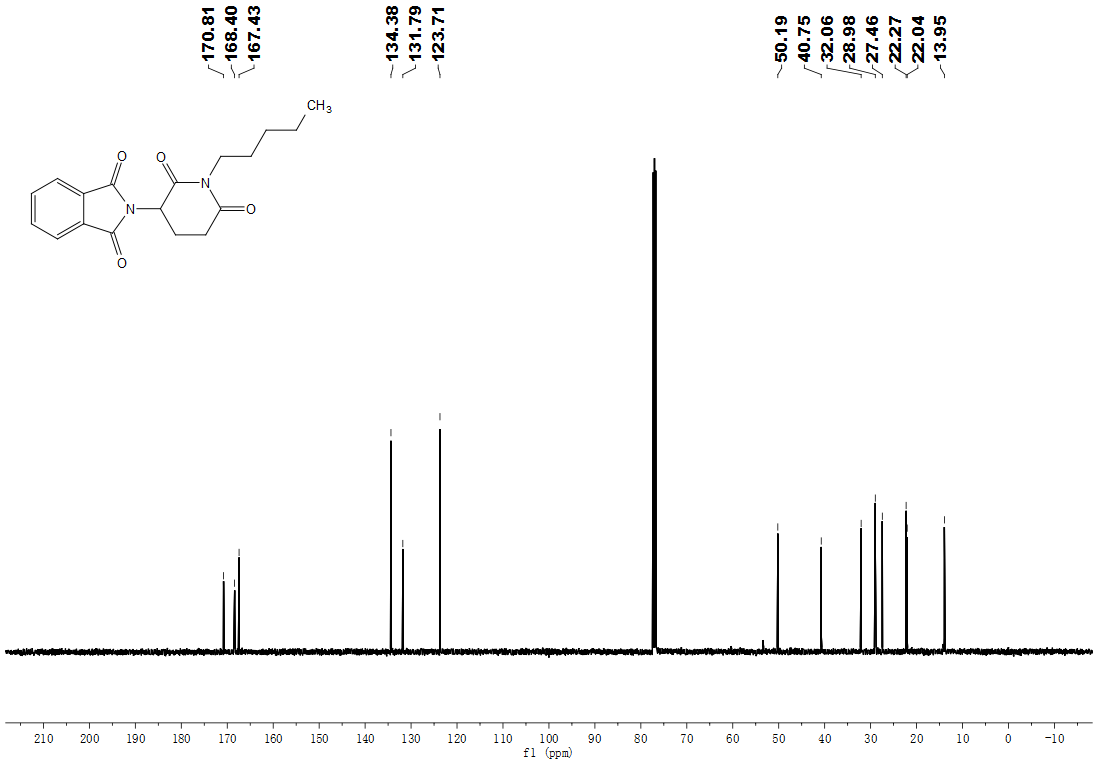
^{1}H NMR of compound **23a** (500 MHz, $CDCl_3$)



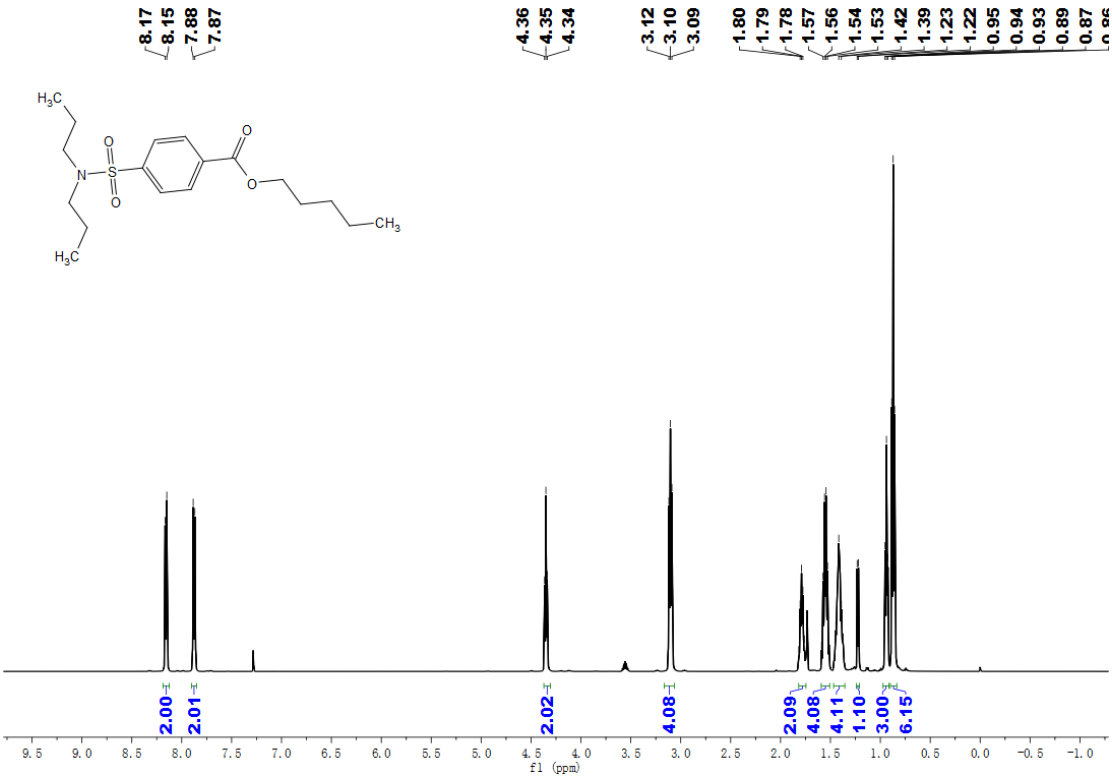
^{13}C NMR of compound **23a** (126 MHz, $CDCl_3$)



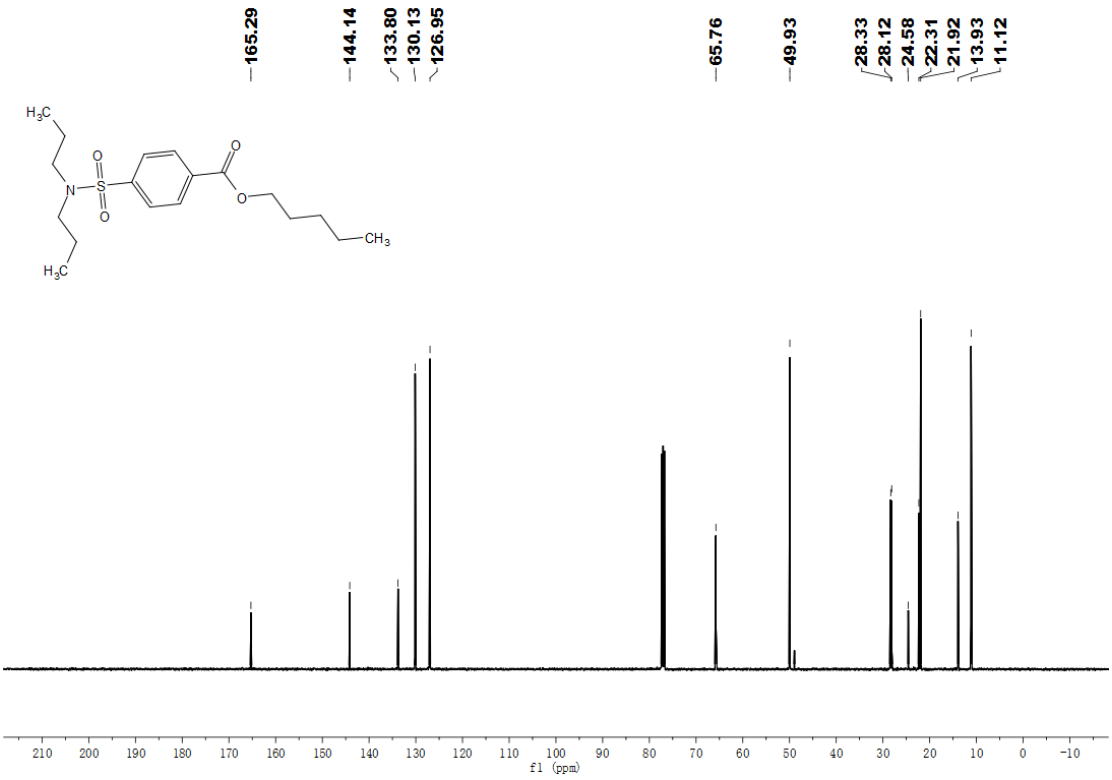
^{1}H NMR of compound **24a** (500 MHz, $CDCl_3$)



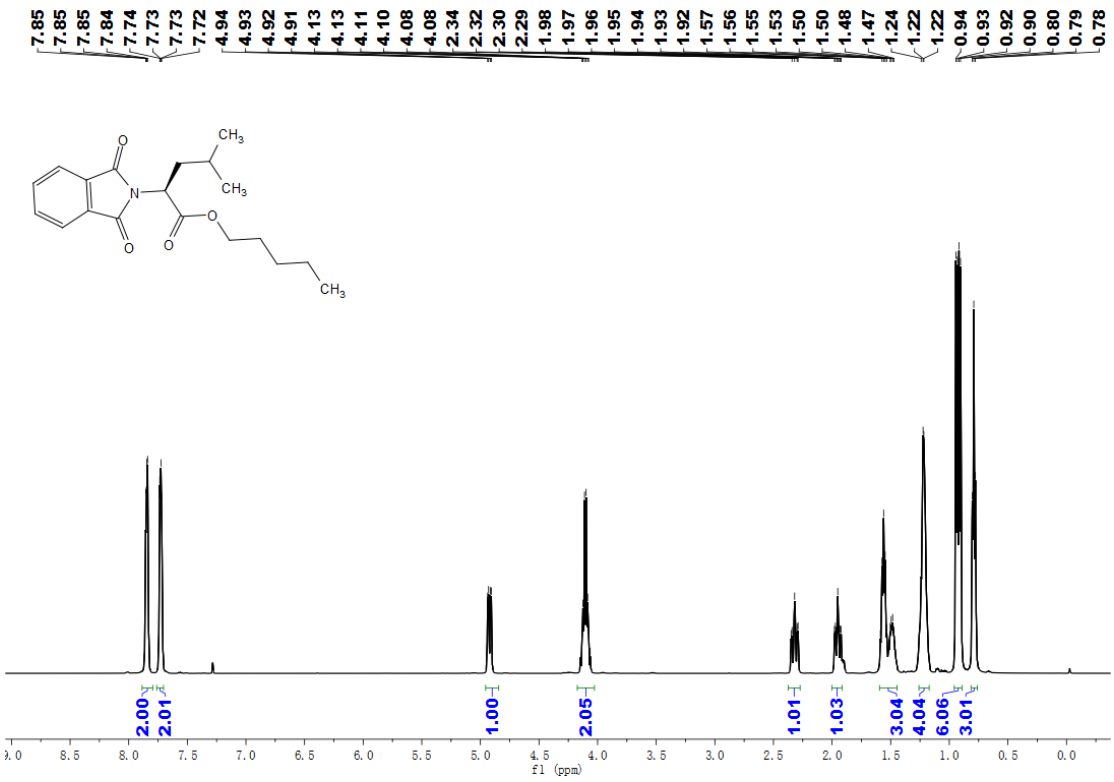
^{13}C NMR of compound **24a** (126 MHz, $CDCl_3$)



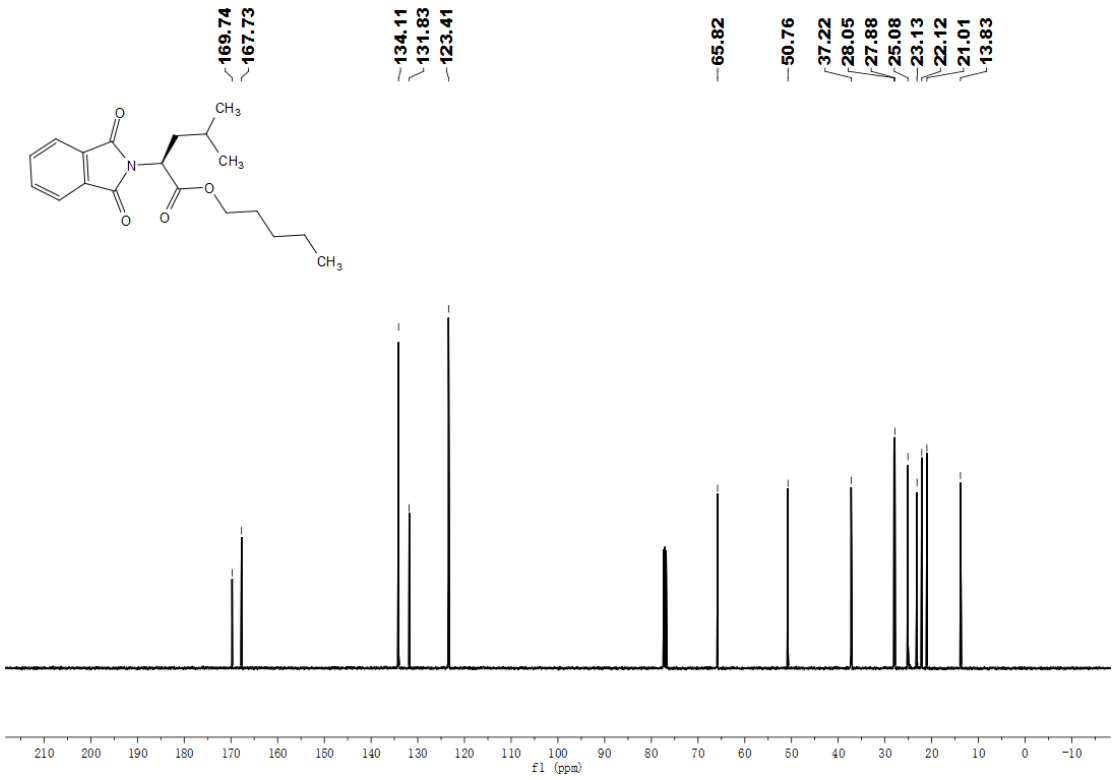
^{1}H NMR of compound **25a** (500 MHz, $CDCl_3$)



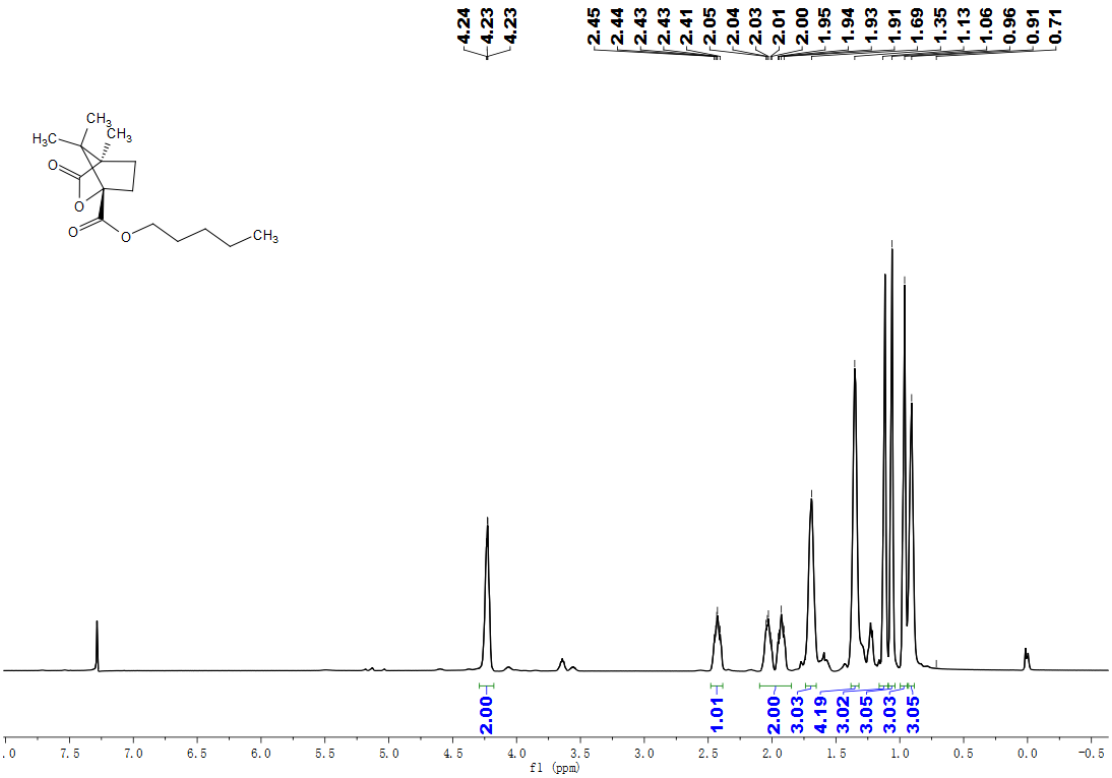
^{13}C NMR of compound **25a** (126 MHz, $CDCl_3$)



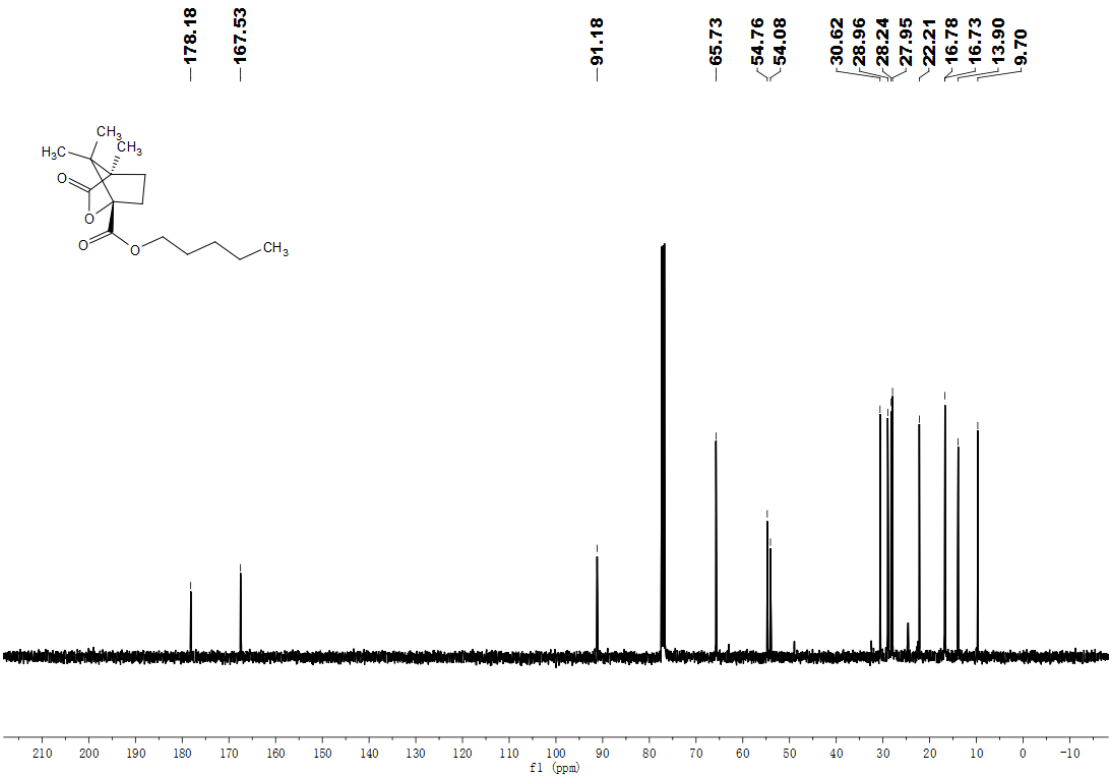
^{1}H NMR of compound **28a** (500 MHz, $CDCl_3$)



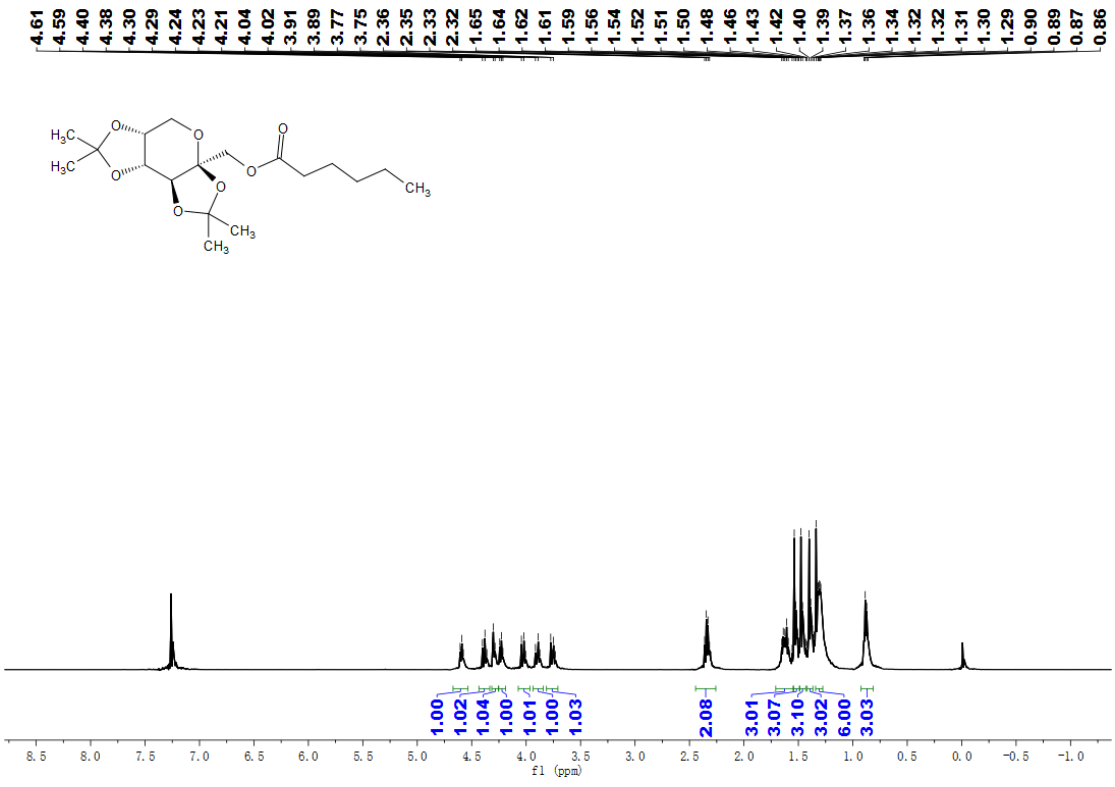
^{13}C NMR of compound **28a** (126 MHz, $CDCl_3$)



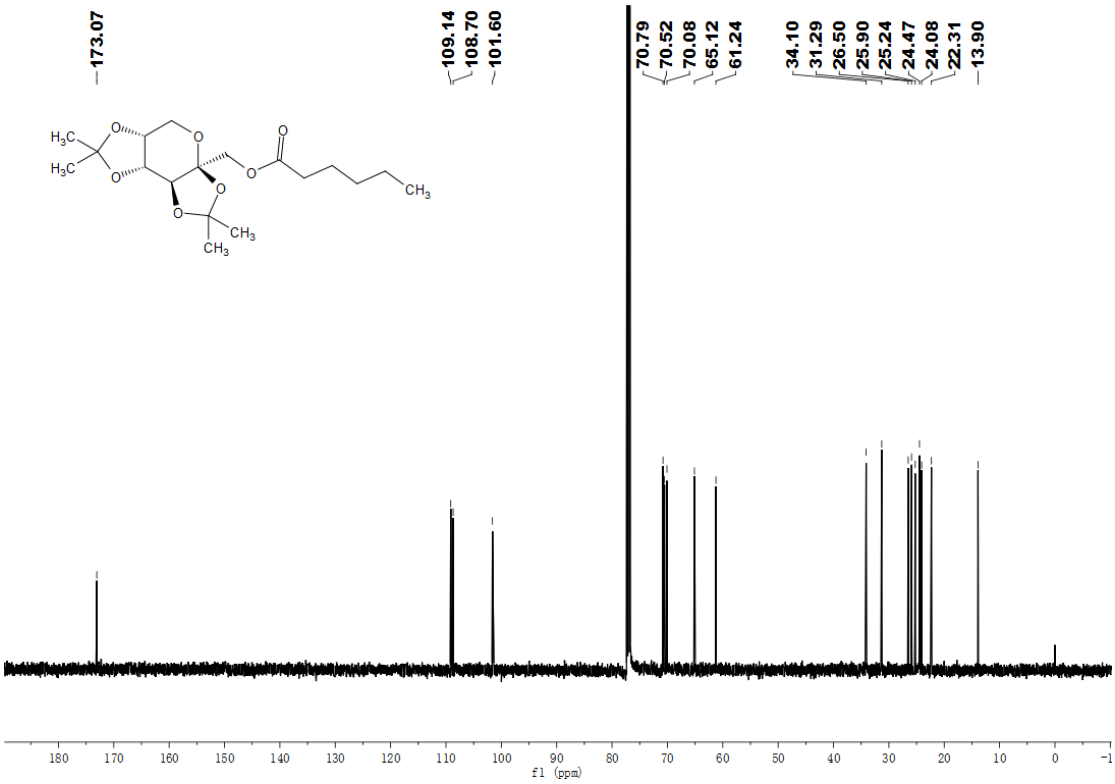
^{1}H NMR of compound **29a** (500 MHz, $CDCl_3$)



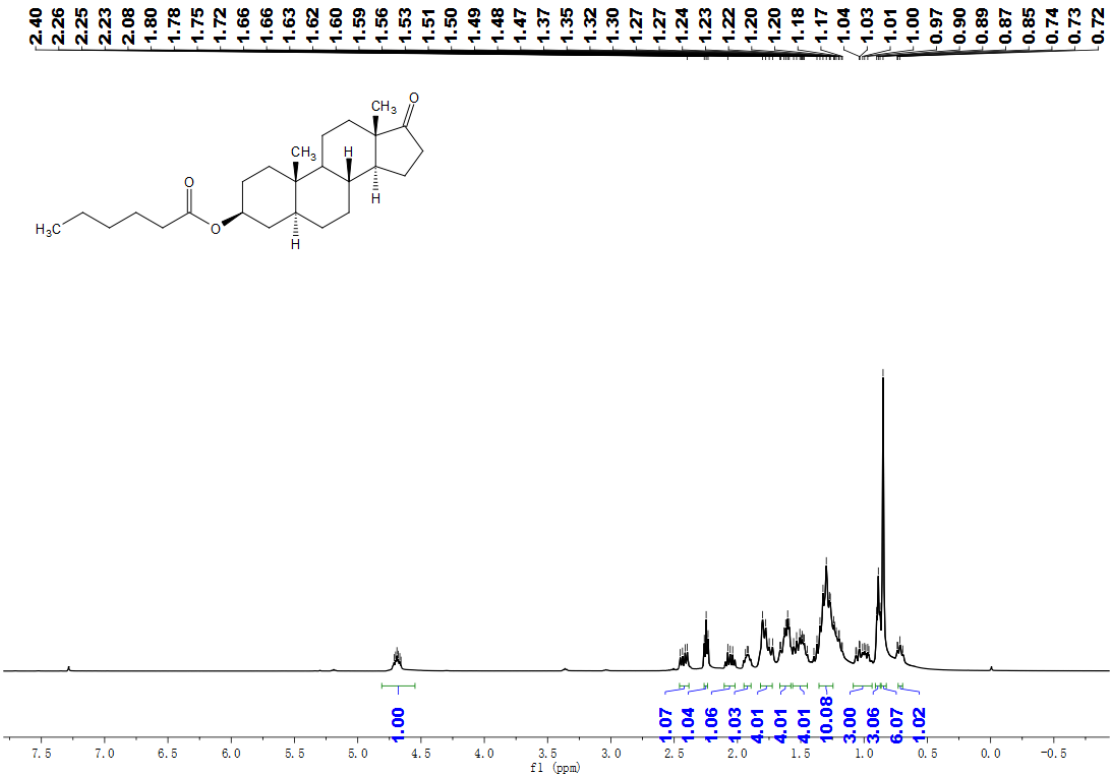
^{13}C NMR of compound **29a** (126 MHz, $CDCl_3$)



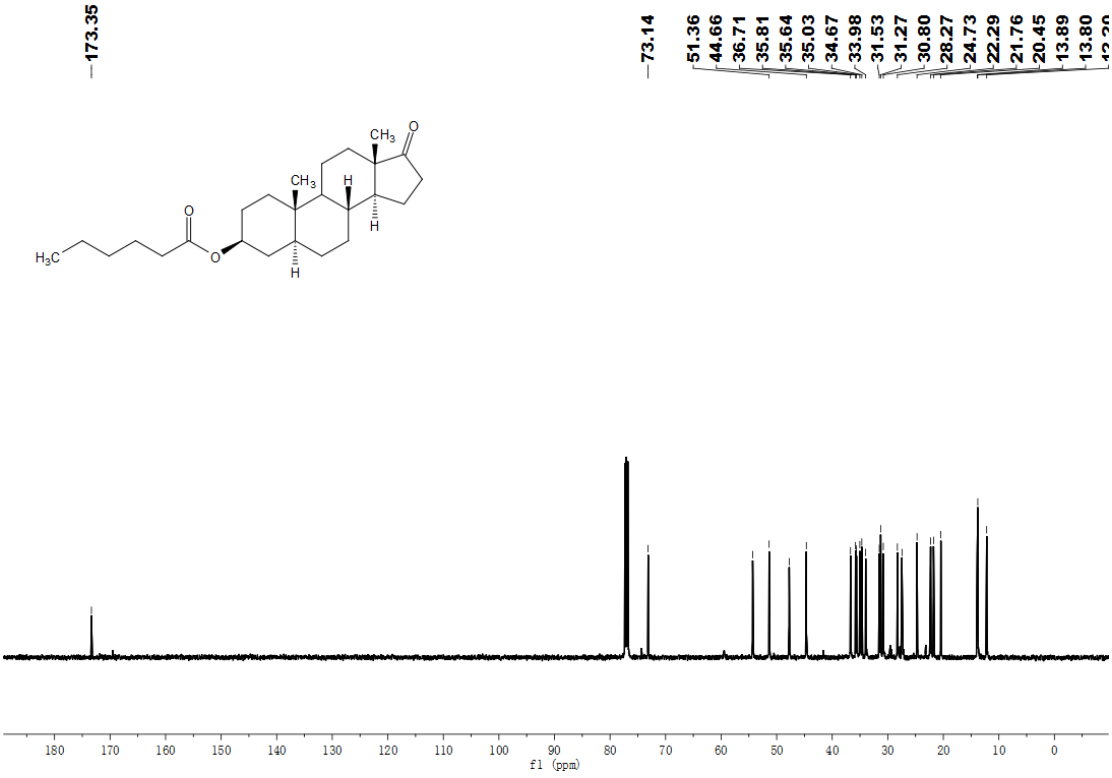
^{1}H NMR of compound **30a** (500 MHz, $CDCl_3$)



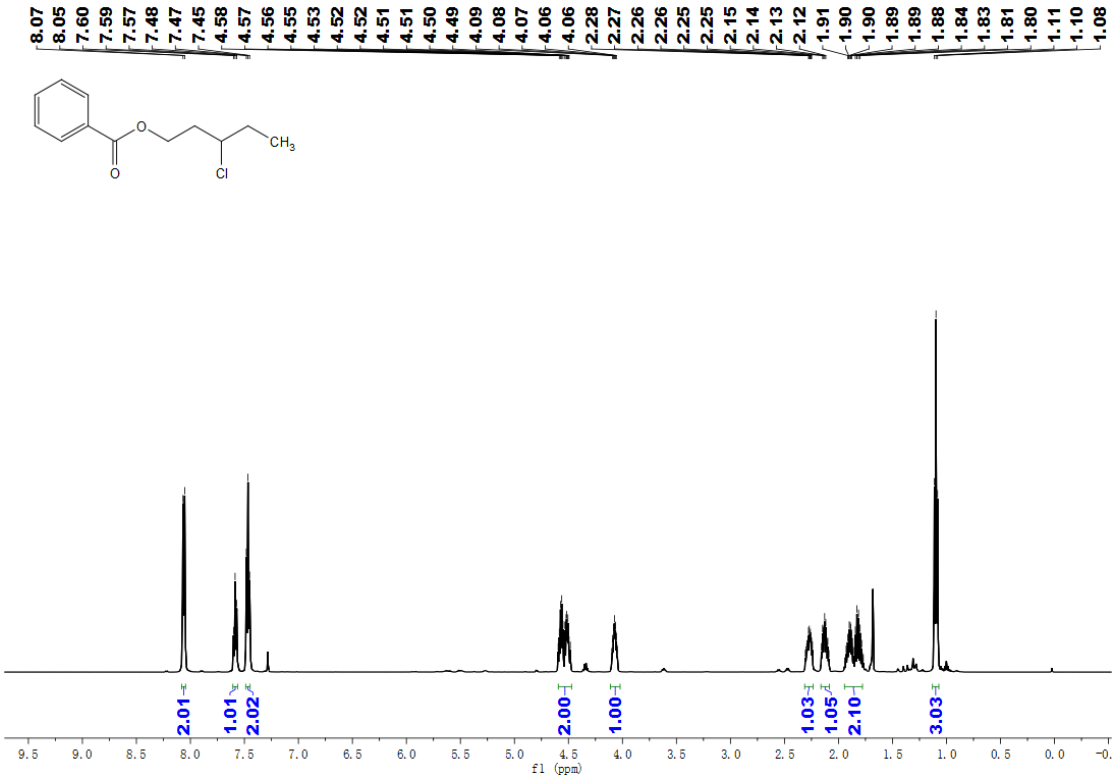
^{13}C NMR of compound **29a** (126 MHz, $CDCl_3$)



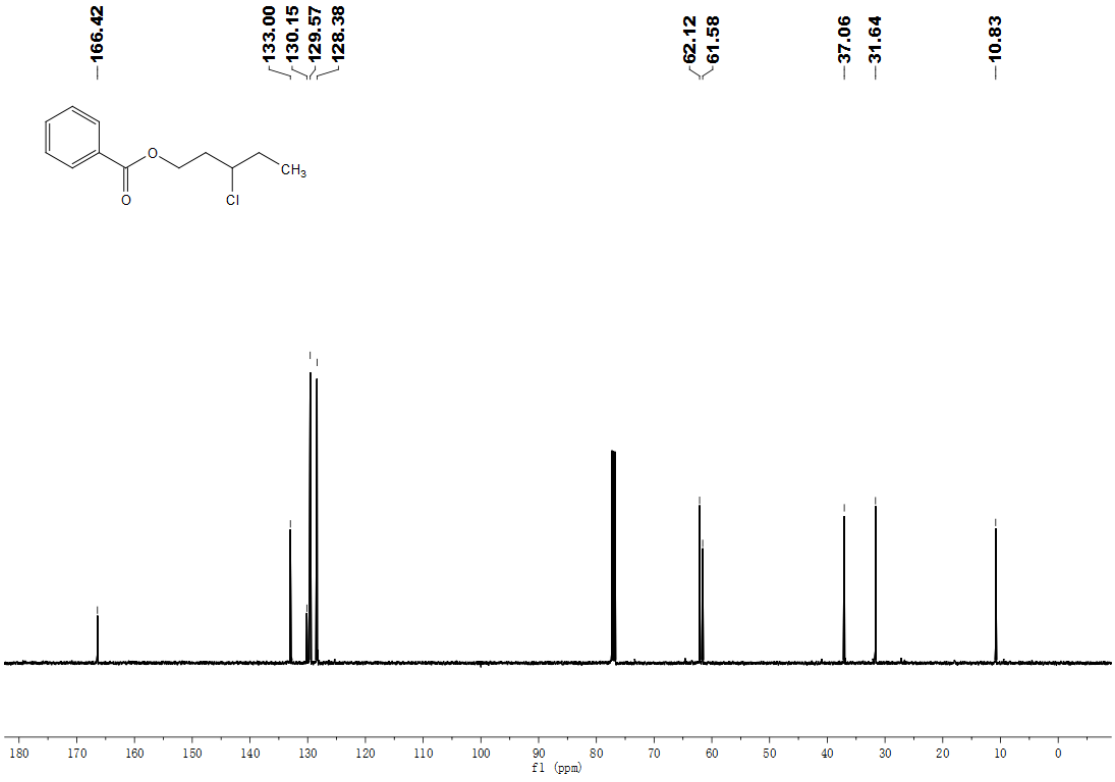
^{1}H NMR of compound **31a** (500 MHz, $CDCl_3$)



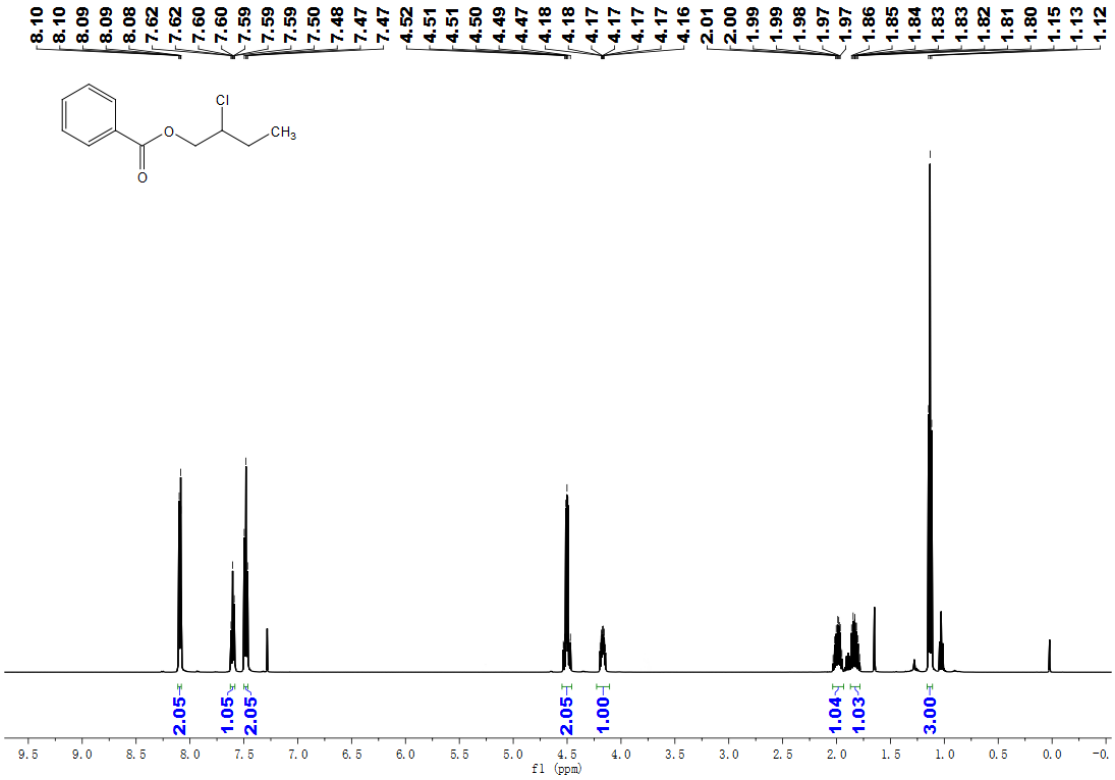
^{13}C NMR of compound **31a** (126 MHz, $CDCl_3$)



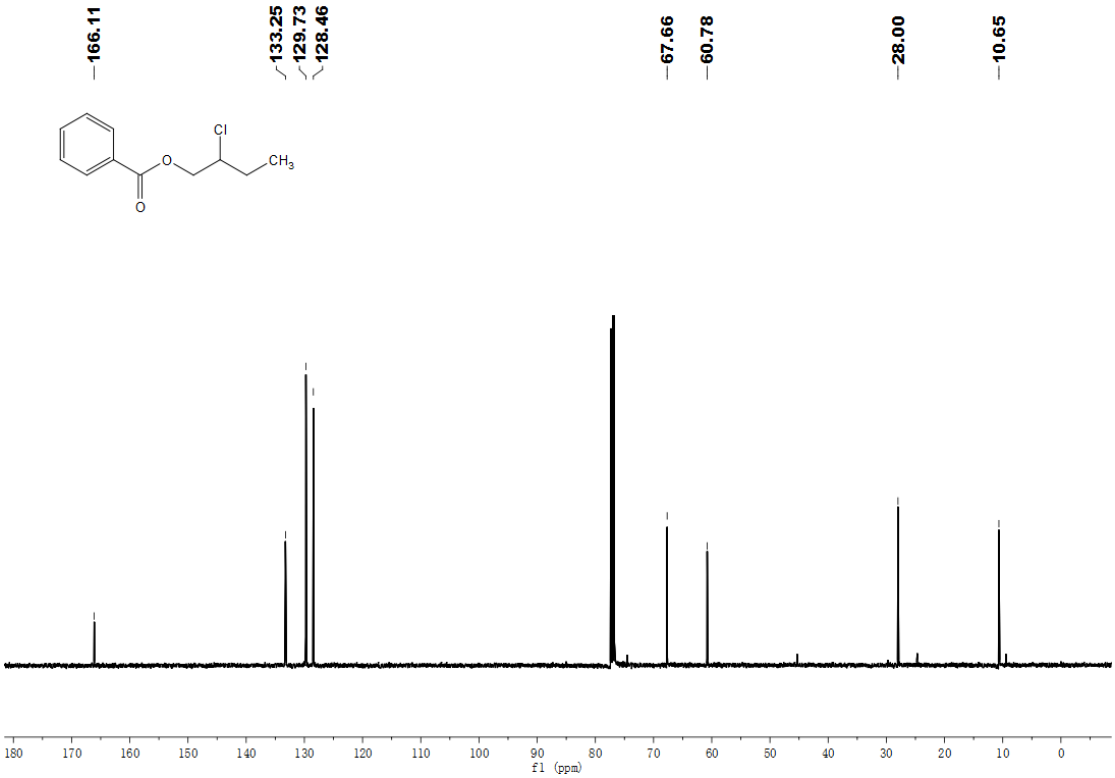
^{1}H NMR of compound **1b'** (500 MHz, $CDCl_3$)



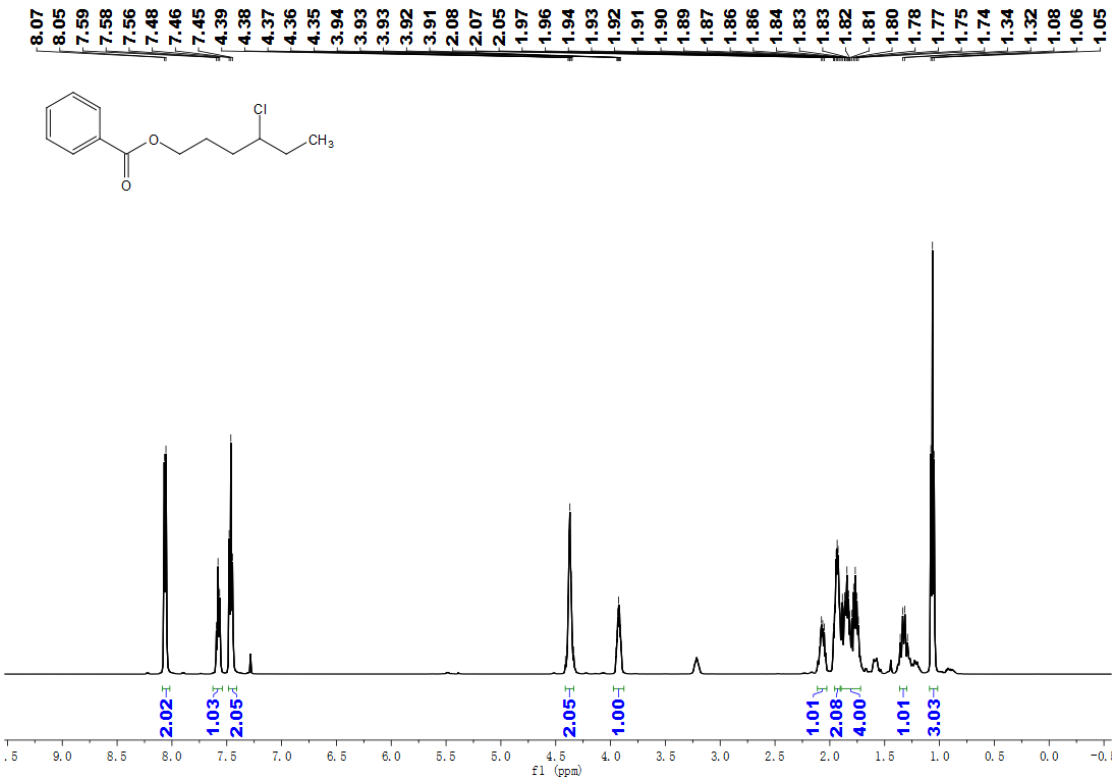
^{13}C NMR of compound **1b'** (126 MHz, $CDCl_3$)



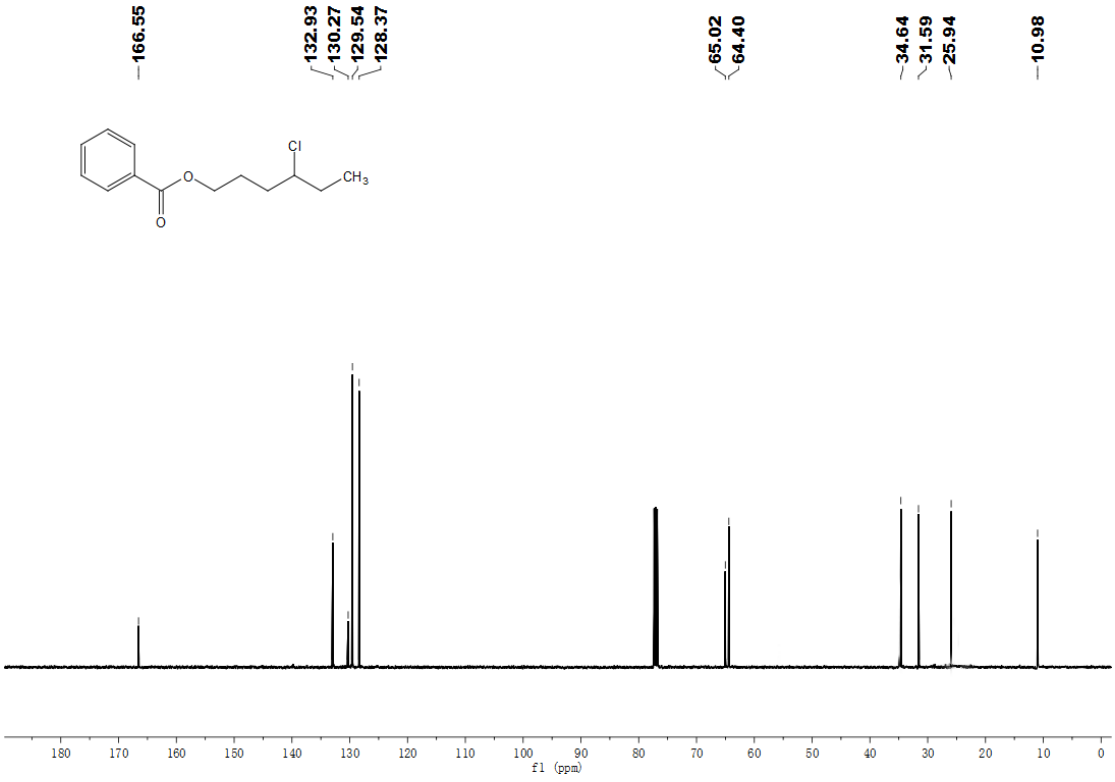
^{1}H NMR of compound **2b'** (500 MHz, $CDCl_3$)



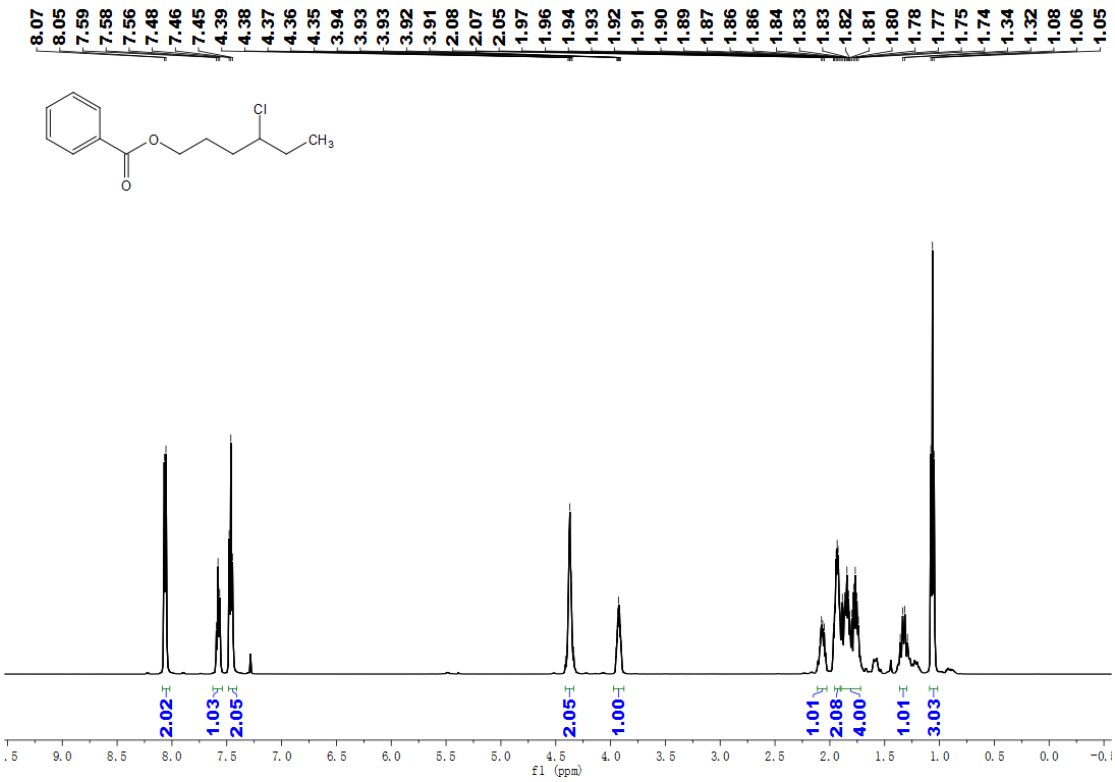
^{13}C NMR of compound **2b'** (126 MHz, $CDCl_3$)



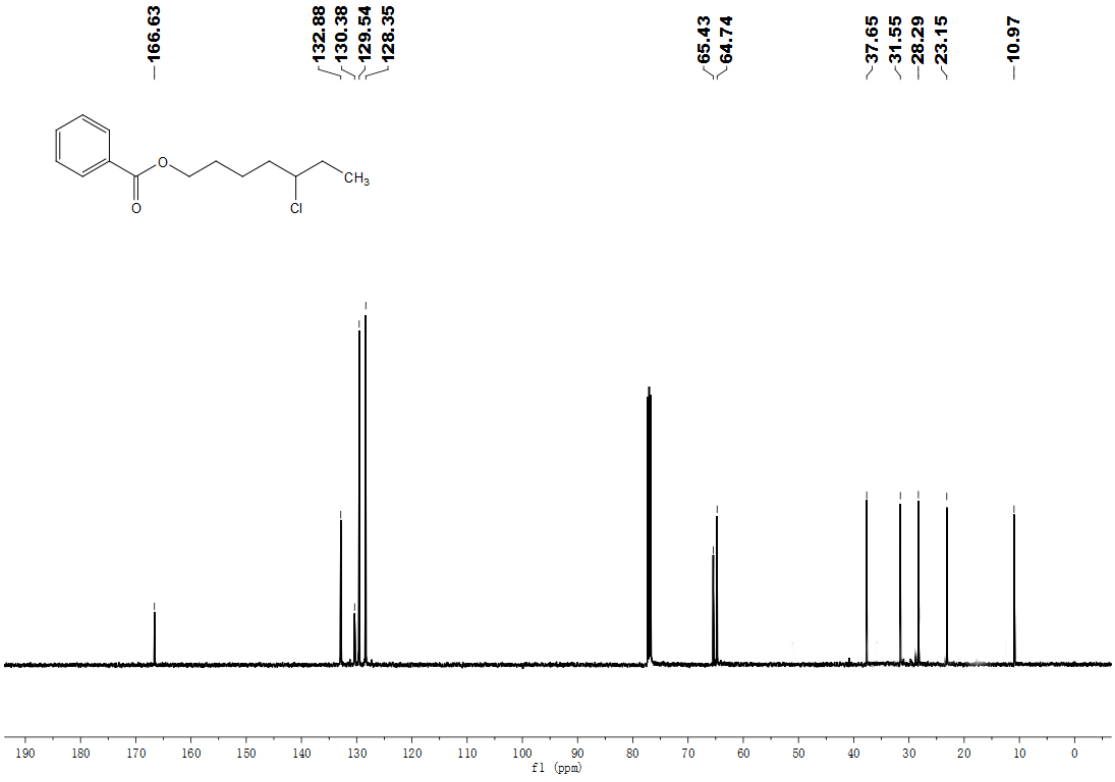
^{1}H NMR of compound **3b'** (500 MHz, $CDCl_3$)



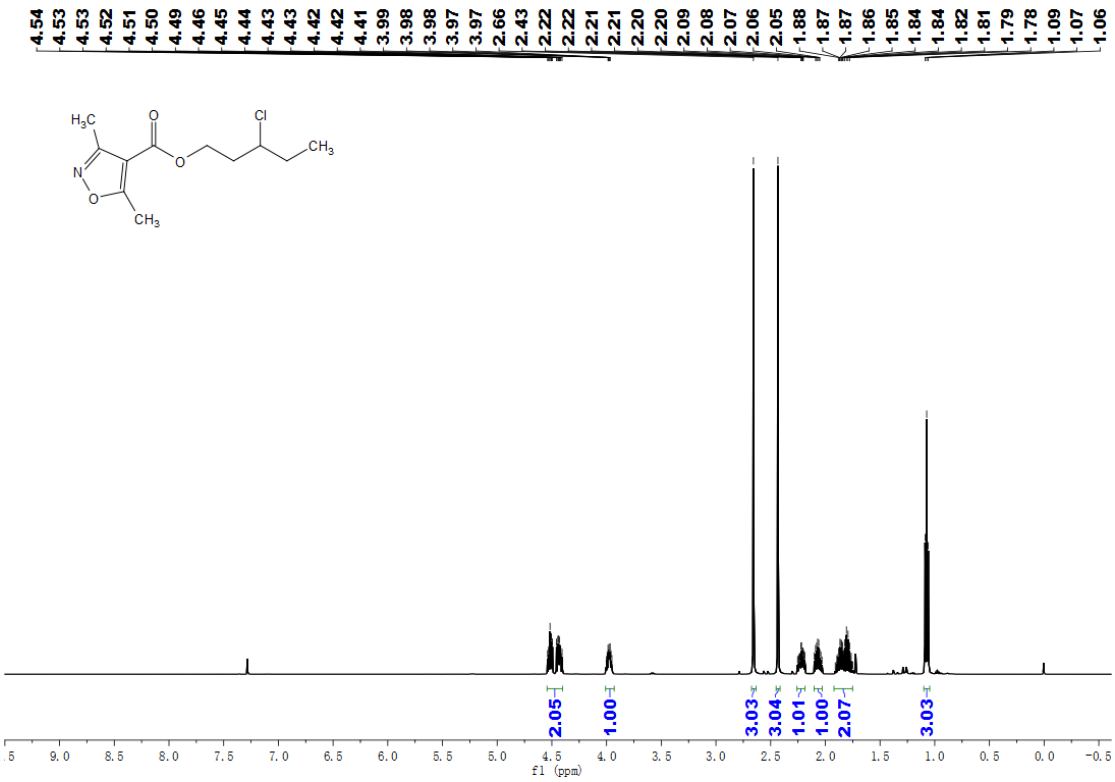
^{13}C NMR of compound **3b'** (126 MHz, $CDCl_3$)



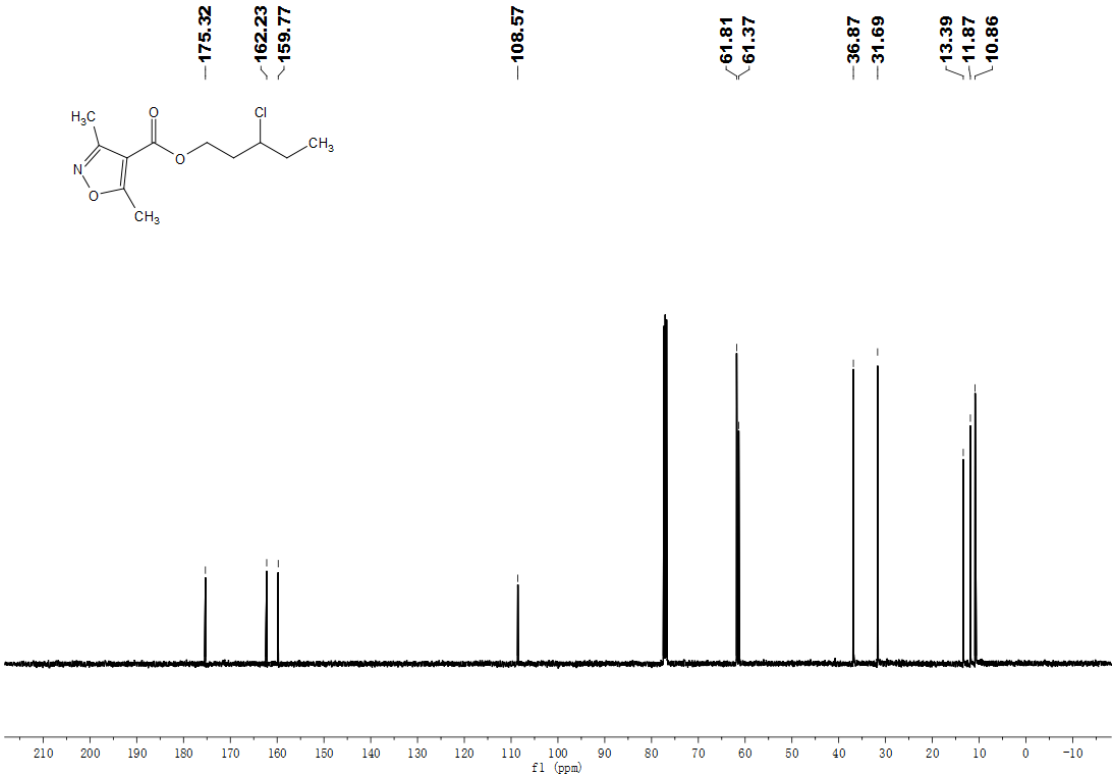
^{1}H NMR of compound **4b'** (500 MHz, $CDCl_3$)



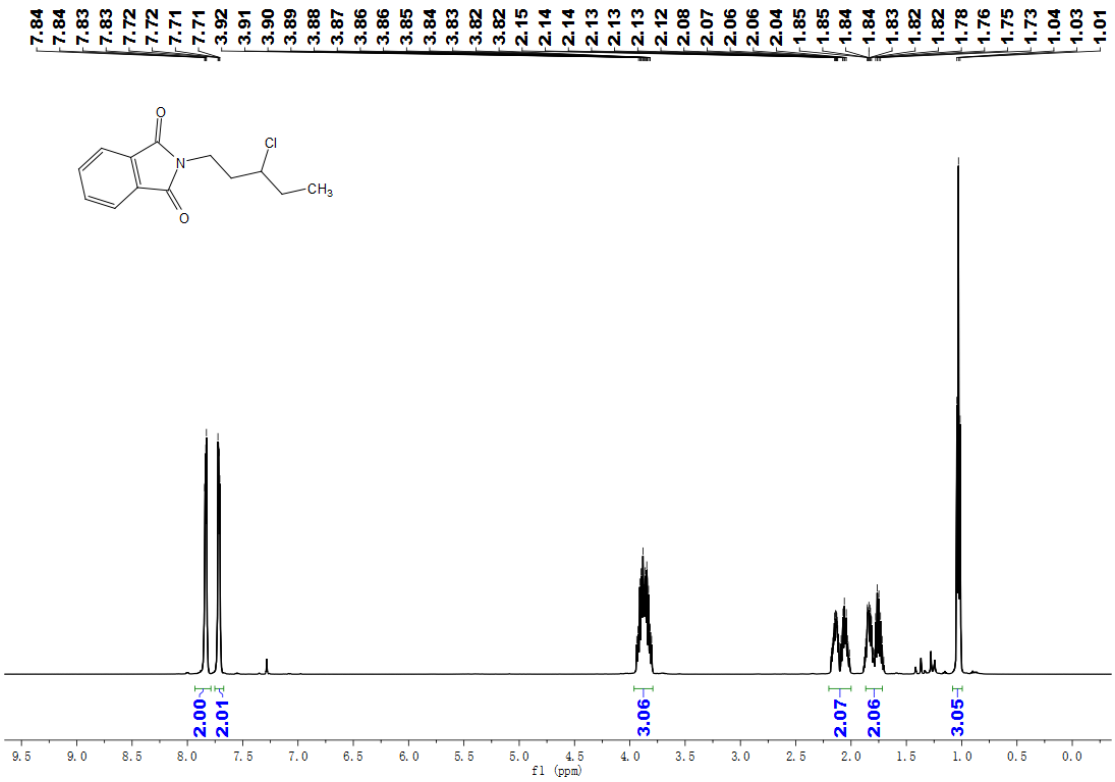
^{13}C NMR of compound **4b'** (126 MHz, $CDCl_3$)



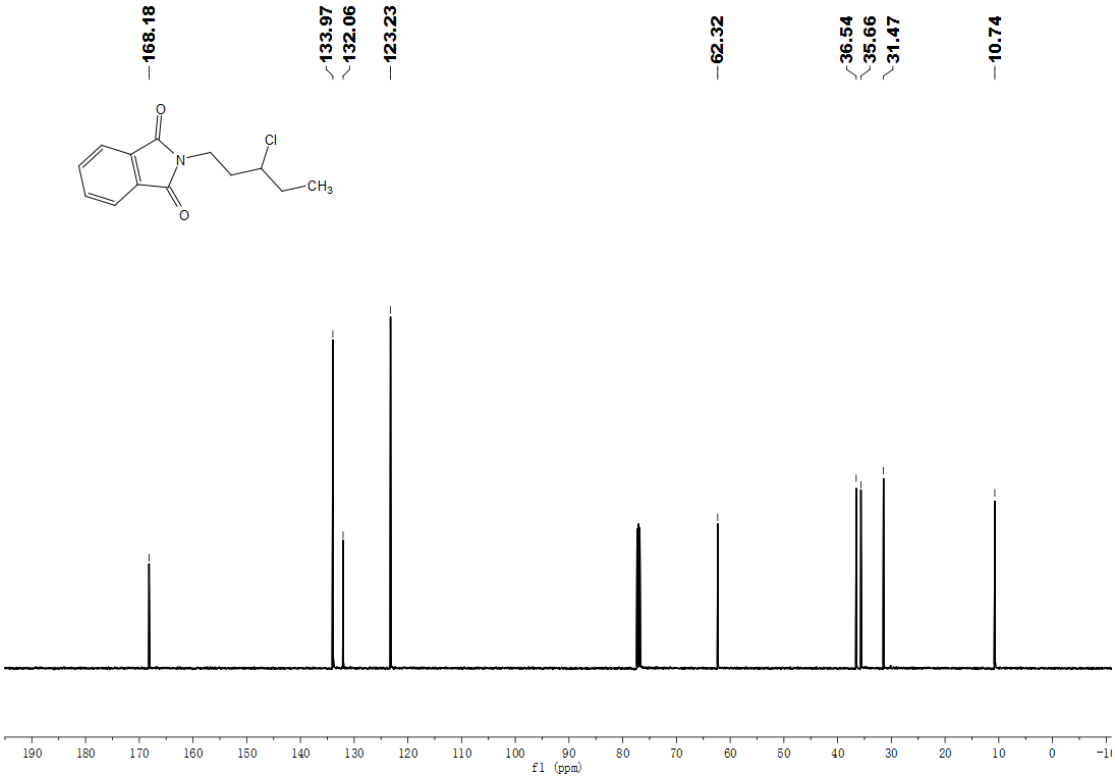
^{1}H NMR of compound **8b'** (500 MHz, $CDCl_3$)



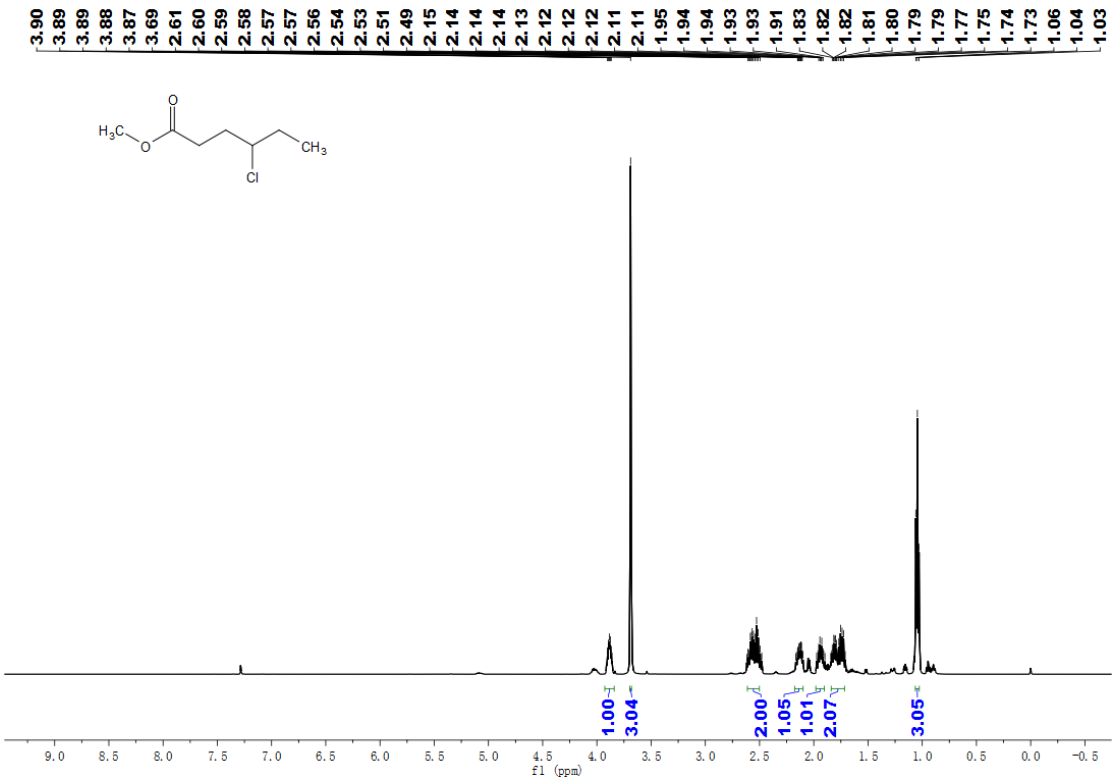
^{13}C NMR of compound **8b'** (126 MHz, $CDCl_3$)



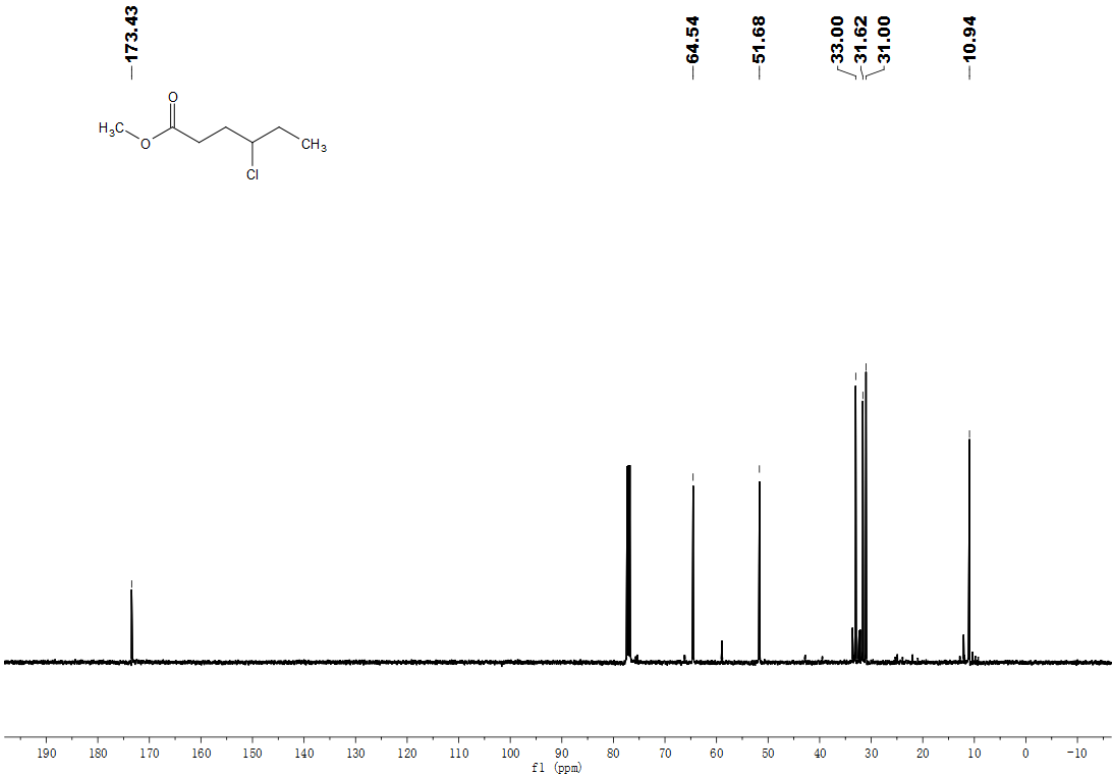
^{1}H NMR of compound **11b'** (500 MHz, $CDCl_3$)



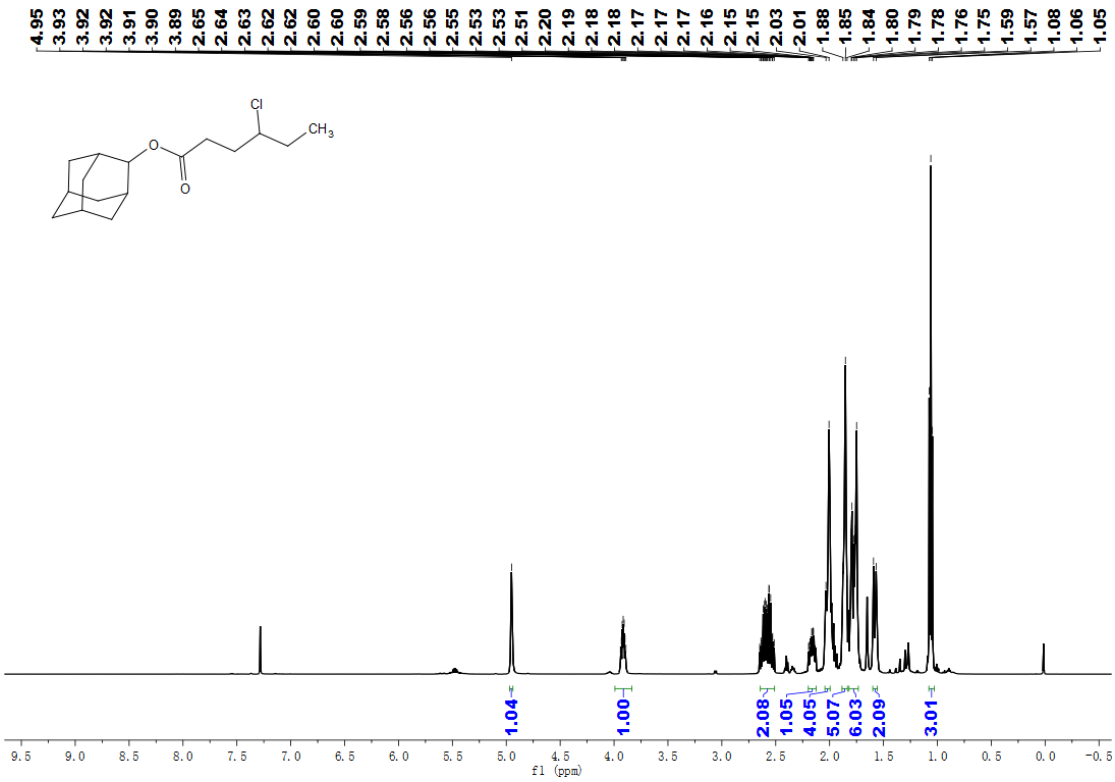
^{13}C NMR of compound **11b'** (126 MHz, $CDCl_3$)



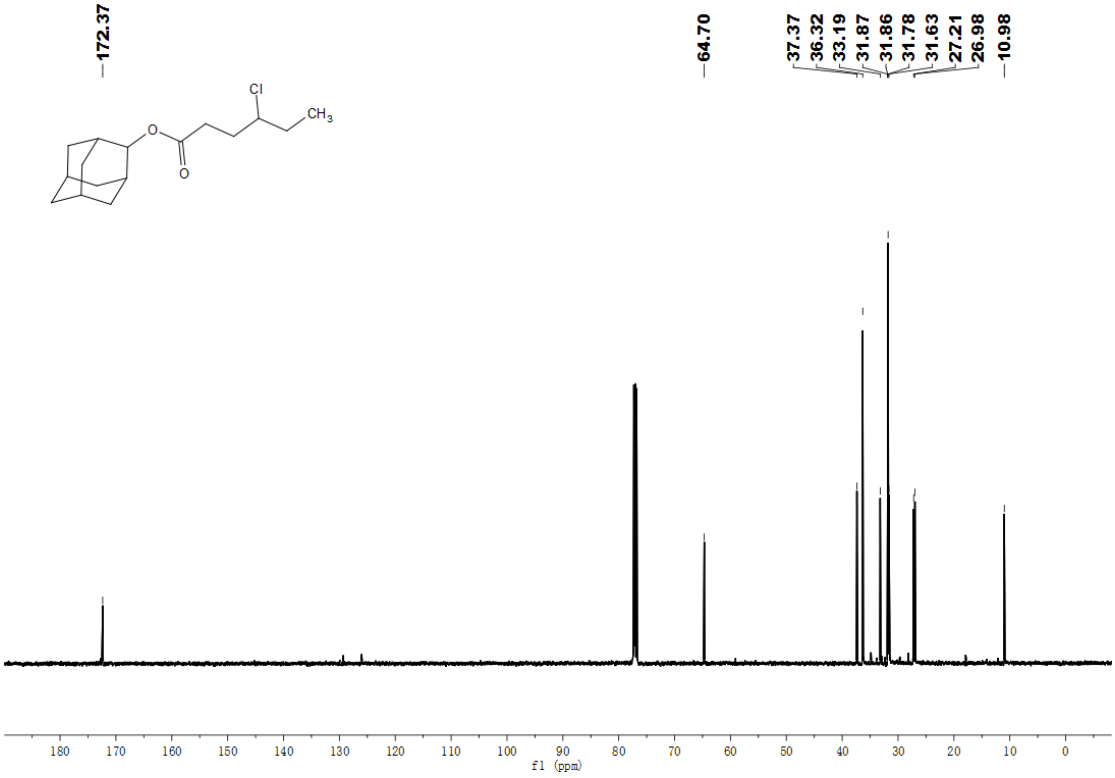
^{1}H NMR of compound **14b'** (500 MHz, $CDCl_3$)



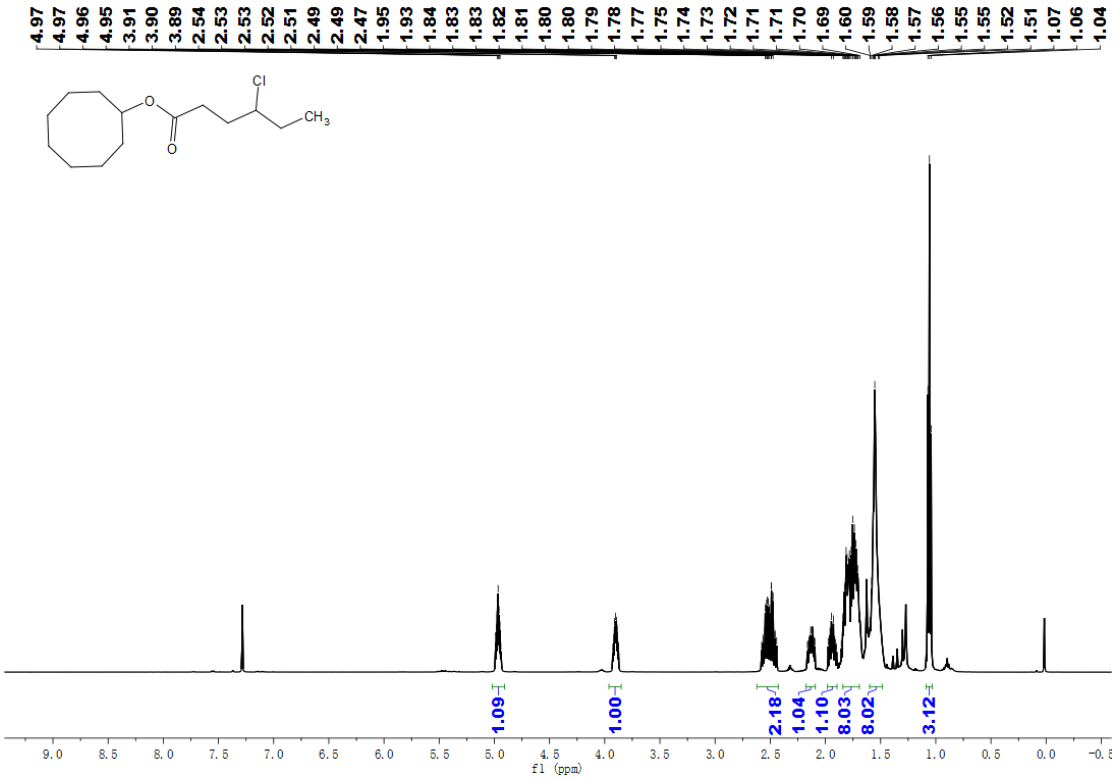
^{13}C NMR of compound **14b'** (126 MHz, $CDCl_3$)



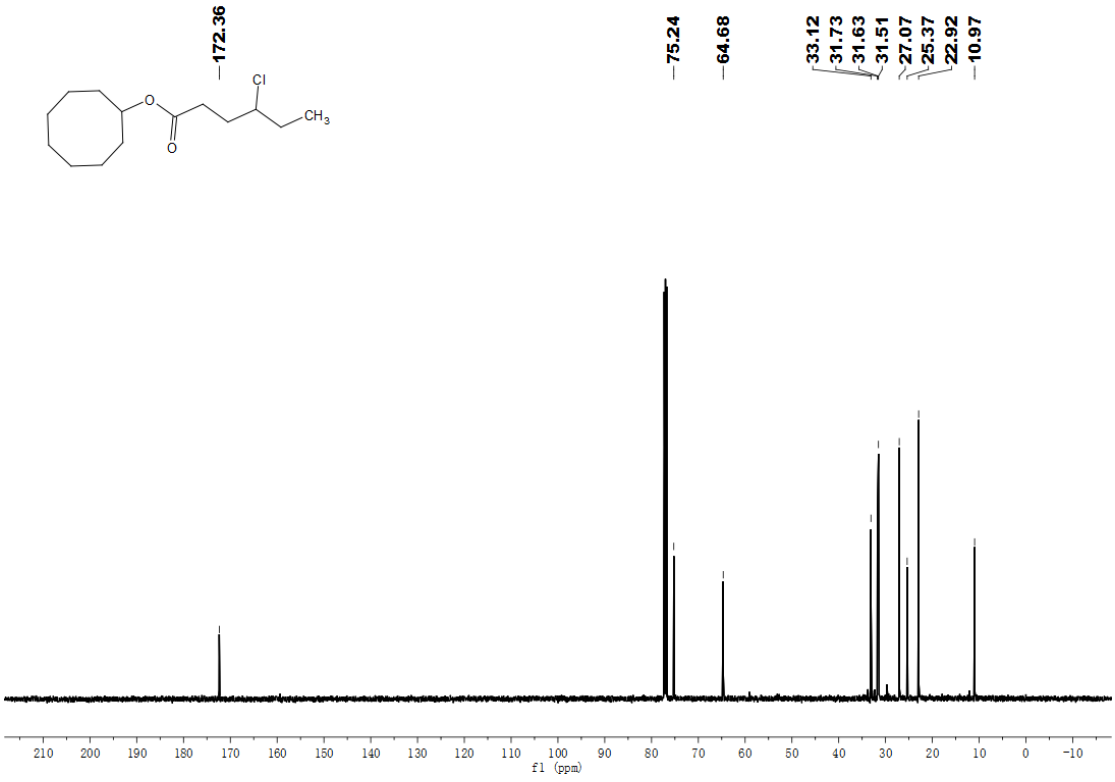
^{1}H NMR of compound **19b'** (500 MHz, $CDCl_3$)



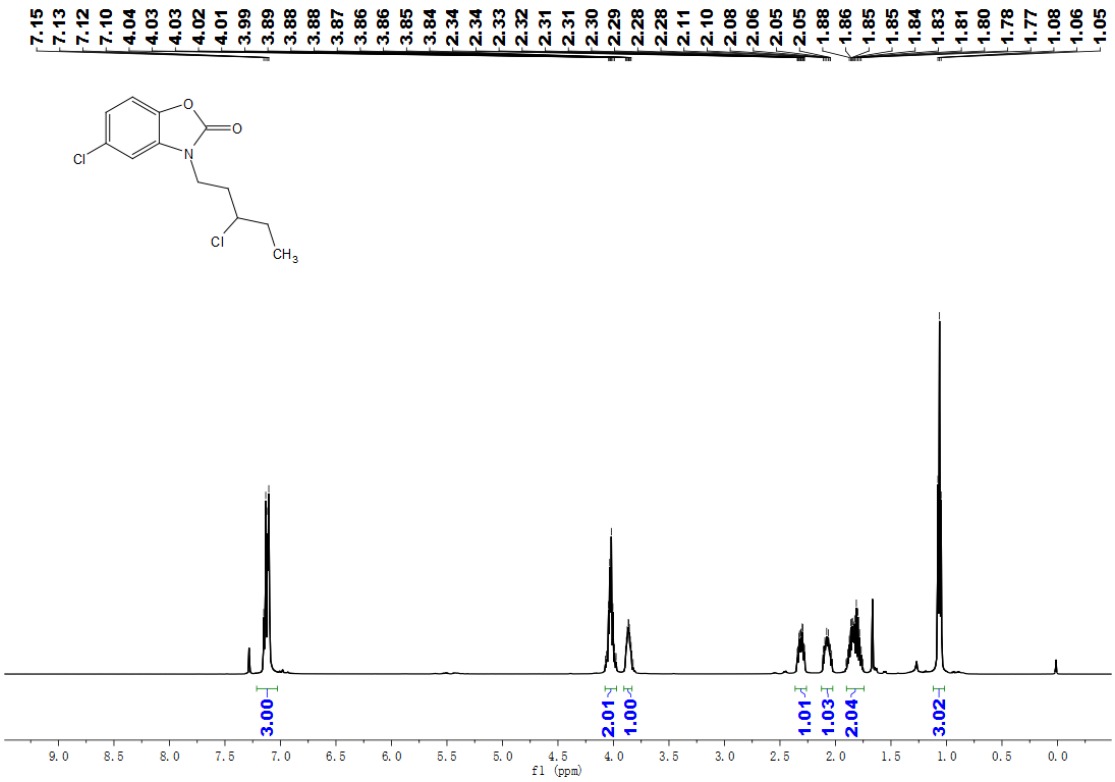
^{13}C NMR of compound **19b'** (126 MHz, $CDCl_3$)



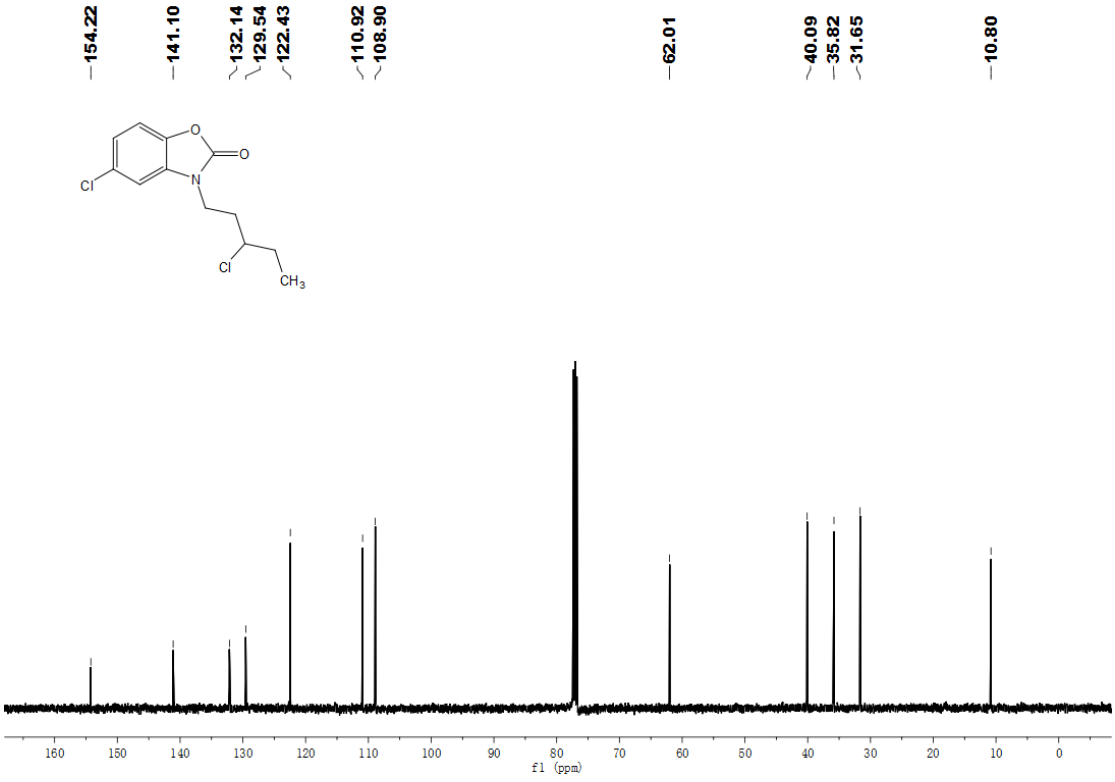
^{1}H NMR of compound **20b'** (500 MHz, $CDCl_3$)



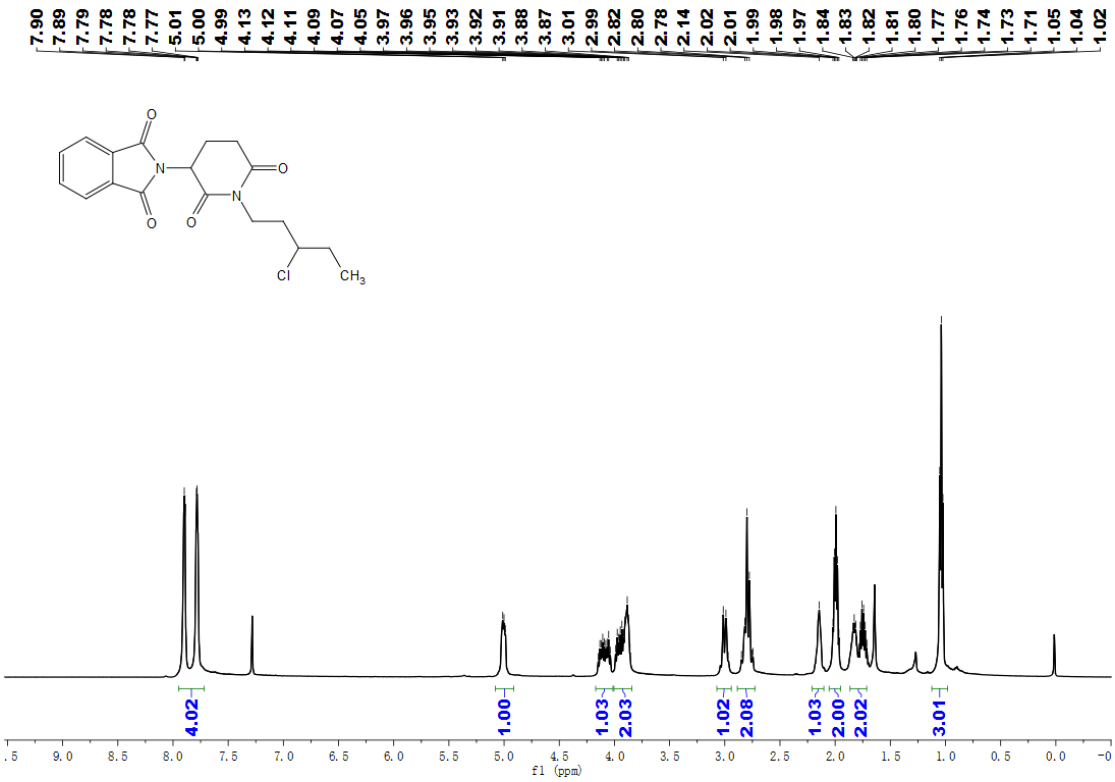
^{13}C NMR of compound **20b'** (126 MHz, $CDCl_3$)



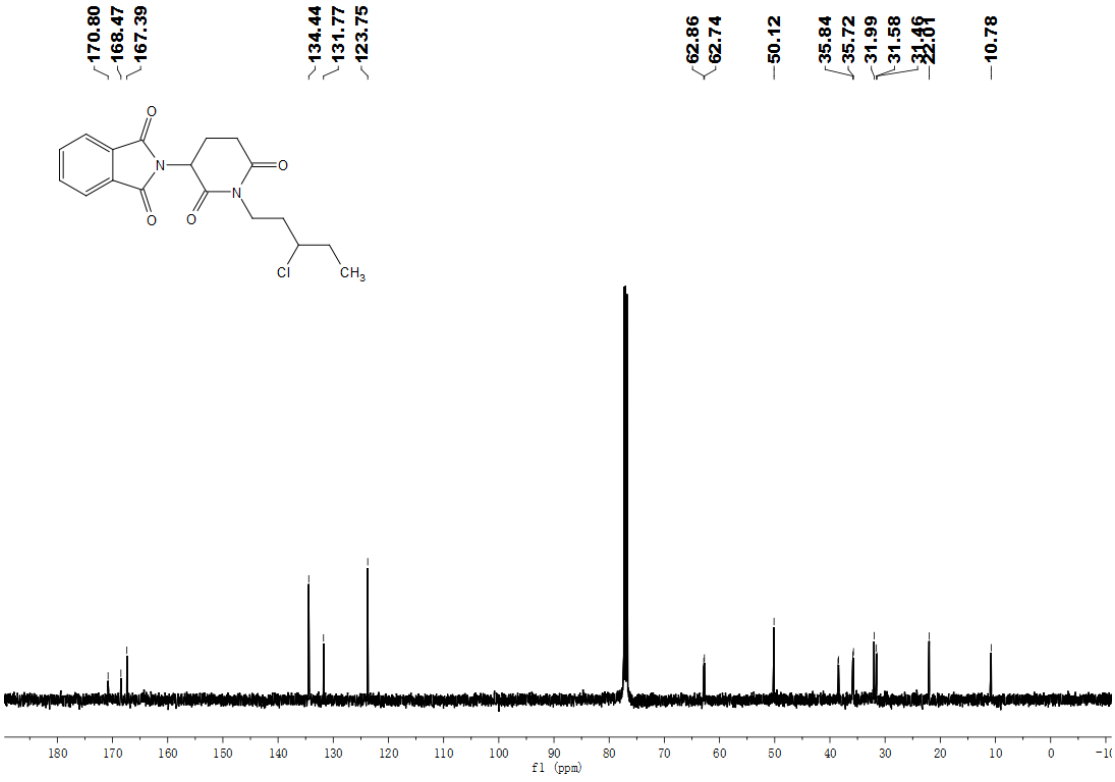
^{1}H NMR of compound **23b'** (500 MHz, $CDCl_3$)



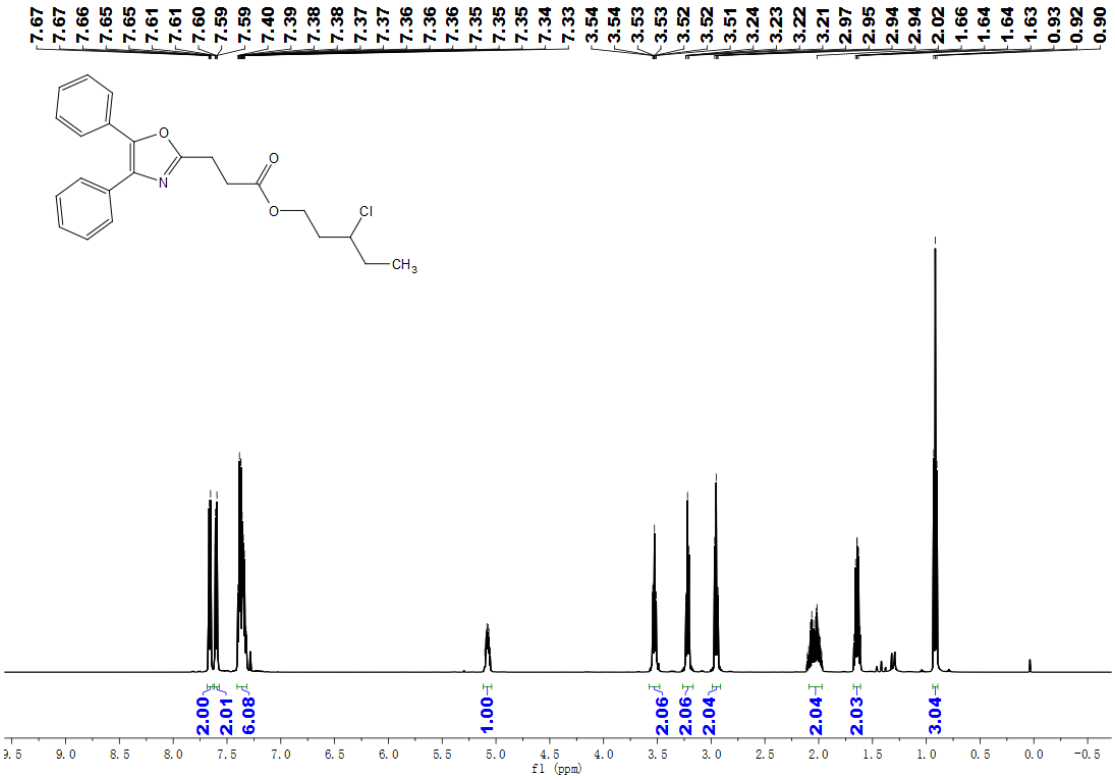
^{13}C NMR of compound **23b'** (126 MHz, $CDCl_3$)



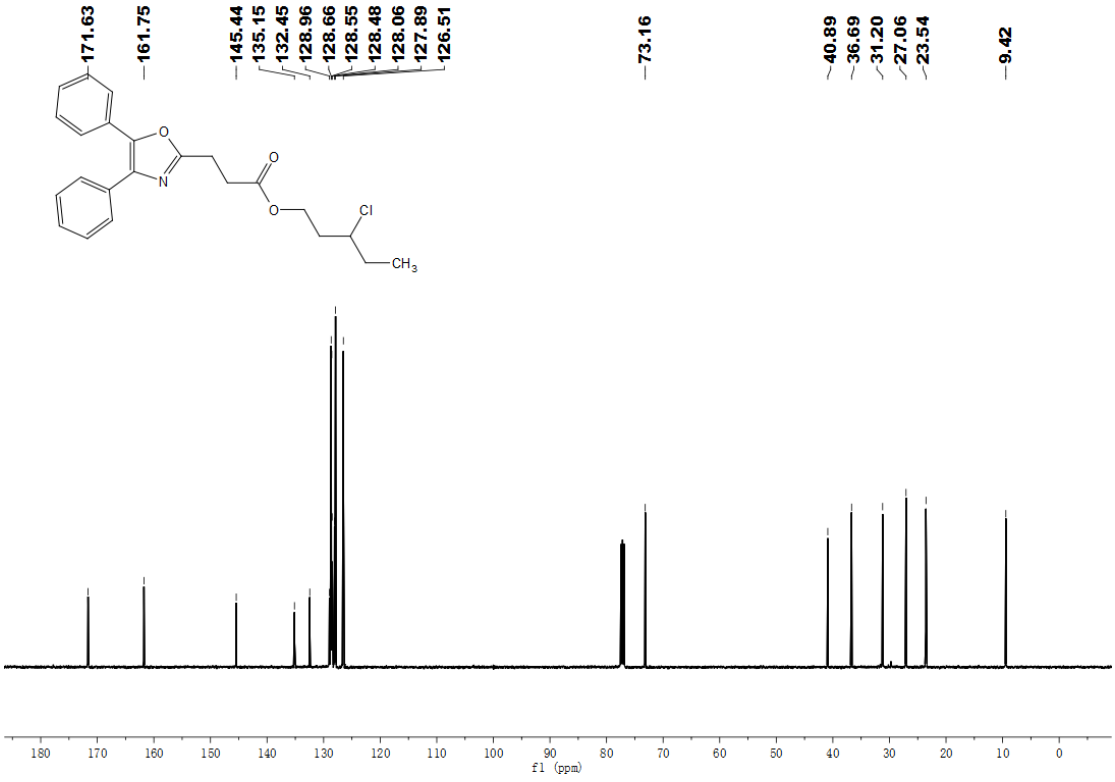
^{1}H NMR of compound **24b'** (500 MHz, $CDCl_3$)



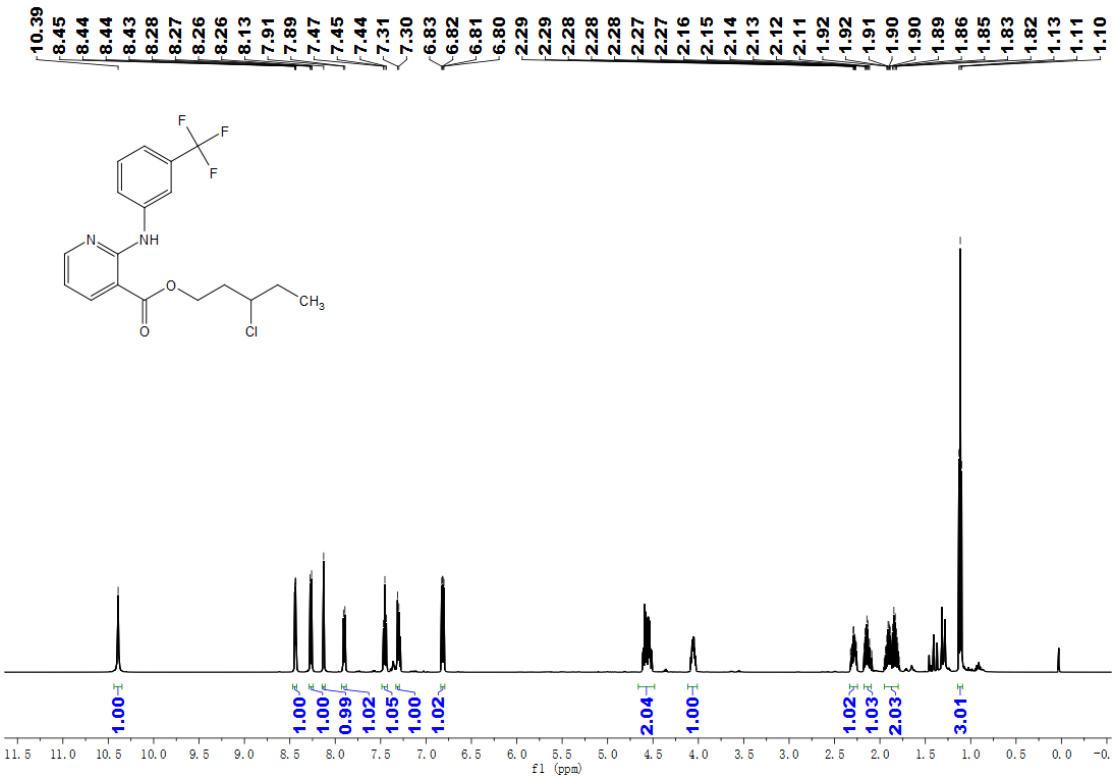
^{13}C NMR of compound **24b'** (126 MHz, $CDCl_3$)



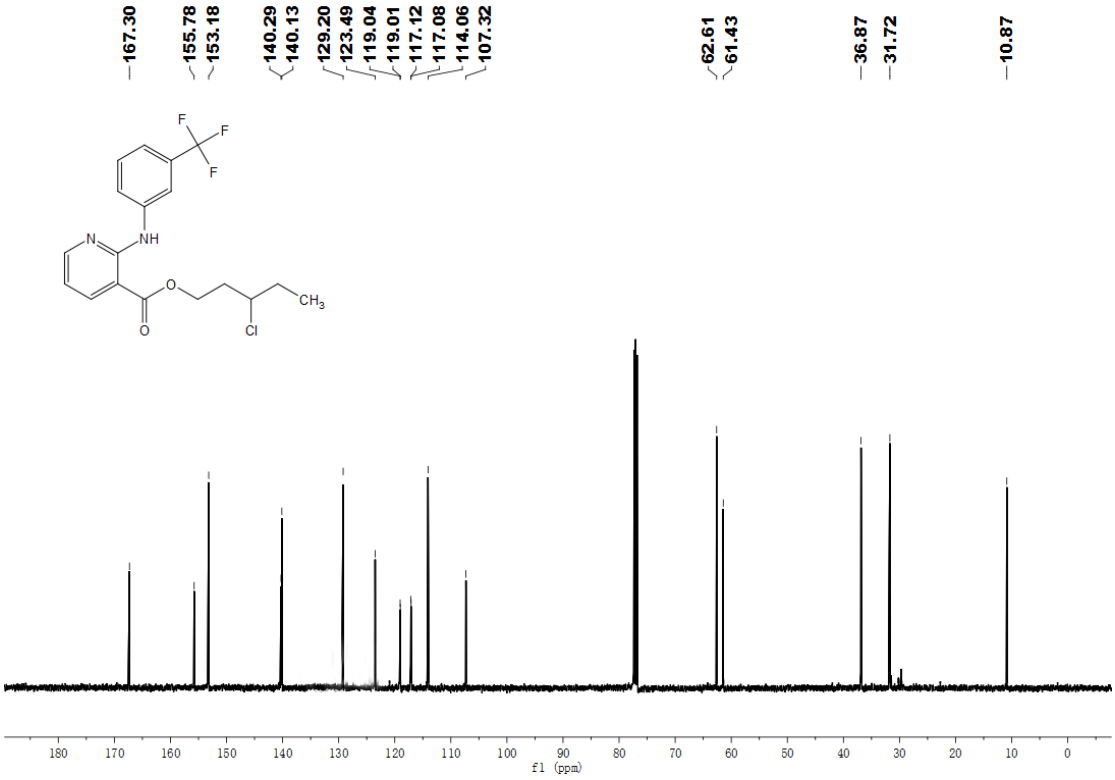
^{1}H NMR of compound **26b'** (500 MHz, $CDCl_3$)



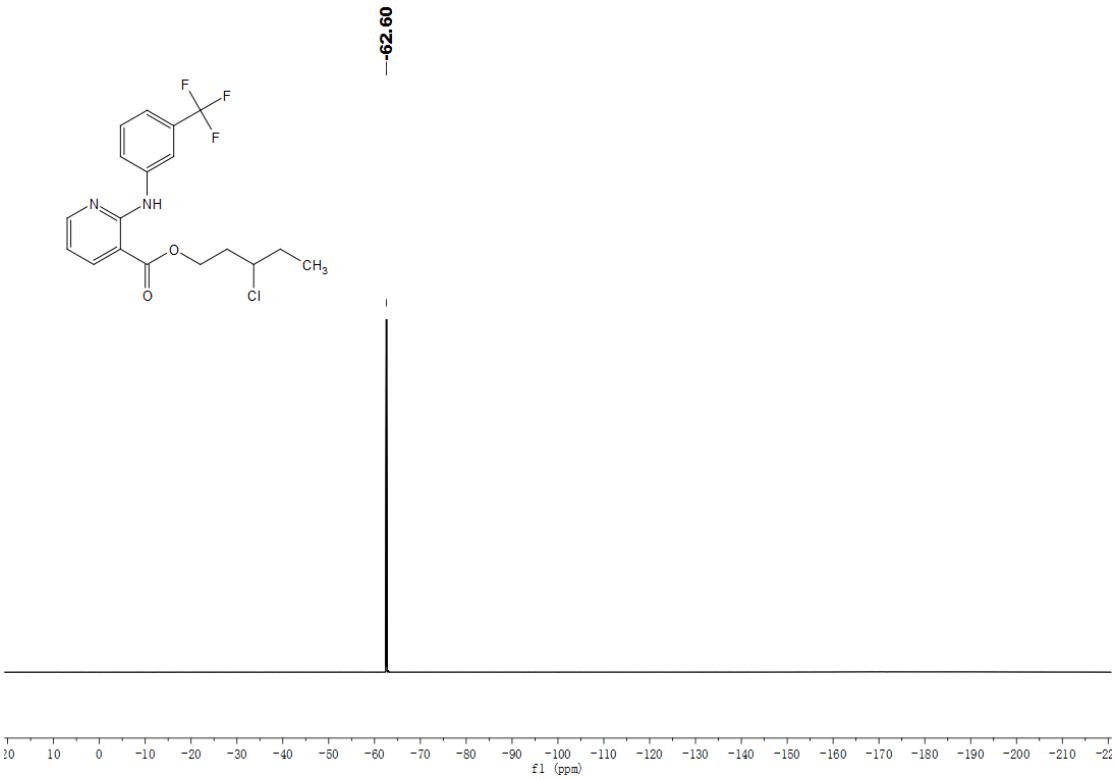
^{13}C NMR of compound **26b'** (126 MHz, $CDCl_3$)



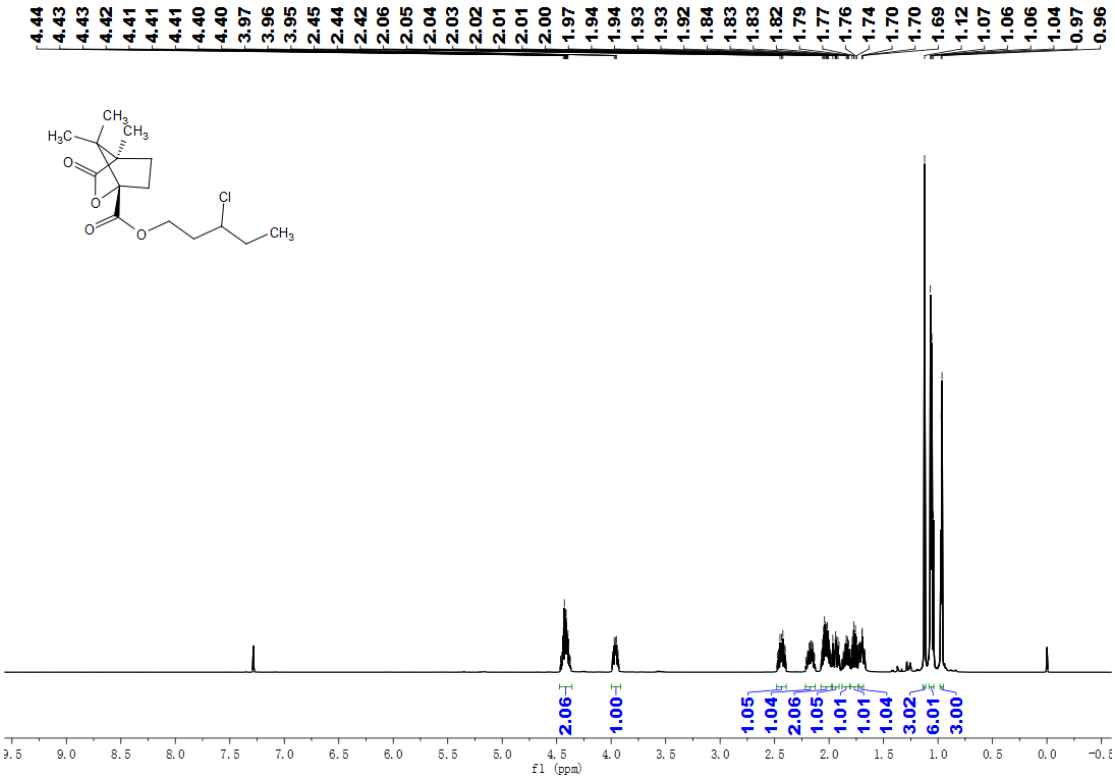
^{1}H NMR of compound **27b'** (500 MHz, $CDCl_3$)



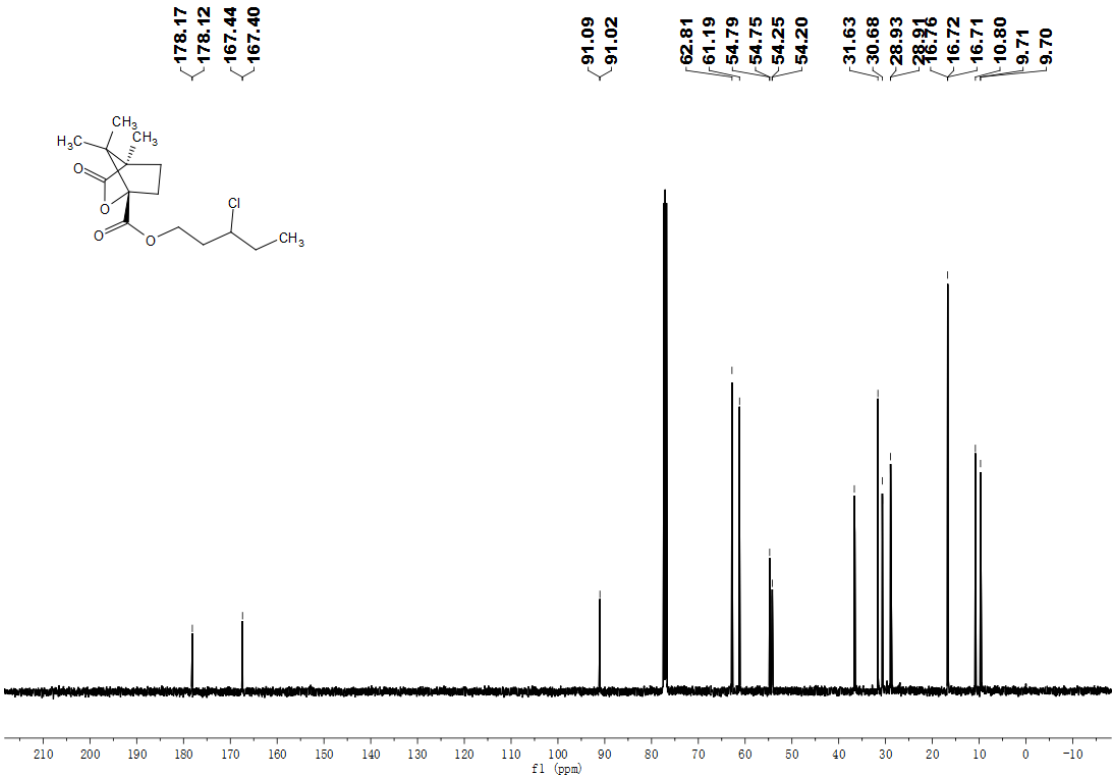
^{13}C NMR of compound **27b'** (126 MHz, $CDCl_3$)



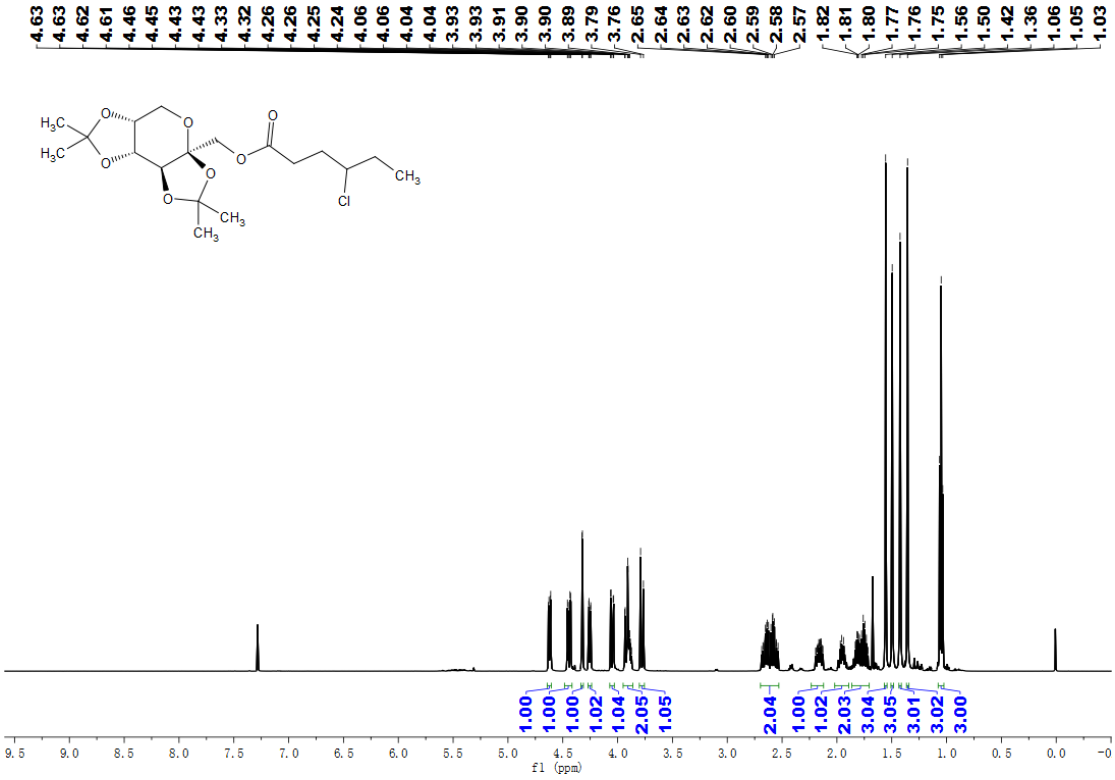
^{19}F NMR of compound **27b'** (471 MHz, $CDCl_3$)



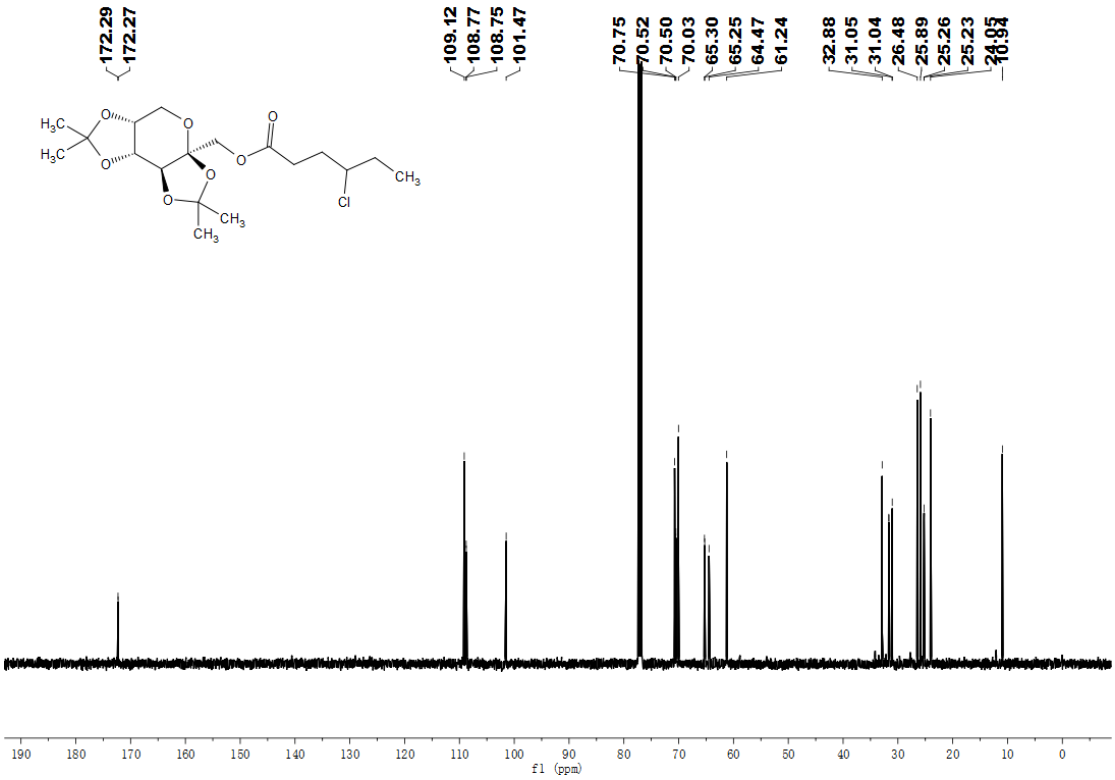
^{1}H NMR of compound **29b'** (500 MHz, $CDCl_3$)



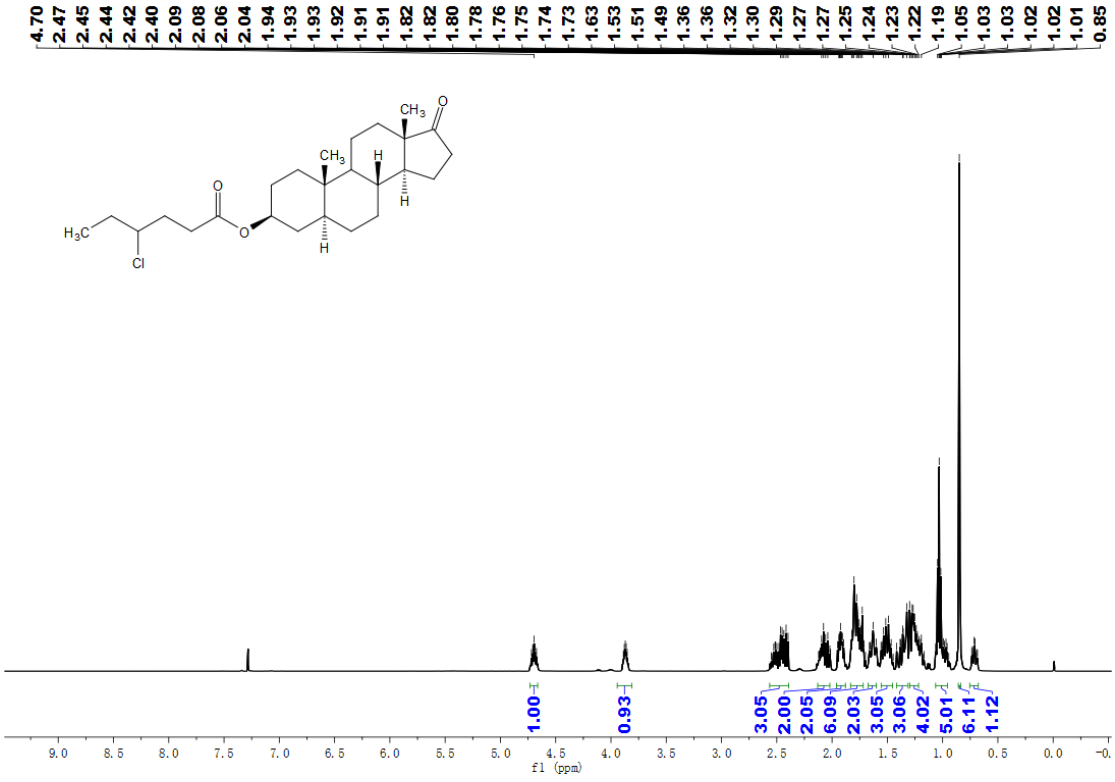
^{13}C NMR of compound **29b'** (126 MHz, $CDCl_3$)



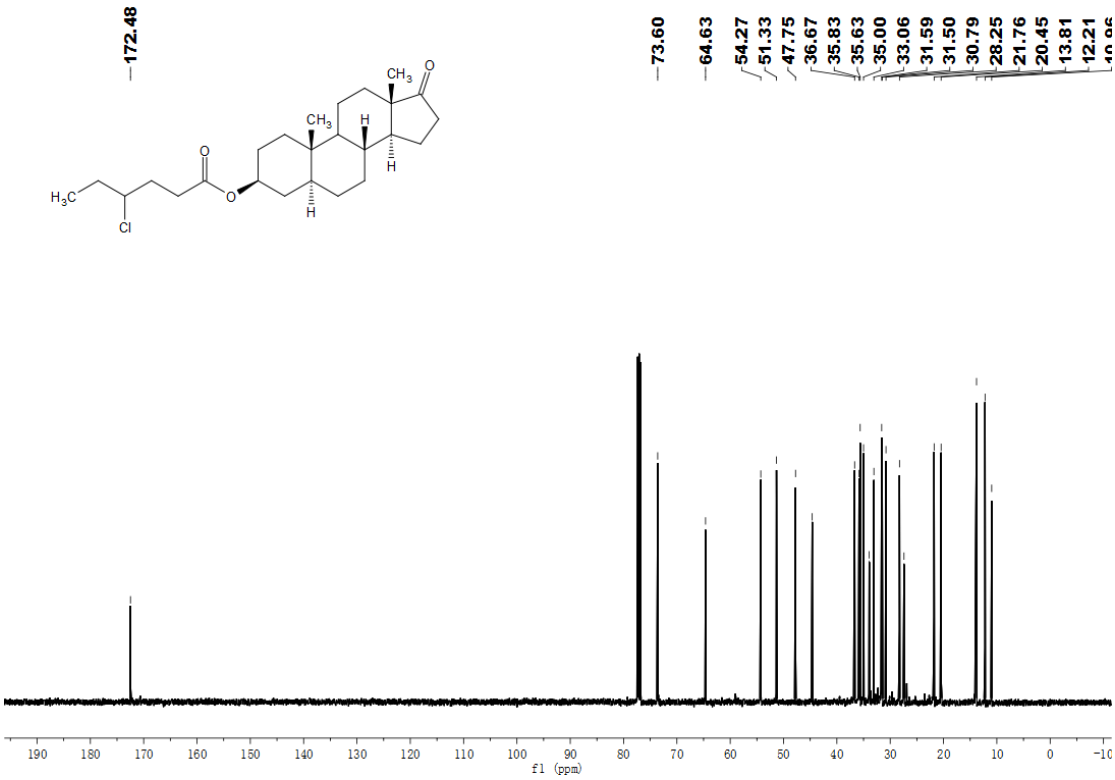
^{1}H NMR of compound **30b'** (500 MHz, $CDCl_3$)



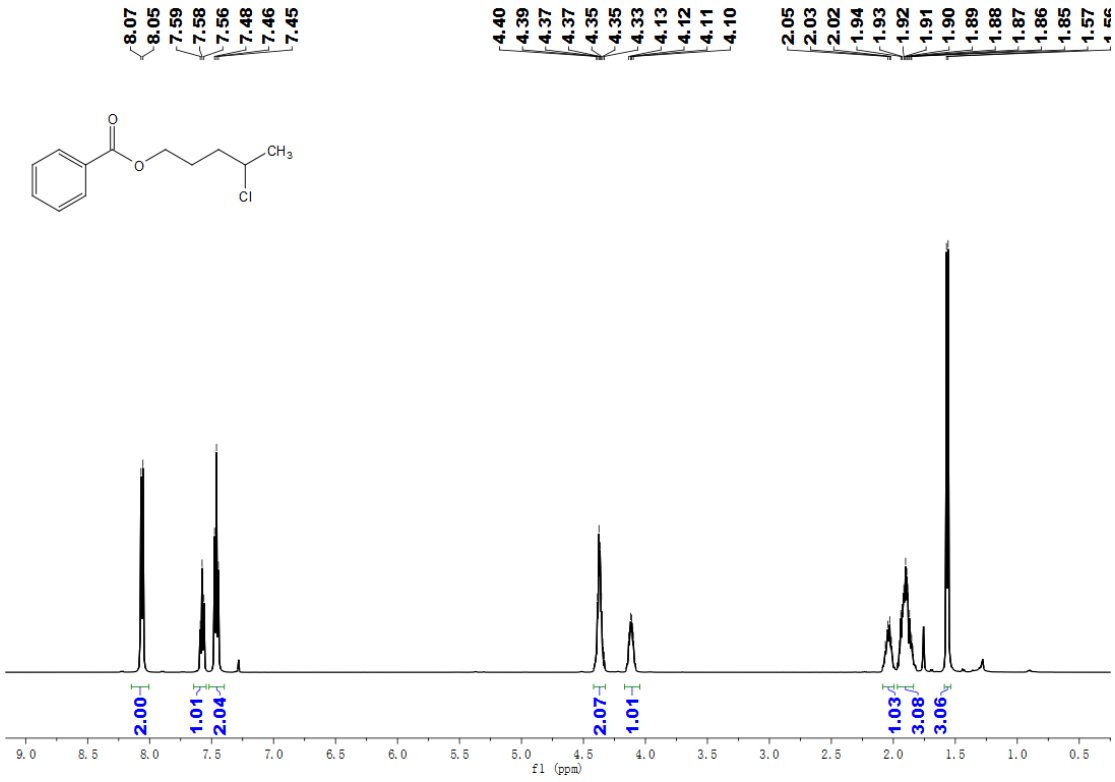
^{13}C NMR of compound **30b'** (126 MHz, $CDCl_3$)



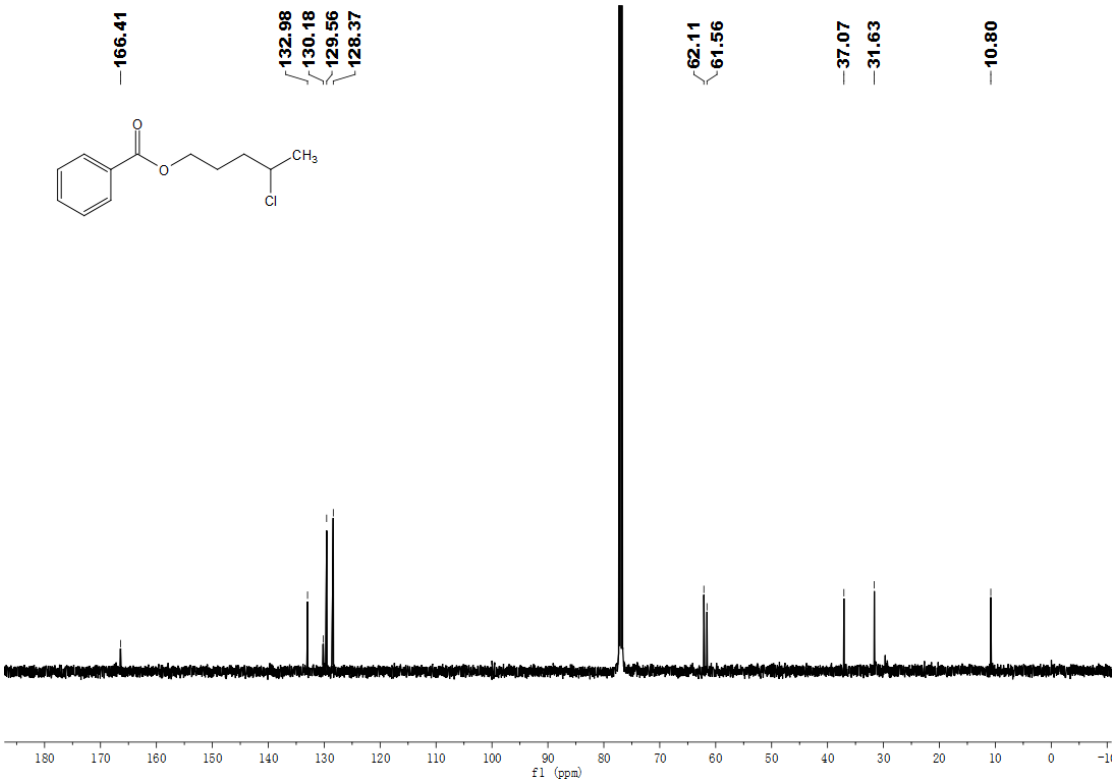
^{1}H NMR of compound **31b'** (500 MHz, $CDCl_3$)



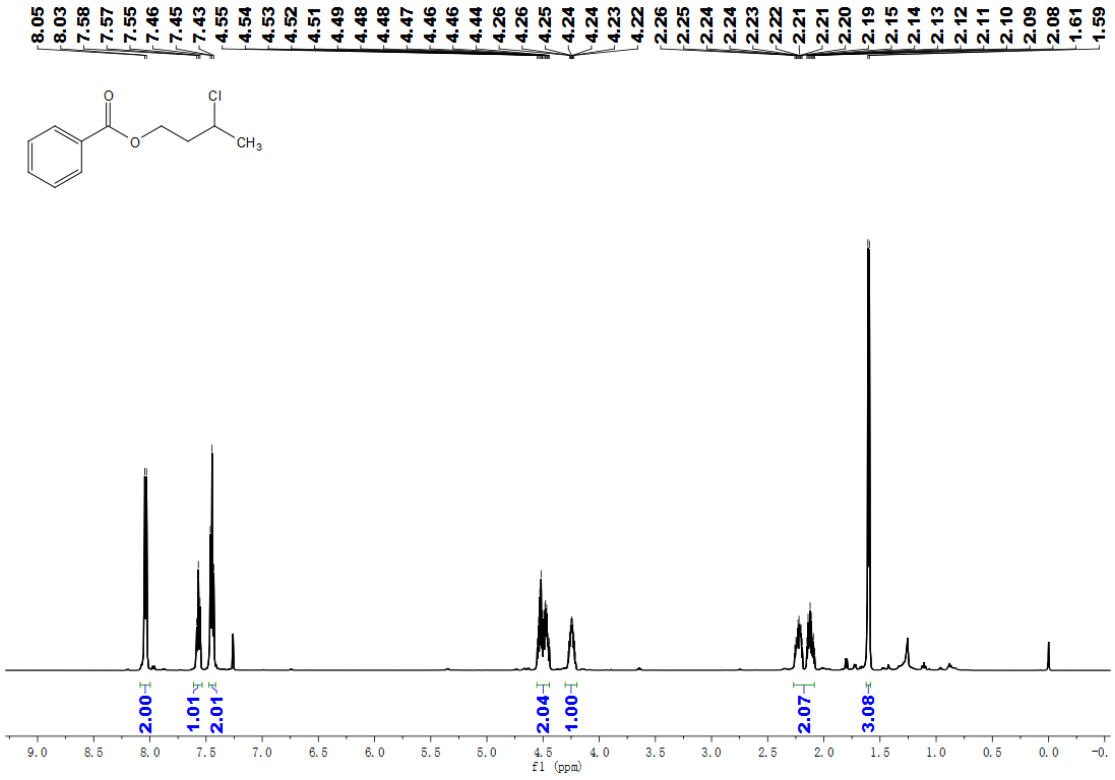
^{13}C NMR of compound **31b'** (126 MHz, $CDCl_3$)



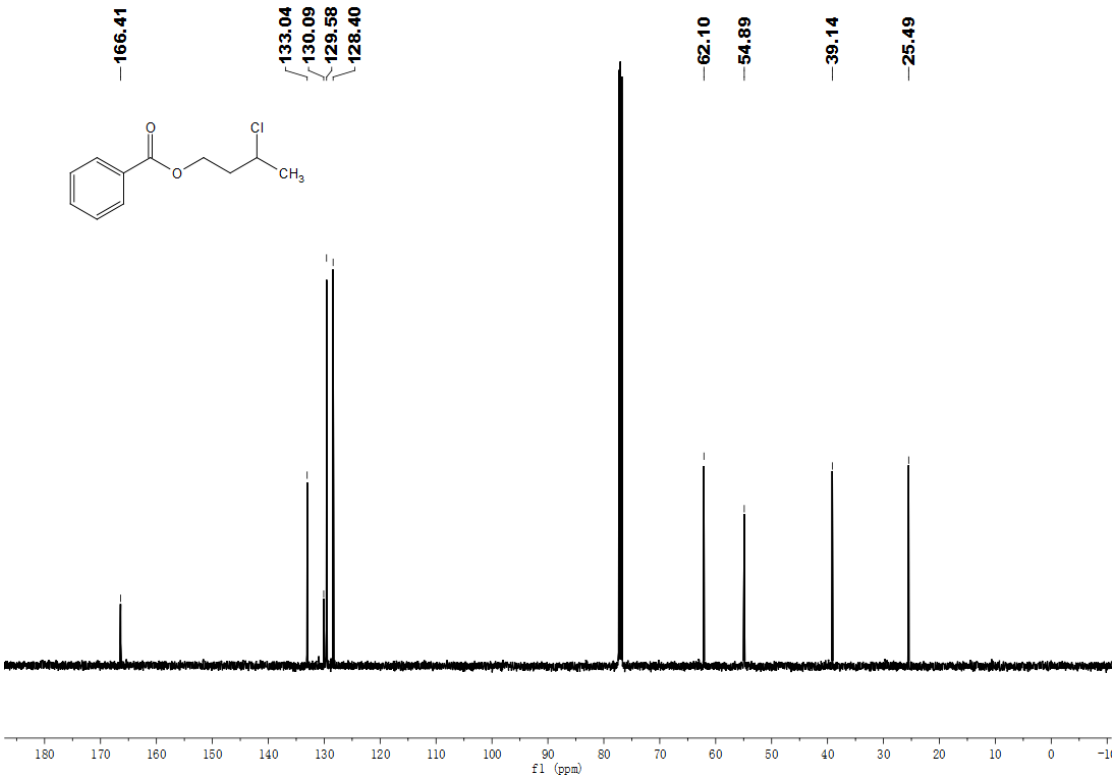
^{1}H NMR of compound **1b** (500 MHz, $CDCl_3$)



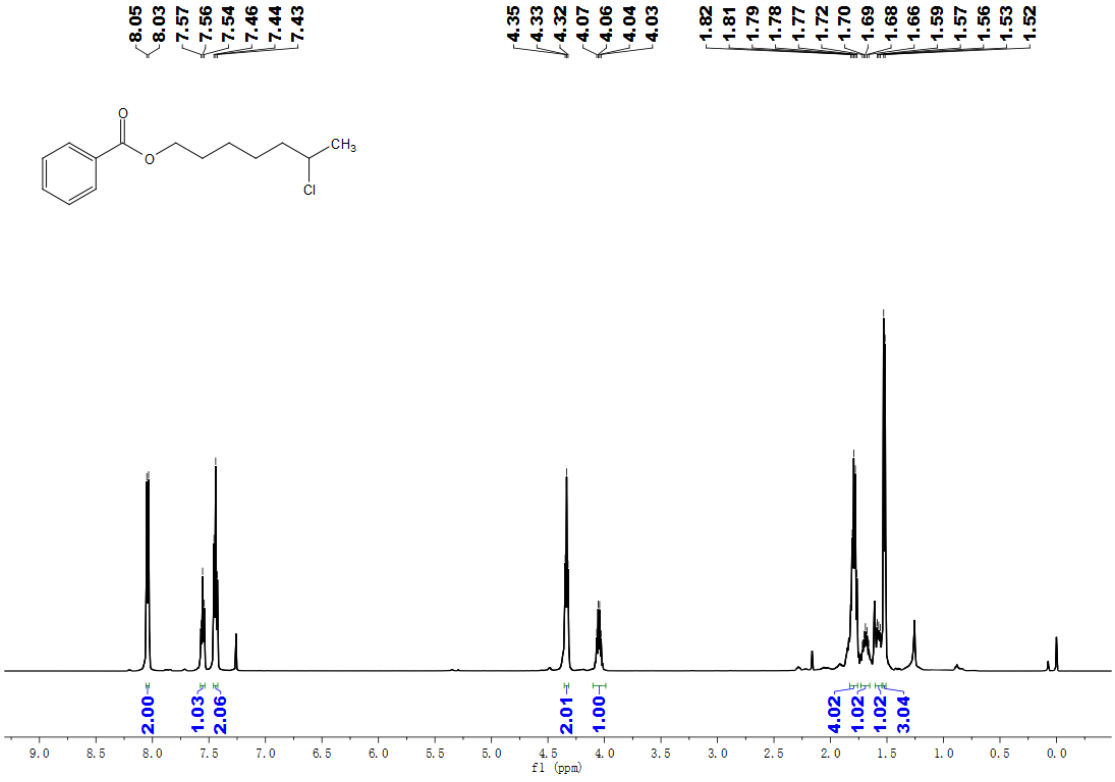
^{13}C NMR of compound **1b** (126 MHz, $CDCl_3$)



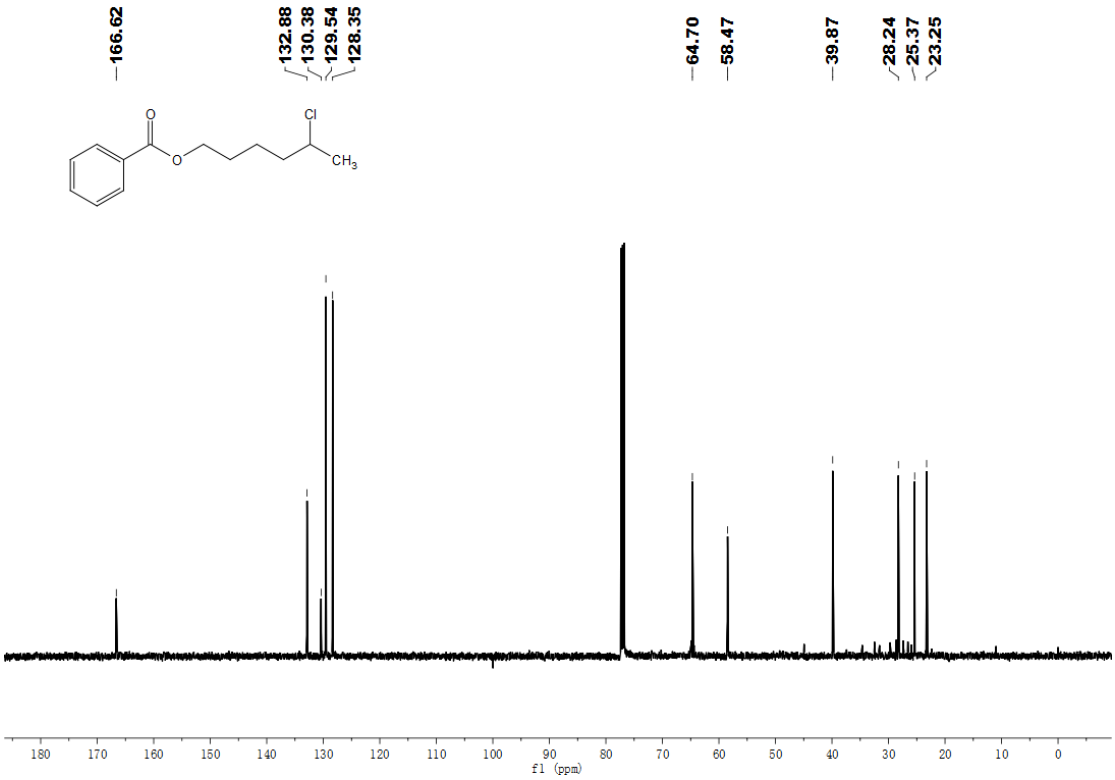
^{1}H NMR of compound **2b** (500 MHz, $CDCl_3$)



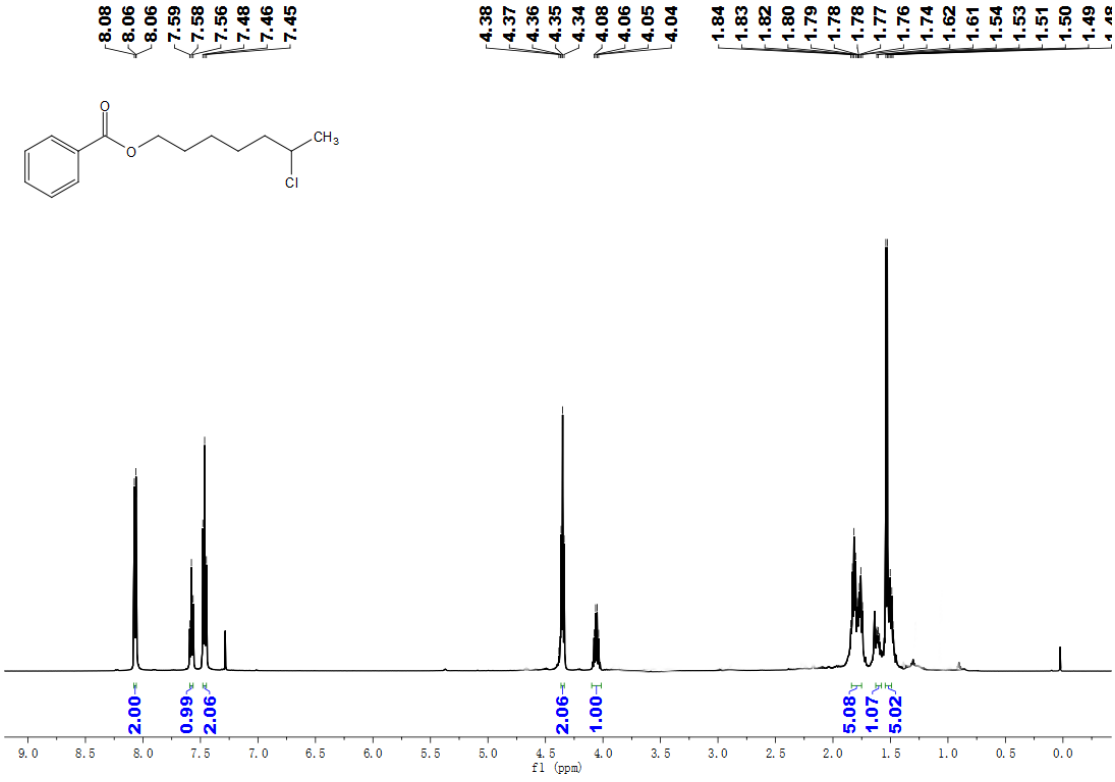
^{13}C NMR of compound **2b** (126 MHz, $CDCl_3$)



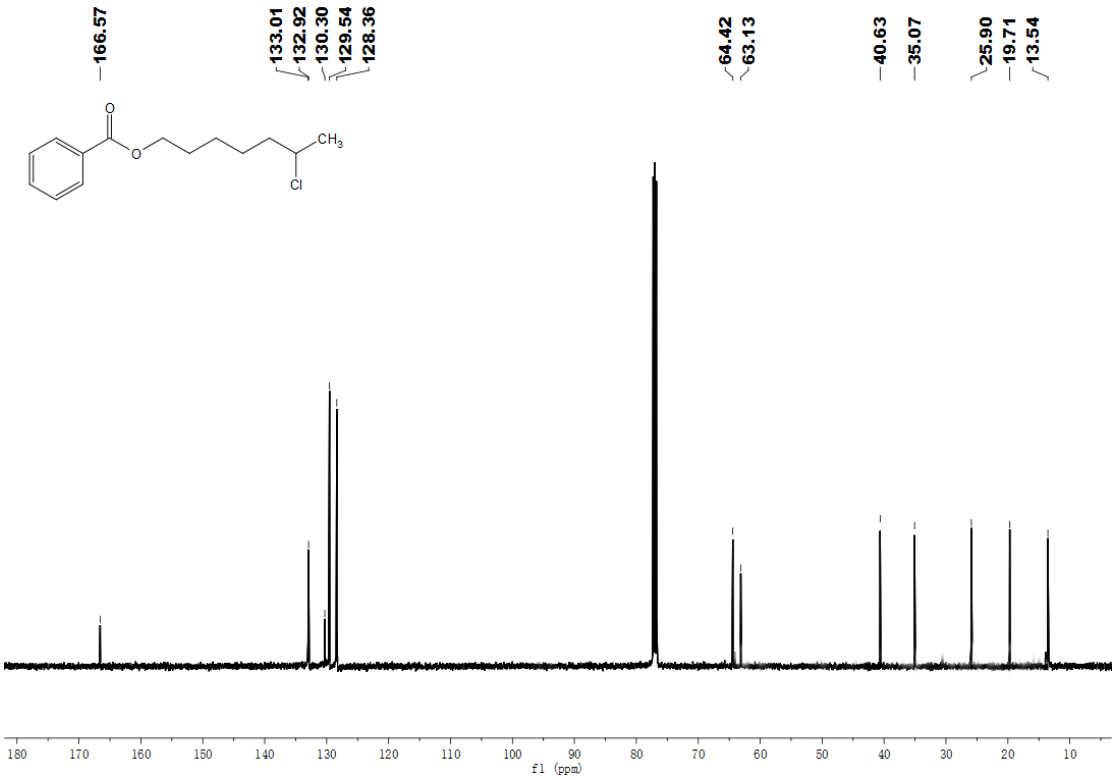
^{1}H NMR of compound **3b** (500 MHz, $CDCl_3$)



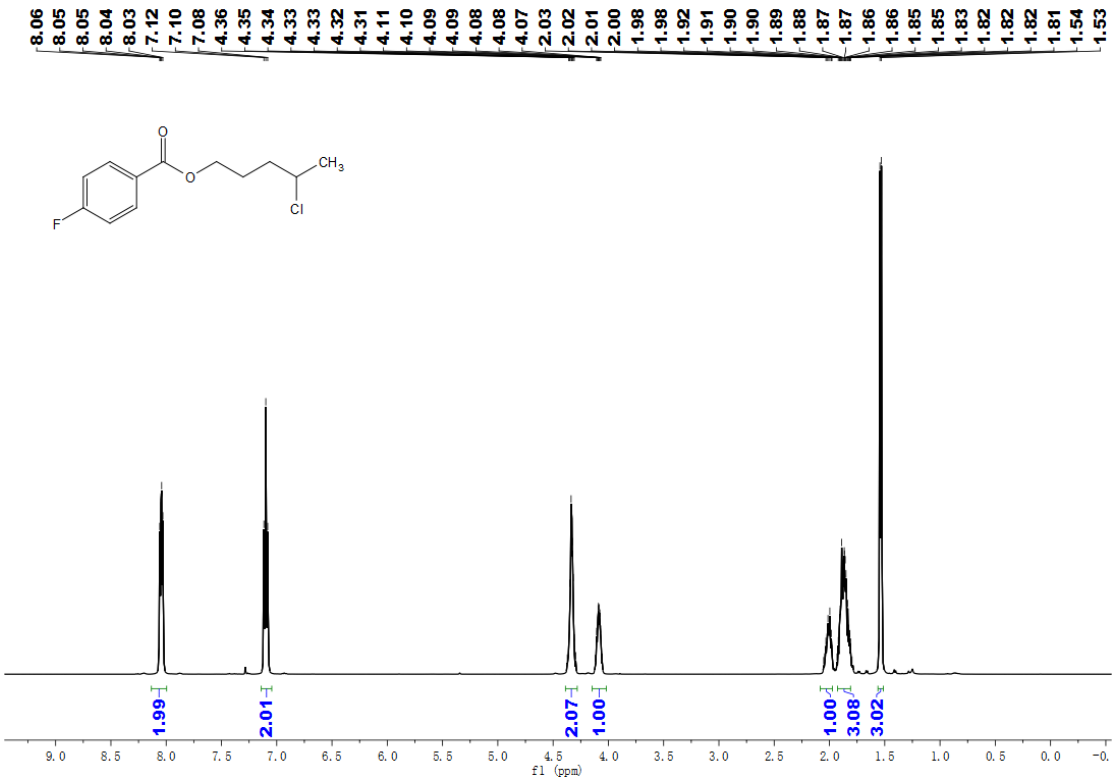
^{13}C NMR of compound **3b** (126 MHz, $CDCl_3$)



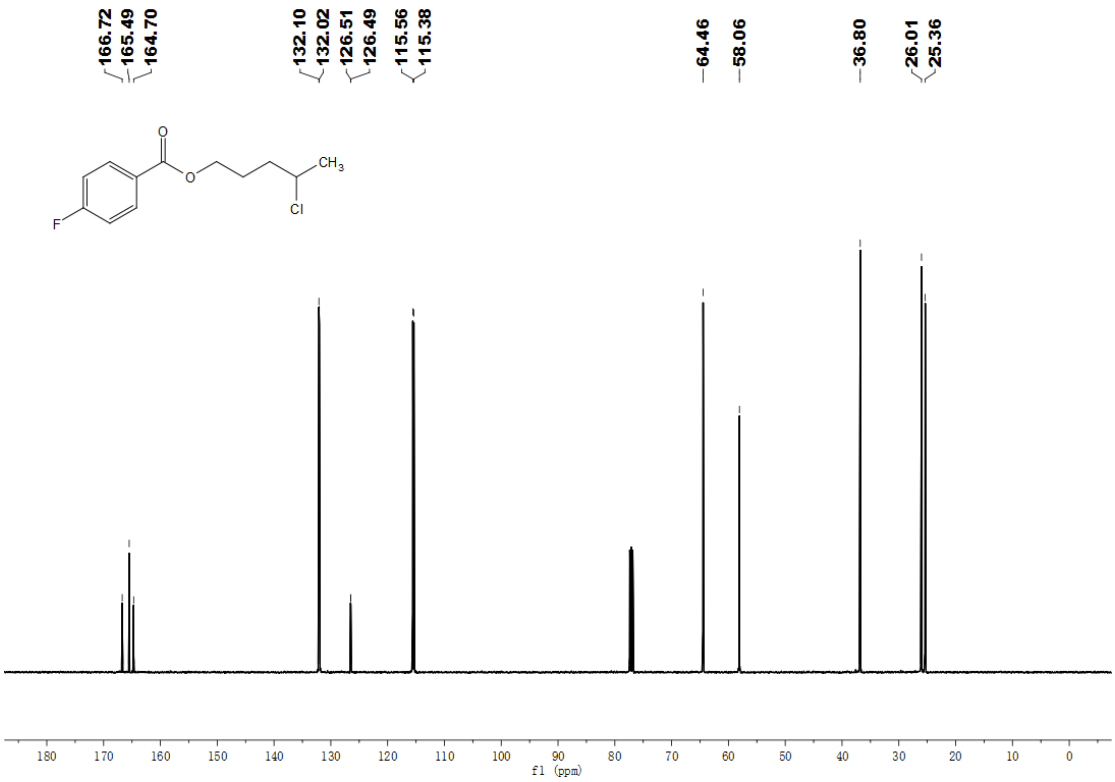
^{1}H NMR of compound **4b** (500 MHz, $CDCl_3$)



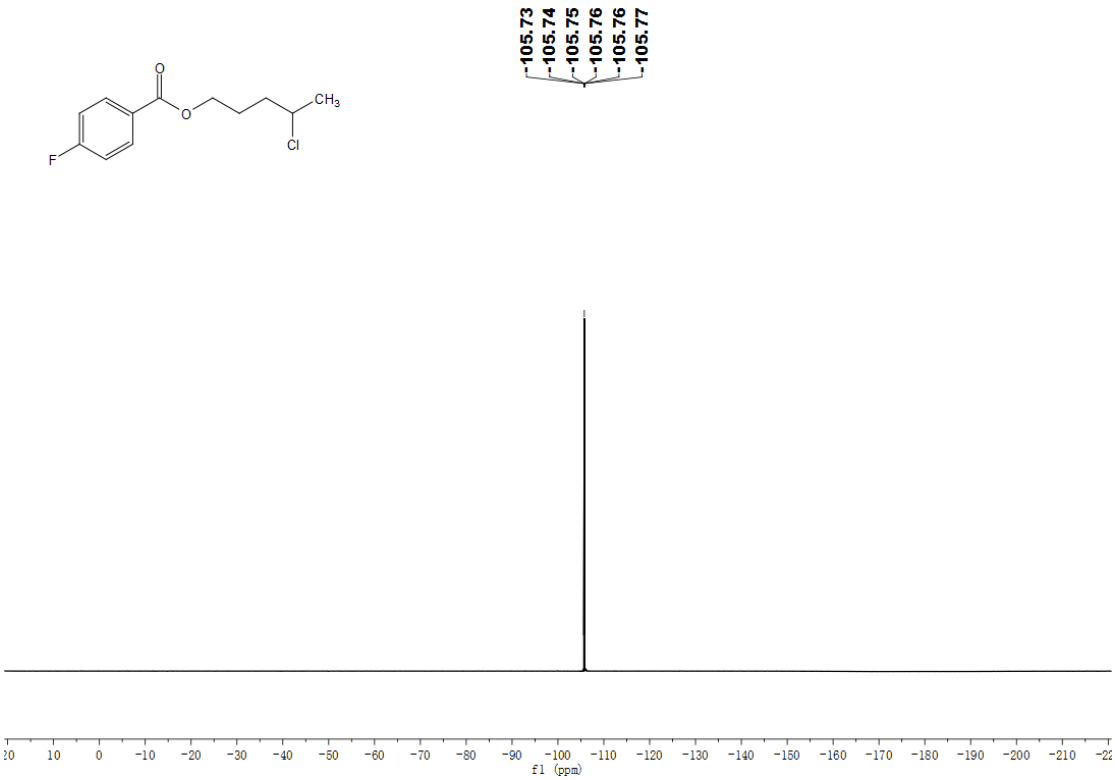
^{13}C NMR of compound **4b** (126 MHz, $CDCl_3$)



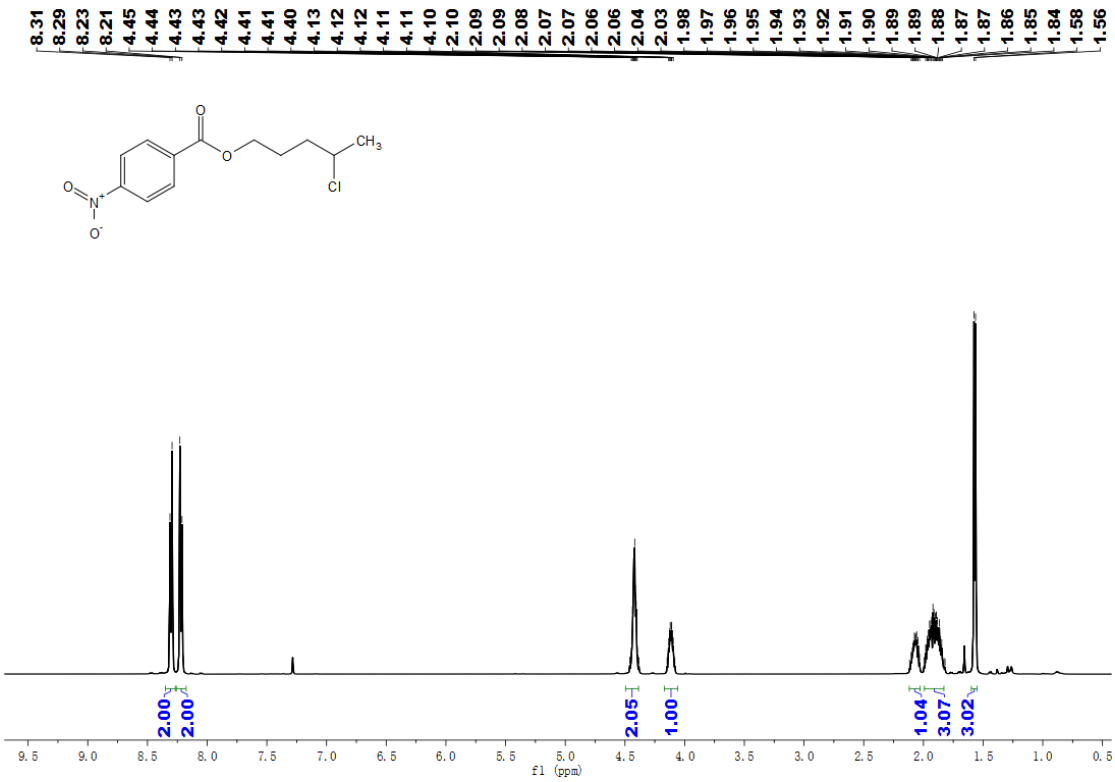
^{1}H NMR of compound **5b** (500 MHz, $CDCl_3$)



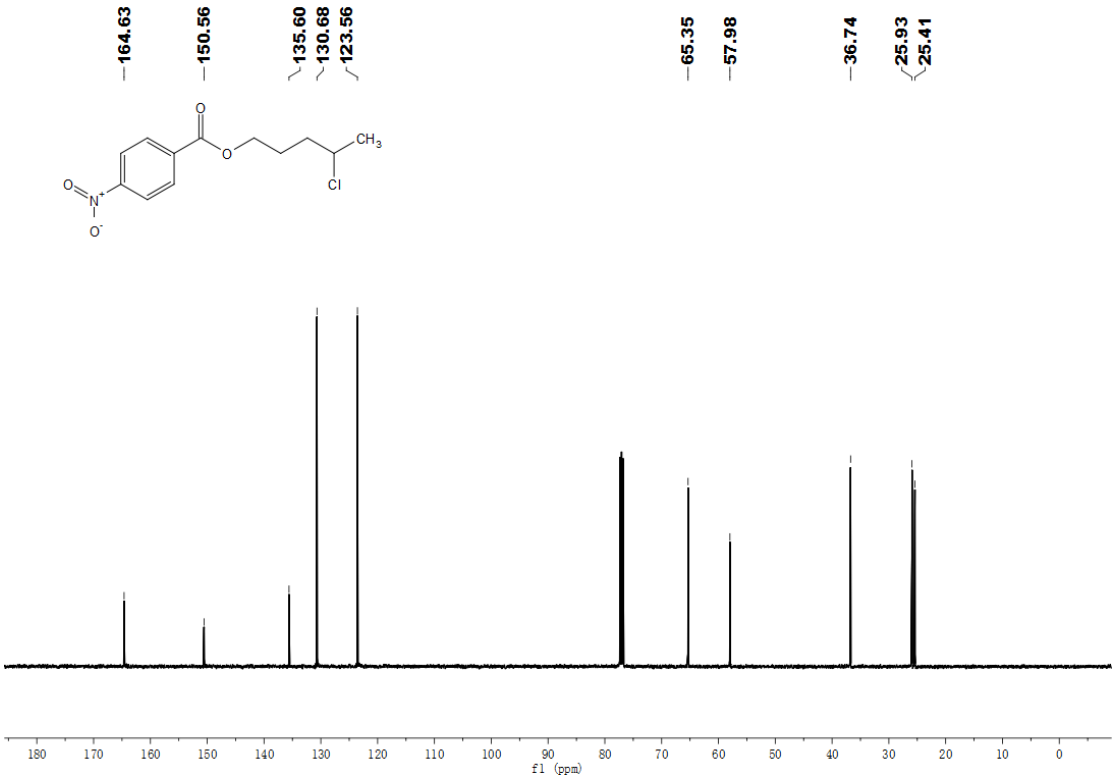
^{13}C NMR of compound **5b** (126 MHz, $CDCl_3$)



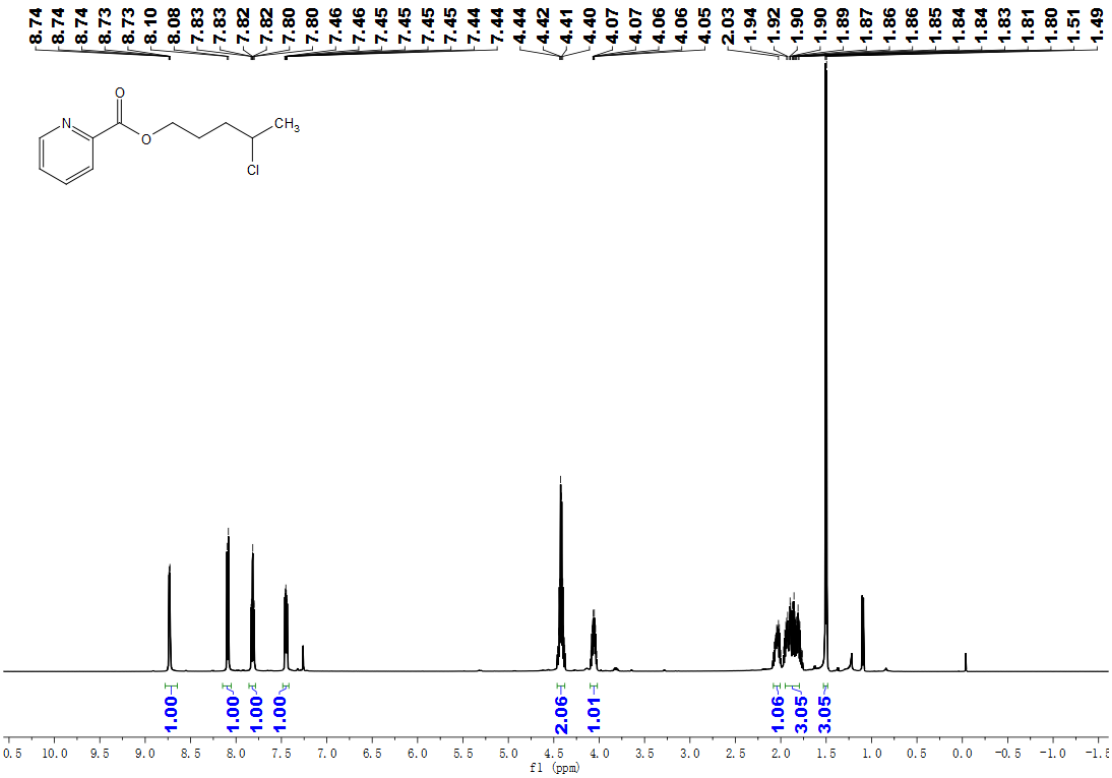
^{19}F NMR of compound **5b** (471 MHz, $CDCl_3$)



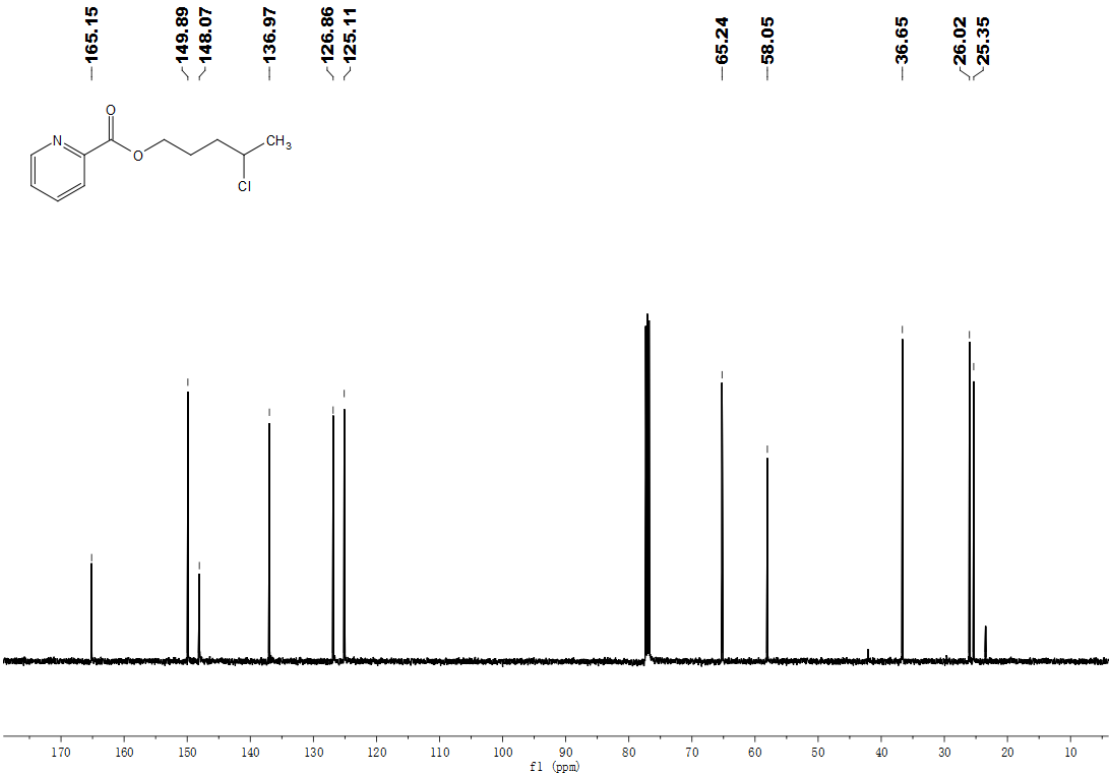
^{1}H NMR of compound **6b** (500 MHz, $CDCl_3$)



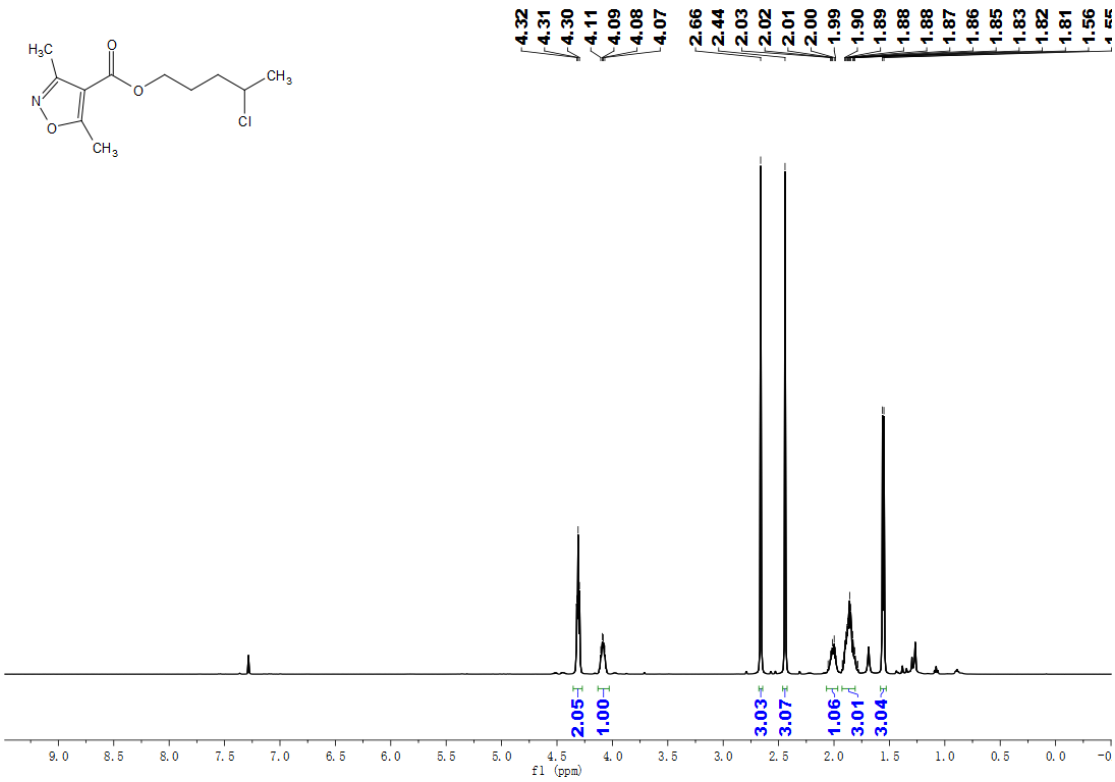
^{13}C NMR of compound **6b** (126 MHz, $CDCl_3$)



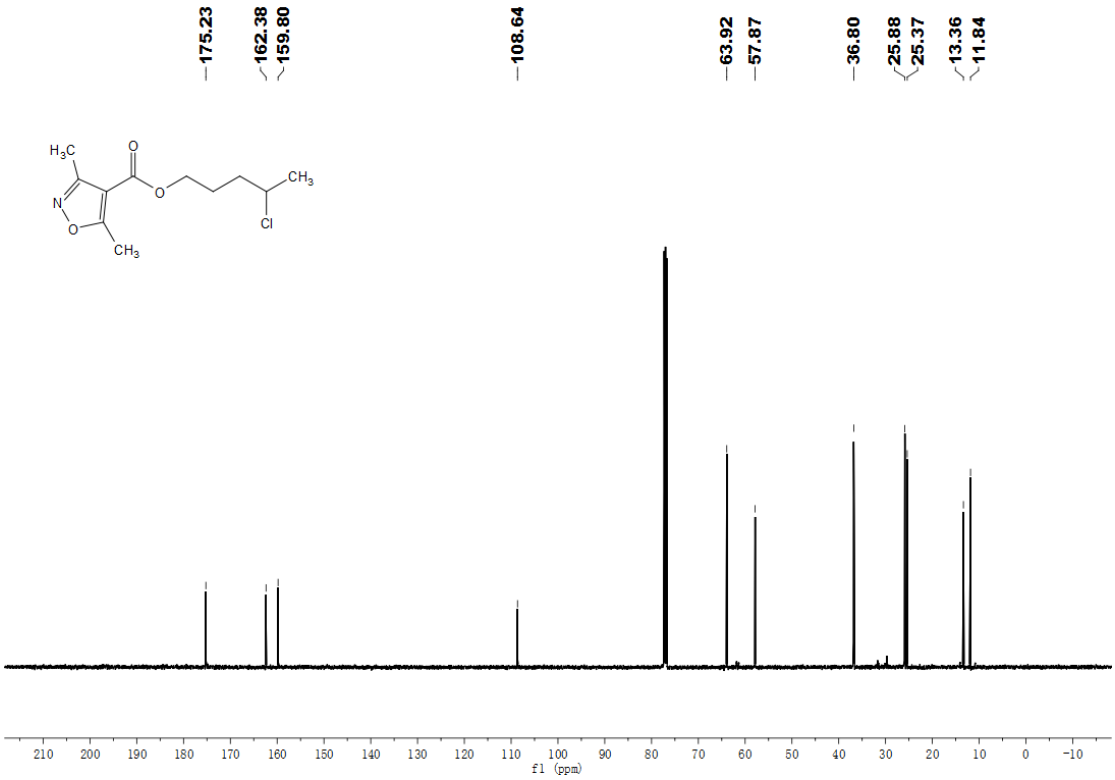
^{1}H NMR of compound **7b** (500 MHz, $CDCl_3$)



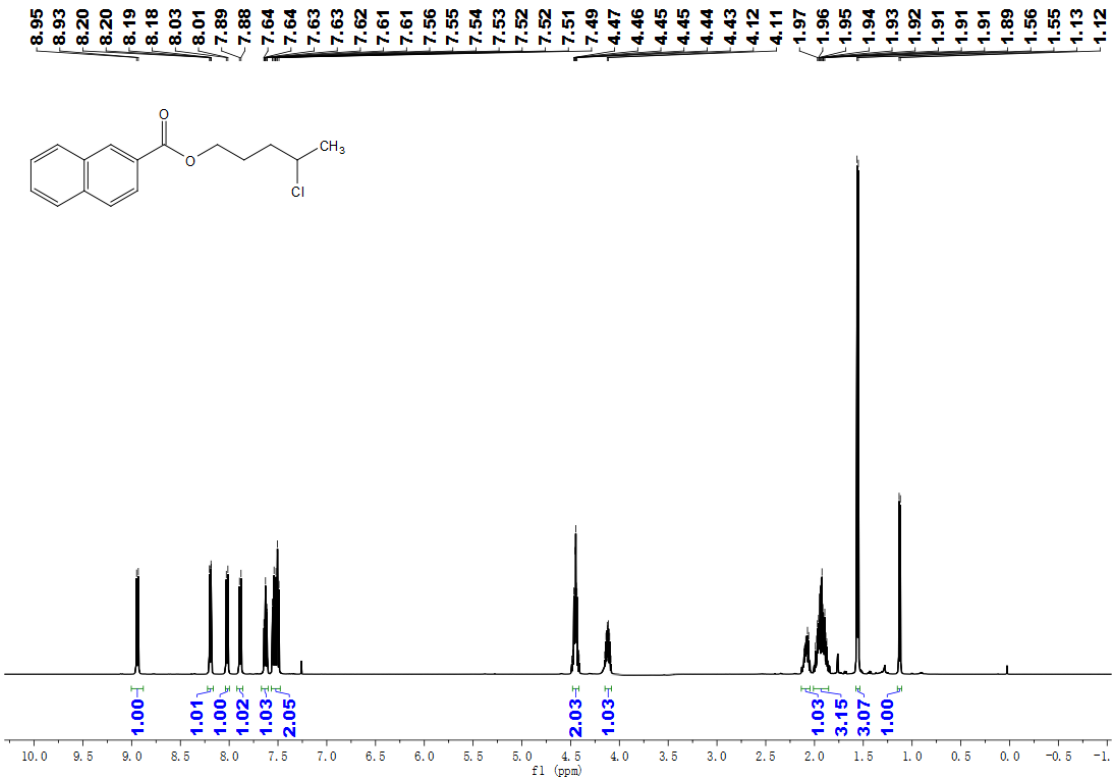
^{13}C NMR of compound **7b** (126 MHz, $CDCl_3$)



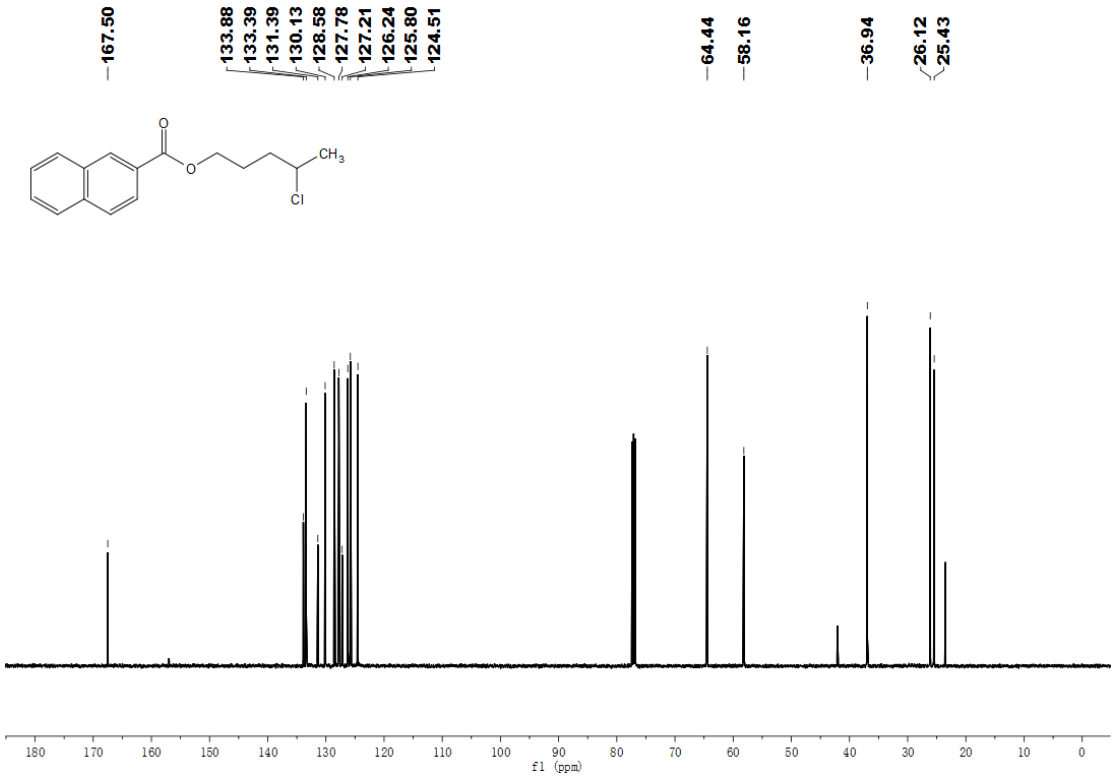
^{1}H NMR of compound **8b** (500 MHz, $CDCl_3$)



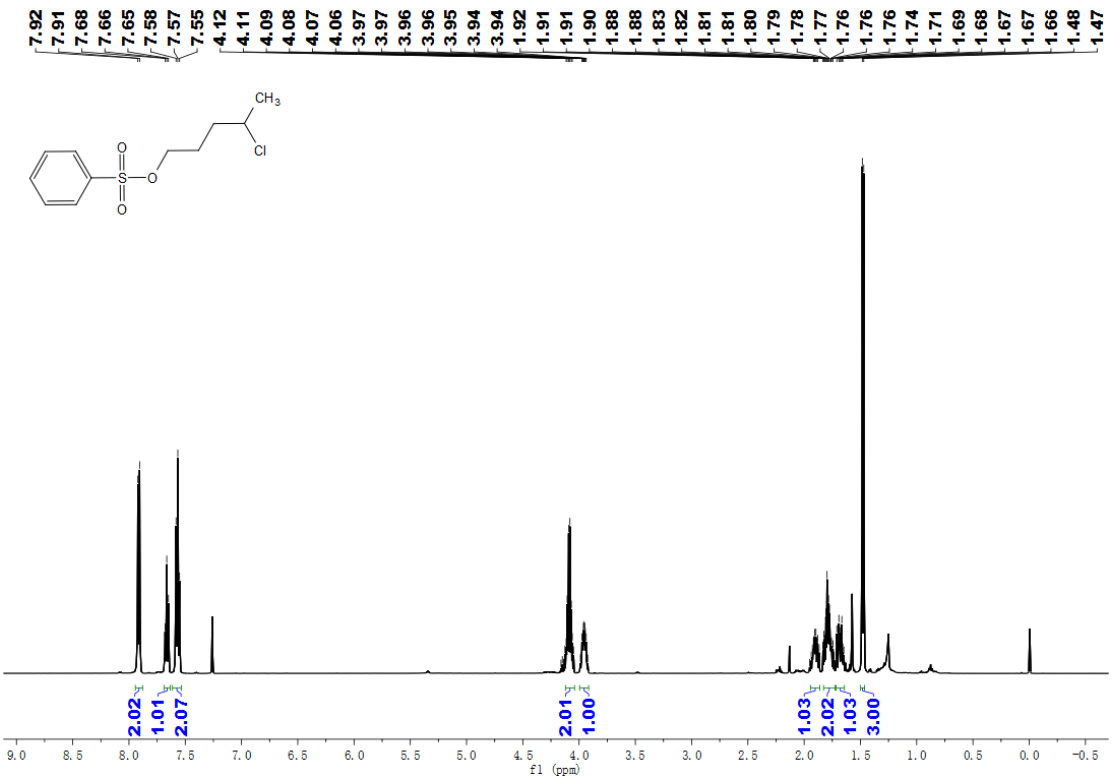
^{13}C NMR of compound **8b** (126 MHz, $CDCl_3$)



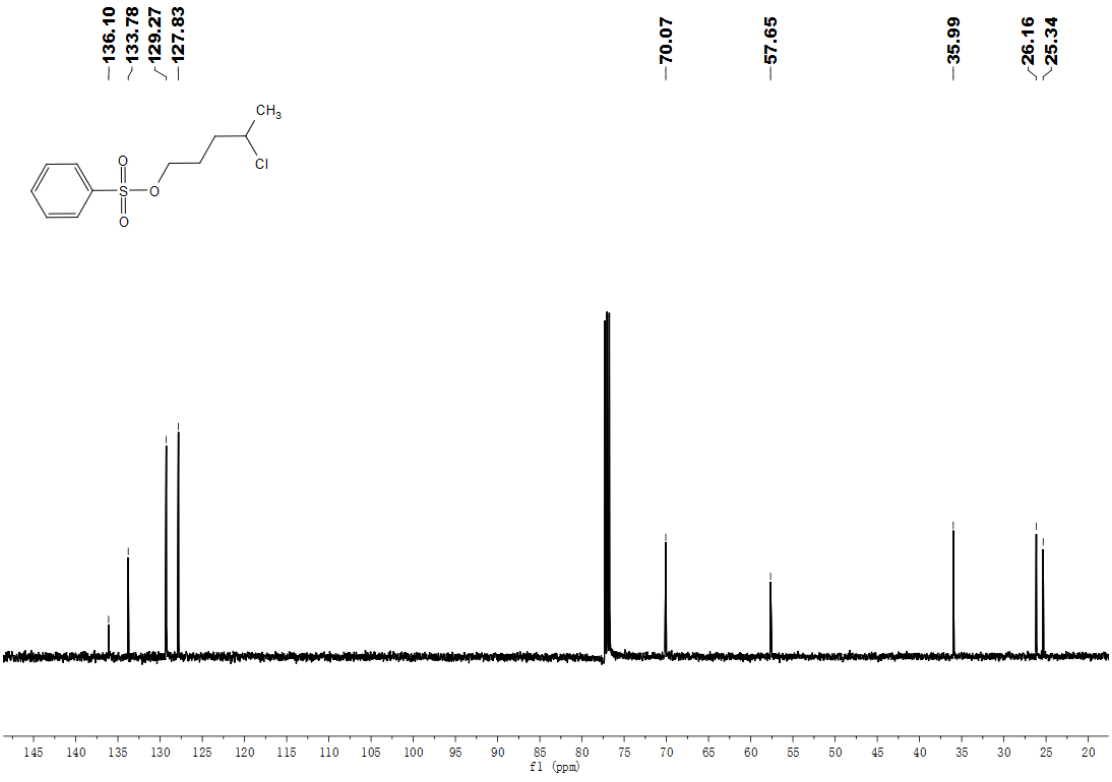
^{1}H NMR of compound **9b** (500 MHz, $CDCl_3$)



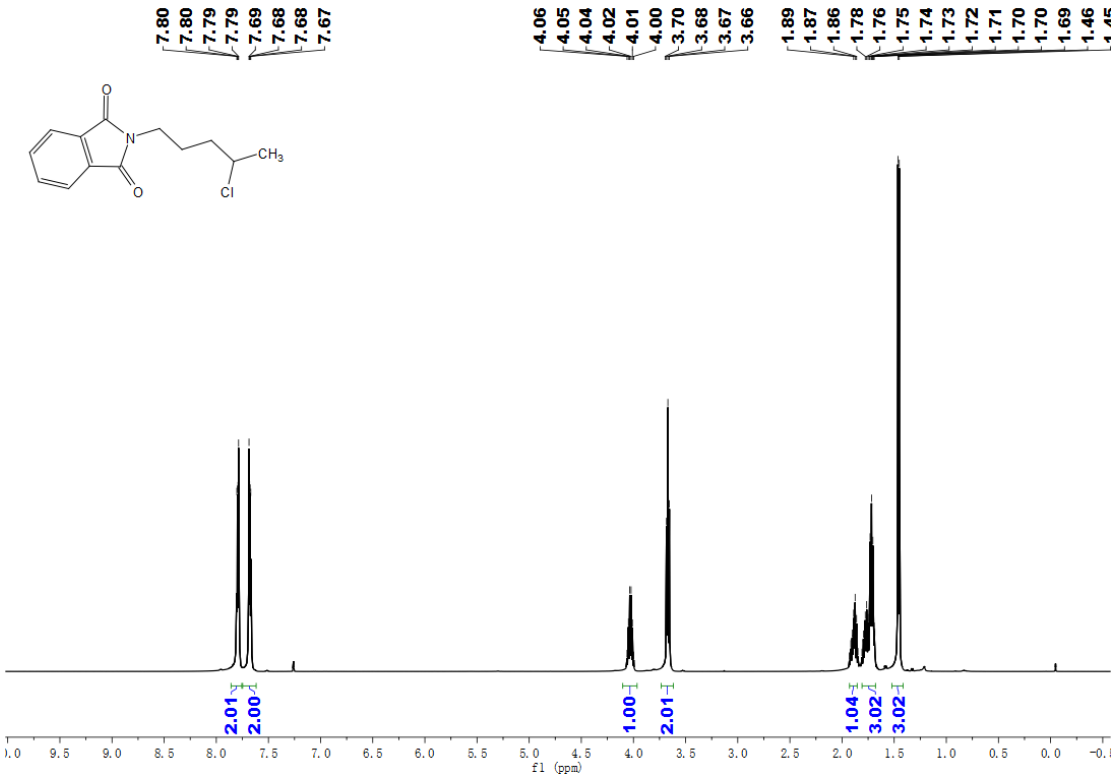
^{13}C NMR of compound **9b** (126 MHz, $CDCl_3$)



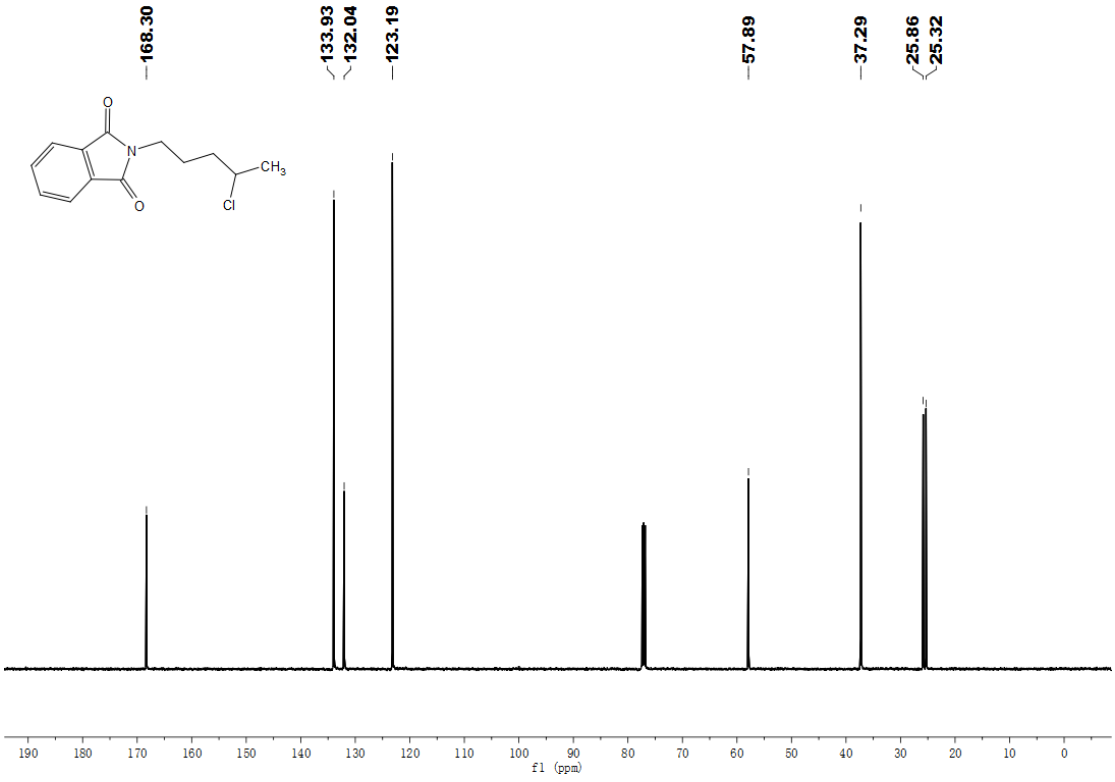
^{1}H NMR of compound **10b** (500 MHz, $CDCl_3$)



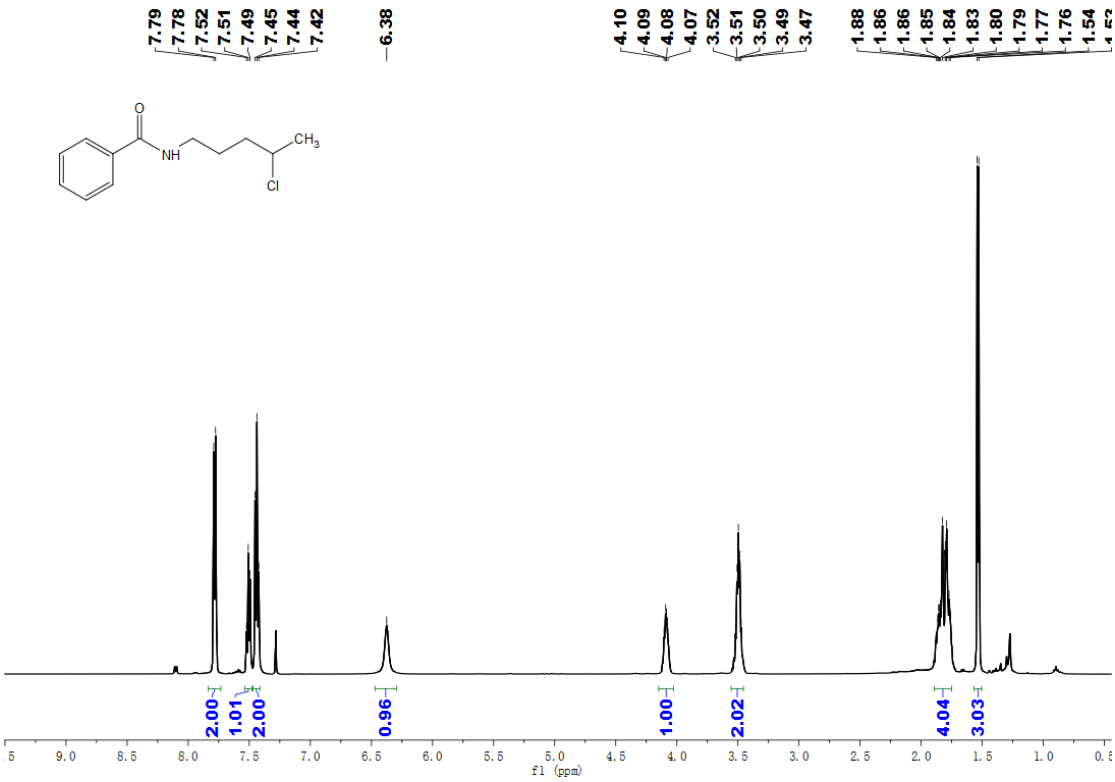
^{13}C NMR of compound **10b** (126 MHz, $CDCl_3$)



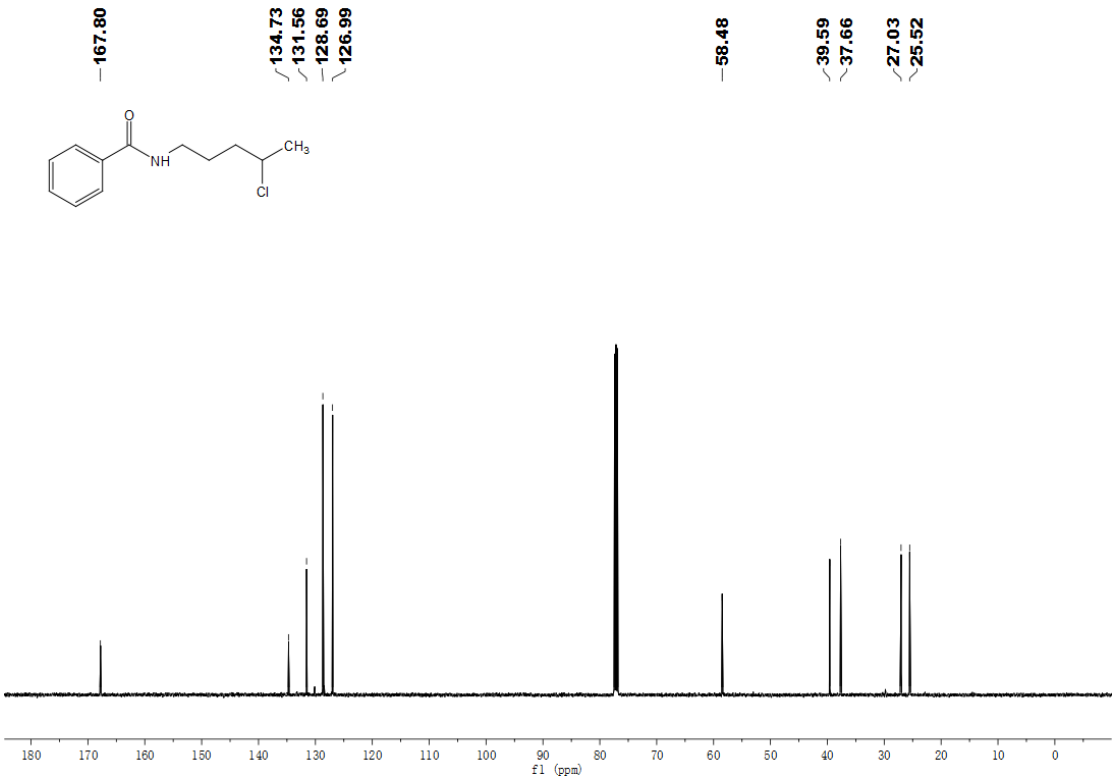
^{1}H NMR of compound **11b** (500 MHz, $CDCl_3$)



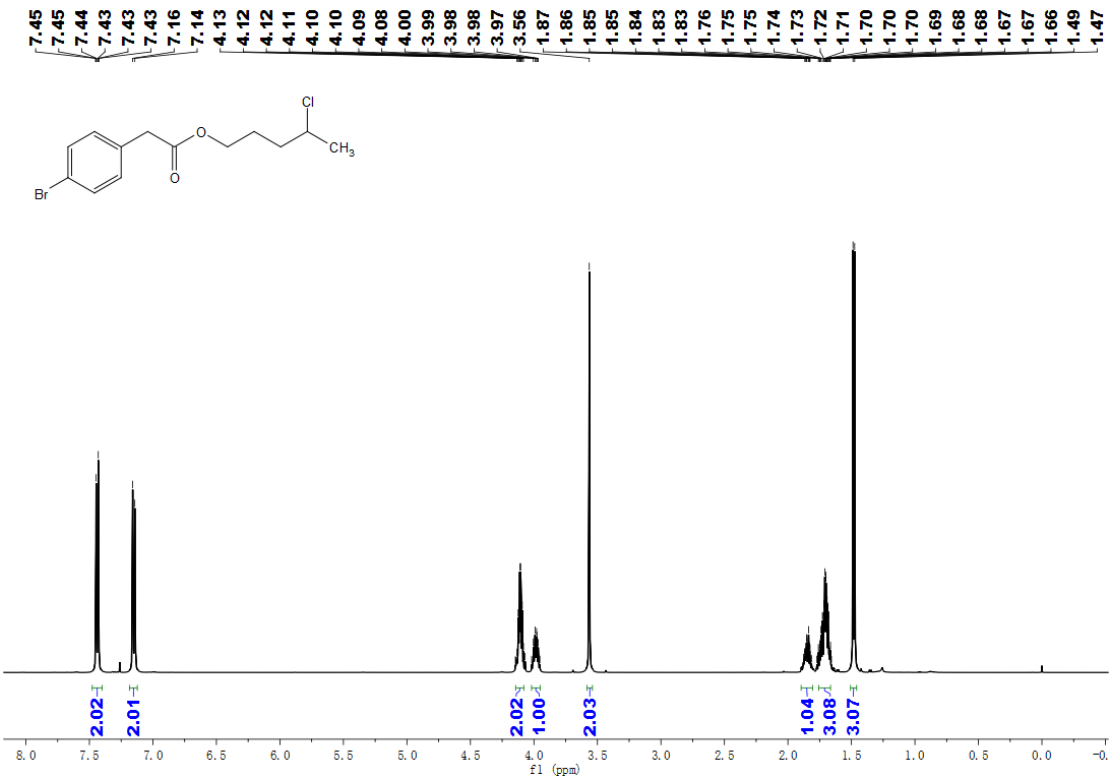
^{13}C NMR of compound **11b** (126 MHz, $CDCl_3$)



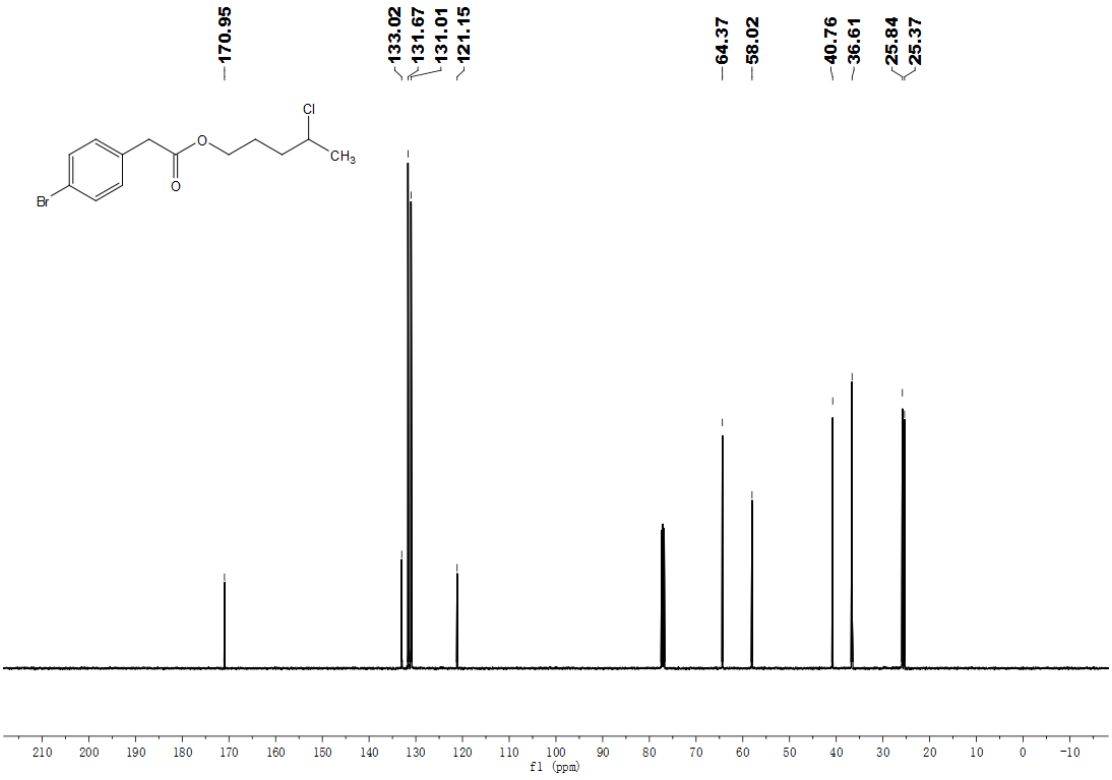
^{1}H NMR of compound **12b** (500 MHz, $CDCl_3$)



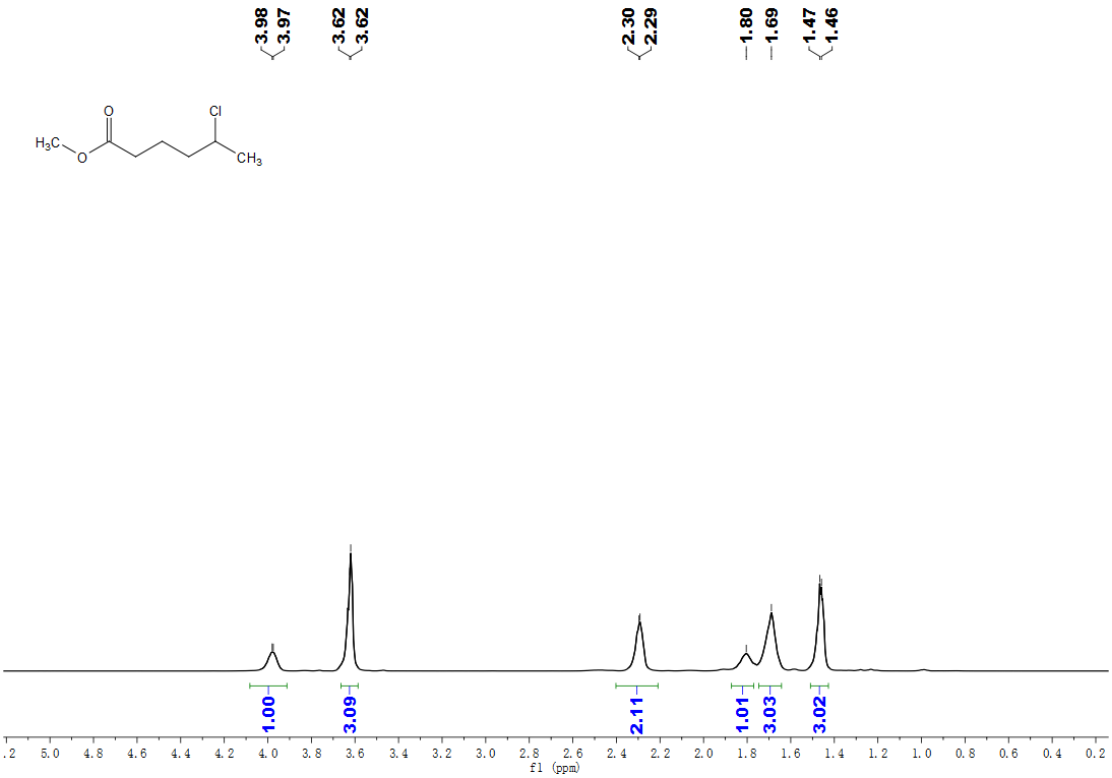
^{13}C NMR of compound **12b** (126 MHz, $CDCl_3$)



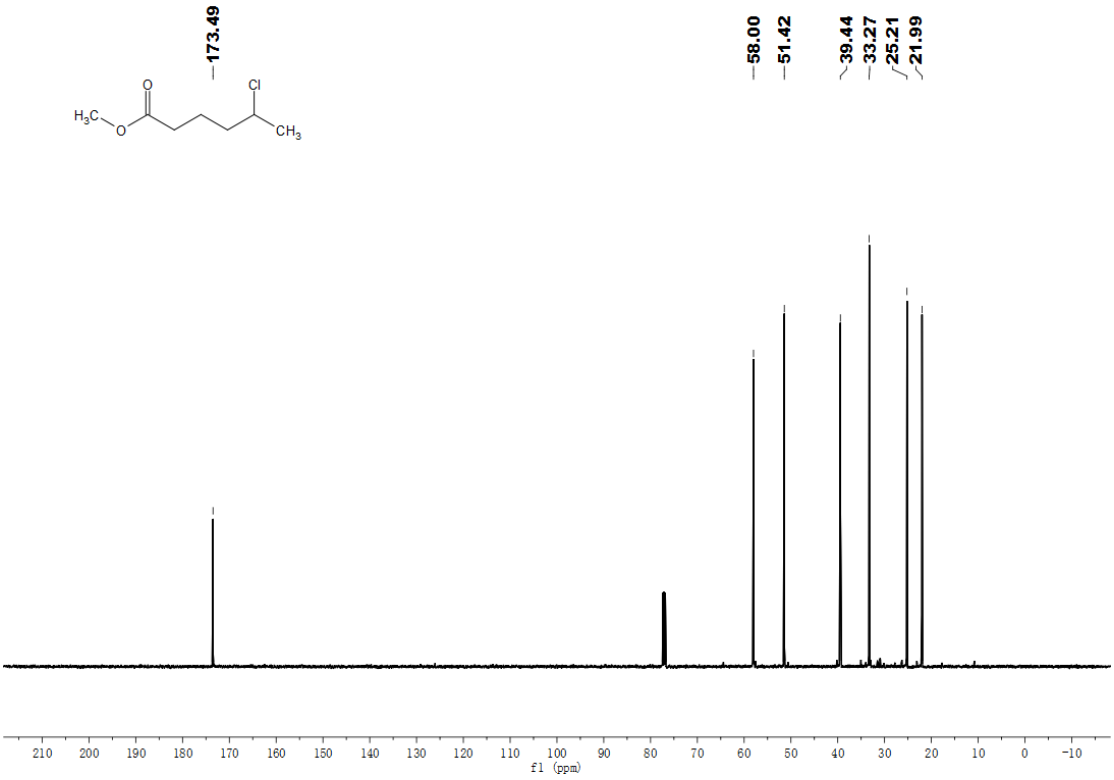
^{1}H NMR of compound **13b** (500 MHz, $CDCl_3$)



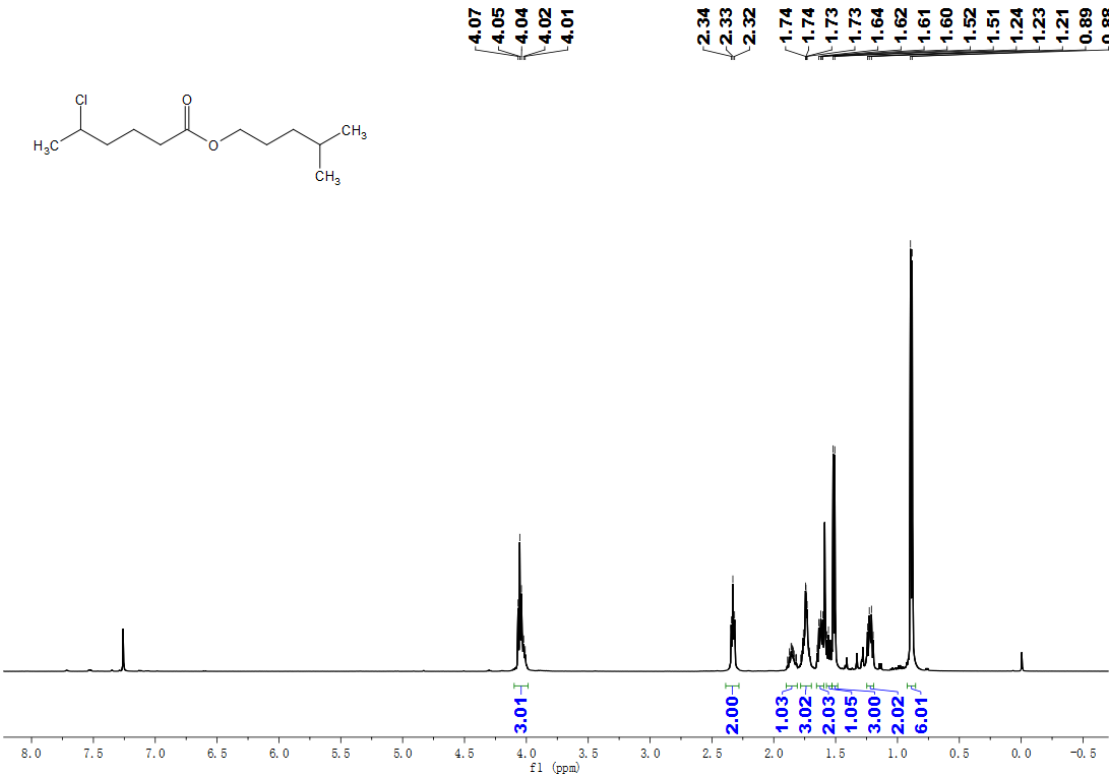
^{13}C NMR of compound **13b** (126 MHz, $CDCl_3$)



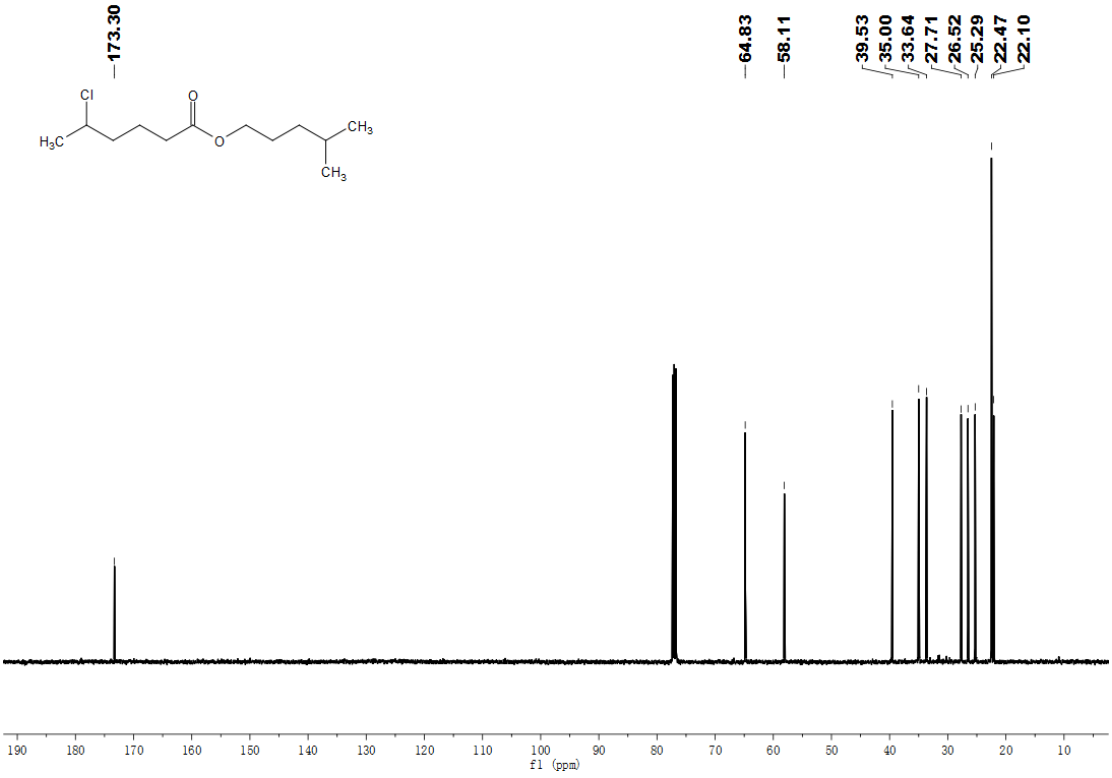
^{1}H NMR of compound **14b** (500 MHz, $CDCl_3$)



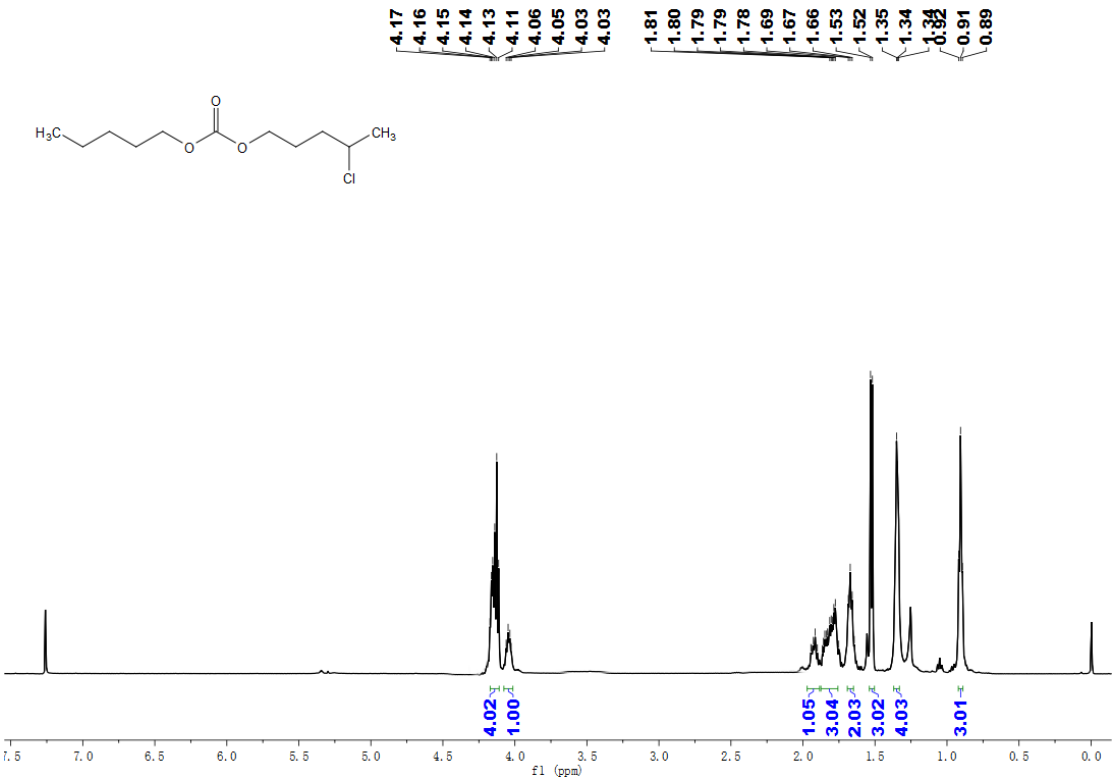
^{13}C NMR of compound **14b** (126 MHz, $CDCl_3$)



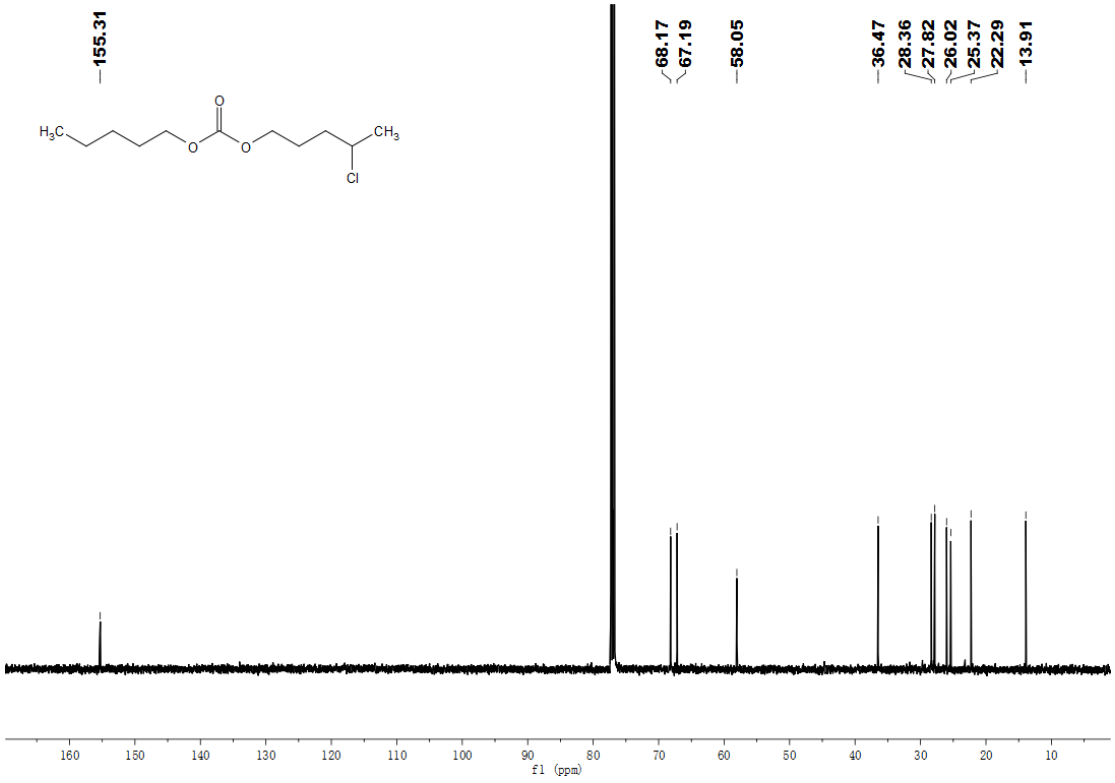
^{1}H NMR of compound **15b** (500 MHz, $CDCl_3$)



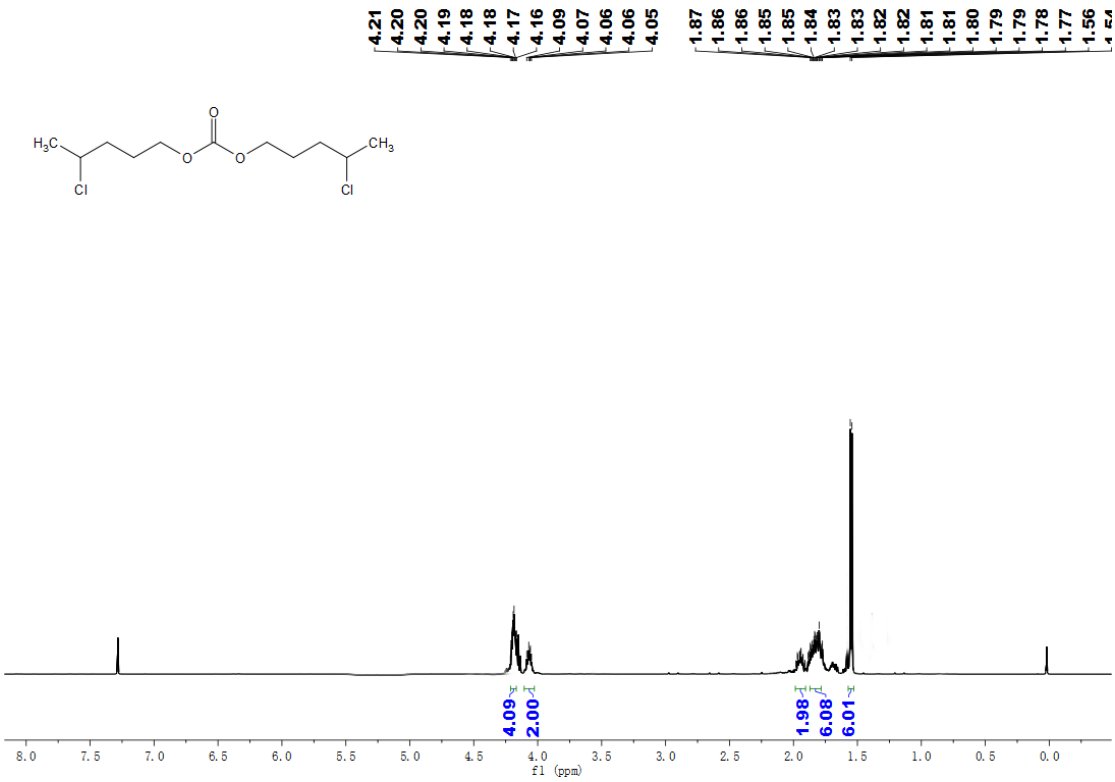
^{13}C NMR of compound **15b** (126 MHz, $CDCl_3$)



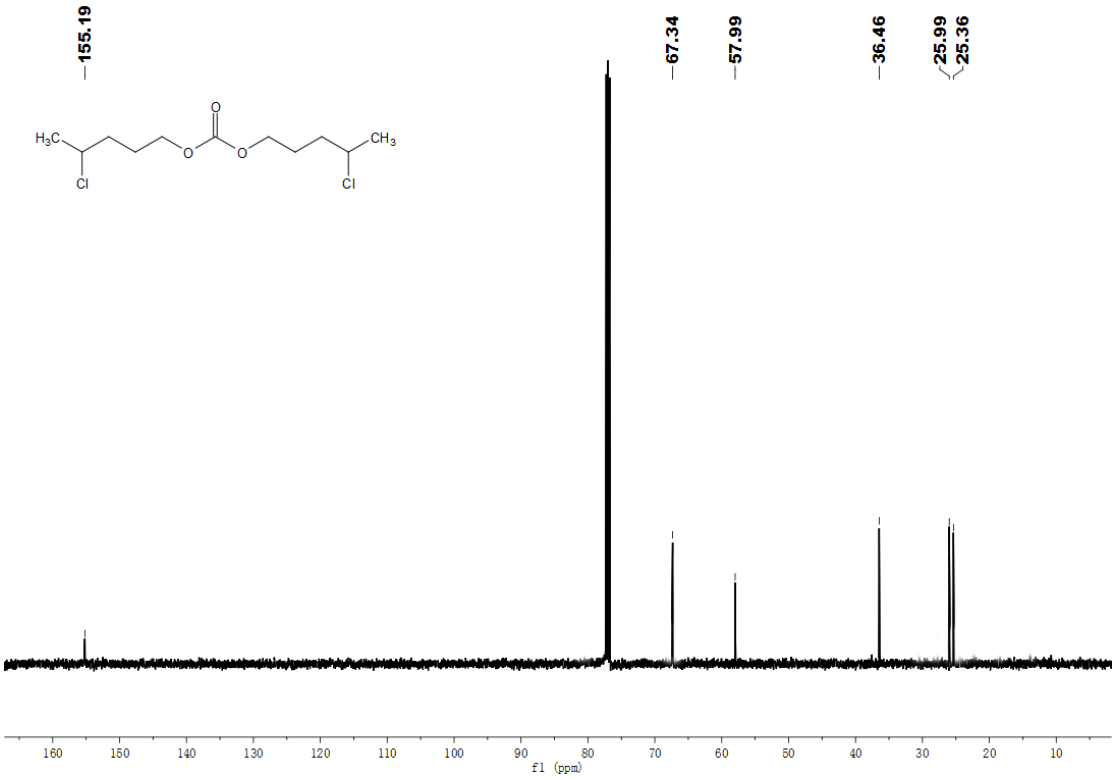
^{1}H NMR of compound **16b** (500 MHz, $CDCl_3$)



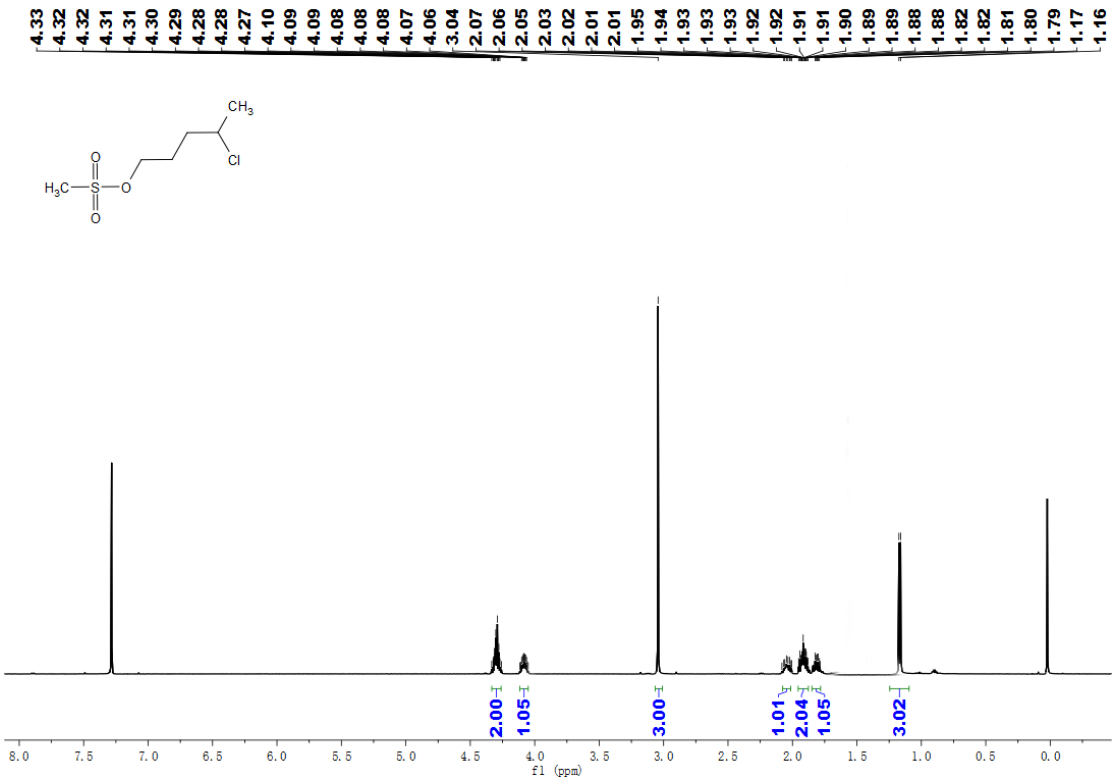
^{13}C NMR of compound **16b** (126 MHz, $CDCl_3$)



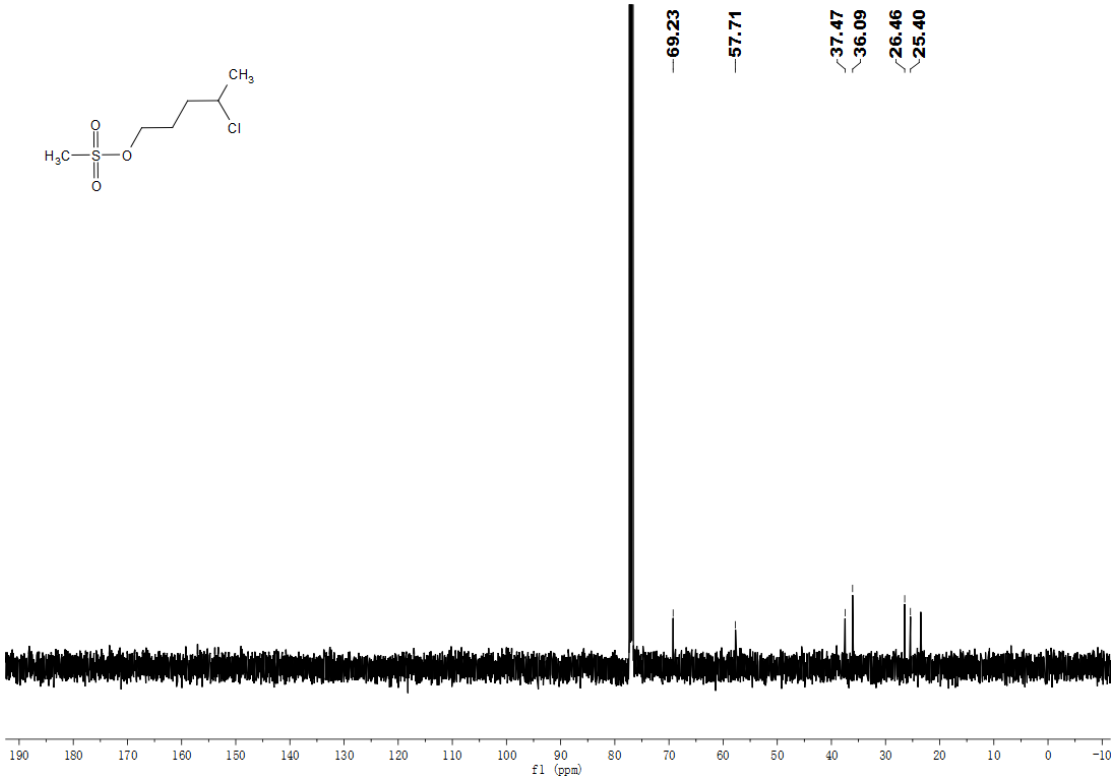
^{1}H NMR of compound **17b** (500 MHz, $CDCl_3$)



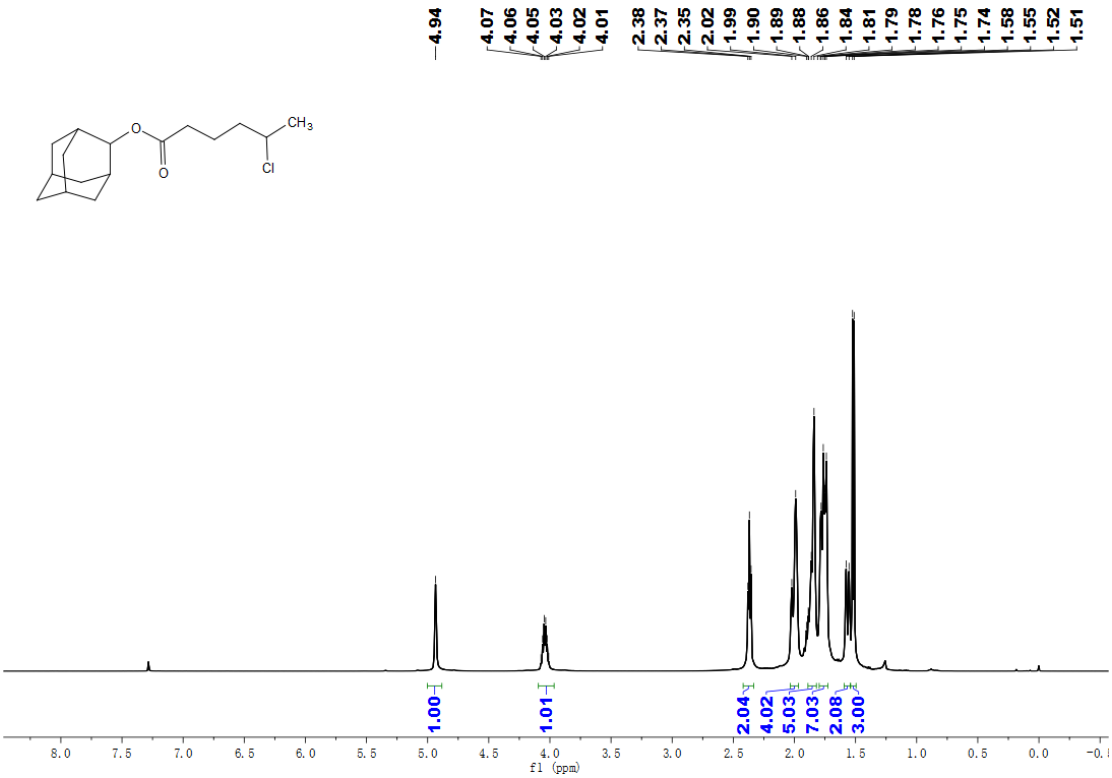
^{13}C NMR of compound **17b** (126 MHz, $CDCl_3$)



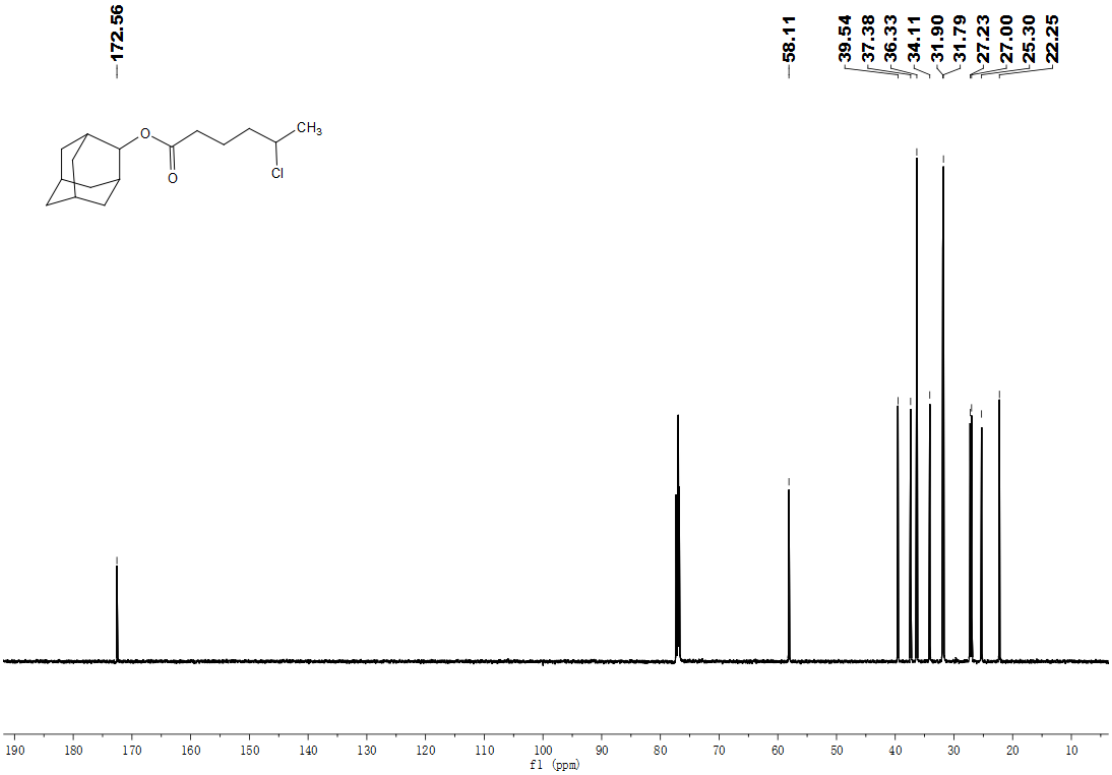
^{1}H NMR of compound **18b** (500 MHz, $CDCl_3$)



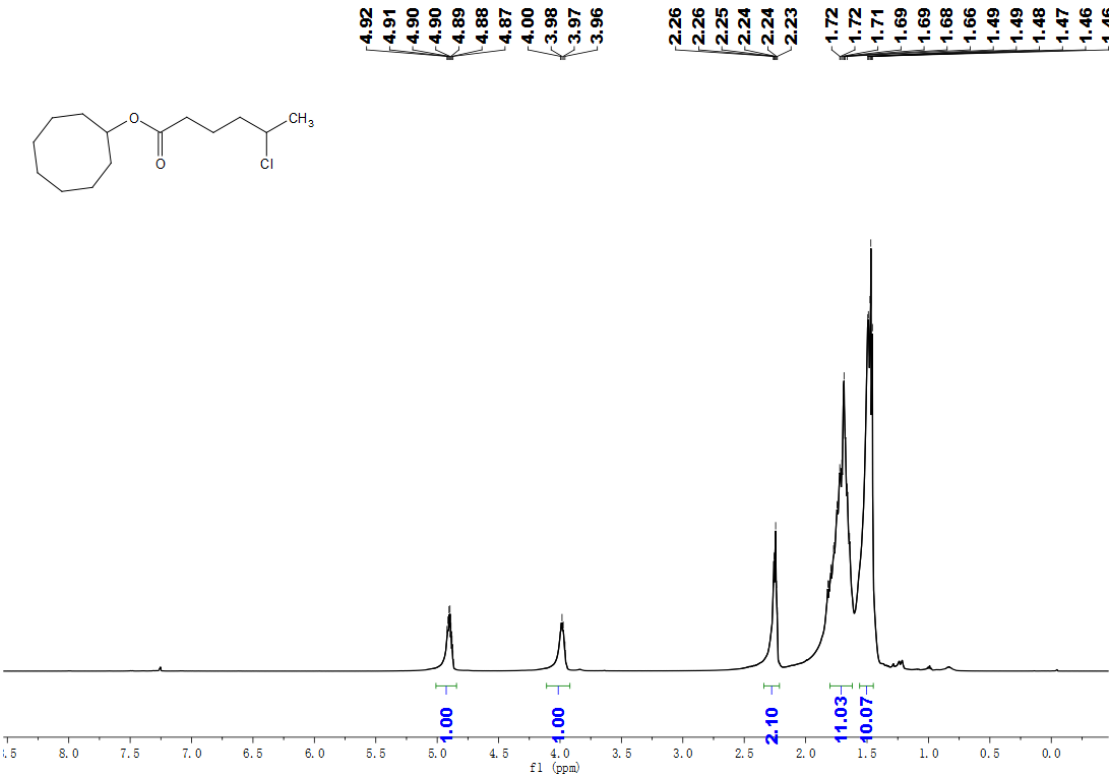
^{13}C NMR of compound **18b** (126 MHz, $CDCl_3$)



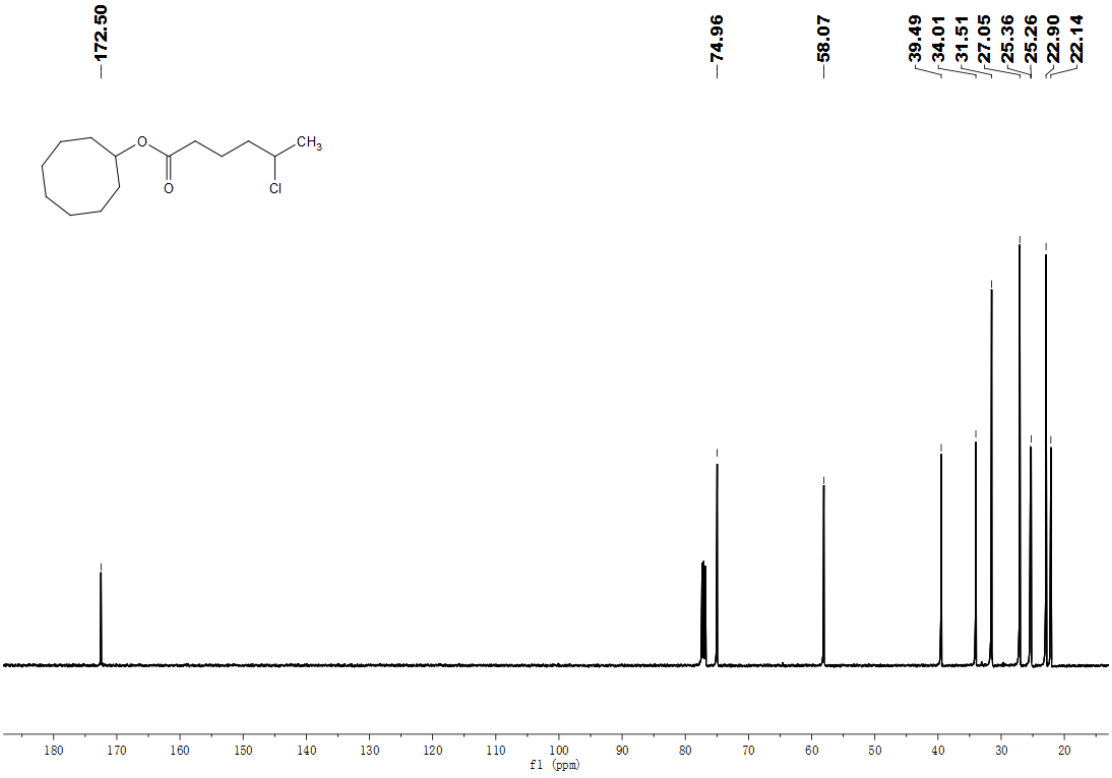
^{1}H NMR of compound **19b** (500 MHz, $CDCl_3$)



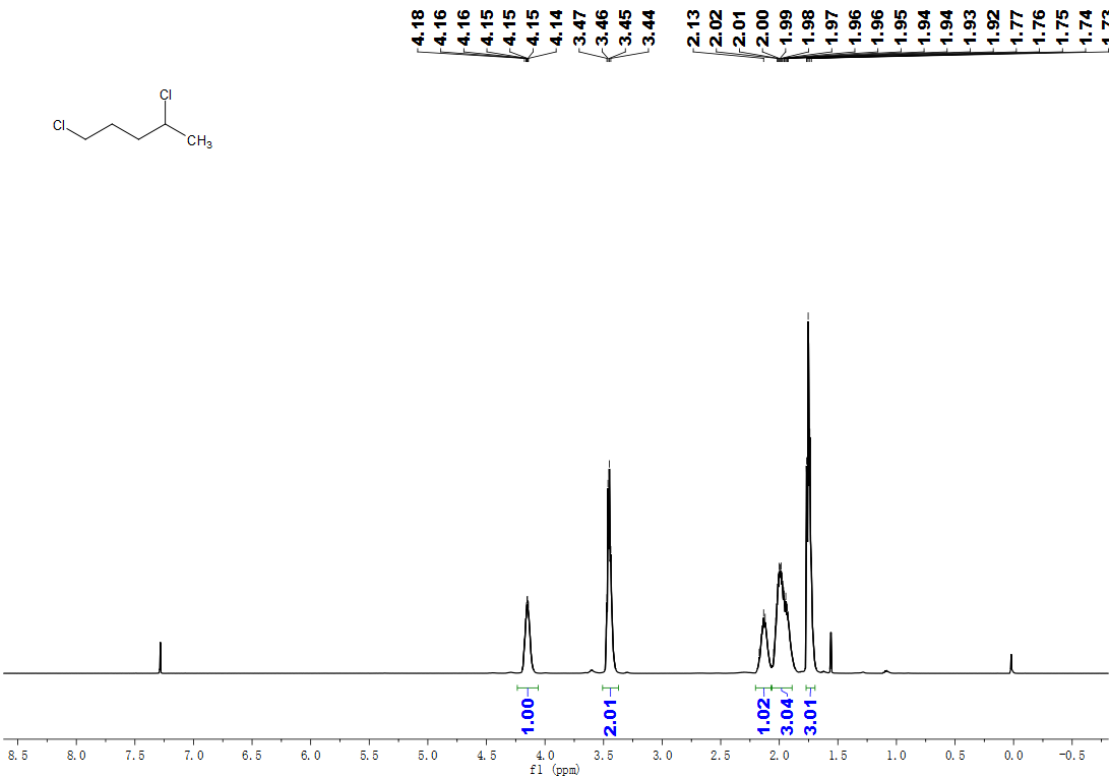
^{13}C NMR of compound **19b** (126 MHz, $CDCl_3$)



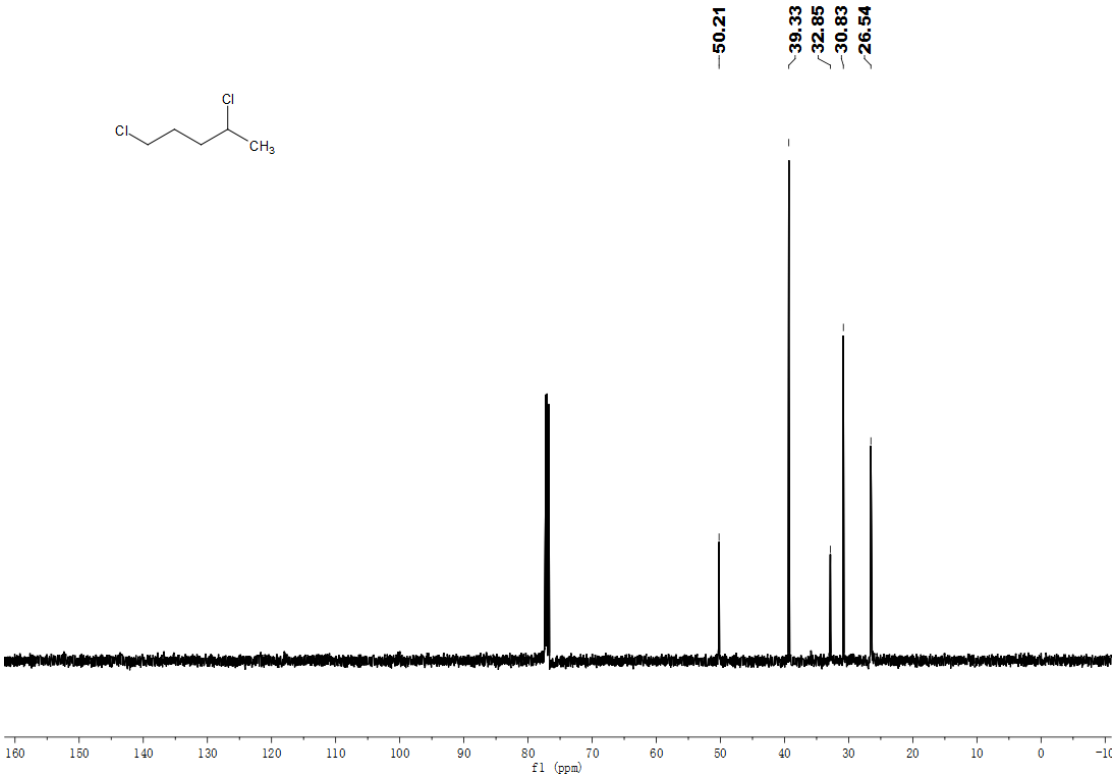
^{1}H NMR of compound **20b** (500 MHz, $CDCl_3$)



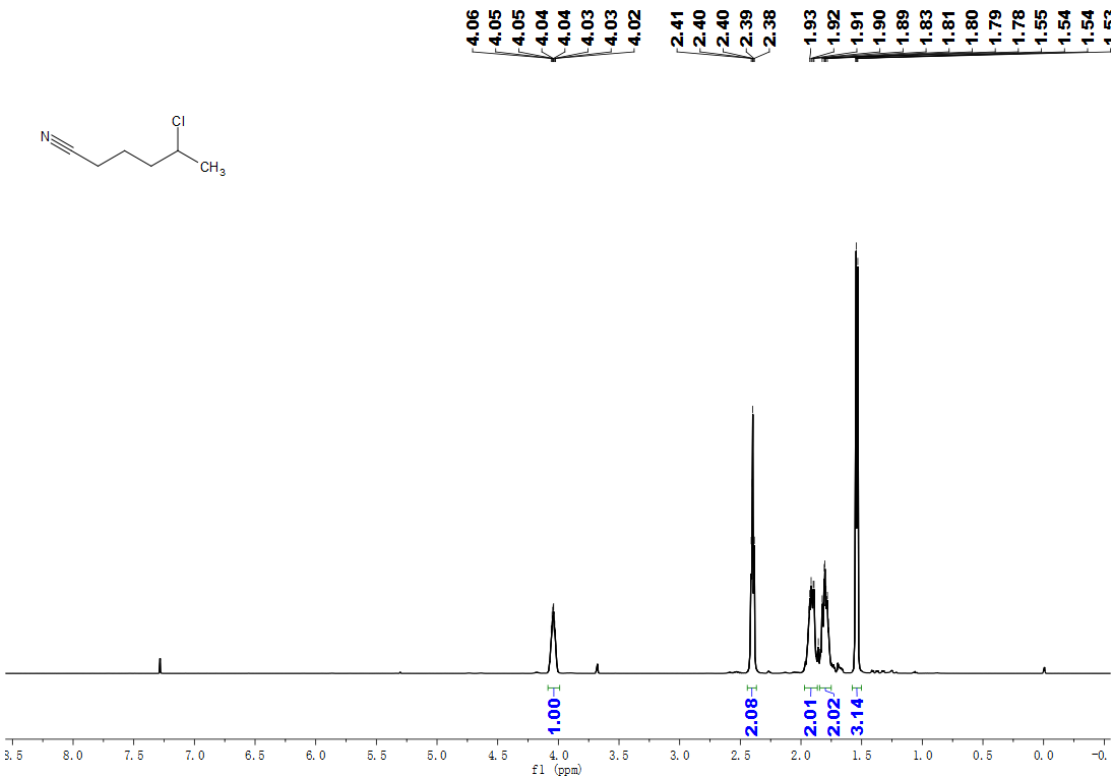
^{13}C NMR of compound **20b** (126 MHz, $CDCl_3$)



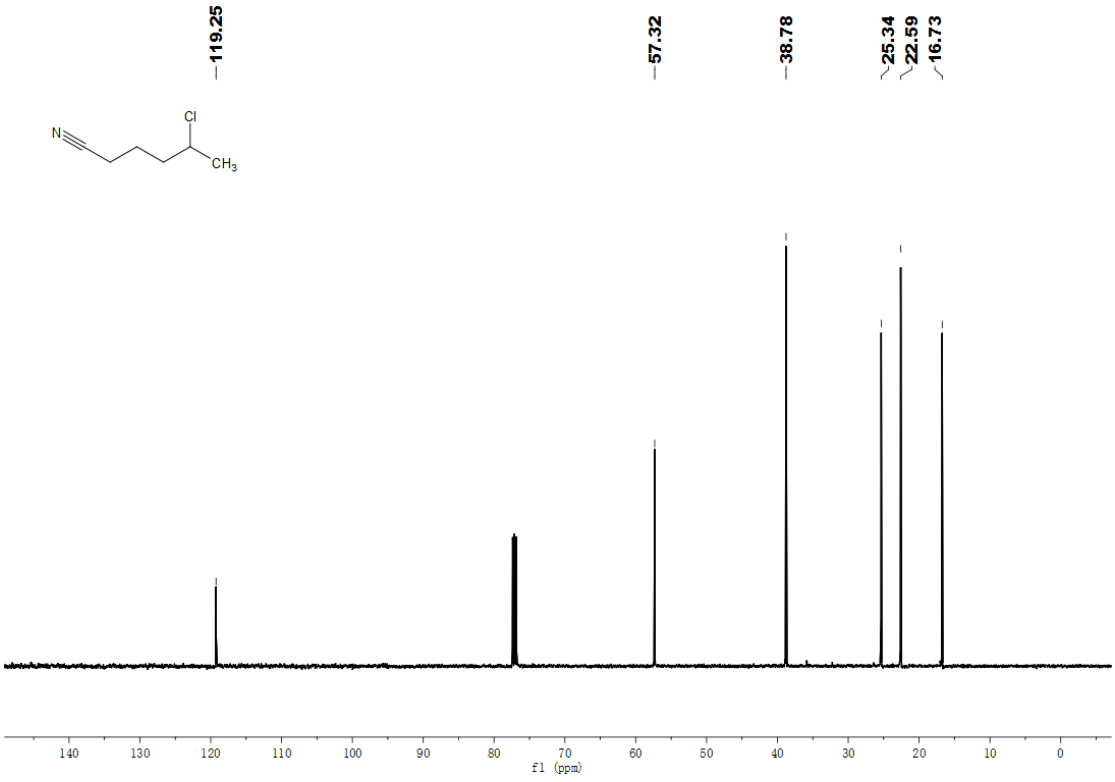
^{1}H NMR of compound **21b** (500 MHz, $CDCl_3$)



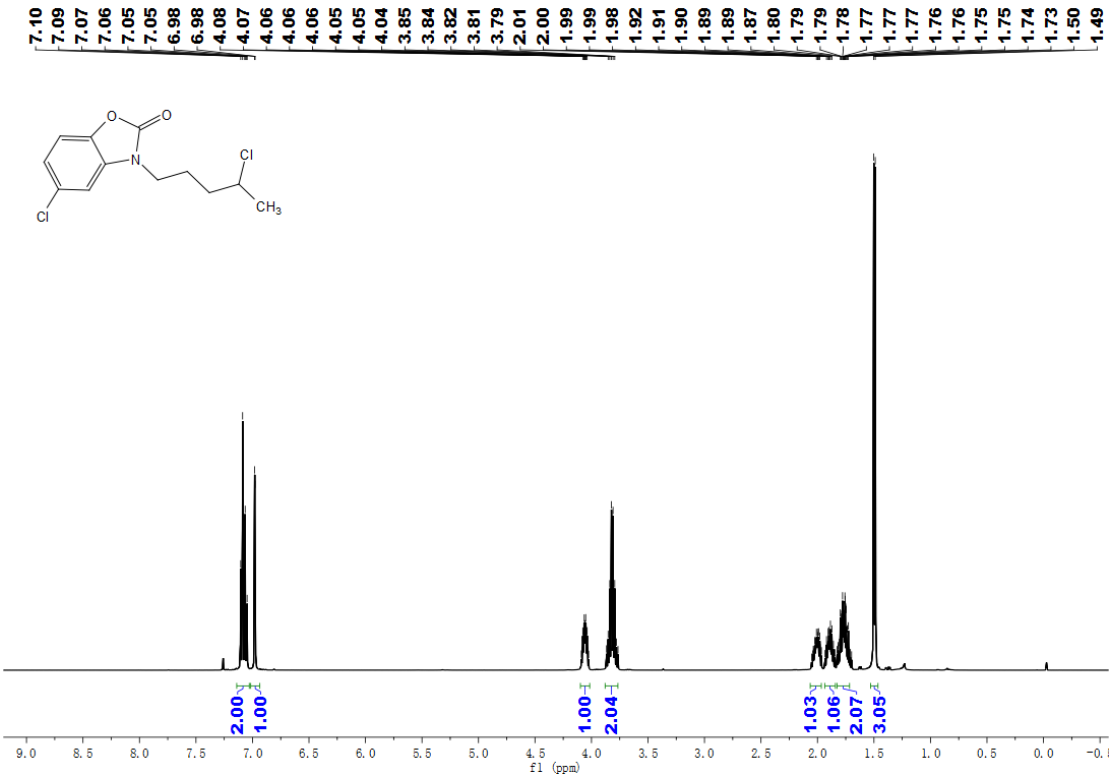
^{13}C NMR of compound **21b** (126 MHz, $CDCl_3$)



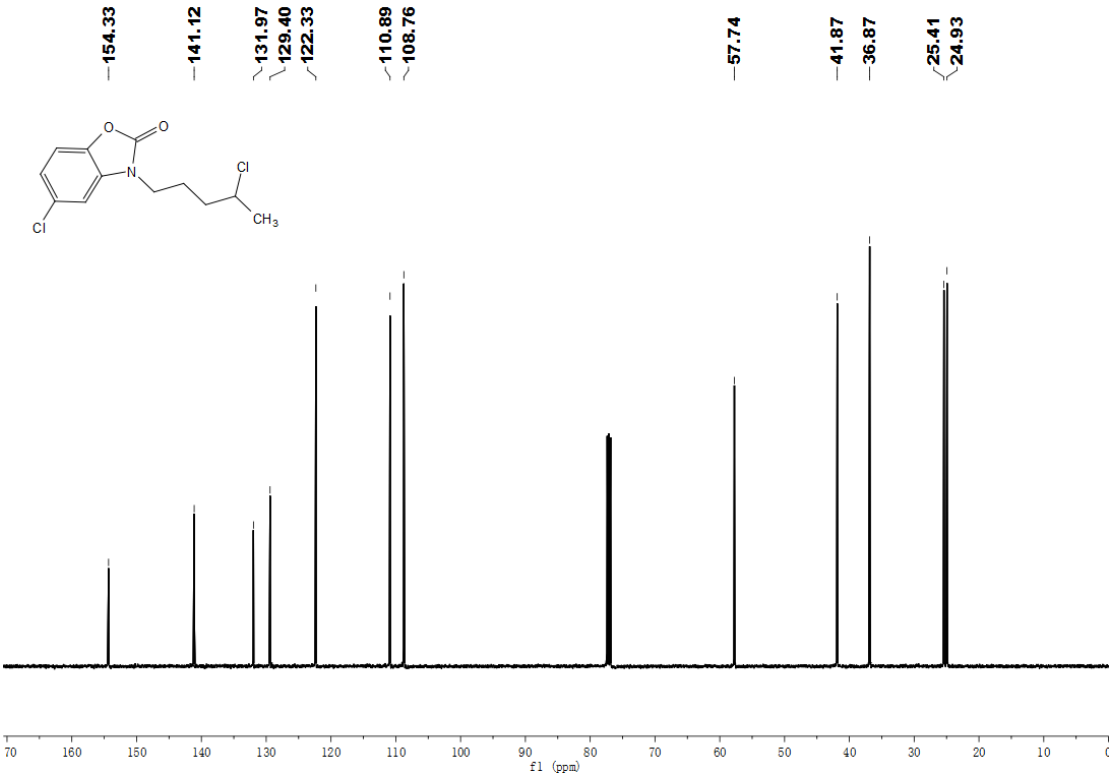
^{1}H NMR of compound **22b** (500 MHz, $CDCl_3$)



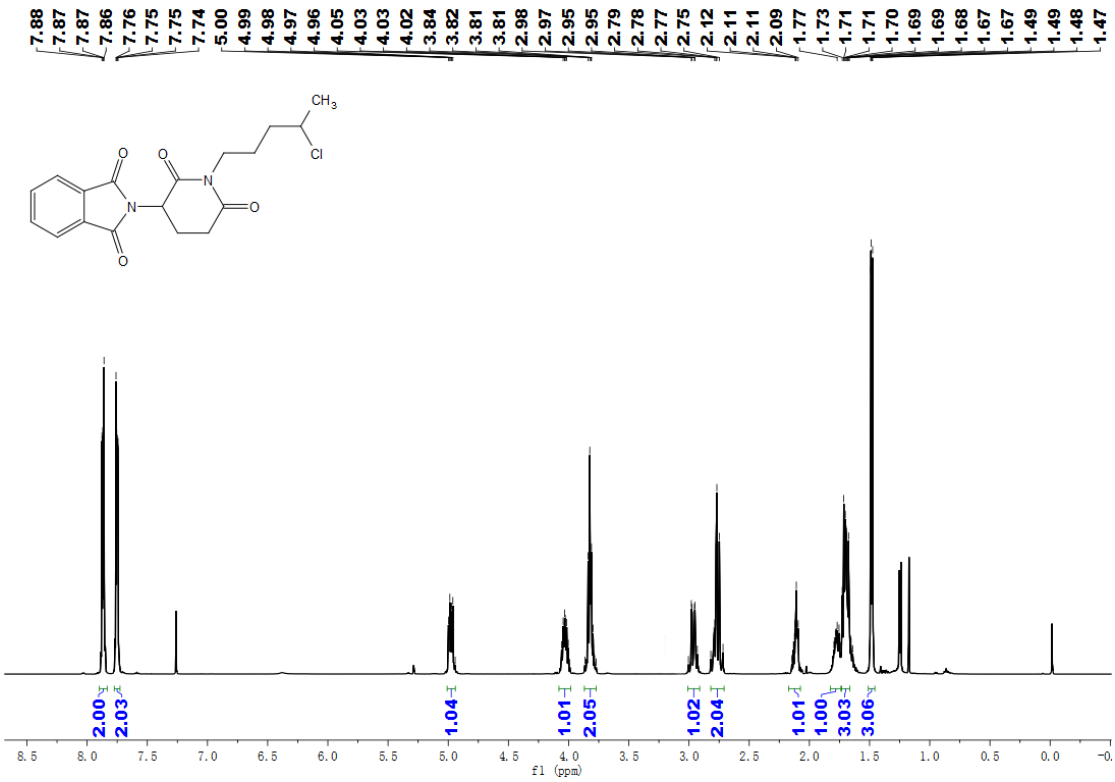
^{13}C NMR of compound **22b** (126 MHz, $CDCl_3$)



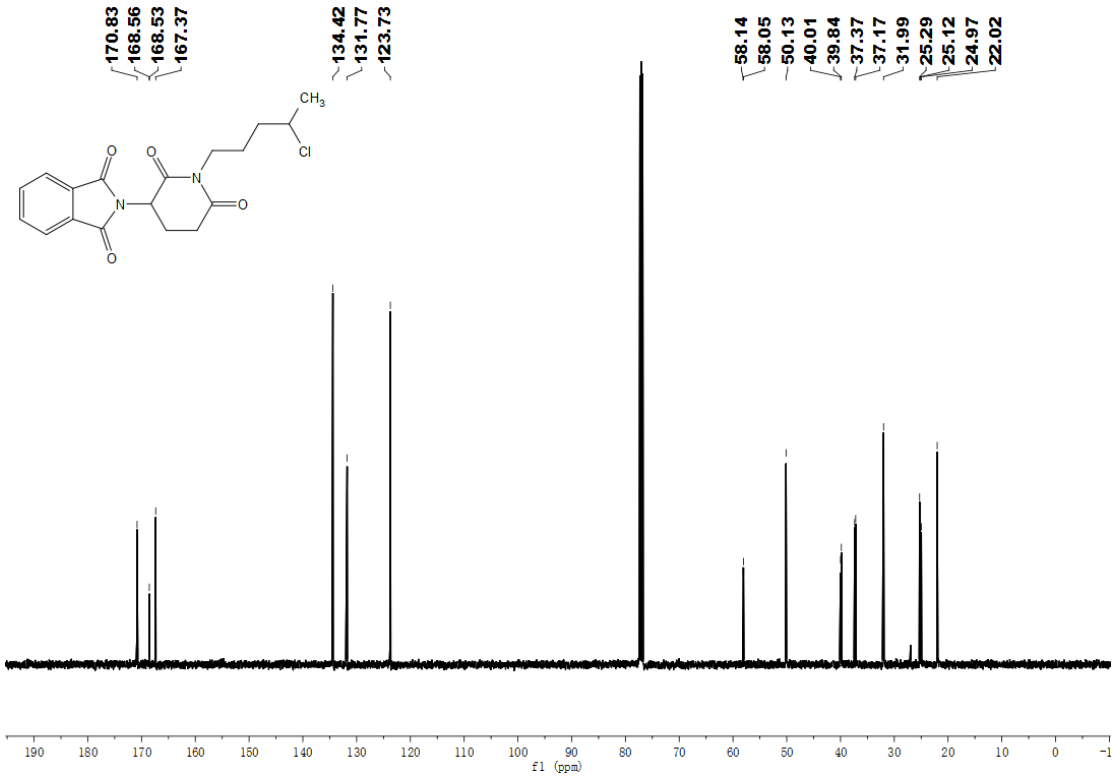
^{1}H NMR of compound **23b** (500 MHz, $CDCl_3$)



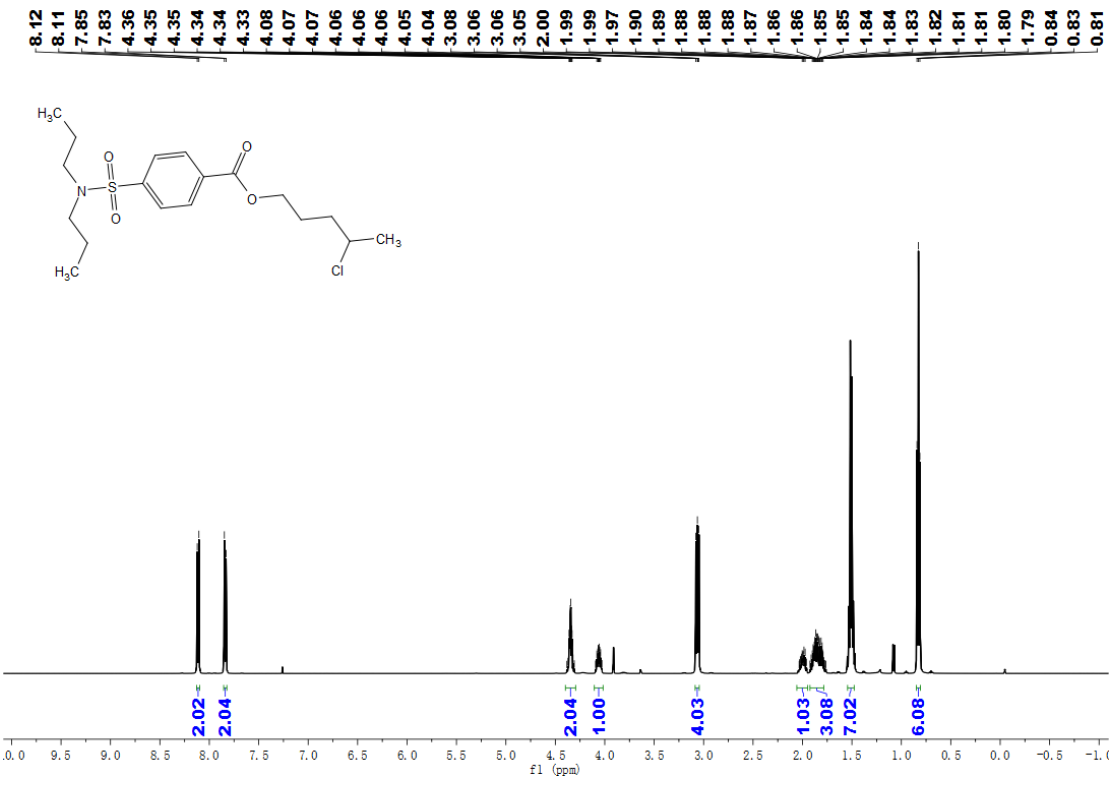
^{13}C NMR of compound **23b** (126 MHz, $CDCl_3$)



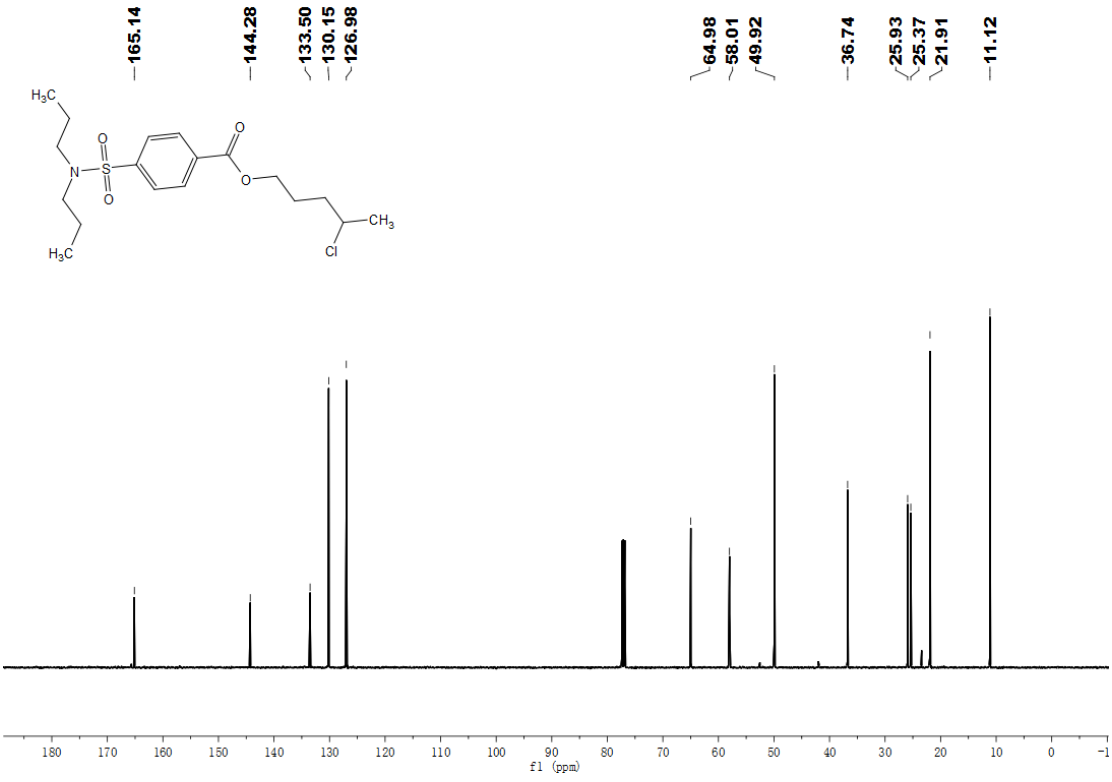
^{1}H NMR of compound **24b** (500 MHz, $CDCl_3$)



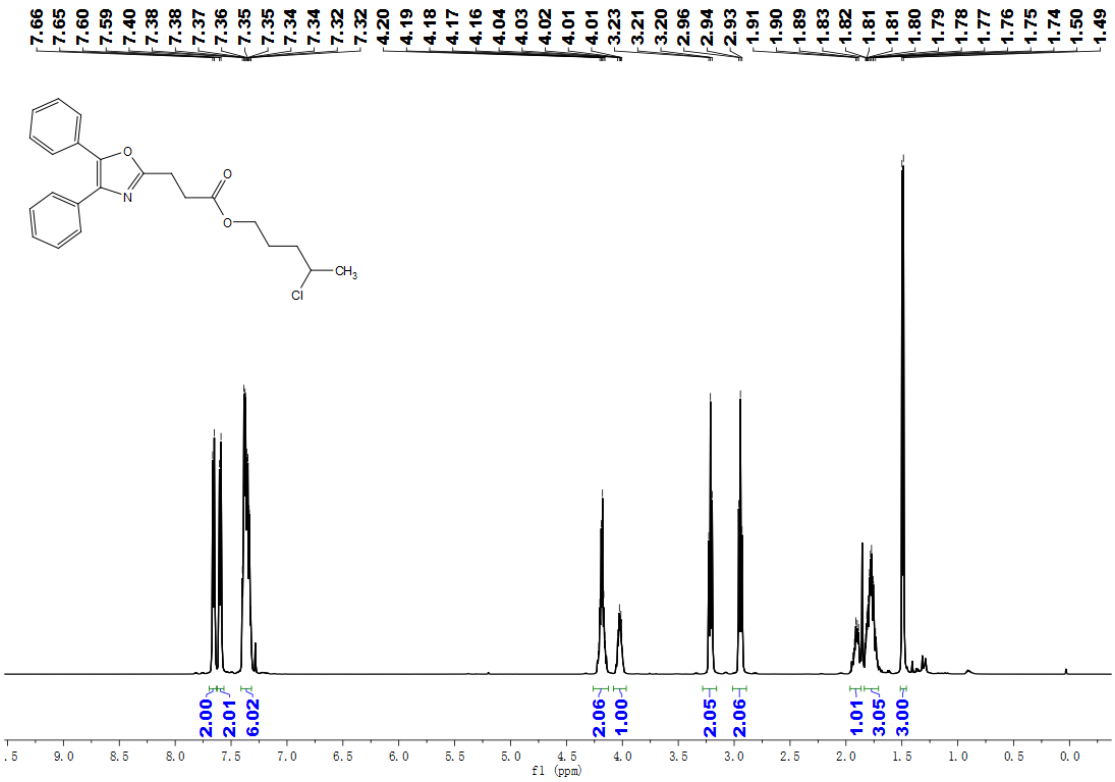
^{13}C NMR of compound **24b** (126 MHz, $CDCl_3$)



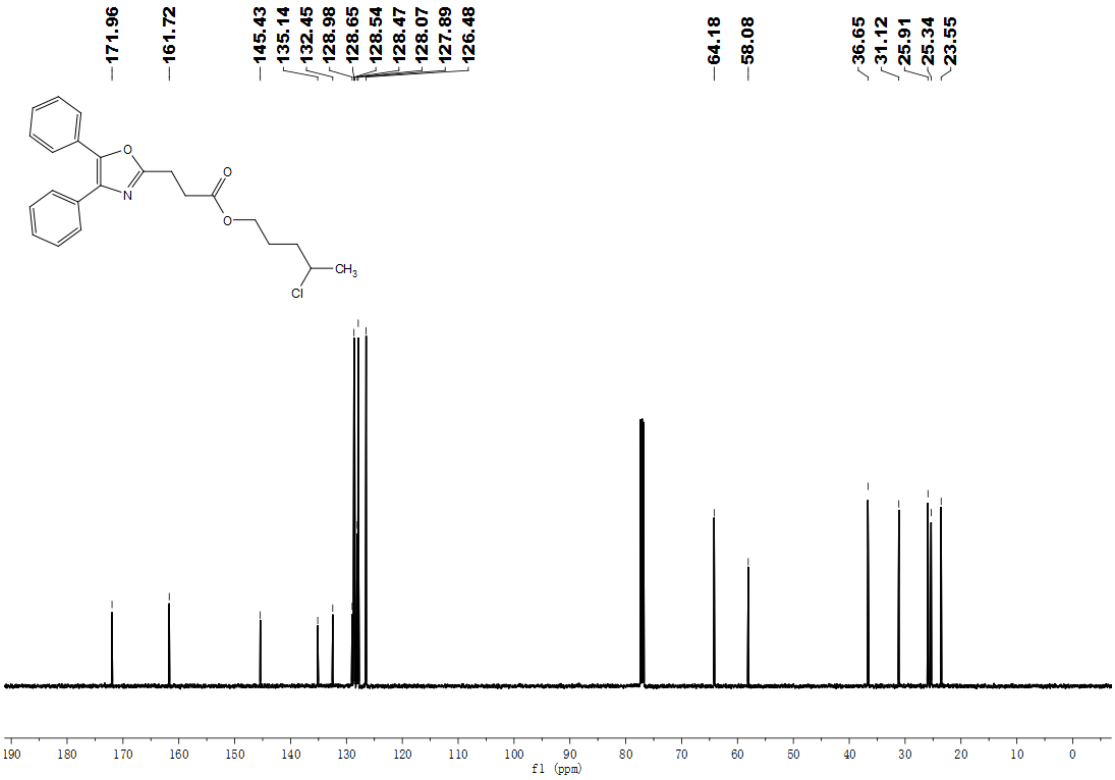
^{1}H NMR of compound **25b** (500 MHz, $CDCl_3$)



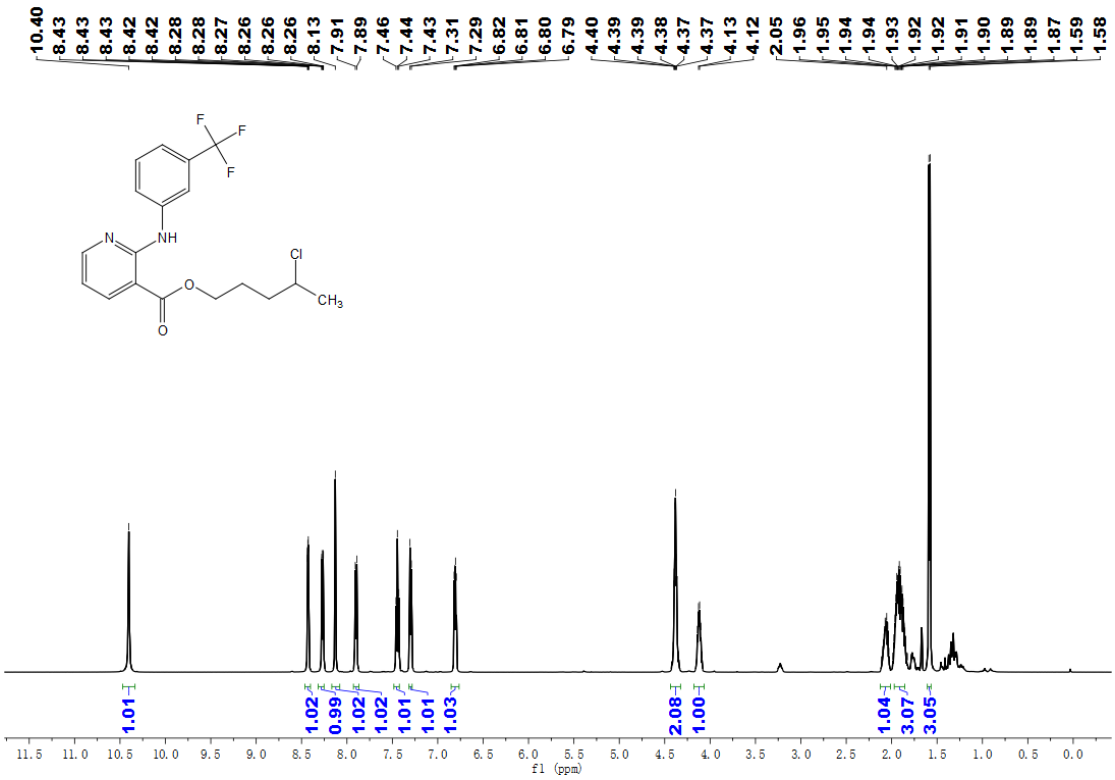
^{13}C NMR of compound **25b** (126 MHz, $CDCl_3$)



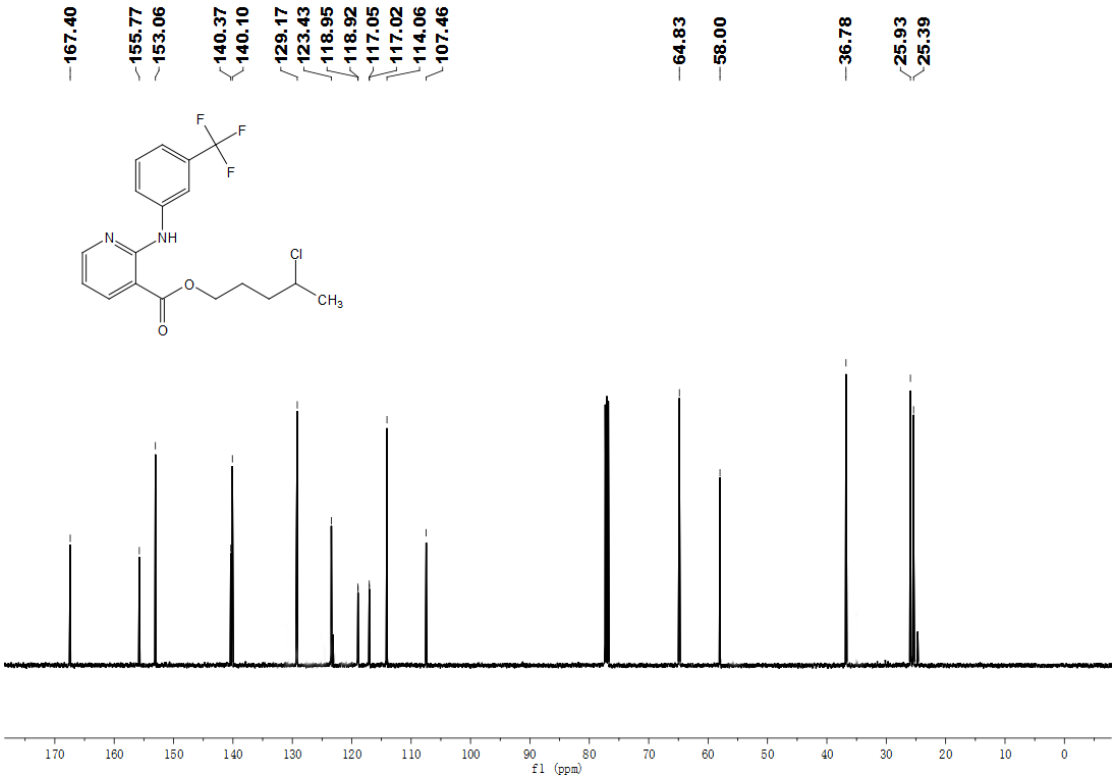
^{1}H NMR of compound **26b** (500 MHz, $CDCl_3$)



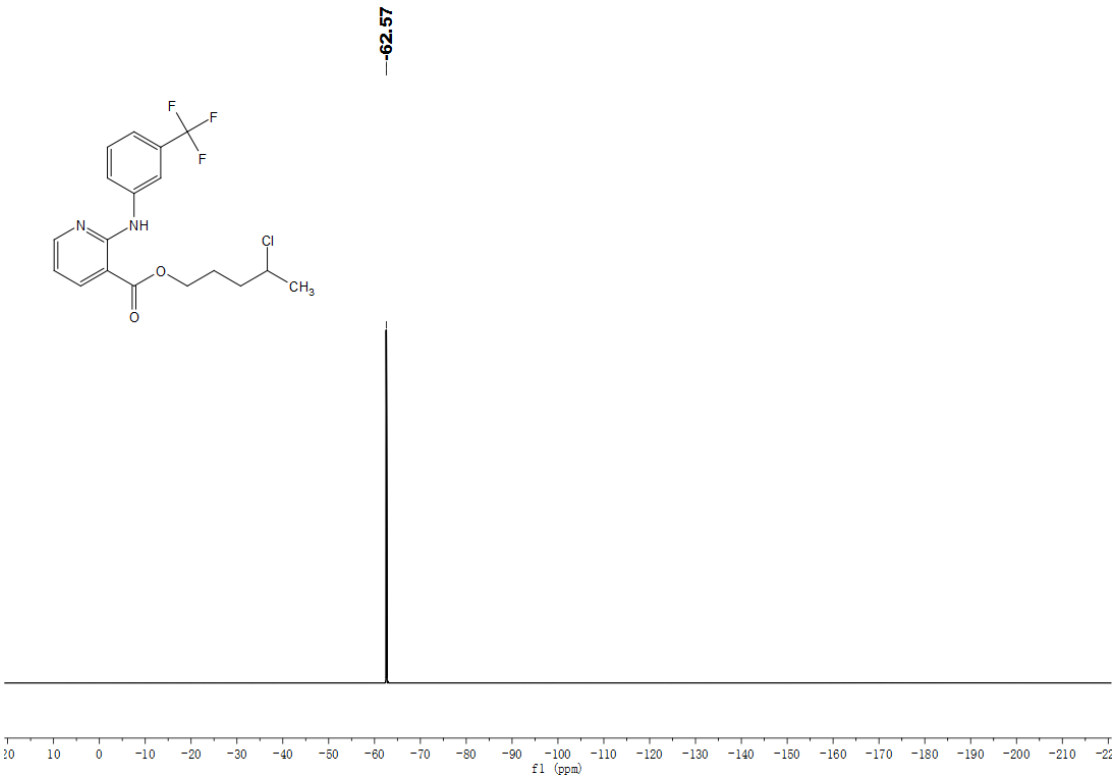
^{13}C NMR of compound **26b** (126 MHz, $CDCl_3$)



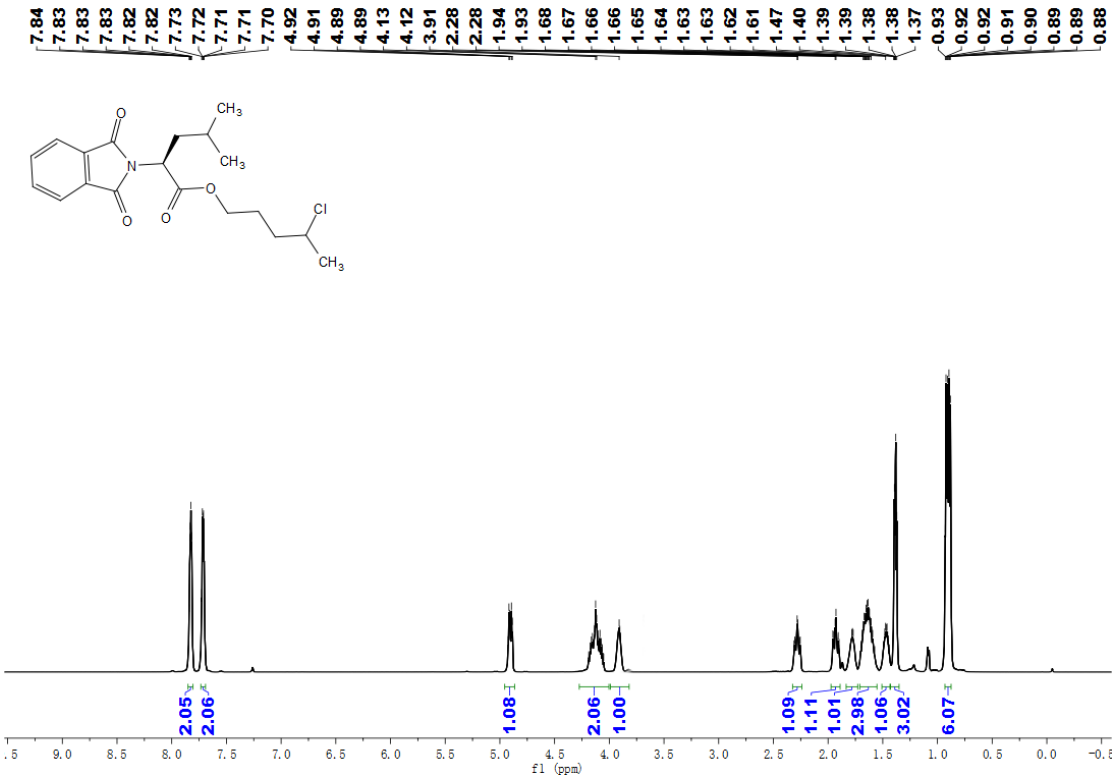
^{1}H NMR of compound **26b** (500 MHz, $CDCl_3$)



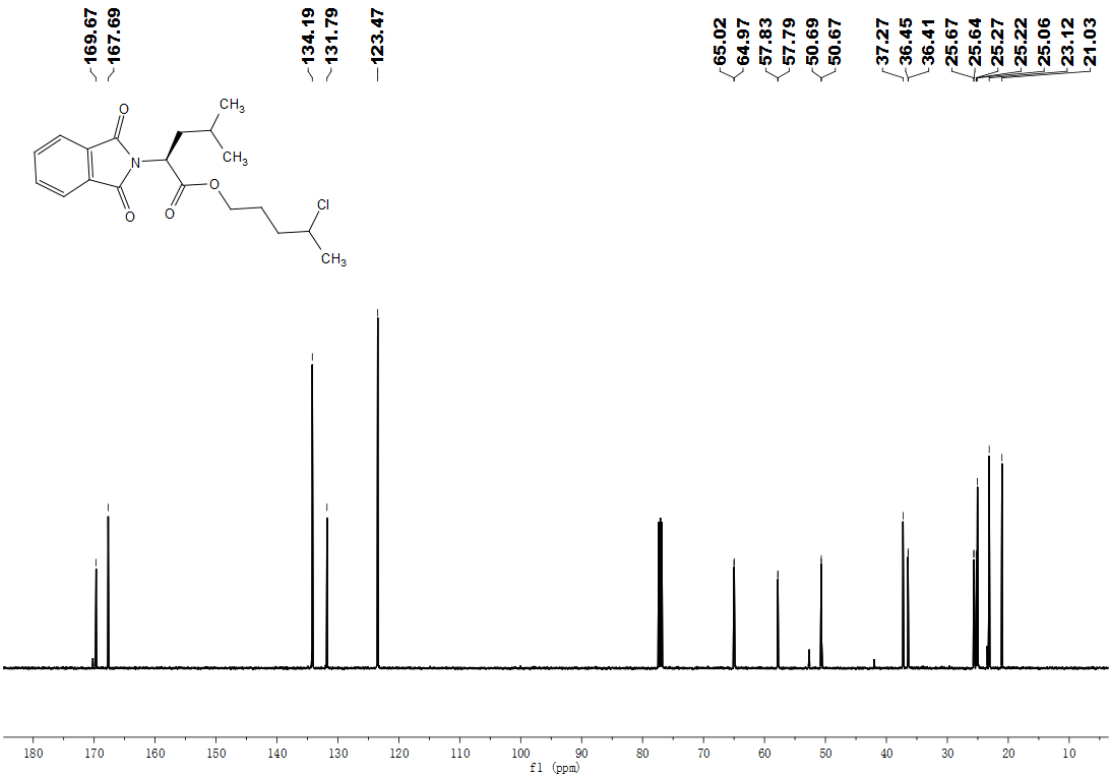
^{13}C NMR of compound **27b** (126 MHz, $CDCl_3$)



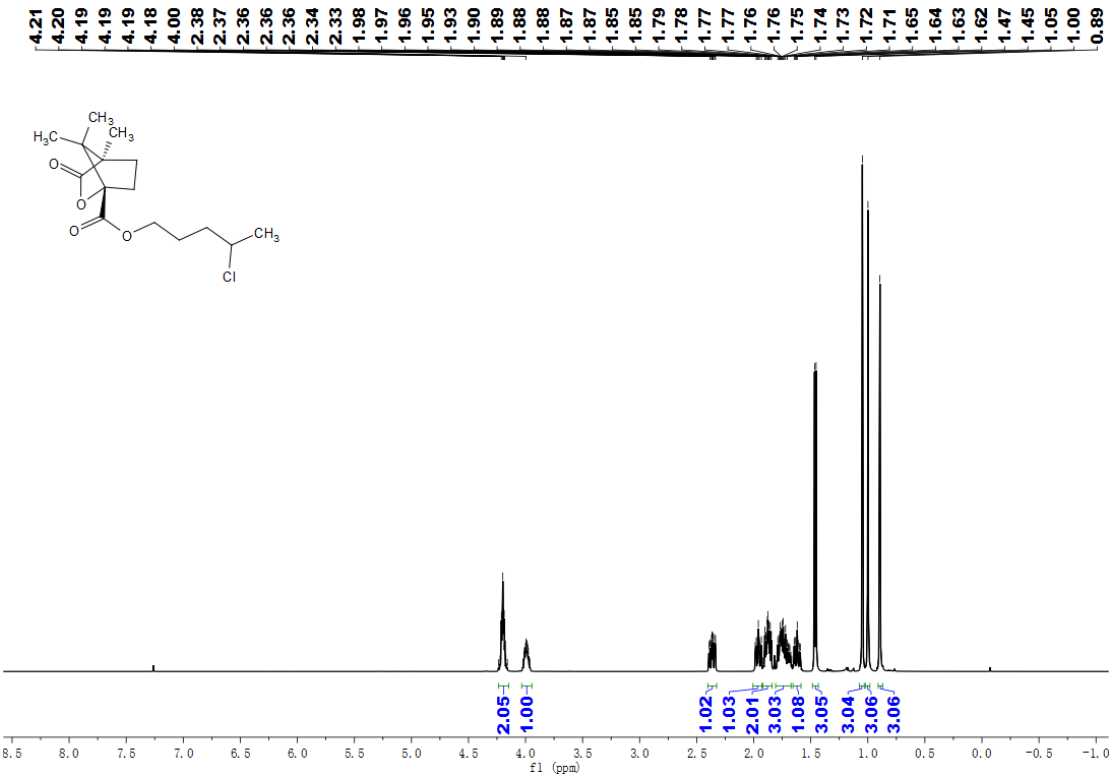
^{19}F NMR of compound **27b** (471 MHz, $CDCl_3$)



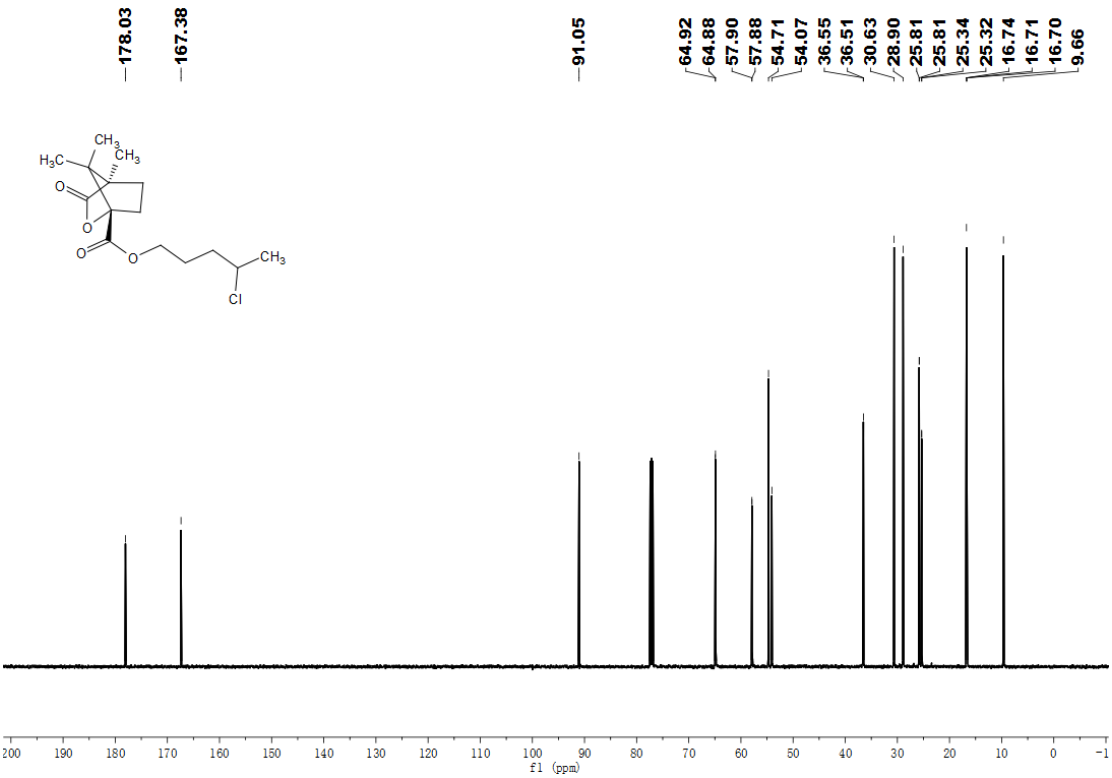
^{1}H NMR of compound **28b** (500 MHz, $CDCl_3$)



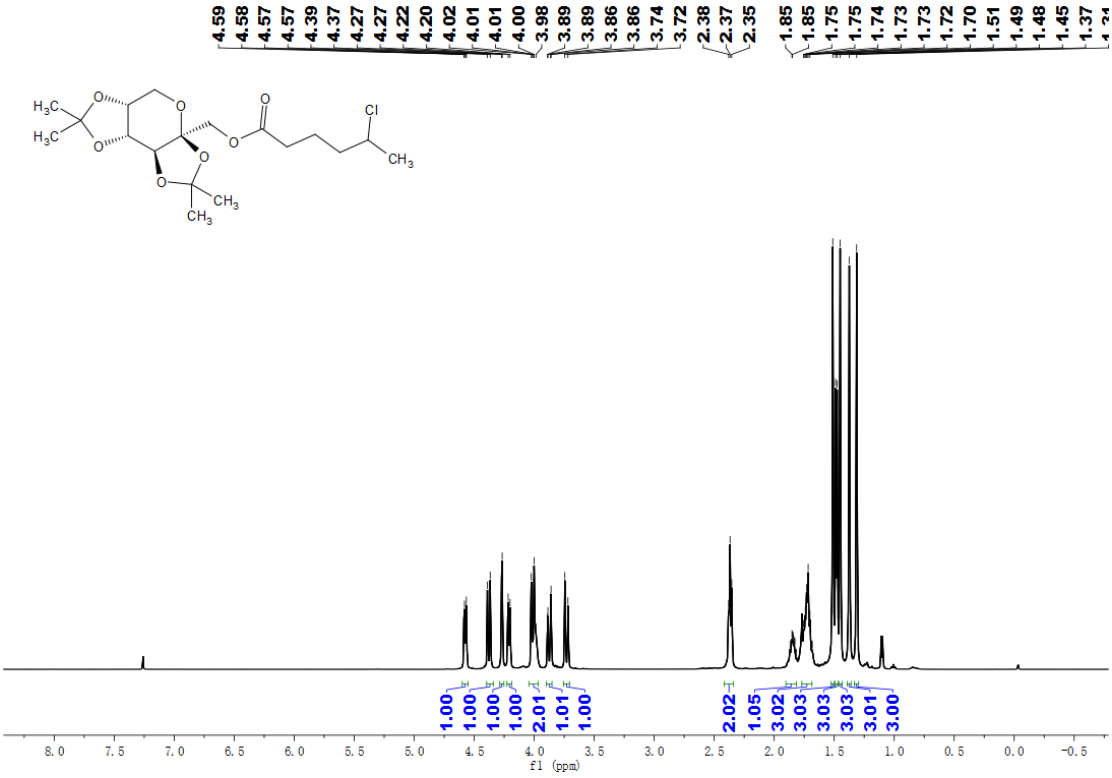
^{13}C NMR of compound **28b** (126 MHz, $CDCl_3$)



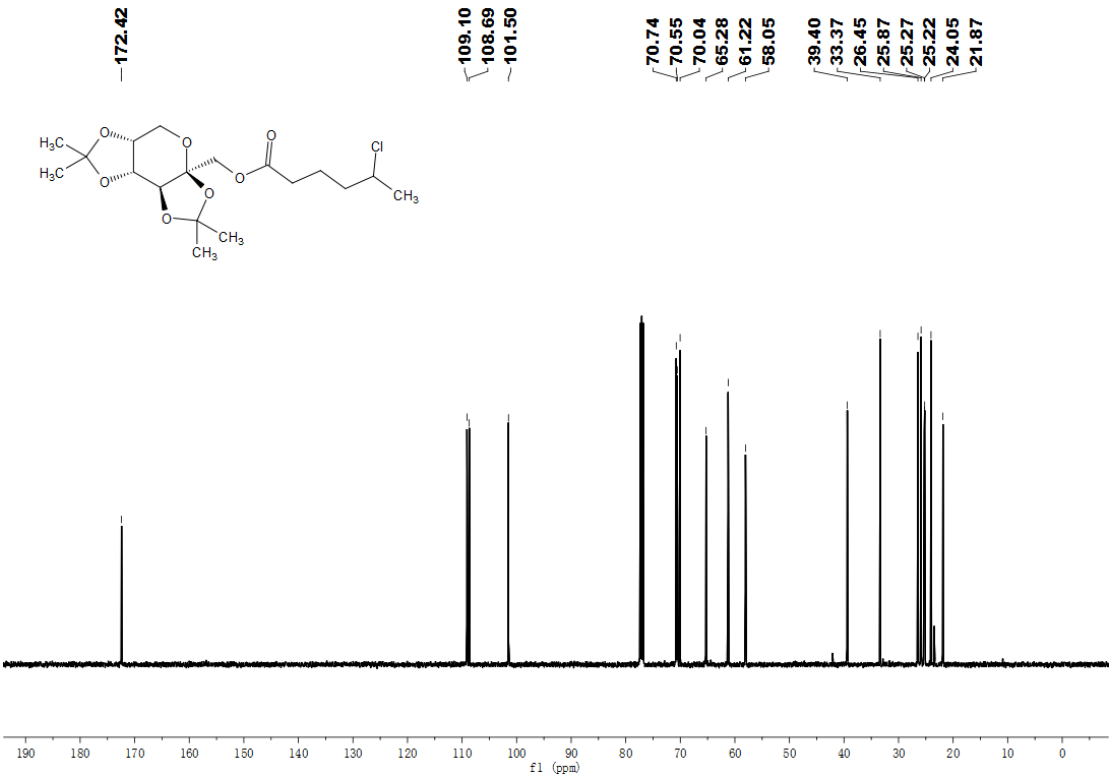
^{1}H NMR of compound **29b** (500 MHz, $CDCl_3$)



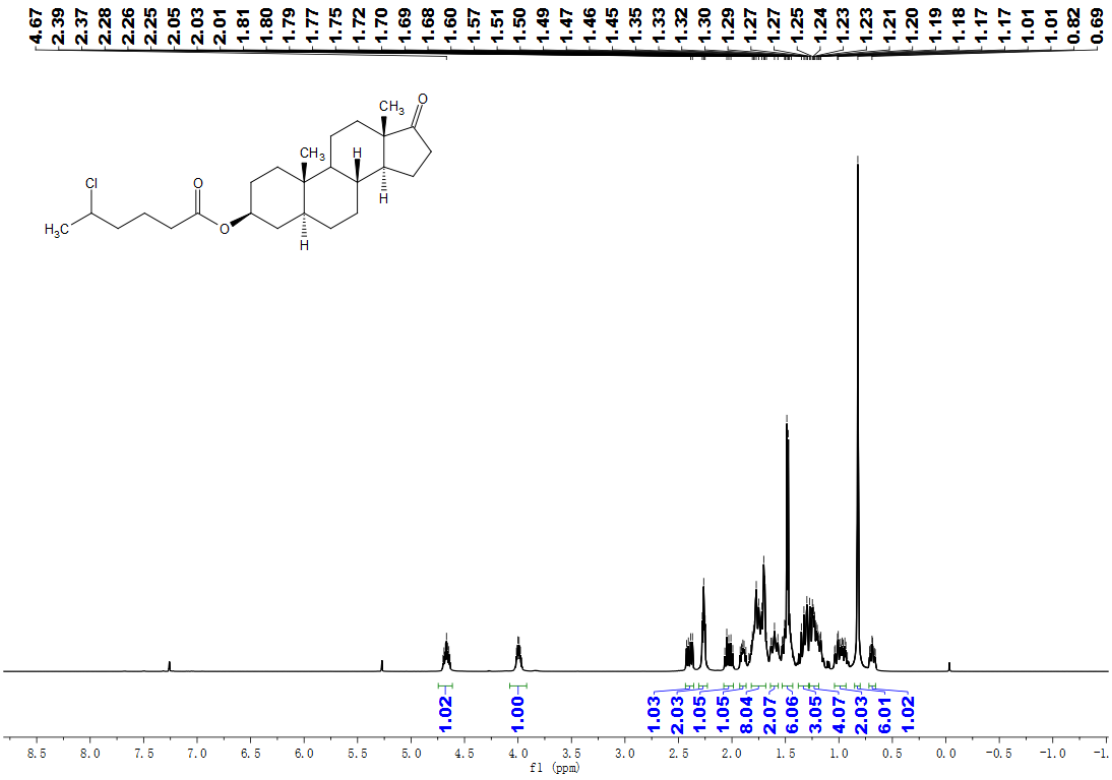
^{13}C NMR of compound **29b** (126 MHz, $CDCl_3$)



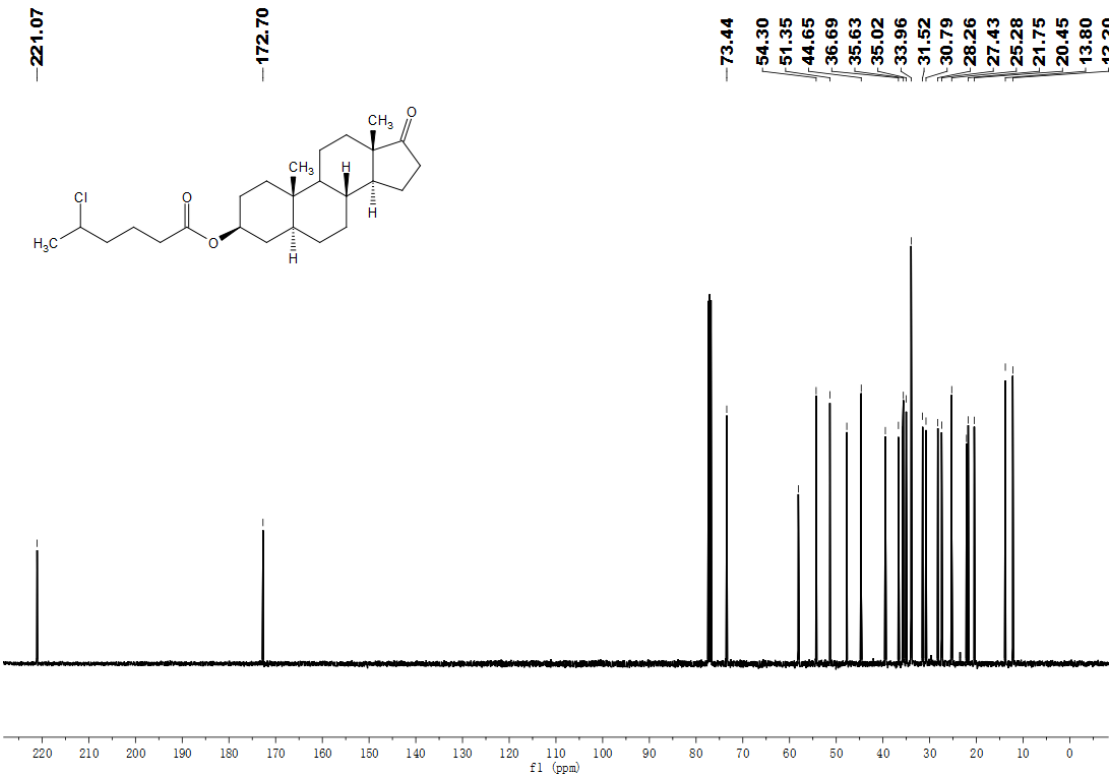
^{1}H NMR of compound **30b** (500 MHz, $CDCl_3$)



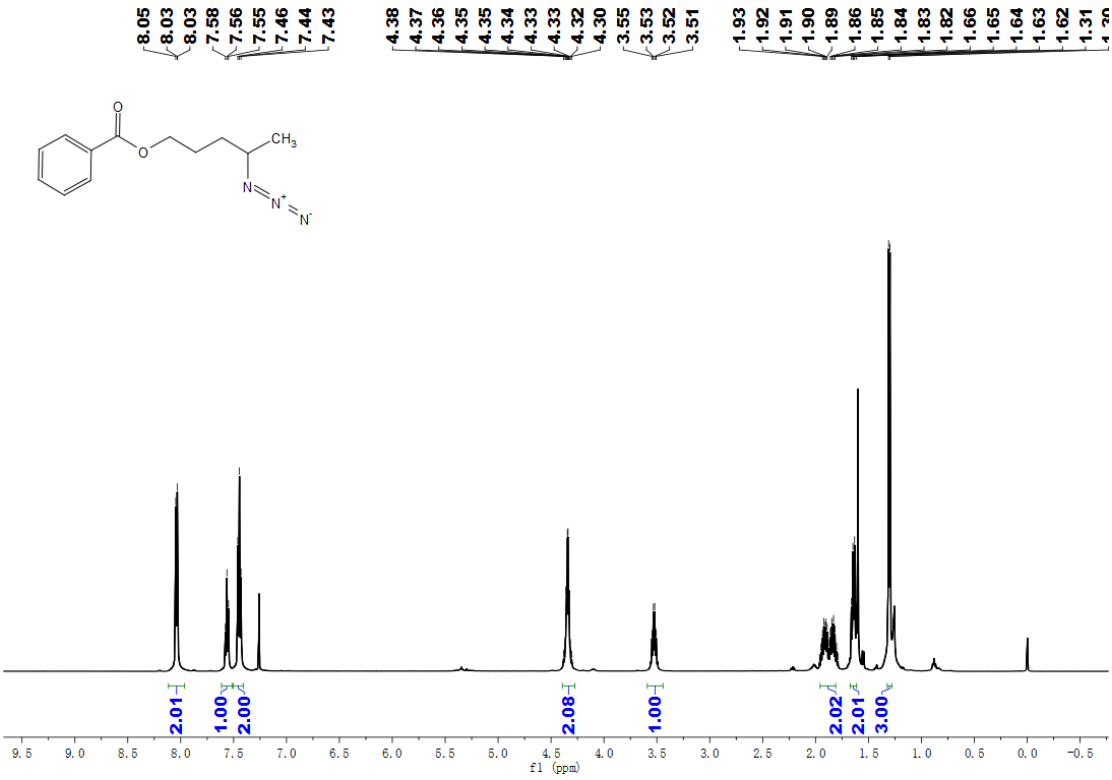
^{13}C NMR of compound **30b** (126 MHz, $CDCl_3$)



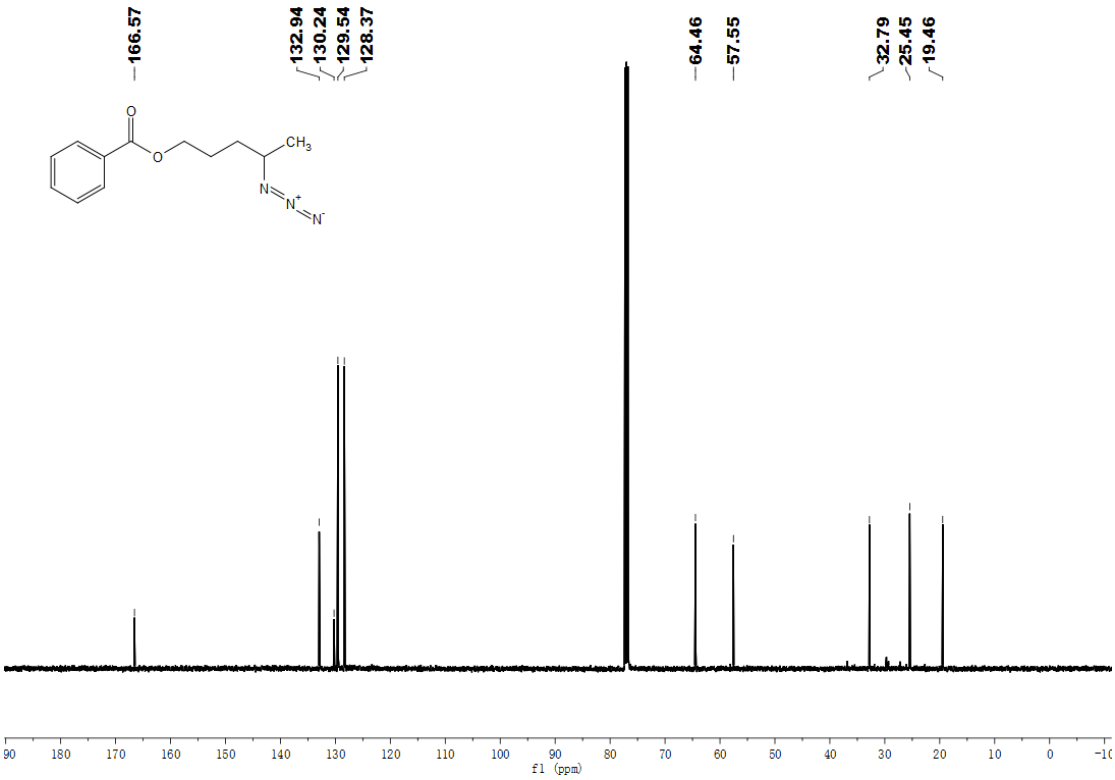
^{1}H NMR of compound **31b** (500 MHz, $CDCl_3$)



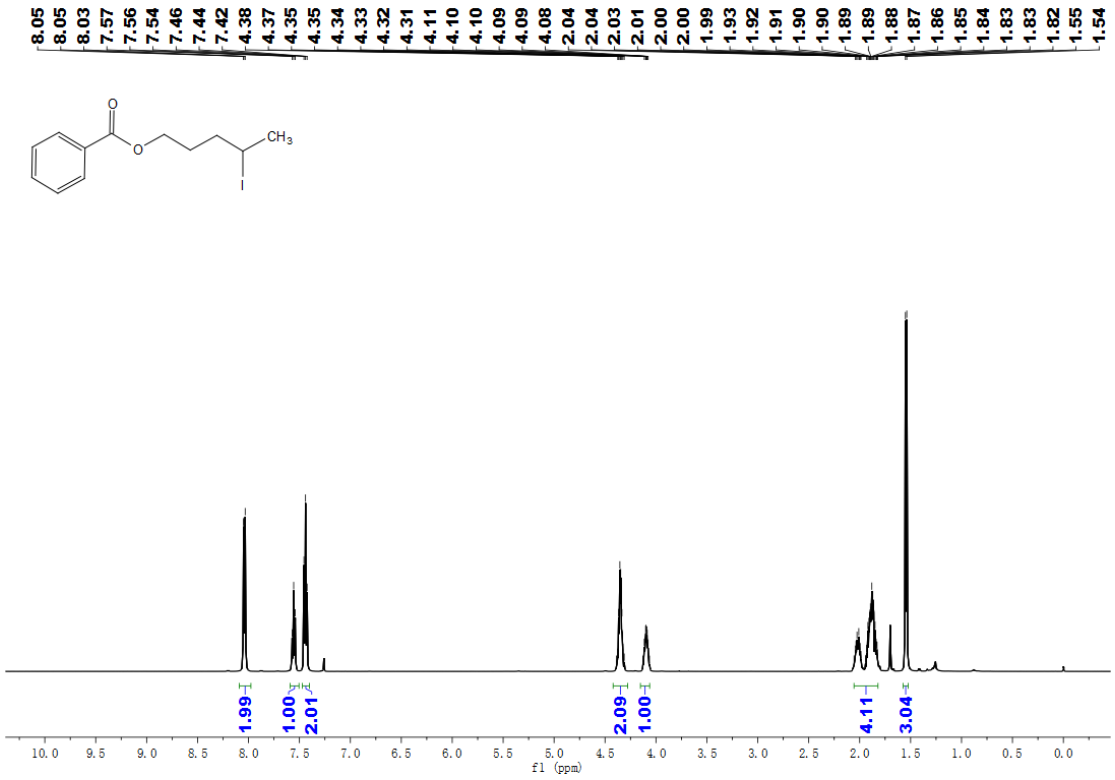
^{13}C NMR of compound **31b** (126 MHz, $CDCl_3$)



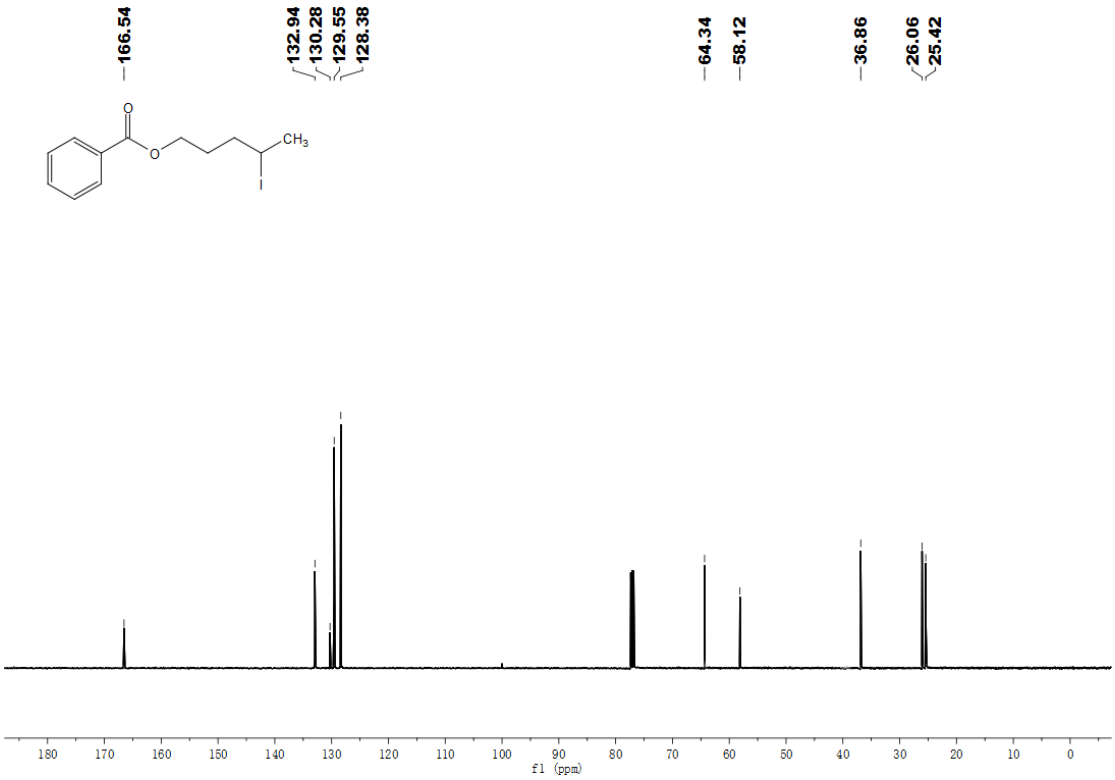
^{1}H NMR of compound **32** (500 MHz, $CDCl_3$)



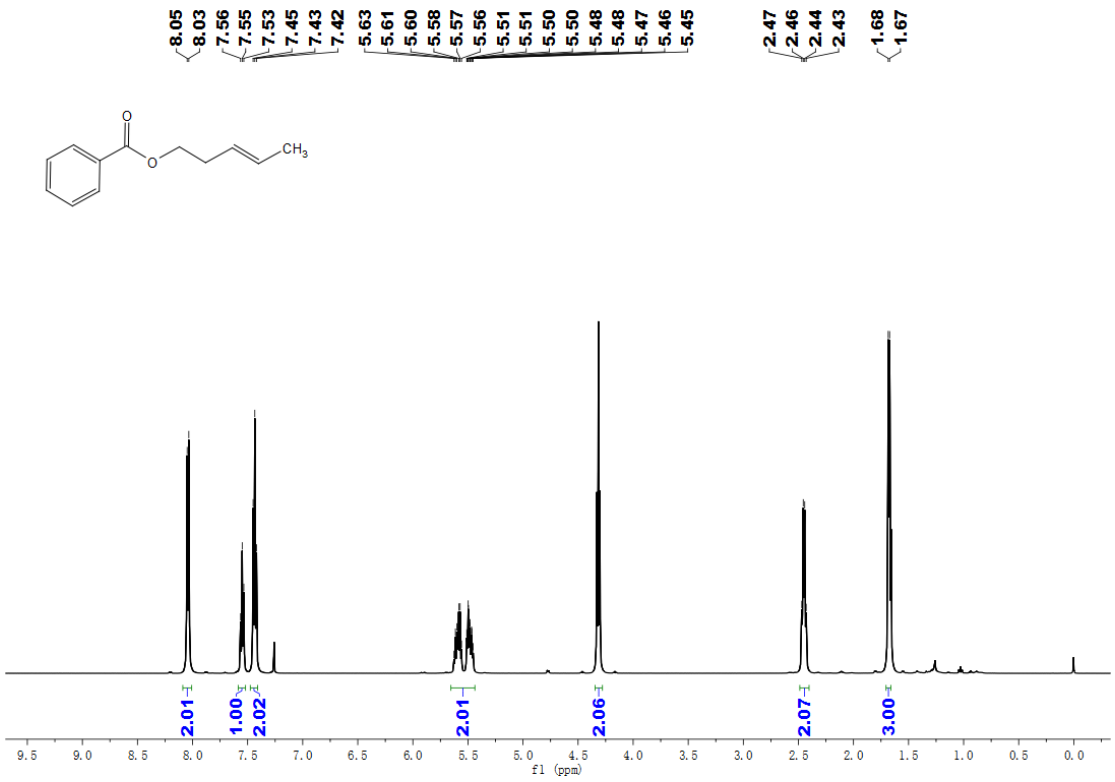
^{13}C NMR of compound **32** (126 MHz, $CDCl_3$)



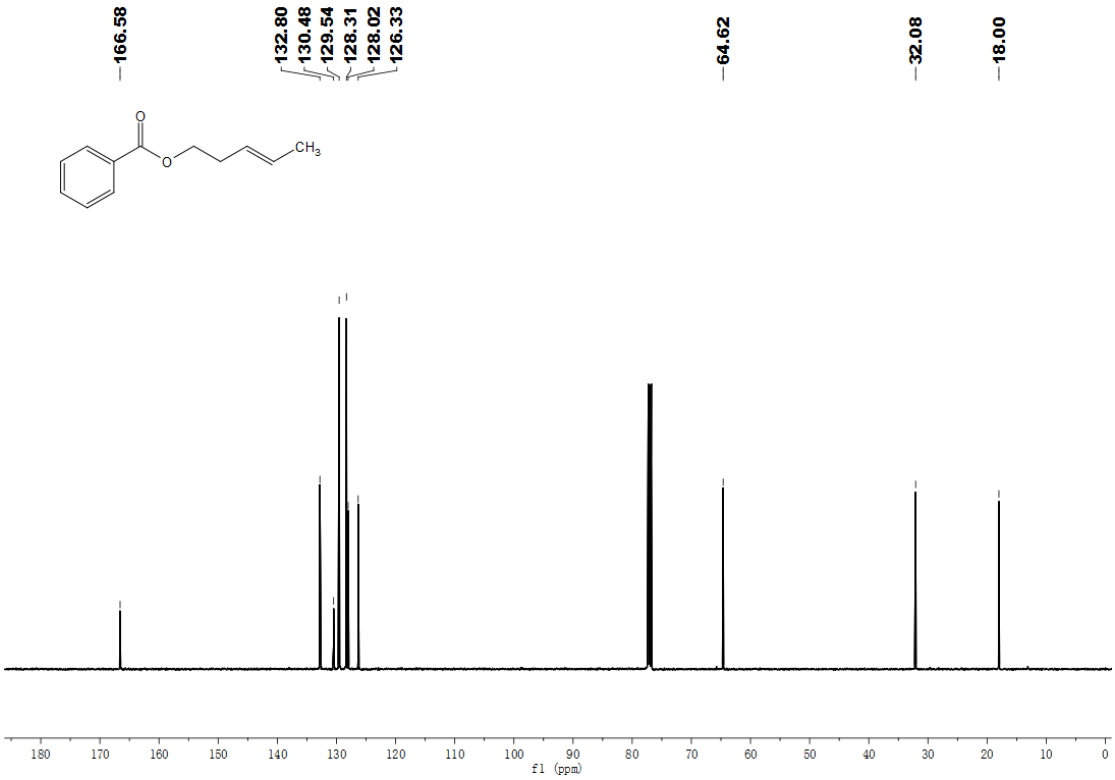
^{1}H NMR of compound **33** (500 MHz, $CDCl_3$)



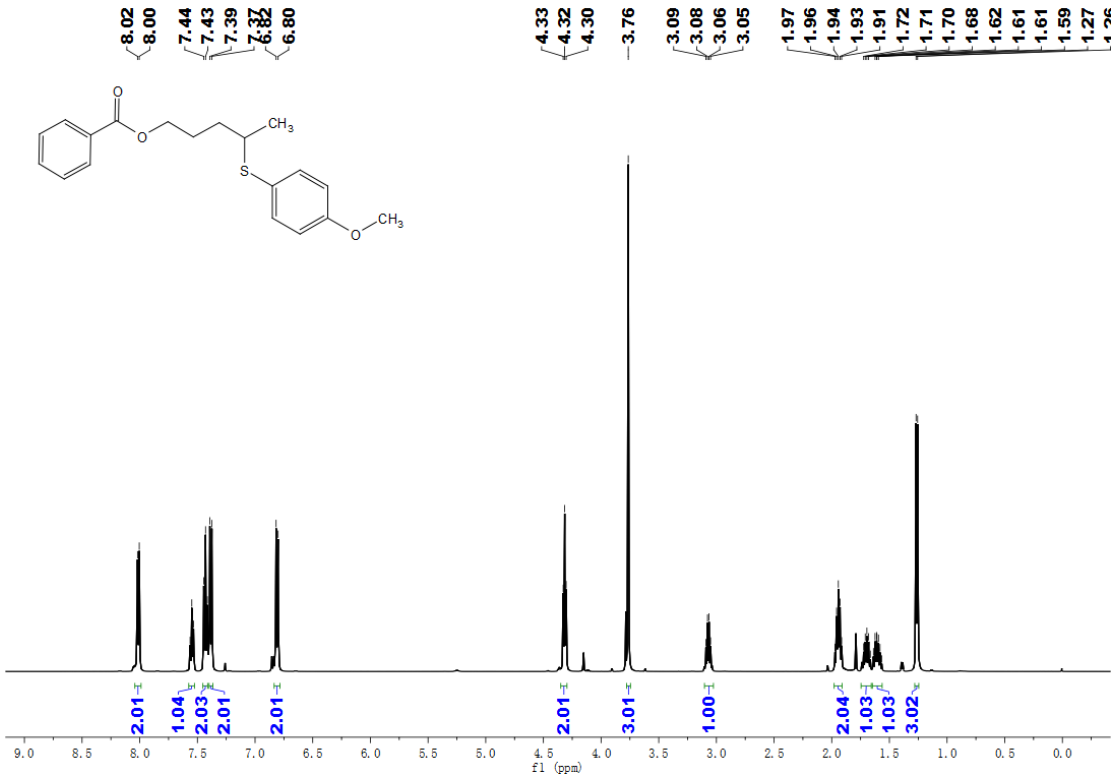
^{13}C NMR of compound **33** (126 MHz, $CDCl_3$)



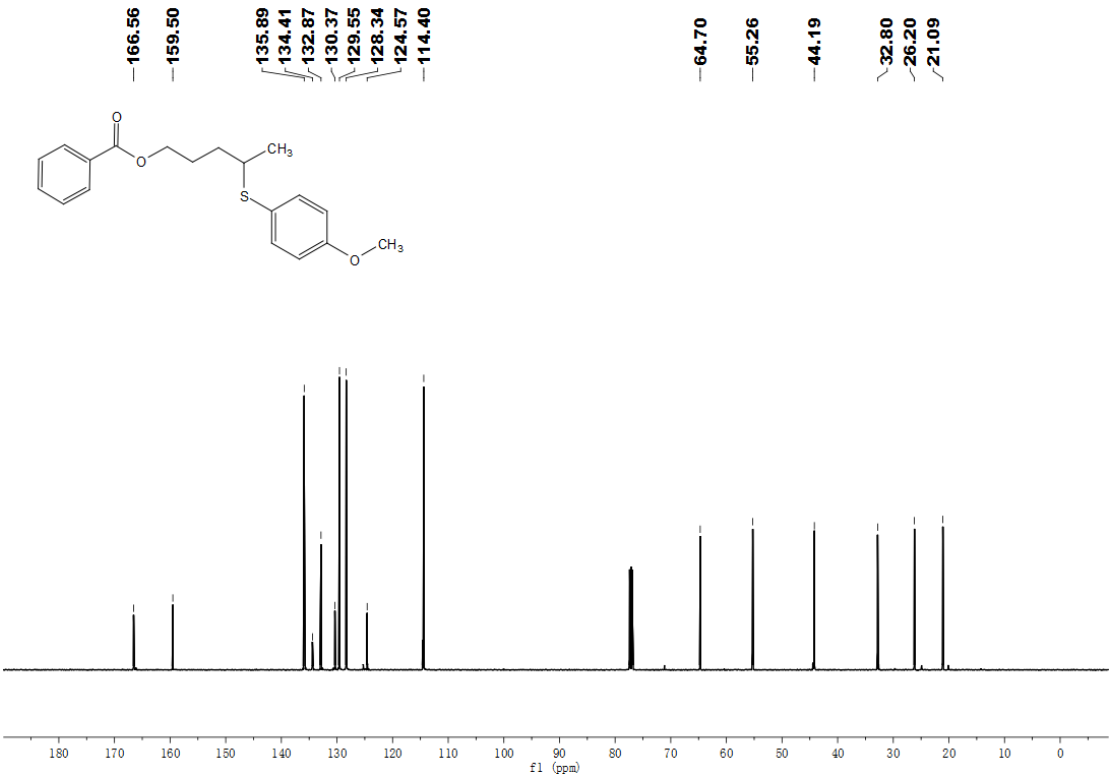
^{1}H NMR of compound **34** (500 MHz, $CDCl_3$)



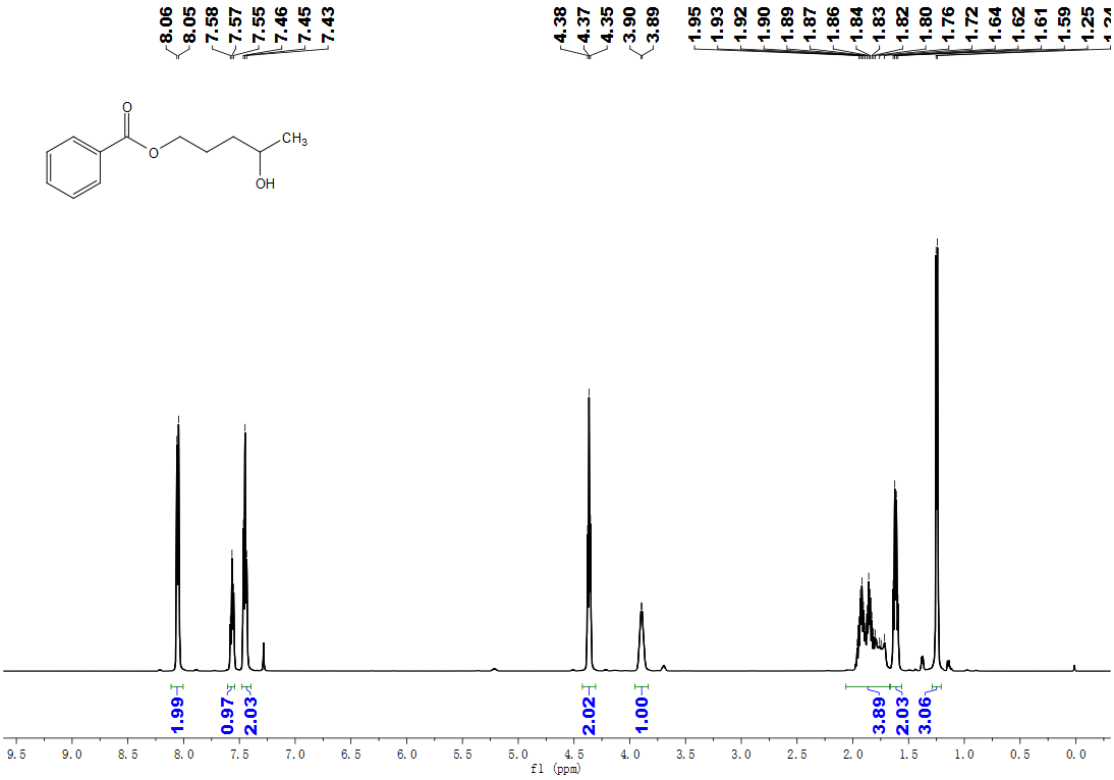
^{13}C NMR of compound **34** (126 MHz, $CDCl_3$)



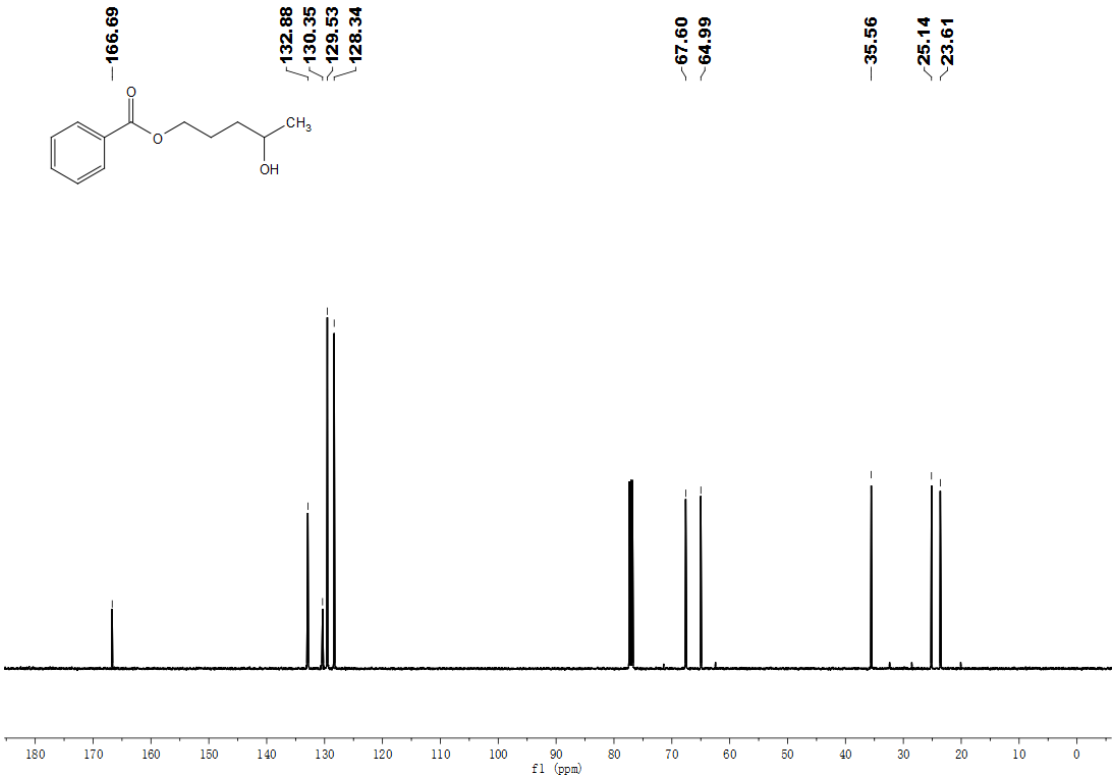
^{1}H NMR of compound **35** (500 MHz, $CDCl_3$)



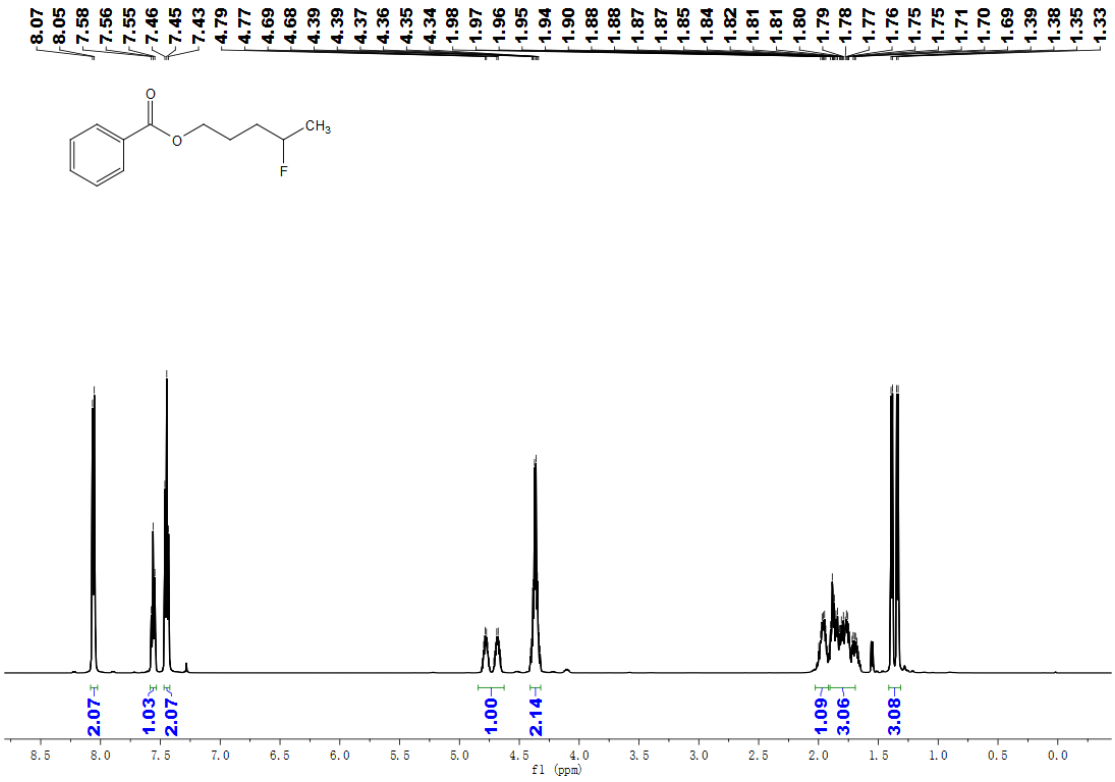
^{13}C NMR of compound **35** (126 MHz, $CDCl_3$)



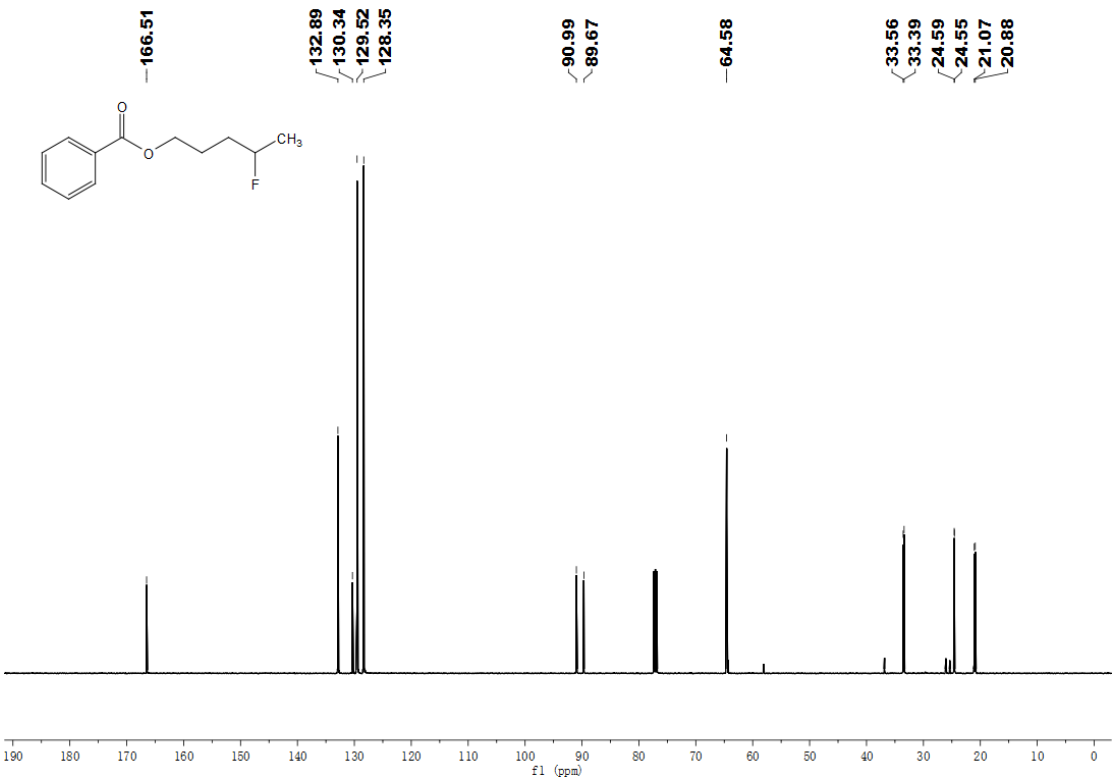
^{1}H NMR of compound **36** (500 MHz, $CDCl_3$)



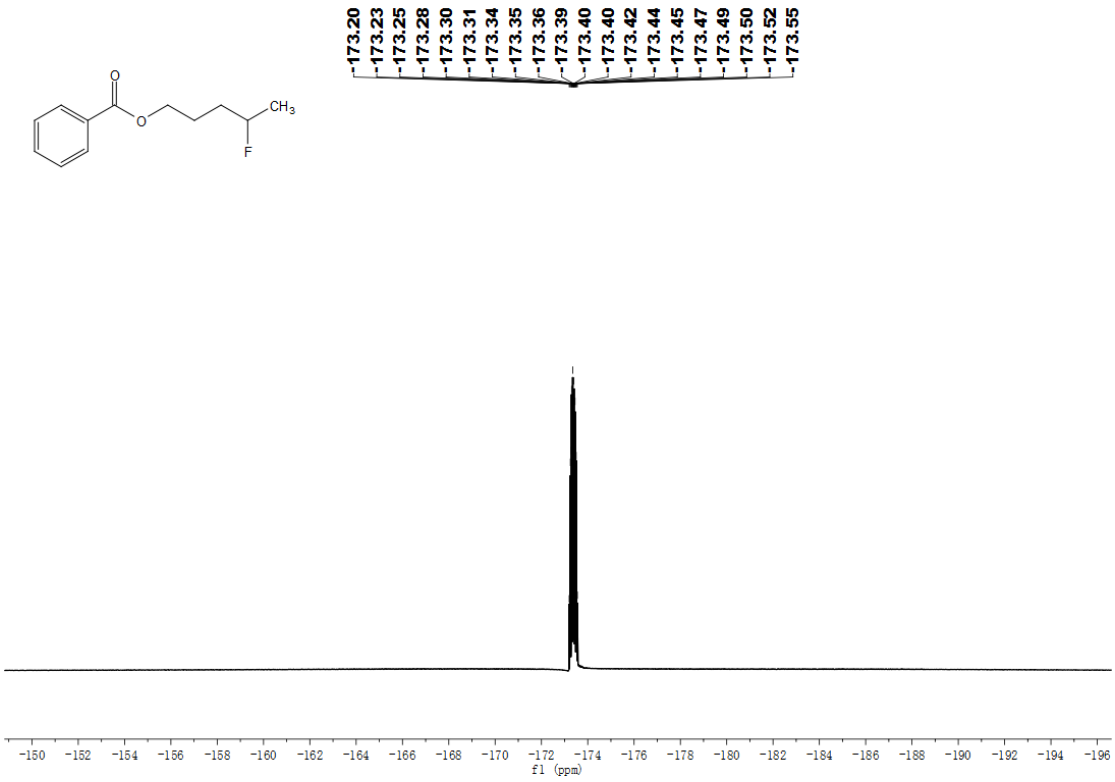
^{13}C NMR of compound **36** (126 MHz, $CDCl_3$)



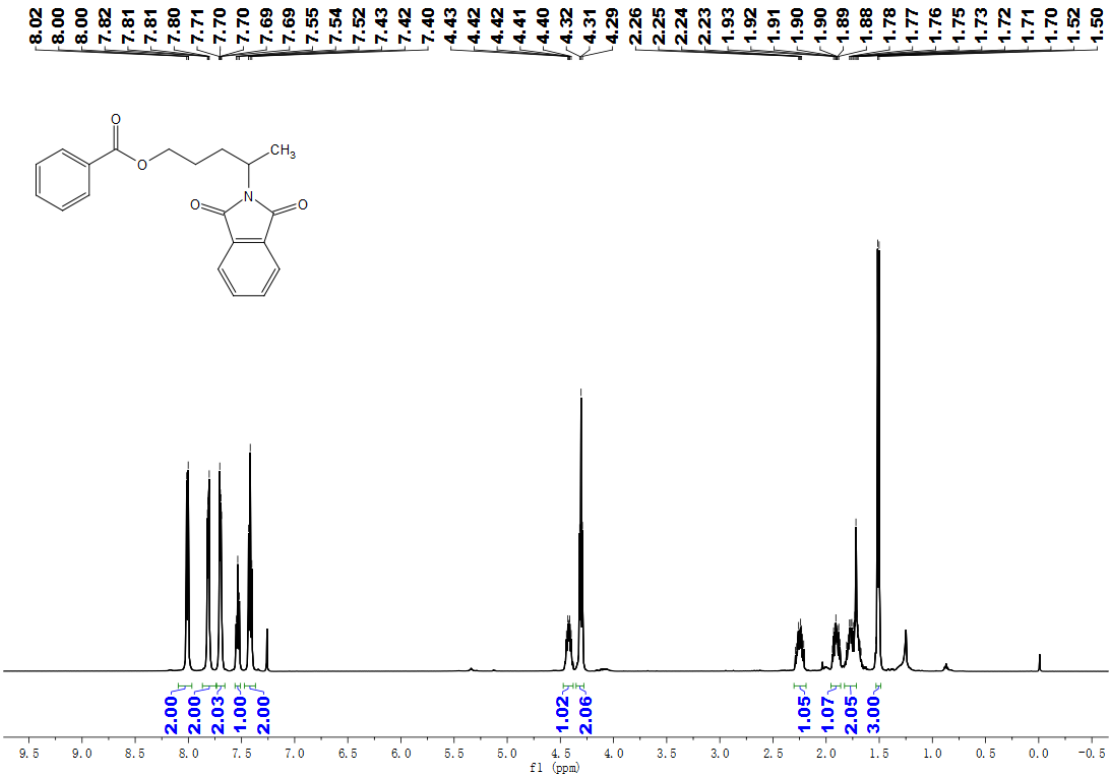
^{1}H NMR of compound **37** (500 MHz, $CDCl_3$)



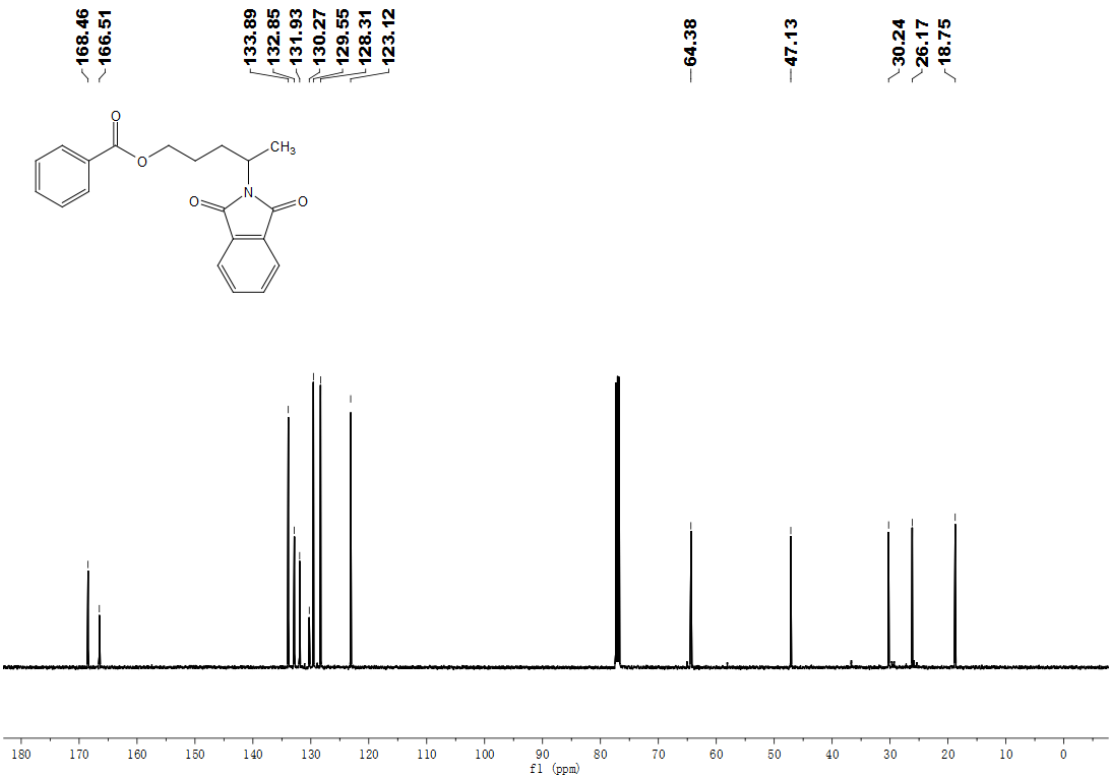
^{13}C NMR of compound **37** (126 MHz, $CDCl_3$)



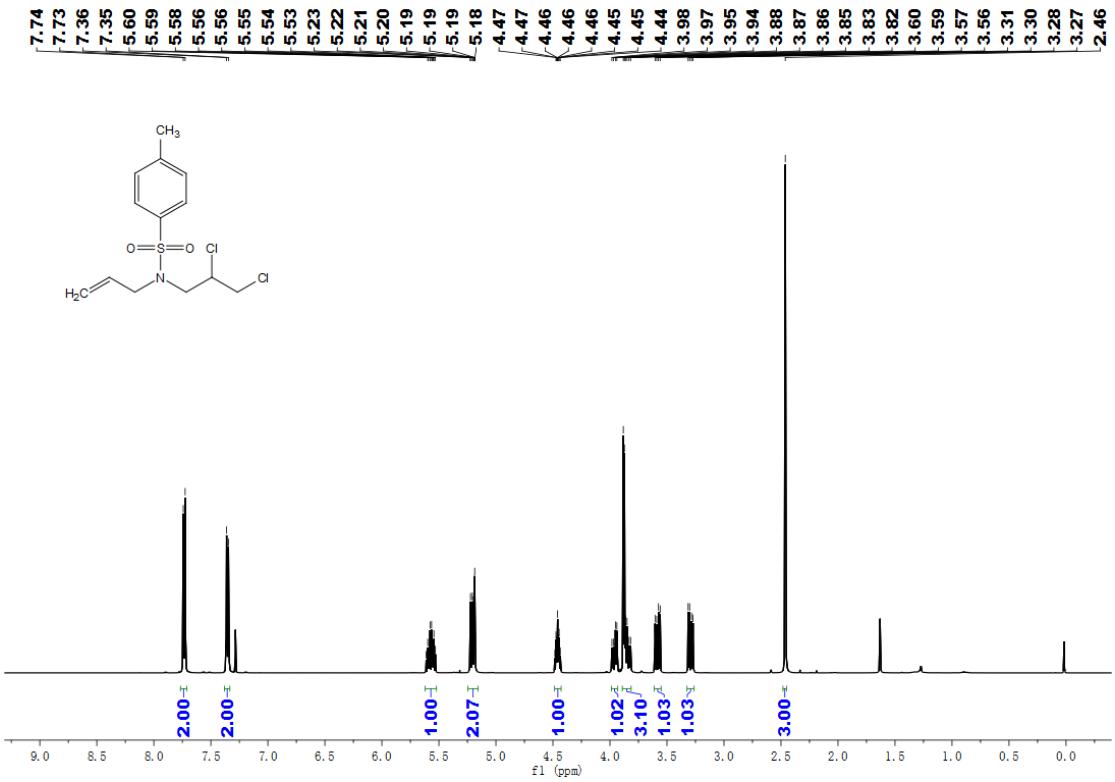
^{19}F NMR of compound **37** (471 MHz, $CDCl_3$)



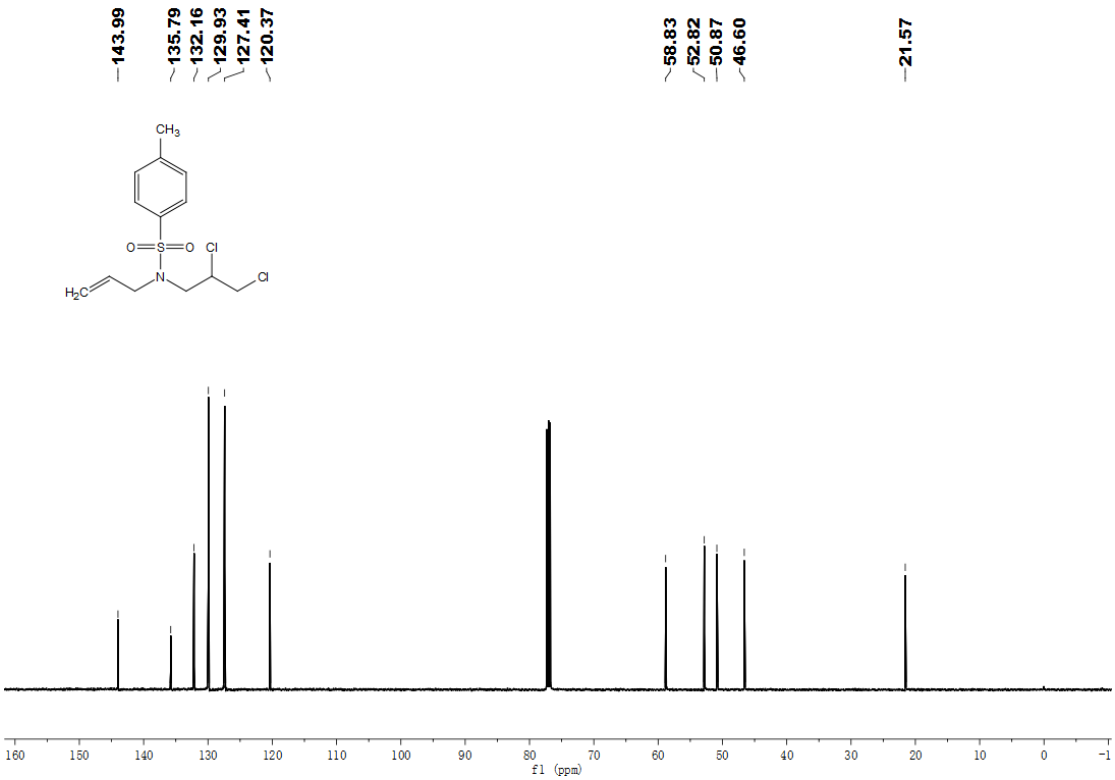
^{1}H NMR of compound **38** (500 MHz, $CDCl_3$)



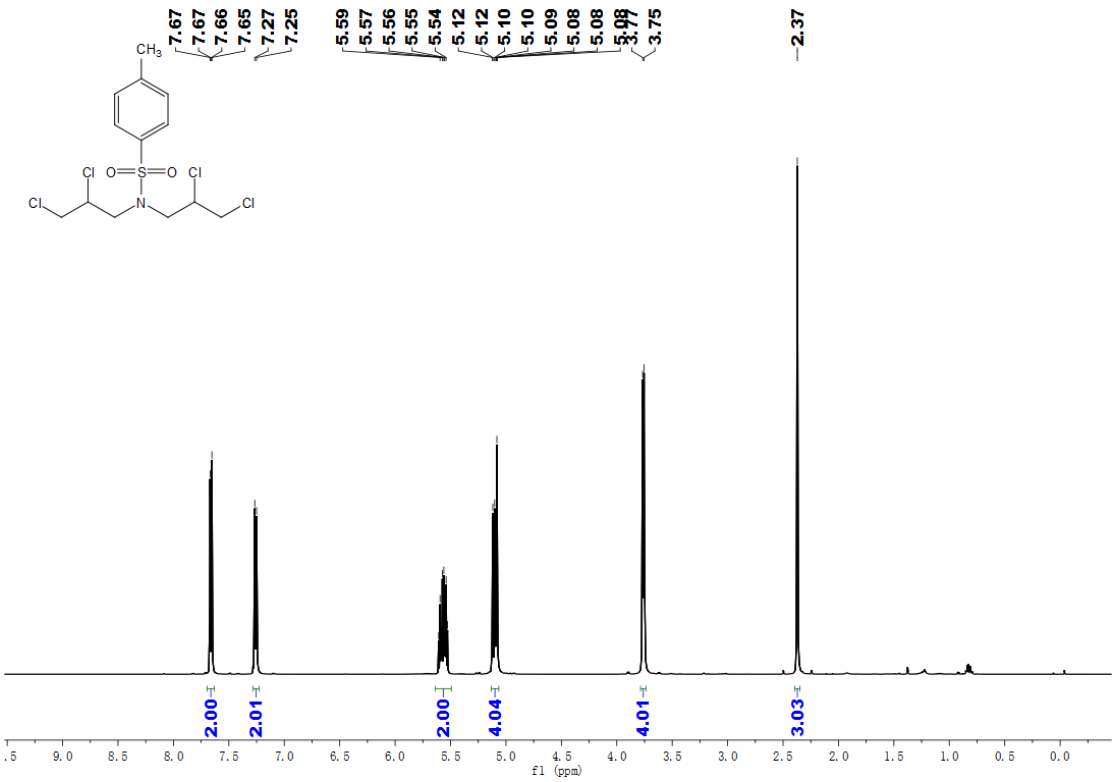
^{13}C NMR of compound **38** (126 MHz, $CDCl_3$)



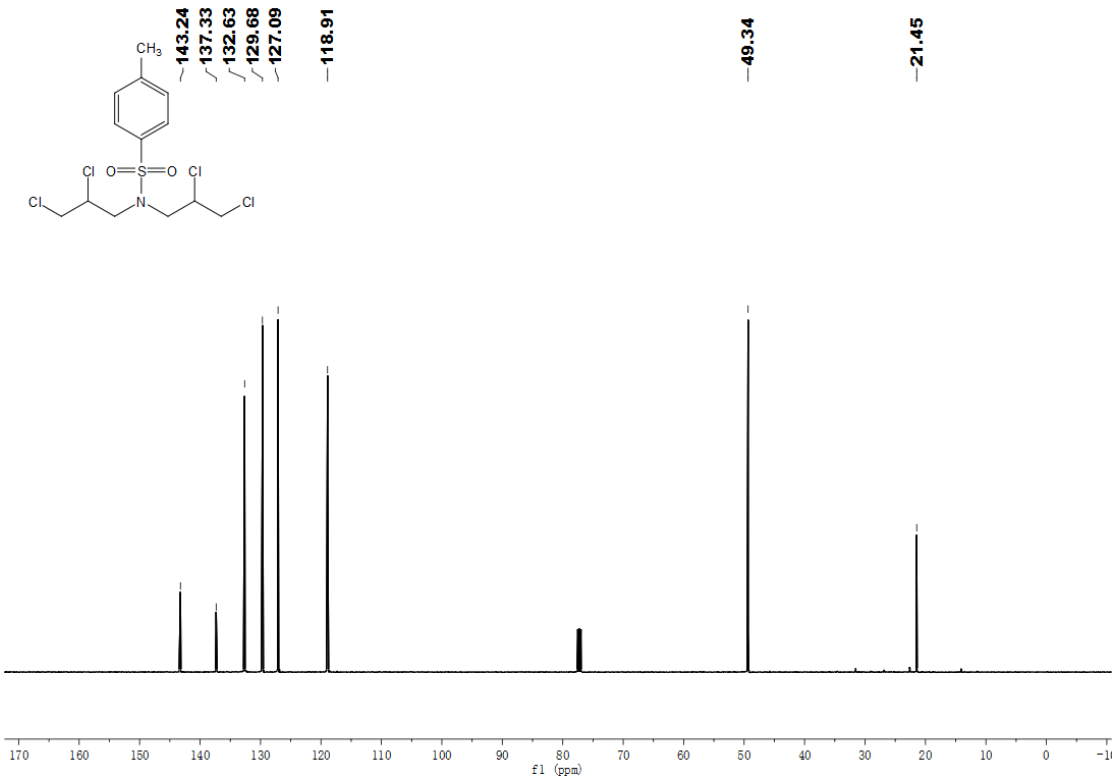
^{1}H NMR of compound **40** (500 MHz, $CDCl_3$)



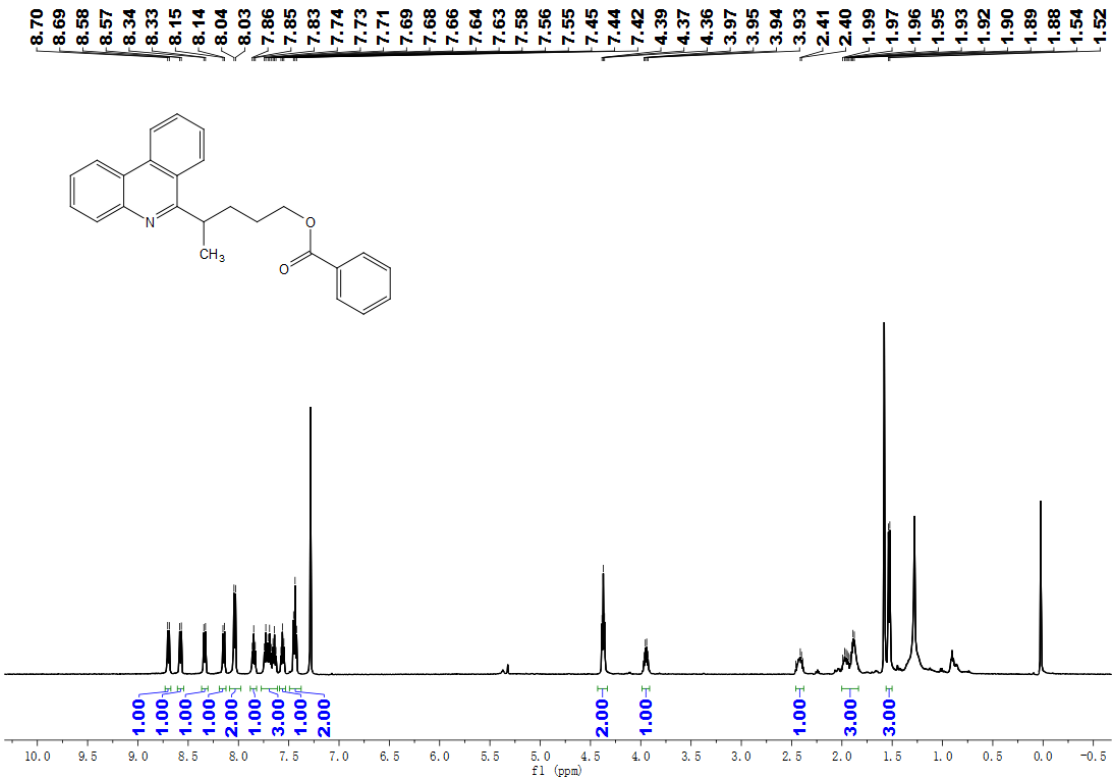
^{13}C NMR of compound **40** (126 MHz, $CDCl_3$)



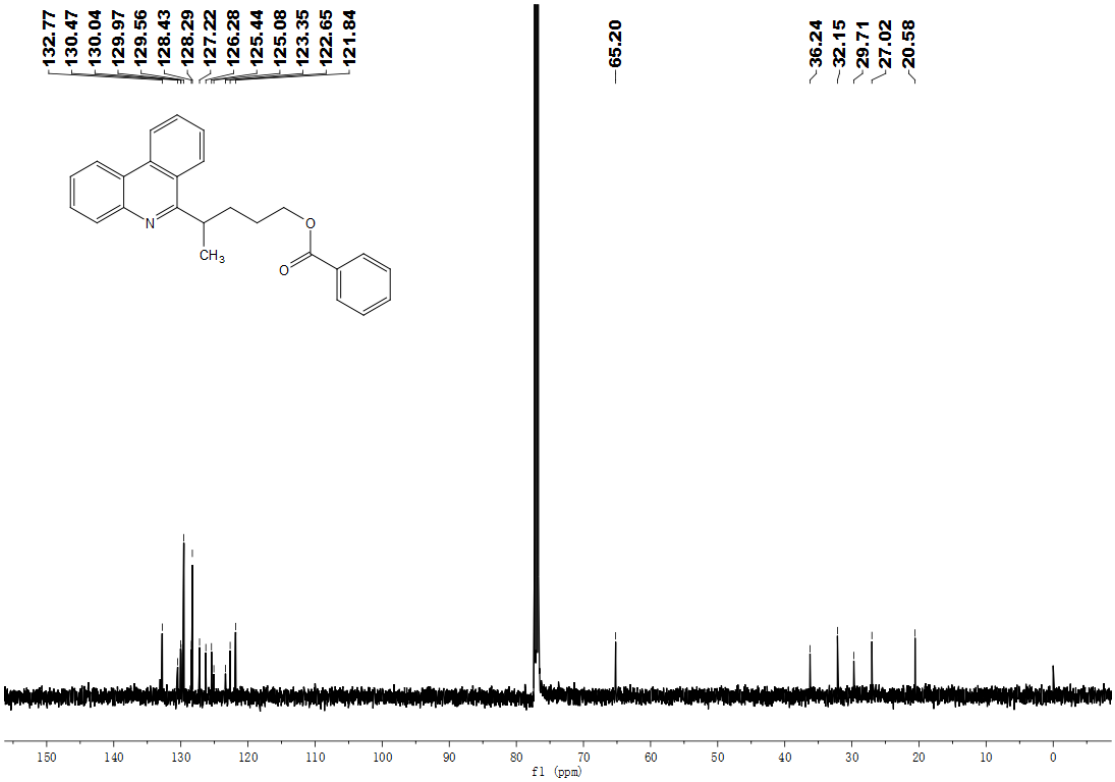
^{1}H NMR of compound **41** (500 MHz, $CDCl_3$)



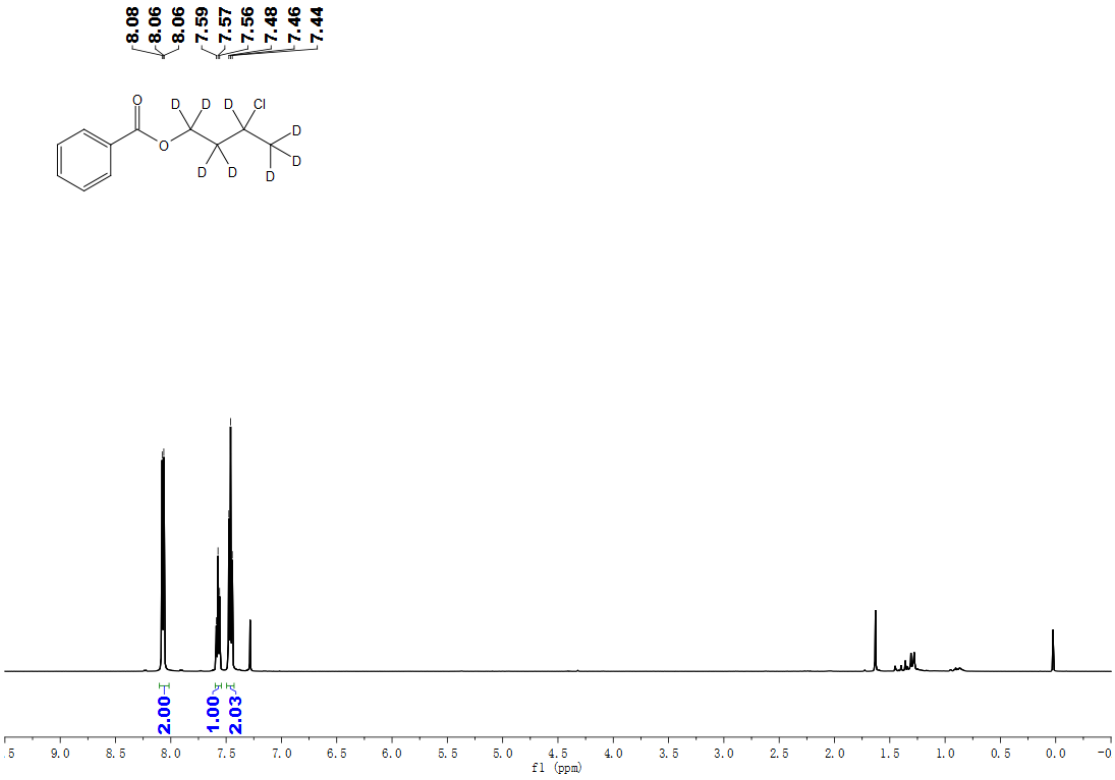
^{13}C NMR of compound **41** (126 MHz, $CDCl_3$)



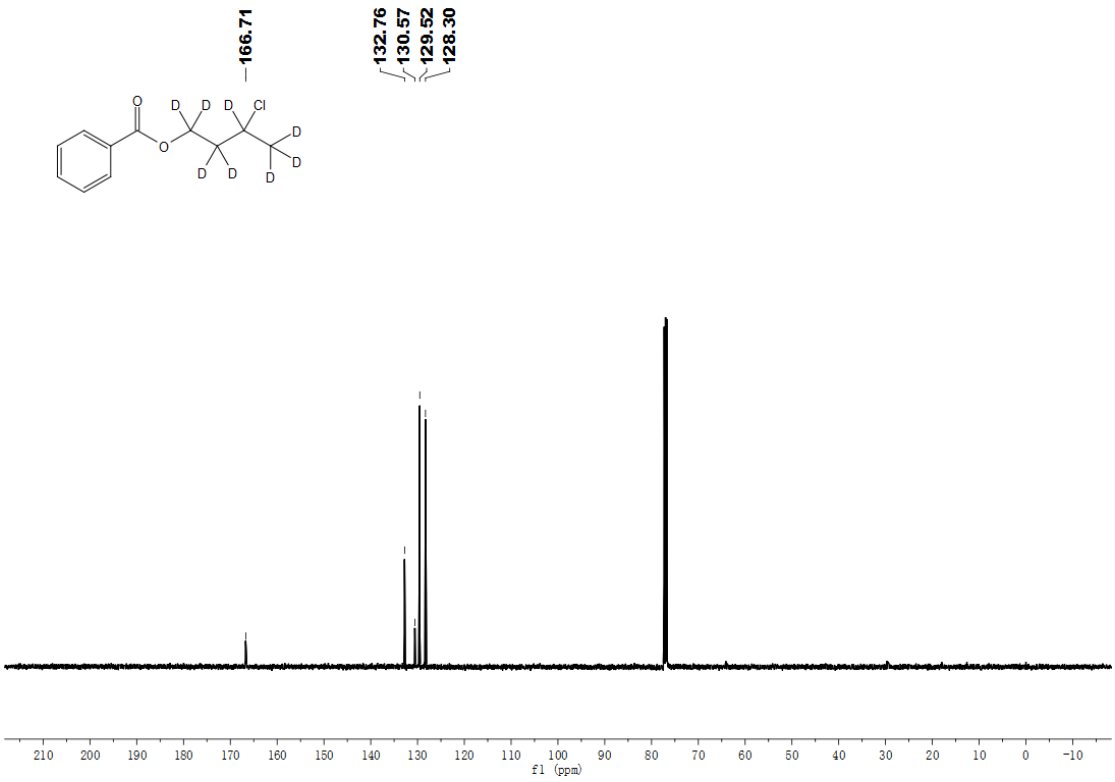
^{1}H NMR of compound **43** (500 MHz, $CDCl_3$)



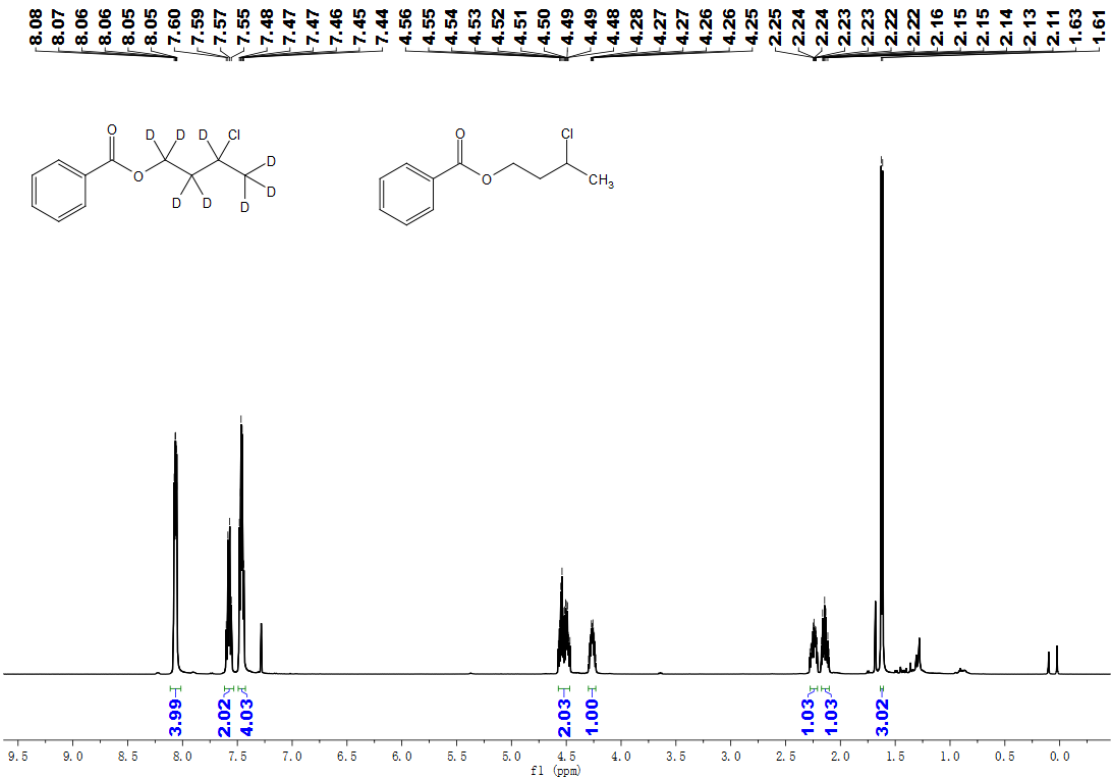
^{13}C NMR of compound **43** (126 MHz, $CDCl_3$)



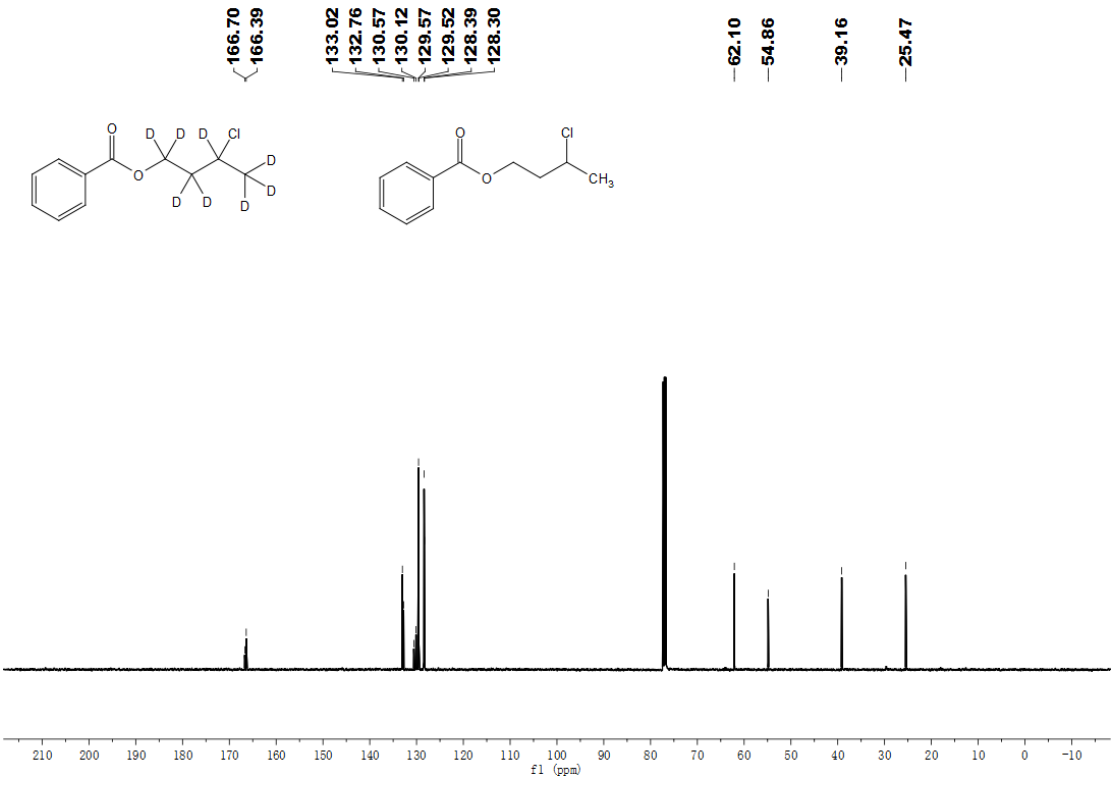
^{1}H NMR of compound **2b^{d8}** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **2b^{d8}** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **2b^{d8}** and **2b** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **2b^{d8}** and **2b** (126 MHz, $CDCl_3$)

15. GC-FID Data and HPLC Data

15.1 GC-FID Data

GC data of 1b

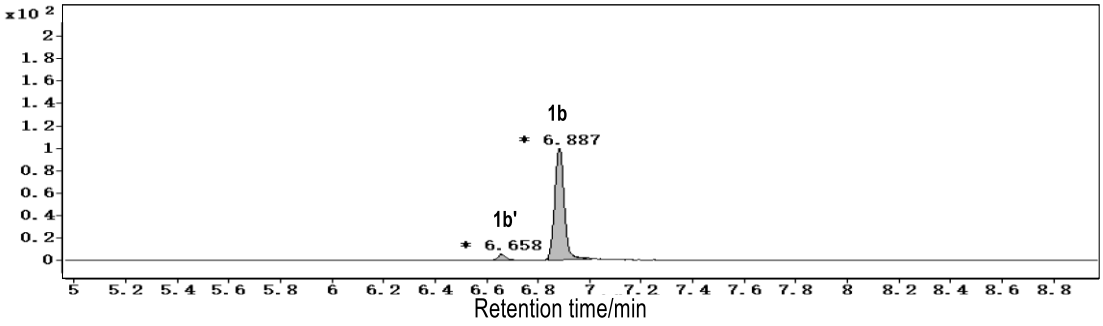


Figure S19. Chromatogram of **1a** reaction (general produce)

Chromatogram of **1a** reaction: Selectivity		
Product	Retention Time	Percent Area
1b'	6.658	3.87
1b	6.887	96.13

Table S8. Date of **1a** reaction (general produce)

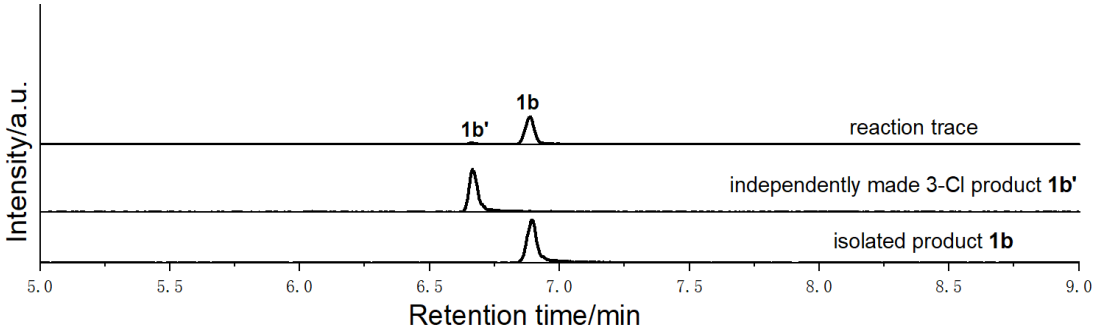


Figure S20. Overlaid Chromatogram: Chlorination of **1a** with authentic 3-Cl product

GC data of 2b

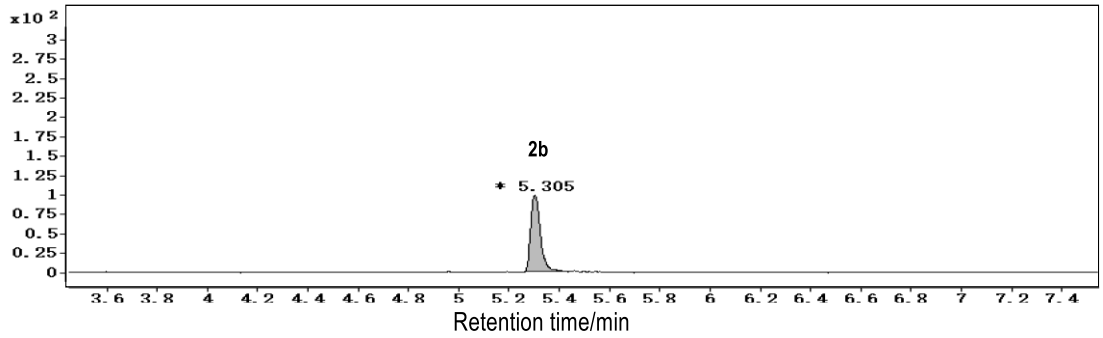


Figure S21. Chromatogram of **2a** reaction (general produce)

Chromatogram of **1a** reaction: Selectivity		
Product	Retention Time	Percent Area
2b'	---	---
1b	5.305	100

Table S9. Date of **1a** reaction (general produce)

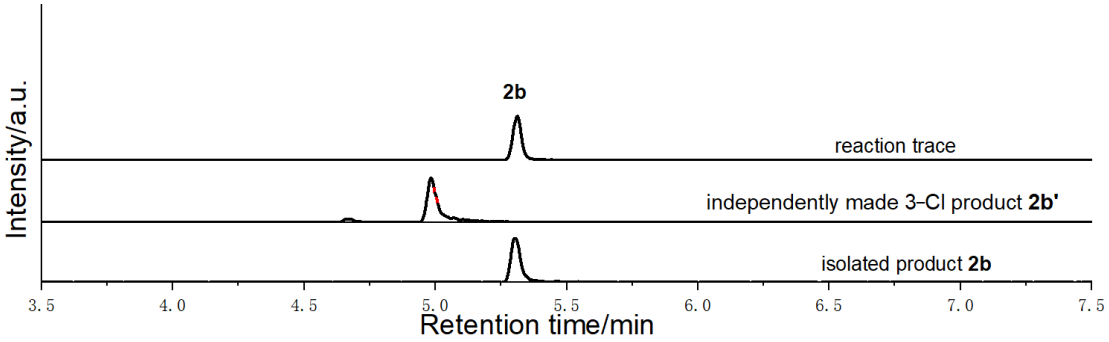


Figure S22. Overlaid Chromatogram: Chlorination of **2a** with authentic 3-Cl product

GC data of 3b

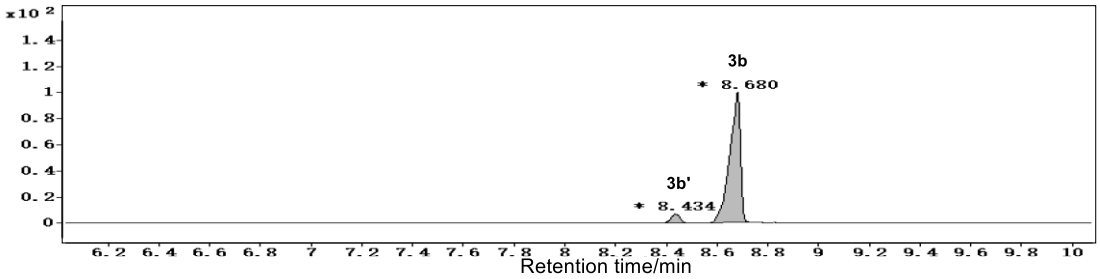


Figure S23. Chromatogram of **3a** reaction (general produce)

Chromatogram of **1a** reaction: Selectivity		
Product	Retention Time	Percent Area
3b'	8.434	5.31
3b	8.680	94.69

Table S10. Date of **3a** reaction (general produce)

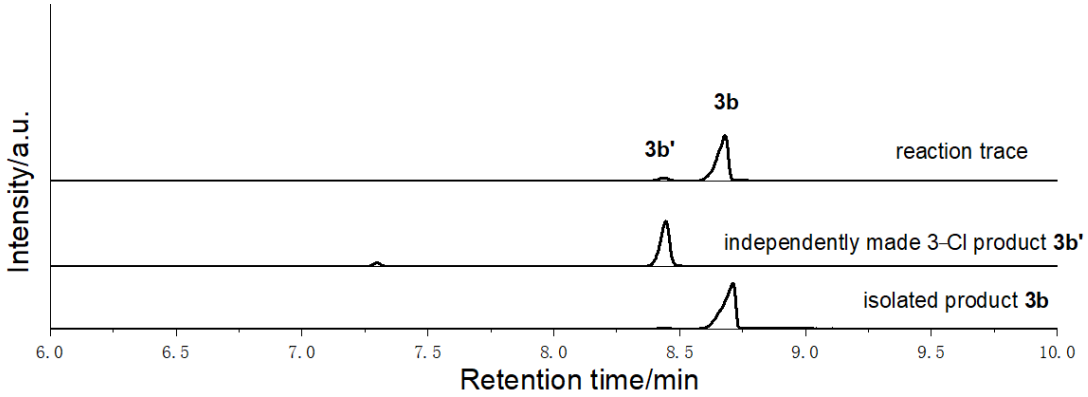


Figure S24. Overlaid Chromatogram: Chlorination of **3a** with authentic 3-Cl product

GC data of 4b

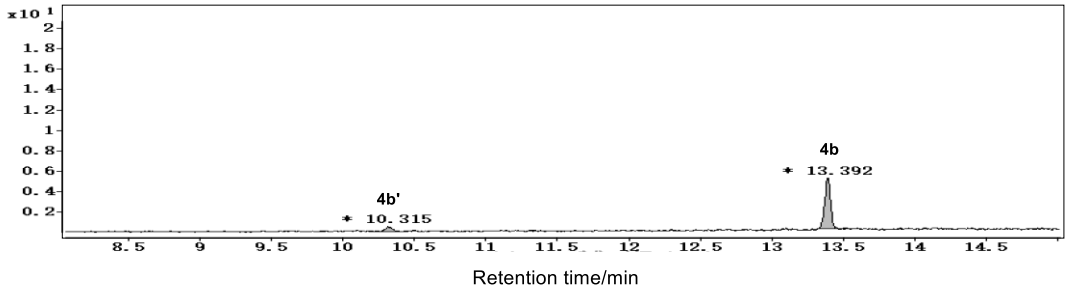


Figure S25. Chromatogram of **4a** reaction (general produce)

Chromatogram of **4a** reaction: Selectivity		
Product	Retention Time	Percent Area
4b'	10.315	8.17
4b	13.392	91.83

Table S11. Date of **4a** reaction (general produce)

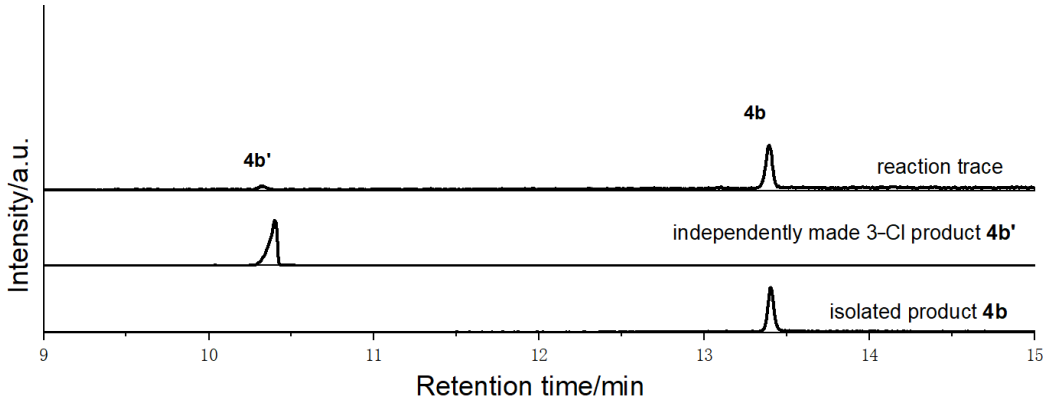


Figure S26. Overlaid Chromatogram: Chlorination of **4a** with authentic 3-Cl product

GC data of 8b

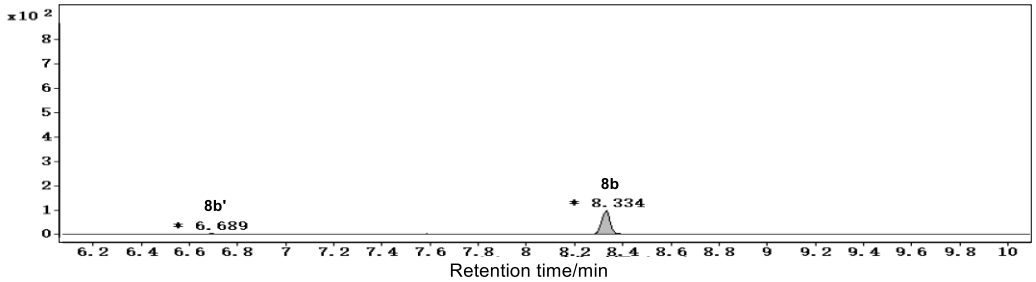


Figure S27. Chromatogram of **8a** reaction (general produce)

Chromatogram of **8a** reaction: Selectivity		
Product	Retention Time	Percent Area
8b'	6.689	2.83
8b	8.334	97.17

Table S12. Date of **8a** reaction (general produce)

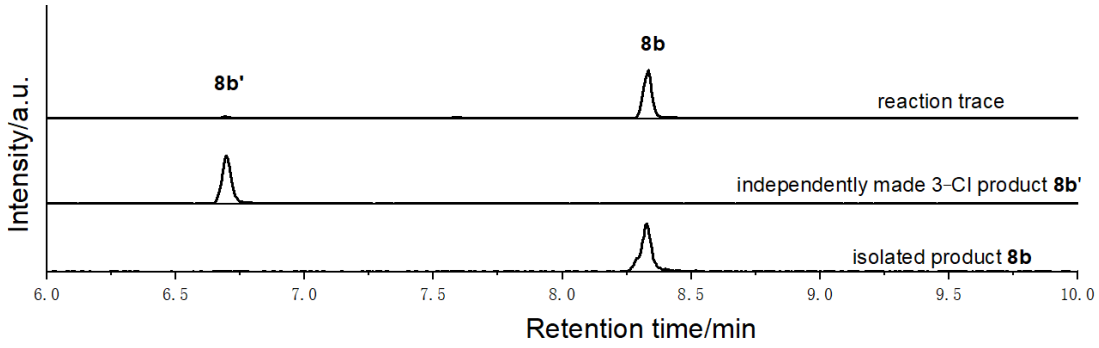


Figure S28. Overlaid Chromatogram: Chlorination of **8a** with authentic 3-Cl product

GC data of 11b

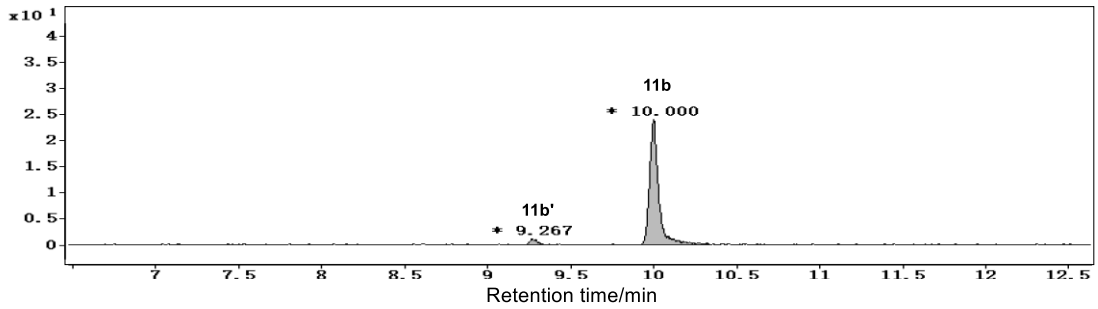


Figure S29. Chromatogram of **11a** reaction (general produce)

Chromatogram of **11a** reaction: Selectivity		
Product	Retention Time	Percent Area
11b'	9.267	3.14
11b	10.000	96.86

Table S13. Date of **8a** reaction (general produce)

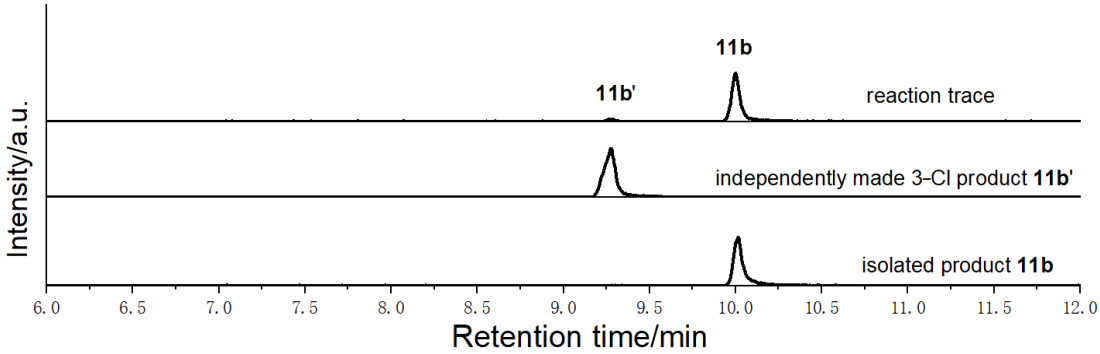


Figure S30. Overlaid Chromatogram: Chlorination of **11a** with authentic 3-Cl product

GC data of 14b

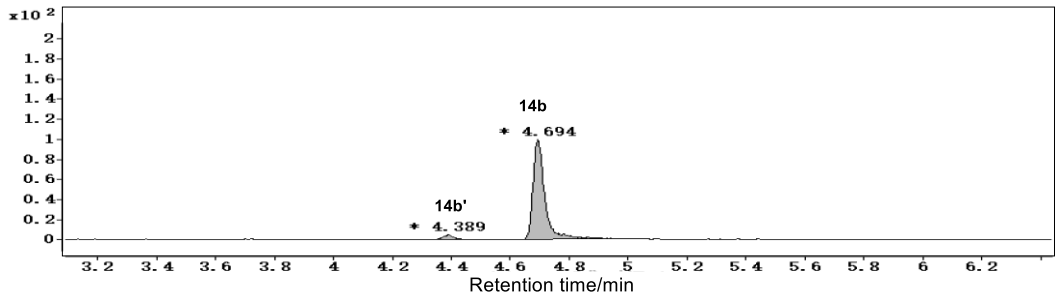


Figure S31. Chromatogram of **14a** reaction (general produce)

Chromatogram of **14a** reaction: Selectivity		
Product	Retention Time	Percent Area
11b'	4.389	4.32
11b	4.694	95.68

Table S14. Date of **14a** reaction (general produce)

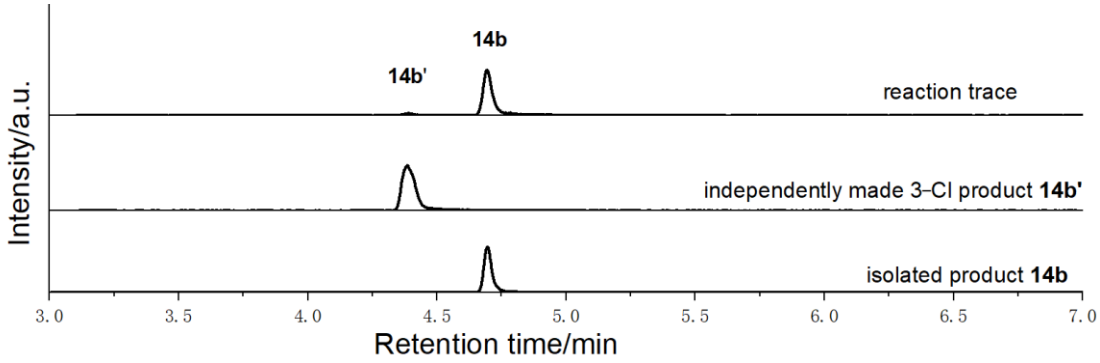


Figure S32. Overlaid Chromatogram: Chlorination of **11a** with authentic 3-Cl product

GC data of 19b

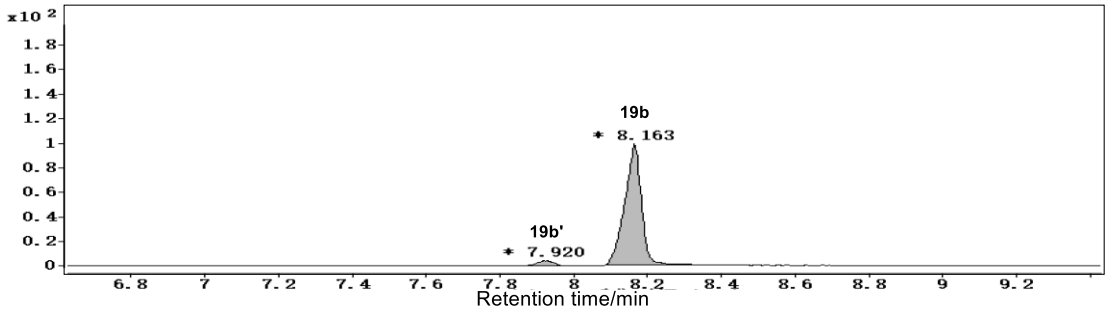


Figure S33. Chromatogram of **19a** reaction (general produce)

Chromatogram of **19a** reaction: Selectivity		
Product	Retention Time	Percent Area
19b'	6.092	3.97
19b	6.251	96.03

Table S15. Date of **20a** reaction (general produce)

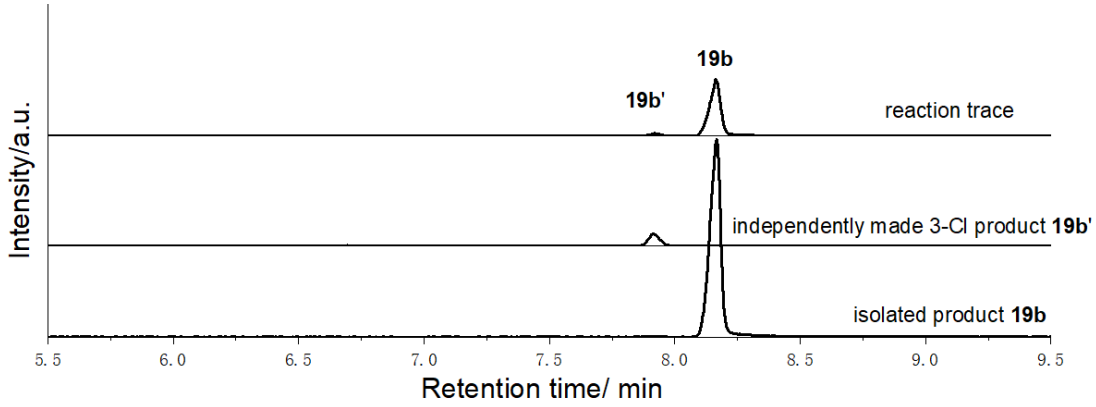


Figure S34. Overlaid Chromatogram: Chlorination of **19a** with authentic 3-Cl product

GC data of 20b

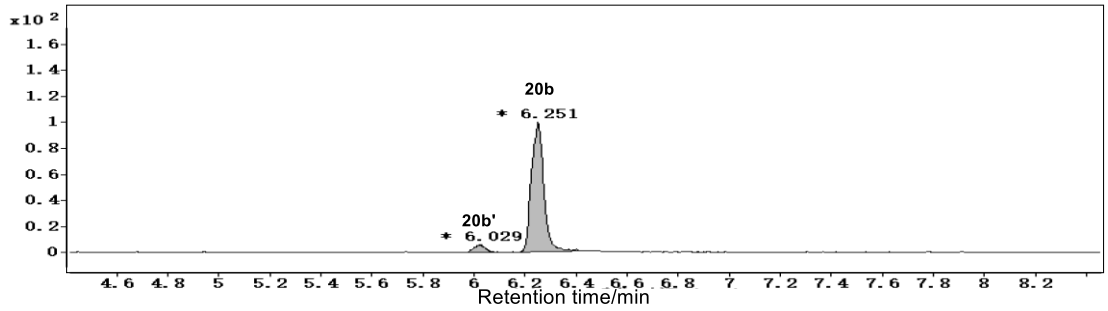


Figure S35. Chromatogram of **20a** reaction (general produce)

Chromatogram of **20a** reaction: Selectivity		
Product	Retention Time	Percent Area
20b'	6.092	3.97
20b	6.251	96.03

Table S16. Date of **20a** reaction (general produce)

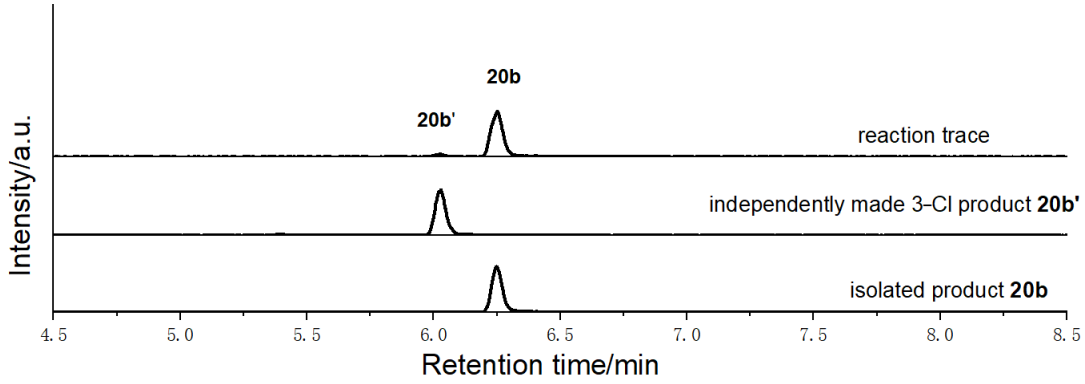


Figure S36. Overlaid Chromatogram: Chlorination of **20a** with authentic 3-Cl product

GC data of 23b

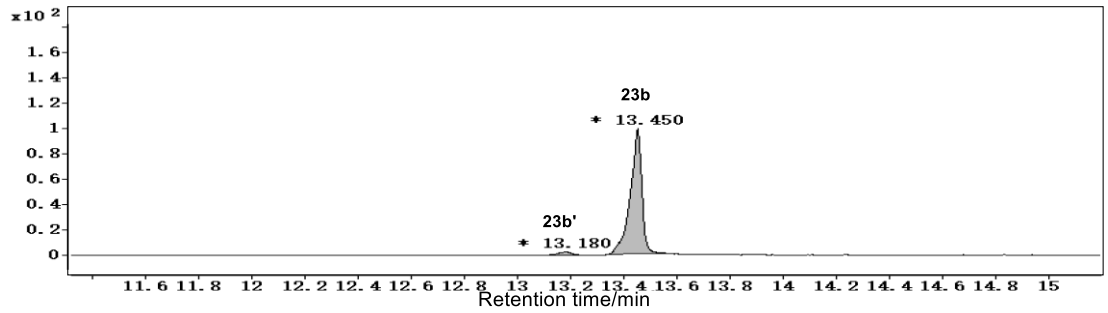


Figure S37. Chromatogram of **23a** reaction (general produce)

Chromatogram of **23a** reaction: Selectivity		
Product	Retention Time	Percent Area
23b'	13.180	3.75
23b	13.450	96.25

Table S17. Date of **23a** reaction (general produce)

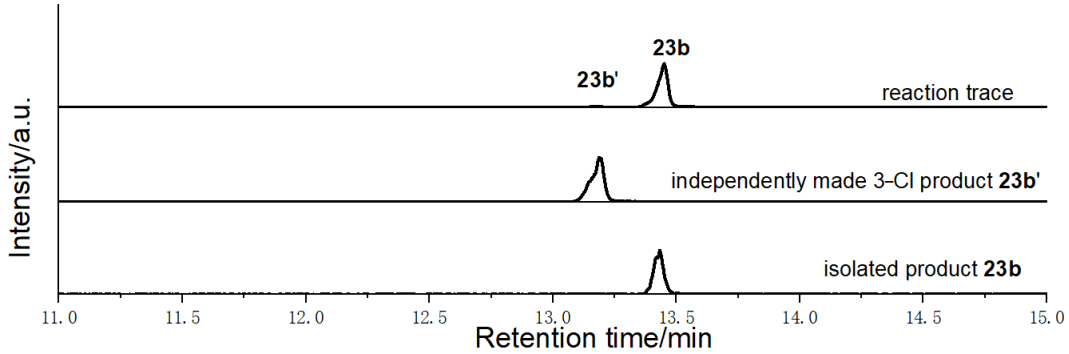


Figure S38. Overlaid Chromatogram: Chlorination of **23a** with authentic 3-Cl product

GC data of 29b

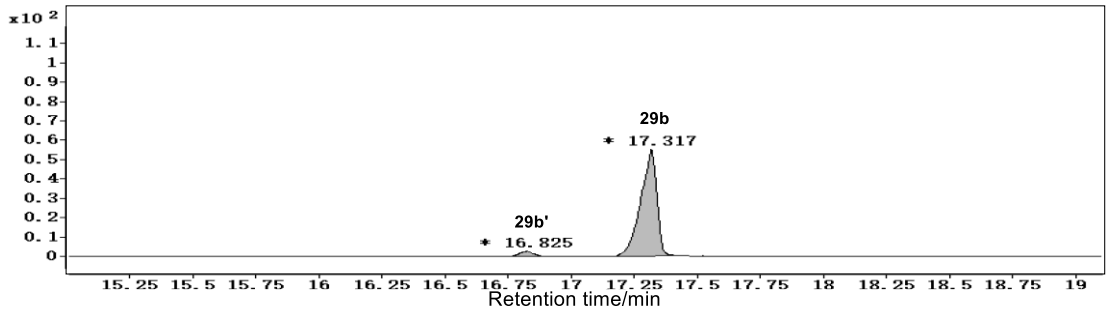


Figure S39. Chromatogram of **29a** reaction (general produce)

Chromatogram of **29a** reaction: Selectivity		
Product	Retention Time	Percent Area
29b'	16.852	3.42
29b	17.317	96.68

Table S18. Date of **29a** reaction (general produce)

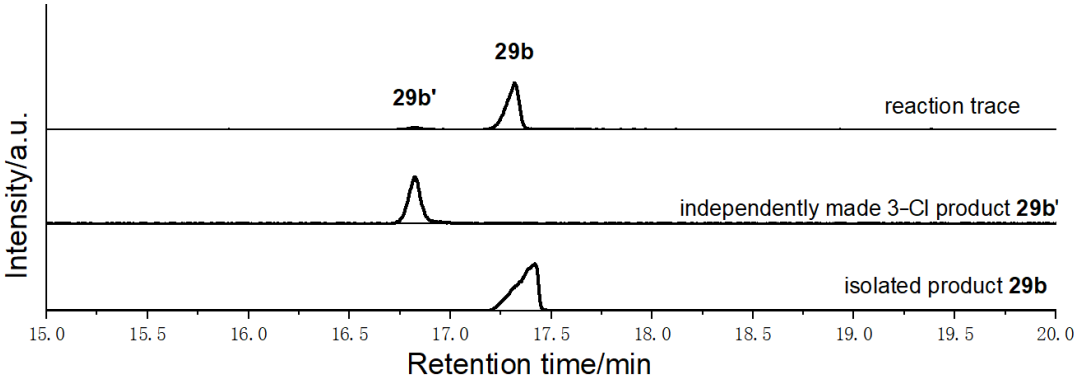


Figure S40. Overlaid Chromatogram: Chlorination of **23a** with authentic 3-Cl product

13.2 HPLC Data

HPLC data of 24b

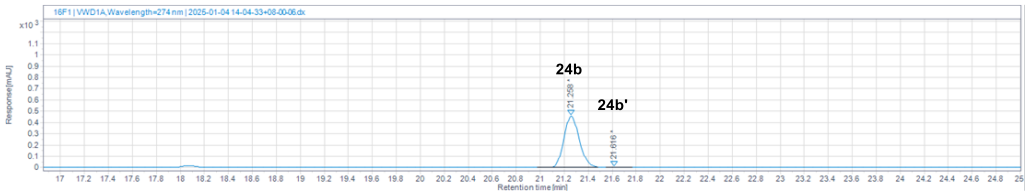


Figure S41. Chromatogram of **24a** reaction (general produce)

Chromatogram of **24a** reaction: Selectivity		
Product	Retention Time	Percent Area
24b	21.258	97.08
24b'	21.616	2.92

Table S19. Date of **24a** reaction (general produce)

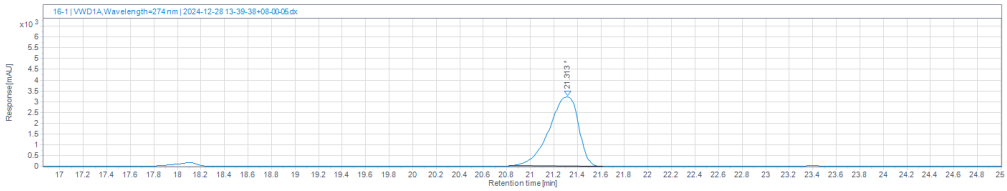


Figure S42. Chromatogram of standard **24b**

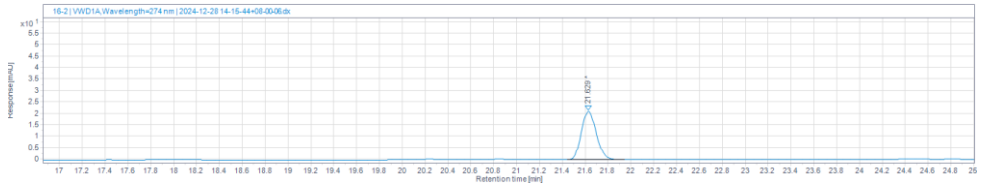


Figure S43. Chromatogram of standard **24b'**

HPLC data of 26b

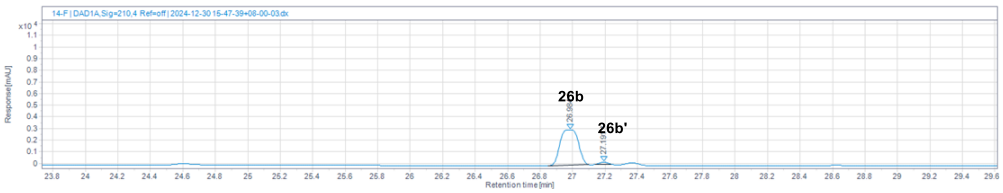


Figure S44. Chromatogram of **26a** reaction (general produce)

Chromatogram of **26a** reaction: Selectivity		
Product	Retention Time	Percent Area
26b	26.772	96.84
26b'	26.923	3.16

Table S20. Date of **26a** reaction (general produce)

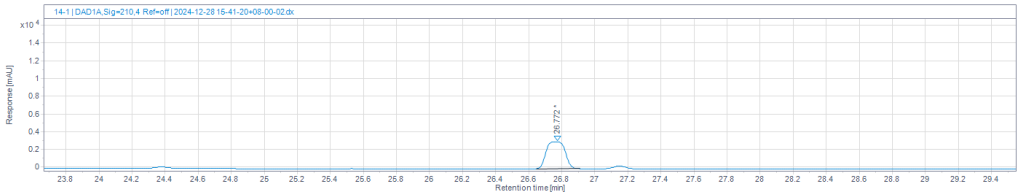


Figure S45. Chromatogram of standard **26b**

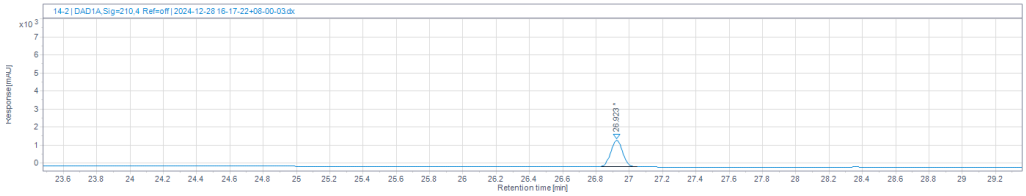


Figure S46. Chromatogram of standard **26b'**

HPLC data of 27b

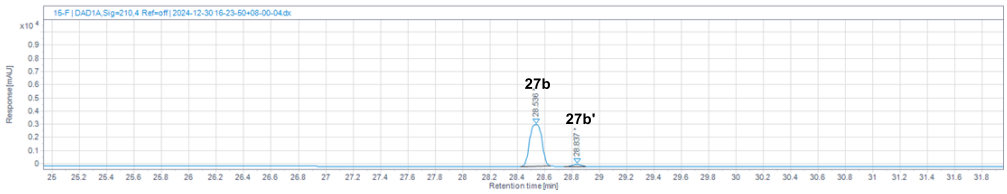


Figure S47. Chromatogram of **27a** reaction (general produce)

Chromatogram of **27a** reaction: Selectivity		
Product	Retention Time	Percent Area
27b	28.399	95.89
27b'	28.977	4.11

Table S21. Date of **27a** reaction (general produce)

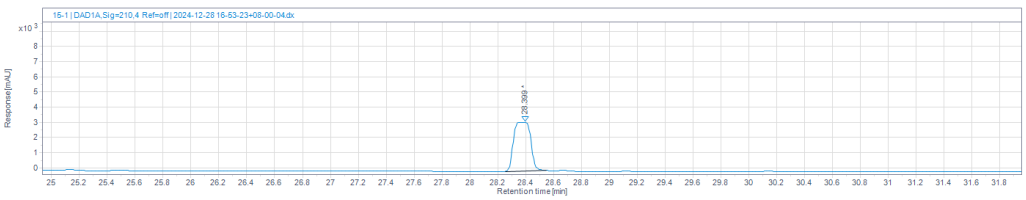


Figure S48. Chromatogram of standard **27b**

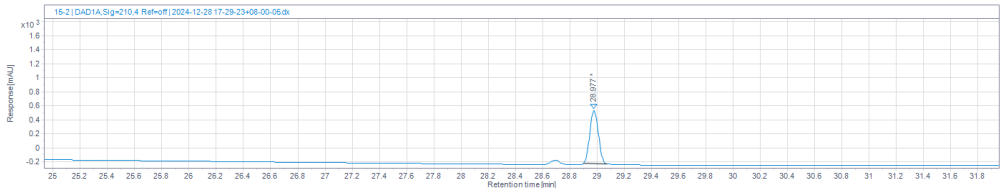


Figure S49. Chromatogram of standard **27b'**

HPLC data of 30b

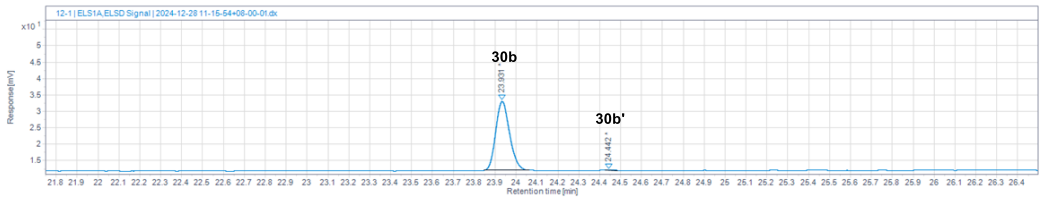


Figure S50. Chromatogram of **30a** reaction (general produce)

Chromatogram of **30a** reaction: Selectivity		
Product	Retention Time	Percent Area
30b	23.908	97.94
30b'	24.577	2.06

Table S22. Date of **27a** reaction (general produce)

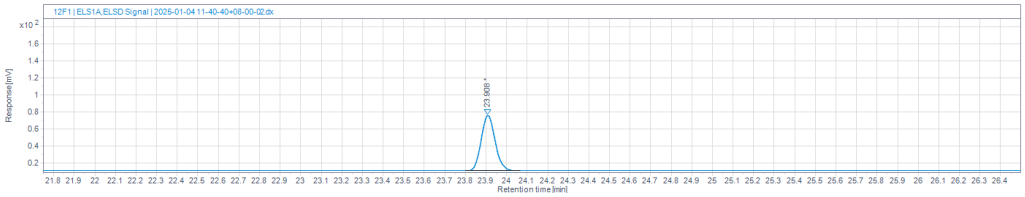


Figure S51. Chromatogram of standard **30b**

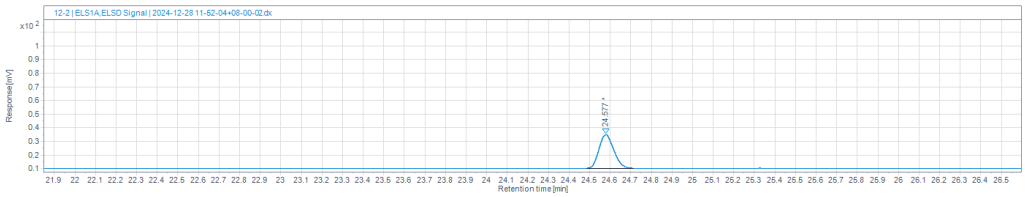


Figure S52. Chromatogram of standard **30b'**

HPLC data of 31b

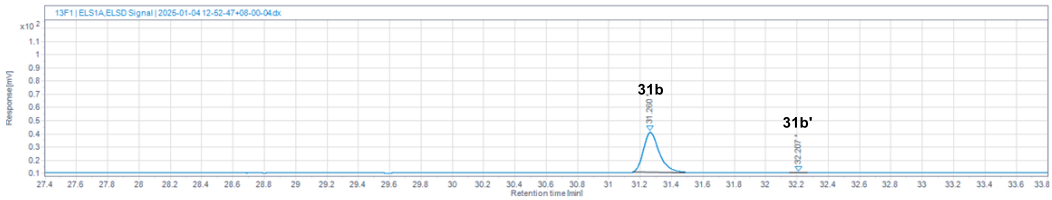


Figure S53. Chromatogram of **31a** reaction (general produce)

Chromatogram of **31a** reaction: Selectivity		
Product	Retention Time	Percent Area
31b	31.365	96.47
31b'	24.577	3.53

Table S23. Date of **31a** reaction (general produce)

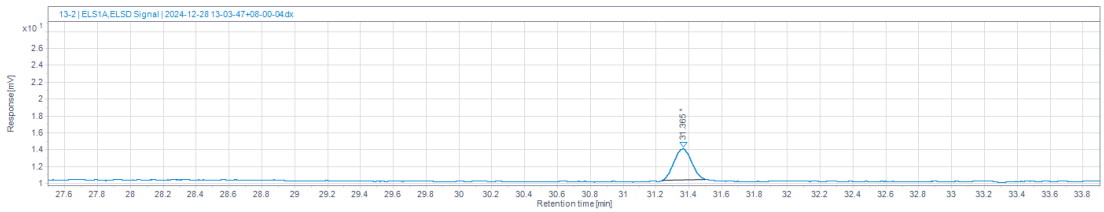


Figure S54. Chromatogram of standard **31b**

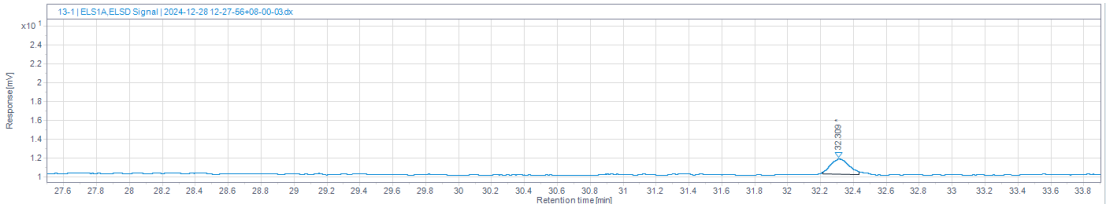


Figure S55. Chromatogram of standard **31b'**