Supporting Information

An Electrochemical Chlorination of Least Hindered Tertiary and Benzylic C(sp^3)-H Bonds

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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. Concentrated hydrochloric acid (aq. 37%, Hushi reagent) were used in the site selective functionalization of C(sp^3)-H bonds.

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.

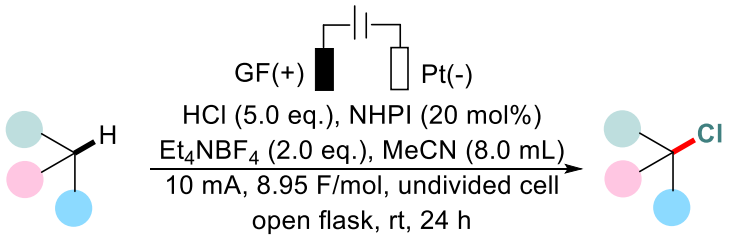
2. Instruments

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). All reactions were carried out in a 10 mL three-necked flask.

3. General Procedure

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

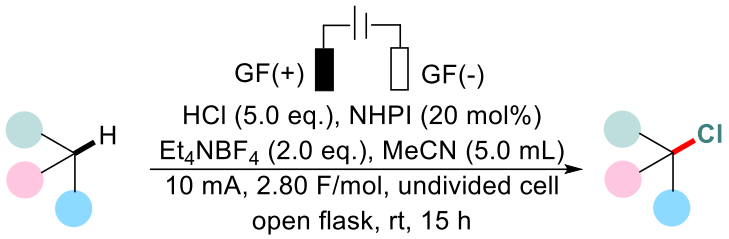
General Procedure A:



The 10 mL three-necked bottle was equipped with two rubber plugs, graphite felt (1

cm x 1 cm x 0.5 cm) and platinum sheet (1 cm x 1 cm x 0.2 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. Substrate (0.5 mmol, 1.0 equiv) and NHPI (0.1 mmol, 20 mol%) were first dissolved in CH_3CN (8.0 mL) and stirred for 5 min at room temperature. Then the mixture was added with Et_4NBF_4 (1.0 mmol, 2.0 equiv). Finally, HCl (concentrated, 2.5 mmol, 5.0 equiv) was added dropwise. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature (23 ^oC). After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (2 mL). Then the mixture was extracted with DCM (3 x 5 mL), the combined organic phase were 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.

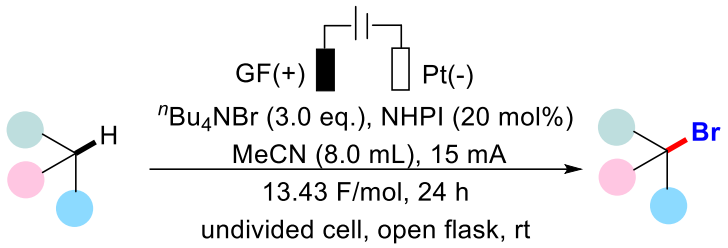
General Procedure B:



The 10 mL three-necked bottle was equipped with two rubber plugs, graphite felt (1.5 cm x 1.5 cm x 0.5 cm) as anode and cathode. The graphite felt anode and cathode attached to a platinum wire. Substrate (1.0 mmol, 1.0 equiv) and NHPI (0.2 mmol, 20 mol%) were first dissolved in CH_3CN (5.0 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, 5.0 mmol, 5.0 equiv) was added dropwise. The reaction mixture was stirred and electrolyzed with a constant current of 10 mA at room temperature (23 ^oC). After the reaction completed as monitored with TLC, the reaction mixture was quenched with 2 M NaOH (4 mL). Then the mixture was extracted with DCM (3 x 8 mL), the combined organic phase were washed with brine and dried over Na_2SO_4. Then the mixture was filtered and concentrated. The residue was purified by

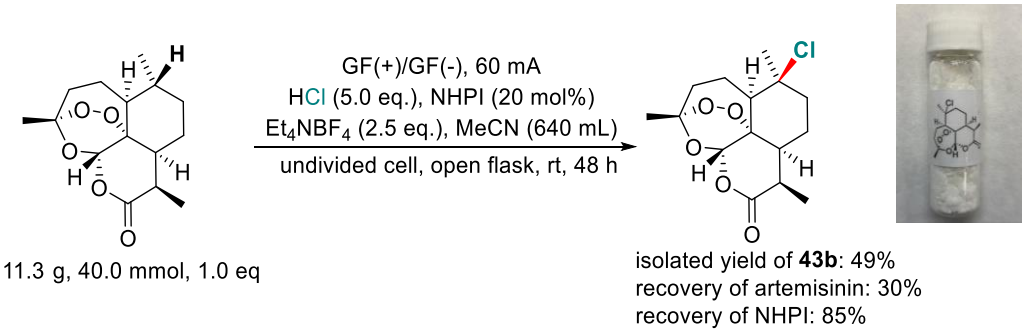
chromatography on silica gel to afford the desired product. It is worth noting that the reaction mixture always opened to air during C(sp^3)-H bonds chlorination reactions.

3.2 Electrochemical bromination of C(sp^3)-H bond



The 10 mL three-necked bottle was equipped with two rubber plugs, graphite felt (1 cm x 1 cm x 0.5 cm) and platinum sheet (1 cm x 1 cm x 0.2 cm) are used as anode and cathode respectively. The graphite felt anode attached to a platinum wire. Substrate (0.5 mmol, 1.0 equiv) and NHPI (0.1 mmol, 20 mol%) were first dissolved in CH_3CN (8.0 mL) and stirred for 5 min at room temperature. Then ^{n}Bu$_4$NBr (1.5 mmol, 3.0 equiv) was added. The reaction mixture was stirred and electrolyzed with a constant current of 15 mA at room temperature (23 ^{o}C). After the reaction completed as monitored with TLC, the reaction mixture was quenched with water (5 mL). Then the mixture was extracted with DCM (3 x 5 mL), the combined organic phase were 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 bromination reactions.

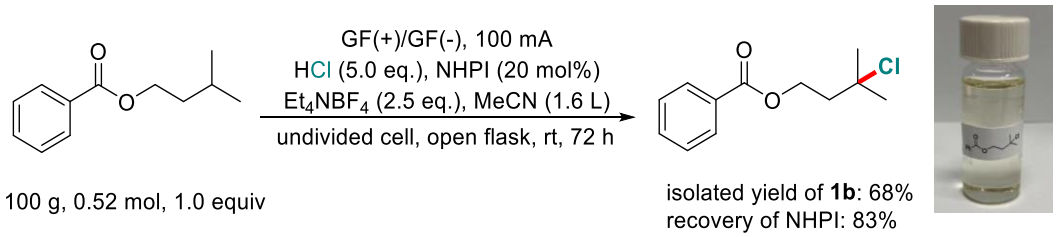
4. Gram-scale experiment:



11.3 g, 40.0 mmol, 1.0 eq

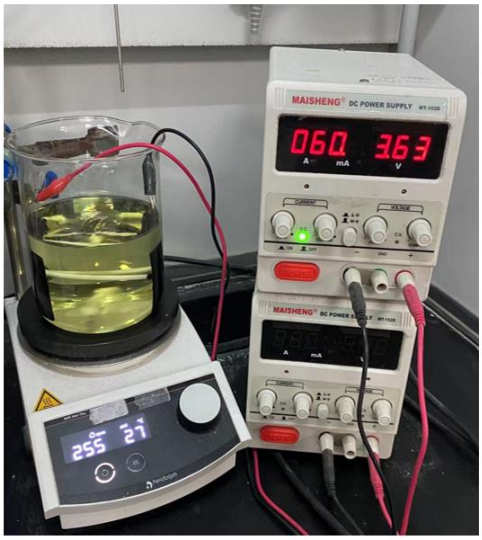
isolated yield of **43b**: 49%
recovery of artemisinin: 30%
recovery of NHPI: 85%

Put two graphite felts (5 cm x 6 cm x 0.5 cm) as both cathode and anode in a 1000 mL of beaker. The graphite felt electrodes attached to a platinum wire. Substrate **43a** (40.0 mmol, 1.0 equiv.) and NHPI (8.0 mmol, 20 mol%) were first dissolved in CH_3CN (640.0 mL) and stirred for 30 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.5 equiv.). Finally, HCl (concentrated, 200.0 mmol, 5.0 equiv.) was added dropwise in multiple portions every 3 hs. The reaction mixture was stirred and electrolyzed with a constant current of 60 mA at room temperature for 48 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 **43b** (6.19 g, 49 %). It is worth noting that the recovery rate of NHPI is 85 %.



Put two graphite felts (6 cm x 9 cm x 0.5 cm) as both cathode and anode in a 3000 mL of beaker. The graphite felt electrode attached to a platinum wire. Substrate **1a** (0.52 mol, 1.0 equiv.) and NHPI (20 mol%) were first dissolved in CH_3CN (1.6 L) and stirred for 30 min at room temperature. Then the mixture was added with Et_4NBF_4 (2.5 equiv). Finally, HCl (concentrated, 2.6 mol, 5.0 equiv) was added in multiple portions every 3 hs. The reaction mixture was stirred and electrolyzed with a constant current of 100 mA at room temperature for 72 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** (79.90 g, 68 %). It is worth noting that the recovery rate of NHPI is 83 %.

Note: The two graphite felts should be avoided direct contact during the reaction.



Graphite felt: 5 cm x 6 cm x 0.5 cm

Platinum wire: 0.5 mm x 10 cm

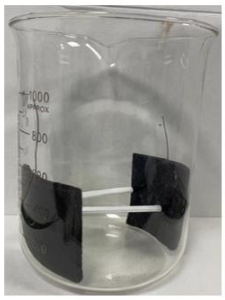
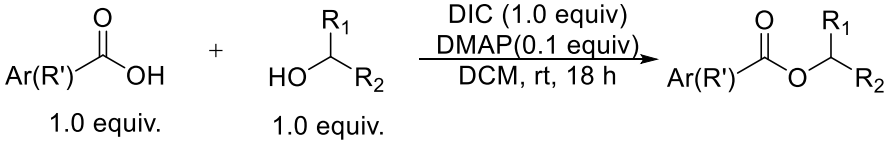


Figure 1. Reaction setup for gram-scale experiments.

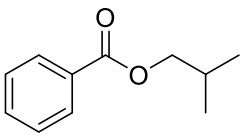
5. Synthesis of substrates

5.1 General procedure for synthesis of benzoates:



Carboxylic acid (10.0 mmol, 1.0 equiv) and 4-dimethylamino pyridine (1.0 mmol, 0.1 equiv) were added to a flask. Dichloromethane (30 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 CH_2Cl_2 (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 ester.

Isobutyl benzoate (2a)

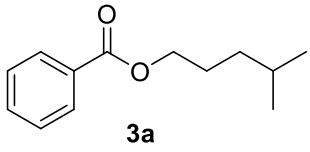


2a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.30 g, 73% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.11 (d, *J* = 6.6 Hz, 2H), 2.09 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.74, 132.92, 130.65, 129.65, 128.45, 71.12, 28.04, 19.33 [1].

4-Methylpentyl benzoate (3a)

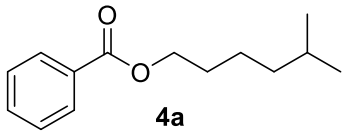


3a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.67 g, 81% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.41 (m, 2H), 4.31 (t, *J* = 6.8 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.61 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.32 (dd, *J* = 15.9, 6.9 Hz, 2H), 0.92 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.81, 132.91, 130.66, 129.65, 128.44, 65.53, 35.26, 27.90, 26.77, 22.66 [2].

5-Methylhexyl benzoate (4a)

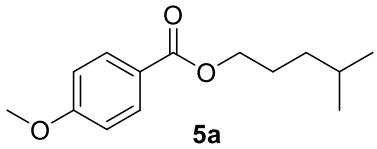


4a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.93 g, 88% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.56 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.44 (dt, *J* = 15.5, 7.6 Hz, 2H), 1.25 (dd, *J* = 15.8, 6.9 Hz, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.82, 132.91, 130.68, 129.66, 128.45, 65.27, 38.70, 29.09, 28.02, 23.97, 22.70. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{21}O_2$ 221.1536; Found: 221.1538.

4-Methylpentyl 4-methoxybenzoate (5a)



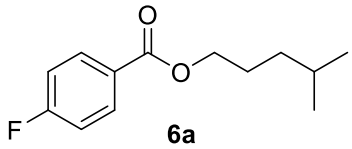
5a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.70 g,

72% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 6.93 – 6.90 (m, 2H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 1.74 (dd, *J* = 15.4, 7.3 Hz, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.31 (dd, *J* = 15.9, 6.9 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.55, 163.35, 131.64, 123.10, 113.67, 65.21, 55.51, 35.27, 27.89, 26.81, 22.65 [3].

4-Methylpentyl 4-fluorobenzoate (6a)

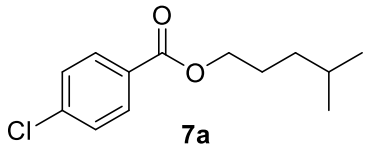


6a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.52 g, 68 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.9, 5.5 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.31 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.81, 165.32 (d, *J* = 130.4 Hz), 132.18 (d, *J* = 9.2 Hz), 126.88 (d, *J* = 3.0 Hz), 115.57 (d, *J* = 21.9 Hz), 65.67, 35.23, 27.90, 26.75, 22.65 [4].

4-Methylpentyl 4-chlorobenzoate (7a)

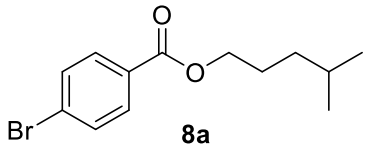


7a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.99 g, 83 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 1.75 (dt, *J* = 12.2, 6.9 Hz, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.30 (dd, *J* = 15.7, 7.1 Hz, 2H), 0.91 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.83, 139.30, 131.01, 129.06, 128.73, 65.72, 35.18, 27.85, 26.69, 22.60 [4].

4-Methylpentyl 4-bromobenzoate (8a)



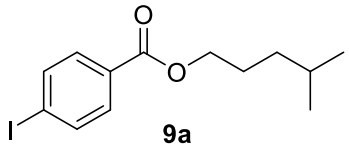
8a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.98 g,

70 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.63 – 1.57 (m, 1H), 1.30 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.05, 131.79, 131.20, 129.53, 128.01, 65.81, 35.21, 27.88, 26.71, 22.65 [4].

4-Methylpentyl 4-iodobenzoate (9a)

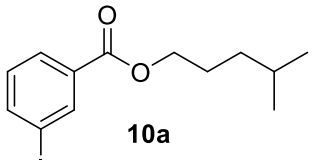


9a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.39 g, 72 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 4.28 (t, *J* = 6.8 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.30 (dd, *J* = 15.8, 7.1 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.25, 137.78, 131.12, 130.09, 100.68, 65.78, 35.19, 27.87, 26.69, 22.65 [4].

4-Methylpentyl 3-iodobenzoate (10a)

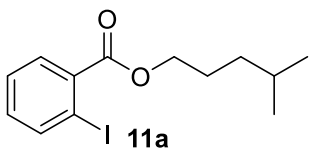


10a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.32 g, 70 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.29 (t, *J* = 6.8 Hz, 2H), 1.79 – 1.73 (m, 2H), 1.63 – 1.57 (m, 1H), 1.30 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.27, 141.75, 138.53, 132.52, 130.14, 128.83, 93.91, 65.95, 35.15, 27.87, 26.70, 22.64. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}IO_2$ 333.0346; Found: 333.0345.

4-Methylpentyl 2-iodobenzoate (11a)

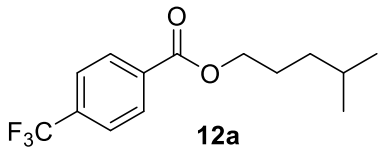


11a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.26 g, 68 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 4.31 (t, *J* = 6.8 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.32 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.74, 141.33, 135.61, 132.57, 130.91, 127.97, 94.08, 66.22, 35.19, 27.85, 26.59, 22.63. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}IO_2$ 333.0346; Found: 333.0344.

4-Methylpentyl 4-(trifluoromethyl)benzoate (12a)

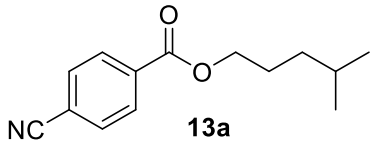


12a

R_f = 0.6, 5% acetone in hexane, yellowish oil (2.19 g, 80 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 4.33 (t, *J* = 6.8 Hz, 2H), 1.77 (dd, *J* = 15.4, 7.3 Hz, 2H), 1.65 – 1.58 (m, 1H), 1.32 (dd, *J* = 15.9, 6.9 Hz, 2H), 0.92 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.56, 134.98 – 133.78 (m), 130.07, 125.50 (q, *J* = 3.7 Hz), 124.88, 122.72, 66.11, 35.21, 27.89, 26.70, 22.63 [4].

4-Methylpentyl 4-cyanobenzoate (13a)

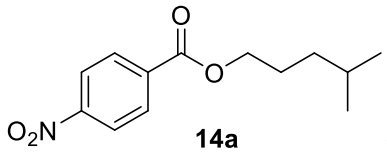


13a

R_f = 0.6, 5% acetone in hexane, yellowish oil (1.89 g, 82 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 4.32 (t, *J* = 6.8 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.60 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.30 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.05, 134.39, 132.27, 130.12, 118.08, 116.35, 66.30, 35.11, 27.81, 26.60, 22.57 [4].

4-Methylpentyl 4-nitrobenzoate (14a)

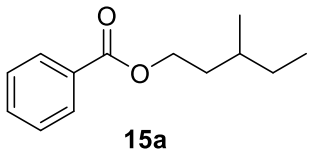


14a

R_f = 0.6, 5% acetone in hexane, yellowish oil (1.88 g, 75 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 9.0 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 1.79 (dd, *J* = 15.2, 7.5 Hz, 2H), 1.62 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.32 (dd, *J* = 15.5, 7.3 Hz, 2H), 0.92 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.89, 150.62, 136.02, 130.80, 123.67, 66.53, 35.18, 27.89, 26.67, 22.64 [4].

3-Methylpentyl benzoate (15a)

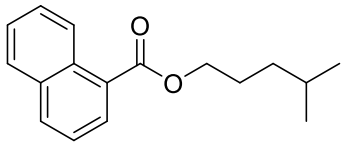


15a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.75 g, 85 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 4.42 – 4.29 (m, 2H), 1.86 – 1.73 (m, 1H), 1.62 – 1.51 (m, 2H), 1.40 (dt, *J* = 12.6, 7.4 Hz, 1H), 1.32 – 1.14 (m, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.64, 132.78, 130.58, 129.55, 128.32, 63.58, 35.23, 31.59, 29.46, 19.12, 11.28 [5].

4-Methylpentyl 1-naphthoate (16a)

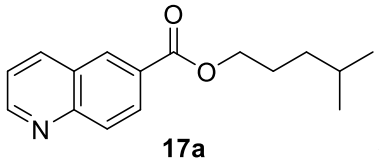


16a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.31 g, 90 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 – 8.90 (m, 1H), 8.19 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.56 – 7.48 (m, 2H), 4.41 (t, *J* = 6.8 Hz, 2H), 1.84 (dt, *J* = 12.2, 6.8 Hz, 2H), 1.65 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.38 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.95 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.83, 133.97, 133.31, 131.47, 130.16, 128.64, 127.79, 127.67, 126.29, 125.97, 124.63, 65.65, 35.35, 27.92, 26.82, 22.68 [4].

4-Methylpentyl quinoline-6-carboxylate (17a)

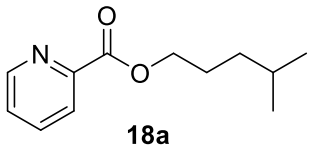


17a

R_f = 0.7, 10% acetone in hexane, yellowish oil (2.00 g, 78 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 – 8.92 (m, 1H), 8.58 – 8.50 (m, 1H), 8.31 – 8.16 (m, 2H), 8.15 – 8.07 (m, 1H), 7.42 (dd, *J* = 18.8, 6.2 Hz, 1H), 4.35 (dd, *J* = 12.2, 6.5 Hz, 2H), 1.79 (t, *J* = 10.2 Hz, 2H), 1.64 – 1.53 (m, 1H), 1.37 – 1.27 (m, 2H), 0.90 (d, *J* = 4.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.17, 152.47, 150.09, 137.36, 130.94, 129.81, 129.02, 128.53, 127.45, 121.85, 65.88, 35.19, 27.86, 26.73, 22.62 [4].

4-Methylpentyl picolinate (18a)

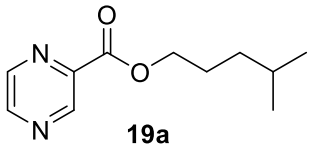


18a

R_f = 0.7, 10% acetone in hexane, yellowish oil (1.59 g, 77 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.82 (t, *J* = 8.6 Hz, 1H), 7.45 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.37 (t, *J* = 7.1 Hz, 2H), 1.85 – 1.75 (m, 2H), 1.58 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.28 (dd, *J* = 15.9, 7.0 Hz, 2H), 0.88 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.35, 149.98, 148.41, 137.04, 126.86, 125.17, 66.45, 34.99, 27.86, 26.70, 22.58 [6].

4-Methylpentyl pyrazine-2-carboxylate (19a)

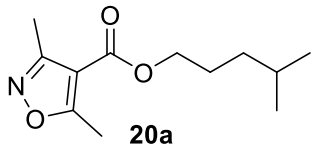


19a

R_f = 0.7, 10% acetone in hexane, yellowish oil (1.83 g, 88 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 – 9.19 (m, 1H), 8.73 (d, *J* = 12.0 Hz, 2H), 4.41 (dd, *J* = 12.3, 5.4 Hz, 2H), 1.81 (dd, *J* = 14.8, 7.7 Hz, 2H), 1.64 – 1.51 (m, 1H), 1.34 – 1.25 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.06, 147.66, 146.36, 144.55, 143.73, 66.87, 34.96, 27.84, 26.63, 22.57 [4].

4-Methylpentyl 3,5-dimethylisoxazole-4-carboxylate (20a)

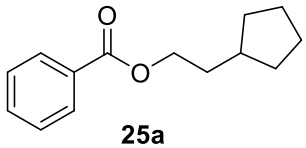


20a

R_f = 0.7, 10% acetone in hexane, yellowish oil (1.37 g, 61 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (t, *J* = 6.7 Hz, 2H), 2.62 (s, 3H), 2.40 (s, 3H), 1.74 – 1.66 (m, 2H), 1.57 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.27 (dd, *J* = 16.0, 6.9 Hz, 2H), 0.88 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.17, 162.59, 159.94, 108.87, 65.03, 35.24, 27.79, 26.59, 22.56, 13.40, 11.92. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{20}NO_3$ 226.1438; Found: 226.1440.

2-Cyclopentylethyl benzoate (25a)

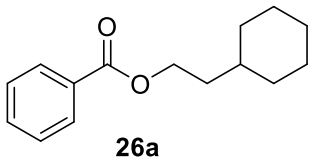


25a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.83 g, 84 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.89 (m, 1H), 1.88 – 1.76 (m, 4H), 1.67 – 1.60 (m, 2H), 1.59 – 1.50 (m, 2H), 1.21 – 1.13 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.78, 132.87, 130.65, 129.63, 128.41, 64.81, 37.19, 34.96, 32.80, 25.19. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{19}O_2$ 219.1380; Found: 219.1382.

2-Cyclohexylethyl benzoate (26a)



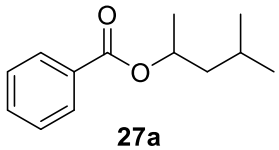
26a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.88 g, 81 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.36 (t, *J* = 6.8 Hz, 2H), 1.78 (d, *J* = 13.3 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.65 (dd, *J* = 14.5, 7.6 Hz, 3H), 1.46 (qd, *J* = 10.8, 7.3 Hz, 1H), 1.22 (dt, *J* = 24.0,

12.3 Hz, 3H), 0.98 (q, *J* = 12.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.82, 132.89, 130.68, 129.65, 128.44, 63.43, 36.21, 34.86, 33.34, 26.62, 26.35 [6].

4-Methylpentan-2-yl benzoate (27a)

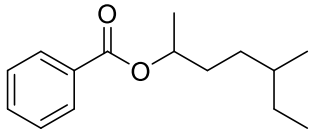


27a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.44 g, 70 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 5.34 – 5.15 (m, 1H), 1.77 – 1.68 (m, 2H), 1.46 – 1.37 (m, 1H), 1.33 (d, *J* = 6.2 Hz, 3H), 0.96 – 0.92 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.35, 132.82, 131.05, 129.64, 128.41, 70.32, 45.41, 24.98, 23.15, 22.53, 20.74 [7].

5-Methylheptan-2-yl benzoate (28a)

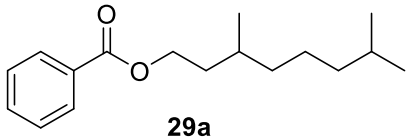


28a

R_f = 0.7, 5% acetone in hexane, yellowish oil (1.78 g, 76 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 7.95 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.25 – 5.04 (m, 1H), 1.78 – 1.55 (m, 2H), 1.48 – 1.37 (m, 1H), 1.34 (d, *J* = 6.2 Hz, 5H), 1.24 – 1.09 (m, 2H), 0.88 – 0.84 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.35, 132.80, 131.07, 129.62, 128.40, 72.15, 34.43, 33.69, 32.19, 29.45, 20.26, 19.28, 11.46. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{23}O_2$ 235.1693; Found: 235.1694.

3,7-Dimethyloctyl benzoate (29a)



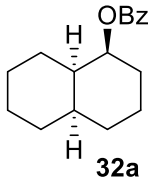
29a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.21 g, 84 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 4.42 – 4.32 (m, 2H), 1.81 (td, *J* = 12.3, 7.1 Hz, 1H), 1.65 (dt, *J* = 12.5, 6.4 Hz, 1H), 1.54 (dtd, *J* = 19.9, 13.4, 6.6 Hz, 2H), 1.37 – 1.26 (m, 3H), 1.20 –

1.12 (m, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.79, 132.89, 130.66, 129.64, 128.42, 63.69, 39.32, 37.28, 35.71, 30.10, 28.08, 24.76, 22.81, 22.72, 19.75 [8].

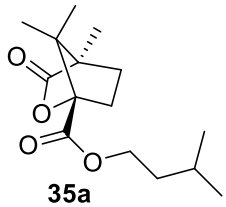
(4a*R*,8a*R*)-Decahydronaphthalen-1-yl benzoate (32a)



32a R_f = 0.7, 5% acetone in hexane, yellowish oil (2.27 g, 88 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 5.08 – 5.02 (m, 1H), 2.12 (q, *J* = 8.4 Hz, 1H), 1.85 – 1.76 (m, 3H), 1.66 – 1.52 (m, 6H), 1.44 (ddd, *J* = 13.1, 9.4, 3.6 Hz, 3H), 1.28 – 1.11 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.04, 132.80, 131.14, 129.67, 128.40, 76.62, 40.28, 35.67, 31.75, 26.26, 26.15, 24.65, 24.27, 21.53, 20.26 [9].

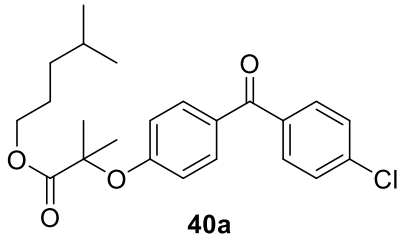
Isopentyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (35a)



35a R_f = 0.7, 10% acetone in hexane, white solid (2.14 g, 80 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (t, *J* = 6.9 Hz, 2H), 2.40 – 2.35 (m, 1H), 1.97 (dd, *J* = 15.7, 7.0 Hz, 1H), 1.88 (dd, *J* = 19.8, 6.7 Hz, 1H), 1.64 (dd, *J* = 18.9, 5.5 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.06 (s, 3H), 1.01 (s, 3H), 0.89 (dd, *J* = 8.0, 6.5 Hz, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.25, 167.60, 91.24, 64.33, 54.83, 54.16, 37.29, 30.69, 29.03, 25.06, 22.47, 22.44, 16.86, 16.80, 9.78. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{25}O_4$ 269.1747; Found: 269.1747.

4-Methylpentyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (40a)

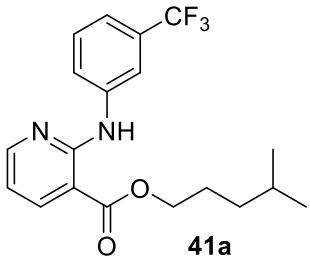


40a

R_f = 0.7, 5% acetone in hexane, yellowish oil (2.73 g, 68 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.12 (dd, *J* = 7.5, 5.8 Hz, 2H), 1.65 (s, 6H), 1.55 (dd, *J* = 15.4, 7.2 Hz, 2H), 1.49 – 1.41 (m, 1H), 1.07 (dd, *J* = 15.8, 7.1 Hz, 2H), 0.79 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.12, 173.74, 159.77, 138.35, 136.45, 132.06, 131.17, 130.30, 128.56, 117.21, 79.45, 66.13, 34.86, 27.62, 26.35, 25.49, 22.47 [4].

4-Methylpentyl 2-((3-(trifluoromethyl)phenyl)amino)nicotinate (41a)

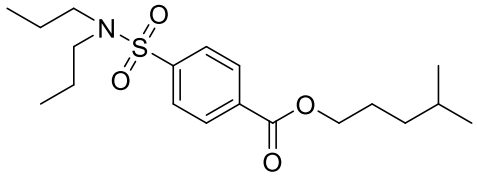


41a

R_f = 0.5, 10% acetone in hexane, yellowish oil (2.05 g, 56 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 8.46 – 8.35 (m, 1H), 8.25 (dd, *J* = 20.4, 8.8 Hz, 1H), 8.10 (s, 1H), 7.88 (t, *J* = 8.2 Hz, 1H), 7.41 (dt, *J* = 16.2, 8.0 Hz, 1H), 7.26 (s, 1H), 6.82 – 6.71 (m, 1H), 4.40 – 4.24 (m, 2H), 1.87 – 1.71 (m, 2H), 1.70 – 1.53 (m, 1H), 1.40 – 1.25 (m, 2H), 0.93 (d, *J* = 15.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.67, 155.90, 153.05, 140.54, 140.29, 131.26 (q, *J* = 32.0 Hz), 129.31, 125.42, 123.54, 119.16 – 118.96 (m), 117.18 (q, *J* = 3.9 Hz), 114.18, 107.88, 66.02, 35.23, 27.91, 26.68, 22.64 [4].

4-Methylpentyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (42a)

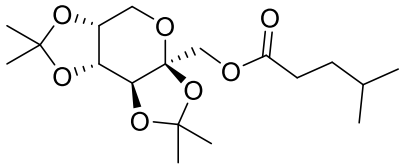


42a

R_f = 0.7, 10% acetone in hexane, yellowish oil (3.03 g, 82 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 4.29 (t, *J* = 6.8 Hz, 2H), 3.14 – 3.01 (m, 4H), 1.79 – 1.68 (m, 2H), 1.61 – 1.46 (m, 5H), 1.28 (dd, *J* = 15.4, 7.3 Hz, 2H), 0.90 – 0.80 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.30, 144.14, 133.82, 130.19, 127.00, 66.07, 49.97, 35.08, 27.77, 26.58, 22.53, 21.98, 11.18. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{32}NO_4S$ 370.2047; Found: 370.2045.

(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-methylpentanoate (44a)

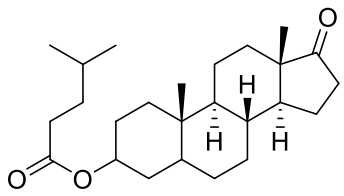


44a

R_f = 0.7, 10% acetone in hexane, colorless oil (2.72 g, 76 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, *J* = 10.5 Hz, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.29 (s, 1H), 4.23 (d, *J* = 8.9 Hz, 1H), 4.02 (d, *J* = 11.7 Hz, 1H), 3.89 (d, *J* = 11.2 Hz, 1H), 3.75 (d, *J* = 13.0 Hz, 1H), 2.38 – 2.29 (m, 2H), 1.58 – 1.50 (m, 6H), 1.47 (s, 3H), 1.39 (s, 3H), 1.33 (s, 3H), 0.88 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.36, 109.24, 108.81, 101.71, 70.90, 70.66, 70.19, 65.30, 61.35, 33.68, 32.29, 27.75, 26.61, 26.01, 25.34, 24.19, 22.32. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{31}O_7$ 359.2064; Found: 359.2065.

(8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 4-methylpentanoate (45a)

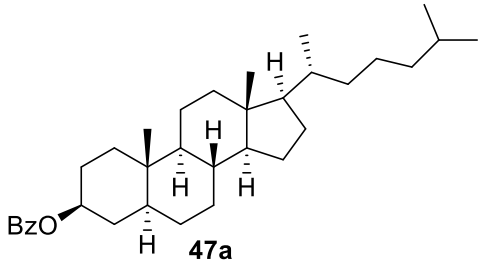


45a

R_f = 0.5, 10% acetone in hexane, white solid (2.21 g, 57 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.71 – 4.61 (m, 1H), 2.40 (dd, *J* = 19.3, 8.5 Hz, 1H), 2.28 – 2.18 (m, 2H), 2.08 – 1.99 (m, 1H), 1.94 – 1.86 (m, 1H), 1.82 – 1.69 (m, 4H), 1.67 – 1.56 (m, 2H), 1.56 – 1.37 (m, 6H), 1.36 – 1.30 (m, 2H), 1.29 – 1.12 (m, 5H), 0.97 (ddd, *J* = 19.8, 18.0, 8.6 Hz, 2H), 0.87 (d, *J* = 6.4 Hz, 6H), 0.83 (d, *J* = 1.4 Hz, 6H), 0.72 – 0.65 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.20, 173.66, 73.27, 54.42, 51.46, 47.85, 44.76, 36.82, 35.92, 35.75, 35.13, 34.07, 33.97, 32.90, 31.63, 30.91, 28.38, 27.80, 27.54, 22.34, 21.87, 20.56, 13.91, 12.31 [10].

(3*S*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl benzoate (47a)

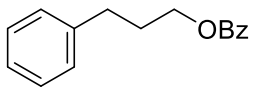


47a

R_f = 0.7, 5% EtOAc in hexane, white solid (3.79 g, 77 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.99 – 4.91 (m, 1H), 1.96 (dd, *J* = 15.9, 12.8 Hz, 2H), 1.86 – 1.71 (m, 3H), 1.66 (t, *J* = 10.7 Hz, 2H), 1.55 (ddd, *J* = 18.9, 16.4, 7.8 Hz, 4H), 1.44 – 1.27 (m, 7H), 1.24 (dd, *J* = 18.4, 10.3 Hz, 3H), 1.11 (dt, *J* = 19.1, 10.7 Hz, 6H), 1.05 – 0.94 (m, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.82 (m, 10H), 0.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.22, 132.75, 131.09, 129.64, 128.35, 74.49, 56.56, 56.42, 54.39, 44.85, 42.74, 40.14, 39.66, 36.95, 36.32, 35.95, 35.66, 35.64, 34.28, 32.15, 28.79, 28.40, 28.15, 27.74, 24.36, 24.00, 22.97, 22.72, 21.38, 18.82, 12.44, 12.22 [11].

3-Phenylpropyl benzoate (51a)

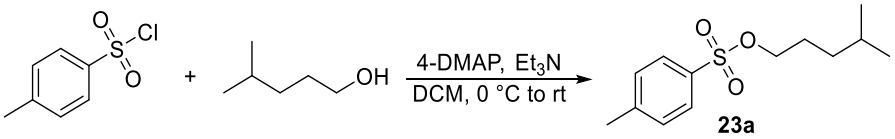


51a

R_f = 0.5, 2% acetone in hexane, white solid (1.99 g, 83 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (dd, *J* = 13.7, 7.1 Hz, 3H), 4.36 (t, *J* = 6.5 Hz, 2H), 2.85 – 2.77 (m, 2H), 2.12 (dt, *J* = 13.1, 6.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.70, 141.30, 133.00, 130.49, 129.67, 128.59, 128.56, 128.47, 126.15, 64.39, 32.43, 30.43 [12].

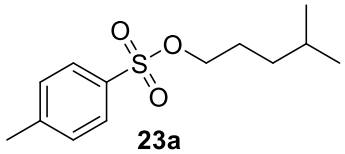
5.2 Synthesis of compound 23a



23a

4-toluenesulfonyl chloride (1.52 g, 8.0 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (100 mL). A solution of 4-Methyl-1-Pentanol (816 mg, 8.0 mmol, 1.0 equiv), 4-DMAP (0.8 mmol, 10 mol%) and triethylamine (9.6 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL) was added to the 4-toluenesulfonyl chloride solution slowly at 0 ℃ under a nitrogen atmosphere. The reaction mixture was stirred at room temperature overnight and then poured into water (50 mL). The water layer was extracted with dichloromethane. The organic layers were combined and washed with 3M HCl (50 mL), sodium bicarbonate (50 mL), and water (50 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 **23a** (1.86 g, 91%), spectra data are consistent with those reported in the literature.

4-Methyl-1-pentyl tosylate (23a)

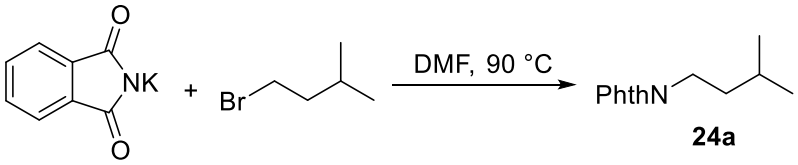


23a

R_f = 0.7, 10% acetone in hexane, yellowish oil (1.86 g, 91% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.62 (dd, *J* = 14.0, 8.6 Hz, 2H), 1.47 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.19 – 1.13 (m, 2H), 0.83 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.75, 133.37, 129.91, 127.99, 71.15, 34.47, 27.62, 26.88, 22.46, 21.75 [13].

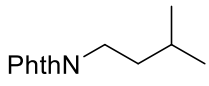
5.3 Synthesis of compound 24a



24a

Potassium phthalimide (22 mmol, 1.1 equiv) was added to a solution of 1-Bromo-3-Methylbutane (20 mmol, 1.0 equiv) in 25 mL of anhydrous DMF. The mixture was heated to 90 ℃ for 16 h. After cooled to room temperature, the reaction mixture was poured into water (75 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phase was washed with 100 mL 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 40:1)) to afford the products **24a** (3.73g, 86%), spectra data are consistent with those reported in the literature.

***N*-Isoamylphthalimide (24a)**

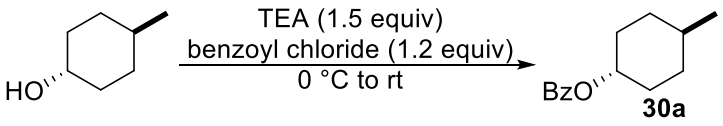


24a

R_f = 0.7, 5% acetone in hexane, yellowish oil (3.73 g, 86% yield)

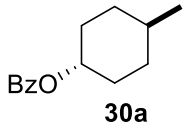
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.70 – 7.65 (m, 2H), 3.71 – 3.62 (m, 2H), 1.63 – 1.50 (m, 3H), 0.96 – 0.91 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46, 133.88, 132.29, 123.18, 37.40, 36.56, 25.98, 22.45 [14].

5.4 Synthesis of compound 30a



To a solution of *trans*-4-methylcyclohexanol (228 mg, 2.0 mmol, 1.0 equiv) and TEA (303 mg, 3.0 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) was added benzoyl chloride (281 mg, 2.4 mmol, 1.2 equiv) at 0 ℃. The reaction mixture was warmed to rt and stirred overnight. The solvent was removed in *vacuo* and the resulting residue was purified by silica gel flash chromatography to give the desired product **30a** (253 mg, 58%), spectra data are consistent with those reported in the literature.

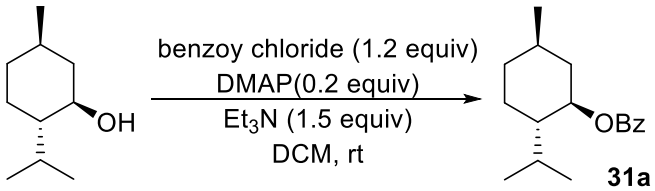
***trans*-4-Methylcyclohexyl benzoate (30a)**



R_f = 0.7, 5% acetone in hexane, white solid (253.0 mg, 58% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.95 – 4.88 (m, 1H), 2.08 (d, *J* = 12.7 Hz, 2H), 1.78 (d, *J* = 12.7 Hz, 2H), 1.55 – 1.38 (m, 3H), 1.11 (q, *J* = 13.6 Hz, 2H), 0.93 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.24, 132.79, 131.07, 129.64, 128.36, 74.15, 33.17, 31.88, 31.84, 21.99 [14].

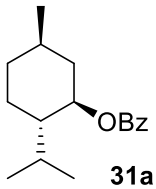
5.5 Synthesis of compound 31a



To a solution of *L*-Menthol (10.0 mmol, 1.0 equiv), DMAP (24.4 mg, 2.0 mmol, 0.2 equiv) and Et_3N (2.0 mL, 15.0 mmol, 1.5 equiv) in CH_2Cl_2 (50.0 mL) at 0 ^oC was added benzoyl chloride (1.68 g, 12.0 mmol, 1.2 equiv). The reaction mixture was stirred at rt for 6 h before quenched with H_2O (10.0 mL) and the mixture was extracted with CH_2Cl_2 (20.0 x 3mL). The combined organic layer was dried over anhydrous $NaSO_4$, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography to afford as a white solid **31a** (2.32 g, 89%). The spectroscopic

data of **31a** were consistent with those previously reported in the literature.

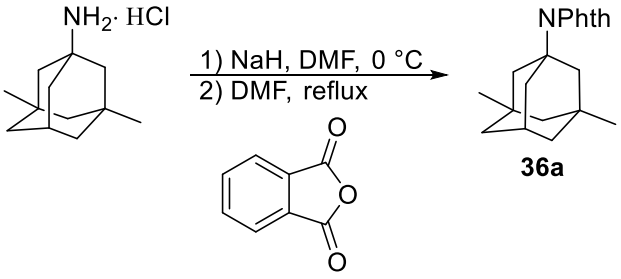
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl benzoate (31a)



31a R_f = 0.7, 10% acetone in hexane, white solid (2.32 g, 89% yield)

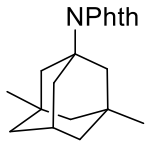
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.94 (td, *J* = 10.9, 4.4 Hz, 1H), 2.13 (d, *J* = 12.0 Hz, 1H), 1.97 (dt, *J* = 13.9, 7.0 Hz, 1H), 1.77 – 1.70 (m, 2H), 1.56 (t, *J* = 11.6 Hz, 2H), 1.17 – 1.05 (m, 2H), 0.94 – 0.91 (m, 6H), 0.80 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.23, 132.82, 131.00, 129.68, 128.42, 74.96, 47.42, 41.11, 34.47, 31.59, 26.63, 23.77, 22.20, 20.93, 16.65 [14].

5.6 Synthesis of compound 36a



Memantine hydrochloride (1.40 g, 5.6 mmol, 1.0 equiv) was dissolved in anhydrous DMF (15 mL) and cooled to 0 ℃. Sodium hydride (134.4 mg, 5.6 mmol, 1.0 equiv) was added portion-wise. The reaction mixture was allowed to stirred at 0 ℃ for 10 min before warmed to rt over 30 min. Phthalic anhydride (1.24 g, 8.37 mmol, 1.5 equiv) was then added and the reaction mixture was heated at reflux overnight. The reaction mixture was then cooled to room temperature, diluted with Et_2O and 1M HCl (aq.). The organic layer was separated and washed 1M HCl (aq.) (2 x 5 mL) and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The crude material was purified by silica gel column chromatography (10% EtOAc/Hexanes) to give *N*-Phth memantine **36a** (1.25 g, 70% yield) as a white solid, spectra data are consistent with those reported in the literature.

***N*-Phth memantine (36a)**

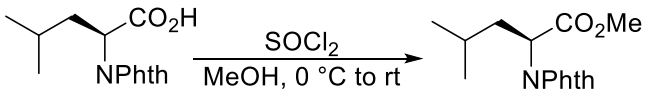


36a

R_f = 0.7, 10% acetone in hexane, white solid (1.25 g, 70% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 2.35 (d, *J* = 2.9 Hz, 2H), 2.22 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.14 (s, 4H), 1.47 (d, *J* = 12.3 Hz, 2H), 1.26 (d, *J* = 10.0 Hz, 4H), 0.89 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.95, 133.76, 132.10, 122.62, 61.94, 50.47, 46.16, 42.59, 38.80, 32.77, 30.50 [14].

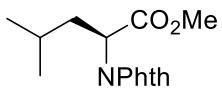
5.7 Synthesis of compound 37a, 38a



37a

To a solution of *N*-phthaloyl-*L*-leucine (1.0 g, 3.8 mmol, 1.0 equiv) in MeOH (10.0 mL) was added thionyl chloride (2.0 mL, 27.7 mmol, 7.2 equiv) at 0 ^oC. The reaction mixture was stirred at room temperature for 10 h before quenched with H_2O (5.0 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20.0 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The residue was purified by chromatography on silica gel (eluted with hexane/acetone (v/v 60:1)) to afford 0.9 g of compound **37a** as a white solid (83% yield), spectra data are consistent with those reported in the literature. The method for synthesizing compound **38a** is the same as that for compound **37a**.

Methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (37a)

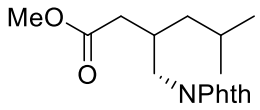


37a

R_f = 0.4, 5% acetone in hexane, white solid (868.0 mg, 83% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.76 – 7.72 (m, 2H), 5.01 – 4.88 (m, 1H), 3.72 (s, 3H), 2.40 – 2.25 (m, 1H), 1.96 (ddd, *J* = 14.4, 10.3, 4.3 Hz, 1H), 1.56 – 1.43 (m, 1H), 0.93 (dd, *J* = 13.5, 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.41, 167.88, 134.30, 131.97, 123.66, 52.87, 50.74, 37.39, 25.19, 23.31, 21.15 [14].

Methyl (*S*)-3-((1,3-dioxoisoindolin-2-yl)methyl)-5-methylhexanoate (38a)

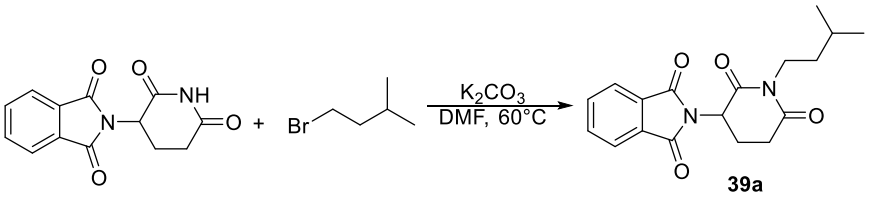


38a

R_f = 0.4, 5% acetone in hexane, white solid (1.02 g, 88% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.72 – 7.68 (m, 2H), 3.68 (dd, *J* = 13.8, 5.1 Hz, 1H), 3.60 (dd, *J* = 13.8, 8.4 Hz, 1H), 3.53 (s, 3H), 2.45 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.28 (tt, *J* = 15.9, 7.9 Hz, 2H), 1.72 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.24 – 1.17 (m, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.04, 168.69, 134.06, 132.12, 123.34, 51.56, 42.06, 41.94, 37.63, 32.87, 25.42, 22.82, 22.65 [14].

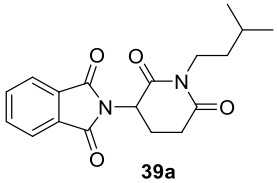
5.8 Synthesis of compound 39a



39a

A mixture of thalidomide (1.0 g, 3.87 mmol, 1.0 equiv), 1-bromo-3-methylbutane (0.56 mL, 4.6 mmol, 1.2 equiv) and K_2CO_3 (803 mg, 5.81 mmol, 1.5 equiv) in anhydrous DMF (5 mL) was vigorously stirred and heated at 60 ^oC (oil bath) for 16 h. The mixture was then allowed to cool to ambient temperature, filtered, and then concentrated under reduced pressure. The solvent was removed in *vacuo* and the resulting residue was purified by silica gel flash chromatography to give the desired product **39a** (1.0 g, 79%), spectra data are consistent with those reported in the literature.

2-(1-Isopentyl-2,6-dioxopiperidin-3-yl)isoindoline-1,3-dione (39a)



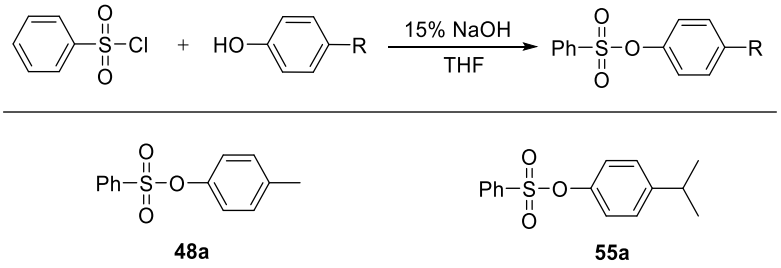
39a

R_f = 0.7, 20% acetone in hexane, white solid (1.0 g, 79% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 5.5 Hz, 2H), 4.97 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.85 – 3.73 (m, 2H), 3.00 – 2.90 (m, 1H), 2.83 – 2.71 (m,

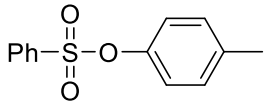
2H), 2.13 – 2.06 (m, 1H), 1.57 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.46 – 1.35 (m, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.86, 168.49, 167.54, 134.49, 131.88, 123.81, 50.30, 39.47, 36.60, 32.17, 26.34, 22.54, 22.46, 22.12 [4].

5.9 Synthesis of compound 48a, 55a



To a solution of substituted phenol (5.0 mmol, 1.0 equiv) in THF (10 mL) was added 15% NaOH (0.66 g, 16.5 mmol). After the resulting solution was cooled to 0 ℃ with an ice water bath, a solution of benzenesulfonyl chloride (1.06 g, 6.0 mmol, 1.2 equiv) in THF (15 mL) was slowly added within 15 min at 0 ℃. After that, the ice-water bath was removed and the reaction mixture was stirred for 2 h. To the mixture was then added ethyl acetate (30 mL). The two-phase mixture was separated. The organic layer was washed with water (20 mL) and dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure gave the rude product. The mixture was concentrated and then purified by flash chromatography to give the pure products. The spectroscopic data of **48a** and **55a** were consistent with those previously reported in the literature.

4-Methylphenyl benzenesulfonate (48a)

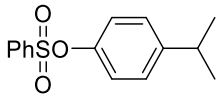


48a

R_f = 0.5, 10% acetone in hexane, yellowish oil (0.82 g, 66% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.52, 137.17, 135.58, 134.23, 130.22, 129.19, 128.61, 122.12, 20.99 [15].

4-Isopropylphenyl benzenesulfonate (55a)

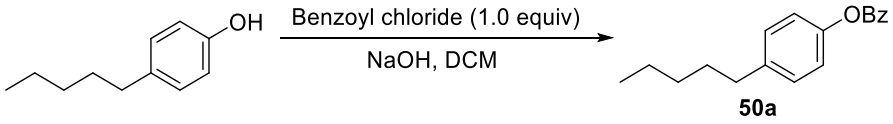


55a

R_f = 0.7, 10% acetone in hexane, yellowish oil (0.77 g, 56% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 2.86 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.20 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.98, 147.57, 135.65, 134.22, 129.17, 128.53, 127.60, 122.09, 33.64, 23.99 [16].

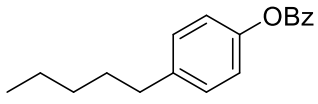
5.10 Synthesis of compound 50a



50a

In a typical procedure, 4-Pentylphenol (15.0 mmol, 1.0 equiv) was dissolved in 20.0 mL of 10% aqueous sodium hydroxide (2.0 g, 50.0 mmol NaOH) solution in a 100.0 mL flask. Solutions of tetra-n-butylammonium chloride (416.9 mg, 1.5 mmol, 0.1 equiv) in 5.0 mL of dichloromethane and Benzoyl chloride (2.1 g, 15.0 mmol, 1.0 equiv) in 15.0 mL of dichloromethane were prepared. After cooling all solutions at 0 ℃, they were mixed at once. The reaction mixture was kept under vigorous magnetic stirring (400 rpm) at 0 ℃ for 5 min and then poured over 50.0 mL of icy water. The organic layer was separated and the aqueous layer was extracted twice with 40.0 mL of diethyl ether. The combined organic extracts were washed with saturated NaCl solution. The combined organic layer was dried over Na_2SO_4, filtered and the filtrate was concentrated in *vacuo*. The residue was purified by flash chromatography to afford as a white solid **50a** (3.74 g, 93%). The spectroscopic data of **50a** were consistent with those previously reported in the literature [17].

4-Pentylphenyl benzoate (50a)



50a

R_f = 0.7, 5% acetone in hexane, white solid (3.74 g, 93%

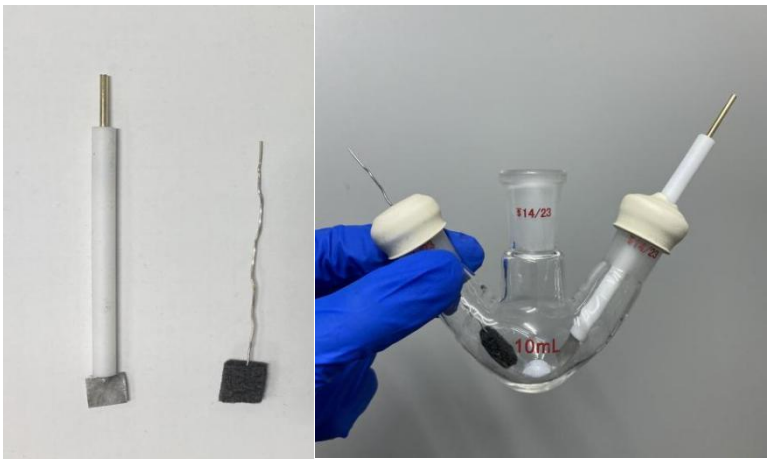
yield)

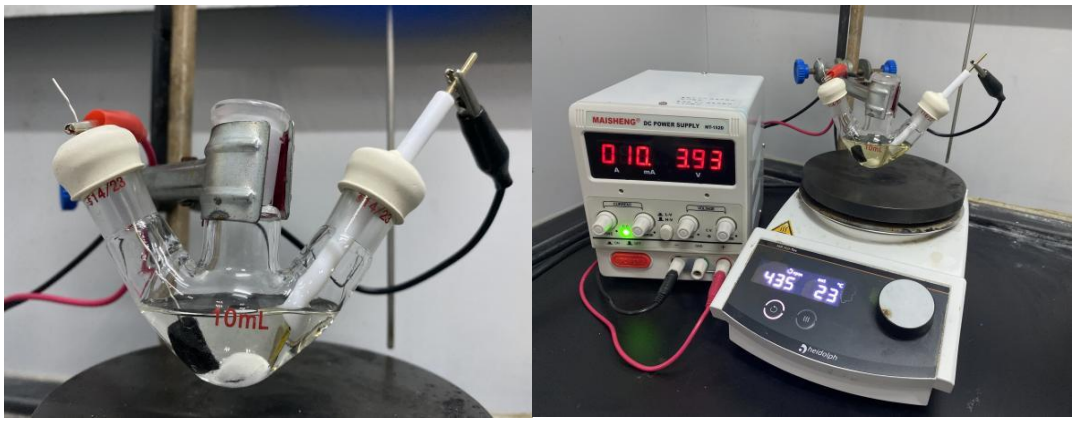
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 2.66 – 2.62 (m, 2H), 1.70 – 1.61 (m, 2H), 1.40 – 1.33 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.46, 148.96, 140.66, 133.60, 130.26, 129.84, 129.45, 128.65, 121.43, 35.48, 31.59, 31.29, 22.67, 14.17.

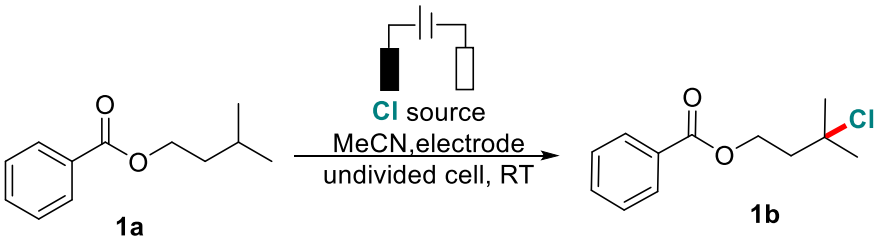
6. Optimization studies

All screening reactions were carried out at a 0.5 mmol scale in a 10 mL three-necked flask unless otherwise noted. Isoamyl Benzoate **1a** (96.1 mg, 0.5 mmol, 1.0 equiv), other specified reagents and a magnetic stir bar were added to a 10 mL three-necked flask. The flask was equipped with two rubber plugs, graphite felt (1 cm x 1 cm x 0.5 cm) and platinum sheet are uesed as anode and cathode respectively. The graphite felt (GF) anode 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 mL). Then the mixture was extracted with DCM (3 x 5 mL), the combined organic phase were 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.

Note: The graphite felt (GF) differs from graphite rod dramatically in the aspects of original material, manufacture process, structure, and properties [18].







entry	reagents (eq.)/ Cl source (eq.)/ electrolyte (eq.)/ current(mA)/ electrode/ solvent (mL)/ atmosphere/ time (h)	Yield of **1b** (%)[b]	RSM (%)[c]
1	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 5/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	62	＜10
2	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	65	＜10
3	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 15/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	54	＜10
4	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 20/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 12	28	＜10
5	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | GF(-)/ MeCN (8)/ open air/ 48	49	17
6	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Ni(-)/ MeCN (8)/ open air/ 48	＜10	87
7	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Zn(-)/ MeCN (8)/ open air/ 48	14	78

8	NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Ag(-)/ MeCN (8)/ open air/ 48	＜10	81
9	NHPI (20 mol%)/ HCl (10)/ CF_3NaSO_3 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	＜10	＞90
10	NHPI (20 mol%)/ HCl (10)/ Bu_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	43	30
11	NHPI (20 mol%)/ HCl (10)/ $LiClO_4$ (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	57	14
12	NHPI (20 mol%)/ NaCl (10)/ Et_4NBF_4(2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	0	100
13	NHPI (20 mol%)/ KCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	0	100
14	NHPI (20 mol%)/ LiCl (10)/ Et_4NBF_4(2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	traces	＞90
15	NHPI (20 mol%)/ NCS (3)/ Et_4NBF_4(2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	traces	＞90
16	NHPI (20 mol%)/ TBAC (3)/ Et_4NBF_4(2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	19	26
17	Cl_4-NHPI (20 mol%)/ HCl (10)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	63	15
18	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	79	＜10
19	NHPI (20 mol%)/ HCl (20)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	39	＜10
20	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN/H_2O (8, 15/1)/ open air/ 24	67	16
21	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) |Pt(-)/ MeCN/H_2O (8, 7/1)/ open air/ 24	44	38
22	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/	18	62

	GF(+) | Pt(-)/ MeCN/H_2O (8, 3/1)/ open air/ 24		
23	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | GF(-)/ MeCN (8)/ open air/ 24	44	35
24	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | GF(-)/ MeCN (5)/ open air/ 24	70	14
25[d]	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | GF(-)/ MeCN (5)/ open air/ 20	70	＜10
26[d,e]	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | GF(-)/ MeCN (5)/ open air/ 15	73	＜10
27	NHPI (10 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 48	64	19
28	NHPI (5 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 72	42	49
29	NHPI (0)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	14	75
30	NHPI (0)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ Air bubbles/ 24	34	18
31	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ N_2/ 24	27	54
32	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (2.0)/ 0/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	0	100
33	NHPI (20 mol%)/ HCl (5)/ Et_4NBF_4 (0)/ 10/ GF(+) | Pt(-)/ MeCN (8)/ open air/ 24	35	47

[a]Reaction conditions: 0.5 mmol substrate, 20% mmol equiv of NHPI, 2.0 equiv of Et_4NBF_4, 5.0 equiv of concentrated HCl, MeCN (8.0 mL), graphite felt anode (1.0 cm × 1.0 cm × 0.5 cm), Pt plate cathode (1.0 cm × 1.0 cm × 0.2 mm), 10 mA, room temperature, open air, 24 h. [b]Isolated yield. [c]RSM is the short for of recovery starting material. [d]1.0 mmol substrate. [e]graphite felt (1.5 cm × 1.5 cm × 0.5 cm).

6.1 Calculation of Faradaic efficiency

The faradaic efficiency of the reaction was calculated using the follow formula [19]

$$\eta = \frac{Q_{theo}}{Q_{exp}} \qquad (1)$$

Where,

$$Q_{theo} = Z_p \cdot N_p \cdot F$$

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

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

η: faradaic efficiency in percent [%]; Q_{theo}: theoretical charge in Coulomb [C]; Q_{exp}: experimental charge in Coulomb [C]; equiv.: electron equivalents (F/mol or equiv.); Z_p :number of electrons per product [-]; N_p: number of moles of the product [mol]; Y: yield in percent [%].

Here, Y=79%, equiv.=8.95 F/mol

The faradaic efficiency was calculated using eq 1:

$$\eta = \frac{Z_p \cdot N_p \cdot F}{Z \cdot N \cdot F \cdot equiv.} = \frac{Y}{equiv.} = \frac{79\%}{8.95} = 9\%$$

If, Y=73%, equiv.=2.80 F/mol

The faradaic efficiency was calculated using eq 1:

$$\eta = \frac{Z_p \cdot N_p \cdot F}{Z \cdot N \cdot F \cdot equiv.} = \frac{Y}{equiv.} = \frac{73\%}{2.80} = 26\%$$

7. Mechanistic studies

7.1 Cyclic voltammetry (CV) experiment

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 mL anhydrous CH_3CN 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/.

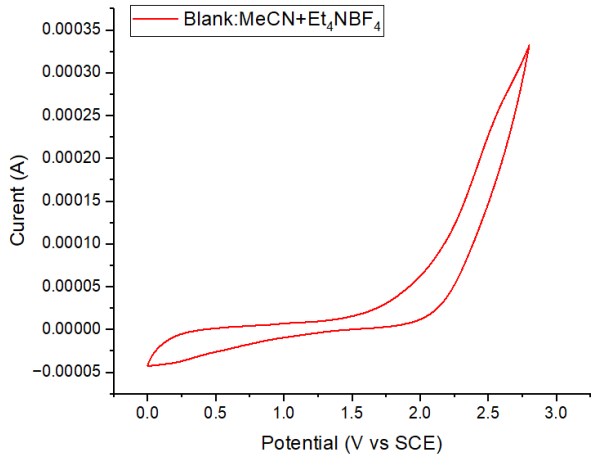


Figure 2. CV curve of blank

2) Cyclic voltammetry experiment of NHPI using glassy carbon working electrode at 100 mV/S.

A solution of NHPI (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous CH_3CN 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.

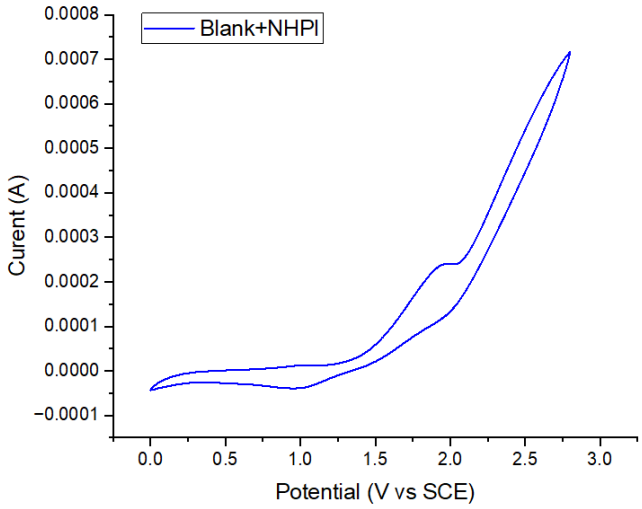


Figure 3. CV curve of NHPI

3) Cyclic voltammetry experiment of concentrated HCl using glassy carbon working electrode at 100 mV/S.

A solution of concentrated HCl (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous CH_3CN 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.

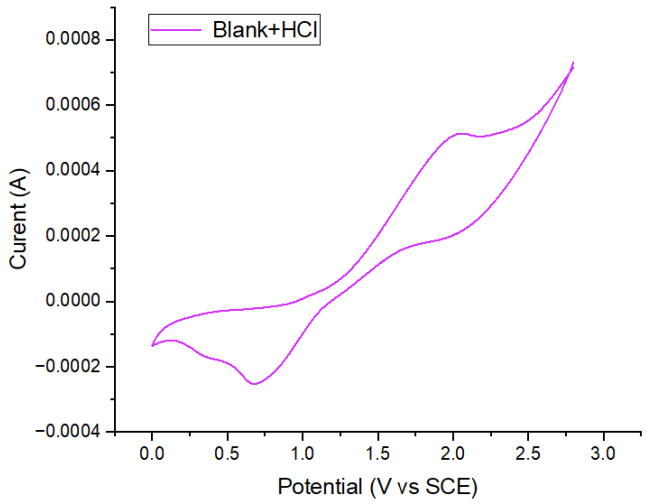


Figure 4. CV curve of concentrated HCl

4) Cyclic voltammetry experiment of NHPI and concentrated HCl using glassy carbon working electrode at 100 mV/S.

A solution of NHPI (0.1 mmol) and concentrated HCl (0.1 mmol) and Et_4NBF_4 (0.1 mmol) in 10 mL anhydrous CH_3CN 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.

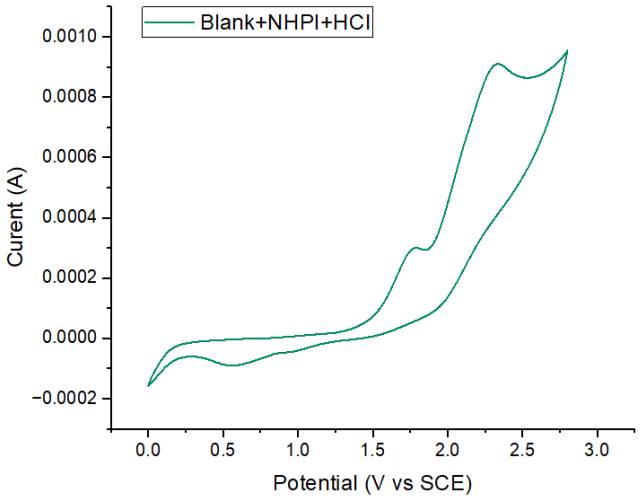


Figure 5. CV curve of NHPI and concentrated HCl

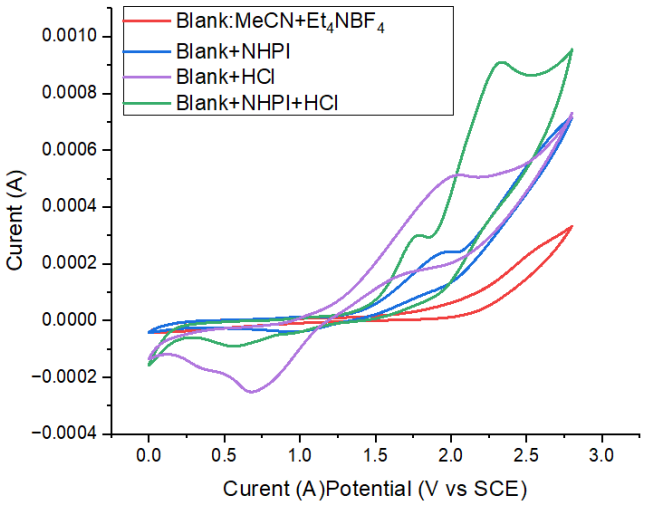


Figure 6. CV curve

Results:

A peak for oxidation of **NHPI** was observed at 1.94 V in CH_3CN (*vs.* SCE).

A peak for oxidation of concentrated **HCl** was observed at 2.02 V in CH_3CN (*vs.* SCE).

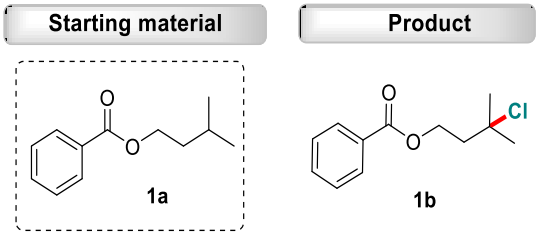
A peak for oxidation of **NHPI** was observed at 1.77 V in CH_3CN with concentrated **HCl**.

A peak for oxidation of concentrated **HCl** was observed at 2.32 V in CH_3CN with

NHPI.

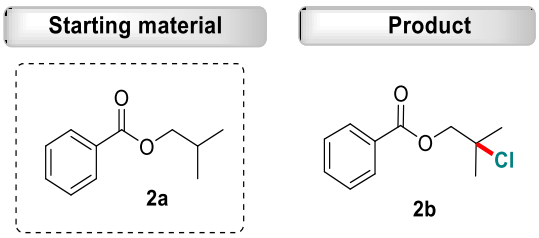
Cyclic voltammetry (CV) of a mixture of **NHPI** and concentrated **HCl** revealed that the oxidation potential of **NHPI** could be effectively lowered under acid conditions.

8. Characterization data of products



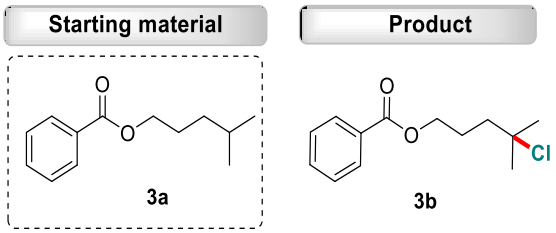
R_f = 0.6 (**1b**), 5% acetone in hexane

Compound **1b** (yellowish oil, 89 mg, 79% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 6.7 Hz, 2H), 2.25 (t, *J* = 6.7 Hz, 2H), 1.67 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.53, 133.08, 130.26, 129.64, 128.48, 68.54, 62.14, 44.18, 33.03 [4].



R_f = 0.6 (**2b**), 5% acetone in hexane

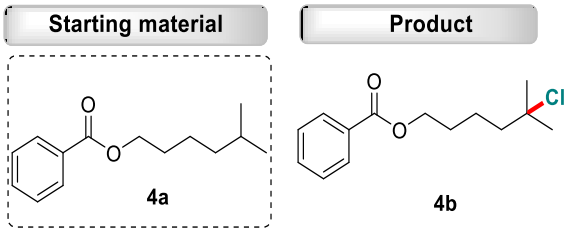
Compound **2b** (yellowish oil, 59 mg, 56% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.39 (s, 2H), 1.69 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.12, 133.39, 131.24, 129.86, 128.62, 72.61, 66.49, 29.58 [20].



R_f = 0.6 (**3b**), 5% acetone in hexane

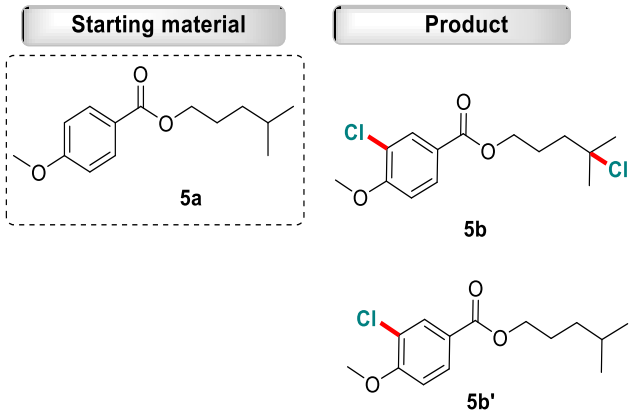
Compound **3b** (yellowish oil, 99 mg, 83% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.36 (t, *J* = 6.4 Hz, 2H), 2.04 – 1.95 (m, 2H), 1.89 (dd, *J* = 11.2, 5.4 Hz, 2H), 1.61 (s, 6H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 166.70, 133.06, 130.40, 129.68, 128.49, 70.39, 64.92, 42.51, 32.59, 24.89 [4].



R_f = 0.6 (**4b**), 5% acetone in hexane

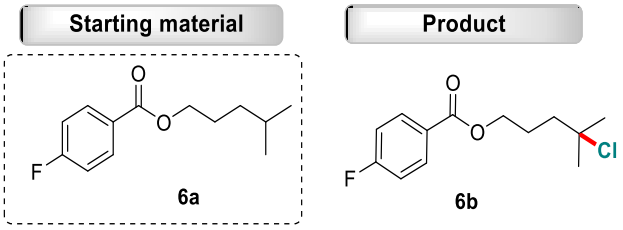
Compound **4b** (yellowish oil, 112 mg, 88% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 1.80 (dt, *J* = 10.7, 6.4 Hz, 4H), 1.69 – 1.62 (m, 2H), 1.58 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.71, 132.97, 130.49, 129.63, 128.45, 70.87, 64.81, 45.67, 32.52, 28.88, 21.81. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{20}ClO_2$ 255.1146; Found: 255.1144.



R_f = 0.5 (**5b**); R_f = 0.6 (**5b'**), 5% acetone in hexane

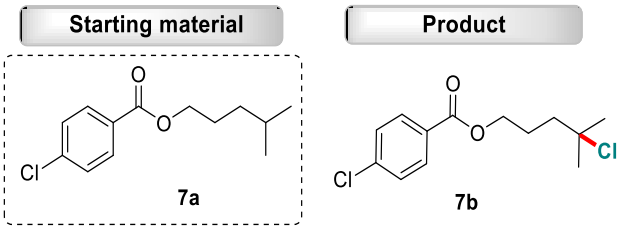
Compound **5b** (yellowish oil, 103 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.1 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.97 (s, 3H), 1.98 (dt, *J* = 10.1, 6.6 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.48, 158.78, 131.74, 130.02, 123.59, 122.63, 111.35, 70.39, 65.05, 56.49, 42.47, 32.60, 24.91. **HRMS (ESI-TOF) m/z:** $[M+Na]^+$ Calcd for $C_{14}H_{18}Cl_2NaO_3$ 327.0525; Found: 327.0527.

Compound **5b'** (yellowish oil, 16 mg, 12% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.1 Hz, 1H), 7.92 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 2H), 3.94 (s, 3H), 1.73 (dd, *J* = 16.5, 8.4 Hz, 2H), 1.59 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.29 (dd, *J* = 15.9, 6.9 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.50, 158.63, 131.66, 129.92, 123.81, 122.51, 111.26, 65.59, 56.40, 35.18, 27.86, 26.74, 22.62. **HRMS (ESI-TOF) m/z:** $[M+Na]^+$ Calcd for $C_{14}H_{19}ClNaO_3$ 293.0915; Found: 293.0917.



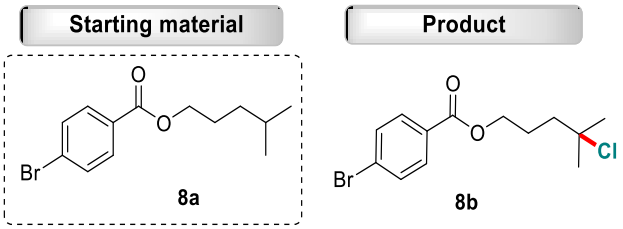
R_f = 0.5 (**6b**), 10% acetone in hexane

Compound **6b** (yellowish oil, 84 mg, 65% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 1.99 (dt, *J* = 10.1, 6.5 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.85, 165.26 (d, *J* = 107.9 Hz), 132.20 (d, *J* = 9.3 Hz), 126.60 (d, *J* = 3.0 Hz), 115.62 (d, *J* = 22.0 Hz), 70.33, 65.03, 42.44, 32.56, 24.83 [4].



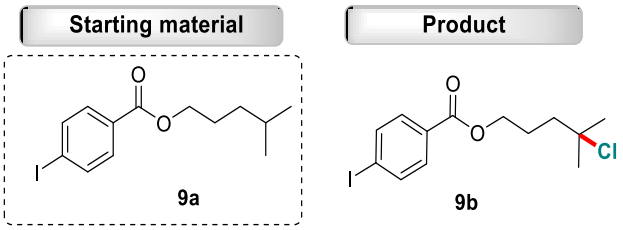
R_f = 0.6 (**7b**), 5% acetone in hexane

Compound **7b** (yellowish oil, 95 mg, 69% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 1.99 (dt, *J* = 10.2, 6.6 Hz, 2H), 1.87 (dd, *J* = 9.3, 7.3 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.80, 139.49, 131.07, 128.90, 128.84, 70.28, 65.15, 42.44, 32.57, 24.83 [4].



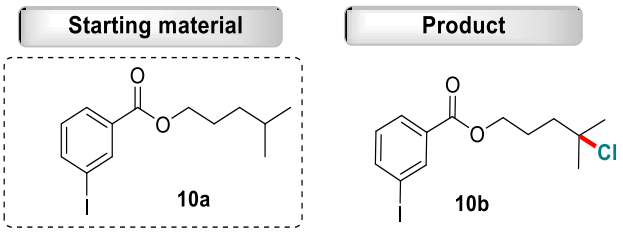
R_f = 0.6 (**8b**), 5% acetone in hexane

Compound **8b** (yellowish oil, 106 mg, 67% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.35 (t, *J* = 6.5 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.87 (dd, *J* = 10.8, 5.2 Hz, 2H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.99, 131.87, 131.24, 129.30, 128.20, 70.33, 65.21, 42.46, 32.60, 24.85 [4].



R_f = 0.6 (**9b**), 5% acetone in hexane

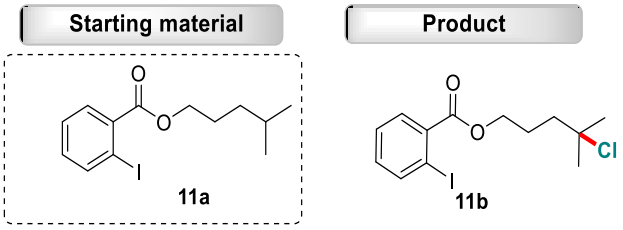
Compound **9b** (yellowish oil, 128 mg, 70% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 1.99 (dt, *J* = 10.2, 6.8 Hz, 2H), 1.87 (dd, *J* = 11.8, 4.2 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.19, 137.85, 131.13, 129.84, 100.87, 70.33, 65.18, 42.42, 32.59, 24.82 [4].



R_f = 0.6 (**10b**), 5% acetone in hexane

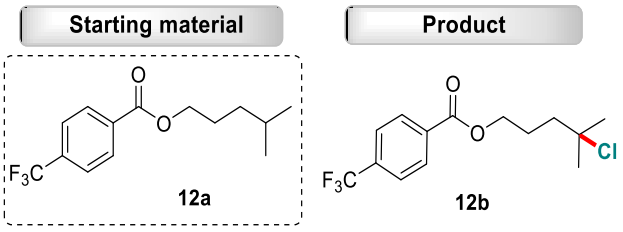
Compound **10b** (yellowish oil, 117 mg, 64% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.6 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 4.35 (t, *J* = 6.5 Hz, 2H), 1.99 (dt, *J* = 13.1, 6.8 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.19, 141.89, 138.56, 132.27,

130.20, 128.85, 93.94, 70.31, 65.36, 42.39, 32.59, 24.84. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{17}ClIO_2$ 366.9956; Found: 366.9954.



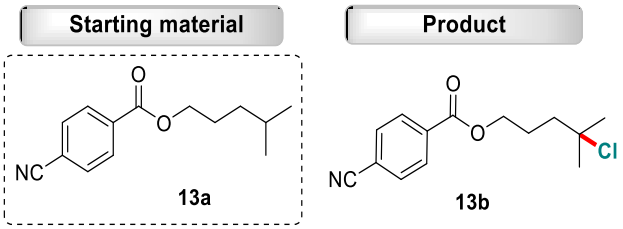
R_f = 0.6 (**11b**), 5% acetone in hexane

Compound **11b** (yellowish oil, 113 mg, 62% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 2.00 (dt, *J* = 9.7, 6.8 Hz, 2H), 1.90 (dd, *J* = 10.8, 4.8 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.66, 141.38, 135.42, 132.71, 130.99, 128.03, 94.10, 70.35, 65.66, 42.52, 32.59, 24.71. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{17}ClIO_2$ 366.9956; Found: 366.9953.



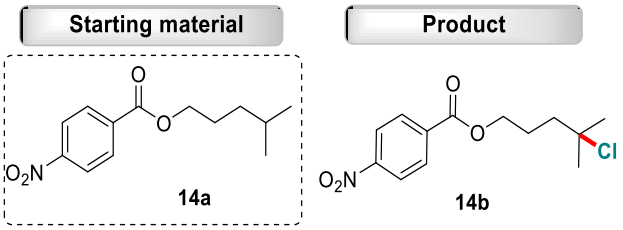
R_f = 0.5 (**12b**), 5% acetone in hexane

Compound **12b** (yellowish oil, 100 mg, 65% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 4.39 (t, *J* = 6.5 Hz, 2H), 2.02 (dt, *J* = 10.4, 6.6 Hz, 2H), 1.88 (dd, *J* = 12.0, 4.4 Hz, 2H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.47, 135.17 – 133.38 (m), 130.10, 125.56 (q, *J* = 3.7 Hz), 124.85, 122.68, 70.25, 65.49, 42.42, 32.58, 24.82. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.11 [4].



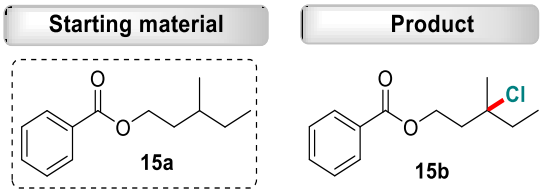
R_f = 0.5 (**13b**), 5% acetone in hexane

Compound **13b** (yellowish oil, 88 mg, 66% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 4.37 (t, *J* = 6.5 Hz, 2H), 2.04 – 1.96 (m, 2H), 1.86 (dd, *J* = 12.0, 4.4 Hz, 2H), 1.59 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.95, 134.13, 132.30, 130.14, 118.03, 116.45, 70.15, 65.67, 42.30, 32.51, 24.71 [4].



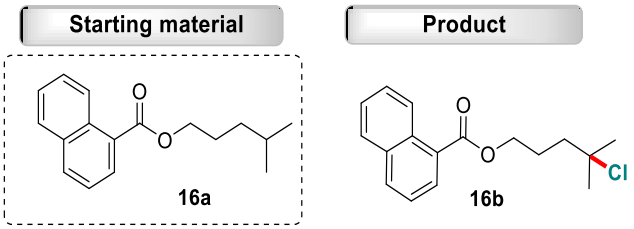
R_f = 0.5 (**14b**), 5% acetone in hexane

Compound **14b** (yellowish oil, 91 mg, 64% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 4.41 (t, *J* = 6.5 Hz, 2H), 2.06 – 1.99 (m, 2H), 1.90 – 1.86 (m, 2H), 1.61 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.79, 150.67, 135.75, 130.82, 123.70, 70.19, 65.89, 42.37, 32.59, 24.77 [4].



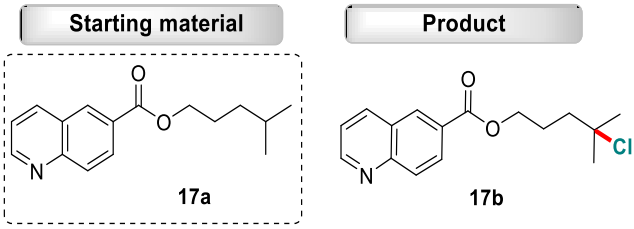
R_f = 0.6 (**15b**), 5% acetone in hexane

Compound **15b** (yellowish oil, 82 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 6.9 Hz, 2H), 2.28 (dt, *J* = 13.7, 6.8 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.88 (tt, *J* = 14.3, 7.2 Hz, 2H), 1.61 (s, 3H), 1.06 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 133.11, 130.30, 129.67, 128.51, 72.88, 62.03, 41.94, 37.55, 29.74, 9.29 [14].



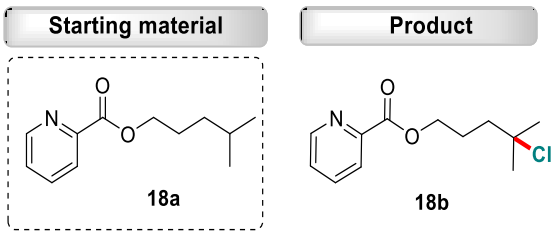
R_f = 0.5 (**16b**), 10% acetone in hexane

Compound **16b** (yellowish oil, 87 mg, 60% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.8 Hz, 1H), 8.19 (d, *J* = 7.3 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 4.46 (t, *J* = 6.4 Hz, 2H), 2.07 (dt, *J* = 10.2, 6.6 Hz, 2H), 1.94 (dd, *J* = 11.0, 5.5 Hz, 2H), 1.63 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.69, 133.99, 133.50, 131.49, 130.26, 128.69, 127.89, 127.36, 126.35, 125.93, 124.64, 70.42, 65.05, 42.63, 32.62, 24.95 [4].



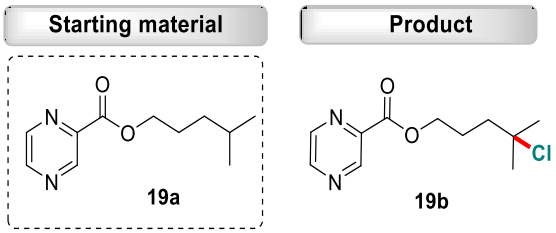
R_f = 0.5 (**17b**), 10% acetone in hexane

Compound **17b** (yellowish oil, 122 mg, 84% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.01 (d, *J* = 2.6 Hz, 1H), 8.59 (s, 1H), 8.29 (t, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H), 4.43 (t, *J* = 6.5 Hz, 2H), 2.05 (dt, *J* = 10.4, 6.7 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.62 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.18, 152.60, 150.15, 137.53, 131.10, 129.92, 129.08, 128.39, 127.55, 121.98, 70.35, 65.36, 42.48, 32.60, 24.91 [4].



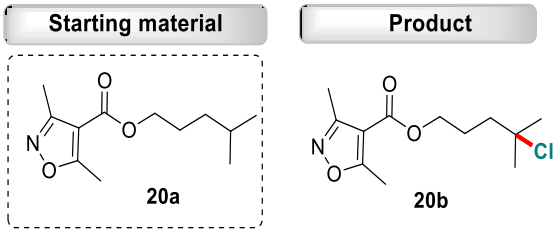
R_f = 0.5 (**18b**), 10% acetone in hexane

Compound **18b** (yellowish oil, 87 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.44 (m, 1H), 4.43 (t, *J* = 6.7 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.86 (dd, *J* = 9.8, 6.5 Hz, 2H), 1.57 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.24, 150.01, 148.14, 137.13, 127.00, 125.24, 70.27, 65.84, 42.26, 32.52, 24.84. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{17}ClNO_2$ 242.0942; Found: 242.0944.



R_f = 0.5 (**19b**), 10% acetone in hexane

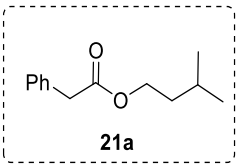
Compound **19b** (yellowish oil, 79 mg, 65% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.70 (d, *J* = 17.3 Hz, 2H), 4.43 (t, *J* = 6.7 Hz, 2H), 2.04 – 1.96 (m, 2H), 1.83 (dd, *J* = 12.0, 4.4 Hz, 2H), 1.54 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.88, 147.69, 146.26, 144.50, 143.45, 70.04, 66.12, 42.12, 32.44, 24.67 [4].



R_f = 0.6 (**20b**), 10% acetone in hexane

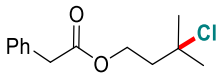
Compound **20b** (yellowish oil, 88 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.29 (t, *J* = 6.4 Hz, 2H), 2.65 (s, 3H), 2.43 (s, 3H), 2.00 – 1.93 (m, 2H), 1.85 (dd, *J* = 10.2, 6.2 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.41, 162.57, 160.00, 108.79, 70.14, 64.51, 42.53, 32.59, 24.74, 13.55, 12.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{12}H_{19}ClNO_3$ 260.1048; Found: 260.1050.

Starting material



21a

Product

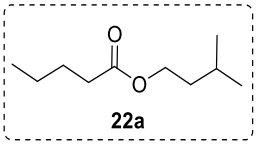


21b

R_f = 0.6 (**21b**); 5% acetone in hexane

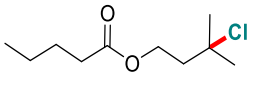
Compound **21b** (yellowish oil, 68 mg, 57% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 3H), 4.33 (t, *J* = 6.9 Hz, 2H), 3.62 (s, 2H), 2.08 (t, *J* = 6.8 Hz, 2H), 1.56 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.56, 133.99, 129.38, 128.70, 127.25, 68.51, 62.11, 43.97, 41.60, 32.91 [4].

Starting material

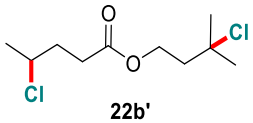


22a

Product



22b

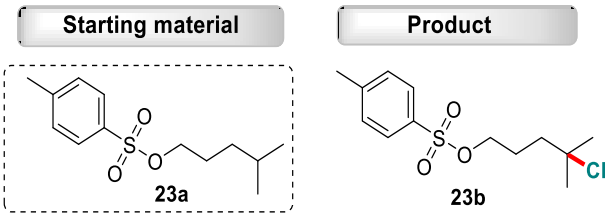


22b'

R_f = 0.7 (**22b**); R_f = 0.6 (**22b'**), 5% acetone in hexane

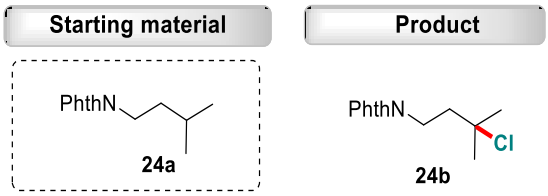
Compound **22b** (yellowish oil, 66 mg, 64% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.29 (t, *J* = 6.9 Hz, 2H), 2.33 – 2.26 (m, 2H), 2.09 (t, *J* = 6.9 Hz, 2H), 1.64 – 1.55 (m, 8H), 1.37 – 1.29 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.84, 68.53, 61.45, 44.10, 34.19, 32.96, 27.11, 22.38, 13.82 [4].

Compound **22b'** (yellowish oil, 8 mg, 7% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.32 (t, *J* = 6.9 Hz, 2H), 4.14 – 4.02 (m, 1H), 2.60 – 2.42 (m, 2H), 2.10 (t, *J* = 7.0 Hz, 3H), 1.98 – 1.90 (m, 1H), 1.62 (d, *J* = 1.5 Hz, 6H), 1.53 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.90, 68.43, 61.80, 57.80, 44.02, 35.16, 32.98, 32.96, 31.47, 25.48. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_{19}Cl_2O_2$ 241.0757; Found: 241.0758.



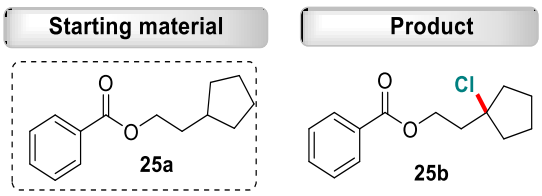
R_f = 0.6 (**23b**); 10% acetone in hexane

Compound **23b** (yellowish oil, 98 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.04 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 1.83 (dt, *J* = 9.9, 6.3 Hz, 2H), 1.71 (dd, *J* = 10.9, 5.5 Hz, 2H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.90, 133.03, 129.93, 127.90, 70.54, 69.96, 41.73, 32.40, 24.92, 21.66. **HRMS (ESI-TOF) m/z:** $[M+Na]^+$ Calcd for $C_{13}H_{19}ClNaO_3S$ 313.0636; Found: 313.0638.



R_f = 0.6 (**24b**), 10% acetone in hexane

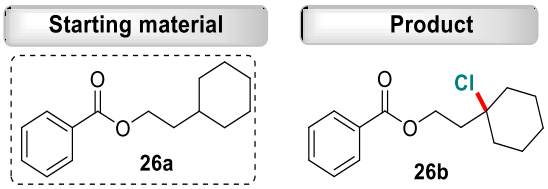
Compound **24b** (yellowish oil, 85 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 3.89 – 3.85 (m, 2H), 2.11 – 2.06 (m, 2H), 1.62 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.14, 133.99, 132.16, 123.24, 68.15, 43.34, 34.65, 32.51 [4].



R_f = 0.6 (**25b**), 5% acetone in hexane

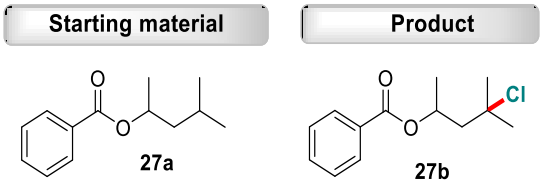
Compound **25b** (yellowish oil, 67 mg, 53% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.63 (t, *J* = 6.7 Hz, 2H), 2.34 (t, *J* = 6.7 Hz, 2H), 2.20 (dd, *J* = 13.7, 7.1 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.88 – 1.70 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.66, 133.09, 130.38,

129.71, 128.53, 80.30, 62.68, 42.95, 41.78, 23.08. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{18}ClO_2$ 253.0990; Found: 253.0989.



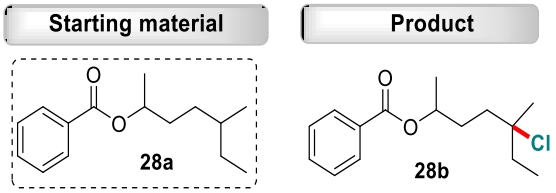
R_f = 0.6 (**26b**), 5% acetone in hexane

Compound **26b** (yellowish oil, 92 mg, 69% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.61 (t, *J* = 6.8 Hz, 2H), 2.25 (t, *J* = 6.8 Hz, 2H), 2.03 (d, *J* = 13.2 Hz, 2H), 1.85 – 1.52 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 133.07, 130.36, 129.67, 128.50, 73.82, 61.70, 43.62, 40.17, 25.39, 22.35. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{20}ClO_2$ 267.1146; Found: 267.1147.



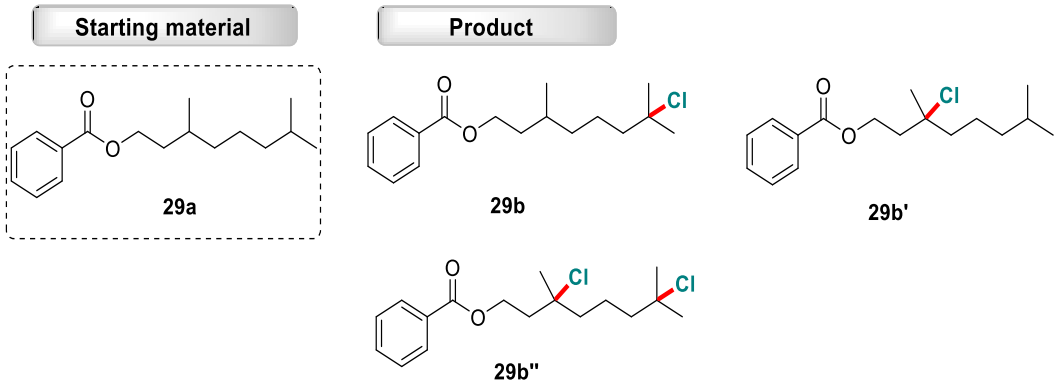
R_f = 0.6 (**27b**), 5% acetone in hexane

Compound **27b** (yellowish oil, 78 mg, 65% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.49 (dq, *J* = 12.4, 6.3 Hz, 1H), 2.33 (dd, *J* = 15.2, 8.4 Hz, 1H), 2.09 (dd, *J* = 15.2, 2.5 Hz, 1H), 1.64 (s, 3H), 1.60 (s, 3H), 1.40 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.93, 133.01, 130.67, 129.66, 128.48, 69.33, 68.84, 51.55, 33.94, 32.05, 21.82. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}ClO_2$ 241.0990; Found: 241.0988.



R_f = 0.6 (**28b**), 5% acetone in hexane

Compound **28b** (yellowish oil, 95 mg, 71% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.16 (dd, *J* = 11.0, 5.9 Hz, 1H), 1.96 – 1.67 (m, 6H), 1.52 (s, 3H), 1.38 (d, *J* = 6.2 Hz, 3H), 1.07 – 0.91 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.25, 132.94, 130.79, 129.63, 128.45, 74.72, 71.60, 39.34, 36.77, 31.38, 29.40, 20.27, 9.26. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{22}ClO_2$ 269.1303; Found: 269.1301.

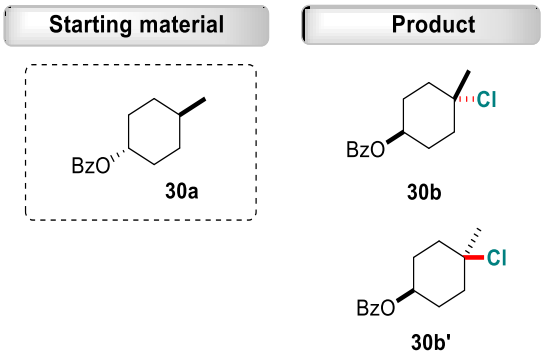


R_f = 0.7 (**29b**); R_f = 0.75 (**29b'**); R_f = 0.6 (**29b''**), 2% acetone in hexane

Compound **29b** (yellowish oil, 101 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.37 (dd, *J* = 13.5, 6.5 Hz, 2H), 1.83 (dd, *J* = 13.5, 5.2 Hz, 1H), 1.73 – 1.67 (m, 3H), 1.61 – 1.48 (m, 9H), 1.42 – 1.35 (m, 1H), 1.23 (dd, *J* = 11.2, 6.7 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.77, 132.94, 130.59, 129.64, 128.45, 71.27, 63.55, 46.30, 37.01, 35.65, 32.55, 30.03, 22.58, 19.66. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{26}ClO_2$ 297.1616; Found: 297.1616.

Compound **29b'** (yellowish oil, 18 mg, 12% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.56 (t, *J* = 6.9 Hz, 2H), 2.33 – 2.17 (m, 2H), 1.80 (dd, *J* = 16.3, 6.1 Hz, 2H), 1.63 (s, 3H), 1.56 – 1.45 (m, 3H), 1.18 (dd, *J* = 15.6, 6.9 Hz, 2H), 0.87 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.64, 133.12, 130.31, 129.70, 128.51, 72.55, 62.08, 45.10, 42.32, 39.06, 30.32, 28.00, 22.71, 22.65. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{26}ClO_2$ 297.1616; Found: 297.1618.

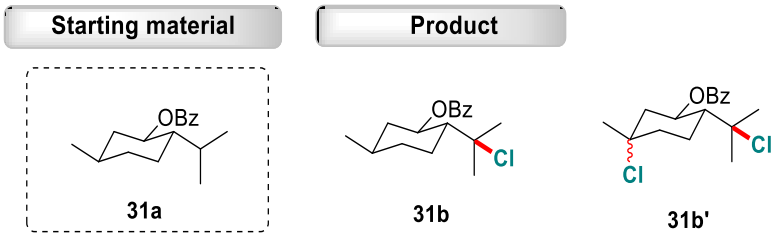
Compound **29b''** (yellowish oil, 13 mg, 8% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 6.8 Hz, 2H), 2.27 (dtd, *J* = 21.5, 14.5, 6.8 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.76 – 1.69 (m, 4H), 1.65 (s, 3H), 1.57 (d, *J* = 2.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 133.17, 130.26, 129.72, 128.55, 72.13, 70.83, 61.99, 46.00, 44.79, 42.35, 32.62, 30.28, 20.62. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{25}Cl_2O_2$ 331.1226; Found: 331.1225.



R_f = 0.5 (**30b**); R_f = 0.45 (**30b'**), 1% acetone in hexane

Compound **30b** (yellowish oil, 32 mg, 25% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 5.44 – 5.24 (m, 1H), 2.11 (td, *J* = 15.1, 8.0 Hz, 2H), 2.02 – 1.85 (m, 6H), 1.70 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.87, 133.03, 130.89, 129.59, 128.52, 71.39, 69.25, 36.49, 33.84, 26.79 [14].

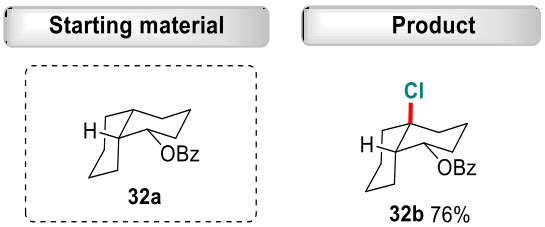
Compound **30b'** (yellowish oil, 40 mg, 32% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.99 – 4.92 (m, 1H), 2.14 – 1.95 (m, 6H), 1.76 – 1.64 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.17, 133.00, 130.69, 129.71, 128.44, 72.42, 70.25, 39.58, 33.12, 27.79 [14].



R_f = 0.7 (**31b**); R_f = 0.65 (**31b'**), 1% acetone in hexane

Compound **31b** (yellowish oil, 76 mg, 52% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 5.17 (td, *J* = 10.6, 4.6 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.16 – 2.11 (m, 1H), 2.04 – 1.99 (m, 1H), 1.80 – 1.75 (m, 1H), 1.66 – 1.60 (m, 8H), 1.41 – 1.32 (m, 1H), 1.13 (dd, *J* = 23.3, 12.3 Hz, 1H), 0.92 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.61, 133.04, 130.76, 129.81, 128.51, 74.92, 73.69, 52.42, 41.55, 34.22, 33.77, 31.29, 27.63, 21.82. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{24}ClO_2$ 295.1459; Found: 295.1460.

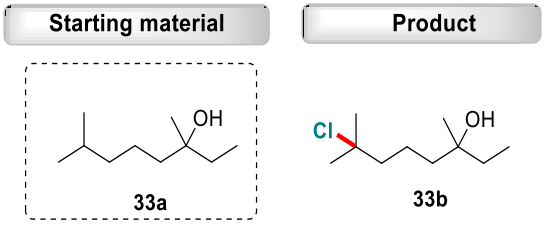
Compound **31b'** (yellowish oil, 20 mg, 12% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 5.56 (td, *J* = 10.5, 4.6 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.23 (dd, *J* = 15.6, 5.3 Hz, 1H), 2.10 – 2.05 (m, 1H), 1.96 (dd, *J* = 9.1, 4.4 Hz, 1H), 1.69 (s, 3H), 1.64 (s, 6H), 1.17 (t, *J* = 12.2 Hz, 1H), 0.99 – 0.85 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.22, 129.85, 128.58, 73.24, 72.19, 70.33, 52.19, 46.94, 40.51, 33.71, 33.52, 30.65, 24.27. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{23}Cl_2O_2$ 329.1070; Found: 329.1071.



R_f = 0.6 (**32b**), 5% acetone in hexane

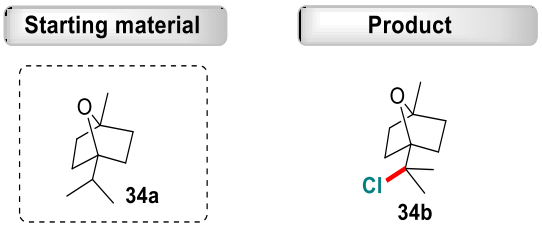
Compound **32b** (yellowish oil, 111 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.21 (t, *J* = 4.4 Hz, 1H), 2.24 (q, *J* = 13.2 Hz, 1H), 2.09 (dd, *J* = 28.7, 14.0 Hz, 2H), 1.95 (d, *J* = 9.2 Hz, 2H), 1.79 (q, *J* = 11.9 Hz, 2H), 1.67 – 1.56 (m, 5H), 1.45 (d, *J* = 10.3 Hz, 1H),

1.37 – 1.24 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 132.89, 130.78, 130.10, 128.44, 74.43, 71.84, 48.42, 43.33, 42.10, 30.67, 26.20, 25.99, 22.01, 17.43. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{22}ClO_2$ 293.1303; Found: 293.1301.



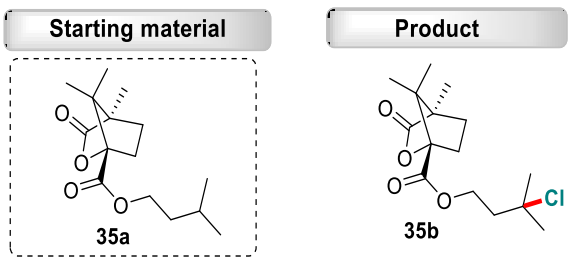
R_f = 0.4 (**33b**); 10% acetone in hexane

Compound **33b** (yellowish oil, 68 mg, 71% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.76 – 1.70 (m, 2H), 1.57 (s, 6H), 1.51 (t, *J* = 5.7 Hz, 4H), 1.43 (d, *J* = 5.6 Hz, 2H), 1.16 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 73.02, 71.26, 46.68, 41.38, 34.51, 32.56, 26.53, 19.67, 8.36 [4].



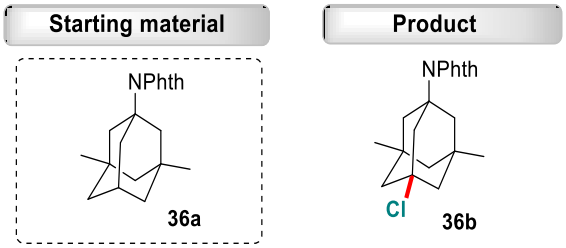
R_f = 0.6 (**34b**); 1% acetone in hexane

Compound **34b** (yellowish oil, 30 mg, 32% yield (^{1}H NMR yield: 77%)): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.02 (t, *J* = 12.5 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.69 – 1.62 (m, 8H), 1.61 – 1.53 (m, 2H), 1.46 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 91.02, 84.04, 71.67, 37.52, 33.19, 29.11, 21.31 [4].



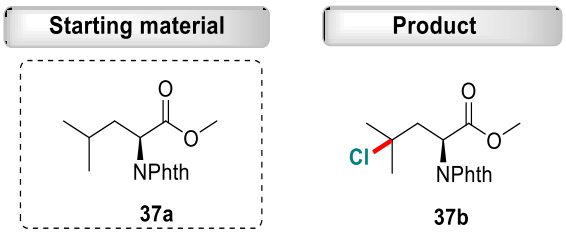
R_f = 0.6 (**35b**); 10% acetone in hexane

Compound **35b** (white solid, 109 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.44 (t, *J* = 6.9 Hz, 2H), 2.40 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.14 (t, *J* = 6.9 Hz, 2H), 1.99 (dd, *J* = 16.0, 6.9 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.66 (t, *J* = 9.1 Hz, 1H), 1.61 (s, 6H), 1.09 (s, 3H), 1.04 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.15, 167.53, 91.07, 68.15, 62.80, 54.86, 54.28, 43.84, 32.95, 30.74, 28.99, 16.86, 9.78. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{24}ClO_4$ 303.1358; Found: 303.1359.



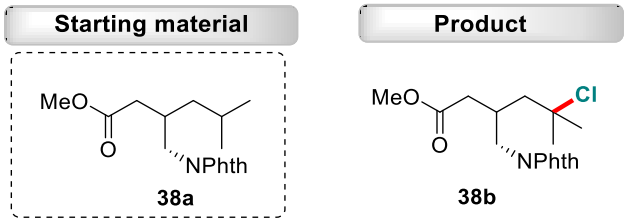
R_f = 0.6 (**36b**); 10% acetone in hexane

Compound **36b** (white solid, 97 mg, 57% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.68 (d, *J* = 5.5 Hz, 2H), 2.74 (s, 2H), 2.18 (d, *J* = 13.9 Hz, 2H), 2.10 (d, *J* = 12.4 Hz, 2H), 1.87 (d, *J* = 12.1 Hz, 2H), 1.75 (d, *J* = 12.0 Hz, 2H), 1.21 (dd, *J* = 28.8, 12.7 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.50, 134.03, 131.83, 122.85, 67.32, 62.39, 52.48, 48.78, 48.01, 44.63, 35.37, 29.43 [14].



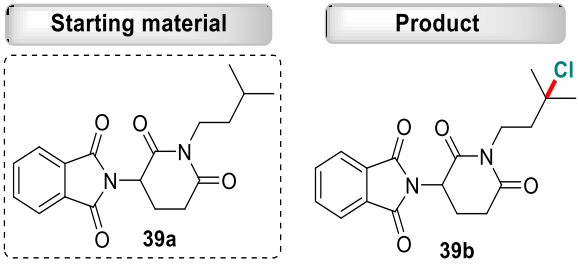
R_f = 0.5 (**37b**); 20% acetone in hexane

Compound **37b** (yellowish oil, 96 mg, 62% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H), 7.75 – 7.72 (m, 2H), 5.21 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.72 (s, 3H), 2.81 (dd, *J* = 15.6, 9.7 Hz, 1H), 2.74 (d, *J* = 15.6 Hz, 1H), 1.65 (s, 3H), 1.56 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.79, 167.72, 134.35, 132.04, 123.74, 68.28, 53.26, 49.38, 43.03, 33.34, 32.07 [4].



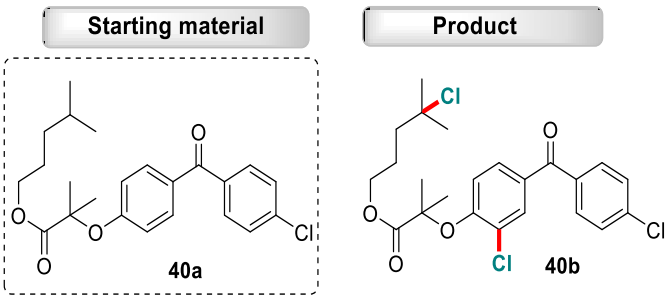
R_f = 0.4 (**38b**); 20% acetone in hexane

Compound **38b** (yellowish oil, 86 mg, 51% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 3.84 (dd, *J* = 13.8, 5.8 Hz, 1H), 3.71 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.58 (s, 3H), 2.66 – 2.58 (m, 1H), 2.45 (t, *J* = 5.9 Hz, 2H), 1.88 (qd, *J* = 15.2, 4.9 Hz, 2H), 1.62 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.48, 168.69, 134.15, 132.05, 123.40, 70.24, 51.67, 47.47, 42.64, 38.41, 32.89, 32.68, 32.23. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{21}ClNO_4$ 338.1154; Found: 338.1156.



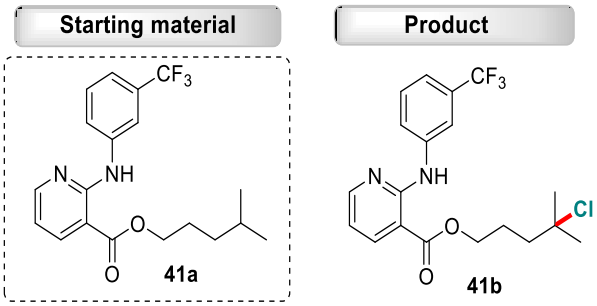
R_f = 0.4 (**39b**); 10% acetone in hexane

Compound **39b** (yellowish oil, 120 mg, 66% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.76 – 7.71 (m, 2H), 4.98 (dd, *J* = 12.7, 5.4 Hz, 1H), 4.10 – 3.91 (m, 2H), 3.05 – 2.89 (m, 1H), 2.84 – 2.67 (m, 2H), 2.19 – 2.05 (m, 1H), 2.04 – 1.86 (m, 2H), 1.57 (d, *J* = 2.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.78, 168.52, 167.48, 134.51, 131.79, 123.78, 68.50, 50.20, 42.60, 37.57, 32.50, 32.43, 32.06, 22.00 [4].



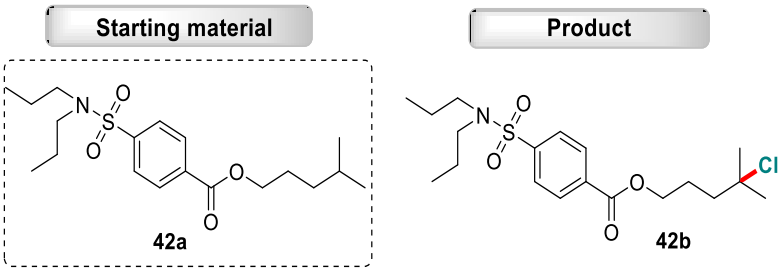
R_f = 0.5 (**40b**); 5% acetone in hexane

Compound **40b** (yellowish oil, 190 mg, 81% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.59 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.87 – 6.81 (m, 1H), 4.19 (t, *J* = 6.4 Hz, 2H), 1.81 (dt, *J* = 12.7, 6.5 Hz, 2H), 1.71 (s, 6H), 1.63 (dt, *J* = 8.1, 4.9 Hz, 2H), 1.50 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.12, 173.33, 155.48, 138.94, 135.78, 132.59, 131.32, 131.24, 129.73, 128.84, 125.61, 116.70, 81.11, 70.04, 65.72, 42.13, 32.47, 25.46, 24.54. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{23}H_{23}Cl_3O_4$ 471.0891; Found: 471.0888.



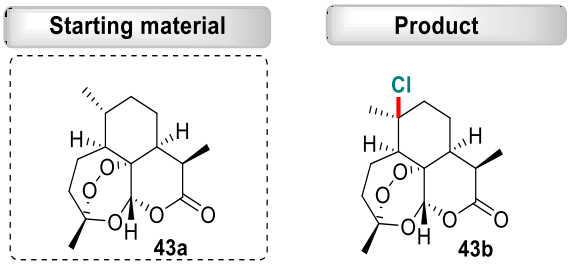
R_f = 0.5 (**41b**); 20% acetone in hexane

Compound **41b** (yellowish oil, 116 mg, 58% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.42 (d, *J* = 6.7 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.10 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 6.82 – 6.78 (m, 1H), 4.37 (t, *J* = 6.5 Hz, 2H), 2.03 (dt, *J* = 10.4, 6.6 Hz, 2H), 1.92 – 1.86 (m, 2H), 1.63 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.56, 155.91, 153.21, 140.47, 140.28, 131.25 (q, *J* = 32.0 Hz), 129.32, 125.41, 123.42 (d, *J* = 44.3 Hz), 119.12 (d, *J* = 3.9 Hz), 117.21 (q, *J* = 4.0 Hz), 114.21, 107.62, 70.22, 65.39, 42.45, 32.59, 24.78. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.60 [4].



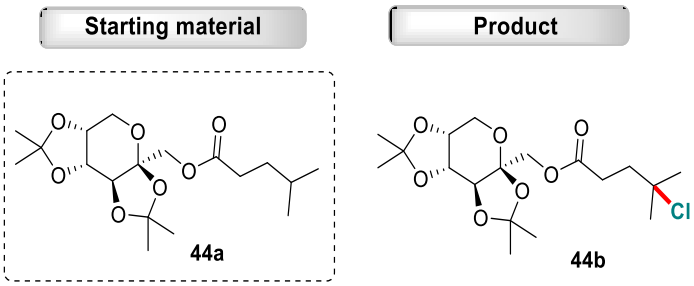
R_f = 0.5 (**42b**); 20% acetone in hexane

Compound **42b** (yellowish oil, 119 mg, 59% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.13 – 3.04 (m, 4H), 2.01 (dt, *J* = 10.3, 6.7 Hz, 2H), 1.88 (dd, *J* = 11.9, 4.4 Hz, 2H), 1.61 (s, 6H), 1.54 (dd, *J* = 15.1, 7.5 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.36, 144.39, 133.65, 130.32, 127.14, 70.27, 65.58, 50.06, 42.41, 32.58, 24.80, 22.07, 11.29. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{19}H_{31}ClNO_4S$ 404.1657; Found: 404.1656.



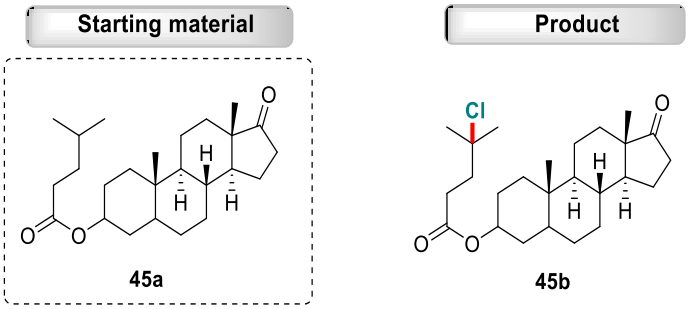
R_f = 0.4 (**43b**); 20% acetone in hexane

Compound **43b** (white solid, 73 mg, 46% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.55 (s, 1H), 3.38 – 3.32 (m, 1H), 2.47 – 2.41 (m, 1H), 2.24 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.19 – 2.13 (m, 2H), 1.98 – 1.91 (m, 2H), 1.84 – 1.79 (m, 3H), 1.66 (s, 3H), 1.46 (s, 3H), 1.22 (t, *J* = 8.3 Hz, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.95, 105.36, 93.52, 79.41, 74.26, 53.81, 45.41, 42.80, 35.51, 33.00, 32.87, 25.36, 21.43, 20.26, 12.70. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{22}ClO_5$ 317.1150; Found: 317.1152.



R_f = 0.4 (**44b**); 5% acetone in hexane

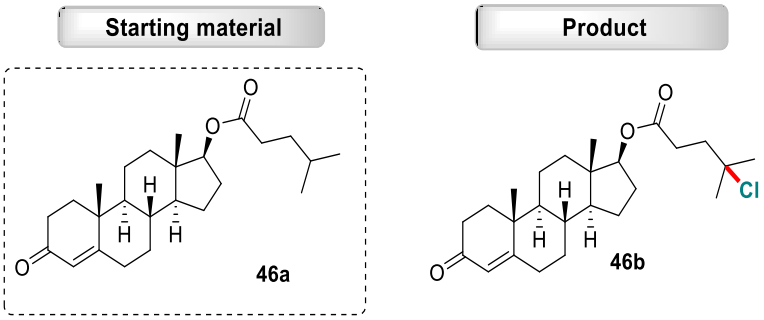
Compound **44b** (yellowish oil, 134 mg, 68% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.60 (d, *J* = 7.9 Hz, 1H), 4.42 (dd, *J* = 11.7, 5.3 Hz, 1H), 4.29 (d, *J* = 12.7 Hz, 1H), 4.24 (d, *J* = 7.9 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.90 (d, *J* = 13.1 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 2.63 – 2.60 (m, 1H), 2.10 (dd, *J* = 9.9, 6.1 Hz, 2H), 1.57 (t, *J* = 16.3 Hz, 8H), 1.48 (s, 3H), 1.41 (t, J = 6.0 Hz, 4H), 1.34 (s, 3H), 1.26 (d, *J* = 14.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.64, 109.28, 108.90, 101.64, 70.89, 70.72, 70.19, 69.63, 65.62, 61.39, 40.38, 32.48, 30.37, 26.62, 26.03, 25.38, 24.20, 21.07. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{30}ClO_7$ 393.1675; Found: 393.1676.



R_f = 0.4 (**45b**); 10% acetone in hexane

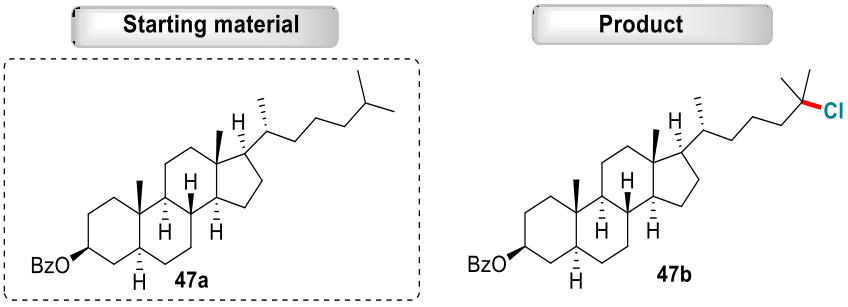
Compound **45b** (white solid, 114 mg, 54% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.75 – 4.64 (m, 1H), 2.51 (s, 1H), 2.43 (dd, *J* = 19.3, 8.6 Hz, 1H), 2.08 – 2.04 (m, 2H), 1.95 – 1.89 (m, 1H), 1.78 (dt, *J* = 8.3, 7.3 Hz, 3H), 1.70 – 1.60 (m, 5H), 1.59 – 1.47 (m, 8H), 1.36 – 1.31 (m, 2H), 1.30 – 1.19 (m, 6H), 1.06 – 0.93 (m, 2H), 0.85 (s, 6H), 0.74 – 0.67 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.41, 172.90, 73.80, 69.87, 54.46, 51.52, 47.93, 44.80, 40.61, 36.84, 35.99, 35.80, 35.18, 34.08, 32.49, 31.67,

30.97, 30.95, 28.42, 27.54, 21.92, 20.61, 13.96, 12.36. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{40}ClO_3$ 423.2660; Found: 423.2659.



R_f = 0.5 (**46b**), 10% EtOAc in hexane

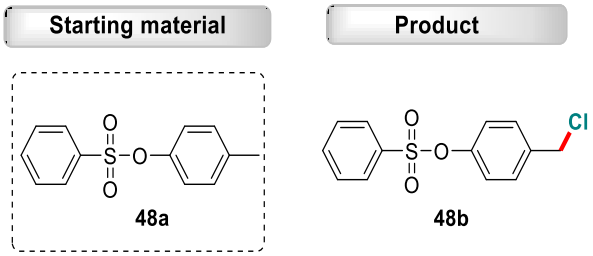
Compound **46b** (white solid, 96 mg, 46% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.70 (s, 1H), 4.64 – 4.56 (m, 1H), 2.53 (dd, *J* = 9.5, 6.8 Hz, 2H), 2.43 – 2.24 (m, 4H), 2.21 – 2.12 (m, 1H), 2.09 – 1.97 (m, 3H), 1.83 (d, *J* = 10.0 Hz, 1H), 1.77 (d, *J* = 12.7 Hz, 1H), 1.66 (dt, *J* = 16.1, 9.4 Hz, 2H), 1.60 – 1.44 (m, 9H), 1.43 – 1.31 (m, 2H), 1.19 – 1.13 (m, 4H), 1.02 (dd, *J* = 18.9, 7.1 Hz, 2H), 0.96 – 0.89 (m, 1H), 0.83 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.49, 173.26, 170.98, 124.03, 82.68, 69.82, 53.77, 50.31, 42.61, 40.53, 38.69, 36.72, 35.78, 35.47, 34.02, 32.81, 32.45, 31.56, 30.65, 27.56, 23.56, 20.61, 17.49, 12.18. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{25}H_{38}ClO_3$ 421.2504; Found: 421.2502.



R_f = 0.6 (**47b**); 2% acetone in hexane

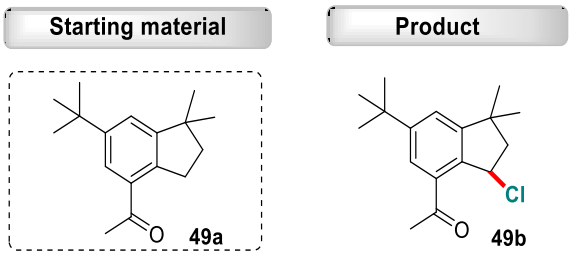
Compound **47b** (white solid, 137 mg, 52% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.99 – 4.90 (m, 1H), 2.00 – 1.89 (m, 2H), 1.87 – 1.64 (m, 6H), 1.61 – 1.45 (m, 9H), 1.43 – 1.23 (m, 9H), 1.17 – 0.99 (m, 6H), 0.96 – 0.79 (m, 10H), 0.66 (s, 3H). **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 166.27, 132.78, 131.10, 129.65, 128.37, 74.51, 71.60, 56.56, 56.37, 54.38, 46.67, 44.86, 42.78, 40.14, 36.96, 36.11, 35.87, 35.65, 34.28, 32.62, 32.58, 32.15, 28.79, 28.41, 27.74, 24.36, 21.84, 21.38, 18.77, 12.45, 12.25. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{34}H_{52}ClO_2$ 527.3650; Found: 527.3651.



R_f = 0.4 (**48b**), 10% acetone in hexane

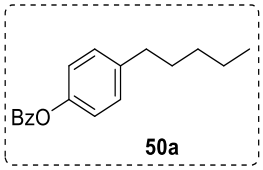
Compound **48b** (yellowish oil, 54 mg, 43% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 4.53 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.45, 136.66, 135.41, 134.45, 130.01, 129.33, 128.59, 122.75, 45.25. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{12}ClO_3S$ 283.0190; Found: 283.0191.



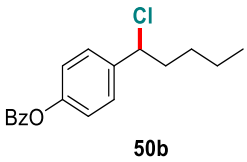
R_f = 0.7 (**49b**), 5% acetone in hexane

Compound **49b** (yellowish oil, 118 mg, 85% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.7 Hz, 1H), 7.40 (s, 1H), 5.59 (d, *J* = 5.8 Hz, 1H), 2.65 (s, 3H), 2.23 – 2.16 (m, 1H), 2.08 (dd, *J* = 13.7, 1.7 Hz, 1H), 1.37 (s, 9H), 1.34 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.95, 154.88, 153.38, 136.29, 134.05, 125.95, 124.09, 63.39, 48.04, 42.88, 35.14, 31.53, 30.81, 29.37, 28.27 [4].

Starting material | Product



50a

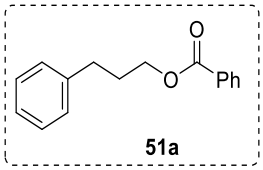


50b

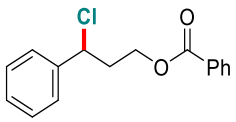
R_f = 0.6 (**50b**), 5% acetone in hexane

Compound **50b** (yellowish oil, 82 mg, 54% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.1 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 4.93 – 4.84 (m, 1H), 2.20 – 2.09 (m, 1H), 2.09 – 2.01 (m, 1H), 1.53 – 1.43 (m, 1H), 1.40 – 1.31 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.17, 150.73, 139.79, 133.81, 130.32, 129.55, 128.73, 128.28, 121.95, 63.30, 39.96, 29.33, 22.27, 14.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{20}ClO_2$ 303.1146; Found: 303.1147.

Starting material | Product



51a

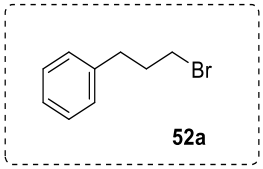


51b

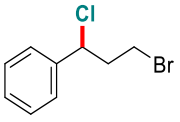
R_f = 0.7 (**51b**), 5% acetone in hexane

Compound **51b** (yellowish oil, 104 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.36 (m, 6H), 7.32 (t, *J* = 7.1 Hz, 1H), 5.26 – 5.06 (m, 1H), 4.57 – 4.47 (m, 1H), 4.41 (dt, *J* = 11.4, 5.7 Hz, 1H), 2.67 – 2.46 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.42, 141.01, 133.21, 130.08, 129.69, 128.94, 128.69, 128.53, 127.05, 62.17, 60.13, 39.05 [4].

Starting material | Product



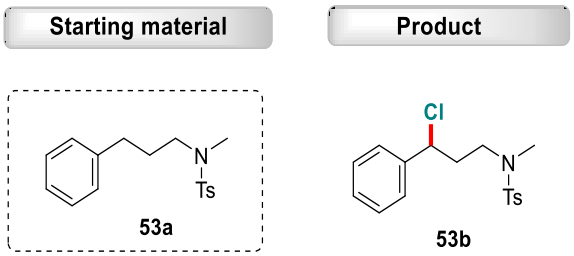
52a



52b

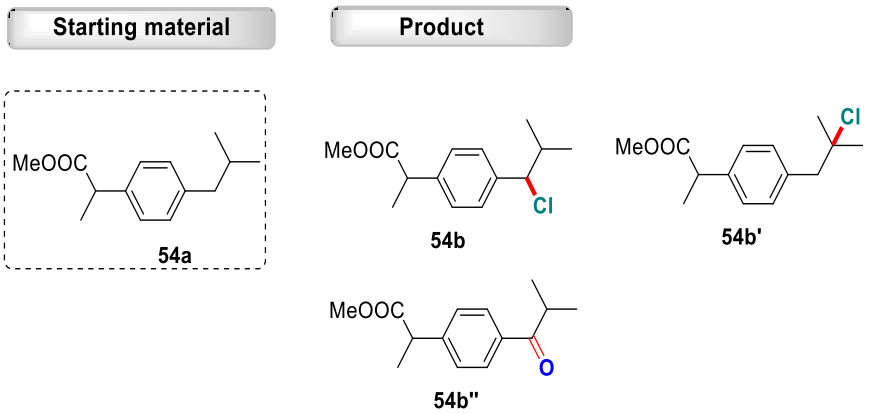
R_f = 0.7 (**52b**), 1% acetone in hexane

Compound **52b** (yellowish oil, 83 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 5H), 5.12 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.59 (dd, *J* = 14.7, 9.2 Hz, 1H), 3.45 – 3.38 (m, 1H), 2.63 (td, *J* = 14.8, 5.8 Hz, 1H), 2.55 – 2.39 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.58, 128.97, 128.80, 127.14, 61.24, 42.46, 30.25 [4].



R_f = 0.6 (**53b**), 5% acetone in hexane

Compound **53b** (yellowish oil, 113 mg, 67% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 3H), 5.01 – 4.96 (m, 1H), 3.20 (dt, *J* = 14.3, 7.3 Hz, 1H), 3.13 – 3.07 (m, 1H), 2.75 (s, 3H), 2.43 (s, 3H), 2.34 – 2.28 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.63, 141.16, 134.27, 129.85, 128.87, 128.64, 127.60, 127.06, 60.64, 48.23, 38.55, 35.87, 21.63. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{21}ClNO_2S$ 338.0976; Found: 338.0978.



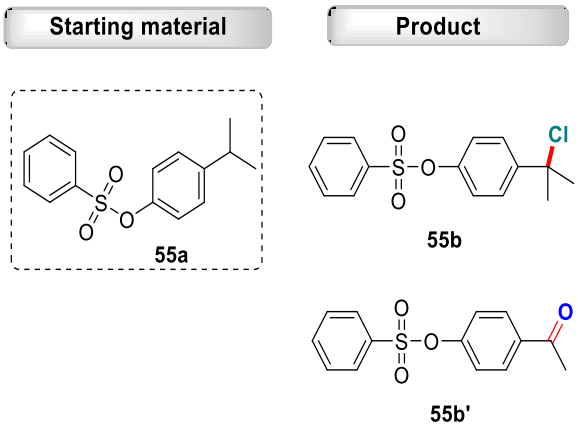
R_f = 0.8 (**54b**); R_f = 0.7 (**54b'**) ; R_f = 0.5 (**54b''**), 5% acetone in hexane

Compound **54b** (yellowish oil, 59 mg, 46% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 5.2 Hz, 2H), 4.62 (d, *J* = 7.6 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 2.22 (dd, *J* = 14.0, 6.7 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H),

1.10 (d, *J* = 6.6 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.00, 140.30, 140.05, 127.86, 127.57, 70.63, 52.22, 45.22, 36.70, 20.34, 19.69, 18.70 [21].

Compound **54b'** (yellowish oil, 18 mg, 14% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (q, *J* = 8.3 Hz, 4H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.04 (s, 2H), 1.57 (s, 6H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.19, 139.15, 135.96, 131.19, 127.18, 70.23, 52.20, 51.54, 45.20, 32.31, 18.74. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{20}ClO_2$ 255.1146; Found: 255.1146.

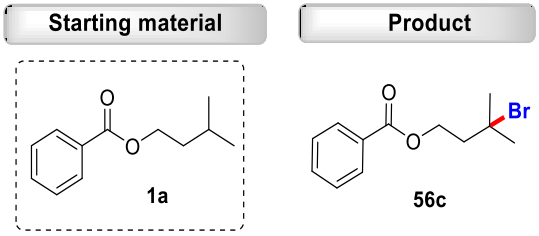
Compound **54b''** (yellowish oil, 12 mg, 10% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 3.79 (q, *J* = 6.8 Hz, 1H), 3.67 (s, 3H), 3.53 (dt, *J* = 13.7, 6.8 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 1.20 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.11, 174.46, 145.59, 135.28, 128.90, 127.95, 52.36, 45.56, 35.49, 19.29, 18.56 [22].



R_f = 0.6 (**55b**); R_f = 0.5 (**55b'**), 10% acetone in hexane

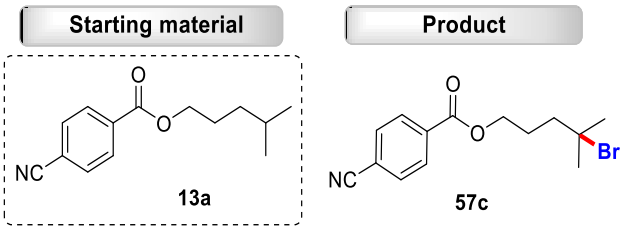
Compound **55b** (yellowish oil, 96 mg, 62% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 1.60 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.73, 143.90, 135.53, 134.40, 129.31, 128.59, 126.72, 122.42, 63.39, 28.48. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{16}ClO_3S$ 311.0503; Found: 311.0504.

Compound **55b'** (yellowish oil, 14 mg, 10% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 2.57 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.73, 152.98, 135.89, 135.24, 134.66, 130.19, 129.43, 128.56, 122.59, 26.74 [16].



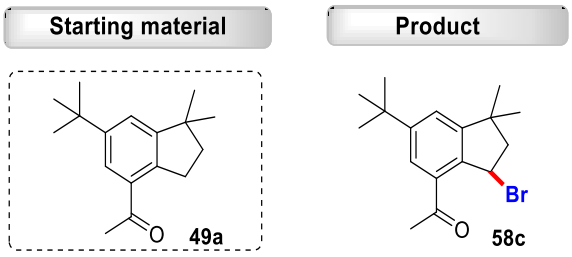
R_f = 0.6 (**56c**), 5% acetone in hexane

Compound **56c** (yellowish oil, 98 mg, 73% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.59 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 6.7 Hz, 2H), 1.86 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.60, 133.15, 130.26, 129.70, 128.54, 64.41, 63.25, 45.61, 34.89 [23].



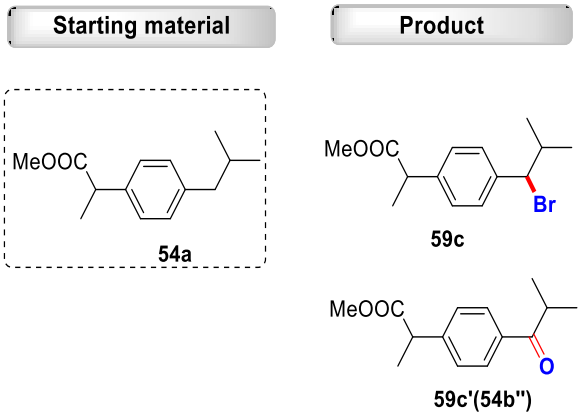
R_f = 0.5 (**57c**), 5% acetone in hexane

Compound **57c** (yellowish oil, 80 mg, 52% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 4.40 (t, *J* = 6.5 Hz, 2H), 2.04 (dd, *J* = 10.1, 5.7 Hz, 2H), 1.91 (dd, *J* = 12.9, 4.5 Hz, 2H), 1.80 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.06, 134.19, 132.40, 130.24, 118.12, 116.58, 66.91, 65.60, 43.88, 34.40, 26.04. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{17}BrNO_2$ 310.0437; Found: 310.0436.



R_f = 0.7 (**58c**), 5% acetone in hexane

Compound **58c** (yellowish oil, 122 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.6 Hz, 1H), 7.40 (s, 1H), 5.59 (d, *J* = 5.8 Hz, 1H), 2.65 (s, 3H), 2.19 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.08 (d, *J* = 13.7 Hz, 1H), 1.37 (s, 9H), 1.34 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.96, 154.88, 153.38, 136.29, 134.03, 125.96, 124.10, 63.39, 48.04, 42.88, 35.14, 31.54, 30.81, 29.37, 28.28. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{17}H_{24}BrO$ 323.1005; Found: 323.1006.



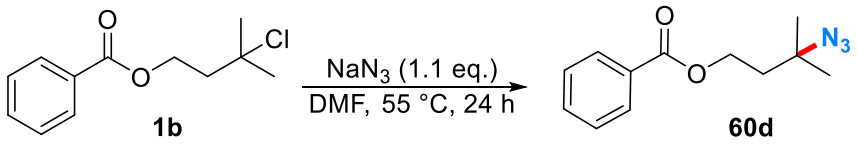
R_f = 0.7 (**59c**); R_f = 0.5 (**59c'**), 5% acetone in hexane

Compound **59c** (yellowish oil, 94 mg, 63% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.25 (t, *J* = 5.4 Hz, 2H), 4.71 (d, *J* = 8.4 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 2.29 (dq, *J* = 13.2, 6.6 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.92, 140.58, 140.32, 128.21, 127.65, 64.12, 52.20, 45.20, 36.65, 21.61, 20.70, 18.67 [24].

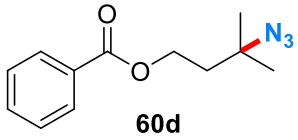
Compound **59c'** (yellowish oil, 15 mg, 13% yield).

9. Conversion of introduced chlorine atom

9.1 Converted to compound 60d



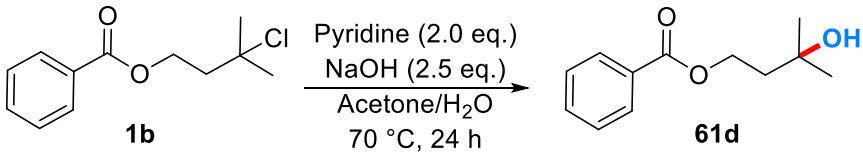
To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv) in DMF (2.0 mL) was added NaN_3 (72 mg, 1.1 mmol, 1.1 equiv) and the reaction mixture was stirred at 55 ^oC for 24 hours. The reaction mixture was extracted with EtOAc. The combined organic layers were washed with bine, dried over Na_2SO_4 and concentrated under reduced preesure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **60d** (193 mg, 83% yield). The spectroscopic data of **60d** were consistent with those previously reported in the literature [14].



R_f = 0.5, 5% acetone in hexane, yellowish oil (193 mg, 83% yield)

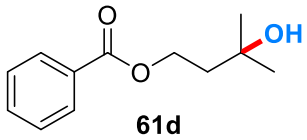
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.43 (t, *J* = 6.8 Hz, 2H), 1.97 (t, *J* = 6.8 Hz, 2H), 1.37 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.52, 133.07, 130.19, 129.61, 128.46, 61.32, 60.33, 39.78, 26.44.

9.2 Converted to compound 61d



To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv) in 20 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 nitroen. 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 tremove most of the acetone.

The product was extracted with EtOAc (3 x 10 mL). The combined EtOAc extracts were washed with 3 M HCl (8 mL) and 10% $NaHCO_3$ (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced preesure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **61d** (133 mg, 64% yield). The spectroscopic data of **61d** were consistent with those previously reported in the literature [25].

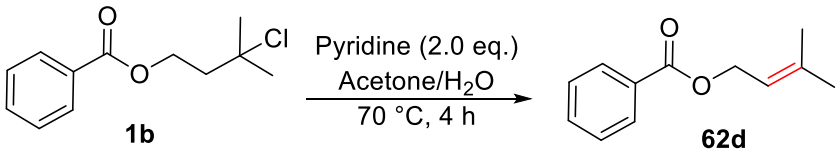


61d

R_f = 0.3, 20% acetone in hexane, yellowish oil (133 mg, 64% yield)

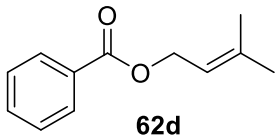
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.50 (t, *J* = 6.8 Hz, 2H), 1.98 (t, *J* = 6.8 Hz, 2H), 1.80 (s, 1H), 1.32 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.76, 133.09, 130.35, 129.63, 128.52, 70.21, 62.09, 41.86, 29.88.

9.3 Converted to compound 62d



1b **62d**

To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv) in 20 mL of 3:1 acetone/water was added Pyridine (2.0 mmol, 2.0 equiv) in a 48.0 mL resealable pressure tube under nitroen. The solution was stirred and heated at 70 ^oC for 4 h. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure tremove most of the acetone. The product was extracted with EtOAc (3 x 10 mL). The combined EtOAc extracts were washed with 3 M HCl (8 mL) and 10% $NaHCO_3$ (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced preesure. The crude residue was purified by flash column chromatography on silica gel to afford the target compound **62d** (131 mg, 69% yield). The spectroscopic data of **62d** were consistent with those previously reported in the literature [26].

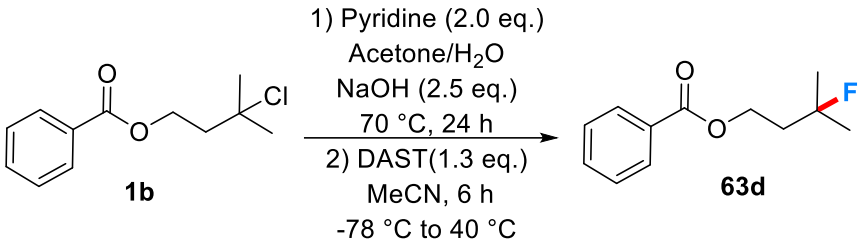


62d

R_f = 0.6, 1% acetone in hexane, yellowish oil (131 mg, 69% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 5.47 (t, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 7.2 Hz, 2H), 1.78 (d, *J* = 8.2 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.77, 139.23, 132.88, 130.62, 129.69, 128.39, 118.80, 61.99, 25.91, 18.22.

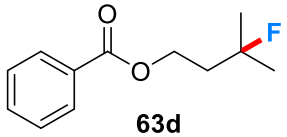
9.4 Converted to compound 63d



To a solution of compound **1b** (226 mg, 1.0 mmol, 1.0 equiv) in 20 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 nitroen. 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 tremove most of the acetone. The product was extracted with EtOAc (3 x 10 mL). The combined EtOAc extracts were washed with 3 M HCl (8 mL) and saturated aqueous $NaHCO_3$ (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced preesure.

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 ^oC under N_2. The reaction mixture was warmed to 40 ^oC and stirred for 6 h. The reaction mixture was extracted with DCM (3 x 10 mL), washed with saturated aqueous $NaHCO_3$ (3 x 5 mL) and brine (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced preesure. The crude residue was purified by flash column

chromatography on silica gel to afford the target compound **63d** (112 mg, 53% yield). The spectroscopic data of **63d** were consistent with those previously reported in the literature [27].

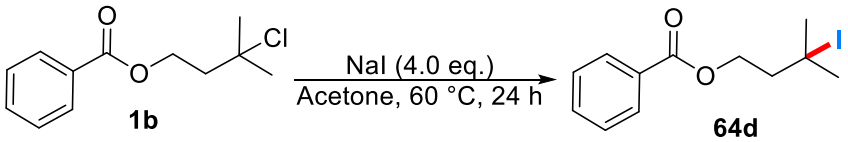


63d

R_f = 0.5, 5% acetone in hexane, yellowish oil (112 mg, 53% yield)

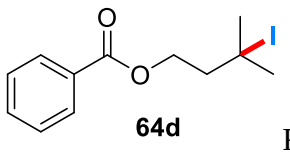
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 4.48 (t, *J* = 6.8 Hz, 2H), 2.12 (dt, *J* = 19.5, 6.8 Hz, 2H), 1.47 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 133.08, 130.31, 129.65, 128.50, 94.39 (d, *J* = 166.1 Hz), 61.05 (d, *J* = 6.2 Hz), 39.95 (d, *J* = 23.2 Hz), 27.21 (d, *J* = 24.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -137.98 – -138.30 (m, 1F).

9.5 Converted to compound 64d



1b **64d**

In a 15 mL resealable pressure tube, **1b** (339 mg, 1.5 mmol, 1.0 equiv) and NaI (6.0 mmol, 4.0 equiv) were dissolved in acetone (5.0 mL). The solution was stirred and heated at 60 ^{o}C for 24 h. After cooling to room temperature, CH_2Cl_2 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 **64d** (271 mg, 57% yield). The spectroscopic data of **64d** were consistent with those previously reported in the literature [28].

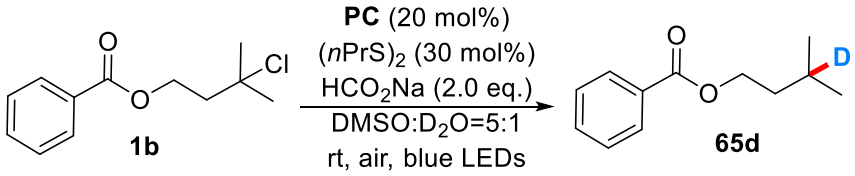


64d

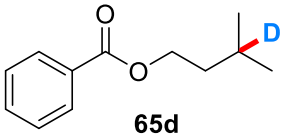
R_f = 0.5, 1% EtOAc in hexane, yellowish oil (271 mg, 57% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.56 (t, *J* = 6.8 Hz, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 2.03 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.59, 133.16, 130.20, 129.70, 128.53, 65.22, 48.32, 46.40, 38.67.

9.6 Converted to compound 65d



A dried 5 mL glass vial was charged with **1b** (45.2 mg, 0.20 mmol, 1.0 equiv), *N*-ethyl-3,6-bis(dimethylamino)carbazole (**PC**) (11.2 mg, 0.040 mmol, 20 mol%), (nPrS)$_2$ (0.060 mmol, 30 mol%), HCO_2Na (0.40 mmol, 2.0 equiv), D_2O (0.2 mL) and DMSO (1.0 mL) under air and then performed in a sealed vessel. The glass vial was positioned approximately 3 cm away from a 50 W blue LEDs lamp (max = 400 nm). After being stirred at room temperature for 72 h, the reaction mixture was purified by flash chromatography to afford as a Yellowish oil **65d** (28.0 mg, 73% yield, 81% D). The spectroscopic data of **65d** were consistent with those previously reported in the literature [29].



R_f = 0.5, 1% EtOAc in hexane, yellowish oil (28.0 mg, 73% yield, 81% D)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 1.78 (d, *J* = 8.0 Hz, 0.19H), 1.65 (d, *J* = 6.2 Hz, 2H), 0.97 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.84, 132.93, 130.65, 129.66, 128.45, 63.76, 37.45, 25.36, 25.13 – 24.60 (m), 22.53.

10. X-ray crystallographic data for compound 43b

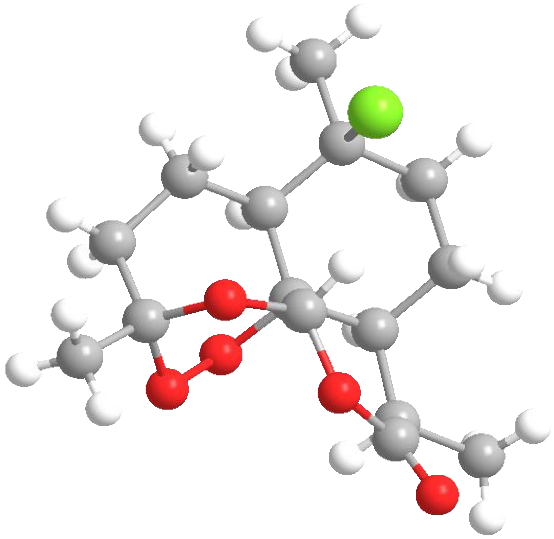


Figure 7. X-ray structure of compound **43b**

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **43b** in a mixture of CH_2Cl_2 and hexane at room temperature. The X-ray data of compound **43b** is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2124132.

11. References

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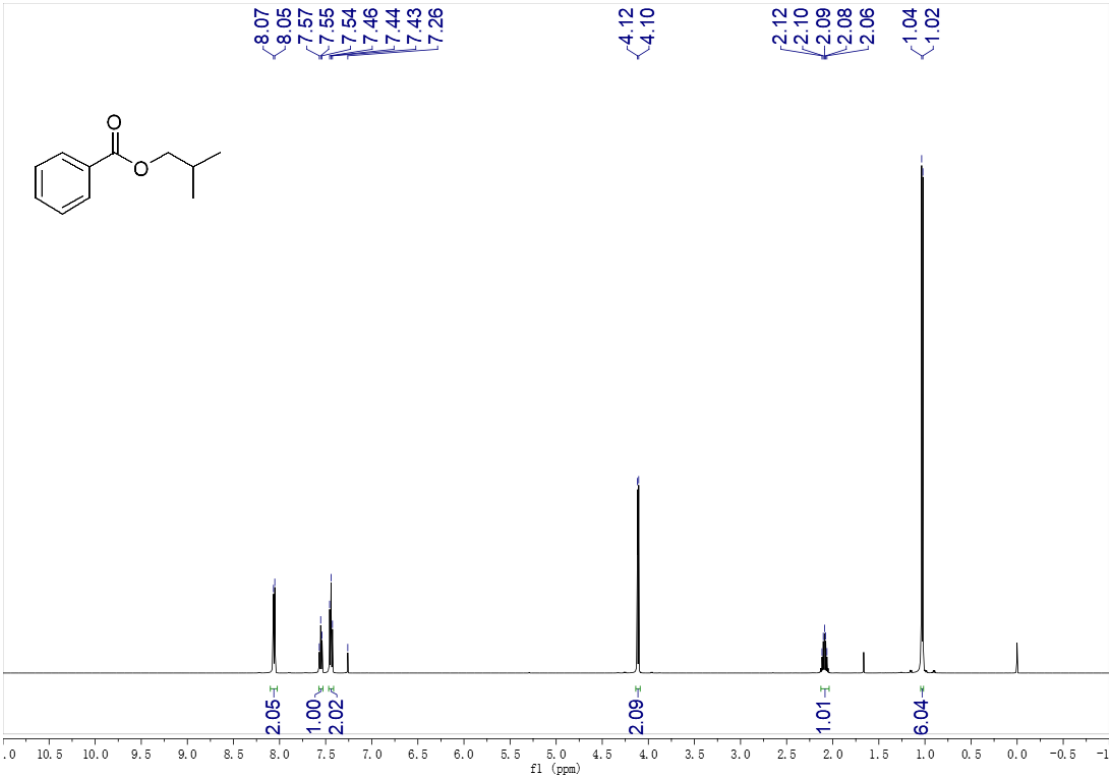
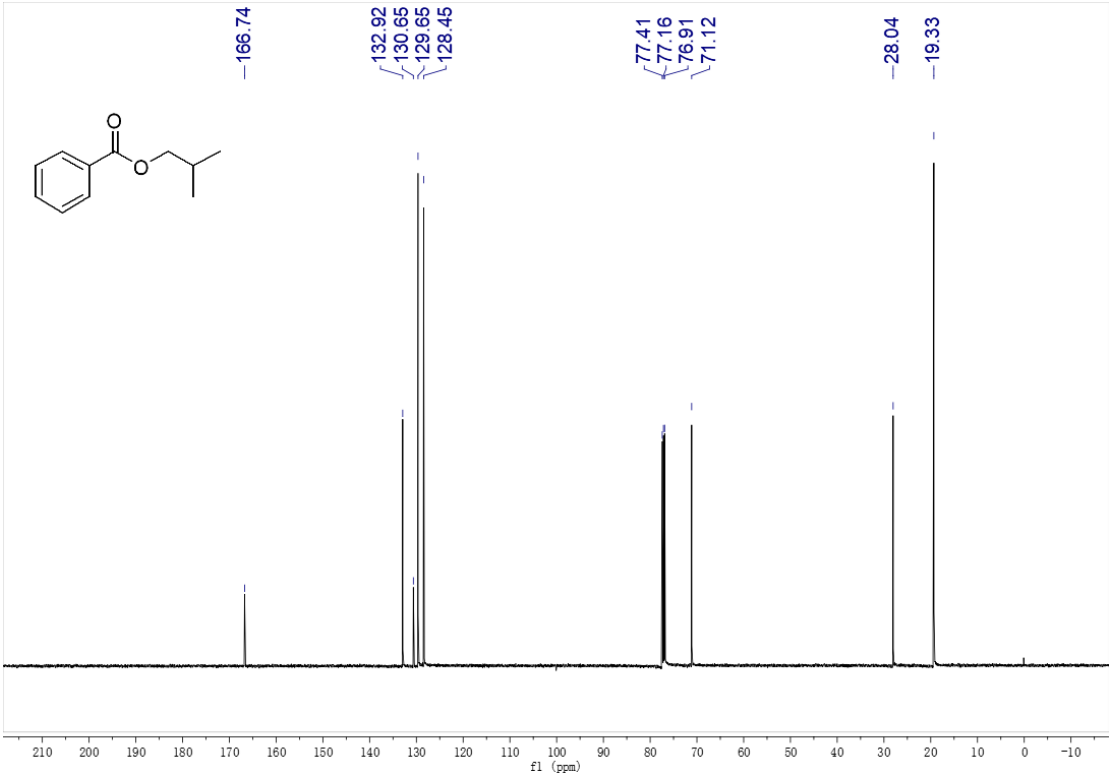
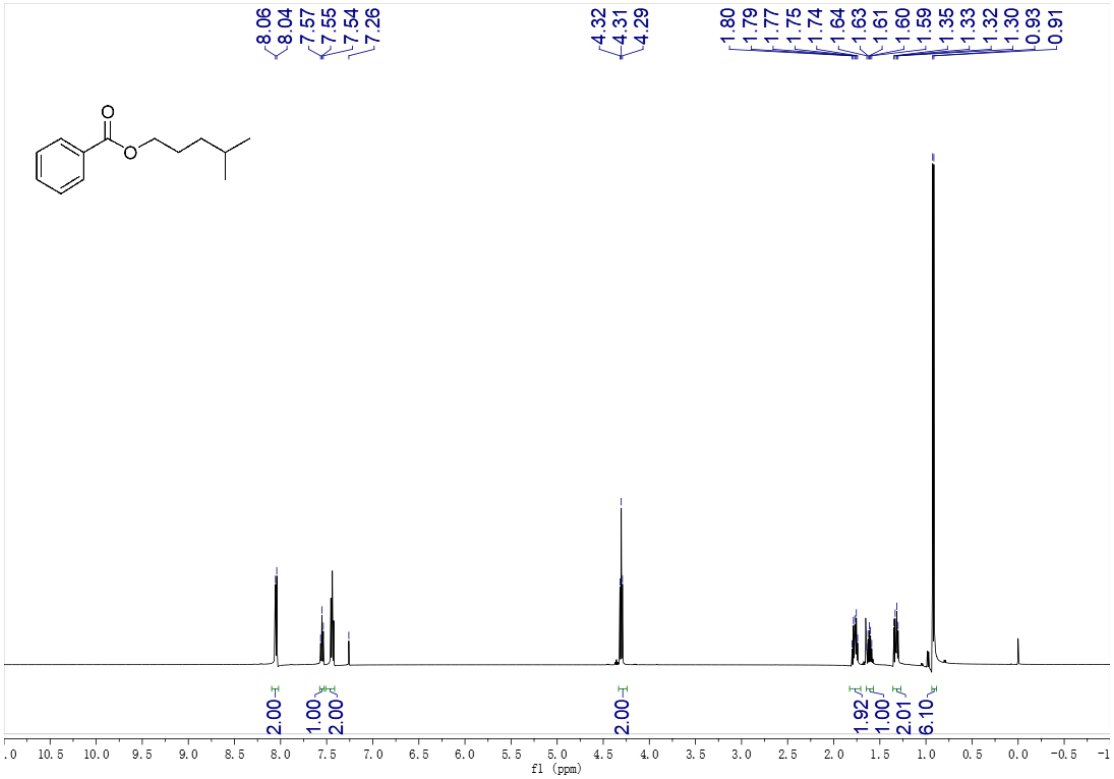
12. ^{1}H-NMR and ^{13}C-NMR spectra



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



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



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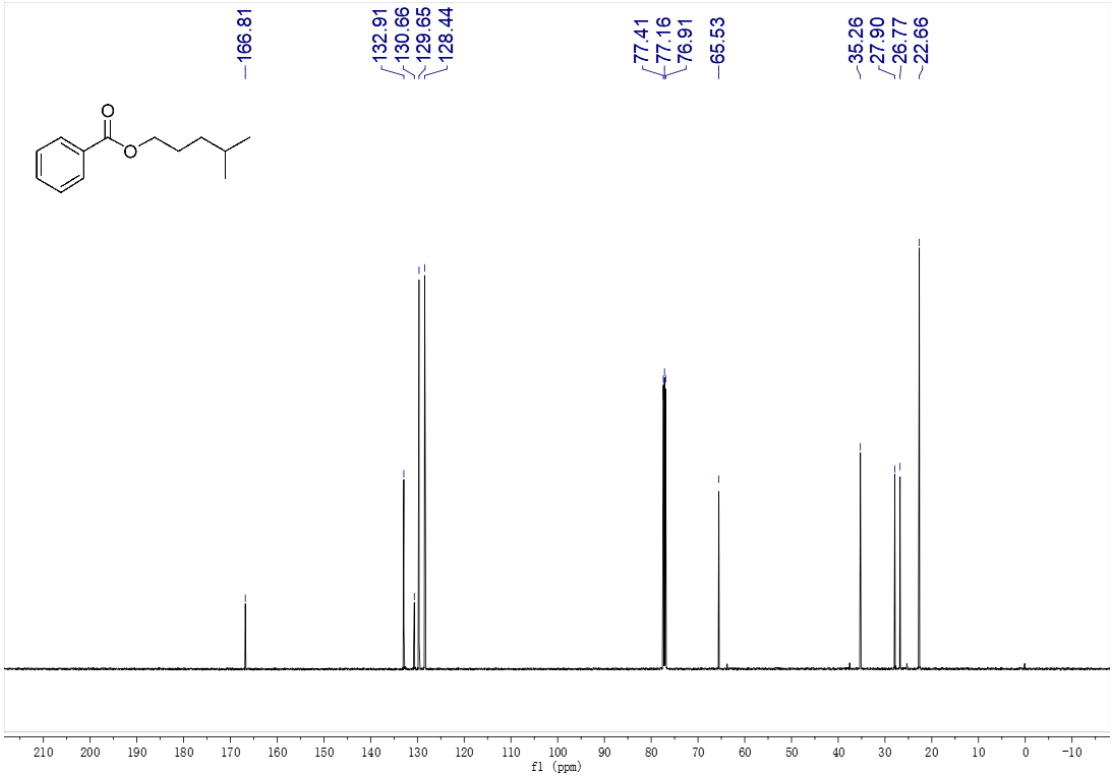
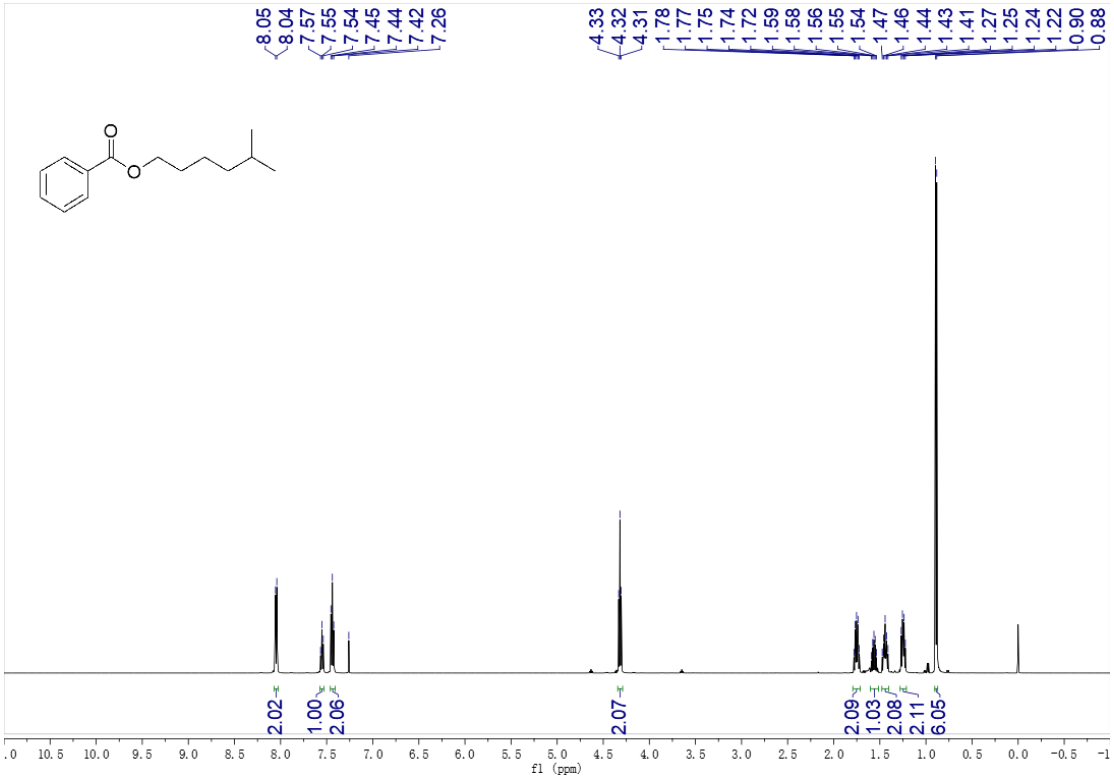


^{13}C NMR of compound **3a** (126 MHz, $CDCl_3$)



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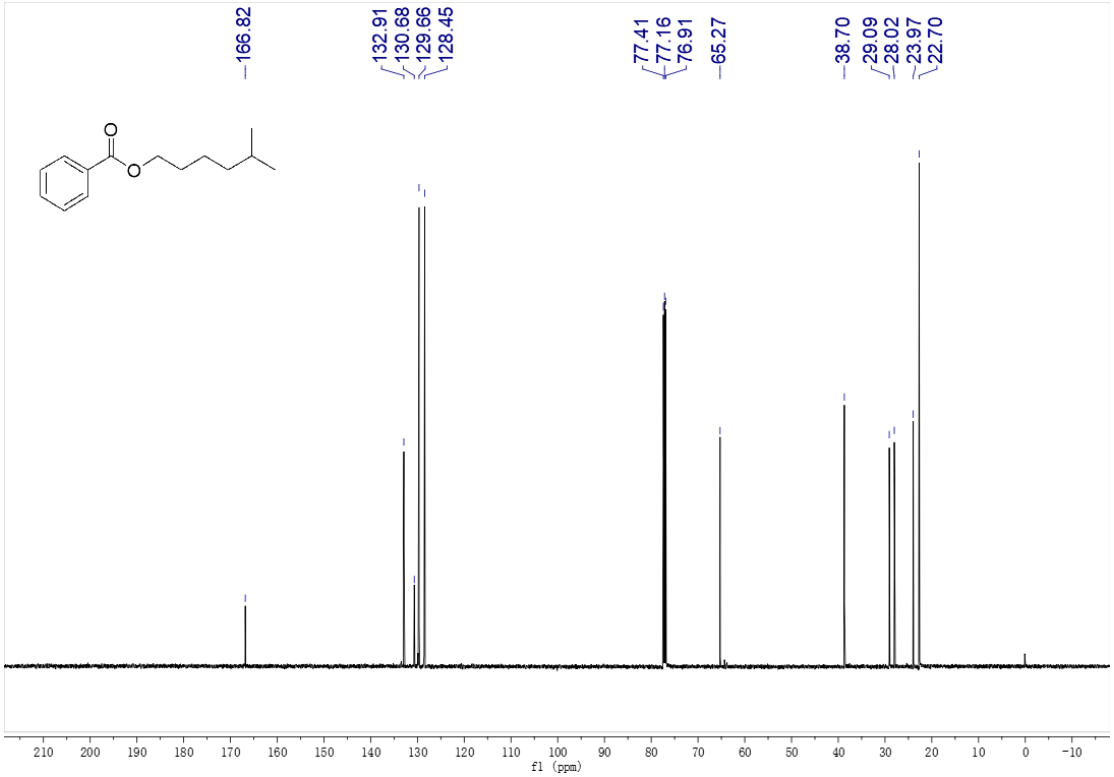

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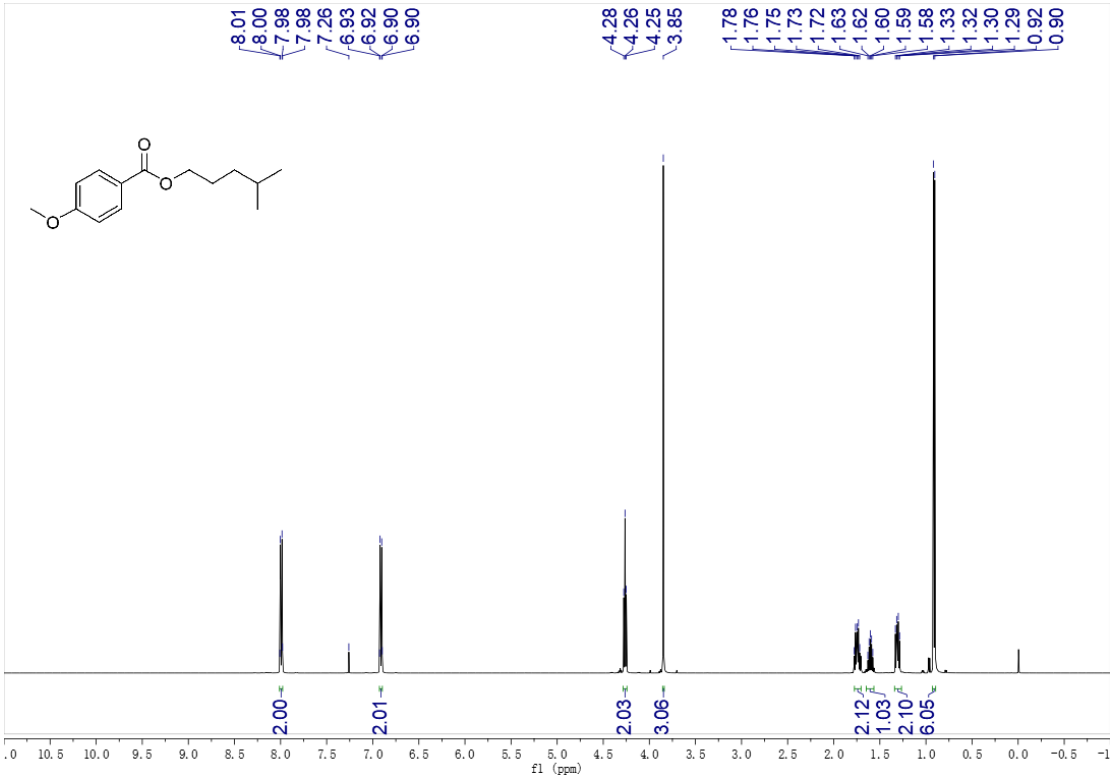

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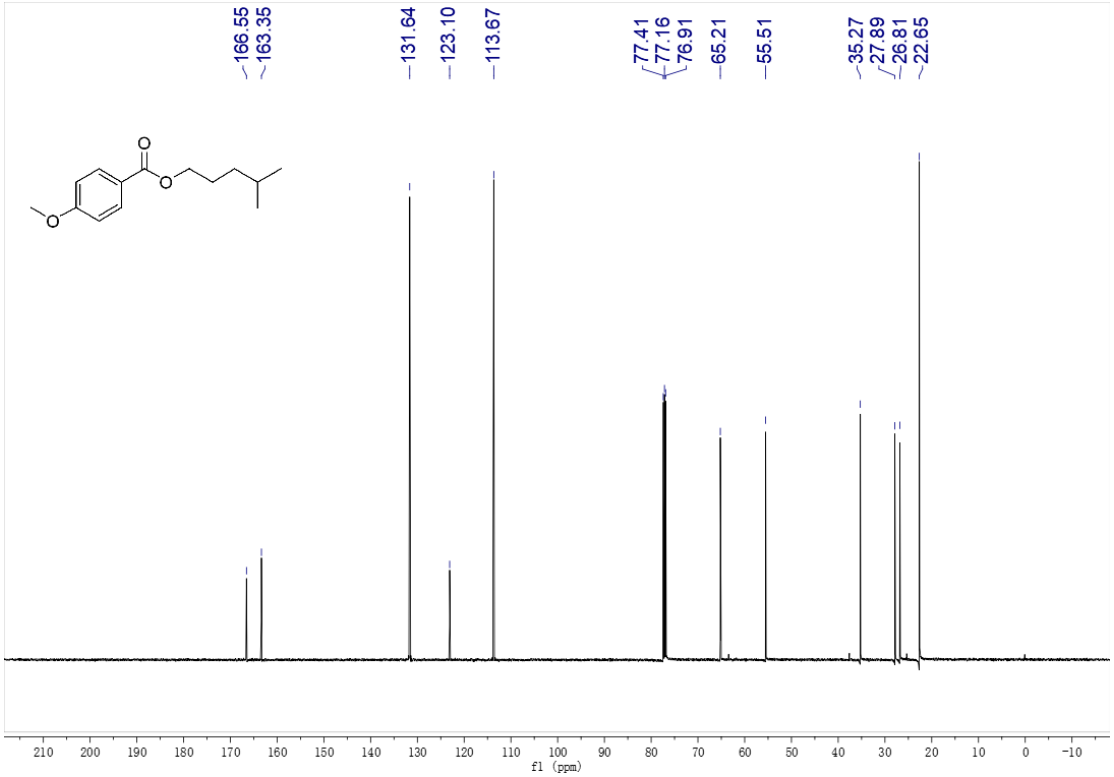
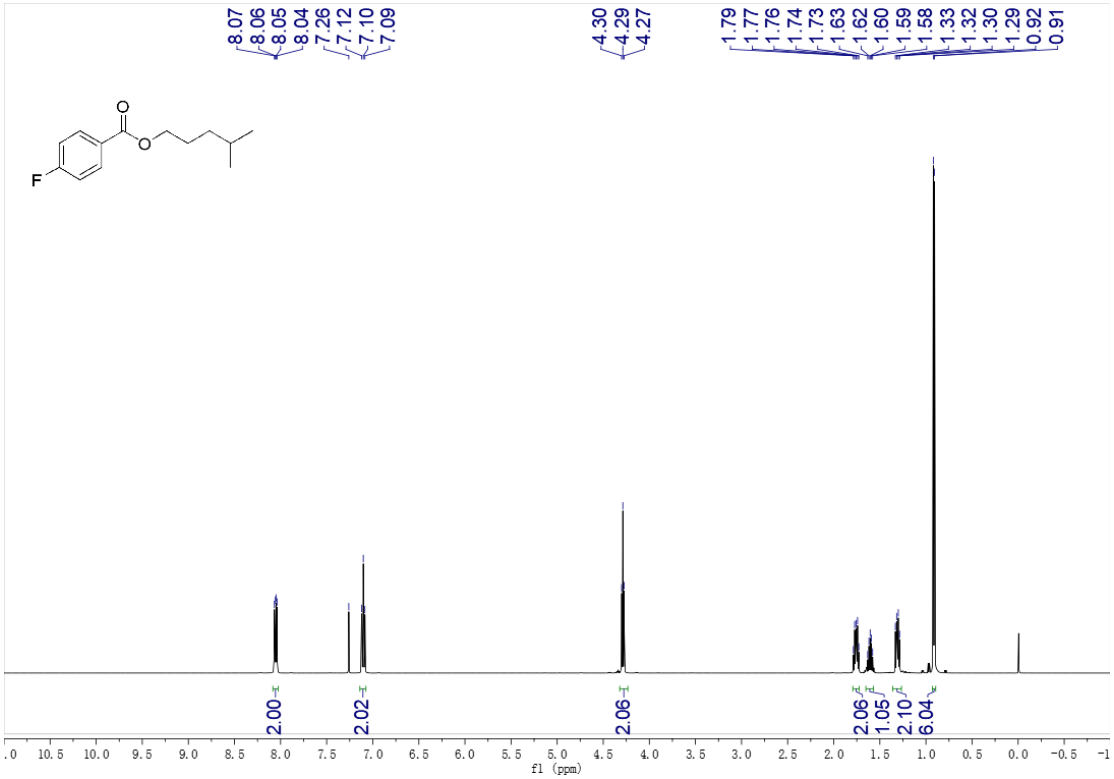


^{13}C NMR of compound **5a** (126 MHz, $CDCl_3$)



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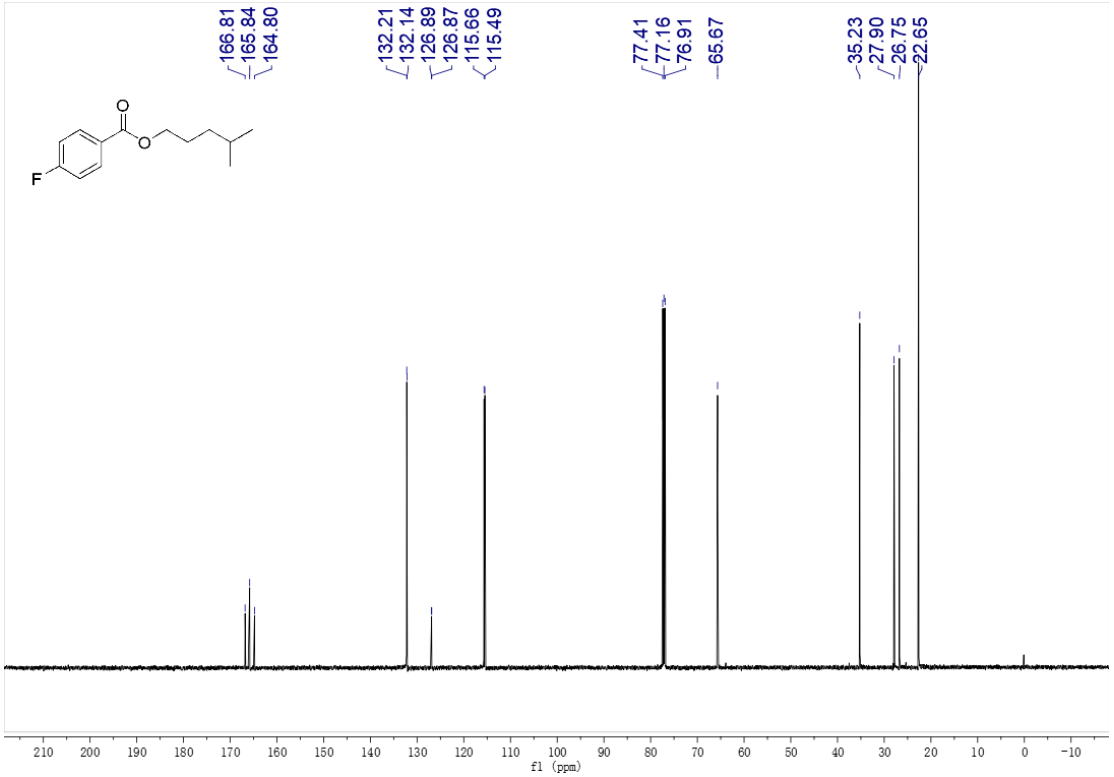

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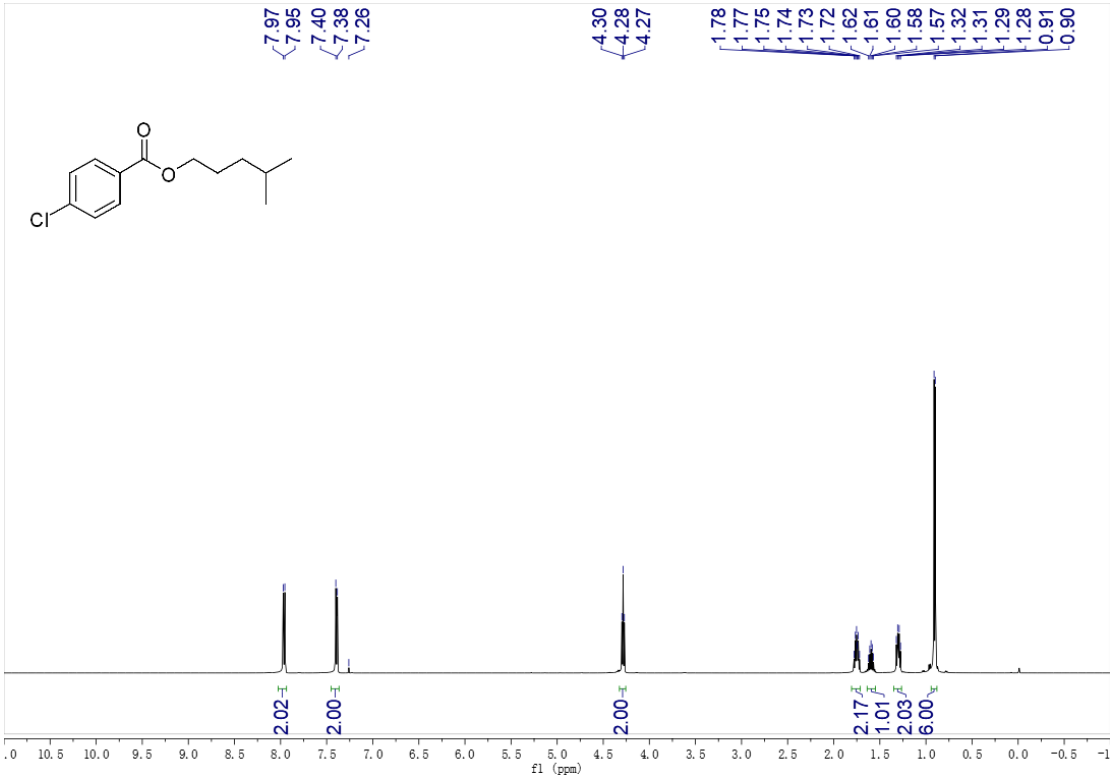

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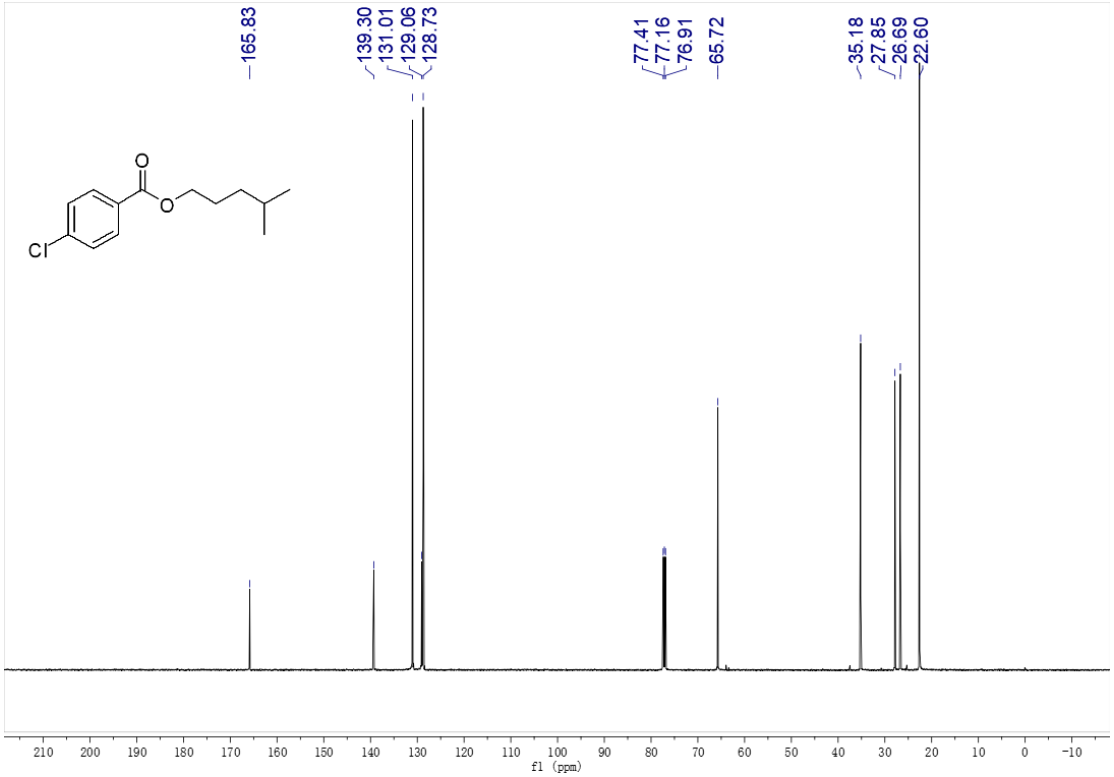

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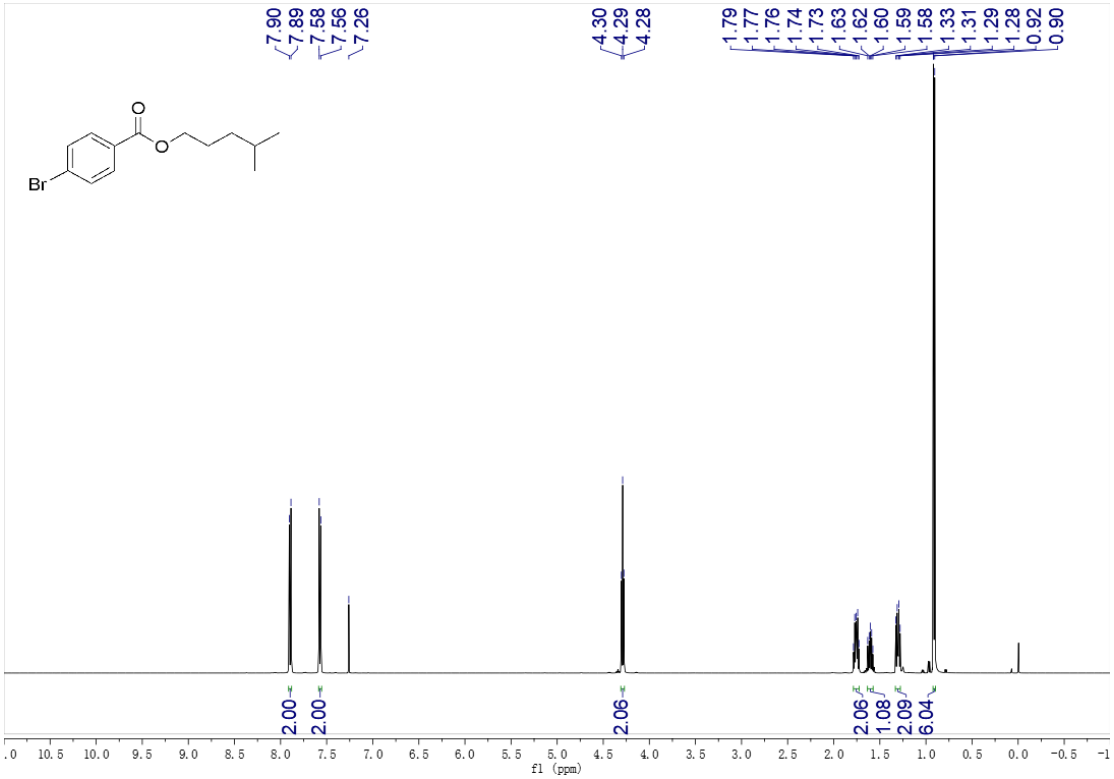

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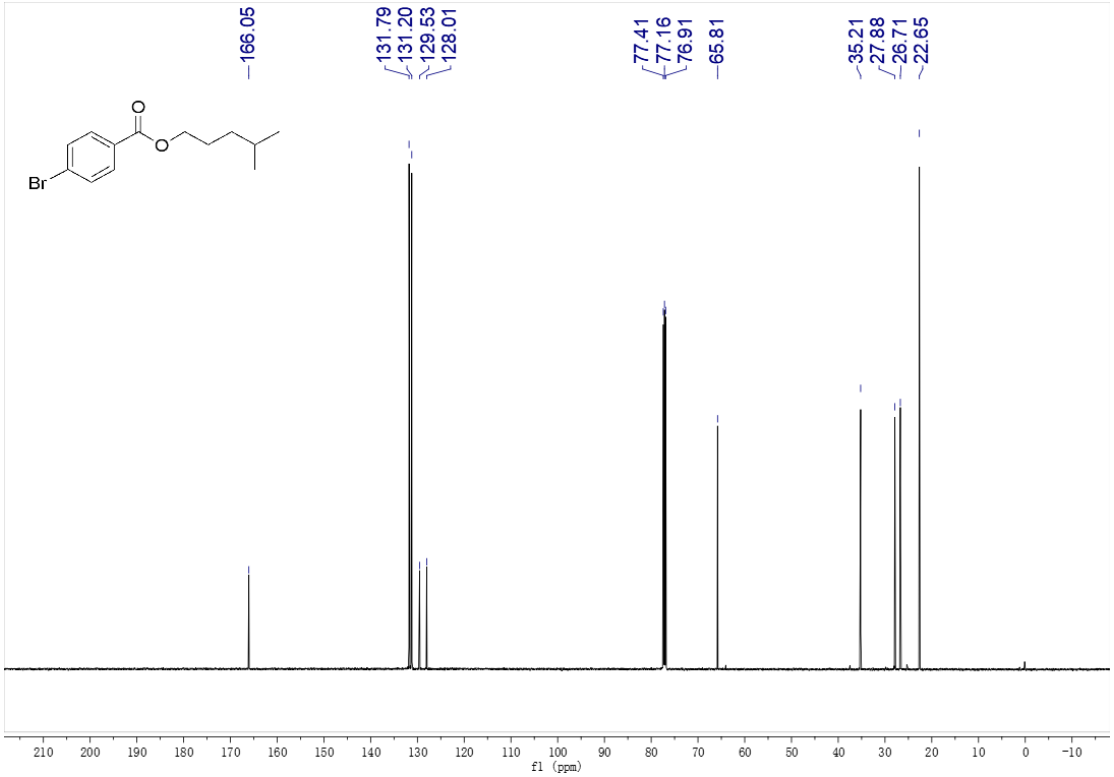

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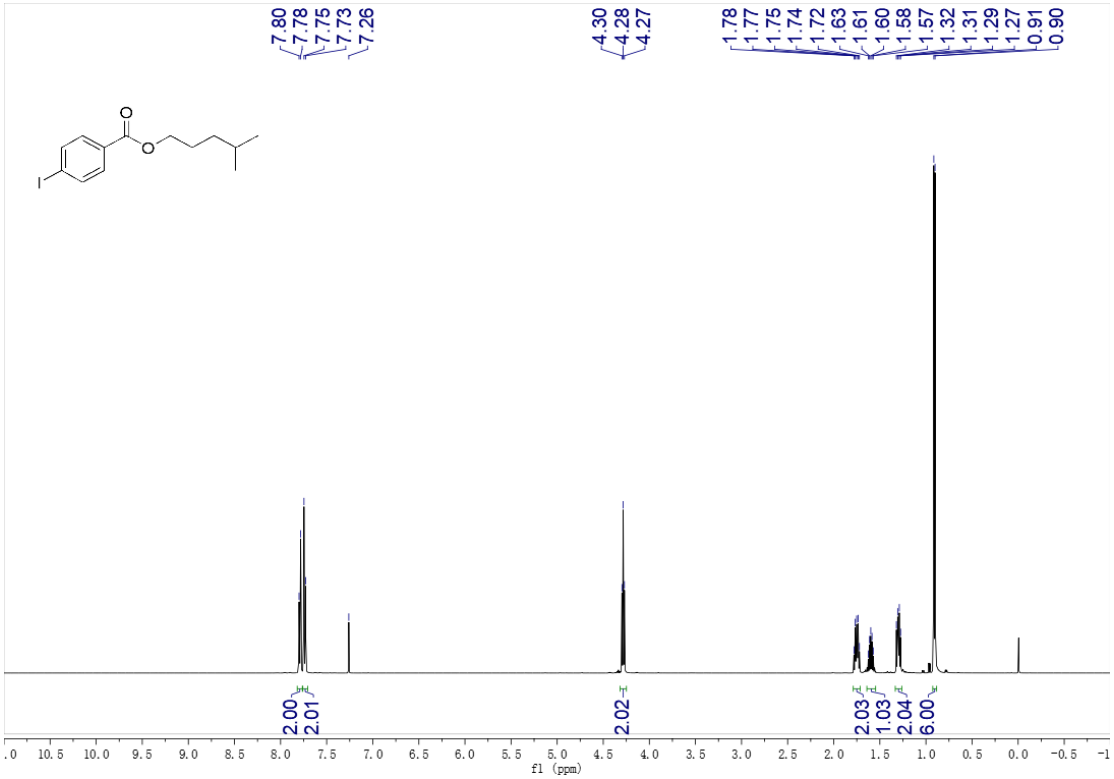

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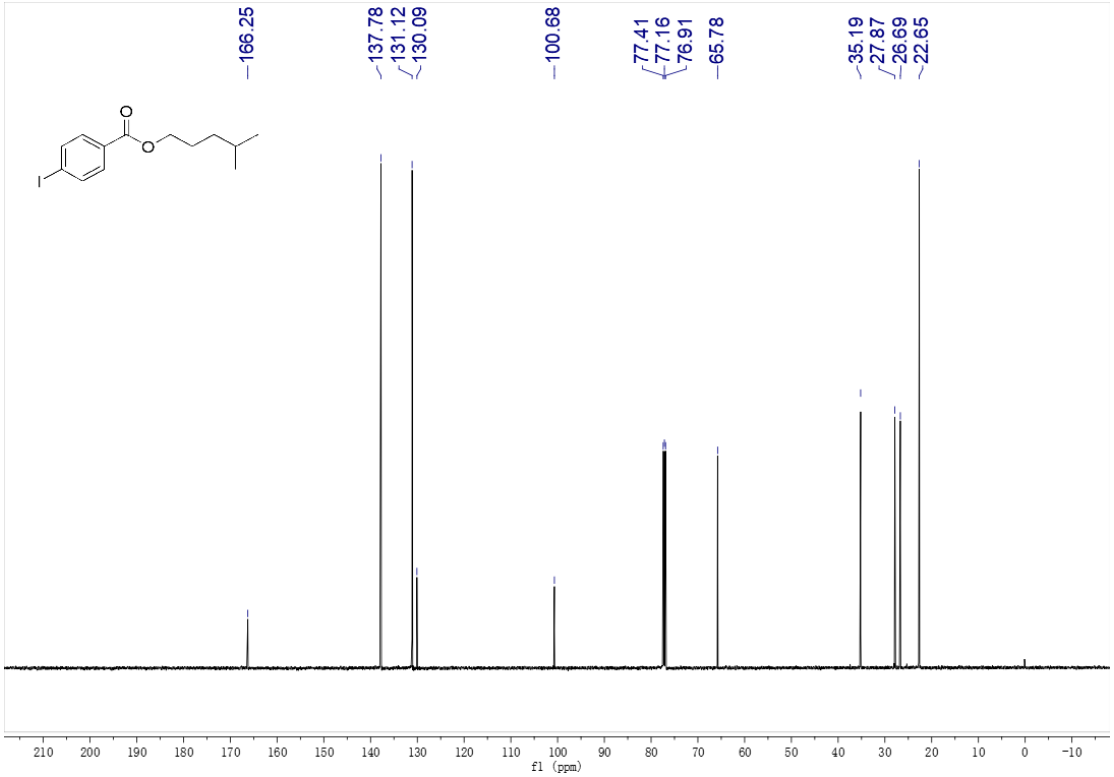

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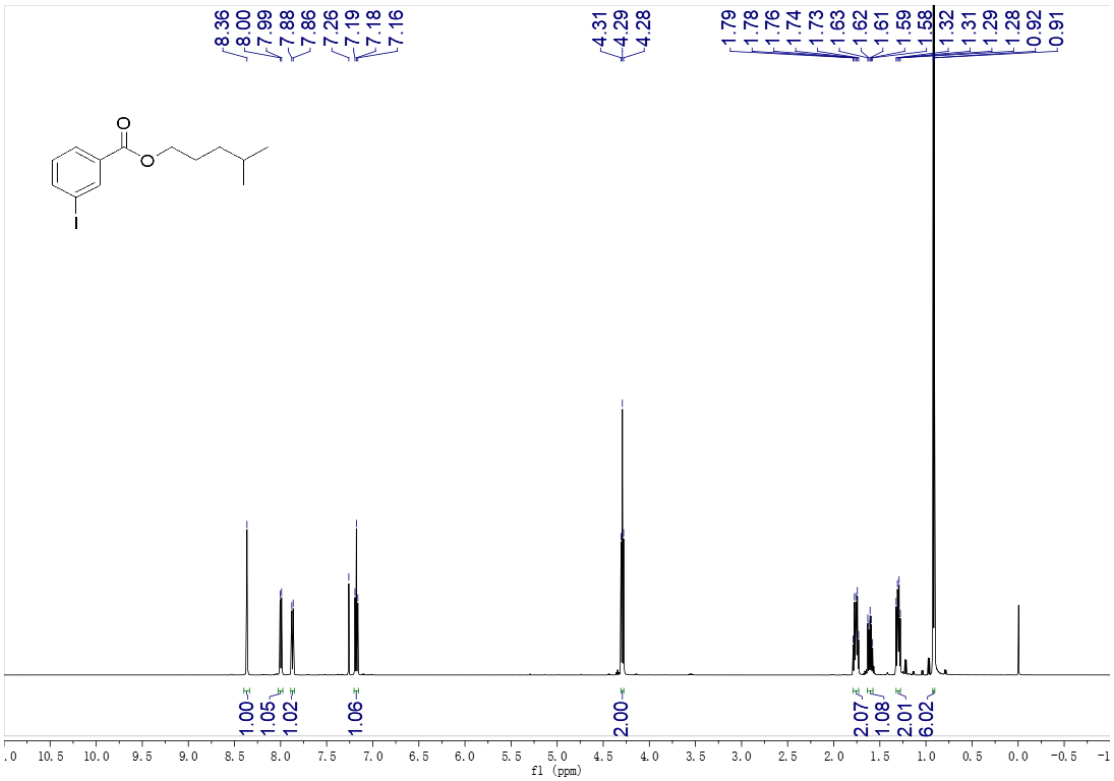

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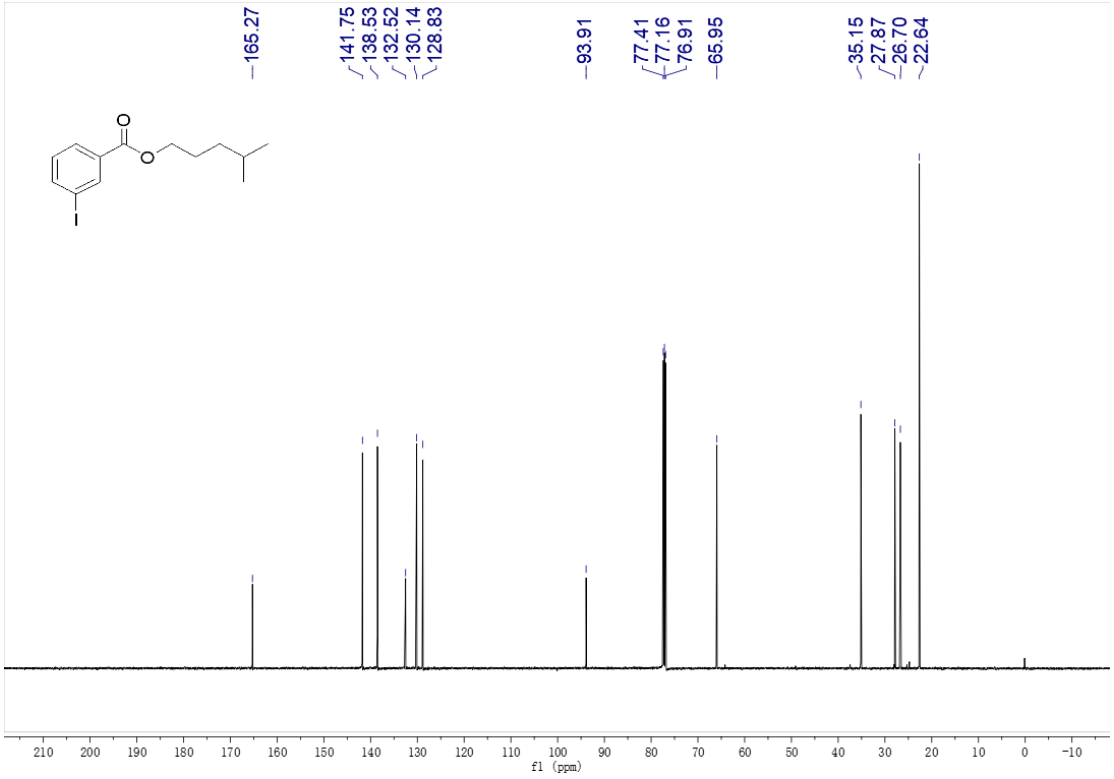

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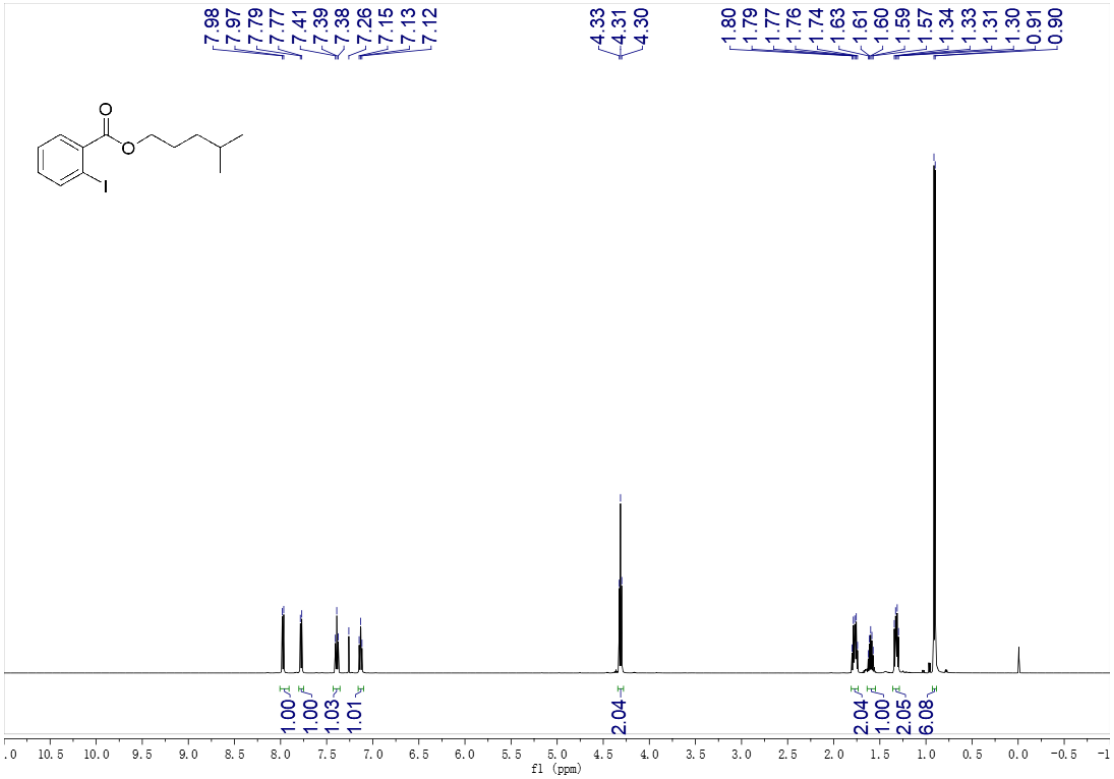

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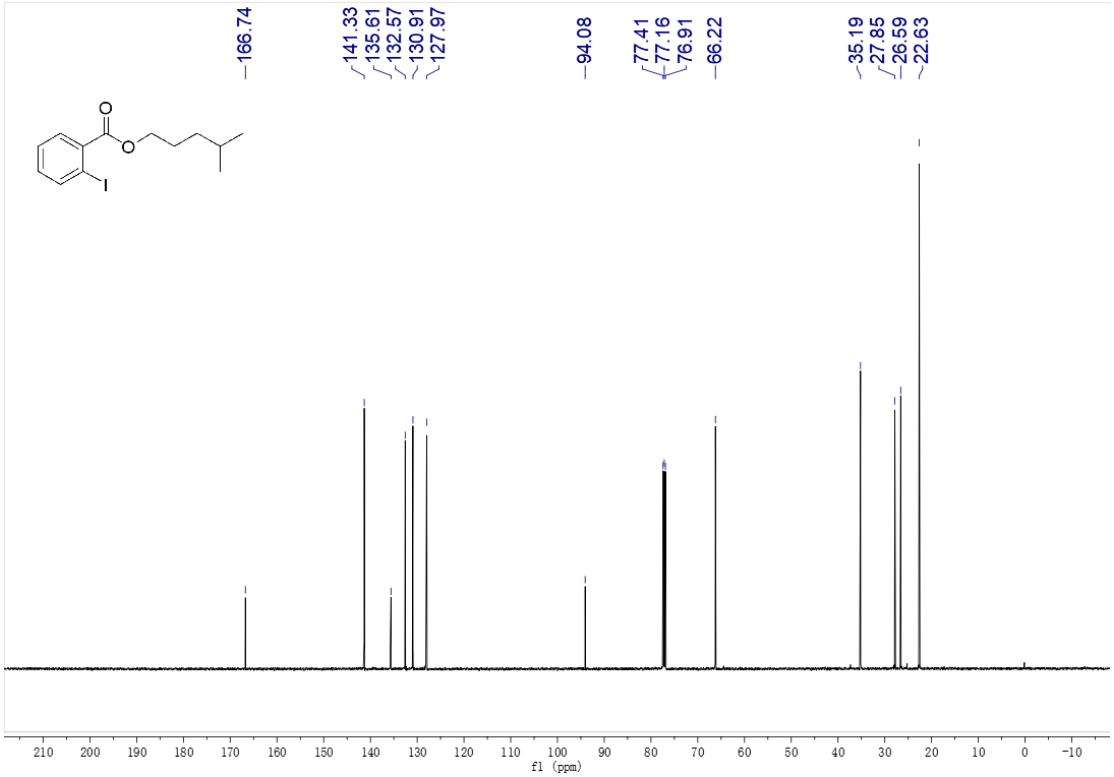

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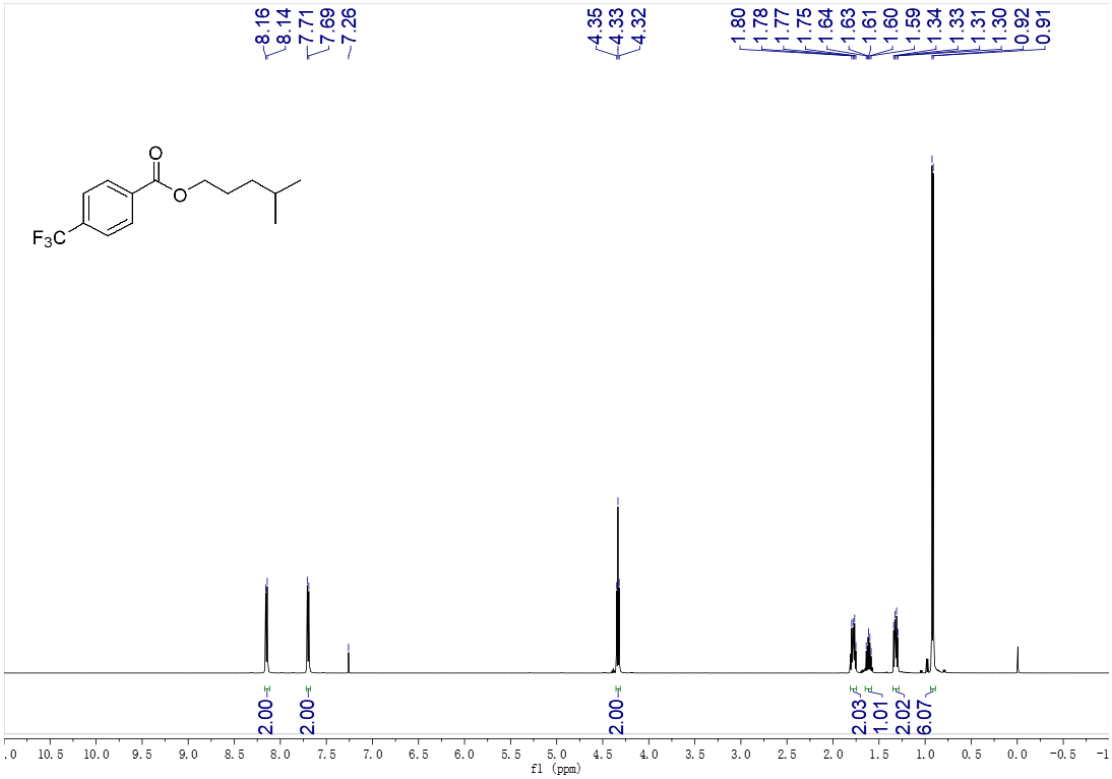

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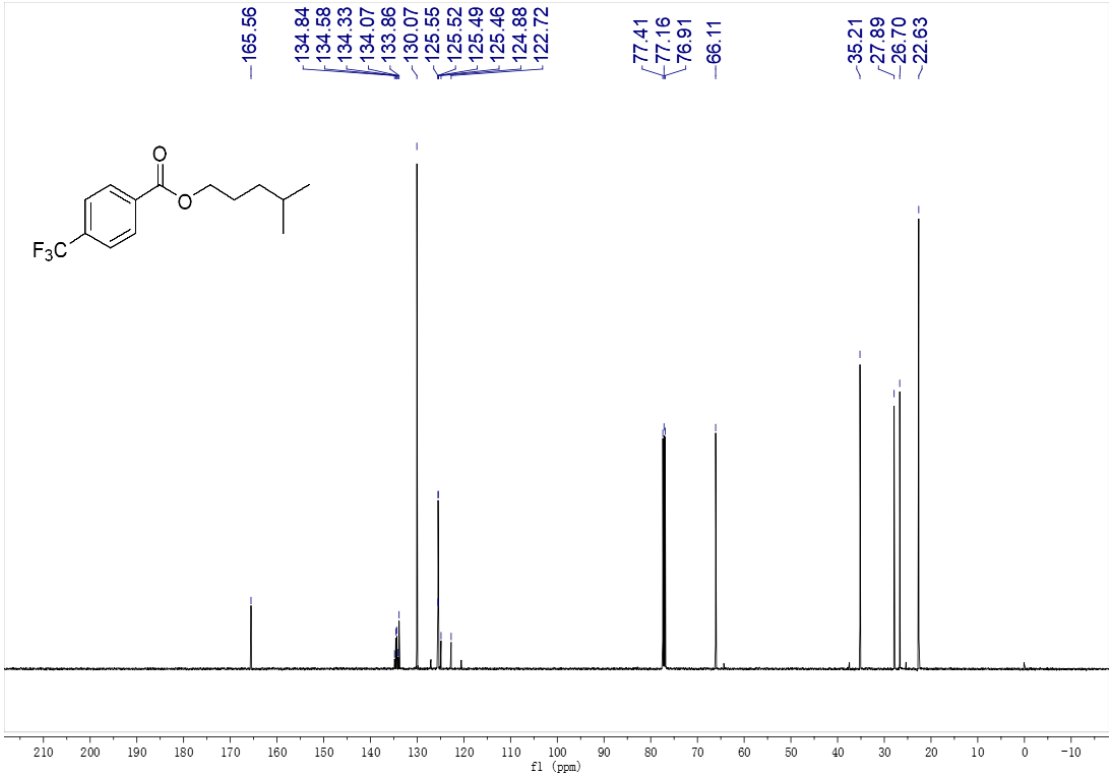

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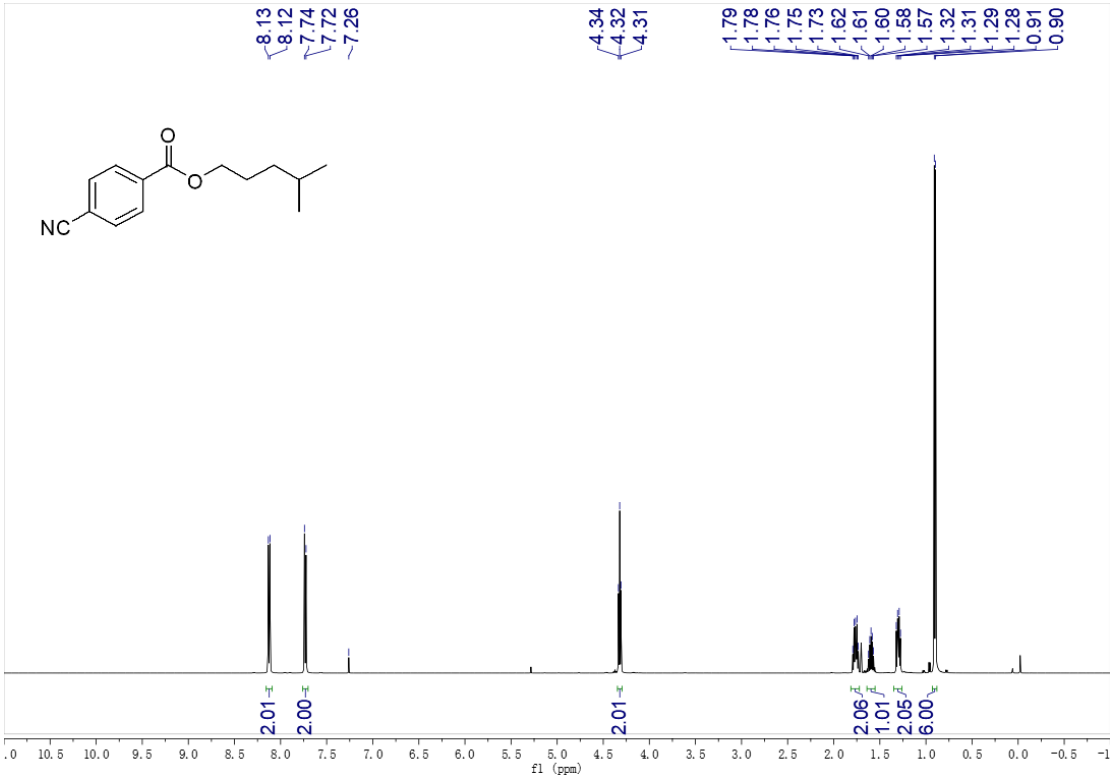

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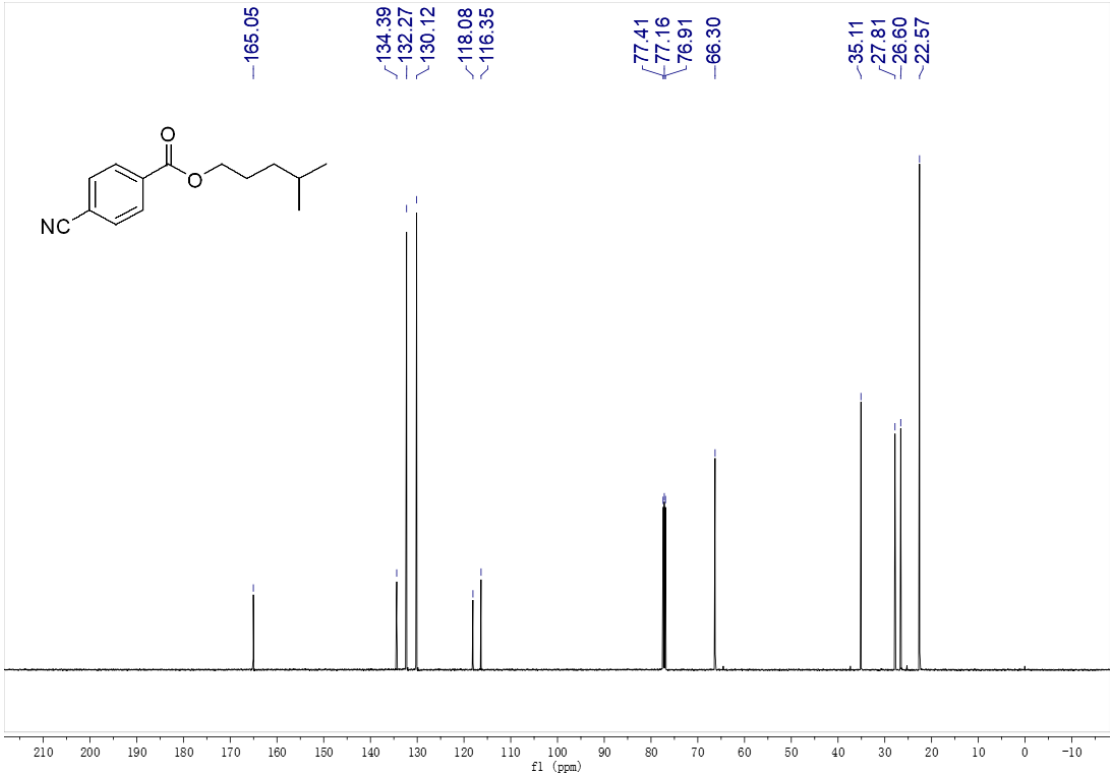

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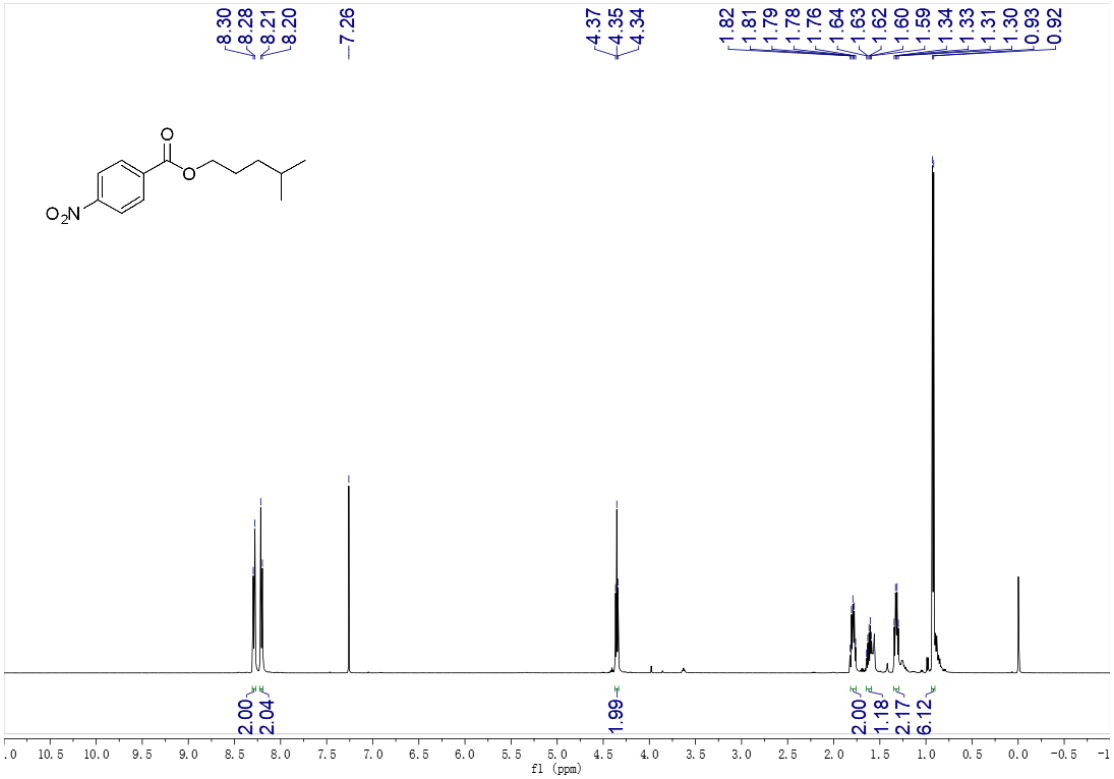

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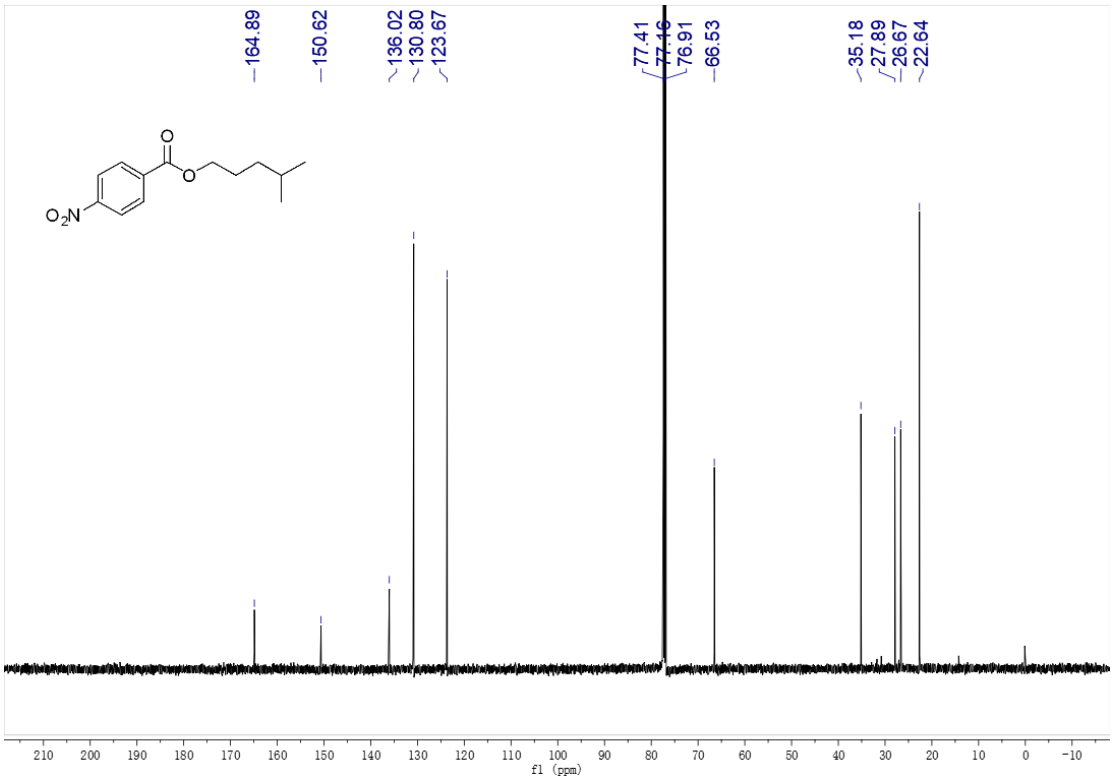

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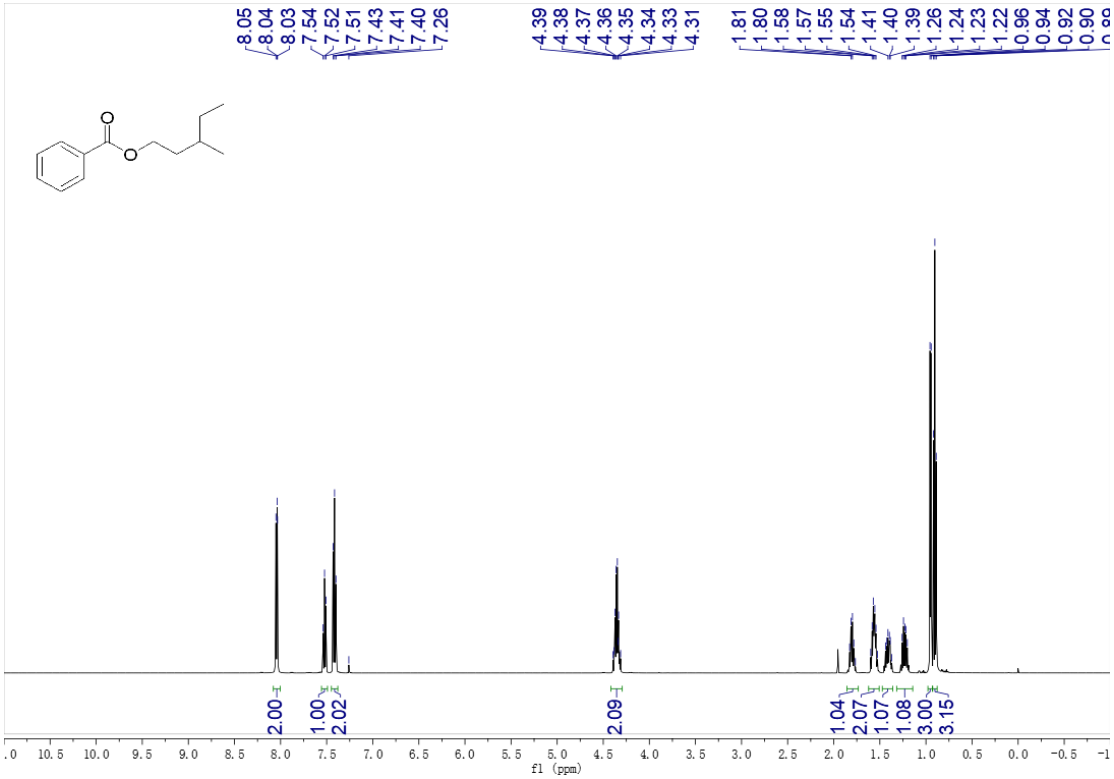

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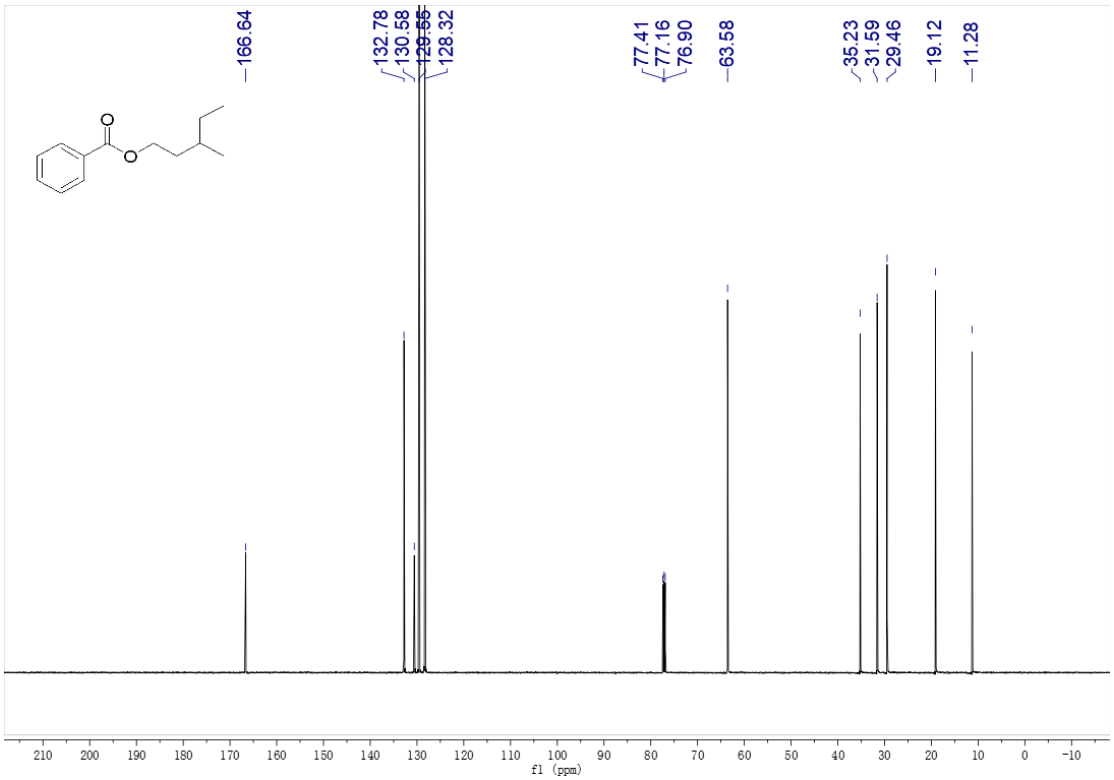

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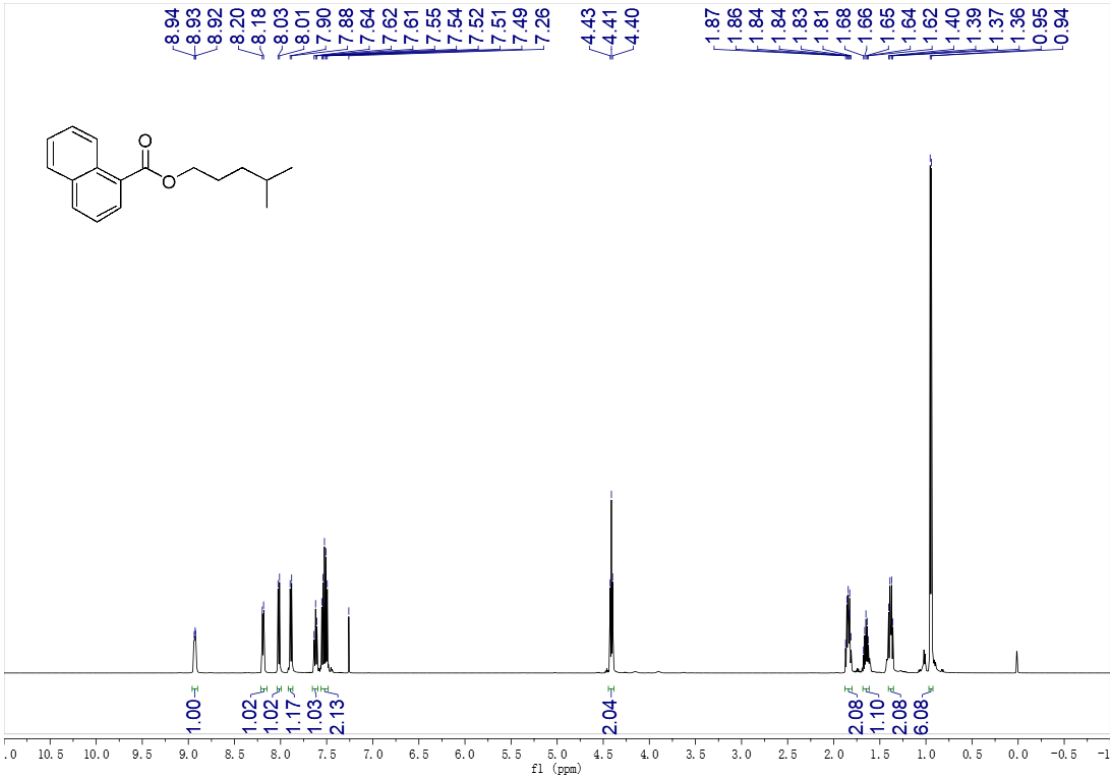

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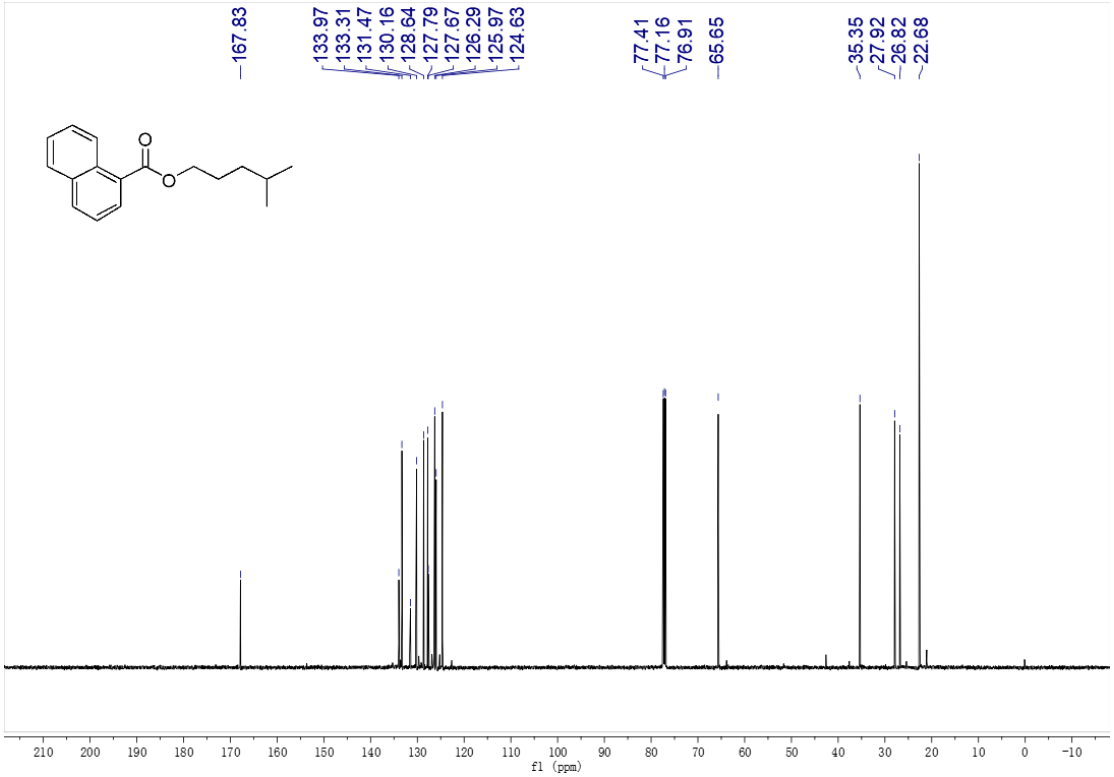
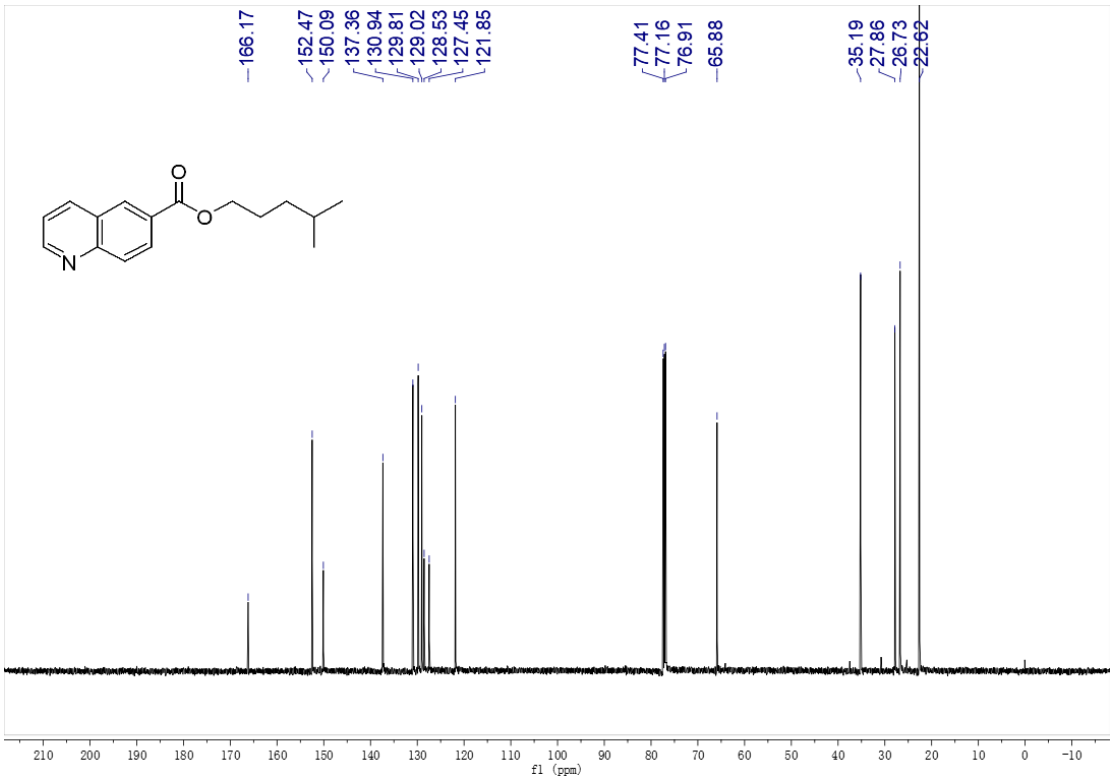


^{13}C NMR of compound **16a** (126 MHz, $CDCl_3$)

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



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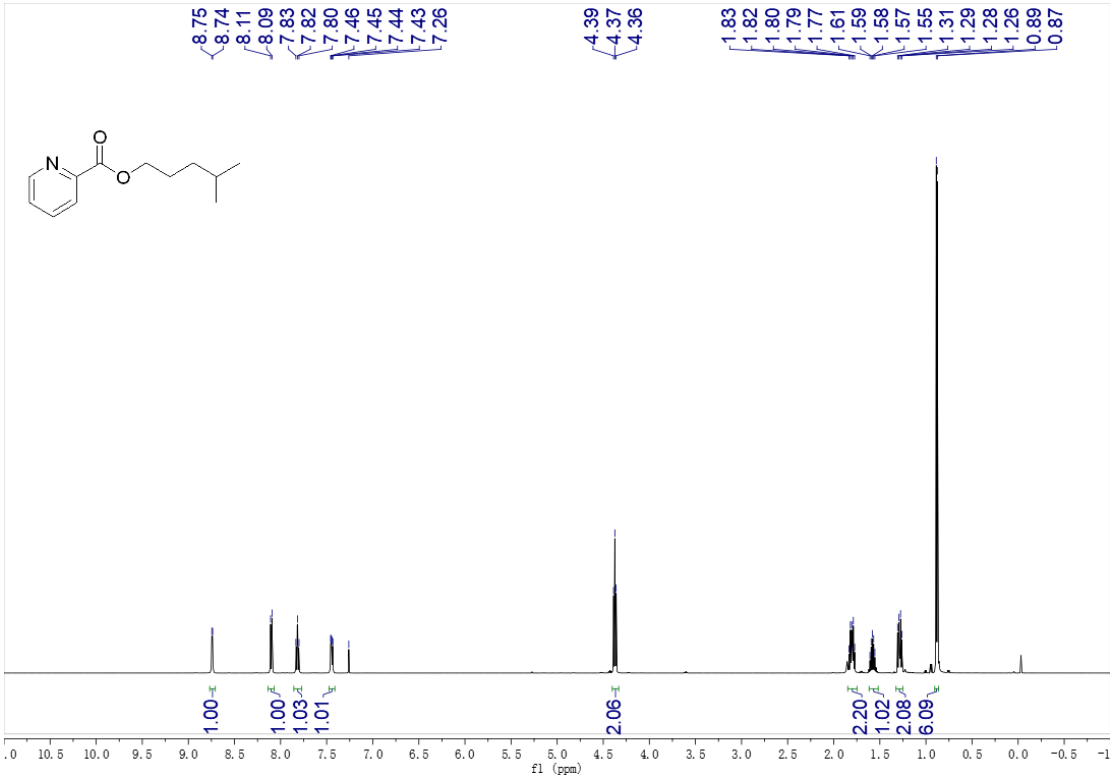

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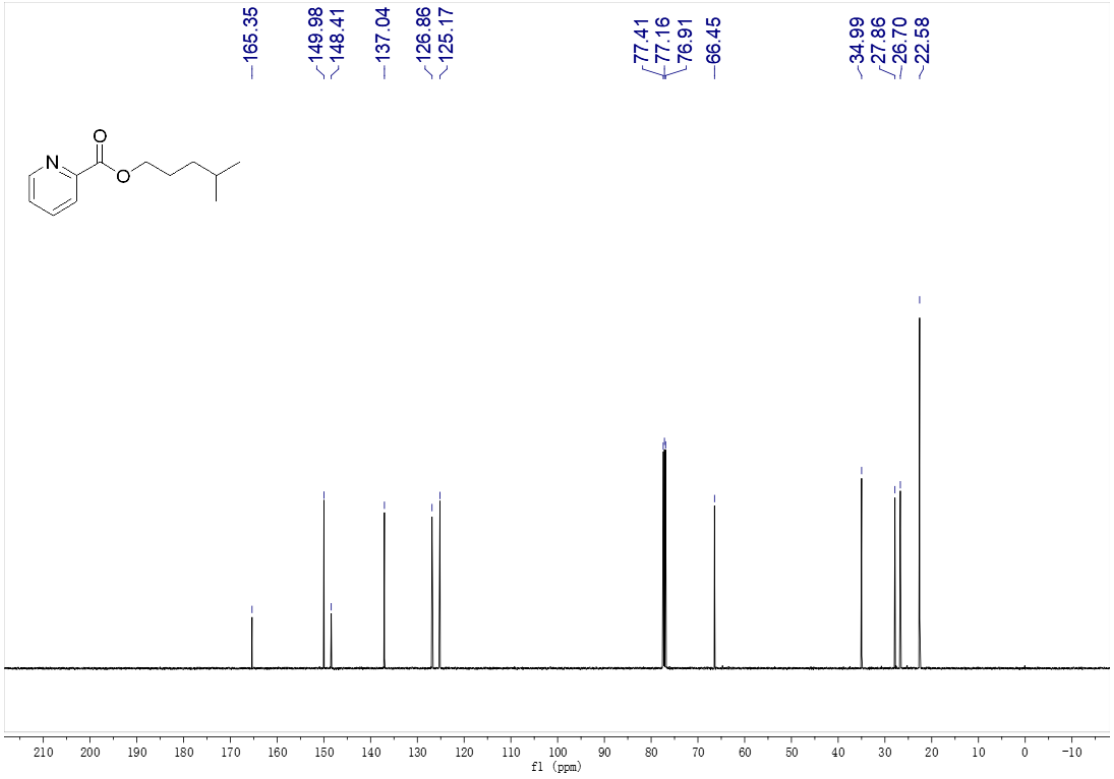

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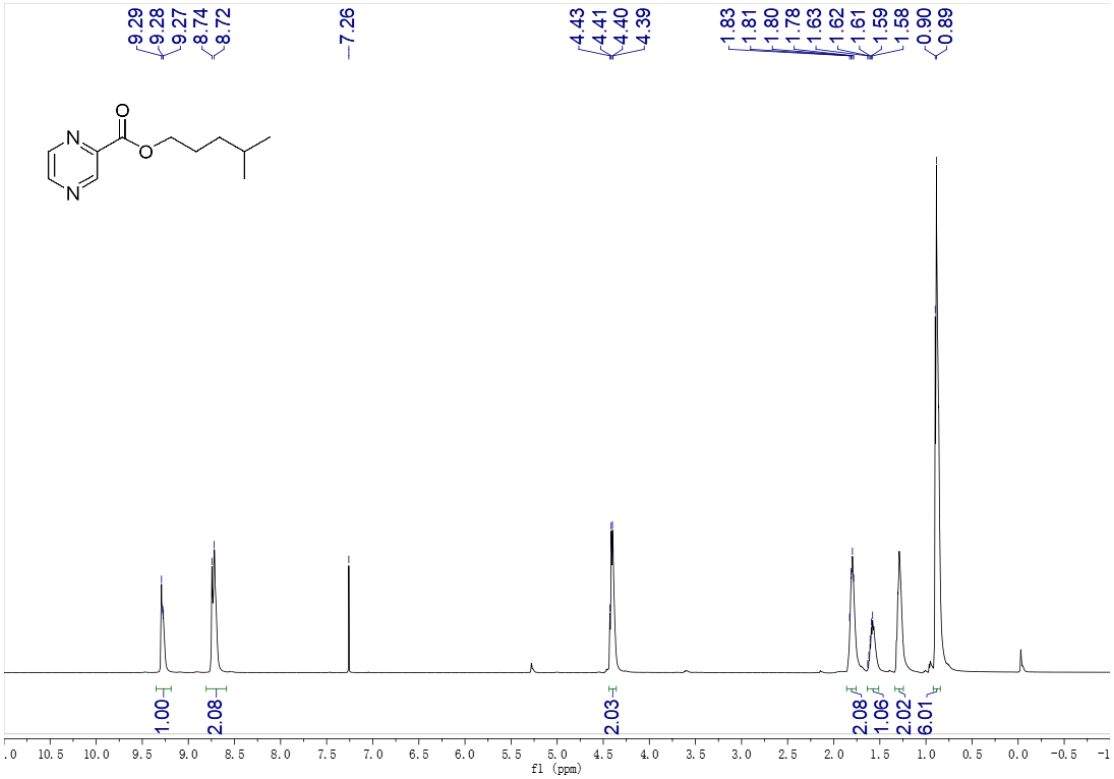

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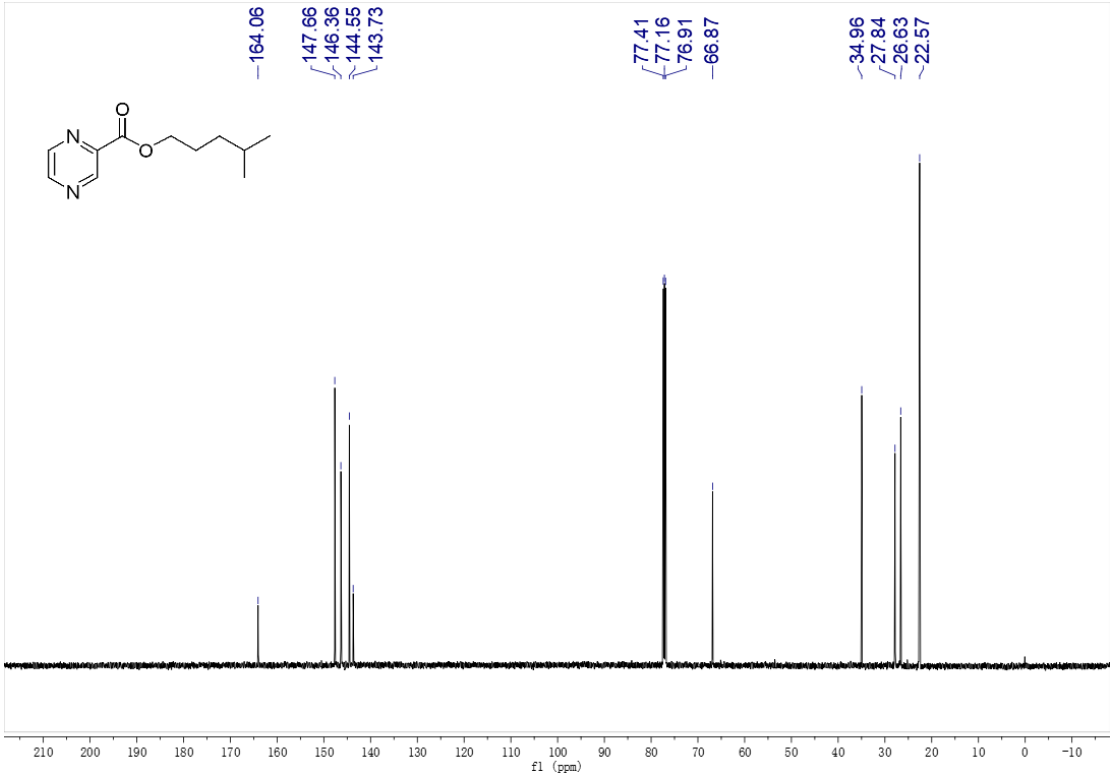

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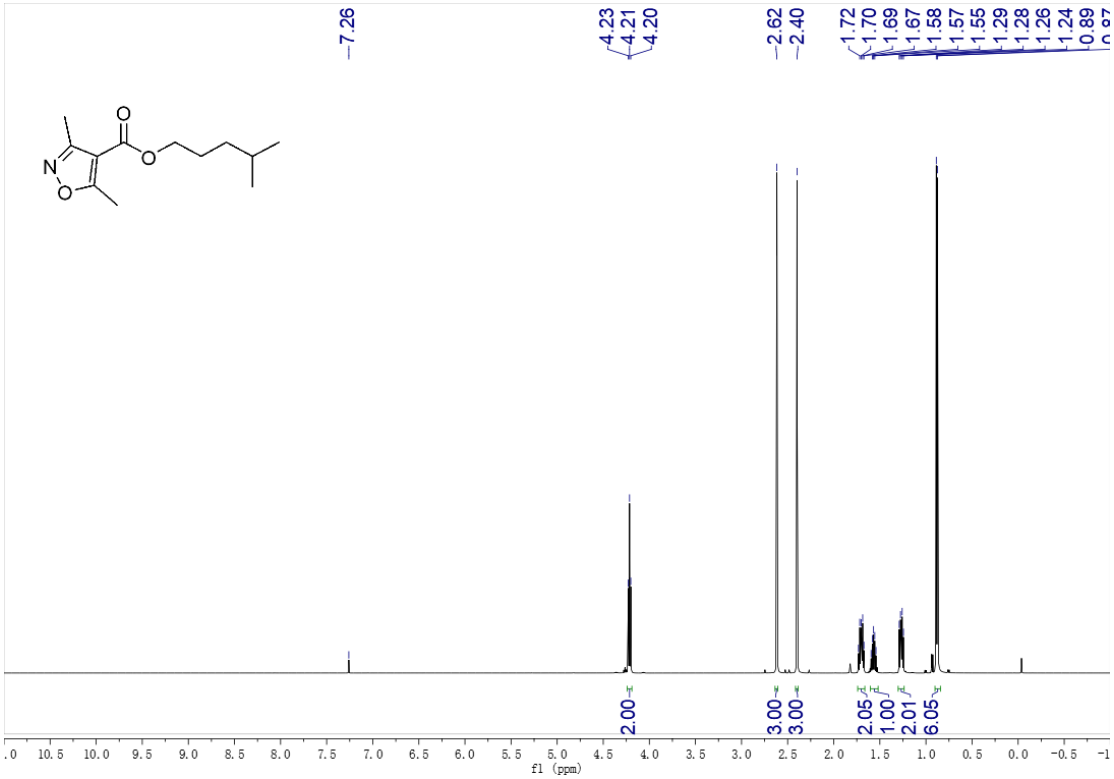

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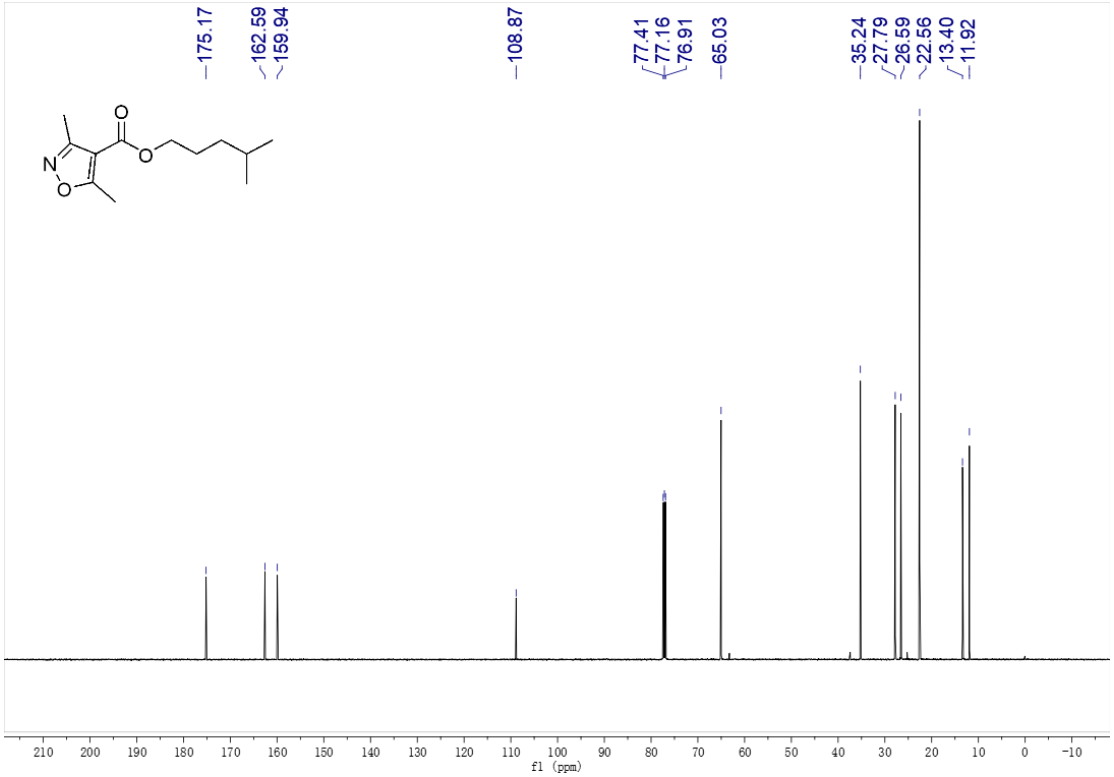

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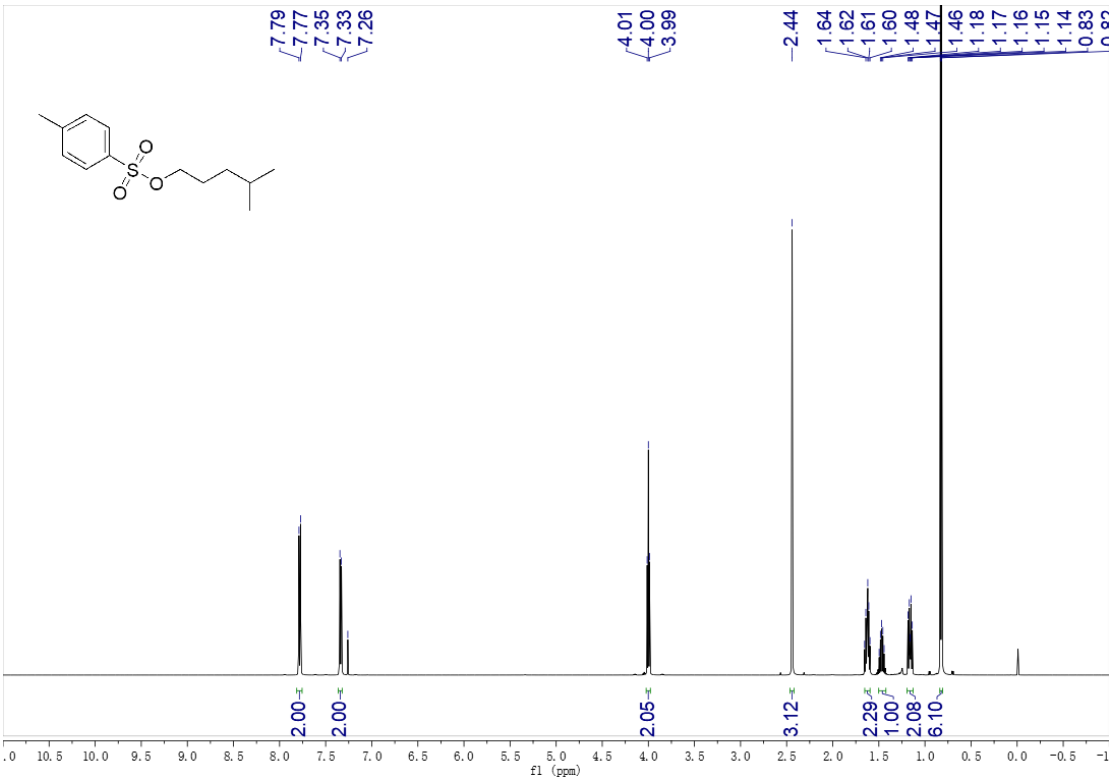

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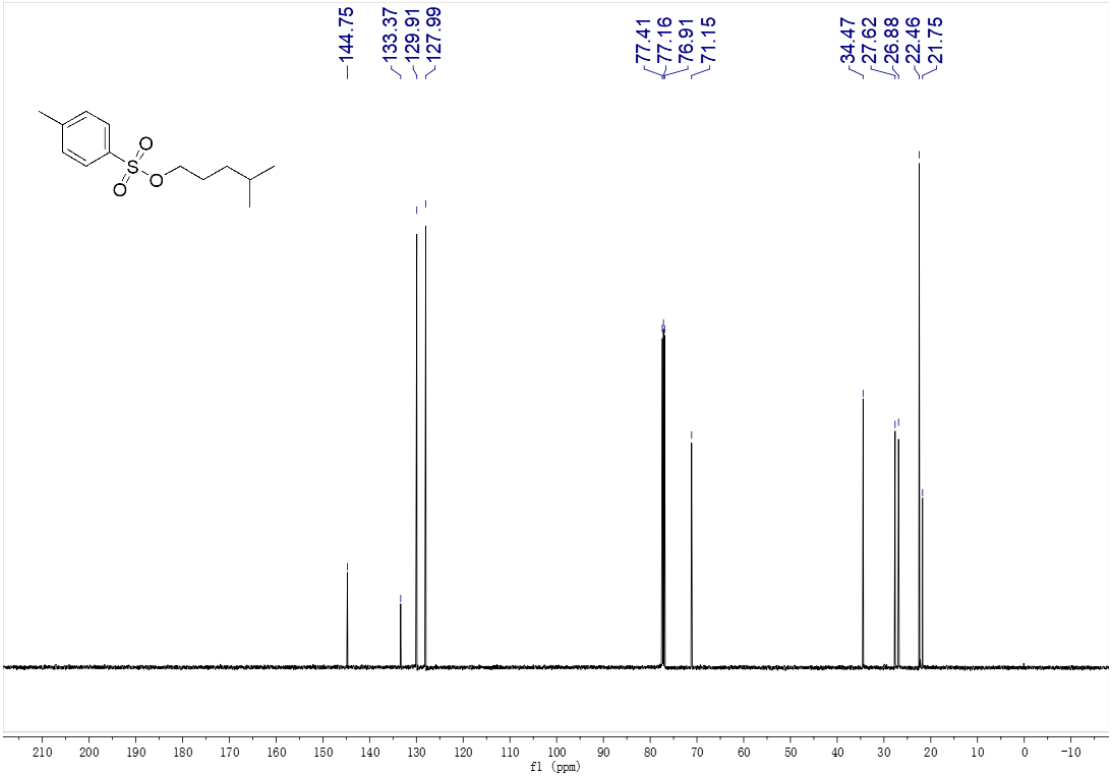

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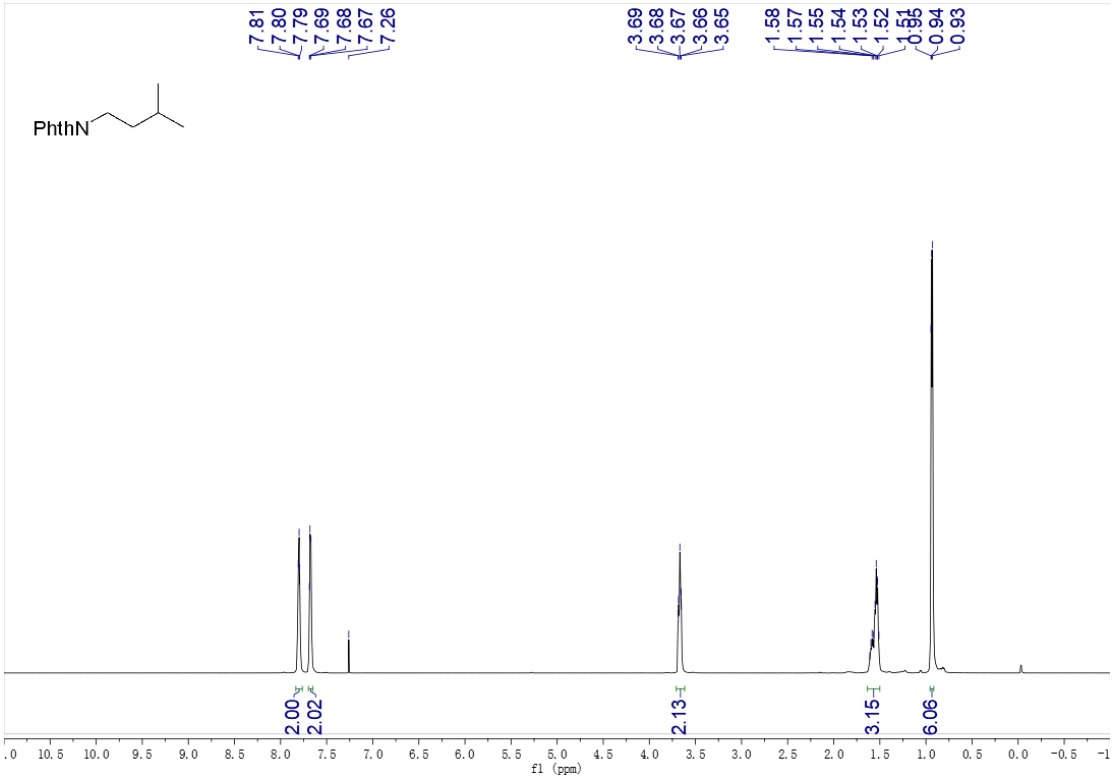

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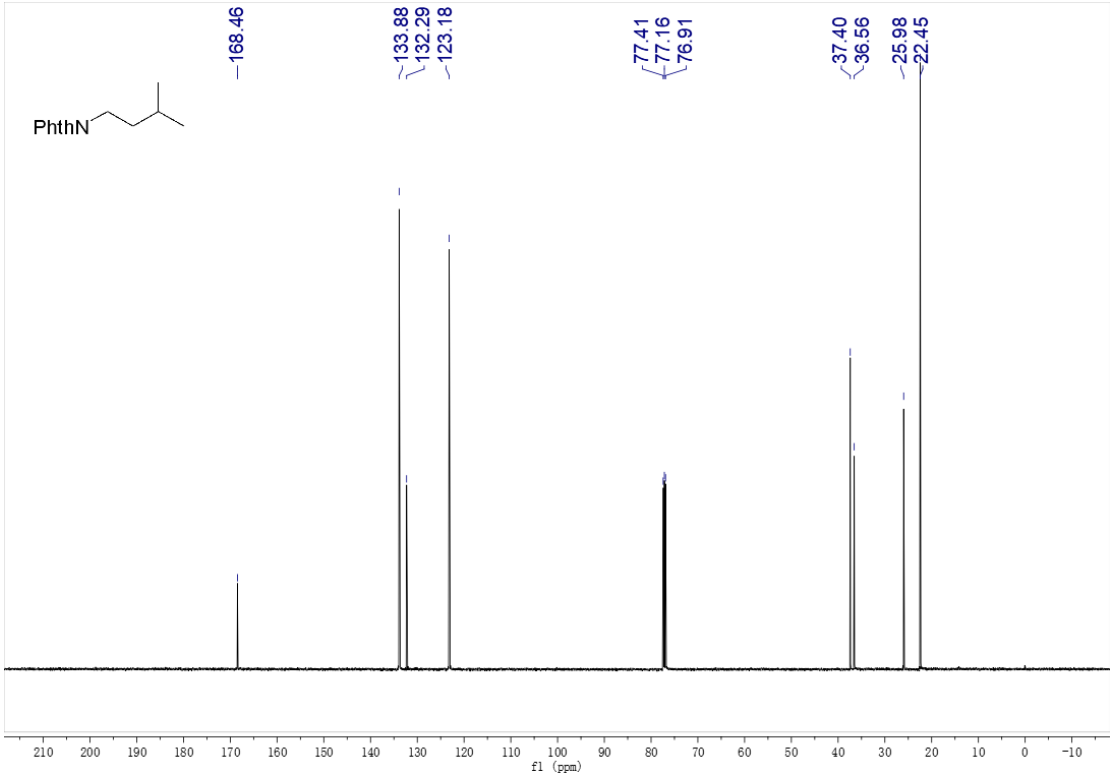

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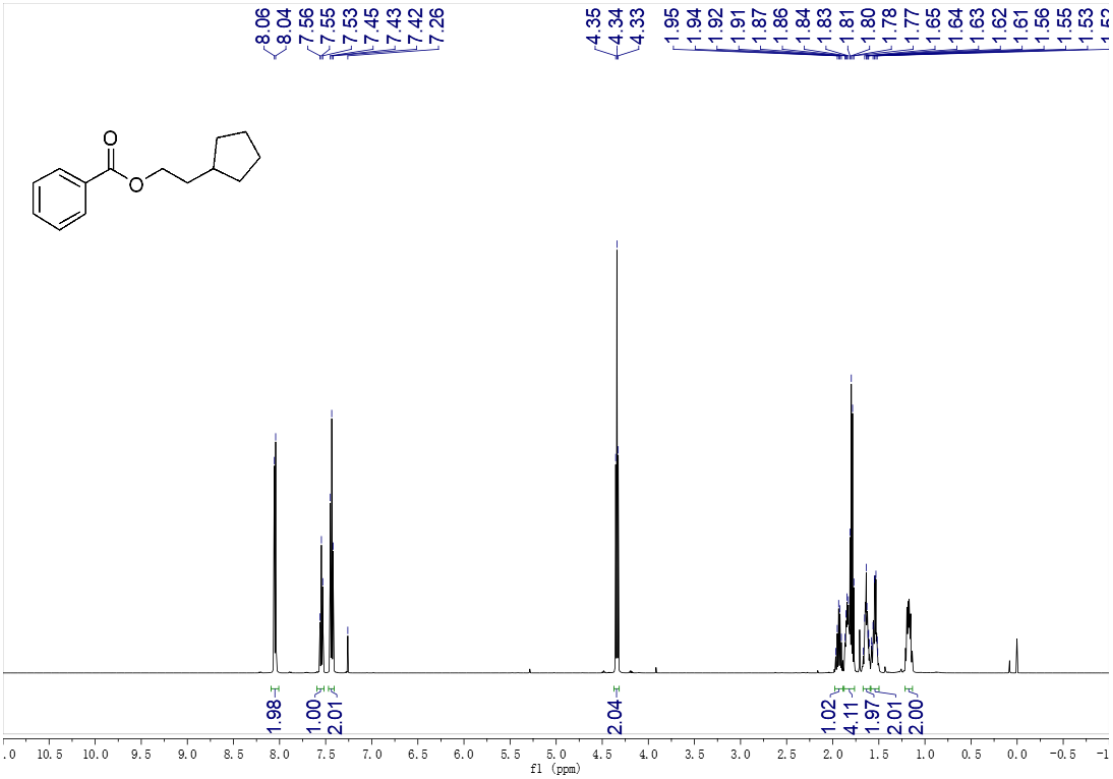

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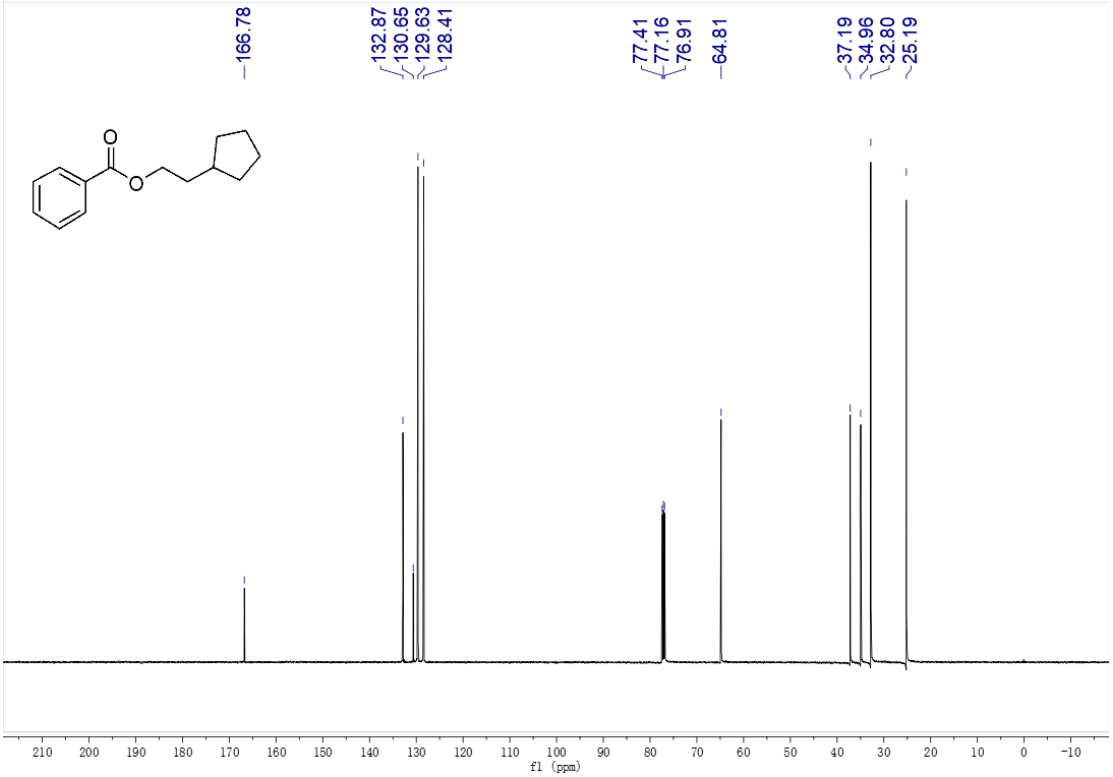

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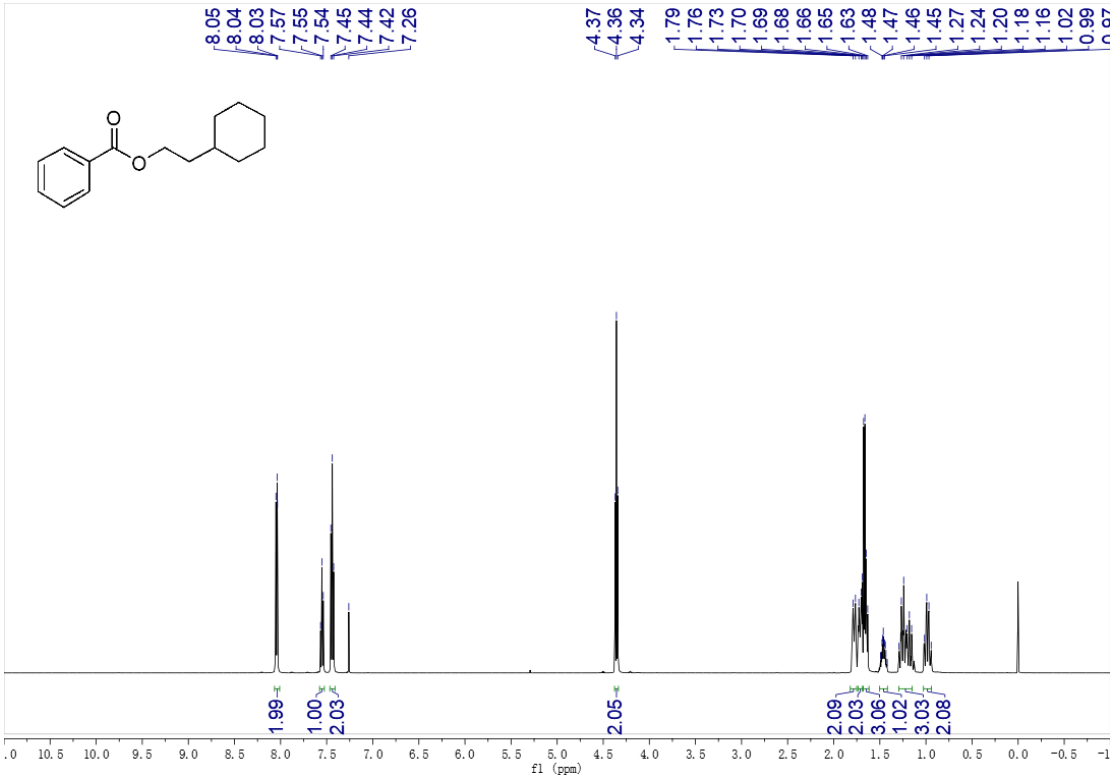

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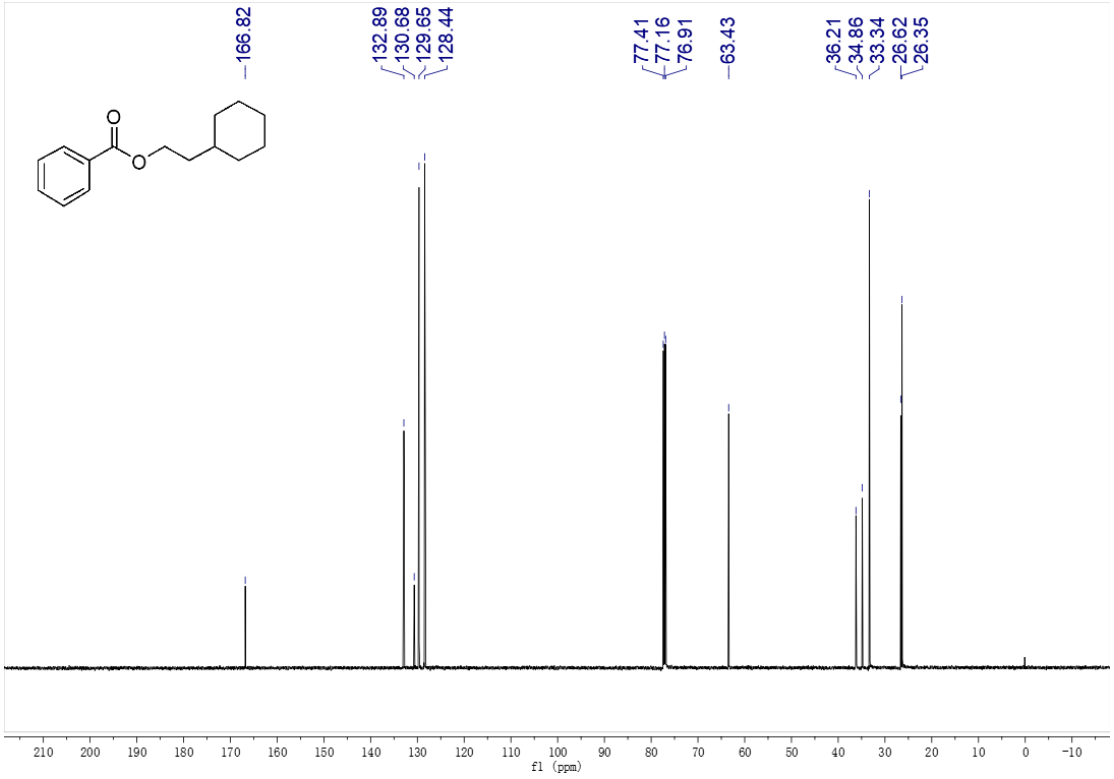

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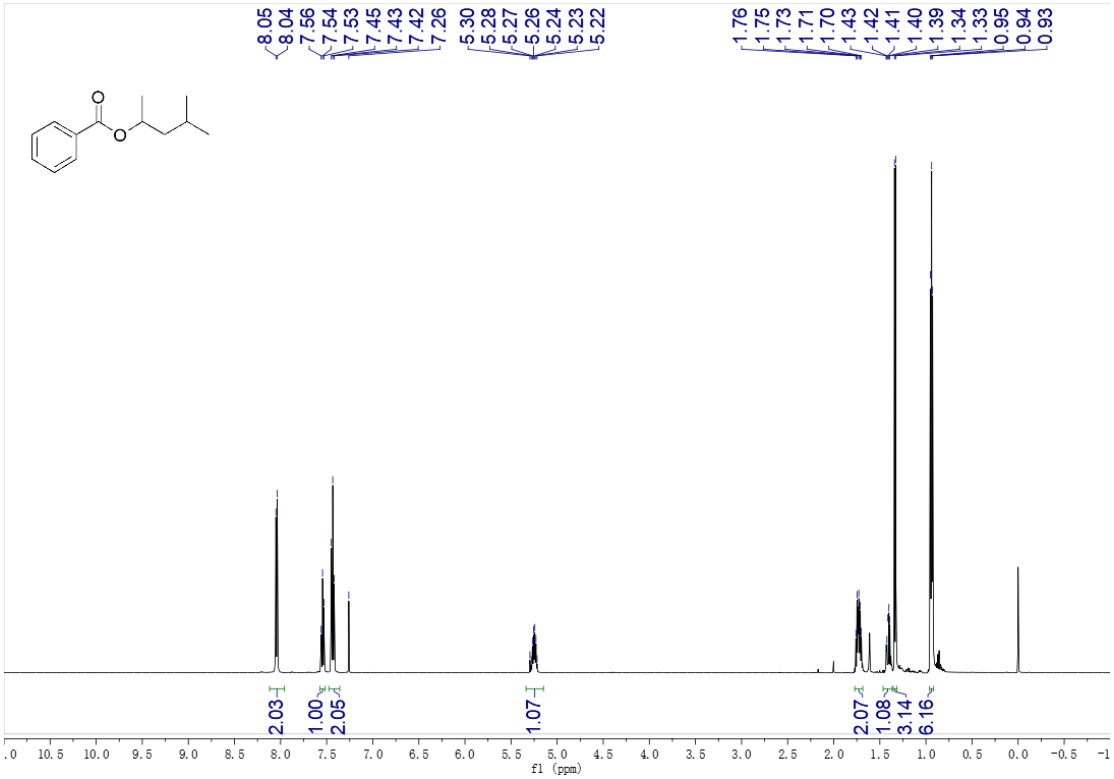

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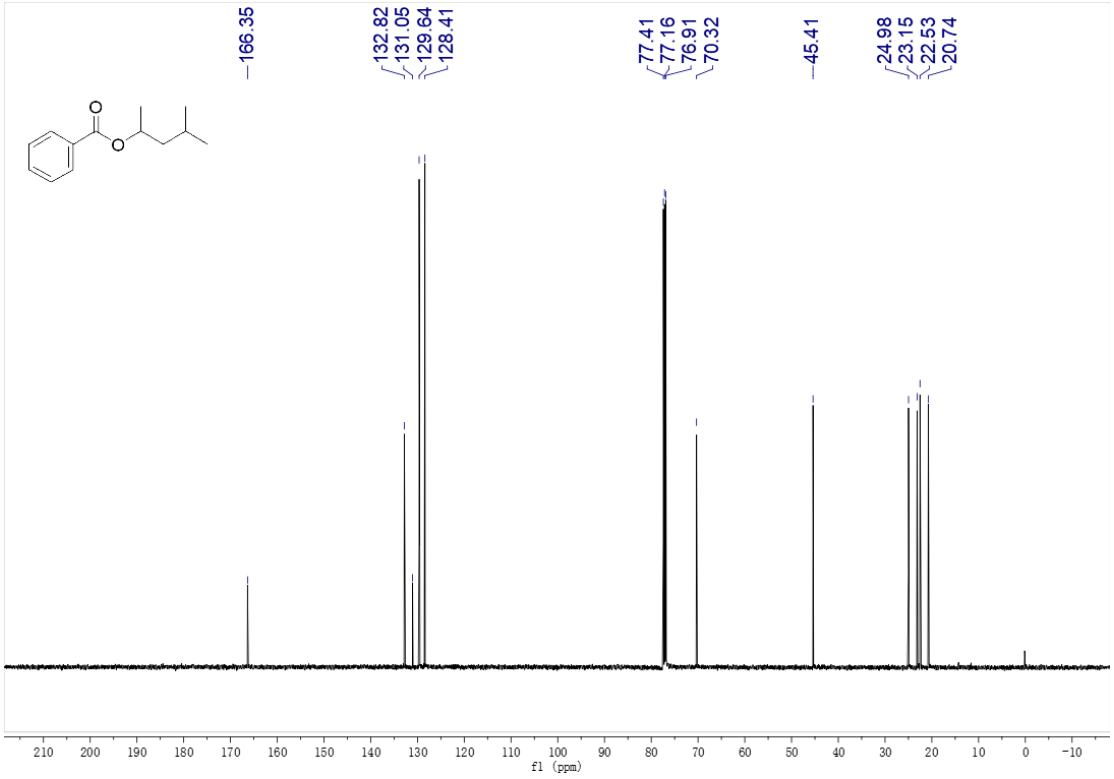

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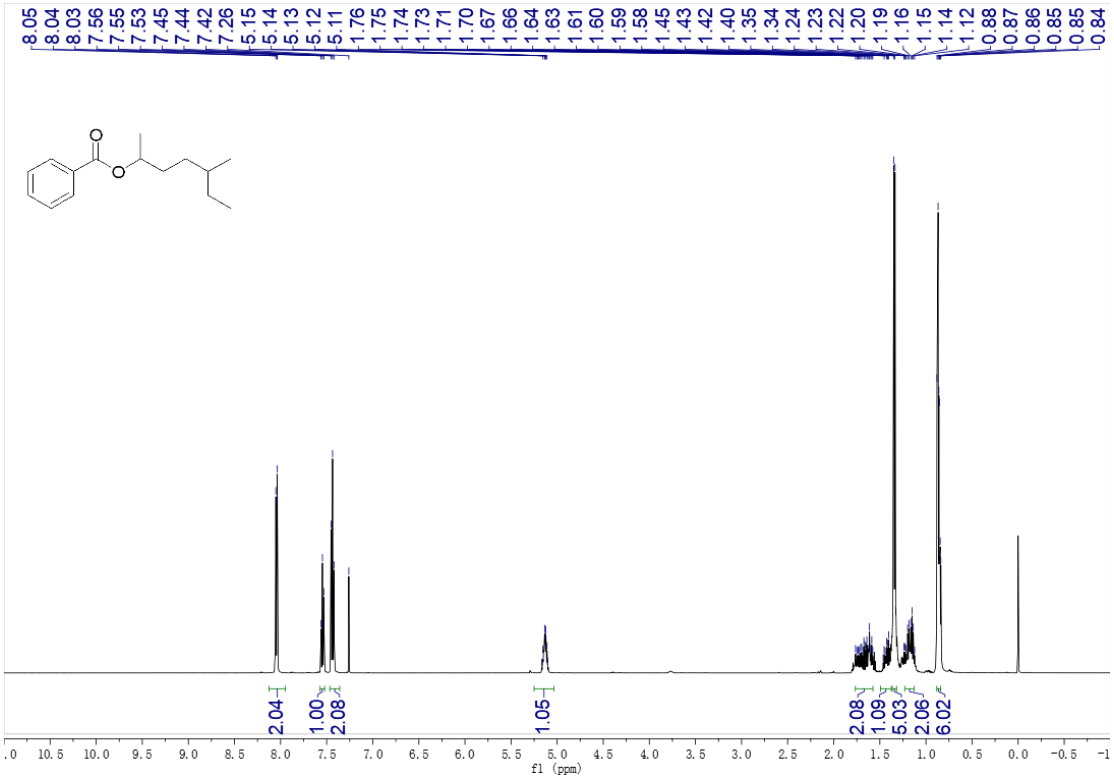
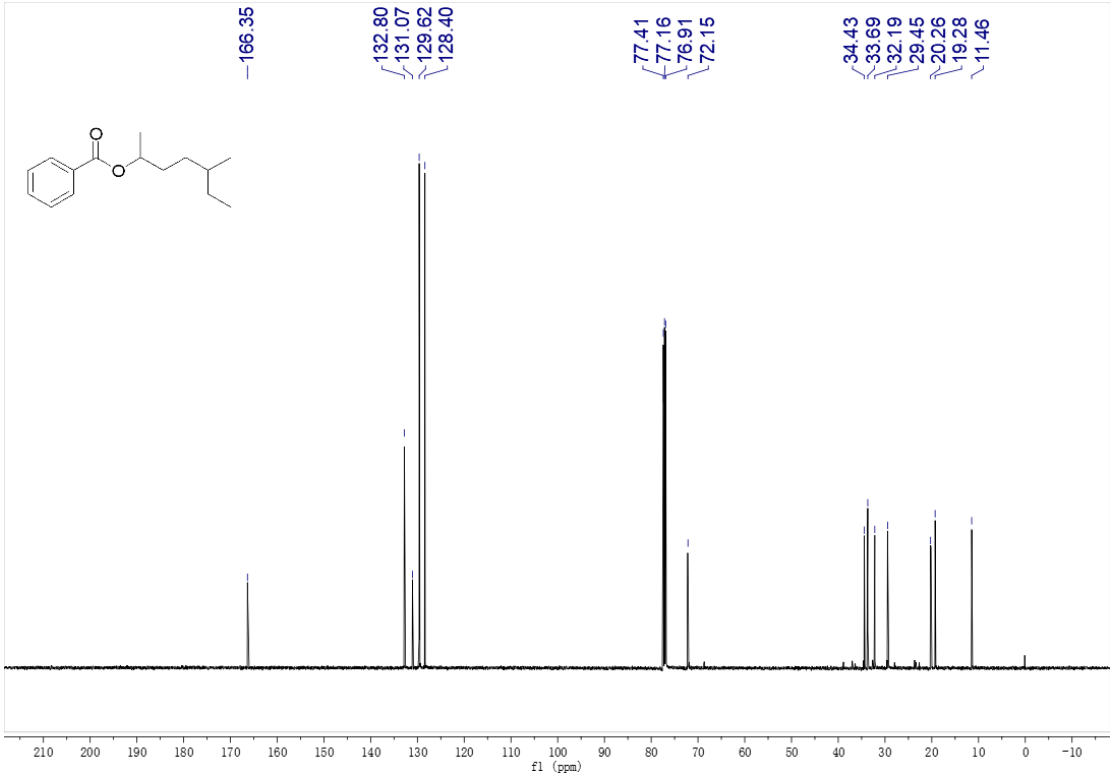
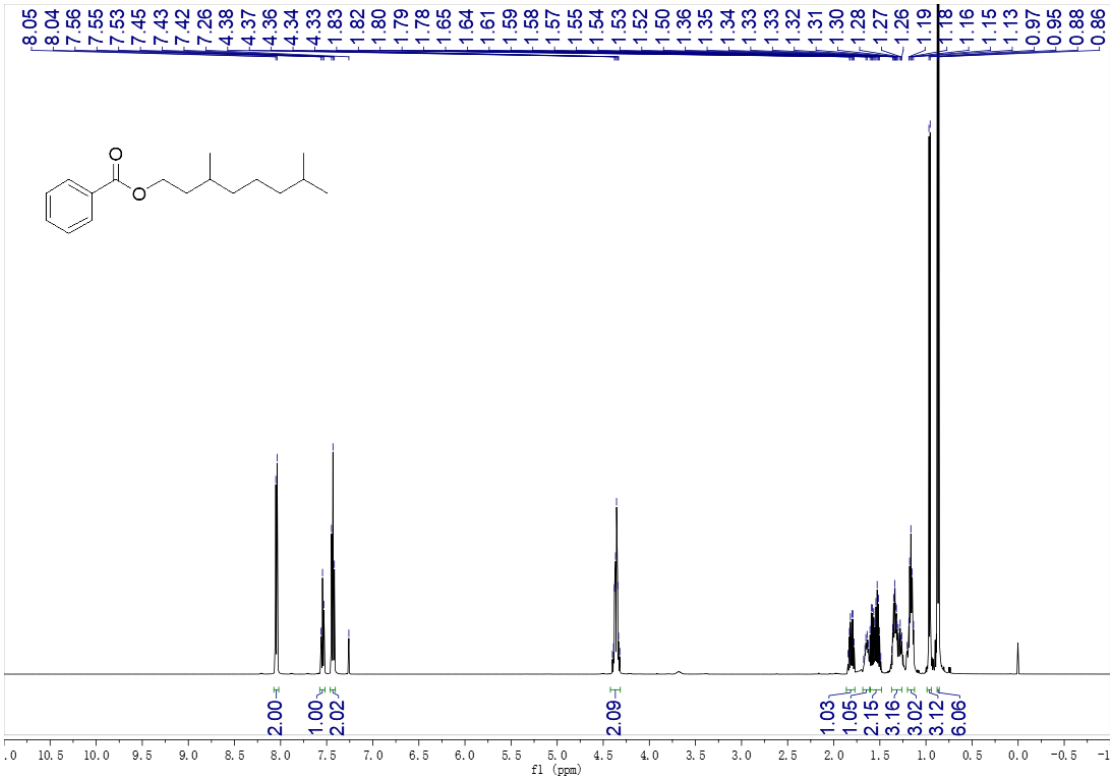


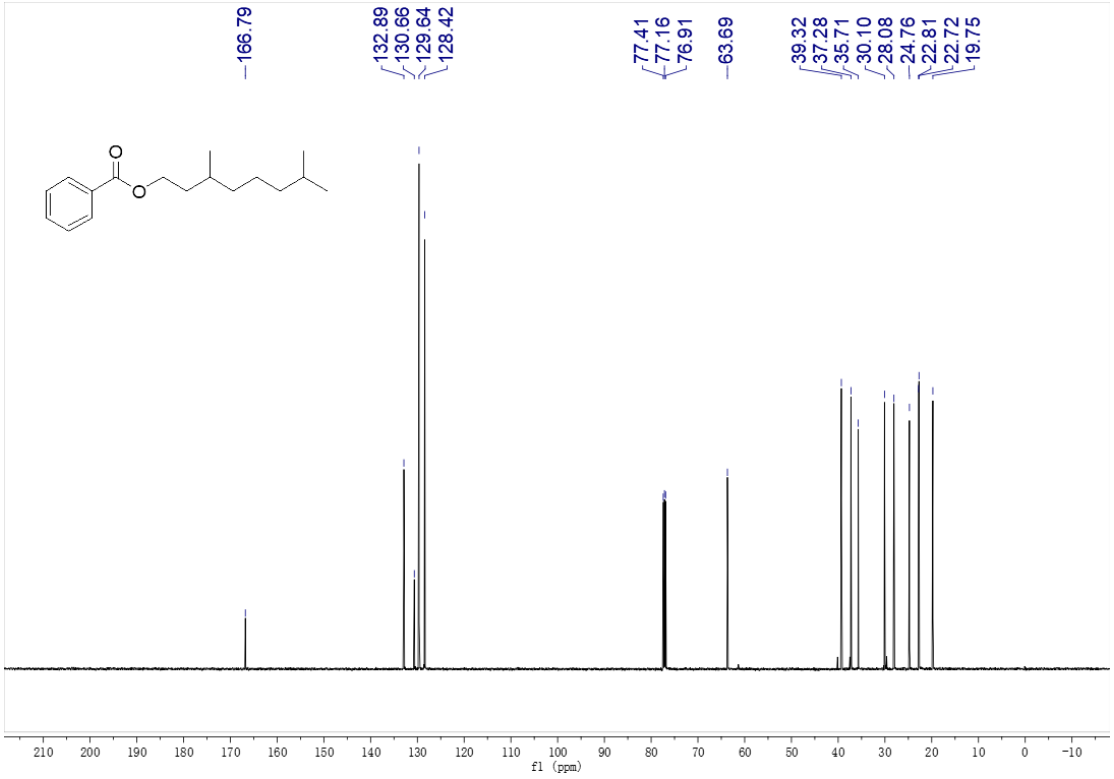
^{1}H NMR of compound **28a** (500 MHz, $CDCl_3$)



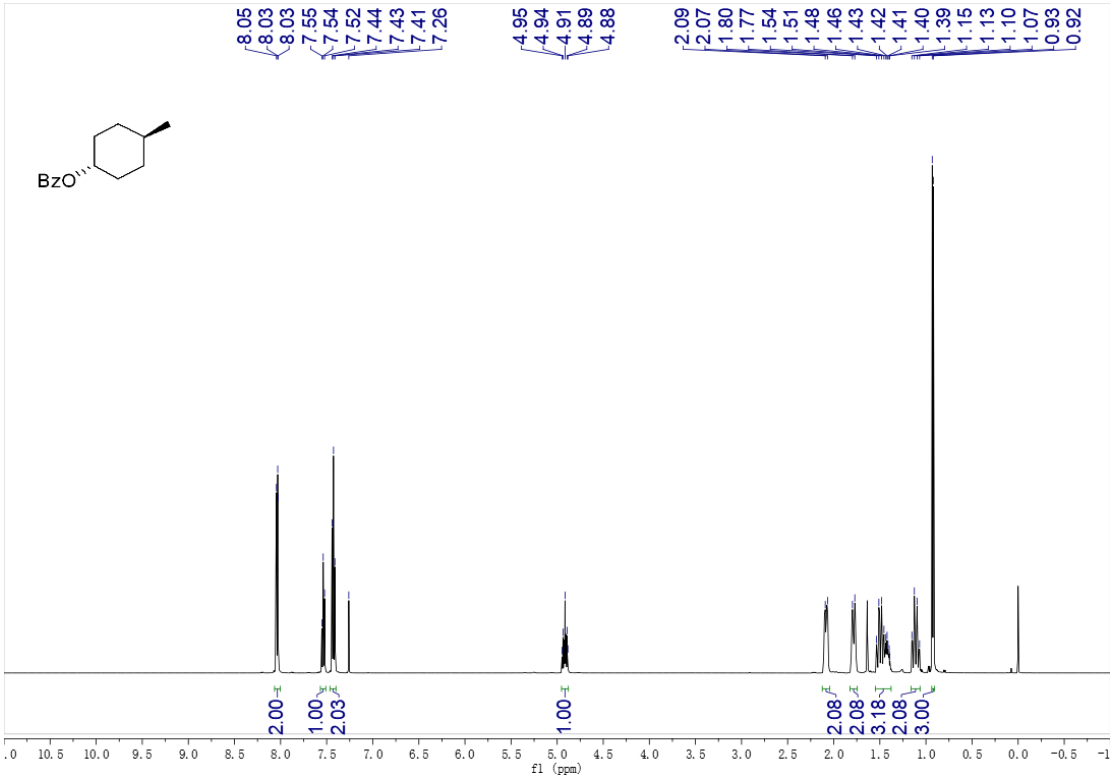
^{13}C NMR of compound **28a** (126 MHz, $CDCl_3$)



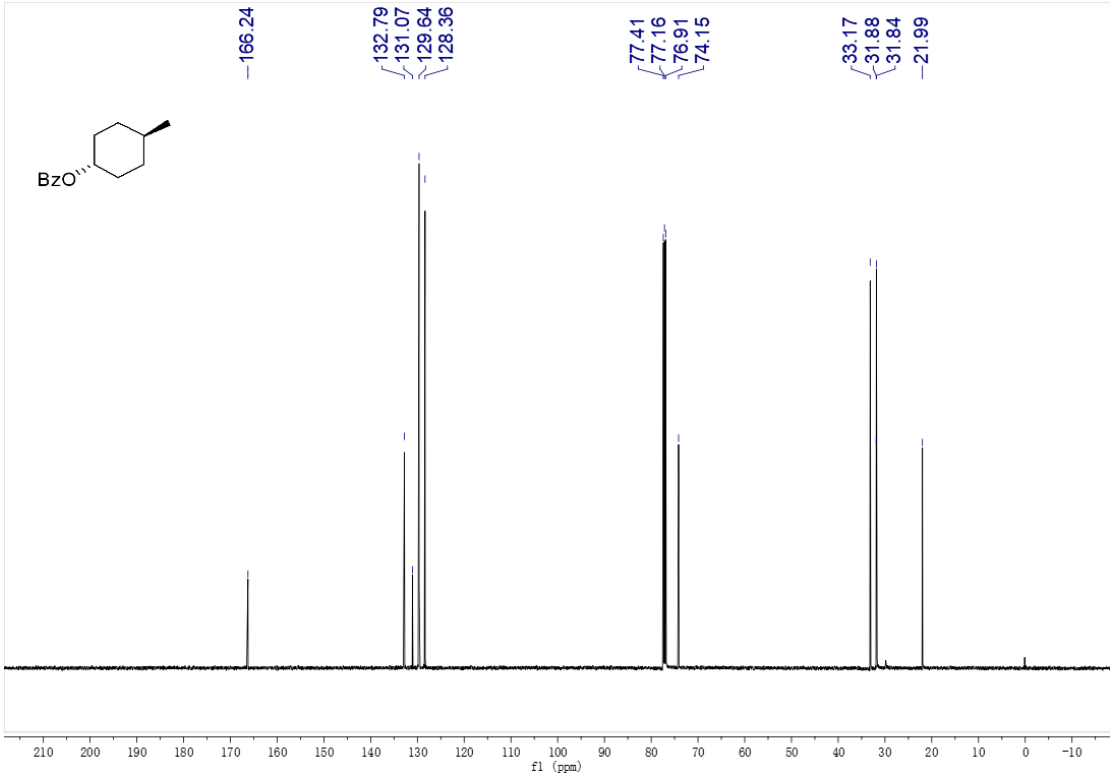
^{1}H NMR of compound **29a** (500 MHz, $CDCl_3$)



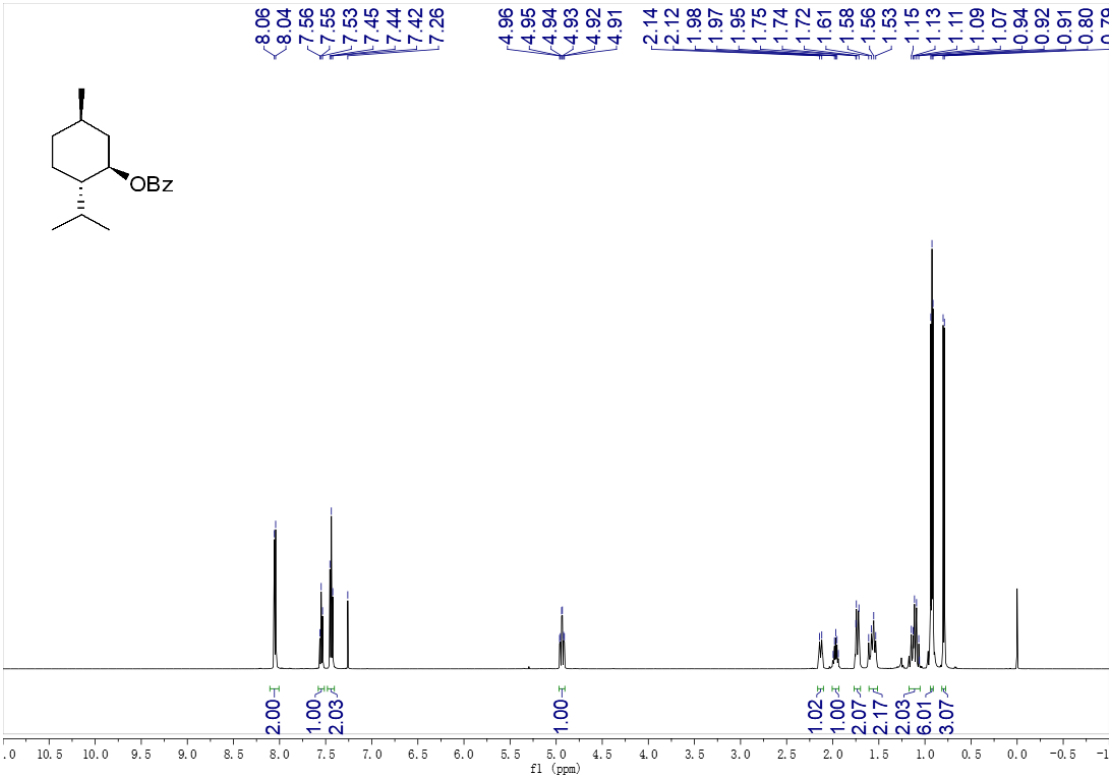
^{13}C NMR of compound **29a** (126 MHz, $CDCl_3$)



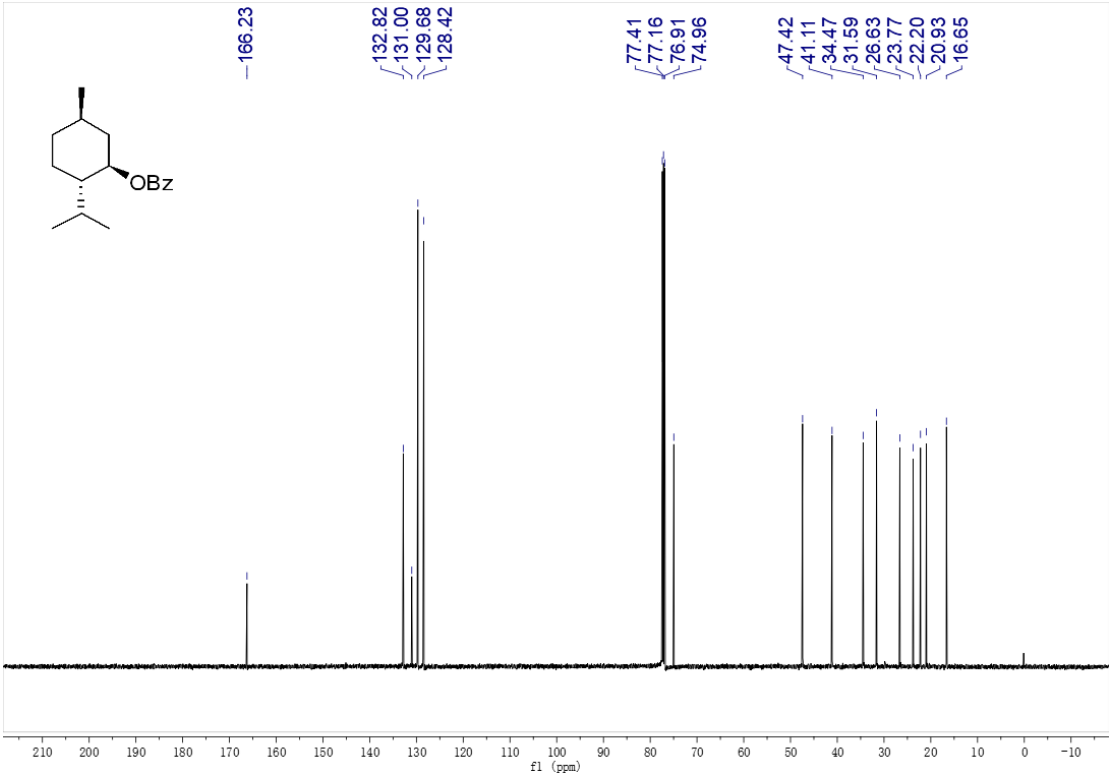
^{1}H NMR of compound **30a** (500 MHz, $CDCl_3$)



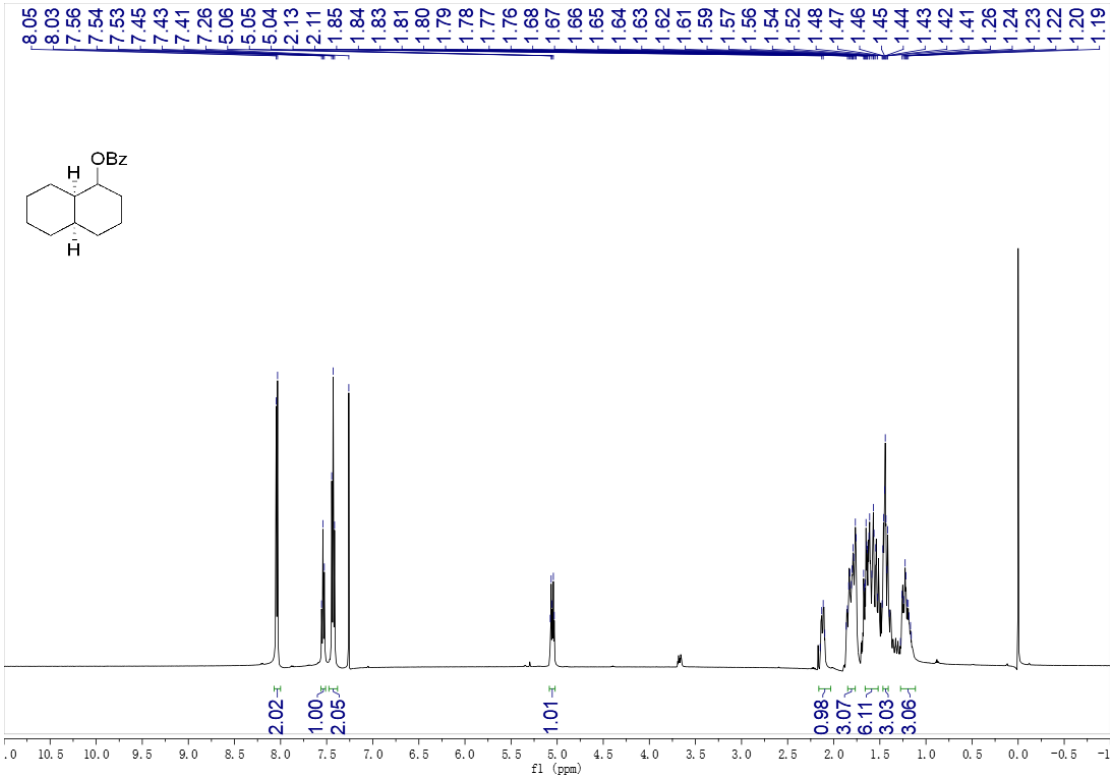
^{13}C NMR of compound **30a** (126 MHz, $CDCl_3$)



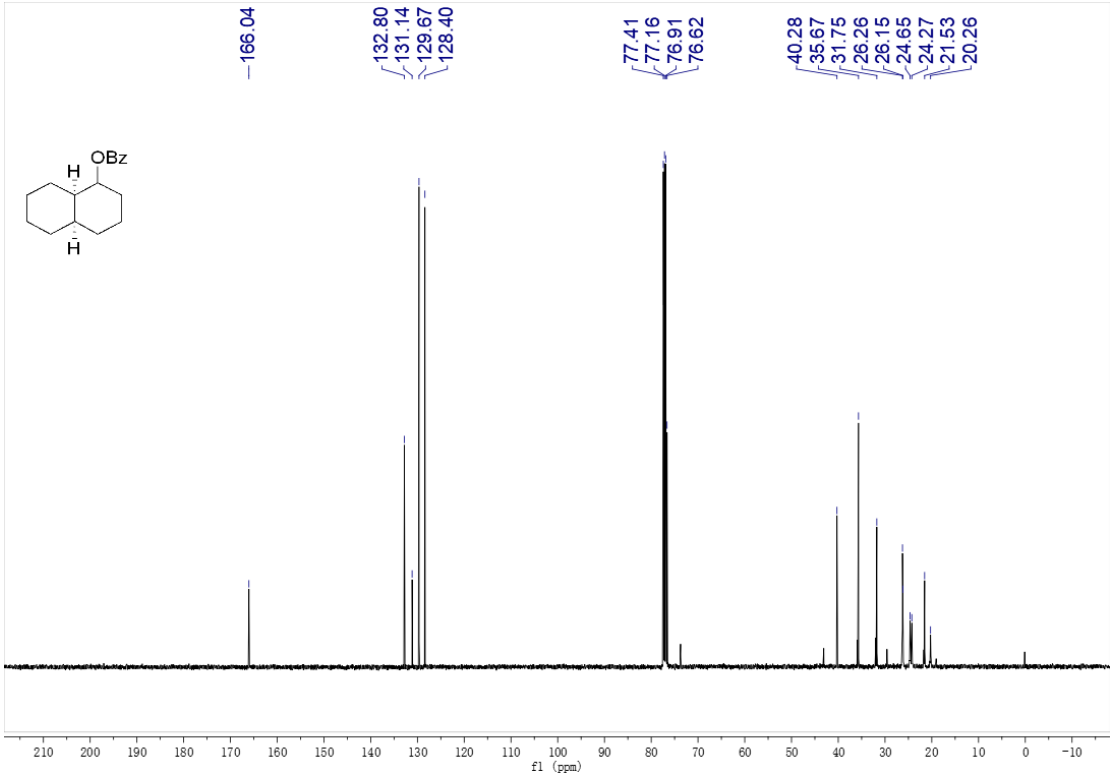
^{1}H NMR of compound **31a** (500 MHz, $CDCl_3$)



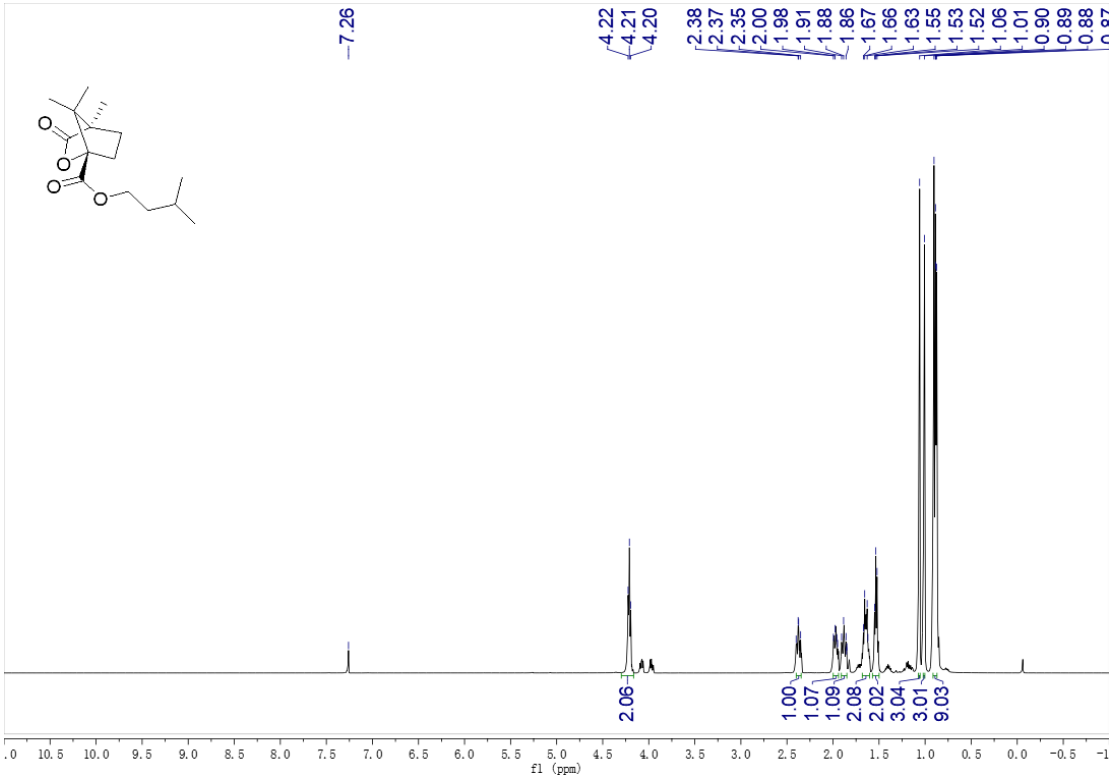
^{13}C NMR of compound **31a** (126 MHz, $CDCl_3$)



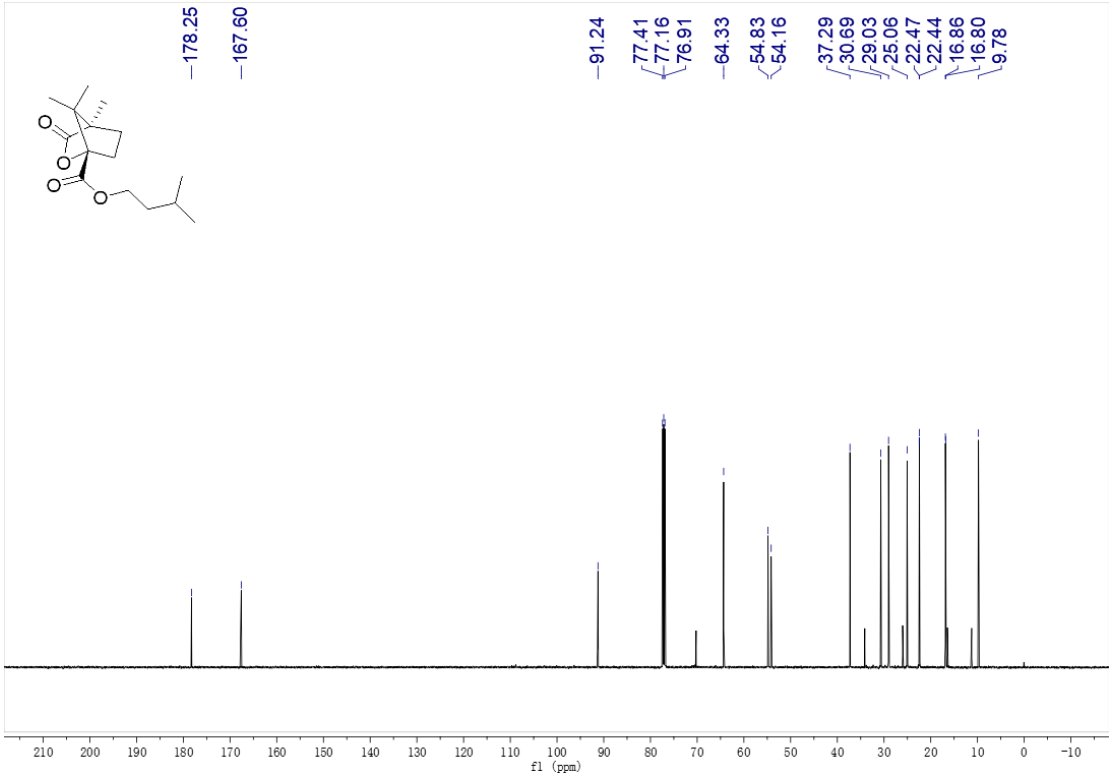
^{1}H NMR of compound **32a** (500 MHz, $CDCl_3$)



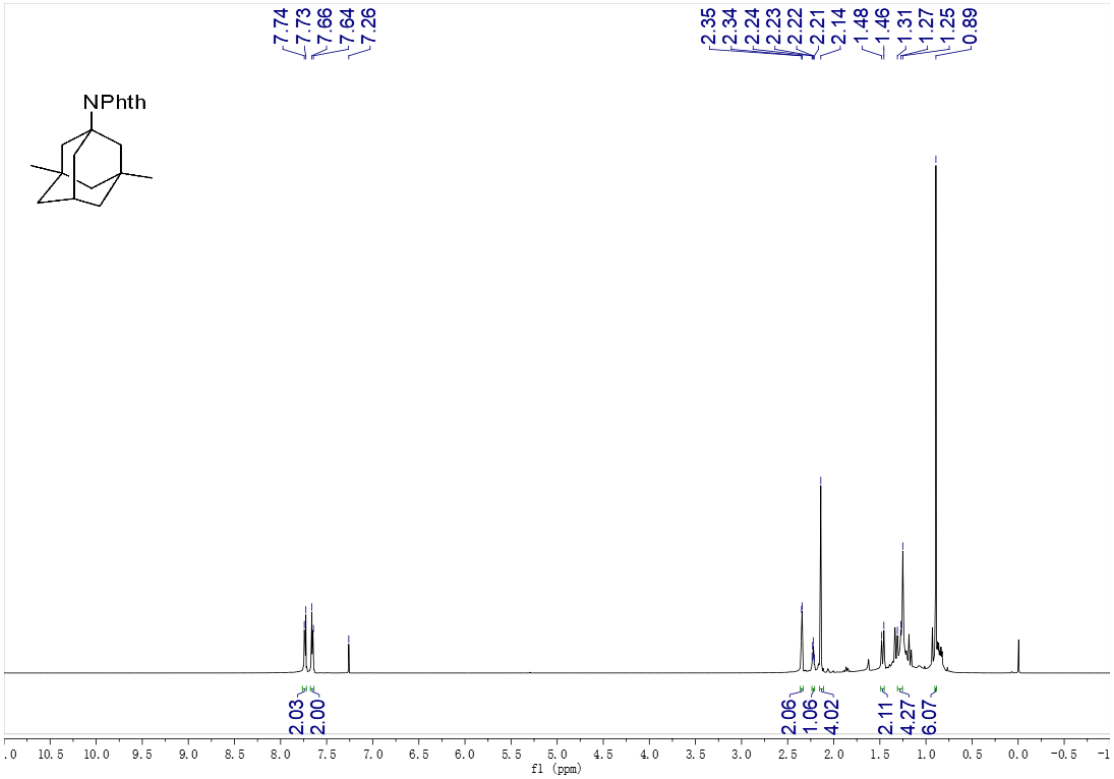
^{13}C NMR of compound **32a** (126 MHz, $CDCl_3$)



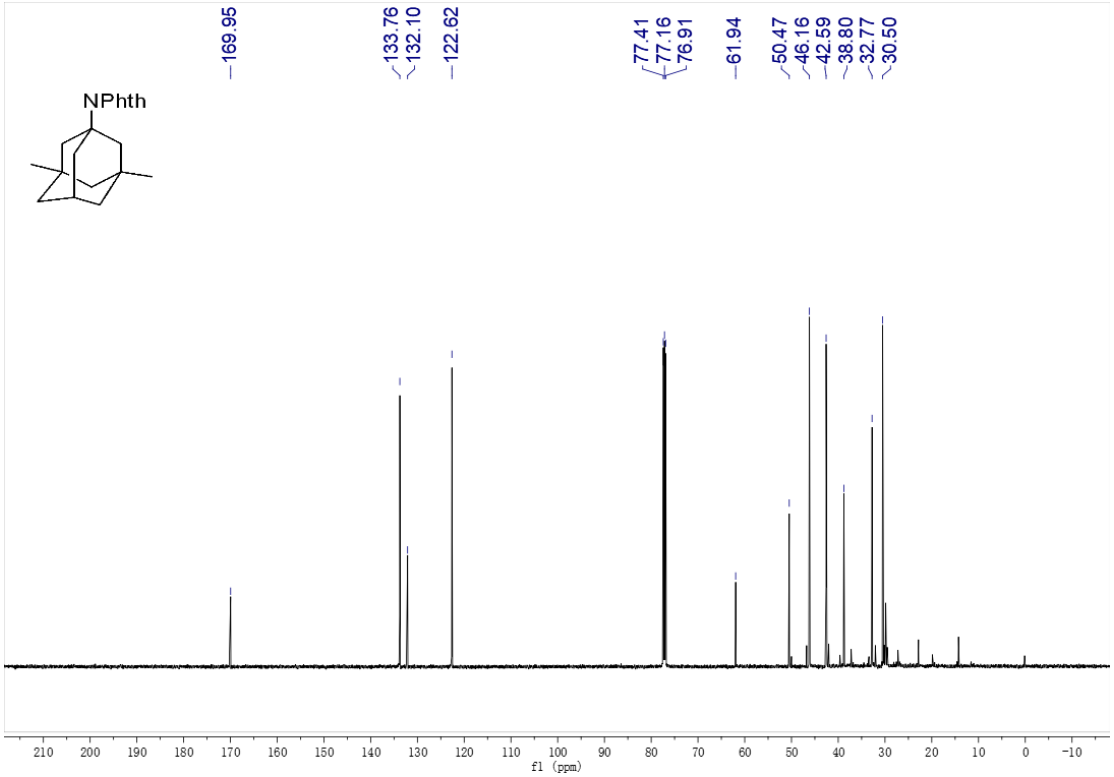
^{1}H NMR of compound **35a** (500 MHz, $CDCl_3$)



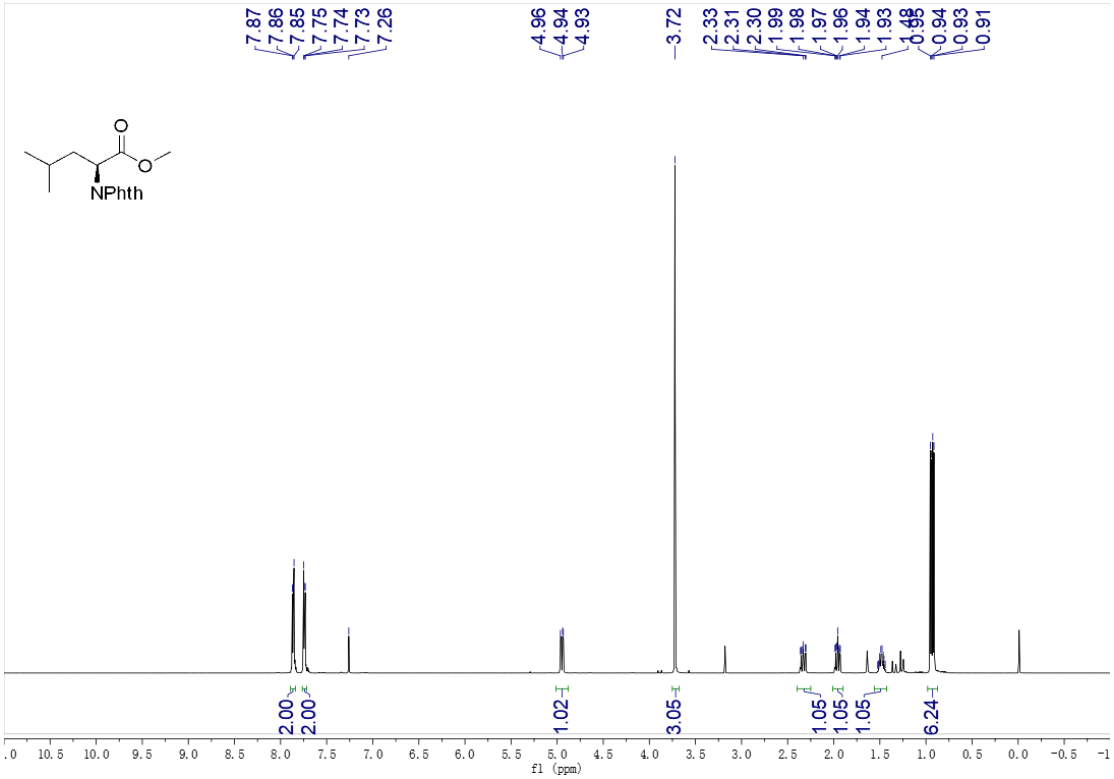
^{13}C NMR of compound **35a** (126 MHz, $CDCl_3$)



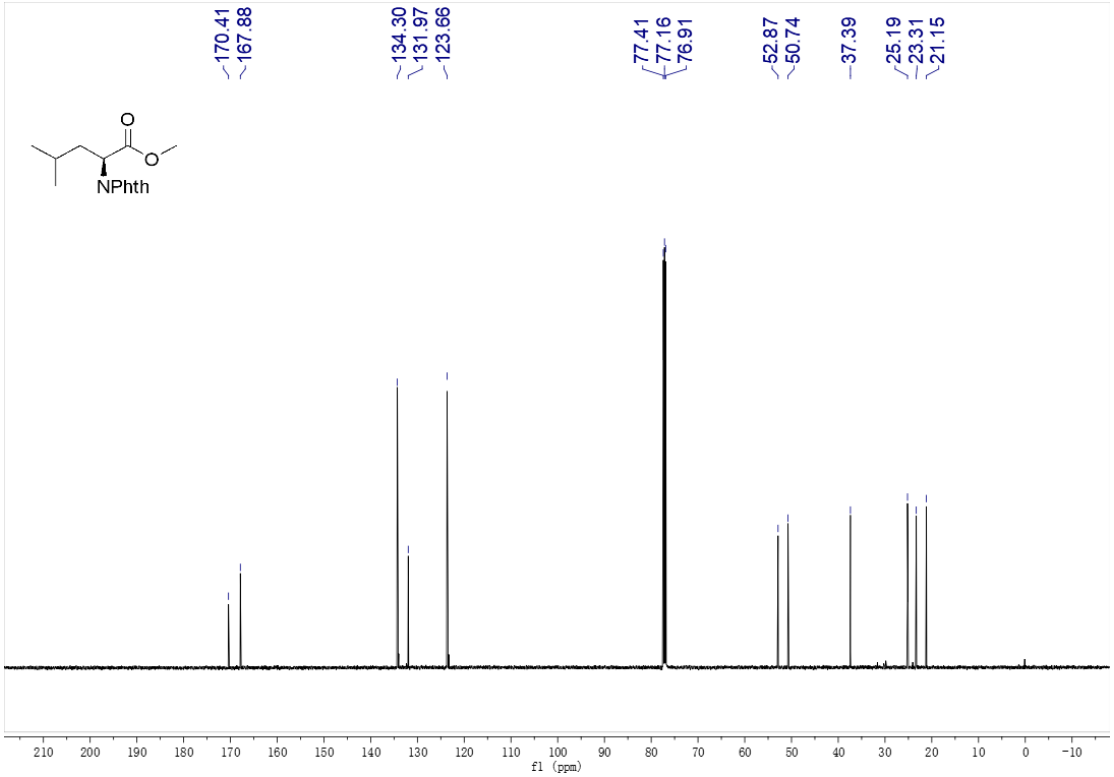
^{1}H NMR of compound **36a** (500 MHz, $CDCl_3$)



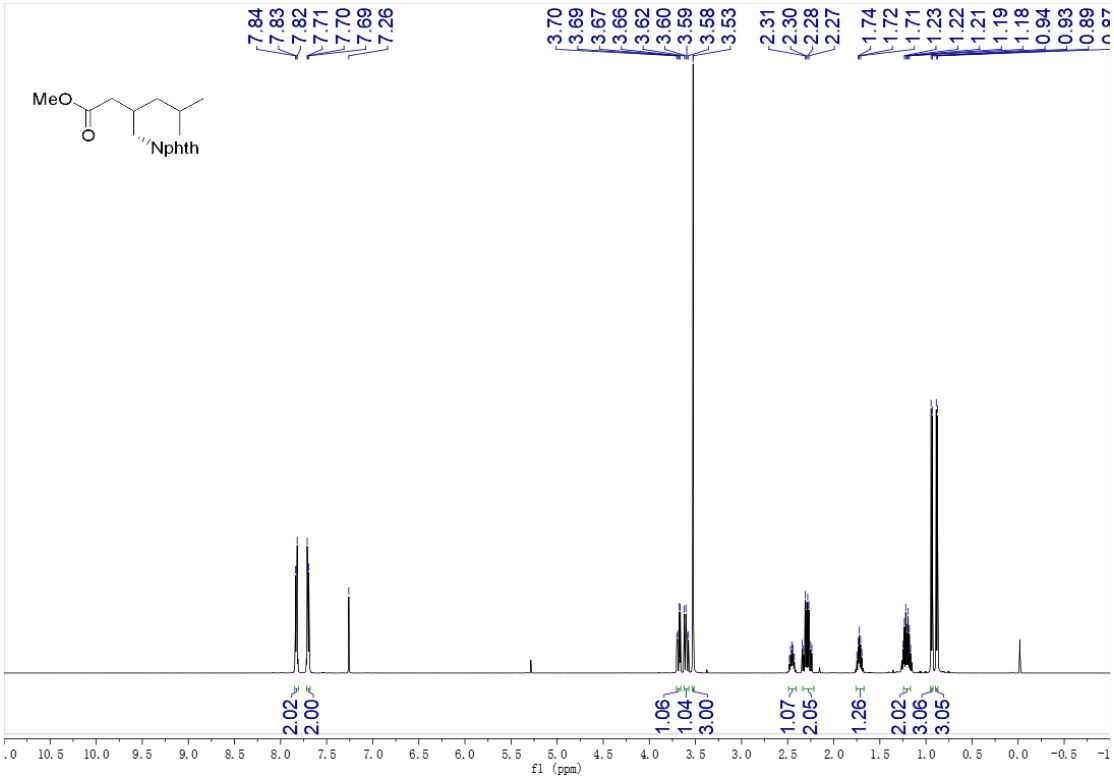
^{13}C NMR of compound **36a** (126 MHz, $CDCl_3$)



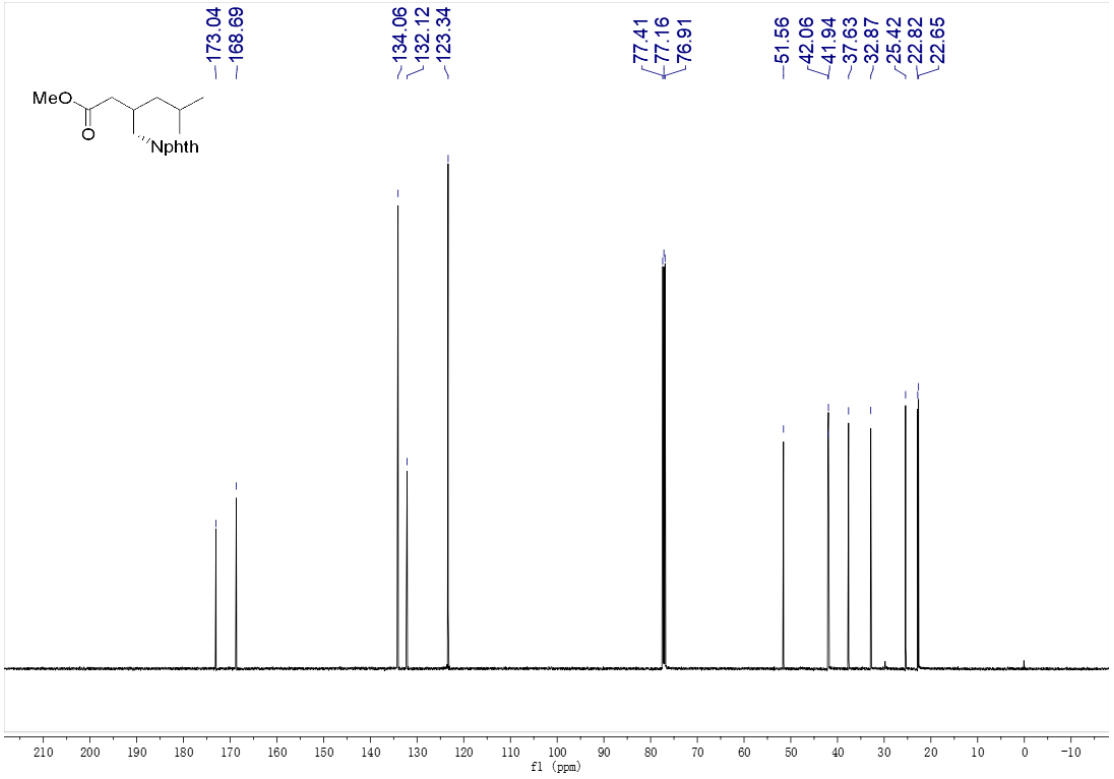
^{1}H NMR of compound **37a** (500 MHz, $CDCl_3$)



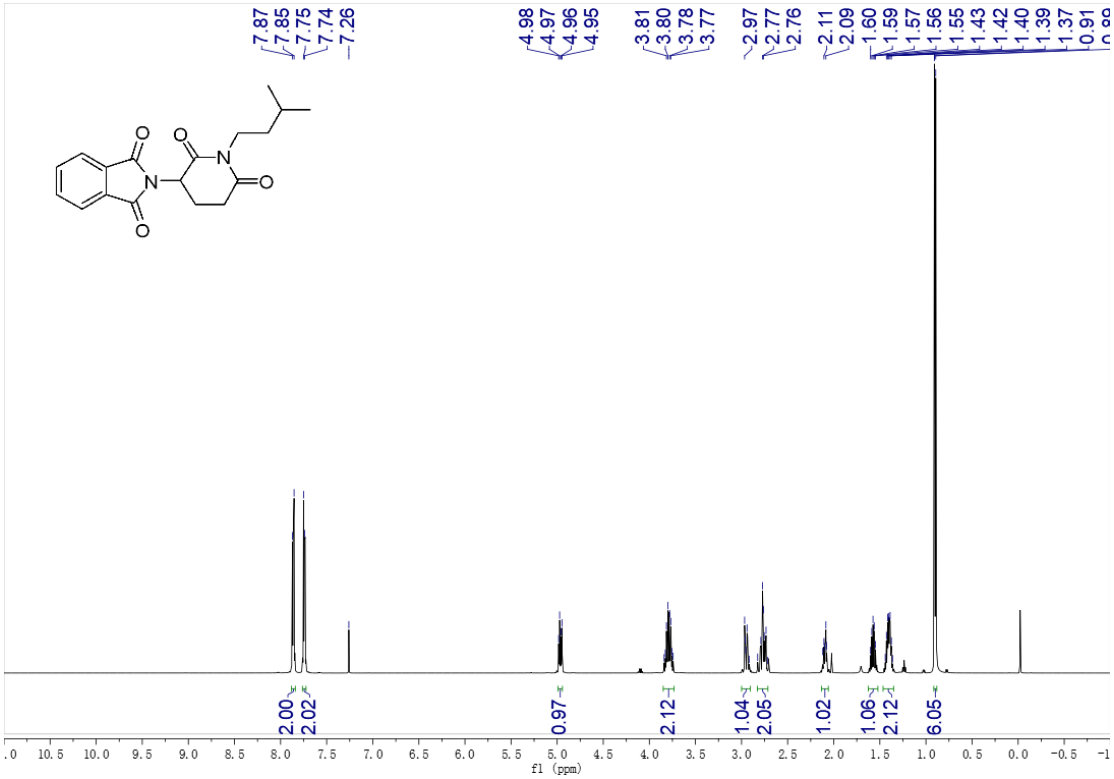
^{13}C NMR of compound **37a** (126 MHz, $CDCl_3$)



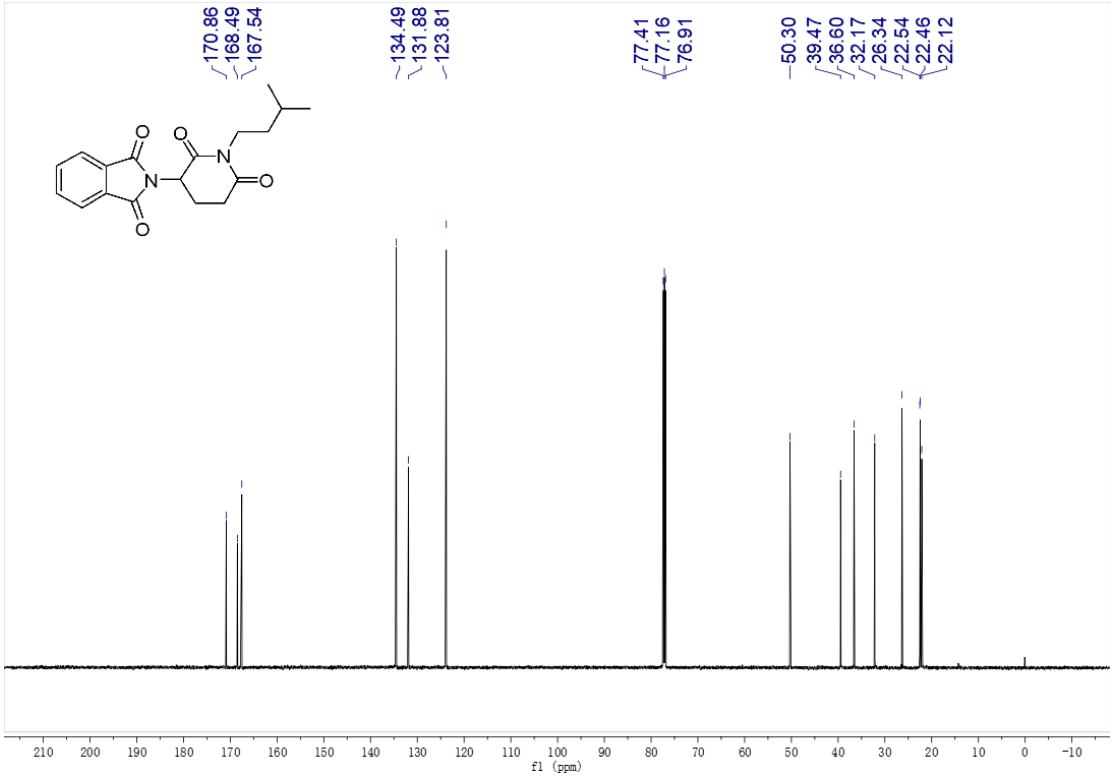
^{1}H NMR of compound **38a** (500 MHz, $CDCl_3$)



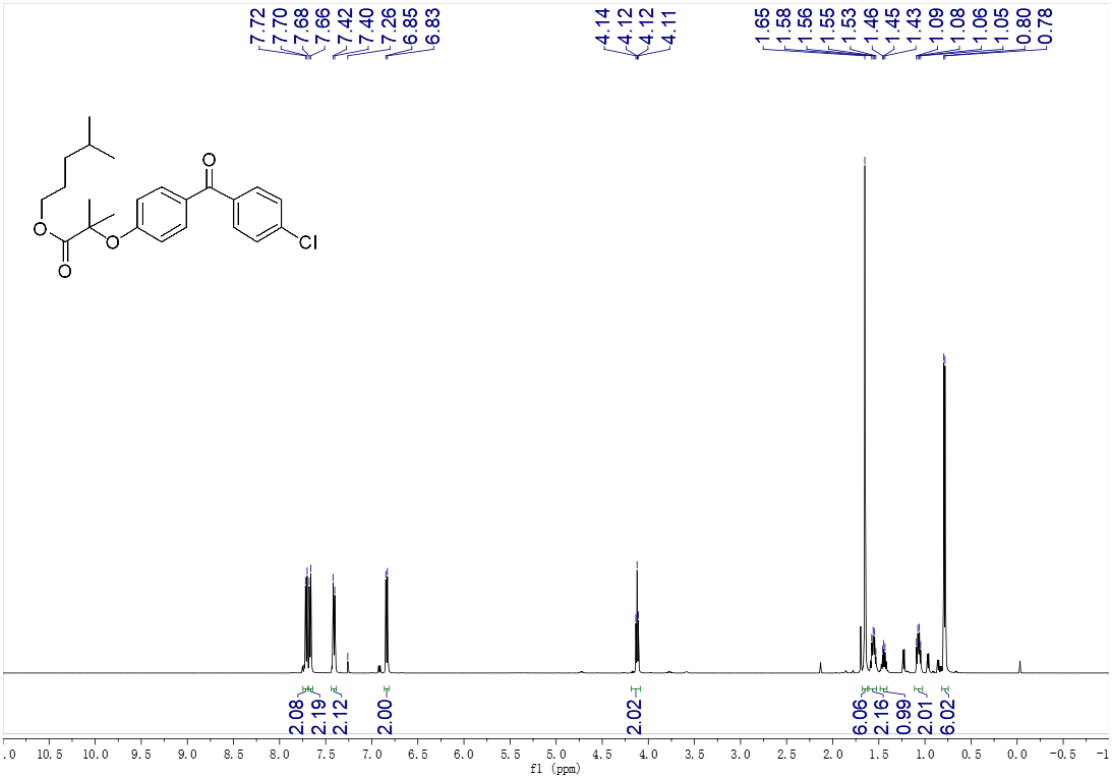
^{13}C NMR of compound **38a** (126 MHz, $CDCl_3$)



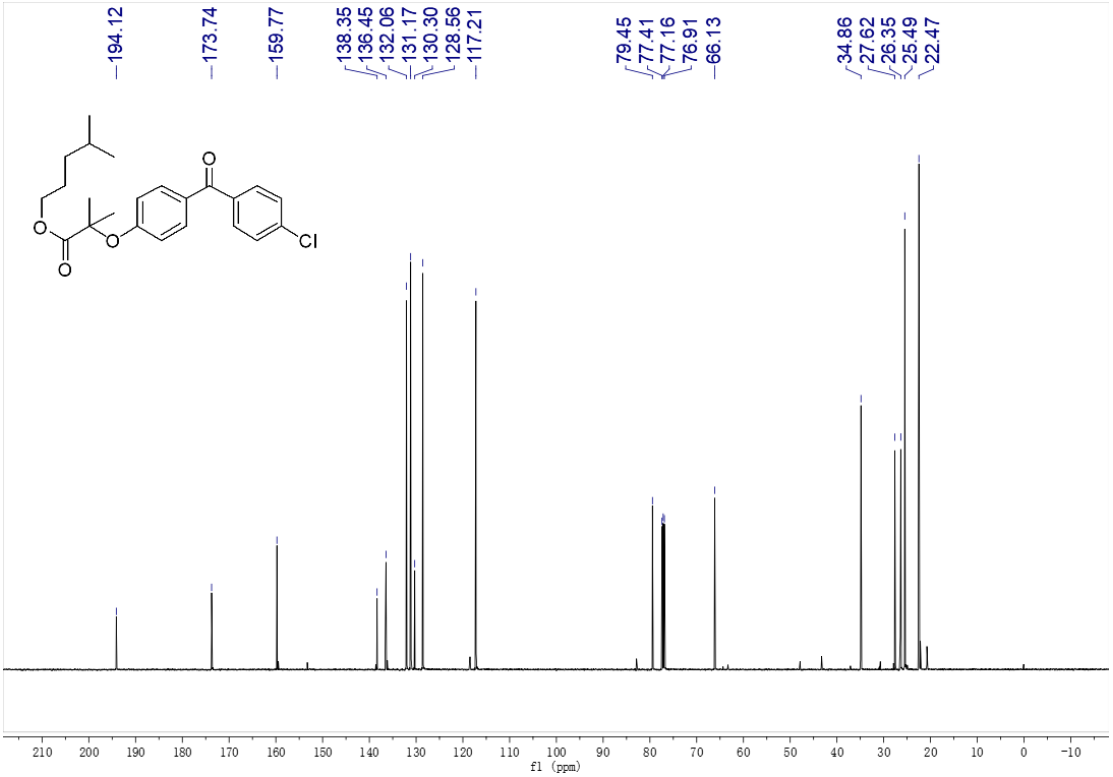
^{1}H NMR of compound **39a** (500 MHz, $CDCl_3$)



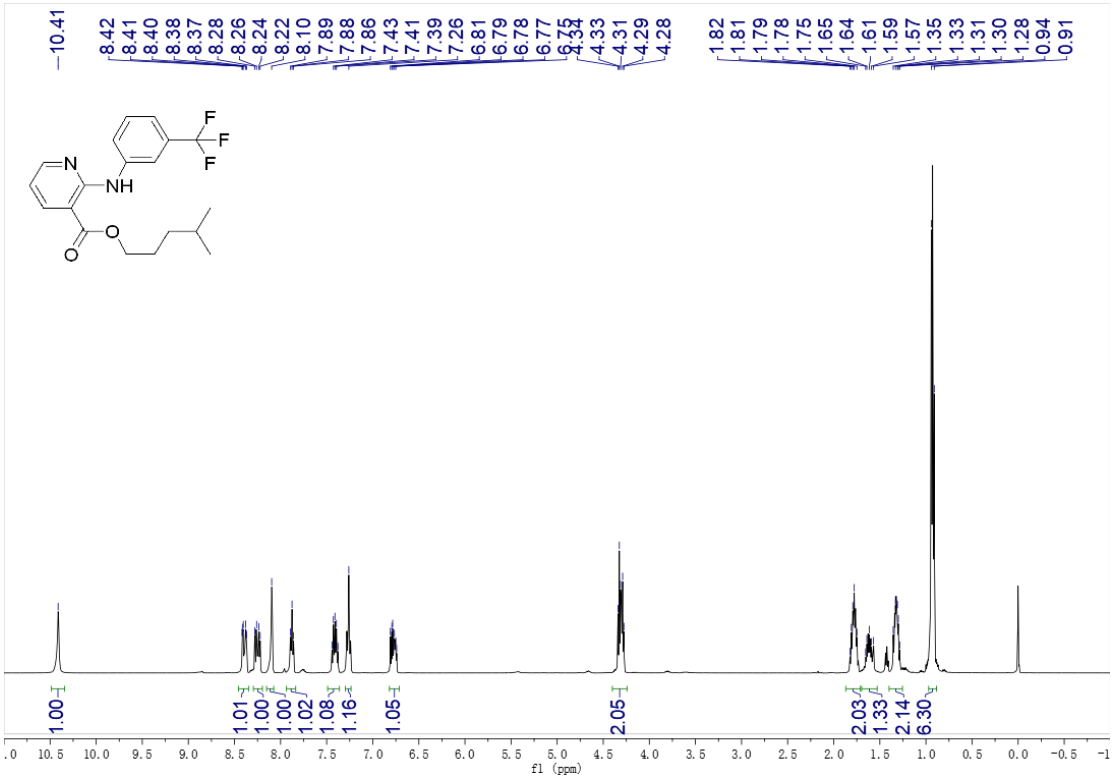
^{13}C NMR of compound **39a** (126 MHz, $CDCl_3$)



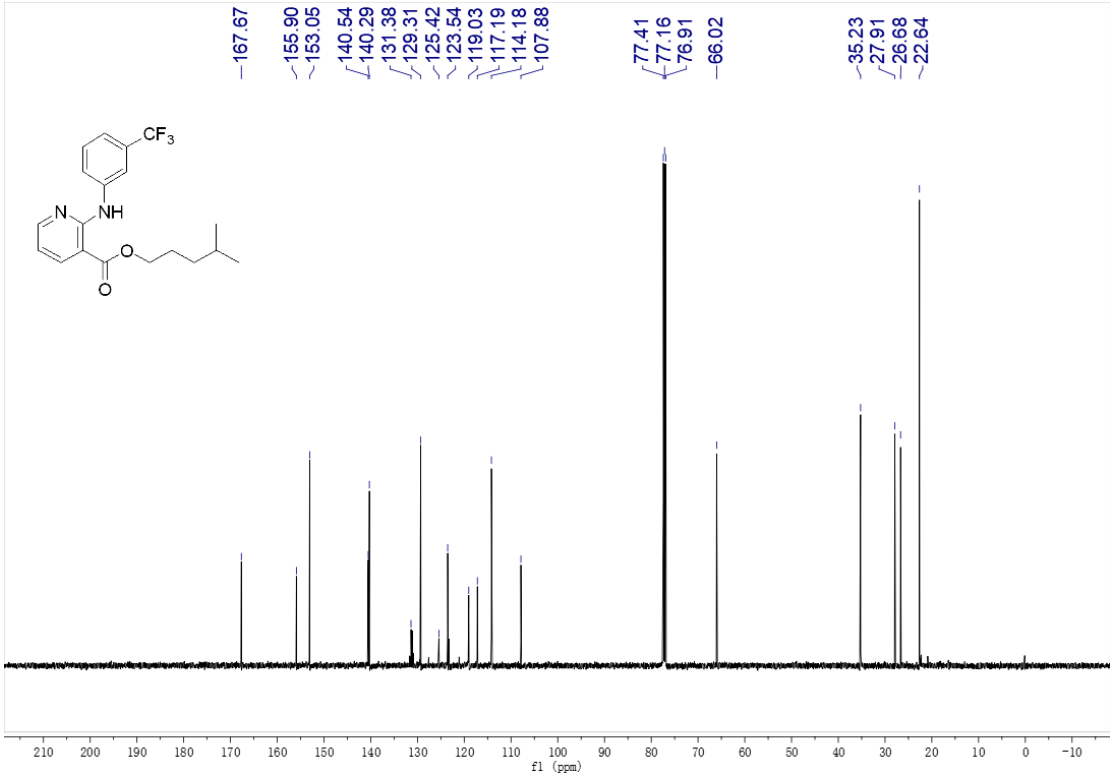
^{1}H NMR of compound **40a** (500 MHz, $CDCl_3$)



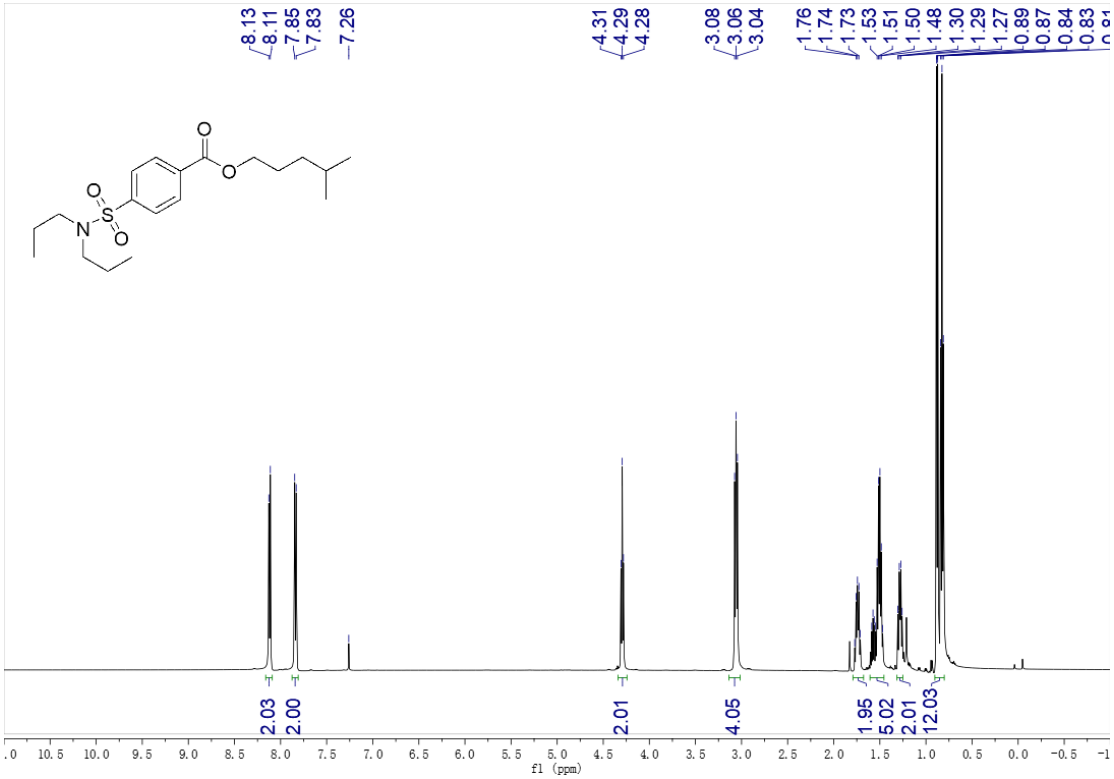
^{13}C NMR of compound **40a** (126 MHz, $CDCl_3$)



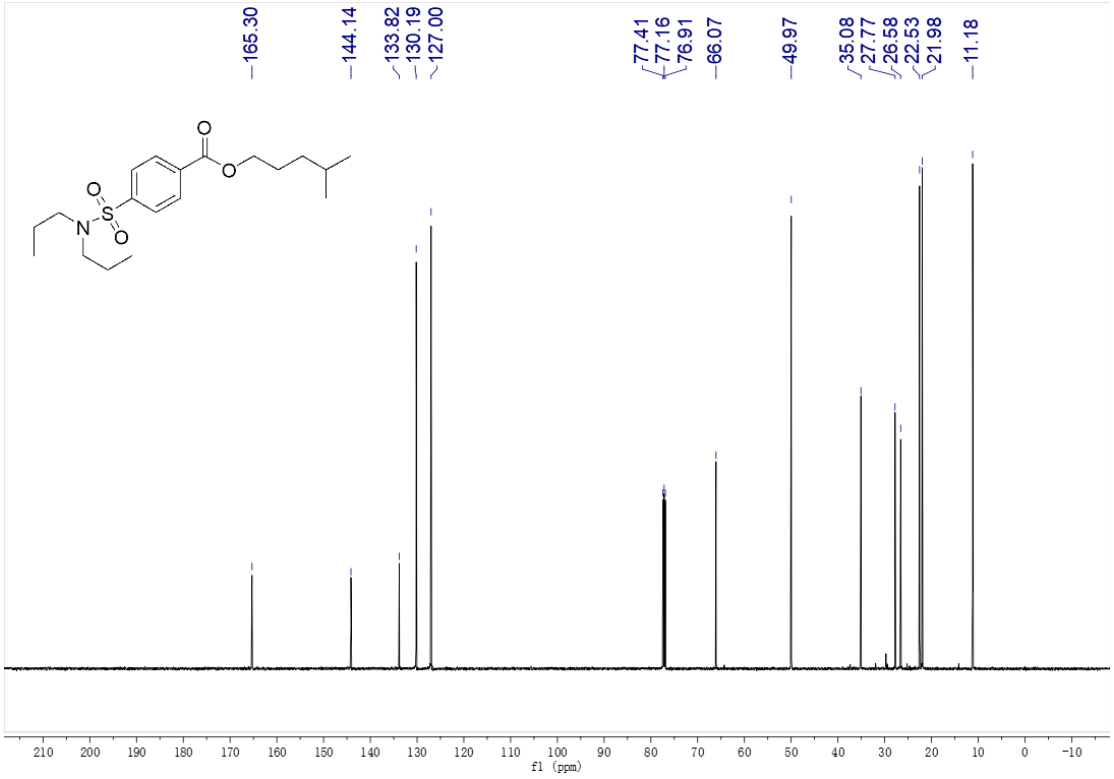
^{1}H NMR of compound **41a** (500 MHz, $CDCl_3$)



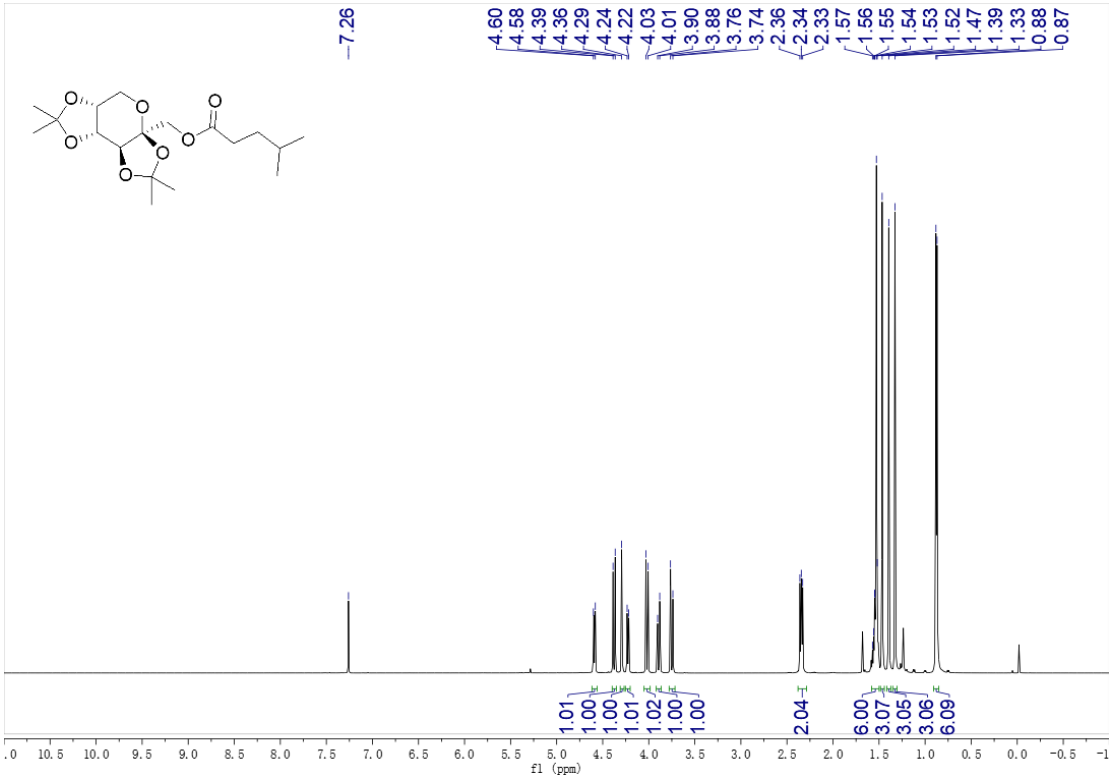
^{13}C NMR of compound **41a** (126 MHz, $CDCl_3$)



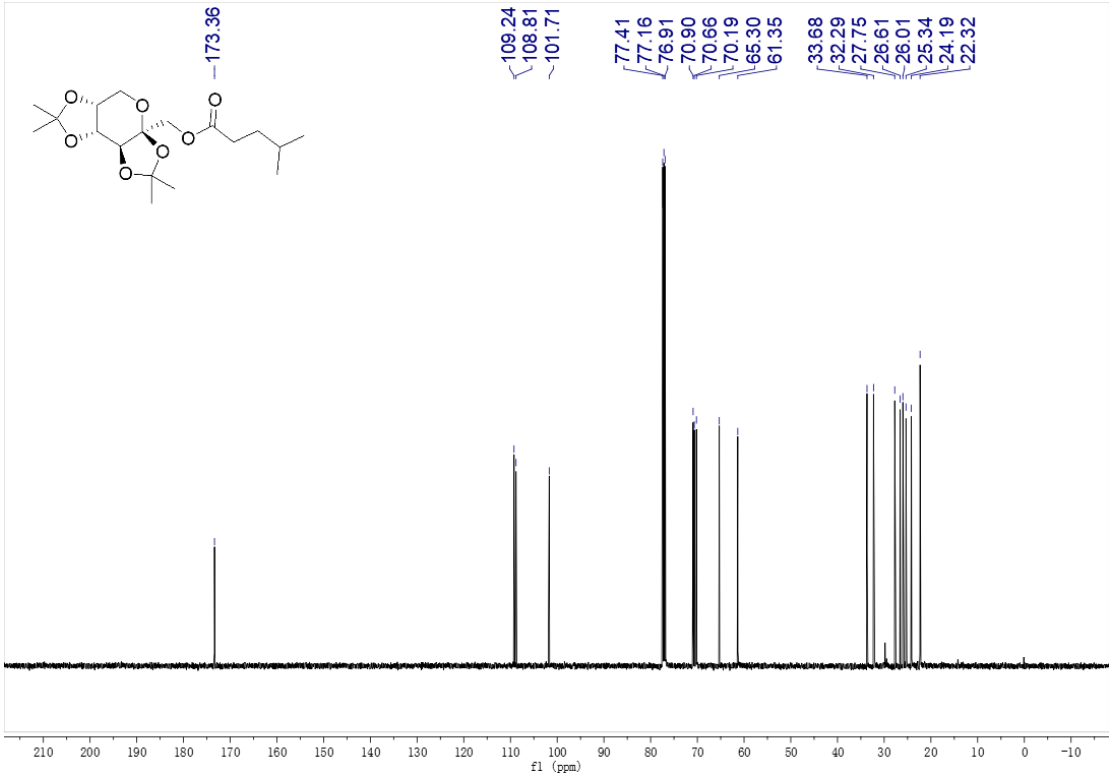
^{1}H NMR of compound **42a** (500 MHz, $CDCl_3$)



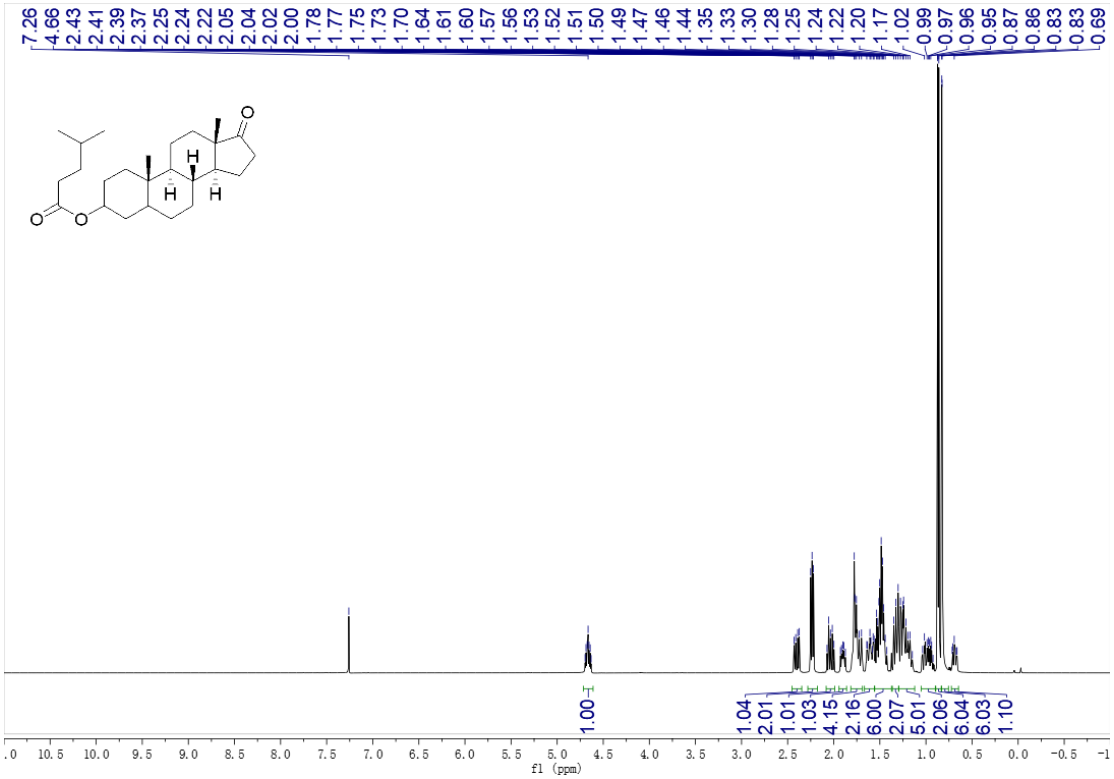
^{13}C NMR of compound **42a** (126 MHz, $CDCl_3$)



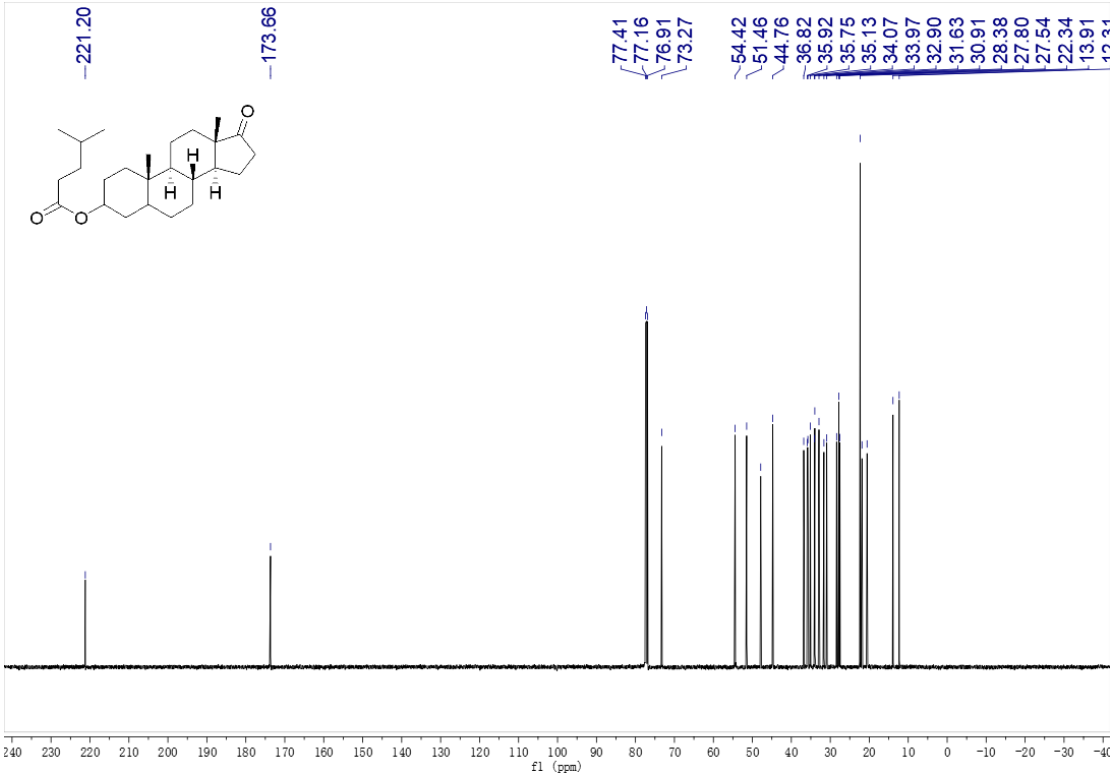
^{1}H NMR of compound **44a** (500 MHz, $CDCl_3$)



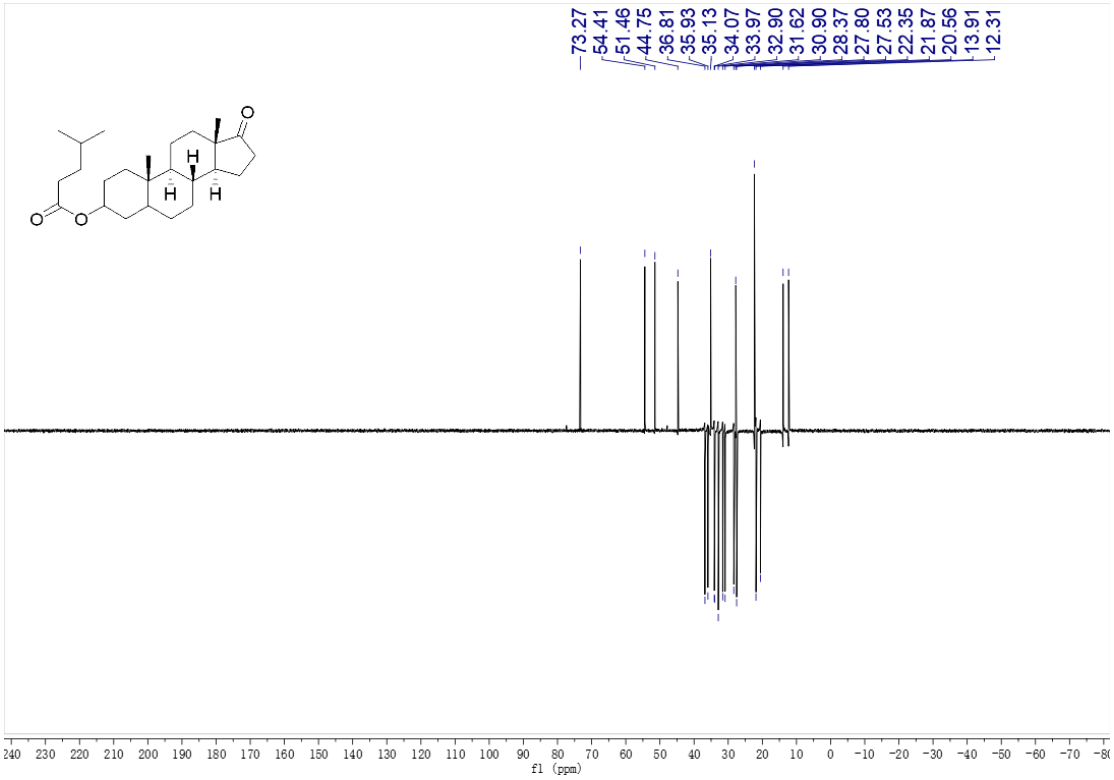
^{13}C NMR of compound **44a** (126 MHz, $CDCl_3$)



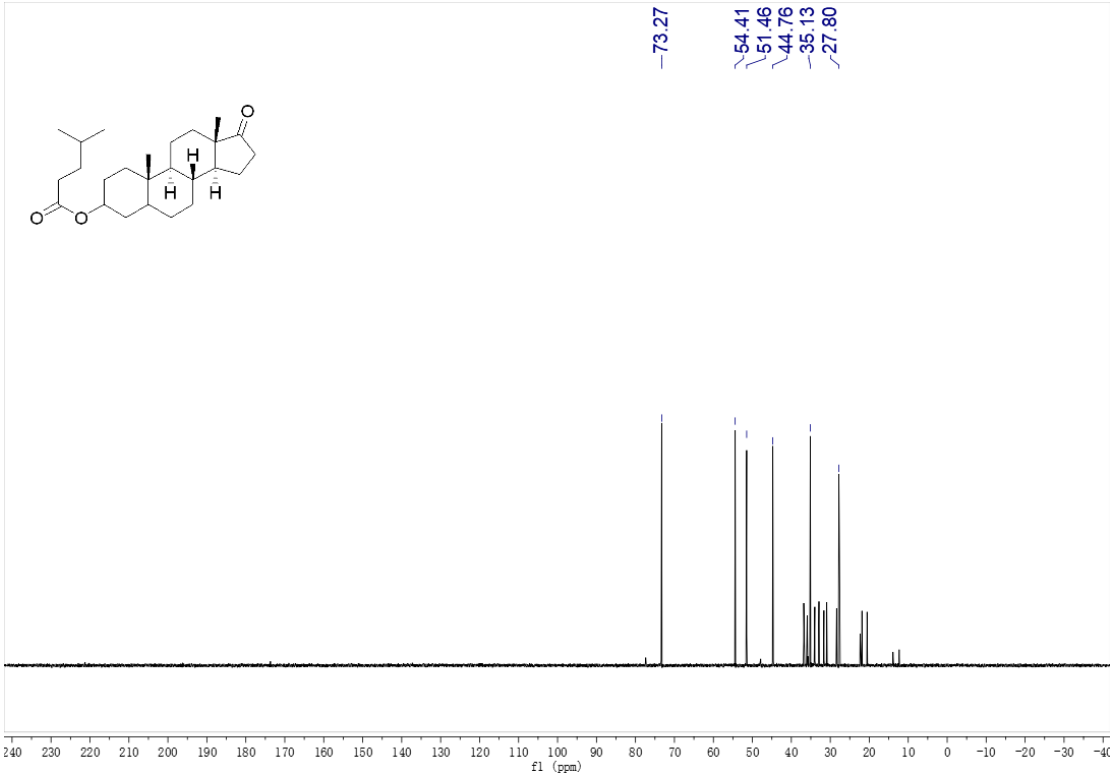
^{1}H NMR of compound **45a** (500 MHz, $CDCl_3$)



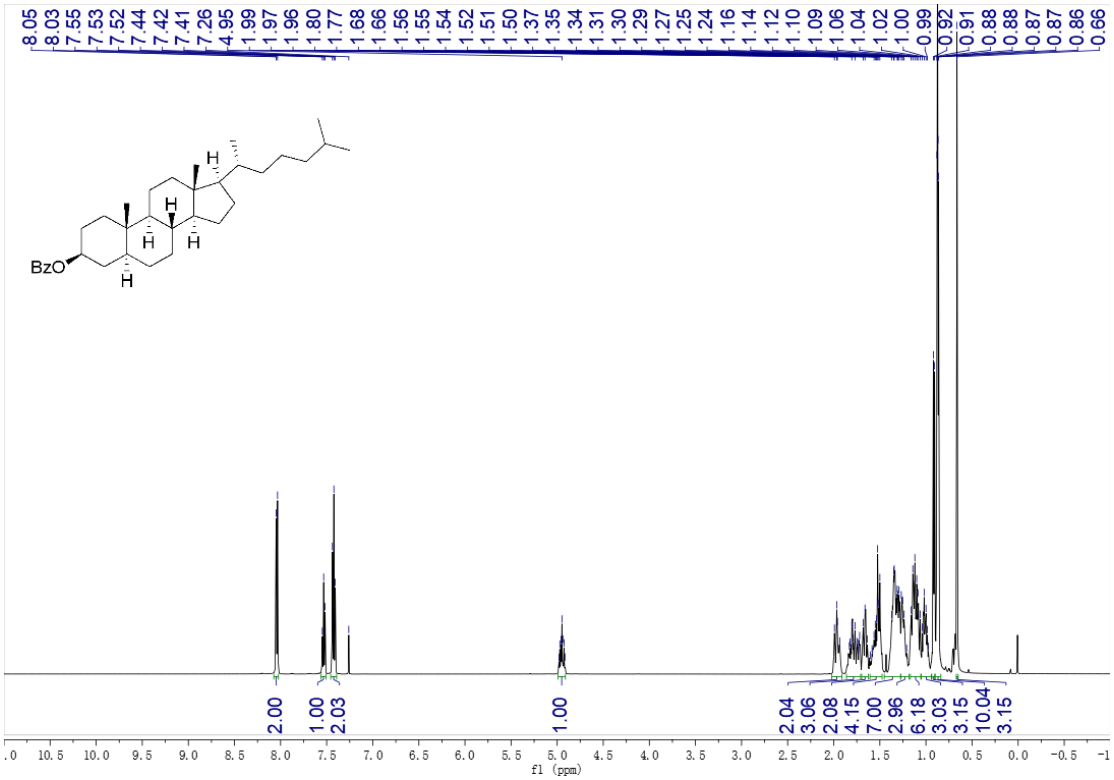
^{13}C NMR of compound **45a** (126 MHz, $CDCl_3$)



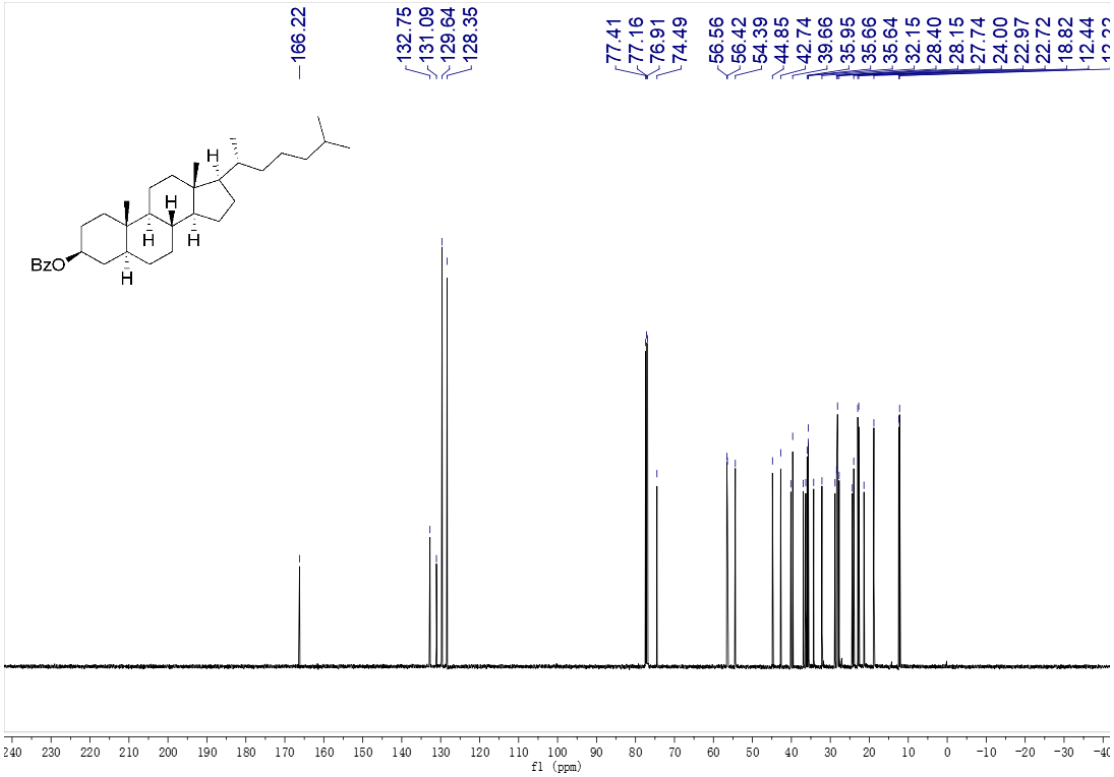
DEPT 135 of compound **45a**



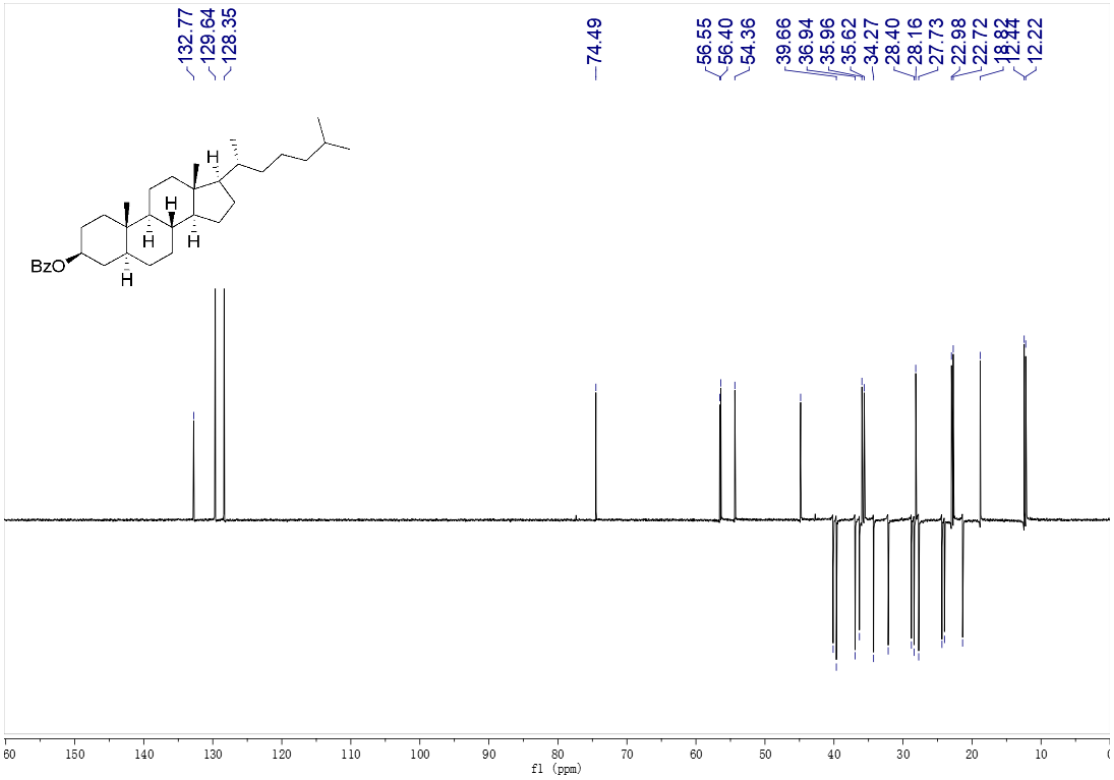
DEPT 90 of compound **45a**



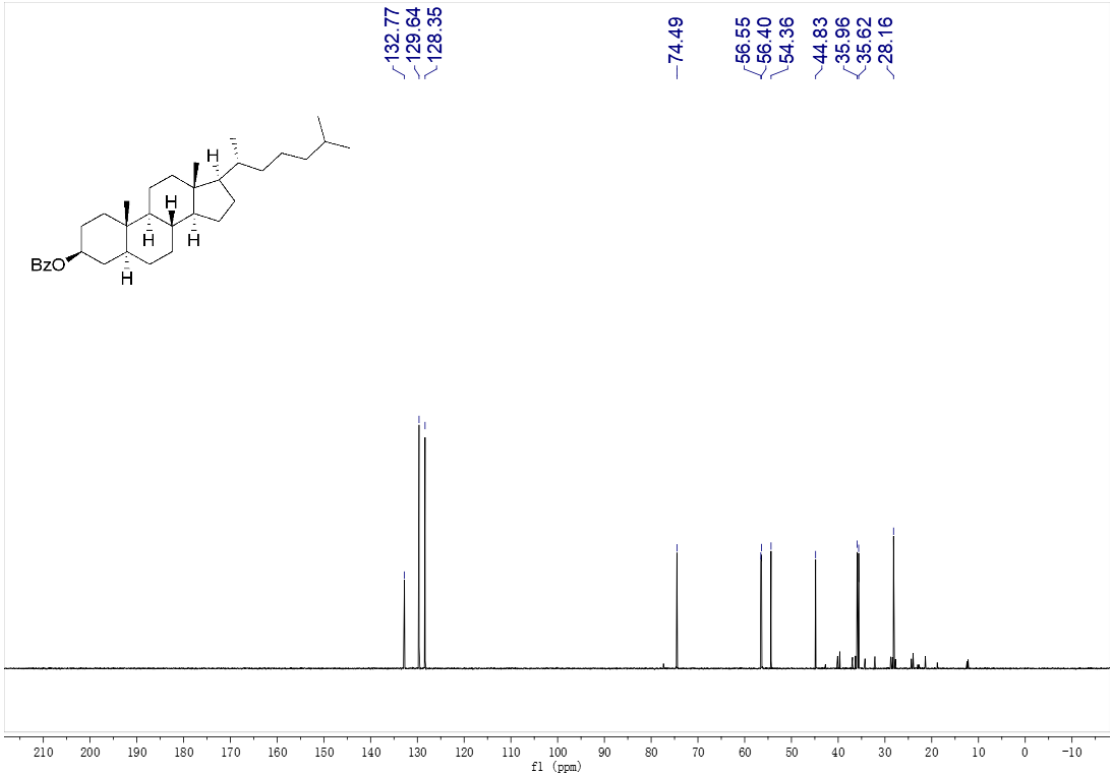
^{1}H NMR of compound **47a** (500 MHz, $CDCl_3$)



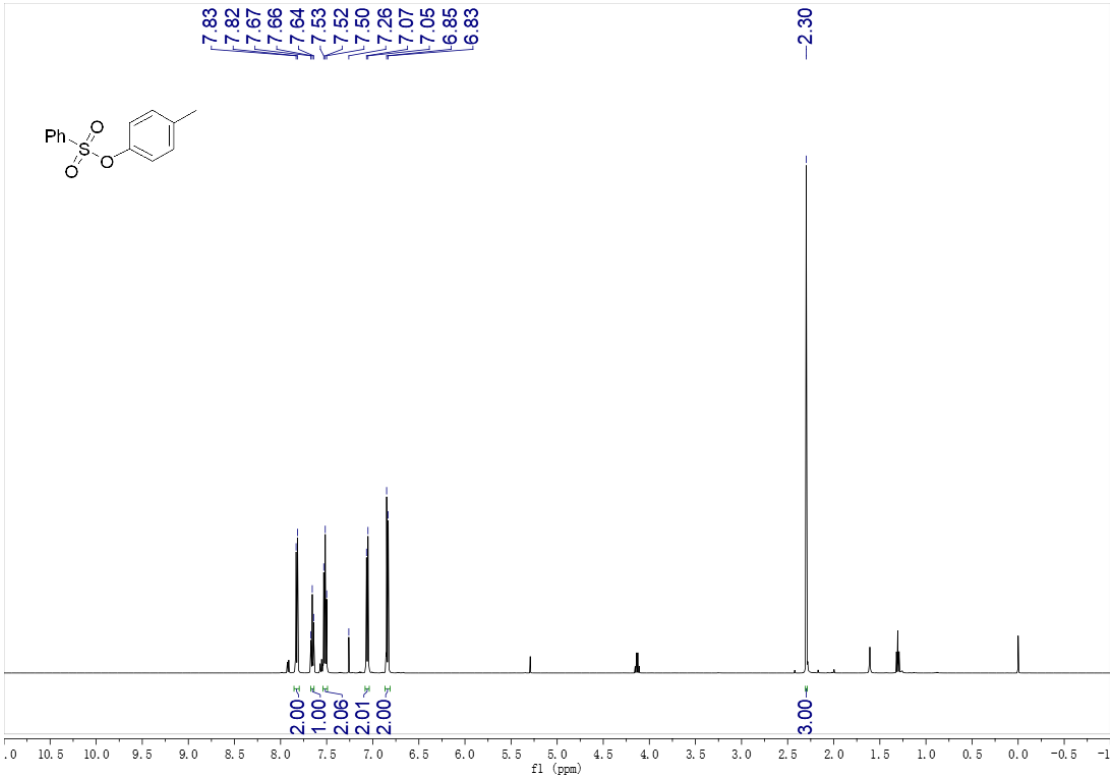
^{13}C NMR of compound **47a** (126 MHz, $CDCl_3$)



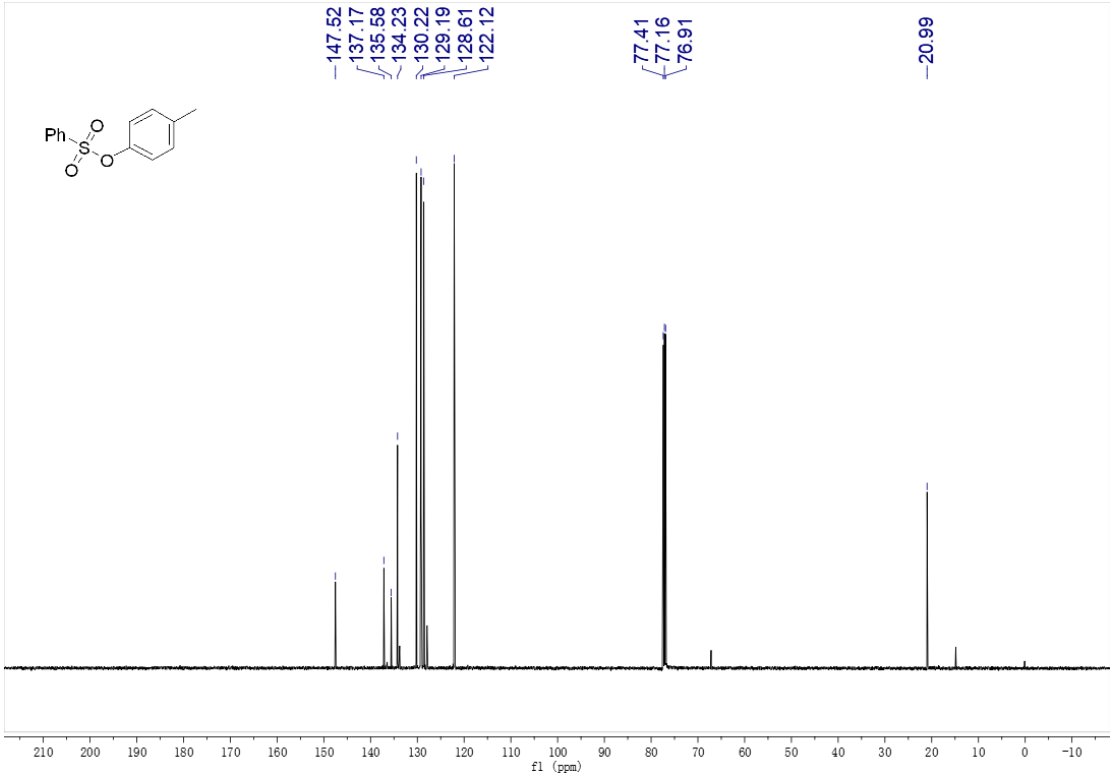
DEPT 135 of compound **47a**



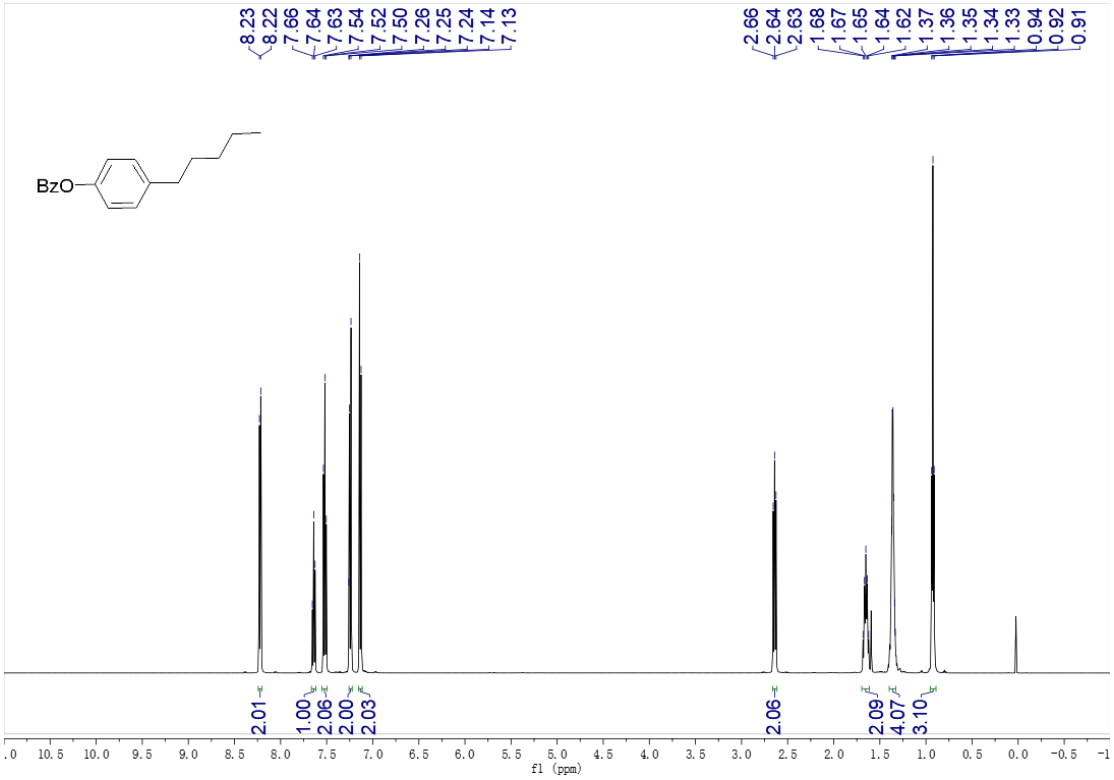
DEPT 90 of compound **47a**



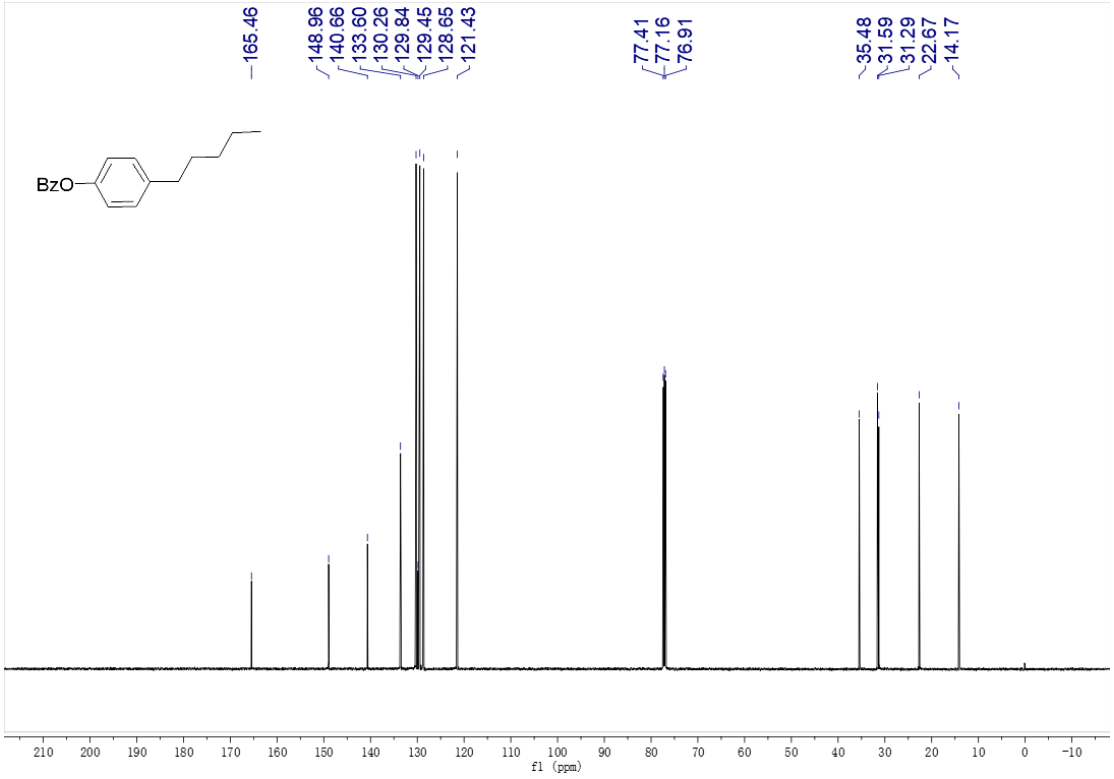
^{1}H NMR of compound **48a** (500 MHz, $CDCl_3$)



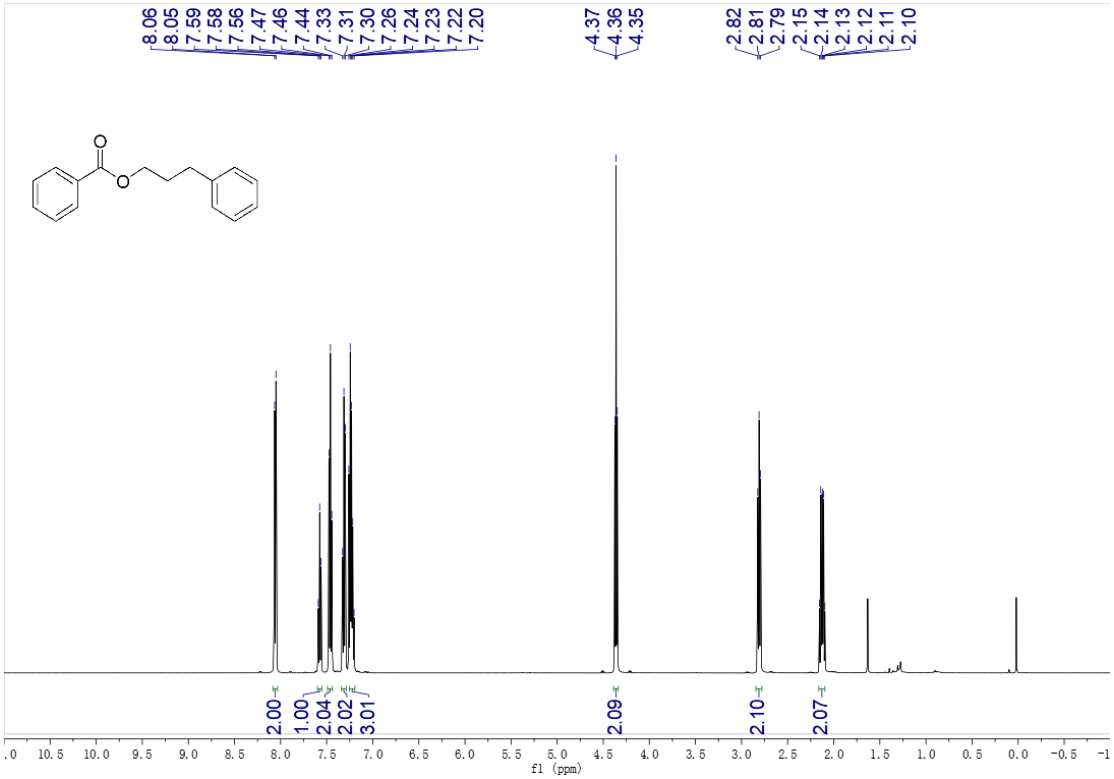
^{13}C NMR of compound **48a** (126 MHz, $CDCl_3$)



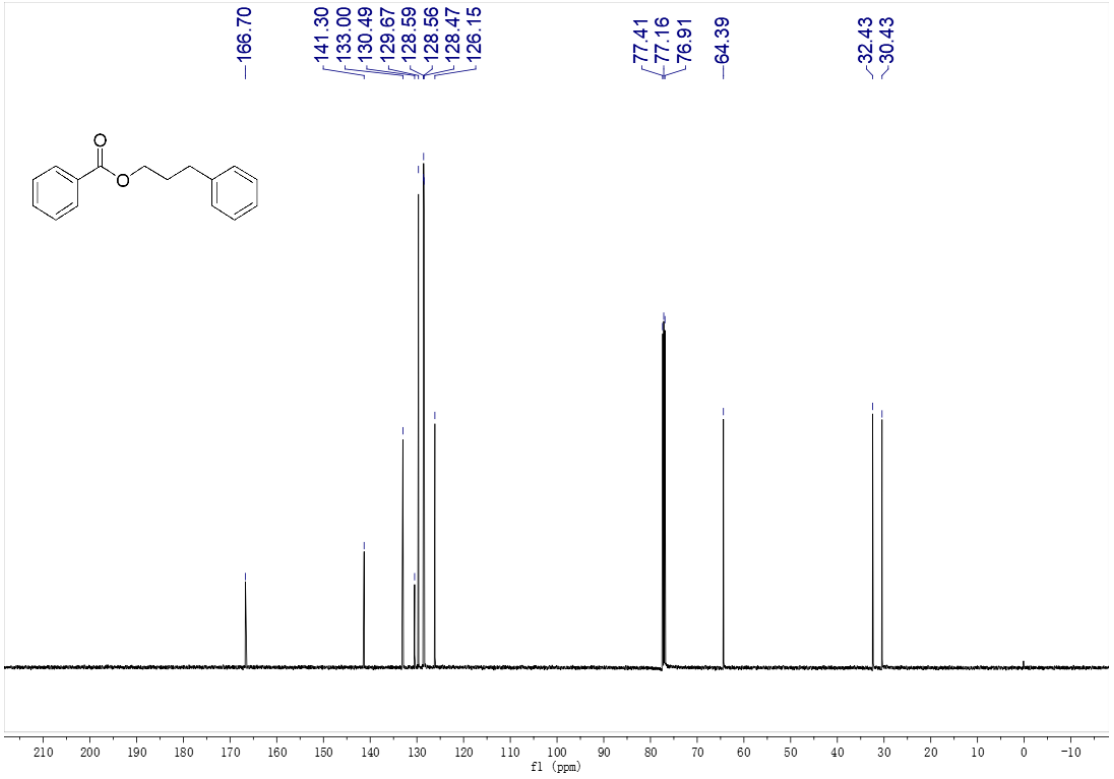
^{1}H NMR of compound **50a** (500 MHz, $CDCl_3$)



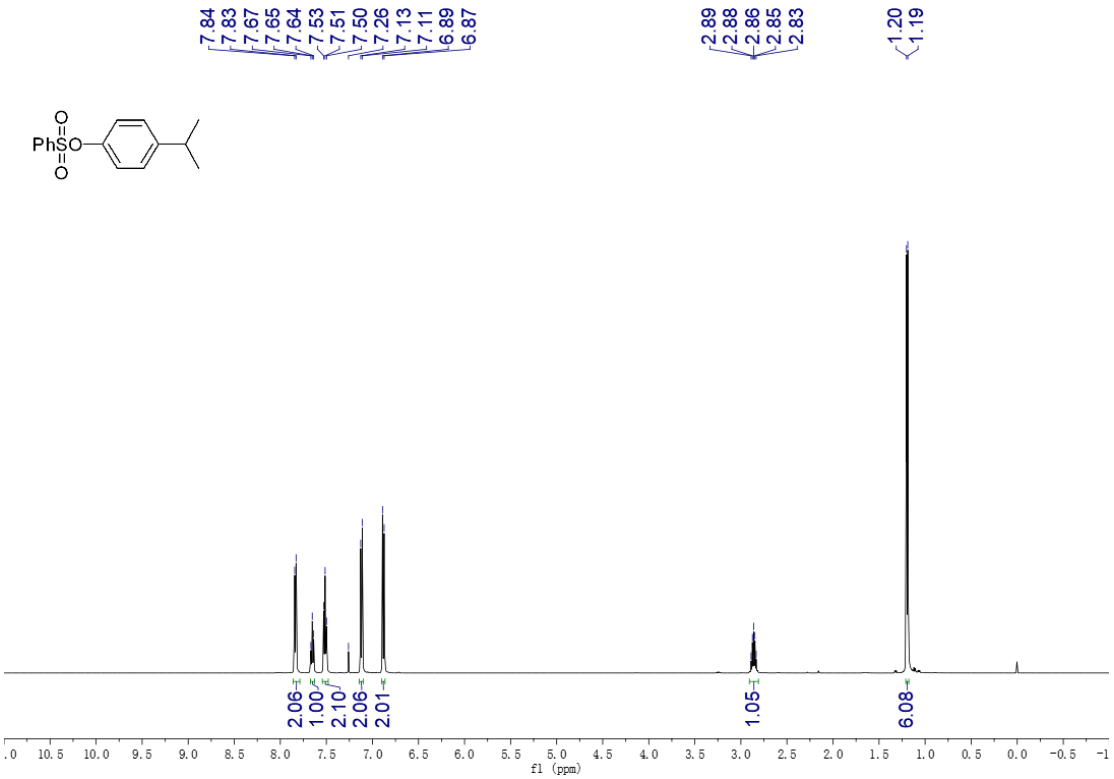
^{13}C NMR of compound **50a** (126 MHz, $CDCl_3$)



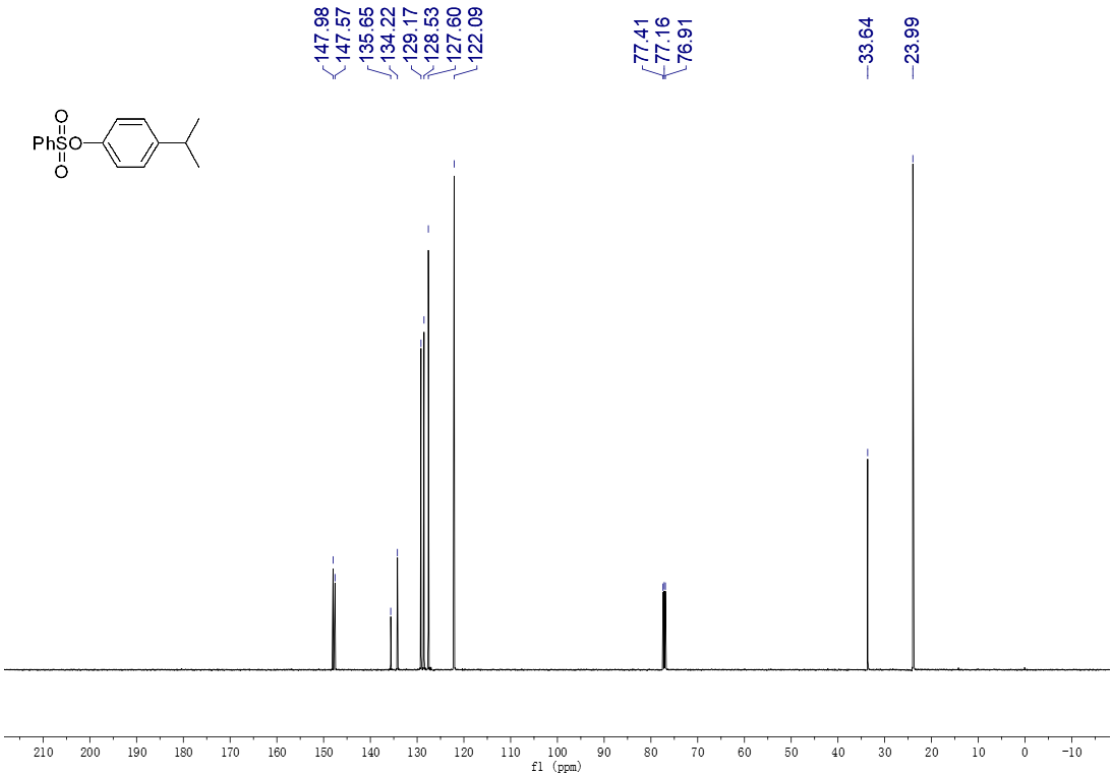
^{1}H NMR of compound **51a** (500 MHz, $CDCl_3$)



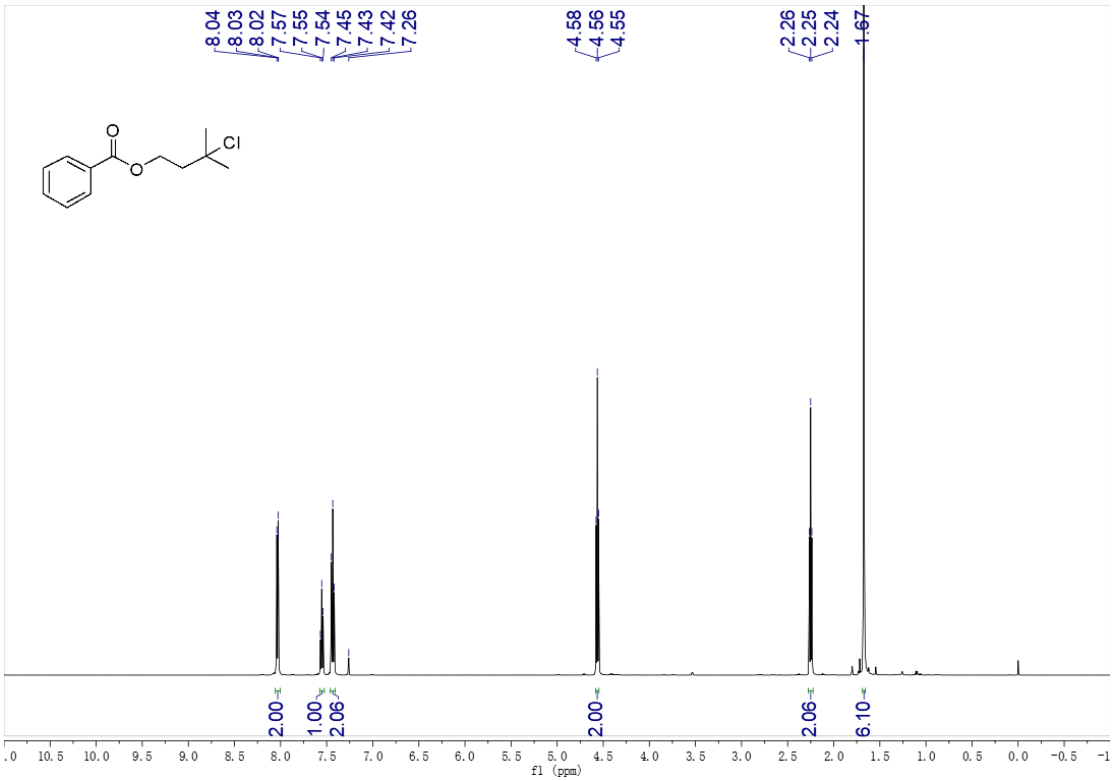
^{13}C NMR of compound **51a** (126 MHz, $CDCl_3$)



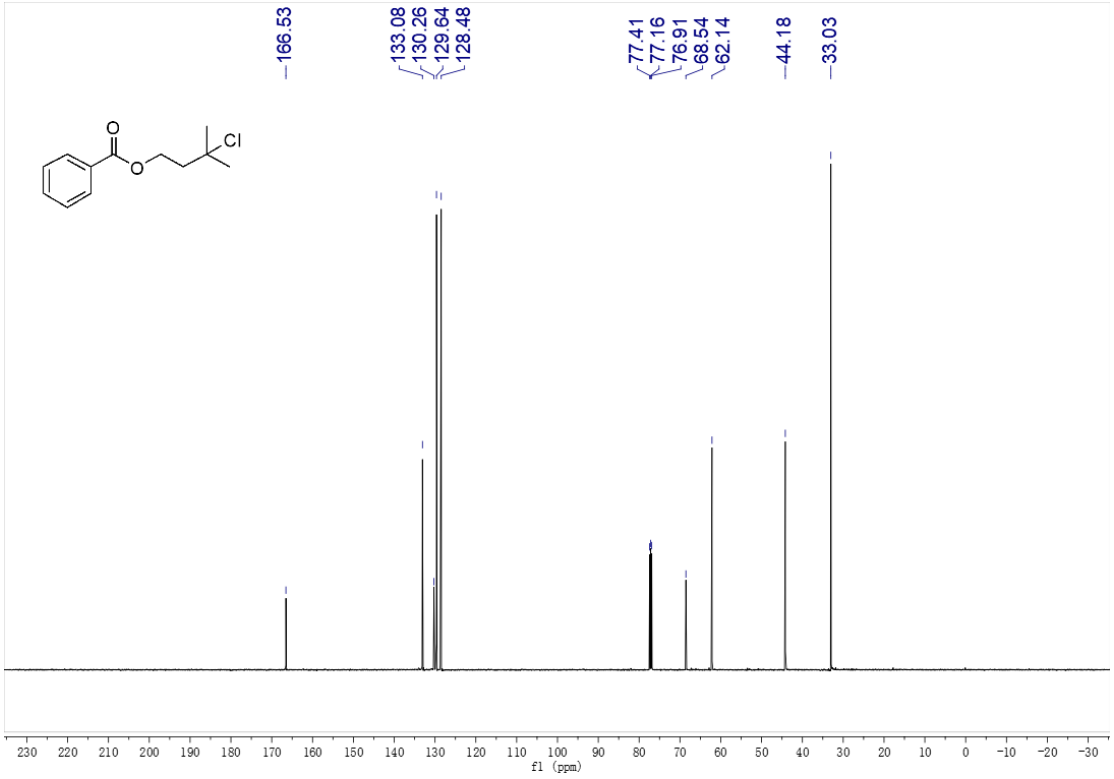
^{1}H NMR of compound **55a** (500 MHz, $CDCl_3$)



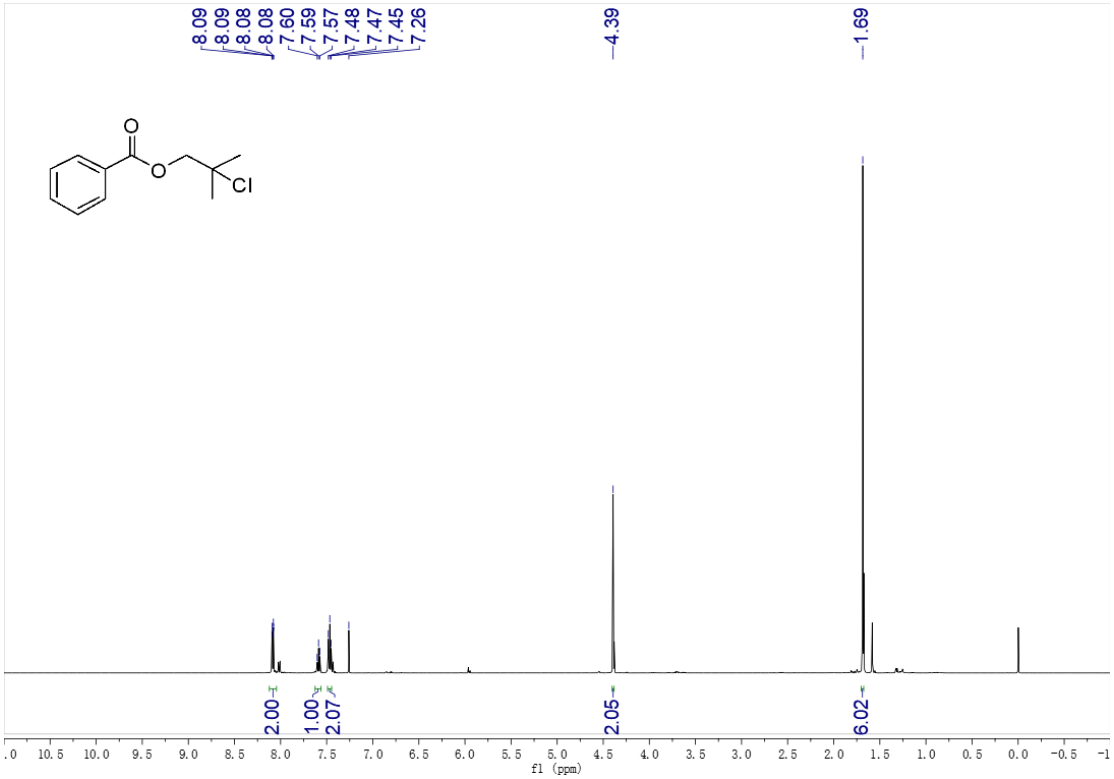
^{13}C NMR of compound **55a** (126 MHz, $CDCl_3$)



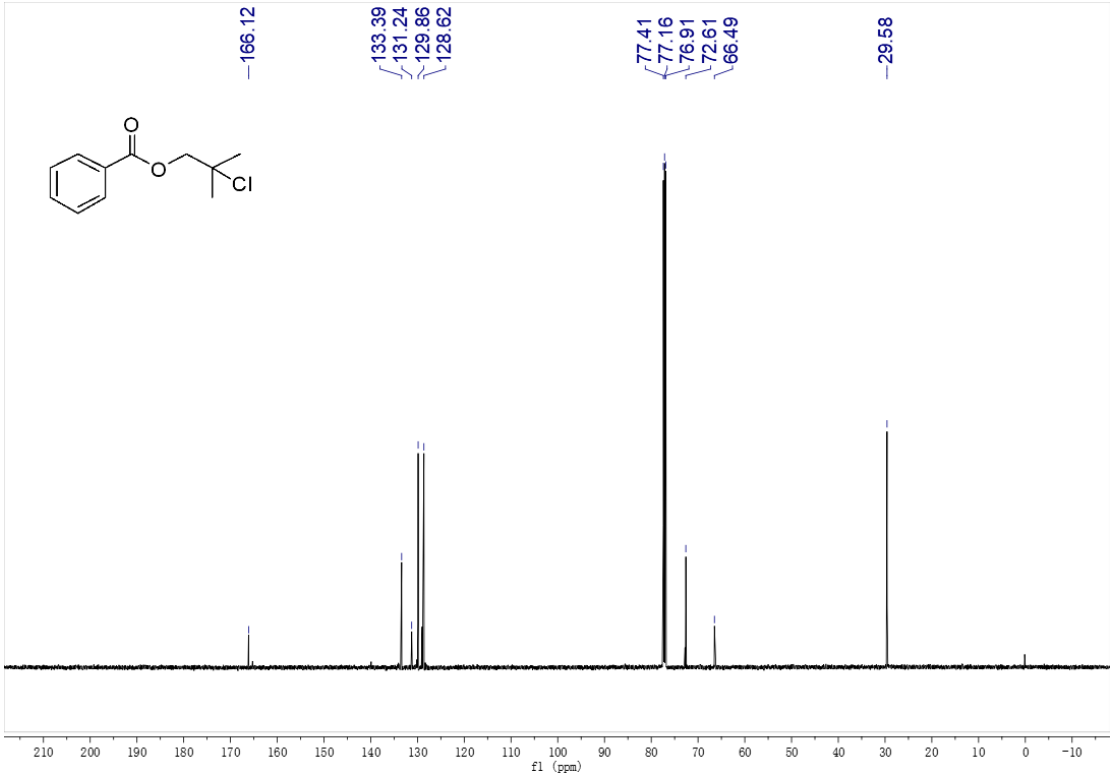
^{1}H NMR of compound **1b** (500 MHz, $CDCl_3$)



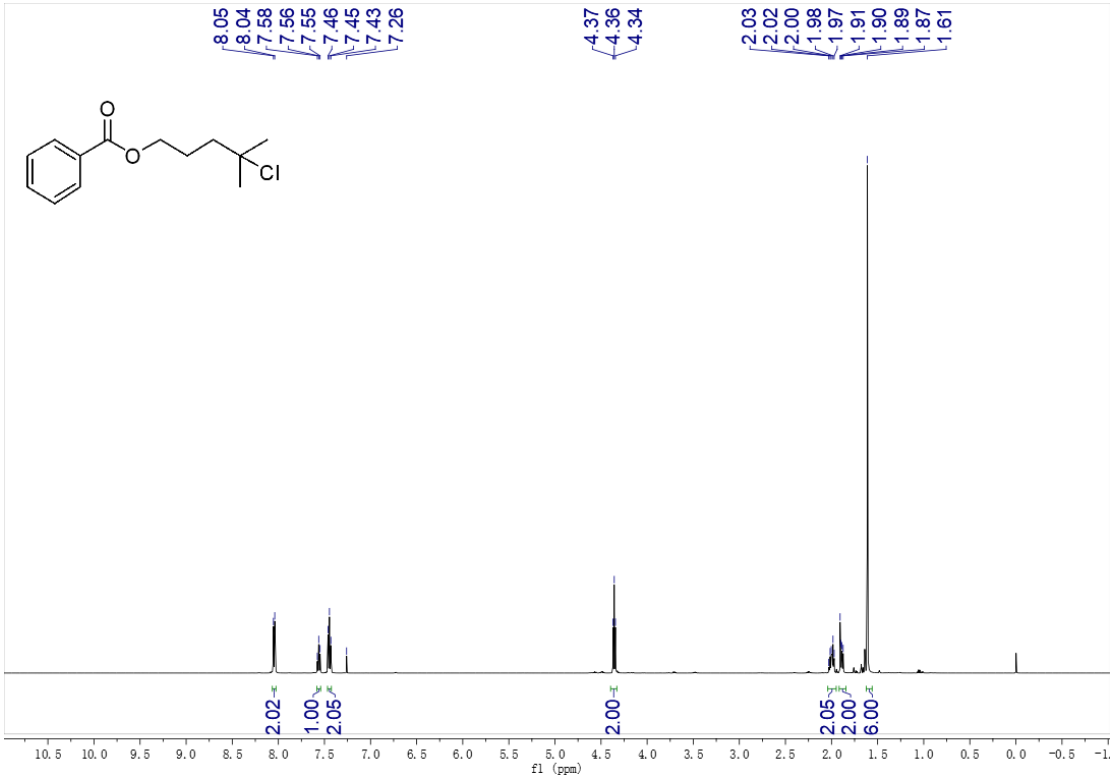
^{13}C NMR of compound **1b** (126 MHz, $CDCl_3$)



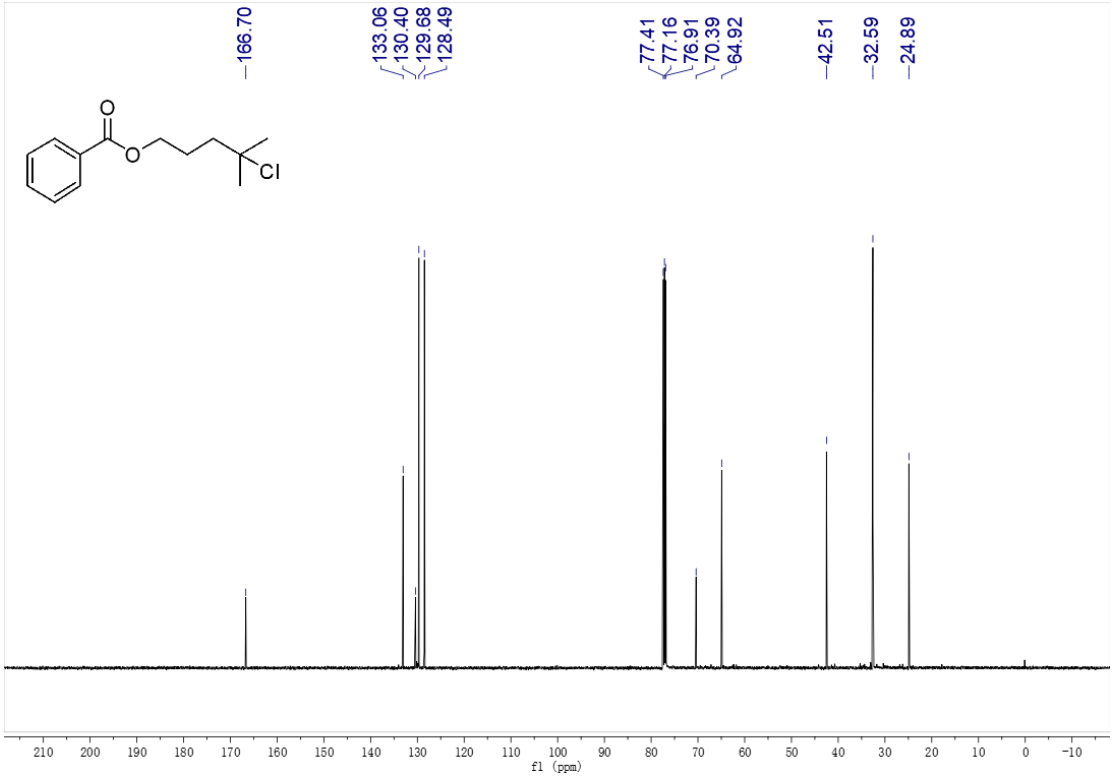
^{1}H NMR of compound **2b** (500 MHz, $CDCl_3$)



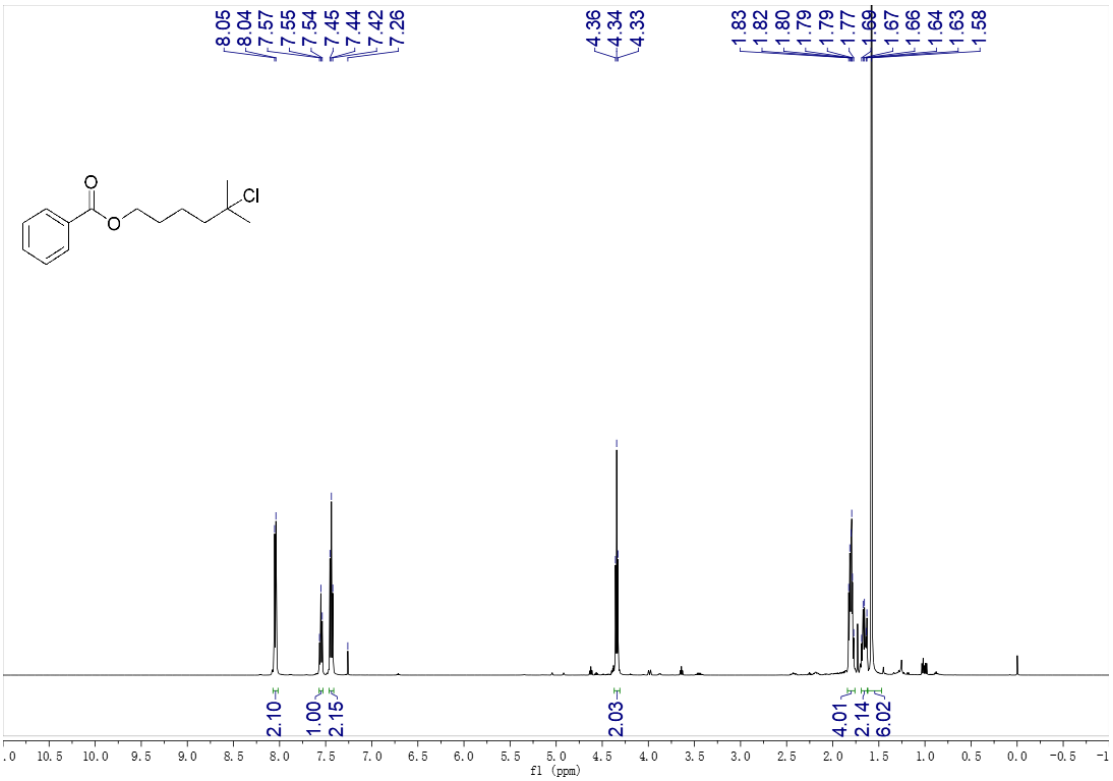
^{13}C NMR of compound **2b** (126 MHz, $CDCl_3$)



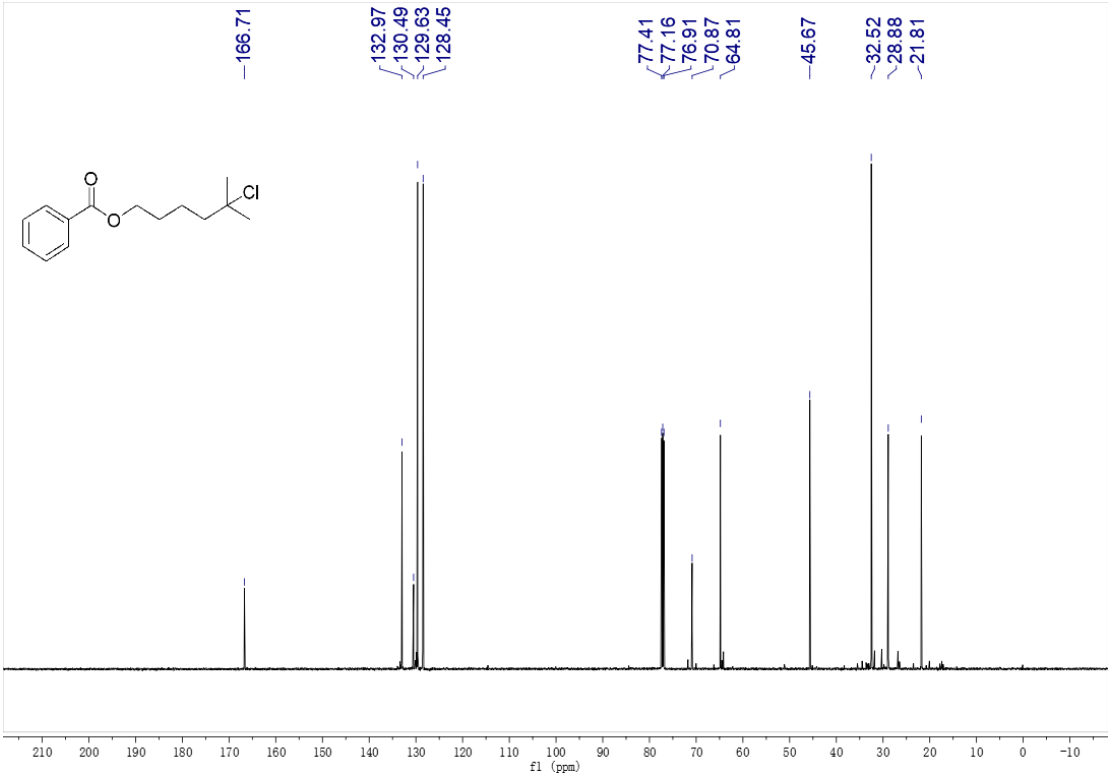
^{1}H NMR of compound **3b** (500 MHz, $CDCl_3$)



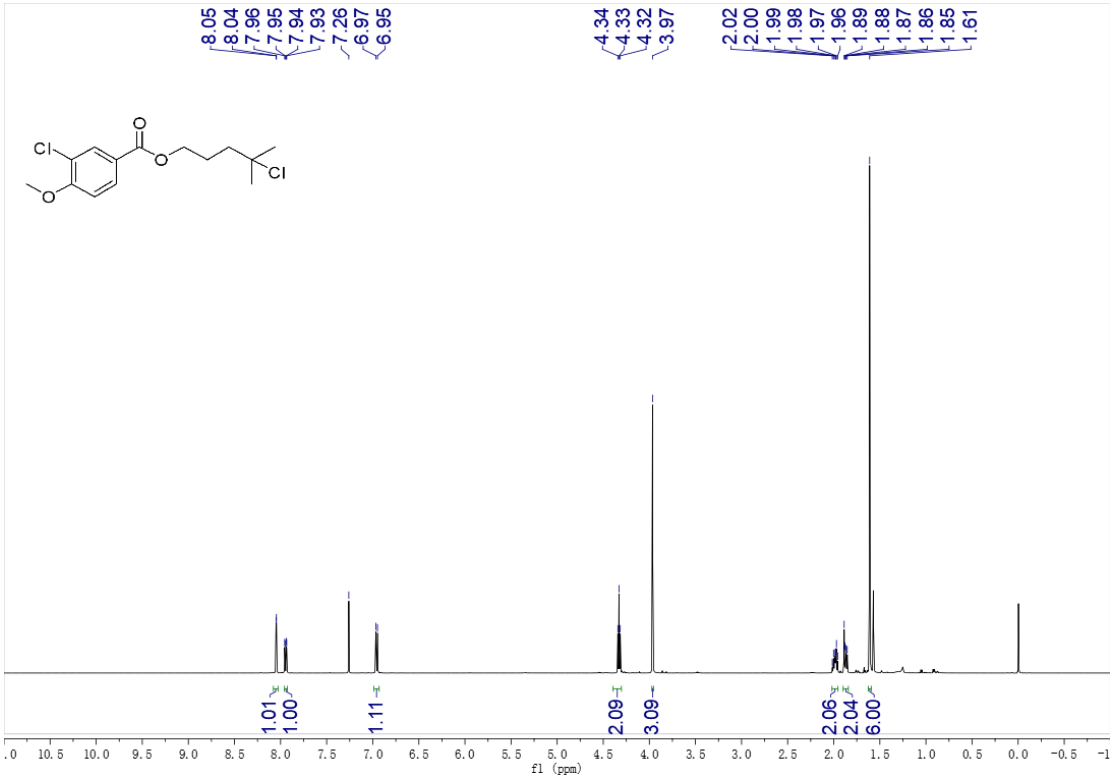
^{13}C NMR of compound **3b** (126 MHz, $CDCl_3$)



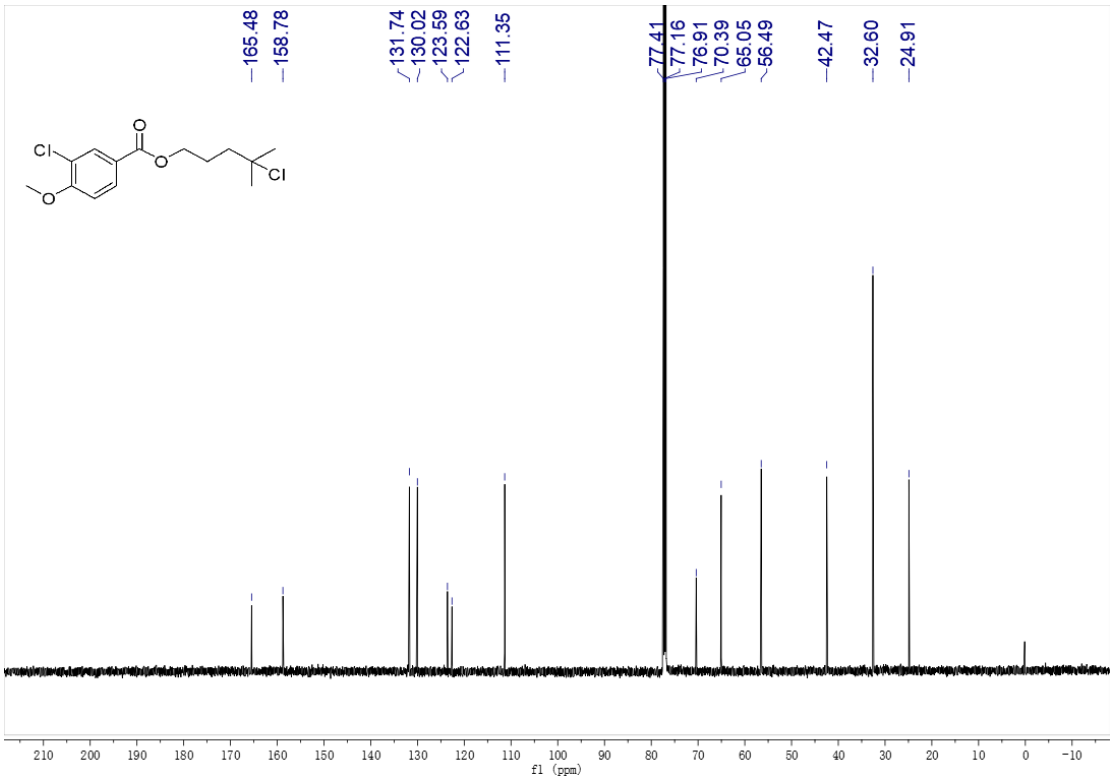
^{1}H NMR of compound **4b** (500 MHz, $CDCl_3$)



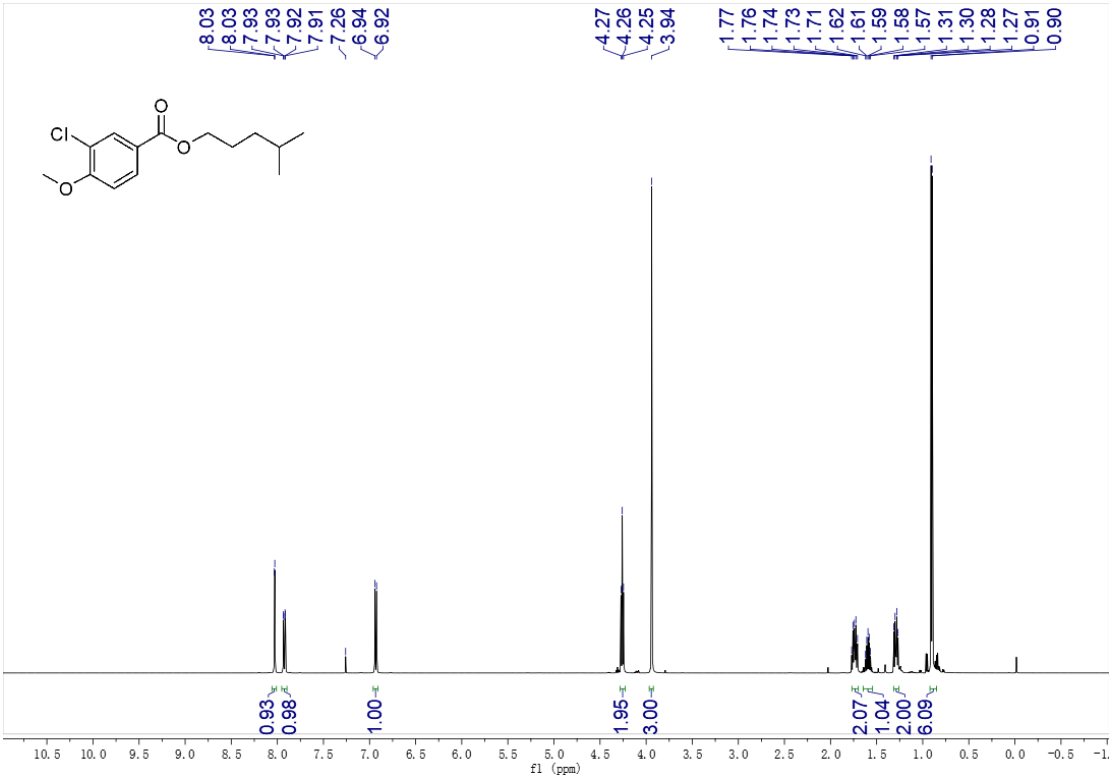
^{13}C NMR of compound **4b** (126 MHz, $CDCl_3$)



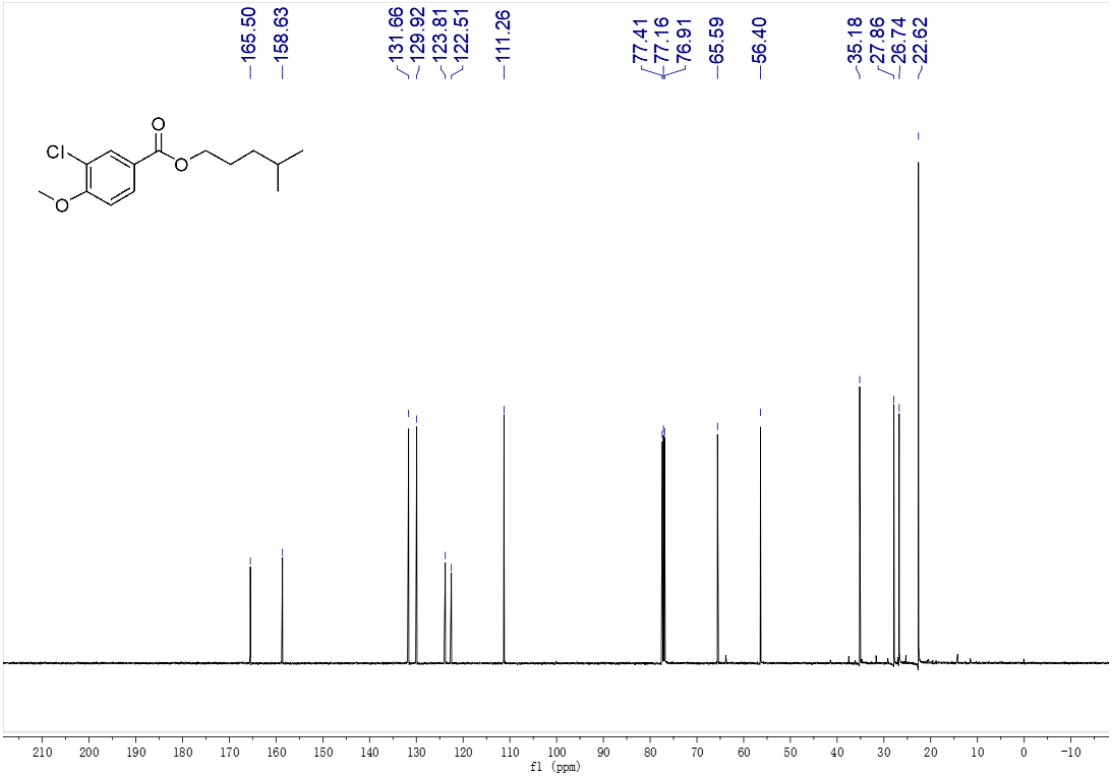
^{1}H NMR of compound **5b** (500 MHz, $CDCl_3$)



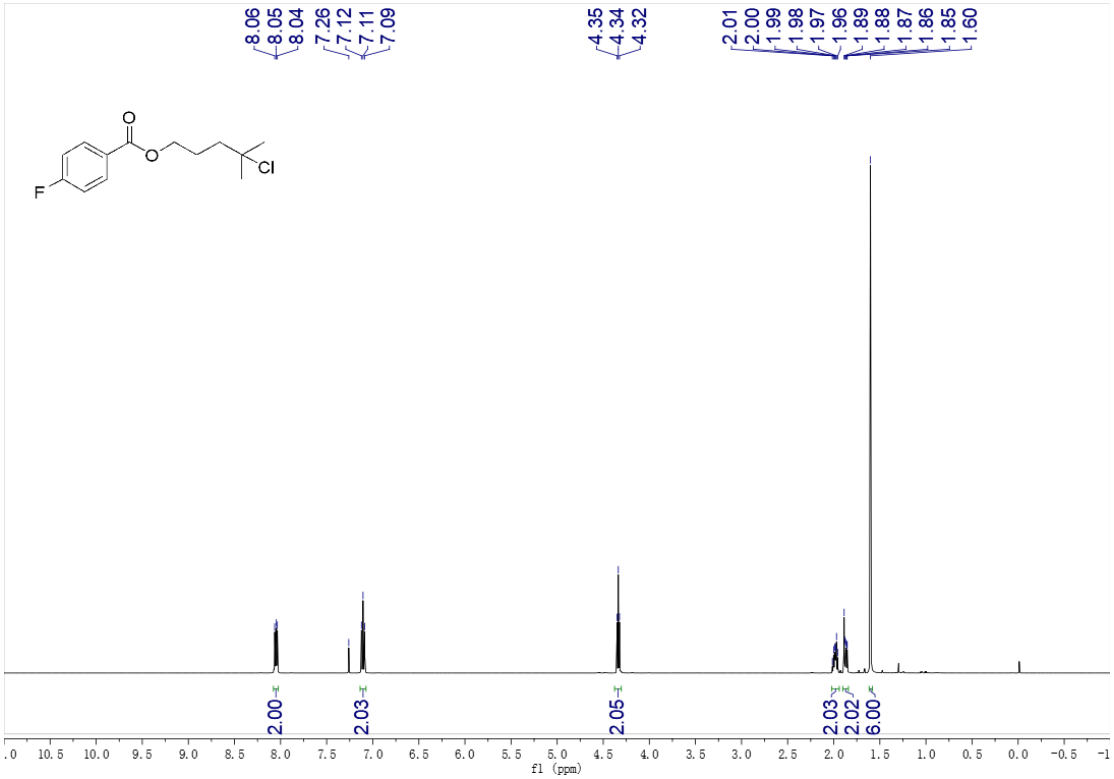
^{13}C NMR of compound **5b** (126 MHz, $CDCl_3$)



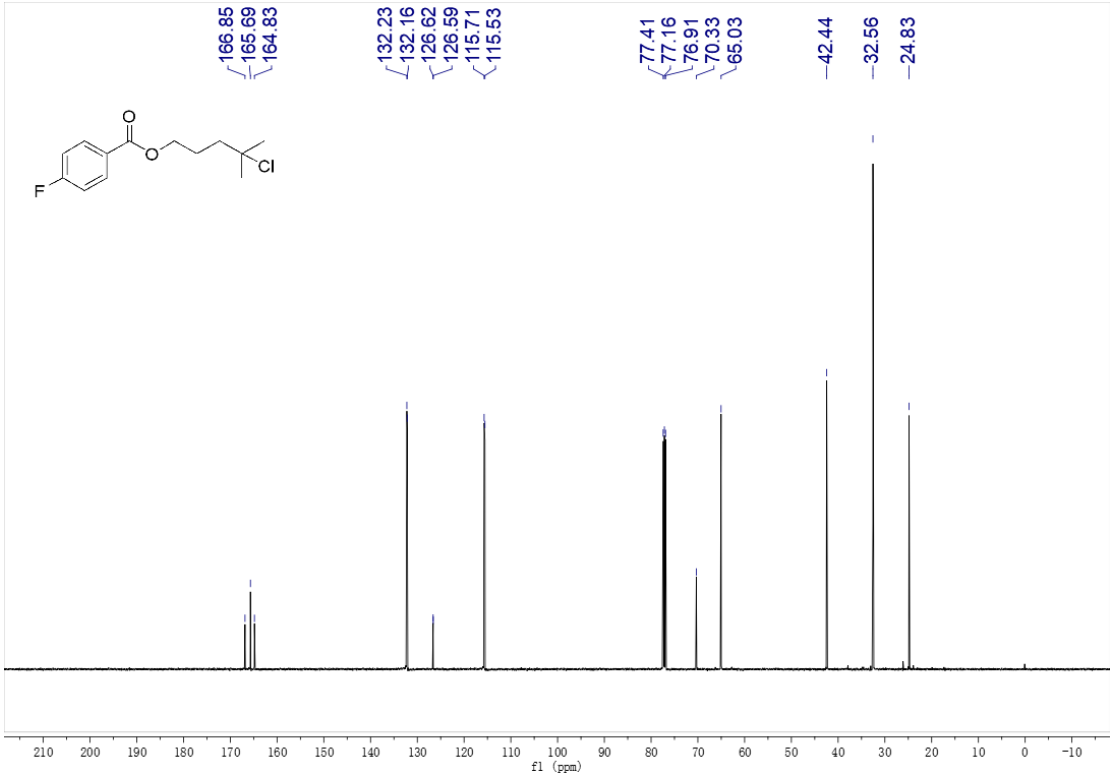
^{1}H NMR of compound **5b'** (500 MHz, $CDCl_3$)



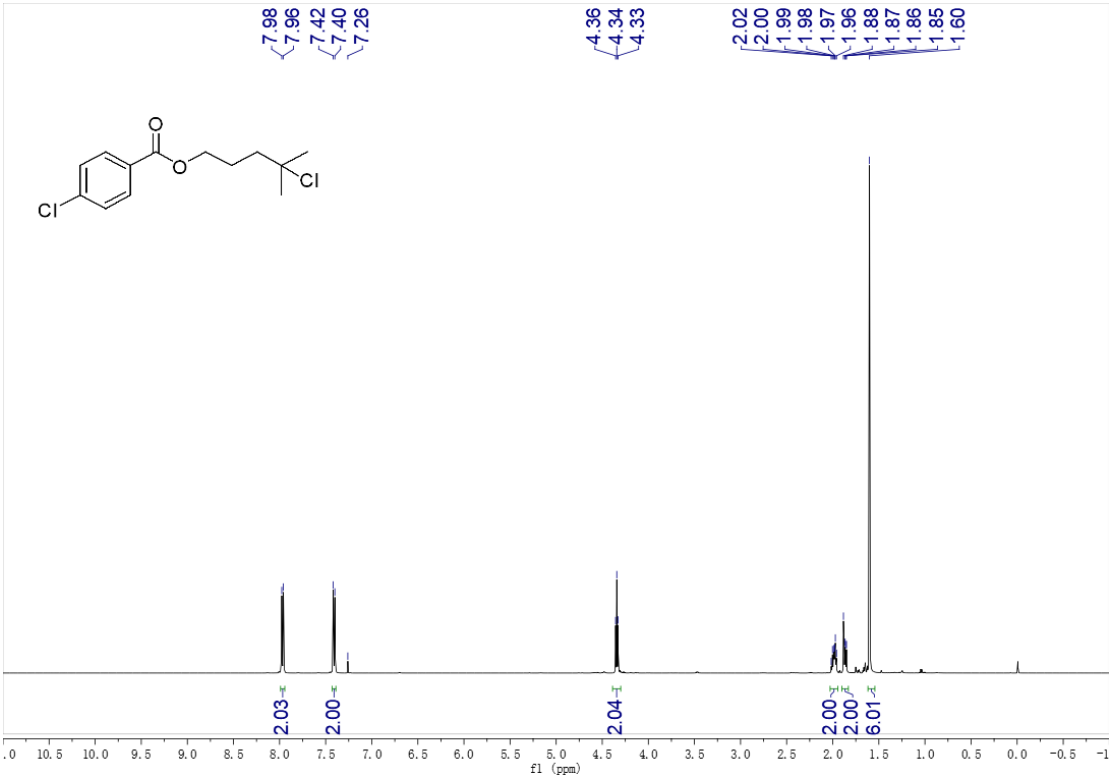
^{13}C NMR of compound **5b'** (126 MHz, $CDCl_3$)



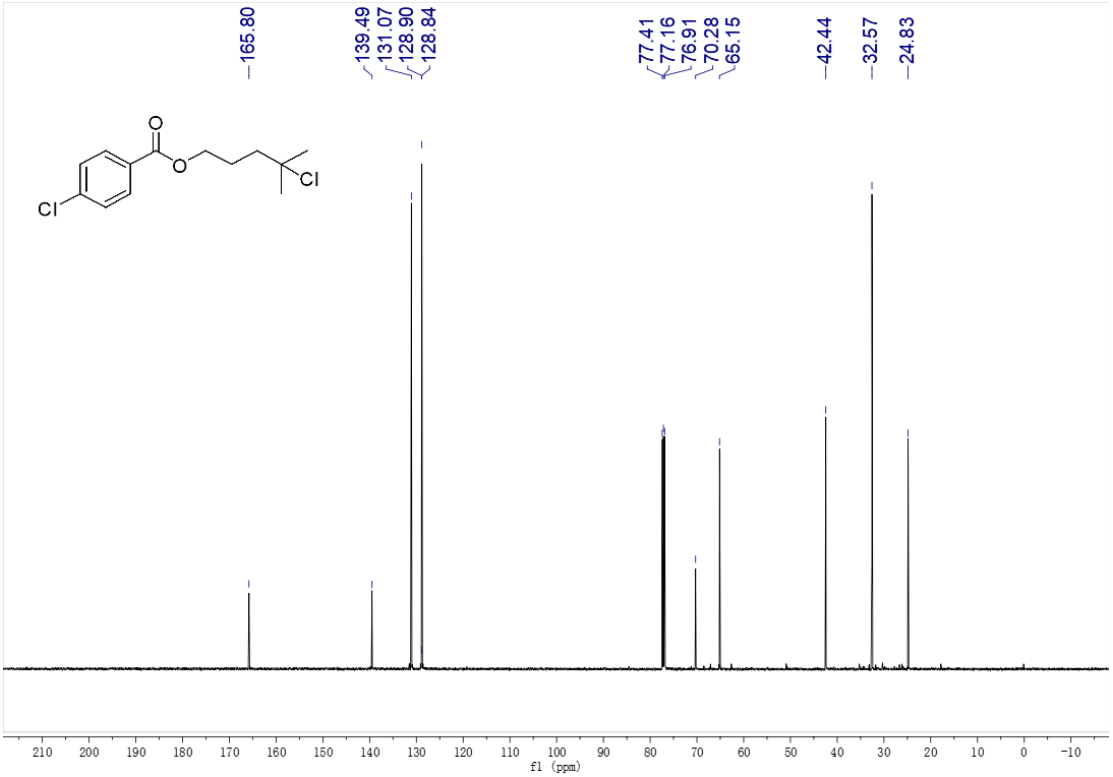
^{1}H NMR of compound **6b** (500 MHz, $CDCl_3$)



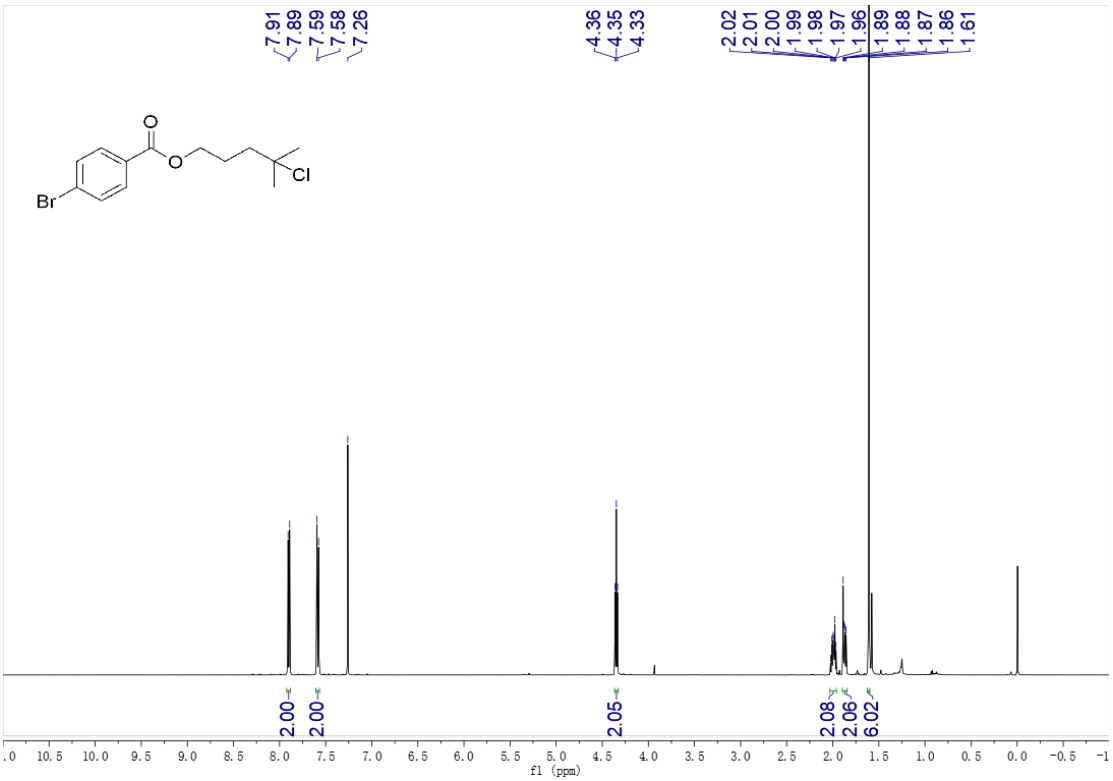
^{13}C NMR of compound **6b** (126 MHz, $CDCl_3$)



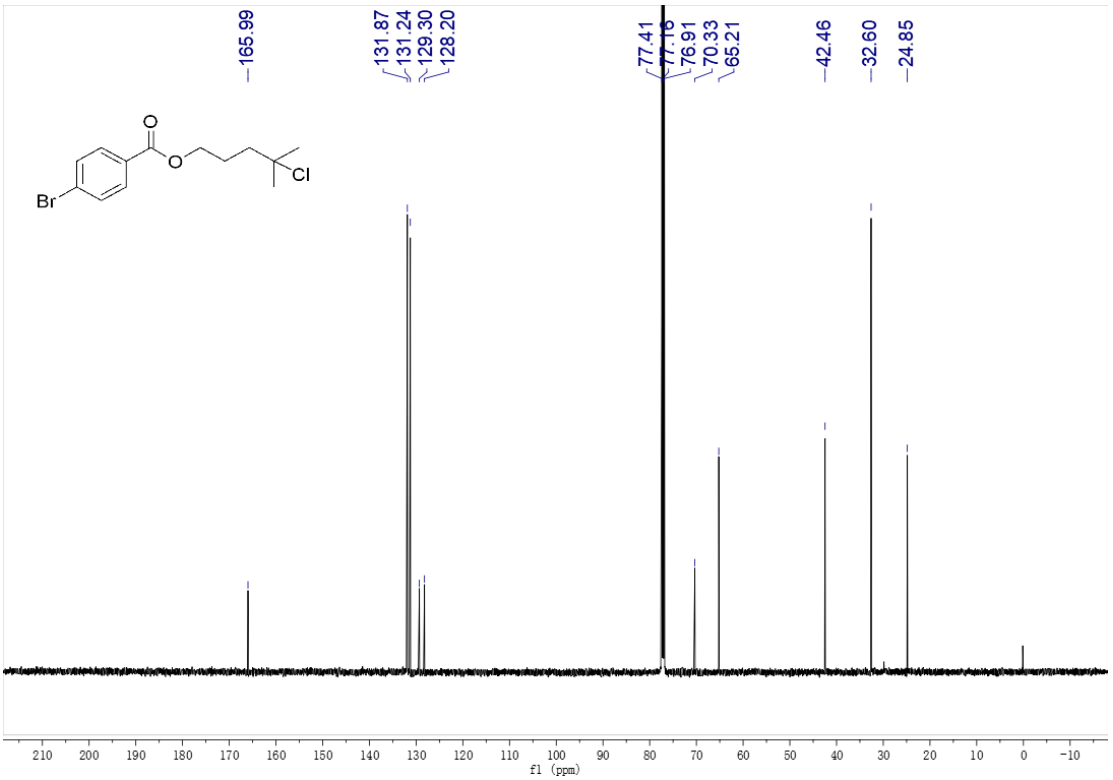
^{1}H NMR of compound **7b** (500 MHz, $CDCl_3$)



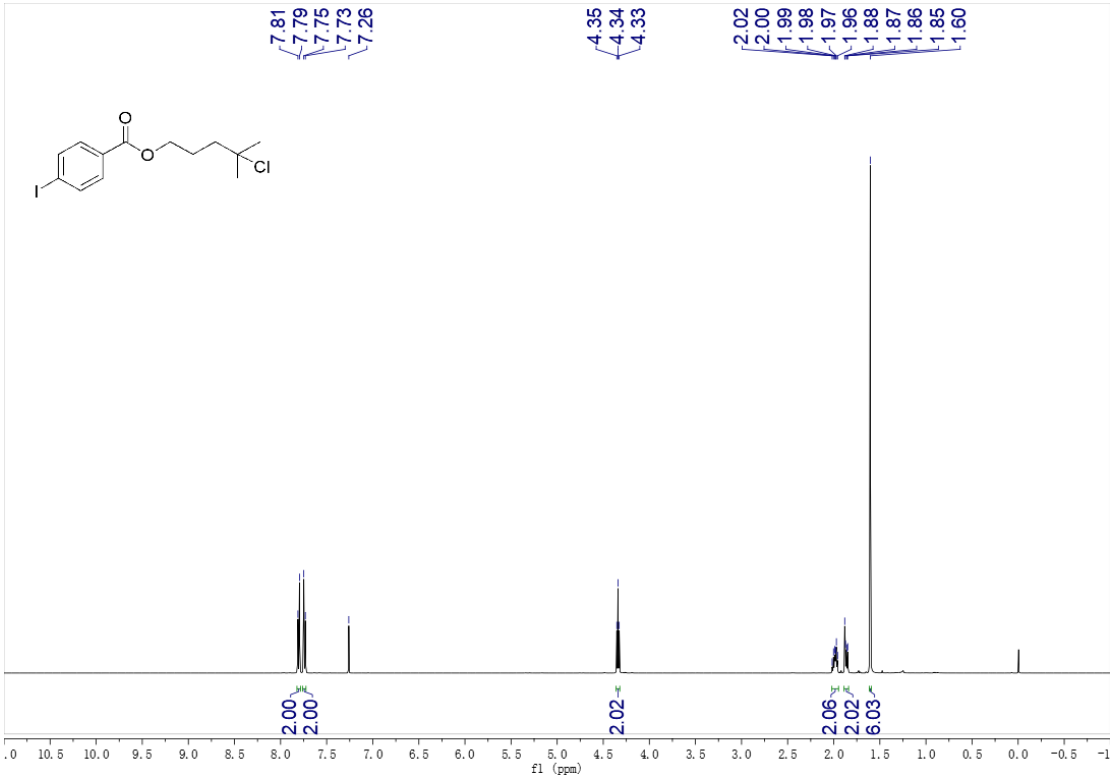
^{13}C NMR of compound **7b** (126 MHz, $CDCl_3$)



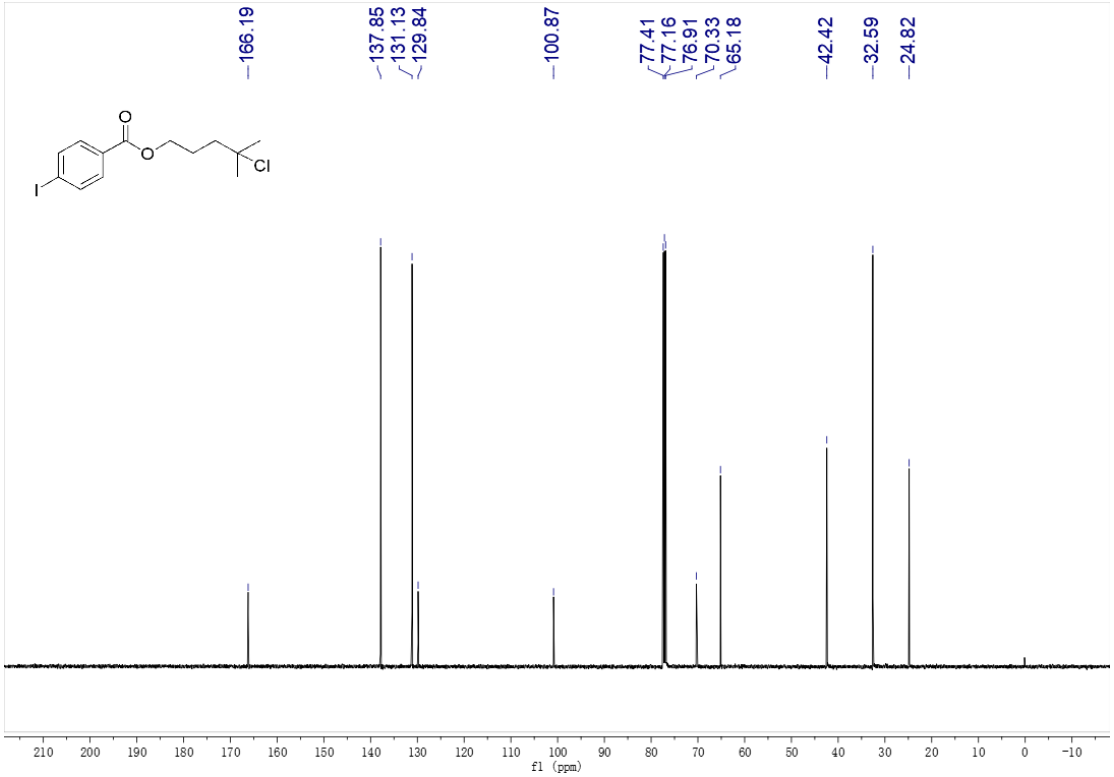
^{1}H NMR of compound **8b** (500 MHz, $CDCl_3$)



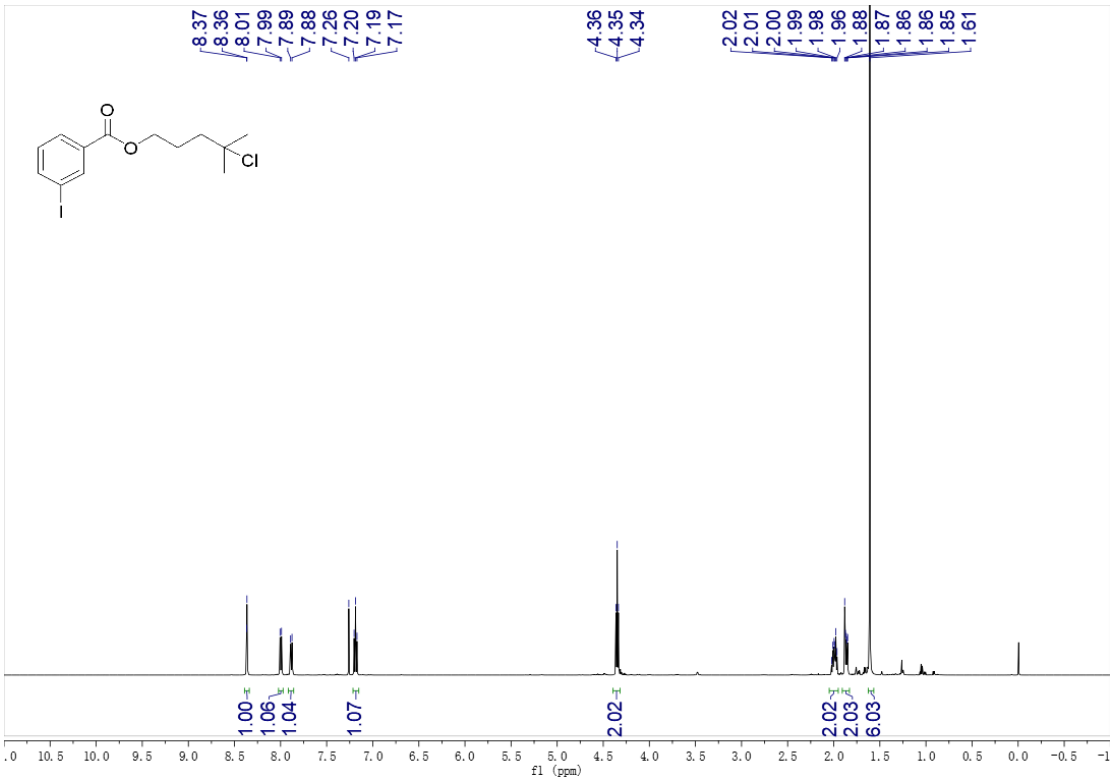
^{13}C NMR of compound **8b** (126 MHz, $CDCl_3$)



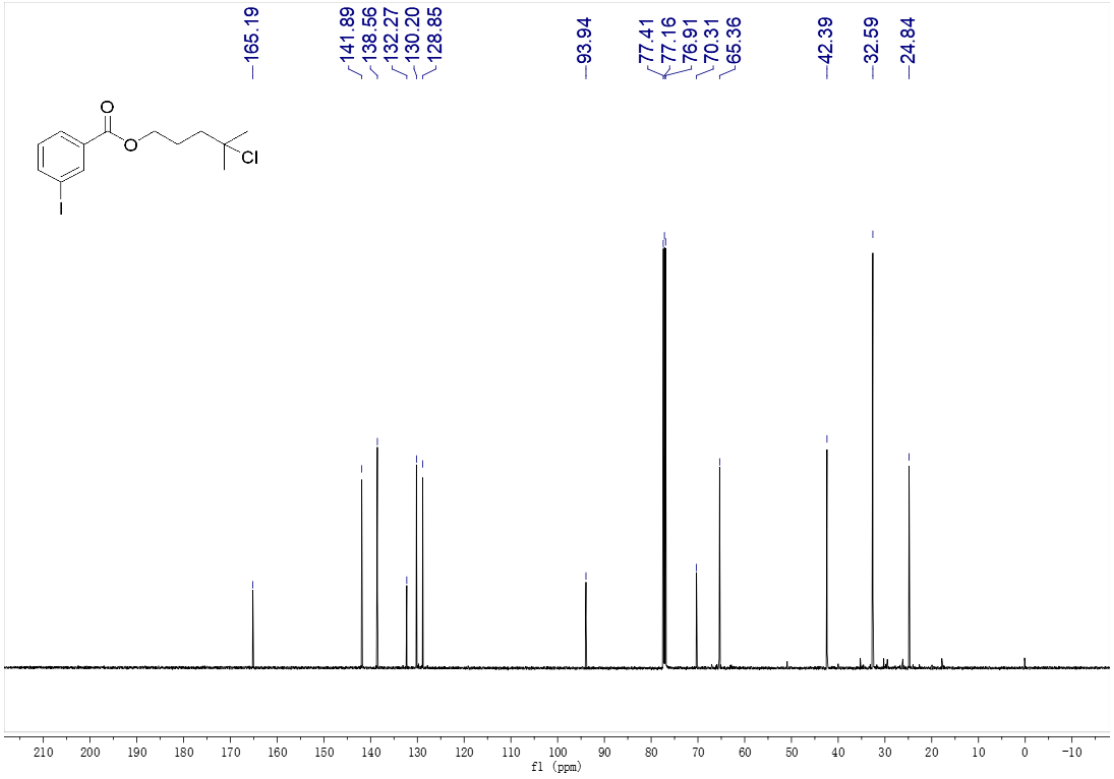
^{1}H NMR of compound **9b** (500 MHz, $CDCl_3$)



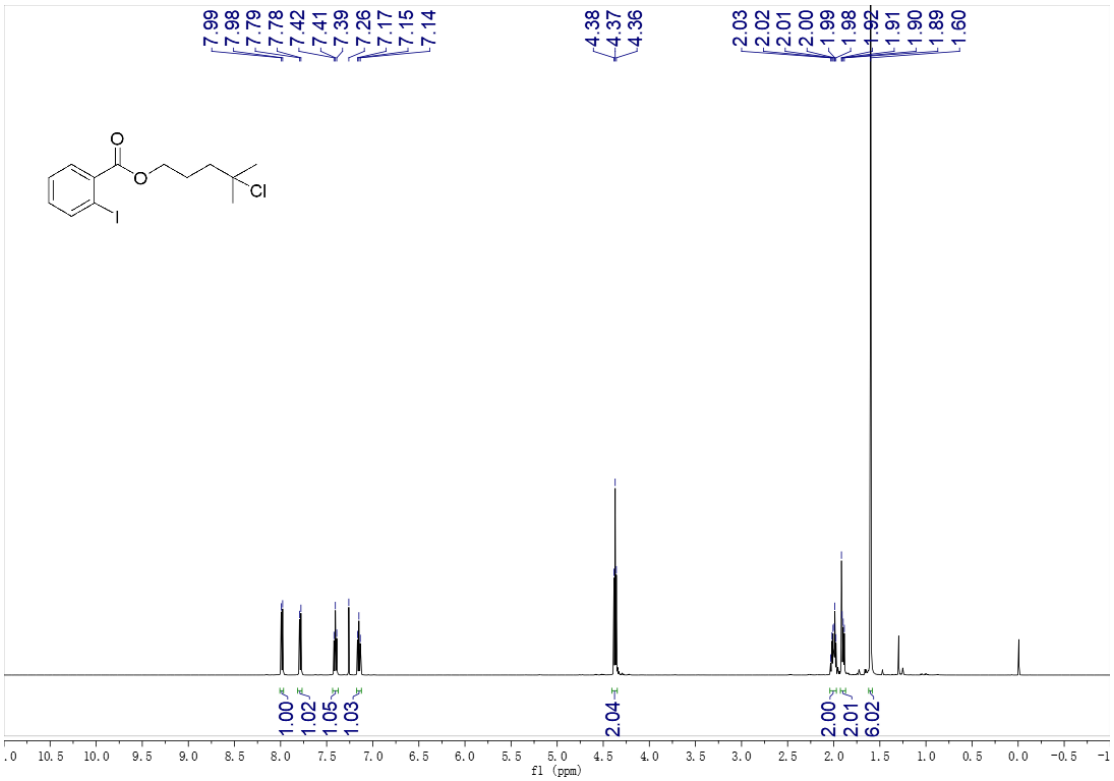
^{13}C NMR of compound **9b** (126 MHz, $CDCl_3$)



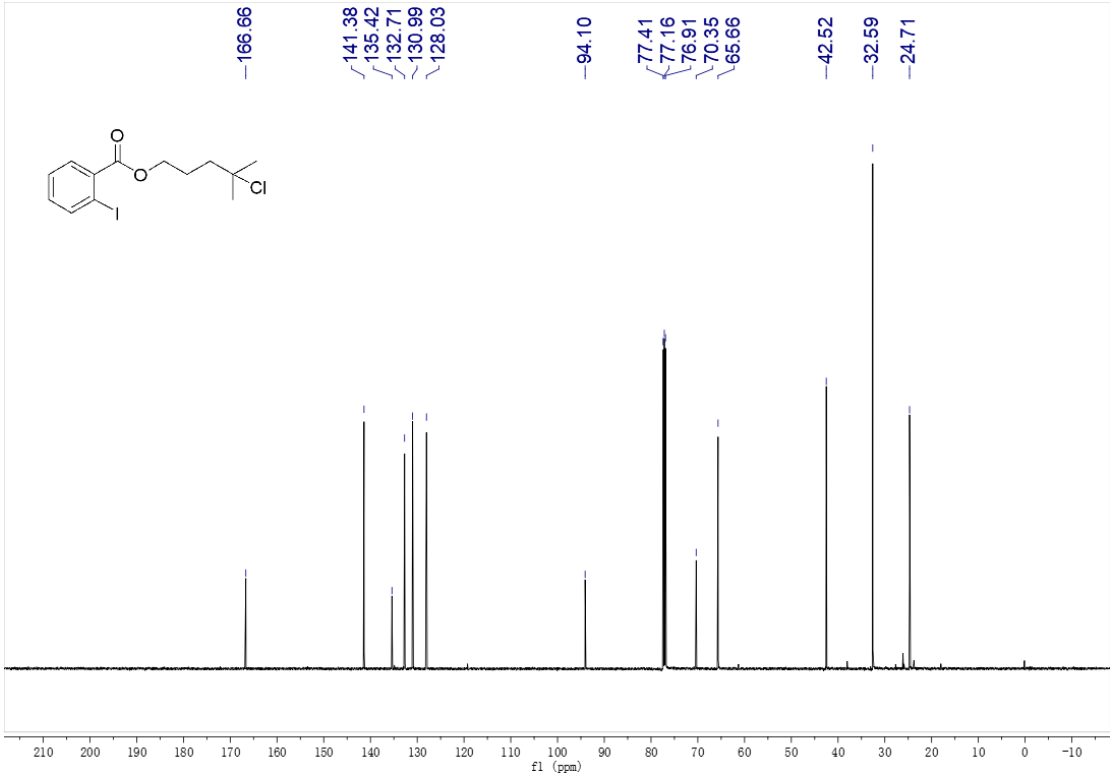
^{1}H NMR of compound **10b** (500 MHz, $CDCl_3$)



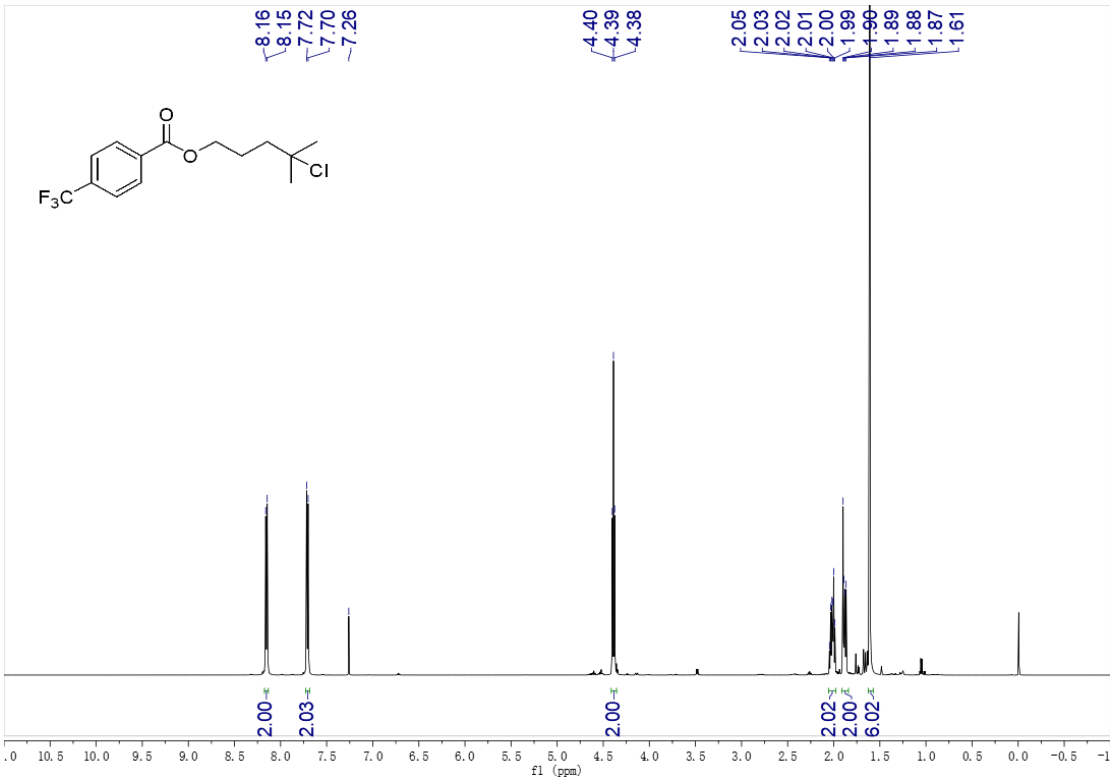
^{13}C NMR of compound **10b** (126 MHz, $CDCl_3$)



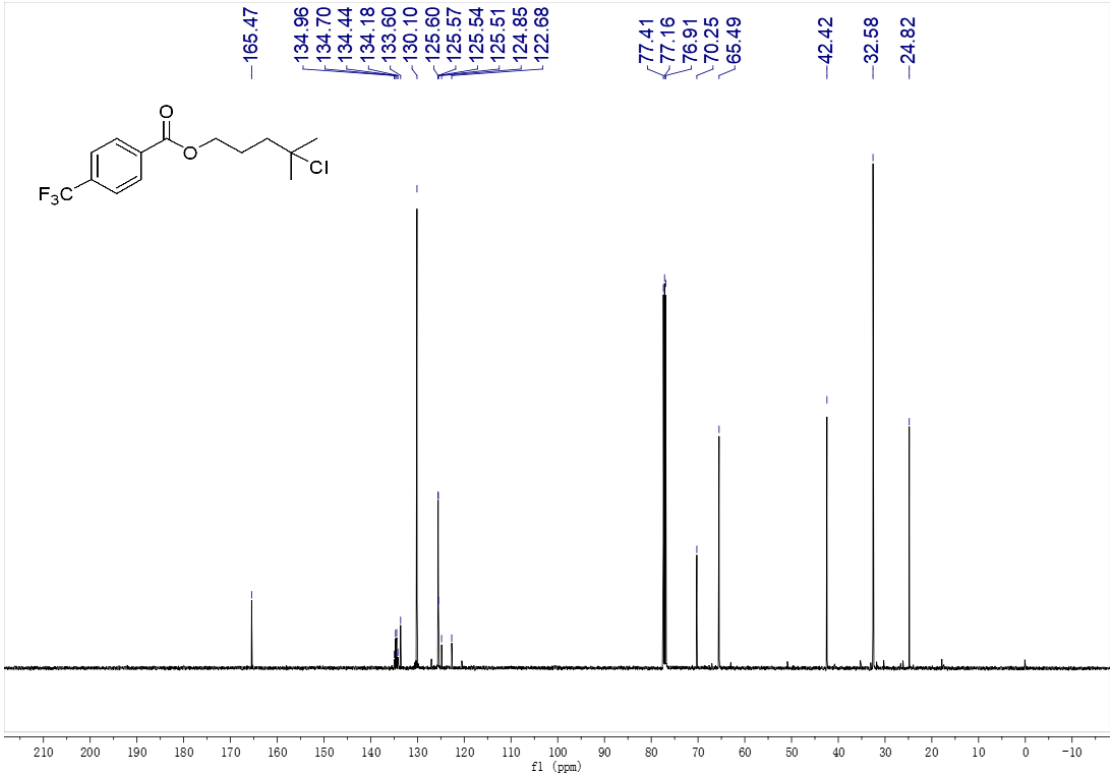
^{1}H NMR of compound **11b** (500 MHz, $CDCl_3$)



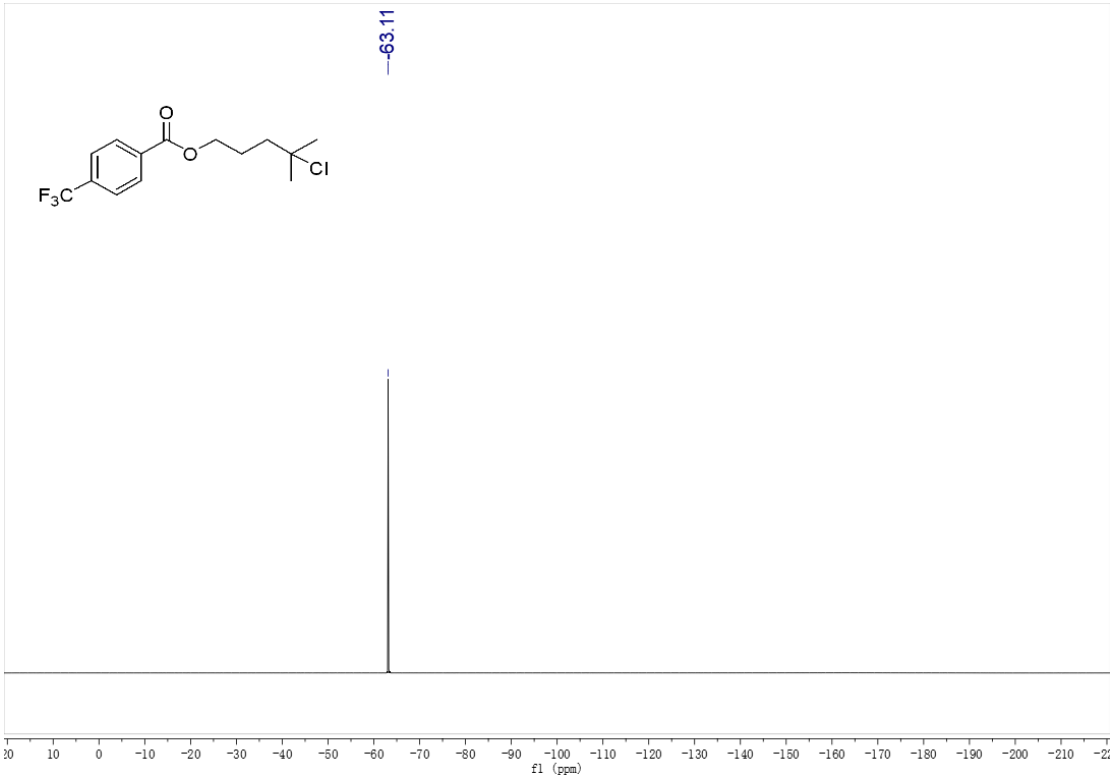
^{13}C NMR of compound **11b** (126 MHz, $CDCl_3$)



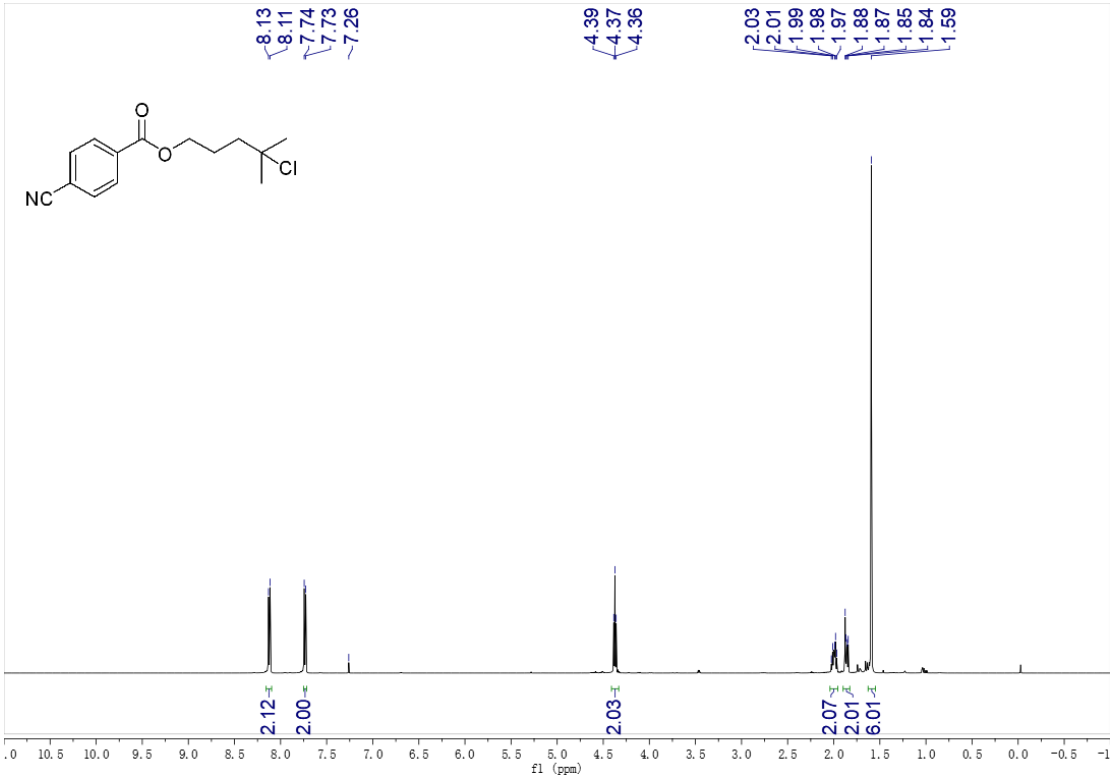
^{1}H NMR of compound **12b** (500 MHz, $CDCl_3$)



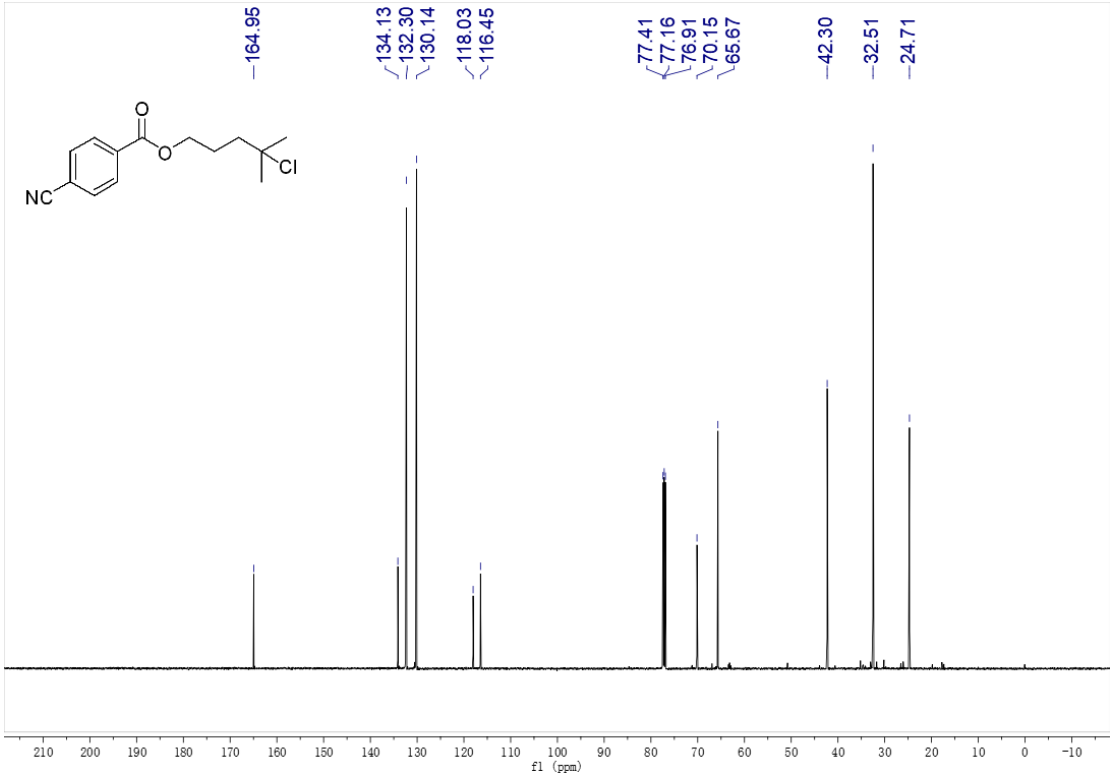
^{13}C NMR of compound **12b** (126 MHz, $CDCl_3$)



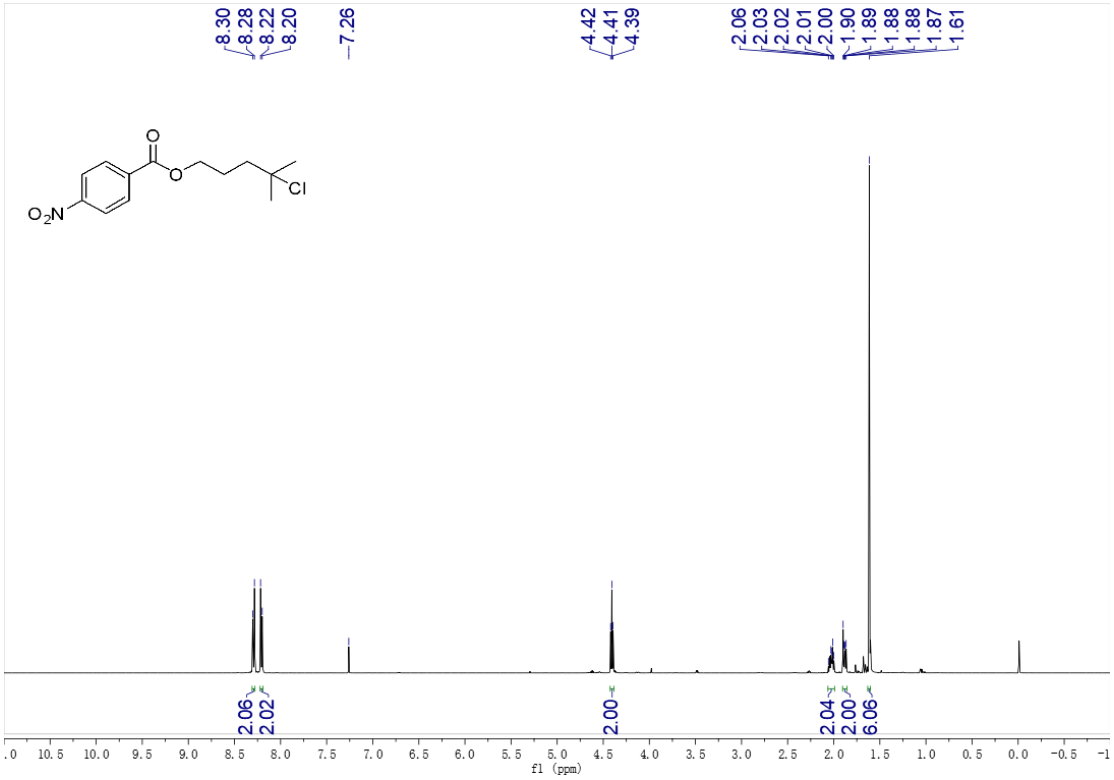
^{19}F NMR of compound **12b** (471 MHz, $CDCl_3$)



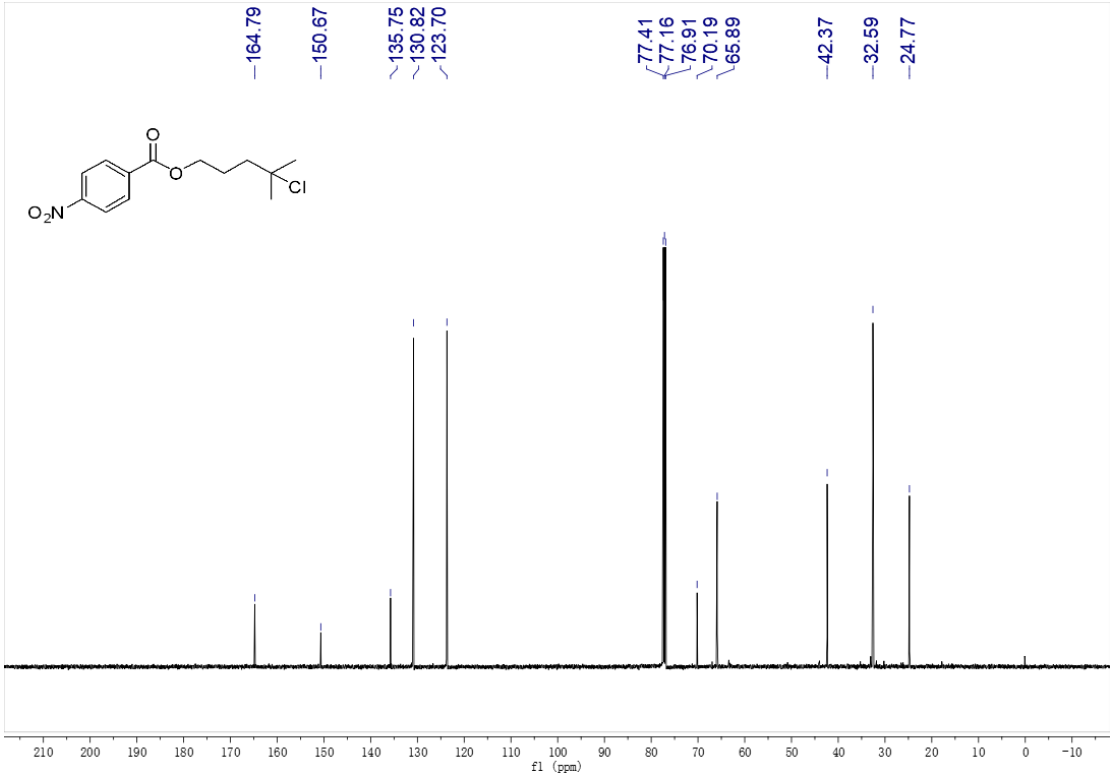
^{1}H NMR of compound **13b** (500 MHz, $CDCl_3$)



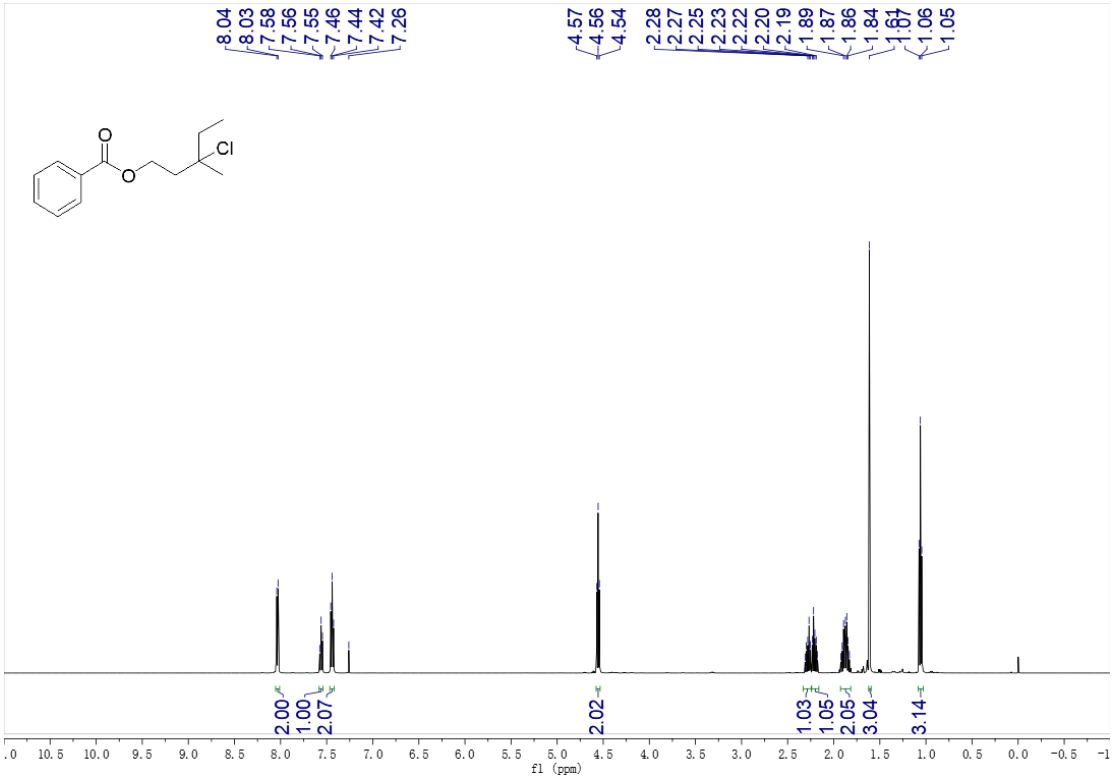
^{13}C NMR of compound **13b** (126 MHz, $CDCl_3$)



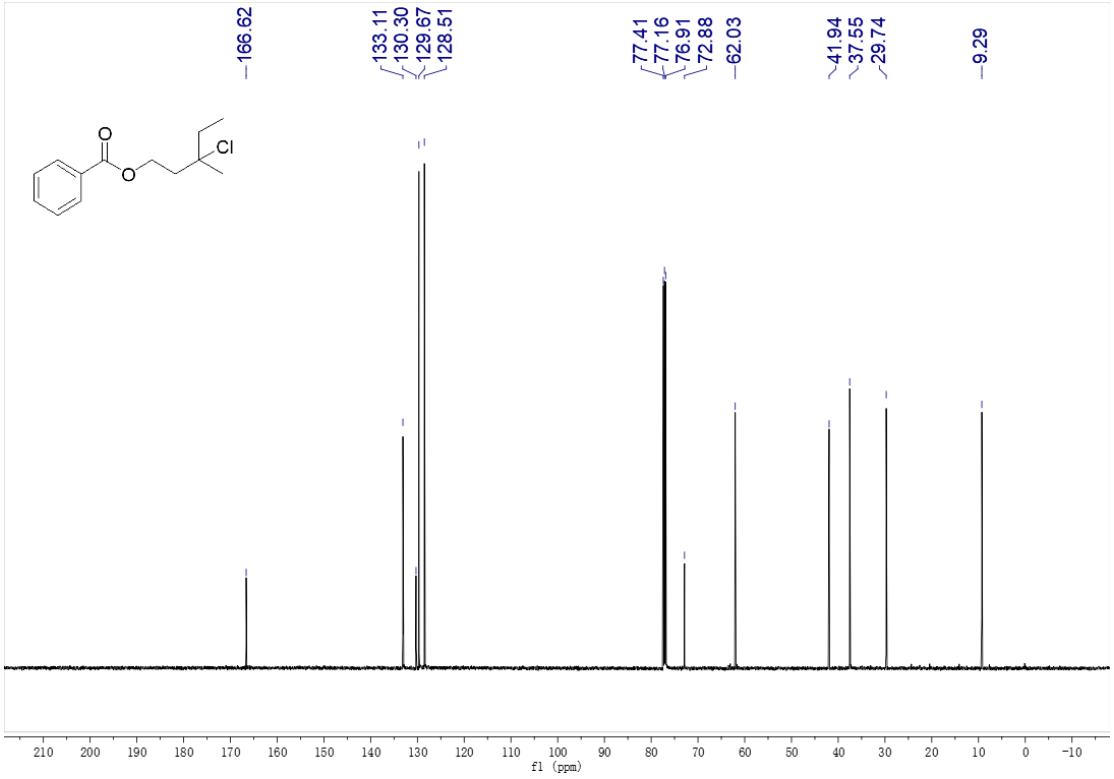
^{1}H NMR of compound **14b** (500 MHz, $CDCl_3$)



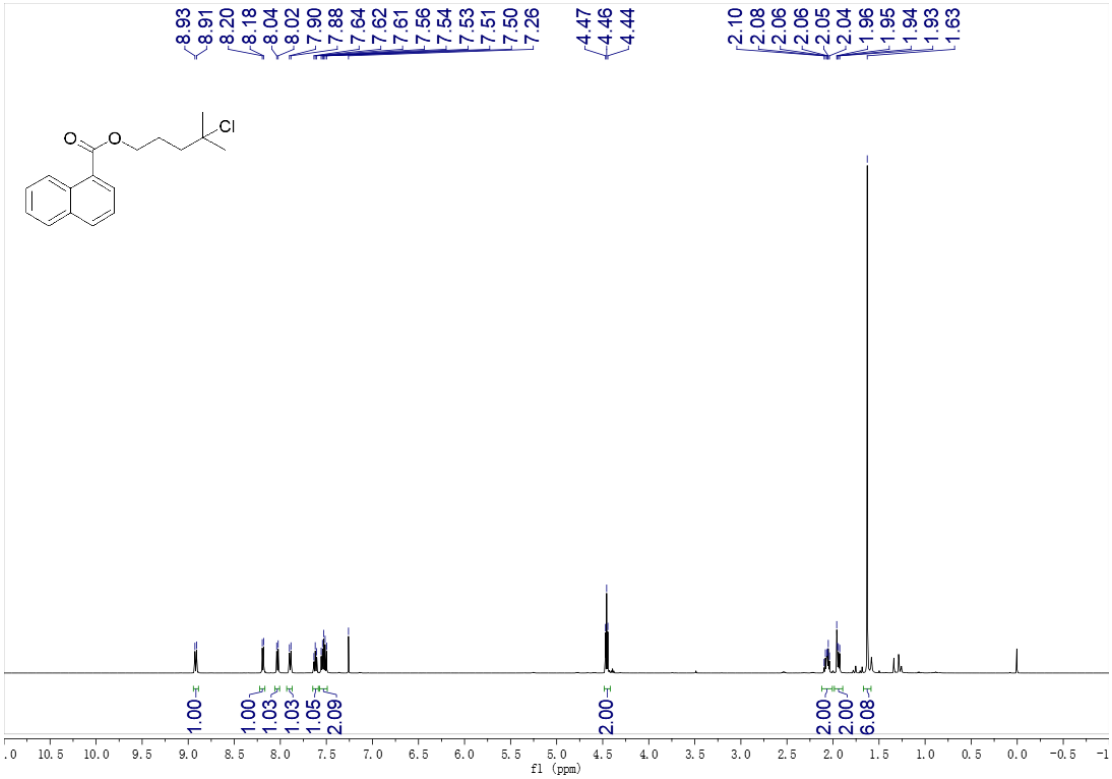
^{13}C NMR of compound **14b** (126 MHz, $CDCl_3$)



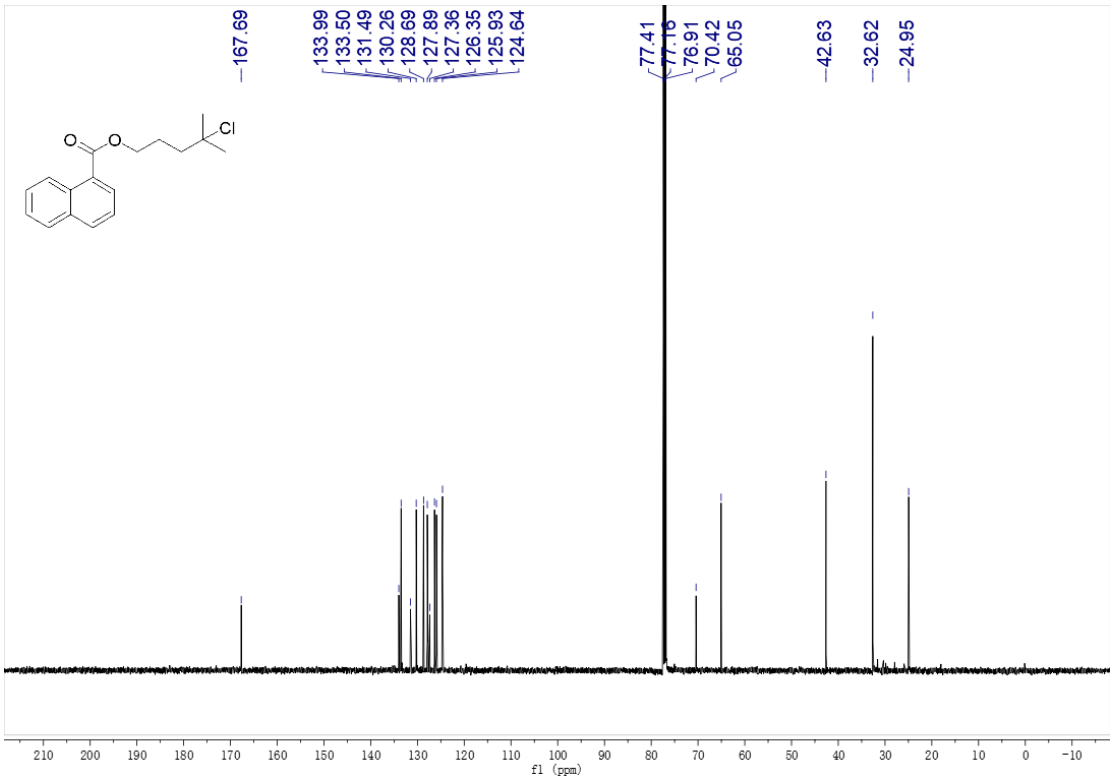
^{1}H NMR of compound **15b** (500 MHz, $CDCl_3$)



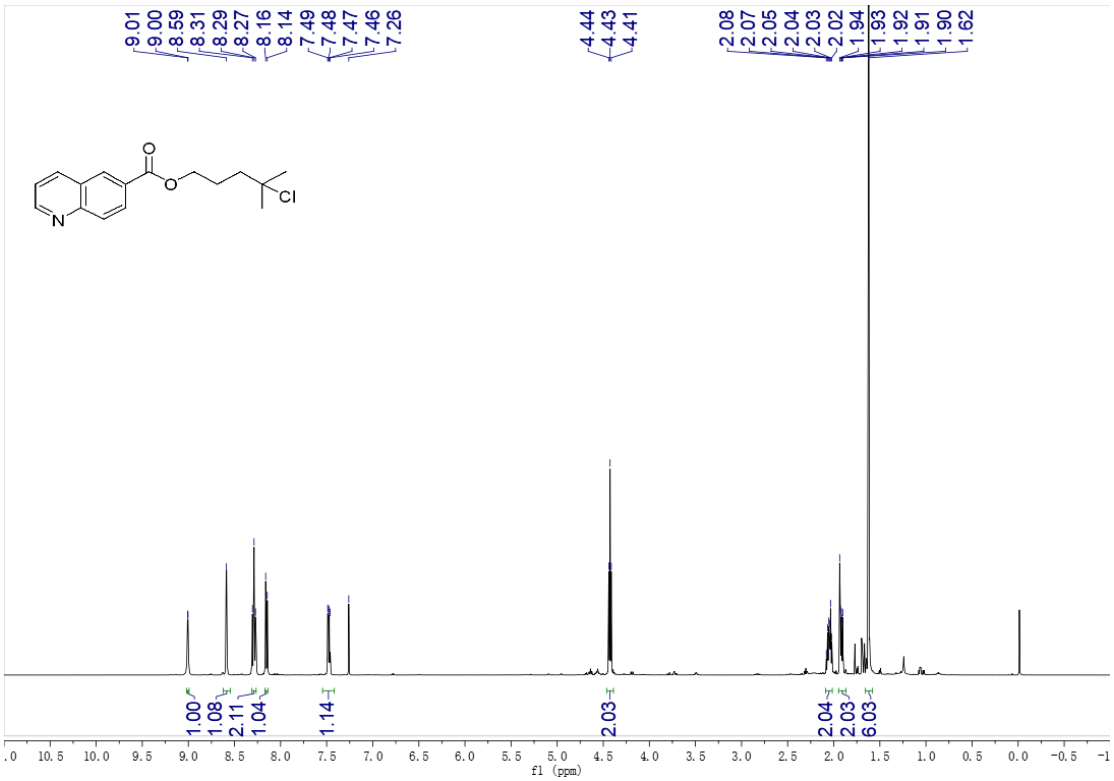
^{13}C NMR of compound **15b** (126 MHz, $CDCl_3$)



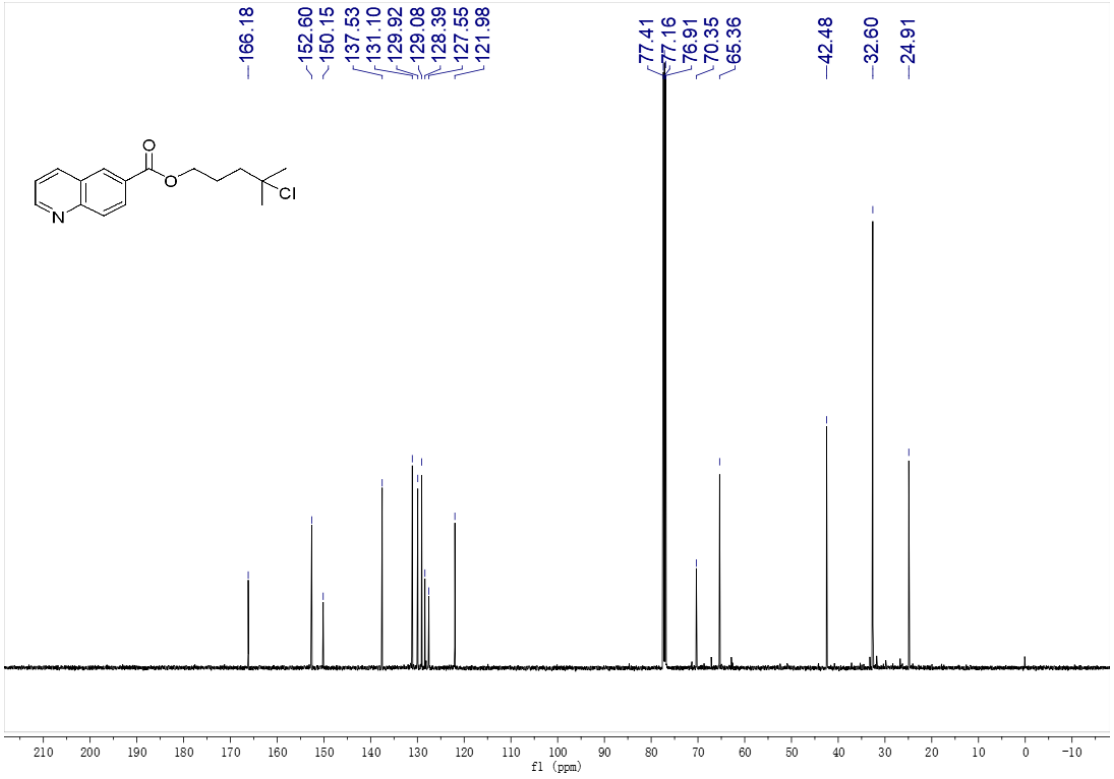
^{1}H NMR of compound **16b** (500 MHz, $CDCl_3$)



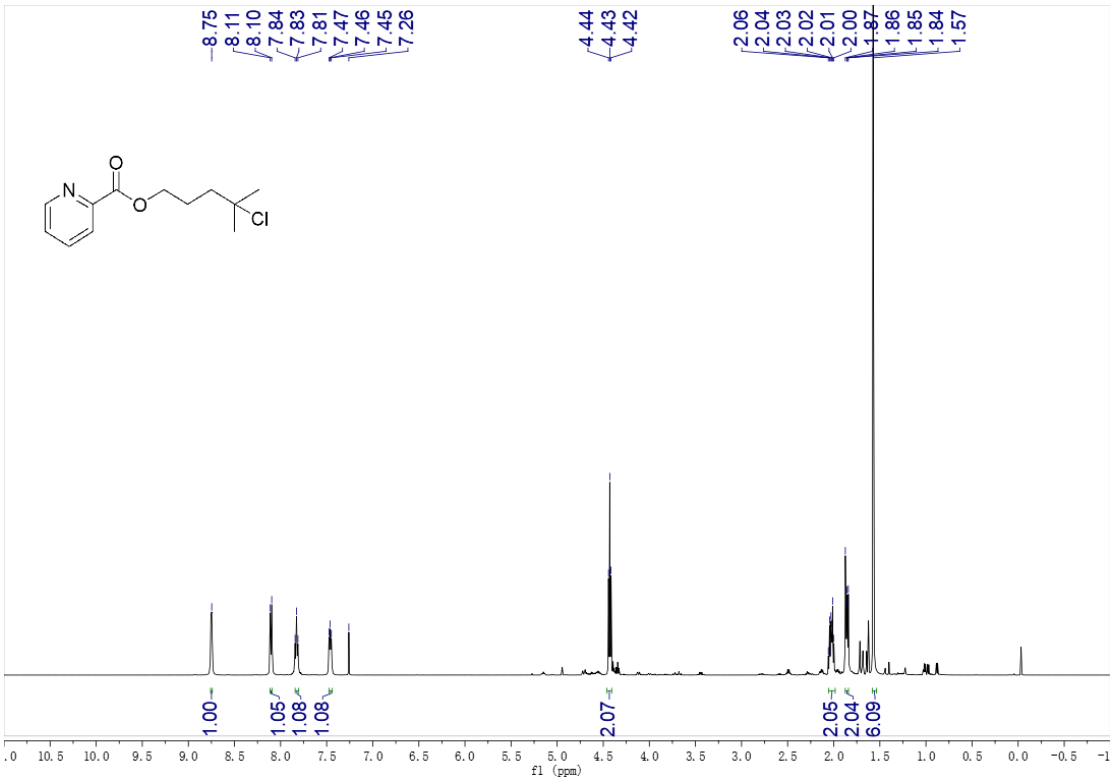
^{13}C NMR of compound **16b** (126 MHz, $CDCl_3$)



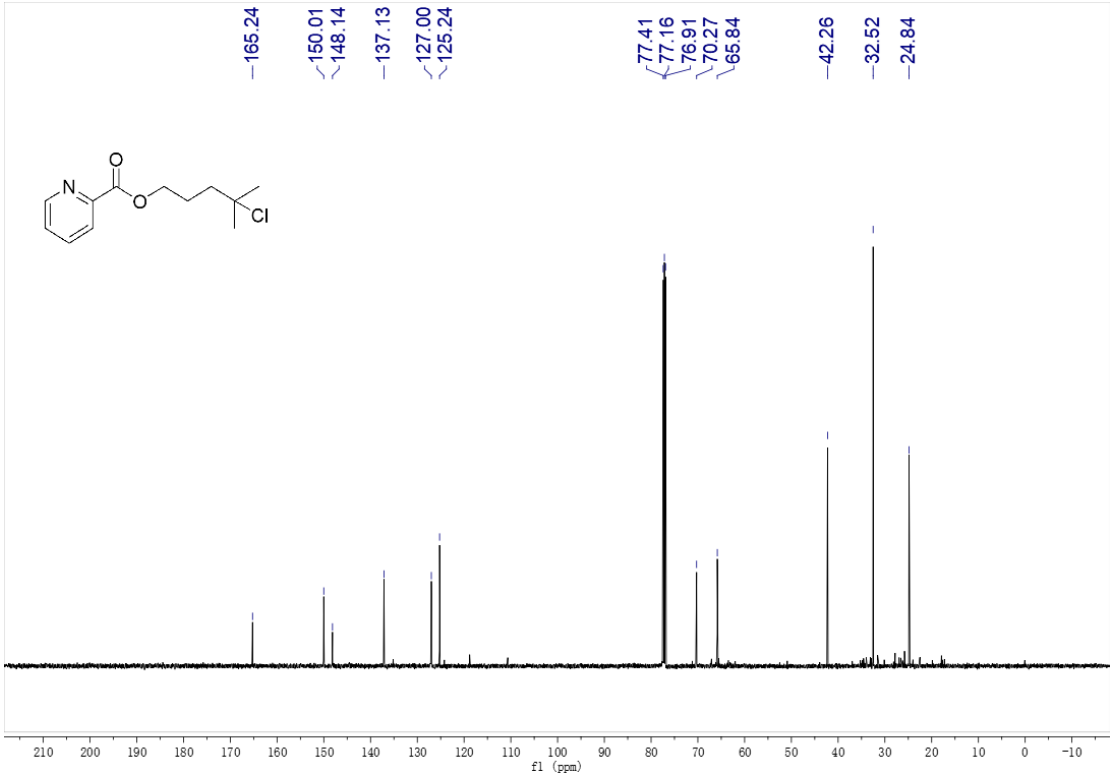
^{1}H NMR of compound **17b** (500 MHz, $CDCl_3$)



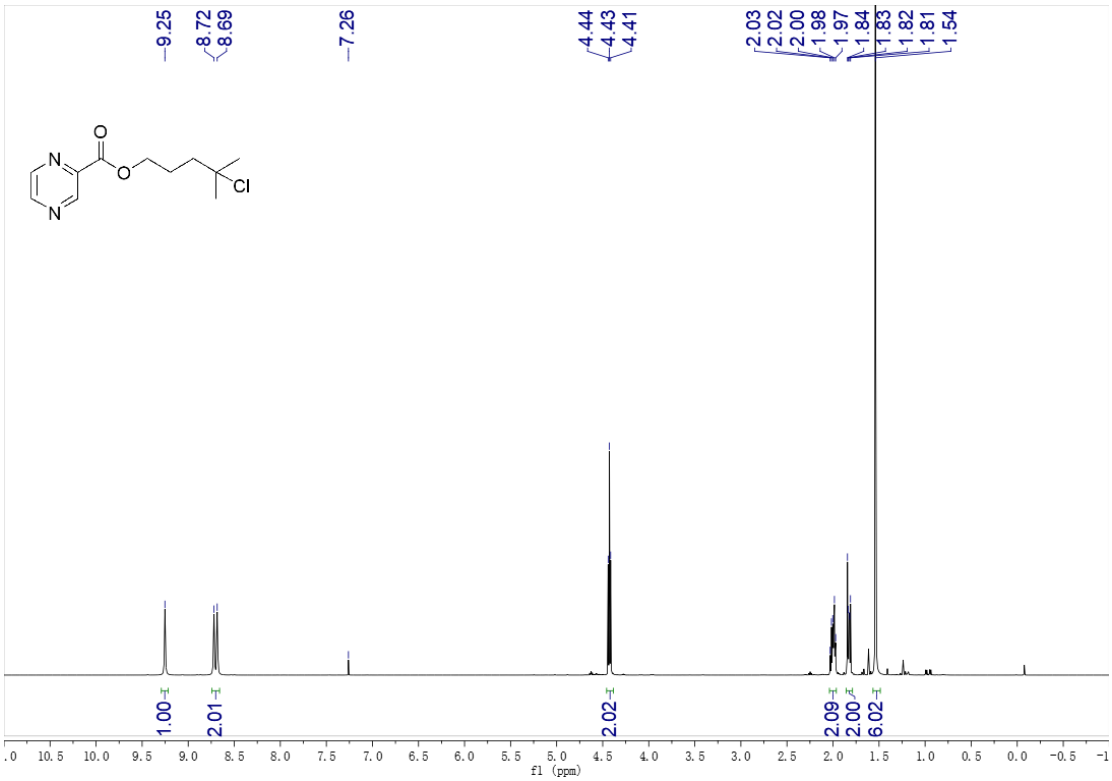
^{13}C NMR of compound **17b** (126 MHz, $CDCl_3$)



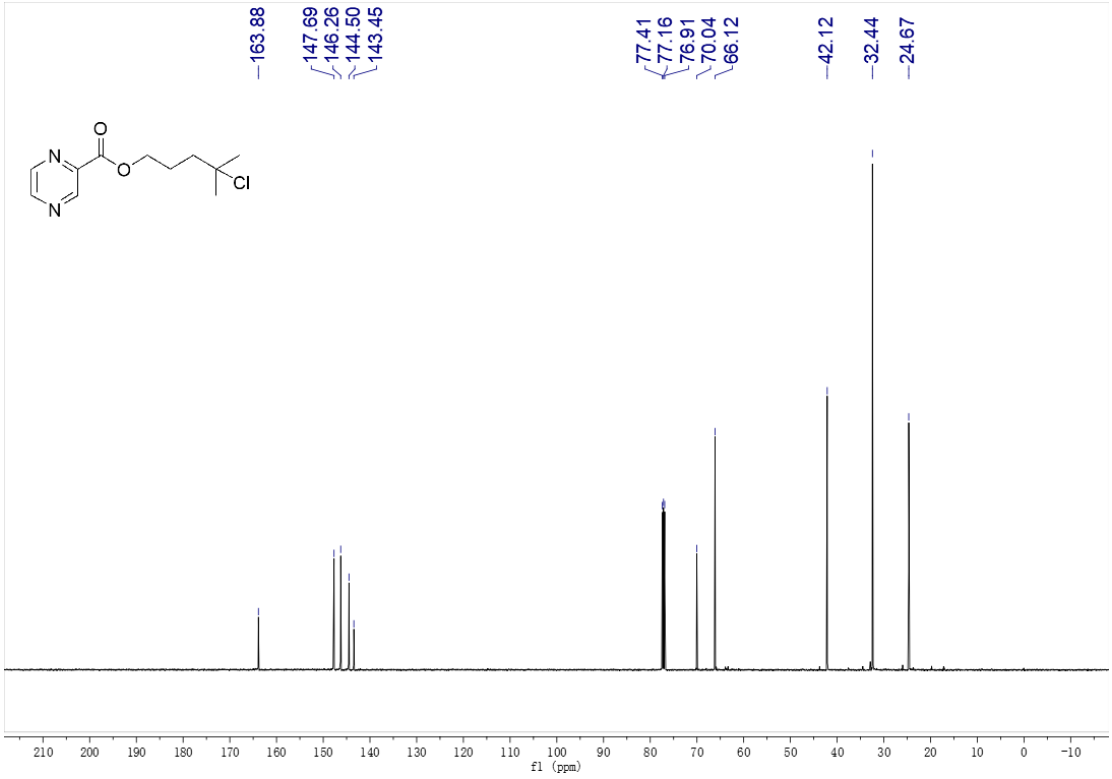
^{1}H NMR of compound **18b** (500 MHz, $CDCl_3$)



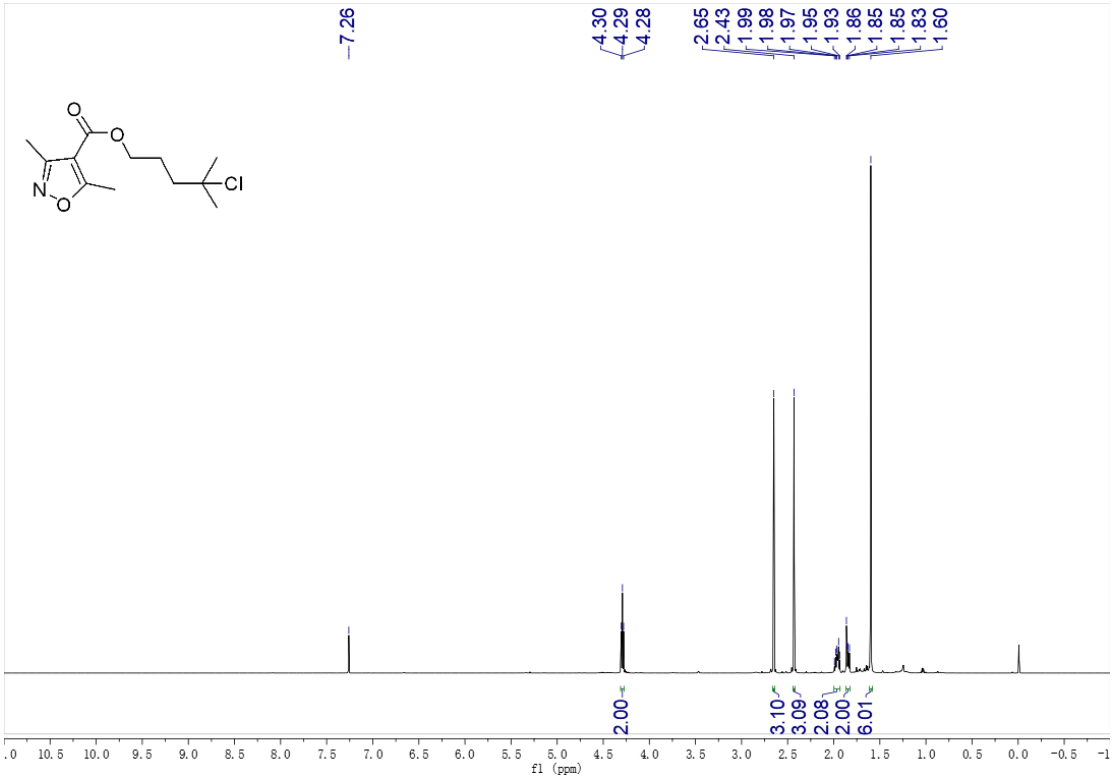
^{13}C NMR of compound **18b** (126 MHz, $CDCl_3$)



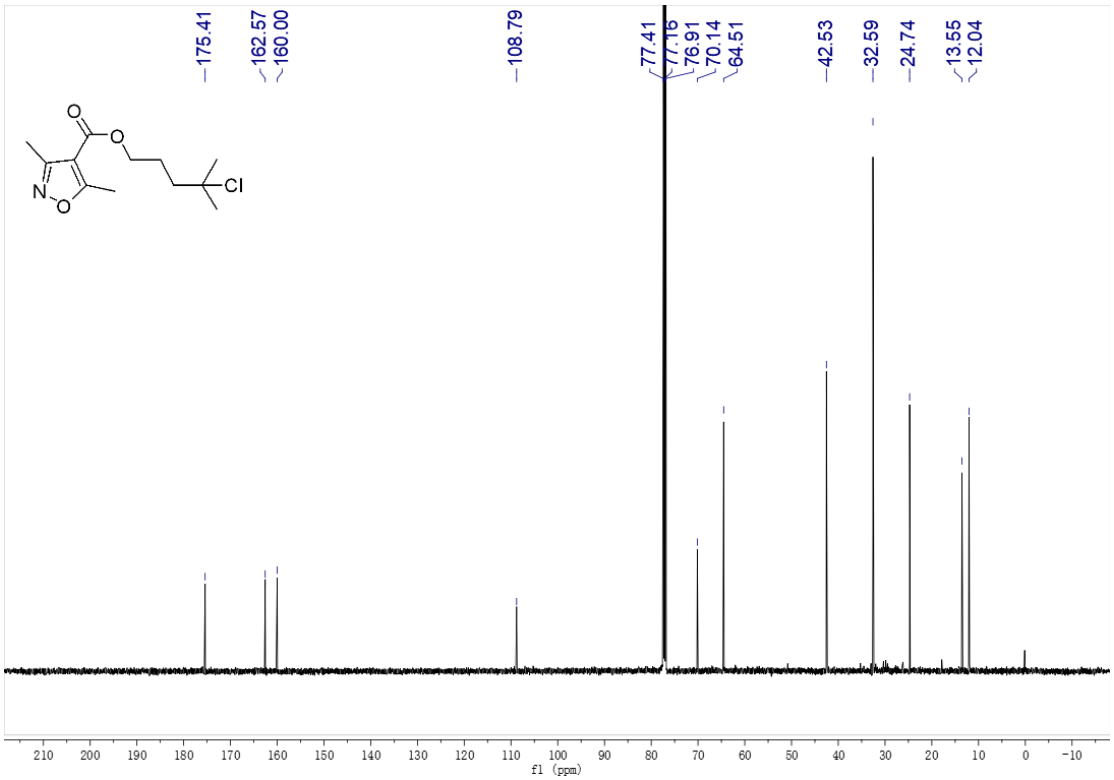
^{1}H NMR of compound **19b** (500 MHz, $CDCl_3$)



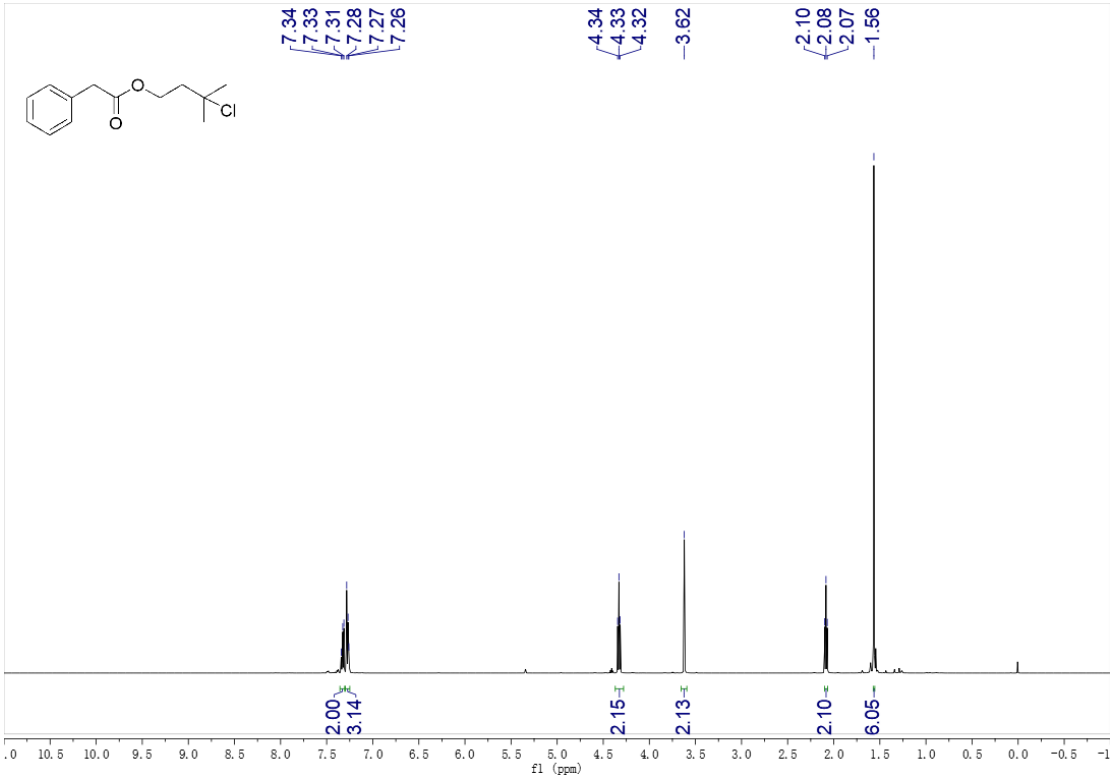
^{13}C NMR of compound **19b** (126 MHz, $CDCl_3$)



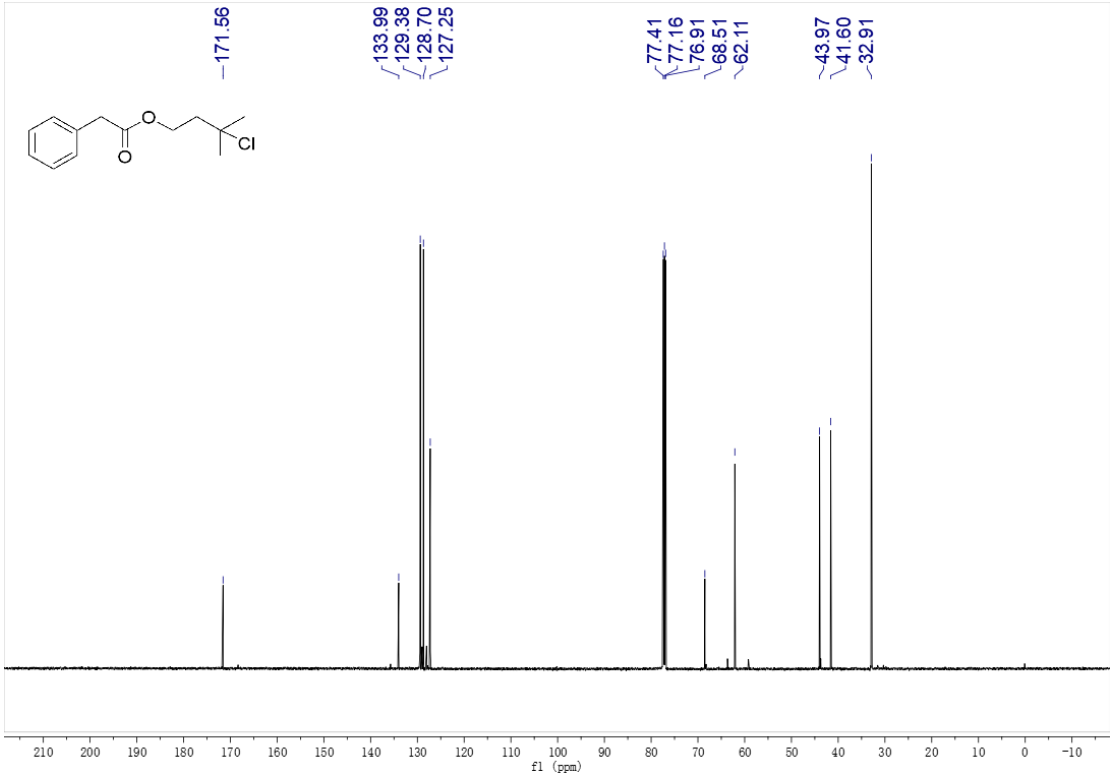
^{1}H NMR of compound **20b** (500 MHz, $CDCl_3$)



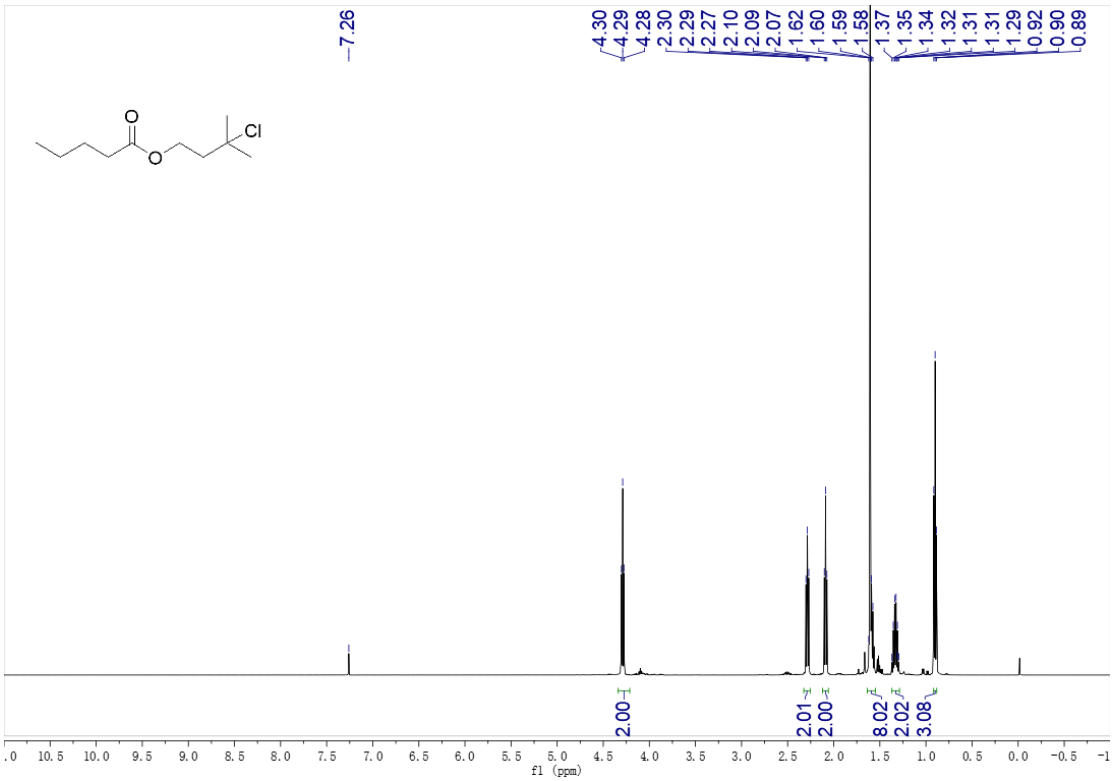
^{13}C NMR of compound **20b** (126 MHz, $CDCl_3$)



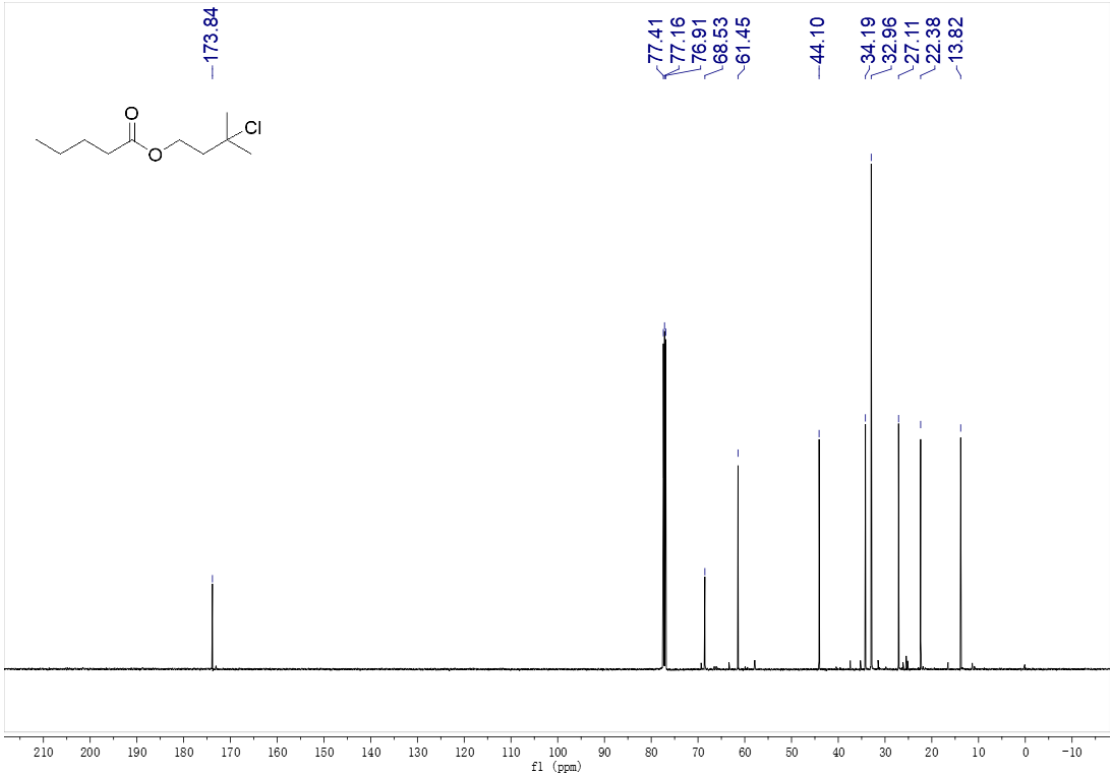
^{1}H NMR of compound **21b** (500 MHz, $CDCl_3$)



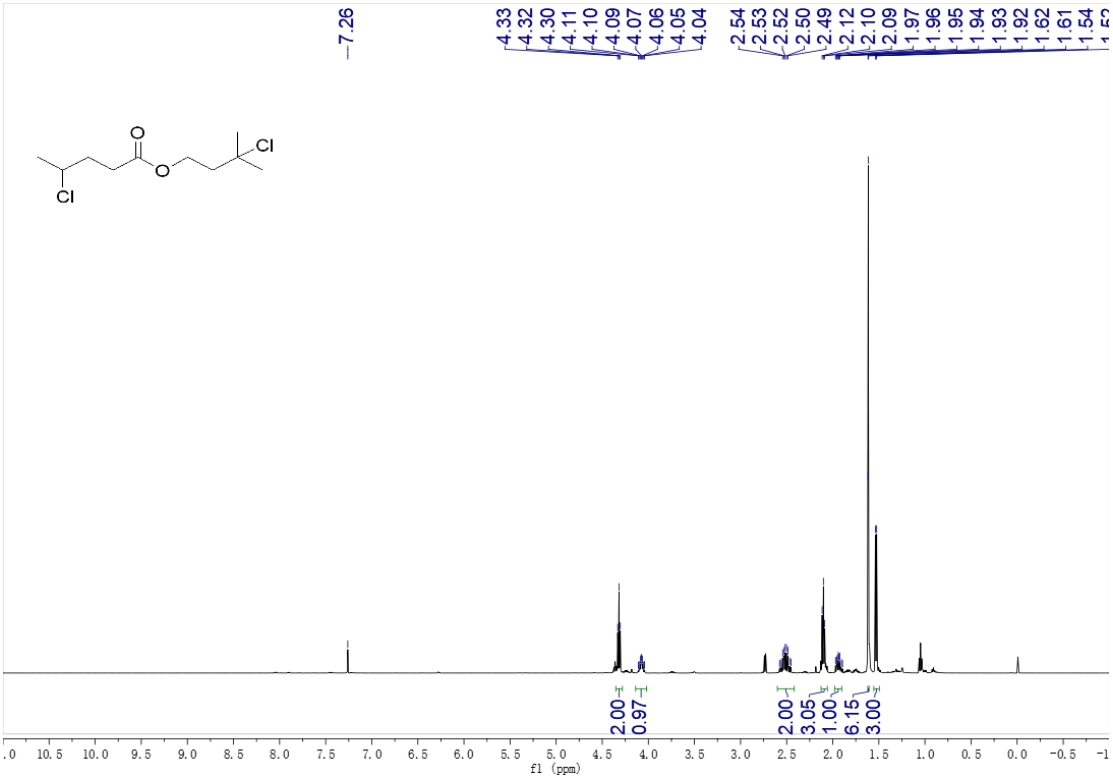
^{13}C NMR of compound **21b** (126 MHz, $CDCl_3$)



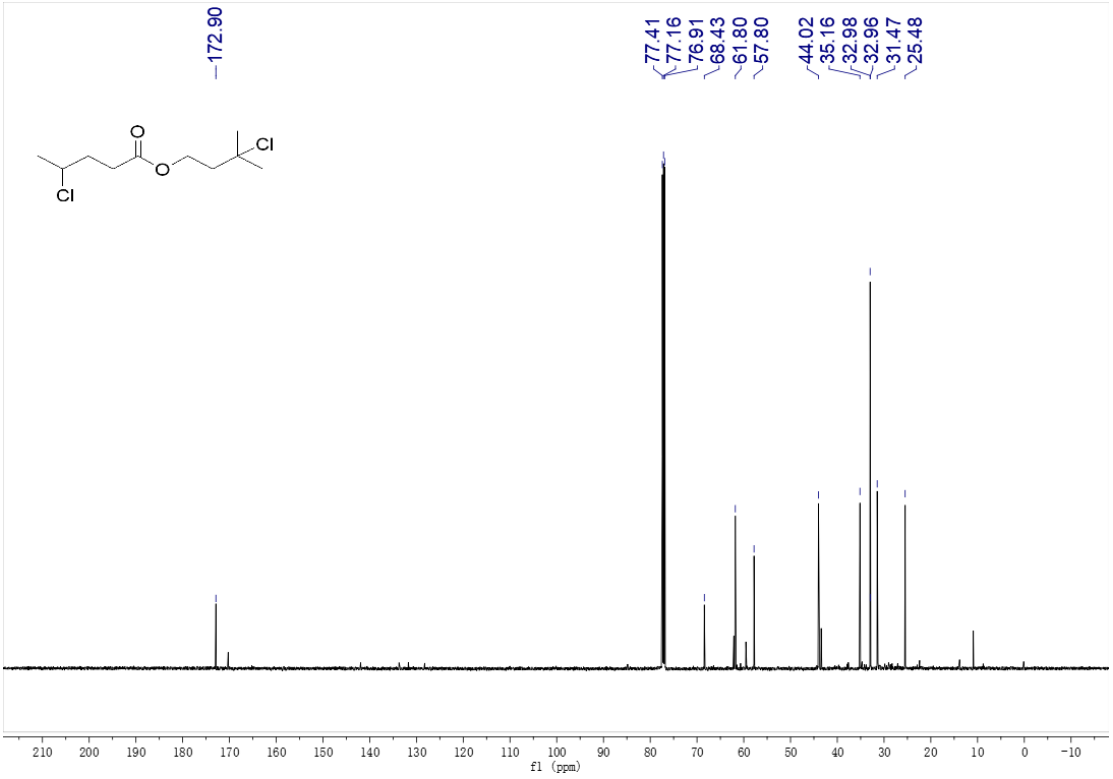
^{1}H NMR of compound **22b** (500 MHz, $CDCl_3$)



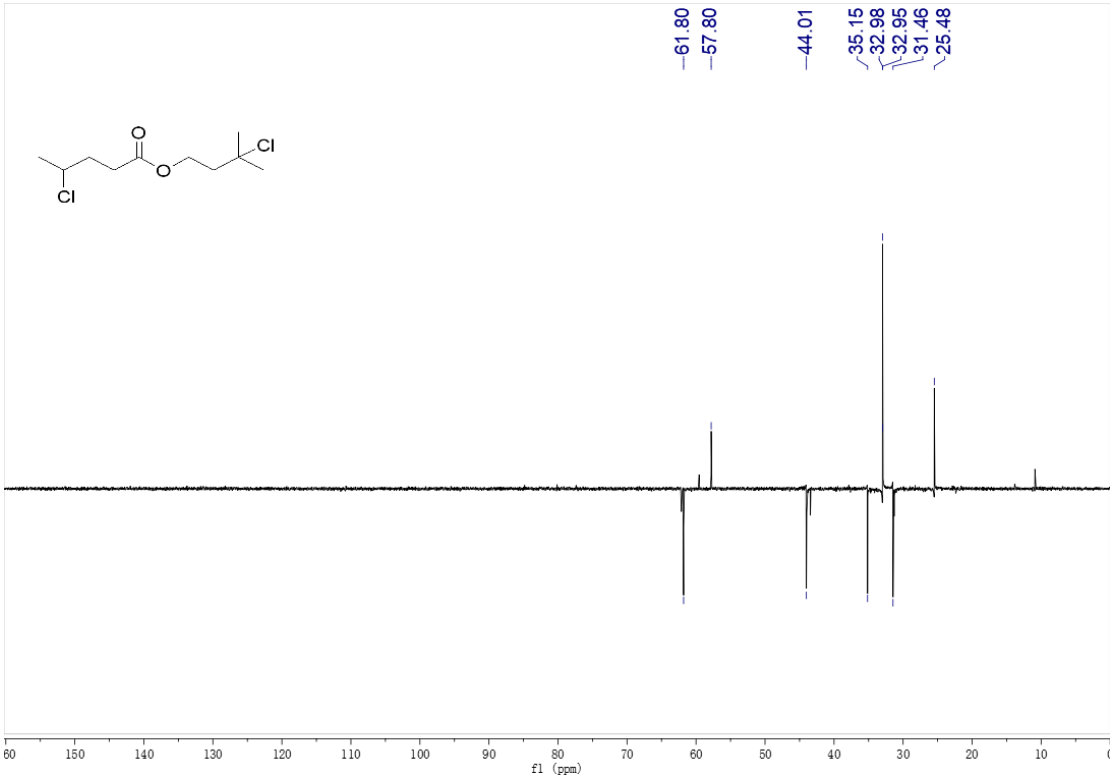
^{13}C NMR of compound **22b** (126 MHz, $CDCl_3$)



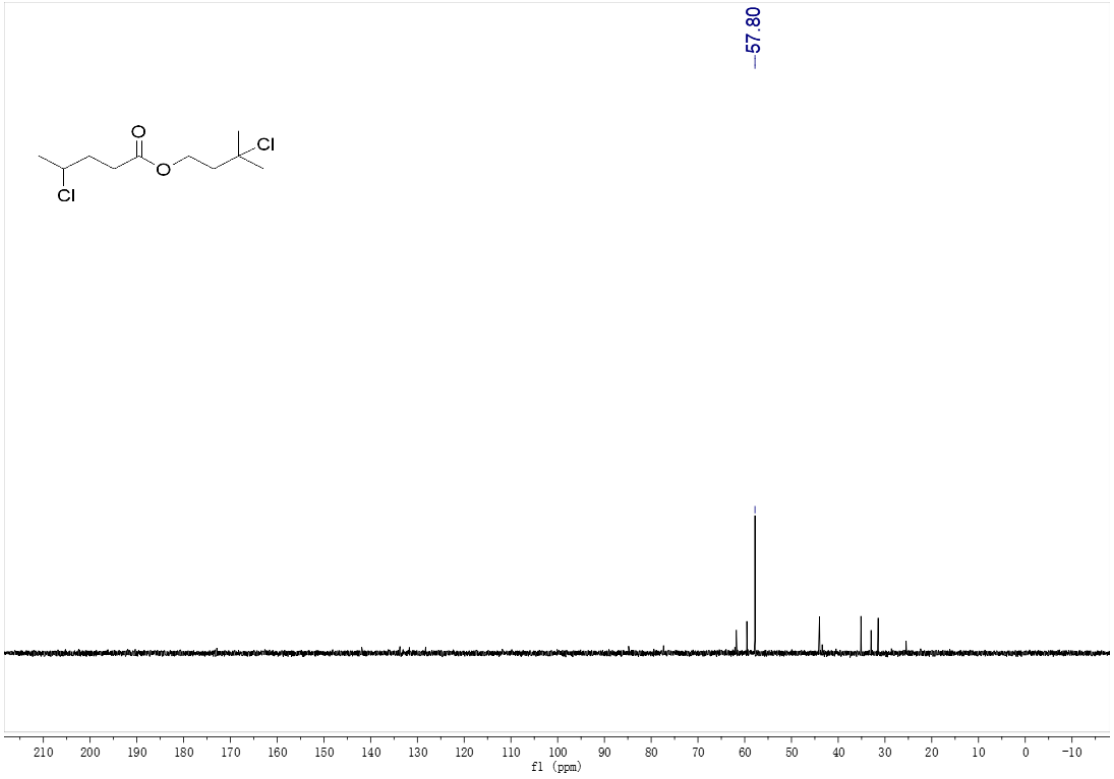
^{1}H NMR of compound **22b'** (500 MHz, $CDCl_3$)



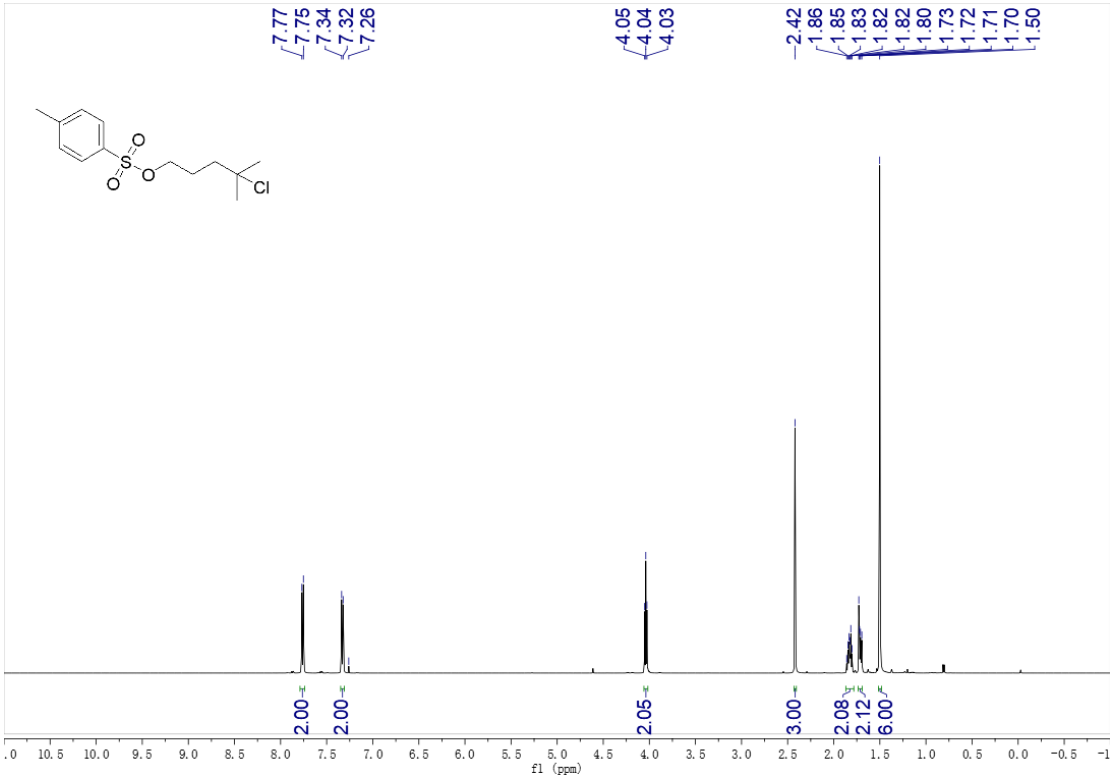
^{13}C NMR of compound **22b'** (126 MHz, $CDCl_3$)



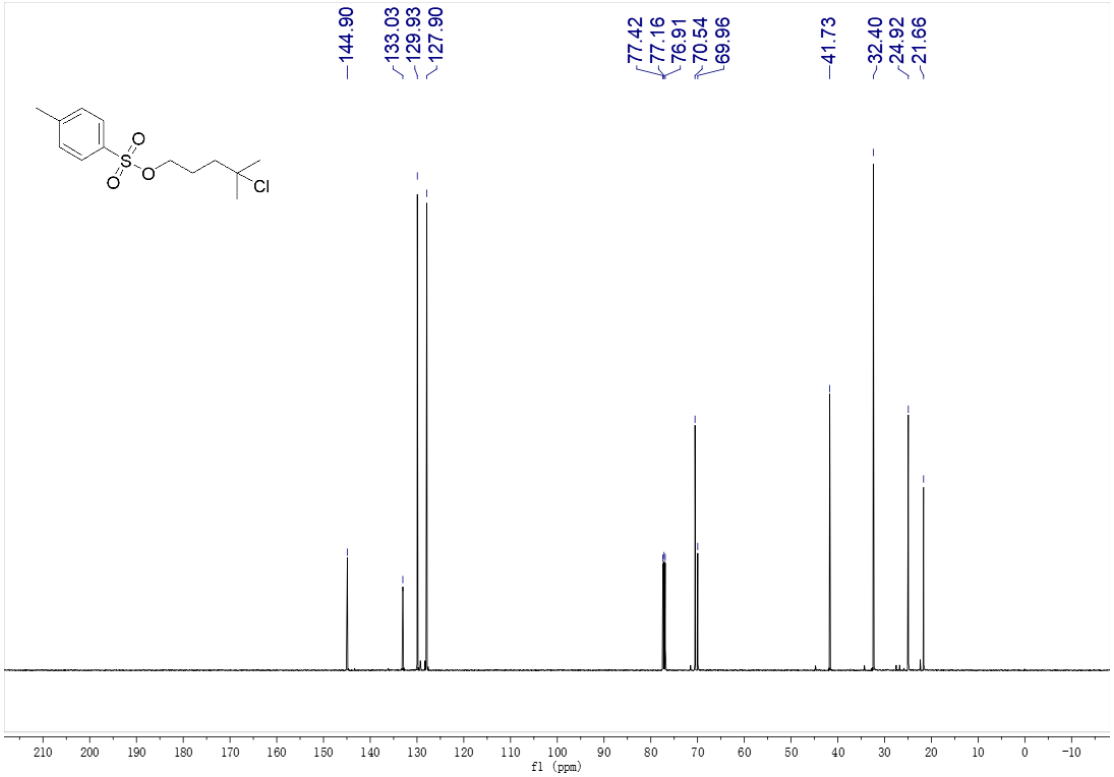
DEPT 135 of compound **22b'**



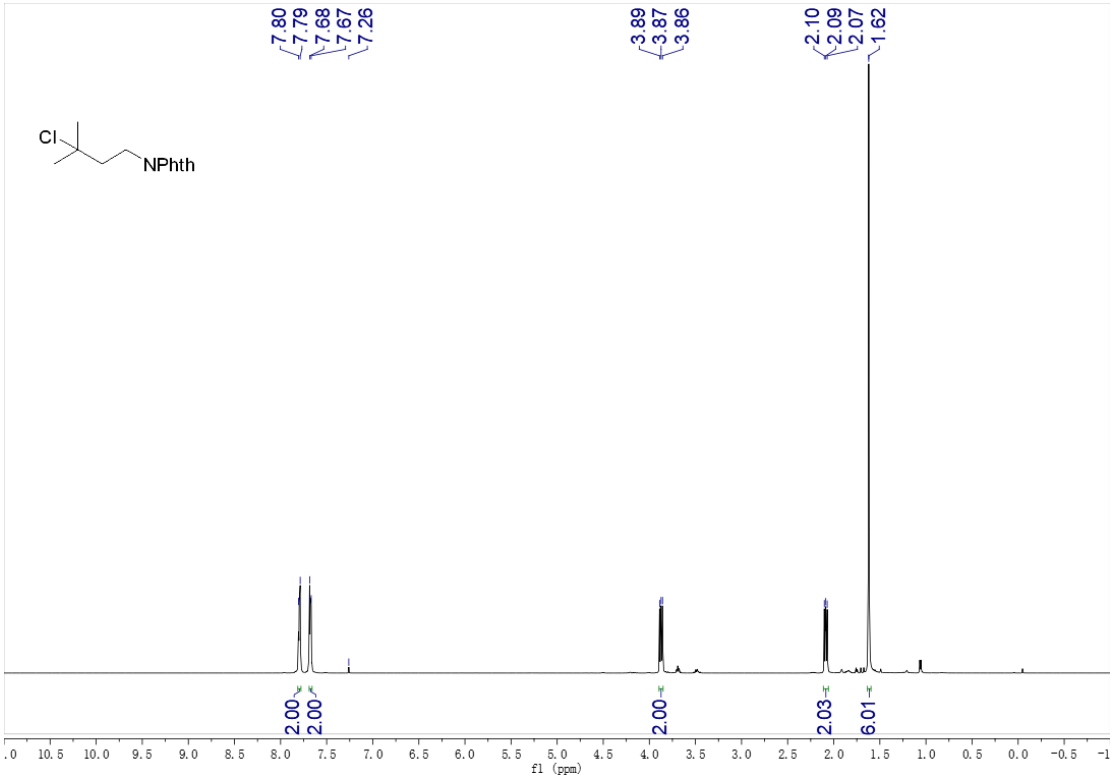
DEPT 90 of compound **22b'**



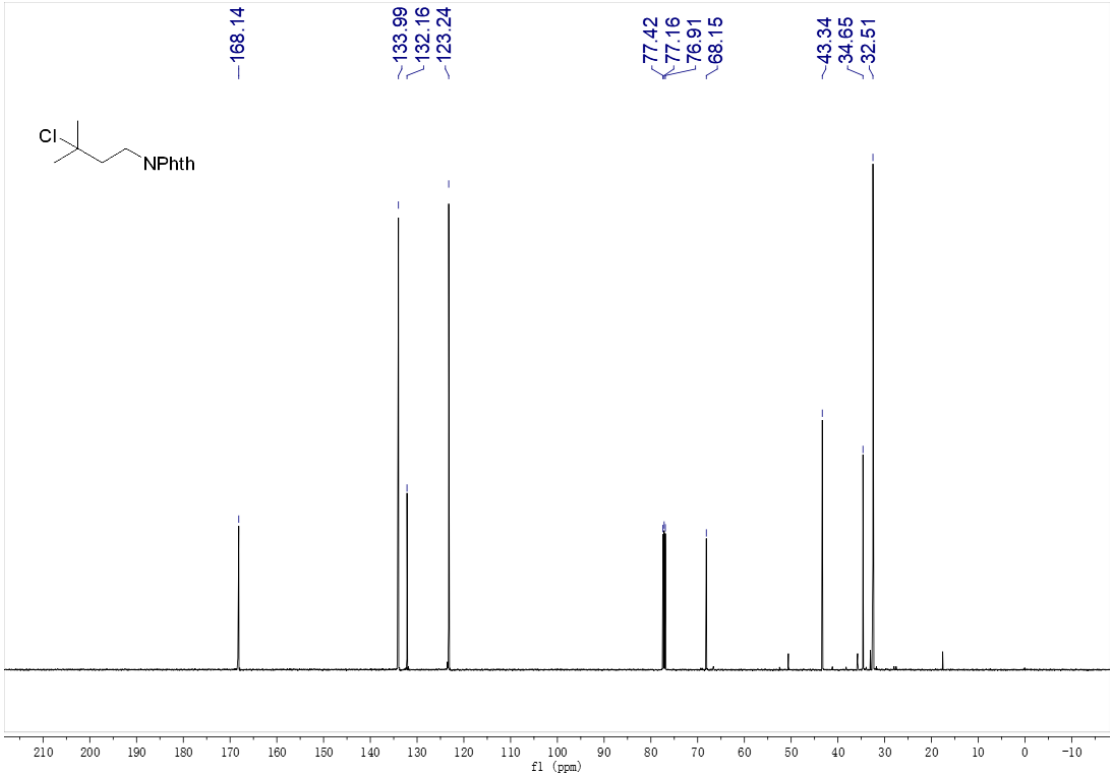
^{1}H NMR of compound **23b** (500 MHz, $CDCl_3$)



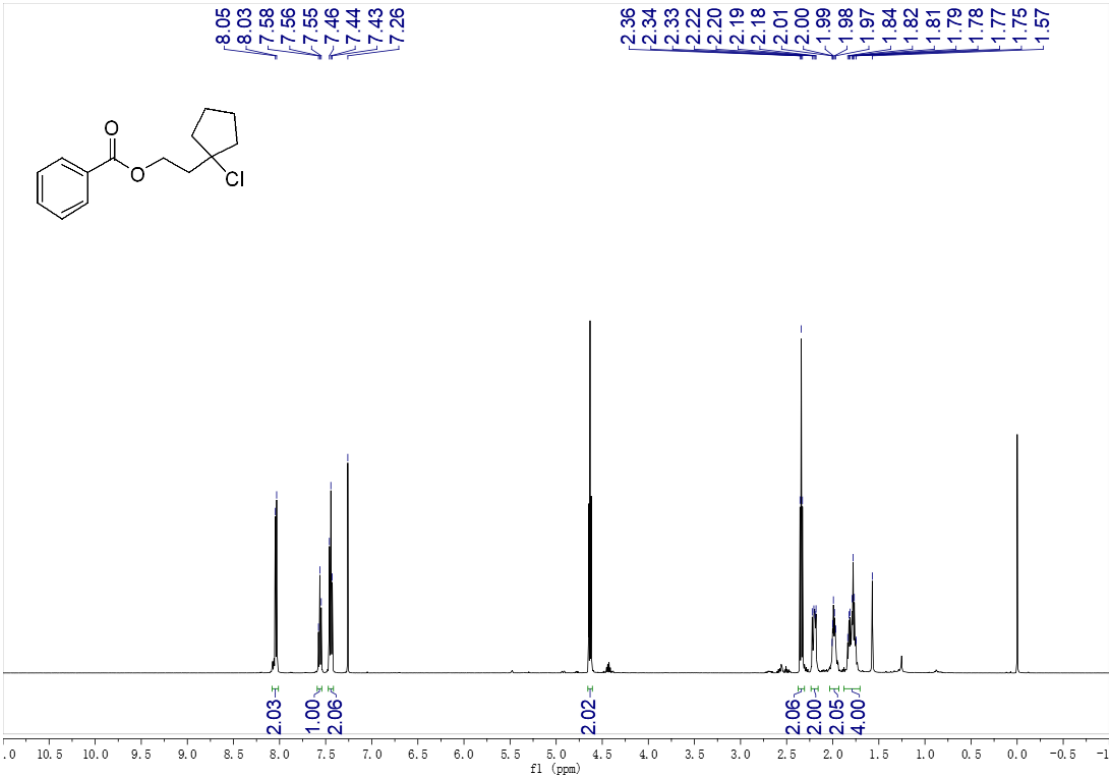
^{13}C NMR of compound **23b** (126 MHz, $CDCl_3$)



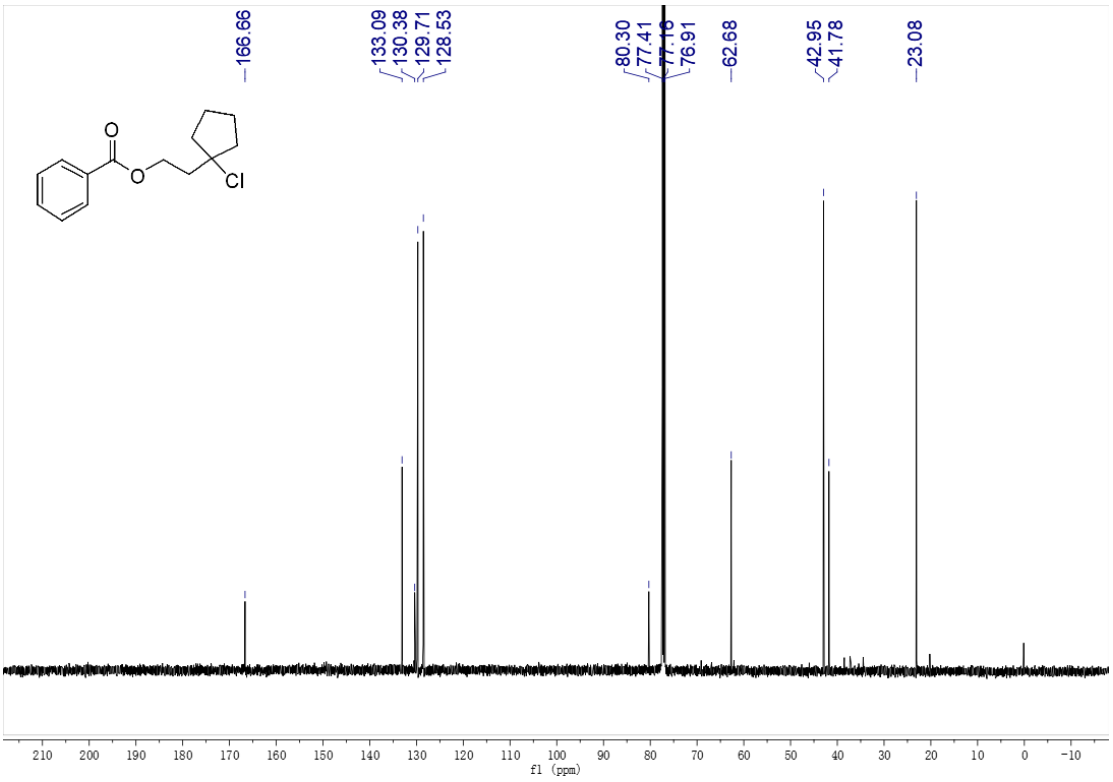
^{1}H NMR of compound **24b** (500 MHz, $CDCl_3$)



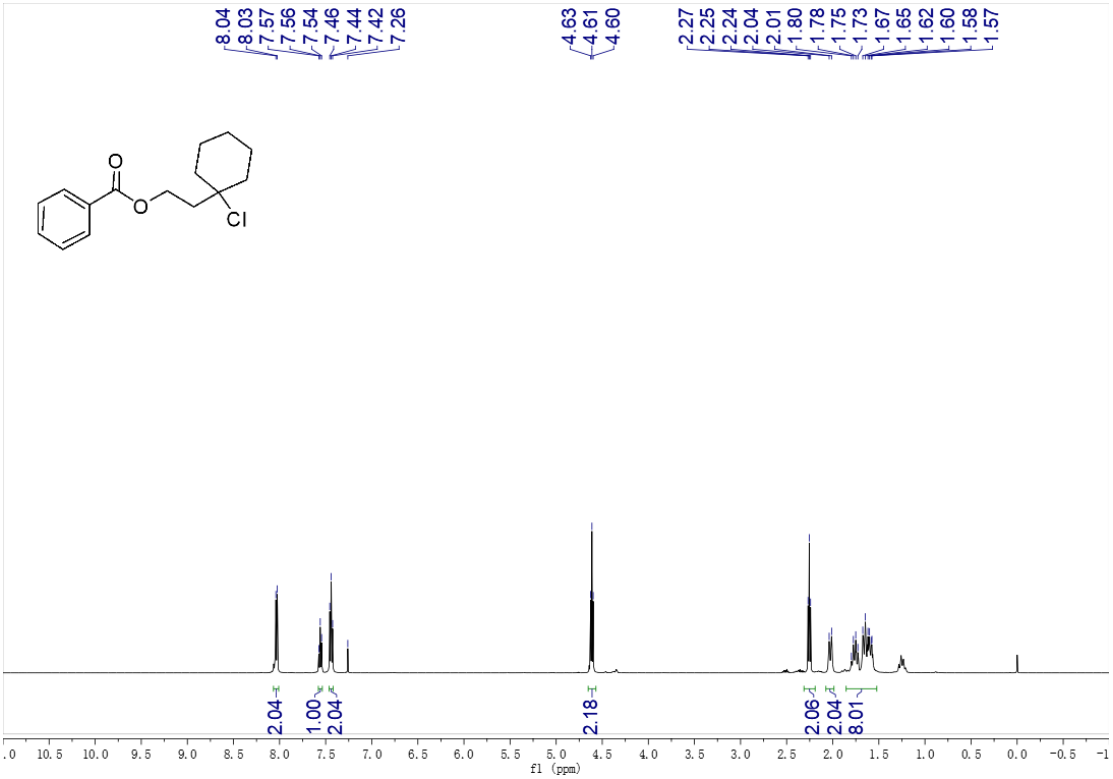
^{13}C NMR of compound **24b** (126 MHz, $CDCl_3$)



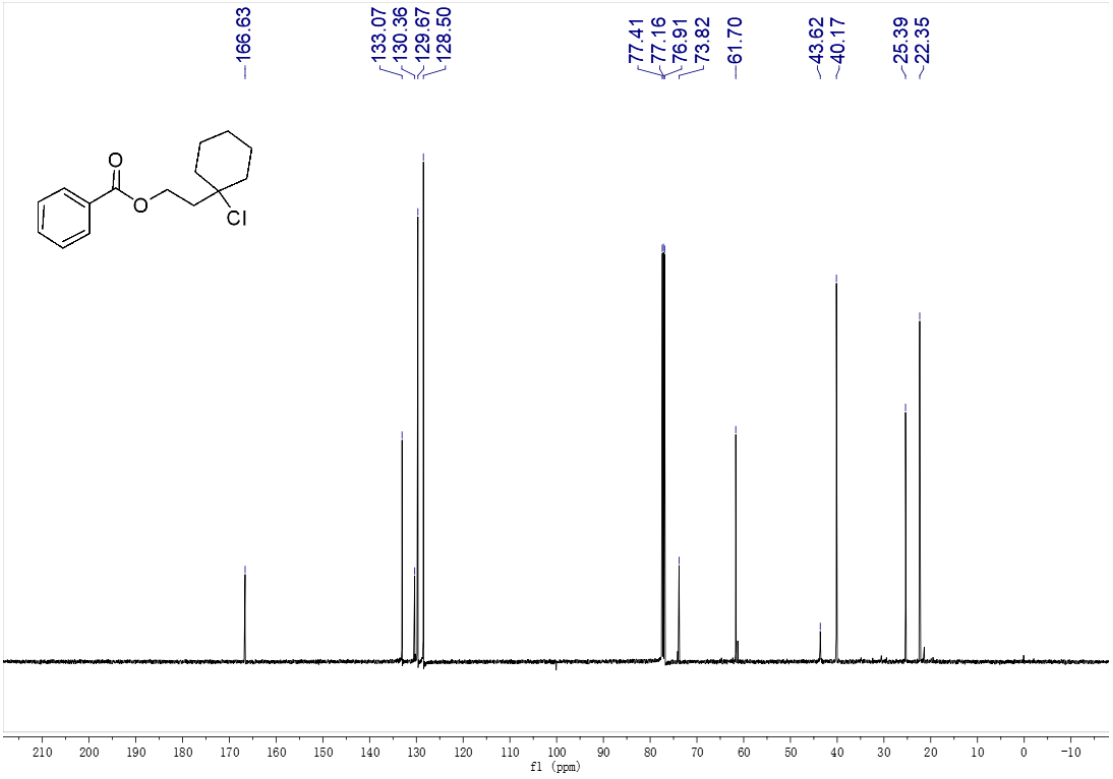
^{1}H NMR of compound **25b** (500 MHz, $CDCl_3$)



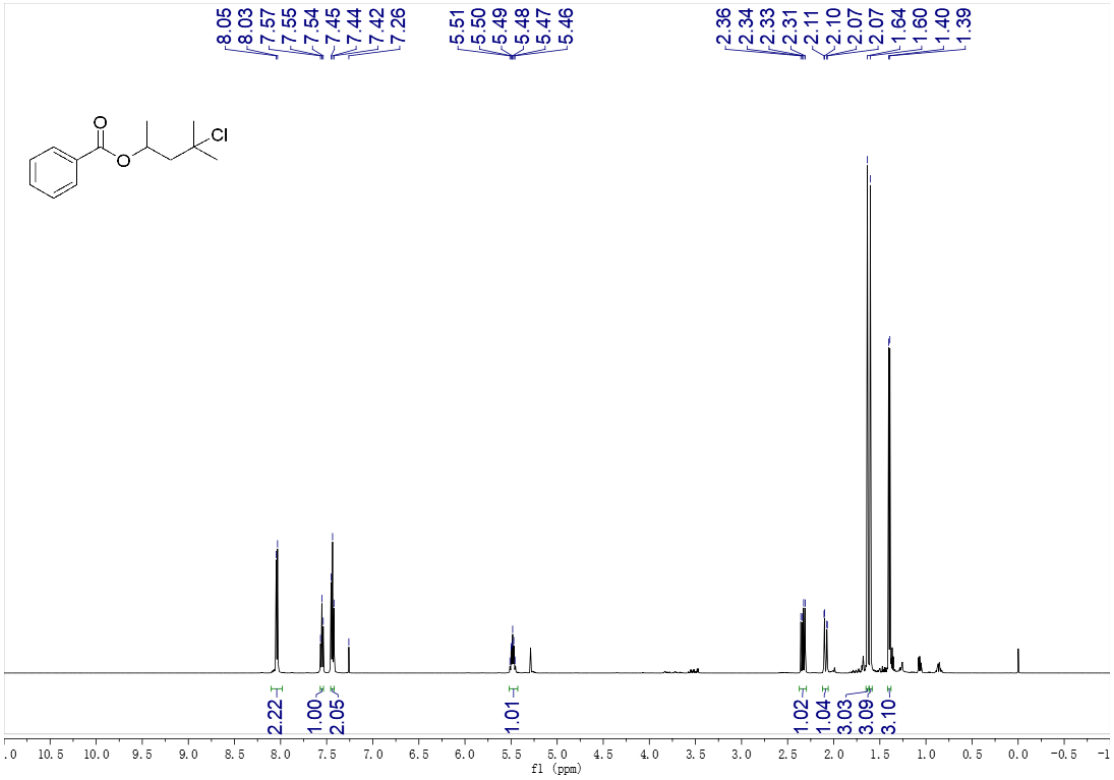
^{13}C NMR of compound **25b** (126 MHz, $CDCl_3$)



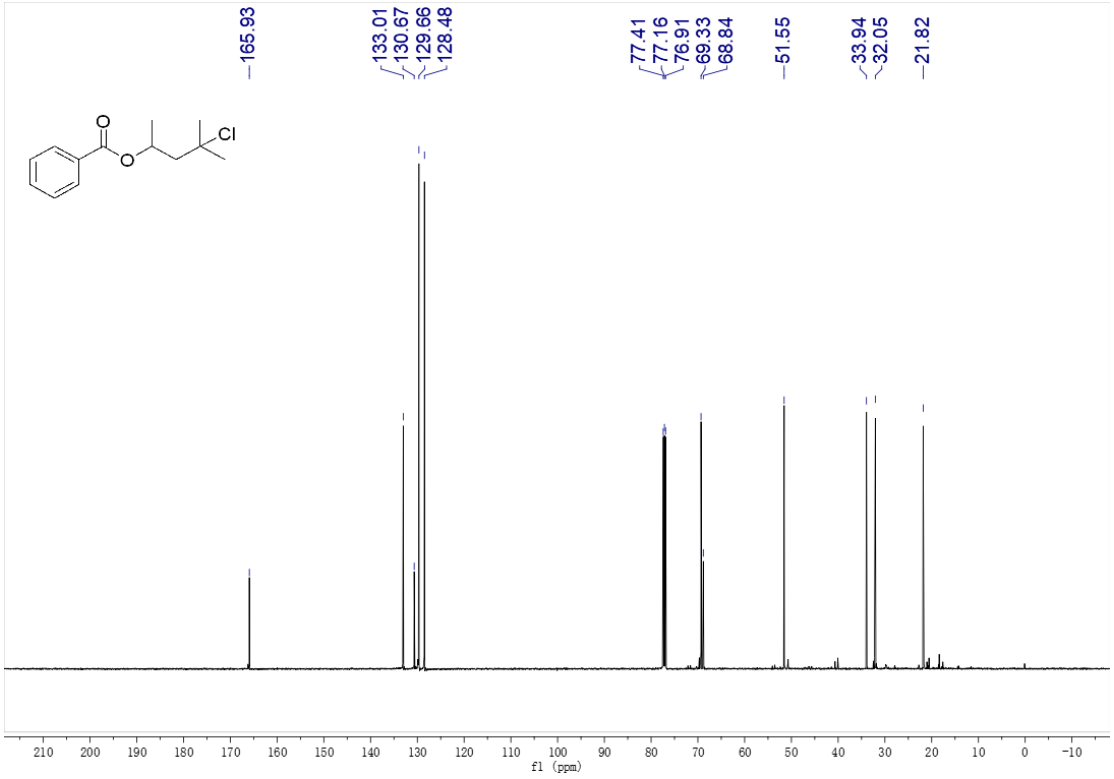
^{1}H NMR of compound **26b** (500 MHz, $CDCl_3$)



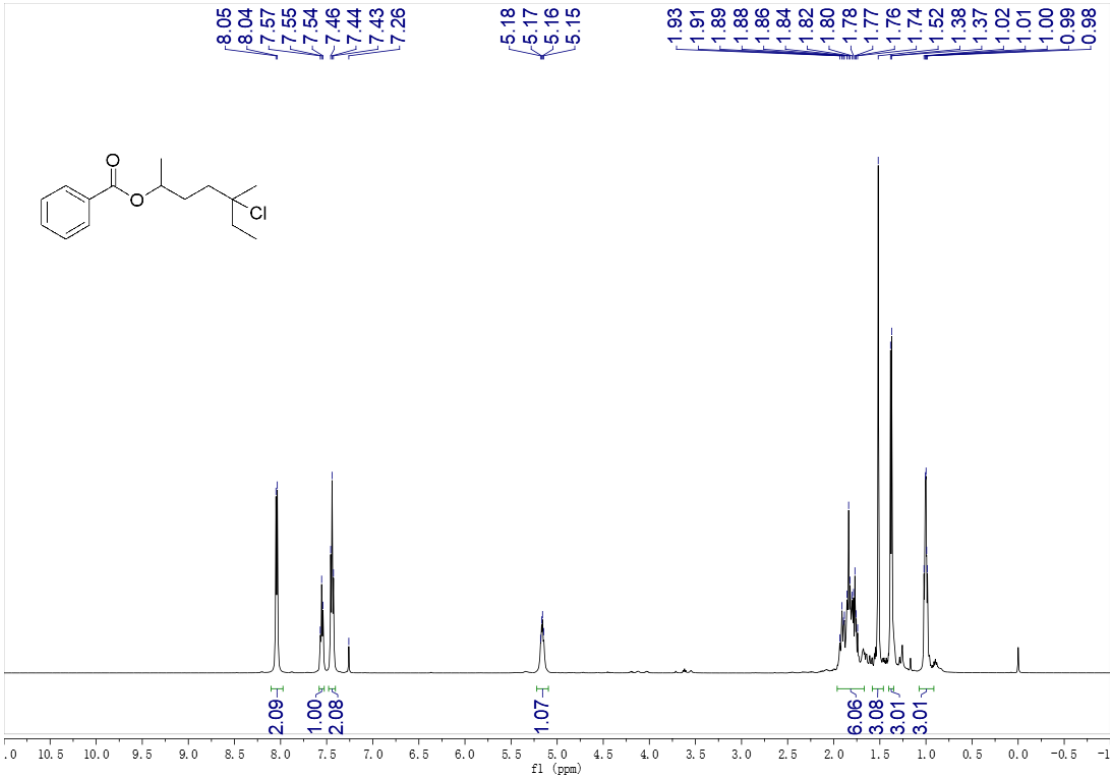
^{13}C NMR of compound **26b** (126 MHz, $CDCl_3$)



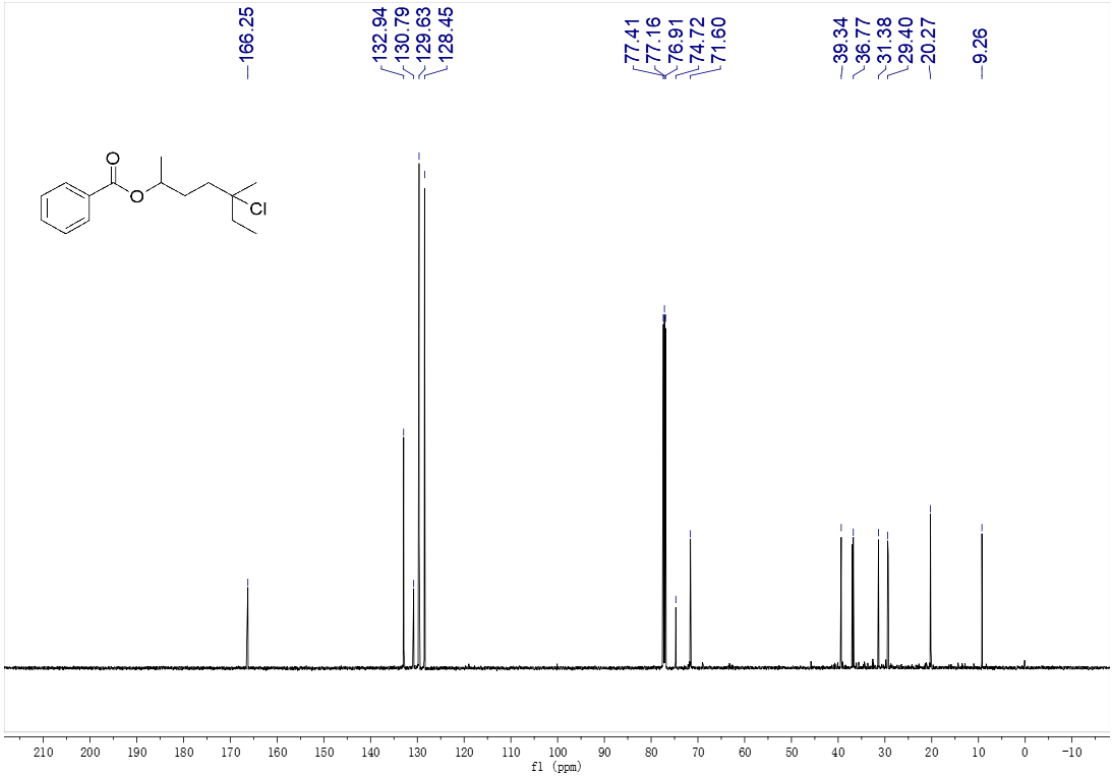
^{1}H NMR of compound **27b** (500 MHz, $CDCl_3$)



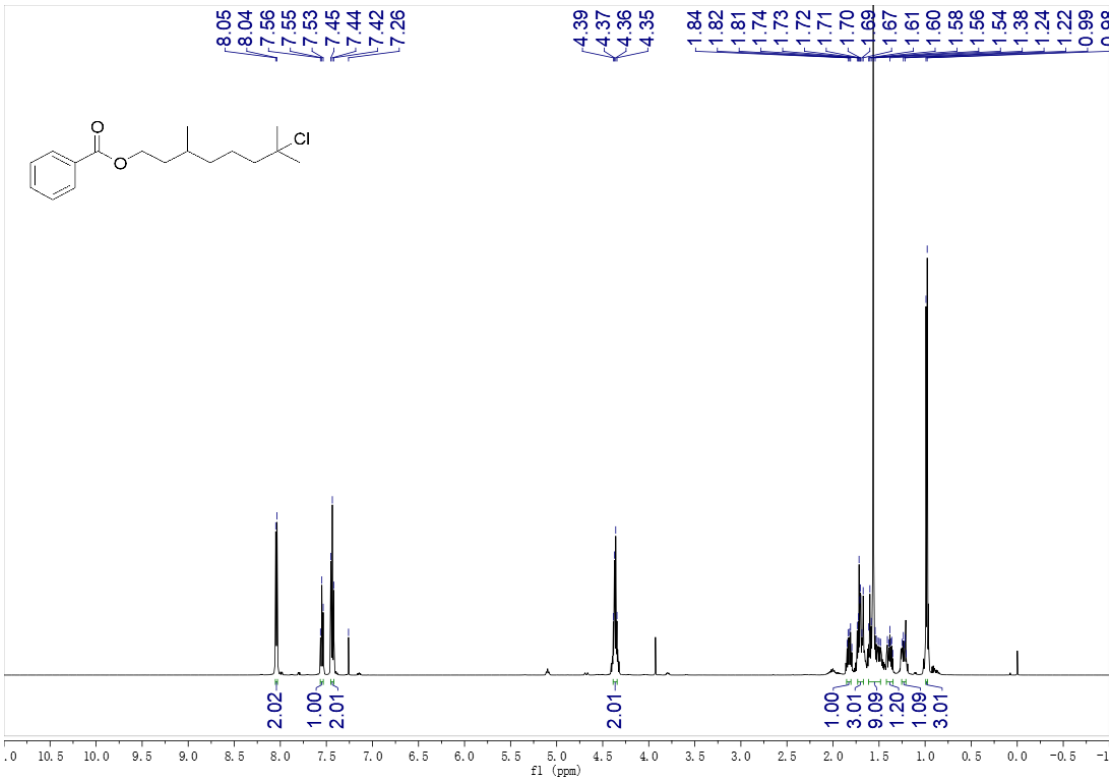
^{13}C NMR of compound **27b** (126 MHz, $CDCl_3$)



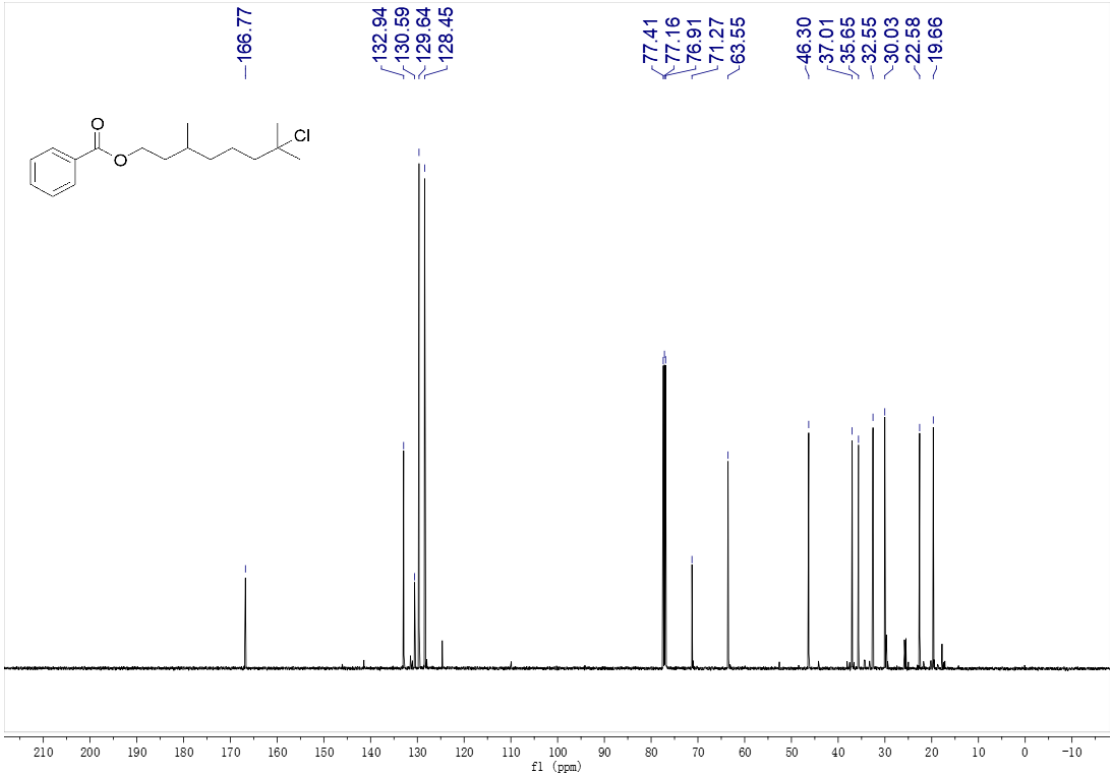
^{1}H NMR of compound **28b** (500 MHz, $CDCl_3$)



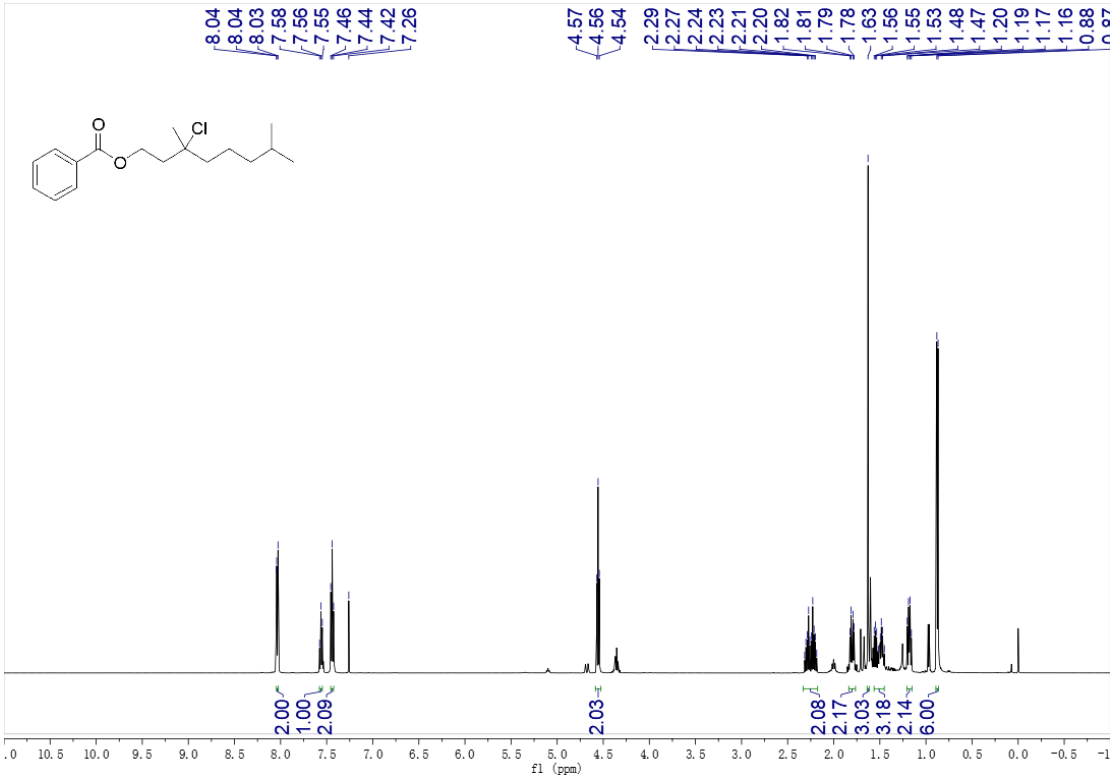
^{13}C NMR of compound **28b** (126 MHz, $CDCl_3$)



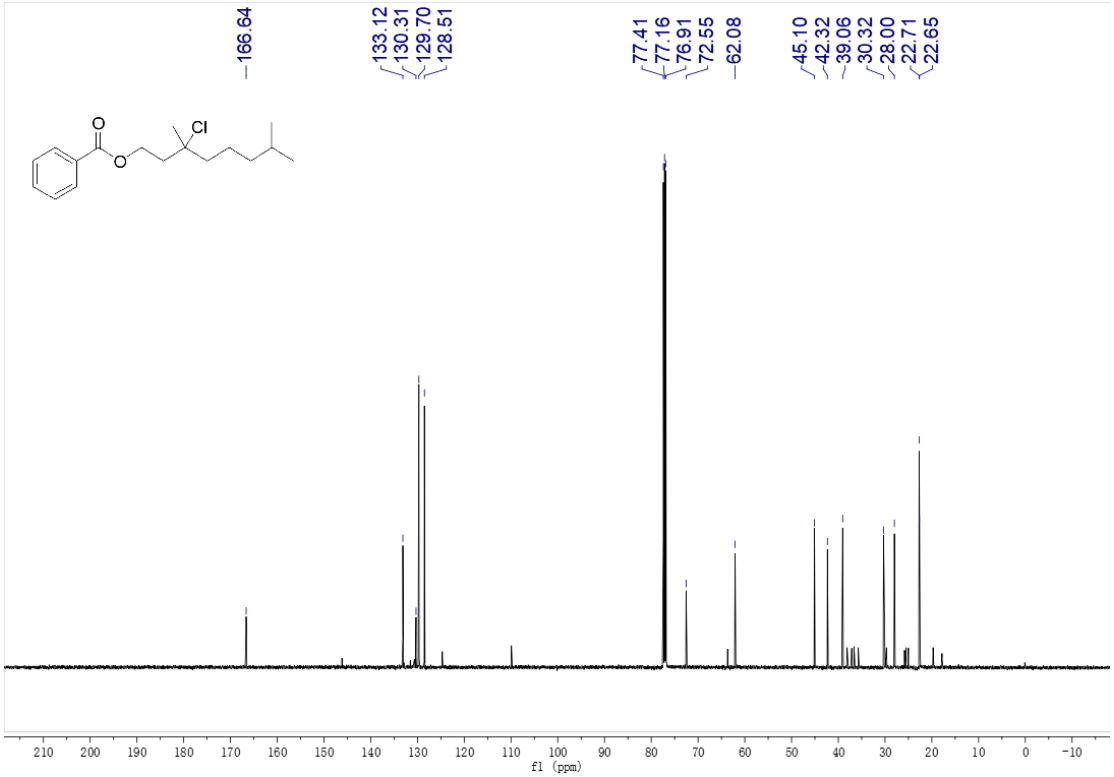
^{1}H NMR of compound **29b** (500 MHz, $CDCl_3$)



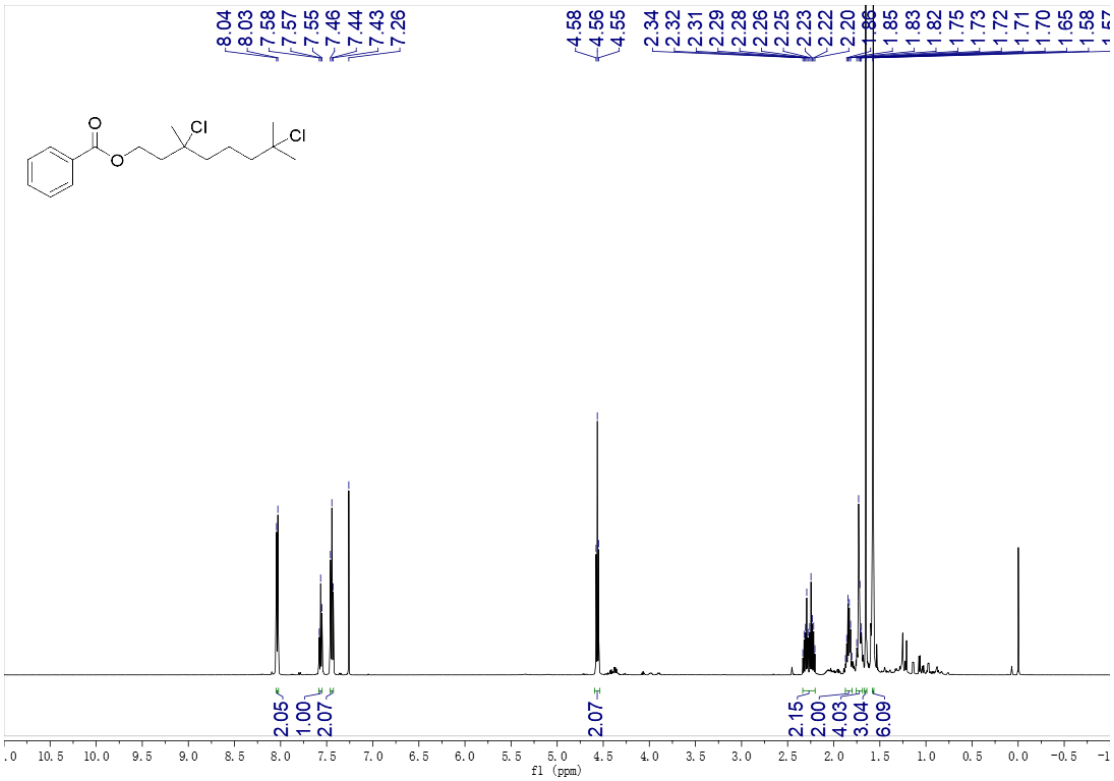
^{13}C NMR of compound **29b** (126 MHz, $CDCl_3$)



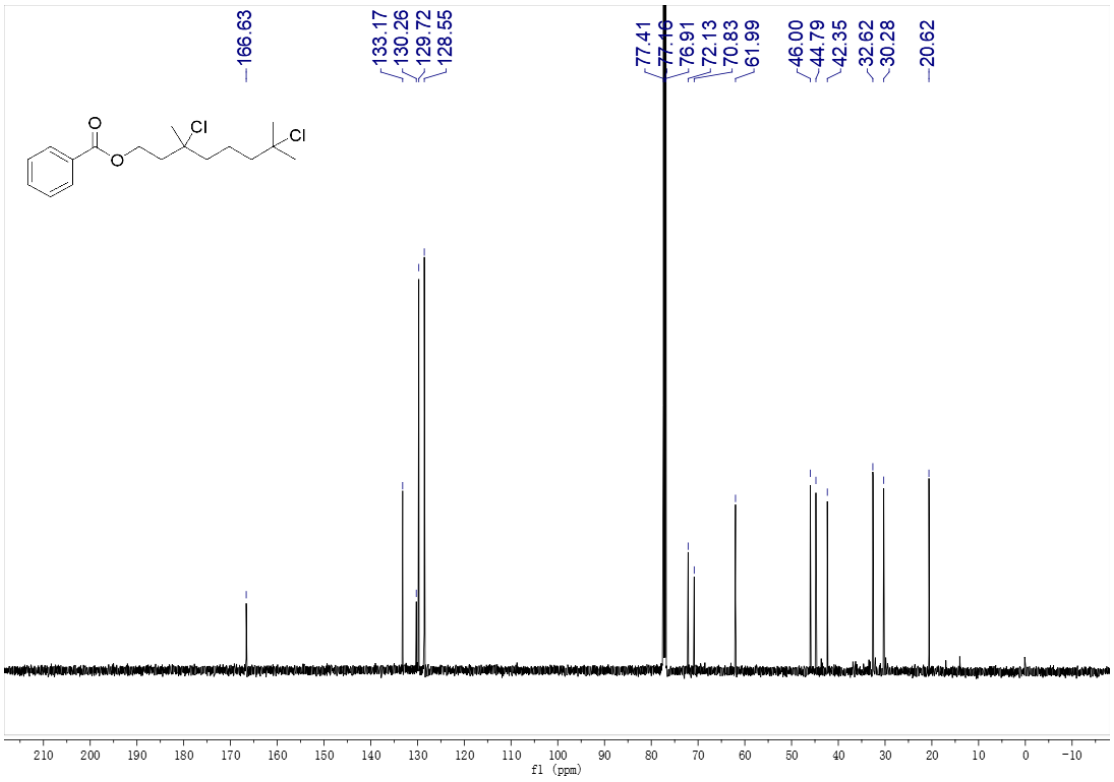
^{1}H NMR of compound **29b'** (500 MHz, $CDCl_3$)



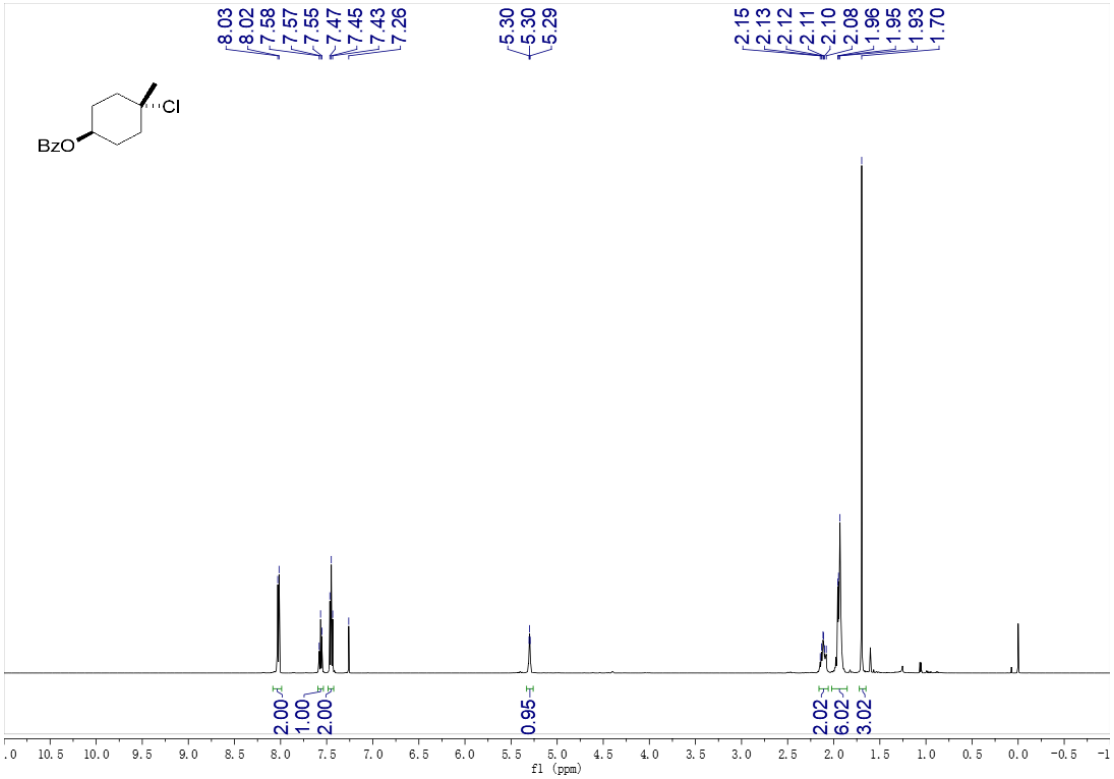
^{13}C NMR of compound **29b'** (126 MHz, $CDCl_3$)



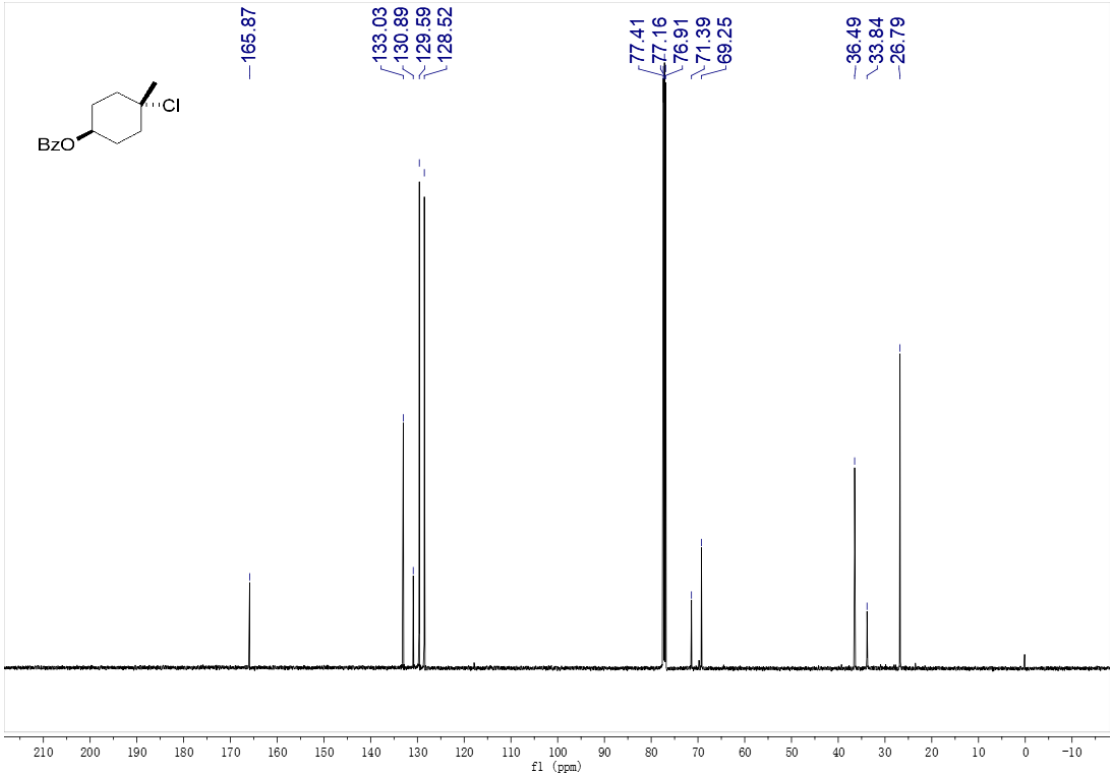
^{1}H NMR of compound **29b''** (500 MHz, $CDCl_3$)



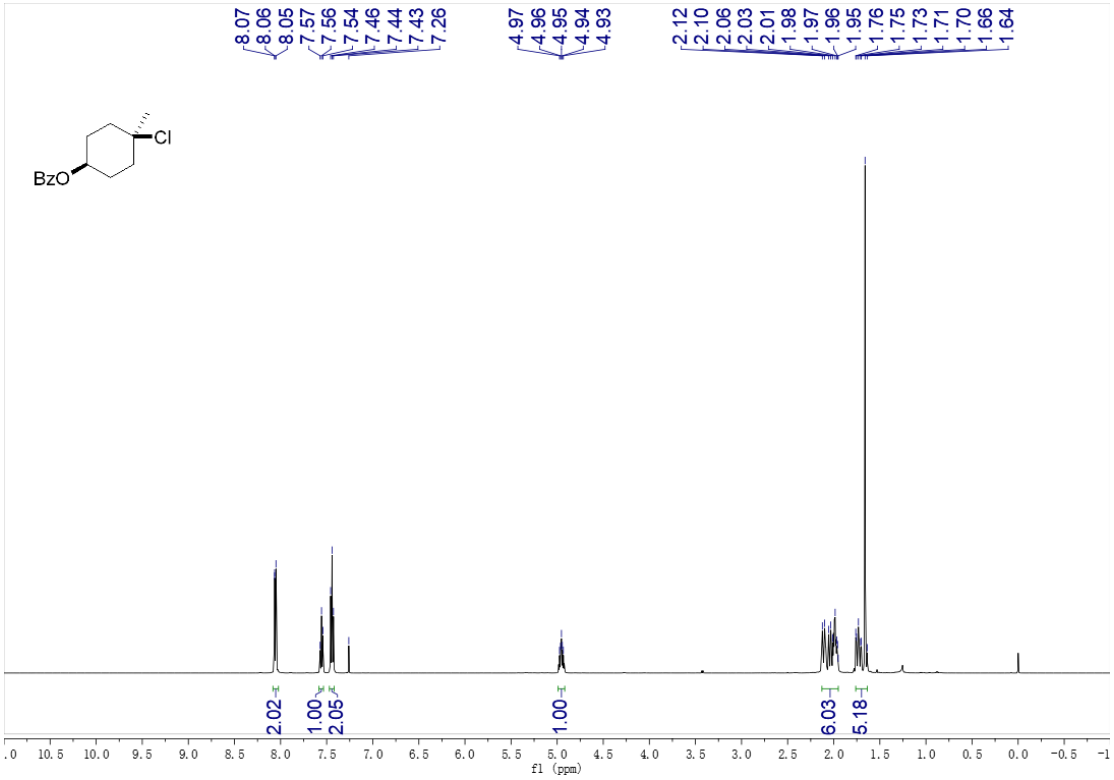
^{13}C NMR of compound **29b''** (126 MHz, $CDCl_3$)



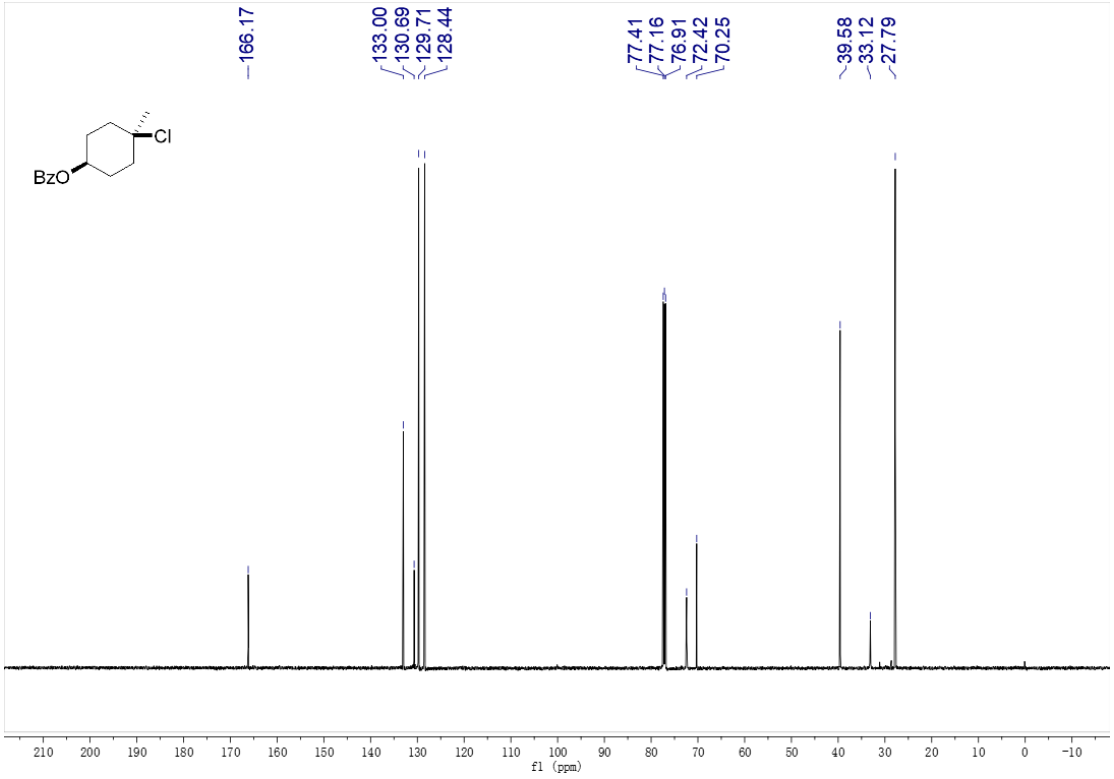
^{1}H NMR of compound **30b** (500 MHz, $CDCl_3$)



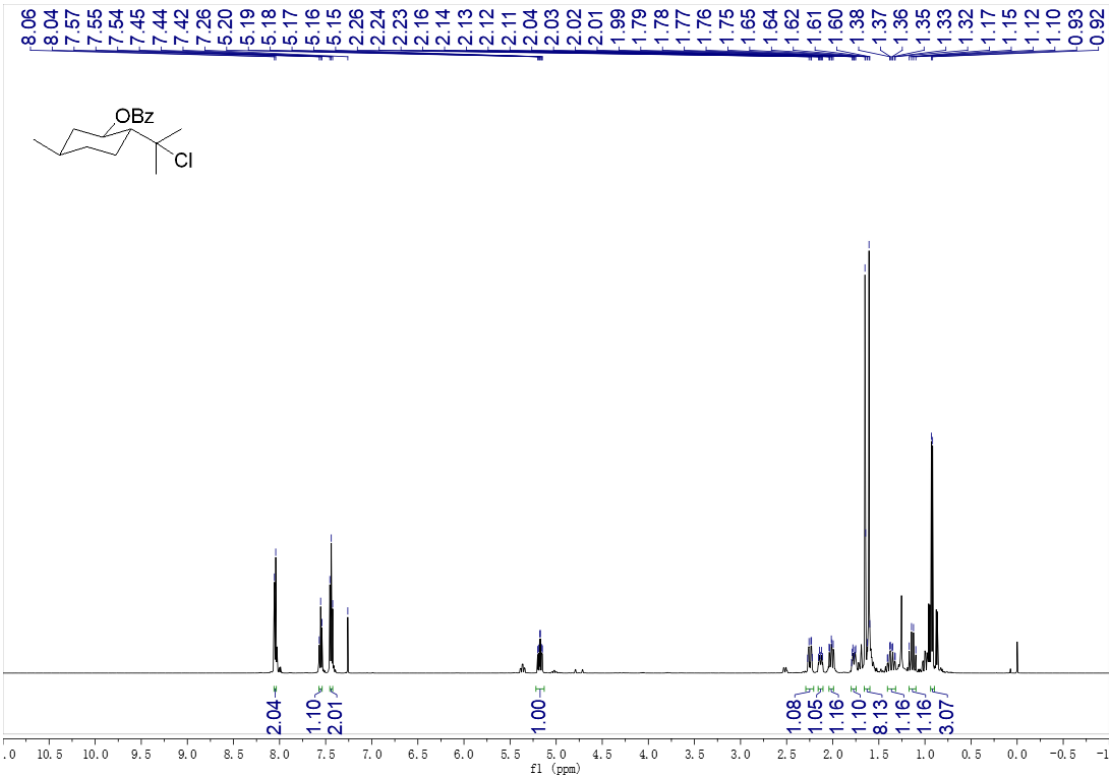
^{13}C NMR of compound **30b** (126 MHz, $CDCl_3$)



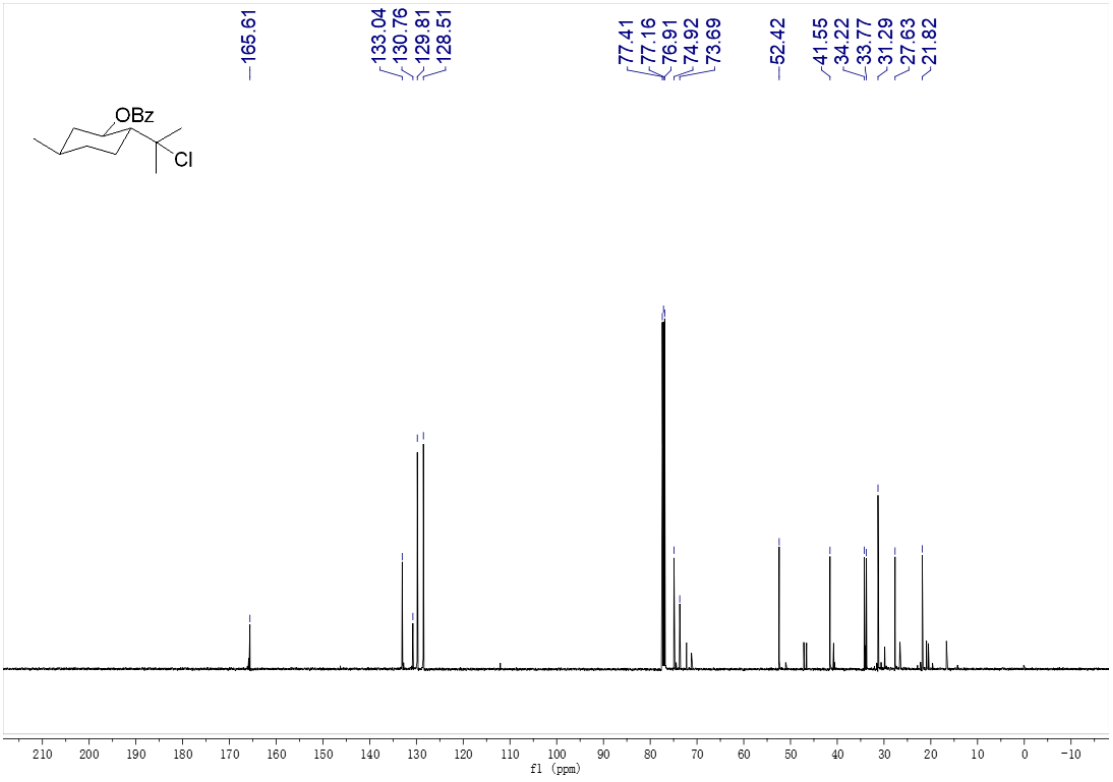
^{1}H NMR of compound **30b'** (500 MHz, $CDCl_3$)



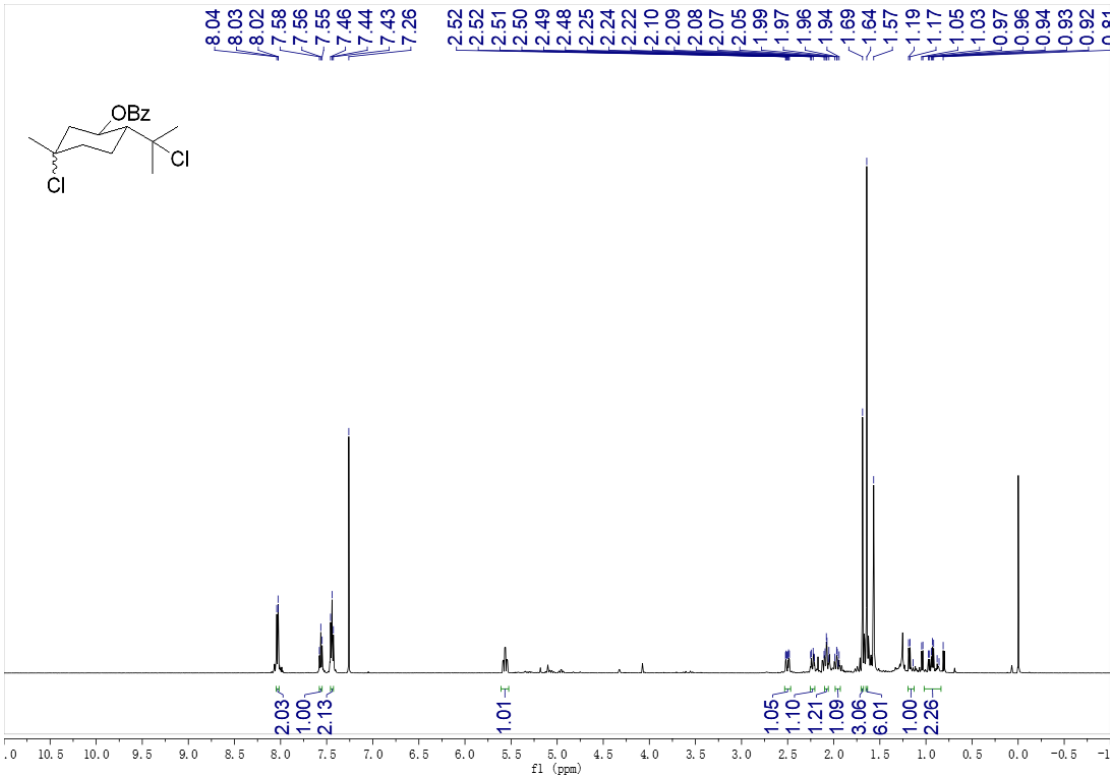
^{13}C NMR of compound **30b'** (126 MHz, $CDCl_3$)



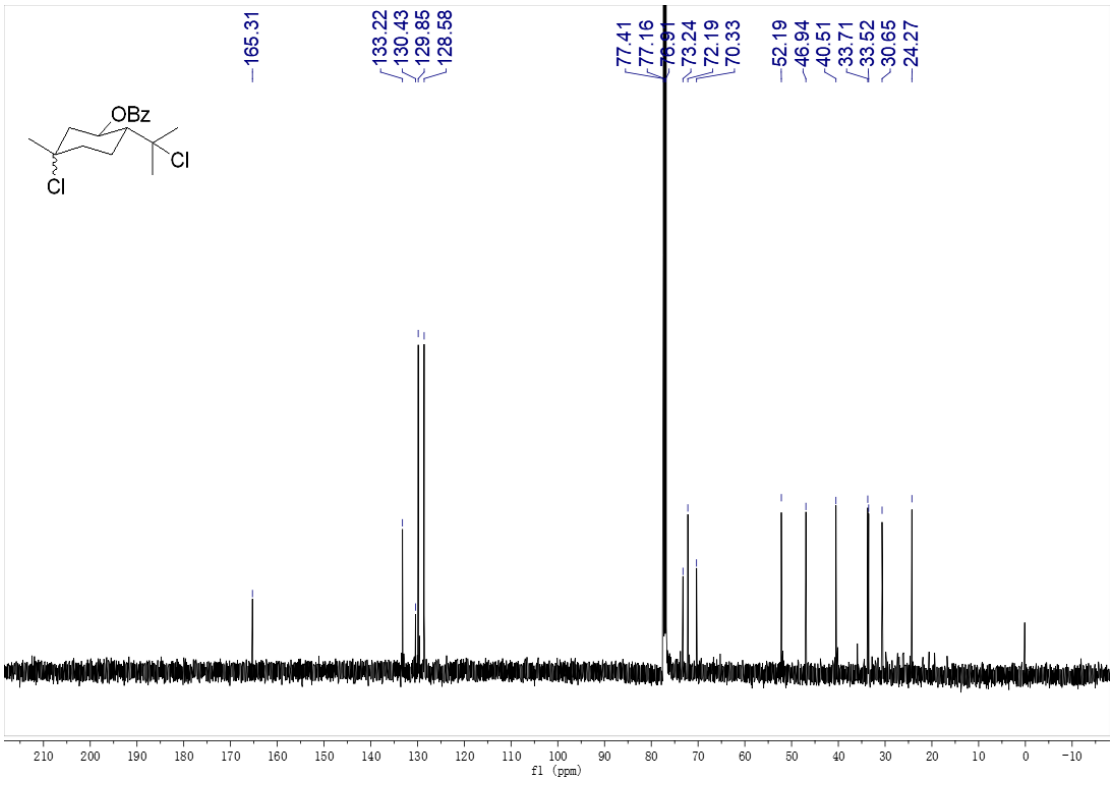
^{1}H NMR of compound **31b** (500 MHz, $CDCl_3$)



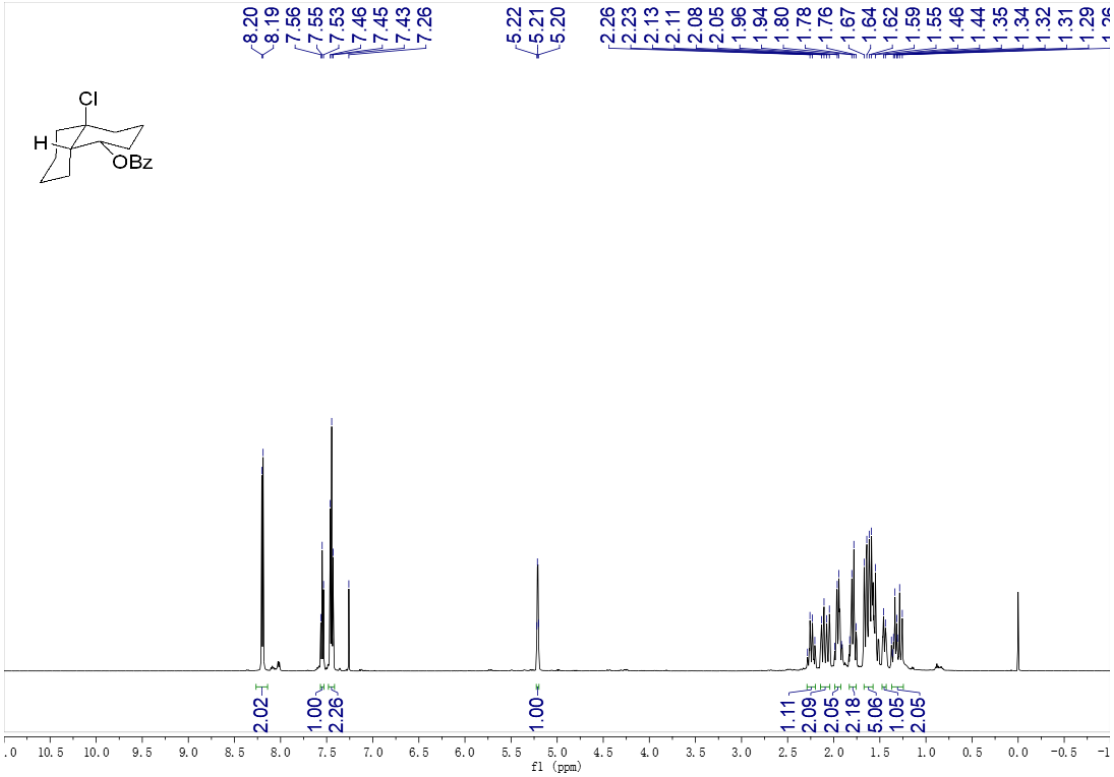
^{13}C NMR of compound **31b** (126 MHz, $CDCl_3$)



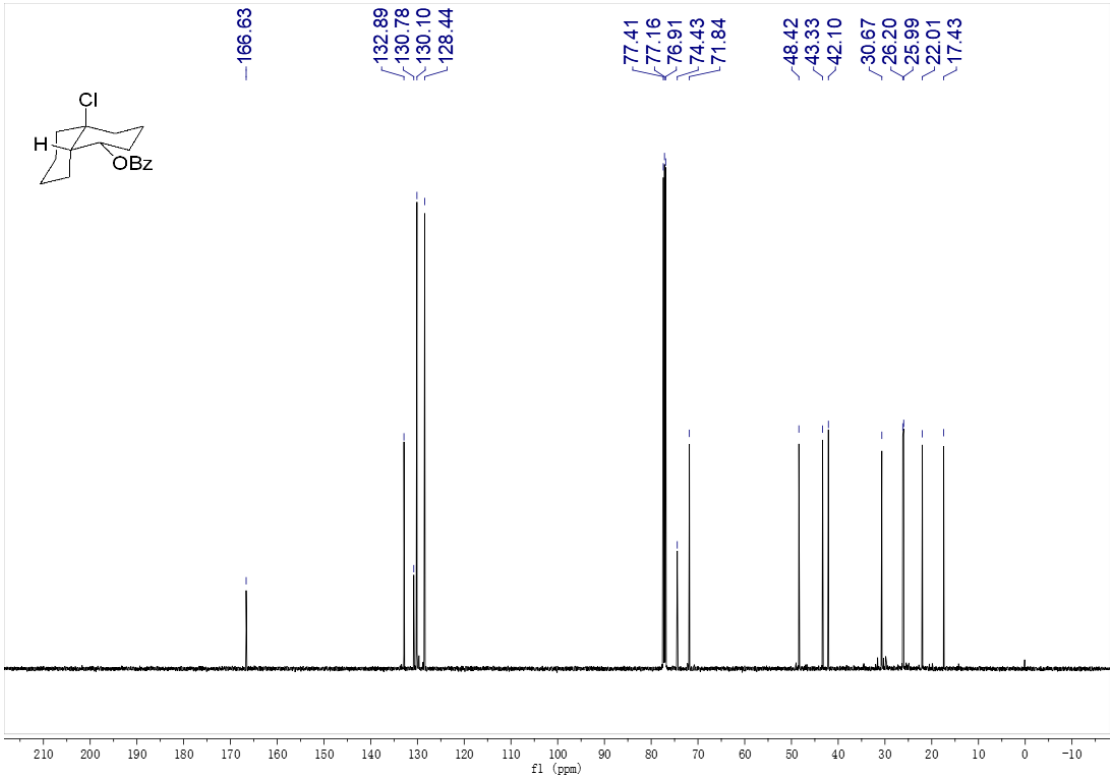
^{1}H NMR of compound **31b'** (500 MHz, $CDCl_3$)



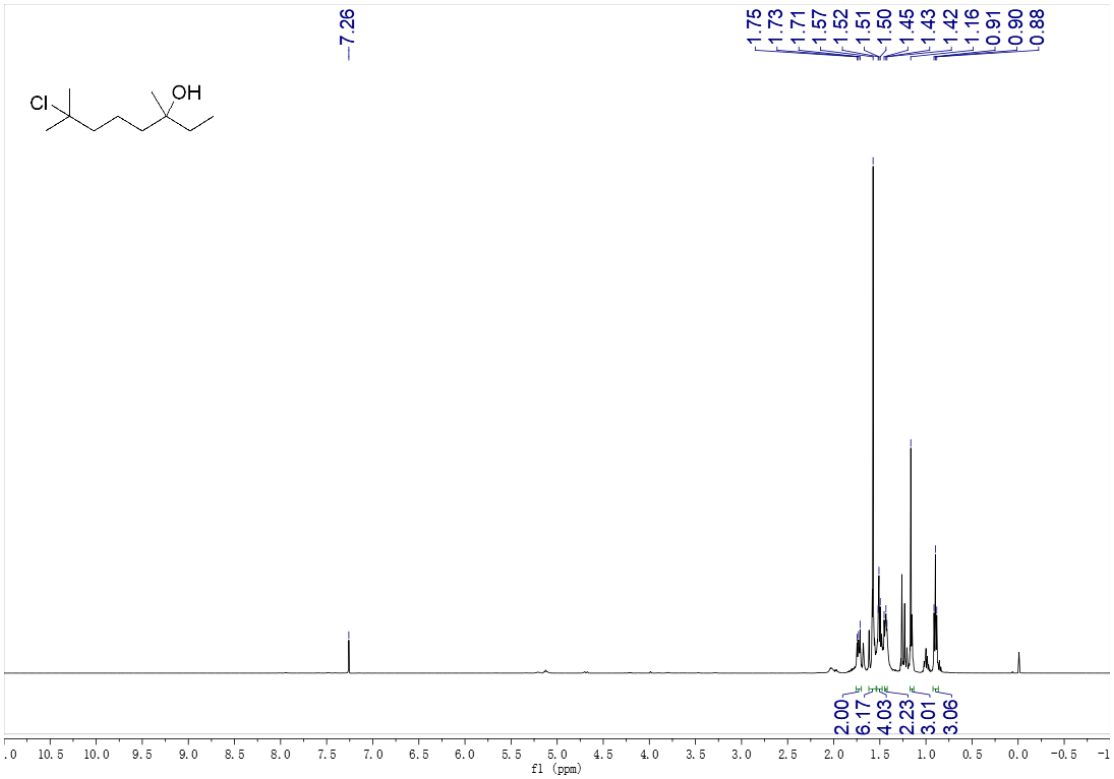
^{13}C NMR of compound **31b'** (126 MHz, $CDCl_3$)



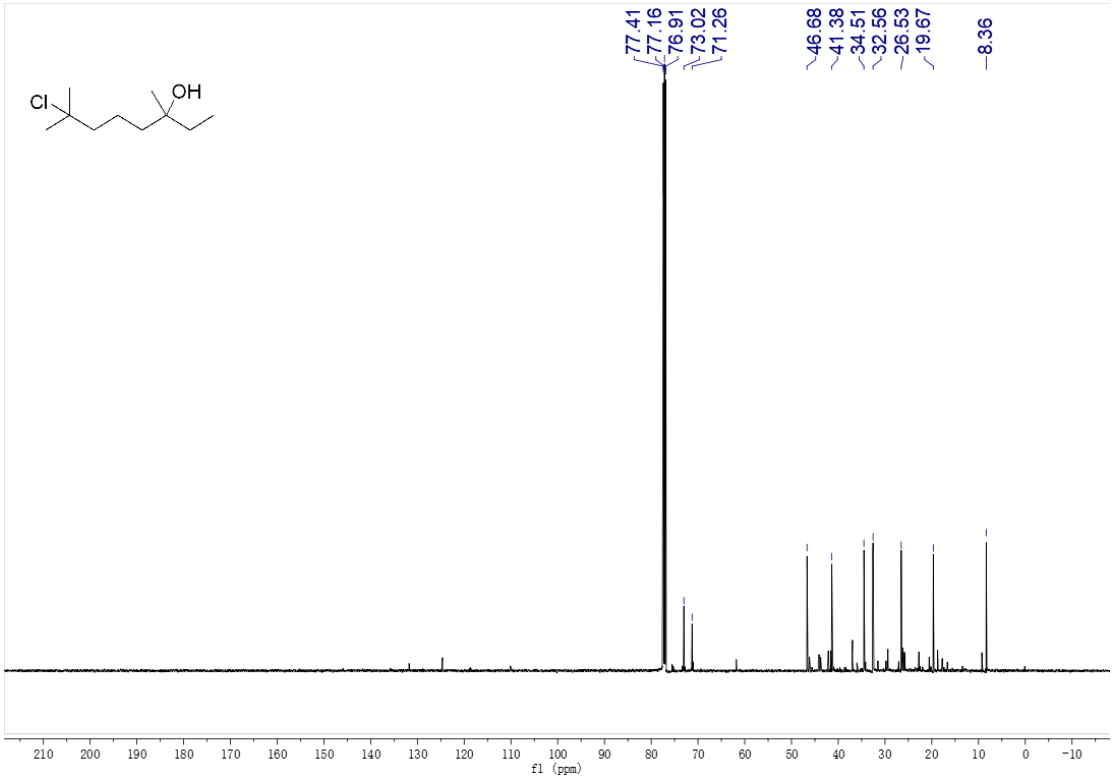
^{1}H NMR of compound **32b** (500 MHz, $CDCl_3$)



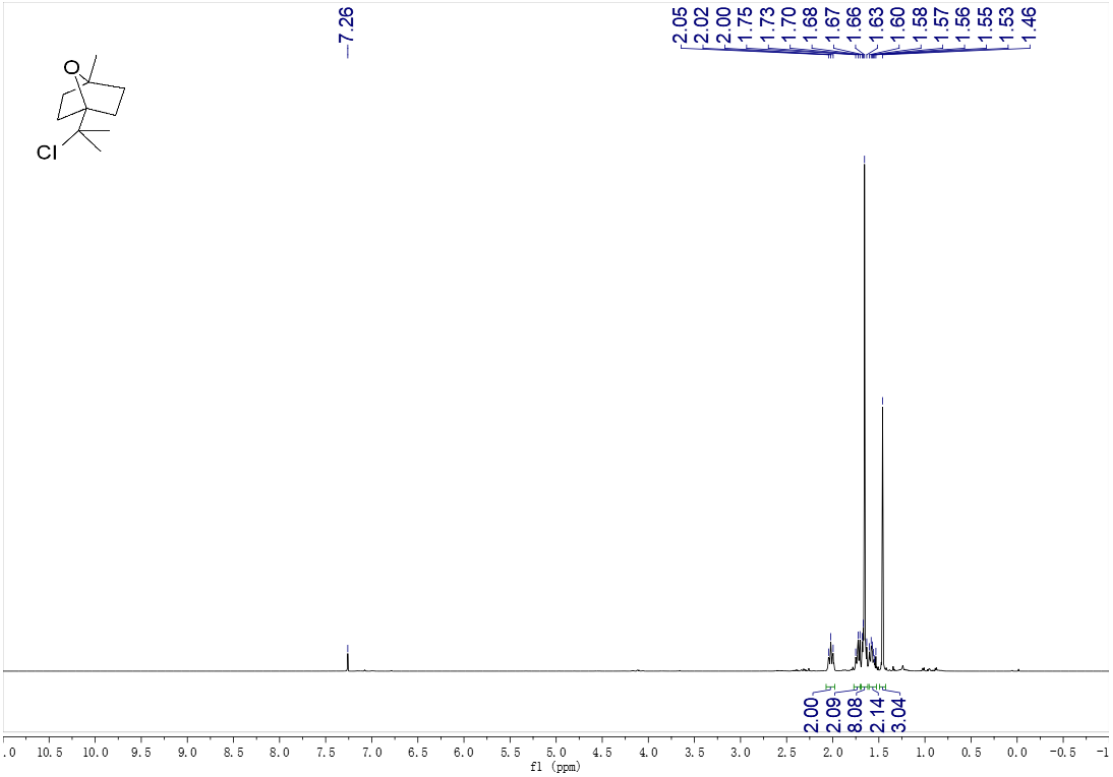
^{13}C NMR of compound **32b** (126 MHz, $CDCl_3$)



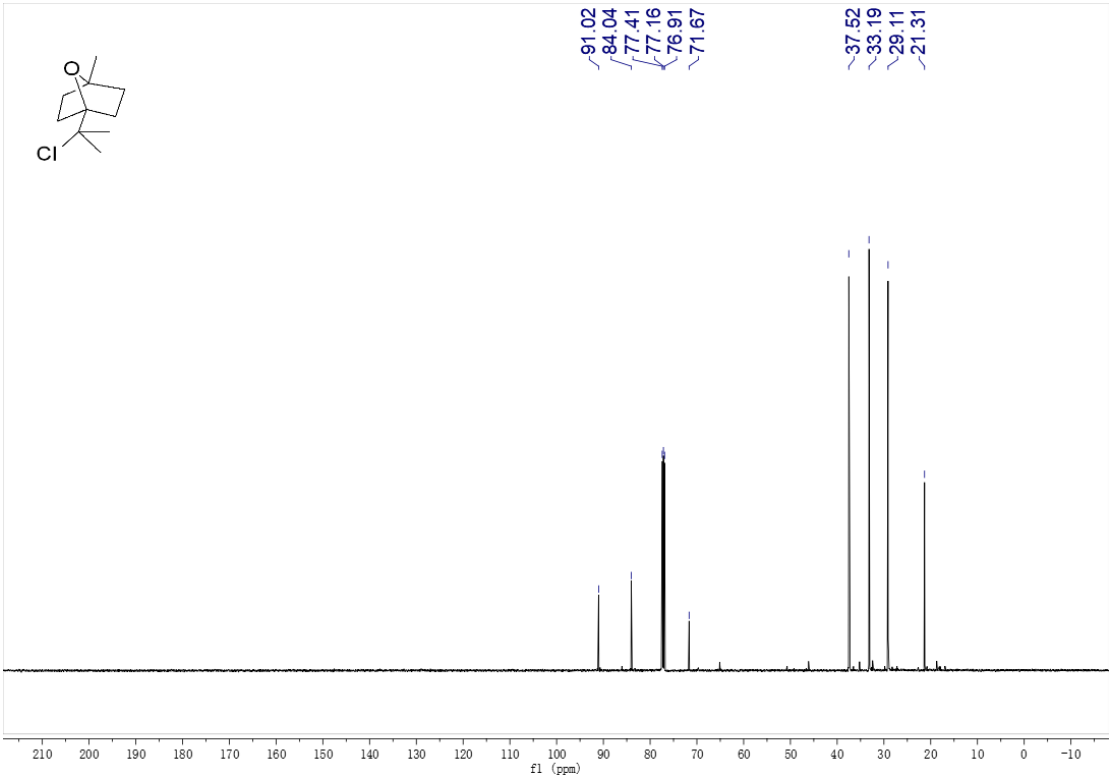
^{1}H NMR of compound **33b** (500 MHz, $CDCl_3$)



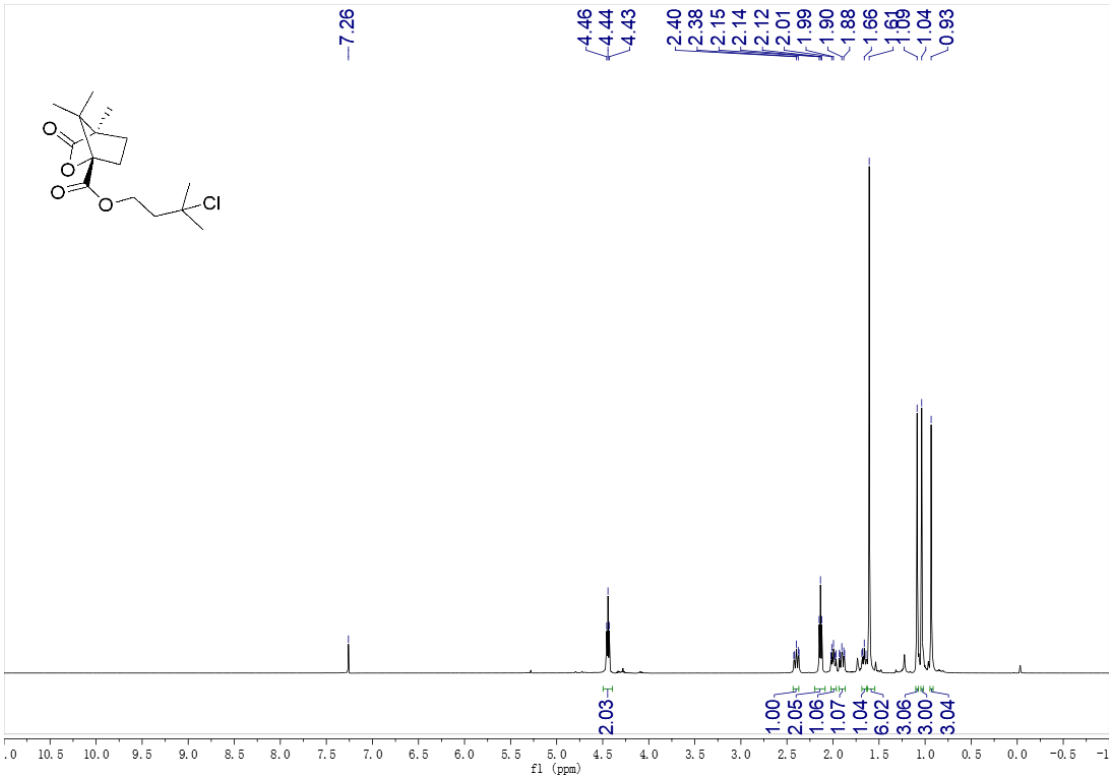
^{13}C NMR of compound **33b** (126 MHz, $CDCl_3$)



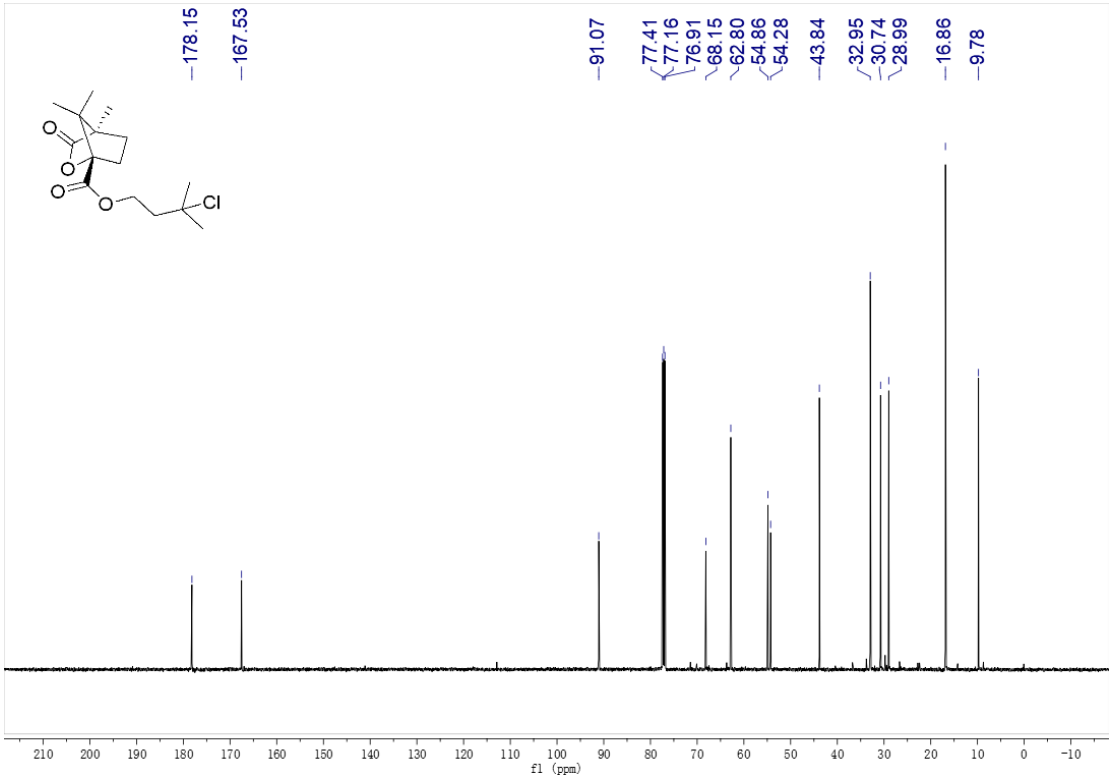
^{1}H NMR of compound **34b** (500 MHz, $CDCl_3$)



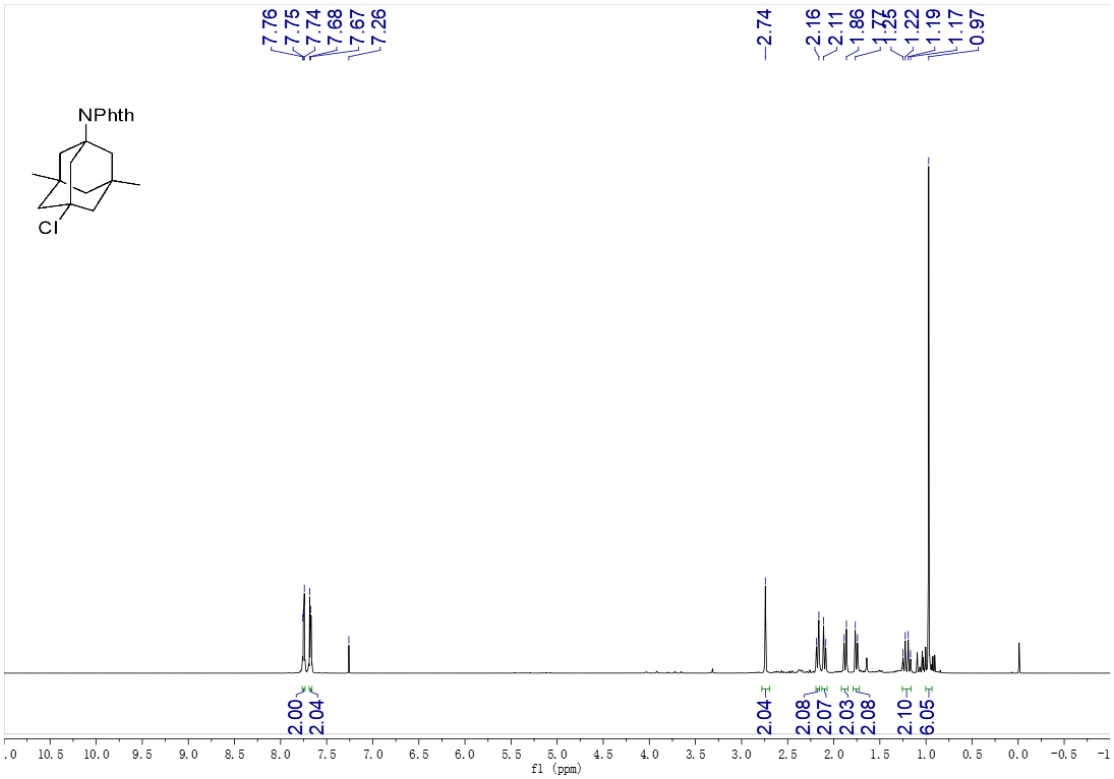
^{13}C NMR of compound **34b** (126 MHz, $CDCl_3$)



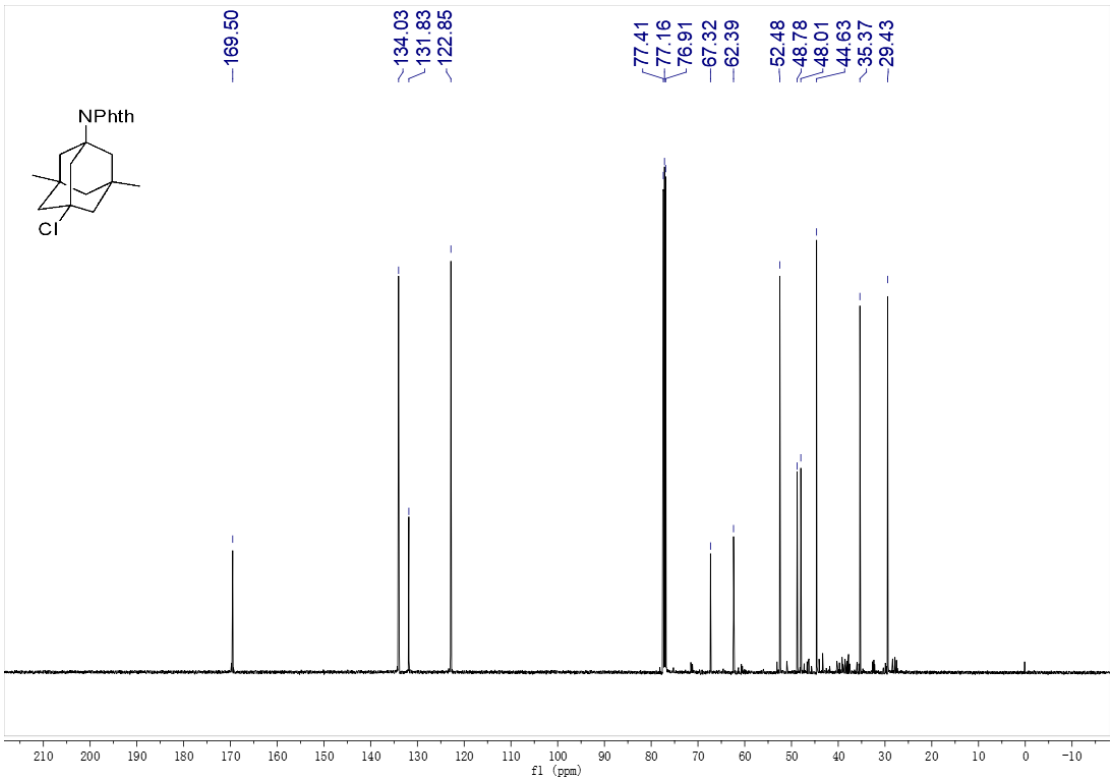
^{1}H NMR of compound **35b** (500 MHz, $CDCl_3$)



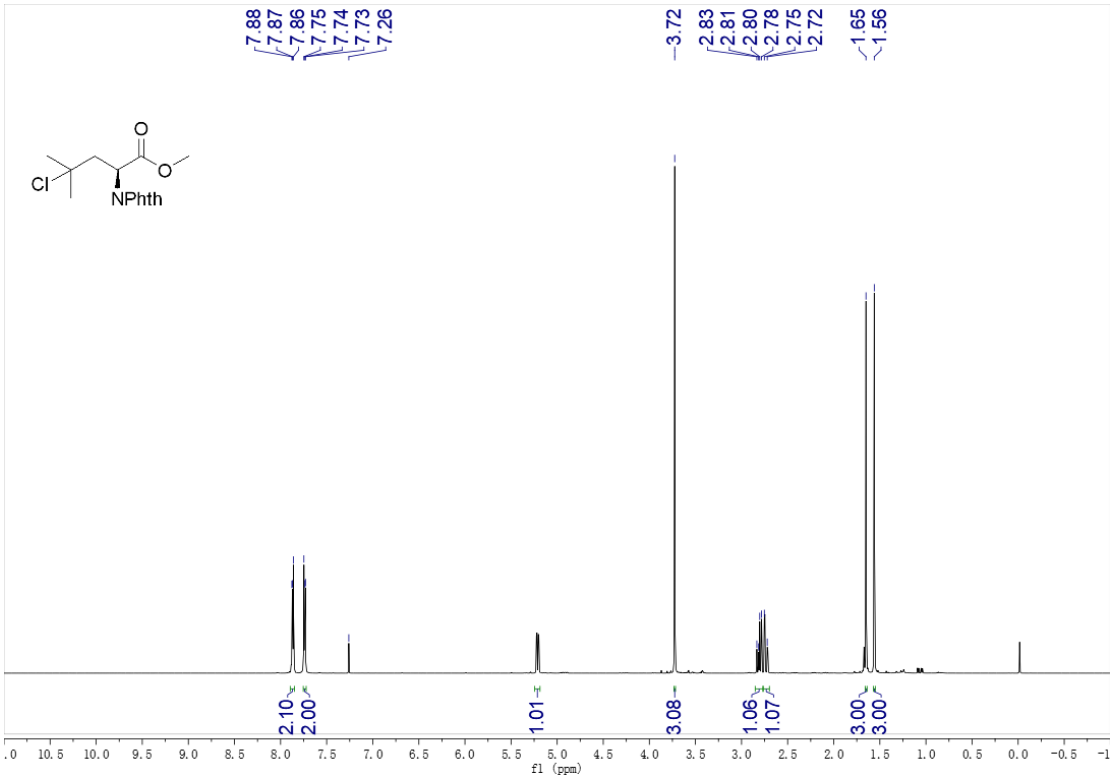
^{13}C NMR of compound **35b** (126 MHz, $CDCl_3$)



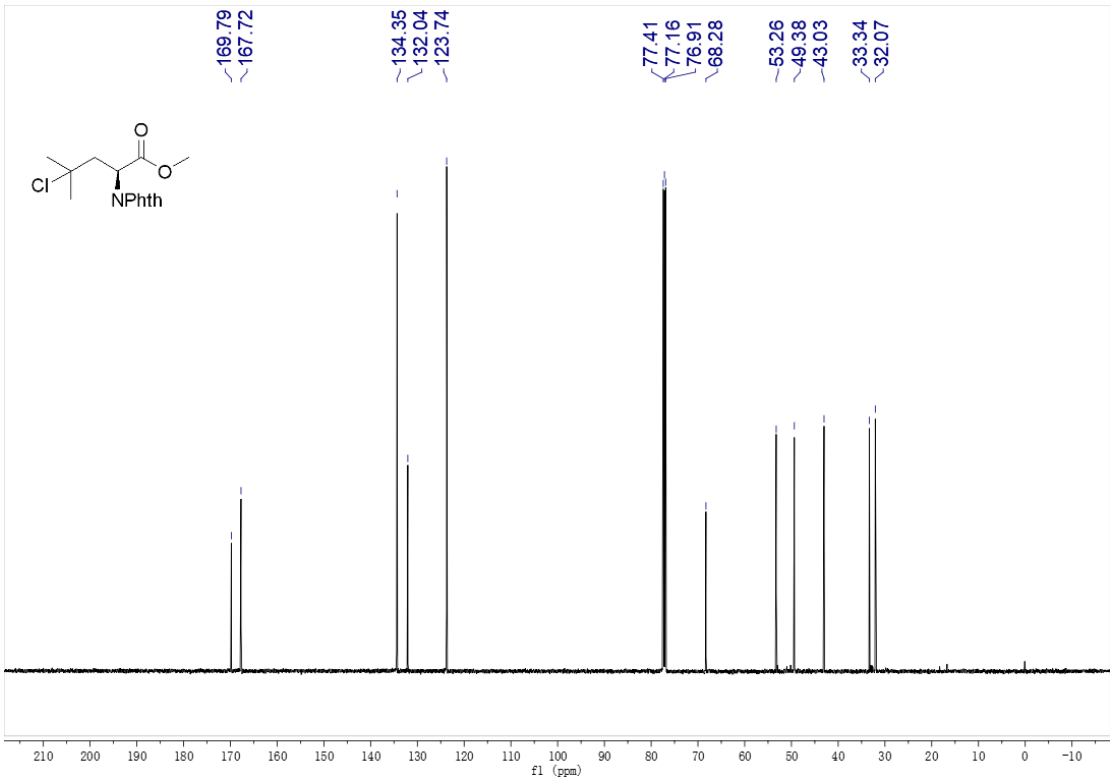
^{1}H NMR of compound **36b** (500 MHz, $CDCl_3$)



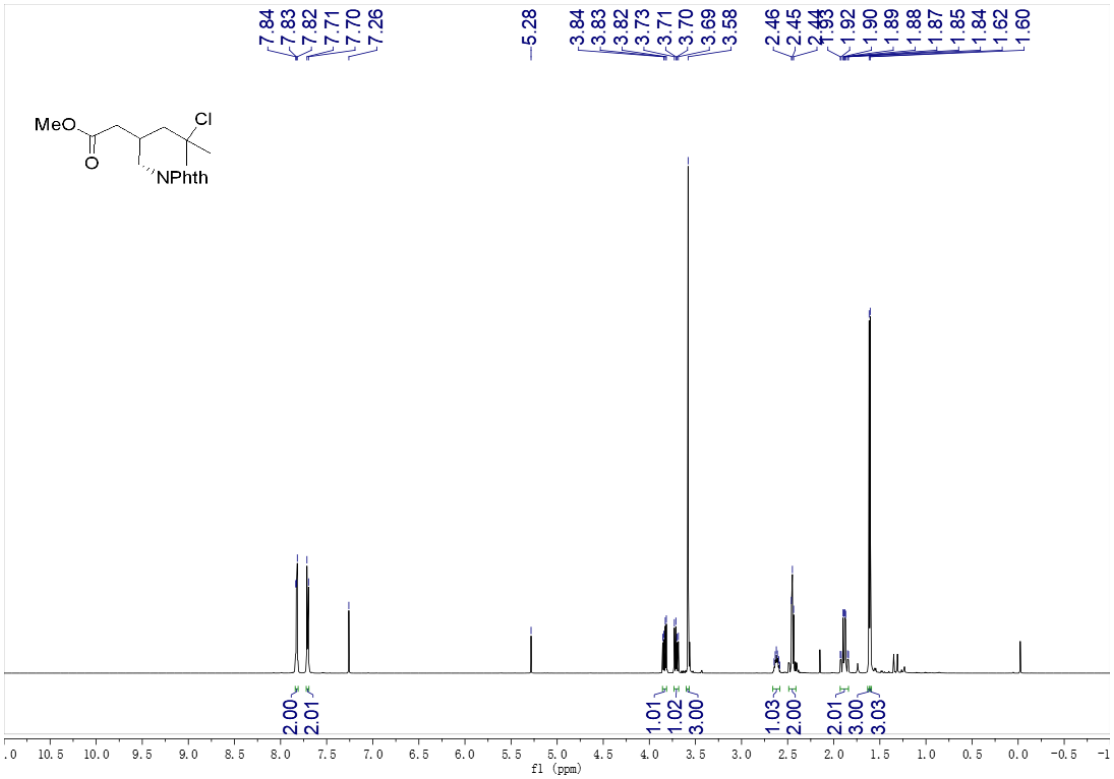
^{13}C NMR of compound **36b** (126 MHz, $CDCl_3$)



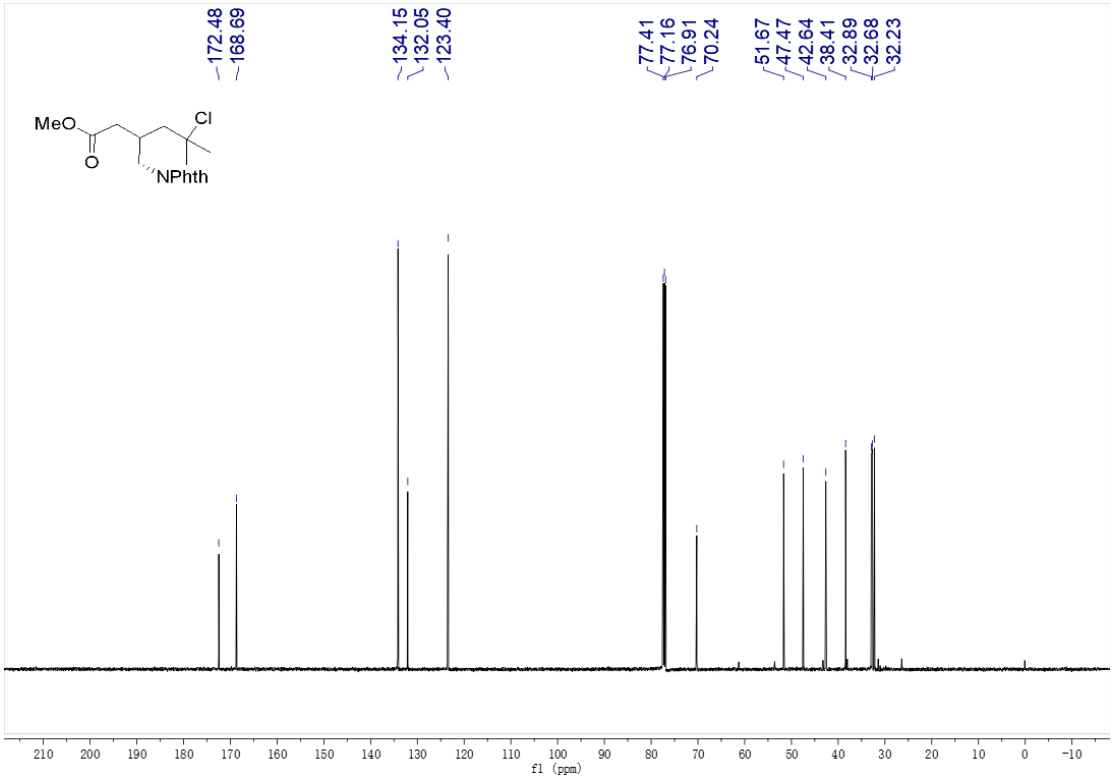
^{1}H NMR of compound **37b** (500 MHz, $CDCl_3$)



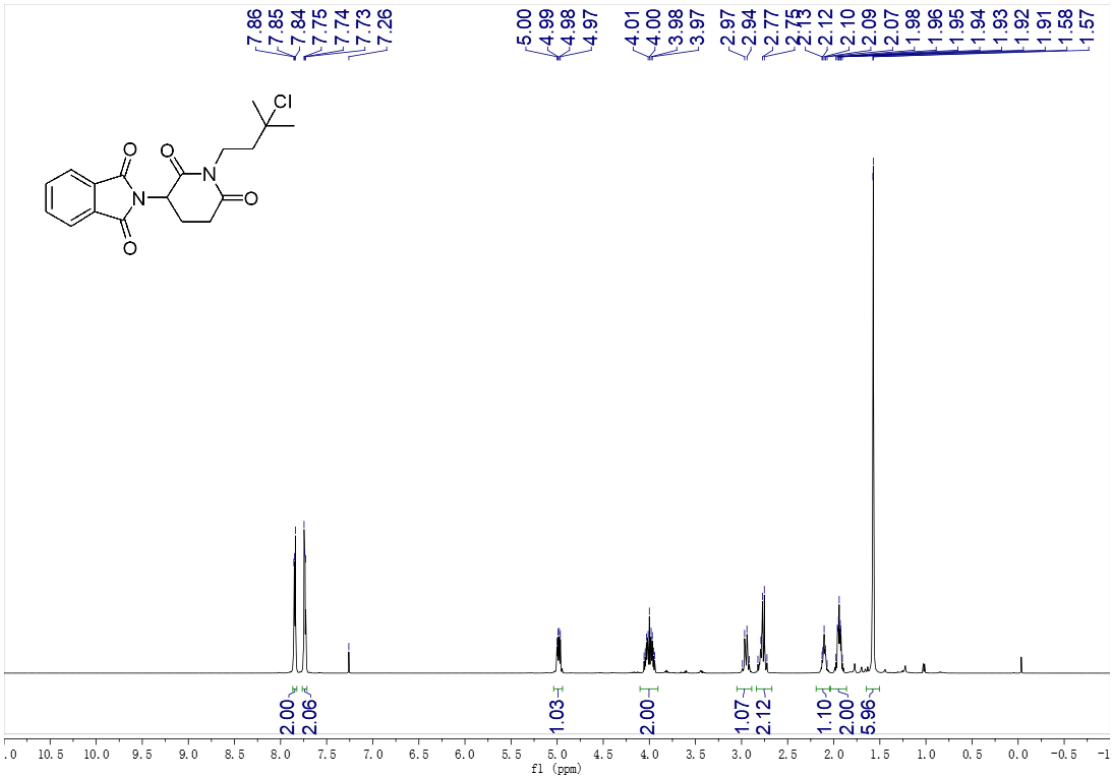
^{13}C NMR of compound **37b** (126 MHz, $CDCl_3$)



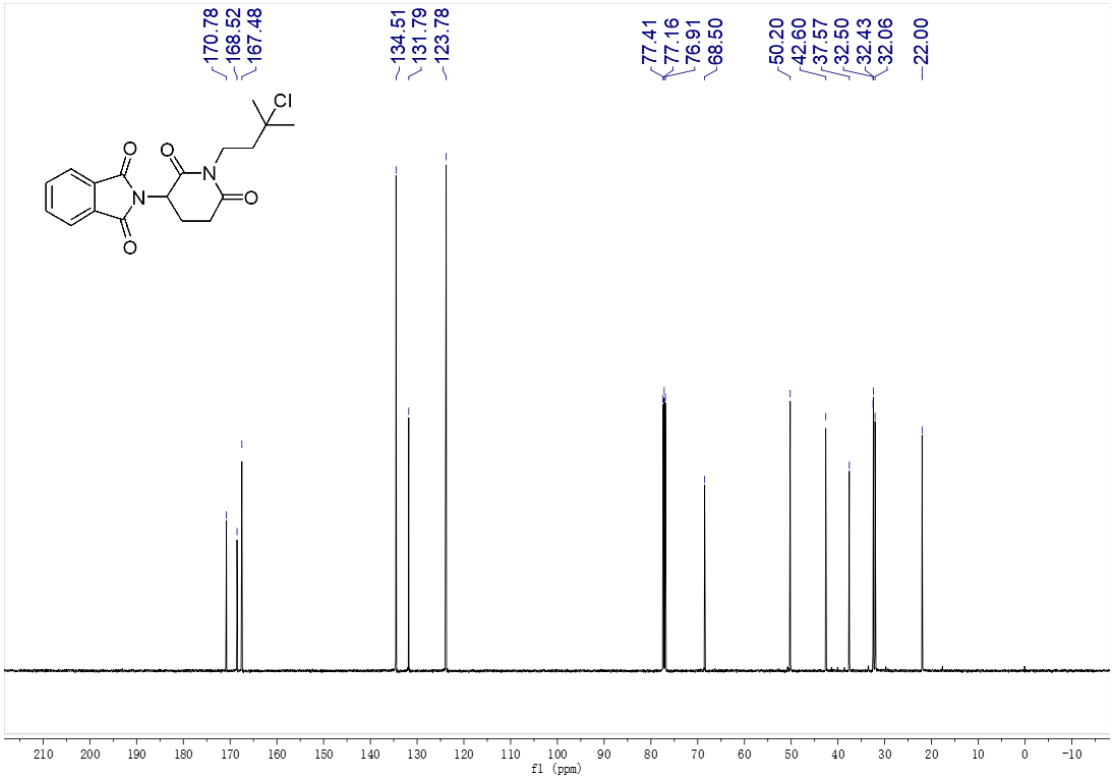
^{1}H NMR of compound **38b** (500 MHz, $CDCl_3$)



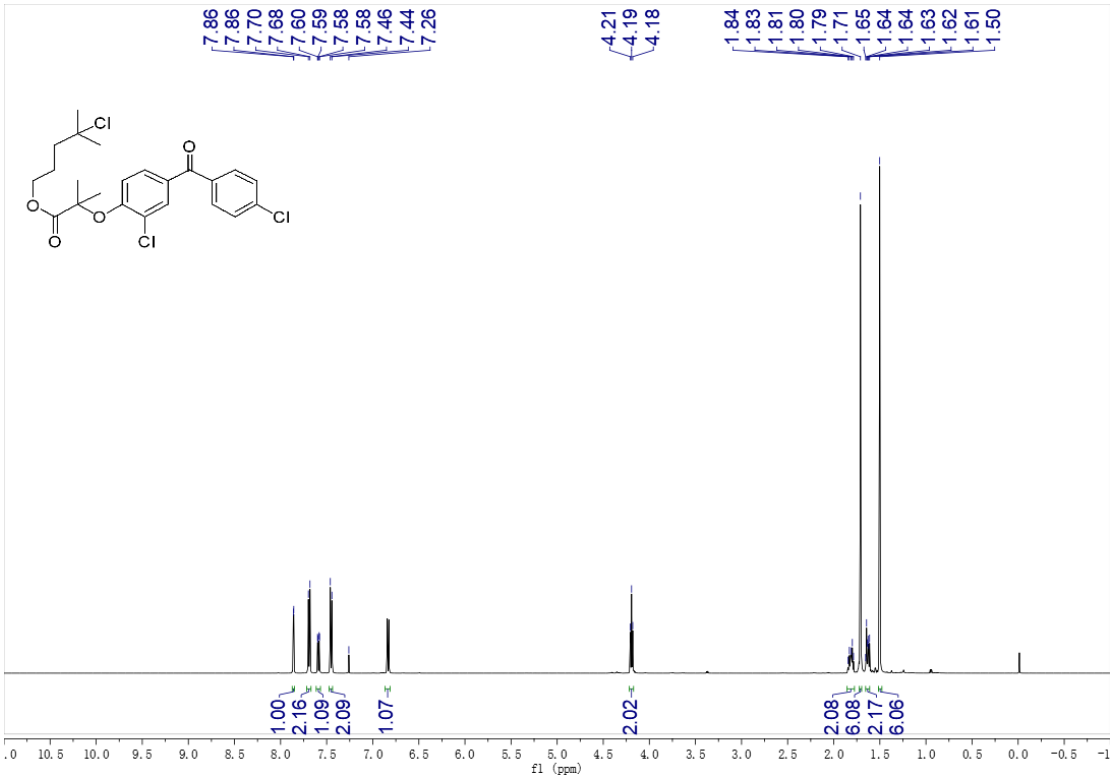
^{13}C NMR of compound **38b** (126 MHz, $CDCl_3$)



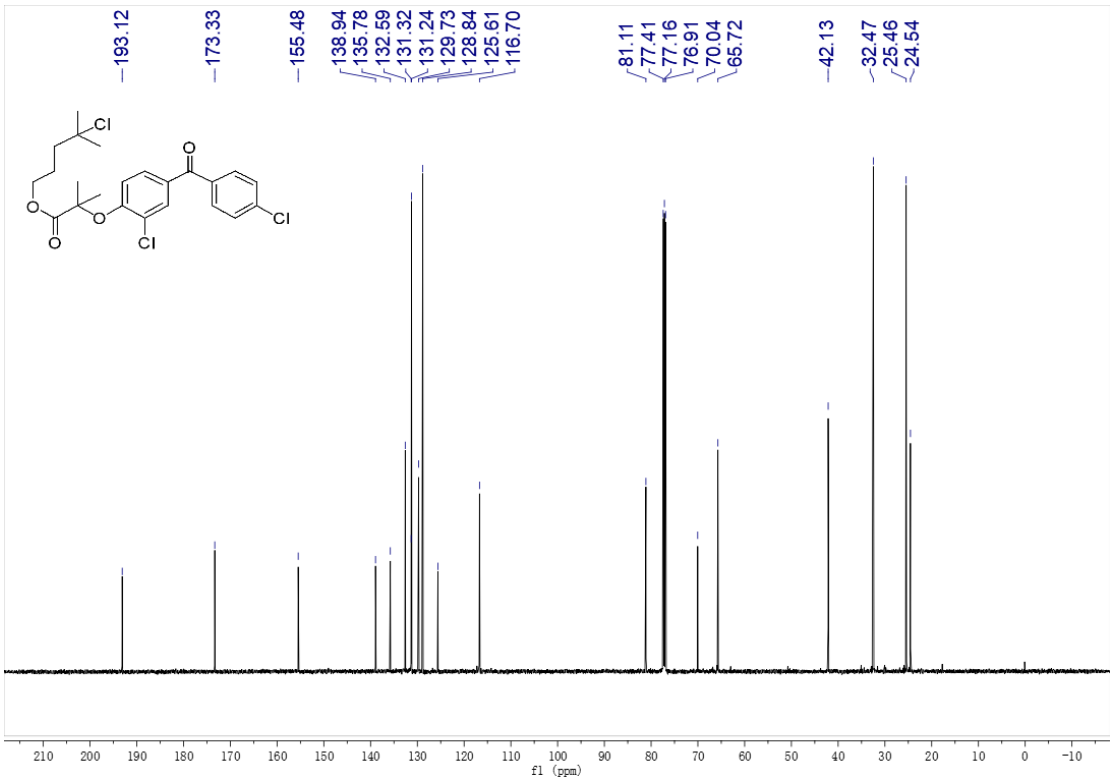
^{1}H NMR of compound **39b** (500 MHz, $CDCl_3$)



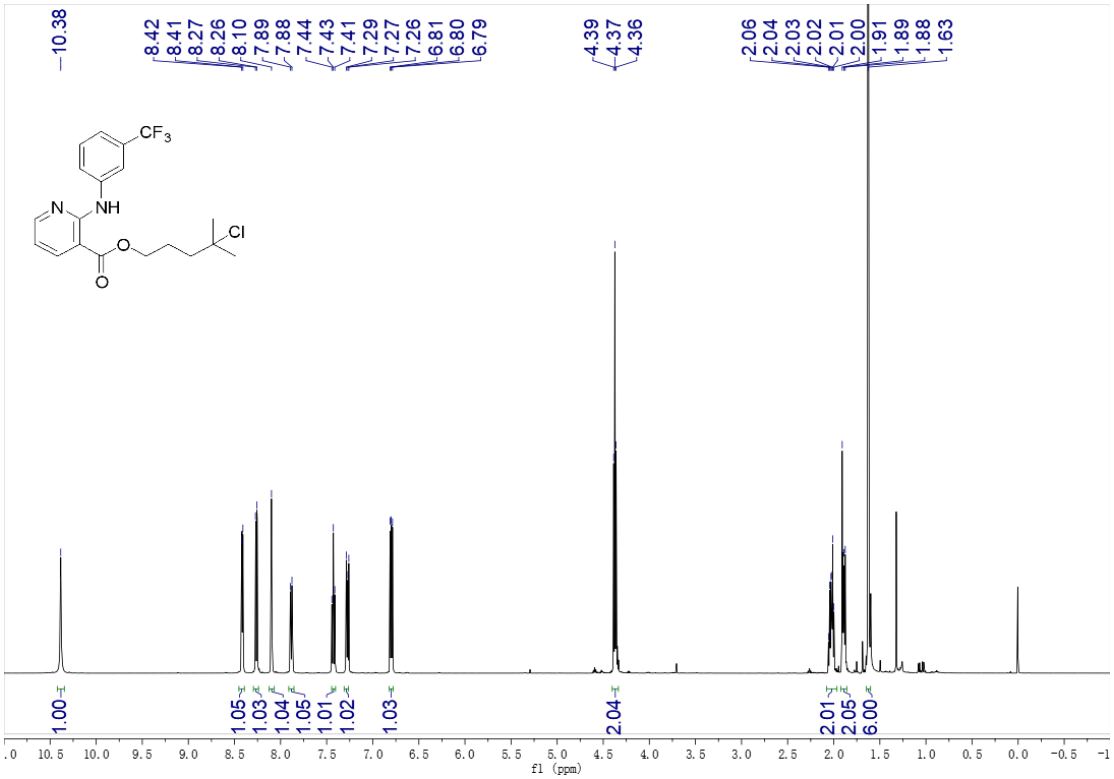
^{13}C NMR of compound **39b** (126 MHz, $CDCl_3$)



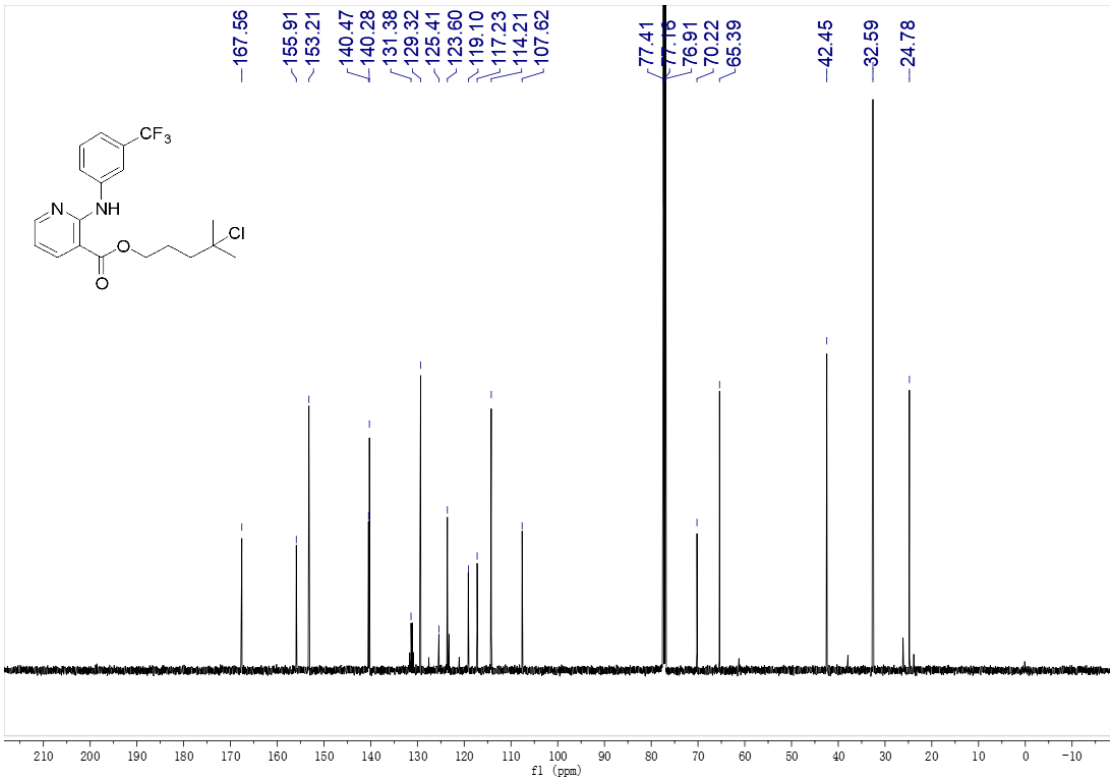
^{1}H NMR of compound **40b** (500 MHz, $CDCl_3$)



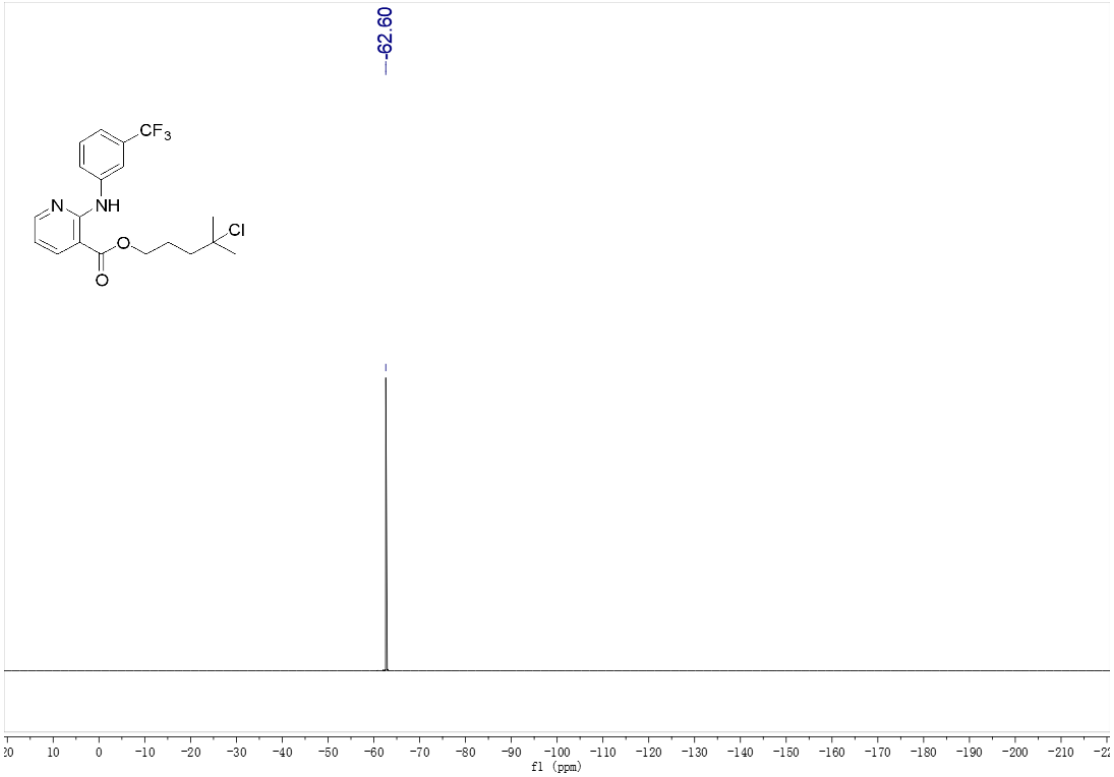
^{13}C NMR of compound **40b** (126 MHz, $CDCl_3$)



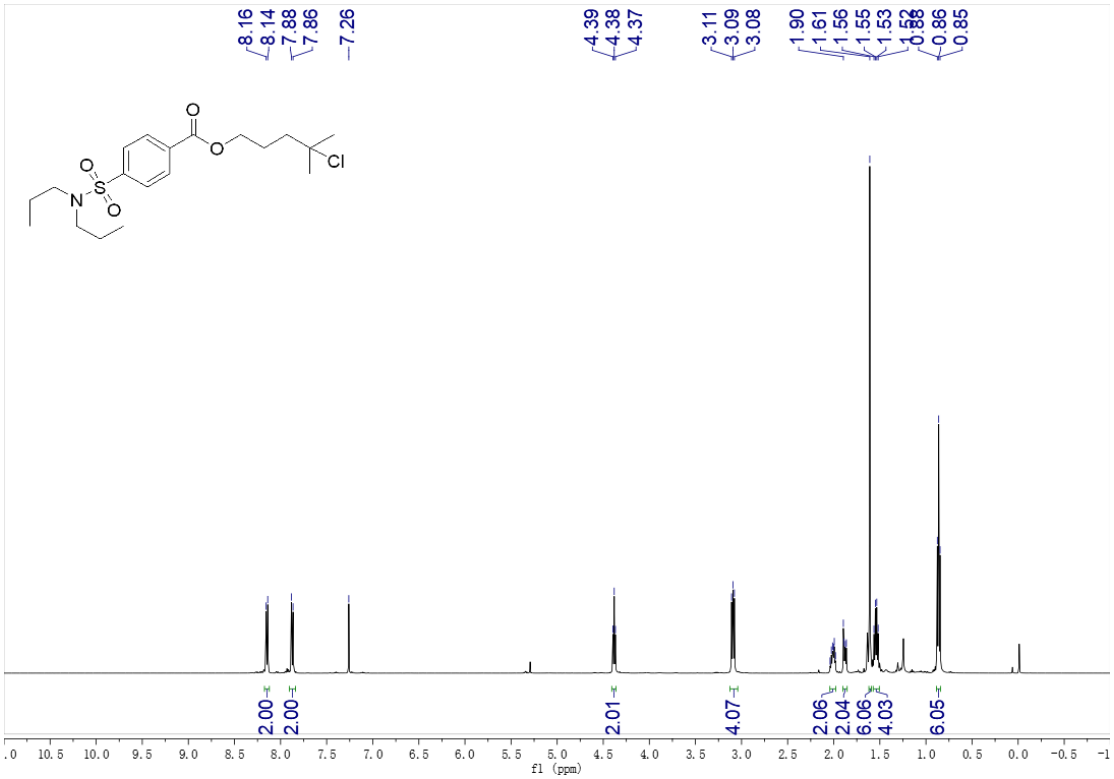
^{1}H NMR of compound **41b** (500 MHz, $CDCl_3$)



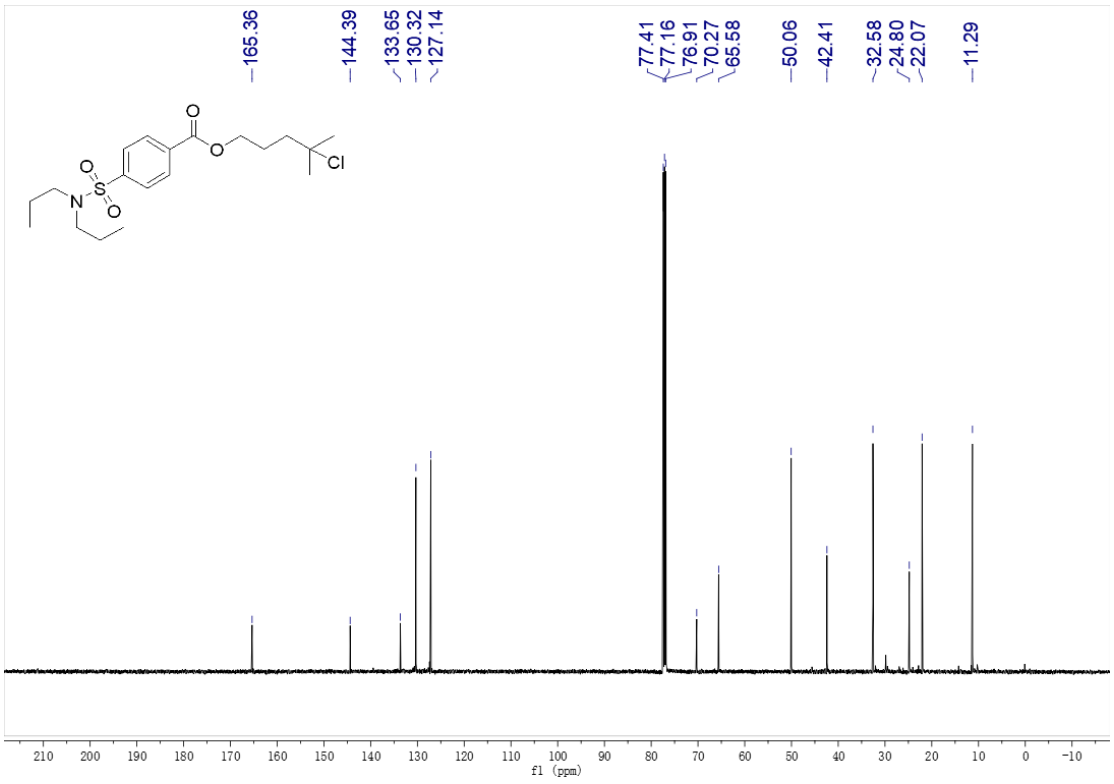
^{13}C NMR of compound **41b** (126 MHz, $CDCl_3$)



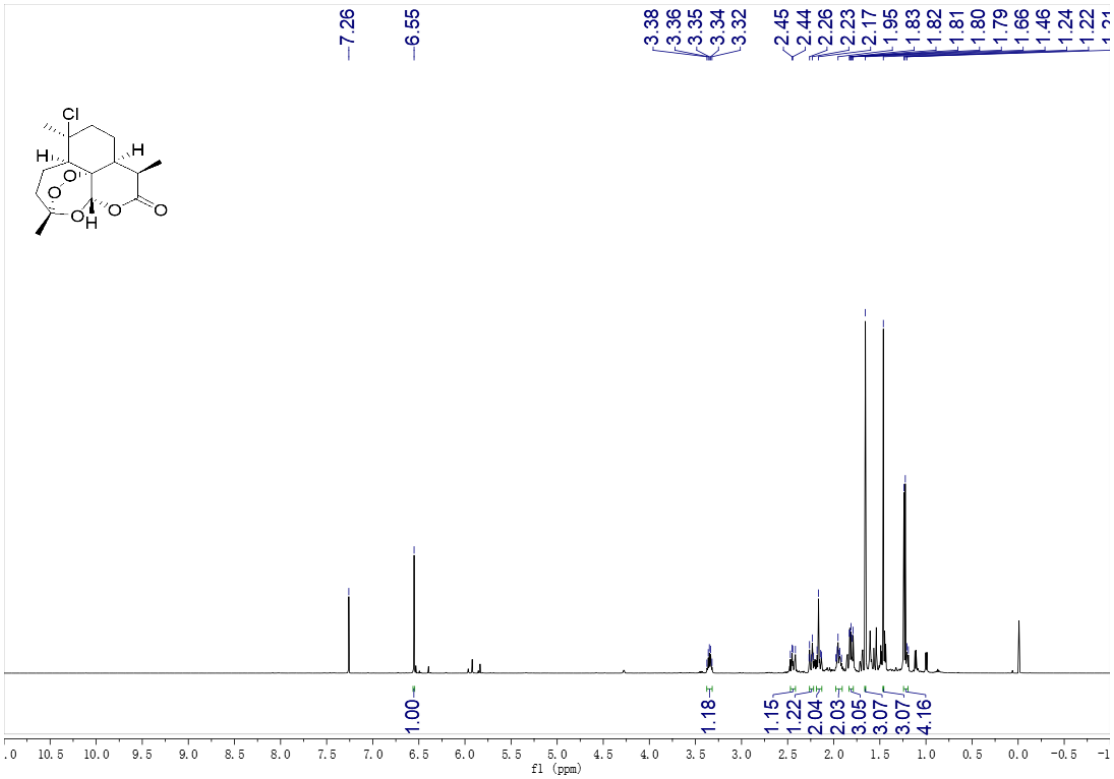
^{19}F NMR of compound **41b** (471 MHz, $CDCl_3$)



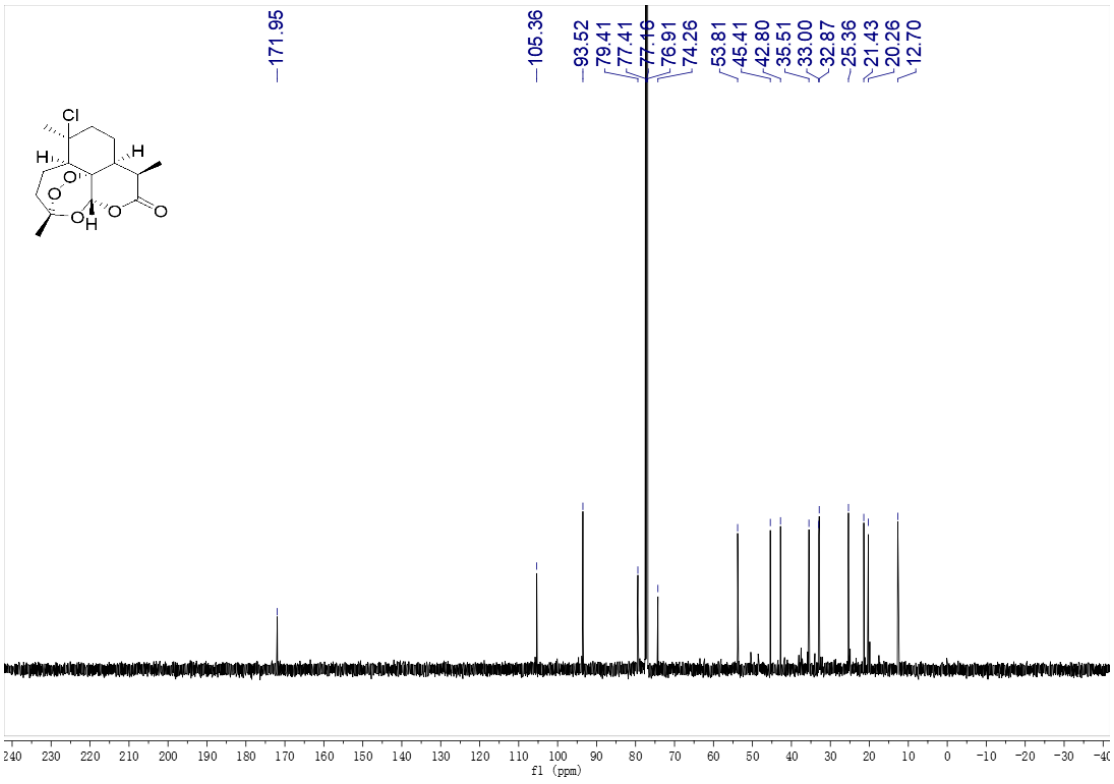
^{1}H NMR of compound **42b** (500 MHz, $CDCl_3$)



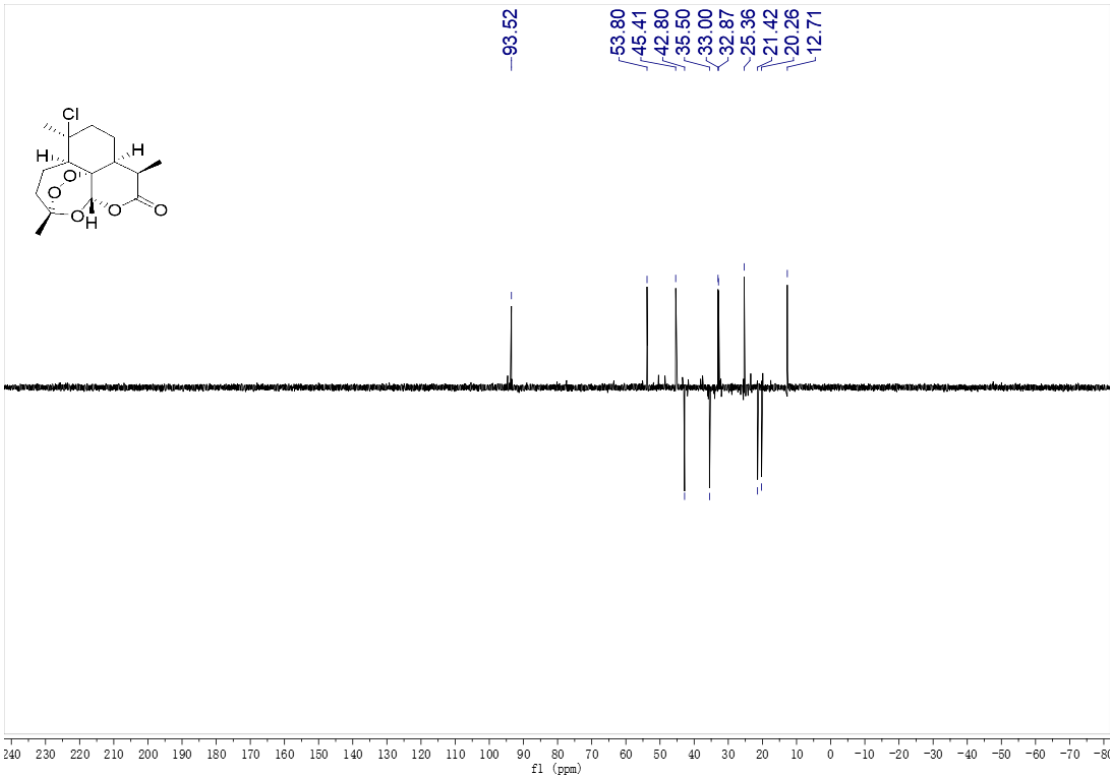
^{13}C NMR of compound **42b** (126 MHz, $CDCl_3$)



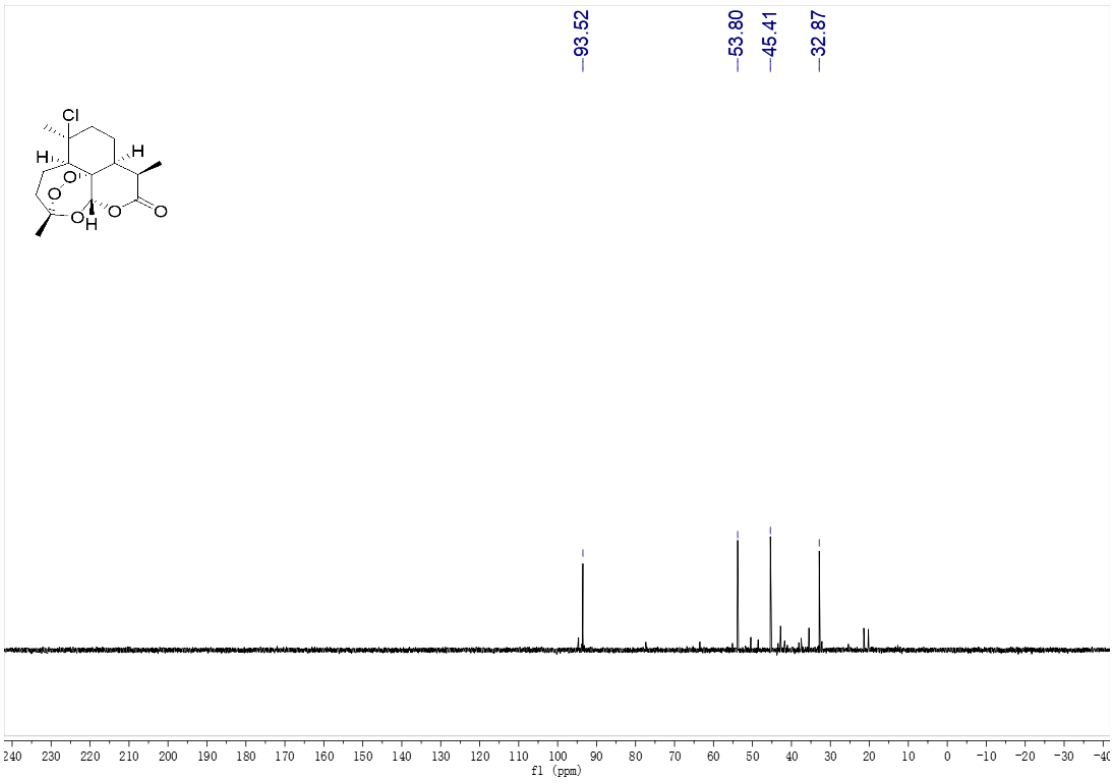
^{1}H NMR of compound **43b** (500 MHz, $CDCl_3$)



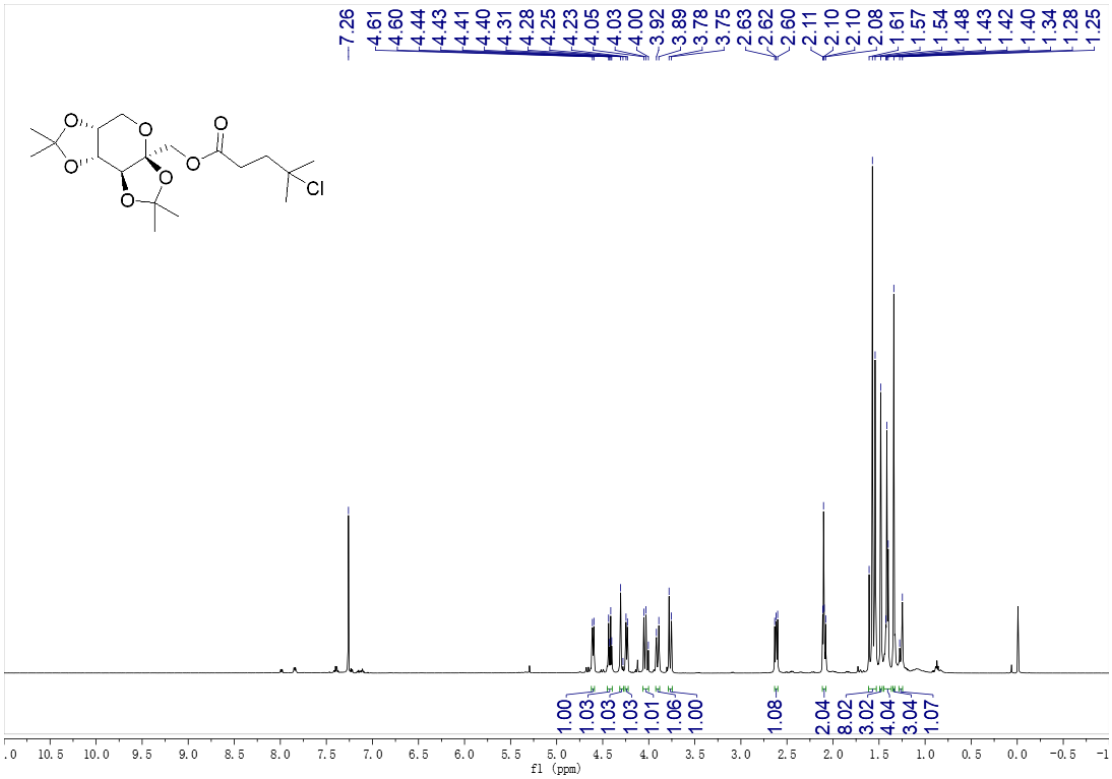
^{13}C NMR of compound **43b** (126 MHz, $CDCl_3$)



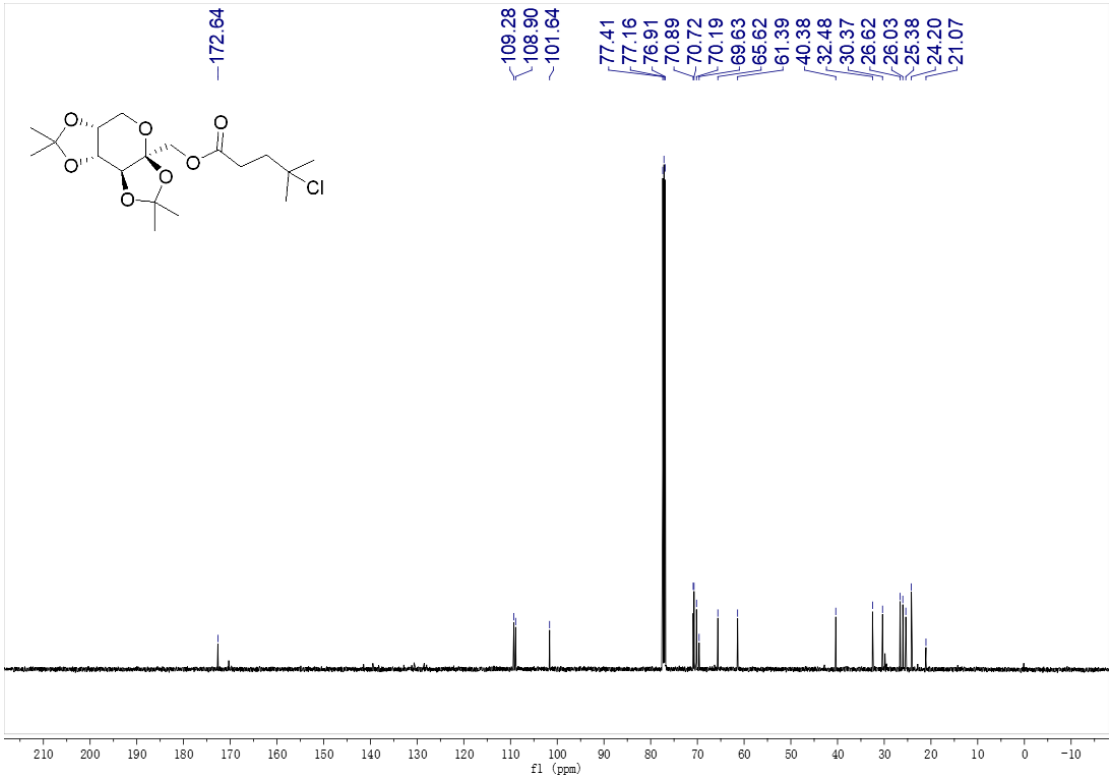
DEPT 135 of compound **43b**



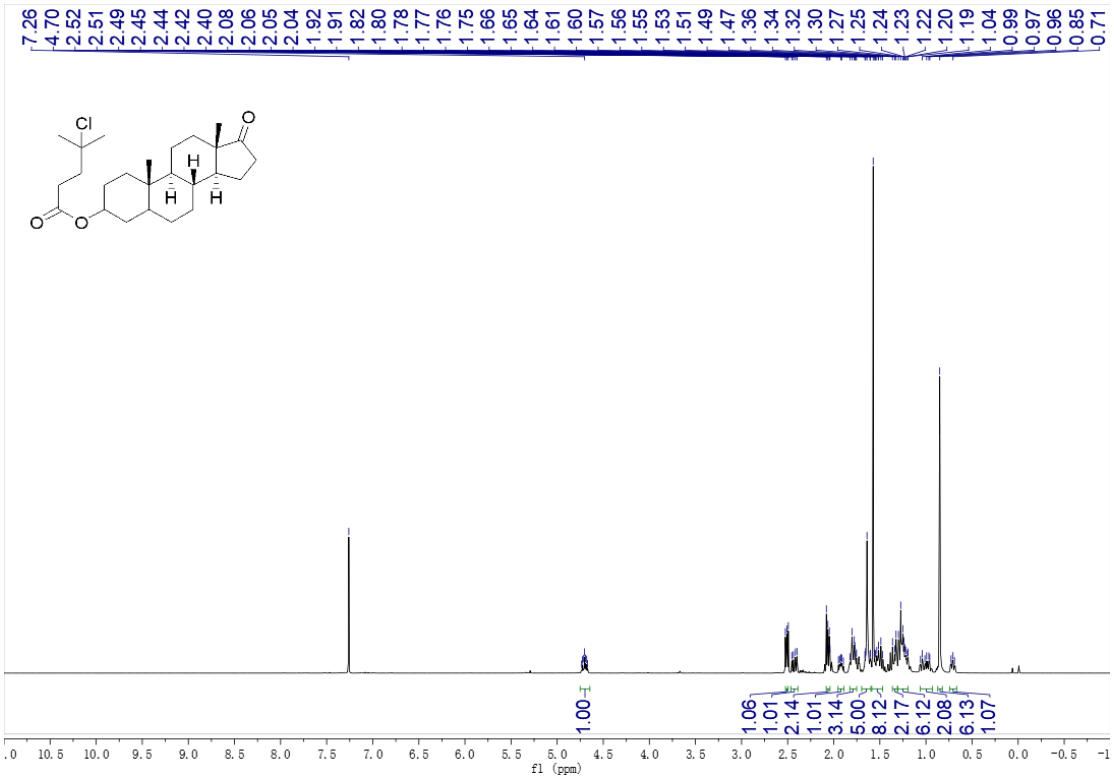
DEPT 90 of compound **43b**



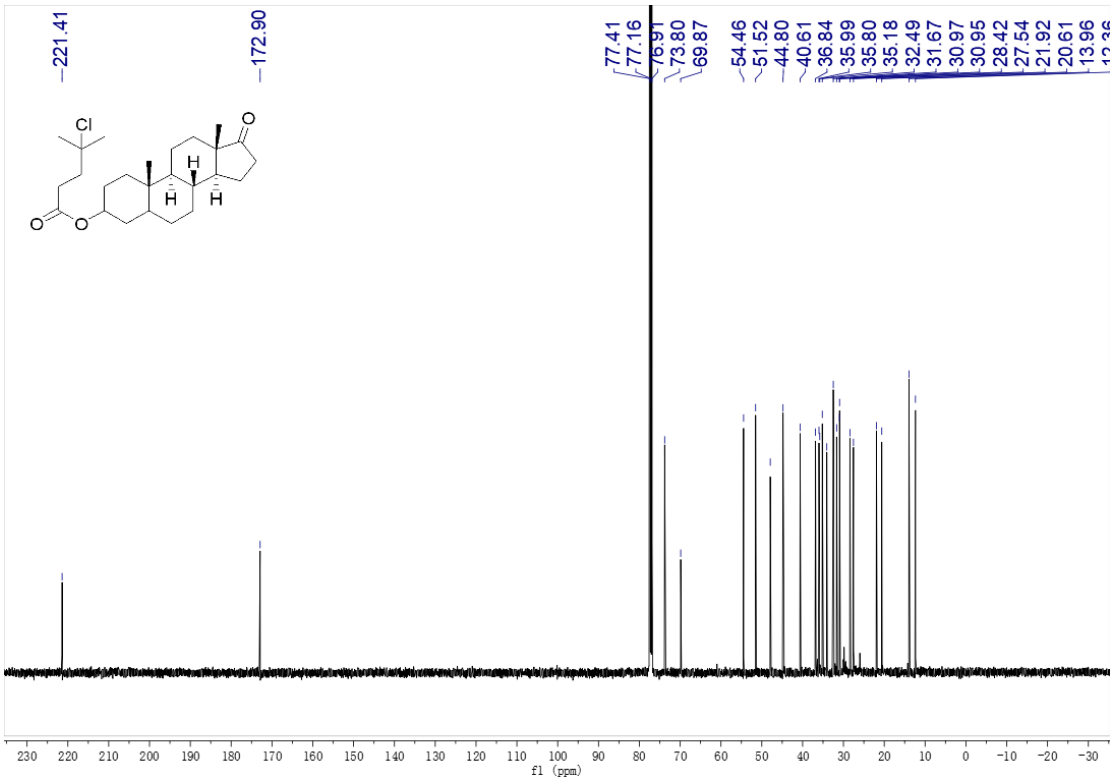
^{1}H NMR of compound **44b** (500 MHz, $CDCl_3$)



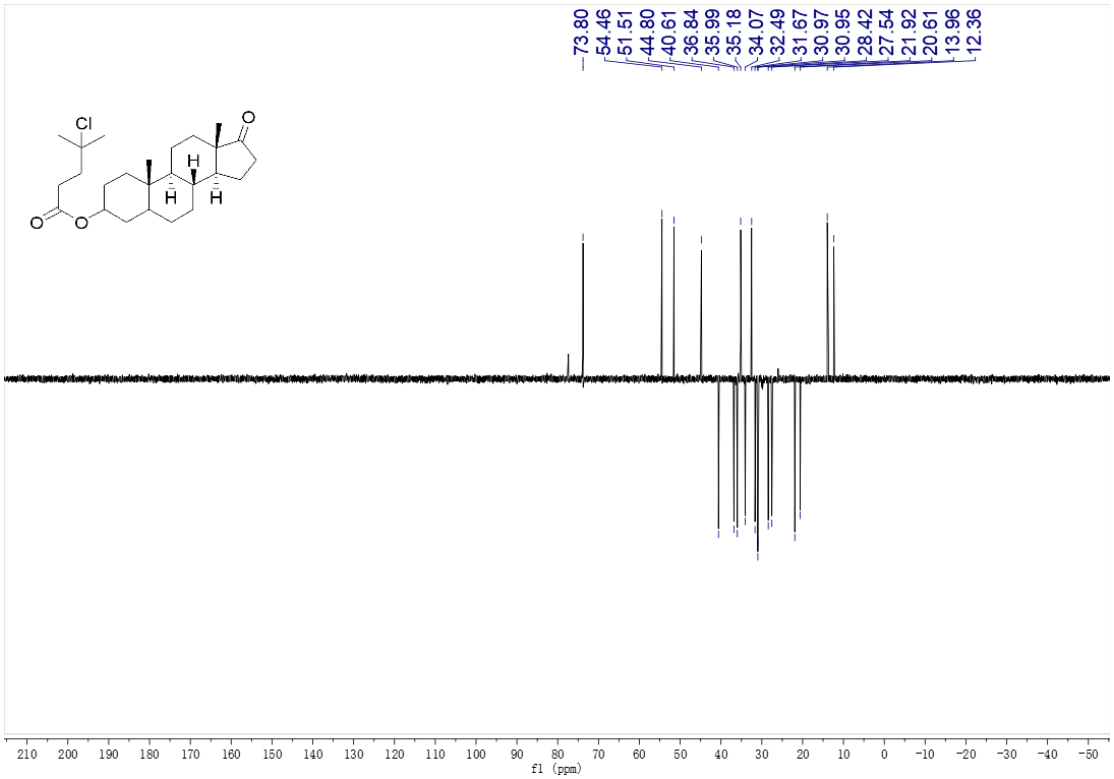
^{13}C NMR of compound **44b** (126 MHz, $CDCl_3$)



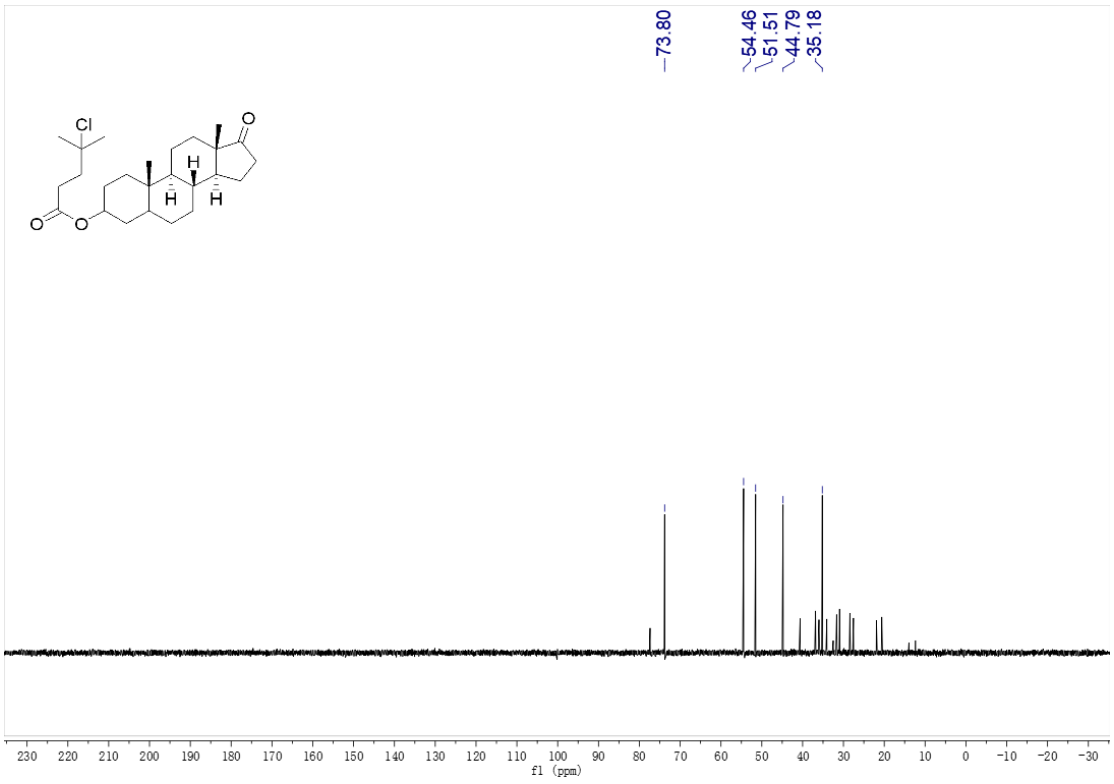
^{1}H NMR of compound **45b** (500 MHz, $CDCl_3$)



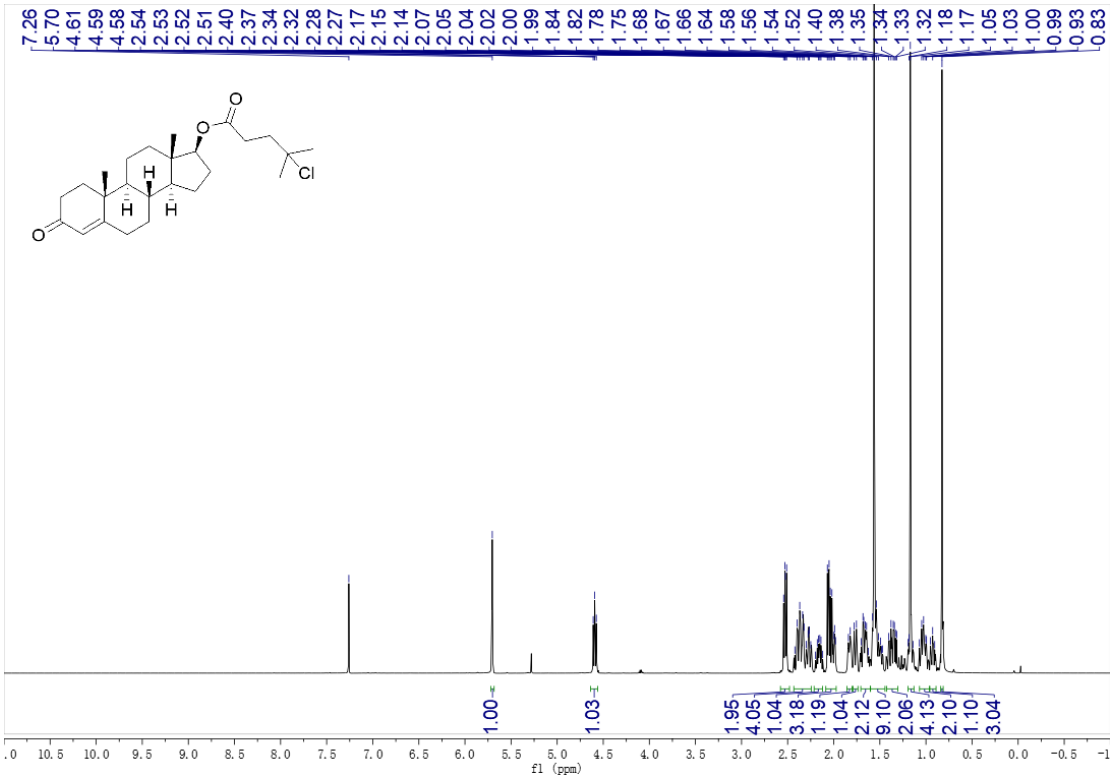
^{13}C NMR of compound **45b** (126 MHz, $CDCl_3$)



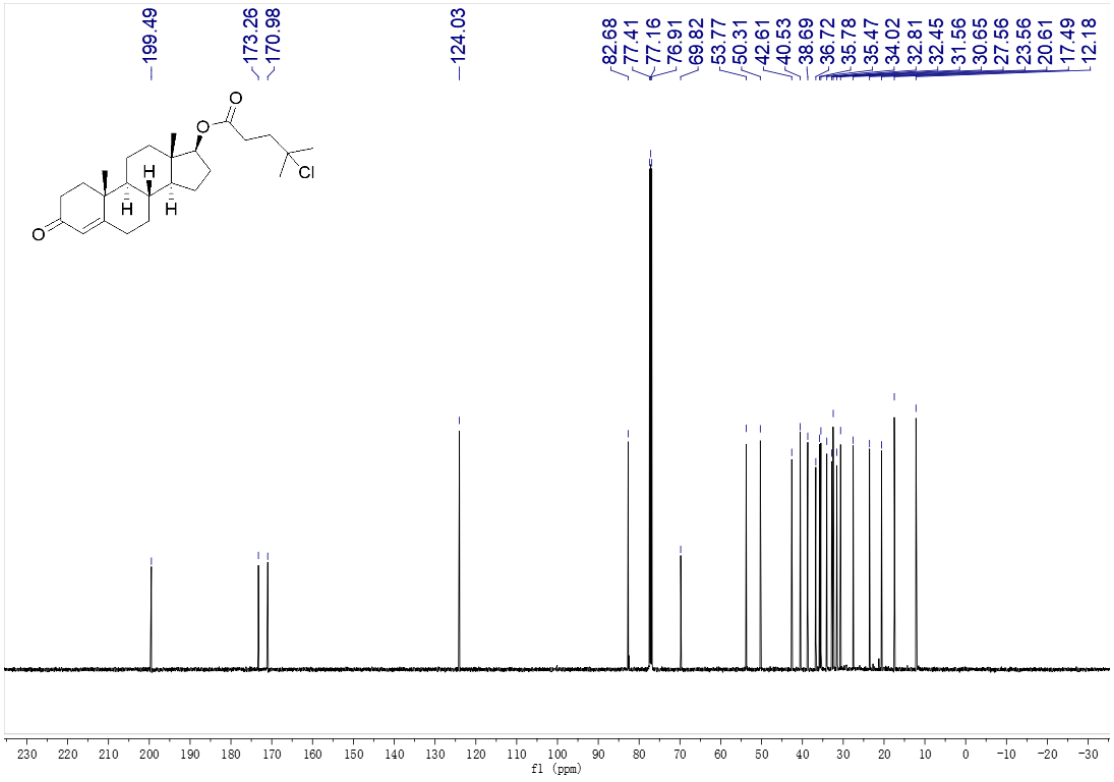
DEPT 135 of compound **45b**



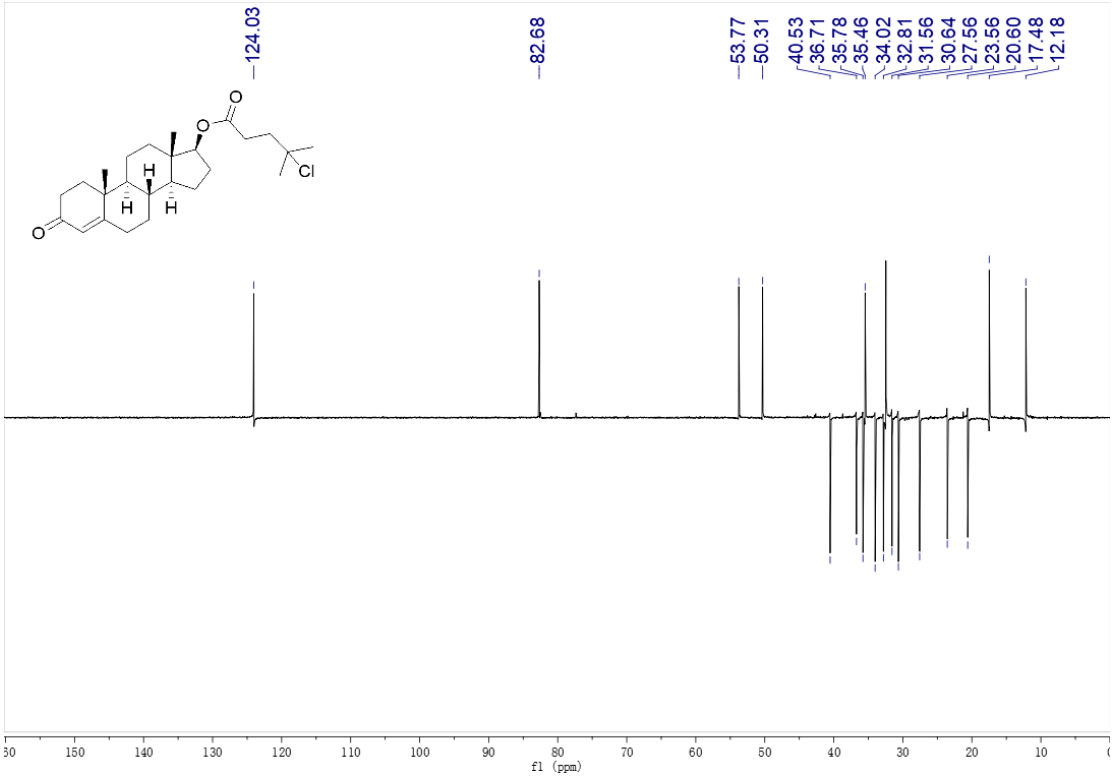
DEPT 90 of compound **45b**



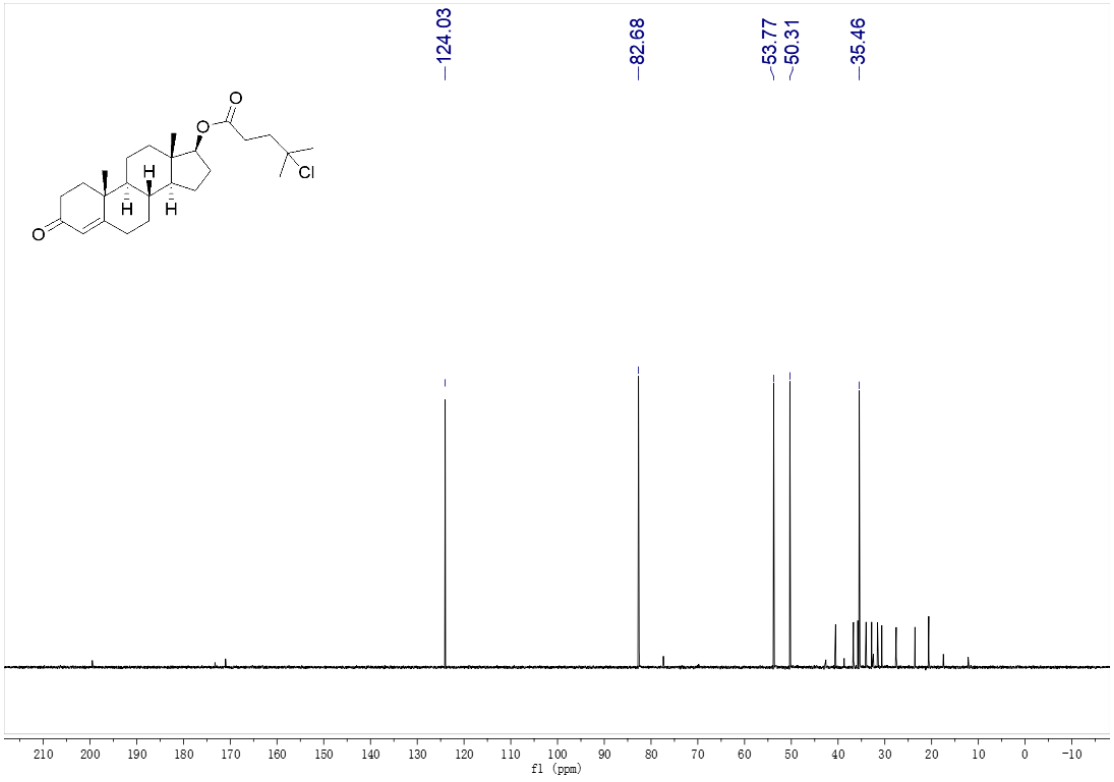
^{1}H NMR of compound **46b** (500 MHz, $CDCl_3$)



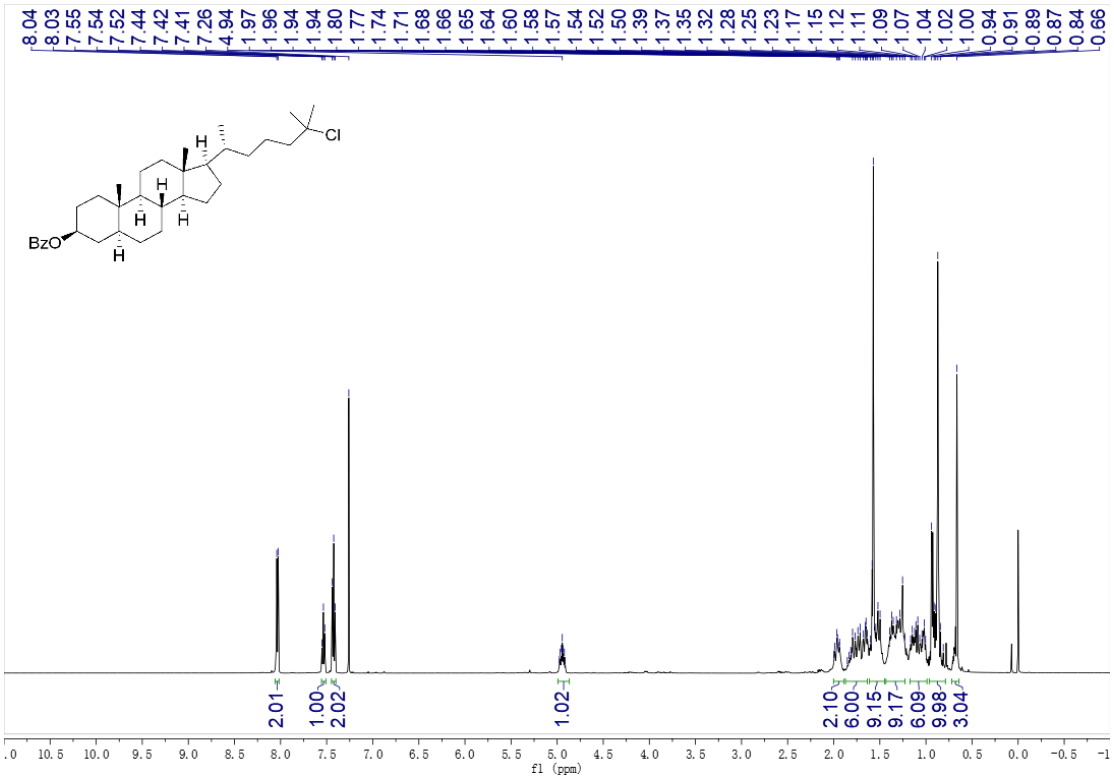
^{13}C NMR of compound **46b** (126 MHz, $CDCl_3$)



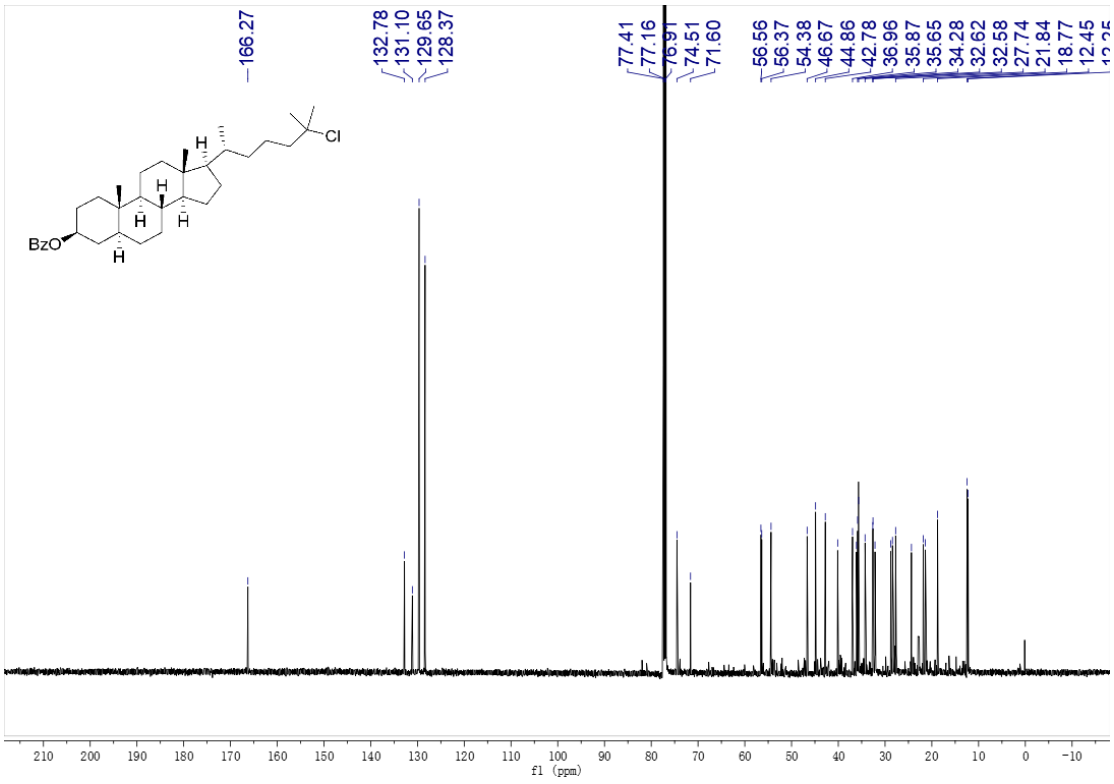
DEPT 135 of compound **46b**



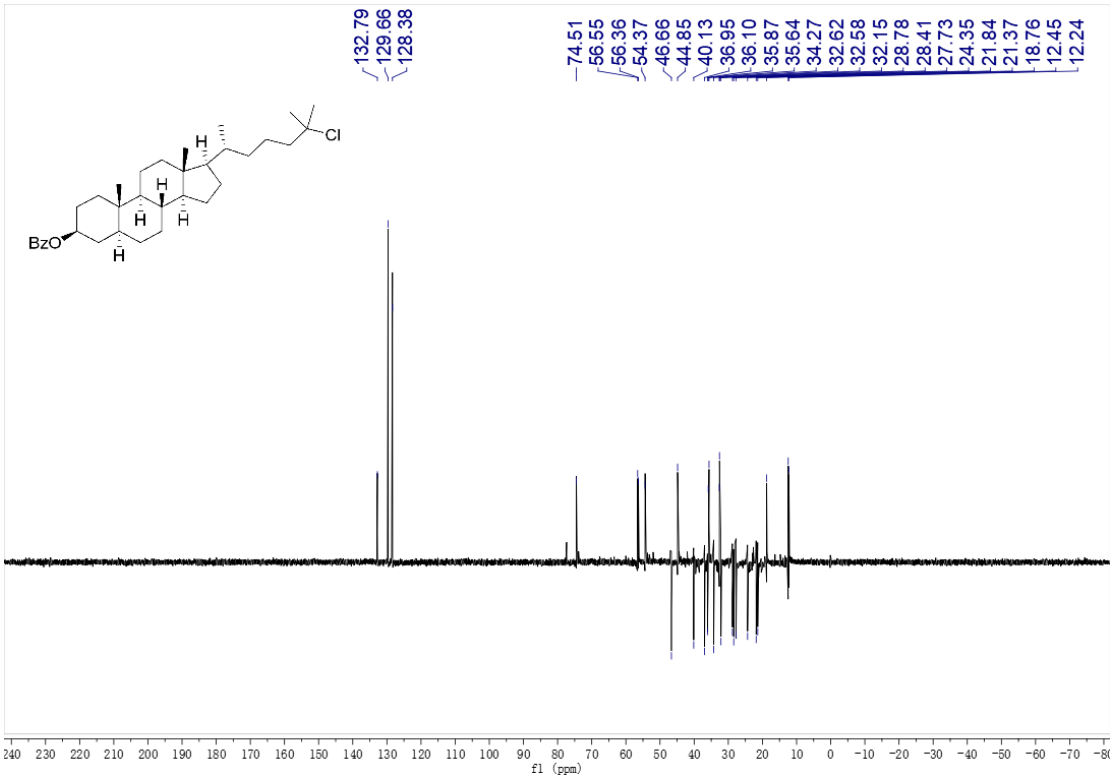
DEPT 90 of compound **46b**



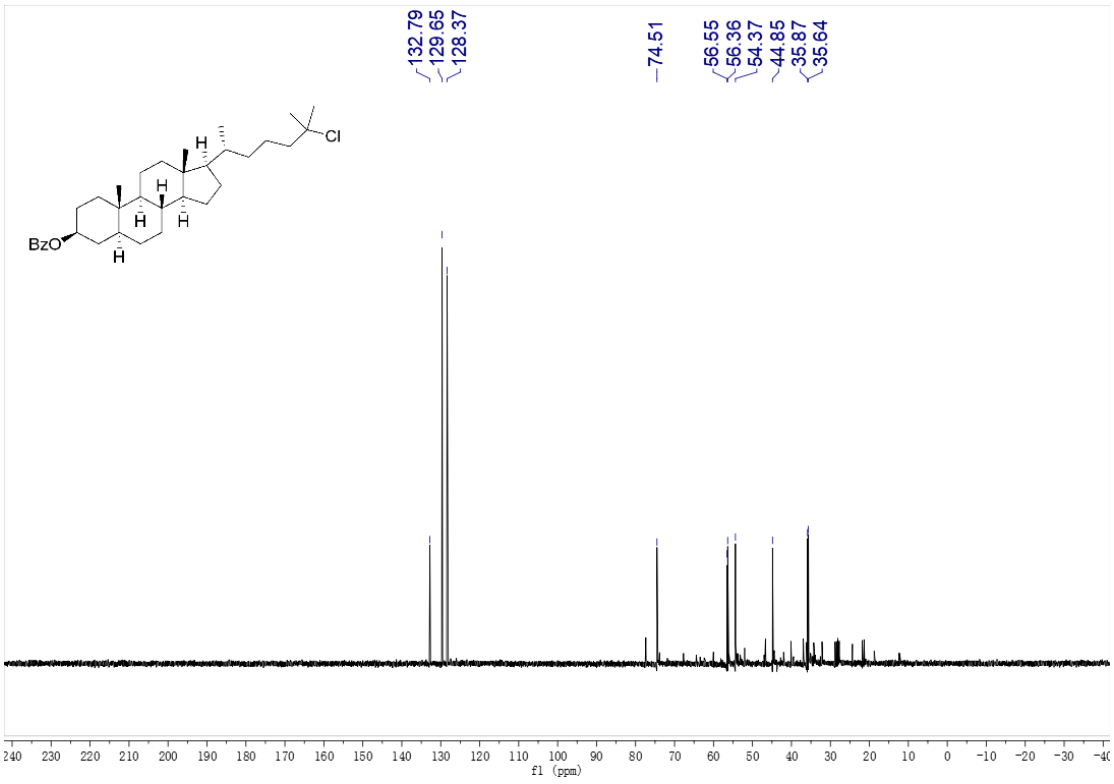
^{1}H NMR of compound **47b** (500 MHz, $CDCl_3$)



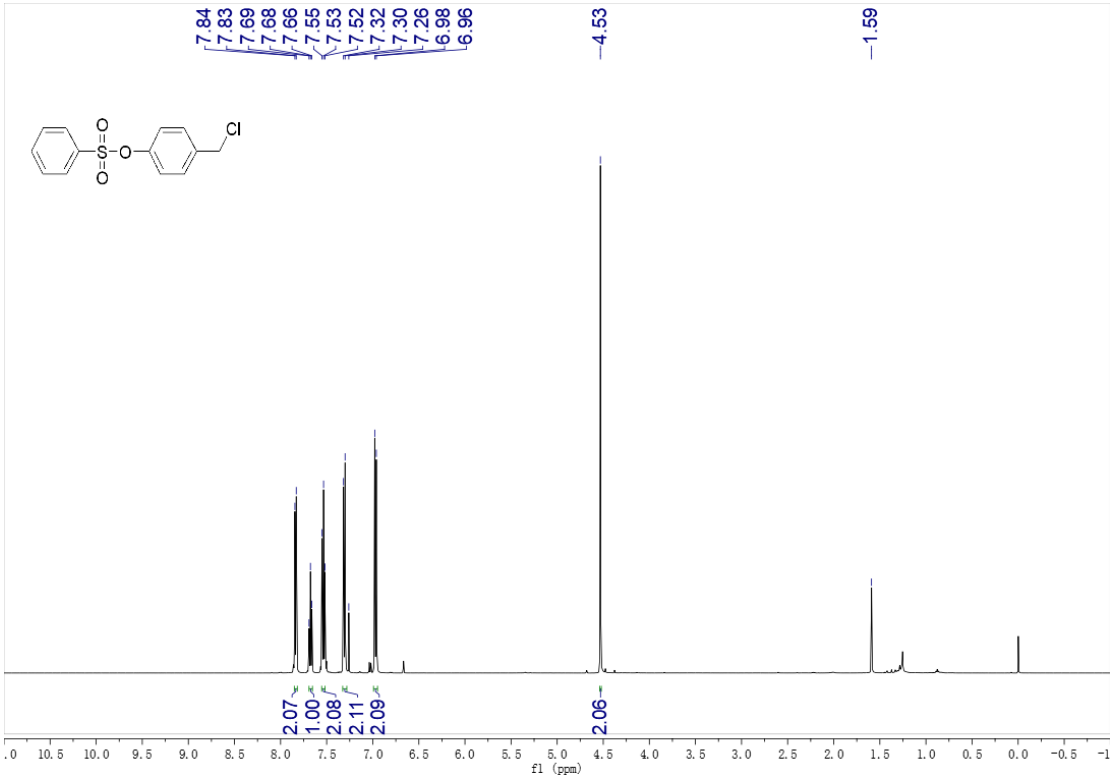
^{13}C NMR of compound **47b** (126 MHz, $CDCl_3$)



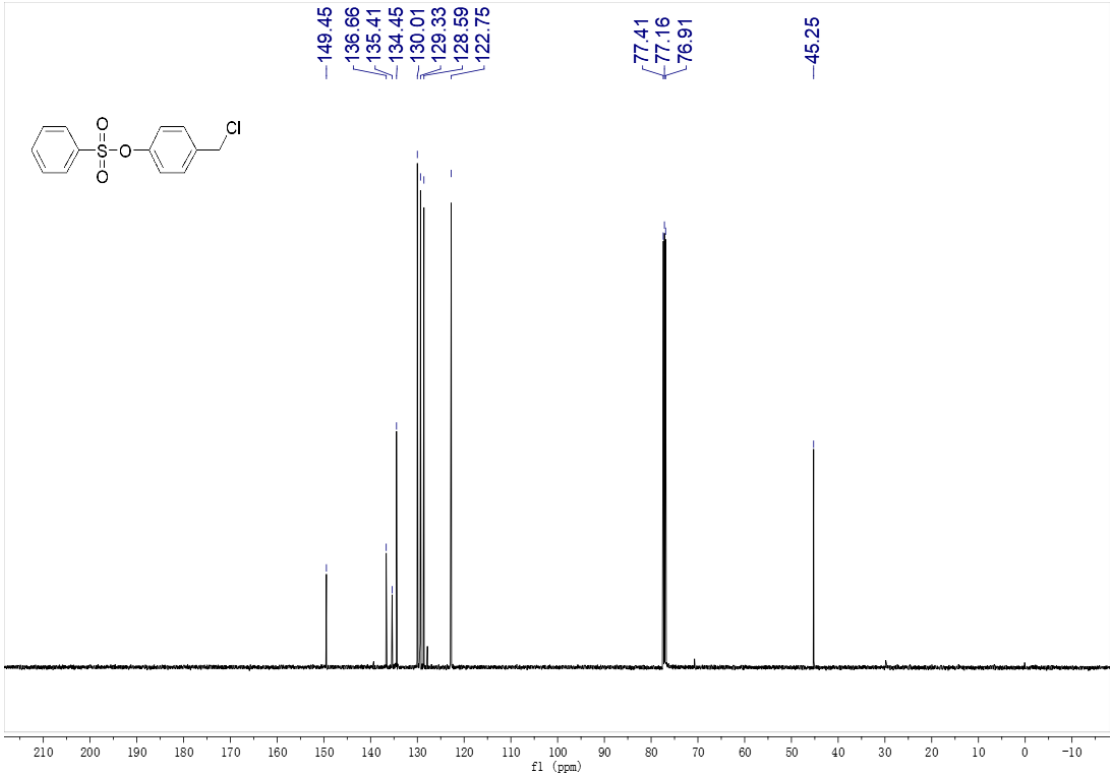
DEPT 135 of compound **47b**



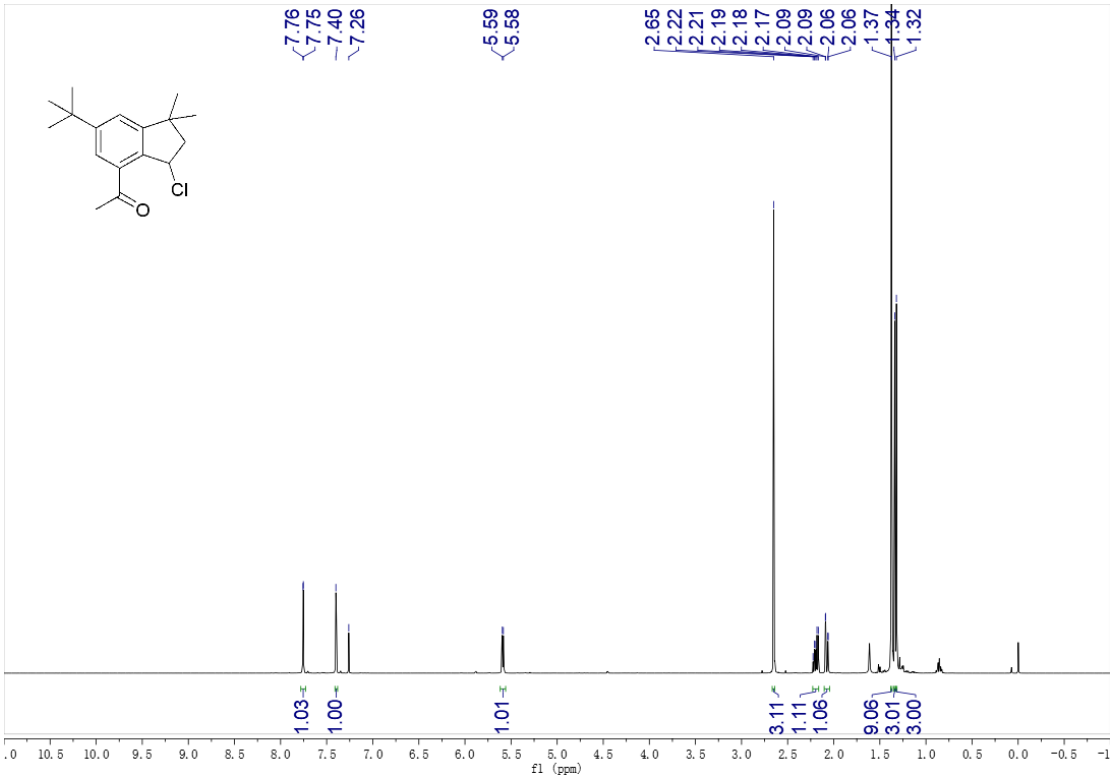
DEPT 90 of compound **47b**



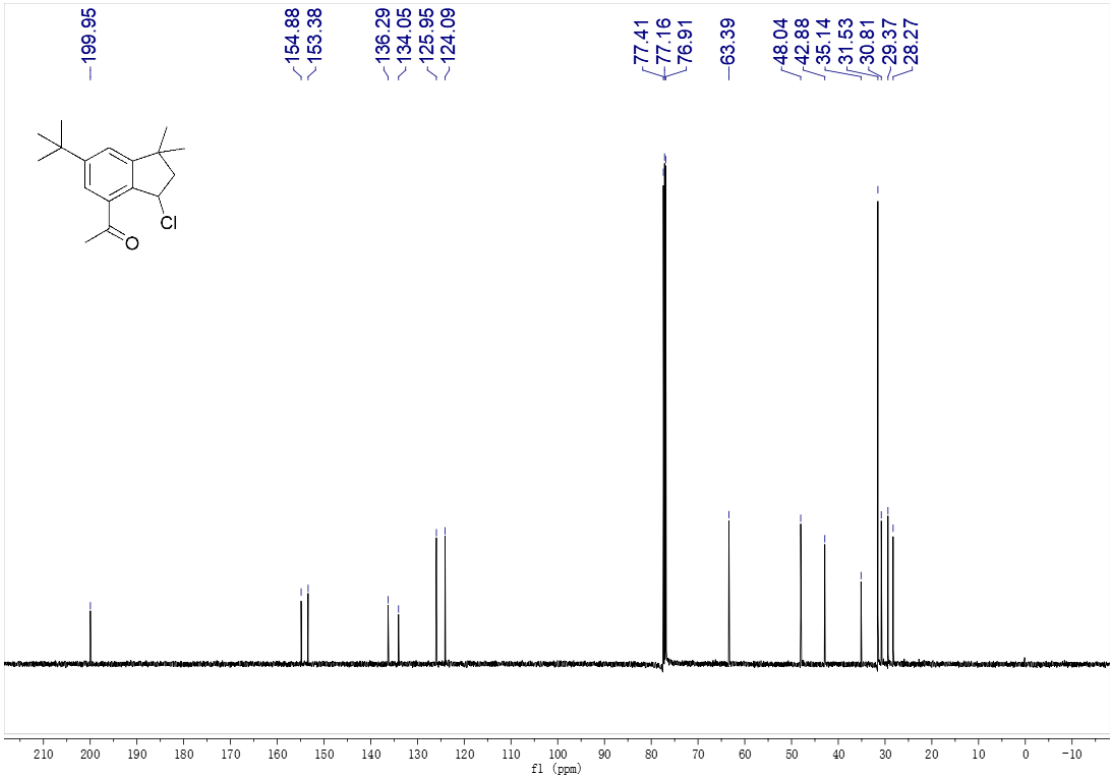
^{1}H NMR of compound **48b** (500 MHz, $CDCl_3$)



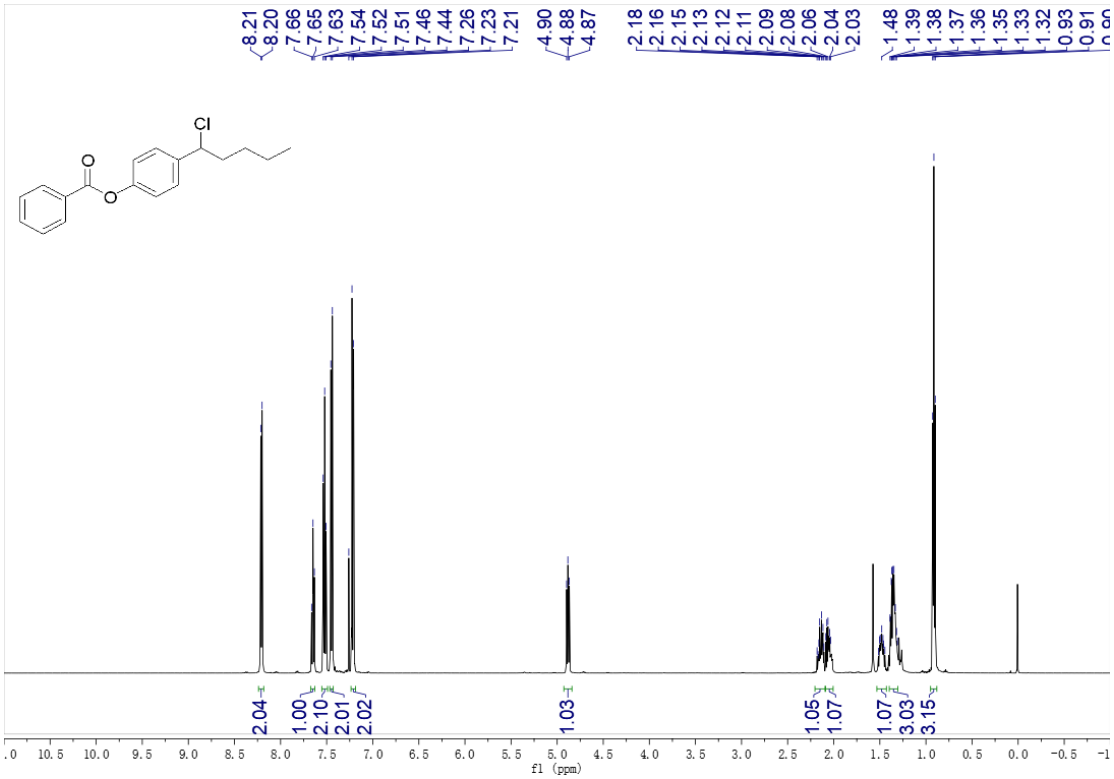
^{13}C NMR of compound **48b** (126 MHz, $CDCl_3$)



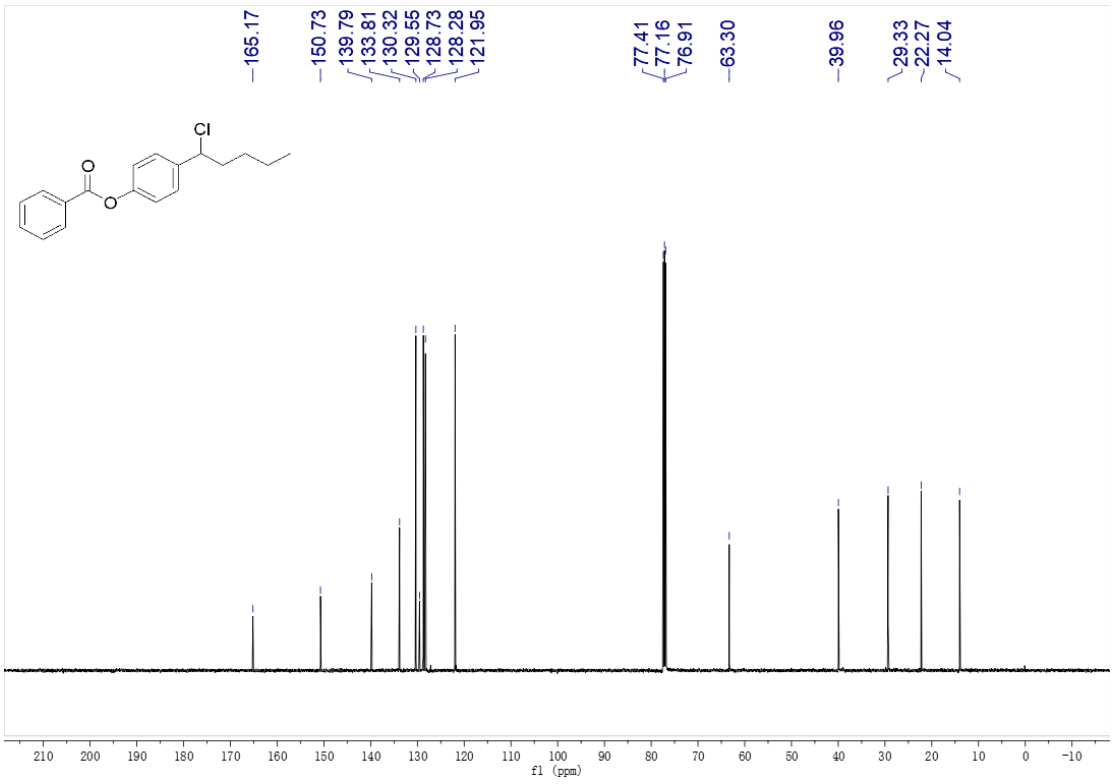
^{1}H NMR of compound **49b** (500 MHz, $CDCl_3$)



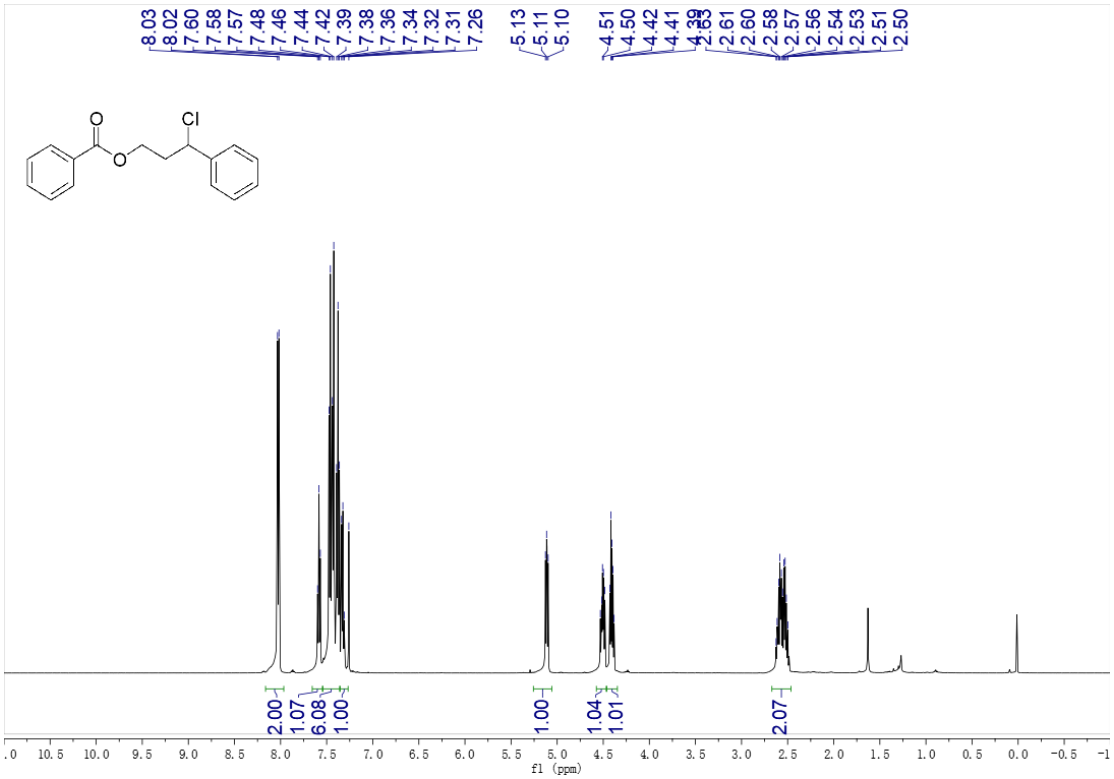
^{13}C NMR of compound **49b** (126 MHz, $CDCl_3$)



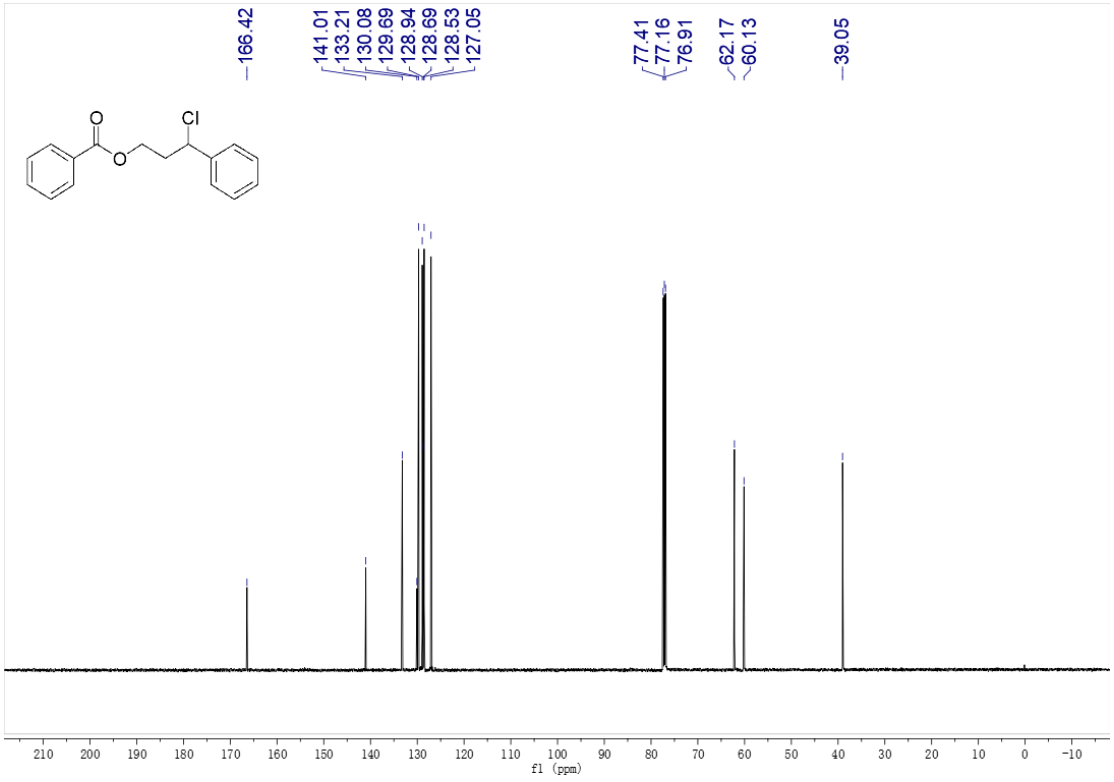
^{1}H NMR of compound **50b** (500 MHz, $CDCl_3$)



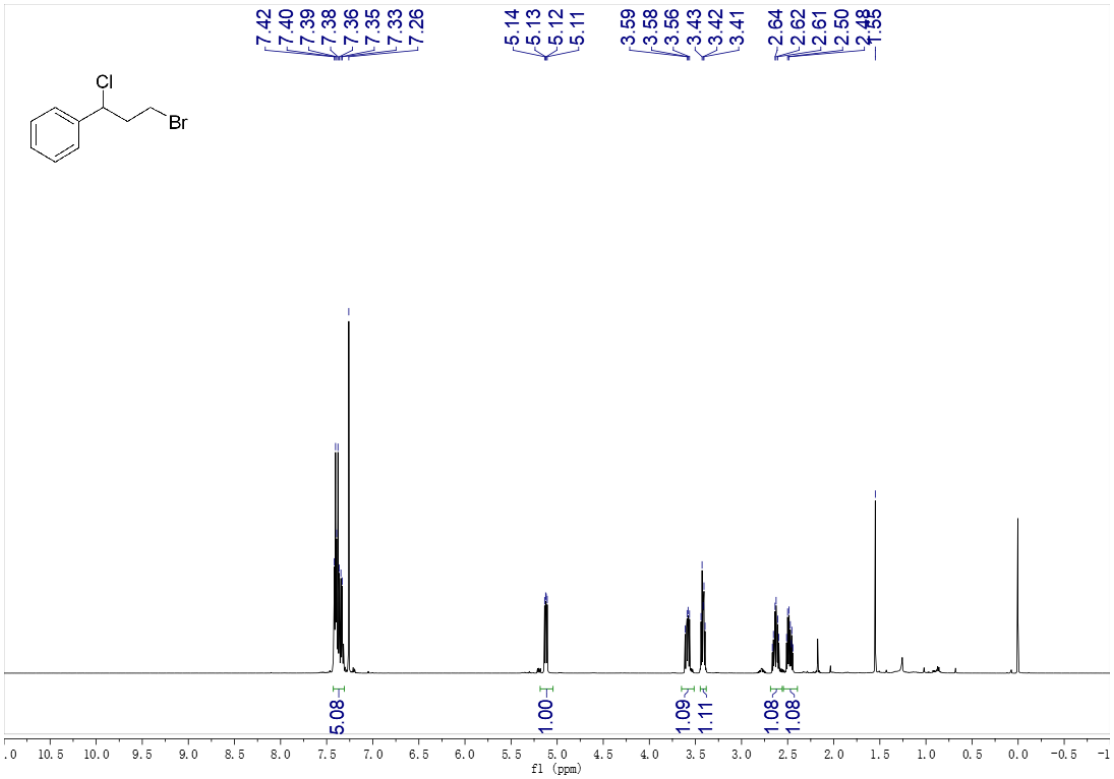
^{13}C NMR of compound **50b** (126 MHz, $CDCl_3$)



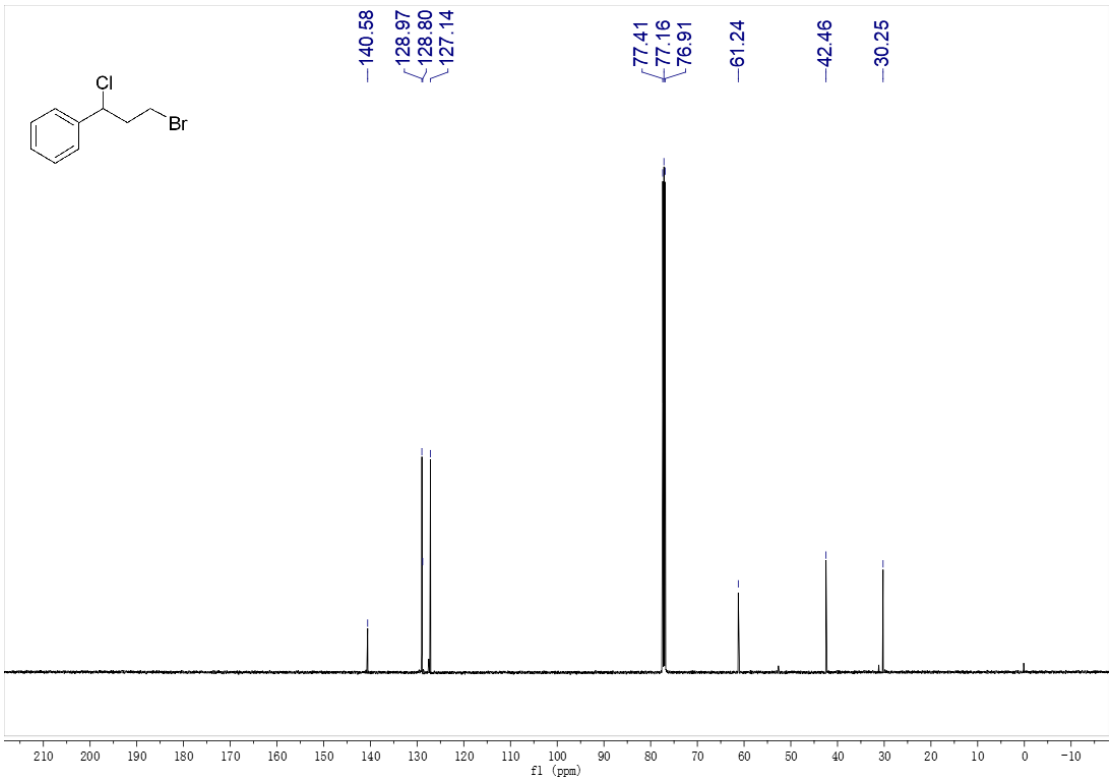
^{1}H NMR of compound **51b** (500 MHz, $CDCl_3$)



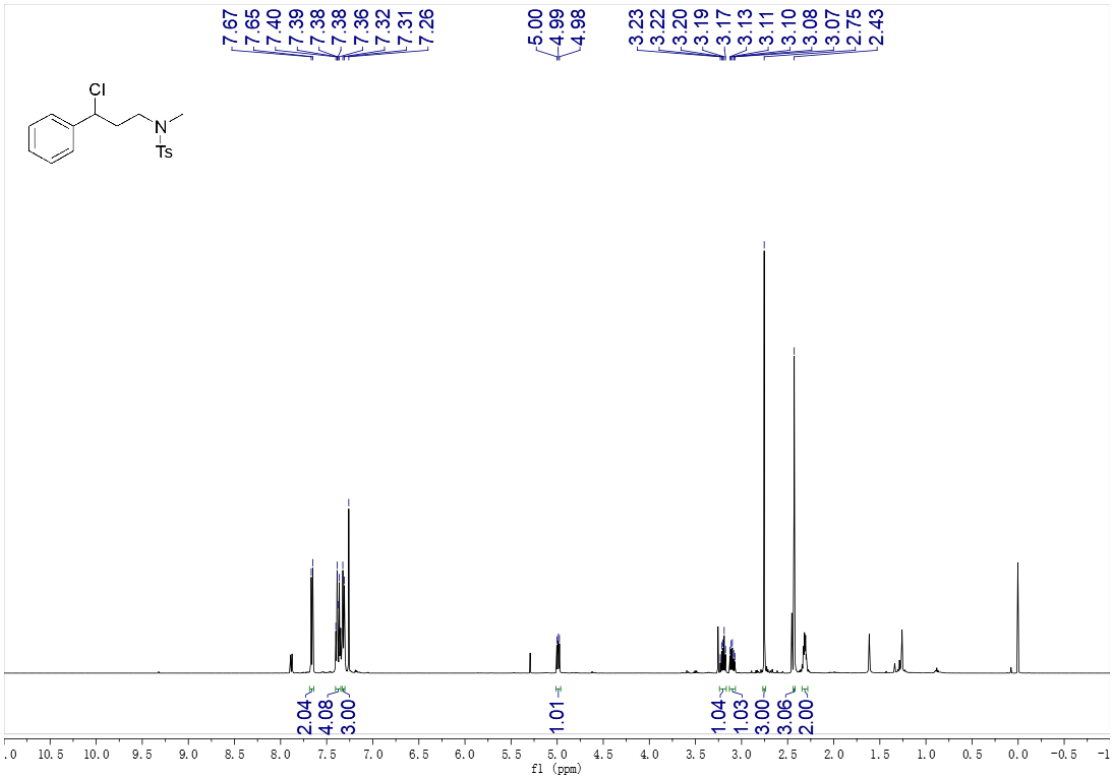
^{13}C NMR of compound **51b** (126 MHz, $CDCl_3$)



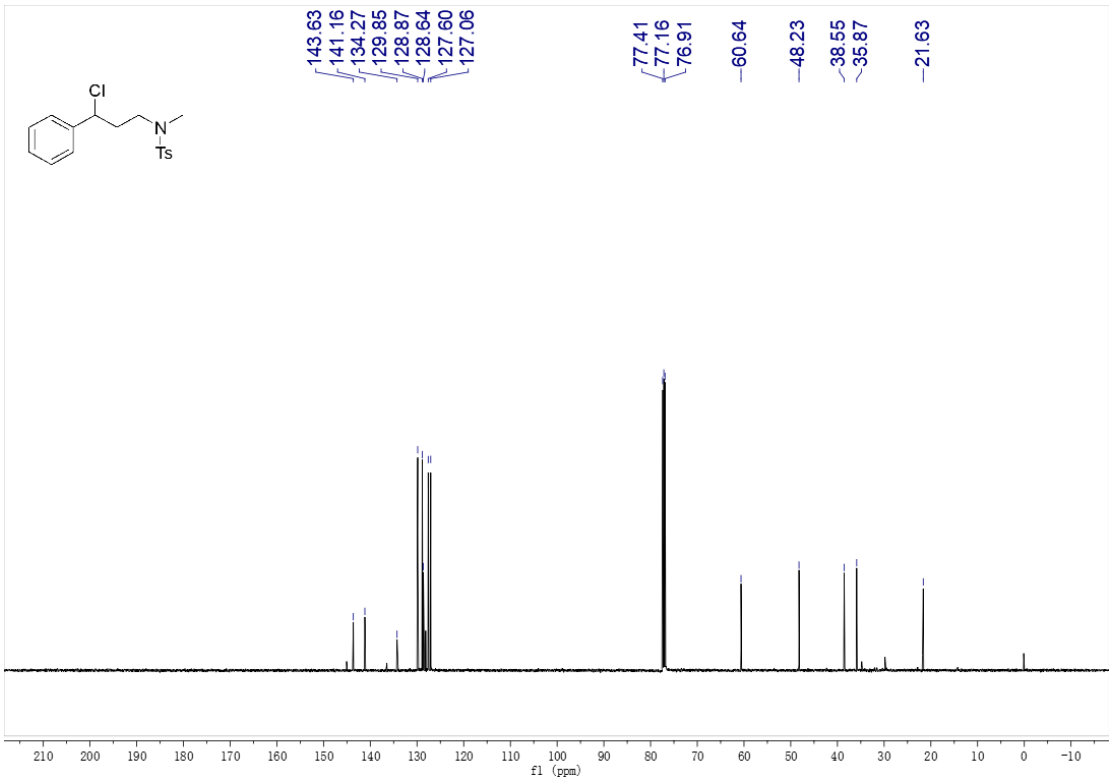
^{1}H NMR of compound **52b** (500 MHz, $CDCl_3$)



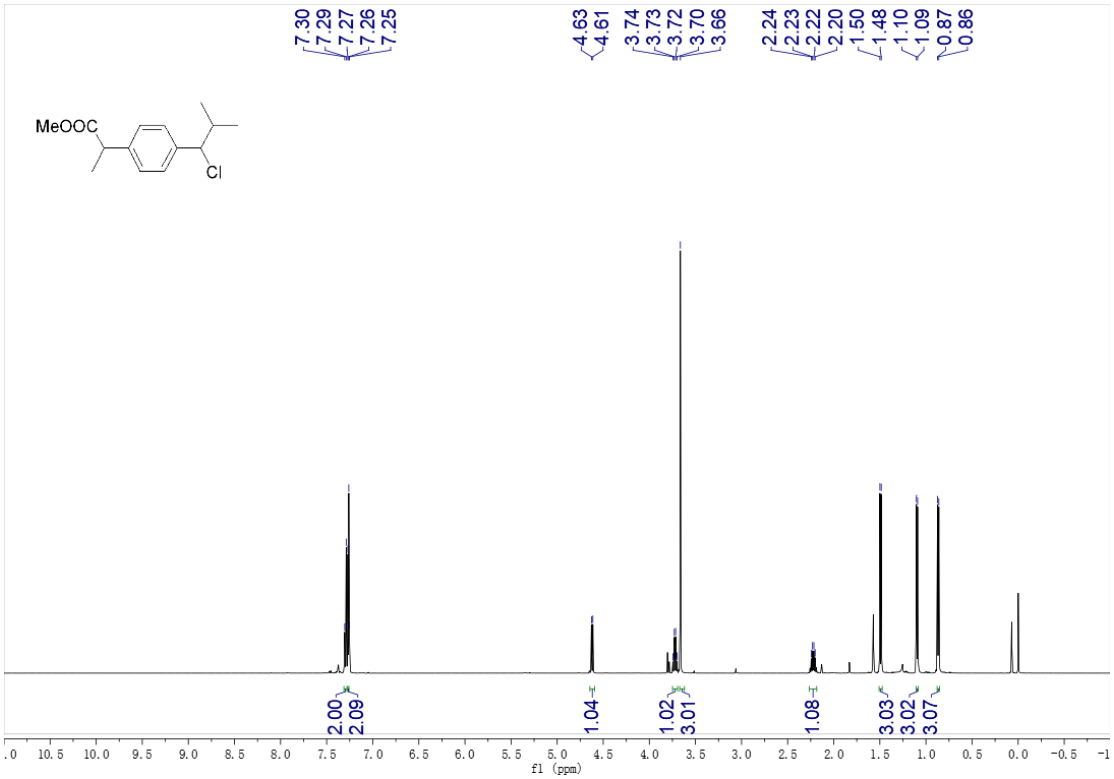
^{13}C NMR of compound **52b** (126 MHz, $CDCl_3$)



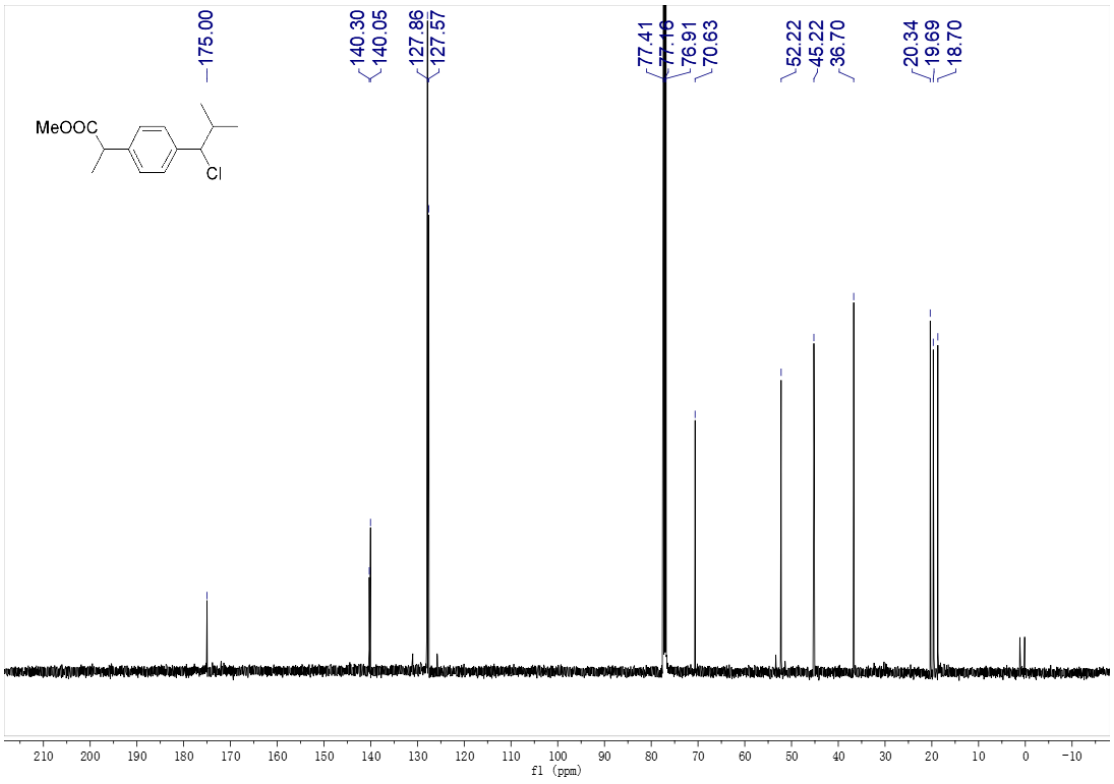
^{1}H NMR of compound **53b** (500 MHz, $CDCl_3$)



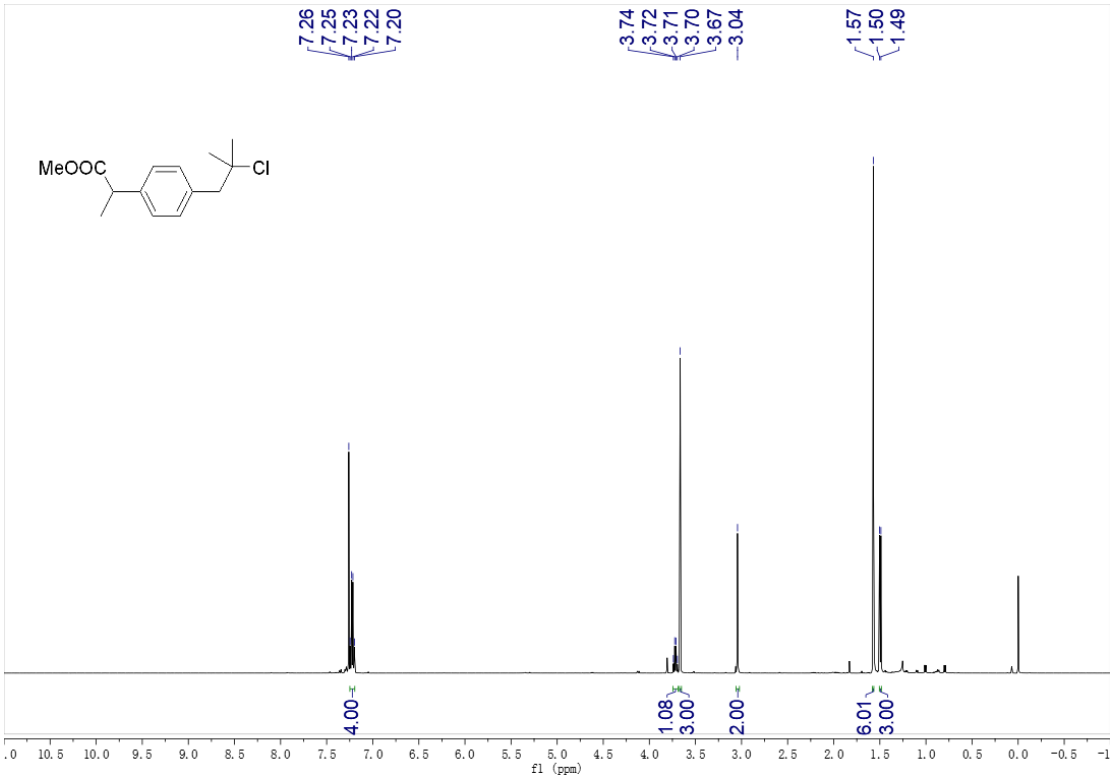
^{13}C NMR of compound **53b** (126 MHz, $CDCl_3$)



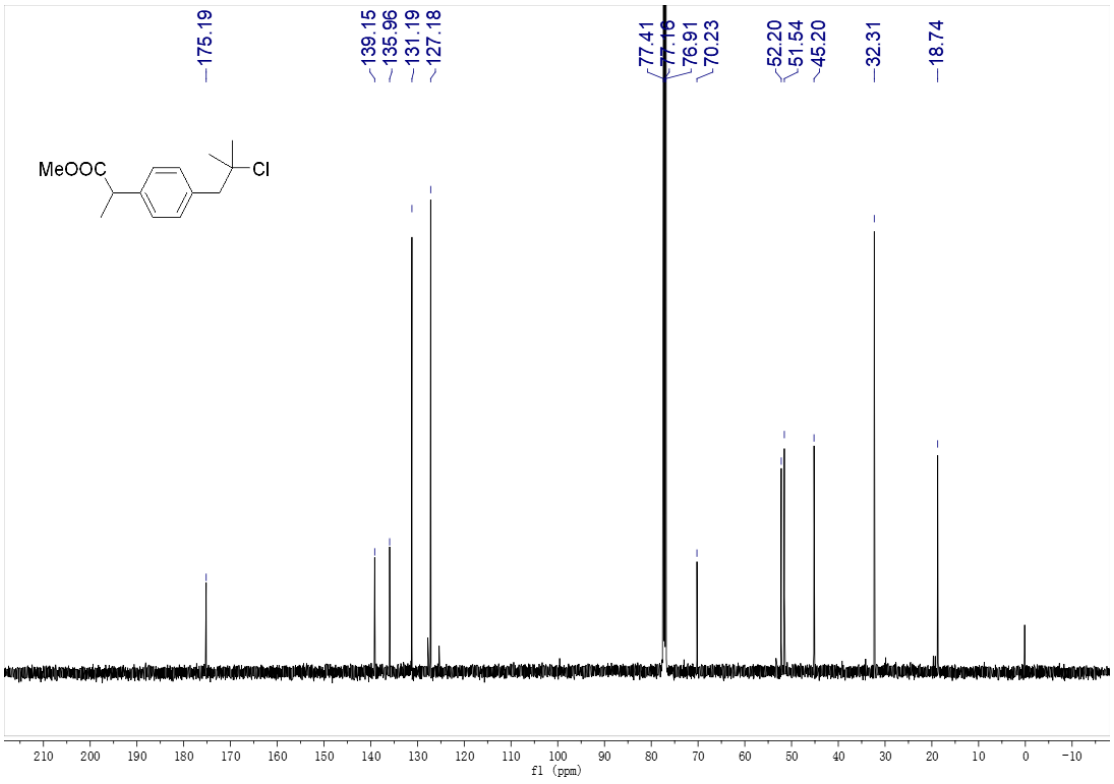
^{1}H NMR of compound **54b** (500 MHz, $CDCl_3$)



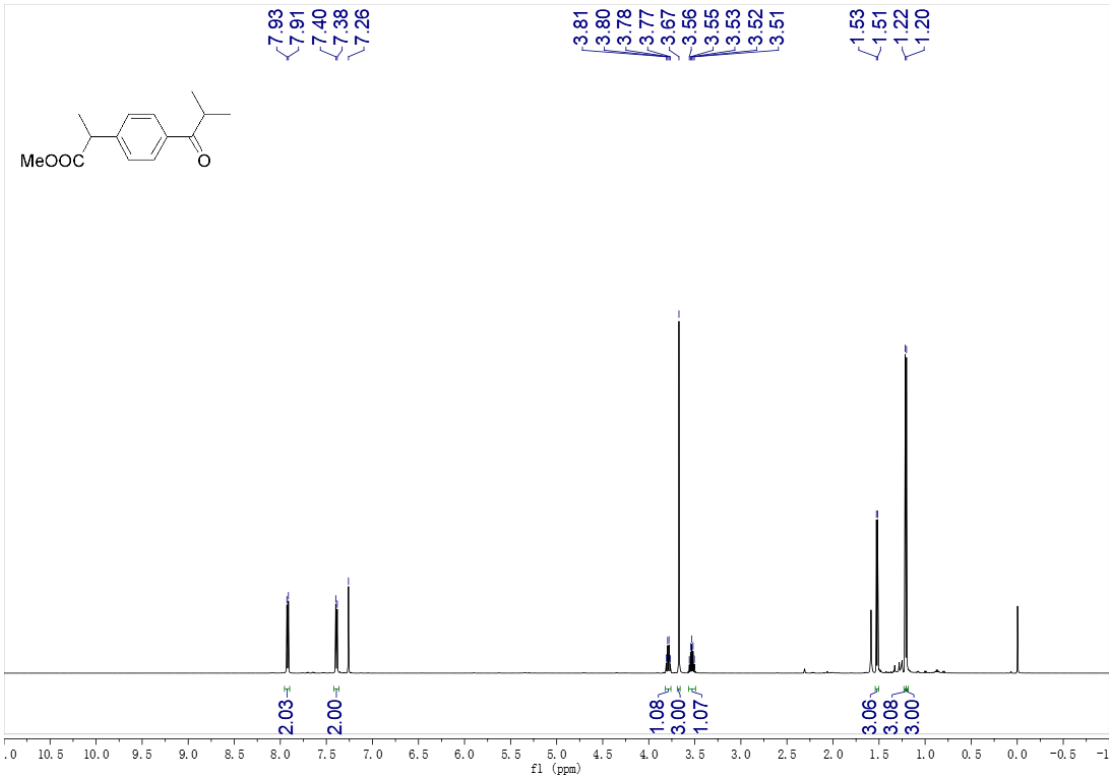
^{13}C NMR of compound **54b** (126 MHz, $CDCl_3$)



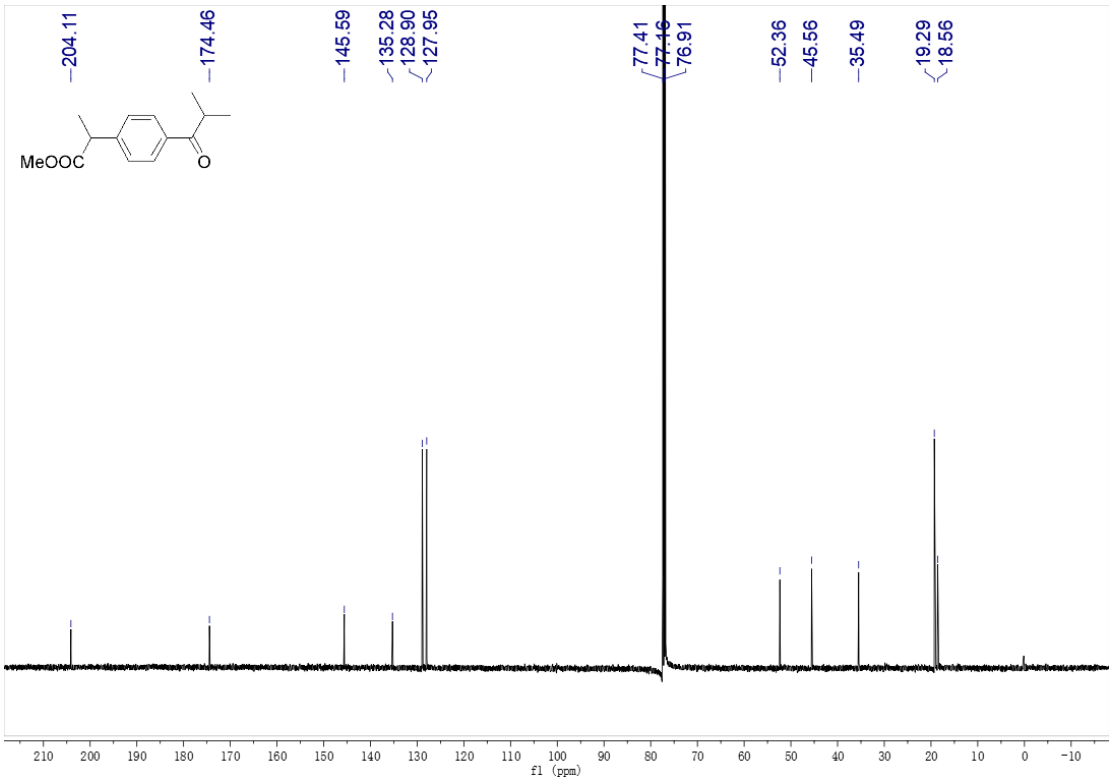
^{1}H NMR of compound **54b'** (500 MHz, $CDCl_3$)



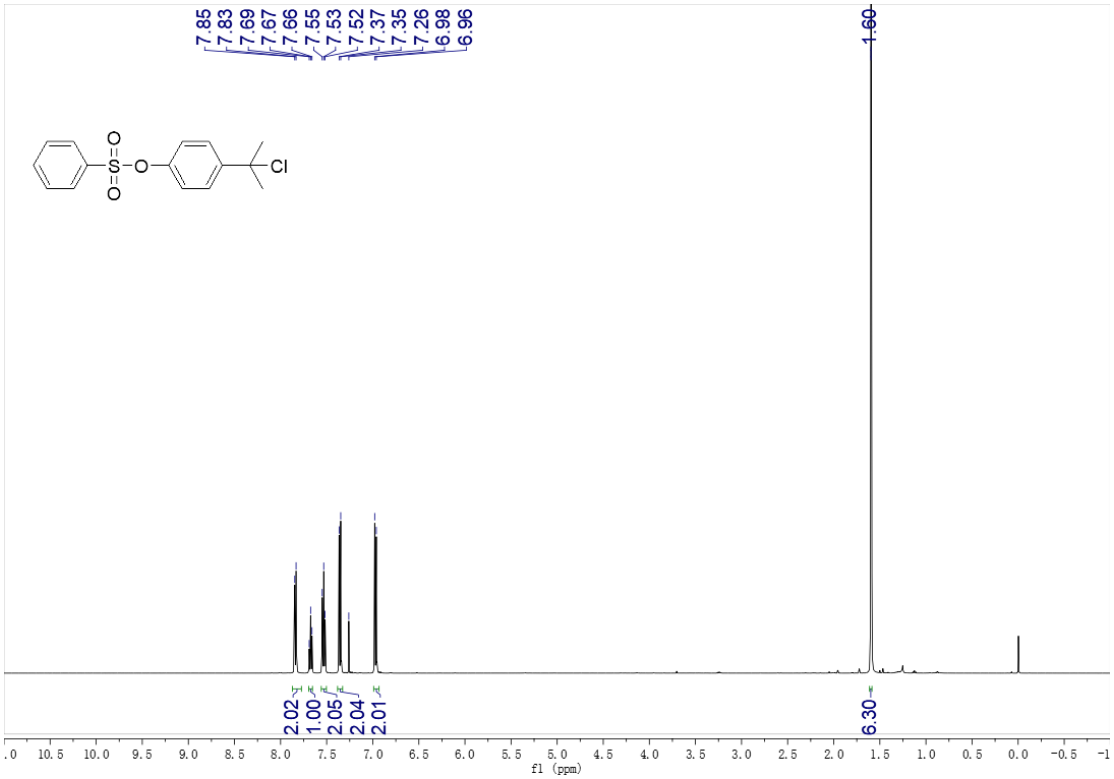
^{13}C NMR of compound **54b'** (126 MHz, $CDCl_3$)



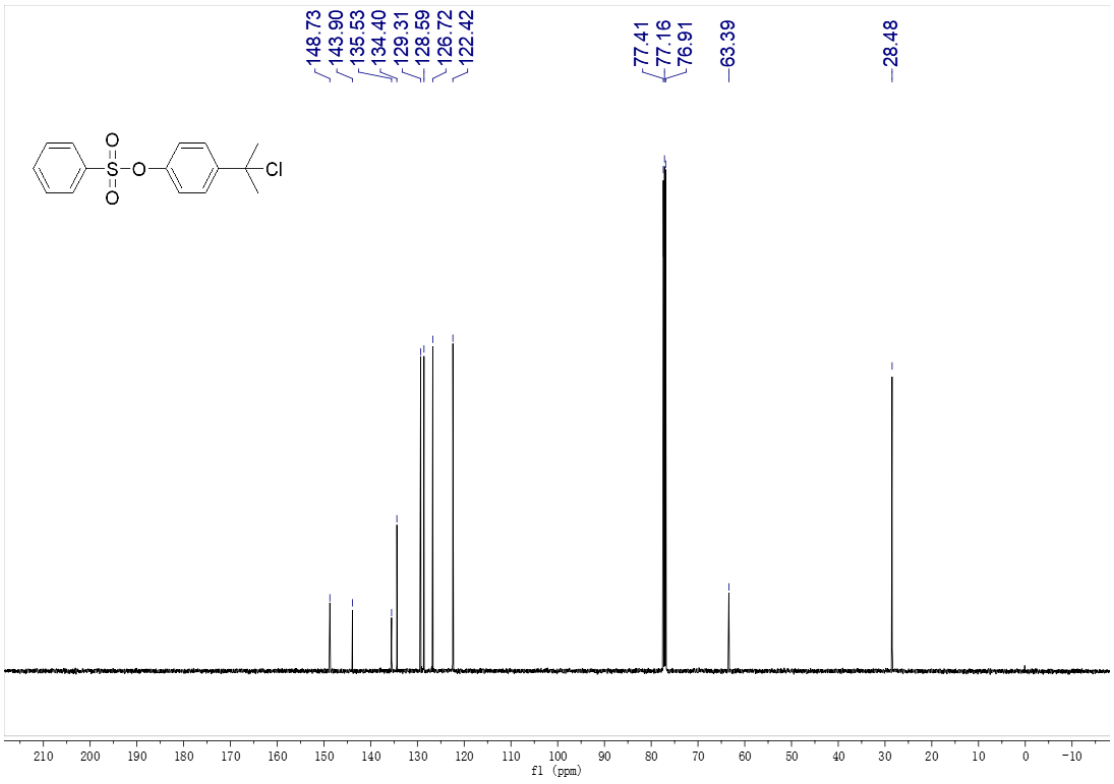
^{1}H NMR of compound **54b''** (500 MHz, $CDCl_3$)



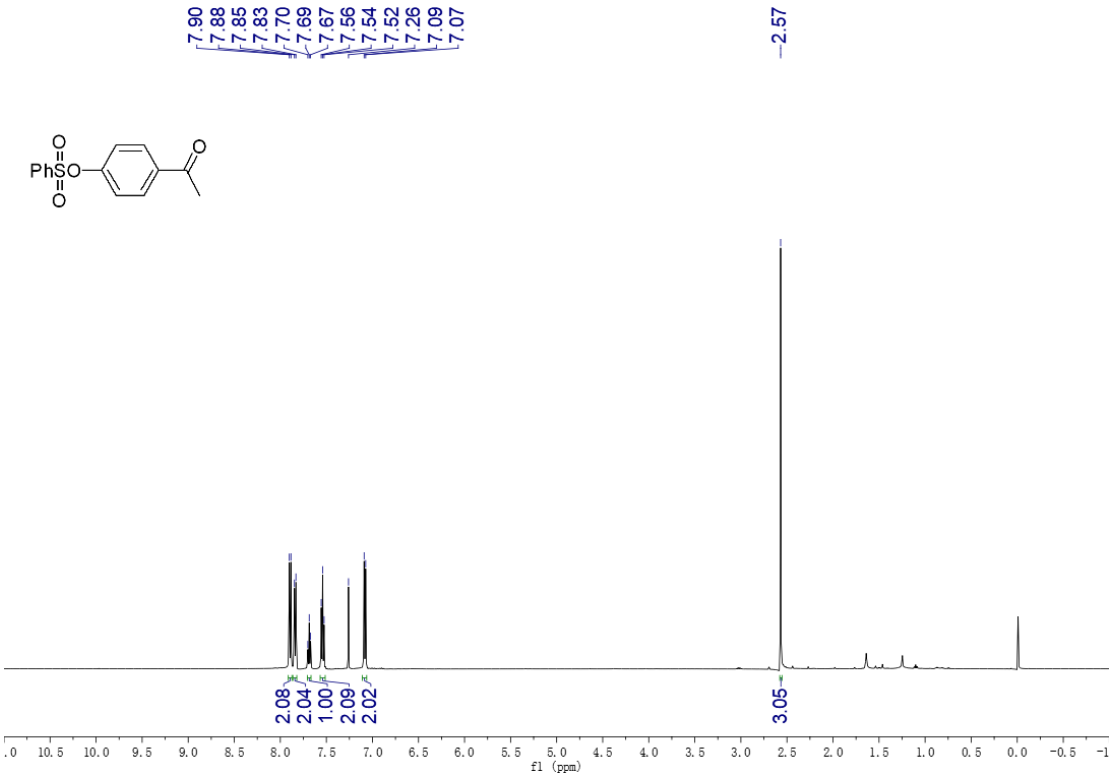
^{13}C NMR of compound **54b''** (126 MHz, $CDCl_3$)



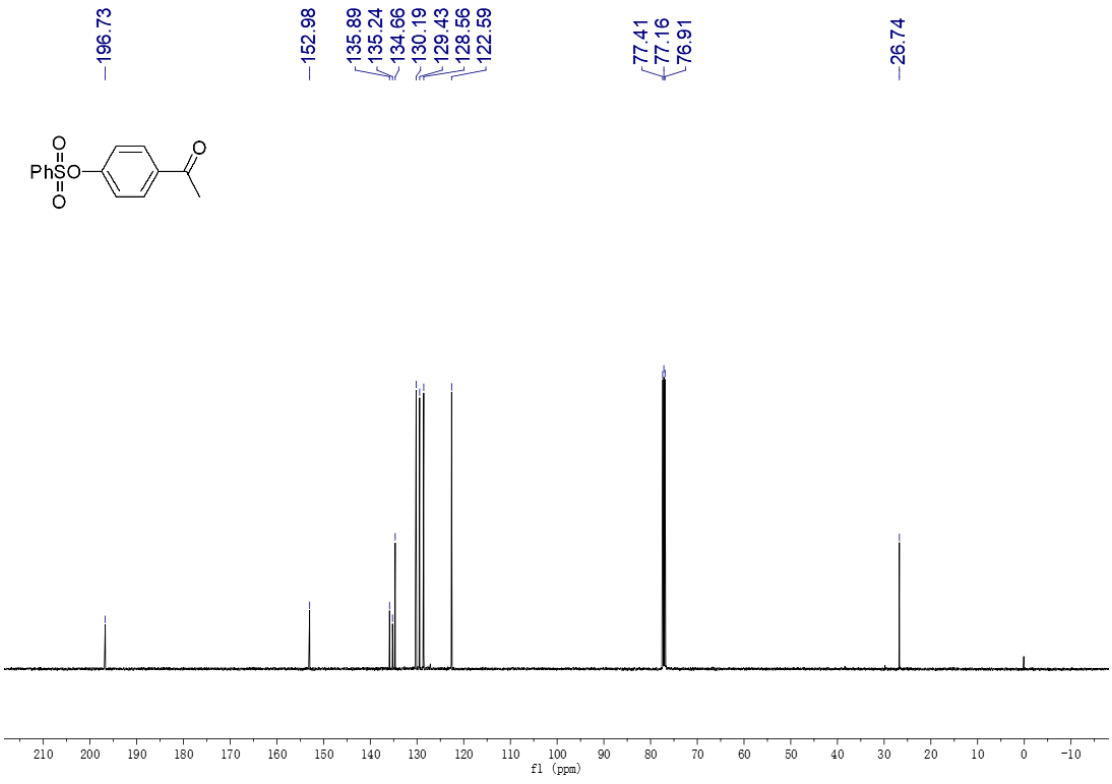
^{1}H NMR of compound **55b** (500 MHz, $CDCl_3$)



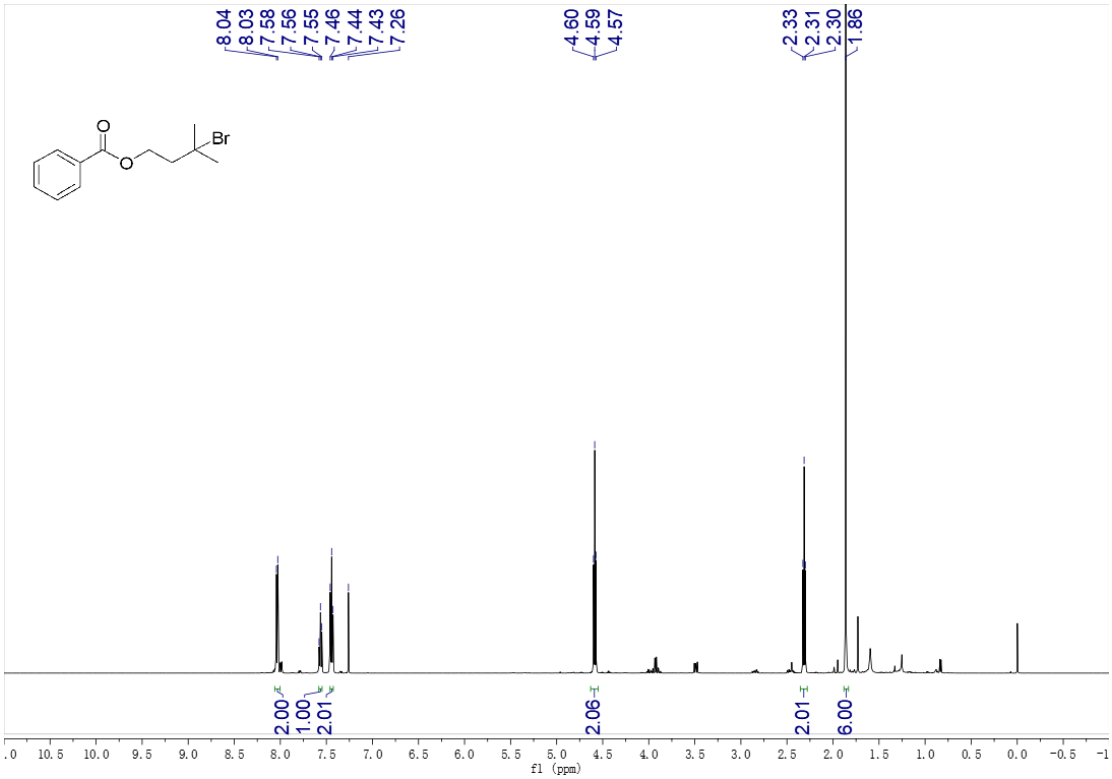
^{13}C NMR of compound **55b** (126 MHz, $CDCl_3$)



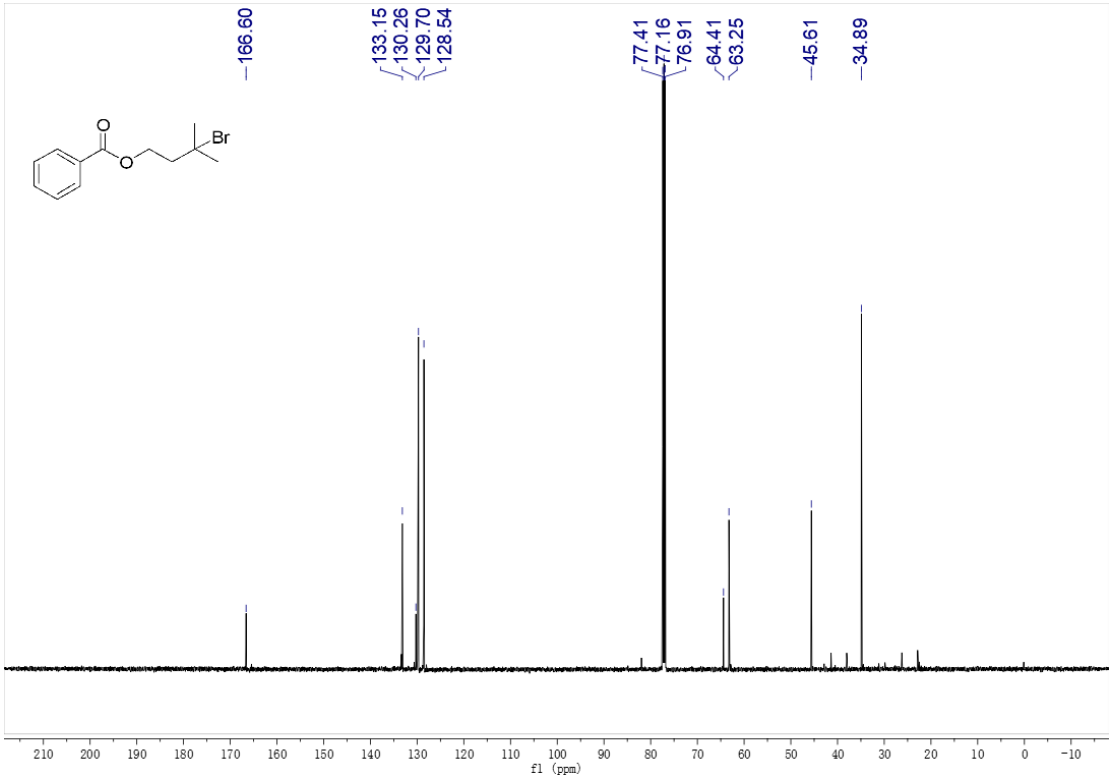
^{1}H NMR of compound **55b'** (500 MHz, $CDCl_3$)



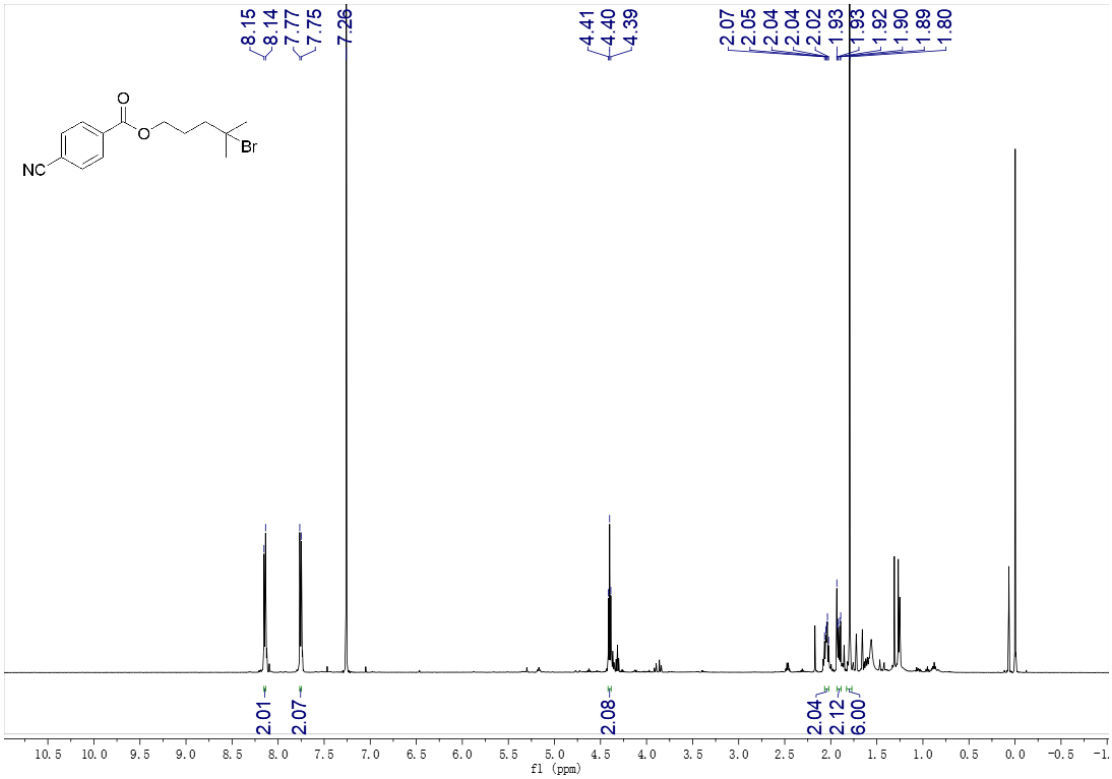
^{13}C NMR of compound **55b'** (126 MHz, $CDCl_3$)



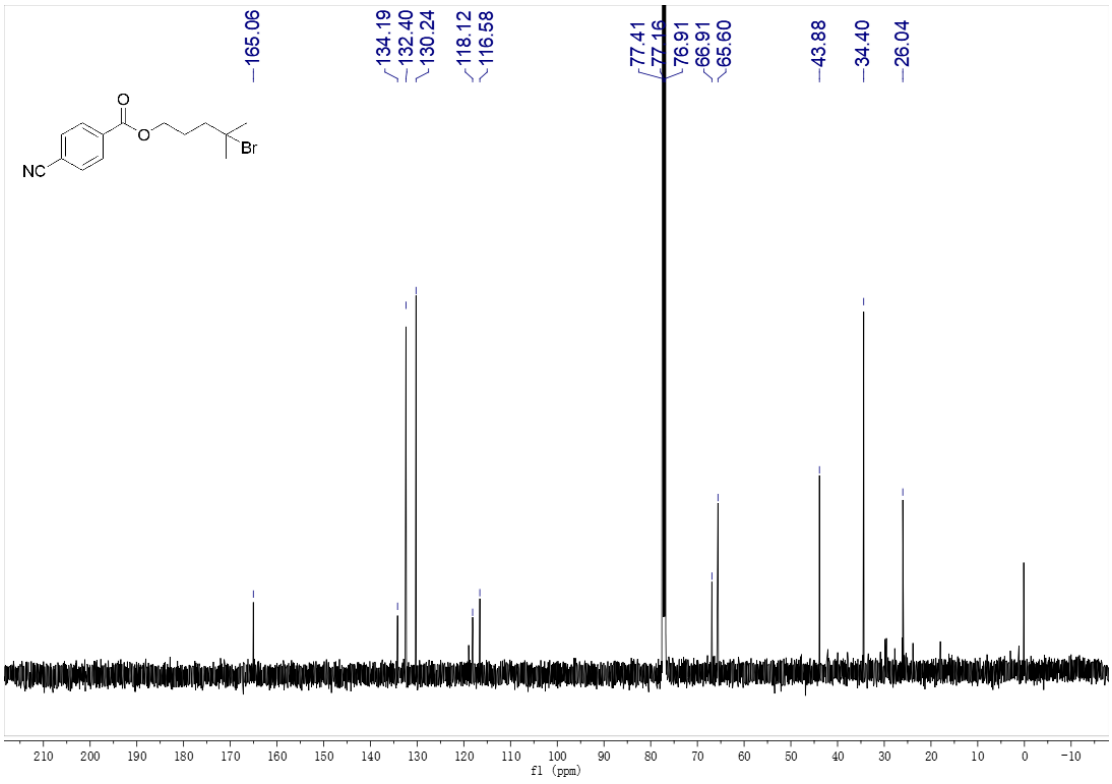
^{1}H NMR of compound **56c** (500 MHz, $CDCl_3$)



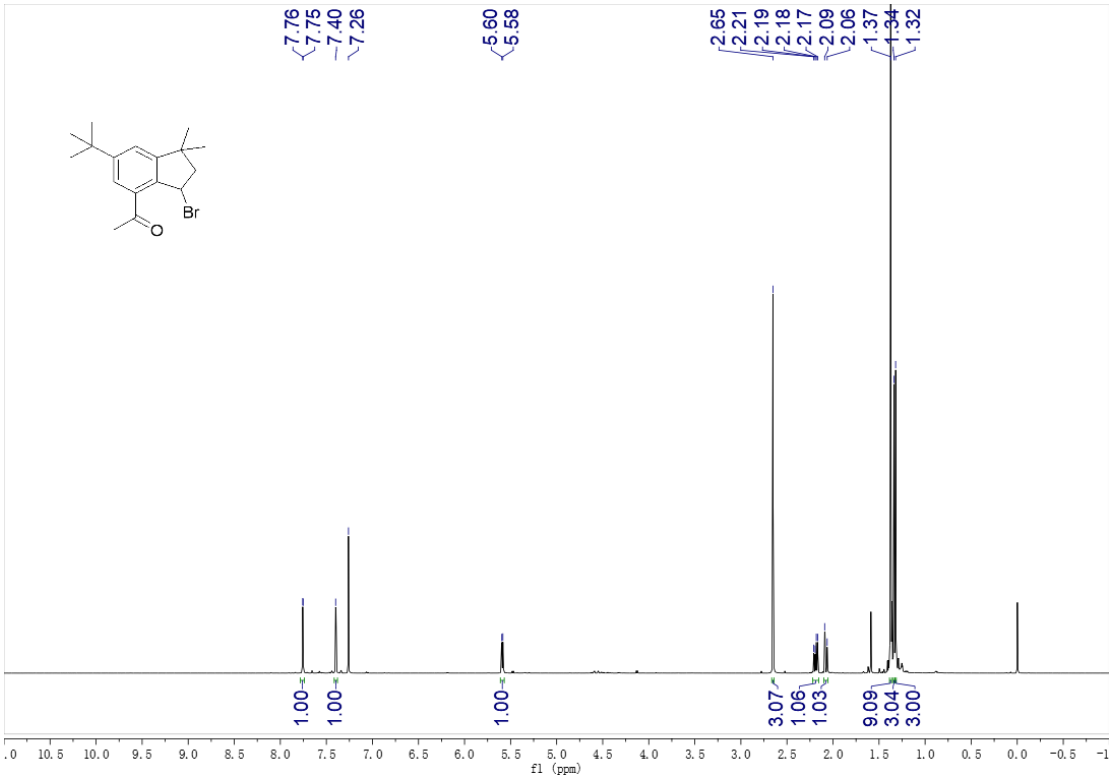
^{13}C NMR of compound **56c** (126 MHz, $CDCl_3$)



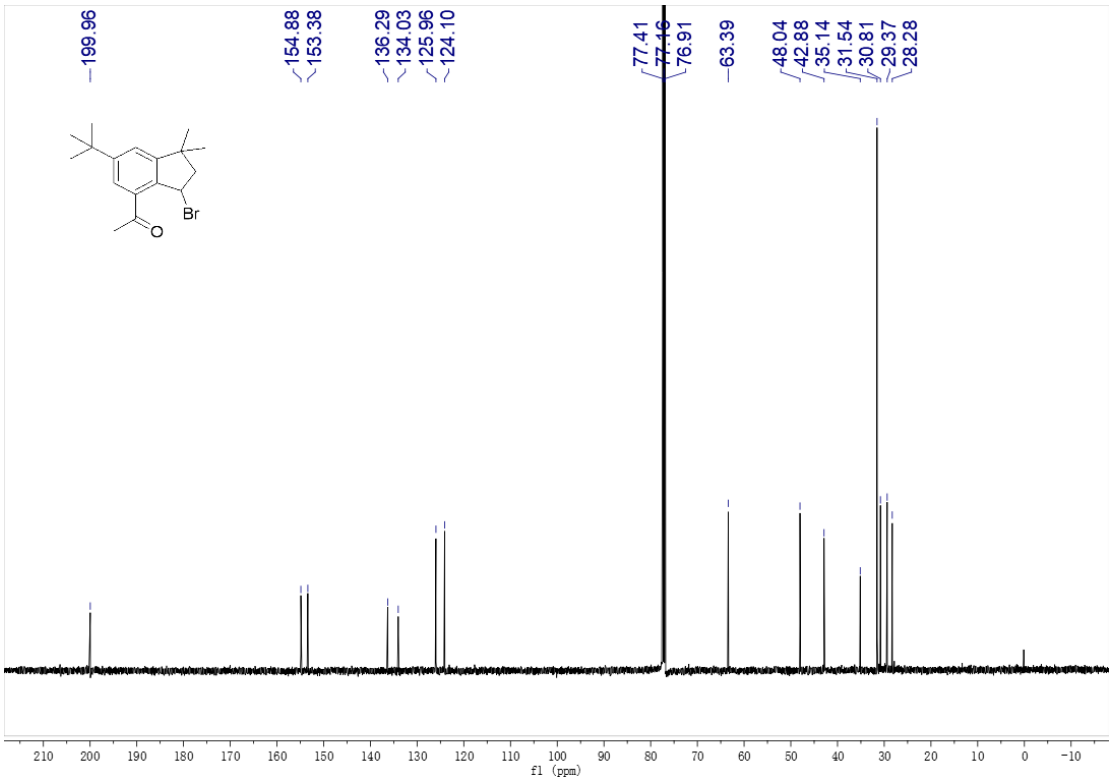
^{1}H NMR of compound **57c** (500 MHz, $CDCl_3$)



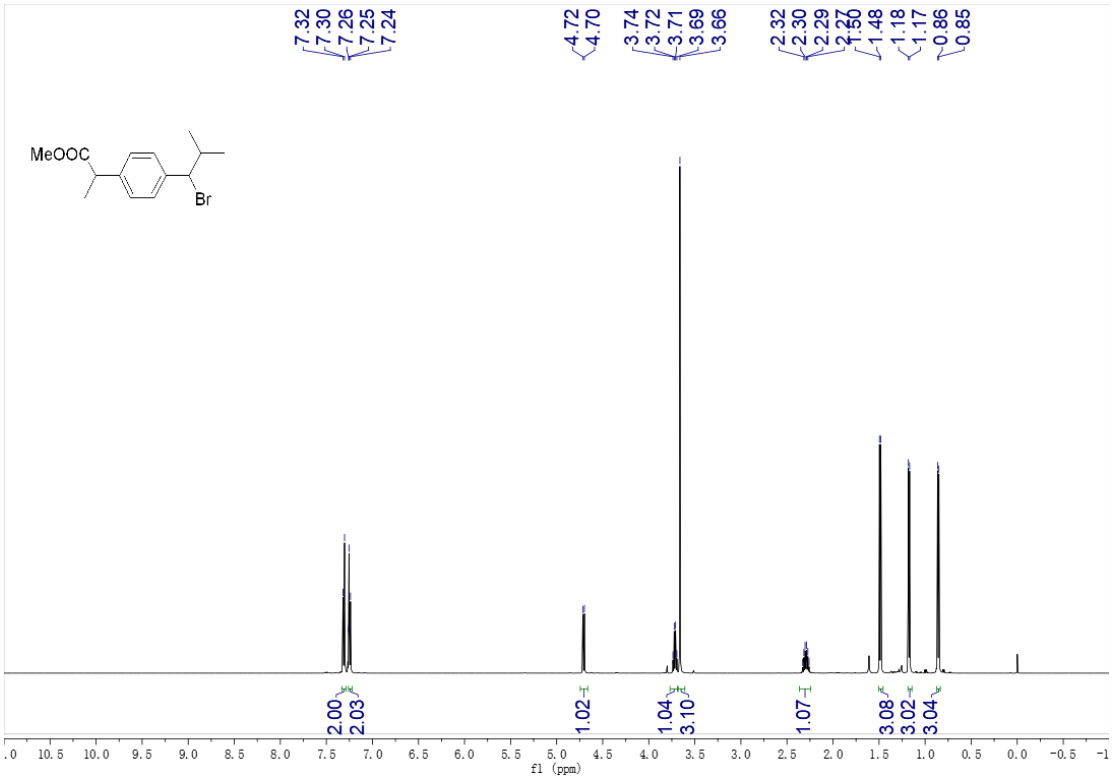
^{13}C NMR of compound **57c** (126 MHz, $CDCl_3$)



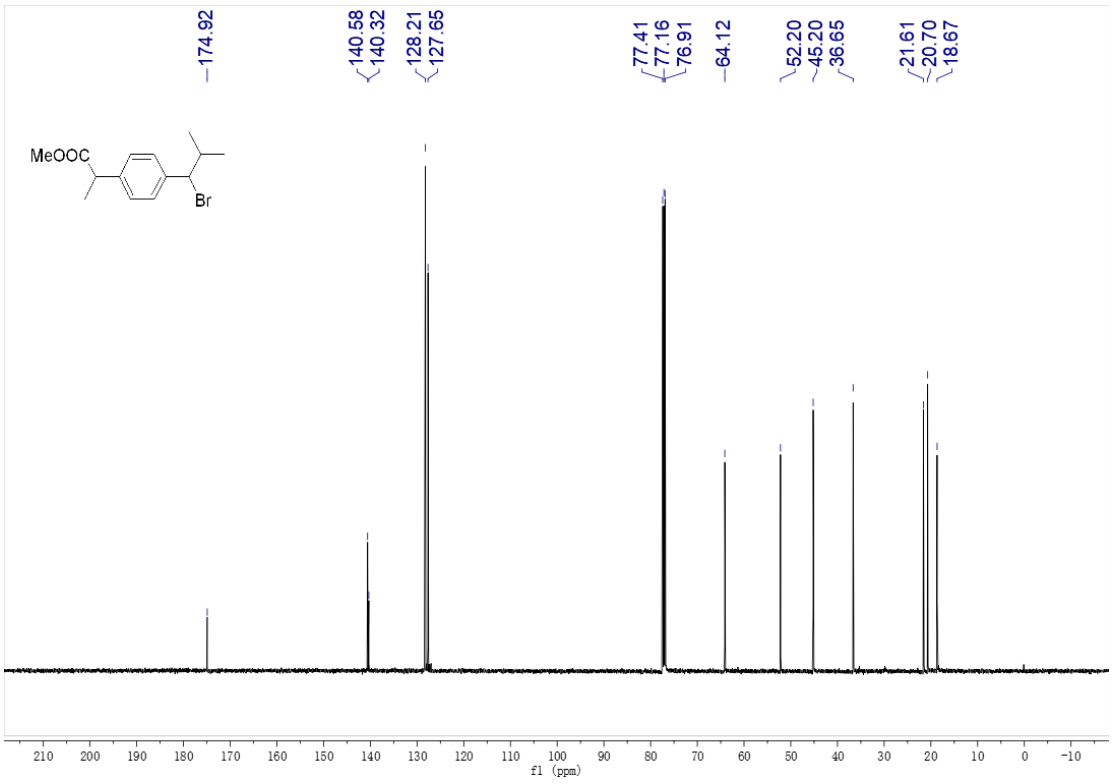
^{1}H NMR of compound **58c** (500 MHz, $CDCl_3$)



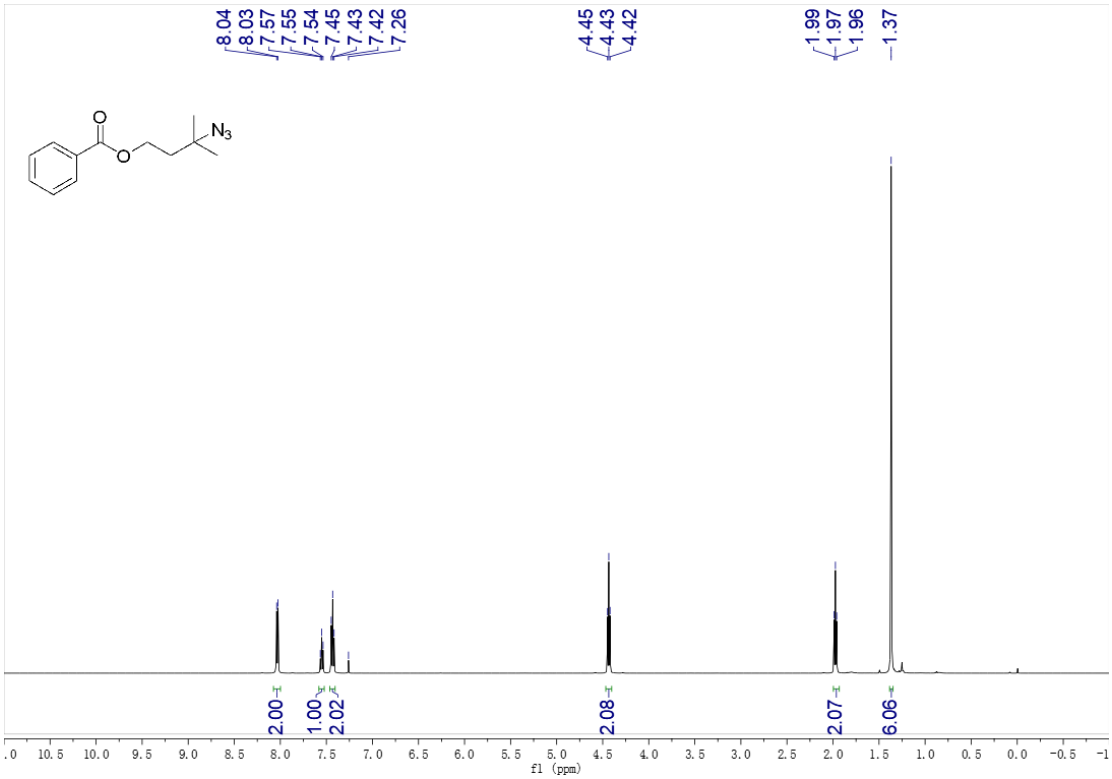
^{13}C NMR of compound **58c** (126 MHz, $CDCl_3$)



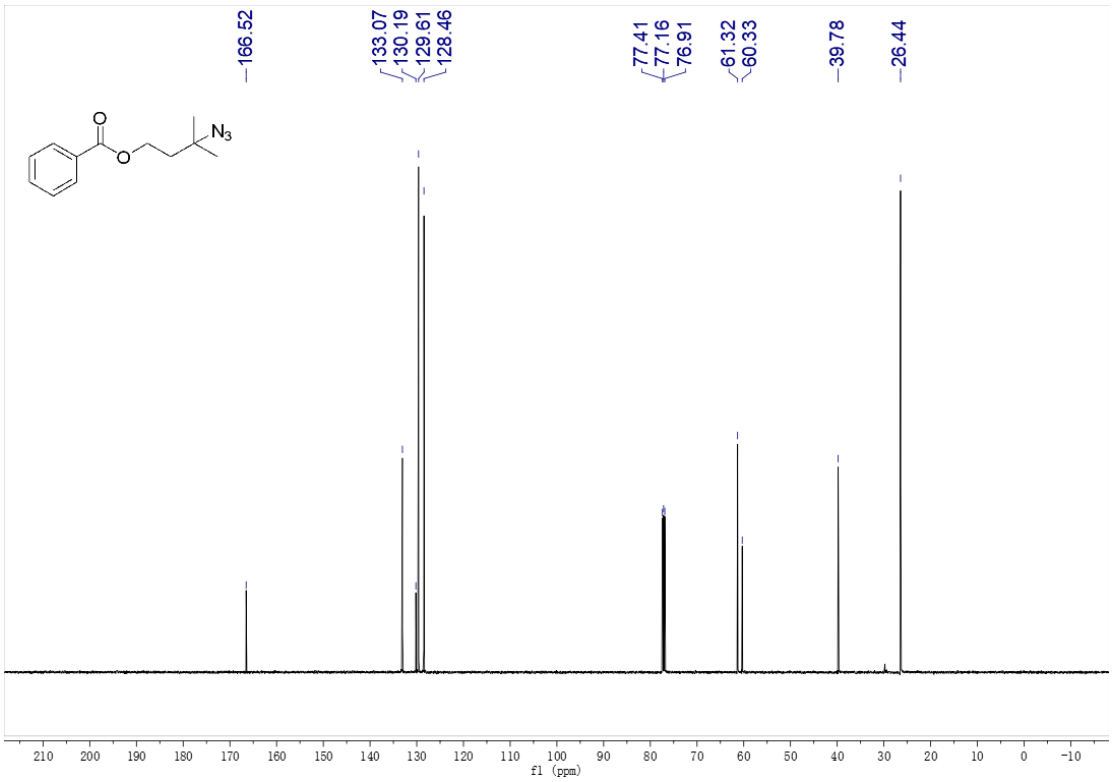
^{1}H NMR of compound **59c** (500 MHz, $CDCl_3$)



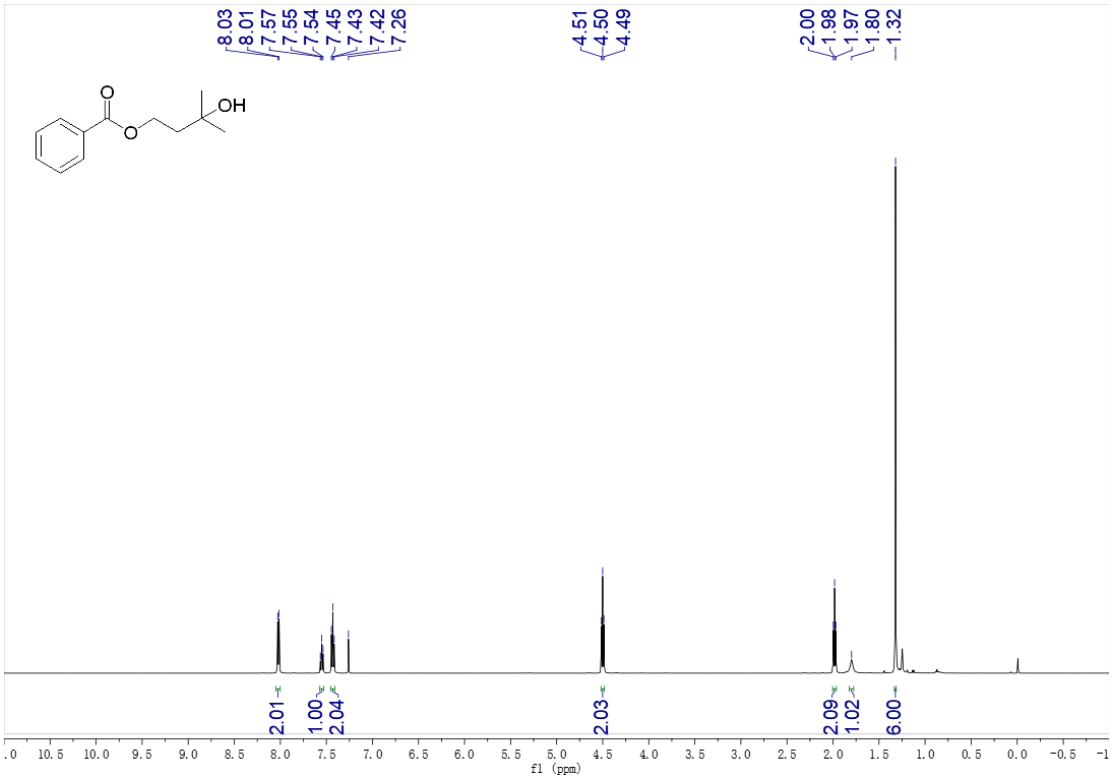
^{13}C NMR of compound **59c** (126 MHz, $CDCl_3$)



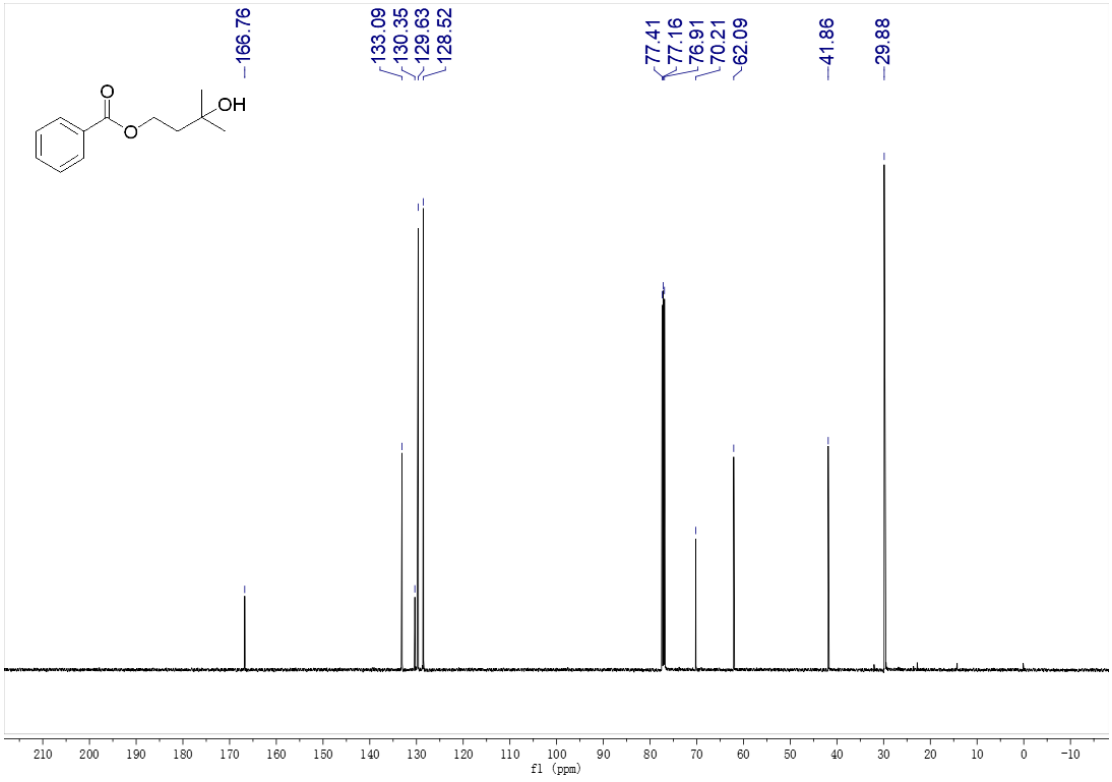
^{1}H NMR of compound **60d** (500 MHz, $CDCl_3$)



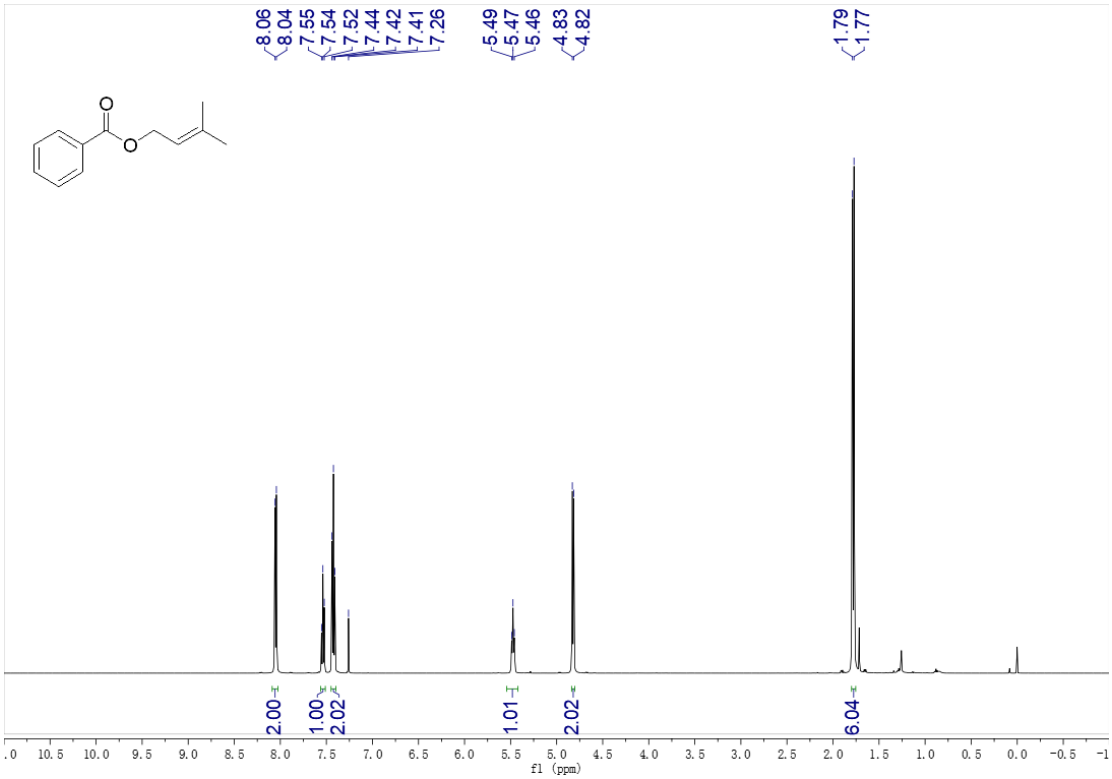
^{13}C NMR of compound **60d** (126 MHz, $CDCl_3$)



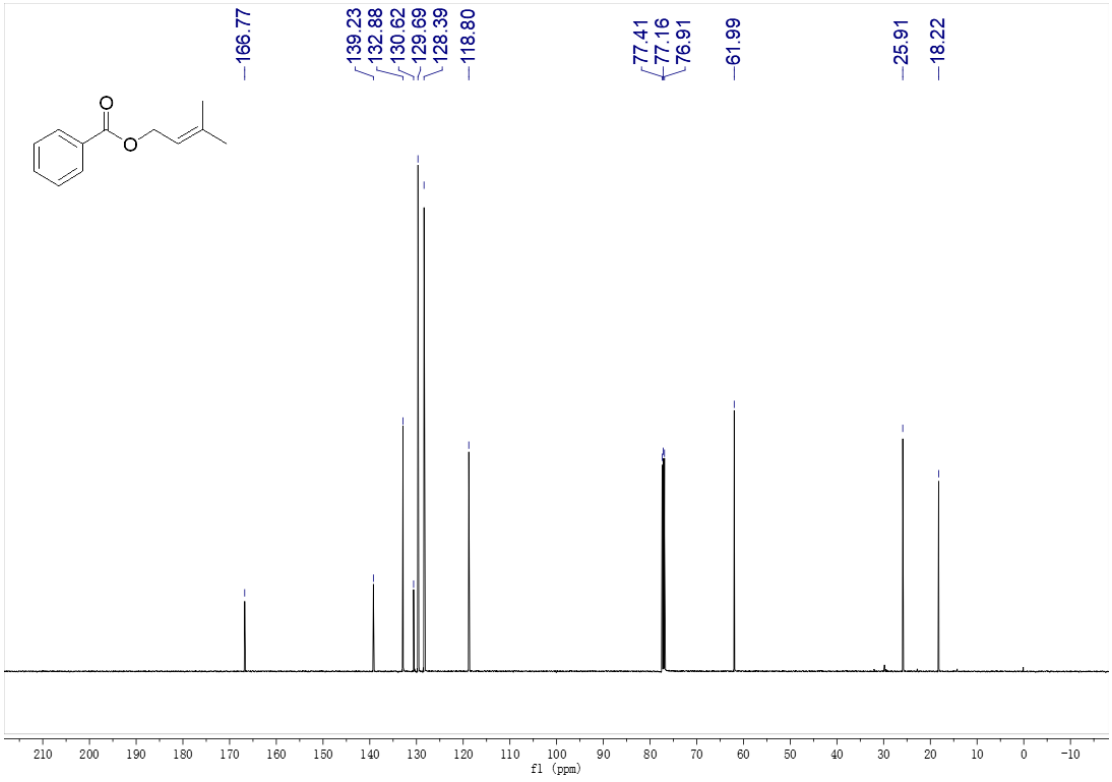
^{1}H NMR of compound **61d** (500 MHz, $CDCl_3$)



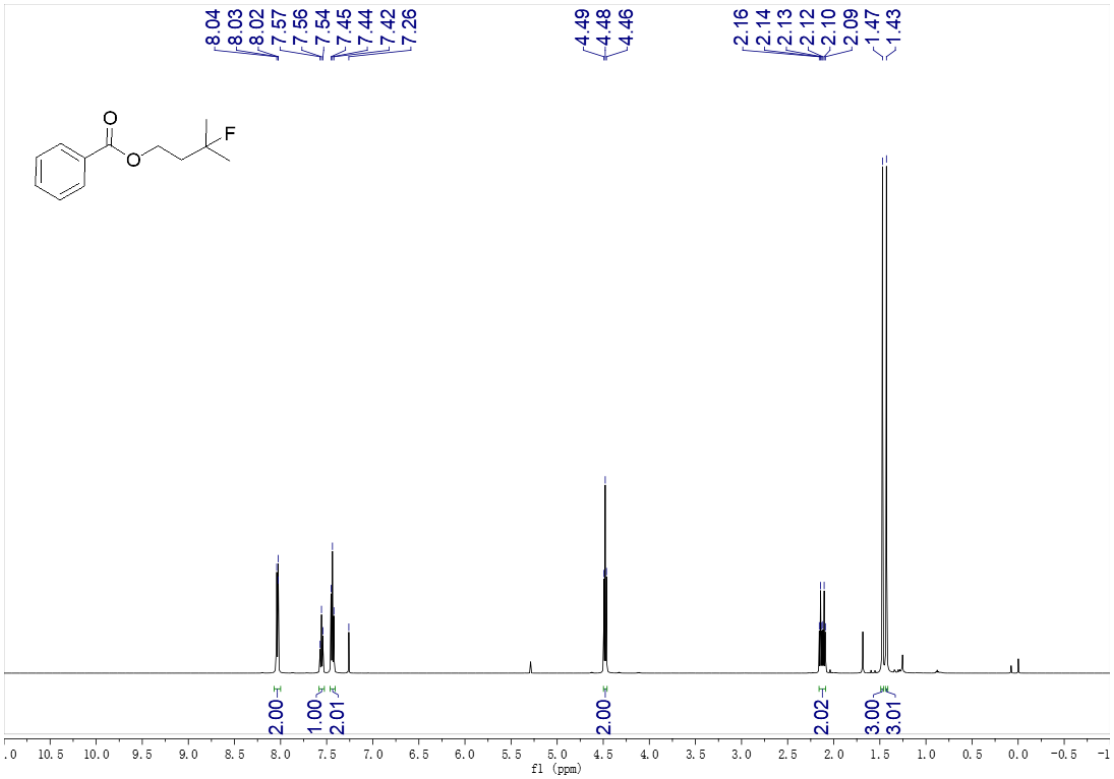
^{13}C NMR of compound **61d** (126 MHz, $CDCl_3$)



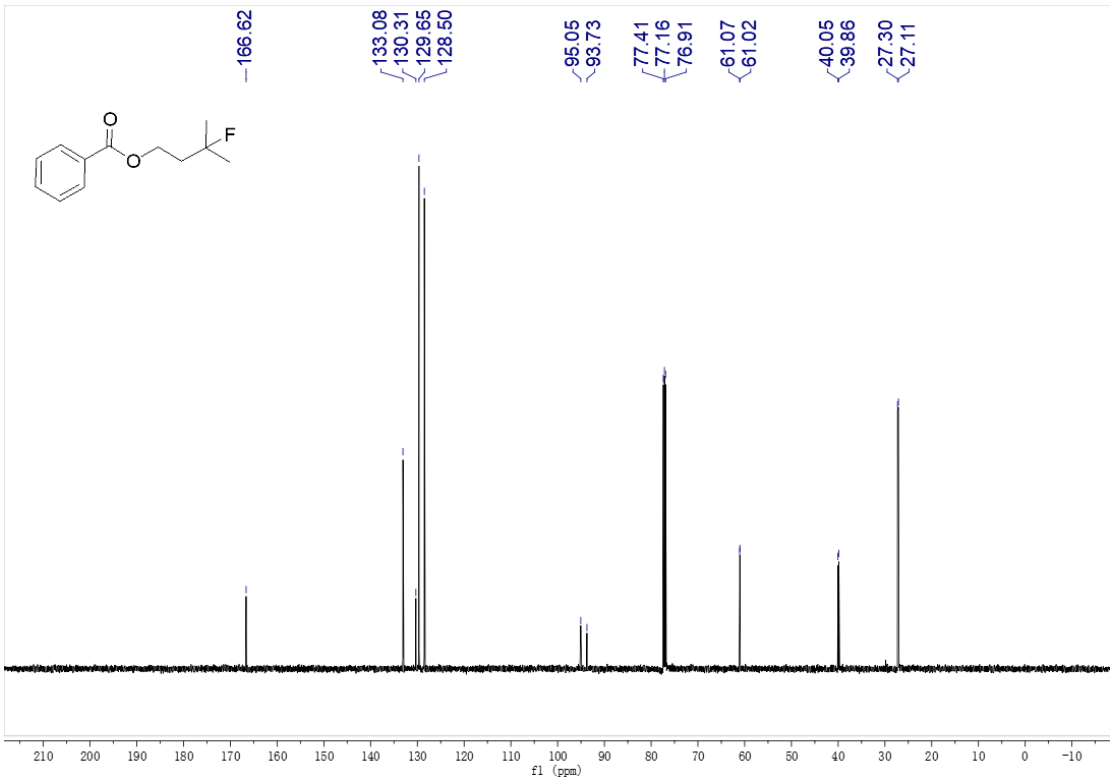
^{1}H NMR of compound **62d** (500 MHz, $CDCl_3$)



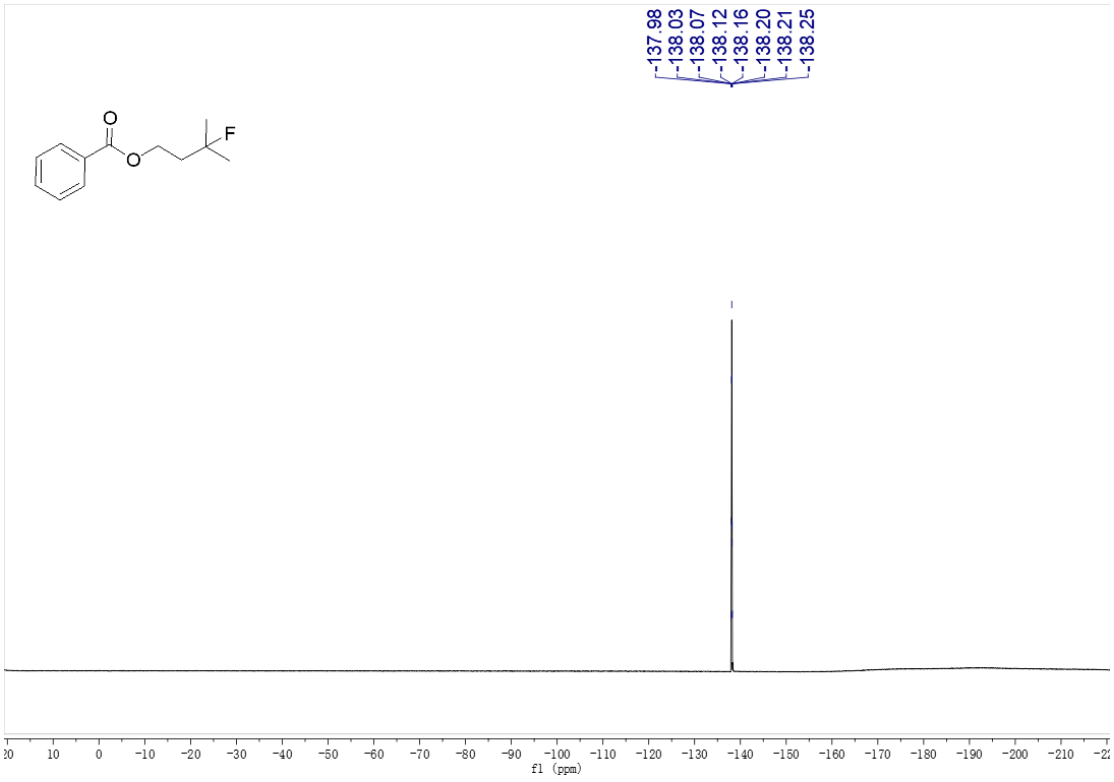
^{13}C NMR of compound **62d** (126 MHz, $CDCl_3$)



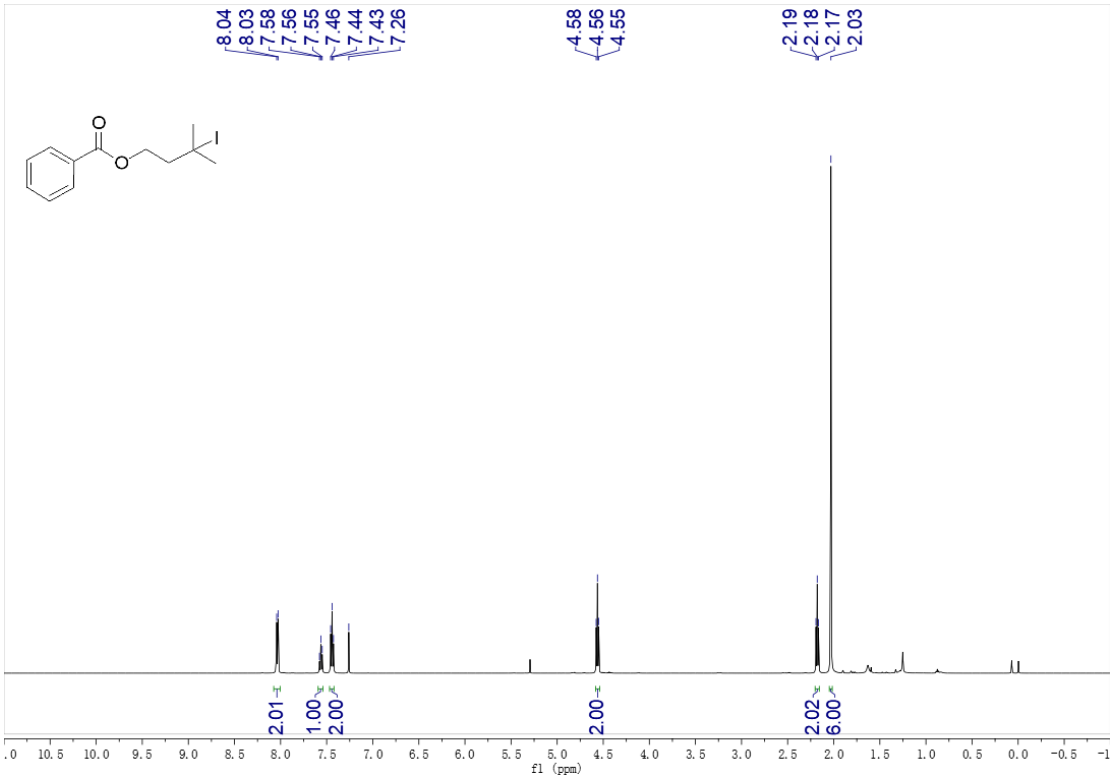
^{1}H NMR of compound **63d** (500 MHz, $CDCl_3$)



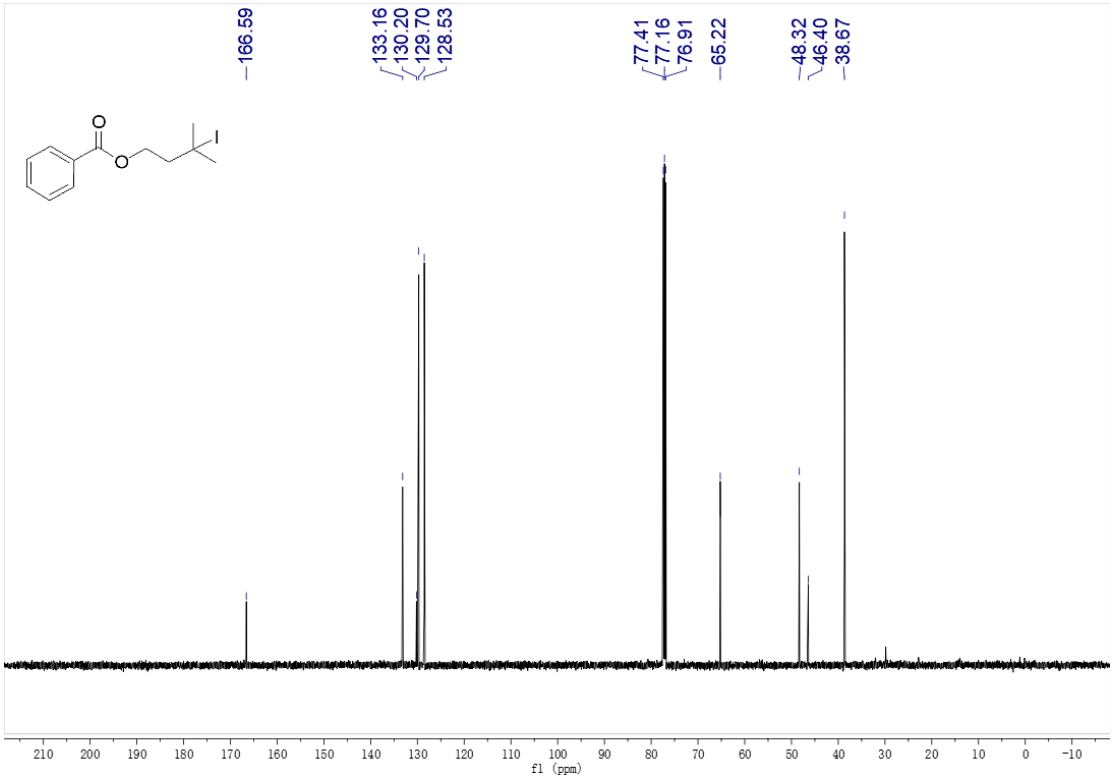
^{13}C NMR of compound **63d** (126 MHz, $CDCl_3$)



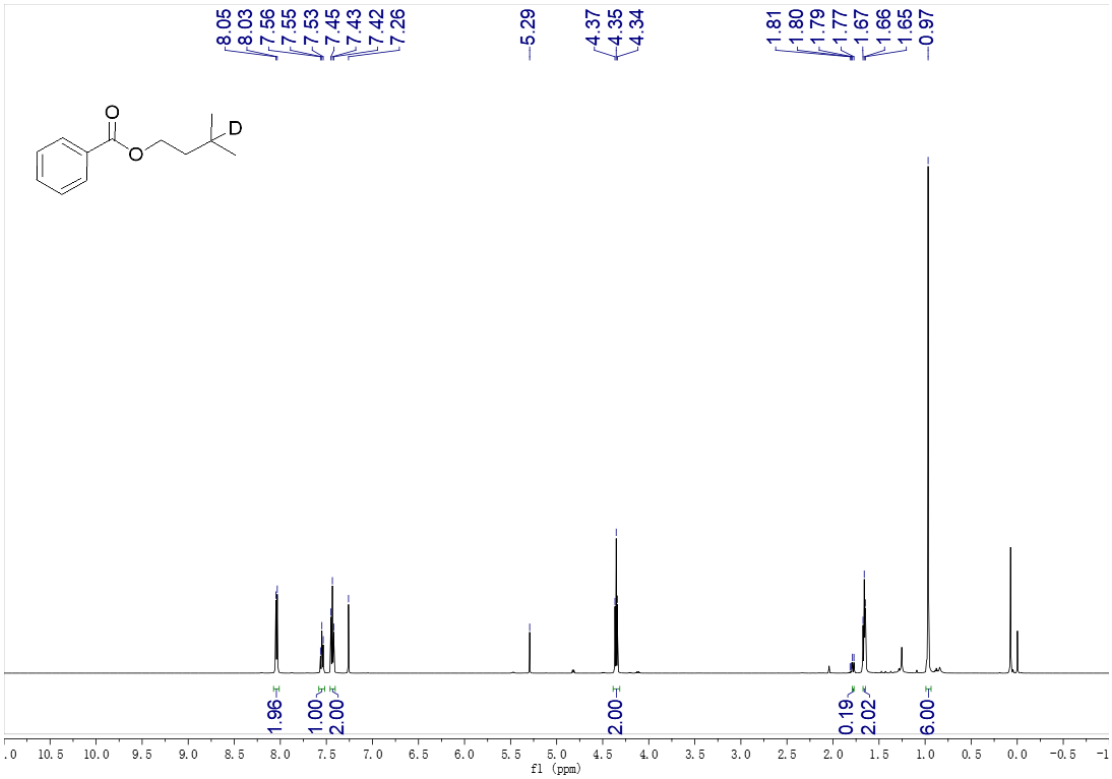
^{19}F NMR of compound **63d** (471 MHz, $CDCl_3$)



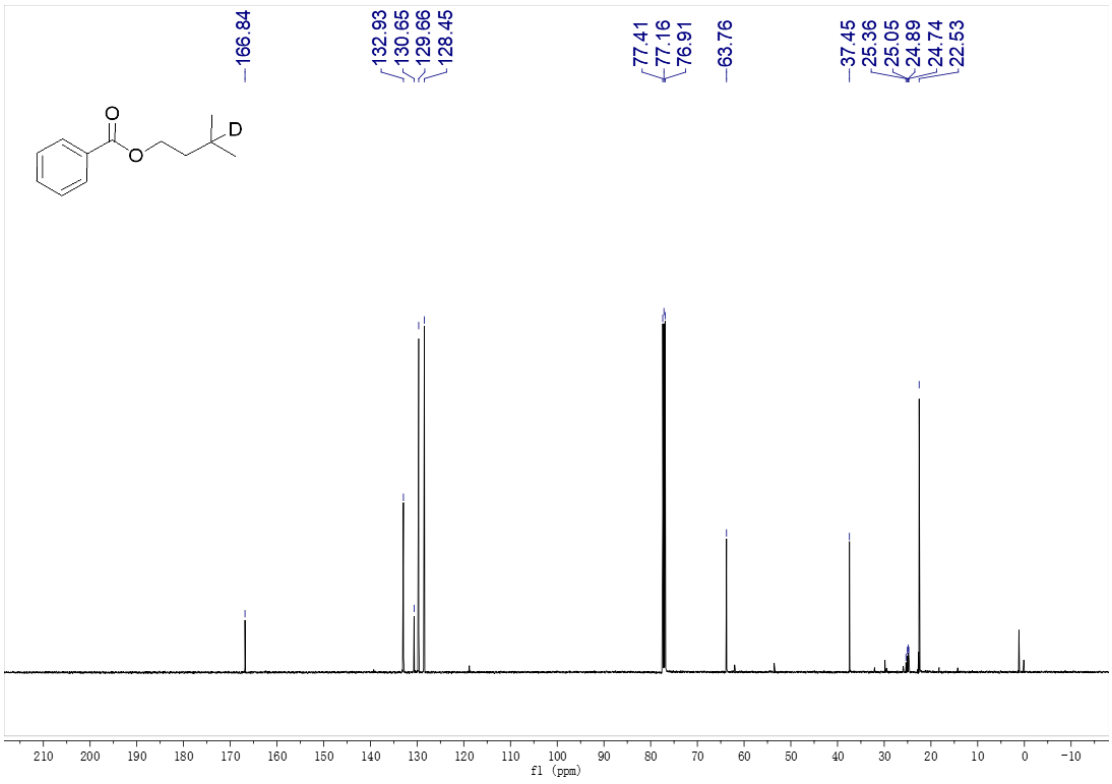
^{1}H NMR of compound **64d** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **64d** (126 MHz, $CDCl_3$)



^{1}H NMR of compound **65d** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **65d** (126 MHz, $CDCl_3$)