Supporting Information

A Catalyst- and Solvent-Free Visible-Light-Promoted Bromination and Chlorination of Tertiary C(sp^3)-H Bond

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Content

1. Reagents

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

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

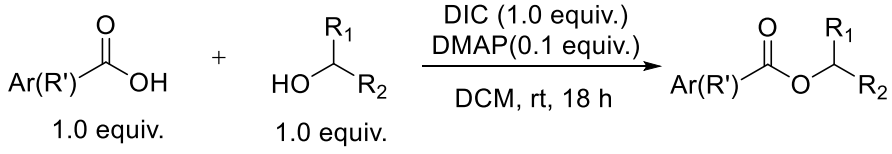
2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectrometry (HRMS) data were obtained on an LC-MS instrument (ESI-HRMS, Agilent 6520 Q-TOF LC/MS).

All reactions were carried out in a 15 mL glass tube.

3. Synthesis of substrates

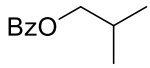
3.1 General procedure for synthesis of benzoates:



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 Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography to yield pure substrate.

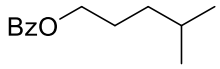
Isobutyl benzoate (2a)



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). Spectra data are consistent with those reported in literature.[1]

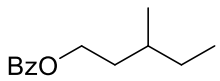
4-Methylpentyl benzoate (3a)



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). Spectra data are consistent with those reported in literature.[2]

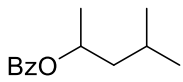
3-Methylpentyl benzoate (4a)



4a 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). Spectra data are consistent with those reported in literature.[3]

4-Methylpentan-2-yl benzoate (5a)

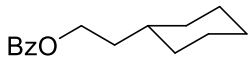


5a R_f = 0.7, 5% acetone in hexane, yellowish oil (1.44 g, 70 % yield).

^{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). Spectra data are consistent with those reported in literature.[4]

2-Cyclohexylethyl benzoate (6a)



6a

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). Spectra data are consistent with those reported in literature.[5]

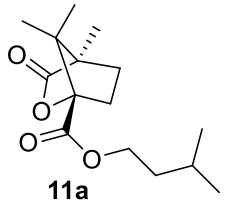
***trans*-4-Methylcyclohexyl benzoate (7a)**

7a

R_f = 0.7, 5% acetone in hexane, white solid (1.48 g, 68% 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). Spectra data are consistent with those reported in literature.[6]

Isopentyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (11a)

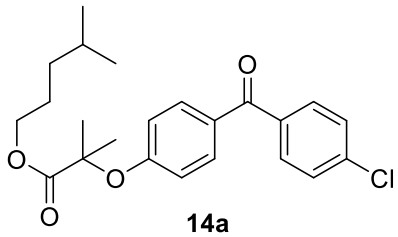


11a

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) spectra data are consistent with those reported in literature.[7]

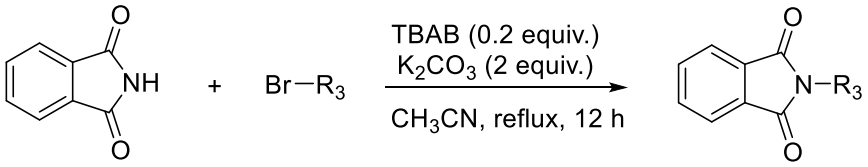
4-Methylpentyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (14a)



14a

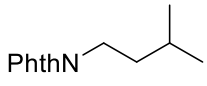
R_f = 0.7, 5% acetone in hexane, yellowish oil (2.73 g, 68 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.12 (dd, J = 7.5, 5.8 Hz, 2H), 1.65 (s, 6H), 1.55 (dd, J = 15.4, 7.2 Hz, 2H), 1.49 – 1.41 (m, 1H), 1.07 (dd, J = 15.8, 7.1 Hz, 2H), 0.79 (d, J = 6.6 Hz, 6H). Spectra data are consistent with those reported in literature.[8]

3.2 General procedure for synthesis of Phth-protected amines:



Phthalimide (10 mmol, 1.0 equiv.) and tetrabutylammonium bromide (TBAB) (2 mmol, 0.2 equiv.) were added to a flask. Alkyl bromide (12 mmol, 1.2 equiv.) and 25 mL of CH_3CN were then added, followed by K_2CO_3 (20 mmol, 2.0 equiv.). The mixture was heated to reflux for 12 h. After cooling to room temperature, the 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 of 0.2 M KOH (aq.) and water. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography to yield the pure substrate.

***N*-Isoamylphthalimide (9a)**

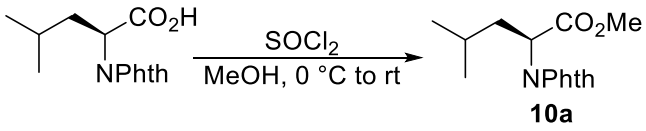


9a

R_f = 0.5, 20% acetone in hexane, yellowish oil (1.87 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). Spectra data are consistent with those reported in literature.[6]

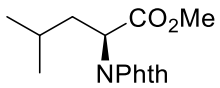
3.3 Synthesis of compound 10a



10a

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 °C. 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 compound **10a** as a white solid.

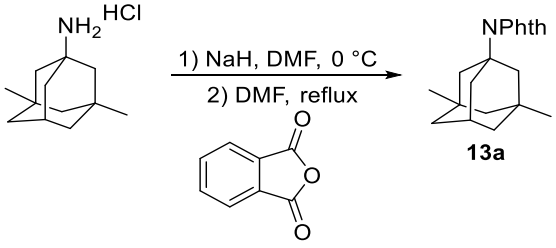
Methyl (*S*)-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (10a)



10a

R_f = 0.4, 20% 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). Spectra data are consistent with those reported in literature.[6]

3.4 Synthesis of compound 13a

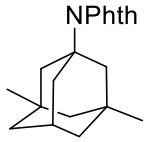


13a

Memantine hydrochloride (1.40 g, 5.6 mmol, 1.0 equiv.) was dissolved in anhydrous DMF (15 mL) and cooled to 0 °C. Sodium hydride (134.4 mg, 5.6 mmol, 1.0 equiv.) was added portion-wise. The reaction mixture was stirred at 0 °C 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 with 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% EA/Hexanes) to give compound **13a** as a white solid.

***N*-Phth memantine (13a)**

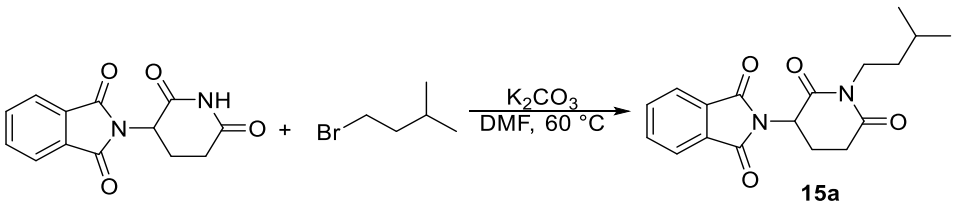


13a

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). Spectra data are consistent with those reported in literature.[6]

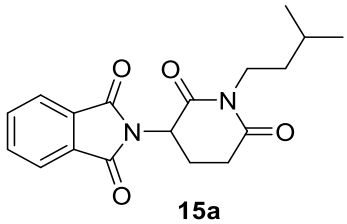
3.5 Synthesis of compound 15a



15a

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 °C 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 **15a** as a white solid.

2-(1-Isopentyl-2,6-dioxopiperidin-3-yl)isoindoline-1,3-dione (15a)



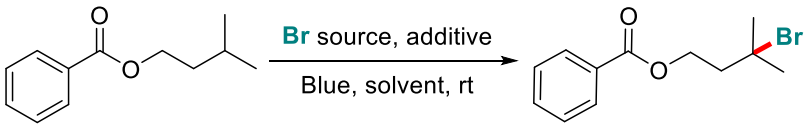
15a

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). Spectra data are consistent with those reported in literature.[8]

4. Optimization studies

4.1 Reaction optimization for C-H bromination of isopentyl benzoate

All screening reactions were carried out at a 0.5 mmol scale in a 15 mL of glass tube. isoamyl benzoate **1a** (96.1 mg, 0.5 mmol, 1.0 equiv.), other specified reagents were added to a 15 mL of glass tube. The reaction carried out at room temperature without magnetic stir bar. After the reaction was completed as monitored with TLC, the solvent of the reaction mixture was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (53 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the methyl peaks at 0.97 ppm (d, J = 6.6 Hz, 6H) for compound **1a**, 1.88 ppm (s, 6H) for compound **1b**.



1a **1b**

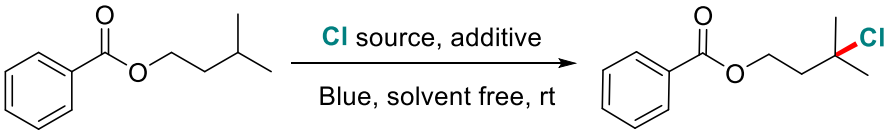
Entry	Reaction conditions	Rsm[a] (%)	Yield of **1b** (%)[b]
1	**NHPI (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), rt, 12 h**	**81**	**12**

2	NHPI (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 12 h	16	74
3	Eosin B (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 12 h	44	47
4	Acid red (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 12 h	100	ND[c]
5	Rhodamine B (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5mL), 465 nm, 6 w, rt, 12 h	100	ND
6	NHPI (0.2 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	<10	90
7	NHPI (0.1 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	<10	91
8	NHPI (0.05 equiv.), DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	<10	89
9	DBDMH (1.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	<5	93 (86[d])
10	DBDMH (1.0 equiv.), DCM (1.5 mL), rt, 12h	100	ND
11	DBDMH (0.75 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	<10	81
12	DBDMH (0.5 equiv.), DCM (1.5mL), 465 nm, 6 w, rt, 1 h	26	68
13	NBS (2.0 equiv.), DCM (1.5 mL), 465 nm, 6 w, rt, 1 h	19	72
14	DBDMH (1.0 equiv.), solvent free, 465 nm, 6 w, rt, 1 h	46	51
15	DBDMH (1.0 equiv.), solvent free, 465 nm, 6 w, rt, 3 h	<10	88 (85[d])
16	DBDMH (1.0 equiv.), solvent free, 465 nm, 6 w, N_2, rt, 3 h	<10	86
17	DBDMH (0.75 equiv.), solvent free, 465 nm, 6 w, rt, 3 h	25	67
18	DBDMH (0.50 equiv.), solvent free, 465 nm, 6 w, rt, 3 h	37	54
19	DBDMH (1.0 equiv.), solvent free, CFL, 6 w, rt, 3 h	44	53
20	DBDMH (1.0 equiv.), solvent free, 365 nm, 6 w, rt, 3 h	<10	79

[a] RSM is the short for of recovery starting material. [b] Yields are based on ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard. [c] ND = not detected. [d] Isolated yield.

4.1 Reaction optimization for C-H chlorination of isopentyl benzoate

All screening reactions were carried out at a 0.5 mmol scale in a 15 mL of glass tube. isoamyl benzoate **1a** (96.1 mg, 0.5 mmol, 1.0 equiv.), other specified reagents were added to a 15 mL of glass tube. The reaction carried out at room temperature without magnetic stir bar. After the reaction was completed as monitored with TLC, the solvent of the reaction mixture was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (53 μL) as an external standard for ^{1}H-NMR analysis. The composition of reaction mixture was based on the methyl peaks at 0.97 ppm (d, J = 6.6 Hz, 6H) for compound **1a**, 1.68 ppm (s, 6H) for compound **1c**.



1a **1c**

Entry	Reaction conditions	Rsm[a] (%)	Yield of **1b** (%)[b]
1	**DCDMH (1.0 equiv.), 465 nm, 6 w, rt, 12 h**	**>90**	**Trace**
2	**DCDMH (1.0 equiv.), 465 nm, 6 w, 40 °C, 12 h**	**>90**	**Trace**
3	**DCDMH (1.0 equiv.), Cs_2CO_3 (2.0 equiv.), 465 nm, 6 w, rt, 6 h**	**76**	**21**
4	**DCDMH (1.0 equiv.), Pyridine (2.0 equiv.), 465 nm, 6 w, rt, 6 h**	**26**	**71(68[c])**
5	**DCDMH (1.0 equiv.), 2,4,6-trimethylpyridine (2.0 equiv.), 465 nm, 6 w, rt, 6 h**	**21**	**62**
6	**Trichloroisocyanuric acid (0.7 equiv.), Pyridine (2.0 equiv.), 465 nm, 6 w, rt, 6 h**	**16**	**60**

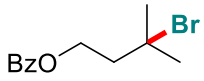
7	**NCS (2.0 equiv.), Pyridine (2.0 equiv.), 465 nm, 6 w, rt, 1 h**	**31**	**58**

[a] RSM is the short for of recovery starting material. [b] Yields are based on ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard. [c] Isolated yield.

5. General procedures and substrate scope for C-H bromination

General conditions A: Substrates (0.5 mmol, 1.0 equiv.) and DBDMH (0.5 mmol) were added to the glass tube. The mixture was irradiated with blue light (465 nm, 6 w) for 3 hours at room temperature without solvent (If it is a solid substrate, DCM (5.0 equiv.) is required as a solvent). The mixture was directly purified by silica gel flash chromatography to give the desired products.

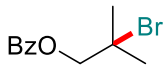
3-bromo-3-methylbutyl benzoate (1b)



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

Compound **1b** (yellowish oil, 115 mg, 85% 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 166.45, 133.01, 130.13, 129.64, 129.56, 128.44, 128.40, 64.26, 63.10, 45.47, 34.75. Spectra data are consistent with those reported in literature.[9]

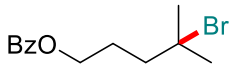
2-bromo-2-methylpropyl benzoate (2b)



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

Compound **2b** (yellowish oil, 86 mg, 67% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 4.47 (s, 2H), 1.88 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.84, 133.27, 129.73(2C), 128.50(2C), 73.31, 60.88, 31.03(2C). **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{11}H_{14}BrO_2^+$ 257.0172; Found: 257.0168.

4-bromo-4-methylpentan-2-yl benzoate (3b)

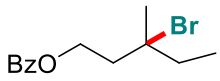


3b

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

Compound **3b** (yellowish oil, 112 mg, 79% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.9 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 4.39 (t, J = 6.2 Hz, 2H), 2.08 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H), 1.82 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.58, 132.95, 130.26, 129.57, 128.38, 67.09, 64.65, 43.87, 34.28, 26.00. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}BrO_2^+$ 285.0485; Found: 285.0488.

3-bromo-3-methylpentyl benzoate (4b)

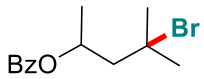


4b

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

Compound **3b** (yellowish oil, 124 mg, 87% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.46 (t, J = 6.9 Hz, 2H), 2.05 – 1.96 (m, 2H), 1.68 (q, J = 7.4 Hz, 2H), 1.36 (s, 3H), 1.01 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl3) δ 166.51, 133.00, 130.14, 129.55, 128.39, 63.15, 61.15, 37.24, 32.52, 23.09, 8.39. Spectra data are consistent with those reported in literature.[9]

4-bromo-4-methylpentan-2-yl benzoate (5b)

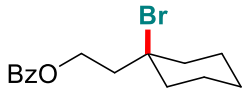


5b

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

Compound **5b** (yellowish oil, 125 mg, 88% yield): **^{1}H NMR** (500 MHz, CDCl3) δ 8.06 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 5.51 (p, J = 6.1 Hz, 1H), 2.41 (dd, J = 15.4, 8.4 Hz, 1H), 2.25 (dd, J = 15.3, 1.5 Hz, 1H), 1.85 (s, 3H), 1.80 (s, 3H), 1.42 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, CDCl3) δ 165.78, 132.93, 130.53, 129.56(2C), 128.38(2C), 70.06, 64.78, 52.86, 35.62, 33.68, 21.66. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{13}H_{18}BrO_2^+$ 285.0485; Found: 285.0483.

2-(1-bromocyclohexyl)ethyl benzoate (6b)

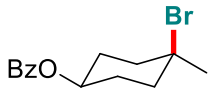


6b

R_f = 0.6 (**6b**), 5% acetone in hexane

Compound **6b** (yellowish oil, 116 mg, 75% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 15.0, 7.8 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 4.70 (dd, J = 9.1, 4.6 Hz, 2H), 2.66 – 2.57 (m, 1H), 2.56 – 2.38 (m, 1H), 2.33 – 1.91 (m, 3H), 1.95 – 1.76 (m, 2H), 1.80 – 1.48 (m, 4H), 1.37 – 1.22 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.50, 132.98, 132.96, 130.22, 130.14, 129.65, 129.56(2C), 128.39(2C), 128.37, 72.71, 62.64, 62.37, 41.34, 31.83, 25.27, 23.05, 22.14. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{20}BrO_2^+$ 311.0641; Found: 311.0644.

(1*s*,4*s*)-4-bromo-4-methylcyclohexyl benzoate (7b)

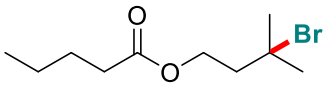


7b

R_f = 0.6 (**7b**), 2% acetone in hexane

Compound **7b** (yellowish oil, 103 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 5.07 – 4.93 (m, 1H), 2.24 (d, J = 13.4 Hz, 2H), 2.06 (ddd, J = 13.0, 10.4, 3.7 Hz, 4H), 1.90 (s, 3H), 1.72 – 1.62 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.04, 132.90, 130.56, 129.61, 128.33, 72.28, 68.46, 41.01(2C), 28.57(3C). **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{14}H_{18}BrO_2^+$ 297.0485; Found: 297.0488.

3-bromo-3-methylbutyl pentanoate (8b)



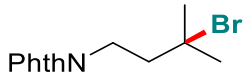
8b

R_f = 0.6 (**8b**), 2% acetone in hexane

Compound **8b** (yellowish oil, 108 mg, 87% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.34 (t, J = 6.9 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 2.17 (t, J = 6.9 Hz, 2H), 1.82 (s, 6H), 1.64 (dd, J = 9.0, 5.8 Hz, 2H), 1.36 (dd, J = 15.0, 7.5 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.72, 64.22, 62.37, 45.35, 34.65(2C), 34.06, 26.98, 22.26,

13.70. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_{20}BrO_2^+$ 251.0641; Found: 251.0638.

2-(3-bromo-3-methylbutyl)isoindoline-1,3-dione (9b)

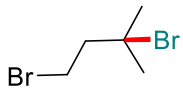


9b

R_f = 0.6 (**9b**), 10% acetone in hexane

Compound **9b** (yellowish oil, 122 mg, 83% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.3, 3.1 Hz, 2H), 7.72 (dd, J = 5.4, 3.0 Hz, 2H), 3.97 – 3.90 (m, 2H), 2.22 – 2.12 (m, 2H), 1.84 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.09, 133.96, 132.11, 123.22, 63.60, 44.71, 35.70, 34.26. Spectra data are consistent with those reported in literature.[9]

1,3-dibromo-3-methylbutane (10b)

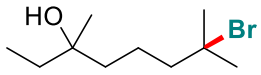


10b

R_f = 0.6 (**10b**), hexane

Compound **10b** (yellowish oil, 173 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.3, 3.1 Hz, 2H), 7.72 (dd, J = 5.4, 3.0 Hz, 2H), 3.97 – 3.90 (m, 2H), 2.22 – 2.12 (m, 2H), 1.84 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.09, 133.96, 132.11, 123.22, 63.60, 44.71, 35.70, 34.26. Spectra data are consistent with those reported in literature.[10]

7-bromo-3,7-dimethyloctan-3-ol (11b)

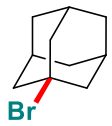


11b

R_f = 0.6 (**11b**), 20% acetone in hexane

Compound **11b** (yellowish oil, 163 mg, 69% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 1.90 – 1.80 (m, 8H), 1.65 – 1.43 (m, 4H), 1.35 – 1.20 (m, 3H), 1.14 (s, 3H), 0.90 (t, J = 13.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ73.94, 68.48, 45.58, 42.62, 34.88, 32.49, 26.00, 19.35, 7.31. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{10}H_{22}BrO^+$ 237.0849; Found: 237.0852.

1-bromoadamantane (12b)

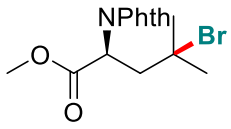


12b

R_f = 0.5 (**12b**), hexane

Compound **12b** (yellowish solid, 171 mg, 81% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.38 (s, 6H), 2.12 (s, 3H), 1.75 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 49.33, 35.54, 32.61. Spectra data are consistent with those reported in literature.[11]

methyl (*S*)-4-bromo-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (13b)

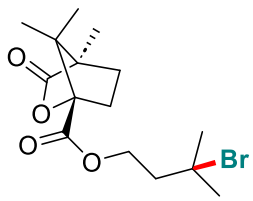


13b

R_f = 0.6 (**13b**), 10% acetone in hexane

Compound **13b** (yellowish oil, 152 mg, 86% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.75 (dd, J = 5.4, 3.0 Hz, 2H), 5.23 (dd, J = 8.6, 3.6 Hz, 1H), 3.73 (s, 3H), 2.89 – 2.80 (m, 2H), 1.82 (s, 3H), 1.74 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.31, 168.61, 134.05, 133.93, 131.94, 123.32, 123.19, 66.72, 51.61, 48.78, 42.41, 38.28, 34.53. Spectra data are consistent with those reported in the literature.[9]

3-bromo-3-methylbutyl (1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (14b)



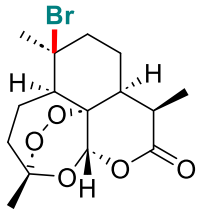
14b

R_f = 0.6 (**14b**), 5% acetone in hexane

Compound **14b** (white solid, 154 mg, 89% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.28 (td, J = 6.3, 2.4 Hz, 2H), 2.48 – 2.38 (m, 1H), 2.03 (ddd, J = 13.6, 9.4, 4.5 Hz, 1H), 1.98 – 1.90 (m, 3H), 1.87 – 1.80 (m, 2H), 1.76 (s, 6H), 1.69 (ddd, J = 13.3, 9.4, 4.2 Hz, 1H), 1.11 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.10, 167.46, 91.10, 66.73, 65.24, 54.77, 54.13, 43.63, 34.24, 30.70, 28.94, 25.86, 16.81,

16.78, 9.71. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{24}BrO_4^+$ 347.0852; Found: 347.0856.

(3*R*,5a*R*,6*S*,8a*S*,9*R*,12*S*,12a*S*)-6-bromo-3,6,9-trimethyloctahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10(3*H*)-one (15b)

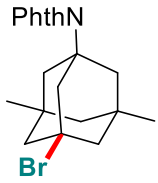


15b

R_f = 0.5 (**15b**), 20% acetone in hexane

Compound **15b** (white solid, 129 mg, 72% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 2.62 (dd, J = 13.5, 4.3 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.13 – 2.06 (m, 2H), 2.04 – 1.99 (m, 4H), 1.81 (dd, J = 13.3, 3.4 Hz, 1H), 1.51 (d, J = 10.1 Hz, 4H), 1.38 (dt, J = 10.2, 5.4 Hz, 1H), 1.32 – 1.20 (m, 2H), 1.18 – 1.11 (m, 1H), 1.01 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.86, 105.66, 94.45, 79.98, 51.92, 51.34, 50.35, 37.22, 35.63, 33.64, 30.16, 26.59, 25.17, 24.82, 19.78. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{15}H_{22}BrO_5^+$ 361.0645; Found: 361.0647.

2-((1*r*,3*s*,5*R*,7*S*)-3-bromo-5,7-dimethyladamantan-1-yl)isoindoline-1,3-dione (16b)

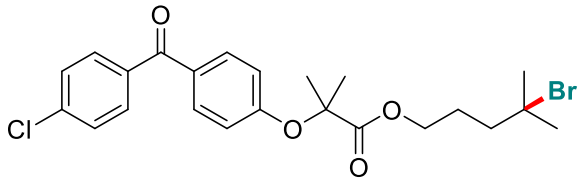


16b

R_f = 0.6 (**16b**), 20% acetone in hexane

Compound **16b** (white solid, 92 mg, 76% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (dd, J = 5.3, 3.1 Hz, 2H), 7.70 (dd, J = 5.3, 3.1 Hz, 2H), 2.95 (s, 2H), 2.25 (d, J = 12.3 Hz, 2H), 2.12 (dd, J = 22.9, 12.2 Hz, 4H), 1.98 (d, J = 12.0 Hz, 2H), 1.34 – 1.23 (m, 2H), 0.99 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.35, 133.91, 131.69, 122.73, 62.82, 62.31, 53.80, 49.17, 48.57, 44.44, 35.94, 29.34. Spectra data are consistent with those reported in literature.[9]

4-bromo-4-methylpentyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (17b)

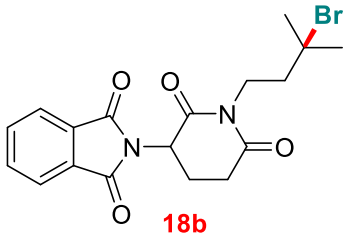


17b

R_f = 0.6 (**17b**), 10% acetone in hexane

Compound **17b** (yellowish oil, 185 mg, 77% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 22.3, 8.6 Hz, 4H), 7.45 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 4.21 (t, J = 6.3 Hz, 2H), 1.87 – 1.74 (m, 2H), 1.70 (s, 6H), 1.68 – 1.63 (m, 8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.06, 173.65, 159.70, 138.36, 136.33, 132.07(2C), 131.12(2C), 130.32, 128.55(2C), 117.09(2C), 79.41, 66.68, 65.36, 43.52, 34.14(2C), 25.67, 25.49(2C). **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{23}H_{27}BrClO_4^+$ 481.0776; Found: 481.0771.

2-(1-(3-bromo-3-methylbutyl)-2,6-dioxopiperidin-3-yl)isoindoline-1,3-dione (18b)



18b

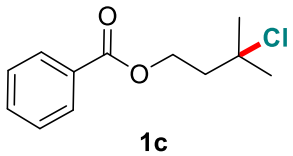
R_f = 0.6 (**18b**), 20% acetone in hexane

Compound **18b** (white solid, 152 mg, 75% yield): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.1, 3.1 Hz, 2H), 7.76 (dd, J = 5.1, 3.0 Hz, 2H), 5.01 (dd, J = 12.3, 5.2 Hz, 1H), 4.24 – 3.87 (m, 2H), 2.99 (d, J = 12.5 Hz, 1H), 2.89 – 2.70 (m, 2H), 2.27 – 1.90 (m, 3H), 1.79 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.74, 168.47, 167.43(2C), 134.46(2C), 131.73, 123.74(2C), 64.10, 50.13, 43.91, 38.60, 34.27, 34.18(2C), 32.00, 21.95. **HRMS (ESI-TOF) m/z:** $[M+H]^+$ Calcd for $C_{18}H_{20}BrN_2O_4^+$ 407.0601; Found: 407.0603.

General conditions B: Substrates (0.5 mmol, 1.0 equiv.), DCDMH (0.5 mmol, 1.0 equiv.) and pyridine (1.0 mmol, 2.0 equiv.) were added to the glass tube. The mixture was irradiated with blue light (465 nm, 6 w) for 3 hours at room temperature without

solvent (If it is a solid substrate, DCM (5.0 equiv.) is required as a solvent). The mixture was directly purified by silica gel flash chromatography to give the desired products.

3-chloro-3-methylbutyl benzoate (1c)

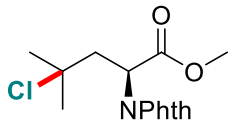


1c

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

Compound **1c** (yellowish oil, 77 mg, 68% 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 166.56, 132.99, 130.19, 129.61, 129.56, 128.44, 128.40, 62.79, 50.78, 32.66, 17.66. Spectra data are consistent with those reported in literature.[4]

methyl (*S*)-4-chloro-2-(1,3-dioxoisoindolin-2-yl)-4-methylpentanoate (2c)

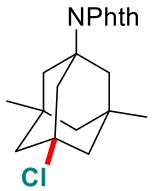


2c

R_f = 0.5 (**2c**); 20% acetone in hexane

Compound **2c** (yellowish oil, 107 mg, 69% 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 169.68, 167.60, 134.24, 131.93, 123.62, 68.17, 53.14, 49.27, 42.91, 33.23, 31.95. Spectra data are consistent with those reported in literature.[4]

3-chloro-5,7-dimethyladamantan-1-yl)isoindoline-1,3-dione (3c)



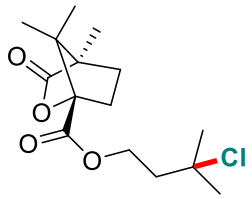
3c

R_f = 0.6 (**3c**); 10% acetone in hexane

Compound **3c** (white solid, 122 mg, 71% 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 169.38, 133.90, 131.71,

122.72, 67.20, 62.27, 52.36, 48.66, 47.88, 44.51, 35.25, 29.31. Spectra data are consistent with those reported in literature.[6]

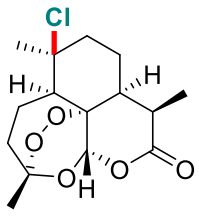
3-chloro-3-methylbutyl(1*S*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (4c)



4c R_f = 0.6 (**4c**); 10% acetone in hexane

Compound **4c** (white solid, 94 mg, 62% 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 178.07, 167.45, 90.98, 68.06, 62.71, 54.77, 54.19, 43.76, 32.87, 30.66, 28.91, 16.77, 9.69. Spectra data are consistent with those reported in literature.[7]

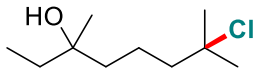
(3*R*,5*aR*,6*S*,8*aS*,9*R*,12*S*,12*aS*)-6-chloro-3,6,9-trimethyloctahydro-12*H*-3,12-epoxy[1,2]dioxepino[4,3-i]isochromen-10(3*H*)-one (5c)



5c R_f = 0.4 (**5c**); 20% acetone in hexane

Compound **5c** (white solid, 84 mg, 53% 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 171.79, 105.22, 93.38, 79.27, 74.12, 53.68, 45.29, 42.68, 35.38, 32.87, 32.73, 25.23, 21.30, 20.13, 12.57. Spectra data are consistent with those reported in literature.[7]

7-chloro-3,7-dimethyloctan-3-ol (6c)

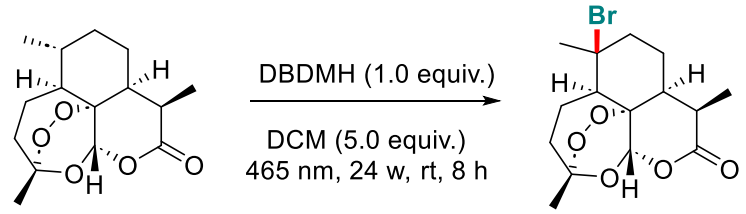


6c

R_f = 0.6 (**6c**); 20% acetone in hexane

Compound **6c** (yellowish oil, 58 mg, 62% 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. Spectra data are consistent with those reported in literature.[7]

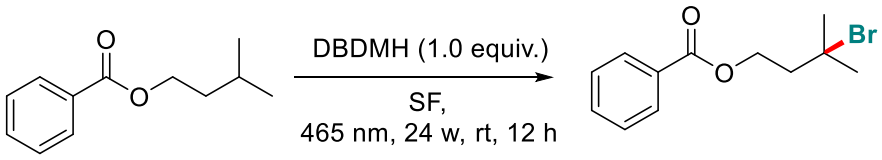
6. Gram-scale experiment



2.8 g, 10 mmol

isolated yield of **12b**: **63%**

Substrates **12a** (10 mmol, 1.0 equiv.) and DBDMH (10 mmol) were added to the glass tube, a solvent DCM (5.0 equiv., 3 mL) needs to be added and then the mixture was irradiated with blue light (465 nm, 6 w) for 8 hours at room temperature. The mixture was directly purified by silica gel flash chromatography to give the desired product **12b** (2.2 g, 63%) as white solid.



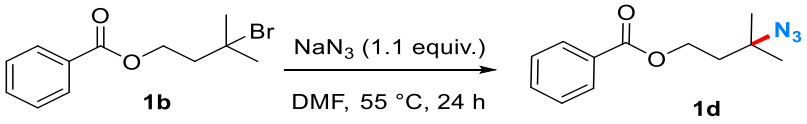
10.0 g, 52 mmol

isolated yield of **1b**: **84%**

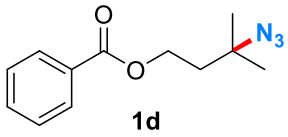
Substrates **1a** (52 mmol, 1.0 equiv.) and DBDMH (52 mmol) were added to the glass tube. The mixture was irradiated with blue light (465 nm, 6 w) for 12 hours at room temperature without solvent. The mixture was directly purified by silica gel flash chromatography to give the desired product **1b** (12.0 g, 84%) as yellowish oil.

7. Conversion of introduced bromine atom

7.1 Converted to compound 1d

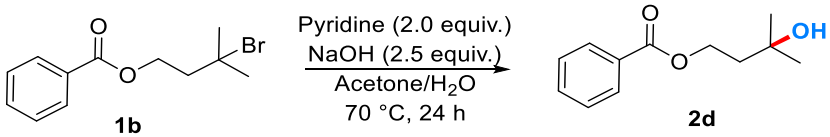


To a solution of compound **1b** (270 mg, 1.0 mmol, 1.0 equiv.) in DMF (2.0 mL) was added NaN_3 (72 mg, 1.1 mmol, 1.1 equiv.) and the reaction mixture was stirred at 55 °C for 24 hours. The reaction mixture was extracted with EA. The combined organic layers were washed with bine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel to afford compound **1d**.



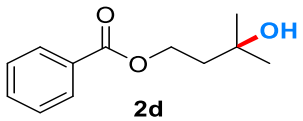
R_f = 0.5, 5% acetone in hexane, yellowish oil (193 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 4.43 (t, J = 6.8 Hz, 2H), 1.97 (t, J = 6.8 Hz, 2H), 1.37 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.46, 133.01, 130.13, 129.55, 128.40, 61.26, 60.27, 39.73, 26.38. Spectra data are consistent with those reported in literature.[6]

7.2 Converted to compound 2d



To a solution of compound **1b** (270 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 N_2. The solution was stirred and heated at 70 °C for 24 hours. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure remove most of the acetone. The product was extracted with EA (3 x 10 mL). The combined EA 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 pressure. The crude residue was

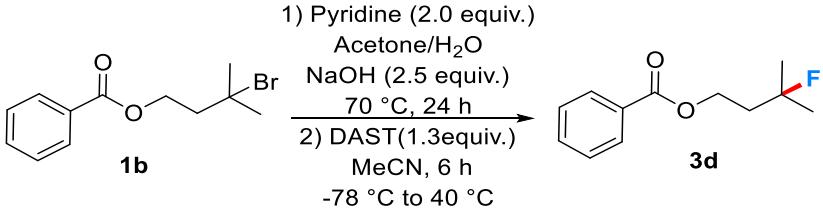
purified by flash column chromatography on silica gel to afford compound **2d**.



2d

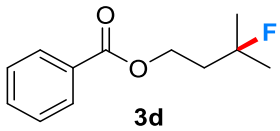
R_f = 0.3, 20% acetone in hexane, yellowish oil (140 mg, 71% yield) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 4.50 (t, J = 6.8 Hz, 2H), 1.98 (t, J = 6.8 Hz, 2H), 1.80 (s, 1H), 1.32 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.65, 132.97, 130.23, 129.52, 128.40, 70.09, 61.97, 41.74, 29.76. Spectra data were consistent with those previously reported in literature.[12]

7.3 Converted to compound 3d



To a solution of compound **1b** (270 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 N_2. The solution was stirred and heated at 70 °C for 24 hours. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure remove most of the acetone. The product was extracted with EA (3 x 10 mL). The combined EA 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 pressure.

To a solution of the crude residue in MeCN (5.0 mL) was added a solution of DAST (209 mg, 1.3 mmol,1.3 equiv.) in MeCN (5.0 mL) at -78 °C under N_2. The reaction mixture was warmed to 40 °C and stirred for 6 hours. 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 pressure. The crude residue was purified by flash column chromatography on silica gel to afford compound **3d**.

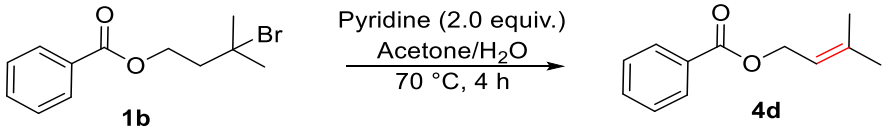


3d

R_f = 0.5, 5% acetone in hexane, yellowish oil (122 mg, 62% yield)

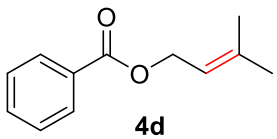
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 4.48 (t, J = 6.8 Hz, 2H), 2.12 (dt, J = 19.5, 6.8 Hz, 2H), 1.47 (s, 3H), 1.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.51, 132.97, 130.21, 129.54, 128.39, 94.94, 93.62, 60.97, 60.92, 39.94, 39.75, 27.20, 27.00. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -138.03, -138.07, -138.07, -138.12, -138.16, -138.16. Spectra data were consistent with those previously reported in literature.[13]

7.3 Converted to compound 4d



1b **4d**

To a solution of compound **1b** (270 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 N_2. The solution was stirred and heated at 70 °C for 4 hours. The pressure tube was cooled to room temperature, and the solution was concentrated under reduced pressure remove most of the acetone. The product was extracted with EA (3 x 10 mL). The combined EA 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 pressure. The crude residue was purified by flash column chromatography on silica gel to afford compound **4d**.



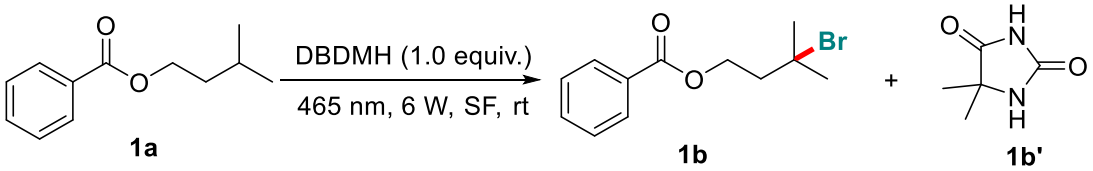
4d

R_f = 0.6, 1% acetone in hexane, yellowish oil (128 mg, 66% 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 166.67, 139.13, 132.78, 130.52, 129.59, 128.29, 118.70, 61.89, 25.81, 18.12. Spectra data were consistent with those previously reported in literature.[14]

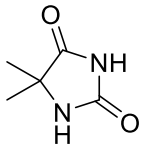
8. Mechanistic studies

8.1 Typical conditions



Substrates **1a** (0.5 mmol, 1.0 equiv.) and DBDMH (0.5 mmol, 1.0 equiv.) were added to the glass tube. The mixture was irradiated with blue light (465 nm, 6 w) for 3 hours at room temperature without solvent. After the reaction was completed, add 2 mL of DCM to the reaction system and filter it directly. Wash the filter cake with a small amount of DCM several times to obtain compound **1b'** (57 mg, 89% yield).

5,5-dimethylimidazolidine-2,4-dione (1b')

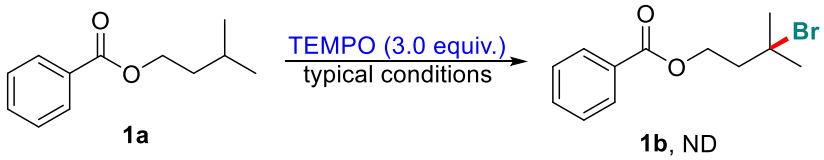


1b'

R_f = 0.4, 5% methyl alcohol in dichloromethane, white solid (57 mg, 89% yield)

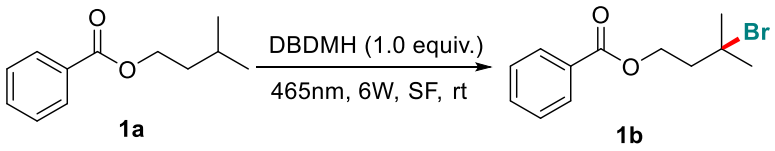
^{1}H NMR (500 MHz, DMSO-*d6*) δ 10.57 (s, 1H), 7.97 (s, 1H), 1.24 (s, 6H). Spectra data are consistent with those reported in literature.[15]

8.2 Spin trapping experiment with TEMPO



Substrates **1a** (0.5 mmol, 1.0 equiv.), TEMPO (1.5 mmol, 3.0 equiv.) and DBDMH (0.5 mmol, 1.0 equiv.) were added to the glass tube. The mixture was irradiated with blue light (465 nm, 6 w) for 3 hours at room temperature without solvent. During this process, we monitored the reaction using TLC and did not observe the formation of compound **1b**, the raw materials are basically not converted.

8.3 Light/dark experiment of C-H bromination of isopentyl benzoate



Six vials were charged with compound **1a** (0.2 mmol, 1.0 equiv.). DBDMH (0.5 mmol, 1.0 equiv.) was added and then the mixture was irradiated with blue light (465 nm, 6 w) for 1 hour at room temperature without solvent. After each interval, one vial was taken out, and the yield was determined by **^{1}H NMR** based on a $Cl_2CHCHCl_2$ (20 μL) as an internal standard.

Vial	Time (h)/conditions						Yield(%)[a]
1	0-1/hv						37
2	0-1/hv	1-2/dark					37
3	0-1/hv	1-2/dark	2-3/hv				68
4	0-1/hv	1-2/dark	2-3/hv	3-4/dark			68
5	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv		90
6	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv	5-6/dark	90

a) NMR yield, average of three experiments.

Table S1. Yields of Light/Dark experiment of C-H bromination of isopentyl benzoate

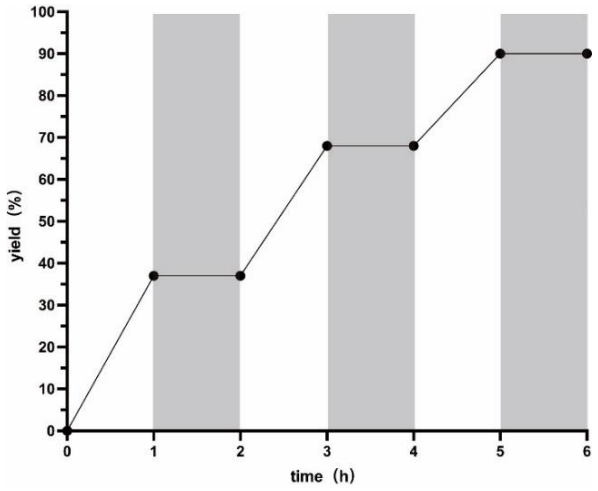


Figure S1. Light/dark experiment of C-H bromination of isopentyl benzoate

8.4 UV visible absorption peaks of DBDMH, substrates(1b) and mixed systems

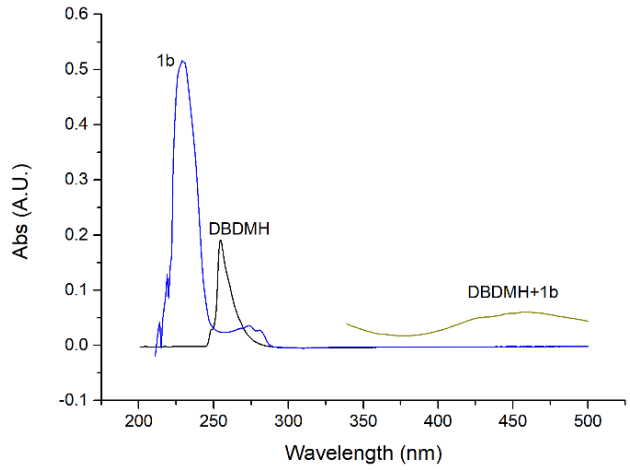


Figure S2. UV visible absorption peaks of **DBDMH**, **1b**, and mixed systems

8.5 The color change of the reaction system with light exposure time

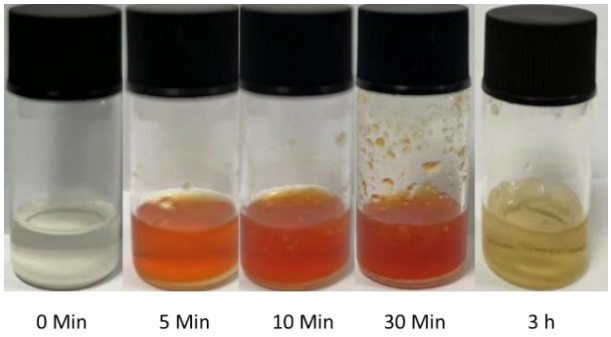


Figure S3. The color change of the reaction system with light exposure time

9. References

[1] C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li, A. Lei, Palladium-Catalyzed Aerobic Oxidative Direct Esterification of Alcohols, *Angew. Chem. Int. Ed.*, 2011, **50**, 5144-5148.

[2] G.-X. Li, X. Hu, G. He, G. Chen, Photoredox-Mediated Minisci-type Alkylation of N-Heteroarenes with Alkanes with High Methylene Selectivity, *ACS Catal*., 2018, **8**, 11847-11853.

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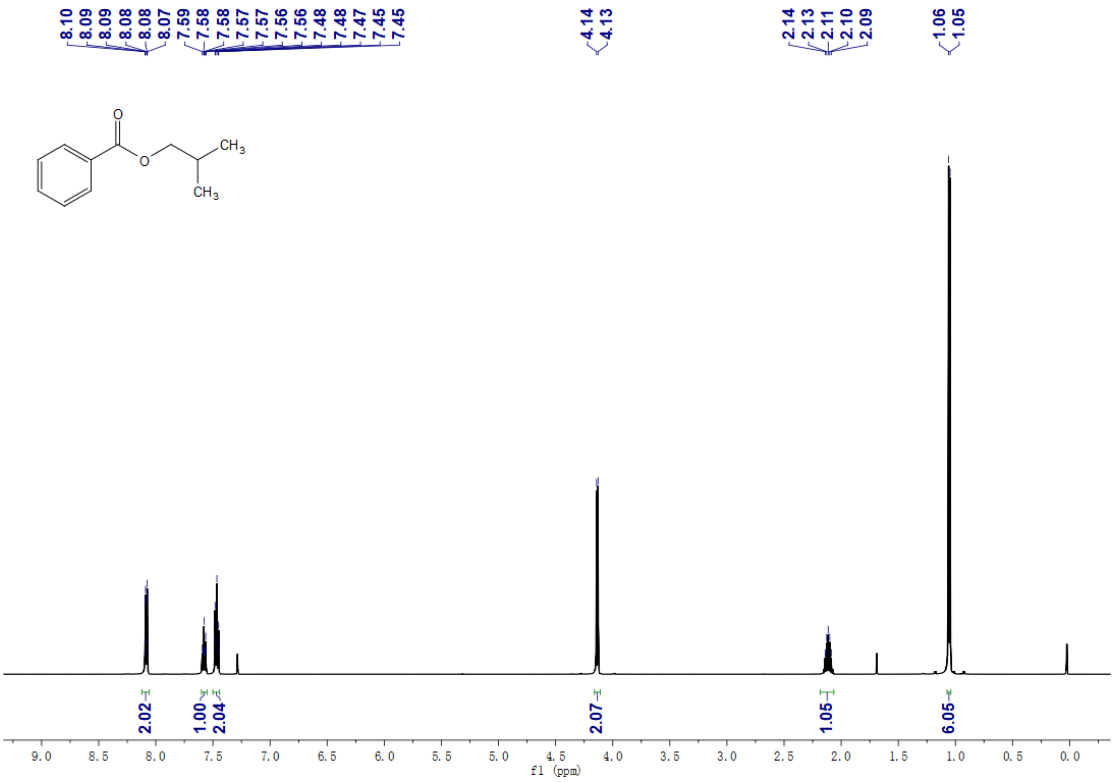
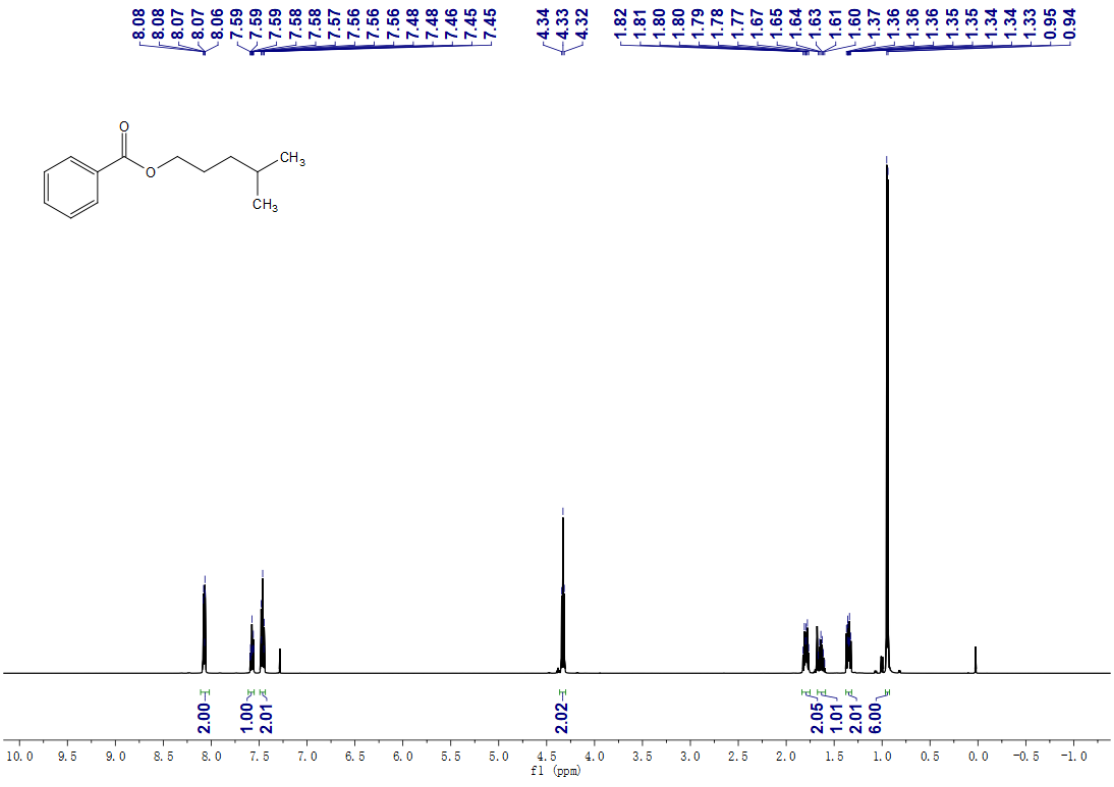
10. ^{1}H-NMR and ^{13}C-NMR spectra



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



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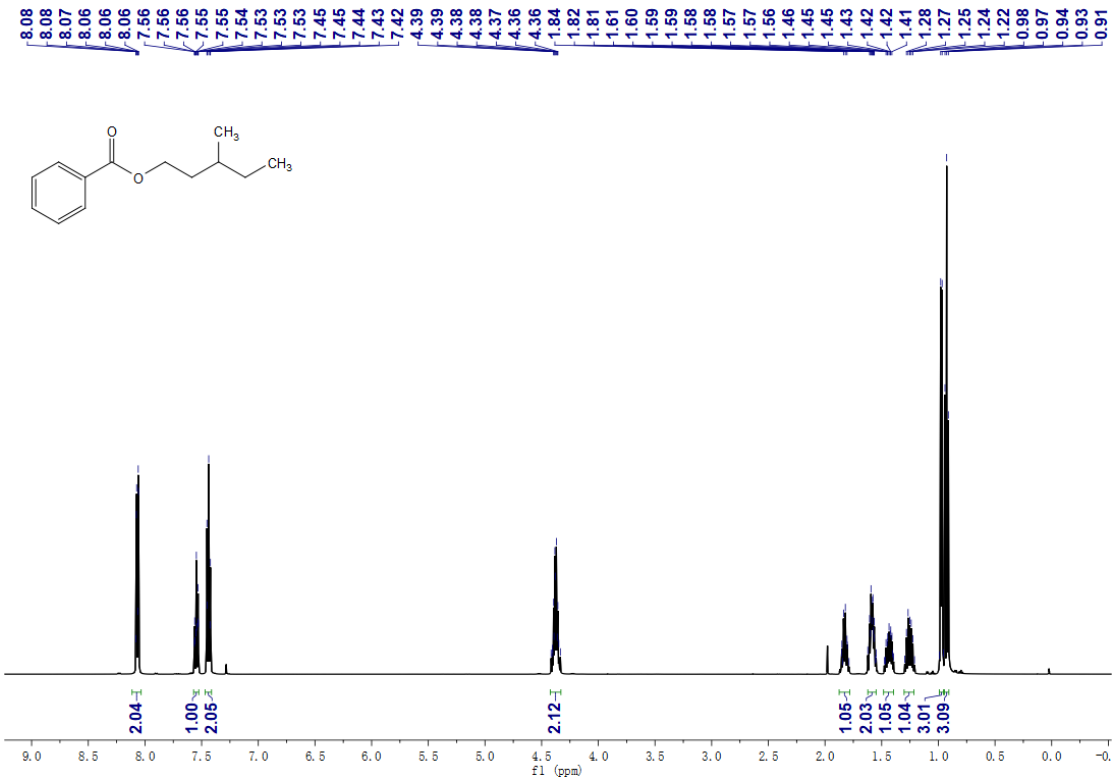

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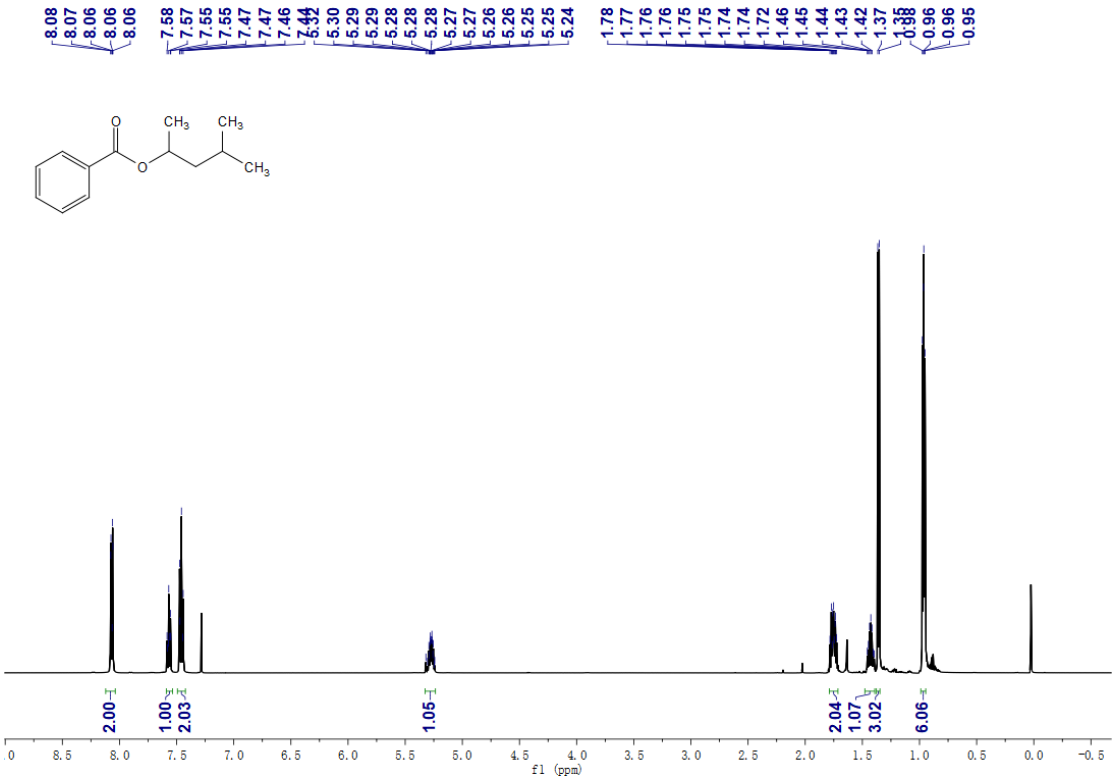

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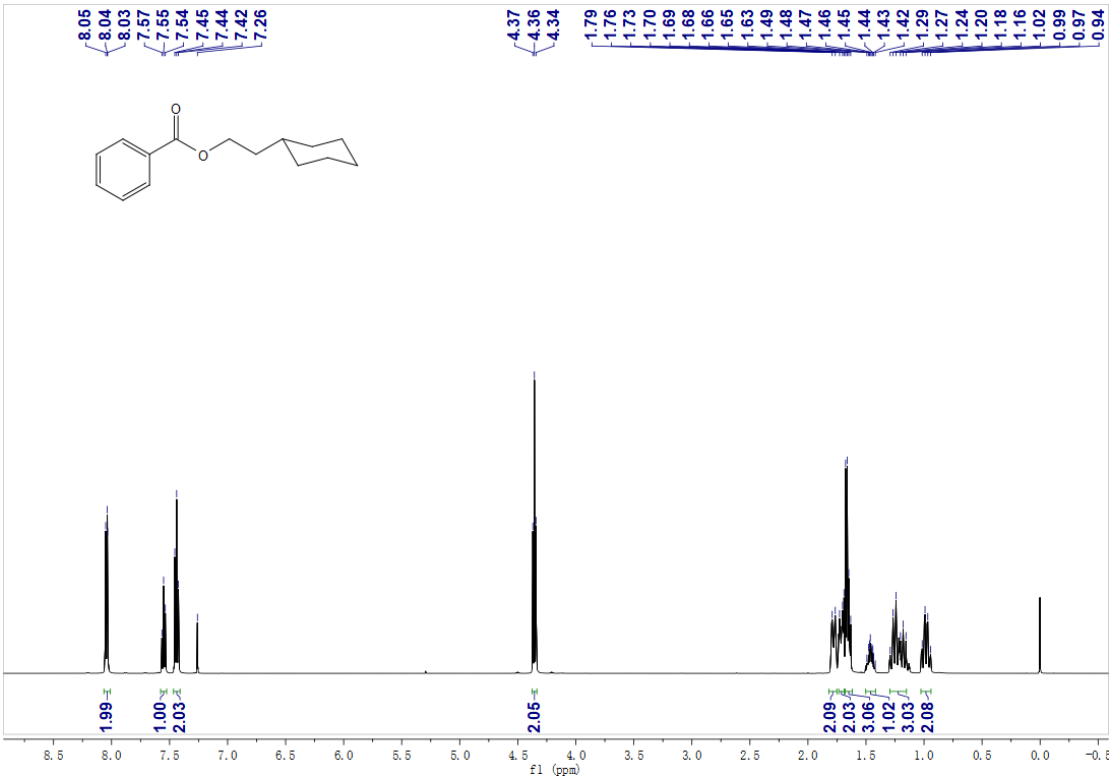

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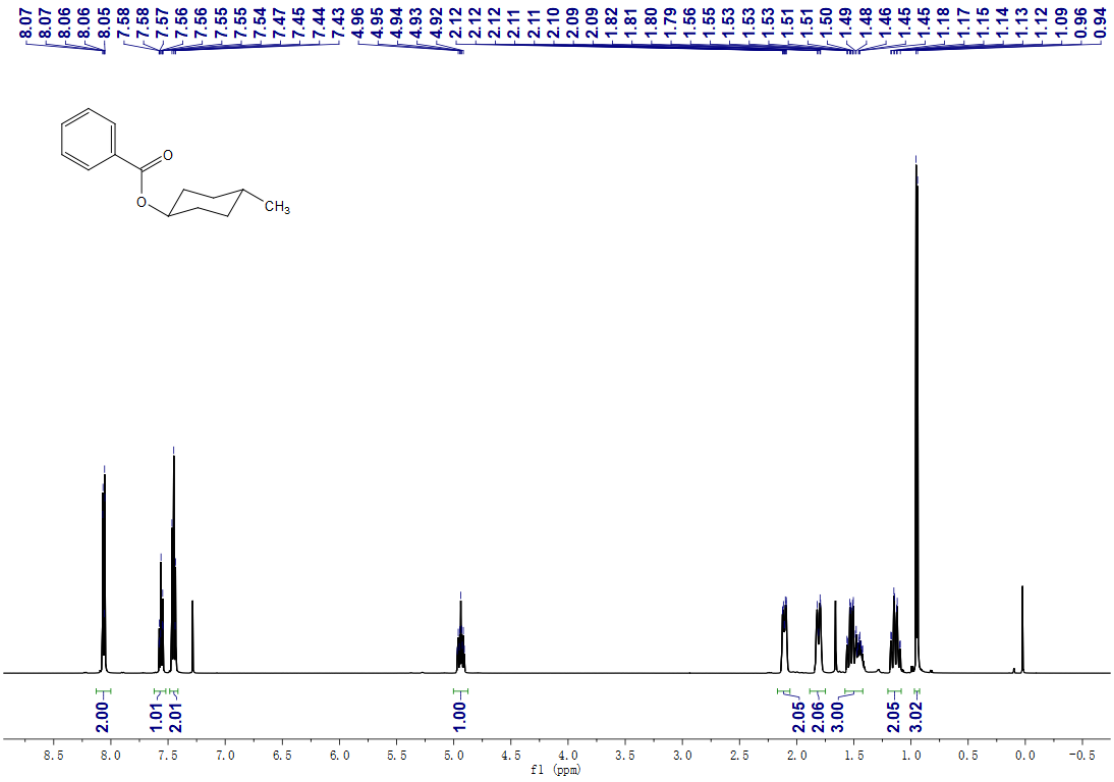

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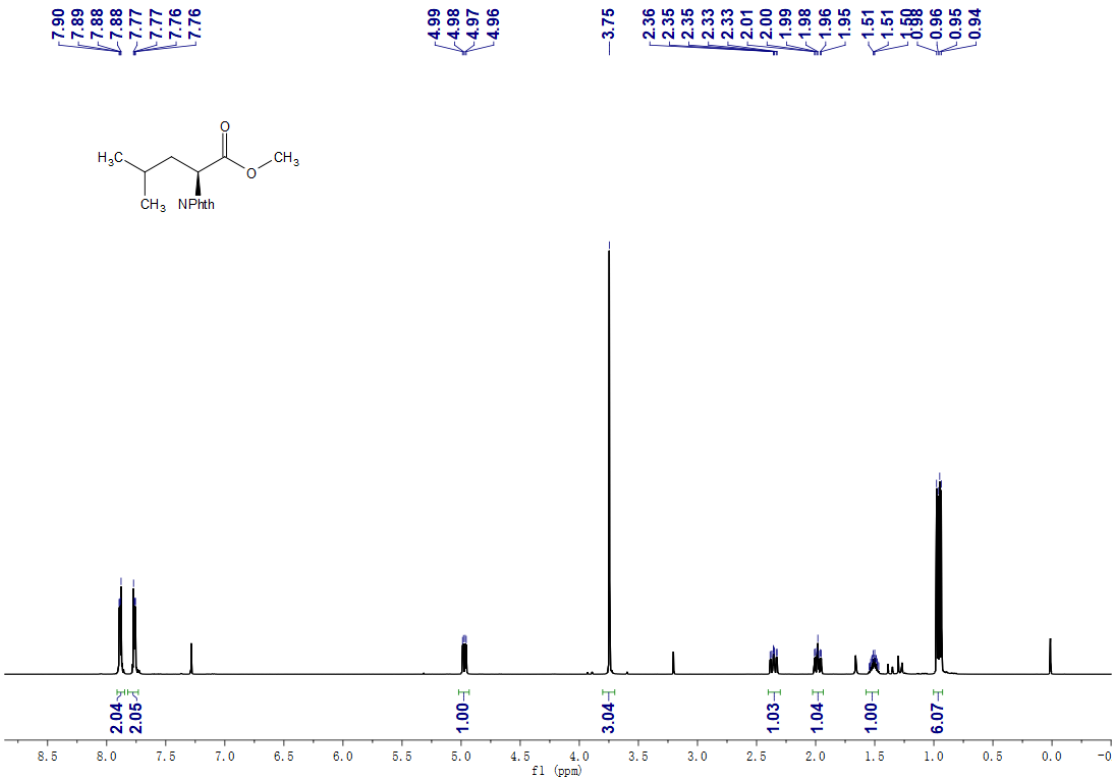
^{1}H NMR of compound **9a** (500 MHz, $CDCl_3$)



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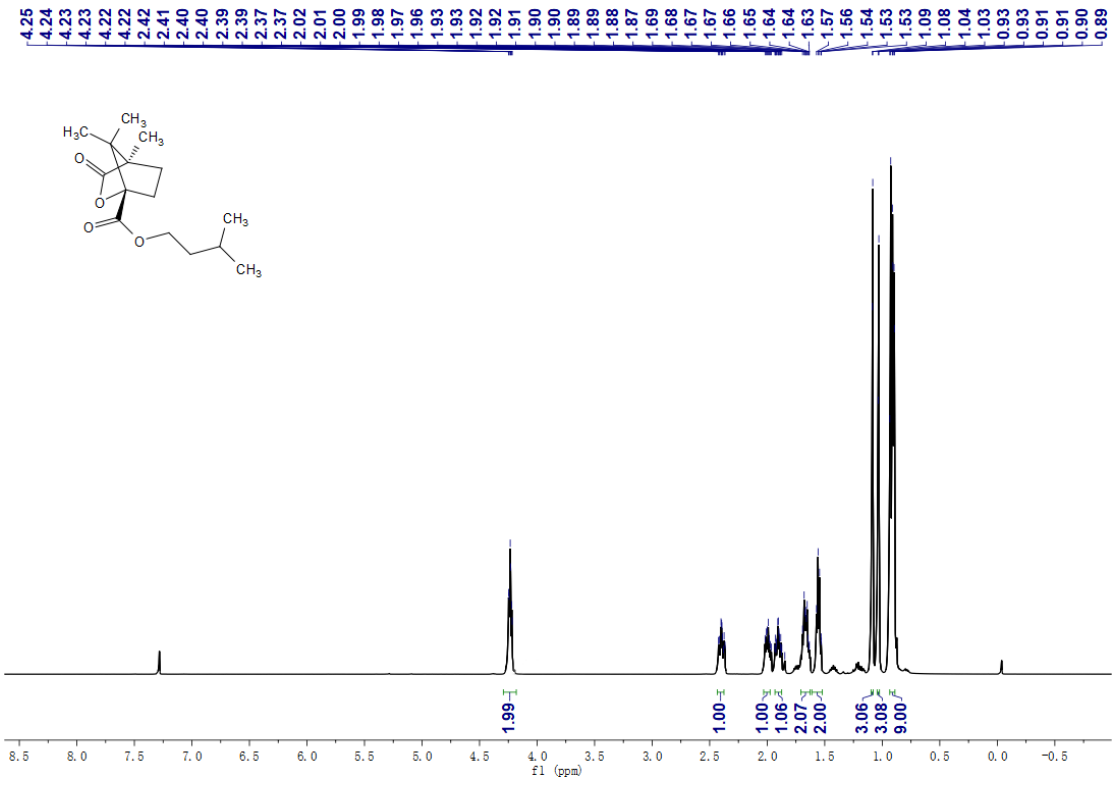

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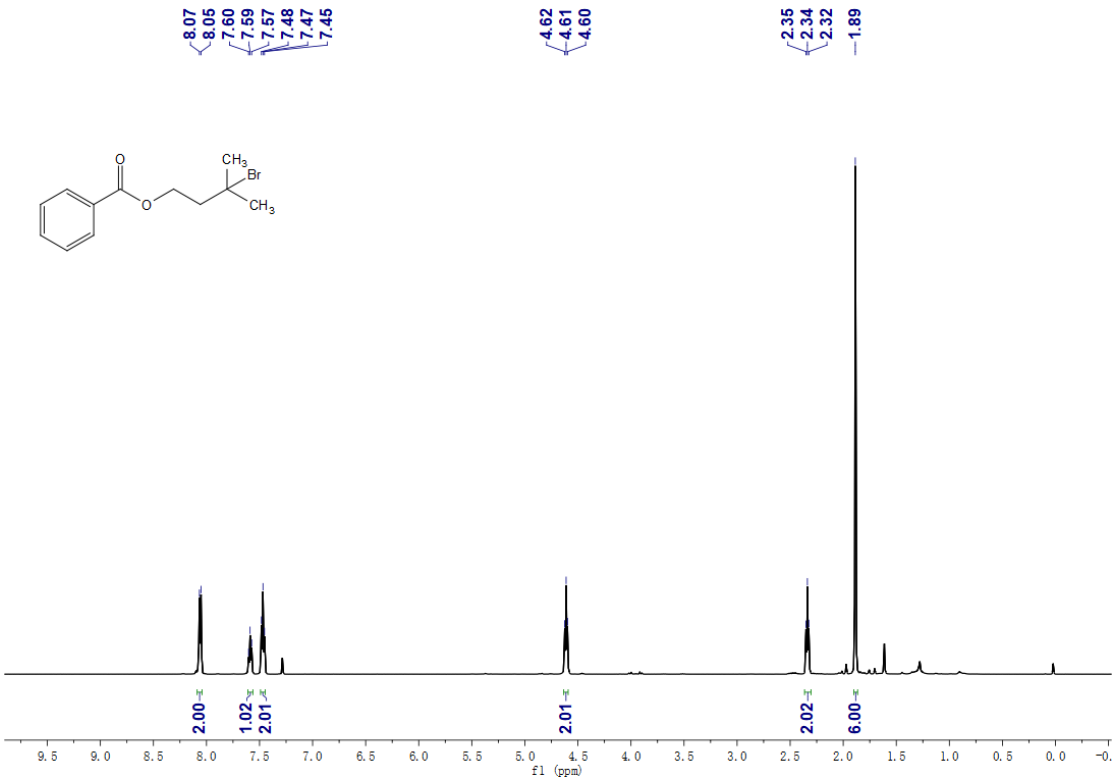

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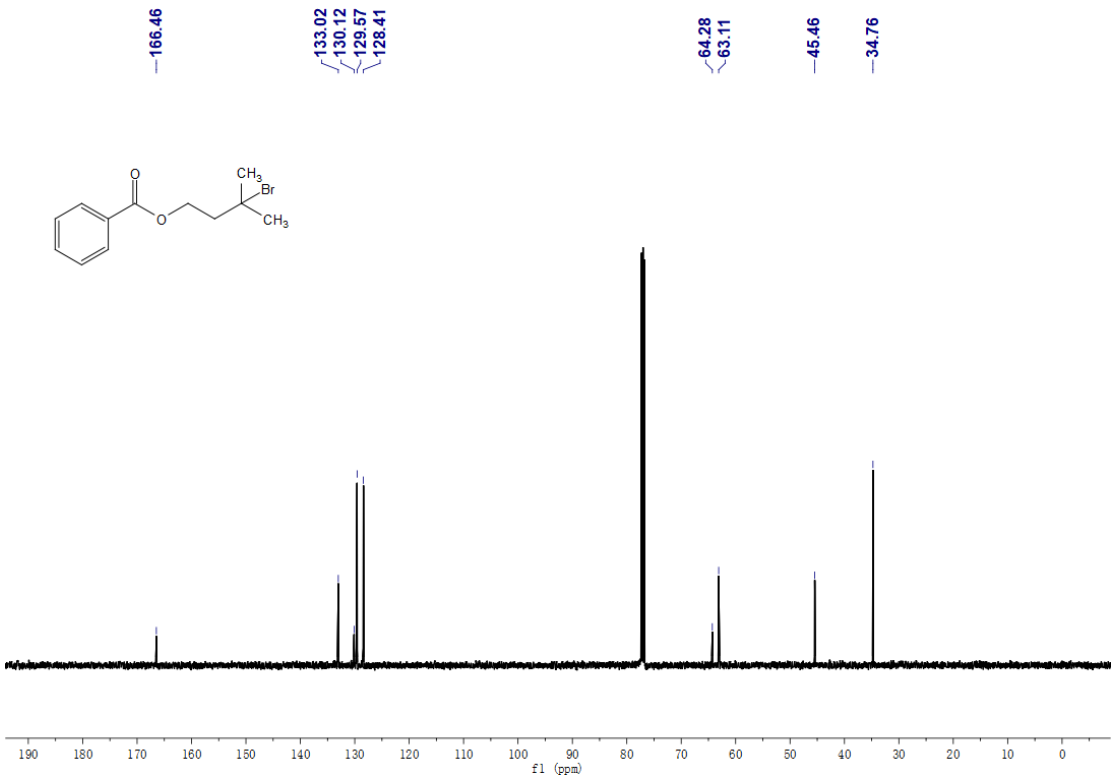

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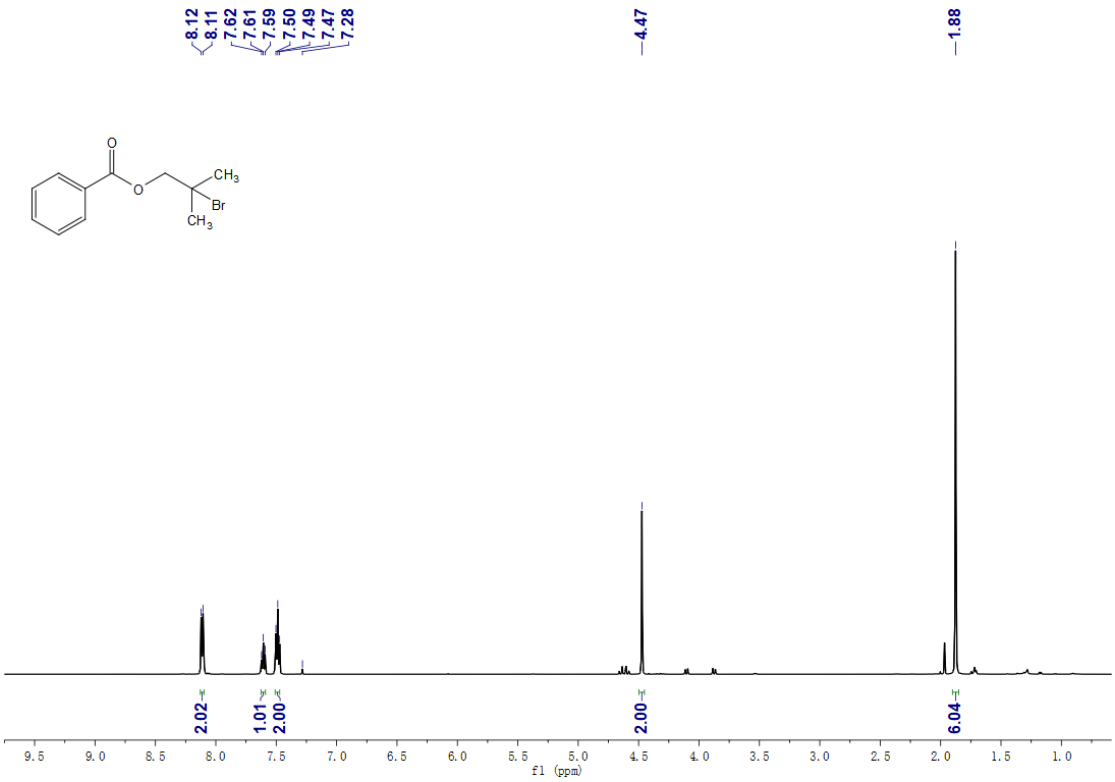

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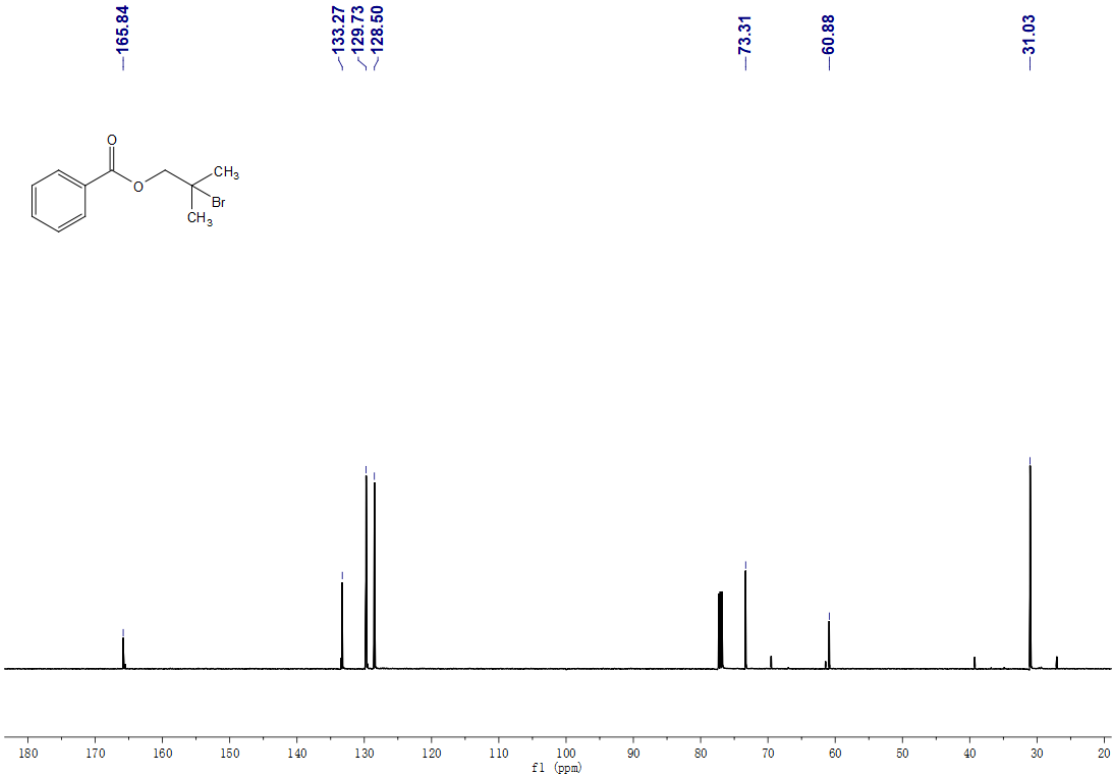

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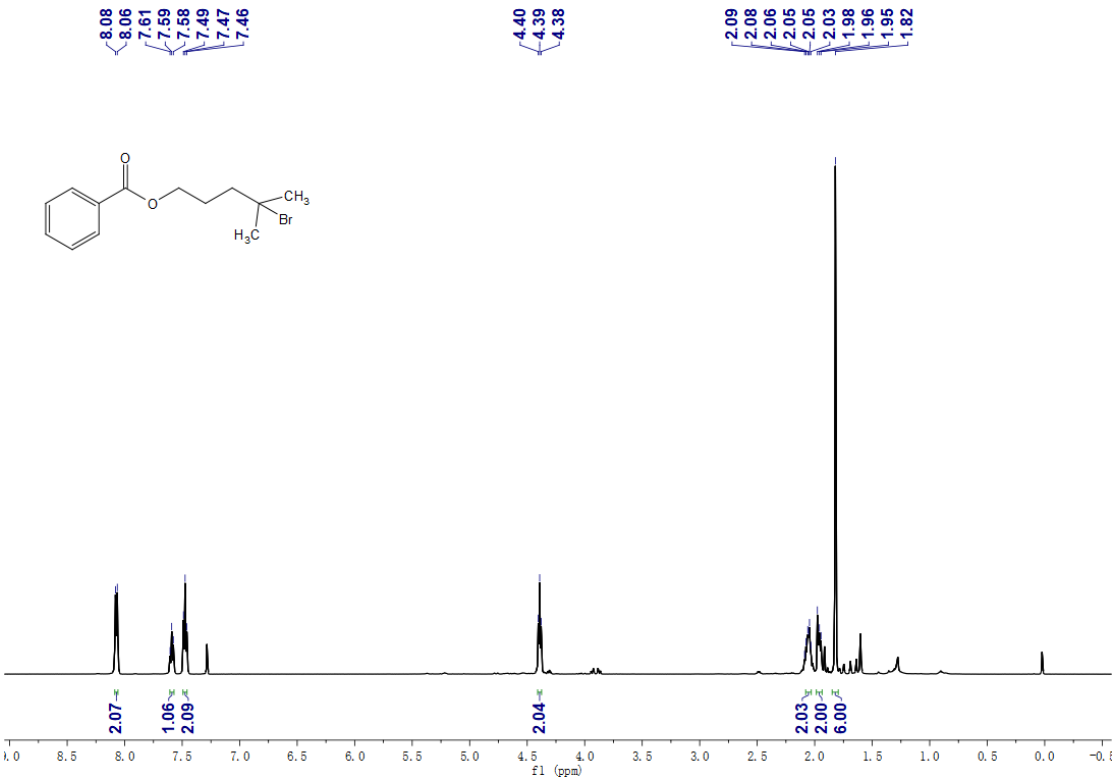

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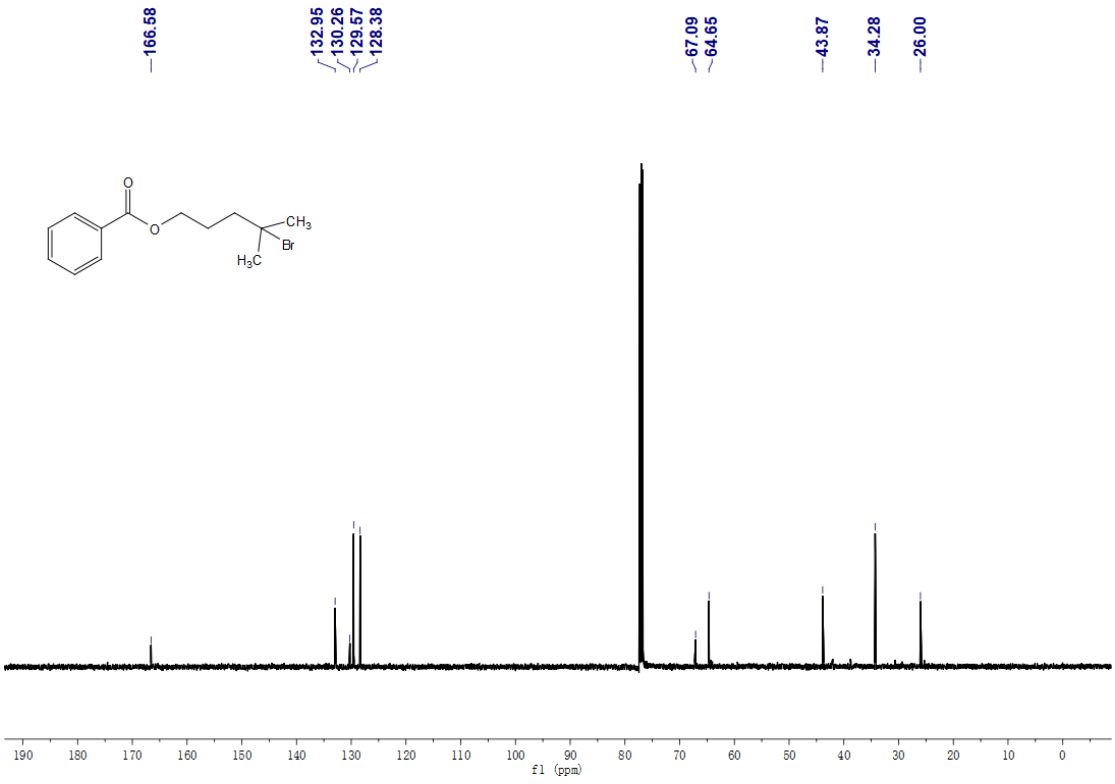

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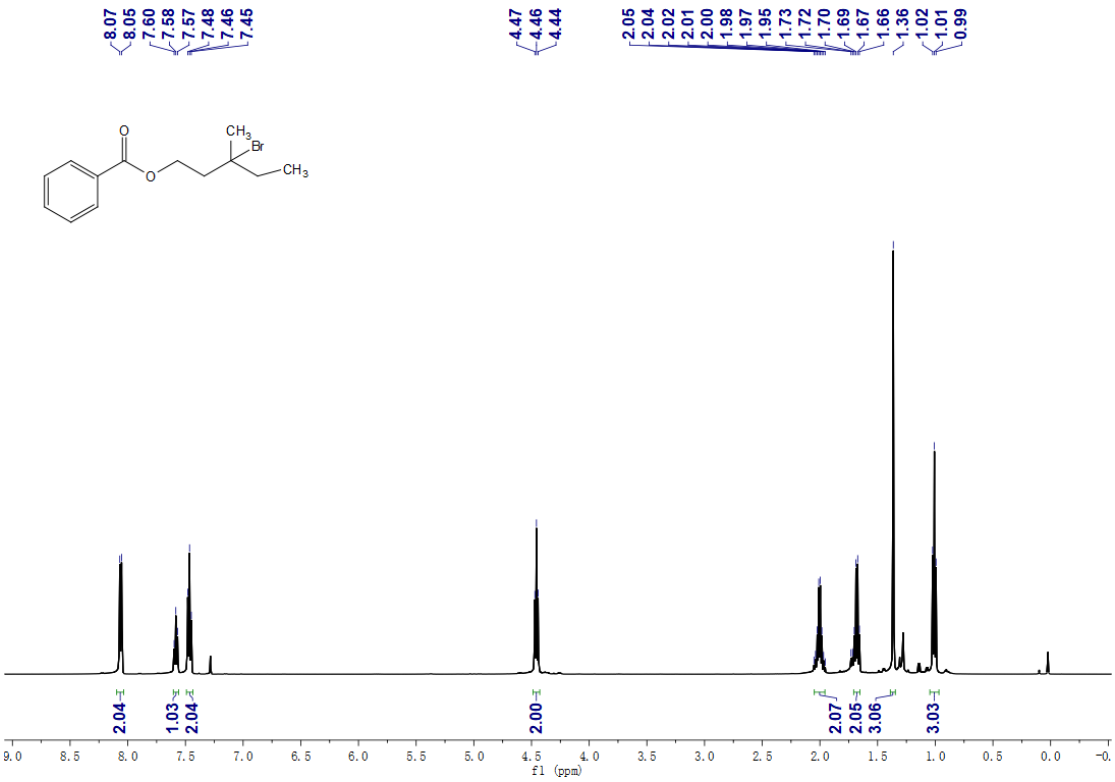

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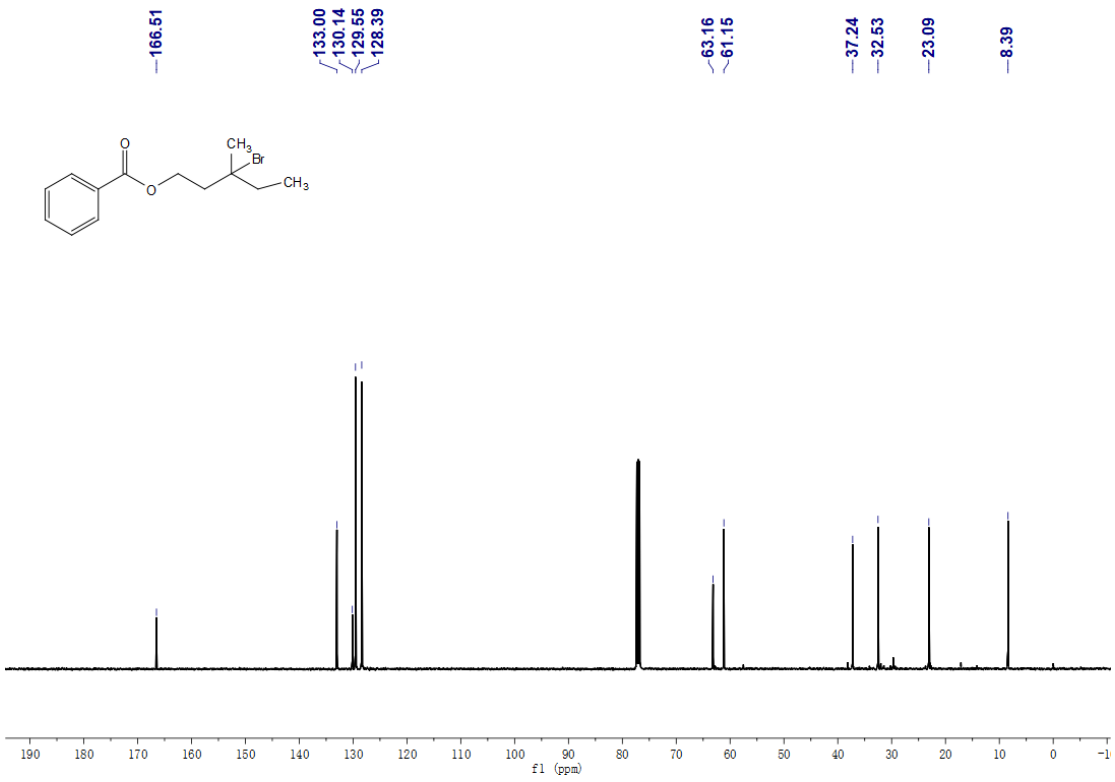

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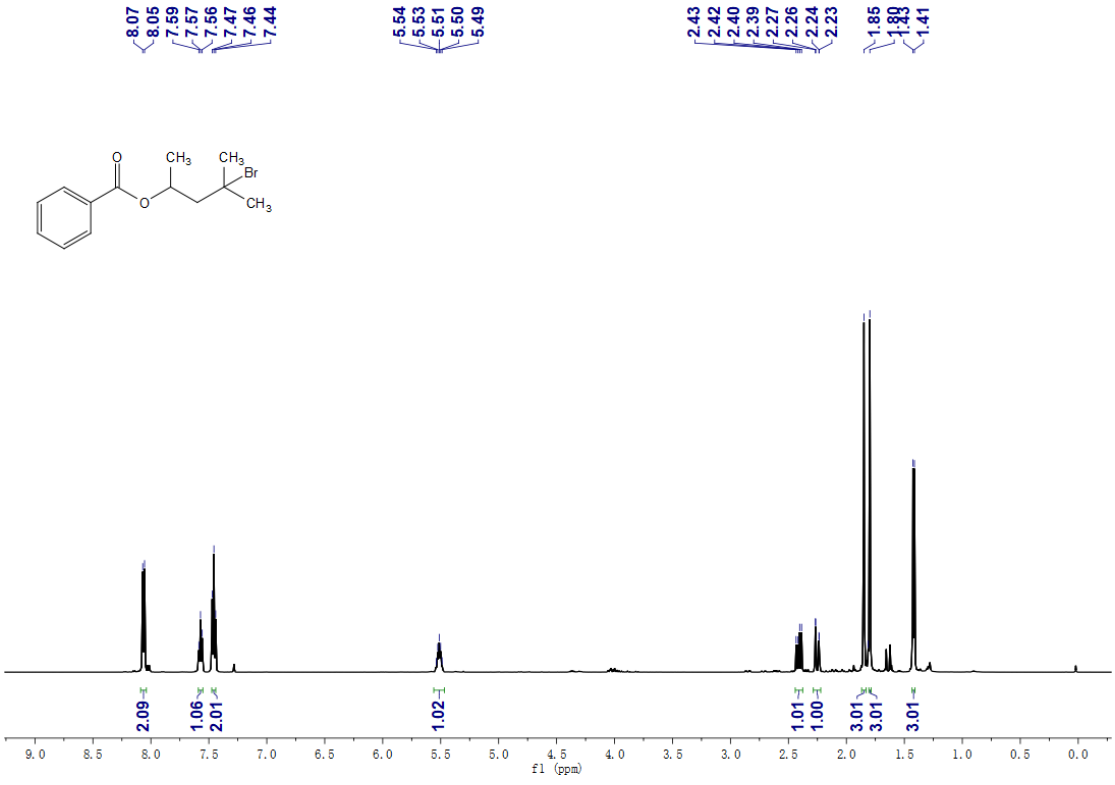

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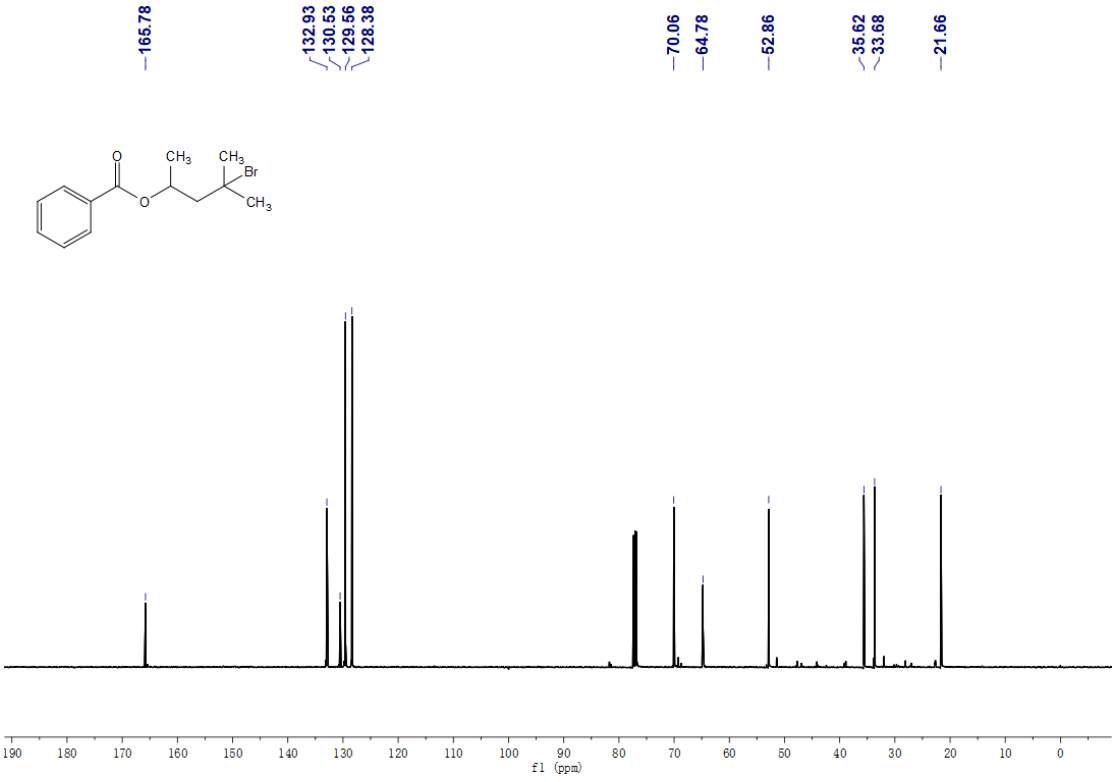

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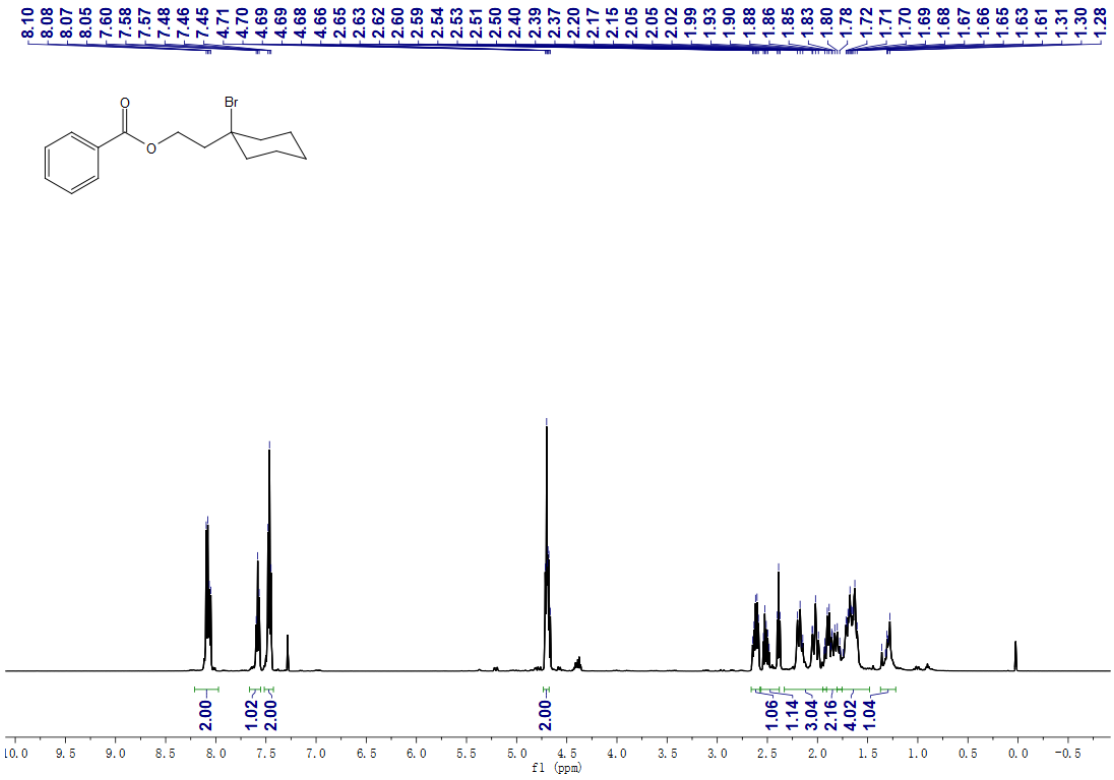

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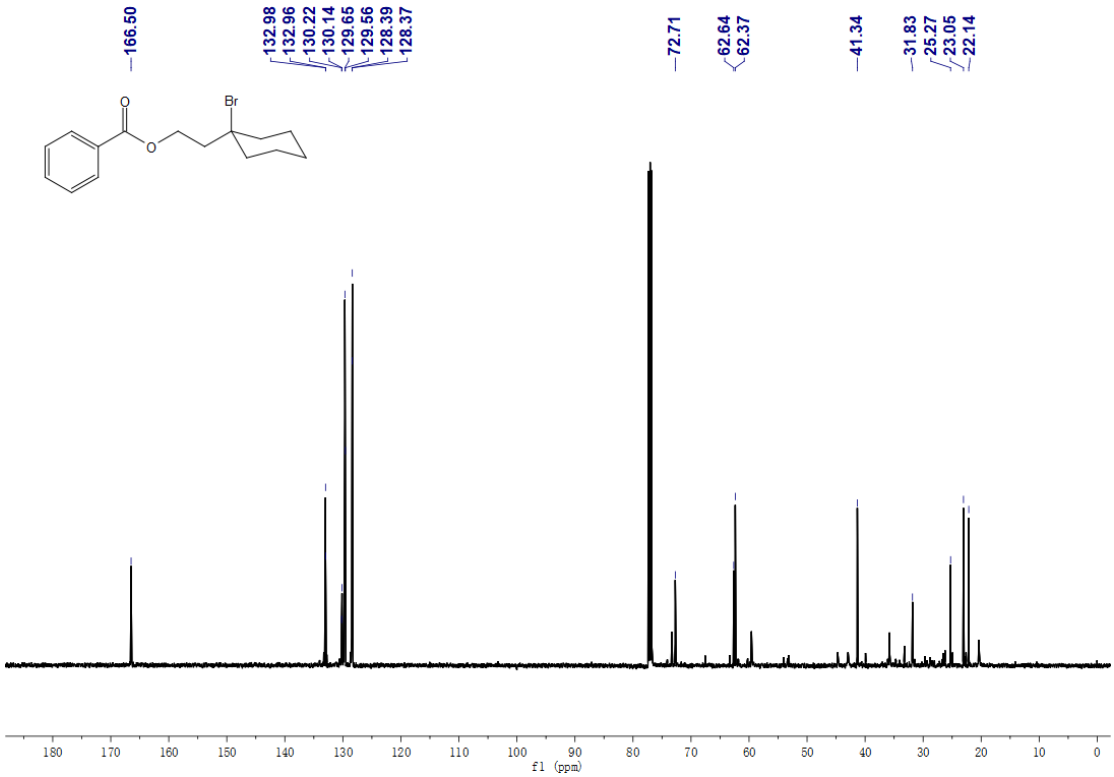

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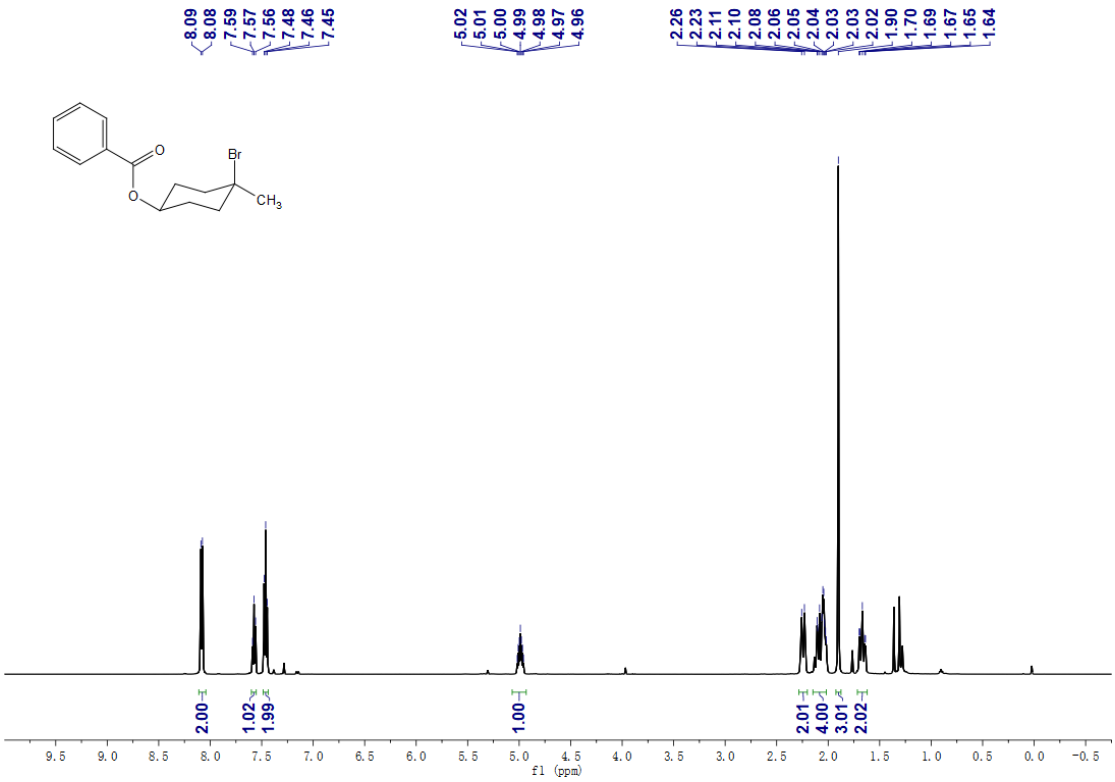

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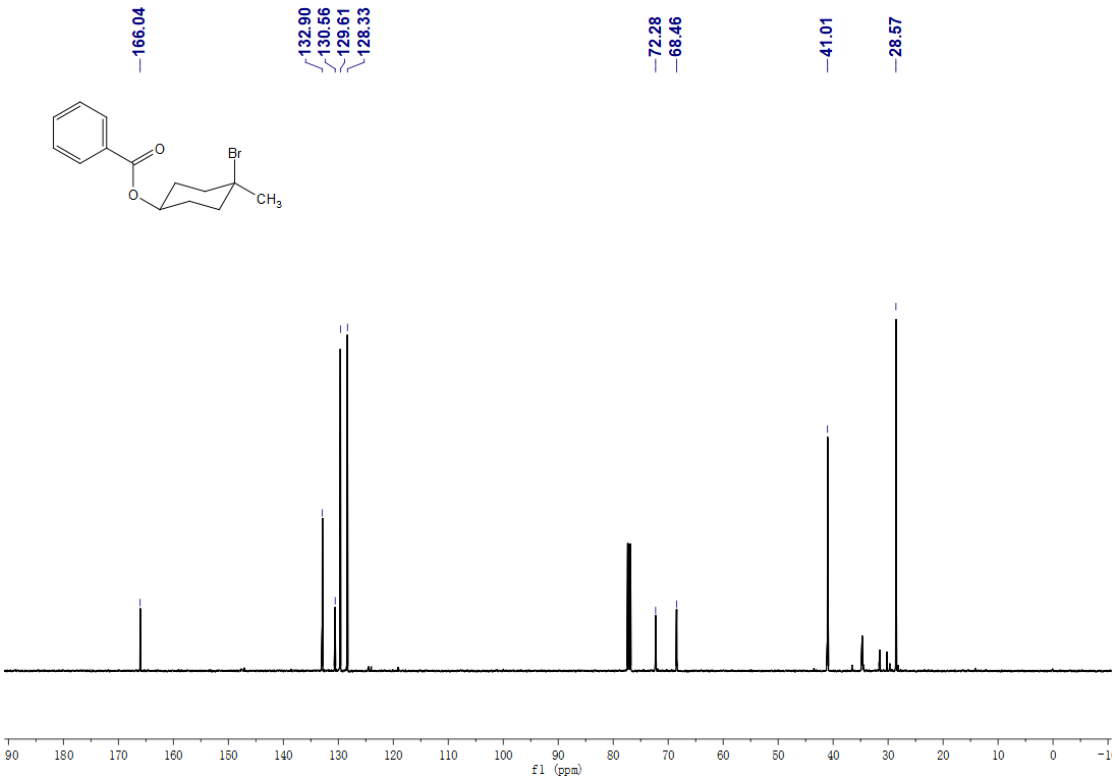

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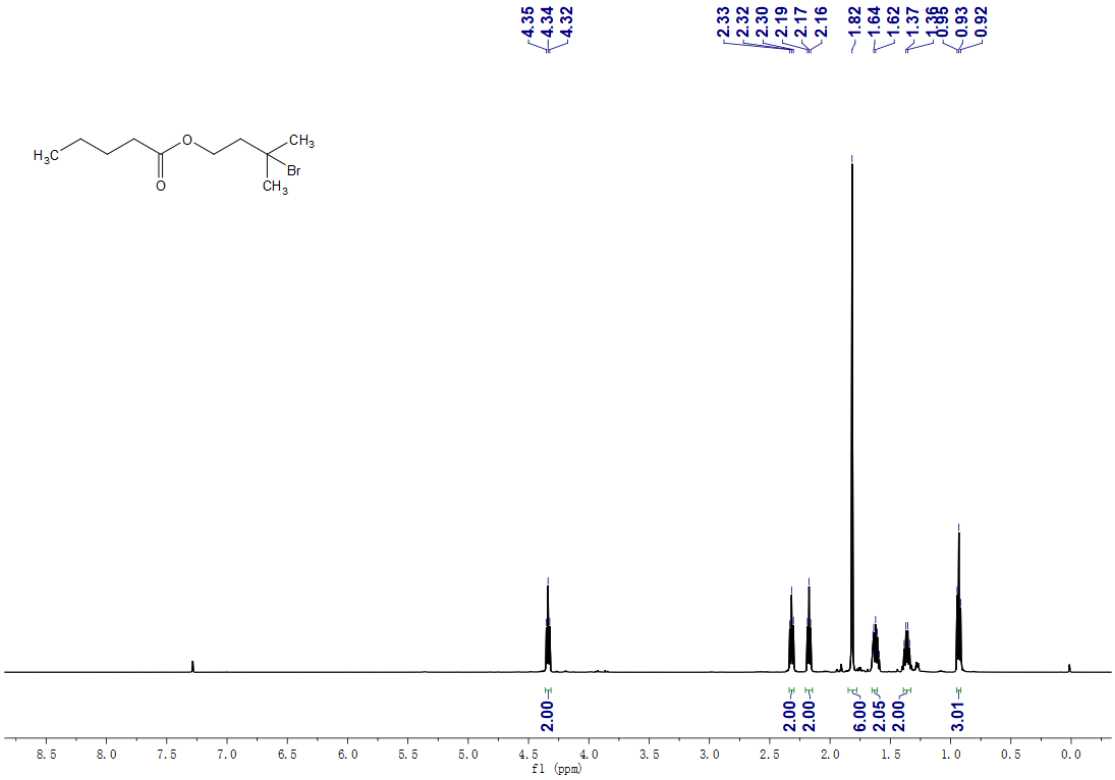

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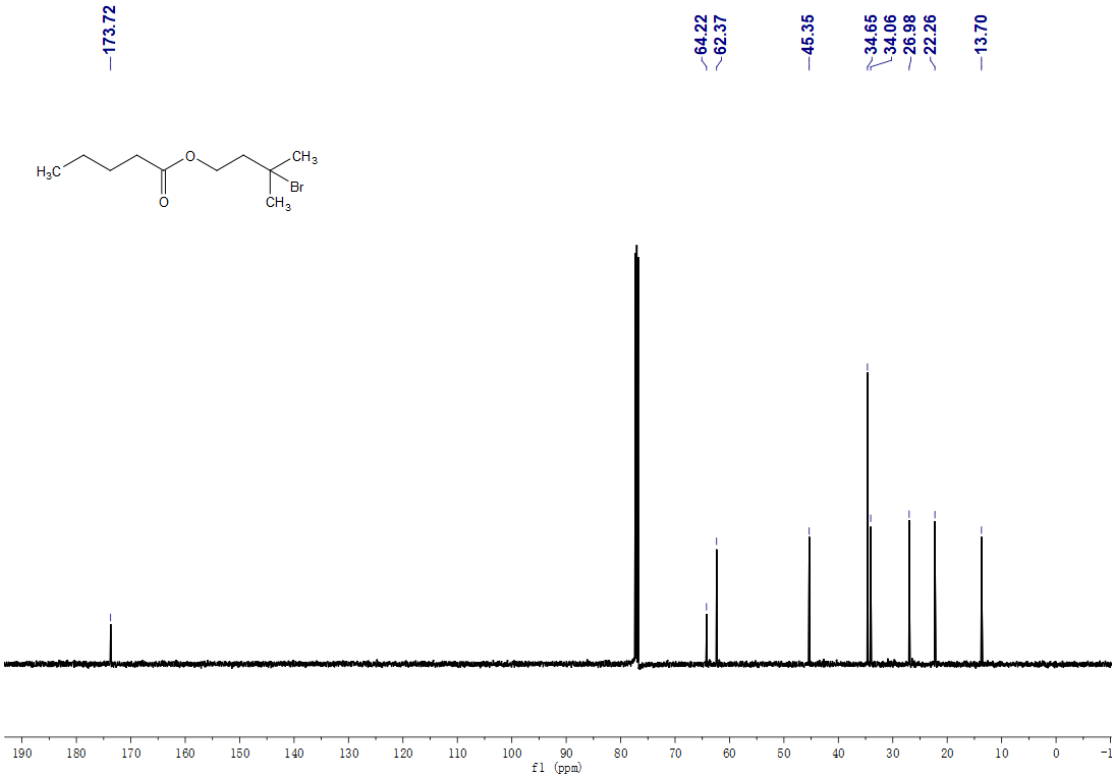

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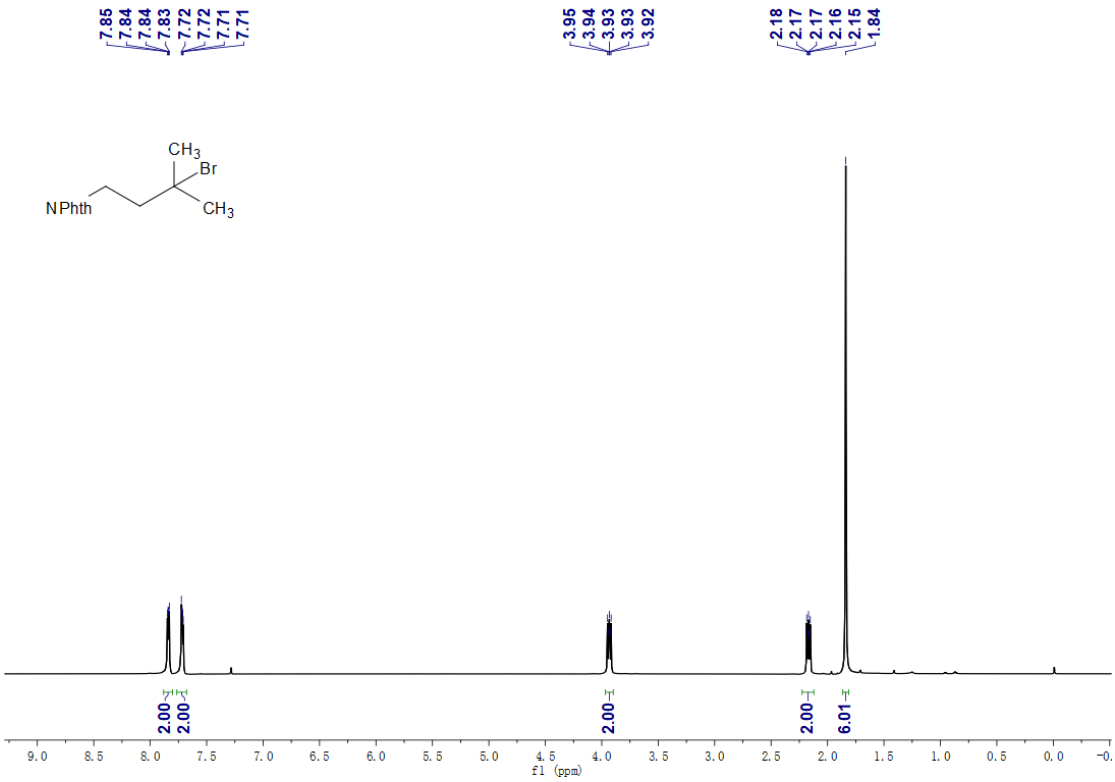

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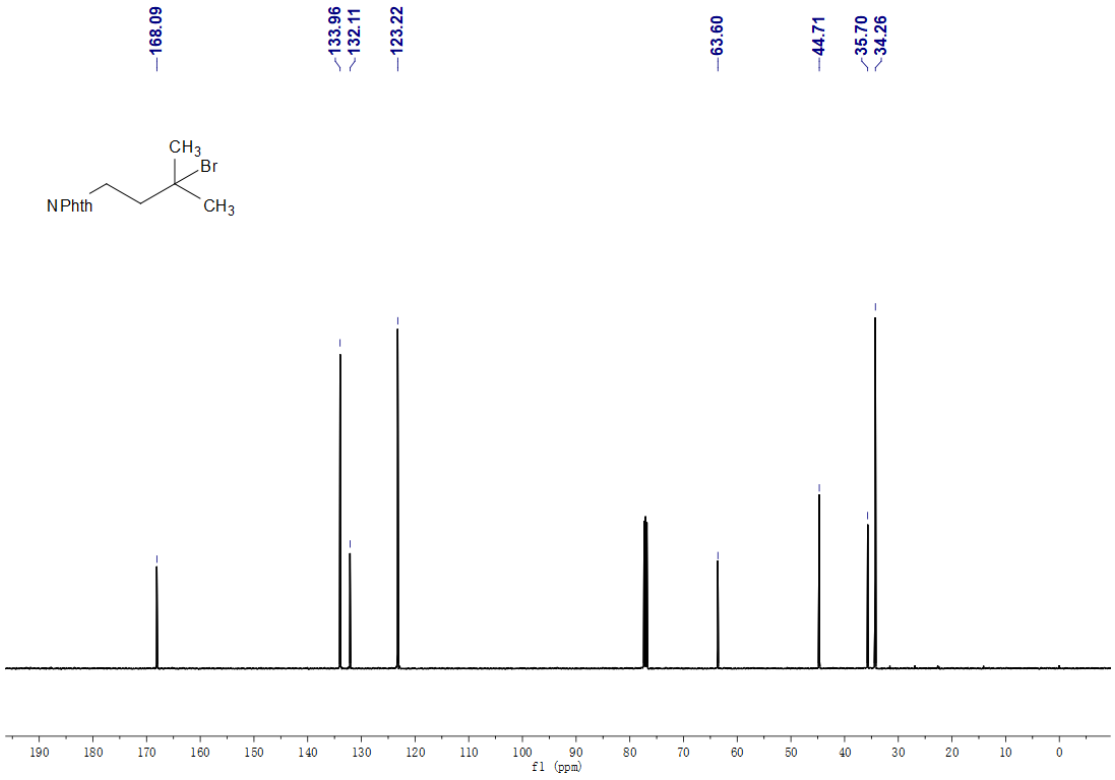

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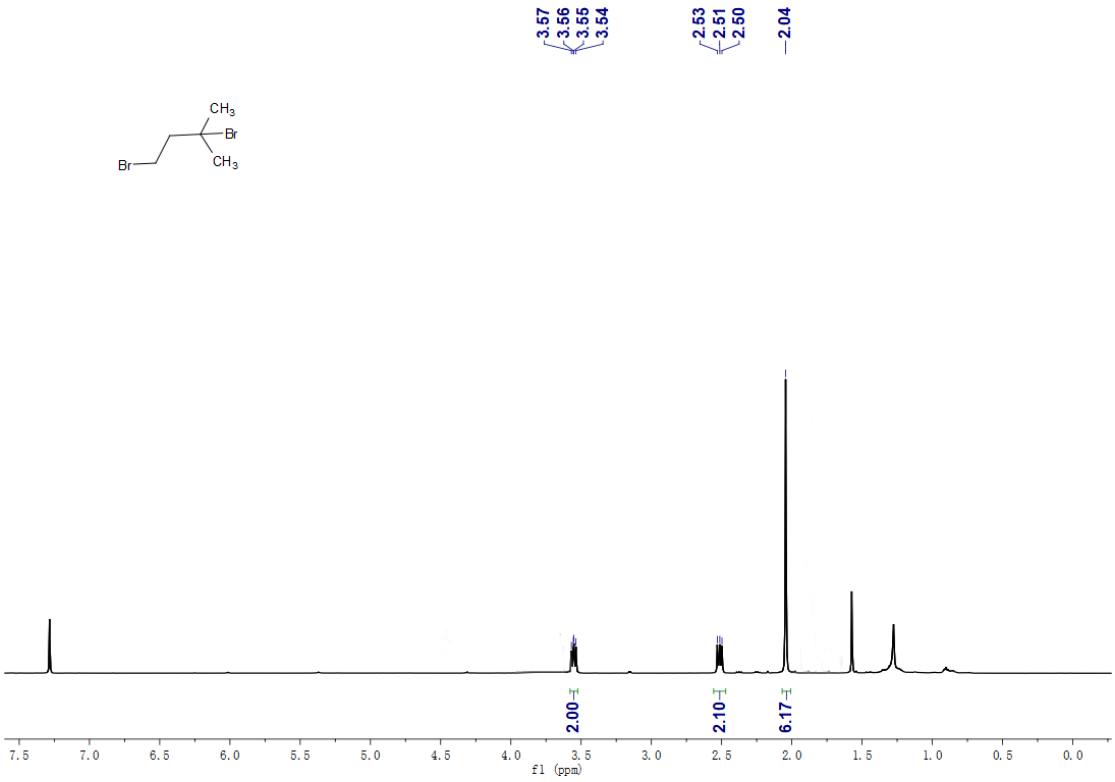

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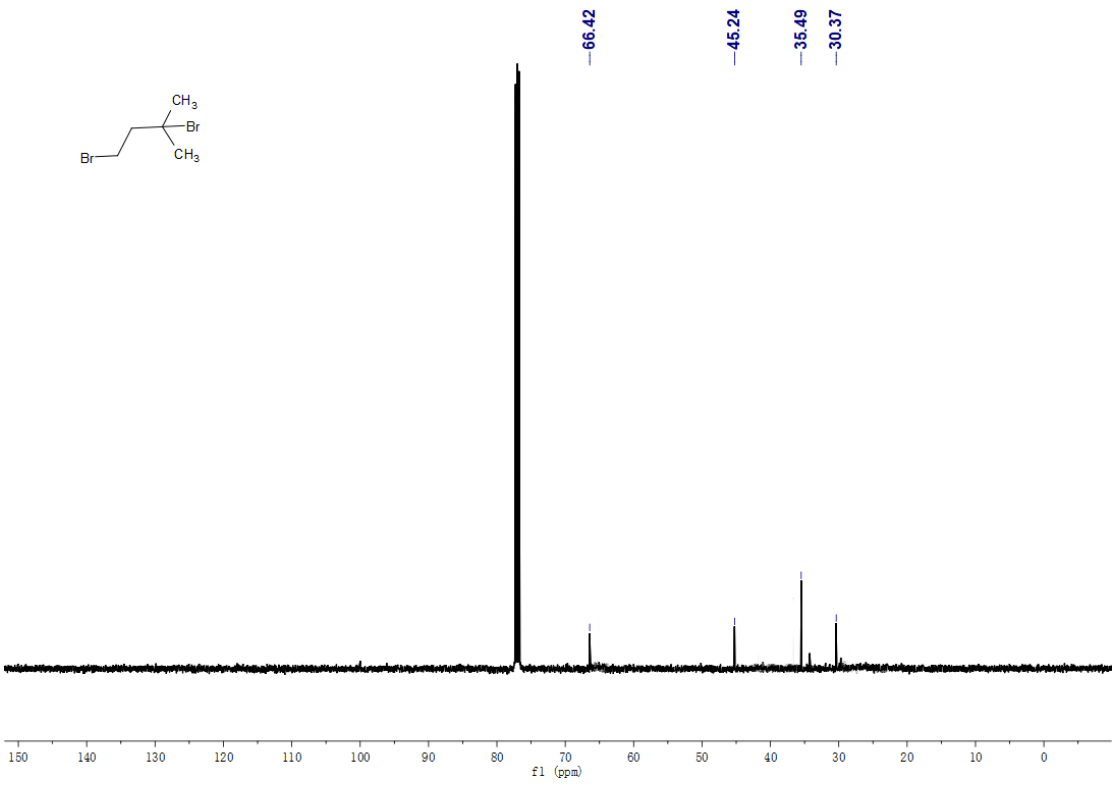

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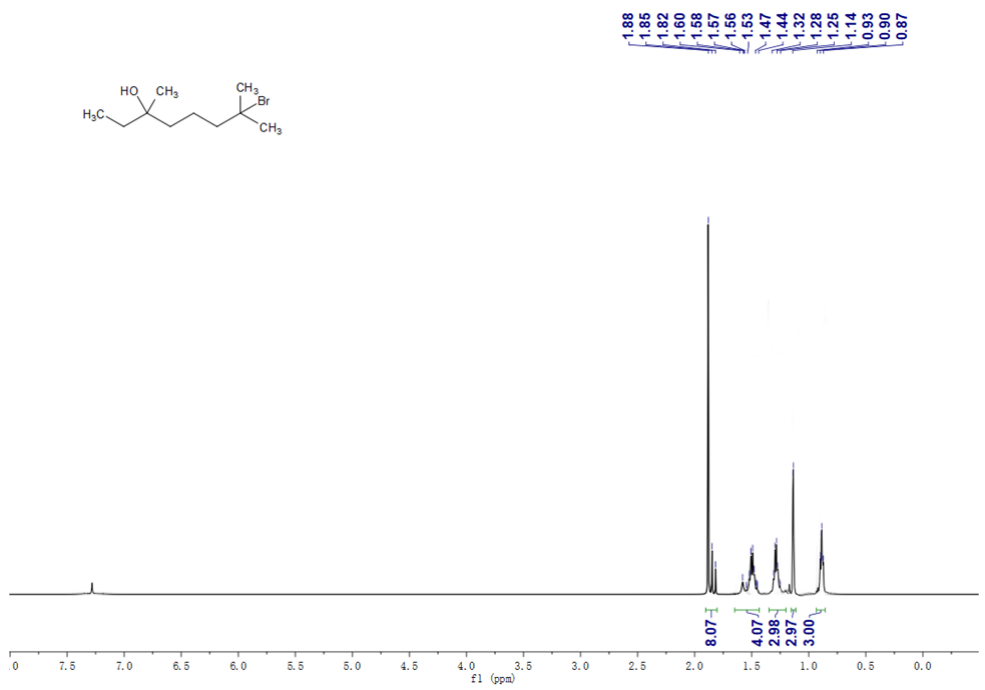

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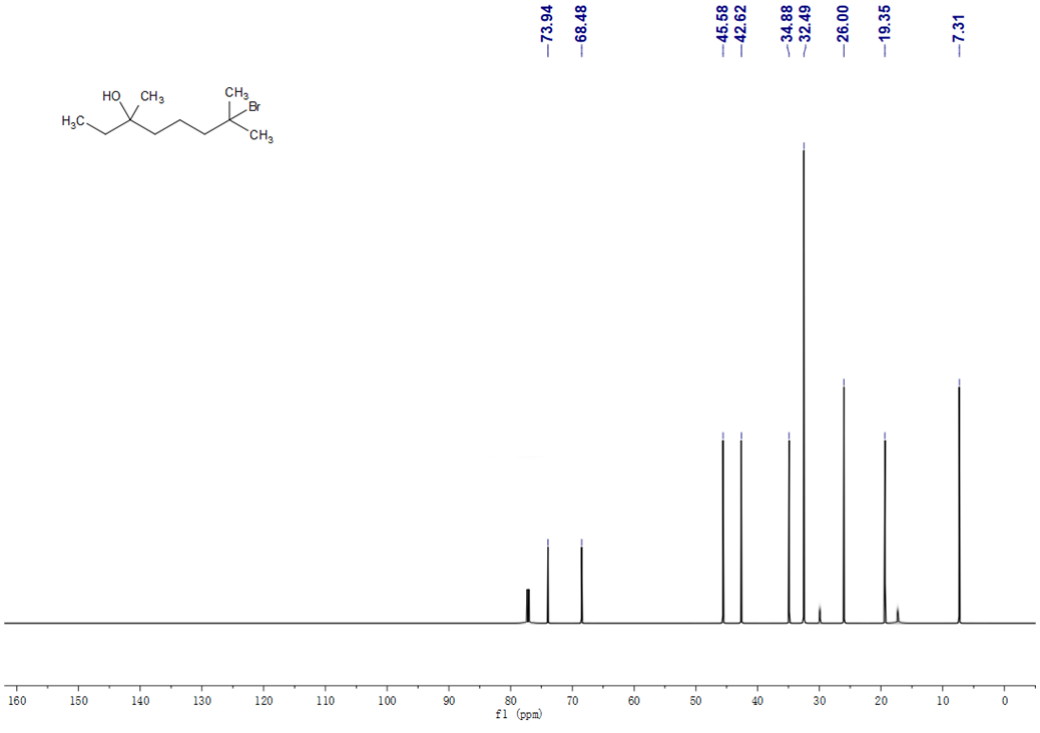

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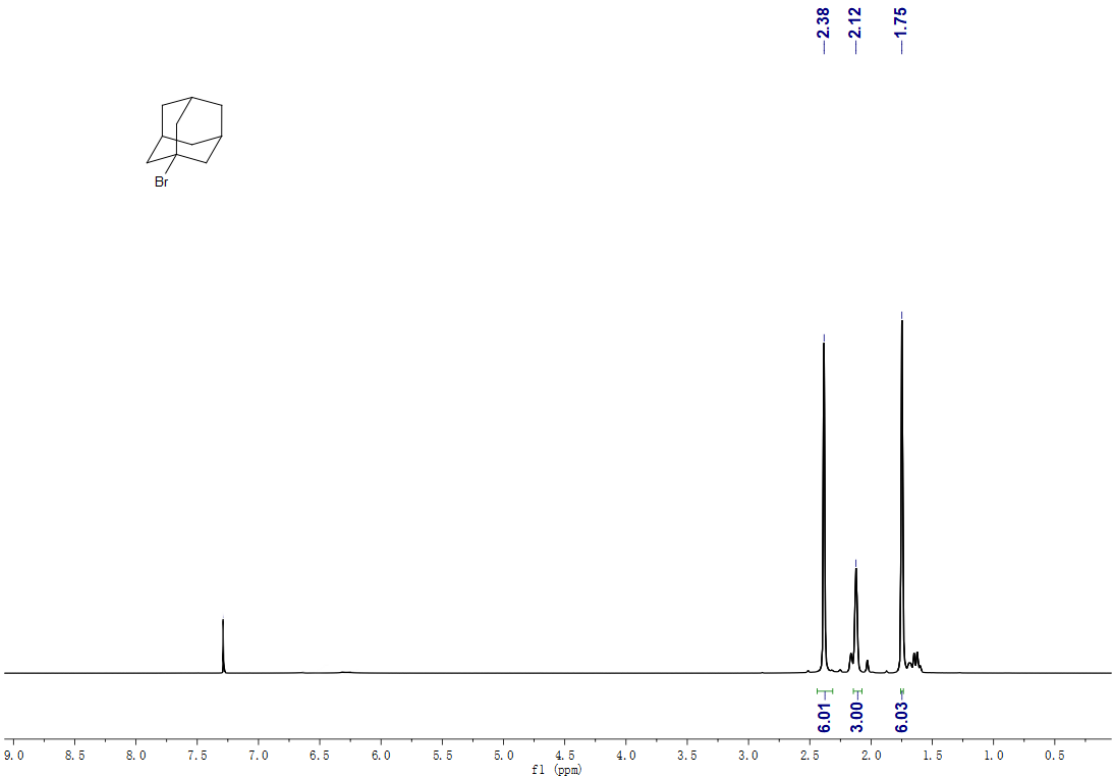

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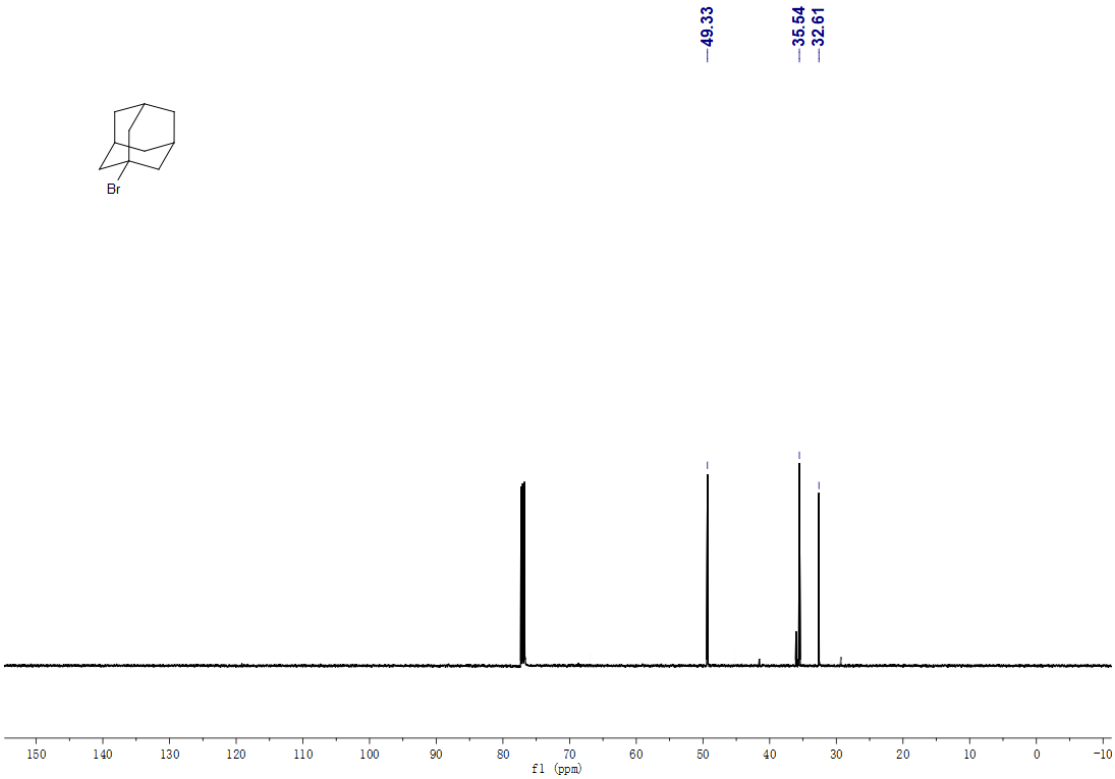

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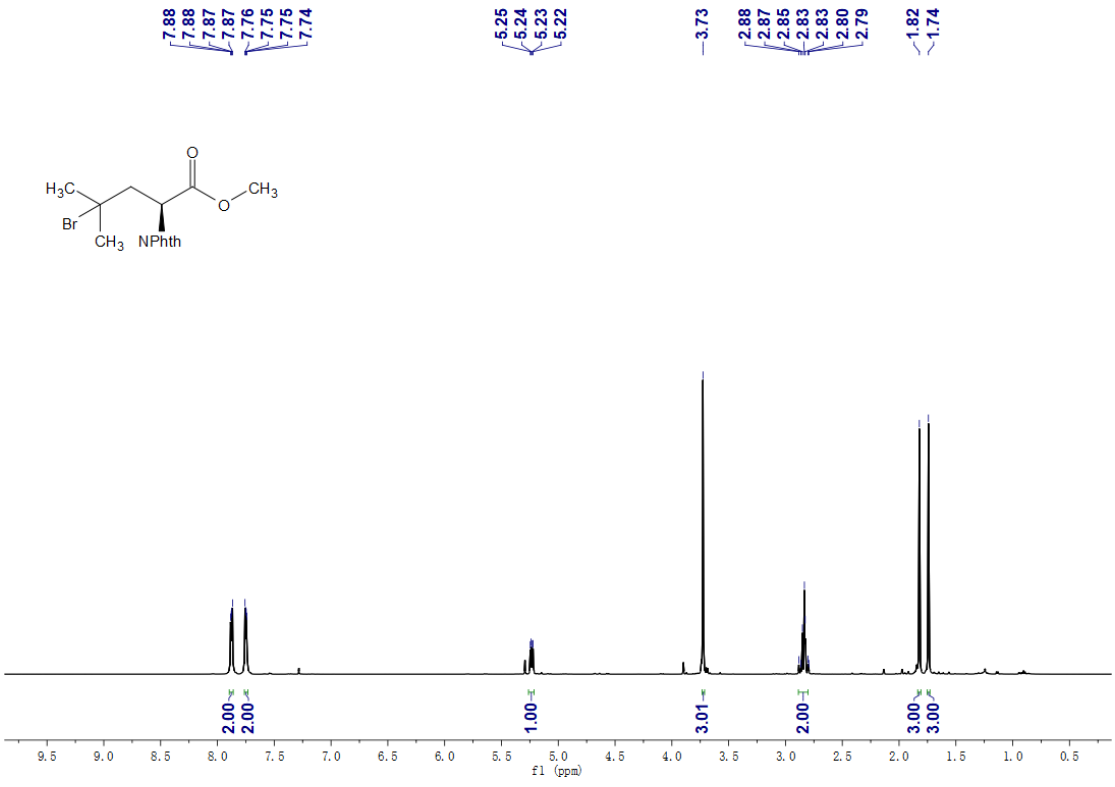

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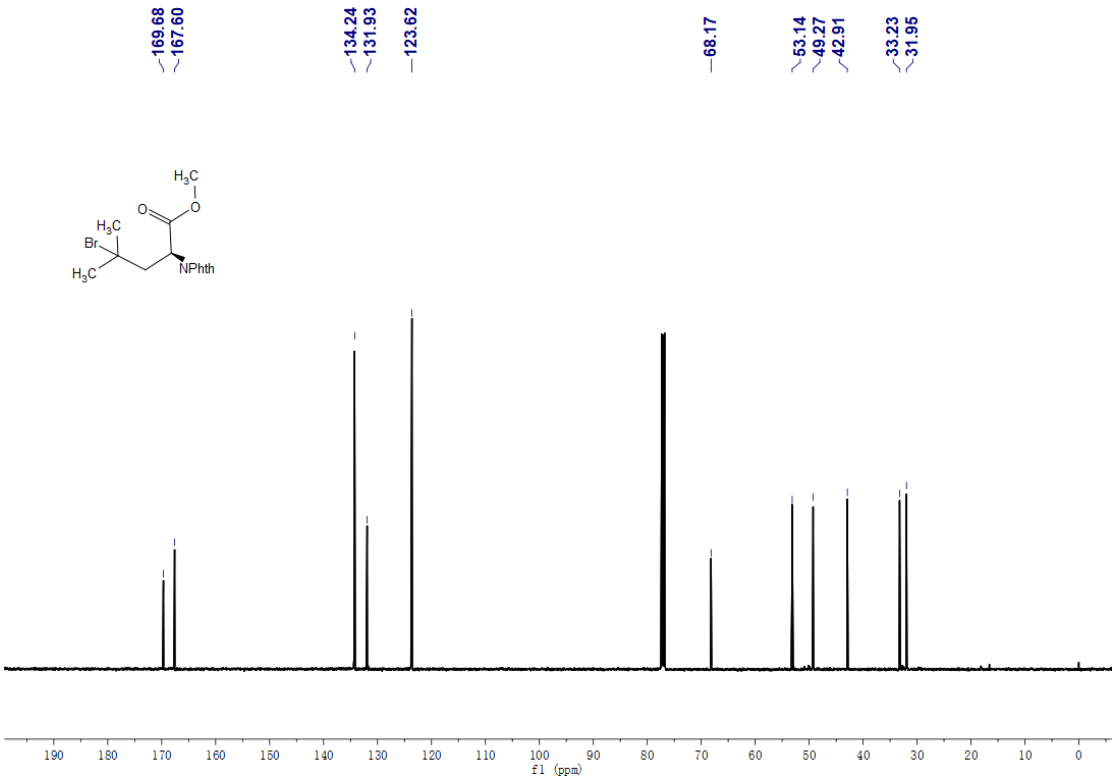

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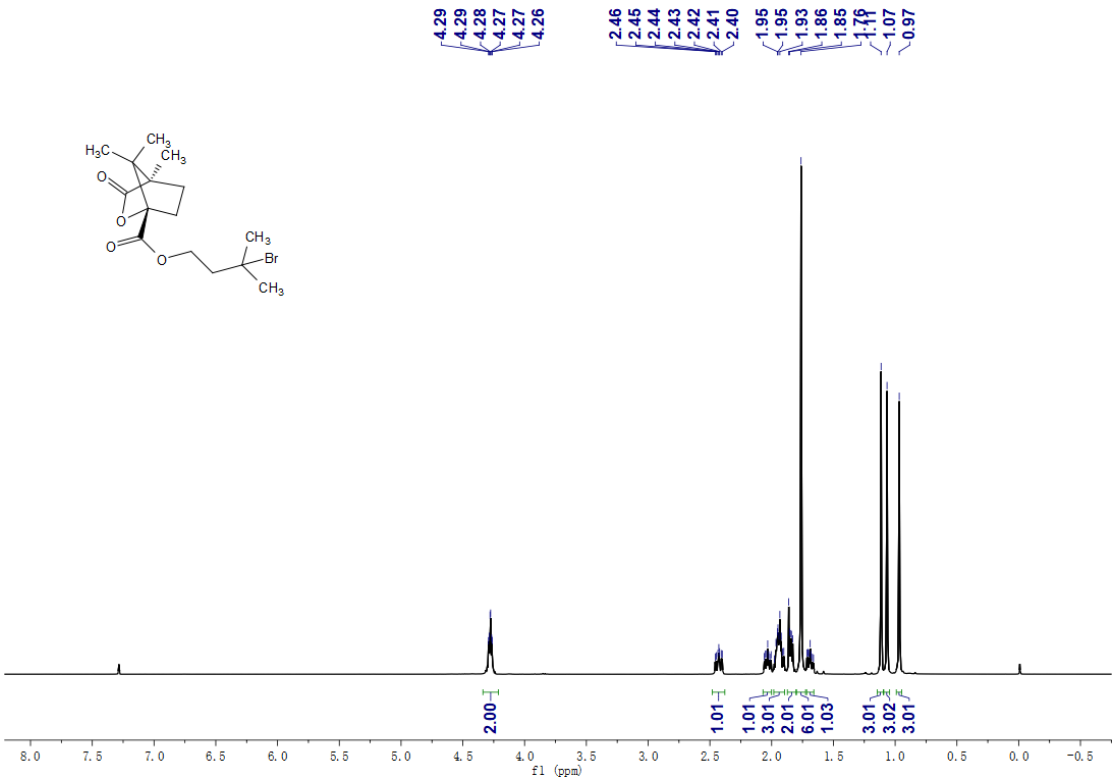

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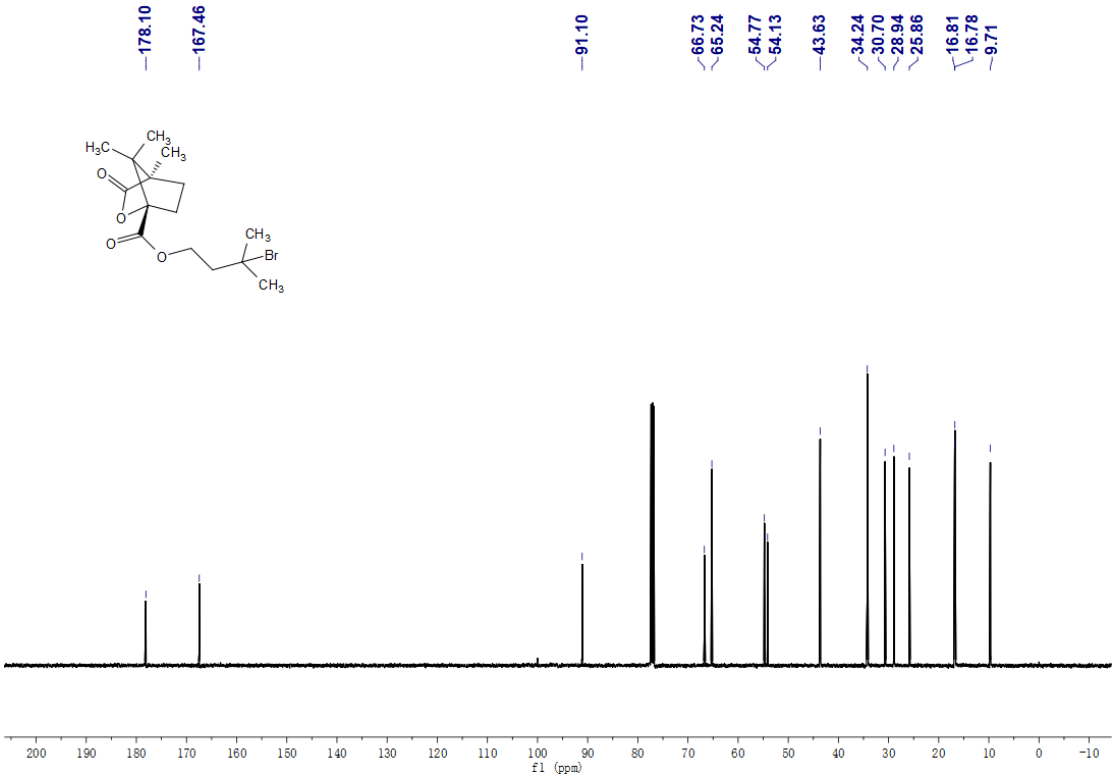

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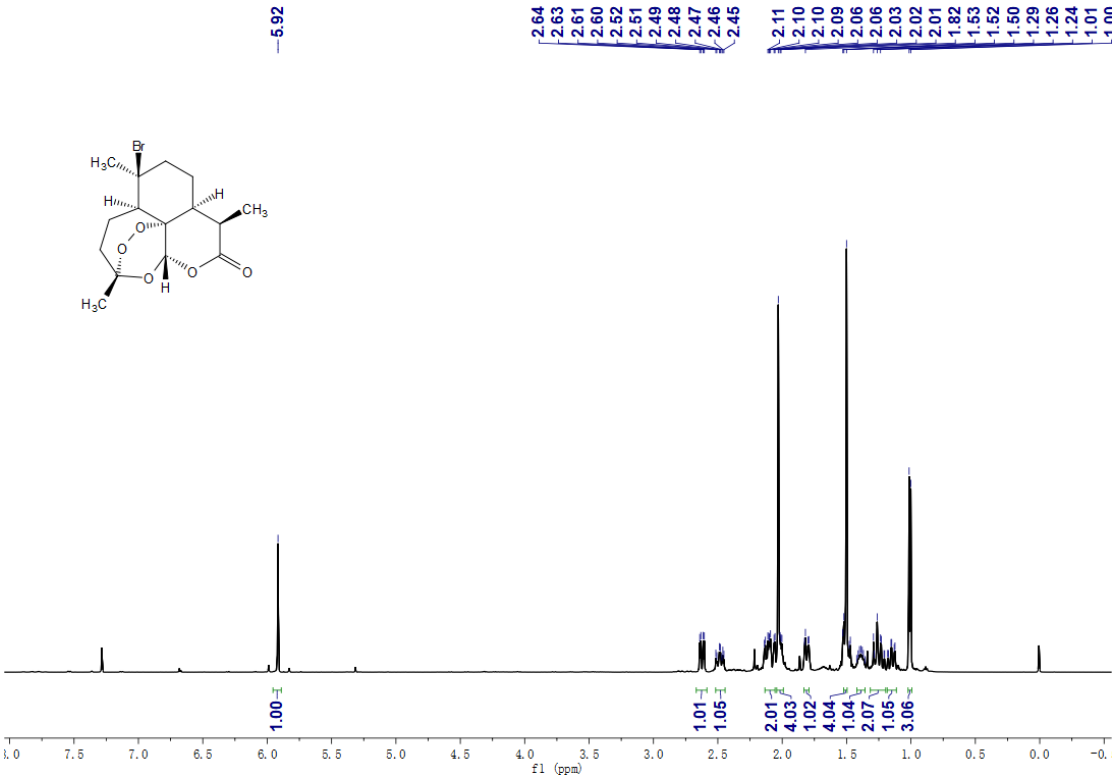

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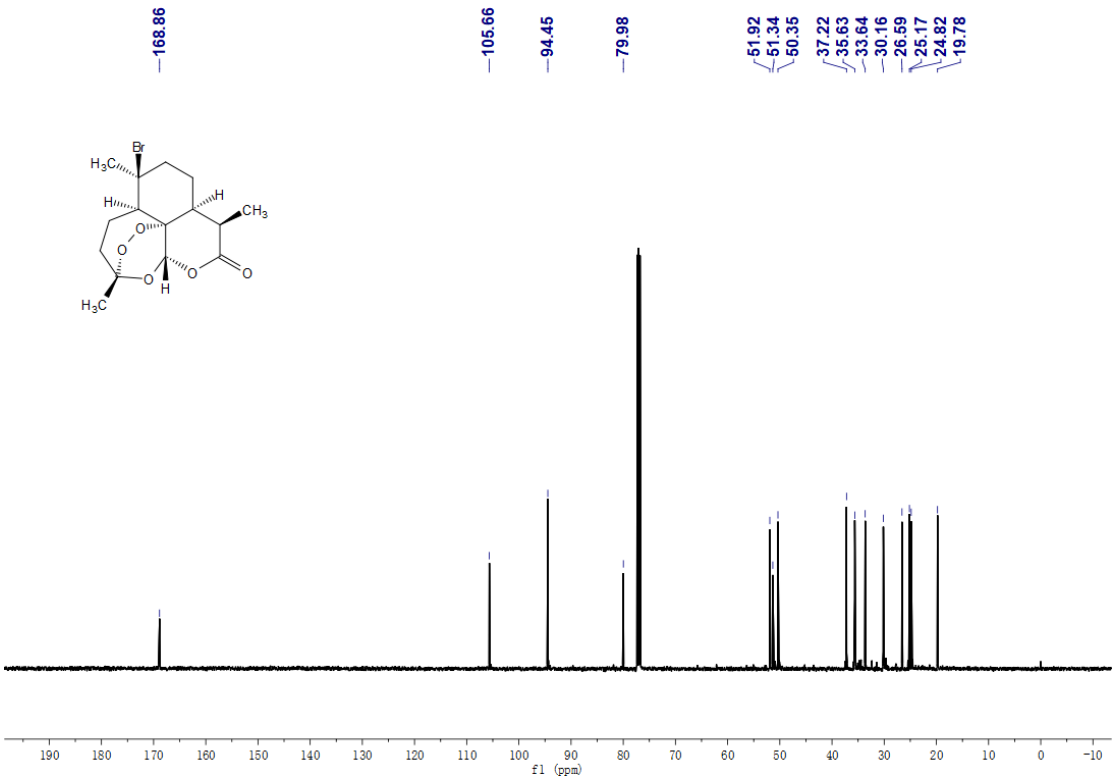

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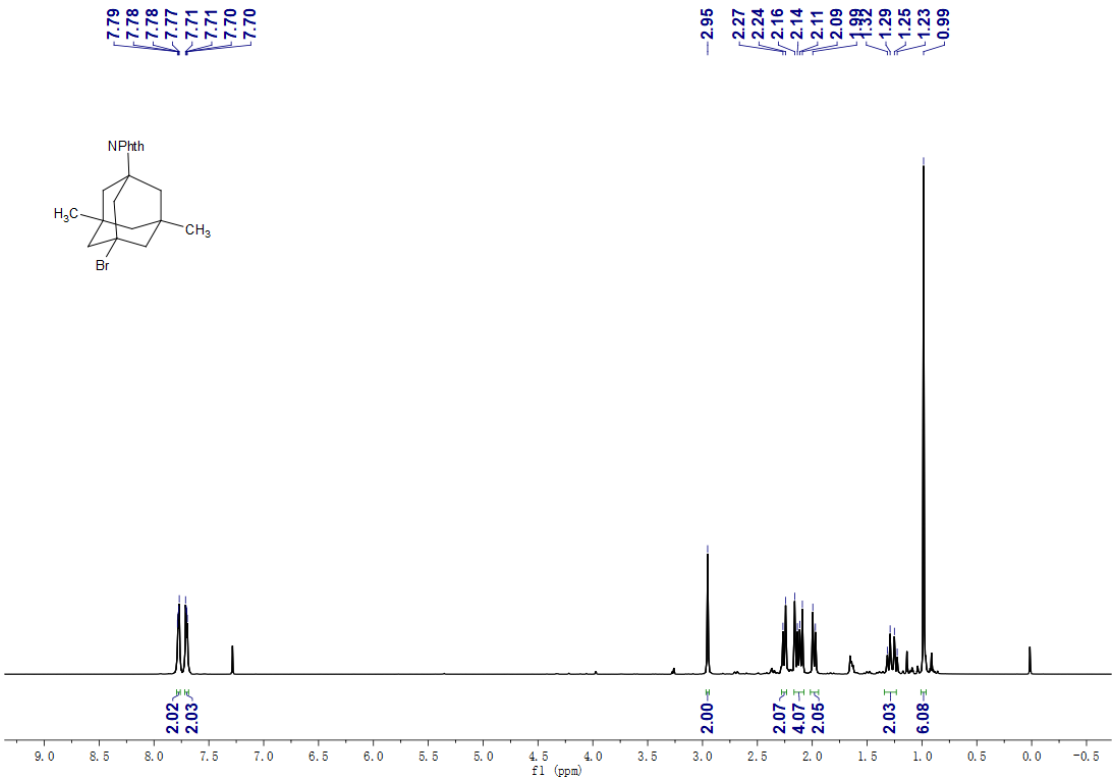

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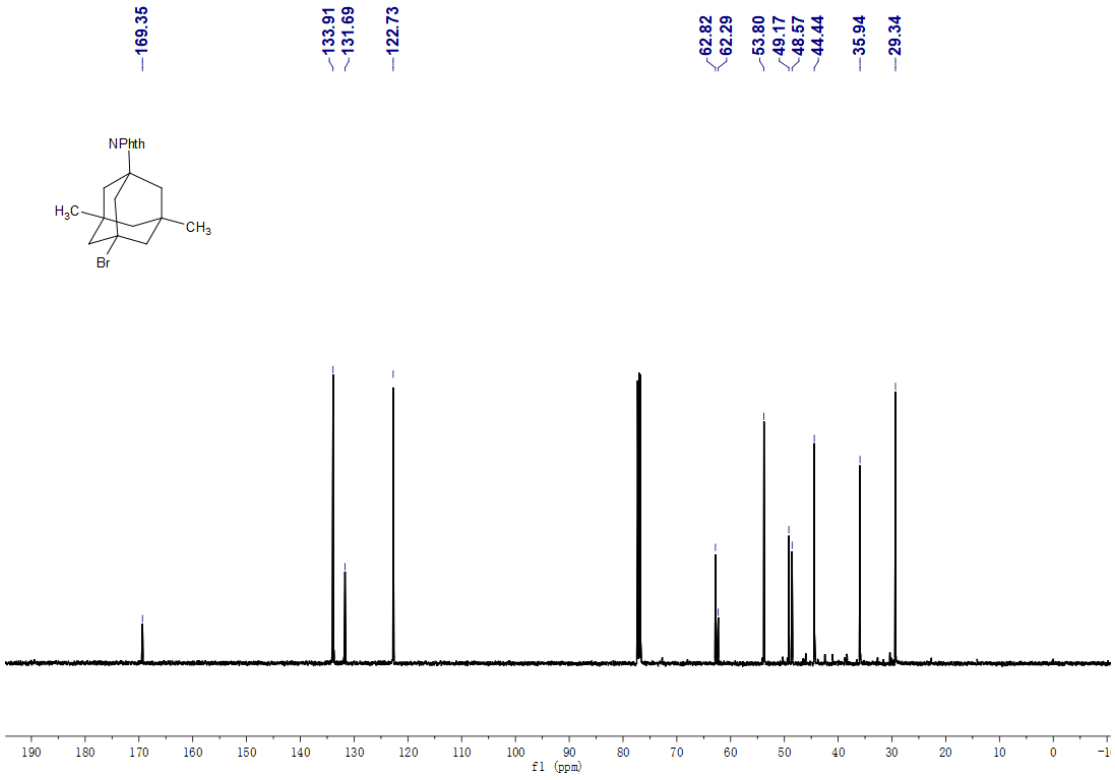

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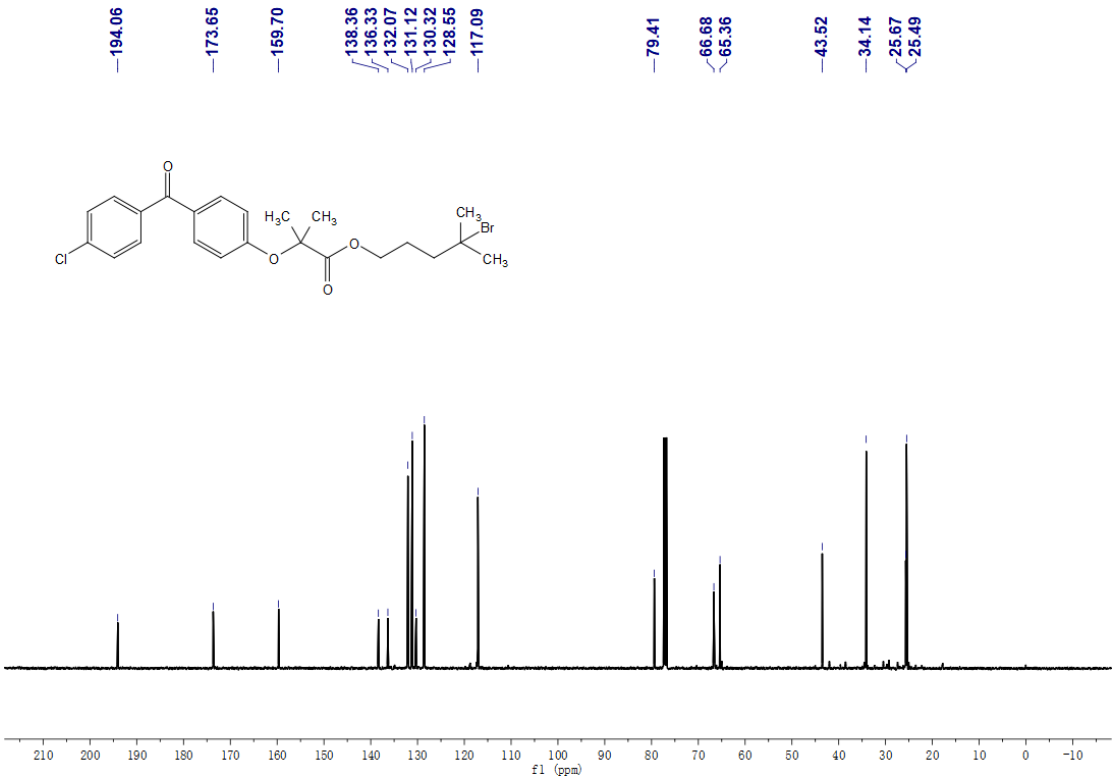

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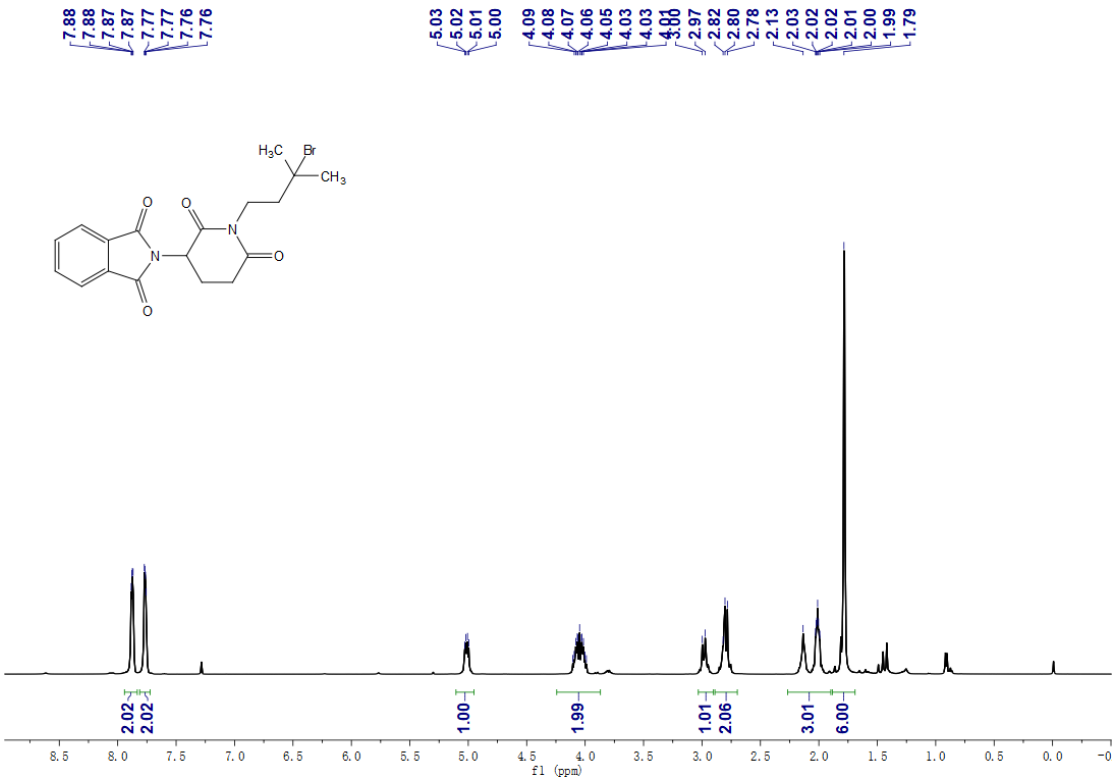

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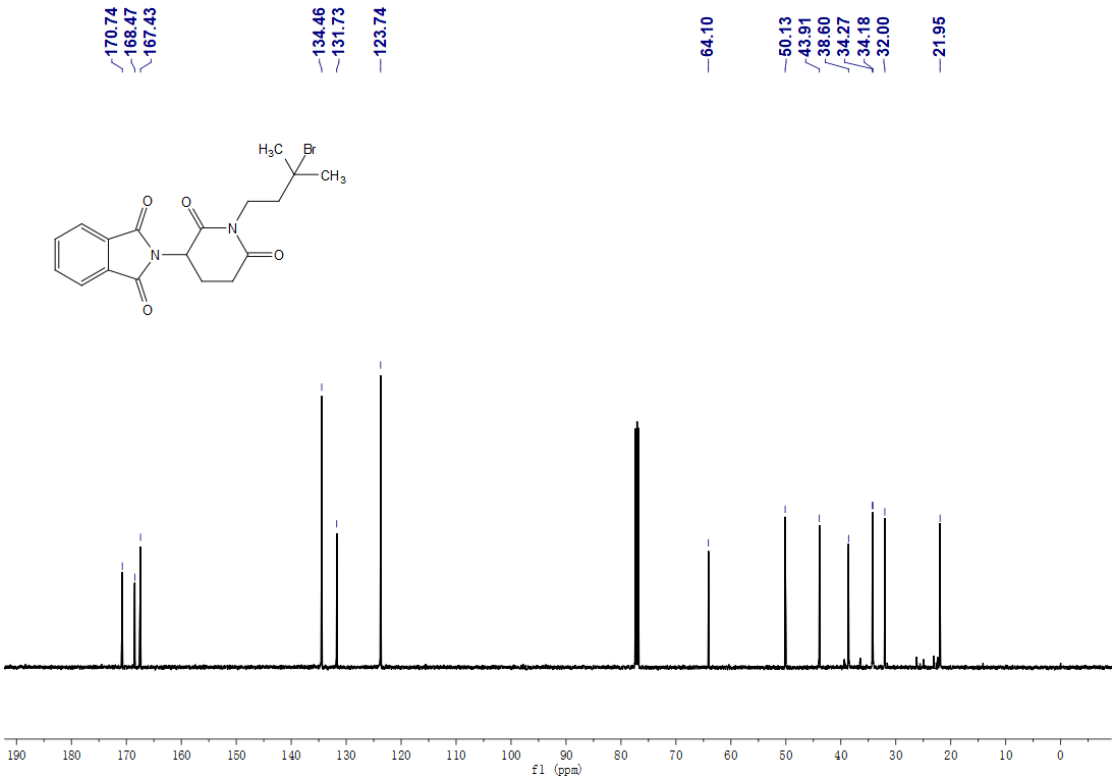

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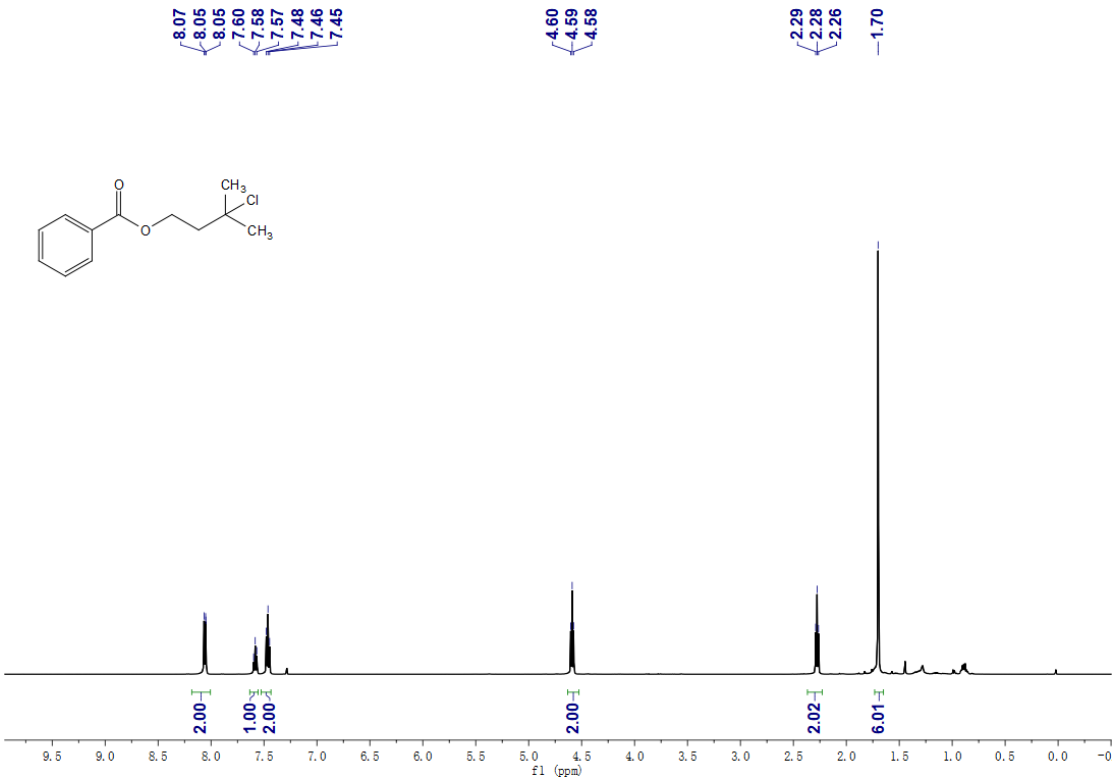

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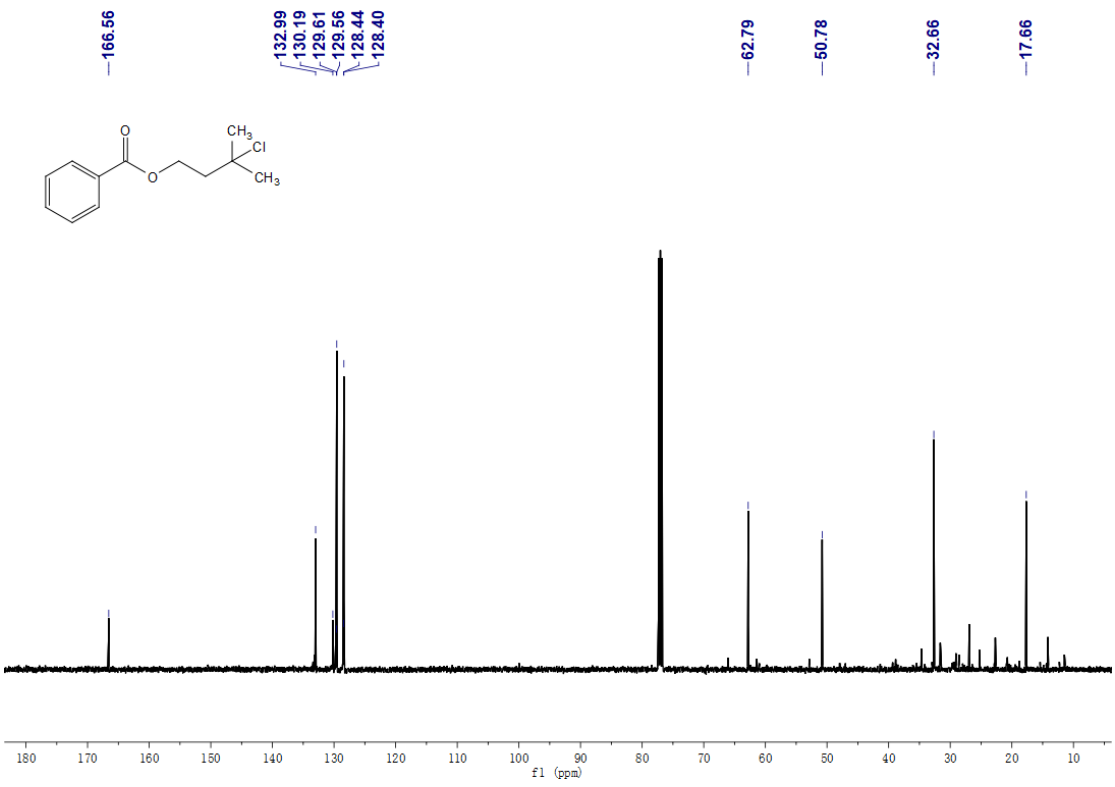

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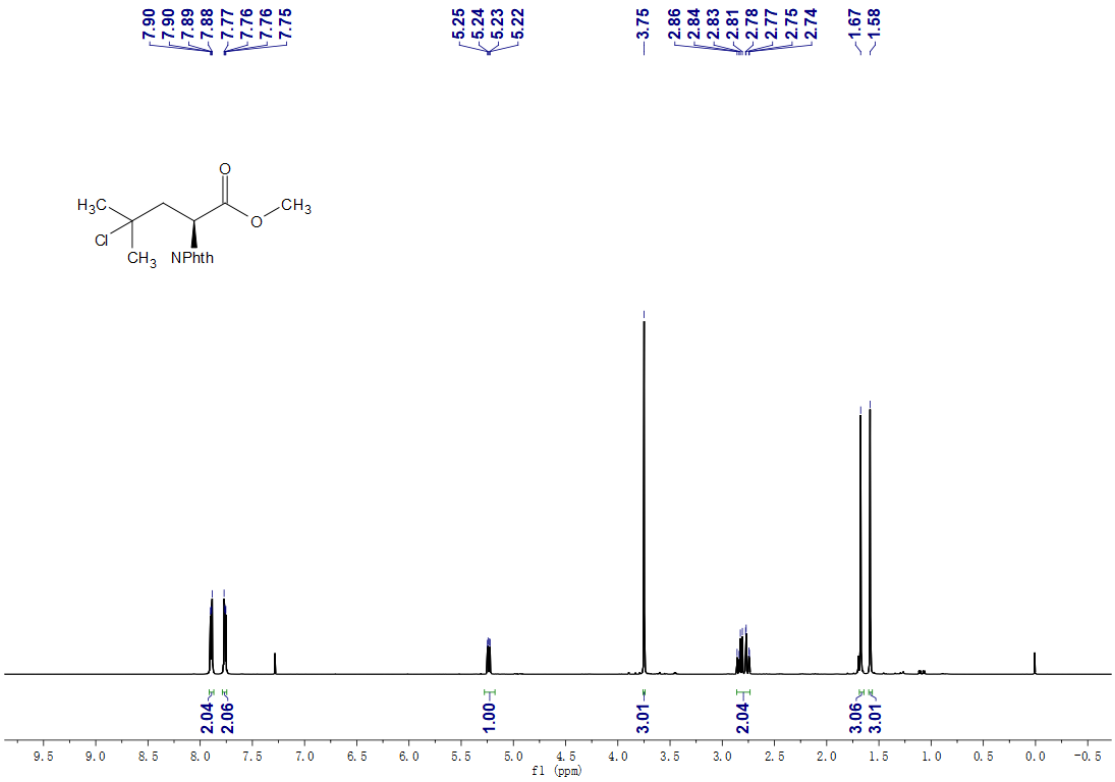

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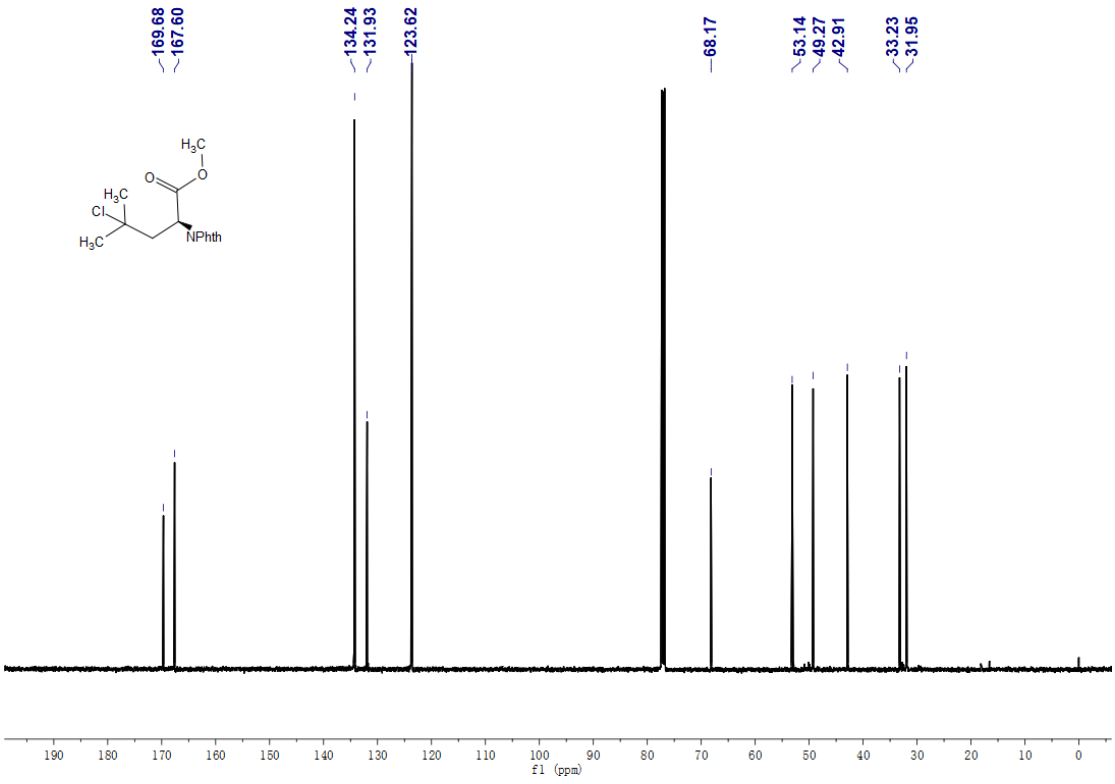
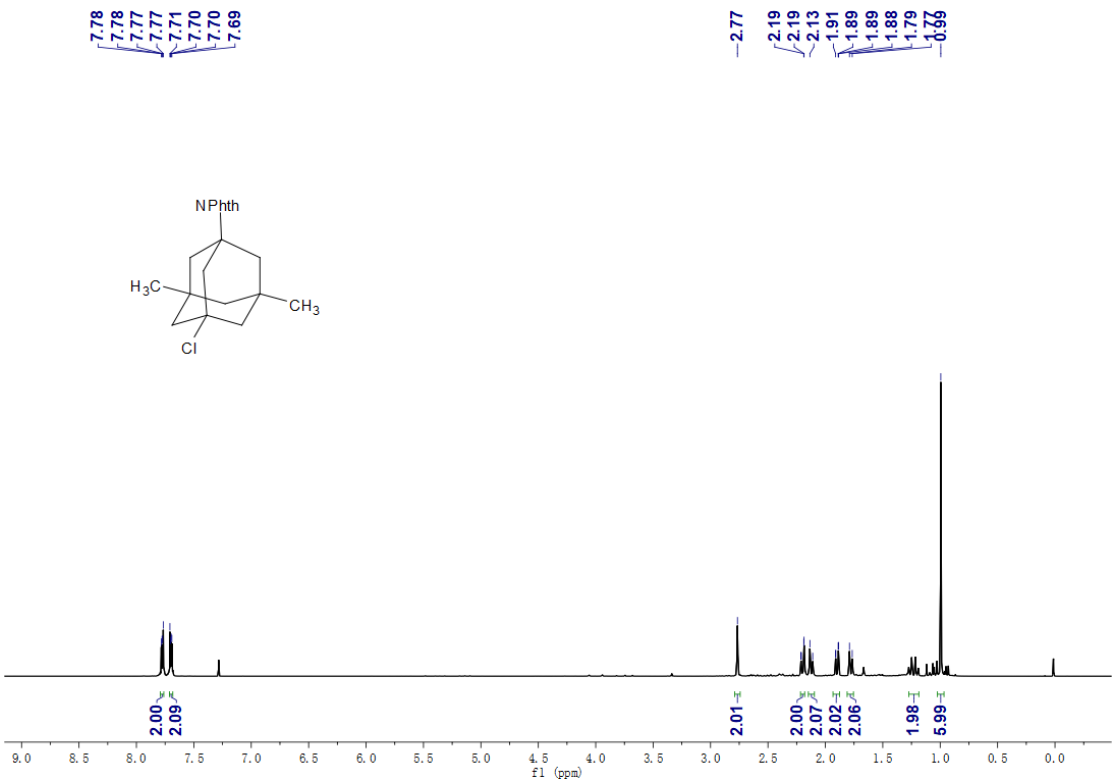
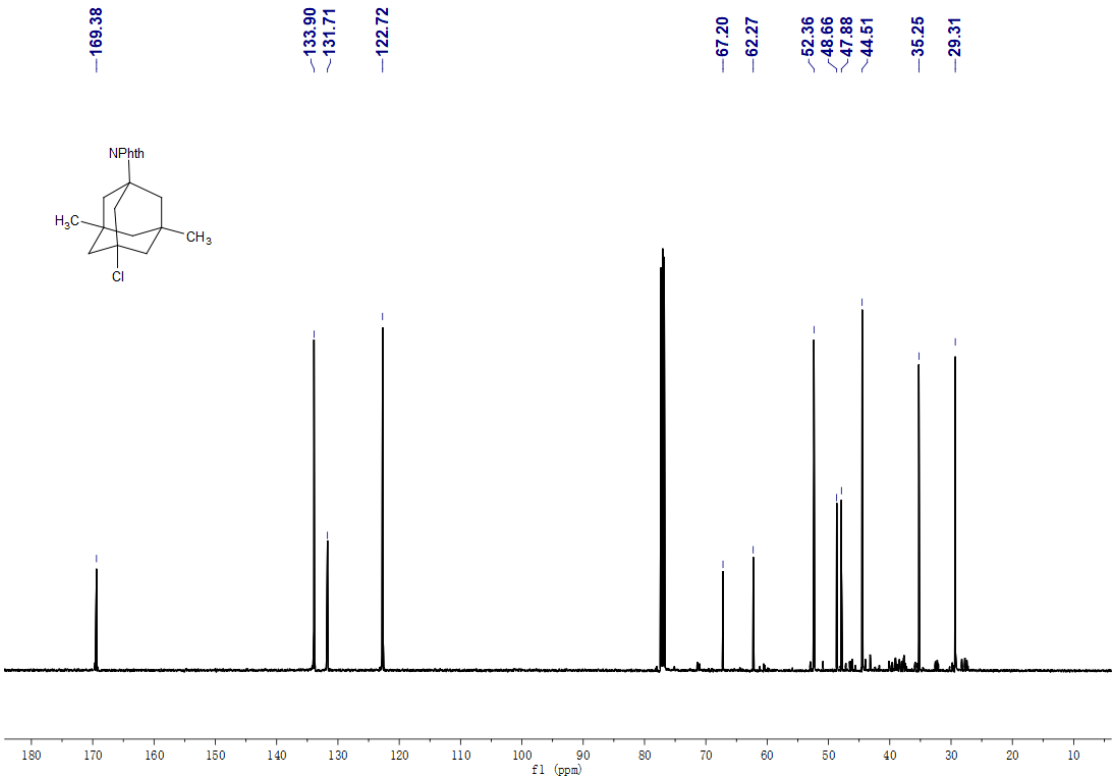


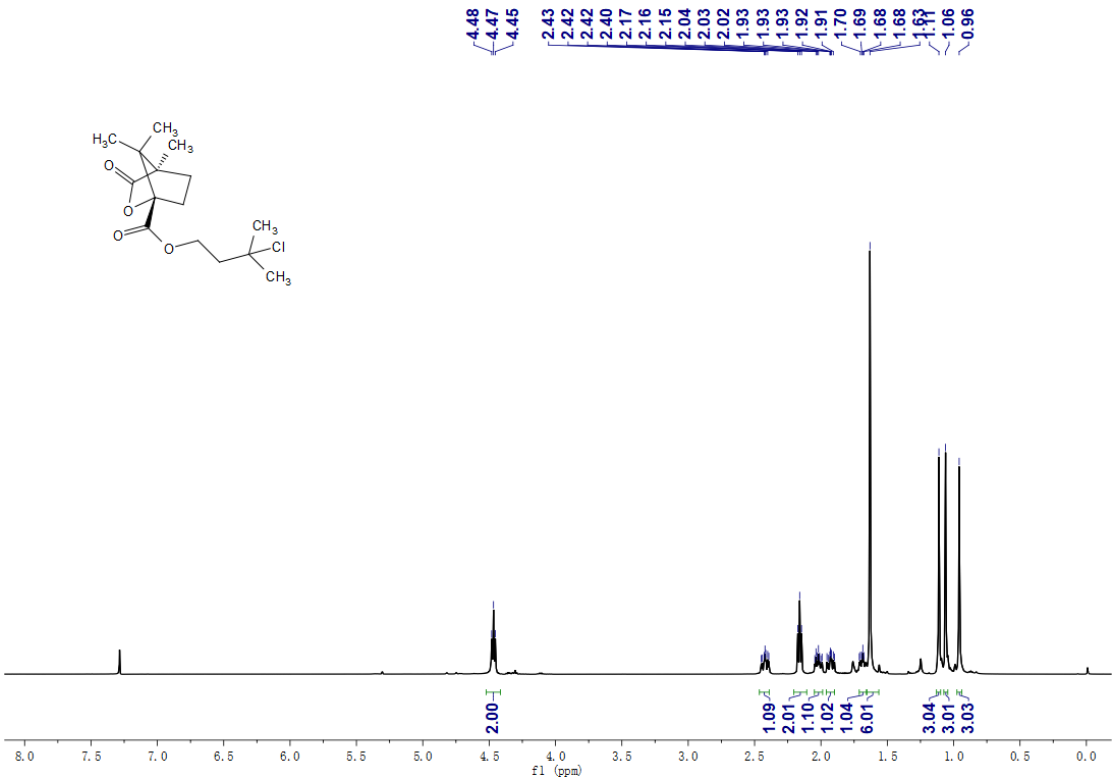
^{13}C NMR of compound **2c** (126 MHz, $CDCl_3$)



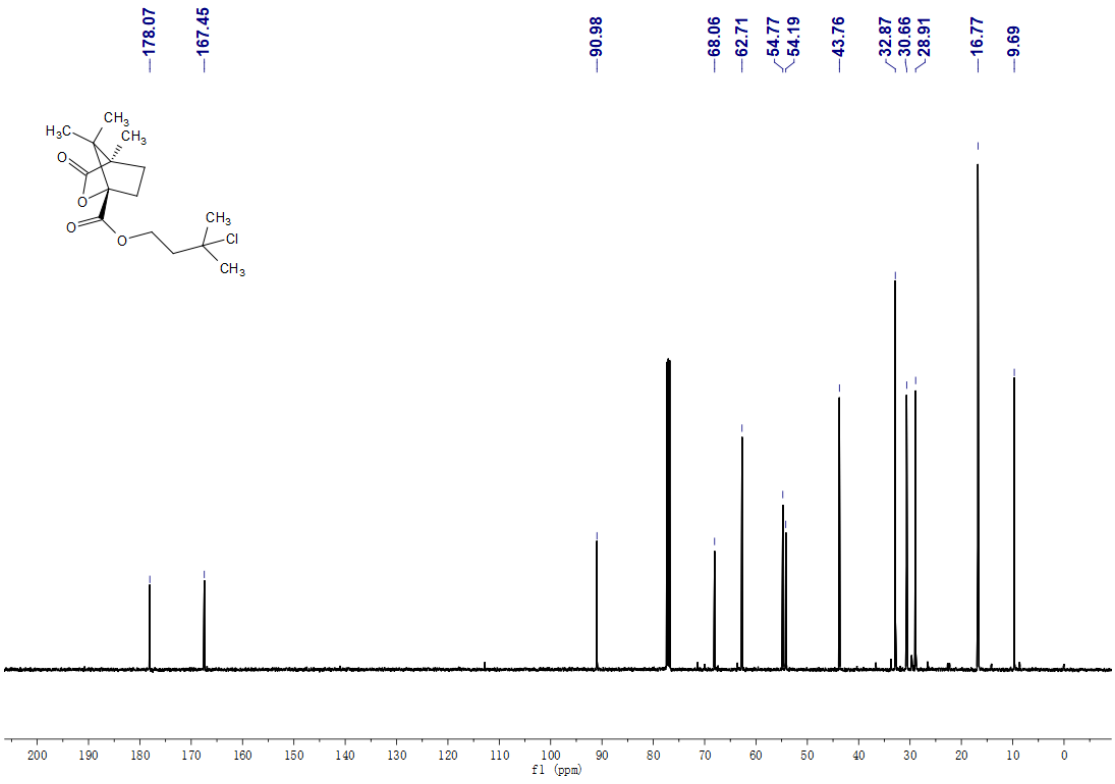
^{1}H NMR of compound **3c** (500 MHz, $CDCl_3$)



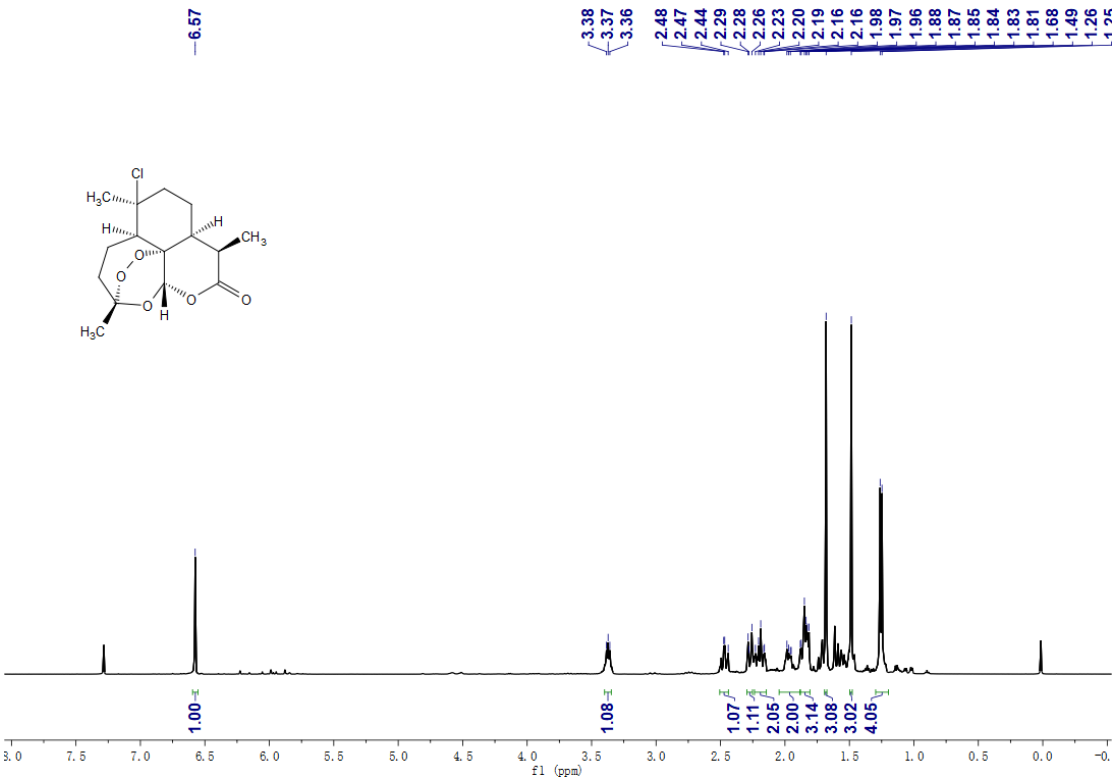
^{13}C NMR of compound **3c** (126 MHz, $CDCl_3$)



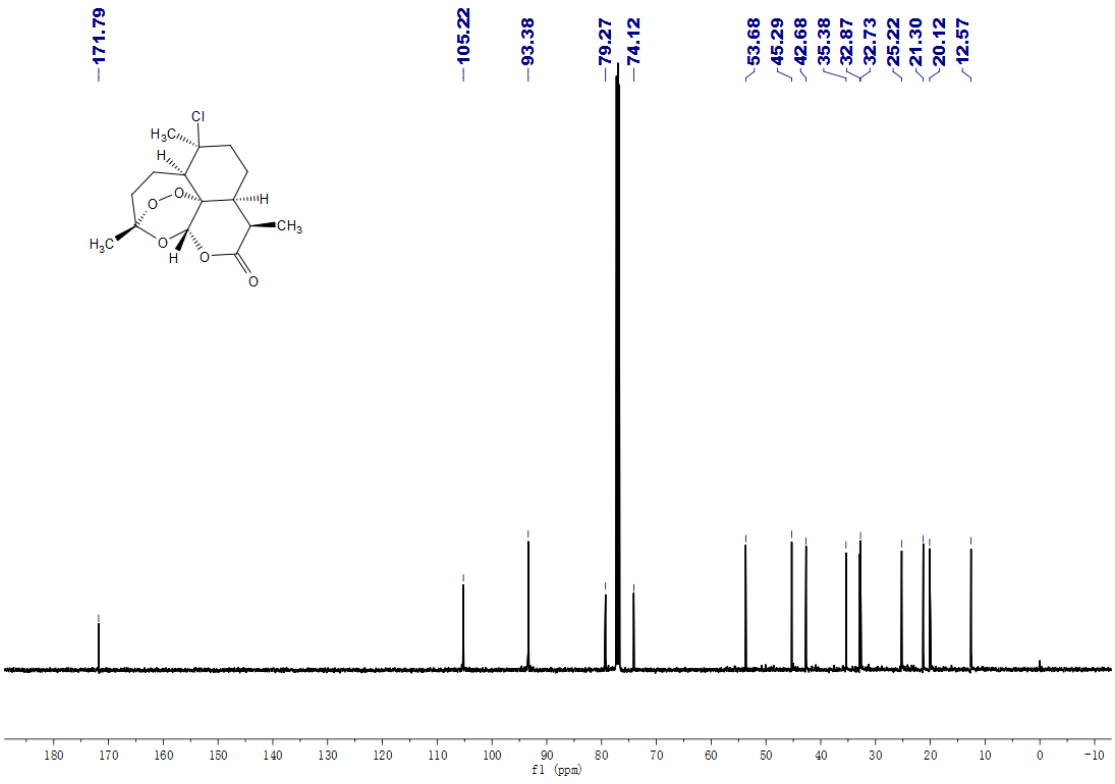
^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)



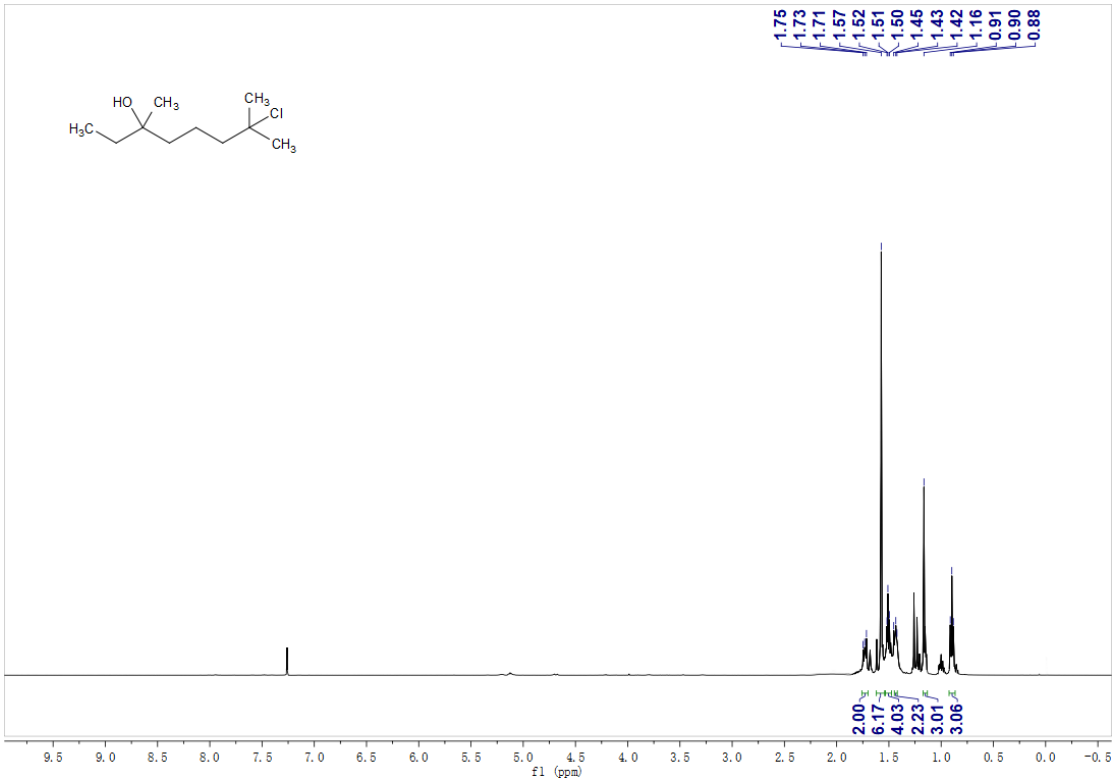
^{13}C NMR of compound **4c** (126 MHz, $CDCl_3$)



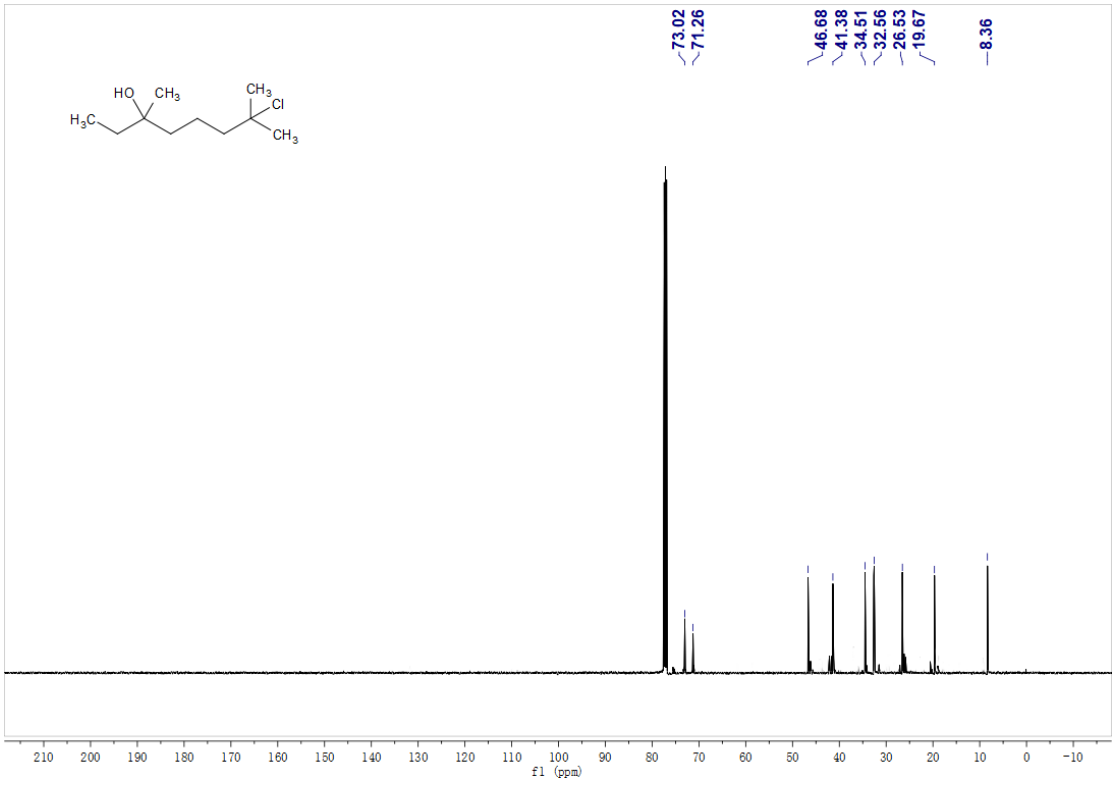
^{1}H NMR of compound **5c** (500 MHz, $CDCl_3$)



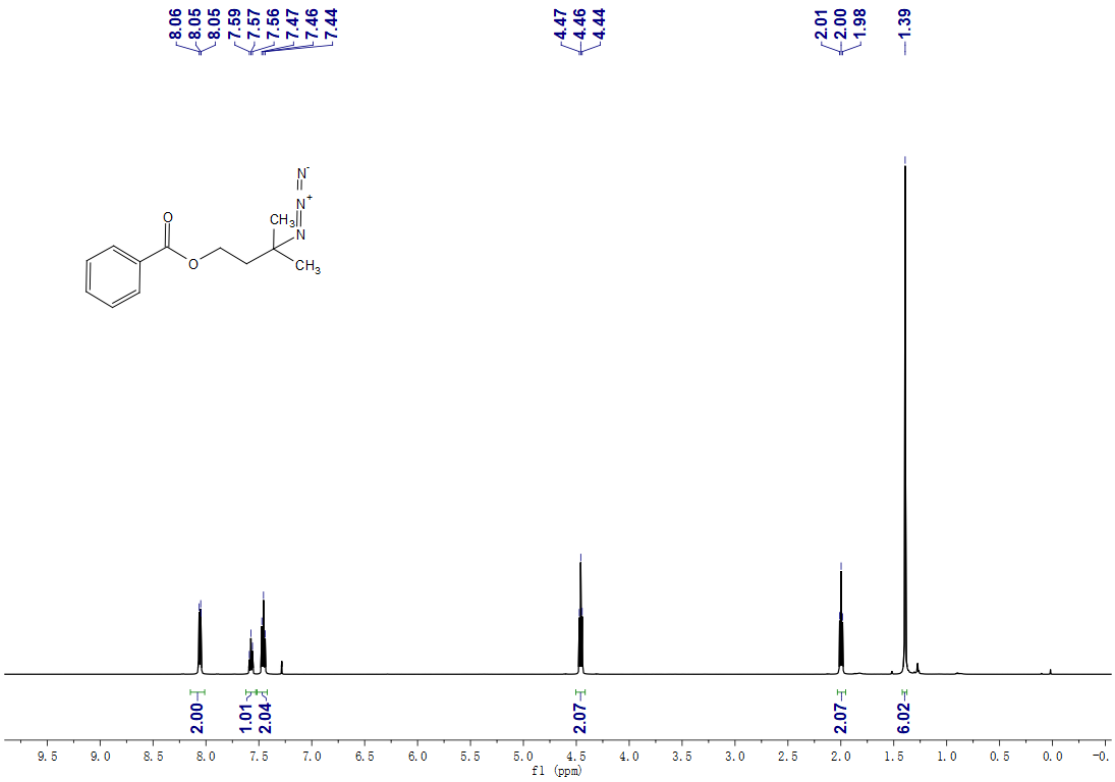
^{13}C NMR of compound **5c** (126 MHz, $CDCl_3$)



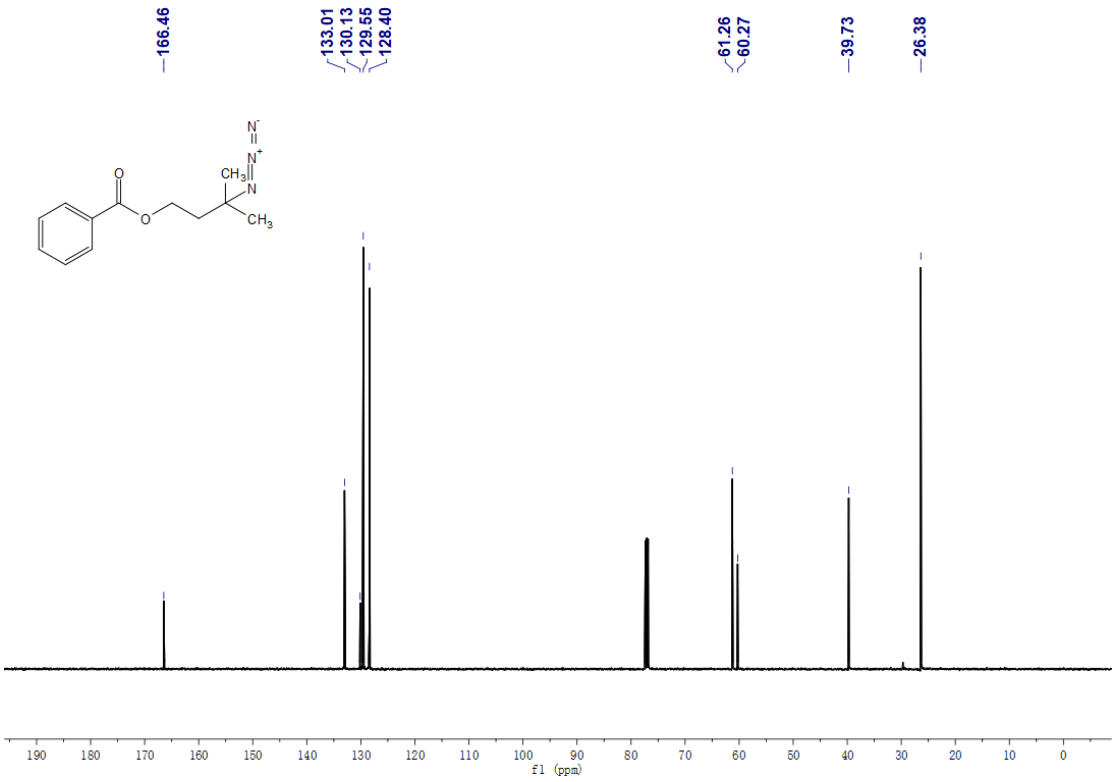
^{1}H NMR of compound **6c** (500 MHz, $CDCl_3$)



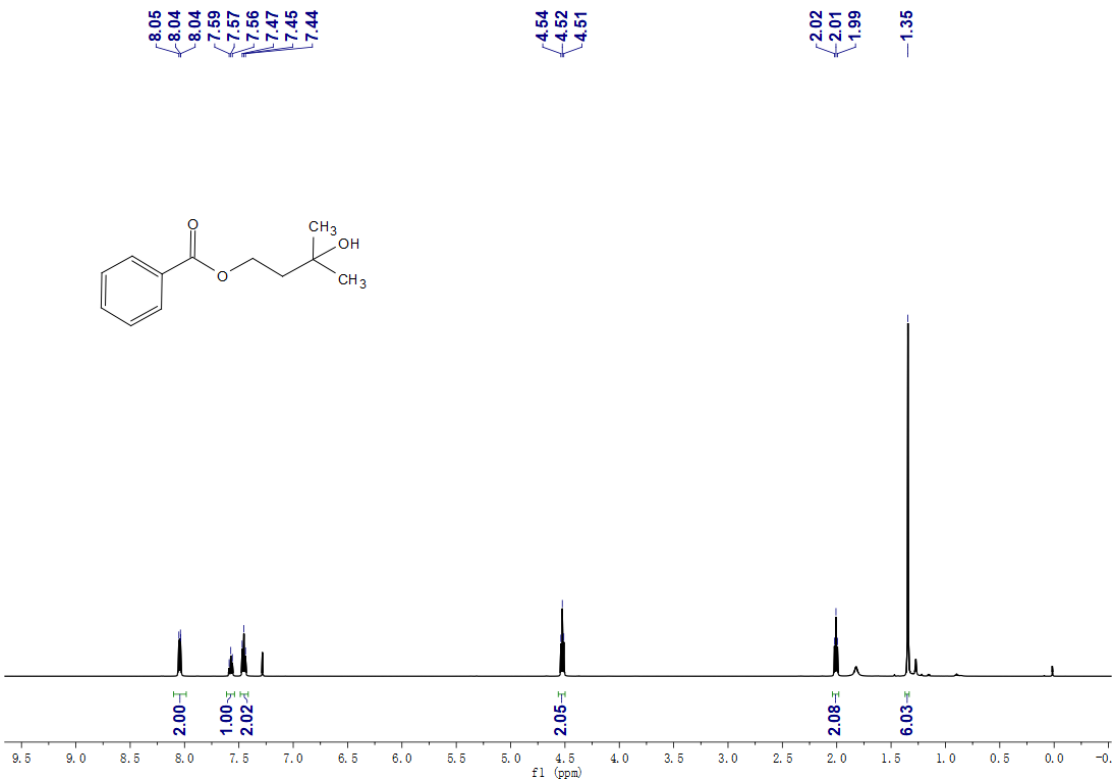
^{13}C NMR of compound **6c** (126 MHz, $CDCl_3$)



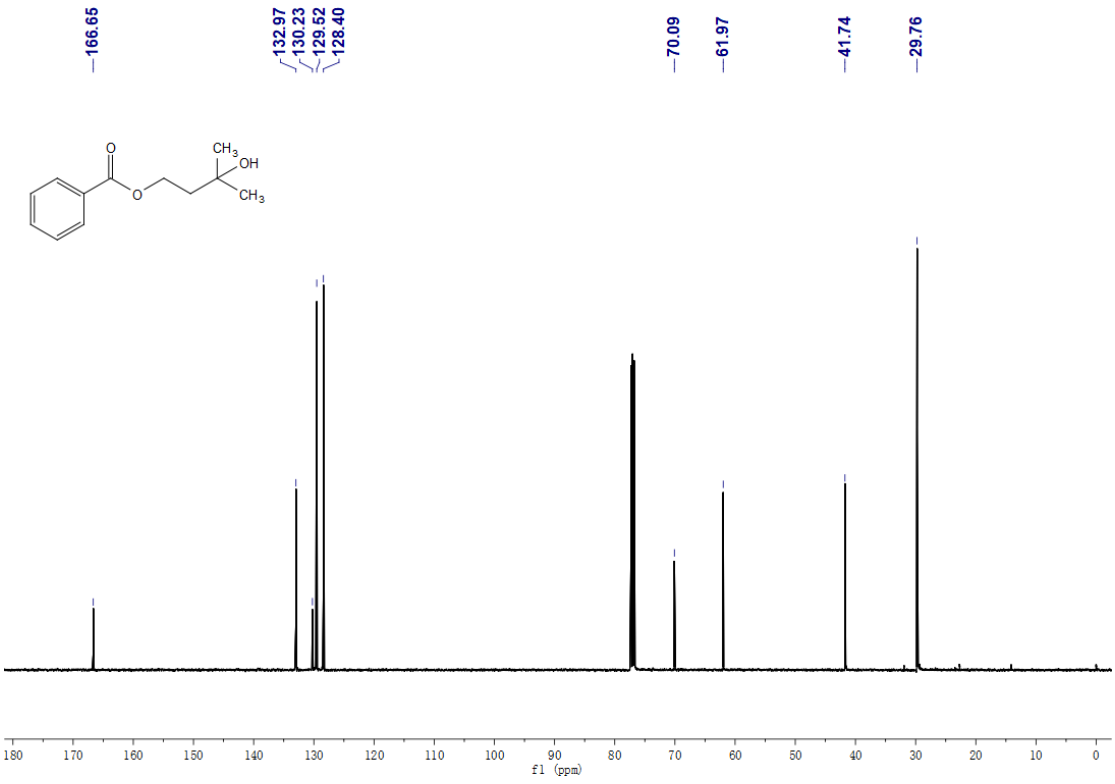
^{1}H NMR of compound **1d** (500 MHz, $CDCl_3$)



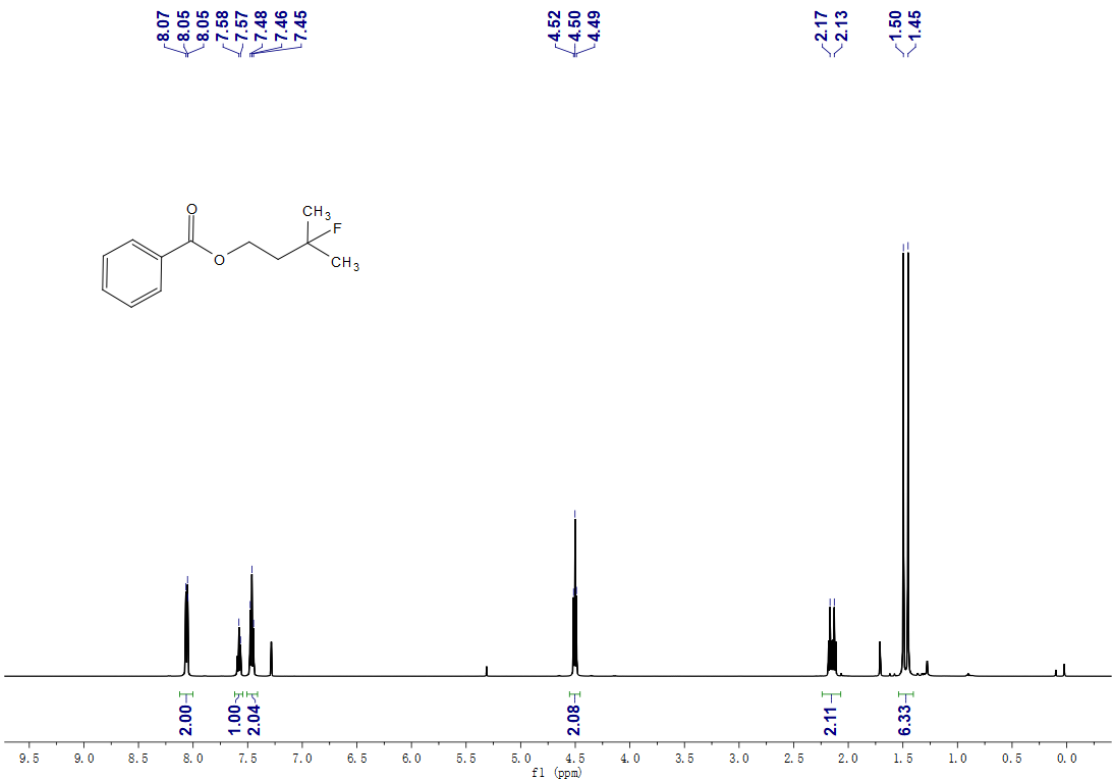
^{13}C NMR of compound **1d** (126 MHz, $CDCl_3$)



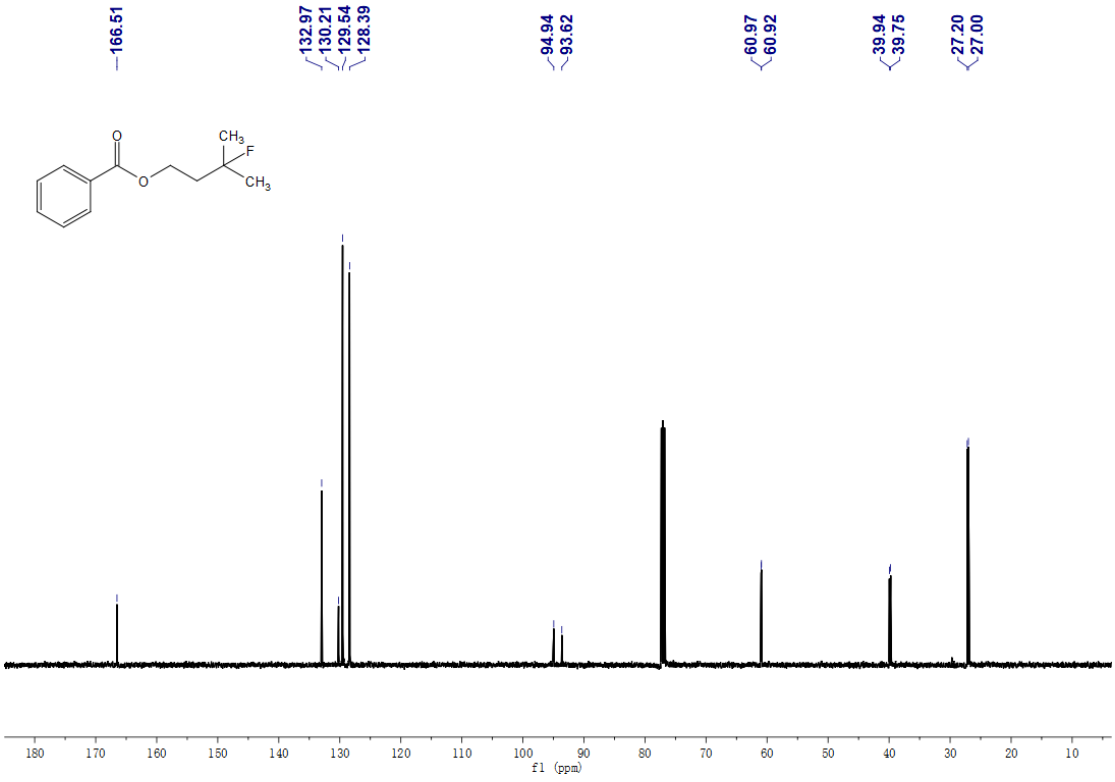
^{1}H NMR of compound **2d** (500 MHz, $CDCl_3$)



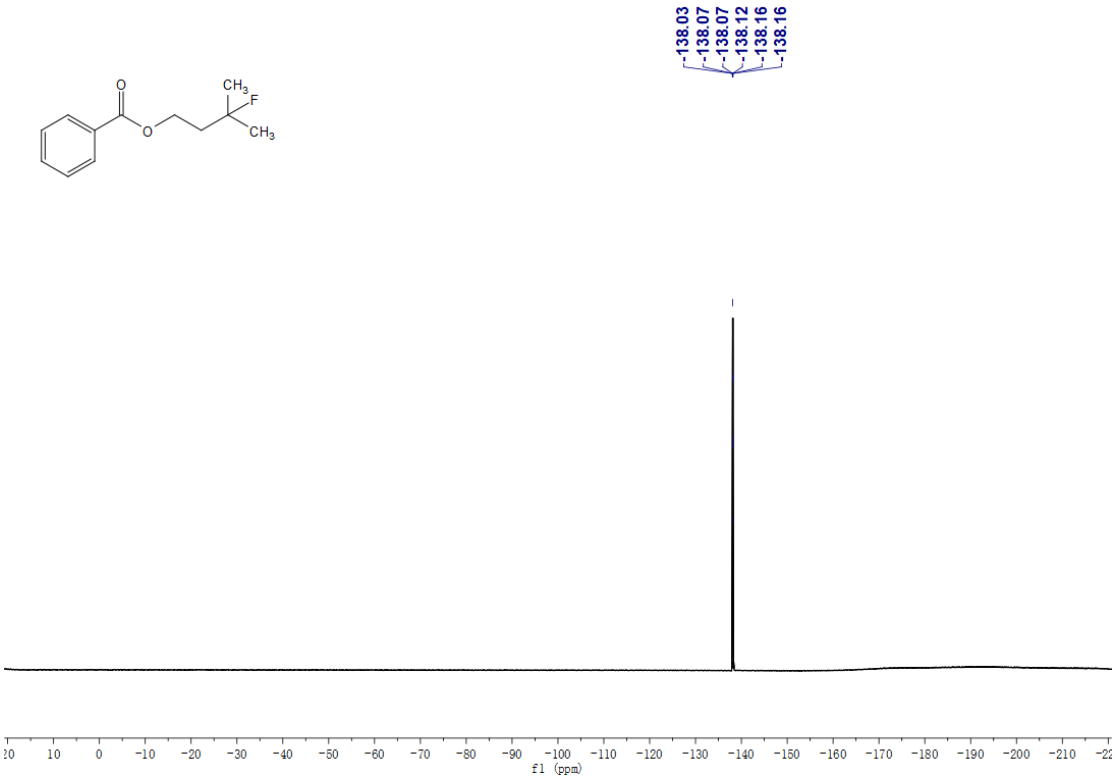
^{13}C NMR of compound **2d** (126 MHz, $CDCl_3$)



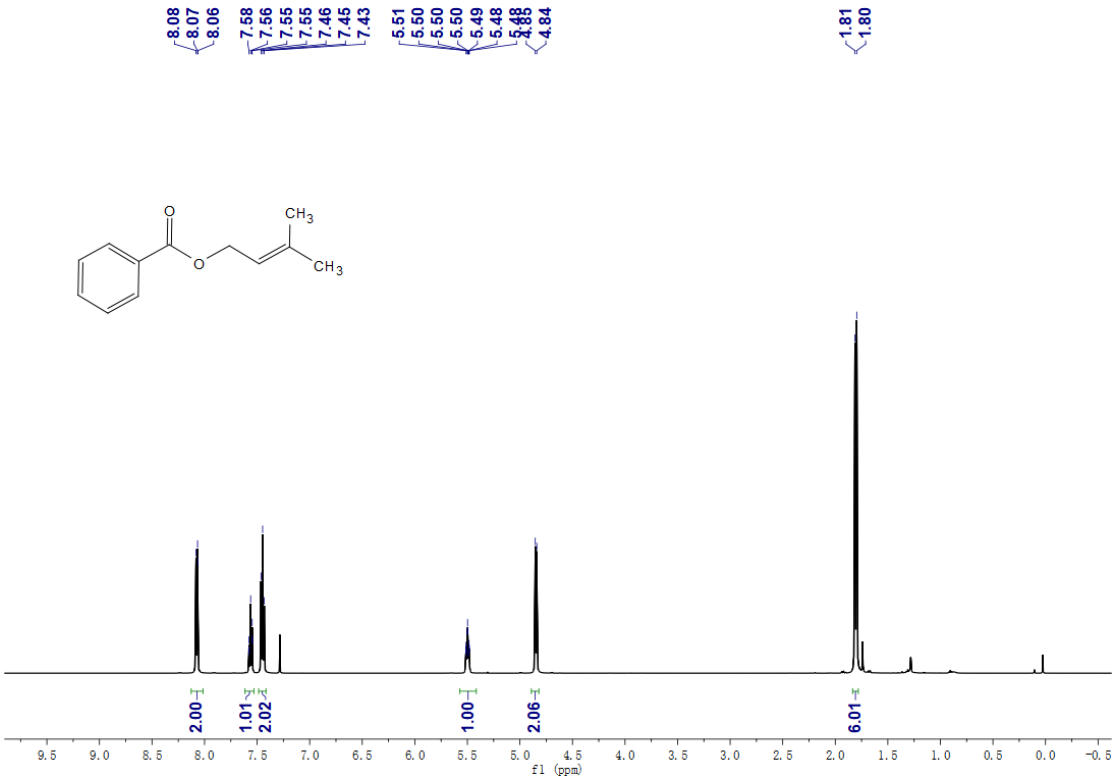
^{1}H NMR of compound **3d** (500 MHz, $CDCl_3$)



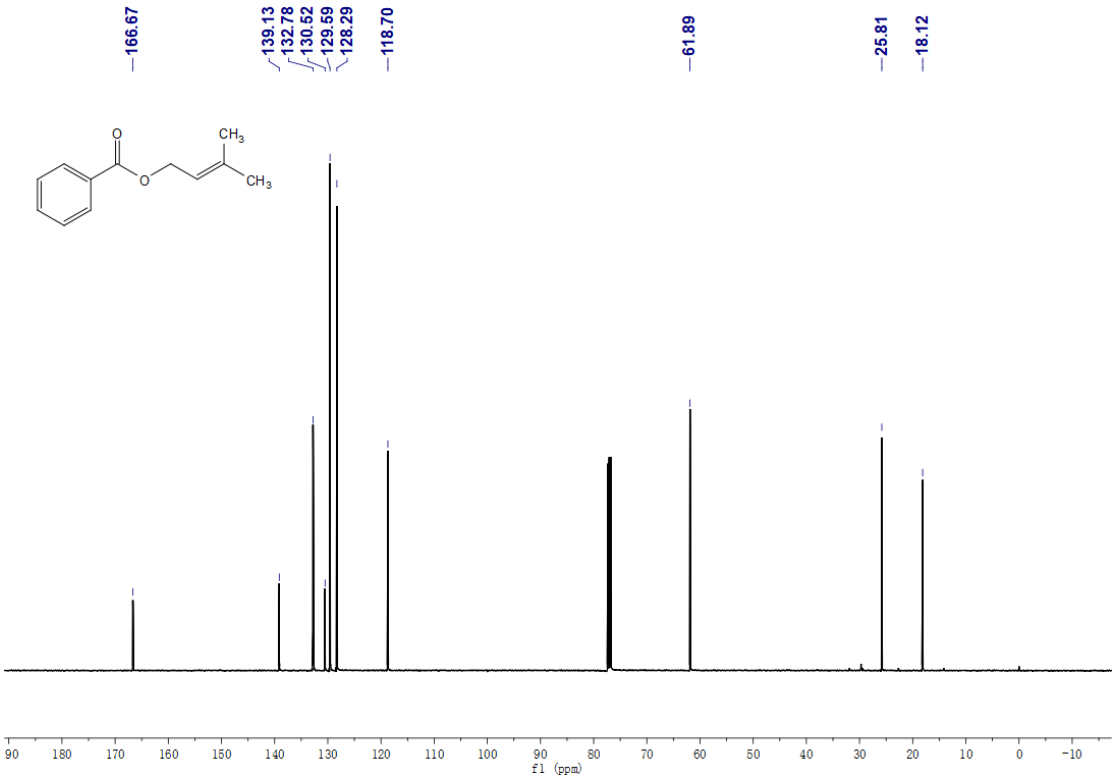
^{13}C NMR of compound **3d** (126 MHz, $CDCl_3$)



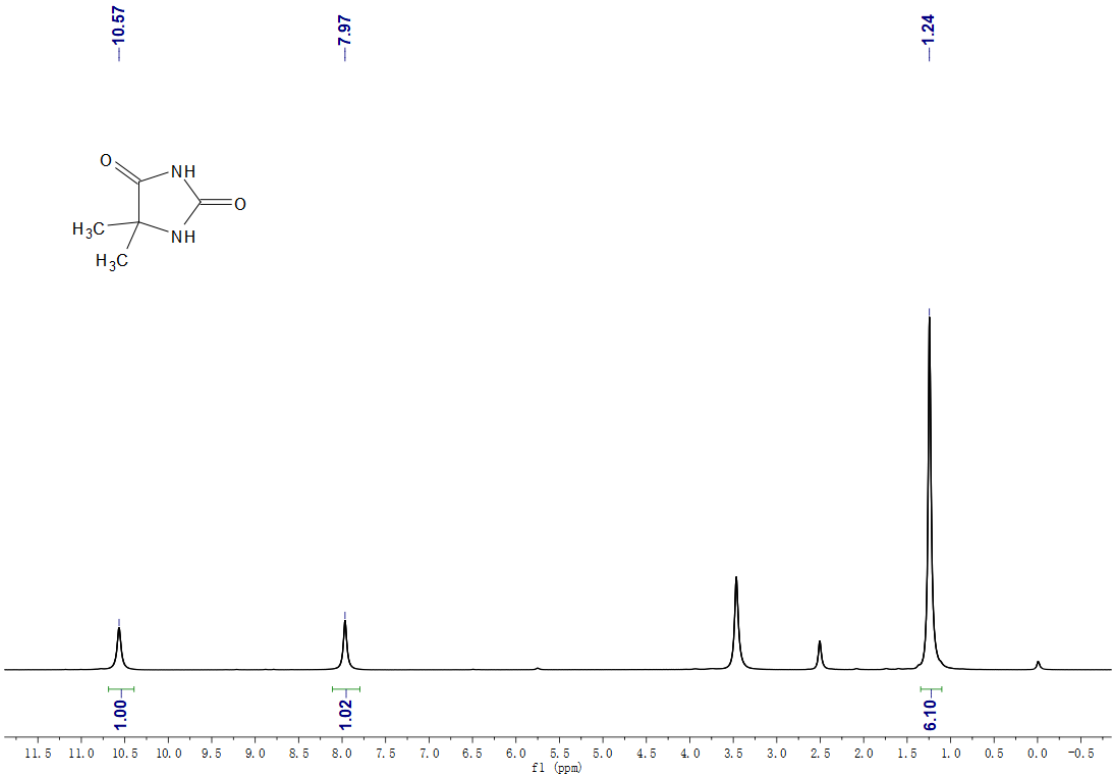
^{19}F NMR of compound **3d** (471 MHz, $CDCl_3$)



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



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



^{1}H NMR of compound **1b'** (500 MHz, DMSO-*d*6)