Supporting Information

Visible-Light-Induced Intramolecular sp^3 C−H Oxidation of *o*-alkyl Substituted Benzamides for Synthesis of Iminoisobenzofurans

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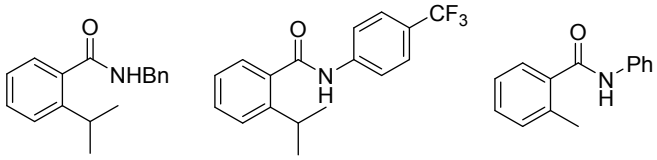
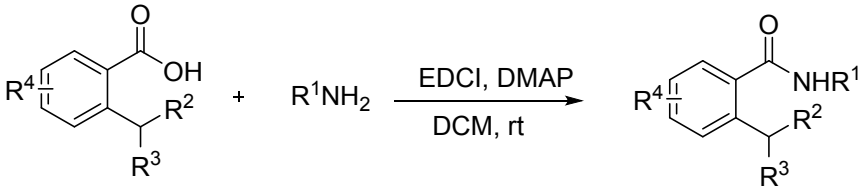
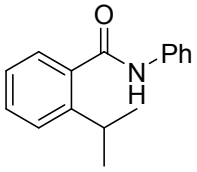
Unsuccessful substrates



General procedure for the preparation of compounds 1.



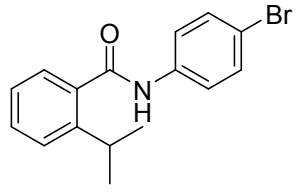
A mixture of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.04g, 6.5 mmol, 1.3 equiv), DMAP (0.92g, 7.5 mmol, 1.5 equiv), acid (5 mmol, 1.0 equiv), and amine (5 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was stirred at room temperature for 6 h. After completing reaction, the mixture was added 30 mL H_2O. The organic layer was separated and the aqueous layer was extracted with dichloromethane (20mL × 3). The combined organic phase was washed with brine (20 mL), and then dried over Na_2SO_4. After filtration, the solvent was concentrated in vacuo. The products were purified by column chromatography with petroleum ether and ethyl acetate as an eluent.



1a

2-isopropyl-*N*-phenylbenzamide (1a)

White solid. M.p. =132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 2H), 7.49 (s, 1H), 7.47 – 7.33 (m, 5H), 7.28 – 7.21 (m, 1H), 7.19– 7.12(m, 1H), 3.48 – 3.35 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.9, 138.0, 136.1, 130.4, 129.1, 126.4, 125.8, 124.6, 119.8, 30.0, 24.2. HRMS (ESI): calcd. for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1383; found 240.1381. (Petroleum ether/EtOAc, 5/1).

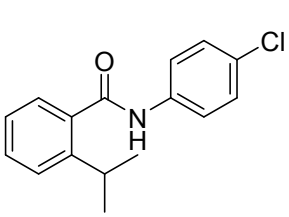


1b

***N*-(4-bromophenyl)-2-isopropylbenzamide (1b)**

White solid. M.p. =180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.39 (m, 7H), 7.32 – 7.22 (m, 1H), 3.53 – 3.14 (m, 1H), 1.30 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.0, 137.1), 135.8, 132.1, 130.6, 126.4, 126.3, 125.8, 121.3, 117.1, 30.0, 24.1. HRMS (ESI): calcd. for $C_{16}H_{17}BrNO$ $[M + H]^+$

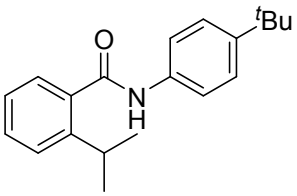
318.0488; found 318.0484. (Petroleum ether/EtOAc, 5/1).



1c

***N*-(4-chlorophenyl)-2-isopropylbenzamide (1c)**

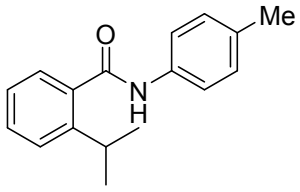
White solid. M.p. =171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, *J* = 11.8 Hz, 3H), 7.47 – 7.35 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.19 (m, 1H), 3.64 – 3.14 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.0, 136.6, 135.8, 130.6, 129.5, 129.1, 126.4, 126.3, 125.9, 121.0, 30.0, 24.1. HRMS (ESI): calcd. for $C_{16}H_{17}ClNO$ $[M + H]^+$ 274.0993; found 274.0990. (Petroleum ether/EtOAc, 5/1).



1d

***N*-(4-(*tert*-butyl)phenyl)-2-isopropylbenzamide (1d)**

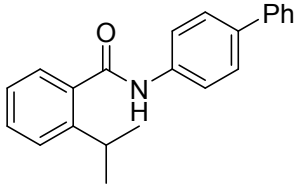
White solid. M.p. =148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55(m, 2H), 7.53 – 7.39 (m, 6H), 7.32 – 7.22 (m, 1H), 3.60 – 3.21 (m, 1H), 1.36 (s, 9H), 1.31 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 147.6, 146.9, 136.2, 135.4, 130.3, 126.3, 126.3, 125.9, 125.8, 119.6, 34.4, 31.4, 30.0, 24.2. HRMS (ESI): calcd. for $C_{20}H_{26}NO$ $[M + H]^+$ 296.2009; found 296.2005. (Petroleum ether/EtOAc, 5/1).



1e

2-isopropyl-*N*-(*p*-tolyl)benzamide (1e)

White solid. M.p. =139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.35 (m, 6H), 7.28 – 7.19 (m, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 3.48 – 3.31 (m, 1H), 2.34 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 146.9, 136.2, 135.4, 134.2, 130.3, 129.6, 126.4, 126.3, 125.8, 119.8, 30.0, 24.2, 20.9. HRMS (ESI): calcd. for $C_{17}H_{20}NO$ $[M + H]^+$ 254.1539; found 254.1536. (Petroleum ether/EtOAc, 5/1).

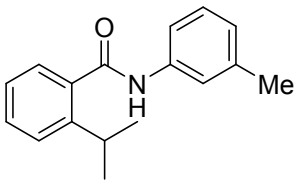


1f

***N*-([1,1'-biphenyl]-4-yl)-2-isopropylbenzamide (1f)**

White solid. M.p. =184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.56 (m, 5H), 7.57 – 7.43 (m, 5H), 7.42 – 7.35 (m, 1H), 7.34-7.24 (m, 1H), 3.60 – 3.34 (m, 6.4 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.0, 140.5, 137.5, 137.3, 136.1, 130.5, 128.8, 127.7, 127.2,

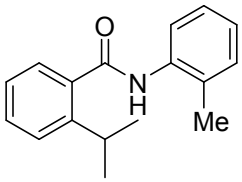
126.9, 126.4, 125.8, 120.1, 30.0, 24.2. HRMS (ESI): calcd. for $C_{22}H_{22}NO$ $[M + H]^+$ 316.1696; found 316.1691. (Petroleum ether/EtOAc, 5/1).



1g

2-isopropyl-*N*-(*m*-tolyl)benzamide (1g)

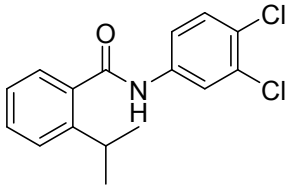
White solid. M.p. =110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.50 – 7.35 (m, 4H), 7.30 – 7.24 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 3.77 – 3.10 (m, 1H), 2.40 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.9, 139.1, 137.9, 136.2, 130.3, 128.9, 126.3, 126.3, 125.8, 125.3, 120.4, 116.8, 30.0, 24.2, 21.5. HRMS (ESI): calcd. for $C_{17}H_{20}NO$ $[M + H]^+$ 254.1539; found 254.1536. (Petroleum ether/EtOAc, 5/1).



1h

2-isopropyl-*N*-(*o*-tolyl)benzamide (1h)

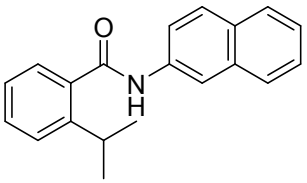
White solid. M.p. =126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.40 (m, 3H), 7.39 – 7.19 (m, 4H), 7.20 – 7.08 (m, 1H), 3.57 – 3.42 (m, 1H), 2.33 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.9, 130.6, 130.4, 128.9, 126.9, 126.4, 126.4, 125.8, 125.4, 122.9, 30.0, 24.2, 17.9. HRMS (ESI): calcd. for $C_{17}H_{20}NO$ $[M + H]^+$ 254.1539; found 254.1535. (Petroleum ether/EtOAc, 5/1).



1i

***N*-(3,4-dichlorophenyl)-2-isopropylbenzamide (1i)**

White solid. M.p. =118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.68 – 7.56 (m, 1H), 7.48 – 7.33 (m, 5H), 7.25 – 7.13 (m, 1H), 3.43 – 3.26 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 147.1, 137.4, 135.3, 132.9, 130.8, 130.5, 127.7, 126.5, 126.2, 125.8, 121.5, 119.0, 30.0, 24.1. HRMS (ESI): calcd. for $C_{16}H_{16}Cl_2NO$ $[M + H]^+$ 308.0603; found 308.0600. (Petroleum ether/EtOAc, 5/1).

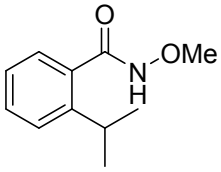


1j

2-isopropyl-*N*-(naphthalen-2-yl)benzamide (1j)

White solid. M.p. =156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.88 – 7.76 (m, 3H), 7.65 (s, 1H), 7.53 – 7.38 (m, 6H), 7.30 – 7.21 (m, 1H), 3.52 – 3.40 (m, 1H), 1.31 (d, *J*

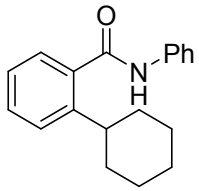
= 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 147.1, 136.1, 135.4, 133.9, 130.7, 130.5, 128.9, 127.7, 127.6, 126.6, 126.4, 125.8, 125.1, 119.7, 116.6, 30.1, 24.2. HRMS (ESI): calcd. for $C_{20}H_{20}NO$ $[M + H]^+$ 290.1539; found 290.1534. (Petroleum ether/EtOAc, 5/1).



1k

2-isopropyl-*N*-methoxybenzamide (1k)

White solid. M.p. =122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.30 – 7.20 (m, 2H), 7.12 – 6.96 (m, 2H), 3.70 (s, 3H), 3.25 – 2.96 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 147.5, 132.1, 130.6, 127.0, 126.1, 125.5, 64.4, 29.9, 24.0. HRMS (ESI): calcd. for $C_{11}H_{16}NO_2$ $[M + H]^+$ 194.1176; found 194.1172. (Petroleum ether/EtOAc, 3/1).

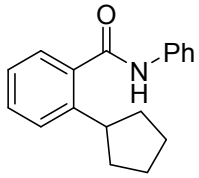


1l

2-cyclohexyl-N-phenylbenzamide (1l)

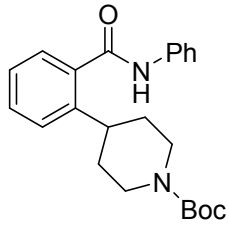
White solid. M.p. =120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.53 (s, 1H), 7.44 – 7.30 (m, 5H), 7.26 – 7.13 (m, 2H), 3.08 – 2.92 (m, 1H), 1.98 – 1.65 (m, 5H), 1.51 – 1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 145.9, 138.0, 136.3, 130.2, 129.1, 127.0, 126.5, 125.8, 124.5, 119.9, 40.5, 34.6, 26.7, 26.1. HRMS (ESI): calcd. for $C_{19}H_{22}NO$ $[M + H]^+$ 280.1696; found 280.1691. (Petroleum ether/EtOAc, 5/1).

2-cyclopentyl-*N*-phenylbenzamide (1m)



1m

White solid. M.p. =123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.41 – 7.30 (m, 5H), 7.23 – 7.10 (m, 2H), 3.46 – 3.34 (m, 1H), 2.16 – 2.00 (m, 2H), 1.81 – 1.73 (m, 2H), 1.71 – 1.54 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 144.7, 138.0, 136.9, 130.3, 129.1, 126.9, 126.4, 125.7, 124.5, 119.8, 41.9, 35.3, 25.9. HRMS (ESI): calcd. for $C_{18}H_{20}NO$ $[M + H]^+$ 266.1539; found 266.1535. (Petroleum ether/EtOAc, 5/1).



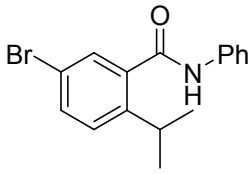
1n

***tert*-butyl-4-(2-(phenylcarbamoyl)phenyl)piperidine-1-carboxylate (1n)**

White solid. M.p. =210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.66 – 7.51 (m, 3H), 7.48 – 7.30 (m, 5H), 7.29 – 7.22 (m, 1H), 7.19 – 7.11 (m, 1H), 4.24 – 4.08 (m, 2H), 3.26 – 3.12 (m, 1H), 2.83 – 2.64 (m, 2H), 1.89 – 1.81 (m, 2H), 1.64 – 1.57 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 154.8, 144.3, 137.9, 136.2, 130.6, 129.2, 127.1, 126.6, 126.3, 124.7, 119.9, 79.4, 38.5, 33.3, 28.4. HRMS (ESI): calcd. for $C_{23}H_{39}N_2O_3$ $[M + H]^+$ 381.2173; found 381.2175. (Petroleum ether/EtOAc, 5/1).

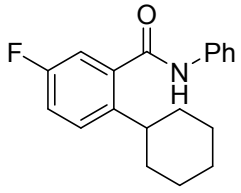
5-bromo-2-isopropyl-*N*-phenylbenzamide (1o)



1o

White solid. M.p. =148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.50 (m, 5H), 7.44 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 7.23 – 7.16 (m, 1H), 3.42 – 3.30 (m, 1H), 1.28 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.9, 137.8, 137.6, 133.3, 129.2, 129.1, 128.3, 124.8, 119.9, 119.2, 29.8, 24.0. HRMS (ESI): calcd. for $C_{16}H_{17}BrNO$ $[M + H]^+$ 318.0488; found 318.0484. (Petroleum ether/EtOAc, 5/1).

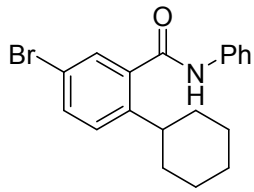
2-cyclohexyl-5-fluoro-*N*-phenylbenzamide (1p)



1p

White solid. M.p. =112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.63 (m, 1H), 7.58 – 7.38 (m, 2H), 7.27 – 7.14 (m, 3H), 7.08 – 6.86 (m, 3H), 2.92 – 2.74 (m, 1H), 1.87 – 1.49 (m, 5H), 1.42 – 0.92 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.30 (d, J = 246.3 Hz), 141.5, 137.7, 137.55 (d, J = 5.9 Hz), 129.1, 128.72 (d, J = 7.4 Hz), 124.7, 120.1, 117.03 (d, J = 20.5 Hz), 113.50 (d, J = 22.4 Hz), 40.0, 34.7, 26.7, 26.0. HRMS (ESI): calcd. for $C_{19}H_{21}FNO$ $[M + H]^+$ 298.1602; found 298.1598. (Petroleum ether/EtOAc, 5/1).

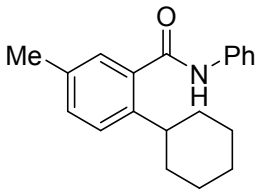
5-bromo-2-cyclohexyl-*N*-phenylbenzamide (1q)



1q

White solid. M.p. =132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.34 (m, 5H), 7.27 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 7.06 – 6.98 (m, 1H), 2.86 – 2.75 (m, 1H), 1.79 – 1.52 (m, 5H), 1.33 – 0.98 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.0, 138.0, 137.6, 133.2, 129.3, 129.2, 128.9, 124.8, 120.0, 119.1, 40.2, 34.4, 26.6, 26.0. HRMS (ESI): calcd. for $C_{19}H_{21}BrNO$ $[M + H]^+$ 358.0801; found 358.0797.

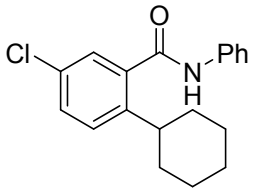
2-cyclohexyl-5-methyl-*N*-phenylbenzamide (1r)



1r

White solid. M.p. =108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.57 (m, 2H), 7.47 (s, 1H), 7.40 – 7.32 (m, 2H), 7.30 – 7.20 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 3.01 – 2.90 (m, 1H), 2.34 (s, 3H), 1.92 – 1.59 (m, 5H), 1.51 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 142.9, 138.0, 136.2, 135.4, 131.0, 129.1, 127.1, 126.9, 124.5, 119.8, 40.1, 34.7, 26.8, 26.1, 20.8. HRMS (ESI): calcd. for $C_{20}H_{24}NO$ $[M + H]^+$ 294.1852; found 294.1850. (Petroleum ether/EtOAc, 5/1).

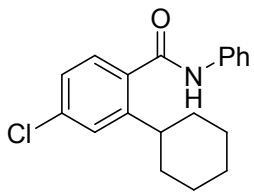
5-chloro-2-cyclohexyl-*N*-phenylbenzamide (1s)



1s

White solid. M.p. =91-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.49 (m, 3H), 7.42 – 7.27 (m, 5H), 7.19 – 7.09 (m, 1H), 3.15 – 2.58 (m, 1H), 1.92 – 1.66 (m, 5H), 1.45 – 1.18 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 144.4, 137.7, 137.6, 131.3, 130.2, 129.2, 128.6, 126.5, 124.8, 120.0, 40.1, 34.5, 26.6, 26.0. HRMS (ESI): calcd. for $C_{19}H_{21}ClNO$ $[M + H]^+$ 314.1306; found 314.1302. (Petroleum ether/EtOAc, 5/1).

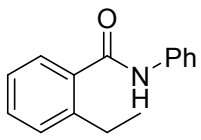
4-chloro-2-cyclohexyl-*N*-phenylbenzamide (1t)



1t

White solid. M.p. =187-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 3H), 7.41 – 7.24 (m, 4H), 7.20 – 7.07 (m, 2H), 3.11 – 2.82 (m, 1H), 1.88 – 1.63 (m, 5H), 1.47 – 1.13 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 148.2, 137.8, 136.3, 134.5, 129.1, 128.0, 127.4, 125.9, 124.7, 120.0, 40.4, 34.4, 26.6, 26.0. HRMS (ESI): calcd. for $C_{19}H_{21}ClNO$ $[M + H]^+$ 314.1306; found 314.1303. (Petroleum ether/EtOAc, 5/1).

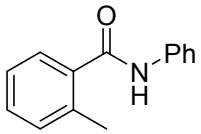
2-ethyl-*N*-phenylbenzamide (1u)



1u

White solid. M.p. =141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.50 (m, 3H), 7.43 – 7.29 (m, 5H), 7.25 – 7.18 (m, 1H), 7.16 – 7.07 (m, 1H), 2.97 – 2.74 (m, 2H), 1.32 – 1.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 142.5, 138.0, 136.2, 130.3, 129.6, 129.1, 126.6, 125.9, 124.5, 119.9, 26.3, 15.9. HRMS (ESI): calcd. for $C_{15}H_{16}NO$ $[M + H]^+$ 226.1226; found

226.1225. (Petroleum ether/EtOAc, 5/1).

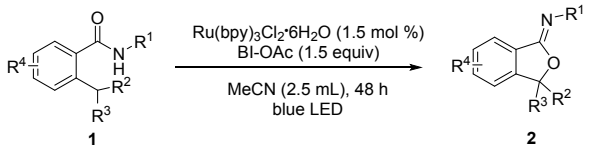


1v

2-methyl-*N*-phenylbenzamide (1v)

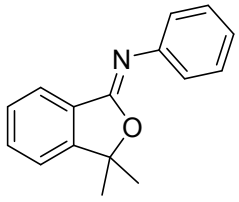
White solid. M.p. =125-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.58 (m, 3H), 7.53 – 7.31 (m, 4H), 7.28 – 7.11 (m, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 138.1, 136.4, 136.3, 131.2, 130.2, 129.0, 126.7, 125.8, 124.5, 120.0, 19.8. HRMS (ESI): calcd. for $C_{14}H_{14}NO$ $[M + H]^+$ 212.1070; found 212.1073. (Petroleum ether/EtOAc, 5/1).

General experimental procedure for 2.



1 2

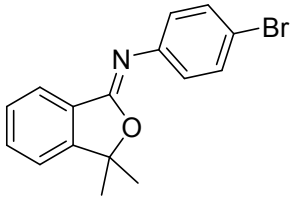
To a 10 mL glass vial was added **1** (0.25 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2•6H_2O$ (2.8 mg, 0.00375 mmol, 1.5 mol %), BI-OAc (115 mg, 0.375 mmol, 1.5 equiv) and 2.5 mL of acetonitrile. The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. And the mixture was stirred under the irradiation with blue LED for 48 h at room temperature. Upon completion, the solvent was removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography to afford the desired product **2**.



2a

(*Z*)-3,3-dimethyl-*N*-phenylisobenzofuran-1(3*H*)-imine (2a)

White solid (48.0 mg, 81%). M.p. = 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 7.4, 0.9 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.38 – 7.28 (m, 5H), 7.15 – 7.04 (m, 1H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 151.5, 146.8, 131.9, 130.2, 128.6, 128.5, 124.0, 123.8, 123.6, 120.2, 88.2, 27.8. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ $[M + H]^+$ 238.1226; found 238.1223. (Petroleum ether/EtOAc, 5/1).

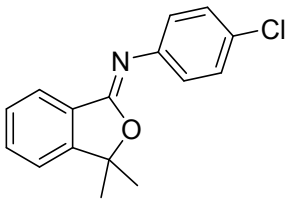


2b

(*Z*)-*N*-(4-bromophenyl)-3,3-dimethylisobenzofuran-1(3*H*)-imine (2b)

White solid (61.2 mg, 82%). M.p. = 109-111 °C. ^{1}H NMR

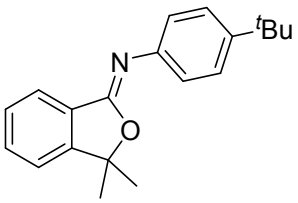
(400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.5, 1.0 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.33 – 7.27 (m, 1H), 7.24 – 7.19 (m, 2H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.5, 145.8, 132.1, 131.5, 129.9, 128.7, 125.5, 124.0, 120.3, 116.7, 88.6, 27.8. HRMS (ESI): calcd. for $C_{16}H_{15}BrNO$ $[M + H]^+$ 316.0332; found 316.0330. (Petroleum ether/EtOAc, 5/1).



2c

(*Z*)-*N*-(4-chlorophenyl)-3,3-dimethylisobenzofuran-1(3*H*)-imine (2c)

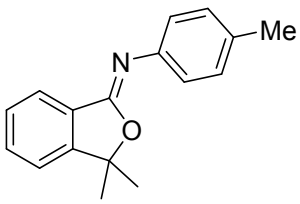
White solid (47.5 mg, 70%). M.p. = 104-105 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.56 (td, *J* = 7.5, 1.0 Hz, 1H), 7.47 (td, *J* = 7.5, 0.9 Hz, 1H), 7.34 – 7.24 (m, 5H), 1.72 – 1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.5, 145.3, 132.1, 129.9, 128.9, 128.7, 128.6, 125.1, 124.0, 120.3, 88.6, 27.8. HRMS (ESI): calcd. for $C_{16}H_{15}ClNO$ $[M + H]^+$ 272.0837; found 272.0834. (Petroleum ether/EtOAc, 5/1).



2d

(*Z*)-*N*-(4-(tert-butyl)phenyl)-3,3-dimethylisobenzofuran-1(3*H*)-imine (2d)

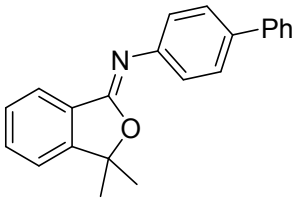
White solid (60.8 mg, 83%). M.p. = 78-80 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 1H), 7.57 (td, *J* = 7.4, 1.1 Hz, 1H), 7.49 (td, *J* = 7.5, 0.9 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.34 – 7.32 (m, 1H), 1.68 (s, 6H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 151.4, 146.6, 143.8, 131.7, 130.5, 128.6, 125.4, 124.0, 123.6, 120.2, 88.1, 34.4, 31.5, 27.9. HRMS (ESI): calcd. for $C_{20}H_{24}NO$ $[M + H]^+$ 294.1852; found 294.1849. (Petroleum ether/EtOAc, 5/1).



2e

(*Z*)-3,3-dimethyl-*N*-(p-tolyl)isobenzofuran-1(3*H*)-imine (2e)

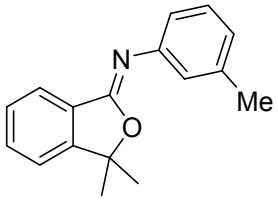
Colourless oil (48.9 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.53 (td, *J* = 7.4, 1.0 Hz, 1H), 7.45 (td, *J* = 7.5, 0.8 Hz, 1H), 7.33 – 7.22 (m, 3H), 7.19 – 7.10 (m, 2H), 2.34 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 151.4, 144.1, 133.3, 131.8, 130.3, 129.2, 128.6, 123.9, 123.6, 120.2, 88.1, 27.9, 21.0. HRMS (ESI): calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383; found 252.1380. (Petroleum ether/EtOAc, 5/1).



2f

(*Z*)-*N*-([1,1'-biphenyl]-4-yl)-3,3-dimethylisobenzofuran-1(3*H*)-imine (2f)

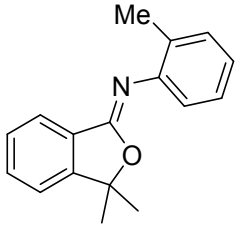
White solid (50.1 mg, 64%). M.p. = 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.55 (dt, *J* = 7.5, 3.7 Hz, 1H), 7.48 (td, *J* = 7.5, 1.0 Hz, 1H), 7.45 – 7.39 (m, 4H), 7.35 – 7.29 (m, 2H), 1.66 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 151.5, 146.0, 141.1, 136.6, 131.9, 130.2, 128.7, 127.2, 126.8, 126.7, 124.2, 124.0, 120.2, 88.4, 27.8. HRMS (ESI): calcd. for $C_{22}H_{20}NO$ $[M + H]^+$ 314.1539; found 314.1535. (Petroleum ether/EtOAc, 5/1).



2g

(*Z*)-3,3-dimethyl-*N*-(*m*-tolyl)isobenzofuran-1(3*H*)-imine (2g)

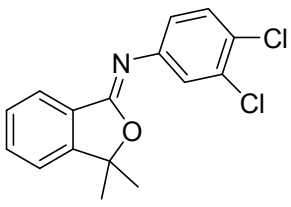
Colourless oil (50.2 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.53 (td, *J* = 7.4, 0.8 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 1H), 7.16 – 7.07 (m, 2H), 6.98 – 6.88 (m, 1H), 2.36 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 151.5, 146.7, 138.2, 131.9, 130.2, 128.6, 128.3, 124.6, 124.3, 124.0, 120.4, 120.2, 88.1, 27.8, 21.5. HRMS (ESI): calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383; found 252.1380. (Petroleum ether/EtOAc, 5/1).



2h

(*Z*)-3,3-dimethyl-*N*-(m-tolyl)isobenzofuran-1(3*H*)-imine (2h)

Yellow oil (43.3 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.4, 1.0 Hz, 1H), 7.48 (td, *J* = 7.5, 0.9 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 16.9, 7.6 Hz, 2H), 7.12 – 7.05 (m, 1H), 7.01 (td, *J* = 7.4, 1.3 Hz, 1H), 2.25 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 151.8, 146.2, 131.9, 130.1, 129.7, 128.6, 125.9, 124.0, 123.4, 121.6, 120.3, 87.8, 27.9, 18.1. HRMS (ESI): calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1383; found 252.1379. (Petroleum ether/EtOAc, 5/1).

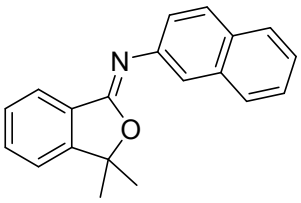


2i

(*Z*)-*N*-(3,4-dichlorophenyl)-3,3-dimethylisobenzofuran-1(3*H*)-imine (2i)

Colourless oil (56.6 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.57 (td, *J* = 7.5, 1.1 Hz, 1H), 7.52 –

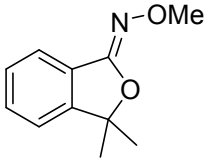
7.44 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.4 Hz, 1H), 1.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 151.6, 146.5, 132.4, 132.0, 130.1, 129.6, 128.8, 127.0, 125.6, 124.1, 123.6, 120.3, 89.1, 27.7. HRMS (ESI): calcd. for $C_{16}H_{14}Cl_2NO$ $[M + H]^+$ 306.0447; found 306.0443. (Petroleum ether/EtOAc, 5/1).



2j

(*Z*)-3,3-dimethyl-*N*-(naphthalen-2-yl)isobenzofuran-1(3*H*)-imine (2j)

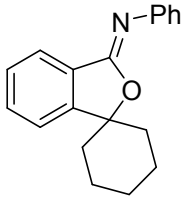
Colourless oil (39.5 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.85 (dd, *J* = 8.7, 4.4 Hz, 3H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.63 – 7.51 (m, 3H), 7.49 – 7.39 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 1.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 151.6, 144.5, 134.1, 132.0, 130.8, 130.1, 128.7, 128.1, 127.6, 125.8, 124.5, 124.1, 124.1, 120.3, 120.2, 88.4, 27.8. HRMS (ESI): calcd. for $C_{20}H_{18}NO$ $[M + H]^+$ 288.1383; found 288.1379. (Petroleum ether/EtOAc, 5/1).



2k

(*Z*)-3,3-dimethylisobenzofuran-1(3*H*)-one *O*-methyl oxime (2k)

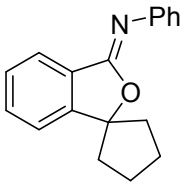
Colourless oil (40.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.46 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38 (td, *J* = 7.6, 0.9 Hz, 1H), 7.30 – 7.21 (m, 1H), 3.96 (s, 3H), 1.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.4, 130.8, 128.5, 127.4, 121.7, 120.4, 90.3, 62.7, 27.9. HRMS (ESI): calcd. for $C_{11}H_{14}NO_2$ $[M + H]^+$ 192.1019; found 192.1017. (Petroleum ether/EtOAc, 4/1).



2l

(*Z*)-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2l)

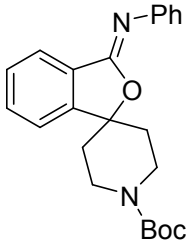
Colourless oil (59.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.52 (td, *J* = 7.4, 1.2 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.40 – 7.32 (m, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.06 (m, 1H), 1.85 – 1.70 (m, 9H), 1.47 – 1.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 151.3, 146.6, 131.6, 130.6, 128.7, 128.5, 124.2, 124.1, 123.9, 120.5, 89.6, 36.7, 24.9, 22.6. HRMS (ESI): calcd. for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1539; found 278.1537. (Petroleum ether/EtOAc, 5/1).



2m

(*Z*)-*N*-phenyl-3'*H*-spiro[cyclopentane-1,1'-isobenzofuran]-3'-imine (2m)

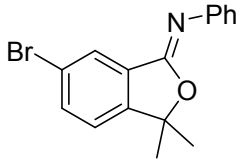
Colourless oil (49.3 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.55 (td, *J* = 7.5, 1.0 Hz, 1H), 7.46 (td, *J* = 7.5, 0.8 Hz, 1H), 7.40 – 7.30 (m, 5H), 7.15 – 7.06 (m, 1H), 2.19 – 1.84 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.3, 146.6, 131.9, 131.1, 128.6, 128.5, 123.9, 123.8, 123.7, 120.4, 98.2, 40.1, 25.0. HRMS (ESI): calcd. for $C_{18}H_{18}NO$ $[M + H]^+$ 264.1383; found 264.1377. (Petroleum ether/EtOAc, 5/1).



2n

***tert*-butyl (*Z*)-3-(phenylimino)-3*H*-spiro[isobenzofuran-1,4'-piperidine]-1'-carboxylate (2n)**

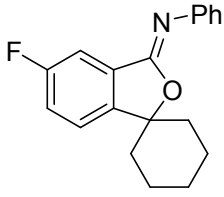
White solid (77.5 mg, 82%). M.p. = 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 1H), 7.53 (dt, *J* = 23.4, 7.4 Hz, 2H), 7.44 – 7.23 (m, 5H), 7.19 – 7.09 (m, 1H), 4.19 (s, 2H), 3.18 (s, 2H), 2.21 – 1.94 (m, 2H), 1.81 – 1.62 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 154.7, 149.6, 146.2, 132.0, 130.6, 129.2, 128.6, 124.3, 124.2, 124.0, 120.5, 87.1, 79.9, 36.0, 28.4. HRMS (ESI): calcd. for $C_{23}H_{27}N_2O_3$ $[M + H]^+$ 379.2016; found 379.2012. (Petroleum ether/EtOAc, 5/1).



2o

(*Z*)-6-bromo-3,3-dimethyl-*N*-phenylisobenzofuran-1(3*H*)-imine (2o)

White solid (60.6 mg, 77%). M.p. = 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.6 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.39 – 7.31 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.07 (m, 1H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 150.1, 146.2, 134.8, 132.5, 128.6, 127.1, 124.2, 123.7, 122.6, 121.9, 88.3, 27.7. HRMS (ESI): calcd. for $C_{16}H_{15}BrNO$ $[M + H]^+$ 316.0332; found 316.0328. (Petroleum ether/EtOAc, 5/1).

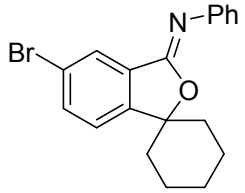


2p

(*Z*)-5'-fluoro-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2p)

White solid (62.7 mg, 85%). M.p. = 102-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.18 (m, 2H), 7.12 (t, *J* = 7.3

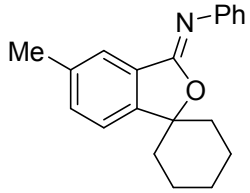
Hz, 1H), 1.85 – 1.65 (m, 9H), 1.45 – 1.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.15 (d, *J* = 246.8 Hz), 156.6, 146.9, 146.1, 132.99 (d, *J* = 9.6 Hz), 128.6, 124.3, 124.2, 122.05 (d, *J* = 8.9 Hz), 119.31 (d, *J* = 24.0 Hz), 110.55 (d, *J* = 24.1 Hz), 89.6, 36.8, 24.8, 22.6. HRMS (ESI): calcd. for $C_{19}H_{19}FNO$ $[M + H]^+$ 296.1445; found 296.1441. (Petroleum ether/EtOAc, 5/1).



2q

(*Z*)-5'-bromo-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2q)

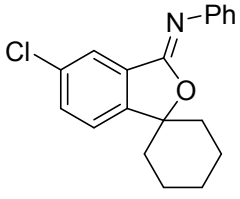
White solid (65.0 mg, 73%). M.p. = 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.6 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.39 – 7.32 (m, 2H), 7.20 – 7.09 (m, 2H), 1.90 – 1.64 (m, 9H), 1.43 – 1.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 149.9, 146.0, 134.6, 132.9, 128.6, 127.1, 124.3, 124.3, 122.5, 122.1, 89.7, 36.6, 24.8, 22.5. HRMS (ESI): calcd. for $C_{19}H_{19}BrNO$ $[M + H]^+$ 356.0645; found 356.0641. (Petroleum ether/EtOAc, 5/1).



2r

(*Z*)-5'-methyl-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2r)

White solid (60.4 mg, 83%). M.p. = 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.34 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.27 – 7.19 (m, 3H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.03 – 6.94 (m, 1H), 2.33 (s, 3H), 1.72 – 1.59 (m, 9H), 1.33 – 1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 148.8, 146.7, 138.7, 132.7, 130.8, 128.5, 124.3, 124.1, 123.8, 120.3, 89.5, 36.7, 24.9, 22.6, 21.2. HRMS (ESI): calcd. for $C_{20}H_{22}NO$ $[M + H]^+$ 292.1696; found 292.1691. (Petroleum ether/EtOAc, 5/1).

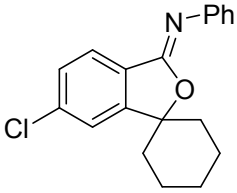


2s

(*Z*)-5'-chloro-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2r)

White solid (62.4 mg, 80%). M.p. = 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.55 – 7.41 (m, 3H), 7.40 – 7.32 (m, 2H), 7.27 – 7.21 (m, 1H), 7.19 – 7.07 (m, 1H), 1.85 – 1.66 (m, 9H), 1.43 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 149.4, 146.1, 134.8, 132.7, 131.8, 128.6, 124.3, 124.2, 124.1, 121.8, 89.6, 36.6, 24.8, 22.5. HRMS (ESI): calcd.

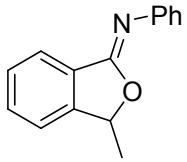
for $C_{19}H_{19}ClNO$ $[M + H]^+$ 312.1150; found 312.1146. (Petroleum ether/EtOAc, 5/1).



2t

(*Z*)-6'-chloro-*N*-phenyl-3'*H*-spiro[cyclohexane-1,1'-isobenzofuran]-3'-imine (2t)

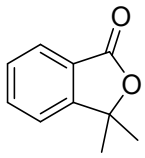
White solid (54.6 mg, 70%). M.p. = 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.39 – 7.32 (m, 2H), 7.29 (d, *J* = 1.5 Hz, 1H), 7.16 – 7.08 (m, 1H), 1.85 – 1.65 (m, 9H), 1.46 – 1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 152.8, 146.2, 137.8, 129.3, 128.6, 125.4, 124.3, 124.1, 121.1, 89.2, 36.6, 24.8, 22.4. HRMS (ESI): calcd. for $C_{19}H_{19}ClNO$ $[M + H]^+$ 312.1150; found 312.1144. (Petroleum ether/EtOAc, 5/1).



2u

(*Z*)-3-methyl-*N*-phenylisobenzofuran-1(3*H*)-imine (2u)

White solid (22.3 mg, 40%). M.p. = 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.60 (td, *J* = 7.4, 1.0 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.17 – 7.10 (m, 1H), 5.68 (q, *J* = 6.6 Hz, 1H), 1.64 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.8, 146.7, 131.9, 130.6, 128.7, 128.6, 124.0, 123.9, 123.3, 121.0, 80.8, 21.0. HRMS (ESI): calcd. for $C_{15}H_{14}NO$ $[M + H]^+$ 224.1070; found 224.1067. (Petroleum ether/EtOAc, 5/1).



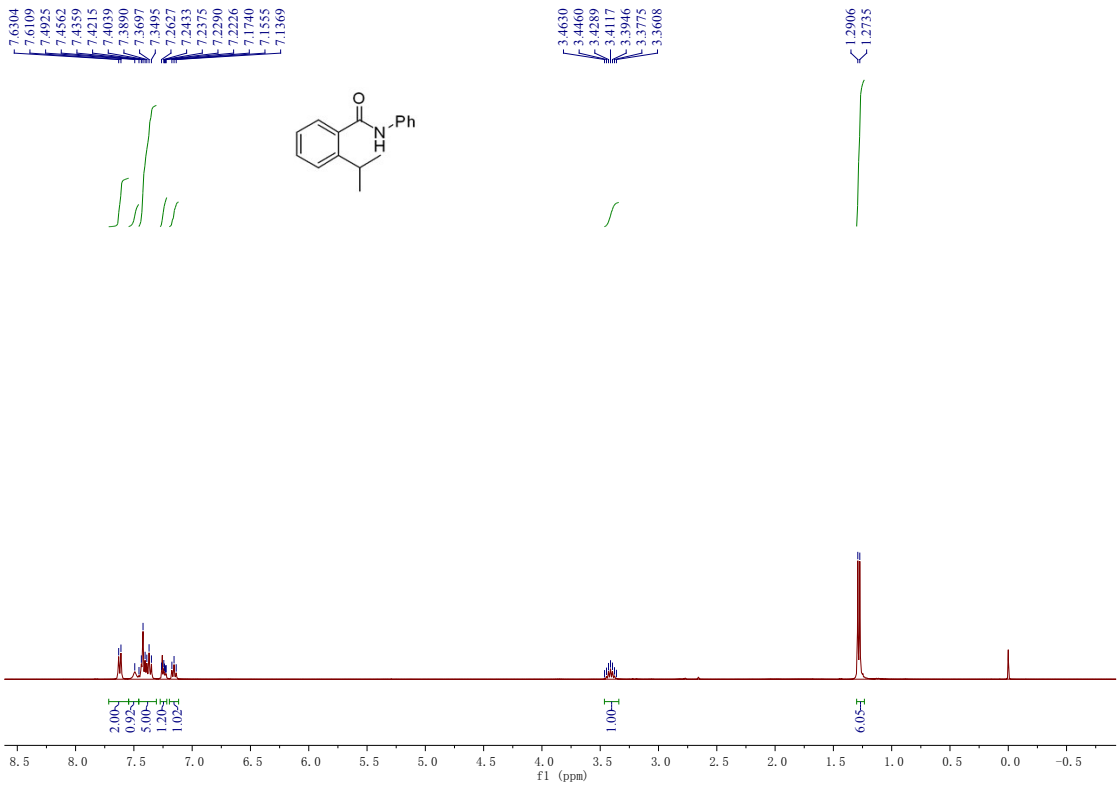
3

3,3-dimethylisobenzofuran-1(3*H*)-one (3)

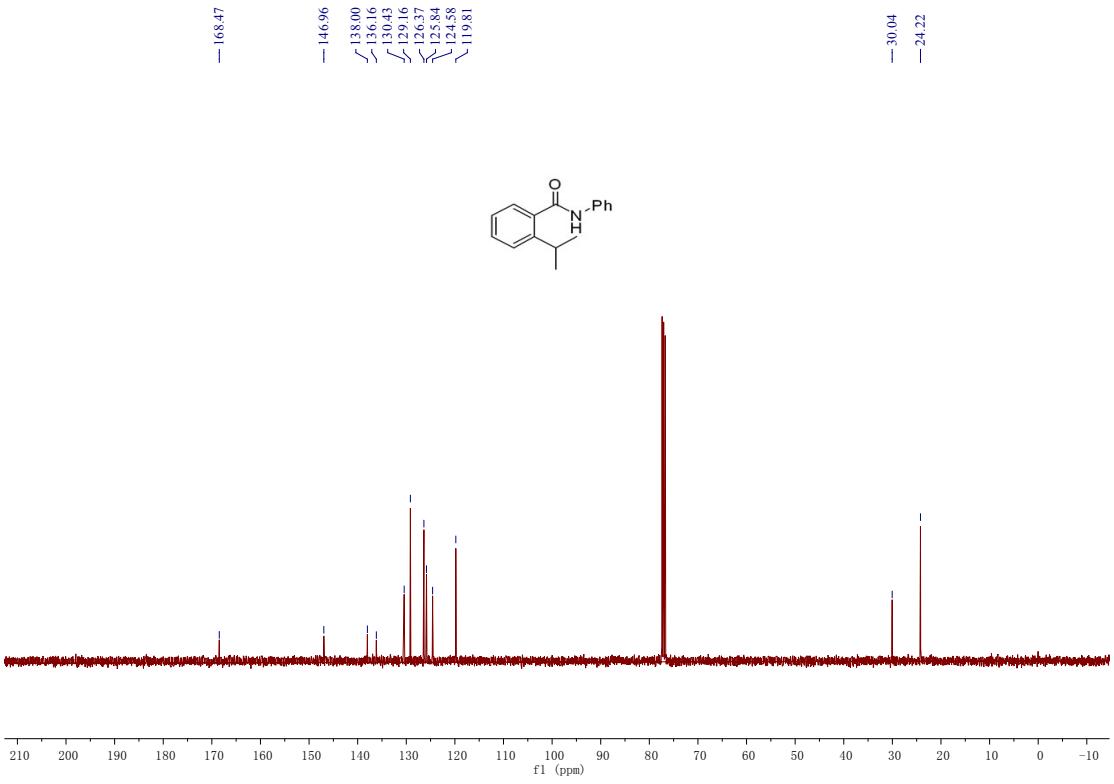
White solid (32.4 mg, 80%). M.p. = 69-71°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.79 (m, 1H), 7.74 – 7.65 (m, 1H), 7.52 (td, *J* = 7.5, 1.7 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.8 Hz, 1H), 1.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 154.9, 134.1, 128.9, 125.6, 125.2, 120.7, 85.4, 27.3. (Petroleum ether/EtOAc, 6/1).

NMR Spectra

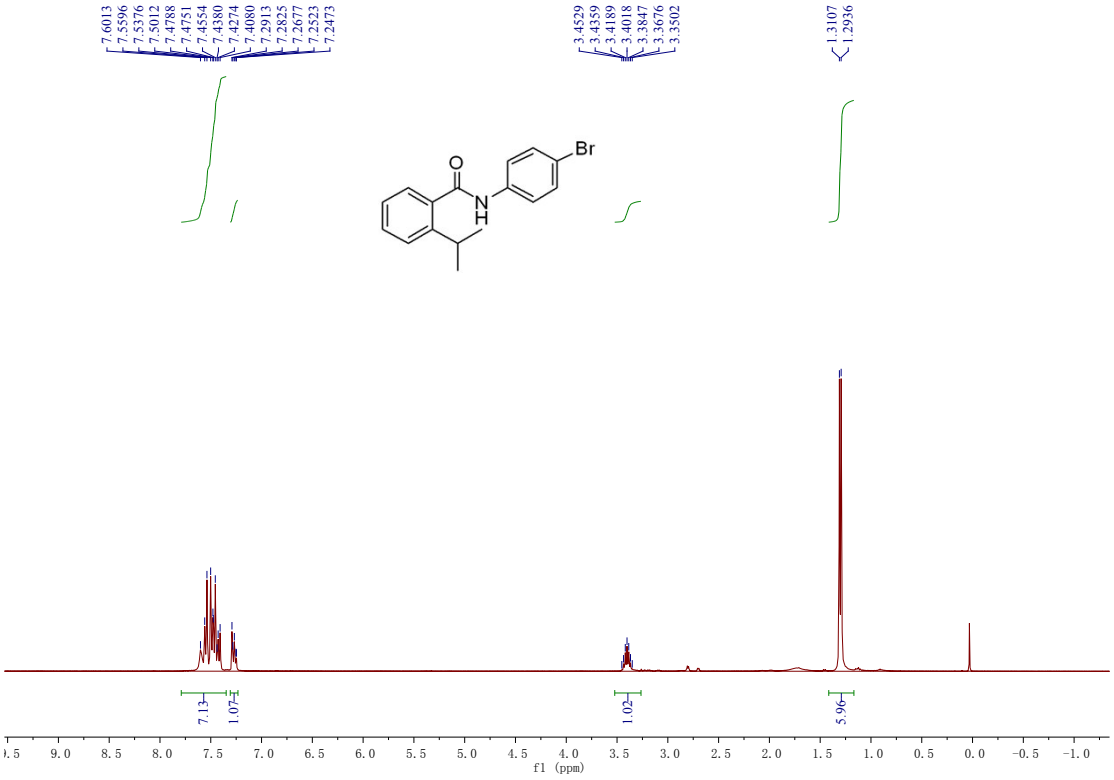
^{1}H NMR spectrum of compound **1a**



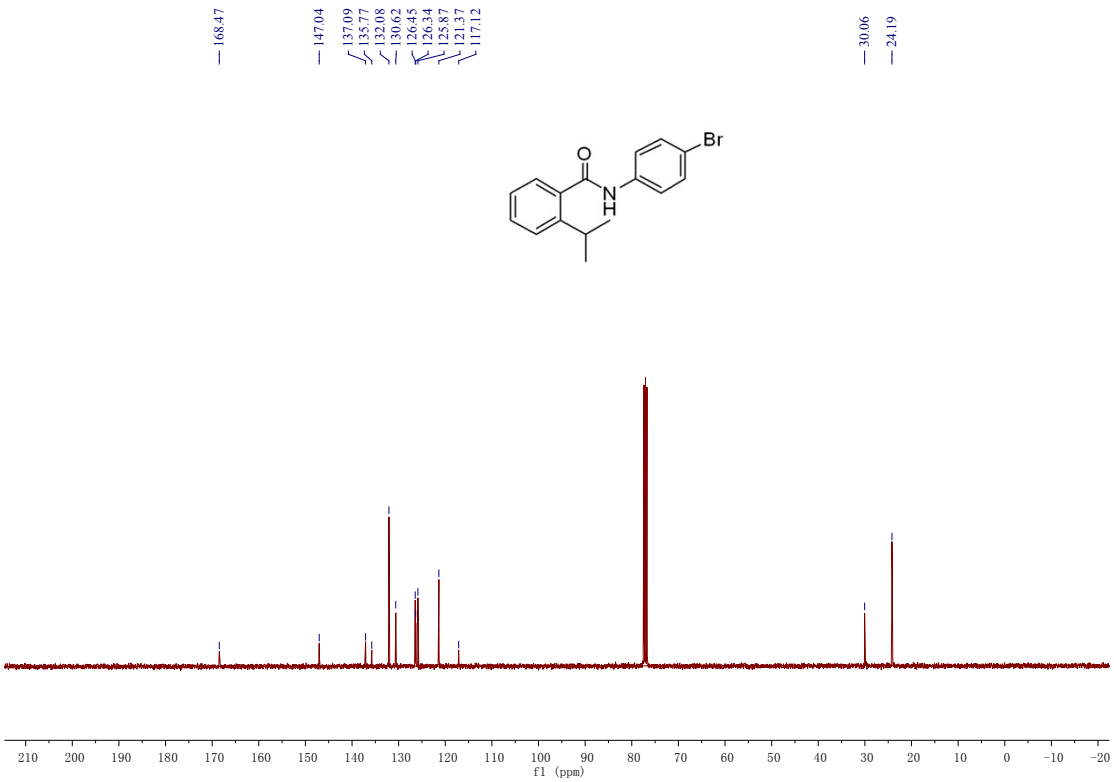
^{13}C NMR spectrum of compound **1a**



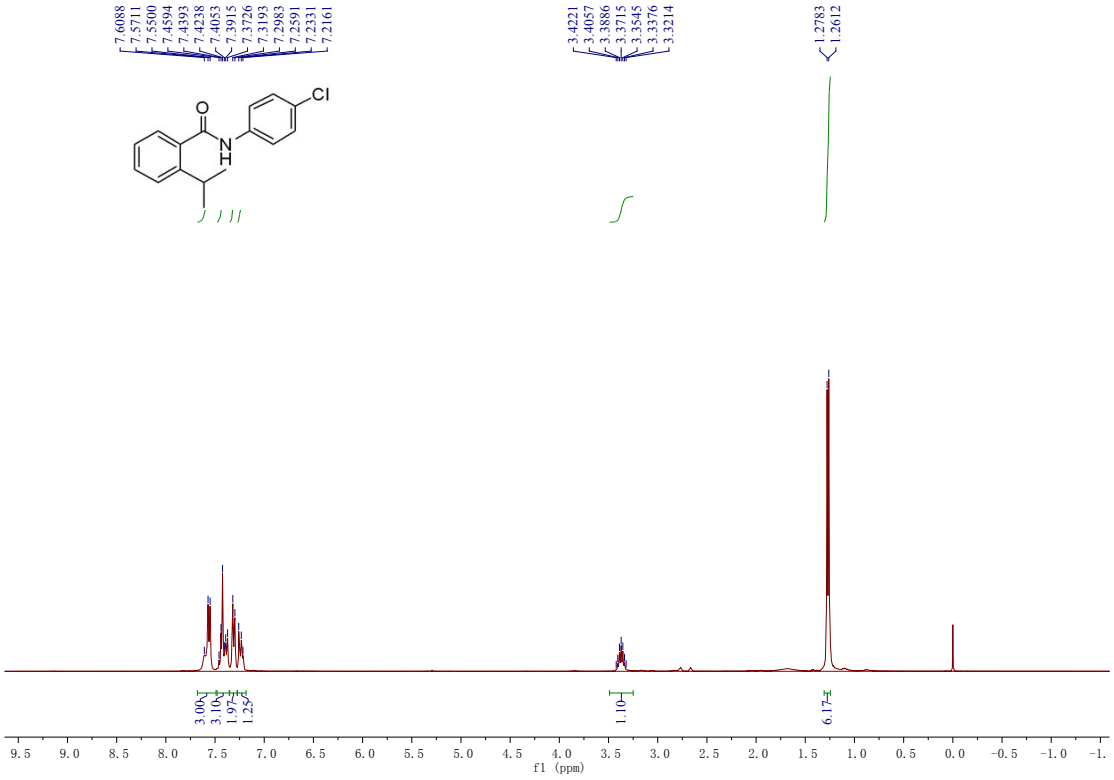
^{1}H NMR spectrum of compound **1b**



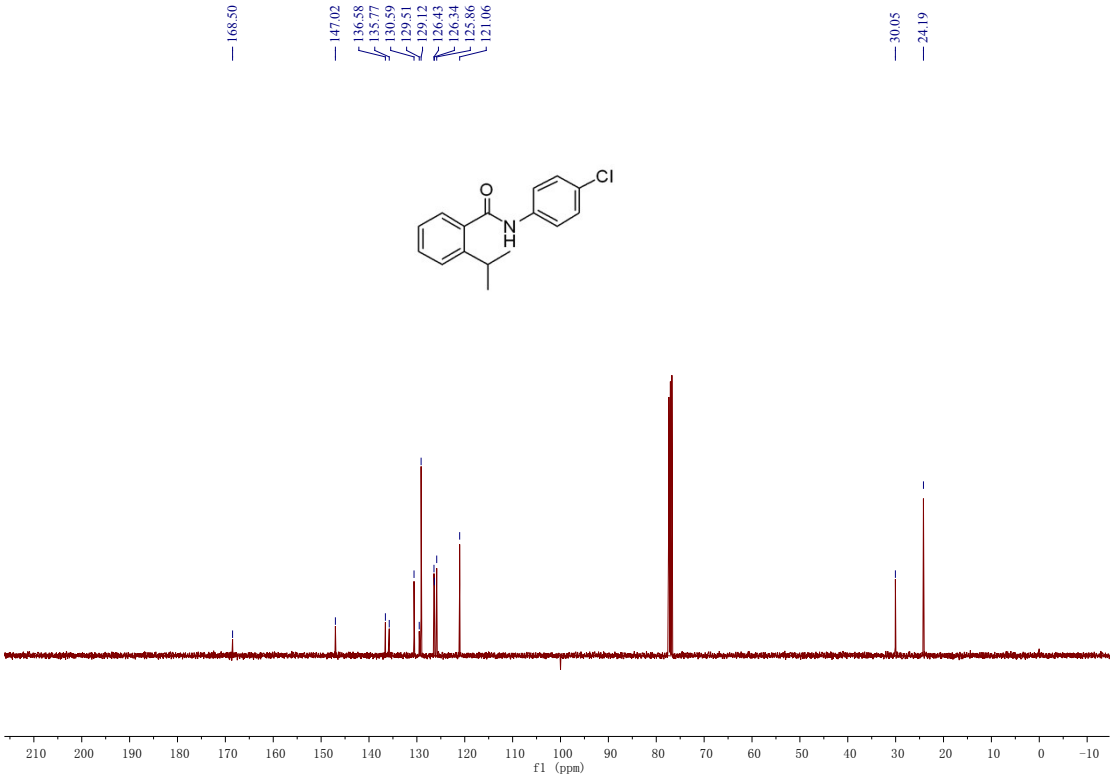
^{13}C NMR spectrum of compound **1b**



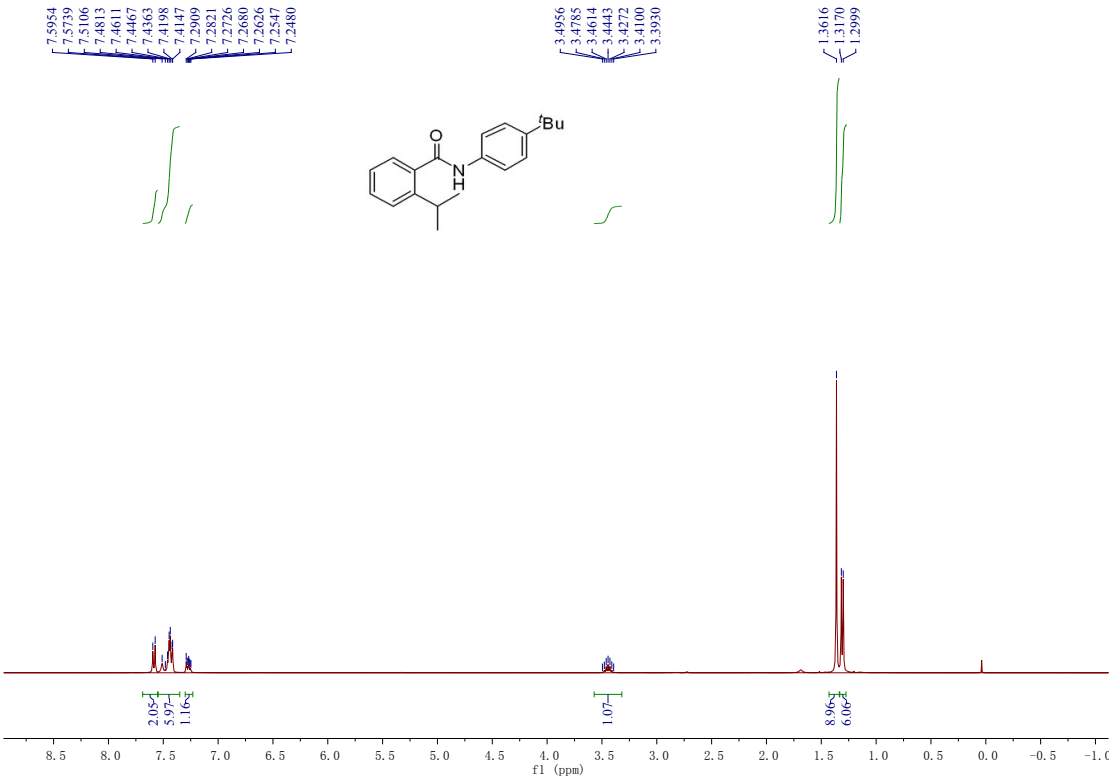
^{1}H NMR spectrum of compound **1c**



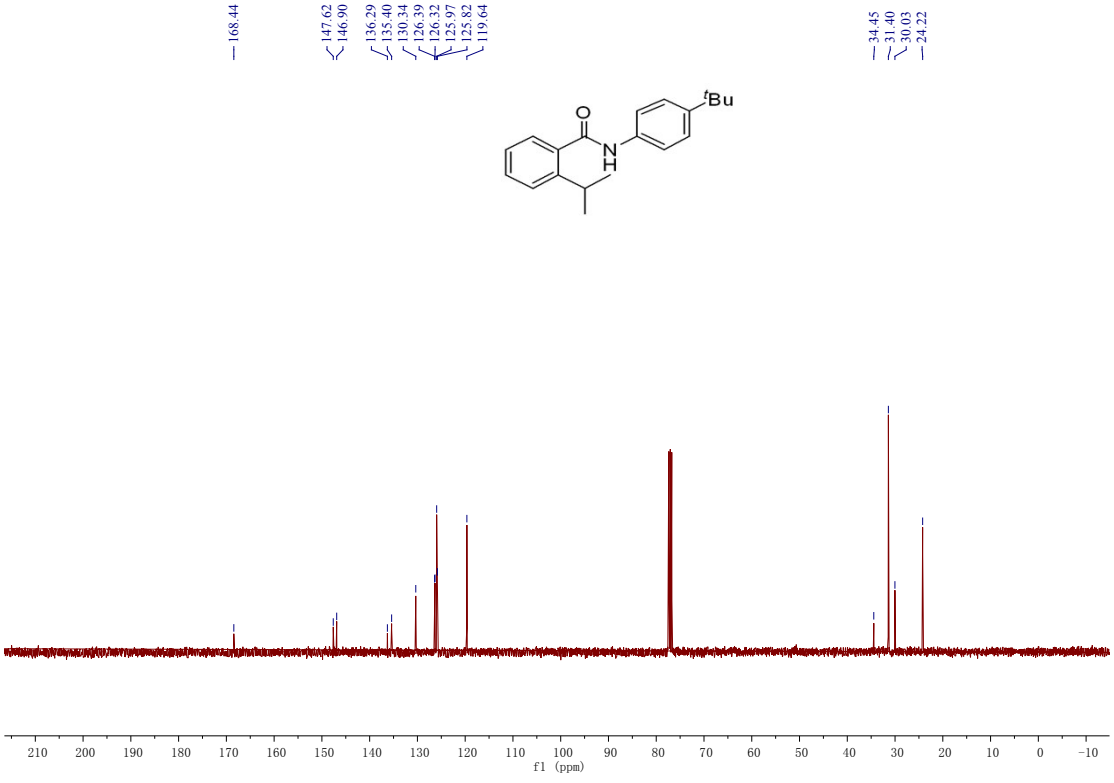
^{13}C NMR spectrum of compound **1c**



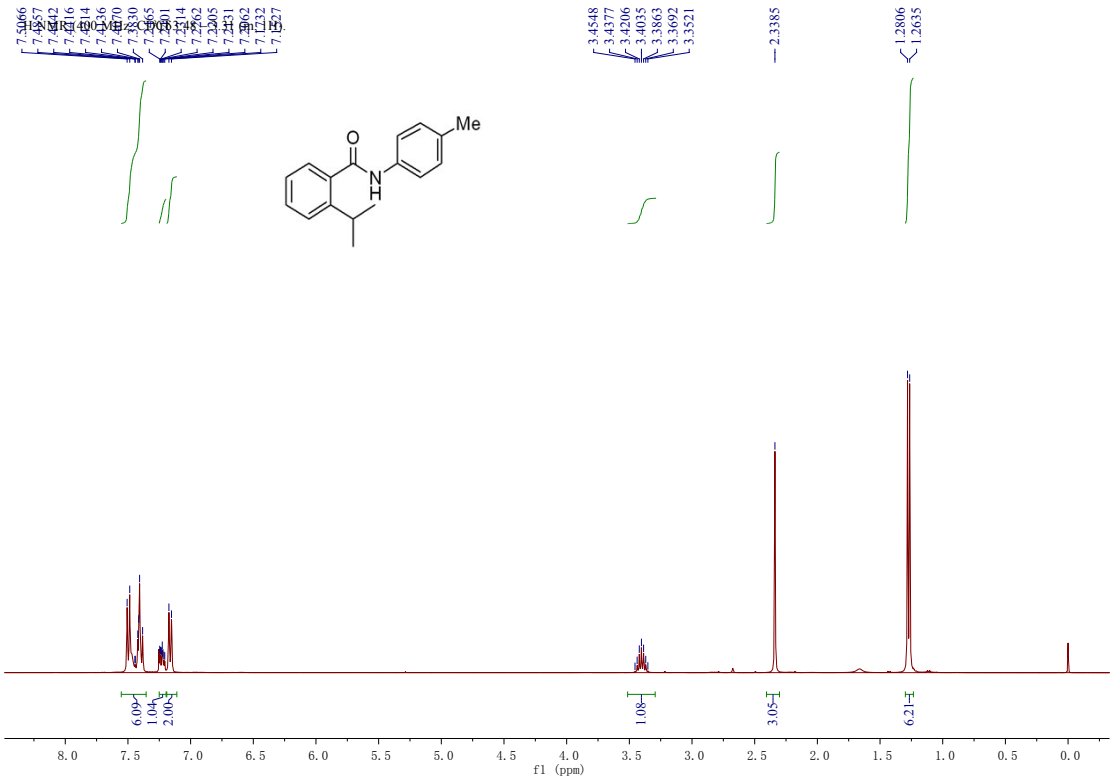
^{1}H NMR spectrum of compound **1d**



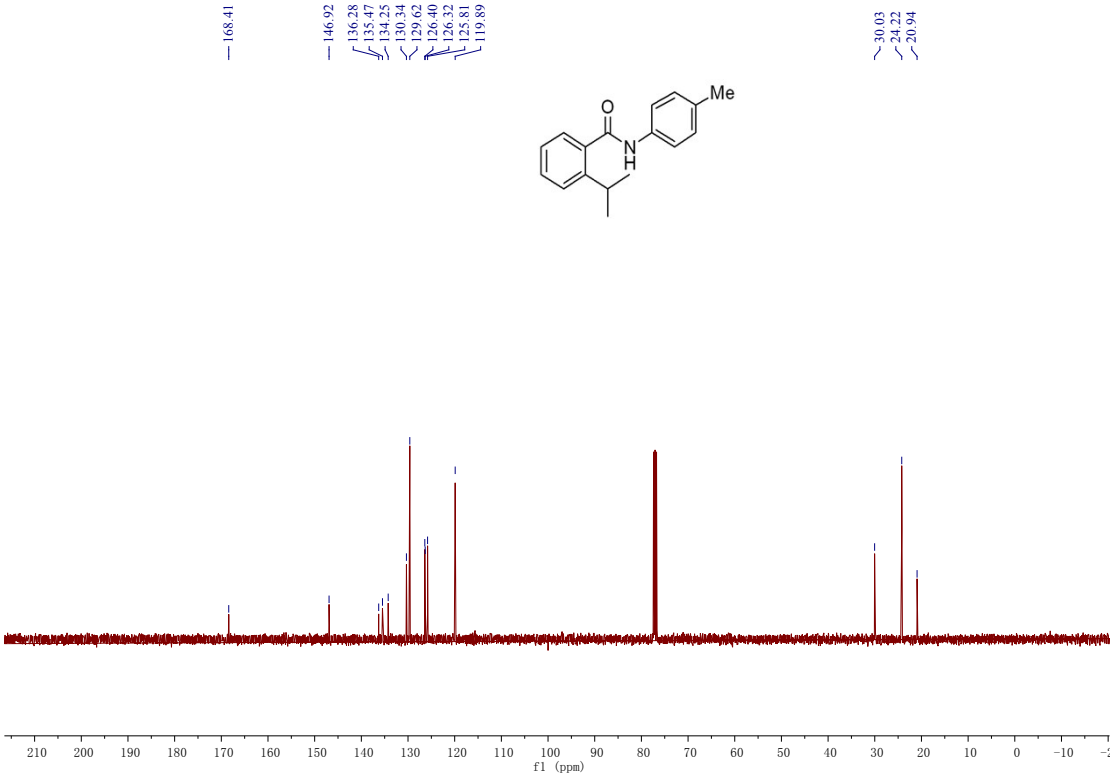
^{13}C NMR spectrum of compound **1d**



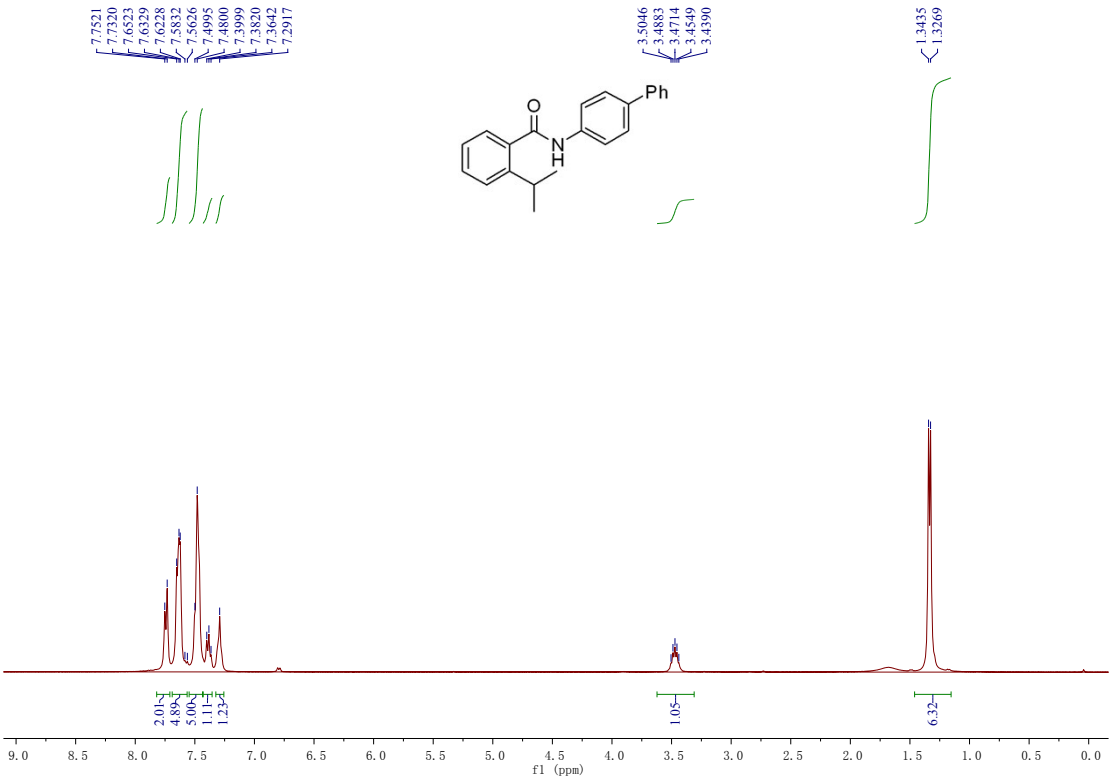
^{1}H NMR spectrum of compound **1e**



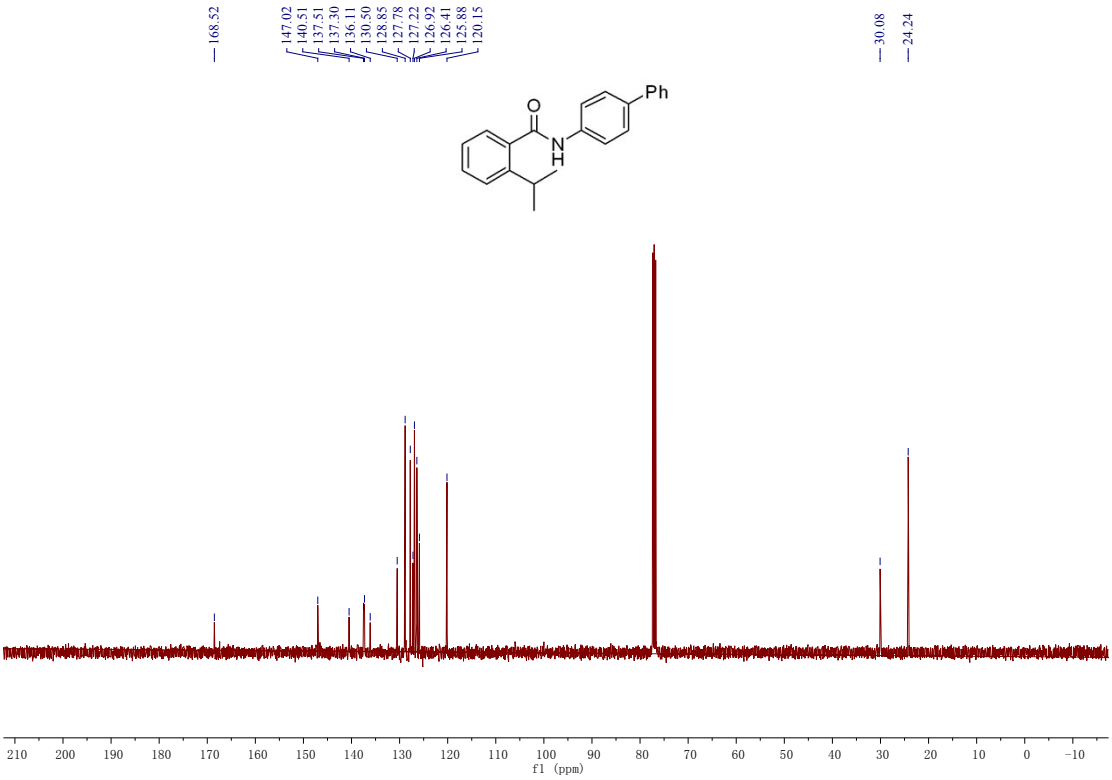
^{13}C NMR spectrum of compound **1e**



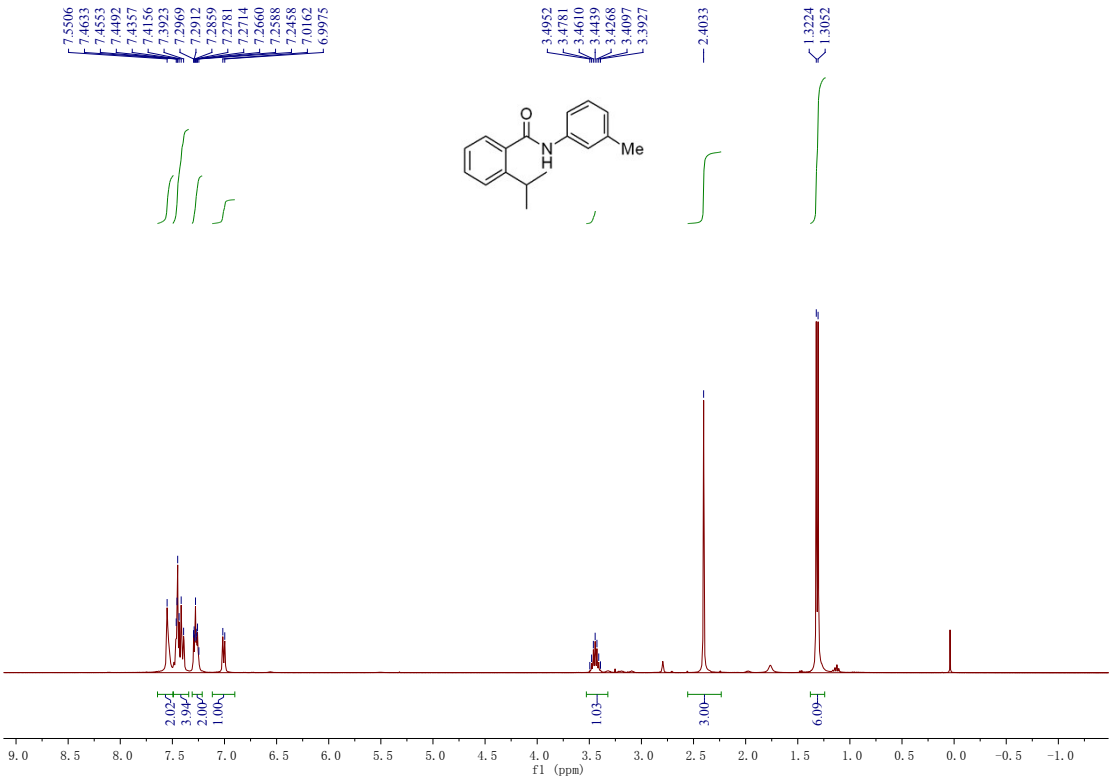
^{1}H NMR spectrum of compound **1f**



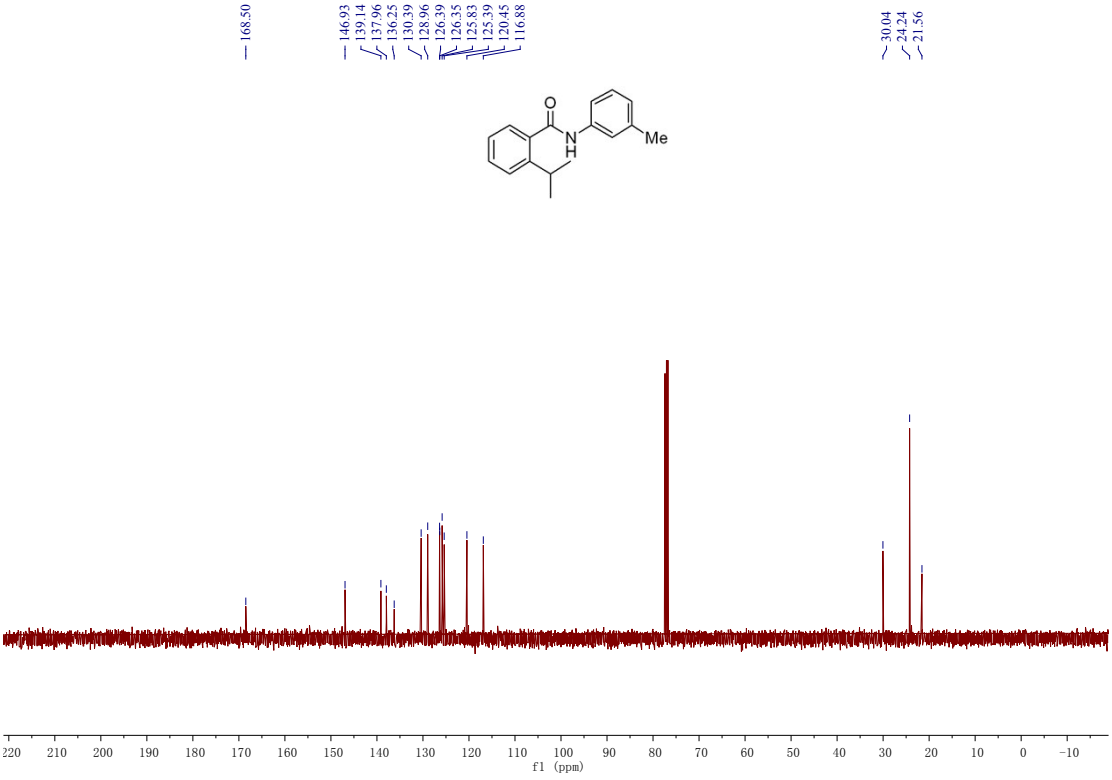
^{13}C NMR spectrum of compound **1f**



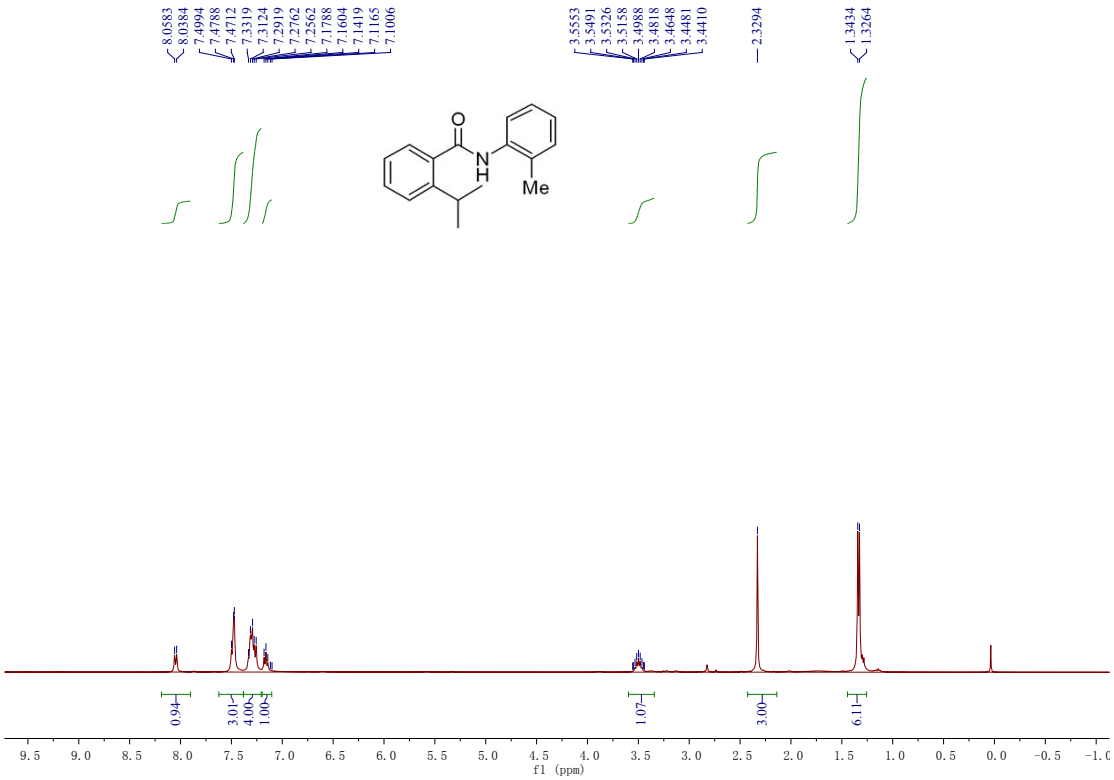
^{1}H NMR spectrum of compound **1g**



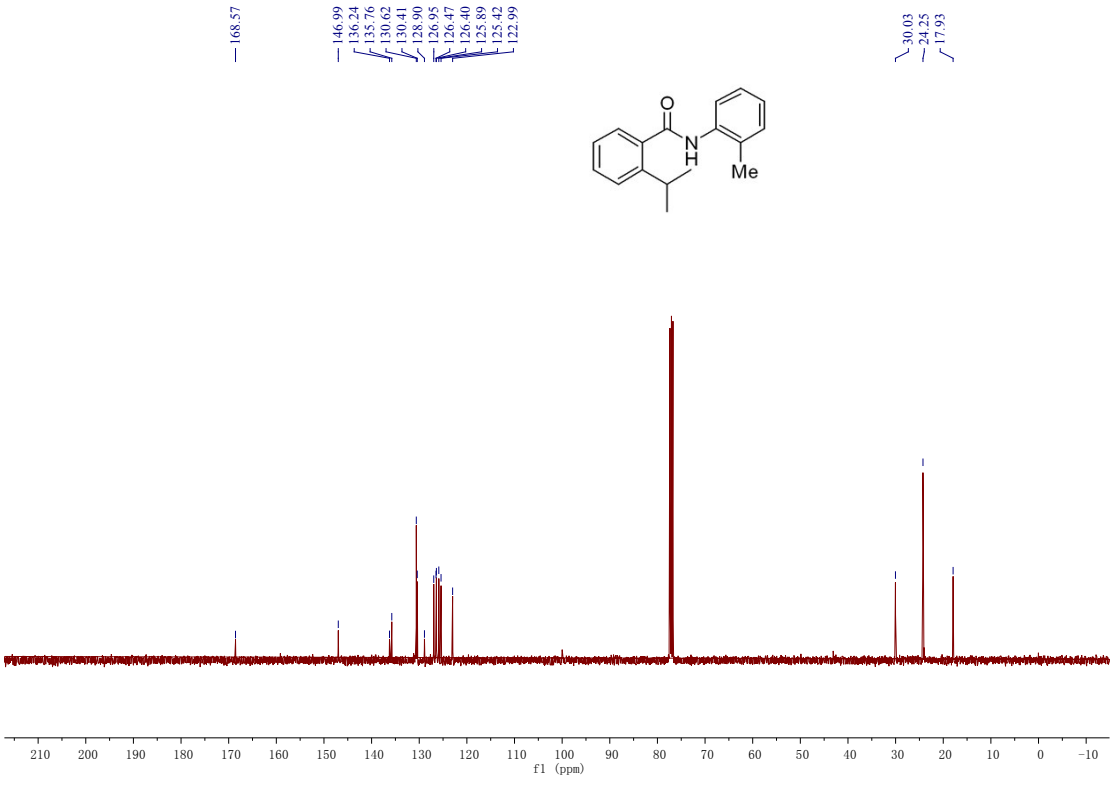
^{13}C NMR spectrum of compound **1g**



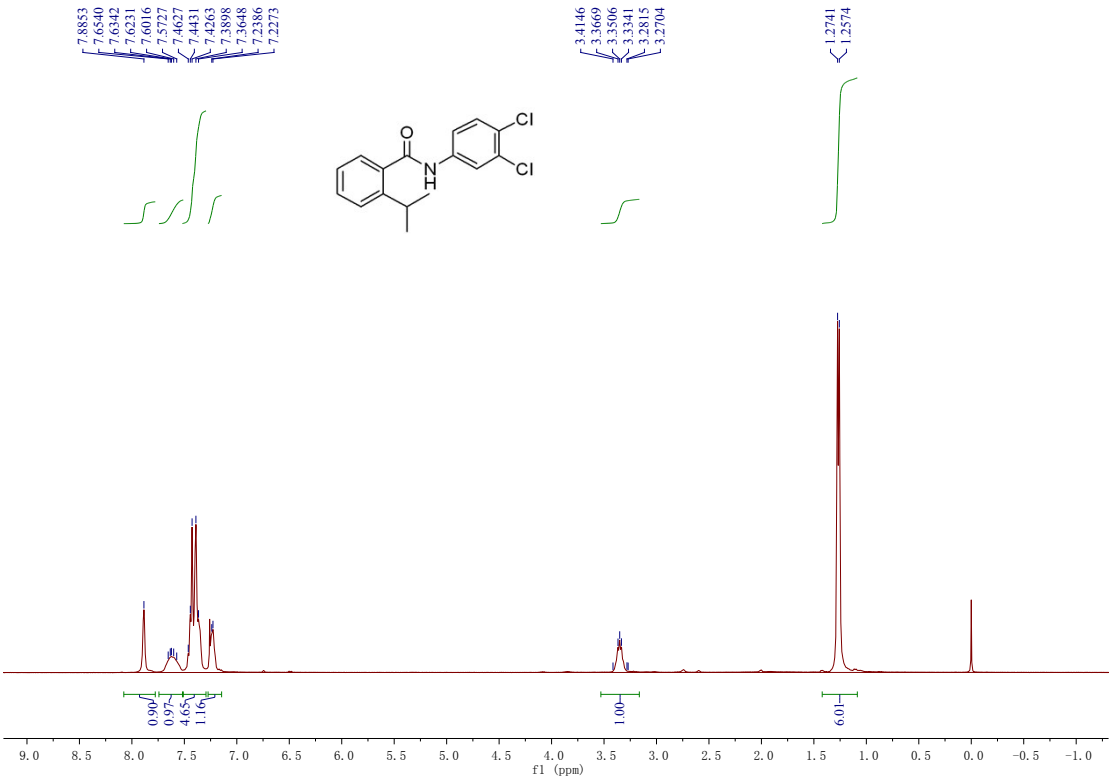
^{1}H NMR spectrum of compound **1h**



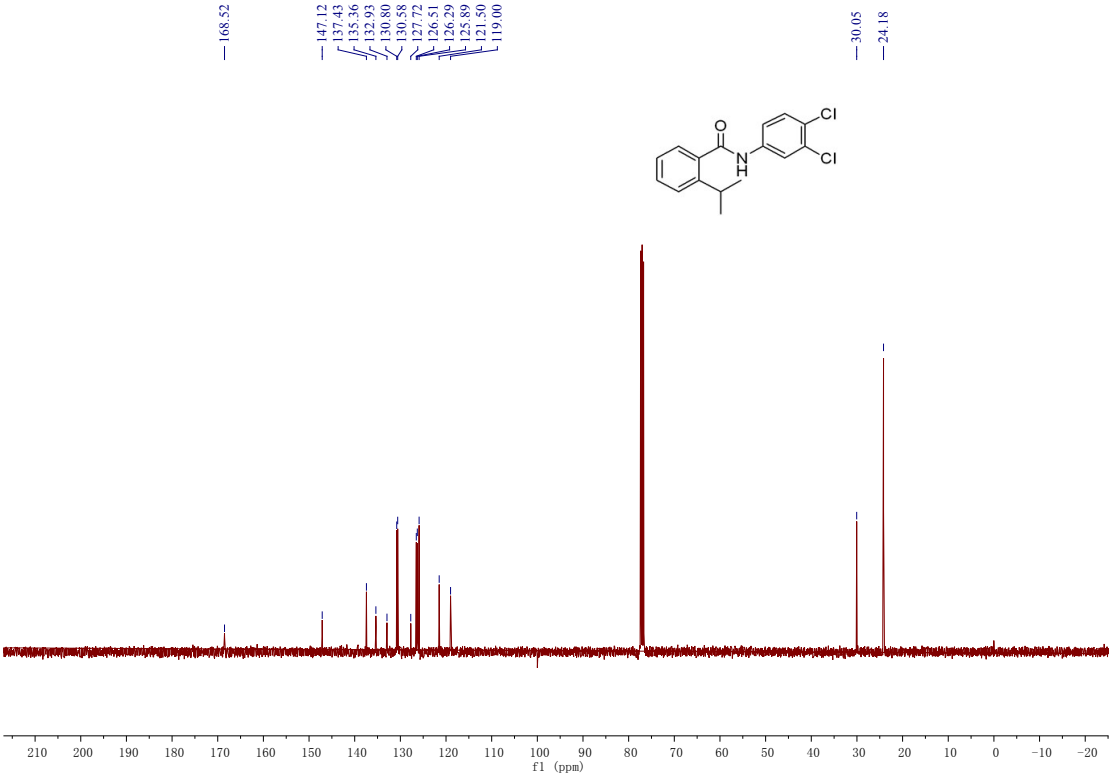
^{13}C NMR spectrum of compound **1h**



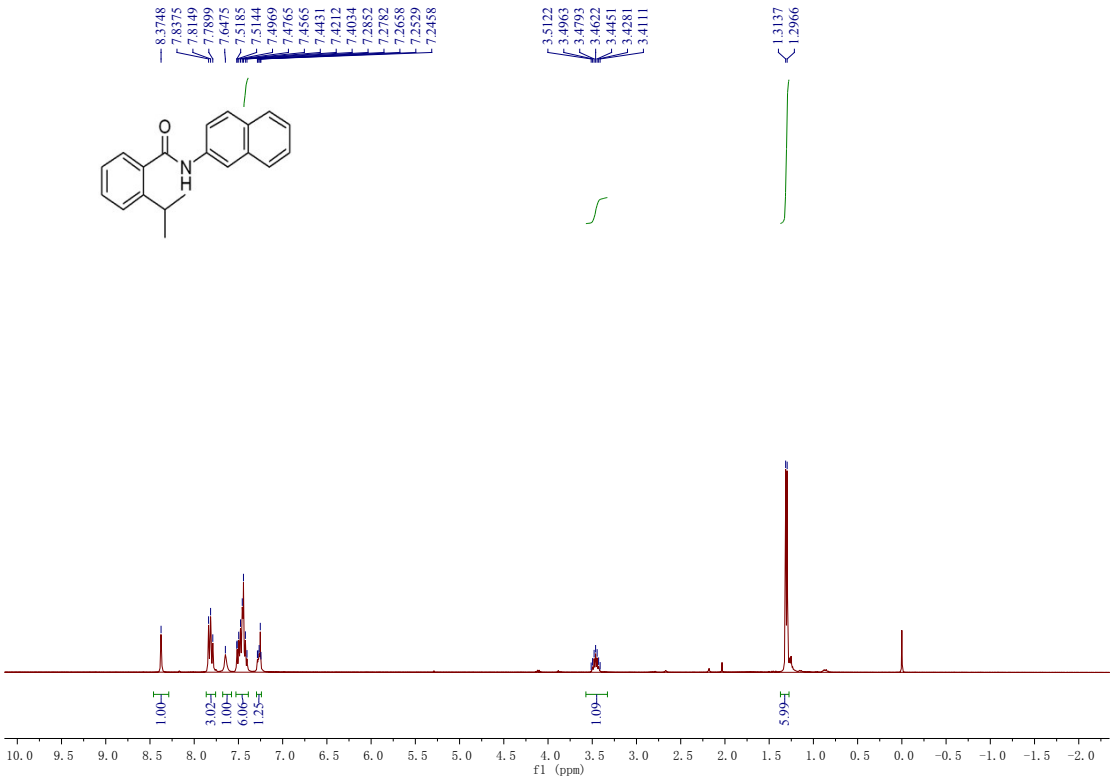
^{1}H NMR spectrum of compound **1i**



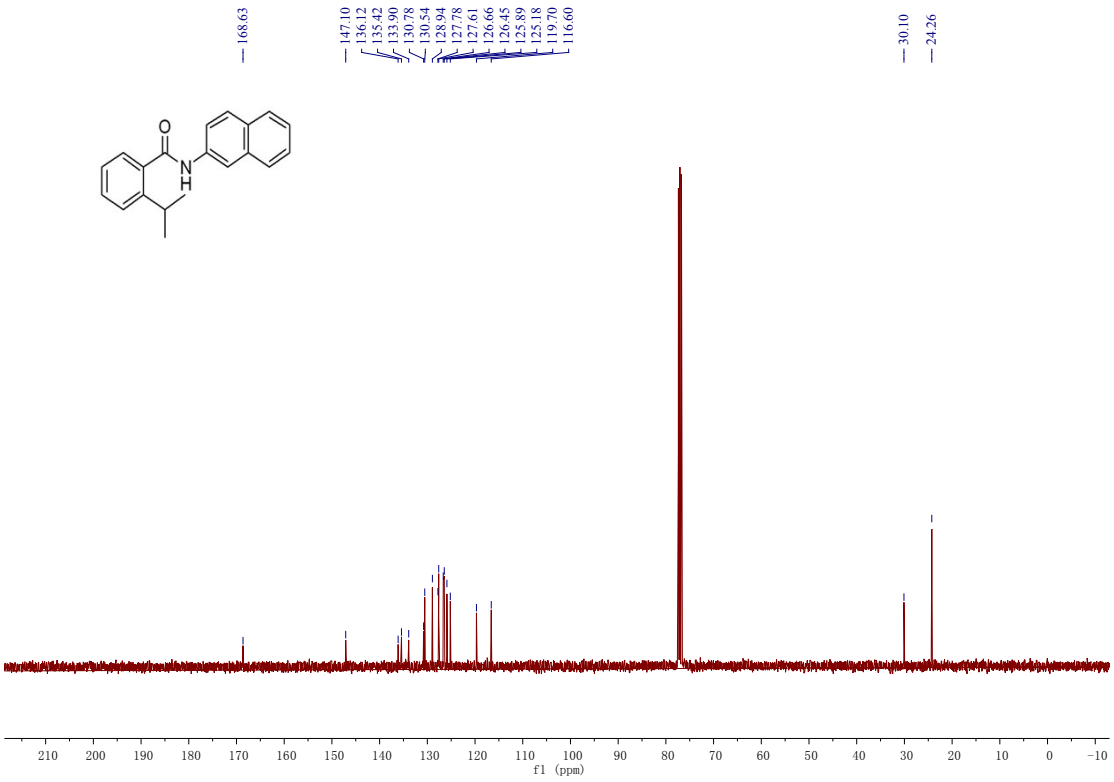
^{13}C NMR spectrum of compound **1i**



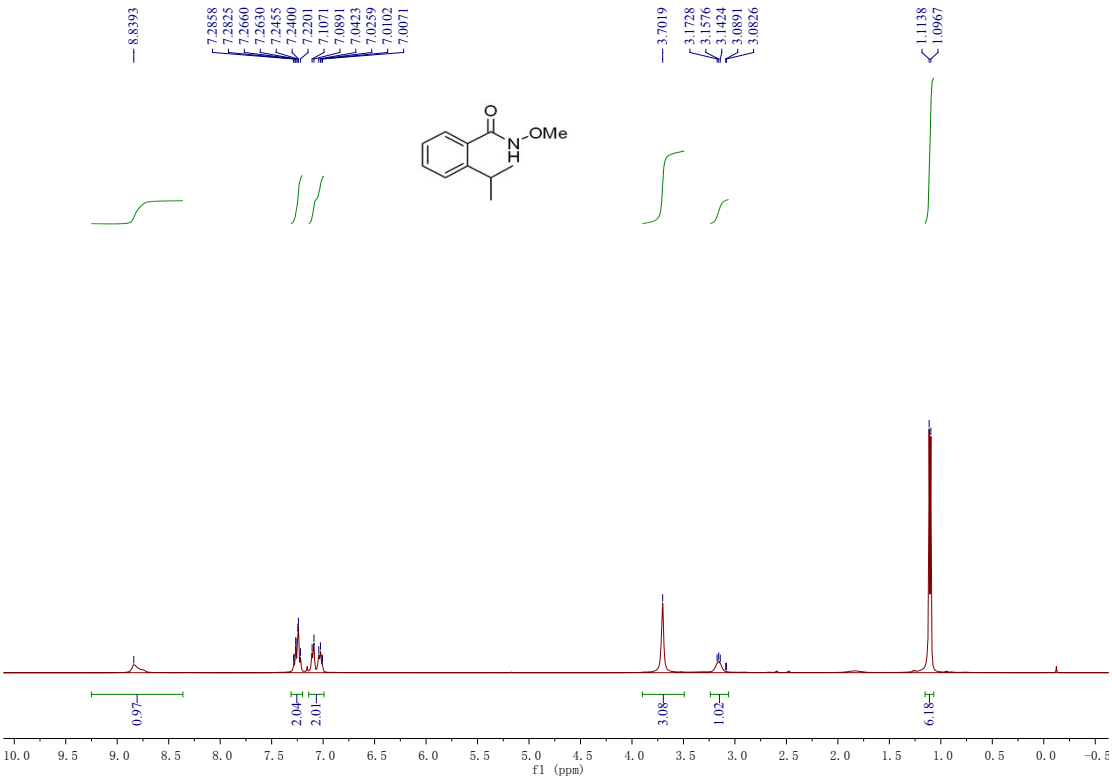
^{1}H NMR spectrum of compound **1j**



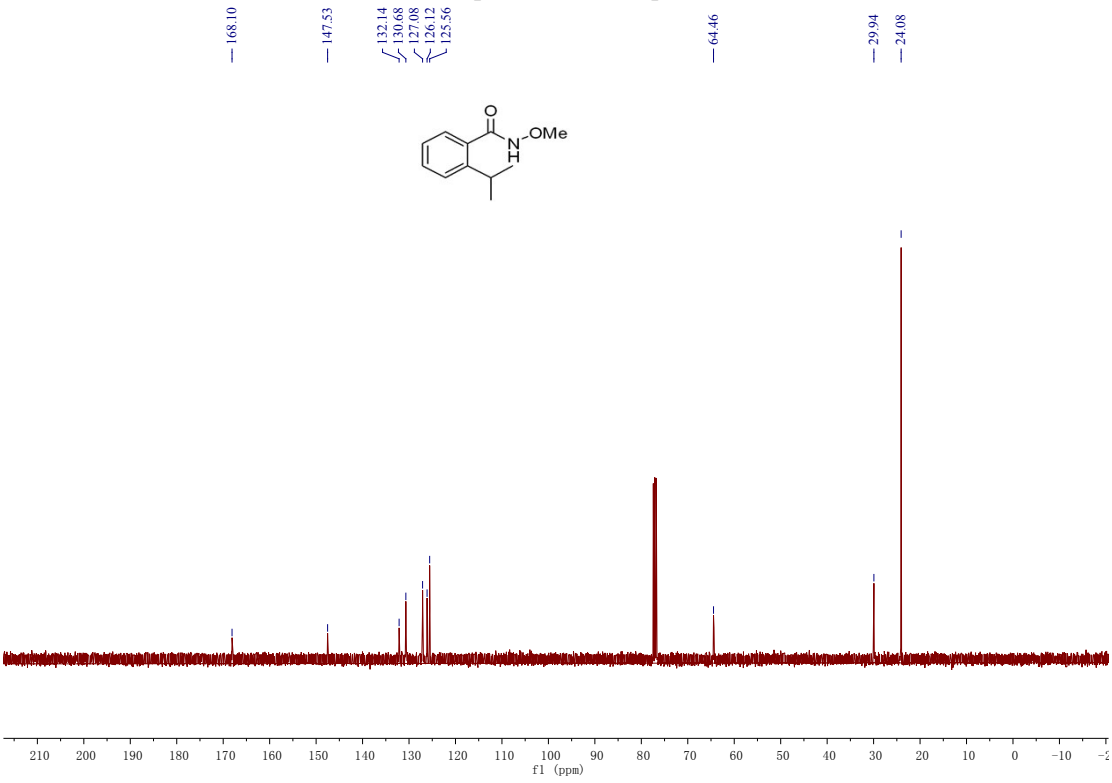
^{13}C NMR spectrum of compound **1j**



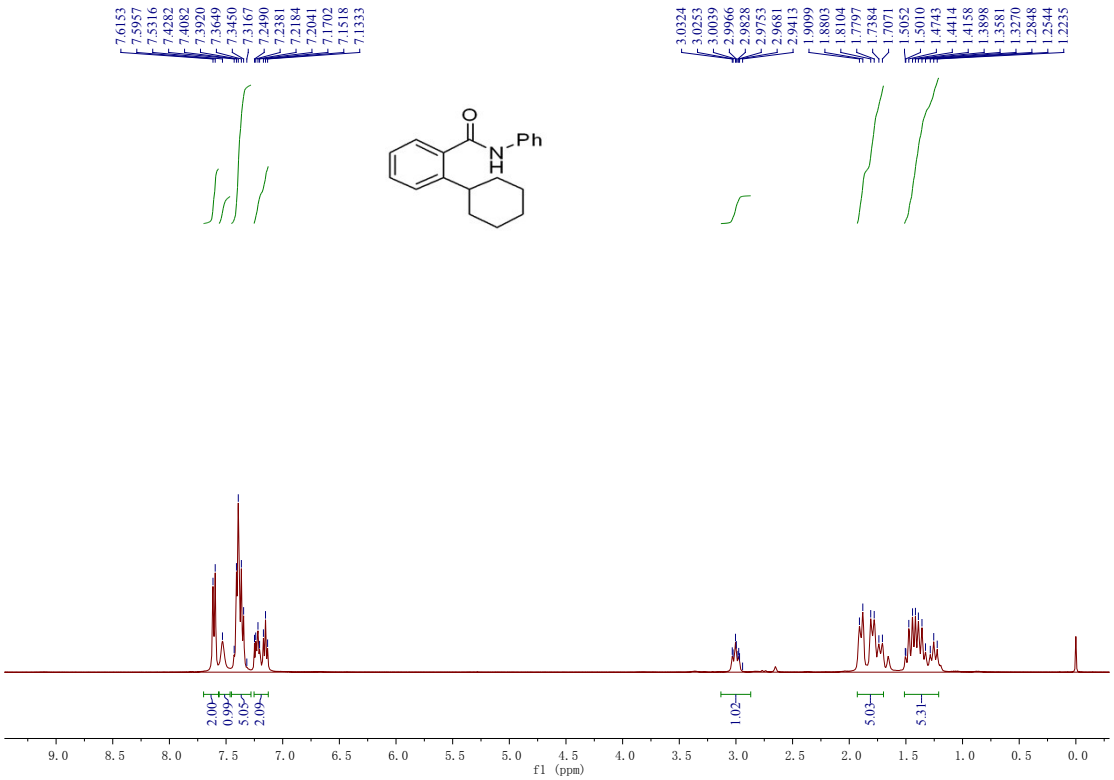
^{1}H NMR spectrum of compound **1k**



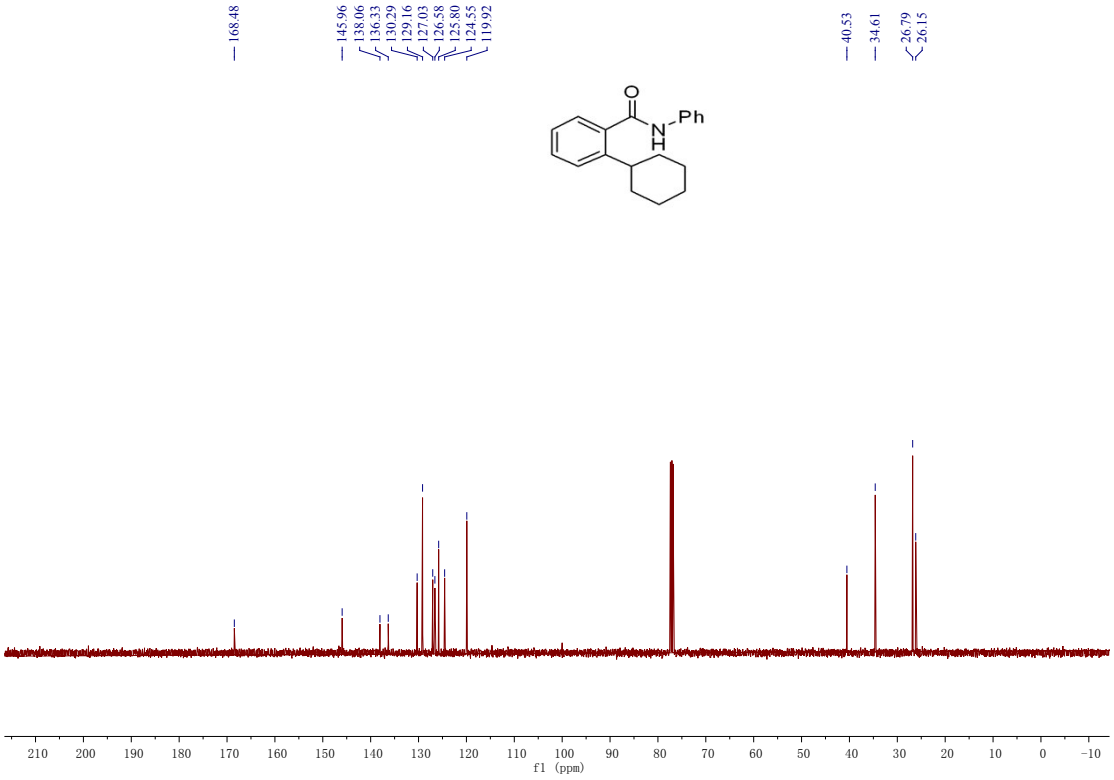
^{13}C NMR spectrum of compound **1k**



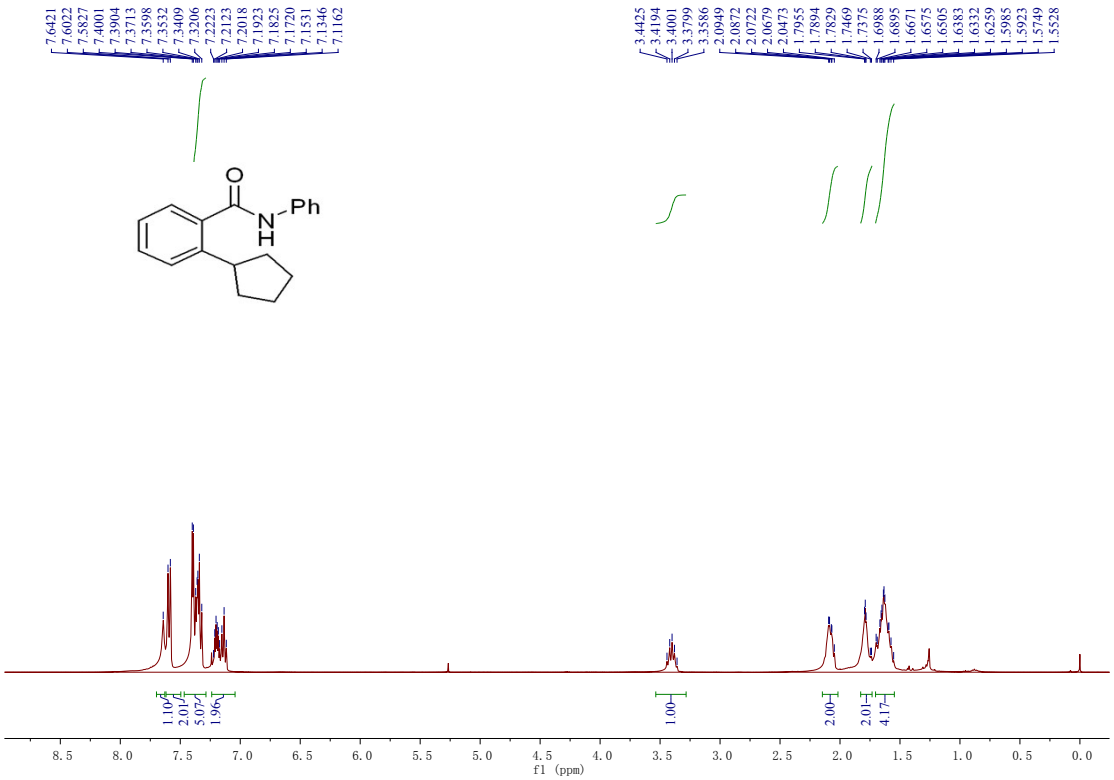
^{1}H NMR spectrum of compound **1l**



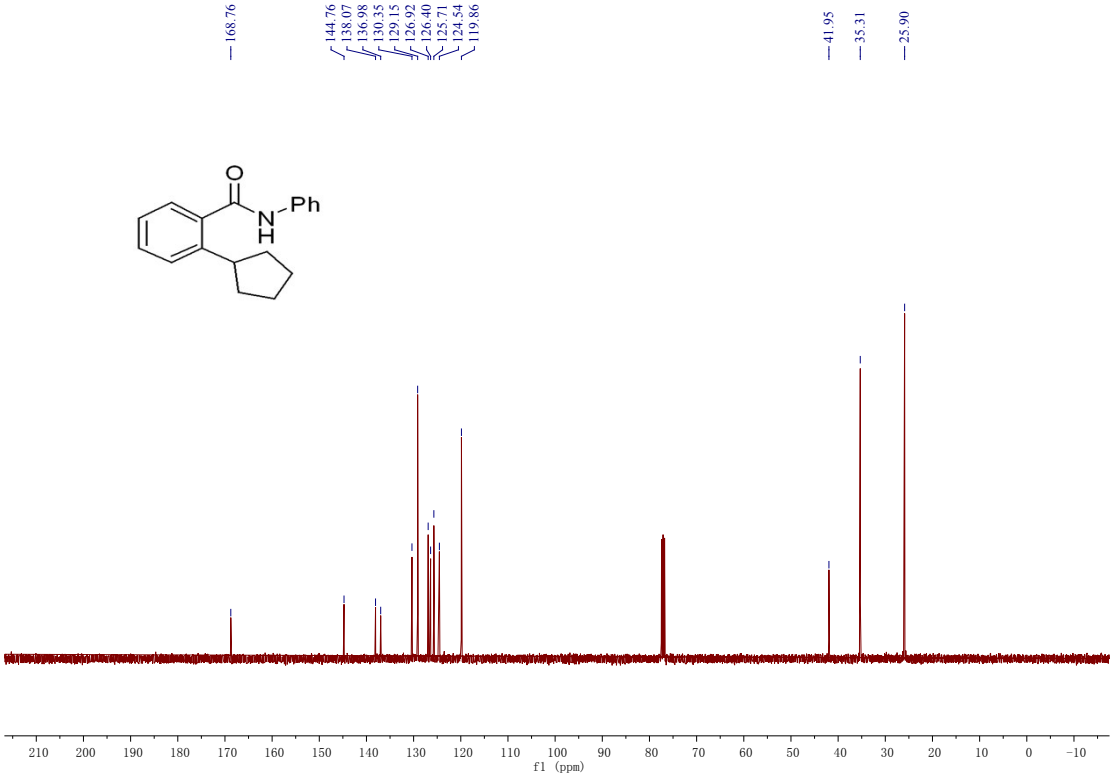
^{13}C NMR spectrum of compound **1l**



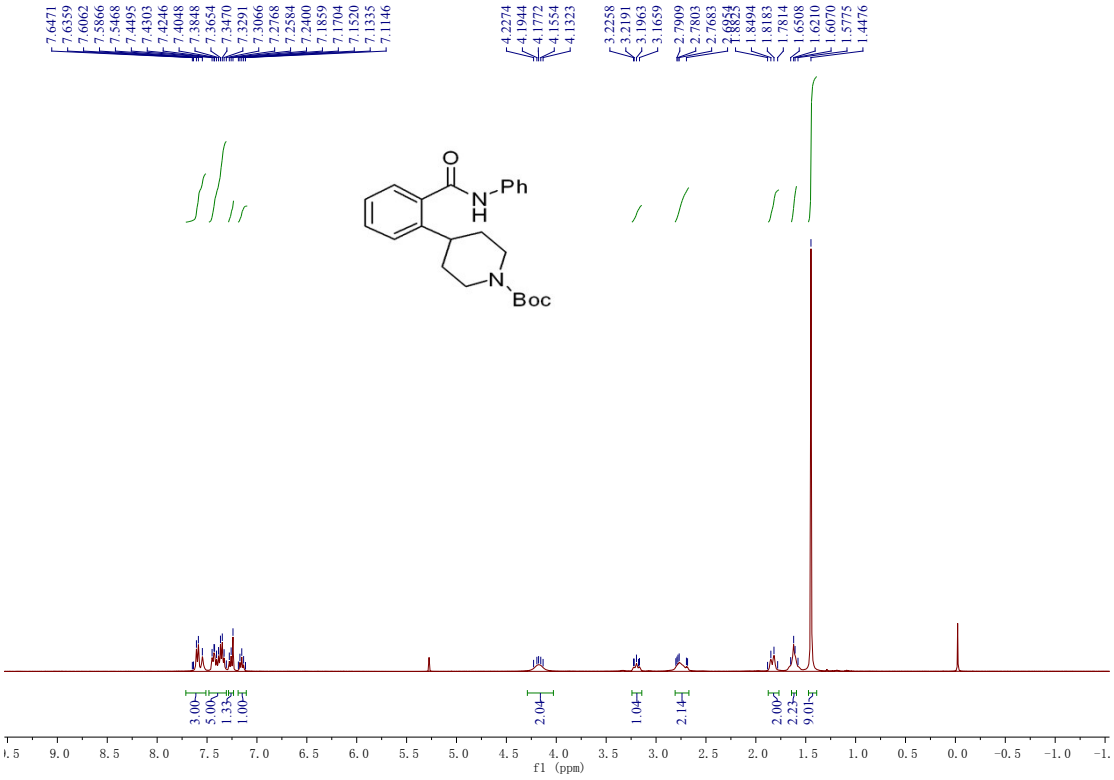
^{1}H NMR spectrum of compound **1m**



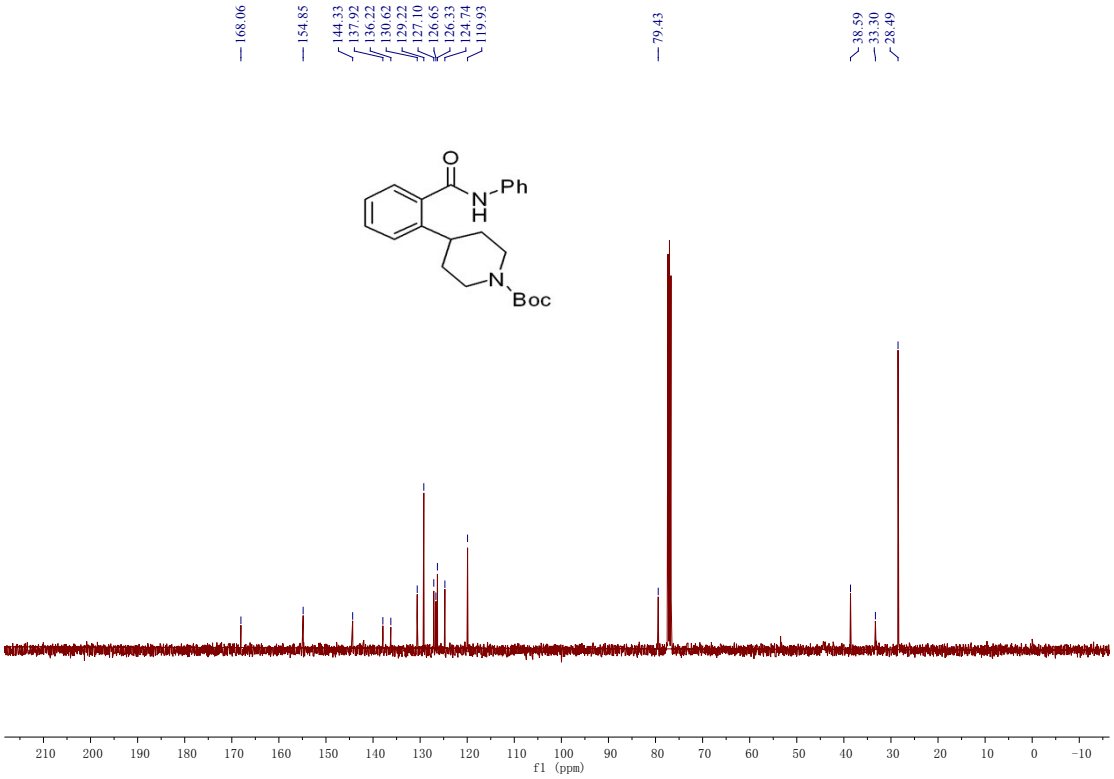
^{13}C NMR spectrum of compound **1m**



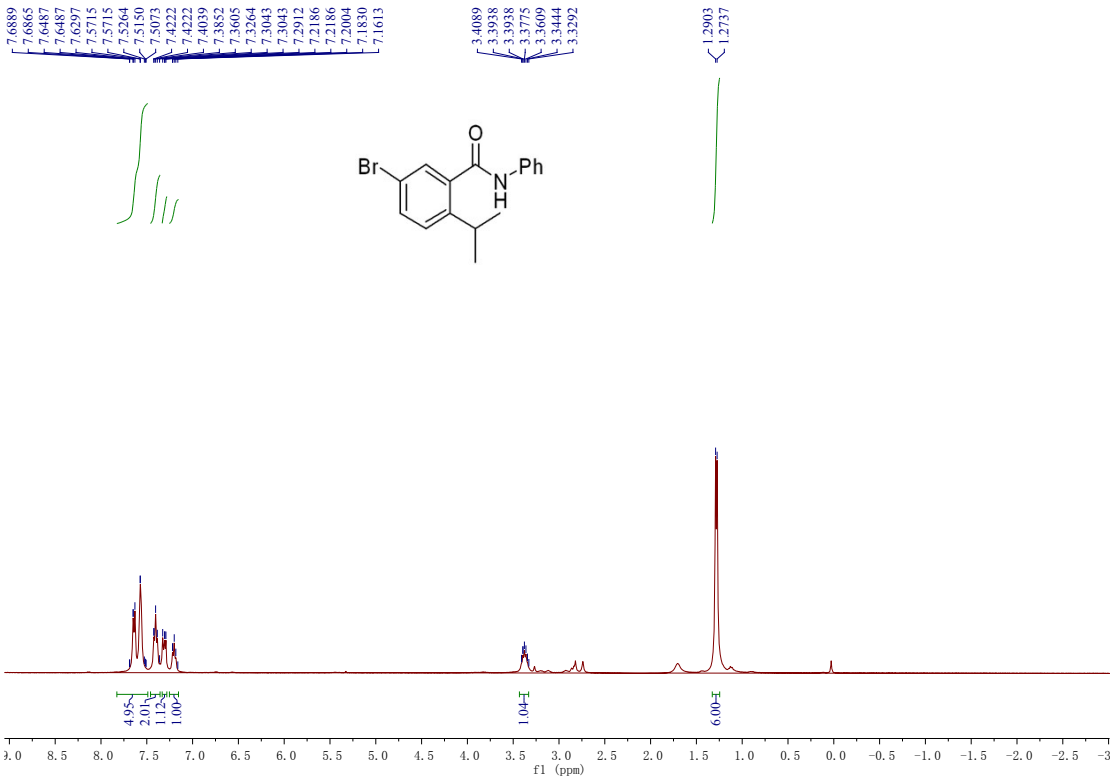
^{1}H NMR spectrum of compound **1n**



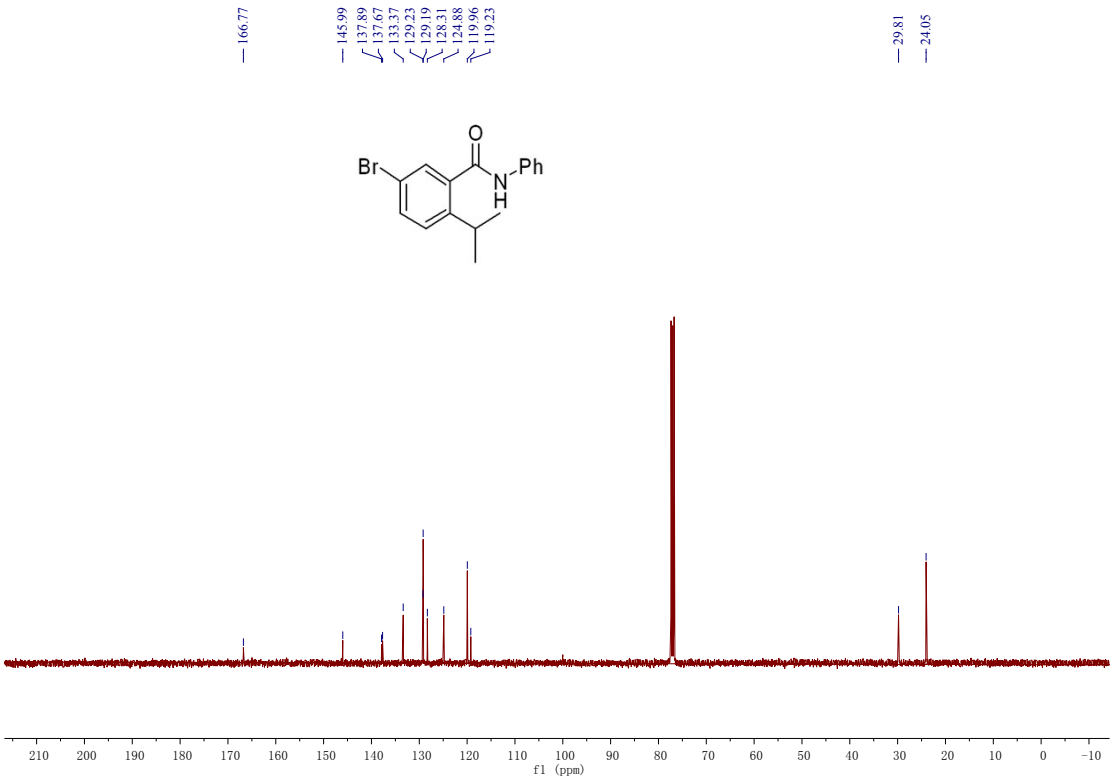
^{13}C NMR spectrum of compound **1n**



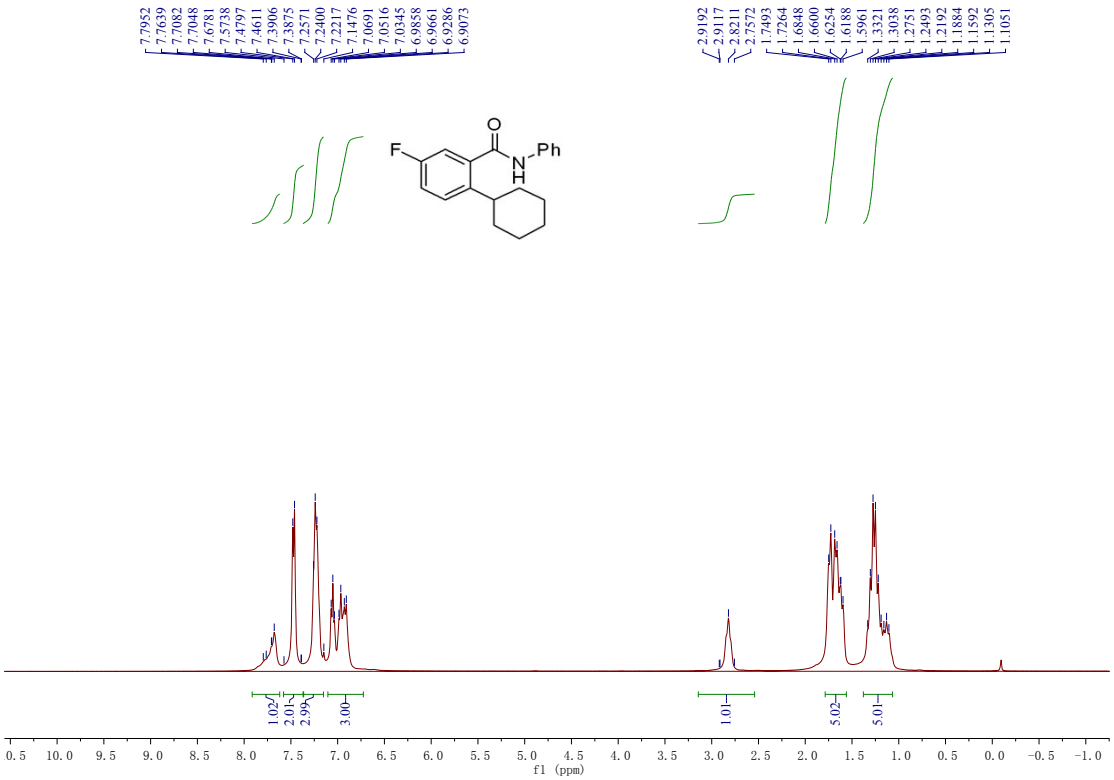
^{1}H NMR spectrum of compound **1o**



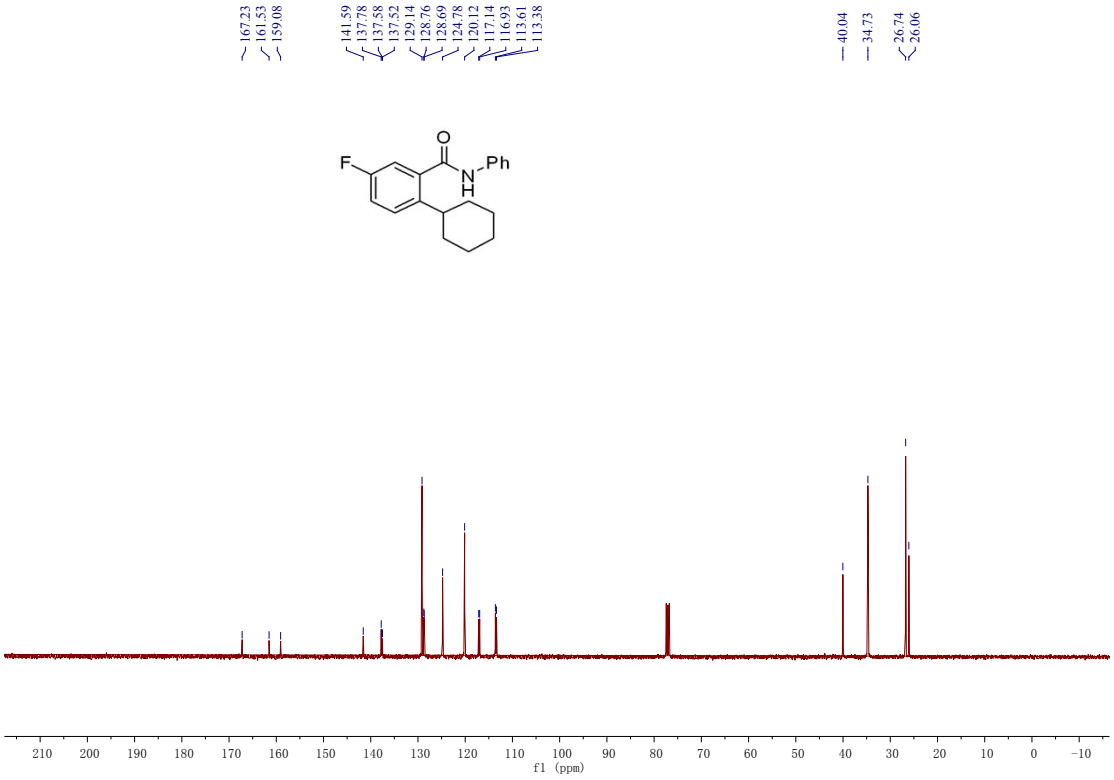
^{13}C NMR spectrum of compound **1o**



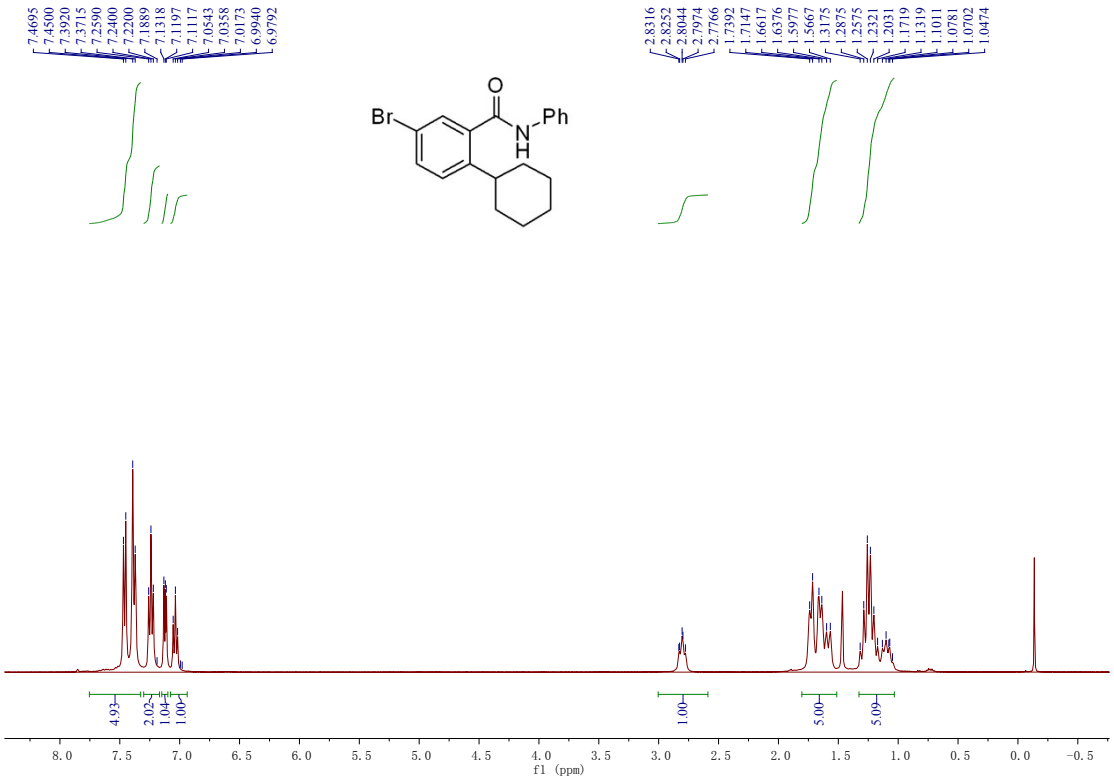
^{1}H NMR spectrum of compound **1p**



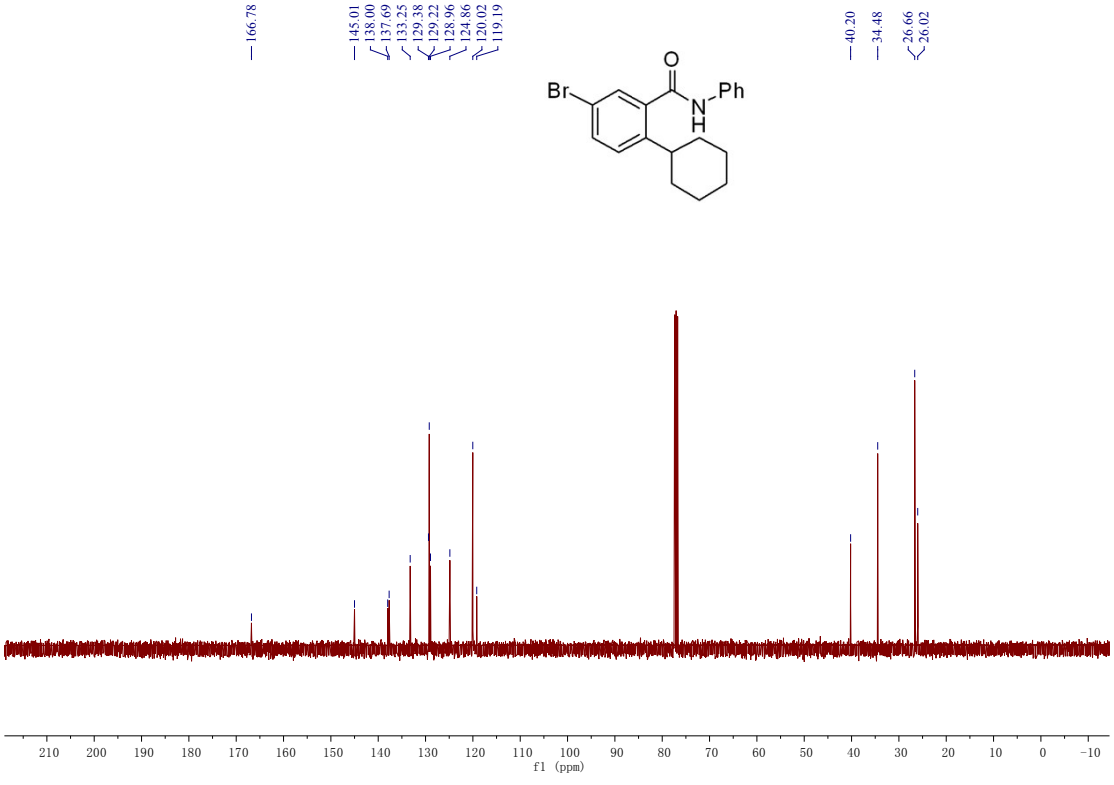
^{13}C NMR spectrum of compound **1p**



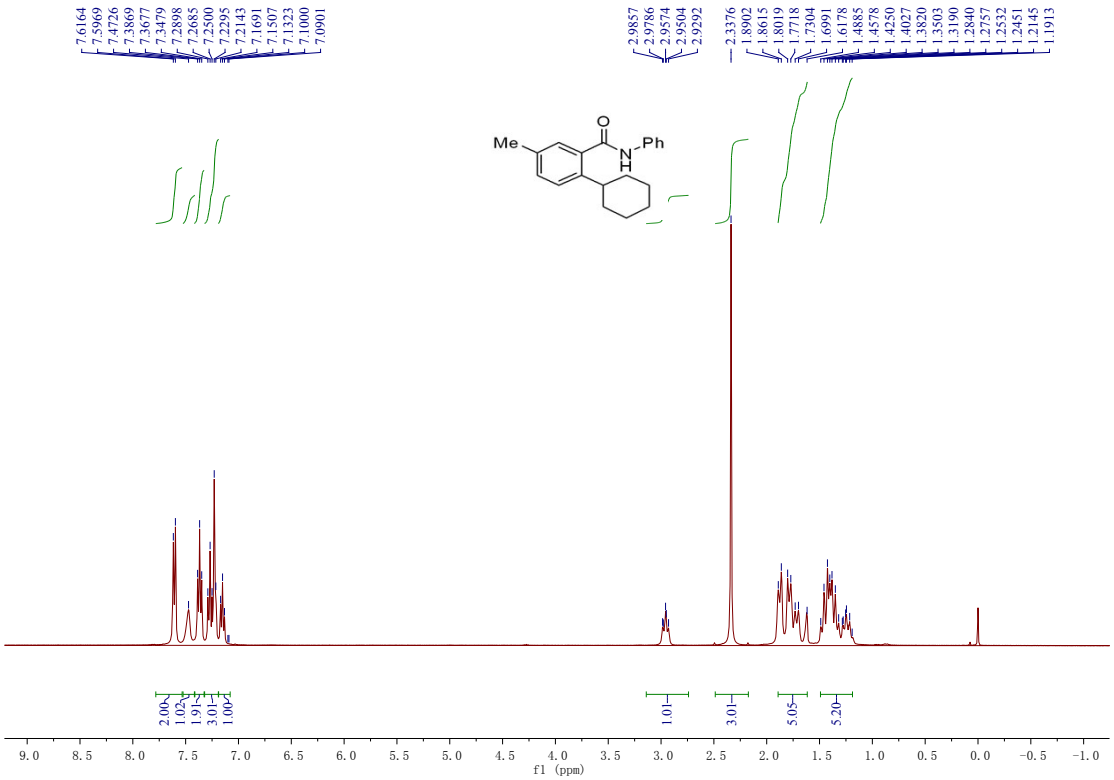
^{1}H NMR spectrum of compound **1q**



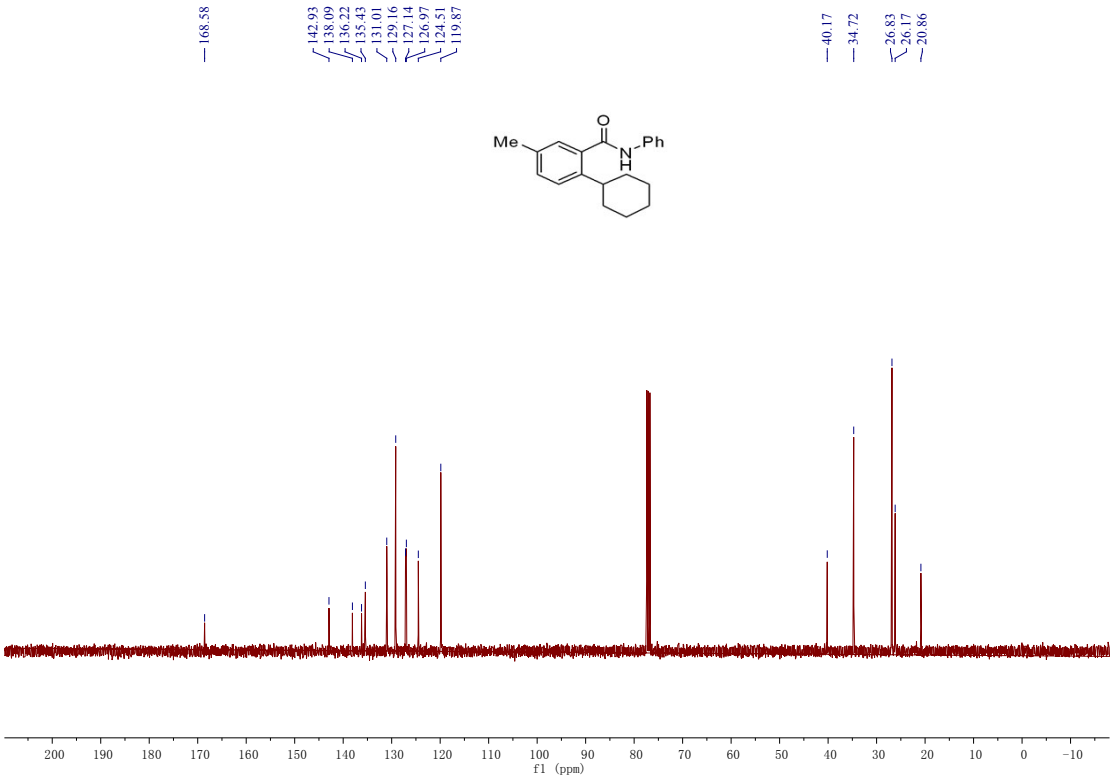
^{13}C NMR spectrum of compound **1q**



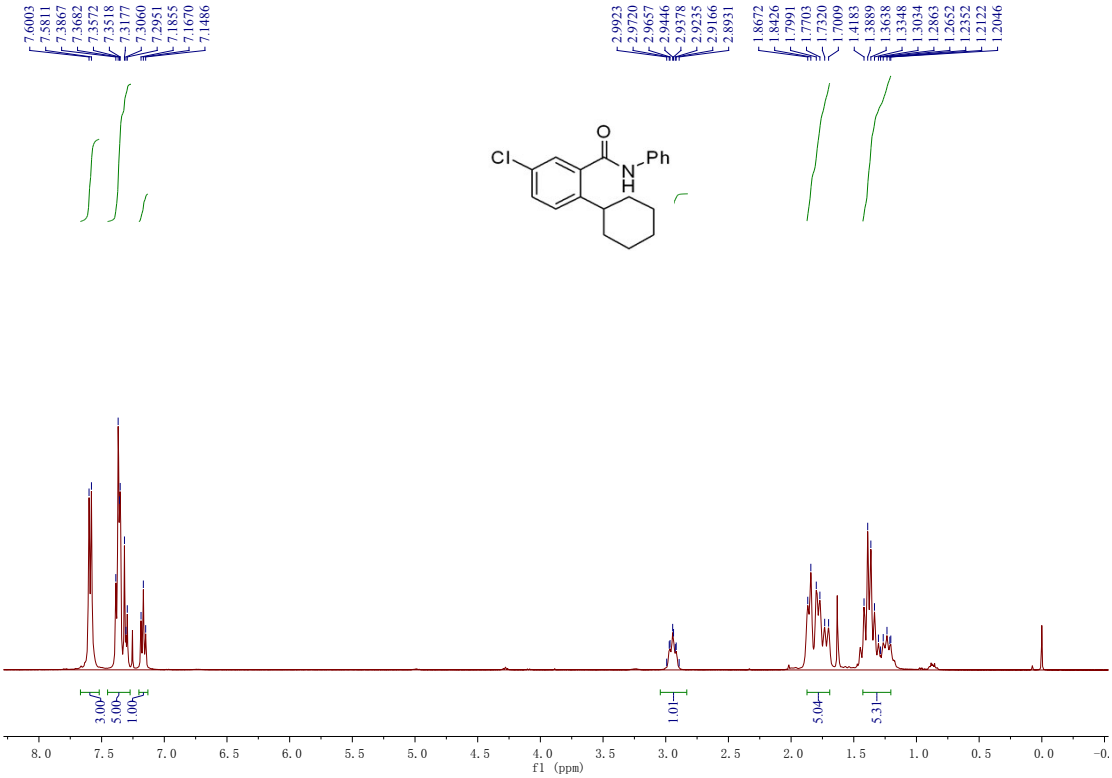
^{1}H NMR spectrum of compound **1r**



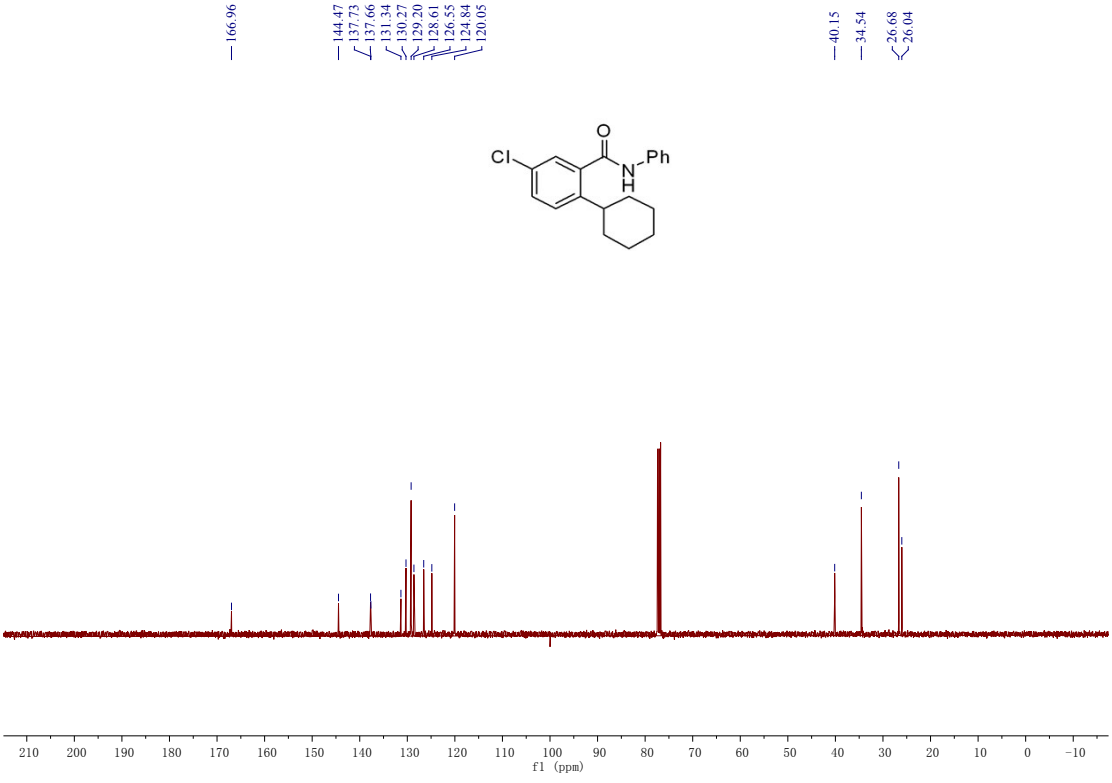
^{13}C NMR spectrum of compound **1r**



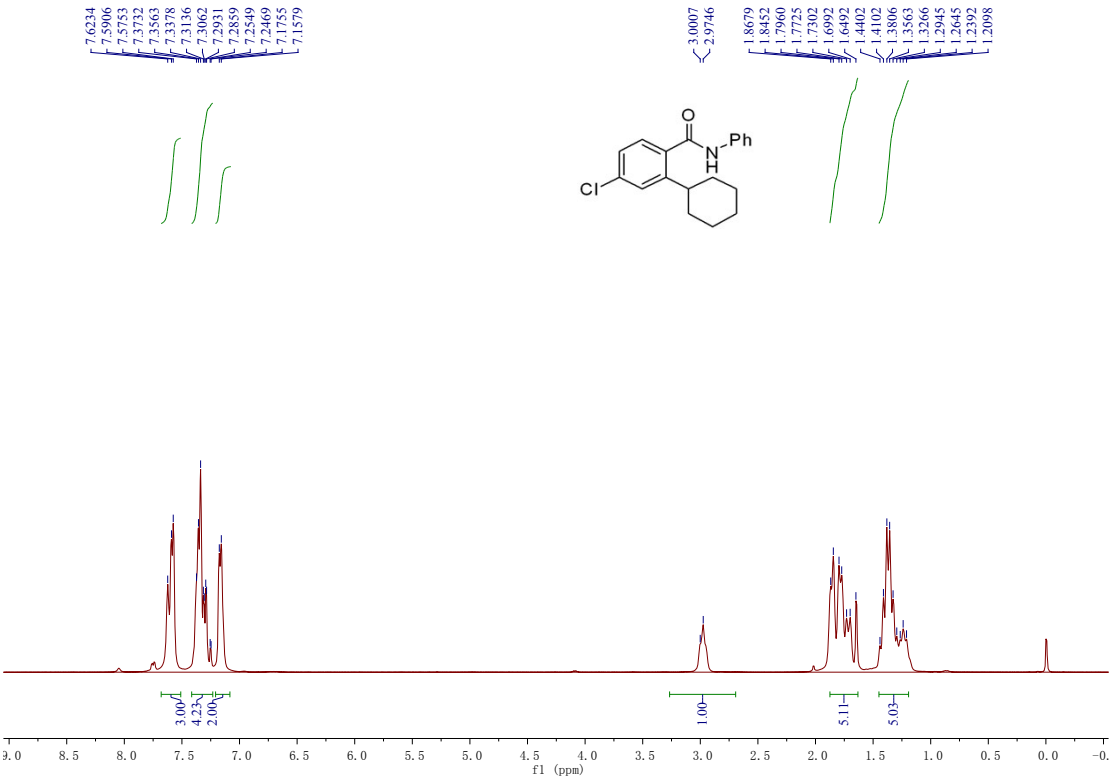
^{1}H NMR spectrum of compound **1s**



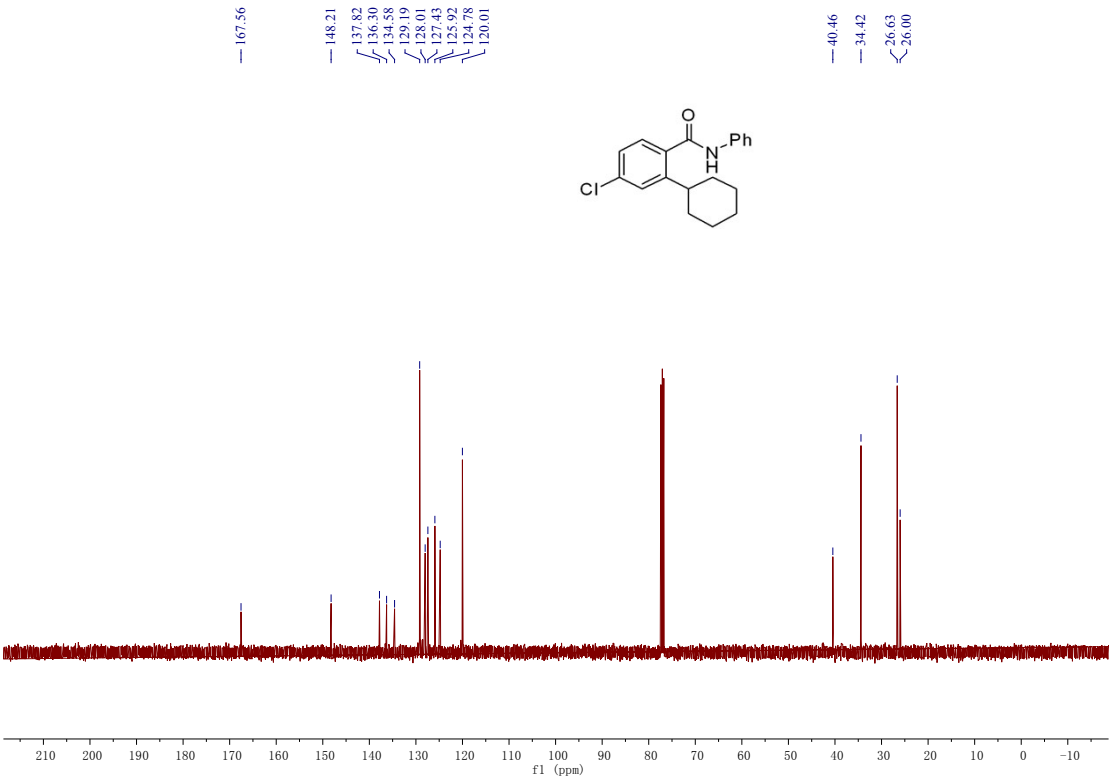
^{13}C NMR spectrum of compound **1s**



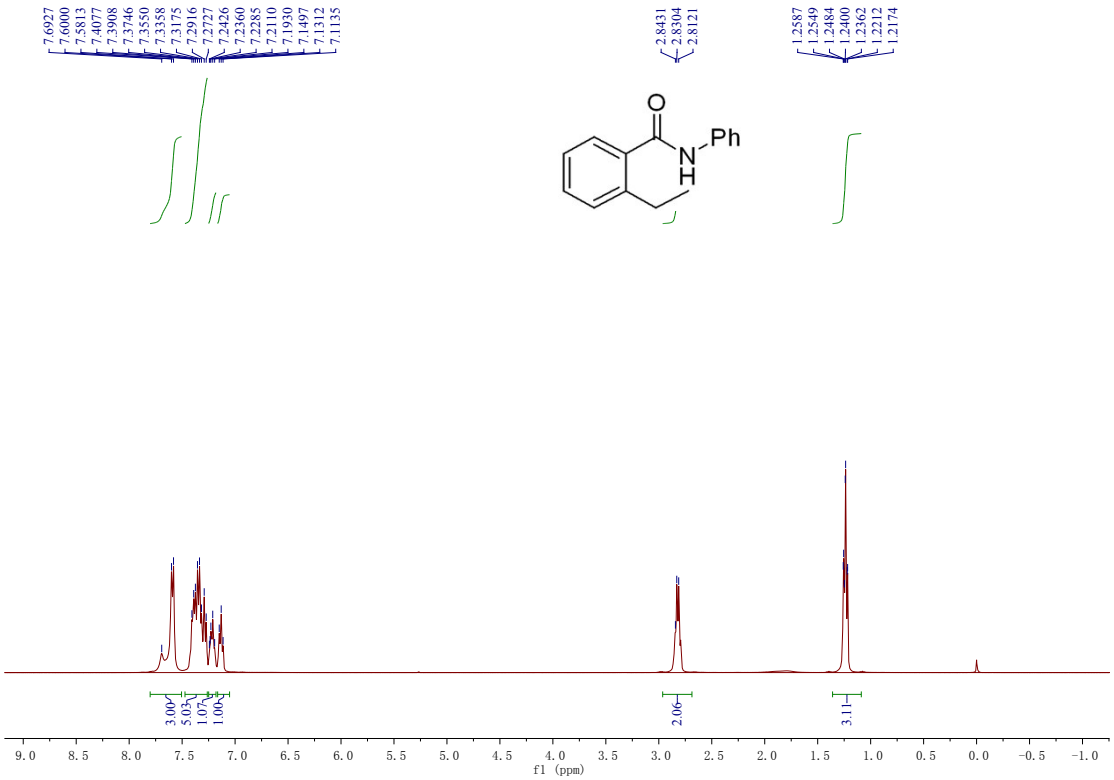
^{1}H NMR spectrum of compound **1t**



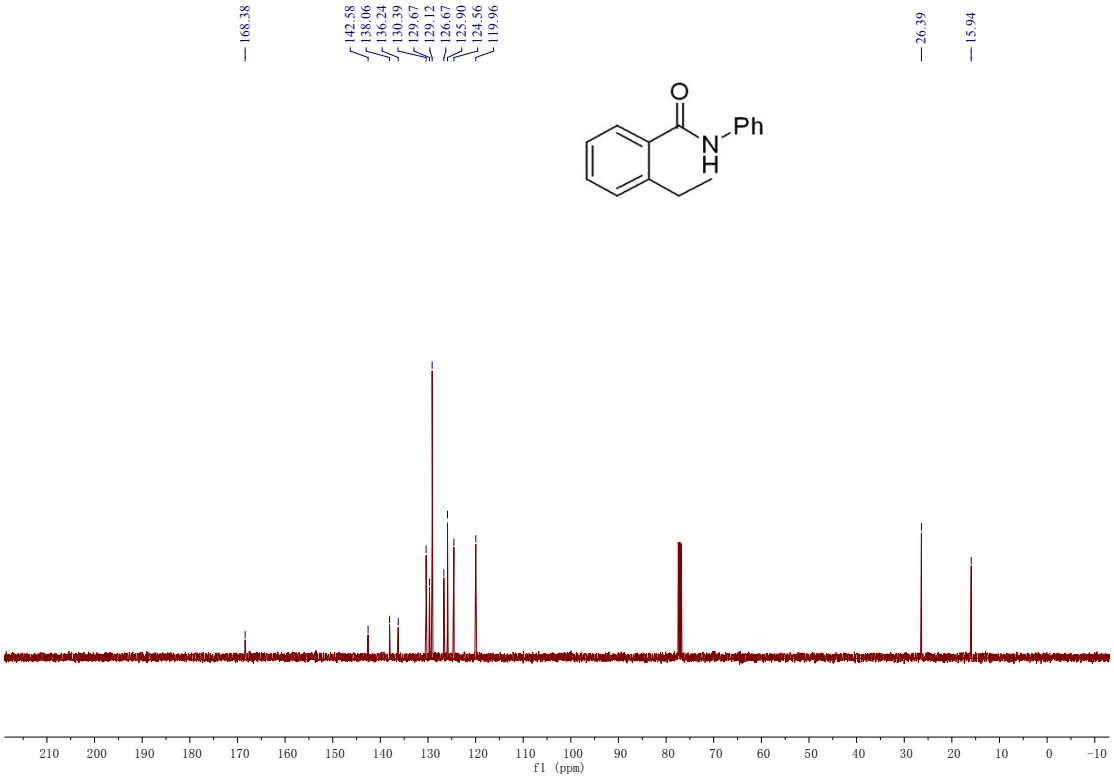
^{13}C NMR spectrum of compound **1t**



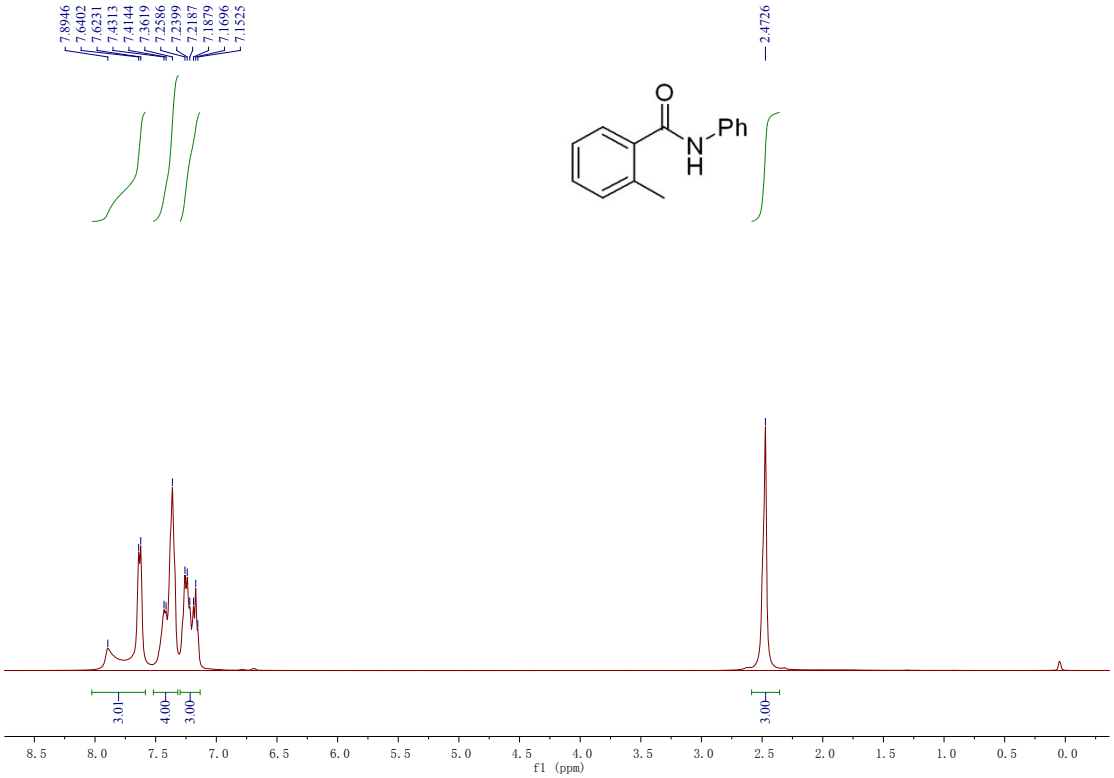
^{1}H NMR spectrum of compound **1u**



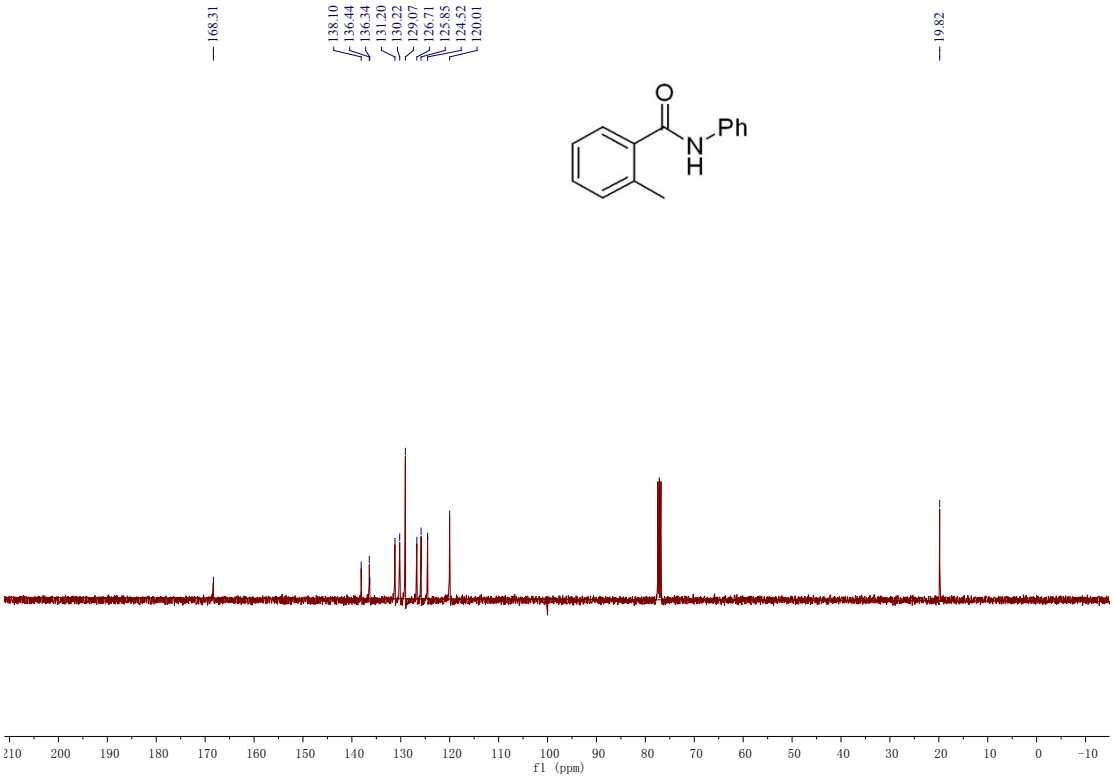
^{13}C NMR spectrum of compound **1u**



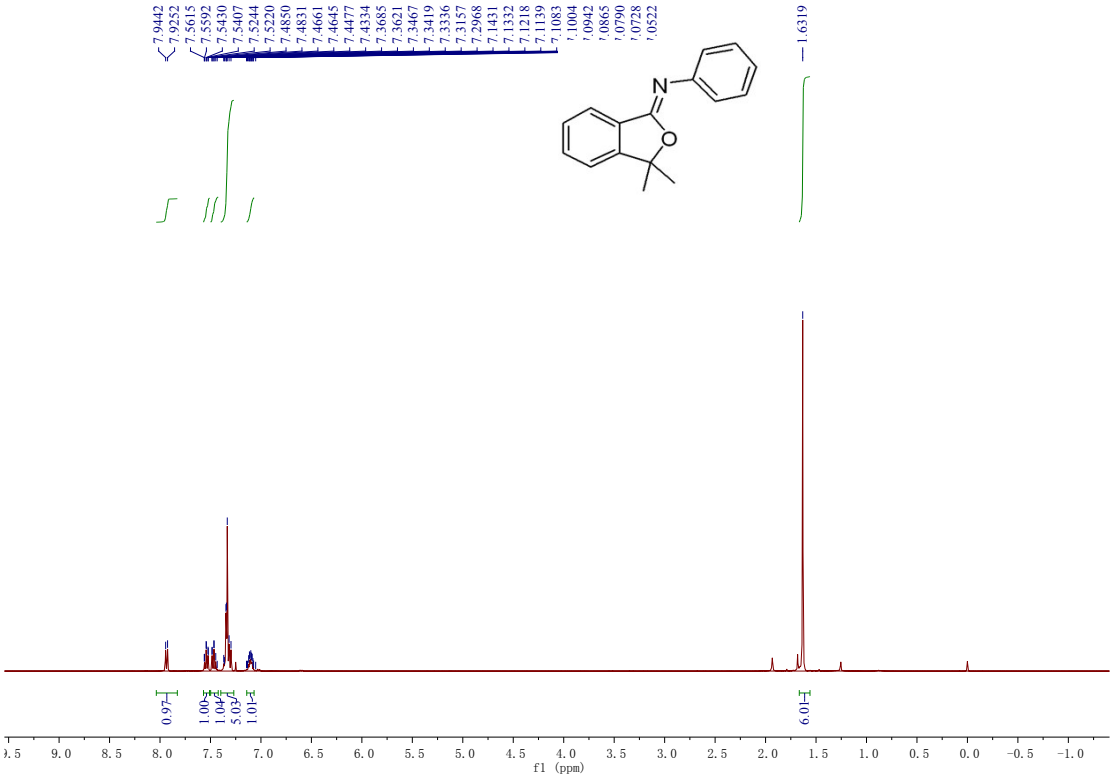
^{1}H NMR spectrum of compound **1v**



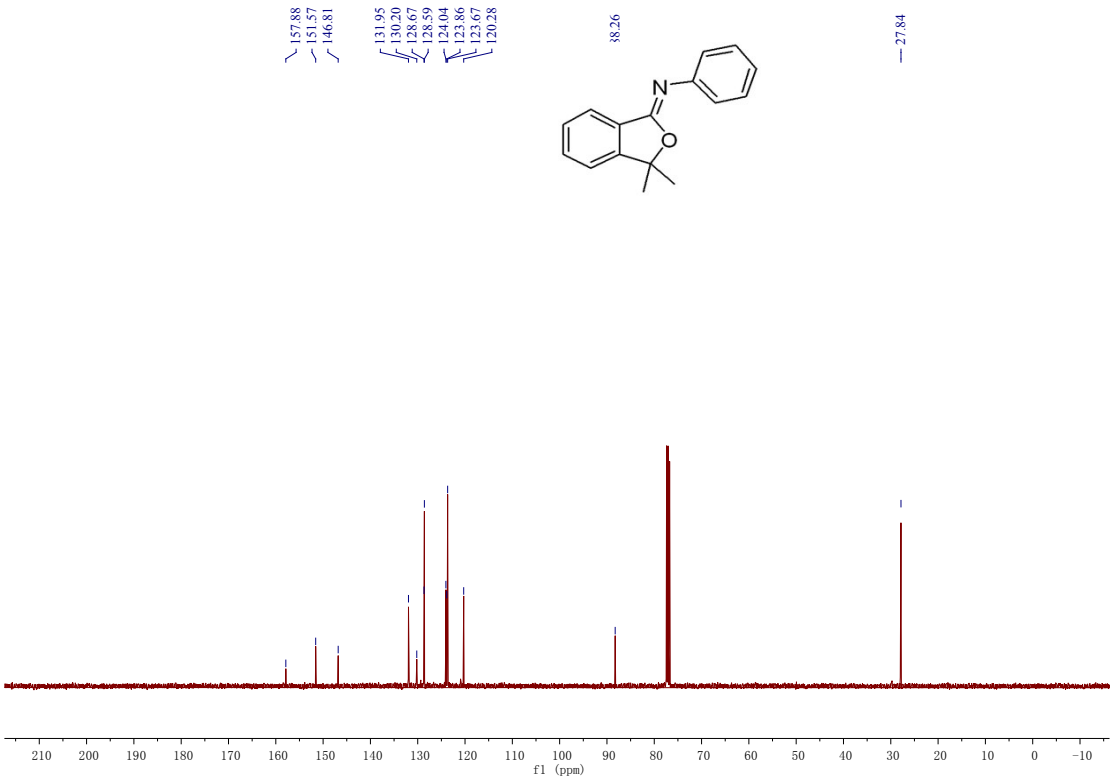
^{13}C NMR spectrum of compound **1v**



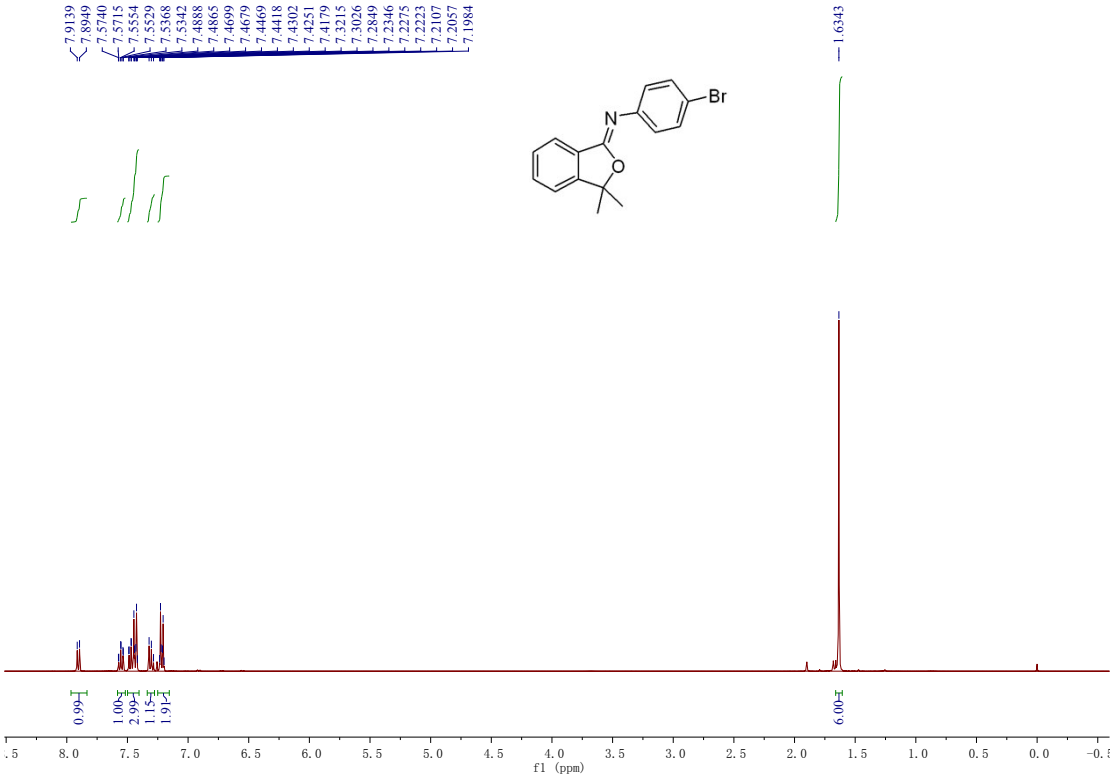
^{1}H NMR spectrum of compound **2a**



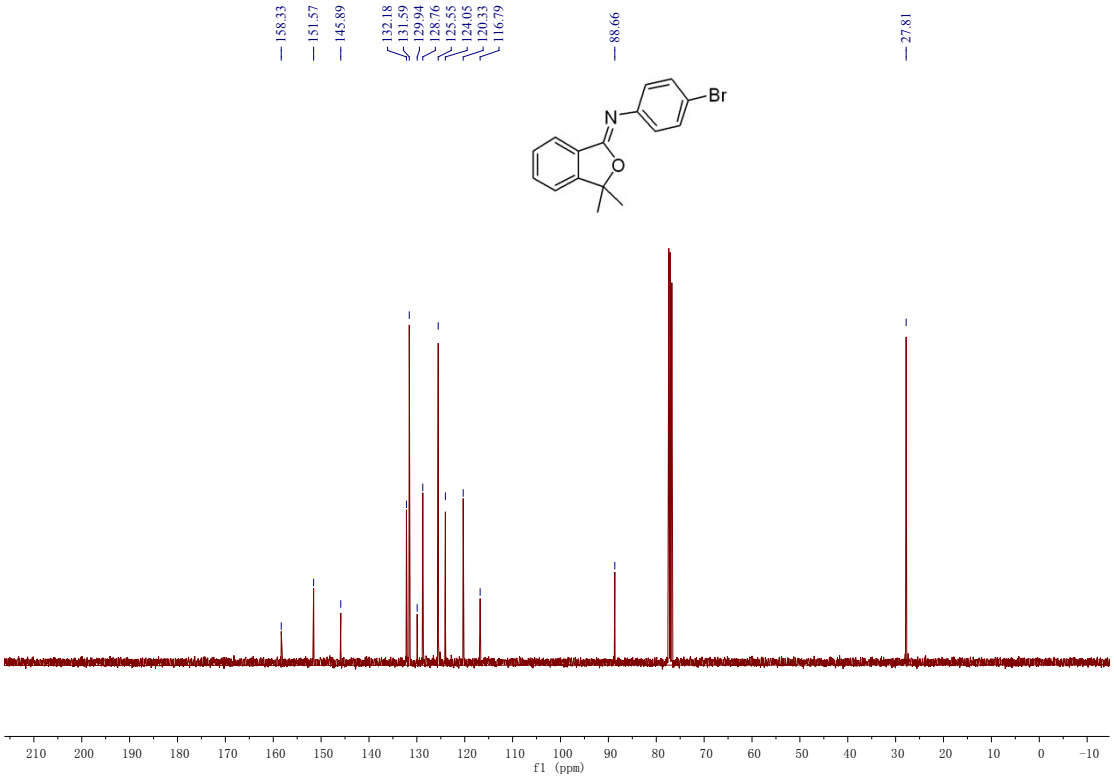
^{13}C NMR spectrum of compound **2a**



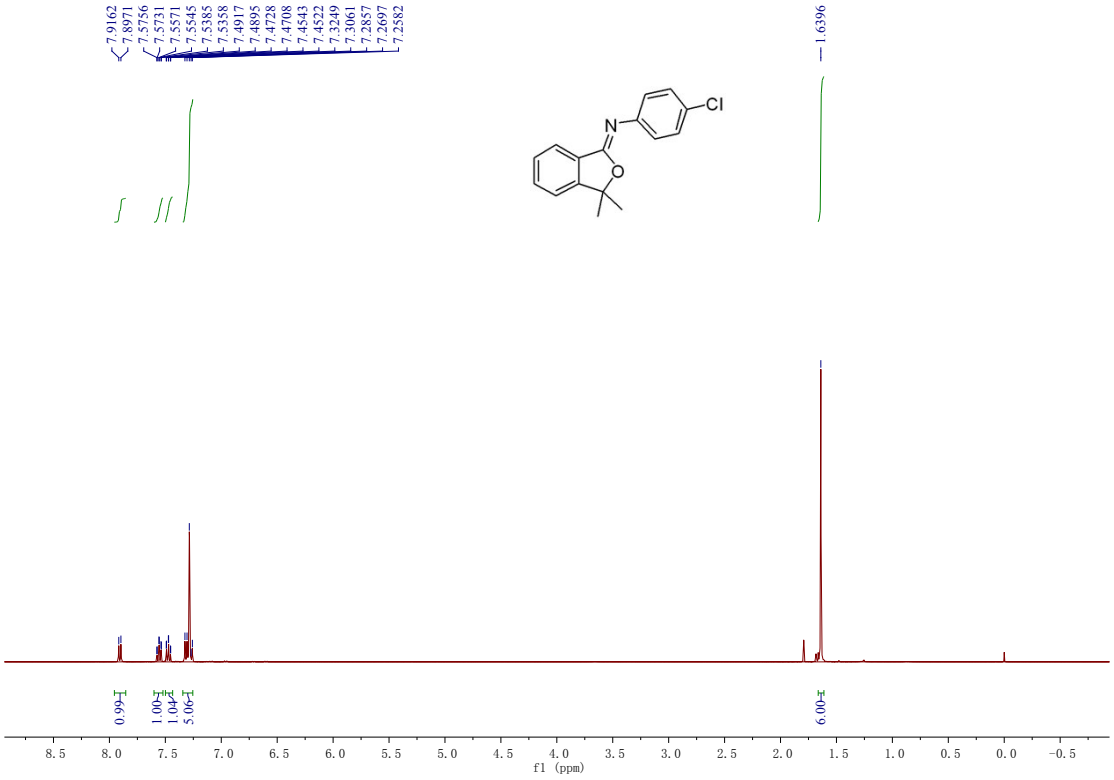
^{1}H NMR spectrum of compound **2b**



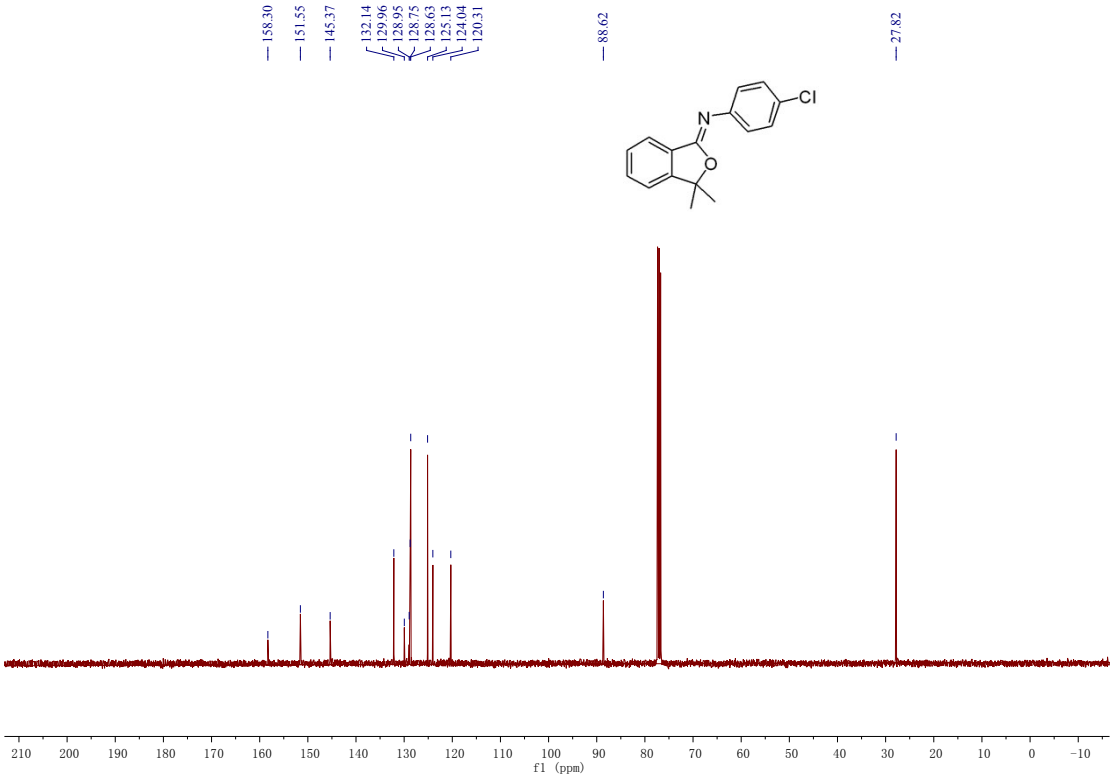
^{13}C NMR spectrum of compound **2b**



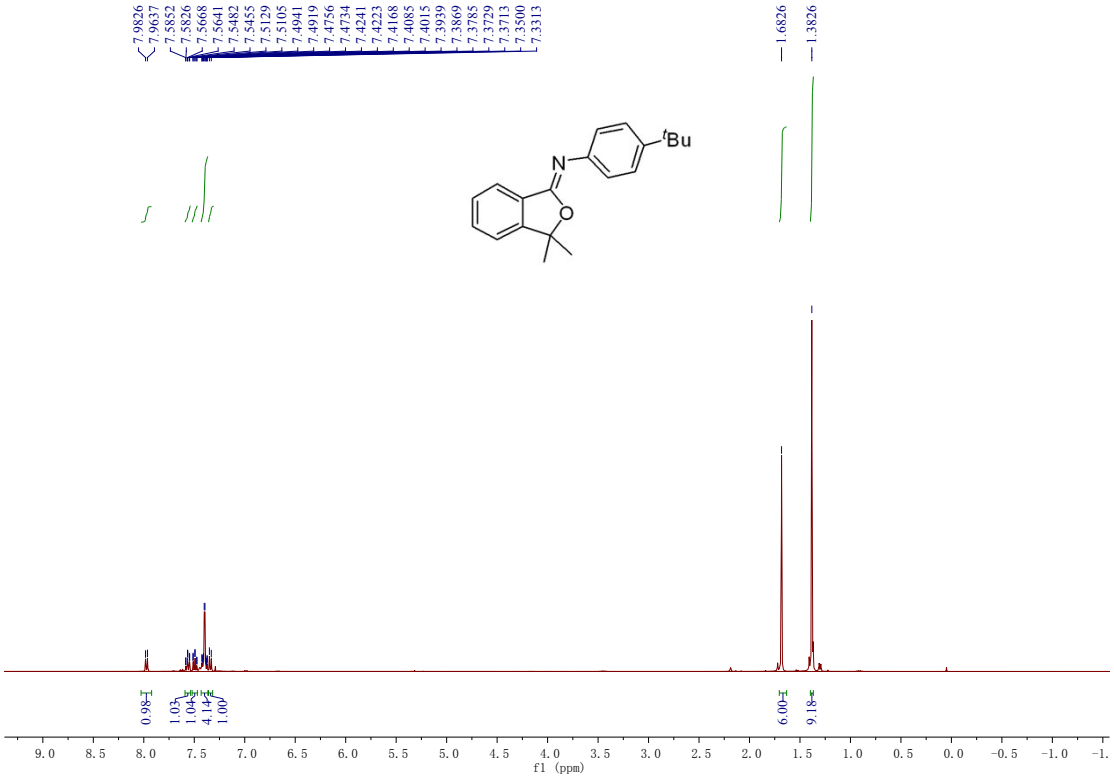
^{1}H NMR spectrum of compound **2c**



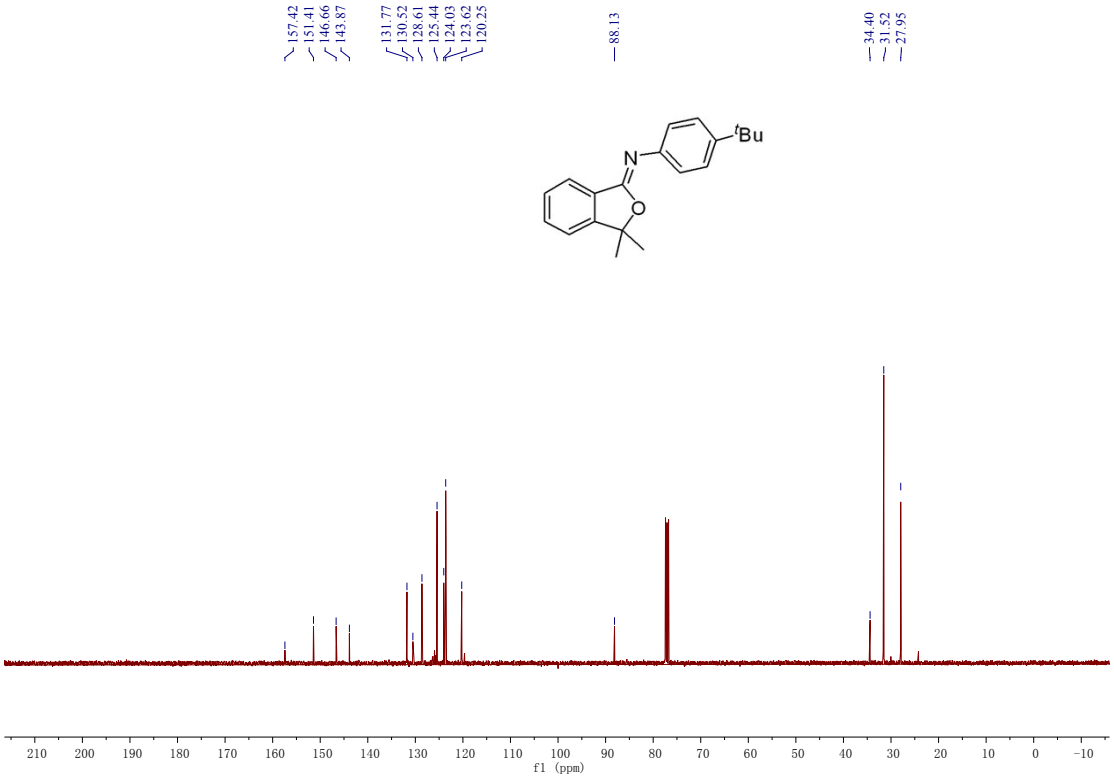
^{13}C NMR spectrum of compound **2c**



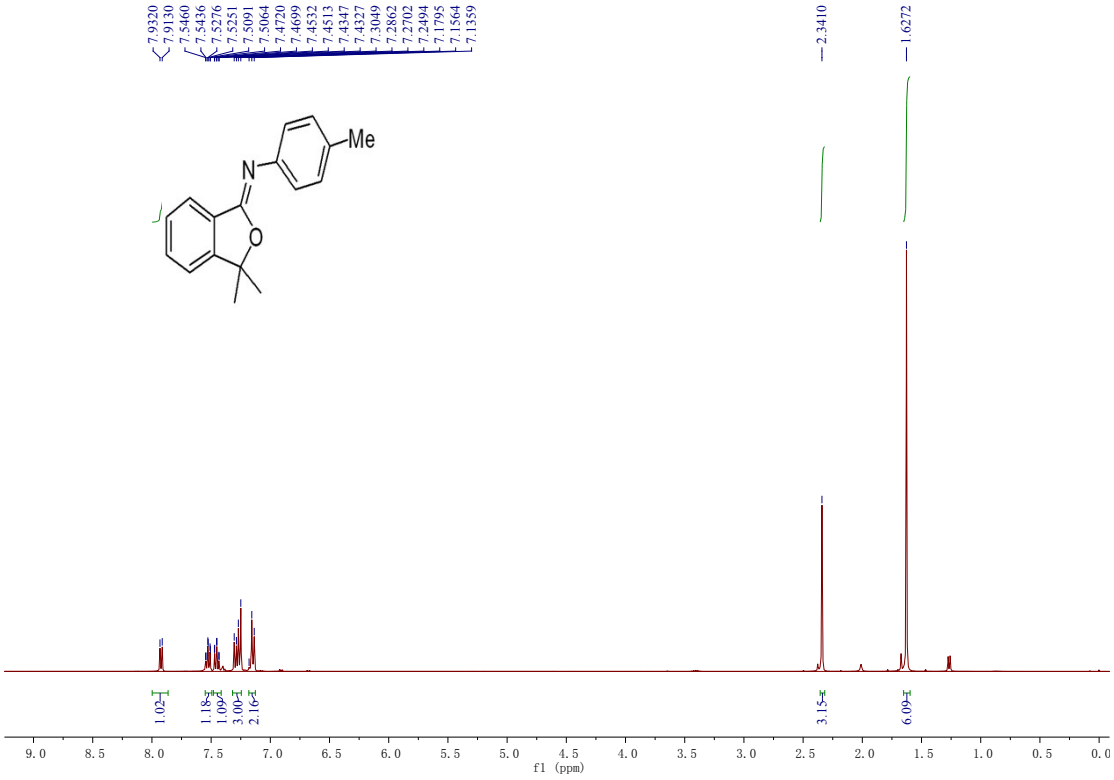
^{1}H NMR spectrum of compound **2d**



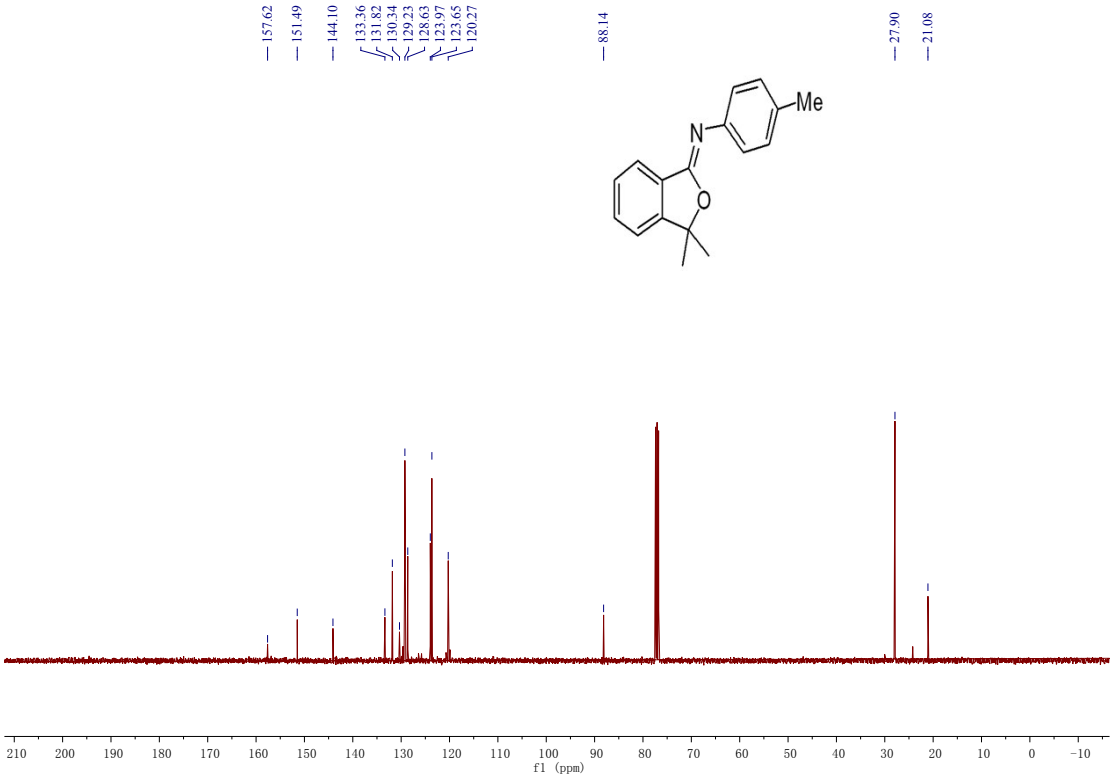
^{13}C NMR spectrum of compound **2d**



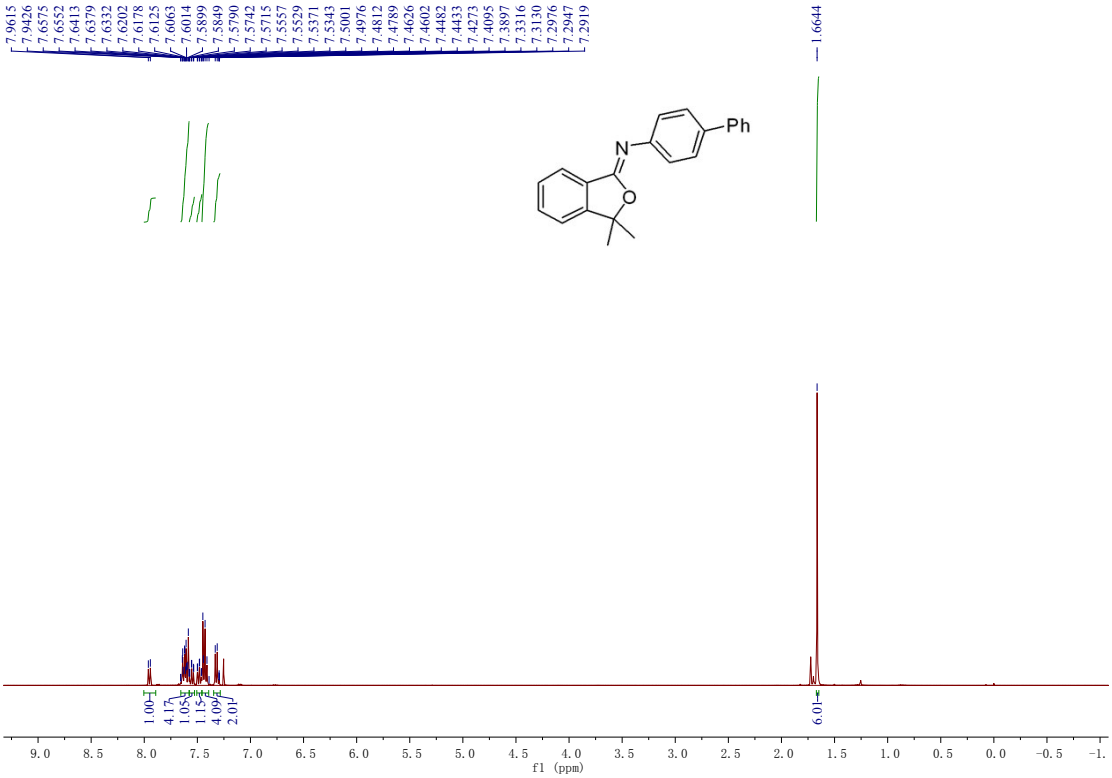
^{1}H NMR spectrum of compound **2e**



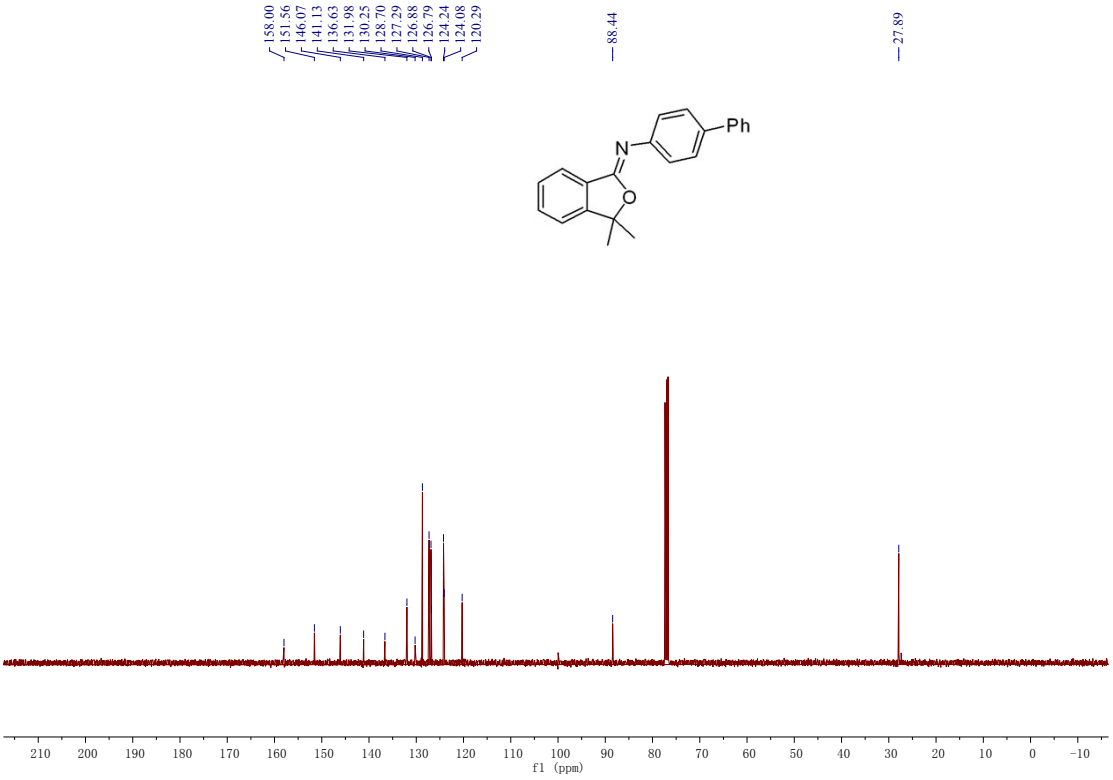
^{13}C NMR spectrum of compound **2e**



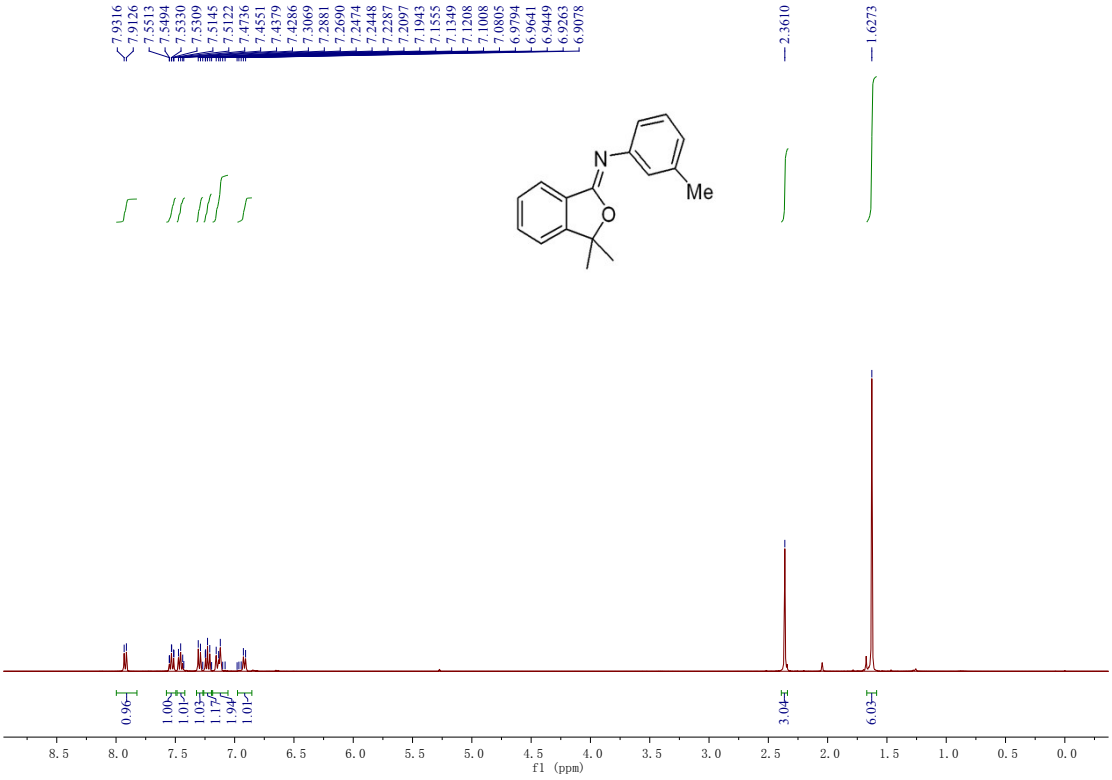
^{1}H NMR spectrum of compound **2f**



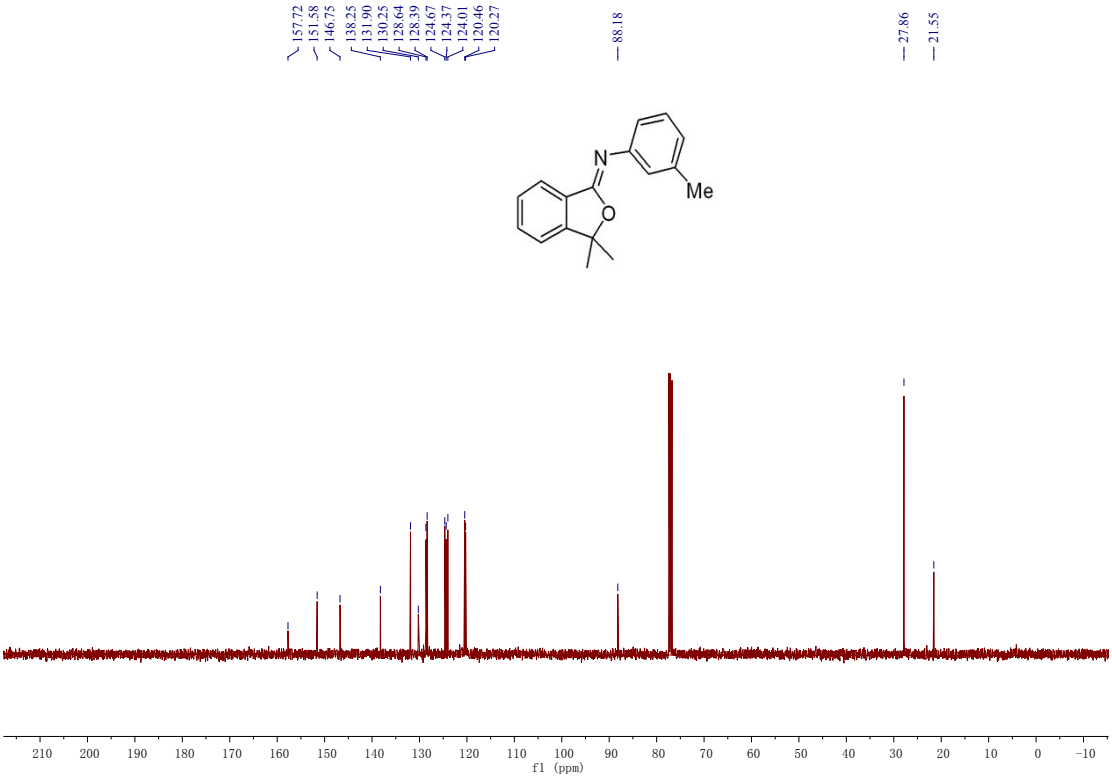
^{13}C NMR spectrum of compound **2f**



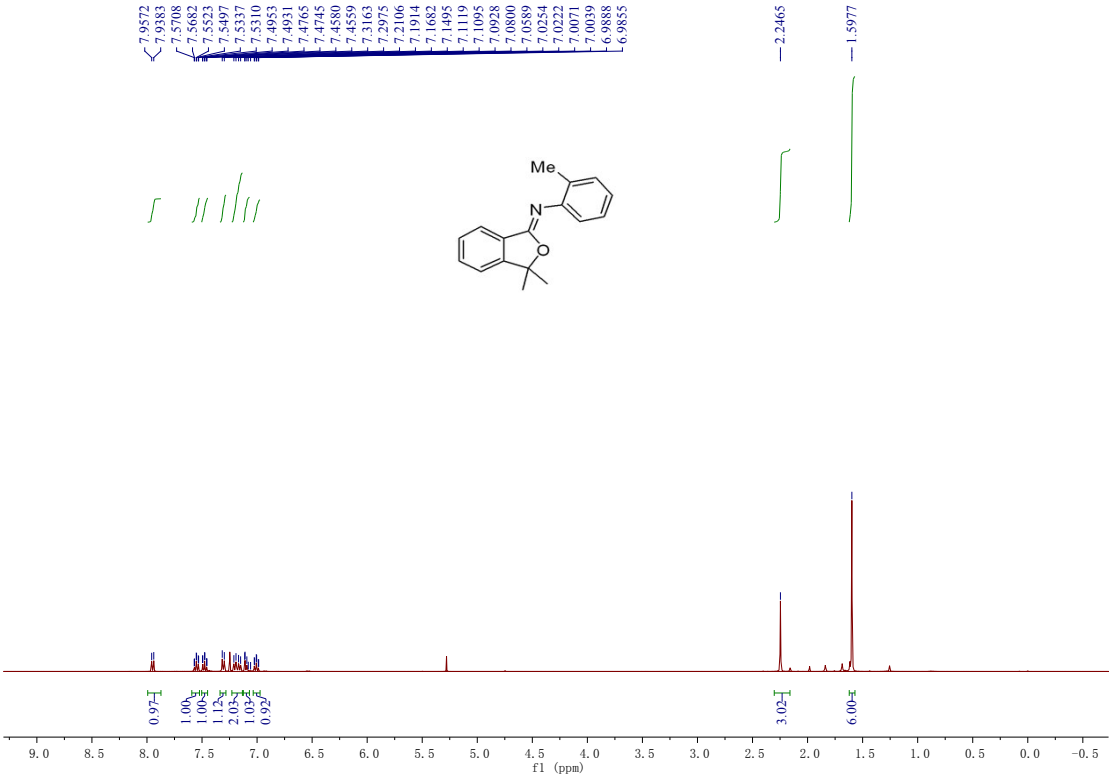
^{1}H NMR spectrum of compound **2g**



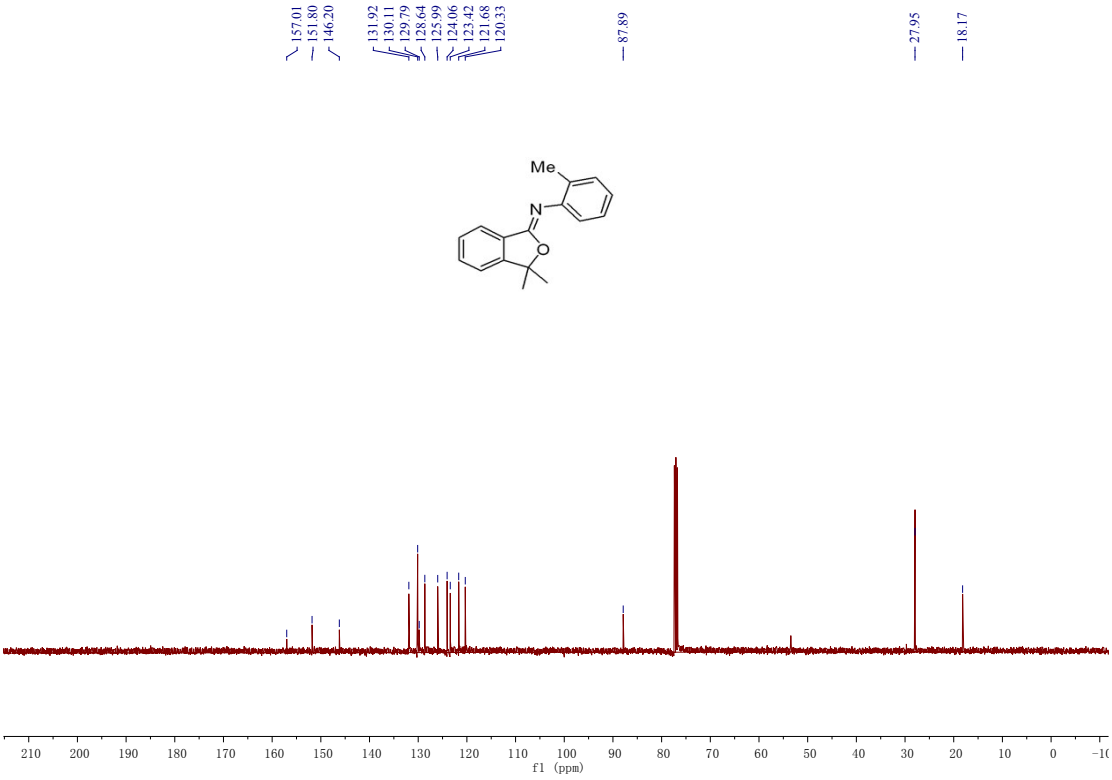
^{13}C NMR spectrum of compound **2g**



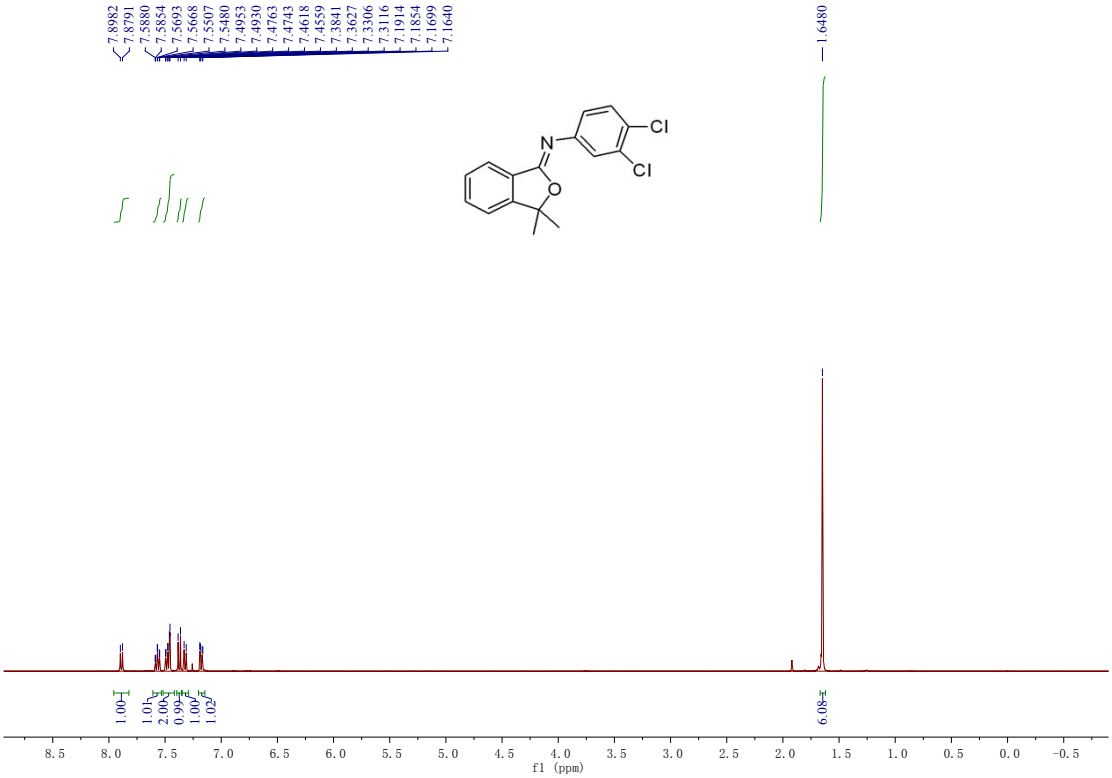
^{1}H NMR spectrum of compound **2h**



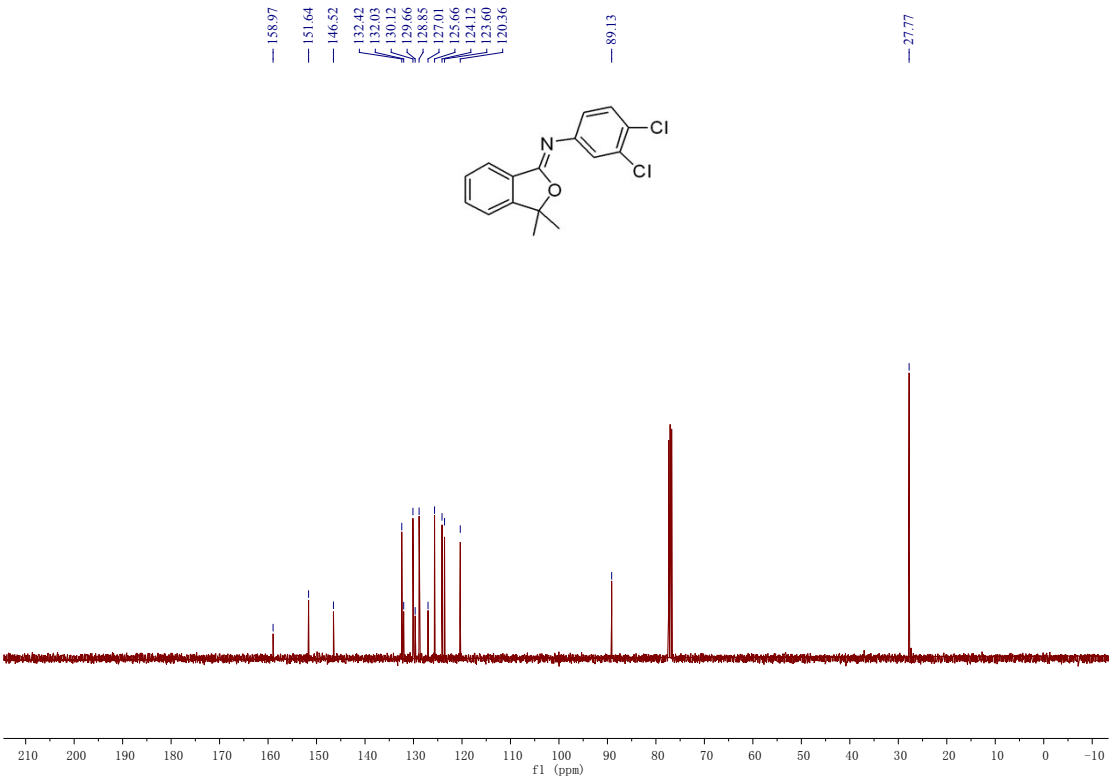
^{13}C NMR spectrum of compound **2h**



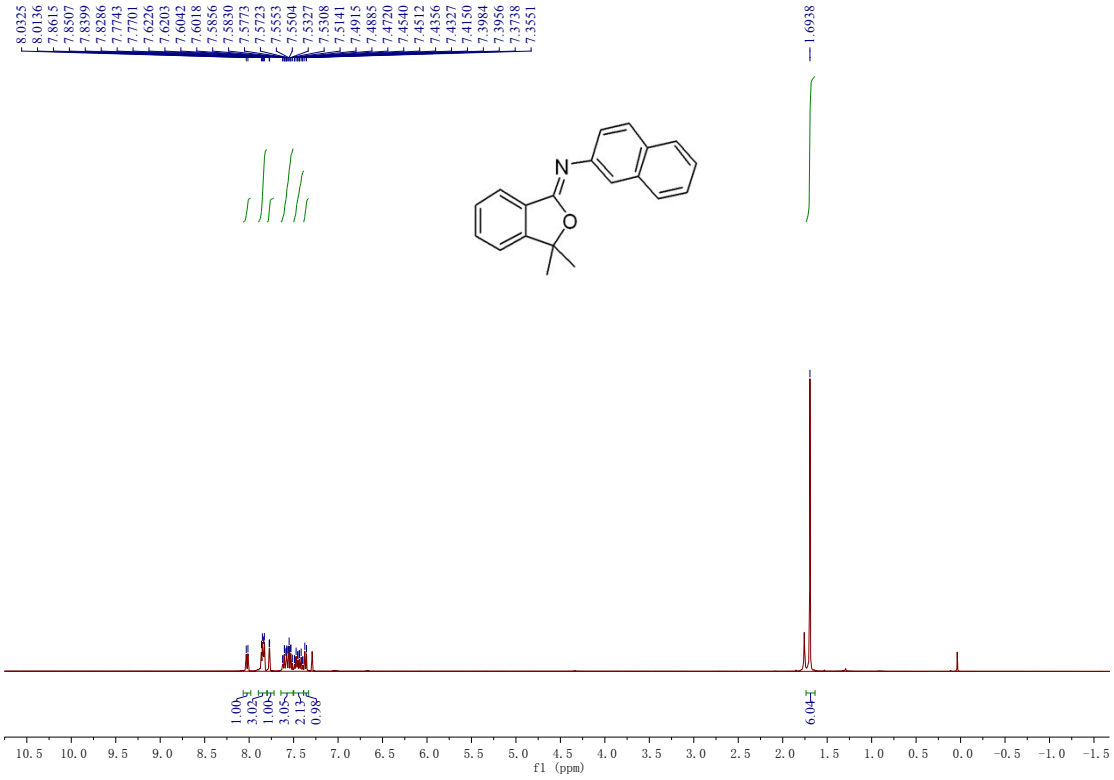
^{1}H NMR spectrum of compound **2i**



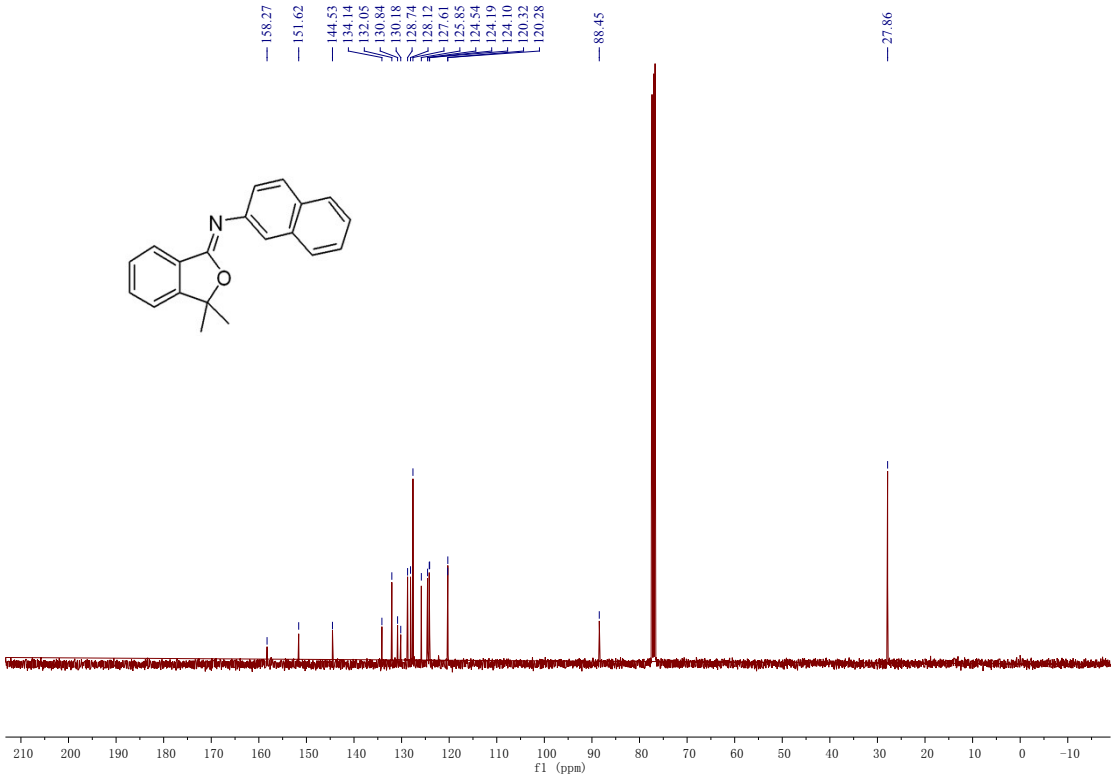
^{13}C NMR spectrum of compound **2i**



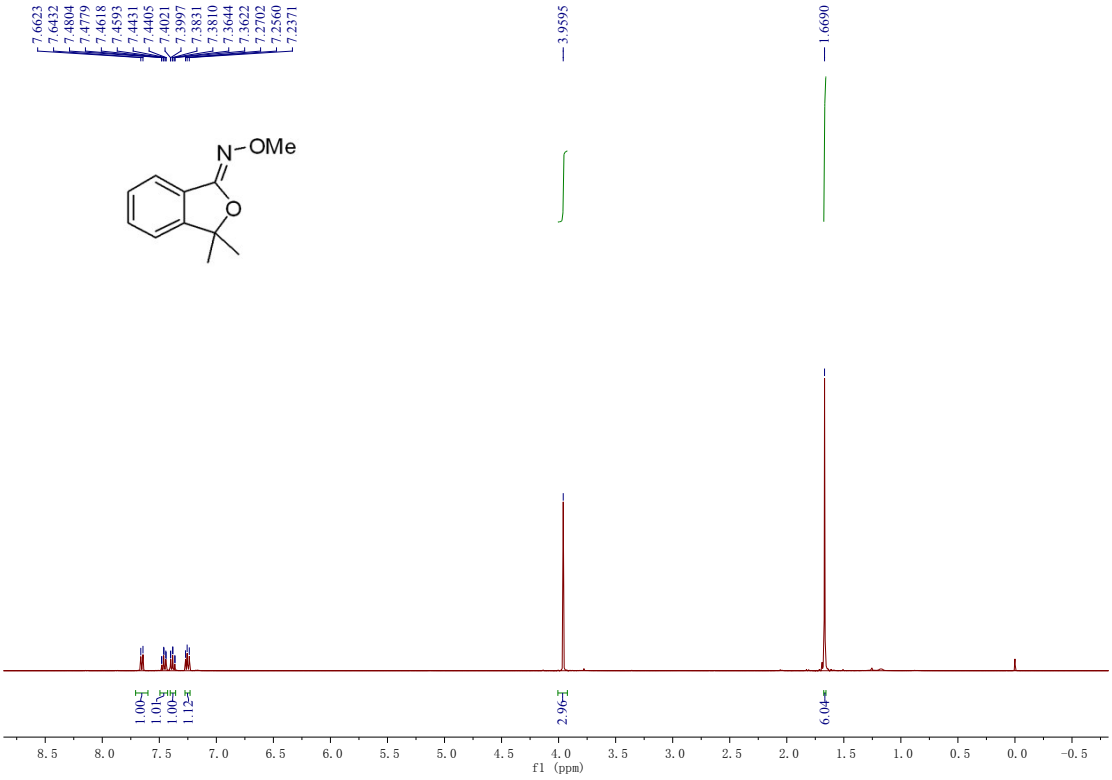
^{1}H NMR spectrum of compound **2j**



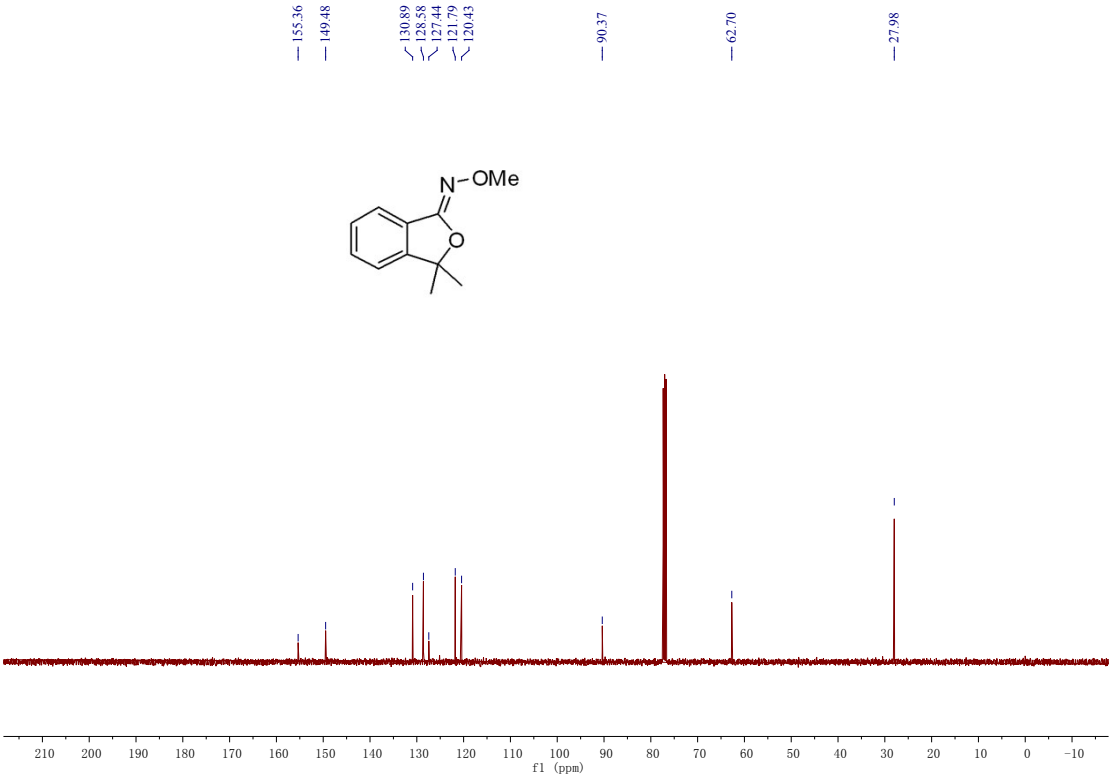
^{13}C NMR spectrum of compound **2j**



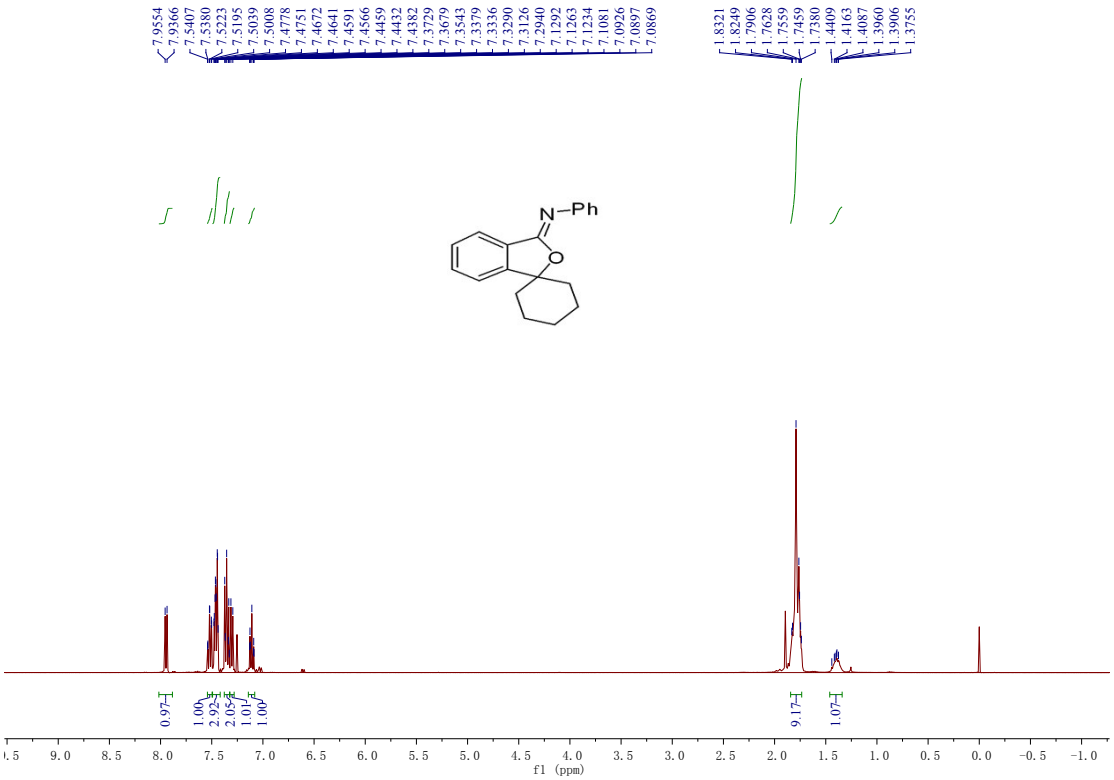
^{1}H NMR spectrum of compound **2k**



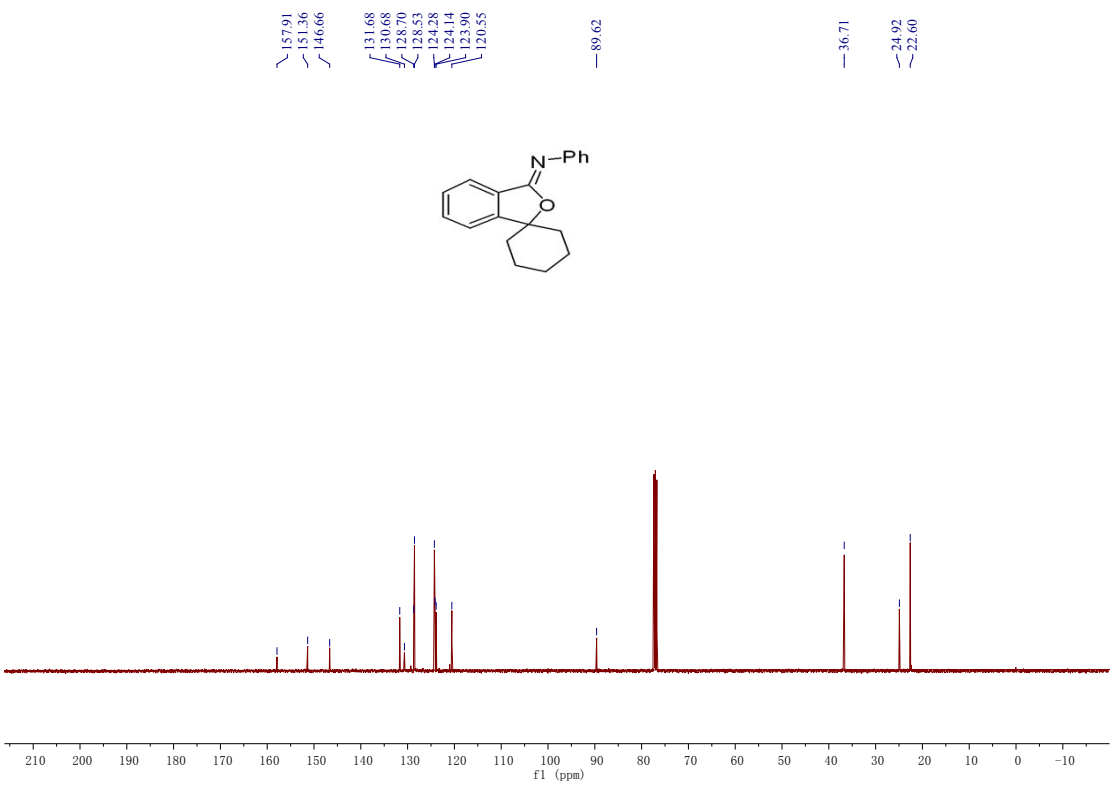
^{13}C NMR spectrum of compound **2k**



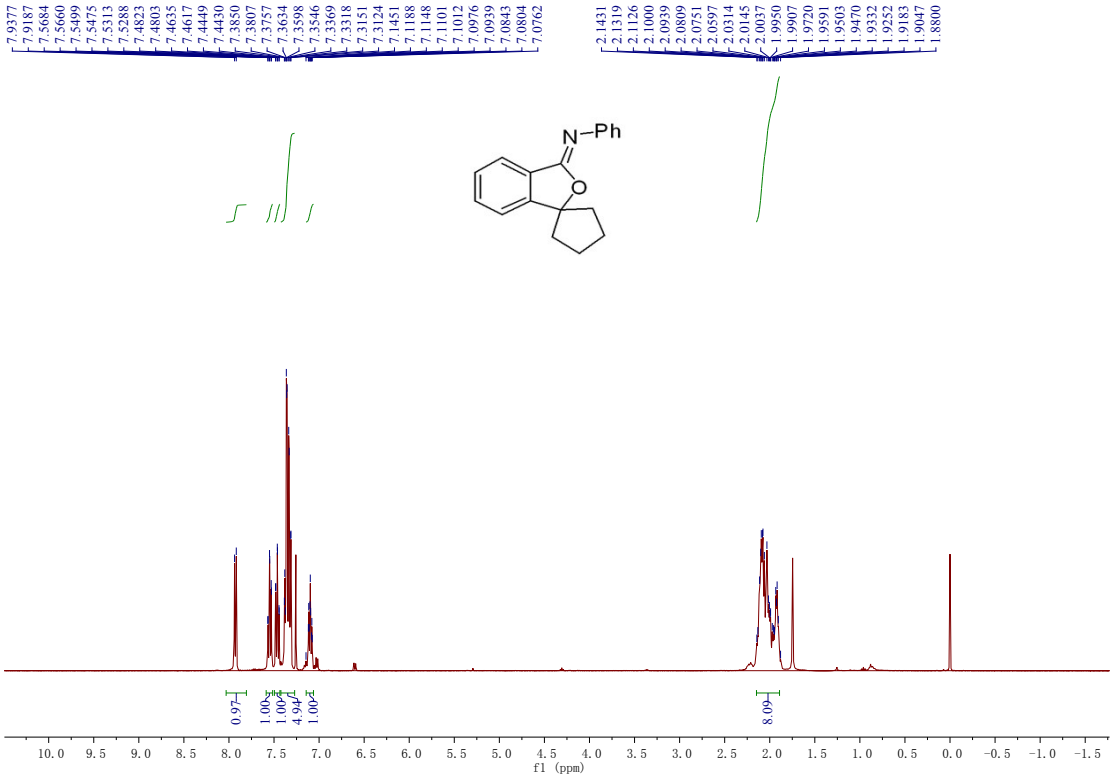
^{1}H NMR spectrum of compound **2l**



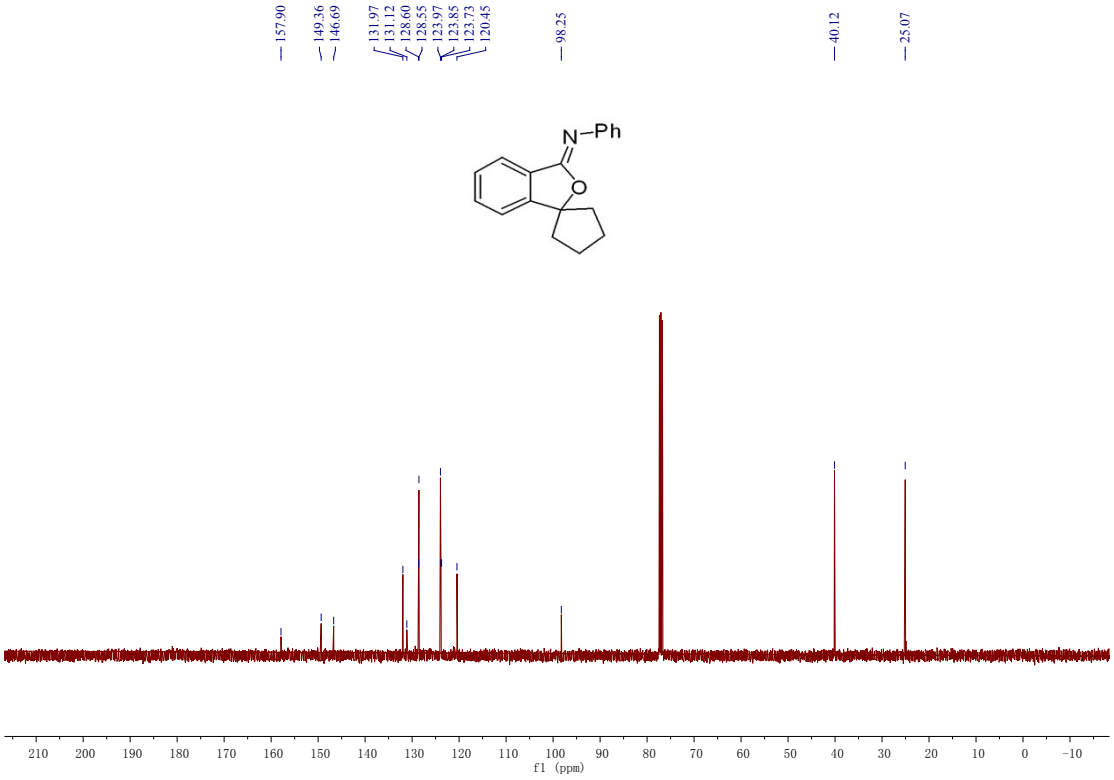
^{13}C NMR spectrum of compound **2l**



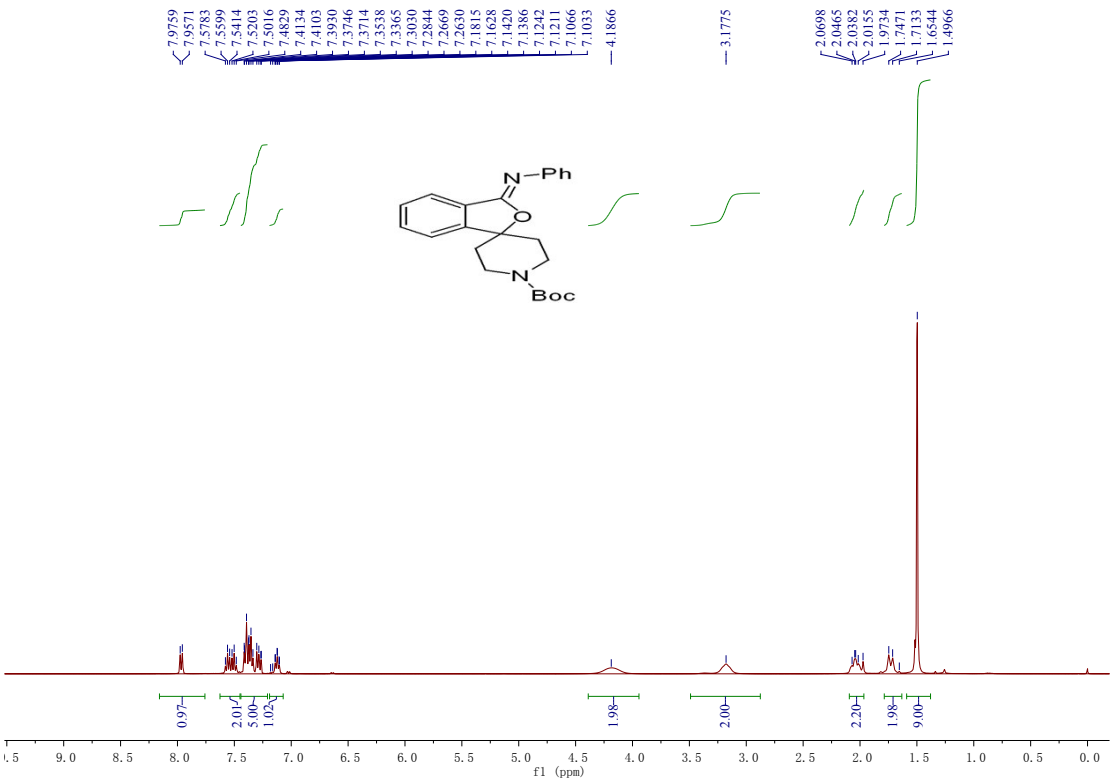
^{1}H NMR spectrum of compound **2m**



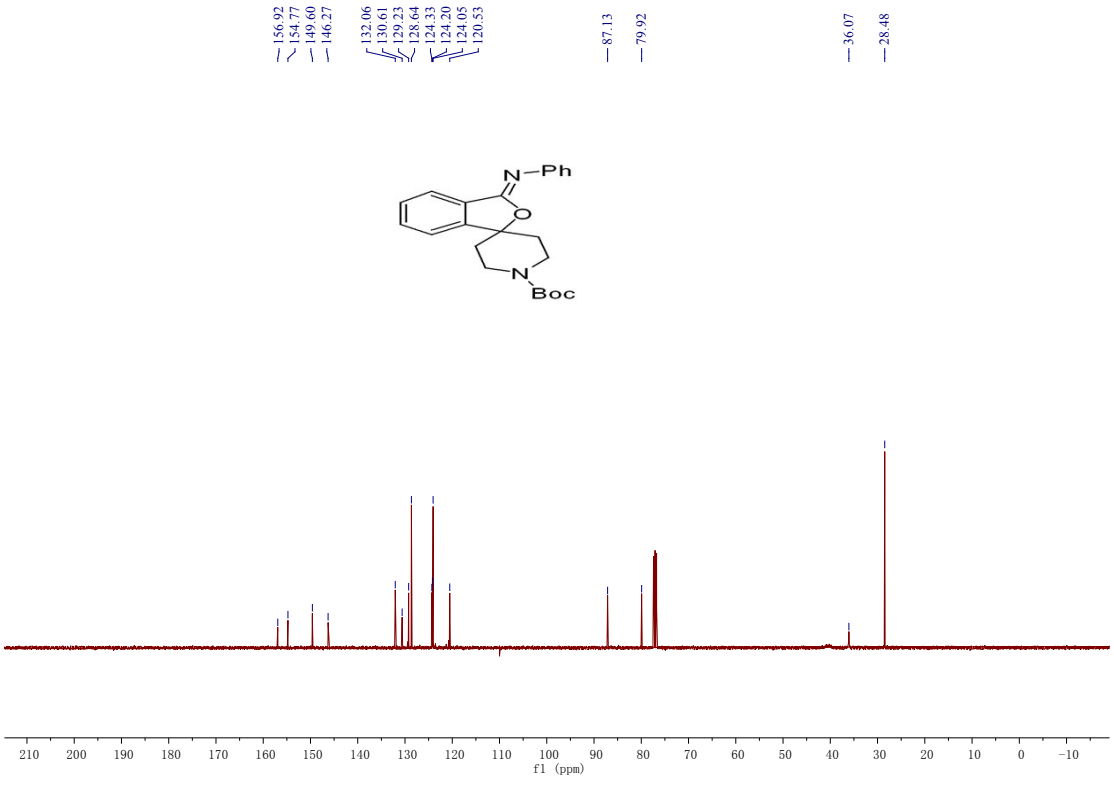
^{13}C NMR spectrum of compound **2m**



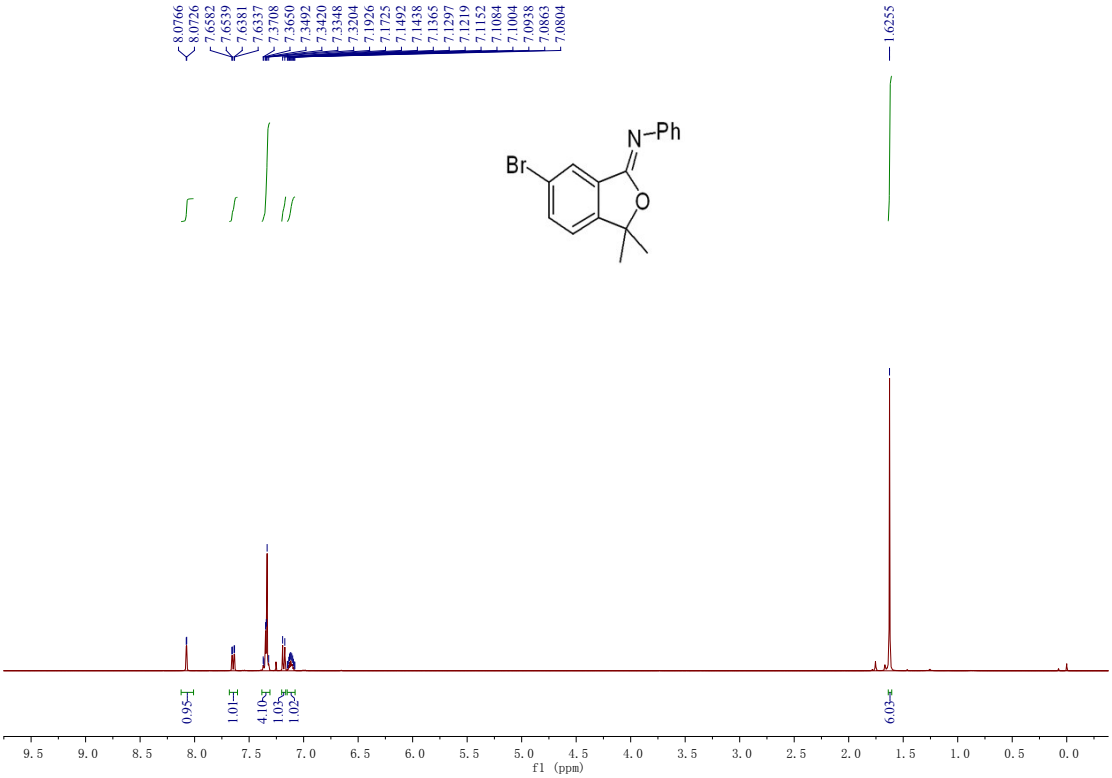
^{1}H NMR spectrum of compound **2n**



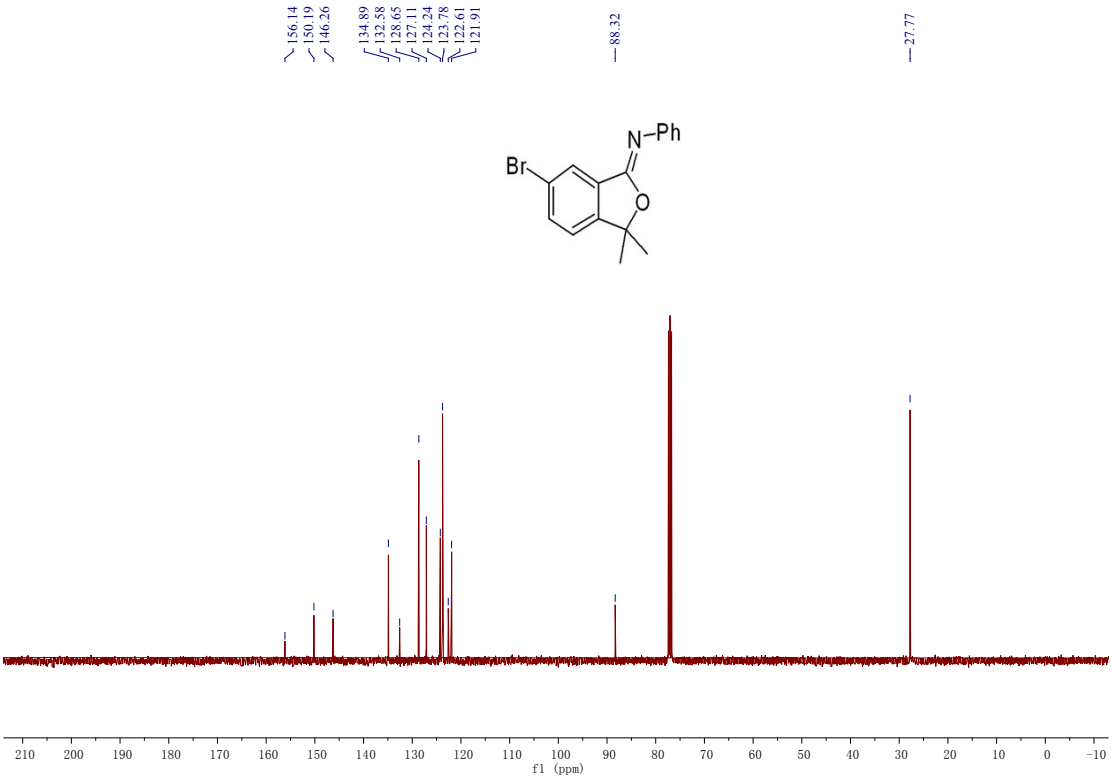
^{13}C NMR spectrum of compound **2n**



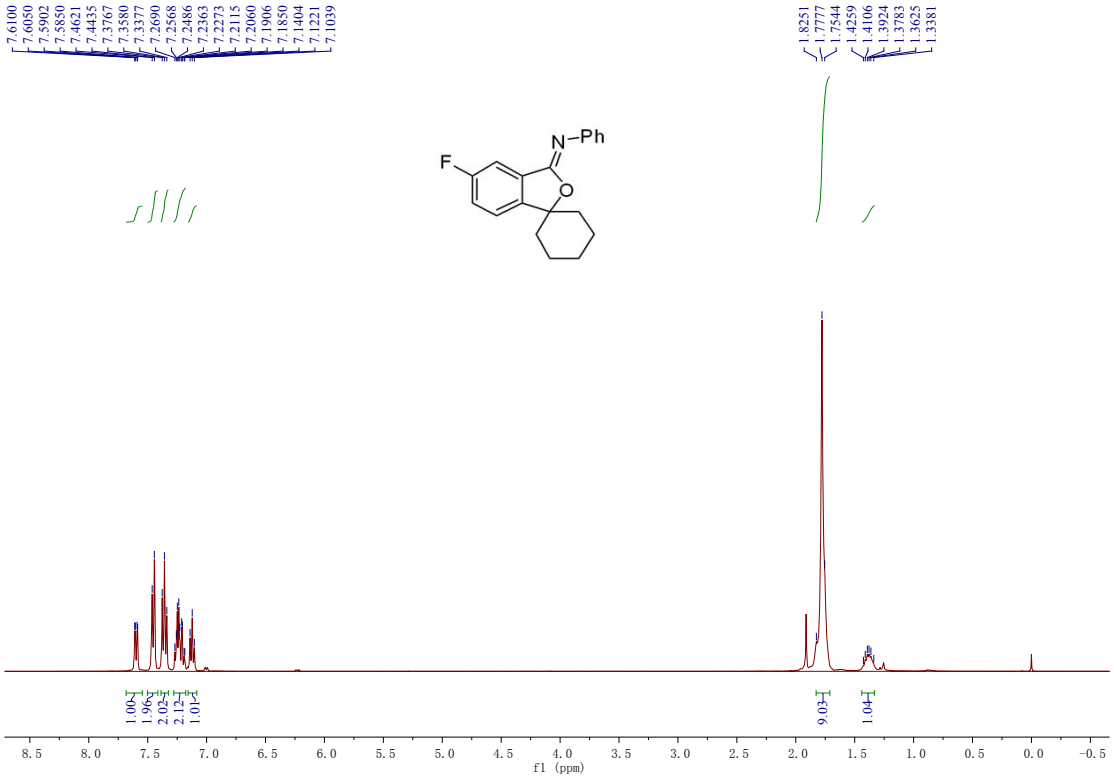
^{1}H NMR spectrum of compound **2o**



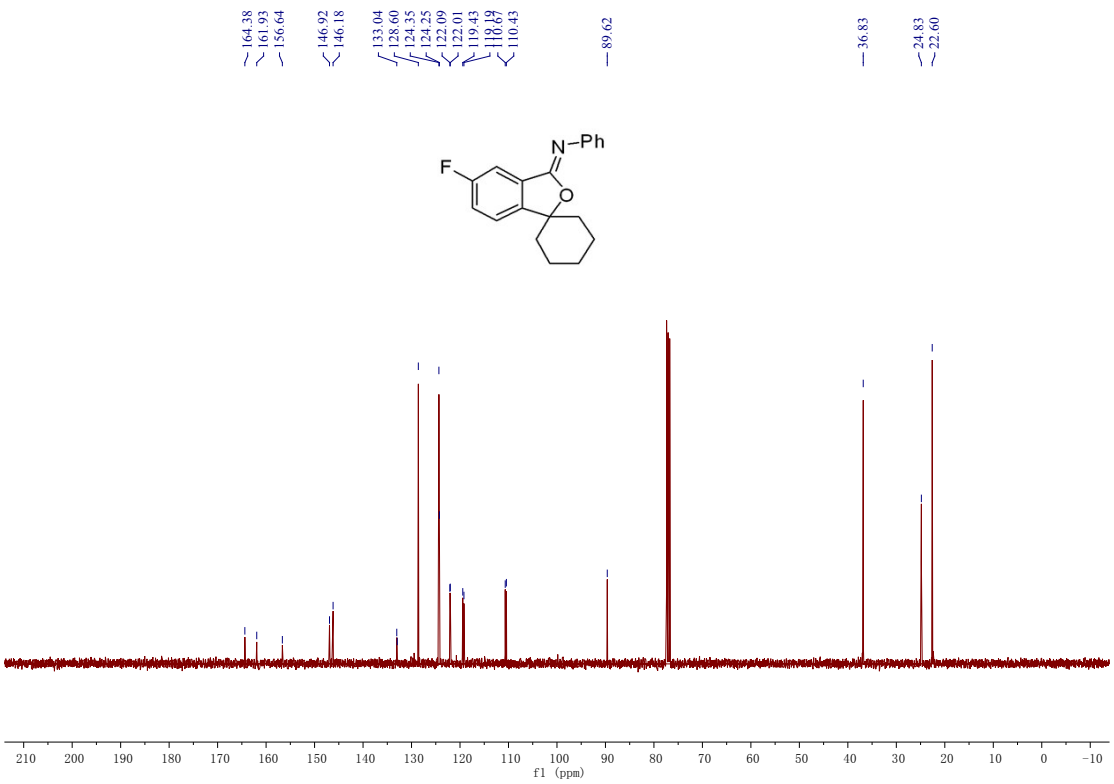
^{13}C NMR spectrum of compound **2o**



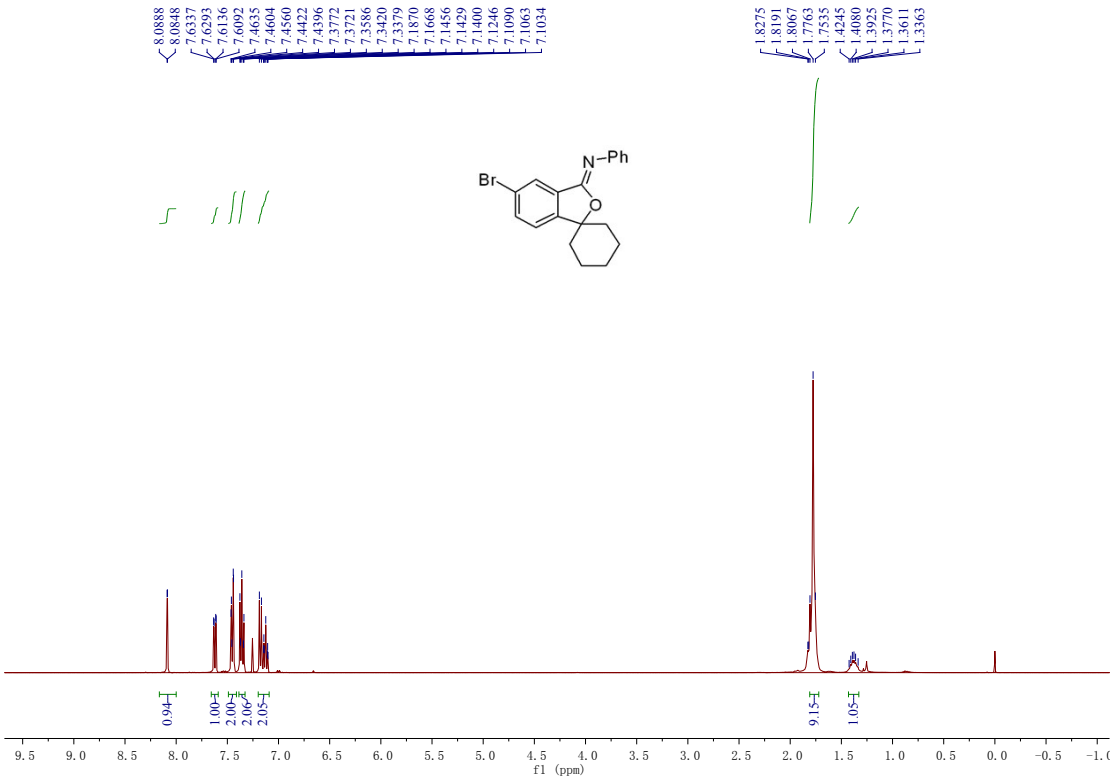
^{1}H NMR spectrum of compound **2p**



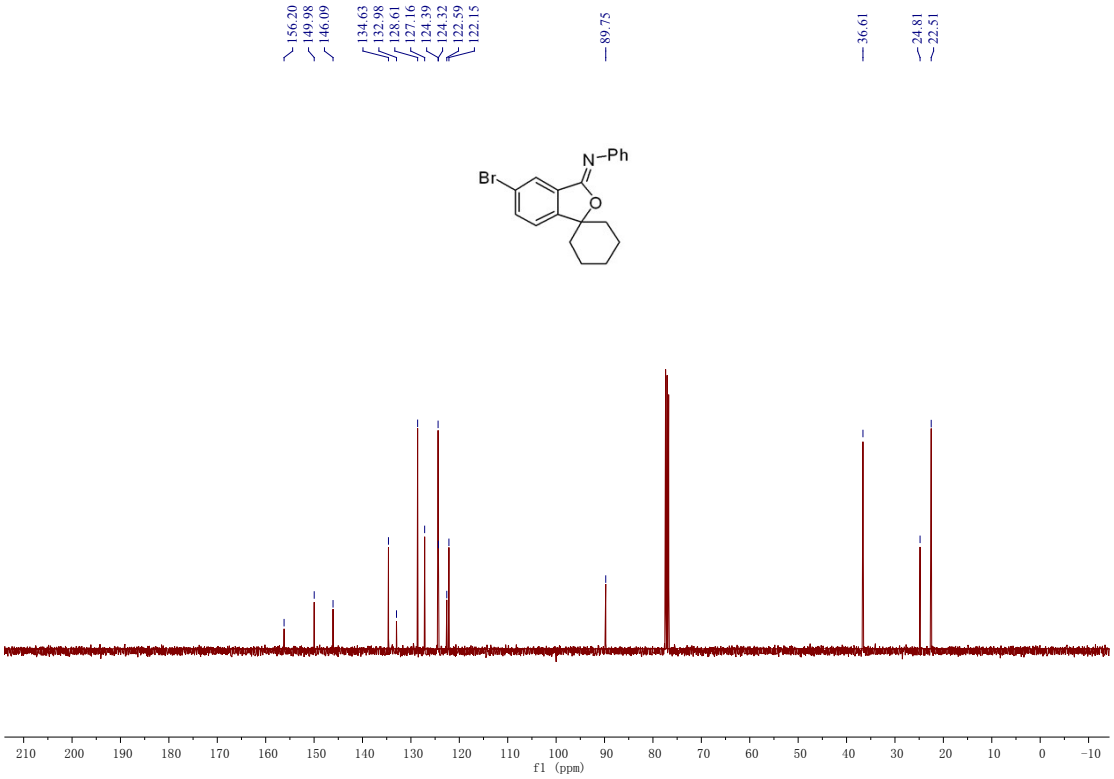
^{13}C NMR spectrum of compound **2p**



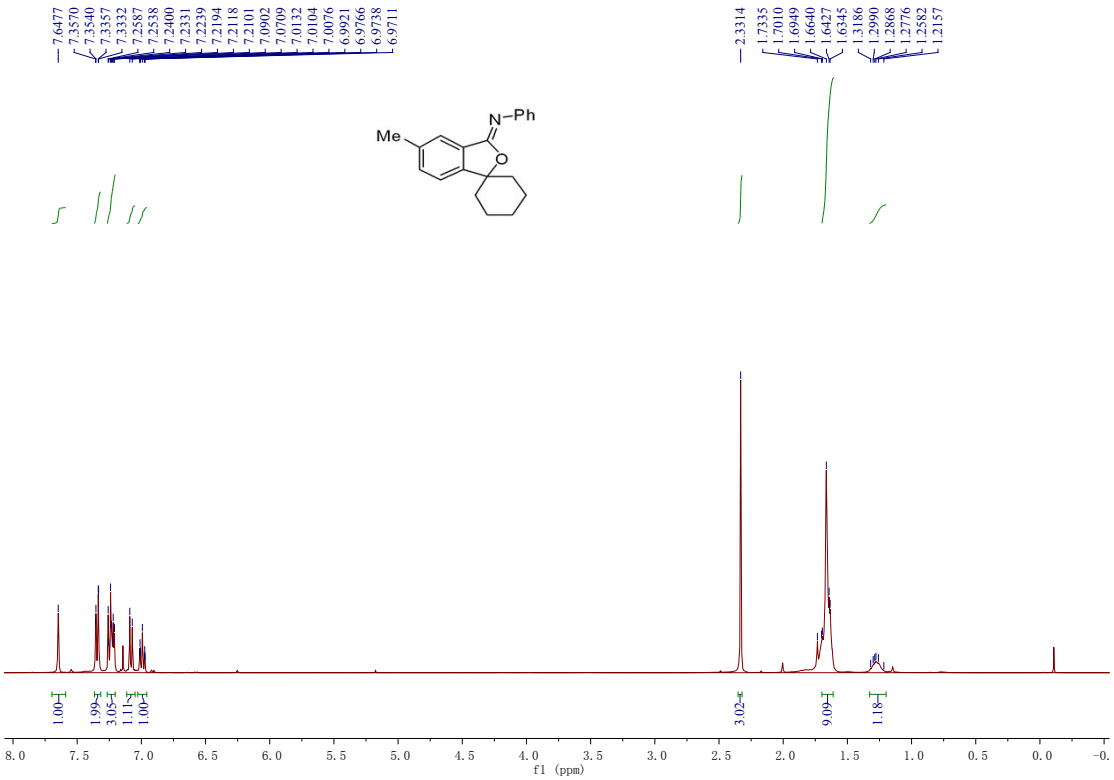
^{1}H NMR spectrum of compound **2q**



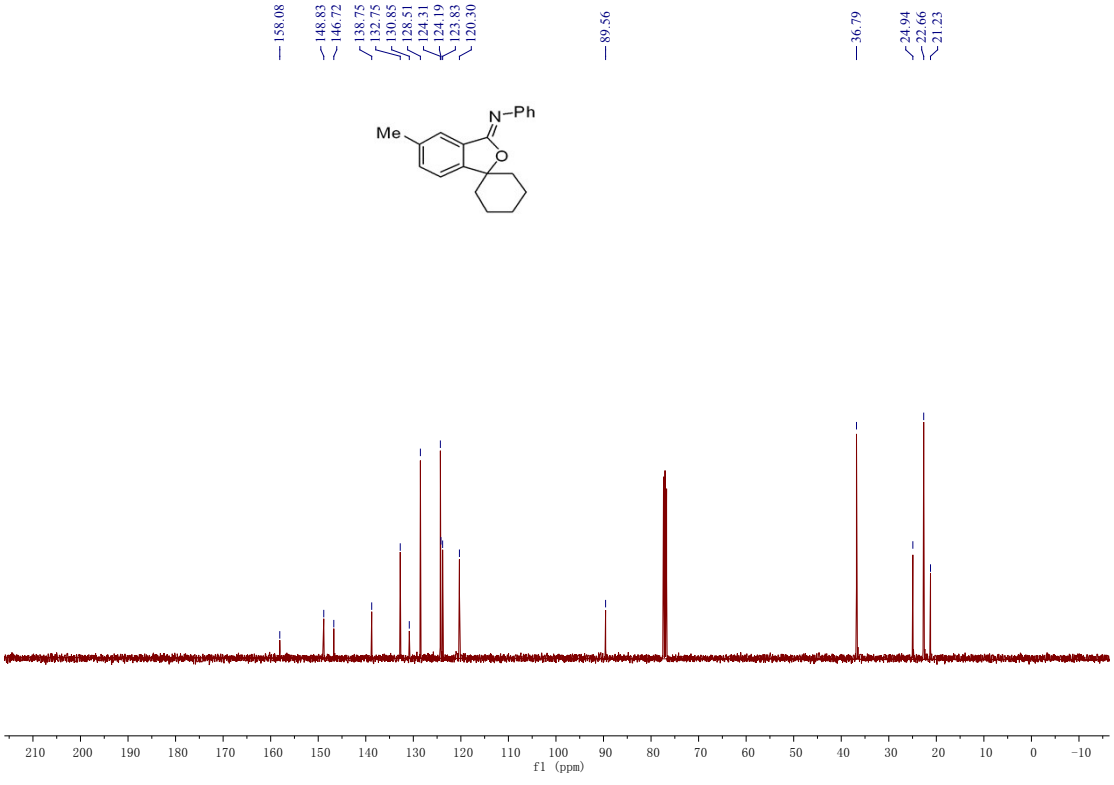
^{13}C NMR spectrum of compound **2q**



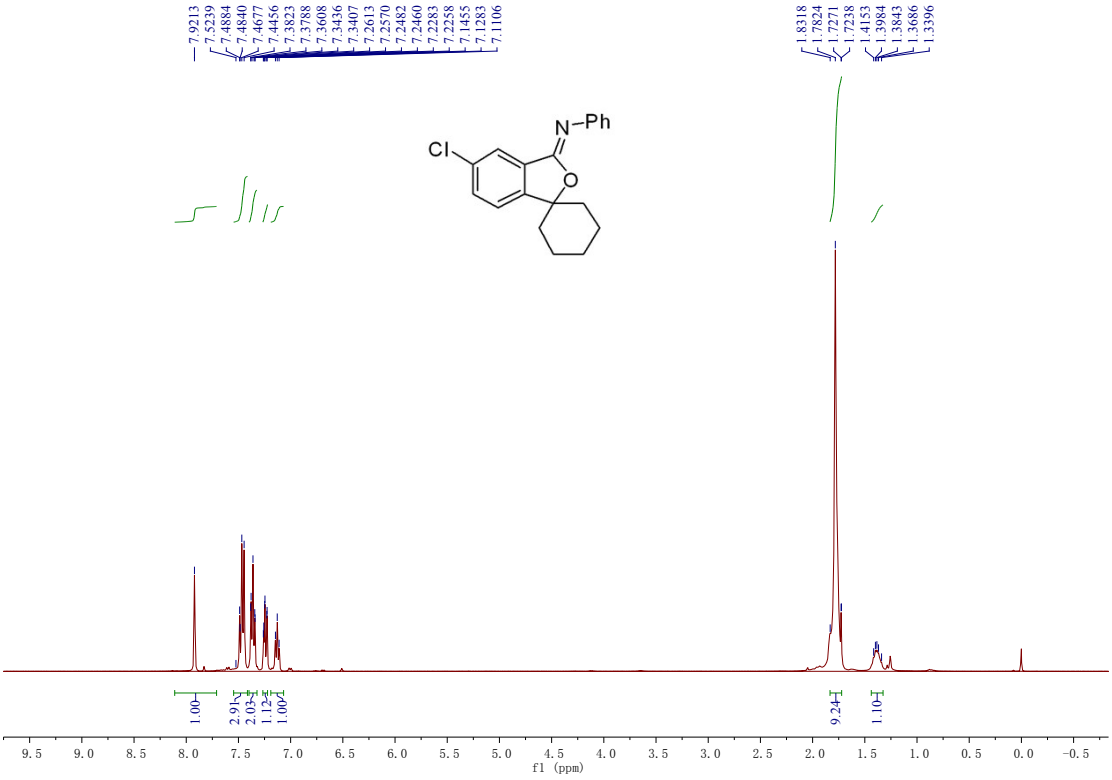
^{1}H NMR spectrum of compound **2r**



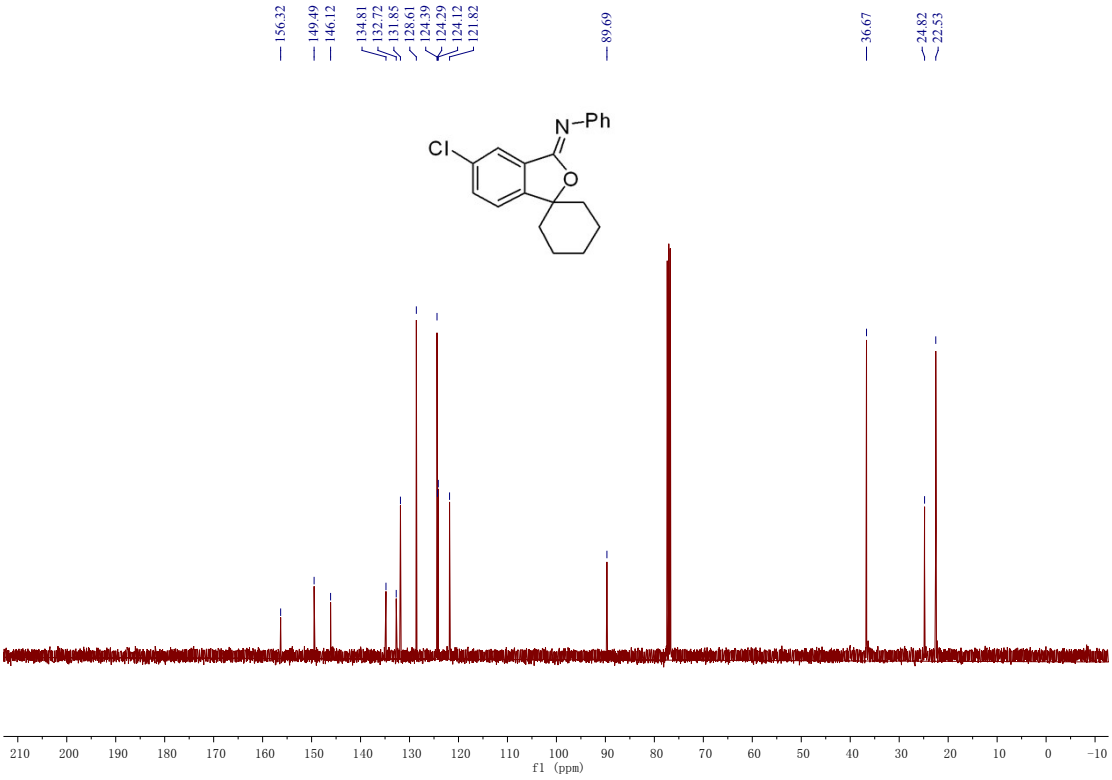
^{13}C NMR spectrum of compound **2r**



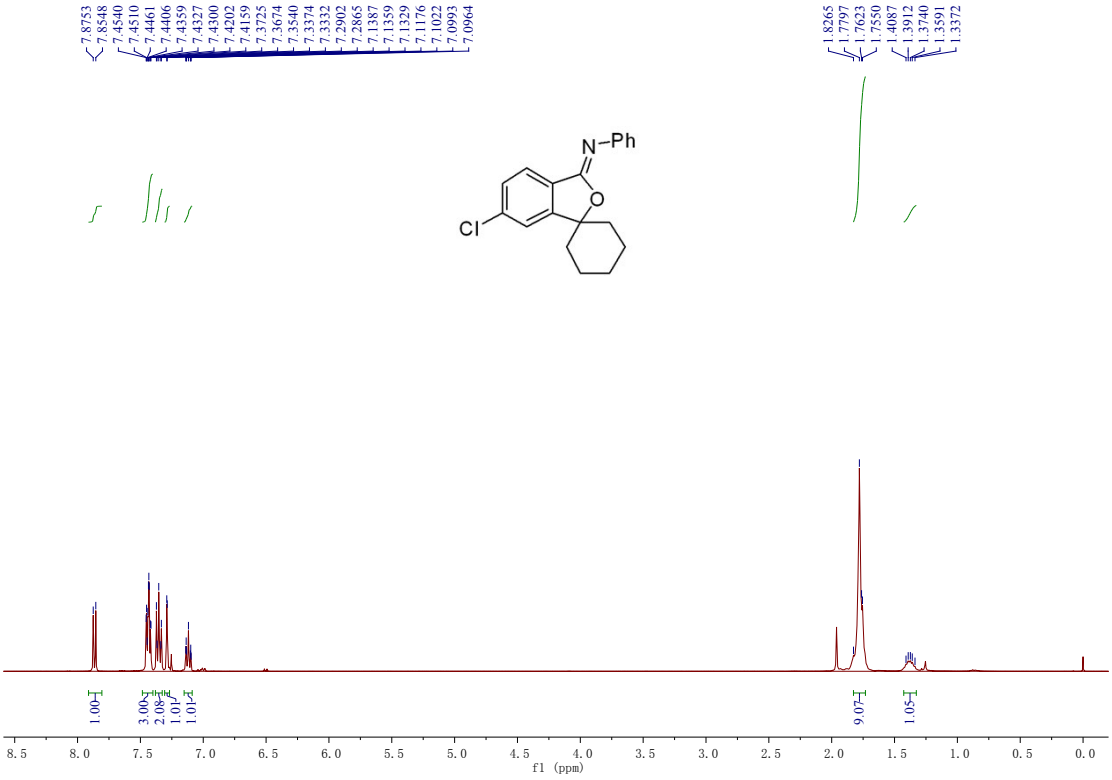
^{1}H NMR spectrum of compound **2s**



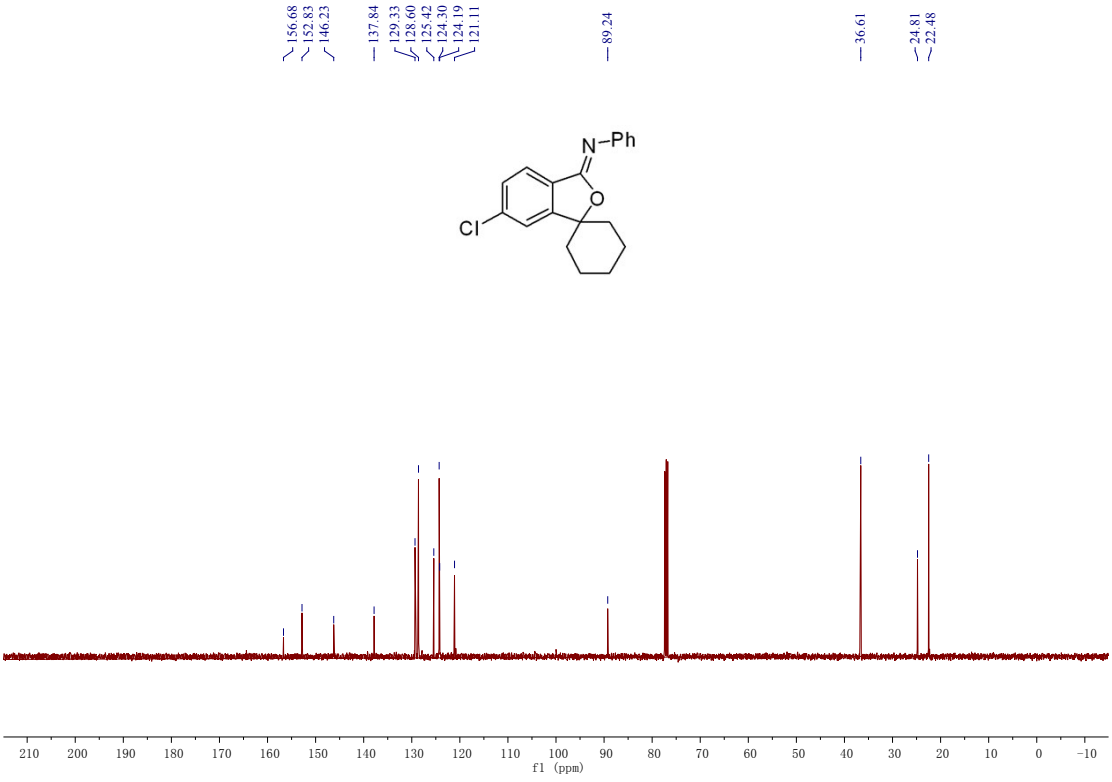
^{13}C NMR spectrum of compound **2s**



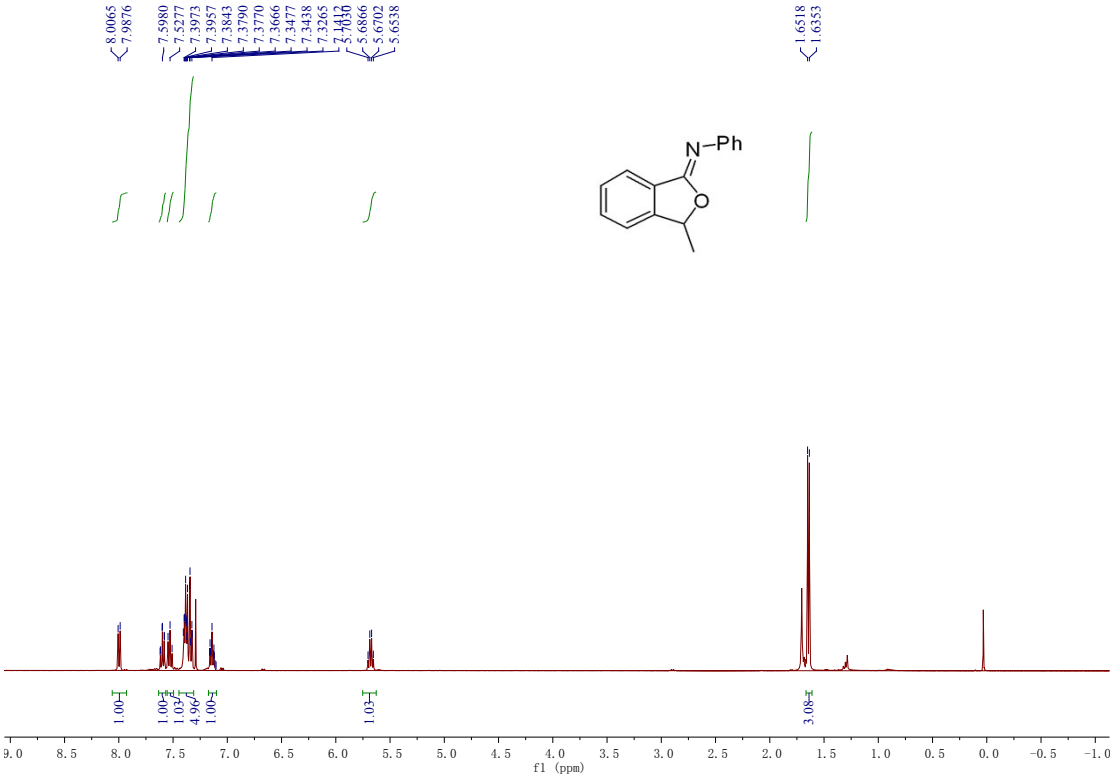
^{1}H NMR spectrum of compound **2t**



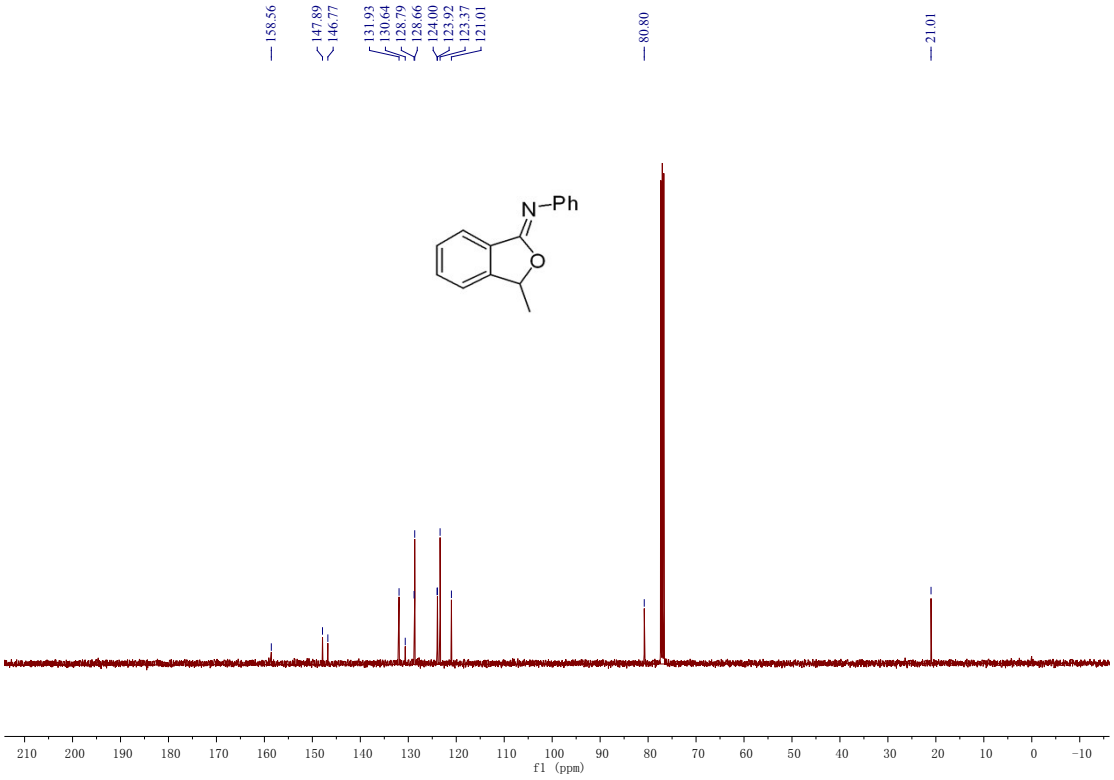
^{13}C NMR spectrum of compound **2t**



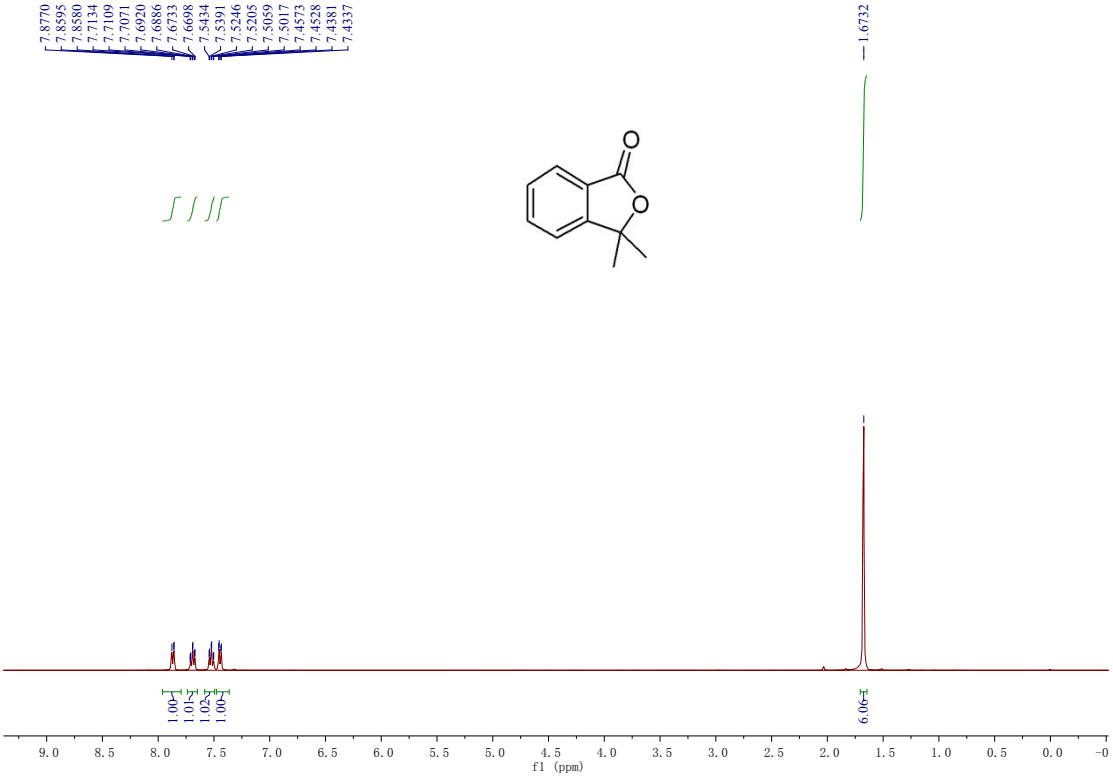
^{1}H NMR spectrum of compound **2u**



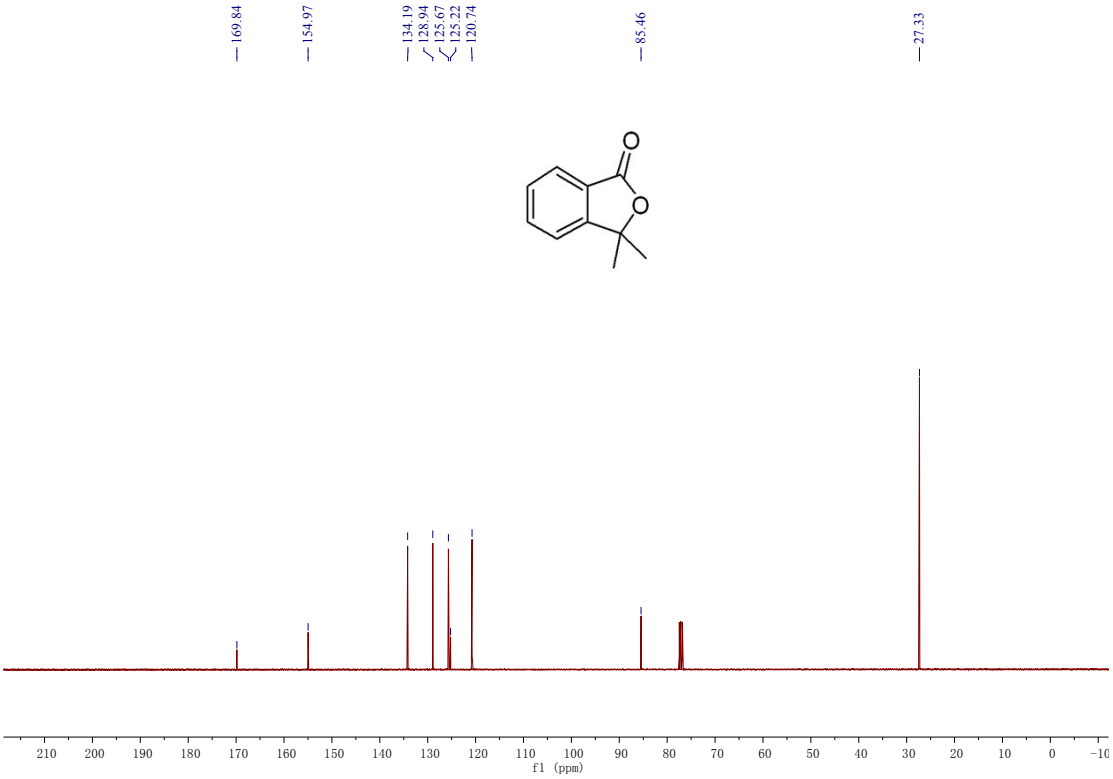
^{13}C NMR spectrum of compound **2u**



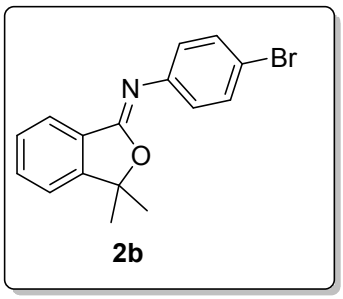
^{1}H NMR spectrum of compound **3**



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



4. X-ray single crystal data for product



2b

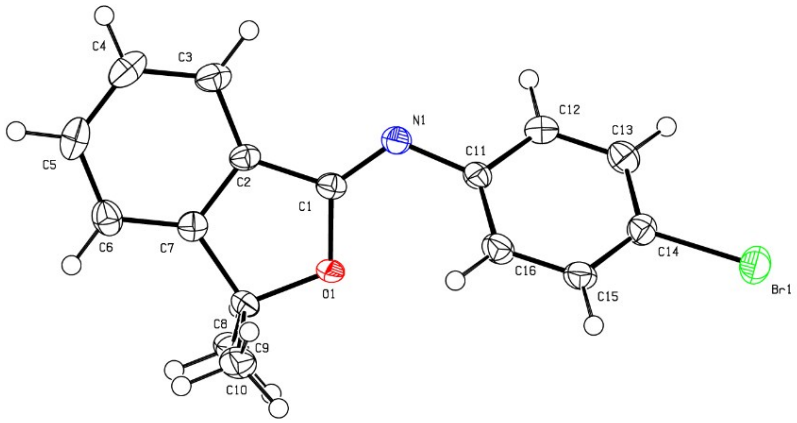


Table 1. Crystal data and structure refinement for **2b**.

Identification code	**2b**
Empirical formula	C16 H14 Br N O
Formula weight	316.19
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 15.304(3) A alpha = 90 deg.
	b = 5.8888(12) A beta = 106.59(3) deg.
	c = 16.007(3) A gamma = 90 deg.
Volume	1382.6(5) A^3
Z, Calculated density	4, 1.519 Mg/m^3
Absorption coefficient	2.964 mm^-1
F(000)	640
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	1.624 to 27.899 deg.

Limiting indices	-19<=h<=20, -7<=k<=7, -21<=l<=21
Reflections collected / unique	14182 / 3309 [R(int) = 0.0632]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.5159
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3309 / 0 / 175
Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0906
R indices (all data)	R1 = 0.0598, wR2 = 0.0978
Extinction coefficient	0.0337(15)
Largest diff. peak and hole	0.745 and -0.584 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for shelxl.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9110(1)	786(1)	8366(1)	34(1)
O(1)	7342(1)	8403(3)	5116(1)	25(1)
N(1)	8868(2)	7289(4)	5356(1)	23(1)
C(1)	8181(2)	8513(4)	4980(2)	21(1)
C(2)	8157(2)	10292(4)	4340(2)	21(1)
C(3)	8844(2)	11115(5)	4011(2)	29(1)
C(4)	8638(2)	12925(5)	3441(2)	35(1)
C(5)	7773(2)	13898(5)	3202(2)	33(1)
C(6)	7094(2)	13071(5)	3536(2)	29(1)
C(7)	7297(2)	11265(4)	4106(2)	22(1)

C(8)	6720(2)	10080(5)	4594(2)	23(1)
C(9)	5912(2)	8828(5)	4010(2)	31(1)
C(10)	6448(2)	11674(5)	5227(2)	34(1)
C(11)	8842(2)	5758(4)	6027(2)	21(1)
C(12)	9350(2)	3764(5)	6096(2)	26(1)
C(13)	9410(2)	2255(5)	6771(2)	27(1)
C(14)	8981(2)	2765(5)	7397(2)	25(1)
C(15)	8480(2)	4730(5)	7352(2)	27(1)
C(16)	8409(2)	6212(5)	6667(2)	28(1)

Table 3. Bond lengths [A] and angles [deg] for shelxl.

Br(1)-C(14)	1.904(3)
O(1)-C(1)	1.363(3)
O(1)-C(8)	1.458(3)
N(1)-C(1)	1.275(3)
N(1)-C(11)	1.412(3)
C(1)-C(2)	1.458(4)
C(2)-C(7)	1.385(4)
C(2)-C(3)	1.391(4)
C(3)-C(4)	1.380(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.391(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.386(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.378(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.507(4)
C(8)-C(9)	1.512(4)

C(8)-C(10)	1.524(4)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.395(4)
C(11)-C(16)	1.395(4)
C(12)-C(13)	1.382(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.378(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.379(4)
C(15)-C(16)	1.382(4)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500

C(1)-O(1)-C(8)	111.57(19)
C(1)-N(1)-C(11)	121.5(2)
N(1)-C(1)-O(1)	125.7(2)
N(1)-C(1)-C(2)	126.2(2)
O(1)-C(1)-C(2)	108.0(2)
C(7)-C(2)-C(3)	121.1(3)
C(7)-C(2)-C(1)	108.6(2)
C(3)-C(2)-C(1)	130.2(2)
C(4)-C(3)-C(2)	117.7(3)
C(4)-C(3)-H(3)	121.2
C(2)-C(3)-H(3)	121.2
C(3)-C(4)-C(5)	121.3(3)

C(3)-C(4)-H(4)	119.3
C(5)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	120.5(3)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(7)-C(6)-C(5)	118.4(3)
C(7)-C(6)-H(6)	120.8
C(5)-C(6)-H(6)	120.8
C(6)-C(7)-C(2)	121.0(3)
C(6)-C(7)-C(8)	130.3(3)
C(2)-C(7)-C(8)	108.7(2)
O(1)-C(8)-C(7)	103.1(2)
O(1)-C(8)-C(9)	108.0(2)
C(7)-C(8)-C(9)	113.7(2)
O(1)-C(8)-C(10)	107.1(2)
C(7)-C(8)-C(10)	111.8(2)
C(9)-C(8)-C(10)	112.5(2)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	118.3(2)

C(12)-C(11)-N(1)	117.5(2)
C(16)-C(11)-N(1)	124.0(2)
C(13)-C(12)-C(11)	121.0(3)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(14)-C(13)-C(12)	119.3(3)
C(14)-C(13)-H(13)	120.4
C(12)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	121.2(3)
C(13)-C(14)-Br(1)	119.9(2)
C(15)-C(14)-Br(1)	118.9(2)
C(14)-C(15)-C(16)	119.2(3)
C(14)-C(15)-H(15)	120.4
C(16)-C(15)-H(15)	120.4
C(15)-C(16)-C(11)	121.1(3)
C(15)-C(16)-H(16)	119.5
C(11)-C(16)-H(16)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for shelxl.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	37(1)	33(1)	32(1)	8(1)	9(1)	0(1)
O(1)	13(1)	36(1)	26(1)	10(1)	6(1)	4(1)
N(1)	20(1)	28(1)	22(1)	1(1)	6(1)	2(1)
C(1)	18(1)	25(1)	19(1)	-3(1)	5(1)	0(1)
C(2)	20(1)	26(1)	19(1)	-3(1)	7(1)	-2(1)

C(3)	23(1)	41(2)	23(1)	-3(1)	8(1)	-4(1)
C(4)	38(2)	43(2)	24(2)	0(1)	10(1)	-16(1)
C(5)	50(2)	24(2)	25(2)	4(1)	10(1)	-3(1)
C(6)	34(2)	24(2)	28(2)	-1(1)	7(1)	6(1)
C(7)	26(1)	22(1)	17(1)	-4(1)	6(1)	0(1)
C(8)	18(1)	26(1)	25(1)	3(1)	7(1)	6(1)
C(9)	20(1)	34(2)	38(2)	1(1)	6(1)	1(1)
C(10)	35(2)	42(2)	29(2)	-2(1)	16(1)	10(1)
C(11)	15(1)	26(1)	20(1)	0(1)	2(1)	-1(1)
C(12)	23(1)	29(2)	28(1)	-2(1)	10(1)	-1(1)
C(13)	29(2)	24(1)	30(2)	-2(1)	9(1)	4(1)
C(14)	23(1)	27(1)	22(1)	1(1)	3(1)	-2(1)
C(15)	22(1)	38(2)	23(1)	0(1)	8(1)	4(1)
C(16)	27(2)	33(2)	26(1)	0(1)	9(1)	8(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for shelxl.

	x	y	z	U(eq)
H(3)	9435	10454	4173	34
H(4)	9095	13519	3206	42
H(5)	7648	15140	2807	40
H(6)	6503	13733	3375	34
H(9A)	6123	7781	3633	47
H(9B)	5485	9923	3650	47
H(9C)	5606	7969	4369	47
H(10A)	6147	10804	5588	51
H(10B)	6029	12832	4899	51
H(10C)	6994	12411	5602	51
H(12)	9659	3439	5673	31

H(13)	9744	881	6804	33
H(15)	8186	5060	7787	33
H(16)	8061	7563	6631	34

Table 6. Torsion angles [deg] for shelxl.

C(11)-N(1)-C(1)-O(1)	-5.1(4)
C(11)-N(1)-C(1)-C(2)	173.9(2)
C(8)-O(1)-C(1)-N(1)	178.6(2)
C(8)-O(1)-C(1)-C(2)	-0.6(3)
N(1)-C(1)-C(2)-C(7)	-178.3(2)
O(1)-C(1)-C(2)-C(7)	0.9(3)
N(1)-C(1)-C(2)-C(3)	-2.0(5)
O(1)-C(1)-C(2)-C(3)	177.2(3)
C(7)-C(2)-C(3)-C(4)	-0.3(4)
C(1)-C(2)-C(3)-C(4)	-176.2(3)
C(2)-C(3)-C(4)-C(5)	0.0(4)
C(3)-C(4)-C(5)-C(6)	0.2(4)
C(4)-C(5)-C(6)-C(7)	-0.1(4)
C(5)-C(6)-C(7)-C(2)	-0.1(4)
C(5)-C(6)-C(7)-C(8)	177.3(3)
C(3)-C(2)-C(7)-C(6)	0.3(4)
C(1)-C(2)-C(7)-C(6)	177.1(2)
C(3)-C(2)-C(7)-C(8)	-177.6(2)
C(1)-C(2)-C(7)-C(8)	-0.8(3)
C(1)-O(1)-C(8)-C(7)	0.1(3)
C(1)-O(1)-C(8)-C(9)	120.7(2)
C(1)-O(1)-C(8)-C(10)	-118.0(2)
C(6)-C(7)-C(8)-O(1)	-177.2(3)
C(2)-C(7)-C(8)-O(1)	0.5(3)

C(6)-C(7)-C(8)-C(9)	66.2(4)
C(2)-C(7)-C(8)-C(9)	-116.2(2)
C(6)-C(7)-C(8)-C(10)	-62.5(4)
C(2)-C(7)-C(8)-C(10)	115.2(2)
C(1)-N(1)-C(11)-C(12)	147.4(3)
C(1)-N(1)-C(11)-C(16)	-38.6(4)
C(16)-C(11)-C(12)-C(13)	1.2(4)
N(1)-C(11)-C(12)-C(13)	175.5(2)
C(11)-C(12)-C(13)-C(14)	-1.8(4)
C(12)-C(13)-C(14)-C(15)	1.2(4)
C(12)-C(13)-C(14)-Br(1)	-176.7(2)
C(13)-C(14)-C(15)-C(16)	-0.1(4)
Br(1)-C(14)-C(15)-C(16)	177.8(2)
C(14)-C(15)-C(16)-C(11)	-0.5(4)
C(12)-C(11)-C(16)-C(15)	0.0(4)
N(1)-C(11)-C(16)-C(15)	-174.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for shelxl [A and deg.].

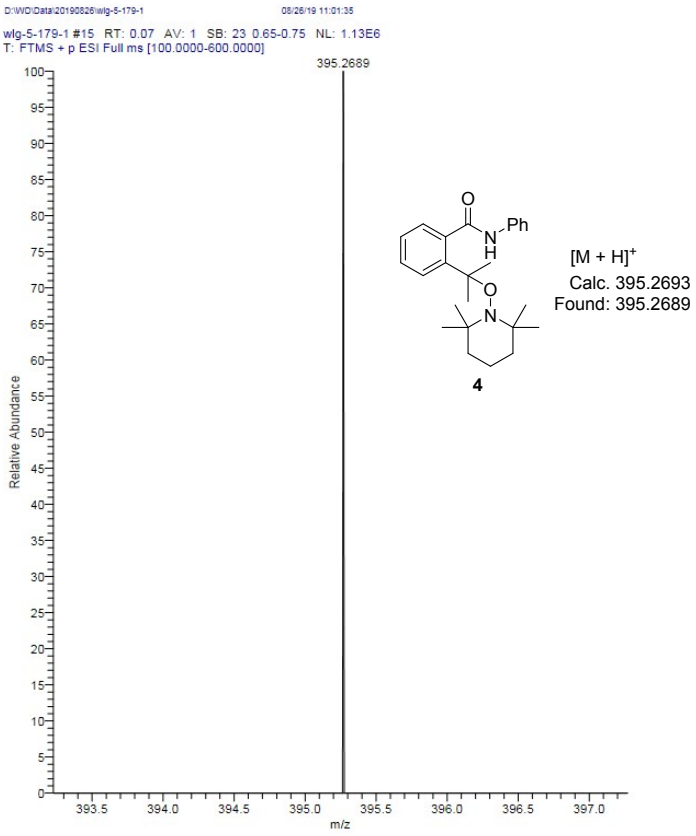
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

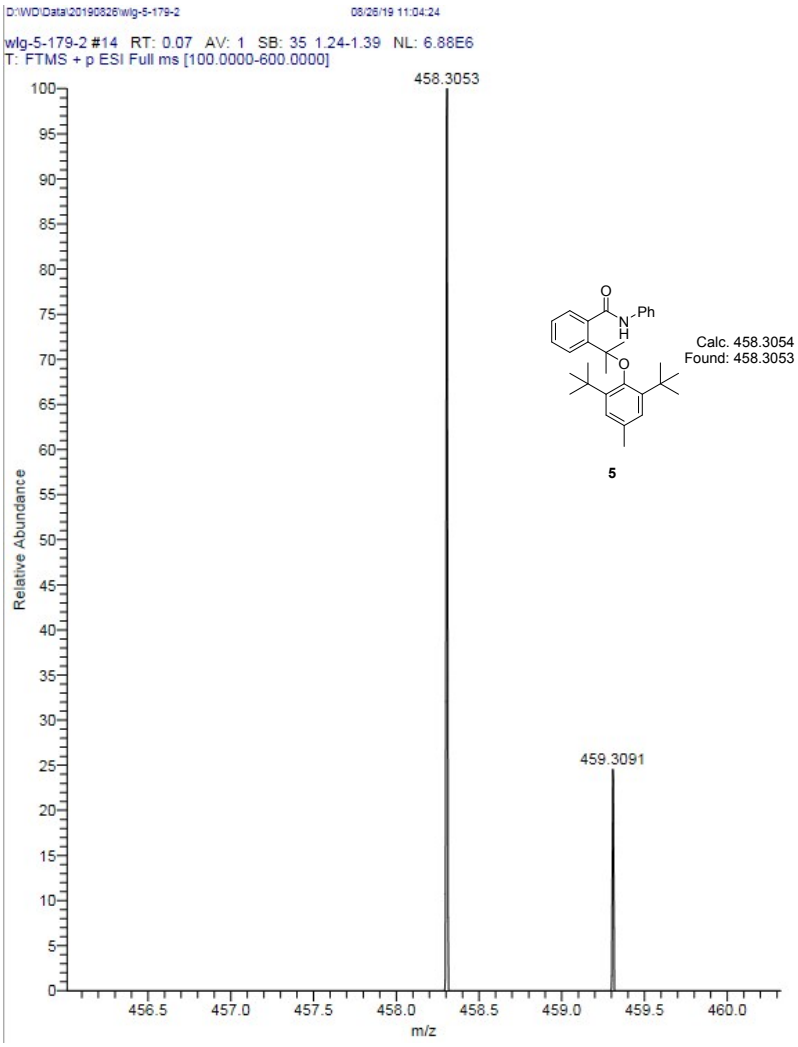
5. Analytical data of HRMS

When 2.0 eq TEMPO or BHT was added to the above reaction mixture, the reaction was inhibited. When 2.0 eq TEMPO or BHT was added to the reaction of **1a**, the reaction was monitored by mass spectrometry experiment. Byproducts **4** and **5** were observed by mass spectrometry, which corresponds to the products of the radical captured by TEMPO and BHT. So we think this is a radical mechanism.

In addition, when we carried out the reaction in the solvent of DCE (Table 1, entry 1), intermolecular oxidation product **6** was detected by mass spectrometry, suggesting

that an alkyl cation had been generated.

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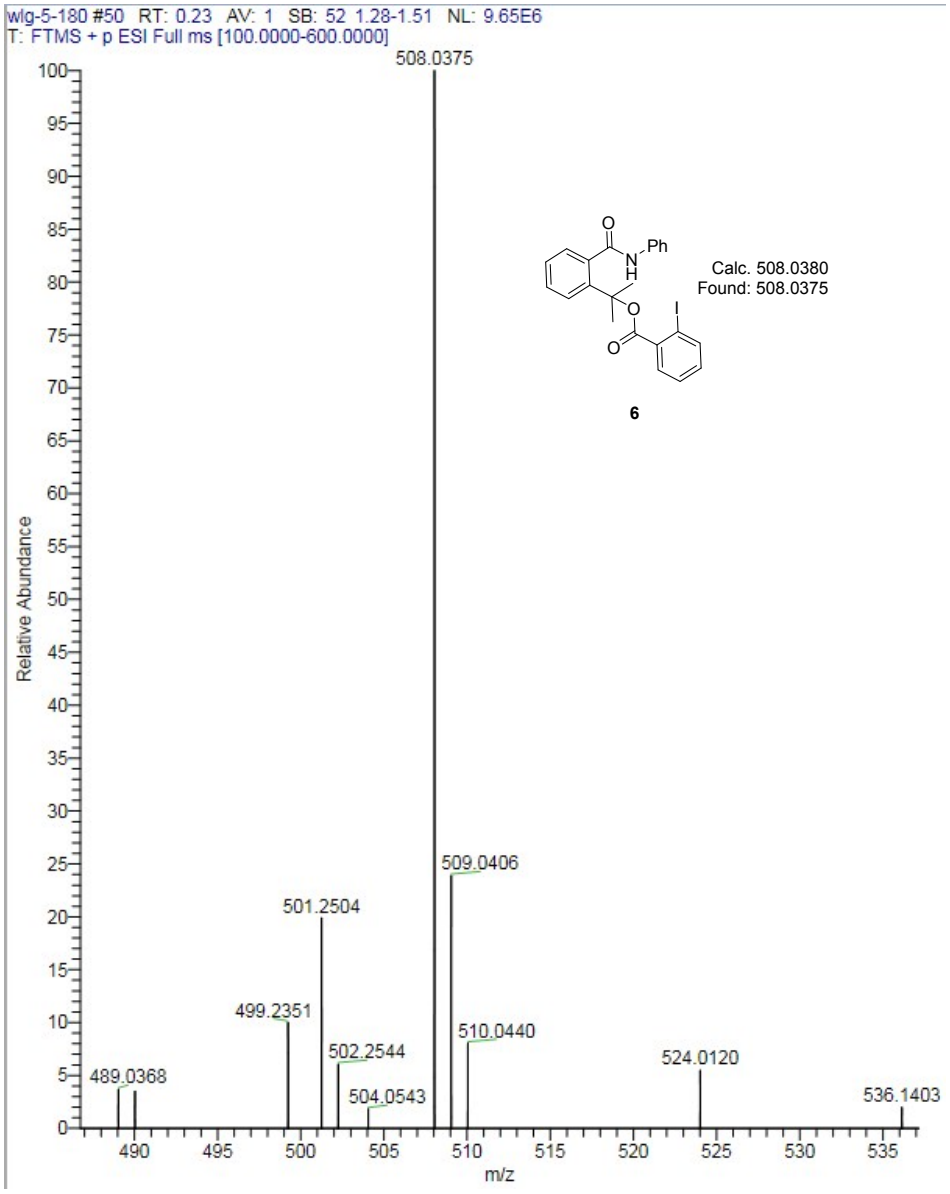
T: FTMS + p ESI Full ms [100.0000-600.0000]
458.3053
459.3091
Relative Abundance
m/z
456.5
457.0
457.5
458.0
458.5
459.0
459.5
460.0
O
N
H
Ph
O
Calc. 458.3054
Found: 458.3053
5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502.2544
524.0120
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504.0543
536.1403
Relative Abundance
m/z
Calc. 508.0380
Found: 508.0375
6