Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Pd(II)-Catalyzed oxidative dearomatization of indoles: substrate-controlled synthesis of indolines and indolones

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1. General information

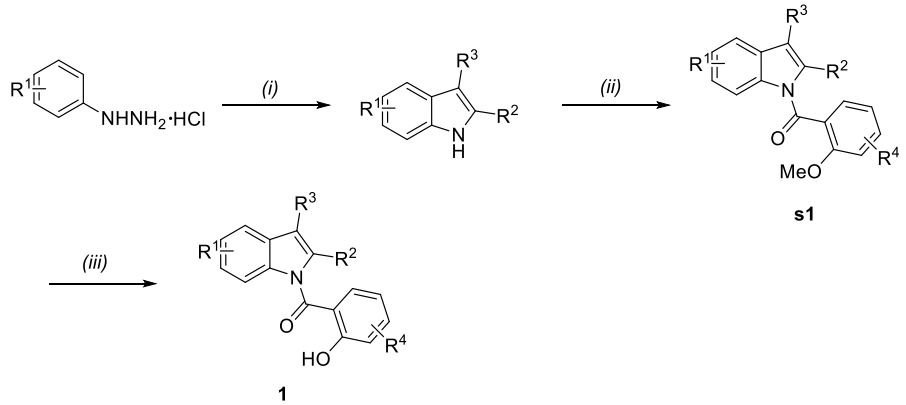
Reagents and solvents: $Pd(OAc)_2$ and 4,5-diaza-9-fluorenone (DAF) are commercially available. PE refers to petroleum ether b. p. 60-90 ℃, EA refers to ethyl acetate and DCM refers to dichloromethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: ^1H and ^{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^1H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.16 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m. p.) was measured on a microscopic melting point apparatus.

2. General procedure for the preparation of N-acylindole substrates

As shown in **Scheme S1**, *N*-acylindole substrates were synthesized from the corresponding phenylhydrazine hydrochlorides as starting materials via Fisher indole synthesis followed by *N*-acylation.



(i) Fisher indole synthesis; (ii) 2-methoxybenzoyl chloride, NaH, DMF; (iii) BBr_3, DCM.

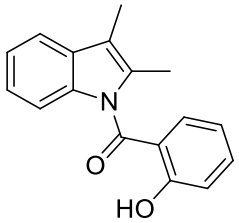
Scheme S1. Preparation of *N*-acylindole substrates

The suspension of substituted phenylhydrazine hydrochloride (40 mmol) in AcOH (40 mL) was heated in 50 °C for 30 min, then butan-2-one (80 mmol, 2 equiv.) was added in one portion and the reaction mixture was refluxed for 3 h. After cooling to room temperature, AcOH was removed under vacum and the residue was dissolved in EA. The organic phase was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give gray residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 200:1 to 60:1) to afford the 2,3-disubstituted indoles.

To a solution of substituted 2,3-dimethyl-1H-indole (3.0 mmol) in DMF (10 mL) at 0 ℃ was added NaH (144 mg, 60% dispersion in mineral oil, 3.6 mmol). The reaction was stirred for 30 min, and 2-methoxybenzoyl chloride (0.45 mL, 3.6 mmol) was added slowly at 0 ℃. The solution was stirred overnight at room temperature, then quenched with aqueous 6M HCl (20 mL) and extracted with EA (4 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 80:1 to 50:1) to produce **s1** (753 mg, 2.7 mmol, 90%) as a yellow solid.

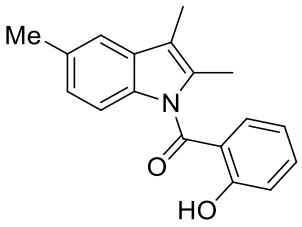
To a solution of **s1** (3.0 mmol) in CH_2Cl_2 (10 mL) at 0 ℃ was added boron tribromide (1.1 mL, 1.0 M solution in DCM, 12 mmol) slowly under argon atmosphere. The solution was stirred overnight at room temperature. The reaction was quenched with cold water (20 mL) and extracted with DCM (50 mL×3). The combined organic layers were washed with saturated brine, dried with Na_2SO_4, concentrated *in vacuo* and purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 500:1 to 300:1) to afford *N*-acylindole substrate **1**.

3. Characterization of the N-acylindole substrates



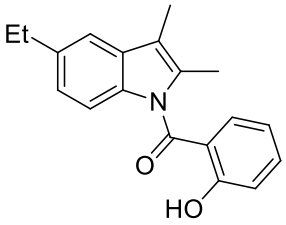
(2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1a)

Yellow solid, m. p. 66 – 67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.67 – 7.28 (m, 3H), 7.28 – 6.94 (m, 4H), 6.94 – 6.71 (m, 1H), 2.37 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 162.1, 136.5, 136.4, 132.9, 130.8, 122.9, 122.4, 119.2, 118.3, 118.3, 116.8, 115.3, 113.4, 12.6, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{15}NO_2\text{-}H]^-$ 264.1030, found 264.1026.



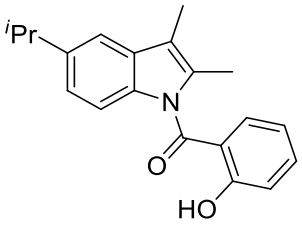
(2-hydroxyphenyl)(2,3,5-trimethyl-1H-indol-1-yl)methanone (1b)

Yellow solid, m. p. 84 – 85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.64 – 7.58 (m, 2H), 7.42 (s, 1H), 7.29 – 7.26 (m, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.03 (dd, J = 8.5, 1.7 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 2.60 (s, 3H), 2.55 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 162.1, 136.2, 134.9, 133.0, 132.9, 132.0, 131.2, 124.4, 119.2, 118.4, 117.1, 115.3, 113.4, 21.5, 12.7, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2+H]^+$ 280.1332, found 280.1332.



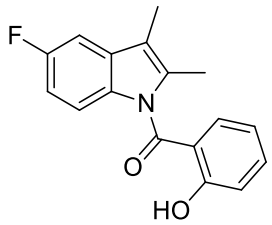
(5-ethyl-2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1c)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.36 – 7.31 (m, 2H), 7.13 (s, 1H), 7.05 – 6.90 (m, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.76 (dd, J = 8.5, 1.8 Hz, 1H), 6.72 – 6.61 (m, 1H), 2.58 (q, J = 7.6 Hz, 2H), 2.23 (s, 3H), 2.09 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 162.0, 138.6, 136.2, 134.9, 133.0, 132.9, 131.1, 123.2, 119.2, 118.3, 117.0, 115.4, 113.4, 28.9, 16.3, 12.6, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{19}NO_2+H]^+$ 294.1489, found 294.1493.



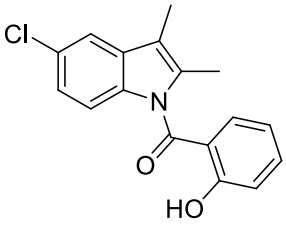
(2-hydroxyphenyl)(5-isopropyl-2,3-dimethyl-1H-indol-1-yl)methanone (1d)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.41 – 7.36 (m, 2H), 7.18 (d, J = 1.8 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.84 (dd, J = 8.5, 1.8 Hz, 1H), 6.79 – 6.62 (m, 1H), 3.07 – 2.58 (m, 1H), 2.26 (s, 3H), 2.14 (s, 3H), 1.20 (s, 3H), 1.17 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 161.9, 147.7, 136.0, 132.3, 130.2, 122.3, 121.6, 120.0, 117.9, 117.7, 114.3, 113.7, 112.8, 29.3, 21.6, 11.9, 8.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{21}NO_2+H]^+$ 308.1645, found 308.1649.



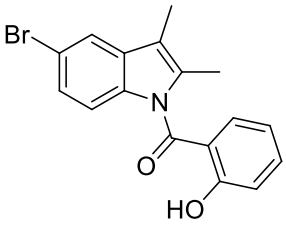
(5-fluoro-2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1e)

Yellow solid, m. p. 79 – 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.46 – 7.40 (m, 1H), 7.31 (dd, J = 8.0, 1.7 Hz, 1H), 7.10 – 6.82 (m, 3H), 6.82 – 6.56 (m, 2H), 2.27 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 162.0, 160.8, 157.6, 136.5, 134.6, 132.6, 131.7, 119.3, 118.4, 116.6, 114.3, 114.2, 110.7, 110.3, 104.0, 103.7, 12.7, 8.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}FNO_2\text{-}H]^-$ 282.0936, found 282.0933.



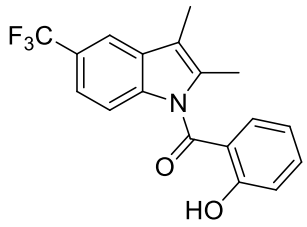
(5-chloro-2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1f)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.36 (brs, 1H), 7.46 – 7.40 (m, 1H), 7.36 – 7.19 (m, 2H), 7.02 (d, J = 8.3 Hz, 1H), 6.90 (d, J = 1.5 Hz, 2H), 6.75 (t, J = 7.6 Hz, 1H), 2.27 (s, 3H), 2.11 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 162.1, 136.6, 134.7, 134.4, 132.6, 132.0, 128.0, 122.9, 119.3, 118.5, 118.0, 116.5, 114.6, 114.3, 12.6, 8.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}ClNO_2\text{-}H]^-$ 298.0640, found 298.0642.



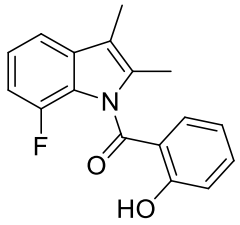
(5-bromo-2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1g)

Yellow solid, m. p. 90 – 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.62 – 7.44 (m, 2H), 7.36 (dd, J = 8.0, 1.7 Hz, 1H), 7.15 – 7.10 (m, 2H), 6.93 (d, J = 8.8 Hz, 1H), 6.88 – 6.76 (m, 1H), 2.36 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 162.2, 136.7, 135.1, 134.2, 132.6, 132.5, 125.5, 121.0, 119.3, 118.5, 116.5, 115.6, 114.7, 114.5, 12.5, 8.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}BrNO_2\text{-}H]^-$ 342.0135, found 342.0130.



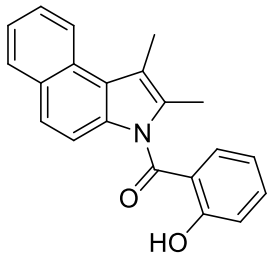
(2,3-dimethyl-5-(trifluoromethyl)-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1h)

Yellow solid, m. p. 73 – 74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.73 (s, 1H), 7.59 – 7.53 (m, 1H), 7.38 – 7.28 (m, 2H), 7.20 – 6.98 (m, 2H), 6.98 – 6.64 (m, 1H), 2.40 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 162.4, 137.8, 137.0, 134.7, 132.6, 130.3, 119.6, 119.6, 119.4, 118.6, 116.3, 115.8, 115.7, 115.0, 113.3, 110.0, 12.4, 8.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{14}F_3NO_2\text{-}H]^-$ 332.0904, found 332.0908.



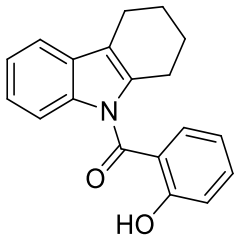
(7-fluoro-2,3-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1i)

Yellow solid, m. p. 66 – 67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.80 (s, 1H), 7.53 – 7.47 (m, 1H), 7.34 – 7.18 (m, 2H), 7.18 – 6.91 (m, 2H), 6.97 – 6.60 (m, 2H), 2.33 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 162.4, 150.8, 147.5, 136.8, 133.8, 131.9, 131.9, 122.5, 122.4, 119.3, 118.2, 114.2, 114.2, 113.5, 109.6, 109.4, 11.8, 8.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}FNO_2\text{-}H]^-$ 282.0936, found 282.0935.



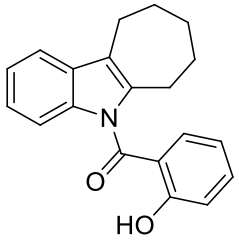
(1,2-dimethyl-3H-benzo[e]indol-3-yl)(2-hydroxyphenyl)methanone (1j)

Yellow solid, m. p. 120 – 121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.53 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.68 – 7.39 (m, 4H), 7.35 (dd, J = 8.0, 1.7 Hz, 1H), 7.30 – 7.20 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 2.67 (s, 3H), 2.43 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 162.6, 136.8, 133.2, 131.2, 130.6, 128.7, 128.5, 126.0, 123.9, 123.6, 123.5, 119.4, 118.4, 116.8, 116.2, 113.8, 12.9, 12.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{17}NO_2\text{-}H]^-$ 314.1187, found 314.1180.



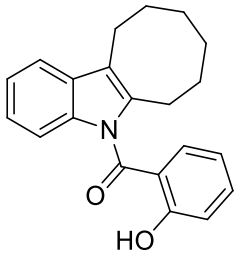
(3,4-dihydro-1H-carbazol-9(2H)-yl)(2-hydroxyphenyl)methanone (1k)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.60 – 7.53 (m, 3H), 7.39 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 3.39 – 2.44 (m, 4H), 1.99 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 161.7, 136.7, 136.1, 132.7, 130.1, 123.2, 122.7, 119.2, 118.3, 118.1, 118.0, 117.1, 114.1, 25.2, 23.6, 22.5, 21.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{17}NO_2+Na]^+$ 314.1151, found 314.1157.



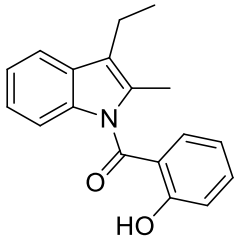
(2-hydroxyphenyl)(7,8,9,10-tetrahydrocyclohepta[b]indol-5(6H)-yl)methanone (1l)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.51 – 7.24 (m, 3H), 7.16 – 7.06 (m, 2H), 7.05 – 6.89 (m, 2H), 6.75 (t, J = 7.6 Hz, 1H), 2.86 – 2.53 (m, 4H), 1.89 – 1.67 (m, 4H), 1.66 – 1.60 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 162.3, 139.3, 136.5, 136.0, 132.8, 130.2, 122.9, 122.3, 122.1, 119.3, 118.3, 117.9, 117.2, 113.2, 31.3, 28.6, 27.3, 27.0, 24.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{19}NO_2-H]^-$ 304.1343, found 304.1336.



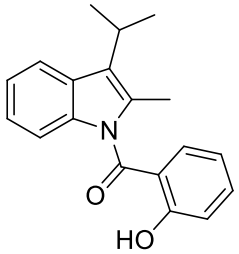
(6,7,8,9,10,11-hexahydro-5H-cycloocta[b]indol-5-yl)(2-hydroxyphenyl)methanone (1m)

Yellow solid, m. p. 128 – 129 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.58 – 7.32 (m, 3H), 7.26 – 7.09 (m, 2H), 7.09 – 6.91 (m, 2H), 6.82 (t, J = 7.6 Hz, 1H), 3.21 – 2.96 (m, 1H), 2.96 – 2.43 (m, 3H), 1.97 – 1.60 (m, 4H), 1.56 – 1.29 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 162.2, 137.6, 136.7, 136.4, 132.8, 129.6, 122.6, 122.2, 120.4, 119.3, 118.4, 118.1, 116.7, 113.6, 29.9, 29.8, 26.5, 25.8, 24.2, 22.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{21}NO_2-H]^-$ 318.1500, found 318.1489.



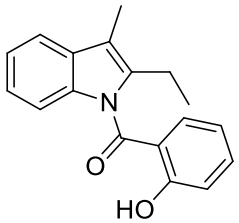
(3-ethyl-2-methyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1n)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.40 – 7.31 (m, 3H), 7.15 – 6.81 (m, 4H), 6.81 – 6.16 (m, 1H), 2.60 (q, J = 7.5 Hz, 2H), 2.26 (s, 3H), 1.13 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 162.1, 136.7, 136.4, 132.9, 132.4, 129.9, 122.8, 122.3, 121.6, 119.3, 118.4, 116.9, 113.6, 17.4, 14.7, 12.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2+H]^+$ 280.1332, found 280.1338.



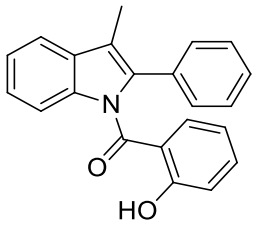
(2-hydroxyphenyl)(3-isopropyl-2-methyl-1H-indol-1-yl)methanone (1o)

Yellow solid, m. p. 61 – 62 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 8.4 Hz, 2H), 7.39 – 7.23 (m, 3H), 7.23 – 7.10 (m, 1H), 6.94 (t, J = 7.6 Hz, 1H), 3.59 – 2.87 (m, 1H), 2.56 (s, 3H), 1.63 (d, J = 7.3 Hz, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 162.4, 137.1, 136.6, 133.0, 131.5, 128.8, 125.1, 122.6, 122.1, 120.0, 119.3, 118.5, 117.0, 113.7, 26.0, 22.4, 12.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{19}NO_2+H]^+$ 294.1489, found 294.1495.



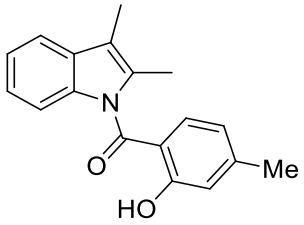
(2-ethyl-3-methyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (1p)

Yellow solid, m. p. 66 – 67 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.59 – 7.36 (m, 3H), 7.27 – 7.08 (m, 2H), 7.06 – 7.00 (m, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.90 – 6.72 (m, 1H), 3.06 – 3.03 (m, 1H)，2.78 – 2.73 (m, 1H), 2.27 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 162.2, 139.3, 136.5, 132.8, 130.7, 122.8, 122.2, 119.3, 118.4, 118.4, 116.7, 114.5, 113.3, 18.9, 14.3, 8.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2-H]^-$ 278.1187, found 278.1191.



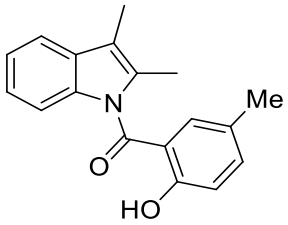
(2-hydroxyphenyl)(3-methyl-2-phenyl-1H-indol-1-yl)methanone (1q)

Yellow solid, m. p. 110 – 111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.56 – 7.42 (m, 1H), 7.51 – 7.48 (m, 2H), 7.29 – 6.98 (m, 8H), 6.85 (dd, J = 8.4, 1.1 Hz, 1H), 6.64 – 6.53 (m, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 161.9, 137.1, 136.4, 136.2, 132.6, 132.3, 130.8, 129.4, 128.4, 127.6, 124.4, 122.9, 119.3, 119.1, 117.9, 117.1, 116.9, 113.4, 9.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{22}H_{17}NO_2\text{-}H]^-$ 326.1187, found 326.1184.



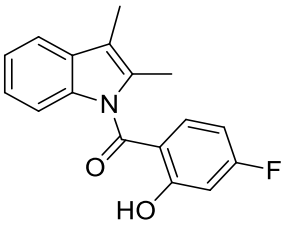
(2,3-dimethyl-1H-indol-1-yl)(2-hydroxy-4-methylphenyl)methanone (1r)

Yellow solid, m. p. 91 – 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.1 Hz, 1H), 7.12 – 6.92 (m, 3H), 6.83 (d, J = 1.7 Hz, 1H), 6.55 (dd, J = 8.2, 1.6 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 2.15 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 162.5, 148.2, 136.6, 132.9, 132.8, 130.8, 122.9, 122.2, 120.5, 118.5, 118.3, 114.9, 114.4, 113.4, 22.1, 12.4, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2\text{+}H]^+$ 280.1332, found 280.1339.



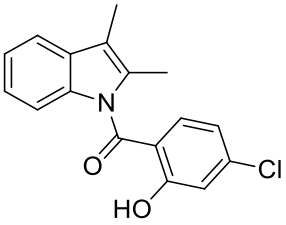
(2,3-dimethyl-1H-indol-1-yl)(2-hydroxy-5-methylphenyl)methanone (1s)

Yellow solid, m. p. 61 – 62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.22 – 7.07 (m, 2H), 7.07 – 6.96 (m, 2H), 6.96 – 6.82 (m, 2H), 2.23 (s, 3H), 2.10 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 160.0, 137.4, 136.6, 132.9, 132.4, 130.8, 128.5, 123.0, 122.4, 118.3, 118.2, 116.6, 115.2, 113.4, 20.3, 12.6, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{17}NO_2\text{+}H]^+$ 280.1332, found 280.1338.



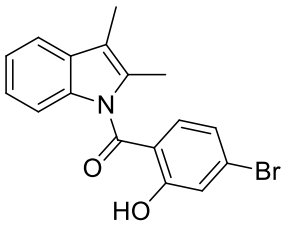
(2,3-dimethyl-1H-indol-1-yl)(4-fluoro-2-hydroxyphenyl)methanone (1t)

Yellow solid, m. p. 66 – 67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.88 (s, 1H), 7.43 – 7.29 (m, 2H), 7.09 – 7.04 (m, 1H), 7.00 – 6.83 (m, 2H), 6.69 (dd, J = 10.2, 2.6 Hz, 1H), 6.51 – 6.37 (m, 1H), 2.27 (s, 4H), 2.13 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 169.3, 165.9, 164.7, 164.6, 136.4, 135.4, 135.2, 132.8, 130.8, 123.0, 122.4, 118.4, 115.4, 113.2, 107.7, 107.4, 105.4, 105.1, 12.4, 8.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}FNO_2\text{-}H]^-$ 282.0936, found 282.0938.



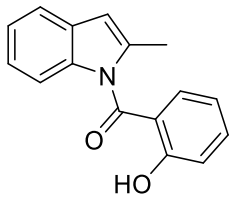
(4-chloro-2-hydroxyphenyl)(2,3-dimethyl-1H-indol-1-yl)methanone (1u)

Yellow solid, m. p. 80 – 81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.45 – 7.27 (m, 3H), 7.22 – 7.08 (m, 1H), 7.08 – 7.01 (m, 2H), 6.98 (d, J = 8.6 Hz, 1H), 2.27 (s, 3H), 2.16 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 160.4, 136.1, 132.5, 131.7, 130.9, 124.1, 123.4, 122.8, 119.9, 118.4, 116.0, 113.3, 12.7, 8.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}ClNO_2\text{+}H]^+$ 345.1155, found 345.1156.



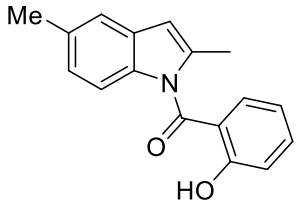
(4-bromo-2-hydroxyphenyl)(2,3-dimethyl-1H-indol-1-yl)methanone (1v)

Yellow solid, m. p. 60 – 61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.25 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 7.00 – 6.88 (m, 2H), 6.84 (dd, J = 8.5, 1.9 Hz, 1H), 2.25 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 162.6, 143.3, 137.5, 136.1, 132.4, 119.6, 118.8, 118.2, 115.9, 115.4, 114.8, 113.0, 12.5, 8.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{14}BrNO_2\text{-}H]^-$ 342.0135, found 342.0136.



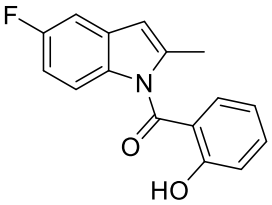
(2-hydroxyphenyl)(2-methyl-1H-indol-1-yl)methanone (3a)

Yellow solid, m. p. 54 – 55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.04 – 6.80 (m, 4H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.28 (s, 1H), 2.29 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 161.0, 136.4, 136.1, 135.4, 131.6, 128.3, 121.6, 121.4, 118.8, 118.1, 117.2, 115.4, 112.3, 107.3, 13.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{13}NO_2+H]^+$ 252.0887, found 252.0881.



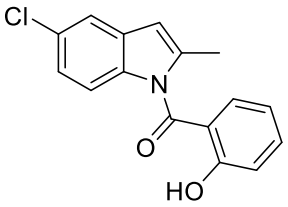
(2,5-dimethyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (3b)

Yellow solid, m. p. 70 – 71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.36 – 7.28 (m, 2H), 7.12 (s, 1H), 7.02 – 6.92 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.78 – 6.62 (m, 2H), 6.23 (s, 1H), 2.31 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 161.6, 137.2, 136.0, 135.1, 132.3, 131.6, 129.3, 123.6, 119.5, 118.7, 117.9, 116.2, 112.8, 107.9, 20.8, 14.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{15}NO_2+H]^+$ 266.1093, found 266.1090.



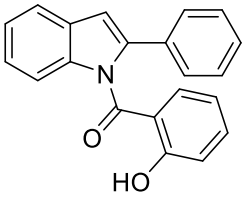
(5-fluoro-2-methyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (3c)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.36 – 7.31 (m, 1H), 7.19 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.86 (dd, *J* = 9.0, 4.4 Hz, 1H), 6.74 – 6.52 (m, 2H), 6.22 (s, 1H), 2.26 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 162.2, 160.8, 157.6, 139.3, 136.8, 133.6, 132.6, 130.4, 130.3, 119.4, 118.5, 116.4, 114.4, 114.3, 110.6, 110.3, 108.2, 108.2, 105.6, 105.3, 15.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{12}FNO_2+H]^+$ 270.0802, found 270.0804.



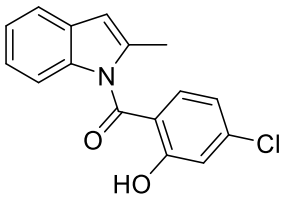
(5-chloro-2-methyl-1H-indol-1-yl)(2-hydroxyphenyl)methanone (3d)

Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.48 – 7.30 (m, 1H), 7.26 (s, 1H), 7.23 – 7.12 (m, 1H), 6.97 (d, J = 8.4 Hz, 1H), 6.83 (s, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.22 (s, 1H), 2.29 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 161.8, 138.6, 136.4, 135.1, 132.1, 130.1, 127.6, 122.3, 119.1, 118.9, 118.1, 115.7, 113.9, 107.1, 14.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{12}ClNO_2+H]^+$ 286.0507, found 286.0510.



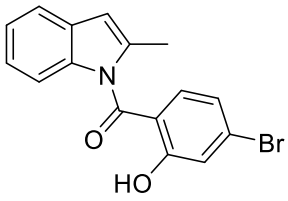
(2-hydroxyphenyl)(2-methyl-1H-indol-1-yl)methanone (3e)

Yellow solid, m. p. 129 – 130 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.57 – 7.45 (m, 1H), 7.38 – 7.34 (m, 1H), 7.33 – 7.20 (m, 4H), 7.18 – 7.06 (m, 5H), 6.89 (d, J = 8.3 Hz, 1H), 6.72 (s, 1H), 6.56 (t, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 1 73.8, 162.3, 141.3, 138.2, 136.7, 132.6, 129.5, 128.6, 127.9, 127.9, 124.2, 123.1, 121.0, 119.3, 118.0, 116.8, 113.3, 109.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{15}NO_2\ NO_2+H]^+$ 314.1093, found 314.1090.



(4-chloro-2-hydroxyphenyl)(2-methyl-1H-indol-1-yl)methanone (3f)

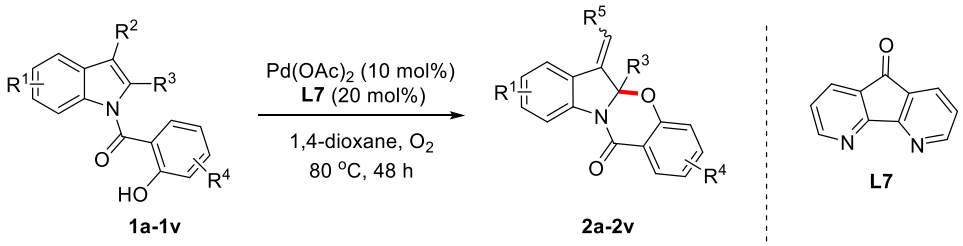
Yellow solid, m. p. 134 – 135 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.29 (s, 1H), 7.45 – 7.35 (m, 2H), 7.33 (d, J = 2.8 Hz, 1H), 7.15 – 6.98 (m, 4H), 6.39 (s, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 160.5, 137.3, 136.4, 131.6, 129.5, 124.2, 123.1, 123.0, 120.2, 120.0, 117.5, 113.4, 109.1, 15.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{12}ClNO_2+H]^+$ 286.0501, found 286.0510.



(4-bromo-2-hydroxyphenyl)(2-methyl-1H-indol-1-yl)methanone (3g)

Yellow solid, m. p. 95 – 96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.24 – 7.12 (m, 2H), 7.06 – 7.01 (m, 1H), 6.99 – 6.90 (m, 2H), 6.86 (dd, J = 8.5, 1.9 Hz, 1H), 6.34 (s, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 162.1, 137.0, 136.6, 133.2, 130.7, 129.0, 122.4, 122.4, 122.3, 121.3, 119.7, 114.9, 112.9, 108.3, 14.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{12}BrNO_2+H]^+$ 330.0017, found 330.0015.

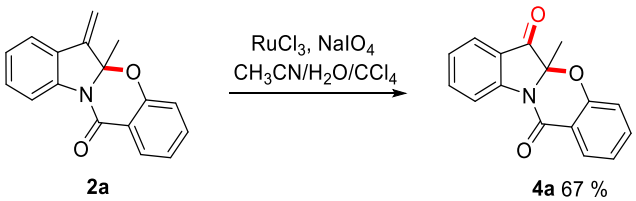
4. General procedure of Pd(II)-catalyzed Wacker cyclization/ dearomatization of indoles



A sealed tube was charged with *N*-acylindole substrate **1** (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), ligand (0.04 mmol, 20 mol%), and 1,4-dioxane (2 mL) under O_2 atmosphere. The reaction mixture was vigorously stirred at 80 °C (oil temperature) for 48 h. After cooling to room temperature, the reaction mixture was diluted with EA (10 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 300:1 to 100:1, TLC: R_f = 0.2 – 0.6, PE/EA = 20:1) to afford dearomatized product **2**.

5. Further functionalization of dearomatized products

5.1 Transformation of C3-exo double bonds

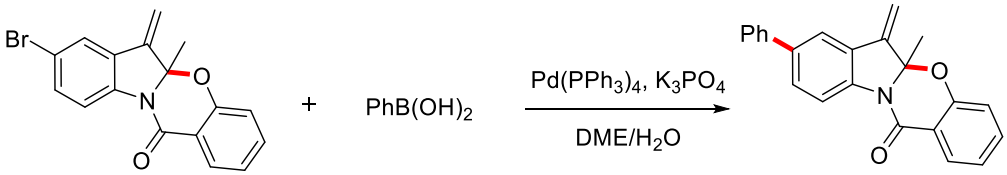


A sealed tube was charged with **2a** (0.2 mmol, 1 equiv.), $RuCl_3$ (0.006 mmol, 3 mol%), $NaIO_4$ (1.2 mmol, 6 equiv.), and $CH_3CN/H_2O/CCl_4$ (2 mL, *v*/*v*/*v* = 1.6:1:1) at room temperature for 1 h. The reaction mixture was diluted with EA (10 mL), quenched with aqueous sodium thiosulfate and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 50:1 to 20:1, TLC: R_f = 0.3, PE/EA = 20:1) to afford **4a**.

5a-methyl-5aH-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12-dione (4a)

35.5 mg, 67% yield, pale yellow solid, m. p. 117 – 118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.96 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.82 – 7.71 (m, 1H), 7.67 – 7.63 (m, 1H), 7.53 – 7.35 (m, 1H), 7.27 – 7.14 (m, 1H), 7.14 – 6.90 (m, 2H), 1.60 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 157.7, 155.5, 150.0, 138.5, 135.3, 128.5, 125.2, 125.0, 123.4, 120.8, 118.2, 118.1, 117.2, 90.7, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{11}NO_3+H]^+$ 266.0812, found 266.0811.

5.2 Cross coupling of 2g with phenylboronic acid



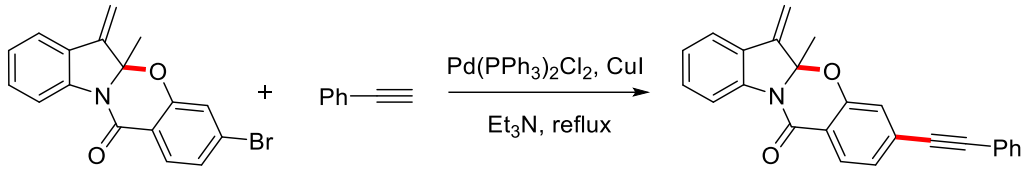
2g **5** 84%

A sealed tube was charged with **2g** (0.2 mmol, 1 equiv.), phenylboronic acid (0.24 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (0.004 mmol, 2 mol%), K_3PO_4 (0.4 mmol, 2 equiv.), and DME/H_2O (2 mL, *v*/*v* = 4:1) under argon atmosphere at 65 °C for 8 h. The reaction mixture was diluted with EA (10 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 200:1 to 150:1, TLC: R_f = 0.5, PE/EA = 20:1) to afford **5**.

5a-methyl-6-methylene-8-phenyl-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (5)

57.0 mg, 84% yield, white solid, m. p. 102 – 103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.55 – 7.43 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 5.84 (s, 1H), 5.58 (s, 1H), 1.67 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.1, 146.5, 140.6, 140.5, 137.8, 134.7, 129.9, 128.8, 128.3, 127.3, 127.0, 126.4, 122.8, 119.6, 118.8, 117.6, 116.5, 106.2, 95.7, 25.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{23}H_{17}NO_2+Na]^+$ 362.1152, found 362.1151.

5.3 Cross coupling of 2v with phenylacetylene



2v **6** 78%

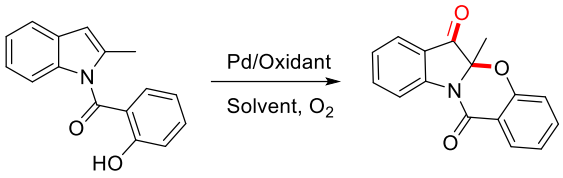
A sealed tube was charged with **2v** (0.2 mmol, 1 equiv.), $Pd(PPh_3)_2Cl_2$ (0.004 mmol, 2 mol%), CuI (0.008 mmol, 4 mol%), phenylacetylene (0.4 mmol, 2 equiv.), and Et_3N (2 mL). The reaction mixture was then vigorously stirred under argon atmosphere at 90 °C (oil temperature) for 4 h. After cooling to room temperature, the reaction mixture was diluted with EA (20 mL) and filtered through a plug of celite. The mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 300:1 to 100:1, TLC: R_f = 0.4, PE/EA = 20:1) to afford the desired product **6**.

5a-methyl-6-methylene-3-(phenylethynyl)-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (6)

56.6 mg, 78% yield, yellow solid, m. p. 129 – 130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.40 – 7.30 (m, 5H), 7.27 – 7.20 (m, 1H), 7.15 (t, J = 7.5 Hz, 1H), 5.78 (s, 1H), 5.54 (s, 1H), 1.68 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 154.9, 146.4, 141.1, 131.8, 130.8, 129.7, 128.9, 128.4, 128.2, 126.0, 125.8, 124.5, 122.5, 121.0, 120.4, 118.4, 116.3, 106.1, 95.6, 92.7, 88.3, 25.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{25}H_{17}NO_2+H]^+$ 364.1332, found 364.1336.

6. Optimization for synthesis of indolones

Table S1 Screening of reaction conditions[a,b]

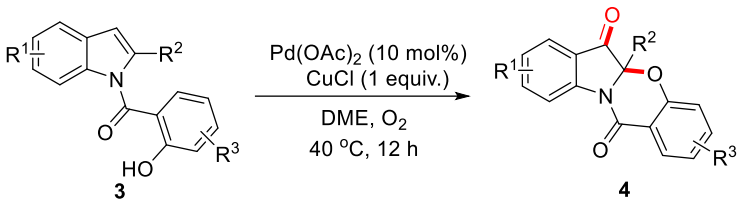


3a **4a**

Entry	Cat.	Oxidant	Solvent (2 mL)	T (°C)	Yield (%)[b]
1	$Pd(OAc)_2$	*p*-BQ	DMF	80	trace
2	$Pd(OAc)_2$	CuCl	DMF	80	48
3	$PdCl_2$	CuCl	DMF	80	48
4	$Pd(PPh_3)_2Cl_2$	CuCl	DMF	80	44
5	$Pd(dppf)Cl_2$	CuCl	DMF	80	45
6	$Pd(OAc)_2$	$CuCl_2$	DMF	80	47
7	$Pd(OAc)_2$	CuBr	DMF	80	trace
8	$Pd(OAc)_2$	$Cu(OAc)_2$	DMF	80	35
9	$Pd(OAc)_2$	$AgSbF_6$	DMF	80	36
10	$Pd(OAc)_2$	CuCl	DME	80	68
11	$Pd(OAc)_2$	CuCl	THF	80	56
12	$Pd(OAc)_2$	CuCl	DMA	80	31
13	$Pd(OAc)_2$	CuCl	MeOH	80	39
14	$Pd(OAc)_2$	CuCl	DCM	80	32
15	$Pd(OAc)_2$	CuCl	1,4-Dioxane	80	39
16	$Pd(OAc)_2$	CuCl	Toluene	80	34
17	$Pd(OAc)_2$	CuCl	DME	70	67
18	$Pd(OAc)_2$	CuCl	DME	60	70
19	$Pd(OAc)_2$	CuCl	DME	50	72
20	$Pd(OAc)_2$	CuCl	DME	40	75
21	$Pd(OAc)_2$	CuCl	DME	rt	27
22[c]	$Pd(OAc)_2$	CuCl	DME	40	69
23[d]	$Pd(OAc)_2$	CuCl	DME	40	trace

[a] Reaction conditions: **3a** (0.2 mmol), catalyst (10 mol%), oxidant (1 equiv.), DME (2 mL), O_2, 12 h. [b] Isolated yield. [c] Under air atmosphere. [d] Under argon atmosphere.

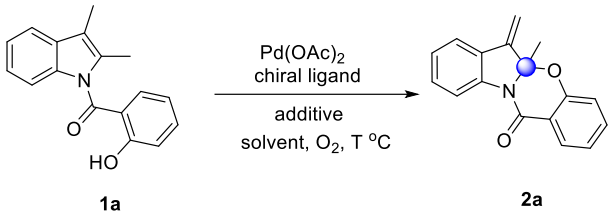
7. General procedure of Pd(II)-catalyzed oxidative dearomatization of 2-substituted indoles



A sealed tube was charged with *N*-acylindole substrate **3** (0.2 mmol, 1 equiv.), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), CuCl (0.2 mmol, 1 equiv.), and DME (2 mL) under O_2 atmosphere. The reaction mixture was vigorously stirred at 40 °C (oil temperature) for 12 h. After cooling to room temperature, the reaction mixture was diluted with EA (10 mL) and filtered through a plug of Celite. The filtrate was washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give dark residue, which was purified by flash chromatography on silica gel with PE/EA (*v*/*v* = 50:1 to 40:1, TLC: R_f = 0.5 – 0.6, PE/EA = 20:1) to afford dearomatized product **4**.

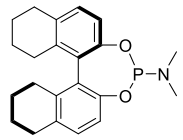
8. Preliminary asymmetric study

Table S2 Preliminary asymmetric study [a-c]

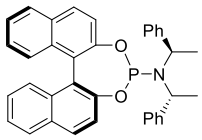


Entry	Ligand	Additive	Solvent	Temperature	Yield (%)	ee (%)
1	**L1**	/	1,4-dioxane	80 °C	trace	/
2	**L2**	/	1,4-dioxane	80 °C	30	5
3	**L3**	/	1,4-dioxane	80 °C	75	2
4[d]	**L4**	/	1,4-dioxane	80 °C	43	6
5	**L5**	/	1,4-dioxane	80 °C	41	2
6	**L6**	/	1,4-dioxane	80 °C	40	8
7	**L7**	/	1,4-dioxane	80 °C	21	18
8	**L8**	/	1,4-dioxane	80 °C	25	16

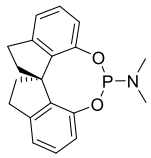
9	**L9**	/	1,4-dioxane	80 °C	18	9
10	**L10**	/	1,4-dioxane	80 °C	trace	/
11[d]	**L7**	**pyridine**	**1,4-dioxane**	**80 °C**	**43**	**36**
12	**L7**	4,5-diaza-9-fluorenone	1,4-dioxane	80 °C	60	7
13	**L7**	2,2'-bipyridine	1,4-dioxane	80 °C	41	4
14	**L7**	pyridine	DME	80 °C	20	14
15	**L7**	pyridine	DMF	80 °C	trace	/
16	**L7**	pyridine	DMA	80 °C	35	7
17	**L7**	pyridine	MeOH	80 °C	trace	/
18	**L7**	pyridine	NMP	80 °C	trace	/
19	**L7**	pyridine	toluene	80 °C	56	11
20	**L7**	pyridine	1,4-dioxane	50 °C	39	31



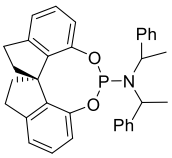
L1



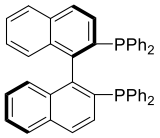
L2



L3

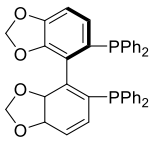


L4

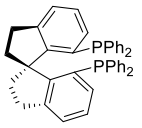


(R)-BINAP

L5

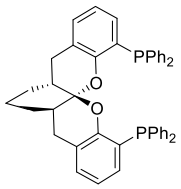


L6

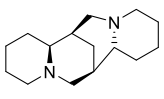


(R)-SDP

L7

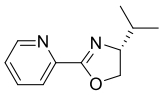


L8



(+)-Sparteine

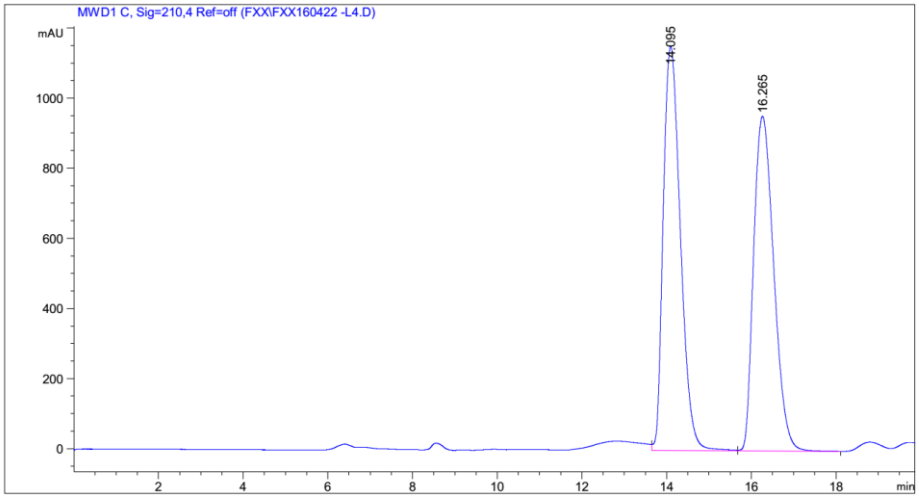
L9



L10

[a] Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%) and ligand (12 mol%) in solvent (2 mL) for 26 h under O_2 atmosphere. [b] Isolated yield. [c] The ee values of the products were determined by chiral-phase HPLC analysis. [d] Pyridine (20 mol%) was added.

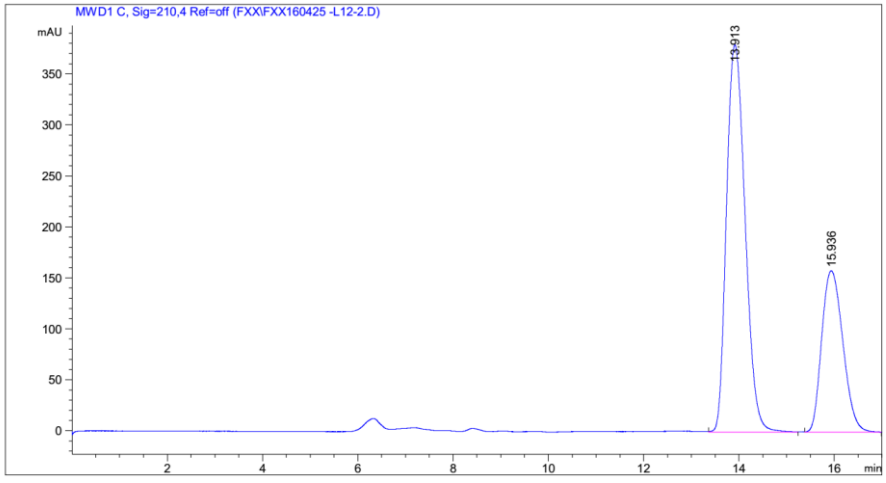
Rac-**2a**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.095	VV	0.4430	3.25052e4	1152.55872	50.8152
2	16.265	VB	0.5135	3.14623e4	954.65234	49.1848

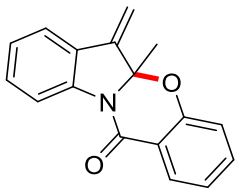
Optically active-**2a** (Table S1 entry 11)

HPLC data for compound **2a**: CHIRALCEL OJ-H, *i*-PrOH: Hexane = 15:85, $[\alpha]_D^{20}$ = +51.7 (c = 0.3, EA), 0.5 mL/min, 210 nm, 36% ee.



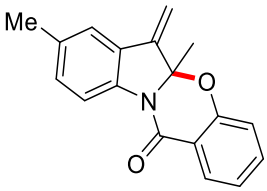
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.913	VB	0.4300	1.03223e4	379.93048	67.8758
2	15.936	VV	0.4589	4885.32813	158.35371	32.1242

9. Characterization of the dearomatized products



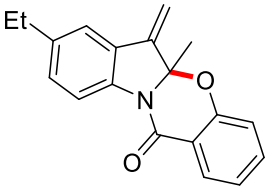
5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2a)

41.0 mg, 78% yield, white solid, m. p. 49 – 50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.1 Hz, 1H), 8.06 (dd, J = 7.7, 1.7 Hz, 1H), 7.66 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.13 (m, 2H), 7.16 – 7.10 (m, 1H), 5.75 (s, 1H), 5.53 (s, 1H), 1.64 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.1, 146.5, 141.2, 134.7, 130.7, 128.3, 125.8, 124.5, 122.7, 121.1, 118.7, 117.6, 116.3, 106.1, 95.4, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{13}NO_2+H]^+$ 264.1019, found 264.1017.



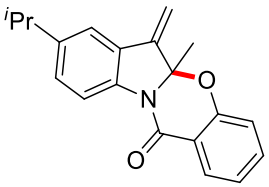
5a,8-dimethyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2b)

41.6 mg, 75% yield, yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.84 (m, 2H), 7.35 – 7.29 (m, 1H), 7.20 (d, J = 1.7 Hz, 1H), 7.04 – 6.96 (m, 2H), 6.91 (d, J = 8.2 Hz, 1H), 5.58 (s, 1H), 5.36 (s, 1H), 2.20 (s, 3H), 1.49 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 155.0, 146.5, 139.0, 134.5, 134.2, 131.5, 128.2, 125.8, 122.7, 121.4, 118.8, 117.5, 116.0, 105.7, 95.5, 25.4, 21.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}NO_2+H]^+$ 278.1176, found 278.1180.



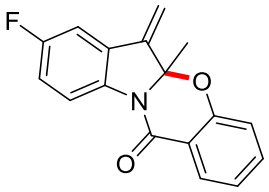
8-ethyl-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2c)

44.2 mg, 76% yield, yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.97 (dd, J = 7.8, 1.7 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.30 (d, J = 1.8 Hz, 1H), 7.21 – 7.02 (m, 2H), 6.98 (dd, J = 8.2, 1.1 Hz, 1H), 5.67 (s, 1H), 5.44 (s, 1H), 2.58 (q, J = 7.6 Hz, 2H), 1.57 (s, 3H), 1.17 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 155.1, 146.7, 140.8, 139.2, 134.5, 130.5, 128.2, 125.9, 122.7, 120.2, 118.8, 117.5, 116.2, 105.6, 95.5, 28.7, 25.4, 15.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{17}NO_2+H]^+$ 292.1332, found 292.1337.



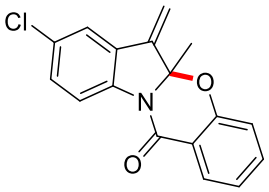
8-isopropyl-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2d)

51.3 mg, 84% yield, white solid, m. p. 79 – 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.3, 1.5 Hz, 1H), 8.01 – 7.93 (m, 1H), 7.45 – 7.34 (m, 1H), 7.32 (d, J = 1.9 Hz, 1H), 7.17 (d, J = 8.1 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 5.68 (s, 1H), 5.43 (s, 1H), 2.89 – 2.80 (m, 1H), 1.56 (s, 3H), 1.19 (d, J = 1.5 Hz, 3H), 1.17 (d, J = 1.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 155.1, 146.8, 145.5, 139.3, 134.5, 129.2, 128.2, 125.8, 122.7, 118.8, 118.7, 117.5, 116.2, 105.6, 95.6, 34.0, 25.4, 24.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{19}NO_2+H]^+$ 306.3704, found 306.3706.



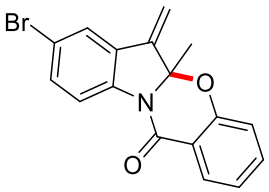
8-fluoro-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2e)

39.9 mg, 71% yield, white solid, m. p. 69 – 70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.8, 4.7 Hz, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.30 – 7.12 (m, 2H), 7.11 – 6.98 (m, 2H), 5.76 (s, 1H), 5.60 (s, 1H), 1.66 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 158.2, 157.7, 154.9, 145.9, 134.7, 128.2, 127.4, 122.9, 118.6, 117.6, 117.4, 117.3, 117.3, 108.1, 107.8, 107.5, 95.6, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}FNO_2+H]^+$ 282.0925, found 282.0922.



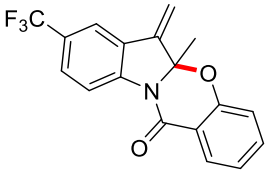
8-chloro-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2f)

38.6 mg, 65% yield, yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 1H), 7.96 (dd, J = 7.8, 1.7 Hz, 1H), 7.48 – 7.34 (m, 2H), 7.23 (dd, J = 8.6, 2.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.01 – 6.85 (m, 1H), 5.68 (s, 1H), 5.50 (s, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 155.0, 145.5, 139.6, 134.8, 130.6, 129.7, 128.3, 127.4, 122.9, 121.2, 118.5, 117.6, 117.3, 107.5, 95.6, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}ClNO_2+H]^+$ 298.0629, found 298.0633.



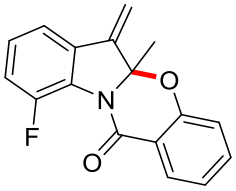
8-bromo-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2g)

40.9 mg, 60% yield, white liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.92 (m, 2H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.32 (m, 2H), 7.13 – 7.03 (m, 1H), 7.03 – 6.92 (m, 1H), 5.68 (s, 1H), 5.50 (s, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.0, 145.4, 140.1, 134.9, 133.4, 128.3, 127.8, 124.1, 122.9, 118.5, 117.7, 117.6, 117.2, 107.6, 95.5, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}BrNO_2+H]^+$ 342.0124, found 342.0129.



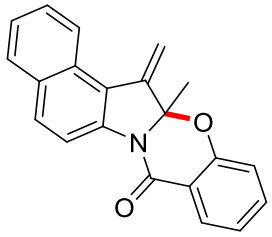
5a-methyl-6-methylene-8-(trifluoromethyl)-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2h)

35.1 mg, 53% yield, white solid, m. p. 94 – 95 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.14 – 7.02 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 5.77 (s, 1H), 5.55 (s, 1H), 1.57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 155.0, 145.3, 143.5, 135.1, 128.4, 127.9, 127.9, 127.8, 127.8, 126.7, 126.2, 125.9, 123.0, 122.3, 118.4, 118.3, 118.3, 118.2, 117.7, 116.1, 108.0, 95.7, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{12}F_3NO_2+H]^+$ 332.0893, found 332.0896.



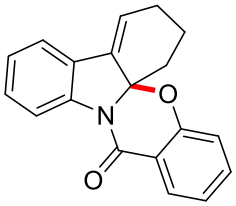
10-fluoro-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2i)

34.8 mg, 62% yield, yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.31 – 7.21 (m, 1H), 7.13 – 6.93 (m, 4H), 5.70 (s, 1H), 5.48 (s, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 154.6, 152.3, 148.9, 146.3, 146.2, 134.5, 130.0, 129.9, 128.8, 126.0, 125.9, 123.0, 119.4, 119.1, 117.3, 116.9, 116.9, 107.0, 96.4, 25.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}FNO_2+H]^+$ 282.0925, found 282.0929.



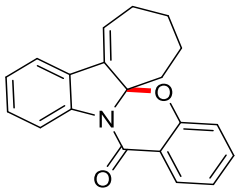
13a-methyl-14-methylene-13a,14-dihydro-8H-benzo[e]benzo[5,6][1,3]oxazino[3,2-a]indol-8-one (2j)

38.8 mg, 62% yield, yellow solid, m. p. 115 – 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 8.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 8.00 (dd, J = 7.8, 1.7 Hz, 1H), 7.89 – 7.65 (m, 2H), 7.59 – 7.21 (m, 3H), 7.14 – 6.87 (m, 2H), 6.05 (s, 1H), 5.66 (s, 1H), 1.58 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.2, 147.4, 141.0, 134.7, 132.1, 131.4, 129.5, 129.3, 128.3, 128.0, 124.8, 123.1, 122.8, 118.8, 118.0, 117.6, 116.1, 108.4, 95.6, 25.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{15}NO_2+H]^+$ 314.1176, found 314.1176.



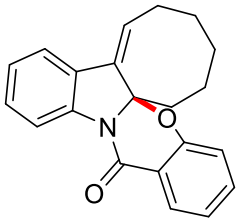
2,3-dihydrobenzo[5,6][1,3]oxazino[2,3-k]carbazol-10(1H)-one (2k)

38.2 mg, 66% yield, yellow solid, m. p. 90 – 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (t, J = 8.5 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.88 (d, J = 8.2 Hz, 1H), 6.24 (t, J = 4.3 Hz, 1H), 2.56 – 2.46 (m, 2H), 2.37 – 2.25 (m, 1H), 2.06 – 1.71 (m, 1H), 1.63 – 1.40 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 154.7, 141.9, 135.0, 134.5, 128.7, 128.0, 126.3, 124.3, 123.6, 122.1, 119.5, 116.9, 114.4, 93.0, 29.2, 23.3, 15.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{15}NO_2+H]^+$ 290.1176, found 290.1177.



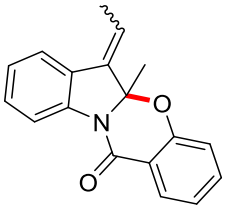
3,4-dihydro-1H-benzo[5,6][1,3]oxazino[3,2-a]cyclohepta[b]indol-11(2H)-one (2l)

44.3 mg, 73% yield, white solid, m. p. 124 – 125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.99 – 7.84 (m, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.27 (s, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.10 – 6.85 (m, 3H), 6.56 – 6.52 (m, 1H), 2.92 – 2.80 (m, 1H), 2.39 – 2.32 (m, 1H), 2.25 – 2.15 (m, 1H), 1.91 – 1.55 (m, 4H), 1.54 – 1.29 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 154.6, 141.6, 140.3, 134.7, 129.3, 128.2, 126.7, 125.6, 124.3, 122.7, 119.7, 119.6, 117.5, 115.7, 98.0, 32.9, 27.8, 26.5, 26.3 ppm. HRMS (ESI) *m/z* calcd for $[C_{20}H_{17}NO_2+H]^+$ 304.1332, found 304.1338.



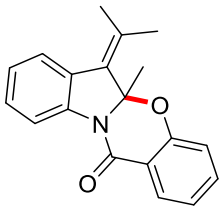
2,3,4,5-tetrahydrobenzo[5,6][1,3]oxazino[3,2-a]cycloocta[b]indol-12(1H)-one (2m)

40.6 mg, 64% yield, white solid, m. p. 159 – 160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 7.95 (dd, J = 7.7, 1.7 Hz, 1H), 7.45 – 7.28 (m, 2H), 7.21 – 7.16 (m, 1H), 7.06 – 6.97 (m, 3H), 6.38 – 6.32 (m, 1H), 3.34 – 3.04 (m, 1H), 2.60 – 2.35 (m, 1H), 2.25 – 2.17 (m, 1H), 1.88 – 1.30 (m, 6H), 1.38 – 1.27 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 154.3, 140.1, 137.5, 134.5, 129.3, 128.0, 127.2, 124.3, 123.3, 122.7, 119.9, 119.1, 117.5, 116.3, 98.3, 37.7, 28.4, 25.4, 23.3, 20.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{19}NO_2+H]^+$ 318.1489, found 318.1489.



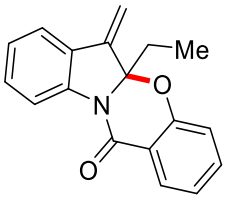
(Z/E)- 6-ethylidene-5a-methyl-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2n)

Inseparable mixture, *Z/E* = 1.6:1, 41.6 mg, 75% yield, pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.17 (m, 0.7H) (minor), 8.10 – 8.07 (m, 1H) (major), 7.95 – 7.92 (m, 1.7H), 7.52 – 7.49 (m, 0.8H), 7.35 – 7.10 (m, 4.6H), 7.06 – 6.95 (m, 2.7H), 6.93 – 6.88 (m, 2.3H), 6.14 – 6.06 (q, J = 7.5 Hz, 1H) (major), 6.04 – 5.96 (q, J = 7.4 Hz, 0.6H) (minor), 2.02 – 1.98 (m, 5H), 1.55 (s, 3H) (major), 1.44 (s, 2H) (minor) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 157.7, 155.0, 154.8, 141.2, 139.9, 138.5, 137.4, 134.6, 134.5, 129.3, 129.2, 128.2, 128.1, 127.2, 126.3, 124.6, 124.4, 124.3, 122.7, 122.6, 121.3, 120.0, 119.7, 118.8, 117.6, 117.5, 116.1, 116.1, 96.1, 95.6, 25.7, 23.1, 14.2, 13.9 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}NO_2+Na]^+$ 300.0995, found 300.0997.



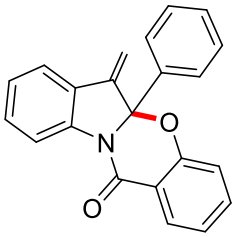
5a-methyl-6-(propan-2-ylidene)-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2o)

35.5 mg, 61% yield, white solid, m. p. 90 – 91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 1H), 7.94 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.16 – 7.11 (m, 1H), 7.03 – 6.94 (m, 2H), 6.93 – 6.84 (m, 1H), 2.15 (s, 3H), 2.04 (s, 3H), 1.54 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 154.7, 140.5, 134.5, 133.4, 131.2, 128.2, 128.0, 127.8, 124.4, 124.1, 122.6, 118.9, 117.5, 115.9, 96.6, 23.3, 23.1, 23.0 ppm. HRMS (ESI) *m/z* calcd for $[C_{19}H_{17}NO_2+H]^+$ 292.1332, found 292.1333.



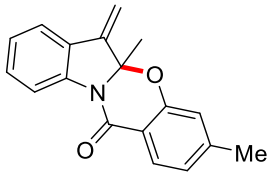
5a-ethyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2p)

36.0 mg, 65% yield, white solid, m. p. 72 – 73 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.64 – 7.33 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.12 – 6.87 (m, 3H), 5.73 (s, 1H), 5.44 (s, 1H), 2.17 – 1.73 (m, 2H), 0.71 – 0.66 (m, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 155.0, 144.5, 142.0, 134.7, 130.6, 128.2, 126.6, 124.4, 122.6, 120.6, 118.8, 117.4, 116.0, 106.8, 97.8, 30.8, 7.1 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}NO_2+Na]^+$ 300.0995, found 300.0996.



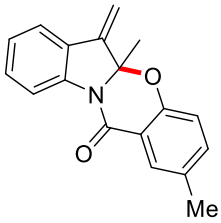
6-methylene-5a-phenyl-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2q)

19.5 mg, 30% yield, white solid, m. p. 174 – 175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 1H), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.49 – 7.27 (m, 5H), 7.19 – 7.08 (m, 5H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.69 (s, 1H), 5.58 (s, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 155.4, 146.5, 142.6, 140.6, 134.7, 130.9, 128.8, 128.7, 128.3, 125.5, 124.9, 124.7, 122.9, 121.5, 119.7, 117.7, 115.5, 107.4, 96.7 ppm. HRMS (ESI) *m/z* calcd for $[C_{22}H_{15}NO_2+H]^+$ 326.1176, found 326.1176.



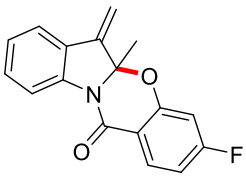
3,5a-dimethyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2r)

45.4 mg, 82% yield, white liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.79 (s, 1H), 5.66 (s, 1H), 5.43 (s, 1H), 2.29 (s, 3H), 1.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 155.1, 146.7, 145.9, 130.7, 128.1, 125.8, 124.2, 124.0, 123.8, 121.0, 120.2, 117.8, 116.2, 105.7, 95.4, 25.4, 21.8 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}NO_2+H]^+$ 278.1176, found 278.1175.



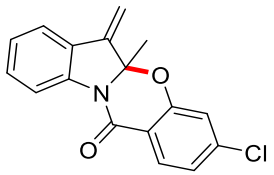
2,5a-dimethyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2s)

41.6 mg, 75% yield, white solid, m. p. 65 – 66 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 2.2 Hz, 1H), 7.60 – 7.47 (m, 1H), 7.39 – 7.33 (m, 1H), 7.27 (dd, J = 8.3, 2.3 Hz, 1H), 7.18 – 7.06 (m, 1H), 6.95 (d, J = 8.3 Hz, 1H), 5.74 (s, 1H), 5.51 (s, 1H), 2.35 (s, 3H), 1.63 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 153.0, 146.6, 141.2, 135.4, 132.3, 130.7, 128.2, 125.8, 124.3, 121.0, 118.4, 117.3, 116.3, 105.9, 95.3, 25.3, 20.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{18}H_{15}NO_2+H]^+$ 278.1176, found 278.1180.



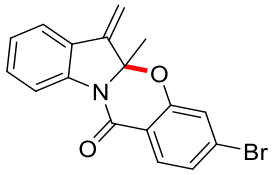
3-fluoro-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2t)

39.9 mg, 71% yield, yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 8.1 Hz, 1H), 8.12 (dd, J = 8.7, 6.4 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.83 (dd, J = 9.4, 2.3 Hz, 1H), 5.81 (s, 1H), 5.57 (s, 1H), 1.72 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 164.8, 157.1, 146.1, 141.0, 130.8, 130.5, 130.3, 125.6, 124.5, 121.1, 116.2, 115.3, 110.7, 110.4, 106.2, 105.2, 104.8, 96.0, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}FNO_2+Na]^+$ 304.0744, found 304.0743.



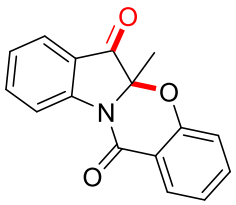
3-chloro-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2u)

34.5 mg, 58% yield, white solid, m. p. 103 – 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 2.7 Hz, 1H), 7.62 – 7.50 (m, 1H), 7.51 – 7.30 (m, 2H), 7.19 – 7.14 (m, 1H), 7.03 (d, J = 8.7 Hz, 1H), 5.78 (s, 1H), 5.53 (s, 1H), 1.66 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 146.1, 140.9, 134.5, 130.8, 128.1, 127.9, 125.8, 124.7, 121.1, 119.9, 119.1, 116.3, 106.2, 95.7, 25.4 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}ClNO_2+Na]^+$ 320.0449, found 320.0450.



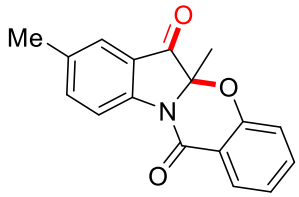
3-bromo-5a-methyl-6-methylene-5aH-benzo[5,6][1,3]oxazino[3,2-a]indol-12(6H)-one (2v)

38.2 mg, 56% yield, white solid, m. p. 75 – 76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.33 – 7.12 (m, 3H), 7.05 (t, J = 7.5 Hz, 1H), 5.67 (s, 1H), 5.42 (s, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 155.5, 146.1, 141.0, 130.8, 129.5, 128.6, 126.2, 125.7, 124.6, 121.1, 120.9, 117.8, 116.3, 106.2, 95.9, 25.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}BrNO_2+Na]^+$ 365.9925, found 365.9929.



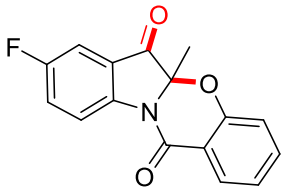
5a-methyl-5aH-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12-dione (4a)

39.8 mg, 75% yield, pale yellow solid, m. p. 117 – 118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 8.3 Hz, 1H), 7.96 (dd, J = 7.7, 1.7 Hz, 1H), 7.82 – 7.71 (m, 1H), 7.67 – 7.63 (m, 1H), 7.53 – 7.35 (m, 1H), 7.27 – 7.14 (m, 1H), 7.14 – 6.90 (m, 2H), 1.60 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 157.7, 155.5, 150.0, 138.5, 135.3, 128.5, 125.2, 125.0, 123.4, 120.8, 118.2, 118.1, 117.2, 90.7, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{11}NO_3+H]^+$ 266.0812, found 266.0811.



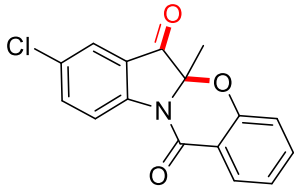
5a,8-dimethyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4b)

41.3 mg, 74% yield, white solid, m. p. 130 – 131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.3 Hz, 1H), 7.97 (dd, J = 7.8, 1.7 Hz, 1H), 7.55 – 7.54 (m, 1H), 7.58 – 7.40 (m, 2H), 7.16 – 7.03 (m, 2H), 2.33 (s, 3H), 1.60 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 157.5, 155.6, 148.1, 139.6, 135.2, 128.4, 128.0, 124.9, 123.3, 120.9, 118.4, 118.1, 117.0, 90.9, 20.9, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{17}H_{13}NO_3+Na]^+$ 302.0788, found 302.0785.



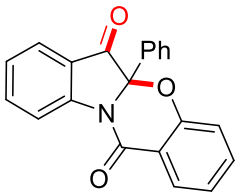
8-fluoro-5a-methyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4c)

38.5 mg, 68% yield, white solid, m. p. 134 – 135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (dd, J = 9.6, 4.3 Hz, 1H), 8.04 (dd, J = 7.8, 1.7 Hz, 1H), 7.58 – 7.44 (m, 3H), 7.28 – 7.10 (m, 2H), 1.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 161.1, 157.9, 157.4, 155.4, 146.4, 135.4, 134.9, 128.5, 128.0, 125.9, 125.6, 123.5, 118.9, 118.8, 118.1, 111.0, 110.7, 91.1, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{10}FNO_3+H]^+$ 284.0717, found 284.0717.



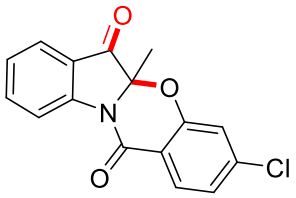
8-chloro-5a-methyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4d)

34.7 mg, 58% yield, white solid, m. p. 173 – 174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, J = 8.7 Hz, 1H), 8.13 – 8.00 (m, 1H), 7.81 (d, J = 2.2 Hz, 1H), 7.71 (dd, J = 8.7, 2.3 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.31 – 7.11 (m, 2H), 1.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 157.6, 155.5, 148.4, 138.3, 135.6, 130.7, 128.6, 124.8, 123.6, 122.2, 118.5, 118.2, 118.0, 91.1, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{10}ClNO_3+Na]^+$ 322.0241, found 322.0238.



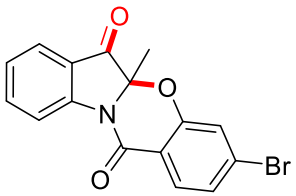
5a-phenyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4e)

30.7 mg, 47% yield, white solid, m. p. 185 – 186 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 8.2 Hz, 1H), 7.94 (dd, J = 7.8, 1.7 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.56 (dd, J = 6.7, 3.0 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.35 – 7.22 (m, 4H), 7.19 (d, J = 8.2 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 158.4, 155.9, 150.9, 138.5, 135.2, 133.6, 129.9, 129.0, 128.4, 126.5, 125.9, 125.3, 123.5, 120.7, 119.2, 118.1, 116.7, 92.2 ppm. HRMS (ESI) *m/z* calcd for $[C_{21}H_{13}NO_3+Na]^+$ 350.0788, found 350.0785.



3-chloro-5a-methyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4f)

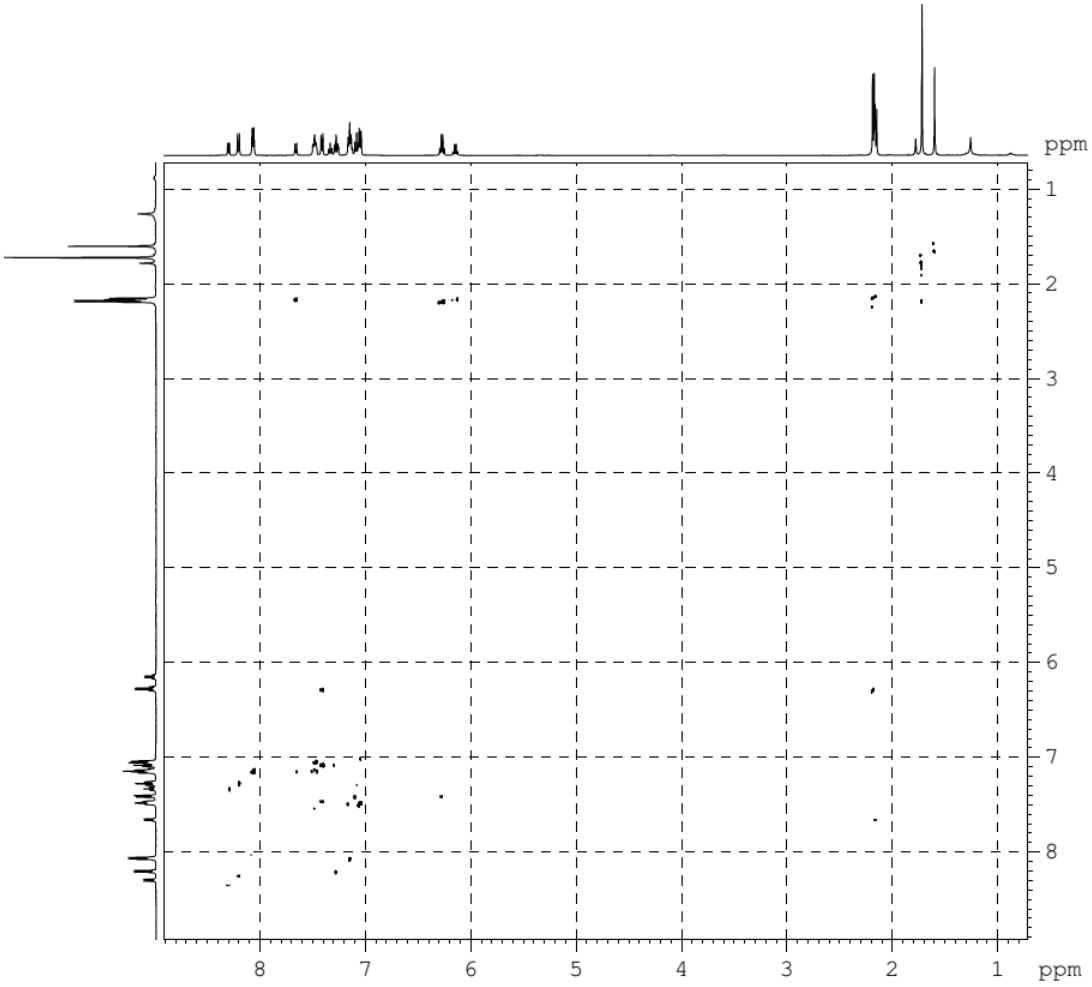
31.7 mg, 53% yield, white solid, m. p. 218 – 219 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 2.6 Hz, 1H), 7.77 (dd, J = 7.8, 1.3 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.41 (dd, J = 8.8, 2.7 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.04 (d, J = 8.7 Hz, 1H), 1.62 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 156.5, 154.0, 149.7, 138.6, 135.2, 128.9, 128.1, 125.3, 120.8, 119.6, 119.4, 117.3, 90.9, 20.5 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{10}ClNO_3+Na]^+$ 322.0241, found 322.0251.

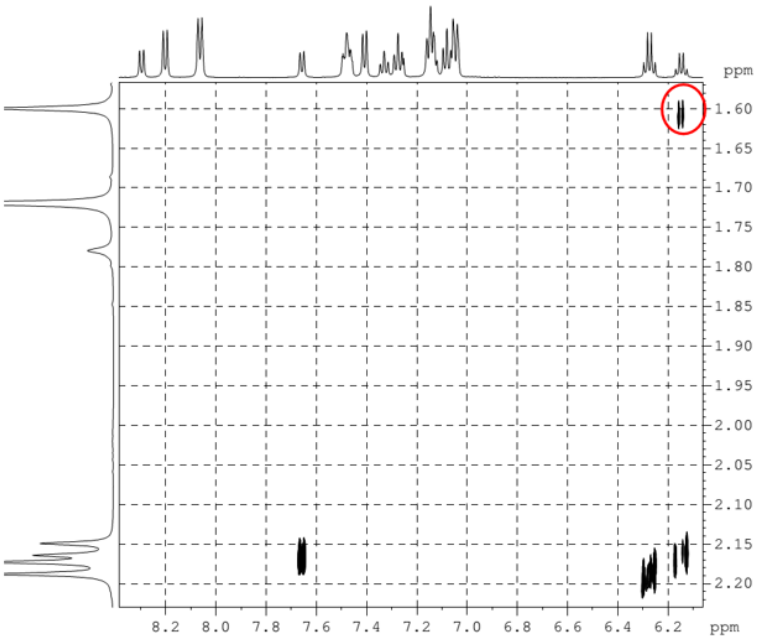


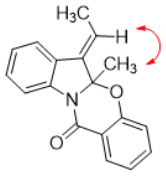
3-bromo-5a-methyl-12H-benzo[5,6][1,3]oxazino[3,2-a]indole-6,12(5aH)-dione (4g)

39.1 mg, 57% yield, white solid, m. p. 120 – 121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.85 (dd, J = 7.8, 1.4 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.39 – 7.27 (m, 3H), 1.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 157.0, 155.9, 149.8, 138.6, 129.7, 129.5, 127.0, 125.3, 125.2, 121.4, 120.8, 117.2, 91.0, 20.6 ppm. HRMS (ESI) *m/z* calcd for $[C_{16}H_{10}BrNO_3+Na]^+$ 365.9736, found 365.9736.

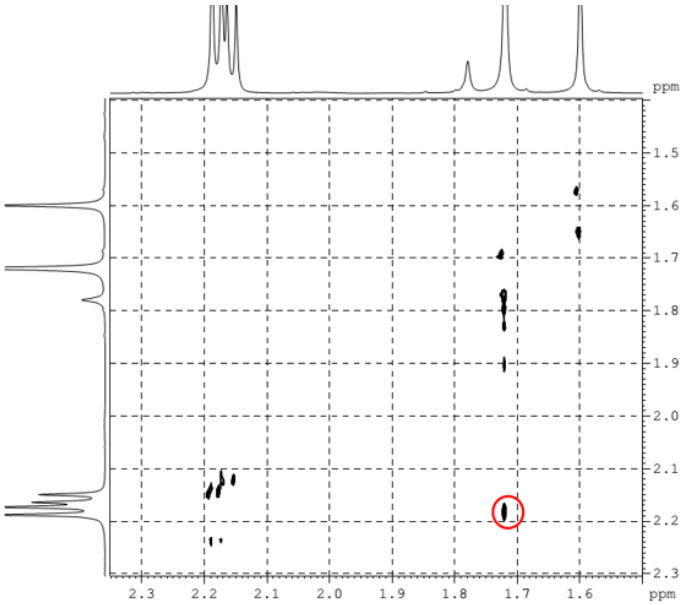
10. NOE analysis of 2n

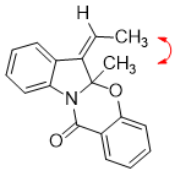



ppm
1.60
1.65
1.70
1.75
1.80
1.85
1.90
1.95
2.00
2.05
2.10
2.15
2.20
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm


H3C
H
CH3
N
O
O

E


ppm
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 ppm


H
CH3
CH3
N
O
O

Z

11. Crystal structures of 2q and 4a

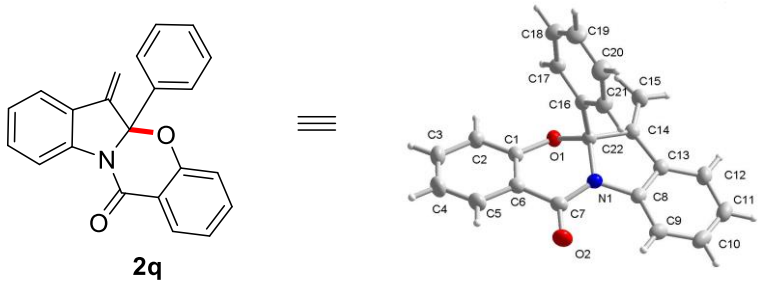


Figure S1. ORTEP plot of the crystal structure of 2q.

X-ray crystallographic data of 2q

CCDC number	1508997
Empirical formula	$C_{22}H_{15}NO_2$
Formula weight	325.35
Temperature	296 K
Wavelength	0.71073 Å
Space group	Pbca
Unit cell dimensions	a= 8.874(6) Å =90 º
	b= 13.733(9) Å =90 º
	c= 27.215(17) Å =90 º
Volume	3317(4) $Å^3$
Z	8
Density (calculated)	1.303 Mg/m^3
F(000)	1360.0
Completeness to theta = 25.010 °	94.1%
Absorption correction	MULTI-SCAN
Max. and min. transmission	0.996 and 0.990
R indices (all data)	R= 0.0354(2726) wR2(reflections)= 0.0962(3390)

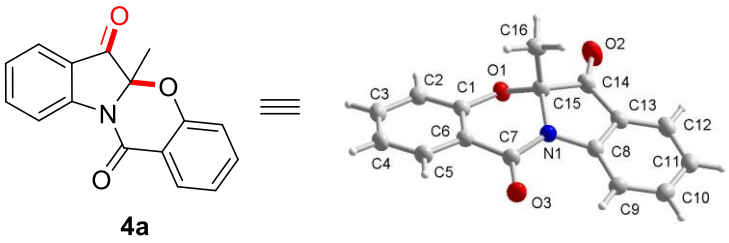
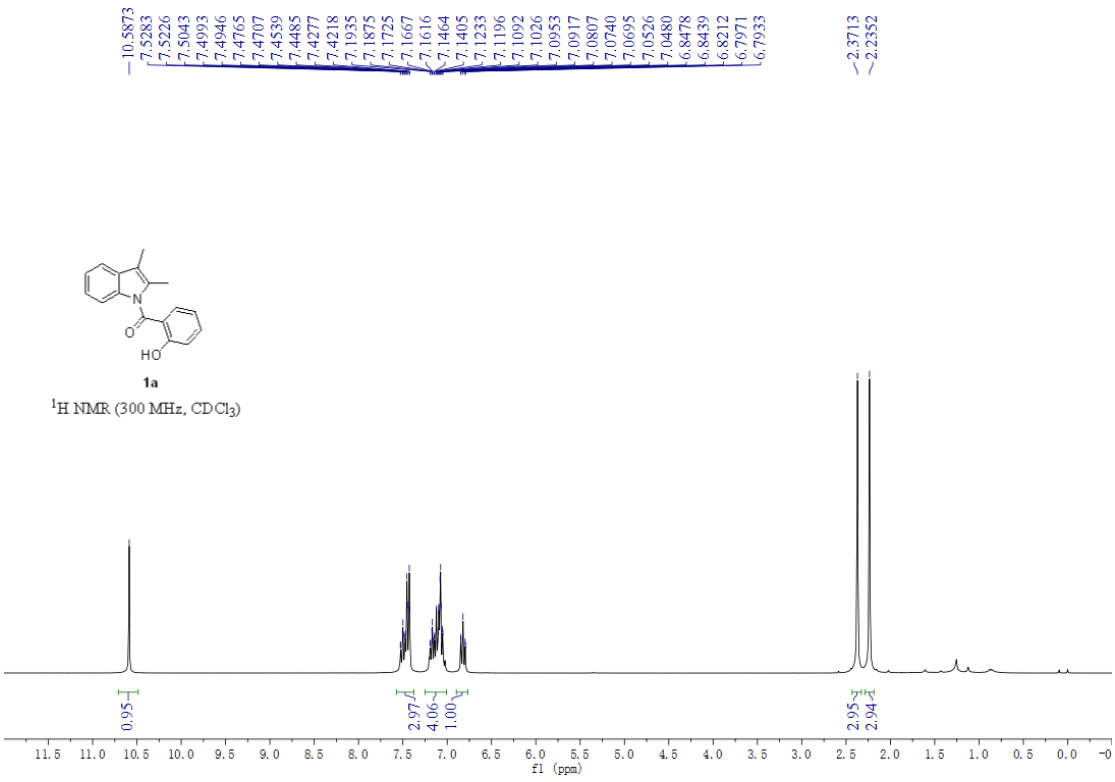


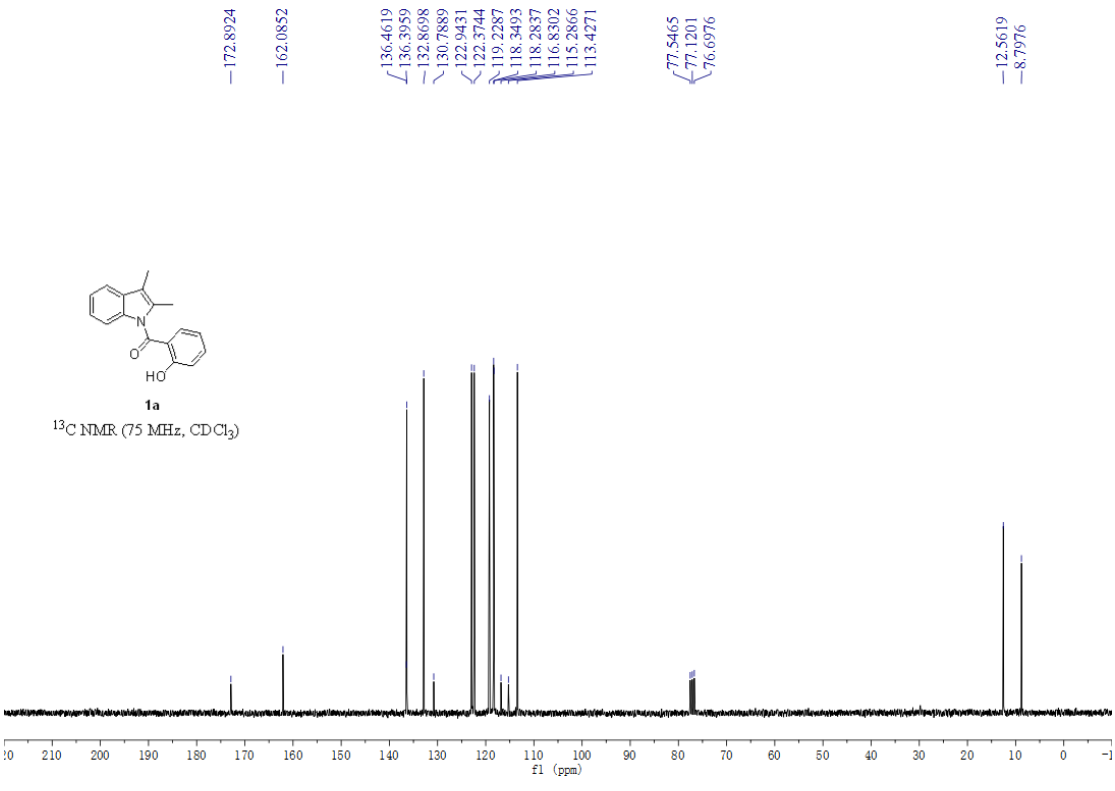
Figure S2. ORTEP plot of the crystal structure of 4a.

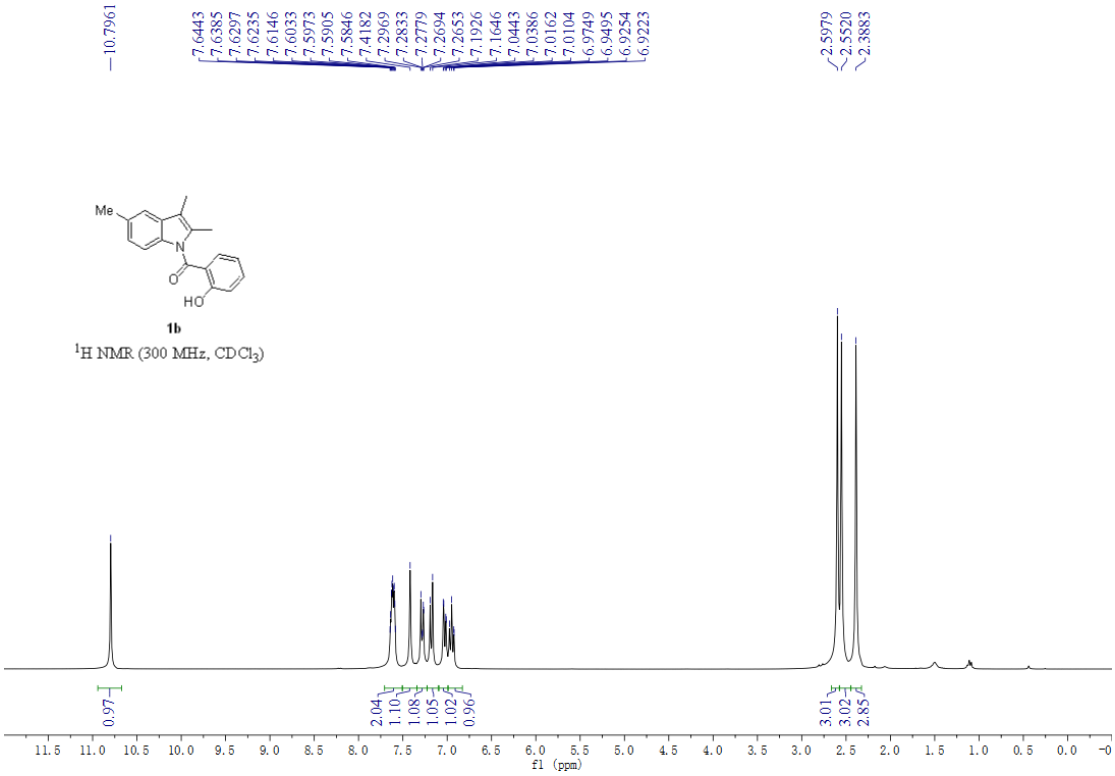
X-ray crystallographic data of 4a

CCDC number	1508996
Empirical formula	$C_{16}H_{11}NO_3$
Formula weight	265.26
Temperature	296 K
Wavelength	0.71073 Å
Space group	P21/c
Unit cell dimensions	a= 8.269(3) Å =90 º
	b= 9.296(4) Å =93.281(4) º
	c= 16.904(7) Å =90 º
Volume	1297.3(9) $Å^3$
Z	4
Density (calculated)	1.358 Mg/m^3
F(000)	552.0
Completeness to theta = 25.010 °	91.1%
Absorption correction	MULTI-SCAN
Max. and min. transmission	0.991 and 0.989
R indices (all data)	R= 0.0372(2113) wR2(reflections)= 0.1039(2581)

12. ^{1}H and ^{13}C NMR spectra of title compounds

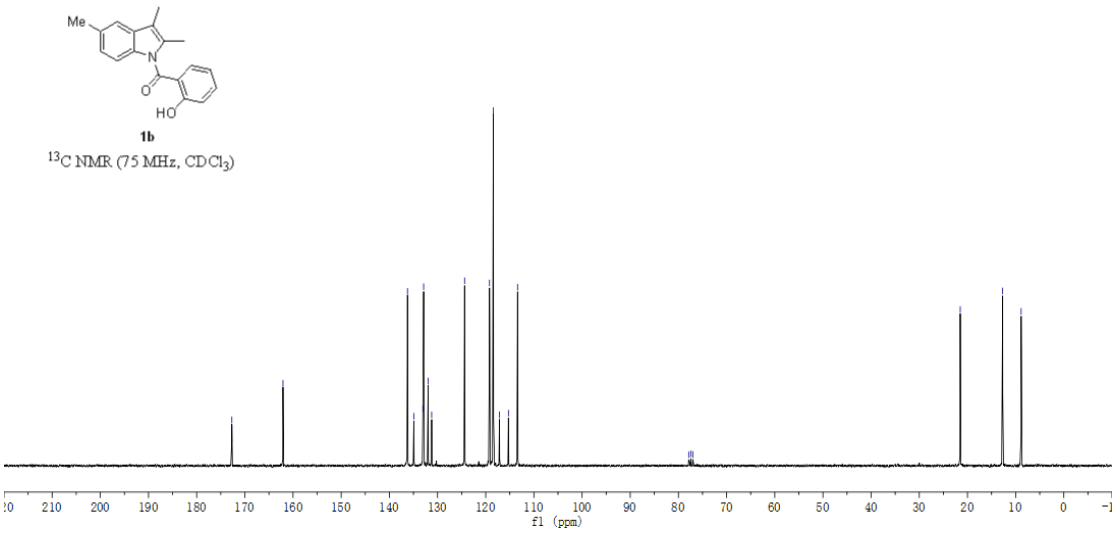






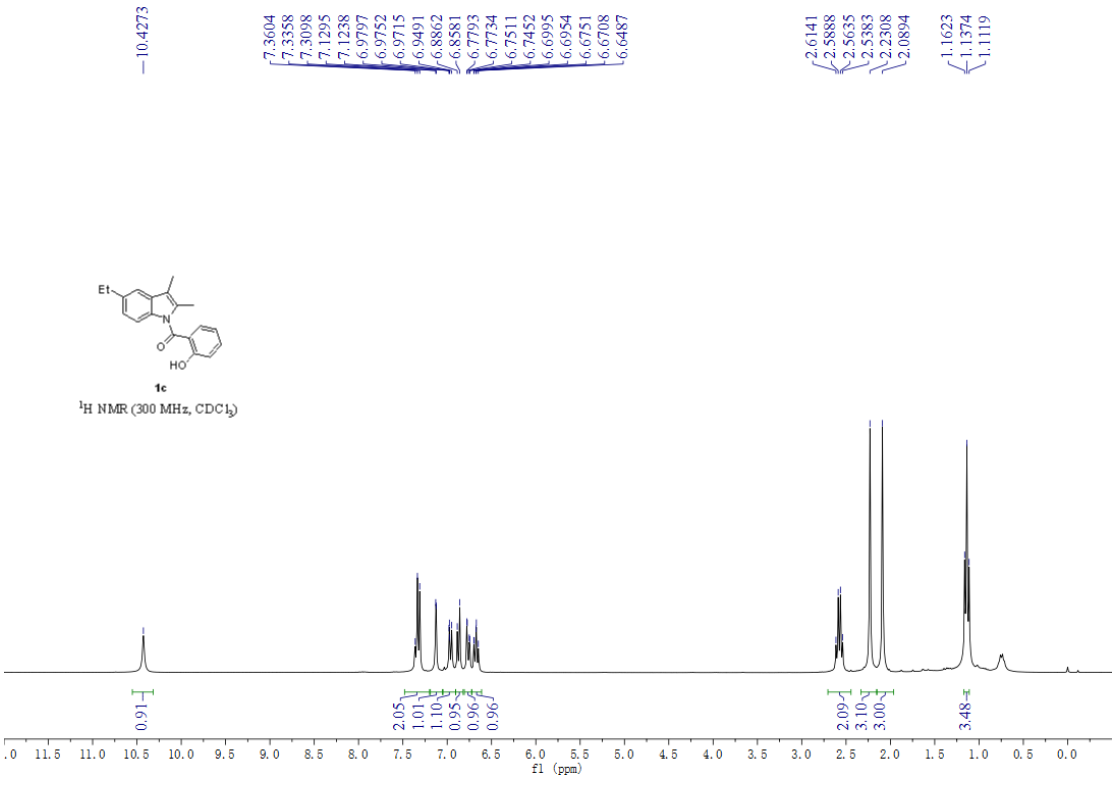
1b

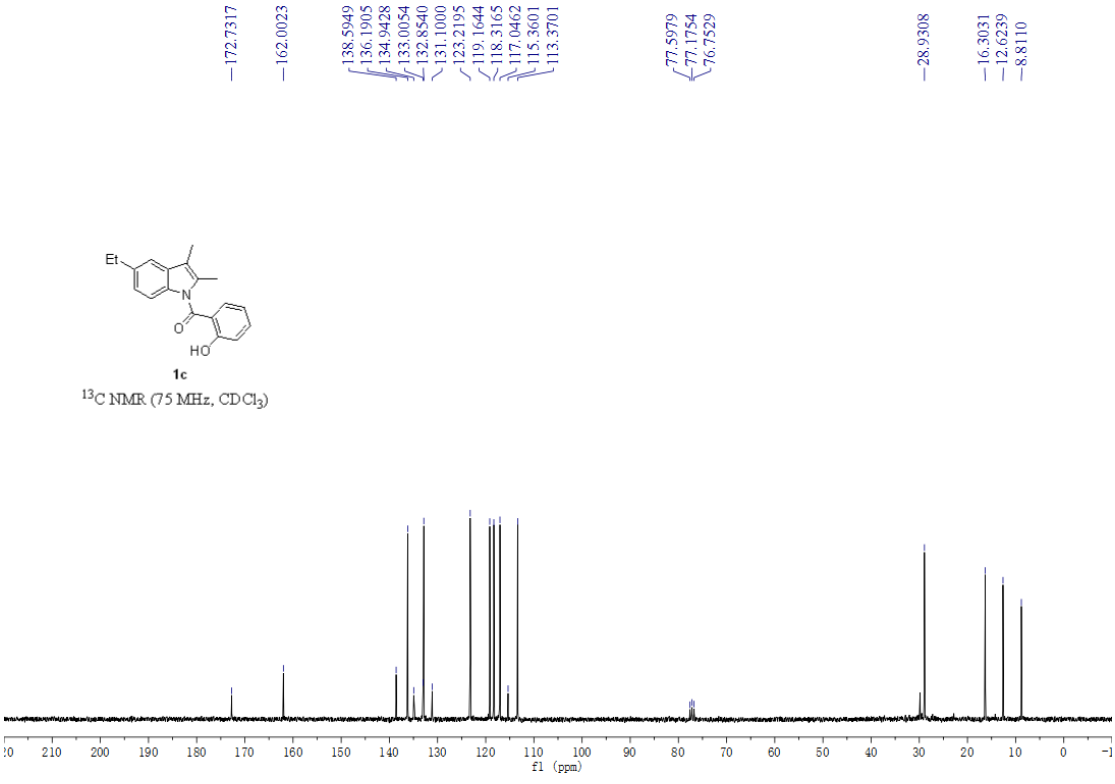
^{1}H NMR (300 MHz, $CDCl_3$)

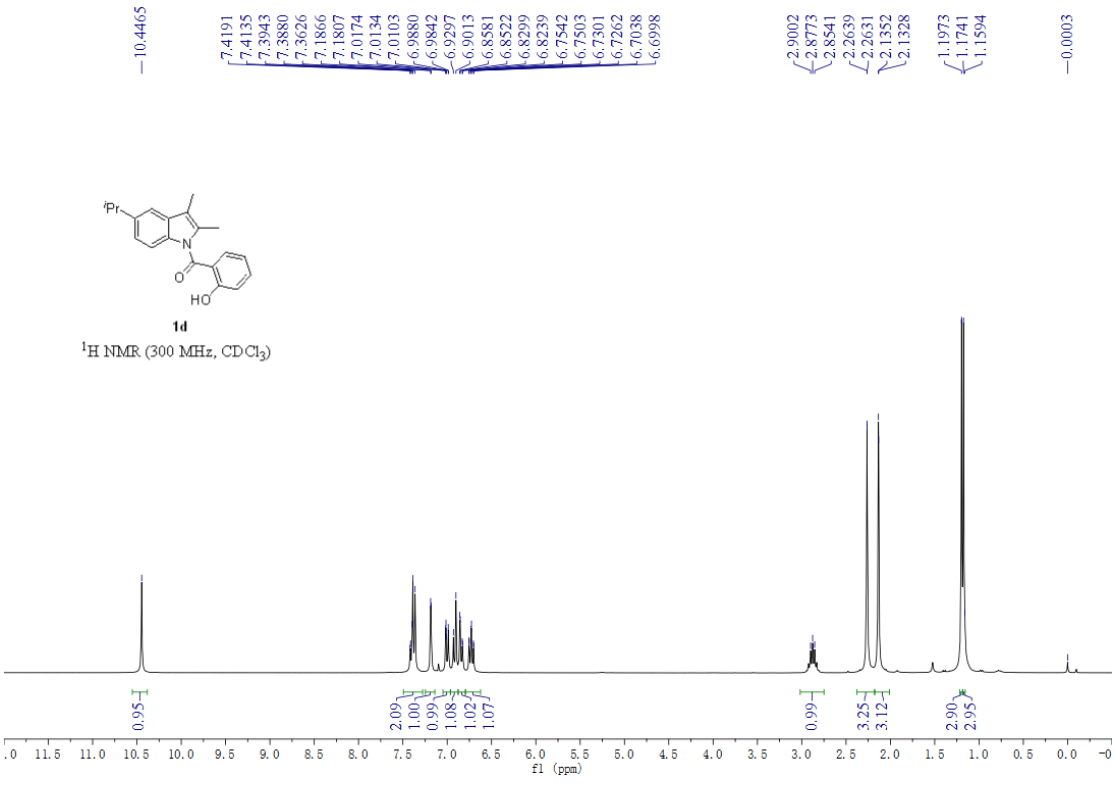


1b

^{13}C NMR (75 MHz, $CDCl_3$)

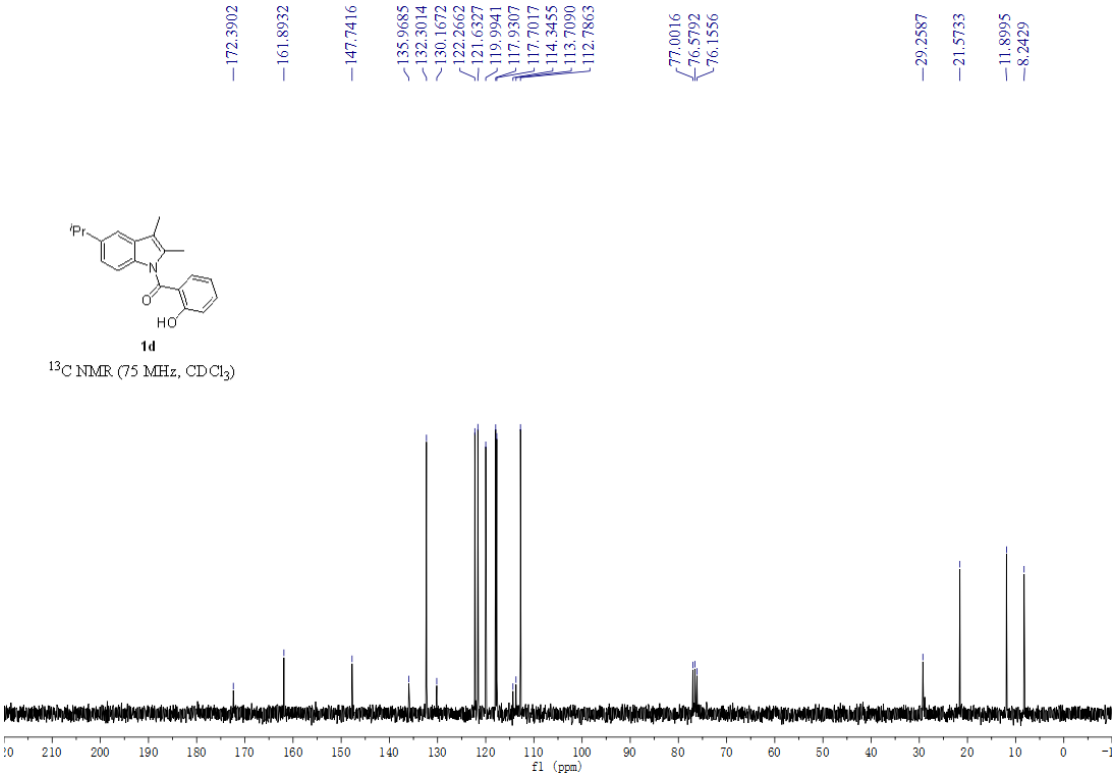

10.4273
7.3604
7.3358
7.3098
7.1295
7.1238
6.9797
6.9752
6.9715
6.9491
6.8862
6.8581
6.7793
6.7734
6.7511
6.7452
6.6995
6.6954
6.6751
6.6708
6.6487
2.6141
2.5888
2.5635
2.5383
2.2308
2.0894
1.1623
1.1374
1.1119
Et
N
O
HO
1c
^{1}H NMR (300 MHz, CDCl$_3$)
0.91
2.05
1.01
1.10
0.95
0.96
0.96
2.09
3.10
3.00
3.48
f1 (ppm)


172.7317
162.0023
138.5949
136.1905
134.9428
133.0054
132.8540
131.1000
123.2195
119.1644
118.3165
117.0462
115.3601
113.3701
77.5979
77.1754
76.7529
28.9308
16.3031
12.6239
8.8110
Et
N
O
HO
1c
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)



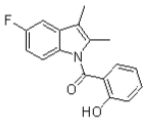
1d

^{1}H NMR (300 MHz, $CDCl_3$)



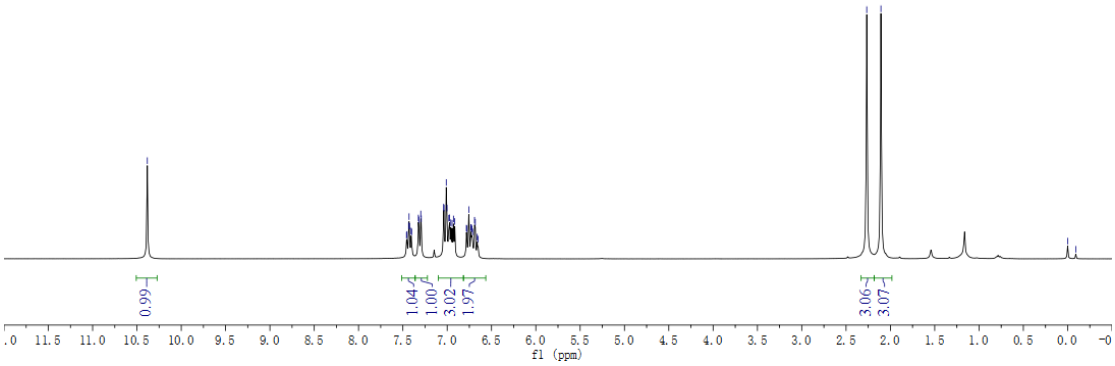
1d

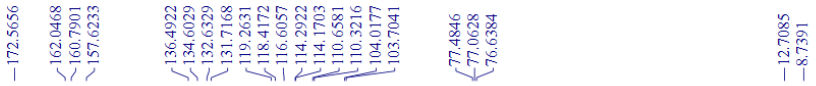
^{13}C NMR (75 MHz, $CDCl_3$)

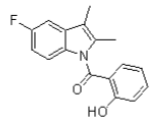


1e

^{1}H NMR (300 MHz, $CDCl_3$)

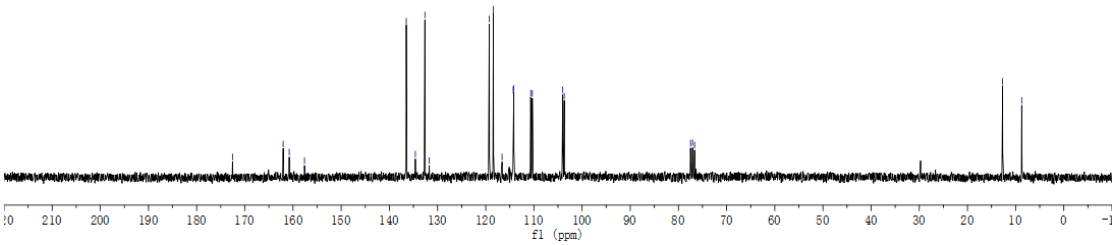


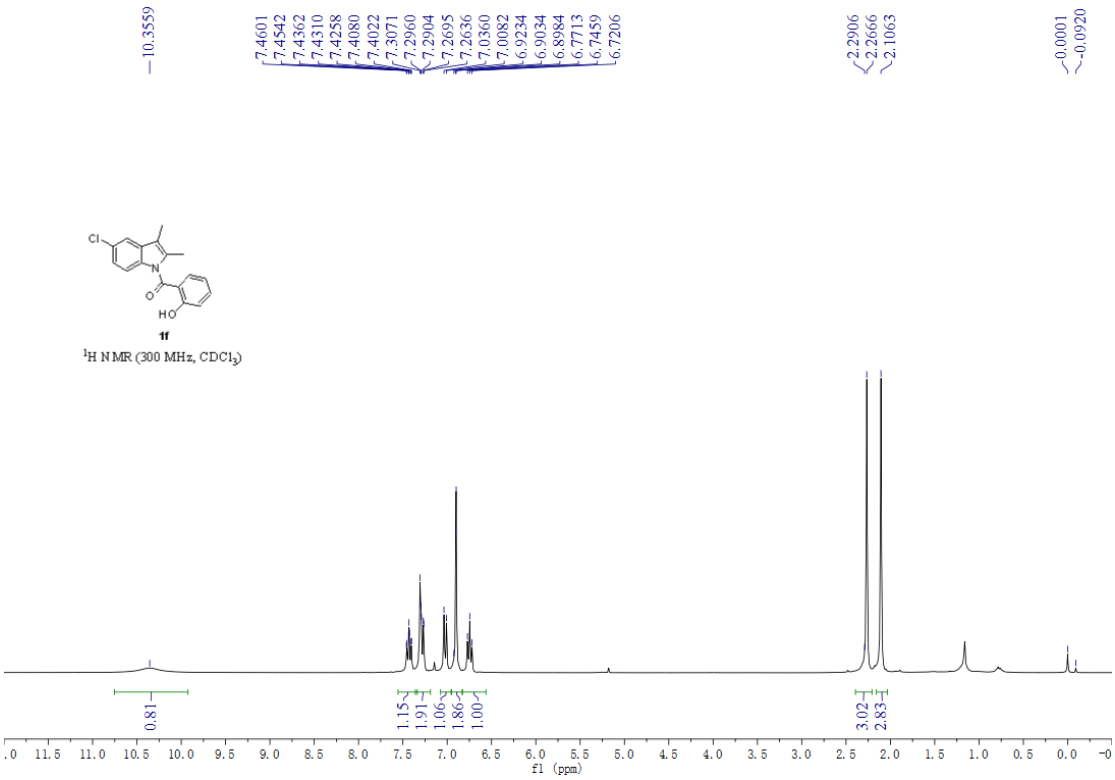




1e

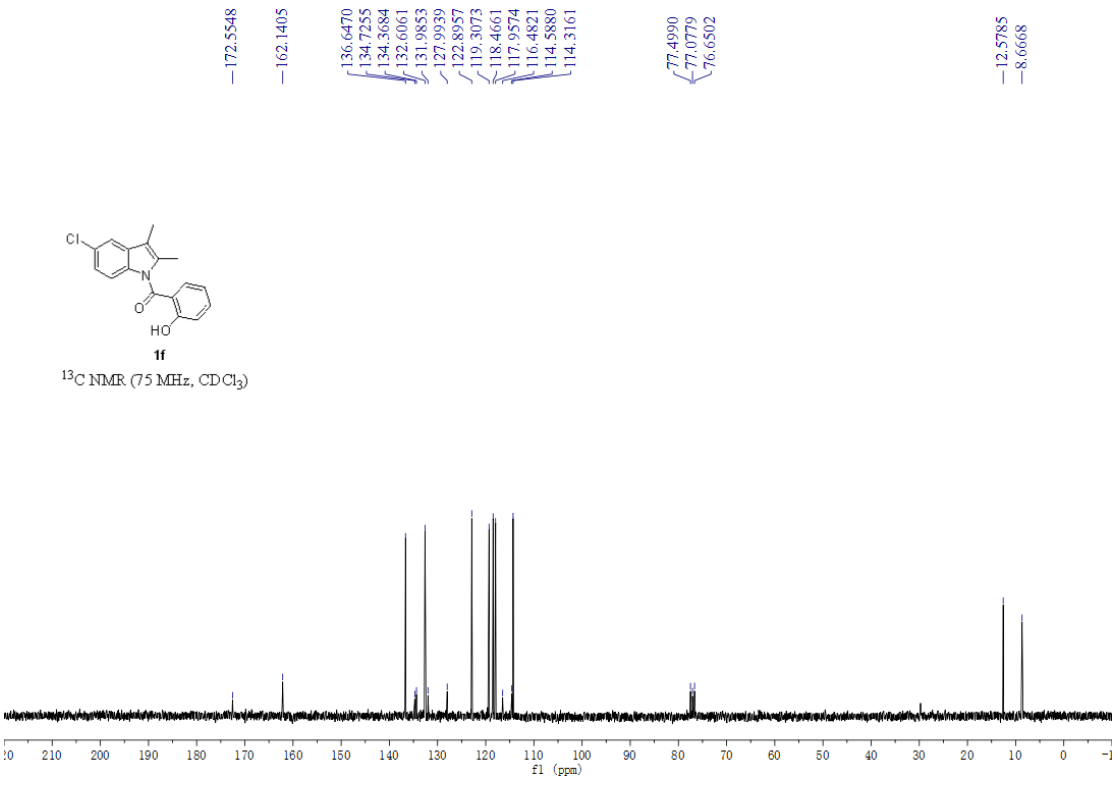
^{13}C NMR (75 MHz, $CDCl_3$)





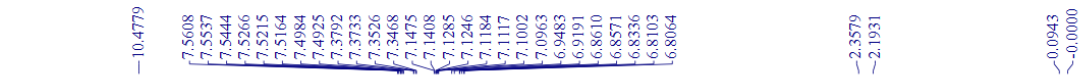
1f

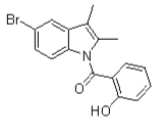
^{1}H NMR (300 MHz, $CDCl_3$)



1f

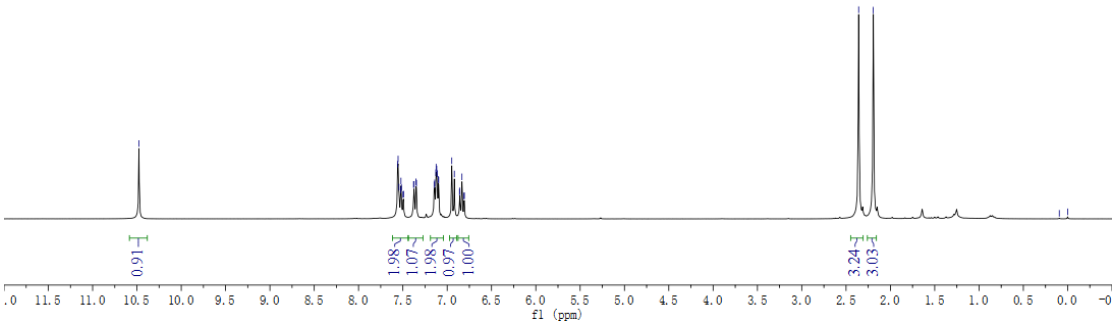
^{13}C NMR (75 MHz, $CDCl_3$)

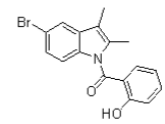




1g

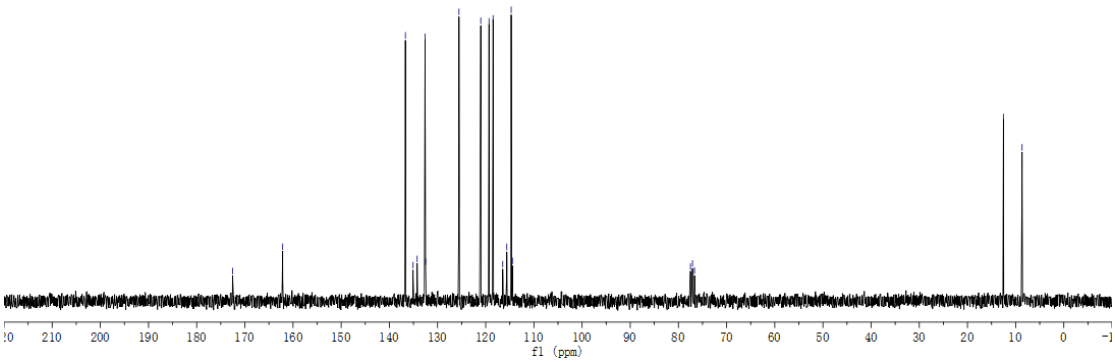
^{1}H NMR (300 MHz, $CDCl_3$)

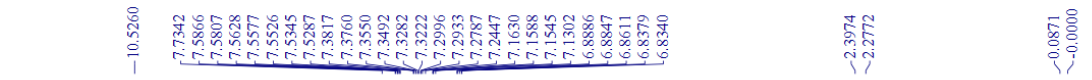


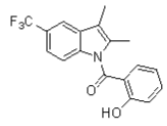


1g

^{13}C NMR (75 MHz, $CDCl_3$)

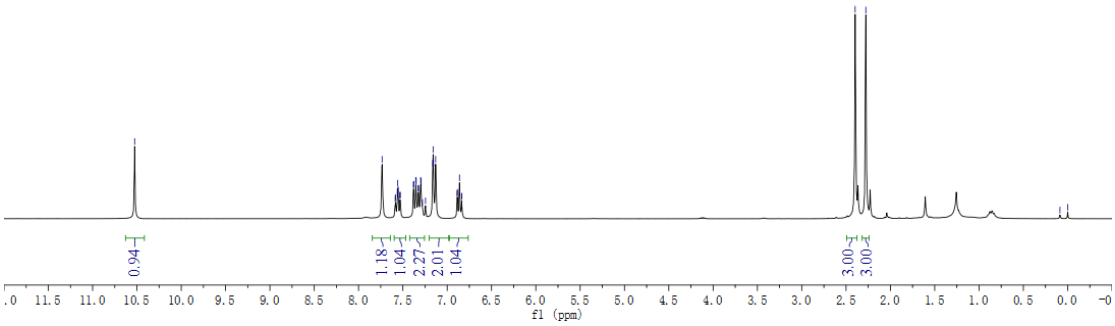


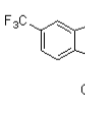




1h

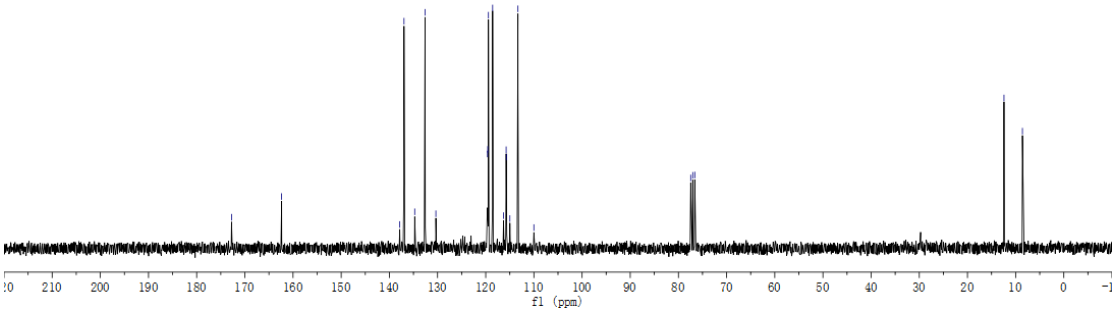
^{1}H NMR (300 MHz, $CDCl_3$)

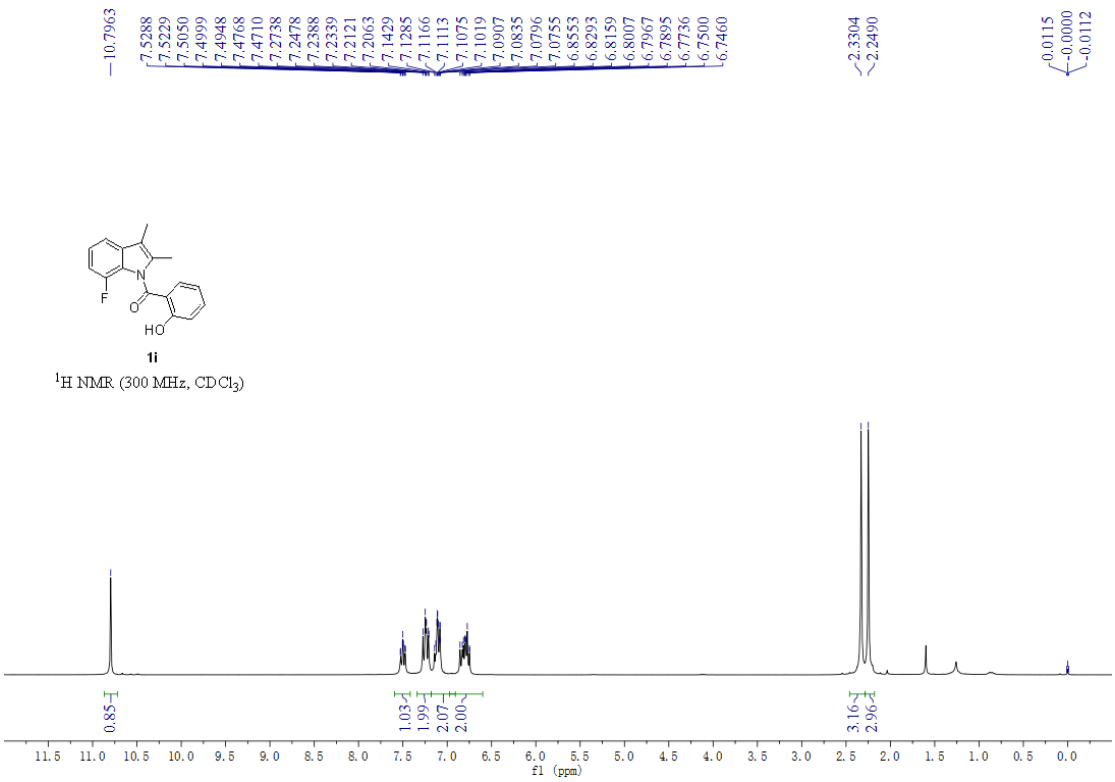




1h

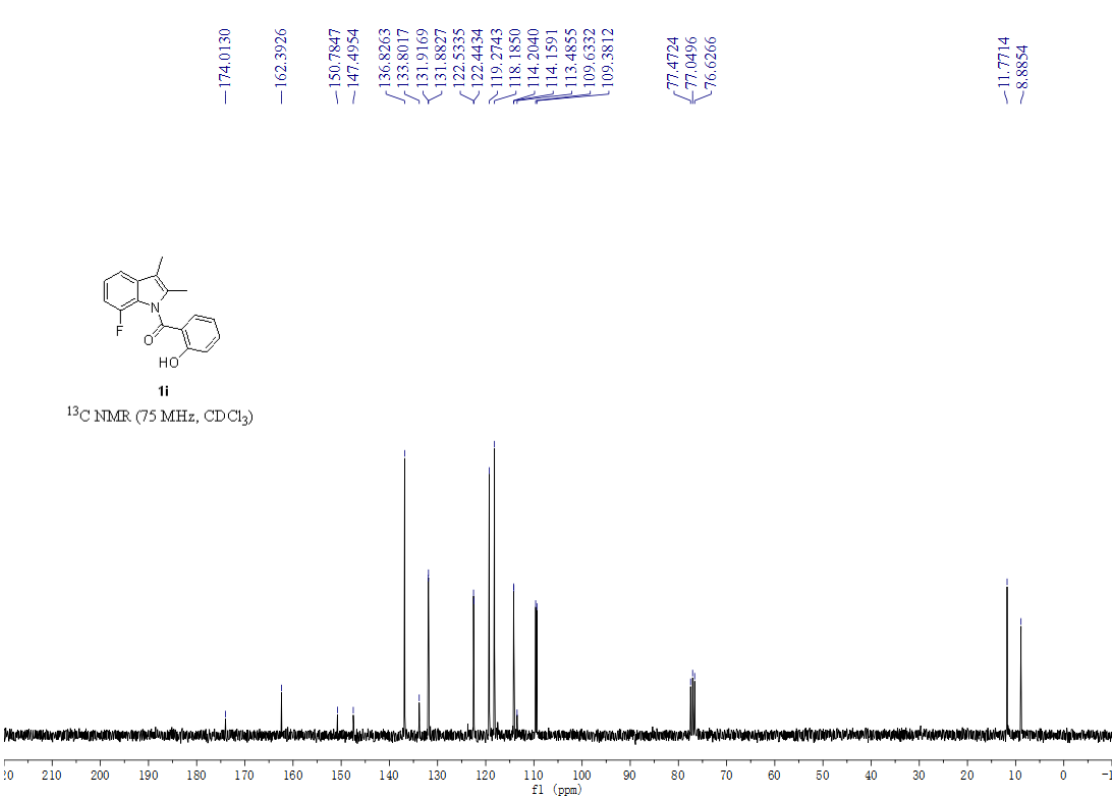
^{13}C NMR (75 MHz, $CDCl_3$)





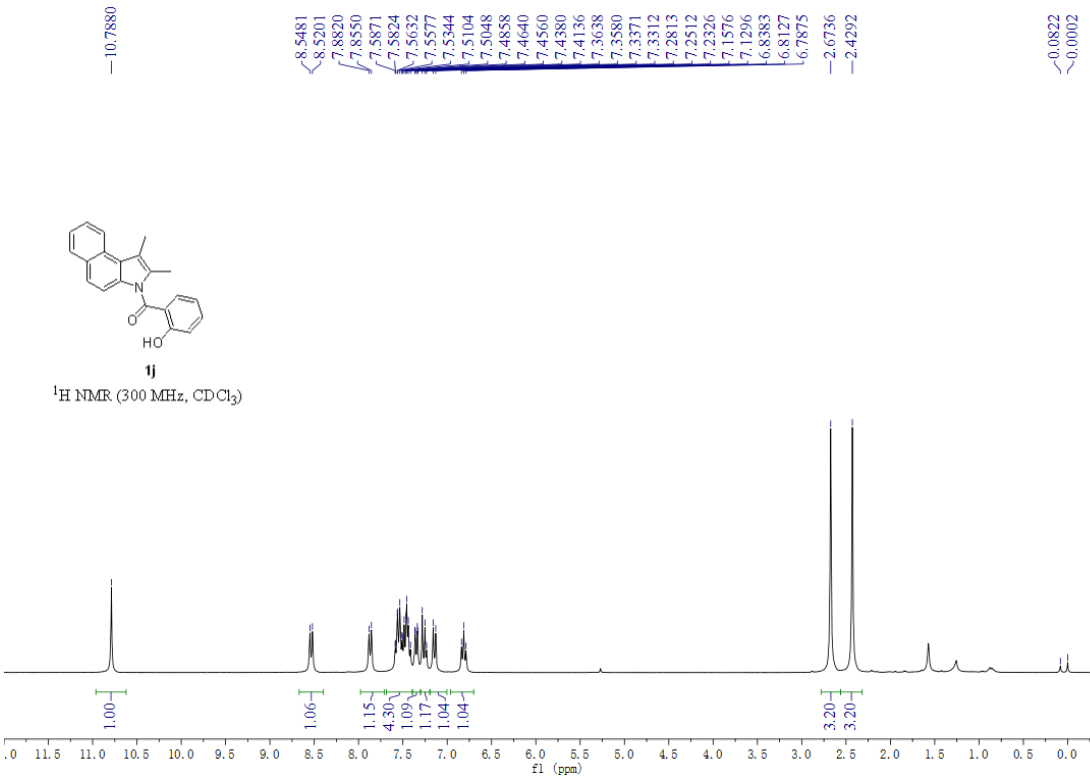
1i

^{1}H NMR (300 MHz, $CDCl_3$)



1i

^{13}C NMR (75 MHz, $CDCl_3$)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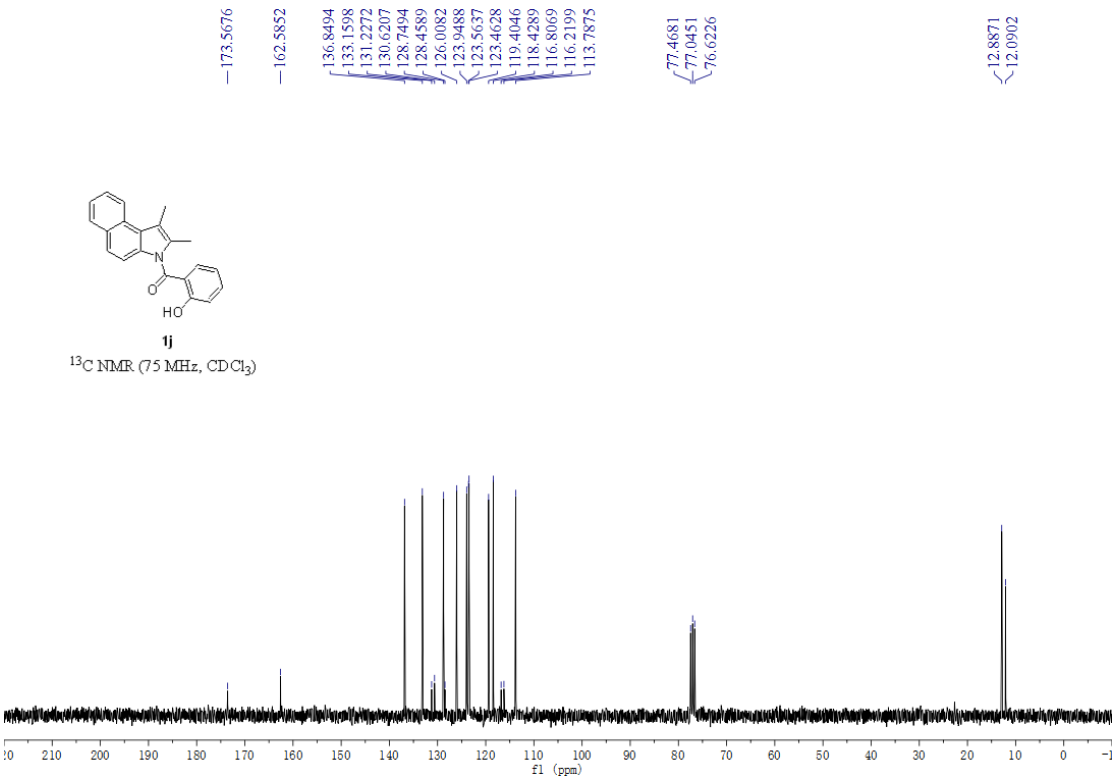
8.5201
7.8820
7.8550
7.5871
7.5824
7.5632
7.5577
7.5344
7.5104
7.5048
7.4858
7.4640
7.4560
7.4380
7.4136
7.3638
7.3580
7.3371
7.3312
7.2813
7.2512
7.2326
7.1576
7.1296
6.8383
6.8127
6.7875
2.6736
2.4292
0.0822
0.0002
HO
1j
1H NMR (300 MHz, CDCl3)
1.00
1.06
1.15
4.30
1.09
1.17
1.04
1.04
3.20
3.20
f1 (ppm)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136.8494
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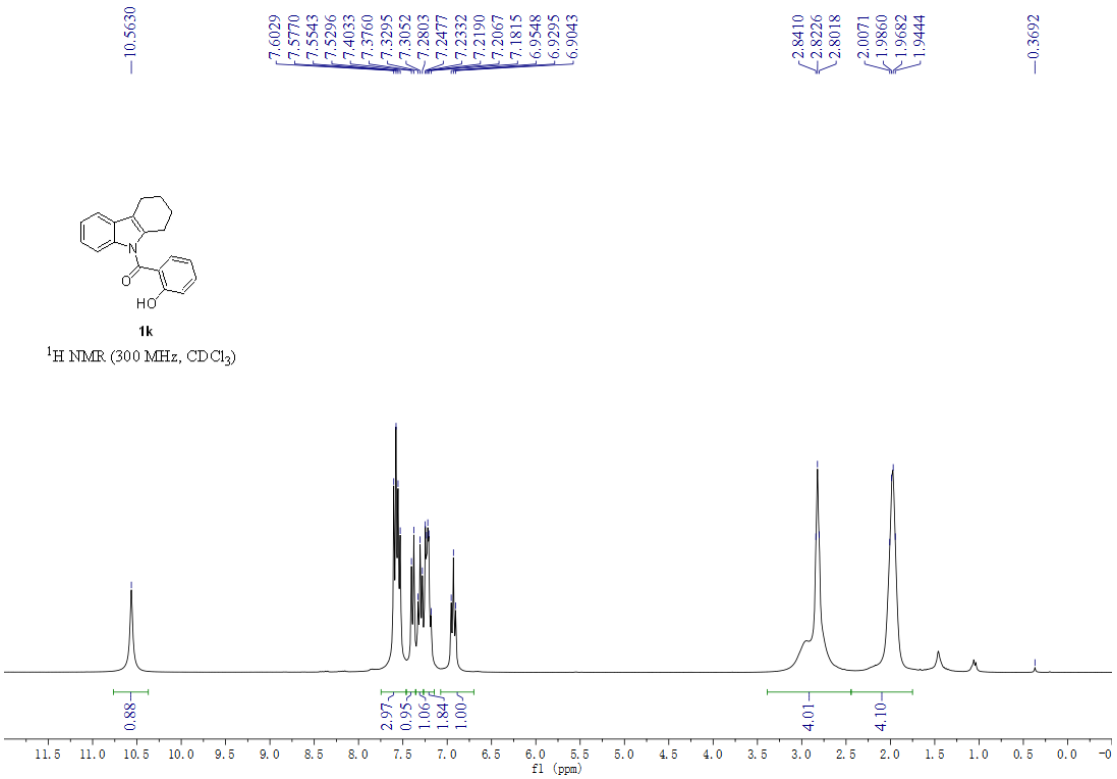
123.9488
123.5637
123.4628
119.4046
118.4289
116.8069
116.2199
113.7875
77.4681
77.0451
76.6226
12.8871
12.0902
HO
1j
13C NMR (75 MHz, CDCl3)
f1 (ppm)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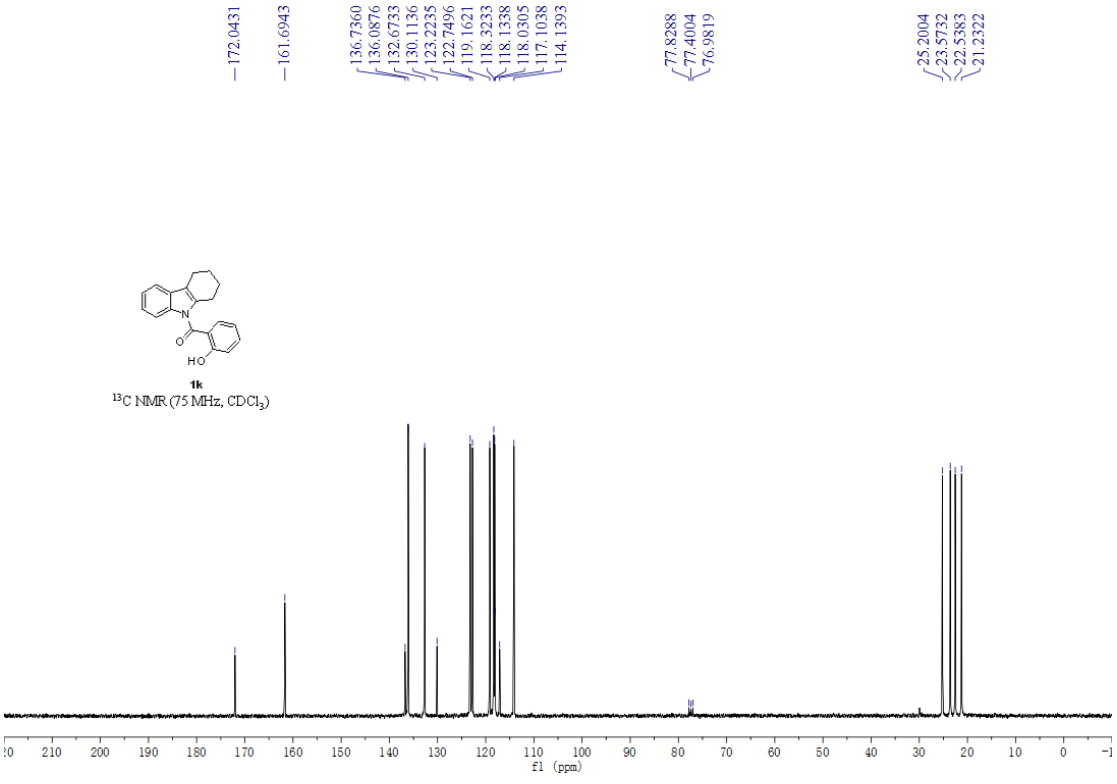
7.5770
7.5543
7.5296
7.4033
7.3760
7.3295
7.3052
7.2803
7.2477
7.2332
7.2190
7.2067
7.1815
6.9548
6.9295
6.9043
2.8410
2.8226
2.8018
2.0071
1.9860
1.9682
1.9444
0.3692
HO
1k
^{1}H NMR (300 MHz, $CDCl_3$)
0.88
2.97
0.95
1.06
1.84
1.00
4.01
4.10
f1 (ppm)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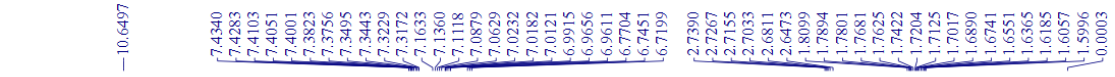
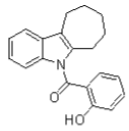
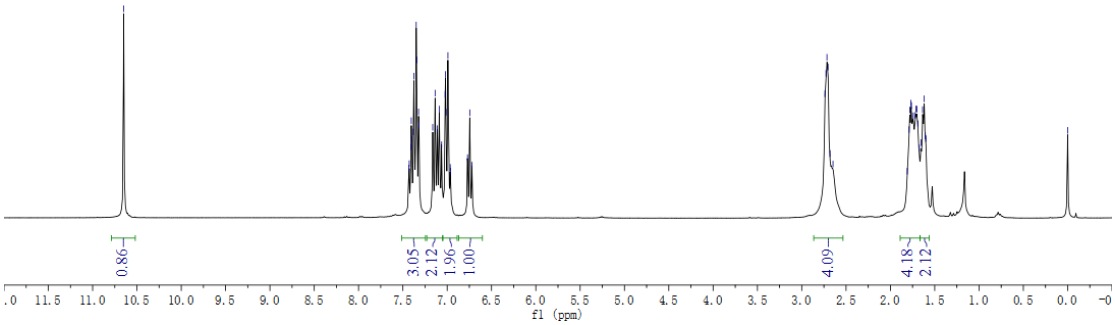
123.2235
122.7496
119.1621
118.3233
118.1338
118.0305
117.1038
114.1393
77.8288
77.4004
76.9819
25.2004
23.5732
22.5383
21.2322
HO
1k
^{13}C NMR (75 MHz, $CDCl_3$)
f1 (ppm)

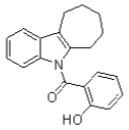




1l

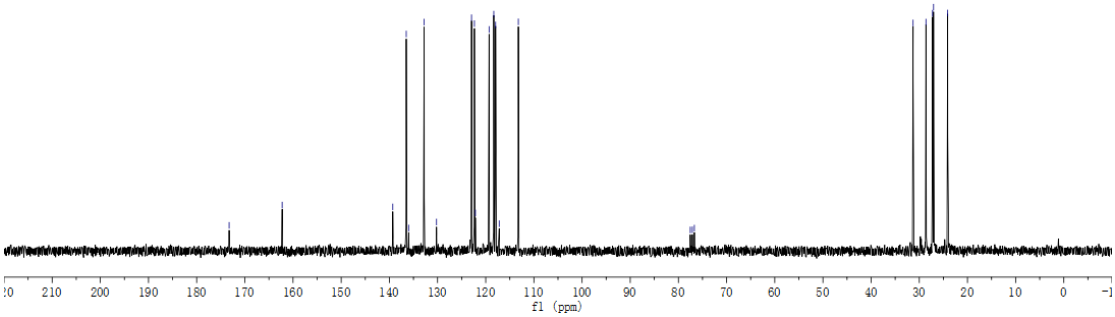
^{1}H NMR (300 MHz, $CDCl_3$)

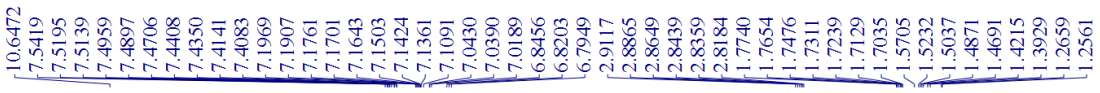


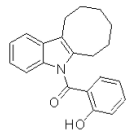


1l

^{13}C NMR (75 MHz, $CDCl_3$)

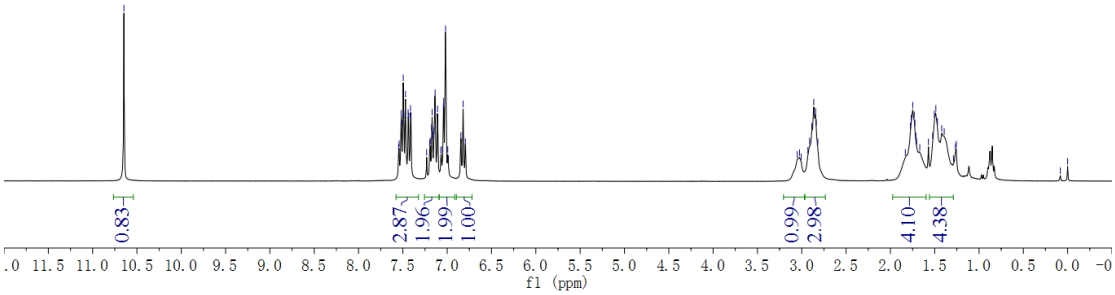


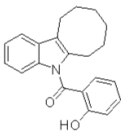




1m

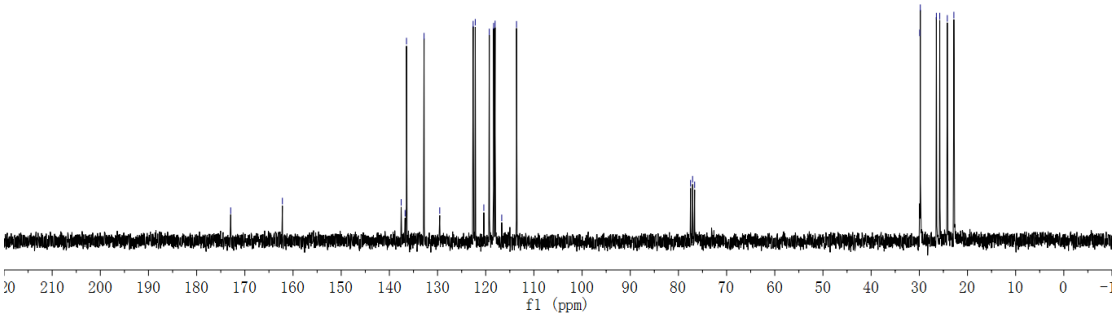
^{1}H NMR (300 MHz, $CDCl_3$)

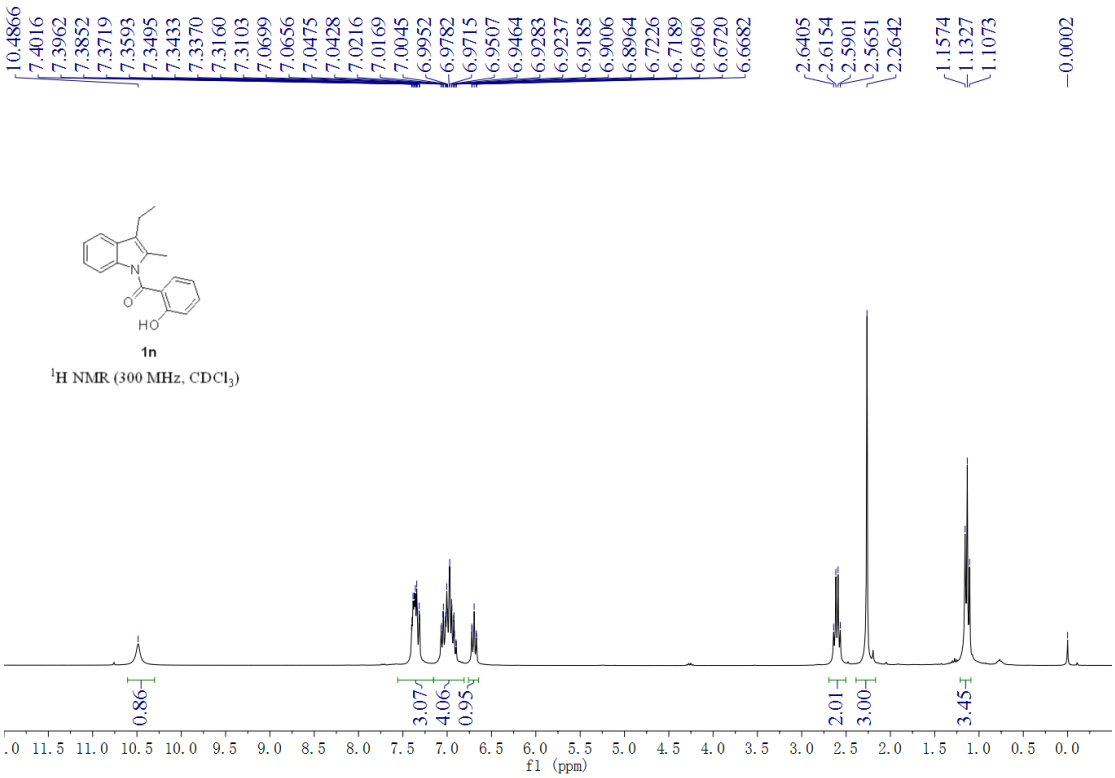




1m

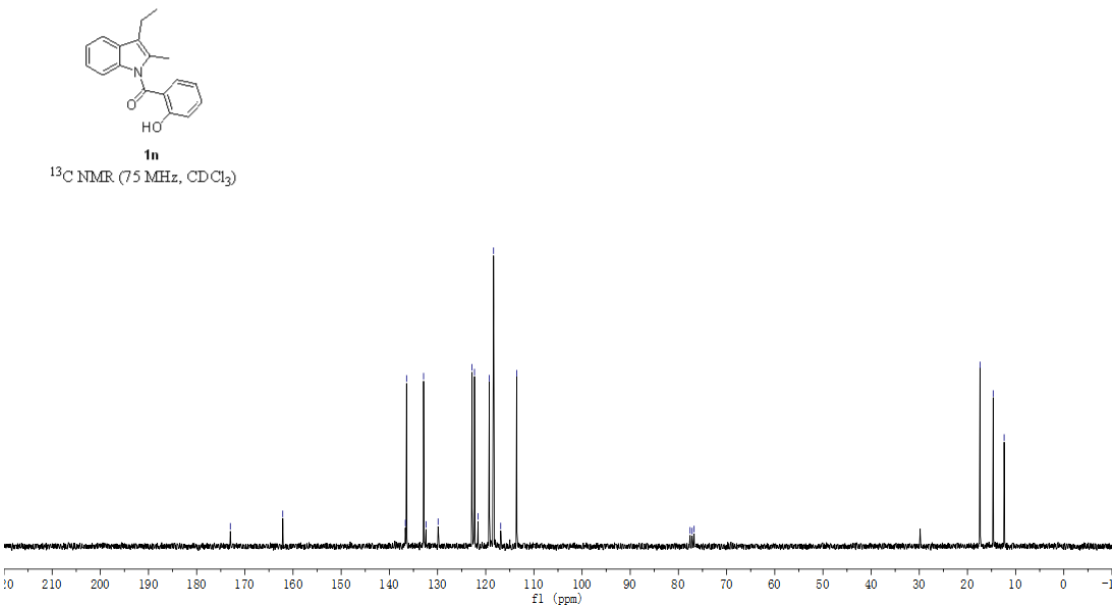
^{13}C NMR (75 MHz, $CDCl_3$)





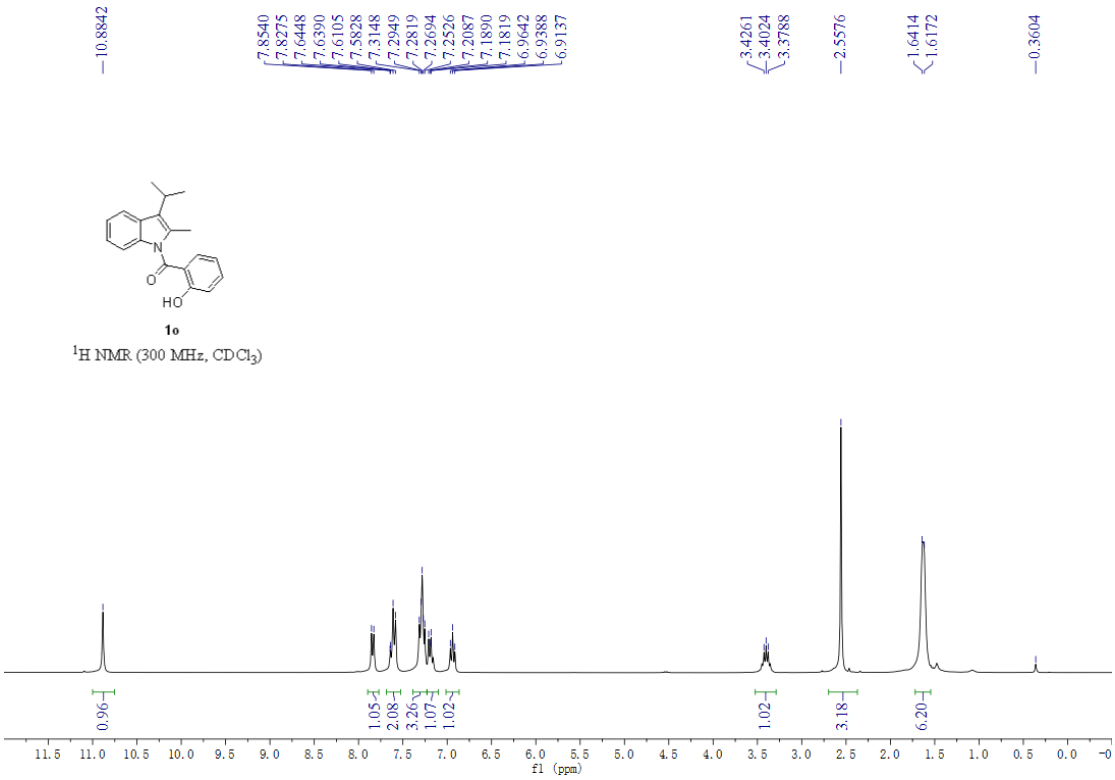
1n

^{1}H NMR (300 MHz, $CDCl_3$)



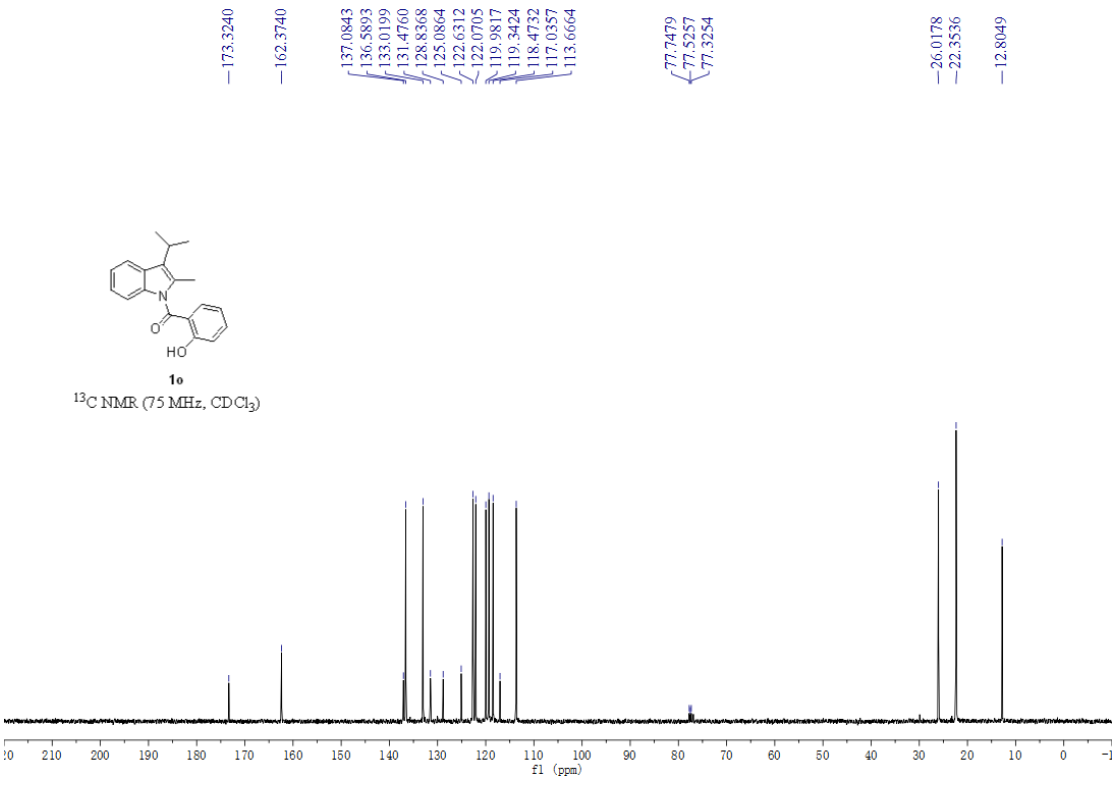
1n

^{13}C NMR (75 MHz, $CDCl_3$)



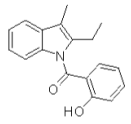
1o

^{1}H NMR (300 MHz, $CDCl_3$)



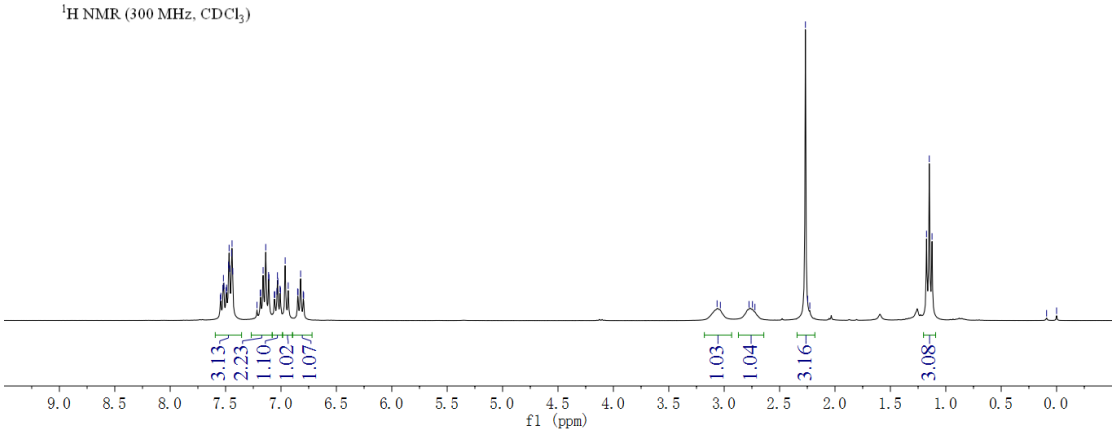
1o

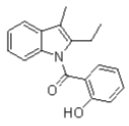
^{13}C NMR (75 MHz, $CDCl_3$)



1p

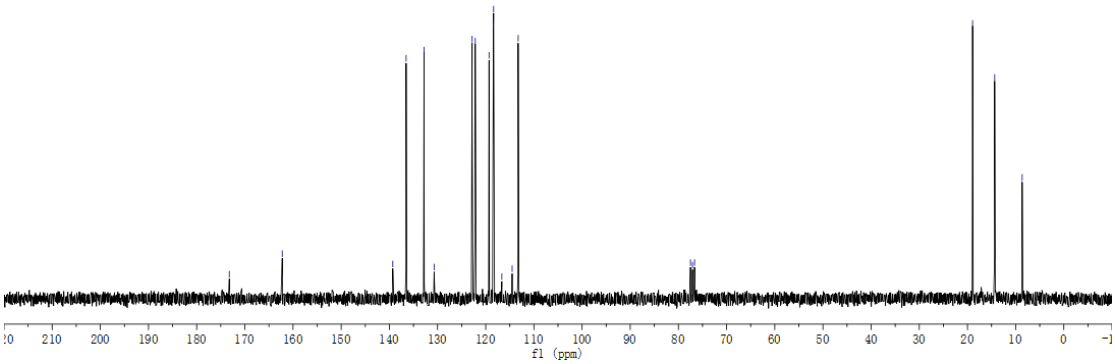
^{1}H NMR (300 MHz, $CDCl_3$)

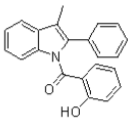




1p

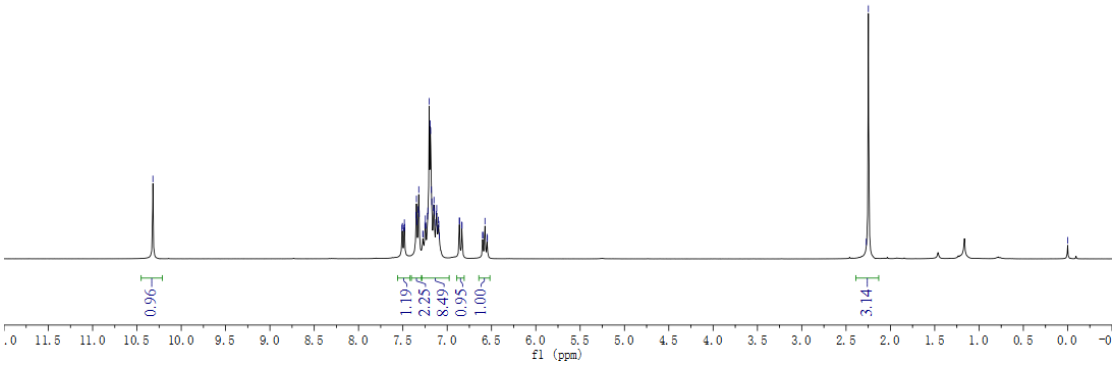
^{13}C NMR (75 MHz, $CDCl_3$)

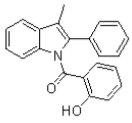




1q

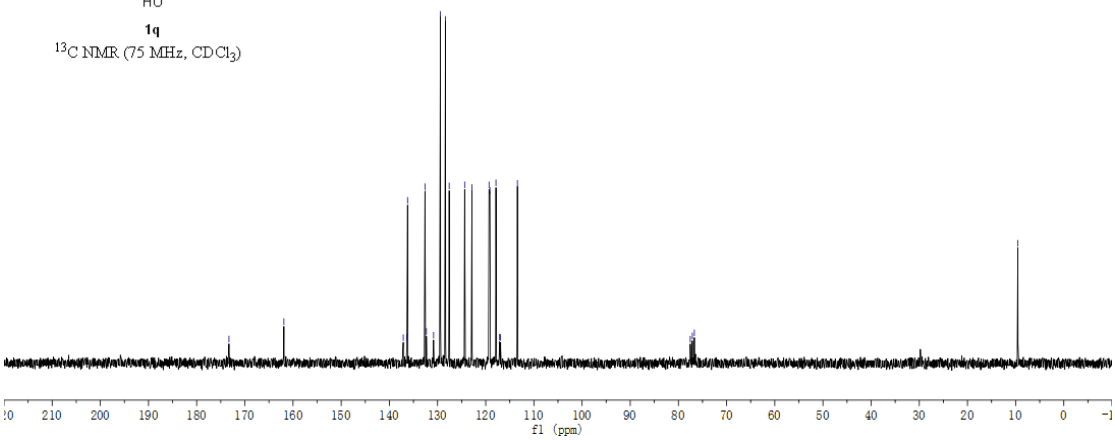
^{1}H NMR (300 MHz, $CDCl_3$)

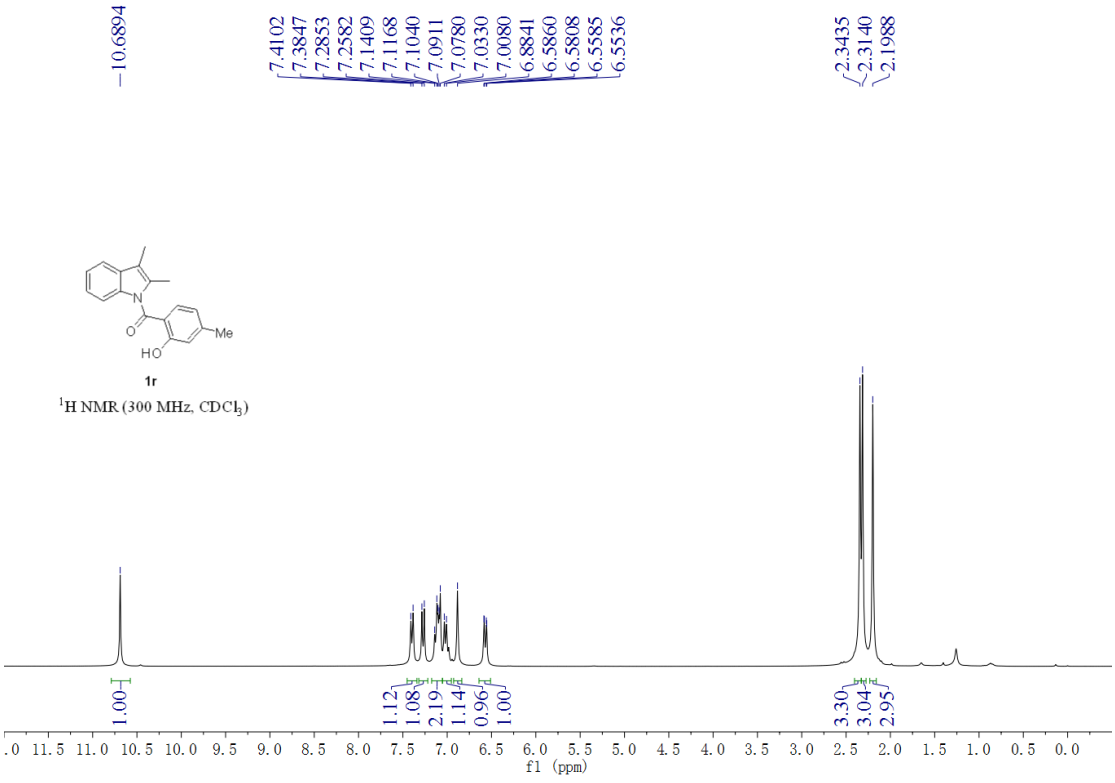




1q

^{13}C NMR (75 MHz, $CDCl_3$)



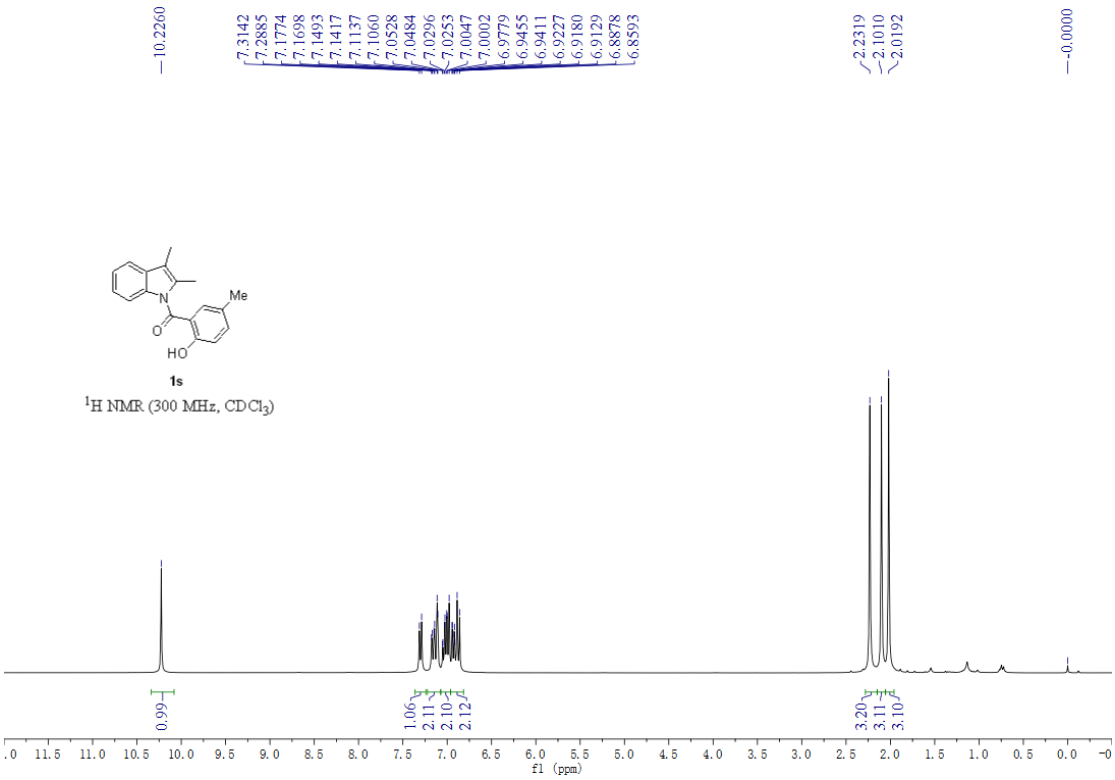


1r

^{1}H NMR (300 MHz, $CDCl_3$)

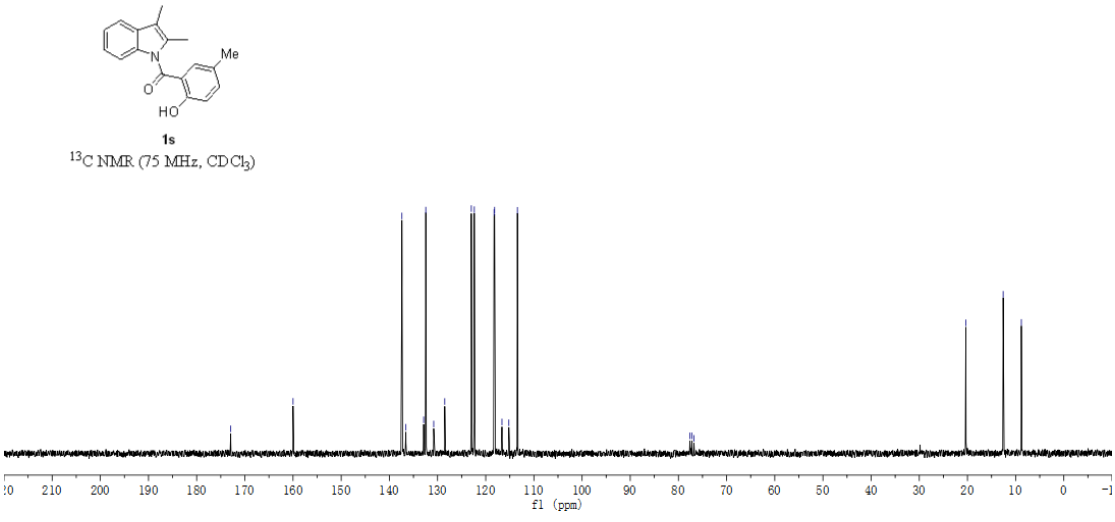
1r

^{13}C NMR (75 MHz, $CDCl_3$)



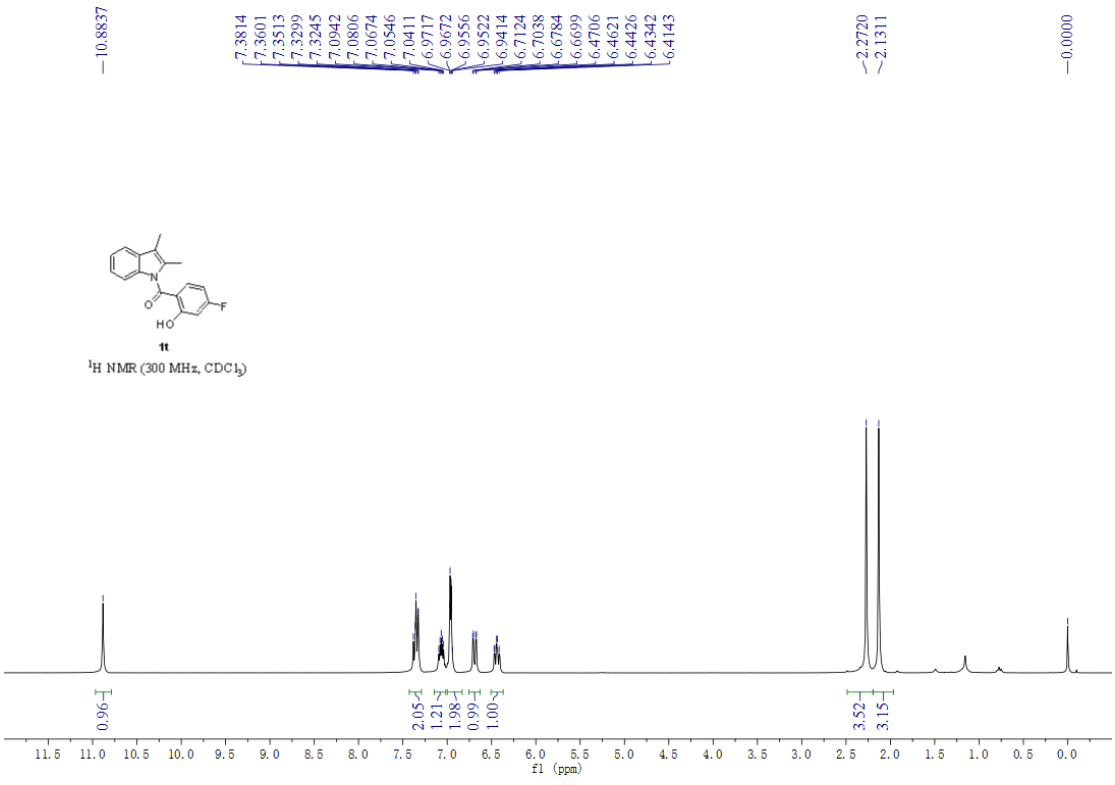
1s

^{1}H NMR (300 MHz, $CDCl_3$)



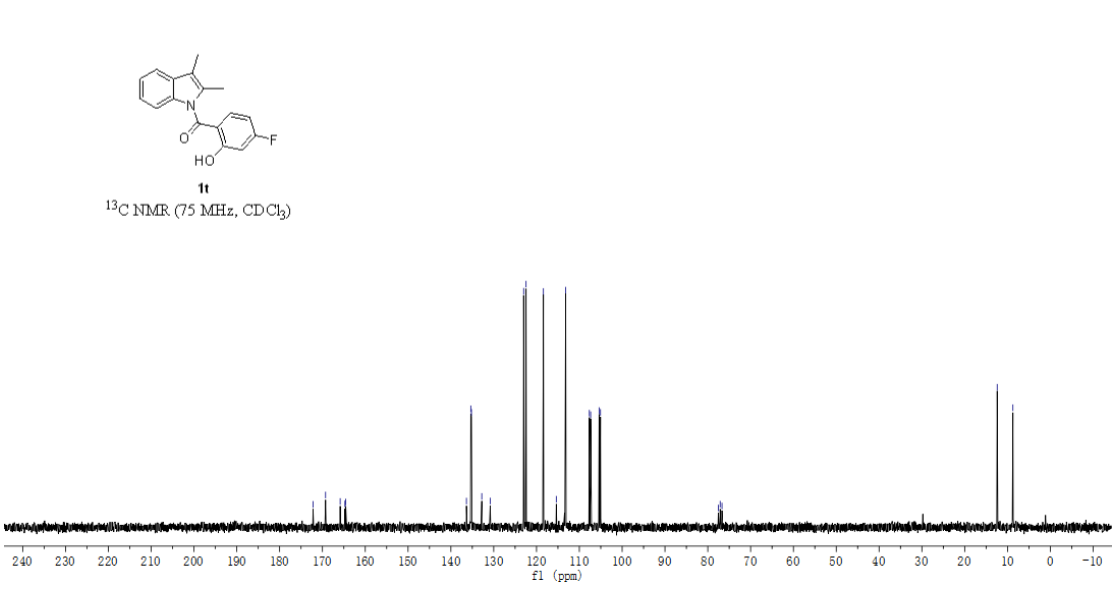
1s

^{13}C NMR (75 MHz, $CDCl_3$)



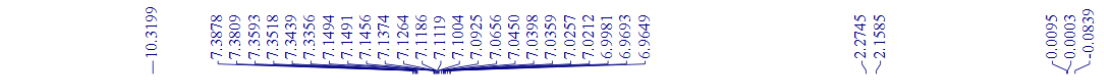
1t

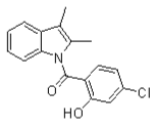
^{1}H NMR (300 MHz, $CDCl_3$)



1t

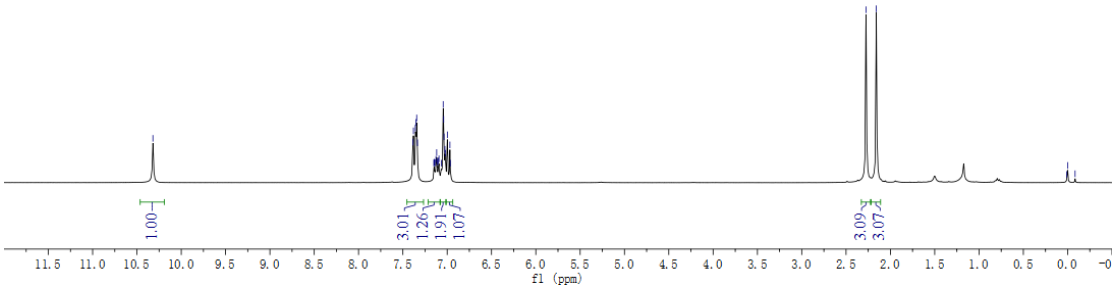
^{13}C NMR (75 MHz, $CDCl_3$)

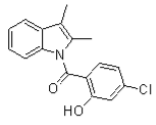




1u

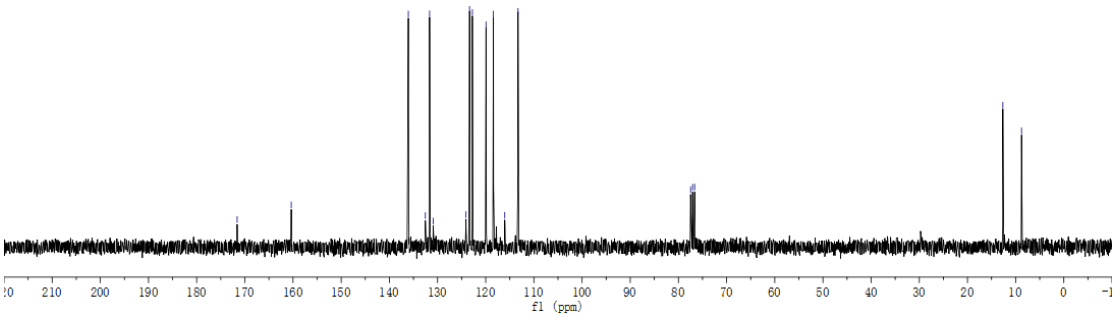
^{1}H NMR (300 MHz, $CDCl_3$)

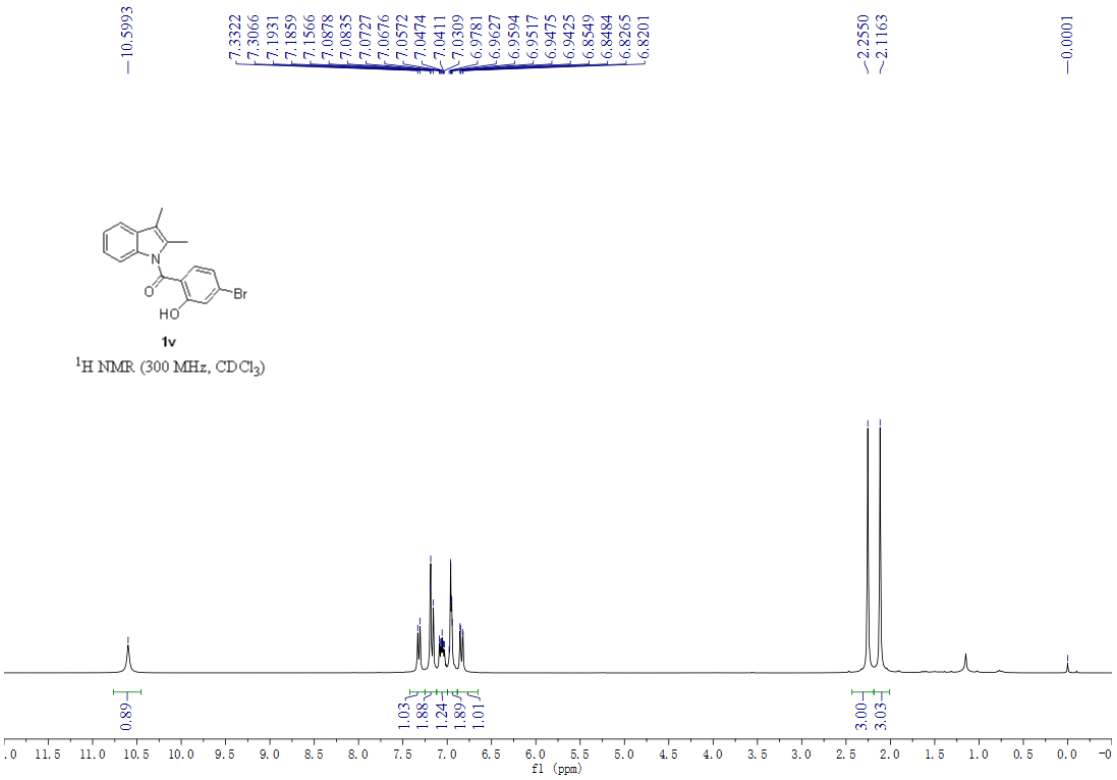




1u

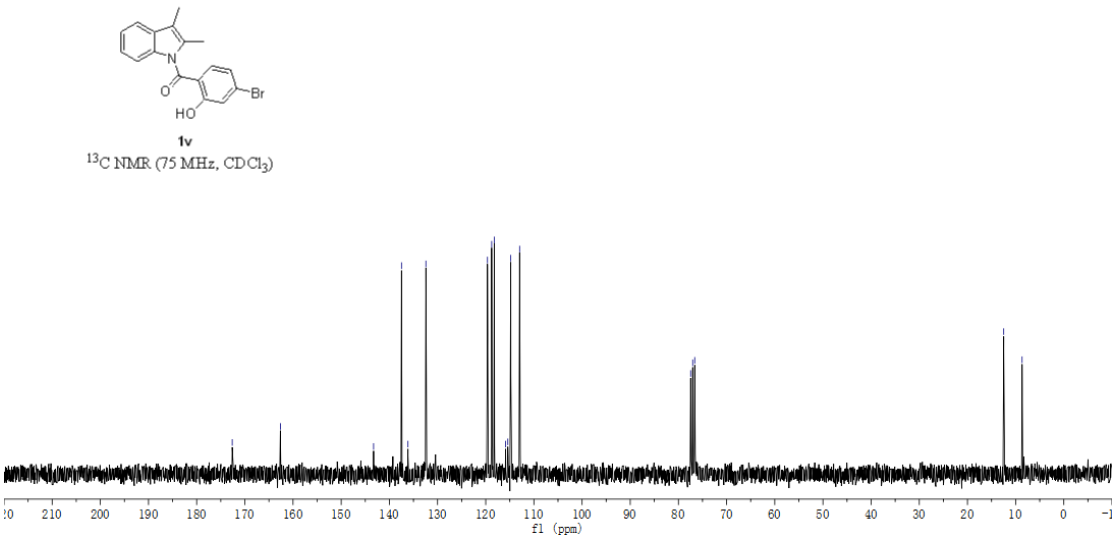
^{13}C NMR (75 MHz, $CDCl_3$)





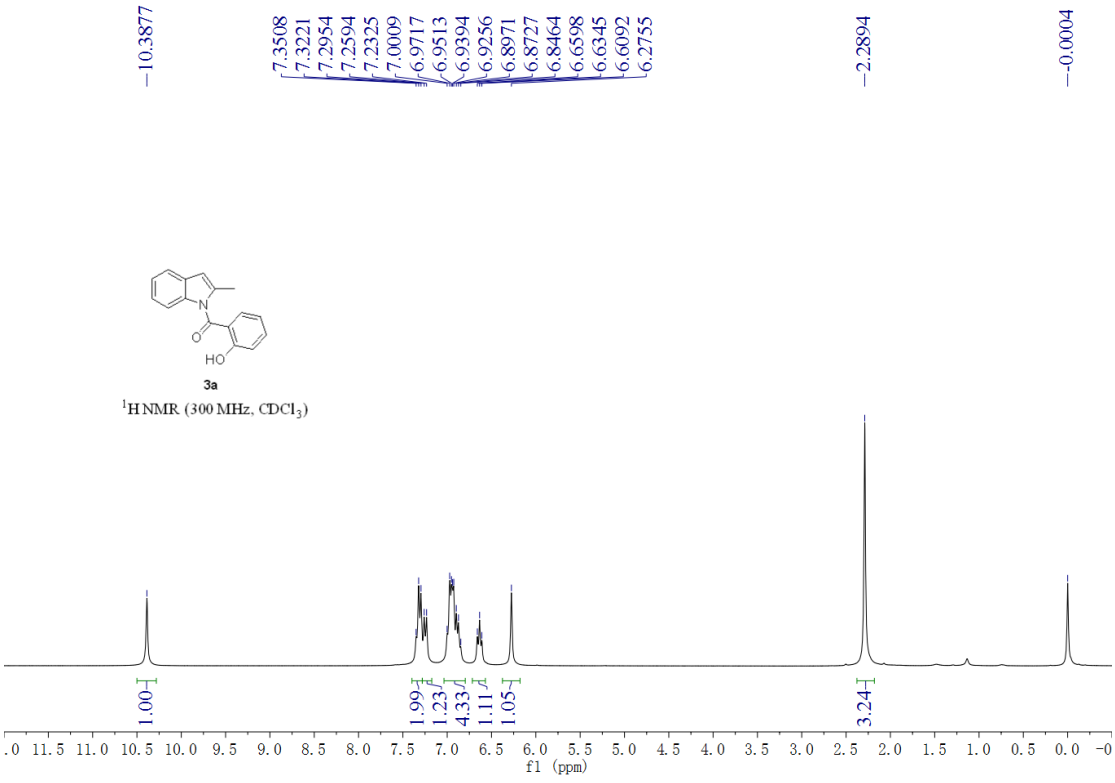
1v

^{1}H NMR (300 MHz, $CDCl_3$)



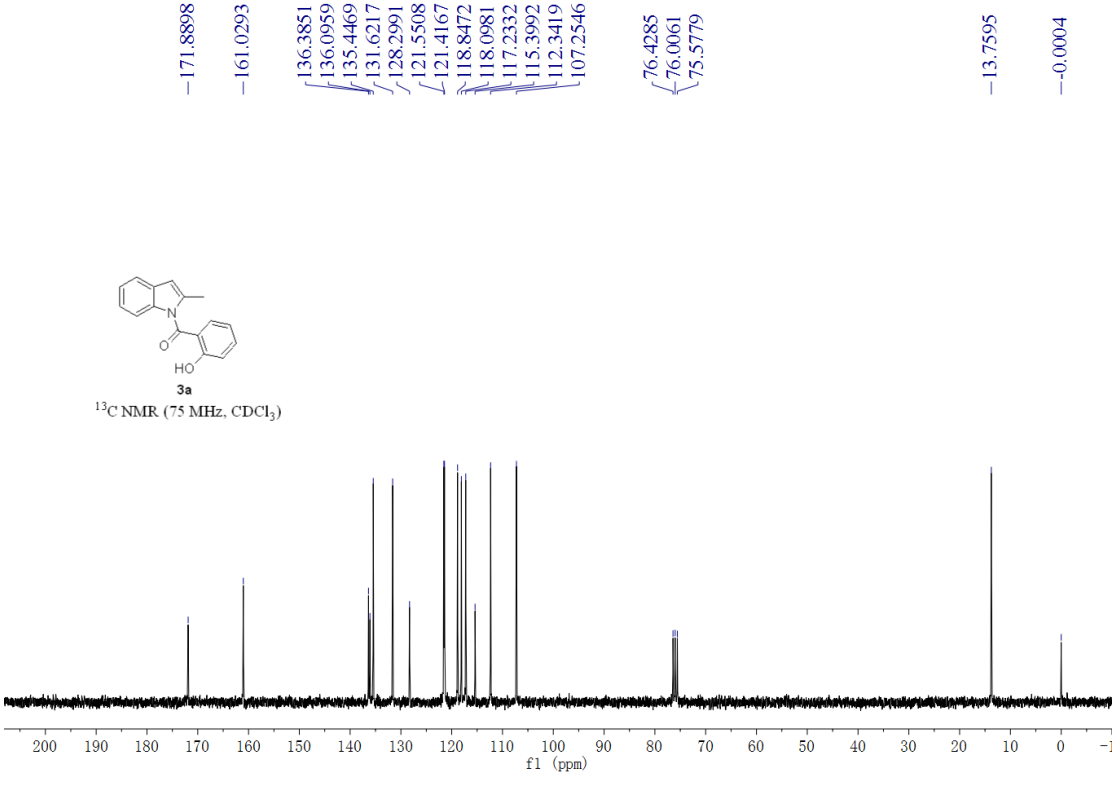
1v

^{13}C NMR (75 MHz, $CDCl_3$)



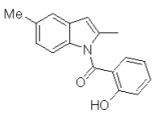
3a

^{1}H NMR (300 MHz, $CDCl_3$)



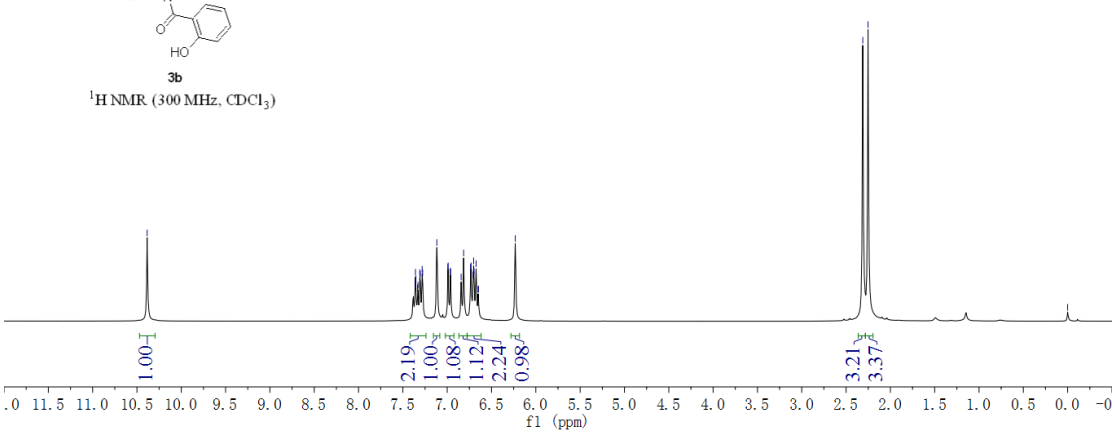
3a

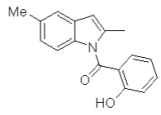
^{13}C NMR (75 MHz, $CDCl_3$)



3b

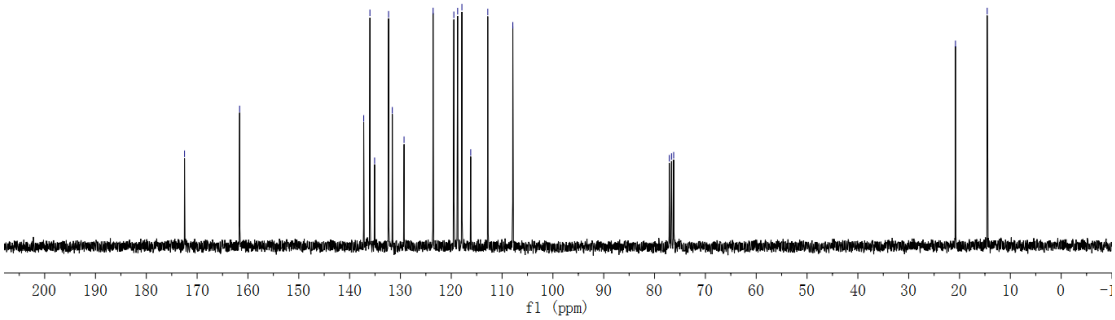
^{1}H NMR (300 MHz, $CDCl_3$)

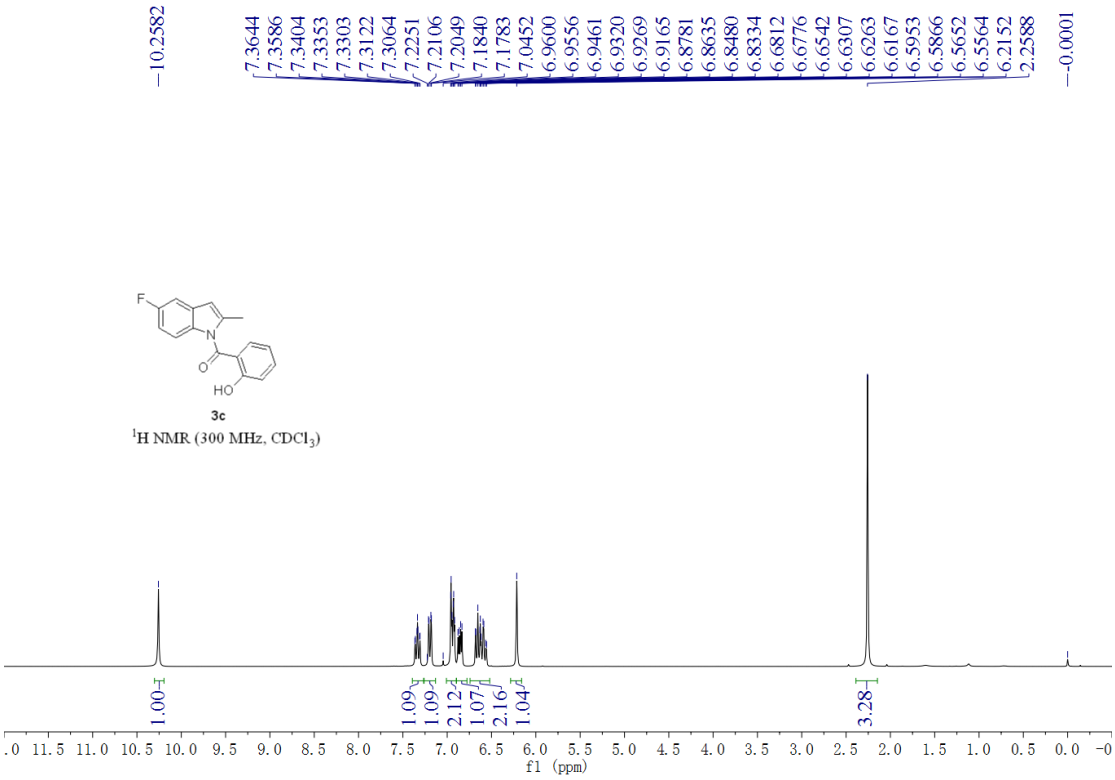




3b

^{13}C NMR (75 MHz, $CDCl_3$)

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7.3303
7.3122
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7.2251
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7.2049
7.1840
7.1783
7.0452
6.9600
6.9556
6.9461
6.9320
6.9269
6.9165
6.8781
6.8635
6.8480
6.8334
6.6812
6.6776
6.6542
6.6307
6.6263
6.6167
6.5953
6.5866
6.5652
6.5564
6.2152
2.2588
0.0001
F
N
O
HO
3c
1H NMR (300 MHz, CDCl3)
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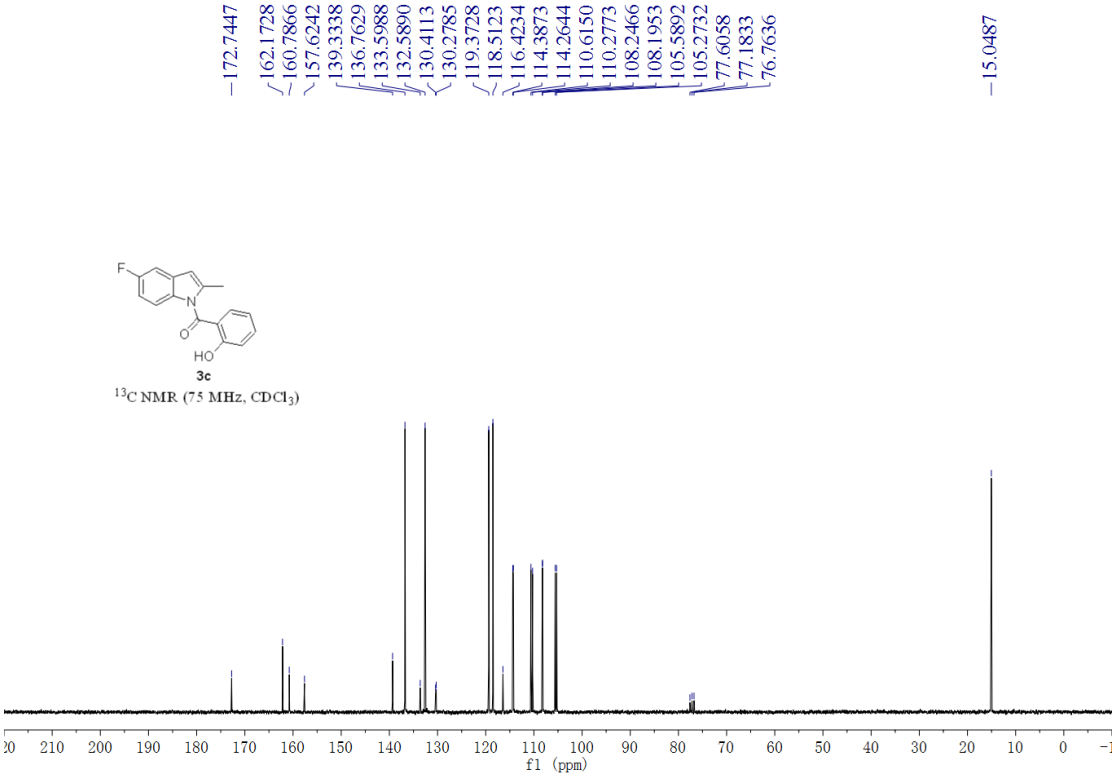
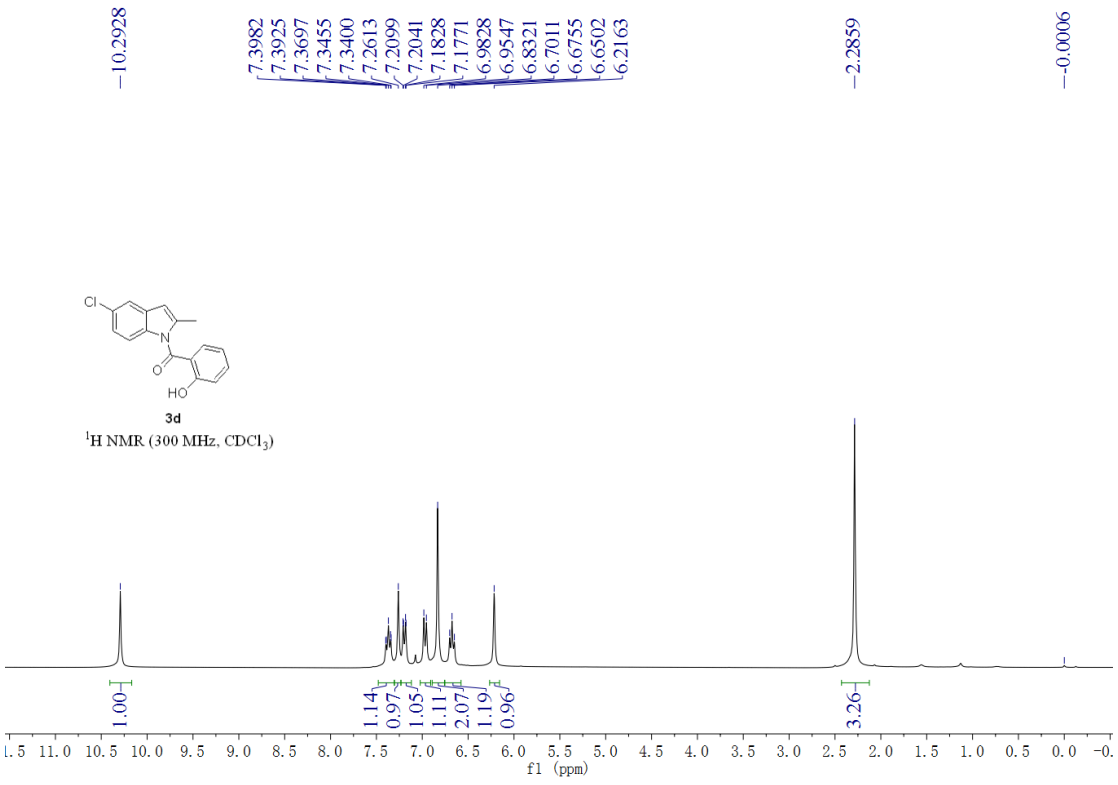
1.09
2.12
1.07
2.16
1.04
3.28
f1 (ppm)


172.7447
162.1728
160.7866
157.6242
139.3338
136.7629
133.5988
132.5890
130.4113
130.2785
119.3728
118.5123
116.4234
114.3873
114.2644
110.6150
110.2773
108.2466
108.1953
105.5892
105.2732
77.6058
77.1833
76.7636
15.0487
F
N
O
HO
3c
13C NMR (75 MHz, CDCl3)
f1 (ppm)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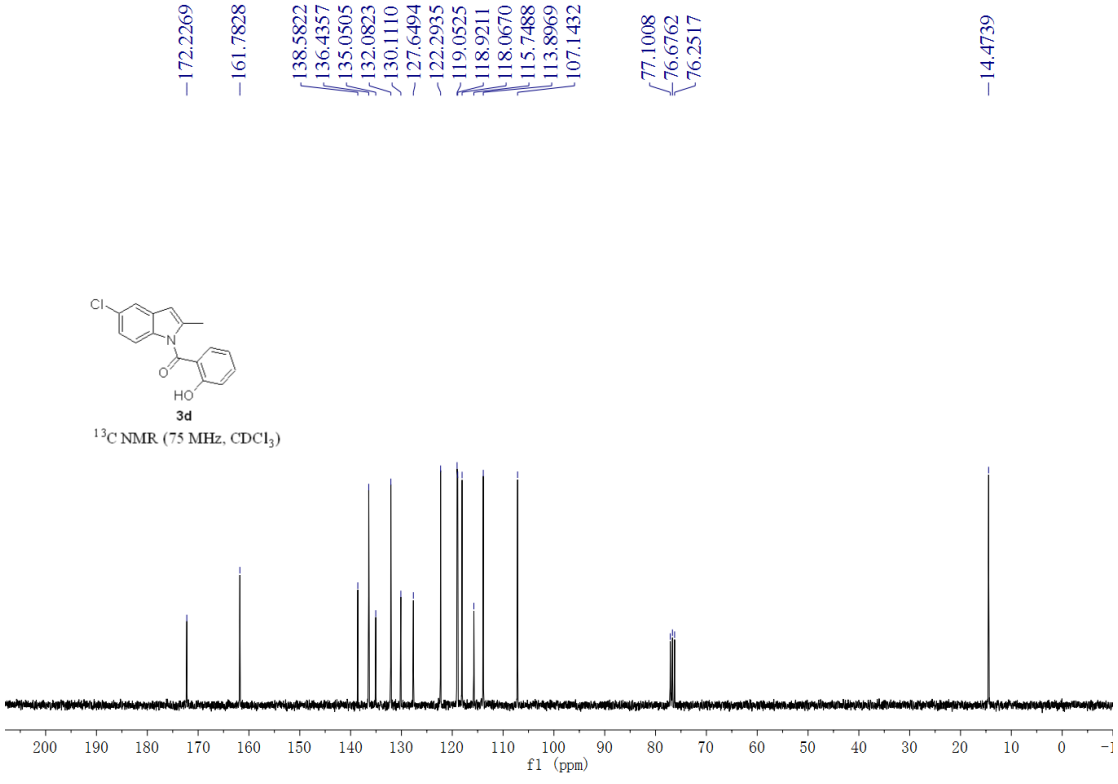
7.3982
7.3925
7.3697
7.3455
7.3400
7.2613
7.2099
7.2041
7.1828
7.1771
6.9828
6.9547
6.8321
6.7011
6.6755
6.6502
6.2163
2.2859
-0.0006
Cl
N
O
HO
3d
1H NMR (300 MHz, CDCl3)
1.00
1.14
0.97
1.05
1.11
2.07
1.19
0.96
3.26
f1 (ppm)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161.7828
138.5822
136.4357
135.0505
132.0823
130.1110
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122.2935
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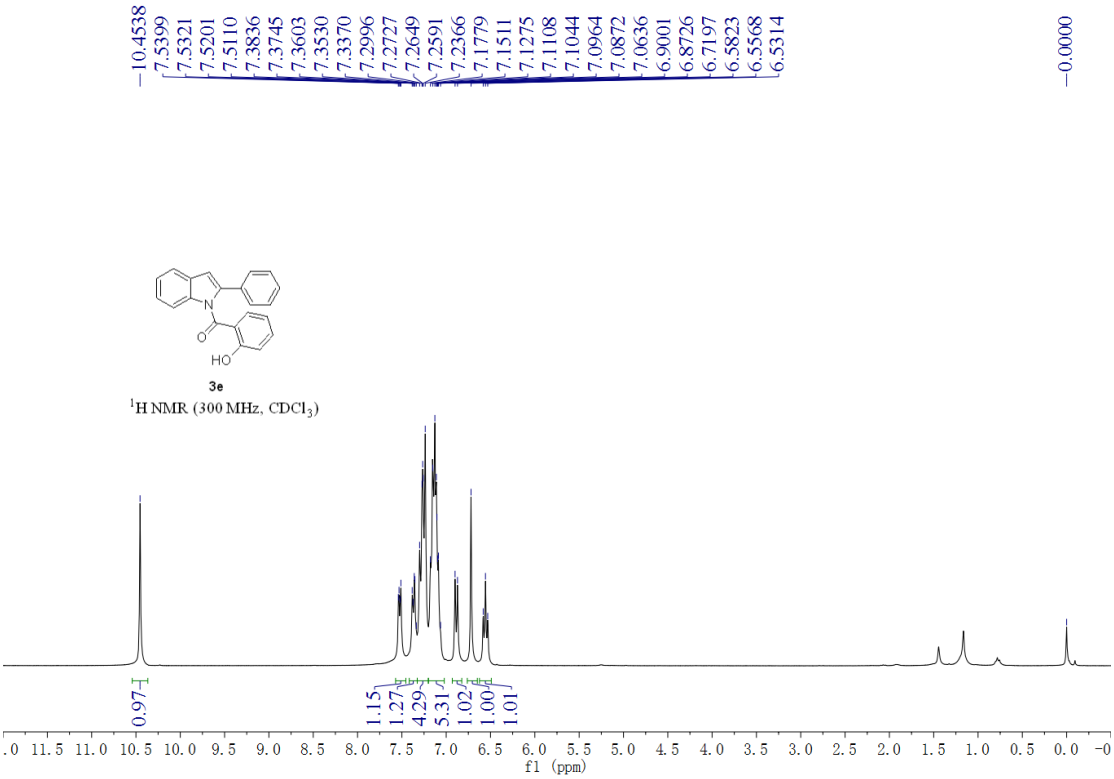
118.9211
118.0670
115.7488
113.8969
107.1432
77.1008
76.6762
76.2517
14.4739
Cl
N
O
HO
3d
13C NMR (75 MHz, CDCl3)
f1 (ppm)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7.5321
7.5201
7.5110
7.3836
7.3745
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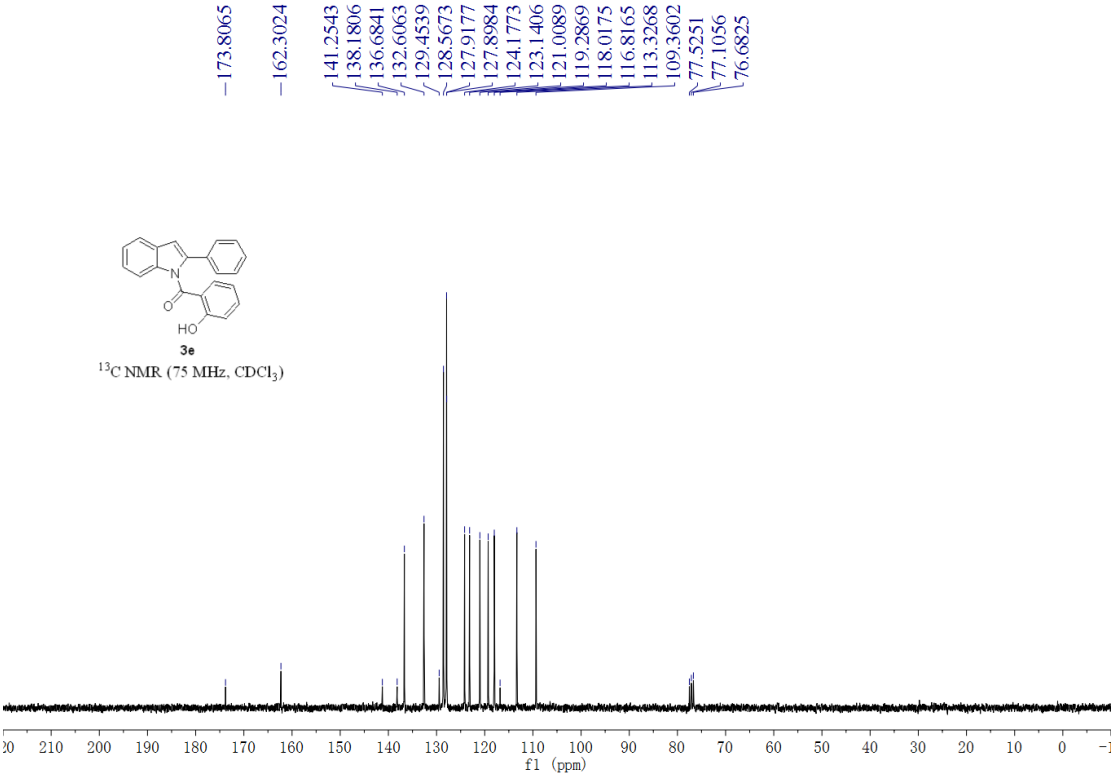
7.3530
7.3370
7.2996
7.2727
7.2649
7.2591
7.2366
7.1779
7.1511
7.1275
7.1108
7.1044
7.0964
7.0872
7.0636
6.9001
6.8726
6.7197
6.5823
6.5568
6.5314
0.0000
HO
3e
1H NMR (300 MHz, CDCl3)
0.97
1.15
1.27
4.29
5.31
1.02
1.00
1.01
f1 (ppm)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141.2543
138.1806
136.6841
132.6063
129.4539
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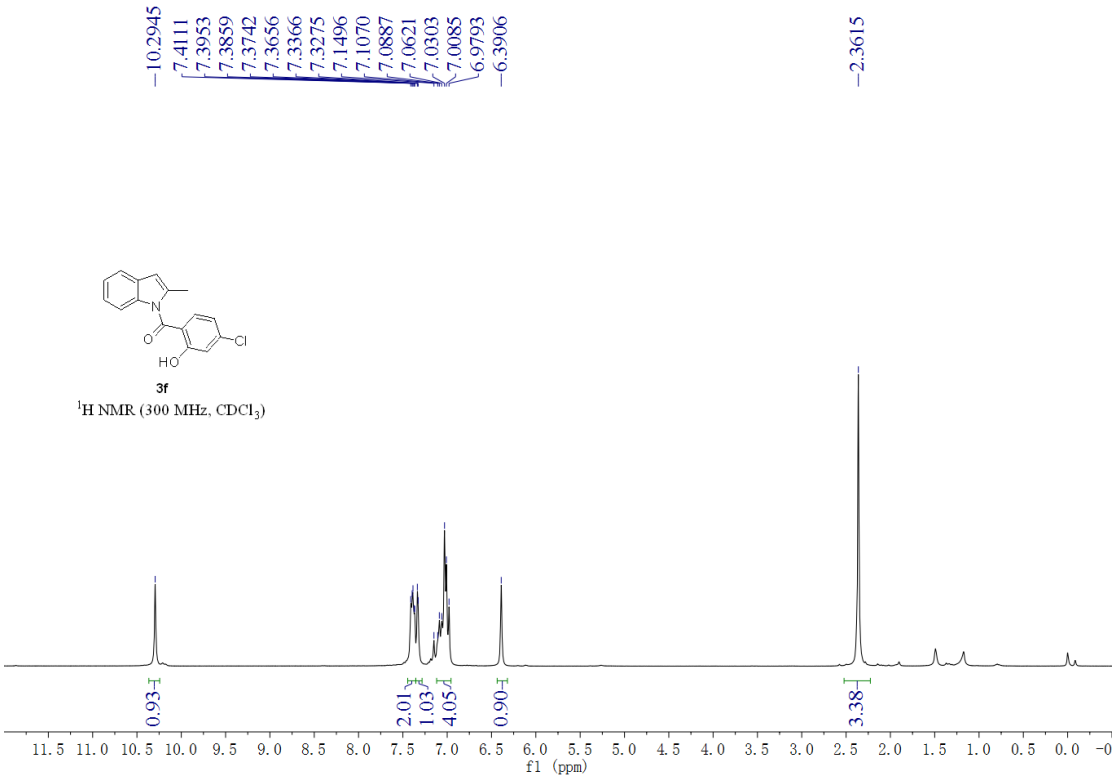
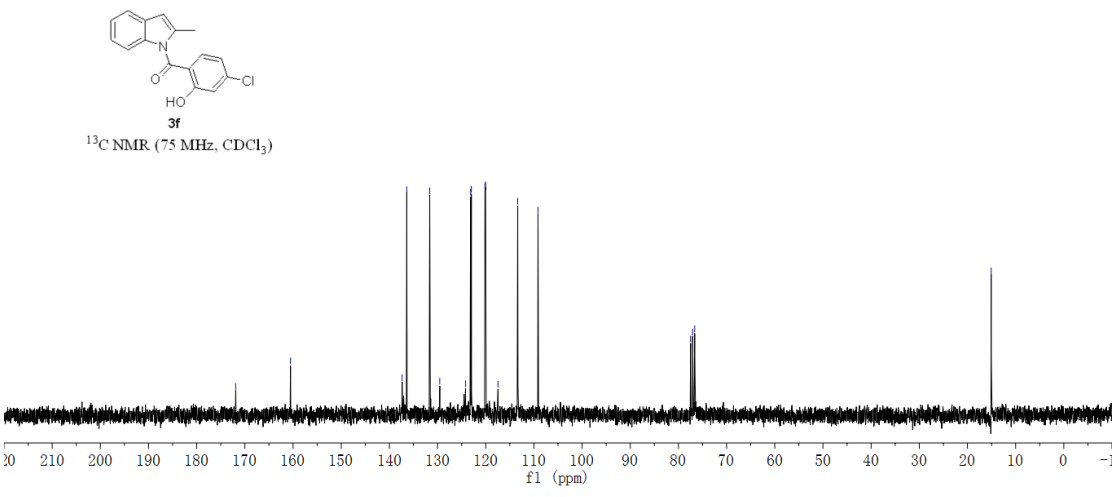
127.9177
127.8984
124.1773
123.1406
121.0089
119.2869
118.0175
116.8165
113.3268
109.3602
77.5251
77.1056
76.6825
HO
3e
13C NMR (75 MHz, CDCl3)
f1 (ppm)



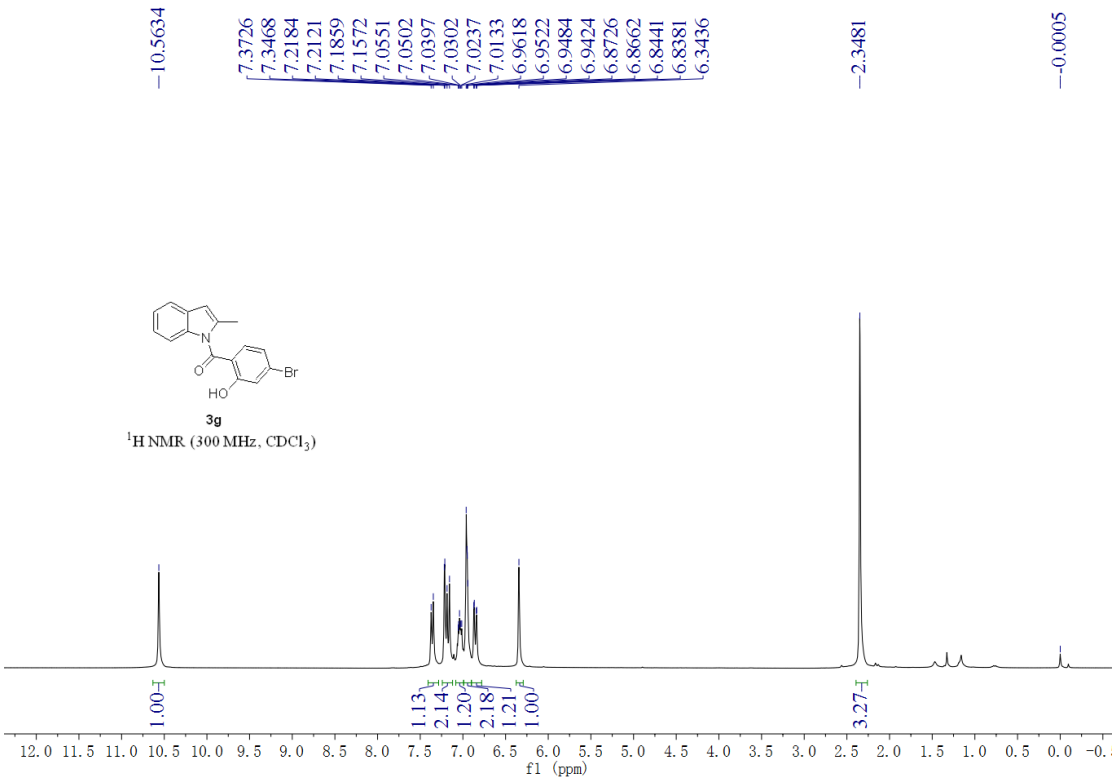
3f

^{1}H NMR (300 MHz, $CDCl_3$)



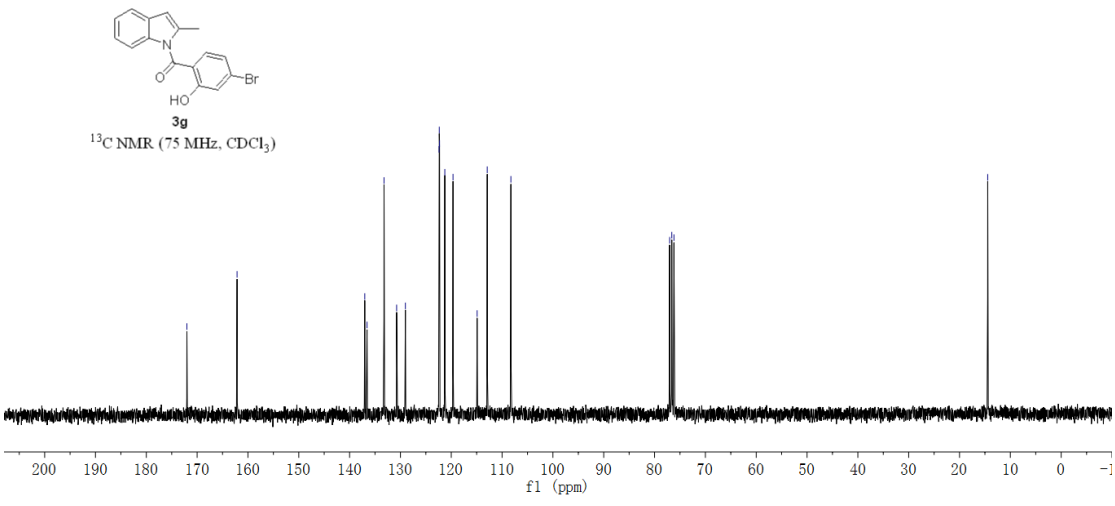
3f

^{13}C NMR (75 MHz, $CDCl_3$)



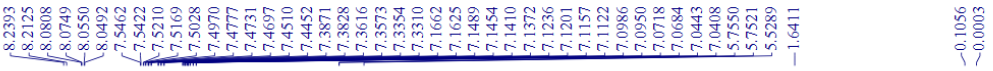
3g

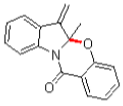
^{1}H NMR (300 MHz, $CDCl_3$)



3g

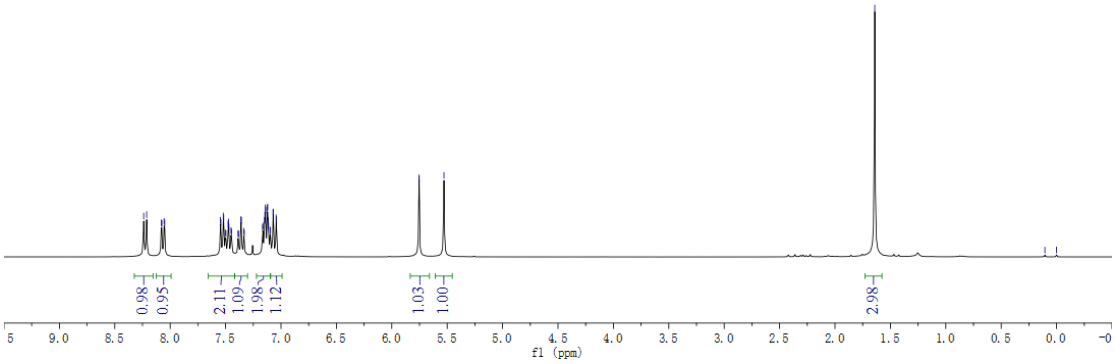
^{13}C NMR (75 MHz, $CDCl_3$)

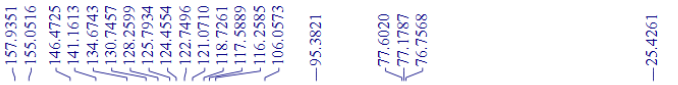


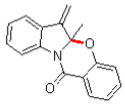


2a

^{1}H NMR (300 MHz, $CDCl_3$)

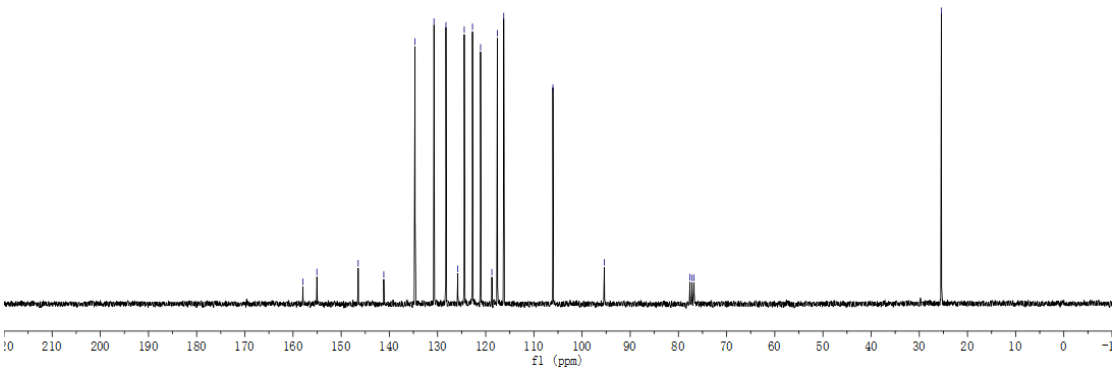


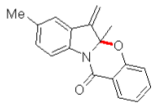




2a

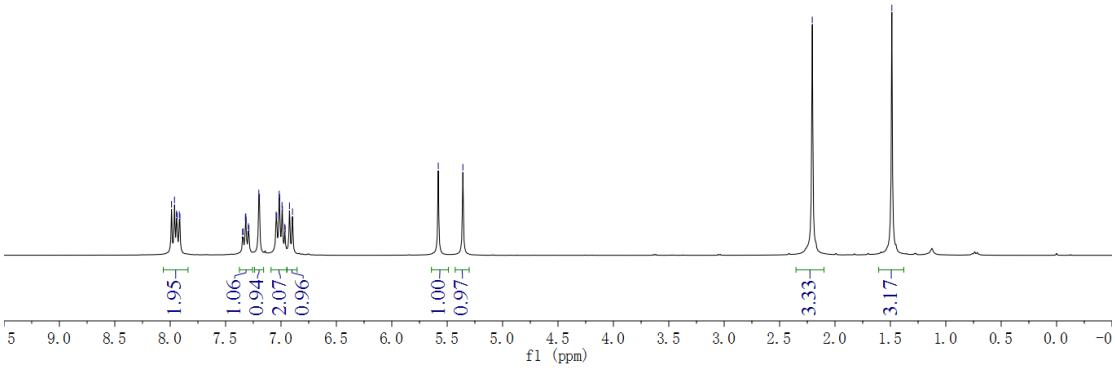
^{13}C NMR (75 MHz, $CDCl_3$)

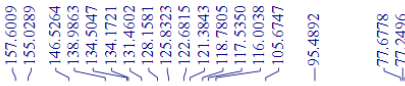


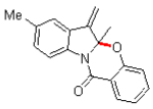


2b

^{1}H NMR (300 MHz, $CDCl_3$)

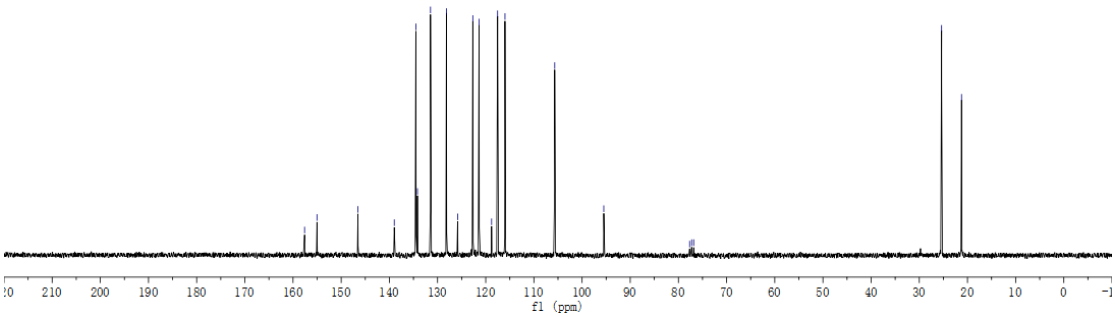


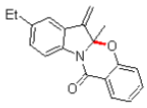




2b

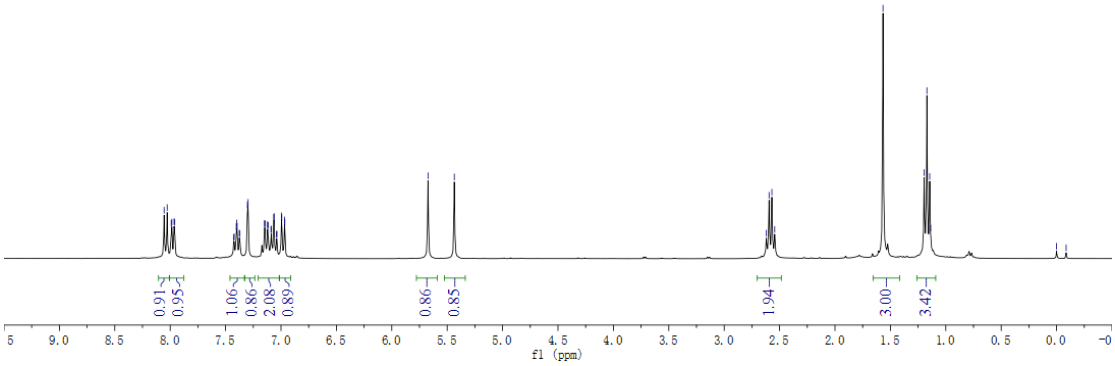
^{13}C NMR (75 MHz, $CDCl_3$)

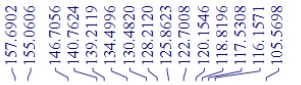


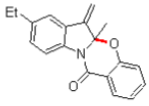


2c

^{1}H NMR (300 MHz, $CDCl_3$)

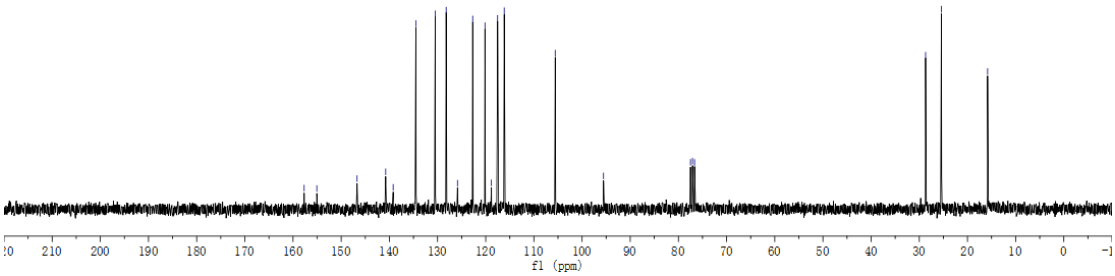


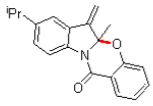




2c

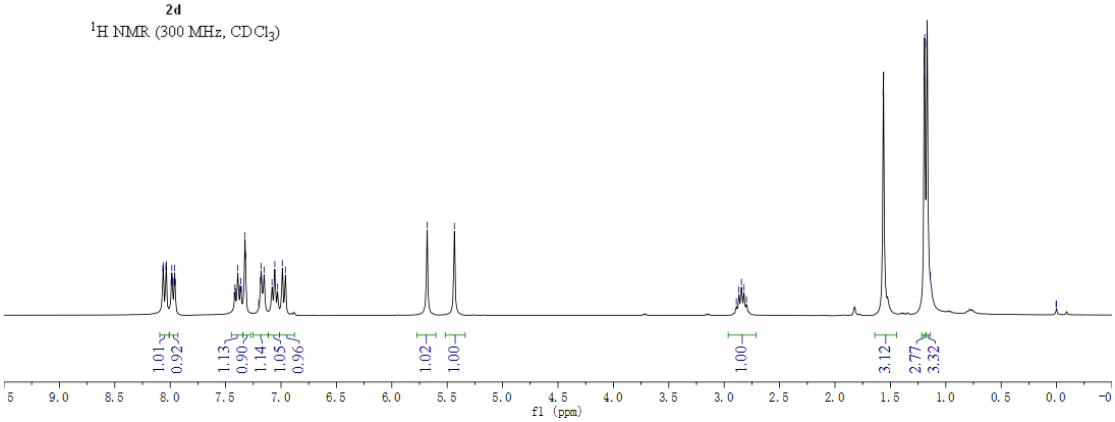
^{13}C NMR (75 MHz, $CDCl_3$)

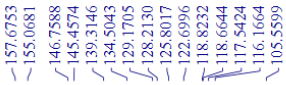


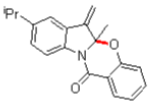


2d

^{1}H NMR (300 MHz, $CDCl_3$)

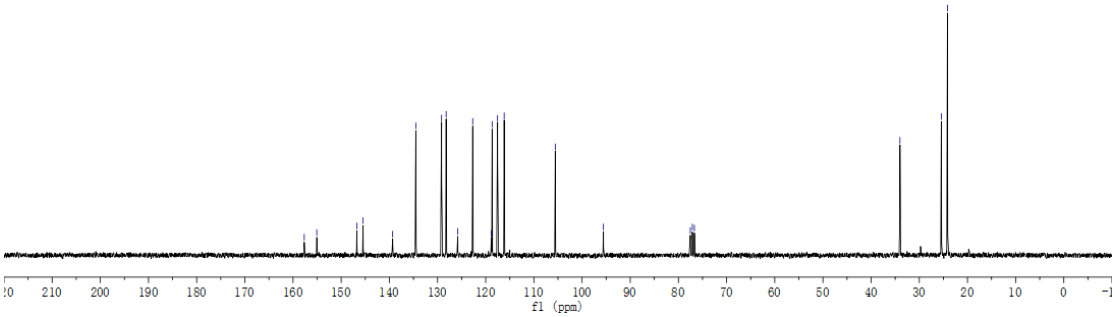


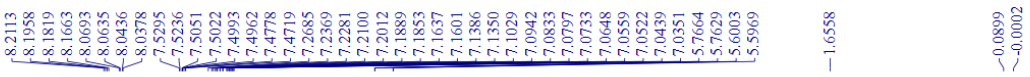


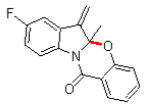


2d

^{13}C NMR (75 MHz, $CDCl_3$)

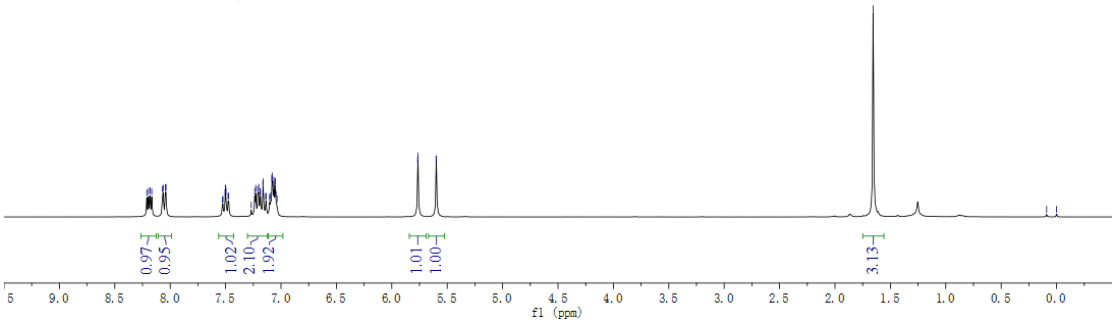


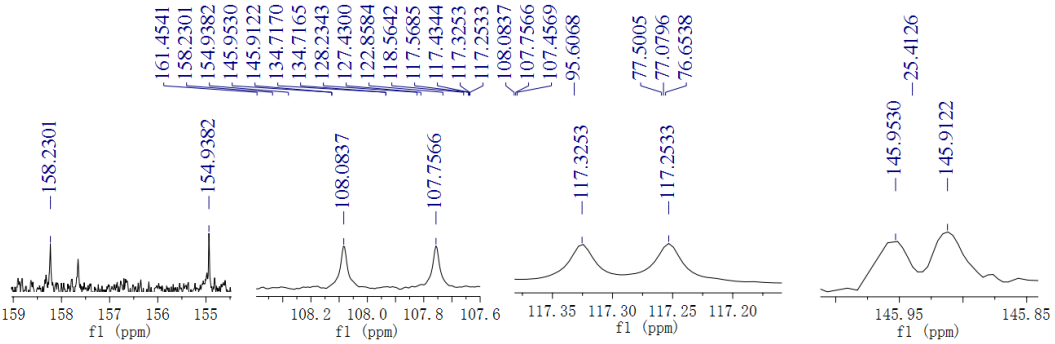


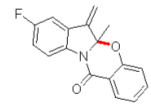


2e

^{1}H NMR (300 MHz, $CDCl_3$)

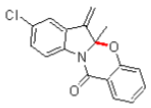






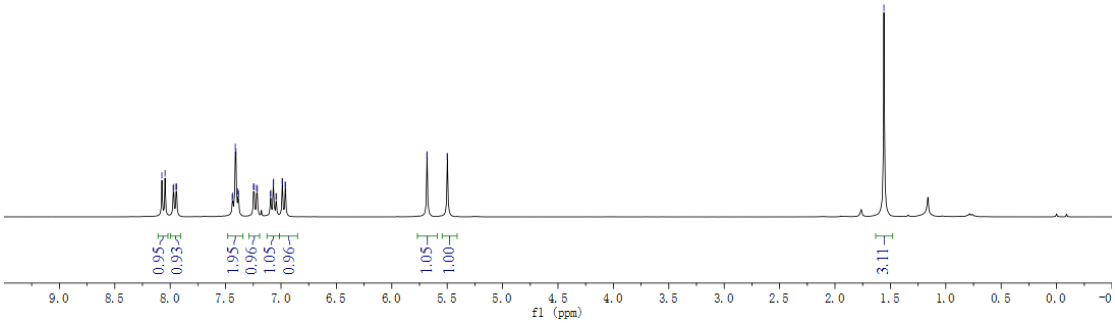
2e

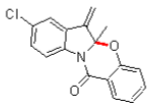
^{13}C NMR (75 MHz, $CDCl_3$)



2f

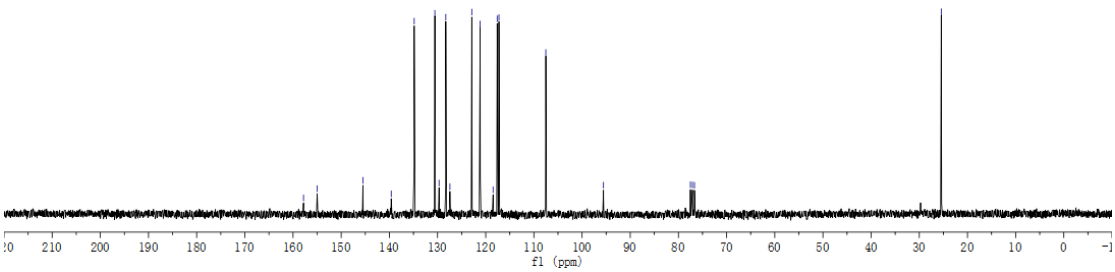
^{1}H NMR (300 MHz, $CDCl_3$)

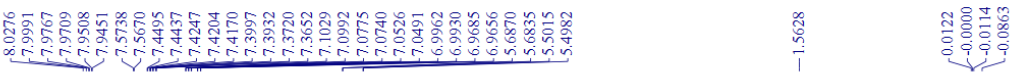


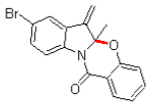


2f

^{13}C NMR (75 MHz, $CDCl_3$)

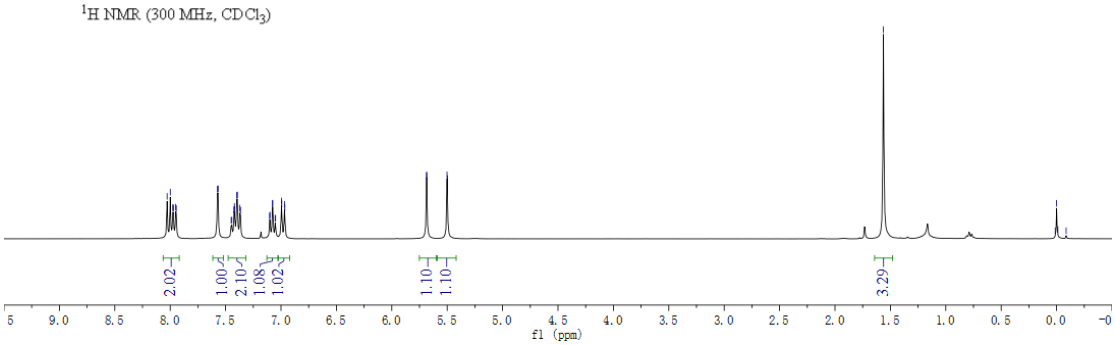


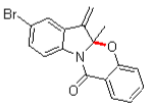




2g

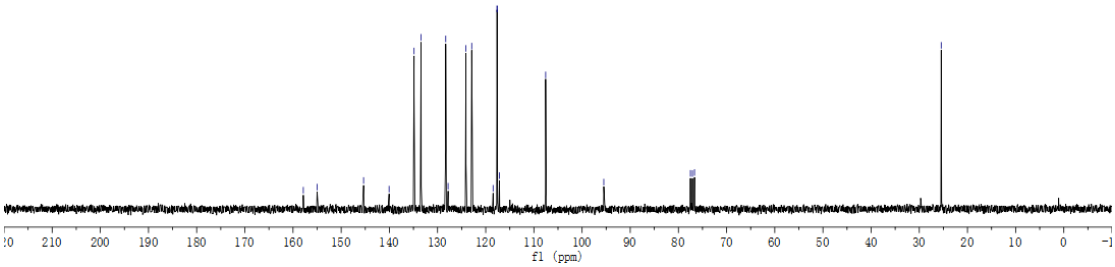
^{1}H NMR (300 MHz, $CDCl_3$)

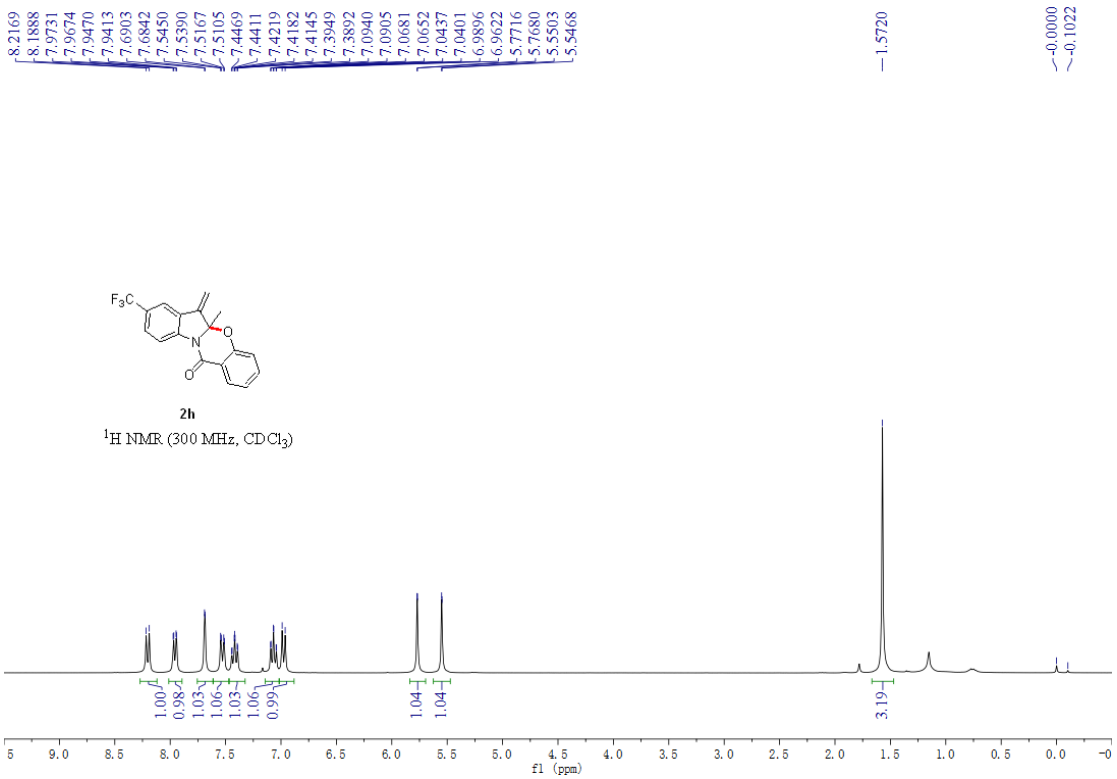




2g

^{13}C NMR (75 MHz, $CDCl_3$)

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7.9413
7.6903
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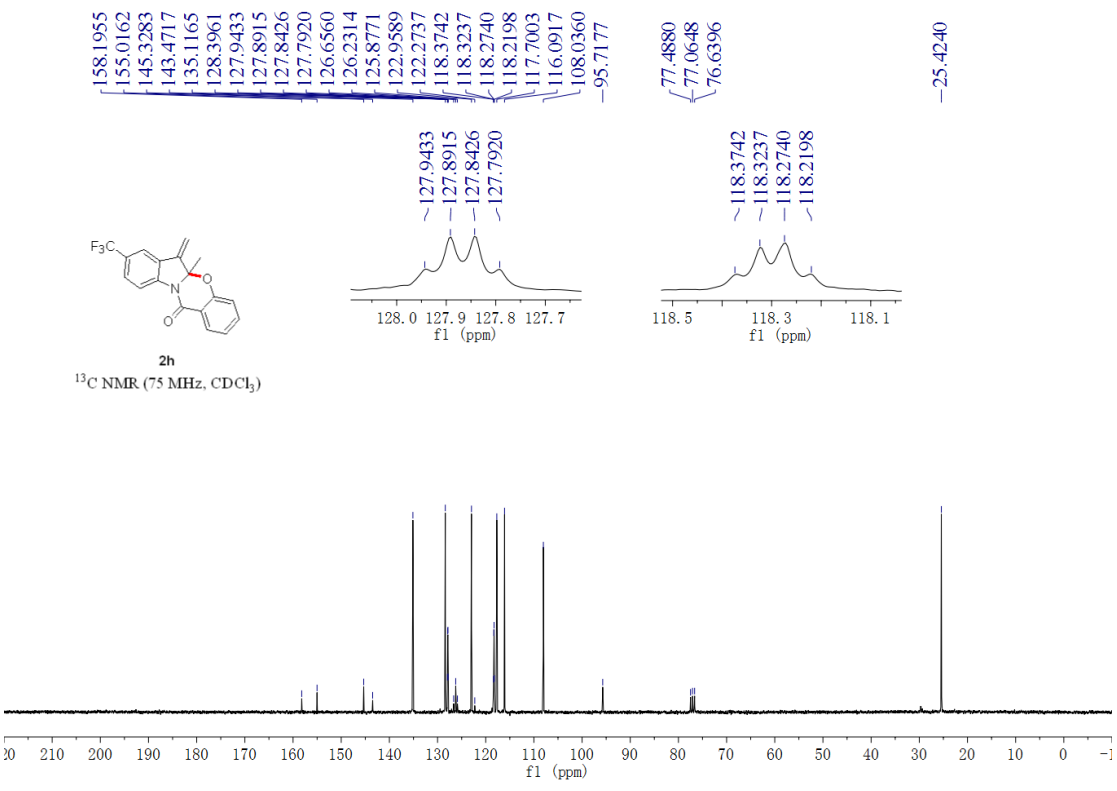
7.5105
7.4469
7.4411
7.4219
7.4182
7.4145
7.3949
7.3892
7.0940
7.0905
7.0681
7.0652
7.0437
7.0401
6.9896
6.9622
5.7716
5.7680
5.5503
5.5468
1.5720
0.0000
0.1022
F3C
O
N
O
2h
1H NMR (300 MHz, CDCl3)
1.00
0.98
1.03
1.06
1.03
1.06
0.99
1.04
1.04
3.19
f1 (ppm)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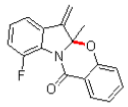
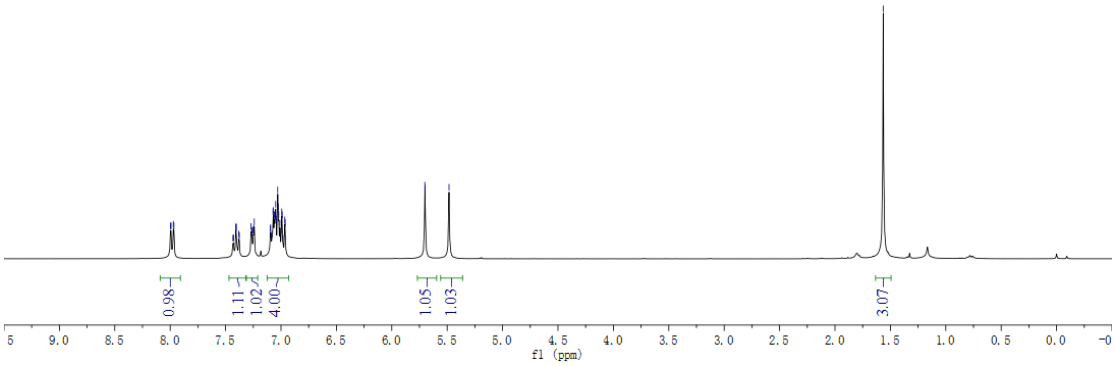
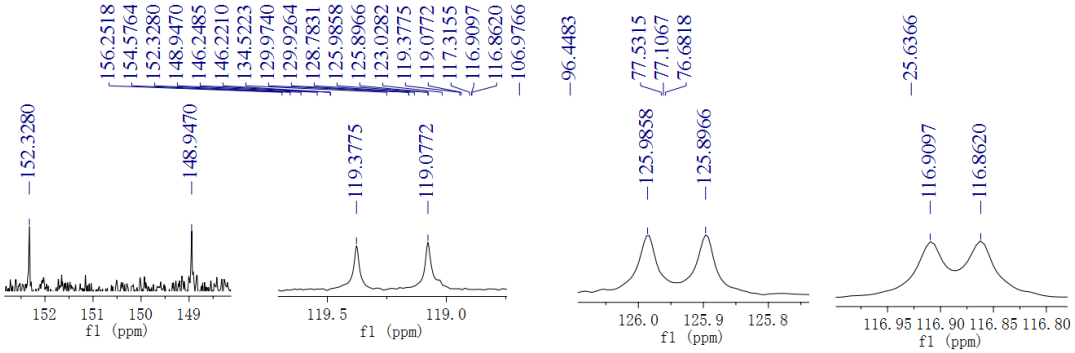
126.2314
125.8771
122.9589
122.2737
118.3742
118.3237
118.2740
118.2198
117.7003
116.0917
108.0360
95.7177
77.4880
77.0648
76.6396
25.4240
127.9433
127.8915
127.8426
127.7920
118.3742
118.3237
118.2740
118.2198
F3C
O
N
O
2h
13C NMR (75 MHz, CDCl3)
128.0 127.9 127.8 127.7
f1 (ppm)
118.5 118.3 118.1
f1 (ppm)
f1 (ppm)

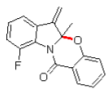


2i

^{1}H NMR (300 MHz, $CDCl_3$)

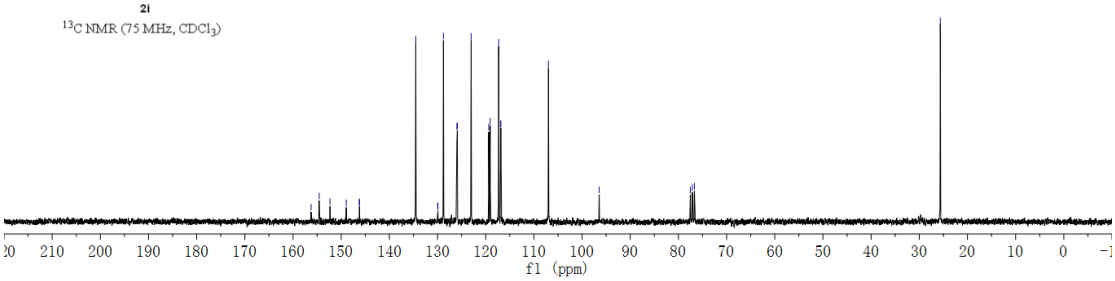


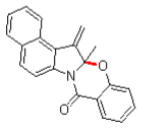




2i

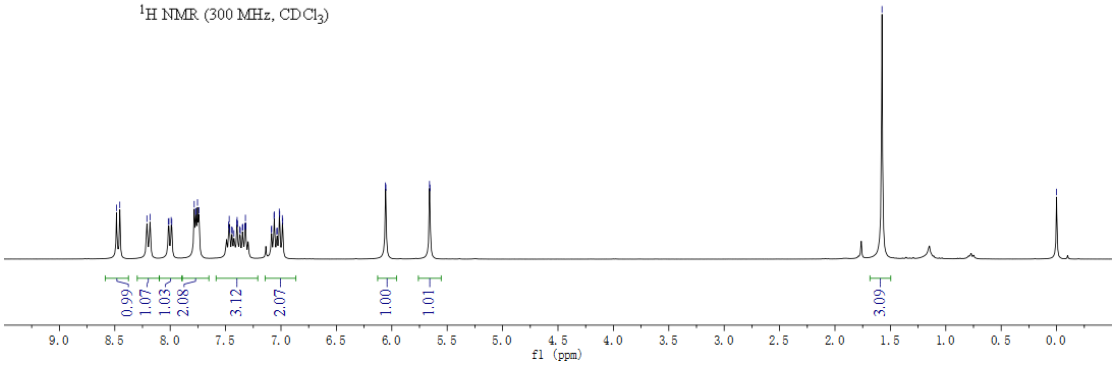
^{13}C NMR (75 MHz, $CDCl_3$)

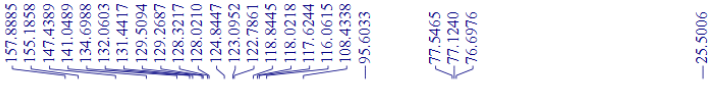


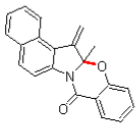


2j

^{1}H NMR (300 MHz, $CDCl_3$)

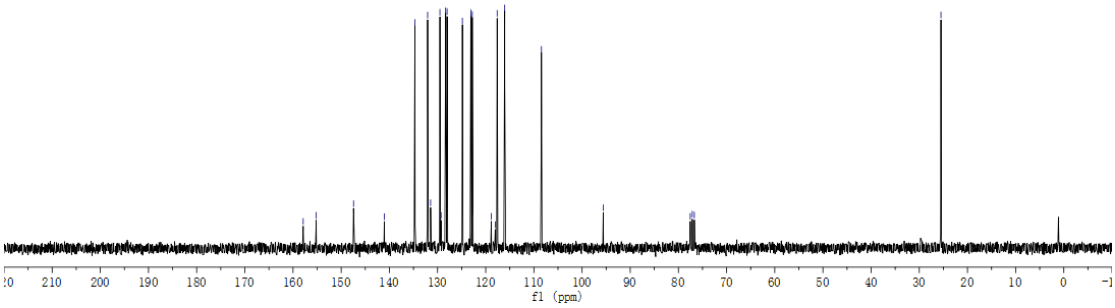


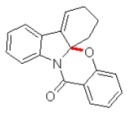




2j

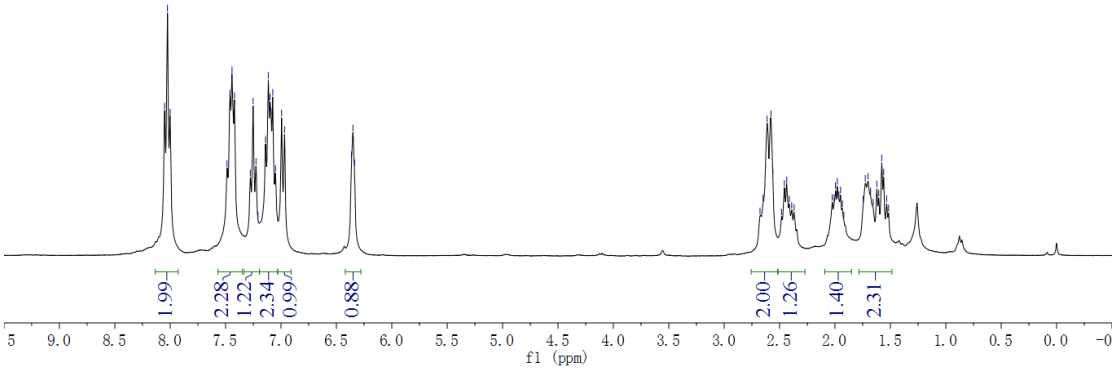
^{13}C NMR (75 MHz, $CDCl_3$)

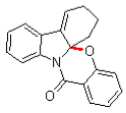




2k

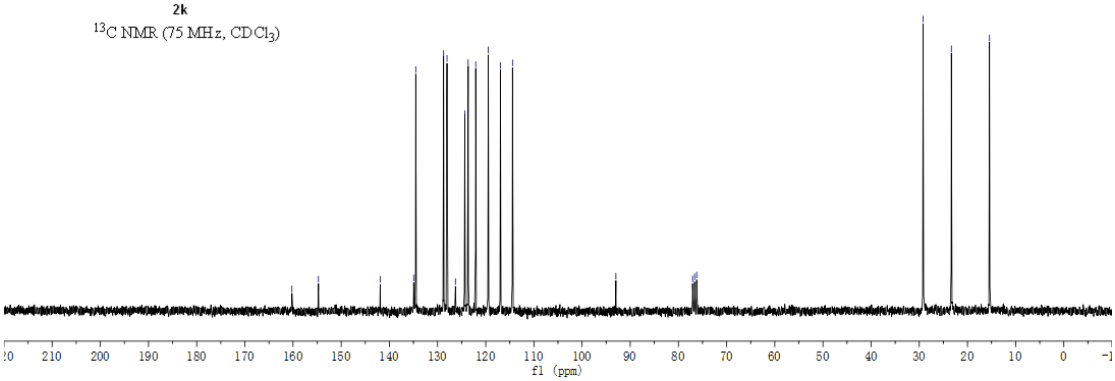
^{1}H NMR (300 MHz, $CDCl_3$)

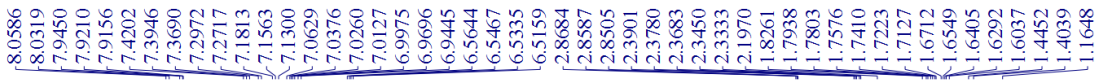


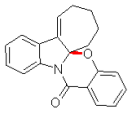


2k

^{13}C NMR (75 MHz, $CDCl_3$)

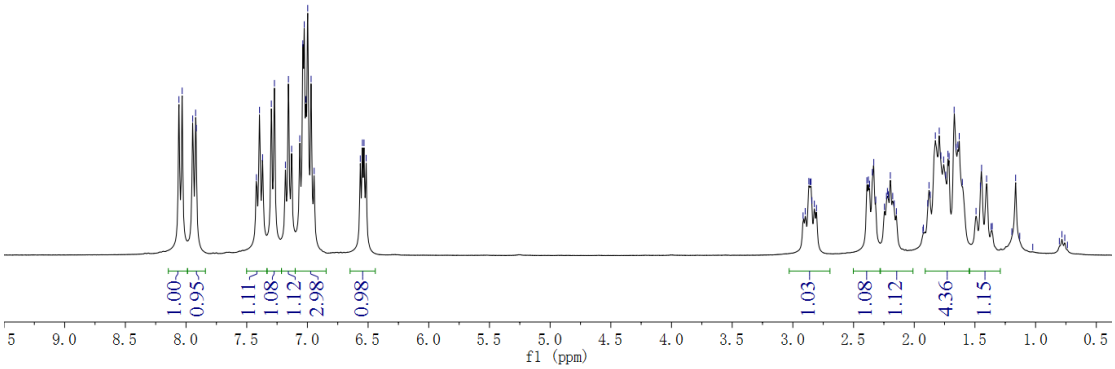


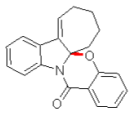




2l

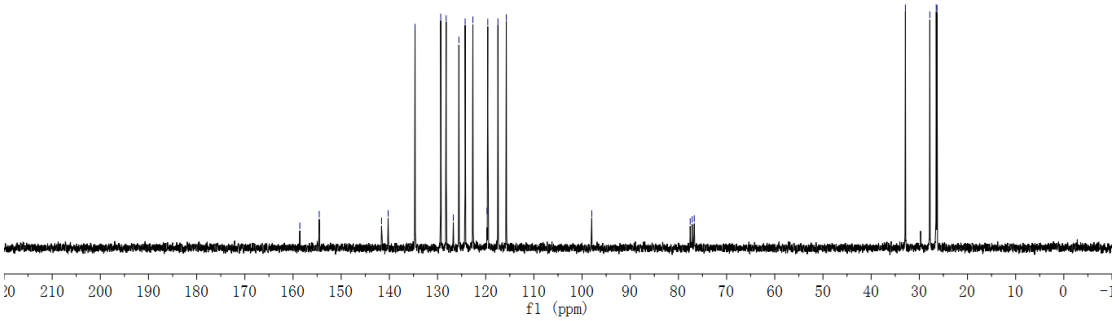
^{1}H NMR (300 MHz, $CDCl_3$)

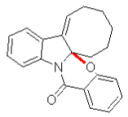




2l

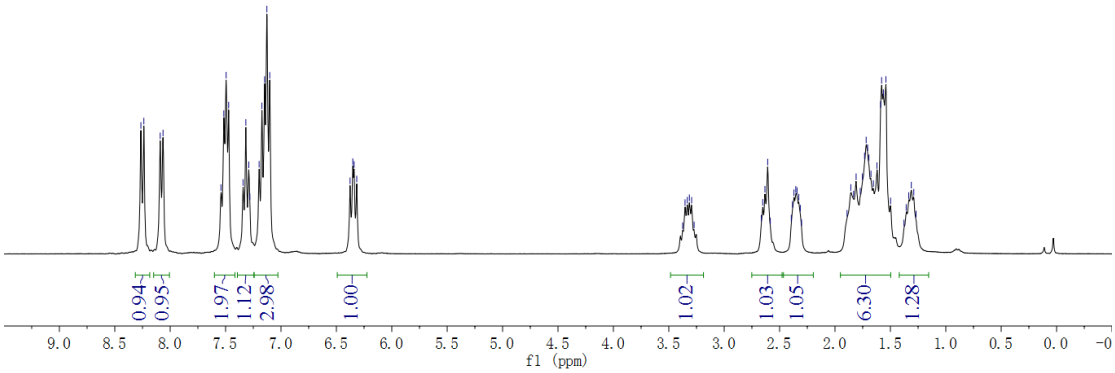
^{13}C NMR (75 MHz, $CDCl_3$)

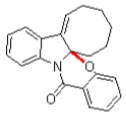




2m

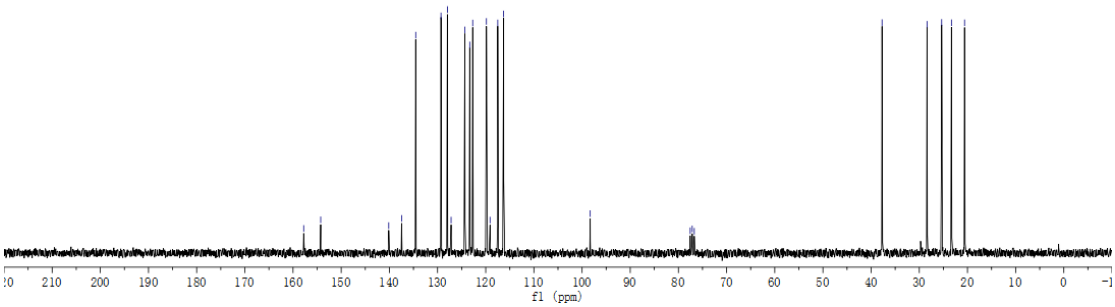
^{1}H NMR (300 MHz, $CDCl_3$)

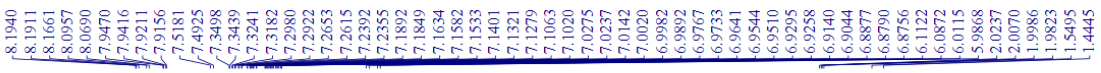


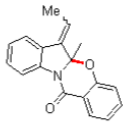


2m

^{13}C NMR (75 MHz, $CDCl_3$)

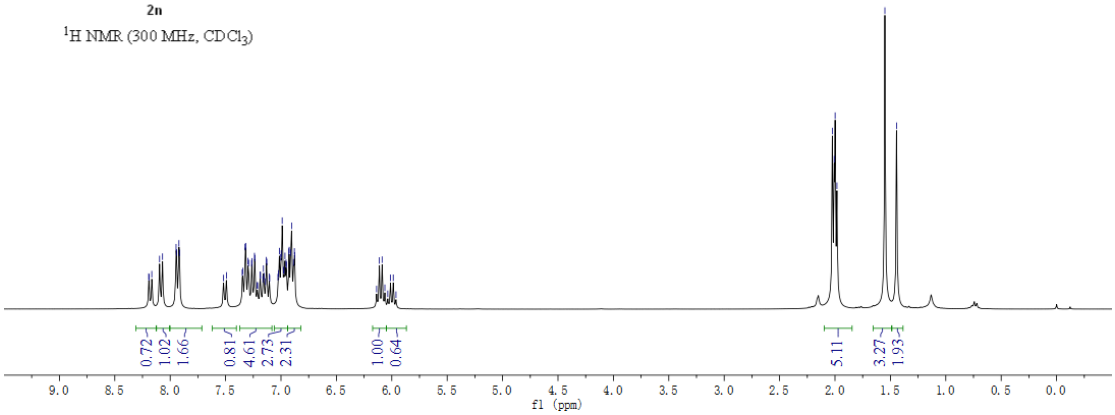


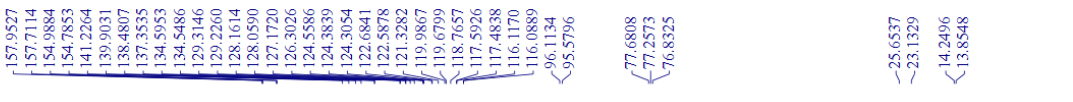


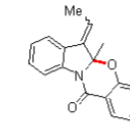


2n

^{1}H NMR (300 MHz, $CDCl_3$)

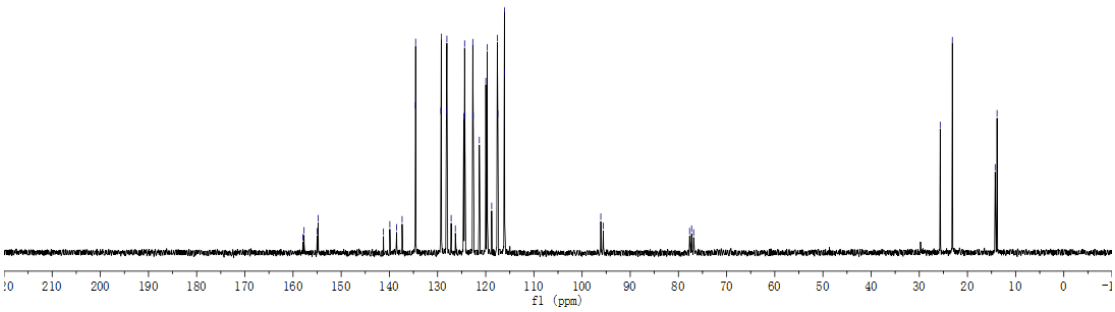


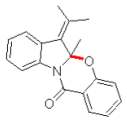




2n

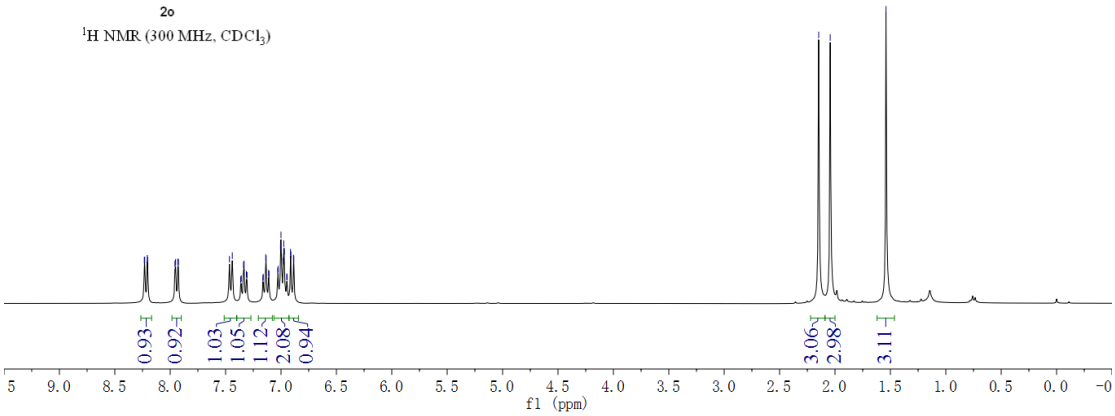
^{13}C NMR (75 MHz, $CDCl_3$)

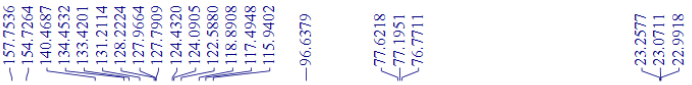


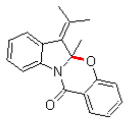


2o

^{1}H NMR (300 MHz, $CDCl_3$)

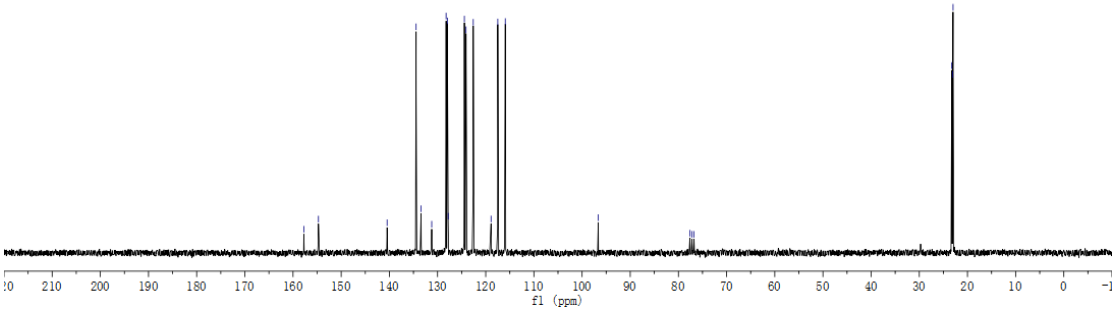


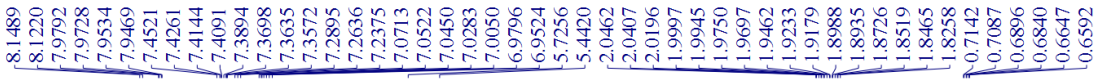


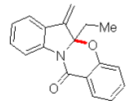


2o

^{13}C NMR (75 MHz, $CDCl_3$)

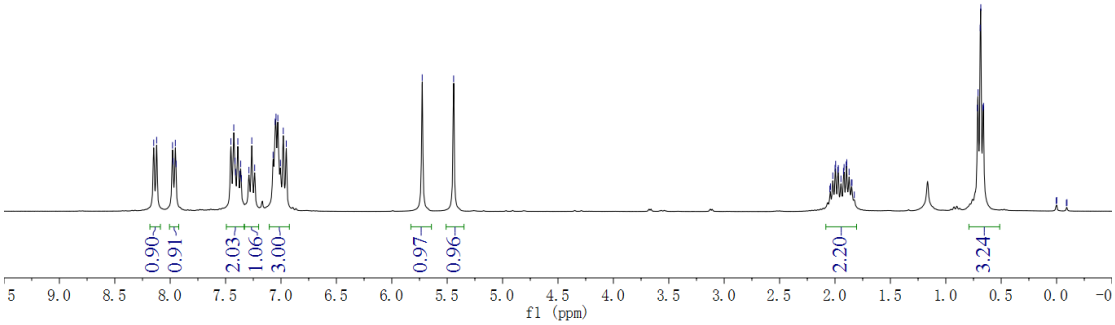


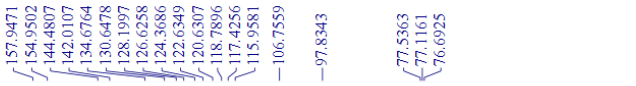


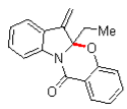


2p

^{1}H NMR (300 MHz, $CDCl_3$)

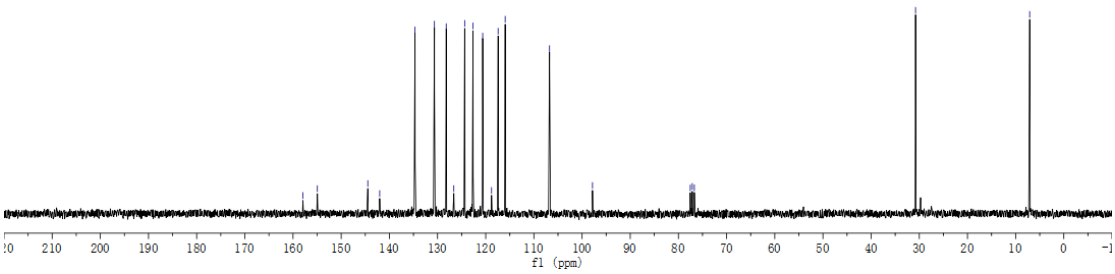


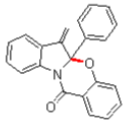




2p

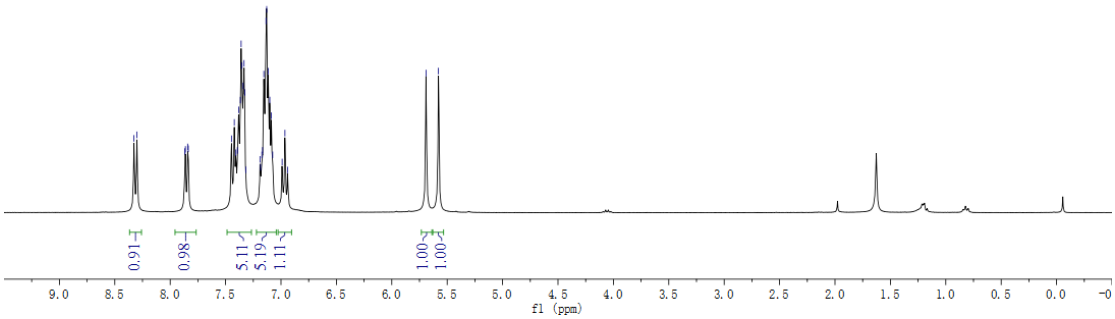
^{13}C NMR (75 MHz, $CDCl_3$)

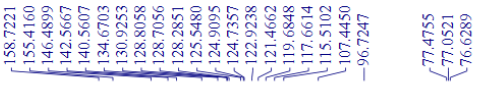


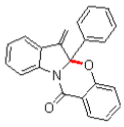


2q

^{1}H NMR (300 MHz, $CDCl_3$)

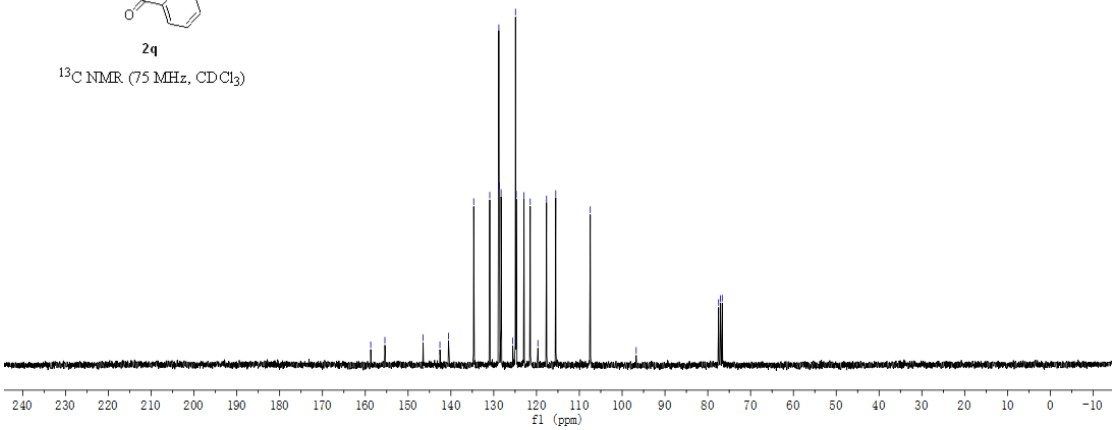


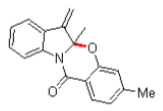




2q

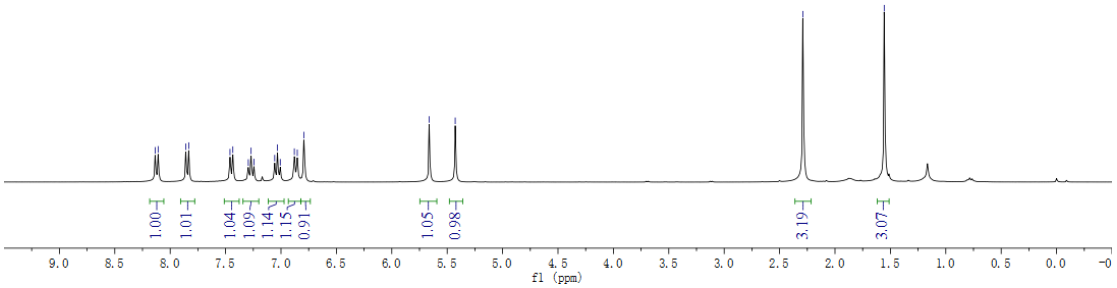
^{13}C NMR (75 MHz, $CDCl_3$)

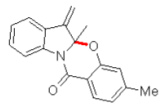




2r

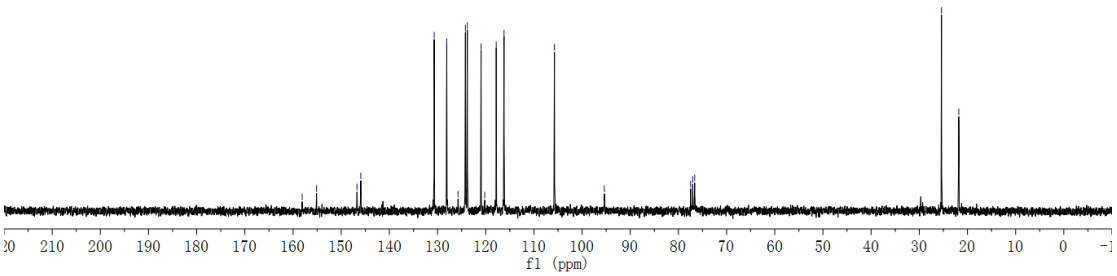
^{1}H NMR (300 MHz, $CDCl_3$)

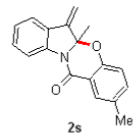




2r

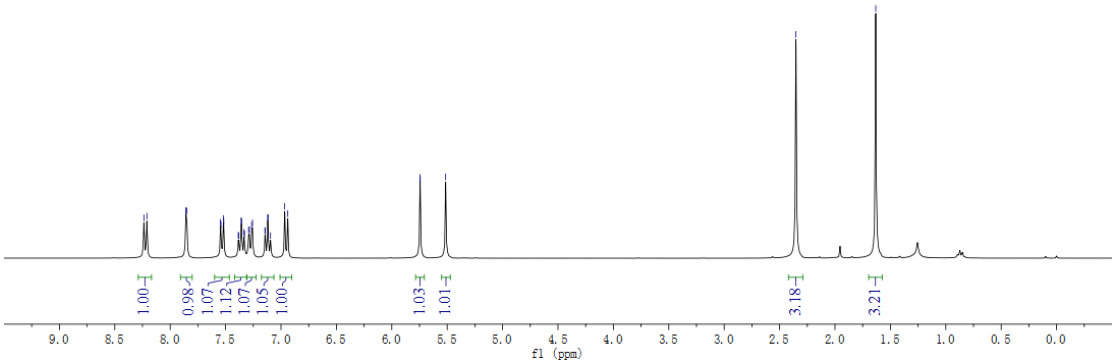
^{13}C NMR (75 MHz, $CDCl_3$)

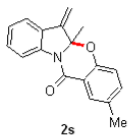




2s

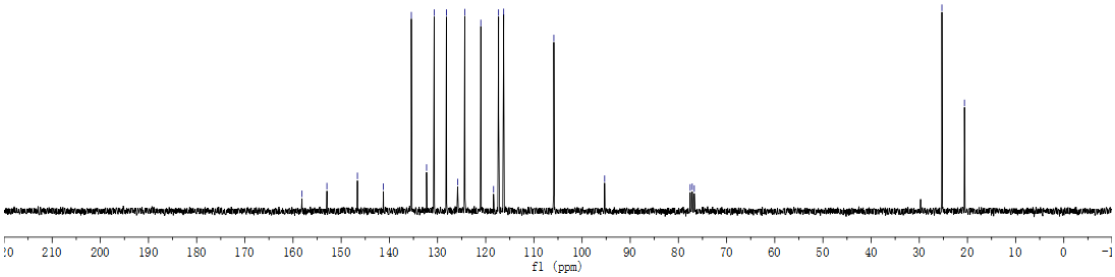
^{1}H NMR (300 MHz, $CDCl_3$)

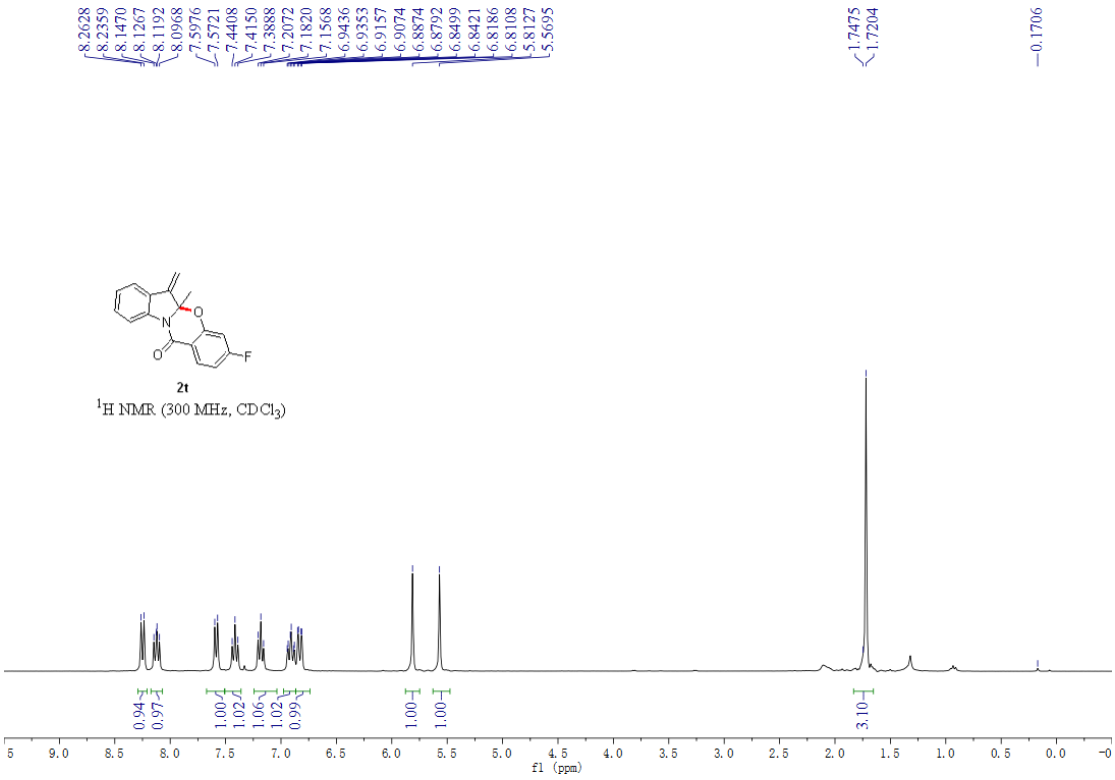




2s

^{13}C NMR (75 MHz, $CDCl_3$)

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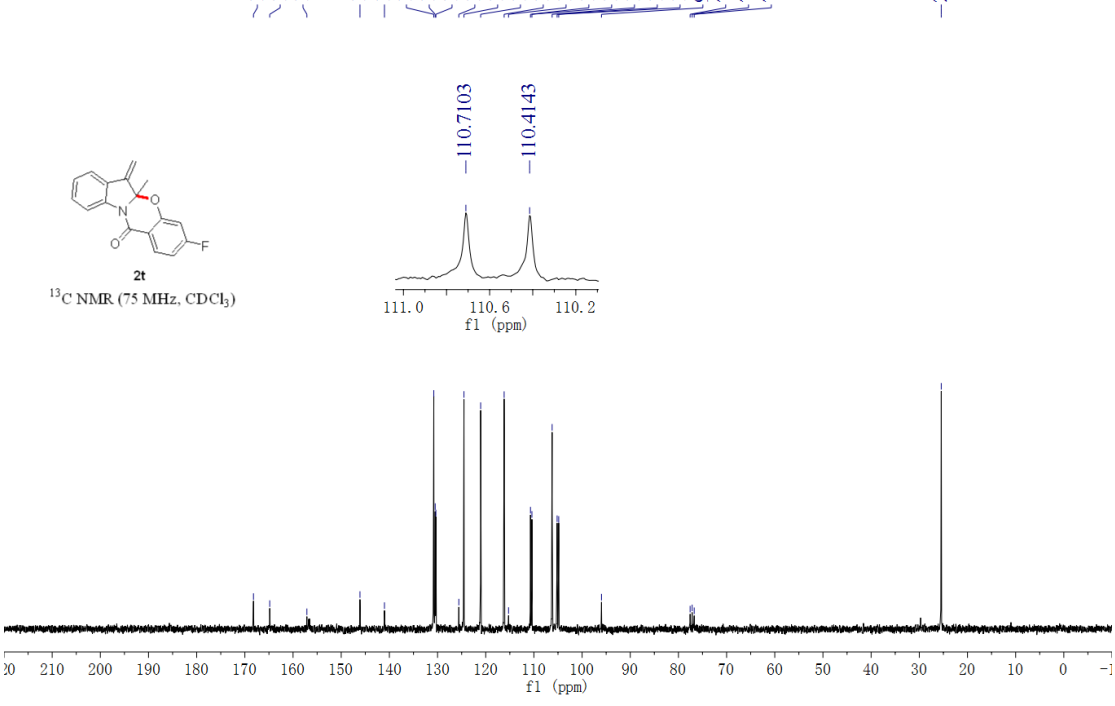
8.2359
8.1470
8.1267
8.1192
8.0968
7.5976
7.5721
7.4408
7.4150
7.3888
7.2072
7.1820
7.1568
6.9436
6.9353
6.9157
6.9074
6.8874
6.8792
6.8499
6.8421
6.8186
6.8108
5.8127
5.5695
1.7475
1.7204
0.1706
2t
1H NMR (300 MHz, CDCl3)
0.94
0.97
1.00
1.02
1.06
1.02
0.99
1.00
1.00
3.10
f1 (ppm)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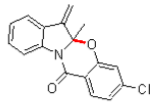
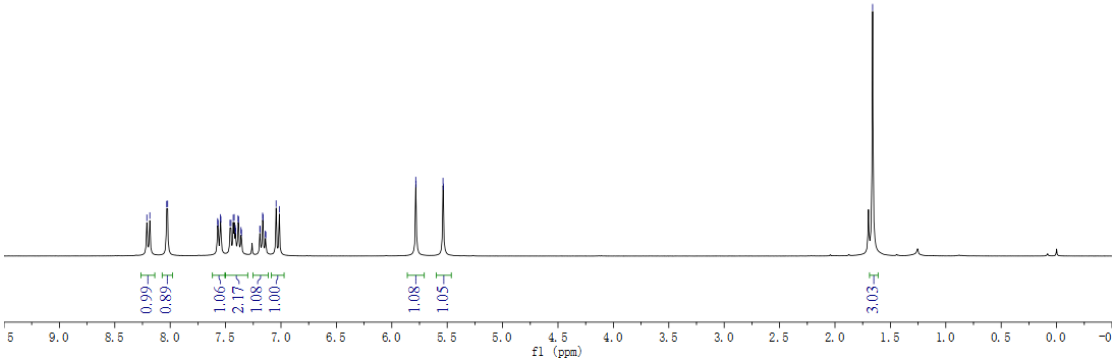
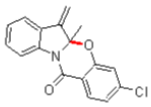
164.8380
157.1237
146.1054
141.0236
130.7819
130.4928
130.3475
125.5847
124.5186
121.0516
116.1790
115.2632
110.7103
110.4143
106.2170
105.1816
104.8477
95.9666
77.5742
77.1501
76.7252
25.4453
110.7103
110.4143
2t
13C NMR (75 MHz, CDCl3)
111.0
110.6
110.2
f1 (ppm)
f1 (ppm)



2u

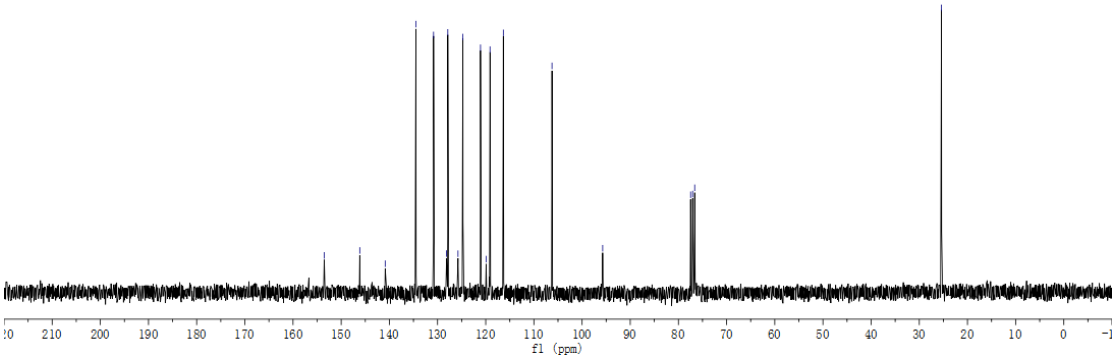
^{1}H NMR (300 MHz, $CDCl_3$)

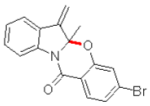




2u

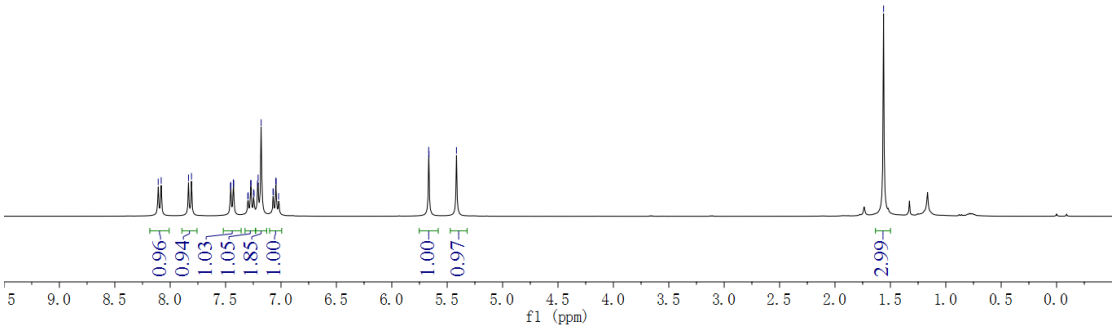
^{13}C NMR (75 MHz, $CDCl_3$)

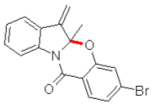




2v

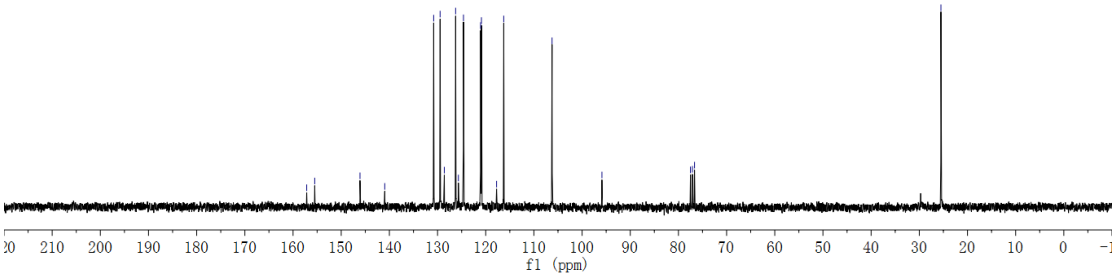
^{1}H NMR (300 MHz, $CDCl_3$)

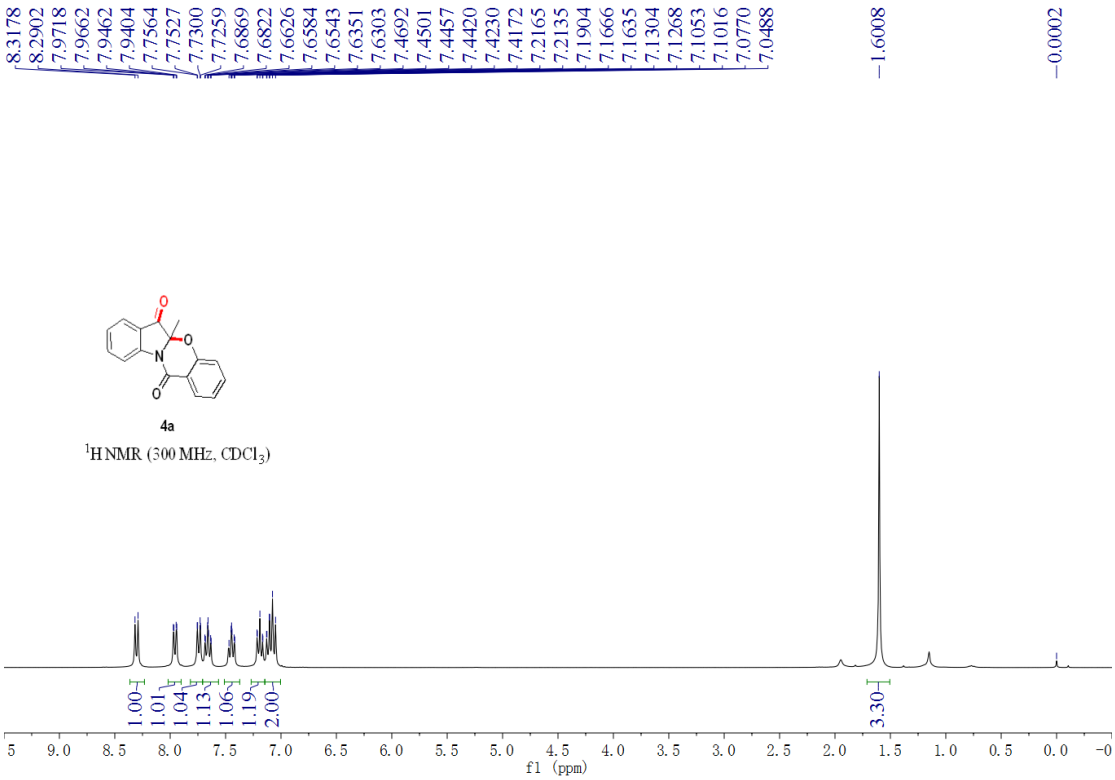


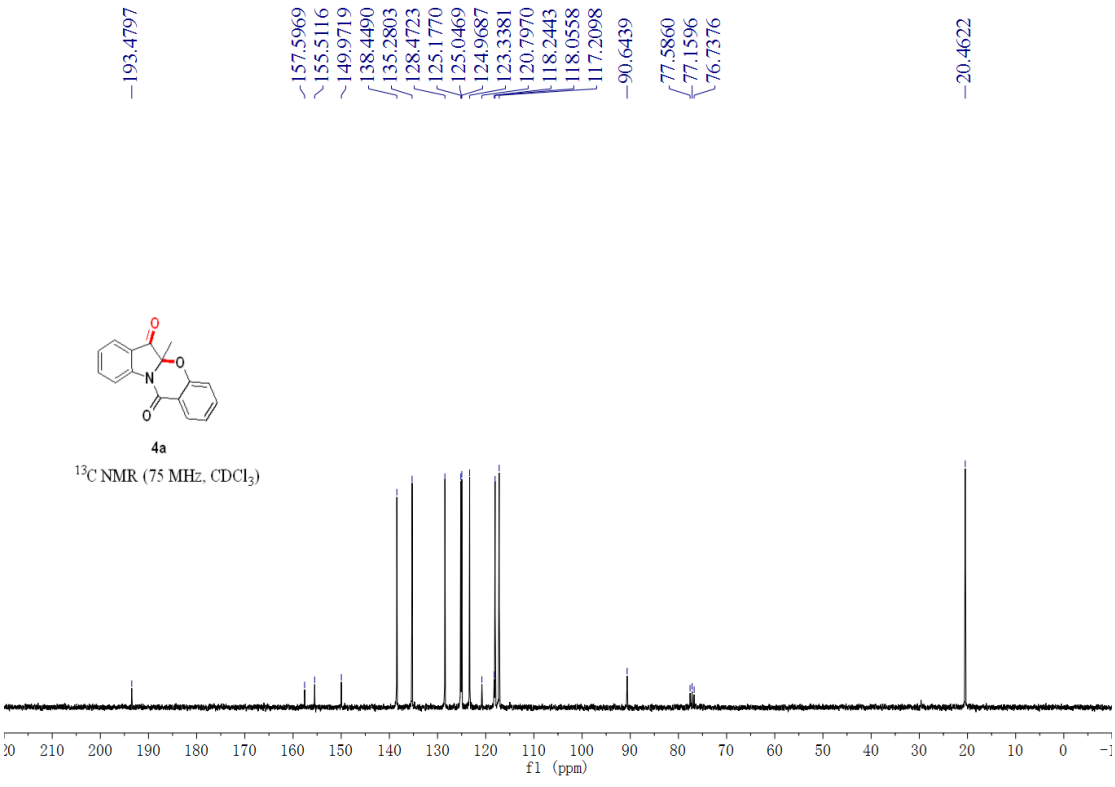


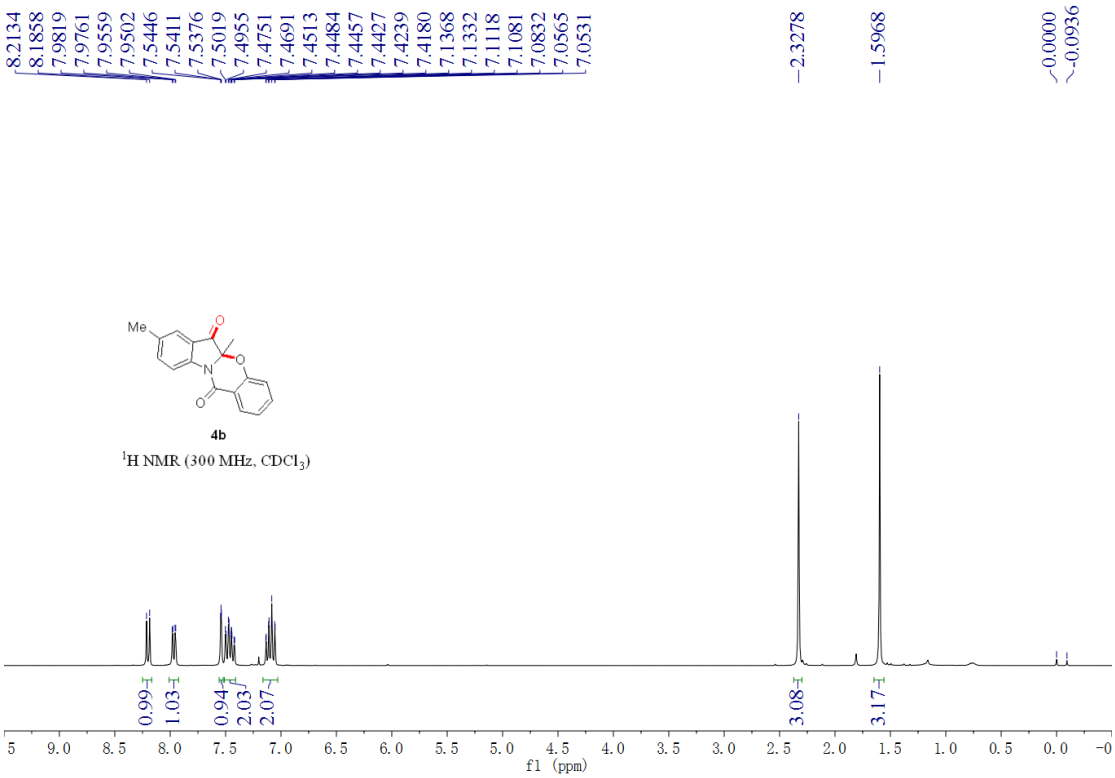
2v

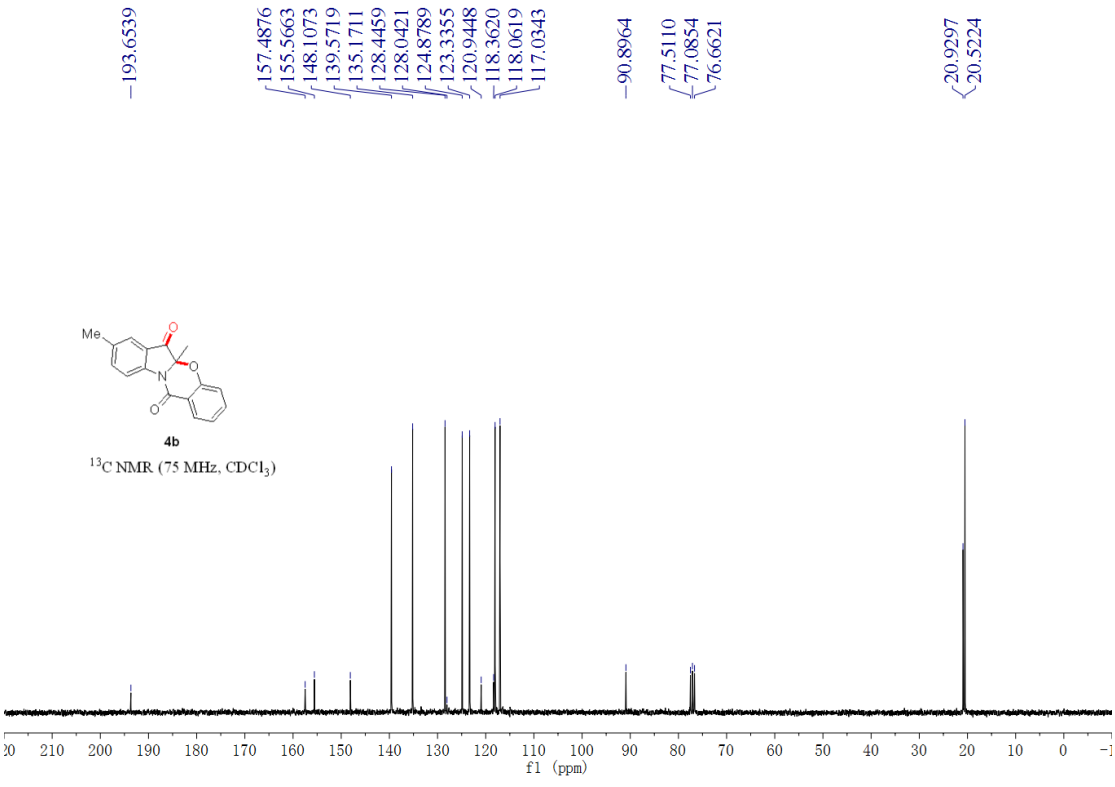
^{13}C NMR (75 MHz, $CDCl_3$)

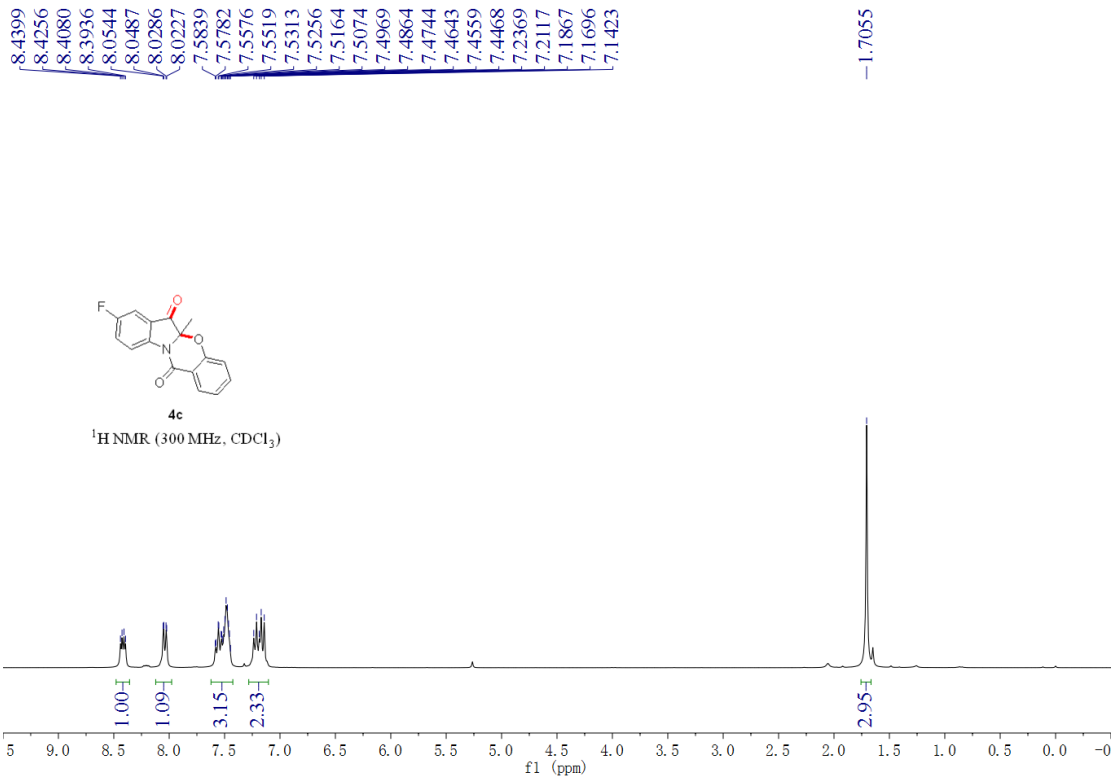


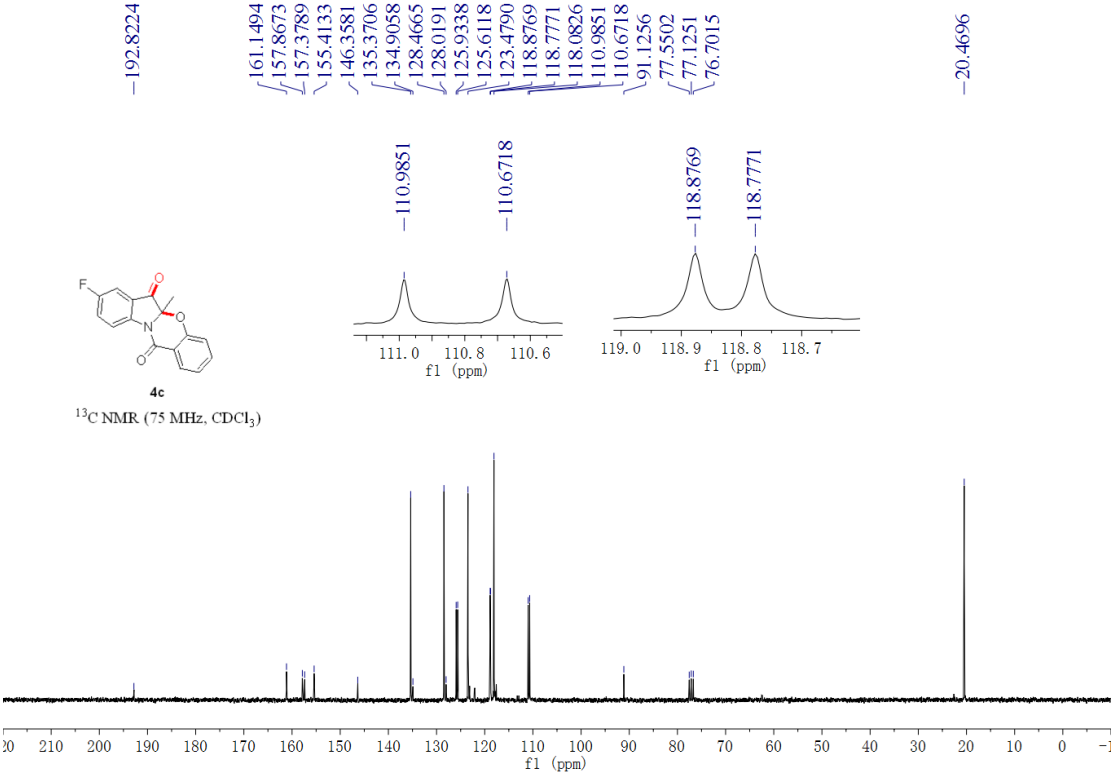

8.3178
8.2902
7.9718
7.9662
7.9462
7.9404
7.7564
7.7527
7.7300
7.7259
7.6869
7.6822
7.6626
7.6584
7.6543
7.6351
7.6303
7.4692
7.4501
7.4457
7.4420
7.4230
7.4172
7.2165
7.2135
7.1904
7.1666
7.1635
7.1304
7.1268
7.1053
7.1016
7.0770
7.0488
1.6008
0.0002
4a
1H NMR (300 MHz, CDCl3)
1.00
1.01
1.04
1.13
1.06
1.19
2.00
3.30
f1 (ppm)

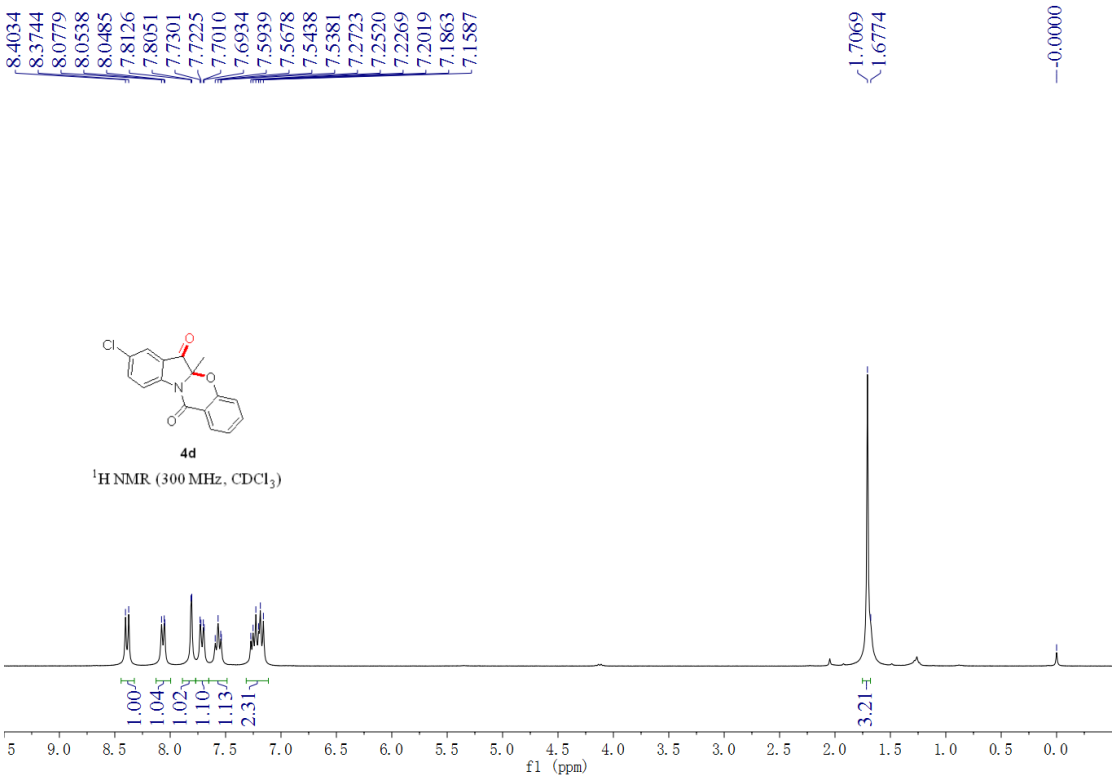

193.4797
157.5969
155.5116
149.9719
138.4490
135.2803
128.4723
125.1770
125.0469
124.9687
123.3381
120.7970
118.2443
118.0558
117.2098
90.6439
77.5860
77.1596
76.7376
20.4622
4a
13C NMR (75 MHz, CDCl3)
f1 (ppm)

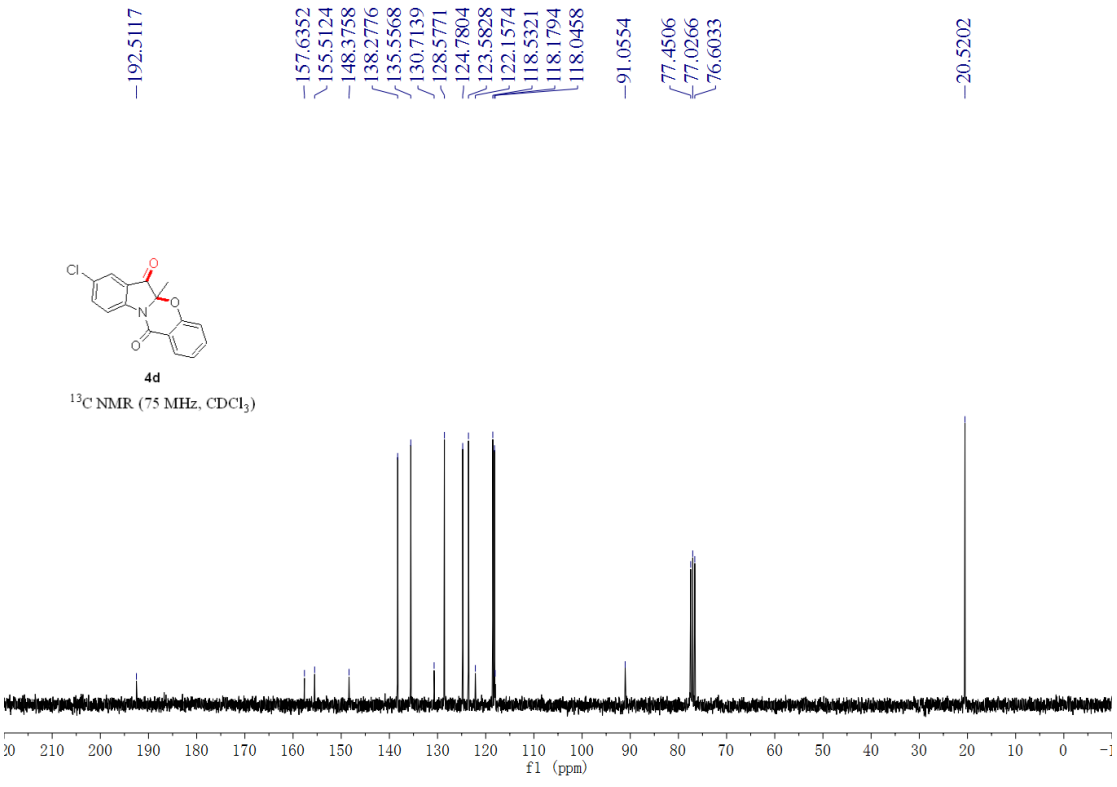

8.2134
8.1858
7.9819
7.9761
7.9559
7.9502
7.5446
7.5411
7.5376
7.5019
7.4955
7.4751
7.4691
7.4513
7.4484
7.4457
7.4427
7.4239
7.4180
7.1368
7.1332
7.1118
7.1081
7.0832
7.0565
7.0531
2.3278
1.5968
0.0000
-0.0936
Me
O
N
O
O
4b
^{1}H NMR (300 MHz, $CDCl_3$)
0.99
1.03
0.94
2.03
2.07
3.08
3.17
f1 (ppm)

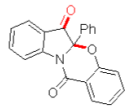

193.6539
157.4876
155.5663
148.1073
139.5719
135.1711
128.4459
128.0421
124.8789
123.3355
120.9448
118.3620
118.0619
117.0343
90.8964
77.5110
77.0854
76.6621
20.9297
20.5224
Me
O
N
O
O
4b
^{13}C NMR (75 MHz, $CDCl_3$)
f1 (ppm)


8.4399
8.4256
8.4080
8.3936
8.0544
8.0487
8.0286
8.0227
7.5839
7.5782
7.5576
7.5519
7.5313
7.5256
7.5164
7.5074
7.4969
7.4864
7.4744
7.4643
7.4559
7.4468
7.2369
7.2117
7.1867
7.1696
7.1423
1.7055
4c
^{1}H NMR (300 MHz, CDCl$_3$)
1.00
1.09
3.15
2.33
2.95
f1 (ppm)


192.8224
161.1494
157.8673
157.3789
155.4133
146.3581
135.3706
134.9058
128.4665
128.0191
125.9338
125.6118
123.4790
118.8769
118.7771
118.0826
110.9851
110.6718
91.1256
77.5502
77.1251
76.7015
20.4696
110.9851
110.6718
118.8769
118.7771
4c
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)

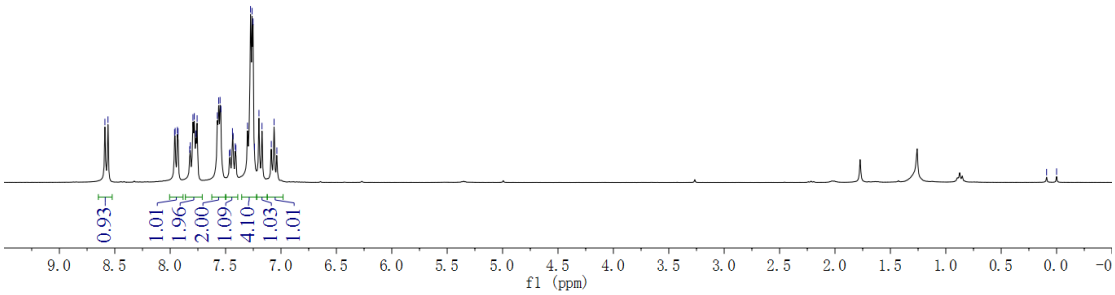

8.4034
8.3744
8.0779
8.0538
8.0485
7.8126
7.8051
7.7301
7.7225
7.7010
7.6934
7.5939
7.5678
7.5438
7.5381
7.2723
7.2520
7.2269
7.2019
7.1863
7.1587
1.7069
1.6774
0.0000
Cl
O
N
O
O
4d
^{1}H NMR (300 MHz, CDCl$_3$)
1.00
1.04
1.02
1.10
1.13
2.31
3.21
f1 (ppm)

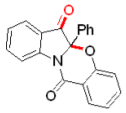

192.5117
157.6352
155.5124
148.3758
138.2776
135.5568
130.7139
128.5771
124.7804
123.5828
122.1574
118.5321
118.1794
118.0458
91.0554
77.4506
77.0266
76.6033
20.5202
Cl
O
N
O
O
4d
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)



4e

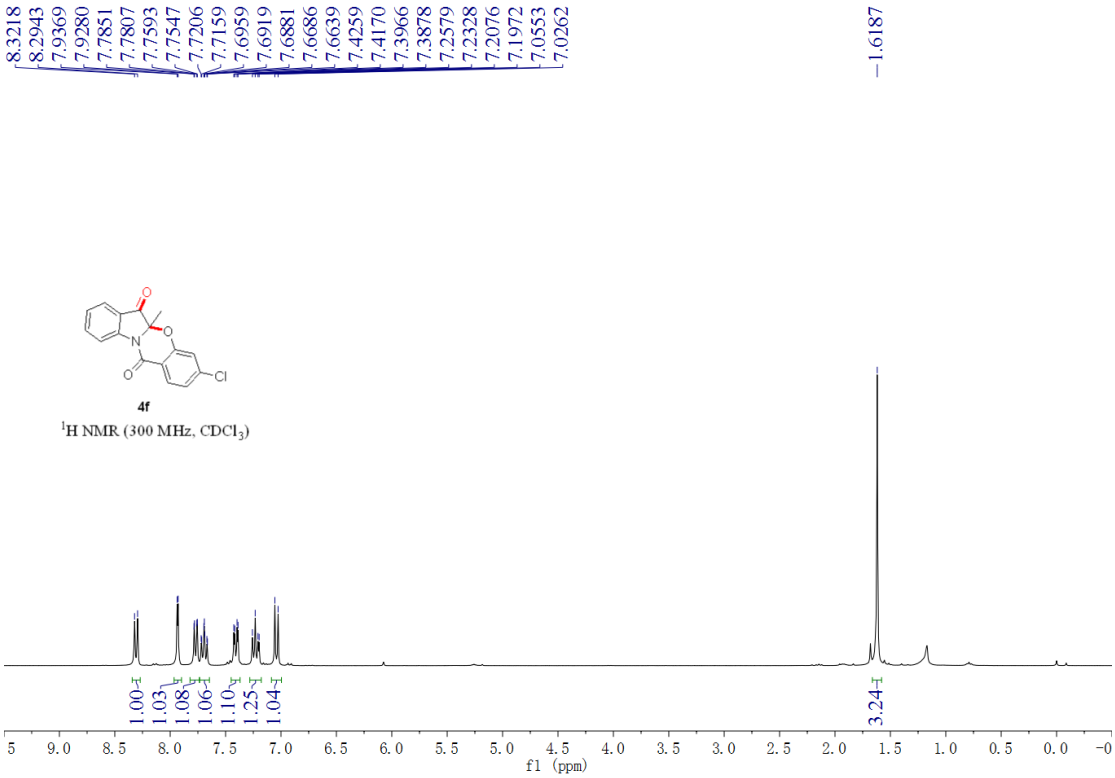
^{1}H NMR (300 MHz, $CDCl_3$)

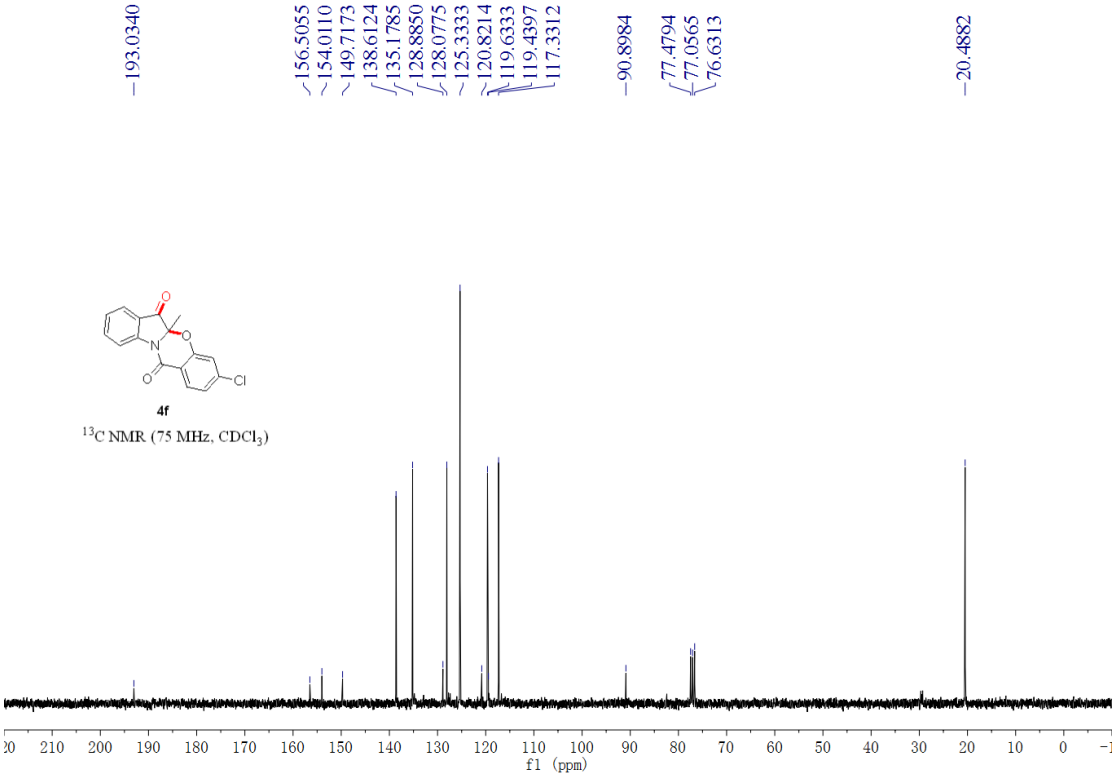


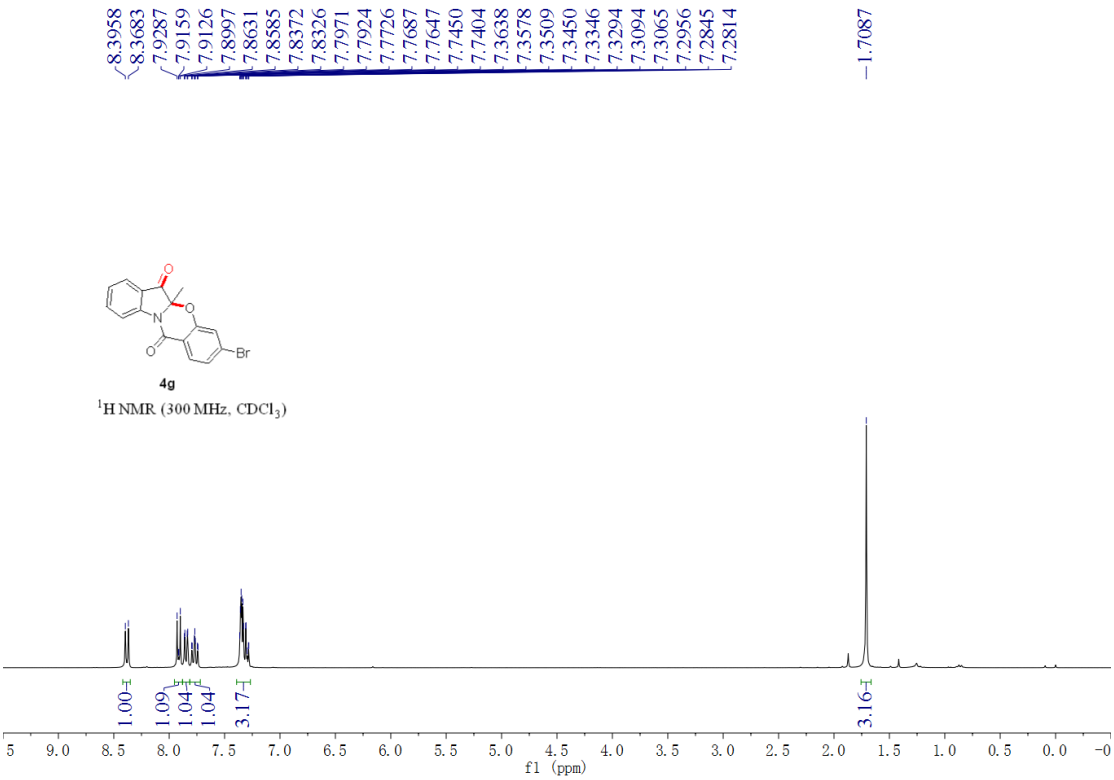


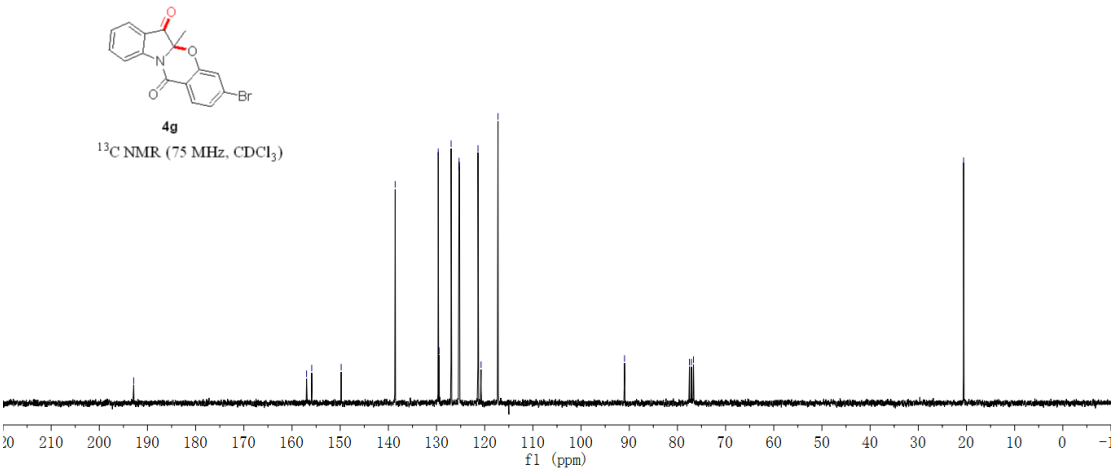
4e

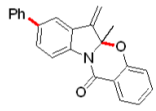
^{13}C NMR (75 MHz, $CDCl_3$)


8.3218
8.2943
7.9369
7.9280
7.7851
7.7807
7.7593
7.7547
7.7206
7.7159
7.6959
7.6919
7.6881
7.6686
7.6639
7.4259
7.4170
7.3966
7.3878
7.2579
7.2328
7.2076
7.1972
7.0553
7.0262
1.6187
4f
1H NMR (300 MHz, CDCl3)
1.00
1.03
1.08
1.06
1.10
1.25
1.04
3.24
f1 (ppm)


193.0340
156.5055
154.0110
149.7173
138.6124
135.1785
128.8850
128.0775
125.3333
120.8214
119.6333
119.4397
117.3312
90.8984
77.4794
77.0565
76.6313
20.4882
4f
13C NMR (75 MHz, CDCl3)
f1 (ppm)

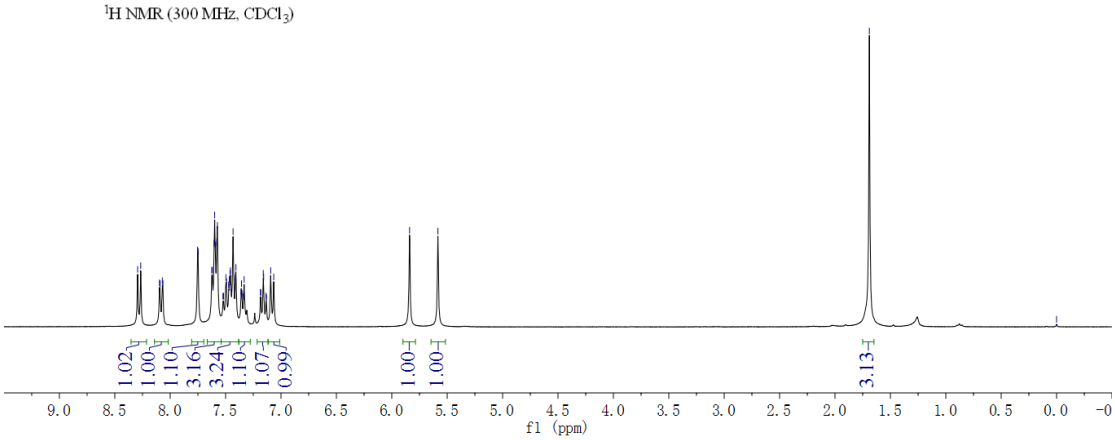

8.3958
8.3683
7.9287
7.9159
7.9126
7.8997
7.8631
7.8585
7.8372
7.8326
7.7971
7.7924
7.7726
7.7687
7.7647
7.7450
7.7404
7.3638
7.3578
7.3509
7.3450
7.3346
7.3294
7.3094
7.3065
7.2956
7.2845
7.2814
1.7087
Br
4g
1H NMR (300 MHz, CDCl3)
1.00
1.09
1.04
1.04
3.17
3.16
f1 (ppm)

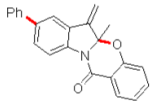

192.8639
156.9828
155.9124
149.8012
138.5873
129.6527
129.4690
126.9786
125.3253
125.2262
121.3988
120.7596
117.2454
90.9798
77.5124
77.0896
76.6660
20.5940
Br
4g
13C NMR (75 MHz, CDCl3)
f1 (ppm)



5

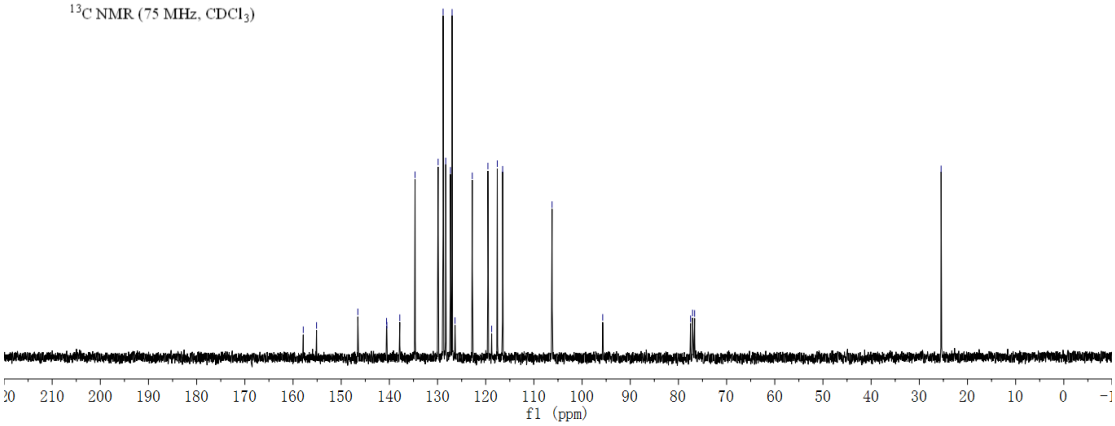
^{1}H NMR (300 MHz, $CDCl_3$)

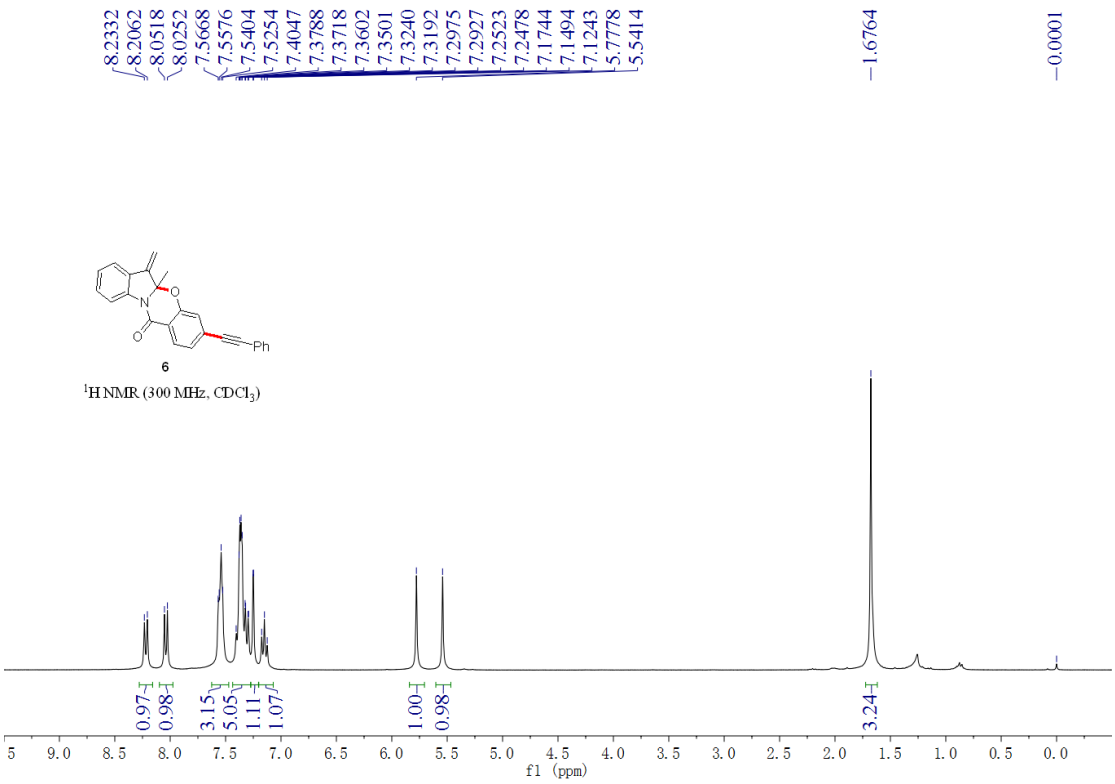


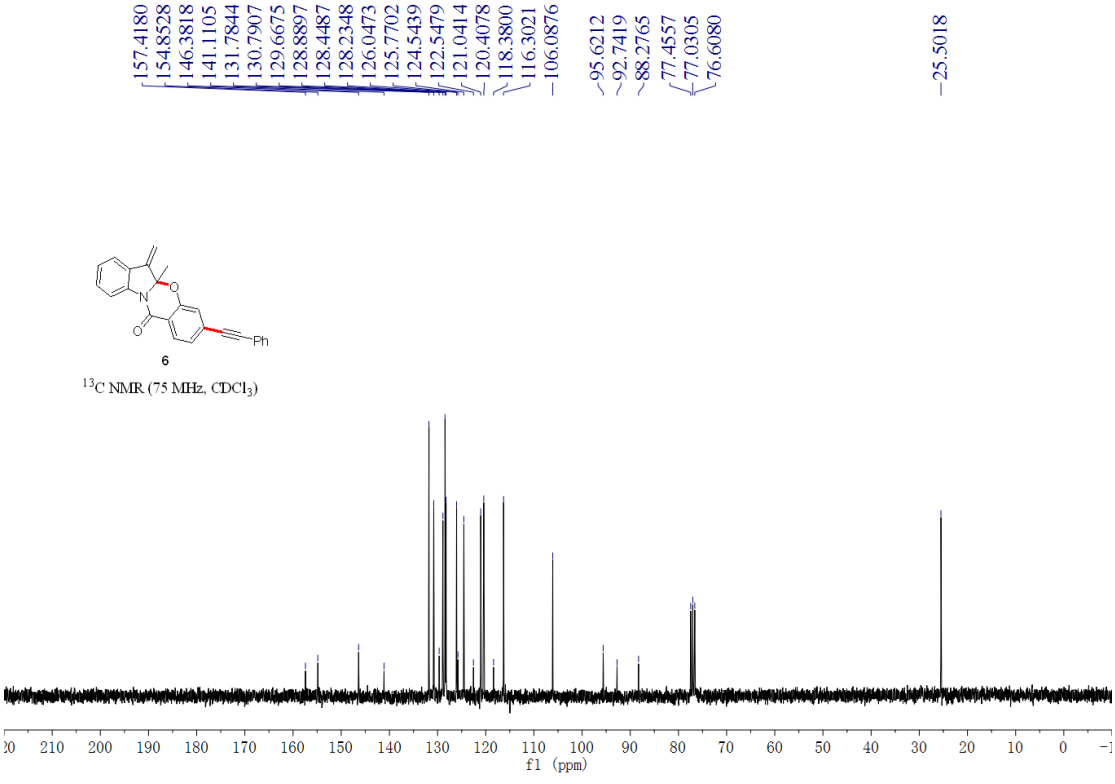


5

^{13}C NMR (75 MHz, $CDCl_3$)




8.2332
8.2062
8.0518
8.0252
7.5668
7.5576
7.5404
7.5254
7.4047
7.3788
7.3718
7.3602
7.3501
7.3240
7.3192
7.2975
7.2927
7.2523
7.2478
7.1744
7.1494
7.1243
5.7778
5.5414
1.6764
0.0001
Ph
6
^{1}H NMR (300 MHz, CDCl$_3$)
0.97
0.98
3.15
5.05
1.11
1.07
1.00
0.98
3.24
f1 (ppm)


157.4180
154.8528
146.3818
141.1105
131.7844
130.7907
129.6675
128.8897
128.4487
128.2348
126.0473
125.7702
124.5439
122.5479
121.0414
120.4078
118.3800
116.3021
106.0876
95.6212
92.7419
88.2765
77.4557
77.0305
76.6080
25.5018
Ph
6
^{13}C NMR (75 MHz, CDCl$_3$)
f1 (ppm)