Supporting information

Rhodium-Catalyzed C–H Functionalization with *N*-Acylsaccharins

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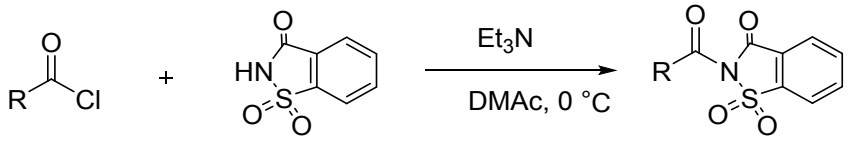
List of Contents

List of Known Compounds/General Methods

The reactions were conducted in sealed tube under the protection of a nitrogen atmosphere. All reactants reported in the manuscript are commercially available and have been prepared by the method reported previously. *N*-Acylsaccharins were prepared by the general methods. All solvents were purchased at the China suppliers and used without any purification. Triethylamine was purified by distillation with calcium hydride. Flash chromatography was performed using 200-300 mesh silica gel. ^{1}H and ^{13}C and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) and Varian (400 MHz) spectrometers in $CDCl_3$ with tetramethylsiliane as an internal standard.

General procedure for N-acylsaccharin synthesis 1a-1p:

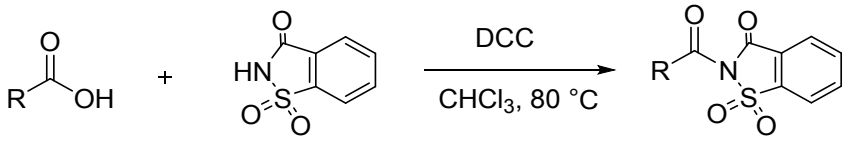
General procedure A:



An oven-dried round-bottomed flask (25 mL) equipped with a stir bar was charged with NEt_3 (10 mmol, 1.0 equiv), DMAc (typically, 8 mL) and saccharin (10 mmol, 1.0 equiv, slowly added into the mixture). Acyl chloride (typically, 1.0 equiv) was added to the reaction mixture with vigorous stirring at 0 ^{o}C, and maintained the temperature at 0 ^{o}C for 1h. After the indicated time, the reaction mixture was poured into 80 ml water and extracted with ethyl acetate three times (20 mL every time). The organic layer was combined and washed with brine three times (30 mL every time), dried, and concentrated. The obtained residue was purified by column

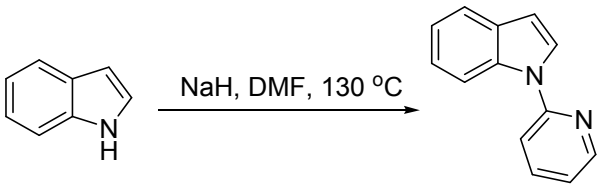
chromatography (Petroleum ether/EtOAc=3/1) to afford *N*-benzoyl saccharin (2.10g, 73.1%).

General procedure B:



An oven-dried round-bottomed flask (100 mL) equipped with a stir bar was charged with $CHCl_3$ (50 mL), saccharin (10 mmol, 1.0 equiv), benzoic acid (1.0 equiv). DCC (1.0 equiv) was added to the reaction mixture with vigorous stirring at 80°C, and the temperature was maintained at 80 ℃ for 12h. After cooling to room temperature, the mixture was filtrated through a short pad of silica gel, then the silica gel was washed with $CHCl_3$ (3 × 20 mL) and the organic phases were combined. After the solvent was removed, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3/1) as eluent afforded *N*-benzoyl saccharin (1.46 g, 51.2%).

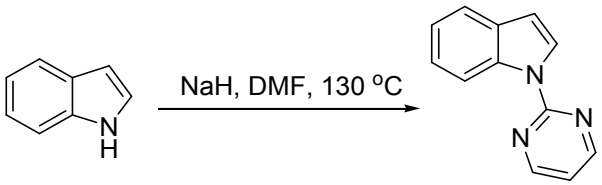
General procedure C



NaH (60% dispersion in mineral oil, 440 mg, 11 mmol) was added to a stirring solution of indole (1.17 g, 10 mmol) in DMF (15 mL) at 0 °C. After stirring for 30 min at 0 °C, 2-bromopyridine (1.37 g, 10.24 mmol) was added and the mixture was stirred at 130 °C for 24 h. The reaction mixture was then cooled to RT, poured into ice and extracted with EtOAc. The organic extract was washed successively with

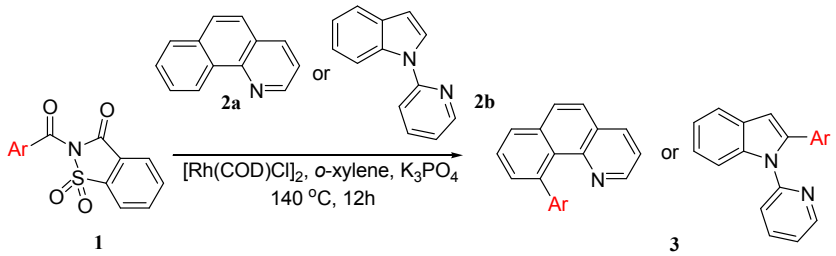
brine. The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. After the solvent was removed, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (30/1) as eluent afforded 1-(2-Pyridinyl)-1H-indole (1.45g, 75%).

General procedure D



NaH (60% dispersion in mineral oil, 440 mg, 1.0 mmol) was added to a stirring solution of indole (117 mg, 1.0 mmol) in DMF (2 mL) at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine (114 mg, 1.0 mmol) was added and the mixture was stirred at 130 °C for 24 h. The reaction mixture was then cooled to RT, poured into ice and extracted with EtOAc. The organic extract was washed successively with brine. The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. After the solvent was removed, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (20/1) as eluent afforded 1-(2-Pyridinyl)-1H-indole (166.1 mg, 85%).

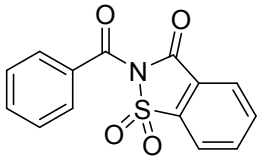
General procedure for C–H Functionalization reaction



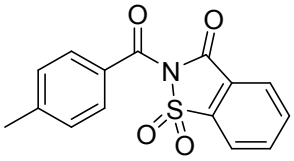
In an oven-dried Teflon septum screw-capped tube (15 mL), benzo[h]quinoline

(17.9 mg, 0.1 mmol, 1.0 equiv) **2a** or 1-(pyridin-2-yl)-1H-indole (19.4 mg, 0.1 mmol, 1.0 equiv) **2b**, *N*-acylsaccharin **1a**-**1q** (1.5 equiv), $[Rh(COD)Cl]_2$ (2.5 mg, 5 mol %), K_3PO_4 (1.5 equiv). The dry *o*-xylene (0.4 mL) was injected into the tube and then the reaction was removed to a 140 ^oC pre-heated oil bath and stirred for 12h. After cooling to room temperature, the solvents was removed, the crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (40/1) as eluent afforded biaryls.

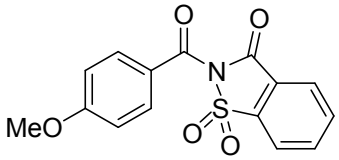
Characterization Data of *N*-Acylsaccharins



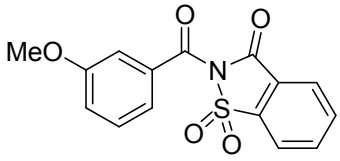
***N*-Benzoylsaccharin (1a)**[1] Following general procedure A, **1a** was isolated as a white solid (2.10 g, 73.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 1H), 7.99 (dd, *J* = 4.7, 0.9 Hz, 2H), 7.93 – 7.87 (m, 1H), 7.79 – 7.70 (m, 2H), 7.66 – 7.61 (m, 1H), 7.52 – 7.46 (m, 2H). mp 152-153 °C



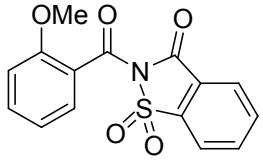
***N*-(4-methylbenzoyl)saccharin (1b)** Following general procedure A, **1b** was isolated as a white solid (2.14 g, 71.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.11 (m, 1H), 8.01 – 7.96 (m, 2H), 7.90 (ddd, *J* = 7.8, 5.1, 3.4 Hz, 1H), 7.83 – 7.79 (m, 2H), 6.98 – 6.95 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.39, 157.42, 138.38, 136.47, 134.94, 133.89, 132.33, 129.53, 128.42, 126.38, 125.43, 121.24, 21.56. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{11}NO_4S$ 301.0409; Found 301.0417. mp 157-158 °C



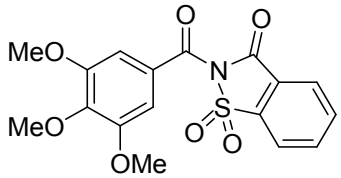
***N*-(4-methoxybenzoyl)saccharin (1c)** Following general procedure A, **1c** was isolated as a white solid (2.64 g, 83.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 8.00 – 7.95 (m, 2H), 7.90 (ddd, *J* = 7.8, 5.1, 3.4 Hz, 1H), 7.84 – 7.79 (m, 2H), 6.99 – 6.95 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.67, 157.92, 138.47, 136.24, 134.82, 132.74, 126.27, 125.79, 124.37, 121.19, 113.92, 109.99, 55.64. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{11}NO_5S$ 317.0358; Found 317.0361. mp 142-143 °C



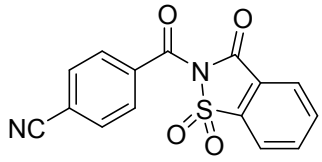
***N*-(3-methoxybenzoyl)saccharin (1d)** Following general procedure A, **1d** was isolated as a white solid (2.58 g, 81.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.94 – 7.90 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.19 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 159.49, 157.46, 138.41, 136.41, 134.90, 133.53, 129.47, 126.39, 121.93, 121.25, 121.09, 120.25, 114.22, 55.54. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{11}NO_5S$ 317.0358; Found 317.0363. mp 144-145 °C



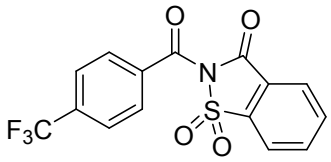
***N*-(2-methoxybenzoyl)saccharin (1e)** Following general procedure B, **1e** was isolated as a white solid (1.57 g, 49.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.91 – 7.87 (m, 1H), 7.60 – 7.47 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.83, 157.19, 156.63, 138.45, 136.28, 134.78, 133.88, 130.04, 126.03, 125.51, 122.96, 121.27, 120.95, 111.09, 55.85. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{11}NO_5S$ 317.0358; Found 317.0360. mp 148-149 °C



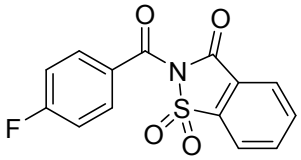
***N*-(3,4,5-trimethoxybenzoyl)saccharin (1f)** Following general procedure A, **1f** was isolated as a white solid (2.47 g, 65.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 1H), 7.99 (t, *J* = 6.0 Hz, 2H), 7.95 – 7.89 (m, 1H), 7.15 (s, 2H), 3.96 (d, *J* = 3.8 Hz, 3H), 3.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.31, 158.19, 152.98, 143.80, 138.42, 136.31, 134.88, 126.89, 126.31, 126.01, 121.28, 107.92, 61.06, 56.37. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{15}NO_7S$ 377.0901; Found 377.0904. mp 138-139 °C



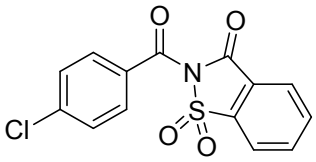
***N*-(4-cyanobenzoyl)saccharin (1g)** Following general procedure A, **1g** was isolated as a white solid (1.68 g, 53.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.97 – 7.93 (m, 1H), 7.79 (d, *J* = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.06, 157.11, 138.34, 136.84, 136.19, 135.16, 132.13, 129.54, 126.58, 124.94, 121.40, 117.57, 116.77. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_8N_2O_4S$ 312.0205; Found 313.0212. mp 166-167 °C



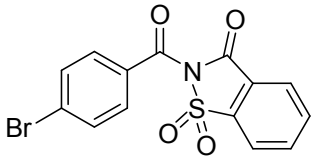
***N*-(4-(trifluoromethyl)benzoyl)saccharin (1h)** Following general procedure A, **1h** was isolated as a white solid (1.62 g, 45.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* =3.9 Hz, 2H), 7.95 (dd, *J* = 7.6, 4.3 Hz,1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.46, 157.19, 138.34(q, J^2 = 37.1 Hz), 136.73, 135.63, 135.10(q, J^3 = 3.8 Hz), 130.55, 129.55, 126.53, 125.46, 125.42, 125.10, 121.36(q, J^1 = 274.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.23. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_8F_3NO_4S$ 355.0126; Found 355.0121. mp 162-163 °C



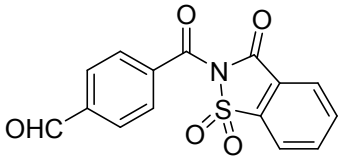
***N*-(4-fluorobenzoyl)saccharin (1i)** Following general procedure A, **1i** was isolated as a white solid (2.25 g, 73.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.6 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.95 – 7.91 (m, 1H), 7.81 (ddd, *J* = 8.0, 5.1, 2.5 Hz, 2H), 7.22 – 7.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.16, 157.52, 138.35(d, J^1 = 258.2 Hz), 136.52, 135.02, 132.54 (d, J^3 = 9.2 Hz), 128.51 (d, J^4 = 2.1 Hz), 126.42, 125.40, 121.28, 115.95, 115.73(d, J^2 = 23.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.62. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_8FNO_4S$ 305.0158; Found 305.0160. mp 170-171 °C



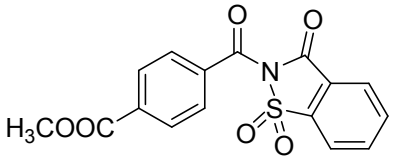
***N*-(4-chlorobenzoyl)saccharin (1j)** Following general procedure A, **1j** was isolated as a white solid (2.19 g, 68.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.00 (t, *J* = 3.6 Hz, 2H), 7.95 – 7.90 (m, 1H), 7.73 – 7.68 (m, 2H), 7.50 – 7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.39, 157.41, 140.51, 138.38, 136.54, 134.98, 130.98, 130.66, 128.85, 126.45, 125.34, 121.29. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_8ClNO_4S$ 321.0201; Found 321.0200. mp 202-203 °C



***N*-(4-bromobenzoyl)saccharin (1k)** Following general procedure B, **1k** was isolated as a white solid (1.80 g, 49.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 3.8 Hz, 2H), 7.95 – 7.91 (m, 1H), 7.67 – 7.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 157.38, 138.40, 136.53, 134.97, 131.82, 131.12, 130.98, 129.17, 126.46, 125.33, 121.29. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_8BrNO_4S$ 364.9357; Found 364.9362. mp 210-211 °C

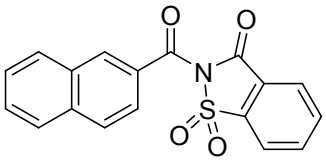


***N*-(4-formylbenzoyl)saccharin (1l)** Following general procedure A, **1l** was isolated as a white solid (1.94 g, 61.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.04 – 7.99 (m, 4H), 7.94 (dt, *J* = 8.1 Hz, 4.2, 1H), 7.86 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.18, 165.66, 157.16, 139.18, 138.39, 137.31, 136.72, 135.08, 129.64, 129.41, 126.54, 125.10, 121.36. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_9NO_5S$ 315.0201; Found 315.0205. mp 166-167 °C

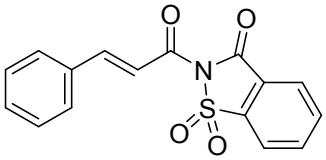


***N*-(4-methoxycarbonyl)saccharin (1m)** Following general procedure B, **1m** was

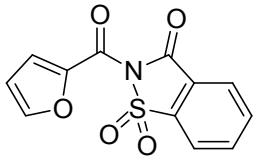
isolated as a white solid (1.65 g, 47.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 12.1, 8.0 Hz, 3H), 8.01 (t, *J* = 6.4 Hz, 2H), 7.96 – 7.91 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 165.82, 157.17, 138.40, 136.62, 136.11, 135.02, 134.31, 129.52, 129.12, 126.50, 125.20, 121.32, 52.57. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{11}NO_6S$ 345.0307; Found 345.0306. mp 169-170 °C



***N*-(2-naphthoyl)saccharin (1n)** Following general procedure A, **1n** was isolated as a white solid (2.24 g, 66.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 8.01 (t, *J* = 7.5 Hz, 2H), 7.98 – 7.94 (m, 1H), 7.92 (t, *J* = 8.2 Hz, 3H), 7.77 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.59 – 7.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.38, 157.59, 138.50, 136.39, 135.83, 134.89, 132.10, 131.88, 129.59, 129.57, 129.12, 128.30, 127.91, 127.13, 126.42, 125.60, 124.69, 121.26. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{11}NO_4S$ 337.0740; Found 337.0743. mp 154-155 °C

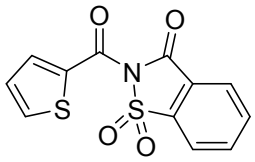


***N*-cinnamoylsaccharin (1o)** Following general procedure A, **1o** was isolated as a white solid (1.98 g, 63.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 15.7 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.95 – 7.90 (m, 1H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.67 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.47 – 7.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.26, 157.82, 149.68, 138.31, 136.42, 134.86, 134.01, 131.53, 129.05, 129.00, 126.27, 125.20, 121.20, 117.03. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{11}NO_4S$ 313.0402; Found 313.0399. mp 230-231 °C

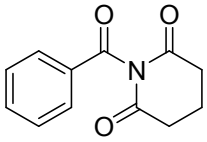


***N*-(furan-2-carbonyl)saccharin (1p)** Following general procedure A, **1p** was

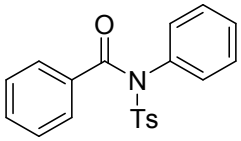
isolated as a white solid (1.96 g, 70.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.98 (dd, *J* = 7.1, 3.7 Hz, 2H), 7.95 – 7.90 (m, 1H), 7.72 (d, *J* = 1.0 Hz, 1H), 7.55 (d, *J* = 3.7 Hz, 1H), 6.65 (dd, *J* = 3.7, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.26, 153.94, 148.66, 145.57, 138.52, 136.23, 134.86, 126.32, 125.75, 123.31, 121.26, 112.99. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_7NO_5S$ 277.0045; Found 277.0047. mp 167-168 °C



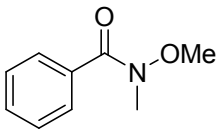
***N*-(thiophene-2-carbonyl)saccharin (1q)** Following general procedure A, **1q** was isolated as a white solid (2.03 g, 69.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 9.4, 3.7 Hz, 1H), 8.01 – 7.90 (m, 4H), 7.84 (d, *J* = 5.0 Hz, 1H), 7.20 – 7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.87, 158.03, 138.47, 137.20, 136.61, 135.79, 135.18, 128.43, 126.56, 125.88, 125.86, 121.48. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{12}H_7NO_4S_2$ 292.9817; Found 292.9808. mp 137-138 °C



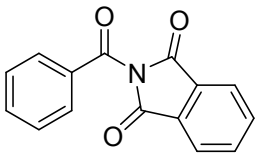
1-Benzoylpiperidine-2,6-dione (1r)[9] Following general procedure of the literature, **1s** was was purified by column chromatography (Petroleum ether/EtOAc = 3/1) to afford a white solid (2.18 g, 75.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 – 7.81 (m, 2H), 7.66 – 7.61 (m, 1H), 7.51 – 7.45 (m, 2H), 2.80 – 2.74 (m, 4H), 2.15 (ddd, *J* = 13.1, 6.5, 2.7, 2H).



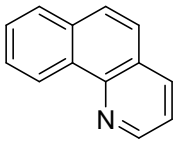
***N*-phenyl-*N*-tosyl benzamide (1s)**[10] Following general procedure of literature, **1s** was was purified by column chromatography (Petroleum ether/EtOAc = 2/1) to afford a white solid (3.05 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 – 7.78 (m, 2H), 7.47 – 7.39 (m, 2H), 7.34 – 7.24 (m, 6H), 7.19 – 7.12 (m, 4H), 2.44 (s, 3H).



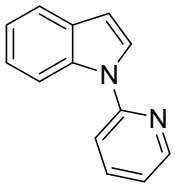
***N*-methoxy-*N*-methylbenzamide (1t)** was purchased from *Energy Chemical* with 98% purity.



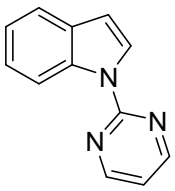
2-Benzoylisoindoline-1,3-dione (1u)[11] Following general procedure of the literature, **1r** was purified by column chromatography (Petroleum ether/EtOAc = 3/1) to afford a white solid (2.10 g, 83.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 4.6, 2.0, 1H), 7.89 – 7.84 (m, 4H), 7.76 (dd, *J* = 5.4, 3.2, 1H), 7.70 – 7.62 (m, 1H), 7.53 – 7.44 (m, 2H).



Benzo[h]quinoline (2a) was purchased from *Energy Chemical* with 98% purity.

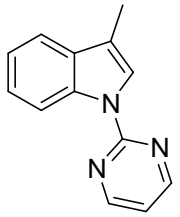


1-(Pyridin-2-yl)-1H-indole (2b)[2] Following general procedure D, **2b** was isolated as a white solid (1.45g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.74 (d, *J* = 3.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.24 (dt, *J* = 11.2, 4.9 Hz, 1H), 7.17 (ddd, *J* = 7.3, 4.9, 0.8 Hz, 1H), 6.73 (d, *J* = 3.5 Hz, 1H).

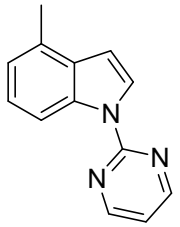


1-(pyrimidin-2-yl)-1H-indole (2c)[8] Following general procedure D, **2c** was isolated as a white solid (166.1 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (dd, *J* = 8.4,

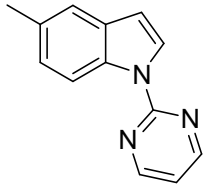
0.6, 1H), 8.68 (d, *J* = 4.8, 2H), 8.30 (d, *J* = 3.7, 1H), 7.65 (d, *J* = 7.8, 1H), 7.40 – 7.35 (m, 1H), 7.29 – 7.24 (m, 1H), 7.00 (t, *J* = 4.8, 1H), 6.76 – 6.70 (m, 1H).



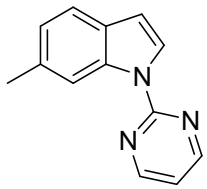
3-methyl-1-(pyrimidin-2-yl)-1H-indole (2d)[8] Following general procedure D, **2d** was isolated as oil (170.3 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 8.8, 1H), 8.70 (d, *J* = 4.8, 2H), 8.41 – 8.26 (m, 2H), 8.02 (d, *J* = 8.8, 1H), 7.08 (t, *J* = 4.8, 1H), 6.76 (d, *J* = 3.6, 1H), 3.95 (s, 3H).



4-methyl-1-(pyrimidin-2-yl)-1H-indole (2e)[8] Following general procedure D, **2e** was isolated as white solid (178.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (dd, *J* = 18.5, 6.6, 3H), 8.27 (d, *J* = 3.7, 1H), 7.25 (d, *J* = 7.9, 1H), 7.04 (dd, *J* = 10.0, 5.5, 2H), 6.74 (d, *J* = 3.2, 1H), 2.58 (s, 3H).

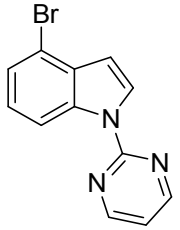


5-methyl-1-(pyrimidin-2-yl)-1H-indole (2f)[8] Following general procedure D, **2f** was isolated as white solid (188.4 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 – 8.63 (m, 3H), 8.24 (d, *J* = 3.6, 1H), 7.42 (s, 1H), 7.17 (d, *J* = 8.5, 1H), 7.00 (t, *J* = 4.8, 1H), 6.64 (d, *J* = 3.5, 1H), 2.48 (s, 3H).

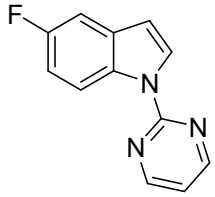


6-methyl-1-(pyrimidin-2-yl)-1H-indole (2g)[8] Following general procedure D, **2g**

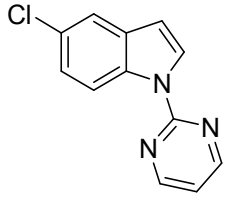
was isolated as white solid (191.3 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 4.8, 2H), 8.64 (s, 1H), 8.21 (d, *J* = 3.6, 1H), 7.51 (d, *J* = 7.9, 1H), 7.09 (d, *J* = 7.9, 1H), 7.02 (t, *J* = 4.8, 1H), 6.66 (d, *J* = 3.7, 1H), 2.56 (s, 3H).



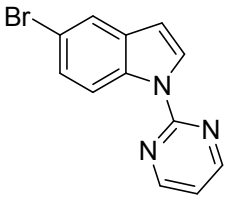
4-bromo-1-(pyrimidin-2-yl)-1H-indole (2h)[8] Following general procedure D, **2h** was isolated as white solid (245.1 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 8.4, 1H), 8.61 (d, *J* = 4.8, 2H), 8.30 (d, *J* = 3.7, 1H), 7.42 – 7.38 (m, 1H), 7.18 (t, *J* = 8.0, 1H), 6.98 (t, *J* = 4.8, 1H), 6.76 (dd, *J* = 3.7, 0.6, 1H).



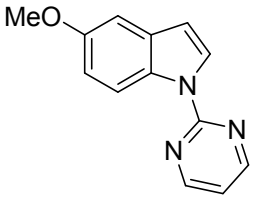
5-fluoro-1-(pyrimidin-2-yl)-1H-indole (2i)[8] Following general procedure D, **2i** was isolated as white solid (199.2 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 (dd, *J* = 9.1, 4.8, 1H), 8.62 (d, *J* = 4.8, 2H), 8.30 (d, *J* = 3.7, 1H), 7.27 (dd, *J* = 9.0, 2.6, 1H), 7.07 (dt, *J* = 9.2, 4.6, 1H), 6.99 – 6.95 (m, 1H), 6.64 (d, *J* = 3.6, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -121.96.



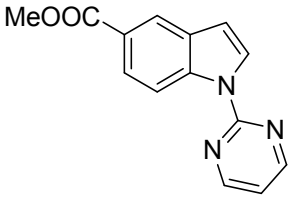
5-chloro-1-(pyrimidin-2-yl)-1H-indole (2j)[8] Following general procedure D, **2j** was isolated as white solid (202.1 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 (d, *J* = 8.9, 1H), 8.69 (d, *J* = 4.8, 2H), 8.29 (d, *J* = 3.7, 1H), 7.58 (d, *J* = 2.0, 1H), 7.27 (dt, *J* = 4.2, 2.1, 1H), 7.06 (t, *J* = 4.8, 1H), 6.63 (dd, *J* = 3.7, 0.5, 1H).



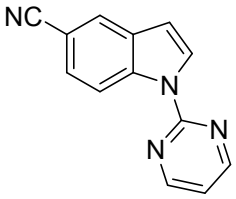
5-bromo-1-(pyrimidin-2-yl)-1H-indole (2k)[8] Following general procedure D, **2k** was isolated as white solid (216.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (t, *J* = 6.4, 3H), 8.25 (d, *J* = 3.7, 1H), 7.73 (d, *J* = 1.9, 1H), 7.40 (dd, *J* = 8.9, 1.9, 1H), 7.02 (t, *J* = 4.8, 1H), 6.61 (d, *J* = 3.7, 1H).



5-methoxy-1-(pyrimidin-2-yl)-1H-indole (2l)[8] Following general procedure D, **2l** was isolated as white solid (196.0 mg g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 9.1, 1H), 8.62 (d, *J* = 4.8, 2H), 8.25 (d, *J* = 3.6, 1H), 7.10 (d, *J* = 2.4, 1H), 7.01 – 6.92 (m, 2H), 6.66 – 6.60 (m, 1H), 3.89 (s, 3H).

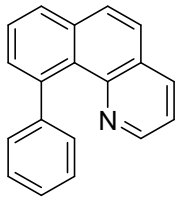


methyl 1-(pyrimidin-2-yl)-1H-indole-5-carboxylate (2m)[8] Following general procedure D, **2m** was isolated as white solid (164.6 mg g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 8.8, 1H), 8.70 (d, *J* = 4.8, 2H), 8.41 – 8.26 (m, 2H), 8.02 (d, *J* = 8.8, 1H), 7.08 (t, *J* = 4.8, 1H), 6.76 (d, *J* = 3.6, 1H), 3.95 (s, 3H).

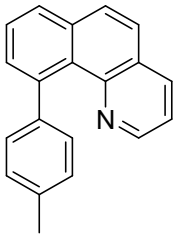


1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (2n)[8] Following general procedure D, **2n** was isolated as white solid (138.6 mg g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.92 (d, *J* = 8.4, 1H), 8.81 – 8.67 (m, 2H), 8.41 (d, *J* = 3.5, 1H), 7.96 (s, 1H), 7.58 (d, *J* = 8.8, 1H), 7.16 (dd, *J* = 6.0, 3.6, 1H), 6.76 (d, *J* = 3.5, 1H).

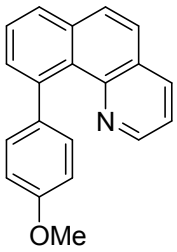
Characterization Data of Products



10-Phenylbenzo[h]quinolone (3a)[3] Following general procedure for C–H Functionalization reaction, **3a** was isolated as oil (23.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.56 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.48 – 7.34 (m, 5H), 7.32 (dd, *J* = 8.0, 4.3 Hz, 1H).

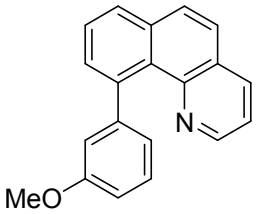


10-*p*-Tolylbenzo[h]quinolone (3b)[3] Following general procedure for C–H Functionalization reaction, **3b** was isolated as a colourless oil (22.9 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.92 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.56 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.33 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H).

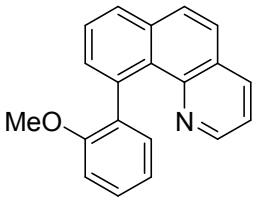


10-(4-Methoxyphenyl)benzo[h]quinolone (3c)[3] Following general procedure for C–H Functionalization reaction, **3c** was isolated as a colourless oil (26.0 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.67 (dd, *J* = 8.3, 6.7 Hz,

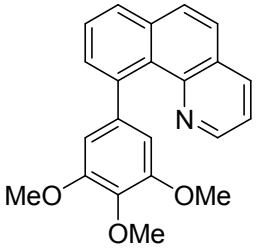
2H), 7.56 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.35 – 7.29 (m, 3H), 6.99 – 6.95 (m, 2H), 3.92 (s, 3H).



10-(3-Methoxyphenyl)benzo[h]quinolone (3d)[3] Following general procedure for C–H Functionalization reaction, **3d** was isolated as a colourless oil (25.4 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.94 – 7.91 (m, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.58 – 7.54 (m, 1H), 7.34 – 7.29 (m, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 (dd, *J* = 7.5, 1.3 Hz, 2H), 3.79 (s, 3H).

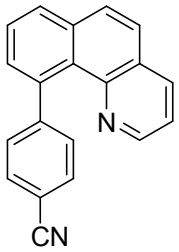


10-(2-Methoxyphenyl)benzo[h]quinolone (3e)[3] Following general procedure for C–H Functionalization reaction, **3e** was isolated as a colourless oil (24.8 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.91 (dd, *J* = 5.8, 4.9 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.69 (t, *J* = 6.3 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.54 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.37 (td, *J* = 8.0, 1.6 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.41 (s, 3H).

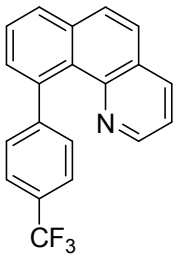


10-(3,4,5-Trimethoxyphenyl)benzo[h]quinolone (3f) Following general procedure for C–H Functionalization reaction, **3f** was isolated as a colourless oil (19.3 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.66 (m,

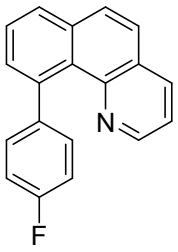
2H), 7.60 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.3 Hz, 1H), 6.59 (s, 2H), 3.96 (s,3H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 152.48, 146.94, 146.64, 141.93, 141.43, 136.29, 135.16, 135.01, 131.20, 128.95, 128.24, 128.04, 127.21, 126.97, 125.99, 121.14, 106.27, 61.05, 56.08. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_8ClNO_4S$ 345.1365; Found 345.1357.



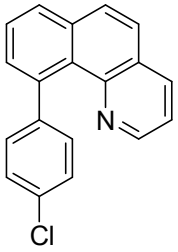
4-(benzo[h]quinolin-10-yl)Benzonitrile (3g)[3] Following general procedure for C–H Functionalization reaction, **3g** was isolated as a colourless oil (22.1 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.71 (dd, *J* = 14.5, 6.9 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.48 – 7.45 (m, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 8.0, 4.3 Hz, 1H).



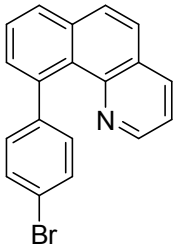
10-(4-(Trifluoromethyl)phenyl)benzo[h]quinolone (3h)[3] Following general procedure for C–H Functionalization reaction, **3h** was isolated as a colourless oil (27.8 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.50 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 (dd, *J* = 8.0, 4.3 Hz, 1H). ^{19}F NMR (376 MHz, CDCl3) δ -61.98.



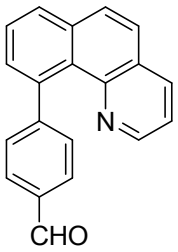
10-(4-Fluorophenyl)benzo[h]quinolone (3i)[3] Following general procedure for C–H Functionalization reaction, **3i** was isolated as a colourless oil (25.1 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.52 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.12 – 7.05 (m, 2H). ^{19}F NMR (376 MHz, CDCl3) δ -118.15.



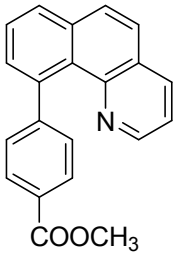
10-(4-Chlorophenyl)benzo[h]quinolone (3j)[3] Following general procedure for C–H Functionalization reaction, **3j** was isolated as a colourless oil (26.7 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 4.3, 1.9 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.87 – 7.84 (m, 1H), 7.72 – 7.65 (m, 2H), 7.51 – 7.49 (m, 1H), 7.40 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H).



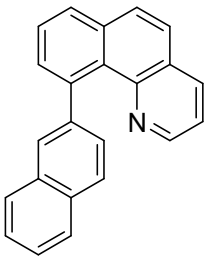
10-(4-Bromophenyl)benzo[h]quinolone (3k)[3] Following general procedure for C–H Functionalization reaction, **3k** was isolated as a colourless oil (29.4 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.57 – 7.45 (m, 3H), 7.34 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.25 – 7.20 (m, 2H).



4-(benzo[h]quinolin-10-yl)Benzaldehyde (3l)[3] Following general procedure for C–H Functionalization reaction, **3l** was isolated as a colourless oil (21.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 8.36 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.90 (dd, *J* = 15.1, 8.5 Hz, 3H), 7.74 – 7.69 (m, 2H), 7.50 (d, *J* = 7.9 Hz, 3H), 7.33 (dd, *J* = 8.0, 4.3 Hz, 1H).

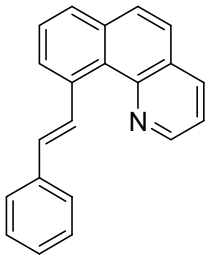


Methyl 4-(benzo[h]quinolin-10-yl)Benzoate (3m)[3] Following general procedure for C–H Functionalization reaction, **3m** was isolated as a white solid (28.5 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.09 (dd, *J* = 10.2, 4.9 Hz, 3H), 7.95 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.71 (dd, *J* = 8.1, 3.0 Hz, 2H), 7.51 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 8.0, 4.3 Hz, 1H), 3.97 (s, 3H).

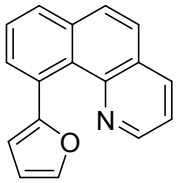


10-(Naphthalen-2-yl)benzo[h]quinolone (3n)[4] Following general procedure for C–H Functionalization reaction, **3n** was isolated as a white solid (25.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.97 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.94 – 7.81 (m, 4H), 7.79 – 7.70 (m, 3H), 7.64 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.30 (dd, *J* =

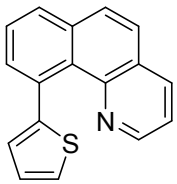
8.0, 4.3 Hz, 1H).



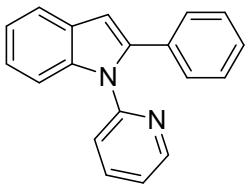
(E)-10-Styrylbenzo[h]quinolone (3o)[5] Following general procedure for C–H Functionalization reaction, **3o** was isolated as a white solid (21.7 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 16.0 Hz, 1H), 9.06 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.19 – 8.15 (m, 1H), 7.90 (dd, *J* = 11.0, 7.7 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.70 (dd, *J* = 14.5, 8.2 Hz, 4H), 7.49 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H).



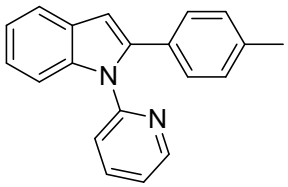
10-(Furan-2-yl)benzo[h]quinolone (3p)[3] Following general procedure for C–H Functionalization reaction, **3p** was isolated as a white solid (21.3 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.82 (dd, *J* = 7.9, 4.2 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.70 – 7.65 (m, 2H), 7.52 (t, *J* = 2.8 Hz, 1H), 7.39 (dd, *J* = 8.0, 4.3 Hz, 1H), 6.60 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.48 (d, *J* = 2.9 Hz, 1H).



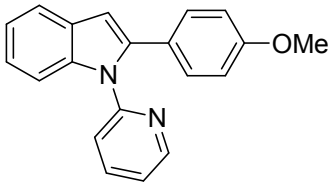
10-(Thiophen-2-yl)benzo[h]quinolone (3q)[3] Following general procedure for C–H Functionalization reaction, **3q** was isolated as a pale yellow oil (20.9 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.72 – 7.63 (m, 3H), 7.40 – 7.33 (m, 2H), 7.11 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.05 – 7.00 (m, 1H).



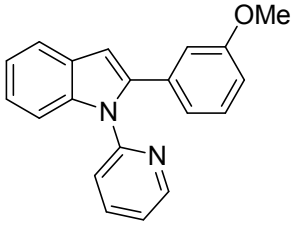
2-Phenyl-1-(pyridin-2-yl)-1H-indole (3r) [2] Following general procedure for C–H Functionalization reaction, **3r** was isolated as a white solid (25.1 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.65 – 7.60 (m, 1H), 7.27 (td, *J* = 5.5, 2.7 Hz, 5H), 7.24 – 7.18 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H).



1-(Pyridin-2-yl)-2-*p*-tolyl-1H-indole (3s)[6] Following general procedure for C–H Functionalization reaction, **3s** was isolated as a white solid (26.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.72 – 7.57 (m, 3H), 7.25 – 7.12 (m, 5H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 2.33 (s, 3H).

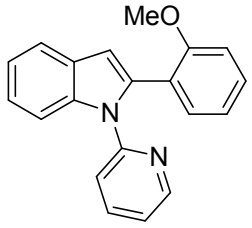


2-(4-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indole (3t)[2] Following general procedure for C–H Functionalization reaction, **3t** was isolated as a colourless oil (27.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.69 – 7.60 (m, 3H), 7.25 – 7.16 (m, 5H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.73 (s, 1H), 3.80 (s, 3H).

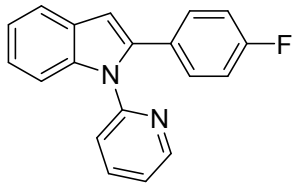


2-(3-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indole (3u)[2] Following general procedure for C–H Functionalization reaction, **3u** was isolated as a colourless oil

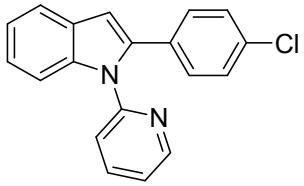
(27.3 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.70 – 7.59 (m, 3H), 7.24 – 7.14 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.83 – 6.76 (m, 3H), 3.67 (s, 3H).



2-(2-Methoxyphenyl)-1-(pyridin-2-yl)-1H-indole (3v)[2] Following general procedure for C–H Functionalization reaction, **3v** was isolated as a white solid (15.3 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 – 8.54 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 7.47 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.31 (td, *J* = 7.9, 1.7 Hz, 1H), 7.23 – 7.12 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 2H), 3.31 (s, 3H).

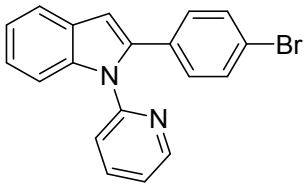


2-(4-Fluorophenyl)-1-(pyridin-2-yl)-1H-indole (3w)[2] Following general procedure for C–H Functionalization reaction, **3w** was isolated as a white solid (25.9 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.66 (tt, *J* = 7.5, 3.9 Hz, 3H), 7.26 – 7.17 (m, 5H), 7.00 – 6.94 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.22.

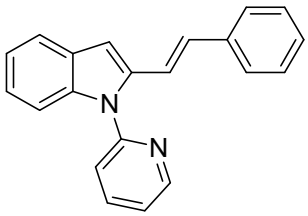


2-(4-Chlorophenyl)-1-(pyridin-2-yl)-1H-indole (3x) Following general procedure for C–H Functionalization reaction, **3x** was isolated as a white solid (28.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 3.8 Hz, 1H), 7.67 (dd, *J* = 16.9, 8.9 Hz, 3H), 7.26 – 7.17 (m, 7H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 0.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.79, 149.36, 138.71, 138.57, 138.14, 137.98, 133.41, 131.19,

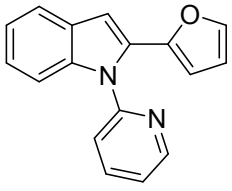
129.83, 128.57, 123.28, 121.93, 121.83, 121.49, 120.67, 111.42, 105.89. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{13}ClN_2$ 304.0767; Found 304.0768. mp 128-129 °C



2-(4-Bromophenyl)-1-(pyridin-2-yl)-1H-indole (3y)[2] Following general procedure for C–H Functionalization reaction, **3y** was isolated as a white solid (31.8 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 7.67 (ddd, *J* = 16.0, 10.3, 5.0 Hz, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 3H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H).

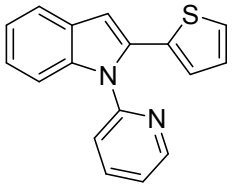


(E)-1-(pyridin-2-yl)-2-styryl-1H-indole (3z)[7] Following general procedure for C–H Functionalization reaction, **3z** was isolated as a pale yellow solid (24.3 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.70 (m, 1H), 7.93 – 7.86 (m, 1H), 7.63 (dt, *J* = 6.6, 2.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.43 – 7.30 (m, 6H), 7.24 – 7.15 (m, 3H), 7.10 (d, *J* = 5.6 Hz, 2H), 6.99 (s, 1H).

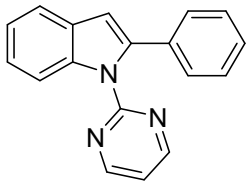


2-(Furan-2-yl)-1-(pyridin-2-yl)-1H-indole (3aa) Following general procedure for C–H Functionalization reaction, **3aa** was isolated as a pale yellow solid (22.6 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dt, *J* = 12.0, 6.0 Hz, 1H), 7.83 (td, *J* = 7.7, 1.9 Hz, 1H), 7.66 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.41 (dd, *J* = 10.1, 3.1 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.25 (d, *J* = 6.5 Hz, 1H), 7.18 (ddd, *J* = 11.5, 5.3, 3.5 Hz, 2H), 6.97 (s, 1H), 6.34 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.96 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.76, 149.41, 146.82, 142.21, 138.45, 138.19, 130.51, 128.31, 123.21,

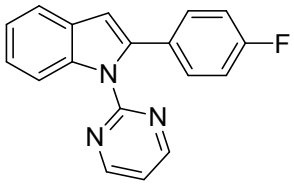
122.58, 121.96, 121.27, 120.79, 111.18, 110.90, 108.21, 104.11. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{12}N_2O$ 260.0950; Found 260.0957. mp 125-126 °C



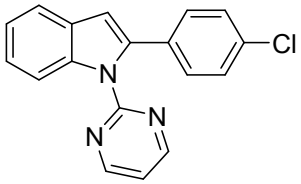
1-(Pyridin-2-yl)-2-(thiophen-2-yl)-1H-indole (3ab) Following general procedure for C–H Functionalization reaction, **3ab** was isolated as a pale yellow oil (22.3 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.75 (td, *J* = 7.7, 1.9 Hz, 1H), 7.64 (dd, *J* = 6.5, 2.3 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.35 – 7.30 (m, 1H), 7.24 – 7.16 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.86 (s, 1H), 6.74 (dt, *J* = 10.4, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 149.39, 138.57, 138.02, 134.30, 133.22, 128.34, 127.29, 126.56, 125.75, 123.17, 122.48, 122.41, 121.35, 120.53, 111.13, 105.55. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{12}N_2S$ 276.0721; Found 276.0720. mp 131-132 °C



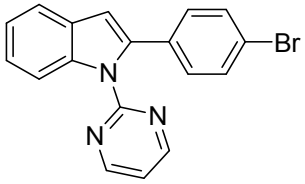
2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ac)[8] Following general procedure for C–H Functionalization reaction, **3ac** was isolated as a white solid (24.6 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 4.8, 2H), 8.16 (d, *J* = 8.2, 1H), 7.67 (d, *J* = 7.6, 1H), 7.35 – 7.25 (m, 7H), 7.10 (t, *J* = 4.8, 1H), 6.83 (s, 1H).



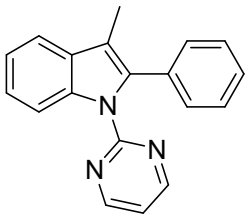
2-(4-fluorophenyl)-1-(pyrimidin-2-yl)-1H-indole (3ad)[8] Following general procedure for C–H Functionalization reaction, **3ad** was isolated as a white solid (26.9 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 – 8.60 (m, 2H), 8.20 – 8.14 (m, 1H), 7.69 – 7.63 (m, 1H), 7.33 – 7.24 (m, 4H), 7.14 – 7.08 (m, 1H), 7.04 – 6.97 (m, 2H), 6.81 – 6.76 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.86.



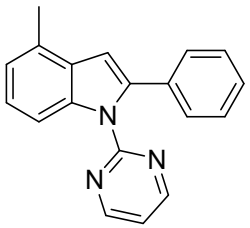
2-(4-chlorophenyl)-1-(pyrimidin-2-yl)-1H-indole (3ae)[8] Following general procedure for C–H Functionalization reaction, **3ae** was isolated as a white solid (27.2 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 – 8.64 (m, 2H), 8.17 (dd, *J* = 8.3, 0.8, 1H), 7.67 – 7.63 (m, 1H), 7.33 – 7.21 (m, 6H), 7.14 – 7.10 (m, 1H), 6.80 (d, *J* = 0.6, 1H).



2-(4-bromophenyl)-1-(pyrimidin-2-yl)-1H-indole (3af)[8] Following general procedure for C–H Functionalization reaction, **3af** was isolated as a white solid (30.4 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 4.8, 2H), 8.17 (d, *J* = 8.0, 1H), 7.65 (d, *J* = 7.6, 1H), 7.43 (dd, *J* = 8.8, 2.2, 2H), 7.33 – 7.22 (m, 2H), 7.18 – 7.10 (m, 3H), 6.80 (s, 1H).

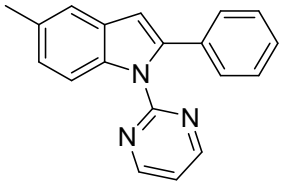


3-methyl-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3da)[8] Following general procedure for C–H Functionalization reaction, **3da** was isolated as a white solid (21.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (t, *J* = 5.4, 2H), 8.23 – 8.17 (m, 1H), 7.66 – 7.61 (m, 1H), 7.38 – 7.26 (m, 7H), 7.01 (t, *J* = 4.8, 1H), 2.37 (s, 3H).

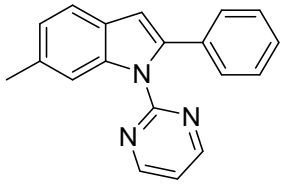


4-methyl-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ea)[8] Following general

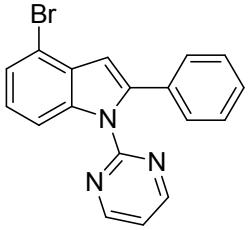
procedure for C–H Functionalization reaction, **3ea** was isolated as a white solid (25.4 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (d, *J* = 4.8, 2H), 7.98 (d, *J* = 8.3, 1H), 7.33 – 7.26 (m, 5H), 7.20 (d, *J* = 7.9, 1H), 7.11 – 7.04 (m, 2H), 6.85 (s, 1H), 2.61 (s, 3H).



5-methyl-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3fa)[8] Following general procedure for C–H Functionalization reaction, **3fa** was isolated as a white solid (26.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (d, *J* = 4.8, 2H), 8.06 (d, *J* = 8.5, 1H), 7.45 (d, *J* = 0.7, 1H), 7.33 – 7.27 (m, 5H), 7.12 (d, *J* = 8.5, 1H), 7.07 (t, *J* = 4.8, 1H), 6.75 (s, 1H), 2.49 (s, 3H).

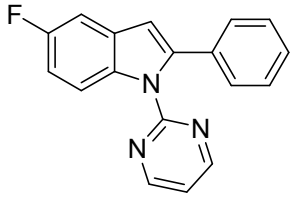


6-methyl-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ga)[8] Following general procedure for C–H Functionalization reaction, **3ga** was isolated as a white solid (25.1 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (d, *J* = 4.8, 2H), 7.95 (s, 1H), 7.54 (d, *J* = 7.9, 1H), 7.32 – 7.25 (m, 5H), 7.09 (dd, *J* = 9.6, 4.9, 2H), 6.78 (s, 1H), 2.51 (s, 3H).

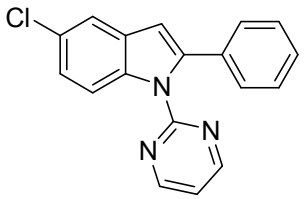


4-bromo-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ha)[8] Following general procedure for C–H Functionalization reaction, **3ha** was isolated as a white solid (32.9 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (dd, *J* = 4.8, 1.9, 2H), 8.01 (dd, *J* = 8.9, 1.4, 1H), 7.77 (d, *J* = 1.9, 1H), 7.36 (dd, *J* = 8.8, 2.0, 1H), 7.32 – 7.26 (m, 5H), 7.13 (dt, *J* = 4.8, 2.4, 1H), 6.73 (d, *J* = 1.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =

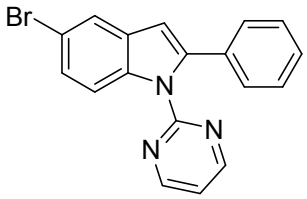
158.33, 157.86, 141.18, 138.20, 133.32, 129.90, 128.22, 128.19, 127.51, 124.93, 124.31, 118.09, 114.42, 111.91, 107.74. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{15}NO_7S$ 349.0215; Found 349.0217. mp 161-162 °C



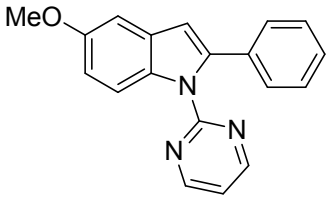
5-fluoro-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ia)[8] Following general procedure for C–H Functionalization reaction, **3ia** was isolated as a white solid (26.0 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 4.8, 2H), 8.09 (dd, *J* = 9.0, 4.6, 1H), 7.34 – 7.26 (m, 6H), 7.12 (t, *J* = 4.8, 1H), 7.01 (td, *J* = 9.1, 2.5, 1H), 6.76 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.86.



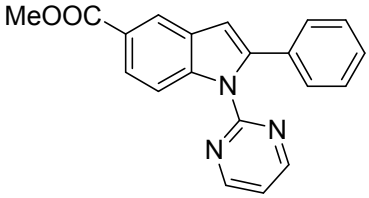
5-chloro-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ja)[8] Following general procedure for C–H Functionalization reaction, **3ja** was isolated as a white solid (28.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 4.8, 2H), 8.06 (d, *J* = 8.9, 1H), 7.61 (d, *J* = 2.1, 1H), 7.38 – 7.26 (m, 5H), 7.23 (dd, *J* = 8.9, 2.1, 1H), 7.13 (t, *J* = 4.8, 1H), 6.73 (s, 1H).



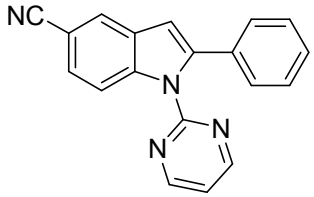
5-bromo-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3ka)[8] Following general procedure for C–H Functionalization reaction, **3ka** was isolated as a white solid (32.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (dd, *J* = 4.8, 1.9, 2H), 8.01 (dd, *J* = 8.9, 1.4, 1H), 7.77 (d, *J* = 1.9, 1H), 7.36 (dd, *J* = 8.8, 2.0, 1H), 7.32 – 7.26 (m, 5H), 7.13 (dt, *J* = 4.8, 2.4, 1H), 6.73 (d, *J* = 1.6, 1H).



5-methoxy-2-phenyl-1-(pyrimidin-2-yl)-1H-indole (3la)[8] Following general procedure for C–H Functionalization reaction, **3la** was isolated as a white solid (26.2 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.64 (d, *J* = 4.8, 2H), 8.08 (d, *J* = 9.0, 1H), 7.27 (d, *J* = 16.1, 5H), 7.08 (dd, *J* = 12.4, 7.6, 2H), 6.93 (dd, *J* = 9.0, 2.3, 1H), 6.74 (s, 1H), 3.88 (s, 3H).



methyl 2-phenyl-1-(pyrimidin-2-yl)-1H-indole-5-carboxylate (3ma)[8] Following general procedure for C–H Functionalization reaction, **3ma** was isolated as a white solid (26.7 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (dd, *J* = 10.1, 4.8, 2H), 8.40 (d, *J* = 1.5, 1H), 8.14 – 8.07 (m, 2H), 7.34 – 7.26 (m, 5H), 7.17 (t, *J* = 4.8, 1H), 6.87 (s, 1H), 3.95 (s, 3H).



2-phenyl-1-(pyrimidin-2-yl)-1H-indole-5-carbonitrile (3na)[8] Following general procedure for C–H Functionalization reaction, **3na** was isolated as a white solid (25.2 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 (dd, *J* = 10.3, 4.4, 2H), 8.14 (d, *J* = 8.7, 1H), 7.98 (d, *J* = 1.0, 1H), 7.51 (dd, *J* = 8.6, 1.6, 1H), 7.31 (q, *J* = 3.6, 3H), 7.25 (ddd, *J* = 16.1, 7.7, 3.0, 3H), 6.83 (s, 1H).

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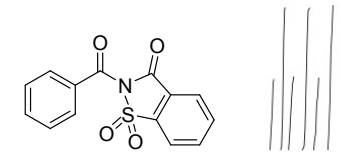
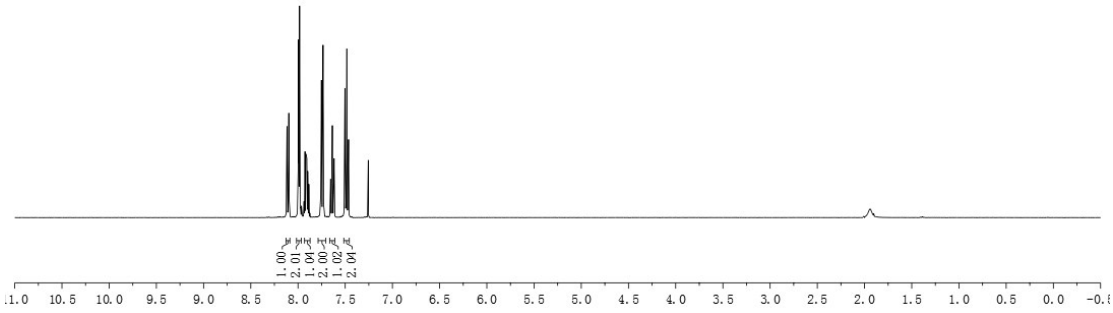
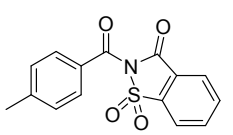


^{1}H NMR (400 MHz, $CDCl_3$)

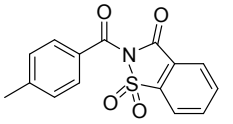
1a





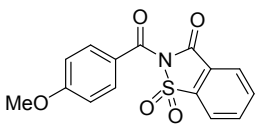
^{1}H NMR (400 MHz, $CDCl_3$)

1b



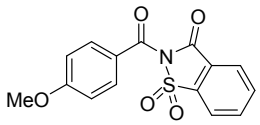
^{13}C NMR (100 MHz, $CDCl_3$)

1b



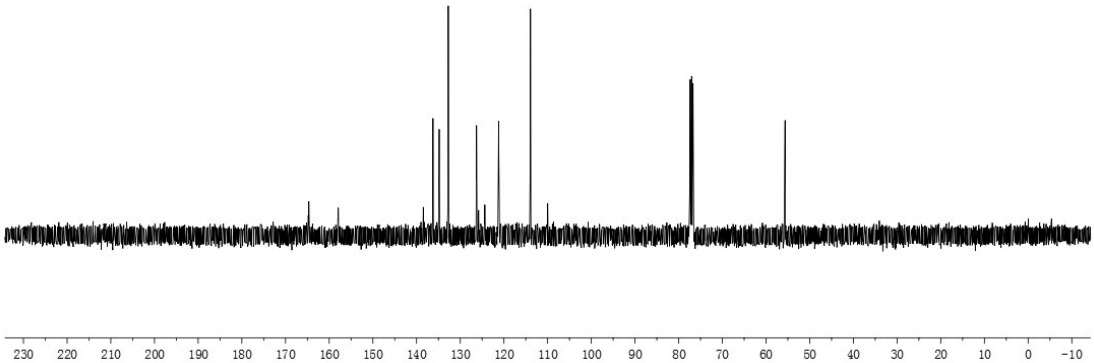
^{1}H NMR (400 MHz, $CDCl_3$)

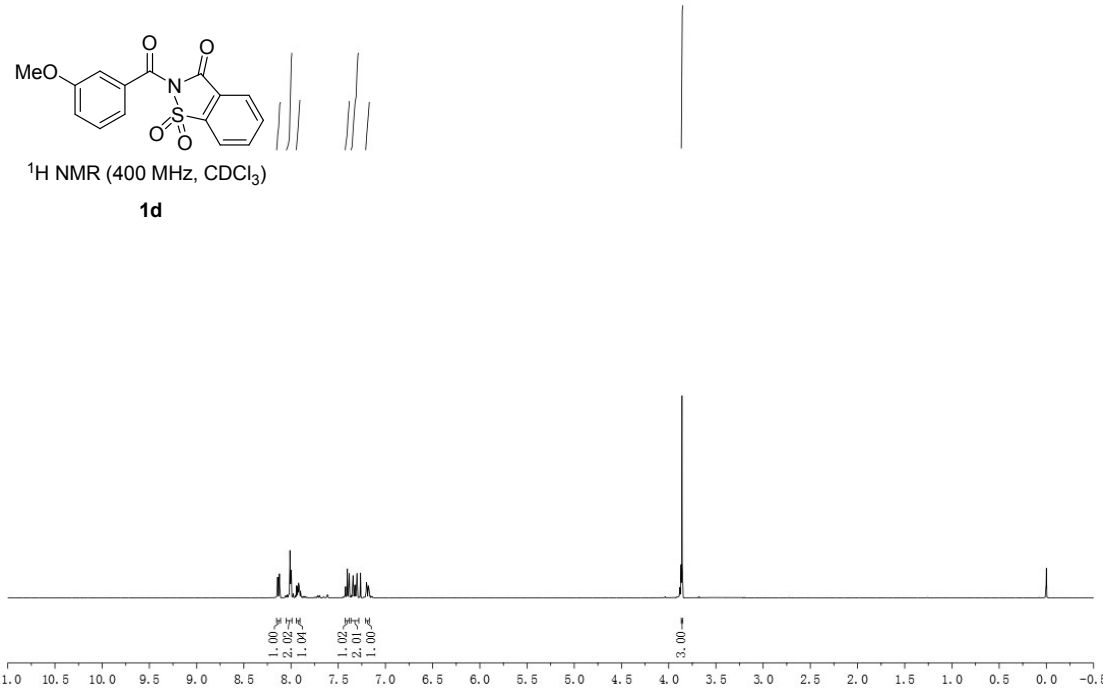
1c



^{13}C NMR (100 MHz, $CDCl_3$)

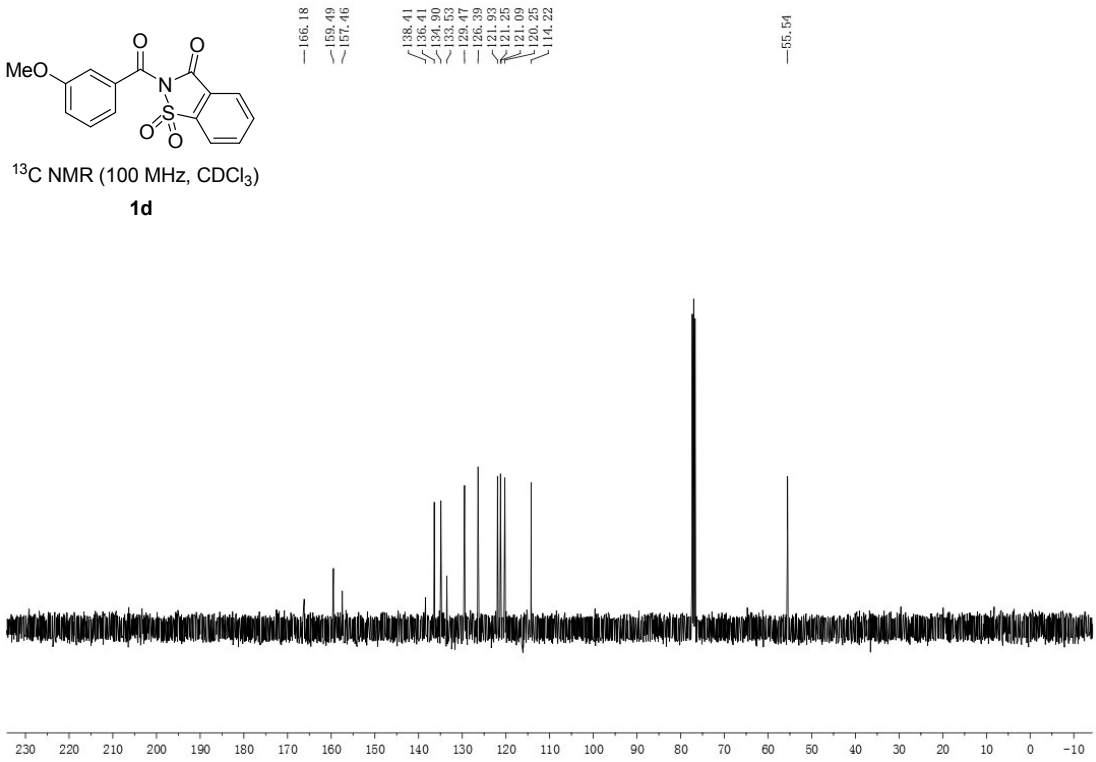
1c





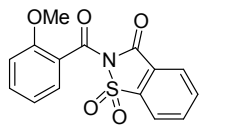
^{1}H NMR (400 MHz, $CDCl_3$)

1d



^{13}C NMR (100 MHz, $CDCl_3$)

1d



^{1}H NMR (400 MHz, $CDCl_3$)

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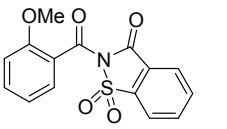
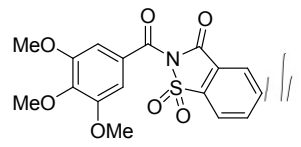


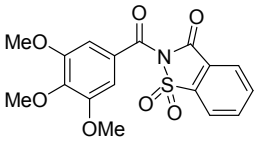
^{13}C NMR (100 MHz, $CDCl_3$)

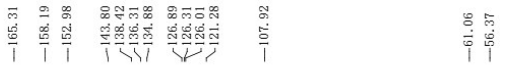
1e



^{1}H NMR (400 MHz, $CDCl_3$)

1f





^{13}C NMR (100 MHz, $CDCl_3$)

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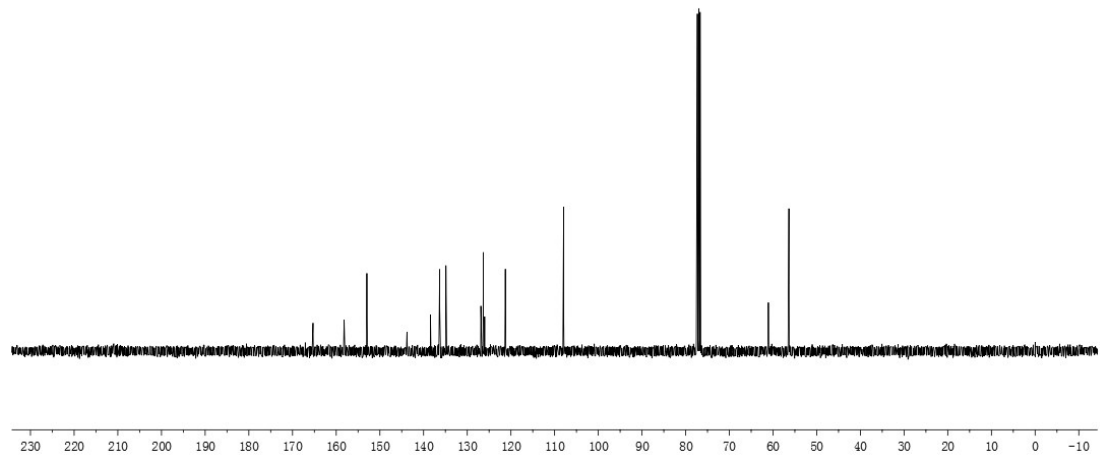
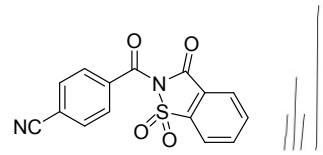
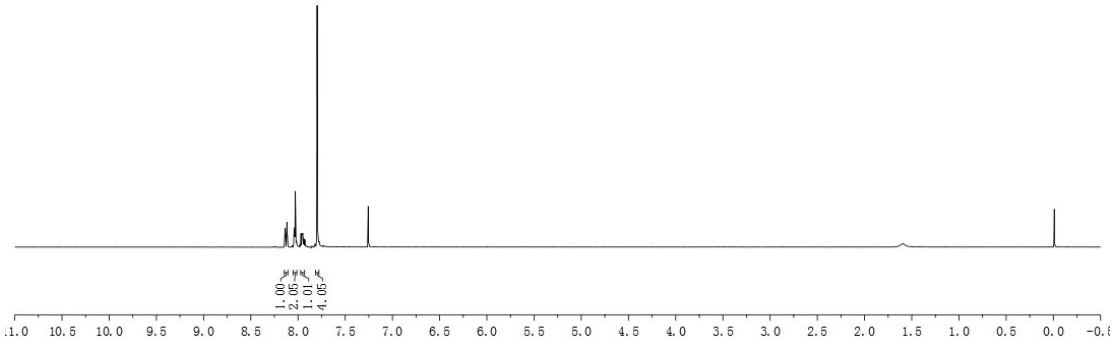
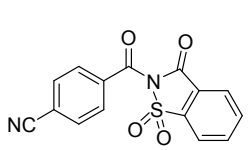




^{1}H NMR (400 MHz, $CDCl_3$)

1g





^{13}C NMR (100 MHz, $CDCl_3$)

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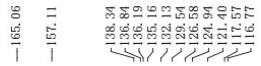
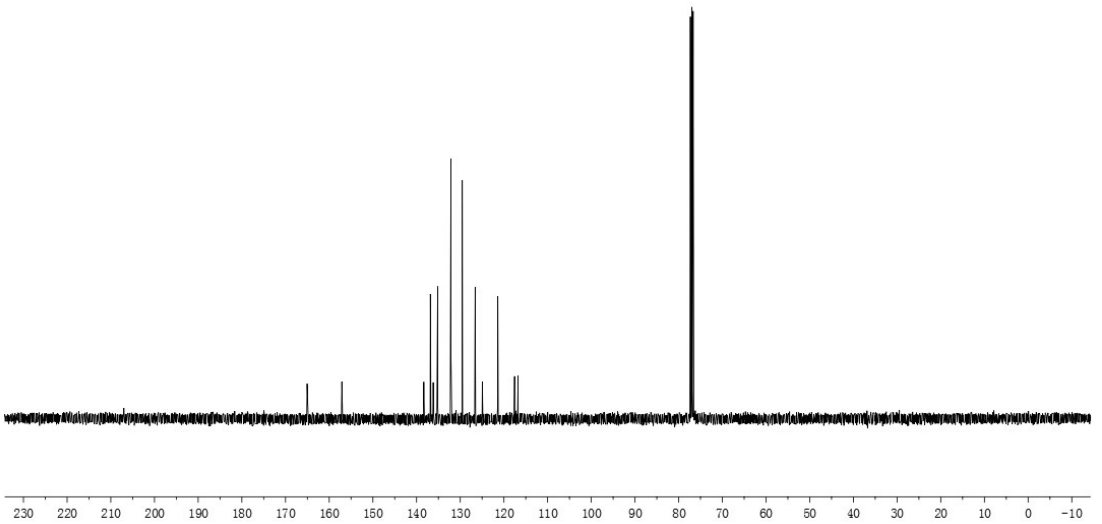
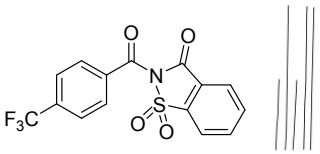
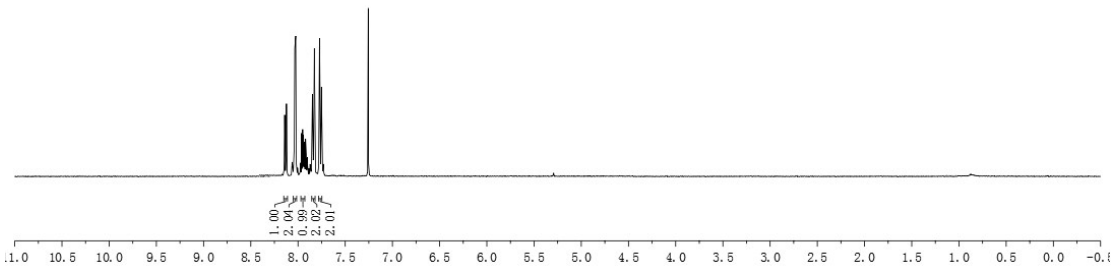


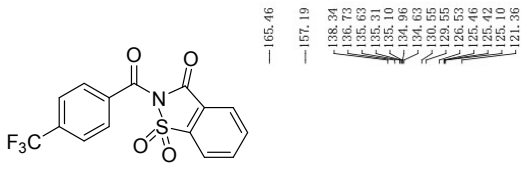




^{1}H NMR (400 MHz, $CDCl_3$)

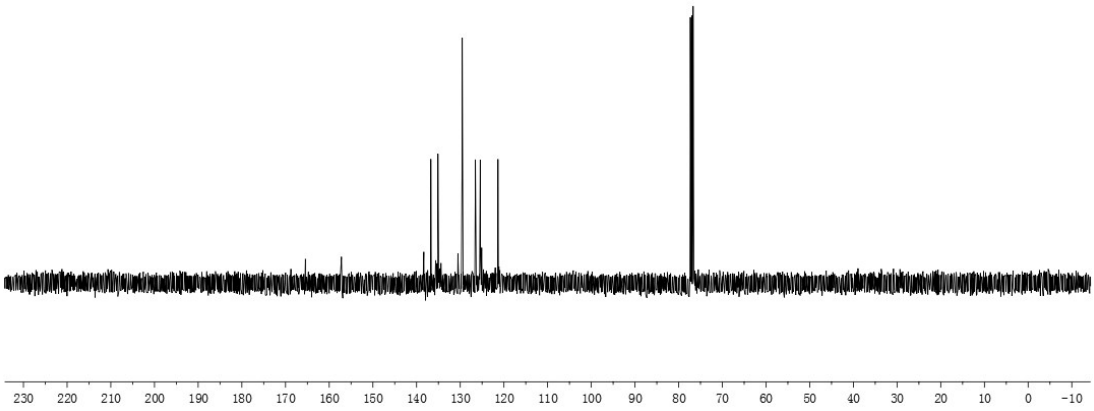
1h

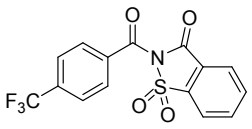




^{13}C NMR (100 MHz, $CDCl_3$)

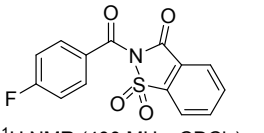
1h





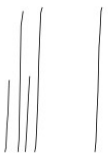
^{19}F NMR (376 MHz, $CDCl_3$)

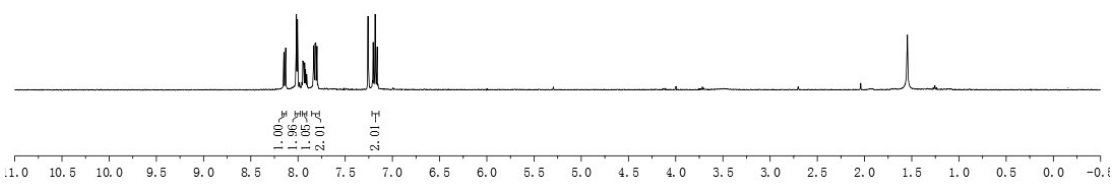
1h

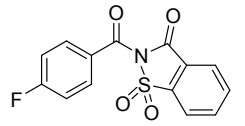


^{1}H NMR (400 MHz, $CDCl_3$)

1i

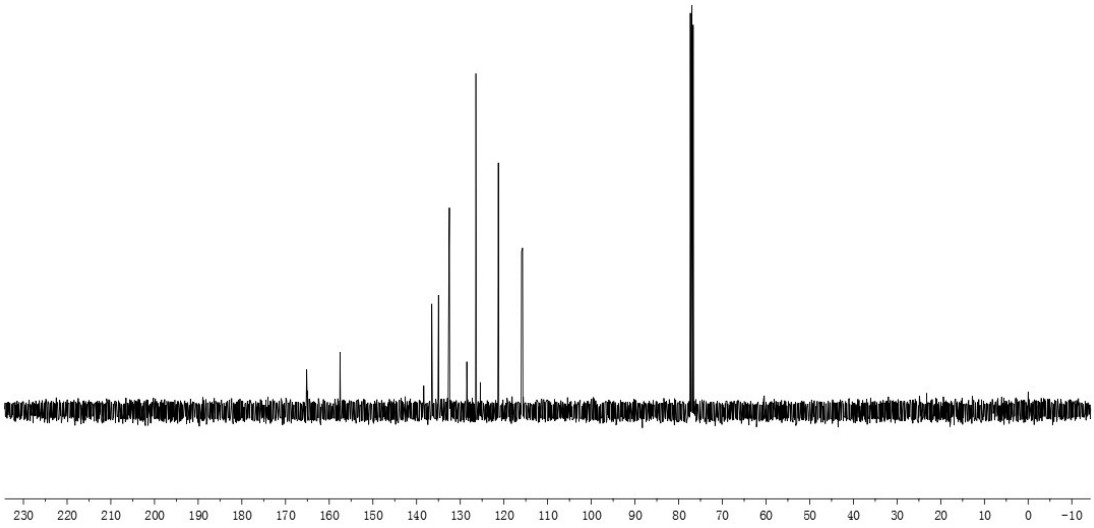


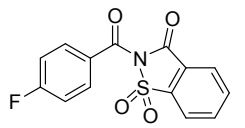


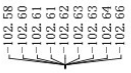


^{13}C NMR (100 MHz, $CDCl_3$)

1i

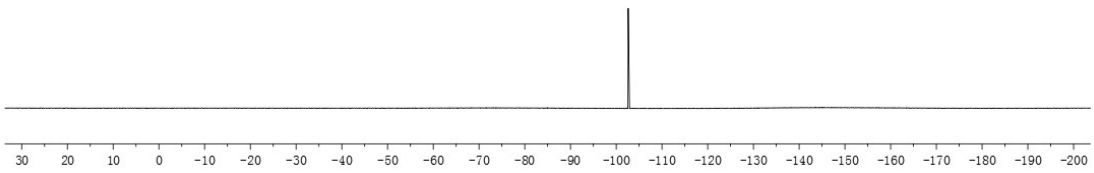


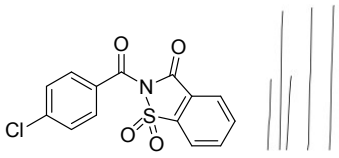




^{19}F NMR (376 MHz, $CDCl_3$)

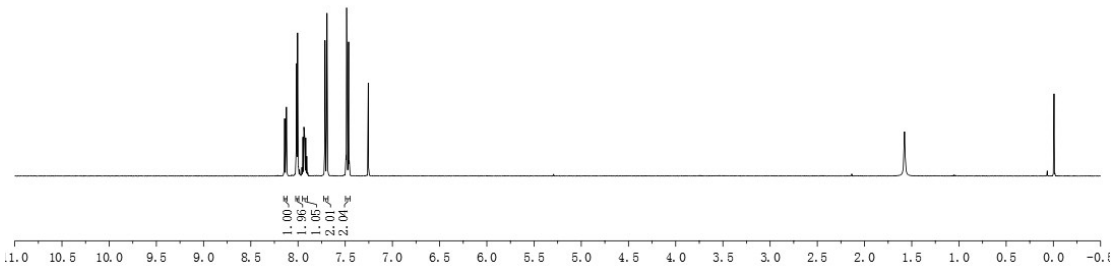
1i

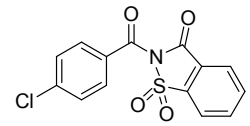




^{1}H NMR (400 MHz, $CDCl_3$)

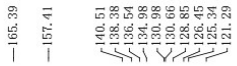
1j

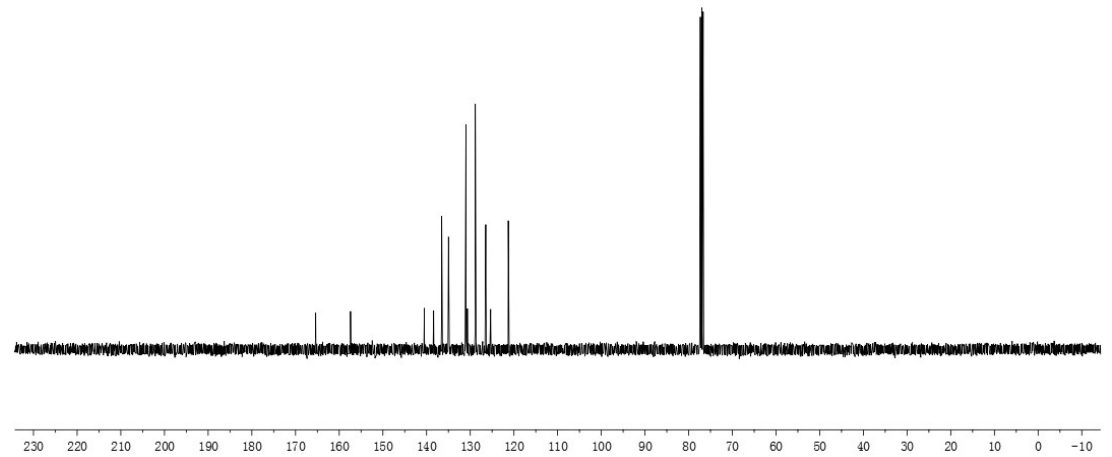


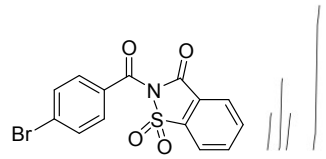


^{13}C NMR (100 MHz, $CDCl_3$)

1j

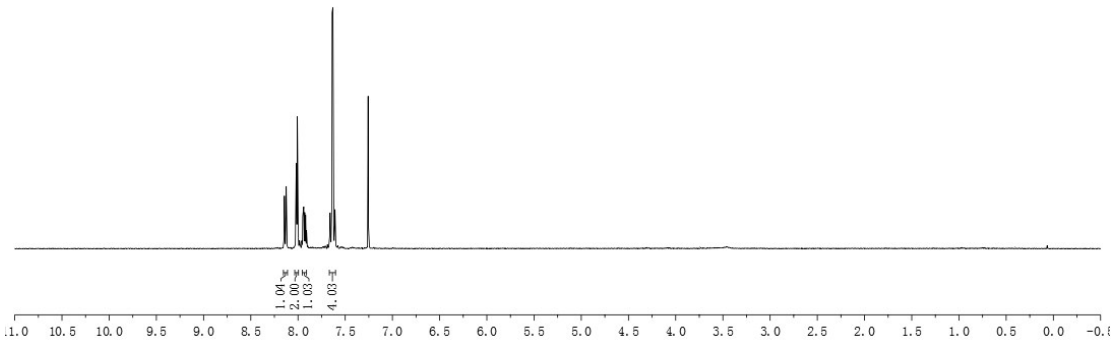


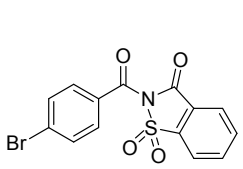




^{1}H NMR (400 MHz, $CDCl_3$)

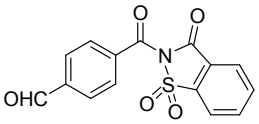
1k





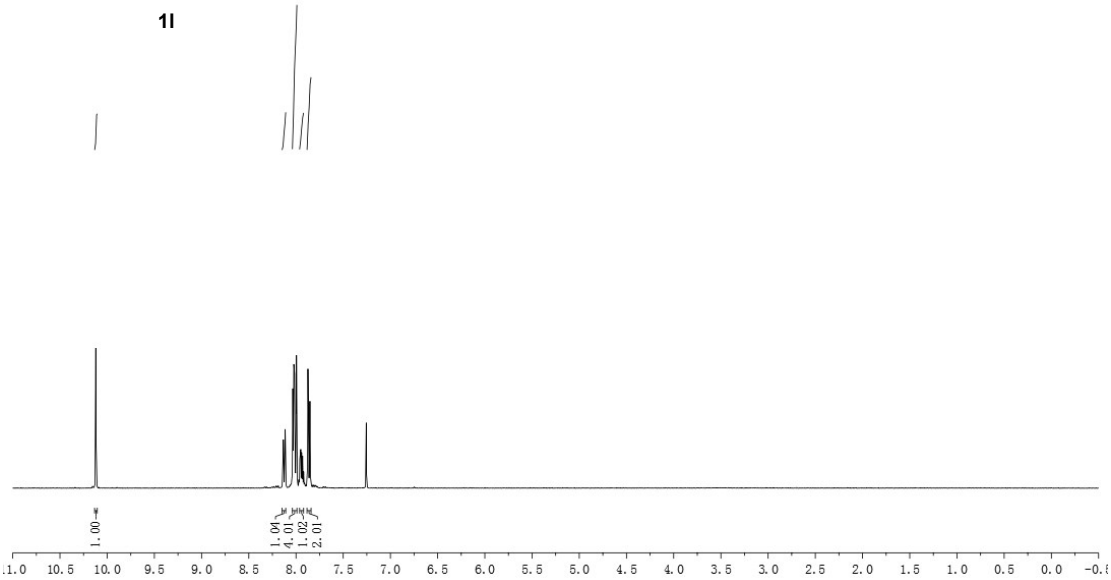
^{13}C NMR (100 MHz, $CDCl_3$)

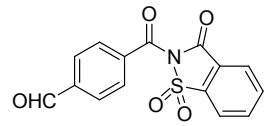
1k



^{1}H NMR (400 MHz, $CDCl_3$)

1l





^{13}C NMR (100 MHz, $CDCl_3$)

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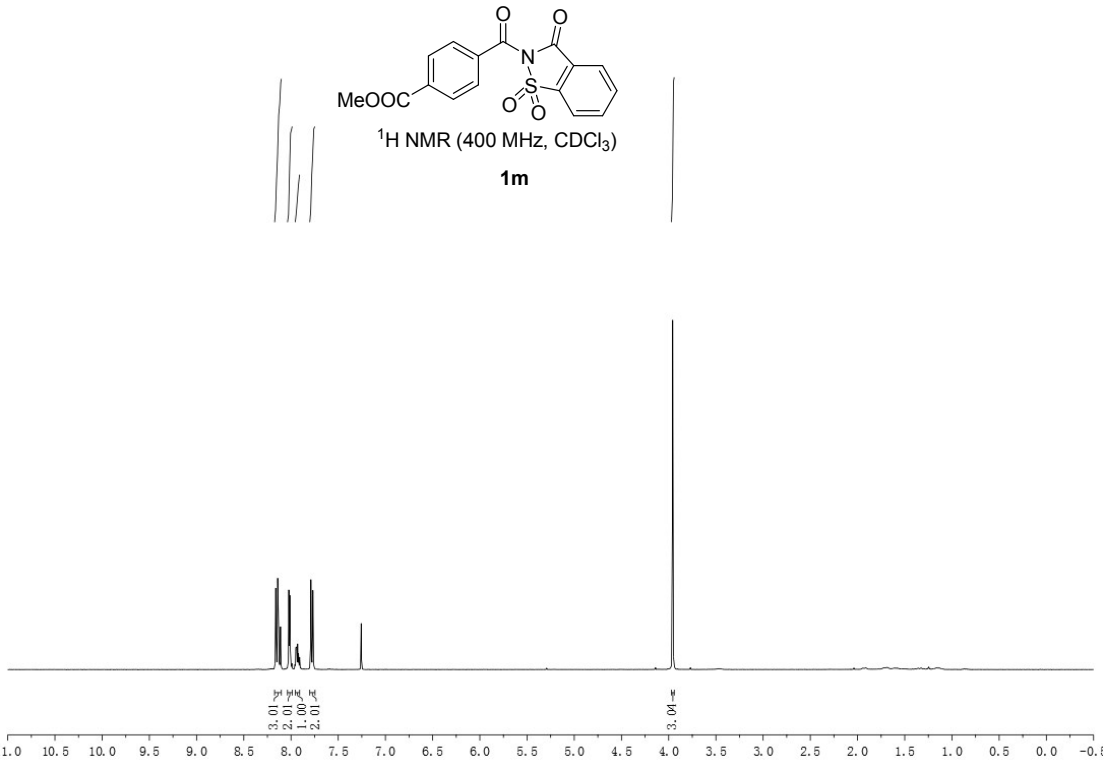

^{1}H NMR (400 MHz, $CDCl_3$)

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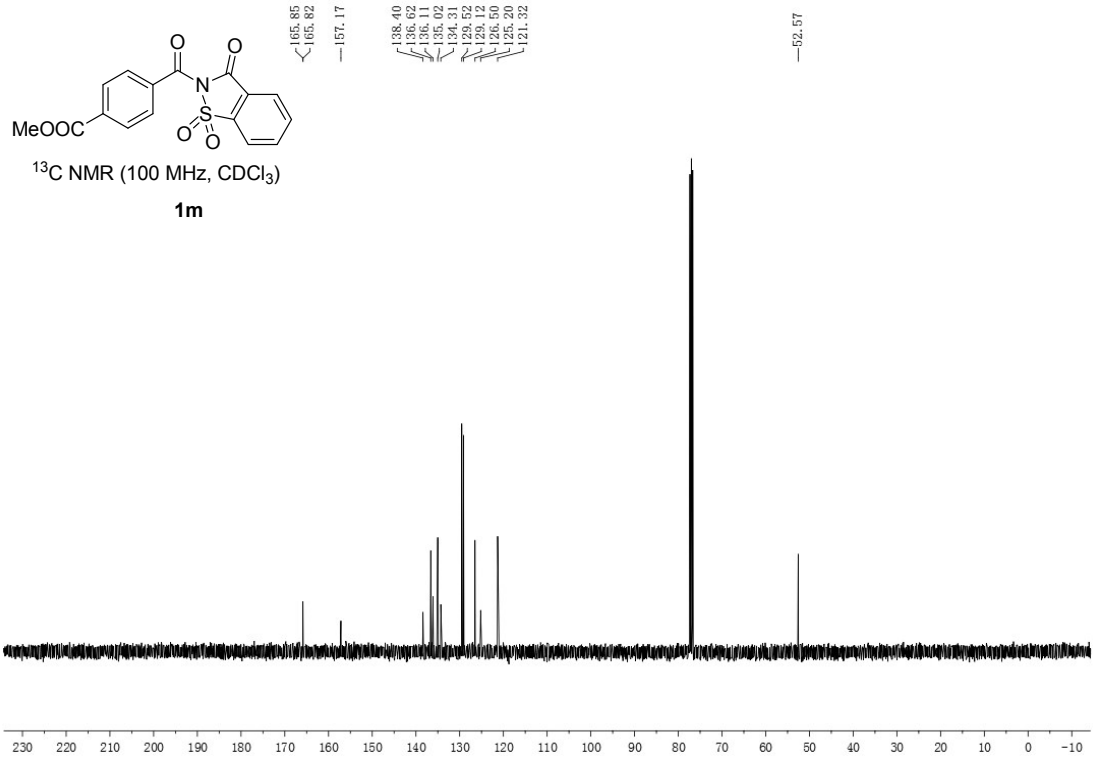
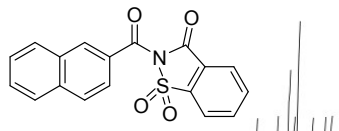


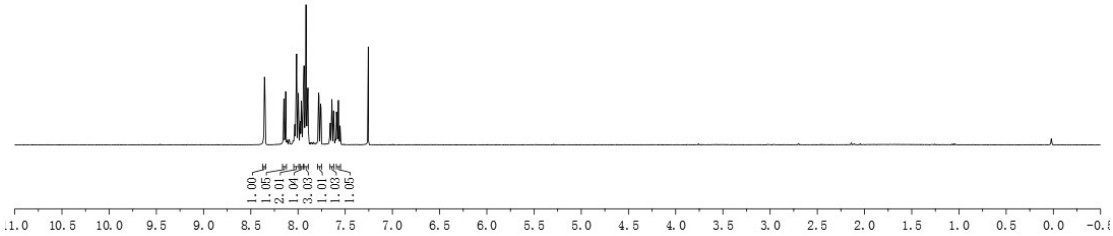
^{13}C NMR (100 MHz, $CDCl_3$)

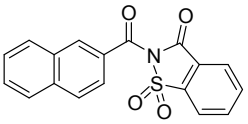
1m



^{1}H NMR (400 MHz, $CDCl_3$)

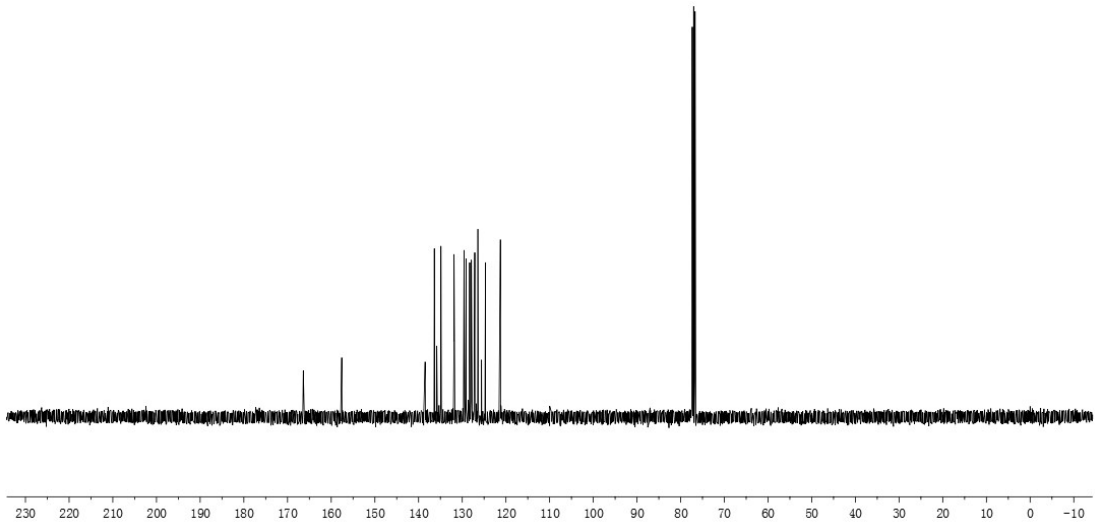
1k

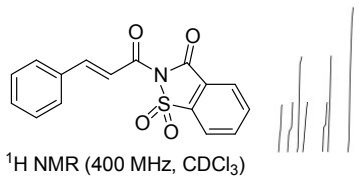




^{13}C NMR (100 MHz, $CDCl_3$)

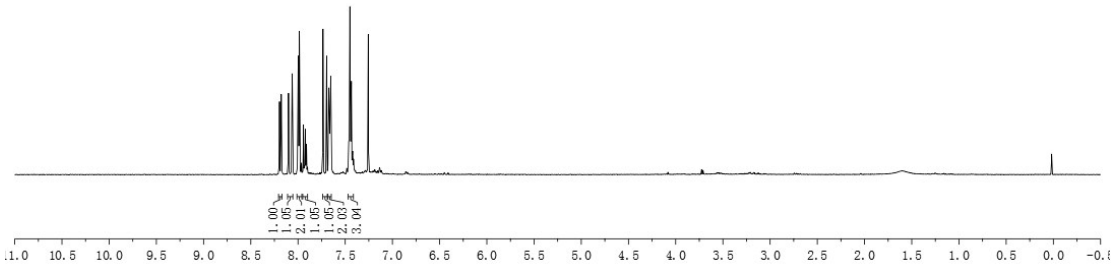
1k

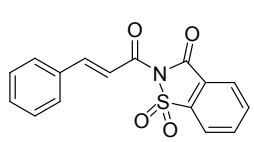




^{1}H NMR (400 MHz, $CDCl_3$)

1l





^{13}C NMR (100 MHz, $CDCl_3$)

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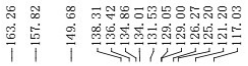
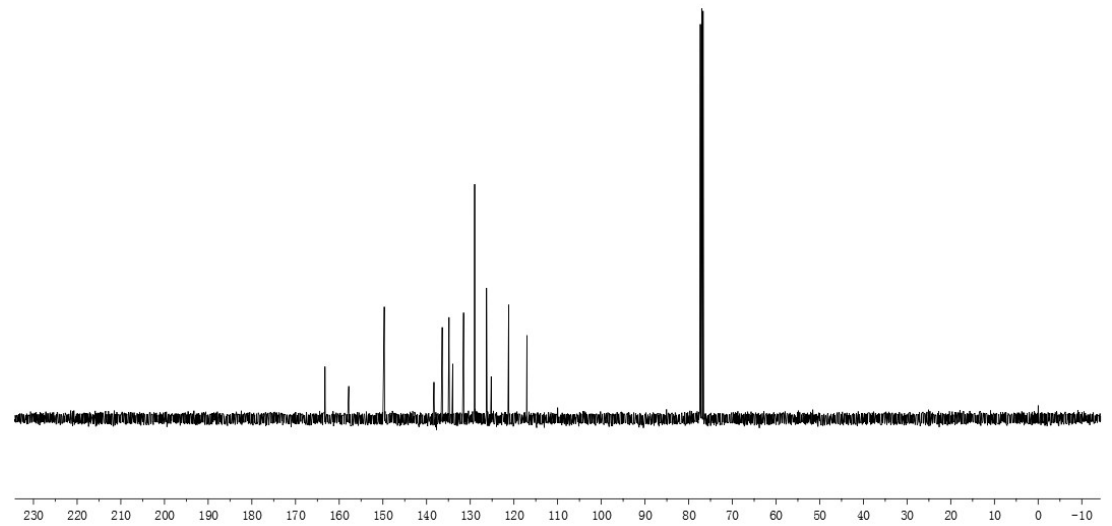
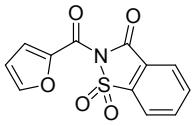
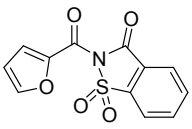






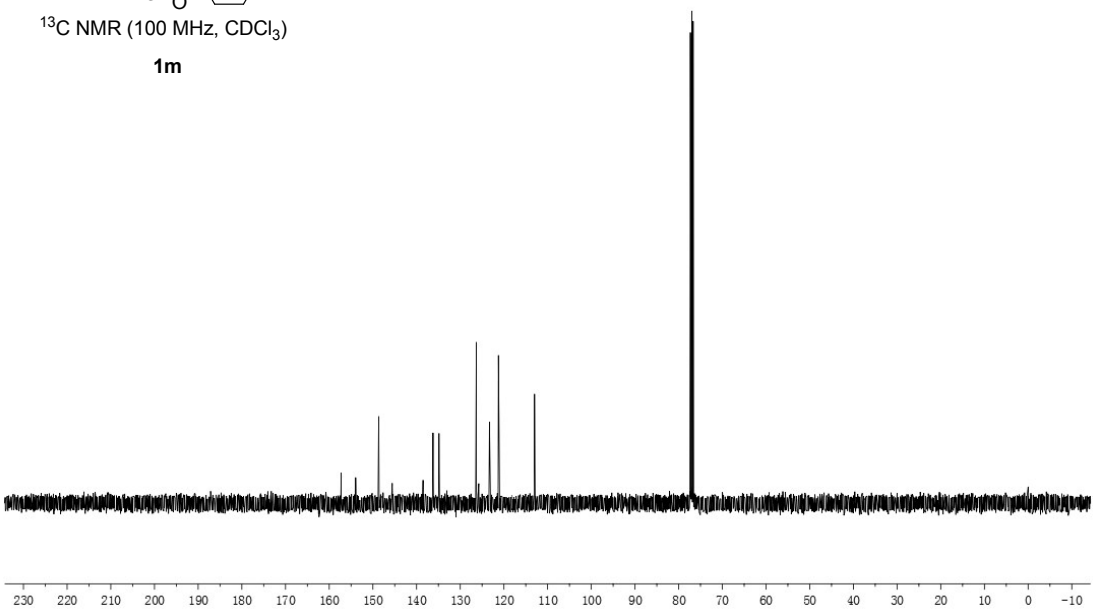
^{1}H NMR (400 MHz, $CDCl_3$)

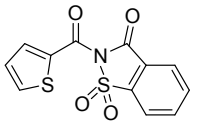
1m



^{13}C NMR (100 MHz, $CDCl_3$)

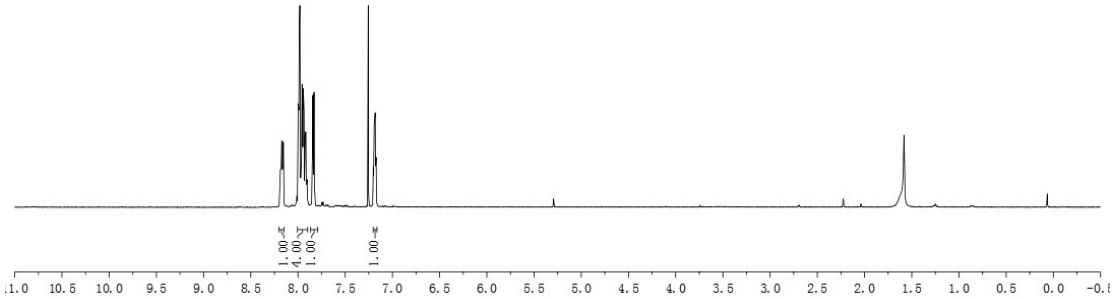
1m

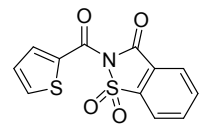




^{1}H NMR (400 MHz, $CDCl_3$)

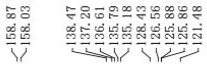
1n

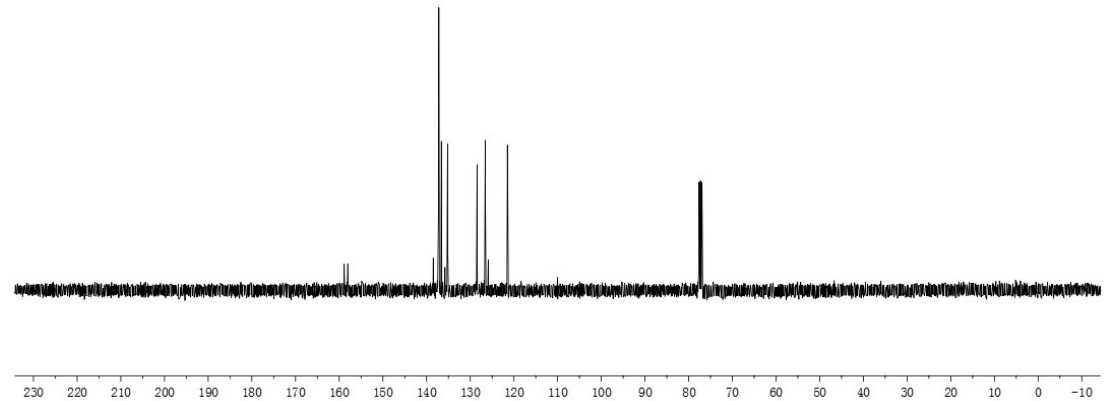


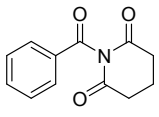


^{13}C NMR (100 MHz, $CDCl_3$)

1n

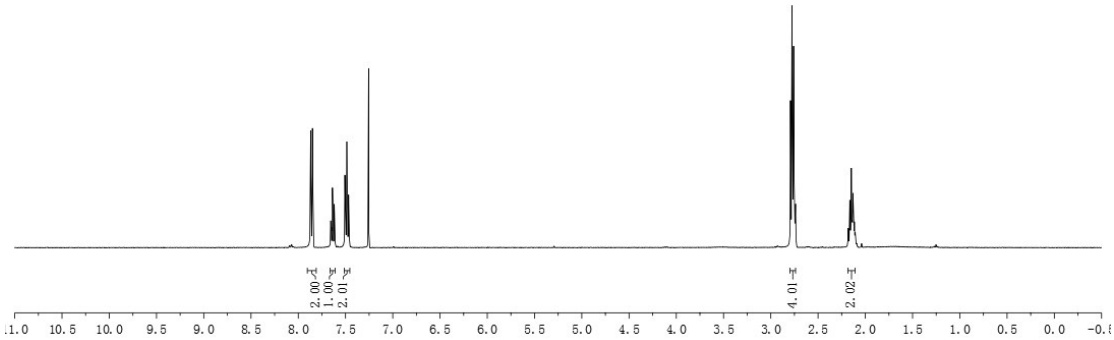


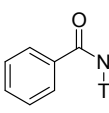




^{1}H NMR (400 MHz, $CDCl_3$)

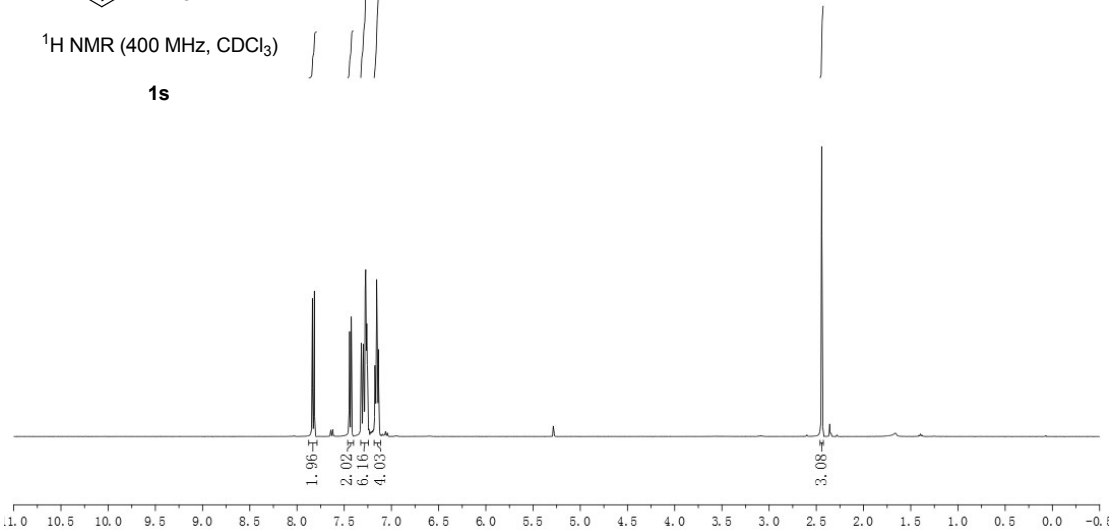
1r

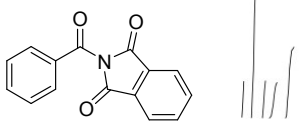




^{1}H NMR (400 MHz, $CDCl_3$)

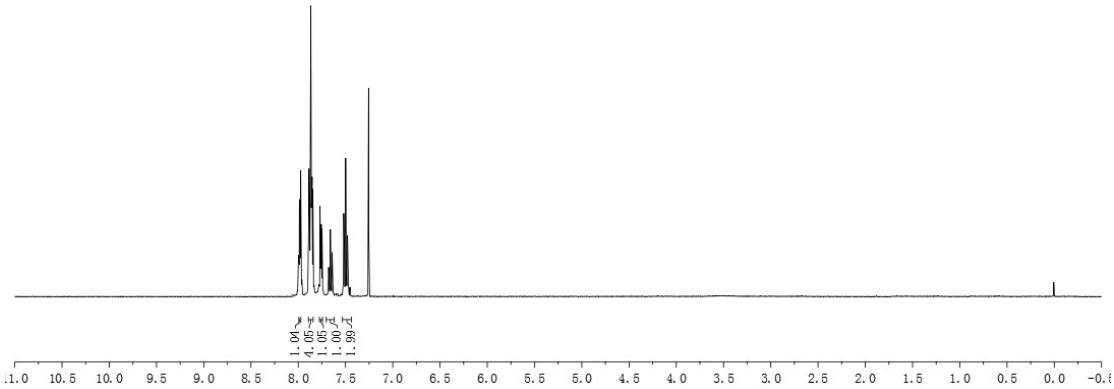
1s

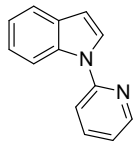




^{1}H NMR (400 MHz, $CDCl_3$)

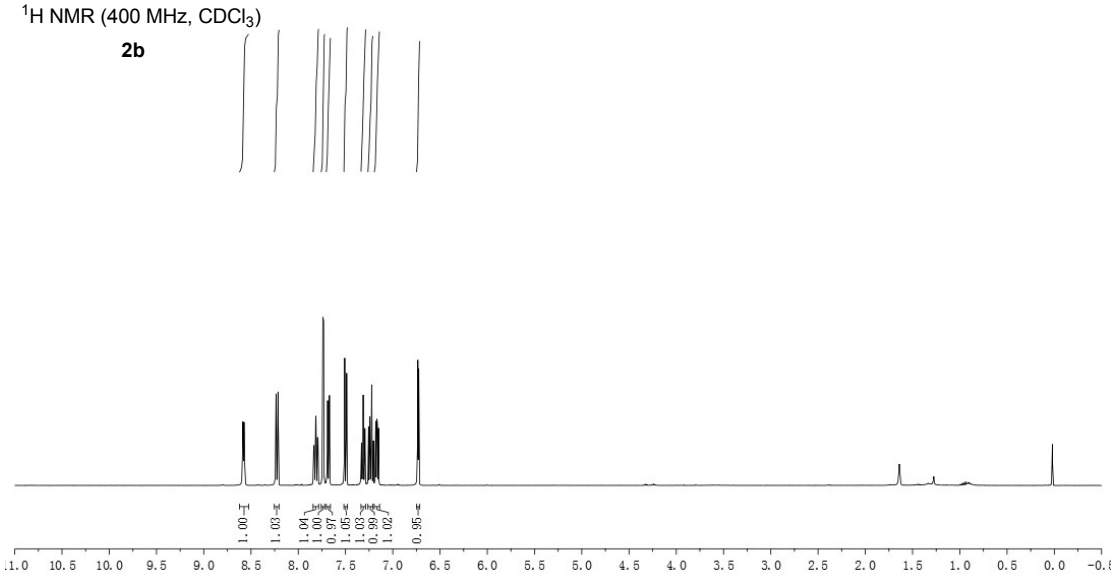
1u

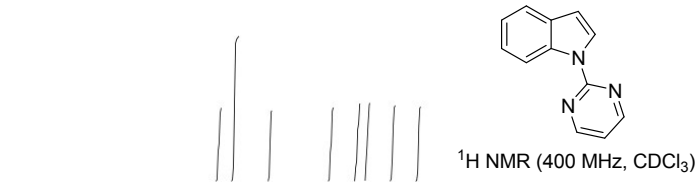




^{1}H NMR (400 MHz, $CDCl_3$)

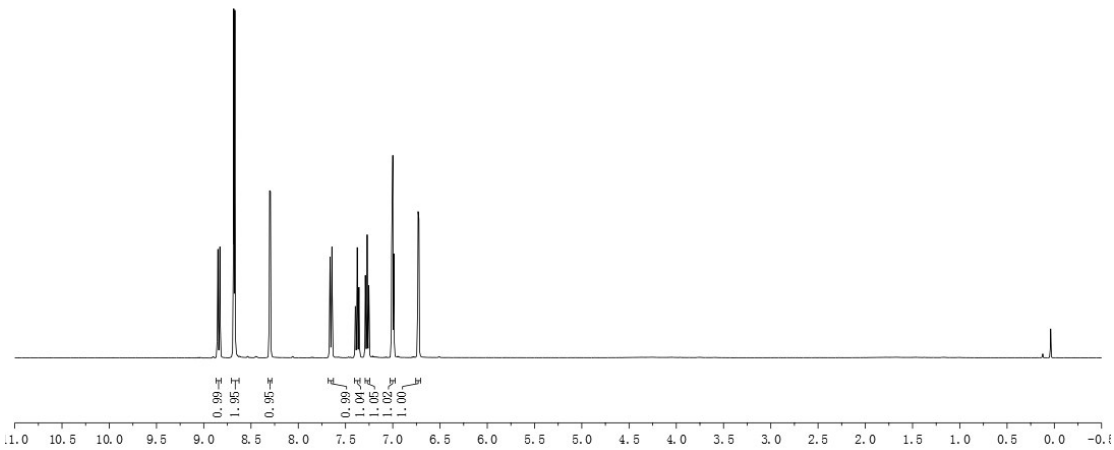
2b

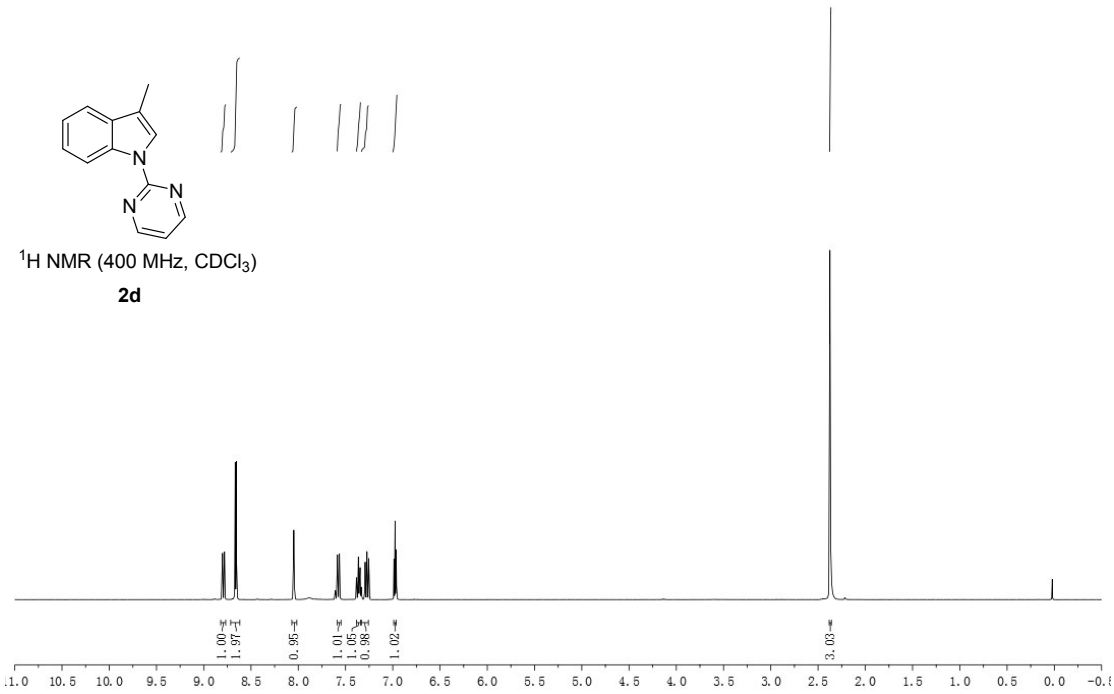




^{1}H NMR (400 MHz, $CDCl_3$)

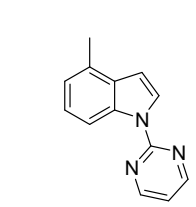
2c





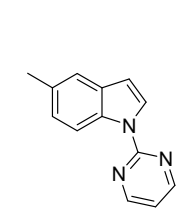
^{1}H NMR (400 MHz, $CDCl_3$)

2d



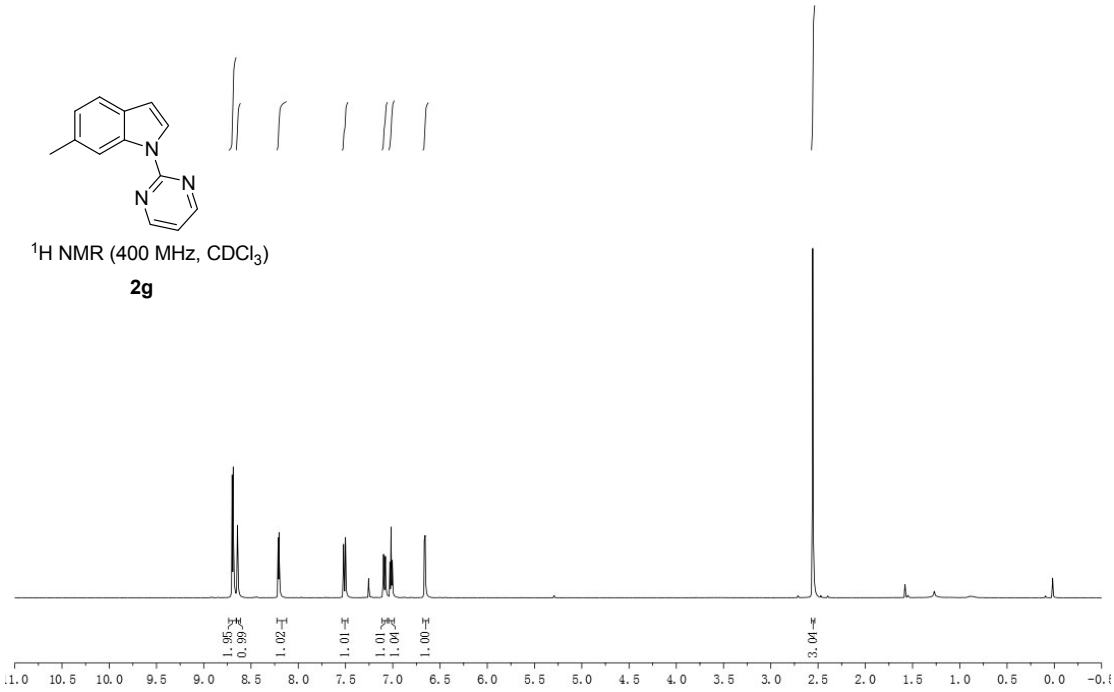
^{1}H NMR (400 MHz, $CDCl_3$)

2e



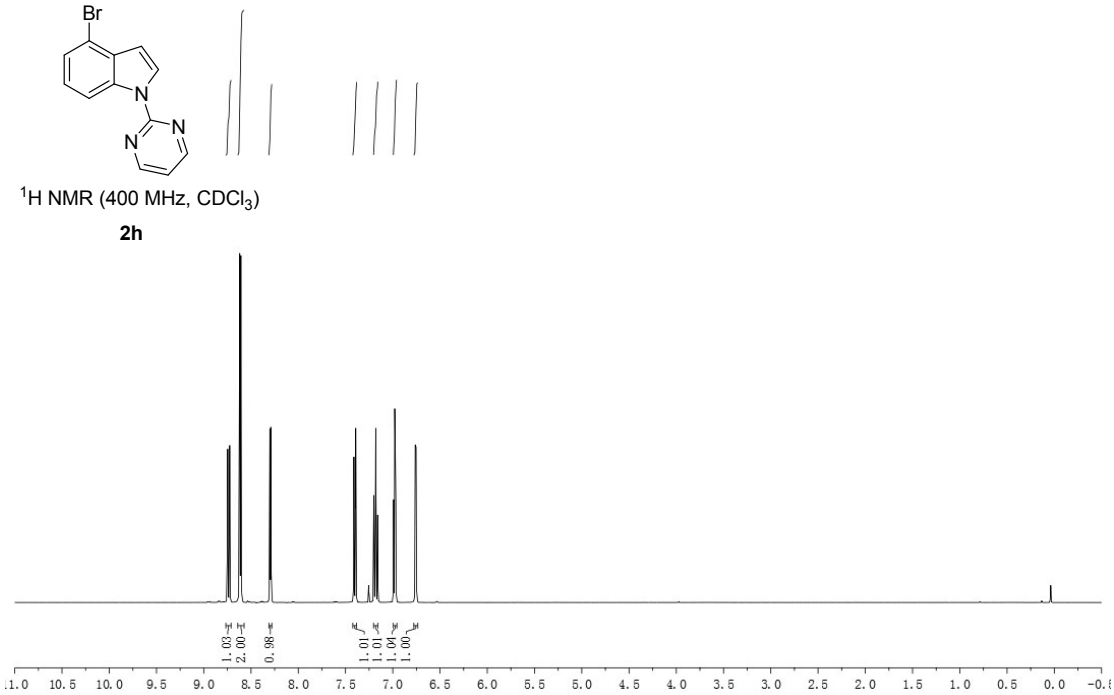
^{1}H NMR (400 MHz, $CDCl_3$)

2f



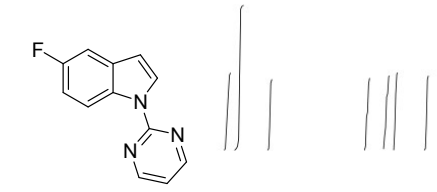
^{1}H NMR (400 MHz, $CDCl_3$)

2g



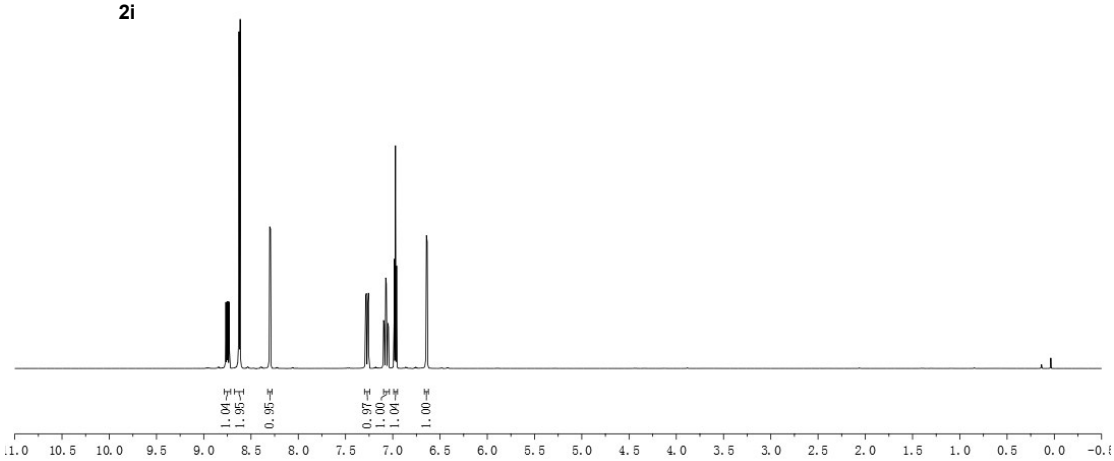
^{1}H NMR (400 MHz, $CDCl_3$)

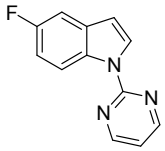
2h



^{1}H NMR (400 MHz, $CDCl_3$)

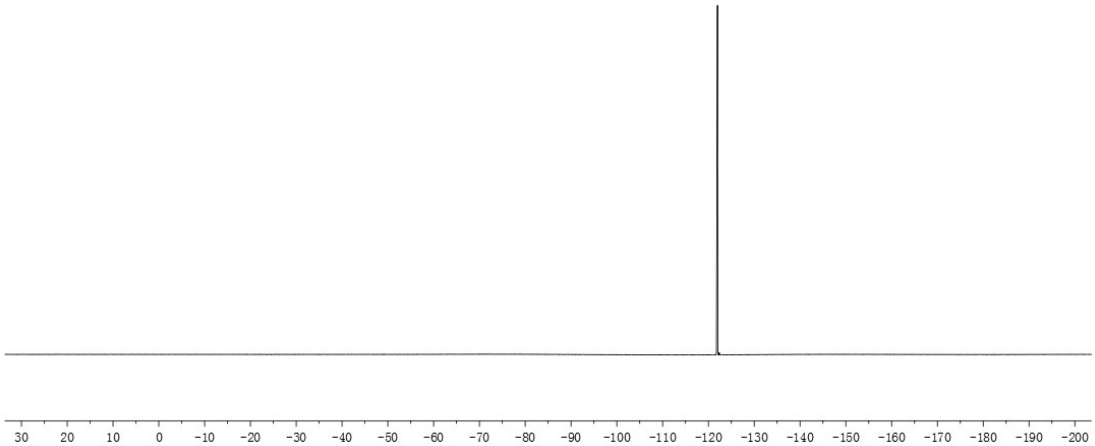
2i

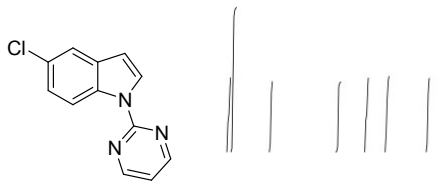




^{19}F NMR (376 MHz, $CDCl_3$)

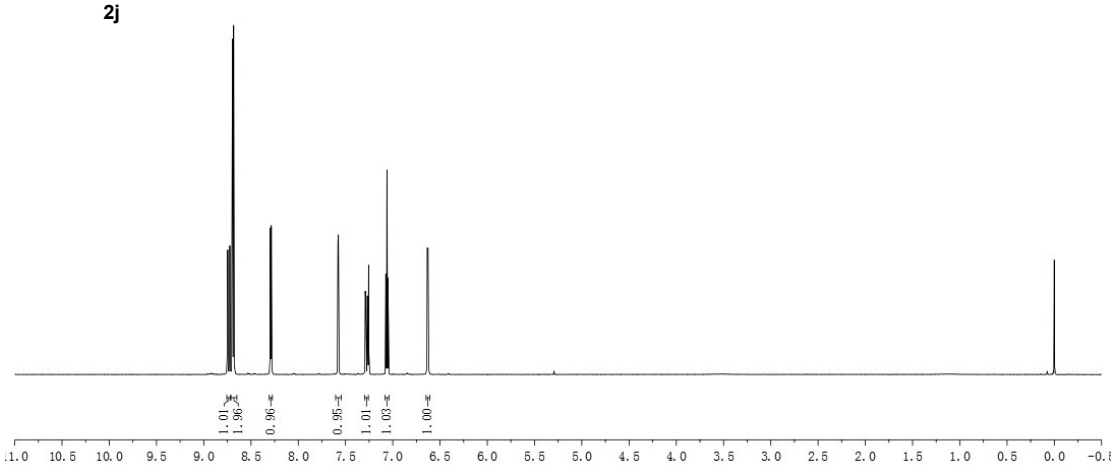
2i

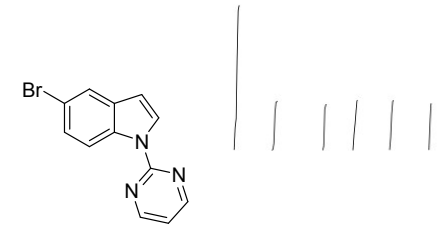




^{1}H NMR (400 MHz, $CDCl_3$)

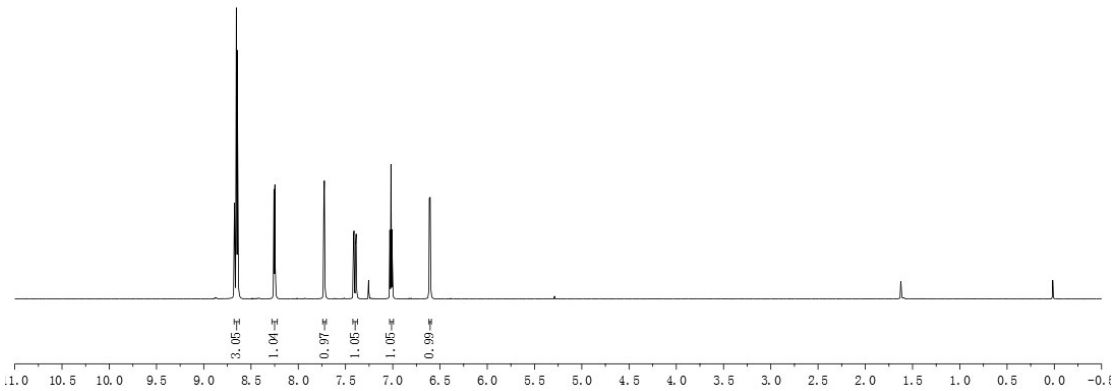
2j

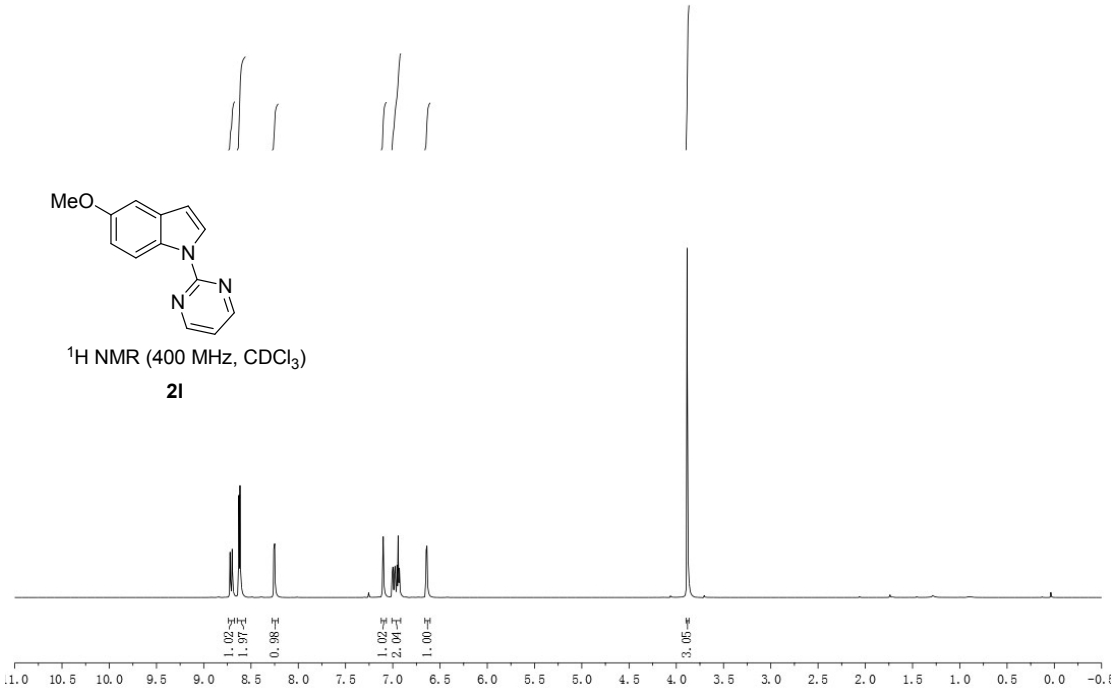




^{1}H NMR (400 MHz, $CDCl_3$)

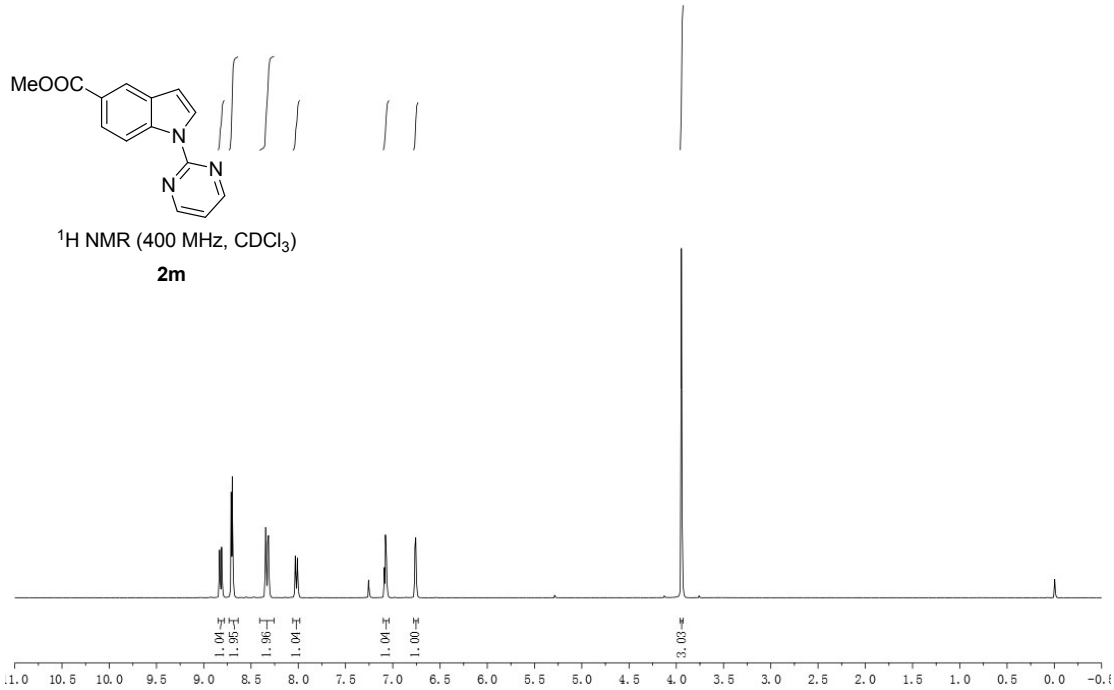
2k





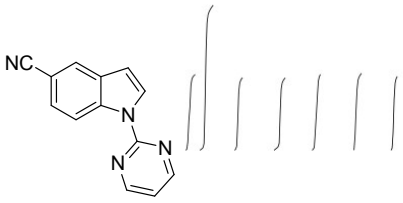
^{1}H NMR (400 MHz, $CDCl_3$)

2l



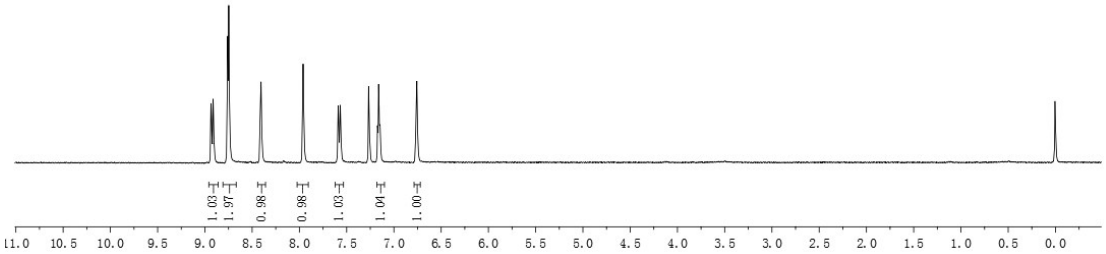
^{1}H NMR (400 MHz, $CDCl_3$)

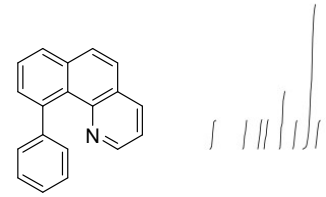
2m



^{1}H NMR (400 MHz, $CDCl_3$)

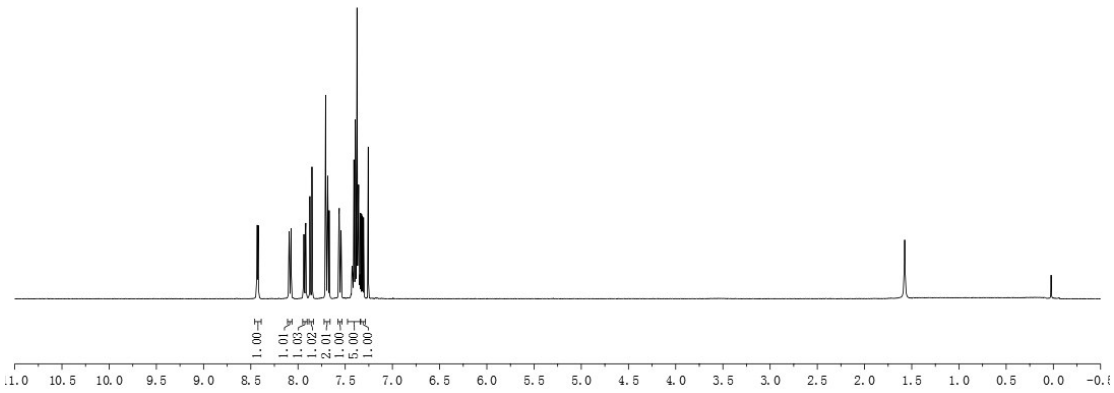
2n

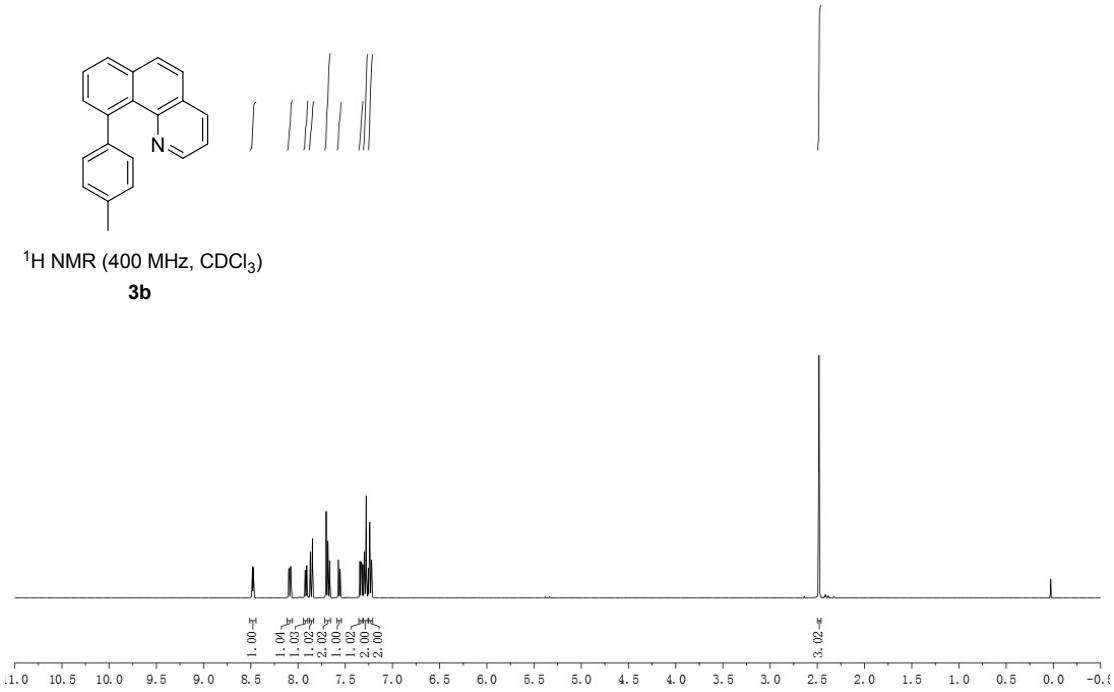




^{1}H NMR (400 MHz, $CDCl_3$)

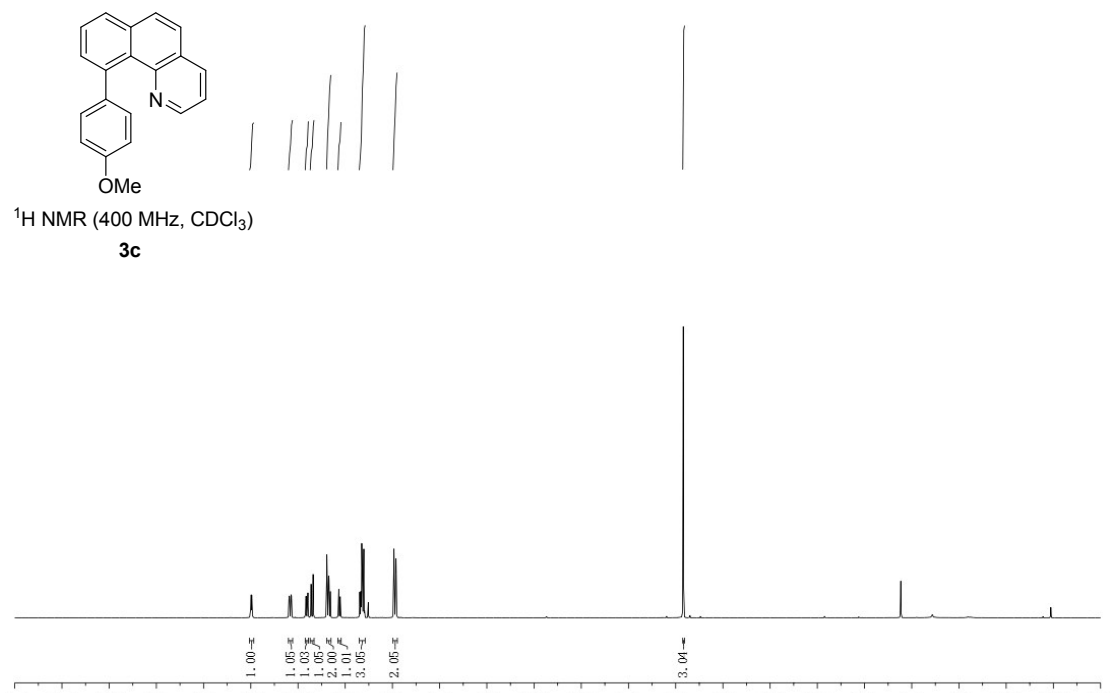
3a





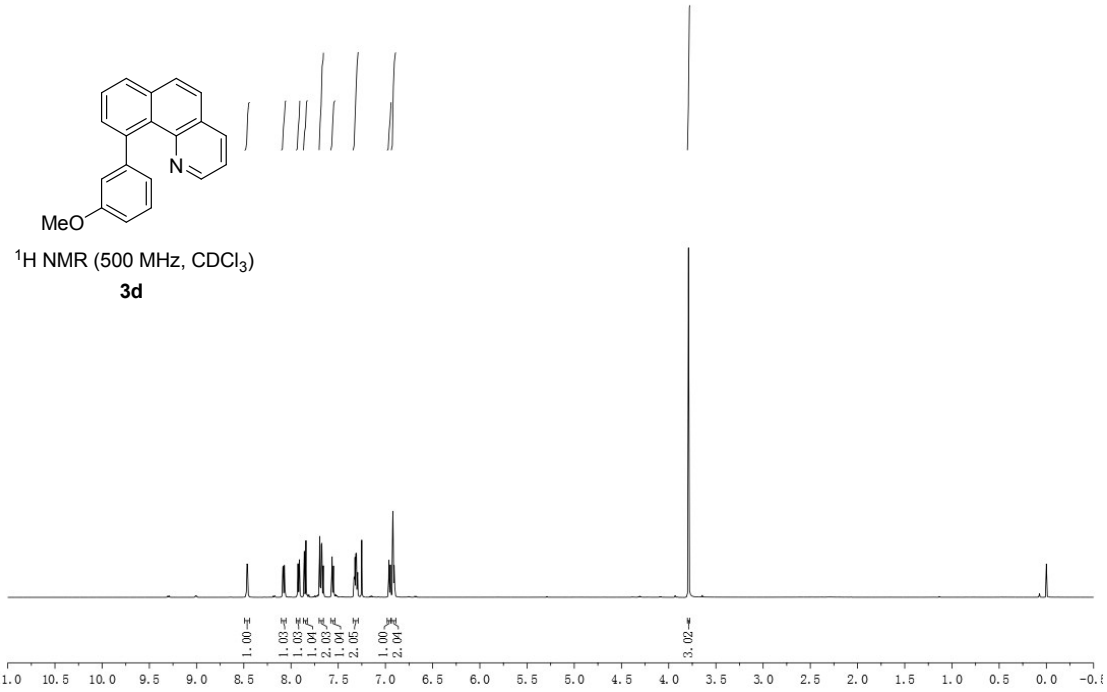
^{1}H NMR (400 MHz, $CDCl_3$)

3b



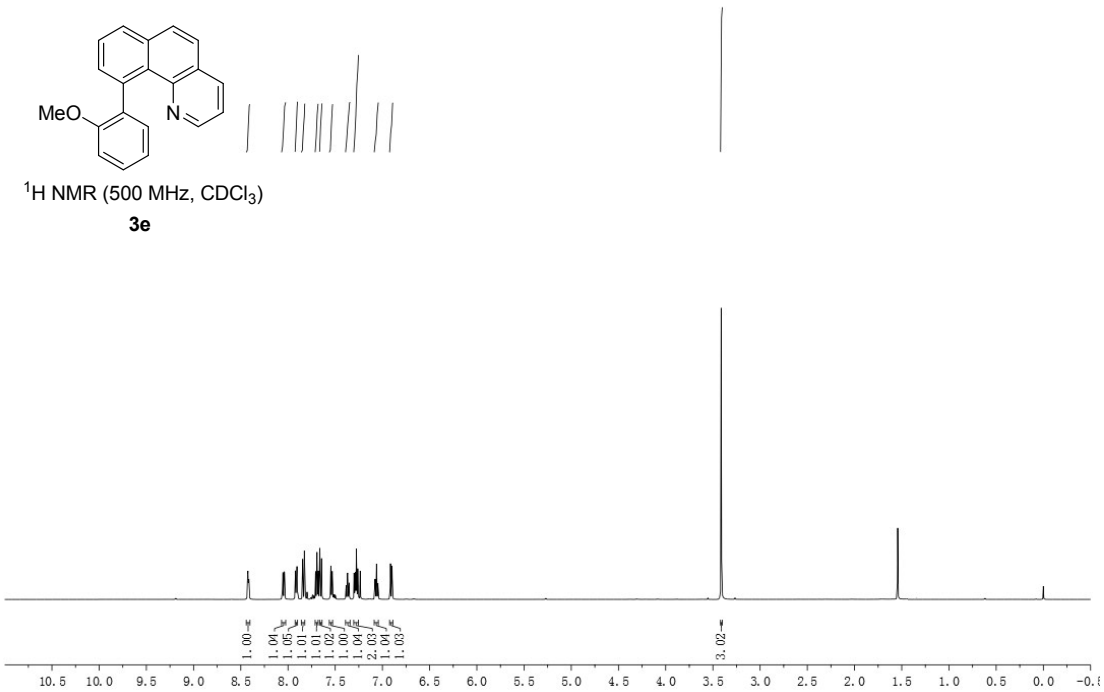
^{1}H NMR (400 MHz, $CDCl_3$)

3c



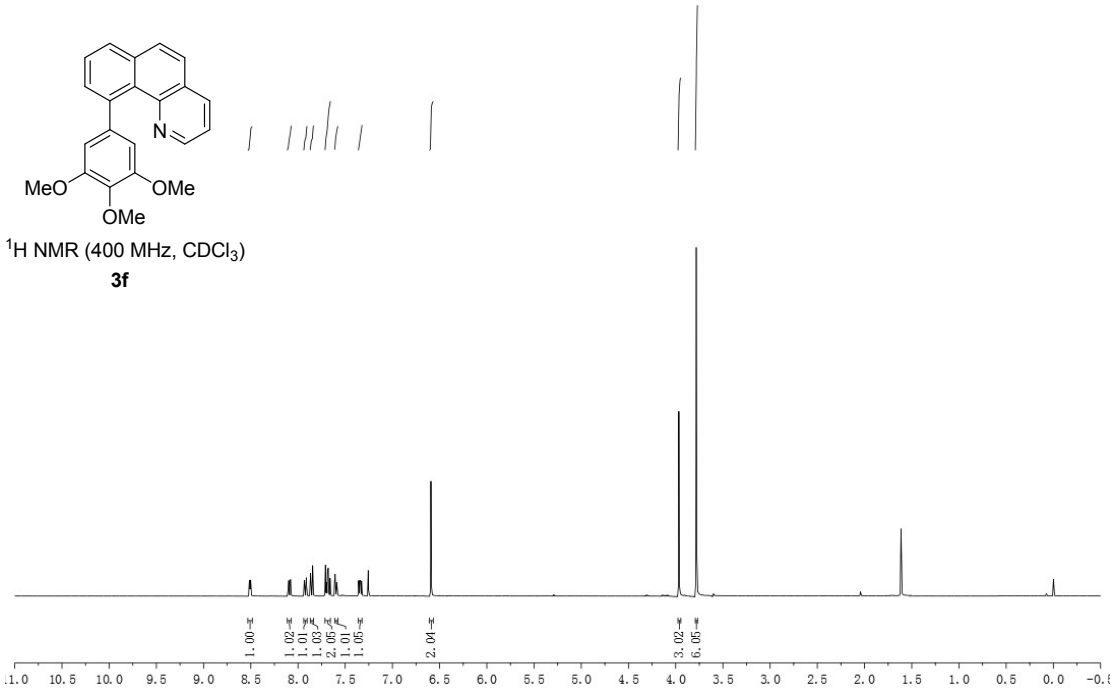
^{1}H NMR (500 MHz, $CDCl_3$)

3d



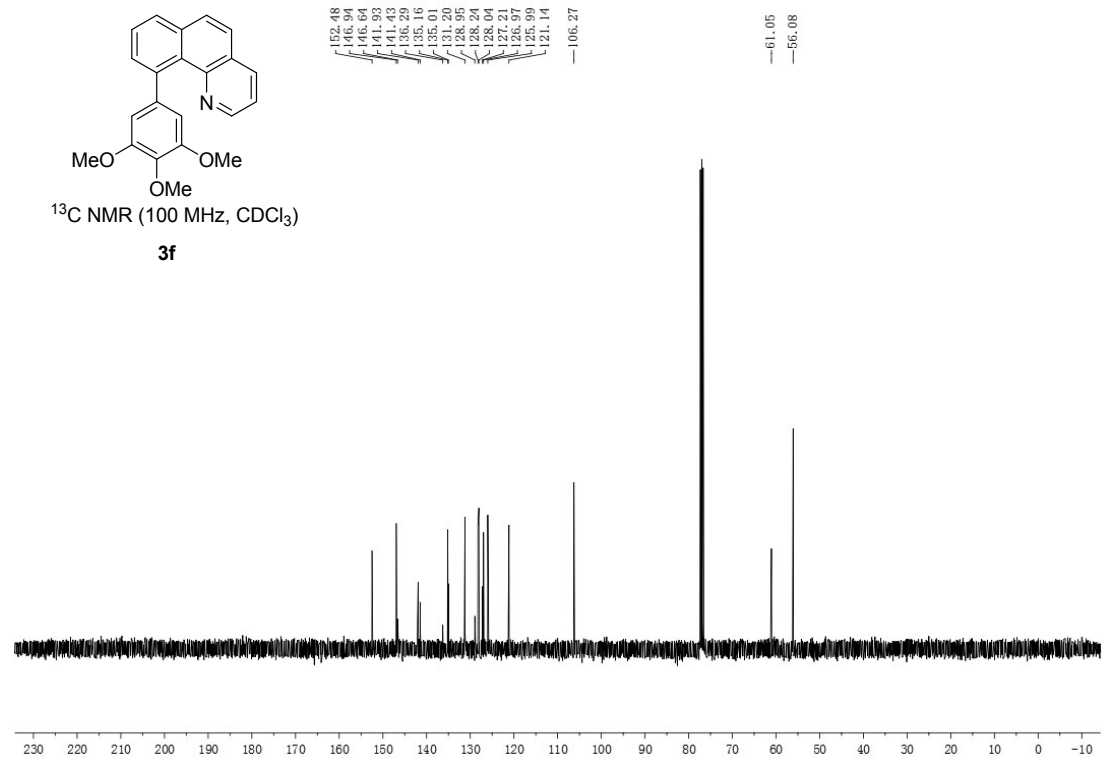
^{1}H NMR (500 MHz, $CDCl_3$)

3e



^{1}H NMR (400 MHz, $CDCl_3$)

3f

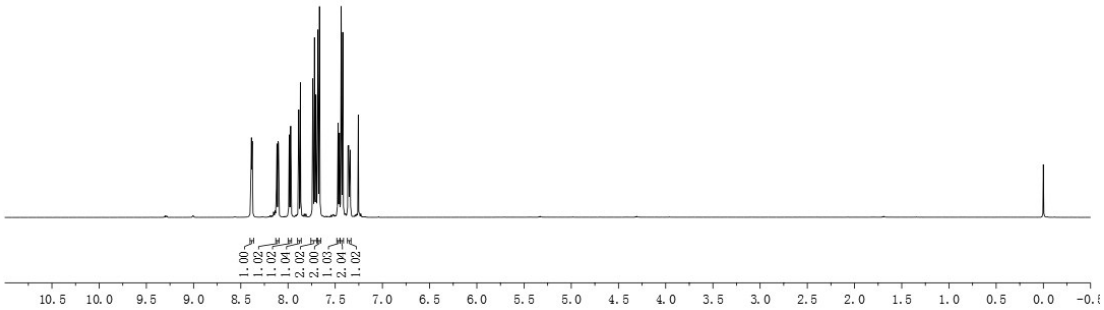


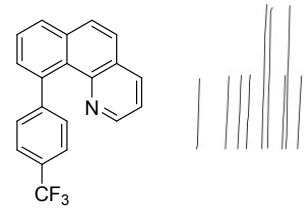
^{13}C NMR (100 MHz, $CDCl_3$)

3f

^{1}H NMR (500 MHz, $CDCl_3$)

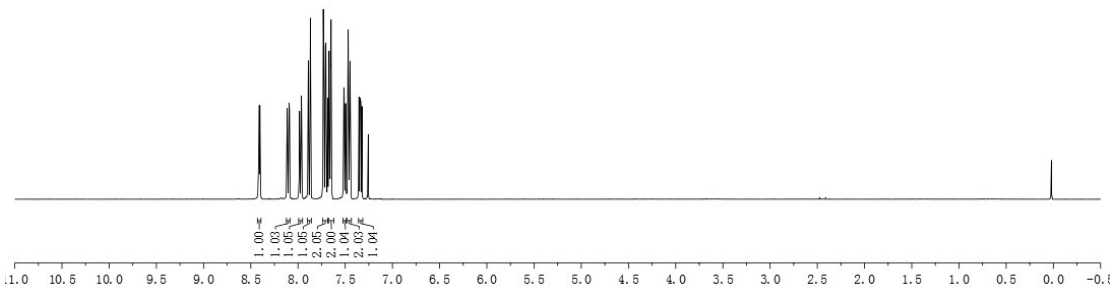
3g

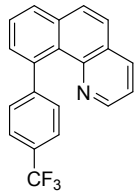




^{1}H NMR (400 MHz, $CDCl_3$)

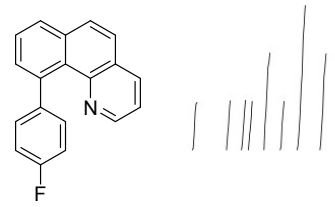
3h





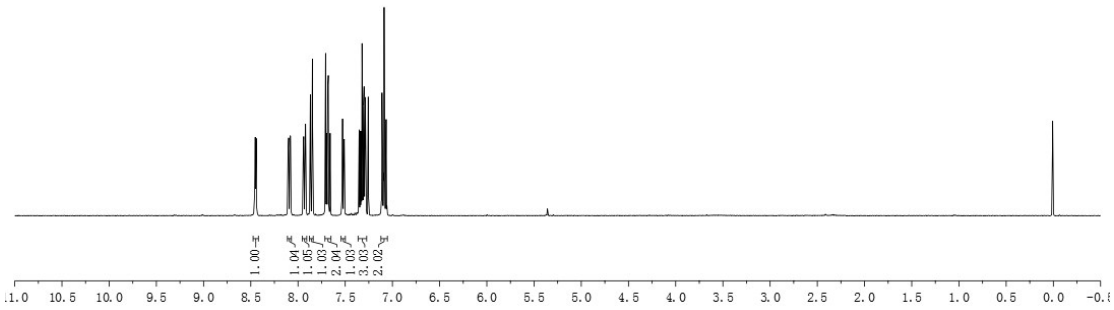
^{19}F NMR (376 MHz, $CDCl_3$)

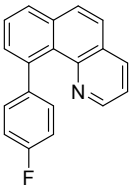
3h



^{1}H NMR (400 MHz, $CDCl_3$)

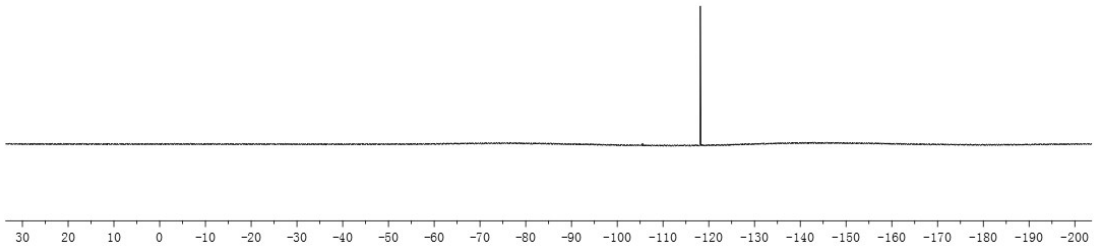
3i

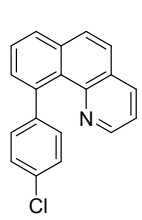




^{19}F NMR (376 MHz, $CDCl_3$)

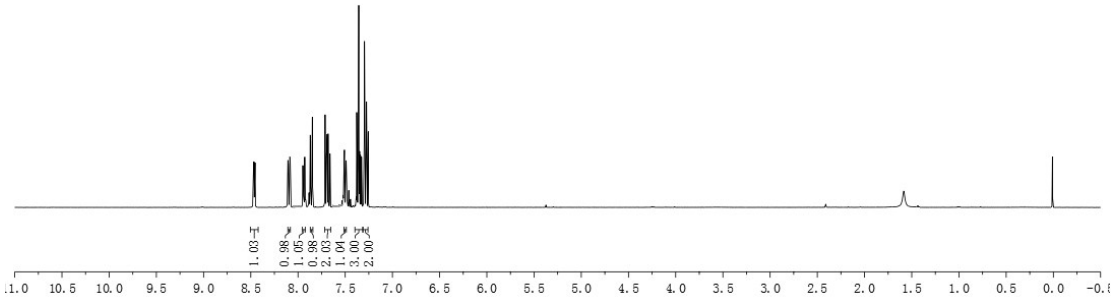
3i

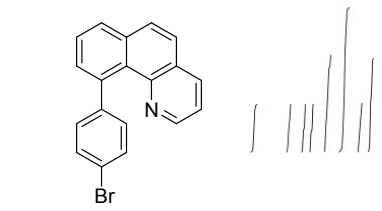




^{1}H NMR (400 MHz, $CDCl_3$)

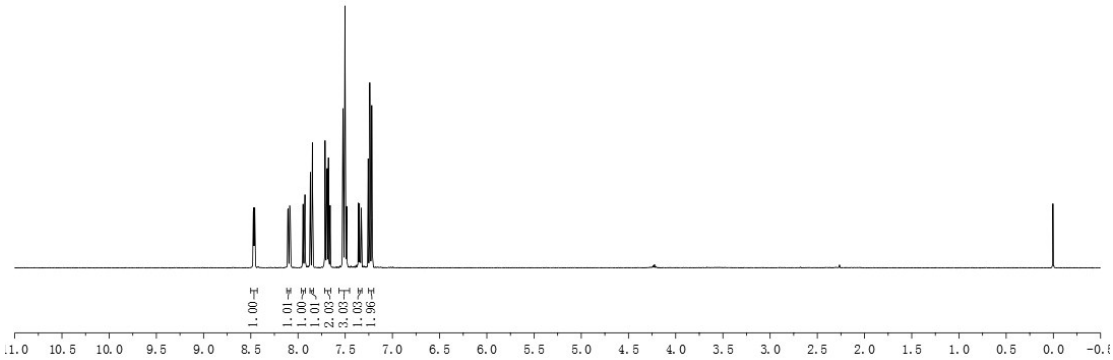
3j

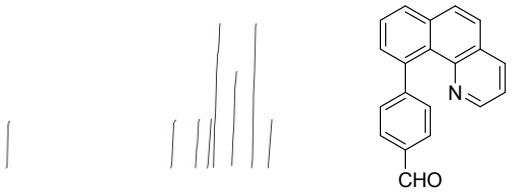




^{1}H NMR (400 MHz, $CDCl_3$)

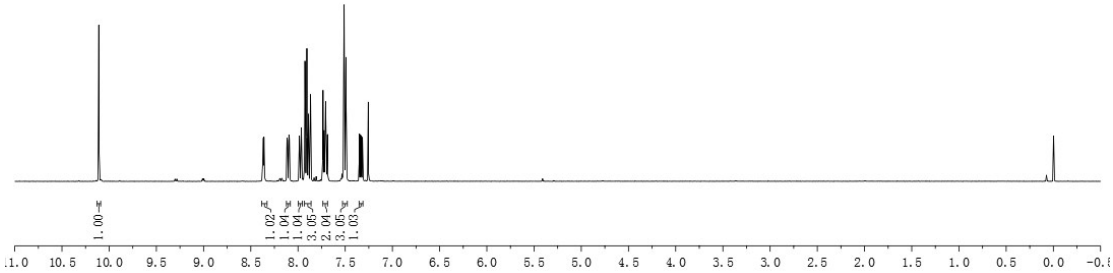
3k

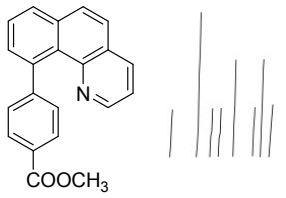




^{1}H NMR (400 MHz, $CDCl_3$)

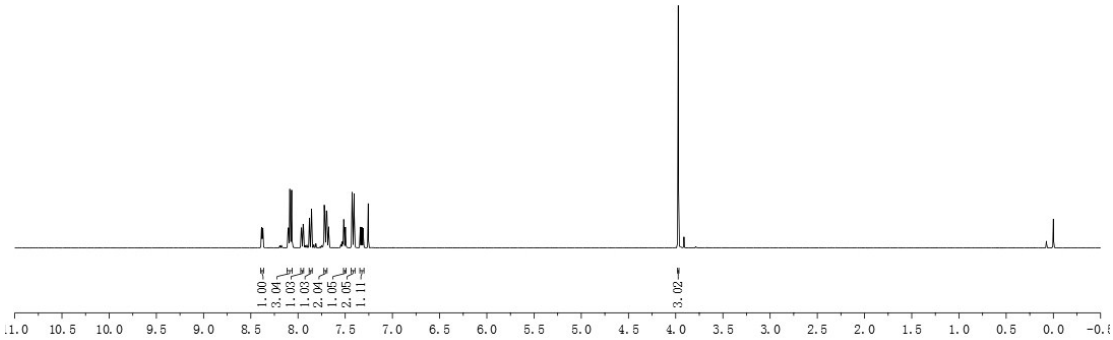
3l

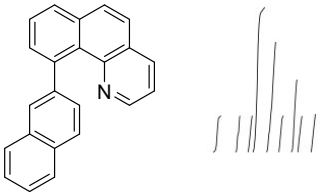




^{1}H NMR (400 MHz, $CDCl_3$)

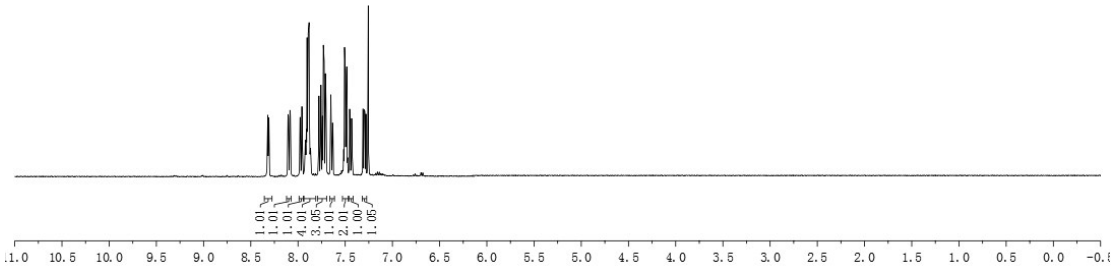
3m

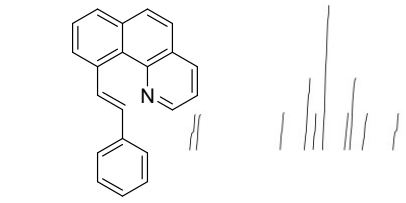




^{1}H NMR (400 MHz, $CDCl_3$)

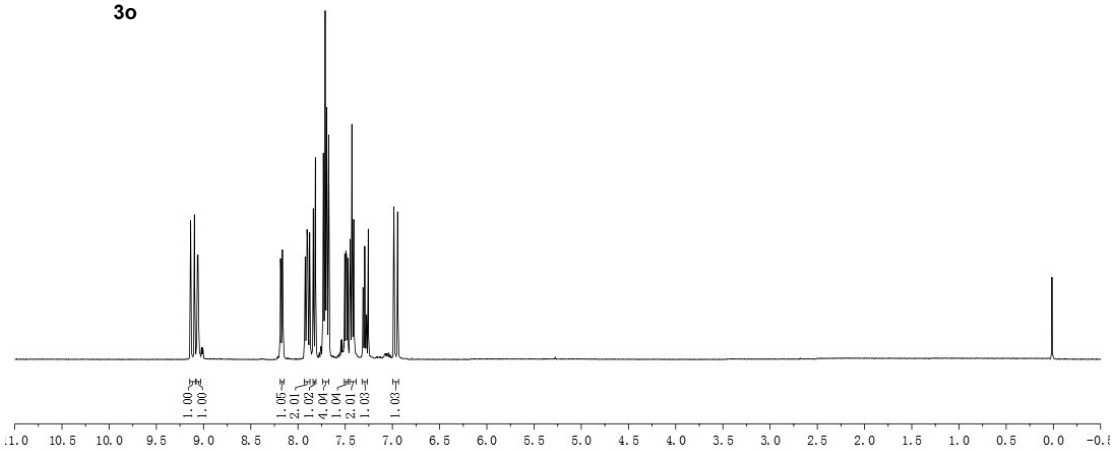
3n

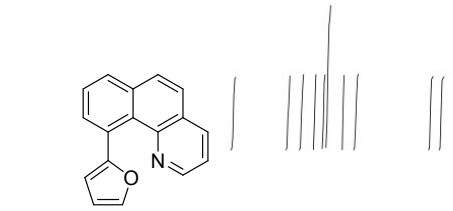




^{1}H NMR (400 MHz, $CDCl_3$)

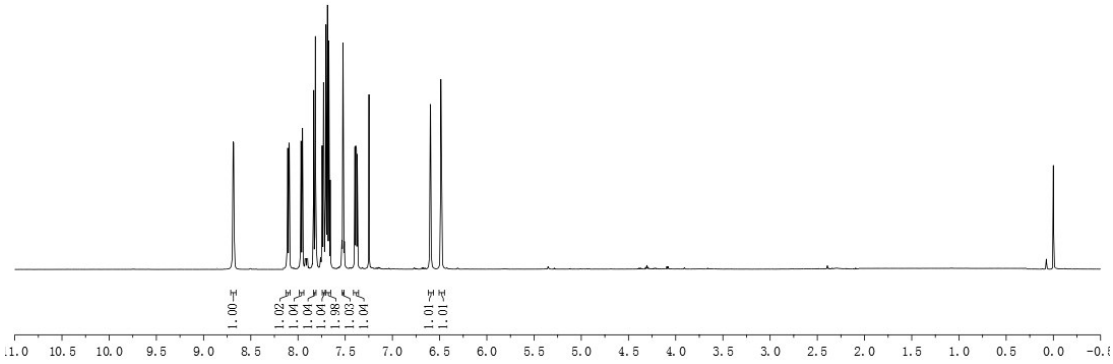
3o

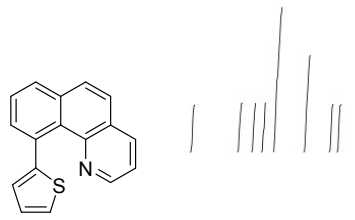




^{1}H NMR (400 MHz, $CDCl_3$)

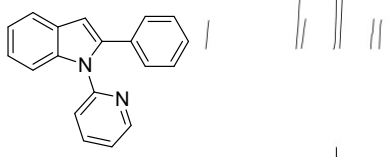
3p





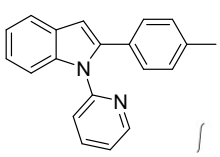
^{1}H NMR (400 MHz, $CDCl_3$)

3q



^{1}H NMR (400 MHz, $CDCl_3$)

3r



^{1}H NMR (400 MHz, $CDCl_3$)

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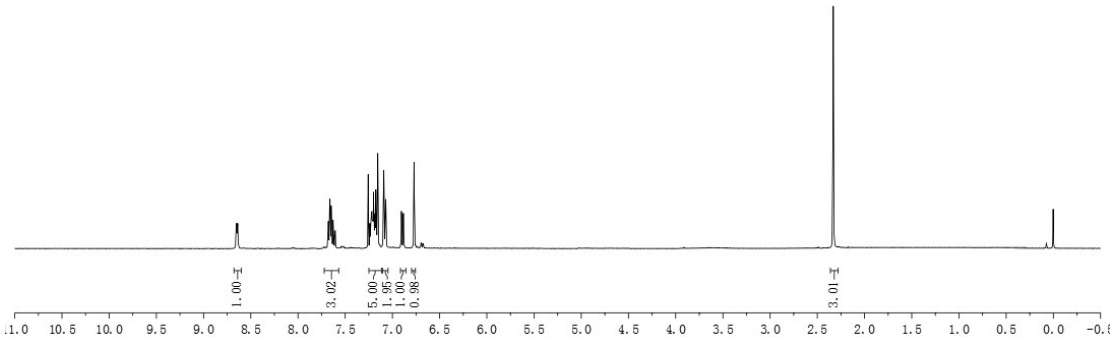

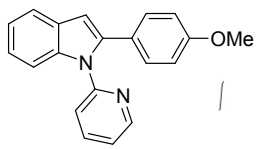

^{1}H NMR (400 MHz, $CDCl_3$)

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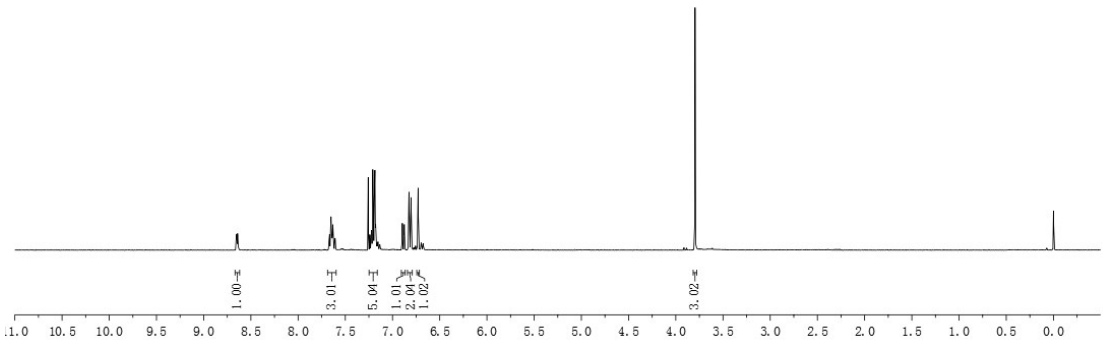

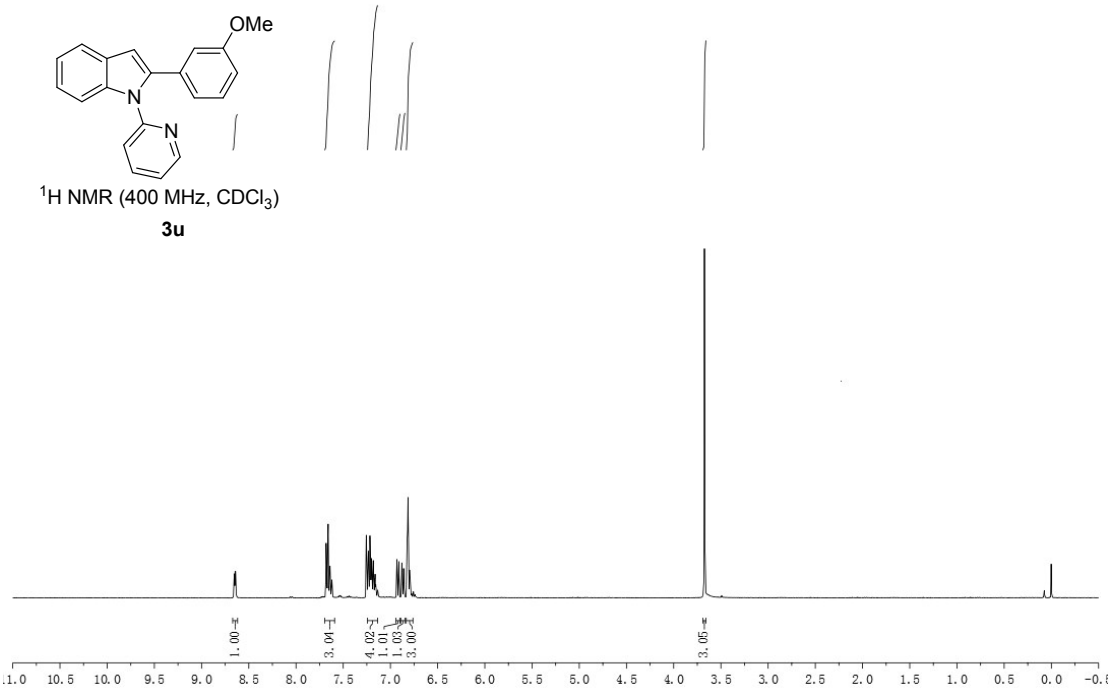

^{1}H NMR (400 MHz, $CDCl_3$)

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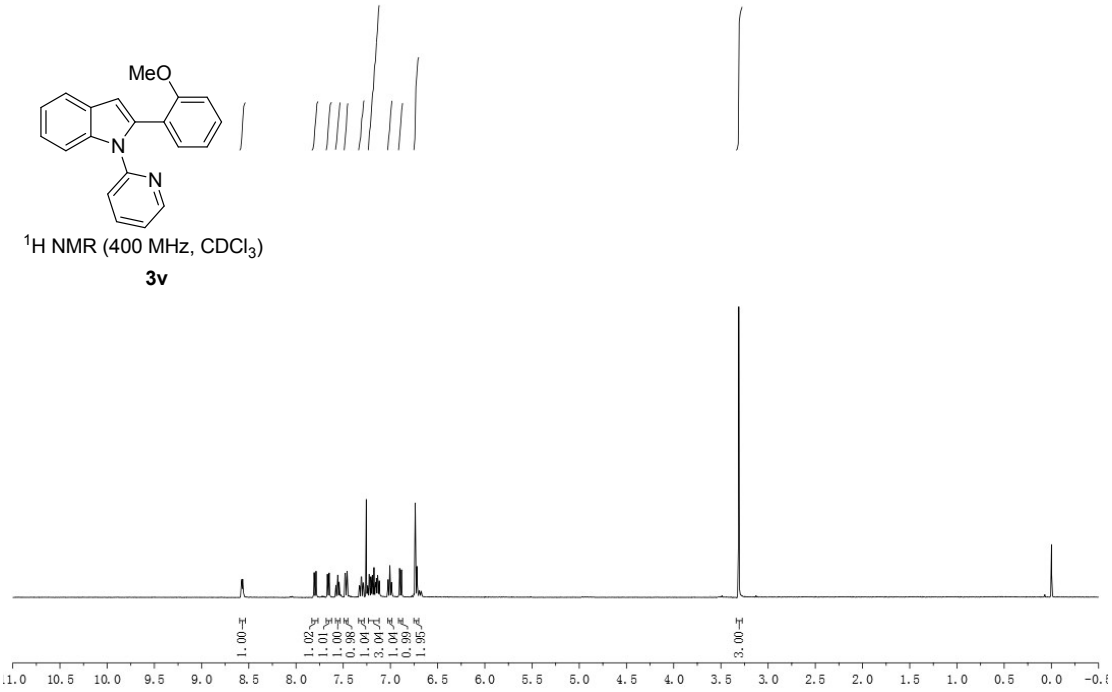

^{1}H NMR (400 MHz, $CDCl_3$)

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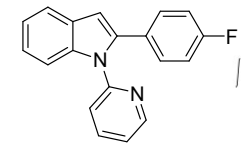
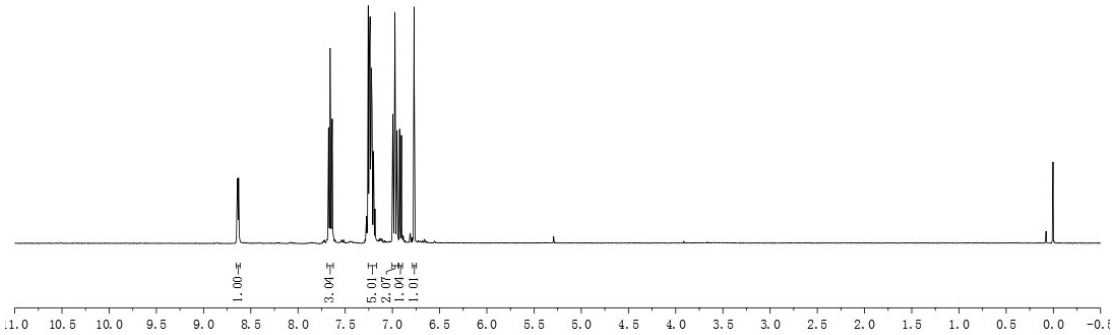
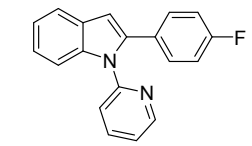


^{1}H NMR (400 MHz, $CDCl_3$)

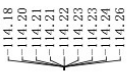
3w

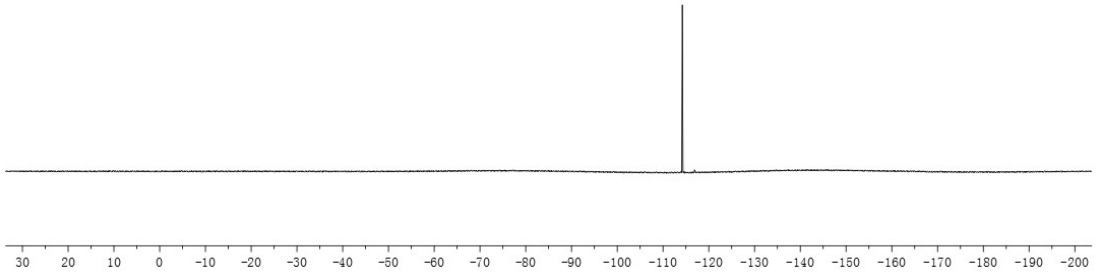


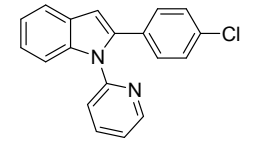


^{19}F NMR (376 MHz, $CDCl_3$)

3w

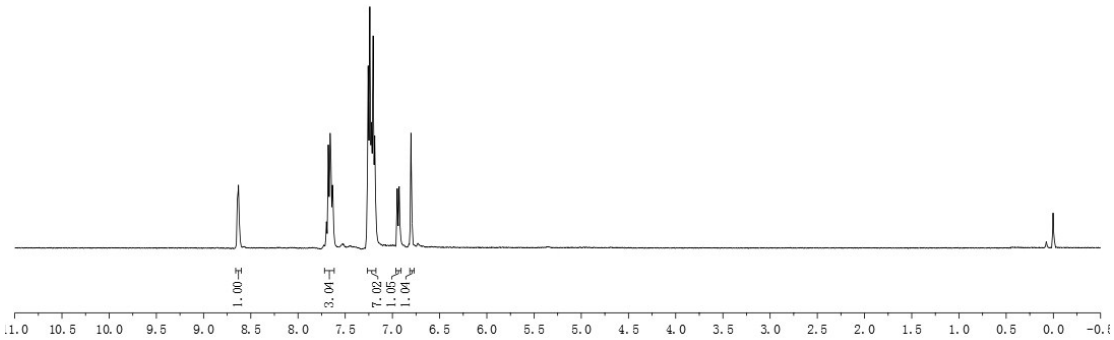


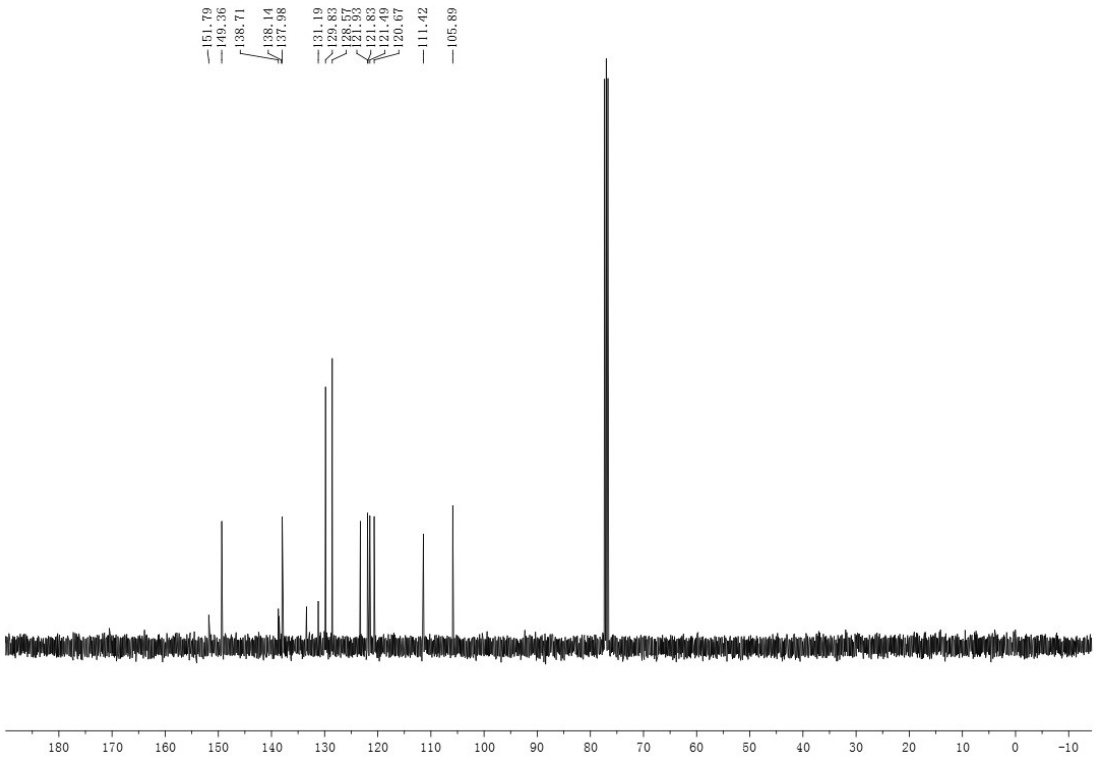


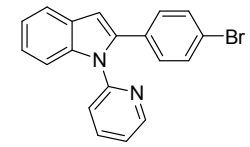


^{13}H NMR (100 MHz, $CDCl_3$)

3x

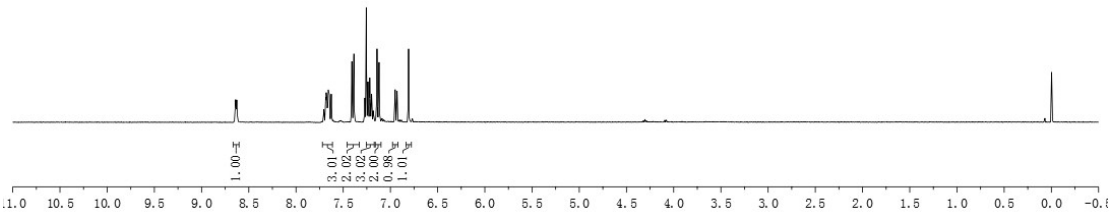


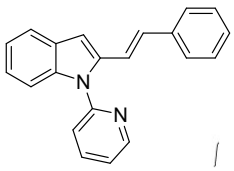




^{1}H NMR (400 MHz, $CDCl_3$)

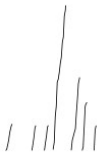
3y

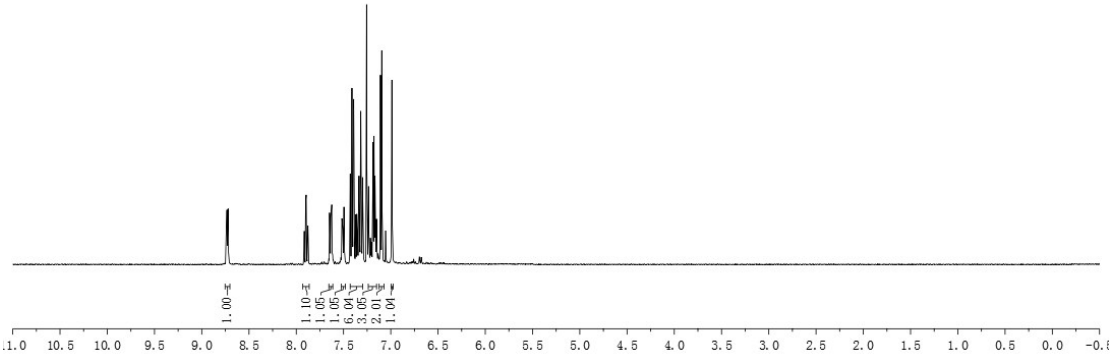


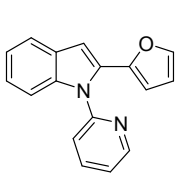


^{1}H NMR (400 MHz, $CDCl_3$)

3z

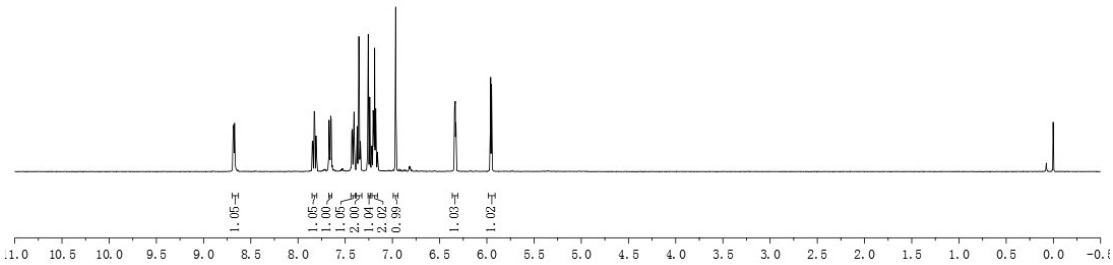


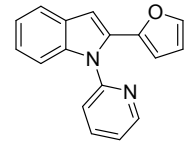




^{1}H NMR (400 MHz, $CDCl_3$)

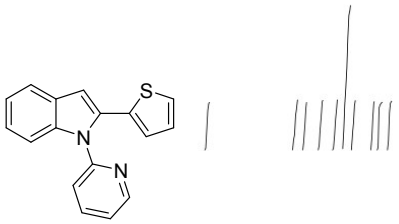
3aa





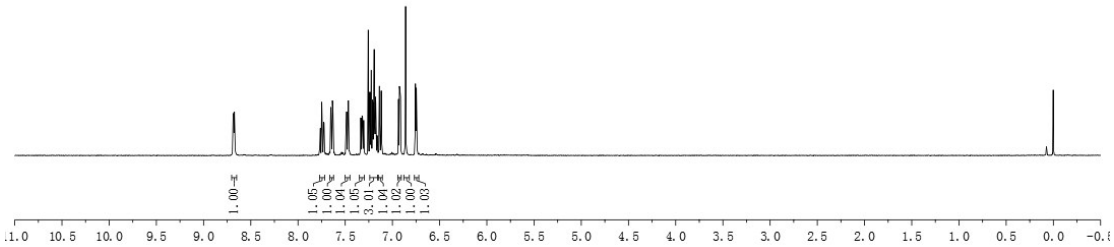
^{13}C NMR (100 MHz, $CDCl_3$)

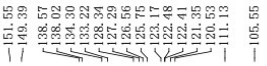
3aa

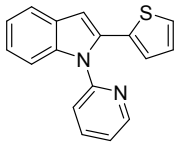


^{1}H NMR (400 MHz, $CDCl_3$)

3ab

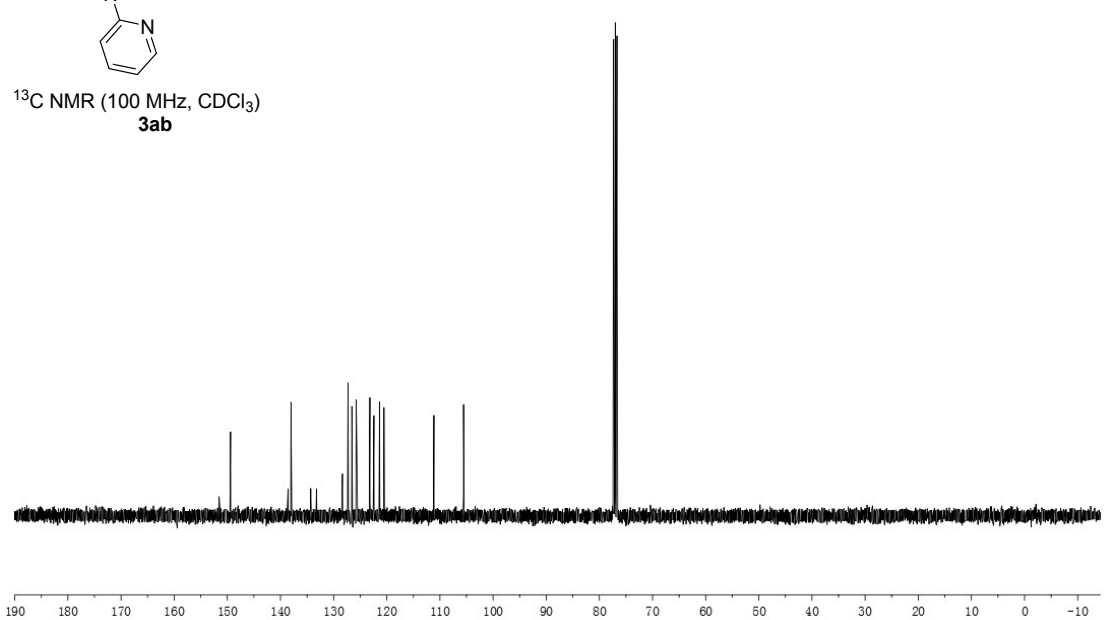


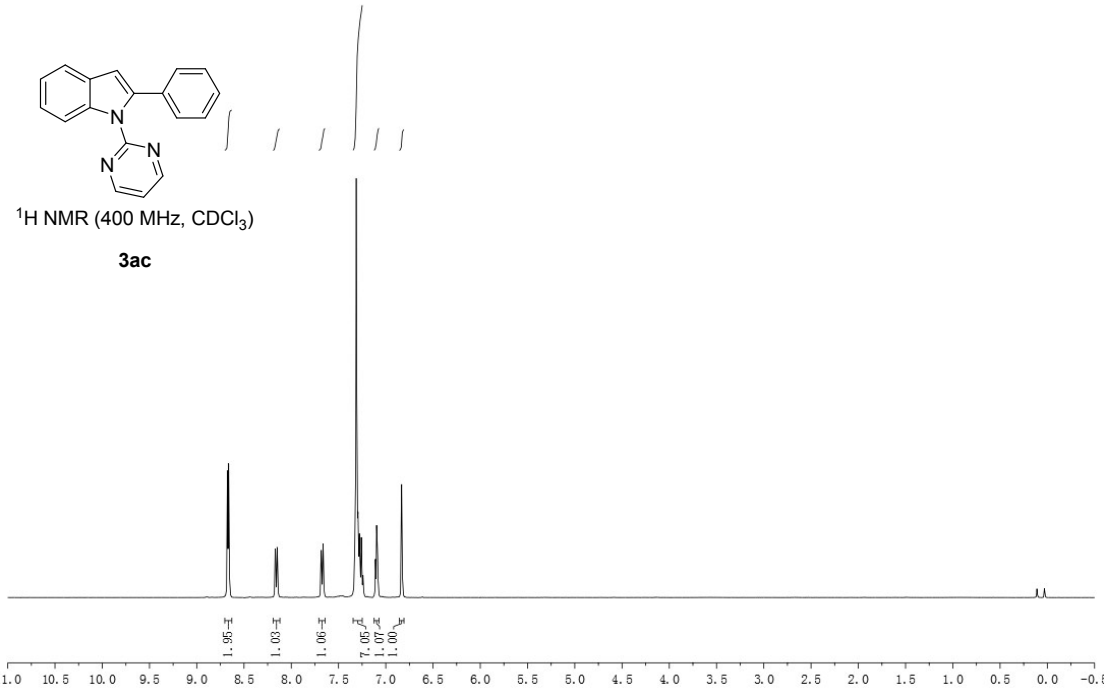




^{13}C NMR (100 MHz, $CDCl_3$)

3ab





^{1}H NMR (400 MHz, $CDCl_3$)

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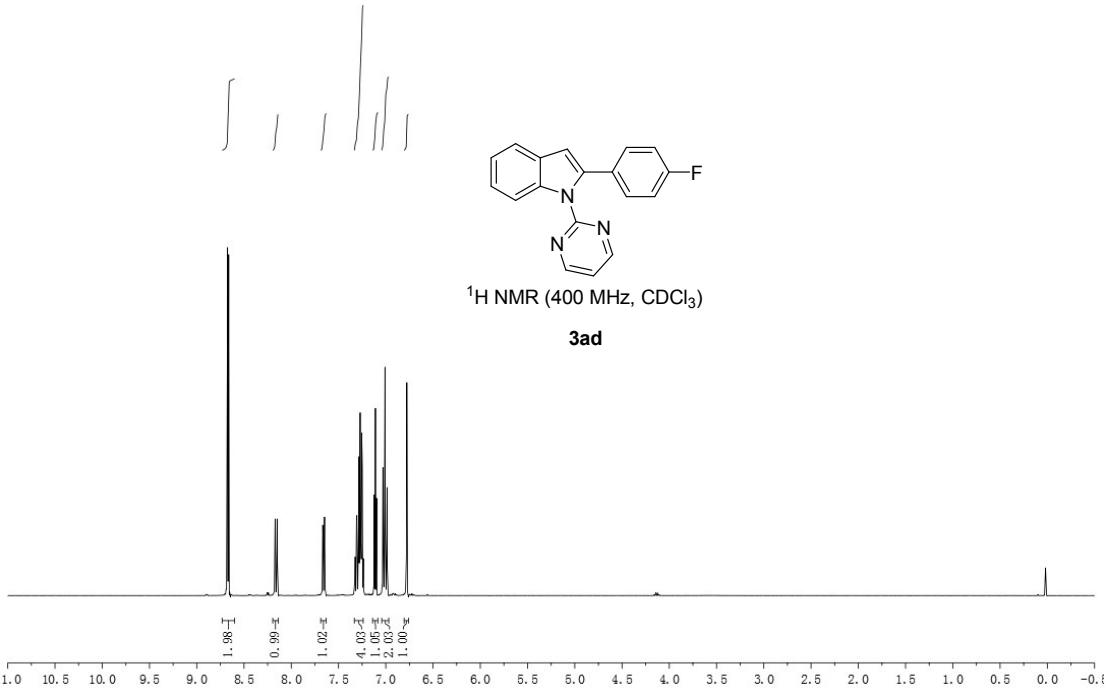

^{1}H NMR (400 MHz, $CDCl_3$)

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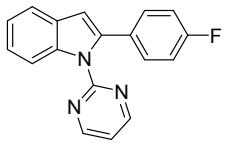

^{19}F NMR (376 MHz, $CDCl_3$)

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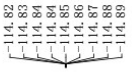

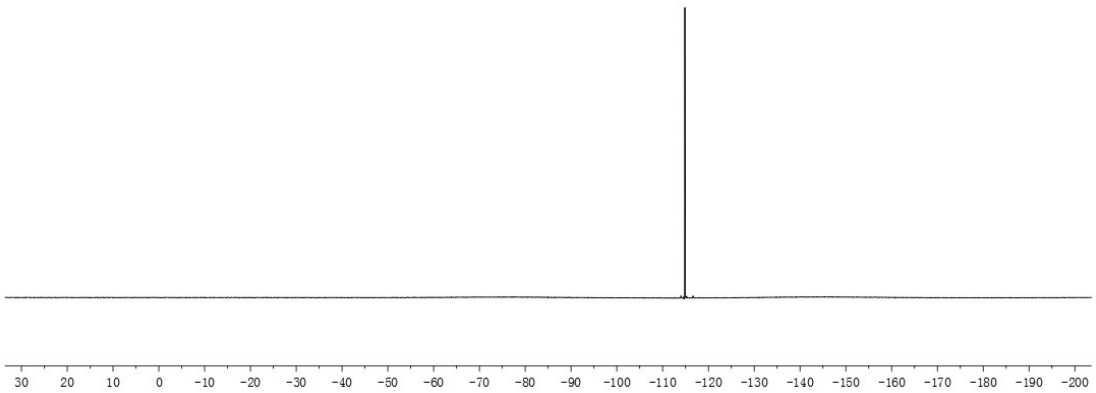

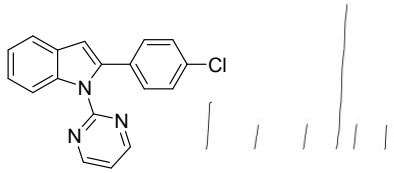

^{1}H NMR (400 MHz, $CDCl_3$)

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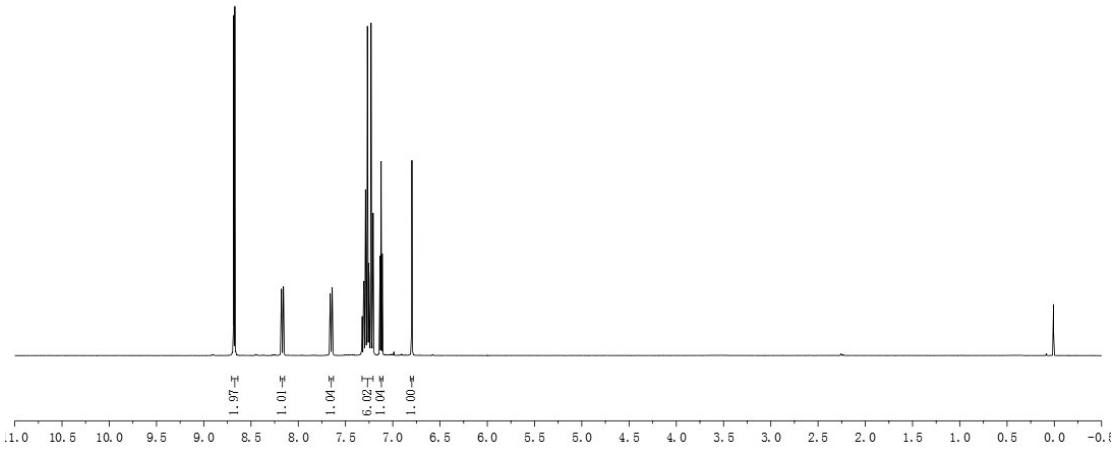

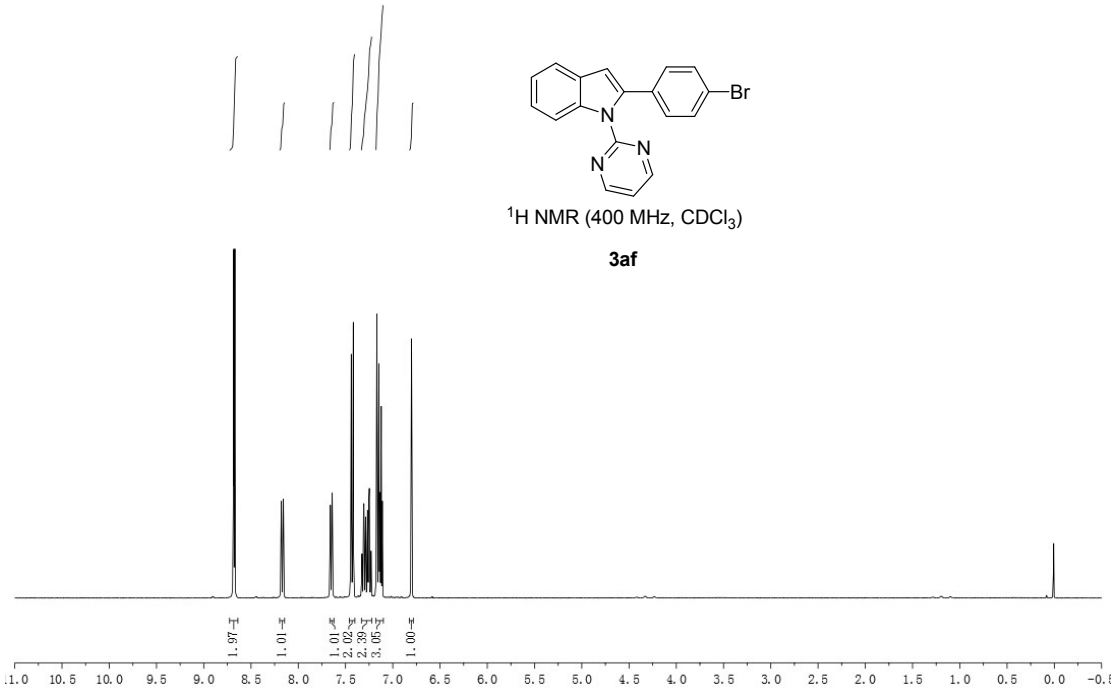

^{1}H NMR (400 MHz, $CDCl_3$)

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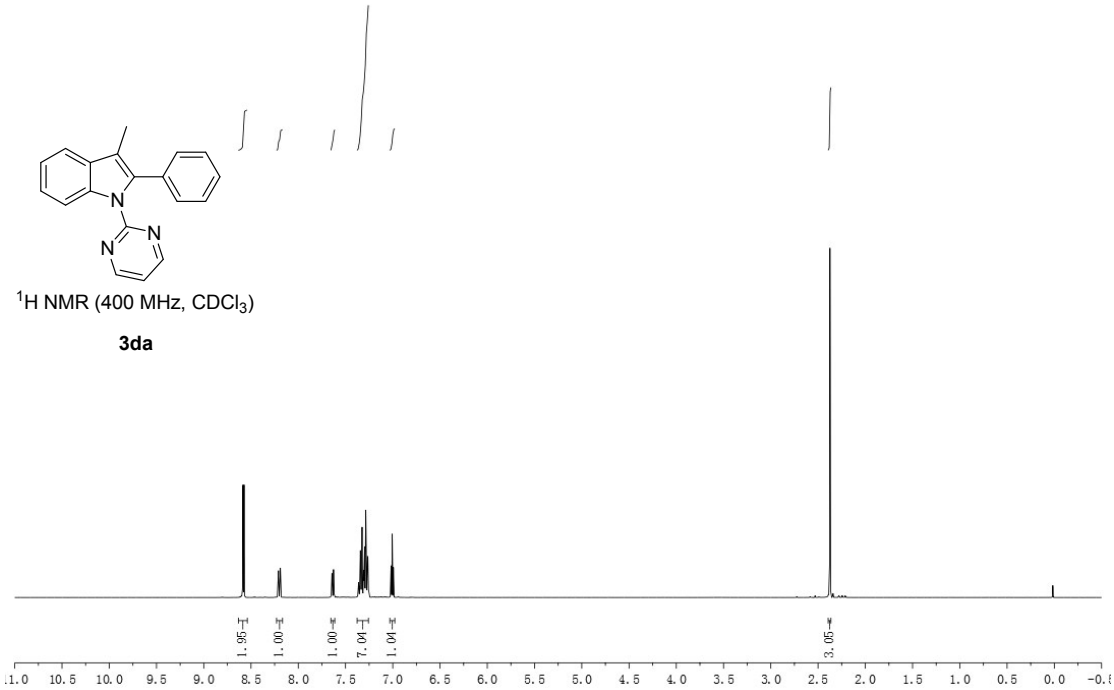

^{1}H NMR (400 MHz, $CDCl_3$)

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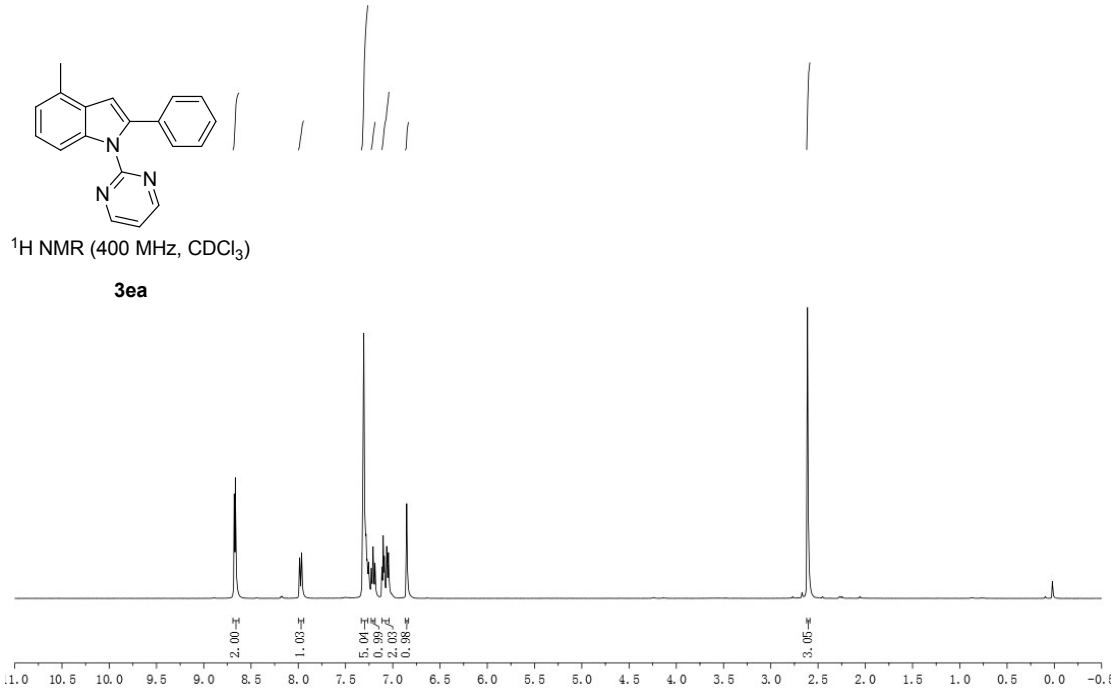
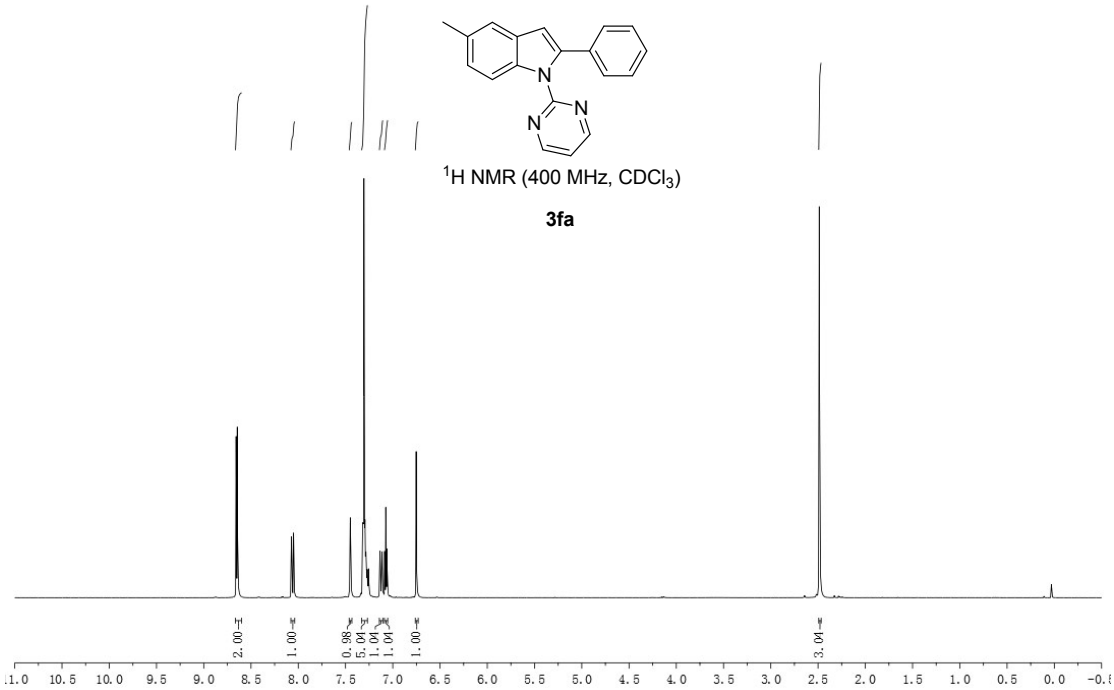


^{1}H NMR (400 MHz, $CDCl_3$)

3ea



^{1}H NMR (400 MHz, $CDCl_3$)

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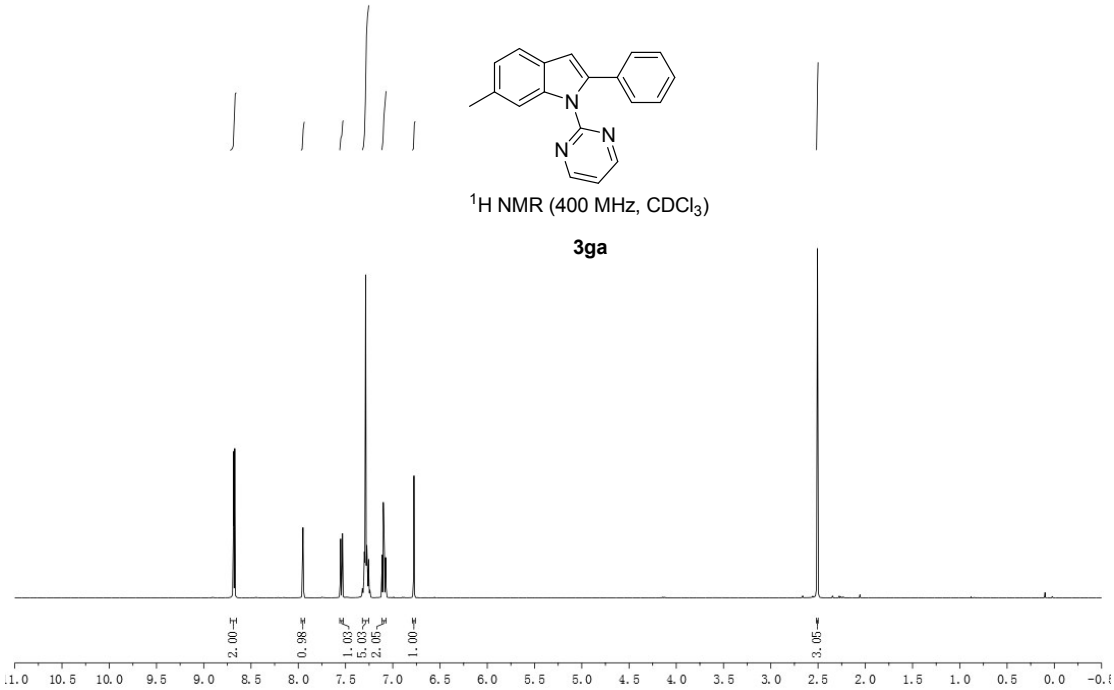

^{1}H NMR (400 MHz, $CDCl_3$)

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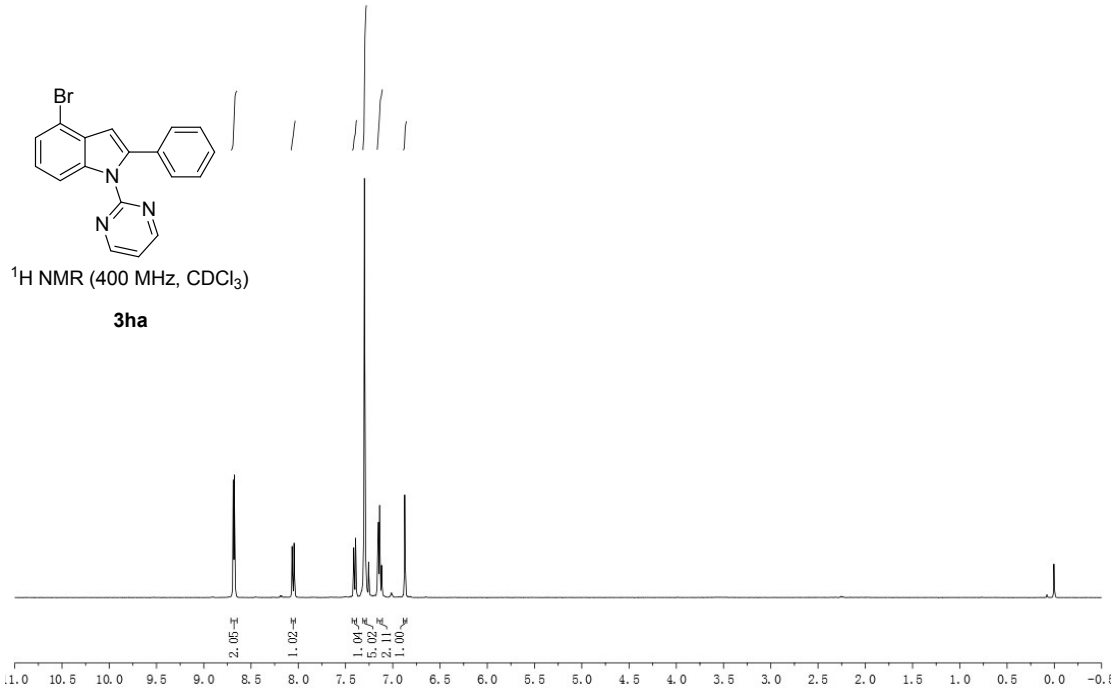
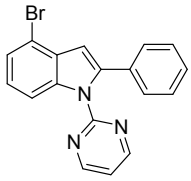


^{1}H NMR (400 MHz, $CDCl_3$)

3ha



^{13}C NMR (100 MHz, $CDCl_3$)

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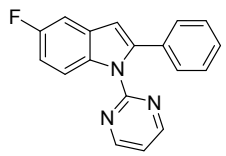
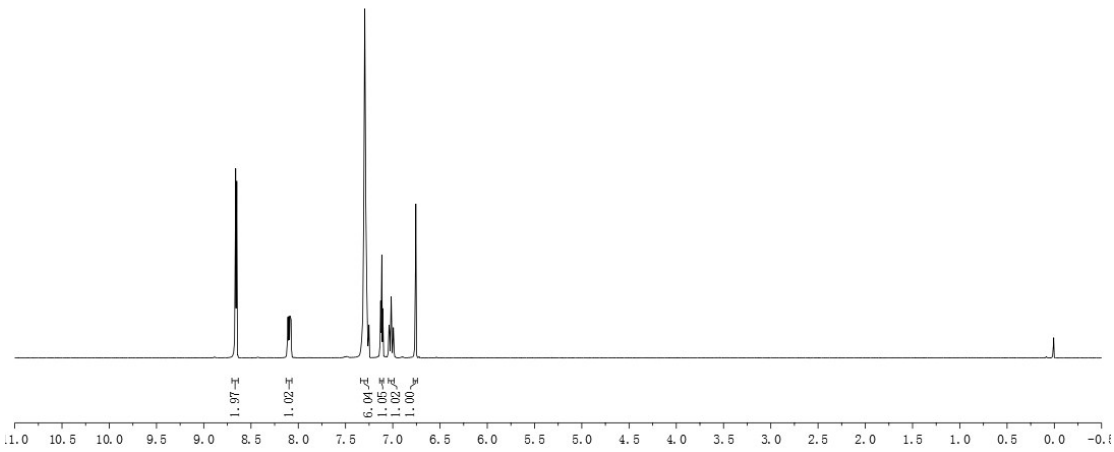
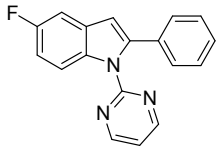


^{1}H NMR (400 MHz, $CDCl_3$)

3ia





^{19}F NMR (376 MHz, $CDCl_3$)

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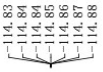

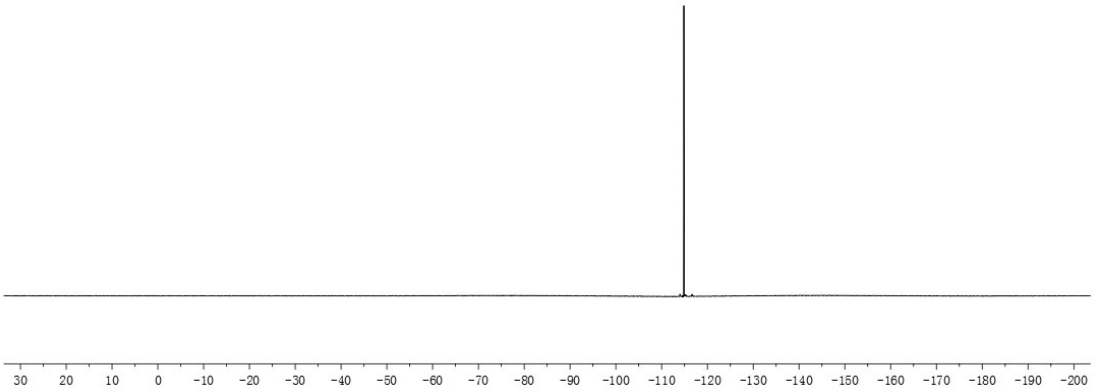

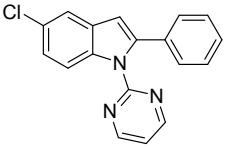

^{1}H NMR (400 MHz, $CDCl_3$)

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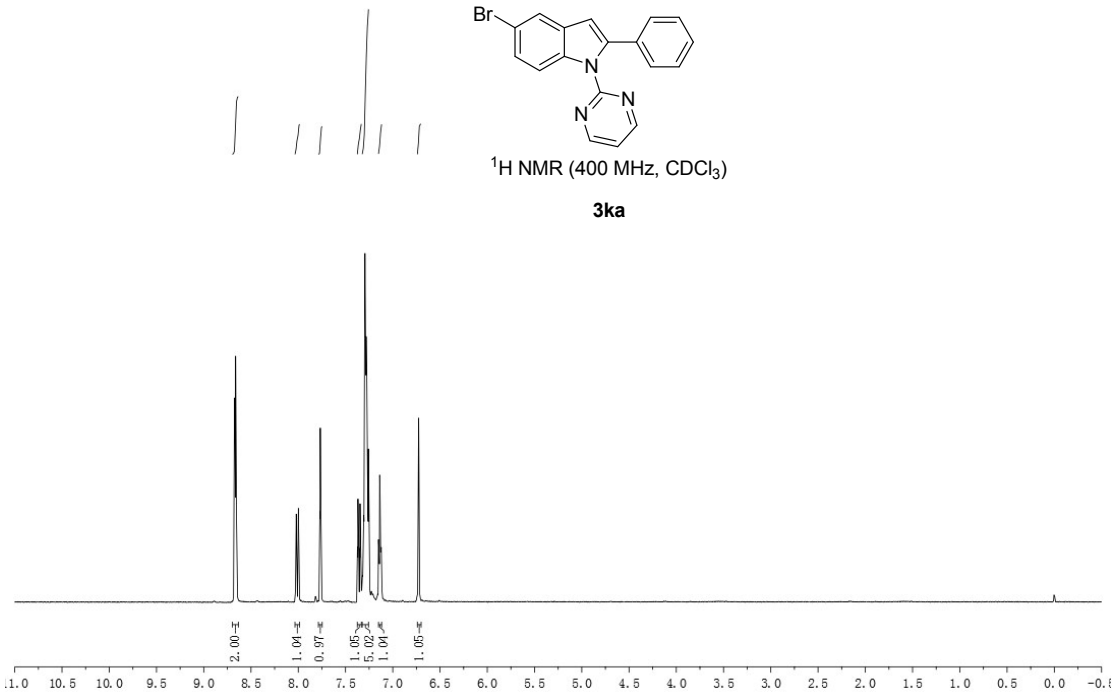
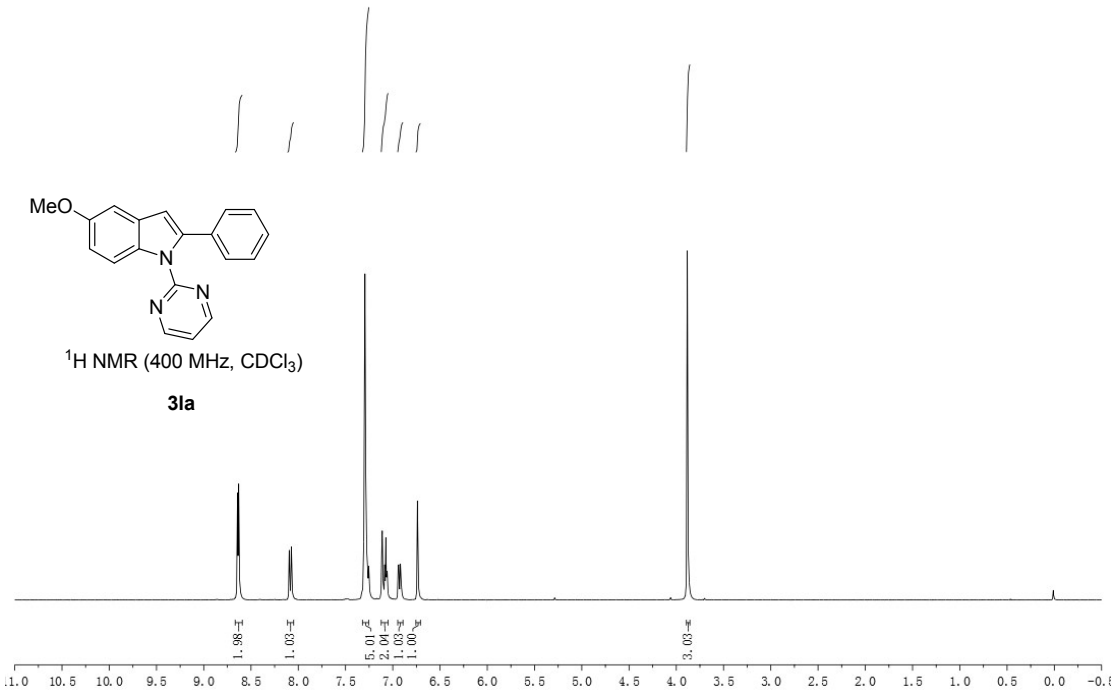


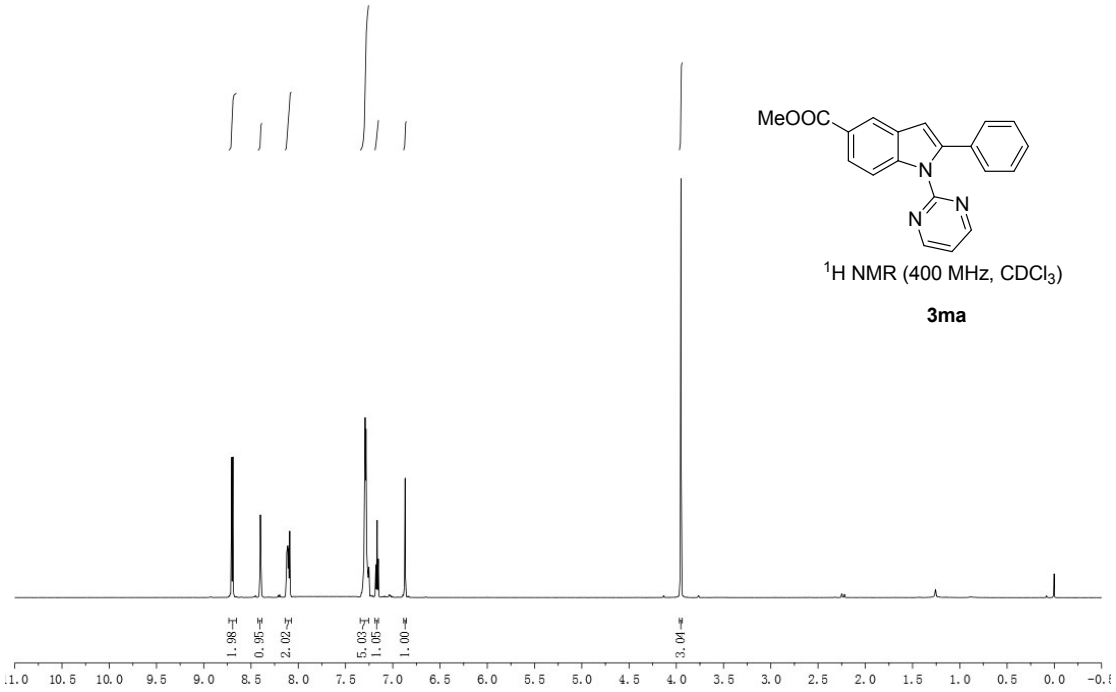
^{1}H NMR (400 MHz, $CDCl_3$)

3ka



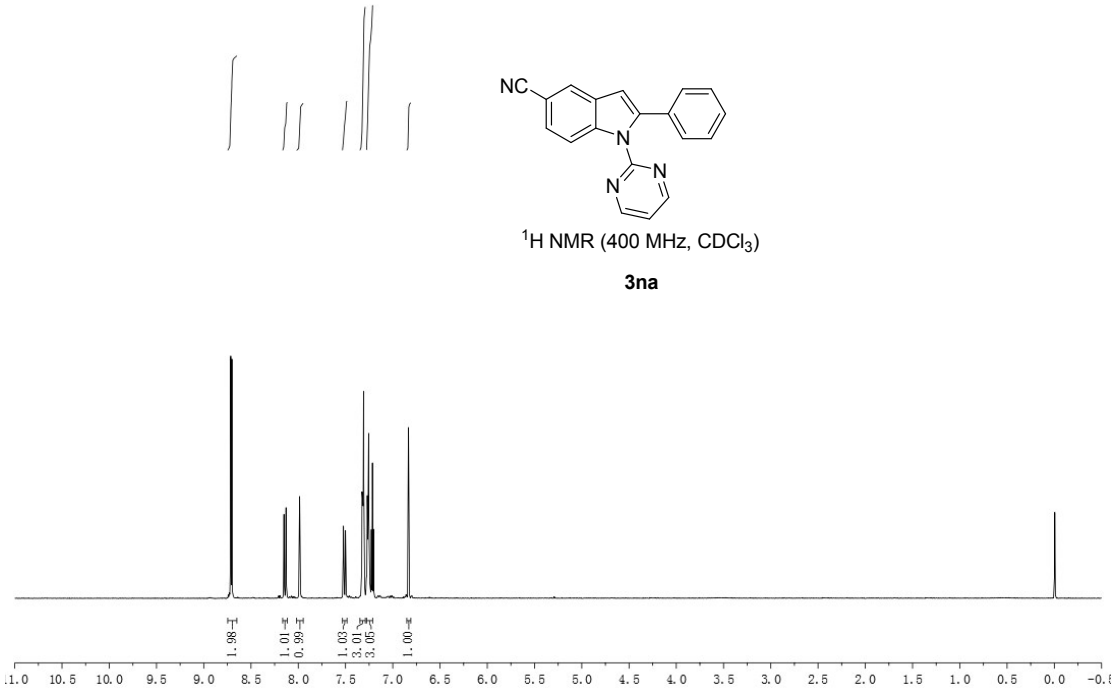
^{1}H NMR (400 MHz, $CDCl_3$)

3la



^{1}H NMR (400 MHz, $CDCl_3$)

3ma



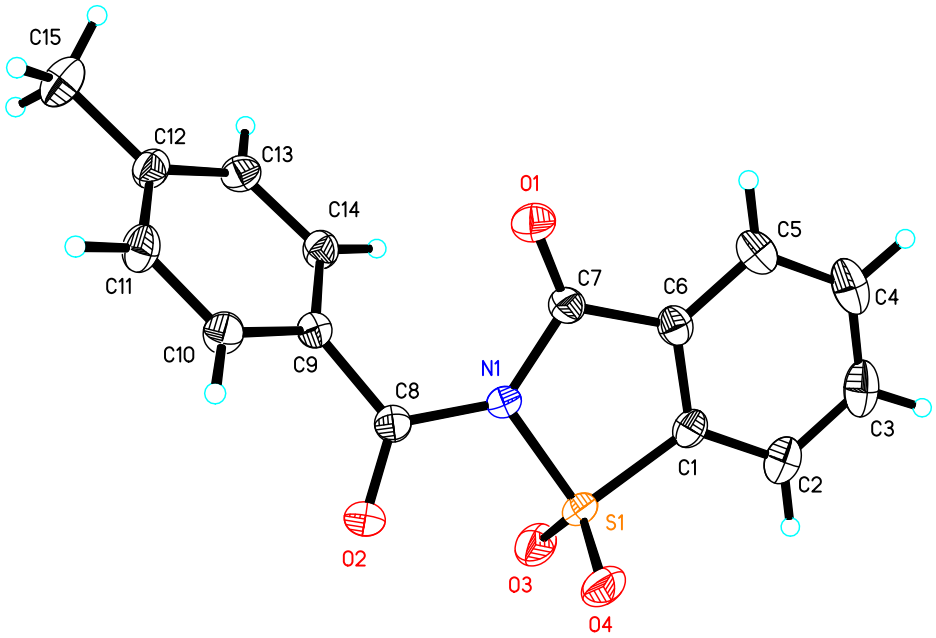
^{1}H NMR (400 MHz, $CDCl_3$)

3na

Crystal Structure of 1j from the Manuscript

The solid state structure of **1b** was confirmed by single crystal X-ray diffraction as shown in **Figure 1.** Suitable colorless plate crystals were obtained by slow concentration of a DCM/Petroleum ether solution of **1b**.

Figure 1. ORTEP Structure of 1j (*CCDC 1508194*)



Selected angles (deg): S1–N1–C9–C8, –163.4; C7–N1–C8–O2, –153.0; S1–N1–C8–O2, 14.8; C7–N1–C8–C9, 28.9 S1–N1–C7–C6, 10.8; C7–N1–C8–O1, 0.9; S1–N1–C7–O1, -167.0; C8–N1–C6–C7, 178.9

Table 1. Crystal data and structure refinement for cd16566.

Identification code	cd16566	
Empirical formula	C15 H11 N O4 S	
Formula weight	301.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.8402(18) Å	α= 90°.
	b = 10.9776(18) Å	β= 90°.
	c = 11.4168(19) Å	γ = 90°.
Volume	1358.6(4) $Å^3$	
Z	4	
Density (calculated)	1.473 Mg/m^3	
Absorption coefficient	0.253 mm^{-1}	
F(000)	624	
Crystal size	0.220 x 0.170 x 0.140 mm^3	
Theta range for data collection	2.574 to 25.495°.	

Index ranges	-13<=h<=12, -13<=k<=13, -13<=l<=13
Reflections collected	7834
Independent reflections	2529 [R(int) = 0.0398]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6641
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2529 / 0 / 192
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0868
R indices (all data)	R1 = 0.0388, wR2 = 0.0888
Absolute structure parameter	0.05(4)
Largest diff. peak and hole	0.212 and -0.225 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for cd16566. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-234(1)	6789(1)	244(1)	37(1)
N(1)	640(2)	7210(2)	1429(2)	35(1)
O(1)	2069(2)	8700(2)	1886(2)	52(1)
O(2)	564(2)	5283(2)	2104(2)	53(1)
O(3)	-1453(2)	6558(2)	620(2)	57(1)
O(4)	397(2)	5899(2)	-426(2)	56(1)
C(1)	-62(2)	8209(3)	-412(2)	36(1)
C(2)	-584(3)	8581(3)	-1454(3)	49(1)
C(3)	-242(4)	9697(4)	-1880(3)	59(1)
C(4)	596(4)	10417(4)	-1282(4)	60(1)
C(5)	1106(3)	10039(3)	-240(3)	51(1)
C(6)	768(3)	8921(3)	193(3)	37(1)
C(7)	1264(3)	8339(3)	1264(2)	36(1)
C(8)	813(3)	6327(3)	2322(2)	37(1)
C(9)	1253(2)	6736(3)	3484(2)	33(1)
C(10)	2032(3)	5957(3)	4088(3)	40(1)
C(11)	2415(3)	6255(3)	5204(3)	43(1)
C(12)	1993(3)	7294(3)	5757(3)	39(1)
C(13)	1199(3)	8054(3)	5154(3)	39(1)
C(14)	842(3)	7795(3)	4015(3)	38(1)
C(15)	2387(4)	7592(4)	6987(3)	60(1)

Table 3. Bond lengths [Å] and angles [°] for cd16566.

S(1)-O(3)	1.412(2)
S(1)-O(4)	1.418(2)
S(1)-N(1)	1.715(2)
S(1)-C(1)	1.740(3)
N(1)-C(8)	1.419(4)
N(1)-C(7)	1.425(4)
O(1)-C(7)	1.192(4)
O(2)-C(8)	1.203(4)
C(1)-C(6)	1.378(4)
C(1)-C(2)	1.379(4)
C(2)-C(3)	1.370(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.383(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.374(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.480(4)
C(8)-C(9)	1.479(4)
C(9)-C(14)	1.385(4)
C(9)-C(10)	1.385(4)
C(10)-C(11)	1.380(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.382(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.382(4)
C(12)-C(15)	1.504(5)
C(13)-C(14)	1.386(4)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
O(3)-S(1)-O(4)	119.49(16)

O(3)-S(1)-N(1)	109.03(13)
O(4)-S(1)-N(1)	110.17(14)
O(3)-S(1)-C(1)	113.05(15)
O(4)-S(1)-C(1)	109.47(14)
N(1)-S(1)-C(1)	92.24(12)
C(8)-N(1)-C(7)	128.8(2)
C(8)-N(1)-S(1)	117.12(19)
C(7)-N(1)-S(1)	113.10(19)
C(6)-C(1)-C(2)	122.2(3)
C(6)-C(1)-S(1)	111.2(2)
C(2)-C(1)-S(1)	126.4(3)
C(3)-C(2)-C(1)	117.4(3)
C(3)-C(2)-H(2)	121.3
C(1)-C(2)-H(2)	121.3
C(2)-C(3)-C(4)	120.9(3)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	121.2(3)
C(5)-C(4)-H(4)	119.4
C(3)-C(4)-H(4)	119.4
C(6)-C(5)-C(4)	118.3(3)
C(6)-C(5)-H(5)	120.9
C(4)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	120.0(3)
C(5)-C(6)-C(7)	125.9(3)
C(1)-C(6)-C(7)	114.0(3)
O(1)-C(7)-N(1)	123.9(3)
O(1)-C(7)-C(6)	127.9(3)
N(1)-C(7)-C(6)	108.2(2)
O(2)-C(8)-N(1)	118.2(3)
O(2)-C(8)-C(9)	123.1(3)
N(1)-C(8)-C(9)	118.7(2)
C(14)-C(9)-C(10)	119.8(3)
C(14)-C(9)-C(8)	122.9(3)
C(10)-C(9)-C(8)	117.1(3)
C(11)-C(10)-C(9)	119.8(3)
C(11)-C(10)-H(10)	120.1
C(9)-C(10)-H(10)	120.1

C(10)-C(11)-C(12)	121.1(3)
C(10)-C(11)-H(11)	119.4
C(12)-C(11)-H(11)	119.4
C(13)-C(12)-C(11)	118.5(3)
C(13)-C(12)-C(15)	120.7(3)
C(11)-C(12)-C(15)	120.7(3)
C(12)-C(13)-C(14)	121.1(3)
C(12)-C(13)-H(13)	119.4
C(14)-C(13)-H(13)	119.4
C(9)-C(14)-C(13)	119.5(3)
C(9)-C(14)-H(14)	120.2
C(13)-C(14)-H(14)	120.2
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for cd16566. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	40(1)	27(1)	-5(1)	-4(1)	-6(1)
N(1)	42(1)	34(1)	30(1)	-1(1)	-6(1)	-8(1)
O(1)	49(1)	60(2)	47(1)	1(1)	-11(1)	-20(1)
O(2)	84(2)	32(1)	43(1)	-3(1)	-7(1)	-9(1)
O(3)	50(1)	78(2)	43(1)	-1(1)	-3(1)	-25(1)
O(4)	86(2)	46(1)	35(1)	-13(1)	-4(1)	7(1)
C(1)	34(2)	43(2)	29(1)	-3(1)	3(1)	5(1)
C(2)	48(2)	62(2)	36(2)	3(2)	0(1)	10(2)
C(3)	64(2)	71(3)	43(2)	19(2)	7(2)	20(2)
C(4)	62(2)	55(2)	65(2)	25(2)	16(2)	9(2)
C(5)	51(2)	44(2)	58(2)	9(2)	6(2)	-7(2)
C(6)	34(1)	39(2)	38(1)	3(1)	7(1)	1(1)
C(7)	37(2)	36(2)	36(2)	0(1)	2(1)	-5(1)
C(8)	42(2)	34(2)	34(2)	-1(1)	1(1)	1(1)
C(9)	35(1)	32(1)	32(1)	1(1)	-1(1)	0(1)
C(10)	44(2)	37(2)	37(2)	-3(1)	2(1)	9(1)
C(11)	43(2)	49(2)	39(2)	5(2)	-4(1)	12(1)
C(12)	40(2)	47(2)	30(1)	0(1)	1(1)	-4(1)
C(13)	42(2)	37(2)	38(2)	-7(1)	2(1)	3(1)
C(14)	40(2)	35(2)	38(2)	2(1)	-2(1)	6(1)
C(15)	64(2)	78(3)	37(2)	-5(2)	-8(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for cd16566.

	x	y	z	U(eq)
H(2)	-1146	8093	-1852	58
H(3)	-577	9975	-2581	71
H(4)	818	11170	-1591	73
H(5)	1665	10529	161	61
H(10)	2296	5236	3742	47
H(11)	2967	5747	5592	52
H(13)	899	8752	5519	47
H(14)	330	8328	3610	45
H(15A)	1764	7324	7527	89
H(15B)	2499	8456	7062	89
H(15C)	3150	7184	7158	89

Table 6. Torsion angles [°] for cd16566.

O(3)-S(1)-N(1)-C(8)	64.3(3)
O(4)-S(1)-N(1)-C(8)	-68.7(2)
C(1)-S(1)-N(1)-C(8)	179.6(2)
O(3)-S(1)-N(1)-C(7)	-126.1(2)
O(4)-S(1)-N(1)-C(7)	100.9(2)
C(1)-S(1)-N(1)-C(7)	-10.8(2)
O(3)-S(1)-C(1)-C(6)	119.3(2)
O(4)-S(1)-C(1)-C(6)	-104.9(2)
N(1)-S(1)-C(1)-C(6)	7.5(2)
O(3)-S(1)-C(1)-C(2)	-66.0(3)
O(4)-S(1)-C(1)-C(2)	69.8(3)
N(1)-S(1)-C(1)-C(2)	-177.8(2)
C(6)-C(1)-C(2)-C(3)	0.3(4)
S(1)-C(1)-C(2)-C(3)	-173.9(3)
C(1)-C(2)-C(3)-C(4)	0.0(5)
C(2)-C(3)-C(4)-C(5)	-0.3(6)
C(3)-C(4)-C(5)-C(6)	0.4(5)
C(4)-C(5)-C(6)-C(1)	-0.1(5)
C(4)-C(5)-C(6)-C(7)	176.8(3)
C(2)-C(1)-C(6)-C(5)	-0.2(4)
S(1)-C(1)-C(6)-C(5)	174.7(2)
C(2)-C(1)-C(6)-C(7)	-177.4(3)
S(1)-C(1)-C(6)-C(7)	-2.5(3)
C(8)-N(1)-C(7)-O(1)	0.9(5)
S(1)-N(1)-C(7)-O(1)	-167.2(3)
C(8)-N(1)-C(7)-C(6)	178.9(3)
S(1)-N(1)-C(7)-C(6)	10.8(3)
C(5)-C(6)-C(7)-O(1)	-4.3(5)
C(1)-C(6)-C(7)-O(1)	172.7(3)
C(5)-C(6)-C(7)-N(1)	177.8(3)
C(1)-C(6)-C(7)-N(1)	-5.2(3)
C(7)-N(1)-C(8)-O(2)	-152.9(3)
S(1)-N(1)-C(8)-O(2)	14.8(4)
C(7)-N(1)-C(8)-C(9)	28.9(4)
S(1)-N(1)-C(8)-C(9)	-163.4(2)
O(2)-C(8)-C(9)-C(14)	-137.8(3)

N(1)-C(8)-C(9)-C(14)	40.3(4)
O(2)-C(8)-C(9)-C(10)	36.7(4)
N(1)-C(8)-C(9)-C(10)	-145.2(3)
C(14)-C(9)-C(10)-C(11)	-1.4(4)
C(8)-C(9)-C(10)-C(11)	-176.2(3)
C(9)-C(10)-C(11)-C(12)	2.9(5)
C(10)-C(11)-C(12)-C(13)	-1.7(5)
C(10)-C(11)-C(12)-C(15)	178.2(3)
C(11)-C(12)-C(13)-C(14)	-0.8(5)
C(15)-C(12)-C(13)-C(14)	179.2(3)
C(10)-C(9)-C(14)-C(13)	-1.1(4)
C(8)-C(9)-C(14)-C(13)	173.4(3)
C(12)-C(13)-C(14)-C(9)	2.2(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd16566 [Å and °].

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

Crystallographic data for 1j (*CCDC 1508194*) are available as CIF files free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.