Supporting Information

Iodine–mediated oxidative triple functionalization of indolines with azoles and diazonium salts

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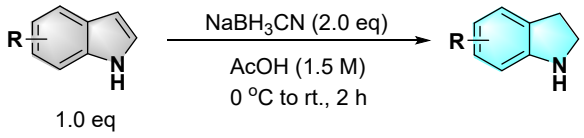
1. General Information

All the reagents were purchased from commercial sources, and used without further purification. All the obtained products were characterized by melting points, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, high resolution mass spectra (HRMS). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus. GC-MS was obtained on ANYEEP TQ1978. ^{1}H NMR spectra, recorded at 600 MHz. ^{13}C NMR spectra, recorded at 151 MHz. ^{19}F NMR spectra, recorded at 565 MHz. The chemical shifts are reported relative to $CDCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.16 for ^{13}C NMR).

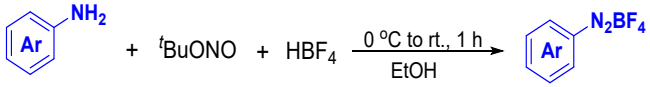
2. Procedure for the synthesis starting materials

2.1 Synthesis of indolines:[1]



To a solution of indole (40 mmol, 1.0 equiv) in acetic acid (1.5 M, 27.0 mL) was added in portions sodium cyanoborohydride (80 mmol, 2.0 equiv) at 0 °C, and the mixture was stirred at room temperature. After 2 h, water (50.0 mL) was added at 0 °C and the mixture was basified with NaOH (5 N aqueous solution). The organic material was extracted with CH_2Cl_2 (100.0 mL × 3), washed with brine, dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator to give crude reaction mixture. The column chromatography gives the pure product.

2.2 Synthesis of diazonium tetrafluoroborate:[2]



Appropriate arylamine (10 mmol) was dissolved in EtOH (3.0 mL) and hydrofluoroboric acid (48% w/w in water, 2.5 mL). The reaction mixture was cooled to 0 °C, tert-Butyl nitrite (2.7 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 hour. The resulting precipitate was collected by filtration. The crude product was dissolved into acetone (about 20.0 mL, for some low solubility product, more acetone was used), and the solution was gently heated, and then diethyl ether was added until the recrystallized product precipitated completely. The diazonium salt was collected by filtration, washed several times by cold diethyl ether and dried

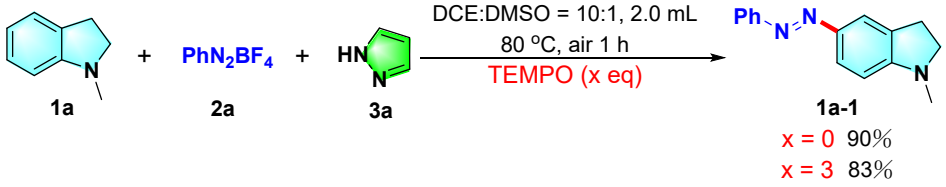
under vacuum.

3. Typical procedure for the synthesis of 4aaa

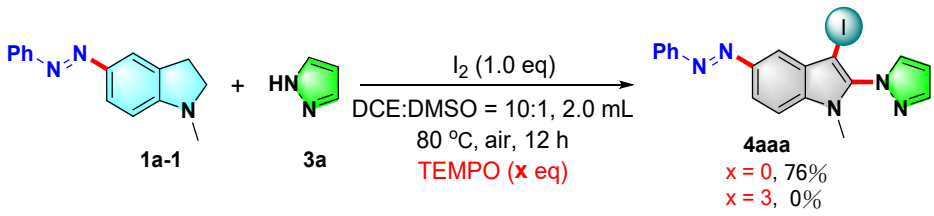
Under air atmosphere, 1-methylindoline **1a** (40.0 mg, 0.30 mmol), aryldiazonium salts **2a** (38.4 mg, 0.2 mmol), azole **3a** (40.8 mg, 0.6 mmol), solvent (2.0 mL, DCE: DMSO = 10:1) were added to a Schlenk tube (50.0 mL) along with a magnetic stirrer bar, and the reaction mixture was heated at 80 °C for 1 h. Then, $\mathbf{I_2}$ (50.8 mg, 0.2 mmol) was added in and heated at 80 °C for another 12 h to complete the transformation. After cooling to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum. The residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (9:1) as the eluent to give **4aaa**.

4. Control experiments

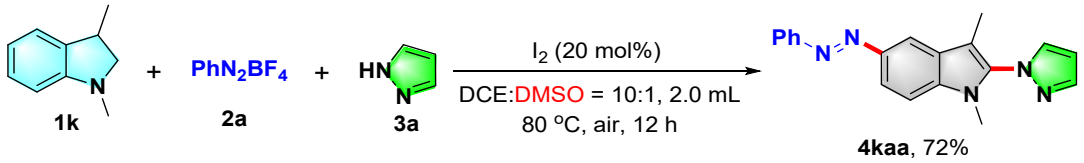
(4a) Under air atmosphere, 1-methylindoline **1a** (40.0 mg, 0.30 mmol), aryl diazonium salts **2a** (38.4 mg, 0.2 mmol), azole **3a** (40.8 mg, 0.6 mmol), solvent (2.0 mL, DCE: DMSO = 10:1) were added to a Schlenk tube (50.0 mL) along with a magnetic stirrer bar, and the reaction mixture was heated at 80 °C for 1 h. After cooling to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum. The residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (10:1) as the eluent to give **1a–1** (42.7 mg, 90% yield). When the 3.0 equiv of TEMPO was added, **1a–1** was isolated in 83% yield.



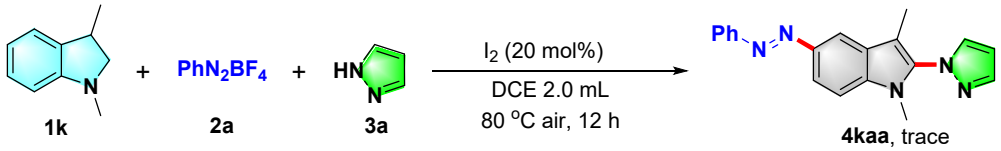
(4b) A mixture of **1a-1** (47.4 mg, 0.2 mmol), **3a** (40.8 mg, 0.3 mmol) and $\mathbf{I_2}$ (50.8 mg, 0.2 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 80 °C in a Schlenk tube (50.0 mL) for 12 h under air. After the transformation completed, the desired product **4aaa** was isolated in 76% yield. When the 3.0 equiv of TEMPO was added, **4aaa** was not detected.



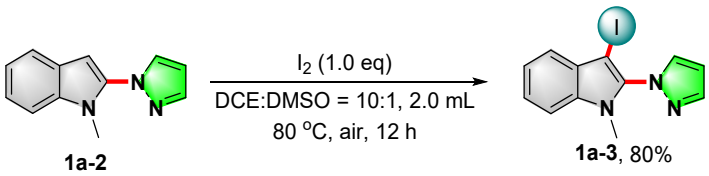
(4c) A mixture of **1e** (44.1 mg, 0.3 mmol), **2a** (38.4 mg, 0.2 mmol), **3a** (40.8 mg, 0.3 mmol) and $\mathbf{I_2}$ (10.2 mg, 0.04 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 80 °C in a Schlenk tube (50.0 mL) for 12 h under air. After the transformation completed, **4kaa** was isolated in 72% yield.



(4d) A mixture of **1e** (44.1 mg, 0.3 mmol), **2a** (38.4 mg, 0.2 mmol), **3a** (40.8 mg, 0.3 mmol) and $\mathbf{I_2}$ (10.2 mg, 0.04 mmol) in DCE (2.0 mL) was stirred at 80 °C in a Schlenk tube (50.0 mL) for 12 h under air. After the transformation was completed, **4kaa** was isolated in trace.

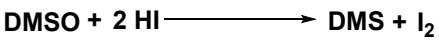


(4e) A mixture of **1a-2**[3] (39.4 mg, 0.2 mmol) and $\mathbf{I_2}$ (50.8 mg, 0.2 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 80 °C in a Schlenk tube (50.0 mL) for 12 h under air. After the transformation was completed, **1a-3** was isolated in 80% yield.



5. GC-MS analysis experiment (EI)

Under the optimized reaction conditions, the model reaction was carried, then the reaction mixture was analyzed by GC-MS (EI), and DMS (Me_2S) could be observed.



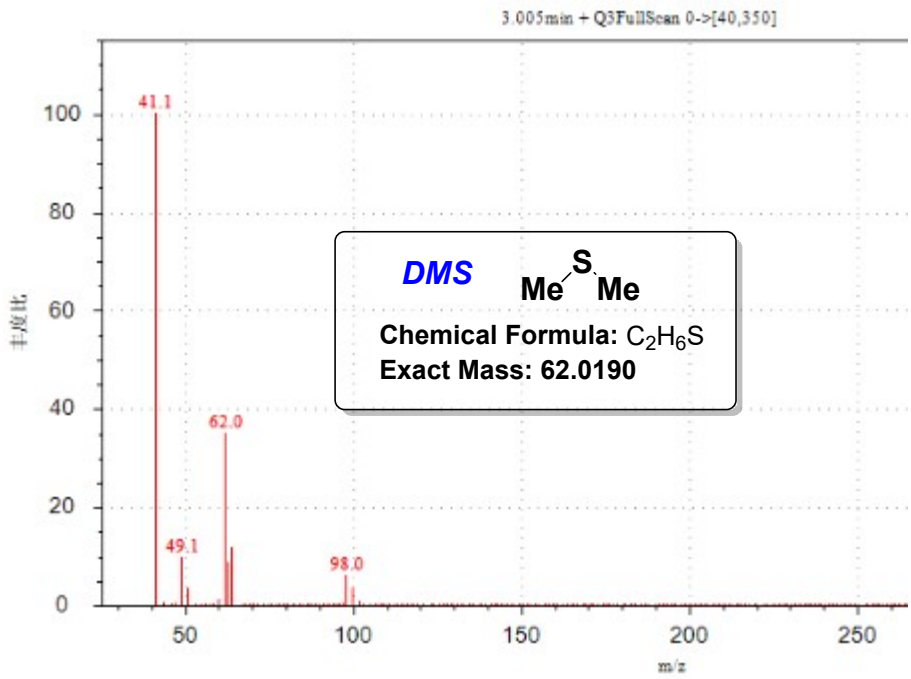
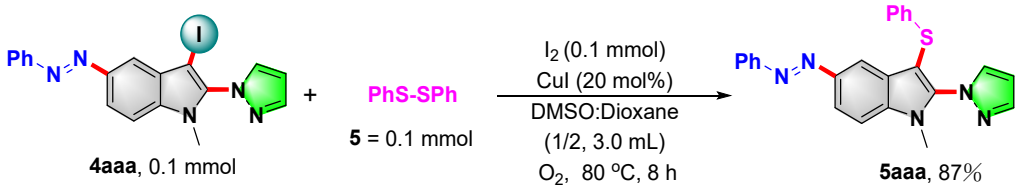
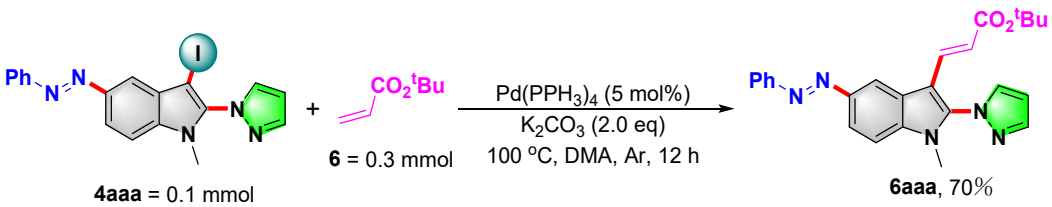


Figure S1. GC-MS analysis experiment report of the reaction mixture

6. Scale-up experiment and synthetic transformations



(5a) A mixture of **4aaa** (42.7 mg, 0.1 mmol), PhSShP (21.8 mg, 0.1 mmol), I_2 (25.4 mg, 0.1 mmol), CuI (3.8 mg, 0.02 mmol) in 3.0 mL solvent (DMSO: Dioxane = 1: 2) was stirred at 80 °C in a 50 mL Schlenk tube for 8 h under O_2. Then the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether /dichloromethane (1:1) as the eluent to give **5aaa** as an orange solid (35.6 mg, 87% yield).

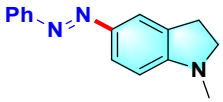


(5b) A mixture of **4aaa** (42.7 mg, 0.1 mmol), tert-butylacrylate (38 mg, 0.3 mmol), K_2CO_3 (27.6 mg, 0.2 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) in DMA (2.0 mL) was stirred at 100 °C in a 50

mL Schlenk tube for 12 h under Ar. Then the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether /dichloromethane (1:2) as the eluent to give **6aaa** as an orange solid (29.8 mg, 70% yield).

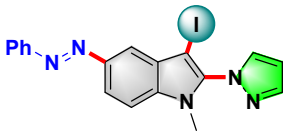
7. Characterization data for the products

(1) (*E*)-1-methyl-5-(phenyldiazenyl)indoline (1a-1)



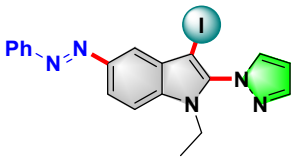
Orange solid, m.p.: 123-125 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.73 (s, 1H), 7.51 – 7.46 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 6.47 (d, *J* = 8.3 Hz, 1H), 3.51 (t, *J* = 8.3 Hz, 2H), 3.05 (t, *J* = 8.3 Hz, 2H), 2.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.89, 153.32, 145.37, 131.13, 129.30, 129.10, 129.03, 122.24, 116.20, 105.06, 55.40, 34.76, 27.90. HRMS (ESI): Calcd. for $C_{15}H_{15}N_3$ $[M+H]^+$: 238.1338; found: 238.1338.

(2) (*E*)-3-iodo-1-methyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aaa)



Orange solid, (63.9 mg, 75% yield), m.p.: 183-184 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.9 Hz, 1H), 8.02 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.88, 148.05, 142.62, 137.52, 137.40, 133.44, 130.58, 129.18, 128.93, 122.78, 120.17, 117.74, 110.81, 107.32, 56.28, 30.94. HRMS (ESI): Calcd. for $C_{18}H_{14}IN_5$ $[M+H]^+$: 428.0366; found: 428.0364.

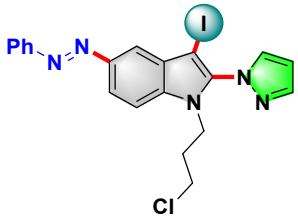
(3) (*E*)-1-ethyl-3-iodo-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4baa)



Orange solid, (53.8 mg, 61% yield), m.p.: 187-188 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.7 Hz, 1H), 8.02 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.84

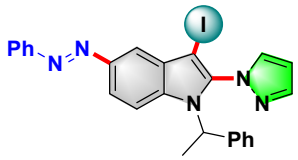
(d, *J* = 2.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.91, 148.02, 142.56, 137.00, 136.40, 133.44, 130.57, 129.19, 129.08, 122.79, 120.45, 117.60, 110.87, 107.29, 56.86, 39.68, 15.57. HRMS (ESI): Calcd. for $C_{19}H_{16}IN_5$ $[M+H]^+$: 442.0523; found: 442.0522.

(4) (*E*)-1-(3-chloropropyl)-3-iodo-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4daa)



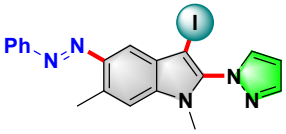
Orange solid, (63.1 mg, 65% yield), m.p.: 189-190 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 4.27 (t, *J* = 7.0 Hz, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 2.16 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.85, 148.15, 142.67, 137.06, 136.88, 133.49, 130.65, 129.19, 128.99, 122.81, 120.25, 117.97, 110.93, 107.48, 57.31, 42.00, 41.91, 32.84. HRMS (ESI): Calcd. for $C_{20}H_{17}ClIN_5$ $[M+H]^+$: 490.0289; found: 490.0287.

(5) (*E*)-3-iodo-5-(phenyldiazenyl)-1-(1-phenylethyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4eaa)



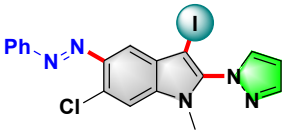
Orange solid, (53.7 mg, 52% yield), m.p.: 189-190 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.9 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.79 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.74 (d, *J* = 2.5 Hz, 1H), 7.52 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.26 (m, 5H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 5.48 (q, *J* = 7.1 Hz, 1H), 1.94 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.90, 147.84, 142.70, 139.86, 137.52, 135.51, 133.73, 130.58, 129.52, 129.17, 128.84, 127.78, 126.54, 122.77, 120.51, 117.22, 113.21, 107.52, 58.79, 54.23, 18.55. HRMS (ESI): Calcd. for $C_{25}H_{20}IN_5$ $[M+H]^+$: 518.0836; found: 518.0835.

(6) (*E*)-3-iodo-1,6-dimethyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4gaa)



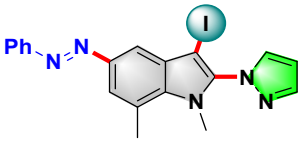
Orange solid, (50.2 mg, 57% yield), m.p.: 187-188 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 5.1 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.24 (s, 1H), 6.55 (t, *J* = 2.1 Hz, 1H), 3.62 (s, 3H), 2.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.25, 146.60, 142.48, 137.76, 137.14, 135.52, 133.43, 130.44, 129.13, 127.23, 122.98, 111.42, 108.57, 107.17, 56.22, 30.73, 18.89. HRMS (ESI): Calcd. for $C_{19}H_{16}IN_5$ $[M+H]^+$: 442.0523; found: 442.0521.

(7) (*E*)-6-chloro-3-iodo-1-methyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4haa)



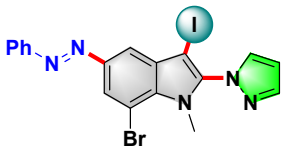
Orange solid, (64.4 mg, 70% yield), m.p.: 209-210 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.89 (d, *J* = 3.6 Hz, 2H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.49 (t, *J* = 7.3 Hz, 1H), 6.58 – 6.55 (m, 1H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.07, 143.98, 142.78, 138.30, 137.39, 133.40, 132.20, 131.16, 129.25, 127.76, 123.37, 111.56, 110.56, 107.47, 77.37, 77.16, 76.95, 56.30, 31.09. HRMS (ESI): Calcd. for $C_{18}H_{13}ClIN_5$ $[M+H]^+$: 461.9976; found: 461.9974.

(8) (*E*)-3-iodo-1,7-dimethyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4iaa)



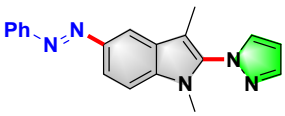
Orange solid, (59.1 mg, 67% yield), m.p.: 208-209 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.89 (d, *J* = 1.8 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.72 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.44 (m, 1H), 6.56 (t, *J* = 2.1 Hz, 1H), 3.78 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.91, 147.59, 142.65, 138.00, 136.50, 133.62, 130.51, 129.60, 129.16, 123.08, 122.73, 119.37, 119.25, 107.33, 57.94, 33.64, 20.07. HRMS (ESI): Calcd. for $C_{19}H_{16}IN_5$ $[M+H]^+$: 442.0523; found: 442.0522.

(9) (*E*)-7-bromo-3-iodo-1-methyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4jaa)



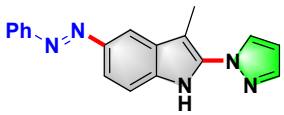
Orange solid, (52.6 mg, 52% yield), m.p.: 199-200 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.8 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.60, 147.85, 142.95, 139.08, 133.75, 133.61, 131.15, 131.05, 129.26, 122.96, 121.65, 120.91, 107.64, 105.36, 58.17, 33.80. HRMS (ESI): Calcd. for $C_{18}H_{13}BrIN_5$ $[M+H]^+$: 505.9471; found: 505.9471.

(10) (*E*)-1,3-dimethyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4kaa)



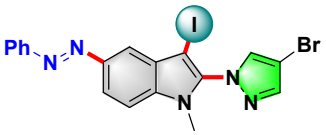
Orange solid, (45.6 mg, 72% yield), m.p.: 146-147 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.9 Hz, 1H), 8.00 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 6.54 (t, *J* = 2.2 Hz, 1H), 3.55 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.02, 147.05, 142.05, 136.58, 133.29, 133.06, 130.22, 129.14, 126.76, 122.62, 117.78, 117.05, 109.99, 107.81, 106.93, 29.82, 8.24. HRMS (ESI): Calcd. for $C_{19}H_{17}IN_5$ $[M+H]^+$: 316.1556; found: 316.1555.

(11)(*E*)-3-methyl-5-(phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4laa)



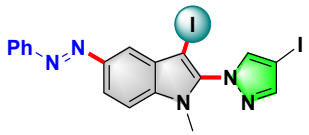
Orange solid, (33.1 mg, 55% yield), m.p.: 141-143 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.98 (d, *J* = 2.5 Hz, 1H), 7.94 (d, *J* = 7.1 Hz, 2H), 7.89 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 6.55 (t, *J* = 2.1 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.05, 147.40, 140.92, 134.83, 132.65, 130.26, 129.38, 129.19, 129.17, 122.65, 117.21, 116.31, 111.39, 107.90, 99.64, 9.00. HRMS (ESI): Calcd. for $C_{18}H_{15}IN_5$ $[M+H]^+$: 302.1400; found: 302.1399.

(12)(*E*)-2-(4-bromo-1*H*-pyrazol-1-yl)-3-iodo-1-methyl-5-(phenyldiazenyl)-1*H*-indole (4aab)



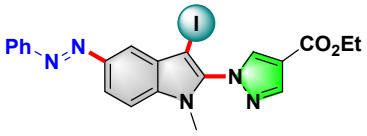
Orange solid, (56.2 mg, 55% yield), m.p.: 195-196 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 13.3 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.49 – 7.45 (m, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.80, 148.10, 143.28, 137.29, 136.56, 133.17, 130.67, 129.19, 128.75, 122.80, 120.25, 118.00, 110.88, 95.51, 56.76, 30.96. HRMS (ESI): Calcd. for $C_{18}H_{13}BrIN_5$ $[M+H]^+$: 505.9471; found: 505.9469.

(13) (*E*)-3-iodo-2-(4-iodo-1*H*-pyrazol-1-yl)-1-methyl-5-(phenyldiazenyl)-1*H*-indole (4aac)



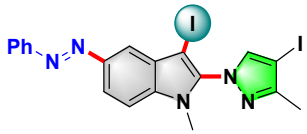
Orange solid, (70.1 mg, 70% yield), m.p.: 199-200 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 2H), 7.91 (d, *J* = 3.1 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.82, 148.11, 147.59, 137.44, 137.32, 136.42, 130.67, 129.20, 128.79, 122.81, 120.25, 118.03, 110.88, 58.84, 56.78, 30.99. HRMS (ESI): Calcd. for $C_{18}H_{13}I_2N_5$ $[M+H]^+$: 553.9333; found: 553.9330.

(14)ethyl*(E)*-1-(3-iodo-1-methyl-5-(phenyldiazenyl)-1*H*-indol-2-yl)-1*H*-pyrazole-4-carboxylate (4aad)



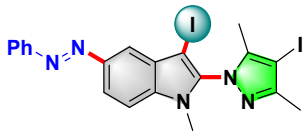
Orange solid, (64.5 mg, 65% yield), m.p.: 203-204 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.26 (s, 1H), 8.14 (d, *J* = 1.9 Hz, 1H), 8.04 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.50, 152.85, 148.23, 143.50, 137.42, 136.81, 136.47, 130.71, 129.21, 128.81, 122.83, 120.35, 118.22, 117.01, 110.94, 60.88, 56.95, 31.09, 14.53. HRMS (ESI): Calcd. for $C_{21}H_{18}IN_5O_2$ $[M+H]^+$: 500.0577; found: 500.0576.

(15)(*E*)-3-iodo-2-(4-iodo-3-methyl-1*H*-pyrazol-1-yl)-1-methyl-5-(phenyldiazenyl)-1*H*-indole (4aae)



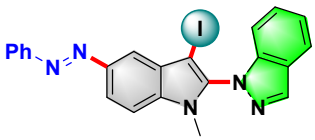
Orange solid, (64.6 mg, 57% yield), m.p.: 201-202 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.95 (d, *J* = 7.0 Hz, 2H), 7.80 (s, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 3.67 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.22, 152.87, 148.08, 138.04, 137.36, 136.86, 130.62, 129.20, 128.85, 122.80, 120.18, 117.92, 110.80, 77.16, 62.65, 56.55, 31.00, 14.03. HRMS (ESI): Calcd. for $C_{19}H_{15}I_2N_5$ $[M+H]^+$: 567.9489; found: 567.9487.

(16)(*E*)-3-iodo-2-(4-iodo-3,5-dimethyl-1*H*-pyrazol-1-yl)-1-methyl-5-(phenyldiazenyl)-1*H* indole (4aaf)



Orange solid, (51.5 mg, 44% yield), m.p.: 209-210 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.04 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 3.55 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.22, 152.86, 148.03, 144.90, 137.31, 136.16, 130.62, 129.18, 128.78, 122.79, 120.27, 117.95, 110.85, 65.20, 59.66, 30.59, 14.56, 12.76. HRMS (ESI): Calcd. for $C_{20}H_{17}I_2N_5$ $[M+H]^+$: 581.9646; found: 581.9643.

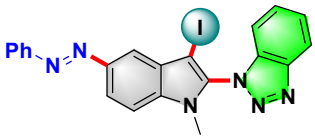
(17) (*E*)-1-(3-iodo-1-methyl-5-(phenyldiazenyl)-1*H*-indol-2-yl)-1*H*-indazole (4aag)



Orange solid, (50.1 mg, 53% yield), m.p.: 225-226 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.22 (d, *J* = 1.8 Hz, 1H), 8.07 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.51 – 7.44 (m, 3H), 7.35 – 7.31 (m, 2H), 3.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.95, 148.07, 141.35, 137.74, 137.68, 136.23, 130.61, 129.23, 129.22,

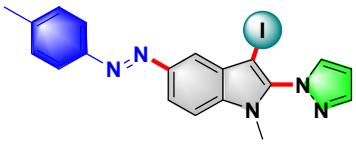
128.06, 124.36, 122.83, 122.43, 121.52, 120.27, 117.78, 111.02, 110.87, 58.50, 30.79. HRMS (ESI): Calcd. for $C_{22}H_{16}IN_5$ $[M+H]^+$: 478.0523; found: 478.0522.

(18) (*E*)-1-(3-iodo-1-methyl-5-(phenyldiazenyl)-1*H*-indol-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4aah)



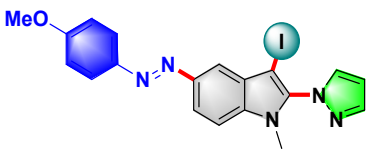
Orange solid, (51.7 mg, 54% yield), m.p.: 221-223 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 – 8.20 (m, 2H), 8.11 (dd, *J* = 8.8, 1.8 Hz, 1H), 8.04 – 7.94 (m, 2H), 7.62 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H), 7.58 – 7.45 (m, 6H), 3.62 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.86, 148.29, 145.54, 137.86, 134.17, 132.97, 130.79, 129.31, 129.25, 129.21, 125.07, 122.88, 120.74, 120.46, 118.40, 111.15, 110.85, 59.07, 30.96. HRMS (ESI): Calcd. for $C_{21}H_{15}IN_6$ $[M+H]^+$: 479.0475; found: 479.0473.

(19) (*E*)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-5-(p-tolyldiazenyl)-1*H*-indole (4aba)



Orange solid, (57.1 mg, 65% yield), m.p.: 203-204 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.90 – 7.85 (m, 4H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 2.2 Hz, 1H), 3.67 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.98, 148.13, 142.61, 141.07, 137.48, 137.28, 133.45, 129.86, 128.96, 122.79, 119.88, 117.75, 110.78, 107.30, 56.23, 30.94, 21.63. HRMS (ESI): Calcd. for $C_{19}H_{16}IN_5$ $[M+H]^+$: 442.0523; found: 442.0521.

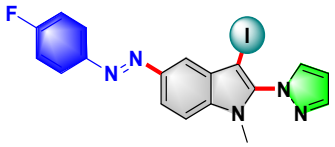
(20)(*E*)-3-iodo-5-((4-methoxyphenyl)diazenyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aca)



Orange solid, (73.1 mg, 80% yield), m.p.: 209-210 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.8 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 2.4 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.04 – 7.01 (m, 2H), 6.56 (t, *J* = 2.2 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.74, 148.11, 147.18, 142.55, 137.37, 137.05,

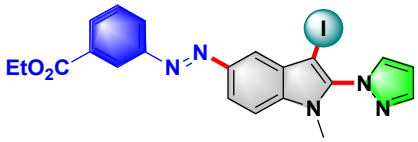
133.43, 128.91, 124.56, 119.35, 117.72, 114.30, 110.73, 107.25, 56.12, 55.68, 30.89. HRMS (ESI): Calcd. for $C_{19}H_{16}IN_5O$ $[M+H]^+$: 458.0472; found: 458.0469.

(21) (*E*)-5-((4-fluorophenyl)diazenyl)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4ada)



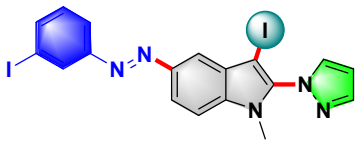
Orange solid, (55 mg, 62% yield), m.p.: 208-209 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.8 Hz, 1H), 8.00 – 7.95 (m, 3H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.20 (t, *J* = 8.6 Hz, 2H), 6.57 (t, *J* = 2.2 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.15 (d, *J* = 251.2 Hz), 149.39 (d, *J* = 3.0 Hz), 147.87, 142.64, 137.58, 137.41, 133.42, 128.95, 124.70 (d, *J* = 8.8 Hz), 120.09, 117.71, 116.09 (d, *J* = 23.0 Hz), 110.83, 107.33, 56.24, 30.96. ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.25. HRMS (ESI): Calcd. for $C_{18}H_{13}FIN_5$ $[M+H]^+$: 446.0272; found: 446.0270.

(22) ethyl(*E*)-3-((3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-5-yl)diazenyl)benzoate (4aea)



Orange solid, (56.8 mg, 57% yield), m.p.: 205-207 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.16 (d, *J* = 1.9 Hz, 1H), 8.15 – 8.11 (m, 2H), 8.03 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.30, 152.84, 147.91, 142.66, 137.66, 137.63, 133.43, 131.74, 131.28, 129.22, 128.98, 126.52, 124.18, 120.59, 117.77, 110.88, 107.35, 61.39, 56.35, 30.98, 14.52. HRMS (ESI): Calcd. for $C_{21}H_{18}IN_5O_2$ $[M+H]^+$: 500.0577; found: 500.0575.

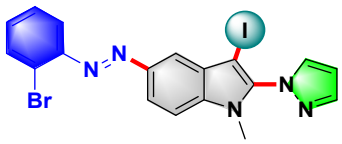
(23)(*E*)-3-iodo-5-((3-iodophenyl)diazenyl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4afa)



Orange solid, (55.2 mg, 50% yield), m.p.: 209-210 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (t, *J* = 1.8 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.88

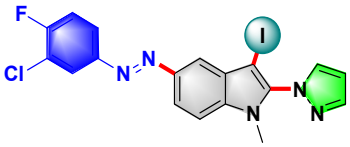
(d, J = 1.9 Hz, 1H), 7.84 (d, J = 2.5 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 1H), 7.25 – 7.23 (m, 1H), 6.55 (t, J = 2.2 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.66, 147.76, 142.67, 139.07, 137.67, 137.66, 133.43, 130.73, 130.54, 128.96, 123.49, 120.70, 117.72, 110.88, 107.36, 94.74, 56.38, 31.00. HRMS (ESI): Calcd. for $C_{18}H_{13}I_2N_5$ $[M+H]^+$: 553.9333; found: 553.9330.

(24) (*E*)-5-((2-bromophenyl)diazenyl)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aga)



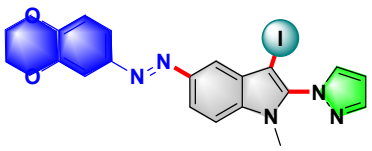
Orange solid, (52.6 mg, 52% yield), m.p.: 209-210 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, J = 1.8 Hz, 1H), 8.07 (dd, J = 8.9, 1.9 Hz, 1H), 7.90 (d, J = 1.9 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H), 7.75 (ddd, J = 9.5, 8.0, 1.5 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.28 (m, 1H), 6.57 (t, J = 2.1 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.88, 148.25, 142.69, 137.71, 137.64, 133.81, 133.45, 131.47, 128.96, 128.13, 125.47, 122.27, 118.00, 117.18, 110.99, 107.37, 56.45, 31.01. HRMS (ESI): Calcd. for $C_{18}H_{13}BrIN_5$ $[M+H]^+$: 505.9471; found: 505.9468.

(25) (*E*)-5-((3-chloro-4-fluorophenyl)diazenyl)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aha)



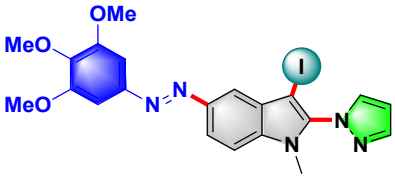
Orange solid, (61.3 mg, 64% yield), m.p.: 205-206 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 1.9 Hz, 1H), 8.03 (dd, J = 7.0, 2.4 Hz, 1H), 7.98 (dd, J = 8.9, 1.9 Hz, 1H), 7.91 – 7.86 (m, 3H), 7.40 (d, J = 8.8 Hz, 1H), 7.29 (t, J = 8.6 Hz, 1H), 6.58 (t, J = 2.2 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.28 (d, J = 253.7 Hz), 149.47 (d, J = 3.4 Hz), 147.67, 142.71, 137.74, 137.68, 133.43, 129.01, 123.98 (d, J = 7.7 Hz), 123.90, 122.17 (d, J = 19.3 Hz), 120.61, 117.74, 116.97 (d, J = 22.5 Hz), 110.93, 107.40, 56.37, 31.01. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.71. HRMS (ESI): Calcd. for $C_{18}H_{12}ClFIN_5$ $[M+H]^+$: 479.9882; found: 479.9881.

(26) (*E*)-5-((2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)diazenyl)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aia)



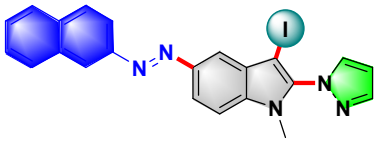
Orange solid, (68.8 mg, 71% yield), m.p.: 208-210 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.9 Hz, 1H), 7.97 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.56 (t, *J* = 2.2 Hz, 1H), 4.33 (t, *J* = 4.9 Hz, 4H), 3.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.00, 147.65, 146.09, 143.97, 142.57, 137.41, 137.13, 133.44, 128.91, 119.54, 117.99, 117.75, 117.48, 110.77, 110.73, 107.27, 64.71, 64.34, 56.14, 30.91. HRMS (ESI): Calcd. for $C_{20}H_{16}IN_5O_2$ $[M+H]^+$: 486.0421; found: 486.0420.

(27) (*E*)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-5-((3,4,5-trimethoxyphenyl)diazenyl)-1*H*-indole (4aja)



Orange solid, (52.7 mg, 51% yield), m.p.: 214-215 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 1.8 Hz, 1H), 7.99 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.86 – 7.84 (m, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.30 (s, 2H), 6.58 – 6.56 (m, 1H), 3.99 (s, 6H), 3.94 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.63, 148.75, 147.89, 142.63, 140.31, 137.55, 137.32, 133.42, 128.97, 119.86, 117.74, 110.84, 107.32, 100.30, 61.16, 56.33, 56.22, 30.94. HRMS (ESI): Calcd. for $C_{21}H_{20}IN_5O_3$ $[M+H]^+$: 518.0683; found: 518.0679.

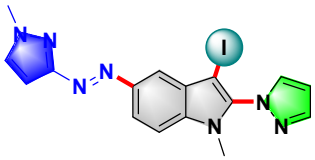
(28)(*E*)-3-iodo-1-methyl-5-(naphthalen-2-yldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aka)



Orange solid, (54 mg, 56% yield), m.p.: 211-213 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 8.14 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.09 (dd, *J* = 8.8, 1.9 Hz, 1H), 8.04 – 8.01 (m, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.90 (q, *J* = 3.7 Hz, 2H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.56 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (151

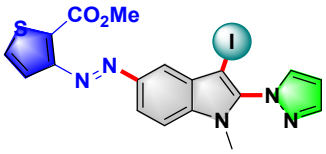
MHz, $CDCl_3$) δ 150.49, 148.21, 142.65, 137.56, 137.45, 134.74, 133.77, 133.46, 129.42, 129.20, 129.03, 128.05, 127.41, 127.30, 126.77, 120.12, 117.87, 117.52, 110.86, 107.34, 56.33, 30.97. HRMS (ESI): Calcd. for $C_{22}H_{16}IN_5$ $[M+H]^+$: 478.0523; found: 478.0521.

(29) (*E*)-3-iodo-1-methyl-5-((1-methyl-1H-pyrazol-3-yl)diazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4ala)



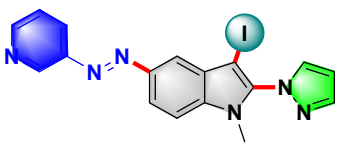
Orange solid, (48.9 mg, 57% yield), m.p.: 235-236 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.8 Hz, 1H), 8.05 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.83 (dd, *J* = 2.5, 0.6 Hz, 1H), 7.40 – 7.37 (m, 2H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.56 – 6.53 (m, 1H), 4.02 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.87, 148.11, 142.57, 137.48, 137.45, 133.42, 131.86, 128.90, 119.98, 117.99, 110.76, 107.27, 95.94, 56.27, 39.73, 30.90. HRMS (ESI): Calcd. for $C_{16}H_{14}IN_7$ $[M+H]^+$: 432.0428; found: 432.0425.

(30) methyl (*E*)-3-((3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-5-yl)diazenyl)thiophene-2-carboxylate (4ama)



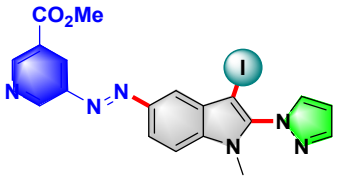
Orange solid, (46.9 mg, 48% yield), m.p.: 206-208 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.9 Hz, 1H), 8.06 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.89 (d, *J* = 1.4 Hz, 1H), 7.85 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 5.4 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.57 – 6.55 (m, 1H), 4.00 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.14, 156.93, 148.41, 142.66, 137.85, 137.62, 133.43, 130.09, 129.49, 128.97, 122.23, 119.01, 117.10, 111.04, 107.35, 56.47, 52.60, 31.00. HRMS (ESI): Calcd. for $C_{18}H_{14}IN_5O_2S$ $[M+H]^+$: 491.9985; found: 491.9981.

(31)(*E*)-3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-5-(pyridin-3-yldiazenyl)-1*H*-indole (4ana)



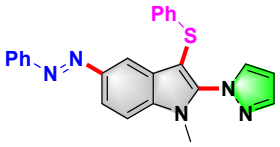
Orange solid, (51.9 mg, 61% yield), m.p.: 205-206 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.69 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.89 (d, *J* = 1.3 Hz, 1H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.45 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 6.58 – 6.55 (m, 1H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.00, 148.17, 147.97, 147.06, 142.70, 137.79, 137.77, 133.41, 128.97, 127.09, 124.15, 120.93, 117.64, 110.94, 107.39, 56.43, 31.01. HRMS (ESI): Calcd. for $C_{17}H_{13}IN_6$ $[M+H]^+$: 429.0319; found: 429.0316.

(32)methyl (*E*)-5-((3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-5-yl)diazenyl)nicotinate (4aoa)



Orange solid, (50.2 mg, 51% yield), m.p.: 210-211 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (s, 1H), 9.27 (s, 1H), 8.72 (t, *J* = 2.1 Hz, 1H), 8.17 (d, *J* = 1.9 Hz, 1H), 8.03 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.88 (dd, *J* = 15.0, 2.0 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.60 – 6.56 (m, 1H), 4.01 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.52, 151.63, 150.30, 147.85, 147.70, 142.72, 137.99, 137.85, 133.42, 128.97, 127.95, 126.78, 121.39, 117.64, 111.01, 107.42, 56.53, 52.77, 31.02. HRMS (ESI): Calcd. for $C_{19}H_{15}IN_6O_2$ $[M+H]^+$: 446.0272; found: 446.0270.

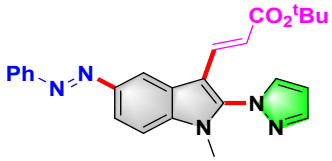
(33)(*E*)-1-methyl-5-(phenyldiazenyl)-3-(phenylthio)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (5aaa)



Orange solid, (35.6 mg, 87% yield), m.p.: 199-200 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.88 – 7.85 (m, 1H), 7.74 (d, *J* = 2.5 Hz, 1H), 7.51 (dd, *J* = 8.4, 6.7 Hz, 3H), 7.46 – 7.42 (m, 1H), 7.18 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.14 – 7.11 (m, 2H), 7.10 – 7.06 (m, 1H), 6.48 – 6.46 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.90, 148.29, 142.61, 140.22, 138.24, 136.92, 133.57, 130.54, 129.15, 129.13, 128.58, 126.28, 125.45, 122.75, 118.57, 117.24, 110.77, 107.15, 97.72, 31.24. HRMS (ESI): Calcd. for $C_{24}H_{19}N_5S$ $[M+H]^+$: 410.1433; found: 410.1430.

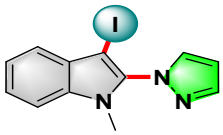
(34)*tert*-butyl(*E*)-3-(1-methyl-5-((*E*)-phenyldiazenyl)-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)

acrylate (6aaa)



Orange solid, (29.8 mg, 70% yield), m.p.: 207-208 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.76 (d, *J* = 2.4 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.49 – 7.45 (m, 2H), 6.59 (t, *J* = 2.2 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.19, 152.94, 148.52, 143.02, 137.48, 137.09, 133.79, 133.49, 130.66, 129.24, 124.21, 122.78, 120.12, 118.39, 116.92, 110.85, 108.26, 107.94, 80.35, 30.36, 28.42. HRMS (ESI): Calcd. for $C_{25}H_{25}N_5O_2$ $[M+H]^+$: 428.2081; found: 428.2082.

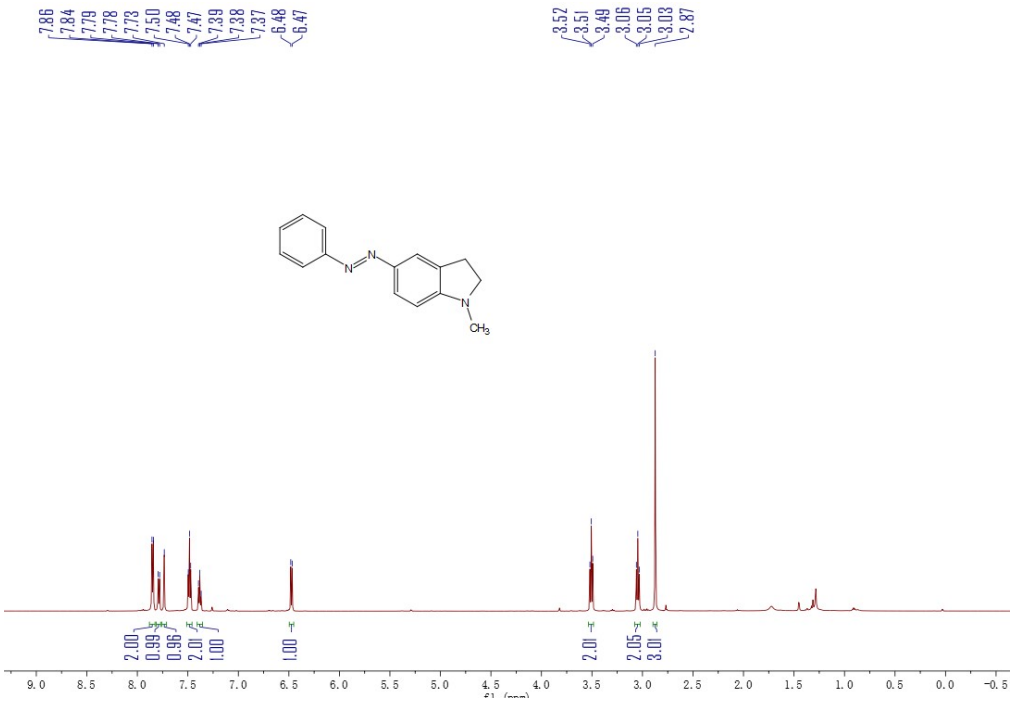
(35)3-iodo-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (1a-3)



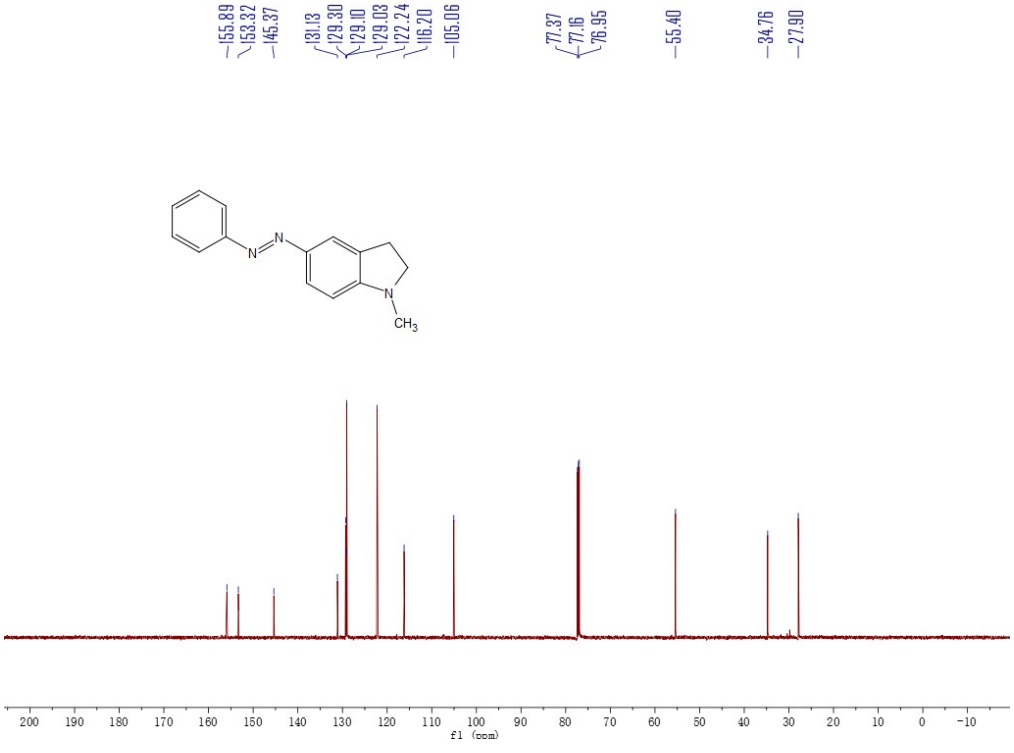
White solid, (51.6 mg, 80% yield), m.p.: 103-105 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.53 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.40 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.35 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.30 (ddd, *J* = 9.5, 7.7, 1.8 Hz, 1H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.40, 136.36, 135.80, 133.44, 128.61, 124.16, 122.02, 121.37, 110.15, 107.09, 54.45, 30.54. HRMS (ESI): Calcd. for $C_{12}H_{10}IN_3$ $[M+H]^+$: 323.9992; found: 323.9991.

8. Copies of NMR spectra

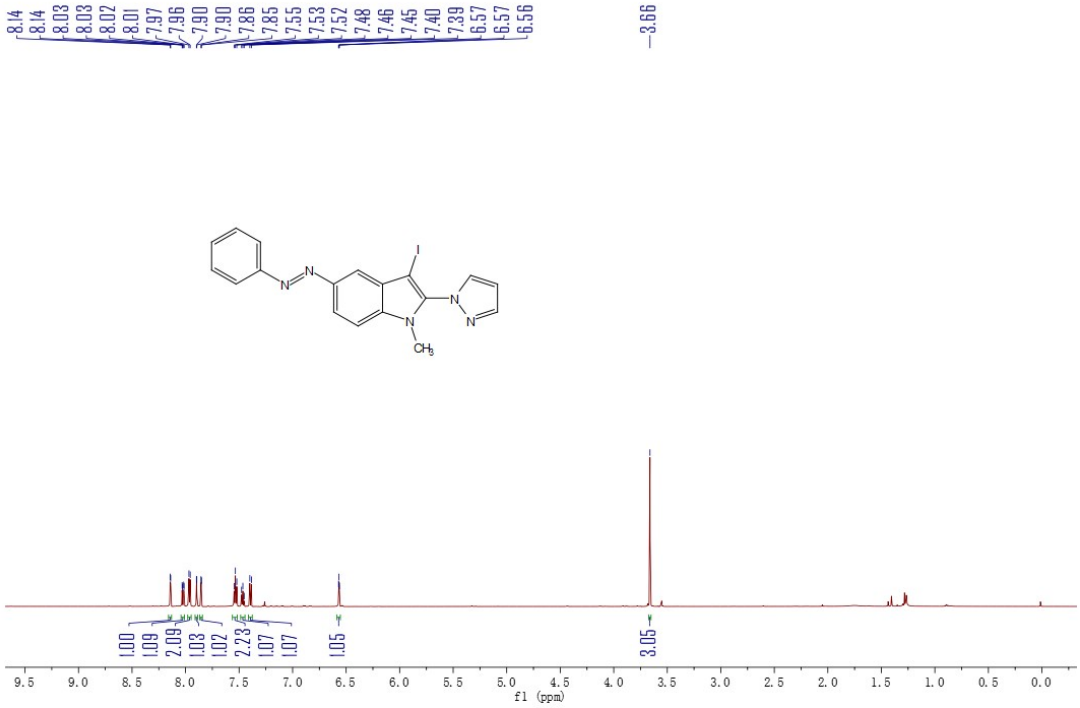
(1) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 1a-1



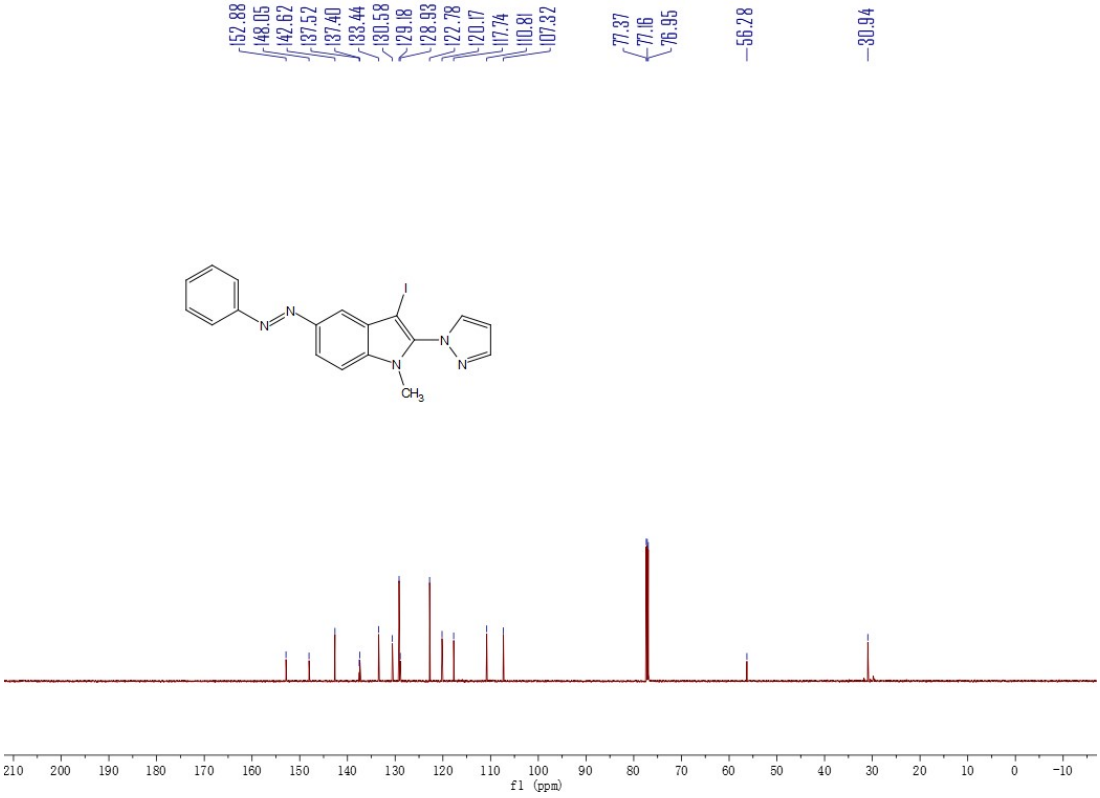
(2) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 1a-1



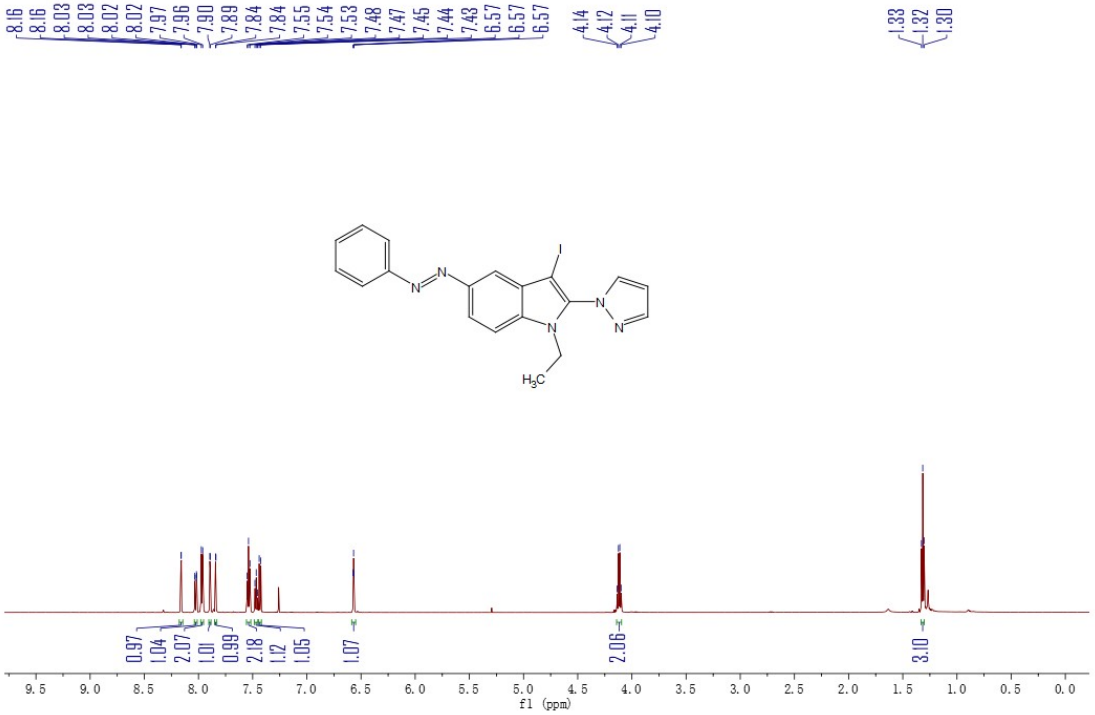
(3) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aaa



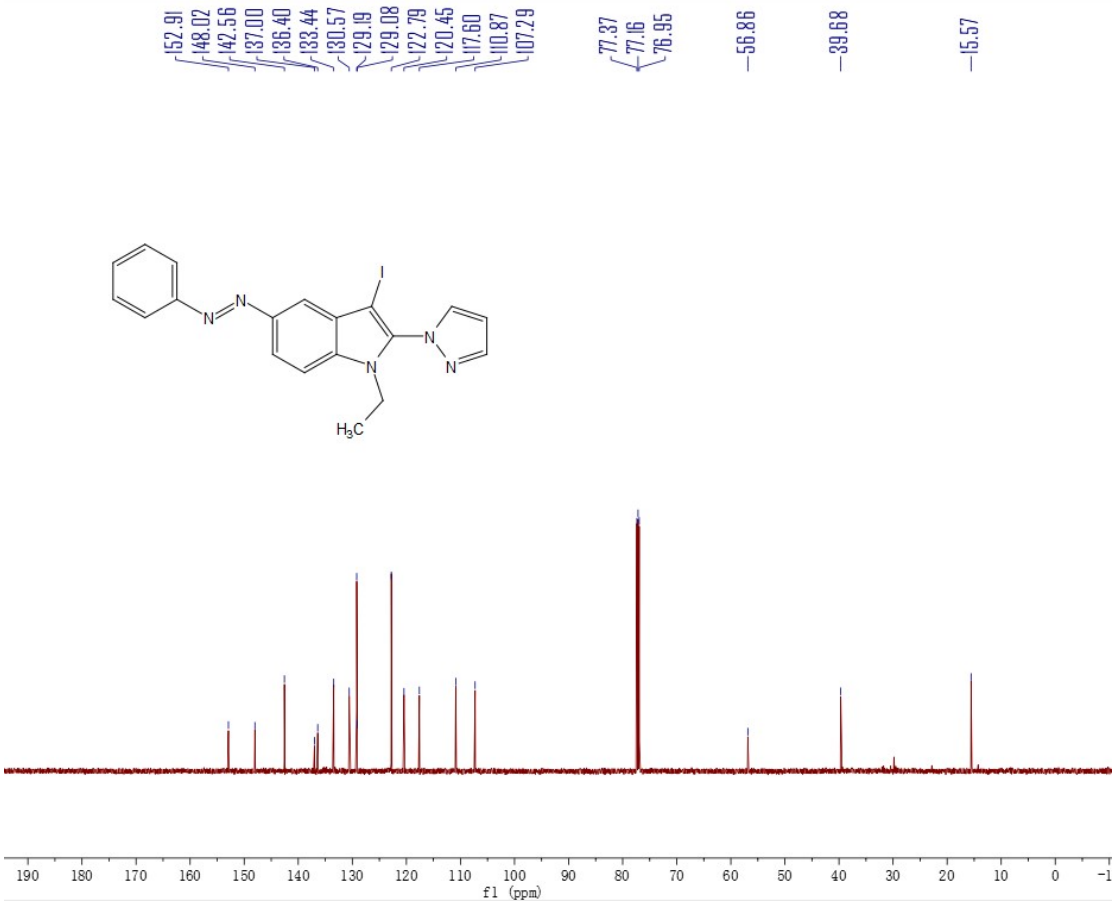
(4) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aaa



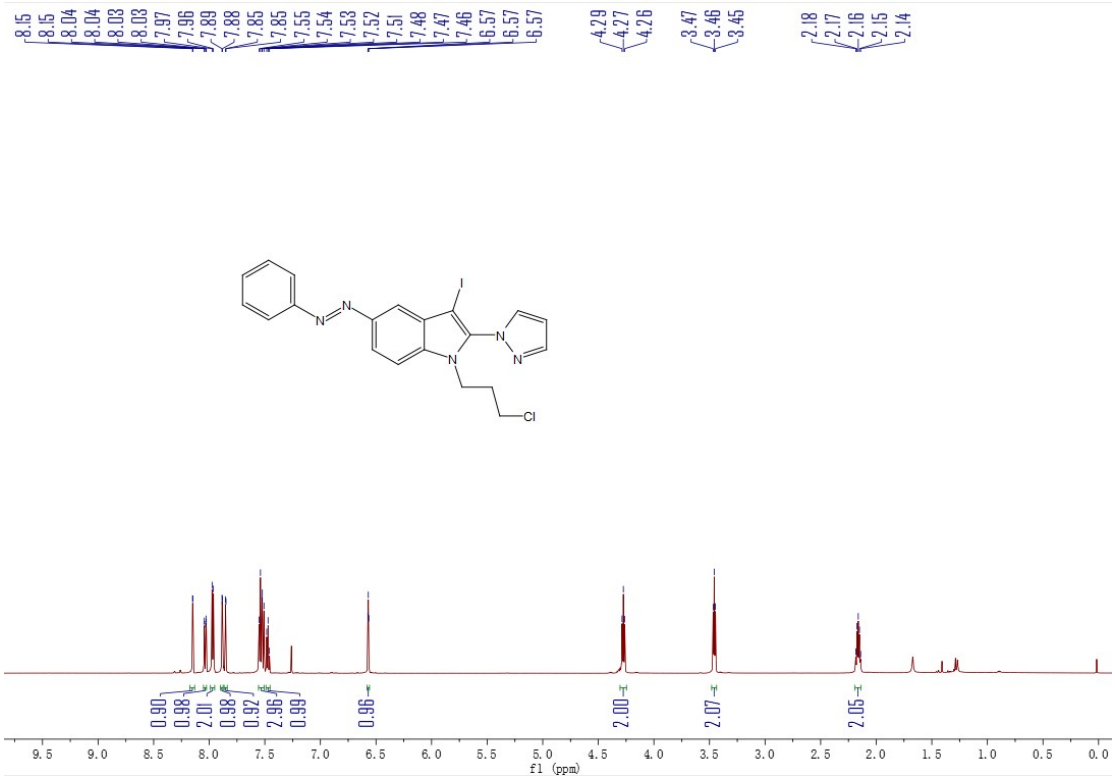
(5) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4baa



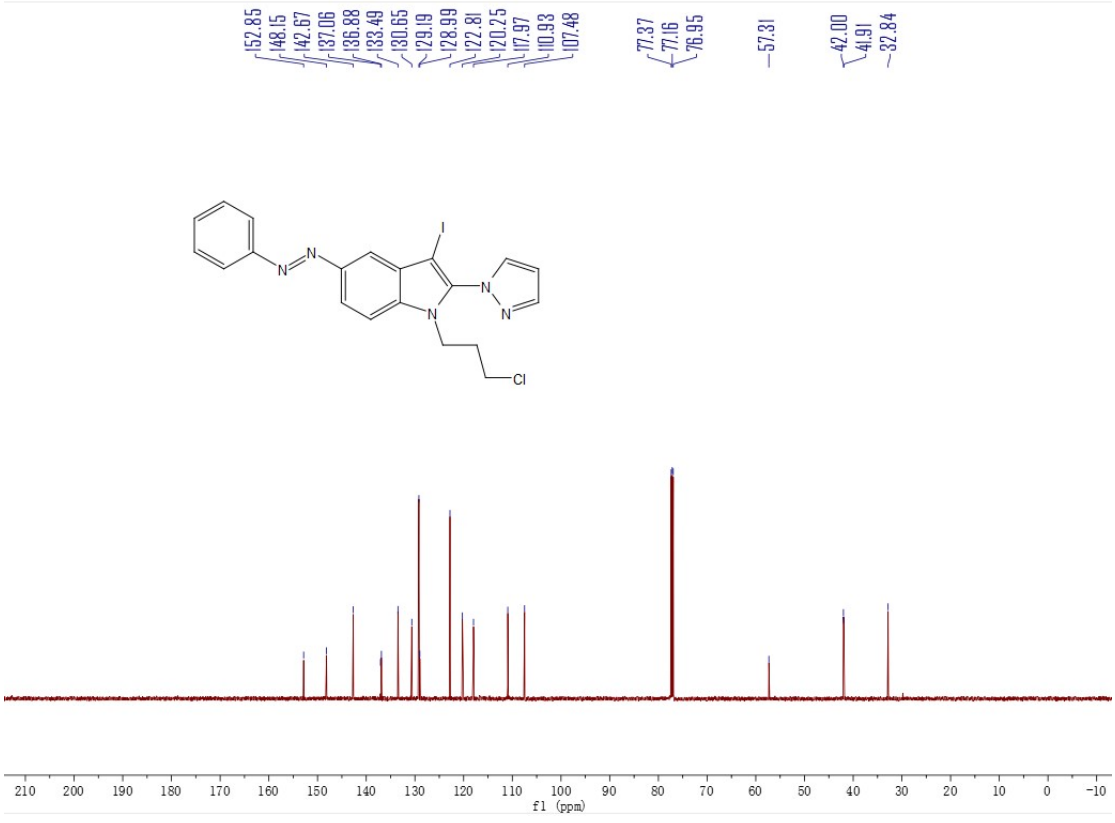
(6) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4baa



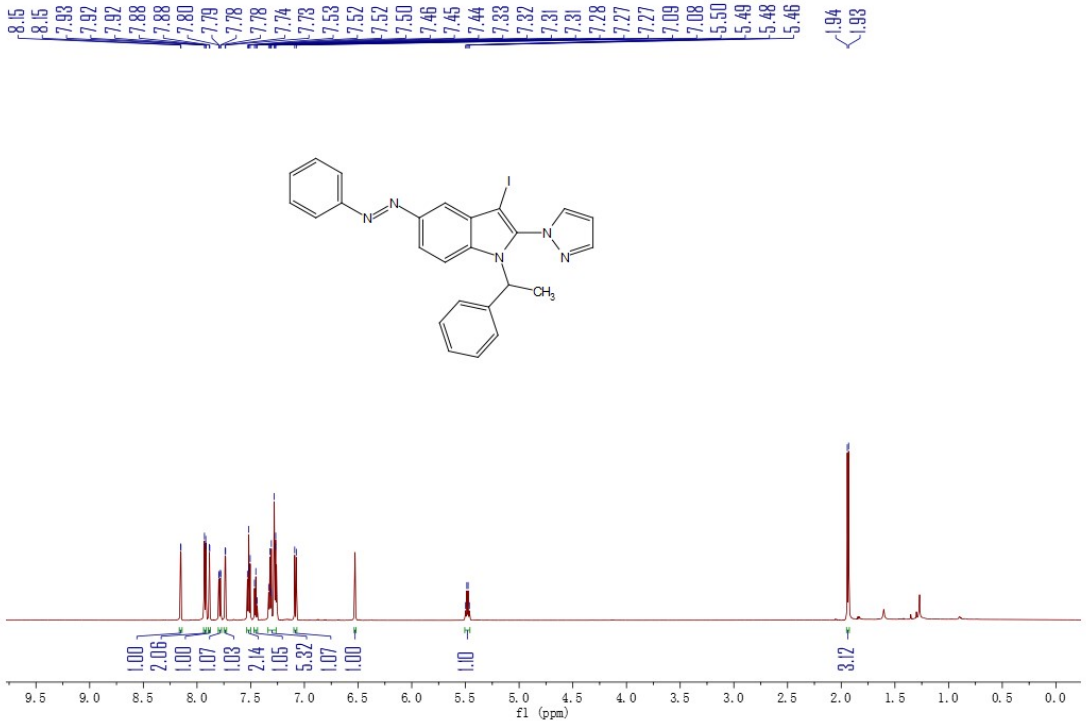
(7) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4daa



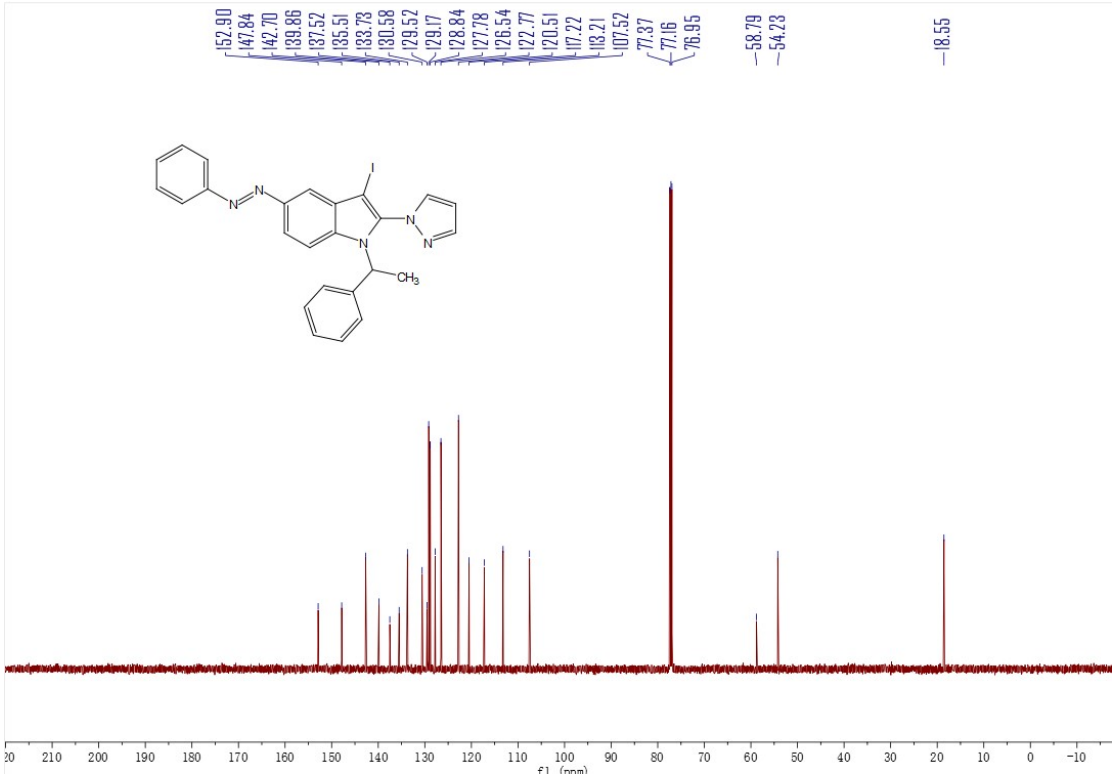
(8) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4daa



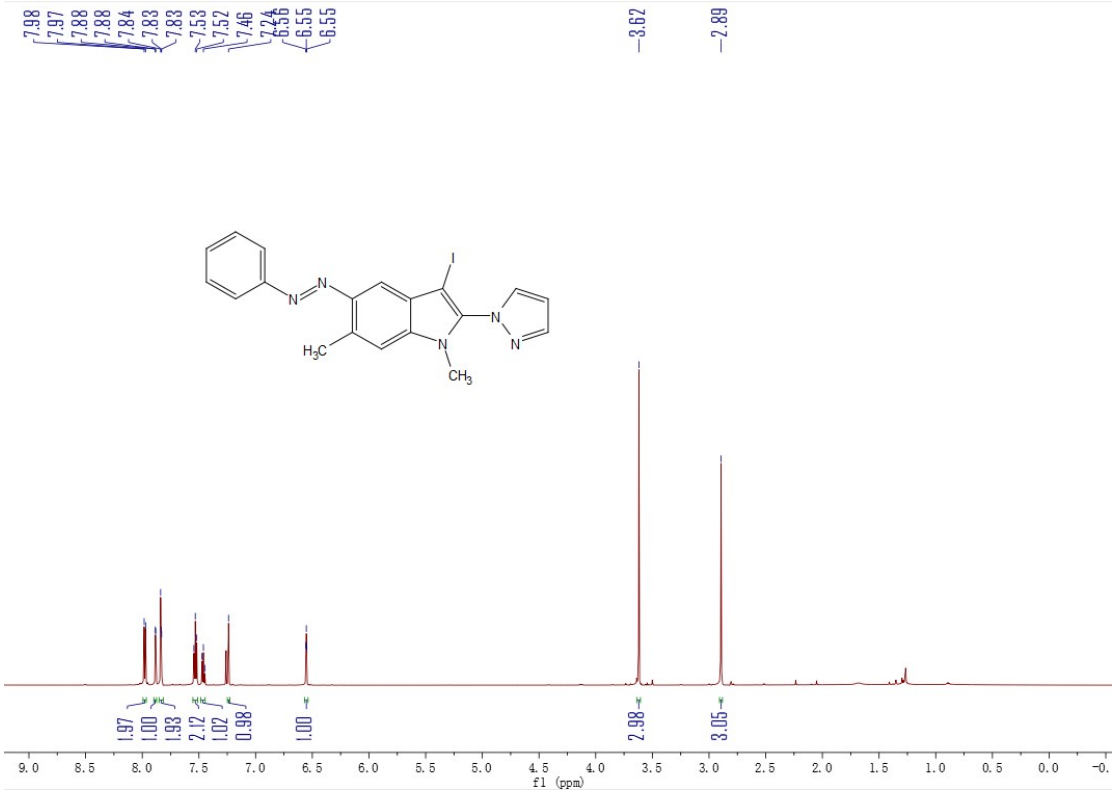
(9) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4eaa



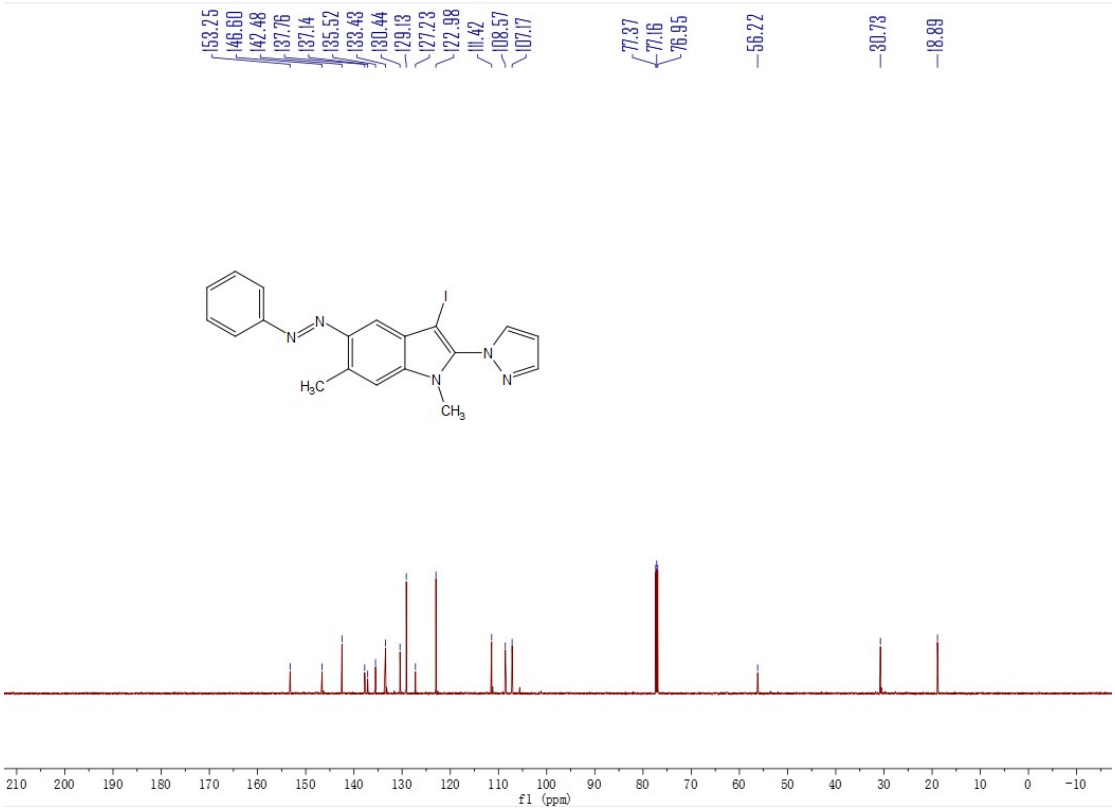
(10)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4eaa



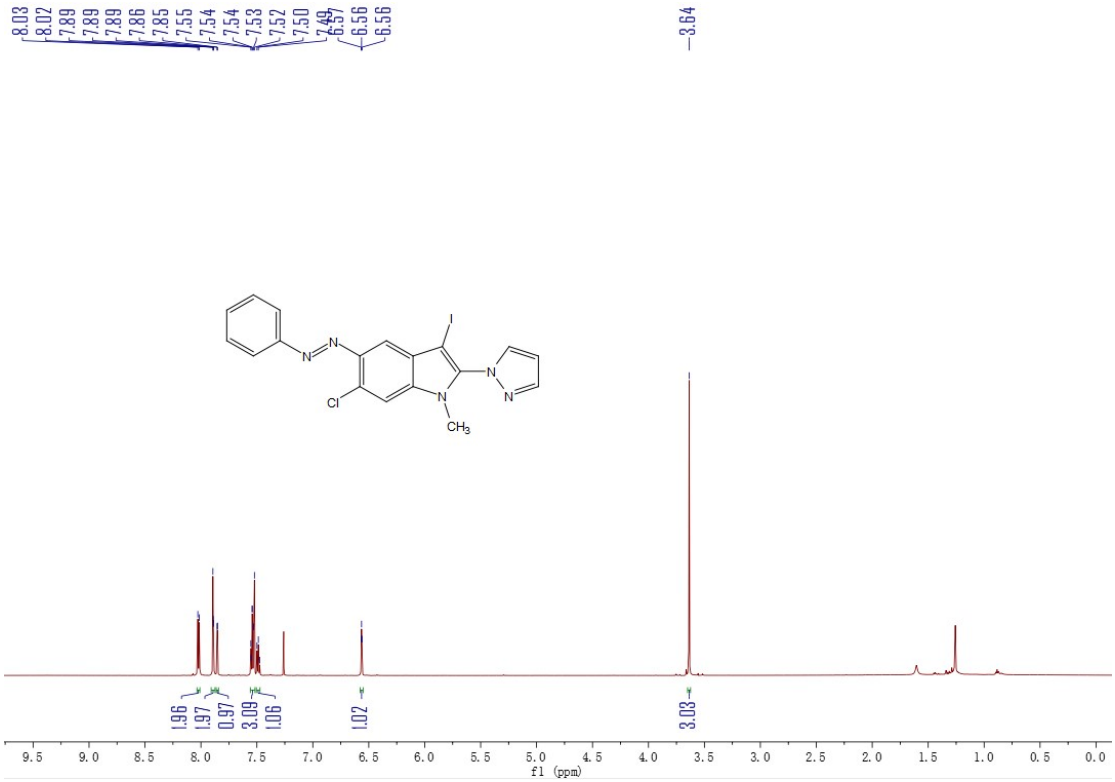
(11)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4gaa



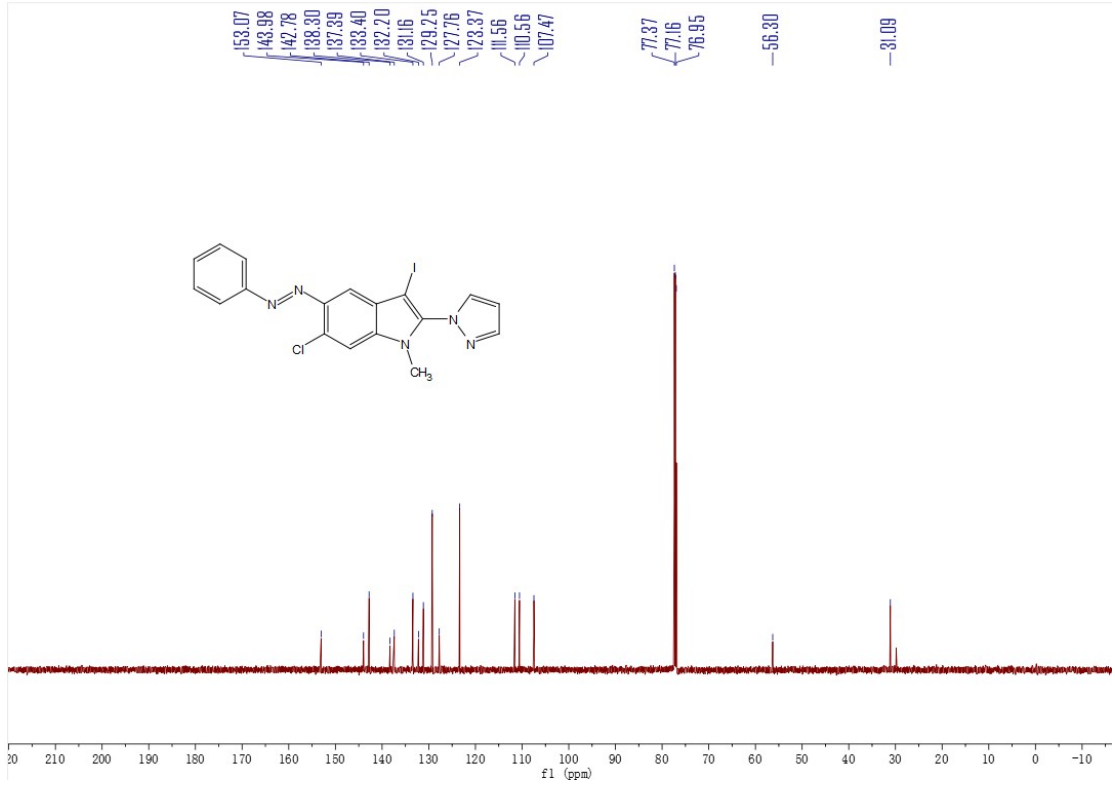
(12)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4gaa



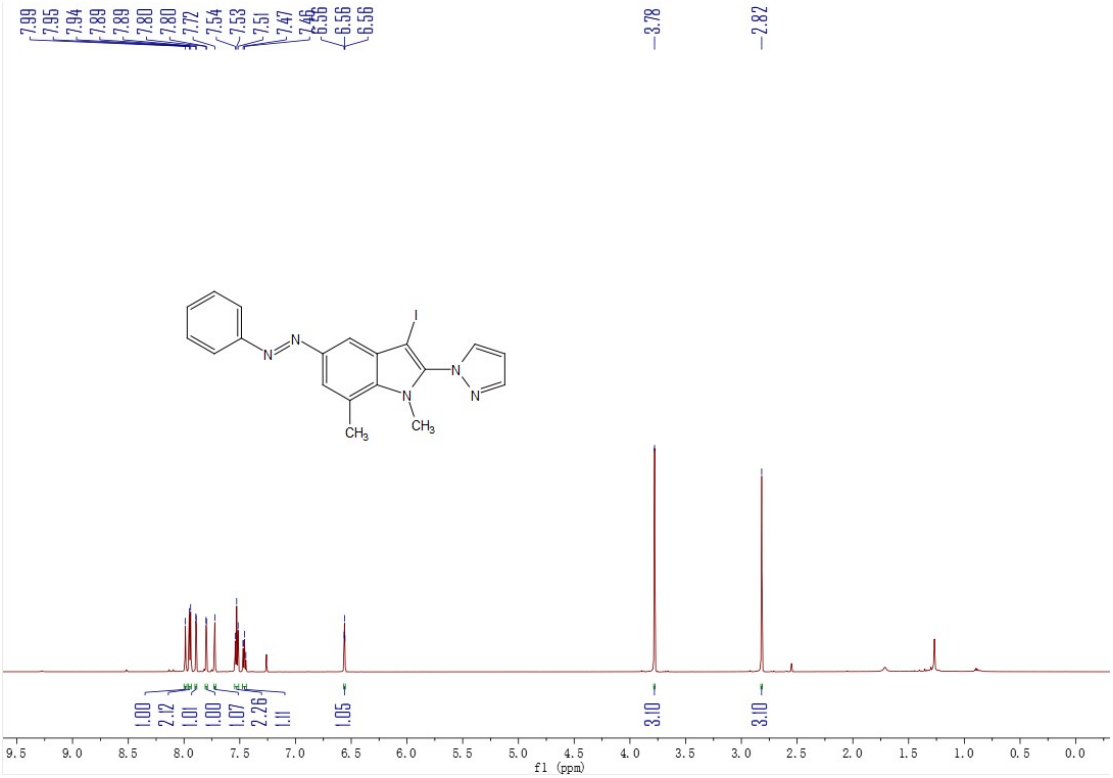
(13)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4haa



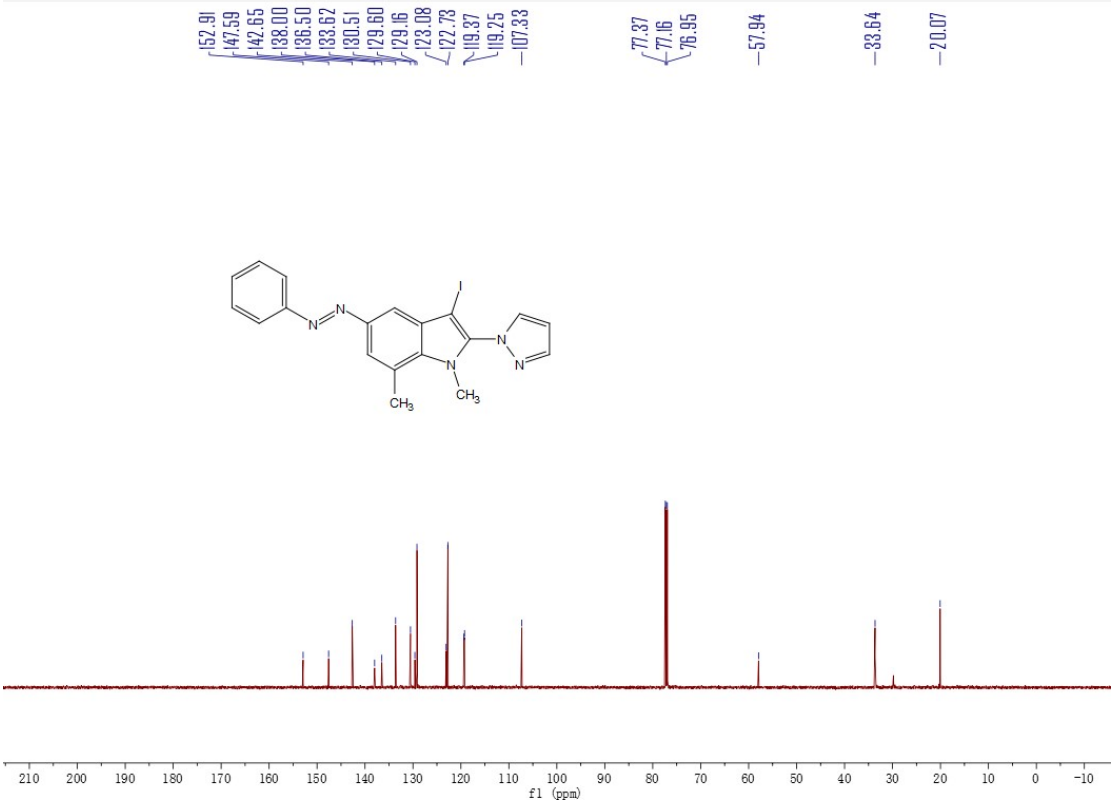
(14)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4haa



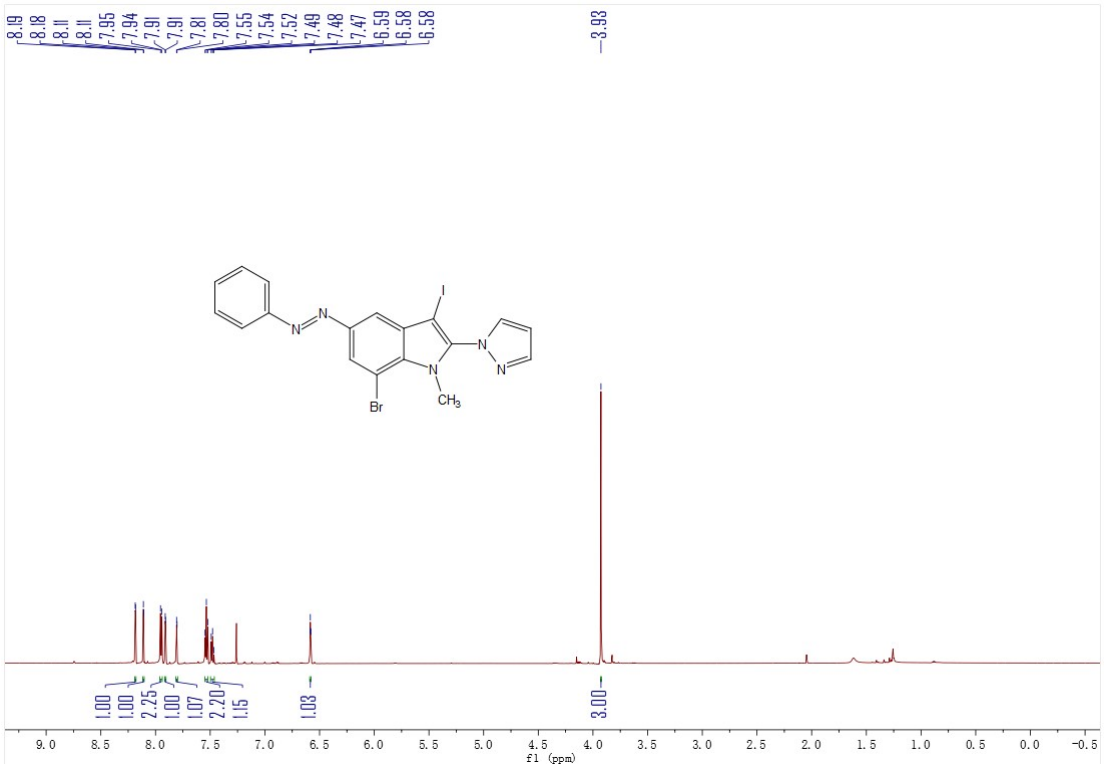
(15)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4iaa



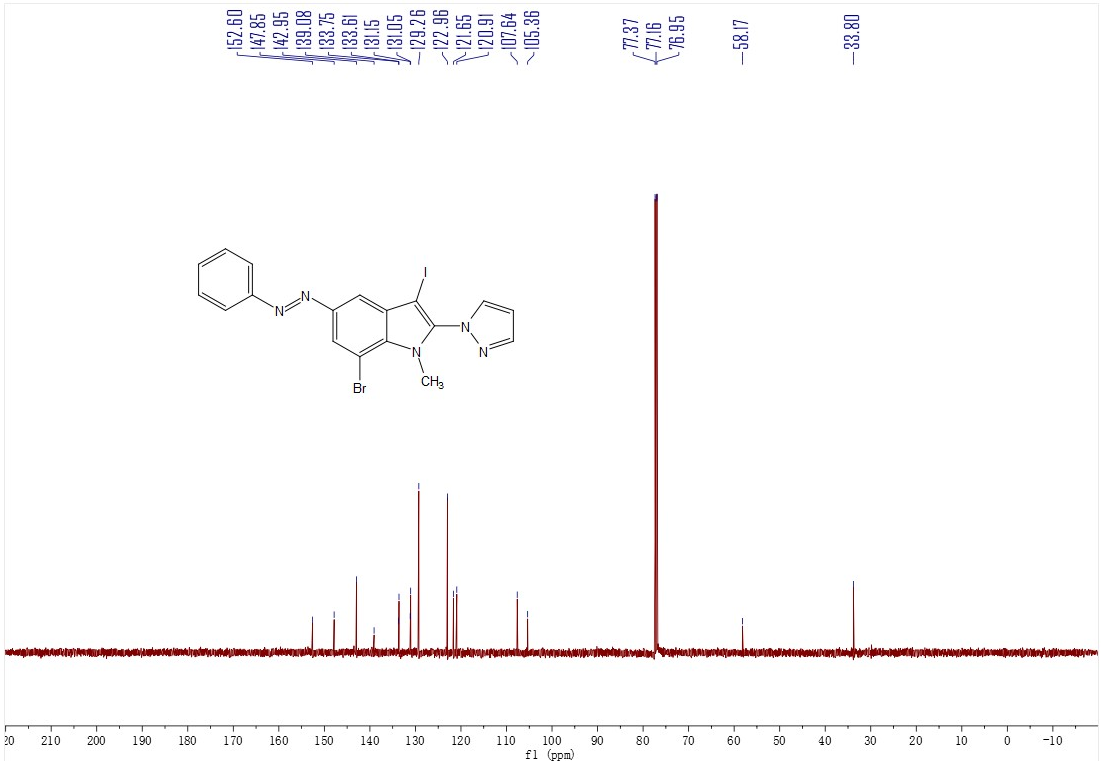
(16)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4iaa



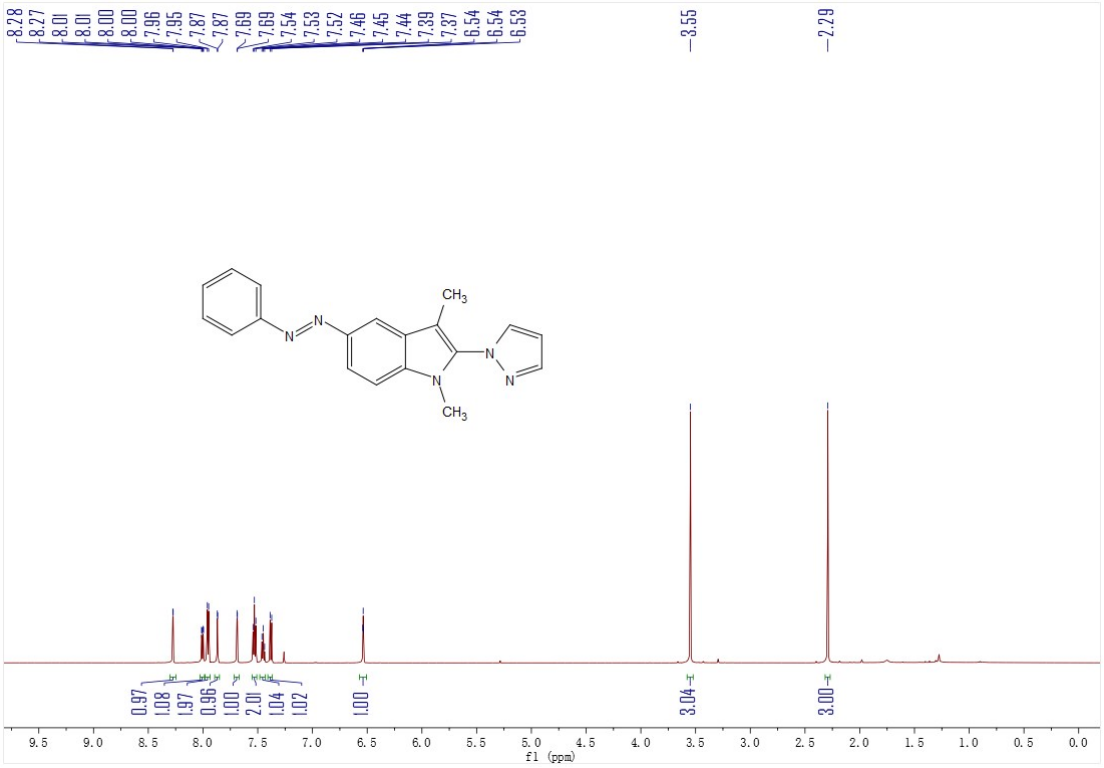
(17)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4jaa



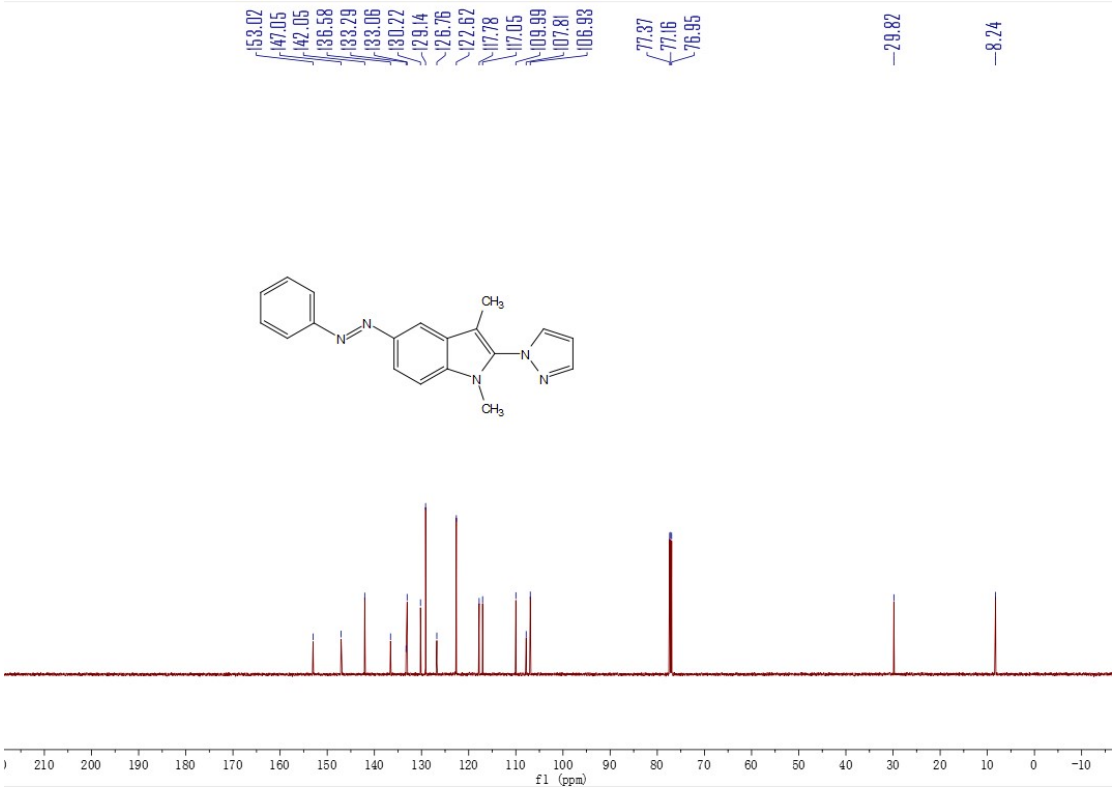
(18)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4jaa



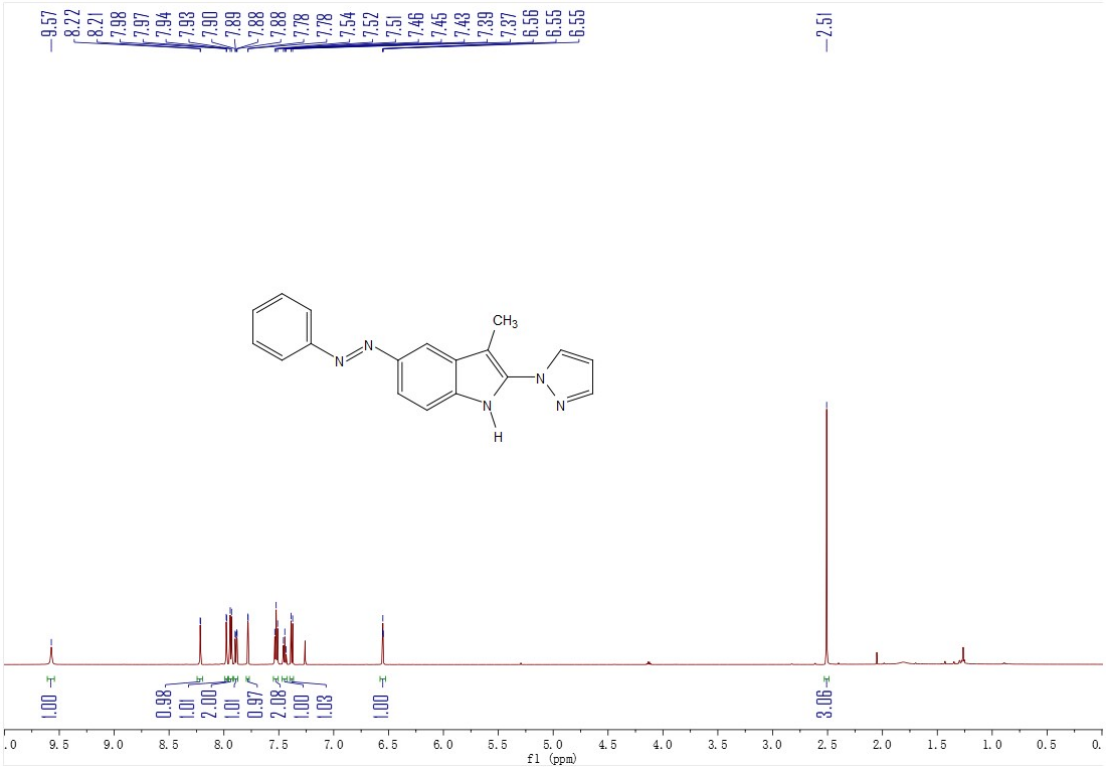
(19)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4kaa



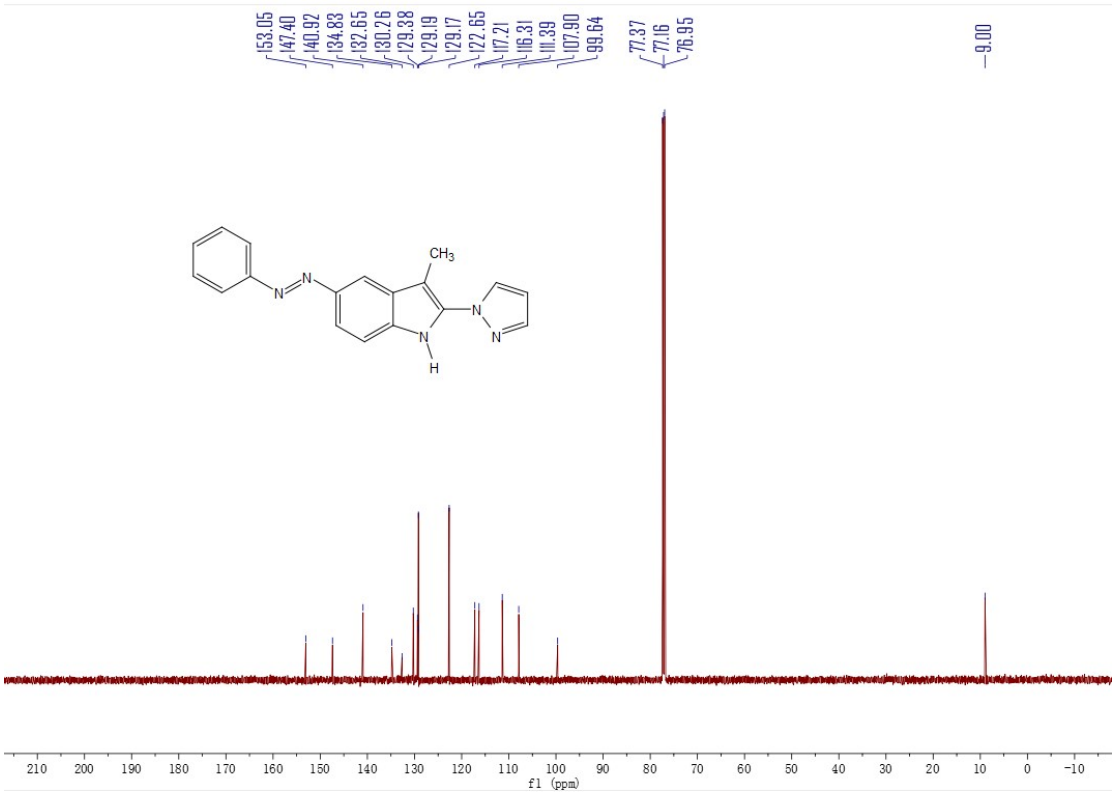
(20)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4kaa



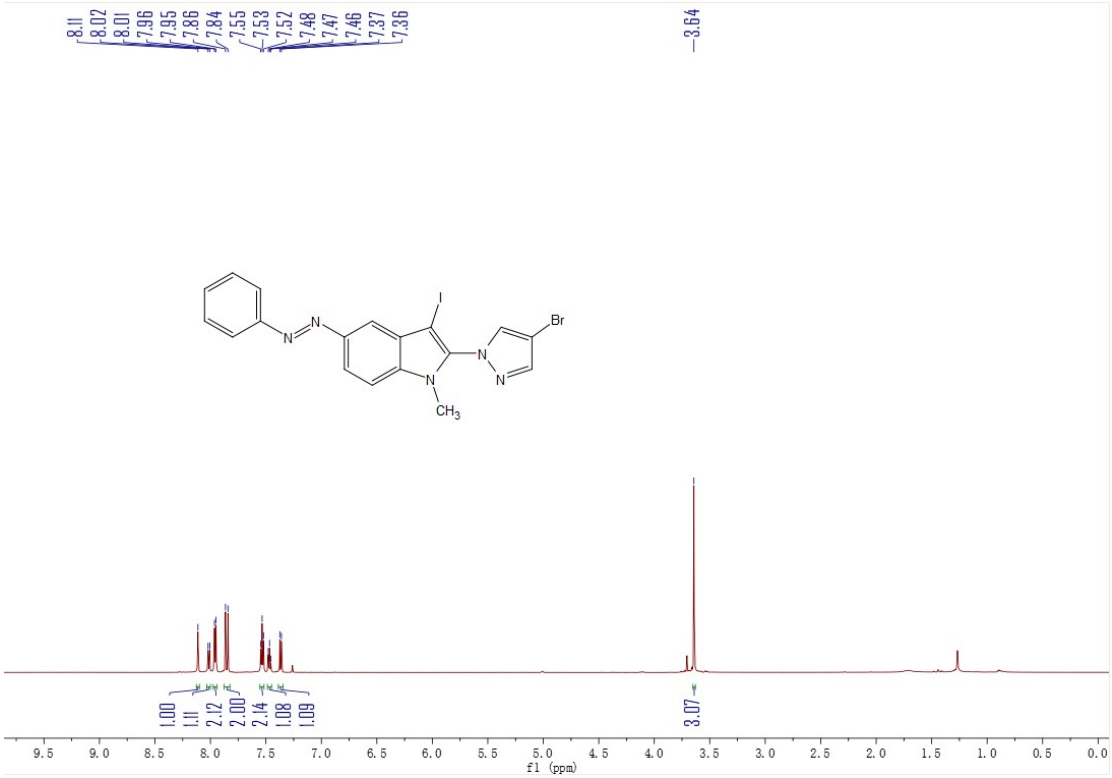
(21)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4laa



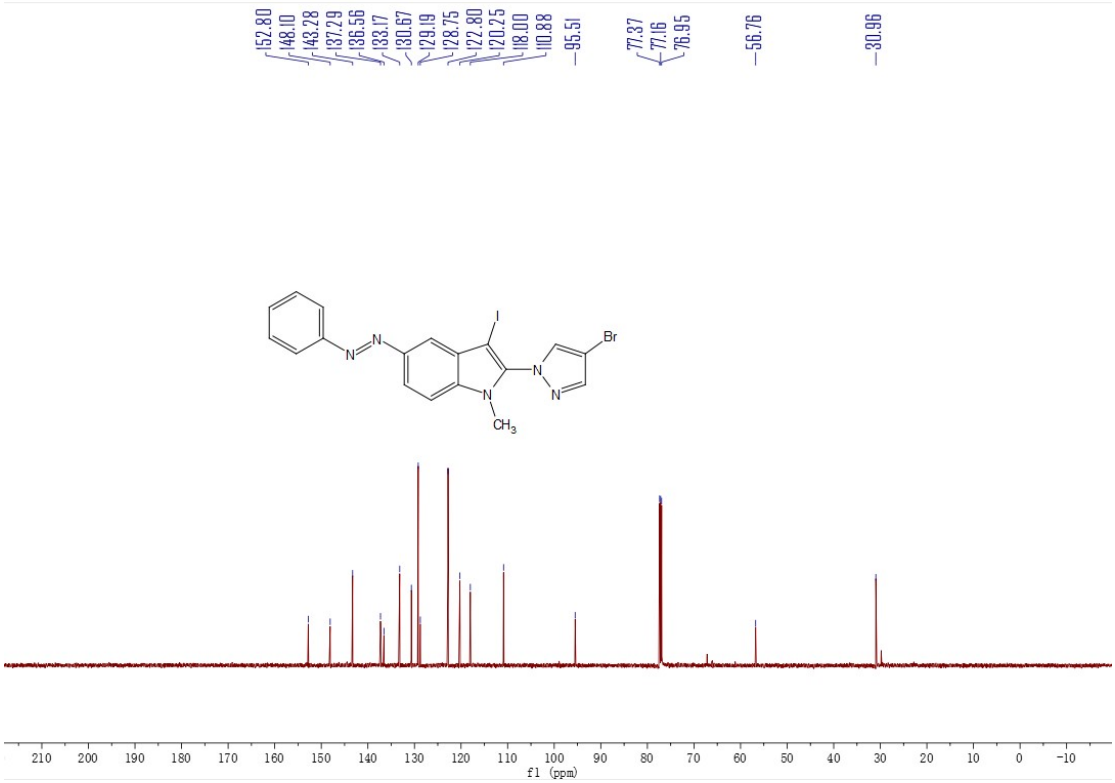
(22)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4laa



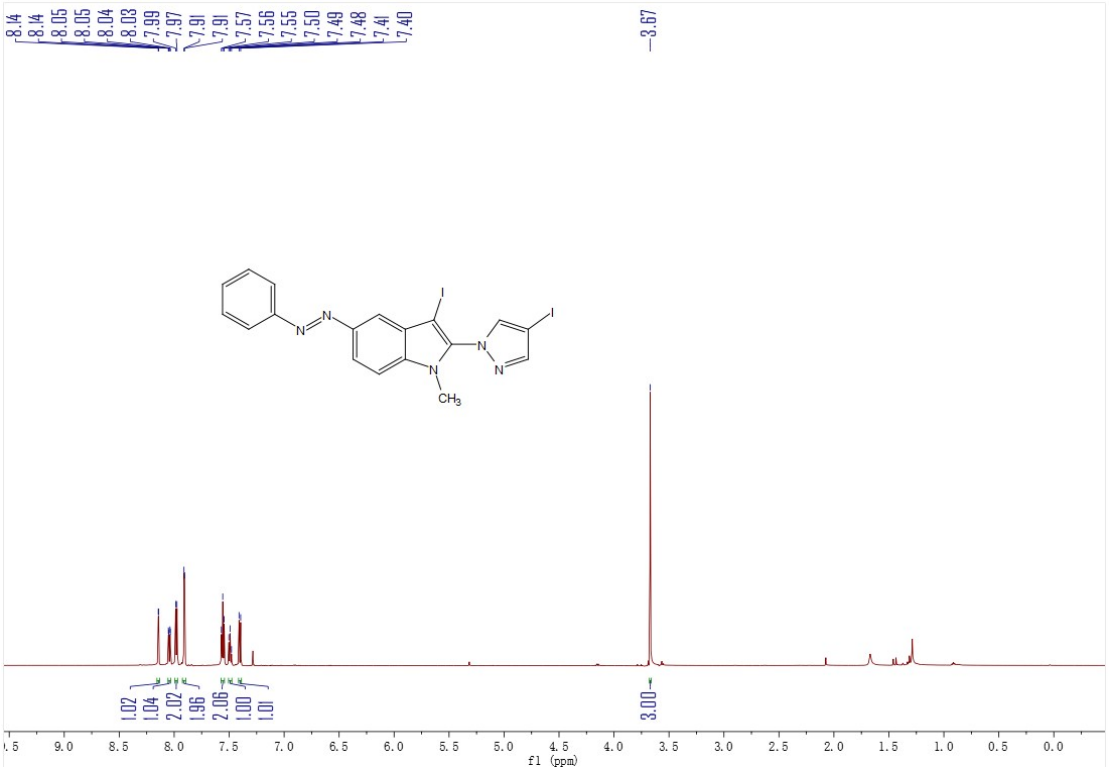
(23)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aab



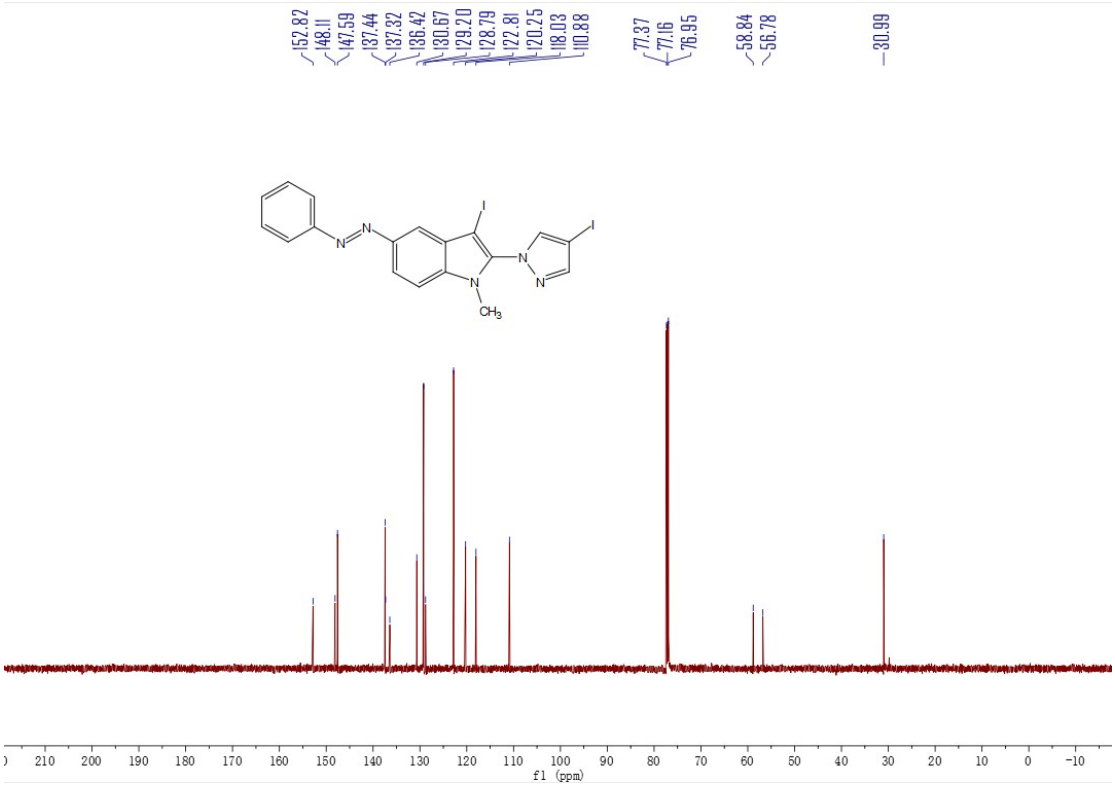
(24)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aab



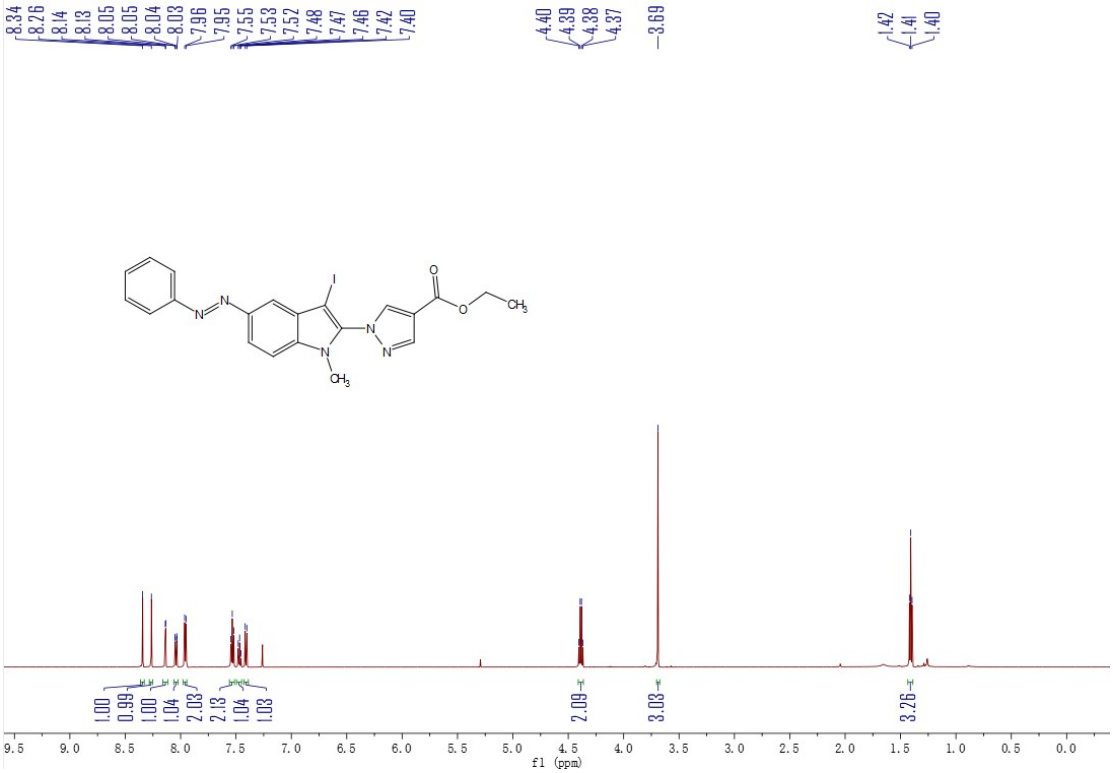
(25)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aac



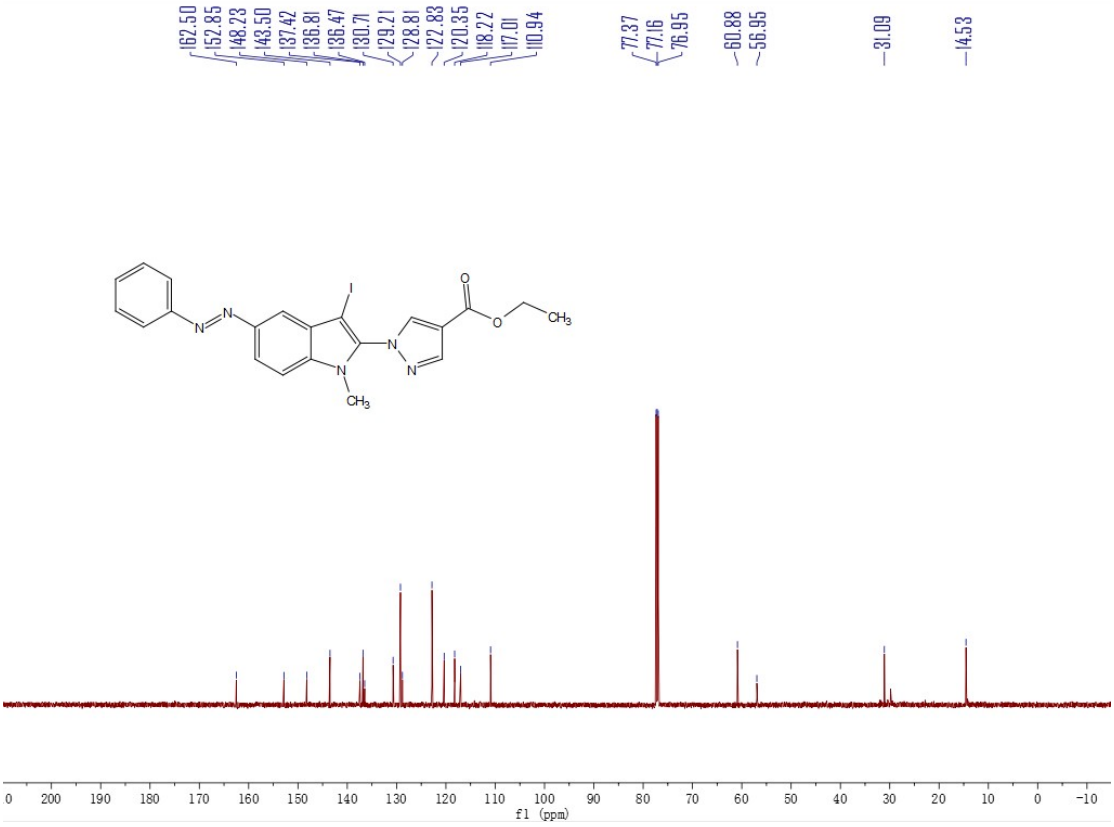
(26)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aac



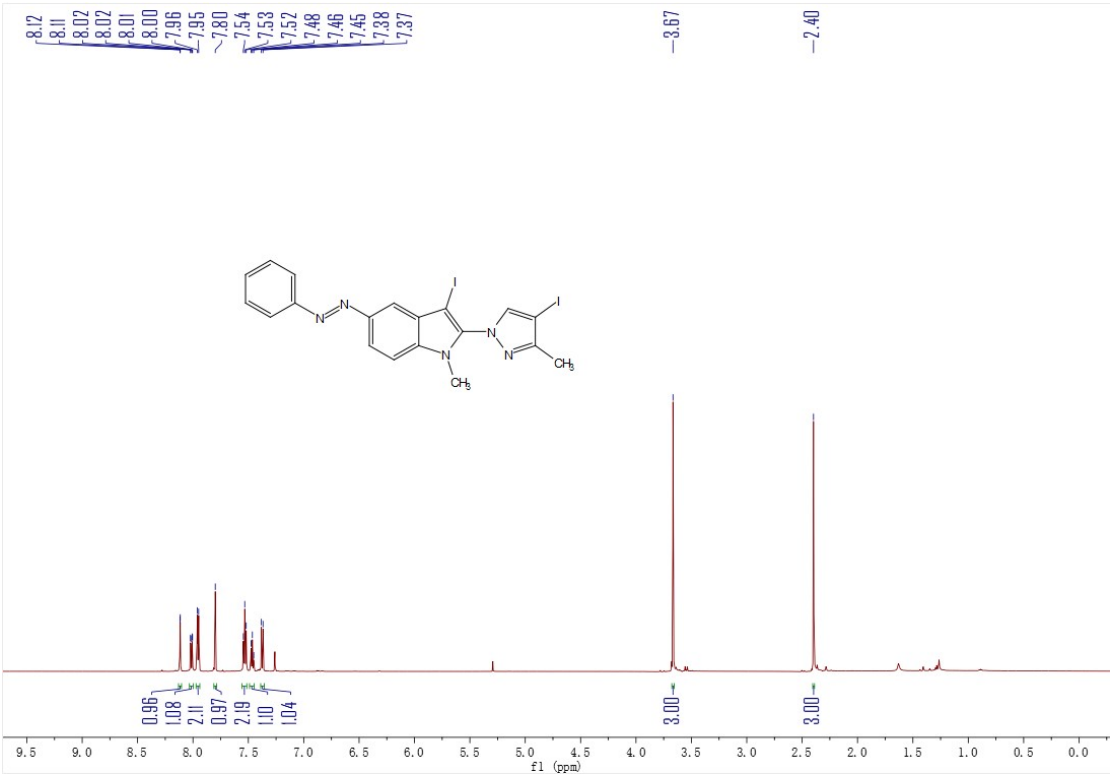
(27)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aad



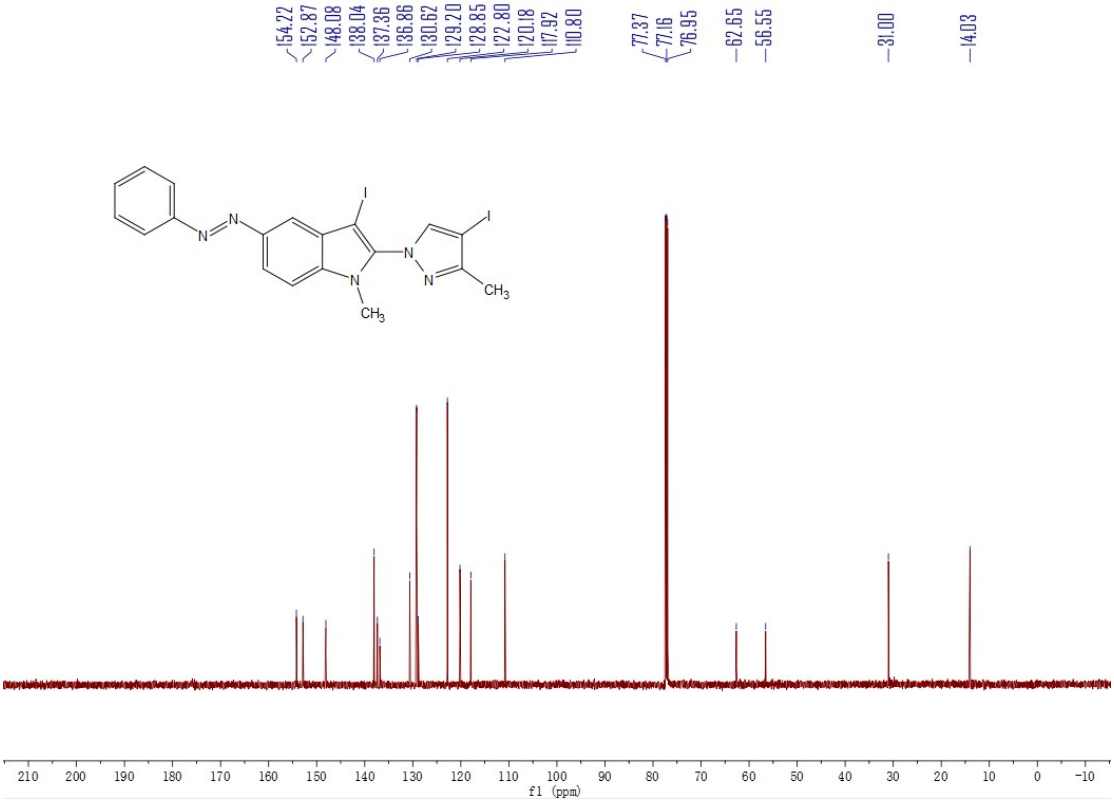
(28)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aad



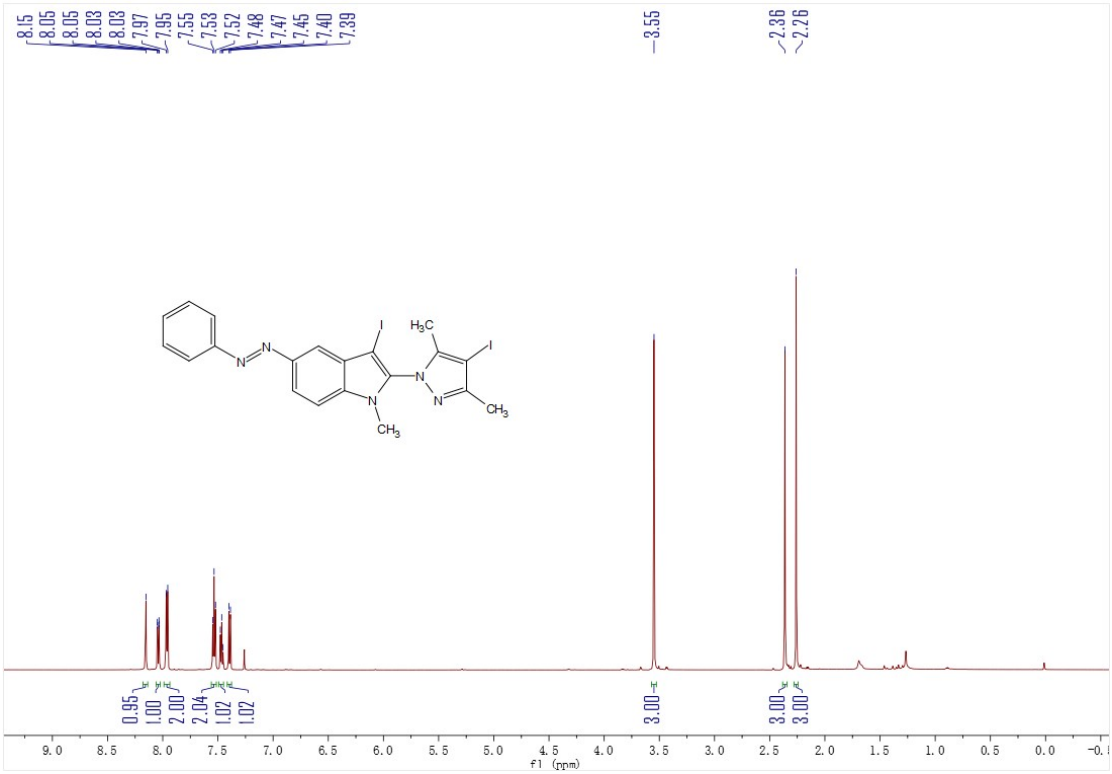
(29)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aae



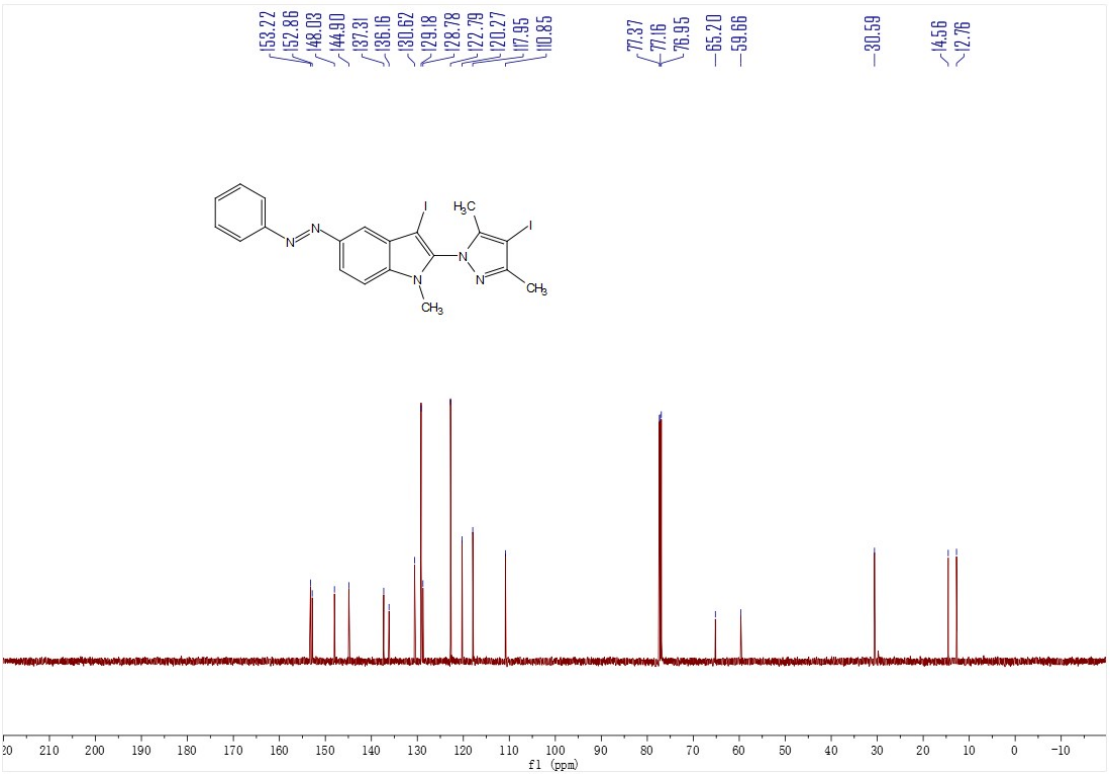
(30)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aae



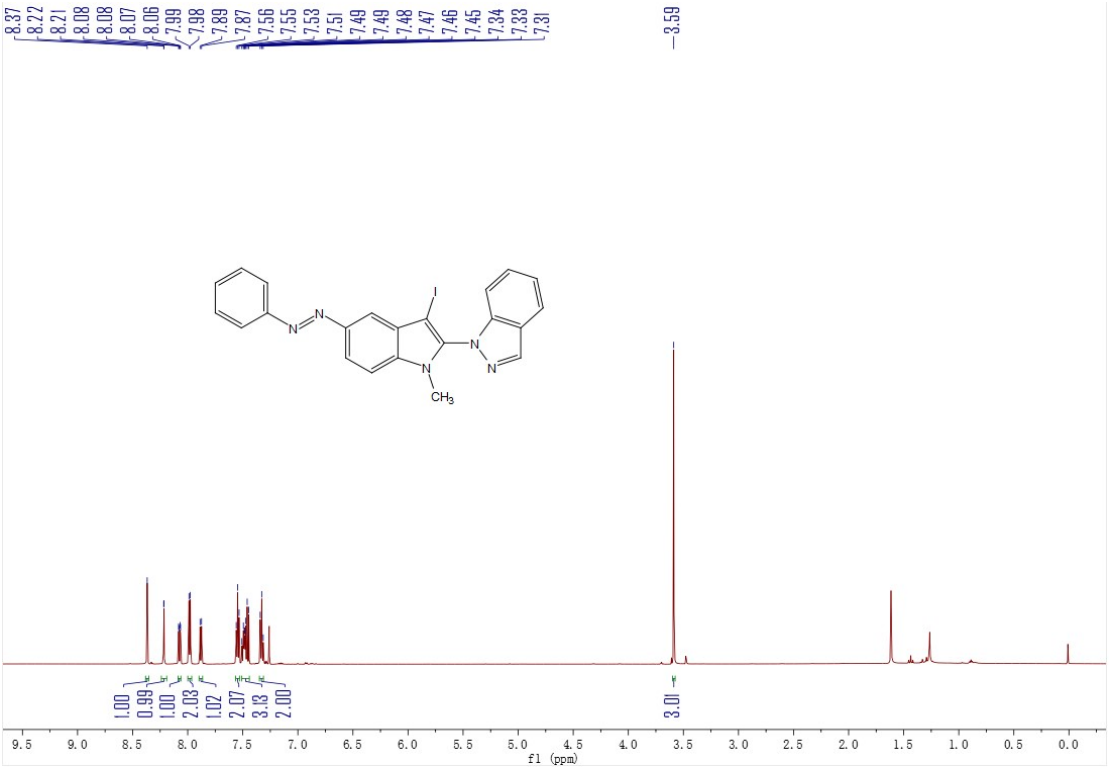
(31)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aaf



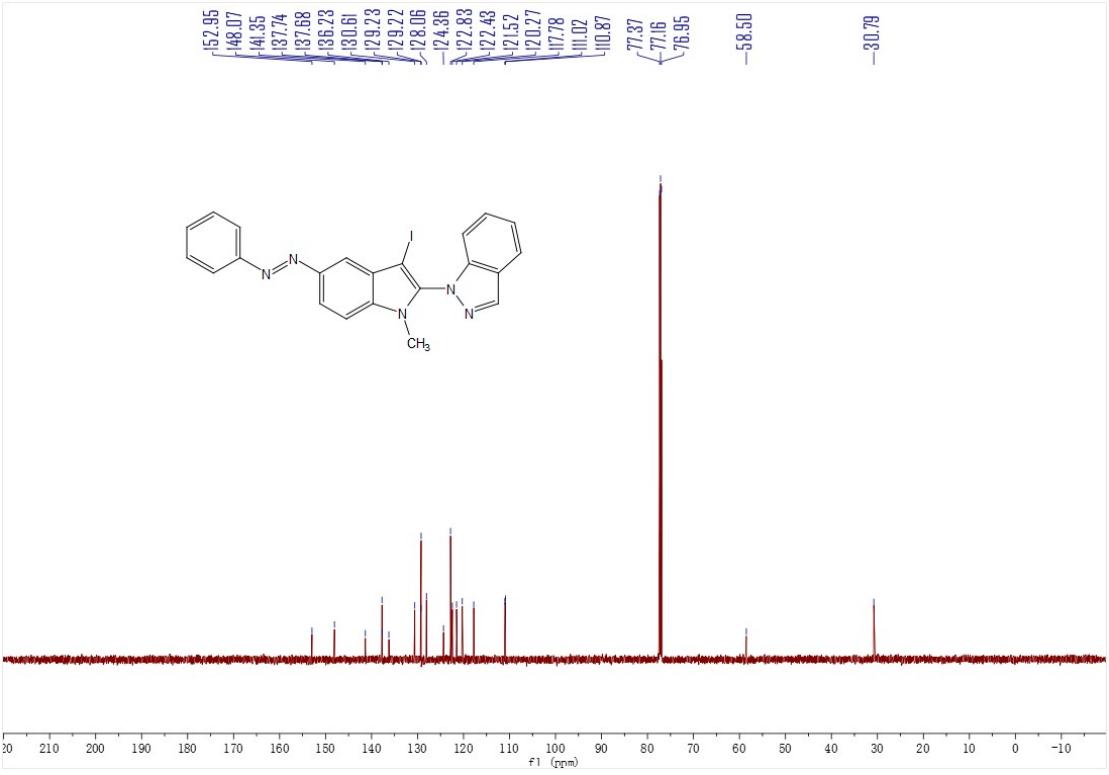
(32)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aaf



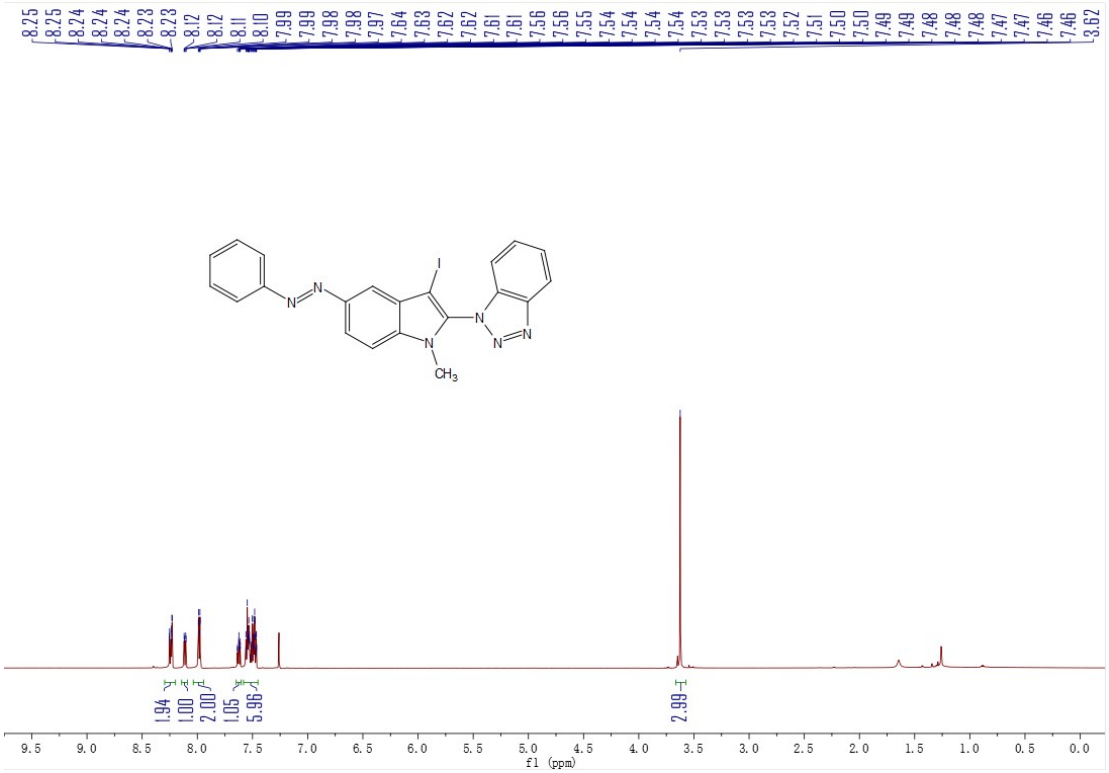
(33)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aag



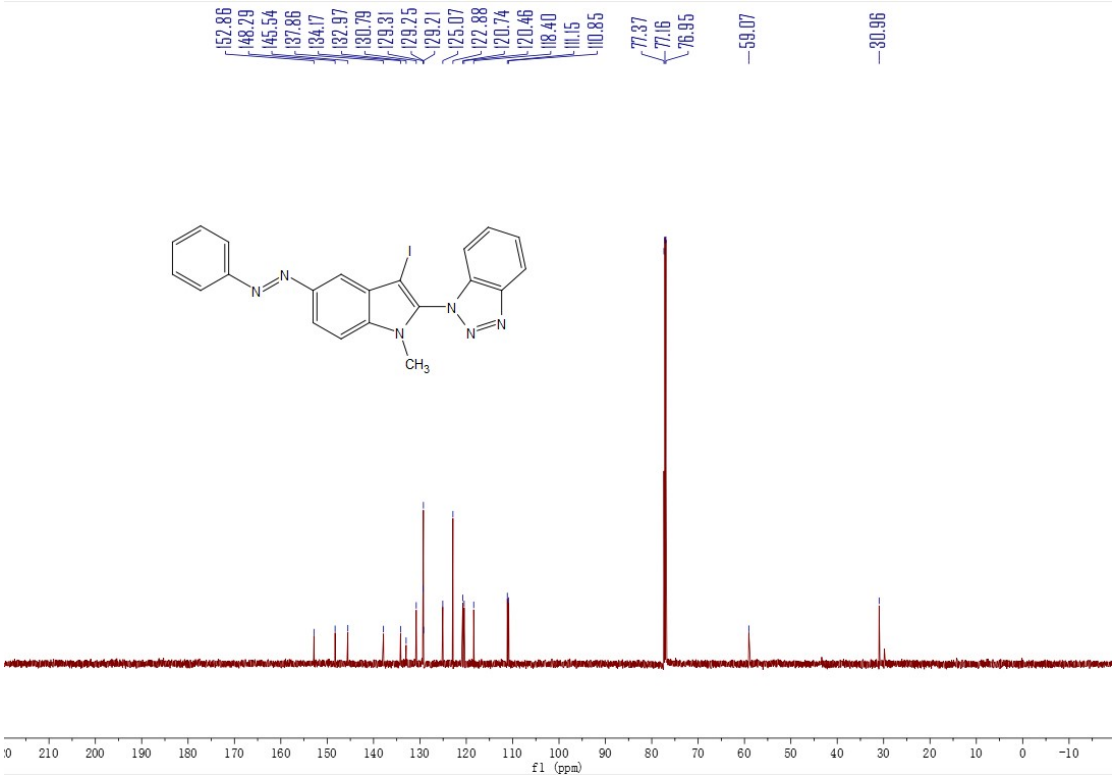
(34)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aag



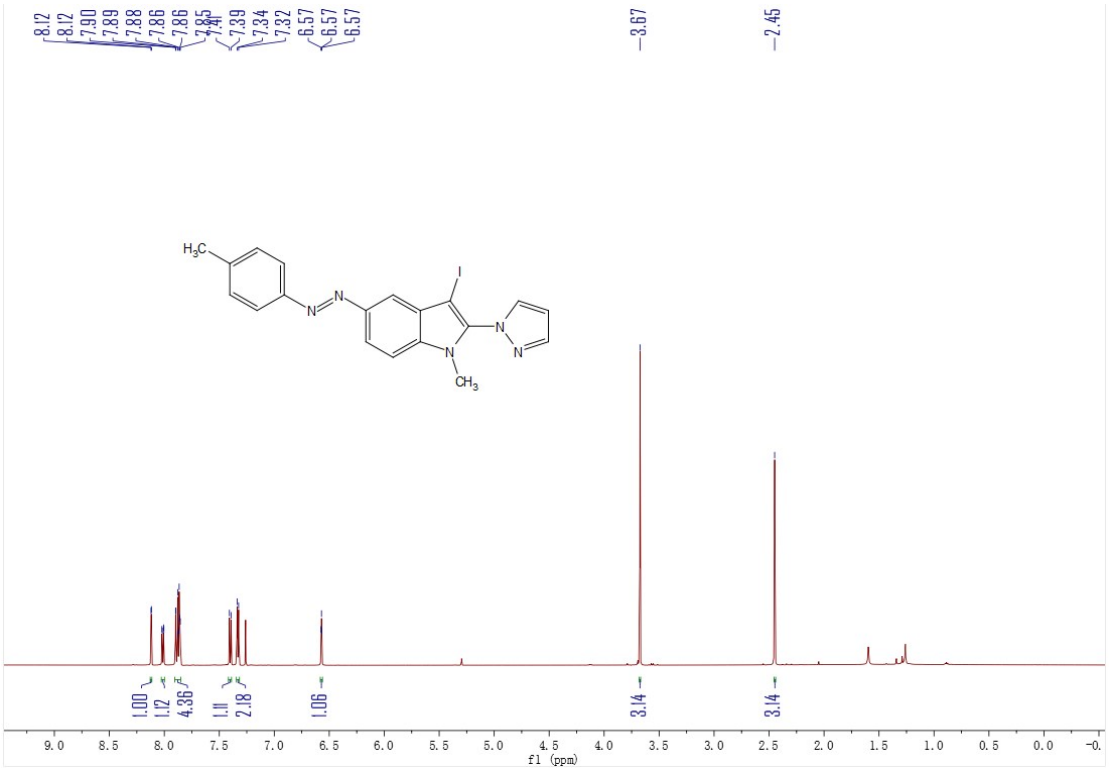
(35)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aah



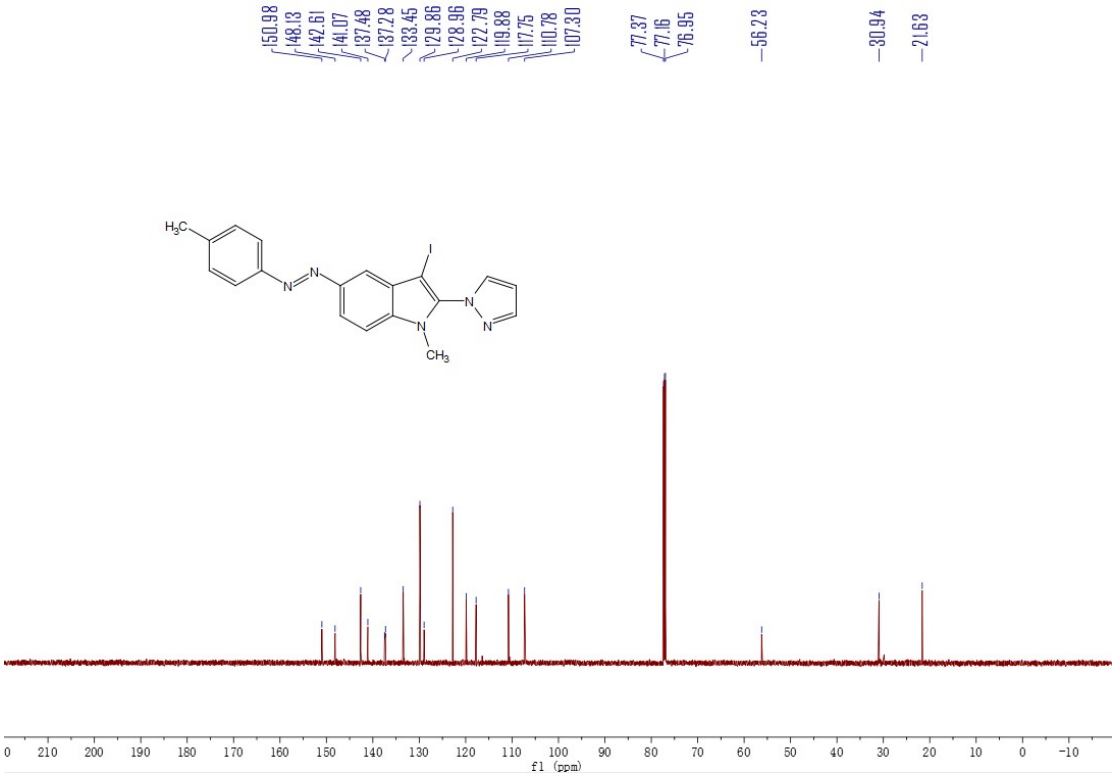
(36)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aag



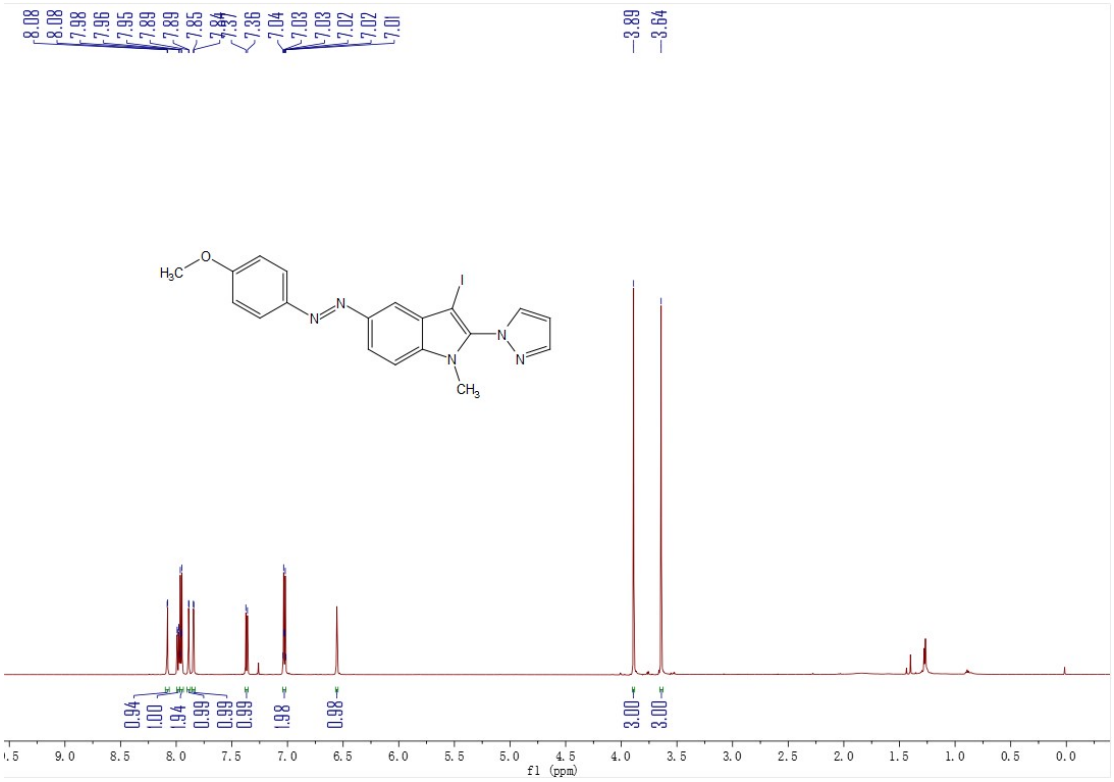
(37)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aba



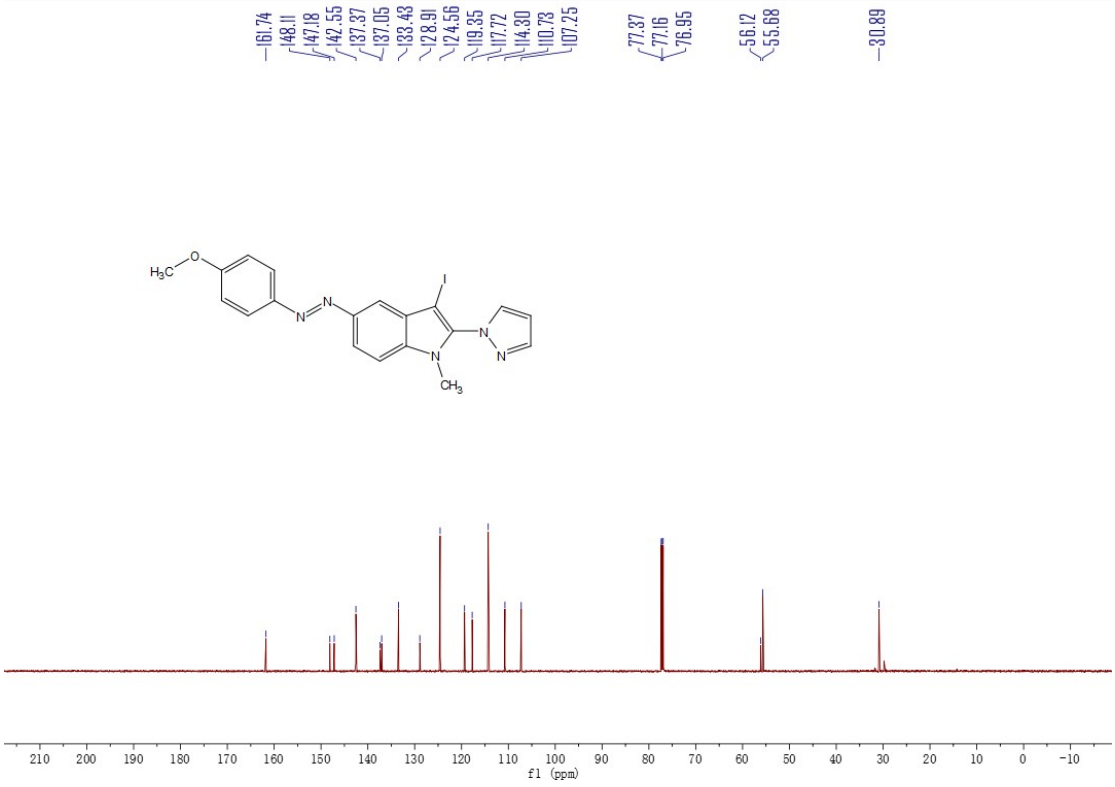
(38)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aba



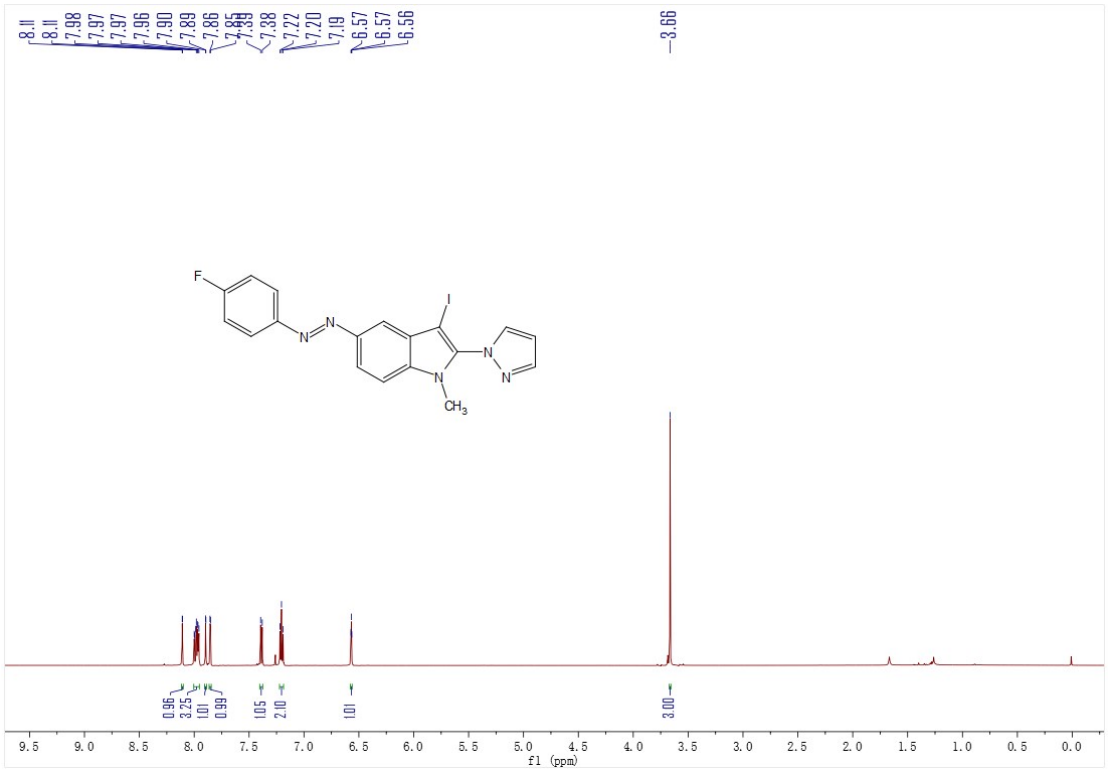
(39)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aca



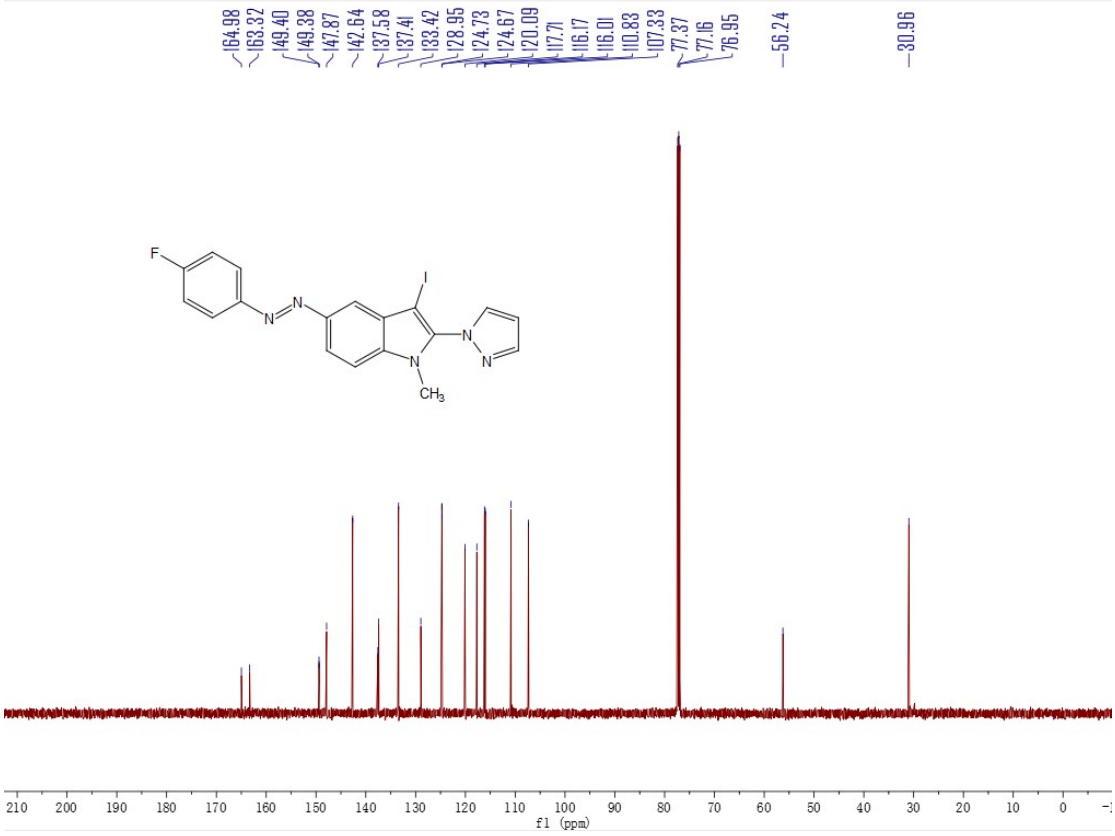
(40)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aca



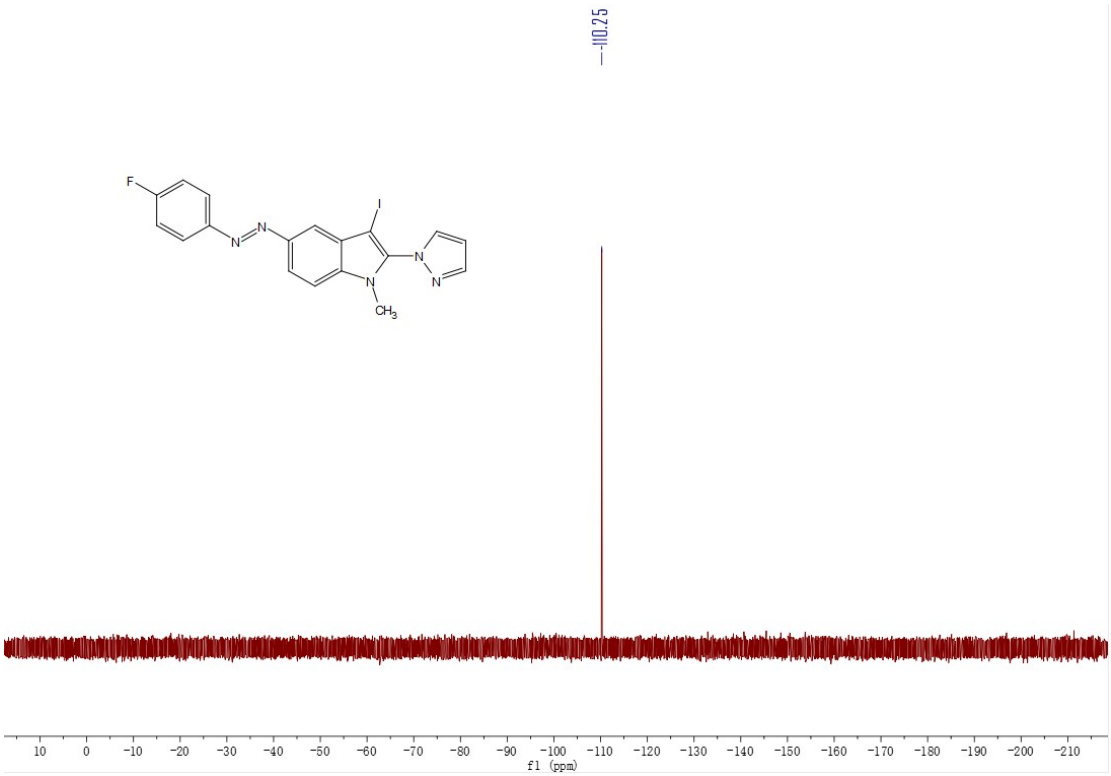
(41)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4ada



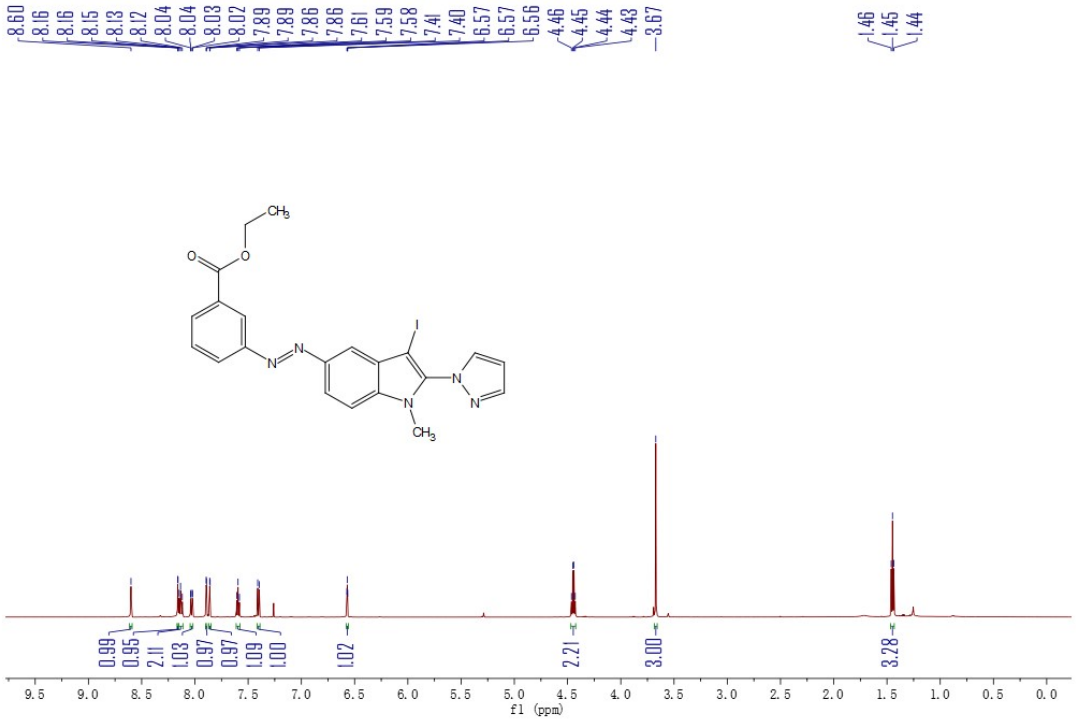
(42)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4ada



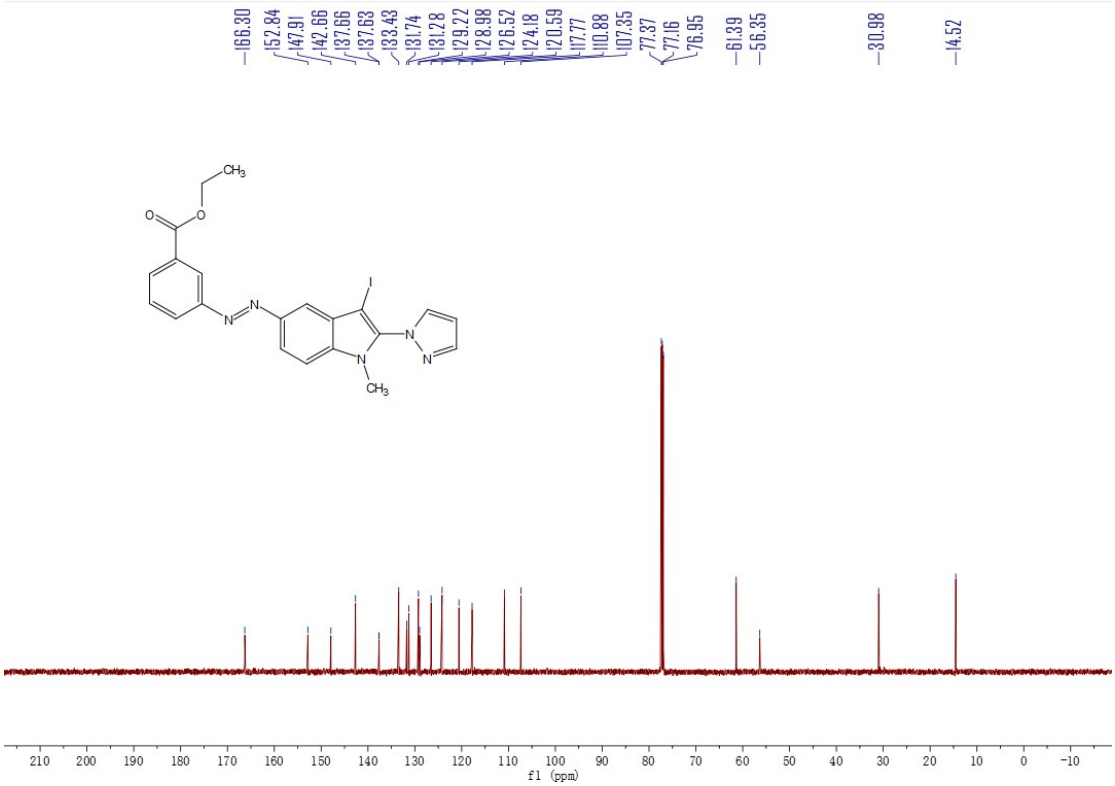
(43)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 4ada



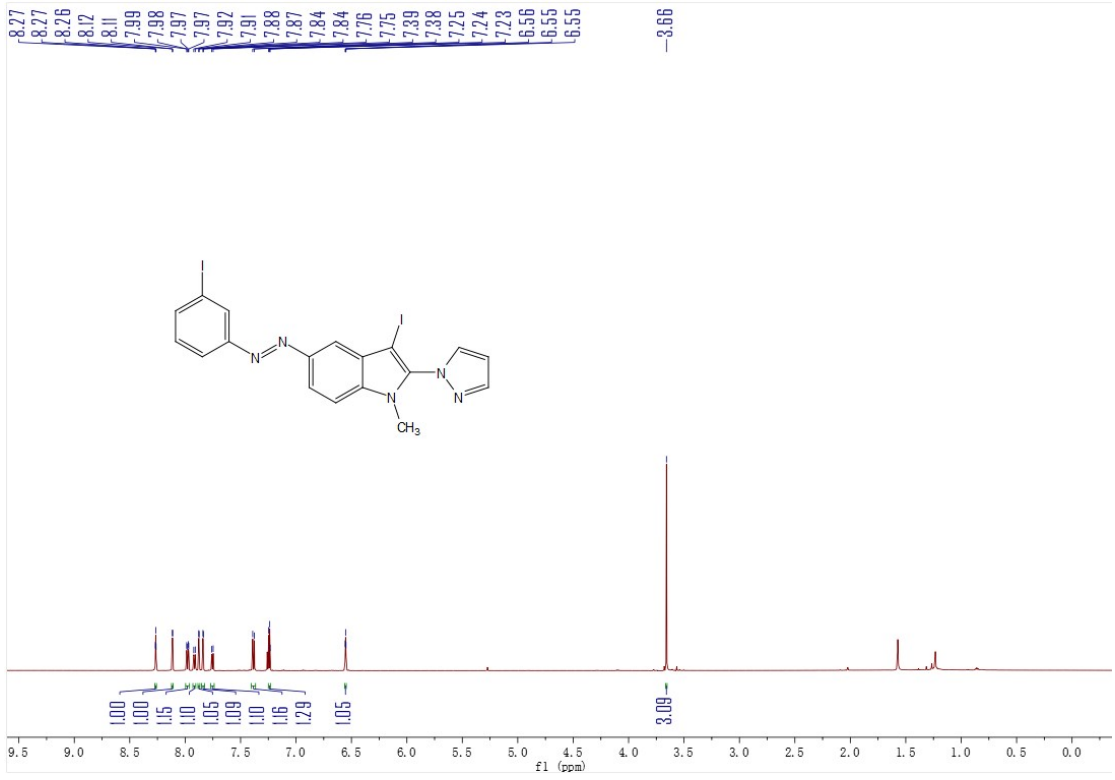
(44)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aea



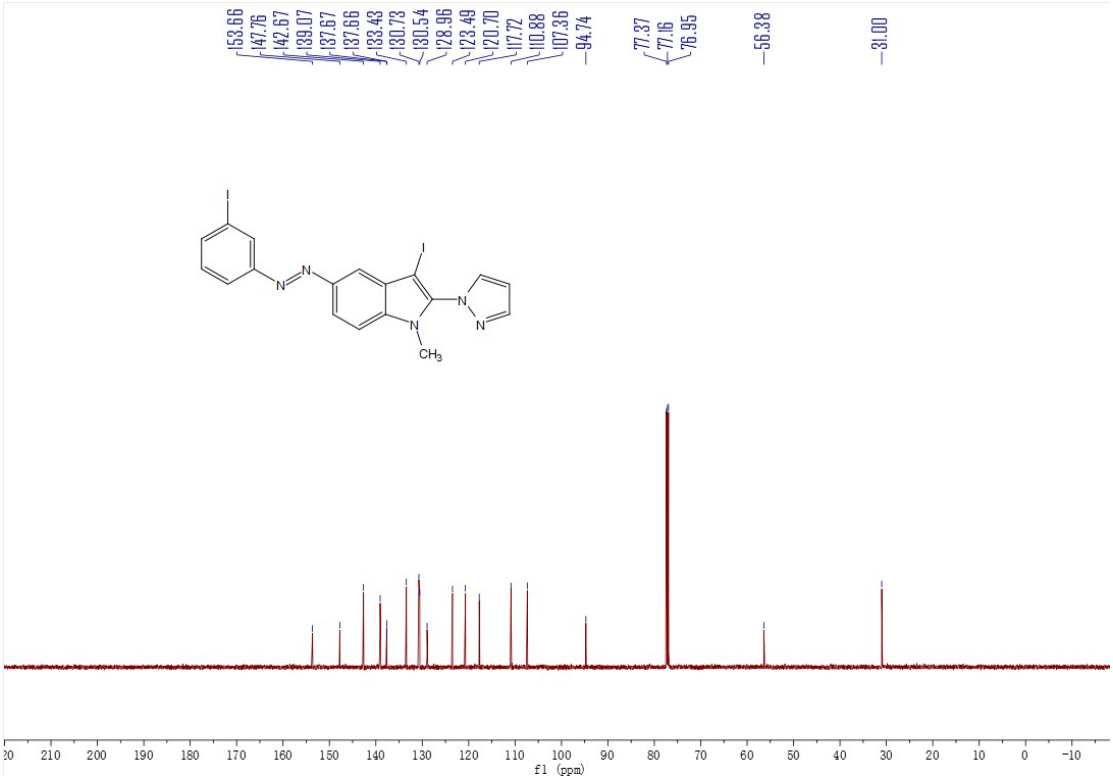
(45)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aea



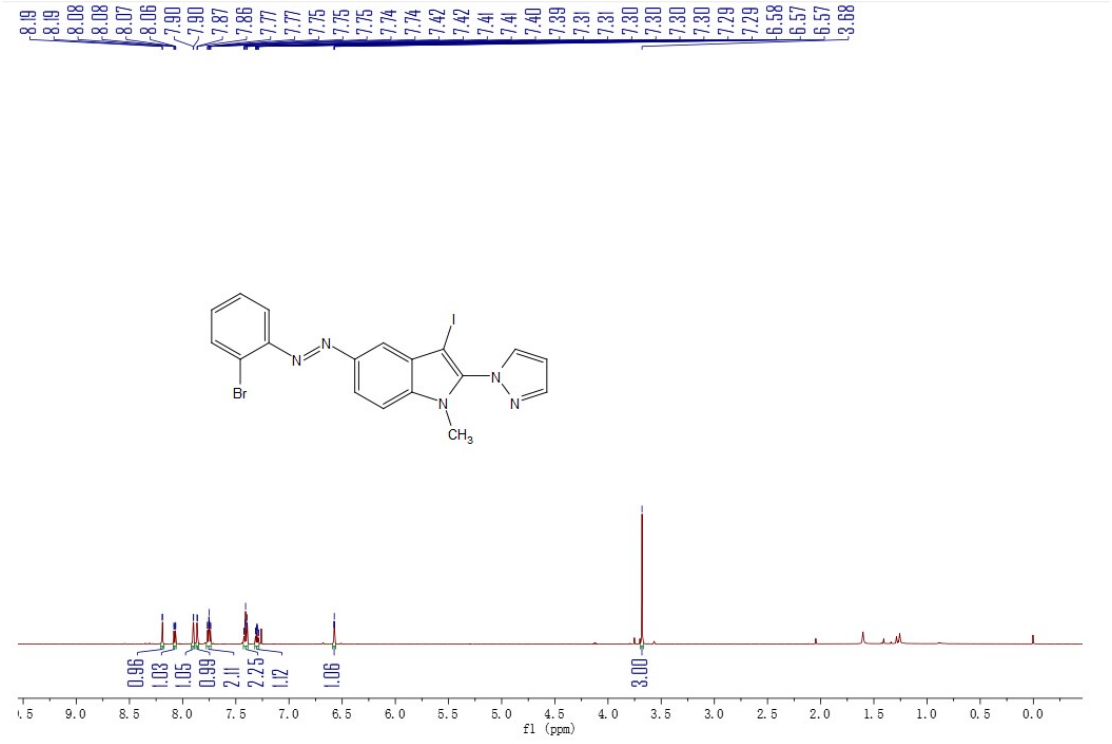
(46)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4afa



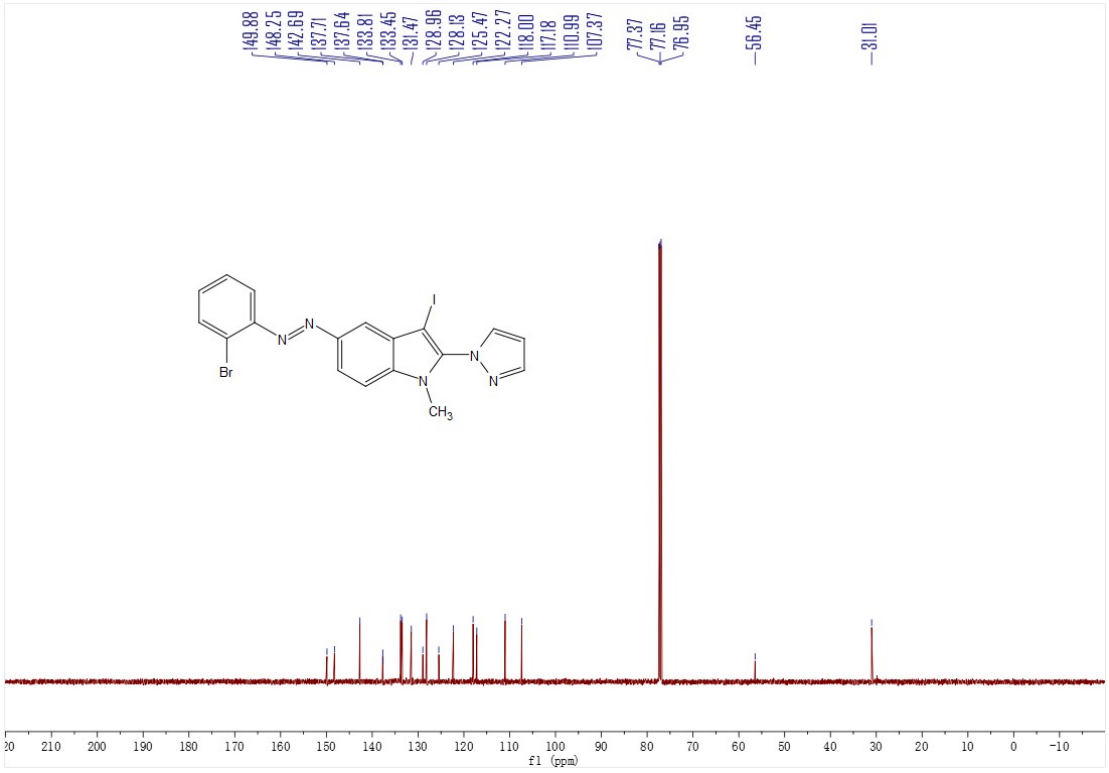
(47)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4afa



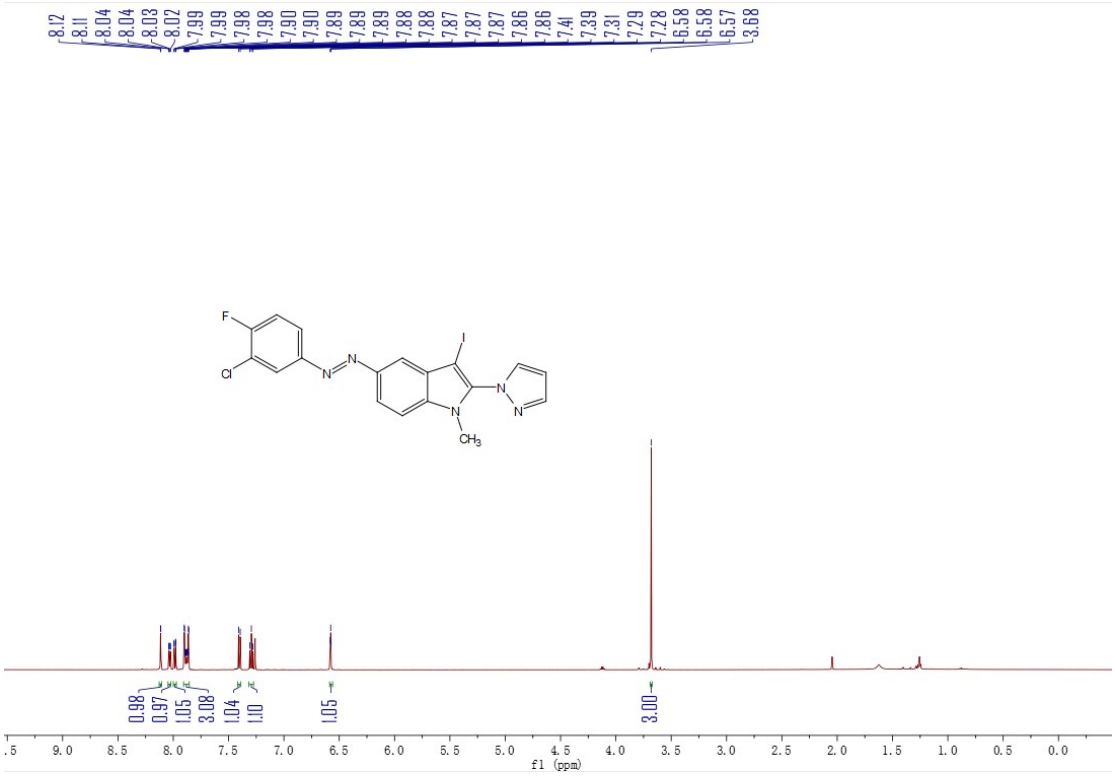
(48)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aga



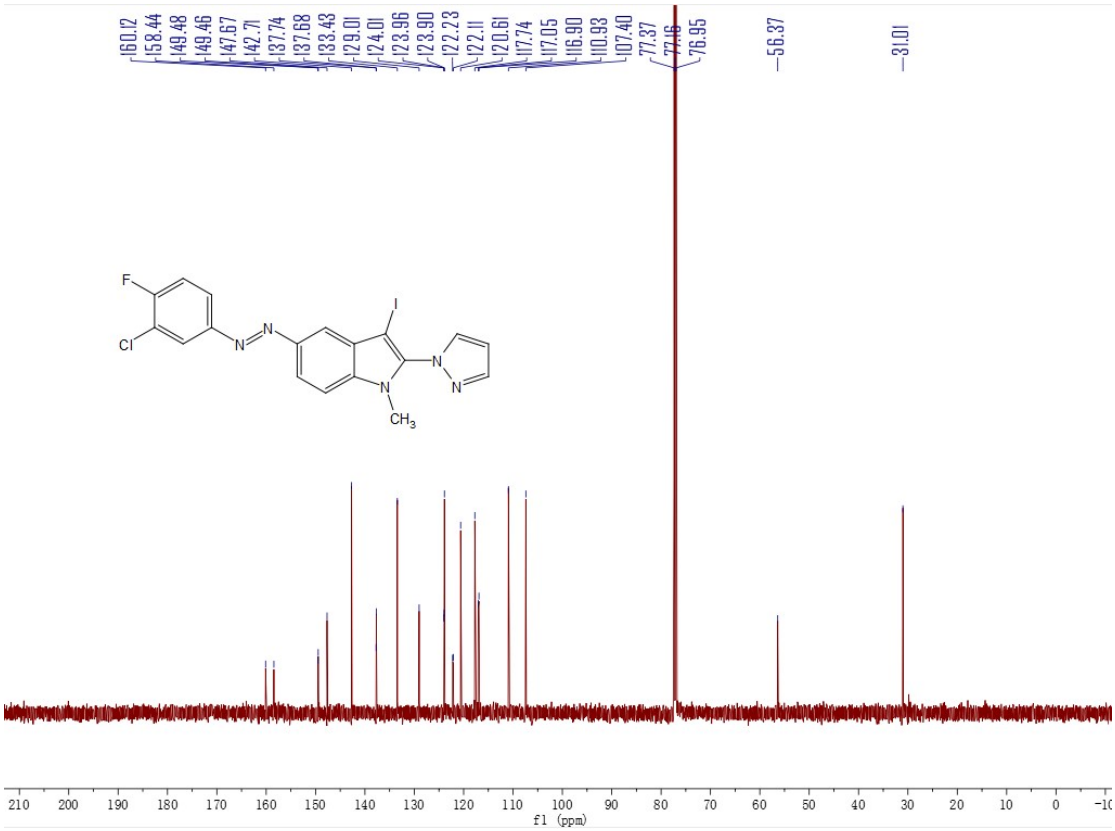
(49)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aga



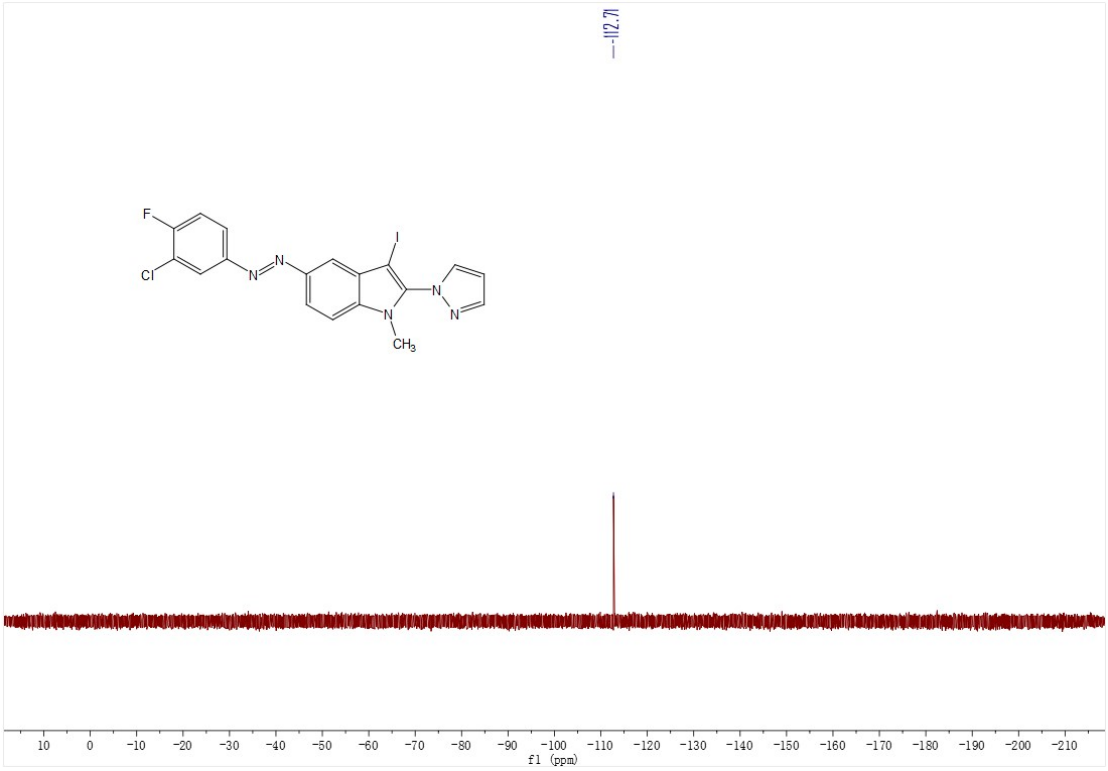
(50)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aha



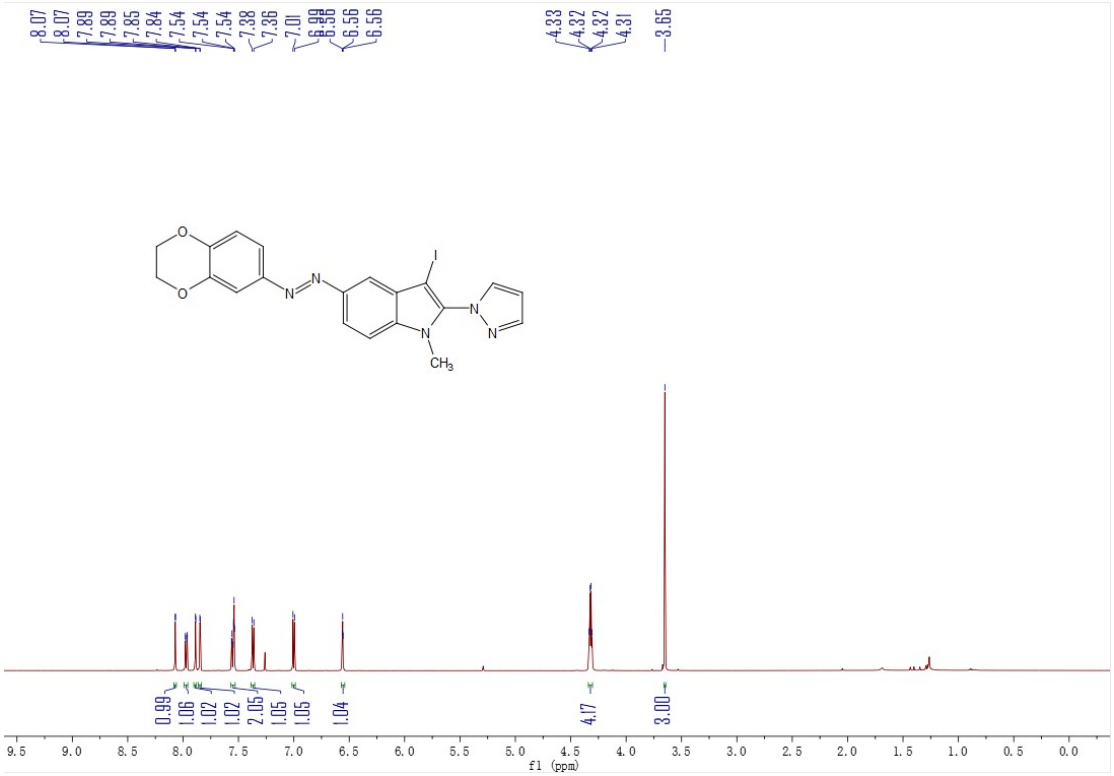
(51)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aha



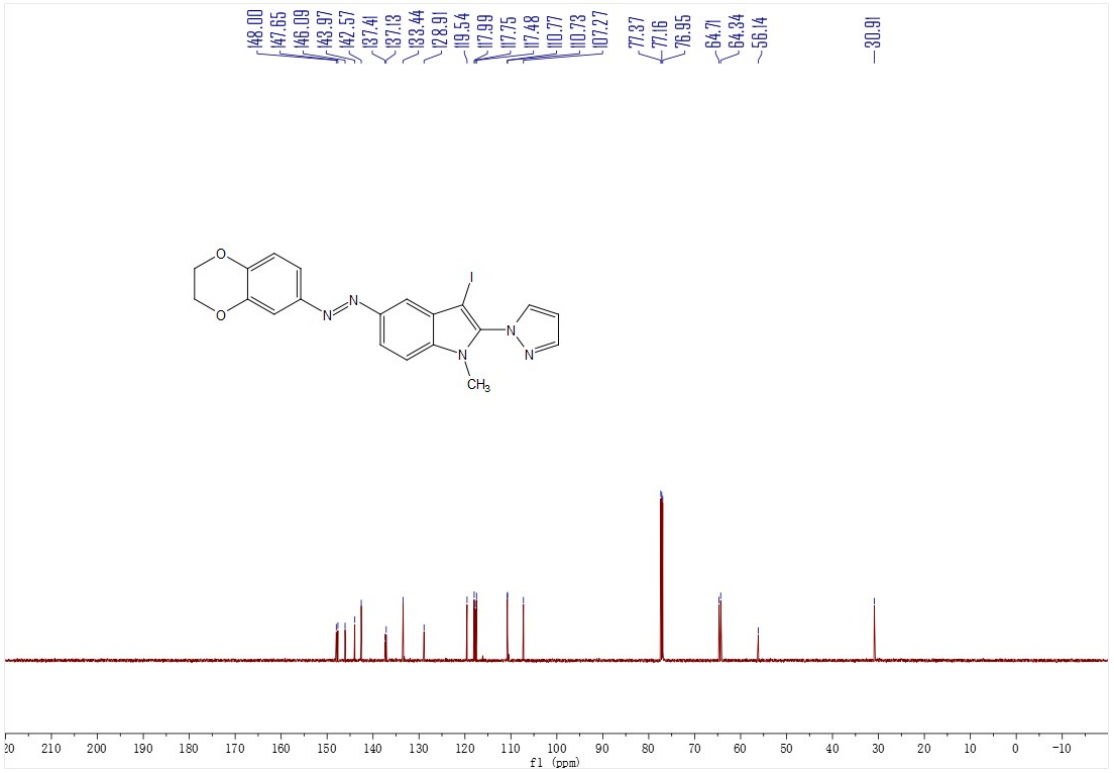
(52)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 4aha



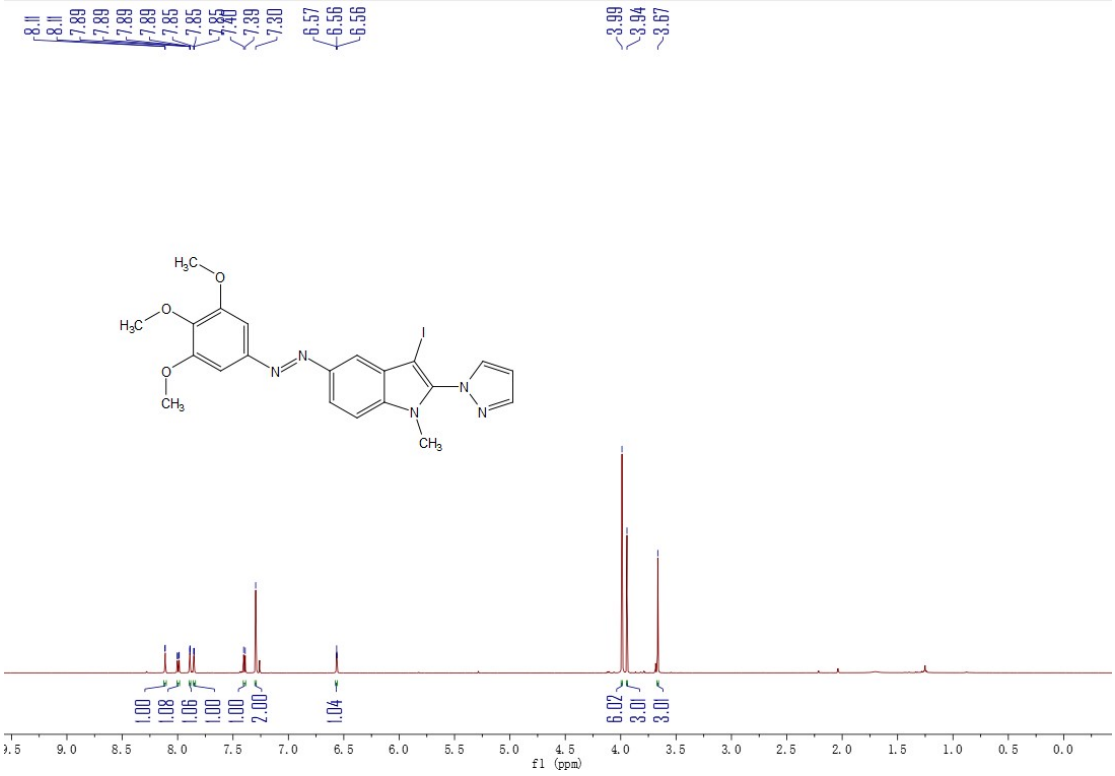
(53)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aia



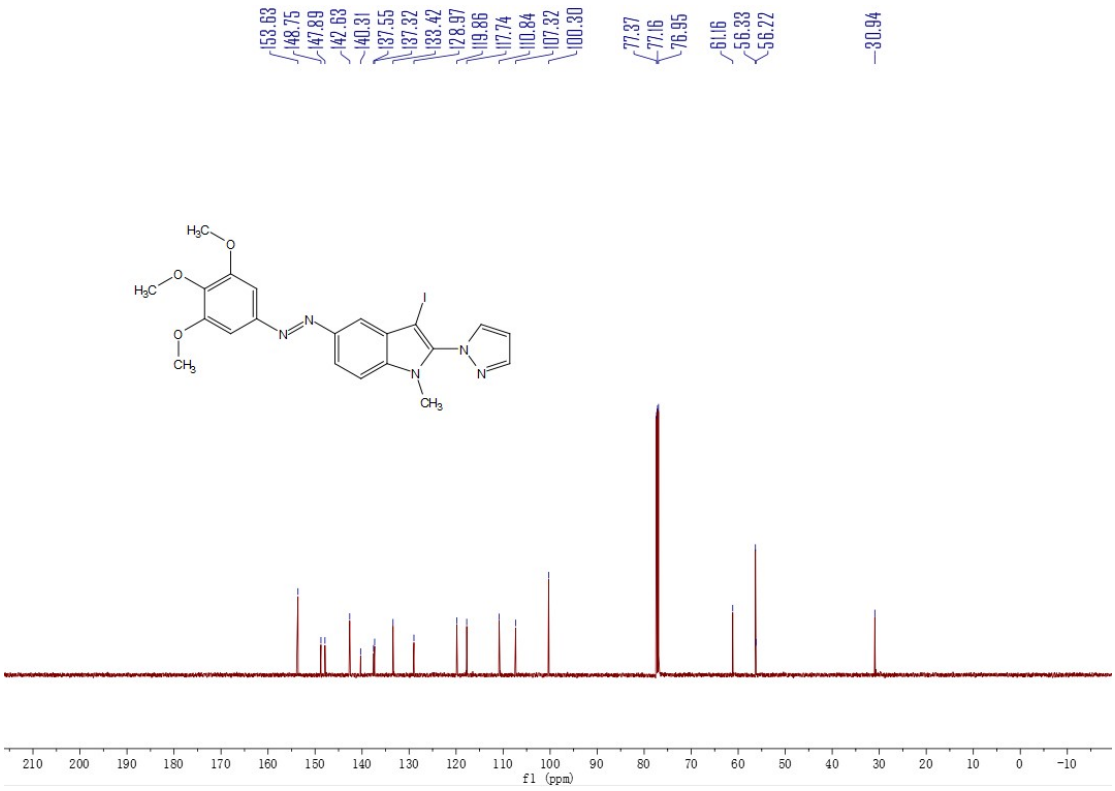
(54)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aia



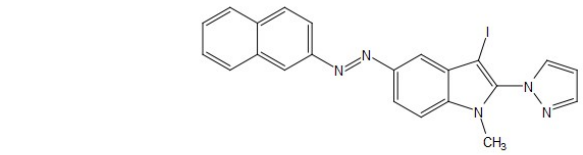
(55)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aja

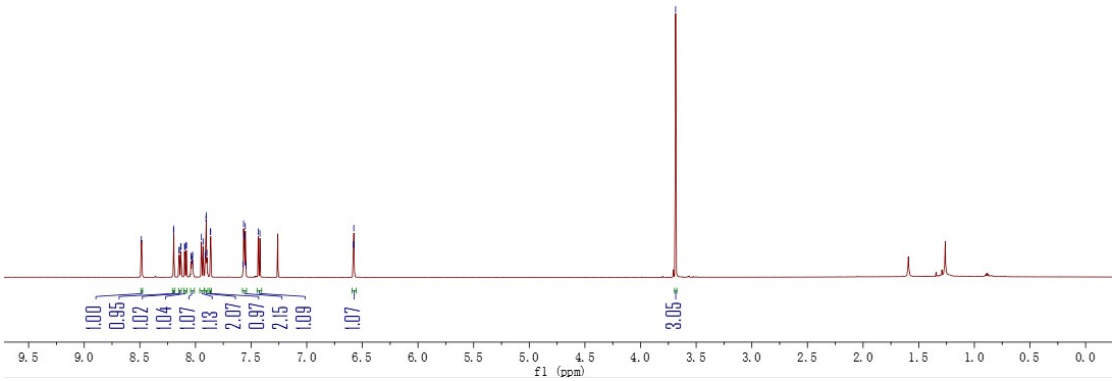


(56)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aja

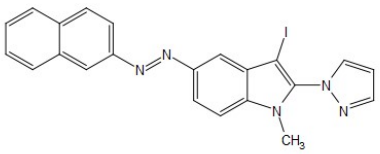


(57)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aka

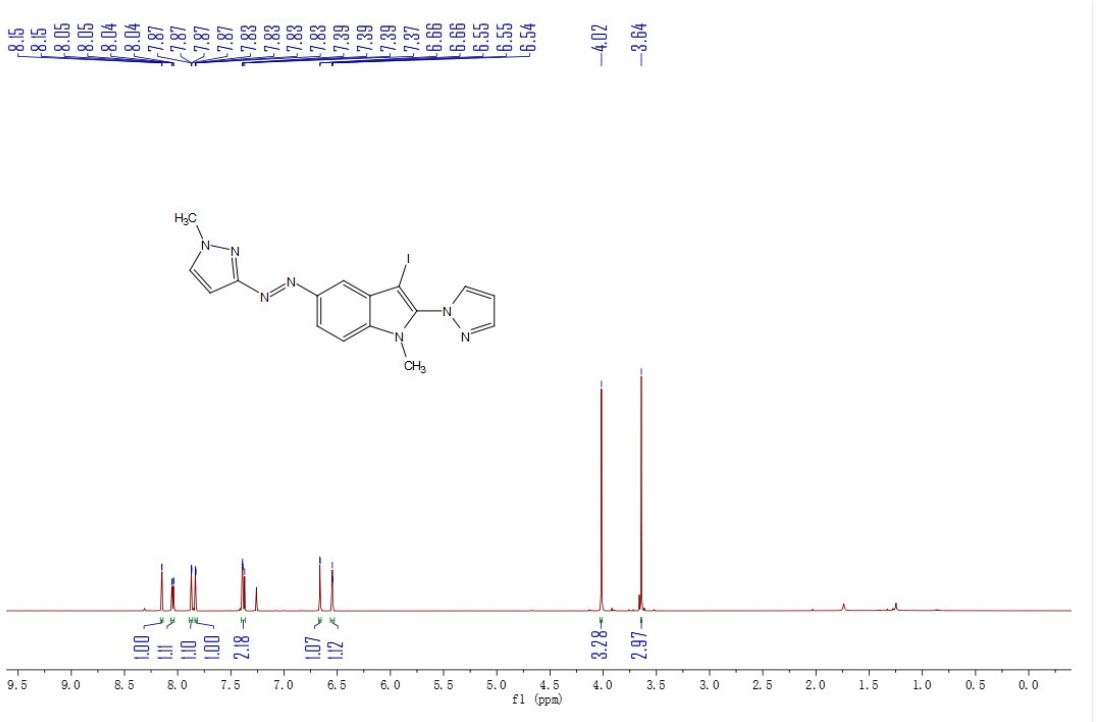




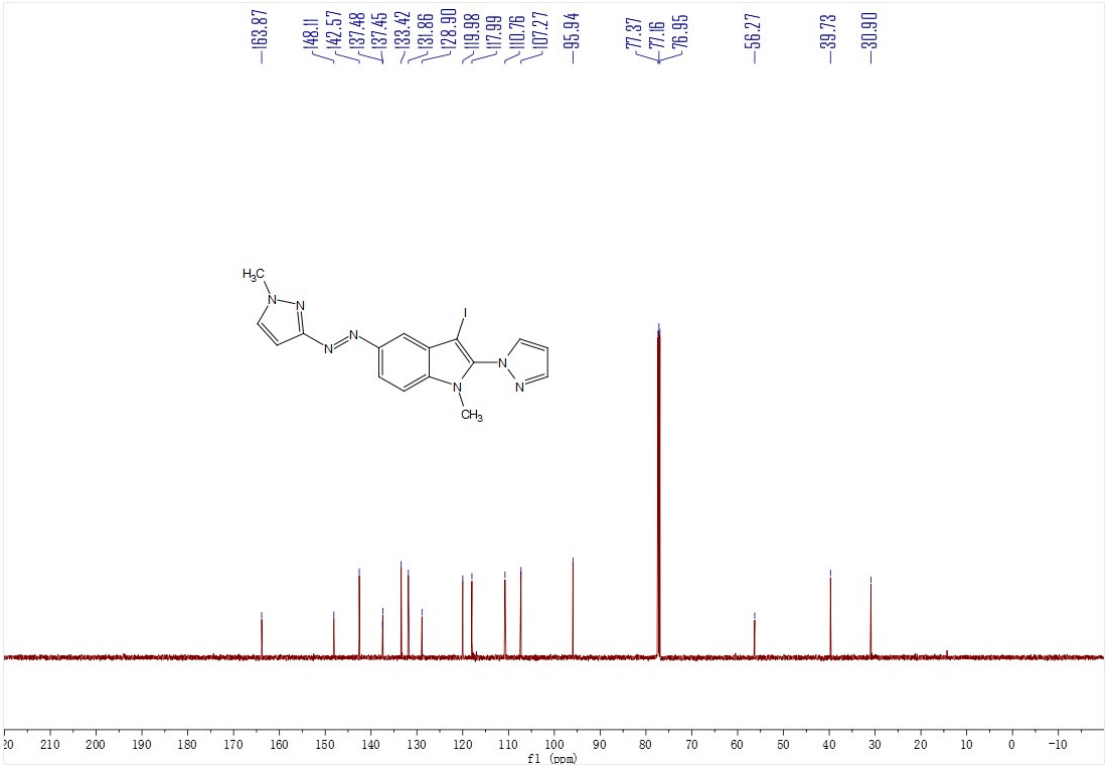
(58)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aka



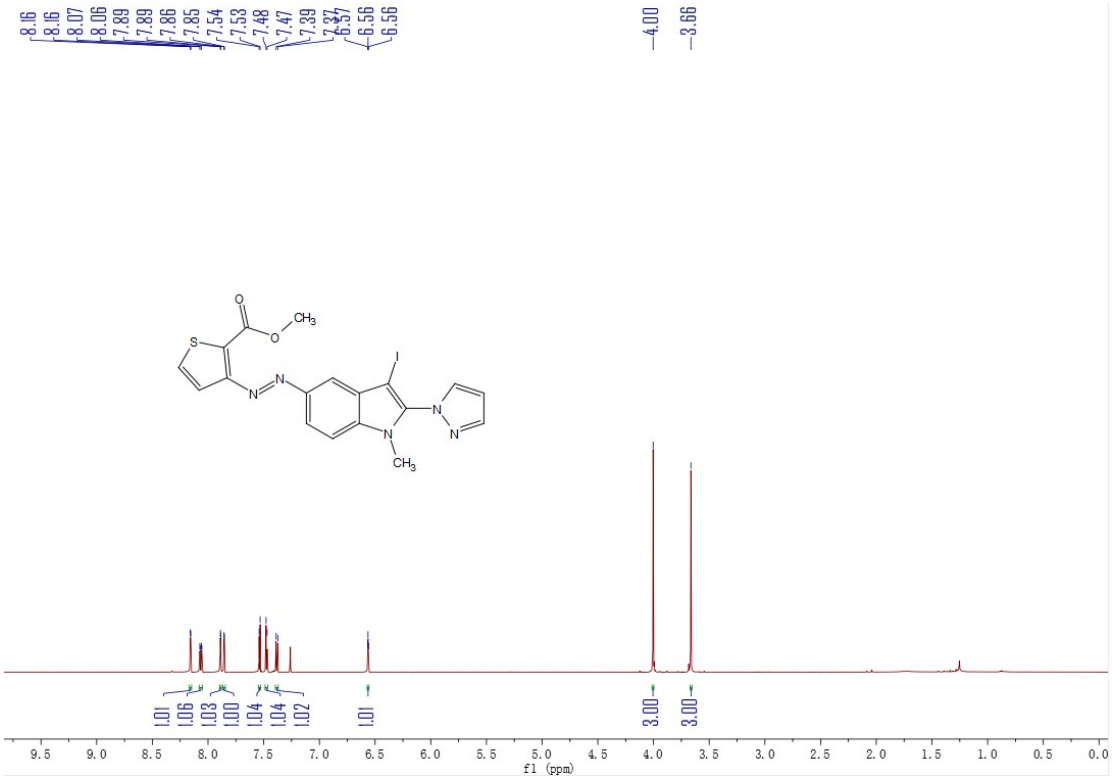
(59)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4ala



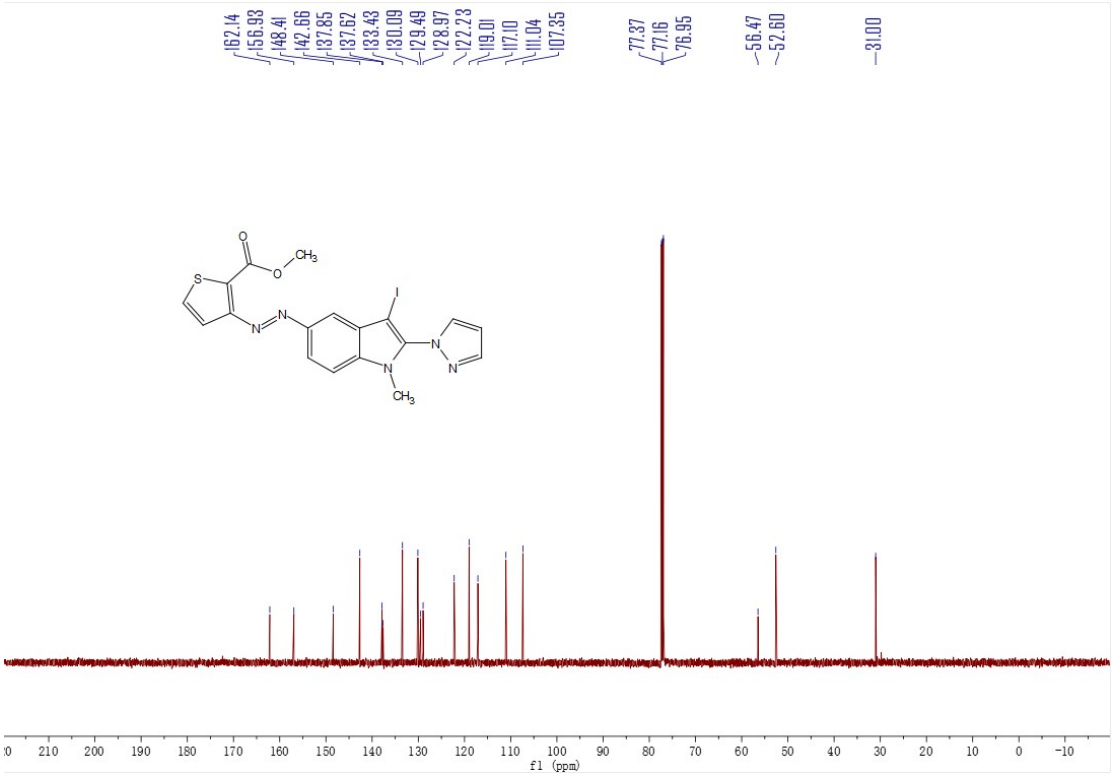
(60)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4ala



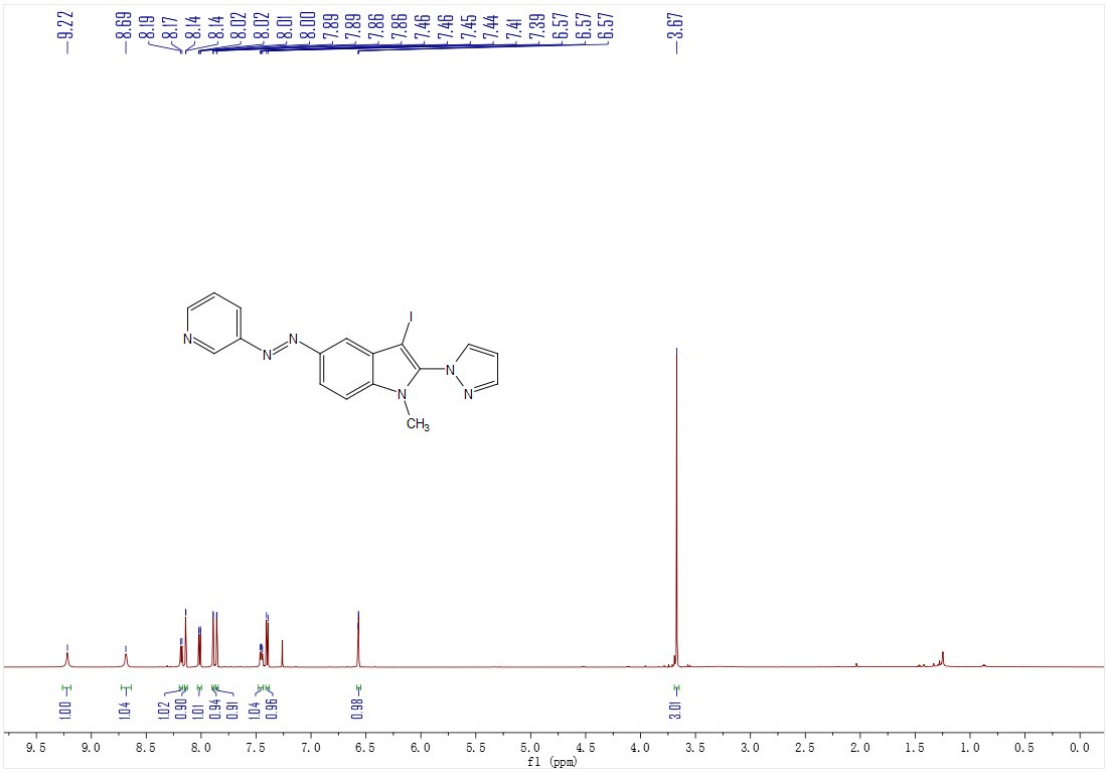
(61)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4ama



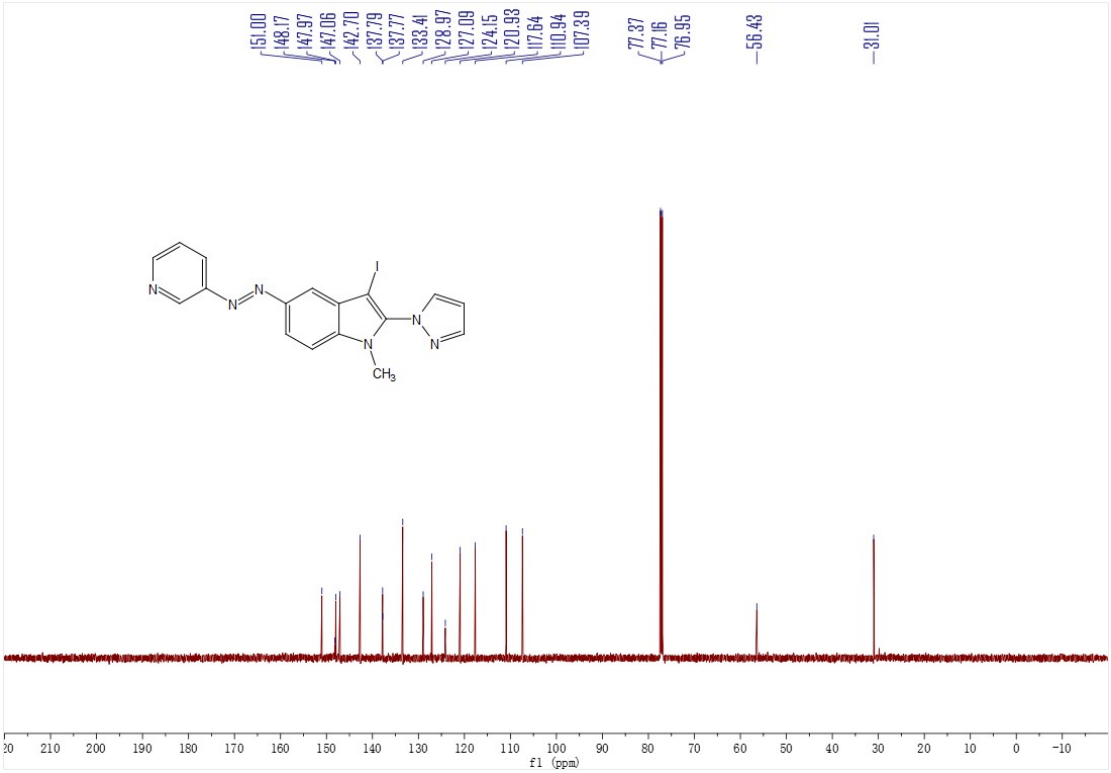
(62)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4ama



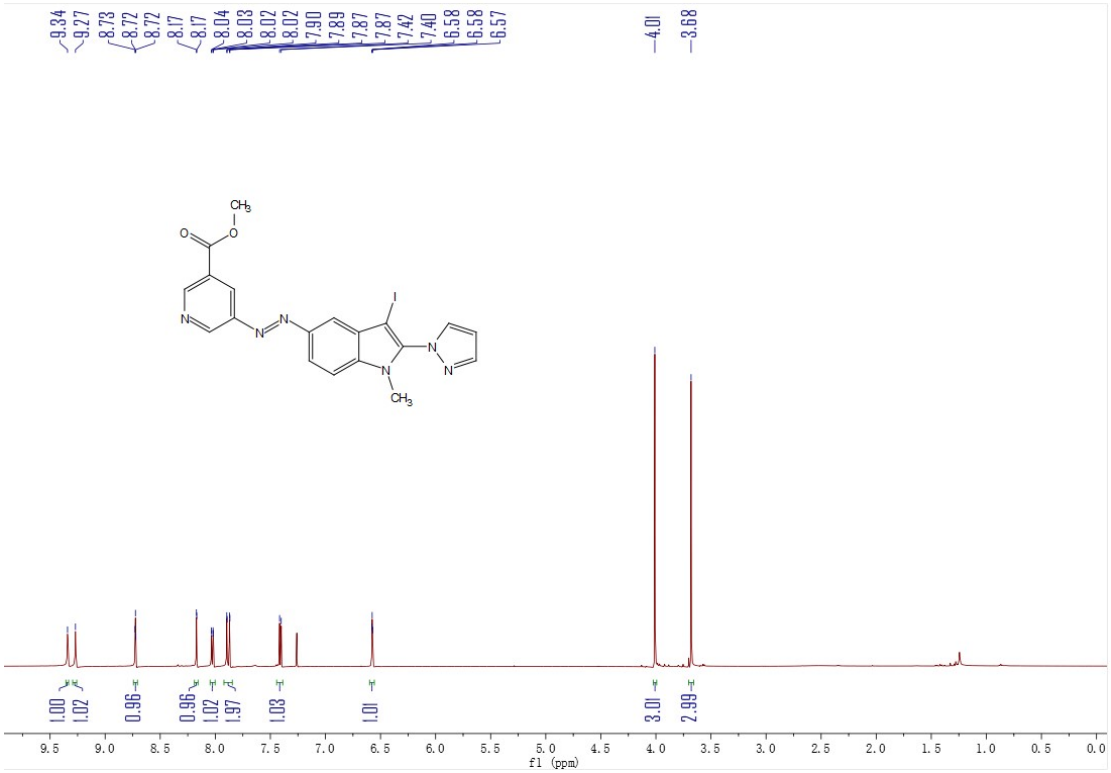
(63)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4ana



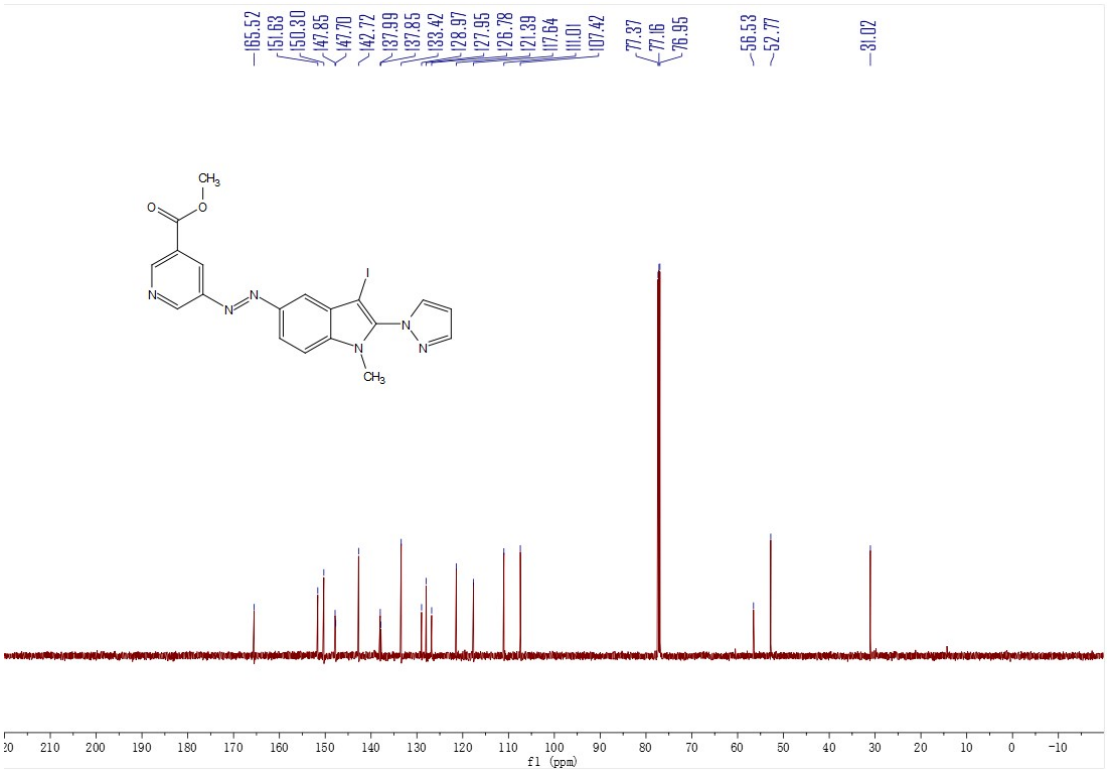
(64)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4ana



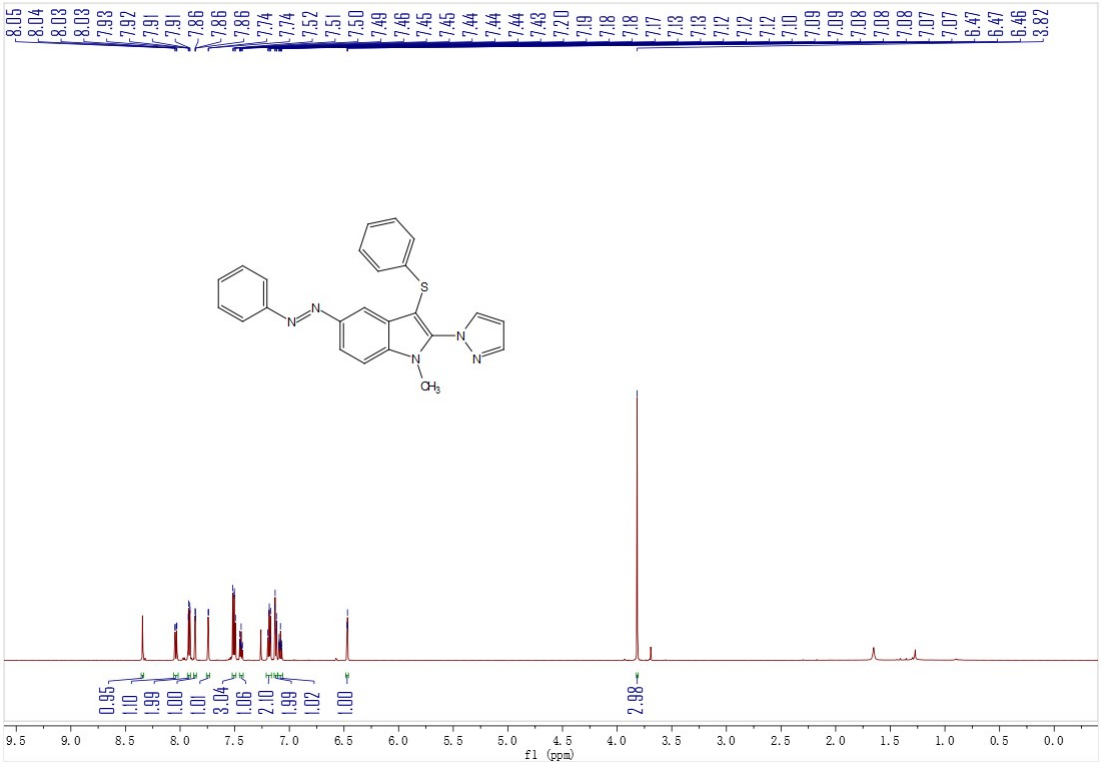
(65)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4aoa



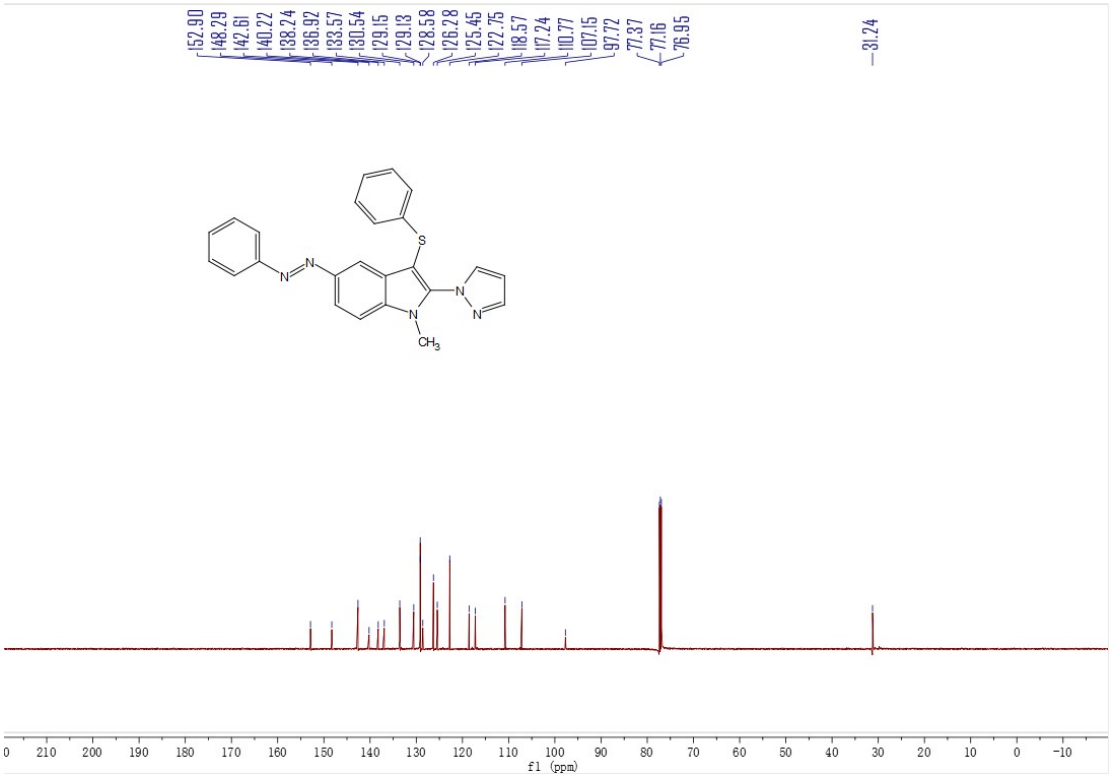
(66)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4aoa



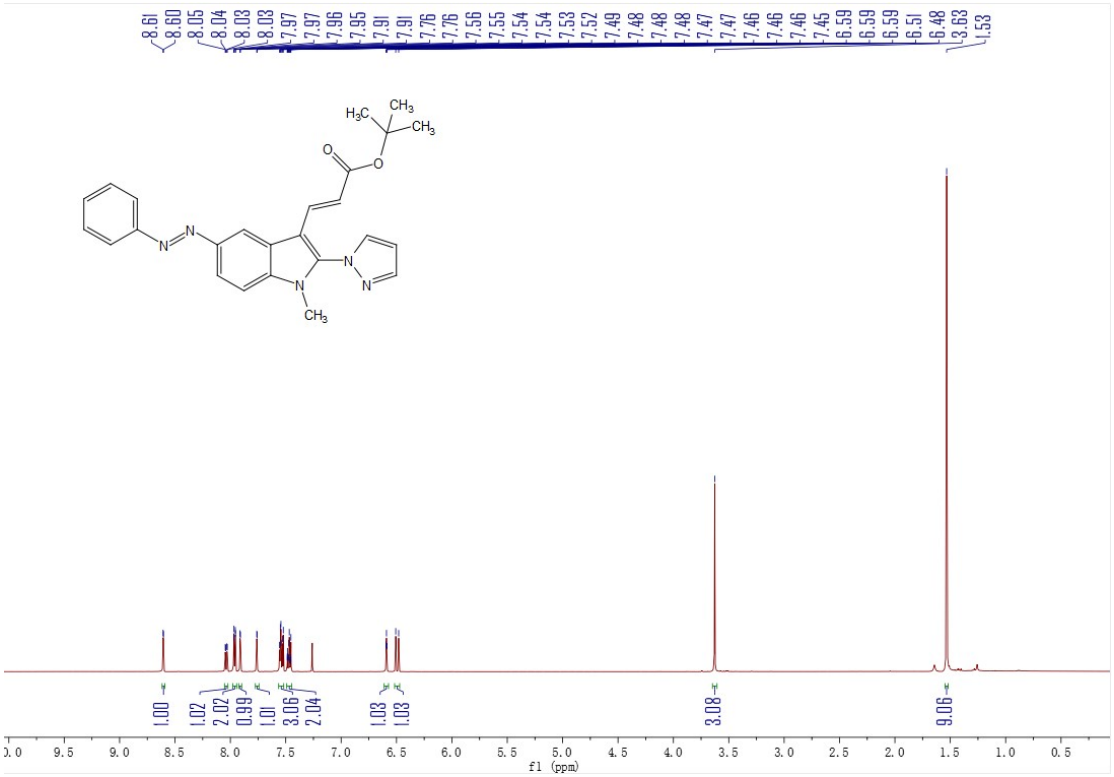
(67)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 5aaa



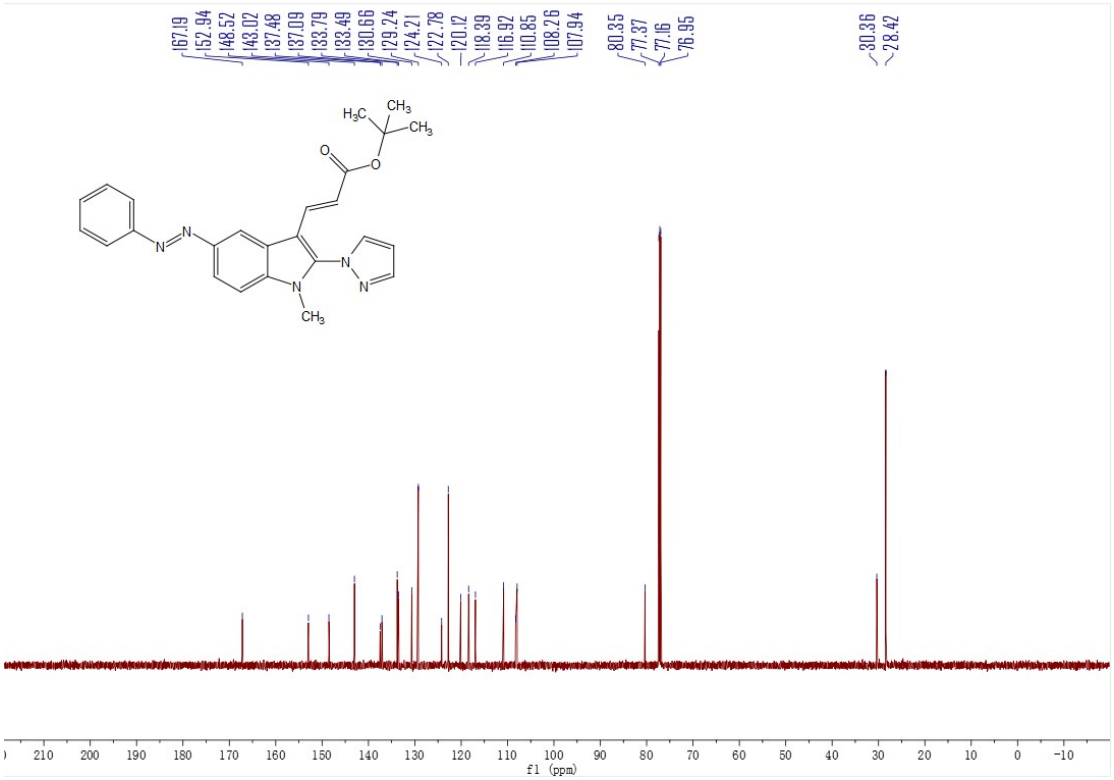
(68)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 5aaa



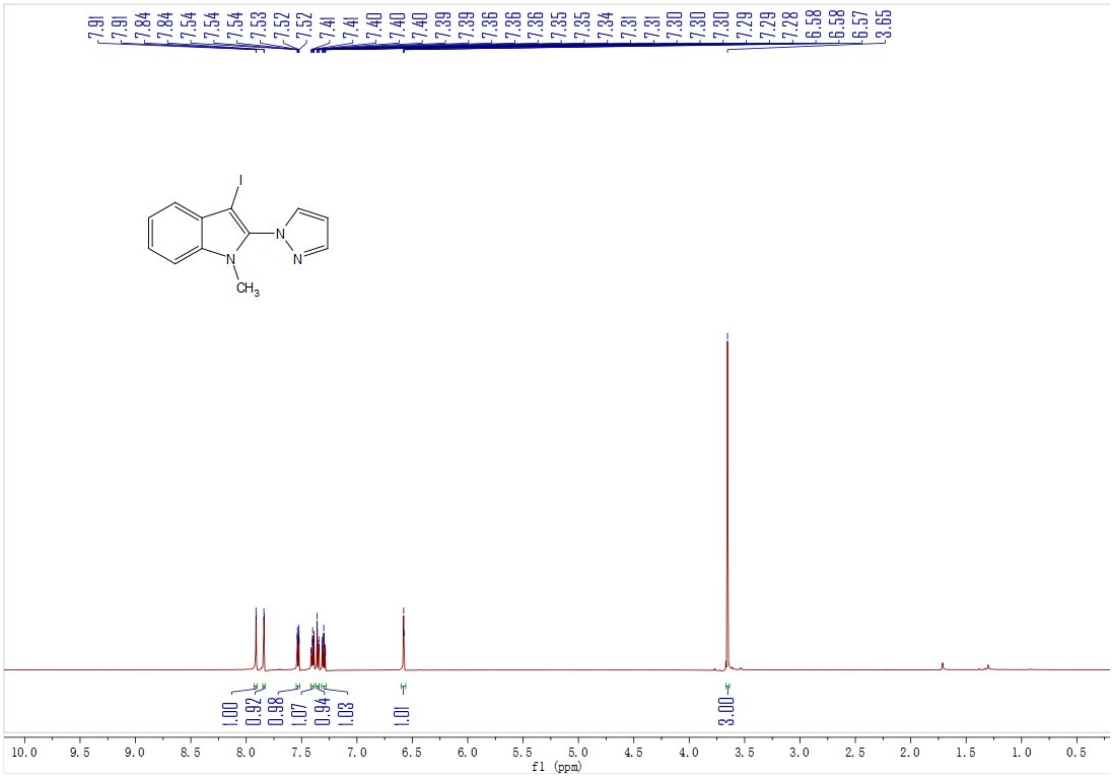
(69)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 6aaa



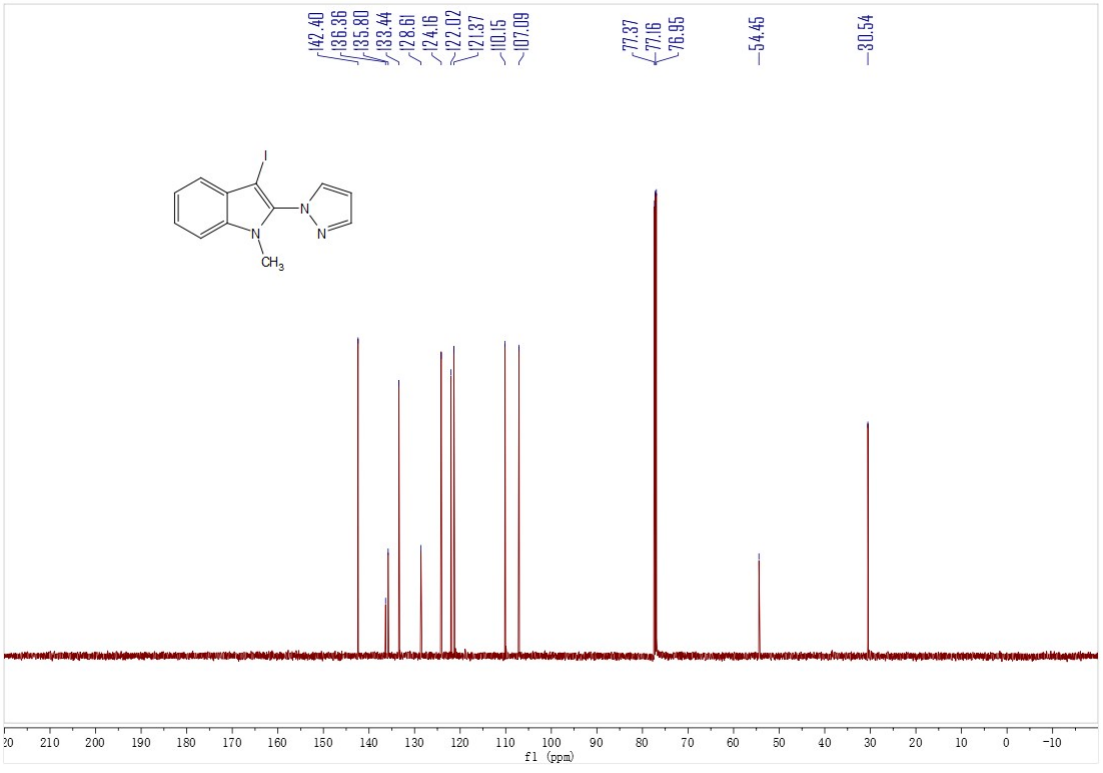
(70)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 6aaa



(71)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 1a-3



(72)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 1a-3



9. References

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[2] P. Wang, Z. Yang, Z. Wang, C. Xu, L. Huang, S. Wang, H. Zhang and A. Lei, *Angew. Chem. Int. Ed*., 2019, **131**, 15894–15898.

[3] D. Beukeaw, K. Udomsasporn and S. Yotphan, *J Org Chem*., 2015, **80**, 3447–3454.