Supporting Information

Transition-Metal-Free Synthesis of C3,5-Difunctionalized Oxindole Derivatives

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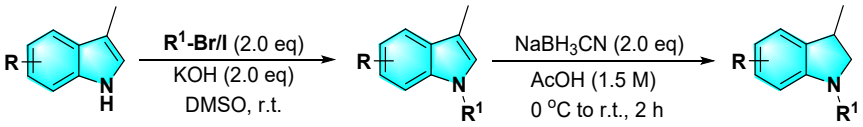
1. General Information

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. ^{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 $CDCl_3$ ($\delta = 7.26$ for ^{1}H NMR and $\delta = 77.16$ for ^{13}C NMR).

2. Procedure for the synthesis starting materials

2.1 Synthesis of 3-substituted indolines:

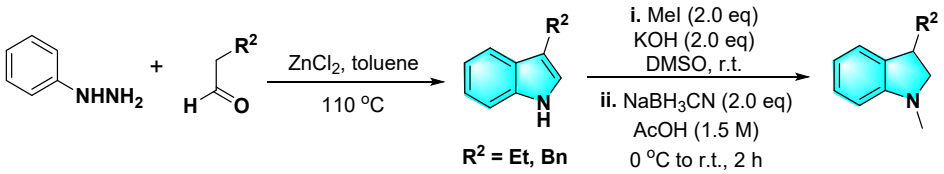
Method for synthesis of compound 1a-1g[1, 5]:



Step 1: A 50.0 mL flask equipped with a stir-bar with 3-Me indole (1.0 eq) and KOH (2.0 eq), DMSO was added to the flask and the solution was stirred under room temperature, then R^1-Br/I (2.0 eq) was added. The reaction mixture was stirred at room temperature and monitored by TLC. Upon finished the reaction mixture was quenched by water and extracted by ethyl acetate. Combined organic phase were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was then purified by chromatography on silica gel with a mixture eluent of petroleum ether and ethyl acetate.

Step 2: To a solution of 3-substituted indole (1.0 equiv.) in acetic acid (1.5 M,) was added in portions sodium cyanoborohydride (2.0 equiv.) at 0 °C, and the mixture was stirred at room temperature. After 2 h, water 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, 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.

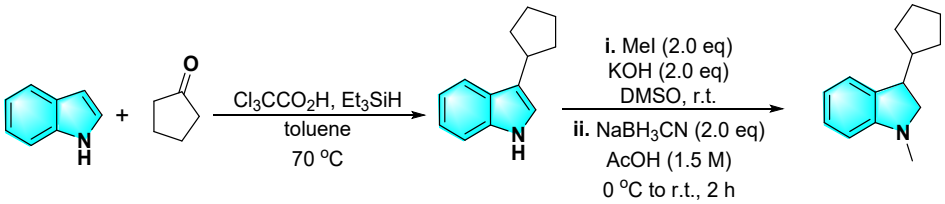
Method for synthesis of compound 1h-1i[2, 5]:



To a solution of phenylhydrazine (10.0 mmol, 1.0 eq) and corresponding aldehyde (10.0 mmol, 1.0 eq) in toluene (40.0 mL) was added AcOH (0.5 mL). The resulting solution was heated at 110 ℃ for 30 min. Then, the mixture was cooled to room temperature and concentrated in vacuo. The remaining orange solid was used without further purification. Zinc chloride (5.0 mmol, 0.5 eq) was added. The resulting solution was heated at 110 ℃ for 3 h, and then cooled to room temperature. The mixture was washed with brine (30.0 mL) and extracted with CH_2Cl_2 (30.0 mL×3). The organic layers were combined and concentrated in vacuo. The residue was purified by silica chromatography to afford product.

Step i and Step ii as mentioned above.

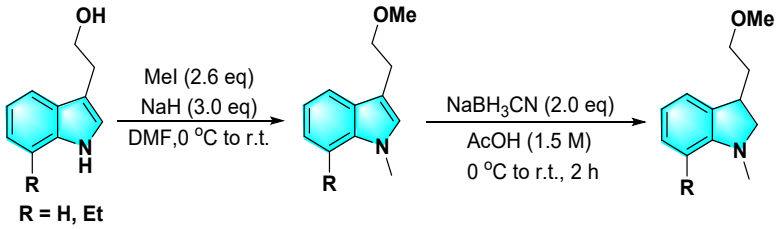
Method for synthesis of compound 1j[3, 5]:



In a 100.0 mL three-neck flask equipped with a magnetic stirrer, 5.0 mL dry toluene, Et_3SiH (3.49 g, 30.0 mmol) and Cl_3CCOOH (2.45g, 15.0 mmol) were added to the flask under N_2 atmosphere. The mixture was stirred to 70 ℃, and the solution of cyclopentanone (0.925 g, 11.0 mmol) and indole (1.17g, 10.0 mmol) in 5.0 mL of toluene was added dropwise. The mixture was heat at 70 ℃ for 20 min to drive reaction to completion as judge by TLC. After the reaction completed, the mixture was cooled to room temperature, and quenched by saturated Na_2CO_3 aqueous solution. Then, the mixture was extracted with Et_2O (20.0 mL×3), and organic layer was dried over anhydrous $MgSO_4$. The solvents were removed under vacuum, and the residue was purified on silica gel to give **1j**.

Step i and Step ii as mentioned above.

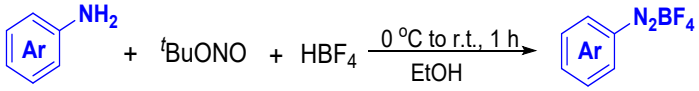
Method for synthesis of compound 1k-1l[4, 5]:



Step 1: a mixture of 3-indole ethanol (1.0 eq.), NaH (3.0 eq.), and MeI (2.6 eq) in DMF afforded N,O-dimethylindole product.

Step 2 as mentioned above.

2.2 Synthesis of aryldiazonium salts[6]:



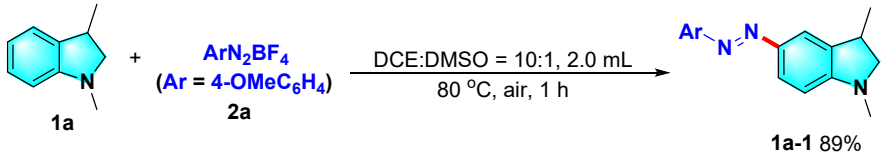
Appropriate arylamine (10.0 mmol) was dissolved in EtOH (3.0 mL) and hydrofluoroboric acid (48% w/w in water, 2.5 mL). The reaction mixture was cooled to 0 °C, tert-Butyl nitrite (2.7 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1.0 hour. The resulting precipitate 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 3aa

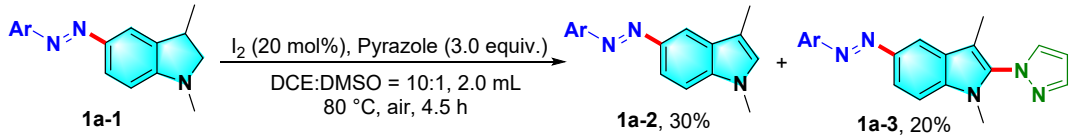
Under air atmosphere, 1,3-dimethylindoline **1a** (36.8 mg, 0.25 mmol), 4-$MeOC_6H_4N_2BF_4$ **2a** (44.4 mg, 0.2 mmol), pyrazole (40.8 mg, 0.6 mmol), I_2 (10.2 mg, 0.04 mmol), solvent (2.0 mL, DCE: DMSO = 10:1) were added to a Schlenk tube (50.0 mL) along with a magnetic stirrer bar, and the reaction mixture was heated at 80 °C for 12.0 h. Then, selectfluor (354.2 mg, 1.0 mmol) was added in and heated at 60 °C for another 3.0 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 (4:1) as the eluent to give **3aa**.

4. Control experiments

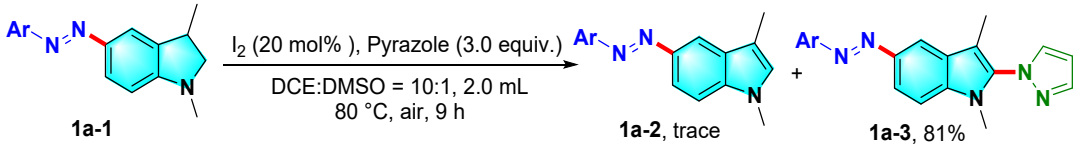
(4a) Under air atmosphere, 1,3-dimethylindoline **1a** (36.8 mg, 0.25 mmol), 4-$MeOC_6H_4N_2BF_4$ **2a** (44.4 mg, 0.2 mmol), solvent (2.0 mL, DCE: DMSO = 10:1) were added to a Schlenk tube (50.0 mL) along with a magnetic stirrer bar, and the reaction mixture was heated at 80 °C for 1.0 h. After cooling 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 as the eluent to give **1a–1** in 89% yield.



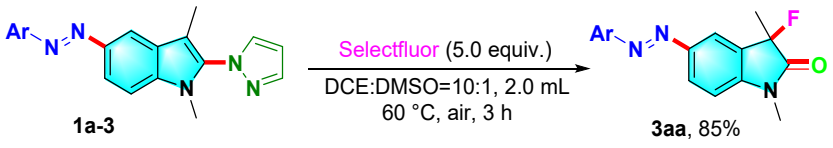
(4b) A mixture of **1a-1** (56.2 mg, 0.2 mmol), pyrazole (40.8 mg, 0.3 mmol) and I_2 (10.2 mg, 0.04 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 80 °C in a Schlenk tube (50.0 mL) for 4.5 h under air. After the transformation completed, the product **1a-2** was isolated in 30% yield and **1a-3** was isolated in 20% yield.



(4c) A mixture of **1a-1** (56.2 mg, 0.2 mmol), pyrazole (40.8 mg, 0.3 mmol) and 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 another 4.5 h under air. After the transformation completed, the product **1a-3** was isolated in 81% yield and **1a-2** was isolated in trace.



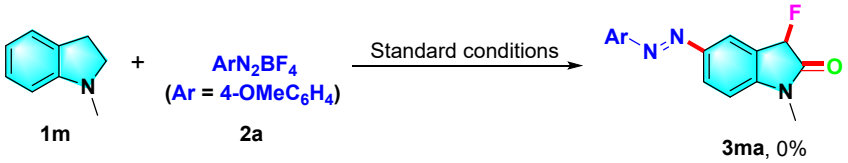
(4d) A mixture of **1a-3** (34.5 mg, 0.1 mmol), selectfluor (177.1 mg, 0.5 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 60 °C in a Schlenk tube (50.0 mL) for 3 h under air. After the transformation was completed, **3aa** was isolated in 85% yield.



(4e) A mixture of **1a-3** (34.5 mg, 0.1 mmol), selectfluor (177.1 mg, 0.5 mmol) and tempo (78.1mg,

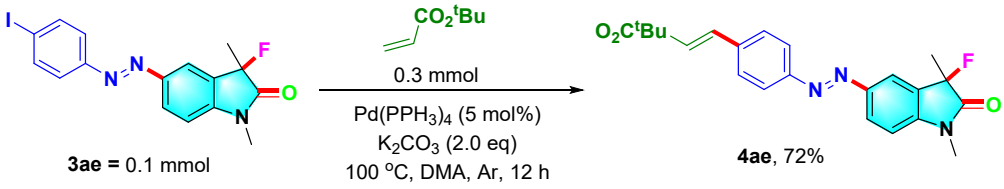
0.5 mmol) in solvent (2.0 mL, DCE: DMSO = 10:1) was stirred at 60 °C in a Schlenk tube (50.0 mL) for 3.0 h under air. After the transformation was completed, **3aa** was isolated in 66% yield.

(4f) A mixture of *N*-methylindoline **1m** (33.3 mg, 0.25 mmol), 4-$MeOC_6H_4N_2BF_4$ **2a** (44.4 mg, 0.2 mmol), pyrazole (40.8 mg, 0.6 mmol), I_2 (10.2 mg, 0.04 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 12.0 h. Then, selectfluor (354.2 mg, 1.0 mmol) was added in and heated at 60 °C for another 3.0 h to complete the transformation. The product **3ma** could not be obtained.



5. Synthetic applications

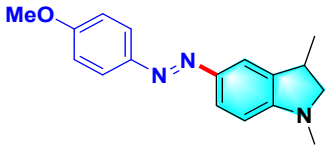
(5a) Under air atmosphere, **1a** (36.8 mg, 0.25 mmol), **2q** (54.8 mg, 0.2 mmol), pyrazole (40.8 mg, 0.6 mmol), I_2 (10.2 mg, 0.04 mmol), solvent (2.0 mL, DCE: DMSO = 10:1) were added to a Schlenk tube (50.0 mL) along with a magnetic stirrer bar, and the reaction mixture was heated at 80 °C for 12.0 h. Then, selectfluor (354.2 mg, 1.0 mmol) was added in and heated at 60 °C for another 3.0 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 (3:1) as the eluent to give **3aq**.



(5b) A mixture of **3ae** (40.9 mg, 0.1 mmol), *tert*-butylacrylate (38.0 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 50.0 mL Schlenk tube for 12.0 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 as the eluent to give **4ae** as an orange solid (29.5 mg, 72% yield).

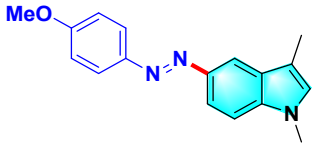
6. Characterization data for the products

(1) (*E*)-5-((4-methoxyphenyl)diazenyl)-1,3-dimethylindoline (1a-1)



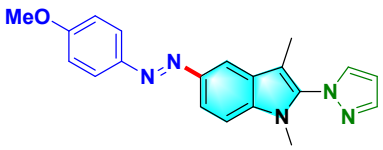
Orange liquid, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.73 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.66 (t, *J* = 1.6 Hz, 1H), 7.02 – 6.97 (m, 2H), 6.48 (d, *J* = 8.3 Hz, 1H), 3.87 (s, 3H), 3.68 (t, *J* = 8.8 Hz, 1H), 3.36 (h, *J* = 7.3 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.85 (s, 3H), 1.37 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 155.0, 147.6, 145.59, 136.2, 128.2, 123.86, 115.0, 114.2, 105.4, 63.6, 55.6, 34.9, 34.88, 18.98. HRMS (ESI): Calcd. for $C_{17}H_{19}N_3O$ $[M+H]^+$: 282.1600; found: 282.1598.

(2) (*E*)-5-((4-methoxyphenyl)diazenyl)-1,3-dimethyl-1H-indole (1a-2)



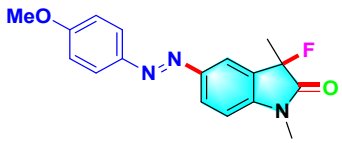
Yellow solid, m.p.: 124-126 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.06 – 7.01 (m, 2H), 6.86 (s, 1H), 3.89 (s, 3H), 3.76 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 147.4, 146.49, 138.46, 128.9, 127.9, 124.2, 116.89, 115.4, 114.26, 112.5, 109.48, 55.66, 32.9, 9.7. HRMS (ESI): Calcd. for $C_{17}H_{17}N_3O$ $[M+H]^+$: 280.1444; found: 280.1442.

(3) (*E*)-5-((4-methoxyphenyl)diazenyl)-1,3-dimethyl-2-(1H-pyrazol-1-yl)-1H-indole (1a-3)



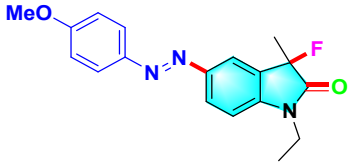
Orange solid, m.p.: 197-199 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.9 Hz, 1H), 7.98 – 7.92 (m, 3H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.54 (t, *J* = 2.2 Hz, 1H), 3.90 (s, 3H), 3.55 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 147.3, 147.1, 142.0, 136.3, 133.2, 133.09, 126.8, 124.38, 117.0, 117.0, 114.3, 109.96, 107.7, 106.9, 55.69, 29.8, 8.27. HRMS (ESI): Calcd. for $C_{20}H_{19}N_5O$ $[M+H]^+$: 346.1662; found: 346.1660.

(4) (*E*)-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1,3-dimethylindolin-2-one (3aa)



Orange solid, (48.5 mg, 77% yield), m.p.: 135-137 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (t, *J* = 2.0 Hz, 1H), 7.98 (dt, *J* = 8.3, 1.8 Hz, 1H), 7.91 – 7.88 (m, 2H), 7.03 – 7.00 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.25 (s, 3H), 1.82 (d, *J* = 22.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.43 (d, *J* = 21.7 Hz) 162.15, 149.43 (d, *J* = 2.8 Hz), 146.91, 145.28 (d, *J* = 4.9 Hz), 128.87 (d, *J* = 2.6 Hz), 128.13 (d, *J* = 18.6 Hz), 124.76, 116.78, 114.39, 108.9, 91.37, 90.1, 55.7, 26.6, 21.3 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.68. HRMS (ESI): Calcd. for $C_{17}H_{16}FN_3O_2$ $[M+H]^+$: 314.1299; found: 314.1297.

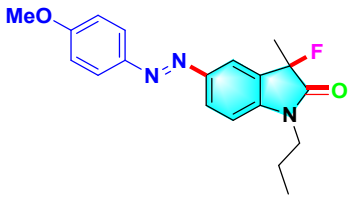
(5) (*E*)-1-ethyl-3-fluoro-5-((4-methoxyphenyl)diazenyl)-3-methylindolin-2-one (3ba)



Orange solid, (37.3 mg, 57% yield), m.p.: 132-134 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (t, *J* = 2.1 Hz, 1H), 7.97 (dt, *J* = 8.3, 1.8 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.79 (qd, *J* = 7.2, 3.4 Hz, 2H), 1.82 (d, *J* = 22.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.09 (d, *J* = 21.6 Hz), 162.1, 149.28 (d, *J* = 2.8 Hz), 146.9, 144.4 (d, *J* = 4.8 Hz), 128.7 (d, *J* = 2.6 Hz), 128.38 (d, *J* = 18.8 Hz), 124.7, 117.0, 114.39,

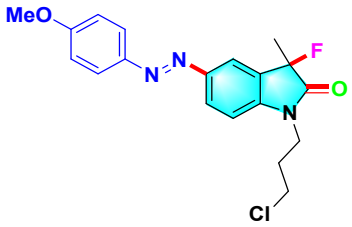
109.0, 91.37, 90.1, 55.7, 35.2, 21.3 (d, J = 29.3 Hz), 12.68. ^{19}F NMR (565 MHz, $CDCl_3$) δ -153.06. HRMS (ESI): Calcd. for $C_{18}H_{18}FN_3O_2$ $[M+H]^+$: 328.1455; found: 328.1453.

(6) (*E*)-3-fluoro-5-((4-methoxyphenyl)diazenyl)-3-methyl-1-propylindolin-2-one (3ca)



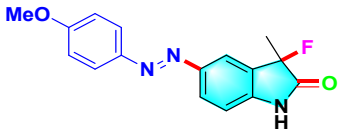
Orange liquid, (47.7mg, 70% yield), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (t, J = 2.1 Hz, 1H), 7.96 (dt, J = 8.3, 1.8 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.03 – 6.99 (m, 2H), 6.97 (d, J = 8.3 Hz, 1H), 3.89 (s, 3H), 3.70 (td, J = 7.2, 2.4 Hz, 2H), 1.82 (d, J = 22.1 Hz, 3H), 1.75 (q, J = 7.4 Hz, 2H), 0.98 (t, J = 7.4 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 173.48 (d, J = 21.4 Hz), 162.1, 149.2 (d, J = 2.8 Hz), 146.9, 144.8 (d, J = 4.9 Hz), 128.7 (d, J = 2.6 Hz), 128.29 (d, J = 18.6 Hz), 124.7, 116.96, 114.39, 109.2, 91.3, 90.1, 55.7, 41.9, 21.4 (d, J = 29.3 Hz), 20.78, 11.39. ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.78. HRMS (ESI): Calcd. for $C_{19}H_{20}FN_3O_2$ $[M+H]^+$: 342.1612; found: 342.1613.

(7) (*E*)-1-(3-chloropropyl)-3-fluoro-5-((4-methoxyphenyl)diazenyl)-3-methylindolin-2-one (3da)



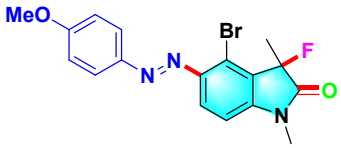
Orange solid, (36 mg, 48% yield), m.p.: 130-132 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (t, J = 2.1 Hz, 1H), 7.99 (dt, J = 8.3, 1.8 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.07 (d, J = 8.3 Hz, 1H), 7.03 – 7.00 (m, 2H), 3.91 (t, J = 7.0 Hz, 2H), 3.89 (s, 3H), 3.62 (t, J = 6.2 Hz, 2H), 2.20 (p, J = 6.5 Hz, 2H), 1.82 (d, J = 22.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 173.57 (d, J = 21.5 Hz), 162.2, 149.46 (d, J = 2.8 Hz), 146.9, 144.4 (d, J = 4.9 Hz), 128.86 (d, J = 2.6 Hz), 128.19 (d, J = 18.7 Hz), 124.8, 117.1, 114.4, 109.1, 91.2, 90.0, 55.7, 42.1, 37.96, 30.38, 21.3 (d, J = 29.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.36. HRMS (ESI): Calcd. for $C_{19}H_{19}ClFN_3O_2$ $[M+H]^+$: 376.1222; found: 376.1222.

(8) (*E*)-3-fluoro-5-((4-methoxyphenyl)diazenyl)-3-methylindolin-2-one (3ea)



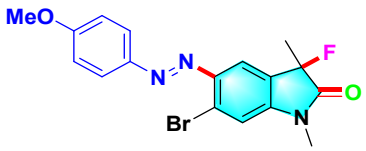
Orange solid, (29 mg, 48% yield), m.p.: 194-196 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.95 (dt, *J* = 8.1, 1.7 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.03 – 7.00 (m, 2H), 3.90 (s, 3H), 1.86 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.59 (d, *J* = 21.5 Hz), 162.2, 149.49 (d, *J* = 2.5 Hz), 146.9, 142.4 (d, *J* = 5.2 Hz), 128.6, 128.49 (d, *J* = 3.2 Hz), 124.8, 117.6, 114.4, 111.0, 91.8, 90.59, 55.7, 21.38 (d, *J* = 29.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.90. HRMS (ESI): Calcd. for $C_{16}H_{14}FN_3O_2$ $[M+H]^+$: 300.1142; found: 300.1139.

(9) (*E*)-4-bromo-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1,3-dimethylindolin-2-one (3fa)



Orange solid, (45.9 mg, 59% yield), m.p.: 198-200 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.78 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.04 – 7.00 (m, 2H), 6.84 (dd, *J* = 8.4, 1.1 Hz, 1H), 3.90 (s, 3H), 3.23 (s, 3H), 2.03 (d, *J* = 21.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.09 (d, *J* = 21.5 Hz), 162.56, 147.2, 146.4 (d, *J* = 4.6 Hz), 145.96 (d, *J* = 2.3 Hz), 126.8 (d, *J* = 17.7 Hz), 125.4, 124.0, 120.18 (d, *J* = 2.3 Hz), 114.48, 108.1, 92.78, 91.5, 55.77, 26.68, 19.6 (d, *J* = 28.1 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -160.99. HRMS (ESI): Calcd. for $C_{17}H_{15}BrFN_3O_2$ $[M+H]^+$: 392.0404; found: 392.0402.

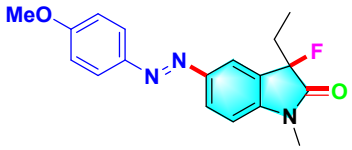
(10) (*E*)-6-bromo-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1,3-dimethylindolin-2-one (3ga)



Orange solid, (54 mg, 69% yield), m.p.: 199-201 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.20 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.23 (s, 3H), 1.80 (d, *J* = 22.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.0 (d, *J* = 21.7 Hz), 162.5, 147.07, 145.77 (d, *J* = 4.5 Hz), 145.7 (d, *J* = 2.7 Hz), 129.8 (d, *J* = 3.0 Hz), 127.26 (d, *J* = 18.8 Hz), 125.39,

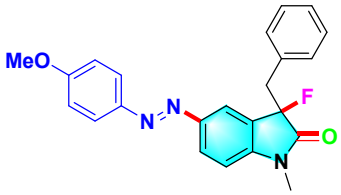
114.4, 114.0, 113.56, 91.0, 89.77, 55.7, 26.6, 21.16 (d, J = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.35. HRMS (ESI): Calcd. for $C_{17}H_{15}BrFN_3O_2$ $[M+H]^+$: 392.0404; found: 392.0401.

(11) (*E*)-3-ethyl-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1-methylindolin-2-one (3ha)



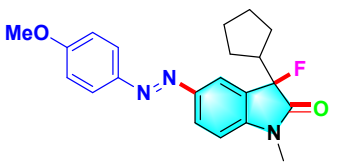
Orange solid, (45.8 mg, 70% yield), m.p.: 133-135 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, J = 7.4, 1.7 Hz, 2H), 7.92 – 7.88 (m, 2H), 7.01 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 3.25 (s, 3H), 2.29 – 2.22 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3 (d, J = 21.7 Hz), 162.1, 149.3 (d, J = 2.8 Hz), 146.9, 145.89 (d, J = 5.0 Hz), 128.5 (d, J = 2.6 Hz), 126.78 (d, J = 18.8 Hz), 124.7, 117.3, 114.38, 108.8, 94.47, 93.2, 55.7, 28.29 (d, J = 27.6 Hz), 26.5, 7.1 (d, J = 8.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -157.18. HRMS (ESI): Calcd. for $C_{18}H_{18}FN_3O_2$ $[M+H]^+$: 328.1455; found: 328.1454.

(12) (*E*)-3-benzyl-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1-methylindolin-2-one (3ia)



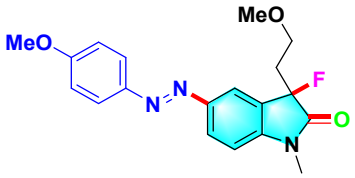
Orange solid, (43.7 mg, 56% yield), m.p.: 155-157 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 3H), 7.75 (t, J = 2.0 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.06 – 7.00 (m, 4H), 6.78 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 3.60 (dd, J = 13.2, 9.8 Hz, 1H), 3.37 (dd, J = 18.8, 13.2 Hz, 1H), 3.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9 (d, J = 21.1 Hz), 162.1, 149.06 (d, J = 2.7 Hz), 146.9, 145.6 (d, J = 5.1 Hz), 132.28 (d, J = 8.5 Hz), 130.6, 128.27, 127.4, 126.1 (d, J = 18.9 Hz), 124.76, 118.3, 114.38, 108.6, 93.9, 92.6, 55.7, 41.36 (d, J = 28.1 Hz), 26.38. ^{19}F NMR (565 MHz, $CDCl_3$) δ -155.74. HRMS (ESI): Calcd. for $C_{23}H_{20}FN_3O_2$ $[M+H]^+$: 390.1612; found: 390.1610.

(13) (*E*)-3-cyclopentyl-3-fluoro-5-((4-methoxyphenyl)diazenyl)-1-methylindolin-2-one (3ja)



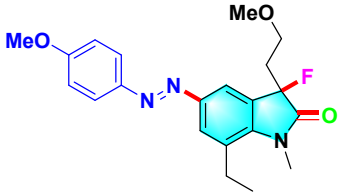
Orange solid, (44.5 mg, 60% yield), m.p.: 150-152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (t, *J* = 2.0 Hz, 1H), 7.97 (dt, *J* = 8.3, 1.7 Hz, 1H), 7.92 – 7.88 (m, 2H), 7.02 – 6.99 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 3.88 (s, 3H), 3.23 (s, 3H), 2.75 (dt, *J* = 12.8, 8.5 Hz, 1H), 1.79 (dtd, *J* = 37.3, 7.5, 6.9, 4.1 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.59 – 1.48 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6 (d, *J* = 22.0 Hz), 162.08, 149.17 (d, *J* = 2.7 Hz), 146.9, 145.89 (d, *J* = 5.4 Hz), 127.8 (d, *J* = 2.5 Hz), 126.9 (d, *J* = 19.4 Hz), 124.7, 118.27, 114.36, 108.66, 95.26, 94.0, 55.69, 45.16 (d, *J* = 25.7 Hz), 26.56 (d, *J* = 3.3 Hz), 26.5, 26.26 (d, *J* = 4.9 Hz), 25.68, 25.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -159.90. HRMS (ESI): Calcd. for $C_{21}H_{22}FN_3O_2$ $[M+H]^+$: 368.1768; found: 368.1766.

(14) (*E*)-3-fluoro-3-(2-methoxyethyl)-5-((4-methoxyphenyl)diazenyl)-1-methylindolin-2-one (3ka)



Orange solid, (47.1 mg, 66% yield), m.p.: 148-150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 6.0, 2.0 Hz, 2H), 7.91 – 7.88 (m, 2H), 7.03 – 7.00 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 3H), 3.50 – 3.44 (m, 1H), 3.32 (td, *J* = 9.3, 5.8 Hz, 1H), 3.24 (s, 3H), 3.15 (s, 3H), 2.70 (dddd, *J* = 13.9, 11.9, 8.8, 6.6 Hz, 1H), 2.41 (dddd, *J* = 15.1, 13.9, 5.8, 4.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.16 (d, *J* = 21.5 Hz), 162.1, 149.2 (d, *J* = 2.9 Hz), 146.9, 146.1 (d, *J* = 4.9 Hz), 128.86 (d, *J* = 2.6 Hz), 126.2 (d, *J* = 18.2 Hz), 124.75, 117.59, 114.39, 108.8, 92.86, 91.6, 67.2 (d, *J* = 9.4 Hz), 58.7, 55.7, 34.7 (d, *J* = 27.5 Hz), 26.6. ^{19}F NMR (565 MHz, $CDCl_3$) δ -155.57. HRMS (ESI): Calcd. for $C_{19}H_{20}FN_3O_3$ $[M+H]^+$: 358.1561; found: 358.1557.

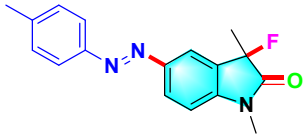
(15) (*E*)-7-ethyl-3-fluoro-3-(2-methoxyethyl)-5-((4-methoxyphenyl)diazenyl)-1-methylindolin-2-one (3la)



Orange liquid, (55.4 mg, 72% yield), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.81 (dt, *J* = 11.9, 2.1 Hz, 2H), 7.04 – 6.99 (m, 2H), 3.89 (s, 3H), 3.50 (s, 3H), 3.48 – 3.43 (m, 1H), 3.28 (td, *J* = 9.2, 5.9 Hz, 1H), 3.15 (s, 3H), 2.99 (qd, *J* = 7.5, 2.5 Hz, 2H), 2.75 – 2.67 (m, 1H), 2.37 (dddd, *J*

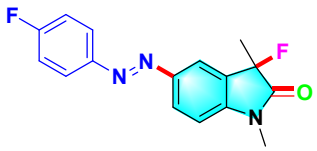
= 15.5, 13.8, 5.9, 4.4 Hz, 1H), 1.35 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1 (d, *J* = 20.5 Hz), 162.09, 148.98 (d, *J* = 3.2 Hz), 146.98, 143.17 (d, *J* = 5.0 Hz), 130.6 (d, *J* = 2.8 Hz), 127.5, 127.28 (d, *J* = 17.7 Hz), 124.7, 115.2, 114.38, 92.2, 90.99, 67.26 (d, *J* = 9.5 Hz), 58.7, 55.7, 35.07 (d, *J* = 28.1 Hz), 29.6, 24.9, 16.68. ^{19}F NMR (565 MHz, $CDCl_3$) δ -154.16. HRMS (ESI): Calcd. for $C_{21}H_{24}FN_3O_3$ $[M+H]^+$: 386.1874; found: 386.1870.

(16) (*E*)-3-fluoro-1,3-dimethyl-5-(p-tolyldiazenyl)indolin-2-one (3ab)



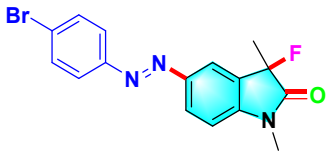
Orange solid, (39.8 mg, 67% yield), m.p.: 130-132 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (t, *J* = 2.0 Hz, 1H), 7.99 (dt, *J* = 8.2, 1.8 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.22 (s, 3H), 2.42 (s, 3H), 1.82 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3 (d, *J* = 21.9 Hz), 150.58, 149.26 (d, *J* = 2.8 Hz), 145.5 (d, *J* = 4.9 Hz), 141.59, 129.8, 129.16 (d, *J* = 2.6 Hz), 128.0 (d, *J* = 18.6 Hz), 122.8, 116.79, 108.9, 91.26, 90.0, 26.5, 21.56, 21.2 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.62. HRMS (ESI): Calcd. for $C_{17}H_{16}FN_3O$ $[M+H]^+$: 298.1350; found: 298.1346.

(17) (*E*)-3-fluoro-5-((4-fluorophenyl)diazenyl)-1,3-dimethylindolin-2-one (3ac)



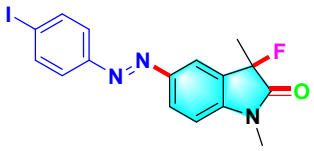
Orange solid, (36.2 mg, 60% yield), m.p.: 163-165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 4.9, 2.7 Hz, 2H), 7.94 – 7.90 (m, 2H), 7.22 – 7.17 (m, 2H), 6.99 (d, *J* = 9.0 Hz, 1H), 3.27 (s, 3H), 1.83 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.6 Hz), δ 164.4 (d, *J* = 252.1 Hz), 149.16 (d, *J* = 2.8 Hz), 149.1 (d, *J* = 3.0 Hz), 145.9 (d, *J* = 4.7 Hz), 129.5 (d, *J* = 2.5 Hz), 128.27 (d, *J* = 18.7 Hz), 124.88 (d, *J* = 8.9 Hz), 116.9, 116.2 (d, *J* = 23.0 Hz), 109.0, 91.29, 90.06, 26.67, 21.3 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -109.33, -152.80. HRMS (ESI): Calcd. for $C_{16}H_{13}F_2N_3O$ $[M+H]^+$: 302.1099; found: 302.1097.

(18) (*E*)-5-((4-bromophenyl)diazenyl)-3-fluoro-1,3-dimethylindolin-2-one (3ad)



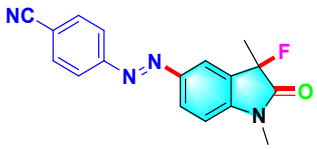
Orange solid, (40.4 mg, 56% yield), m.p.: 170-172 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.81 – 7.73 (m, 2H), 7.69 – 7.61 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 1H), 3.27 (s, 3H), 1.83 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.7 Hz), 151.29, 149.1 (d, *J* = 2.7 Hz), 146.19 (d, *J* = 4.6 Hz), 132.5, 129.8 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 18.8 Hz), 125.4, 124.38, 116.9, 109.0, 91.2, 90.0, 26.67, 21.3 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.79. HRMS (ESI): Calcd. for $C_{16}H_{13}BrFN_3O$ $[M+H]^+$: 362.0298; found: 362.0296.

(19) (*E*)-3-fluoro-5-((4-iodophenyl)diazenyl)-1,3-dimethylindolin-2-one (3ae)



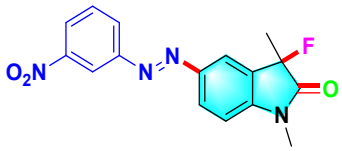
Orange solid, (57.9 mg, 71% yield), m.p.: 185-187 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 6.0, 2.0 Hz, 2H), 7.88 – 7.81 (m, 2H), 7.66 – 7.59 (m, 2H), 6.97 (d, *J* = 8.6 Hz, 1H), 3.26 (s, 3H), 1.83 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.37 (d, *J* = 21.7 Hz), 151.8, 149.09 (d, *J* = 2.7 Hz), 146.19 (d, *J* = 4.9 Hz), 138.49, 129.8 (d, *J* = 2.5 Hz), 128.26 (d, *J* = 18.6 Hz), 124.48, 116.9, 109.0, 97.6, 91.2, 89.97, 26.66, 21.3 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.75. HRMS (ESI): Calcd. for $C_{16}H_{13}FIN_3O$ $[M+H]^+$: 410.0160; found: 410.0157.

(20) (*E*)-4-((3-fluoro-1,3-dimethyl-2-oxoindolin-5-yl)diazenyl)benzonitrile (3af)



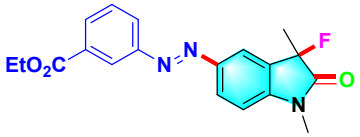
Orange solid, (31.7 mg, 51% yield), m.p.: 180-182 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 8.2, 1.7 Hz, 1H), 8.06 (t, *J* = 2.0 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.29 (s, 3H), 1.84 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3 (d, *J* = 21.6 Hz), 154.5, 149.06 (d, *J* = 2.7 Hz), 147.0 (d, *J* = 4.7 Hz), 133.37, 130.7 (d, *J* = 2.4 Hz), 128.4 (d, *J* = 19.0 Hz), 123.39, 118.6, 117.0, 113.9, 109.1, 91.09, 89.86, 26.7, 21.29 (d, *J* = 29.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.89. HRMS (ESI): Calcd. for $C_{17}H_{13}FN_4O$ $[M+H]^+$: 309.1146; found: 309.1142.

(21) (*E*)-3-fluoro-1,3-dimethyl-5-((3-nitrophenyl)diazenyl)indolin-2-one (3ag)



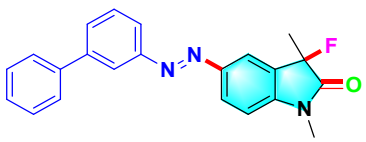
Orange solid, (39 mg, 59% yield), m.p.: 183-185 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (t, *J* = 2.1 Hz, 1H), 8.31 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.26 – 8.23 (m, 1H), 8.11 (dt, *J* = 8.3, 1.8 Hz, 1H), 8.08 (t, *J* = 2.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 3.29 (s, 3H), 1.84 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.37 (d, *J* = 21.7 Hz), 153.0, 149.19, 148.8 (d, *J* = 2.8 Hz), 146.9 (d, *J* = 4.6 Hz), 130.67 (d, *J* = 2.5 Hz), 130.1, 129.49, 128.4 (d, *J* = 18.7 Hz), 124.89, 117.0, 116.8, 109.1, 91.1, 89.89, 26.7, 21.29 (d, *J* = 29.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.86. HRMS (ESI): Calcd. for $C_{16}H_{13}FN_4O$ $[M+H]^+$: 329.1044; found: 329.1042.

(22) ethyl (*E*)-3-((3-fluoro-1,3-dimethyl-2-oxoindolin-5-yl)diazenyl)benzoate (3ah)



Orange solid, (40.3 mg, 57% yield), m.p.: 155-157 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (t, *J* = 1.8 Hz, 1H), 8.14 (dt, *J* = 7.7, 1.5 Hz, 1H), 8.10 – 8.06 (m, 3H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.27 (s, 3H), 1.84 (d, *J* = 22.1 Hz, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.9 Hz), 166.17, 152.5, 149.1 (d, *J* = 2.7 Hz), 146.27 (d, *J* = 4.9 Hz), 131.8, 131.7, 129.9 (d, *J* = 2.3 Hz), 129.3, 128.29 (d, *J* = 18.8 Hz), 126.7, 124.1, 117.0, 109.0, 91.2, 89.99, 61.4, 26.67, 21.3 (d, *J* = 29.3 Hz), 14.48. ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.79. HRMS (ESI): Calcd. for $C_{19}H_{18}FN_3O_3$ $[M+H]^+$: 356.1404; found: 356.1402.

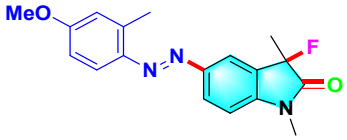
(23) (*E*)-5-([1,1'-biphenyl]-3-yldiazenyl)-3-fluoro-1,3-dimethylindolin-2-one (3ai)



Orange solid, (34.5 mg, 48% yield), m.p.: 150-152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (t, *J* = 1.9 Hz, 1H), 8.10 – 8.06 (m, 2H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.68 (m, 3H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.28 (s, 3H), 1.85 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, J = 21.6 Hz), 153.0, 149.3 (d, J = 2.8

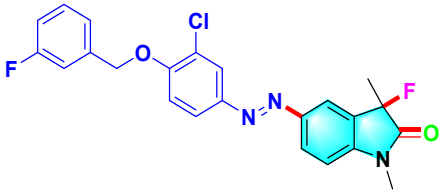
Hz), 145.99 (d, J = 4.6 Hz), 142.39, 140.47, 129.67, 129.66, 129.6 (d, J = 2.5 Hz), 129.0, 128.2 (d, J = 18.7 Hz), 127.86, 127.3, 121.7, 121.6, 117.0, 109.0, 91.29, 90.06, 26.66, 21.3 (d, J = 29.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.71. HRMS (ESI): Calcd. for $C_{22}H_{18}FN_3O$ $[M+H]^+$: 360.1506; found: 360.1504.

(24) (*E*)-3-fluoro-5-((4-methoxy-2-methylphenyl)diazenyl)-1,3-dimethylindolin-2-one (3ak)



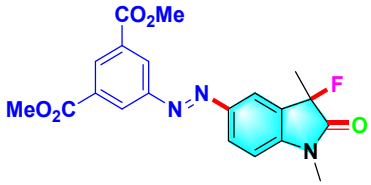
Orange solid, (33.4 mg, 51% yield), m.p.: 144-146 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 2.7 Hz, 1H), 6.79 (dd, *J* = 8.9, 2.8 Hz, 1H), 3.87 (s, 3H), 3.26 (s, 3H), 2.73 (s, 3H), 1.83 (d, *J* = 22.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.47 (d, *J* = 21.6 Hz), 162.06, 149.9 (d, *J* = 2.7 Hz), 145.06 (d, *J* = 4.7 Hz), 145.0, 140.88, 128.7 (d, *J* = 2.7 Hz), 128.1 (d, *J* = 18.7 Hz), 117.17, 116.9, 115.48, 112.6, 108.9, 91.4, 90.2, 55.6, 26.6, 21.37 (d, *J* = 29.4 Hz), 18.0. ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.83. HRMS (ESI): Calcd. for $C_{18}H_{18}FN_3O_2$ $[M+H]^+$: 328.1455; found: 328.1453.

(25) (*E*)-5-((3-chloro-4-((3-fluorobenzyl)oxy)phenyl)diazenyl)-3-fluoro-1,3-dimethylindolin-2-one (3al)



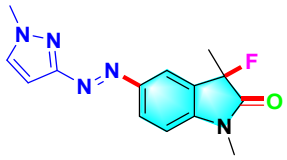
Orange solid, (57.4 mg, 65% yield), m.p.: 155-157 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 3H), 7.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.37 (td, *J* = 7.9, 5.8 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 9.2 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 2H), 3.26 (s, 3H), 1.82 (d, *J* = 22.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.6 Hz), δ 163.1 (d, *J* = 246.6 Hz), 155.99, 149.1 (d, *J* = 2.7 Hz), 146.99, 145.8 (d, *J* = 4.8 Hz), 138.6 (d, *J* = 7.7 Hz), 130.4 (d, *J* = 8.0 Hz), 129.47 (d, *J* = 2.4 Hz), 128.2 (d, *J* = 18.7 Hz), 124.85, 124.38, 123.2, 122.5 (d, *J* = 2.8 Hz), 116.78, 115.2 (d, *J* = 21.1 Hz), 114.0 (d, *J* = 22.2 Hz), 113.3, 109.0, 91.28, 90.06, 70.2 (d, *J* = 2.0 Hz), 26.6, 21.3 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.37, -152.74. HRMS (ESI): Calcd. for $C_{23}H_{18}F_2N_3O_2$ $[M+H]^+$: 442.1128; found: 442.1127.

(26) dimethyl (*E*)-5-((3-fluoro-1,3-dimethyl-2-oxoindolin-5-yl)diazenyl)isophthalate (3am)



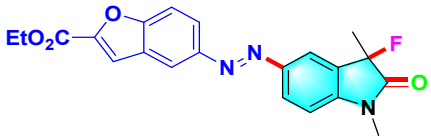
Orange solid, (39.7 mg, 50% yield), m.p.: 161-163 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.70 (d, *J* = 1.6 Hz, 2H), 8.12 – 8.06 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.99 (s, 6H), 3.28 (s, 3H), 1.83 (d, *J* = 22.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.39 (d, *J* = 21.7 Hz), 165.8, 152.66, 148.9 (d, *J* = 2.8 Hz), 146.66 (d, *J* = 4.9 Hz), 132.2, 131.86, 130.3 – 130.2 (m), 128.34 (d, *J* = 18.8 Hz), 127.78, 117.07, 109.09, 91.1, 89.9, 52.7, 26.68, 21.27 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.82. HRMS (ESI): Calcd. for $C_{20}H_{18}FN_3O_5$ $[M+H]^+$: 400.1303; found: 400.1301.

(27) (*E*)-3-fluoro-1,3-dimethyl-5-((1-methyl-1H-pyrazol-3-yl)diazenyl)indolin-2-one (3an)



Orange solid, (37.3 mg, 65% yield), m.p.: 150-152 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (t, *J* = 2.1 Hz, 1H), 8.03 (dt, *J* = 8.3, 1.8 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H), 4.01 (s, 3H), 3.24 (s, 3H), 1.79 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, J = 21.6 Hz), 163.57, 149.4 (d, *J* = 2.8 Hz), 145.9 (d, *J* = 4.5 Hz), 132.0, 129.3 (d, *J* = 2.4 Hz), 128.16 (d, *J* = 18.7 Hz), 117.1, 108.9, 96.18, 91.2, 89.98, 39.79, 26.6, 21.17 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.64. HRMS (ESI): Calcd. for $C_{14}H_{14}FN_5O$ $[M+H]^+$: 288.1255; found: 288.1252.

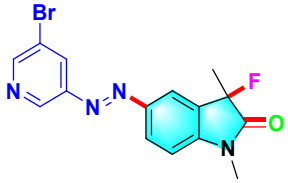
(28) ethyl (*E*)-5-((3-fluoro-1,3-dimethyl-2-oxoindolin-5-yl)diazenyl)benzofuran-2-carboxylate (3ao)



Yellow solid, (42.3 mg, 53% yield), m.p.: 195-197 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.0 Hz, 1H), 8.08 – 8.03 (m, 3H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.62 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.27 (s, 3H), 1.84 (d, *J* = 22.1 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR

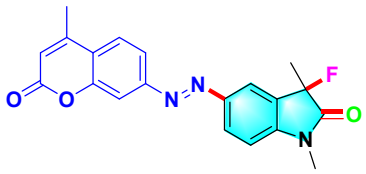
(151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.6 Hz), 159.3, 157.0, 149.46, 149.1 (d, *J* = 2.7 Hz), 147.2, 145.9 (d, *J* = 4.7 Hz), 129.5 (d, *J* = 2.6 Hz), 128.26 (d, *J* = 18.7 Hz), 127.68, 122.08, 118.7, 116.89, 114.57, 113.0, 109.0, 91.29, 90.06, 61.89, 26.66, 21.3 (d, *J* = 29.2 Hz), 14.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.77. HRMS (ESI): Calcd. for $C_{21}H_{18}FN_3O_4$ $[M+H]^+$: 396.1354; found: 396.1351.

(29) (*E*)-5-((5-bromopyridin-3-yl)diazenyl)-3-fluoro-1,3-dimethylindolin-2-one (3ap)



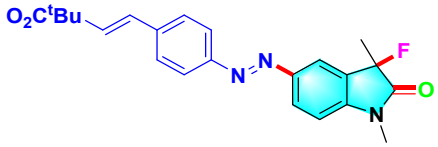
Orange solid, (30 mg, 41% yield), m.p.: 197-199 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.0 Hz, 1H), 8.75 (d, *J* = 2.1 Hz, 1H), 8.27 (t, *J* = 2.1 Hz, 1H), 8.09 (dt, *J* = 8.3, 1.8 Hz, 1H), 8.06 (t, *J* = 2.1 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.29 (s, 3H), 1.84 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.36 (d, *J* = 21.6 Hz), 152.39, 149.0 (d, *J* = 2.7 Hz), 148.3, 147.07 (d, *J* = 4.6 Hz), 146.2, 130.6 (d, *J* = 2.6 Hz), 128.8, 128.47 (d, *J* = 18.8 Hz), 121.46, 117.06, 109.1, 91.07, 89.8, 26.7, 21.28 (d, *J* = 29.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.89. HRMS (ESI): Calcd. for $C_{15}H_{12}BrFN_4O$ $[M+H]^+$: 363.0251; found: 363.0248.

(30) (*E*)-3-fluoro-1,3-dimethyl-5-((4-methyl-2-oxo-2H-chromen-7-yl)diazenyl)indolin-2-one (3aq)



Orange solid, (38 mg, 52% yield), m.p.: 190-192 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 8.2, 1.8 Hz, 1H), 8.06 (t, *J* = 2.0 Hz, 1H), 7.84 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.34 (d, *J* = 1.0 Hz, 1H), 3.28 (s, 3H), 2.48 (d, *J* = 1.3 Hz, 3H), 1.84 (d, *J* = 22.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.38 (d, *J* = 21.6 Hz), 160.7, 154.2, 151.98, 149.09 (d, *J* = 2.8 Hz), 146.76 (d, *J* = 4.8 Hz), 130.5 (d, *J* = 2.4 Hz), 128.36 (d, *J* = 18.7 Hz), 125.4, 121.7, 119.07, 117.0, 116.0, 110.8, 109.1, 91.1, 89.9, 26.7, 21.29 (d, *J* = 29.2 Hz), 18.9. ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.83. HRMS (ESI): Calcd. for $C_{20}H_{16}FN_3O_3$ $[M+H]^+$: 366.1248; found: 366.1247.

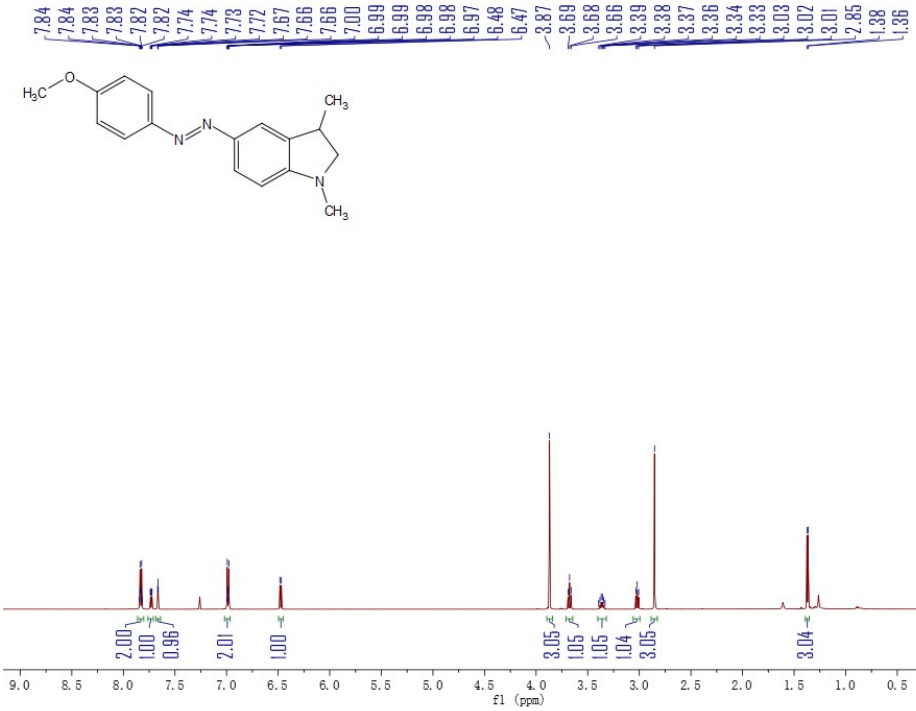
(31) 5-((*E*)-(4-((*E*)-3,3-dimethylbut-1-en-1-yl)phenyl)diazenyl)-3-fluoro-1,3-dimethylindolin-2-one (4ae)



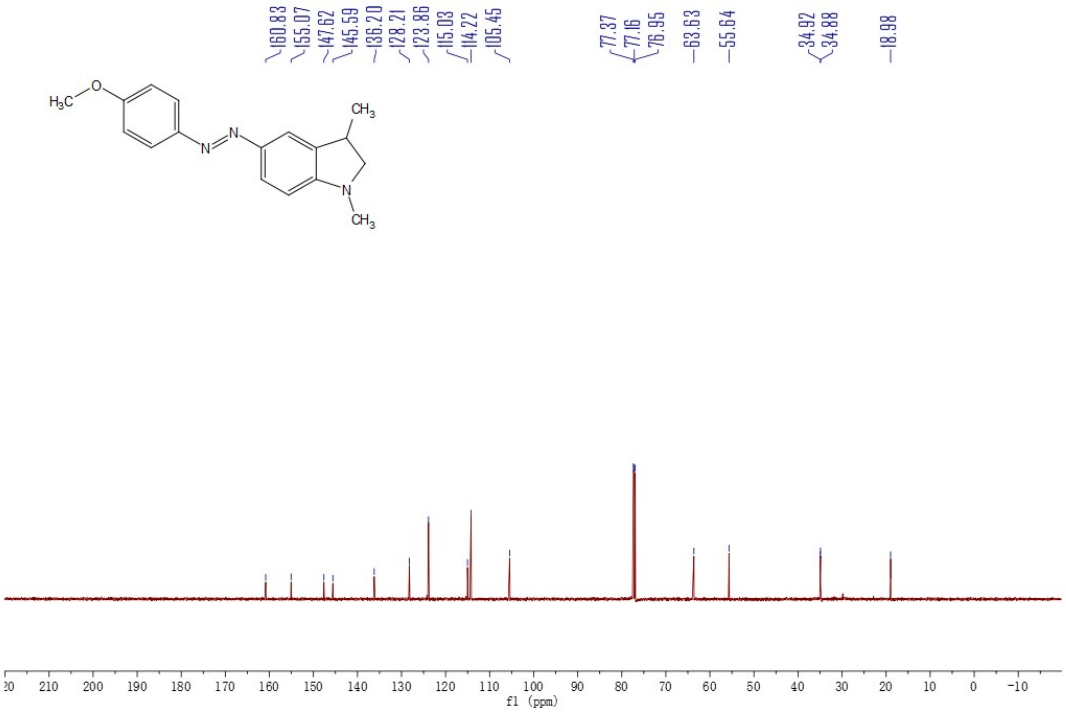
Orange solid, (29.5 mg, 72% yield), m.p.: 205-207 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.58 (m, 3H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 3.28 (s, 3H), 1.83 (d, *J* = 22.2 Hz, 3H), 1.55 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4 (d, *J* = 21.5 Hz), 166.17, 153.2, 149.39 (d, *J* = 2.7 Hz), 146.2 (d, *J* = 4.7 Hz), 142.5, 137.2, 129.87 (d, *J* = 2.6 Hz), 128.9, 128.3 (d, *J* = 18.8 Hz), 123.4, 121.7, 117.0, 109.0, 91.2, 90.0, 80.9, 28.3, 26.69, 21.3 (d, *J* = 29.4 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -152.79. HRMS (ESI): Calcd. for $C_{23}H_{24}FN_3O_3$ $[M+H]^+$: 410.1874; found: 410.1871.

7. Copies of NMR spectra

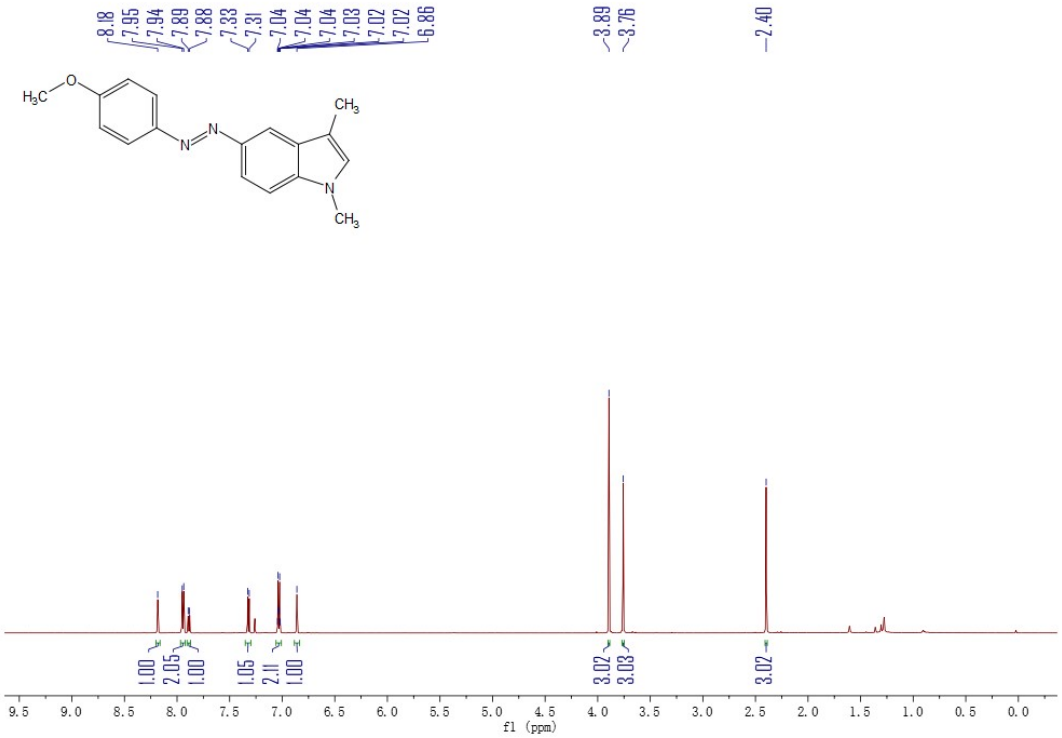
(1) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 1a-1



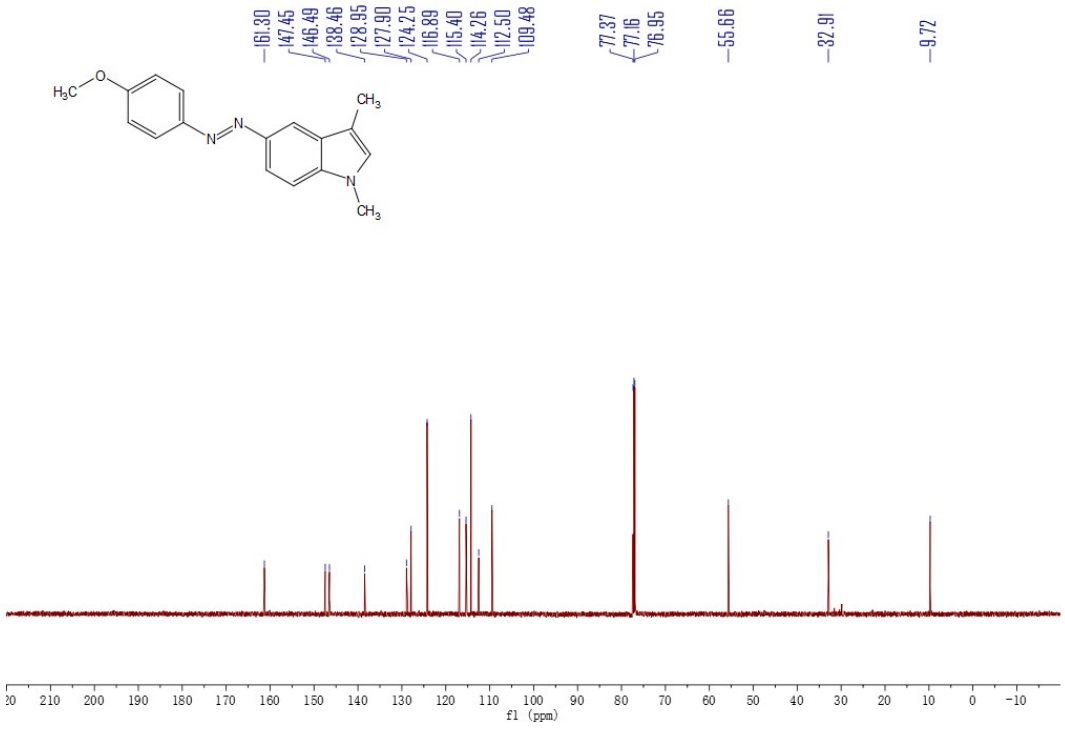
(2) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 1a-1



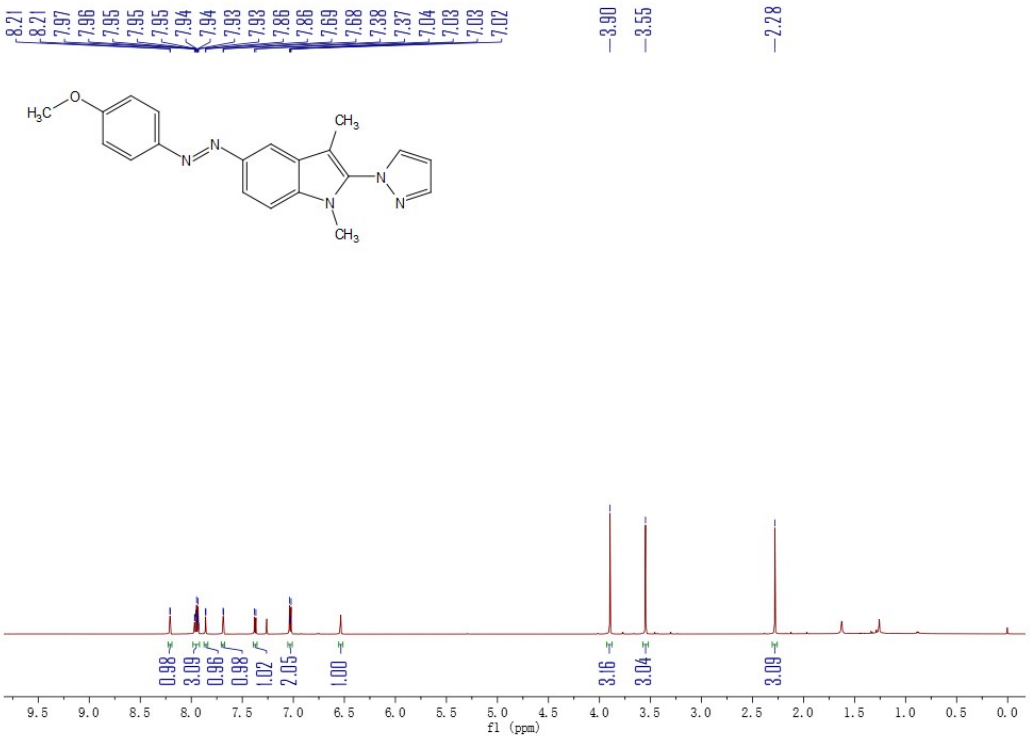
(3) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 1a-2



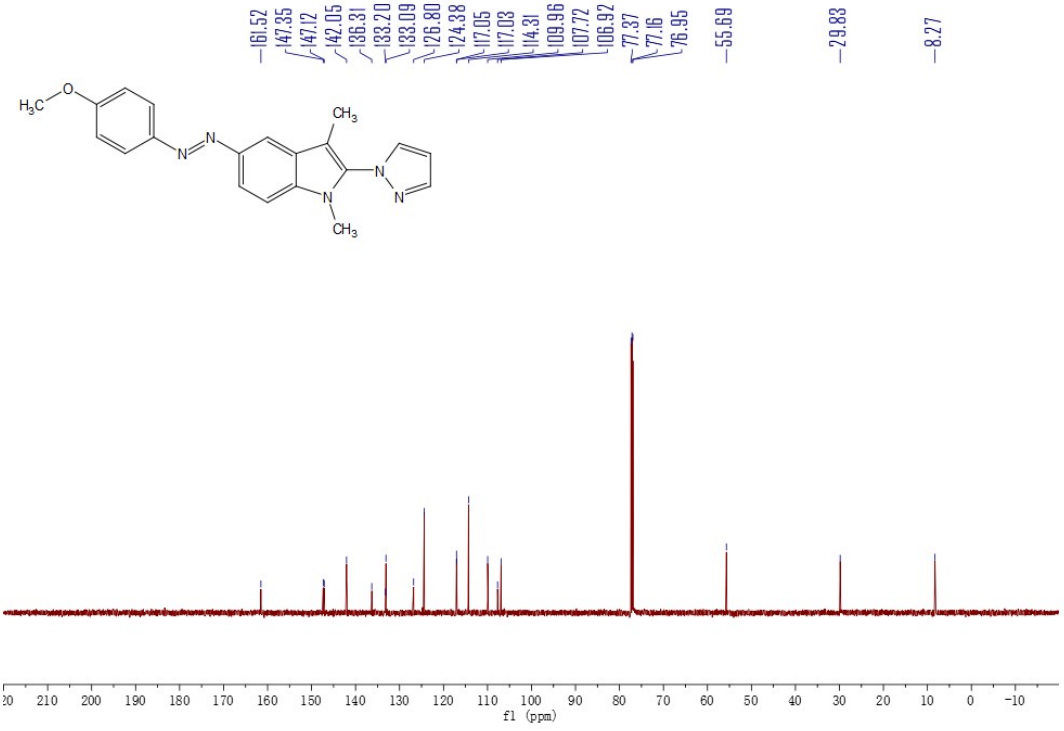
(4) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 1a-2



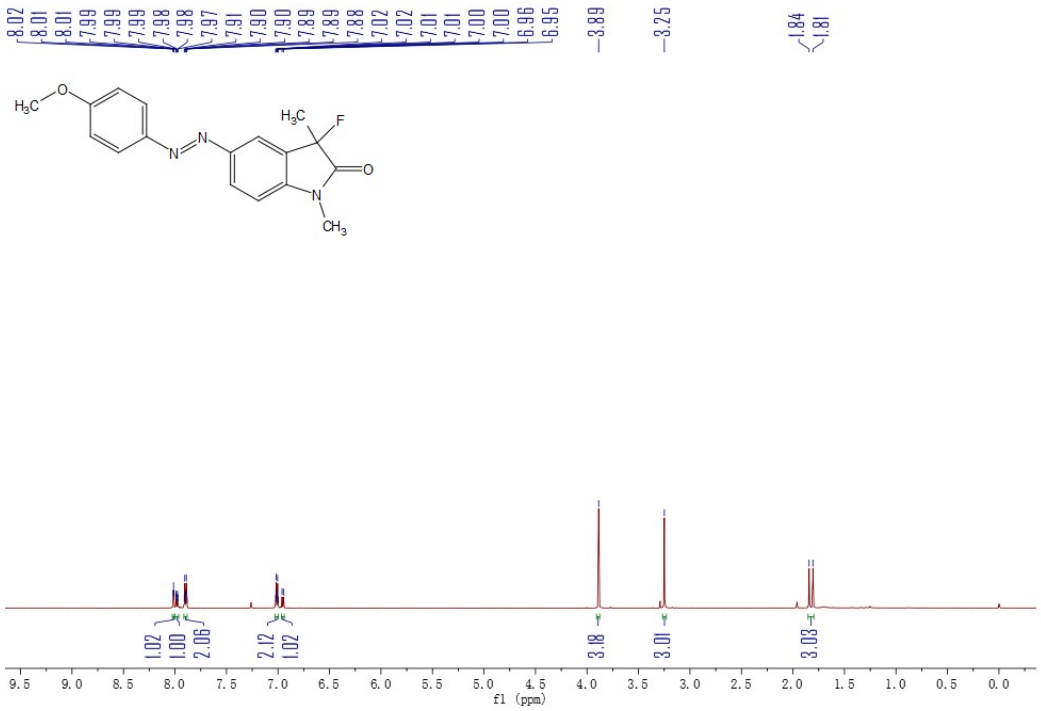
(5) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 1a-3



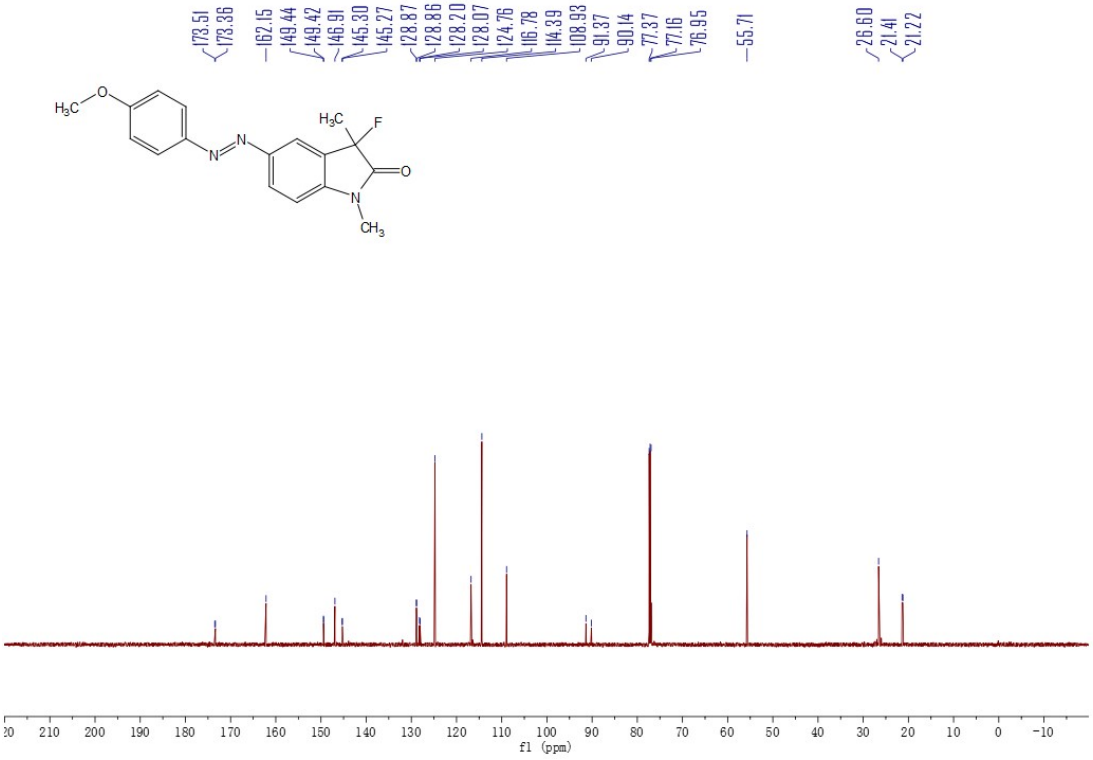
(6) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 1a-3



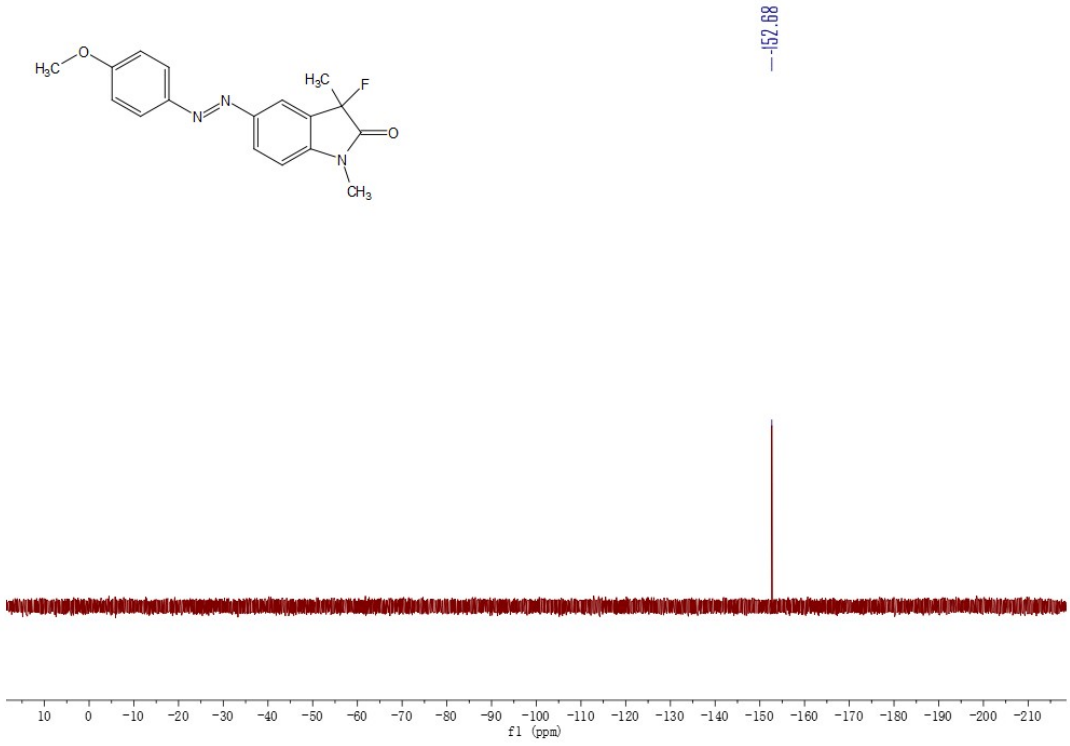
(7) ^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3aa



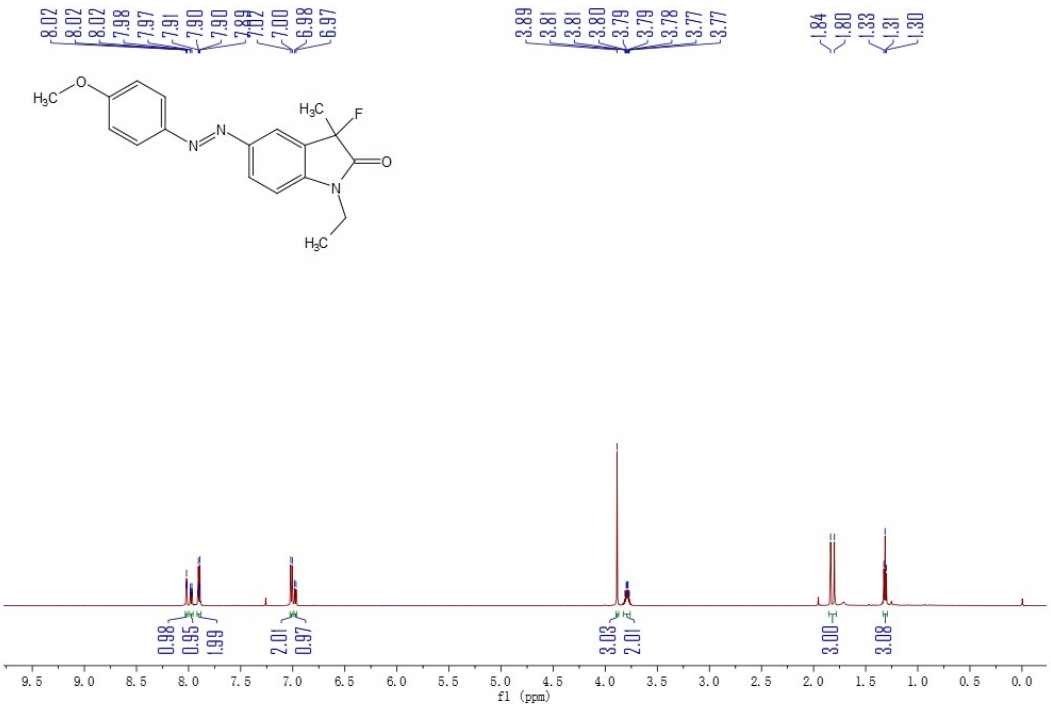
(8) ^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3aa



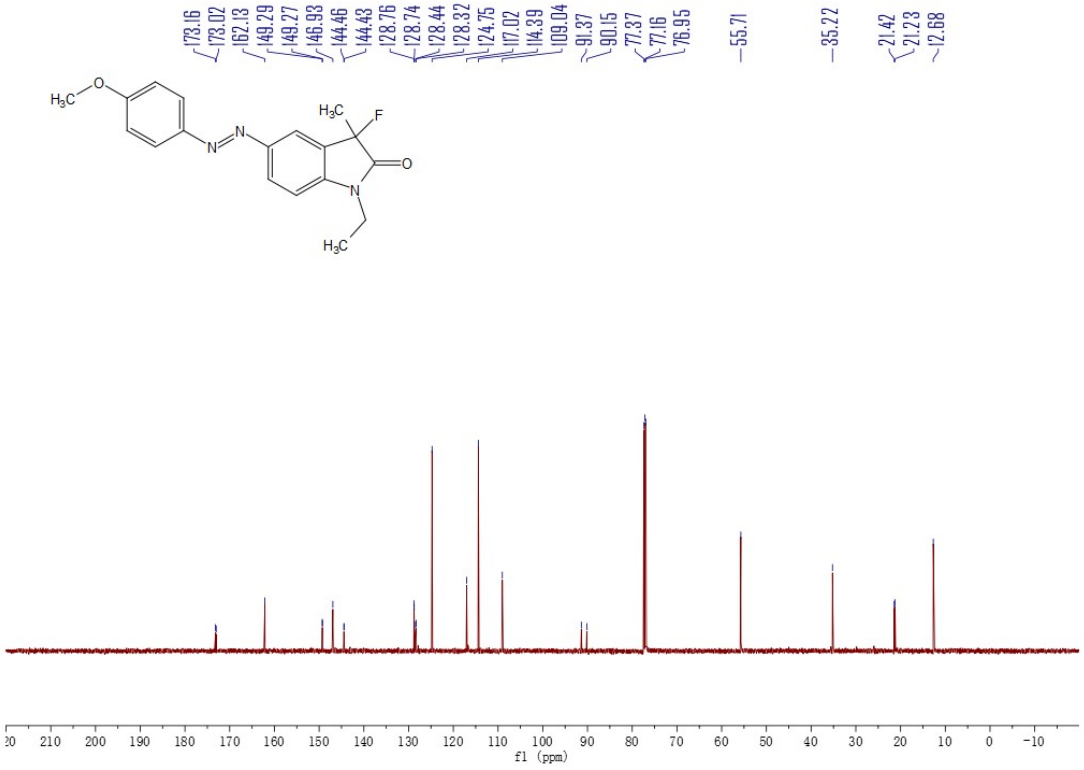
(9) ^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3aa



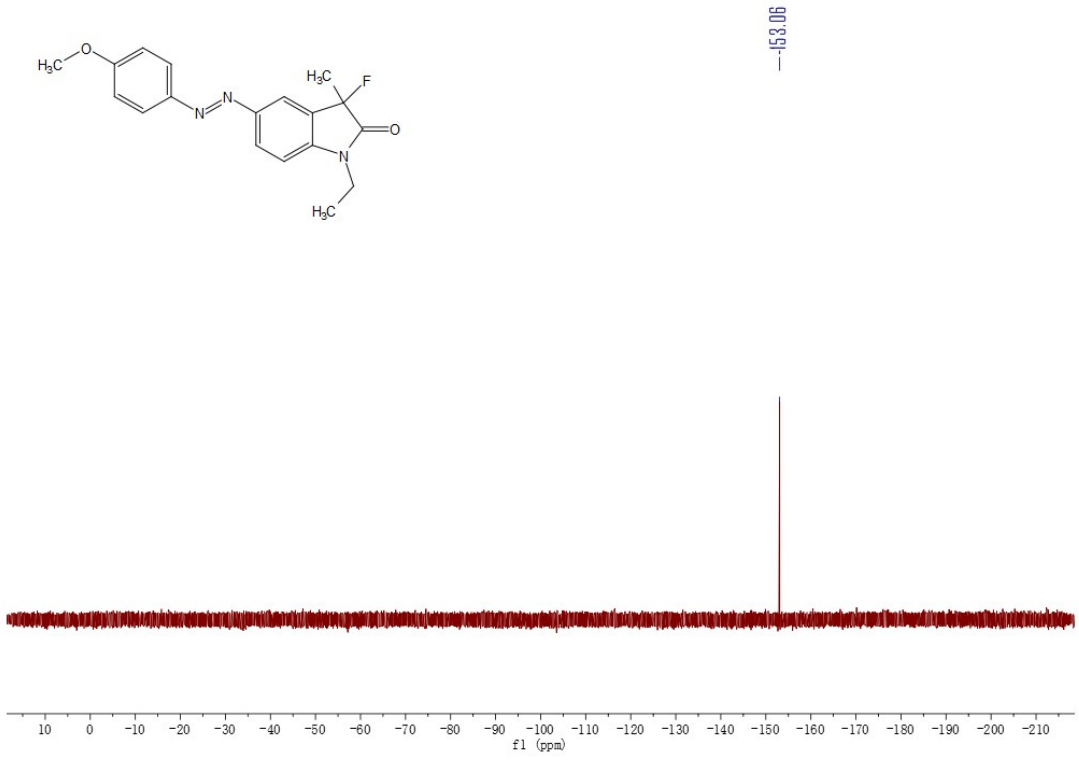
(10)^{1}H-NMR (600, $CDCl_3$) spectra of 3ba



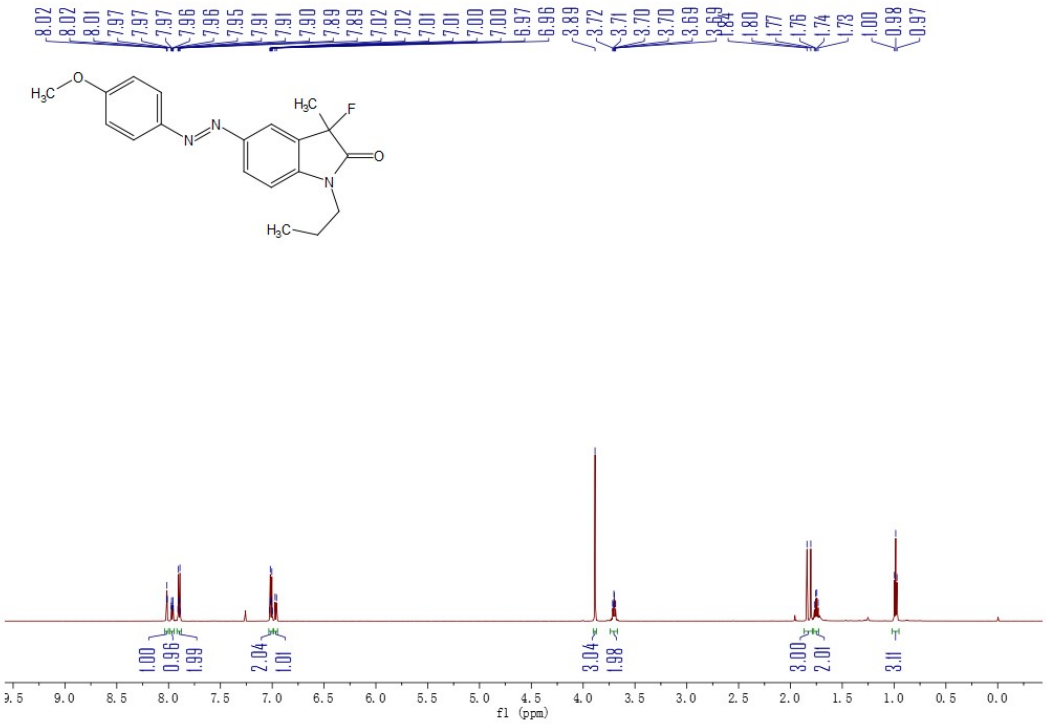
(11)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ba



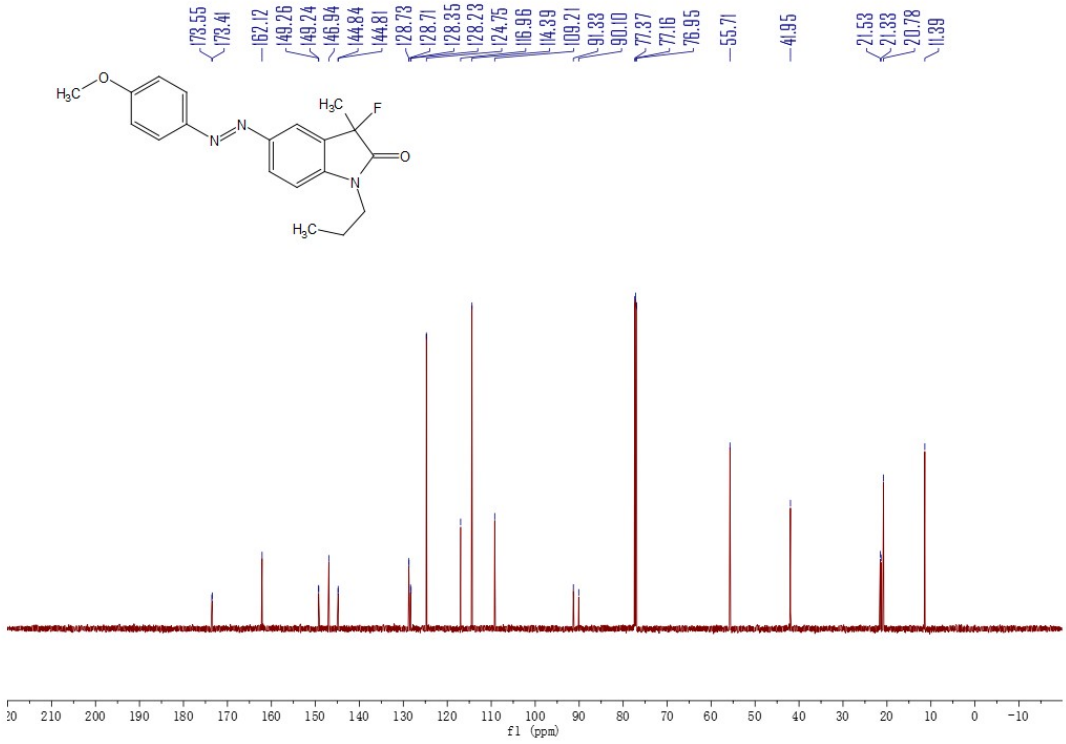
(12)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3aa



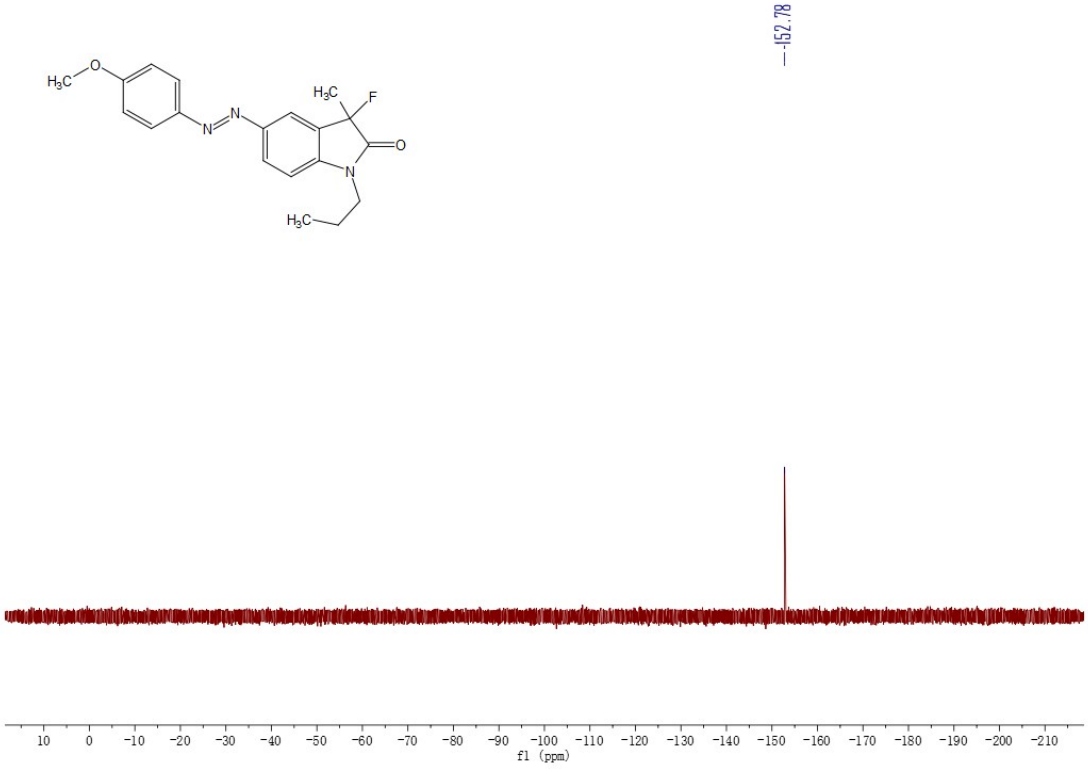
(13)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ca



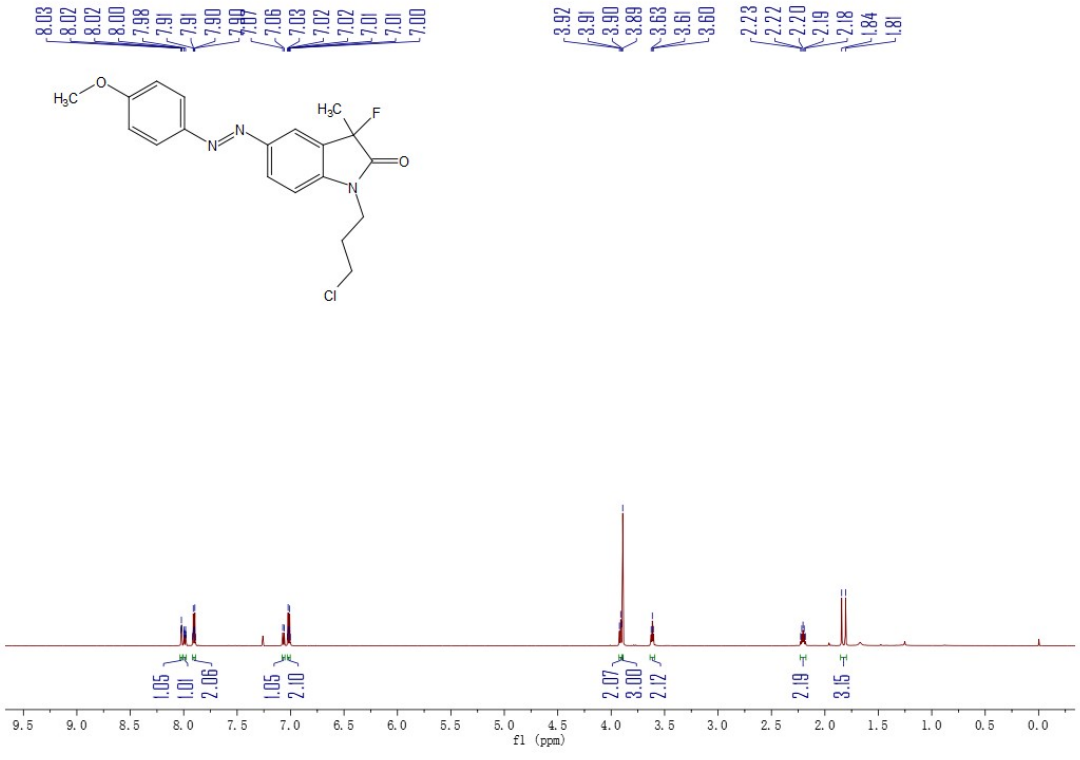
(14)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ca



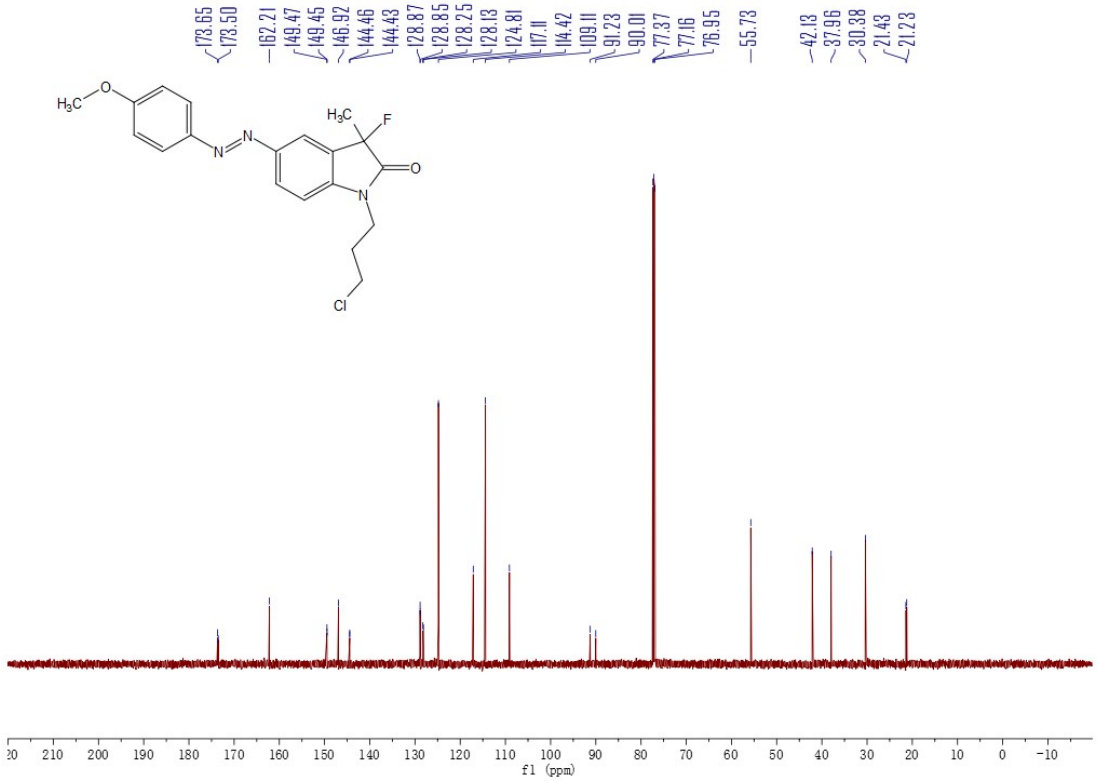
(15)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ca



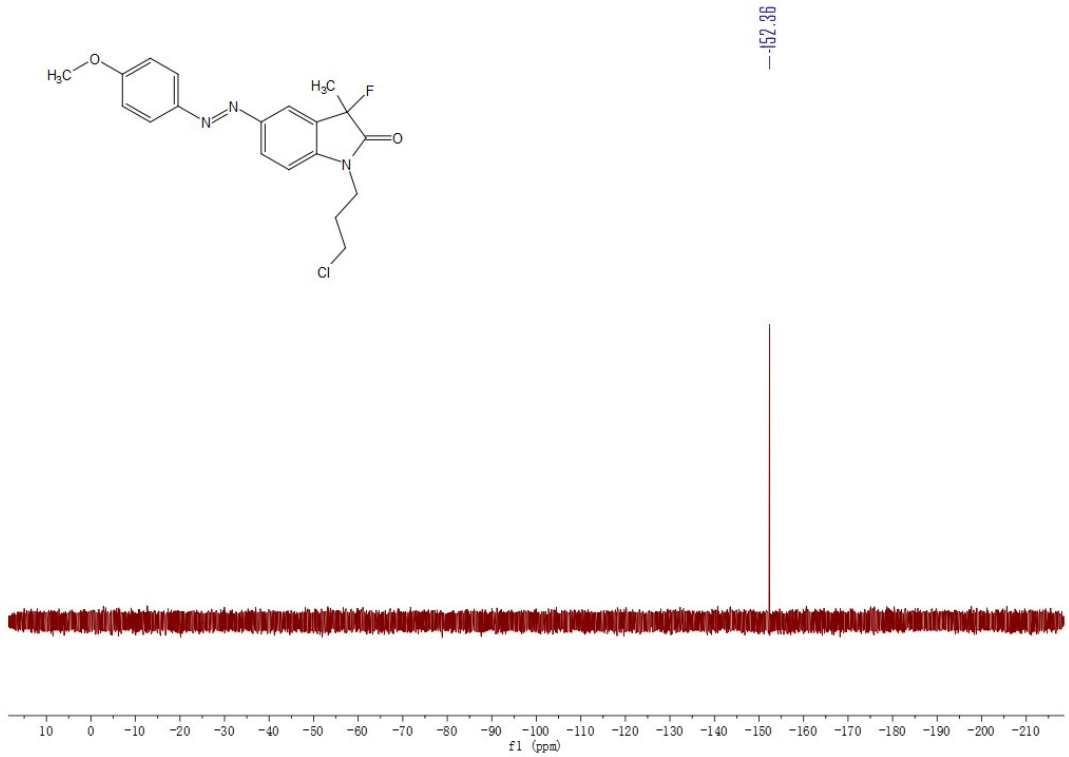
(16)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3da



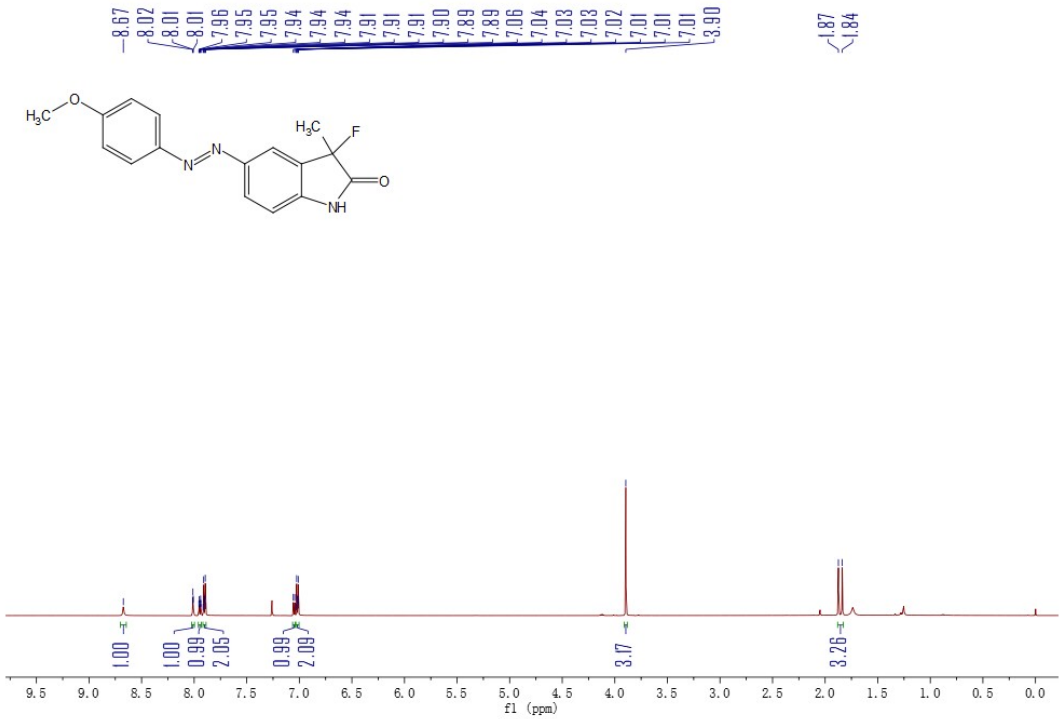
(17)^{13}NMR (151MHz, $CDCl_3$) spectra of 3da



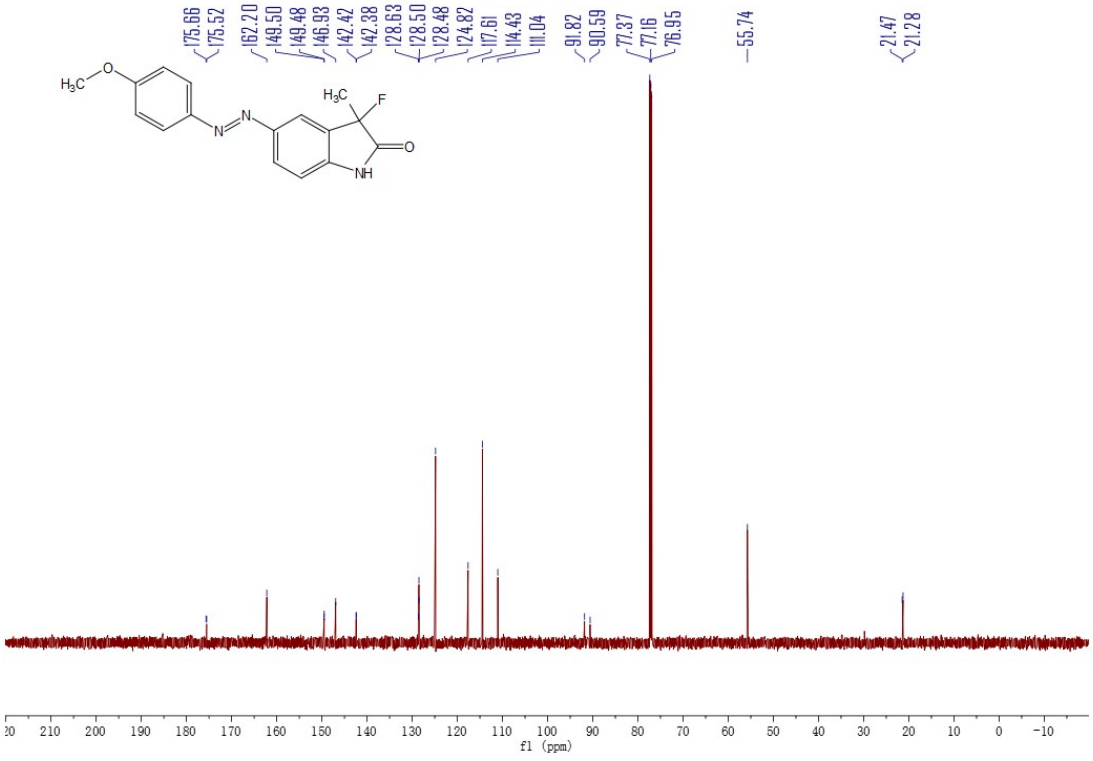
(18)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3da



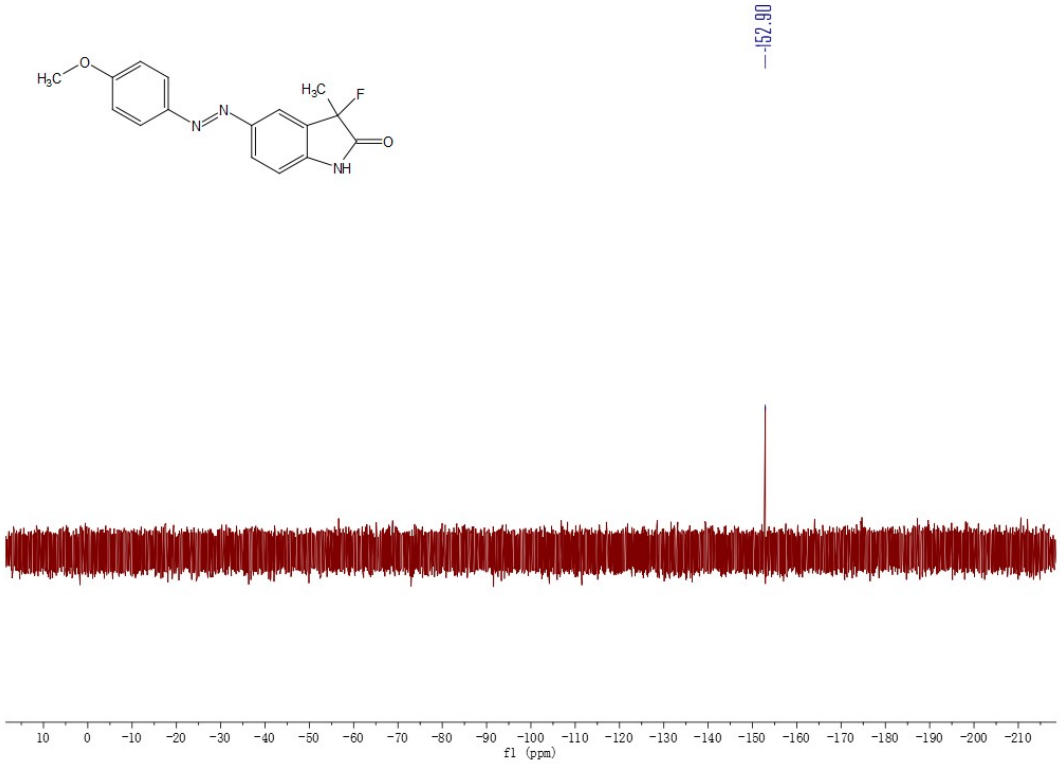
(19)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ea



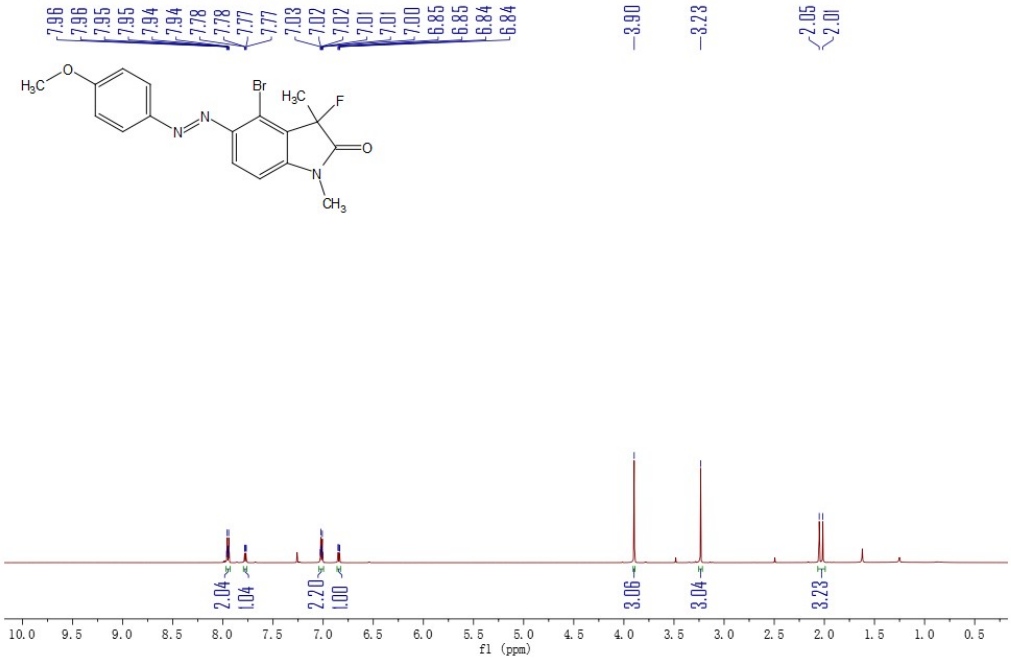
(20)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ea



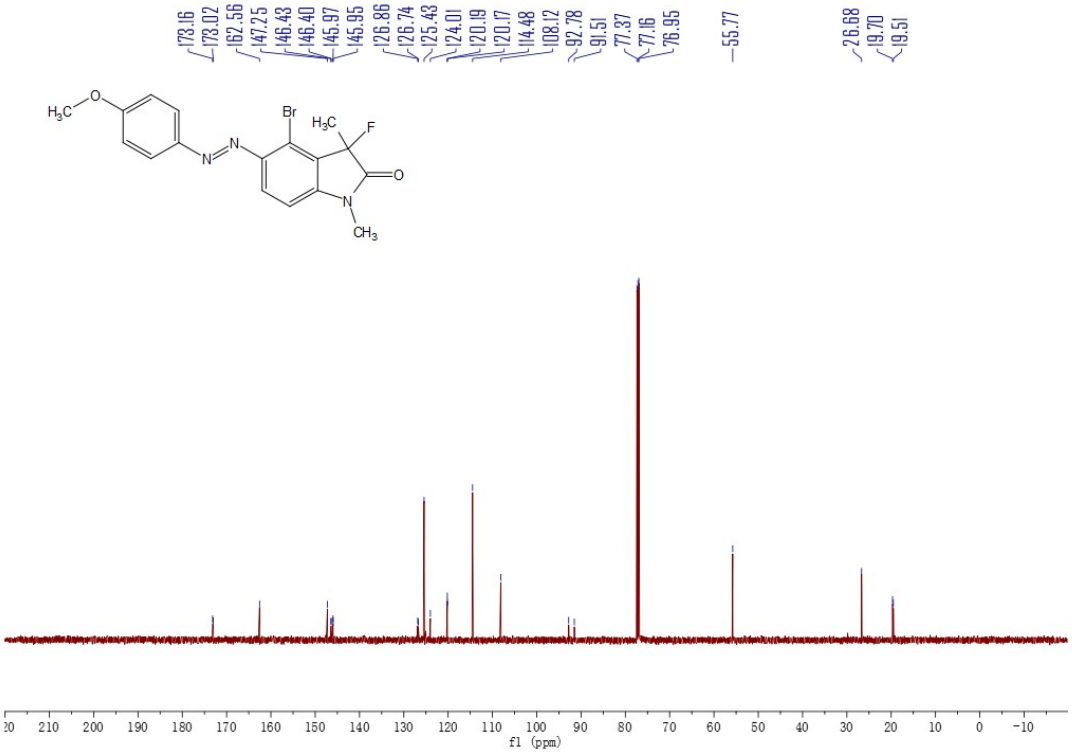
(21)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ea



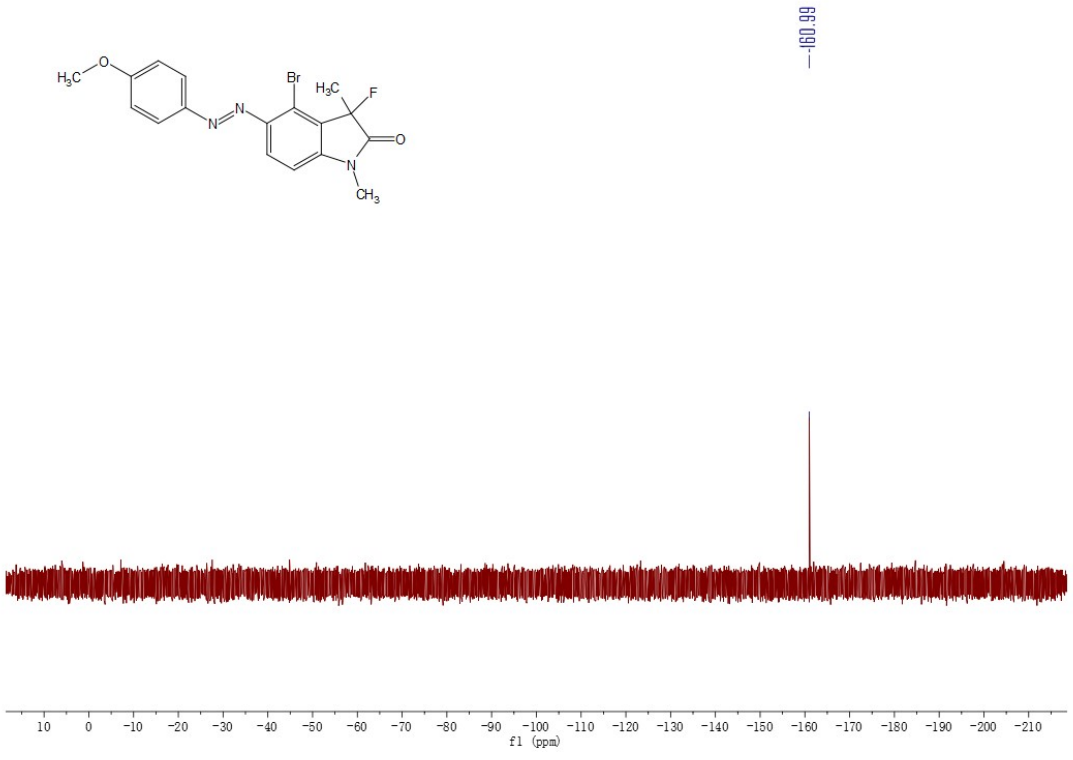
(22)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3fa



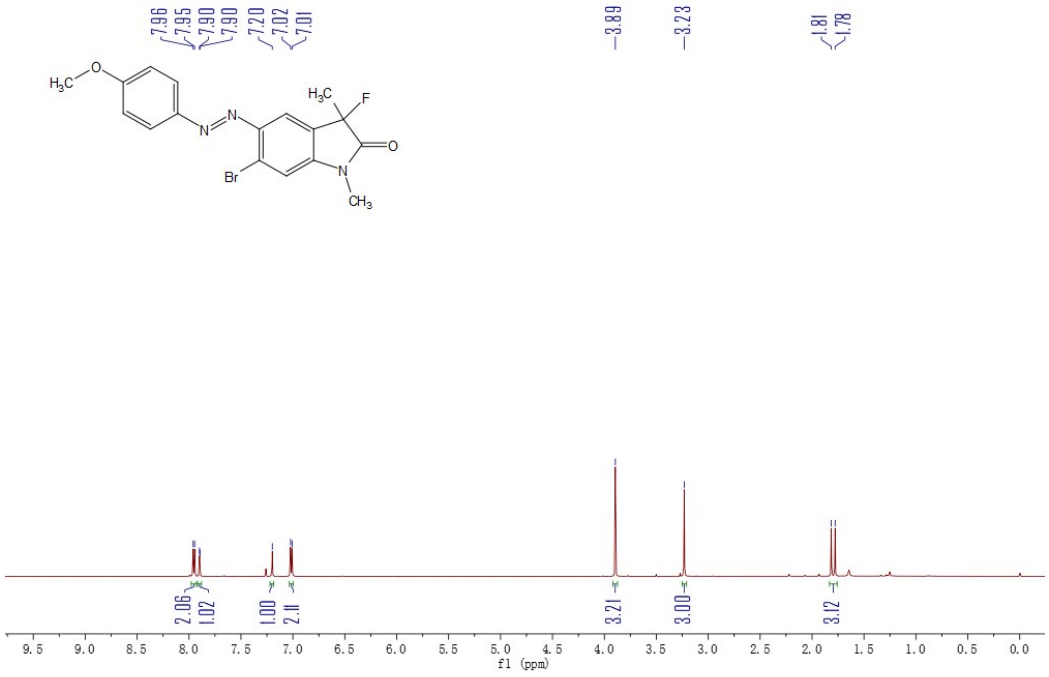
(23)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3fa



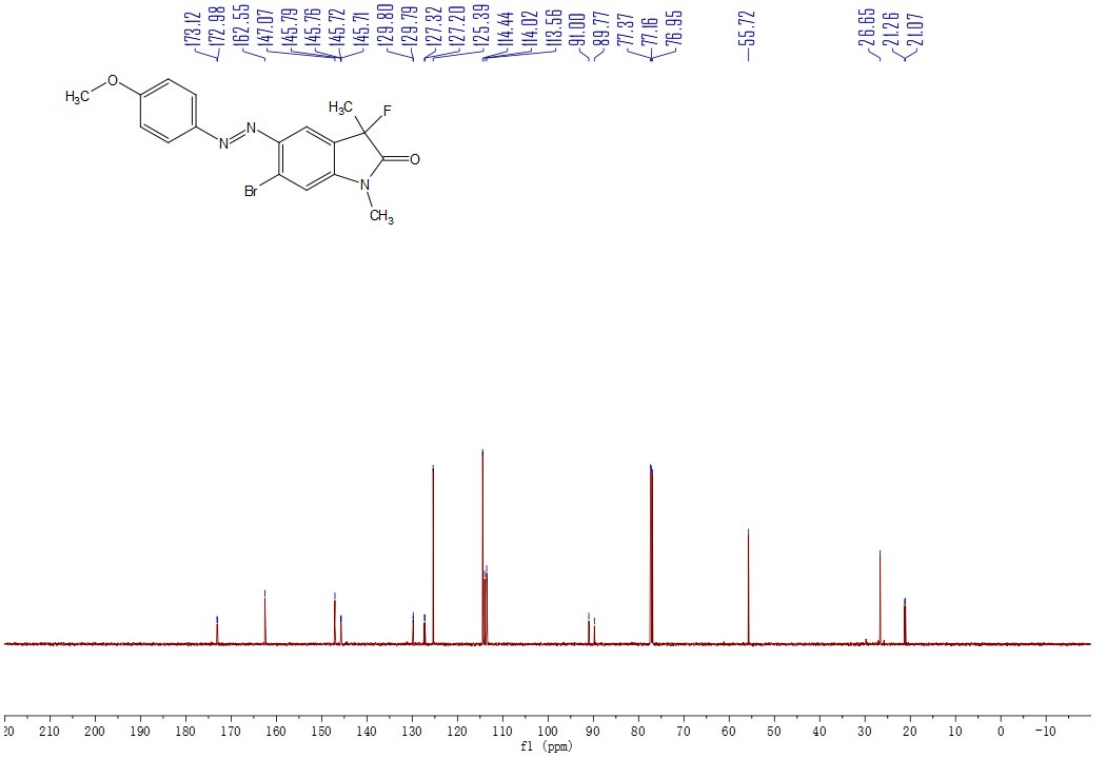
(24)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3fa



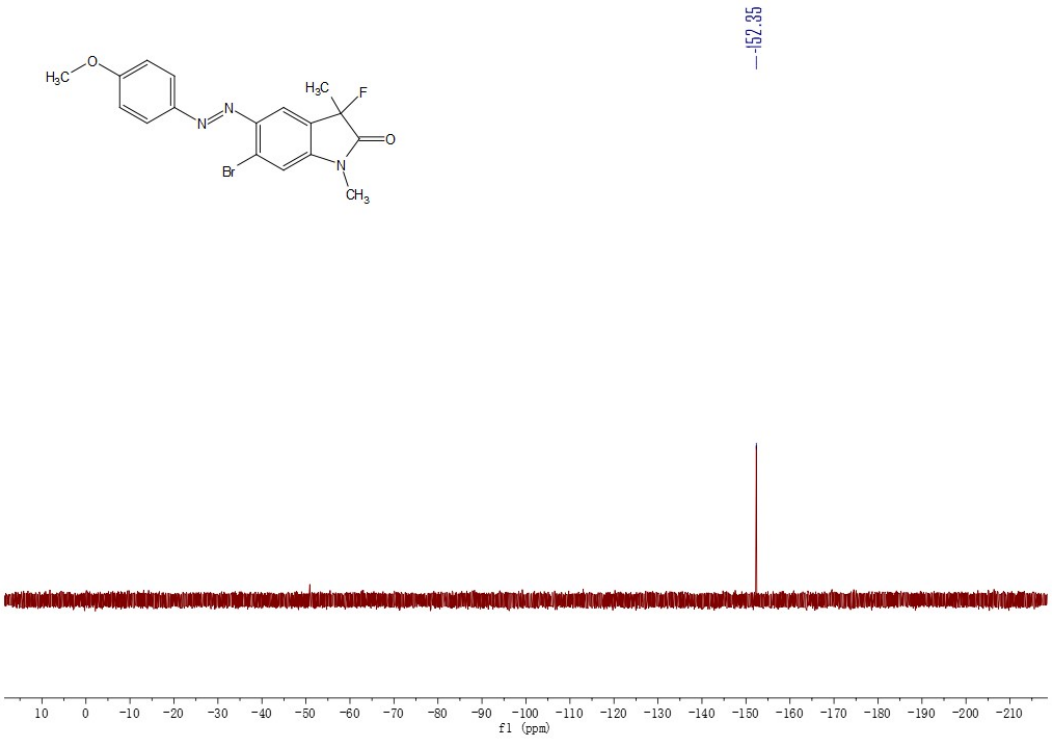
(25)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ga



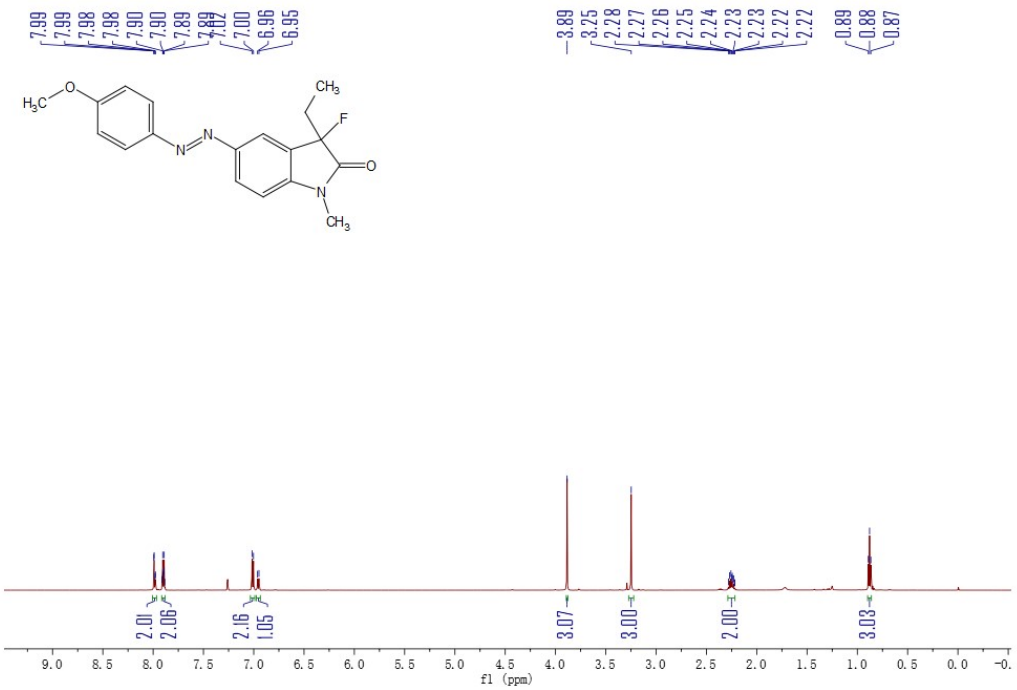
(26)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ga



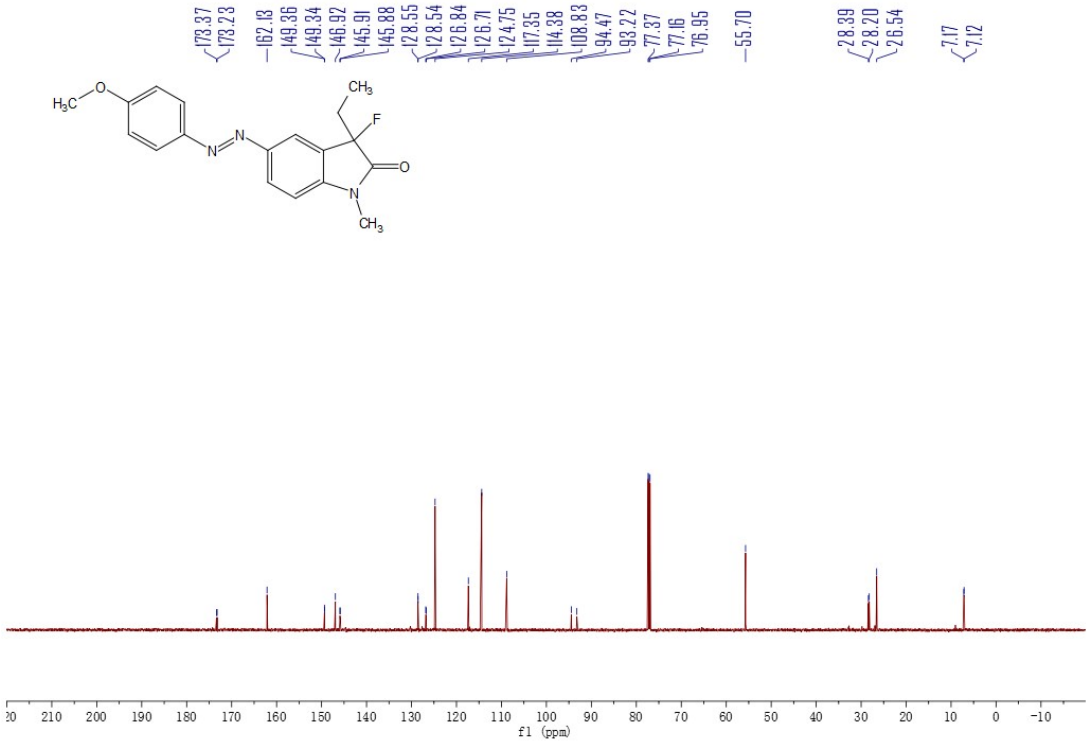
(27)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ga



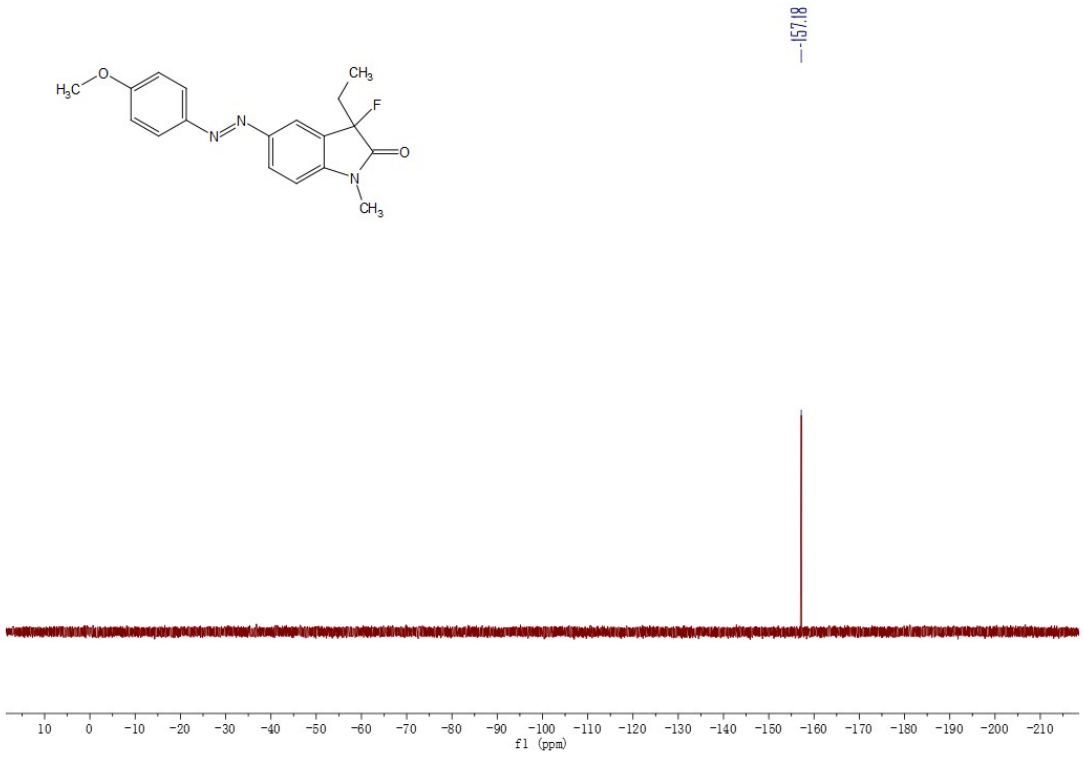
(28)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ha



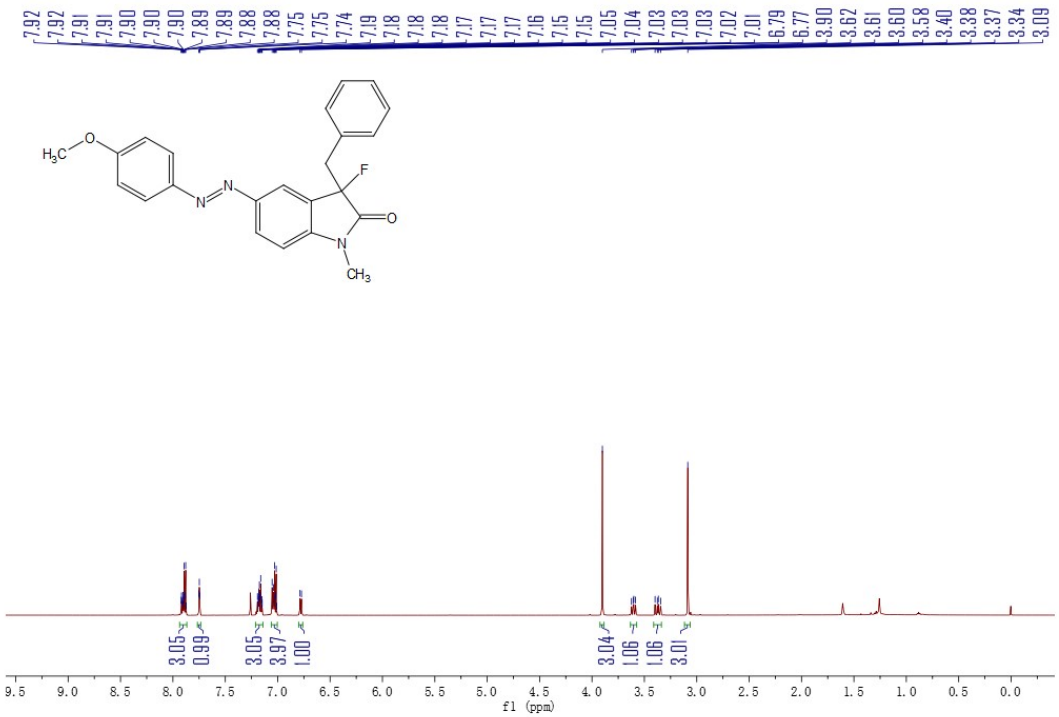
(29)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ha



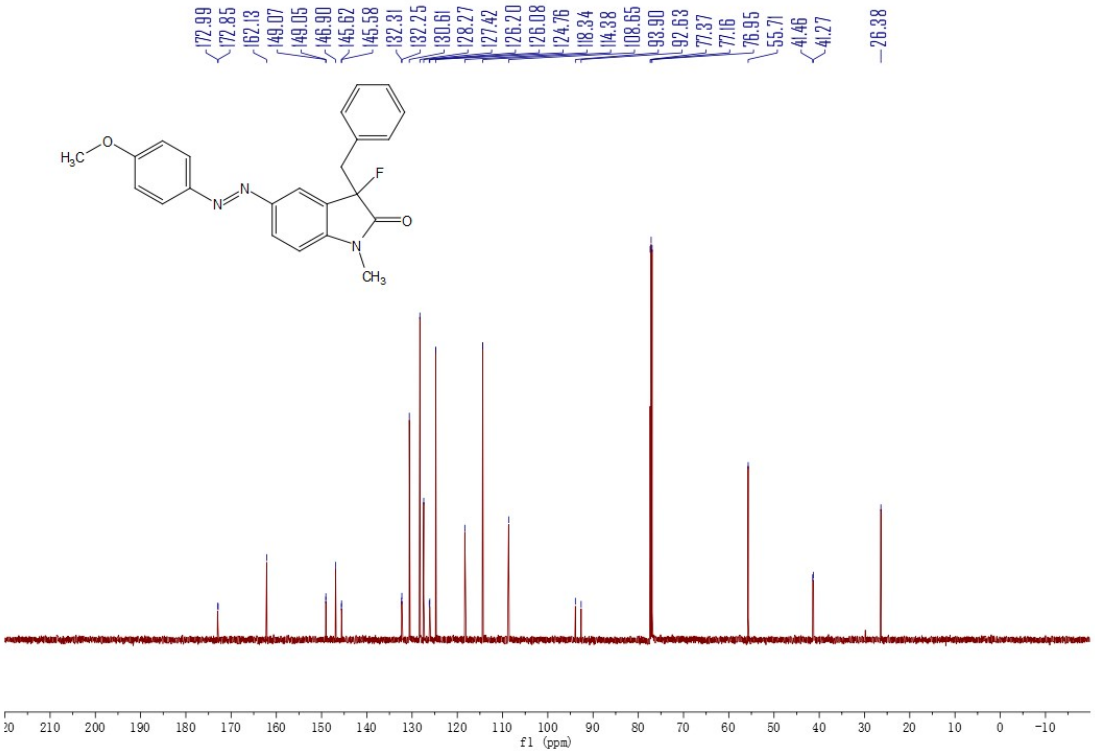
(30)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ha



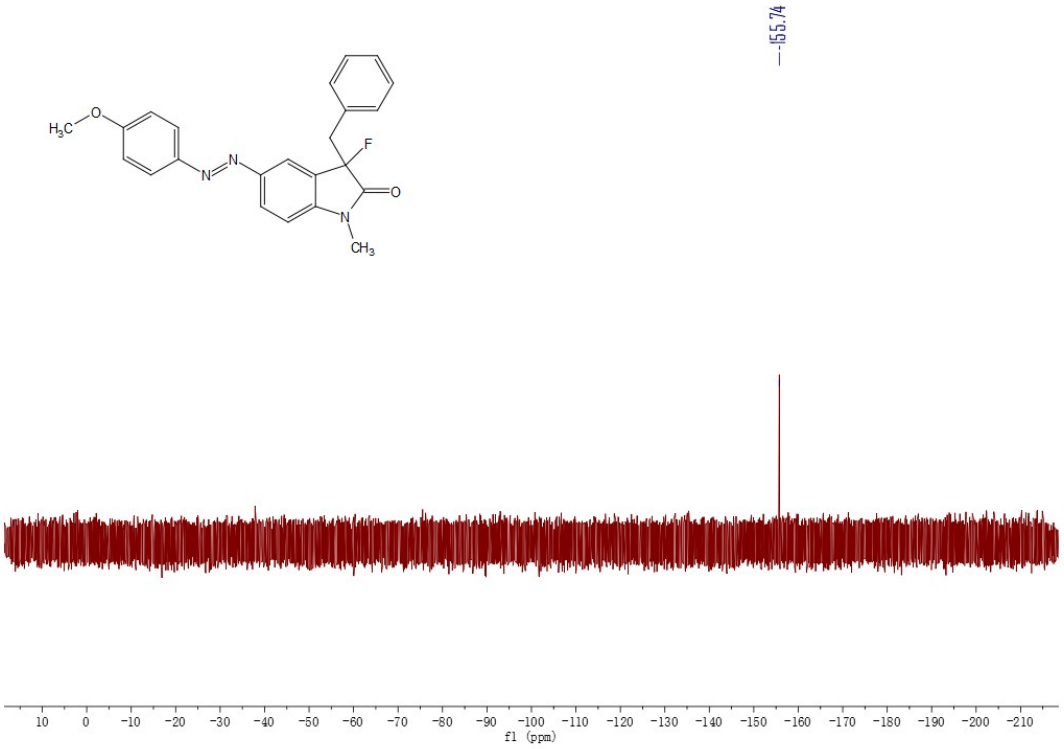
(31)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ia



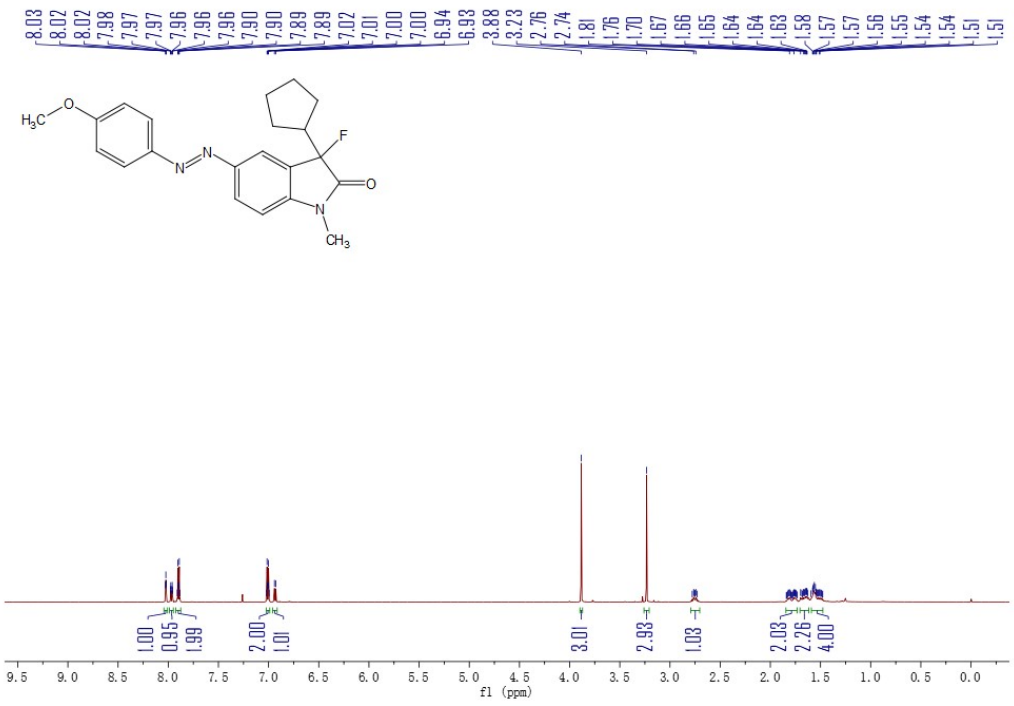
(32)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ia



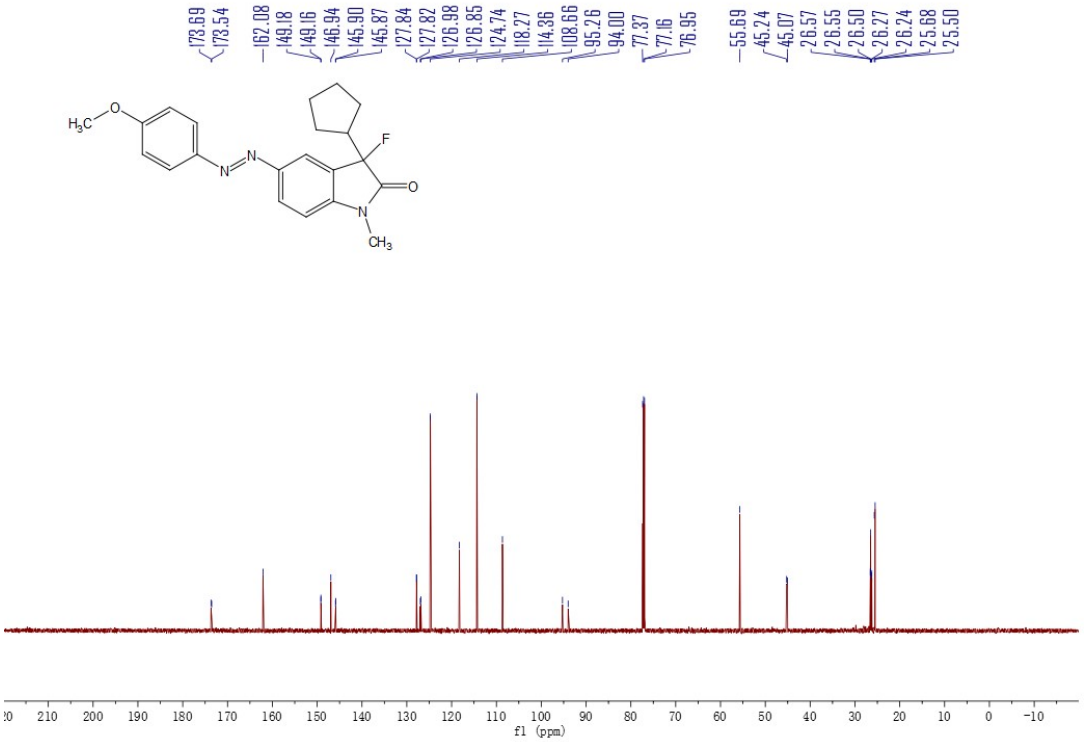
(33)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ia



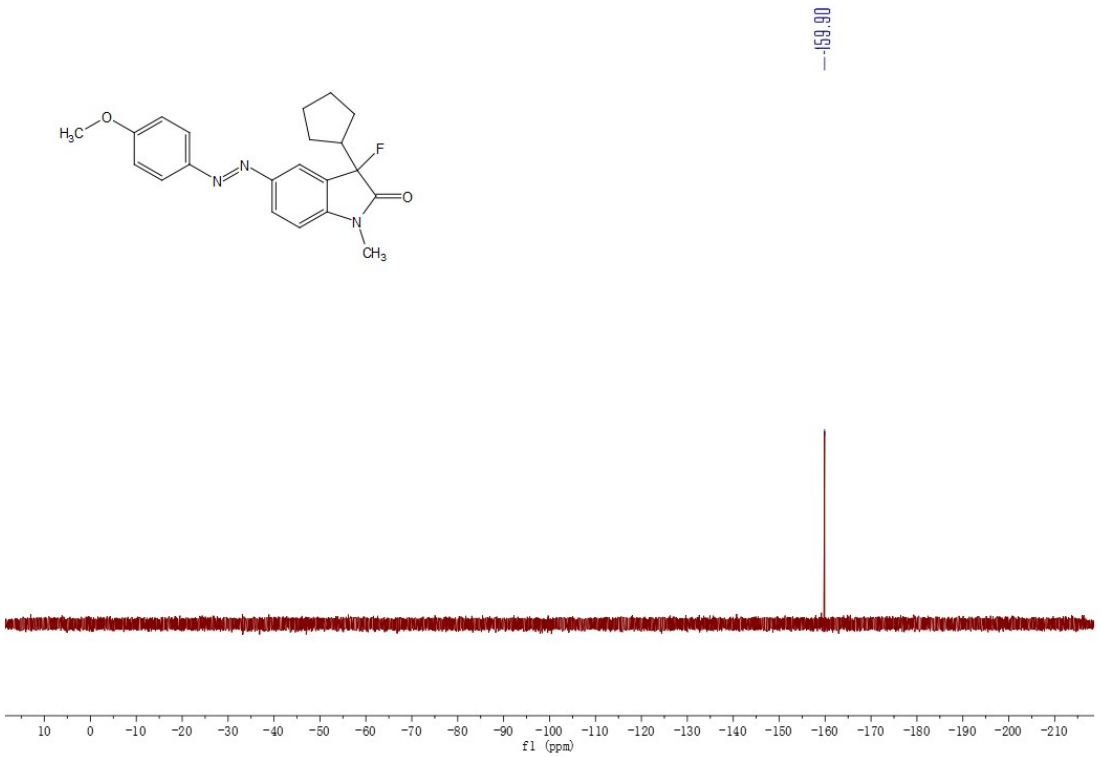
(34)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ja



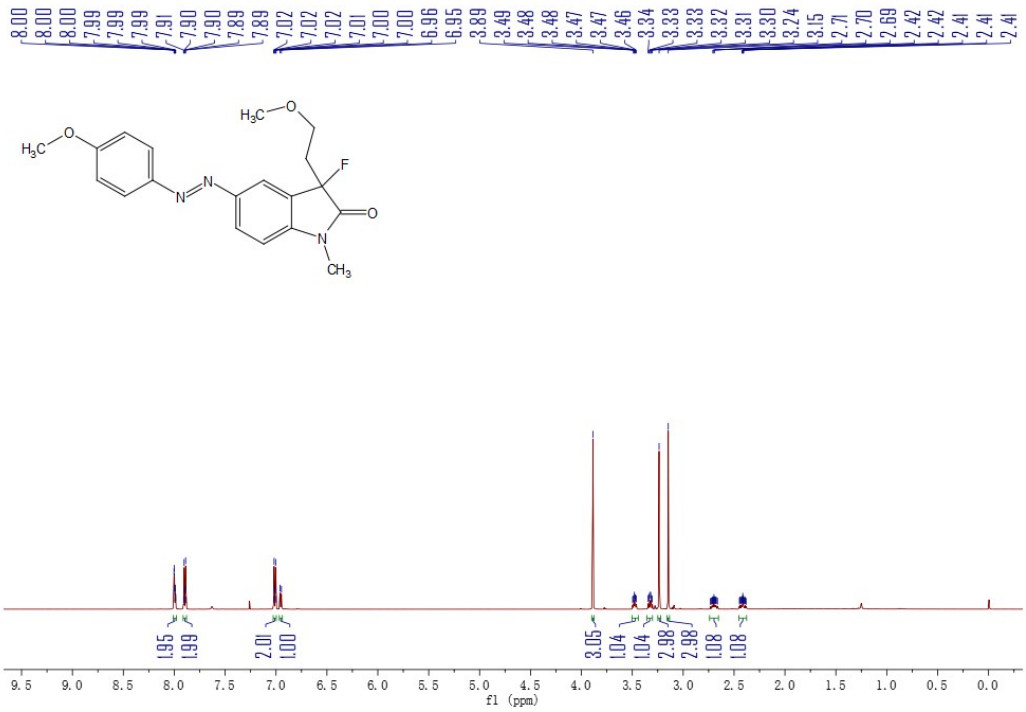
(35)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ja



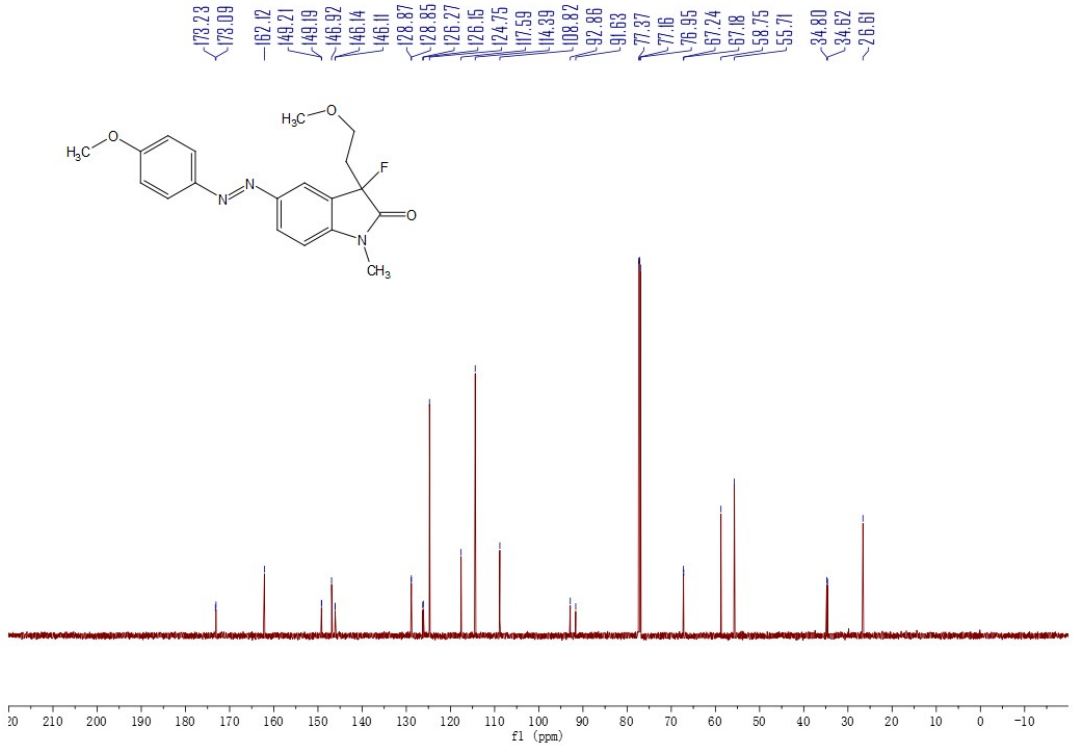
(36)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ja



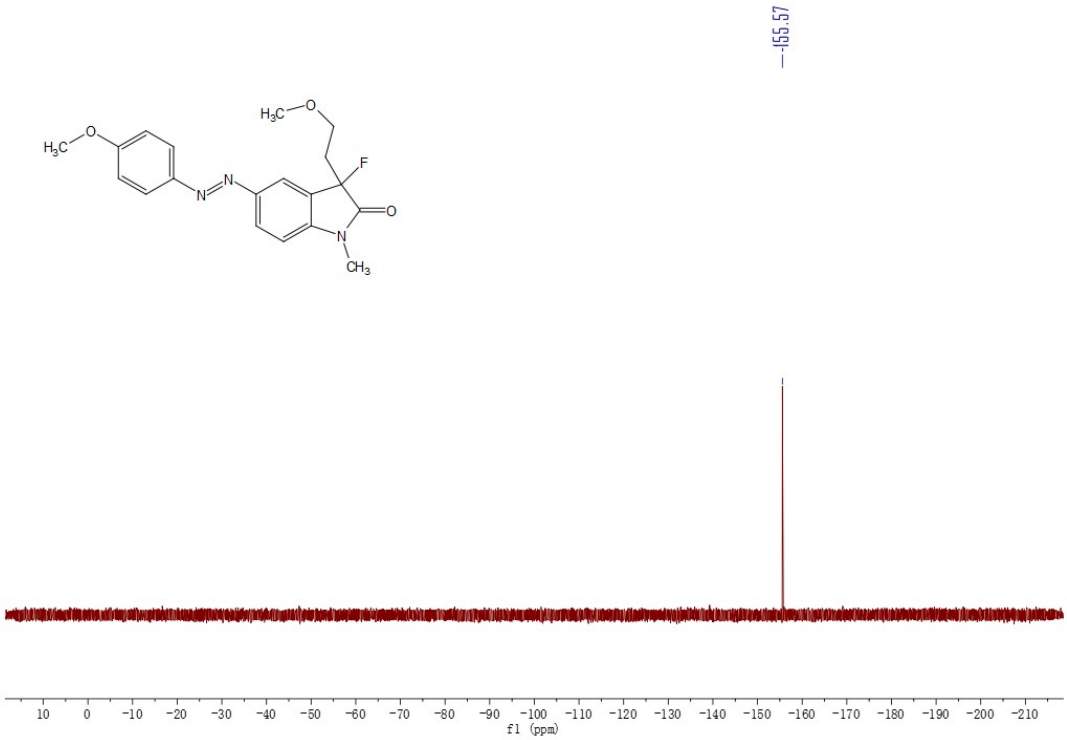
(37)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ka



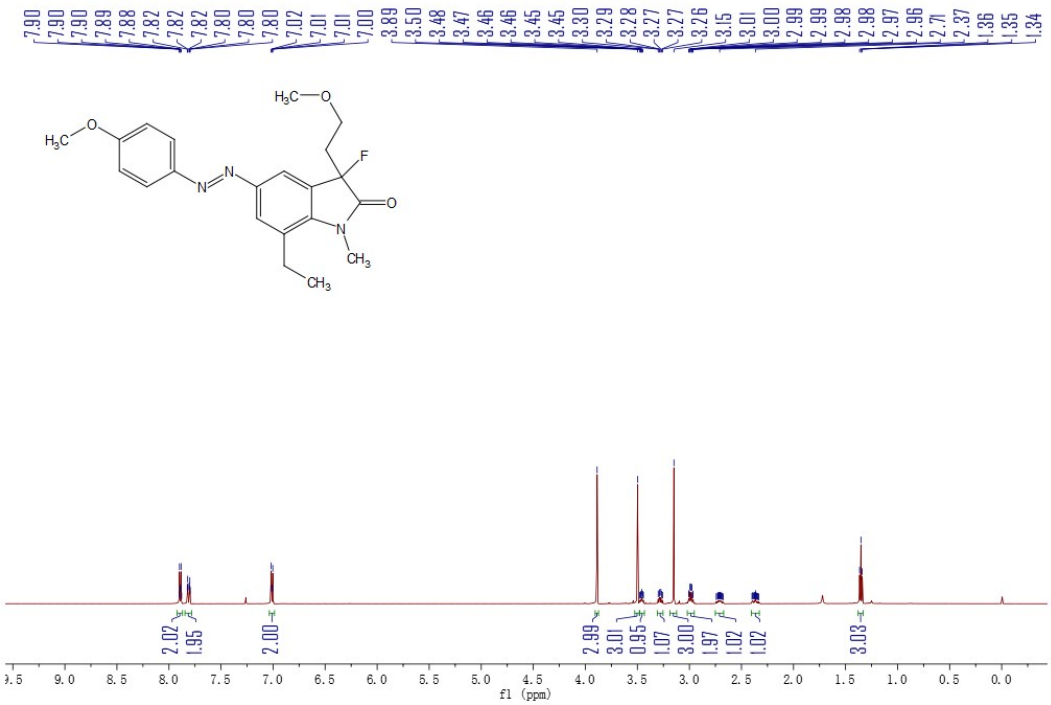
(38)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ka



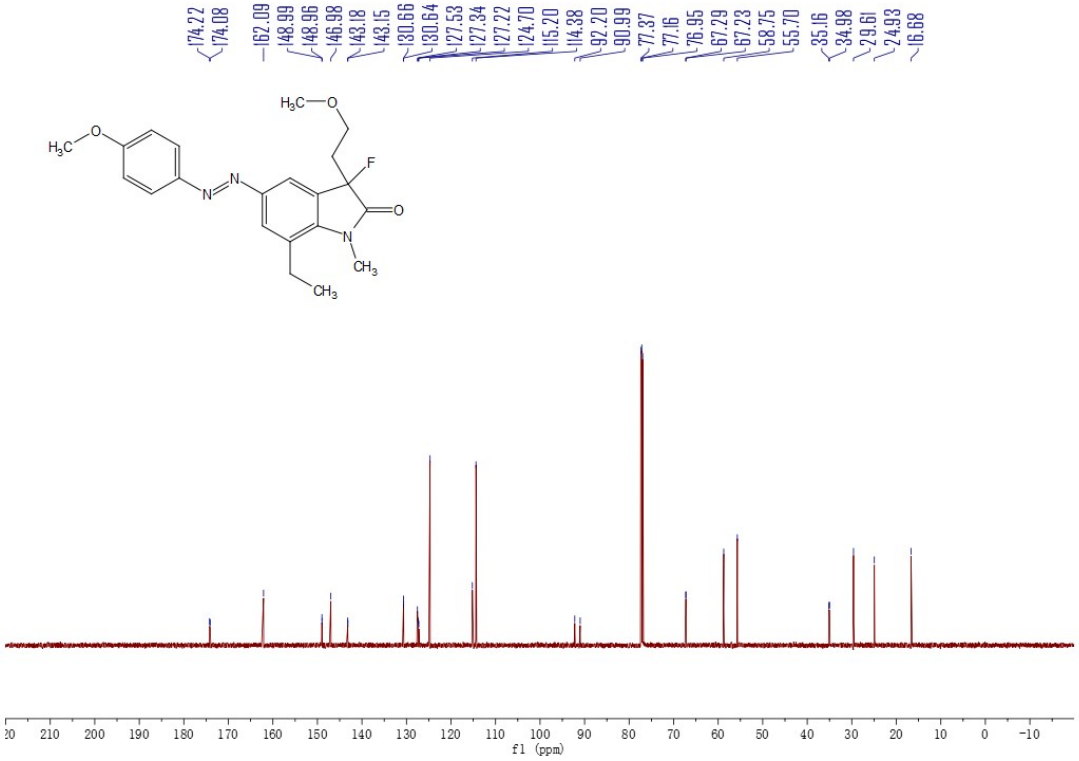
(39)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ka



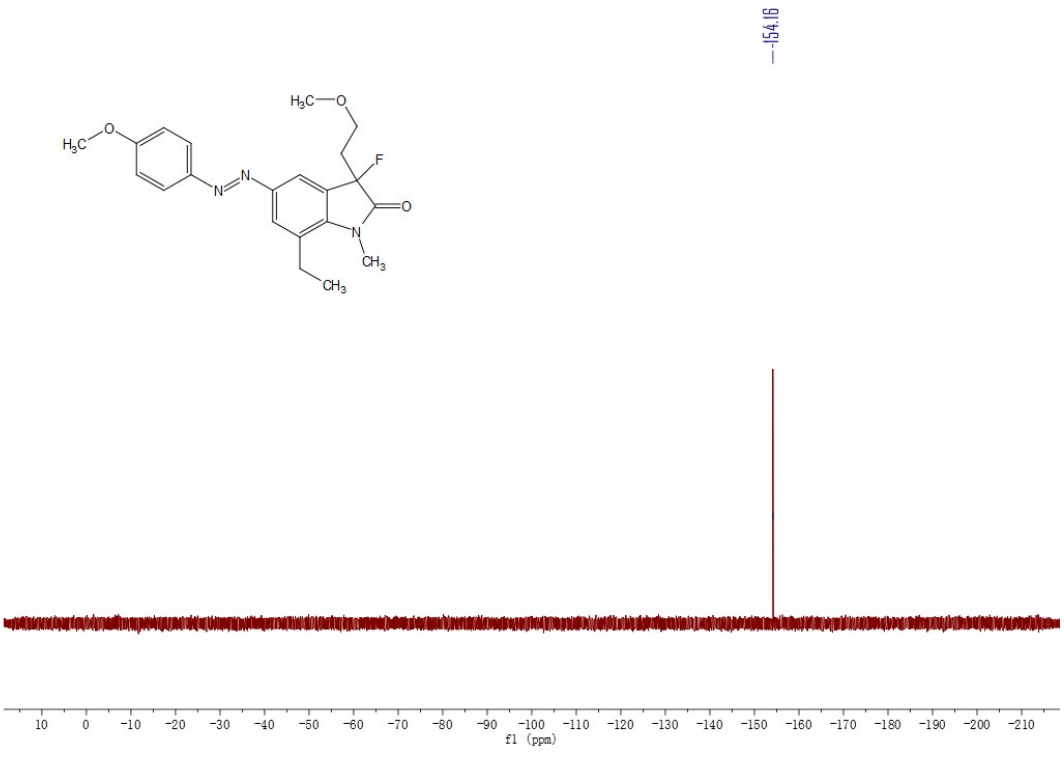
(40)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3la



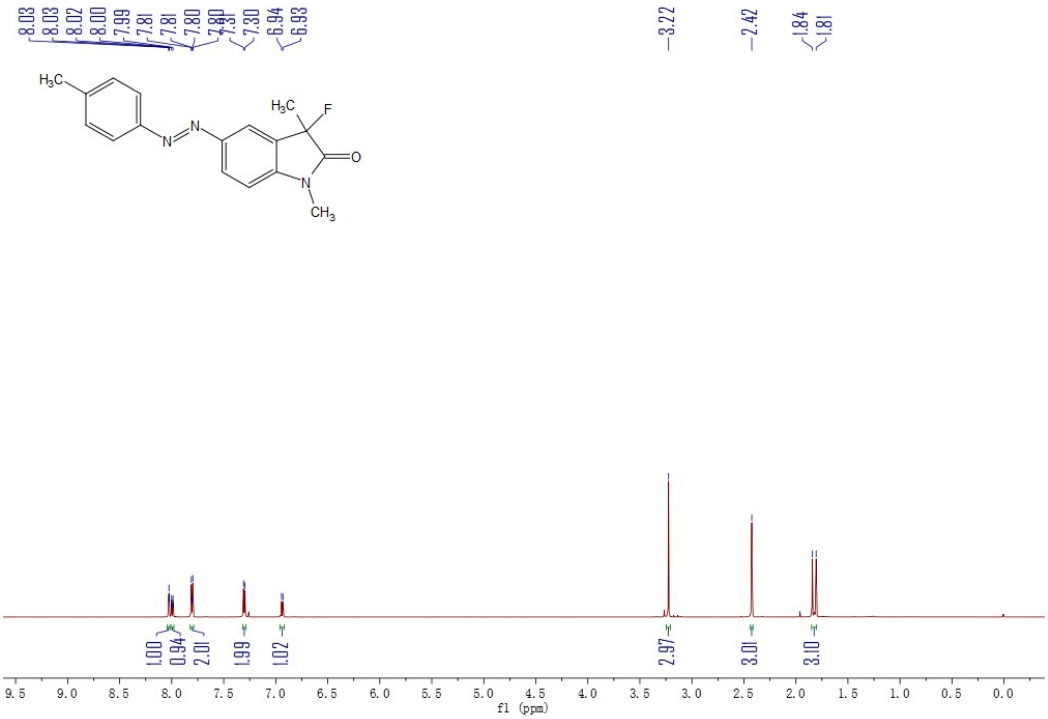
(41)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3la



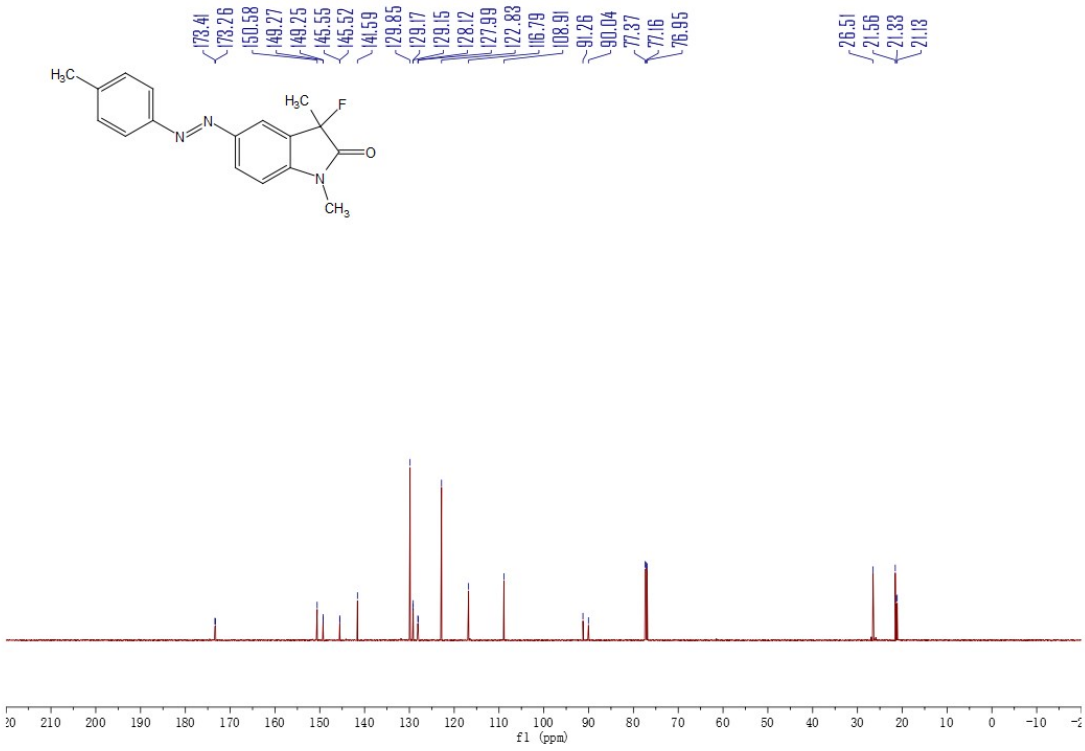
(42)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3la



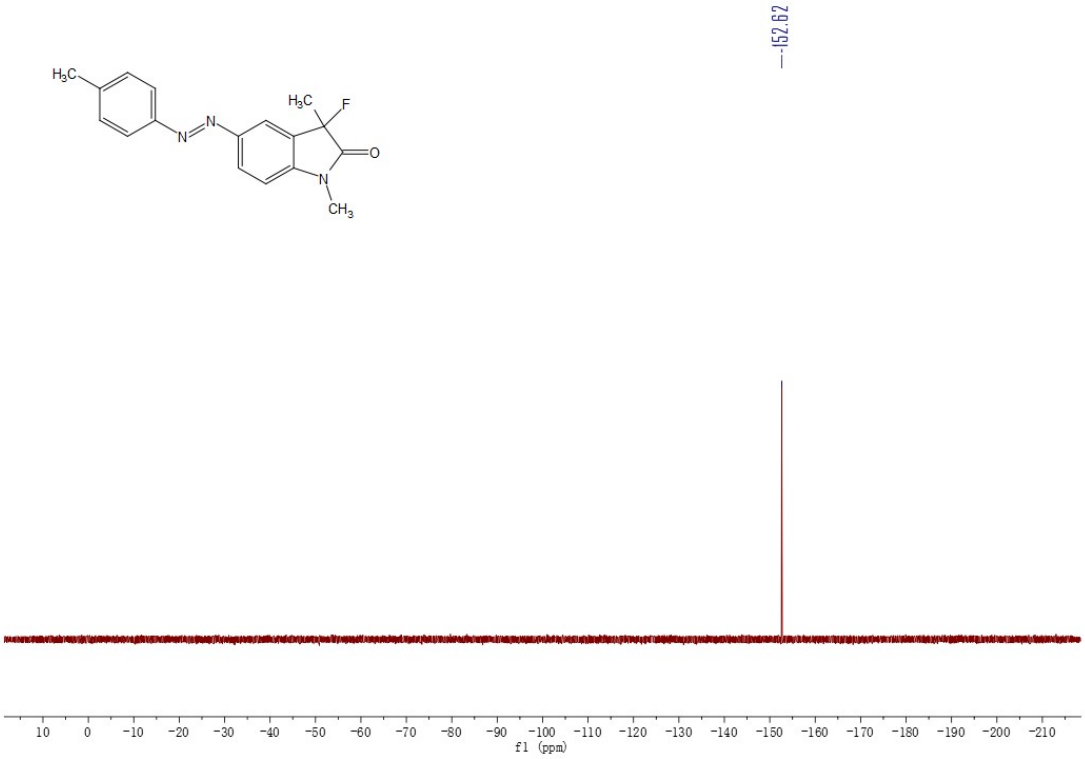
(43)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ab



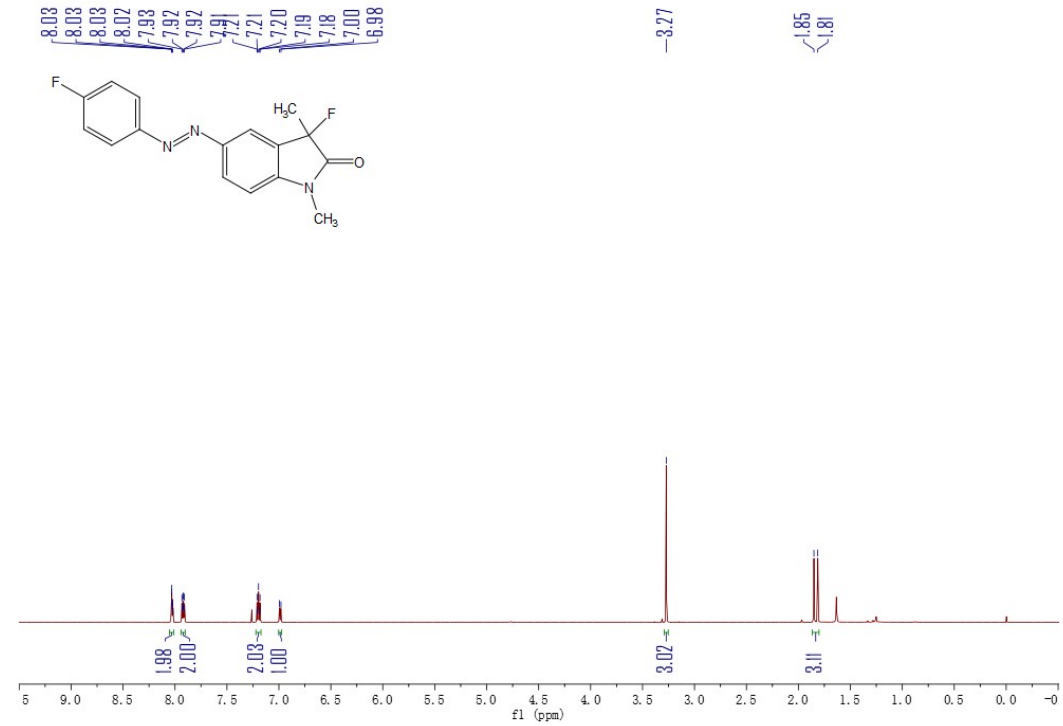
(44)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ab



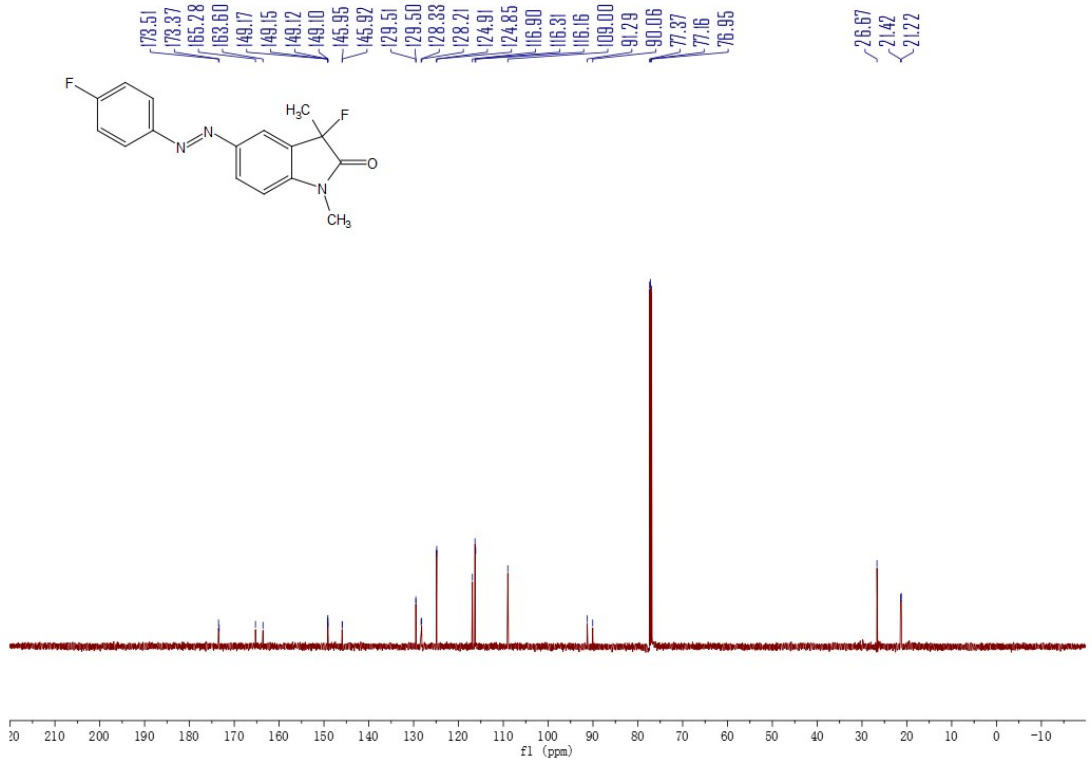
(45)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ab



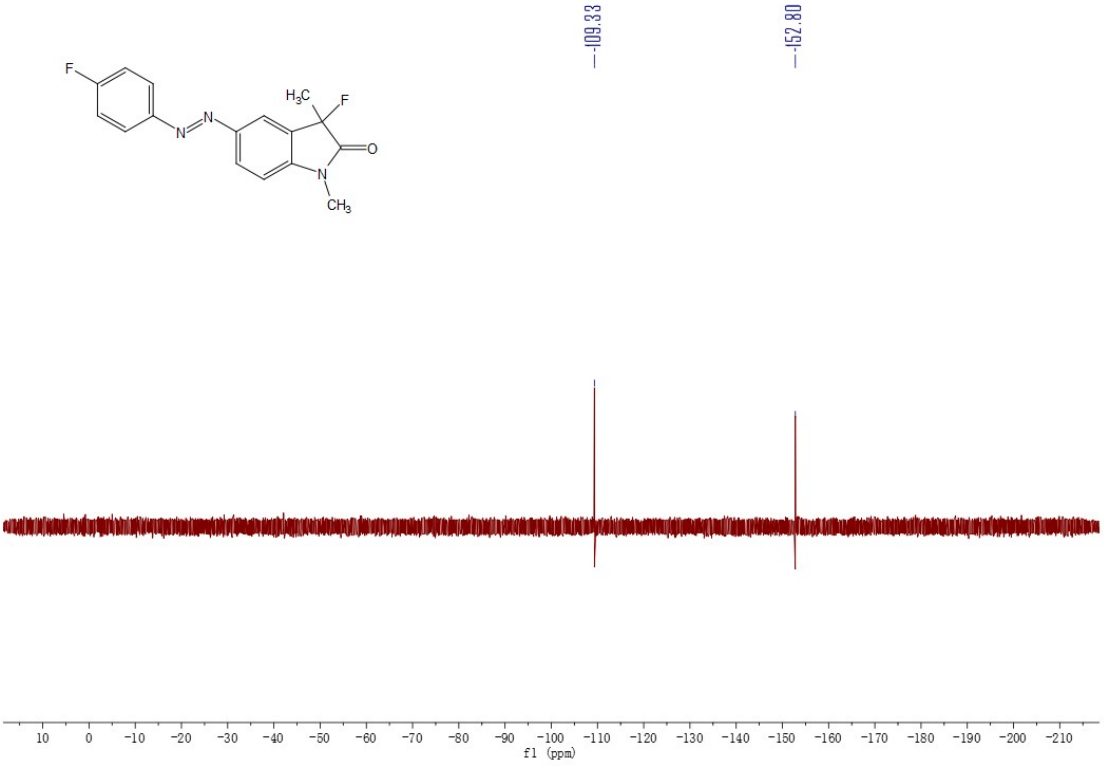
(46)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ac



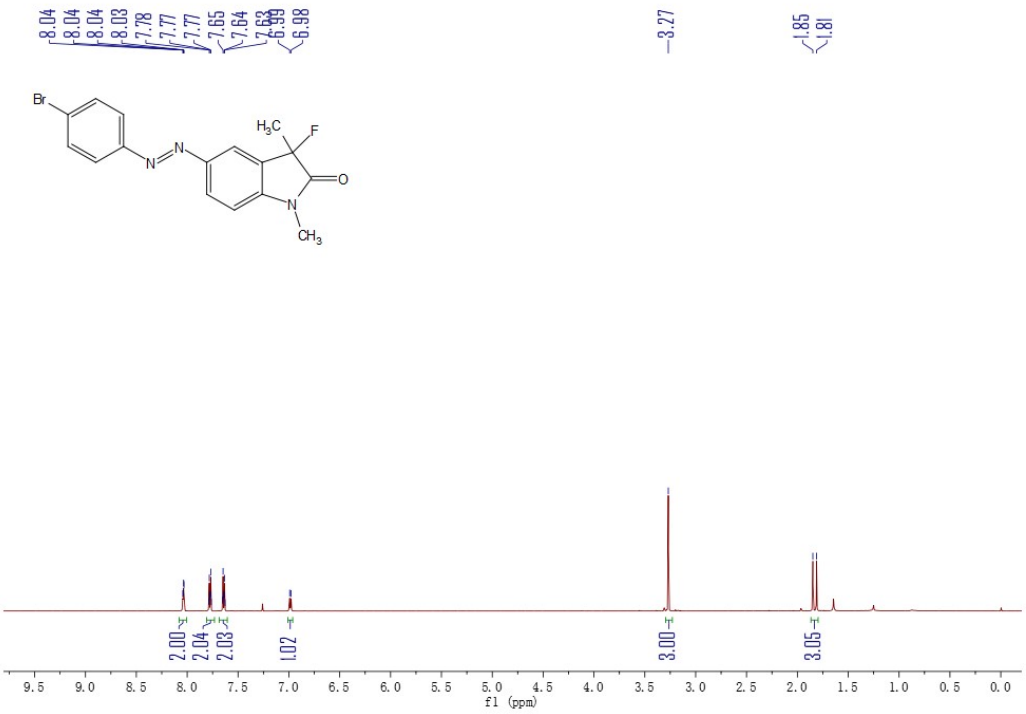
(47)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ac



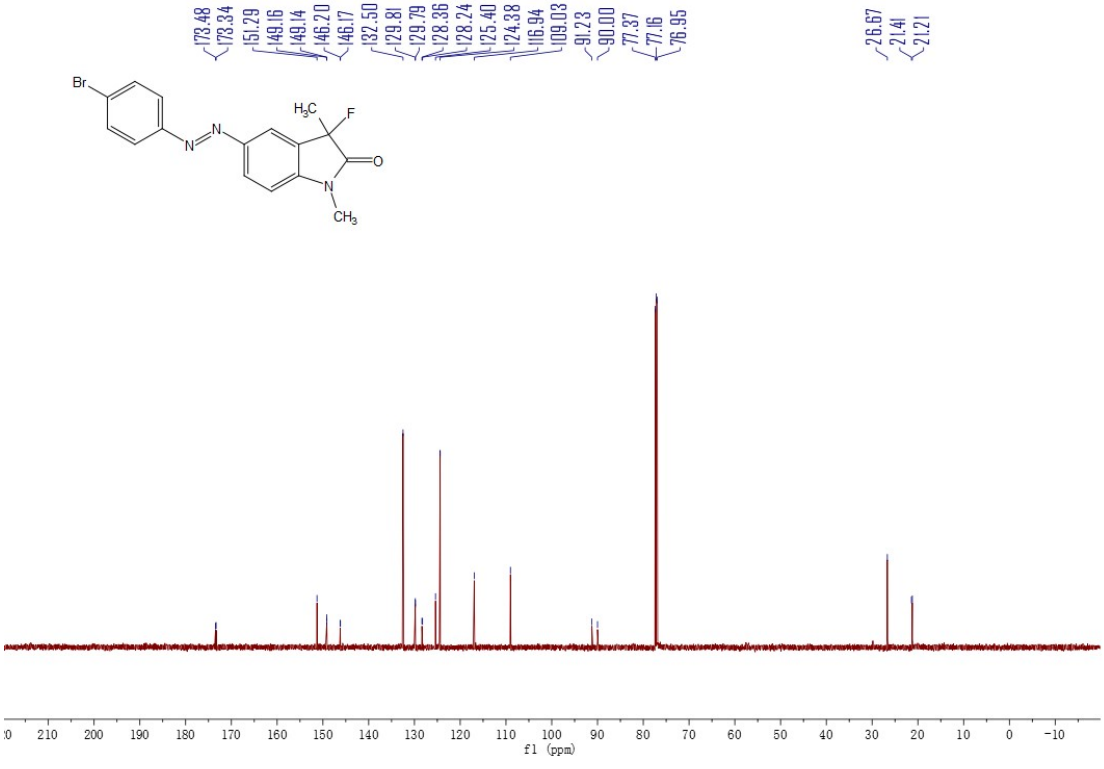
(48)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ac



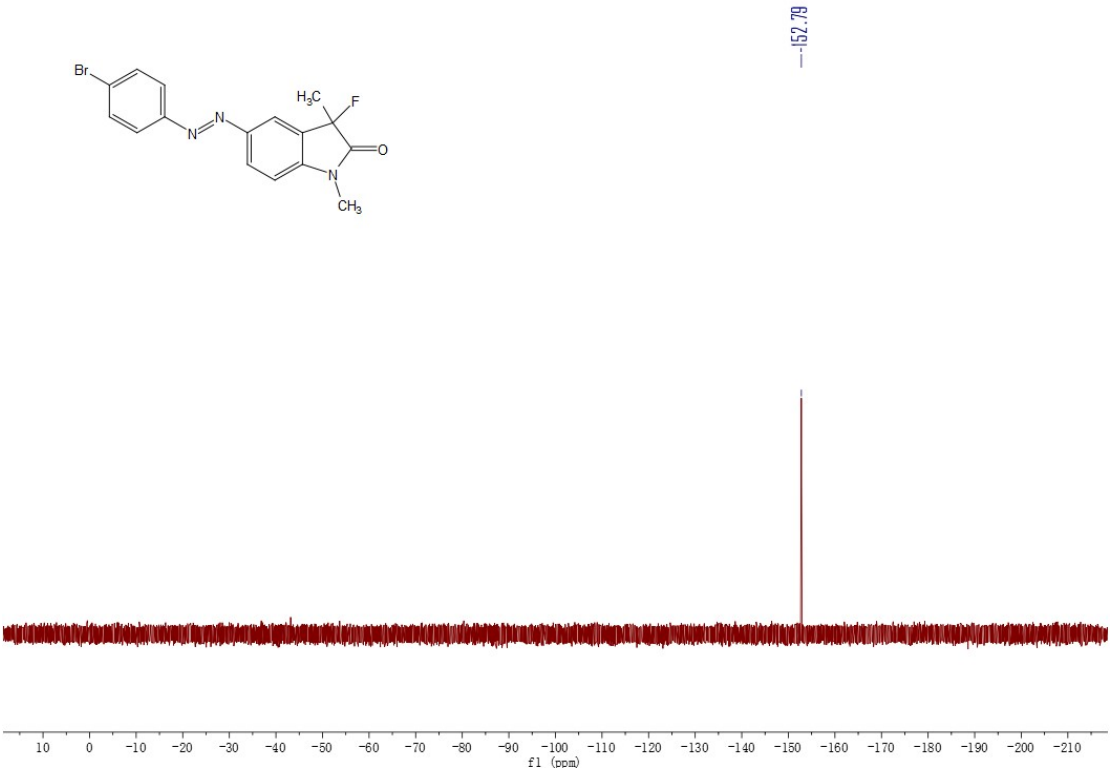
(49)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ad



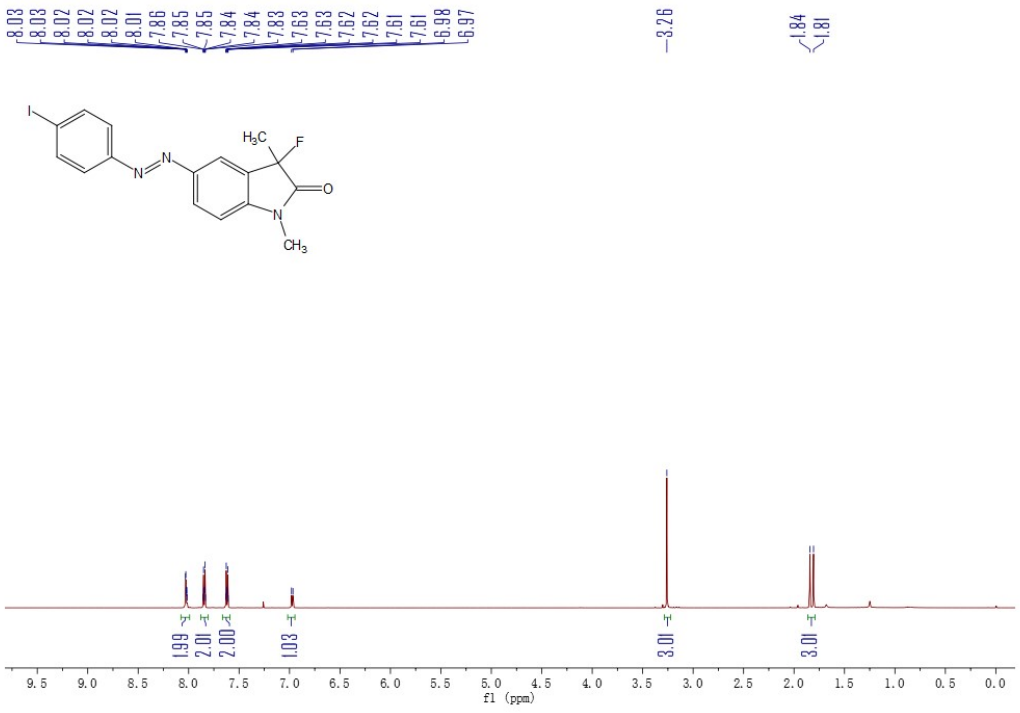
(50)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ad



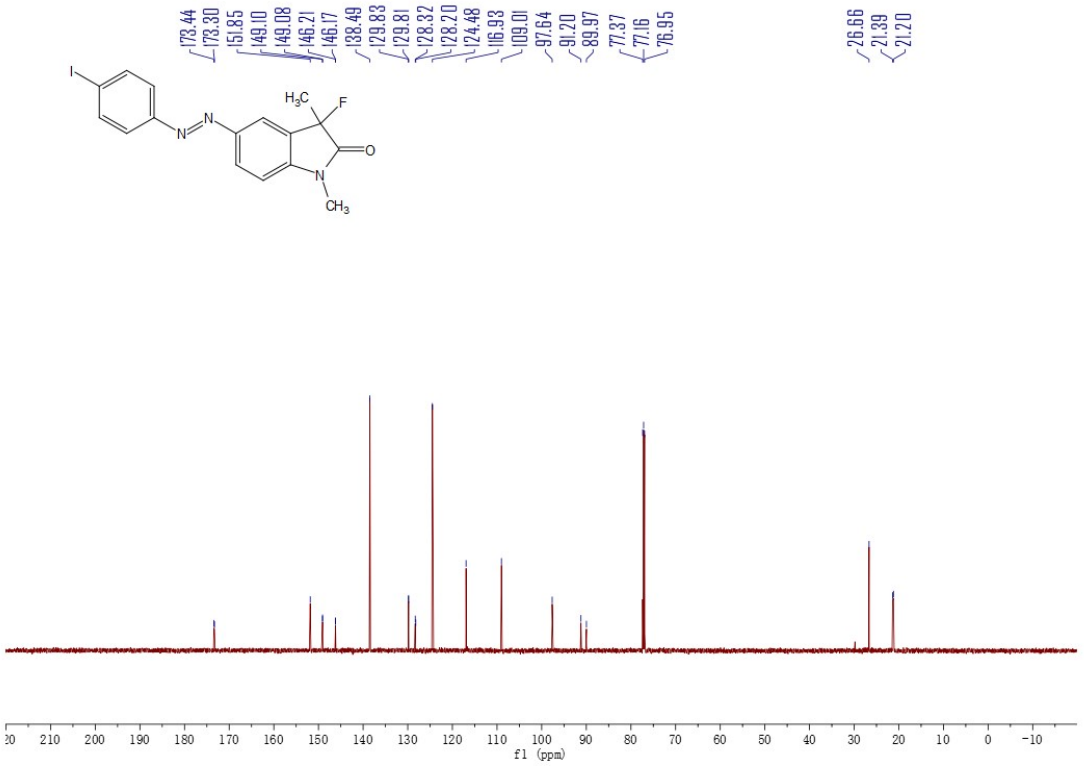
(51)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ad



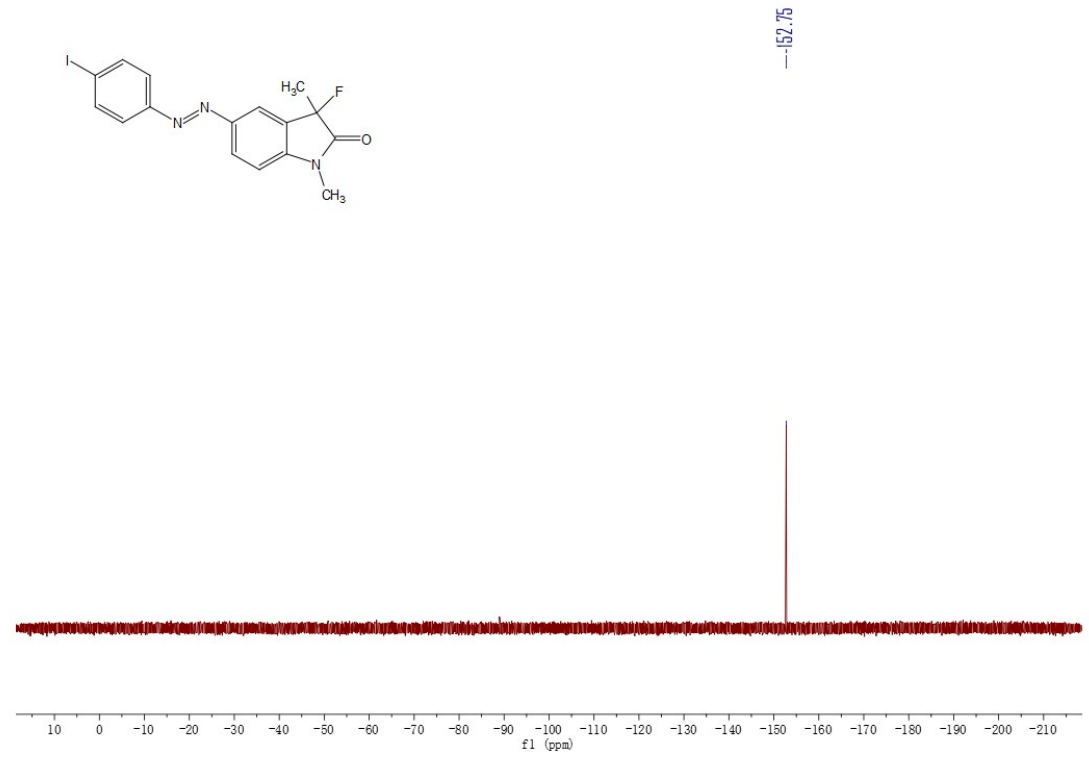
(52)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ae



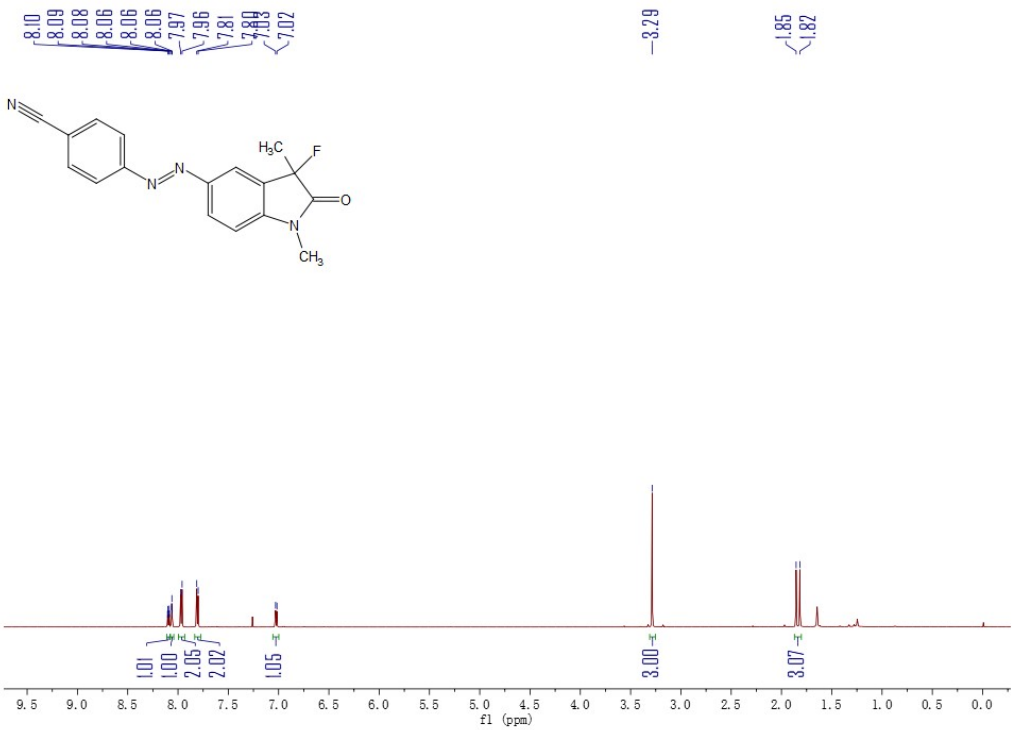
(53)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ae



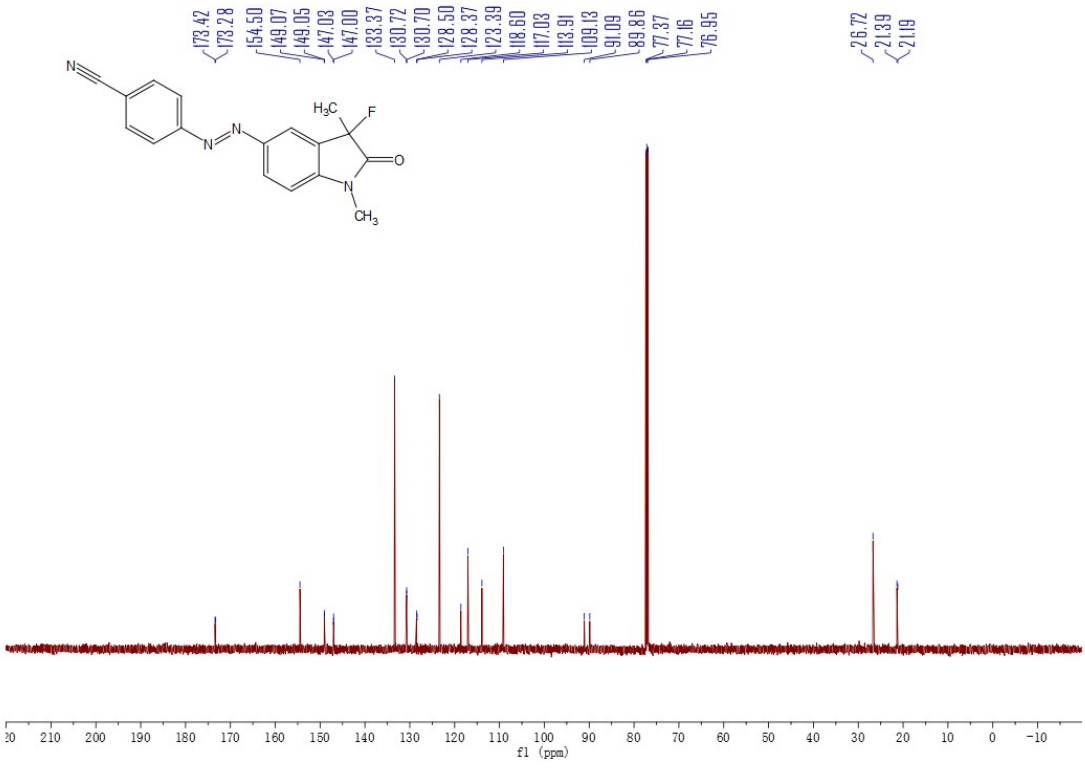
(54)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ae



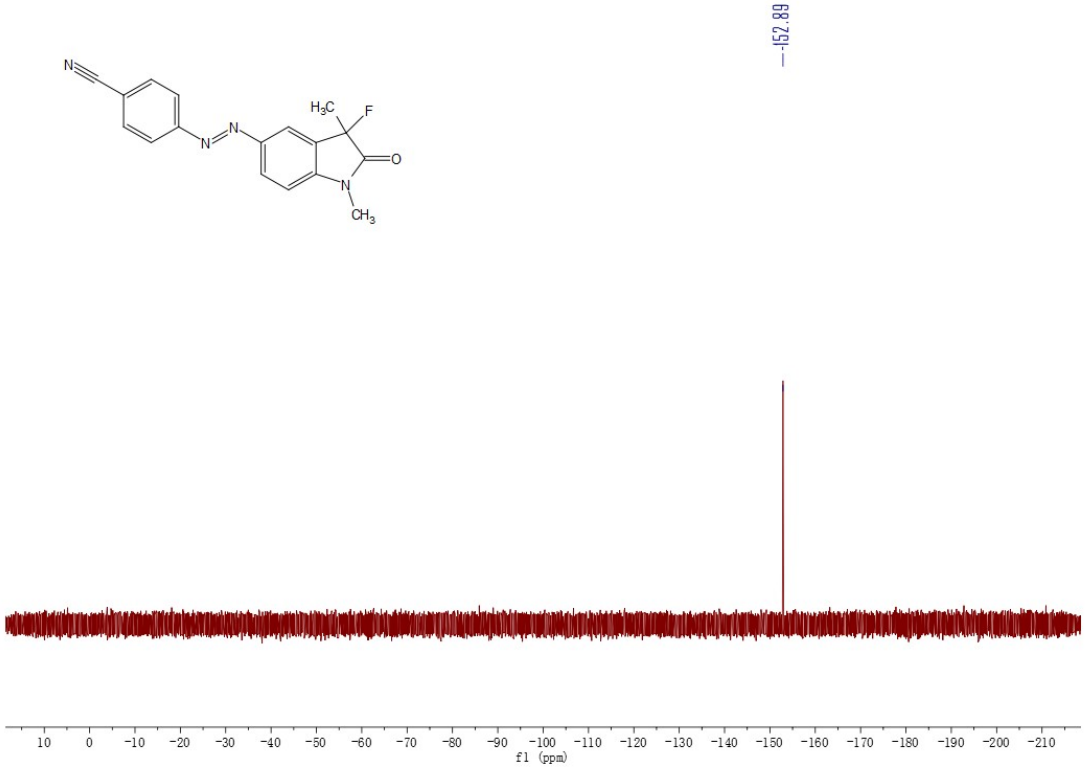
(55)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3af



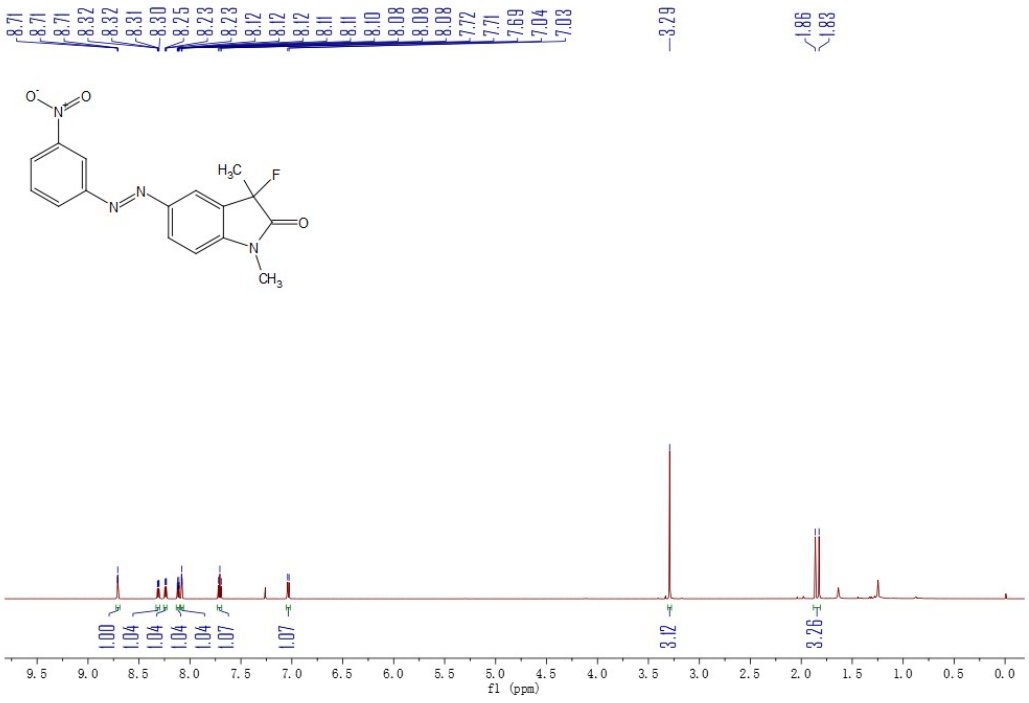
(56)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3af



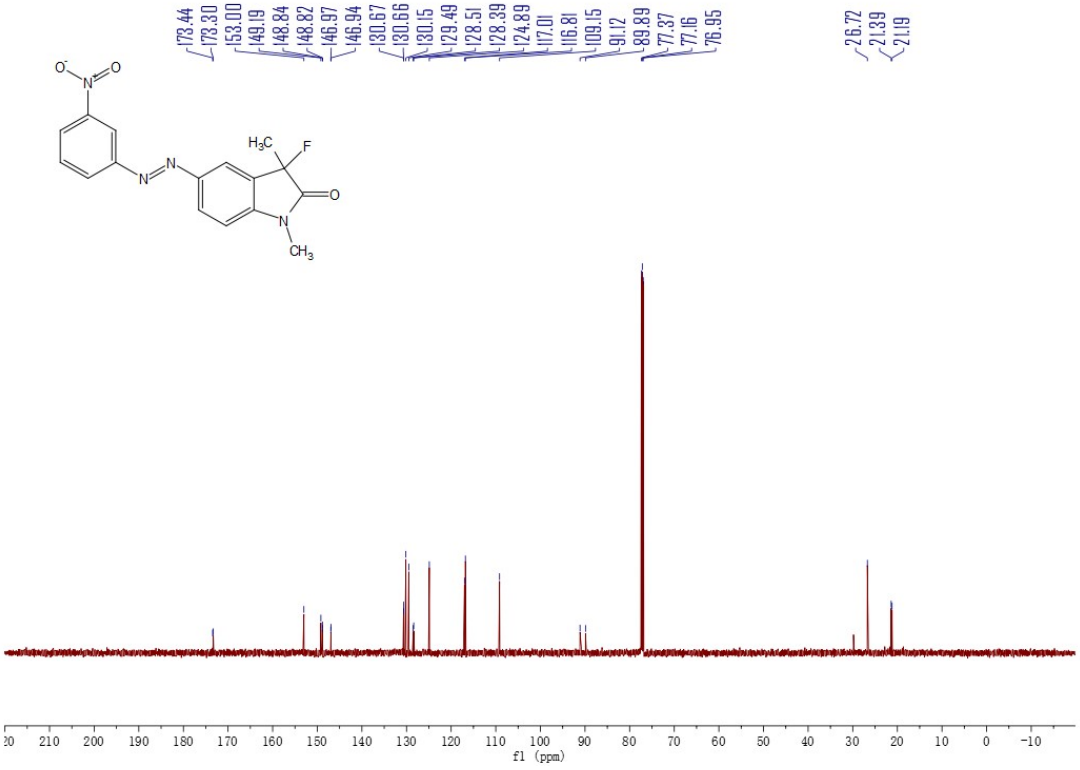
(57)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3af



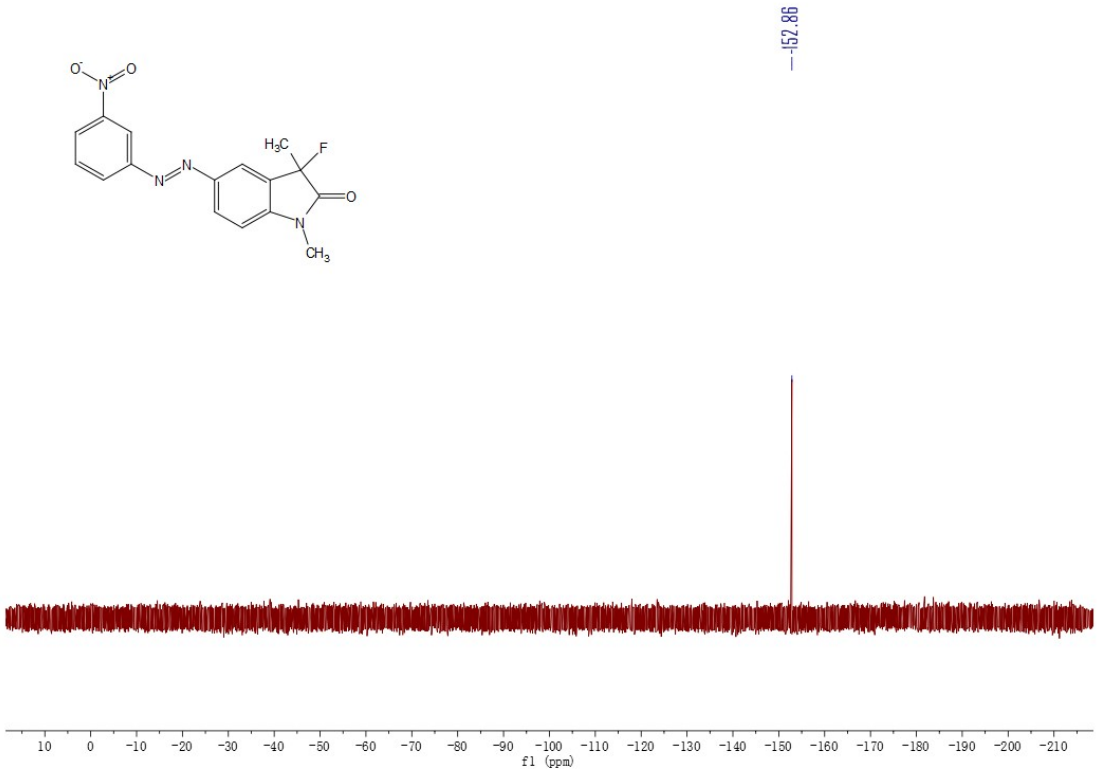
(58)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ag



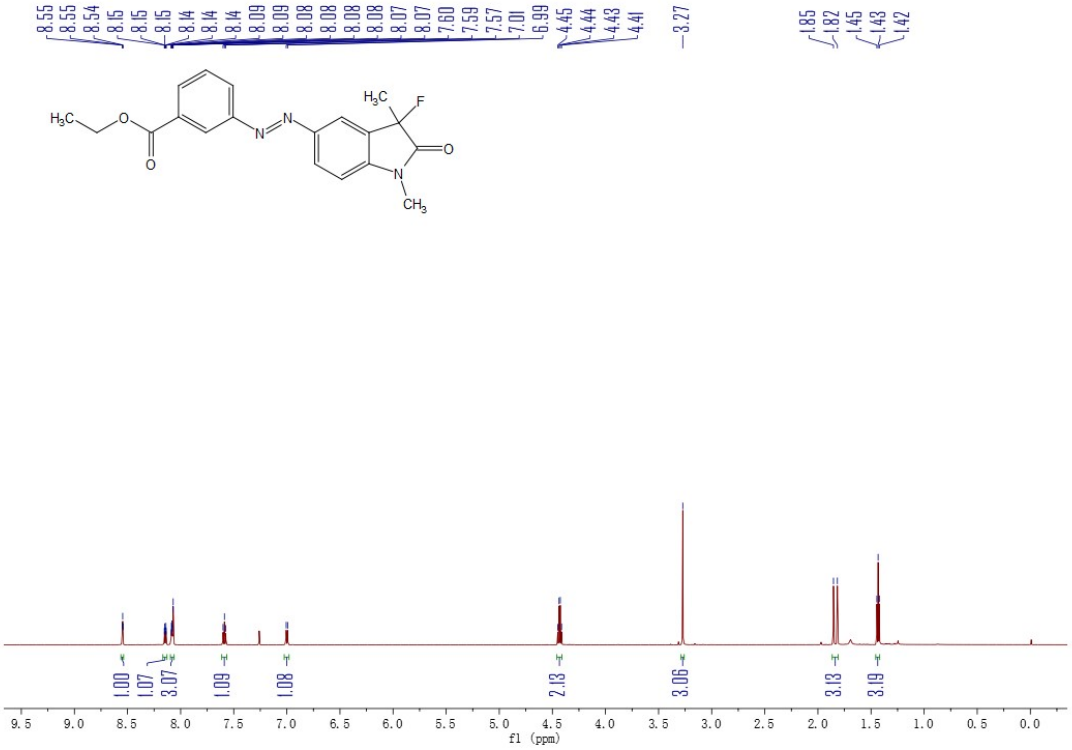
(59)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ag



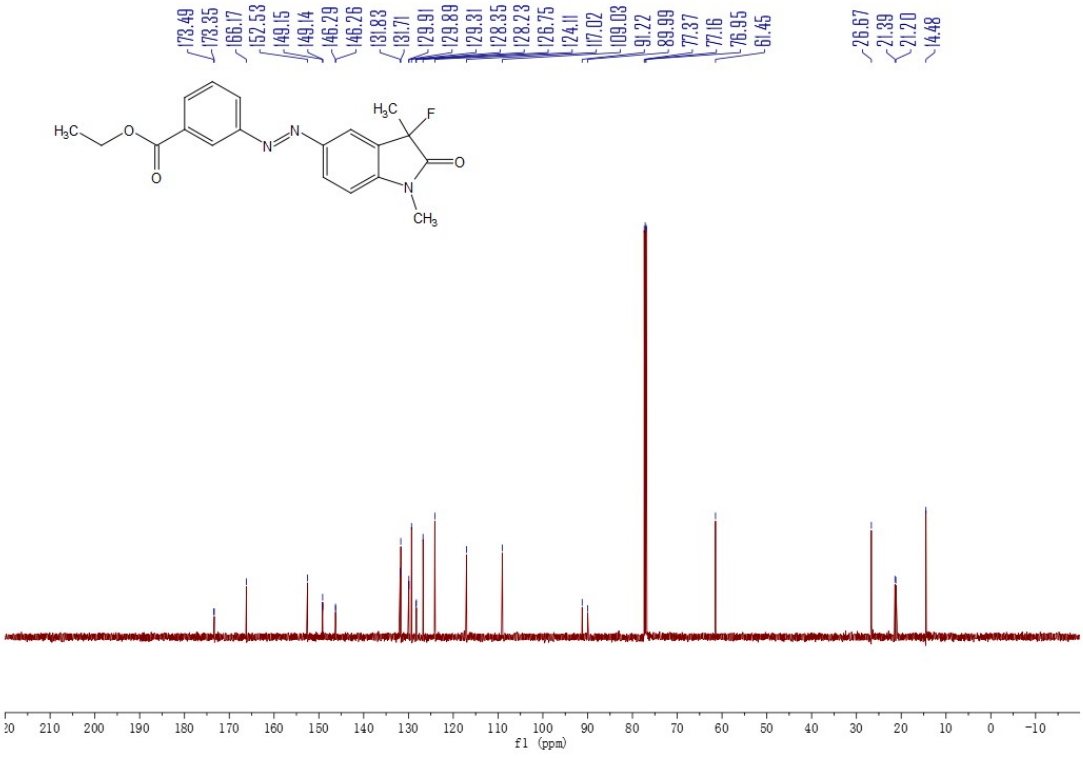
(60)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ag



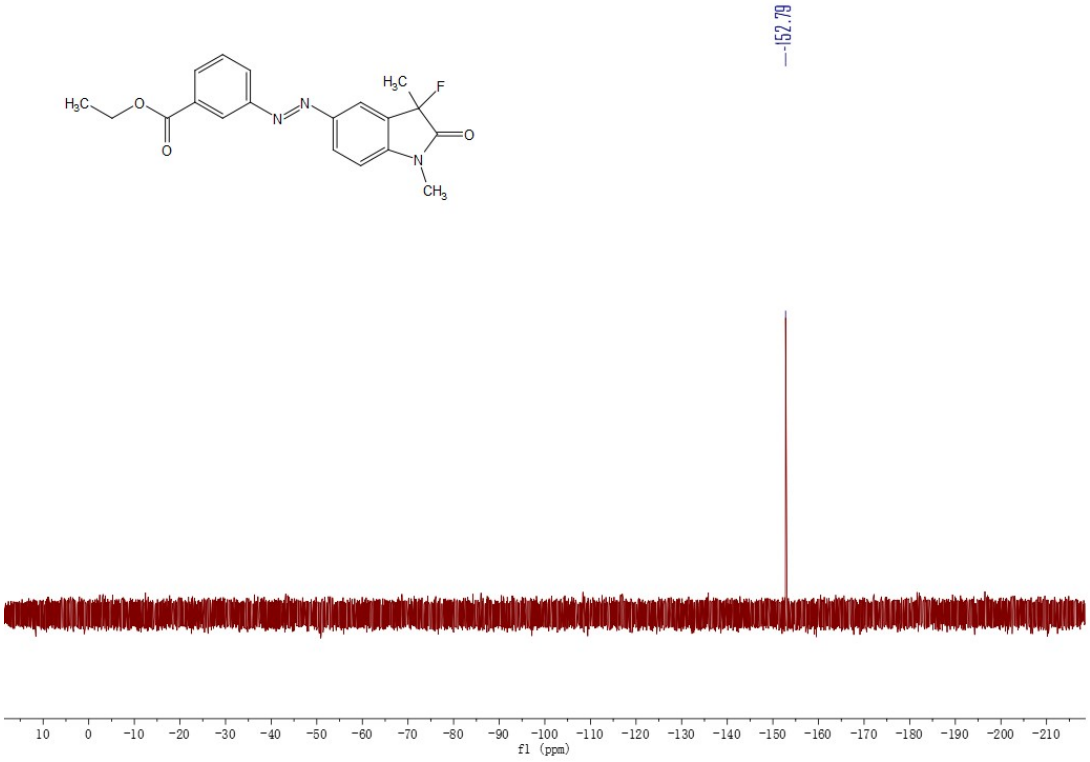
(61)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ah



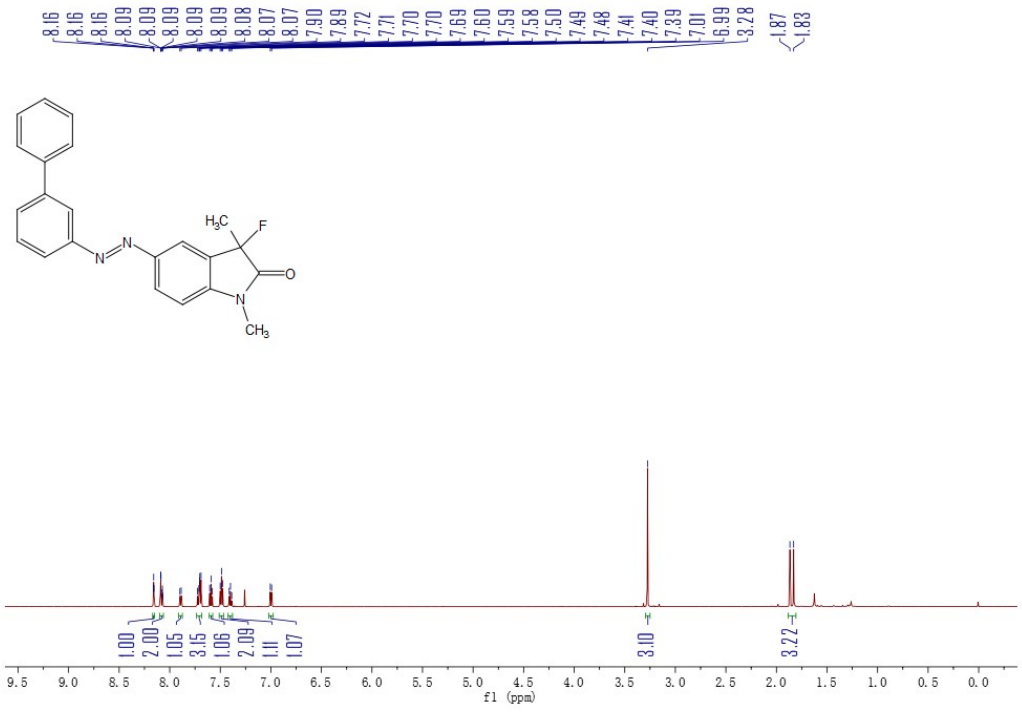
(62)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ah



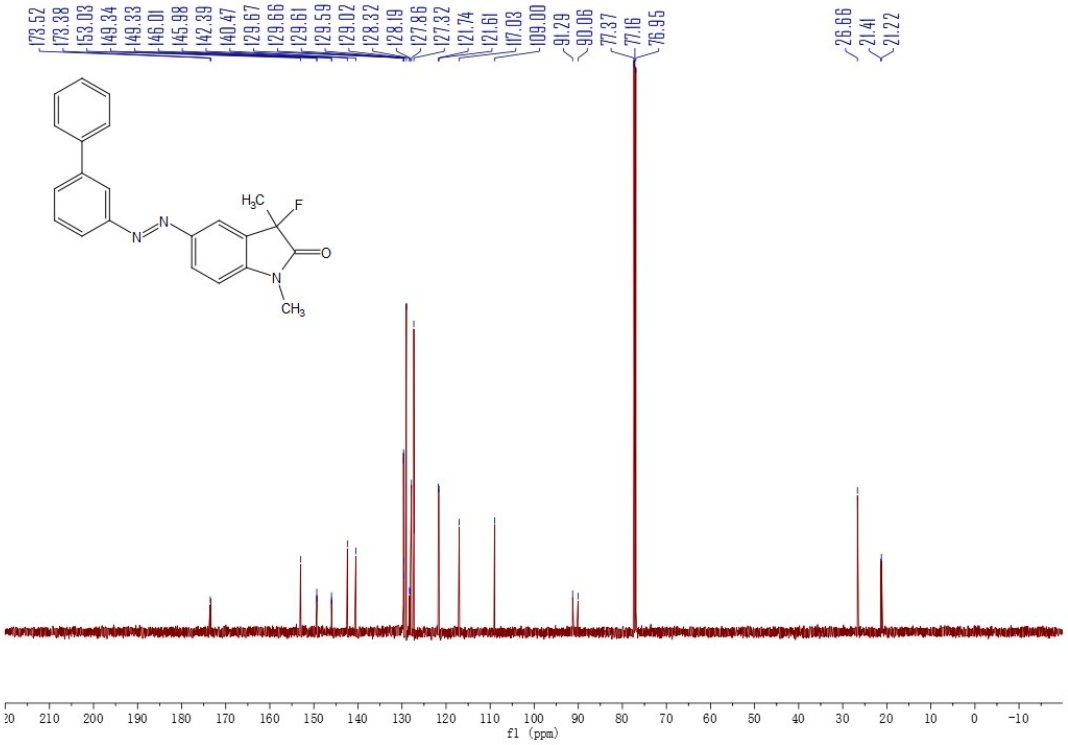
(63)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ah



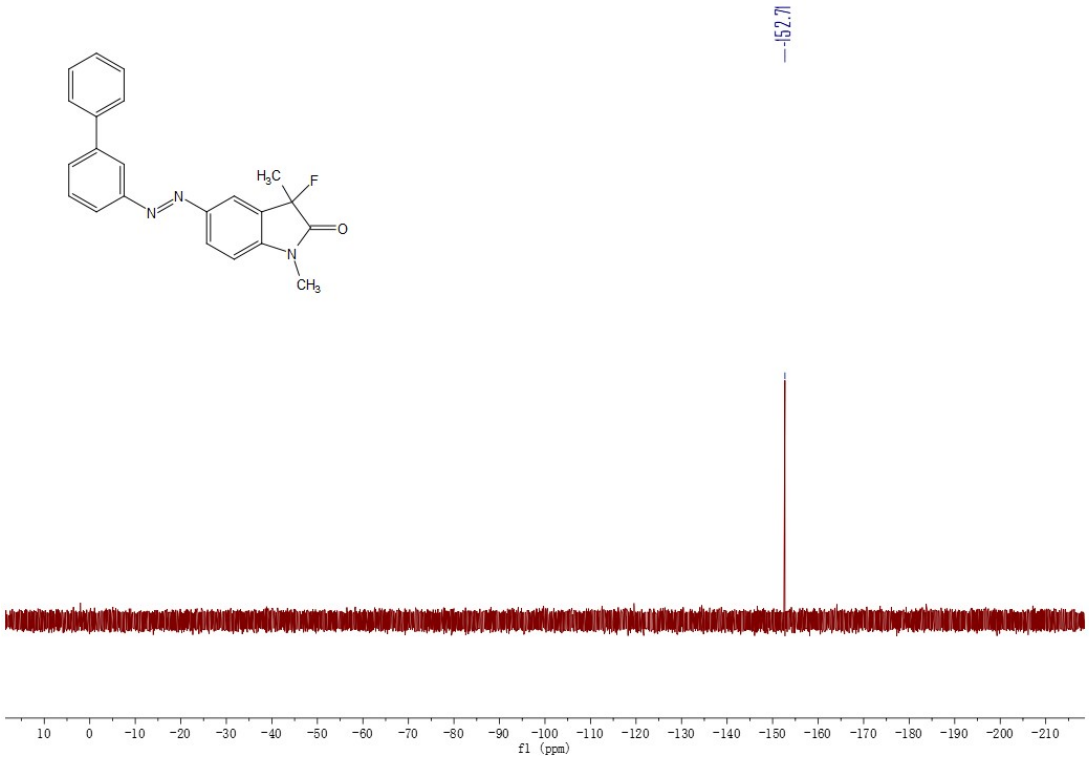
(64)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ai



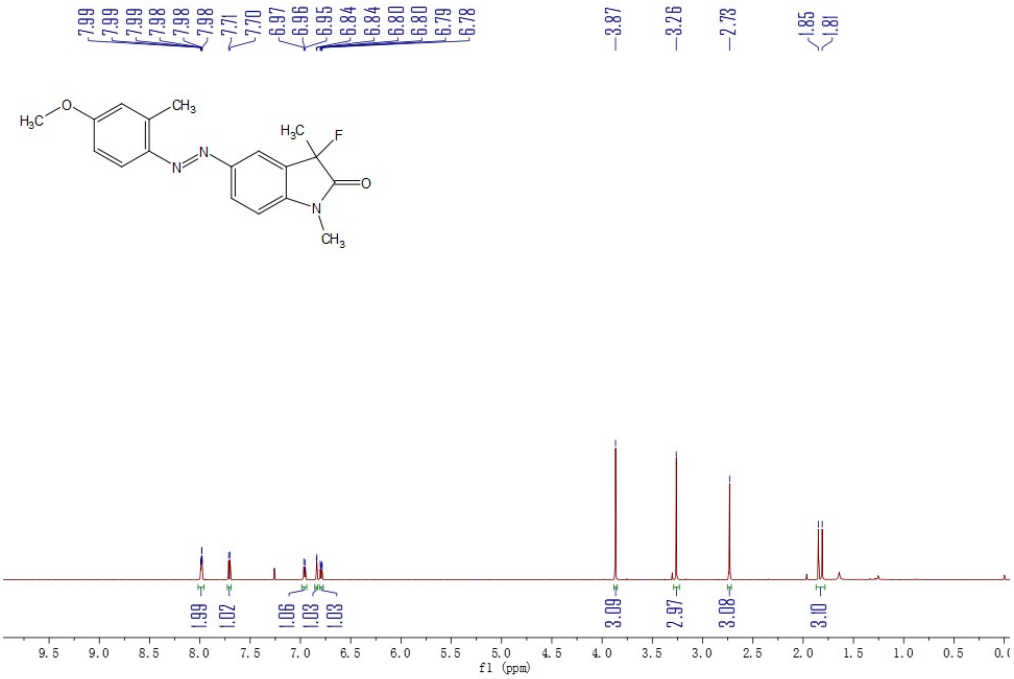
(65)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ai



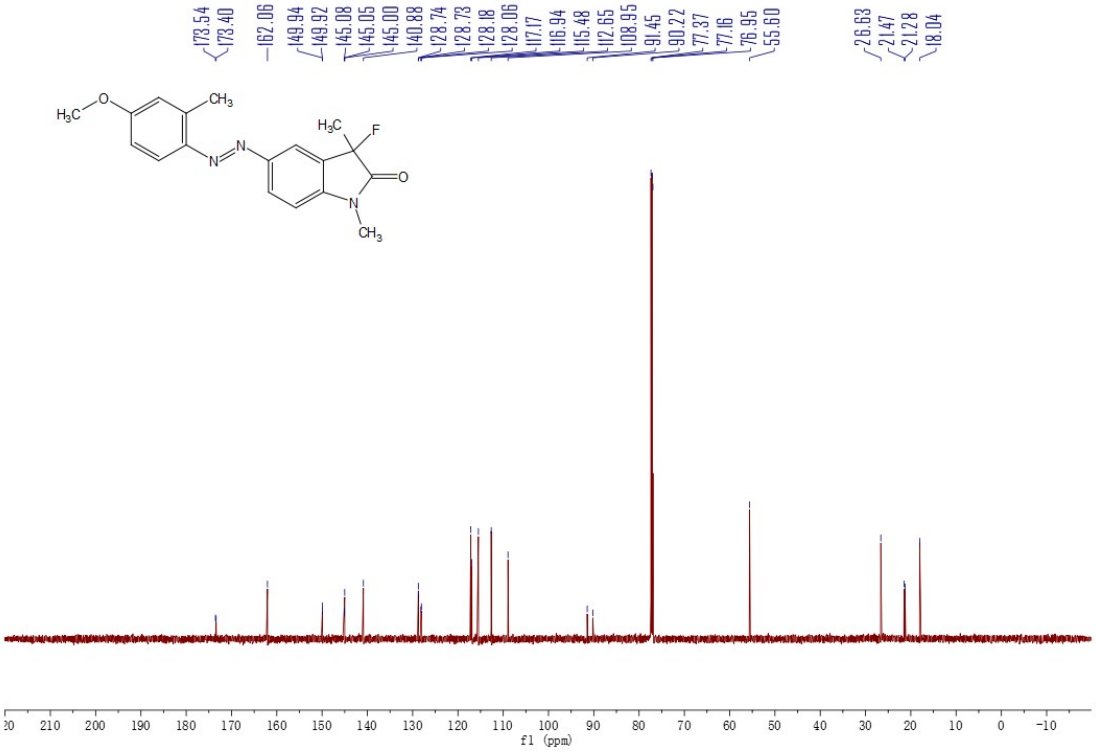
(66)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ai



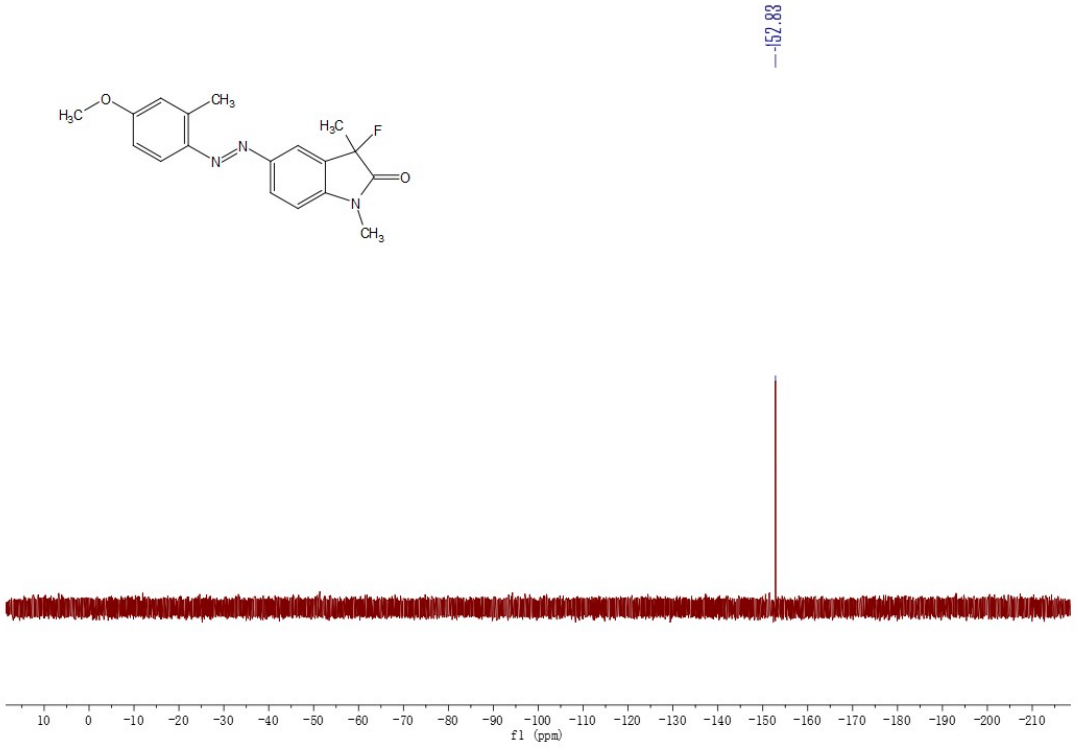
(67)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ak



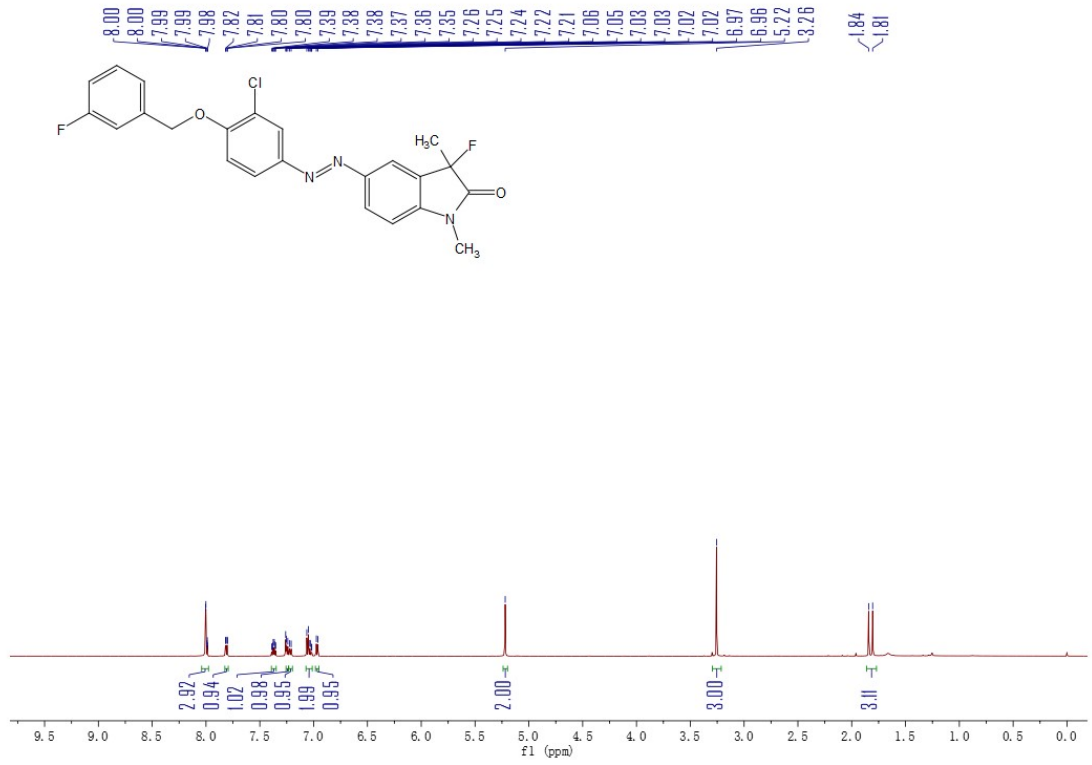
(68)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ak



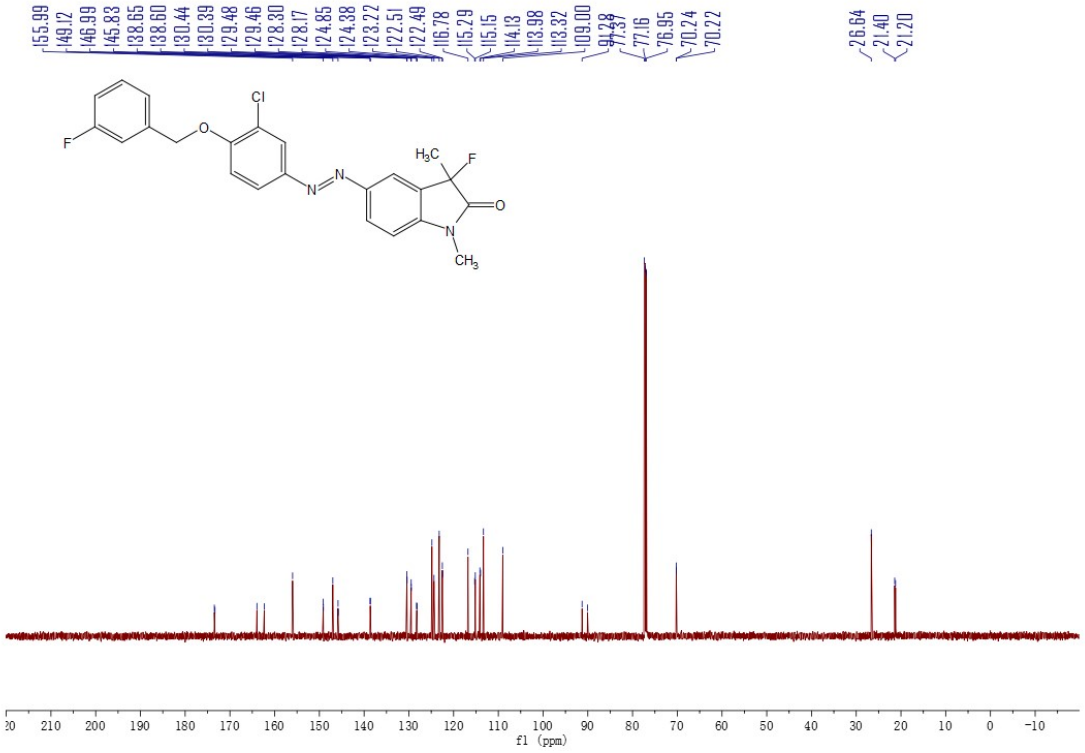
(69)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ak



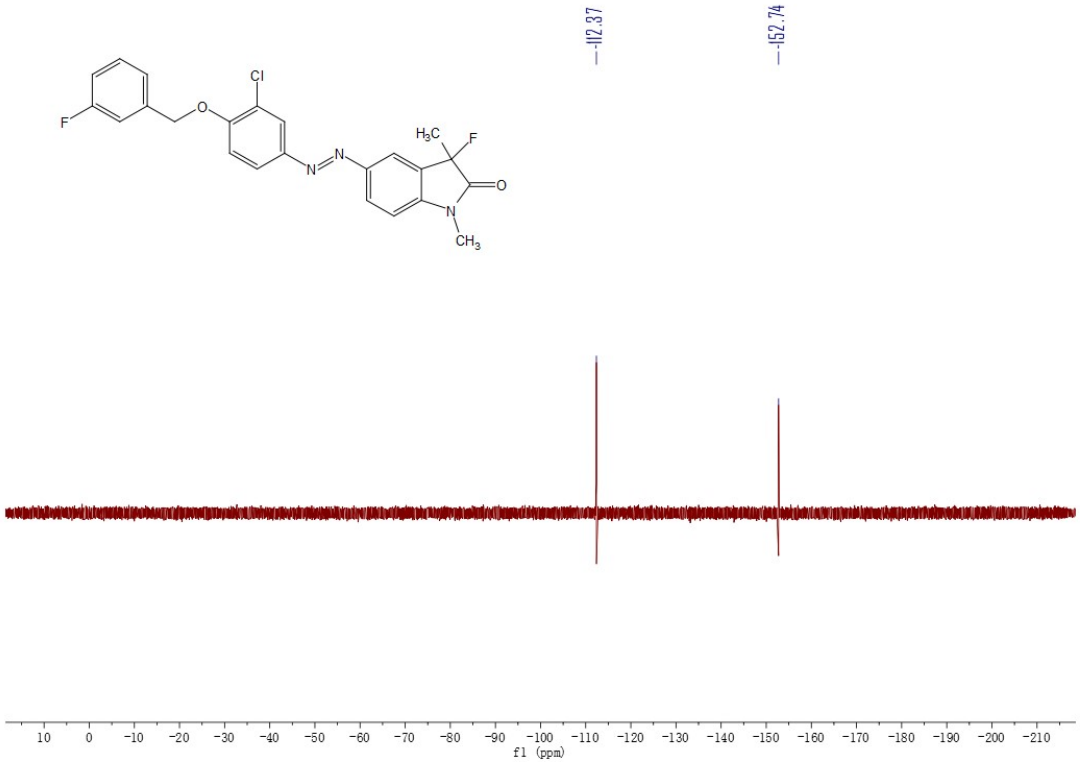
(70)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3al



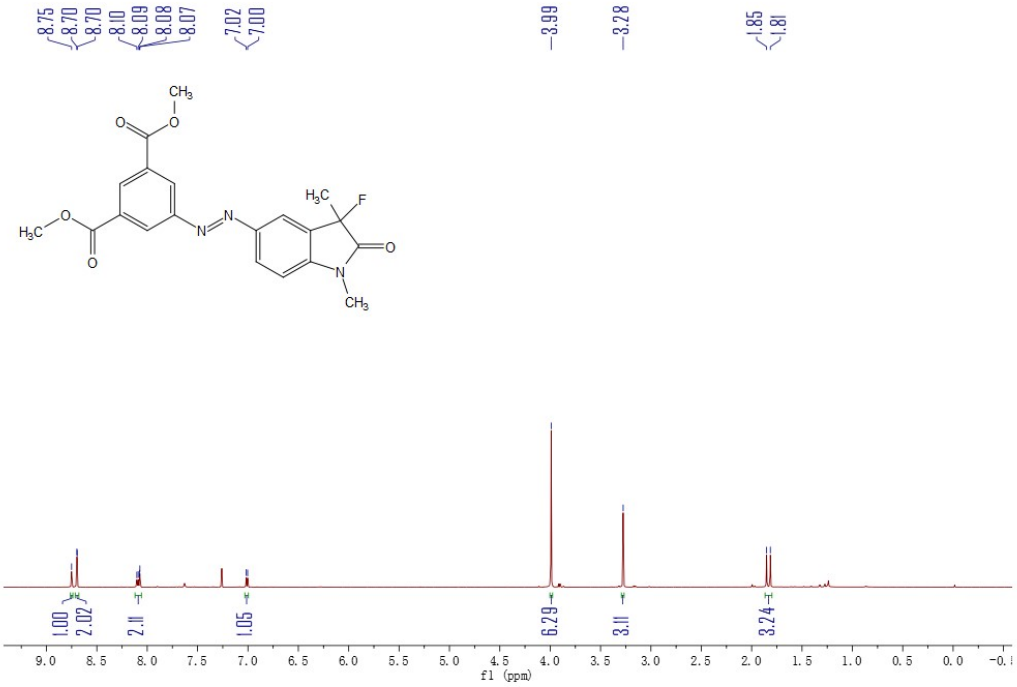
(71)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3al



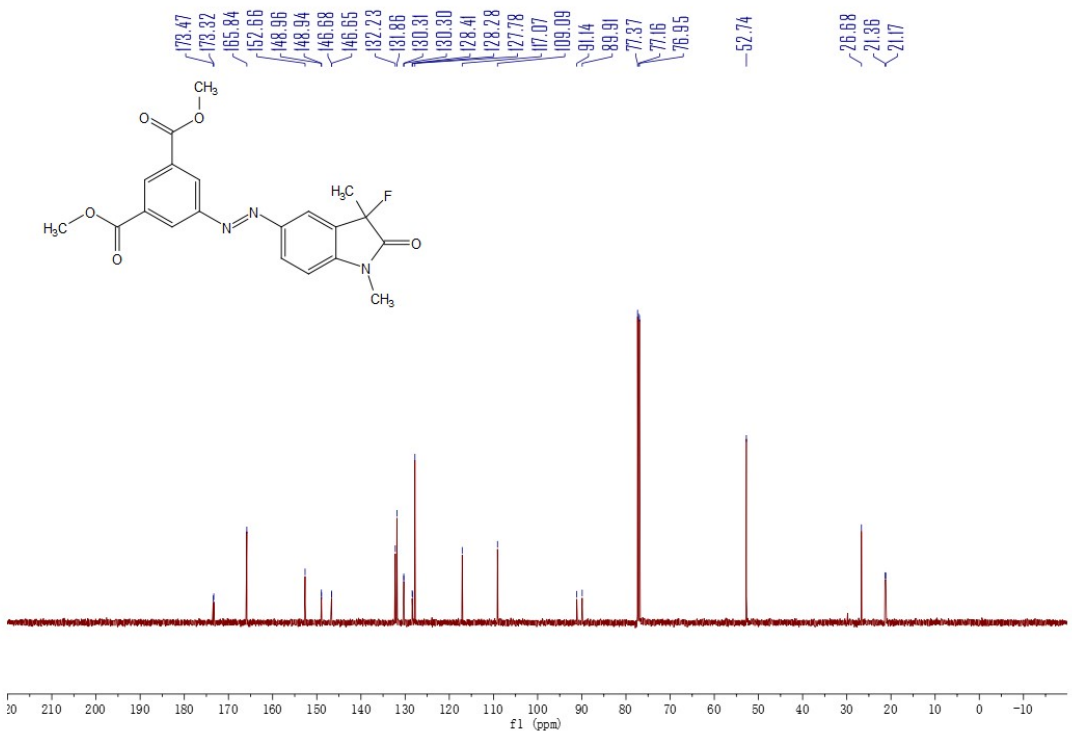
(72)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3al



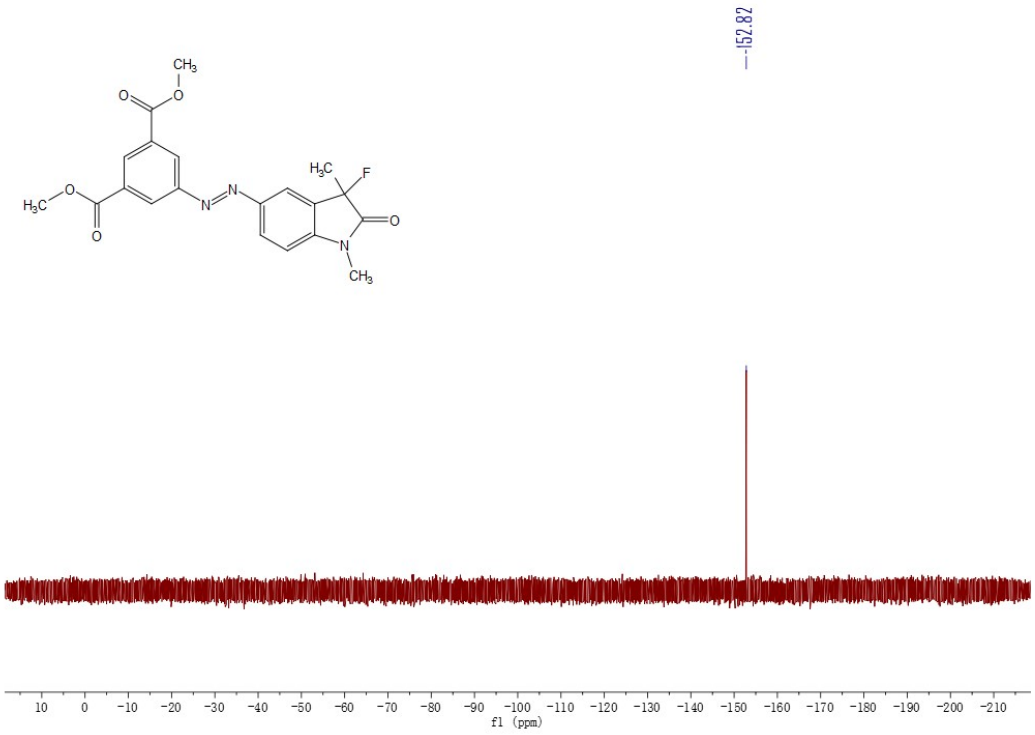
(73)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3am



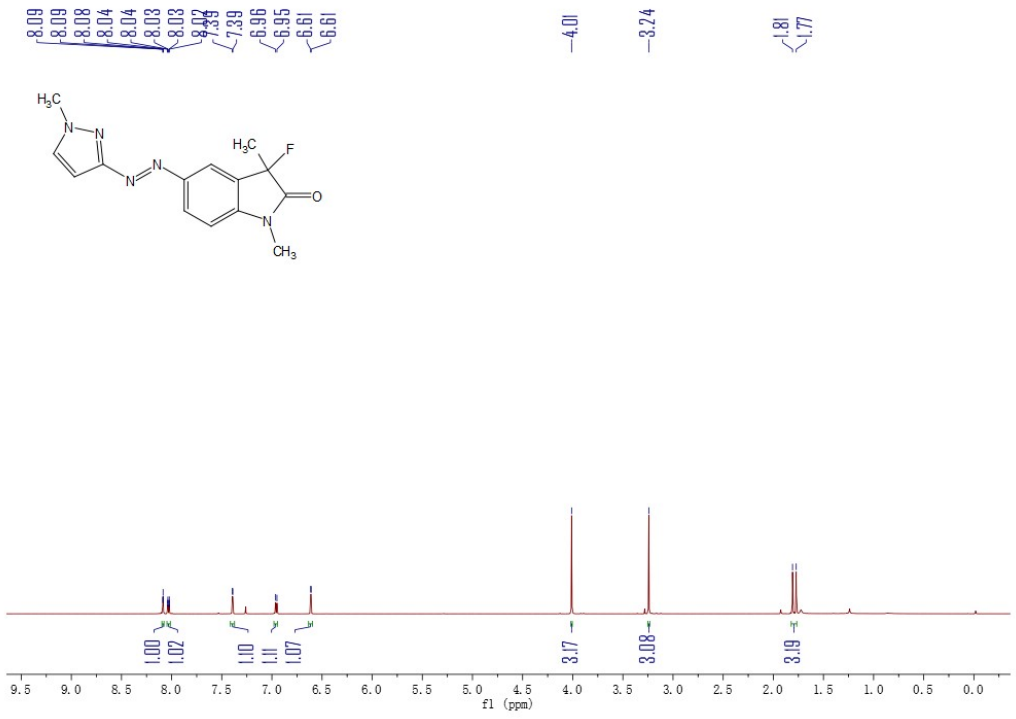
(74)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3am



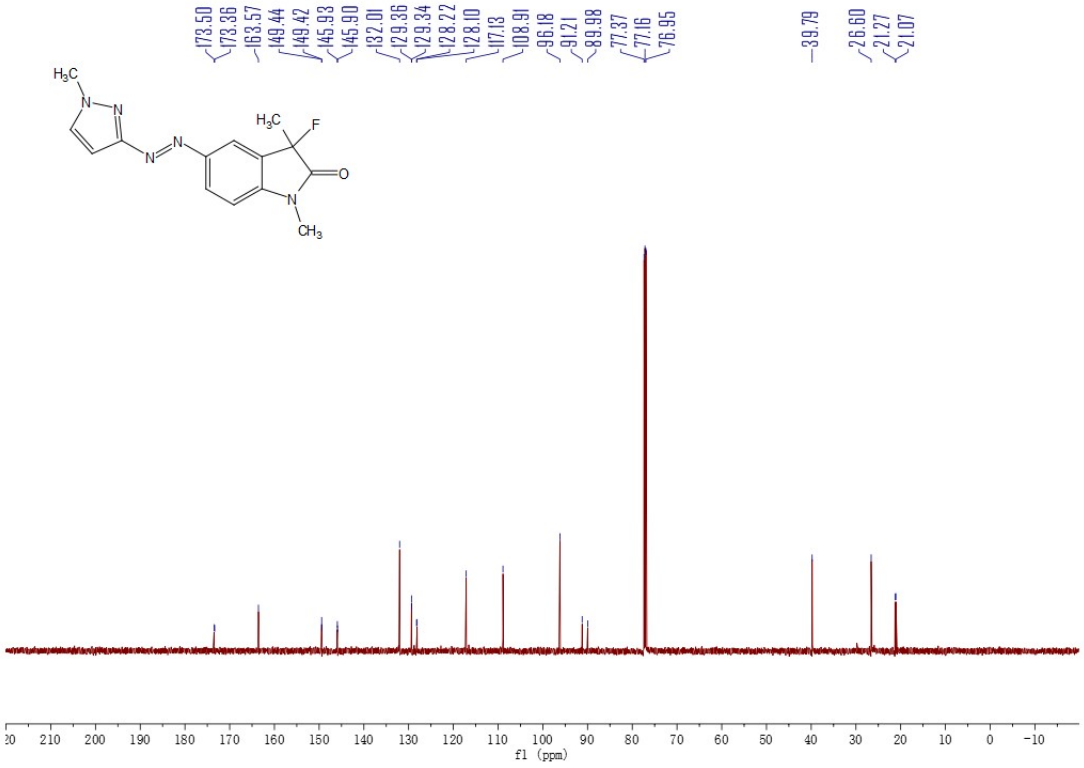
(75)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3am



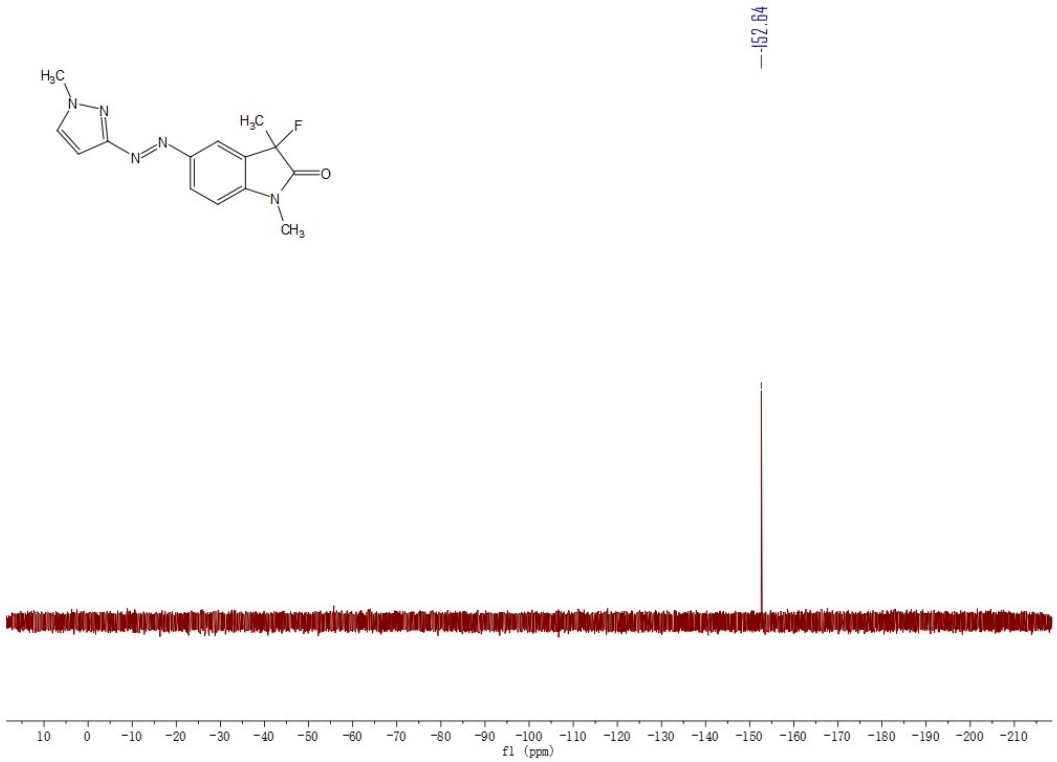
(76)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3an



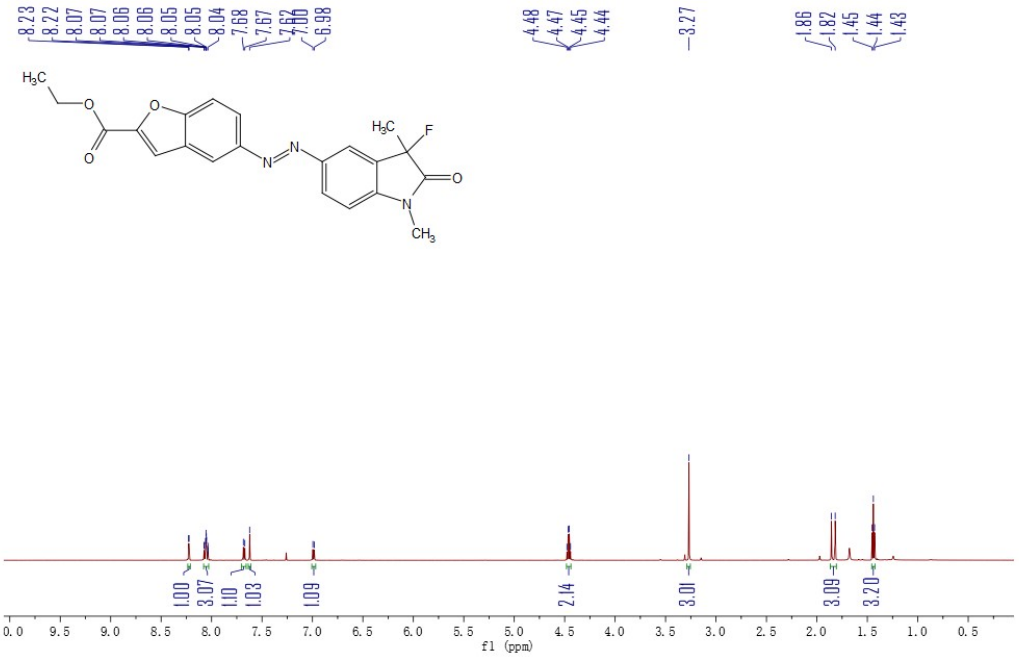
(77)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3an



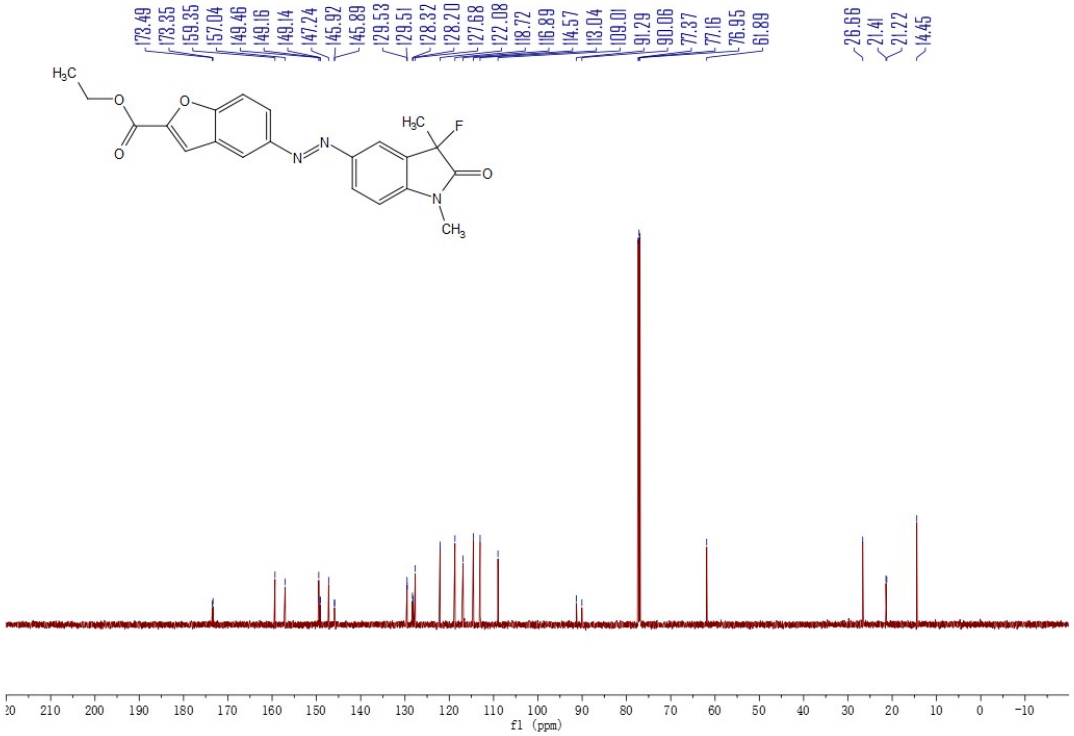
(78)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3an



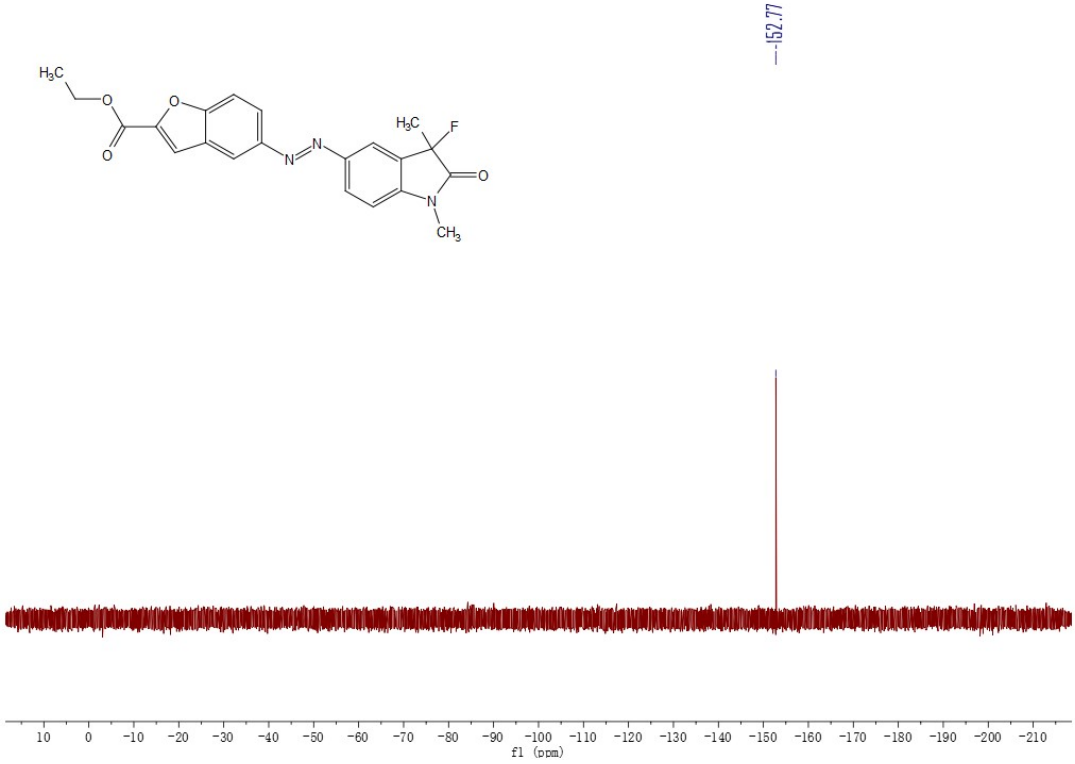
(79)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ao



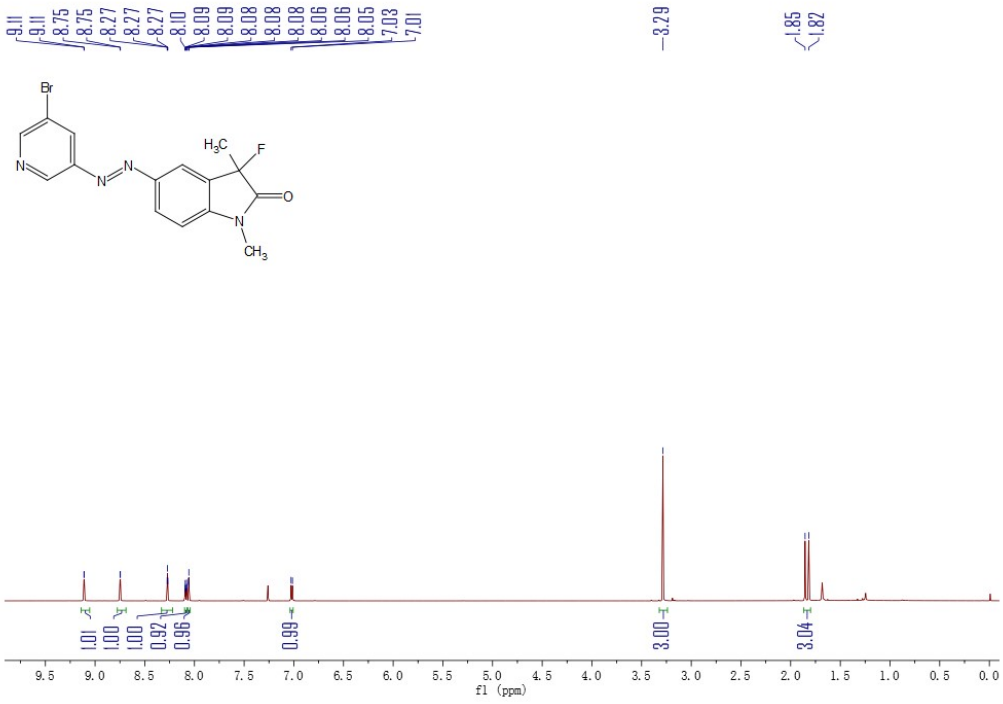
(80)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ao



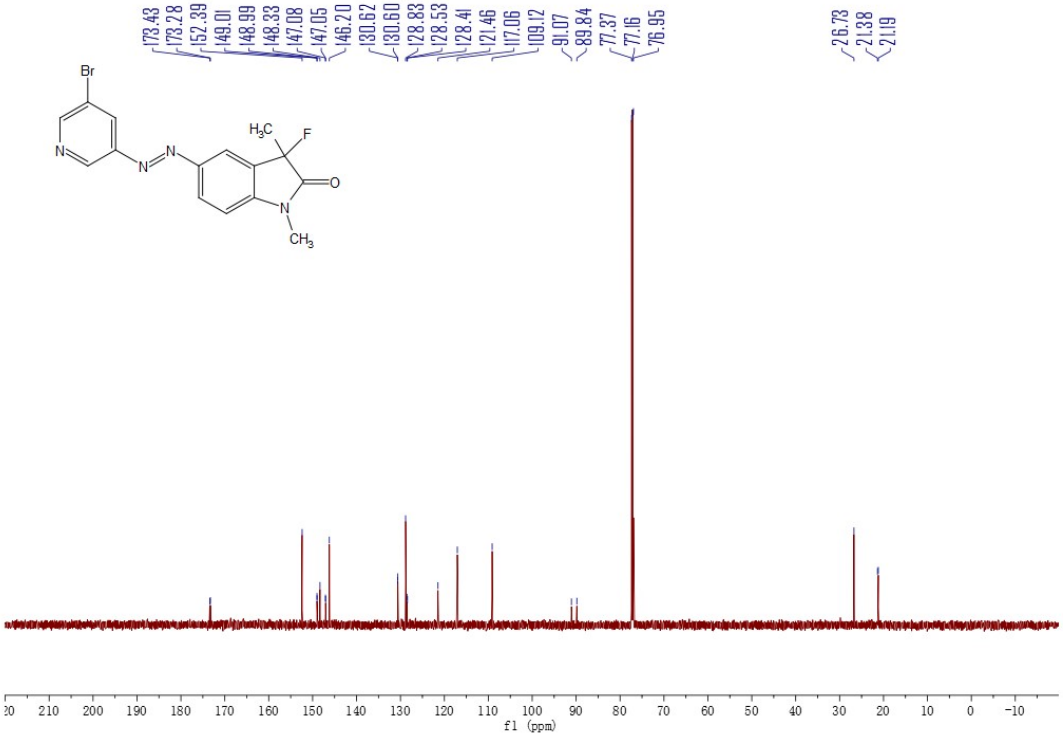
(81)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ao



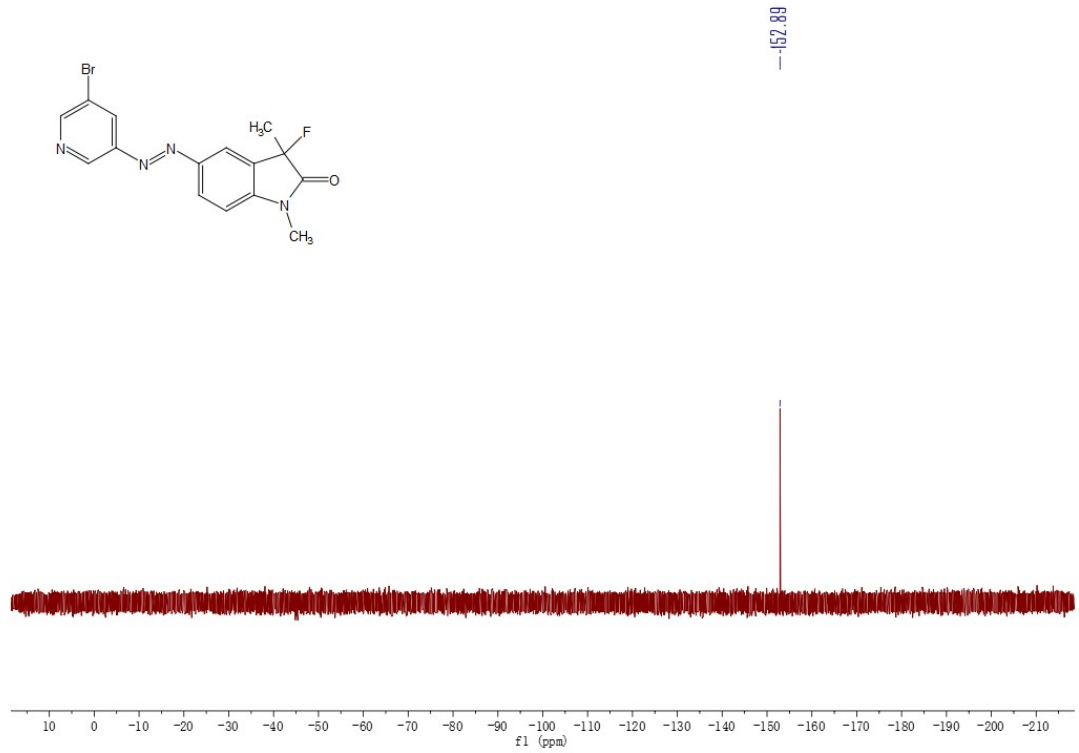
(82)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3ap



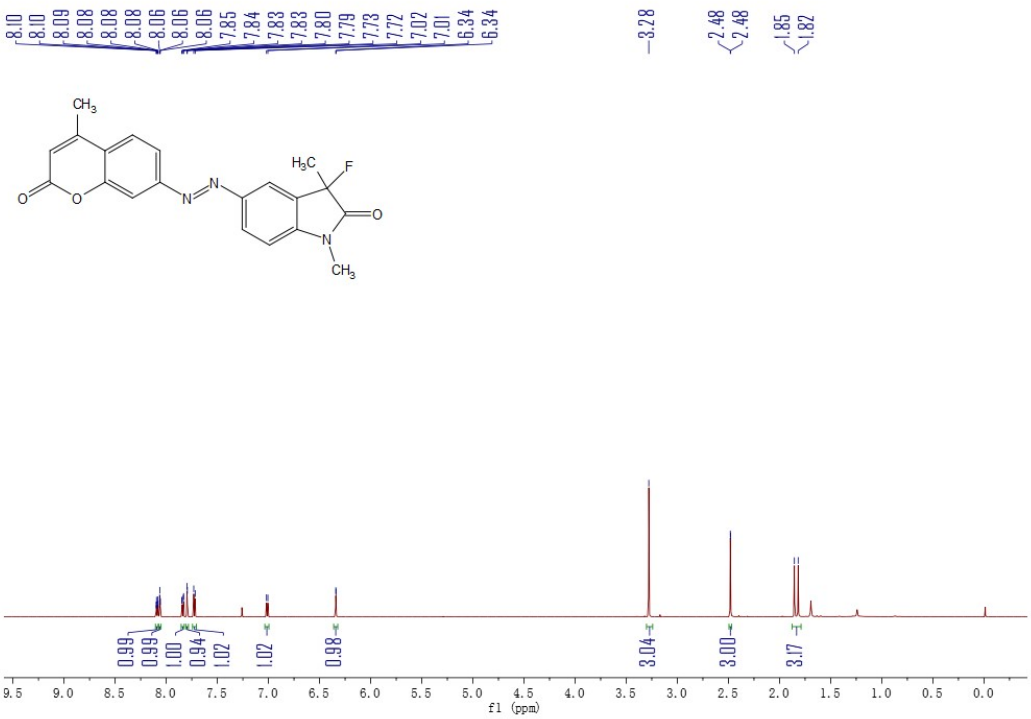
(83)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3ap



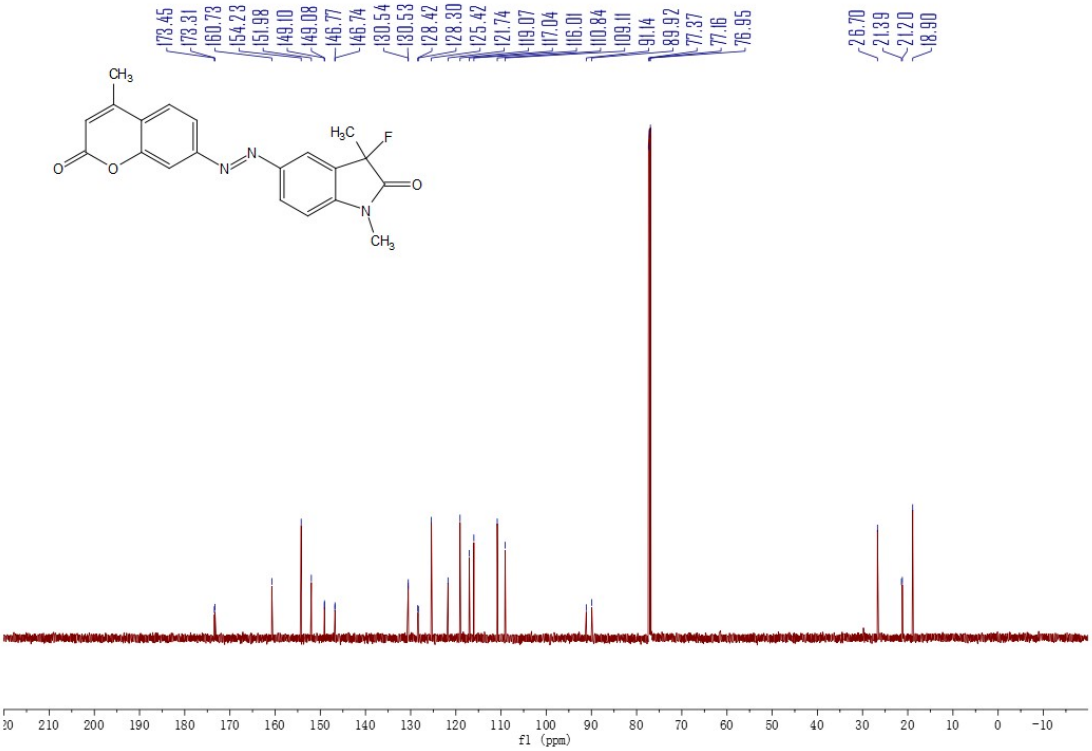
(84)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3ap



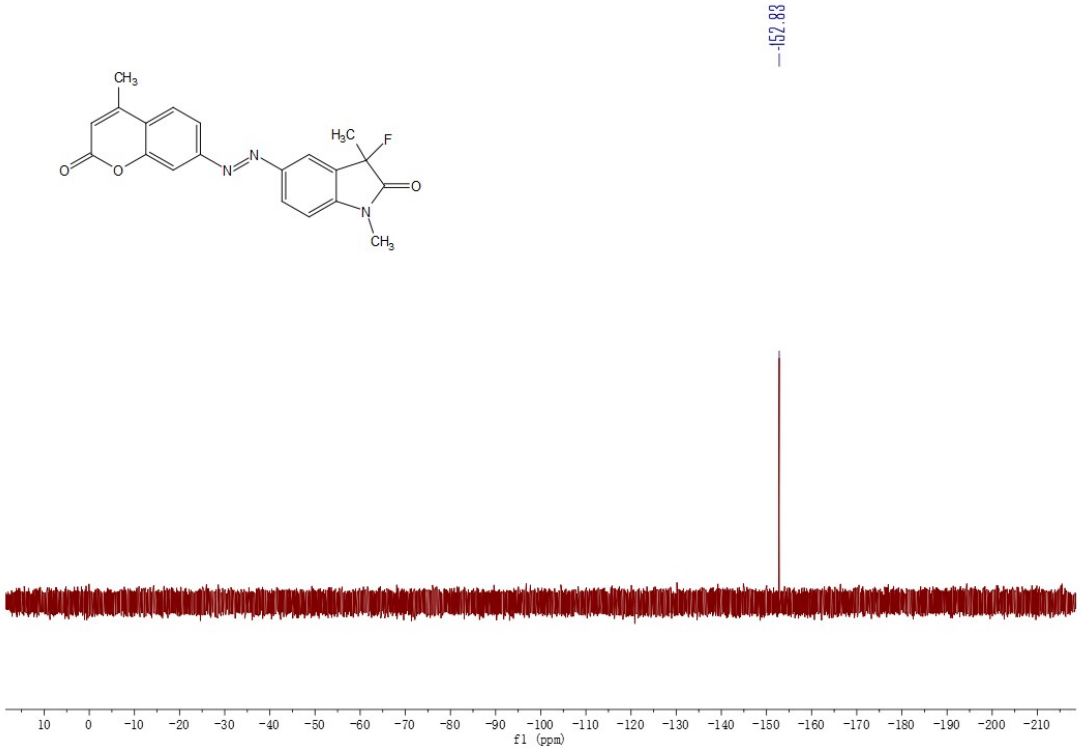
(85)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 3aq



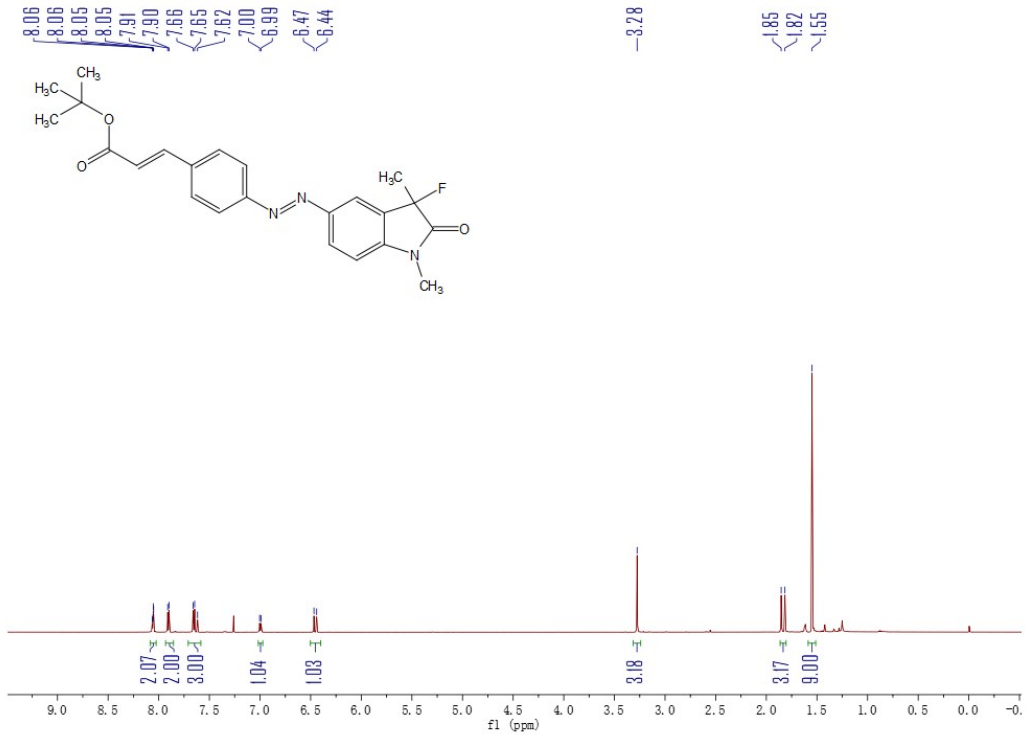
(86)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 3aq



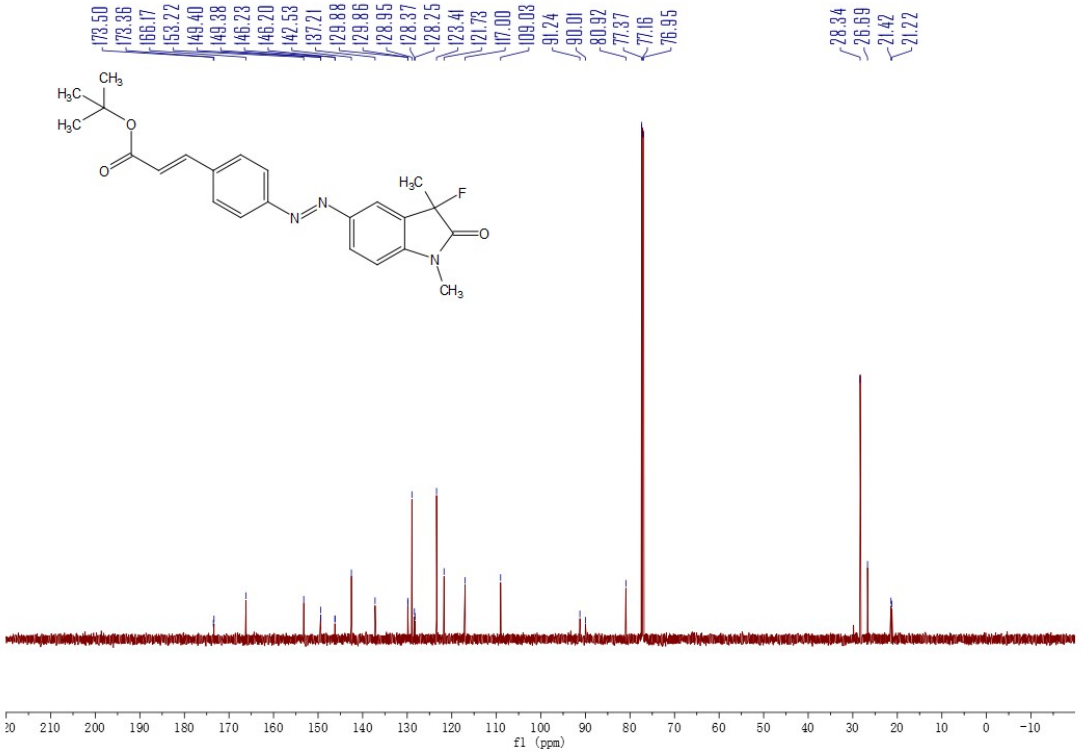
(87)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 3aq



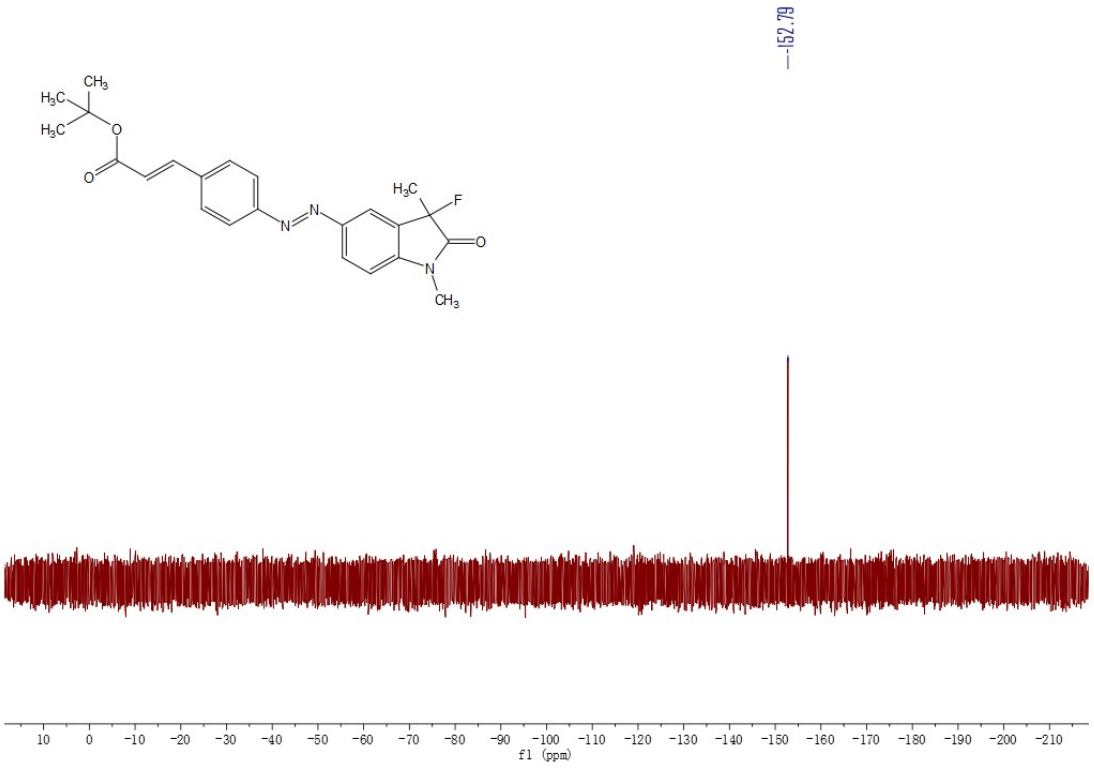
(88)^{1}H-NMR (600MHz, $CDCl_3$) spectra of 4ae



(89)^{13}C-NMR (151MHz, $CDCl_3$) spectra of 4ae



(90)^{19}F-NMR (565MHz, $CDCl_3$) spectra of 4ae



8. References

[1] Y. Dong, J. Yang, H. Zhang, X.-Y. Zhan, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, Cobalt-Catalyzed Cycloamination: Synthesis and Photophysical Properties of Polycyclic *N*-Heterocycles, *Org. Lett*., 2020, **22**, 5151–5156.

[2] M. Cao, H. Wang, Y. Ma, C.-H. Tung and L. Liu, Site- and Enantioselective Manganese-Catalyzed Benzylic C–H Azidation of Indolines, *J. Am. Chem. Soc*., 2022, **144**, 15383–15390.

[3] J. Rizzo, C. Alt and T. Zhang, An Expedient Synthesis of 3-Substituted Indoles via Reductive Alkylation with Ketones, *Tetrahedron Lett*., 2008, **49**, 6749–6751.

[4] M. DiPoto, R. Hughes and J. Wu, Dearomative Indole (3+2) Reactions with Azaoxyallyl Cations–New Method for the Synthesis of Pyrroloindolines, *J. Am. Chem. Soc*., 2015, **137**, 14861−14864.

[5] X. Jiang, W. Tang, D. Xue, J. Xiao and C. Wang, Divergent Dehydrogenative Coupling of Indolines with Alcohols, *ACS Catal*., 2017, **7**, 1831–1835.

[6] P. Wang, Z. Yang, Z. Wang, C. Xu, L. Huang, S. Wang, H. Zhang and A. Lei, Electrochemical Arylation of Electron-Deficient Arenes through Reductive Activation, *Angew. Chem*. *Int. Ed*., 2019, **58**, 15747–15751.