Platform for 3-Fluoro-3-Hydroxyoxindoles: Photocatalytic C-N Cross-Coupling and Deaminative Oxidation-Fluorohydroxylation

Letian Zhang,[a,b] Yibin Wang,[a,b] Jiabin Shen,[a] Hao Xu[a] and Chao Shen*[a]

[a] *Key Laboratory of Pollution Exposure and Health Intervention of Zhejiang Province, College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou 310015, China.*

[b] *College of Petroleum Chemical Industry, Changzhou University, Changzhou 213164, China.*

E-mail address: shenchaozju@163.com

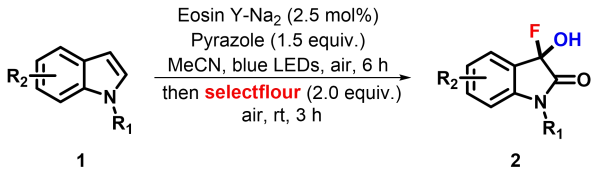
Supporting Information

1. General Informaton

All reagents were obtained commercially and used without any prior purification. All products were separated by silica gel (200-300 mesh) column chromatography with petroleum ether (PE) (60-90°C) and ethyl acetate (EA). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance 400 and 500 MHz spectrometer at ambient temperature with $CDCl_3$ or CD_3SOCD_3 solvent and tetramethylsilane (TMS) as the internal standard. Melting points were determined on an X-5 Data microscopic melting point apparatus. The small-angle X-ray diffraction (SAXRD) data was taken on a German Bruker D4 X-ray diffractometer. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. High-resolution mass spectra were recorded on a micromass ESI-TOF MS.

2. Experimental Section

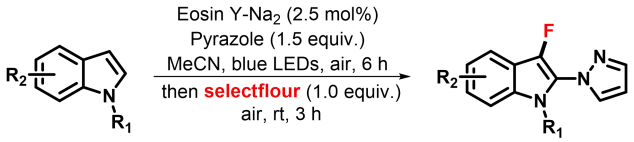
2.1 General produce for the synthesis of product 2



1 2

To a 15 mL tube was added indoles **1** (0.2 mmol, 1.0 equiv.), pyrazole (0.3 mmol, 1.5 equiv.), Eosin Y-Na_2 (2.5 mol%), and MeCN (2.0 mL). The mixture was stirred at room temperature under the irradiation of blue LEDs for 6 h; then, selectflour (0.4 mmol, 2.0 equiv.) was directly added to the reaction mixture and reacted at room temperature for another 3 h. After the completion (as indicated by TLC), the solvent was removed under reduced pressure, and the obtained residue was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 20:1) to provide the products **2**.

2.2 General produce for the synthesis of product 4a and 4b

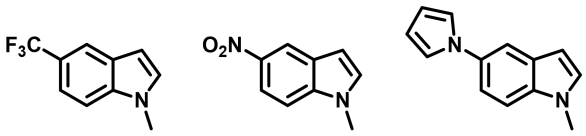


1

4a, R_1 = Bn, R_2 = H
4b, R_1 = Me, R_2 = 4-F

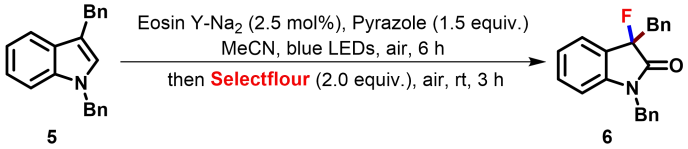
To a 15 mL tube was added indoles **1** (0.2 mmol, 1.0 equiv.), pyrazole (0.3 mmol, 1.5 equiv.), Eosin Y-Na_2 (2.5 mol%), and MeCN (2.0 mL). The mixture was stirred at room temperature under the irradiation of blue LEDs for 6 h; then, selectflour (0.2 mmol, 1.0 equiv.) was added in portions to the reaction mixture and reacted at room temperature for another 3 h. After the completion (as indicated by TLC), the solvent was removed under reduced pressure, and the obtained residue was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 15:1) to provide the product **4a** or **4b**.

2.3 Other unsuccessful substrates



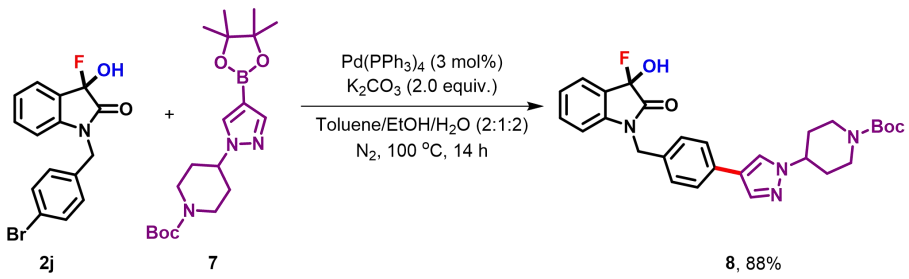
Indoles containing strong electron withdrawing groups such as CF_3 and NO_2 could not be smoothly converted into target products under standard conditions, and only trace amounts of target products could be detected. Therefore, no subsequent separation operation was carried out. When indole with 5-pyrrole motif was employed as a substrate, resulting in messy reaction system with no target product observed, which might due to the electron rich pyrrole motif reduce the reaction selectivity.

2.4 General produce for the synthesis of product 6



To a 15 mL tube was added indoles **4** (0.2 mmol, 1.0 equiv.), pyrazole (0.3 mmol, 1.5 equiv.), Eosin Y-Na_2 (2.5 mol%), and MeCN (2.0 mL). The mixture was stirred at room temperature under the irradiation of blue LEDs for 6 h; then, Selectflour (0.4 mmol, 2.0 equiv.) was directly added to the reaction mixture and reacted at room temperature for another 3 h. After the completion (as indicated by TLC), the solvent was removed under reduced pressure, and the obtained residue was further purified by silica gel column chromatography (200-300 mesh silica gel, PE/EA = 15:1) to provide the products **6**.

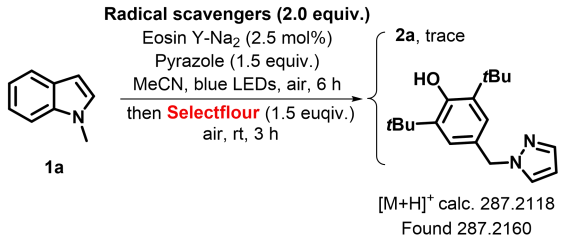
2.5 General produce for the synthesis of compound 8



To a 50 mL round-bottom flask with a nitrogen balloon was added **2j** (0.5 mmol), **6** (0.6 mmol), $Pd(PPh_3)_4$ (3 mol%), K_2CO_3 (1.0 mmol), and Tolune/EtOH/H_2O (2:1:2, 10 mL). The mixture was stirred at 100 °C under nitrogen for 16 h. After the completion (as indicated by TLC), the mixture

was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was evaporated to dryness under reduced pressure, and the crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc 2:1) to obtain the desired product **8**.

2.6 General produce for the radical trapping experiment



A solution of **1a** (0.2 mmol, 1.0 equiv.), pyrazole (0.3 mmol), Eosin Y-Na_2 (2.5 mol%), and radical scavengers (0.4 mmol) in MeCN (3.0 mL) was stirred at room temperature under the irradiation of blue LEDs for 6 h; then, Selectflour (0.3 mmol, 1.5 equiv.) was added slowly in portions to the reaction mixture and reacted at room temperature for another 3 h. The reaction mixture was detected by the LC-MS, and no target product **2a** was obtained in the presence of the radical scavengers including DPE (1,1-diphenylethylene) and BHT (2,6-ditert-butyl-4-methyl phenol), indicated that a radical pathway should be involved.

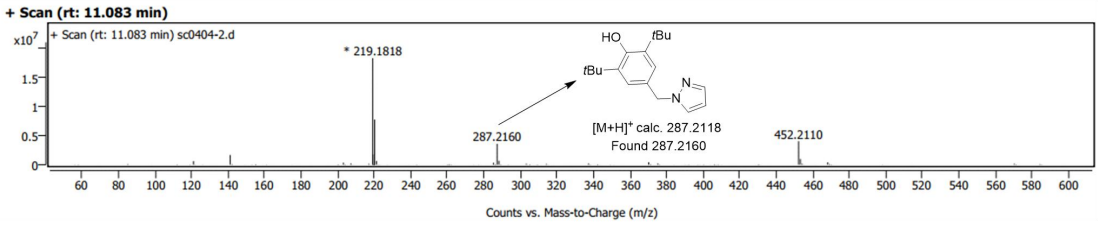
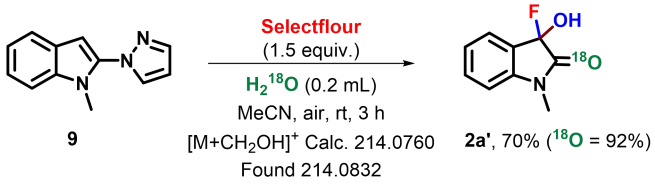


Figure S1. MS spectrum analysis of reaction in the presence of BHT.

2.7 ^{18}O Labeling Experiment

We have performed an $H_2{}^{18}O$ experiment under the standard condition (98% purity of $H_2{}^{18}O$ was filled in the reaction system). HRMS mass showed the formation of ^{18}O atom product. Thus, O-atom in the product is from the H_2O.



HRMS (ESI+) Calculated for $C_{10}H_{11}FN^{18}O_3$ $[M+CH_2OH]^+$: 214.0760, found: 214.0832.

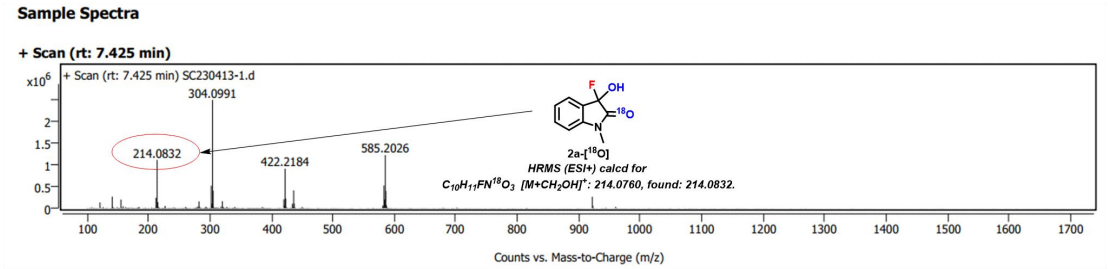


Figure S2. HRMS spectrum analysis of reaction in the presence of $H_2{}^{18}O$.

3. X-ray Structure and Data of 2a and 6

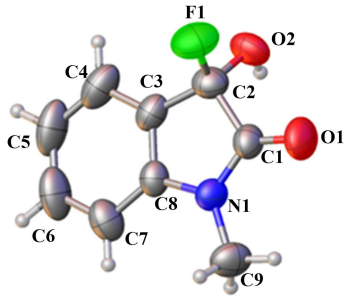


Figure S3. X-Ray crystal structure of **2a**

Table S1. Crystallographic data and structure refinement for **2a**

CCDC	2256847
Empirical formula	$C_9H_8FNO_2$
Formula weight	181.16
Temperature, K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a, b, c, Å	10.8781(12), 9.1314(10), 16.6641(18)
α, β, γ, °	90, 90.030(2), 90
Volume, Å^3	1655.3(3)
Z	8
Calculated density, g/cm^3	1.454
Absorption coefficient, mm^{-1}	0.118
F (000)	752.0
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection, °	3.744 to 55.234
Index ranges	-14 ≤ h ≤ 8, -10 ≤ k ≤ 11, -20 ≤ l ≤ 18
Reflections collected	9757
Independent reflections	3770 [R_{int} = 0.0828, R_{sigma} = 0.0645]
Data/restraints/parameters	3770/0/240
Goodness-of-fit on F^2	1.003
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1601
Final R indexes [all data]	R_1 = 0.0942, wR_2 = 0.1887

Compound was add to a 10 mL sample bottle, following to add DCM (2 mL) and n-hexane (6 mL), then seal the bottle with a parafilm, and poke 6 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXD-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

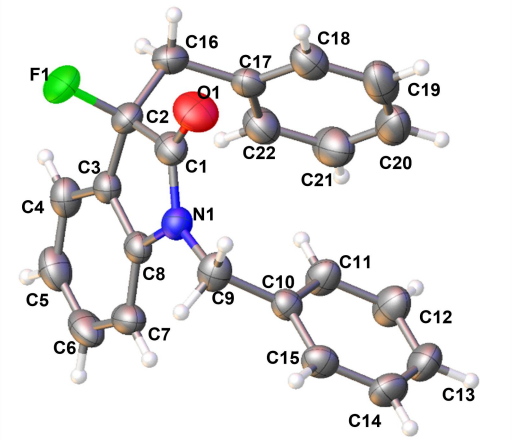


Figure S4. X-Ray crystal structure of **6**

Table S2. Crystallographic data and structure refinement for **6**

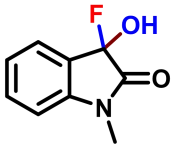
CCDC	2267747
Empirical formula	$C_{22}H_{18}FNO$
Formula weight	331.3904
Temperature, K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a, b, c, Å	8.3849(14), 9.8150(16), 11.0999(18)
α, β, γ, °	94.254(3), 101.852(3), 101.824(2)

Volume, $Å^3$	868.6(2)
Z	1
Calculated density, g/cm^3	1.267
Absorption coefficient, mm^{-1}	0.085
F (000)	348.00
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	5.096 to 55.074
Index ranges	$-8 \leq h \leq 10$, $-12 \leq k \leq 12$, $-14 \leq l \leq 10$
Reflections collected	5177
Independent reflections	3766 [R_{int} = 0.0210, R_{sigma} = 0.0303]
Data/restraints/parameters	3776/0/227
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1086
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1187

Compound was add to a 10 mL sample bottle, following to add DCM (2 mL) and n-hexane (6 mL), then seal the bottle with a parafilm, and poke 6 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXD-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

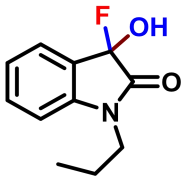
4. Characterization of the products

3-Fluoro-3-hydroxy-1-methylindolin-2-one (2a)



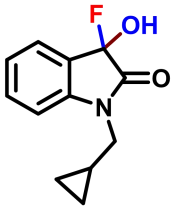
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 75 °C. (31.5 mg, 87% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.51 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 3.25 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.34 (t, *J* = 30.3 Hz), 144.00 (t, *J* = 7.0 Hz), 133.66, 124.68, 123.99, 120.15 (t, *J* = 23.0 Hz), 113.40, 110.92, 109.53, 108.45, 26.36; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.34; **HRMS** (ESI) *m/z*: $[M+CH_2OH]^+$ Calcd for $C_{10}H_{11}FNO_3$: 212.0717, Found 212.0726.

3-Fluoro-3-hydroxy-1-propylindolin-2-one (2b)



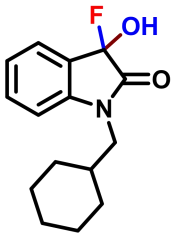
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 71 °C. (35.1 mg, 84% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (dt, *J* = 7.4, 1.7 Hz, 1H), 7.51 (ddd, *J* = 9.1, 7.3, 1.4 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 3.69 (t, *J* = 7.3 Hz, 2H), 1.76 (h, *J* = 7.4 Hz, 2H), 1.01 (td, *J* = 7.4, 1.1 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.39 (t, *J* = 30.0 Hz), 143.55 (t, *J* = 7.2 Hz), 133.55, 124.81, 123.73, 120.30 (t, *J* = 23.1 Hz), 113.38, 110.90, 109.80, 108.43, 41.82, 20.51, 11.24; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.35; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{12}FNO_2Na$: 232.0744, Found 232.0748.

1-(Cyclopropylmethyl)-3-fluoro-3-hydroxyindolin-2-one (2c)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 65 °C. (31.4 mg, 71% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.72 (dt, *J* = 7.5, 1.7 Hz, 1H), 7.63 (tt, *J* = 7.8, 1.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 3.62 (d, *J* = 7.1 Hz, 2H), 1.18 (tt, *J* = 7.7, 4.9 Hz, 1H), 0.59 – 0.46 (m, 2H), 0.41 – 0.29 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.94 (t, *J* = 29.8 Hz), 143.90 (t, J = 7.2 Hz), 134.81, 125.15, 124.36, 119.27 (t, *J* = 22.8 Hz), 114.05, 111.59, 111.54, 109.13, 44.54, 9.65, 3.98; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -111.06; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{12}FNO_2Na$: 244.0744, Found 244.0749.

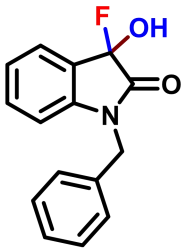
1-(Cyclohexylmethyl)-3-fluoro-3-hydroxyindolin-2-one (2d)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 60 °C. (33.2 mg, 63% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.69 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 3.55 (d, *J* = 7.3 Hz, 2H), 1.75 (dtd, *J* = 10.9, 7.5, 3.6 Hz, 1H), 1.68 – 1.55 (m, 5H), 1.20 – 1.08 (m, 3H), 0.98 (dp, *J* = 12.3, 4.5, 3.3 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.61 (t, *J* = 30.1 Hz), 143.95 (t, *J* = 7.1 Hz), 143.95, 143.88, 133.60, 124.64, 123.68, 120.11 (t, *J* = 23.0

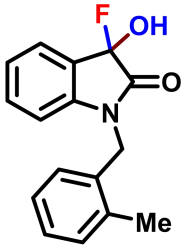
Hz), 113.41, 110.93, 110.17, 108.46, 46.47, 36.02, 30.77, 26.14, 25.64; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -110.06; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{18}FNO_2Na$: 286.1214, Found 286.1214.

1-Benzyl-3-fluoro-3-hydroxyindolin-2-one (2e)



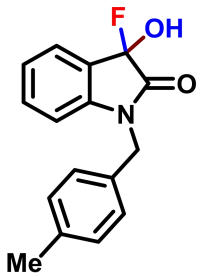
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:40 (v/v)) as a white solid. M.p. 80 °C. (41.7 mg, 81% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 1H), 7.45 – 7.29 (m, 6H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 4.93 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.56 (t, *J* = 30.5 Hz), 143.19 (t, *J* = 7.0 Hz), 134.36, 133.56, 129.11, 128.21, 127.34, 124.77, 124.01, 120.22 (t, *J* = 23.1 Hz), 113.50, 111.02, 110.62, 108.54, 44.03; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.64; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{13}FNO_2$: 258.0925, Found 258.0929.

3-Fluoro-3-hydroxy-1-(2-methylbenzyl)indolin-2-one (2f)



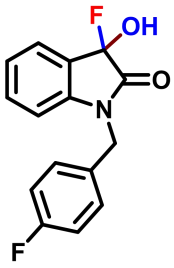
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:40 (v/v)) as a white solid. M.p. 79 °C. (43.4 mg, 80% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.25 – 7.10 (m, 4H), 6.72 (t, *J* = 6.2 Hz, 1H), 4.95 (s, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.48 (t, *J* = 30.4 Hz), 143.40 (t, *J* = 7.0 Hz), 135.89, 133.59, 131.73, 130.98, 128.06, 126.53 (d, *J* = 5.6 Hz), 124.74, 124.00, 120.21 (t, *J* = 23.1 Hz), 113.46, 110.98, 110.83, 108.50, 42.34, 19.31; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.56; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{14}FNO_2Na$: 294.0901, Found 294.0906.

3-Fluoro-3-hydroxy-1-(4-methylbenzyl)indolin-2-one (2g)



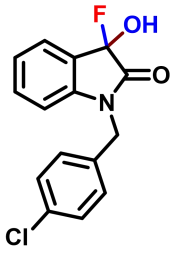
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 76 °C. (45.0 mg, 83% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.41 (td, *J* = 7.8, 1.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.83 (d, *J* = 7.9 Hz, 1H), 4.89 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.53 (t, *J* = 30.2 Hz), 143.25 (t, *J* = 7.1 Hz), 138.02, 133.55, 131.33, 129.77, 127.39, 124.71, 123.95, 120.23 (t, *J* = 23.1 Hz), 113.53, 111.05, 110.67, 108.57, 43.82, 21.15; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.75; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{14}FNO_2Na$: 294.0901, Found 294.0903.

3-Fluoro-1-(4-fluorobenzyl)-3-hydroxyindolin-2-one (2h)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:15 (v/v)) as a white solid. M.p. 102 °C. (41.3 mg, 75% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.33 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 16.9 Hz, 2H), 6.82 (d, *J* = 7.9 Hz, 1H), 4.90 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.51 (t, *J* = 30.5 Hz), 163.78, 161.32, 142.96 (t, *J* = 7.0 Hz), 133.55, 130.16 (d, *J* = 3.2 Hz), 129.17 (d, *J* = 8.3 Hz), 124.90, 124.12, 120.25 (t, *J* = 23.0 Hz), 116.09 (d, *J* = 21.7 Hz), 113.38, 110.90, 110.39, 108.42, 43.36; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.69, -113.63; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{11}F_2NO_2Na$: 298.0650, Found 298.0656.

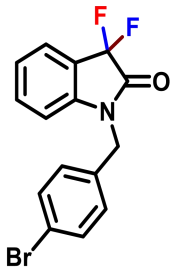
1-(4-Chlorobenzyl)-3-fluoro-3-hydroxyindolin-2-one (2i)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether =

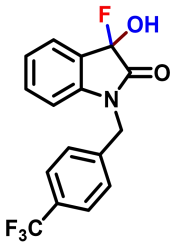
1:20 (v/v)) as a white solid. M.p. 89 °C. (46.1 mg, 79% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.48 (m, 1H), 7.40 (p, *J* = 6.5, 5.1 Hz, 1H), 7.35 – 7.24 (m, 3H), 7.15 (dp, *J* = 21.6, 7.5, 6.5 Hz, 2H), 6.83 – 6.66 (m, 1H), 4.96 – 4.69 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.52 (t, *J* = 30.1 Hz), 142.87 (t, *J* = 7.0 Hz), 134.18, 133.59, 132.87, 129.33, 128.75, 124.93, 124.19, 120.21 (t, *J* = 23.1 Hz), 113.37, 110.89, 110.40, 108.41, 43.41; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.60; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{11}ClFNO_2Na$: 314.0355, Found 314.0357.

1-(4-Bromobenzyl)-3-fluoro-3-hydroxyindolin-2-one (2j)



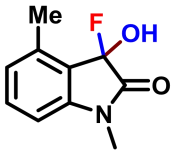
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a yellow solid. M.p. 82 °C. (55.1 mg, 82% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (dq, *J* = 7.5, 1.7 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.42 (td, *J* = 7.9, 1.4 Hz, 1H), 7.25 – 7.15 (m, 3H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.87 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.52 (t, *J* = 30.3 Hz), 142.83 (t, *J* = 7.1 Hz), 133.61, 133.38, 132.28, 129.05, 124.94, 124.21, 122.24, 120.18 (t, *J* = 23.2 Hz), 113.36, 110.88, 110.40, 108.40, 43.45; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.56; **HRMS** (ESI) *m/z*: $[M+MeCN+H]^+$ Calcd for $C_{17}H_{15}BrFN_2O_2$: 379.0275, Found 379.0279.

3-Fluoro-3-hydroxy-1-(4-(trifluoromethyl)benzyl)indolin-2-one (2k)



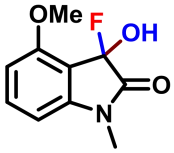
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 110 °C. (48.1 mg, 74% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.57 (m, 3H), 7.44 (dd, *J* = 12.1, 8.0 Hz, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.99 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.55 (t, *J* = 30.7 Hz), 142.81 (t, *J* = 6.9 Hz), 138.47, 133.61, 130.65 (q, *J* = 32.7 Hz), 127.58, 126.11 (q, *J* = 3.8 Hz), 125.25, 124.98, 124.26, 122.54, 120.27 (t, *J* = 23.2 Hz), 113.33, 110.84, 110.21, 108.36, 43.54; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.70, -111.50; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{11}F_4NO_2Na$: 348.0618, Found 348.0618.

3-Fluoro-3-hydroxy-1,4-dimethylindolin-2-one (2m)



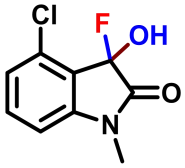
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:40 (v/v)) as a white solid. M.p. 76 °C. (32.8 mg, 84% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 3.50 (s, 3H), 2.59 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.17 (t, *J* = 29.7 Hz), 141.57 (t, *J* = 6.8 Hz), 137.27, 123.94, 123.92, 123.90, 122.46, 120.97 (t, *J* = 22.6 Hz), 120.74, 112.98, 110.53, 108.08, 29.71, 18.77; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.25; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{10}FNO_2Na$: 218.0588, Found 218.0589.

3-Fluoro-3-hydroxy-4-methoxy-1-methylindolin-2-one (2n)



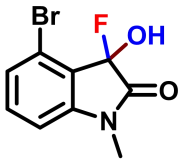
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 81 °C. (36.3 mg, 86% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.58 (td, *J* = 8.3, 7.4, 1.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.80 (dd, *J* = 7.8, 1.9 Hz, 1H), 3.91 (s, 3H), 3.16 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.97 (t, *J* = 30.1 Hz), 157.39, 145.80 (t, *J* = 6.7 Hz), 136.50, 114.43, 112.07, 109.62, 108.46, 105.30, 104.87 (t, *J* = 23.1 Hz), 56.44, 26.92; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -112.86; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{10}FNO_3Na$: 234.0537, Found 234.0538.

4-Chloro-3-fluoro-3-hydroxy-1-methylindolin-2-one (2o)



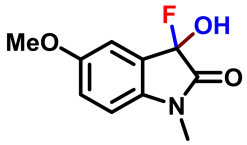
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 116 °C. (32.8 mg, 76% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 (t, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 3.24 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.60 (t, *J* = 30.3 Hz), 145.66 (t, *J* = 6.1 Hz), 134.63, 132.60, 124.96, 117.61 (t, *J* = 22.5 Hz), 112.98, 110.48, 107.98, 107.87, 26.56; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.96; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_7ClFNO_2Na$: 238.0042, Found 238.0046.

4-Bromo-3-fluoro-3-hydroxy-1-methylindolin-2-one (2p)



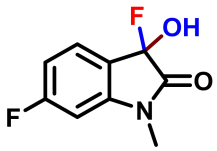
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:25 (v/v)) as a white solid. M.p. 105 °C. (38.0 mg, 73% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.54 (t, *J* = 30.1 Hz), 145.85 (t, *J* = 5.9 Hz), 134.69, 127.91, 120.18 (t, *J* = 23.2 Hz), 113.17, 110.66, 108.41, 108.16, 26.47; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.10; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_7BrFNO_2Na$: 281.9536, Found 281.9539.

3-Fluoro-3-hydroxy-5-methoxy-1-methylindolin-2-one (2q)



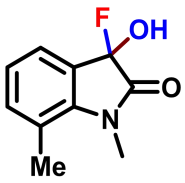
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 82 °C. (34.2 mg, 81% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (q, *J* = 2.0 Hz, 1H), 7.03 (ddt, *J* = 8.5, 2.5, 1.2 Hz, 1H), 6.84 (dt, *J* = 8.6, 1.5 Hz, 1H), 3.84 (s, 3H), 3.21 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.17 (t, *J* = 30.5 Hz), 156.78, 137.02 (t, *J* = 7.1 Hz), 120.96 (t, *J* = 22.9 Hz), 118.37, 113.61, 111.19, 111.12, 110.33, 108.63, 55.99, 26.39; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -112.88; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{10}FNO_3Na$: 234.0537, Found 234.0539.

3,6-Difluoro-3-hydroxy-1-methylindolin-2-one (2r)



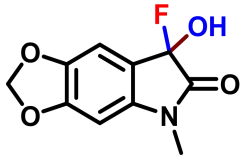
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:25 (v/v)) as a white solid. M.p. 116 °C. (23.3 mg, 64% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (ddt, *J* = 8.5, 5.2, 1.8 Hz, 1H), 6.88 (td, *J* = 8.7, 2.2 Hz, 1H), 6.68 (ddd, *J* = 8.5, 2.4, 1.2 Hz, 1H), 3.25 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.49, 165.44 (t, *J* = 29.6 Hz), 146.24 (t, *J* = 5.8 Hz), 126.61 (d, *J* = 10.6 Hz), 115.90 (t, *J* = 22.1 Hz), 112.78, 110.34 (d, *J* = 6.8 Hz), 110.14, 107.82, 98.74, 98.46, 26.43; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -102.65, -111.38; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_9H_7F_2NO_2Na$: 222.0337, Found 222.0339.

3-Fluoro-3-hydroxy-1,7-dimethylindolin-2-one (2s)



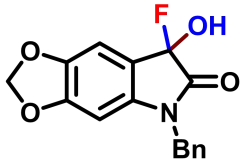
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 77 °C. (32.0 mg, 82% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.51 (d, J = 2.4 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.11 (dd, J = 8.1, 1.5 Hz, 1H), 3.16 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.75 (t, J = 30.1 Hz), 142.02 (t, J = 7.3 Hz), 134.74, 133.89, 125.27, 119.25 (t, J = 22.3 Hz), 114.27, 111.81, 110.91, 109.34, 26.77, 20.77; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -111.03; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{10}FNO_2Na$: 218.0588, Found 218.0589.

7-Fluoro-7-hydroxy-5-methyl-5,7-dihydro-6*H*-[1,3]dioxolo[4,5-f]indol-6-one (2t)



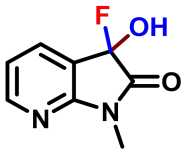
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 86 °C. (23.4 mg, 52% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 (t, J = 1.5 Hz, 1H), 6.50 (s, 1H), 6.06 (s, 2H), 3.20 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.95 (t, J = 30.3 Hz), 152.10, 144.41, 140.17 (t, J = 7.3 Hz), 113.85, 111.62 (t, J = 23.9 Hz), 108.92, 105.81, 102.32, 93.38, 26.67; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -110.60; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_8FNO_4Na$: 248.0330, Found 248.0335.

5-Benzyl-7-fluoro-7-hydroxy-5,7-dihydro-6*H*-[1,3]dioxolo[4,5-f]indol-6-one (2u)



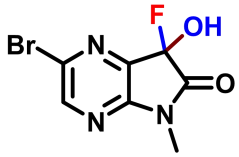
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:30 (v/v)) as a white solid. M.p. 92 °C. (29.5 mg, 49% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 5H), 7.03 (d, J = 2.1 Hz, 1H), 6.35 (s, 1H), 5.99 (s, 2H), 4.87 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.99 (t, J = 30.5 Hz), 151.72, 144.29, 139.04 (t, J = 7.8 Hz), 134.31, 129.16, 128.24, 127.23, 113.75, 111.51 (t, J = 24.1 Hz), 108.81, 105.54, 102.07, 94.24, 44.08; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -109.95; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{12}FNO_4Na$: 324.0643, Found 324.0646.

3-Fluoro-3-hydroxy-1-methyl-1,3-dihydro-2*H*-pyrrolo[2,3-b]pyridin-2-one (2v)



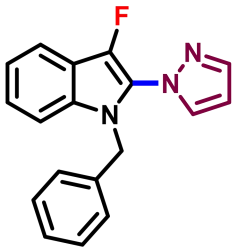
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 112 °C. (17.1 mg, 47% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.50 – 8.34 (m, 1H), 7.83 (dq, *J* = 7.3, 1.6 Hz, 1H), 7.13 (dd, *J* = 7.4, 5.3 Hz, 1H), 3.34 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.18 (t, *J* = 29.6 Hz), 157.23 (t, *J* = 6.8 Hz), 152.23, 132.58, 119.27, 115.05 (t, *J* = 23.2 Hz), 112.69, 110.19, 107.69, 25.35; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.23; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_8H_8FN_2O_2Na$: 205.0384, Found 205.0389.

2-Bromo-7-fluoro-7-hydroxy-5-methyl-5,7-dihydro-6*H*-pyrrolo[2,3-b]pyrazin-6-one (2w)



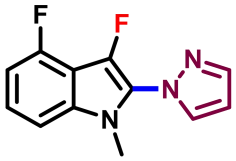
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a yellow solid. M.p. 131 °C. (23.5 mg, 45% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 3.35 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.86 (t, *J* = 29.0 Hz), 148.79, 146.90 (t, *J* = 6.0 Hz), 134.18, 106.75, 104.18, 25.48; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -119.80; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_7H_5BrFN_3O_2Na$: 283.9441, Found 283.9446.

1-Benzyl-3-fluoro-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4a)



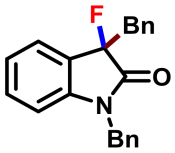
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:40 (v/v)) as a white solid. M.p. 136 °C. (10.0 mg, 17% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.20 (m, 4H), 7.00 (dd, *J* = 7.1, 2.5 Hz, 2H), 6.48 (t, *J* = 2.1 Hz, 1H), 5.33 (s, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.38, 137.94, 137.15, 135.46, 133.32, 130.60 (d, *J* = 5.5 Hz), 128.69, 127.56, 126.61, 124.06, 120.61, 119.08 (d, *J* = 19.6 Hz), 117.50 (d, *J* = 2.5 Hz), 115.67 (d, *J* = 14.5 Hz), 110.39, 107.31, 46.84; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -175.49; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{14}FN_3Na$: 314.1064, Found 314.1068.

3,4-Difluoro-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4b)



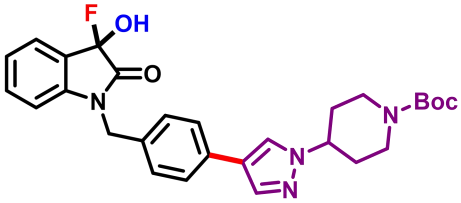
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 150 °C. (7.0 mg, 15% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.83 (t, *J* = 2.9 Hz, 1H), 7.33 – 7.08 (m, 2H), 6.98 – 6.84 (m, 1H), 6.59 (t, *J* = 2.2 Hz, 1H), 3.62 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.78, 155.29, 142.49, 138.18 (d, *J* = 9.2 Hz), 136.73, 133.46, 133.16, 124.03 (d, *J* = 8.1 Hz), 123.99, 116.90 (d, *J* = 17.3 Hz), 107.41, 107.14, 106.48, 106.31, 106.29, 106.27, 105.70, 30.83; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -125.53, -174.31; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_9F_2N_3Na$: 256.0657, Found 256.0658.

1,3-Dibenzyl-3-fluoroindolin-2-one (6)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 128 °C. (53.7 mg, 81% yield); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.0 Hz, 3H), 7.21 (s, 2H), 7.19 (s, 1H), 7.08 (d, *J* = 7.8 Hz, 3H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.52 (d, *J* = 7.9 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 4.53 (d, *J* = 15.8 Hz, 1H), 3.73 – 3.45 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.62 (d, *J* = 21.1 Hz), 143.37 (d, *J* = 5.4 Hz), 134.70, 132.40 (d, *J* = 9.9 Hz), 131.19 (d, *J* = 2.9 Hz), 130.79, 128.79, 128.38, 127.54, 127.33, 126.72, 125.39, 125.26, 125.20, 123.03 (d, *J* = 2.4 Hz), 109.84, 94.59, 92.70, 43.72, 41.19 (d, *J* = 28.7 Hz); **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -152.00; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{18}FNONa$: 354.1265, Found 354.1267.

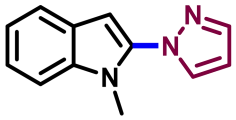
Tert-butyl 4-(4-(4-((3-fluoro-3-hydroxy-2-oxoindolin-1-yl)methyl)phenyl)-1*H*-pyrazol-1-yl) piperidine-1-carboxylate (8)



The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:3 (v/v)) as a white solid. M.p. 139 °C. (200.1 mg, 79% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.25 (s, 1H), 7.88 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 9.1 Hz, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.23 (q, *J* = 7.8 Hz, 2H), 4.95 (s, 2H), 4.37 (dq, *J* = 15.4, 4.0 Hz, 1H), 4.06 (d, *J* = 13.1 Hz, 2H), 2.93 (s, 2H), 2.09 – 1.95 (m, 2H), 1.82 (tt, *J* = 12.4, 6.3 Hz, 2H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.07 (t, *J* = 30.2 Hz), 154.33, 143.44 (t, *J* = 7.3 Hz), 136.33, 134.76, 133.05,

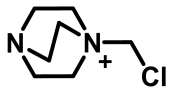
132.91, 128.45, 125.93, 125.72, 125.25, 124.64, 121.57, 119.33, 111.82, 79.35, 58.74, 43.43, 32.47, 28.58; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -111.65; **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{31}FN_4O_4Na$: 529.2222, Found 529.2226.

1-Methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole[1] (9)



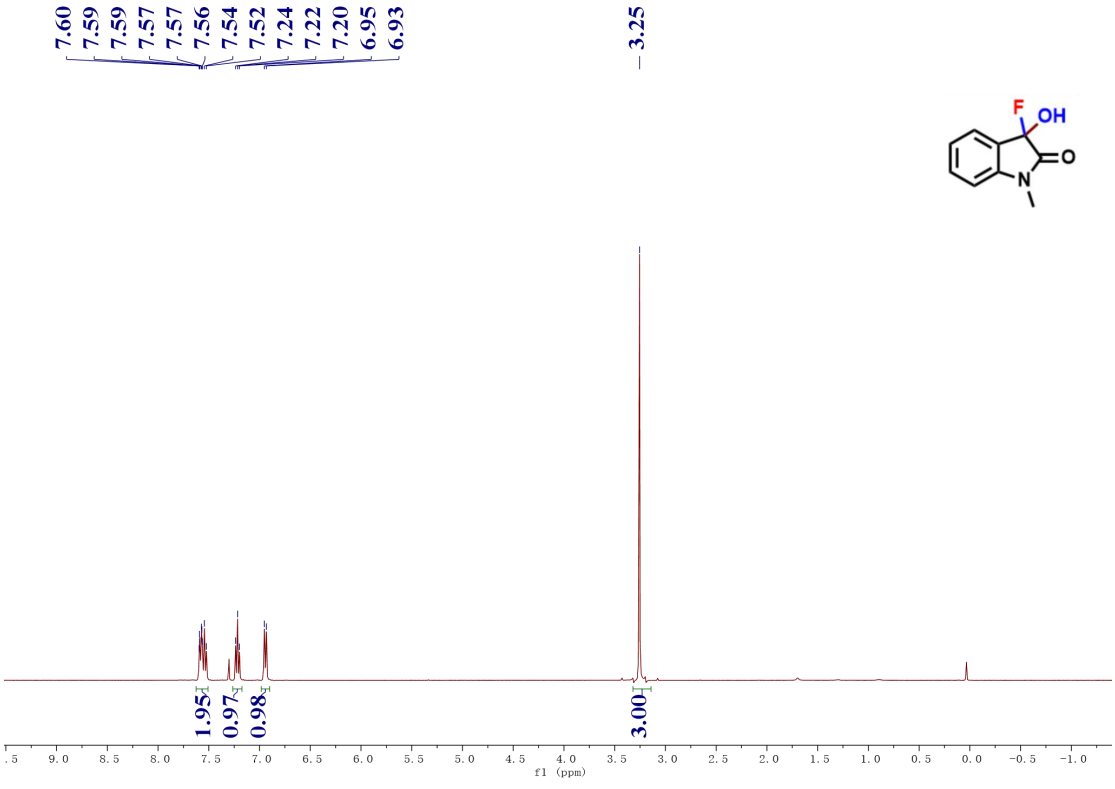
The product was obtained after purification by column chromatography (EtOAc/petroleum ether = 1:20 (v/v)) as a white solid. M.p. 59 °C. (35.1 mg, 89% yield); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.16 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 6.50 (s, 1H), 6.45 (t, *J* = 2.1 Hz, 1H), 3.65 (s, 3H); **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{11}N_3Na$: 220.0845, Found 220.0849.

1-(Chloromethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium (E)

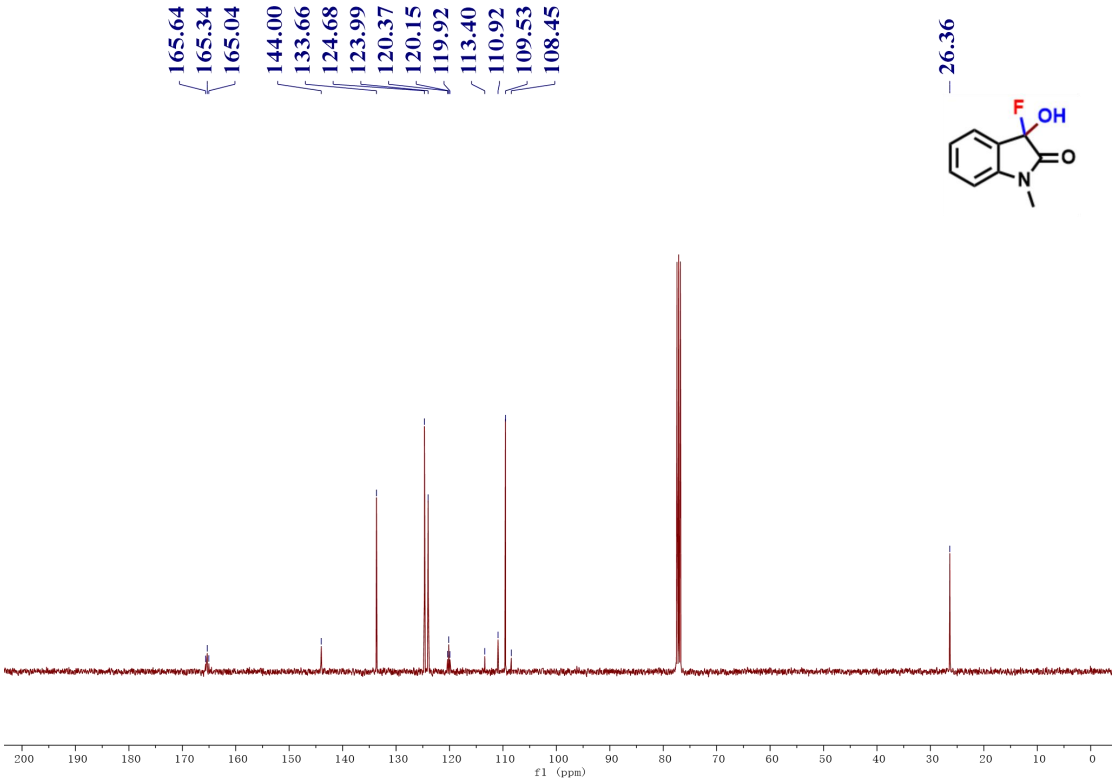


The product was obtained by recrystallization from acetonitrileas a yellow solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 5.34 (s, 2H), 3.49 (dd, *J* = 8.9, 6.2 Hz, 6H), 3.25 (dd, *J* = 8.9, 6.1 Hz, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 68.17, 50.99, 44.58.

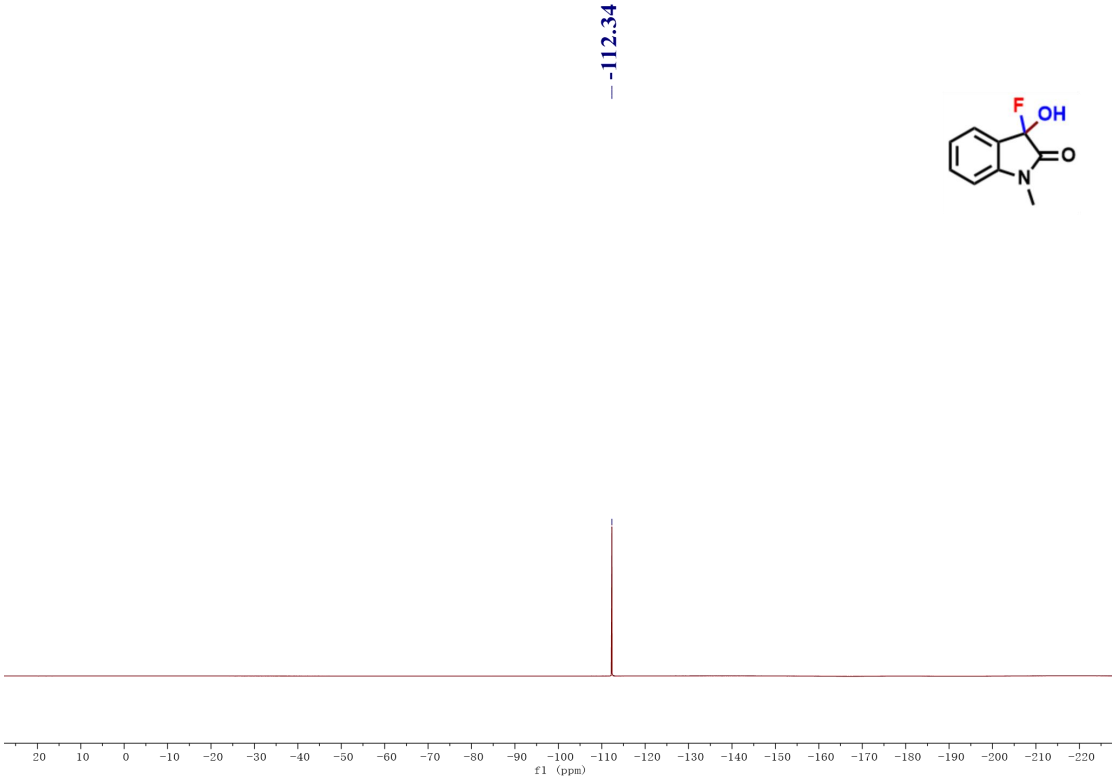
5. ^{1}H, ^{13}C, and ^{19}F NMR Spectra



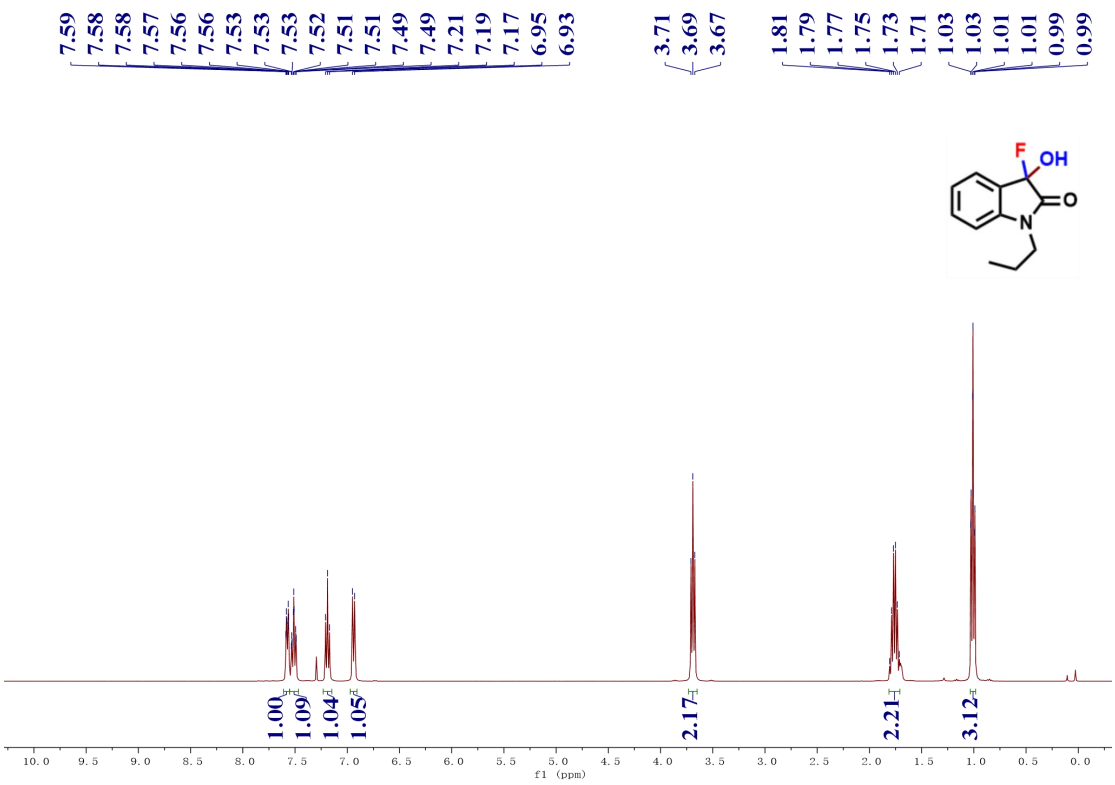
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2a**



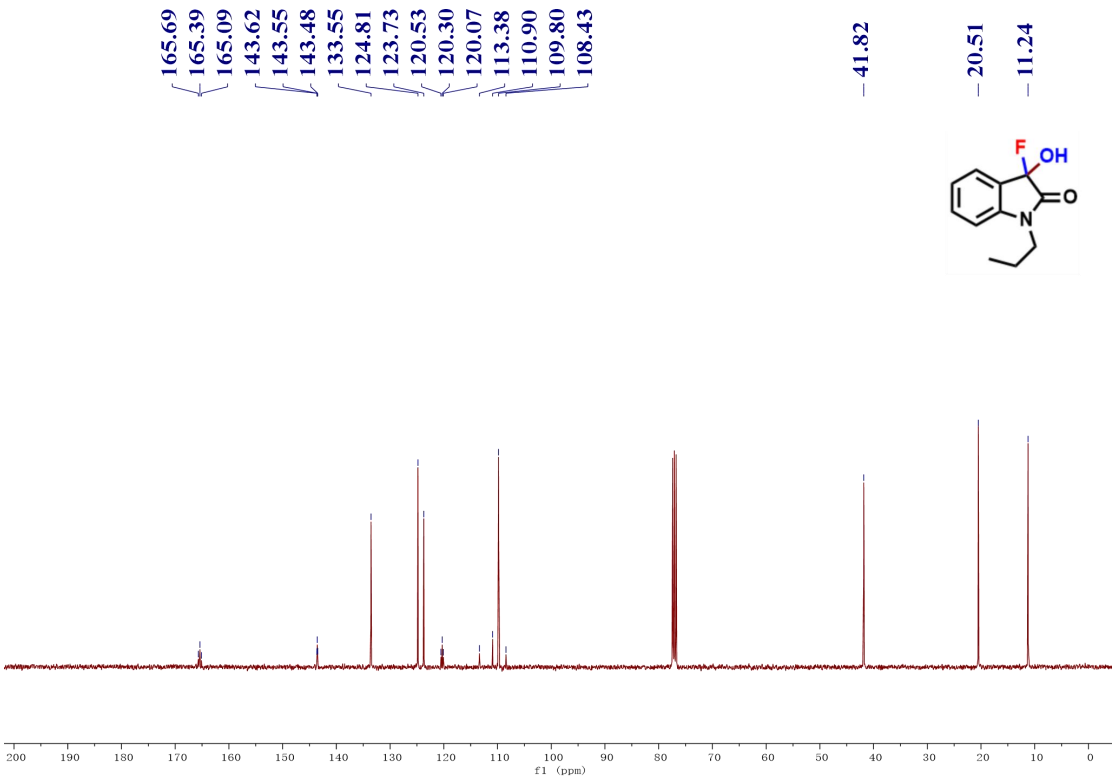
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2a**



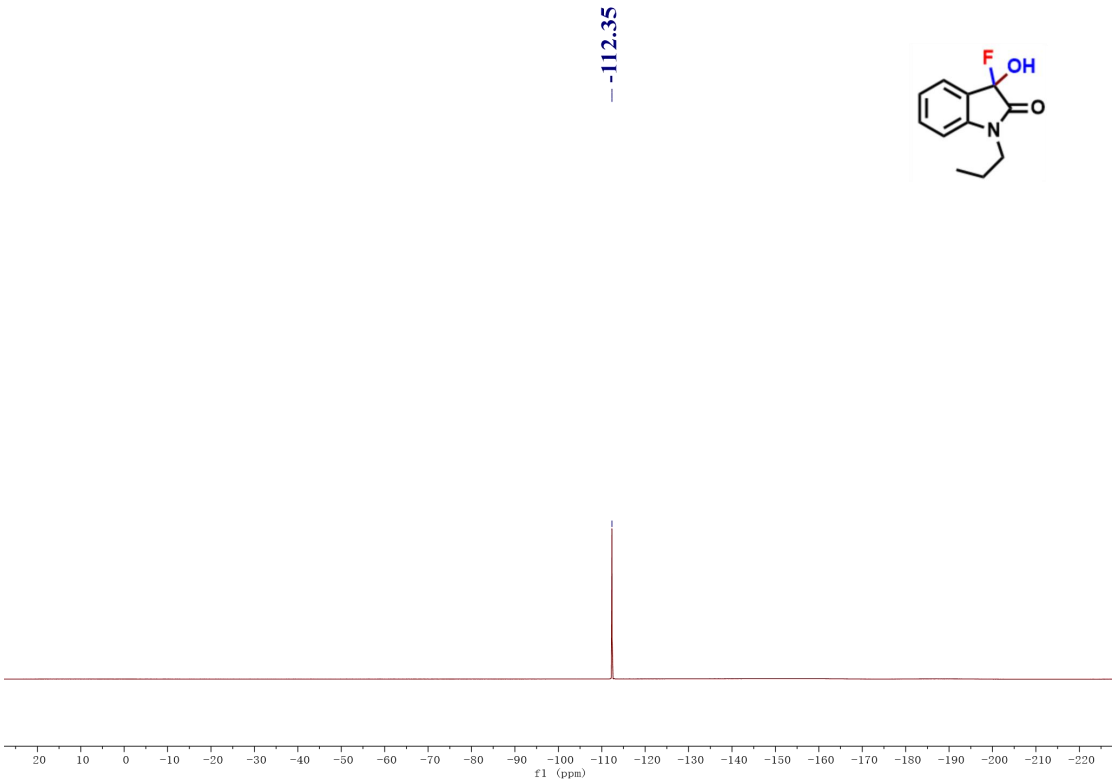
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2a**



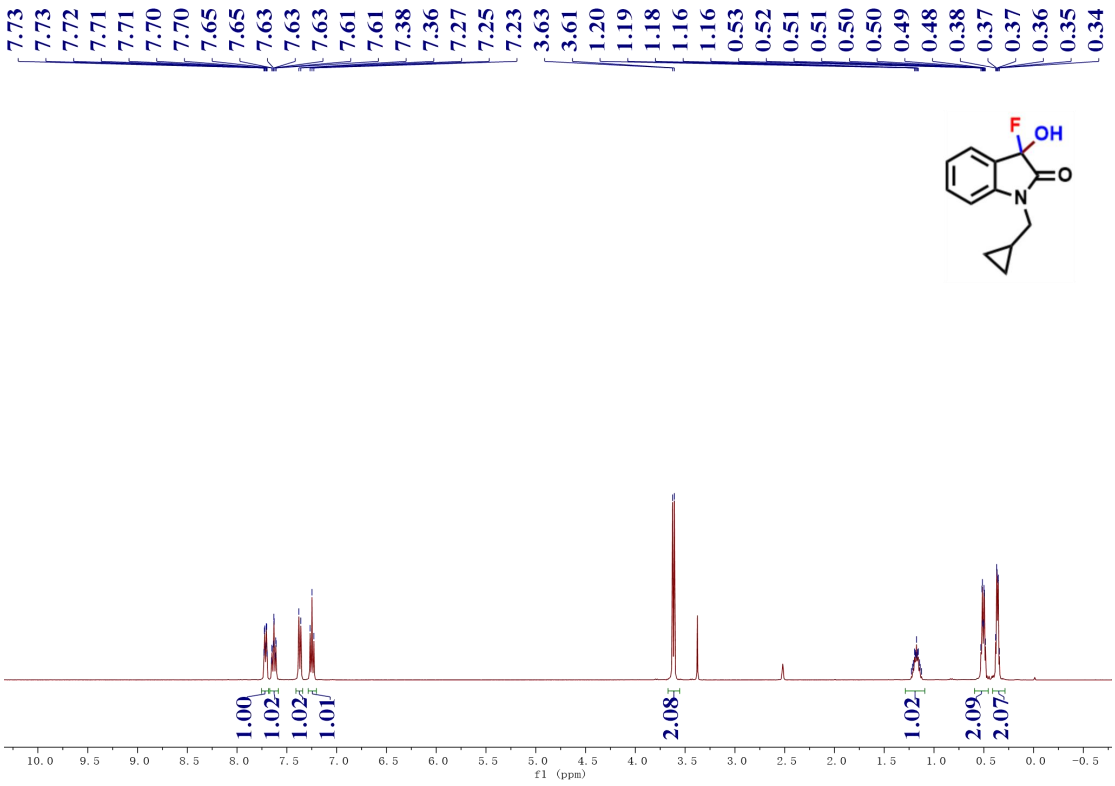
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2b**



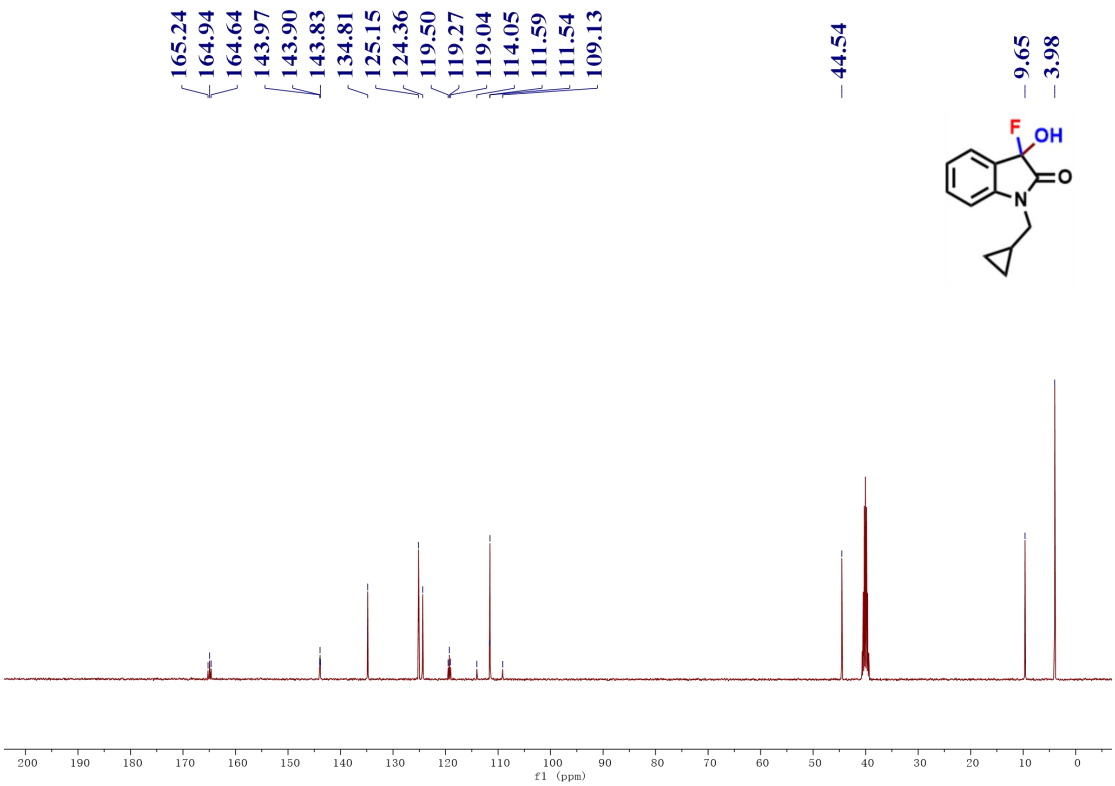
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2b**



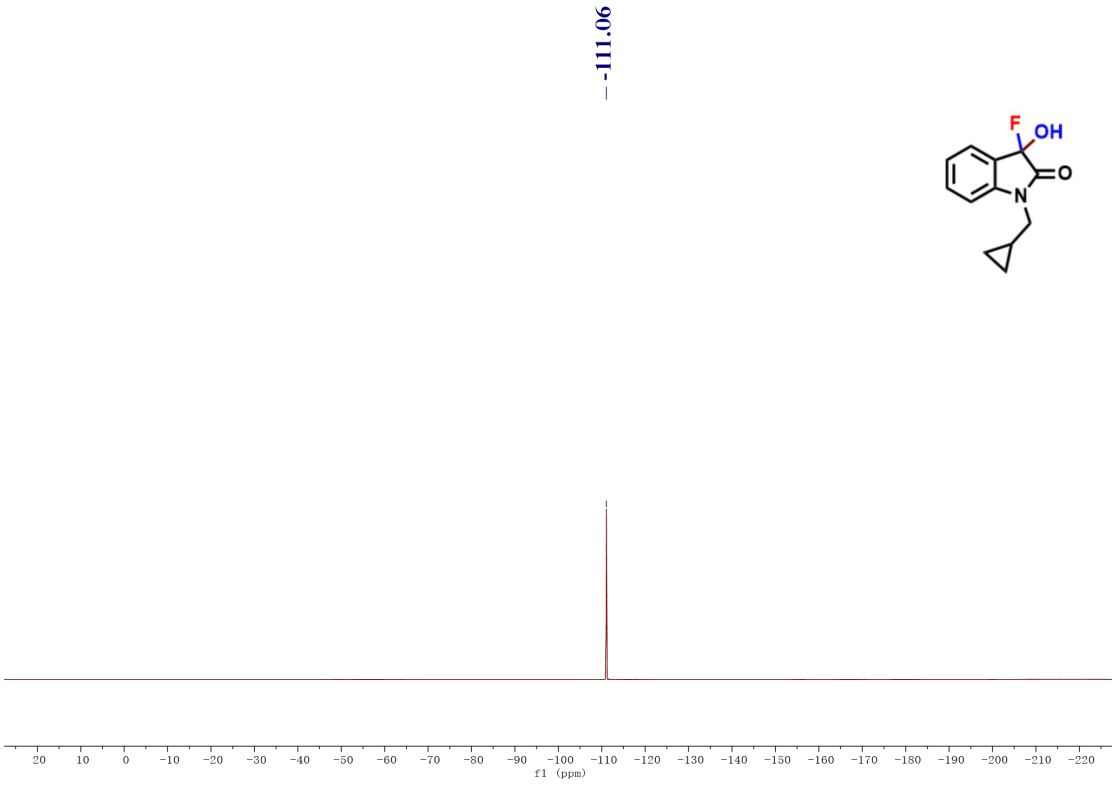
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2b**



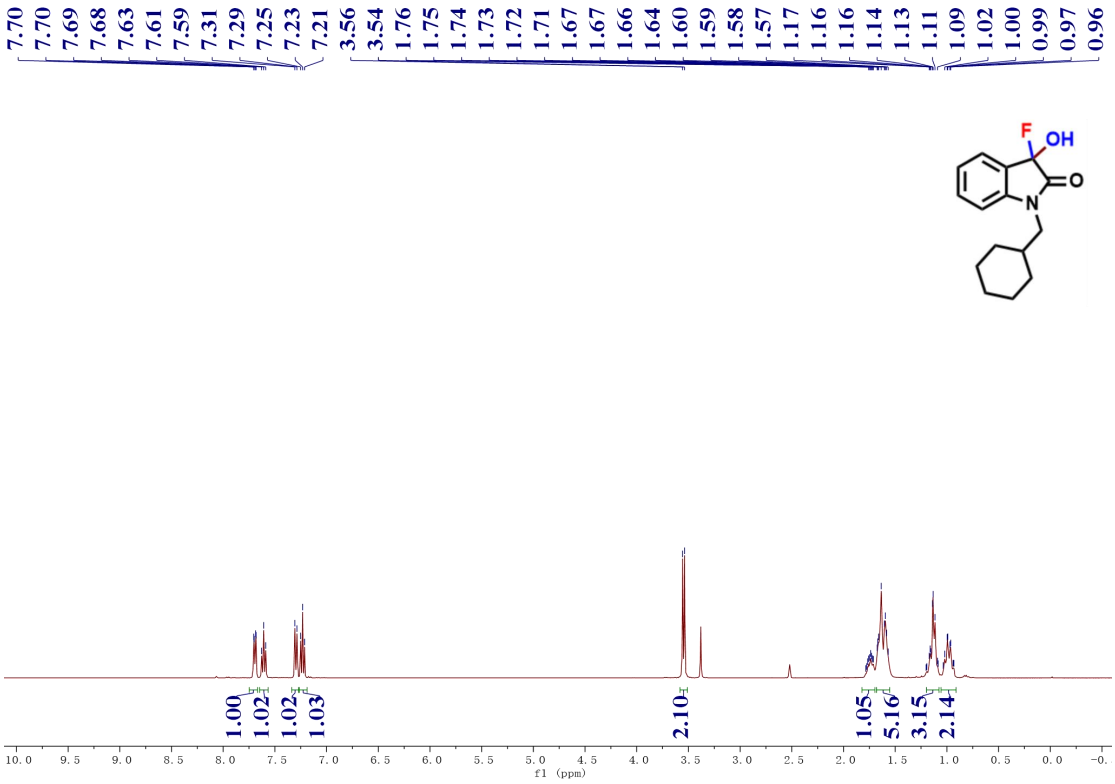
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2c**



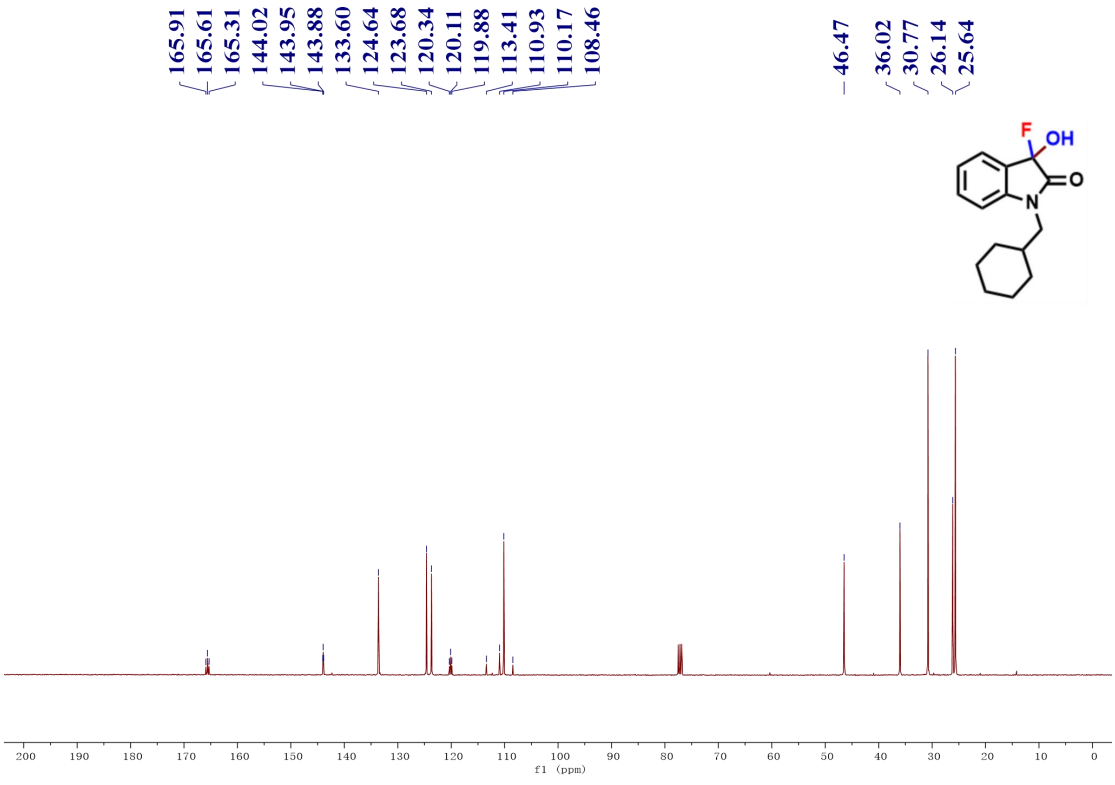
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2c**



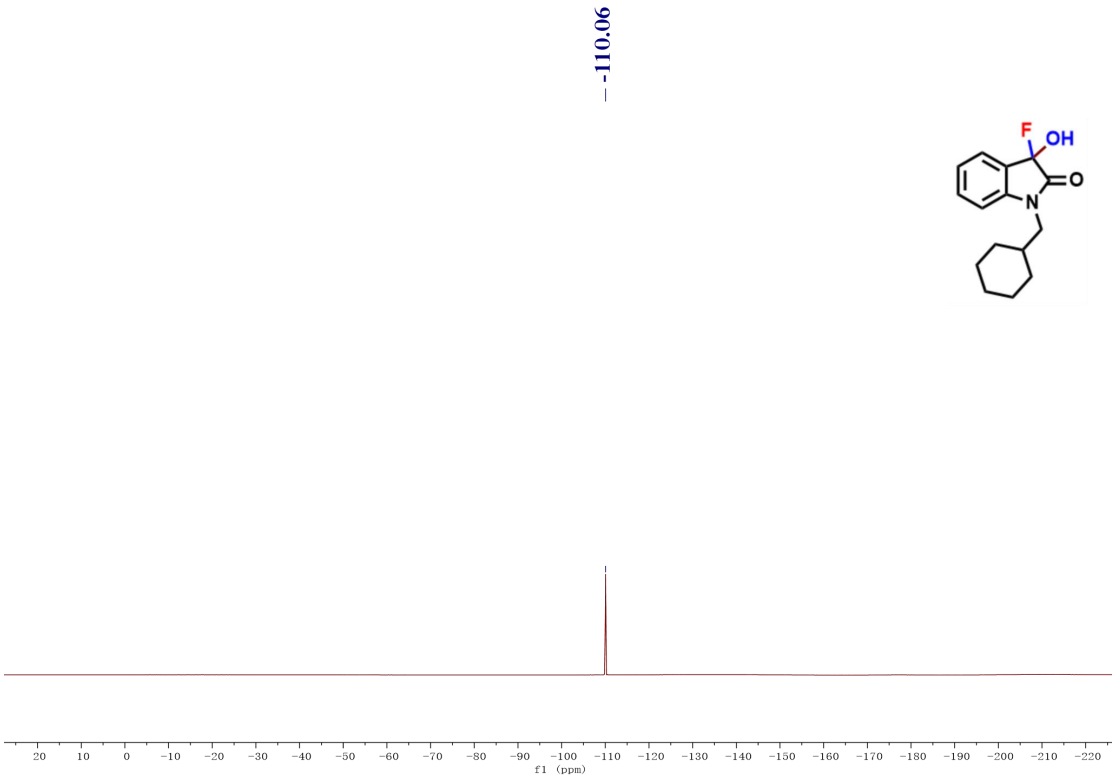
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of compound **2c**



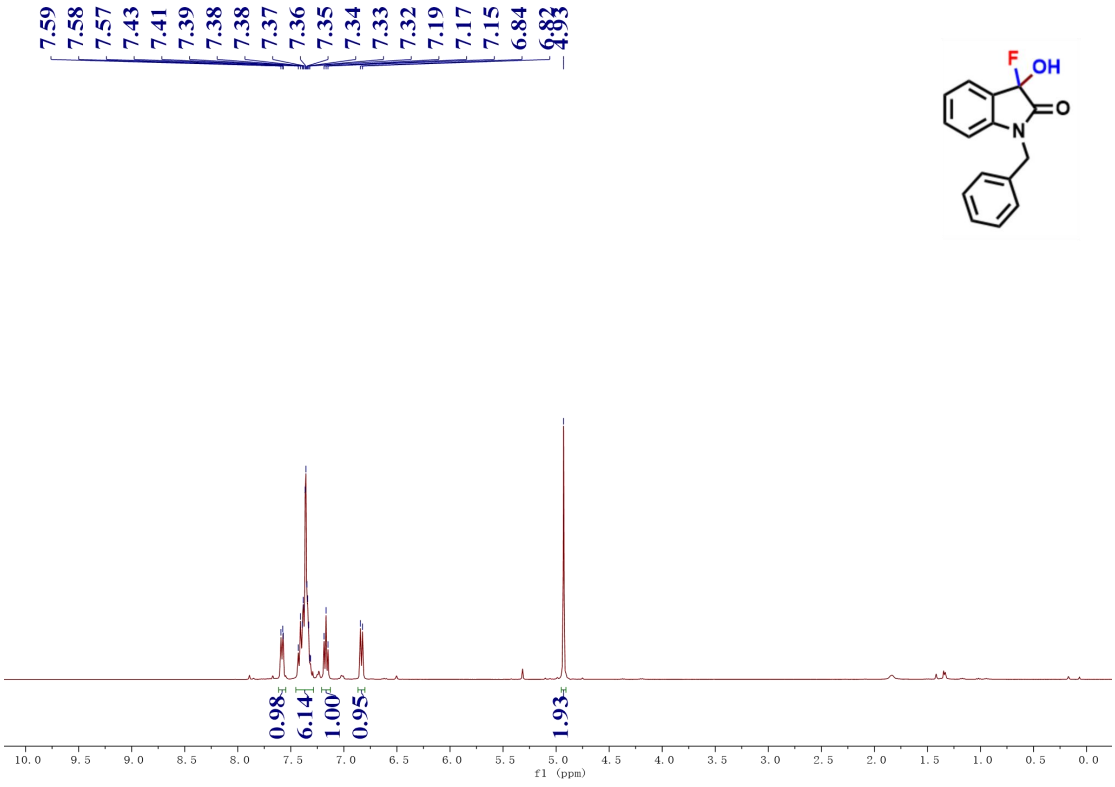
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2d**



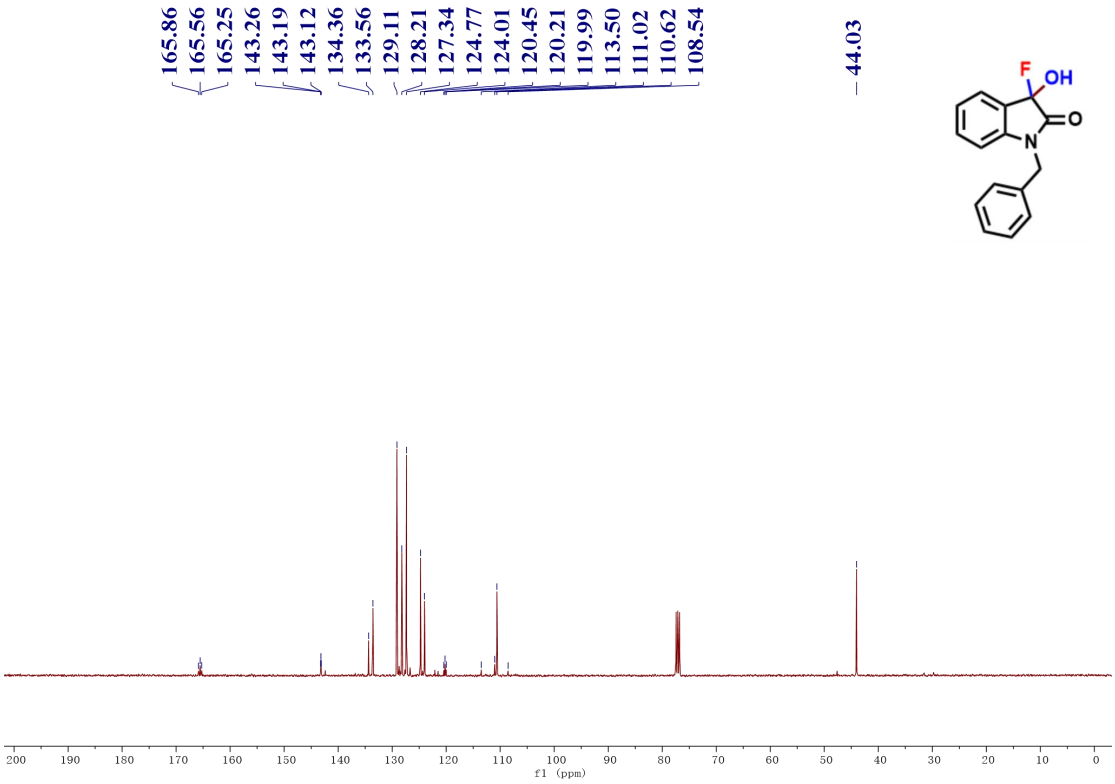
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2d**



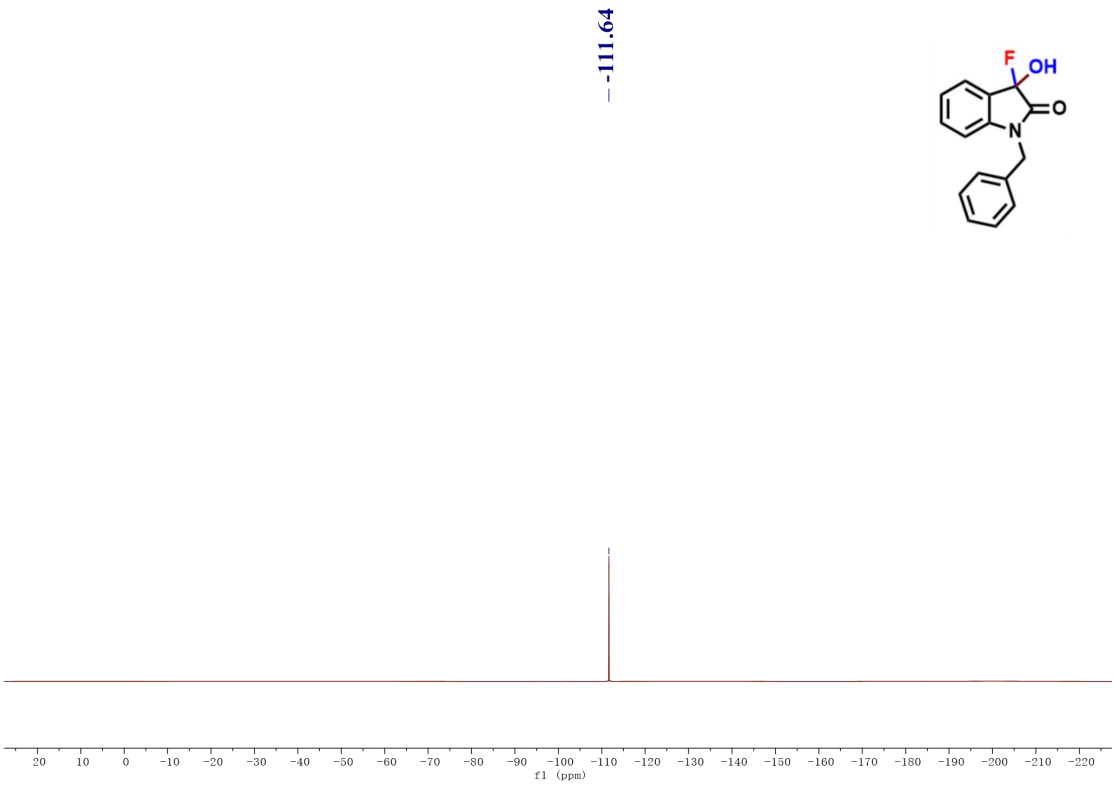
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2d**



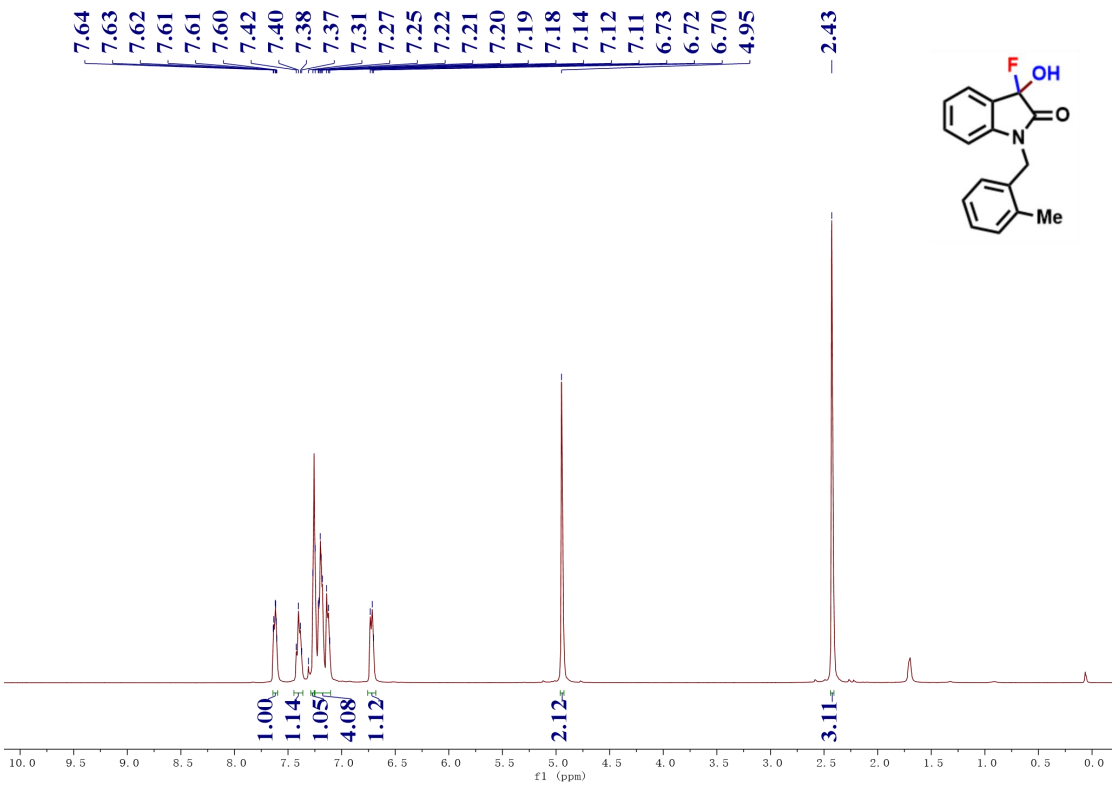
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2e**



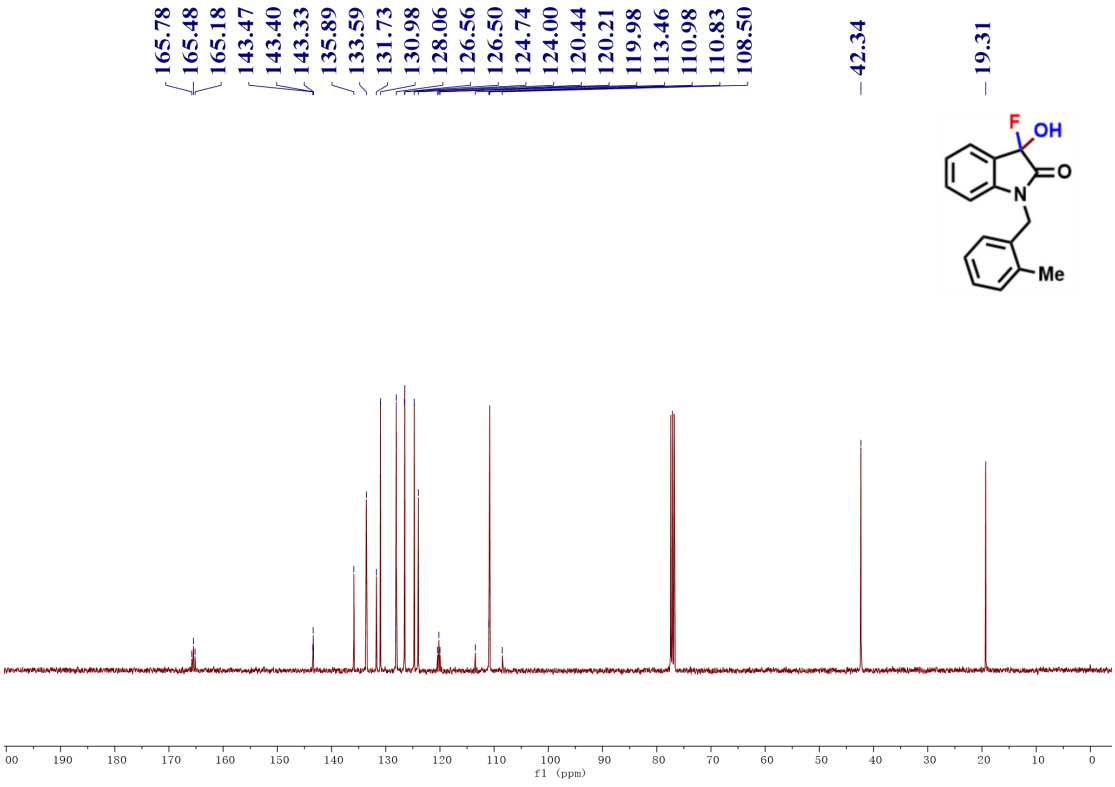
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2e**



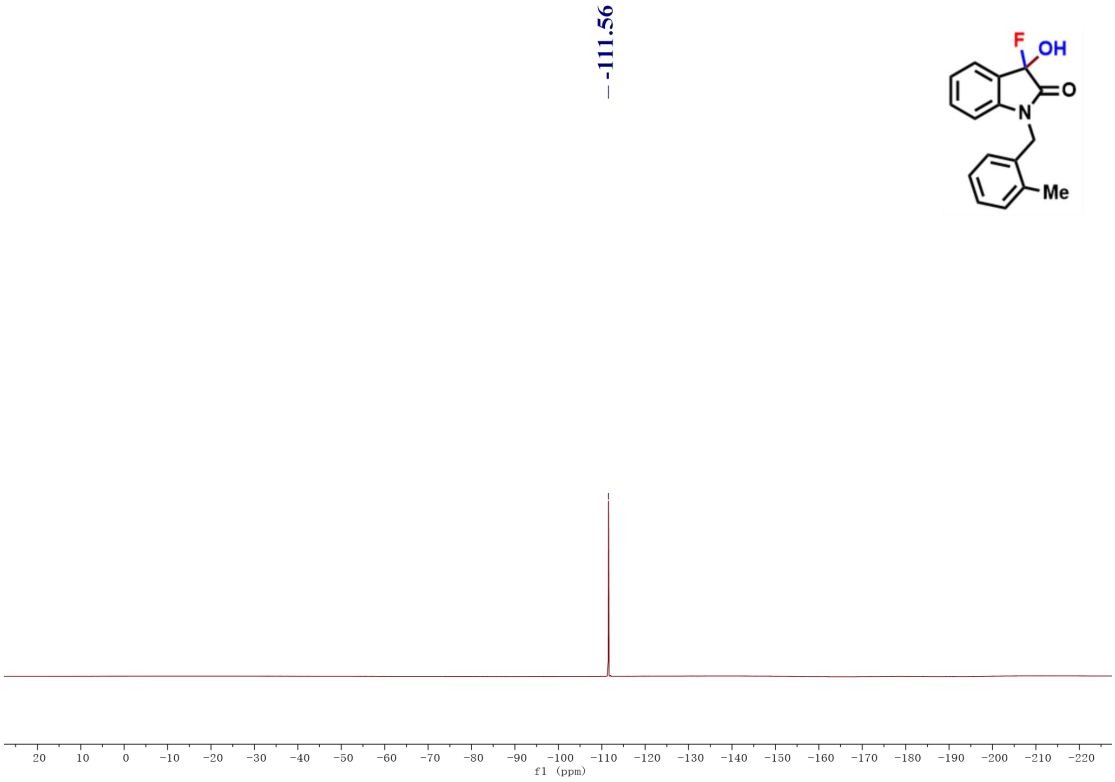
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2e**



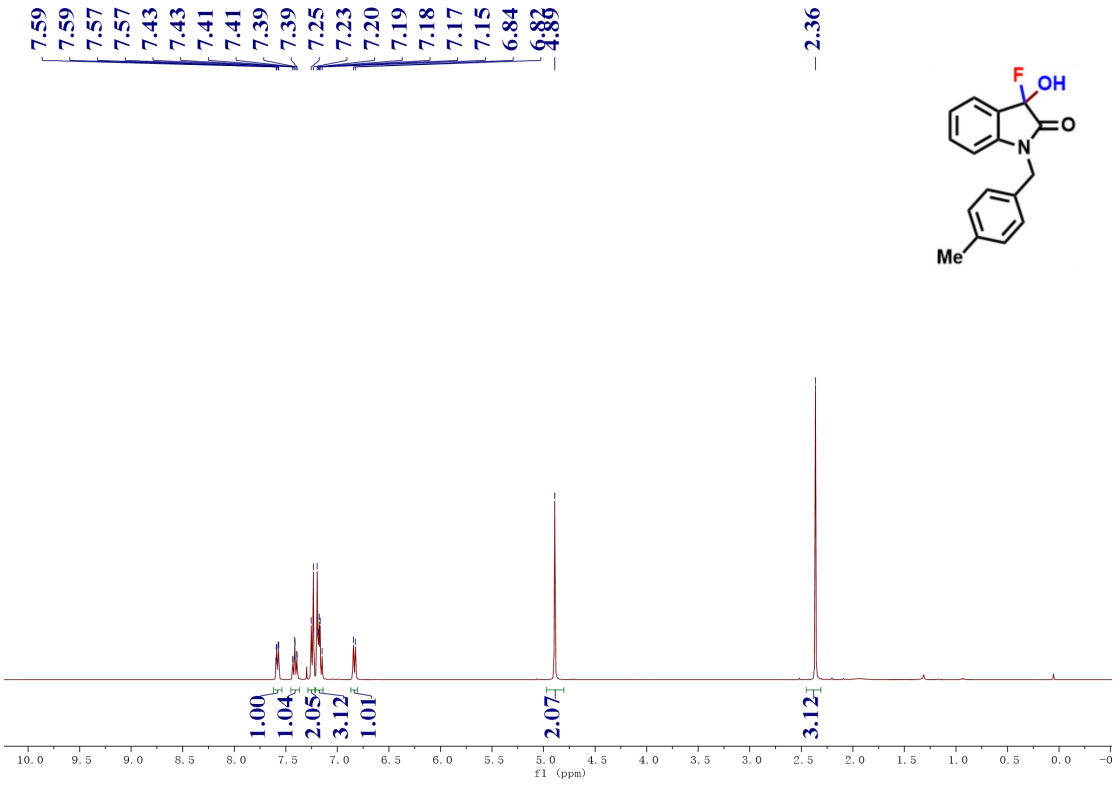
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2f**



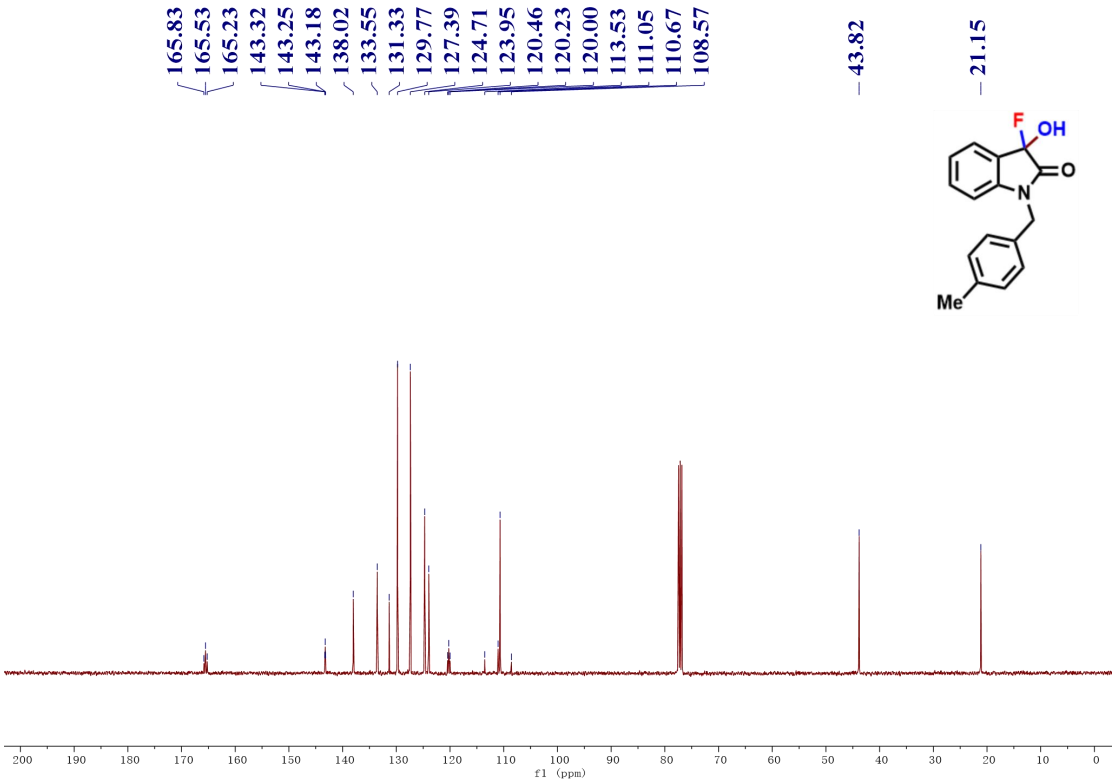
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2f**



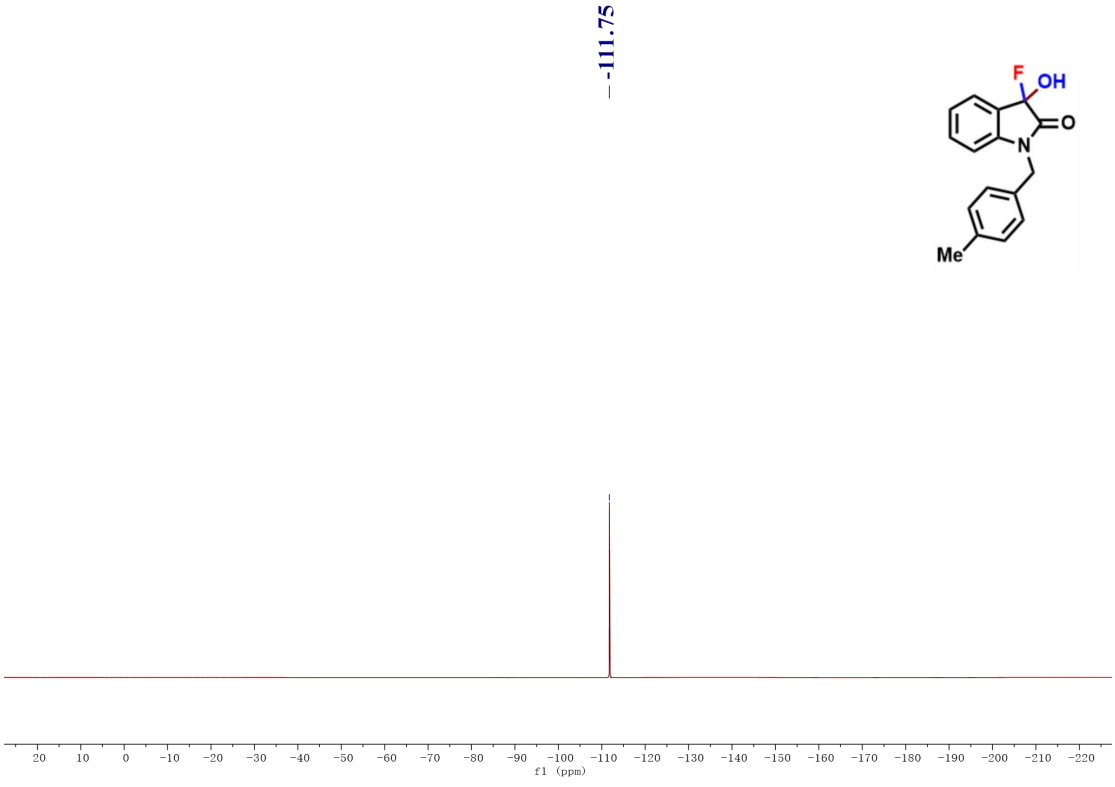
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2f**



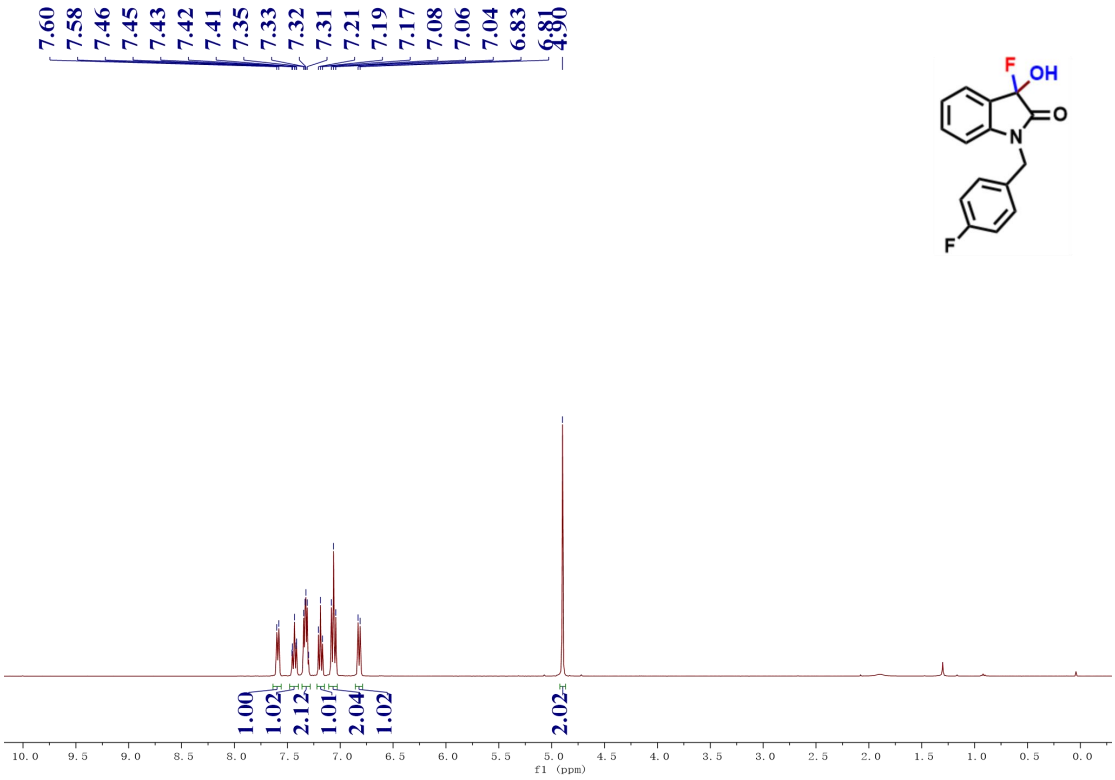
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2g**



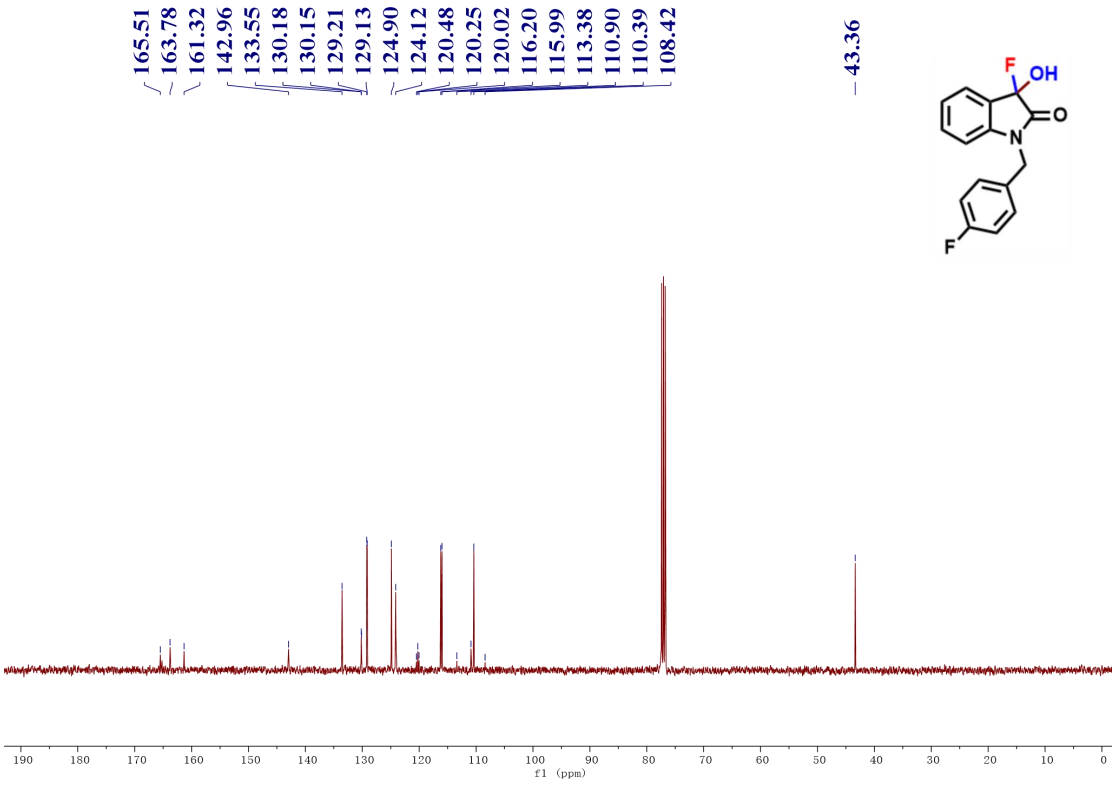
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2g**



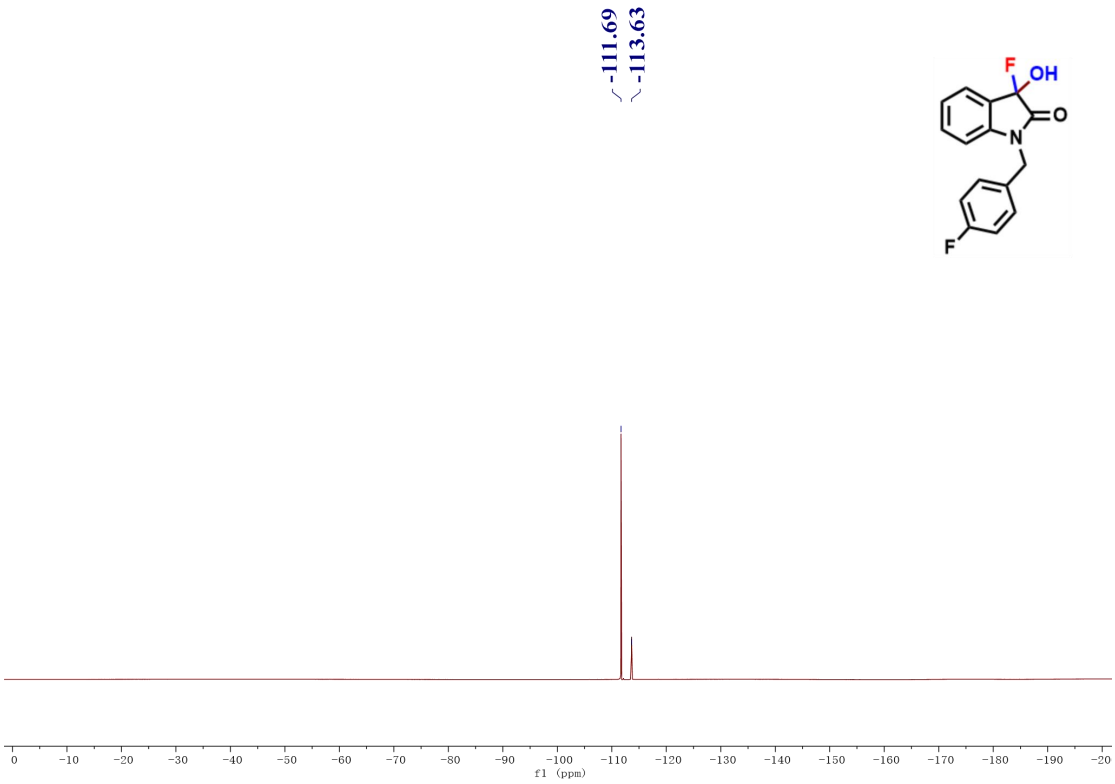
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2g**



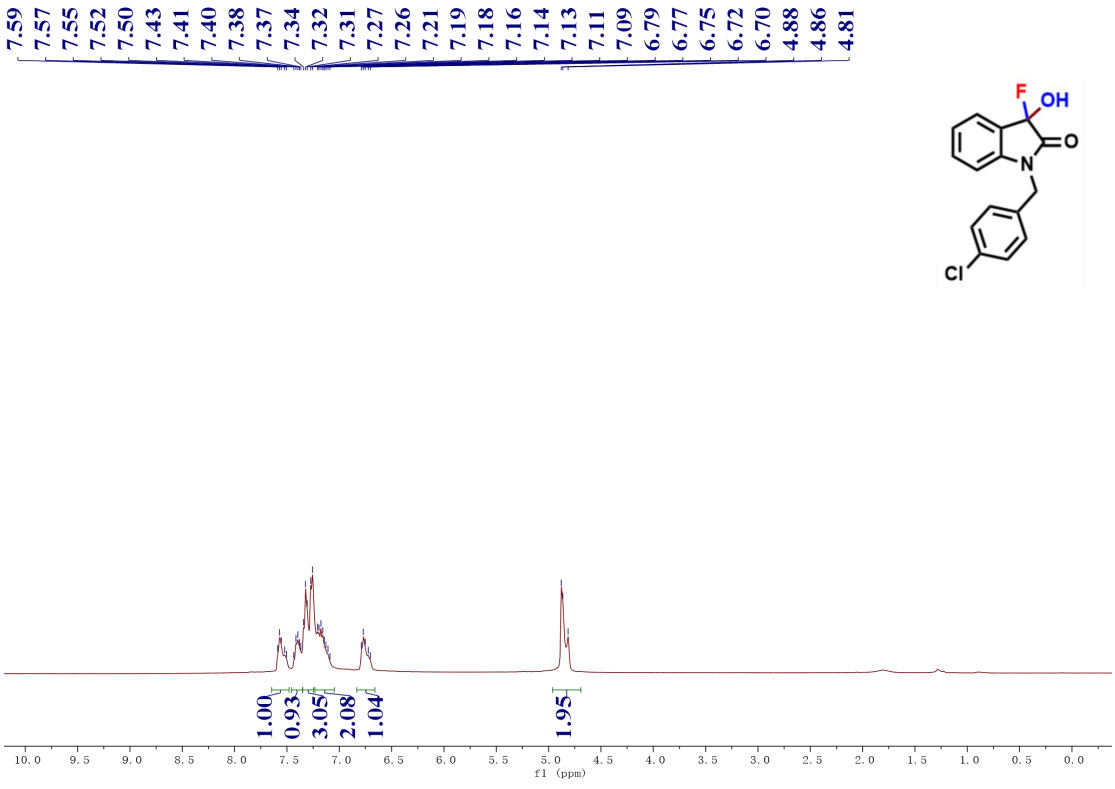
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2h**



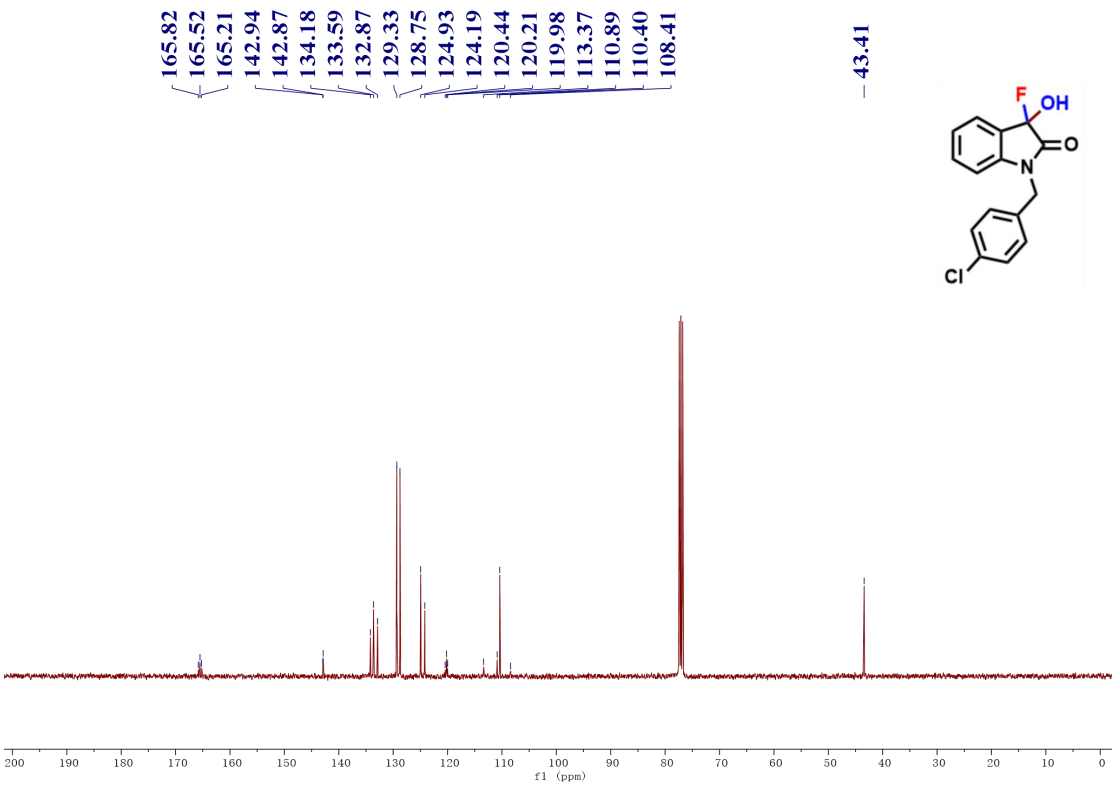
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2h**



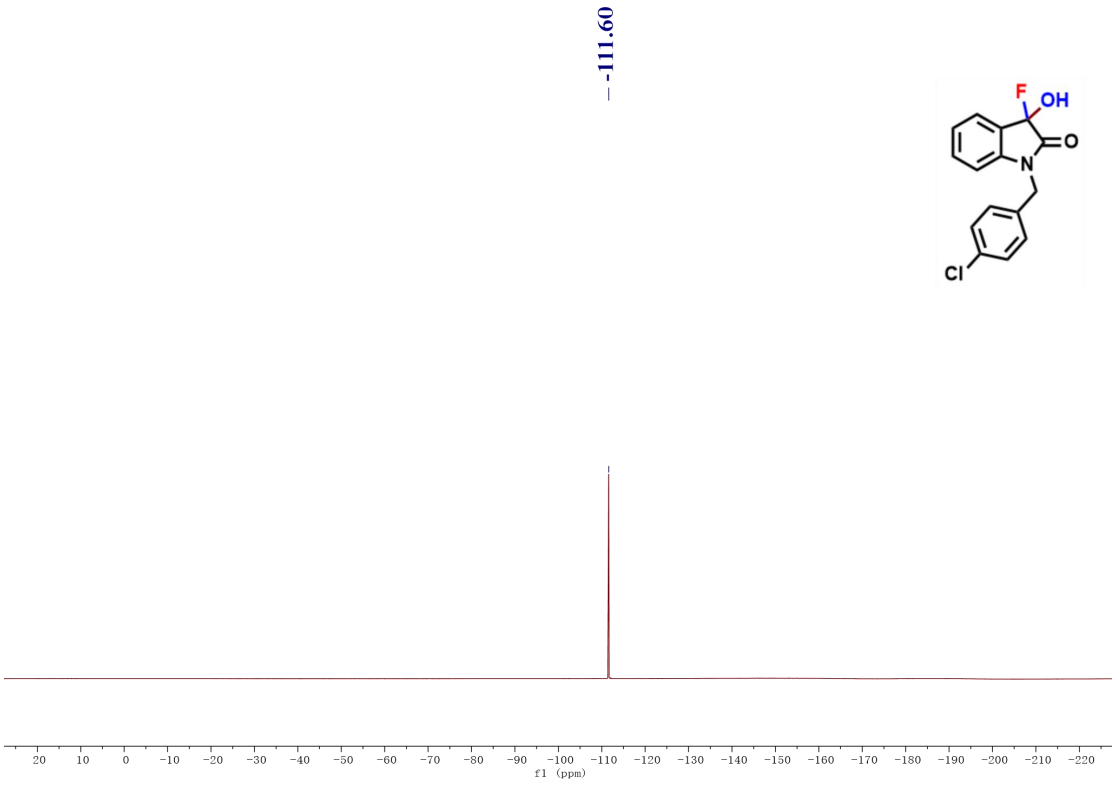
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2h**



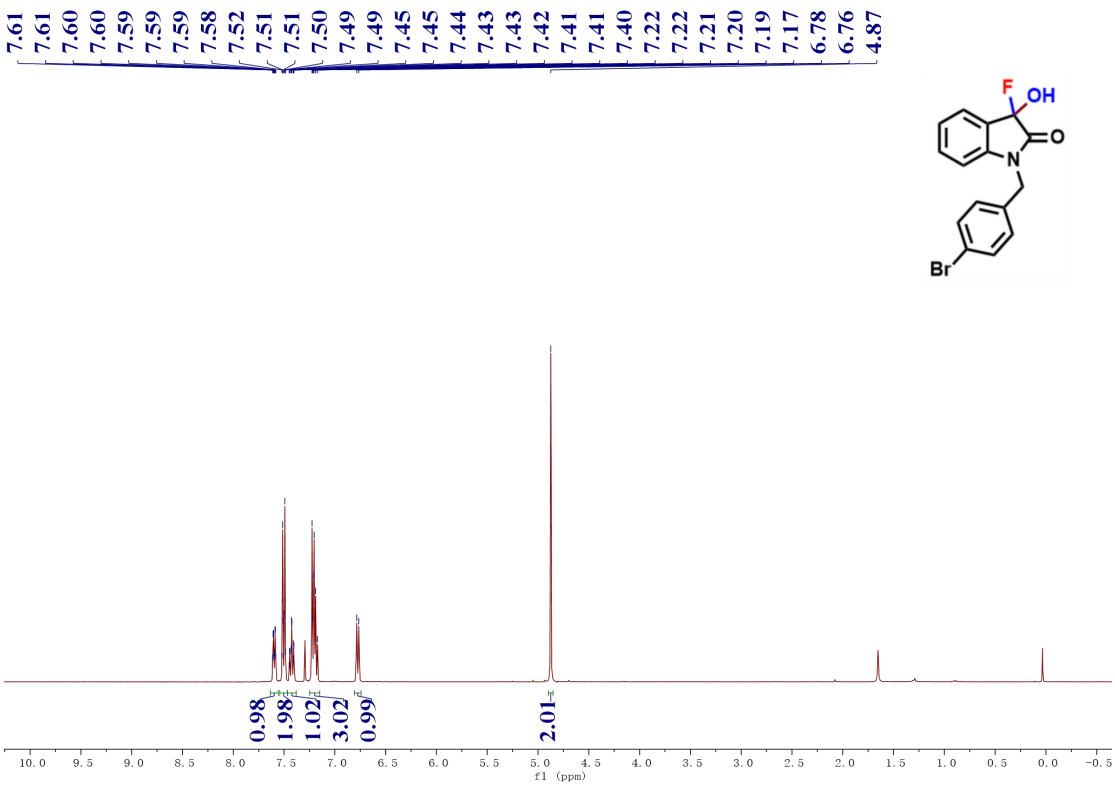
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2i**



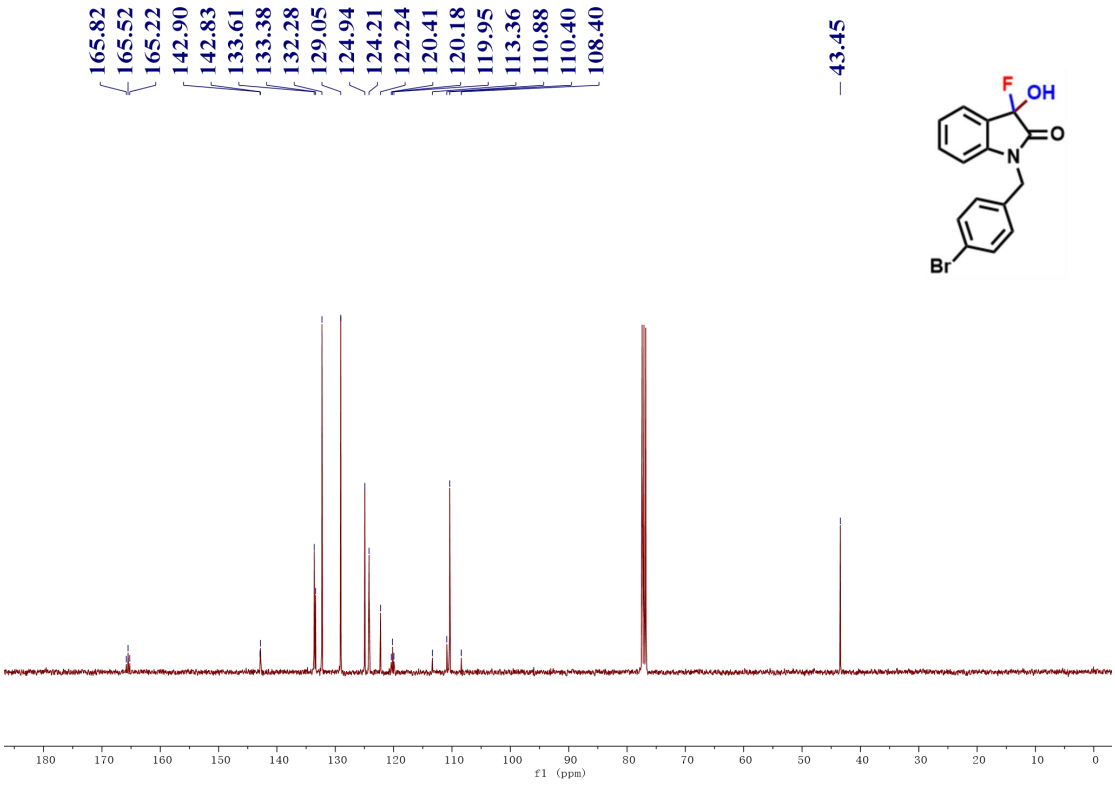
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2i**



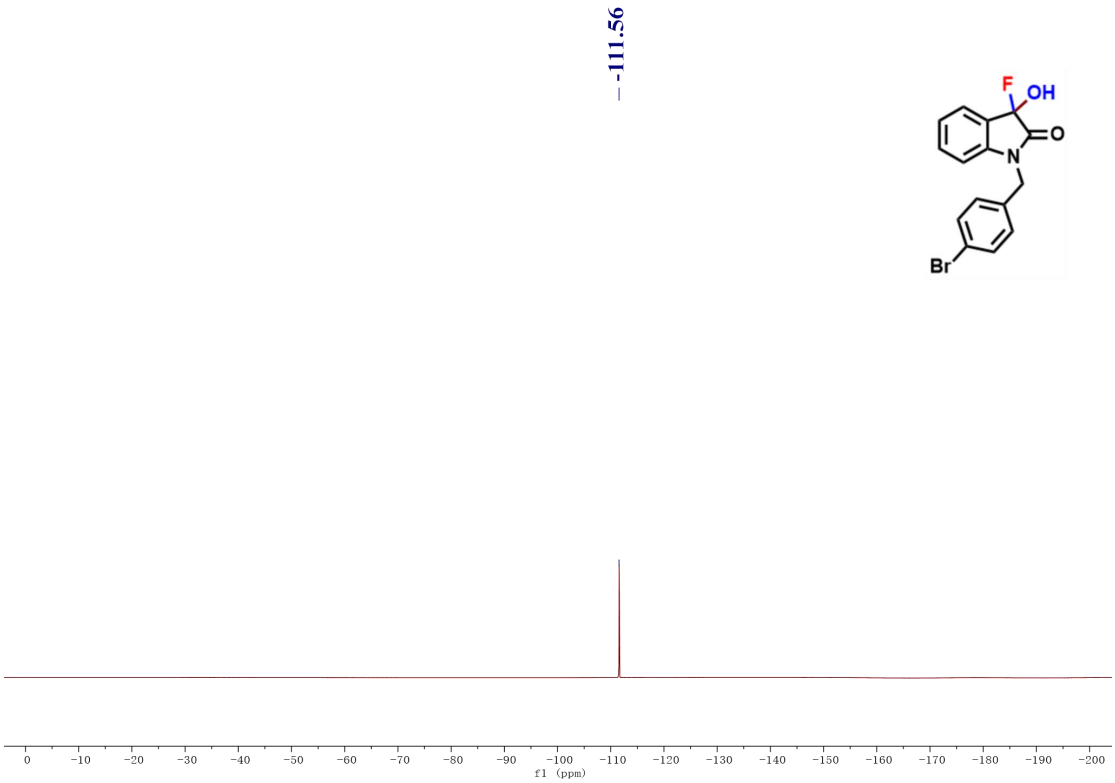
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2i**



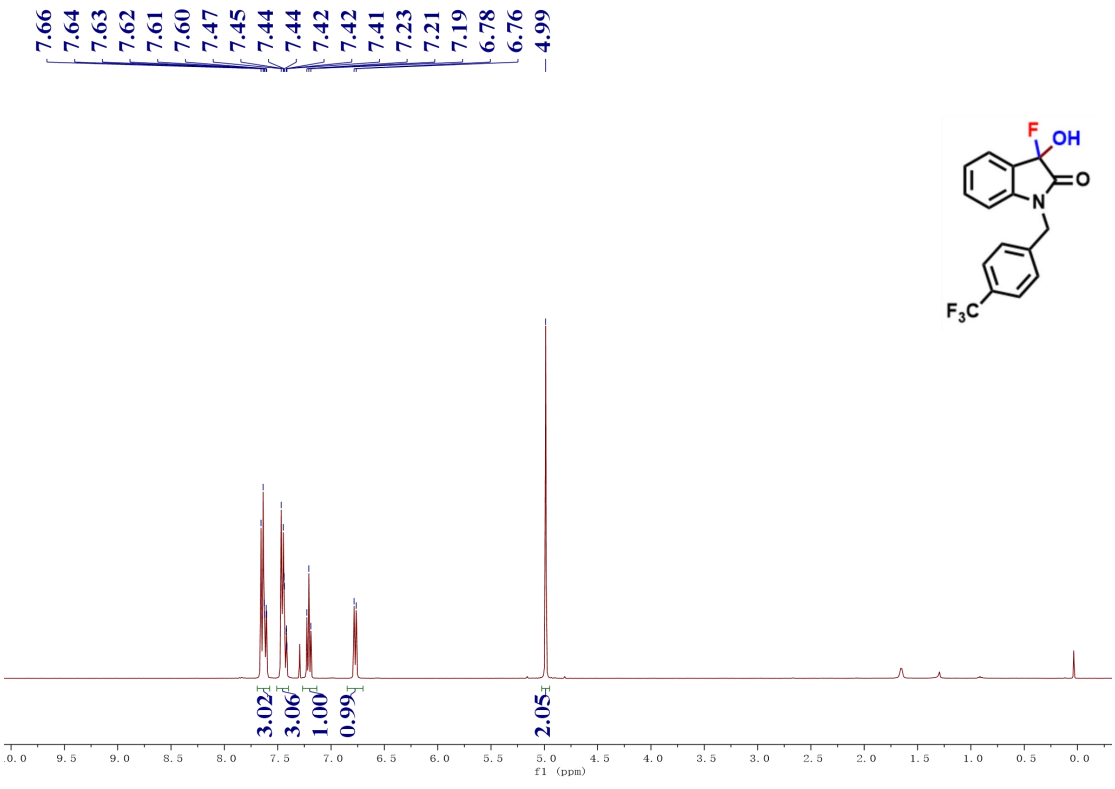
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2j**



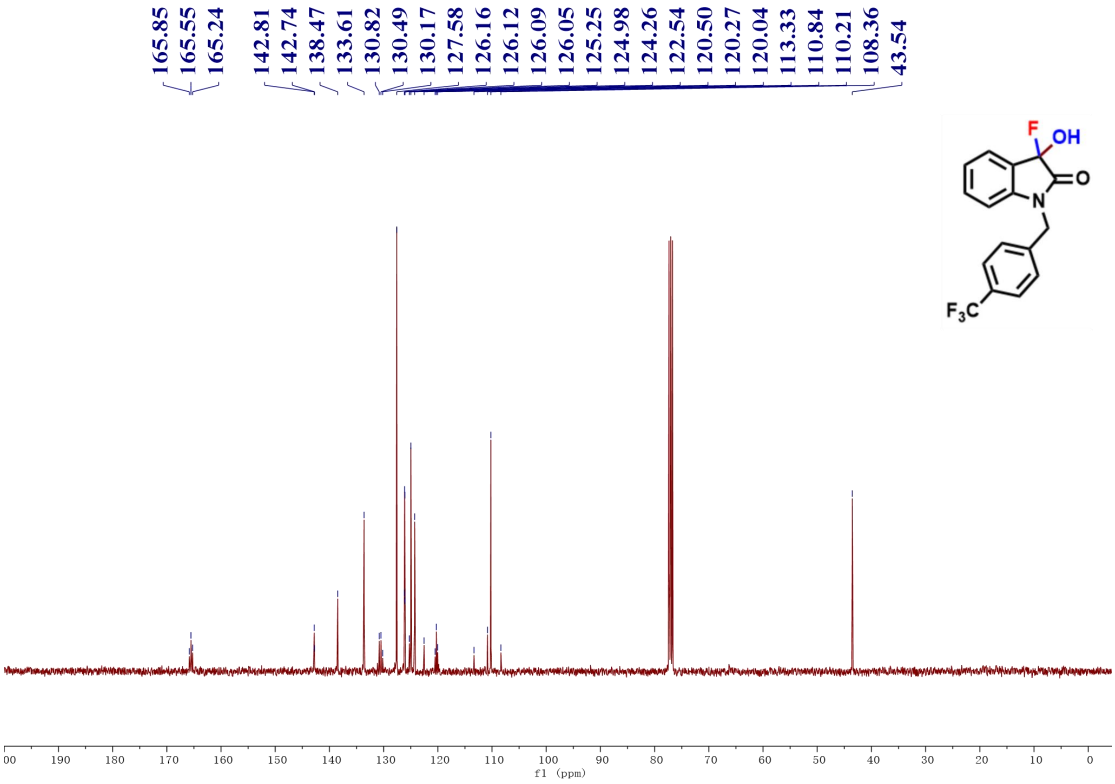
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2j**



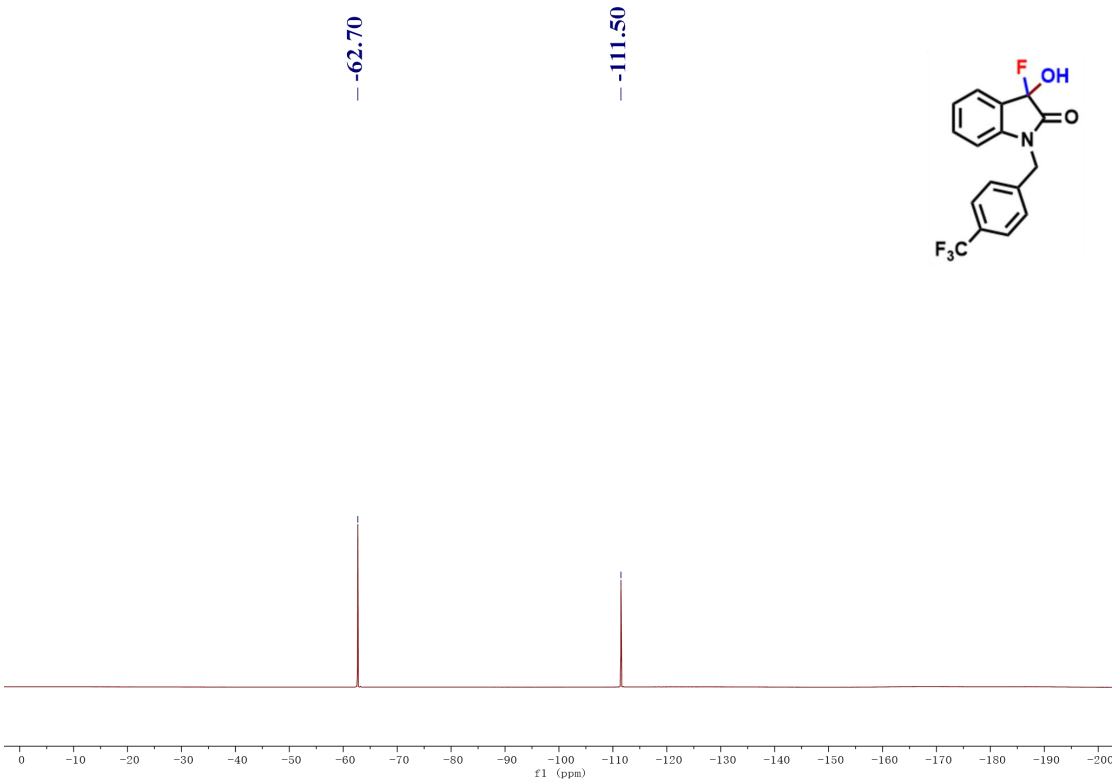
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2j**



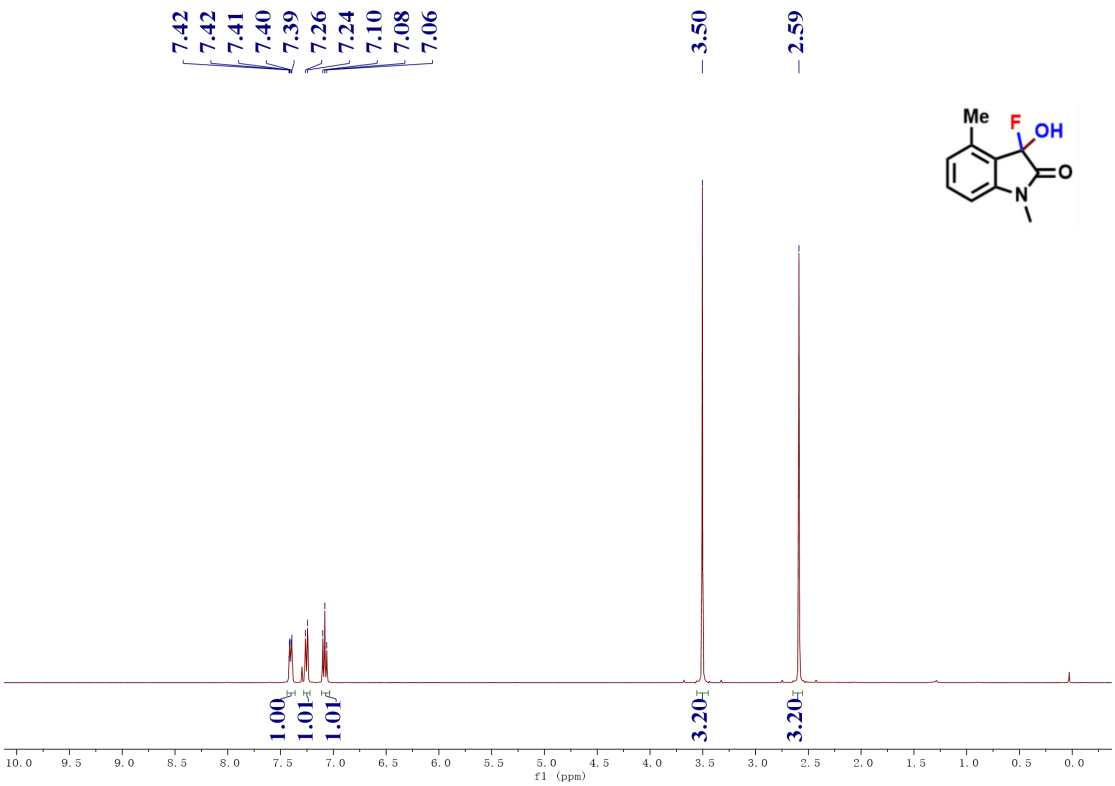
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2k**



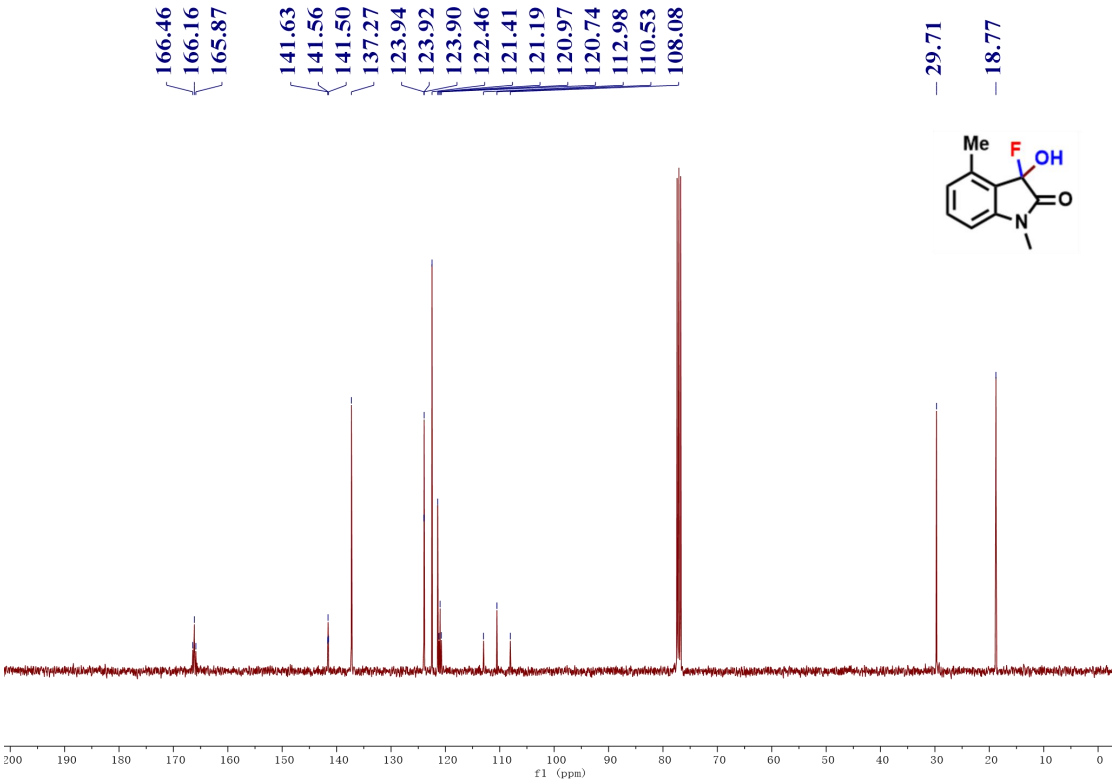
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2k**



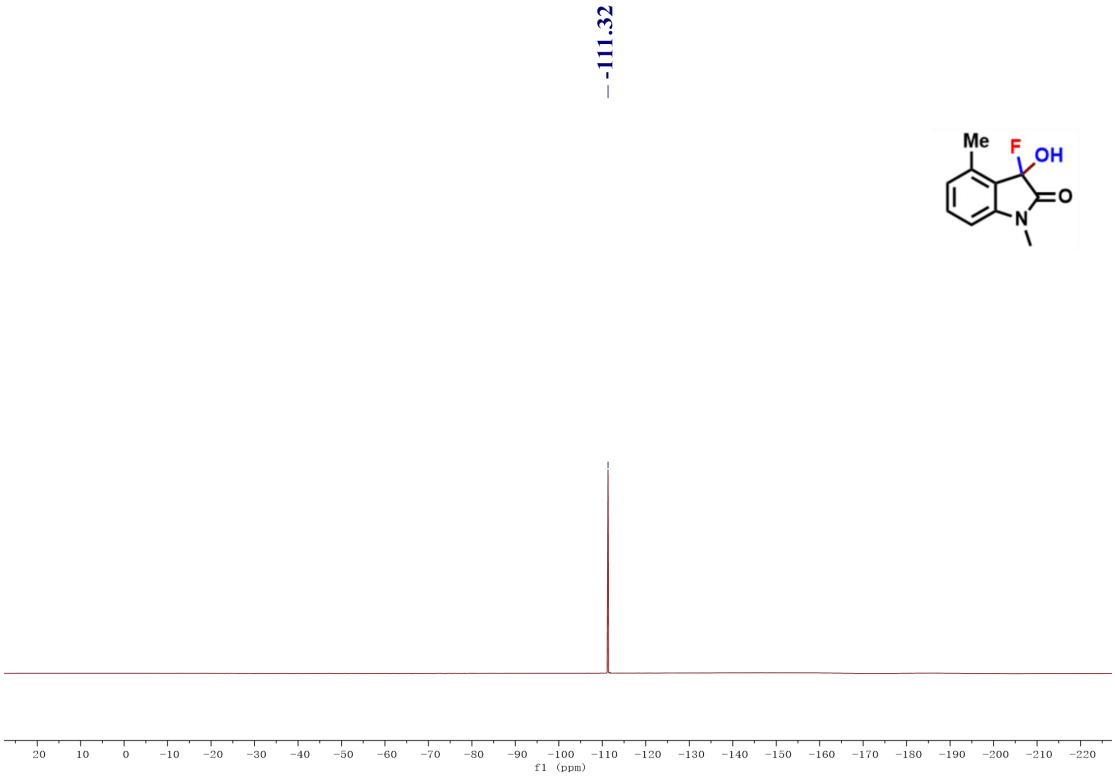
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2k**



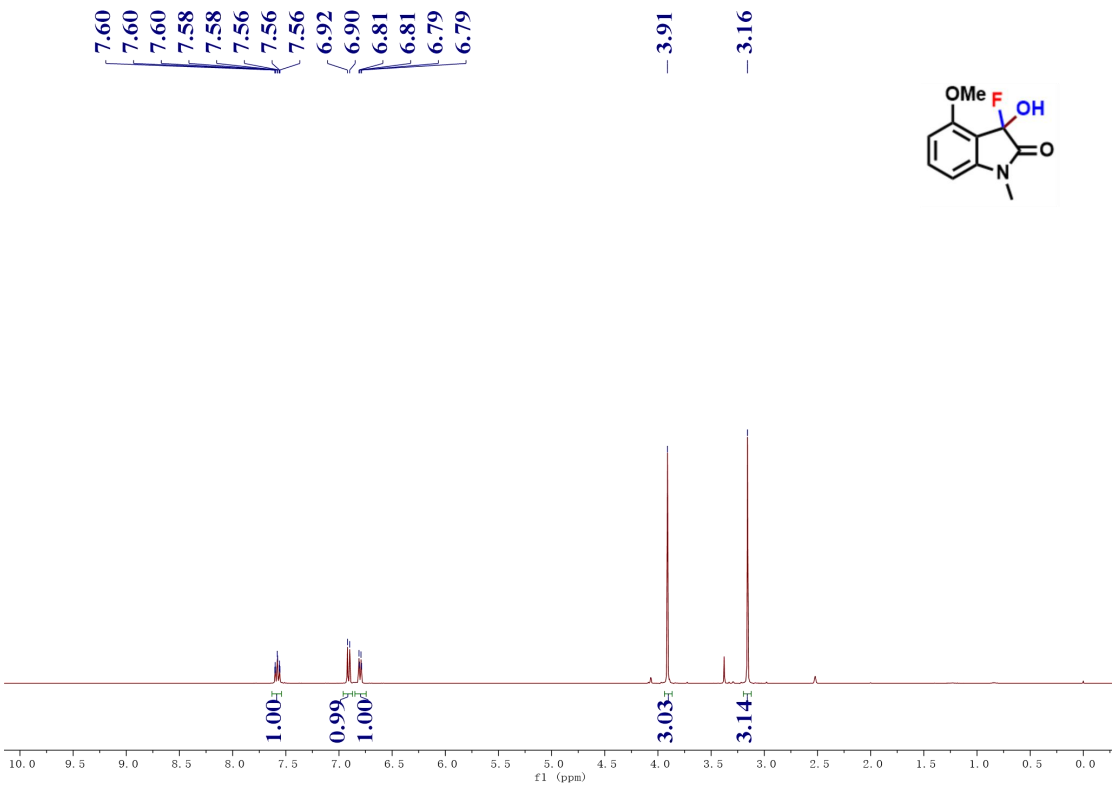
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2m**



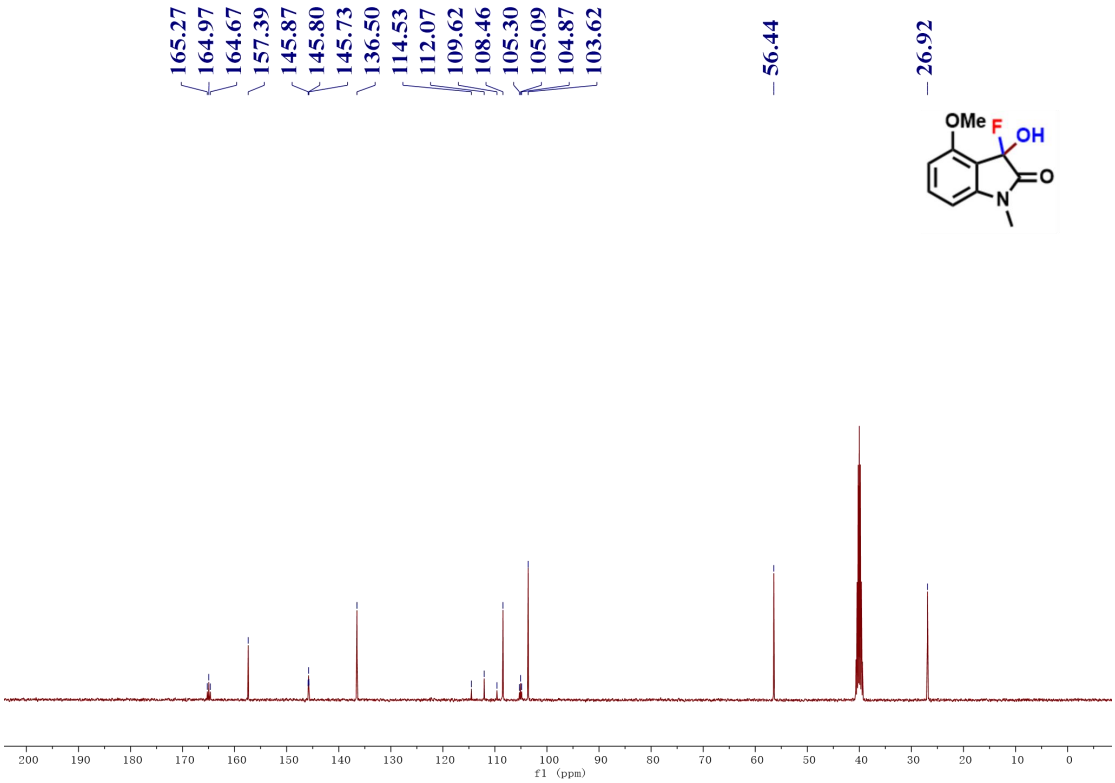
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2m**



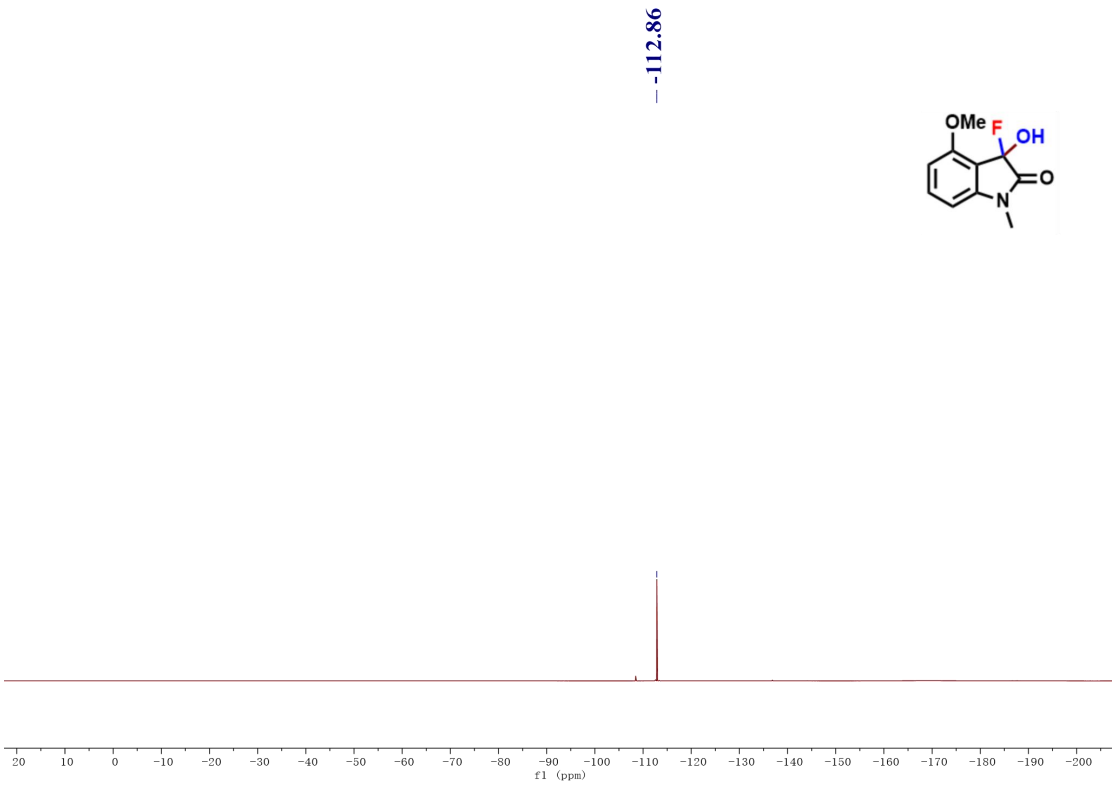
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2m**



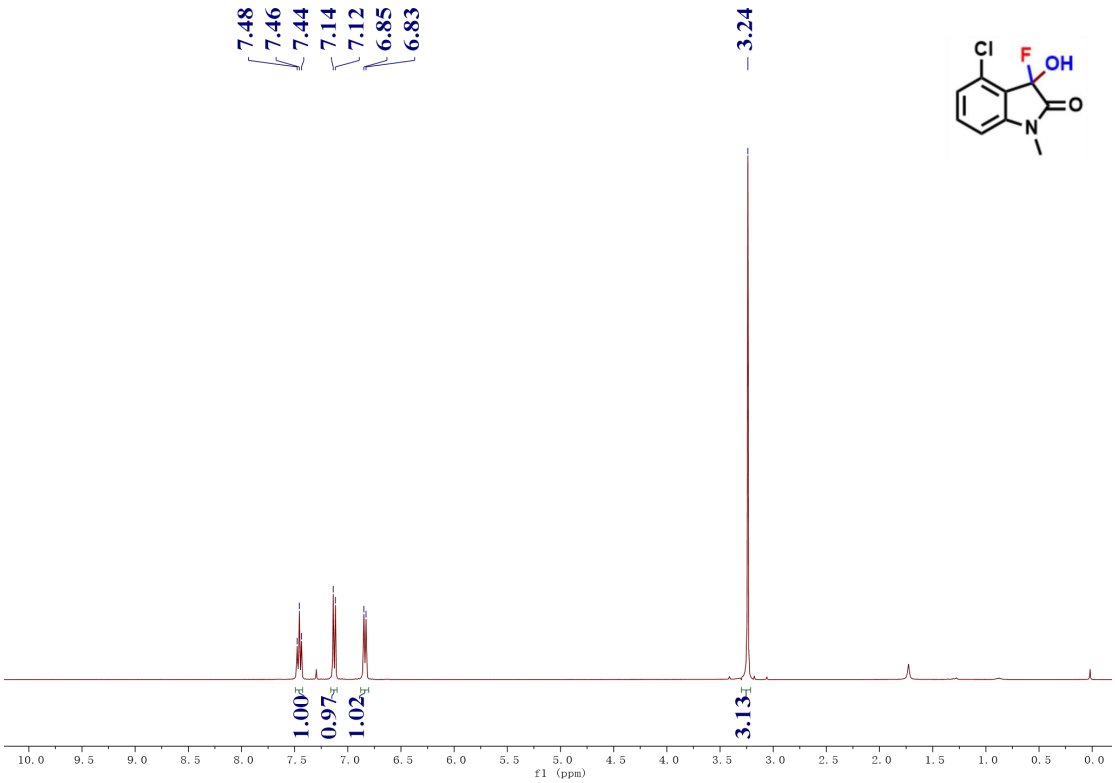
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2n**



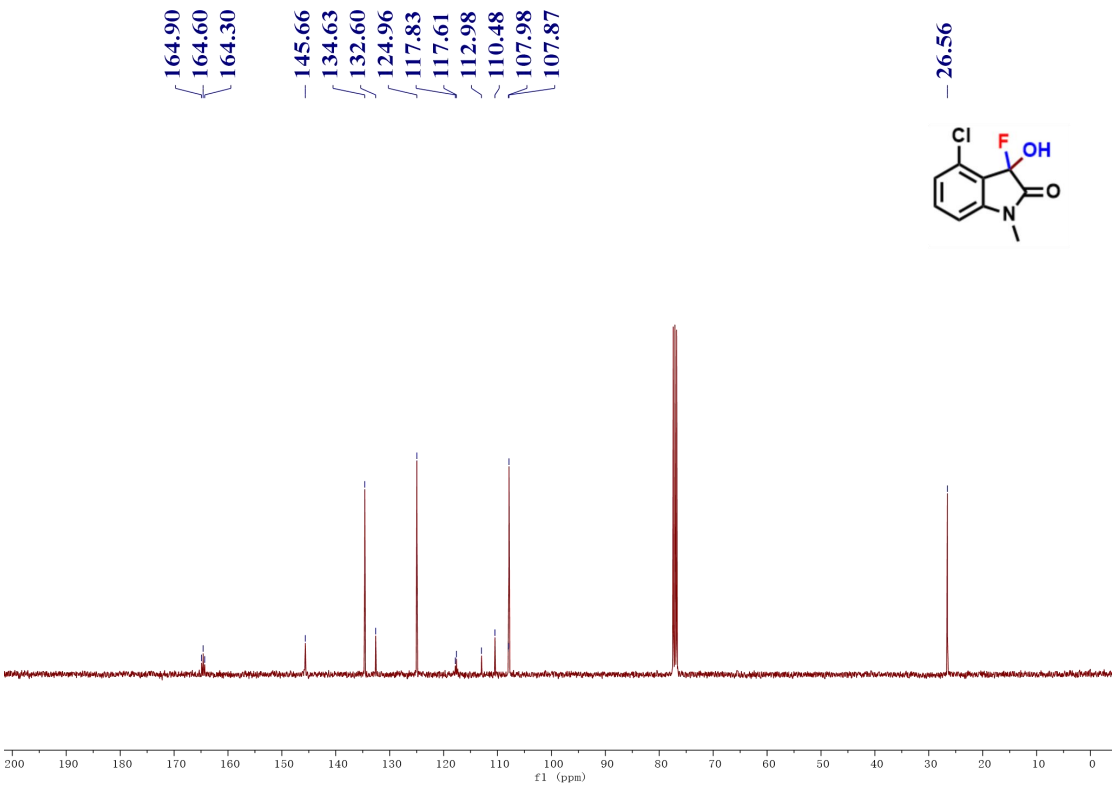
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2n**



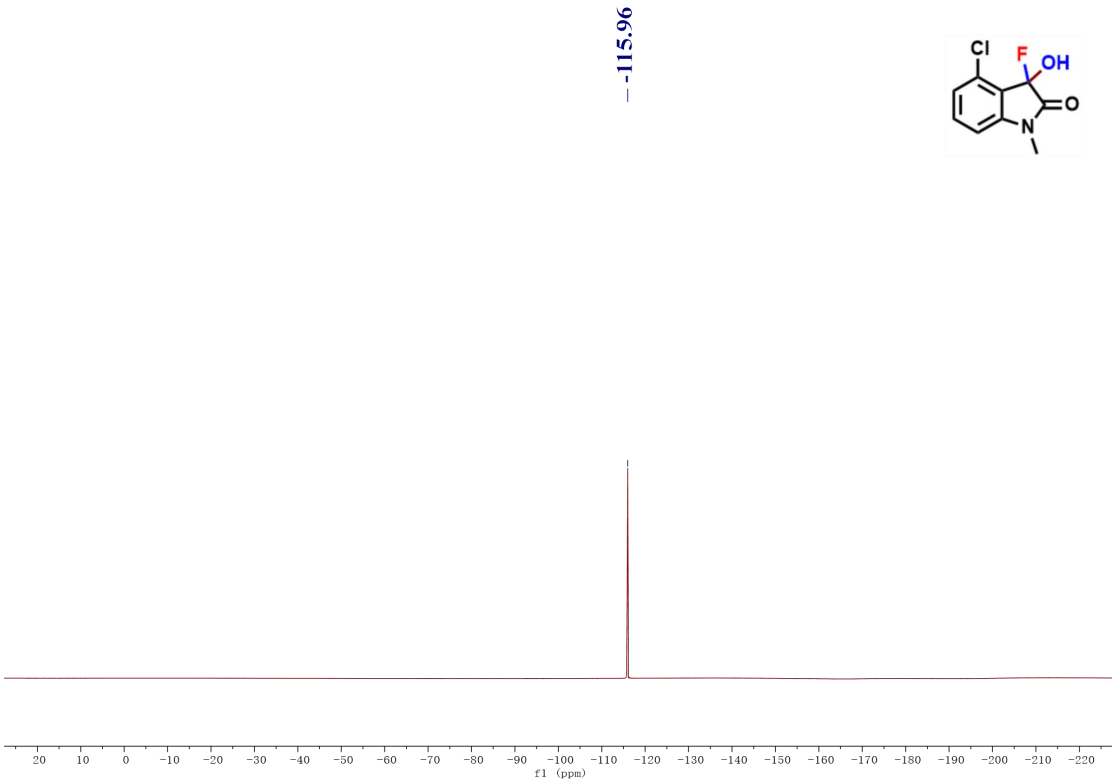
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of compound **2n**



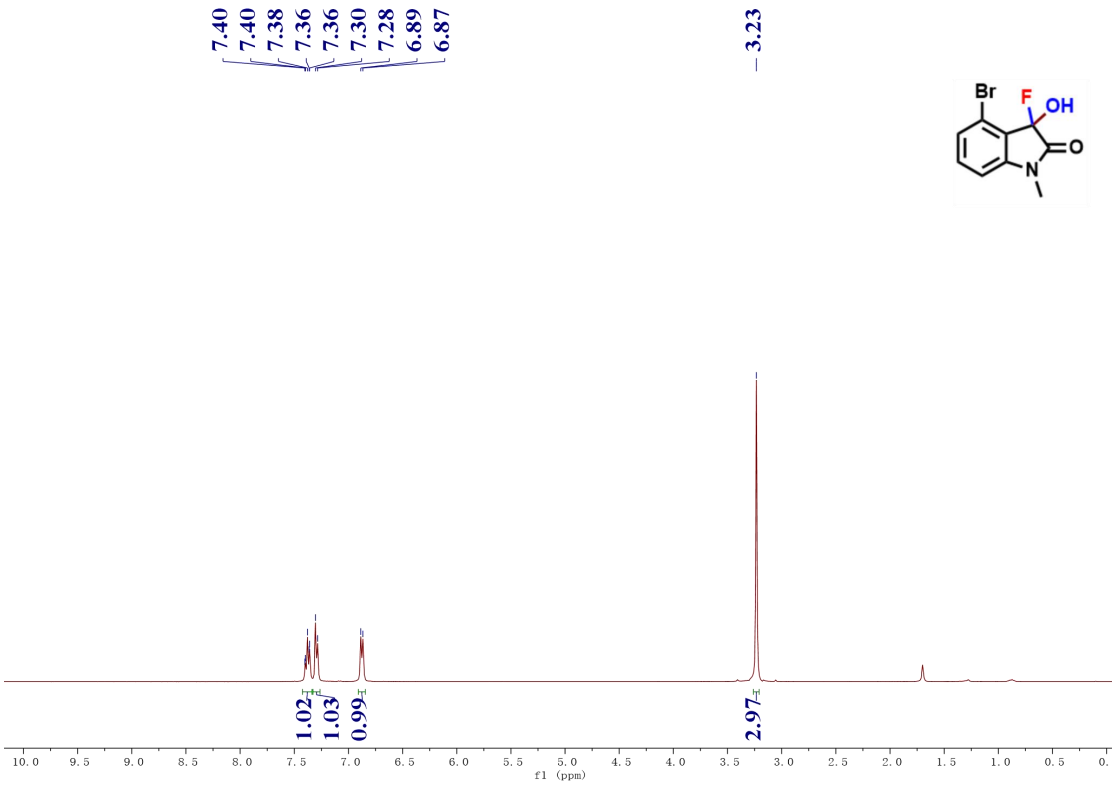
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2o**



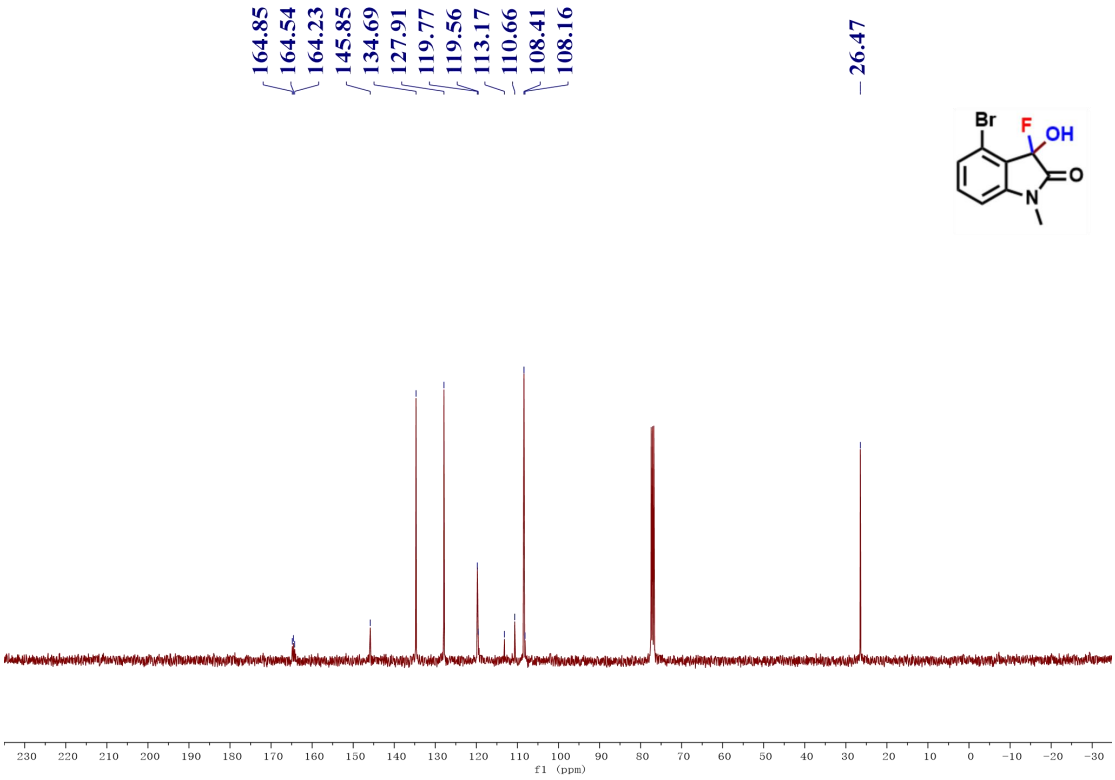
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2o**



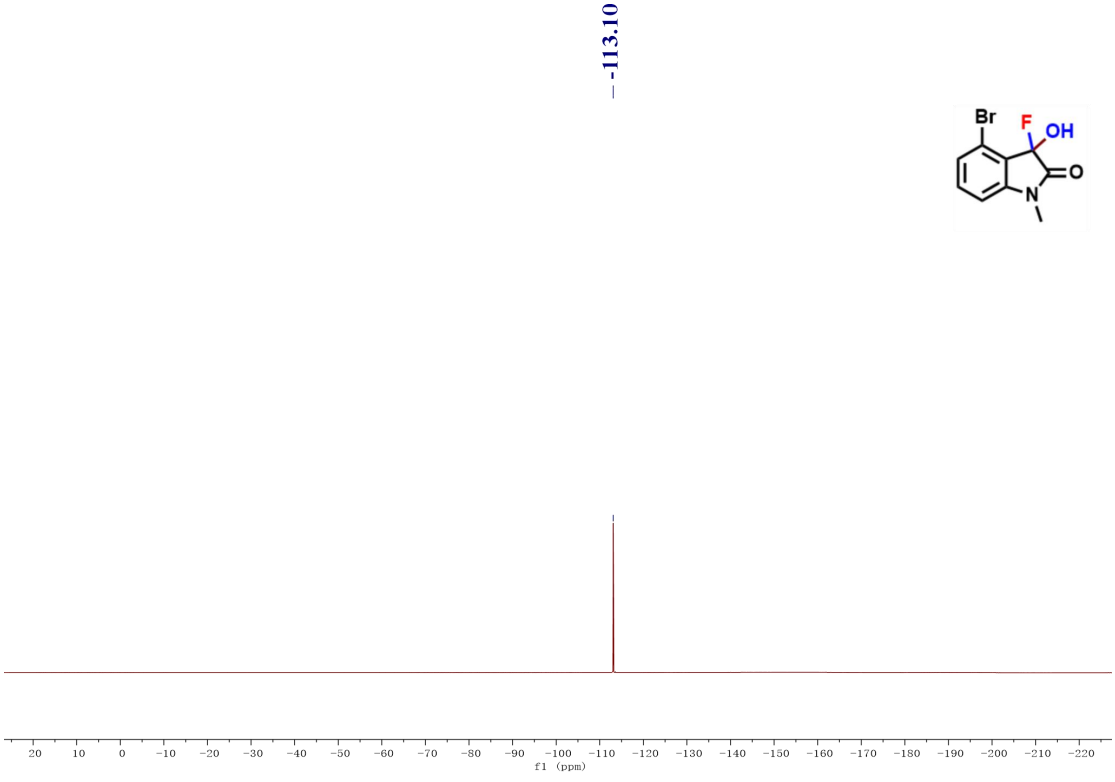
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2o**



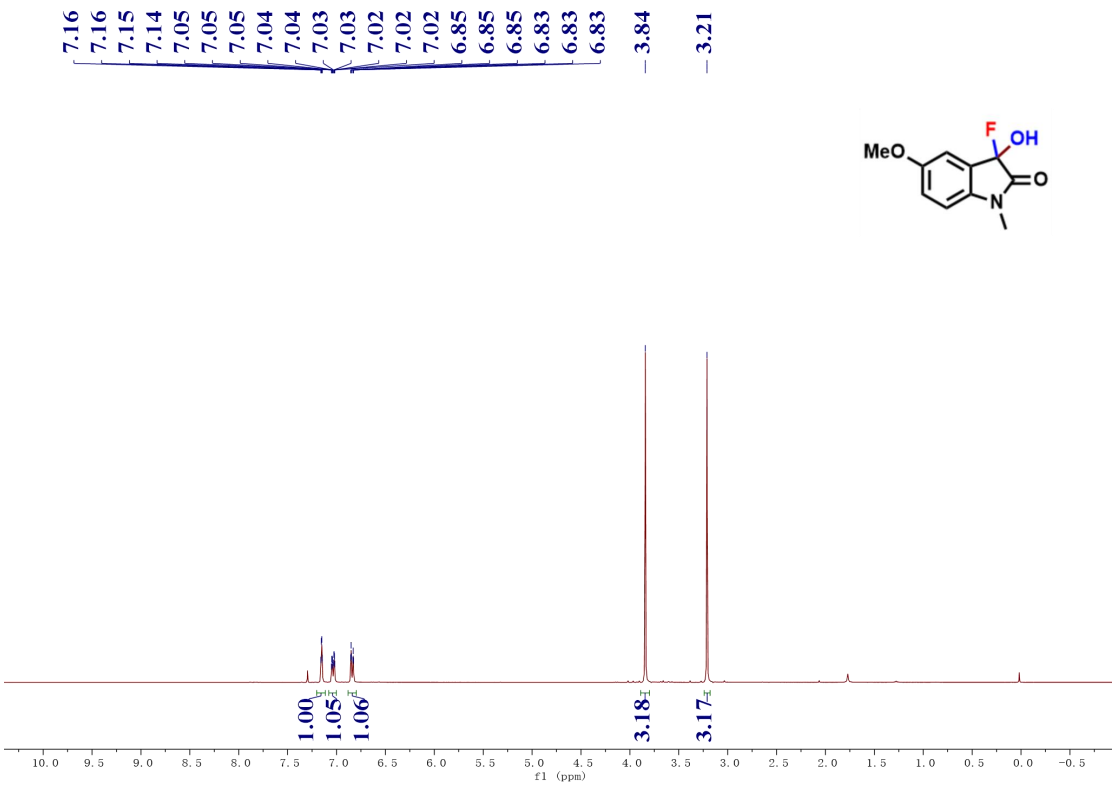
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2p**



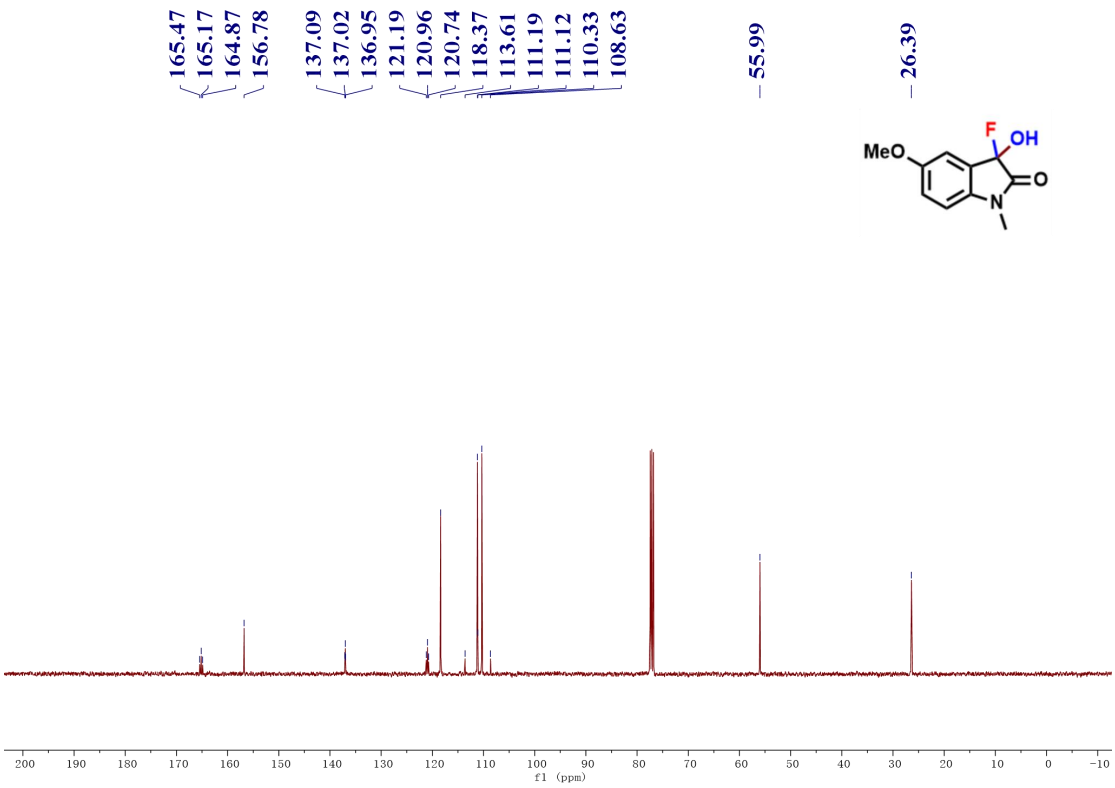
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2p**



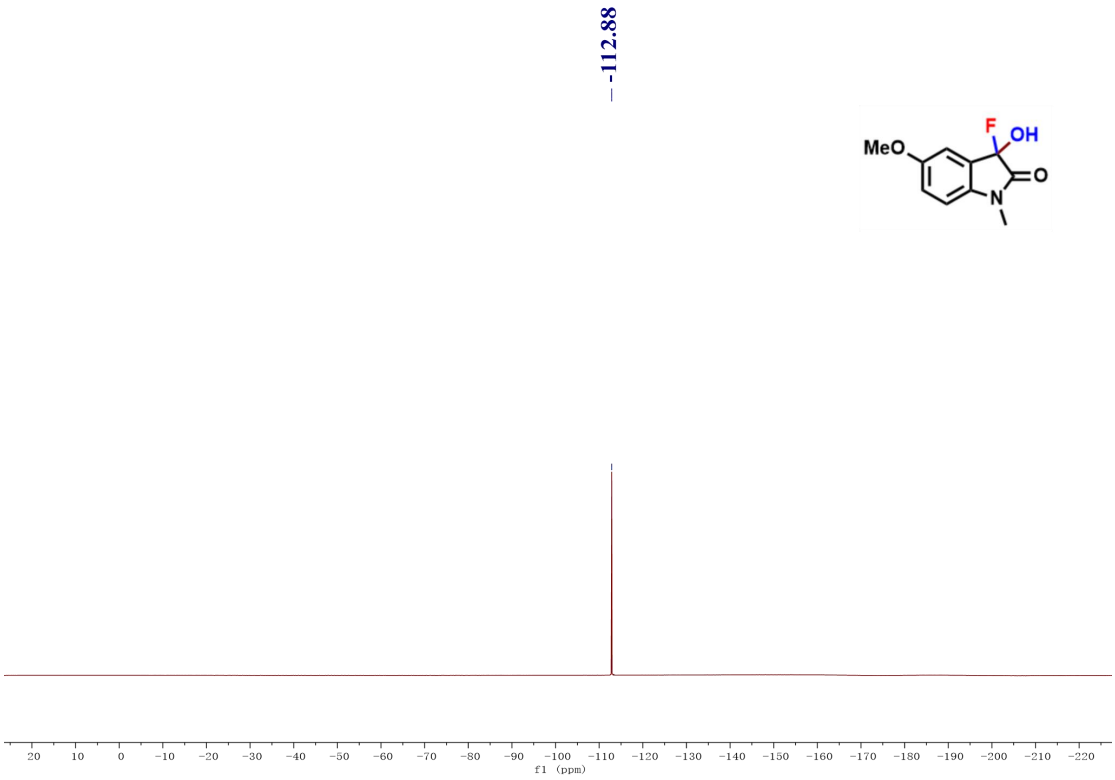
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2p**



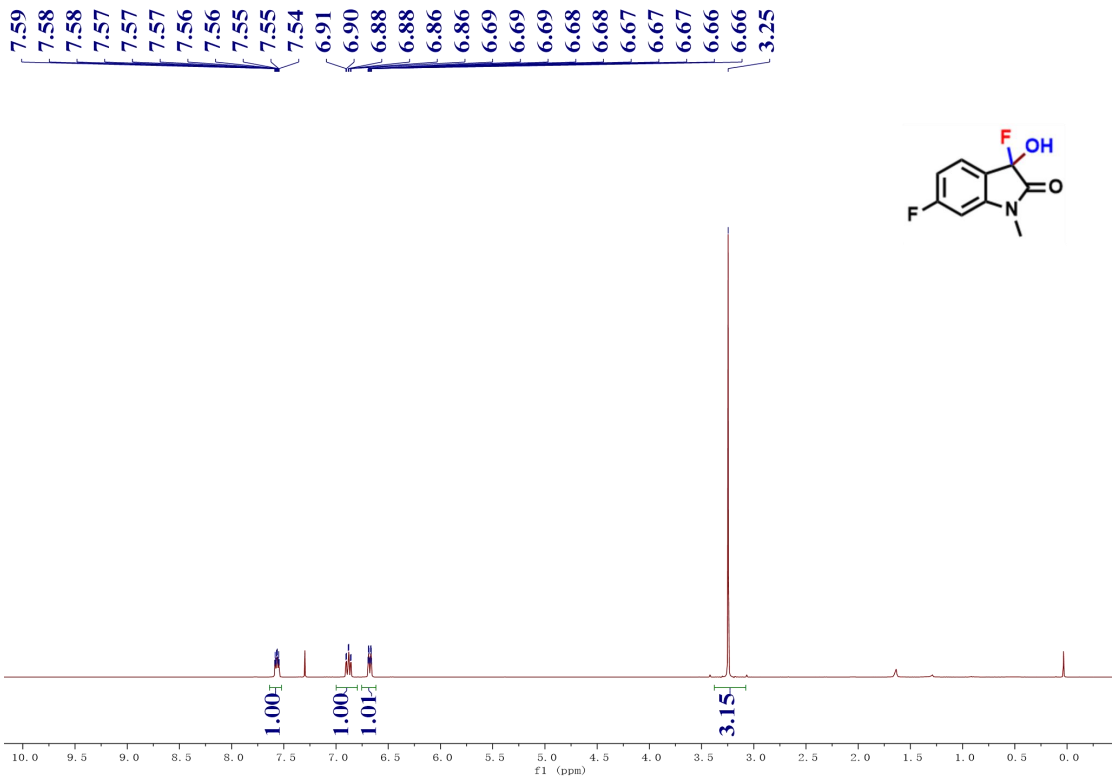
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2q**



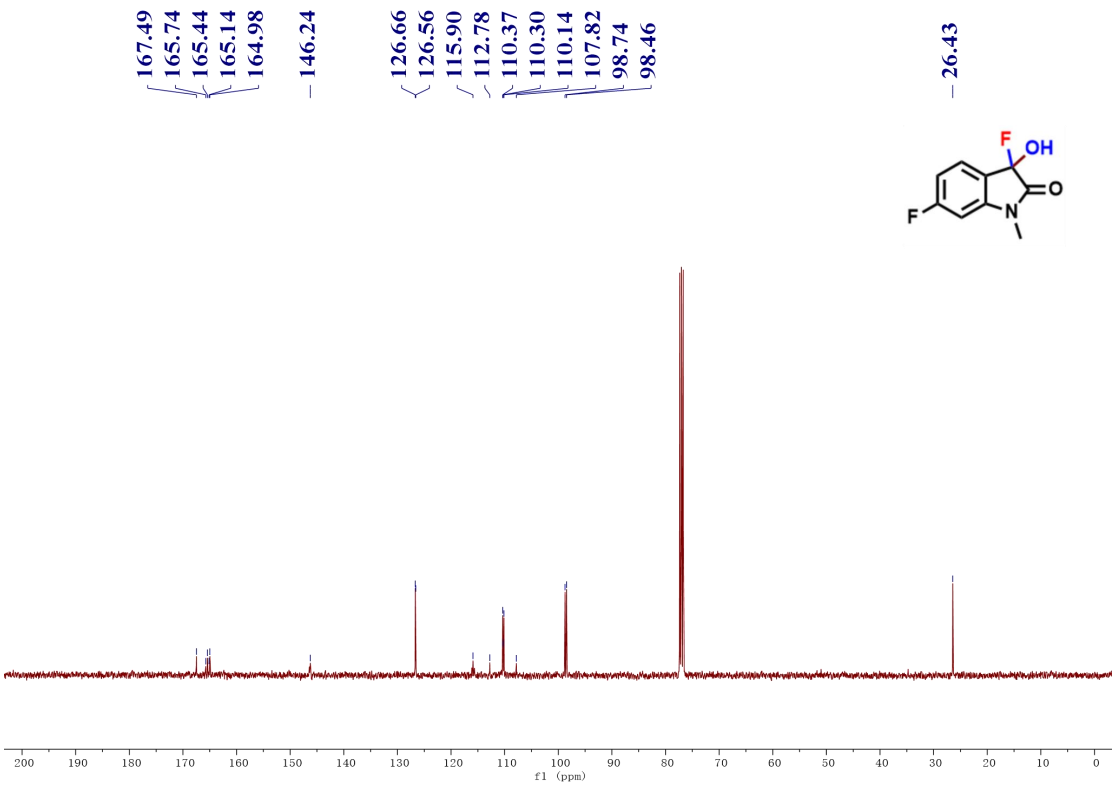
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2q**



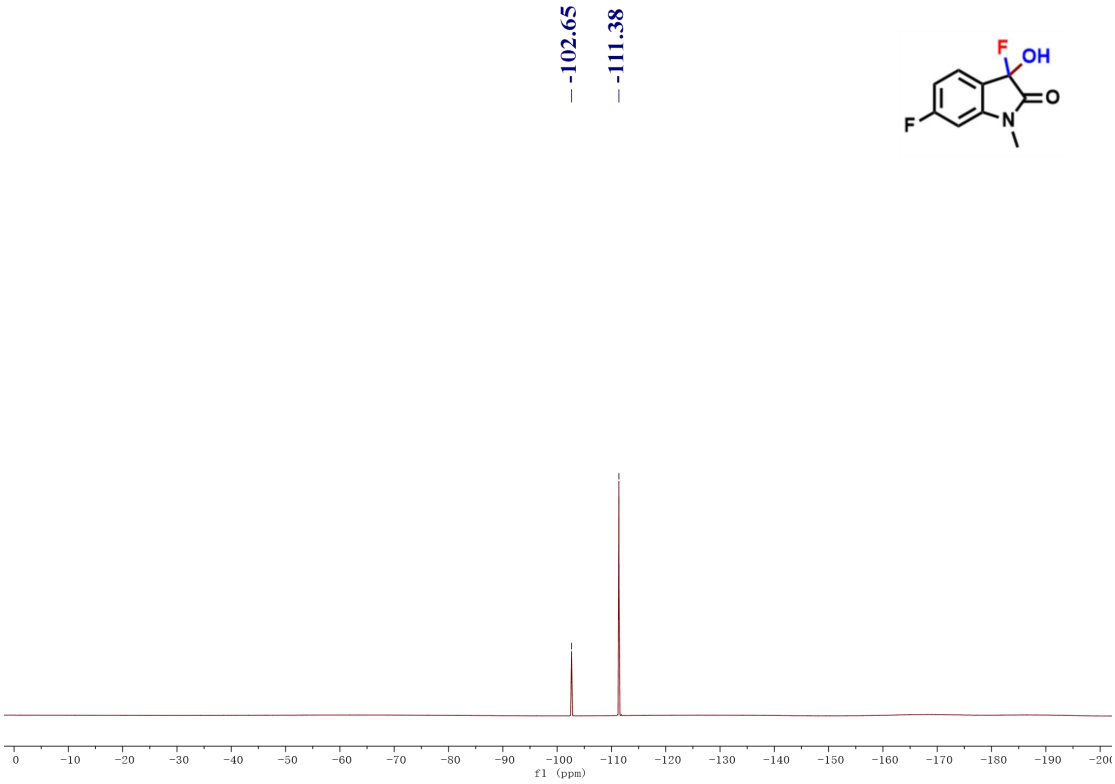
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2q**



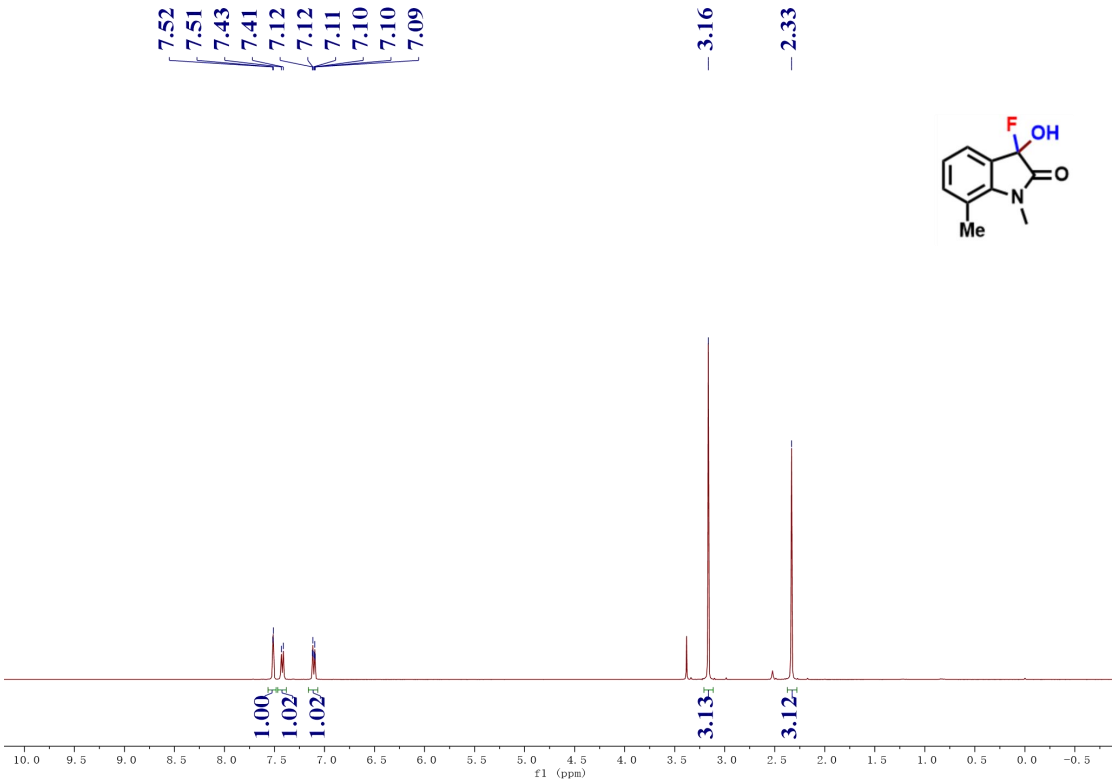
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2r**



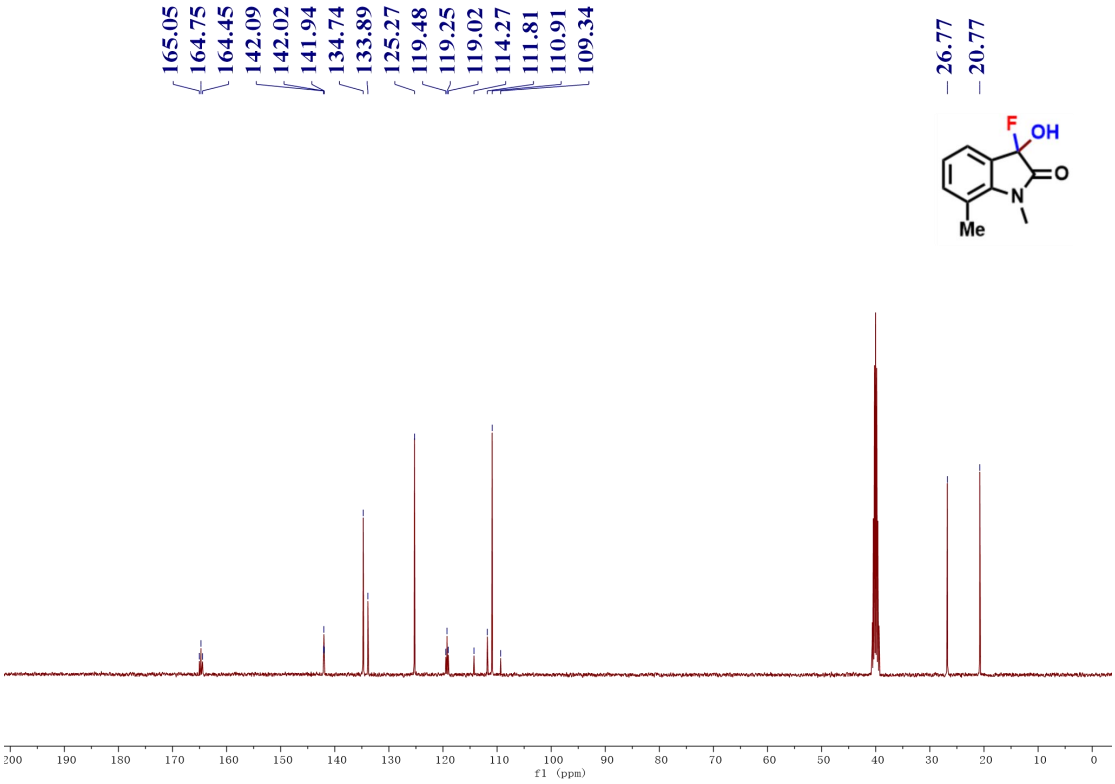
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2r**



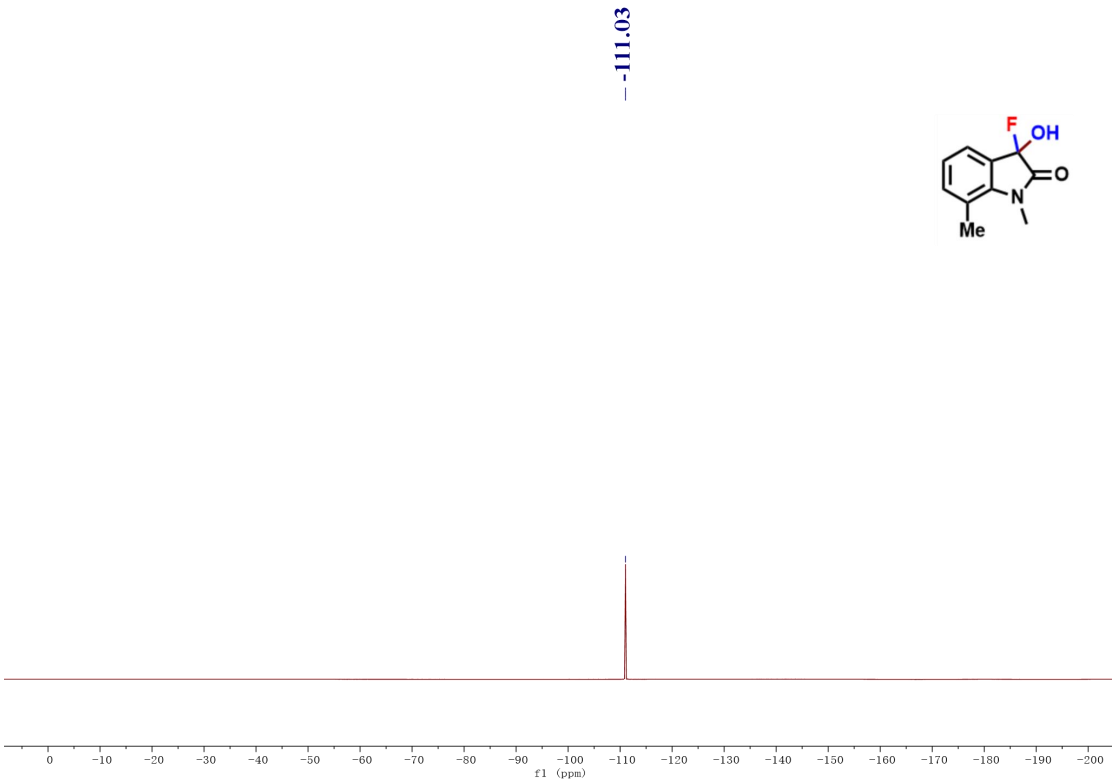
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2r**



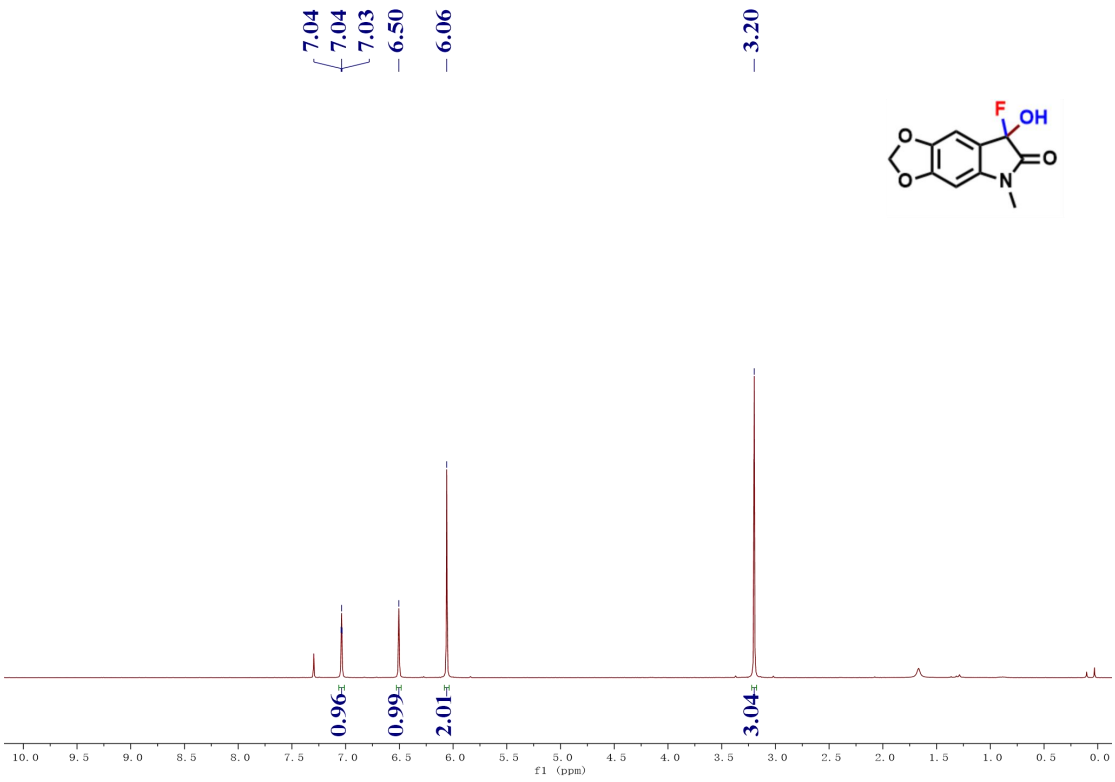
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **2s**



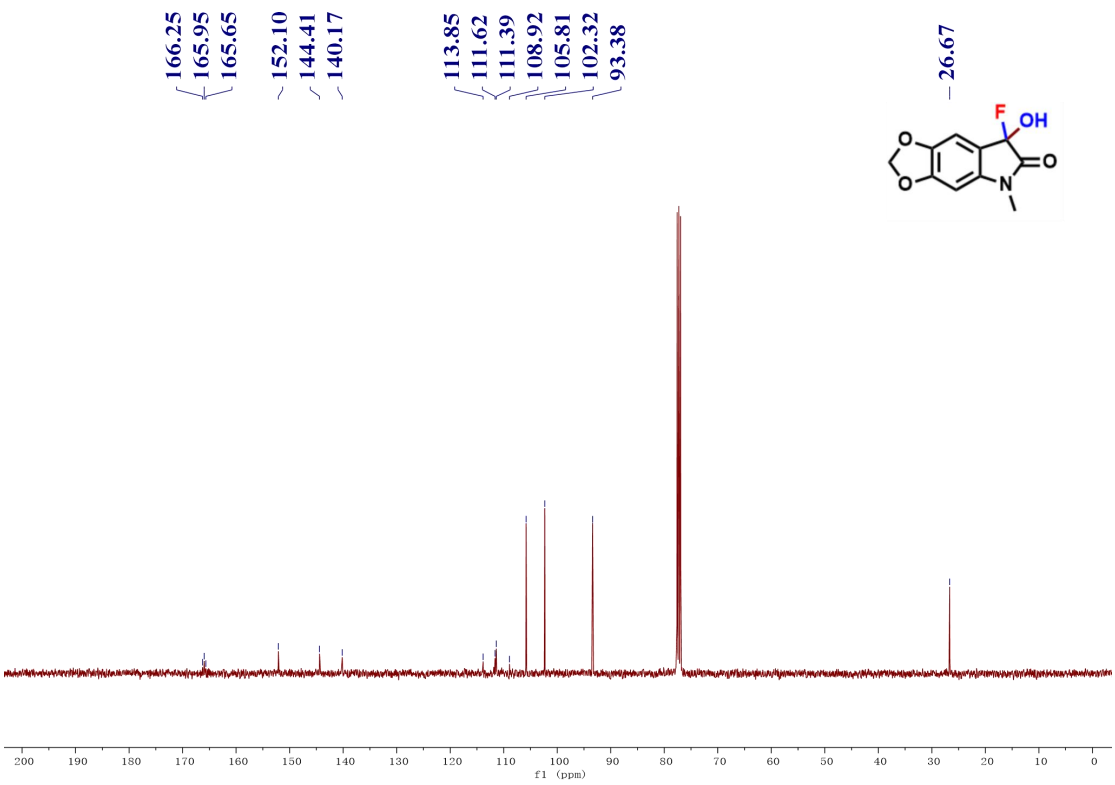
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **2s**



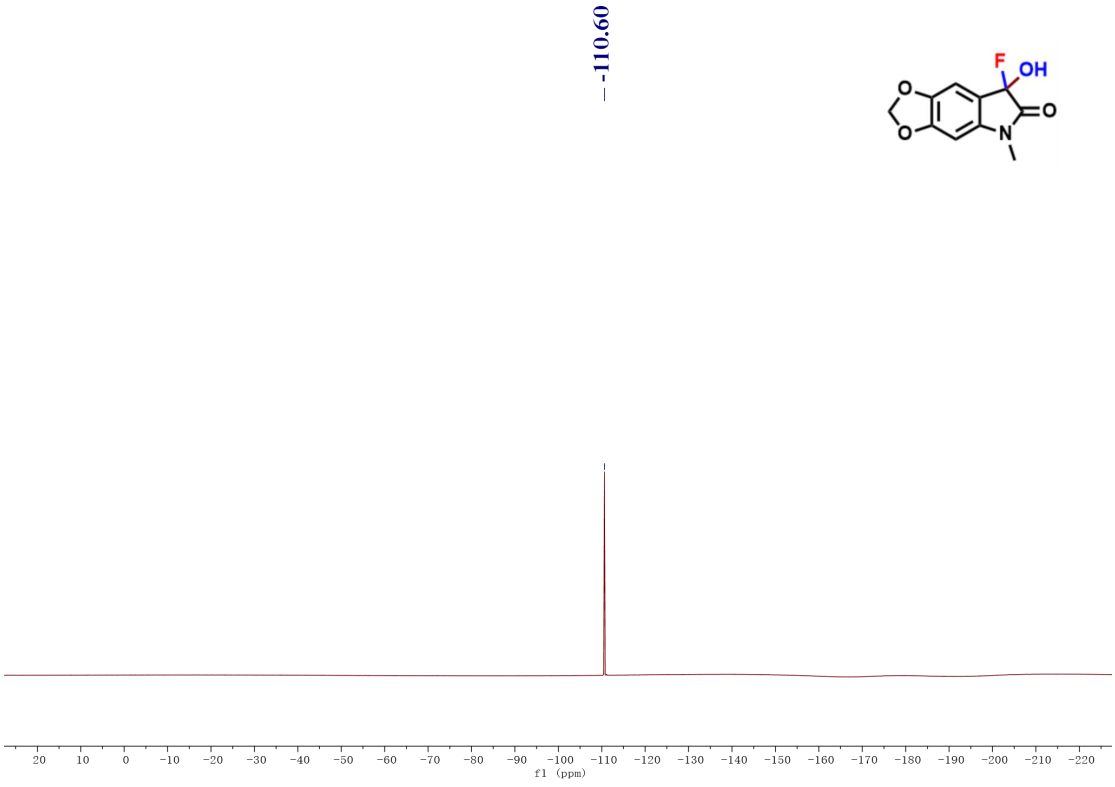
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of compound **2s**



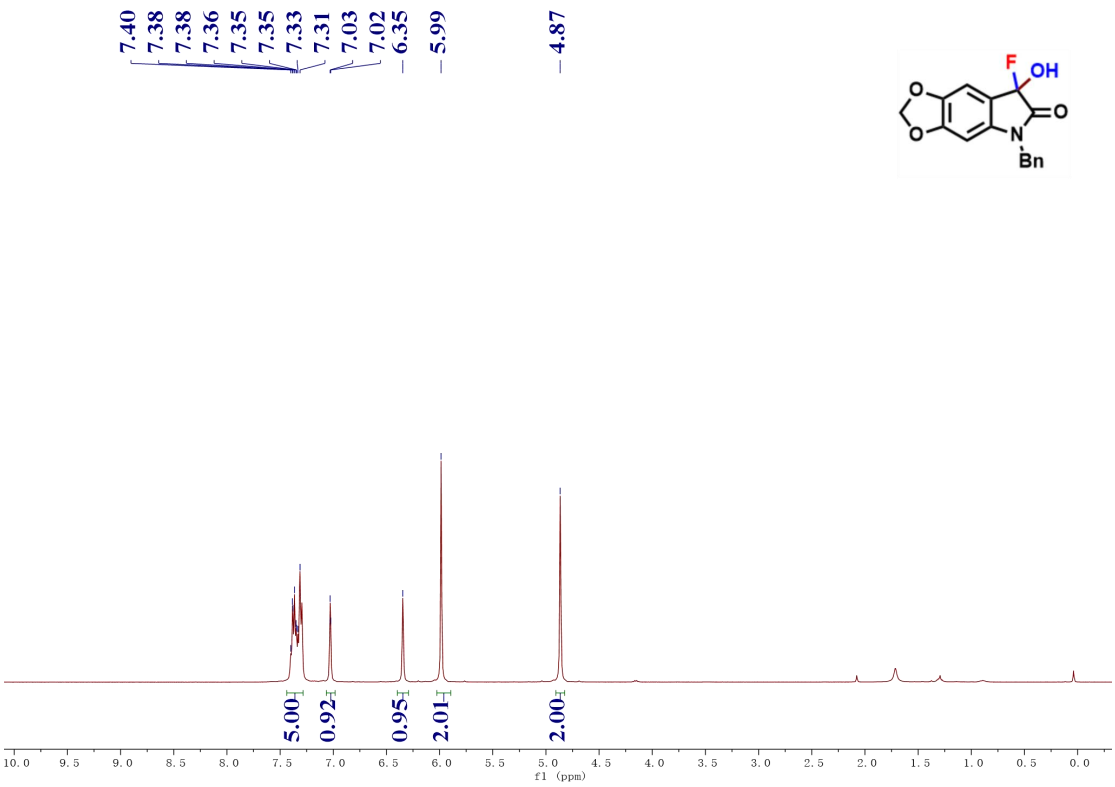
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2t**



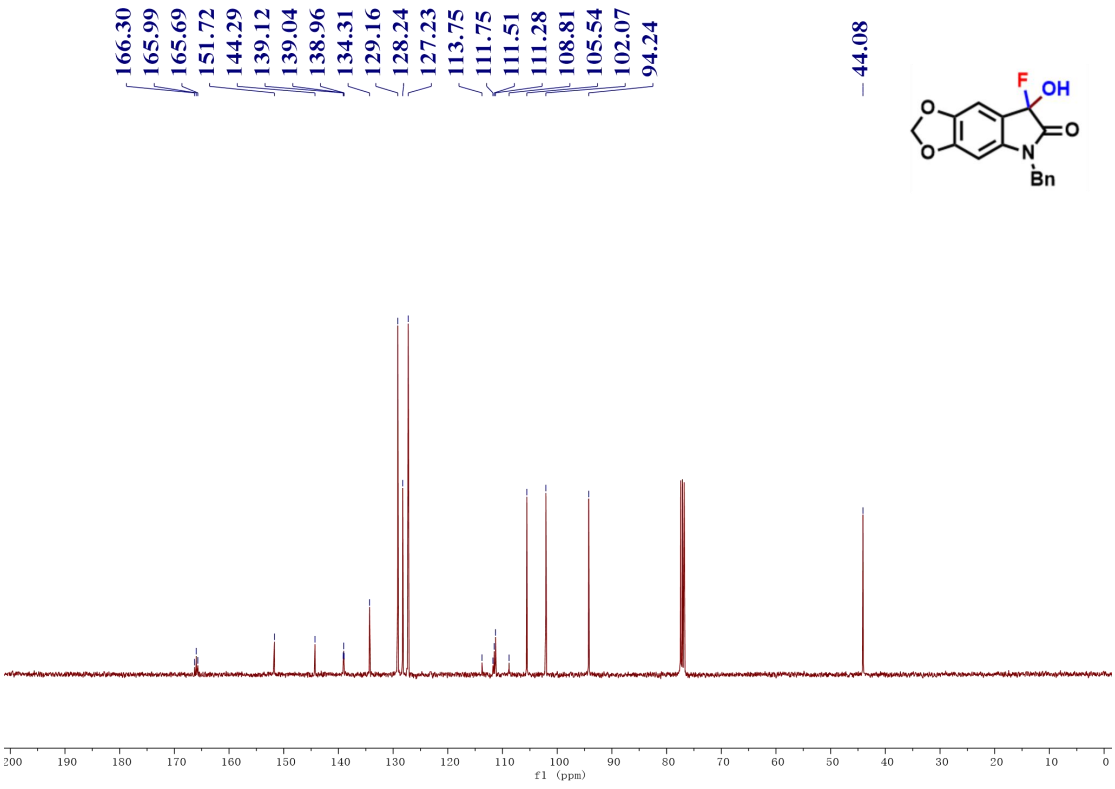
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2t**



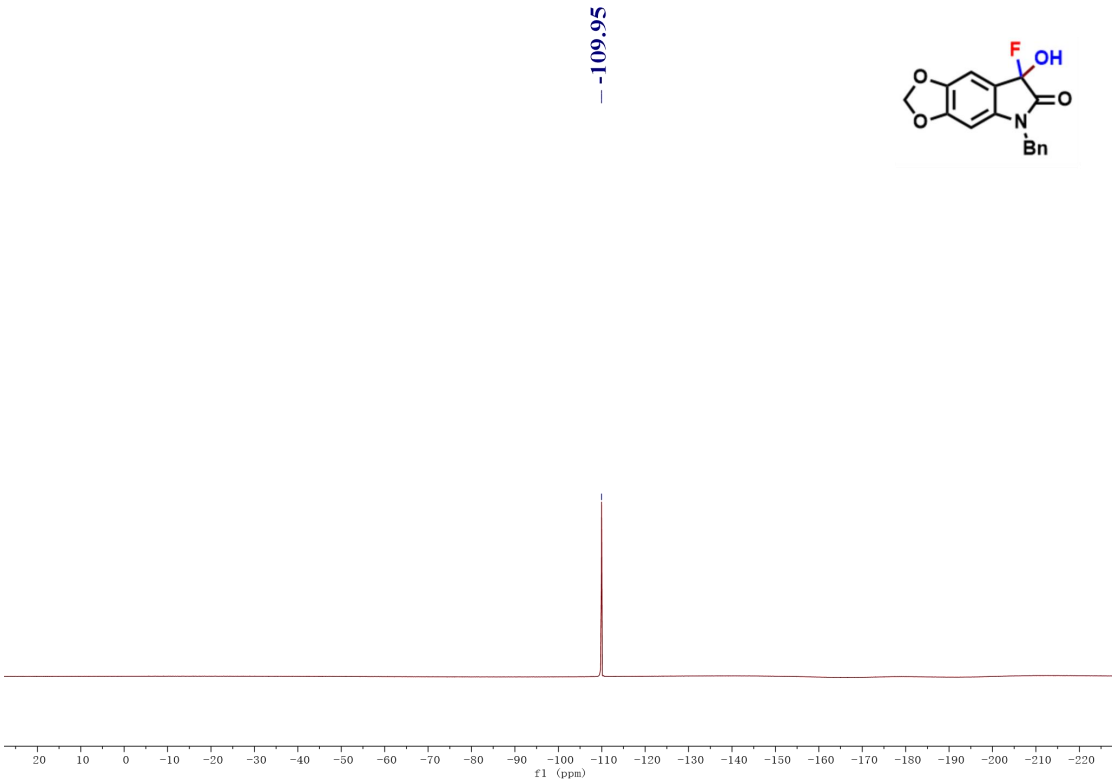
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2t**



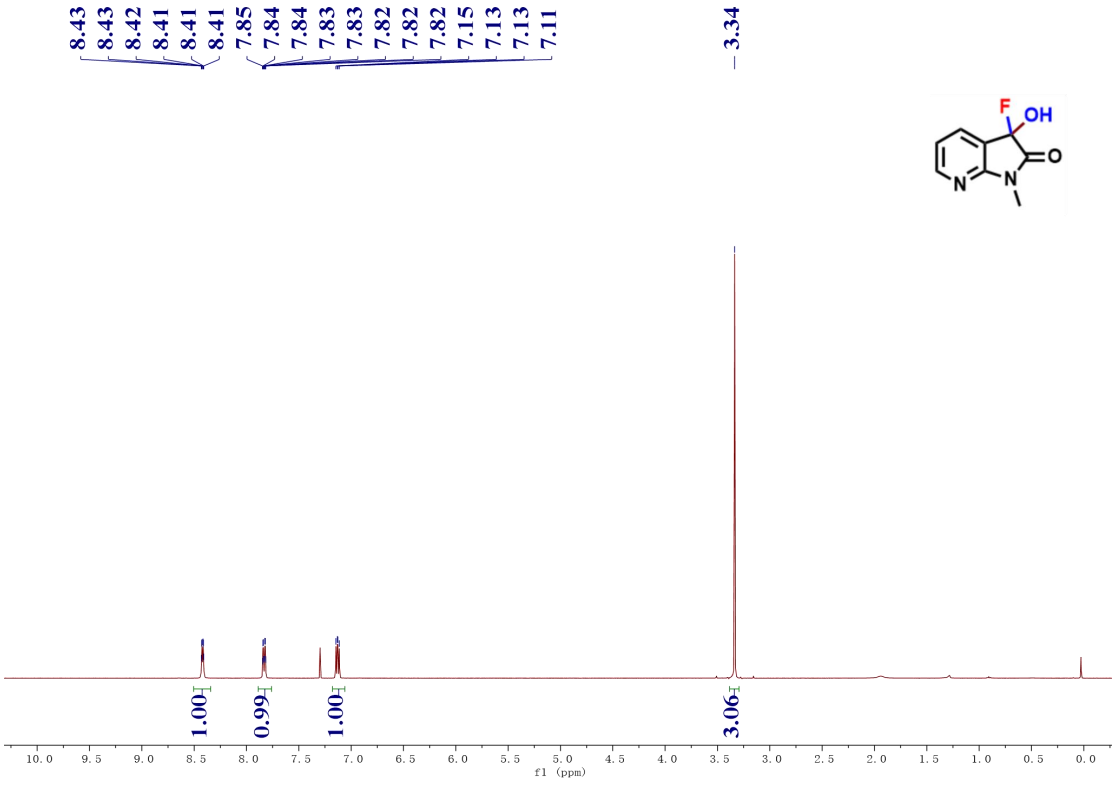
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2u**



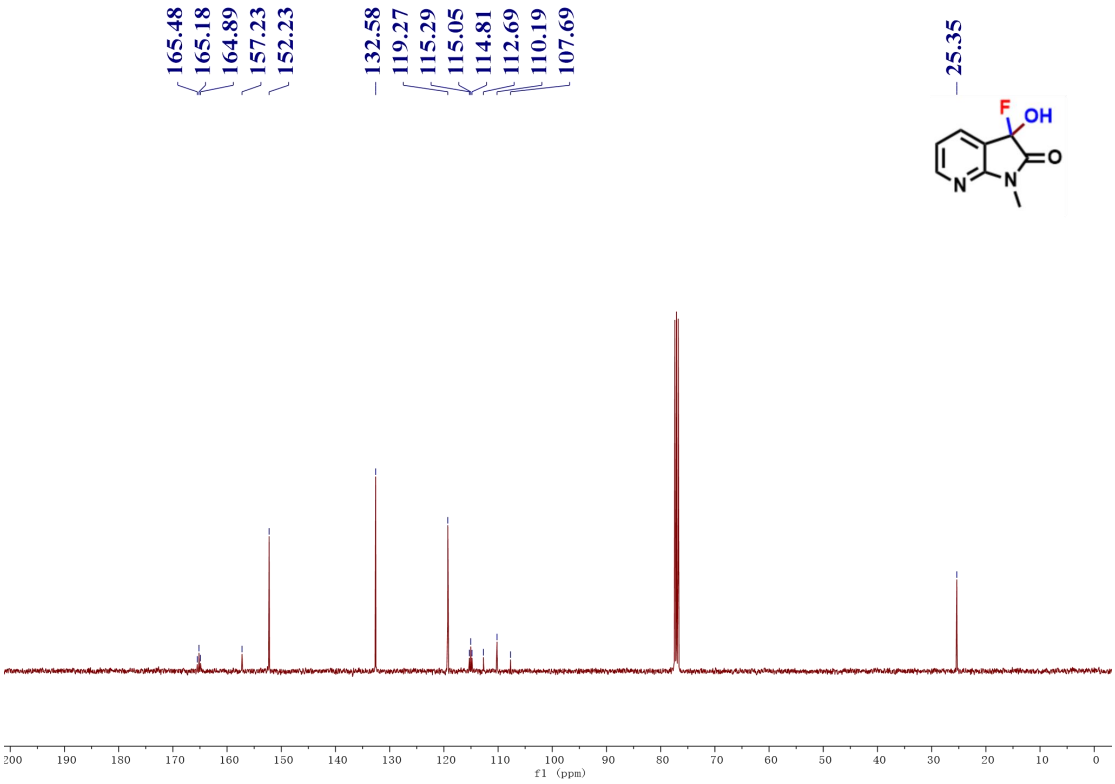
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2u**



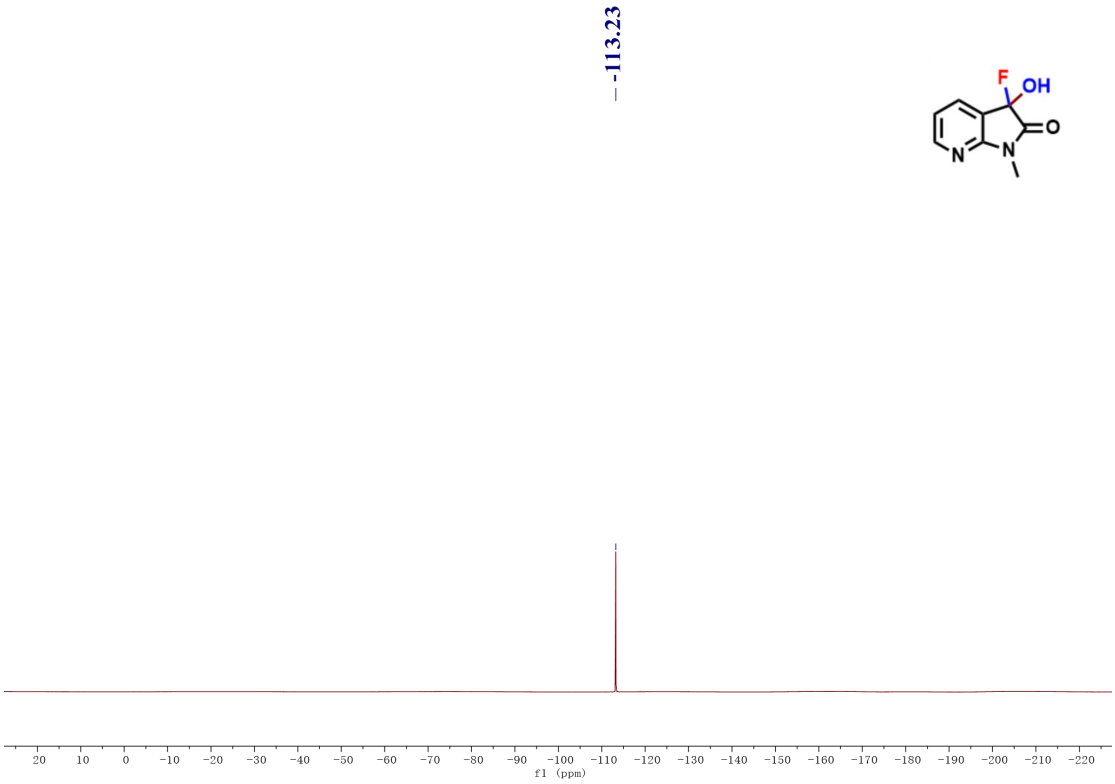
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2u**



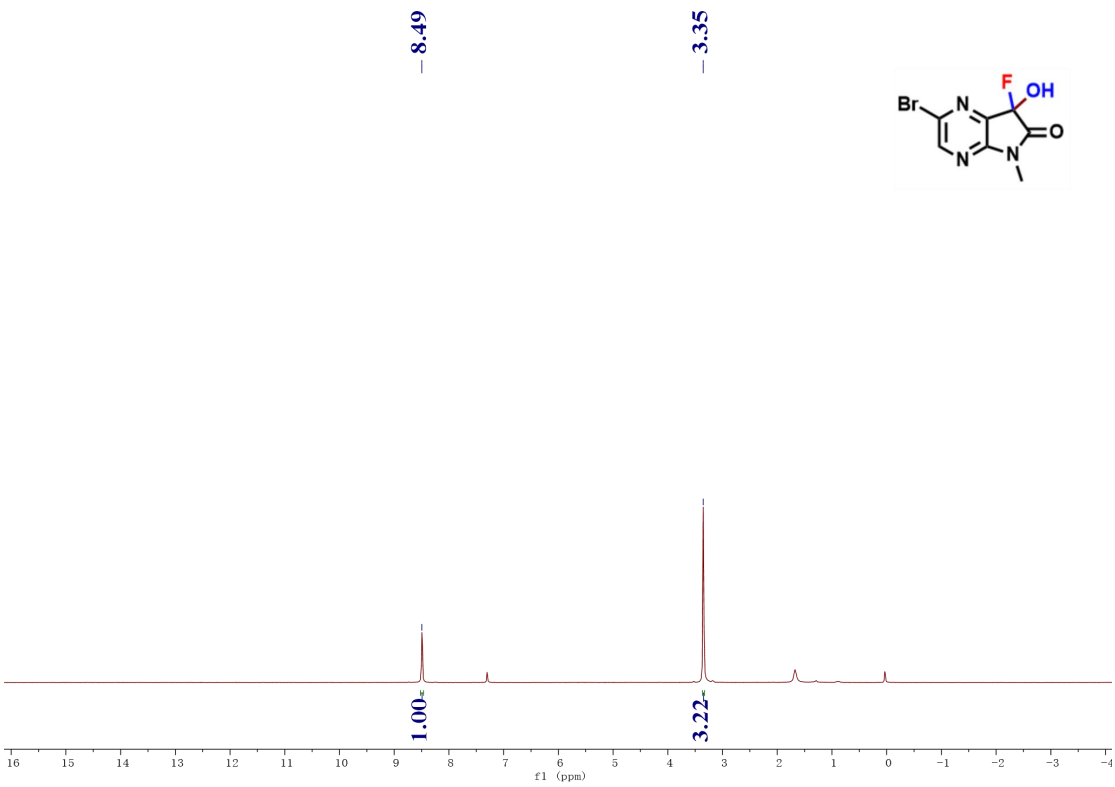
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2v**



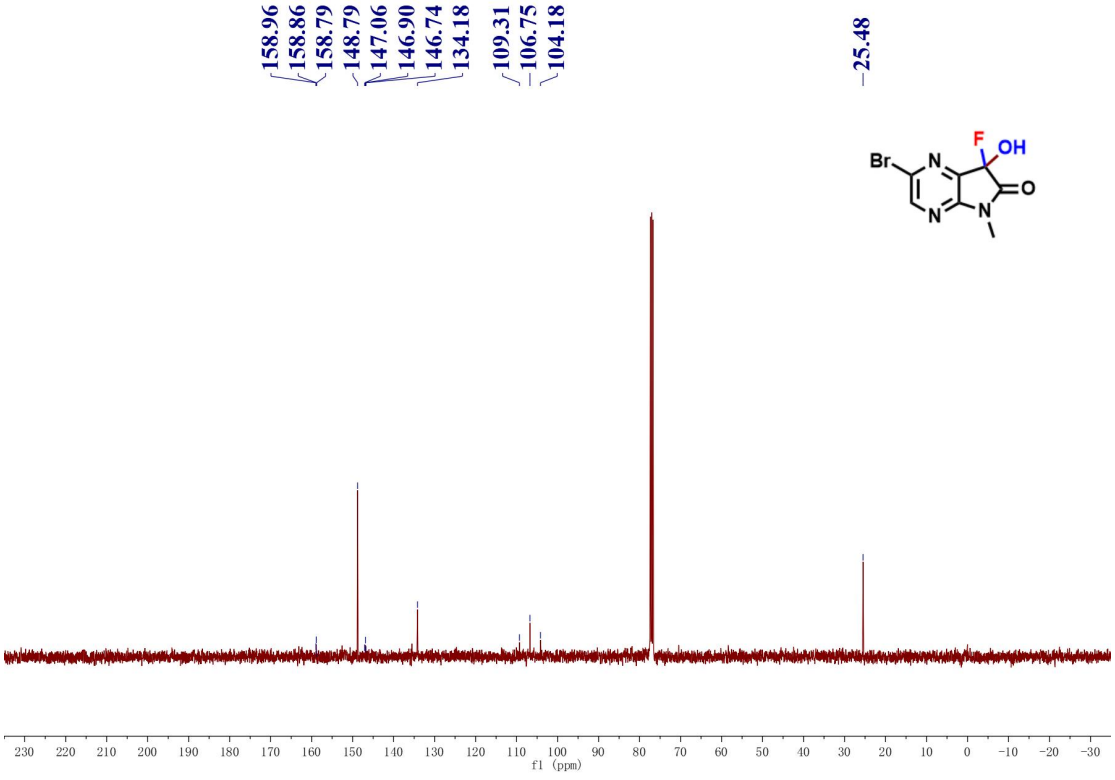
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2v**



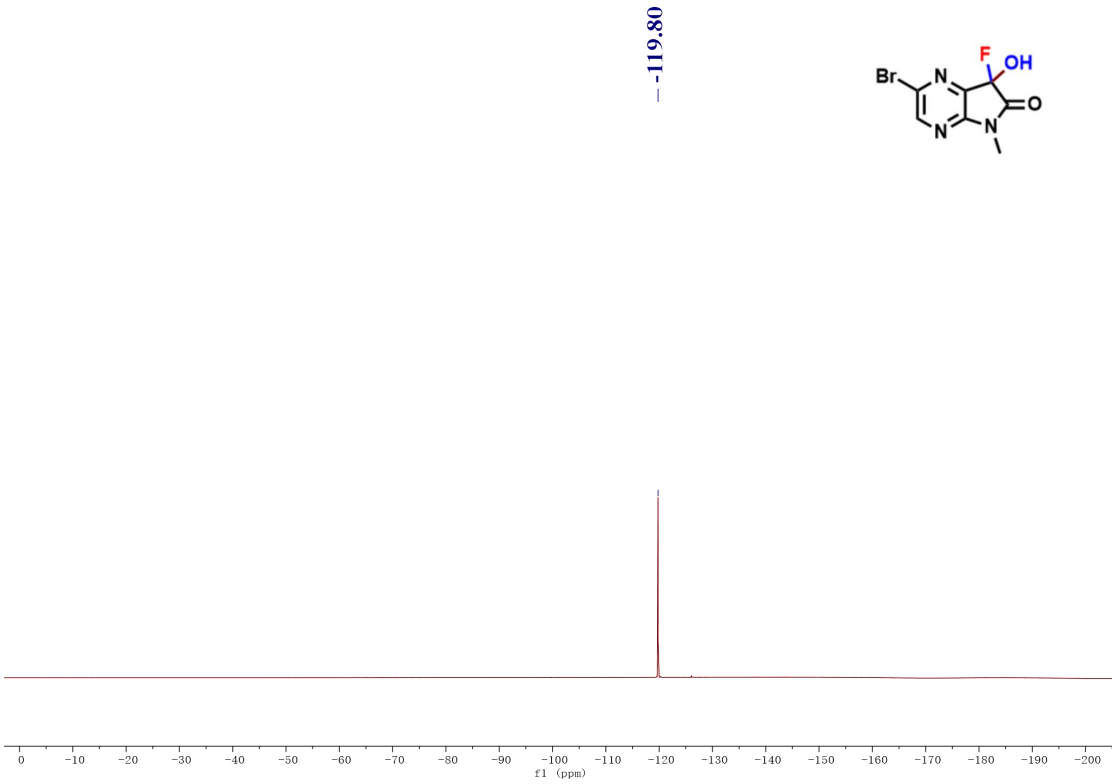
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2v**



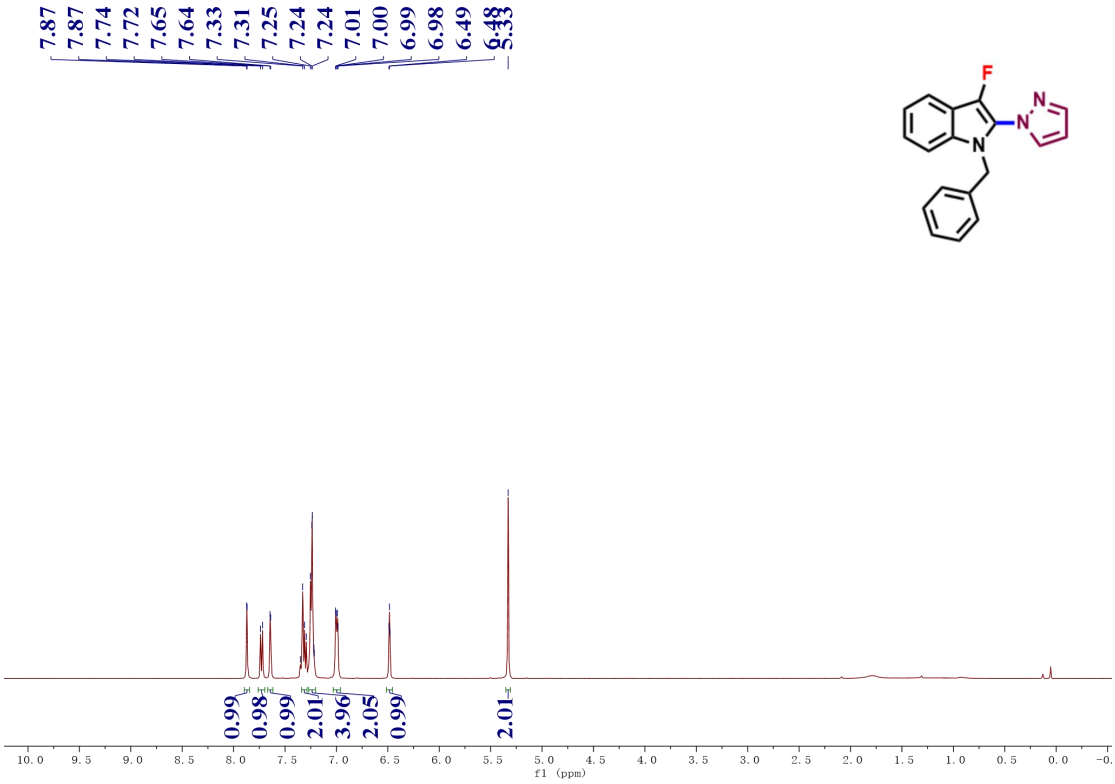
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **2w**



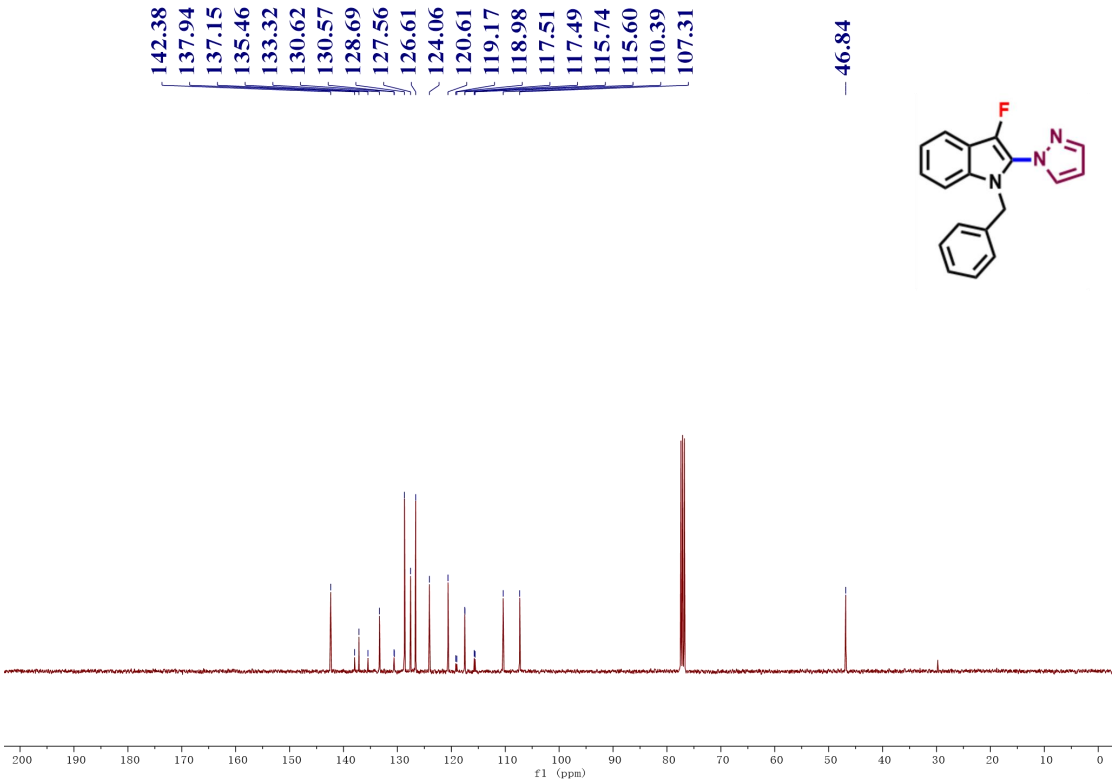
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **2w**



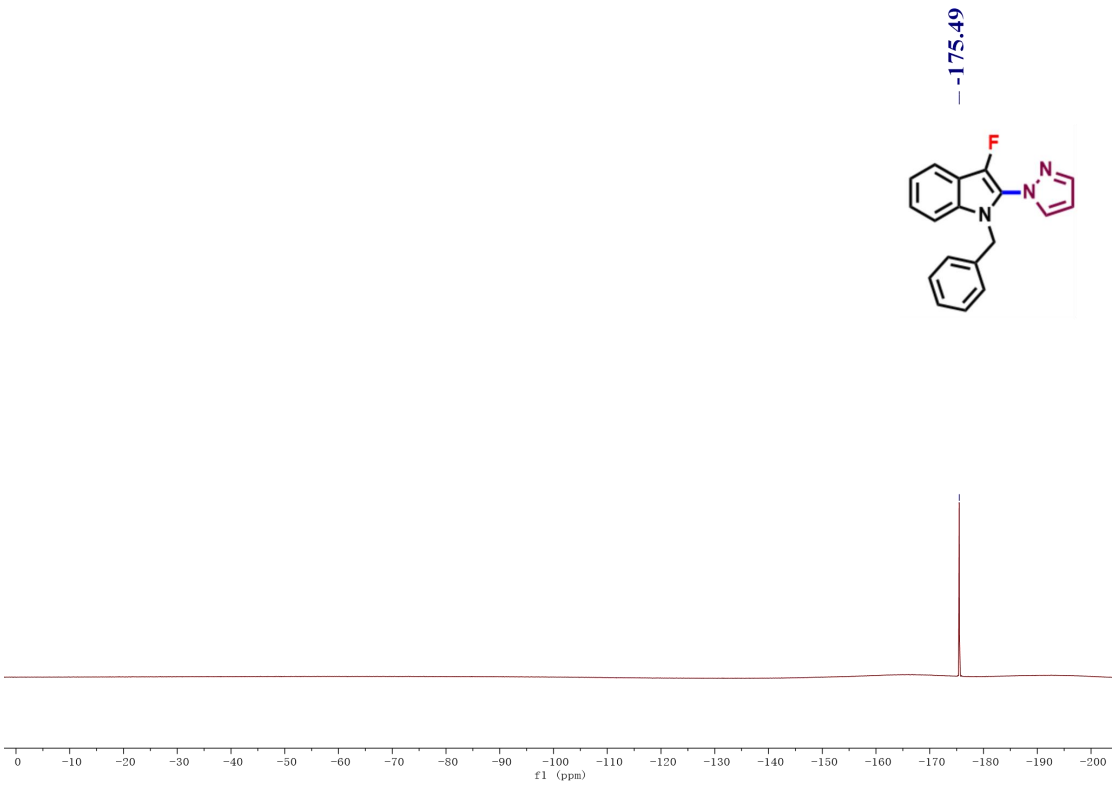
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **2w**



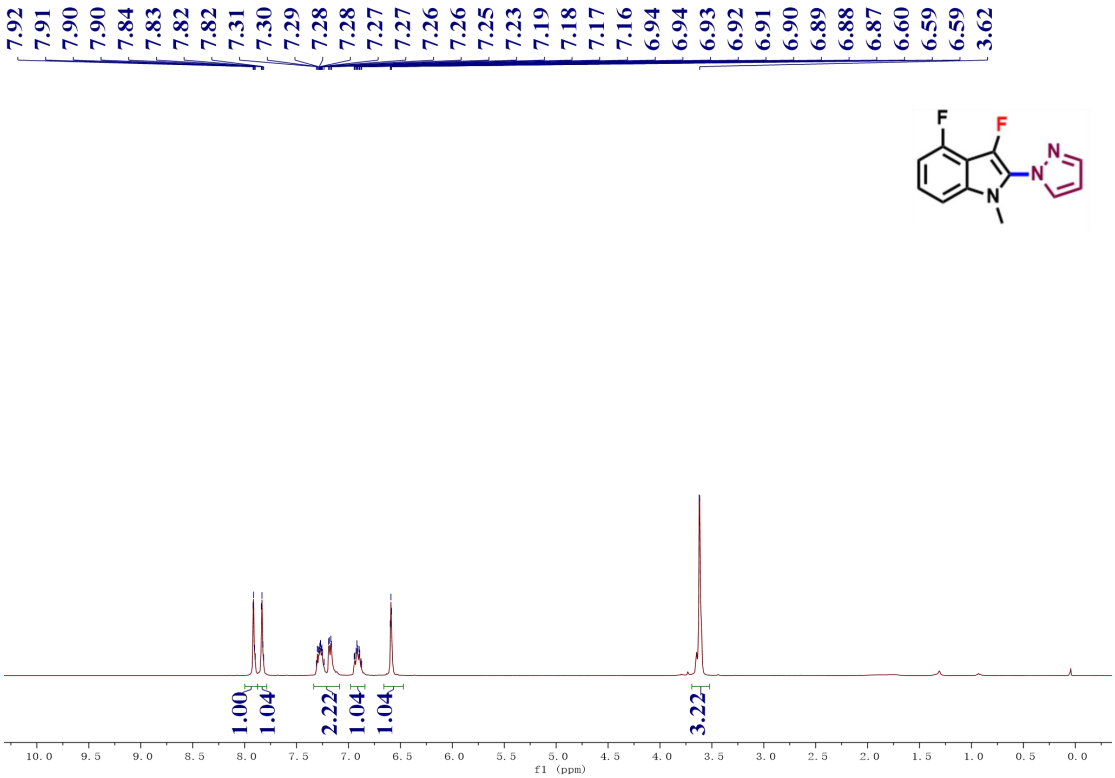
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **4a**



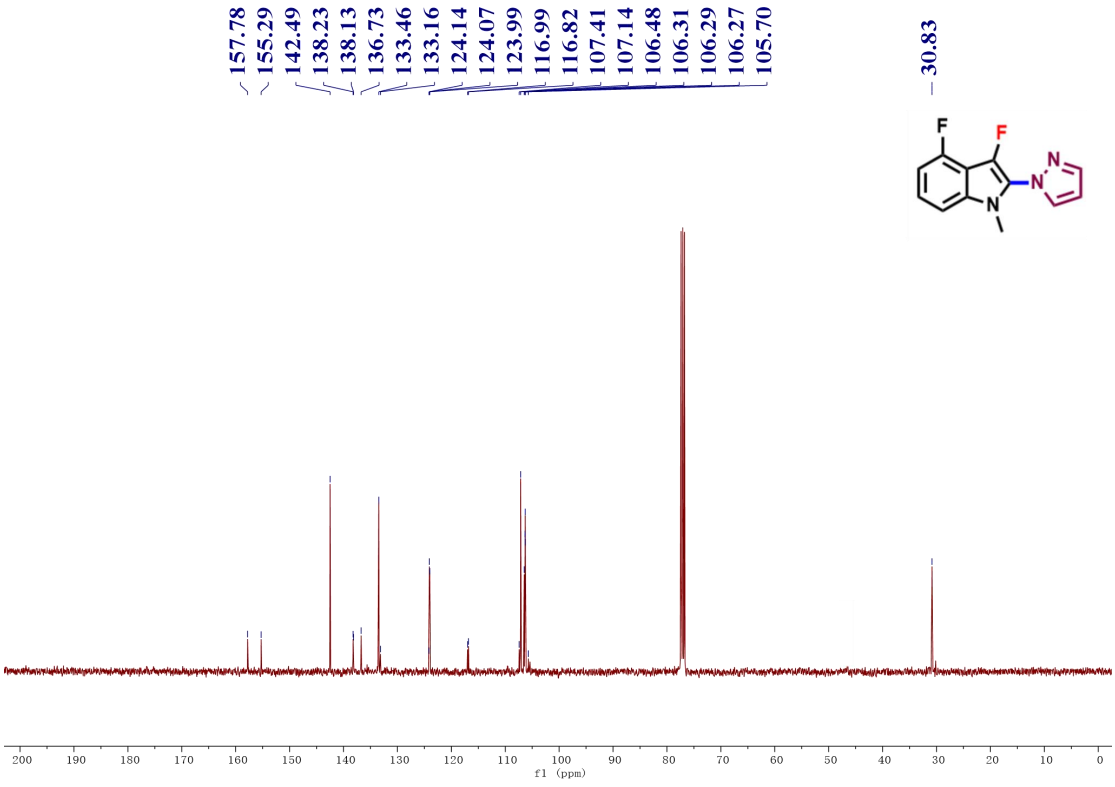
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **4a**



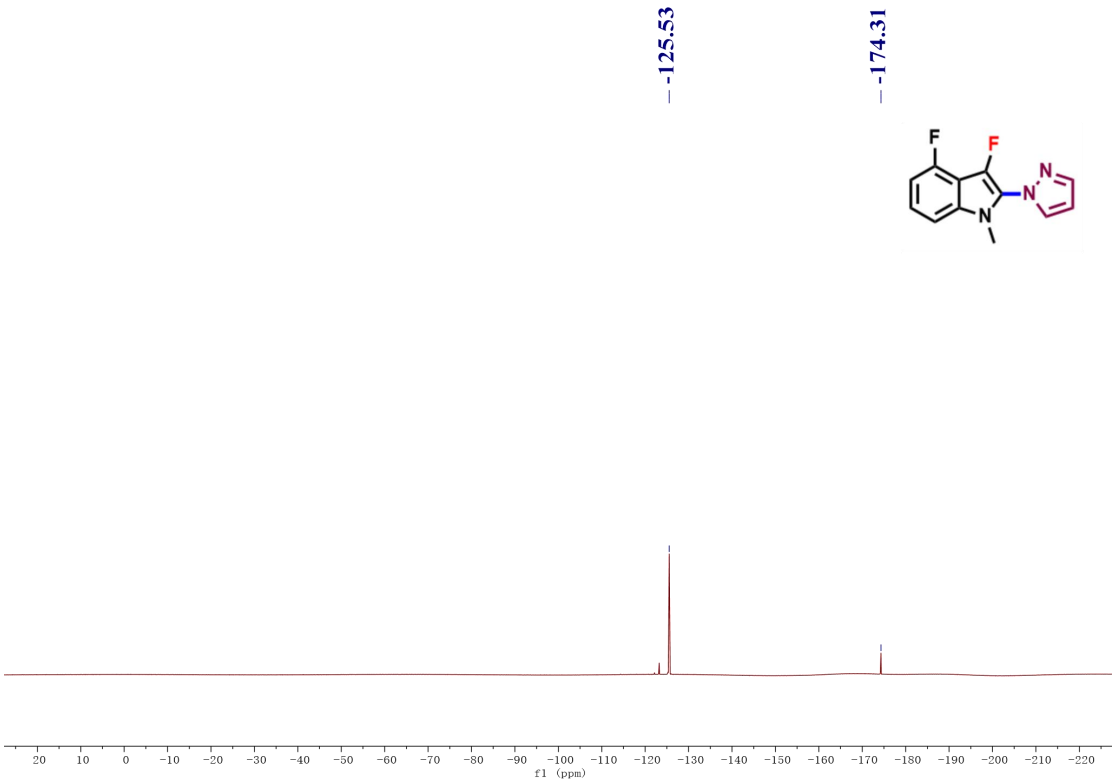
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **4a**



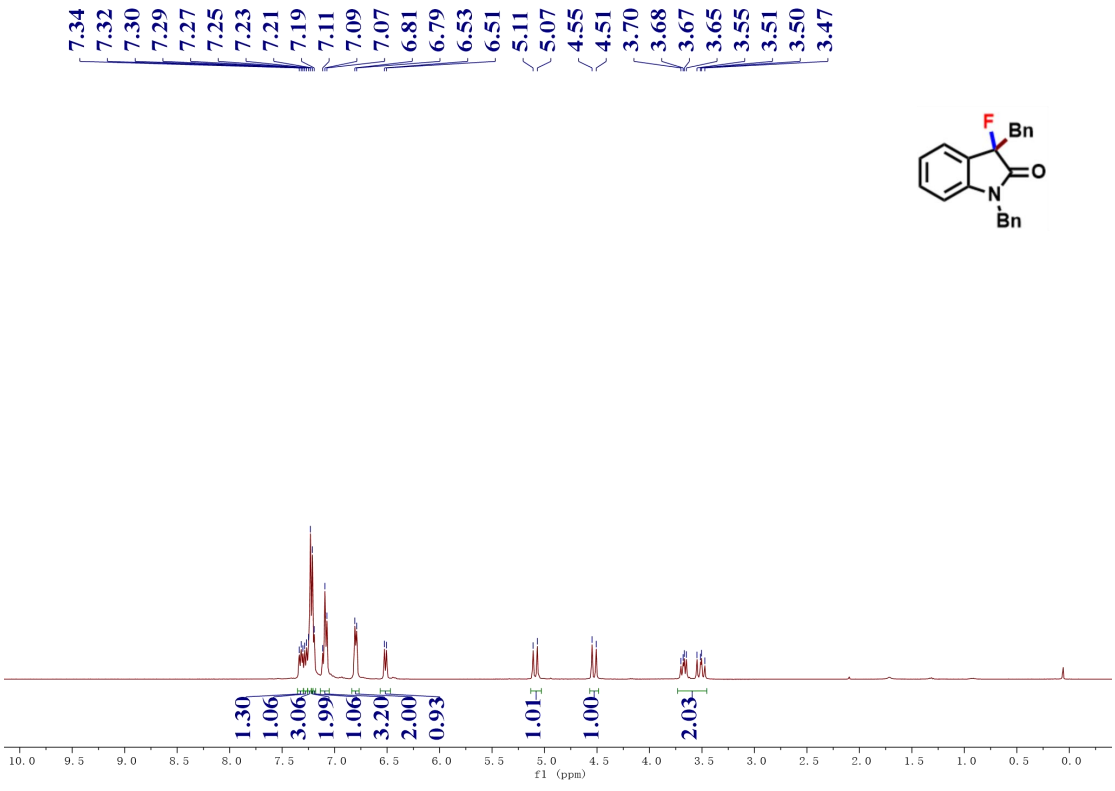
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **4b**



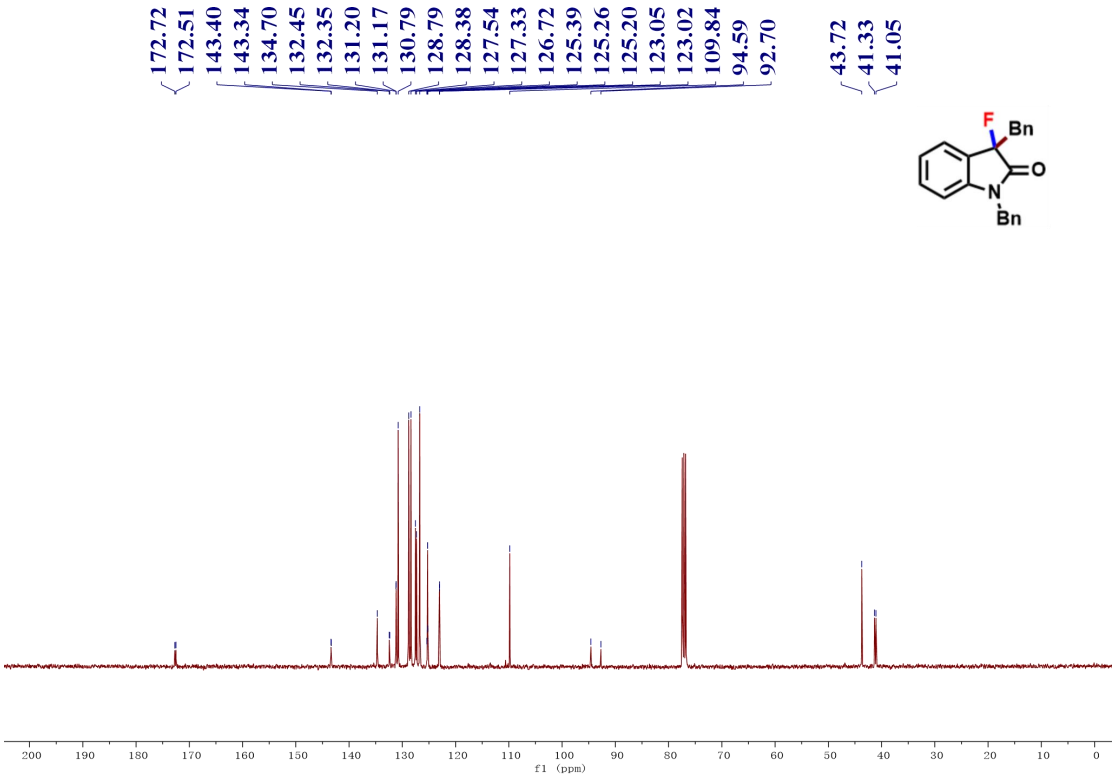
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **4b**



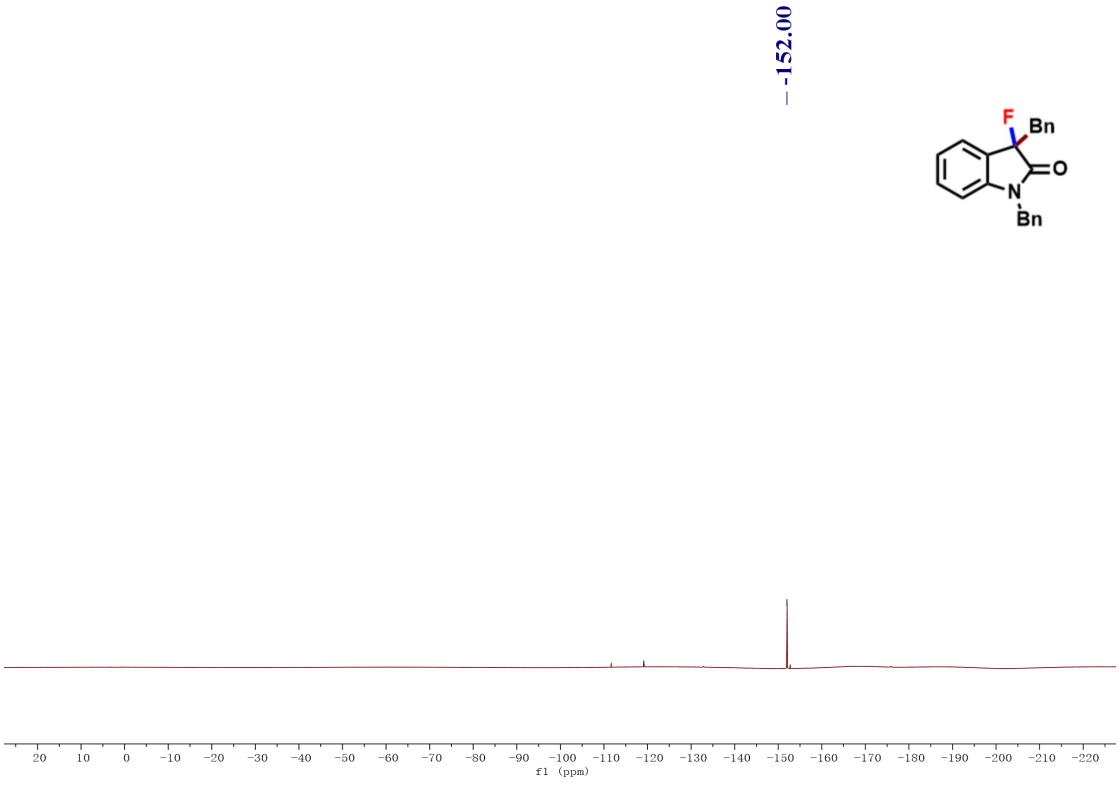
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **4b**



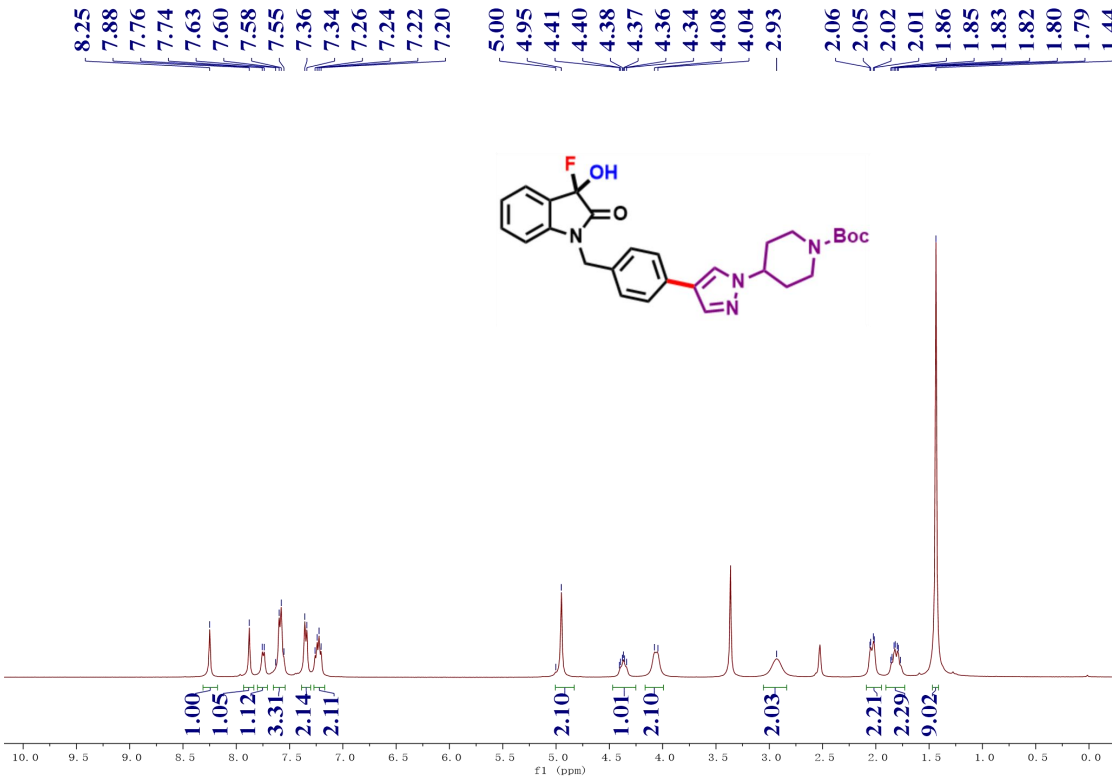
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **6**



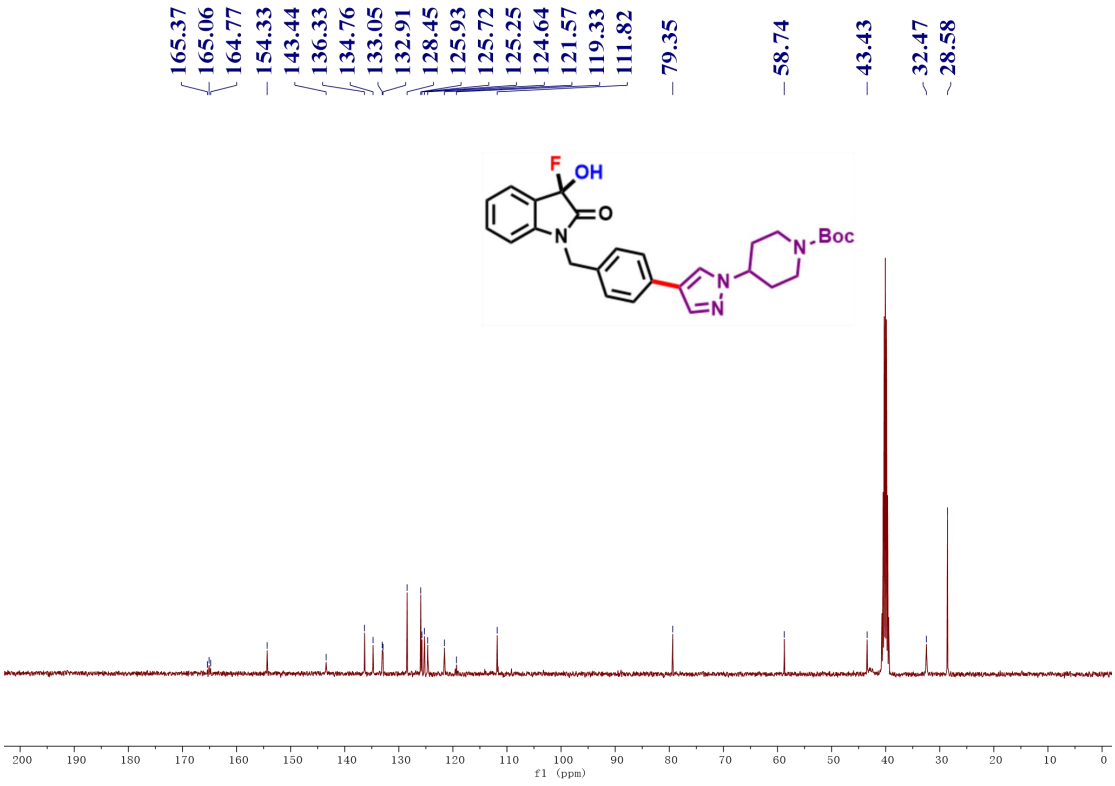
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **6**



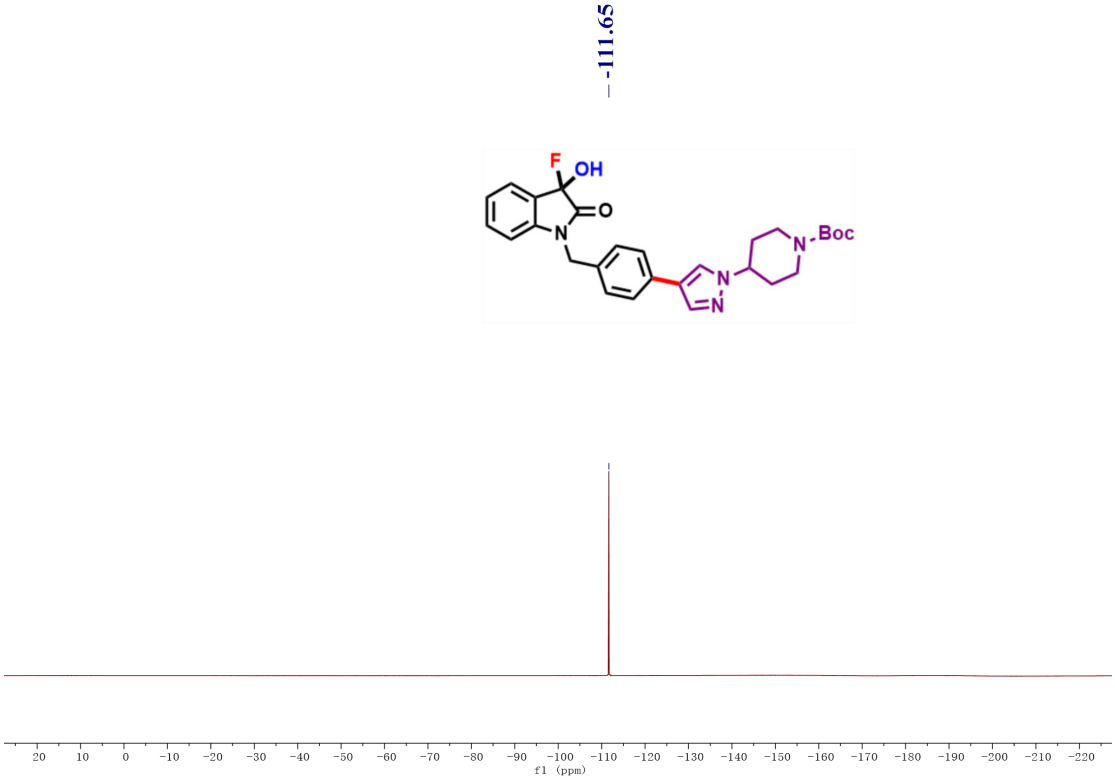
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **6**



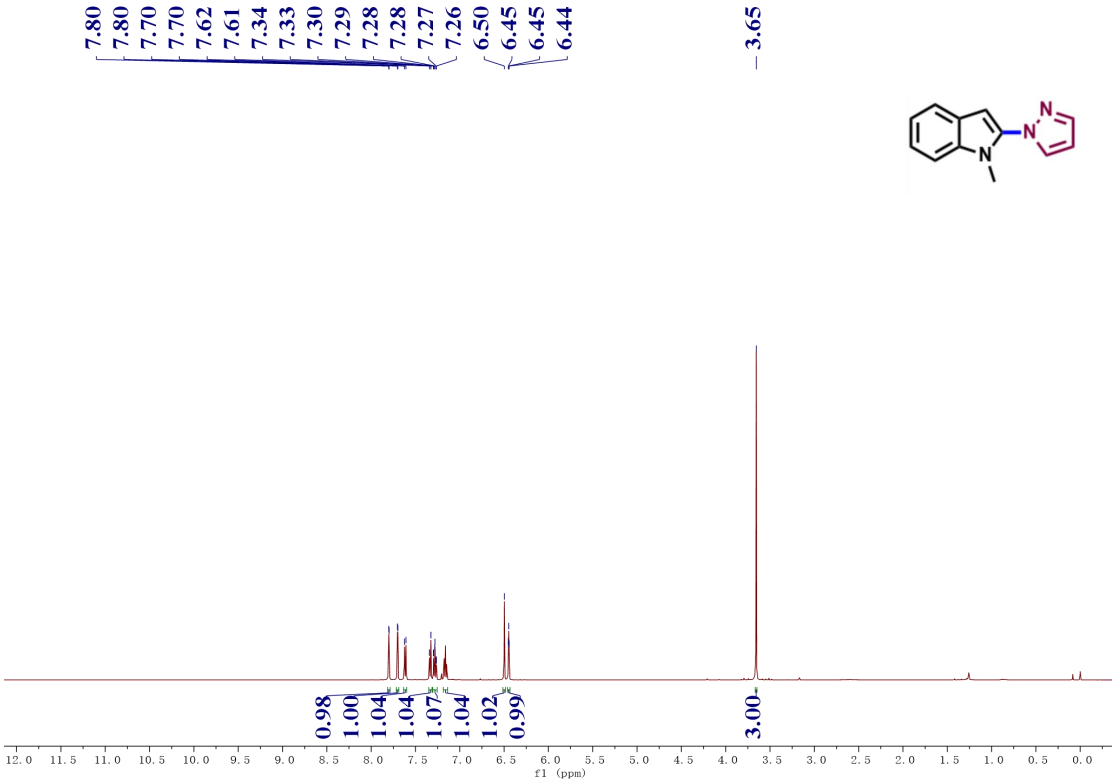
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **8**



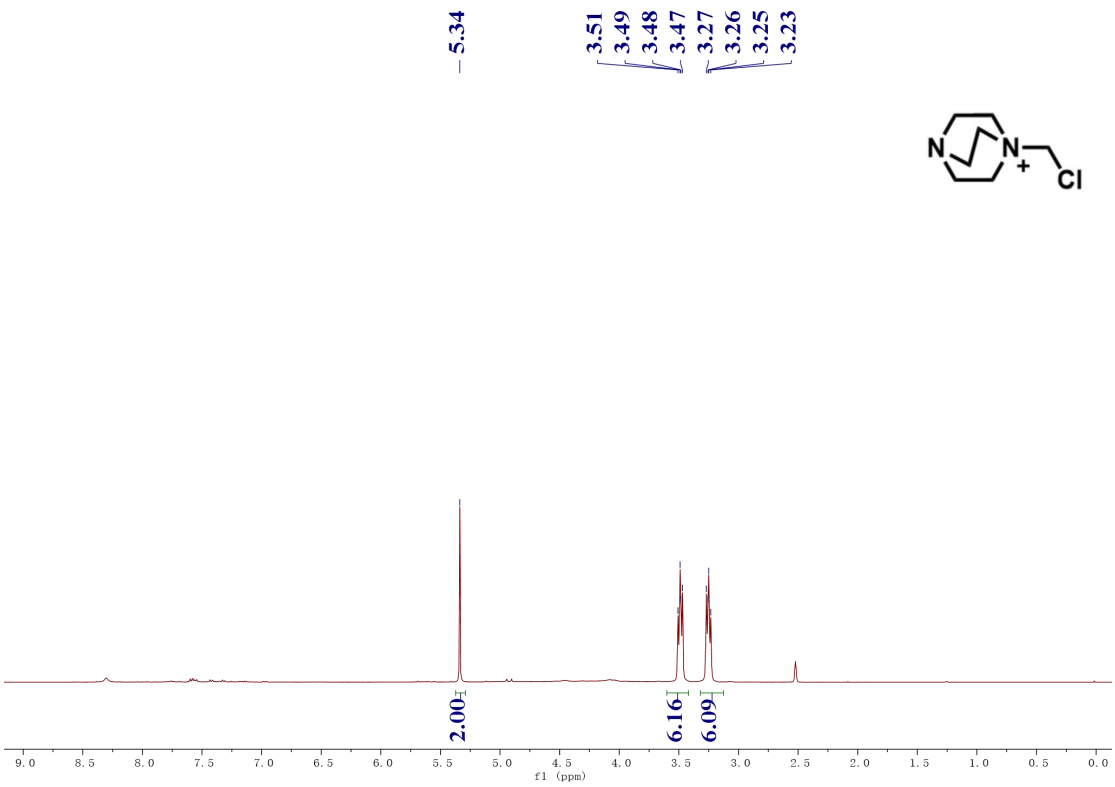
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **8**



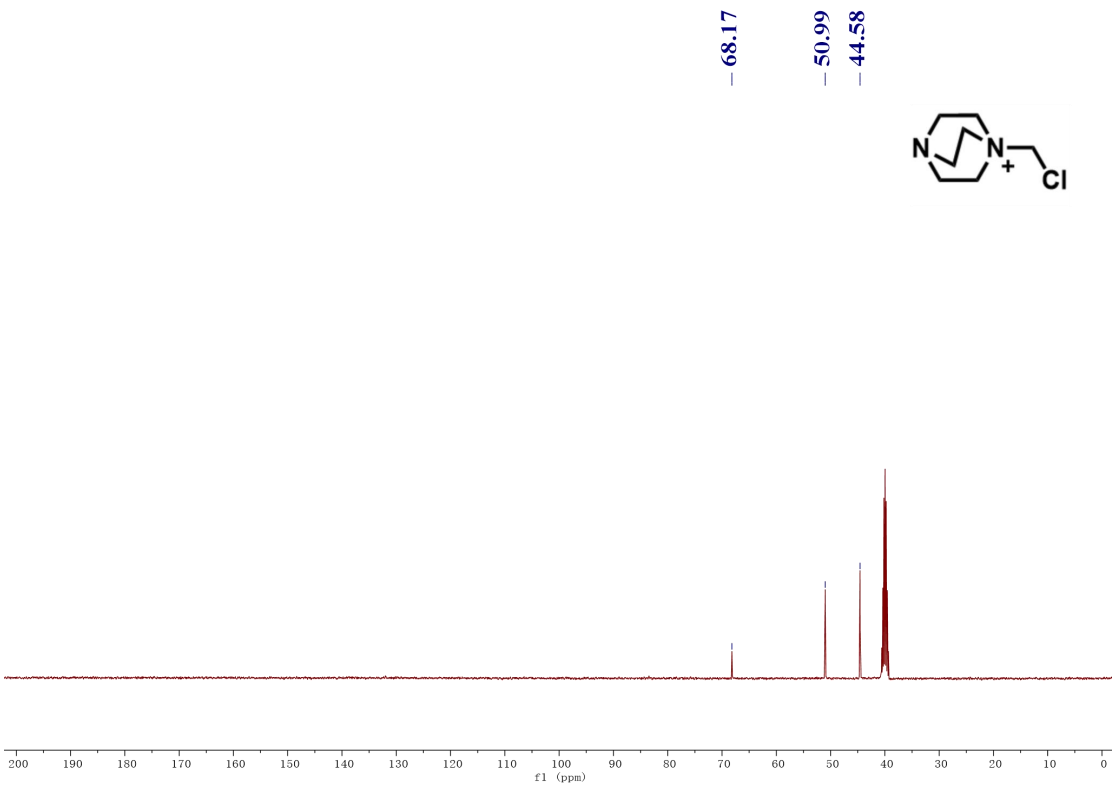
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **8**



^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **9**



^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **E**



^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **E**

6. References

[1] Beukeaw D.; Udomsasporn K.; Yotphan S. Iodine-Catalyzed Oxidative Cross-Coupling of Indoles and Azoles: Regioselective Synthesis of *N*-Linked 2-(Azol-1-yl)indole Derivatives. *J. Org. Chem.* **2015**, *80*, 3447–3454.