Highly efficient synthesis of C3-heteroaryl 3-fluorooxindoles *via* one-pot stepwise Ce(III)/photoassisted cross-dehydrogenative coupling/fluorooxidation process

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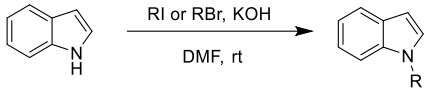
Supporting Information

1. Experimental Section

1.1 General Information

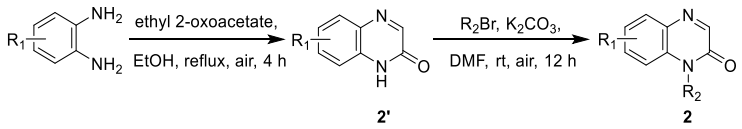
All reagents were obtained commercially and used without any prior purification. Indoles (**1**) were purchased from Aladdin. All products were isolated by recrystallization from ethanol/water, unless otherwise noted. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance 400 and 500 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.

1.2 General produce for the synthesis of *N*-protected indoles



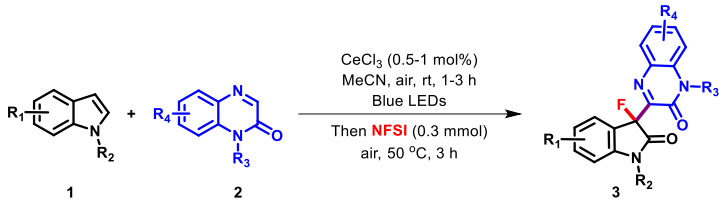
In a 50 mL flask, halogenoalkane (11 mmol in 10 mL DMF) was added in dropped-wised at 0 ℃ to a stirred solution of the corresponding indoles (10 mmol) and KOH (15 mmol) in DMF (20 mL). After stirring at 0 ℃ for 30 min, the reaction system was moved to room temperature to react for 6 h. After the completion (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 removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc 50:1-40:1) to give the desired product.

1.3 General produce for the synthesis of quinoxalin-(1*H*)-ones [1]



A mixture of o-phenylenediamine (5 mmol), ethyl 2-oxoacetate (6 mmol) and ethanol (20 mL) in a dried 50 mL round-bottom flask was stirred at reflux for 4 h. After the completion (as indicated by TLC), the reaction mixture was filtered, washed with ethanol and then dried to give quinoxalin-2(1*H*)-one 2'. Subsequently, A mixture of quinoxalin-2(*1H*)-one 2', K_2CO_3 (1.2 equiv.), corresponding halogenoalkane (1.1 equiv.) and DMF (20 ml) in a dried 50 mL round-bottom flask was stirred at room temperature overnight. 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 removed under reduced pressure, and the crude product was further purified by recrystallisation using the mixture of ethyl acetate and petroleum ether to afford desired substrates 2. All the substrates 2 are known compounds.

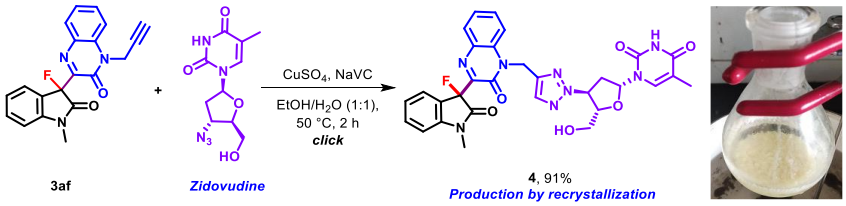
1.4 General produce for the synthesis of compound 3



To a 15 mL tube was added indoles **1** (0.2 mmol, 1.0 equiv.), quinoxalin-2(1*H*)-ones **2** (0.22 mmol, 1.1 equiv.), $CeCl_3$ (0.5-1 mol%), and MeCN (3.0 mL). The mixture was stirred at room temperature under the irradiation of blue LEDs for 1-3 h; then, NFSI (0.3 mmol, 1.5 equiv.) was added slowly in portions to the reaction mixture and reacted at 50 °C for another 3 h. After the completion (as indicated by TLC), the solvent was removed under reduced pressure. The mixed solid was subsequently dissolved by adding ethanol (10 mL), which was allowed to dissolve completely by warming to 50 °C. After falling to room temperature, water was slowly added dropwise on one side with stirring, and when the solution was turbid, cooled to 5 °C and stirred for another 20 min followed by suction filtration. The filter cake was washed twice with a mixed solution of ethyl acetate/petroleum ether (1:3), and dried in vacuo to obtain the desired products.

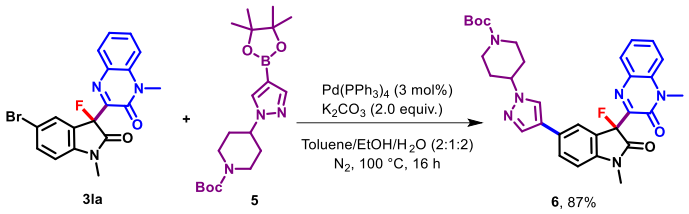
Figure S1. The product precipitated by recrystallization.

1.5 General produce for the synthesis of compound 4



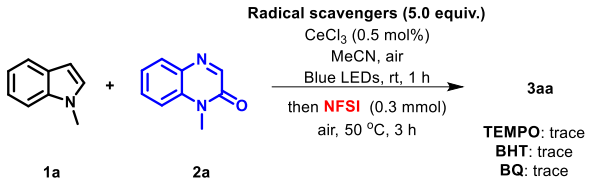
To a 50 mL round-bottom flask was added **3af** (1.0 mmol), Zidovudine (1.2 mmol), $CuSO_4$ (0.2 mmol), NaVC (Sodium ascorbate) (1.0 mmol), and EtOH/H_2O (1:1, 10 mL). Then, the reaction system reacted at 50 °C for 2 h. After the completion (as indicated by TLC), the mixture was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by recrystallisation using the mixture of ethyl acetate and petroleum ether to afford the desired product.

1.6 General produce for the synthesis of compound 6



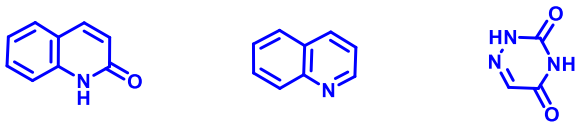
To a 50 mL round-bottom flask with a nitrogen balloon was added **3al** (1.0 mmol), **5** (1.2 mmol), $Pd(PPh_3)_4$ (3 mol%), K_2CO_3 (2.0 mmol), and Tolune/EtOH/H_2O (2:1:2, 10 mL). The mixture was stirred at 100 °C under nitrogen for 16 h. After the completion (as indicated by TLC), the mixture was then extracted with ethyl acetate and the collected organic layer was washed with brine, dried with $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc 1:1) to give the desired product.

1.7 General produce for the radical inhibition experiment



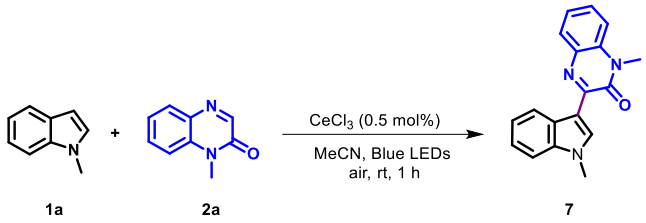
Under the optimized reaction conditions, the reaction of **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.22 mmol, 1.1 equiv.), $CeCl_3$ (0.5 mol%), and radical scavengers (5.0 equiv.) were carried under blue LEDs irradiation at room temperature for 1 h; then, NFSI (0.3 mmol, 1.5 equiv.) was added slowly in portions to the reaction mixture and reacted at 50 °C for another 3 h. No target product **3aa** was obtained in the presence of the radical scavengers including TEMPO (2,2,6,6-tetramethylpiperidine1-oxyl), BHT (2,6-ditert-butyl-4-methyl phenol), and BQ (*p*-benzoquinone), indicated that a radical pathway should be involved.

Table S1 Unreactive substrates



2r, 0% **2s**, 0% **2t**, 0%

Table S2 Study on the effect of blue light irradiation on cross-dehydrogenative coupling.



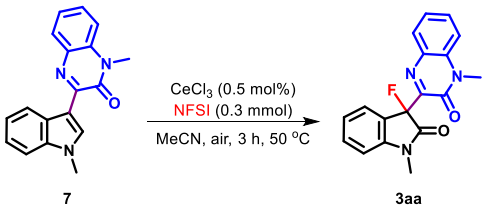
1a 2a 7

Entry	Deviation from above conditions	Yield[a,b] (%)
1	None	89
2	At 25 °C under darkness	34
3	At 55 °C under darkness	39

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.22 mmol, 1.1 equiv.), $CeCl_3$ (0.5 mol%), MeCN (3.0 mL) were stirred under blue LEDs irradiation at room temperature for 1 h. [b] Isolated yields.

The reaction of **1a** (0.2 mmol, 1.0 equiv.) and **2a** (0.22 mmol, 1.1 equiv.) were carried out under blue light irradiation or darkness to explore the effect of light irradiation on this transformation. As it can been see, the compound **7** was obtained in good yield of 89% under the blue light irradiation (entry 1), while only 34% yield of **7** formed under darkness at room temperature (entry 2). It should been noted that the yield increased to 39% when conducting the reaction under darkness at 55 °C compared to that under darkness at 25 °C (entry 3). These results suggested that the thermal pathway coexisted with the main photoassisted pathway in this transformation.

Table S3 Screening of temperature, light irradiation, and atmosphere on fluorooxidation process.



7 3aa

Entry	Deviation from above conditions	Yield[a,b] (%)
1	None	89
2	At 25 °C	54
3	Under blue LEDs at 25 and 50 °C, respectively	51, 83
4	Under N_2	85

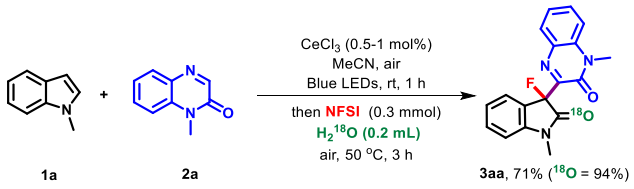
[a] Reaction conditions: **7** (0.2 mmol, 1.0 equiv.), NFSI (0.3 mmol, 1.5 equiv.),

$CeCl_3$ (0.5 mol%), MeCN (3.0 mL) were stirred at room temperature under air for 3 h. [b] Isolated yields.

A series of control experiments were carried out to investigate the effect of temperature, light irradiation, and atmosphere on fluorooxidation process. As showed in Table S3, performing the reaction at 50 °C in MeCN for 3 h produced the product **3aa** in the highest yield of 89% (entry 1), while lower yield of 51% was obtained at 25 °C (entry 2); it indicated that the heating promoted the occurrence of this process. Considering the great optical activity of compound **7** (absorption in the λ = 425-500nm) and complex **7**-Ce(III) (absorption in the λ = 425-525nm), control experiments were conducted to determine whether the blue light irradiation was capable to promote the fluorooxidation process of compound **7**. However, the yield of the reaction between **7** and NFSI did not improve under the light irradiation, indicating the light irradiation had no effect on this transformation (entry 3). Finally, studies on the atmosphere were conducted to investigate whether the oxidation process existed in the reaction, and under an inert N_2 atmosphere, the fluorooxidation process could still be carried out and afforded the product **3aa** with a satisfied yield of 85% (entry 4).

1.8 ^{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 $C_{18}H_{14}FN_3Na^{18}O_2$ $[M+Na]^+$: 348.0962, found: 348.1019.

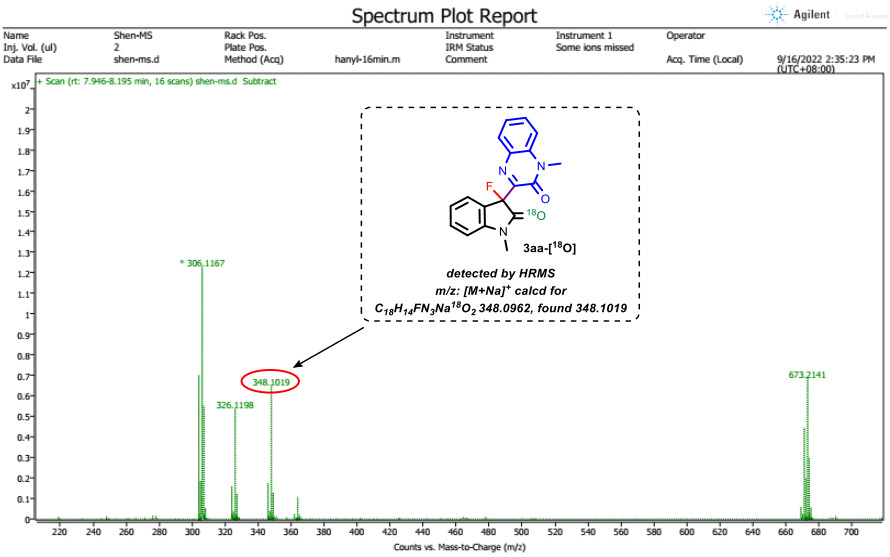


Figure S2. HRMS spectrum analysis of reaction in the presence of $H_2{}^{18}O$.

2. X-ray Structure and Data of 3aa

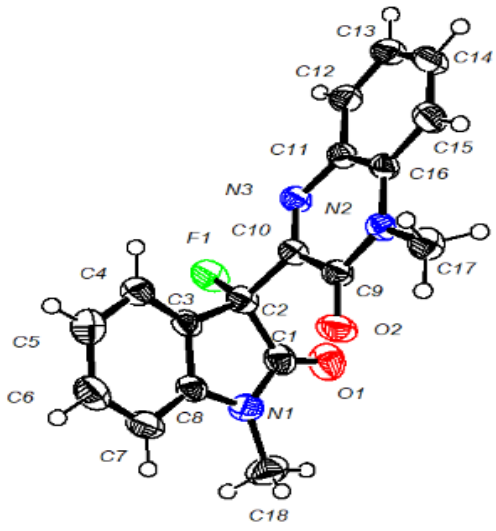


Figure S3. X-Ray crystal structure of **3aa**

Table S1. Crystallographic data and structure refinement for **4la**

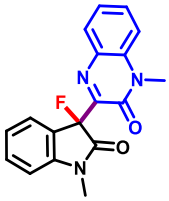
CCDC	2151231
Empirical formula	$C_{18}H_{14}FN_3O_2$
Formula weight	323.32
Temperature, K	296.15
Crystal system	monoclinic

Space group	$P2_1/c$
a, b, c, Å	11.3251(15), 11.4665(15), 11.4636(15)
α, β, γ, °	90, 93.247(2), 90
Volume, $Å^3$	1486.3(3)
Z	4
Calculated density, g/cm^3	1.445
Absorption coefficient, mm^{-1}	0.105
F (000)	672.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection, °	5.028 to 56.254
Index ranges	$-13 \leq h \leq 15$, $-14 \leq k \leq 14$, $-14 \leq l \leq 7$
Reflections collected	8881
Independent reflections	3425 [R_{int} = 0.0417, R_{sigma} = 0.0384]
Data/restraints/parameters	3425/0/219
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0643, wR_2 = 0.1333

Compound **3aa** (20 mg) was add to a 10 mL sample bottle, following to add DCM (3 mL) and n-hexane (7 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.

3. Characterization of Products

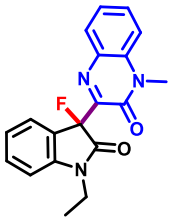
3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3aa)



Obtained as a yellow solid in 87% yield, 56.3 mg; M.p. 168-169 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.08 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.68 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.26 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.08 – 7.03 (m, 1H), 3.58 (s, 3H), 3.28 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.44, 170.24,

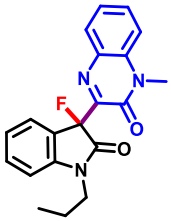
152.38, 152.16, 146.12, 146.07, 135.92, 134.68, 133.34, 132.52, 132.16, 132.13, 131.62, 131.02, 129.86, 129.53, 128.99, 127.78, 124.75, 124.36, 124.13, 123.02, 122.98, 113.87, 109.09, 26.68; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -156.16; **HRMS** (ESI+) Calculated for $C_{18}H_{14}FN_3NaO_2$ $[M+Na]^+$: 346.0962, found: 346.0971.

3-(1-Ethyl-3-fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ba)



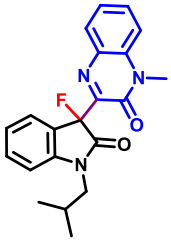
Obtained as a yellow solid in 83% yield, 56 mg; M.p. 176-177 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.65 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.52 – 7.39 (m, 2H), 7.38 – 7.27 (m, 2H), 7.07 – 6.94 (m, 2H), 4.03 – 3.81 (m, 2H), 3.60 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.00, 169.80, 152.52, 152.35, 152.31, 145.30, 145.25, 133.38, 132.48, 132.07, 132.04, 131.55, 130.99, 124.94, 124.40, 124.27, 122.77, 122.74, 113.84, 109.19, 92.92, 91.00, 35.23, 29.01, 12.22; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -157.38; **HRMS** (ESI+) Calculated for $C_{19}H_{16}FN_3NaO_2$ $[M+Na]^+$: 360.1119, found: 360.1126.

3-(3-Fluoro-2-oxo-1-propylindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ca)



Obtained as a yellow solid in 74% yield, 52 mg; M.p. 181-182 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 9.3 Hz, 2H), 7.31 (dd, *J* = 14.5, 7.7 Hz, 2H), 7.05 – 6.87 (m, 2H), 3.80 (t, *J* = 7.3 Hz, 2H), 3.58 (s, 3H), 1.87 (h, *J* = 7.5 Hz, 2H), 1.09 (td, *J* = 7.4, 2.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.38, 170.18, 152.46, 152.32, 152.29, 145.69, 145.63, 133.35, 132.42, 132.06, 132.02, 131.58, 130.91, 130.69, 124.86, 124.27, 124.15, 123.85, 122.76, 122.72, 113.88, 109.33, 92.93, 91.02, 42.18, 29.01, 20.59, 11.50; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -158.95; **HRMS** (ESI+) Calculated for $C_{20}H_{18}FN_3NaO_2$ $[M+Na]^+$: 374.1275, found: 374.1279.

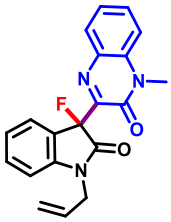
3-(3-Fluoro-1-isobutyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3da)



Obtained as a yellow solid in 71% yield, 51.9 mg; M.p. 178-179 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.1, 2.7 Hz, 1H), 7.79 – 7.66 (m, 1H), 7.58 – 7.44 (m, 2H), 7.44 – 7.33 (m, 2H), 7.06 (ddd, *J* = 21.3, 8.1, 2.6 Hz, 2H), 3.71 (dd, *J* = 7.5, 2.6 Hz, 2H), 3.67 (d, *J*

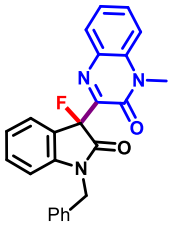
= 2.7 Hz, 3H), 2.36 (dtd, *J* = 13.6, 6.9, 2.6 Hz, 1H), 1.19 (dd, *J* = 6.6, 2.6 Hz, 3H), 1.15 (dd, *J* = 6.7, 2.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.72, 170.52, 152.54, 152.38, 152.32, 146.15, 146.10, 133.47, 132.52, 132.06, 132.02, 131.63, 131.05, 124.90, 124.43, 124.33, 124.25, 122.80, 122.77, 113.91, 109.61, 93.00, 91.10, 48.30, 29.08, 27.35, 20.49; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -161.87; **HRMS** (ESI+) Calculated for $C_{21}H_{20}FN_3NaO_2$ $[M+Na]^+$: 388.1432, found: 388.1427.

3-(1-Allyl-3-fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ea)



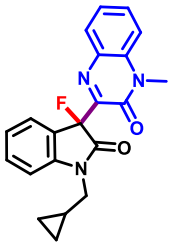
Obtained as a yellow solid in 64% yield, 44.7 mg; M.p. 171-172 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 8.1, 3.3 Hz, 1H), 7.67 (dd, *J* = 9.3, 6.4 Hz, 1H), 7.48 (td, *J* = 7.6, 3.0 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.30 (dd, *J* = 8.5, 3.5 Hz, 1H), 7.02 (dp, *J* = 8.1, 5.1, 4.1 Hz, 1H), 6.95 (dt, *J* = 8.2, 4.0 Hz, 1H), 6.08 – 5.91 (m, 1H), 5.53 (dd, *J* = 18.9, 4.3 Hz, 1H), 5.34 (dt, *J* = 8.9, 4.1 Hz, 1H), 4.59 – 4.50 (m, 1H), 4.49 – 4.39 (m, 1H), 3.63 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.17, 169.89, 152.44, 152.34, 145..36, 133.41, 132.53, 131.98, 131.57, 131.09, 130.95, 129.52, 124.80, 124.32, 122.94, 118.15, 113.81, 110.04, 42.89, 29.05; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -159.42; **HRMS** (ESI+) Calculated for $C_{20}H_{16}FN_3NaO_2$ $[M+Na]^+$: 372.1119, found: 372.1127.

3-(1-Benzyl-3-fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3fa)



Obtained as a white solid in 75% yield, 59.9 mg; M.p. 186-187 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 9.0 Hz, 1H), 7.68 (t, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (q, *J* = 7.3 Hz, 3H), 7.33 (t, *J* = 6.8 Hz, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.19 – 5.00 (m, 2H), 3.66 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.66, 170.47, 152.45, 152.22, 145.29, 145.24, 135.26, 133.45, 132.56, 132.00, 131.97, 131.62, 131.08, 128.89, 127.73, 127.39, 124.85, 124.33, 123.05, 123.02, 113.86, 110.24, 44.42, 29.06; **^{19}F NMR** (471 MHz, DMSO-d_6) δ -160.41; **HRMS** (ESI+) Calculated for $C_{24}H_{18}FN_3NaO_2$ $[M+Na]^+$: 422.1275, found: 422.1279.

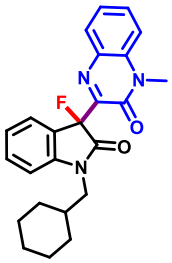
3-(1-(Cyclopropylmethyl)-3-fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ga)



Obtained as a white solid in 75% yield, 54.5 mg; M.p. 181-182 °C. **^{1}H NMR** (400

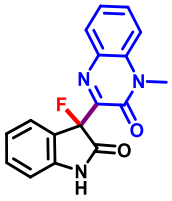
MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.67 (td, *J* = 7.9, 7.2, 1.6 Hz, 1H), 7.51 – 7.41 (m, 2H), 7.38 – 7.29 (m, 2H), 7.11 – 6.99 (m, 2H), 3.77 (dd, *J* = 6.8, 1.8 Hz, 2H), 3.62 (s, 3H), 1.33 (dp, *J* = 13.9, 7.5 Hz, 1H), 0.65 (p, *J* = 8.8 Hz, 2H), 0.51 (dd, *J* = 4.9, 2.6 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.44, 170.24, 152.57, 152.34, 145.88, 145.83, 133.45, 132.51, 132.04, 132.01, 131.52, 131.06, 130.68, 124.93, 124.26, 124.14, 123.91, 122.77, 122.74, 113.80, 109.55, 44.98, 44.83, 29.02, 9.34, 4.12, 4.07, 4.03, 3.97; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -157.52; **HRMS** (ESI+) Calculated for $C_{21}H_{18}FN_3NaO_2$ $[M+Na]^+$: 386.1275, found: 386.1284.

3-(1-(Cyclohexylmethyl)-3-fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ha)



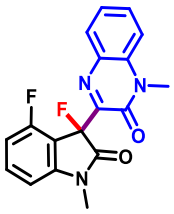
Obtained as a white solid in 71% yield, 57.6 mg; M.p. 191-192 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.9 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.52 – 7.40 (m, 2H), 7.39 – 7.28 (m, 2H), 7.06 – 6.94 (m, 2H), 3.69 (tt, *J* = 14.0, 7.2 Hz, 2H), 3.62 (d, *J* = 3.2 Hz, 3H), 2.04 – 1.94 (m, 2H), 1.93 – 1.85 (m, 1H), 1.85 – 1.77 (m, 2H), 1.72 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.30 (tt, *J* = 22.5, 10.5 Hz, 3H), 1.21 – 1.09 (m, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.40, 170.20, 152.11, 152.06, 151.90, 146.32, 146.27, 133.70, 132.56, 132.53, 132.24, 132.13, 130.40, 125.04, 124.71, 124.32, 124.15, 123.10, 123.07, 115.69, 110.48, 46.43, 36.41, 30.73, 30.69, 29.40, 26.39, 25.81, 25.78; **^{19}F NMR** (471 MHz, DMSO-d_6) δ -159.67; **HRMS** (ESI+) Calculated for $C_{24}H_{24}FN_3NaO_2$ $[M+Na]^+$: 428.1745, found: 428.1751.

3-(3-Fluoro-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ia)



Obtained as a yellow solid in 73% yield, 45.2 mg; M.p. 241-242 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.96 (s, 1H), 8.11 – 7.98 (m, 1H), 7.80 – 7.69 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.44 – 7.33 (m, 1H), 7.20 (dt, *J* = 7.4, 1.9 Hz, 1H), 7.07 – 6.88 (m, 2H), 3.58 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.60, 171.41, 152.32, 152.15, 152.11, 145.22, 145.16, 133.64, 132.52, 132.49, 132.14, 130.40, 125.29, 125.12, 124.94, 124.68, 122.63, 122.60, 115.64, 111.10, 93.72, 91.84, 29.36; **^{19}F NMR** (471 MHz, DMSO-d_6) δ -162.11; **HRMS** (ESI+) Calculated for $C_{17}H_{12}FN_3NaO_2$ $[M+Na]^+$: 332.0806, found: 332.0812.

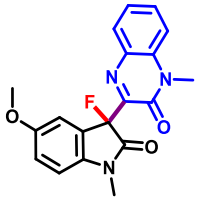
3-(3,4-Difluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ja)



Obtained as a yellow solid in 67% yield, 45.7 mg; M.p. 213-214 °C. **^{1}H NMR** (400

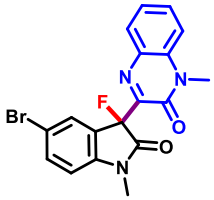
MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.52 – 7.36 (m, 3H), 6.83 – 6.70 (m, 2H), 3.64 (d, *J* = 1.4 Hz, 3H), 3.38 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.73, 169.53, 160.66, 158.14, 152.38, 151.14, 150.92, 148.07, 134.08, 133.99, 133.29, 132.69, 131.69, 131.27, 124.45, 113.82, 111.08, 111.05, 110.88, 105.10, 91.58, 89.65, 29.03, 27.14; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -116.21, -165.78; **HRMS** (ESI+) Calculated for $C_{18}H_{13}F_2N_3NaO_2$ $[M+Na]^+$: 364.0868, found: 364.0872.

3-(3-Fluoro-5-methoxy-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ka)



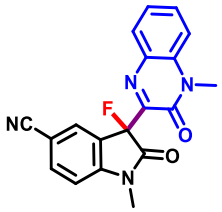
Obtained as a white solid in 81% yield, 57.2 mg; M.p. 197-198 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.05 (m, 1H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.01 – 6.81 (m, 3H), 3.73 (s, 3H), 3.62 (s, 3H), 3.35 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.13, 169.93, 156.15, 156.12, 152.37, 139.48, 133.39, 132.51, 131.63, 131.08, 125.09, 124.37, 116.59, 116.56, 113.85, 111.84, 109.57, 55.88, 29.04, 26.77; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -160.86; **HRMS** (ESI+) Calculated for $C_{19}H_{16}FN_3NaO_3$ $[M+Na]^+$: 376.1068, found: 376.1076.

3-(5-Bromo-3-fluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3la)



Obtained as a yellow solid in 72% yield, 57.9 mg; M.p. 201-202 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.64 (m, 1H), 7.57 (dt, *J* = 8.4, 2.1 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.43 – 7.34 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 3.64 (s, 3H), 3.37 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.84, 169.64, 152.36, 151.73, 151.51, 145.18, 145.13, 134.82, 134.79, 133.37, 132.56, 131.85, 131.16, 127.95, 125.95, 124.51, 115.43, 115.39, 113.91, 110.53, 90.34, 29.09, 26.79; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -163.51; **HRMS** (ESI+) Calculated for $C_{18}H_{13}BrFN_3NaO_2$ $[M+Na]^+$: 424.0067, found: 424.0059.

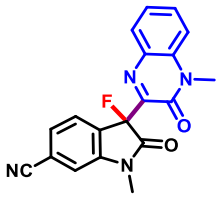
3-Fluoro-1-methyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-oxoindoline-5-carbonitrile (3ma)



Obtained as a yellow solid in 69% yield, 48 mg; M.p. 207-208 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 (dt, *J* = 8.2, 1.6 Hz, 1H), 7.74 – 7.68 (m, 1H), 7.56 (q, *J* = 1.6 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J*

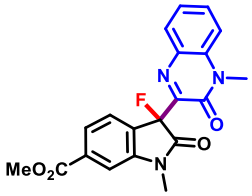
= 8.2 Hz, 1H), 3.64 (s, 3H), 3.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.02, 169.82, 152.37, 152.34, 151.07, 149.79, 149.74, 137.11, 137.08, 133.30, 132.55, 132.16, 131.19, 128.12, 125.23, 125.05, 124.74, 118.39, 114.04, 109.61, 106.29, 106.26, 91.52, 89.59, 29.14, 26.98; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -164.41; **HRMS** (ESI+) Calculated for $C_{19}H_{13}FN_4NaO_2$ $[M+Na]^+$: 371.0915, found: 371.0910.

3-Fluoro-1-methyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-oxoindoline-6-carbonitrile (3na)



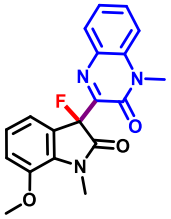
Obtained as a yellow solid in 71% yield, 49.5 mg; M.p. 210-211 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 – 8.11 (m, 1H), 7.75 – 7.67 (m, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.19 (s, 1H), 3.64 (s, 3H), 3.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.59, 169.39, 152.35, 151.21, 150.99, 146.85, 133.33, 132.58, 132.08, 131.21, 128.79, 128.61, 127.50, 127.47, 125.25, 124.67, 118.11, 115.61, 113.99, 111.52, 91.79, 89.86, 29.09, 26.93; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -165.12; **HRMS** (ESI+) Calculated for $C_{19}H_{13}FN_4NaO_2$ $[M+Na]^+$: 371.0915, found: 371.0911.

Methyl 3-fluoro-1-methyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-oxoindoline-6-carbo-xylate (3oa)



Obtained as a yellow solid in 73% yield, 55.7 mg; M.p. 215-216 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.65 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.59 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.29 (m, 2H), 3.93 (s, 3H), 3.58 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.97, 169.81, 166.10, 166.09, 152.31, 152.28, 151.68, 151.50, 146.32, 146.28, 133.69, 133.67, 133.26, 132.46, 131.81, 131.00, 128.57, 128.43, 124.76, 124.74, 124.51, 124.45, 113.91, 109.63, 92.06, 90.53, 52.51, 28.98, 26.83; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -164.44; **HRMS** (ESI+) Calculated for $C_{20}H_{16}FN_3NaO_4$ $[M+Na]^+$: 404.1017, found: 404.1012.

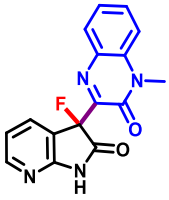
3-(3-Fluoro-7-methoxy-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3pa)



Obtained as a white solid in 83% yield, 58.7 mg; M.p. 197-198 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.02 – 6.94 (m, 2H), 6.90 (dt, *J* = 7.1, 1.9 Hz, 1H), 3.90 (s, 3H), 3.63 (s,

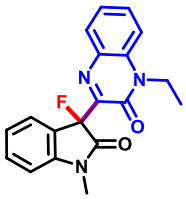
3H), 3.61 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.64, 170.44, 152.36, 145.73, 133.32, 132.51, 131.57, 130.98, 124.32, 123.67, 123.64, 117.15, 115.97, 115.94, 113.86, 92.76, 90.86, 56.05, 30.03, 29.02; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -161.94; **HRMS** (ESI+) Calculated for $C_{19}H_{16}FN_3NaO_3$ $[M+Na]^+$: 376.1068, found: 376.1071.

3-(3-Fluoro-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3qa)



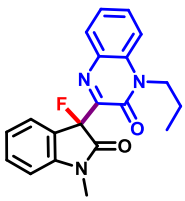
Obtained as a white solid in 47% yield, 29.2 mg; M.p. 259-260 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 8.23 – 8.18 (m, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.65 (s, 1H), 7.54 (dq, J = 7.3, 4.7, 3.9 Hz, 2H), 6.97 (dd, J = 7.4, 5.3 Hz, 1H), 3.59 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 172.74, 157.62, 152.22, 150.93, 149.45, 133.97, 132.44, 132.04, 131.98, 130.49, 124.78, 123.99, 118.87, 115.71, 68.27, 55.41, 29.66; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -163.49; **HRMS** (ESI+) Calculated for $C_{17}H_{13}FN_4NaO_2$ $[M+Na]^+$: 347.0915, found: 347.0924.

1-Ethyl-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)quinoxalin-2(1*H*)-one (3ab)



Obtained as a yellow solid in 82% yield, 55.3 mg; M.p. 167-168 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.44 (dt, J = 24.3, 7.9 Hz, 3H), 7.32 (d, J = 7.0 Hz, 1H), 7.13 – 6.87 (m, 2H), 4.24 (q, J = 7.2 Hz, 2H), 3.39 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.41, 170.21, 152.42, 152.20, 151.87, 146.11, 146.06, 132.83, 132.35, 132.12, 132.08, 131.55, 131.34, 124.75, 124.24, 124.16, 123.00, 122.97, 113.72, 109.09, 92.85, 90.94, 37.40, 26.71, 12.50; **HRMS** (ESI+) Calculated for $C_{19}H_{16}FN_3NaO_2$ $[M+Na]^+$: 360.1119, found: 360.1124.

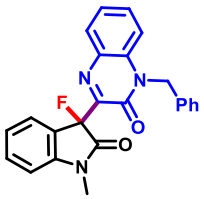
3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-1-propylquinoxalin-2(1*H*)-one (3ac)



Obtained as a yellow solid in 78% yield, 54.8 mg; M.p. 172-173 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.9 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.34 (dd, J = 21.7, 7.8 Hz, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 4.12 (t, J = 8.3 Hz, 2H), 3.39 (s, 3H), 1.74 (dt, J = 15.4, 8.0 Hz, 2H), 0.98 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.40, 170.20, 152.10, 146.11, 132.79, 132.60, 132.06, 132.03, 131.43, 131.31, 124.69, 124.30, 124.11, 122.97, 122.94, 113.84, 109.08, 92.84, 90.93, 43.76, 26.70, 20.58, 11.23; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -162.12; **HRMS** (ESI+) Calculated for $C_{20}H_{18}FN_3NaO_2$

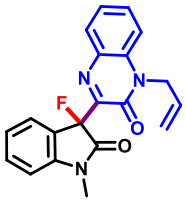
[M+Na]$^+$: 374.1275, found: 374.1280.

1-Benzyl-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)quinoxalin-2(1*H*)-one (3ad)



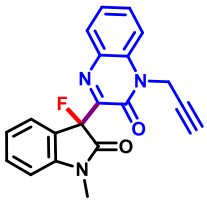
Obtained as a white solid in 76% yield, 60.7 mg; M.p. 187-188 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.34 (tt, *J* = 7.9, 1.7 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.19 – 7.16 (m, 2H), 7.16 – 7.12 (m, 2H), 7.02 – 6.98 (m, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.41 – 5.19 (m, 2H), 3.26 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.29, 169.13, 151.45, 145.09, 133.41, 131.71, 131.56, 131.11, 130.44, 130.06, 127.96, 126.76, 125.58, 123.64, 123.30, 123.14, 121.94, 113.65, 108.07, 91.67, 90.14, 44.70, 25.64; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -162.51; **HRMS** (ESI+) Calculated for $C_{24}H_{18}FN_3NaO_2$ [M+Na]$^+$: 422.1275, found: 422.1268.

1-Allyl-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)quinoxalin-2(1*H*)-one (3ae)



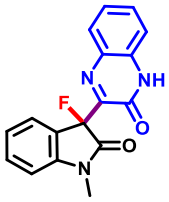
Obtained as a yellow solid in 67% yield, 46.8 mg; M.p. 179-180 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.44 (q, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.8 Hz, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.83 (ddt, *J* = 15.7, 10.3, 5.1 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.11 (d, *J* = 17.3 Hz, 1H), 4.88 – 4.74 (m, 2H), 3.37 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.37, 170.17, 152.43, 152.20, 151.98, 146.10, 146.05, 132.68, 132.62, 132.15, 132.12, 131.48, 131.11, 130.21, 124.71, 124.32, 124.19, 124.01, 123.03, 123.00, 118.46, 114.48, 109.14, 92.86, 90.95, 44.46, 26.70; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -163.11; **HRMS** (ESI+) Calculated for $C_{20}H_{16}FN_3NaO_2$ [M+Na]$^+$: 372.1119, found: 372.1124.

3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3af)



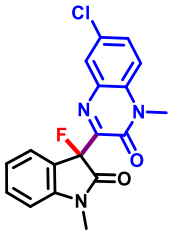
Obtained as a white solid in 72% yield, 50.0 mg; M.p. 186-187 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.60 – 7.40 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 5.07 – 4.83 (m, 2H), 3.38 (s, 3H), 2.29 (s, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.26, 170.06, 152.30, 152.07, 151.39, 146.09, 132.70, 132.23, 132.19, 131.88, 131.66, 131.21, 124.90, 124.71, 124.01, 123.83, 123.08, 123.05, 114.44, 109.11, 92.80, 90.88, 76.15, 73.96, 31.48, 26.70; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -162.52; **HRMS** (ESI+) Calculated for $C_{20}H_{14}FN_3NaO_2$ [M+Na]$^+$: 370.0962, found: 370.0968.

3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)quinoxalin-2(1*H*)-one (3ag)



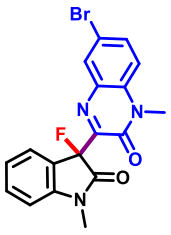
Obtained as a yellow solid in 71% yield, 43.9 mg; M.p. 260-261 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.70 (s, 1H), 7.99 (dd, J = 8.2, 1.4 Hz, 1H), 7.64 (ddd, J = 8.5, 7.3, 1.4 Hz, 1H), 7.49 (tt, J = 7.8, 1.7 Hz, 1H), 7.42 (ddd, J = 16.1, 8.0, 1.3 Hz, 2H), 7.27 (ddd, J = 7.5, 2.6, 1.2 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 3.26 (s, 3H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 170.06, 169.90, 153.44, 152.52, 146.28, 132.61, 131.92, 131.64, 129.59, 124.94, 124.47, 124.14, 123.35, 116.31, 110.07, 92.90, 91.39, 26.88; **^{19}F NMR** (471 MHz, DMSO-d_6) δ -161.45; **HRMS** (ESI+) Calculated for $C_{17}H_{12}FN_3NaO_2$ $[M+Na]^+$: 332.0806, found: 332.0813.

6-Chloro-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ah)



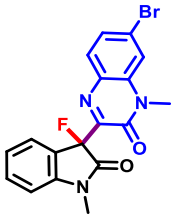
Obtained as a yellow solid in 67% yield, 47.9 mg; M.p. 213-214 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.13 (d, J = 2.0 Hz, 1H), 7.62 (dd, J = 8.9, 2.0 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 3.60 (s, 3H), 3.37 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 170.09, 169.88, 153.72, 153.49, 151.96, 146.02, 132.86, 132.23, 132.19, 131.96, 131.54, 130.20, 129.70, 124.70, 123.75, 123.57, 123.00, 122.97, 114.99, 109.07, 92.69, 90.77, 29.15, 26.62; **^{19}F NMR** (471 MHz, Chloroform-d) δ -163.37; **HRMS** (ESI+) Calculated for $C_{18}H_{13}ClFN_3NaO_2$ $[M+Na]^+$: 380.0573, found: 380.0579.

6-Bromo-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ai)



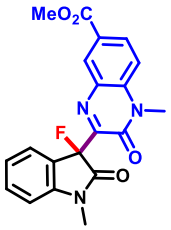
Obtained as a yellow solid in 73% yield, 58.7 mg; M.p. 219-220 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.30 (s, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.25 (d, J = 8.9 Hz, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 3.60 (s, 3H), 3.38 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 170.18, 169.98, 153.78, 153.55, 152.05, 146.13, 134.32, 133.40, 133.26, 132.51, 132.28, 132.25, 124.79, 123.90, 123.72, 123.07, 123.04, 116.97, 115.29, 109.13, 92.75, 90.82, 29.20, 26.70; **^{19}F NMR** (376 MHz, Chloroform-d) δ -163.49; **HRMS** (ESI+) Calculated for $C_{18}H_{13}BrFN_3NaO_2$ $[M+Na]^+$: 424.0067, found: 424.0074.

7-Bromo-3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)-1-methylquinoxalin-2(1*H*)-one (3aj)



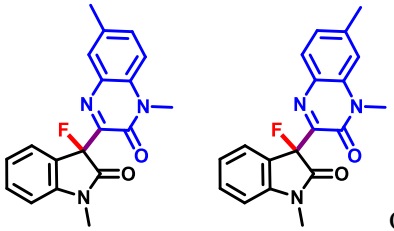
Obtained as a yellow solid in 74% yield, 59.5 mg; M.p. 217-218 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.30 (s, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.59 (s, 3H), 3.38 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.18, 169.98, 152.72, 152.49, 152.08, 146.12, 134.35, 132.27, 132.23, 131.35, 127.75, 125.93, 124.78, 123.90, 123.72, 123.08, 123.05, 116.96, 109.13, 92.80, 90.88, 29.15, 26.70; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -163.51; **HRMS** (ESI+) Calculated for $C_{18}H_{13}BrFN_3NaO_2$ $[M+Na]^+$: 424.0067, found: 424.0076.

Methyl 3-(3-fluoro-1-methyl-2-oxoindolin-3-yl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (3ak)



Obtained as a yellow solid in 65% yield, 49.6 mg; M.p. 223-224 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.3 Hz, 1H), 8.16 – 8.02 (m, 2H), 7.47 (tt, *J* = 7.8, 1.6 Hz, 1H), 7.32 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 4.04 (s, 3H), 3.68 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.86, 165.86, 154.85, 154.62, 152.22, 146.17, 134.95, 133.21, 132.40, 132.32, 131.18, 124.92, 124.81, 123.86, 123.08, 115.59, 109.16, 92.85, 90.93, 52.85, 29.27, 26.71; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -162.95; **HRMS** (ESI+) Calculated for $C_{20}H_{16}FN_3NaO_4$ $[M+Na]^+$: 404.1017, found: 404.1012.

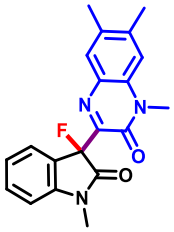
3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-1,6(7)-dimethylquinoxalin-2(1*H*)-one (3al & 3al')



Obtained as a yellow solid in 80% yield, 54 mg; M.p. 176-177 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.42 (dt, *J* = 7.8, 1.7 Hz, 2H), 7.30 (d, *J* = 2.8 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.14 (s, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 3.58 (s, 6H), 3.37 (s, 6H), 2.56 (s, 3H), 2.51 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.54, 170.49, 170.34, 170.29, 152.51, 152.48, 152.29, 152.26, 152.04, 146.10, 142.72, 134.30, 133.26, 132.84, 132.45, 132.08, 131.15, 130.75, 125.73, 124.72, 122.94, 113.91, 113.61, 109.04, 92.81, 90.90, 29.00, 26.66, 20.73; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -161.77; **HRMS** (ESI+) Calculated for $C_{19}H_{16}FN_3NaO_2$ $[M+Na]^+$: 360.1119,

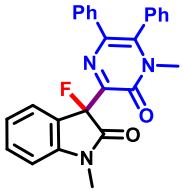
found: 360.1126.

3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-1,6,7-trimethylquinoxalin-2(1*H*)-one (3am)



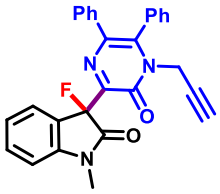
Obtained as a yellow solid in 76% yield, 53.4 mg; M.p. 188-189 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.31 (tdd, *J* = 7.8, 2.1, 1.3 Hz, 1H), 7.19 – 7.16 (m, 1H), 7.01 (s, 1H), 6.91 (tt, *J* = 7.6, 1.0 Hz, 1H), 6.84 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.46 (s, 3H), 3.26 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 170.58, 170.42, 152.40, 150.91, 146.04, 141.81, 133.40, 132.00, 131.36, 130.90, 124.67, 124.29, 122.88, 114.27, 108.97, 92.57, 91.05, 28.88, 26.60, 20.72, 19.25; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -162.83; **HRMS** (ESI+) Calculated for $C_{20}H_{18}FN_3NaO_2$ $[M+Na]^+$: 374.1275, found: 374.1276.

3-Fluoro-1-methyl-3-(4-methyl-3-oxo-5,6-diphenyl-3,4-dihydropyrazin-2-yl)indolin-2-one (3an)



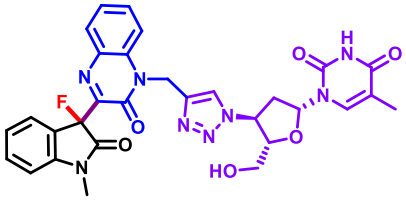
Obtained as a yellow solid in 62% yield, 53 mg; M.p. 211-212 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 (q, *J* = 12.4, 9.9 Hz, 5H), 7.27 (s, 3H), 7.21 (s, 4H), 7.10 (q, *J* = 6.6, 6.1 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 3.41 (s, 3H), 3.28 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.96, 170.76, 153.03, 149.12, 148.89, 146.00, 139.28, 137.23, 133.55, 131.97, 129.96, 129.89, 129.83, 129.57, 129.44, 129.13, 127.94, 127.34, 125.18, 124.19, 122.97, 108.99, 92.71, 90.79, 34.04, 26.69; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -162.13; **HRMS** (ESI+) Calculated for $C_{26}H_{20}FN_3NaO_2$ $[M+Na]^+$: 448.1432, found: 448.1429.

3-Fluoro-1-methyl-3-(3-oxo-5,6-diphenyl-4-(prop-2-yn-1-yl)-3,4-dihydropyrazin-2-yl)indolin-2-one (3ao)



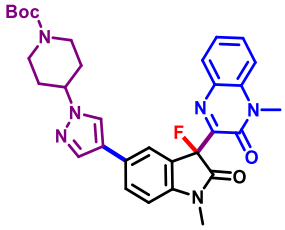
Obtained as a yellow solid in 56% yield, 50.3 mg; M.p. 189-190 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.42 (m, 6H), 7.34 – 7.28 (m, 3H), 7.25 – 7.18 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 4.48 (ddd, *J* = 74.8, 16.6, 2.5 Hz, 2H), 3.41 (s, 3H), 2.27 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.81, 170.61. 152.05, 149.57, 145.98, 138.53, 137.02, 133.65, 131.99, 131.17, 130.41, 130.27, 130.18, 129.57, 129.25, 129.00, 127.95, 127.44, 125.35, 123.02, 109.11, 92.80, 90.88, 77.27, 73.33, 36.12, 26.74; **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -162.44; **HRMS** (ESI+) Calculated for $C_{28}H_{20}FN_3NaO_2$ $[M+Na]^+$: 472.1432, found: 472.1441.

1-((2R,4S,5S)-4-(4-((3-(3-Fluoro-1-methyl-2-oxoindolin-3-yl)-2-oxoquinoxalin-1(2*H*)-yl)methyl)-1*H*-1,2,3-triazol-1-yl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methyl pyrimidine-2,4(1*H*,3*H*)-dione (4)



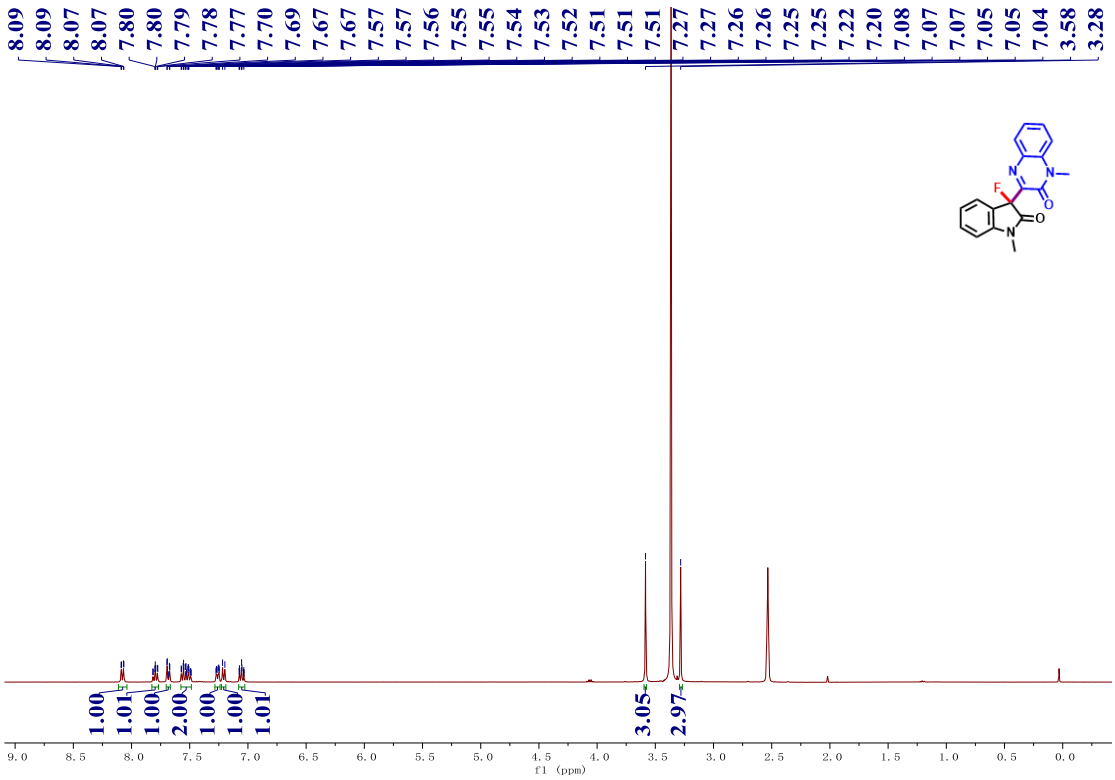
Obtained as a white solid in 91% yield, 559.3 mg; M.p. 278-279 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.36 (s, 1H), 8.18 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.30 (d, J = 6.9 Hz, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.38 (t, J = 6.5 Hz, 1H), 5.48 (d, J = 5.7 Hz, 2H), 5.36 – 5.28 (m, 1H), 5.25 (t, J = 5.0 Hz, 1H), 4.14 (d, J = 4.3 Hz, 1H), 3.69 – 3.55 (m, 2H), 3.28 (s, 3H), 2.63 (tt, J = 14.3, 6.7 Hz, 2H), 1.81 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.04, 169.84, 164.23, 152.12, 151.94, 151.90, 150.93, 146.31, 141.85, 136.70, 132.89, 132.75, 132.39, 132.29, 130.64, 125.07, 124.93, 124.18, 123.98, 123.45, 116.17, 110.14, 93.19, 91.31, 84.89, 84.38, 61.22, 59.85, 37.91, 37.61, 26.98, 12.75; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -160.06; **HRMS** (ESI+) Calculated for $C_{30}H_{27}FN_8NaO_6$ $[M+Na]^+$: 637.1930, found: 637.1937.

Tert-butyl 4-(4-(3-fluoro-1-methyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-2-oxoindolin-5-yl)-1*H*-pyrazol-1-yl)piperidine-1-carboxylate (6)

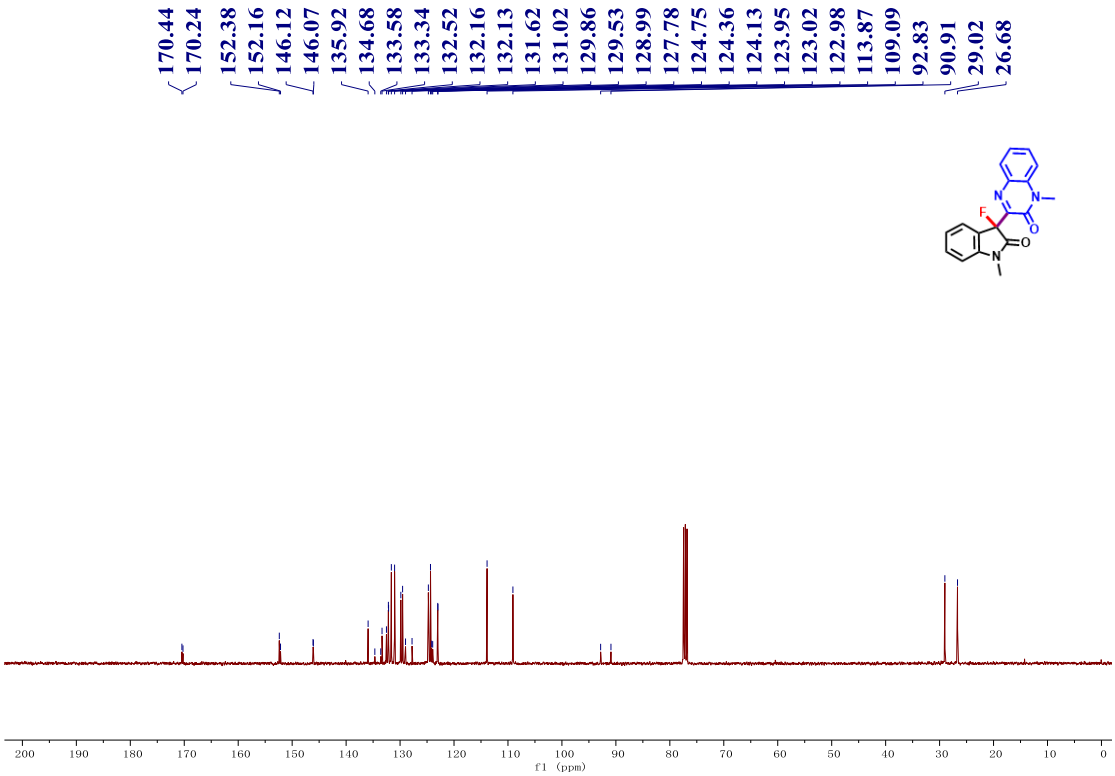


Obtained as a yellow solid in 87% yield, 498.2 mg; M.p. 246-247 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.14 (d, J = 6.2 Hz, 1H), 7.67 (s, 2H), 7.61 – 7.52 (m, 2H), 7.48 (t, J = 6.4 Hz, 1H), 7.43 – 7.34 (m, 2H), 6.96 (d, J = 5.4 Hz, 1H), 4.40 – 4.10 (m, 3H), 3.61 (s, 3H), 3.39 (s, 3H), 2.99 – 2.79 (m, 2H), 2.12 (d, J = 9.8 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.48 (d, J = 1.4 Hz, 9H); **^{13}C NMR** (101 MHz, Chloroform-d) δ 170.23, 170.03, 154.57, 152.36, 144.45, 136.12, 133.40, 132.53, 131.67, 131.06, 128.96, 127.96, 124.63, 124.40, 123.53, 122.26, 122.06, 113.91, 109.44, 92.82, 90.91, 79.95, 59.54, 32.45, 29.09, 28.46, 26.79, 24.90; **^{19}F NMR** (376 MHz, Chloroform-d) δ -162.82; **HRMS** (ESI+) Calculated for $C_{31}H_{33}FN_6NaO_4$ $[M+Na]^+$: 595.2440, found: 595.2447.

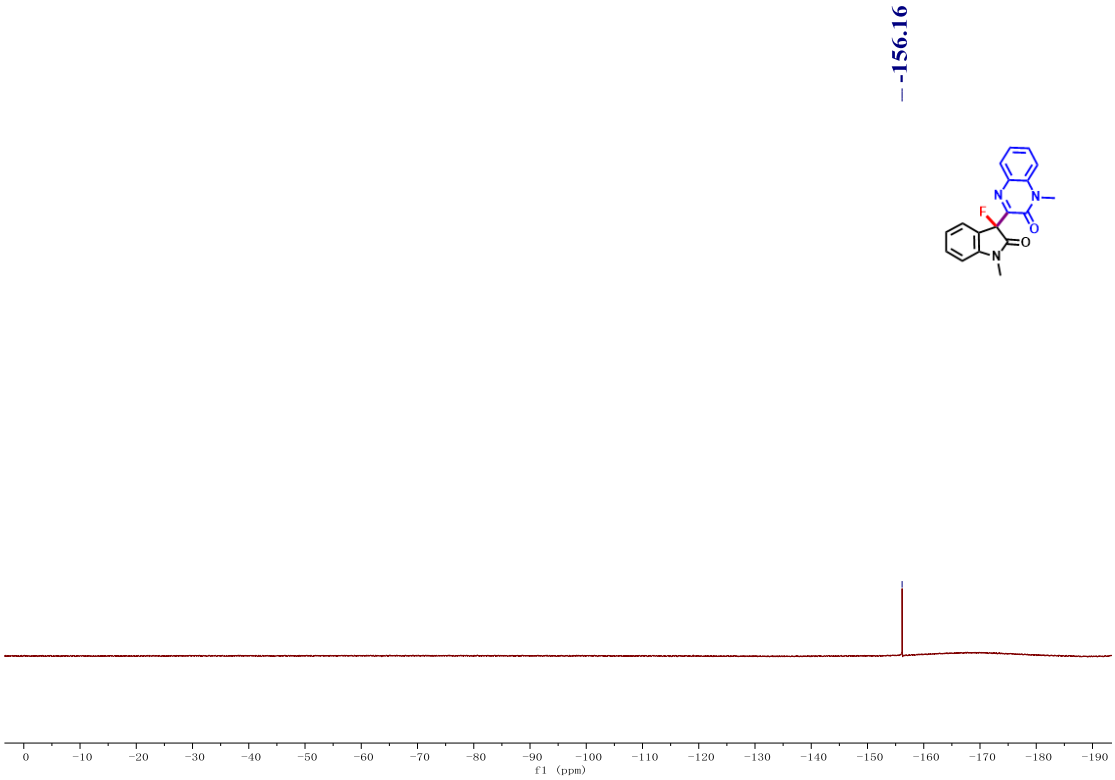
4. ^{1}H, ^{13}C, and F^{19} NMR Spectra of These Compounds



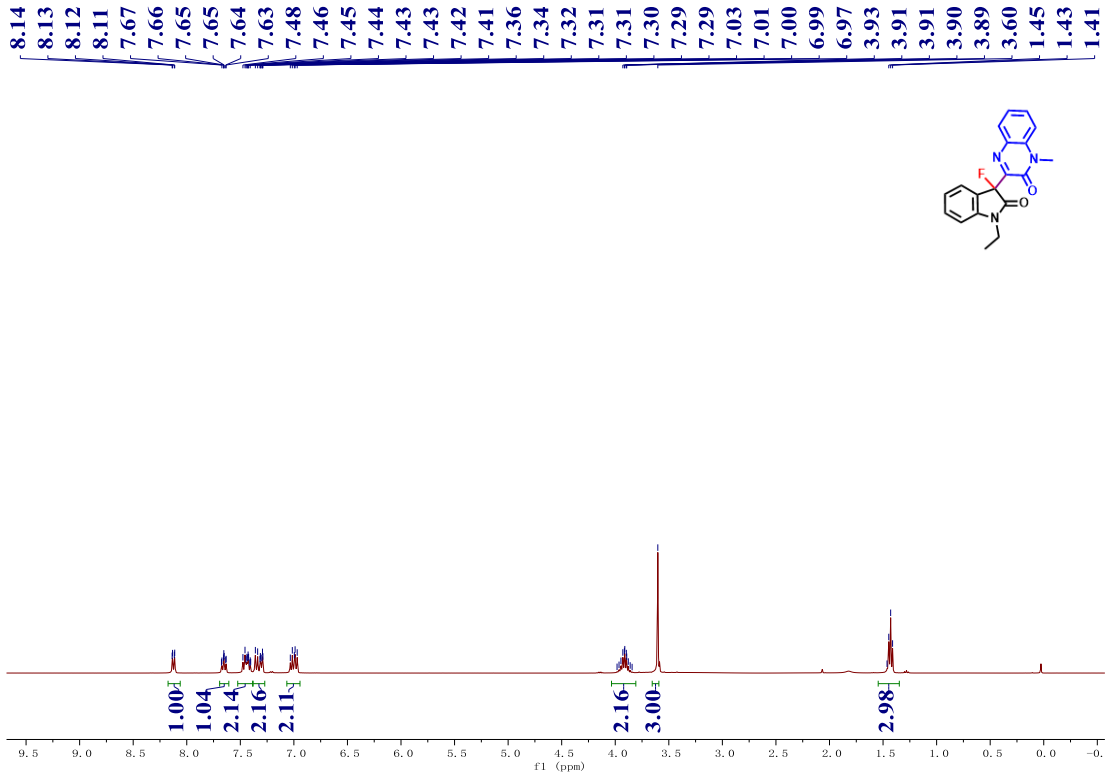
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **3aa**



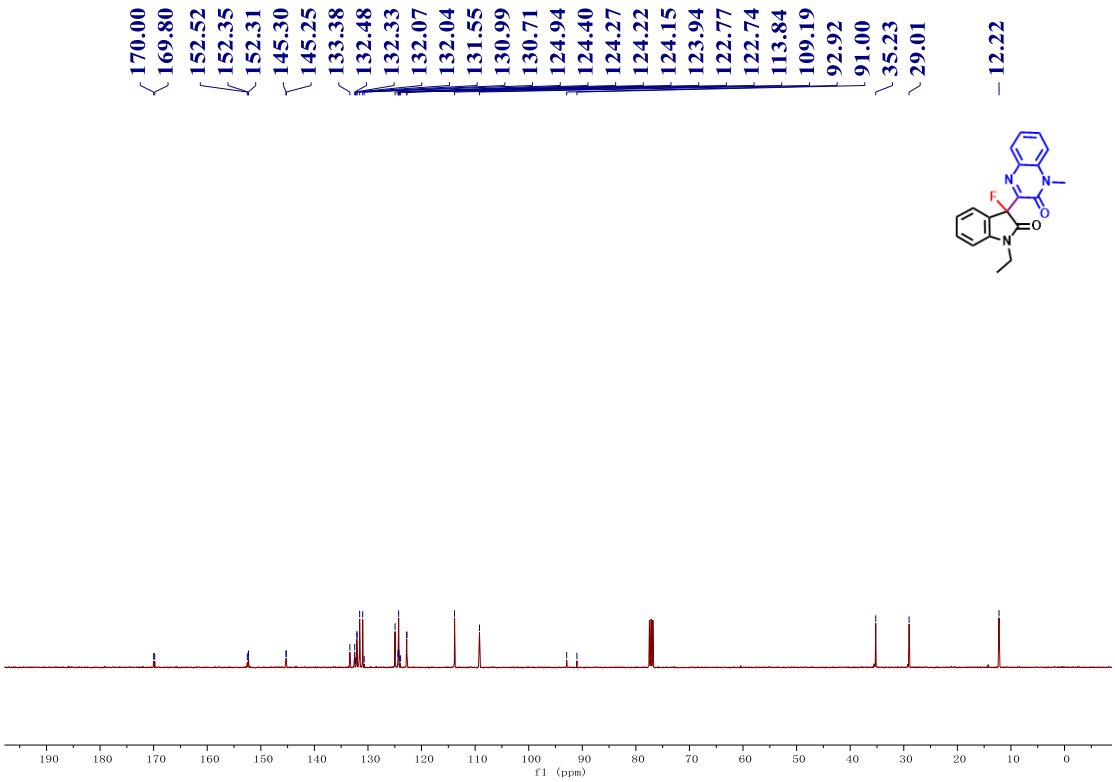
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3aa**



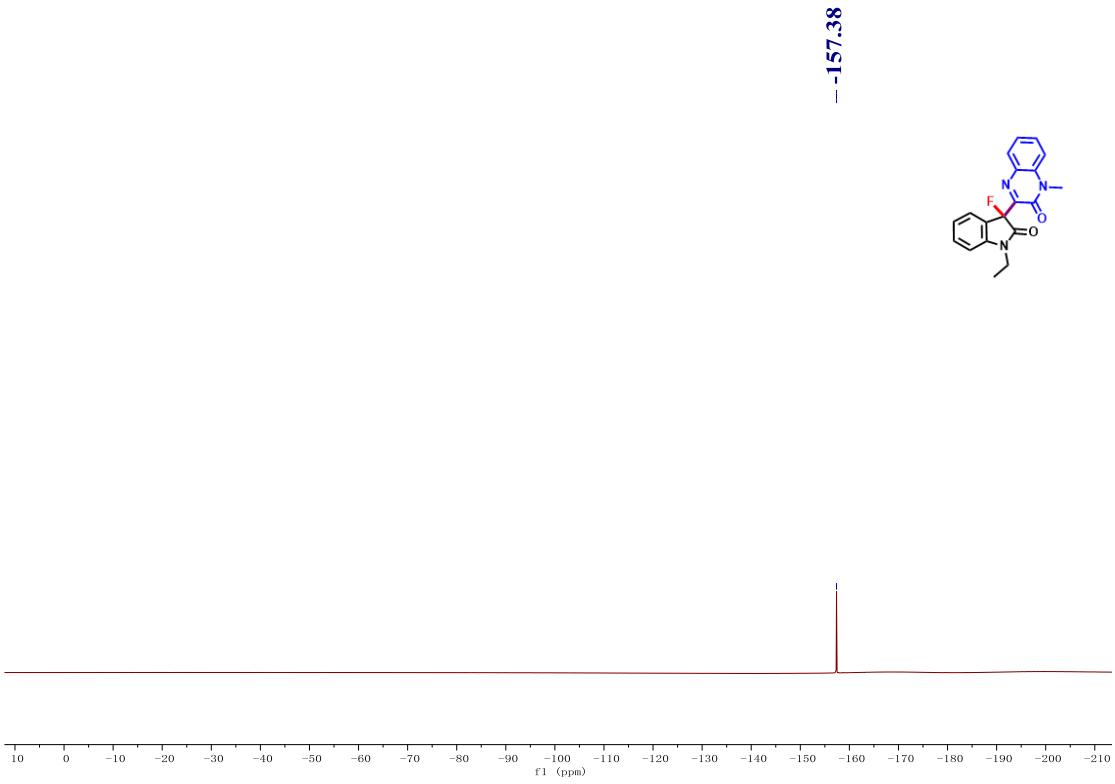
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3aa**



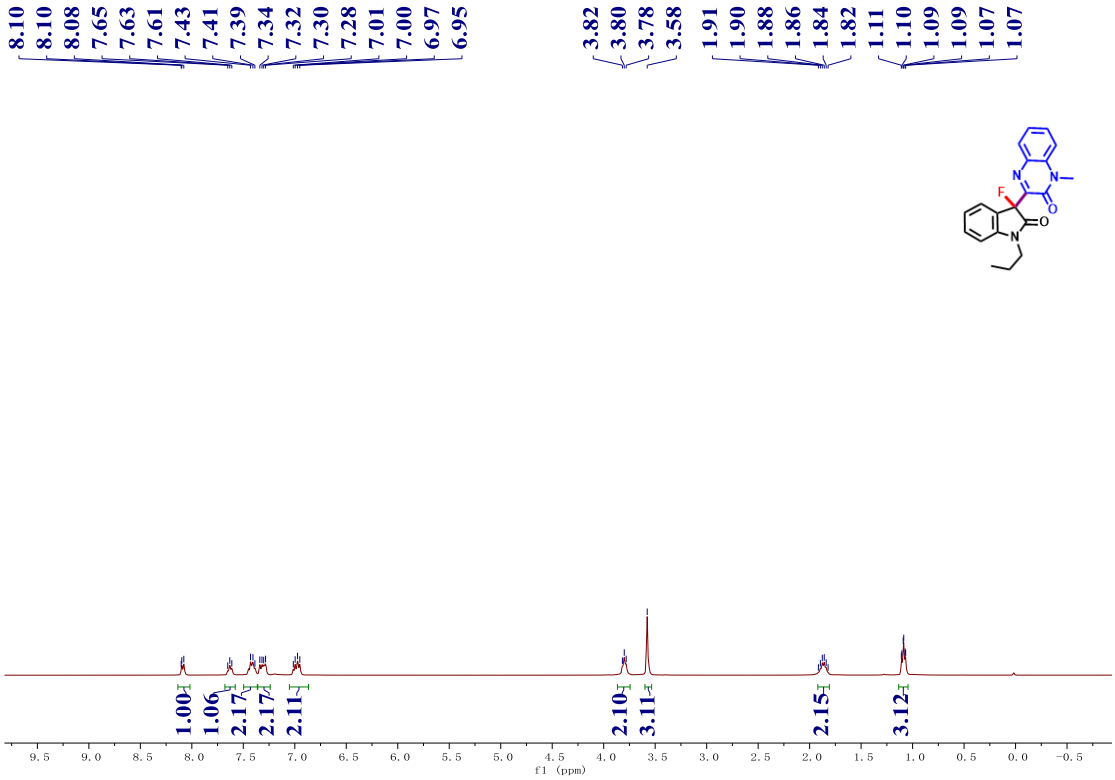
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ba**



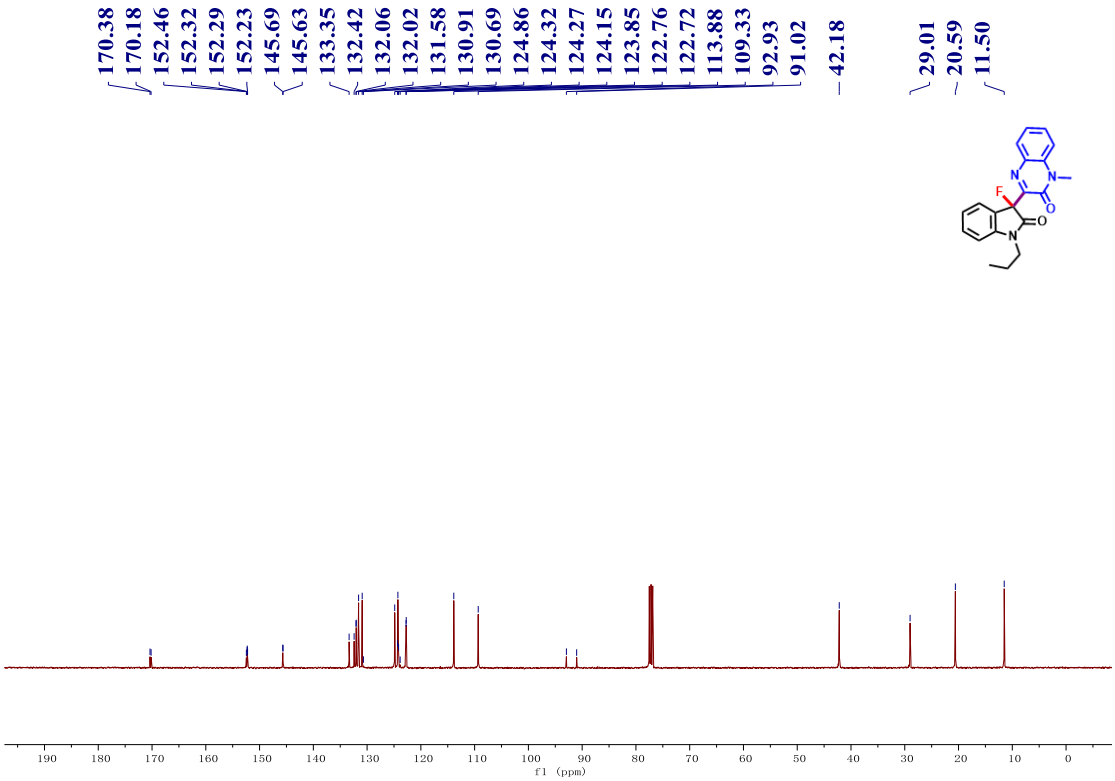
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ba**



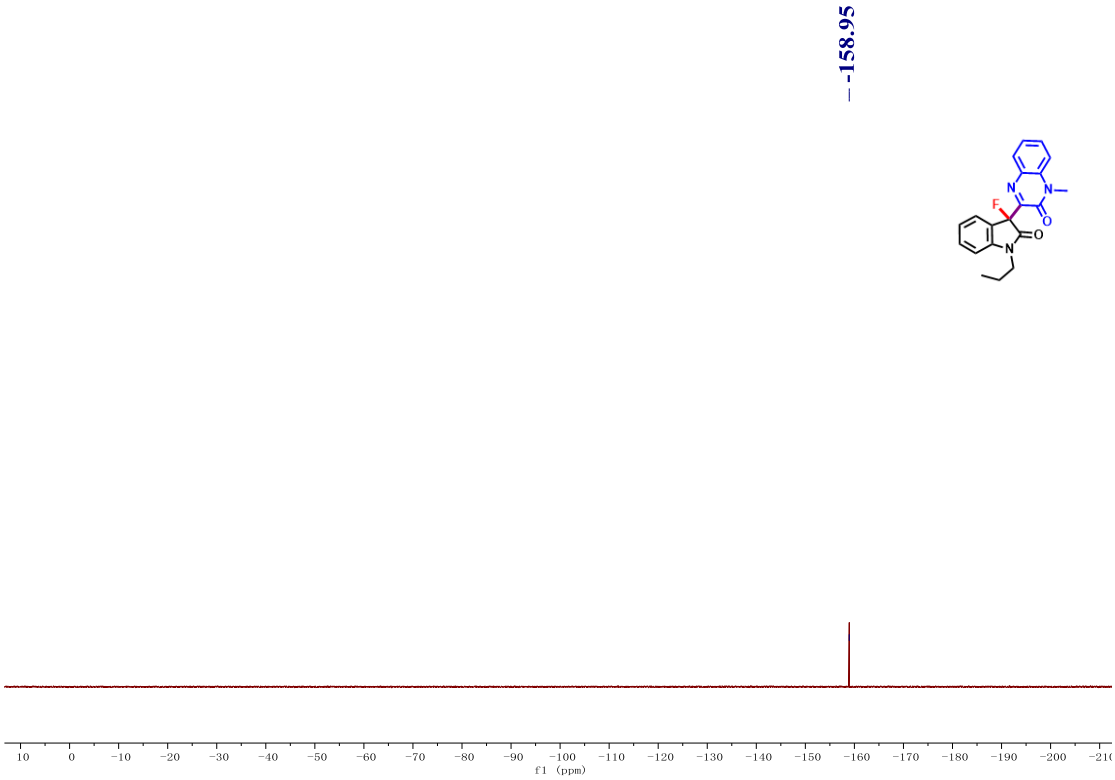
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of compound **3ba**



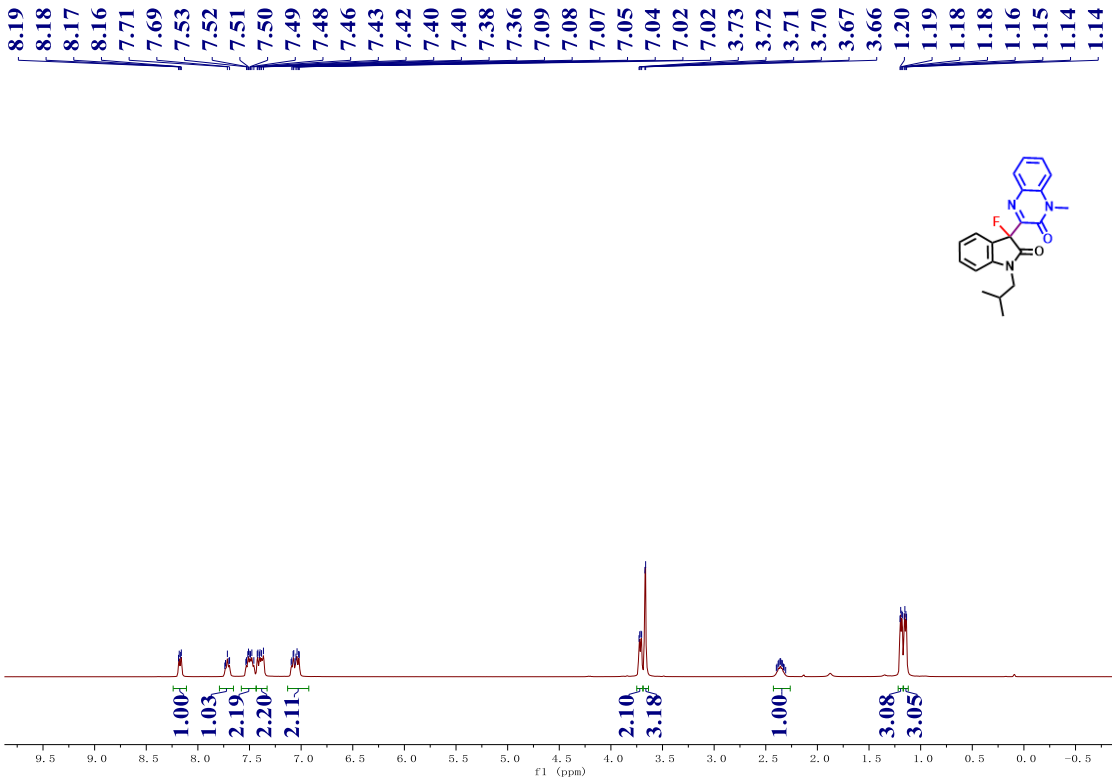
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ca**



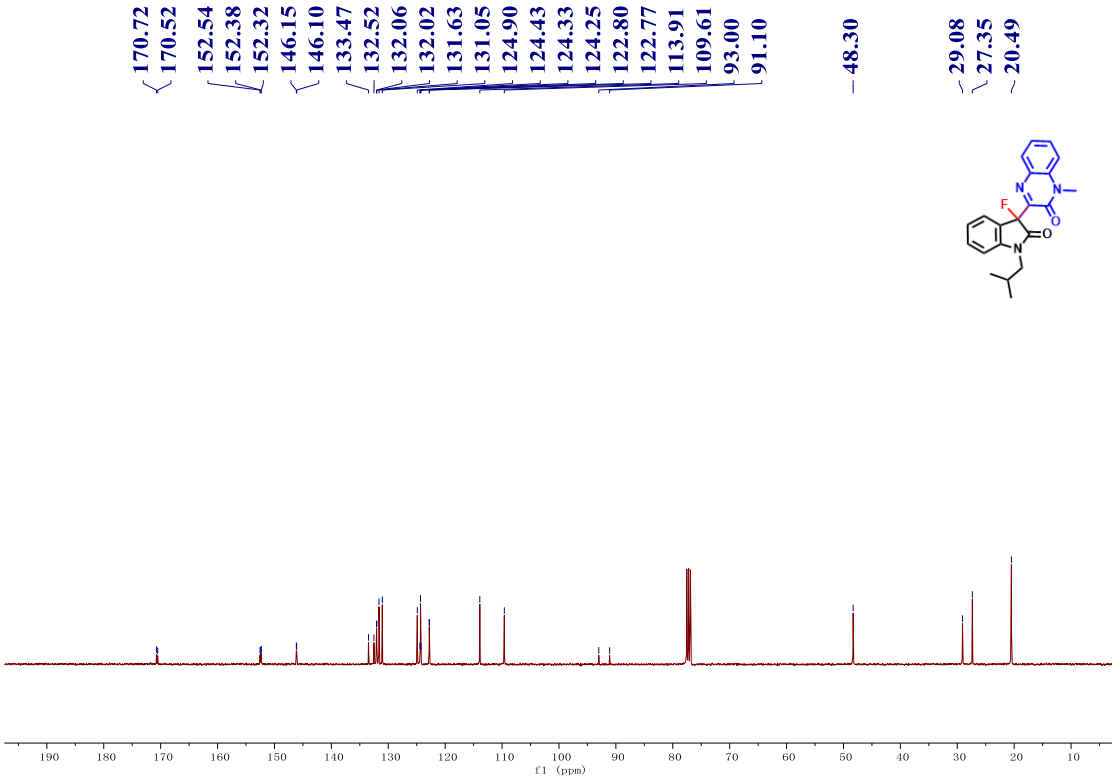
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ca**



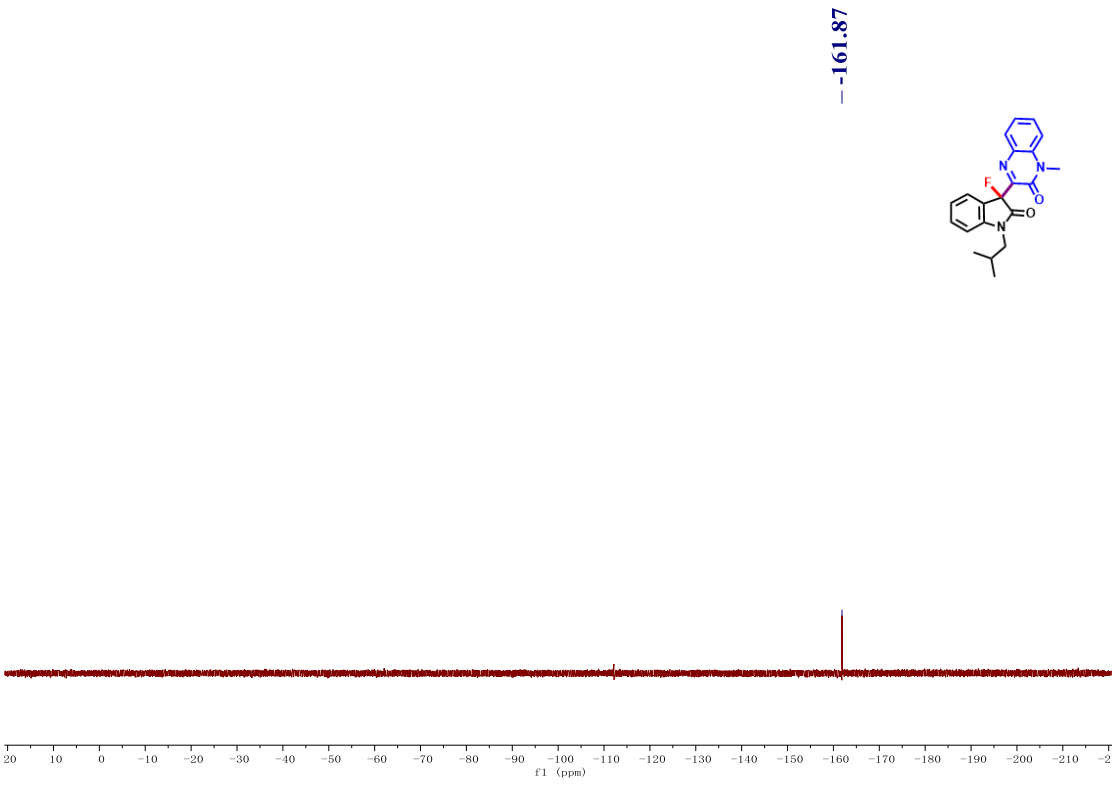
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ca**



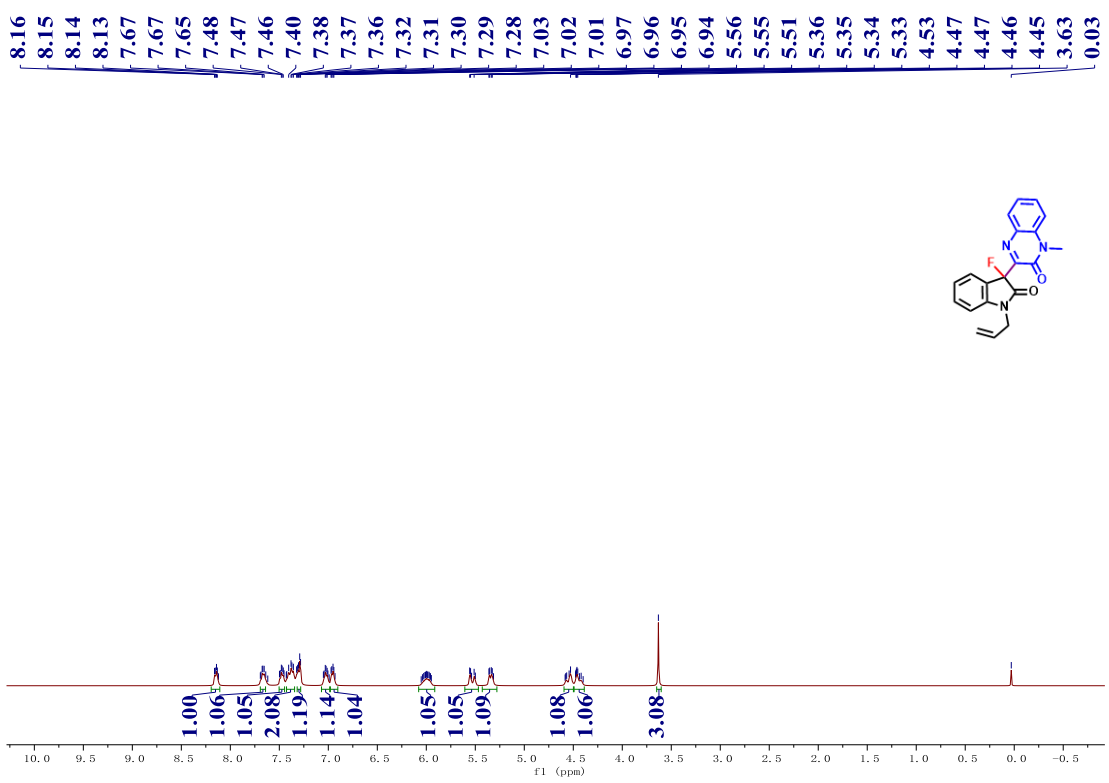
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3da**



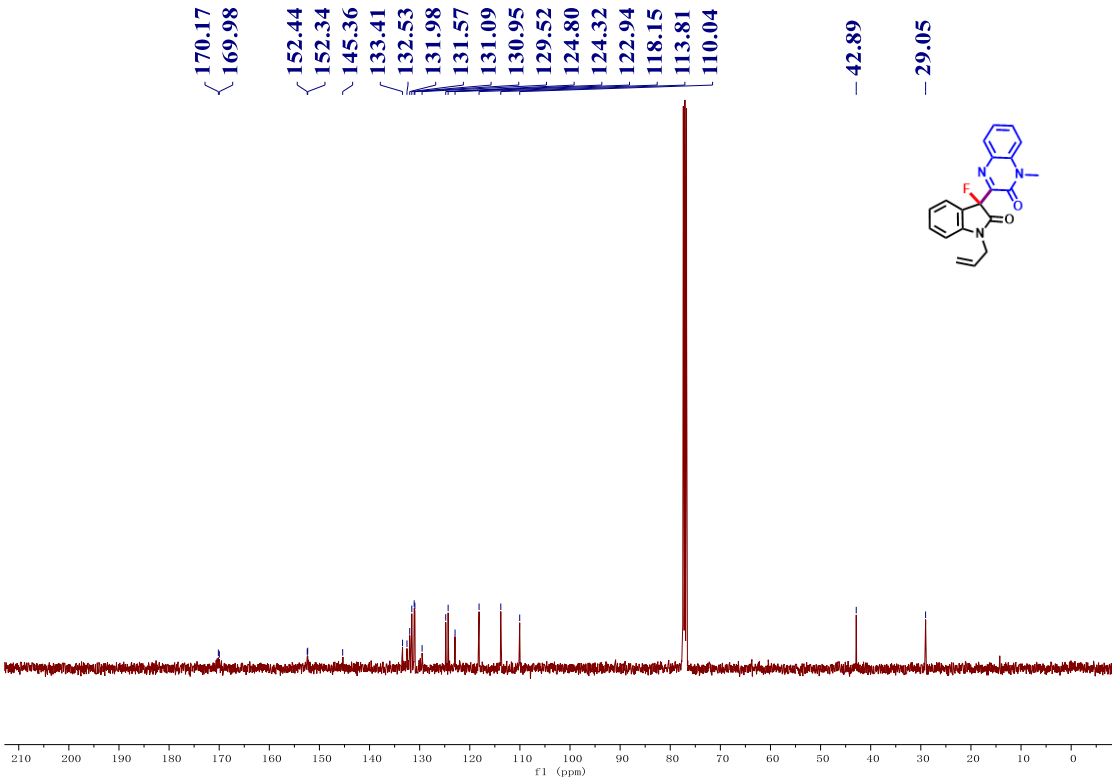
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3da**



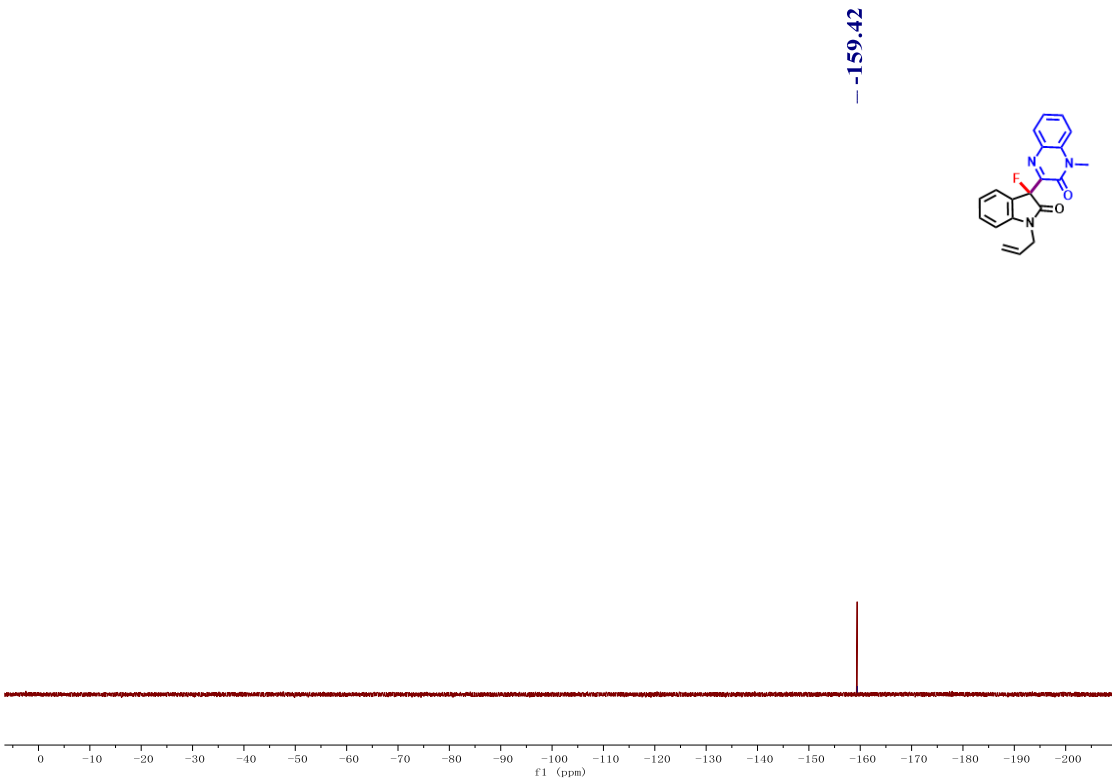
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3da**



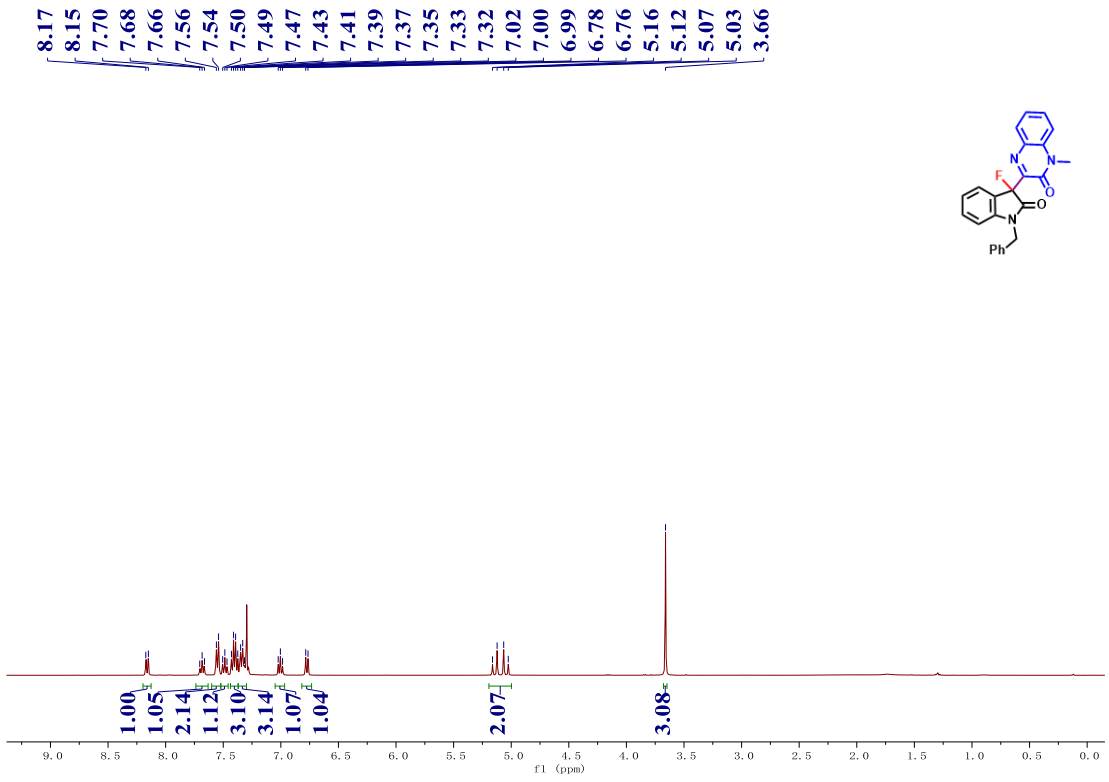
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ea**



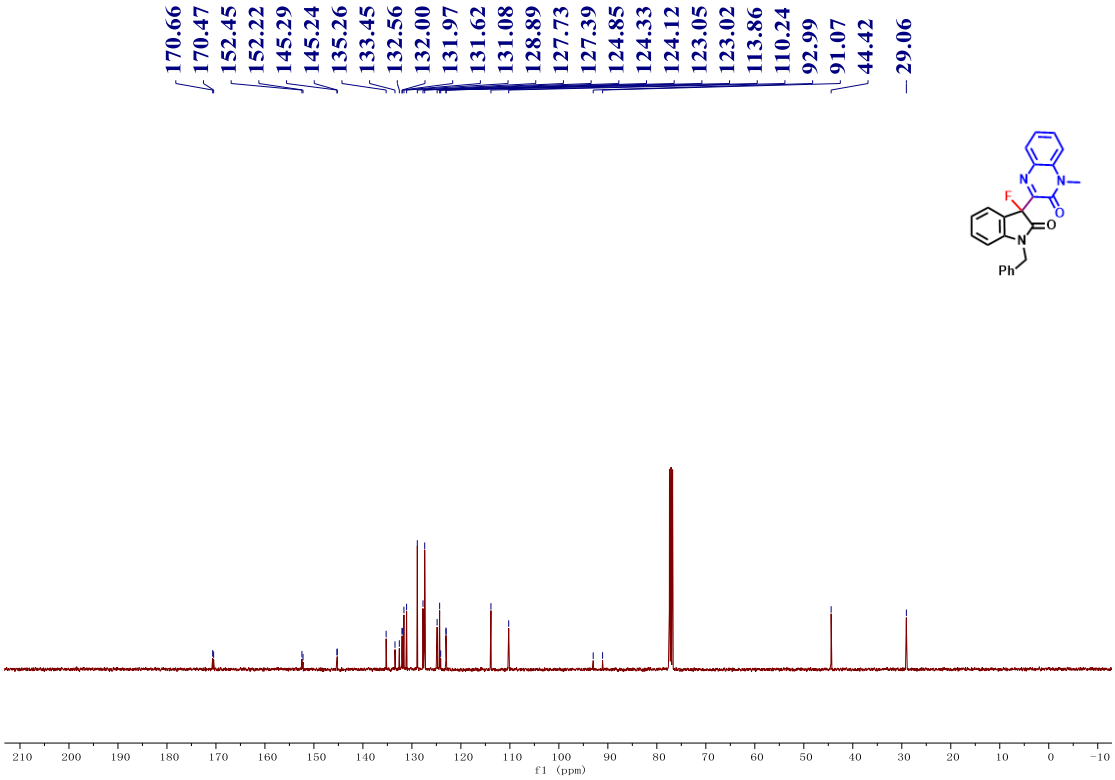
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ea**



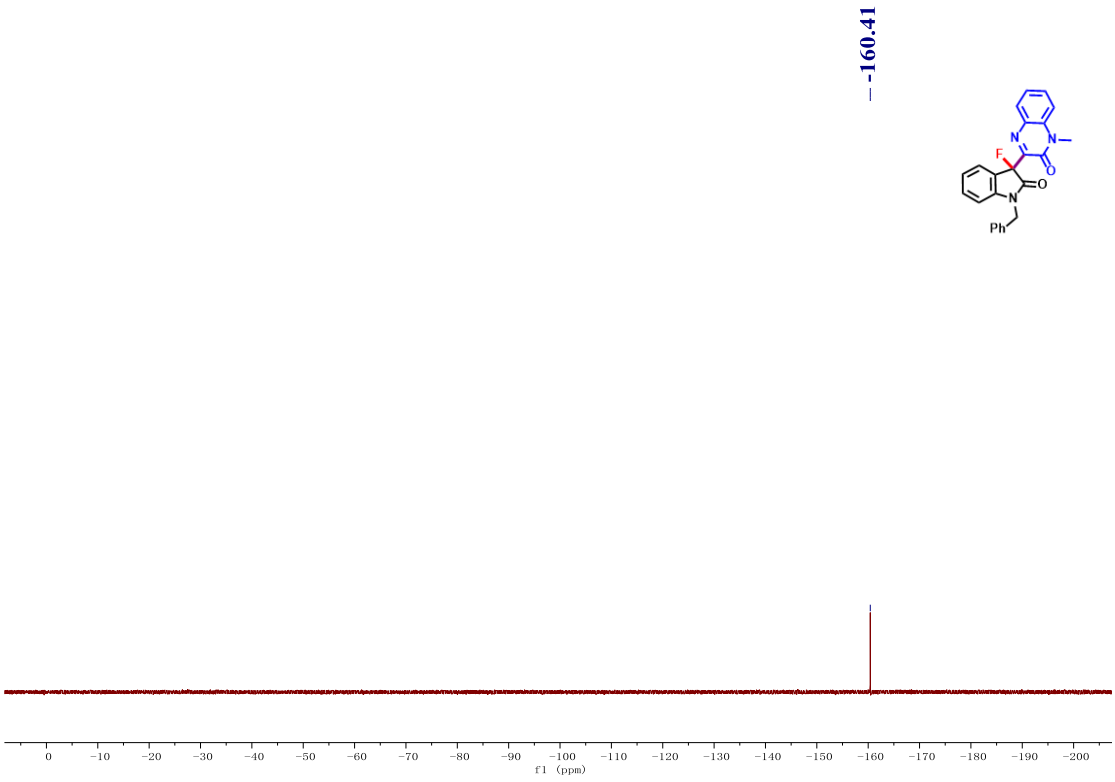
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ea**



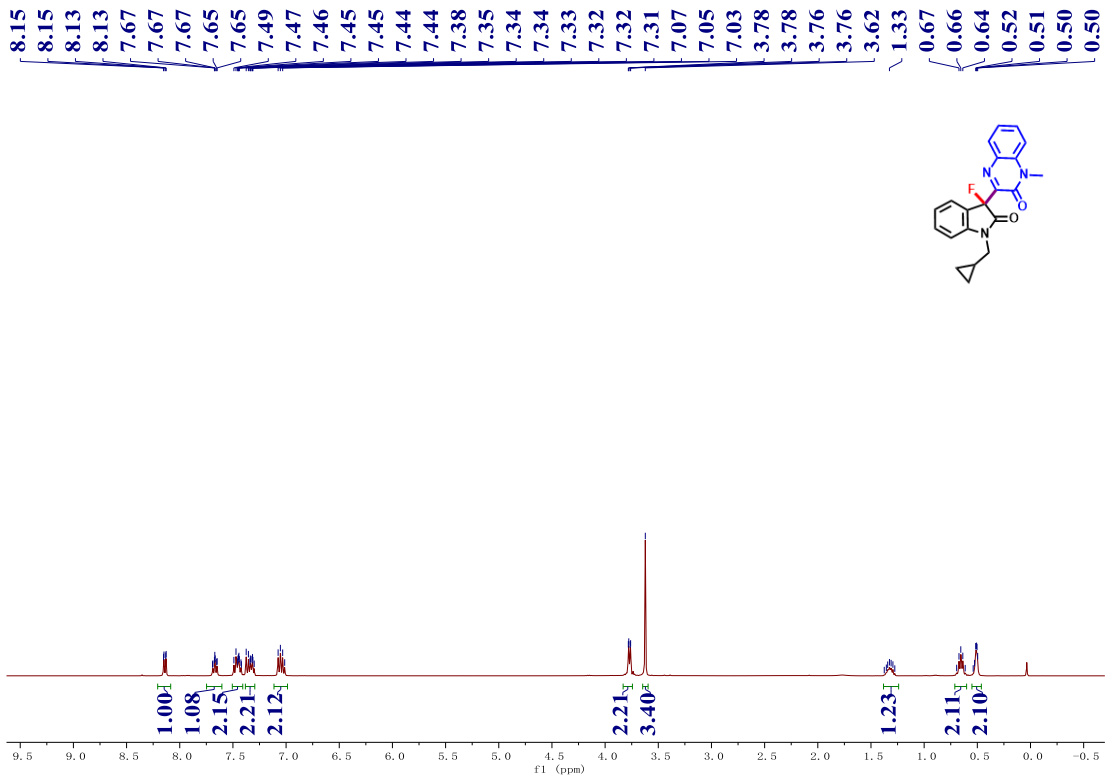
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3fa**



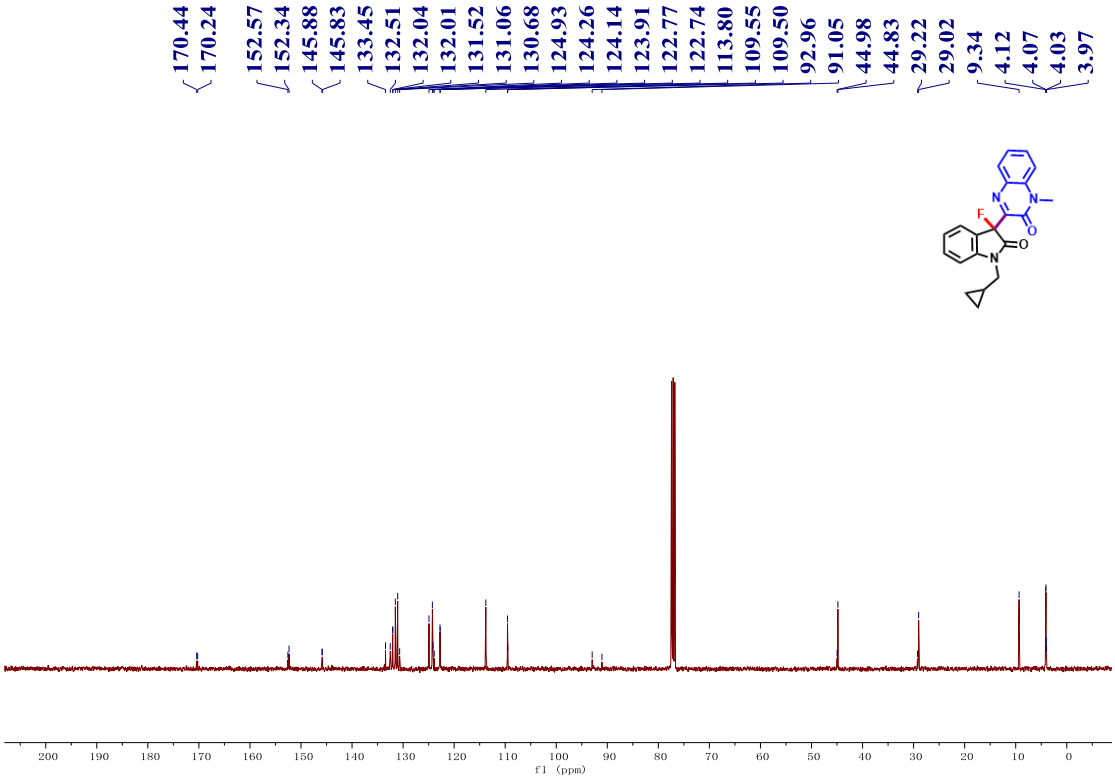
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3fa**



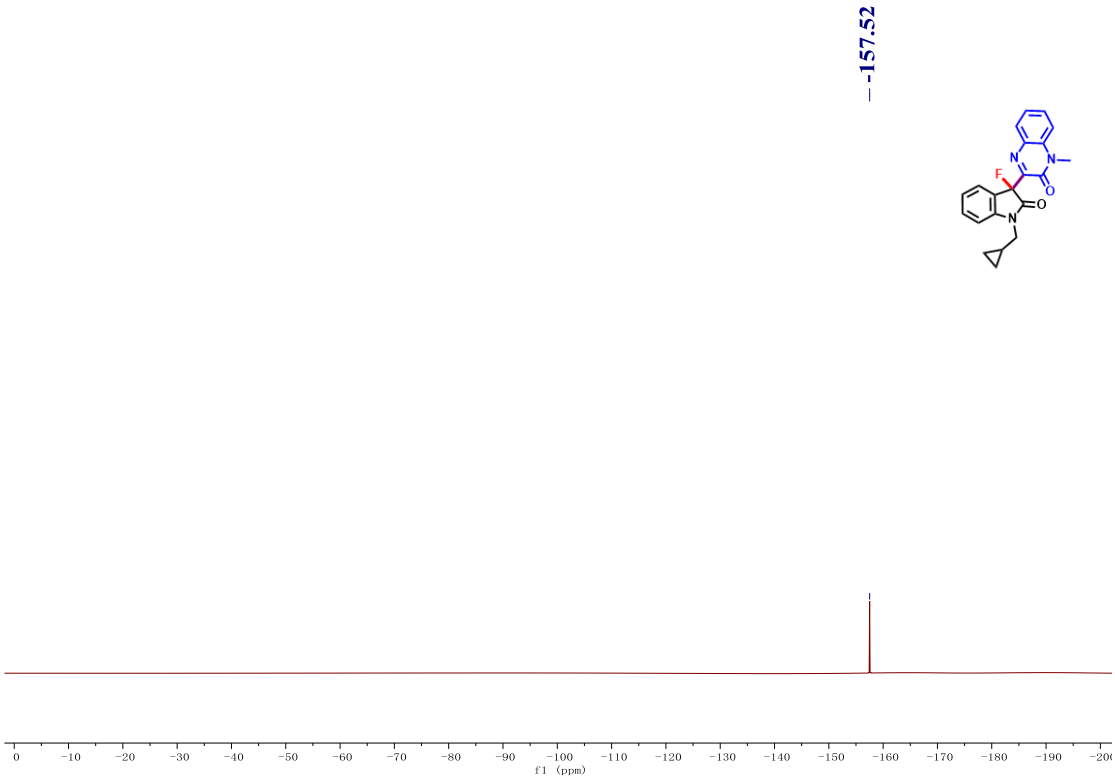
^{19}F NMR (471 MHz, DMSO-d_6) Spectra of compound **3fa**



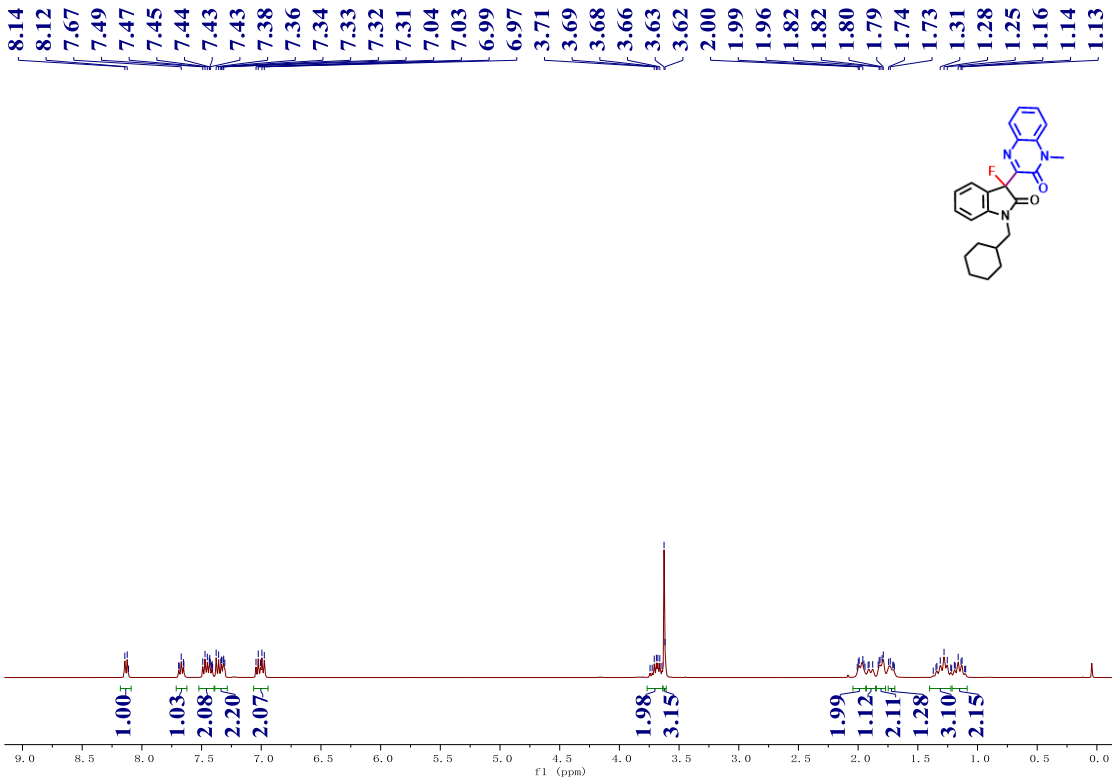
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ga**



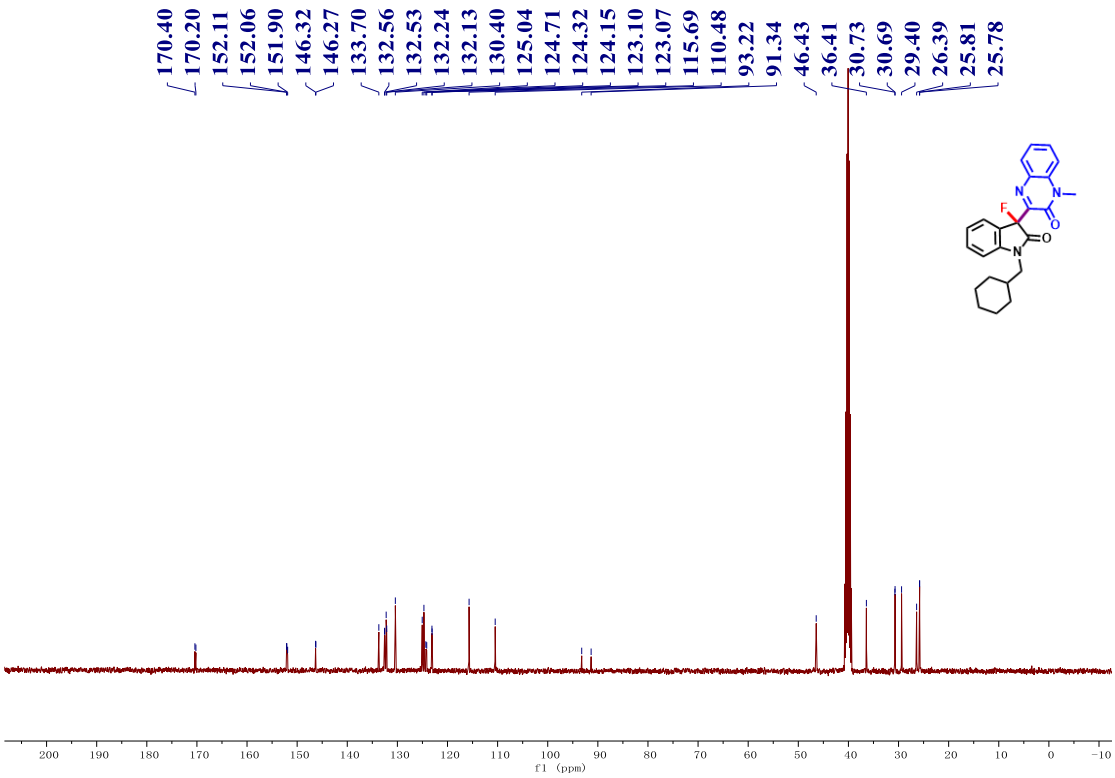
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ga**



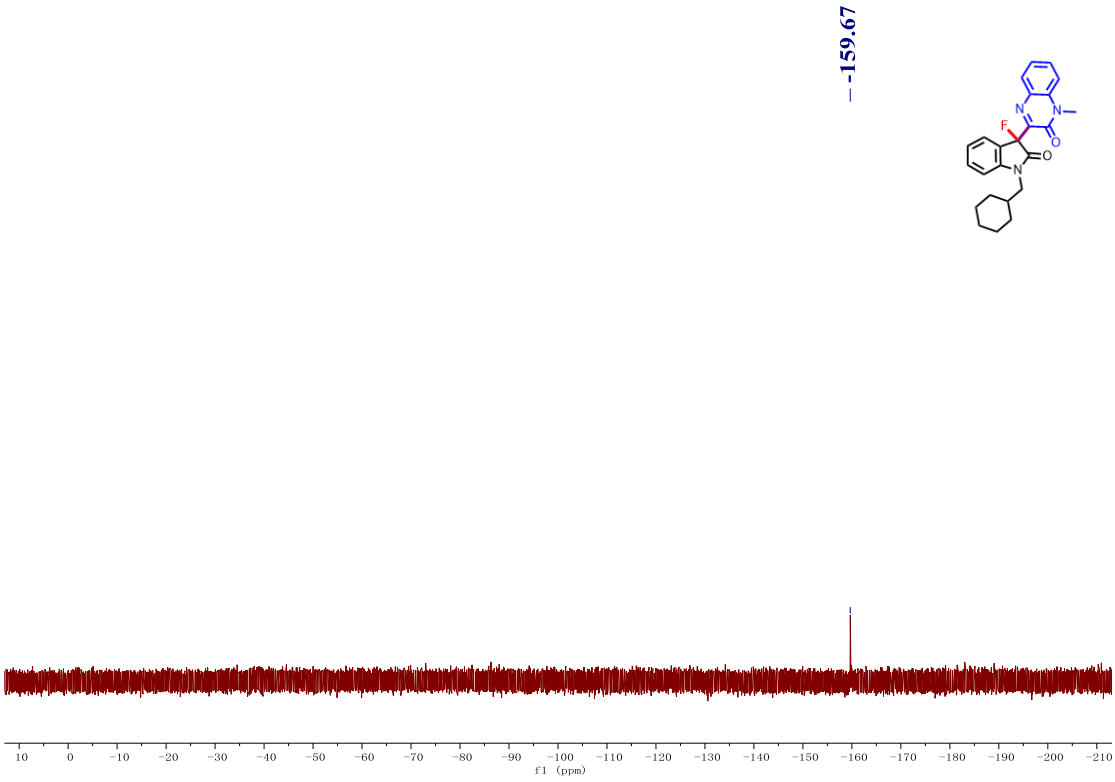
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3ga**



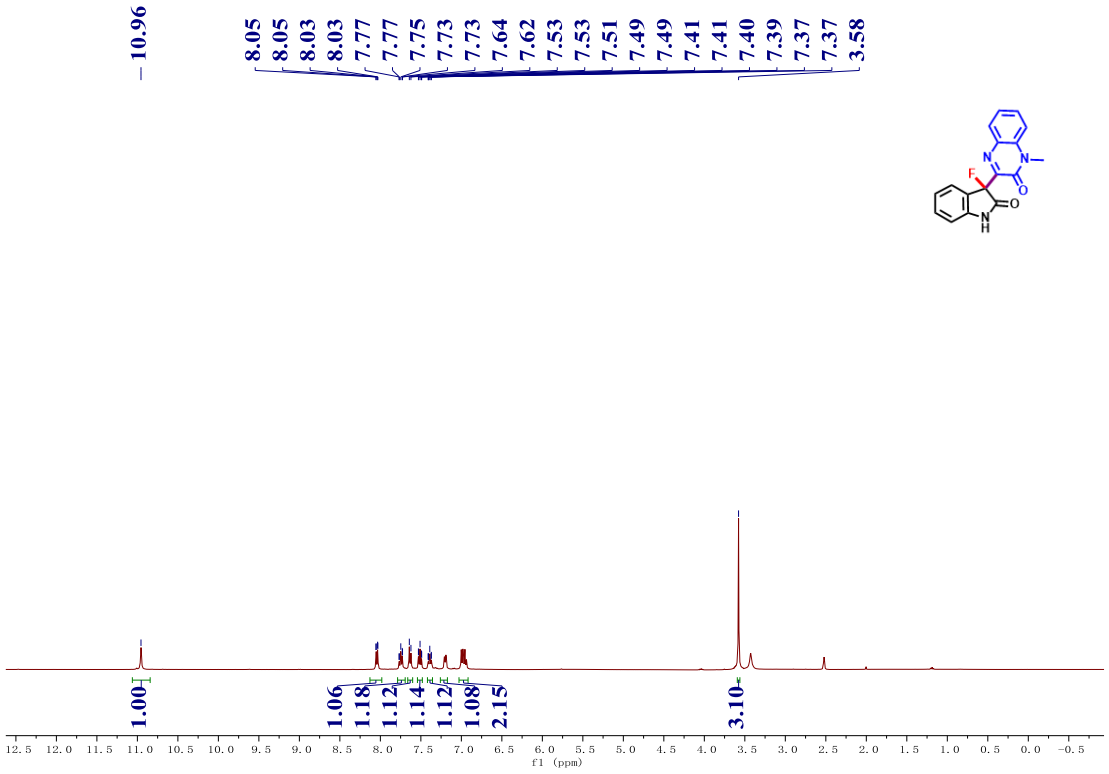
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **3ha**



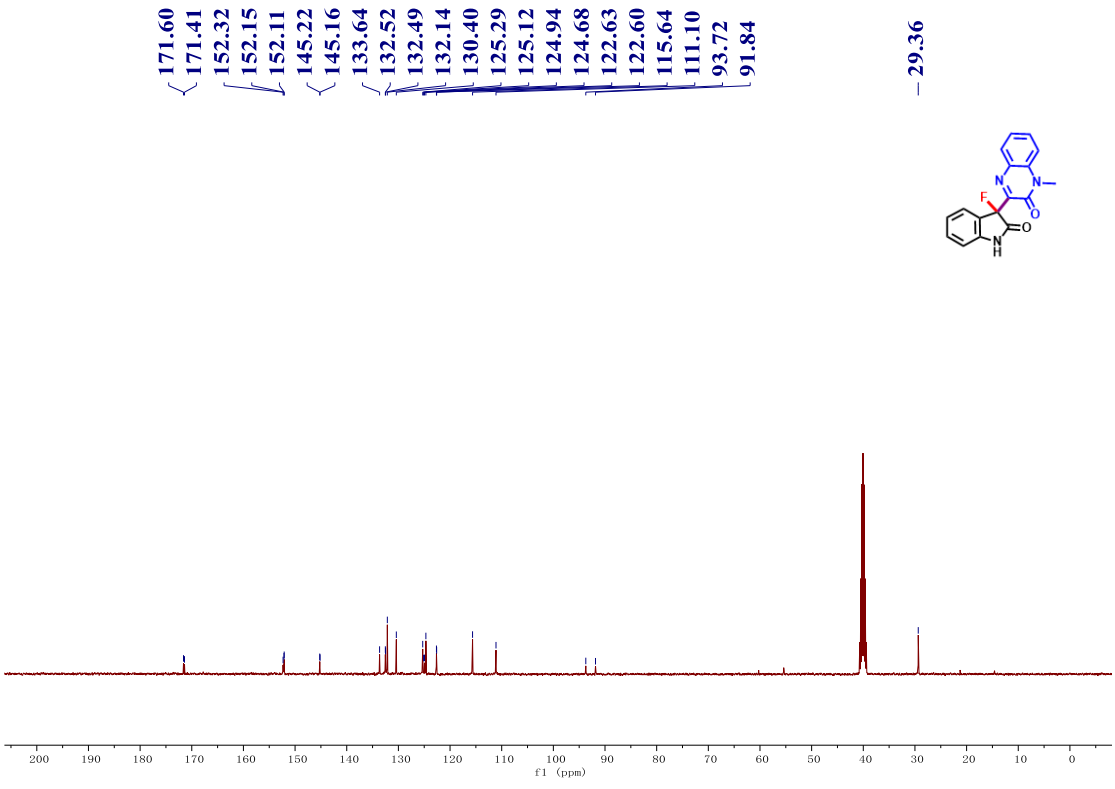
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **3ha**



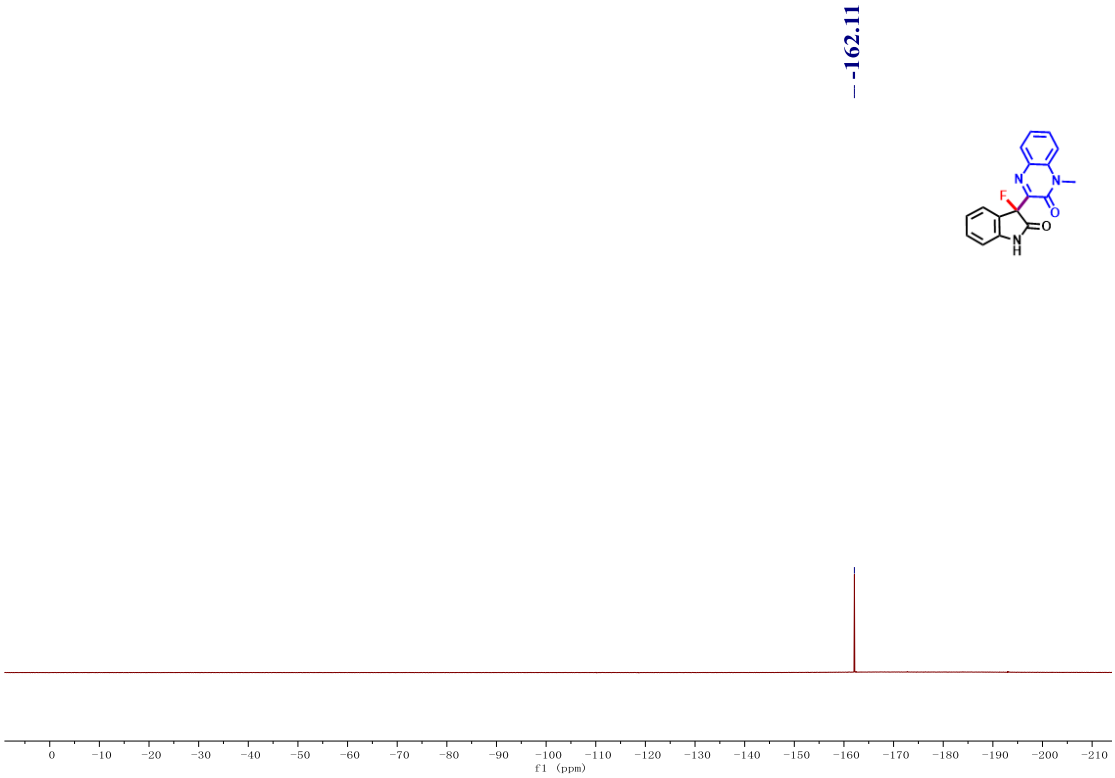
^{19}F NMR (471 MHz, DMSO-d_6) Spectra of compound **3ha**



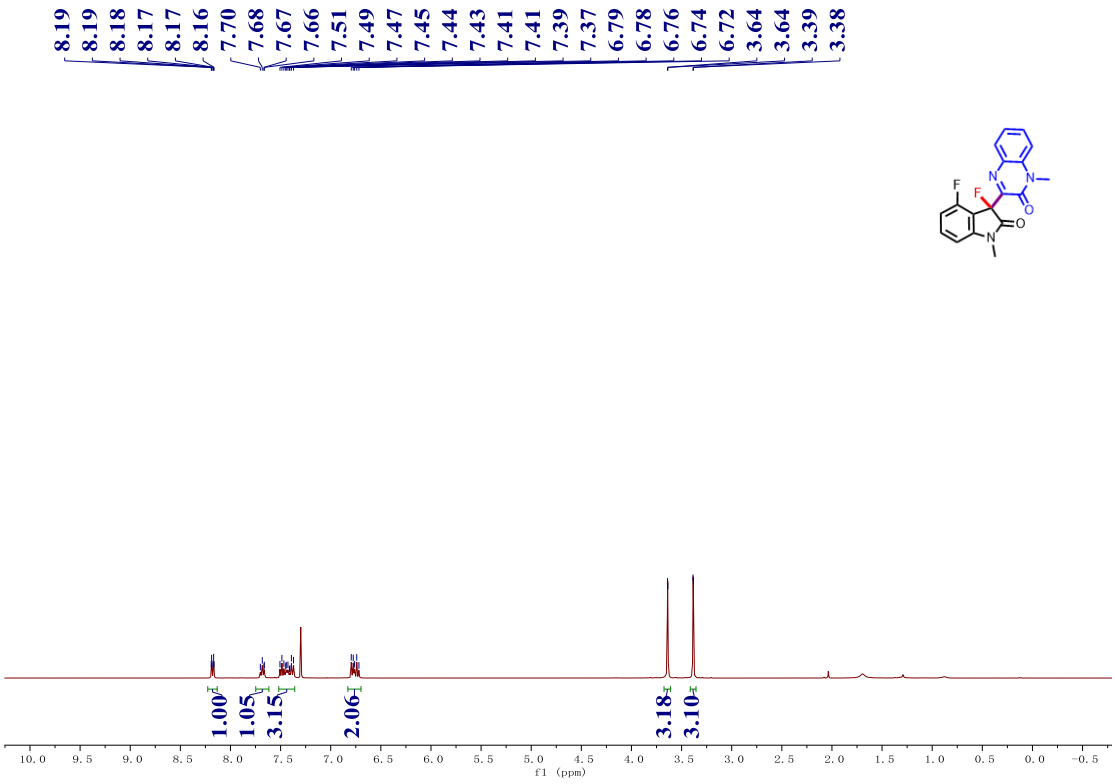
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **3ia**



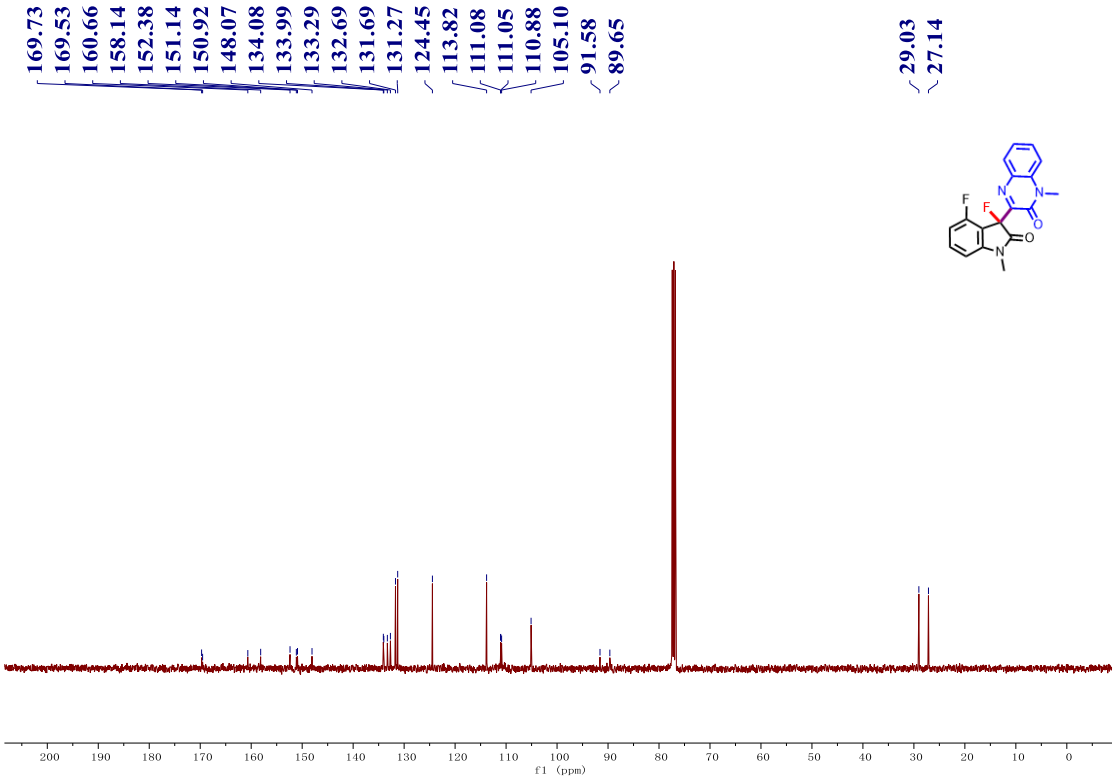
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **3ia**



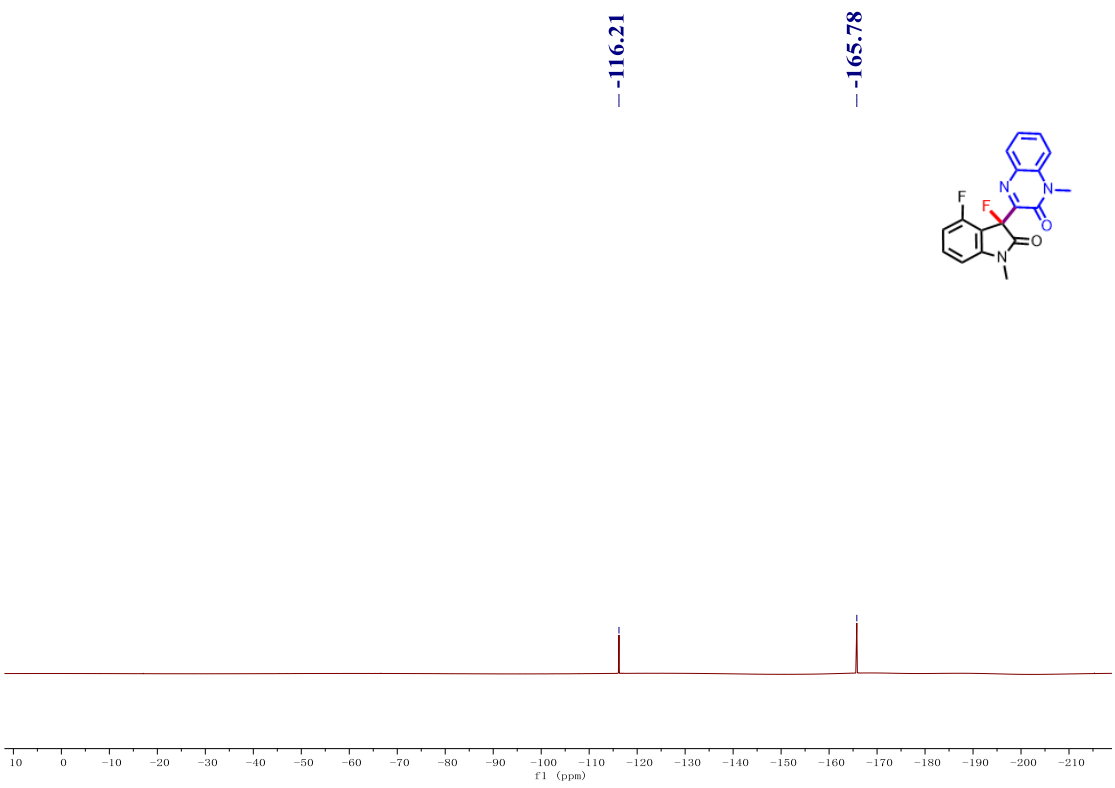
^{19}F NMR (471 MHz, DMSO-d_6) Spectra of compound **3ia**



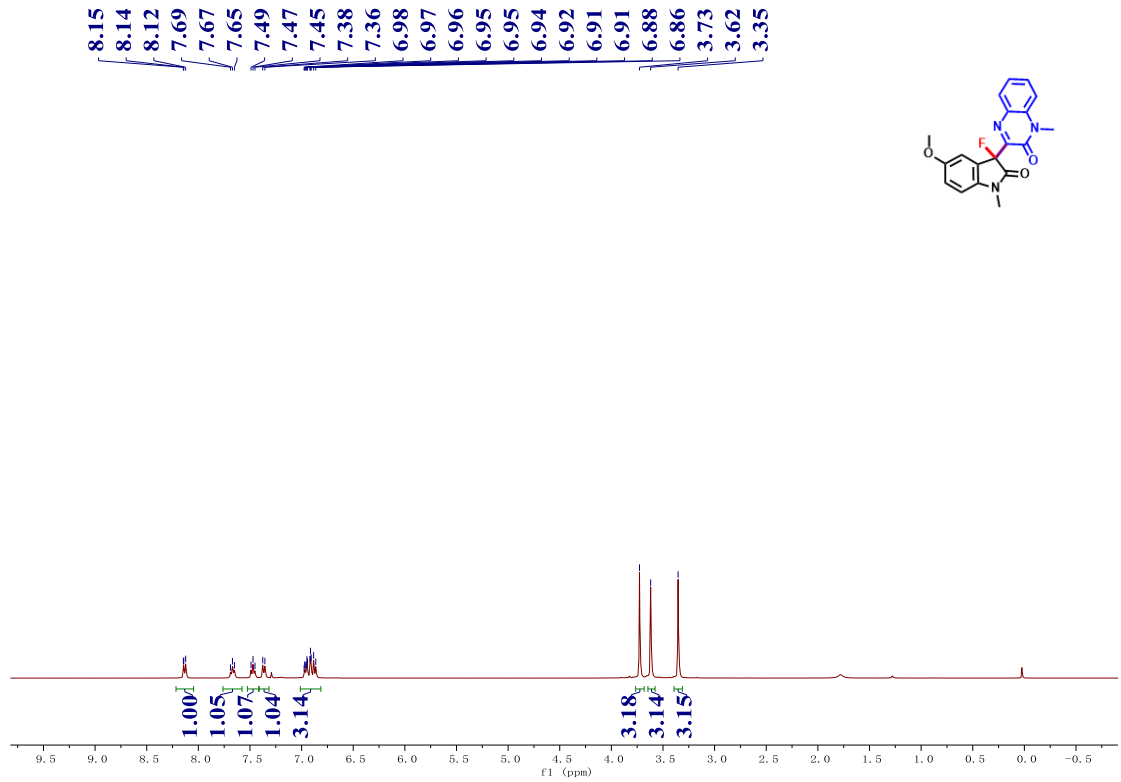
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ja**



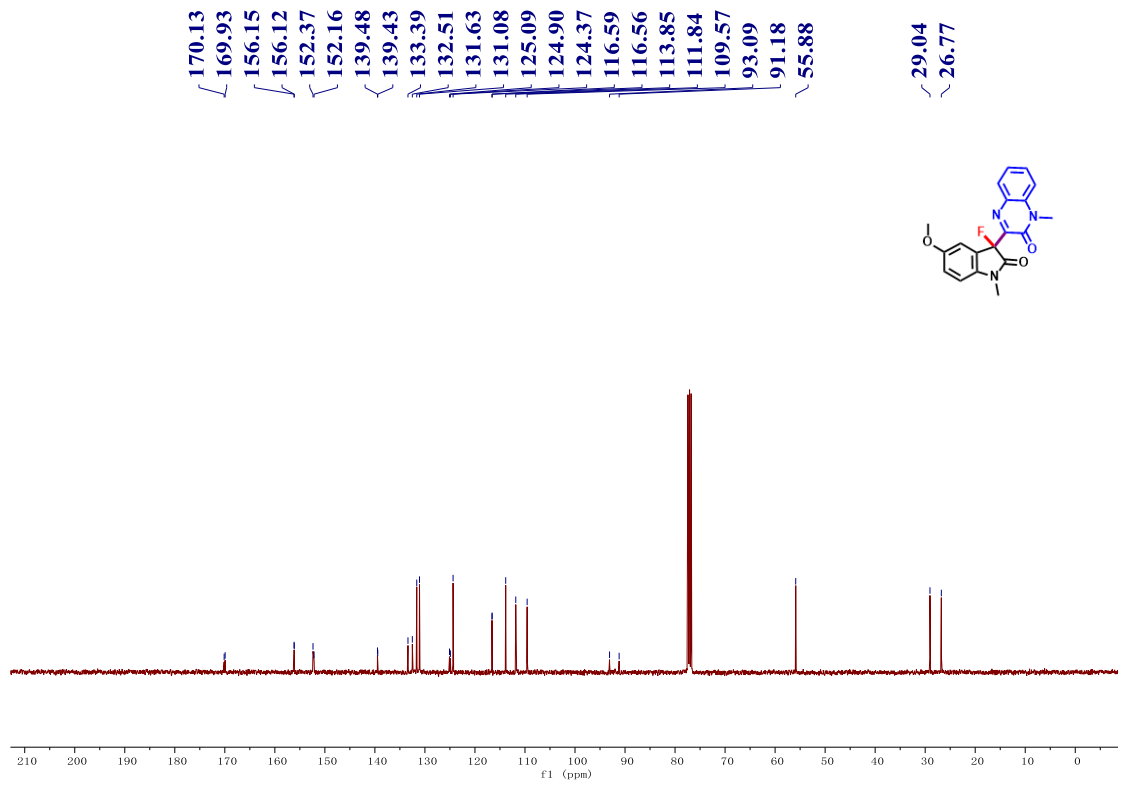
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ja**



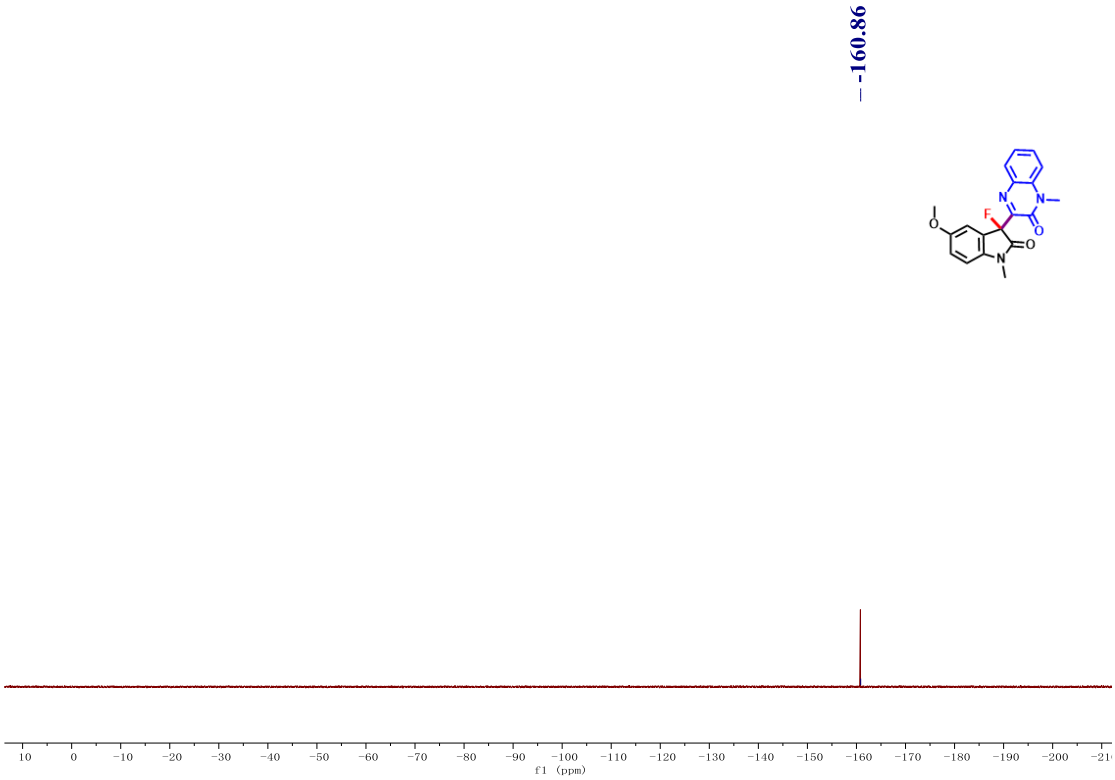
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3ja**



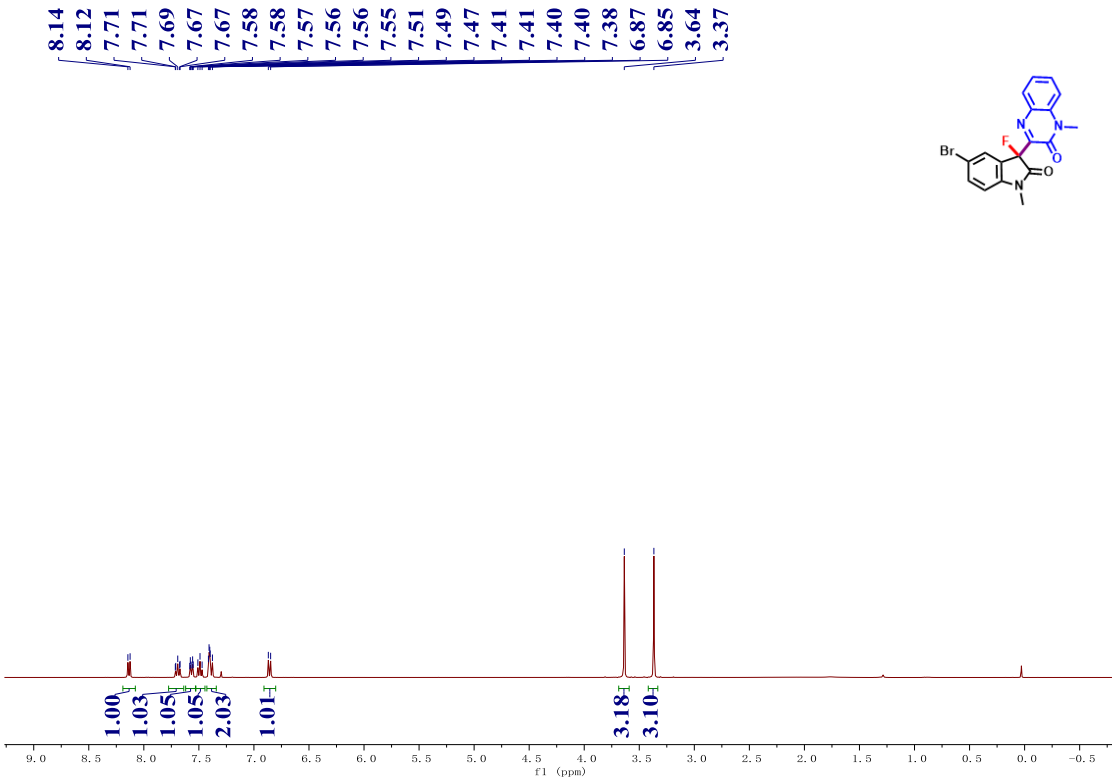
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ka**



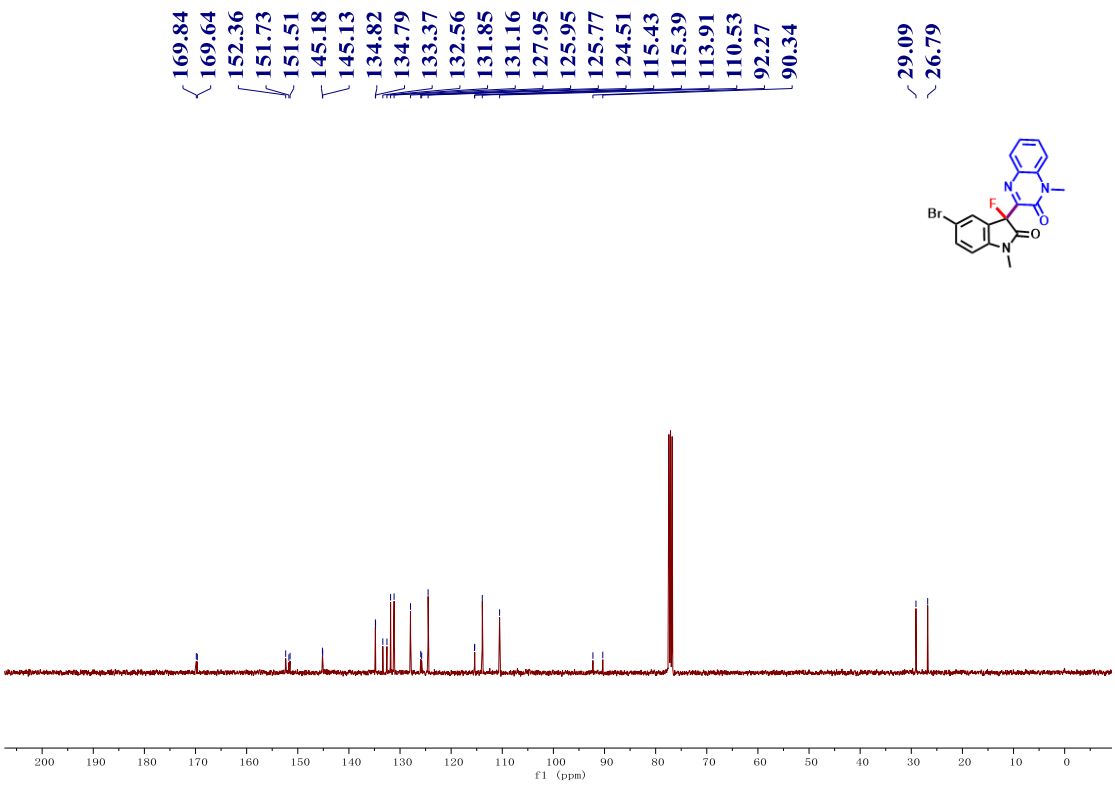
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ka**



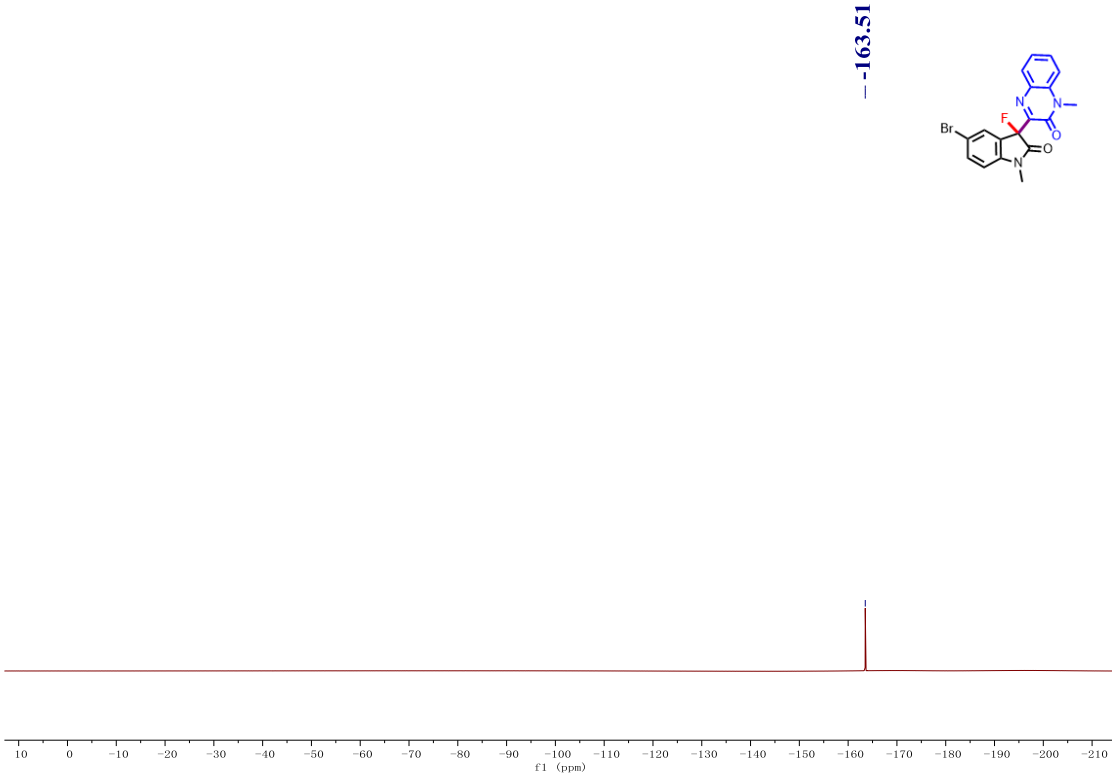
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ka**



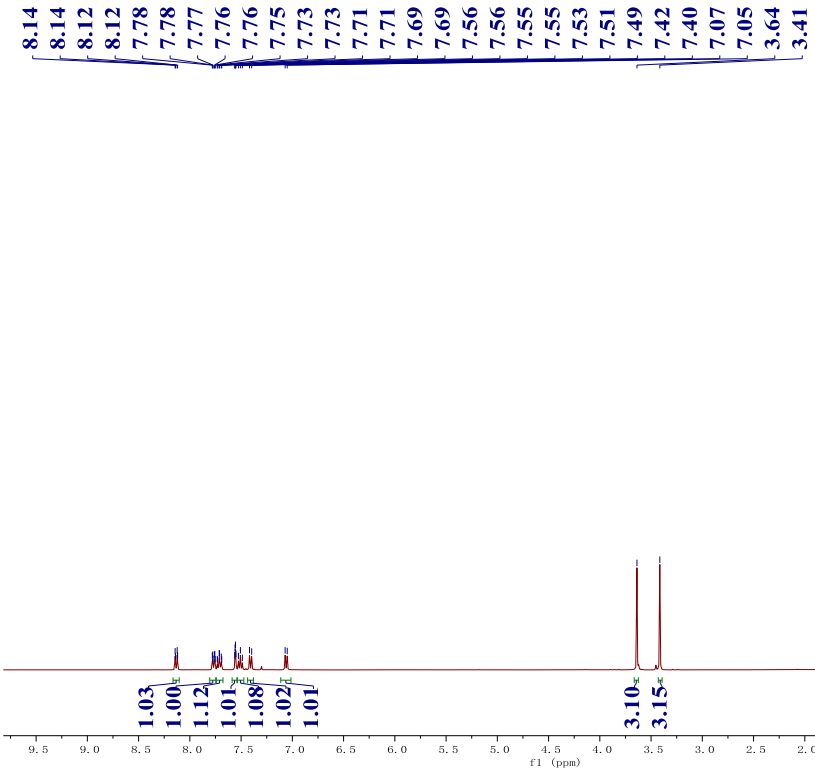
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3la**



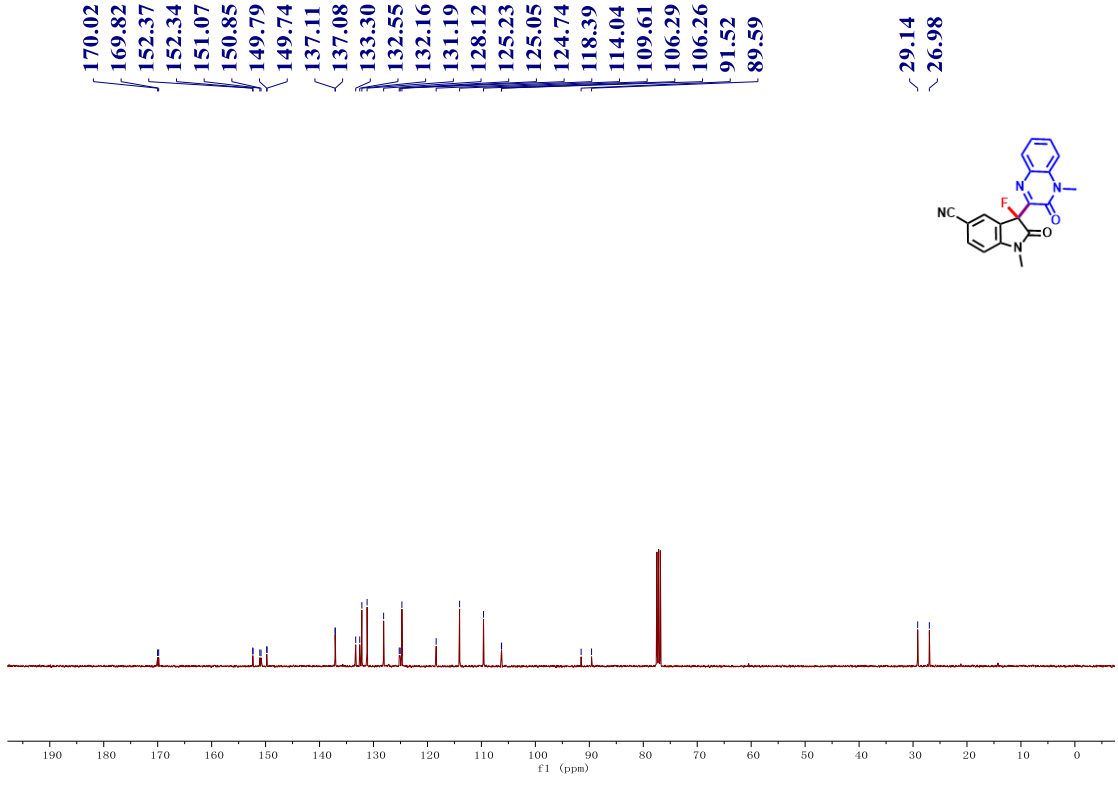
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3la**



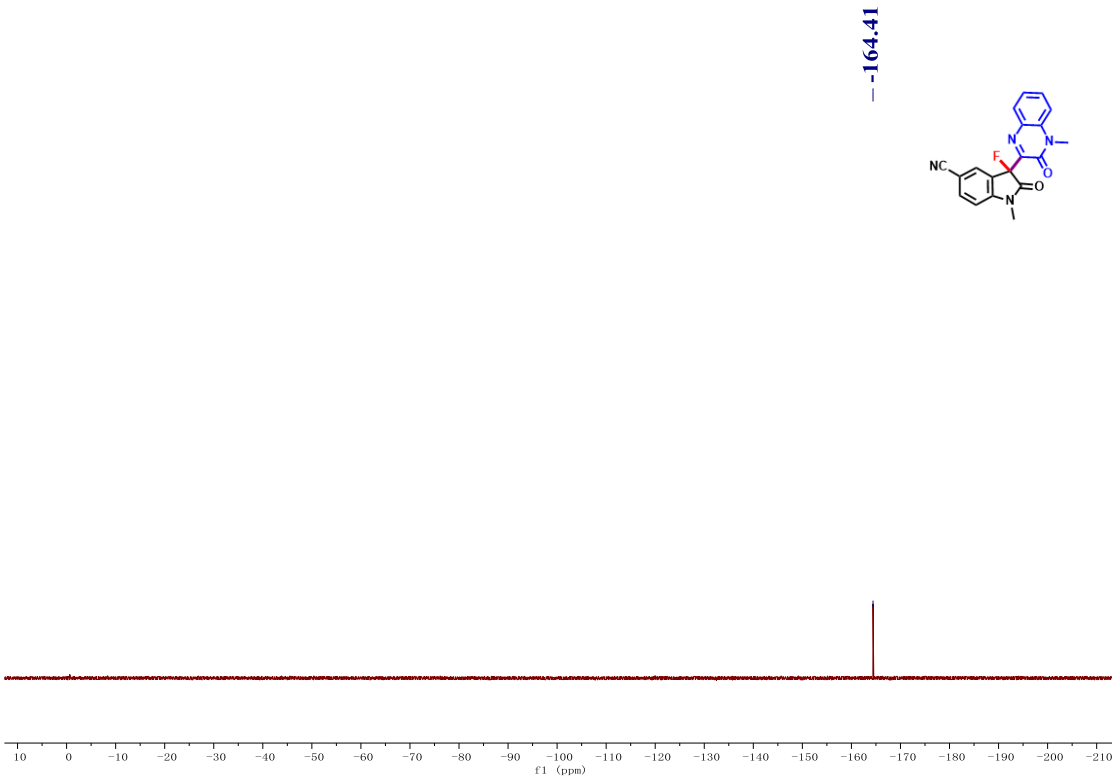
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3la**



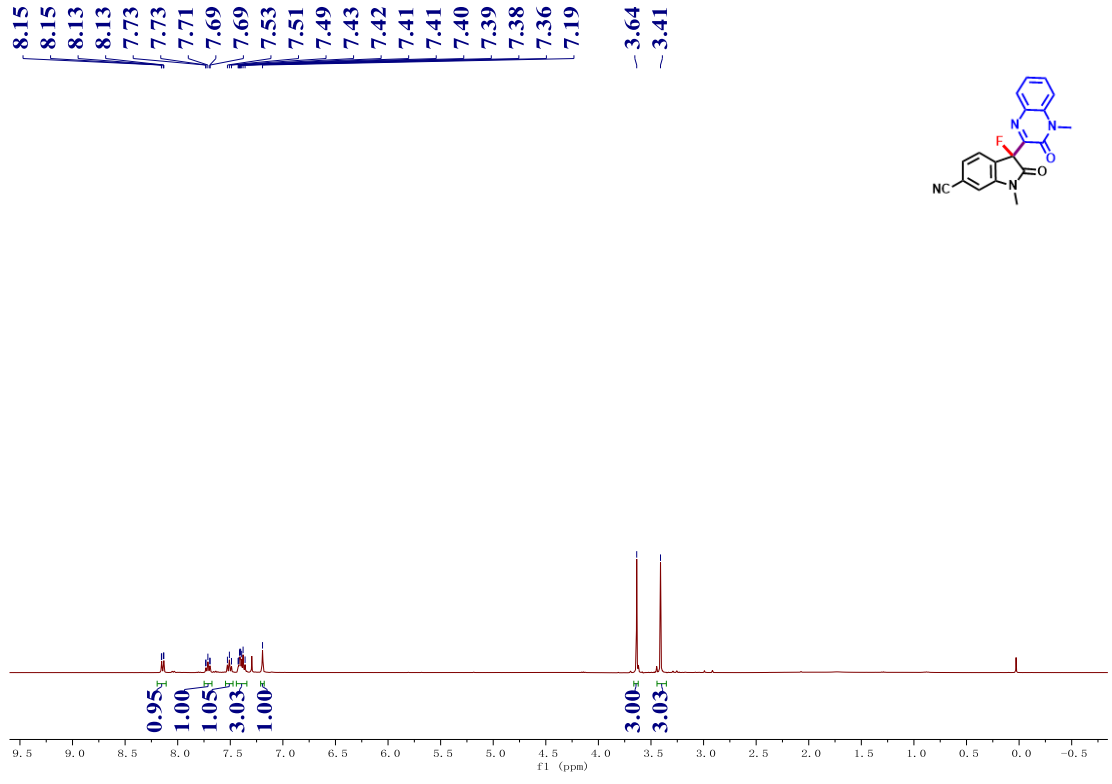
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3ma**



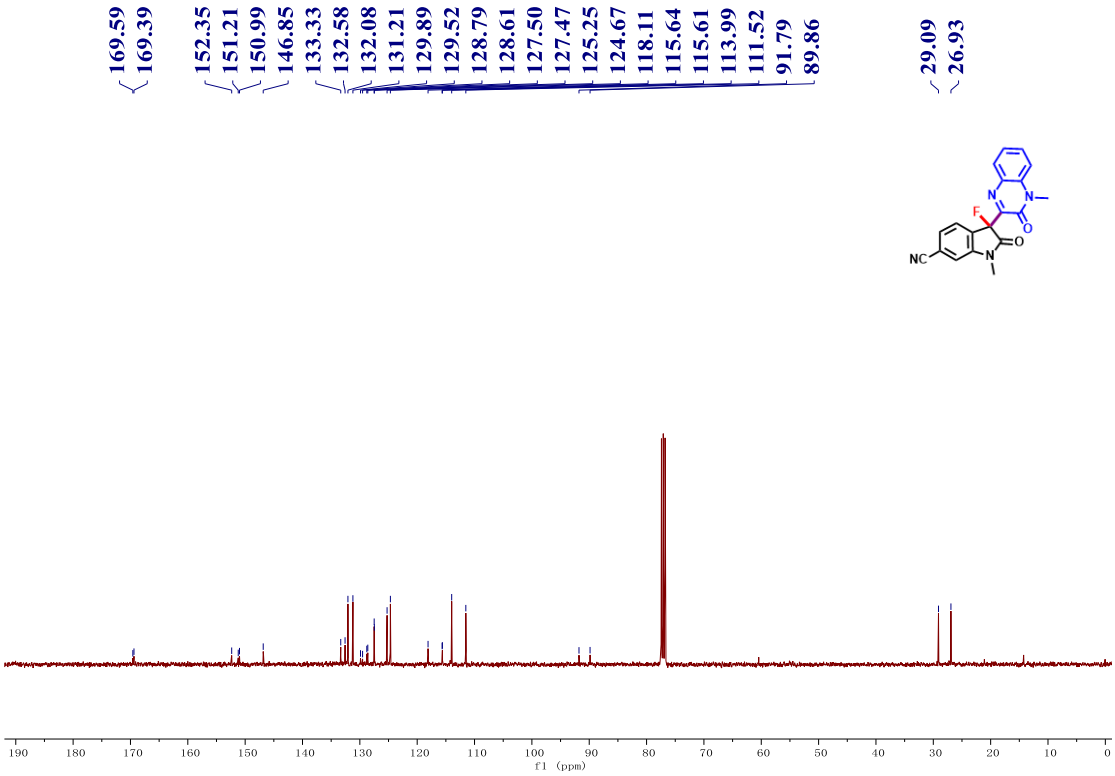
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3ma**



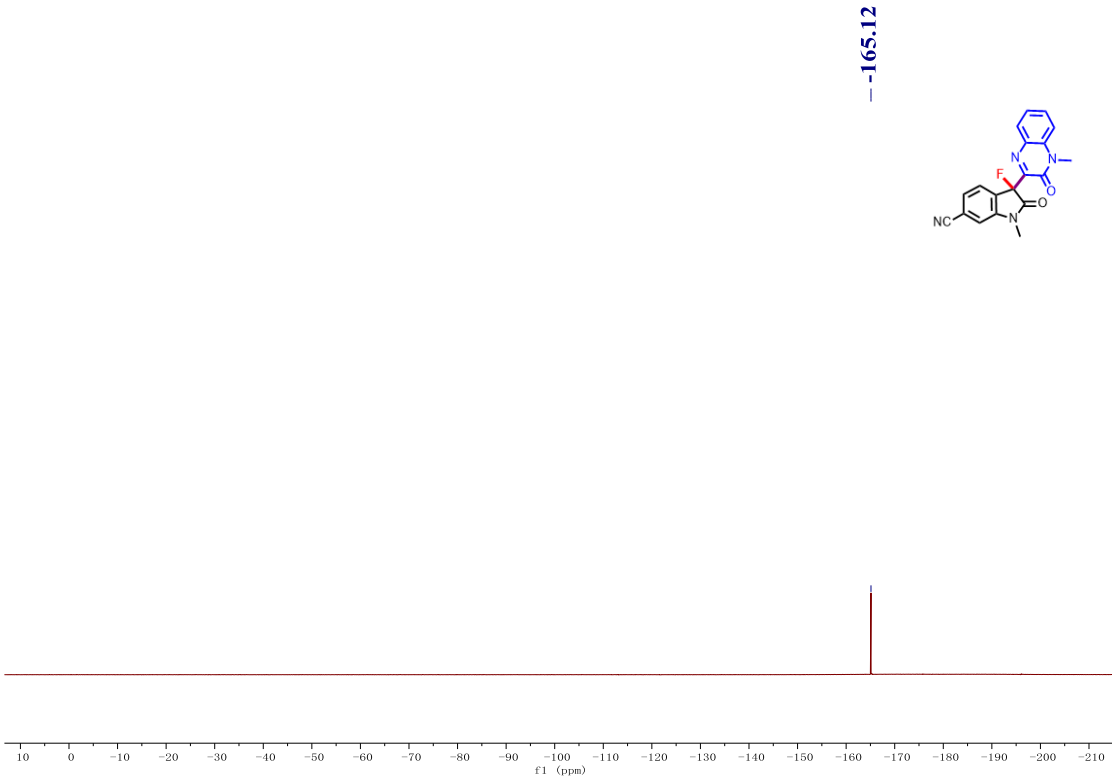
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ma**



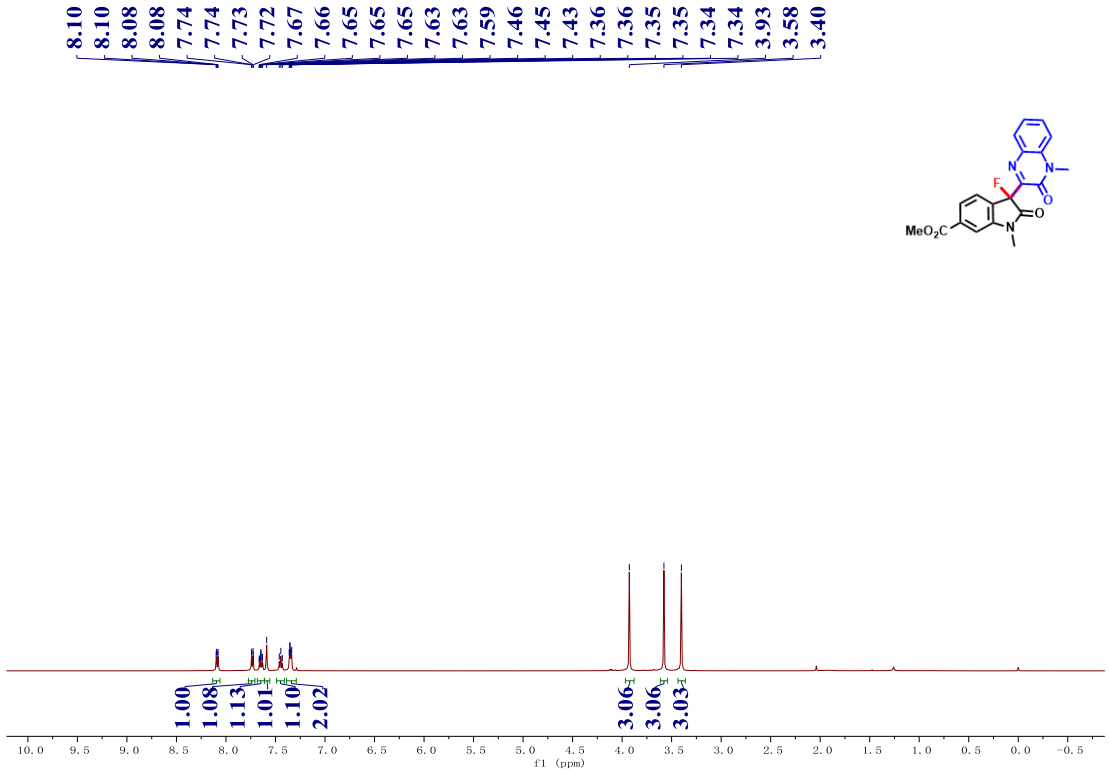
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3na**



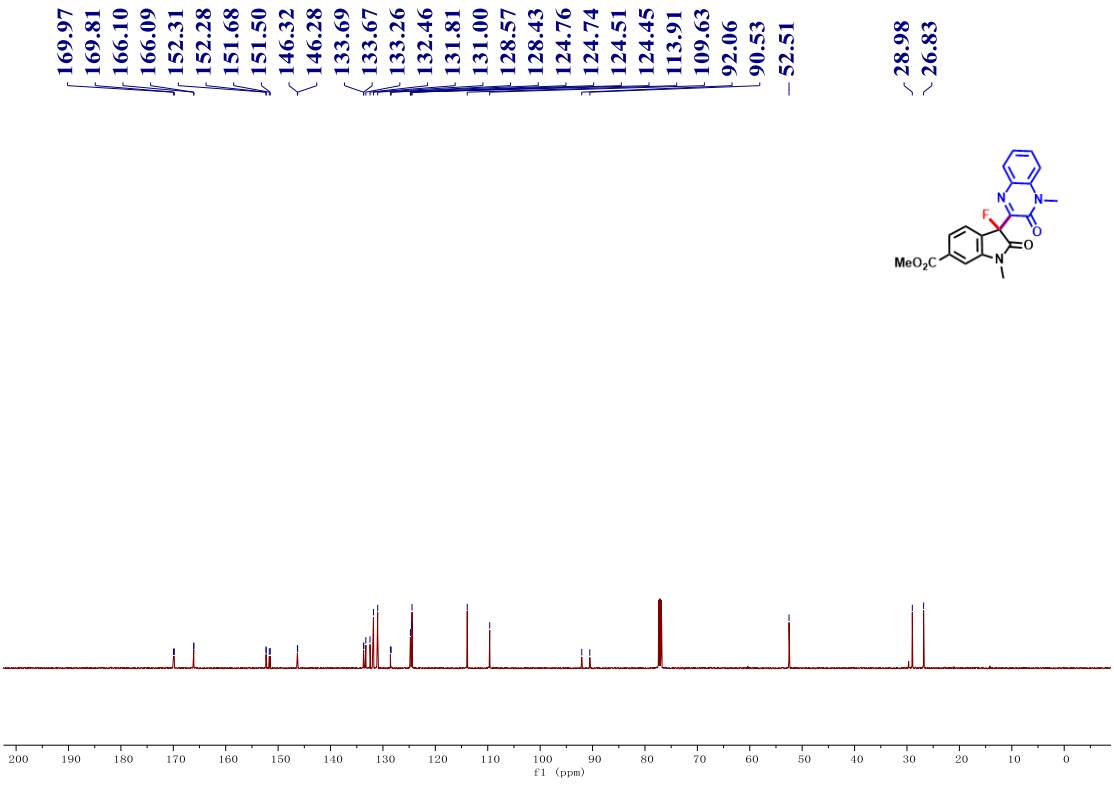
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3na**



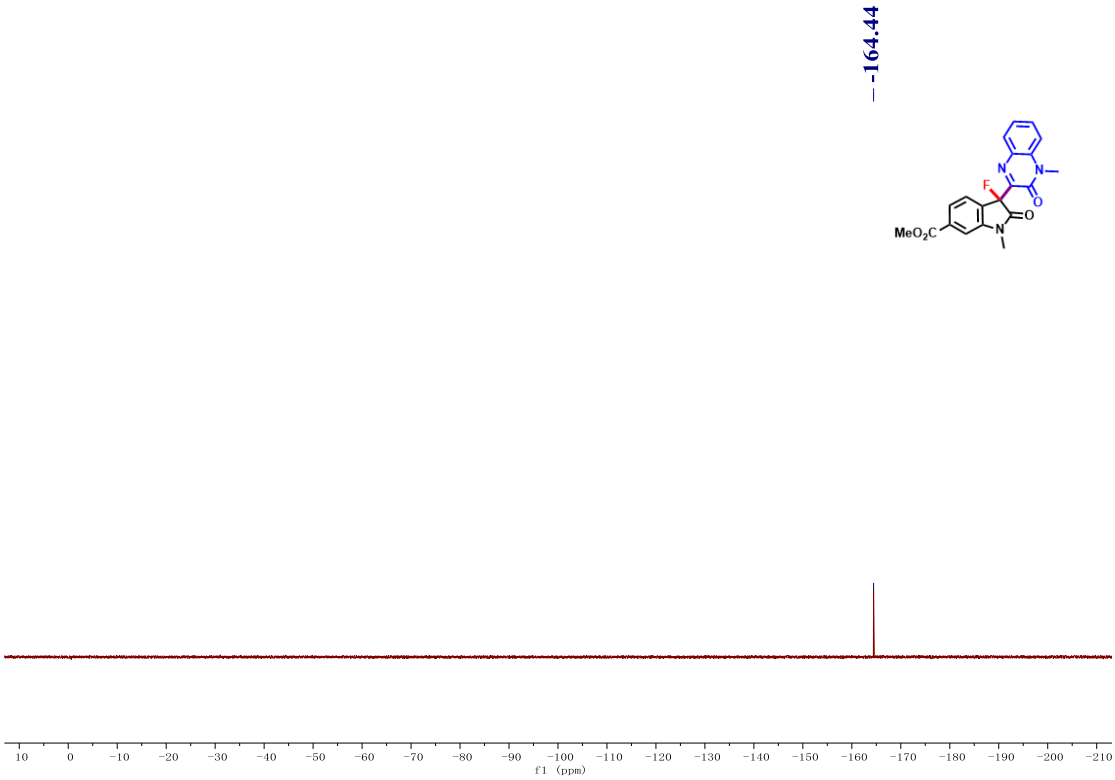
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3na**



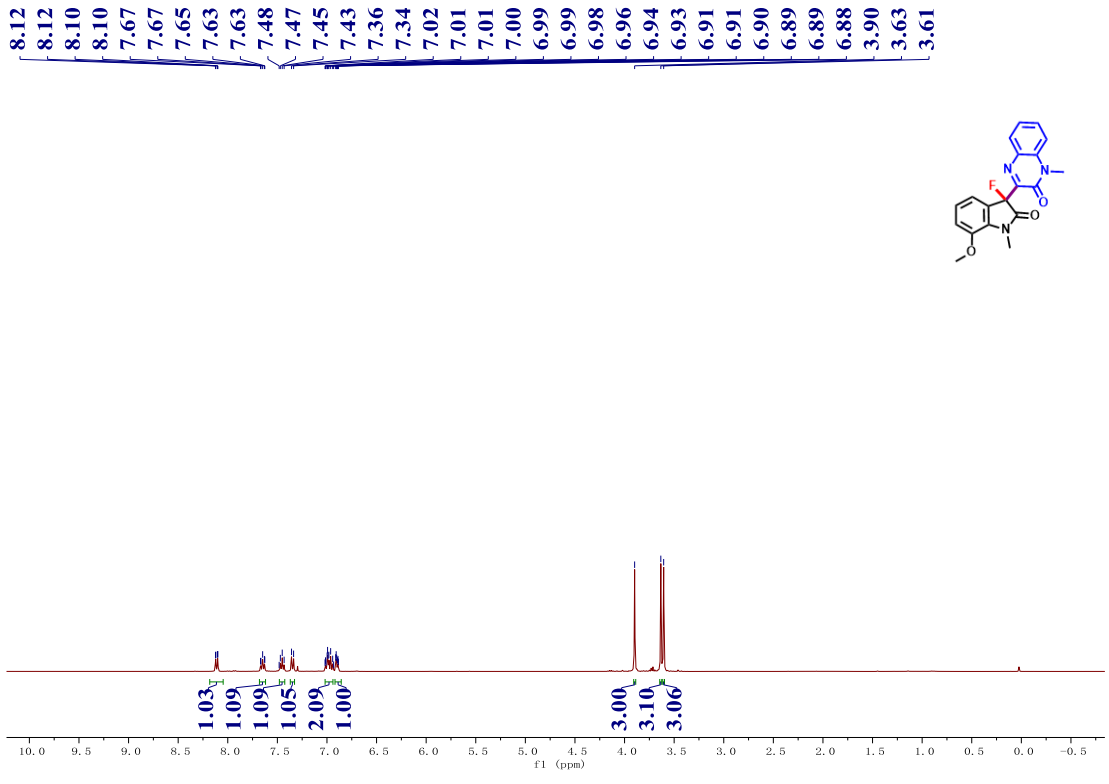
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3oa**



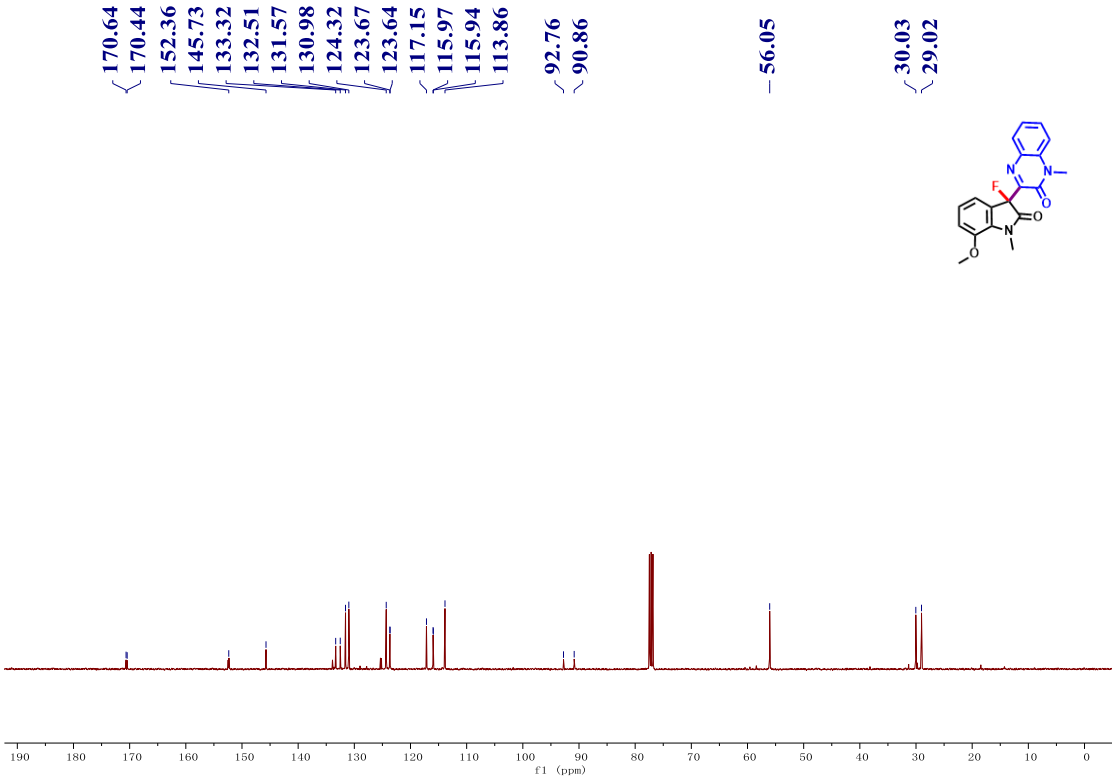
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3oa**



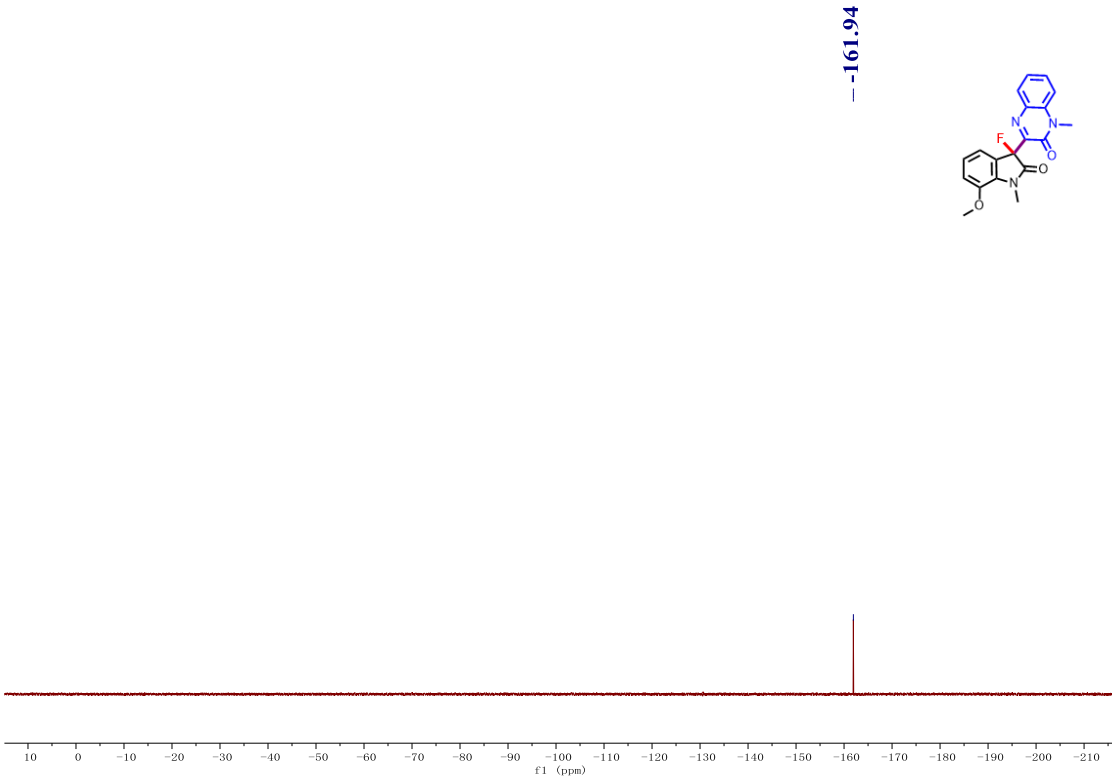
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3oa**



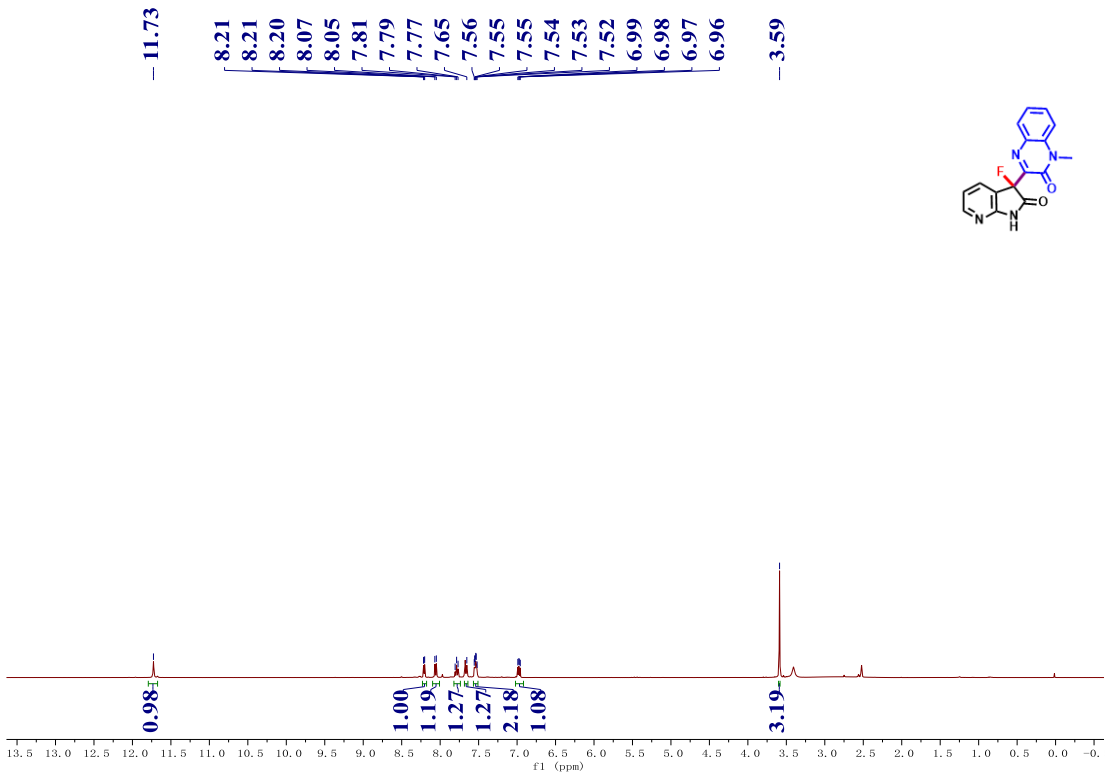
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3pa**



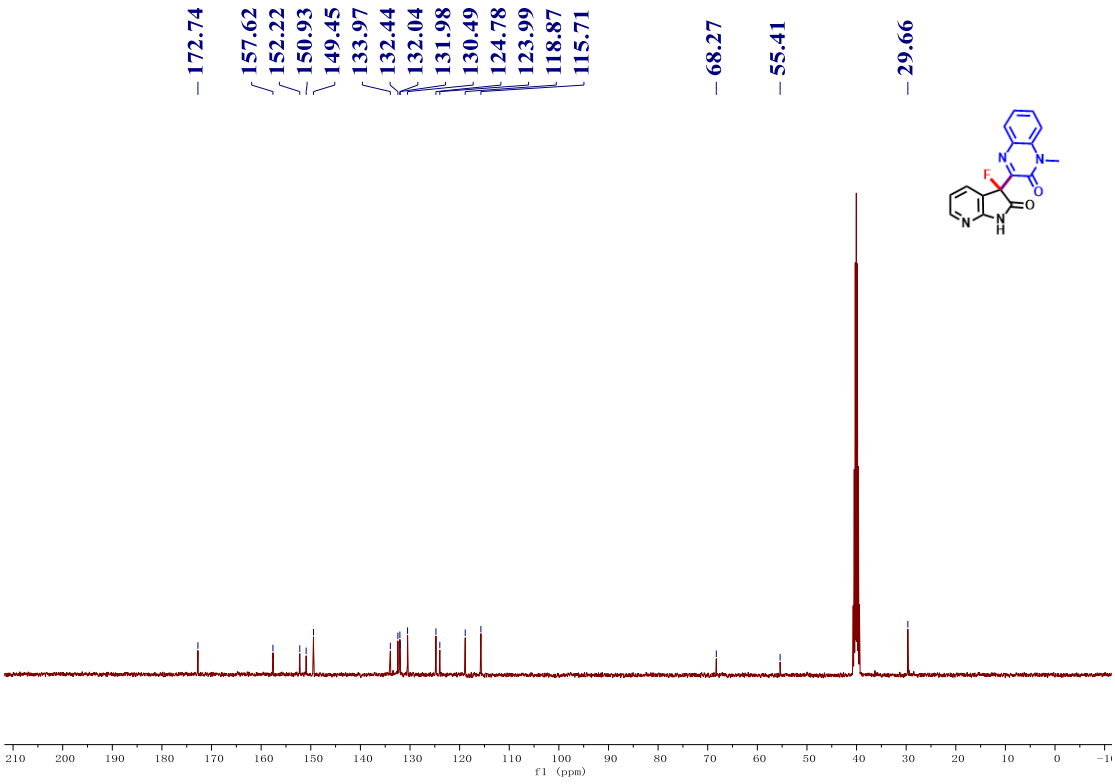
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3pa**



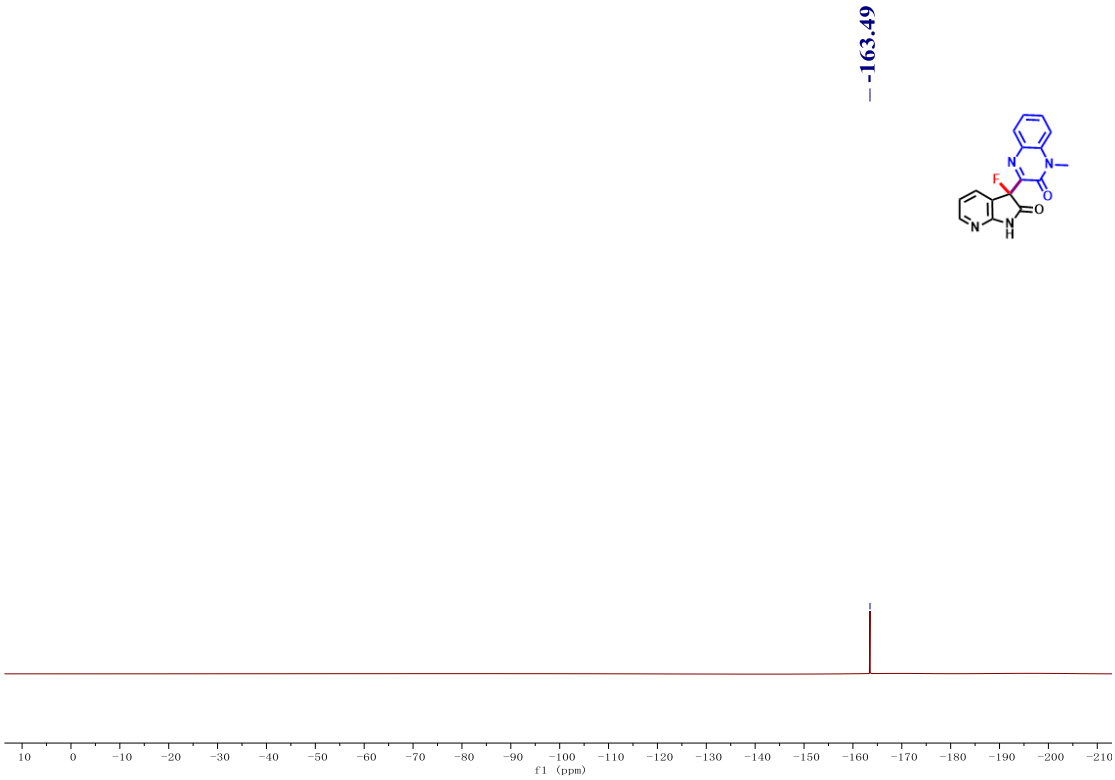
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3pa**



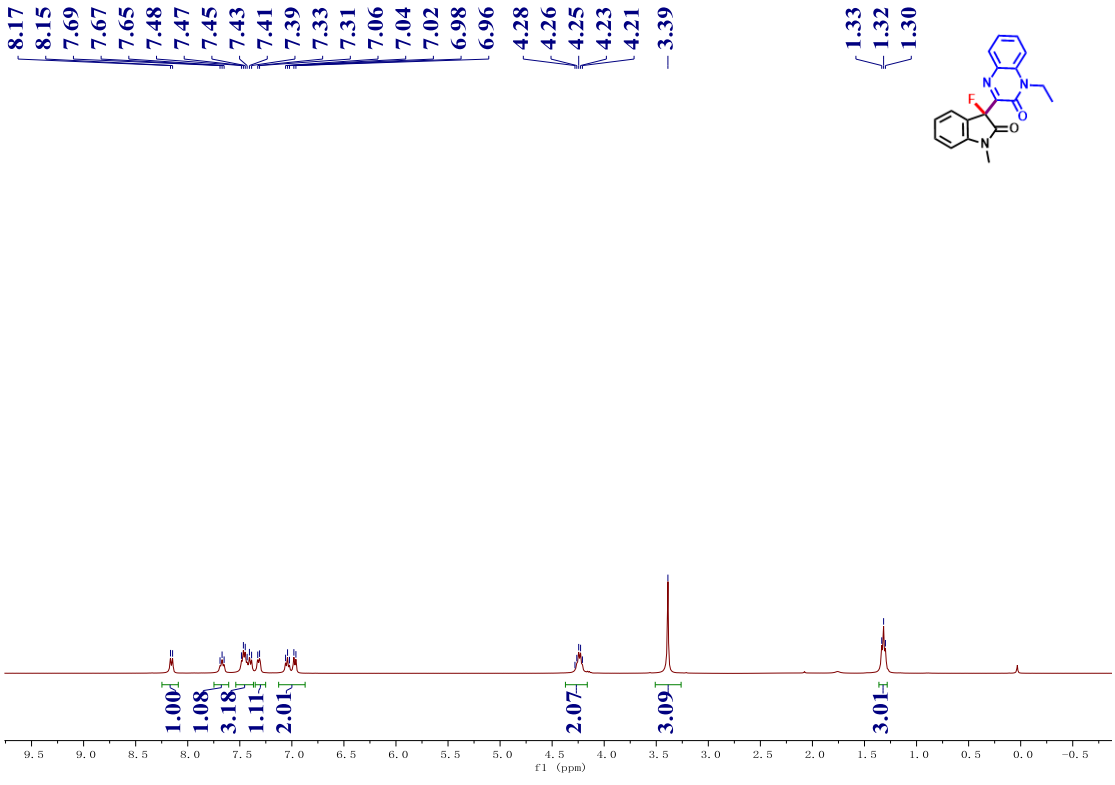
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **3qa**



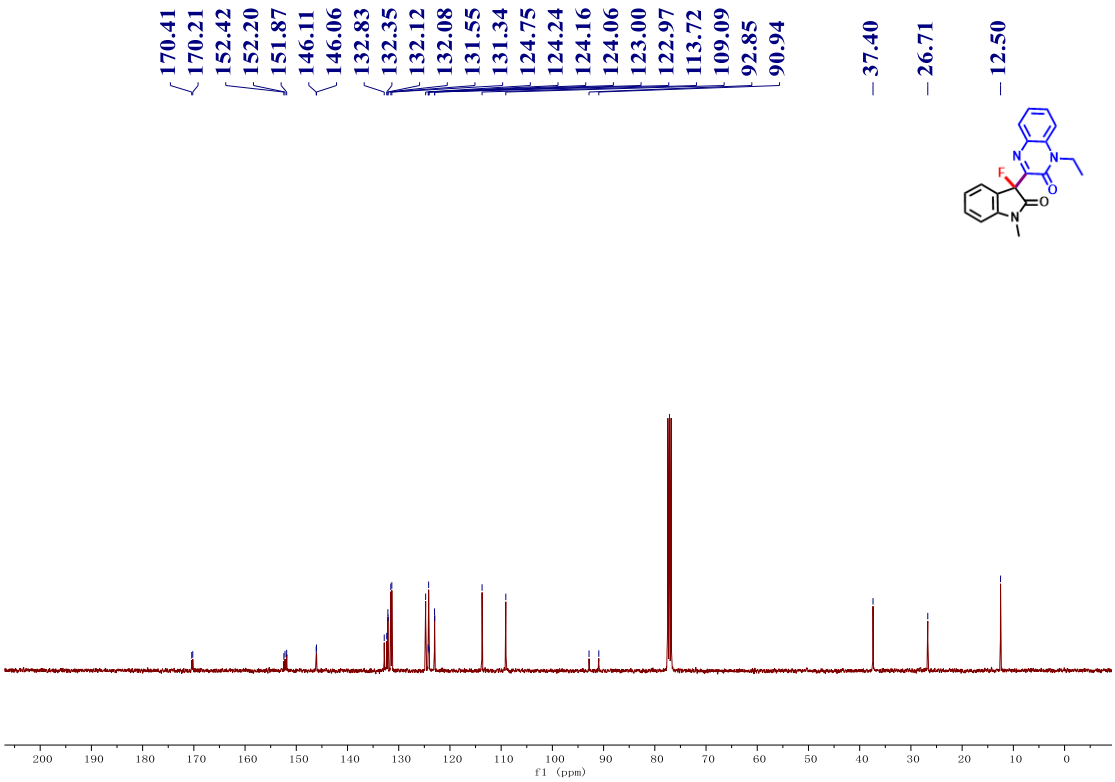
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **3qa**



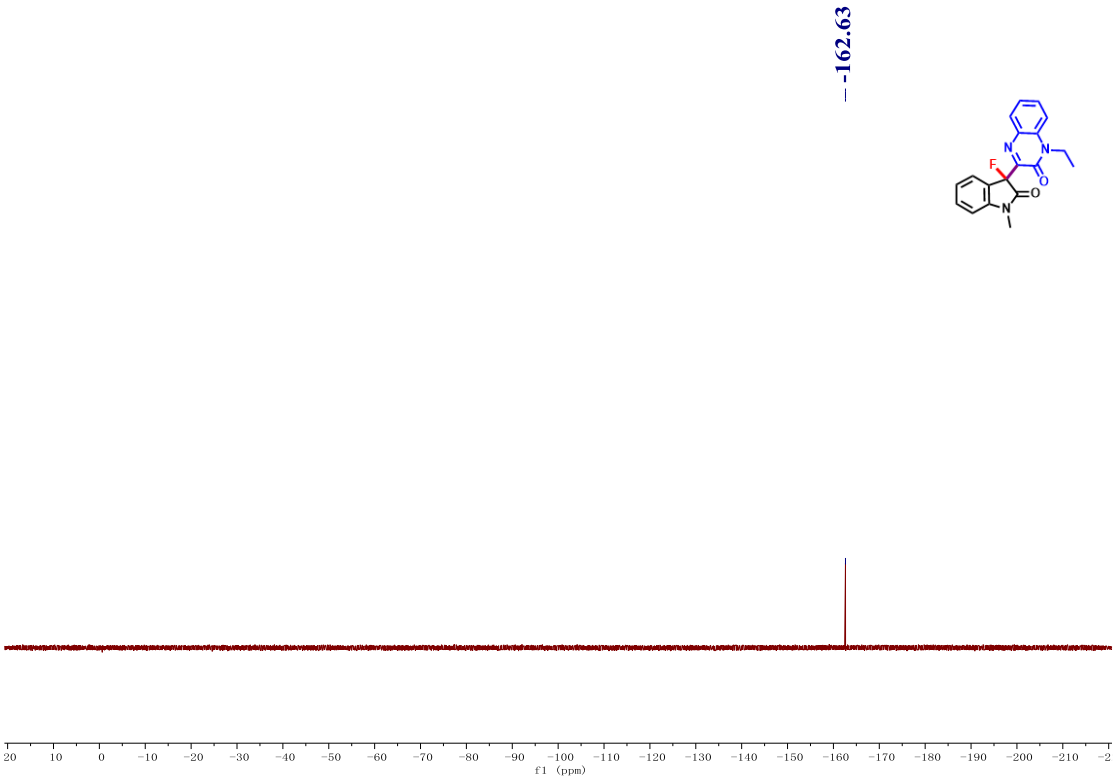
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3qa**



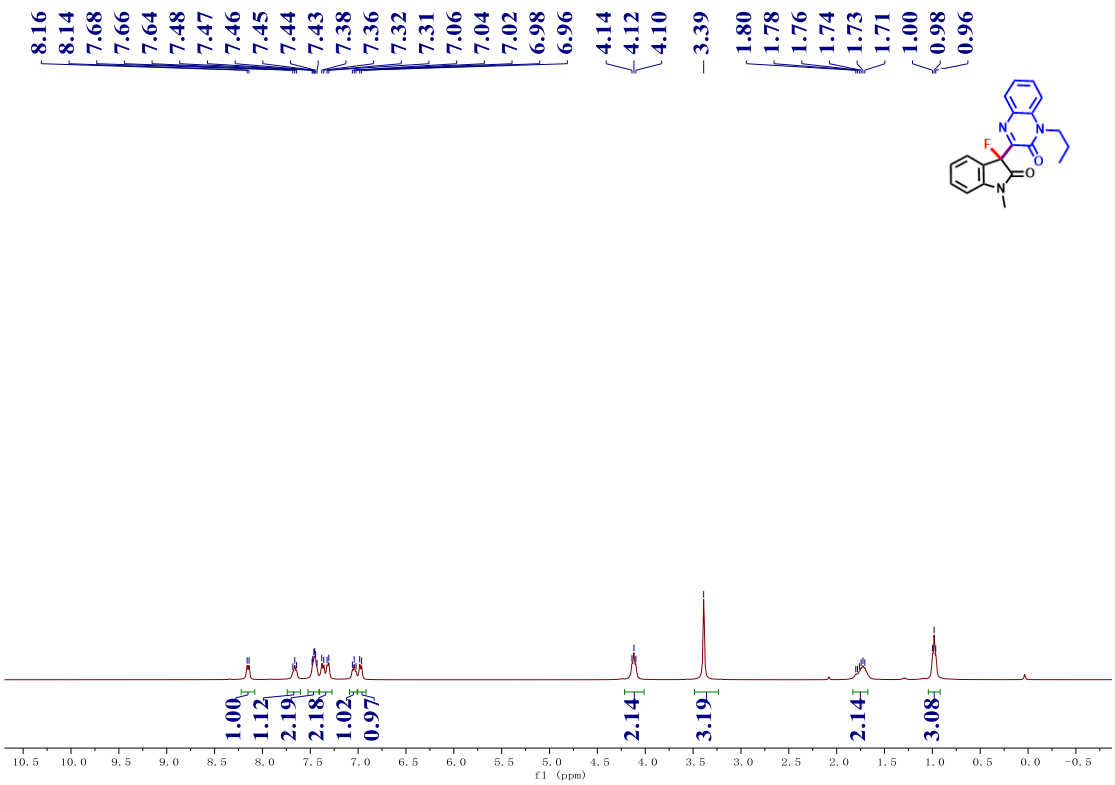
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3ab**



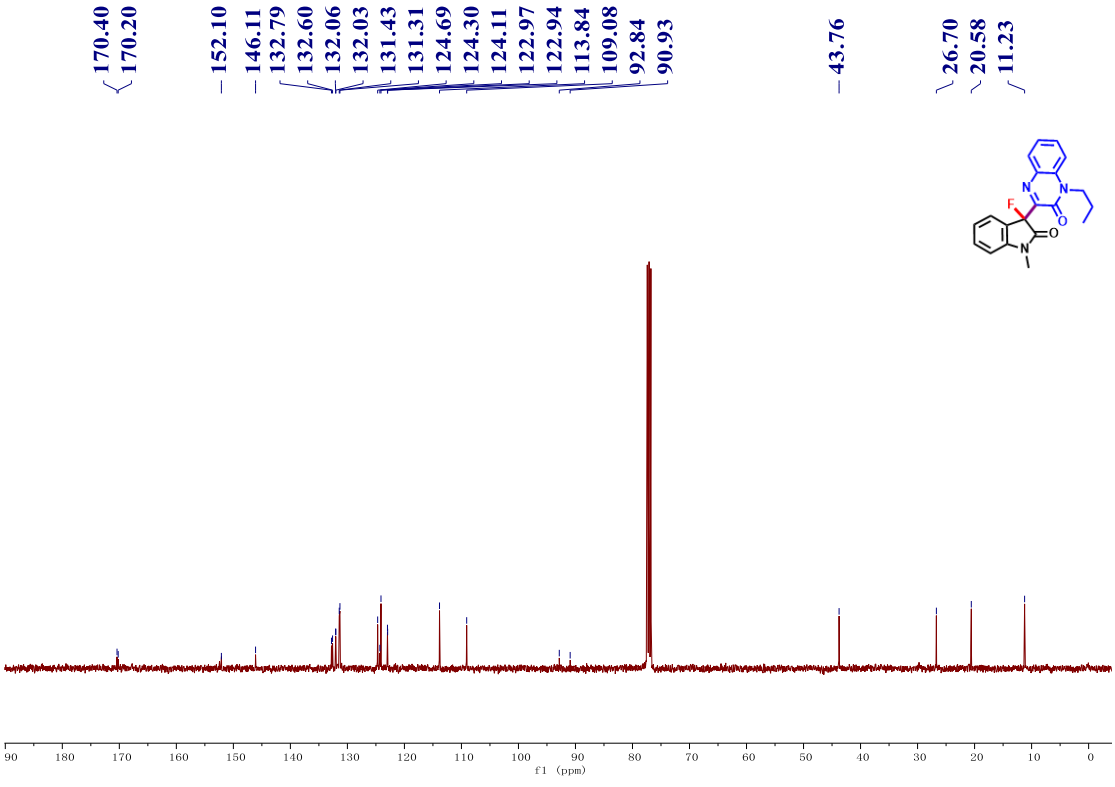
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3ab**



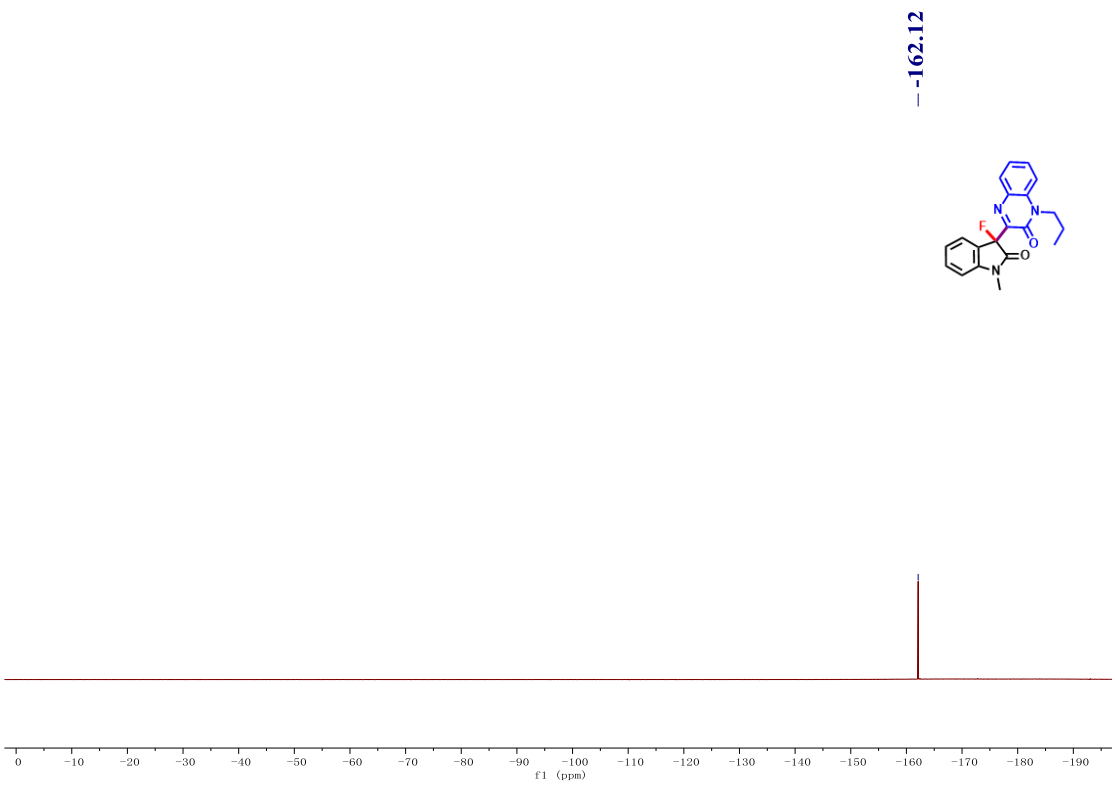
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ab**



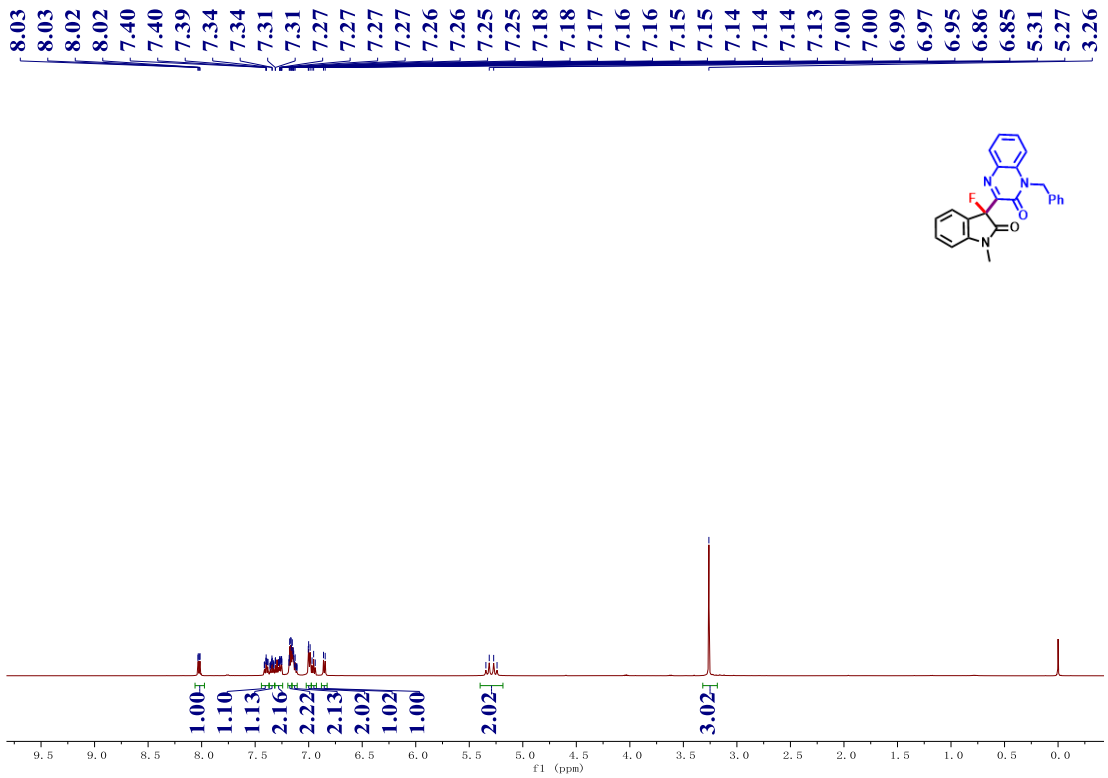
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ac**



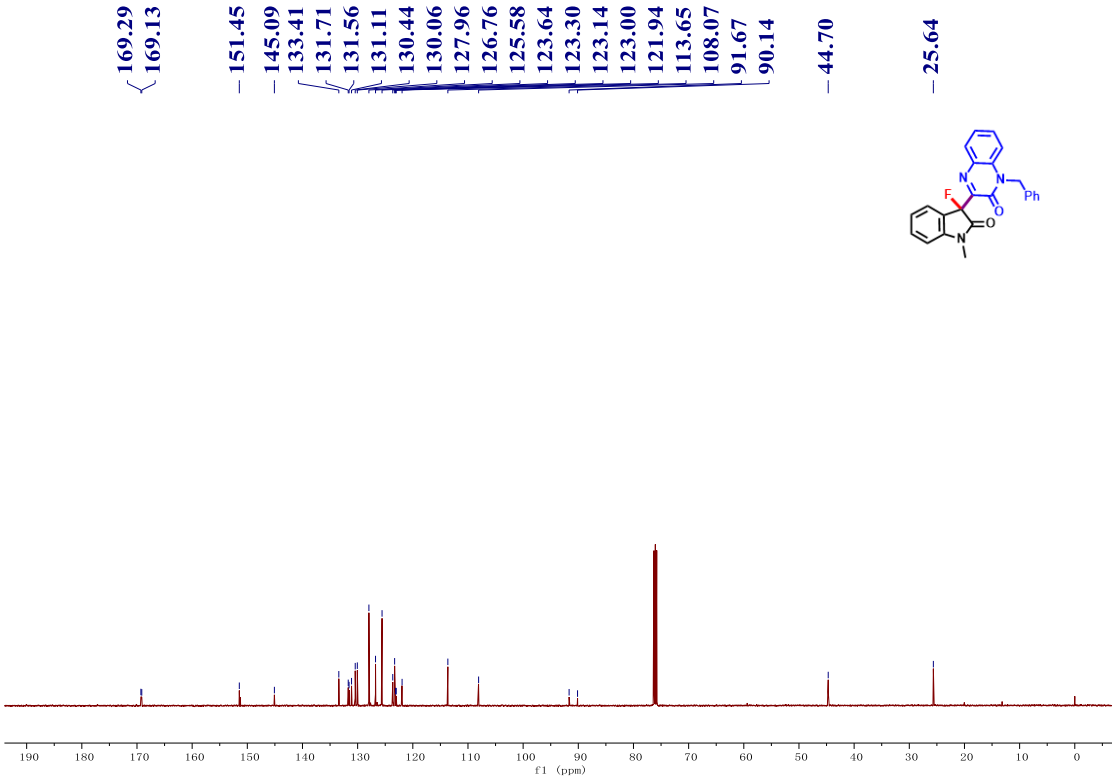
^{13}C NMR (101 MHz, $CDCl_3$) Spectra of compound **3ac**



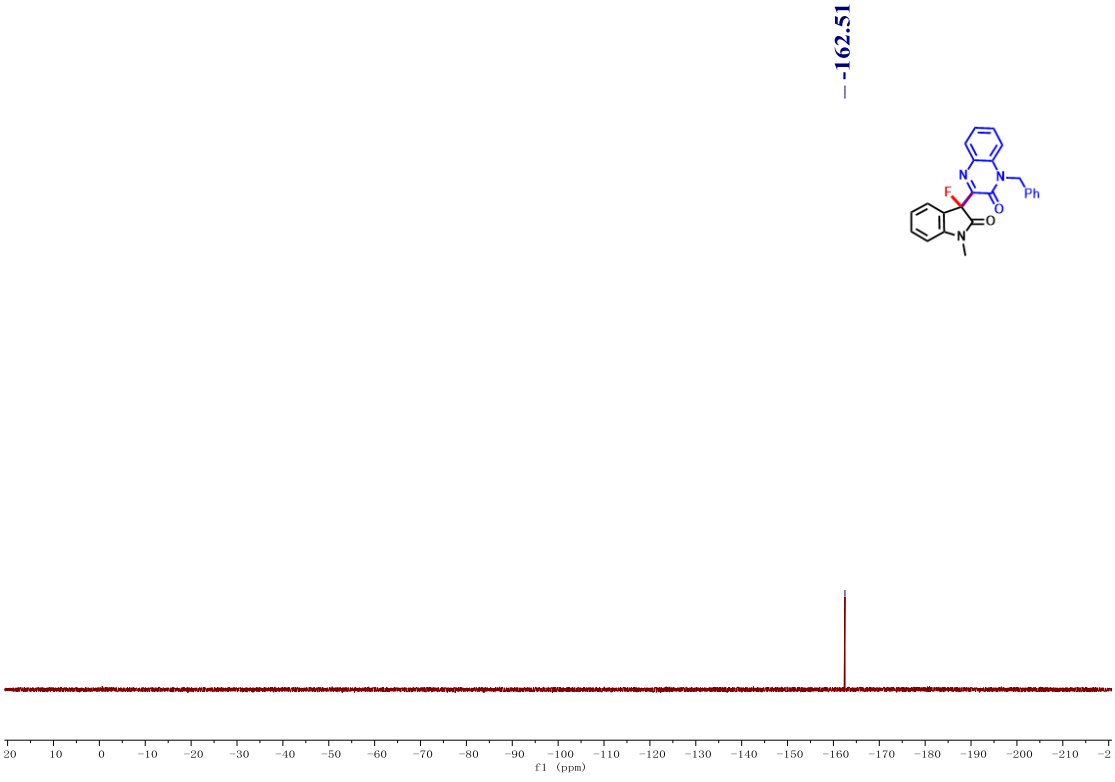
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ac**



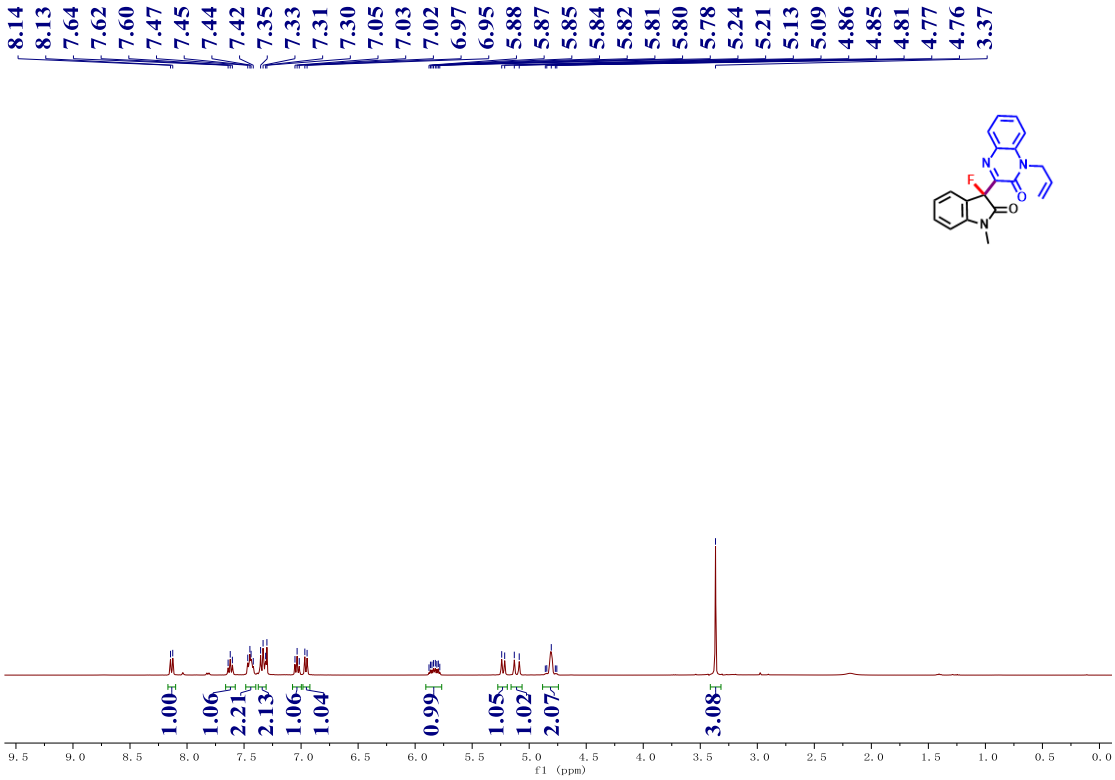
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3ad**



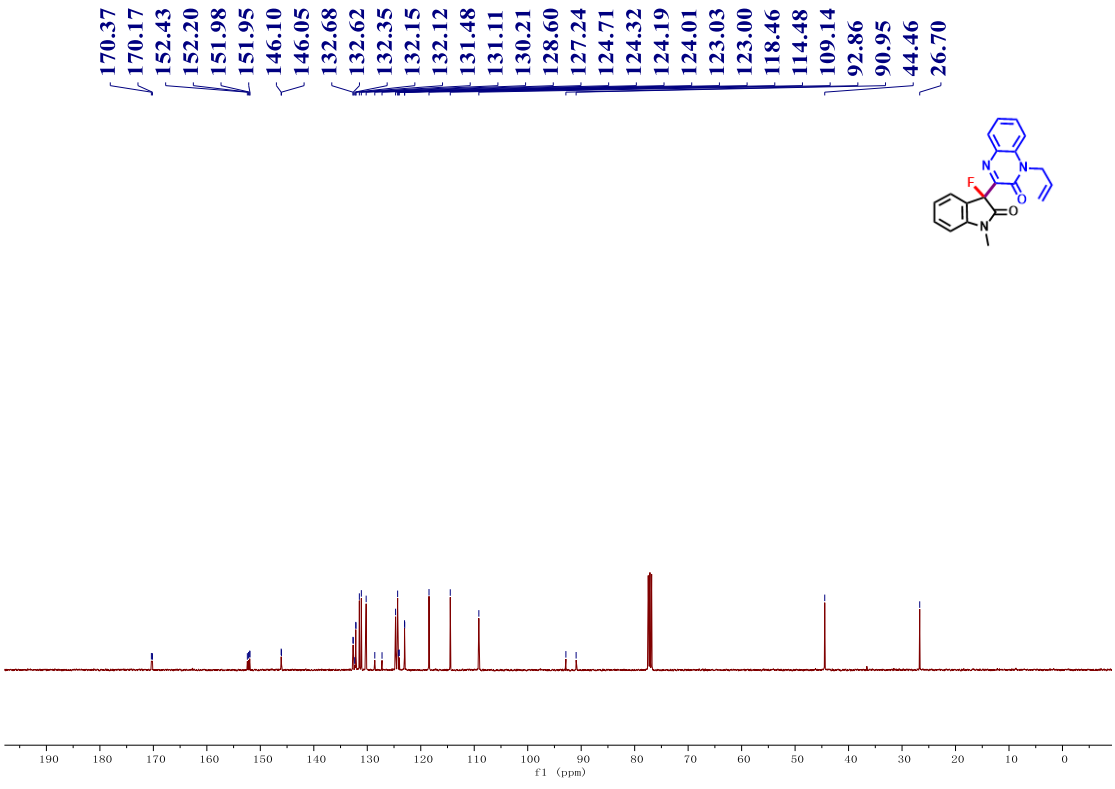
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3ad**



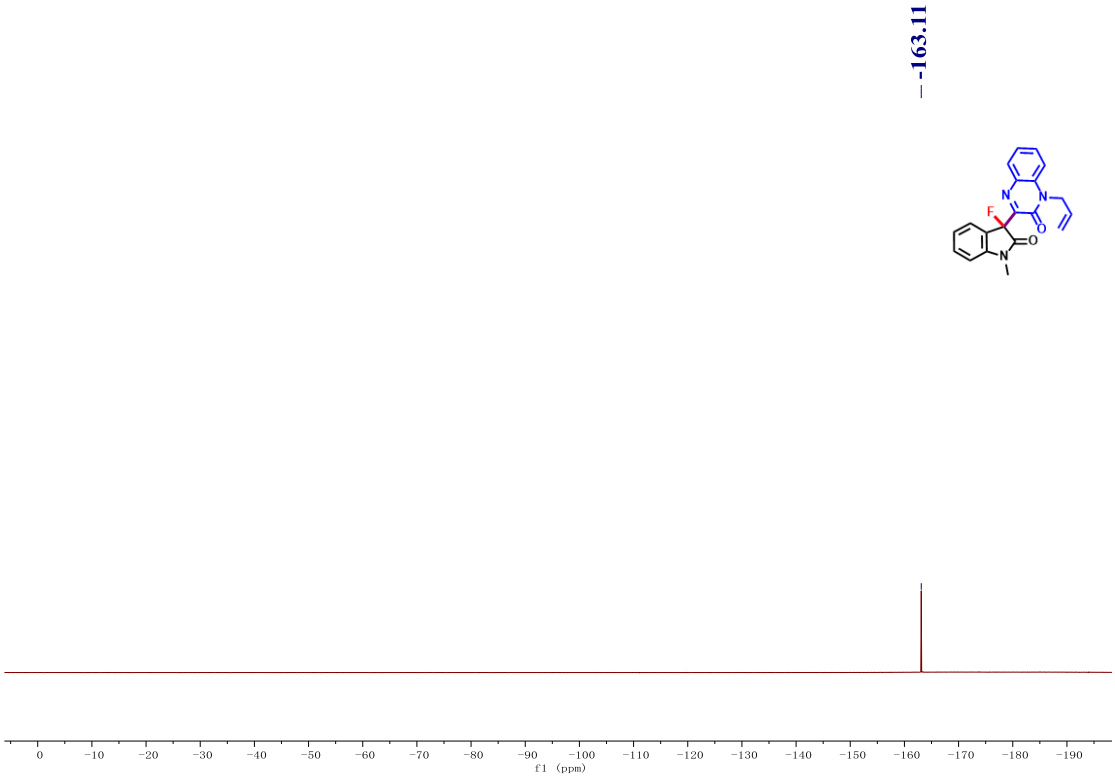
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ad**



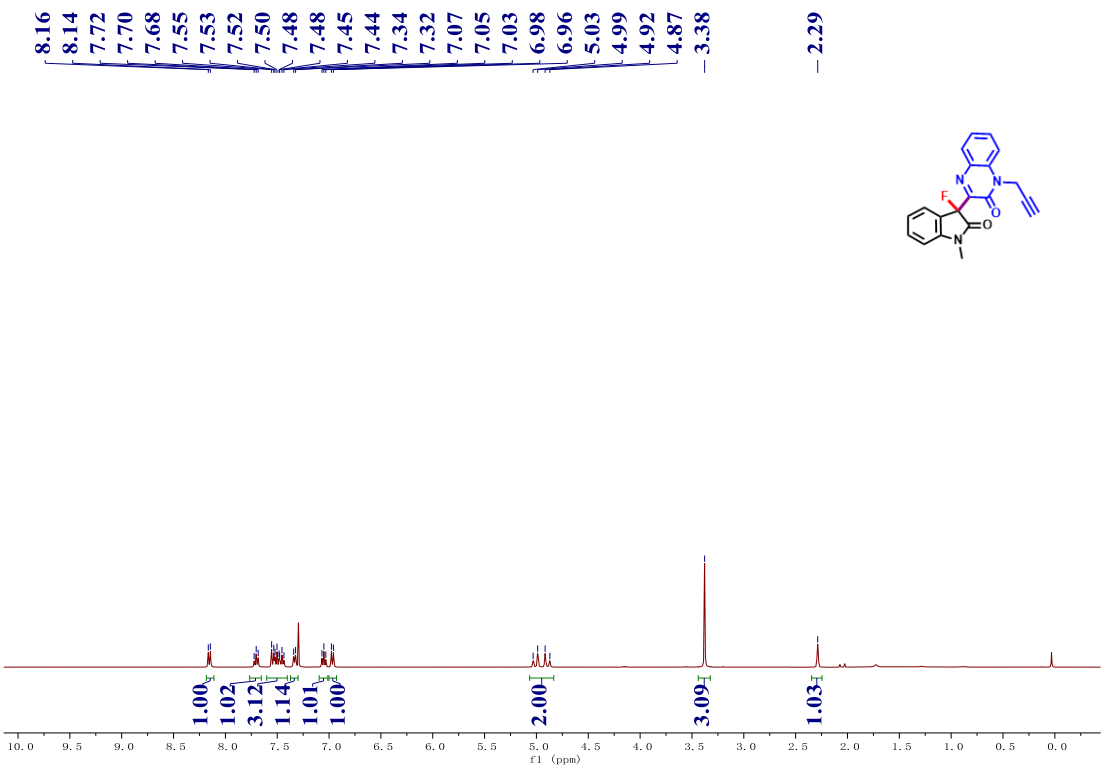
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ae**



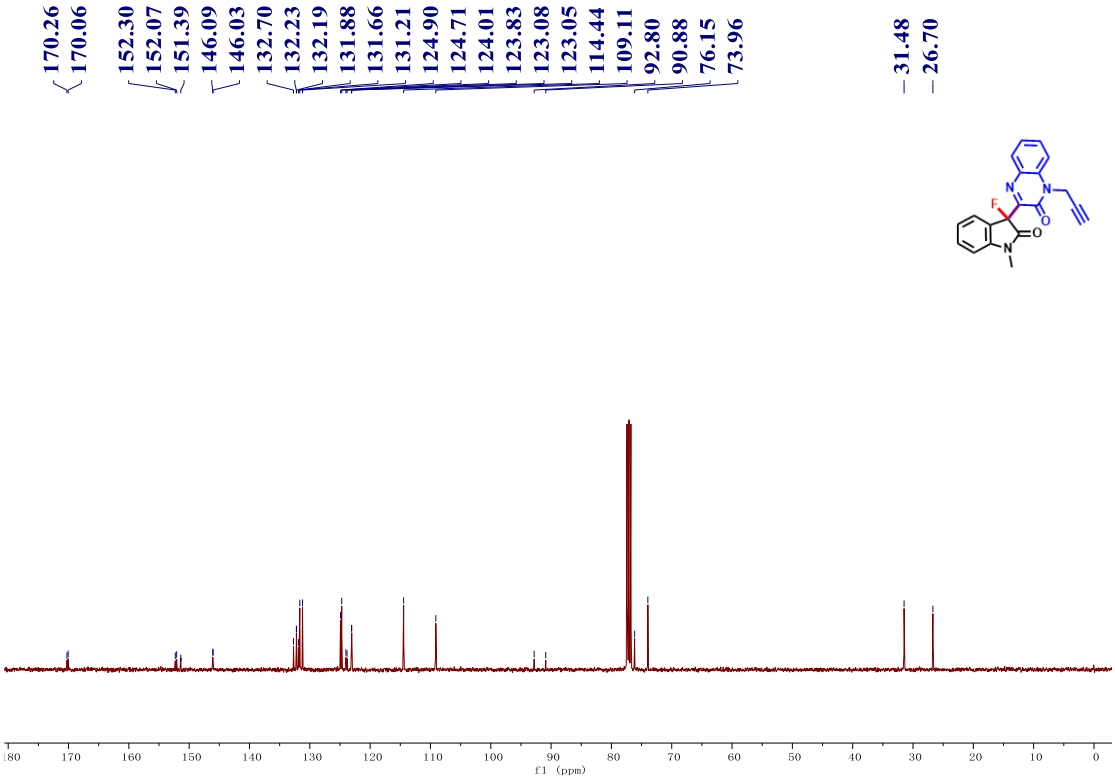
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ae**



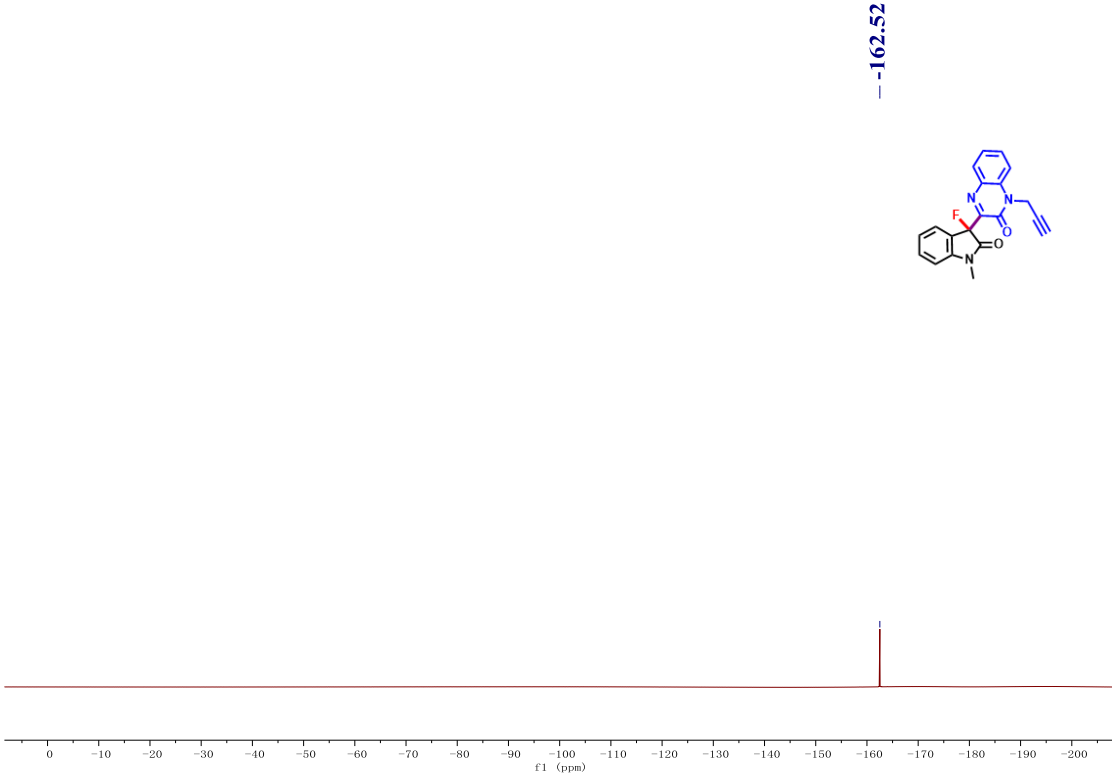
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ae**



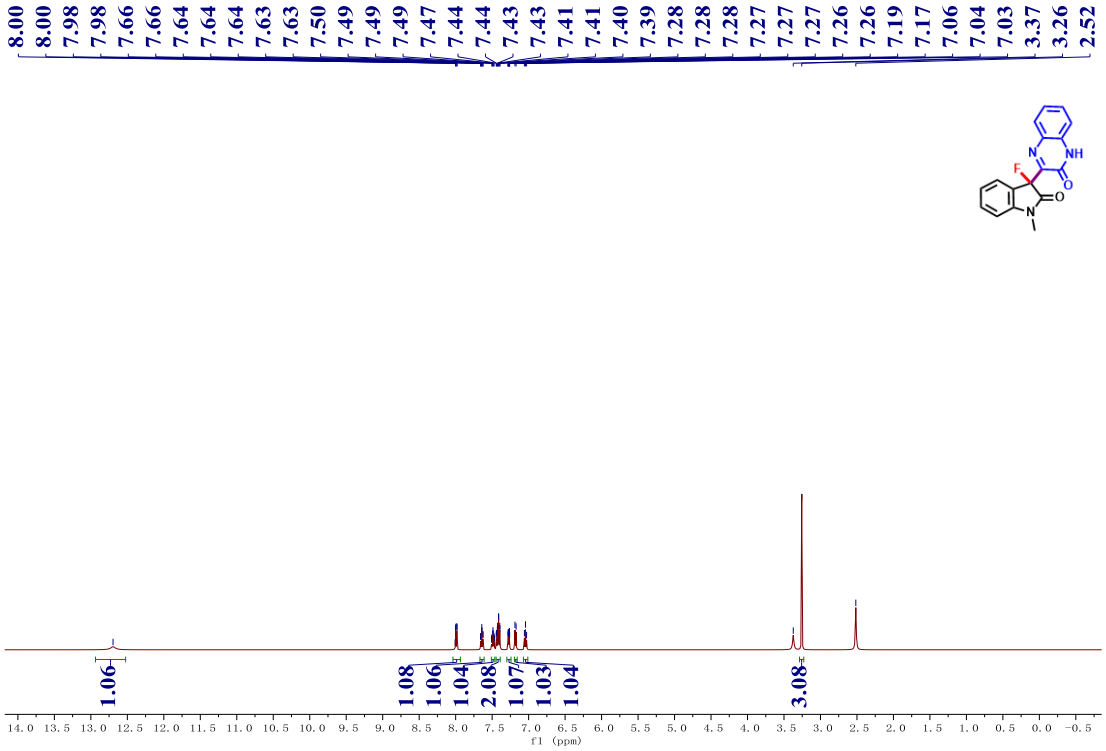
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3af**



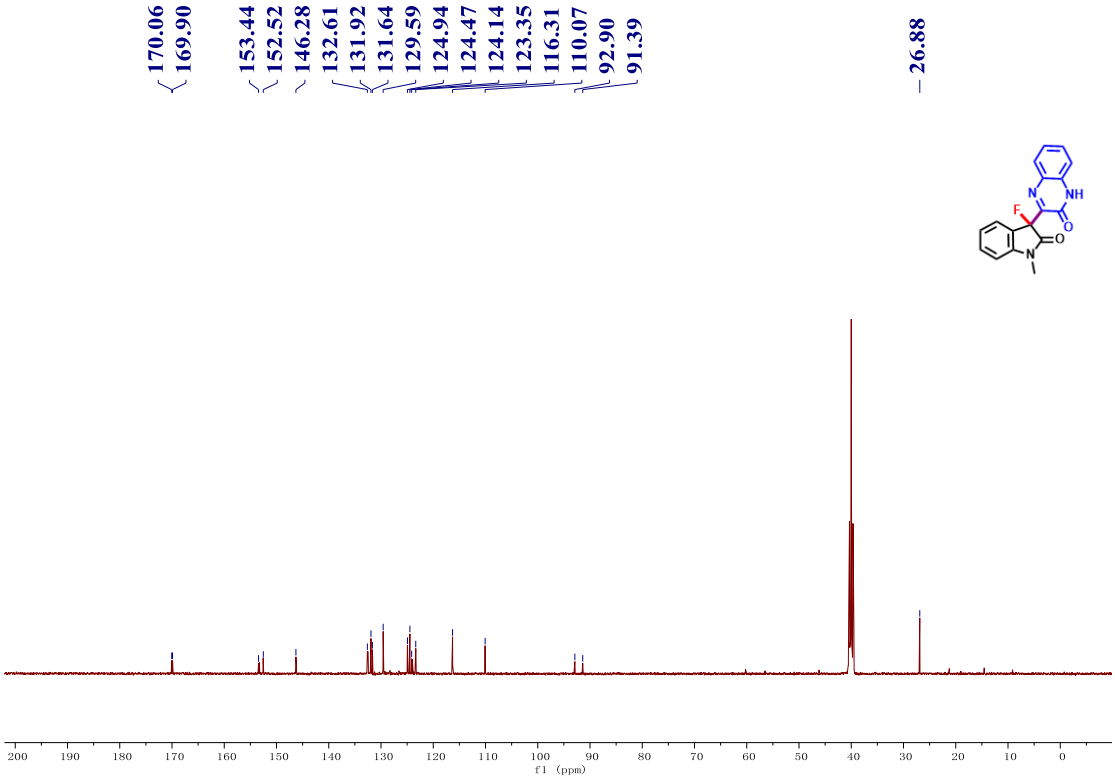
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3af**



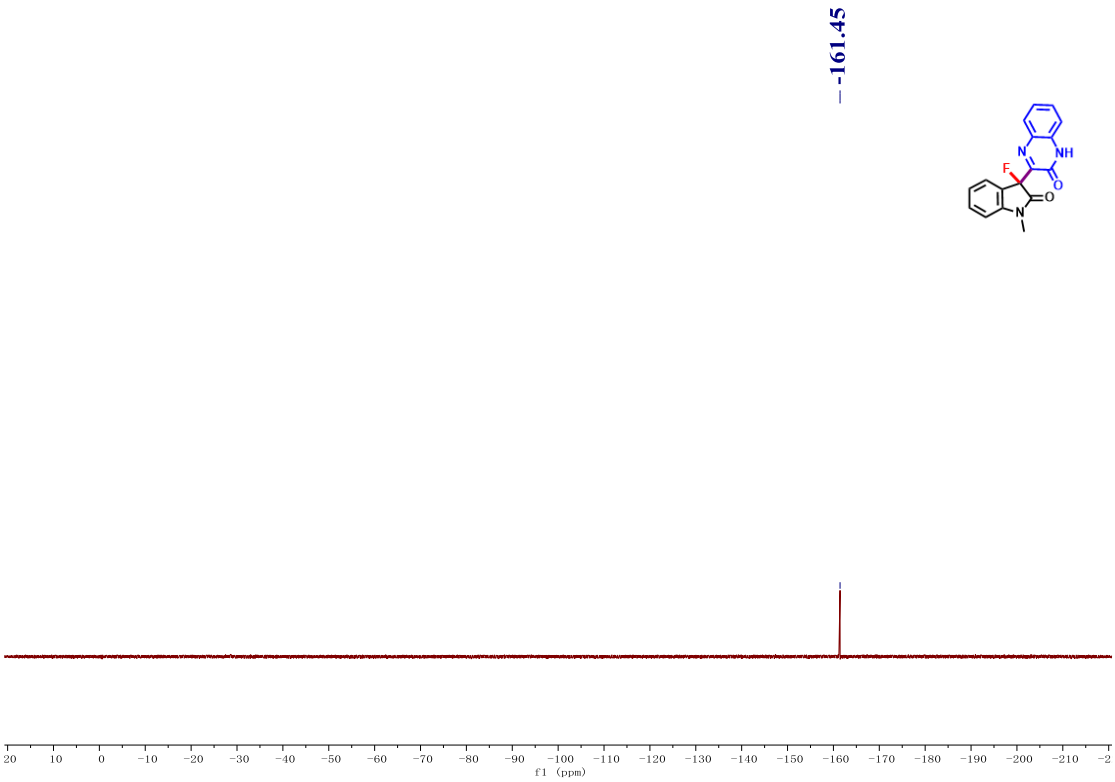
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3af**



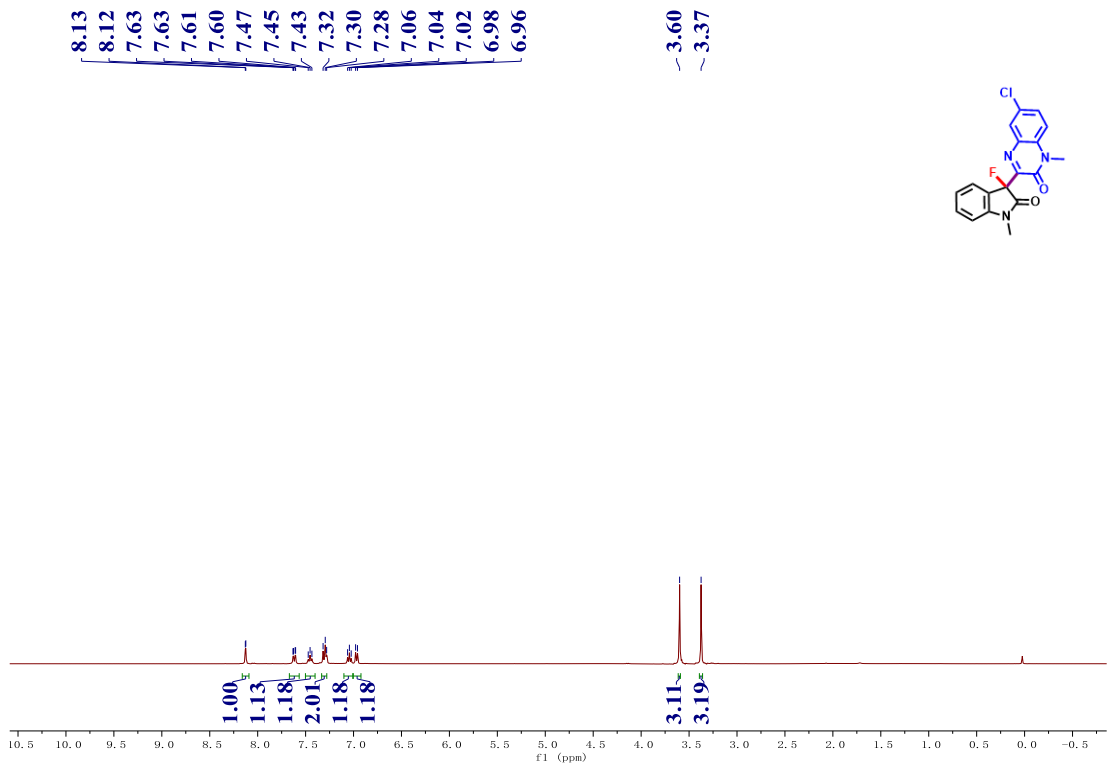
^{1}H NMR (500 MHz, DMSO-d_6) Spectra of compound **3ag**



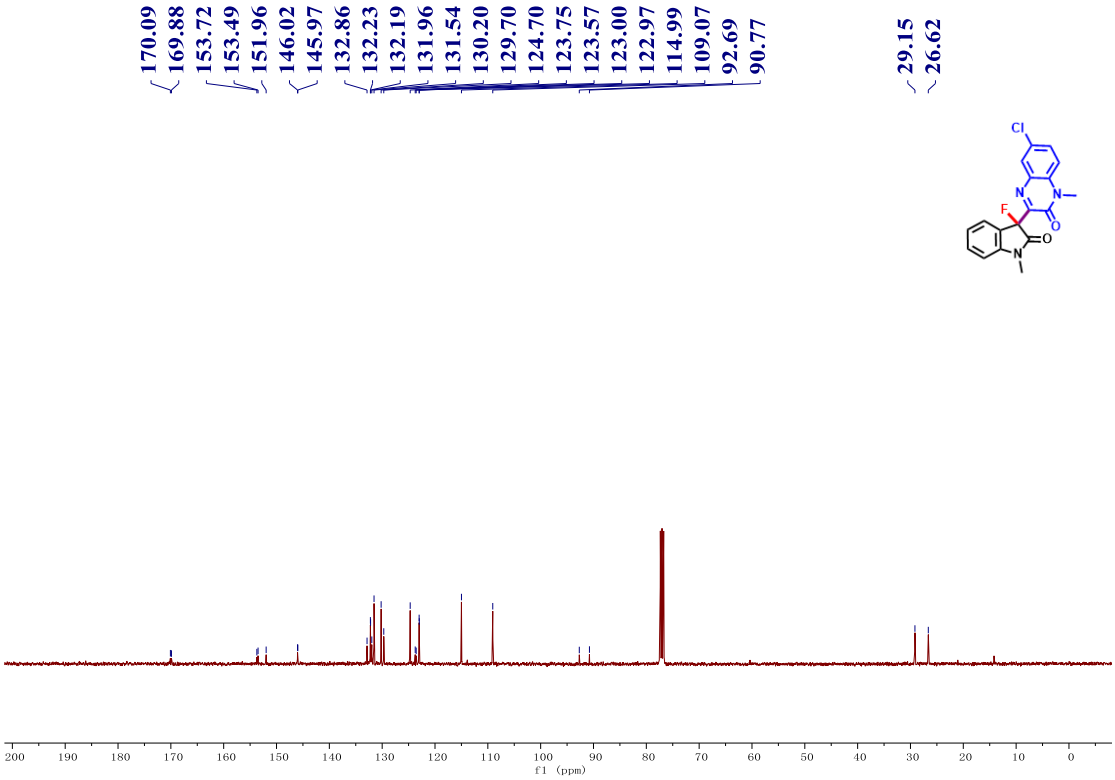
^{13}C NMR (126 MHz, DMSO-d_6) Spectra of compound **3ag**



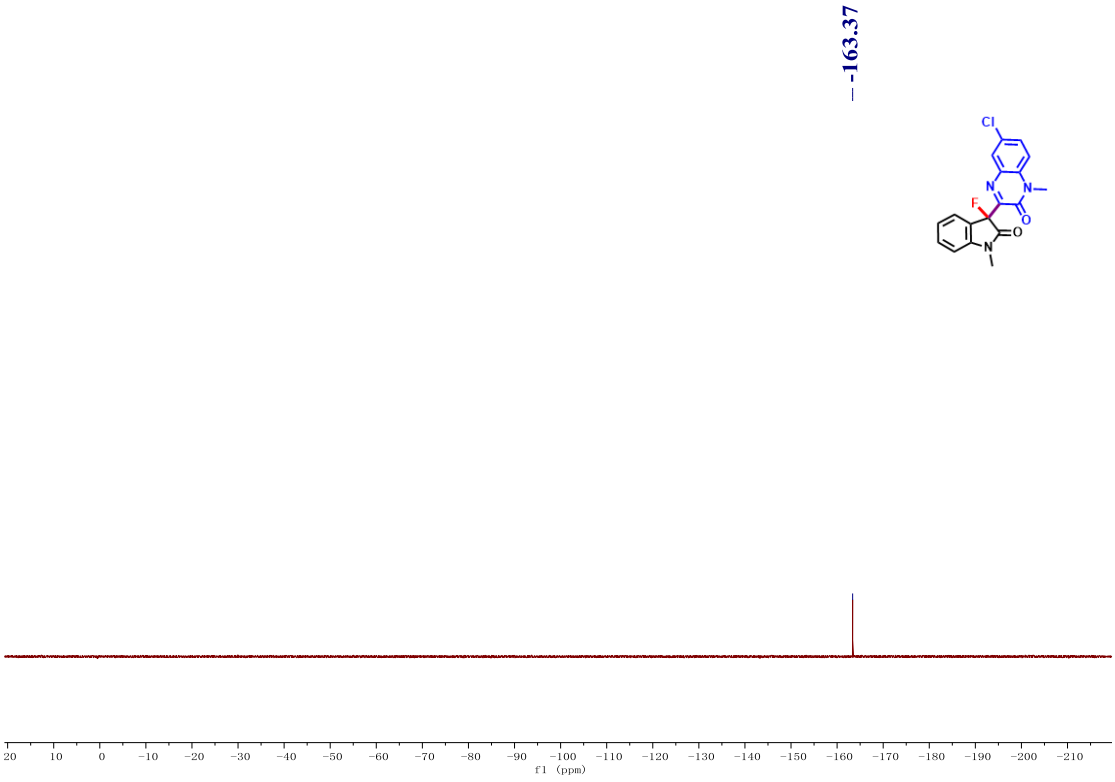
^{19}F NMR (471 MHz, DMSO-d_6) Spectra of compound **3ag**



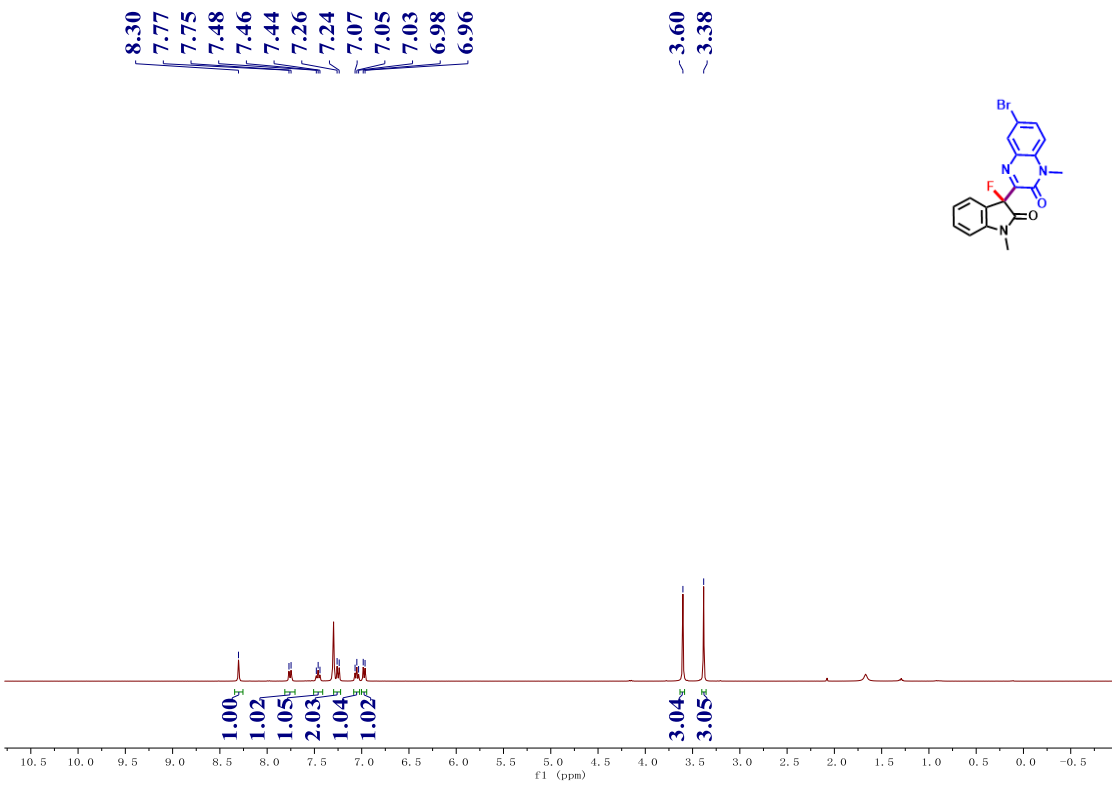
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ah**



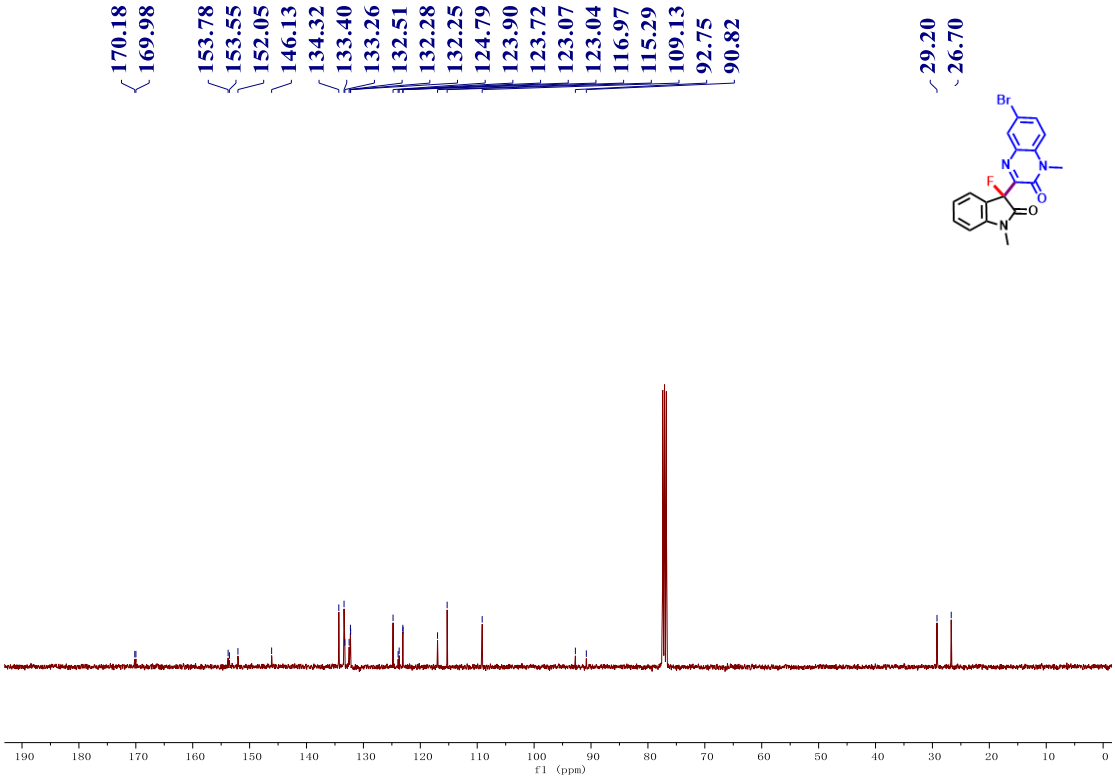
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ah**



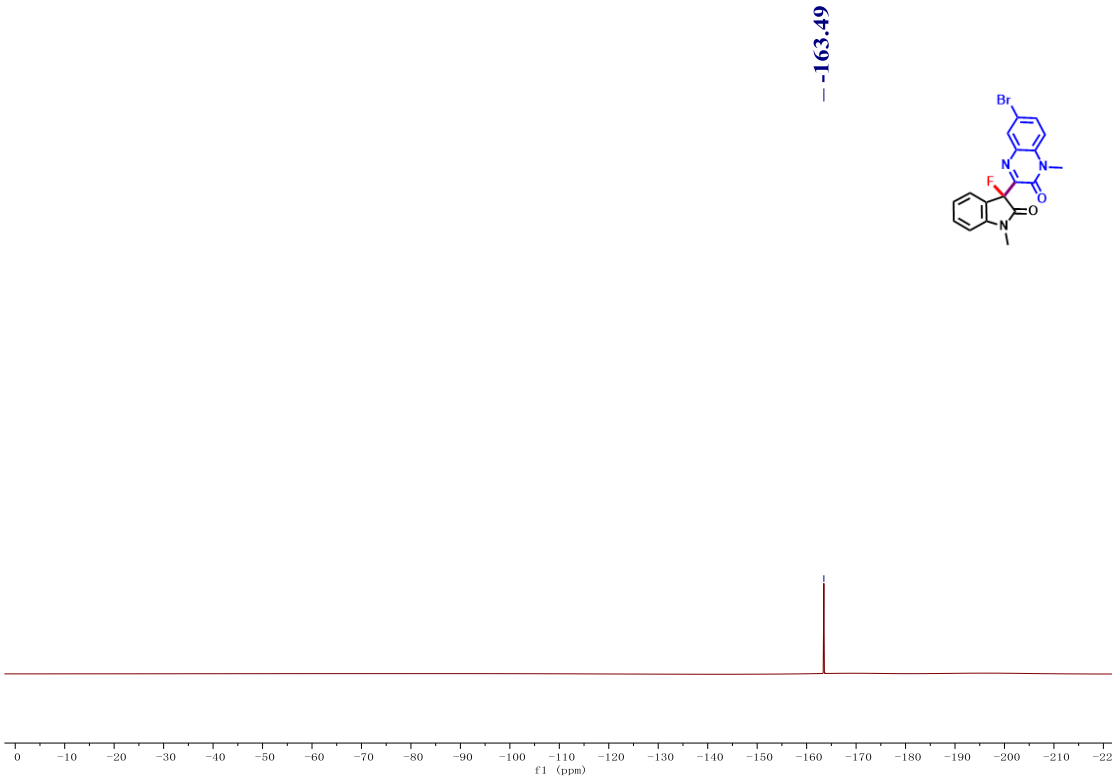
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ah**



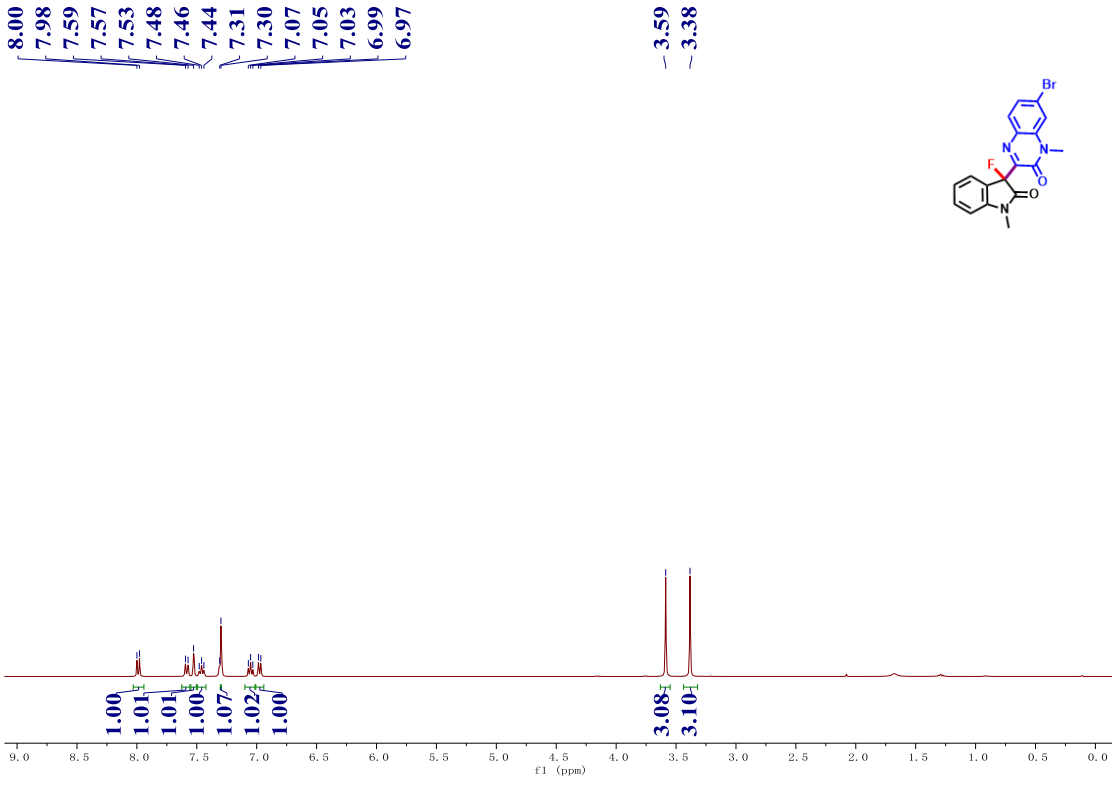
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ai**



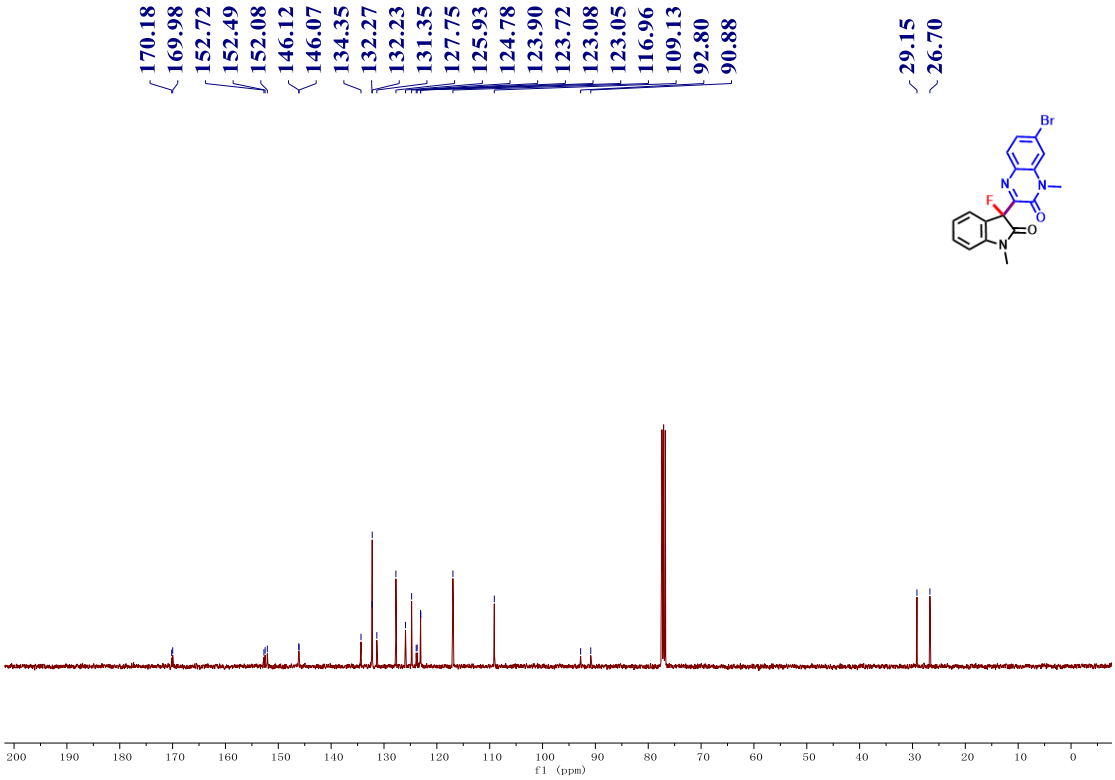
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ai**



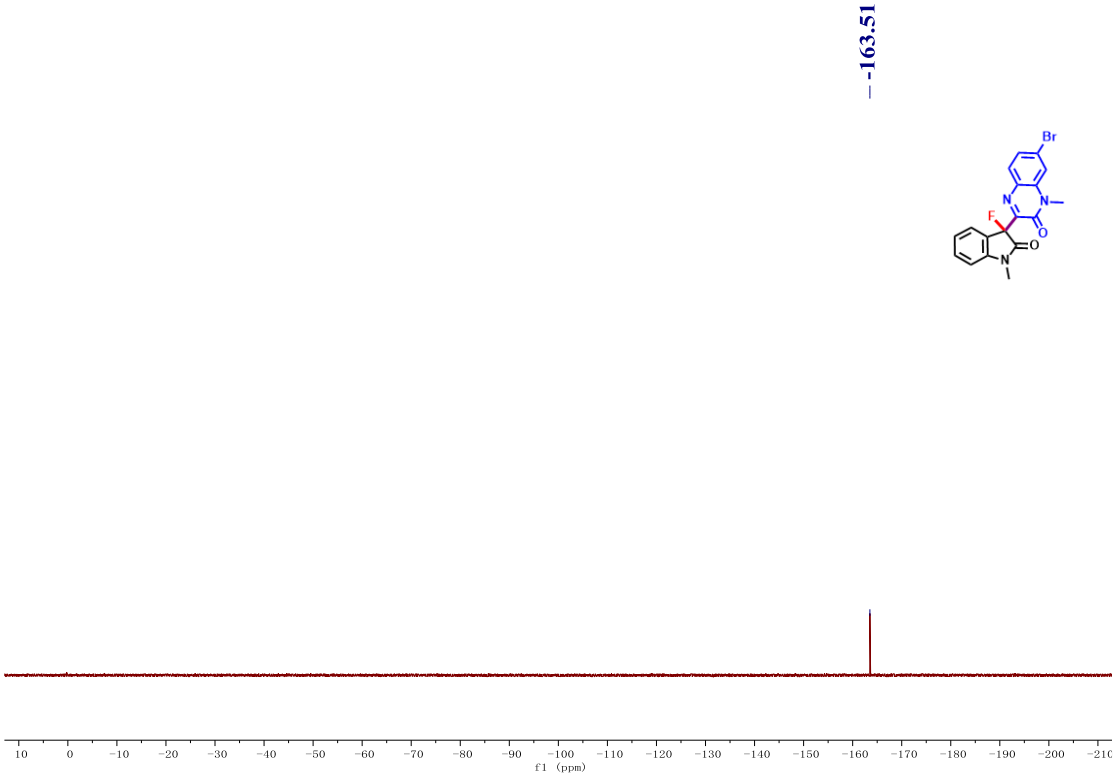
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3ai**



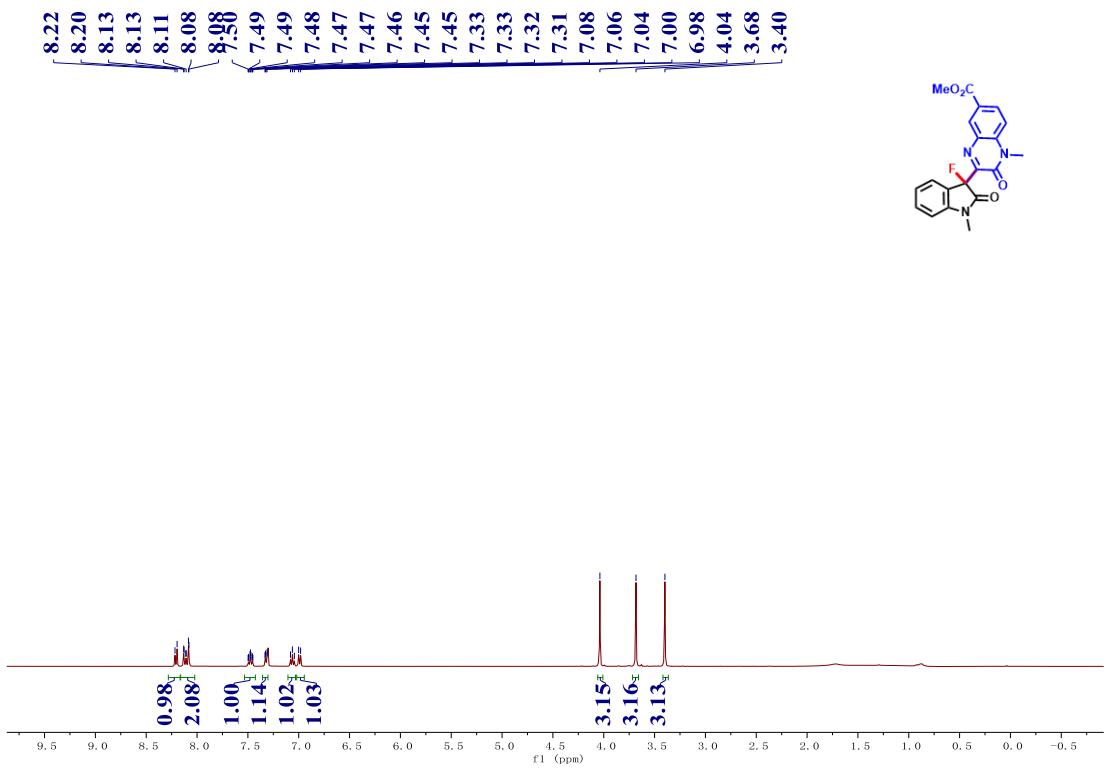
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3aj**



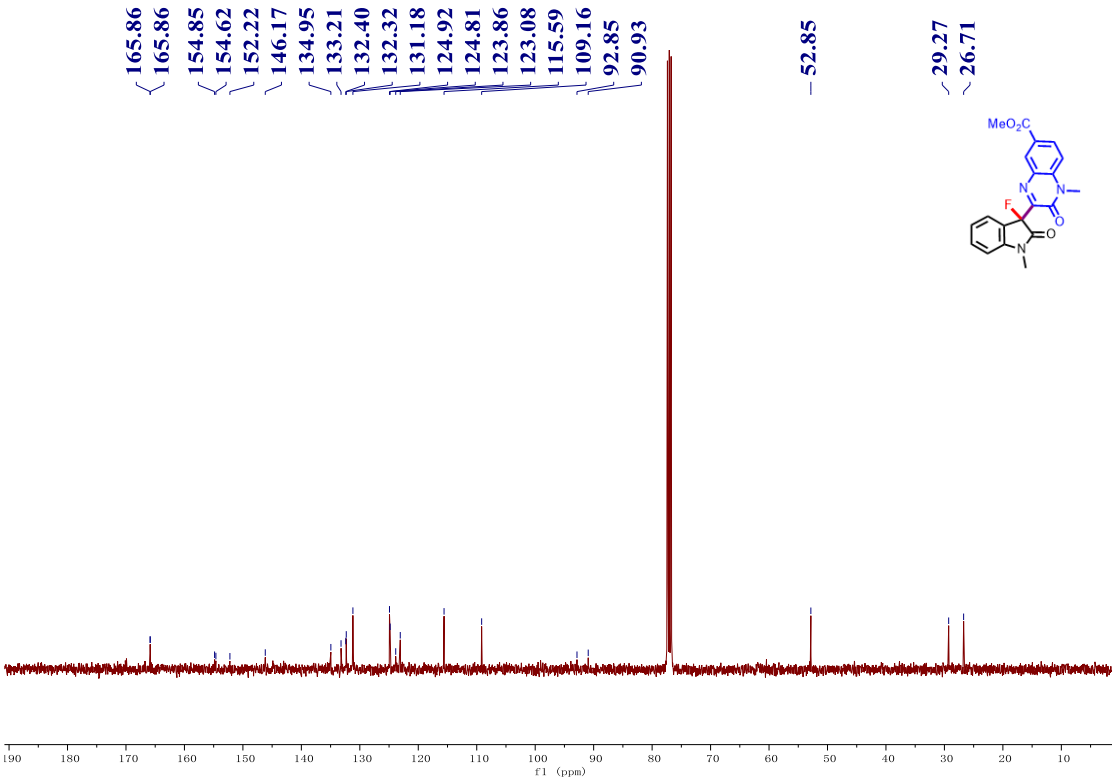
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3aj**



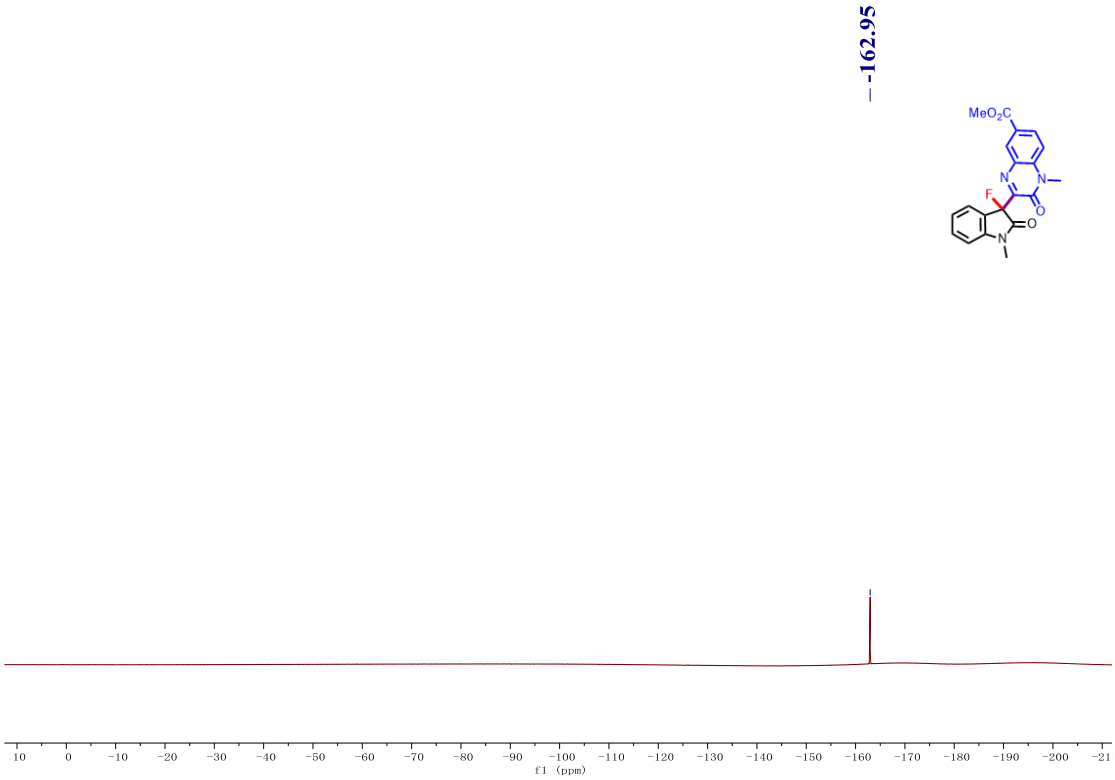
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3aj**



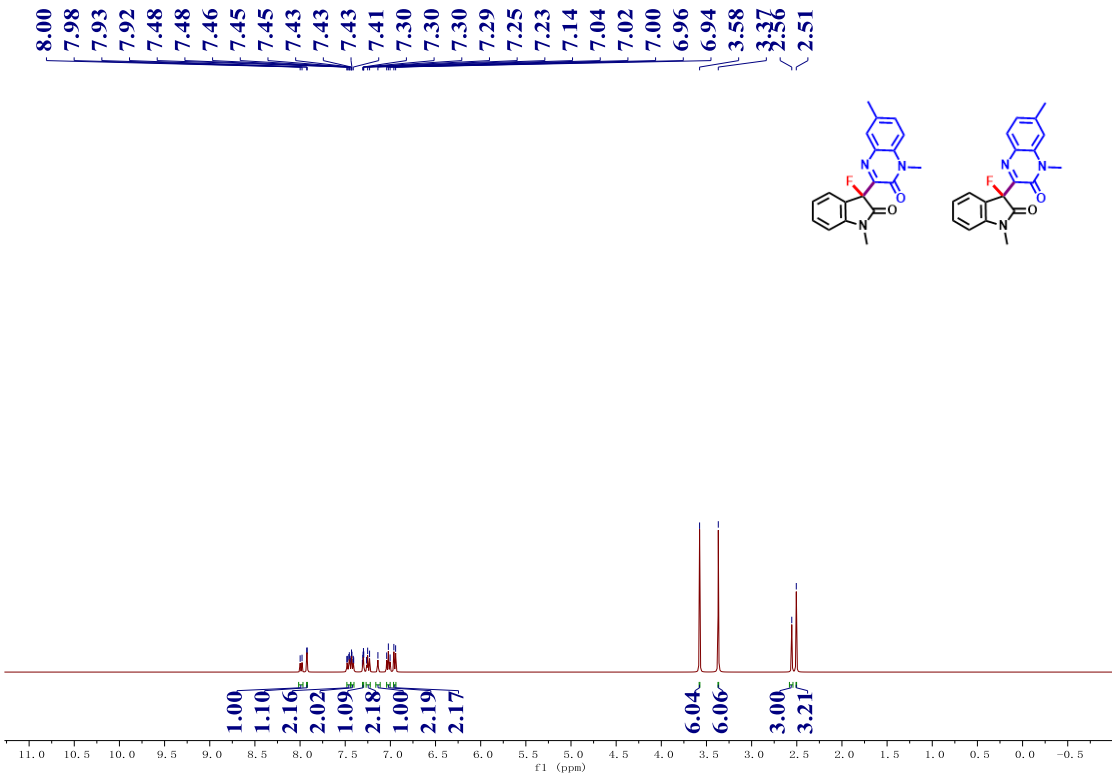
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ak**



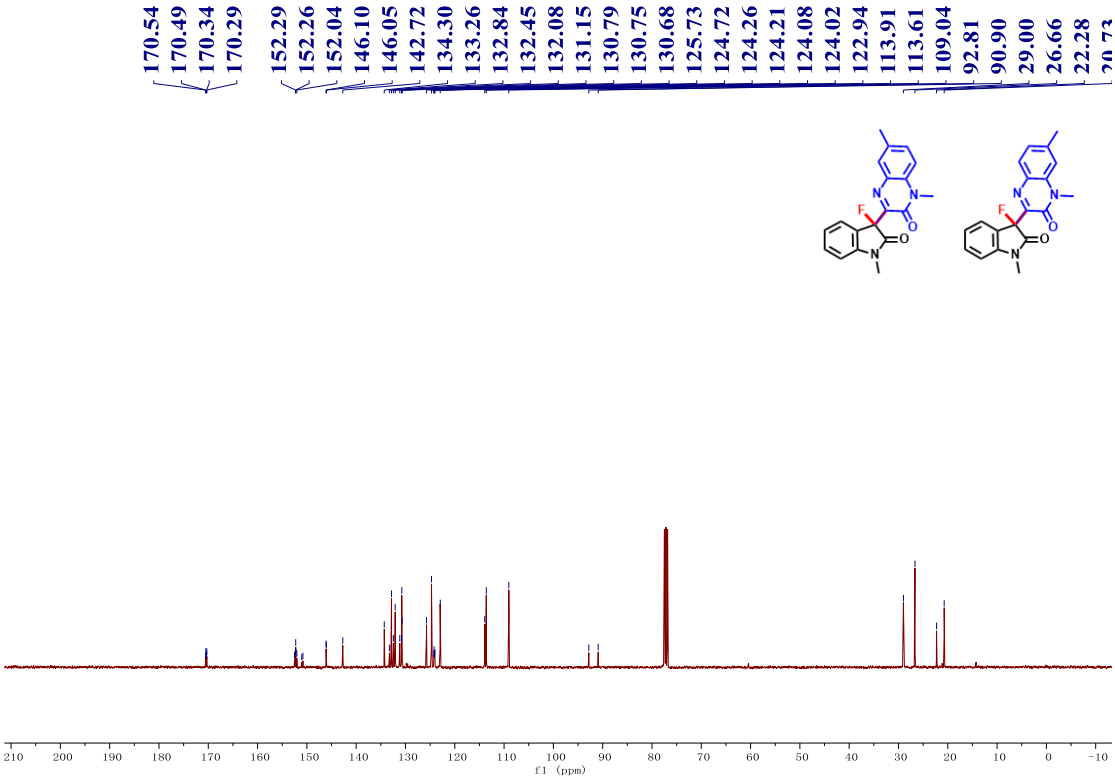
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ak**



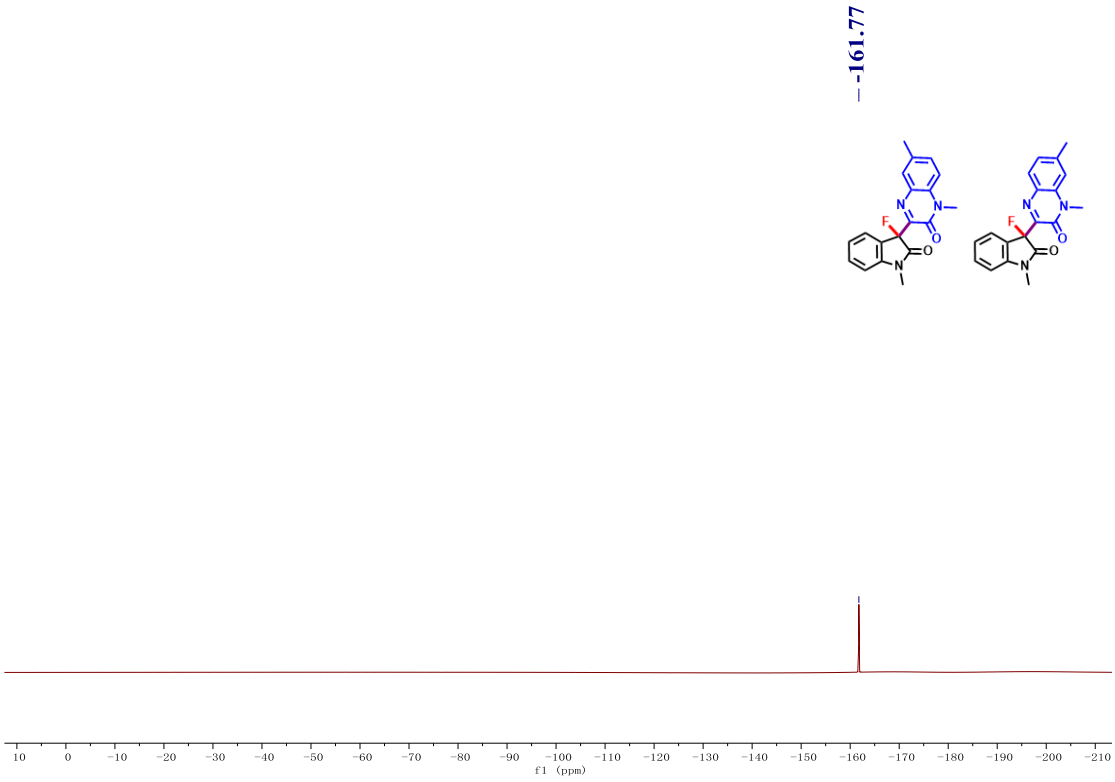
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3ak**



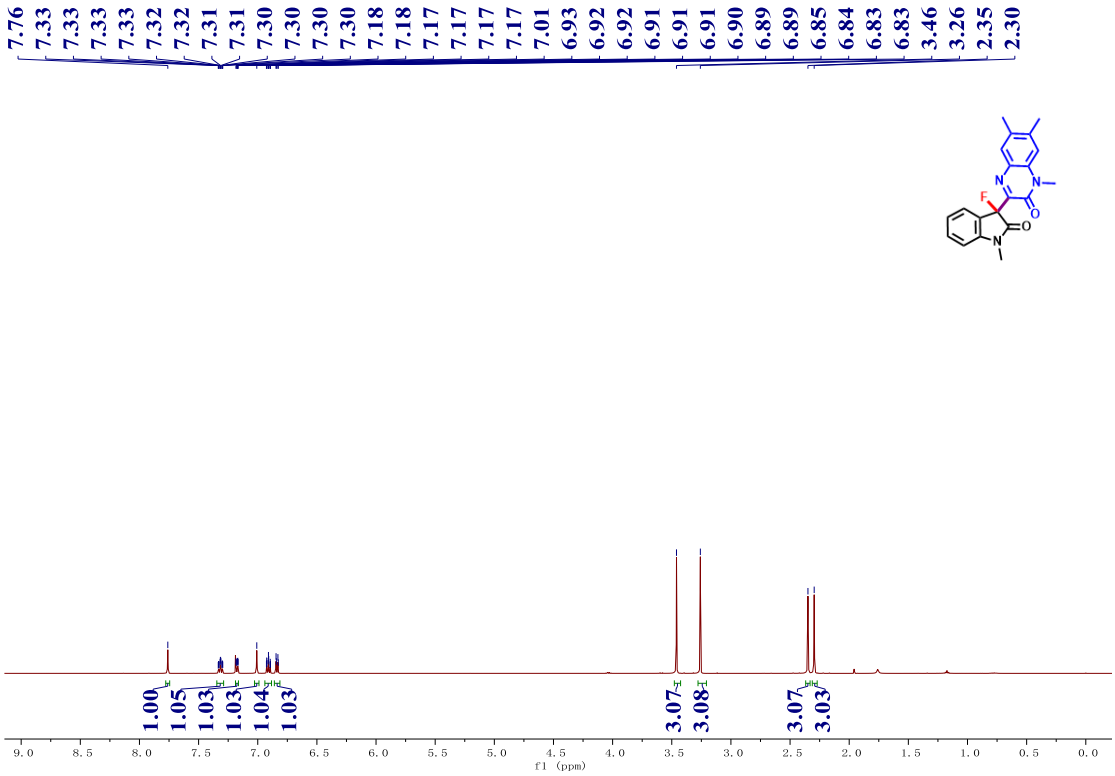
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3al & 3al'**



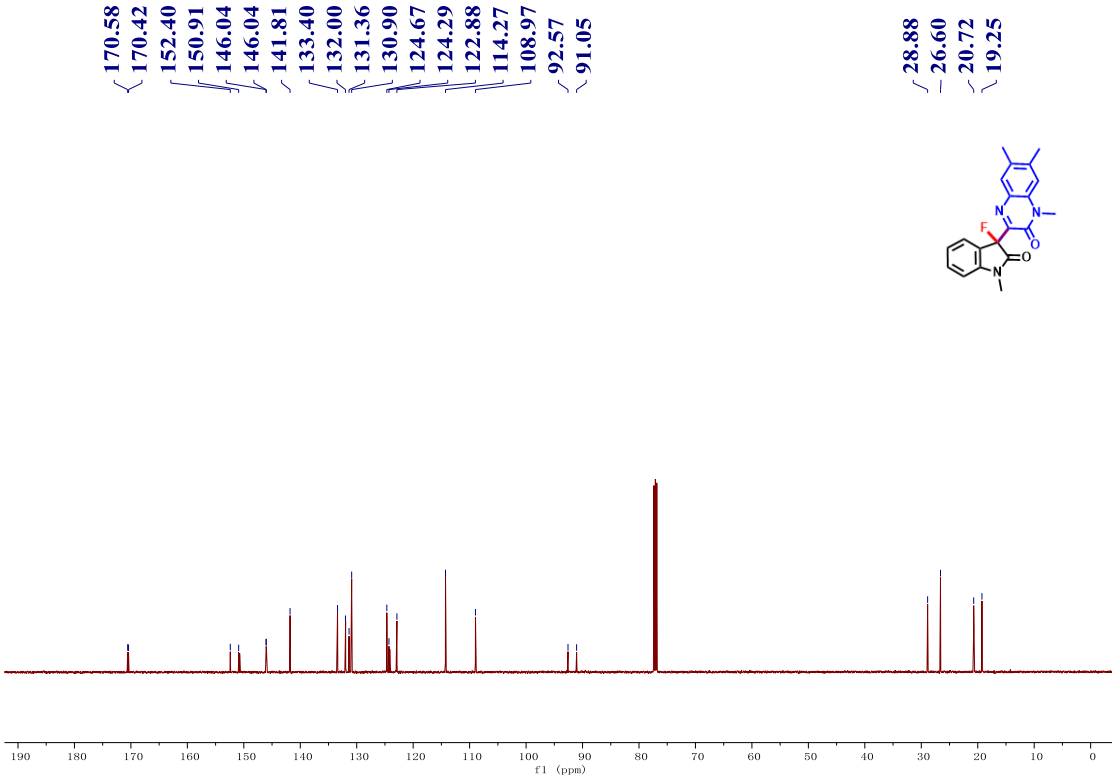
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3al & 3al'**



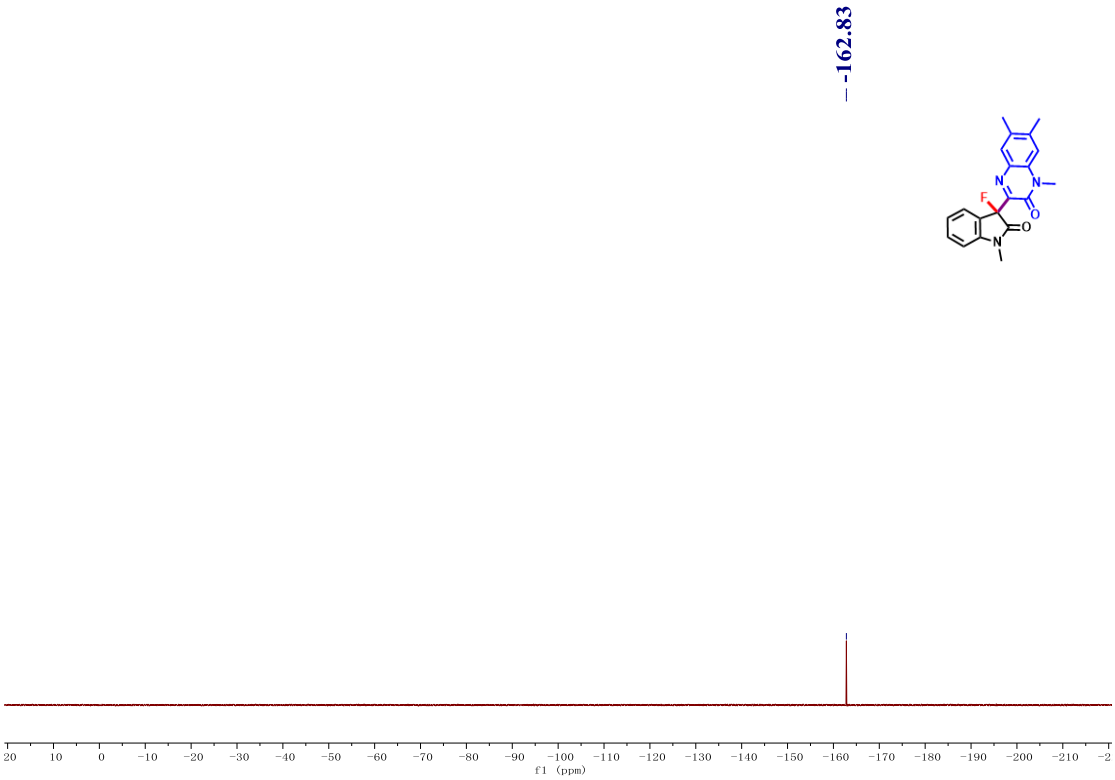
^{19}F NMR (376 MHz, Chloroform-*d*) Spectra of compound **3al & 3al'**



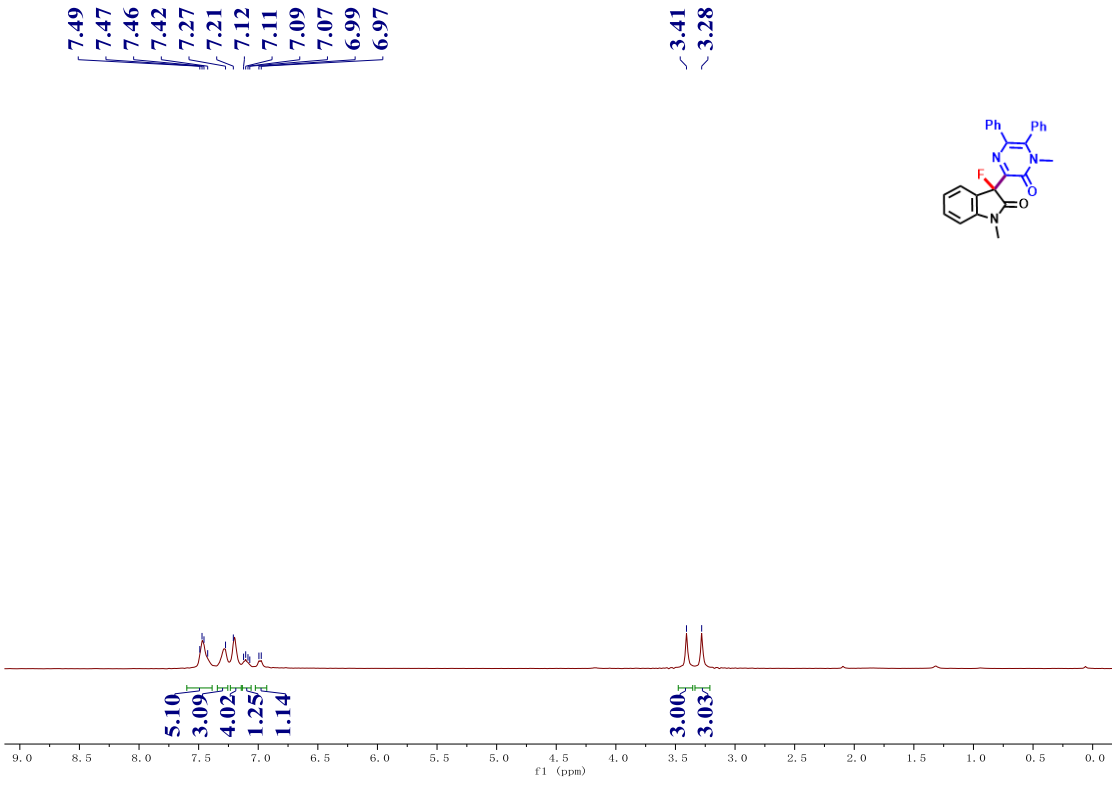
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of compound **3am**



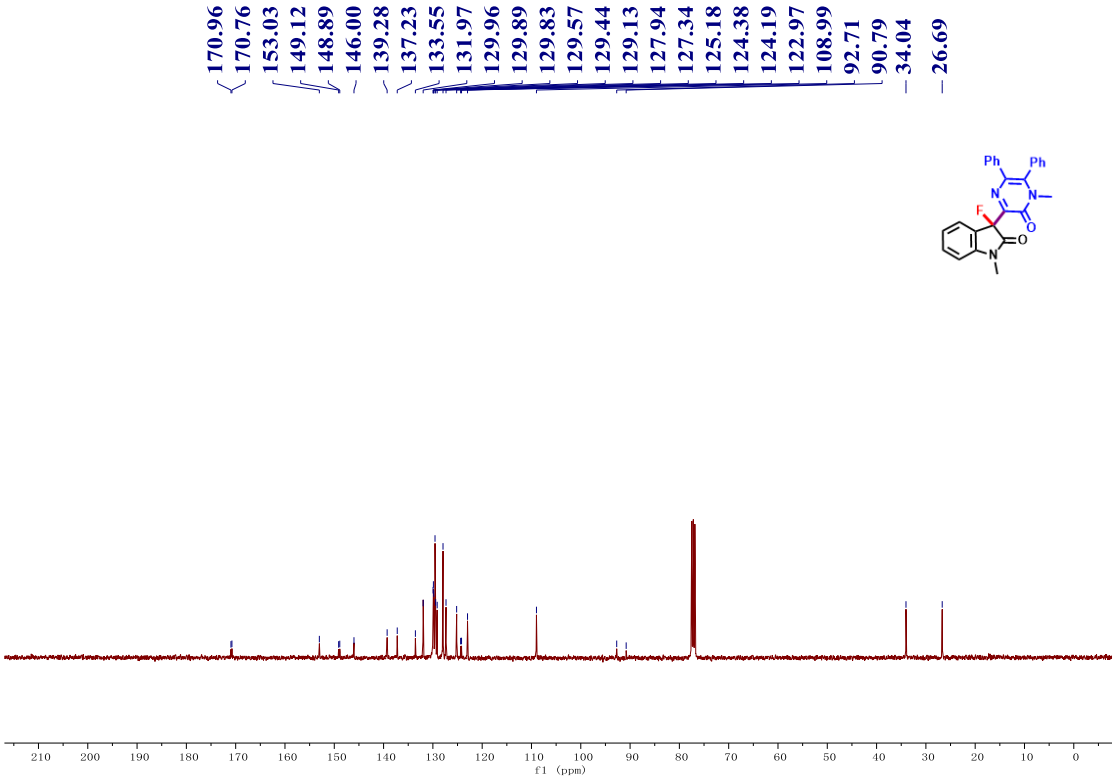
^{13}C NMR (126 MHz, Chloroform-*d*) Spectra of compound **3am**



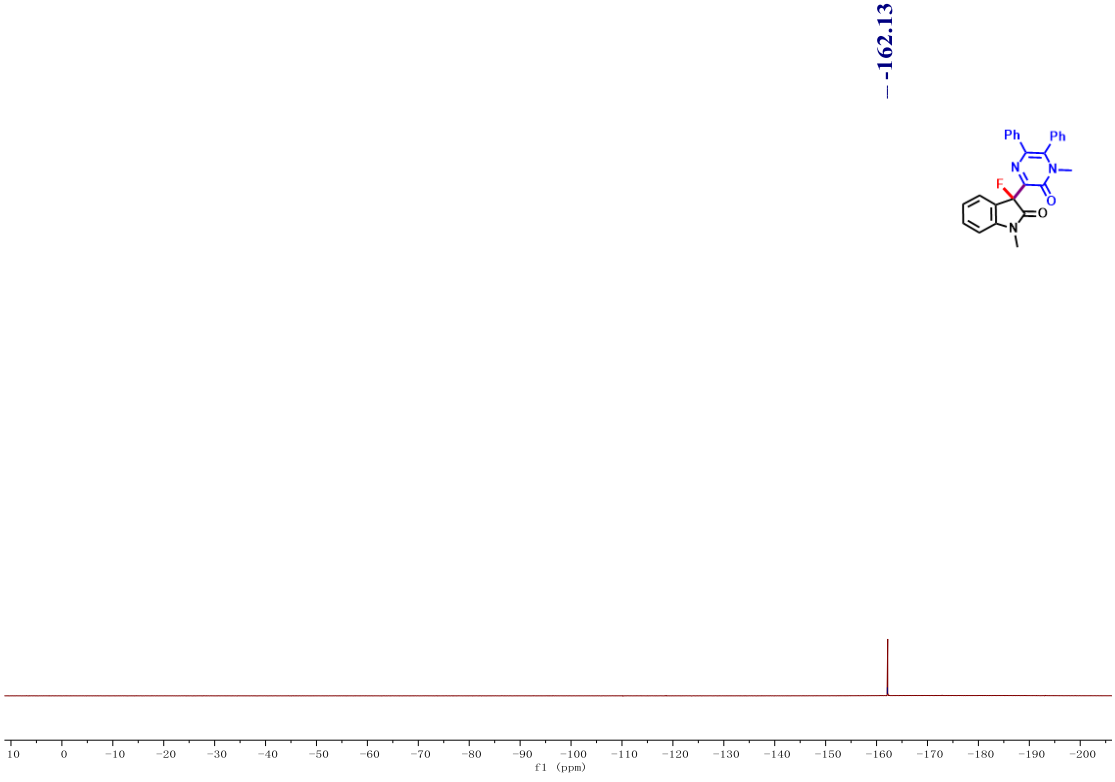
^{19}F NMR (471 MHz, Chloroform-d) Spectra of compound **3am**



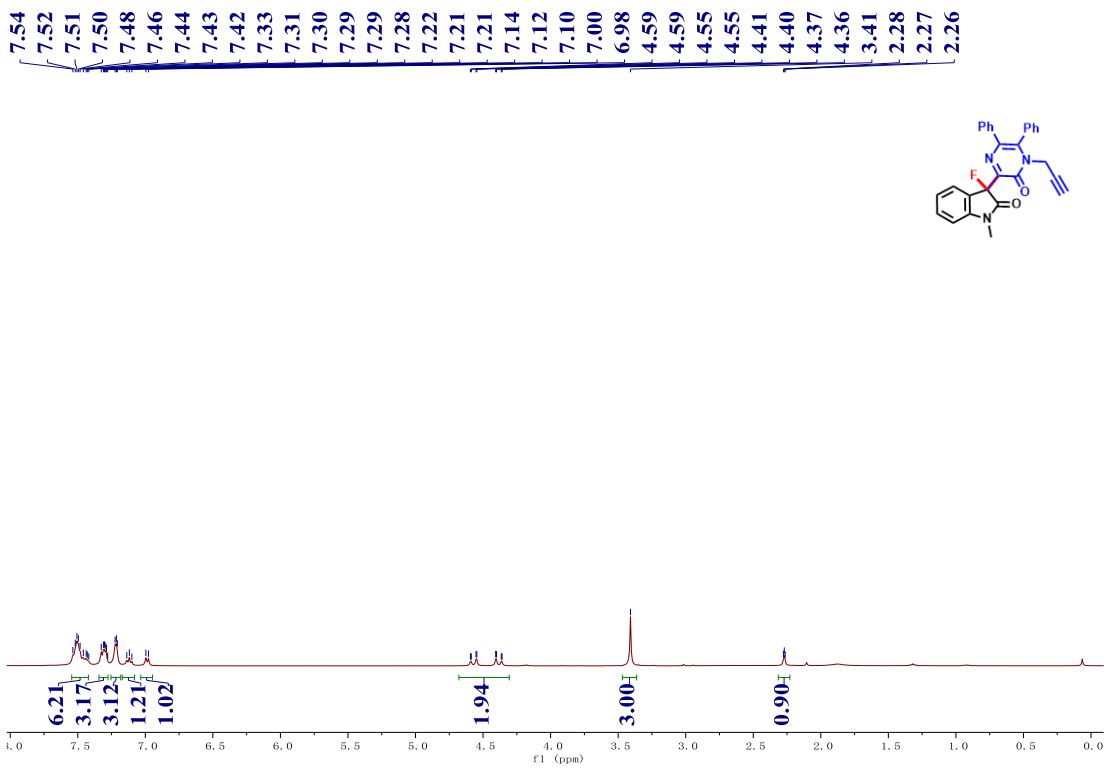
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3an**



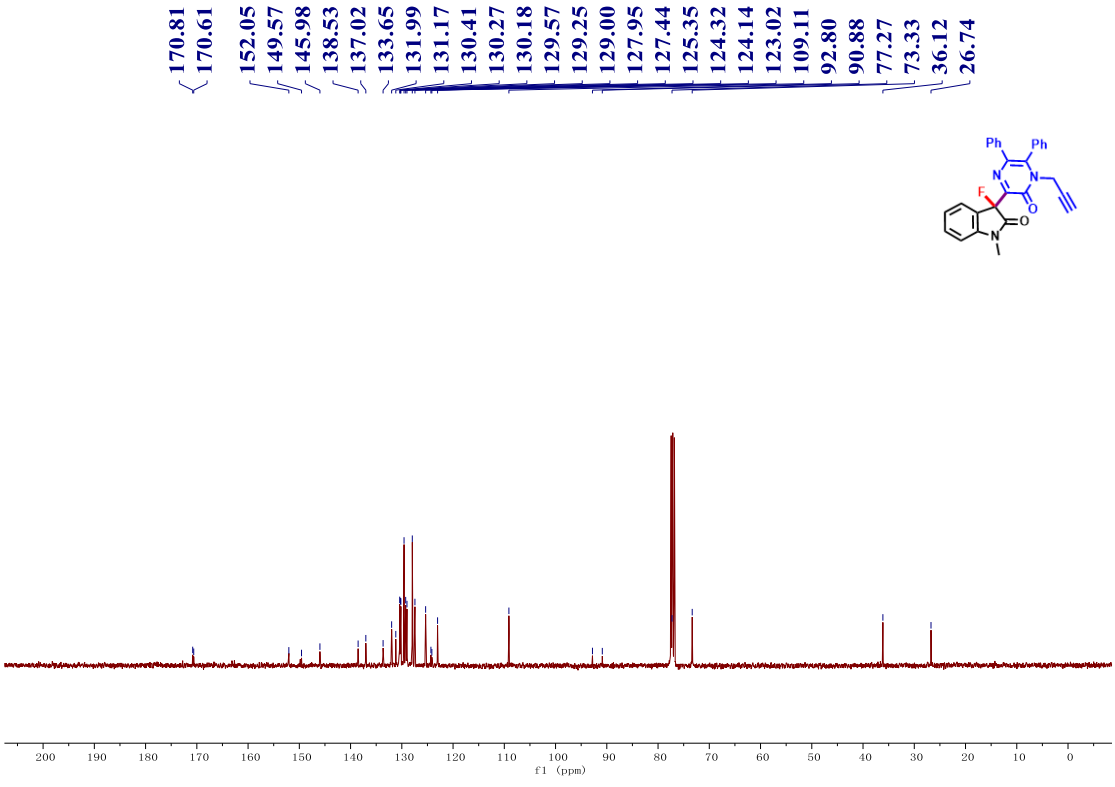
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3an**



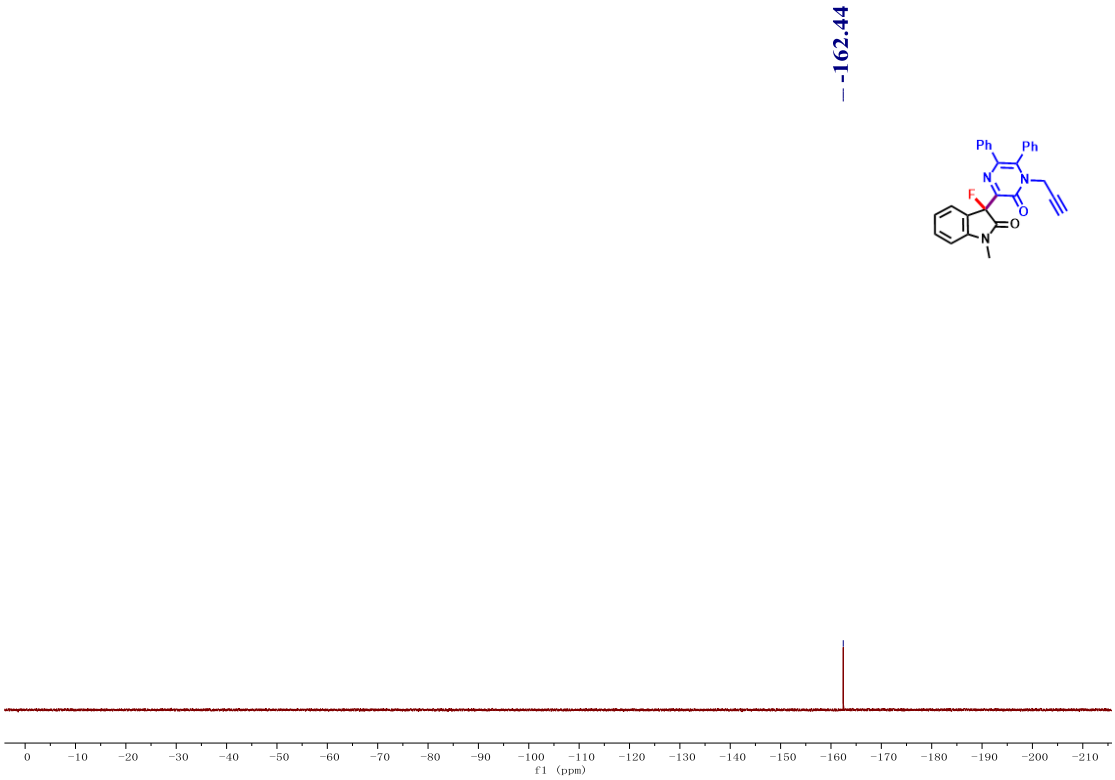
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3an**



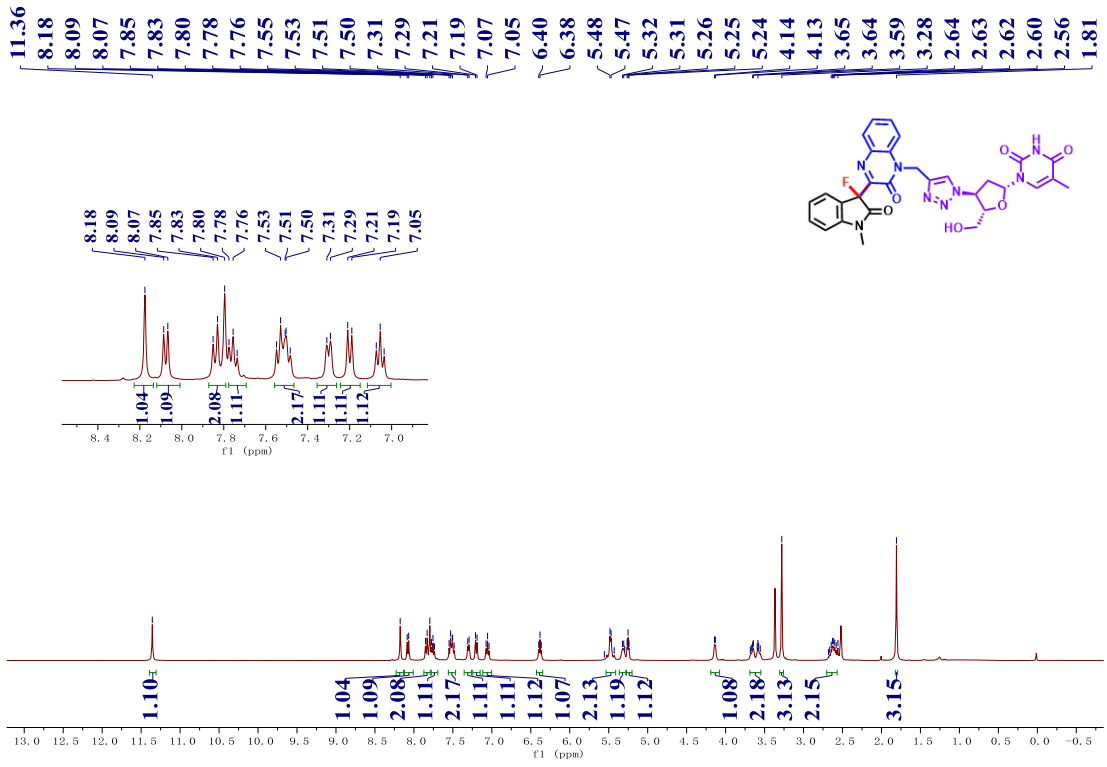
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of compound **3ao**



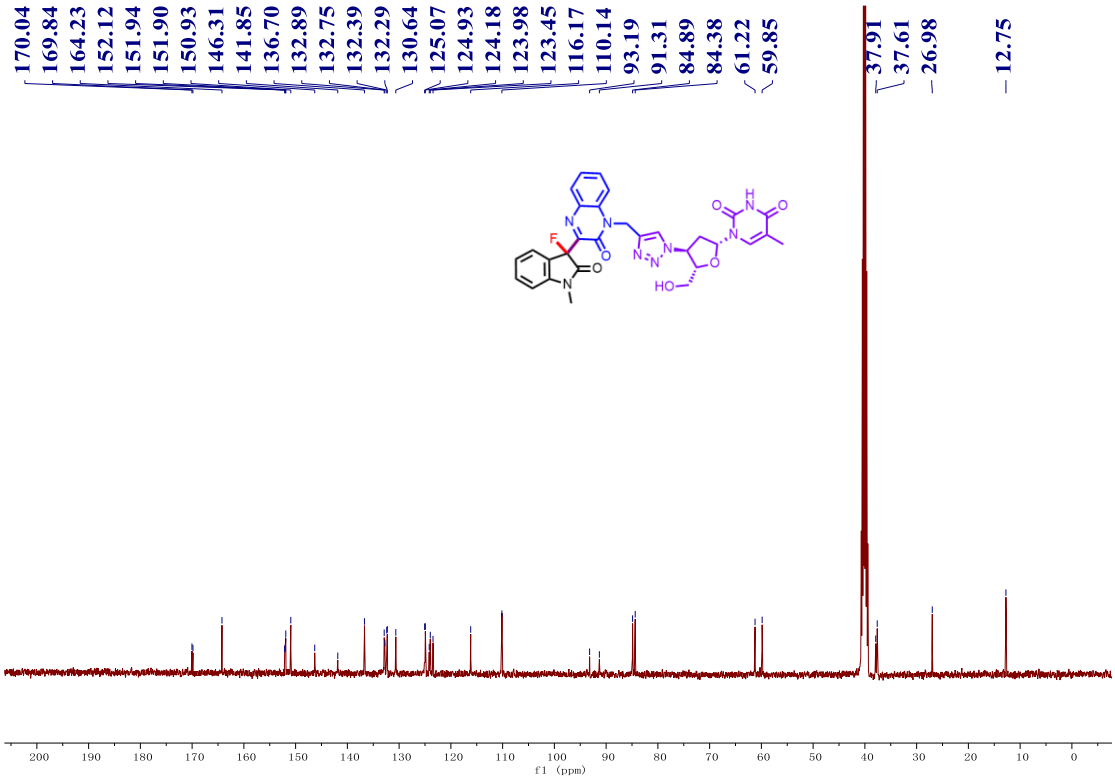
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of compound **3ao**



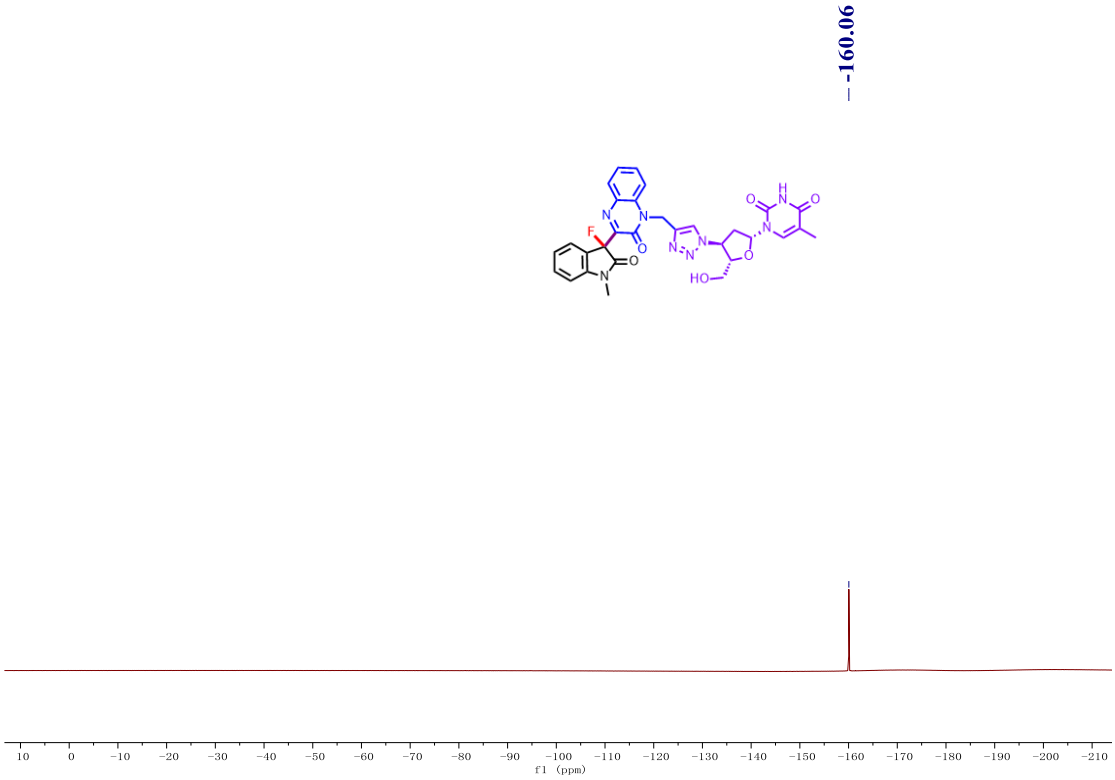
^{19}F NMR (471 MHz, Chloroform-*d*) Spectra of compound **3ao**



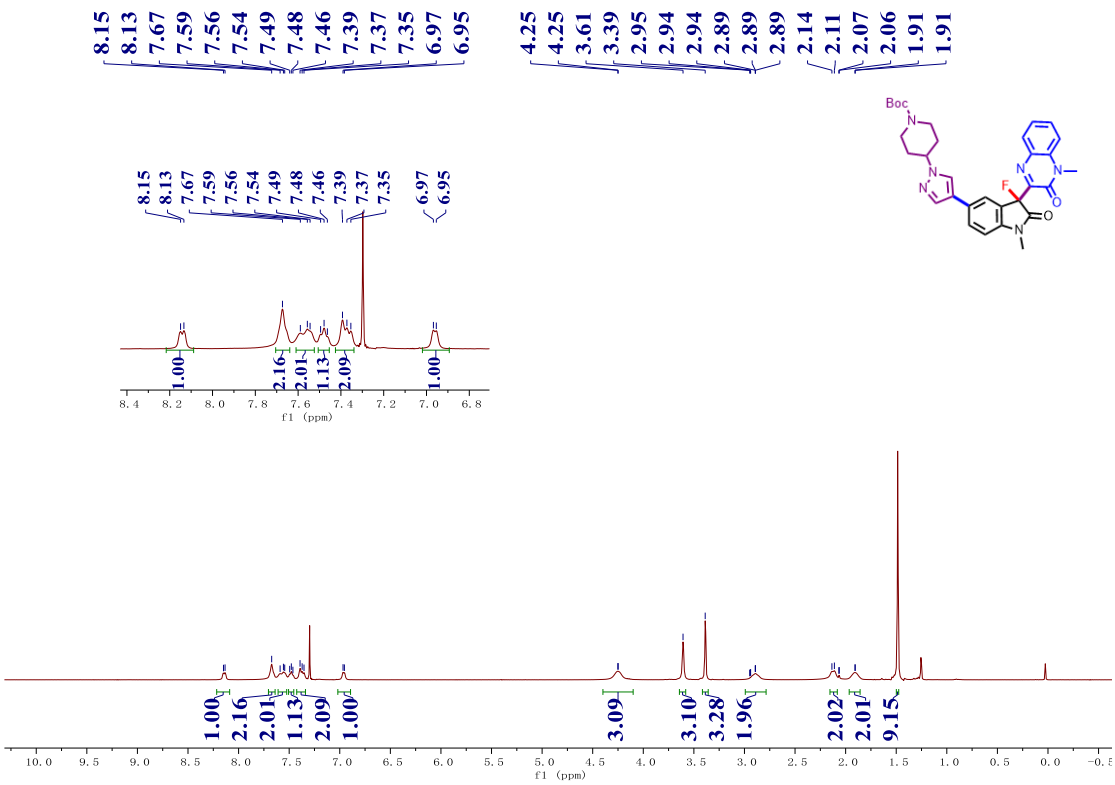
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of compound **4**



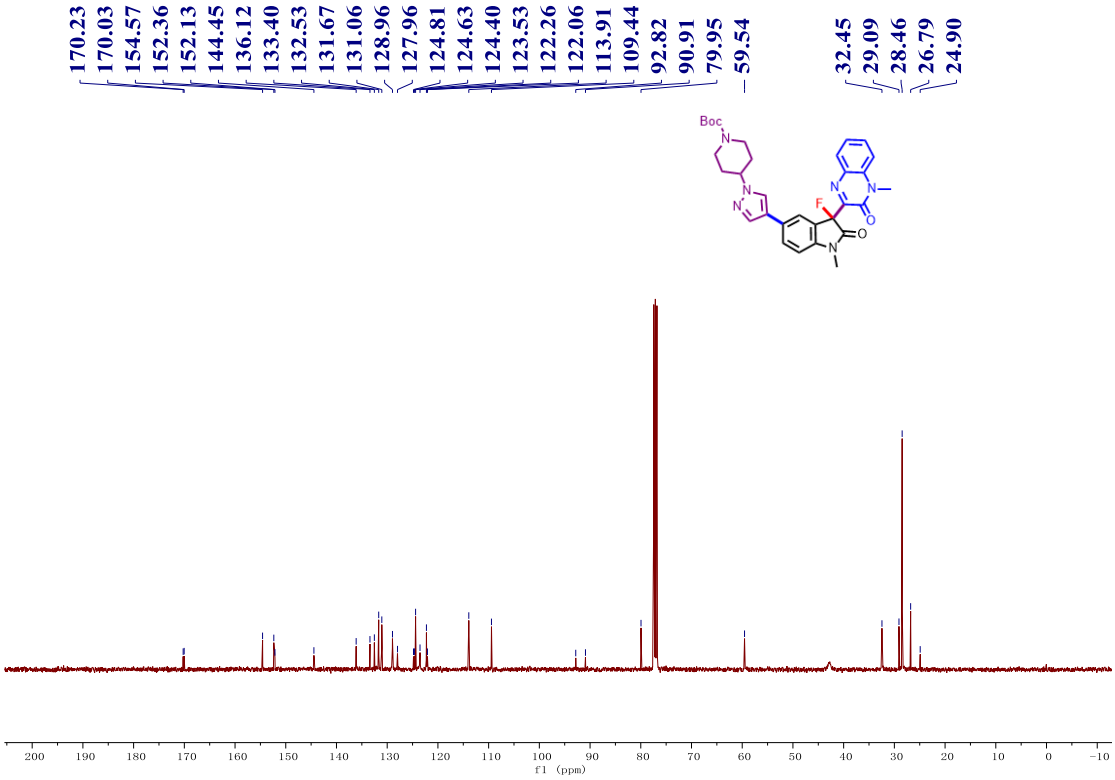
^{13}C NMR (101 MHz, DMSO-d_6) Spectra of compound **4**



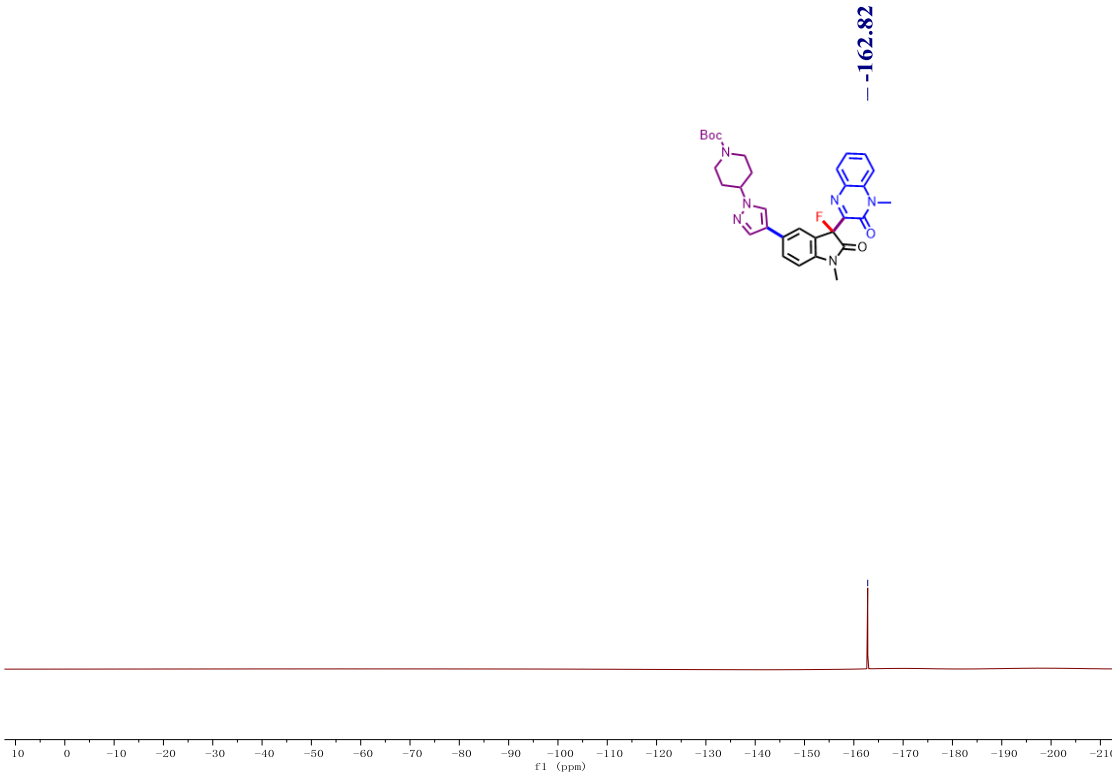
^{19}F NMR (376 MHz, DMSO-d_6) Spectra of compound **4**



^{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**

5. References

1 J. Xu, H. Yang, L. He, L. Huang, J. Shen, W. Li and P. Zhang, Synthesis of (*E*)-Quinoxalinone Oximes through a Multicomponent Reaction under Mild Conditions, *Org. Lett.,* 2021, **23**, 195-201.