Supporting Information

Direct C-H Fluorination/Heteroarylation of Oxindoles with Quinoxalin-2(1H)-ones Using Selectfluor

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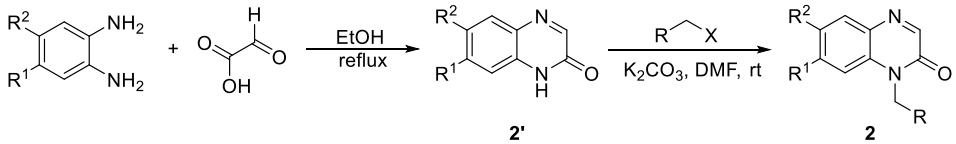
1. General information

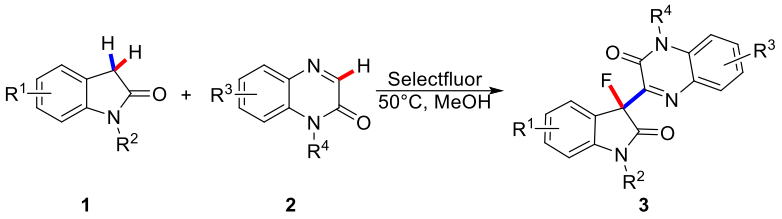
Unless stated otherwise, all reactions for preparing compound **3a-aj** were carried out under an air atmosphere. All reagents and solvents were of commercial quality and were used without further purification. Purification was carried out according to standard laboratory methods[1]. All reactions were monitored by TLC analysis with silica gel-coated plates with fluorescent indicator UV254. ^{1}H and ^{13}C NMR spectra were obtained on either a Bruker AV 300 at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are reported in Hz with TMS at 0.0 ppm (^{1}H and ^{13}C) or $CDCl_3$ referenced at 7.26 (^{1}H) and 77.0 ppm (^{13}C) and DMSO-d_6 referenced at 2.50 (^{1}H) and 39.5 (^{13}C). Mass spectra were measured with an Orbitrap Exploris™ 120 mass spectrometer using ESI ionization.

2. General procedure for the synthesis of starting materials[2]



Glyoxylic acid (1.1 equiv.) was added into a suspension of *o*-arylenediamine (1. 0 equiv.) in ethanol (1 mol/L). The reaction mixture was stirred and heated at reflux in an oil bath for 2 h, then at room temperature for 1 h until the reaction completed. The precipitated solid was filtered and washed with ethanol, then dried to give quinoxalinone **2'**. For alkylation, the corresponding alkyl halide (1.6 equiv.) was added to a suspension of quinoxalinone **2'** (1 equiv.) and potassium carbonate (1.2 equiv.) in DMF. The reaction mixture was stirred at room temperature overnight. When TLC analysis indicated that the quinoxalinone disappeared, the reaction mixture was washed with saturated solution of ammonium chloride, ethyl acetate and water. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting organic residue was purified by column chromatography over silica gel to afford the desired product **2**.

3. General procedure for the synthesis of 3a-3ar

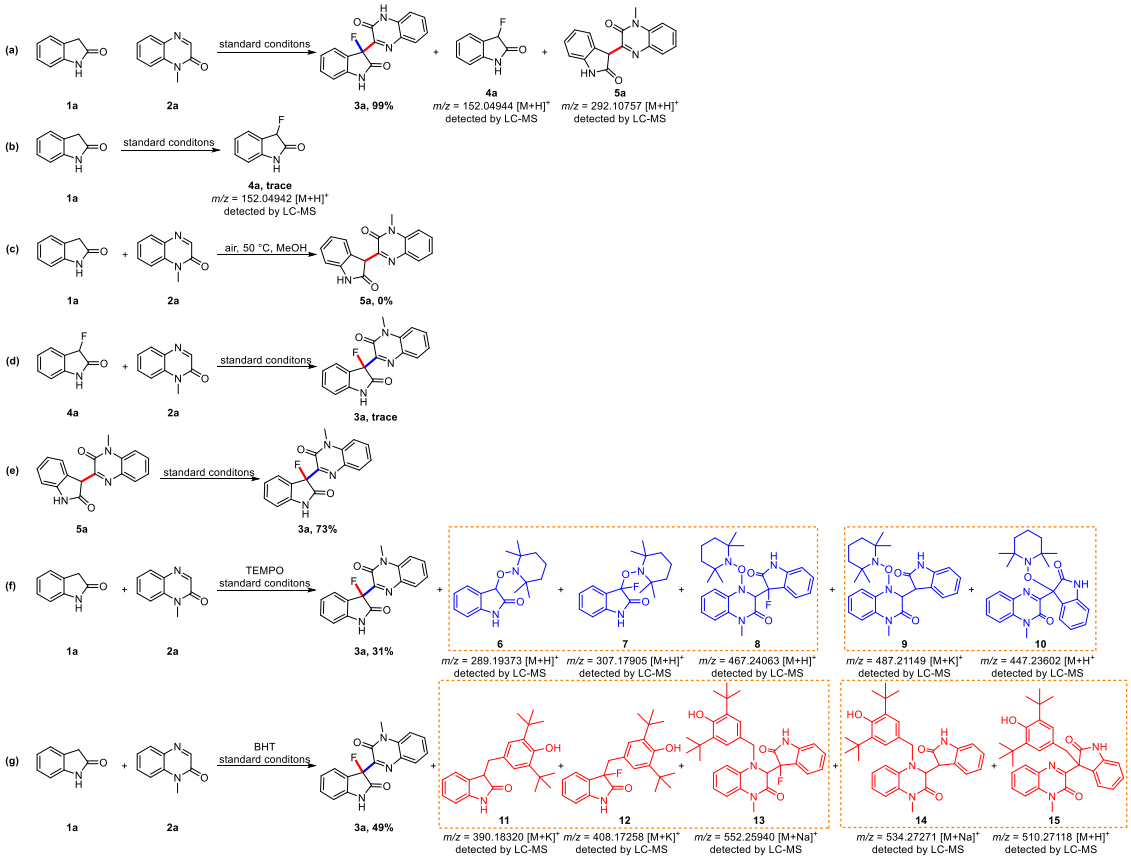


1 2 3

Different substituted oxindole **1** (0.2 mmol, 1.0 equiv.) and various quinoxalin-2-one **2** (0.24 mmol, 1.2 equiv.) was dissolved with 2 ml methanol (MeOH) and was treated with Selectfluor (0.4 mmol, 2.0 equiv.) at 50 °C under air atmosphere in a 10 mL thick-walled ground test tube. Then mixture was stirred until the reaction completed. The progress of the reaction was monitored by TLC. After that, the reaction mixture was washed with saturated solution of ammonium chloride, dichloromethane (DCM) and water. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The resulting organic residue was purified using column chromatography over silica gel to give the desired product **3** with dichloromethane/methanol (50:0 to 20:1).

4. The mechanistic studies

4.1 The Control experiments



(a) Oxindole (**1a**, 0.2 mmol), 1-methylquinoxalin-2-one (**2a**, 0.24 mmol, 1.2 equiv.), selectfluor (0.4 mmol, 2.0 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 4 h until the reaction completed. the desired product **3a** was obtained in 99% yield. Meanwhile, **4a** and **5a** were detected by HRMS from the reaction solution, indicating that they might be intermediates in the reaction.

(b) Oxindole (**1a**, 0.5 mmol) and selectfluor (1.0 mmol, 2.0 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 30 h. the desired product **4a** was not obtained from the reaction. However, **4a** was detected by HRMS from the reaction solution, indicating that **4a** might be a secondary intermediate of the reaction and participated in a secondary pathway.

(c) Oxindole (**1a**, 0.2 mmol) and 1-methylquinoxalin-2-one (**2a**, 0.24 mmol, 1.2 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 12 h. the desired product **5a** was not observed in reaction process via TLC monitored and was not afforded from the reaction. Meanwhile, **5a** was not detected by HRMS from the reaction solution, indicating that it could not react in the absence of selectfluor.

(d) 3-Fluoro-2-oxindole (**4a**, 0.1 mmol), 1-methylquinoxalin-2-one (**2a**, 0.12 mmol, 1.2 equiv.), selectfluor (0.2 mmol, 2.0 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 12 h until the reaction completed. the desired product **3a** was observed in reaction process via TLC monitored and was not afforded from the reaction, illustrating that **4a** might be a secondary intermediate of the reaction and participated in a secondary pathway.

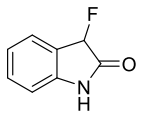
(e) 3-(1-Methylquinoxalin-2-one) indolin-2-one (**5a**, 0.1 mmol) and selectfluor (0.2 mmol, 2.0 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 12 h until the reaction completed. the desired product **3a** was afforded in 73% yield indicating that **5a** was main intermediate and involve in the main reaction pathway in the reaction process.

(f) Oxindole (**1a**, 0.2 mmol), 1-methylquinoxalin-2-one (**2a**, 0.24 mmol, 1.2 equiv.), selectfluor (0.4 mmol, 2.0 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.4 mmol, 2.0 equiv.) were added to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 6 h until the reaction completed. the desired product **3a** was obtained in 31% yield. Furthermore, some free radical-trapping adducts **6-10** were detected by HRMS from the reaction solution, indicating that the reaction mechanism might consist of two radical reaction pathways, a primary pathway and a secondary pathway.

(g) Oxindole (**1a**, 0.2 mmol), 1-methylquinoxalin-2-one (**2a**, 0.24 mmol, 1.2 equiv.), selectfluor (0.4 mmol, 2.0 equiv.) and Butylated hydroxytoluene (BHT, 0.4 mmol, 2.0 equiv.) were added

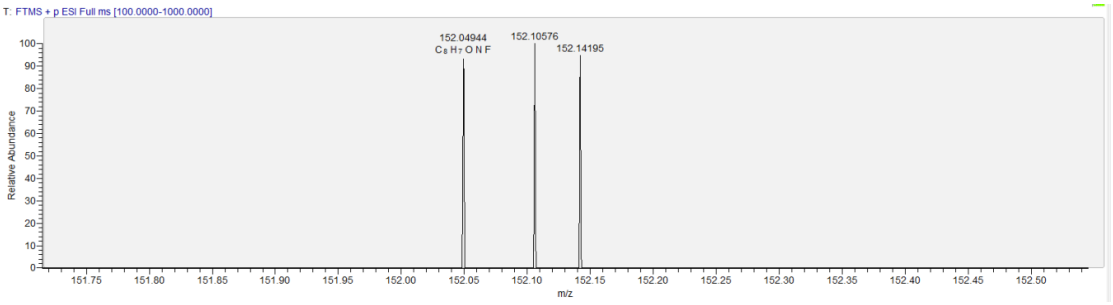
to a 10 mL thick-walled ground test tube with a magnetic stirring bar, then the reaction mixture was dissolved and stirred at 50 ℃ for 6 h until the reaction completed. the desired product **3a** was obtained in 49% yield. Furthermore, some free radical-trapping adducts **11**-**15** were detected by HRMS from the reaction solution, indicating that the reaction mechanism might consist of two radical reaction pathways, a primary pathway and a secondary pathway.

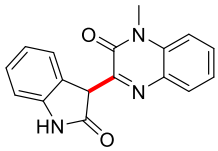
4.2 The HRMS spectra of compounds 4a, 5a, 6-15



4a

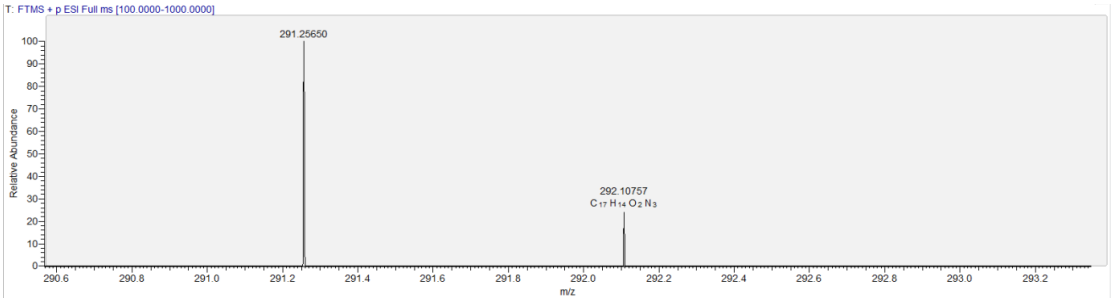
Compound 4a: HRMS (m/z) [ESI]: calculated for $C_8H_7ONF^+$ [M+H] $^+$: 152.0506, found 152.04944.

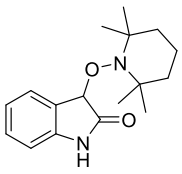




5a

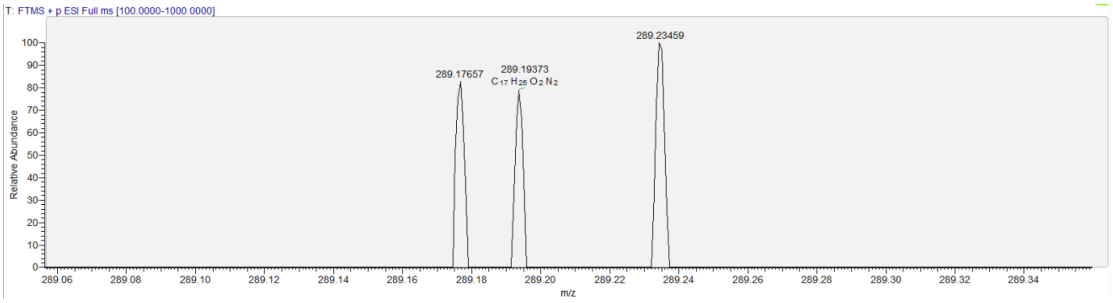
Compound 5a: HRMS (m/z) [ESI]: calculated for $C_{17}H_{14}O_2N_3^+$ [M+H] $^+$: 292.1081, found 292.10757.

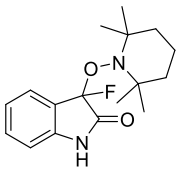




6

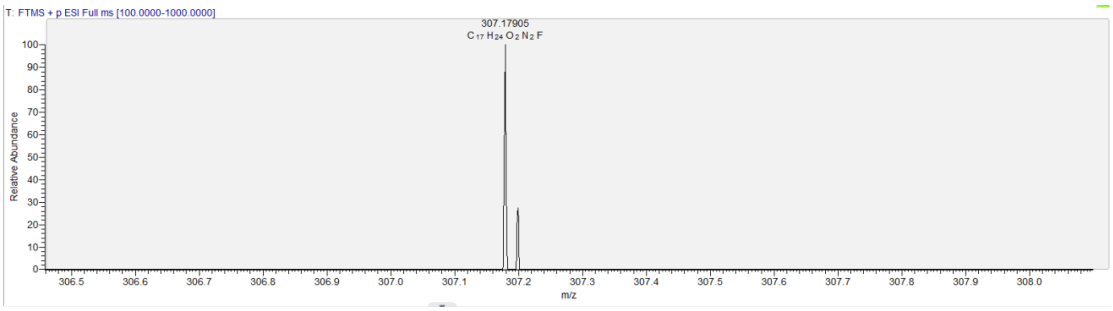
Compound 6: HRMS (m/z) [ESI]: calculated for $C_{17}H_{25}O_2N_2$ $^+$ [M+H] $^+$: 289.1911, found 289.19373.

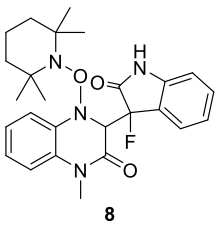




7

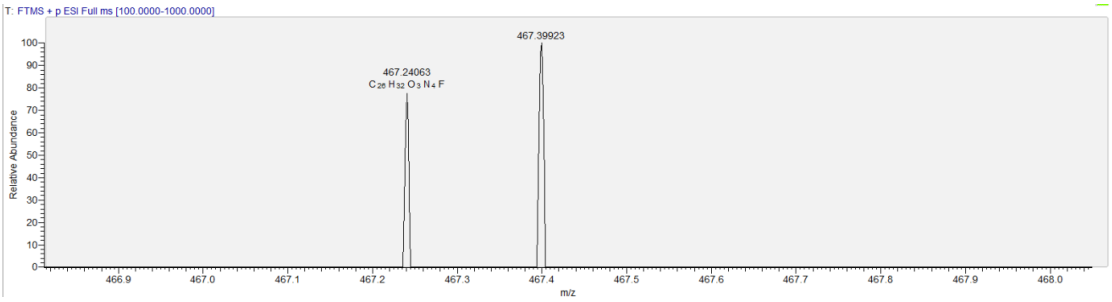
Compound 7: HRMS (m/z) [ESI]: calculated for $C_{17}H_{24}O_2N_2F$ $^+$ [M+H] $^+$: 307.1816, found 307.17905.

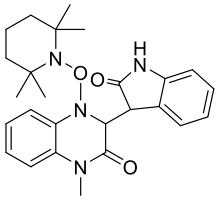




8

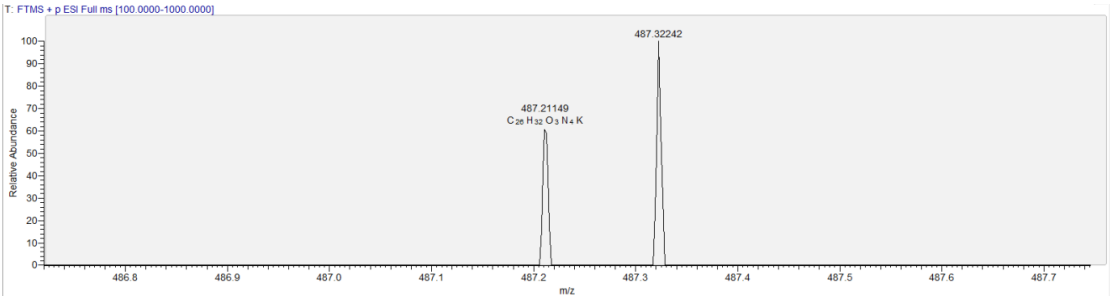
Compound 8: HRMS (m/z) [ESI]: calculated for $C_{26}H_{32}O_3N_4F$ $^+$ [M+H] $^+$: 467.2453, found 467.24063.

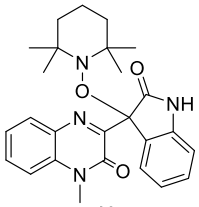




9

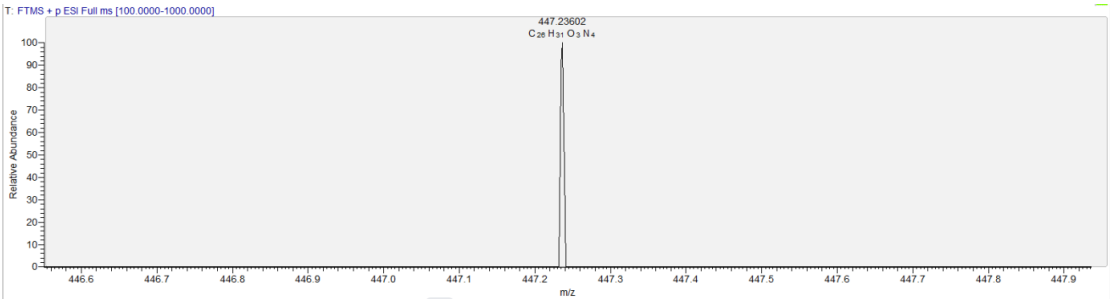
Compound 9: HRMS (m/z) [ESI]: calculated for $C_{26}H_{32}O_3N_4K^+$ [M+K] $^+$: 487.2106, found 487.21149.

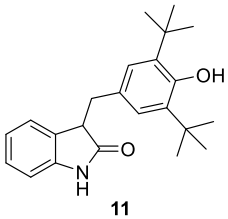




10

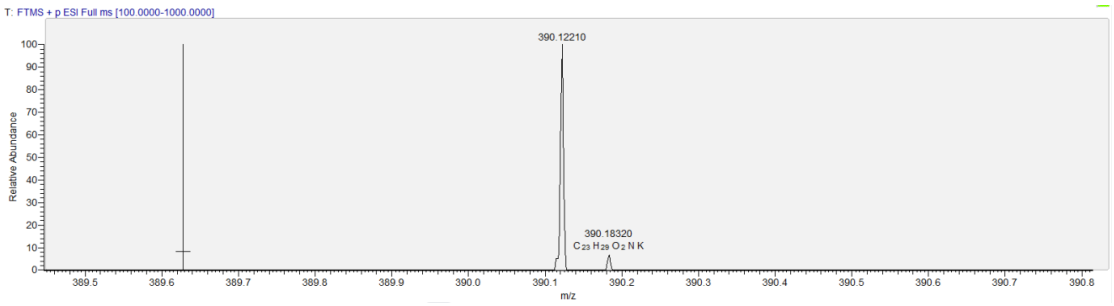
Compound 10: HRMS (m/z) [ESI]: calculated for $C_{26}H_{31}O_3N_4^+$ [M+H] $^+$: 447.2391, found 447.23602.

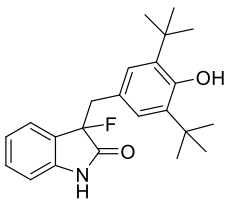




11

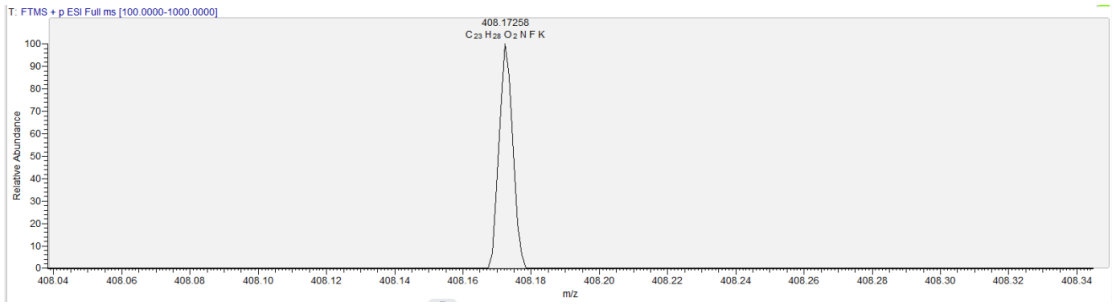
Compound 11: HRMS (m/z) [ESI]: calculated for $C_{23}H_{29}O_2NK^+$ [M+K] $^+$: 390.1830, found 390.18320.

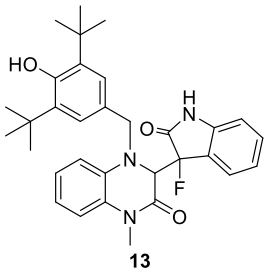




12

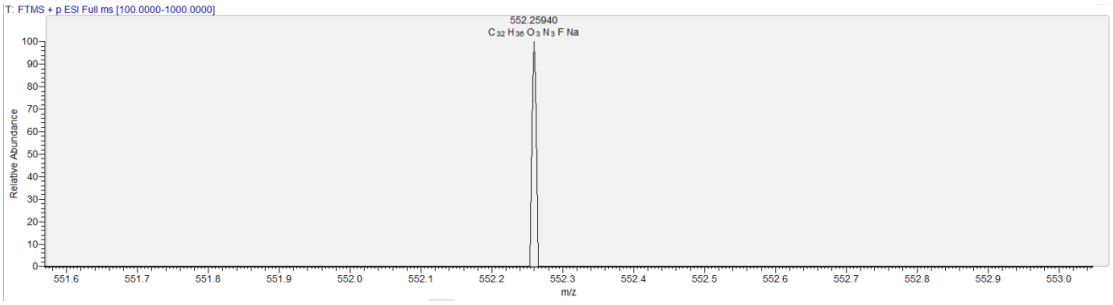
Compound 12: HRMS (m/z) [ESI]: calculated for $C_{23}H_{28}O_2NFK^+$ [M+K] $^+$: 408.1736, found 408.17258.

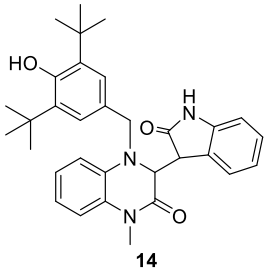




13

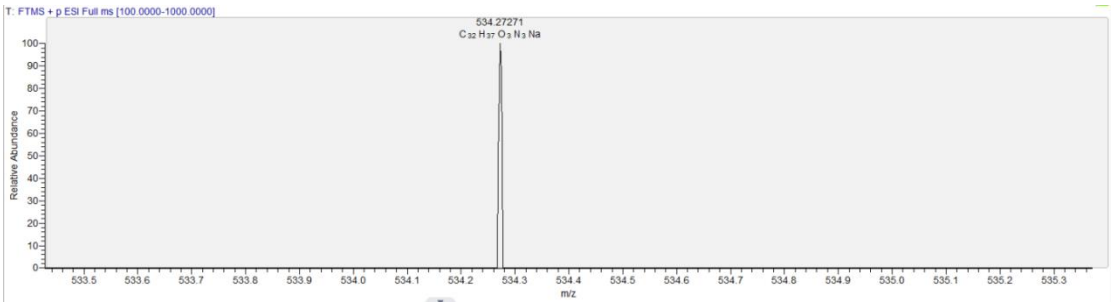
Compound 13: HRMS (m/z) [ESI]: calculated for $C_{32}H_{36}O_3N_3FNa^+$ [M+Na] $^+$: 552.2633, found 552.25940.

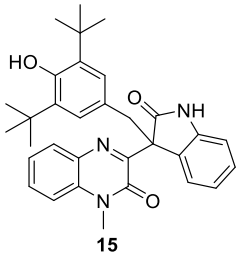




14

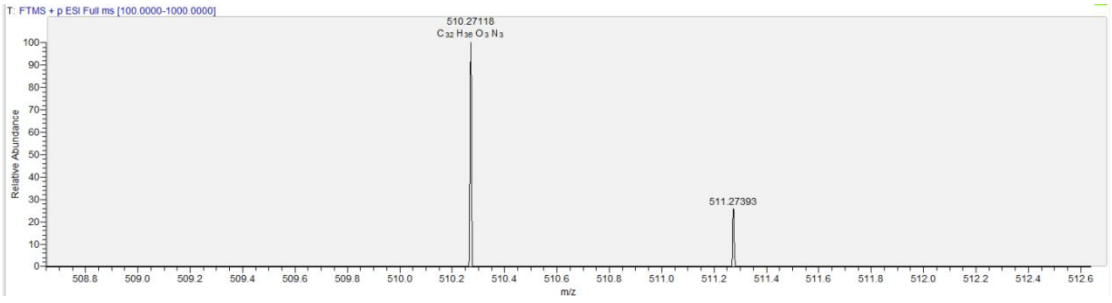
Compound 14: HRMS (m/z) [ESI]: calculated for $C_{32}H_{37}O_3N_3Na^+$ [M+Na] $^+$: 534.2727, found 534.27271.



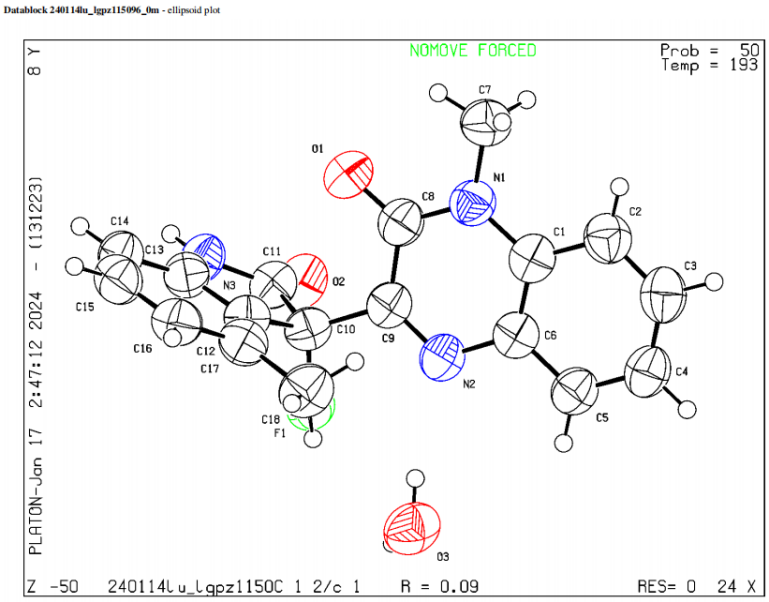


15

Compound 15: HRMS (m/z) [ESI]: calculated for $C_{32}H_{36}O_3N_3^+$ [M+H] $^+$: 510.2751, found 510.27118.



5. X-ray Structure and Data of 3m



240114LU_LGPZ115096_0m

Table 1 Crystal data and structure refinement for 240114LU_LGPZ115096_0m.

Identification code	240114LU_LGPZ115096_0m
Empirical formula	$C_{18}H_{16}FN_3O_3$
Formula weight	341.34
Temperature/K	193.00
Crystal system	monoclinic
Space group	C2/c
a/Å	24.355(17)
b/Å	8.370(6)
c/Å	15.766(12)
α/°	90
β/°	100.14(2)
γ/°	90
Volume/Å^3	3164(4)
Z	8
ρ_{calc}g/cm^3	1.433
μ/mm^{-1}	0.573
F(000)	1424.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	9.738 to 121.496
Index ranges	-31 ≤ h ≤ 26, -10 ≤ k ≤ 10, -19 ≤ l ≤ 20
Reflections collected	17700
Independent reflections	3535 [R_{int} = 0.0814, R_{sigma} = 0.0722]
Data/restraints/parameters	3535/0/229
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0885, wR_2 = 0.2547
Final R indexes [all data]	R_1 = 0.1329, wR_2 = 0.2953
Largest diff. peak/hole / e Å^{-3}	0.36/-0.31

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 240114LU_LGPZ115096_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F(1)	5388.7(8)	4746(2)	5969.1(13)	73.8(6)
O(1)	6944.8(11)	6834(3)	6770.7(16)	74.4(8)
O(2)	5813.5(11)	7441(3)	5127.3(15)	78.0(8)
N(1)	7371.7(12)	4471(3)	6540.3(17)	65.9(8)
N(2)	6303.8(12)	3193(3)	5978.6(17)	64.3(8)
N(3)	5716.4(13)	8382(3)	6458.1(18)	67.7(8)
C(1)	7314.7(16)	2903(4)	6211(2)	66.6(9)
C(2)	7783.0(17)	1941(5)	6158(2)	73.8(10)
C(3)	7700.5(19)	425(5)	5830(2)	79.7(11)
C(4)	7167.1(17)	-189(4)	5547(2)	73.4(10)
C(5)	6710.6(17)	739(4)	5593(2)	67.8(9)
C(6)	6777.5(16)	2296(4)	5925(2)	63.6(9)
C(7)	7925.0(16)	5136(5)	6879(3)	78.9(10)
C(8)	6913.0(15)	5420(4)	6541(2)	66.1(9)
C(9)	6370.5(14)	4636(4)	6269(2)	62.5(9)
C(10)	5860.8(15)	5606(4)	6364(2)	64.4(9)
C(11)	5811.7(16)	7251(4)	5888(2)	65.8(9)
C(12)	5810.1(15)	6066(4)	7271(2)	64.3(9)
C(13)	5726.5(15)	7721(4)	7285(2)	65.1(9)
C(14)	5659.7(16)	8529(5)	8022(2)	71.5(10)
C(15)	5679.1(16)	7594(5)	8762(2)	75.2(10)
C(16)	5752.9(16)	5958(5)	8758(2)	71.6(10)
C(17)	5818.9(15)	5148(4)	8000(2)	69.7(9)
C(18)	5884(2)	3357(4)	7996(3)	85.2(12)
O(3)	5247.5(12)	1293(3)	5866.4(19)	89.5(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 240114LU_LGPZ115096_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	71.7(14)	68.2(12)	78.9(13)	-5.8(9)	6.0(10)	-0.6(9)
O(1)	85.1(18)	59.5(14)	77.5(16)	-3.4(11)	11.7(13)	-4.2(11)
O(2)	99(2)	71.7(16)	62.6(15)	4.4(11)	12.9(13)	5.9(13)
N(1)	67.8(19)	67.3(17)	62.0(16)	-3.8(12)	9.4(13)	-1.8(13)
N(2)	71(2)	59.9(16)	61.6(16)	2.2(12)	9.8(13)	3.2(12)
N(3)	80(2)	56.5(15)	67.0(17)	0.6(12)	13.8(14)	3.7(13)
C(1)	77(3)	64.9(19)	57.7(18)	4.1(14)	11.6(16)	3.0(16)
C(2)	71(2)	78(2)	72(2)	0.5(17)	9.2(18)	5.7(17)
C(3)	84(3)	78(2)	76(2)	1.9(18)	13(2)	18.2(19)
C(4)	87(3)	60.3(19)	73(2)	3.2(16)	14.6(19)	8.2(17)
C(5)	77(2)	60.6(19)	65.4(19)	3.8(14)	12.6(17)	0.0(16)
C(6)	70(2)	62.9(18)	57.8(17)	4.5(14)	11.3(15)	1.0(15)
C(7)	71(3)	83(2)	81(2)	-6.5(19)	8.8(18)	-6.9(18)
C(8)	73(2)	65(2)	60.2(18)	-0.8(15)	10.8(16)	0.9(16)
C(9)	71(2)	58.4(18)	57.6(17)	2.8(13)	11.2(15)	0.9(15)
C(10)	65(2)	62.6(19)	63.1(18)	-2.0(14)	6.0(15)	-5.0(14)
C(11)	72(2)	64.7(19)	58.4(19)	1.0(15)	4.3(15)	2.0(15)
C(12)	63(2)	64.2(19)	64.7(19)	1.3(15)	9.4(15)	-2.5(15)
C(13)	63(2)	68(2)	64.1(19)	-3.5(15)	8.9(15)	0.6(15)
C(14)	73(2)	73(2)	69(2)	-9.1(16)	14.6(17)	0.0(17)
C(15)	70(3)	96(3)	60(2)	-10.5(19)	12.8(16)	-2.8(19)
C(16)	72(2)	84(2)	59.1(19)	1.5(16)	12.0(16)	-7.4(17)
C(17)	65(2)	76(2)	67(2)	4.4(16)	8.6(16)	-0.6(16)
C(18)	105(3)	73(2)	79(2)	12.2(18)	18(2)	-2(2)
O(3)	96(2)	64.5(15)	102(2)	12.2(13)	3.6(16)	2.0(13)

Table 4 Bond Lengths for 240114LU_LGPZ115096_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(1)	C(10)	1.405(4)	C(4)	C(5)	1.369(5)
O(1)	C(8)	1.237(4)	C(5)	C(6)	1.403(5)
O(2)	C(11)	1.210(4)	C(8)	C(9)	1.470(5)
N(1)	C(1)	1.409(4)	C(9)	C(10)	1.513(5)
N(1)	C(7)	1.469(5)	C(10)	C(11)	1.563(5)
N(1)	C(8)	1.371(5)	C(10)	C(12)	1.507(5)
N(2)	C(6)	1.391(5)	C(12)	C(13)	1.401(5)
N(2)	C(9)	1.292(4)	C(12)	C(17)	1.379(5)
N(3)	C(11)	1.353(4)	C(13)	C(14)	1.379(5)
N(3)	C(13)	1.412(4)	C(14)	C(15)	1.399(5)
C(1)	C(2)	1.410(5)	C(15)	C(16)	1.381(6)
C(1)	C(6)	1.402(5)	C(16)	C(17)	1.408(5)
C(2)	C(3)	1.372(5)	C(17)	C(18)	1.508(5)
C(3)	C(4)	1.395(6)			

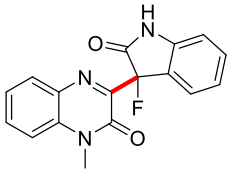
Table 5 Bond Angles for 240114LU_LGPZ115096_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1)	N(1)	C(7)	120.8(3)	F(1)	C(10)	C(9)	107.6(3)
C(8)	N(1)	C(1)	120.8(3)	F(1)	C(10)	C(11)	104.5(3)
C(8)	N(1)	C(7)	118.4(3)	F(1)	C(10)	C(12)	110.7(3)
C(9)	N(2)	C(6)	118.2(3)	C(9)	C(10)	C(11)	114.9(3)
C(11)	N(3)	C(13)	111.2(3)	C(12)	C(10)	C(9)	115.9(3)
N(1)	C(1)	C(2)	121.6(3)	C(12)	C(10)	C(11)	102.6(3)
C(6)	C(1)	N(1)	118.8(3)	O(2)	C(11)	N(3)	126.7(3)
C(6)	C(1)	C(2)	119.6(3)	O(2)	C(11)	C(10)	125.3(3)
C(3)	C(2)	C(1)	118.9(4)	N(3)	C(11)	C(10)	107.7(3)
C(2)	C(3)	C(4)	121.8(4)	C(13)	C(12)	C(10)	107.7(3)
C(5)	C(4)	C(3)	119.5(3)	C(17)	C(12)	C(10)	131.0(3)
C(4)	C(5)	C(6)	120.3(4)	C(17)	C(12)	C(13)	121.3(3)
N(2)	C(6)	C(1)	121.5(3)	C(12)	C(13)	N(3)	110.6(3)
N(2)	C(6)	C(5)	118.7(3)	C(14)	C(13)	N(3)	126.9(3)
C(1)	C(6)	C(5)	119.8(3)	C(14)	C(13)	C(12)	122.5(3)
O(1)	C(8)	N(1)	123.1(3)	C(13)	C(14)	C(15)	115.9(4)
O(1)	C(8)	C(9)	121.3(3)	C(16)	C(15)	C(14)	122.4(3)
N(1)	C(8)	C(9)	115.6(3)	C(15)	C(16)	C(17)	121.1(3)
N(2)	C(9)	C(8)	124.8(3)	C(12)	C(17)	C(16)	116.9(3)
N(2)	C(9)	C(10)	118.9(3)	C(12)	C(17)	C(18)	122.5(3)
C(8)	C(9)	C(10)	116.3(3)	C(16)	C(17)	C(18)	120.7(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 240114LU_LGPZ115096_0m.

Atom	*x*	*y*	*z*	U(eq)
H(3)	5655.97	9397.35	6330.37	81
H(2)	8149.7	2337.37	6347.19	89
H(3A)	8015.36	-225.33	5795.1	96
H(4)	7121.04	-1244.02	5323.86	88
H(5)	6346.66	327.19	5400.04	81
H(7A)	8149.3	5157.49	6420.53	118
H(7B)	8110.95	4469.48	7355.34	118
H(7C)	7884.01	6225.19	7087.49	118
H(14)	5603.91	9651.68	8026.96	86
H(15)	5640.01	8103.01	9286.98	90
H(16)	5759.24	5370	9275.09	86
H(18A)	5581.23	2887.66	7578.94	128
H(18B)	5870.69	2935.42	8571.94	128
H(18C)	6243.4	3082.73	7834.87	128
H(3B)	4991.05	1740.07	5486.37	134
H(3C)	5531.35	1936.97	5909.07	134

6. Characterization of products



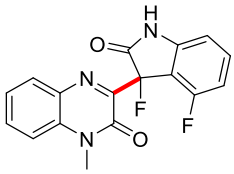
3-Fluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3a) was purified by silica column with dichloromethane/methanol = 50:1-20:1, yellow solid, 61.3 mg, 99% yield;

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.95 (s, 1H, NH), 8.04 (dd, J = 1.50, 8.02 Hz, 1H, ArH), 7.75 (ddd, J = 1.52, 7.16, 8.6 Hz, 1H, ArH), 7.64 (dd, J = 1.26, 8.54 Hz, 1H, ArH), 7.50 (ddd, J = 1.24, 7.16, 8.20 Hz, 1H, ArH), 7.35-7.40 (m, 1H, ArH), 7.19 (d, J = 7.44 Hz, 1H, ArH), 6.92-6.98 (m, 2H, ArH), 3.56 (s, 3H, NCH_3);

^{13}C NMR (75 MHz, DMSO-d_6): δ = 171.35-171.54 (d, $J_{C\text{-}F}$ = 19.53 Hz), 152.09-152.26 (d, $J_{C\text{-}F}$ = 16.90 Hz), 152.03-152.05 (d, $J_{C\text{-}F}$ = 2.01 Hz), 145.10-145.16 (d, $J_{C\text{-}F}$ = 5.60 Hz), 133.60, 132.46-132.49 (d, $J_{C\text{-}F}$ = 3.67 Hz), 132.13, 132.08, 130.36, 125.24-125.26 (d, $J_{C\text{-}F}$ = 1.68 Hz), 124.87-125.05 (d, $J_{C\text{-}F}$ = 17.80 Hz), 124.66, 122.57-122.60 (d, $J_{C\text{-}F}$ = 3.28 Hz), 115.64, 111.04-111.06 (d, $J_{C\text{-}F}$ = 2.07 Hz), 91.78-93.66 (d, $J_{C\text{-}F}$ = 188.05 Hz), 29.32;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.99;

HRMS (ESI-TOF) calcd for $C_{17}H_{13}N_3O_2F$ $[M + H]^+$: 310.0986; found: 310.0966.



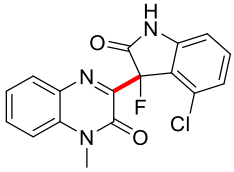
3, 4-Difluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3b) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 39.9 mg, 61% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.24 (s, 1H, NH), 8.06 (dd, J = 1.50, 7.96 Hz, 1H, ArH), 7.77 (ddd, J = 1.58, 7.22, 8.60 Hz, 1H, ArH), 7.67 (dd, J = 1.22, 8.58 Hz, 1H, ArH), 7.52 (ddd, J = 1.22, 7.24, 8.24 Hz, 1H, ArH), 7.41-7.47 (m, 1H, ArH), 6.85 (d, J = 7.96 Hz, 1H, ArH), 6.78 (t, J = 8.98 Hz, 1H, ArH), 3.59 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.63-170.82 (d, $J_{C\text{-}F}$ = 19.34 Hz), 157.83-160.34 (d, $J_{C\text{-}F}$ = 250.82 Hz), 152.05 (d, $J_{C\text{-}F}$ = 3.86 Hz), 150.93-151.15 (d, $J_{C\text{-}F}$ = 22.08 Hz), 147.06 (dd, $J_{C\text{-}F}$ = 5.11, 7.26 Hz), 135.07 (d, $J_{C\text{-}F}$ = 3.30 Hz), 134.97 (d, $J_{C\text{-}F}$ = 3.28 Hz)133.52, 132.37, 132.06, 130.43, 124.85, 115.80, 109.90-110.09 (d, $J_{C\text{-}F}$ = 19.48 Hz), 107.69, 92.28-94.41 (d, $J_{C\text{-}F}$ = 213.27 Hz), 29.41;

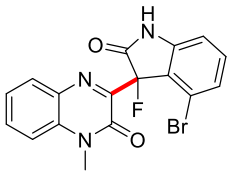
^{19}F NMR (376 MHz, DMSO-d_6): δ = -117.74 (d, $J_{C\text{-}F}$ = 4.77 Hz), -163.38 (d, $J_{C\text{-}F}$ = 3.53 Hz);

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2F_2$ $[M + H]^+$: 328.0892; found: 328.0869.

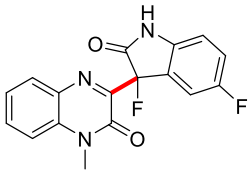


3-Fluoro-4-chloro-3-(1-methylquinoxalin-2-one) indolin-2-one (3c) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow, 37.5 mg, 55% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.26 (s, 1H, NH), 8.07 (dd, J = 1.48, 8.00 Hz, 1H, ArH), 7.77 (ddd, J = 1.54, 7.22, 8.62 Hz, 1H, ArH), 7.67 (dd, J = 1.30, 8.54 Hz, 1H, ArH), 7.52 (ddd, J = 1.28, 7.22, 8.28 Hz, 1H, ArH), 7.41 (dt, J = 2.20, 8.08 Hz, 1H, ArH), 6.95-7.00 (m, 2H, ArH), 3.60 (s, 3H, NCH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.33-170.52 (d, $J_{C\text{-}F}$ = 19.10 Hz), 151.97-152.01 (d, $J_{C\text{-}F}$ = 3.87 Hz), 150.89-151.11 (d, $J_{C\text{-}F}$ = 21.60 Hz), 146.92-146.97 (d, $J_{C\text{-}F}$ = 5.06 Hz), 134.05-134.08 (d, $J_{C\text{-}F}$ = 3.46 Hz), 133.45, 132.32, 132.12, 130.78-130.81 (d, $J_{C\text{-}F}$ = 2.34 Hz), 130.48, 124.84, 123.19-123.22 (d, $J_{C\text{-}F}$ = 2.82 Hz), 122.22-122.39 (d, $J_{C\text{-}F}$ = 16.73 Hz), 115.77, 110.13, 91.68-93.58 (d, $J_{C\text{-}F}$ = 190.55 Hz), 29.37;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -166.56;
HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2ClF$ $[M + H]^+$: 344.0597; found: 344.0581.



3-Fluoro-4-bromo -3-(1-methylquinoxalin-2-one) indolin-2-one (3d) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 49.1 mg, 65% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.24 (s, 1H, NH), 8.08 (dd, J = 1.48, 8.04 Hz, 1H, ArH), 7.28 (t, J = 7.82 Hz, 1H, ArH), 7.69 (d, J = 8.44 Hz, 1H, ArH), 7.53 (t, J = 7.56 Hz, 1H, ArH), 7.33 (dt, J = 2.16, 7.99 Hz, 1H, ArH), 7.14 (d, J = 8.16 Hz, 1H, ArH), 7.00 (d, J = 7.72 Hz, 1H, ArH), 3.60 (s, 3H, NCH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.22-170.41 (d, $J_{C\text{-}F}$ = 19.20 Hz), 151.93-151.97 (d, $J_{C\text{-}F}$ = 3.99 Hz), 150.92-151.14 (d, $J_{C\text{-}F}$ = 21.35 Hz), 147.00-147.05 (d, $J_{C\text{-}F}$ = 5.04 Hz), 134.12-134.15 (d, $J_{C\text{-}F}$ = 3.40 Hz), 133.45, 132.32, 132.14, 130.52, 126.26-126.29 (d, $J_{C\text{-}F}$ = 2.83 Hz), 124.86, 124.26-124.43 (d, $J_{C\text{-}F}$ = 16.47 Hz), 119.09-119.11 (d, $J_{C\text{-}F}$ = 2.44 Hz), 115.77, 110.53, 92.39-94.30 (d, $J_{C\text{-}F}$ = 190.94 Hz), 29.36;
HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2BrF$ $[M + H]^+$: 388.0091; found: 388.0078.

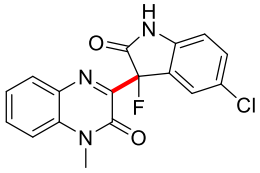


3, 5-Difluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3e) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brown solid, 51.2 mg, 78% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.99 (s, 1H, NH), 8.04 (dd, J = 1.50, 8.02 Hz, 1H, ArH), 7.76 (ddd, J = 1.56, 7.20, 8.60 Hz, 1H, ArH), 7.66 (dd, J = 1.26, 8.50 Hz, 1H, ArH), 7.51 (ddd, J = 1.24, 7.22, 8.26 Hz, 1H, ArH), 7.20-7.25 (m, 1H, ArH), 7.15 (td, J = 2.51, 7.81 Hz, 1H, ArH), 6.98 (ddd, J = 1.29, 4.27, 5.52 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.24-171.43 (d, $J_{C\text{-}F}$ = 19.25 Hz), 157.10-159.51 (d, $J_{C\text{-}F}$ = 240.59 Hz), 152.13-152.16 (d, $J_{C\text{-}F}$ = 3.53 Hz), 151.44-151.66 (d, $J_{C\text{-}F}$ = 21.96 Hz), 141.32-141.36 (d, $J_{C\text{-}F}$ = 4.07 Hz), 133.71, 132.15, 132.19, 130.44, 124.64, 118.81-118.85 (d, $J_{C\text{-}F}$ = 3.57 Hz),

118.58-118.61 (d, J_{C-F} = 2.78 Hz), 115.64, 113.43-113.18 (d, J_{C-F} = 24.87 Hz), 111.93-112.01 (d, J_{C-F} = 7.66 Hz), 91.74-93.63 (d, J_{C-F} = 188.43 Hz), 29.34;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -120.98, -160.88;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}F_2N_3O_2$ $[M + H]^+$: 328.0892; found: 328.0871.



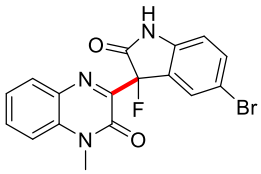
3-Fluoro-5-chloro-3-(1-methylquinoxalin-2-one) indolin-2-one (3f) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brown solid, 36 mg, 52% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.11 (s, 1H, NH), 8.03 (dd, J = 1.46, 8.06 Hz, 1H, ArH), 7.75 (ddd, J = 1.58, 7.22, 8.62 Hz, 1H, ArH), 7.65 (dd, J = 1.26, 8.54 Hz, 1H, ArH), 7.51 (ddd, J = 1.24, 7.20, 8.24 Hz, 1H, ArH), 7.44 (td, J = 2.19, 8.32 Hz, 1H, ArH), 7.29 (t, J = 2.32 Hz, 1H, ArH), 7.00 (dd, J = 1.26, 8.30 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.01-171.20 (d, J_{C-F} = 19.28 Hz), 152.17-152.21 (d, J_{C-F} = 3.42 Hz), 151.32-151.54 (d, J_{C-F} = 22.06 Hz), 146.92-146.97 (d, J_{C-F} = 5.44 Hz), 133.73, 132.21, 132.18, 130.43, 126.81, 126.64, 126.48-126.52 (d, J_{C-F} = 3.65 Hz), 125.51, 124.63, 115.63, 112.54, 91.49-93.38 (d, J_{C-F} = 189.02 Hz), 29.36;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.86;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2ClF$ $[M + H]^+$: 344.0597; found: 344.0583.



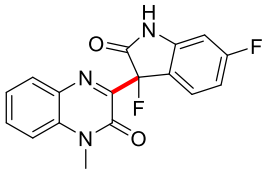
3-Fluoro-5-bromo-3-(1-methylquinoxalin-2-one) indolin-2-one (3g) was purified by silica column with dichloromethane/methanol = 50:0-20:1, Brownish yellow solid, 60.1 mg, 79% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.12 (s, 1H, NH), 8.04 (dd, J = 1.48, 8.00 Hz, 1H, ArH), 7.75 (ddd, J = 1.56, 7.22, 8.62 Hz, 1H, ArH), 7.65 (dd, J = 1.28, 8.64 Hz, 1H, ArH), 7.58 (td, J = 2.14, 8.32 Hz, 1H, ArH), 7.51 (ddd, J = 1.26, 7.20, 8.24 Hz, 1H, ArH), 7.39 (t, J = 2.26 Hz, 1H, ArH), 6.96 (dd, J = 1.28, 8.32 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.90-171.09 (d, J_{C-F} = 19.33 Hz), 152.18-152.22 (d, J_{C-F} = 3.53 Hz), 151.32-151.53 (d, J_{C-F} = 21.92 Hz), 144.35-144.40 (d, J_{C-F} = 5.34 Hz), 135.07-135.11 (d, J_{C-F} = 3.62 Hz), 133.75, 132.23, 132.18, 130.43, 128.16, 127.01-27.19 (d, J_{C-F} = 17.61 Hz), 124.63, 115.64, 114.01-114.05 (d, J_{C-F} = 3.61 Hz), 113.03-113.04 (d, J_{C-F} = 1.81 Hz), 91.43-93.32 (d, J_{C-F} = 189.21 Hz), 29.37;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.71;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2BrF$ $[M + H]^+$: 388.0091; found: 388.0091.



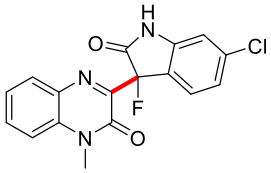
3, 5-Difluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3h) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 28.4 mg, 41% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.14 (s, 1H, NH), 8.04 (dd, J = 1.46, 8.06 Hz, 1H, ArH), 7.75 (ddd, J = 1.58, 7.20, 8.62 Hz, 1H, ArH), 7.65 (dd, J = 1.26, 8.54 Hz, 1H, ArH), 7.51 (ddd, J = 1.22, 7.20, 8.24 Hz, 1H, ArH), 7.22-7.26 (m, 1H, ArH), 6.79-6.83 (m, 1H, ArH), 6.71-6.77 (m, 1H, ArH), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.57-171.77 (d, $J_{C\text{-}F}$ = 19.56 Hz), 163.63-166.08 (d, $J_{C\text{-}F}$ = 245.23 Hz), 152.08-152.12 (d, $J_{C\text{-}F}$ = 3.49 Hz), 151.68-151.91 (d, $J_{C\text{-}F}$ = 22.60 Hz), 147.04-147.23 (dd, $J_{C\text{-}F}$ = 5.56, 12.90 Hz), 133.62, 132.19, 132.10, 130.39, 127.23-127.33 (d, $J_{C\text{-}F}$ = 10.58 Hz), 124.69, 120.89-121.06 (d, $J_{C\text{-}F}$ = 17.24 Hz), 115.67, 108.67-108.92 (dd, $J_{C\text{-}F}$ = 3.25, 22.15 Hz), 99.32-99.60 (d, $J_{C\text{-}F}$ = 27.11 Hz), 91.10-92.99 (d, $J_{C\text{-}F}$ = 188.70 Hz), 29.36;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -107.02 (d, $J_{C\text{-}F}$ = 6.99 Hz), -159.31 (d, $J_{C\text{-}F}$ = 7.06 Hz);

HRMS (ESI-TOF) calcd for $C_{17}H_{12}F_2N_3O_2$ $[M + H]^+$: 328.0892; found: 328.0871.



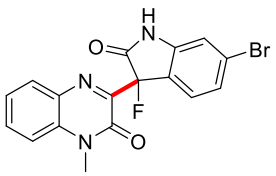
3-Fluoro-6-chloro-3-(1-methylquinoxalin-2-one) indolin-2-one (3i) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light brown solid, 49.8 mg, 70% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.16 (s, 1H, NH), 8.04 (dd, J = 1.50, 7.98 Hz, 1H, ArH), 7.75 (ddd, J = 1.54, 7.18, 8.60 Hz, 1H, ArH), 7.65 (dd, J = 1.22, 8.58 Hz, 1H, ArH), 7.51 (ddd, J = 1.24, 7.16, 8.24 Hz, 1H, ArH), 7.21-7.23 (m, 1H, ArH), 6.98-7.01 (m, 2H, ArH), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.24-171.43 (d, $J_{C\text{-}F}$ = 19.42 Hz), 152.10-152.13 (d, $J_{C\text{-}F}$ = 3.51 Hz), 151.49-151.71 (d, $J_{C\text{-}F}$ = 22.25 Hz), 146.57-146.62 (d, $J_{C\text{-}F}$ = 5.42 Hz), 136.78-136.83 (d, $J_{C\text{-}F}$ = 4.11 Hz), 133.63, 132.24, 132.13, 130.40, 126.86, 124.72, 123.65-123.83 (d, $J_{C\text{-}F}$ = 18.25 Hz), 122.37-122.40 (d, $J_{C\text{-}F}$ = 3.13 Hz), 115.68, 111.20, 91.11-93.00 (d, $J_{C\text{-}F}$ = 188.92 Hz), 29.37;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.52;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2ClF$ $[M + H]^+$: 344.0597; found: 344.0573.



3-Fluoro-6-bromo-3-(1-methylquinoxalin-2-one) indolin-2-one (3j) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 60.5 mg, 75% yield;

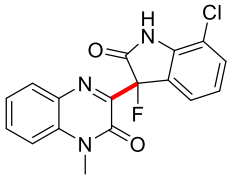
^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.15 (s, 1H, NH), 8.04 (dd, J = 1.52, 8.04 Hz, 1H, ArH),

7.76 (ddd, J = 1.54, 7.22, 8.62 Hz, 1H, ArH), 7.65 (dd, J = 1.28, 8.56 Hz, 1H, ArH), 7.51 (ddd, J = 1.22, 7.18, 8.24 Hz, 1H, ArH), 7.13-7.15 (m, 3H, ArH), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.12-171.32 (d, $J_{C\text{-}F}$ = 19.50 Hz), 152.10-152.13 (d, $J_{C\text{-}F}$ = 3.54 Hz), 151.45-151.68 (d, $J_{C\text{-}F}$ = 22.33 Hz), 146.64-146.69 (d, $J_{C\text{-}F}$ = 5.49 Hz), 133.63, 132.25, 132.13, 130.40, 127.13, 125.38, 125.30-125.33 (d, $J_{C\text{-}F}$ = 3.05 Hz), 124.72, 124.06-124.24 (d, $J_{C\text{-}F}$ = 17.94 Hz), 115.69, 113.95, 91.18-93.07 (d, $J_{C\text{-}F}$ = 189.11 Hz), 29.37;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.83;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2BrF$ $[M + H]^+$: 388.0091; found: 388.0092.



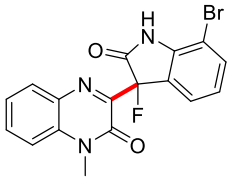
3-Fluoro-7-chloro-3-(1-methylquinoxalin-2-one) indolin-2-one (3k) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 62.9 mg, 90% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.46 (s, 1H, NH), 8.05 (dd, J = 1.50, 7.98 Hz, 1H, ArH), 7.76 (ddd, J = 1.54, 7.18, 8.62 Hz, 1H, ArH), 7.66 (dd, J = 1.12, 8.44 Hz, 1H, ArH), 7.52 (ddd, J = 1.26, 7.22, 8.26 Hz, 1H, ArH), 7.45-7.48 (m, 1H, ArH), 7.17-7.20 (m, 1H, ArH), 6.98 (ddd, J = 1.04, 7.38, 8.34 Hz, 1H, ArH), 3.58 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.17-171.36 (d, $J_{C\text{-}F}$ = 19.09 Hz), 152.11-152.15 (d, $J_{C\text{-}F}$ = 3.46 Hz), 151.40-151.63 (d, $J_{C\text{-}F}$ = 22.15 Hz), 142.79-142.84 (d, $J_{C\text{-}F}$ = 5.47 Hz), 133.62, 132.44, 132.47, 132.30, 132.14, 130.44, 126.45-126.63 (d, $J_{C\text{-}F}$ = 17.98 Hz), 124.76, 123.98-124.01 (d, $J_{C\text{-}F}$ = 3.05 Hz), 115.72, 115.16-115.18 (d, $J_{C\text{-}F}$ = 1.94 Hz), 91.83-93.72 (d, $J_{C\text{-}F}$ = 189.21 Hz), 29.39;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.02;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2ClF$ $[M + H]^+$: 344.0597; found: 344.0574.



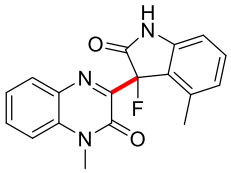
3-Fluoro-7-bromo-3-(1-methylquinoxalin-2-one) indolin-2-one (3l) was purified by silica column with dichloromethane/methanol = 50:0-20:1, red solid, 52.0 mg, 66% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.30 (s, 1H, NH), 8.05 (dd, J = 1.54, 8.02 Hz, 1H, ArH), 7.77 (ddd, J = 1.56, 7.22, 8.62 Hz, 1H, ArH), 7.64-7.67 (m, 1H, ArH), 7.60 (d, J = 8.32 Hz, 1H, ArH), 7.52 (t, J = 7.64 Hz, 1H, ArH), 7.21 (dd, J = 2.22, 7.02 Hz, 1H, ArH), 6.91 (t, J = 7.76 Hz, 1H, ArH), 3.58 (s, 3H, NCH_3);

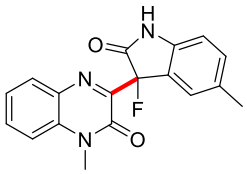
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.08-171.27 (d, $J_{C\text{-}F}$ = 19.22 Hz), 152.11-152.14 (d, $J_{C\text{-}F}$ = 3.62 Hz), 151.46-151.68 (d, $J_{C\text{-}F}$ = 21.91 Hz), 144.50-144.55 (d, $J_{C\text{-}F}$ = 5.43 Hz), 135.34-135.38 (d, $J_{C\text{-}F}$ = 3.72 Hz), 133.62, 132.30, 132.15, 130.44, 126.39-126.57 (d, $J_{C\text{-}F}$ = 17.96 Hz), 124.77, 124.43, 124.32-124.36 (d, $J_{C\text{-}F}$ = 3.11 Hz), 115.72, 103.21-103.23 (d, $J_{C\text{-}F}$ = 1.99 Hz), 92.07-93.96 (d, $J_{C\text{-}F}$ = 189.21 Hz), 29.39;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.68;

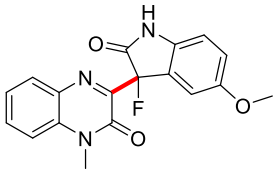
HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2BrF$ $[M + H]^+$: 388.0091; found: 388.0089.



3-Fluoro-4-methyl-3-(1-methylquinoxalin-2-one) indolin-2-one (3m) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 42.8 mg, 67% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.96 (s, 1H, NH), 8.04 (dd, J = 1.52, 8.00 Hz, 1H, ArH), 7.75 (ddd, J = 1.57, 7.16, 8.62 Hz, 1H, ArH), 7.66 (dd, J = 1.26, 8.58 Hz, 1H, ArH), 7.50 (ddd, J = 1.24, 7.20, 8.20 Hz, 1H, ArH), 7.24 (dt, J = 2.29, 7.76 Hz, 1H, ArH), 6.79 (d, J = 7.76 Hz, 1H, ArH), 6.74 (d, J = 7.80 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3), 1.98 (d, J = 2.32 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.16-171.35 (d, $J_{C\text{-}F}$ = 18.93 Hz), 152.36-152.58 (d, $J_{C\text{-}F}$ = 21.80 Hz), 151.96-152.00 (d, $J_{C\text{-}F}$ = 3.87 Hz), 145.23-145.29 (d, $J_{C\text{-}F}$ = 5.81 Hz), 136.69-136.70 (d, $J_{C\text{-}F}$ = 1.77 Hz), 133.57, 132.15, 132.00-132.03 (d, $J_{C\text{-}F}$ = 14.00 Hz), 131.94, 130.30, 124.66, 124.54-124.57 (d, $J_{C\text{-}F}$ = 11.72 Hz), 122.75-122.92 (d, $J_{C\text{-}F}$ = 16.94 Hz), 115.69, 108.58, 92.57-94.46 (d, $J_{C\text{-}F}$ = 188.62 Hz), 29.35, 17.41;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -165.69;
HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_2F$ $[M + H]^+$: 324.1143; found: 324.1121.



3-Fluoro-5-methyl-3-(1-methylquinoxalin-2-one) indolin-2-one (3n) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light brown solid, 58.9 mg, 90% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.86 (s, 1H, NH), 8.04 (dd, J = 1.52, 8.04 Hz, 1H, ArH), 7.75 (ddd, J = 1.56, 7.22, 8.60 Hz, 1H, ArH), 7.64 (dd, J = 1.26, 8.54 Hz, 1H, ArH), 7.51 (ddd, J = 1.22, 7.16, 8.22 Hz, 1H, ArH), 7.15-7.18 (m, 1H, ArH), 6.99-7.00 (m, 1H, ArH), 6.87 (dd, J = 1.22, 7.89 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3), 2.17 (s, 3H, CH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.35-171.54 (d, $J_{C\text{-}F}$ = 19.90 Hz), 152.16-152.38 (d, $J_{C\text{-}F}$ = 22.21 Hz), 152.03-152.07 (d, $J_{C\text{-}F}$ = 3.62 Hz), 142.64-142.69 (d, $J_{C\text{-}F}$ = 5.66 Hz), 133.62, 132.57-132.61 (d, $J_{C\text{-}F}$ = 3.74 Hz), 132.09, 131.65-13168 (d, $J_{C\text{-}F}$ = 3.33 Hz), 130.34, 125.75, 125.10, 124.92, 124.64, 115.64, 110.79-110.82 (d, $J_{C\text{-}F}$ = 2.04 Hz), 91.95-93.83 (d, $J_{C\text{-}F}$ = 187.89 Hz), 29.32, 20.77;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.70;
HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_2F$ $[M + H]^+$: 324.1143; found: 324.1122.



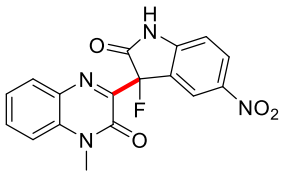
3-Fluoro-5-methoxy-3-(1-methylquinoxalin-2-one) indolin-2-one (3o) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brown solid, 66.6 mg, 99% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.76 (s, 1H, NH), 8.04 (dd, J = 1.48, 8.08 Hz, 1H, ArH), 7.75 (ddd, J = 1.58, 7.22, 8.62 Hz, 1H, ArH), 7.65 (dd, J = 1.26, 8.50 Hz, 1H, ArH), 7.50 (ddd, J = 1.26, 7.16, 8.24 Hz, 1H, ArH), 6.94 (dt, J = 2.40, 8.52 Hz, 1H, ArH), 6.80 (t, J = 2.44 Hz, 1H, ArH), 3.64 (s, 3H, CH_3), 3.57 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.25-171.44 (d, $J_{C\text{-}F}$ = 19.33 Hz), 155.41-155.44 (d, $J_{C\text{-}F}$ = 3.35 Hz), 151.98-152.20 (d, $J_{C\text{-}F}$ = 21.98 Hz), 152.07-152.11 (d, $J_{C\text{-}F}$ = 3.53 Hz), 138.20-138.26 (d, $J_{C\text{-}F}$ = 5.79 Hz), 133.69, 132.15, 132.07, 130.39, 126.07, 125.90, 124.59, 117.26-117.30 (d, $J_{C\text{-}F}$ = 3.95 Hz), 115.60, 111.61-111.74 (d, $J_{C\text{-}F}$ = 12.20 Hz), 92.21-94.09 (d, $J_{C\text{-}F}$ = 188.20 Hz), 55.99, 29.30;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.92;

HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_3F$ $[M + H]^+$: 340.1092; found: 340.1072.



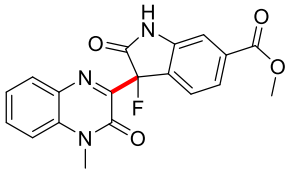
3-Fluoro-5-nitro-3-(1-methylquinoxalin-2-one) indolin-2-one (3p) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brick red solid, 25 mg, 36% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.91 (s, 1H, NH), 8.03 (dt, J = 8.71, 2.11 Hz, 1H, ArH), 8.04-8.07 (m, 2H, ArH), 7.77 (ddd, J = 1.56, 7.20, 8.62 Hz, 1H, ArH), 7.67 (dd, J = 1.26, 8.54 Hz, 1H, ArH), 7.52 (ddd, J = 1.24, 7.22, 8.24 Hz, 1H, ArH), 7.24 (dd, J = 1.16, 8.72 Hz, 1H, ArH), 3.56 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.47-171.67 (d, $J_{C\text{-}F}$ = 19.36 Hz), 152.32-152.35 (d, $J_{C\text{-}F}$ = 3.33 Hz), 151.27-151.32 (d, $J_{C\text{-}F}$ = 4.86 Hz), 150.83-151.05 (d, $J_{C\text{-}F}$ = 22.00 Hz), 142.77-142.80 (d, $J_{C\text{-}F}$ = 3.17 Hz), 133.82, 132.36, 132.31, 130.48, 129.41-129.45 (d, $J_{C\text{-}F}$ = 3.11 Hz), 125.37-125.55 (d, $J_{C\text{-}F}$ = 18.20 Hz), 124.70, 121.33, 115.68, 111.40, 90.79-92.69 (d, $J_{C\text{-}F}$ = 189.59 Hz), 29.39;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -161.84;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_4O_4F$ $[M + H]^+$: 355.0837; found: 355.0818.



3-Fluoro-3-(1-methylquinoxalin-2-one)-2-oxoindoline-6-carboxylate (3q) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 75.5 mg, 99% yield;

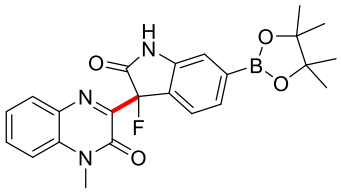
^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.22 (s, 1H, NH), 8.05 (dd, J = 1.46, 8.10 Hz, 1H, ArH), 7.76 (ddd, J = 1.54, 7.12, 8.58 Hz, 1H, ArH), 7.65 (d, J = 8.44 Hz, 1H, ArH), 7.58 (dt, J = 7.84, 1.32 Hz, 1H, ArH), 7.51 (ddd, J = 1.22, 7.24, 8.24 Hz, 1H, ArH), 7.46-7.47 (brs, 1H, ArH), 7.37 (dd, J = 2.46, 7.74 Hz, 1H, ArH), 3.86 (s, 3H, OCH_3), 3.56 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.99-171.18 (d, $J_{C\text{-}F}$ = 19.26 Hz), 166.00, 152.12-152.15

(d, $J_{C\text{-}F}$ = 3.52 Hz), 151.38-151.60 (d, $J_{C\text{-}F}$ = 21.85 Hz), 145.45-145.51 (d, $J_{C\text{-}F}$ = 5.31 Hz), 133.62, 132.15-132.32 (d, $J_{C\text{-}F}$ = 3.43 Hz), 132.32, 132.15, 130.42, 129.46-129.63 (d, $J_{C\text{-}F}$ = 17.27 Hz), 125.59, 124.77, 123.94-123.97 (d, $J_{C\text{-}F}$ = 3.15 Hz), 115.69, 110.85, 91.24-93.13 (d, $J_{C\text{-}F}$ = 188.65 Hz), 52.97, 29.36;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -162.02;

HRMS (ESI-TOF) calcd for $C_{19}H_{15}N_3O_4F$ $[M + H]^+$: 368.1041; found: 368.1019.



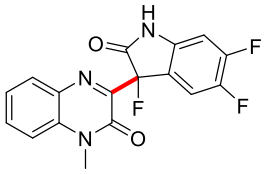
6-(4′,4′,5′,5′-Tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-3-Fluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3r) was purified by silica column with dichloromethane/methanol = 50:0-20:1, red solid, 50.7 mg, 57% yield;

^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.20 (s, 1H, NH), 8.03 (dd, J = 1.50, 8.06 Hz, 1H, ArH), 7.75 (ddd, J = 1.56, 7.20, 8.64 Hz, 1H, ArH), 7.65 (dd, J = 1.24, 8.56 Hz, 1H, ArH), 7.50 (ddd, J = 1.28, 7.22, 8.30 Hz, 1H, ArH), 7.23-7.28 (m, 2H, ArH), 7.19 (dd, J = 2.38, 7.42 Hz, 1H, ArH), 3.55 (3H, NCH_3), 1.29 (s, 12H, 4×CH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.05-171.25 (d, $J_{C\text{-}F}$ = 19.32 Hz), 152.06 (d, $J_{C\text{-}F}$ = 4.71 Hz), 151.86-152.03 (d, $J_{C\text{-}F}$ = 17.19 Hz), 144.77-144.82 (d, $J_{C\text{-}F}$ = 5.58 Hz), 133.60, 132.18, 132.10, 130.36, 128.93 (d, $J_{C\text{-}F}$ = 2.94 Hz), 128.06, 127.89, 124.70, 124.66, 115.93, 115.67, 91.69-93.58 (d, $J_{C\text{-}F}$ = 188.49 Hz), 84.44, 29.31, 25.10, 25.05;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -161.18;

HRMS (ESI-TOF) calcd for $C_{23}H_{24}N_3O_4BF$ $[M + H]^+$: 436.1838; found: 436.1815.



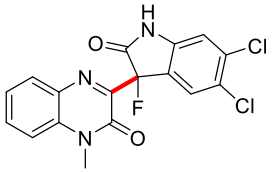
3, 5, 6-Trifluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3s) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brick red solid, 57.3 mg, 80% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.24 (s, 1H, NH), 8.03 (dd, J = 1.46, 8.06 Hz, 1H, ArH), 7.76 (ddd, J = 1.54, 7.22, 8.62 Hz, 1H, ArH), 7.66 (dd, J = 1.28, 8.56 Hz, 1H, ArH), 7.51 (ddd, J = 1.22, 7.18, 8.24 Hz, 1H, ArH), 7.43 (ddd, J = 2.32, 7.98, 9.84 Hz, 1H, ArH), 7.06 (ddd, J = 1.19, 6.54,10.50 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3);

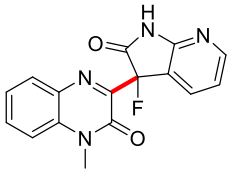
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.23-171.42 (d, $J_{C\text{-}F}$ = 19.16 Hz), 152.14-152.17 (d, $J_{C\text{-}F}$ = 3.54 Hz), 151.16-151.38 (d, $J_{C\text{-}F}$ = 22.13 Hz), 144.63, 142.19, 133.71, 132.24, 132.16, 130.44, 128.81, 124.67, 120.58, 115.65, 115.48, 101.06-101.29 (d, $J_{C\text{-}F}$ = 22.93 Hz), 91.25-93.14 (d, $J_{C\text{-}F}$ = 189.57 Hz), 29.36;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -132.61 (dd, $J_{C\text{-}F}$ = 6.99, 20.91 Hz), -146.96 (d, $J_{C\text{-}F}$ = 21.43 Hz), -160.30 (d, $J_{C\text{-}F}$ = 7.32 Hz);

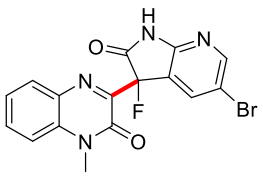
HRMS (ESI-TOF) calcd for $C_{17}H_{11}N_3O_2F_3$ $[M + H]^+$: 346.0798; found: 346.0780.



3-Fluoro-5, 6-dichloro-3-(1-methylquinoxalin-2-one) indolin-2-one (3t) was purified by silica column with dichloromethane/methanol = 50:0-20:1, brown solid, 50.4 mg, 53% yield;
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 11.41 (s, 1H, NH), 8.03 (dd, *J* = 1.42, 8.04 Hz, 1H, ArH), 7.76 (ddd, *J* = 1.54, 7.12, 8.60 Hz, 1H, ArH), 7.67 (dd, *J* = 1.26, 8.62 Hz, 1H, ArH), 7.49-7.53 (m, 2H, ArH), 7.22 (d, *J* = 1.20 Hz, 1H, ArH), 3.57 (s, 3H, NCH_3);
^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 170.81-171.01 (d, $J_{C\text{-}F}$ = 19.45 Hz), 152.22-152.26 (d, $J_{C\text{-}F}$ = 3.53 Hz), 150.93-151.15 (d, $J_{C\text{-}F}$ = 21.92 Hz), 145.10-145.15 (d, $J_{C\text{-}F}$ = 5.13 Hz), 134.74-134.78 (d, $J_{C\text{-}F}$ = 16.04 Hz), 133.76, 132.26, 130.46, 127.45, 125.36-125.54 (d, $J_{C\text{-}F}$ = 17.96 Hz), 124.68, 124.53-124.57 (d, $J_{C\text{-}F}$ = 3.39 Hz), 12.53-124.57 (d, $J_{C\text{-}F}$ = 3.39 Hz), 115.66, 112.83, 91.01-92.91 (d, $J_{C\text{-}F}$ = 190.02 Hz), 29.38;
^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ = -161.17;
HRMS (ESI-TOF) calcd for $C_{17}H_{11}N_3O_2Cl_2F$ $[M + H]^+$: 378.0207; found: 378.0198.



3-Fluoro-3-(1-methylquinoxalin-2-one)-1*H*-pyrrolo[2,3-b] pyridine-2-one (3u) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light red solid, 54.9 mg, 92% yield;
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 11.66 (s, 1H, NH), 8.25 (dt, *J* = 5.29, 1.89 Hz, 1H, ArH), 8.02 (dd, *J* = 1.50, 8.02 Hz, 1H, ArH), 7.76 (ddd, *J* = 1.58, 7.20, 8.60 Hz, 1H, ArH), 7.62-7.66 (m, 2H, ArH), 7.51 (ddd, *J* = 1.22, 7.20, 8.24 Hz, 1H, ArH), 6.96-7.00 (m, 1H, ArH), 3.57 (s, 3H, NCH_3);
^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ = 171.01-171.21 (d, $J_{C\text{-}F}$ = 19.20 Hz), 159.52-159.58 (d, $J_{C\text{-}F}$ = 5.65 Hz), 152.17-152.20 (d, $J_{C\text{-}F}$ = 3.61 Hz), 151.16-151.38 (d, $J_{C\text{-}F}$ = 22.01 Hz), 150.72-150.75 (d, $J_{C\text{-}F}$ = 3.72 Hz), 133.66, 133.41, 132.31, 132.14, 130.43, 124.74, 119.49-119.67 (d, $J_{C\text{-}F}$ = 18.40 Hz), 118.75-118.77 (d, $J_{C\text{-}F}$ = 2.76 Hz), 115.71, 91.44-93.33 (d, $J_{C\text{-}F}$ = 189.80 Hz), 29.40;
^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ = -162.39;
HRMS (ESI-TOF) calcd for $C_{16}H_{12}N_4O_2F$ $[M + H]^+$: 311.0939; found: 311.0922.



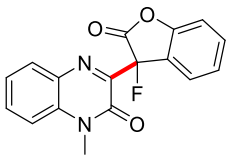
3-Fluoro-5-bromo-3-(1-methylquinoxalin-2-one)-1*H*-pyrrolo[2,3-b] pyridine-2-one (3v) was purified by silica column with dichloromethane/methanol = 50:0-20:1, red solid, 65.4 mg, 83% yield;
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 11.88 (s, 1H, NH), 8.40 (t, *J* = 2.22 Hz, 1H, ArH), 8.04 (dd,

J = 1.50, 8.04 Hz, 1H, ArH), 7.93 (t, J = 2.28 Hz, 1H, ArH), 7.78 (t, J = 7.90 Hz, 1H, ArH), 7.69 (d, J = 4.44 Hz, 2H, ArH), 7.53 (t, J = 7.60 Hz, 1H, ArH), 3.58 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.73, 158.44, 152.31, 151.06, 142.83, 136.19, 133.78, 132.34, 130.49, 124.73, 121.26, 115.69, 113.25, 91.22, 29.43;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -163.30;

HRMS (ESI-TOF) calcd for $C_{16}H_{11}N_4O_2FBr$ $[M + H]^+$: 389.0044; found: 389.0046.



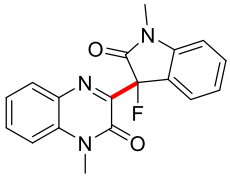
3-Fluoro-3-(1-methylquinoxalin-2-one)-Benzofuran-2-one (3w) was purified by silica column with dichloromethane/methanol = 50:0-20:1, solid, 24.4 mg, 23% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.98 (dd, J = 1.20, 6.40 Hz, 1H, ArH), 7.80 (ddd, J = 1.20, 5.72, 6.84 Hz, 1H, ArH), 7.70 (dd, J = 0.96, 6.84 Hz, 1H, ArH), 7.60-7.63 (m, 1H, ArH), 7.55 (ddd, J = 0.96, 5.76, 6.60 Hz, 2H, ArH), 7.43-7.46 (m, 2H, ArH), 7.24 (tt, J = 0.76, 6.08 Hz, 1H, ArH), 3.59 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.88-169.06 (d, $J_{C\text{-}F}$ = 13.10 Hz), 155.49-155.54 (d, $J_{C\text{-}F}$ = 3.81 Hz), 152.33-152.36 (d, $J_{C\text{-}F}$ = 2.17 Hz), 150.26-150.44 (d, $J_{C\text{-}F}$ = 13.93 Hz), 134.13-134.16 (d, $J_{C\text{-}F}$ = 2.21 Hz), 133.71, 132.76, 130.64, 126.09, 125.64-125.67 (d, $J_{C\text{-}F}$ = 9.68 Hz), 125.08, 122.65-122.80 (d, $J_{C\text{-}F}$ = 11.84 Hz), 115.99, 112.11-112.13 (d, $J_{C\text{-}F}$ = 1.2 Hz), 89.79-91.33 (d, $J_{C\text{-}F}$ = 115.68 Hz), 29.65;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -155.05;

HRMS (ESI-TOF) calcd for $C_{16}H_{11}N_4O_2FBr$ $[M + H]^+$: 311.0826; found: 311.0807.



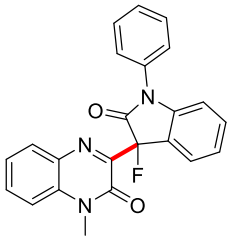
1-Methyl-3-fluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3x) was purified by silica column with dichloromethane/methanol = 50:0-20:1, pale solid, 59.9 mg, 91% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02 (dd, J = 1.50, 8.06 Hz, 1H, ArH), 7.74 (ddd, J = 1.52, 7.18, 8.62 Hz, 1H, ArH), 7.60 (dd, J = 1.18, 8.58 Hz, 1H, ArH), 7.51 (ddd, J = 1.24, 7.24, 8.30 Hz, 1H, ArH), 7.44-7.47 (m, 1H, ArH), 7.18-7.21 (m, 1H, ArH), 7.15 (d, J = 7.88 Hz, 1H, ArH), 7.03 (tt, J = 1.08, 7.52 Hz, 1H, ArH), 3.51 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.04-170.24 (d, $J_{C\text{-}F}$ = 19.95 Hz), 152.02 (d, $J_{C\text{-}F}$ = 3.66 Hz), 151.59-151.81 (d, $J_{C\text{-}F}$ = 22.20 Hz), 146.09-146.14 (d, $J_{C\text{-}F}$ = 5.18 Hz), 133.44, 132.79-132.83 (d, $J_{C\text{-}F}$ = 3.60 Hz), 132.48, 132.00, 130.32, 124.96, 124.82, 123.74-123.92 (d, $J_{C\text{-}F}$ = 17.86 Hz), 123.55-123.58 (d, $J_{C\text{-}F}$ = 3.02 Hz), 115.59, 110.12, 91.25-93.14 (d, $J_{C\text{-}F}$ = 188.24 Hz), 29.34, 26.82;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.94;

HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_2F$ $[M + H]^+$: 324.1143; found: 324.1125.



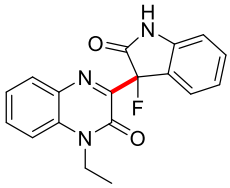
1-Phenyl-3-fluoro-3-(1-methylquinoxalin-2-one) indolin-2-one (3y) was purified by silica column with dichloromethane/methanol = 50:0-20:1, pale solid, 69.1 mg, 86% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.09 (dd, J = 1.52, 8.04 Hz, 1H, ArH), 7.77 (ddd, J = 1.56, 7.14, 8.60 Hz, 1H, ArH), 7.63-7.68 (m, 3H, ArH), 7.51-7.59 (m, 4H, ArH), 7.44-7.47 (tt, J = 1.72, 7.72 Hz, 1H, ArH), 7.33-7.36 (m, 1H, ArH), 7.09 (t, J = 7.58 Hz, 1H, ArH), 6.86 (d, J = 7.96 Hz, 1H, ArH), 3.60 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.36-169.56 (d, $J_{C\text{-}F}$ = 19.87 Hz), 152.27-152.31 (d, $J_{C\text{-}F}$ = 3.67 Hz), 151.80-152.03 (d, $J_{C\text{-}F}$ = 22.37 Hz), 146.20-146.26 (d, $J_{C\text{-}F}$ = 5.13 Hz), 134.18, 133.64, 132.74-132.78 (d, $J_{C\text{-}F}$ = 3.60 Hz), 132.35, 132.20, 130.47, 130.35, 129.07, 127.03, 125.63, 124.83, 123.93-123.99 (d, $J_{C\text{-}F}$ = 3.06 Hz), 123.59-123.77 (d, $J_{C\text{-}F}$ = 18.15 Hz), 115.79, 110.44, 91.25-93.14 (d, $J_{C\text{-}F}$ = 189.49 Hz), 29.56;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.29;

HRMS (ESI-TOF) calcd for $C_{23}H_{17}N_3O_2F$ $[M + H]^+$: 386.1299; found: 386.1280.



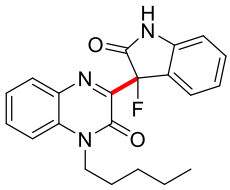
3-Fluoro-3-(1-ethylquinoxalin-2-one) indolin-2-one (3ab) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light brown solid, 59.4 mg, 90% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.94 (s, 1H, NH), 8.05 (dd, J = 1.46, 8.06 Hz, 1H, ArH), 7.69-7.77 (m, 2H, ArH), 7.50 (ddd, J = 1.50, 6.86, 8.22 Hz, 1H, ArH), 7.35-7.40 (m, 1H, ArH), 7.18-7.21 (m, 1H, ArH), 6.92-6.98 (m, 2H, ArH), 4.16-4.22 (m, 2H, $N\underline{CH_2}CH_3$), 1.15 (t, J = 7.10 Hz, 1H, $NCH_2\underline{CH_3}$);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.36-171.56 (d, $J_{C\text{-}F}$ = 19.23 Hz), 152.04-152.26 (d, $J_{C\text{-}F}$ = 22.29 Hz), 151.64-151.68 (d, $J_{C\text{-}F}$ = 3.39 Hz), 145.08-145.13 (d, $J_{C\text{-}F}$ = 5.63 Hz), 132.51, 132.47, 132.37-132.41 (d, $J_{C\text{-}F}$ = 3.73 Hz), 132.26, 130.72, 125.24, 124.92-125.10 (d, $J_{C\text{-}F}$ = 17.84 Hz), 124.61, 122.62-122.65 (d, $J_{C\text{-}F}$ = 3.25 Hz), 115.30, 111.07-111.09 (d, $J_{C\text{-}F}$ = 1.92 Hz), 91.79-93.67 (d, $J_{C\text{-}F}$ = 187.93 Hz), 37.35, 12.77;

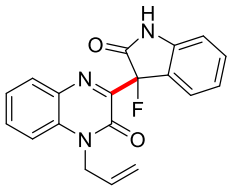
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.80;

HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_2F$ $[M + H]^+$: 324.1143; found: 324.1125.

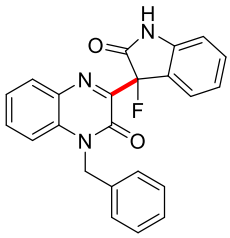


3-Fluoro-3-(1-pentylquinoxalin-2-one) indolin-2-one (3ac) was purified by silica column with dichloromethane/methanol = 50:0-20:1, red solid, 65.2 mg, 97% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.94 (s, 1H, NH), 8.05 (dd, J = 1.48, 8.04 Hz, 1H, ArH), 7.74 (ddd, J = 1.52, 6.96, 8.52 Hz, 1H, ArH), 7.69 (dd, J = 1.38, 8.70 Hz, 1H, ArH), 7.49 (ddd, J = 1.32, 7.04, 8.22 Hz, 1H, ArH), 7.35-7.39 (m, 1H, ArH), 7.17-7.19 (m, 1H, ArH), 6.91-6.98 (m, 2H, ArH), 4.10-4.18 (m, 2H, $NCH_2\underline{CH_2}(CH_2)_2CH_3$), 1.52-1.55 (m, 2H, $N\underline{CH_2}CH_2(CH_2)_2CH_3$) 1.21-1.26 (m, 4H, $NCH_2CH_2\underline{(CH_2)_2}CH_3$), 0.77-0.80 (m, 3H, $NCH_2CH_2(CH_2)_2\underline{CH_3}$);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.33-171.53 (d, $J_{C\text{-}F}$ = 19.42 Hz), 152.02-152.24 (d, $J_{C\text{-}F}$ = 22.29 Hz), 151.89-151.92 (d, $J_{C\text{-}F}$ = 3.43 Hz), 145.08-145.14 (d, $J_{C\text{-}F}$ = 5.56 Hz), 132.58, 132.44-132.48 (d, $J_{C\text{-}F}$ = 3.70 Hz), 132.35, 132.22, 130.70, 125.16, 124.92-125.10 (d, $J_{C\text{-}F}$ = 3.70 Hz), 124.61, 122.58-122.61 (d, $J_{C\text{-}F}$ = 3.18 Hz), 115.54, 111.08-111.10 (d, $J_{C\text{-}F}$ = 1.84 Hz), 91.78-93.66 (d, $J_{C\text{-}F}$ = 188.01 Hz), 41.94, 28.69, 26.98, 22.18, 14.27;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.98;
HRMS (ESI-TOF) calcd for $C_{21}H_{21}N_3O_2F$ $[M + H]^+$: 366.1612; found: 366.1593.

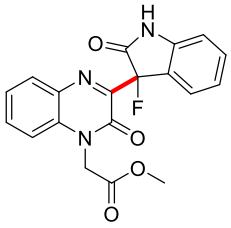


3-Fluoro-3-(1-allylquinoxalin-2-one) indolin-2-one (3ad) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light brown solid, 59.7 mg, 88% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.94 (s, 1H, NH), 8.06 (dd, J = 1.50, 8.06 Hz, 1H, ArH), 7.72 (ddd, J = 1.58, 7.20, 8.66 Hz, 1H, ArH), 7.59 (dd, J = 1.20, 8.60 Hz, 1H, ArH), 7.50 (ddd, J = 1.18, 7.24, 8.22 Hz, 1H, ArH), 7.35-7.40 (m, 1H, ArH), 7.20-7.22 (m, 1H, ArH), 6.92-6.98 (m, 2H, ArH), 5.80-5.88 (m, 1H, $NCH_2\underline{CH}{=}CH_2$), 5.15 (dd, J = 1.38, 10.50 Hz, 1H, $NCH_2CH{=}\underline{CH_2}$), 4.98 (dd, J = 1.40, 17.24 Hz, 1H, $NCH_2CH{=}\underline{CH_2}$), 4.80-4.83 (m, 2H, $N\underline{CH_2}CH{=}CH_2$);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.30-171.49 (d, $J_{C\text{-}F}$ = 19.37 Hz), 152.09-152.31 (d, $J_{C\text{-}F}$ = 22.43 Hz), 151.89-151.92 (d, $J_{C\text{-}F}$ = 5.51 Hz), 145.07-145.13 (d, $J_{C\text{-}F}$ = 5.51 Hz), 132.64, 132.49-132.53 (d, $J_{C\text{-}F}$ = 3.72 Hz), 132.28, 132.11, 131.48, 130.59, 125.24, 124.89-125.07 (d, $J_{C\text{-}F}$ = 17.75 Hz), 124.74, 122.64-122.67 (d, $J_{C\text{-}F}$ = 3.27 Hz), 117.86, 115.87, 110.10, 91.79-93.67 (d, $J_{C\text{-}F}$ = 188.14 Hz), 44.14;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.76;
HRMS (ESI-TOF) calcd for $C_{19}H_{15}N_3O_2F$ $[M + H]^+$: 336.1143; found: 336.1125.

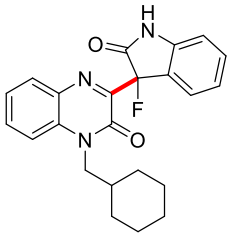


3-Fluoro-3-(1-benzylquinoxalin-2-one) indolin-2-one (3ae) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 31.5 mg, 40% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.00 (s, 1H, NH), 8.05 (dd, J = 1.50, 8.02 Hz, 1H, ArH), 7.65 (ddd, J = 1.56, 7.16, 8.62 Hz, 1H, ArH), 7.57 (dd, J = 1.28, 8.68 Hz, 1H, ArH), 7.48 (ddd, J = 1.24, 7.20, 8.24 Hz, 1H, ArH), 7.36-7.41 (m, 1H, ArH), 7.23-7.28 (m, 5H, ArH), 7.12-7.14 (m, 1H,

ArH), 6.95-6.99 (m, 2H, ArH), 5.47 (d, J = 15.92 Hz, 1H, NC$\underline{H}_2$), 5.37 (d, J = 15.96 Hz, 1H, NC$\underline{H}_2$);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.33-171.53 (d, $J_{C\text{-}F}$ = 19.30 Hz), 152.24-152.47 (d, $J_{C\text{-}F}$ = 22.30 Hz), 151.89-151.92 (d, $J_{C\text{-}F}$ = 3.38 Hz), 145.13-145.18 (d, $J_{C\text{-}F}$ = 5.49 Hz), 135.79, 132.68, 132.54-132.58 (d, $J_{C\text{-}F}$ = 3.65 Hz), 132.42, 132.19, 130.70, 129.23, 128.00, 127.12, 125.29, 125.07, 124.88, 122.66-122.69 (d, $J_{C\text{-}F}$ = 3.01 Hz), 115.91, 111.16, 91.87-93.75 (d, $J_{C\text{-}F}$ = 188.29 Hz), 45.10;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.74;
HRMS (ESI-TOF) calcd for $C_{23}H_{17}N_3O_2F$ $[M + H]^+$: 386.1299; found: 386.1278.



3-Fluoro-3-(1-methylacetatequinoxalin-2-one) indolin-2-one (3af) was purified by silica column with dichloromethane/methanol = 50:0-20:1, red solid, 68.7 mg, 93% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.96 (s, 1H, NH), 8.08 (dd, J = 1.44, 8.04 Hz, 1H, ArH), 7.73 (ddd, J = 1.52, 7.24, 8.62 Hz, 1H, ArH), 7.62 (dd, J = 1.18, 8.62 Hz, 1H, ArH), 7.53 (ddd, J = 1.16, 7.16, 8.18 Hz, 1H, ArH), 7.36-7.40 (m, 1H, ArH), 7.20-7.22 (m, 1H, ArH), 6.93-6.98 (m, 2H, ArH), 5.08 (s, 2H, NCH_2), 3.66 (s, 3H, OCH_3);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.14-171.33 (d, $J_{C\text{-}F}$ = 19.35 Hz), 168.04, 151.82-152.04 (d, $J_{C\text{-}F}$ = 22.60 Hz), 151.90-151.94 (d, $J_{C\text{-}F}$ = 3.46 Hz), 145.04-145.10 (d, $J_{C\text{-}F}$ = 5.55 Hz), 132.90, 132.61-132.65 (d, $J_{C\text{-}F}$ = 3.66 Hz), 132.36, 132.09, 130.66, 125.29, 125.02, 124.69-124.87 (d, $J_{C\text{-}F}$ = 17.88 Hz), 122.71-122.74 (d, $J_{C\text{-}F}$ = 3.28 Hz), 115.50, 111.17, 91.70-93.58 (d, $J_{C\text{-}F}$ = 188.70 Hz), 53.01, 43.84;
^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.98;
HRMS (ESI-TOF) calcd for $C_{19}H_{15}N_3O_4F$ $[M + H]^+$: 368.1041; found: 368.1021.

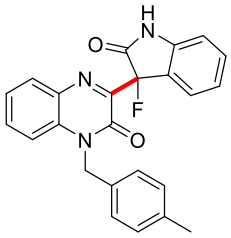


3-Fluoro-3-(1-cyclohexylmethylquinoxalin-2-one) indolin-2-one (3ag) was purified by silica column with dichloromethane/methanol = 50:0-20:1, tawny solid, 67.5 mg, 83% yield;
^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.93 (s, 1H, NH), 8.04 (dd, J = 1.44, 8.04 Hz, 1H, ArH), 7.67-7.75 (m, 2H, ArH), 7.49 (t, J = 7.40 Hz, 1H, ArH), 7.37 (t, J = 7.70 Hz, 1H, ArH), 7.16-7.19 (m, 1H, ArH), 6.91-6.97 (m, 2H, ArH), 3.93-4.12 (m, 2H, NCH_2), 1.69-1.75 (m, 1H, $NCH_2\underline{CH}$), 1.45-1.57 (m, 6H, 3×CH_2), 1.01-1.07 (m, 4H, 2×CH_2);
^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.34-171.54 (d, $J_{C\text{-}F}$ = 19.40 Hz), 152.32-152.36 (d, $J_{C\text{-}F}$ = 3.54 Hz), 152.08-152.30 (d, $J_{C\text{-}F}$ = 22.27 Hz), 145.08-145.14 (d, $J_{C\text{-}F}$ = 5.59 Hz), 132.94, 132.42-132.46 (d, $J_{C\text{-}F}$ = 3.72 Hz), 132.31, 132.09, 130.68, 125.09, 124.94-125.12 (d, $J_{C\text{-}F}$ = 17.85 Hz), 124.57, 122.53-122.56 (d, $J_{C\text{-}F}$ = 3.10 Hz), 115.84, 111.07-111.09 (d, $J_{C\text{-}F}$ = 1.82 Hz), 91.81-93.69

(d, $J_{C\text{-}F}$ = 187.77 Hz), 47.34, 36.12, 30.40, 30.35, 26.16, 25.63;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.07;

HRMS (ESI-TOF) calcd for $C_{23}H_{23}N_3O_2F$ $[M + H]^+$: 392.1769; found: 392.1749.



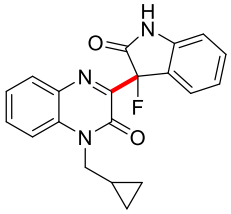
3-Fluoro-3-(1-(*p*-methylphenyl)-quinoxalin-2-one) indolin-2-one (3ah) was purified by silica column with dichloromethane/methanol = 50:0-20:1, tawny solid, 63.7 mg, 75% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.98 (s, 1H, NH), 8.06 (dd, J = 1.50, 8.00 Hz, 1H, ArH), 7.65 (ddd, J = 1.56, 7.18, 8.62 Hz, 1H, ArH), 7.57 (dd, J = 1.28, 8.68 Hz, 1H, ArH), 7.47 (ddd, J = 1.22, 7.14, 8.20 Hz, 1H, ArH), 7.36-7.41 (m, 1H, ArH), 6.95-7.09 (m, 6H, ArH), 5.31-5.46 (m, 2H, NCH_2), 3.38 (s, 3H, NCH_3), 2.21 (s, 3H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.34-171.54 (d, $J_{C\text{-}F}$ = 19.35 Hz), 152.23-152.46 (d, $J_{C\text{-}F}$ = 22.39 Hz), 152.30-152.34 (d, $J_{C\text{-}F}$ = 3.29 Hz), 145.11-145.17 (d, $J_{C\text{-}F}$ = 5.53 Hz), 137.26, 132.76, 132.65, 132.54-132.58 (d, $J_{C\text{-}F}$ = 3.80 Hz), 132.40, 132.15, 130.68, 129.76, 127.15, 125.27, 124.89-125.07 (d, $J_{C\text{-}F}$ = 17.85 Hz), 124.83, 122.66-122.69 (d, $J_{C\text{-}F}$ = 3.28 Hz), 115.94, 111.15, 91.86-93.74 (d, $J_{C\text{-}F}$ = 188.40 Hz), 44.86, 21.05;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.80;

HRMS (ESI-TOF) calcd for $C_{24}H_{19}N_3O_2F$ $[M + H]^+$: 400.1456; found: 400.1434.



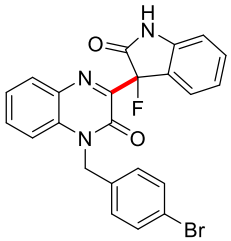
3-Fluoro-3-(1-cyclopropylmethylquinoxalin-2-one) indolin-2-one (3ai) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 64.2 mg, 92% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.96 (s, 1H, NH), 8.06 (dd, J = 1.46, 7.98 Hz, 1H, ArH), 7.81 (dd, J = 1.40, 8.64 Hz, 1H, ArH), 7.75 (dt, J = 1.50, 7.02 Hz, 1H, ArH), 7.50 (ddd, J = 1.34, 6.96, 8.20 Hz, 1H, ArH), 7.35-7.39 (m, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 6.92-6.98 (m, 2H, ArH), 4.06-4.16 (m, 2H, NCH_2), 1.15-1.22 (m, 1H, CH), 0.27-0.42 (m, 4H, 2×CH_2);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.33-171.53 (d, $J_{C\text{-}F}$ = 19.45 Hz), 152.22-152.45 (d, $J_{C\text{-}F}$ = 22.49 Hz), 152.19-152.22 (d, $J_{C\text{-}F}$ = 3.77 Hz), 145.08-145.14 (d, $J_{C\text{-}F}$ = 5.59 Hz), 132.83, 132.45-132.49 (d, $J_{C\text{-}F}$ = 3.68 Hz), 132.28, 132.20, 130.67, 125.13, 124.90-125.08 (d, $J_{C\text{-}F}$ = 17.81 Hz), 124.66, 122.58-122.62 (d, $J_{C\text{-}F}$ = 3.28 Hz), 115.77, 111.08-111.10 (d, $J_{C\text{-}F}$ = 2.04 Hz), 91.82-93.70 (d, $J_{C\text{-}F}$ = 188.02 Hz), 45.80, 10.00, 4.16, 4.11;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.99;

HRMS (ESI-TOF) calcd for $C_{20}H_{17}N_3O_2F$ $[M + H]^+$: 350.1299; found: 350.1280.



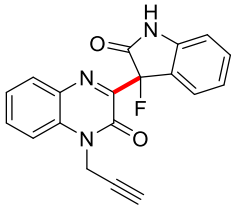
3-Fluoro-3-(1-(4-bromobenzyl)-quinoxalin-2-one) indolin-2-one (3aj) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 35.7 mg, 37% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.98 (s, 1H, NH), 8.07 (dd, J = 1.52, 8.00 Hz, 1H, ArH), 7.66 (ddd, J = 1.52, 7.18, 8.64 Hz, 1H, ArH), 7.56 (dd, J = 1.21, 8.68 Hz, 1H, ArH), 7.47-7.50 (m, 3H, ArH), 7.36-7.41 (m, 1H, ArH), 7.25-7.27 (m, 1H, ArH), 7.10 (d, J = 8.56 Hz, 2H, ArH), 6.99 (dd, J = 1.16, 7.86 Hz, 2H, ArH), 5.35-5.48 (m, 2H, NCH_2);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.30-171.50 (d, $J_{C\text{-}F}$ = 19.32 Hz), 152.42 (d, $J_{C\text{-}F}$ = 22.64 Hz), 152.28-152.31 (d, $J_{C\text{-}F}$ = 3.23 Hz), 145.09-145.14 (d, $J_{C\text{-}F}$ = 5.54 Hz), 135.27, 132.61, 132.55 (d, $J_{C\text{-}F}$ = 3.68 Hz), 132.43, 132.26, 132.12, 130.75, 129.40, 125.35, 124.95, 124.84-125.02 (d, $J_{C\text{-}F}$ = 17.68 Hz), 122.71 (d, $J_{C\text{-}F}$ = 3.11 Hz), 121.13, 115.81, 111.14, 91.85-93.73 (d, $J_{C\text{-}F}$ = 188.25 Hz), 45.80, 10.00, 4.16, 4.11;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.69;

HRMS (ESI-TOF) calcd for $C_{23}H_{16}N_3O_2FBr$ $[M + H]^+$: 464.0404; found: 464.0379.



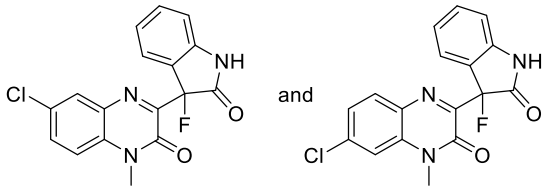
3-Fluoro-3-(1-(2-Propynyl)-quinoxalin-2-one) indolin-2-one (3ak) was purified by silica column with dichloromethane/methanol = 50:0-20:1, orange solid, 64.1 mg, 96% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.98 (s, 1H, NH), 8.09 (dd, J = 1.48, 8.00 Hz, 1H, ArH), 7.81 (ddd, J = 1.50, 7.18, 8.60 Hz, 1H, ArH), 7.16 (dd, J = 1.20, 8.56 Hz, 1H, ArH), 7.55 (ddd, J = 1.20, 7.24, 8.20 Hz, 1H, ArH), 7.36-7.41 (m, 1H, ArH), 7.21-7.23 (m, 1H, ArH), 6.93-6.99 (m, 2H, ArH), 4.97-5.09 (m, 2H, NCH_2), 5.35-5.48 (m, 2H, NCH_2), 3.36 (m, 1H, CH);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.21-171.40 (d, $J_{C\text{-}F}$ = 19.35 Hz), 151.97-152.19 (d, $J_{C\text{-}F}$ = 22.34 Hz), 151.17-151.20 (d, $J_{C\text{-}F}$ = 3.45 Hz), 145.07-145.13 (d, $J_{C\text{-}F}$ = 5.57 Hz), 132.61-132.65 (d, $J_{C\text{-}F}$ = 3.84 Hz), 132.31, 132.28, 131.94, 130.68, 125.38, 125.15, 124.68-124.86 (d, $J_{C\text{-}F}$ = 17.75 Hz), 122.73-122.70 (d, $J_{C\text{-}F}$ = 3.12 Hz), 115.82, 111.14-111.16 (d, $J_{C\text{-}F}$ = 1.96 Hz), 91.75-93.64 (d, $J_{C\text{-}F}$ = 188.80 Hz), 77.93, 76.19, 31.66;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.79;

HRMS (ESI-TOF) calcd for $C_{19}H_{12}N_3O_2F$ $[M + H]^+$: 334.0986; found: 334.0970.



(regioisomeric mixture with 2:1 ratio)

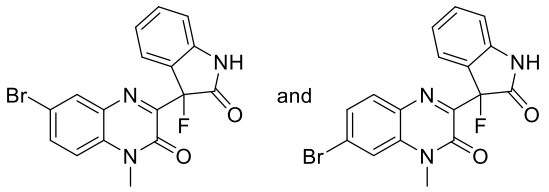
3-Fluoro-3-(6-chloro-1-methylquinoxalin-2-one) indolin-2-one and 3-fluoro-3-(7-chloro-1-methylquinoxalin-2-one) indolin-2-one (3al1 and 3al2) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 46.1 mg, 66% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.98 (s, 1.53H, NH), 8.12 (d, J = 2.48 Hz, 1H, ArH), 8.04 (d, J = 8.60 Hz, 0.46H, ArH), 7.75-7.81 (m, 1.68H, ArH), 7.68 (d, J = 9.12 Hz, 1.11H, ArH), 7.55 (dd, J = 2.16, 8.60 Hz, 0.53H, ArH), 7.35-7.40 (m, 1.74H, ArH), 7.17-7.18 (m, 1.63H, ArH), 6.93-6.98 (m, 3.34H, ArH), 3.55 (s, 2.98H, NCH_3), 3.55 (s, 1.52H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.12-171.32 (d, $J_{C\text{-}F}$ = 19.48 Hz), 153.50-153.73 (d, $J_{C\text{-}F}$ = 22.25 Hz), 151.17-151.20 (d, $J_{C\text{-}F}$ = 3.37 Hz), 145.12-145.17 (d, $J_{C\text{-}F}$ = 5.45 Hz), 136.62, 134.79, 132.71-132.75 (d, $J_{C\text{-}F}$ = 3.40 Hz), 132.60, 132.56, 131.89, 131.77, 130.88, 129.21, 128.55, 125.35, 124.79-124.81 (d, $J_{C\text{-}F}$ = 2.21 Hz), 124.63, 122.58-122.62 (d, $J_{C\text{-}F}$ = 3.18 Hz), 117.60, 115.59, 111.09, 91.77-93.66 (d, $J_{C\text{-}F}$ = 188.81 Hz), 29.60;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.87, -159.98;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2FCl$ $[M + H]^+$: 344.0597; found: 344.0575.



(regioisomeric mixture with 2:1 ratio)

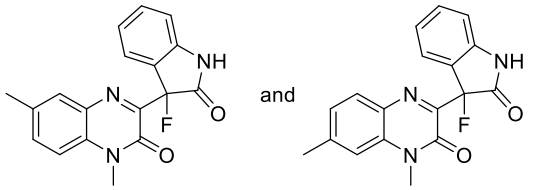
3-Fluoro-3-(6-bromo-1-methylquinoxalin-2-one) indolin-2-one and 3-fluoro-3-(7-bromo-1-methylquinoxalin-2-one) indolin-2-one (3am1 and 3am2) was purified by silica column with dichloromethane/methanol = 50:0-20:1, maroon solid, 74.2 mg, 92% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.97 (s, 1.59H, NH), 8.24 (d, J = 2.24 Hz, 1H, ArH), 7.96 (d, J = 8.56 Hz, 0.49H, ArH), 7.87-7.92 (m, 1.59H, ArH), 7.67 (dd, J = 1.98, 8.58 Hz, 0.51H, ArH), 7.62 (d, J = 9.00 Hz, 1.06H, ArH), 7.35-7.40 (m, 1.72H, ArH), 7.16-7.18 (m, 1.77H, ArH), 6.93-6.98 (m, 3.38H, ArH), 3.55 (s, 4.59H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.13-171.32 (d, $J_{C\text{-}F}$ = 19.48 Hz), 153.40-153.63 (d, $J_{C\text{-}F}$ = 22.28 Hz), 151.89 (d, $J_{C\text{-}F}$ = 3.29 Hz), 145.11-145.17 (d, $J_{C\text{-}F}$ = 5.08 Hz), 134.88, 134.48, 133.12, 133.04, 132.57 (d, $J_{C\text{-}F}$ = 4.00 Hz), 132.19, 131.97, 131.15, 127.66, 125.41, 125.37, 124.81 (d, $J_{C\text{-}F}$ = 1.39 Hz), 124.63 (d, $J_{C\text{-}F}$ = 1.49 Hz), 122.59-122.62 (d, $J_{C\text{-}F}$ = 2.93 Hz), 118.45, 117.85, 116.28, 111.08-111.10 (d, $J_{C\text{-}F}$ = 1.98 Hz), 91.76-93.64 (d, $J_{C\text{-}F}$ = 188.66 Hz), 29.57;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.88, -159.98;

HRMS (ESI-TOF) calcd for $C_{17}H_{12}N_3O_2FBr$ $[M + H]^+$: 388.0091; found: 388.0092.



(regioisomeric mixture with 1:2 ratio)

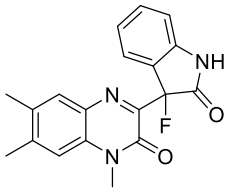
3-Fluoro-3-(1-methyl-6-methylquinoxalin-2-one) indolin-2-one and 3-fluoro-3-(1-methyl-7-methylquinoxalin-2-one) indolin-2-one (3an1 and 3an2) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 67 mg, 98% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.92 (s, 1.77H, NH), 7.92 (d, J = 8.20 Hz, 0.62H, ArH), 7.84-7.85 (m, 1H, ArH), 7.47-7.60 (m, 3.21H, ArH), 7.32-7.39 (m, 2.49H, ArH), 7.14-7.16 (m, 1.86H, ArH), 6.91-6.97 (m, 3.52H, ArH), 3.55 and 3.54 (s, 4.95H, NCH_3), 2.52 (s, 1.64H, CH_3), 2.47 (s, 3.20H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.40-171.60 (d, $J_{C\text{-}F}$ = 19.33 Hz), 171.46 (d, $J_{C\text{-}F}$ = 19.18 Hz), 152.16 (d, $J_{C\text{-}F}$ = 2.58 Hz), 151.94-151.97 (d, $J_{C\text{-}F}$ = 3.22 Hz), 150.73-150.95 (d, $J_{C\text{-}F}$ = 22.29 Hz), 145.10-145.16 (d, $J_{C\text{-}F}$ = 5.83 Hz), 142.79, 134.18, 133.22, 132.42-132.46 (d, $J_{C\text{-}F}$ = 3.66 Hz), 132.04, 131.43, 130.37, 130.08, 129.96, 125.91, 125.18, 124.93-125.11 (d, $J_{C\text{-}F}$ = 17.94 Hz), 122.54-122.57 (d, $J_{C\text{-}F}$ = 3.19 Hz), 115.42, 115.36, 111.03, 91.77-93.65 (d, $J_{C\text{-}F}$ = 188.05 Hz), 29.29, 29.23, 22.07, 20.58;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.05, -160.06;

HRMS (ESI-TOF) calcd for $C_{18}H_{15}N_3O_2F$ $[M + H]^+$: 324.1143; found: 324.1124.



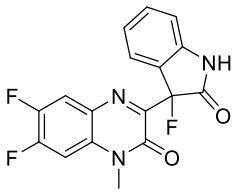
3-Fluoro-3-(1-methyl-6, 7-dimethylquinoxalin-2-one) indolin-2-one (3ao) was purified by silica column with dichloromethane/methanol = 50:0-20:1, light yellow solid, 73 mg, 100% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.90 (s, 1.77H, NH), 7.81 (s, 1H, ArH), 7.46 (s, 1H, ArH), 7.34-7.38 (m, 1H, ArH), 7.12-7.15 (m, 1H, ArH), 6.91-6.96 (m, 2H, ArH), 3.54 (m, 3H, ArH), 3.54 (m, 3H, NCH_3), 2.43 (s, 3H, CH_3), 2.37 (s, 3H, CH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.53-171.72 (d, $J_{C\text{-}F}$ = 19.35 Hz), 152.04-152.08 (d, $J_{C\text{-}F}$ = 3.51 Hz), 150.66-150.88 (d, $J_{C\text{-}F}$ = 22.33 Hz), 145.07-145.12 (d, $J_{C\text{-}F}$ = 5.49 Hz), 142.07, 133.48, 132.36-132.39 (d, $J_{C\text{-}F}$ = 3.68 Hz), 131.61, 130.56, 130.13, 125.11, 125.05-125.23 (d, $J_{C\text{-}F}$ = 17.98 Hz), 122.52-122.52 (d, $J_{C\text{-}F}$ = 3.09 Hz), 115.72, 111.01, 91.75-93.62 (d, $J_{C\text{-}F}$ = 187.61 Hz), 29.21, 20.53, 19.15;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -160.11;

HRMS (ESI-TOF) calcd for $C_{19}H_{17}N_3O_2F$ $[M + H]^+$: 338.1299; found: 338.1280.



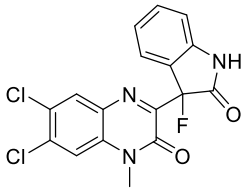
3-Fluoro-3-(1-methyl-6, 7-difluoroquinoxalin-2-one) indolin-2-one (3ap) was purified by silica column with dichloromethane/methanol = 50:0-20:1, white solid, 50.7 mg, 73% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.97 (s, 1.77H, NH), 8.21 (dd, J = 8.34, 10.74 Hz, 1H, ArH), 7.87 (dd, J = 7.48, 12.36 Hz, 1H, ArH), 7.35-7.40 (m, 1H, ArH), 7.15-7.17 (m, 1H, ArH), 6.92-6.97 (m, 2H, ArH), 3.53 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.11-171.31 (d, $J_{C\text{-}F}$ = 19.37 Hz), 150.55-153.05 (dd, $J_{C\text{-}F}$ = 14.51, 249.44 Hz), 152.63-152.85 (d, $J_{C\text{-}F}$ = 22.38 Hz), 151.83-151.86 (d, $J_{C\text{-}F}$ = 3.28 Hz), 145.39-147.82 (dd, $J_{C\text{-}F}$ = 14.39, 242.99 Hz), 145.09-145.14 (d, $J_{C\text{-}F}$ = 5.47 Hz), 132.59-132.56 (d, $J_{C\text{-}F}$ = 3.81 Hz), 131.62-13172 (d, $J_{C\text{-}F}$ = 9.88 Hz), 128.61-128.71 (dd, $J_{C\text{-}F}$ = 2.38, 9.98 Hz), 125.34, 124.60-124.77 (d, $J_{C\text{-}F}$ = 17.72 Hz), 122.59-122.62 (d, $J_{C\text{-}F}$ = 3.22 Hz), 117.93-118.11 (d, $J_{C\text{-}F}$ = 18.34 Hz), 111.09, 104.77-105.01 (d, $J_{C\text{-}F}$ = 23.42 Hz), 91.73-93.62 (d, $J_{C\text{-}F}$ = 188.60 Hz), 30.13;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -130.57 (d, $J_{C\text{-}F}$ = 23.76 Hz), -142.43 (d, $J_{C\text{-}F}$ = 23.84 Hz), -159.91;

HRMS (ESI-TOF) calcd for $C_{17}H_{11}N_3O_2F_3$ $[M + H]^+$: 346.0798; found: 346.0778.



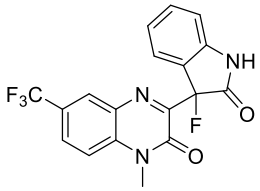
3-Fluoro-3-(1-methyl-6, 7-dichloroquinoxalin-2-one) indolin-2-one (3aq) was purified by silica column with dichloromethane/methanol = 50:0-20:1, yellow solid, 57.7 mg, 75% yield;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.08 (s, 1H, NH), 8.32 (s, 1H, ArH), 7.97 (s, 1H, ArH), 7.35-7.40 (m, 1H, ArH), 7.15-7.18 (m, 1H, ArH), 6.93-6.99 (m, 2H, ArH), 3.54 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.97-171.17 (d, $J_{C\text{-}F}$ = 19.40 Hz), 153.67-153.89 (d, $J_{C\text{-}F}$ = 22.41 Hz), 151.76-151.79 (d, $J_{C\text{-}F}$ = 3.53 Hz), 145.14-145.20 (d, $J_{C\text{-}F}$ = 5.80 Hz), 134.35, 133.65, 132.60-132.64 (d, $J_{C\text{-}F}$ = 3.73 Hz), 131.50, 131.02, 126.69, 125.39, 124.50-124.67 (d, $J_{C\text{-}F}$ = 17.74 Hz), 122.58-122.61 (d, $J_{C\text{-}F}$ = 3.27 Hz), 117.59, 111.17, 91.78-93.67 (d, $J_{C\text{-}F}$ = 188.99 Hz), 29.85;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -159.83;

HRMS (ESI-TOF) calcd for $C_{17}H_{11}N_3O_2FCl_2$ $[M + H]^+$: 378.0207; found: 378.0197.



3-Fluoro-3-(1-methyl-6-trifluoromethyl-2-one) indolin-2-one (3ar) was purified by silica column with dichloromethane/methanol = 50:0-20:1, maroon solid, 49.2 mg, 64% yield;

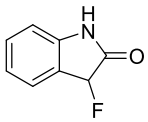
^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.01 (s, 1H, NH), 8.25 (dd, J = 0.98, 8.46 Hz, 1H, ArH),

7.95 (d, J = 1.84 Hz, 1H, ArH), 7.82 (dd, J = 1.84, 8.48 Hz, 1H, ArH), 7.36-7.41 (m, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 6.93-6.99 (m, 2H, ArH), 3.62 (s, 3H, NCH_3);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.01-171.20 (d, $J_{C\text{-}F}$ = 19.34 Hz), 154.82-155.04 (d, $J_{C\text{-}F}$ = 22.24 Hz), 151.97-152.00 (d, $J_{C\text{-}F}$ = 3.59 Hz), 145.13-145.18 (d, $J_{C\text{-}F}$ = 5.55 Hz), 134.05, 133.99, 132.63-132.67 (d, $J_{C\text{-}F}$ = 3.67 Hz), 131.58, 131.20-131.52 (d, $J_{C\text{-}F}$ = 32.04 Hz), 125.45, 124.51-124.68 (d, $J_{C\text{-}F}$ = 17.76 Hz), 122.80-125.52 (d, $J_{C\text{-}F}$ = 271.41 Hz), 122.62-122.65 (d, $J_{C\text{-}F}$ = 3.17 Hz), 120.77, 113.33-113.37 (d, $J_{C\text{-}F}$ = 4.09 Hz), 111.14, 91.83-93.72 (d, $J_{C\text{-}F}$ = 189.04 Hz), 29.65;

^{19}F NMR (376 MHz, DMSO-d_6): δ = -60.76, -159.89;

HRMS (ESI-TOF) calcd for $C_{18}H_{11}N_3O_2F_4$ $[M + H]^+$: 378.0860; found: 378.0839.

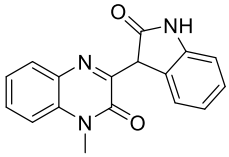


3-Fluoro-2-oxindole (4a)[3] black solid, 53.6 mg;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.63 (s, 1H, NH), 7.45 (d, J = 7.48 Hz, 1H, ArH), 7.95 (t, J = 7.76 Hz, 1H, ArH), 7.03 (t, J = 7.02 Hz, 1H, ArH), 6.88 (d, J = 7.80 Hz, 1H, ArH), 5.93 (d, $J_{H\text{-}F}$= 50.52 Hz, 1H, CH);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.75-172.92 (d, $J_{C\text{-}F}$ = 17.39 Hz), 143.76-143.82 (d, $J_{C\text{-}F}$ = 5.83 Hz), 131.77-131.80 (d, $J_{C\text{-}F}$ = 3.65 Hz), 126.62, 123.74-123.90 (d, $J_{C\text{-}F}$ = 15.91 Hz), 122.63-122.66 (d, $J_{C\text{-}F}$ = 3.21 Hz), 110.80-110.82 (d, $J_{C\text{-}F}$ = 1.71 Hz), 85.63-87.45 (d, $J_{C\text{-}F}$ = 181.41 Hz);

^{19}F NMR (376 MHz, DMSO-d_6): δ = -192.05.



3-(2-Hydroxy-1*H*-indol-3-yl)-1-methylquinoxalin-2-one (5a)[4] orange solid, 64 mg;

^{1}H NMR (400 MHz, DMSO-d_6): δ = 14.50 (s, 1H), 10.94 (s, 1H), 8.70 (dd, J = 1.16, 8.00 Hz, 1H), 7.35-7.37 (m, 1H), 7.26-7.29 (m, 1H), 7.16-7.20 (m, 2H), 7.05 (dt, J = 1.26, 7.50 Hz, 1H), 6.88-6.95 (m, 2H), 3.58 (s, 3H);

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.20, 156.43, 140.23, 137.49, 128.75, 125.91, 125.63, 125.17, 124.54, 124.04, 123.01, 121.01, 116.47, 115.28, 109.52, 97.82, 30.03.

7. Reference

[1] W. L. F. Armarego, C. Chai, in *Purification of Laboratory Chemicals (Seventh Edition)*, Butterworth-Heinemann, Boston, **2013**, pp. 103-554.

[2] J. Zhou, Q. Ren, N. Xu, C. Wang, S. Song, Z. Chen, J. Li, *Green Chem.* **2021**, *23*, 5753-5758.

[3] Q. Yang, G.-L. Dai, Y.-M. Yang, Z. Luo, Z.-Y. Tang, *J. Org. Chem.* **2018**, *83*, 6762-6768.

[4] Y.-Y. Han, Z.-J. Wu, X.-M. Zhang, W.-C. Yuan, *Tetrahedron Lett.* **2010**, *51*, 2023-2028.

8. Copies of $^{1}H/^{13}C$ NMR and HR-ESI-MS Spectra

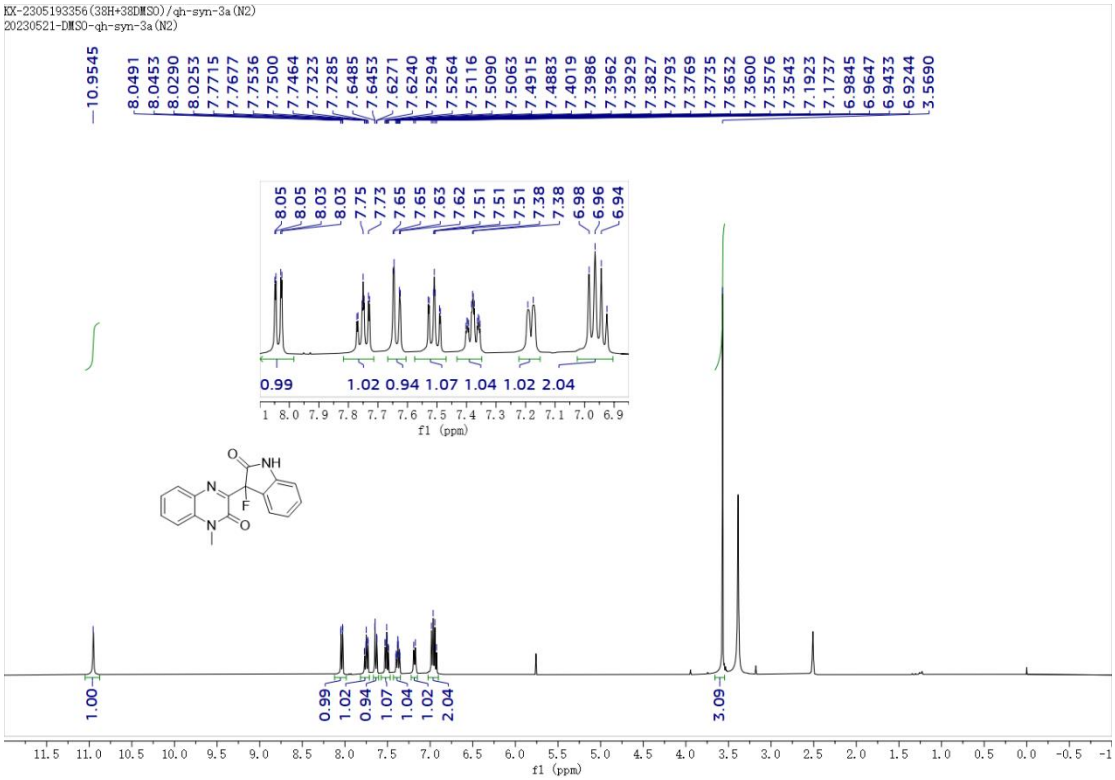


Figure S1. The ^{1}H NMR Spectrum of Compound **3a** in DMSO-d_6

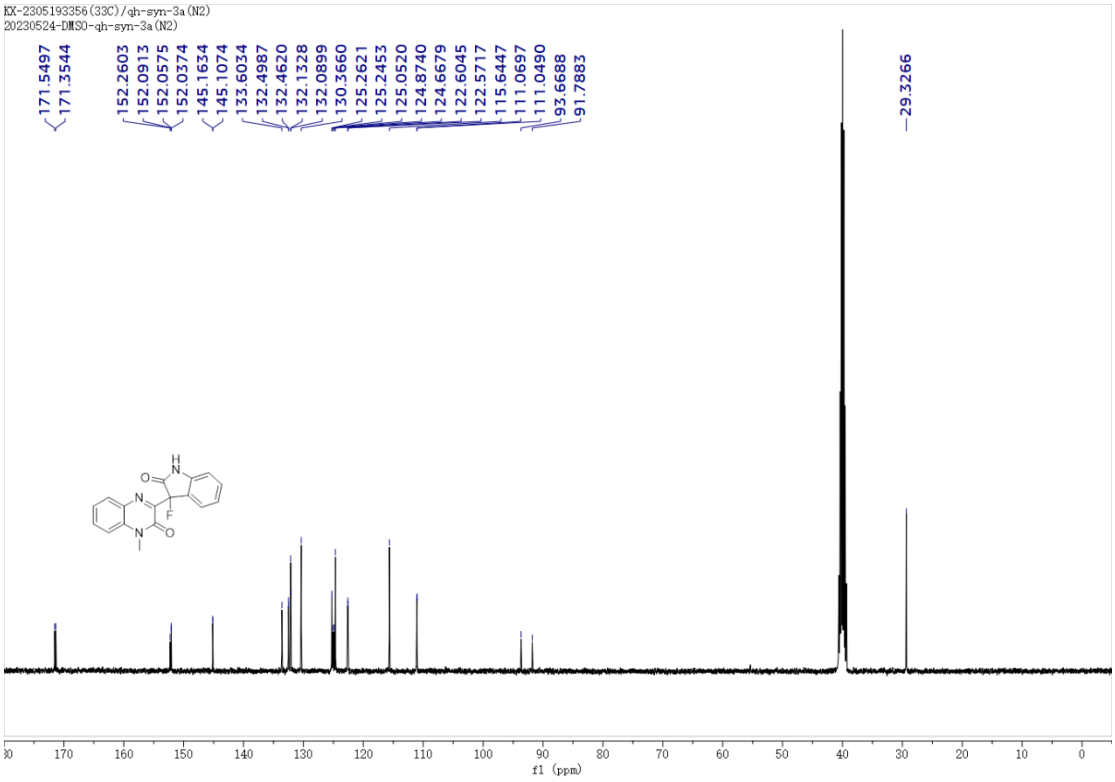


Figure S2. The ^{13}C NMR Spectrum of Compound **3a** in DMSO-d_6

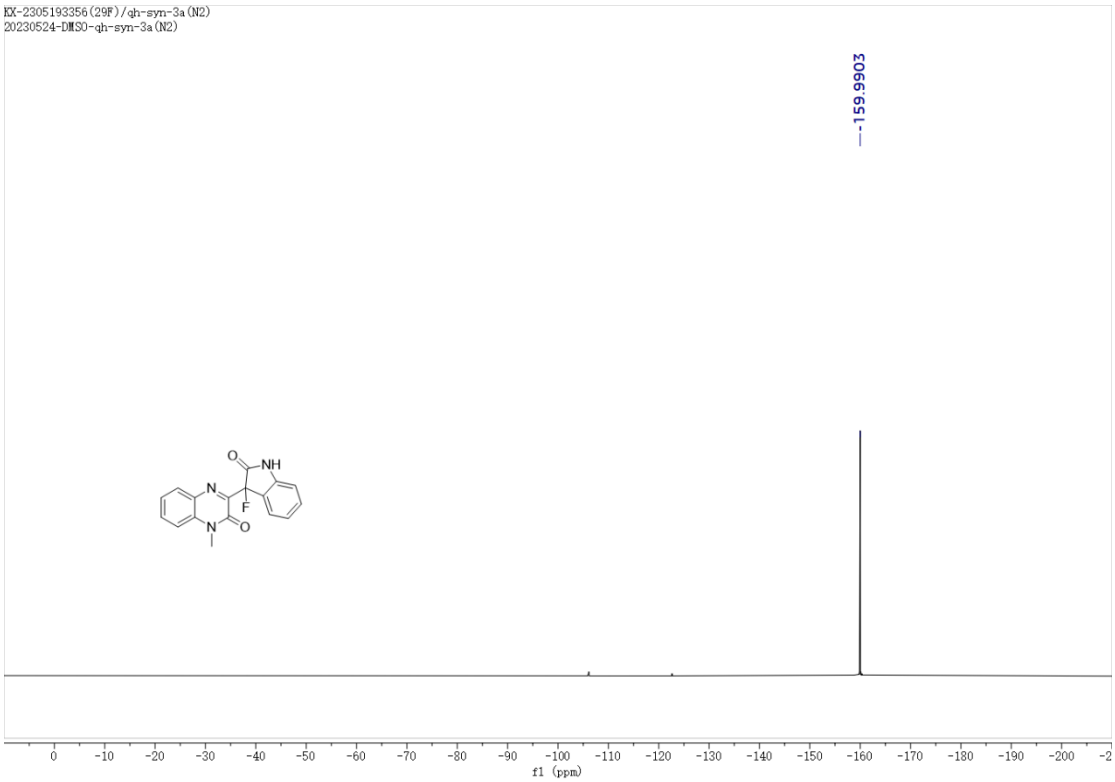


Figure S3. The ^{19}F NMR Spectrum of Compound **3a** in DMSO-d_6

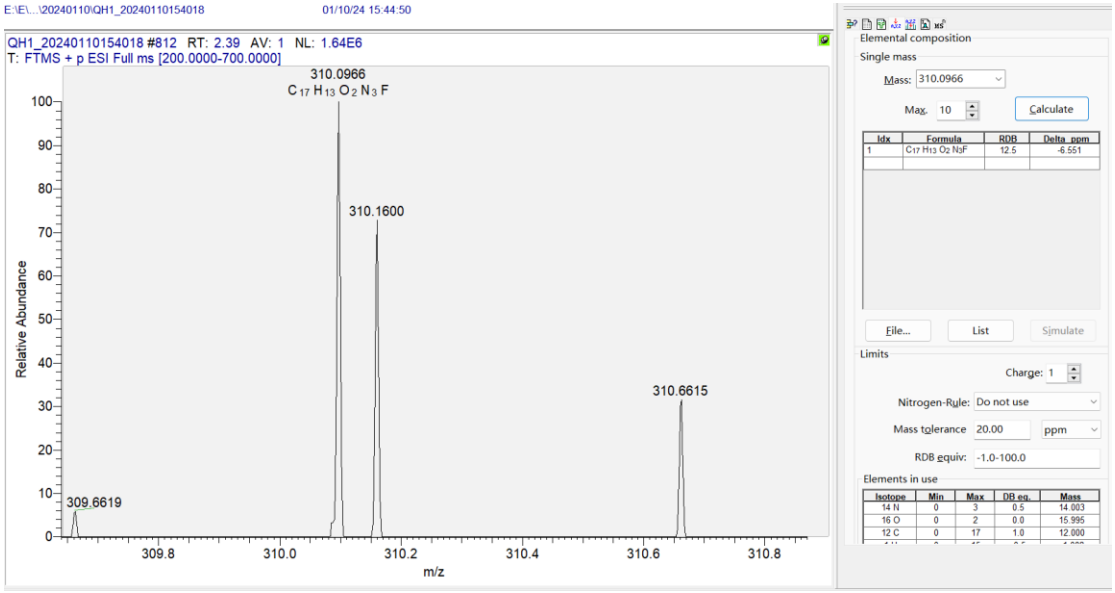


Figure S4. The HR-ESI-MS Spectrum of Compound **3a**

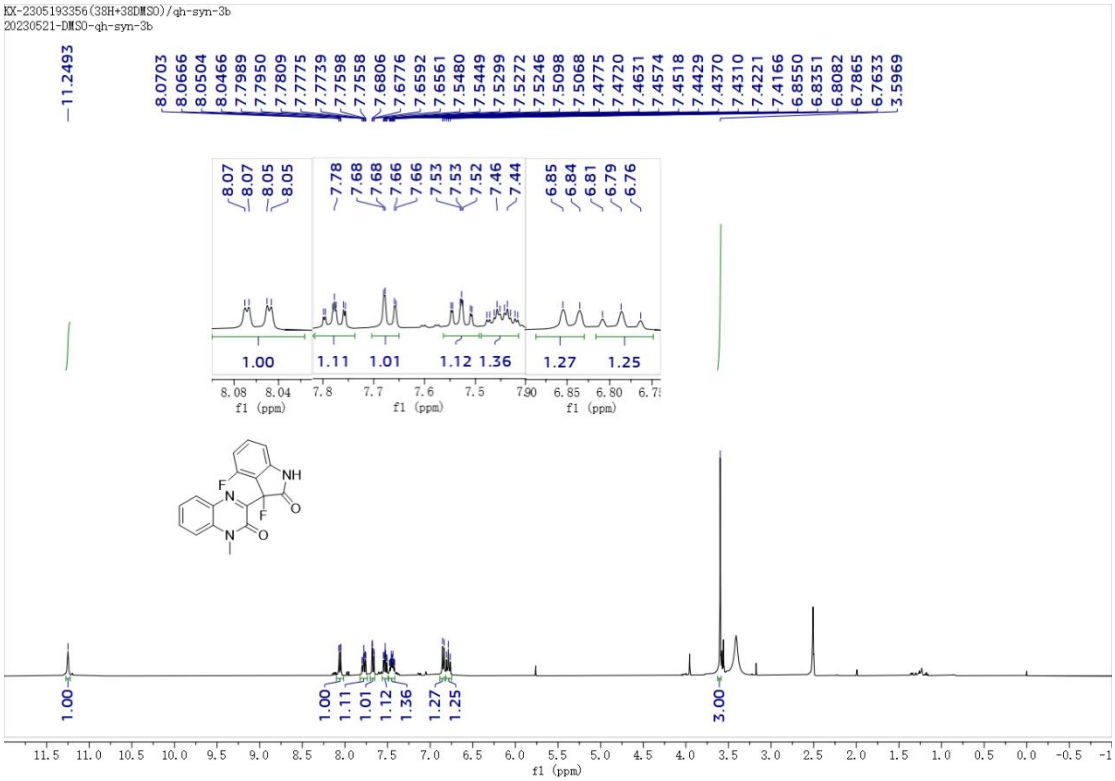


Figure S5 The ^{1}H NMR Spectrum of Compound **3b** in DMSO-d_6

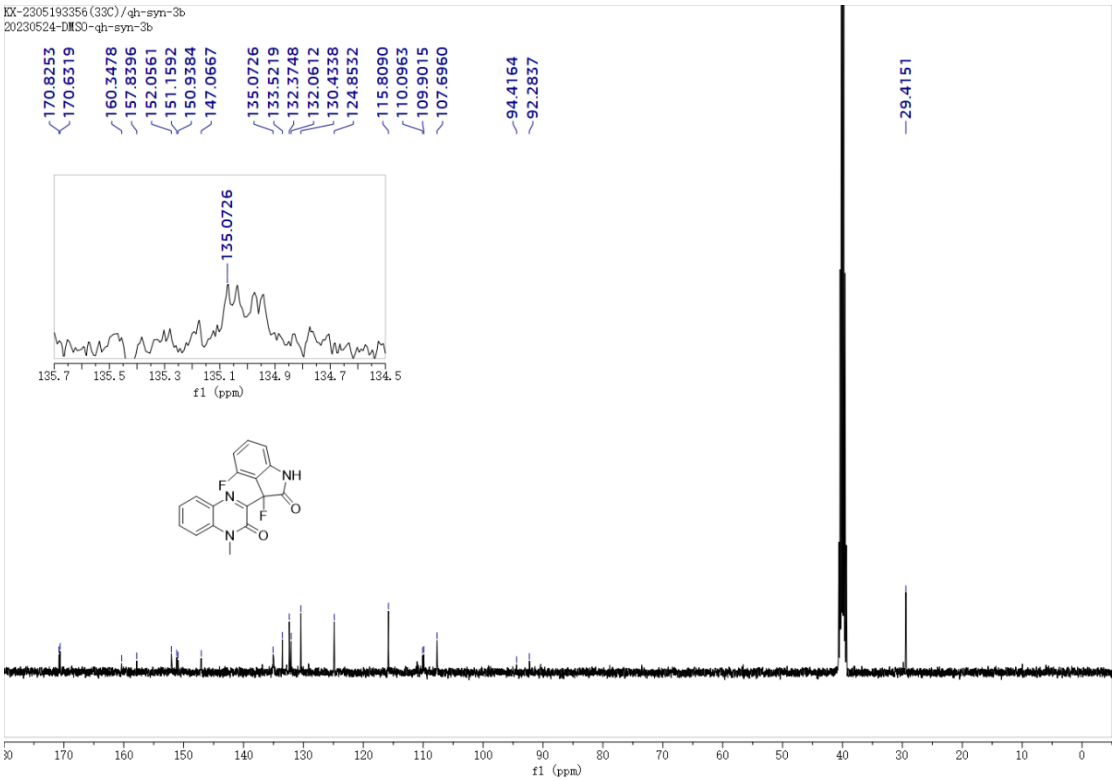


Figure S6. The ^{13}C NMR Spectrum of Compound **3b** in DMSO-d_6

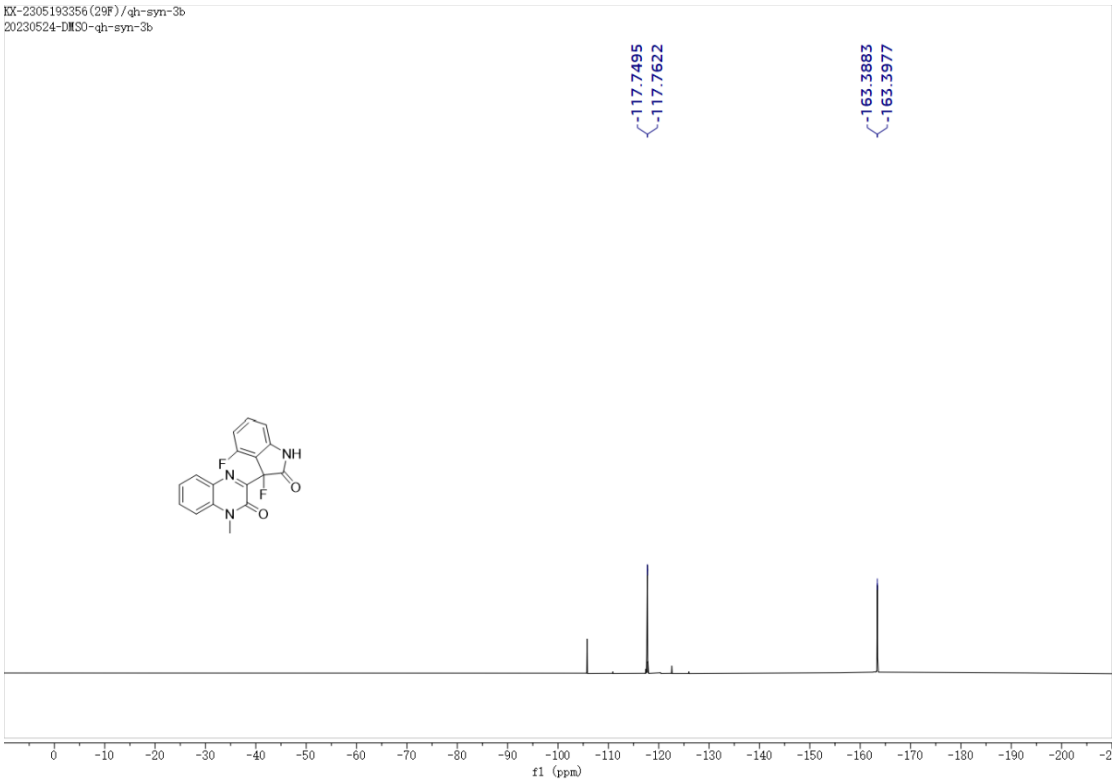


Figure S7. The ^{19}F NMR Spectrum of Compound **3b** in DMSO-d_6

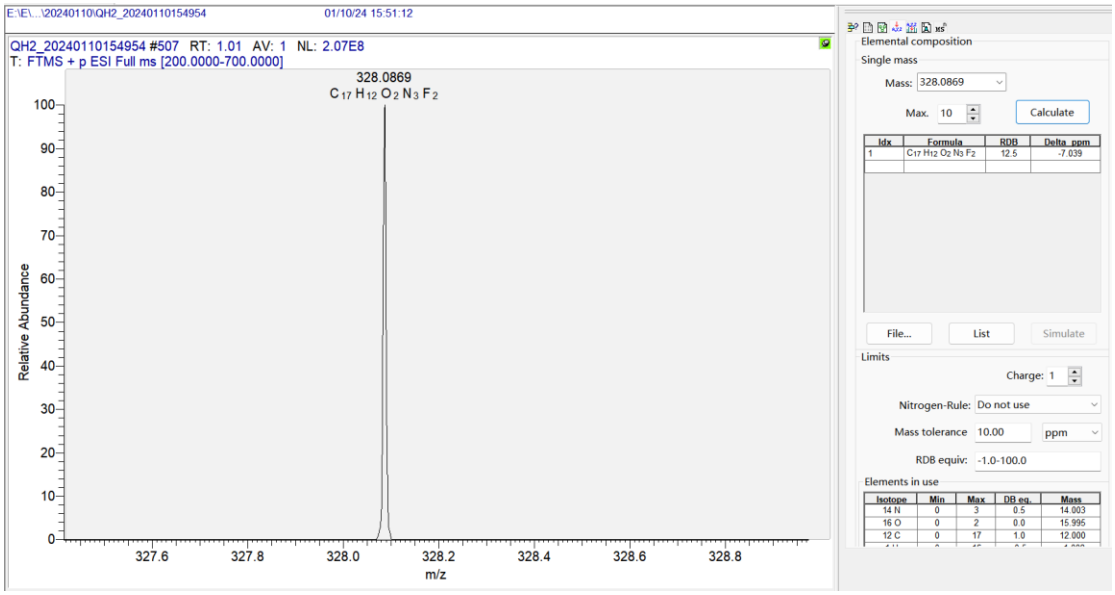


Figure S8. The HR-ESI-MS Spectrum of Compound **3b**

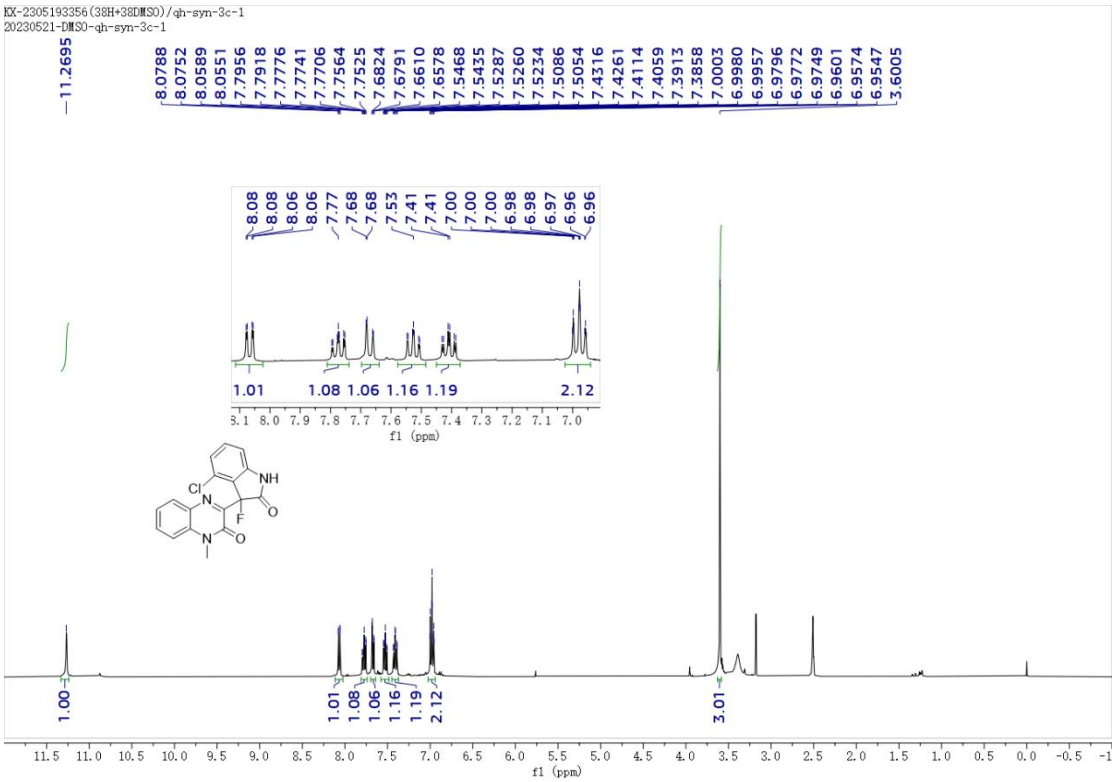


Figure S9. The ^{1}H NMR Spectrum of Compound **3c** in DMSO-d_6

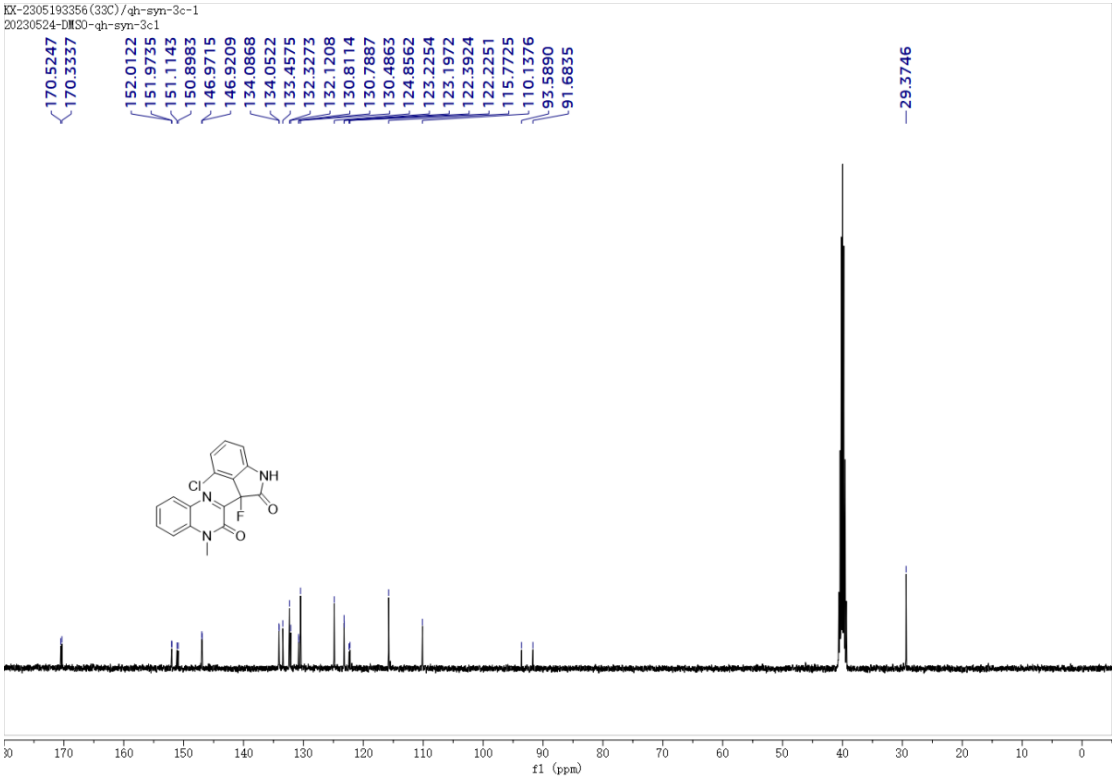


Figure S10. The ^{13}C NMR Spectrum of Compound **3c** in DMSO-d_6

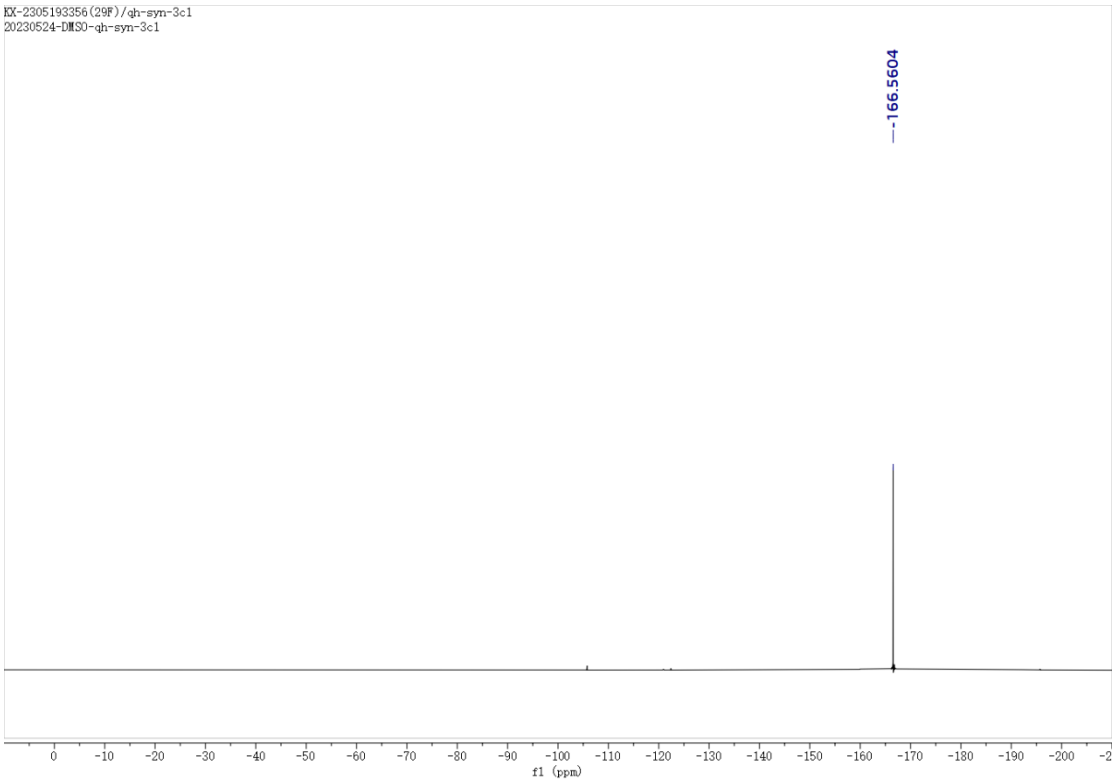


Figure S11. The ^{19}F NMR Spectrum of Compound **3c** in DMSO-d_6

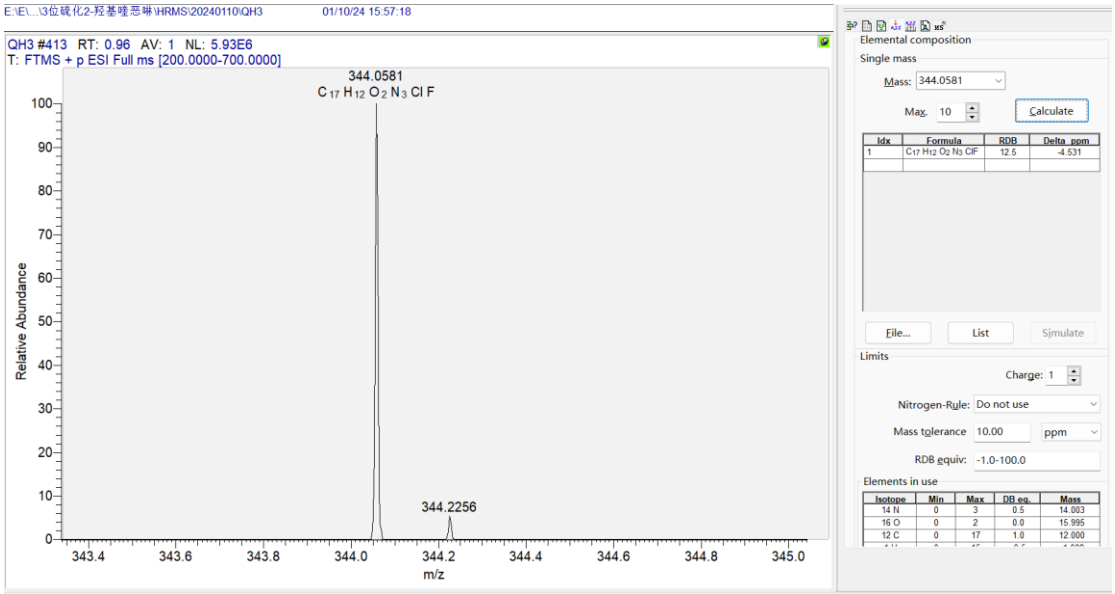


Figure S12. The HR-ESI-MS Spectrum of Compound **3c**

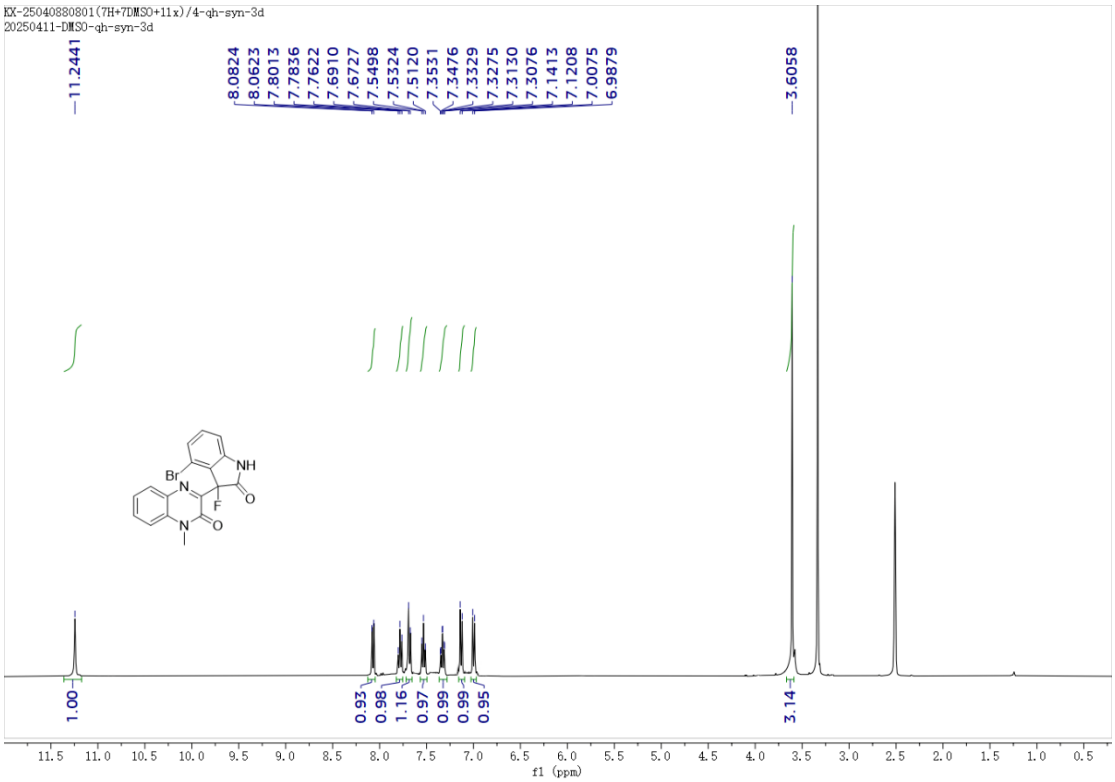


Figure S13. The ^{1}H NMR Spectrum of Compound **3d** in DMSO-d_6

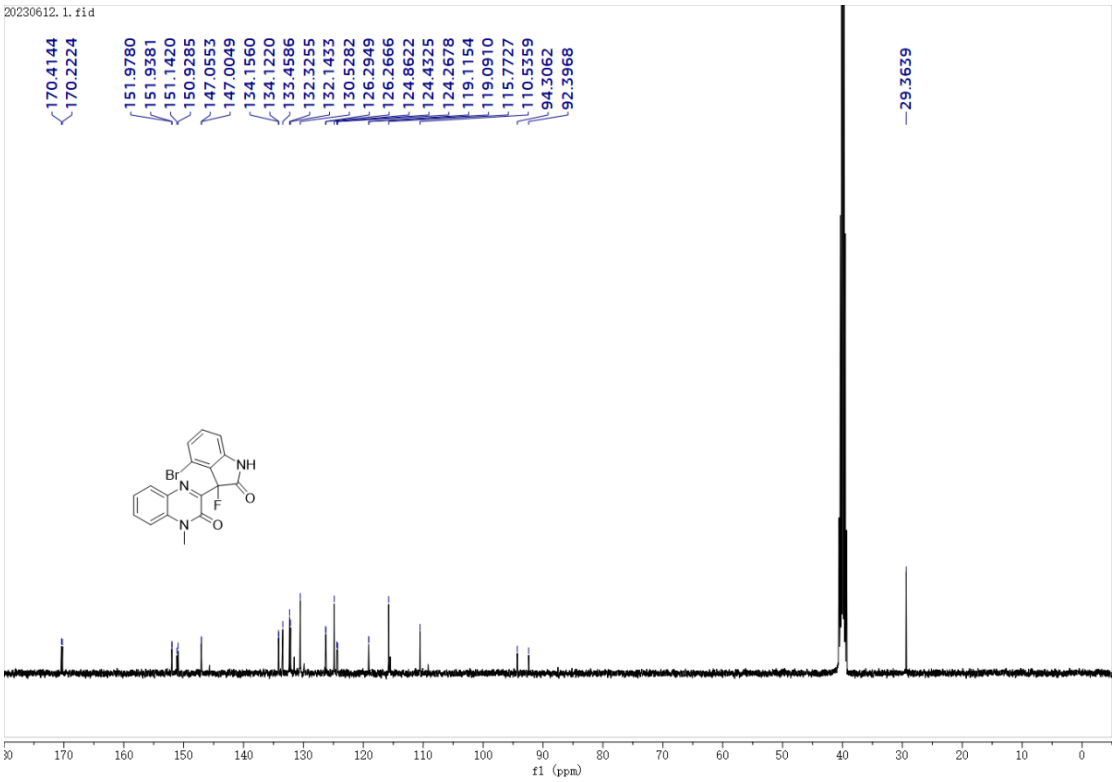


Figure S14. The ^{13}C NMR Spectrum of Compound **3d** in DMSO-d_6

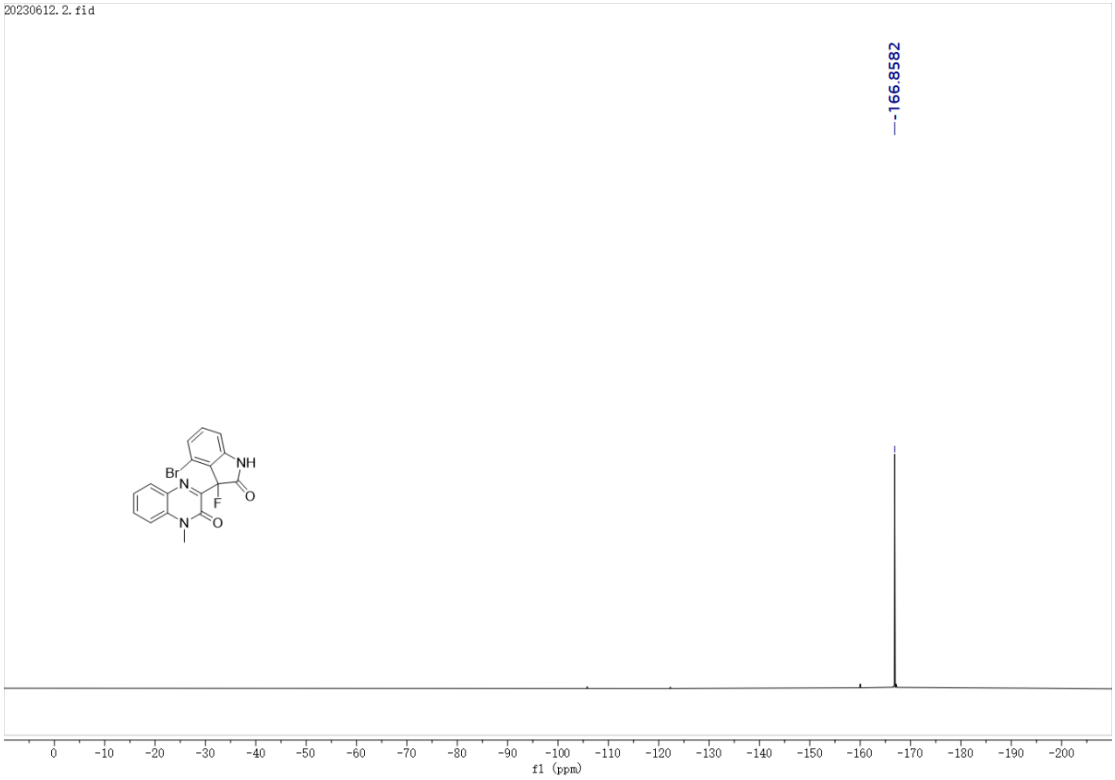


Figure S15. The ^{19}F NMR Spectrum of Compound **3d** in DMSO-d_6

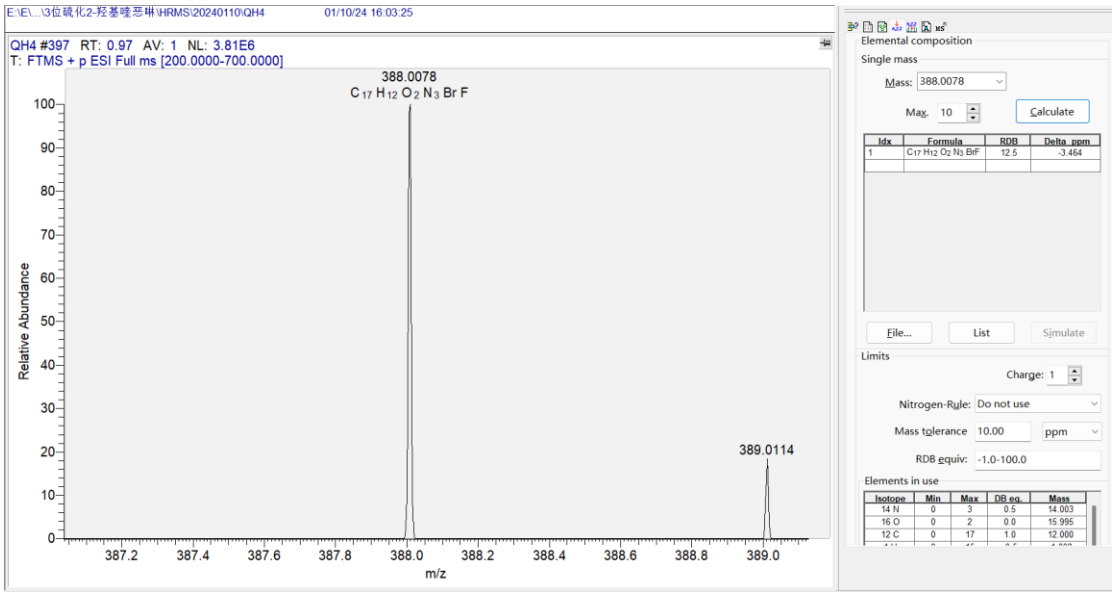


Figure S16. The HR-ESI-MS Spectrum of Compound **3d**

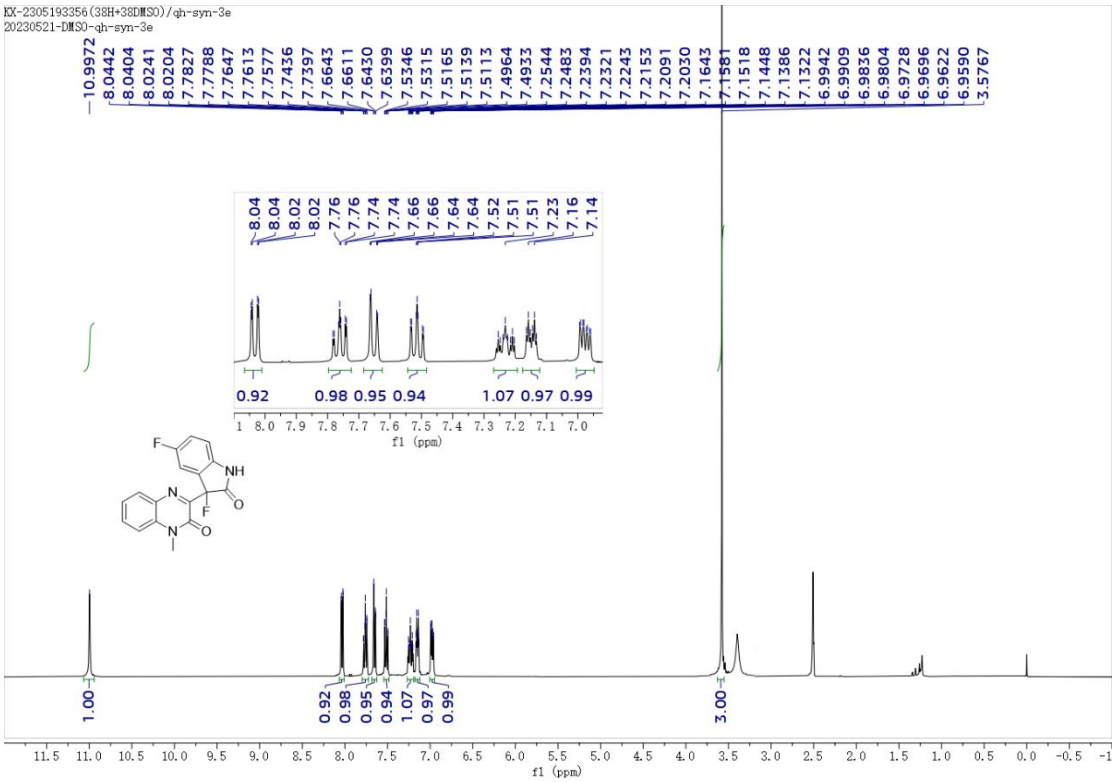


Figure S17. The ^{1}H NMR Spectrum of Compound **3e** in DMSO-d_6

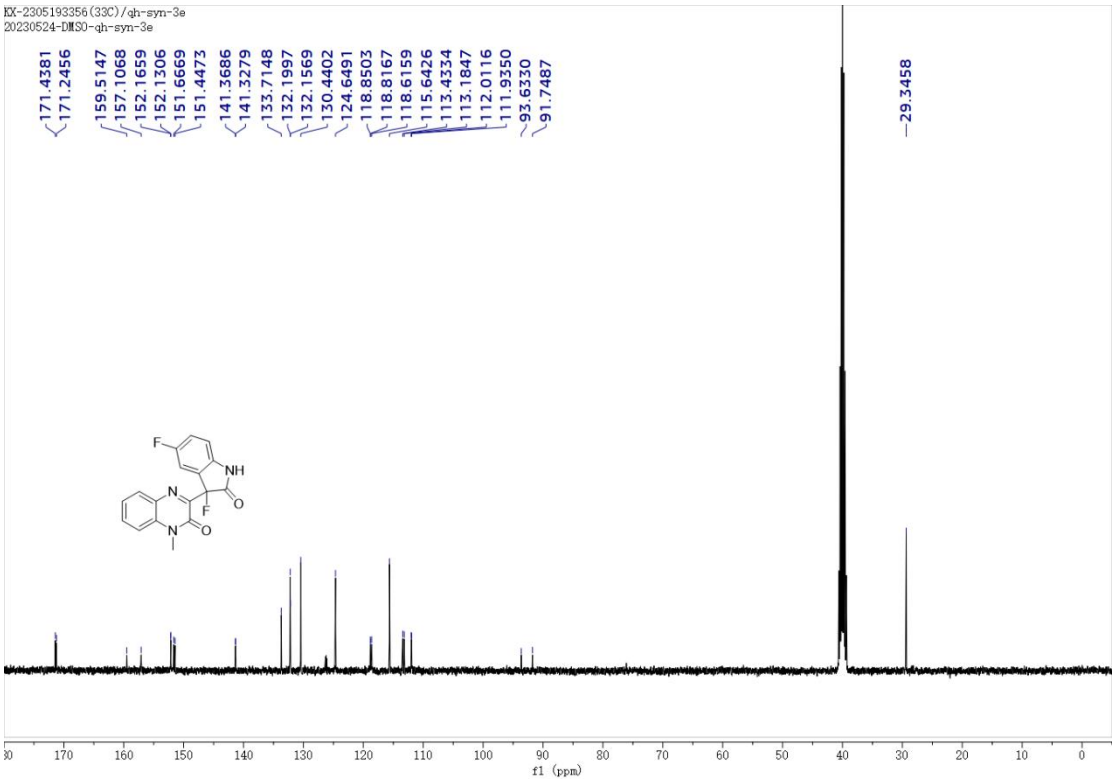


Figure S18. The ^{13}C NMR Spectrum of Compound **3e** in DMSO-d_6

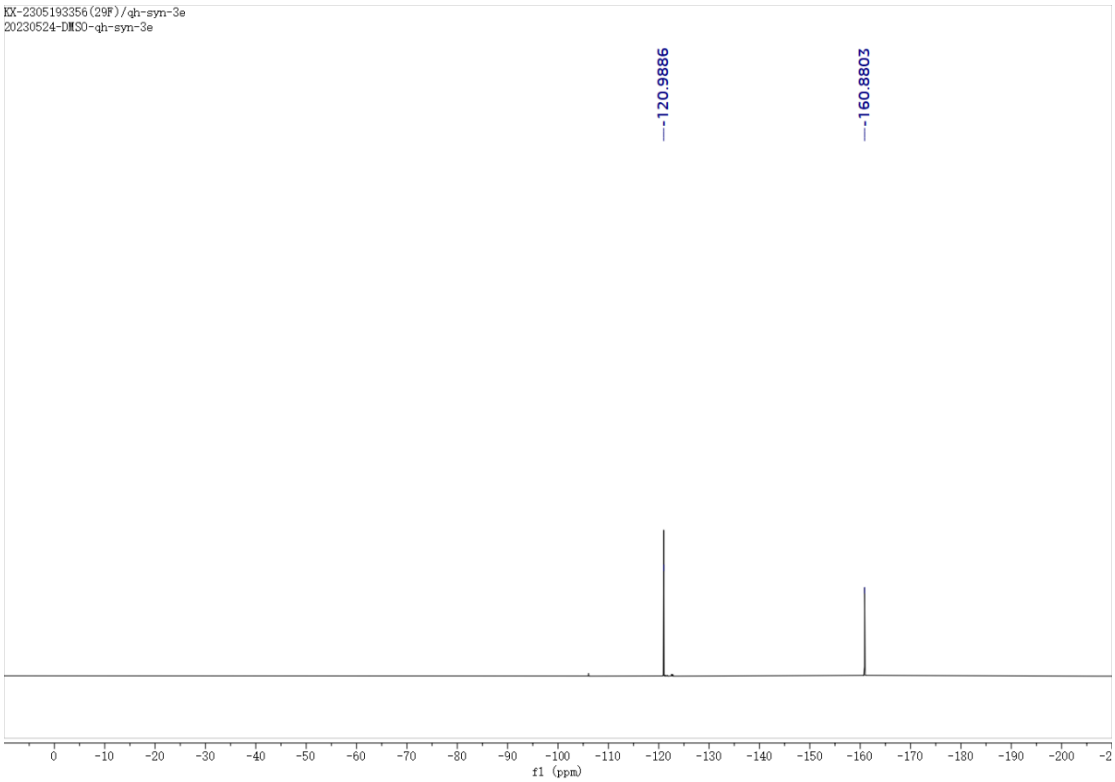


Figure S19. The ^{19}F NMR Spectrum of Compound **3e** in DMSO-d_6

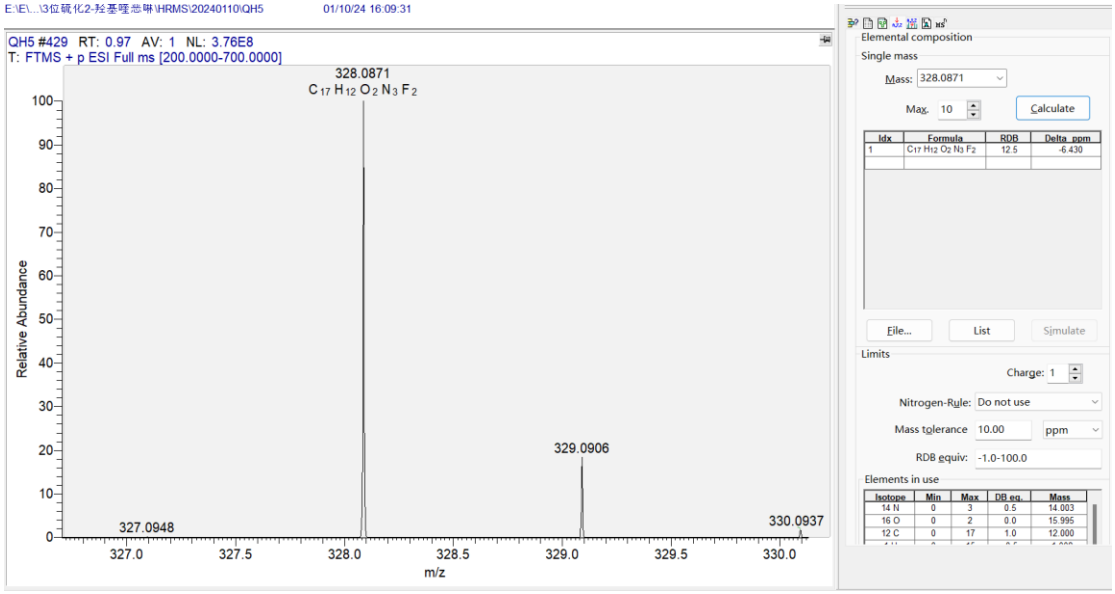


Figure S20. The HR-ESI-MS Spectrum of Compound **3e**

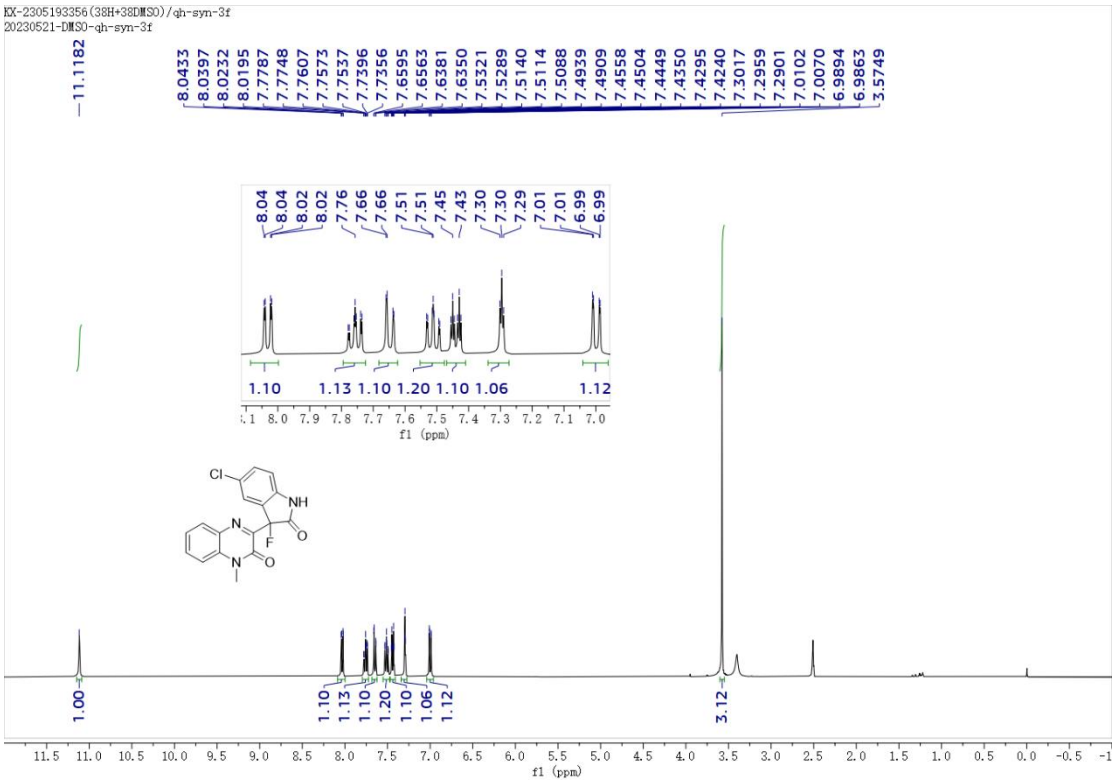


Figure S21. The ^{1}H NMR Spectrum of Compound **3f** in DMSO-d_6

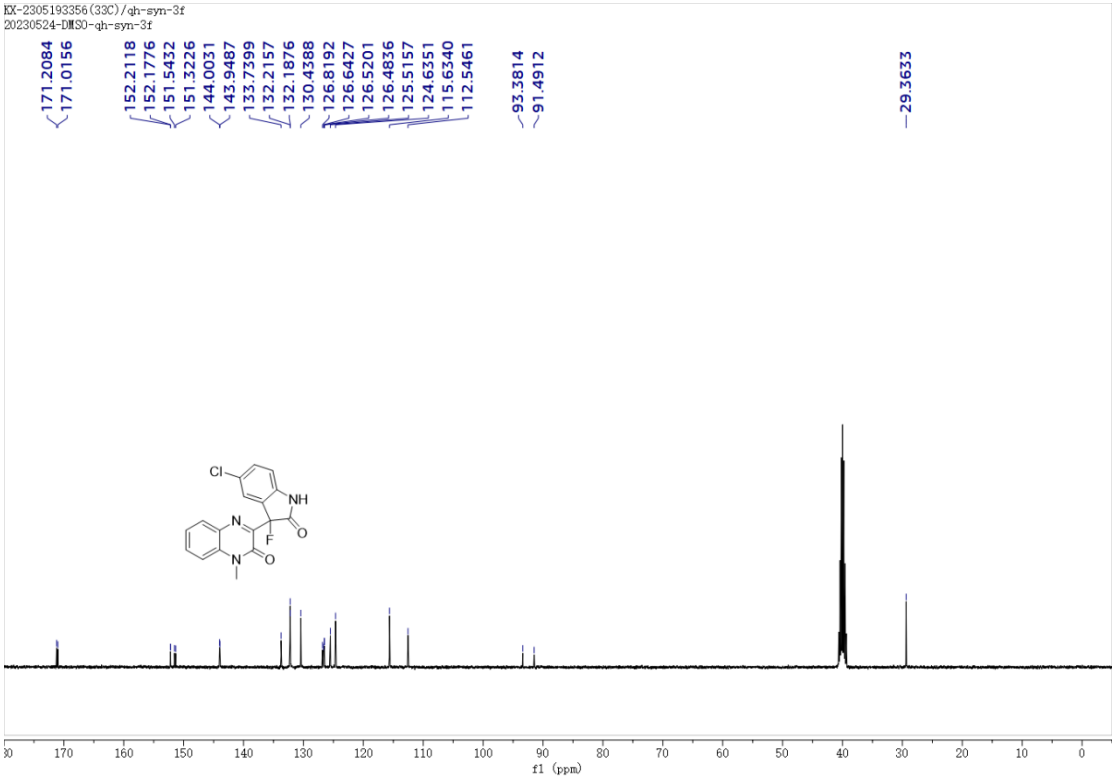


Figure S22. The ^{13}C NMR Spectrum of Compound **3f** in DMSO-d_6

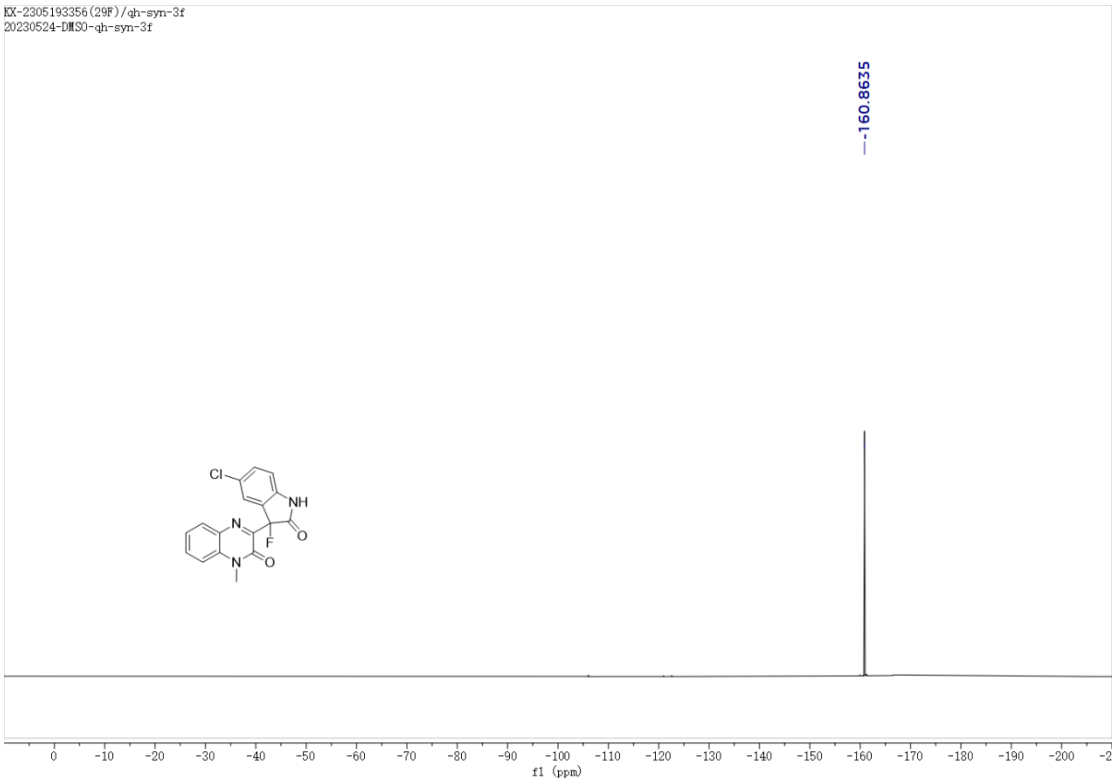


Figure S23. The ^{19}F NMR Spectrum of Compound **3f** in DMSO-d_6

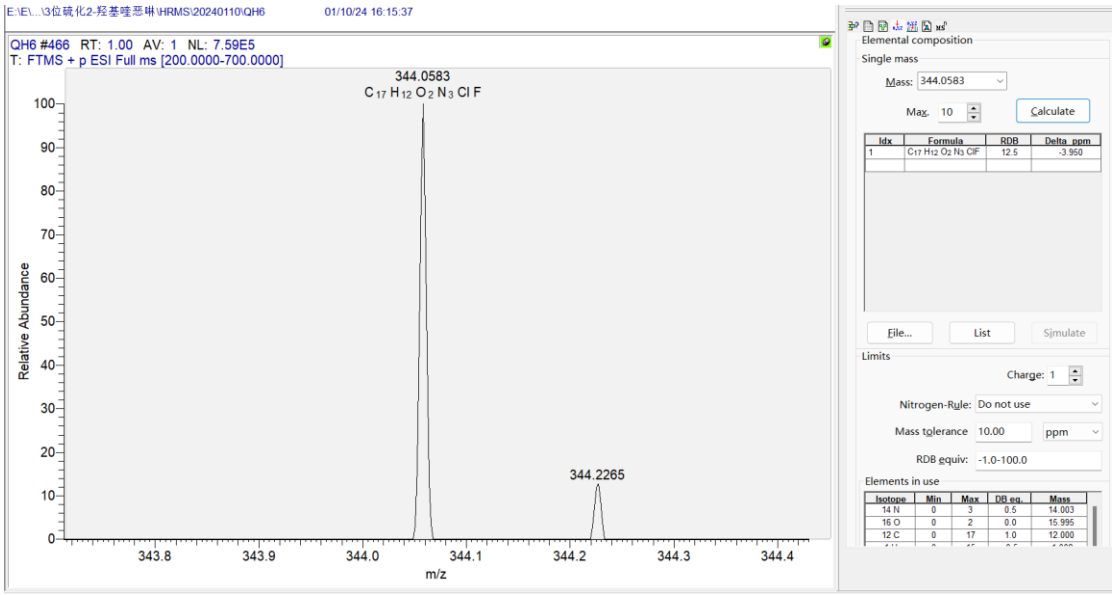


Figure S24. The HR-ESI-MS Spectrum of Compound **3f**

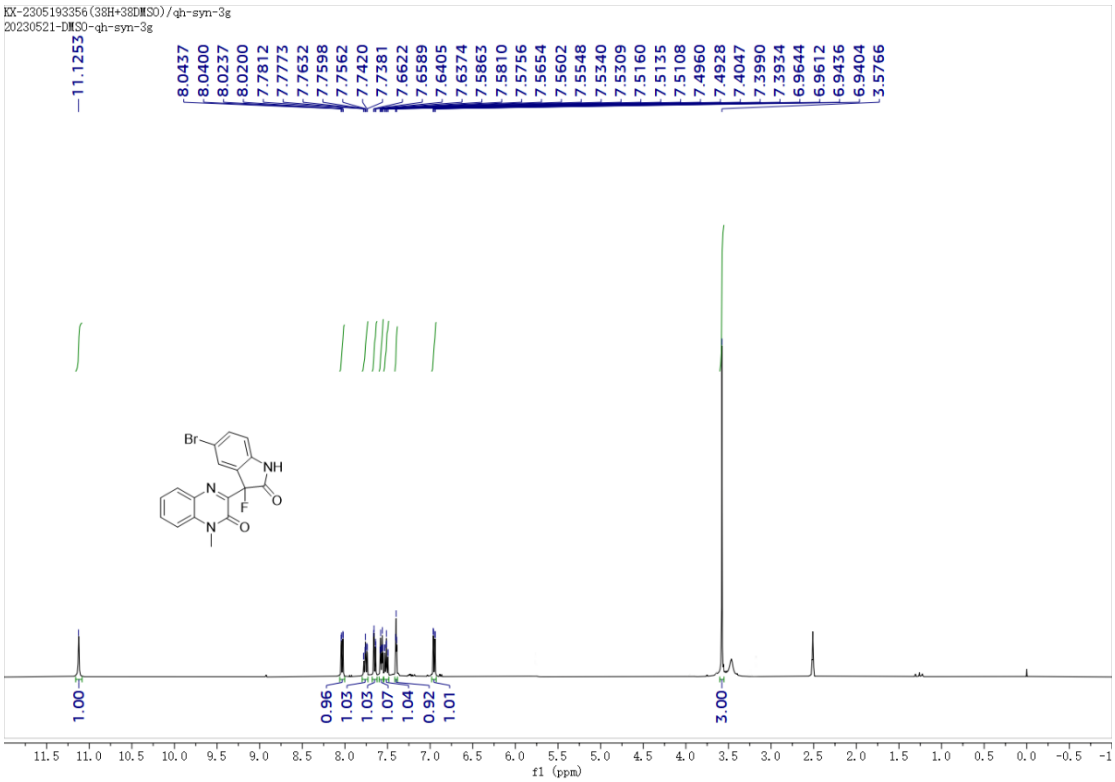


Figure S25. The ^{1}H NMR Spectrum of Compound **3g** in DMSO-d_6

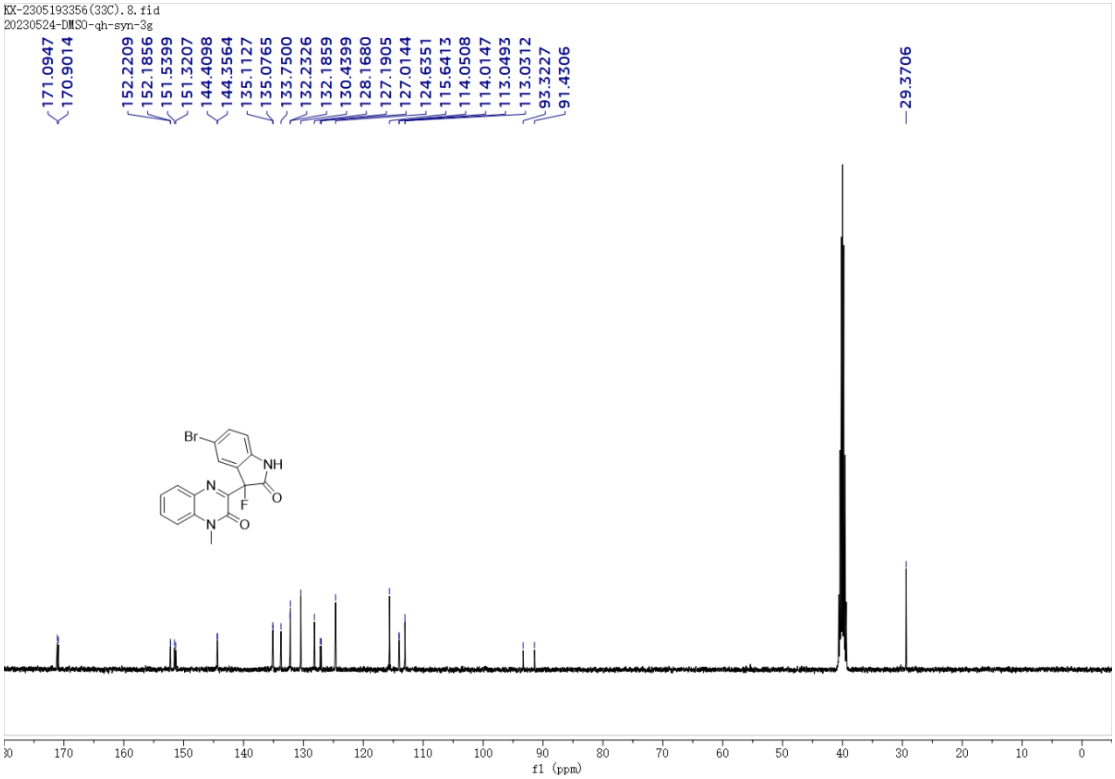


Figure S26. The ^{13}C NMR Spectrum of Compound **3g** in DMSO-d_6

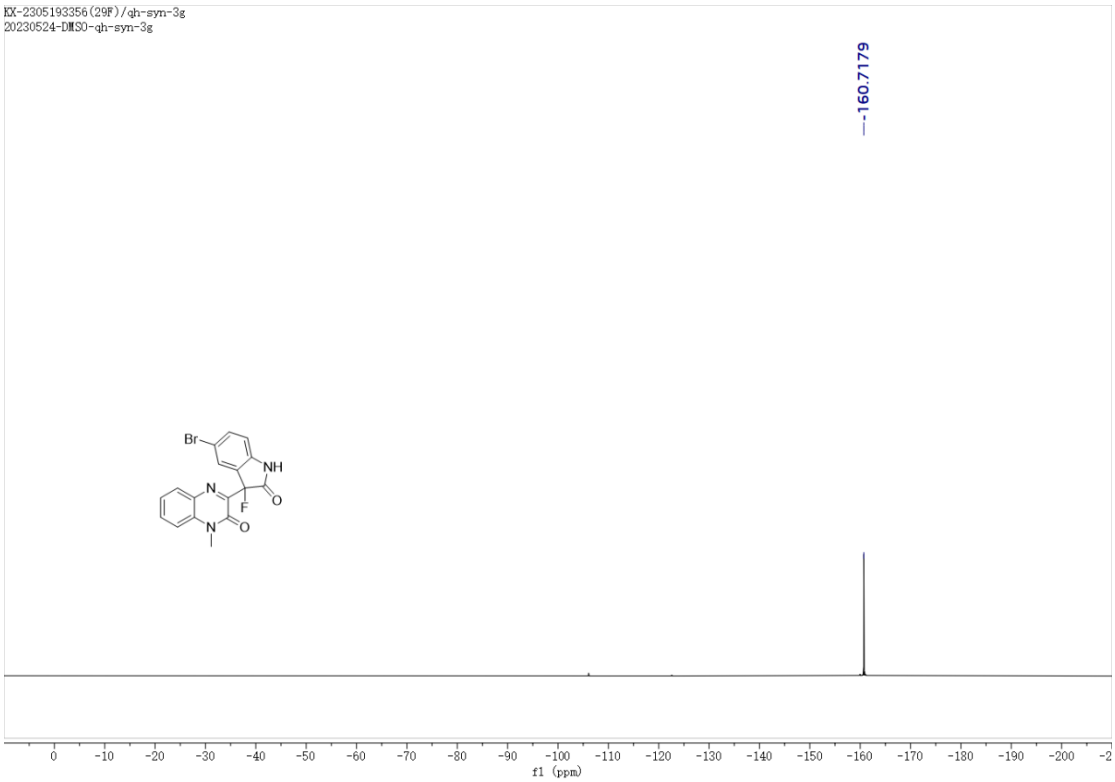


Figure S27. The ^{19}F NMR Spectrum of Compound **3g** in DMSO-d_6

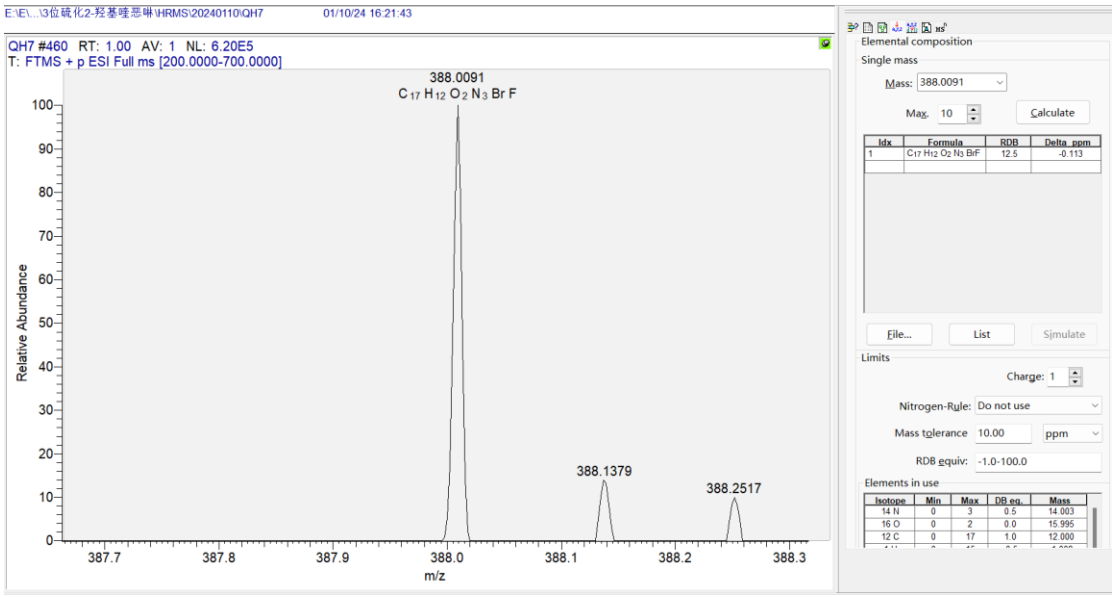


Figure S28. The HR-ESI-MS Spectrum of Compound **3g**

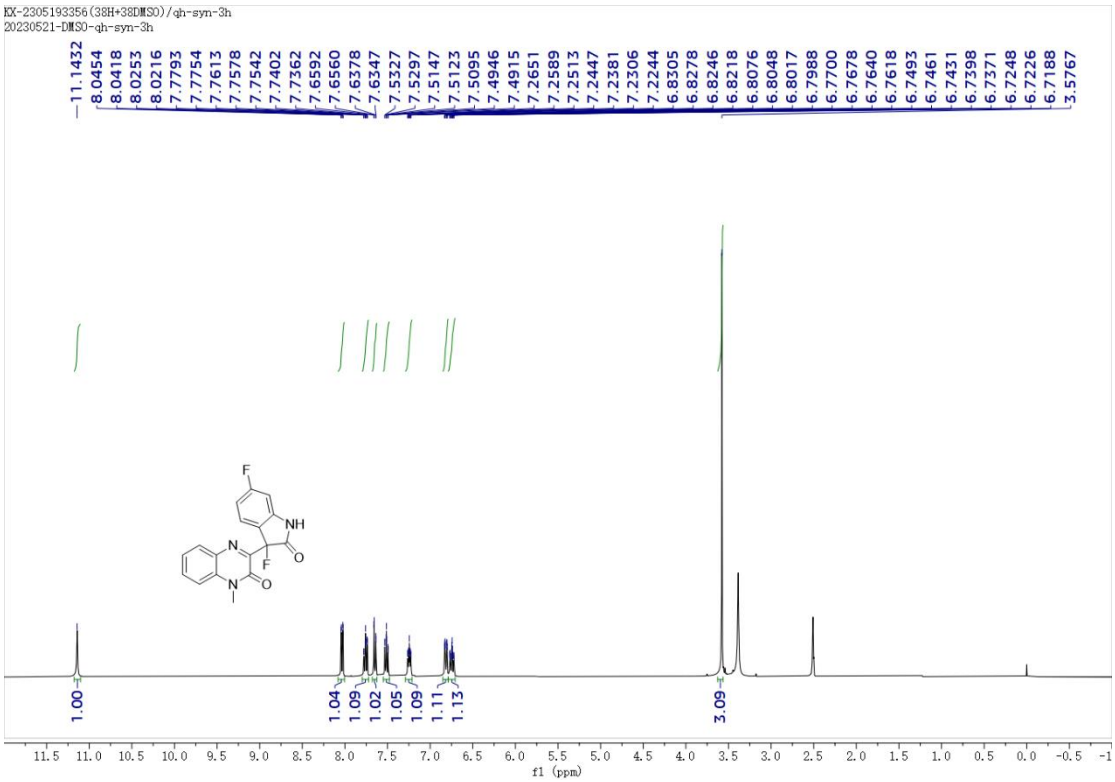


Figure S29. The ^{1}H NMR Spectrum of Compound **3h** in DMSO-d_6

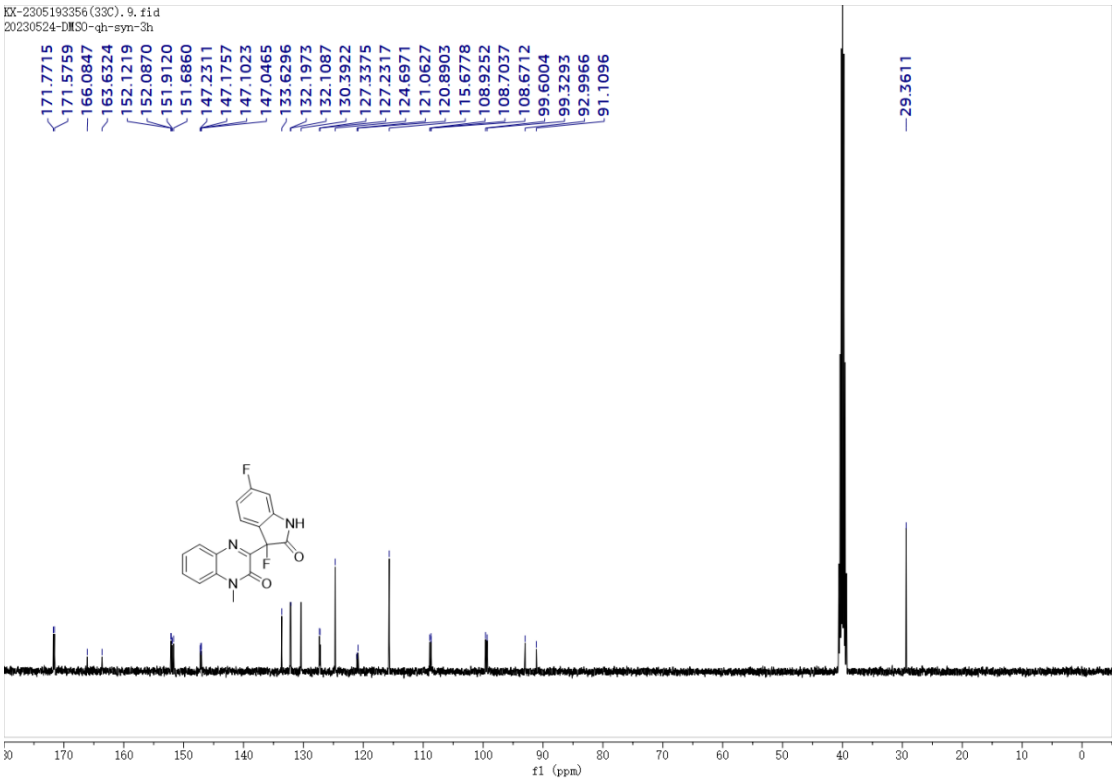


Figure S30. The ^{13}C NMR Spectrum of Compound **3h** in DMSO-d_6

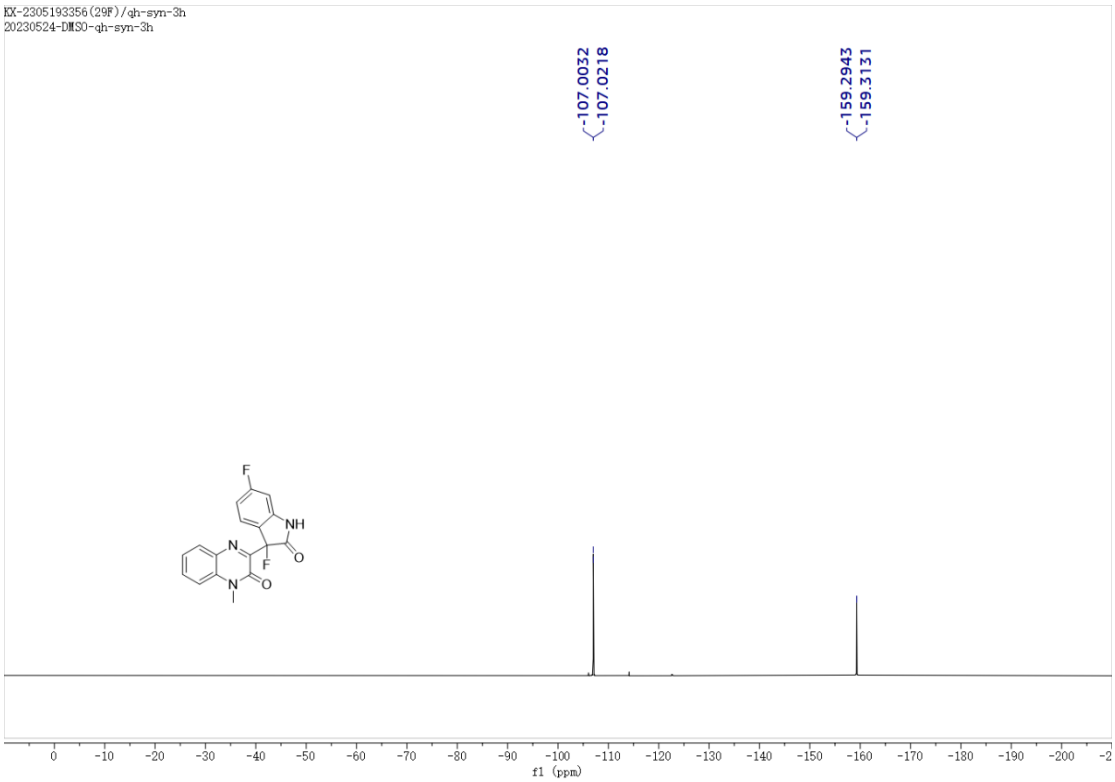


Figure S31. The ^{19}F NMR Spectrum of Compound **3h** in DMSO-d_6

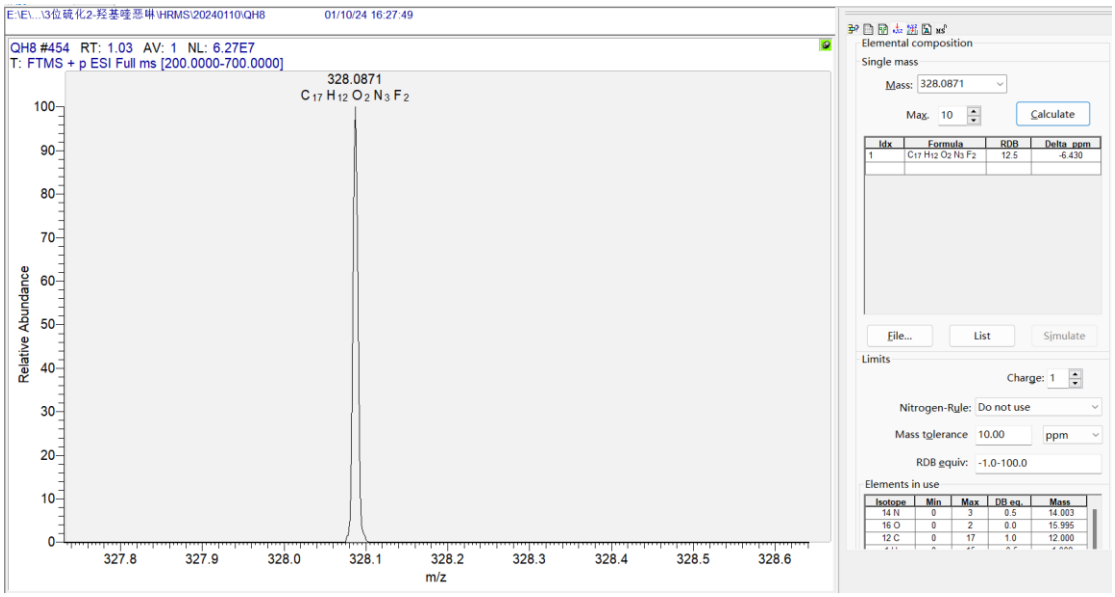


Figure S32. The HR-ESI-MS Spectrum of Compound **3h**

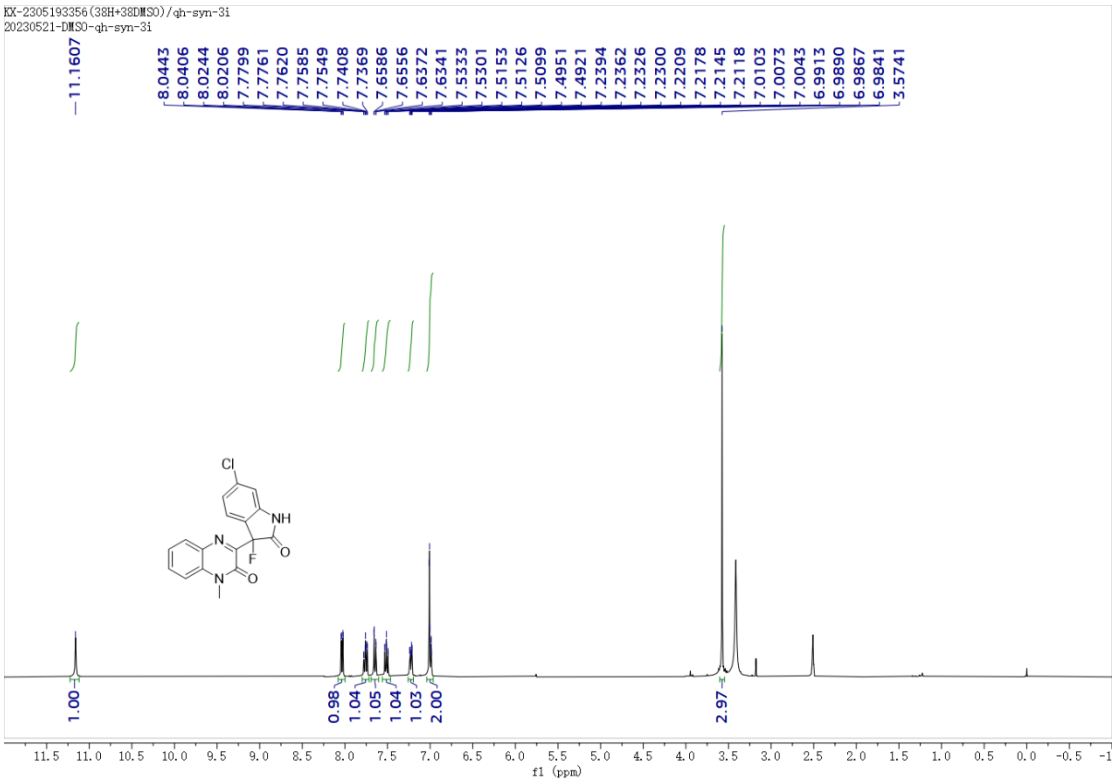


Figure S33. The ^{1}H NMR Spectrum of Compound **3i** in DMSO-d_6

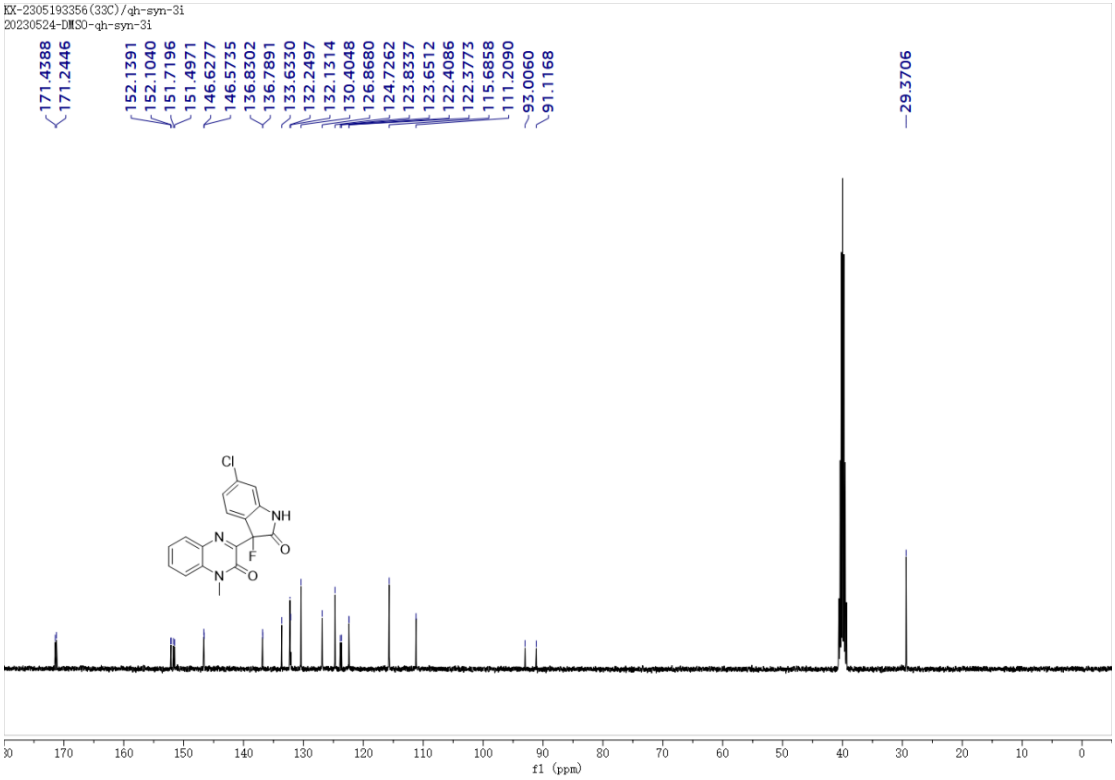


Figure S34. The ^{13}C NMR Spectrum of Compound **3i** in DMSO-d_6

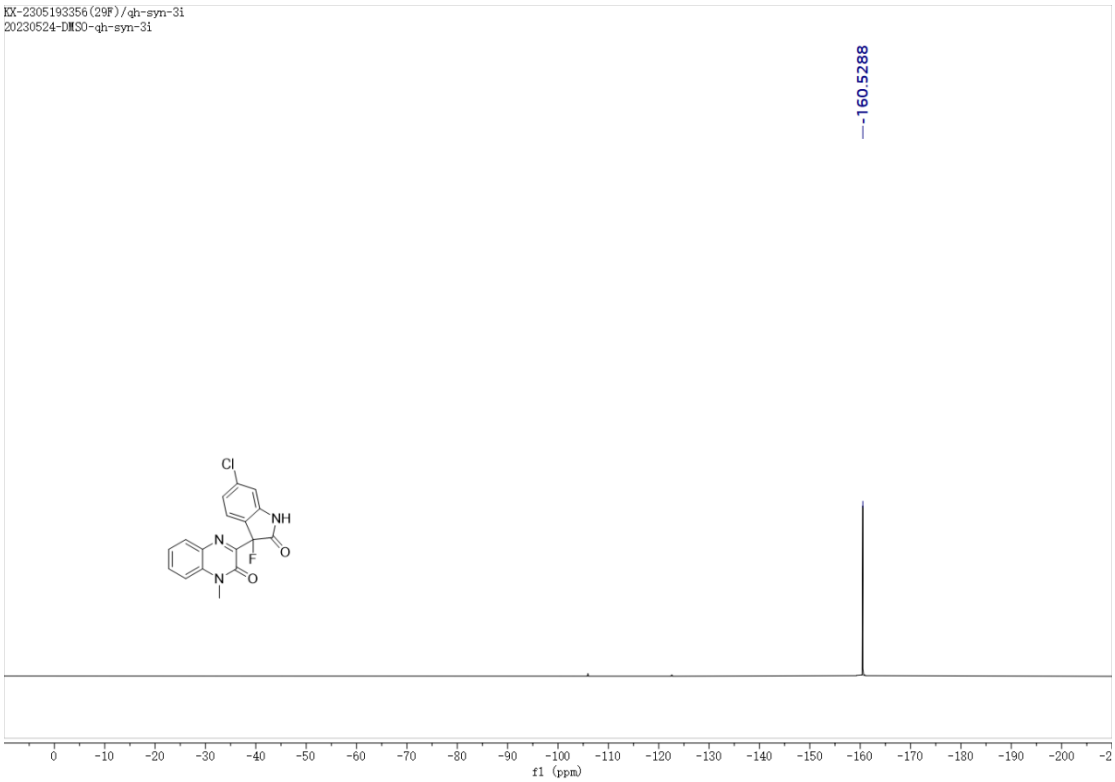


Figure S35. The ^{19}F NMR Spectrum of Compound **3i** in DMSO-d_6

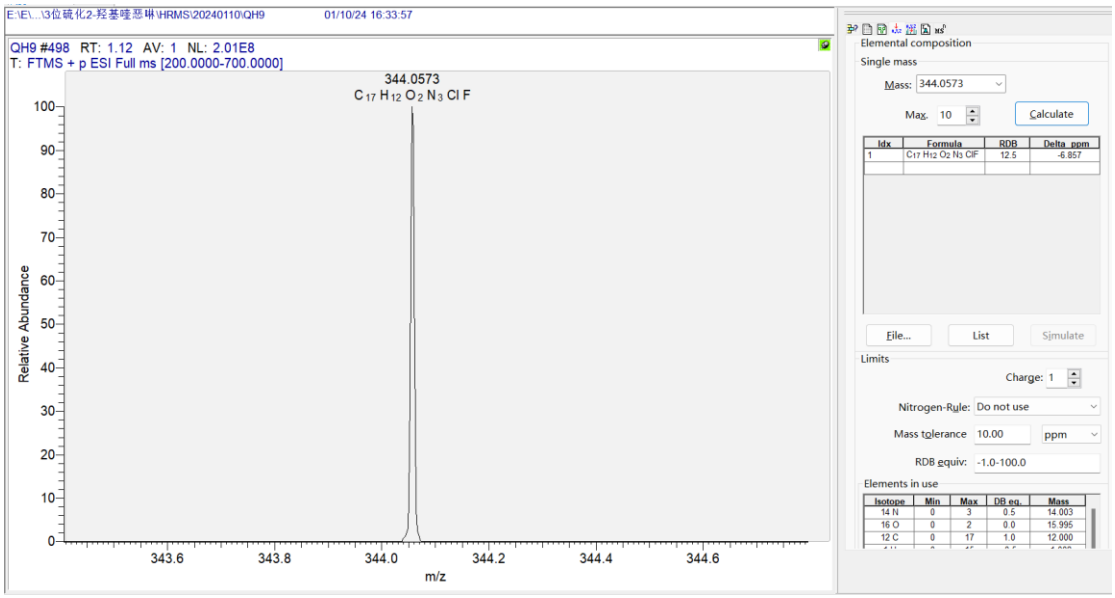


Figure S36. The HR-ESI-MS Spectrum of Compound **3i**

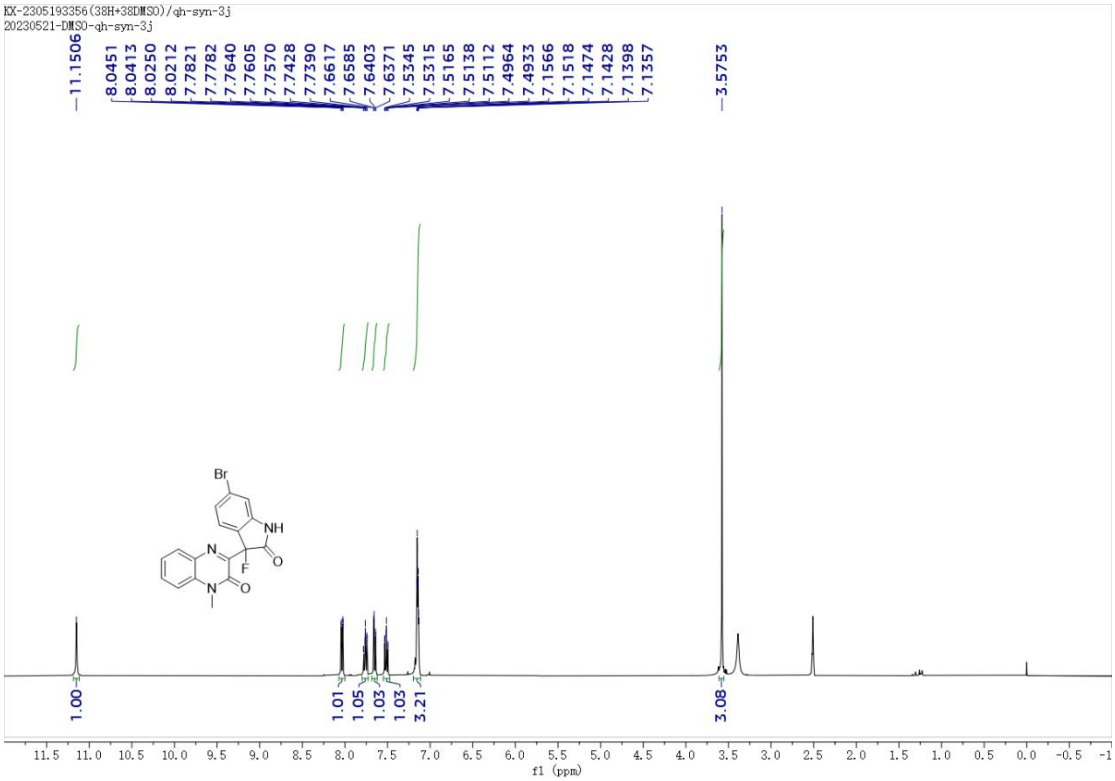


Figure S37. The ^{1}H NMR Spectrum of Compound **3j** in DMSO-d_6

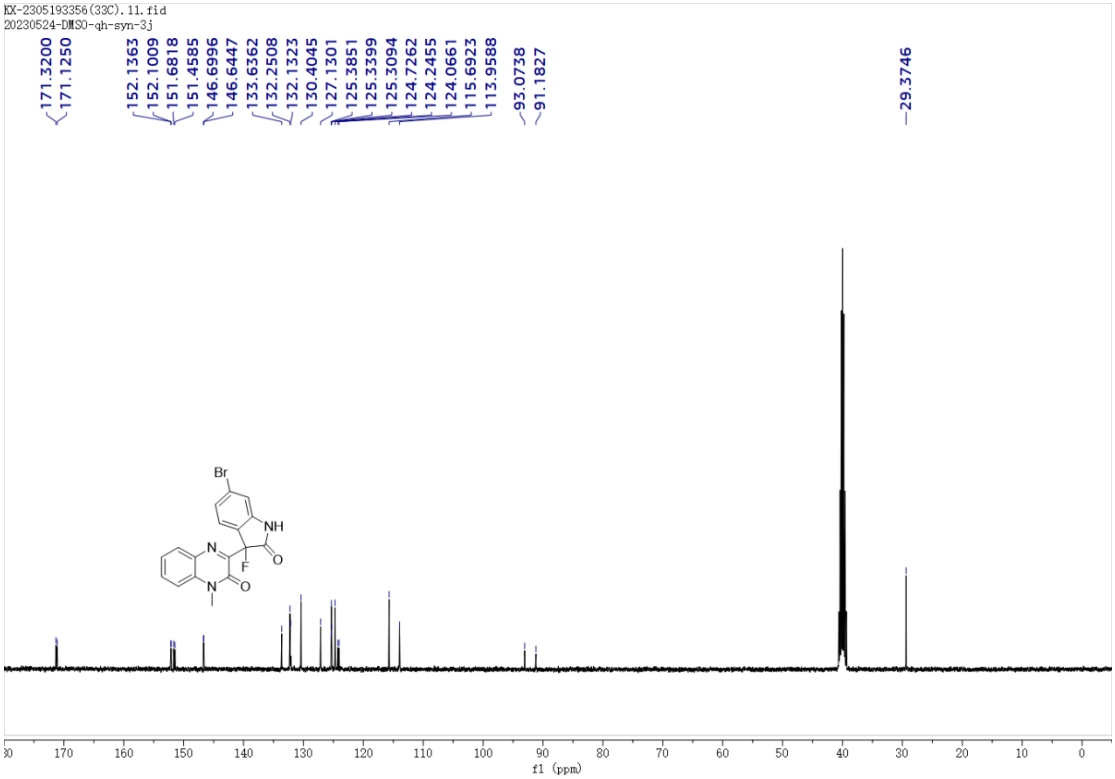


Figure S38. The ^{13}C NMR Spectrum of Compound **3j** in DMSO-d_6

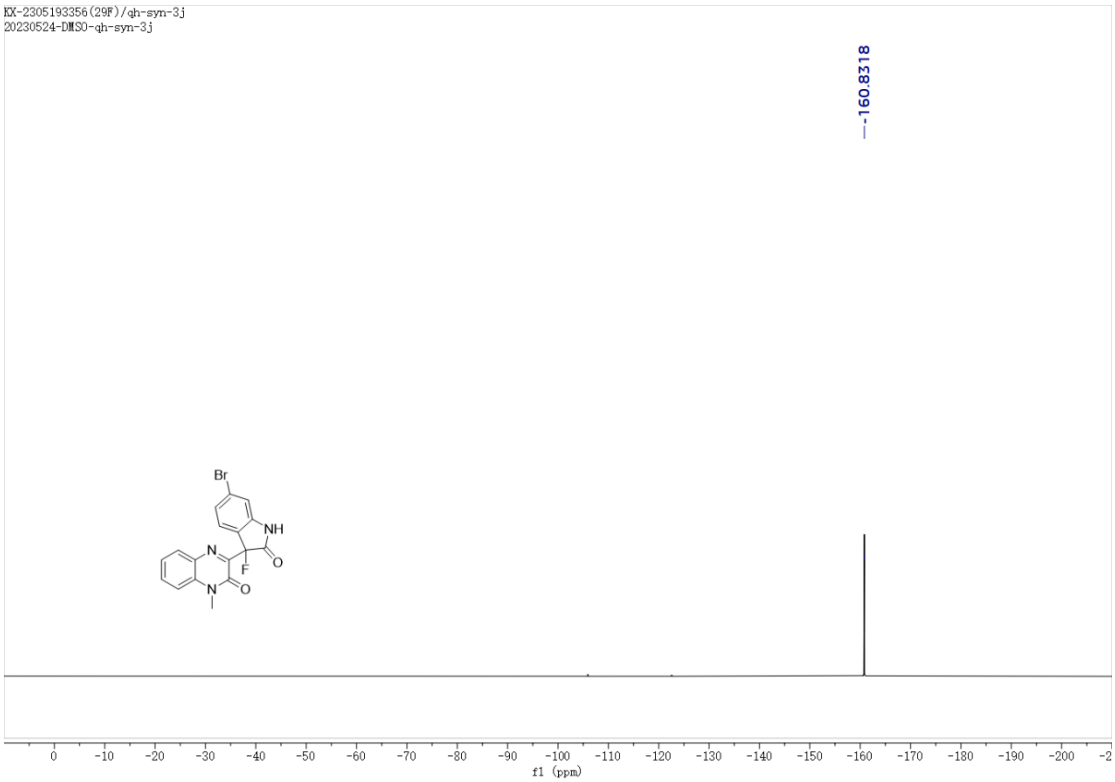


Figure S39. The ^{19}F NMR Spectrum of Compound **3j** in DMSO-d_6

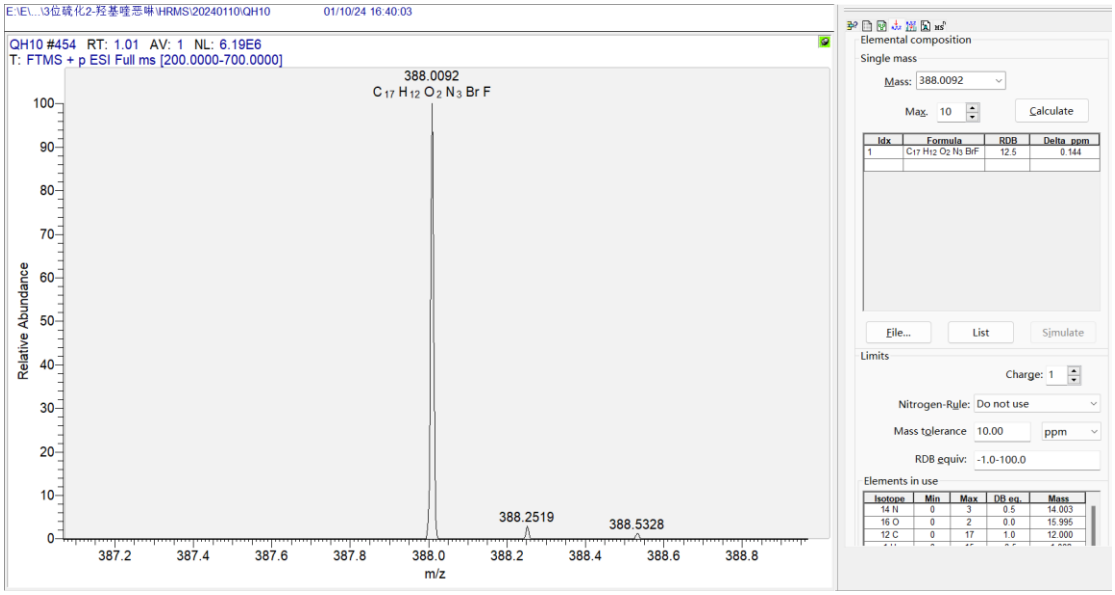


Figure S40. The HR-ESI-MS Spectrum of Compound **3j**

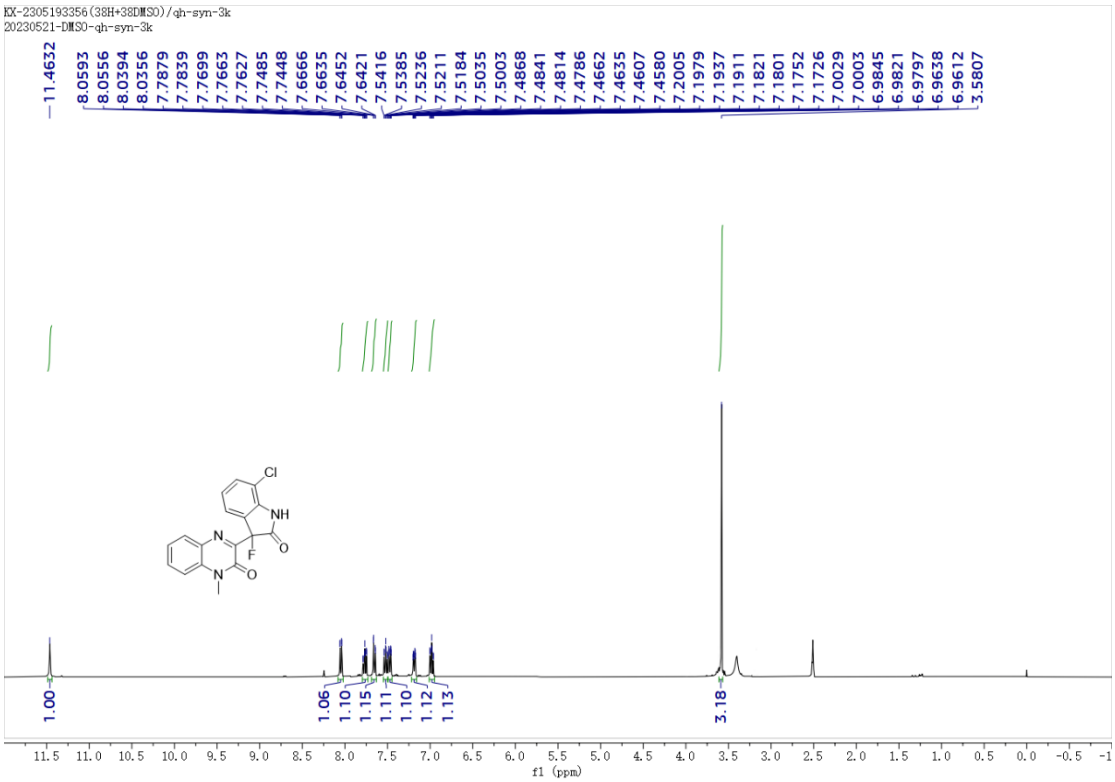


Figure S41. The ^{1}H NMR Spectrum of Compound **3k** in DMSO-d_6

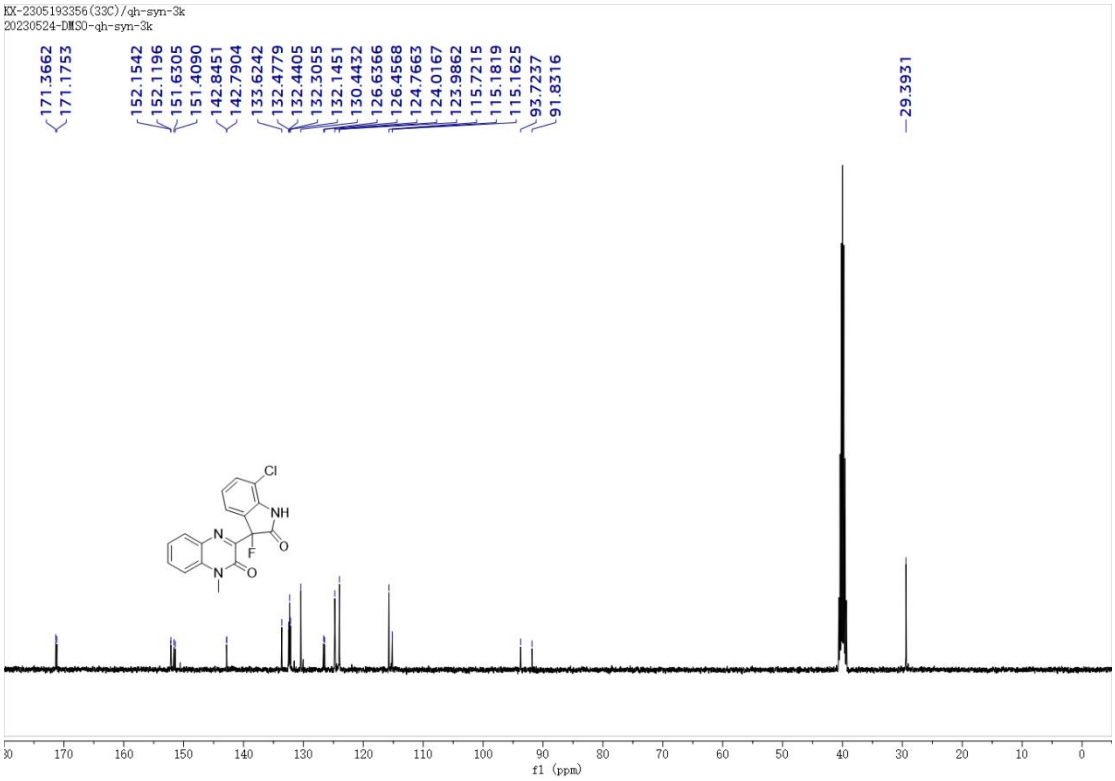


Figure S42. The ^{13}C NMR Spectrum of Compound **3k** in DMSO-d_6

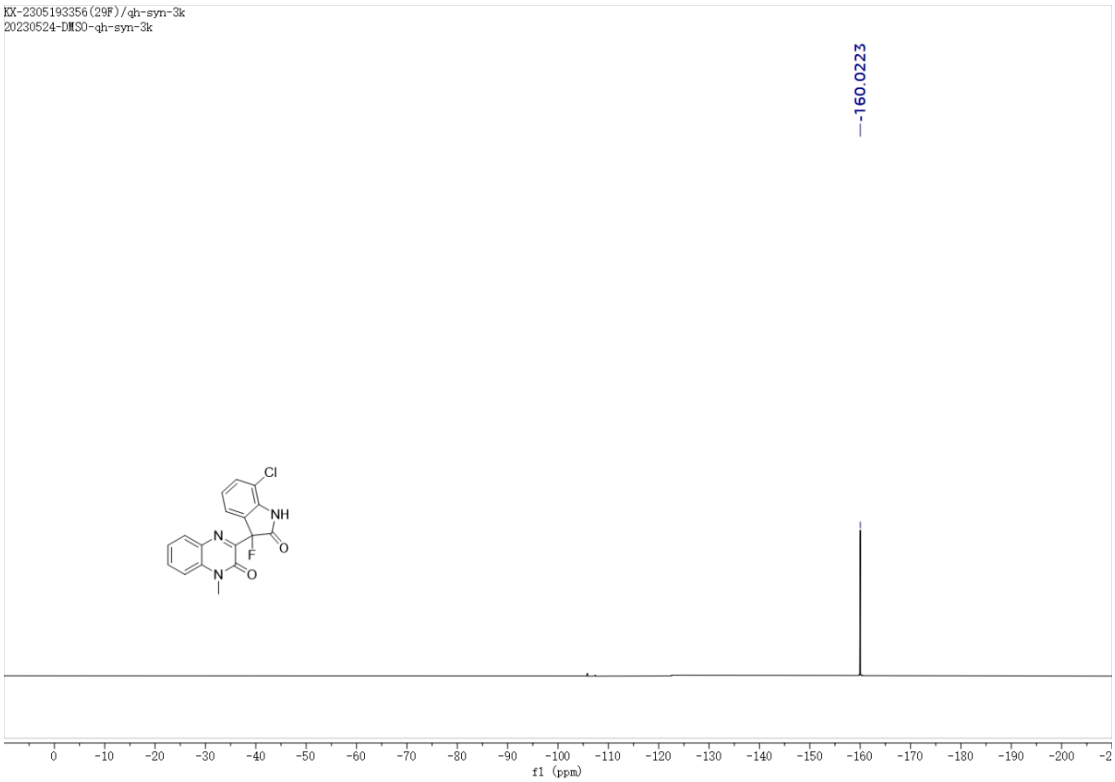


Figure S43. The ^{19}F NMR Spectrum of Compound **3k** in DMSO-d_6

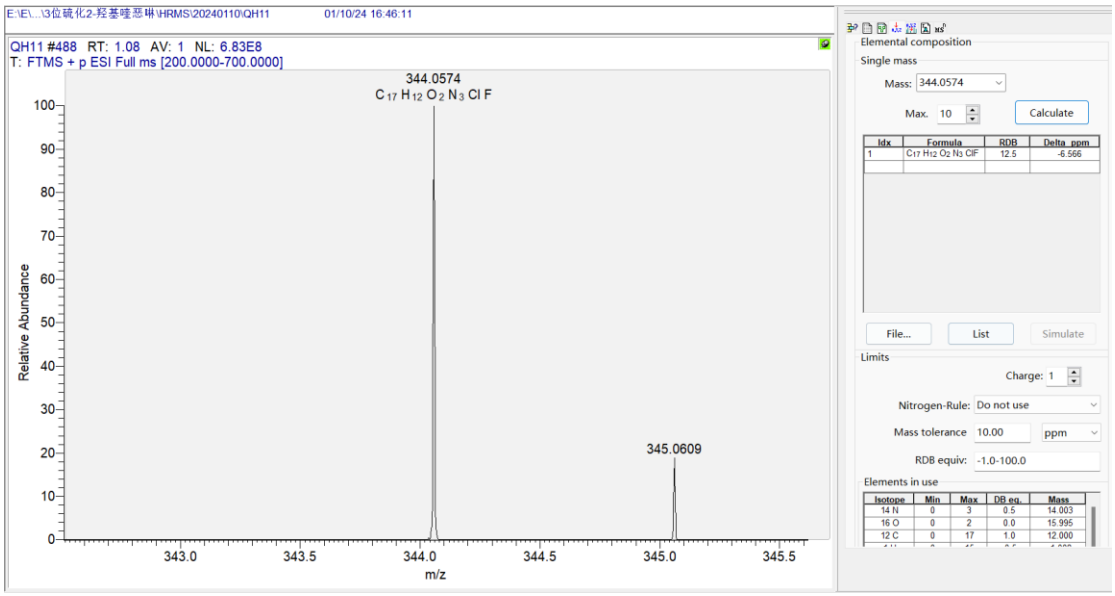


Figure S44. The HR-ESI-MS Spectrum of Compound **3k**

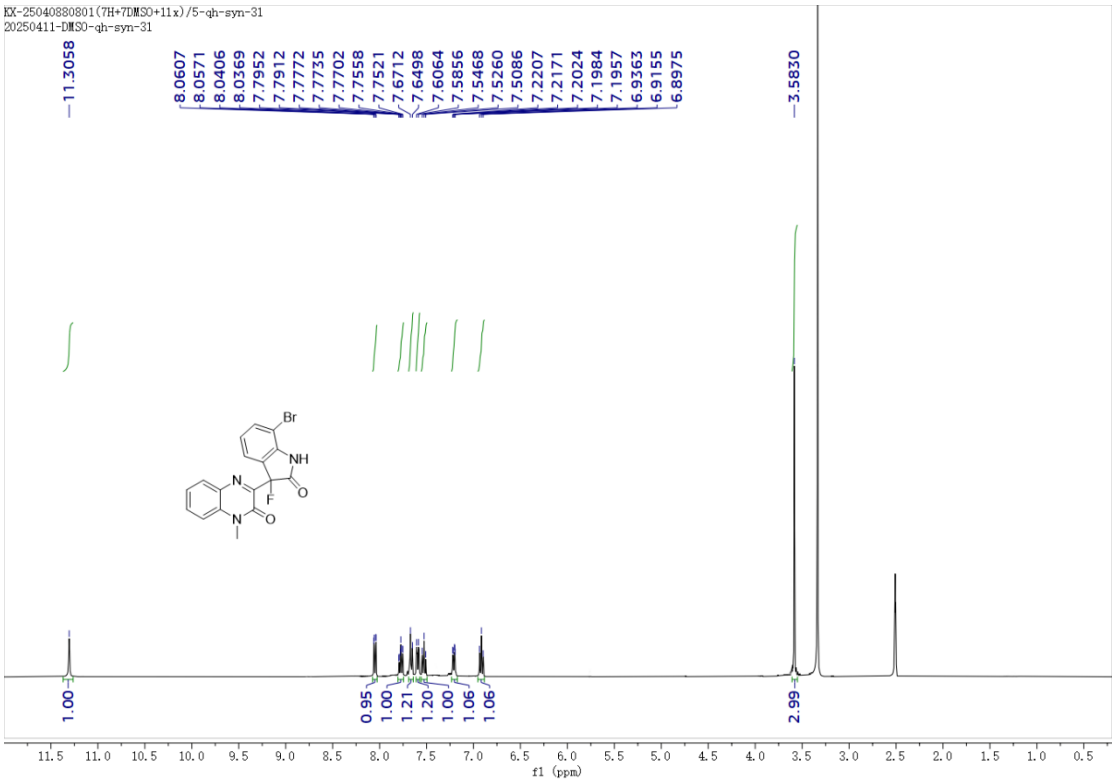


Figure S45. The ^{1}H NMR Spectrum of Compound **3l** in DMSO-d_6

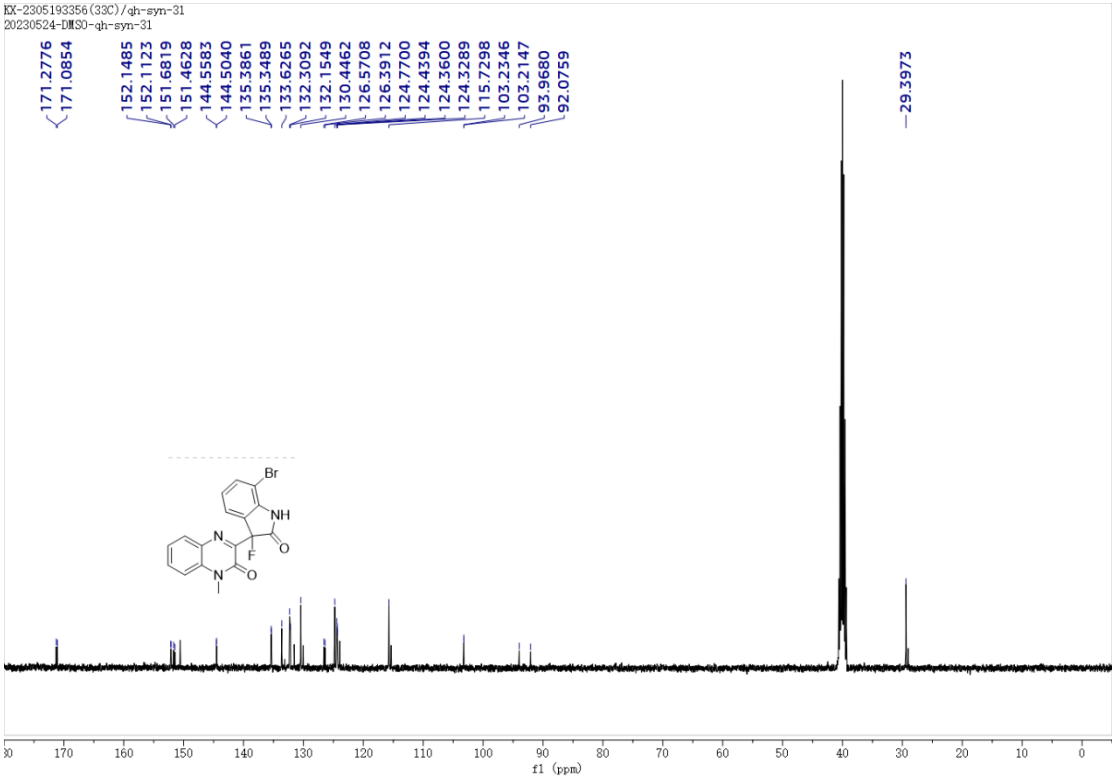


Figure S46. The ^{13}C NMR Spectrum of Compound **3l** in DMSO-d_6

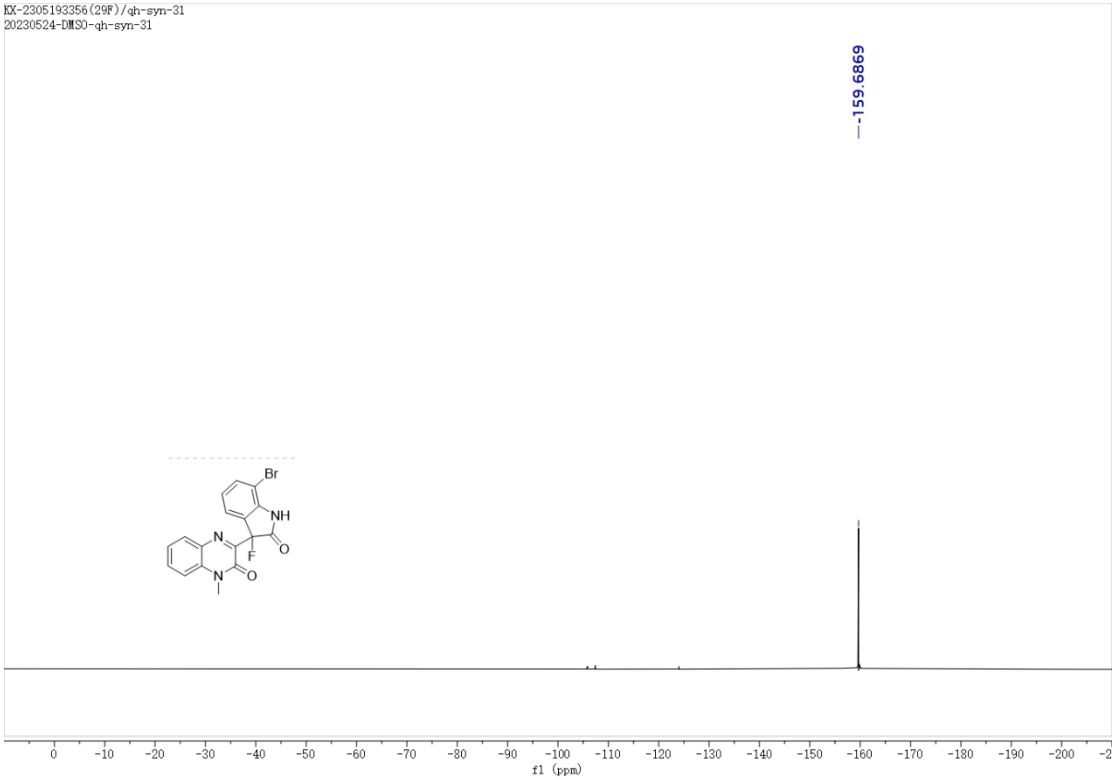


Figure S47. The ^{19}F NMR Spectrum of Compound **3l** in DMSO-d_6

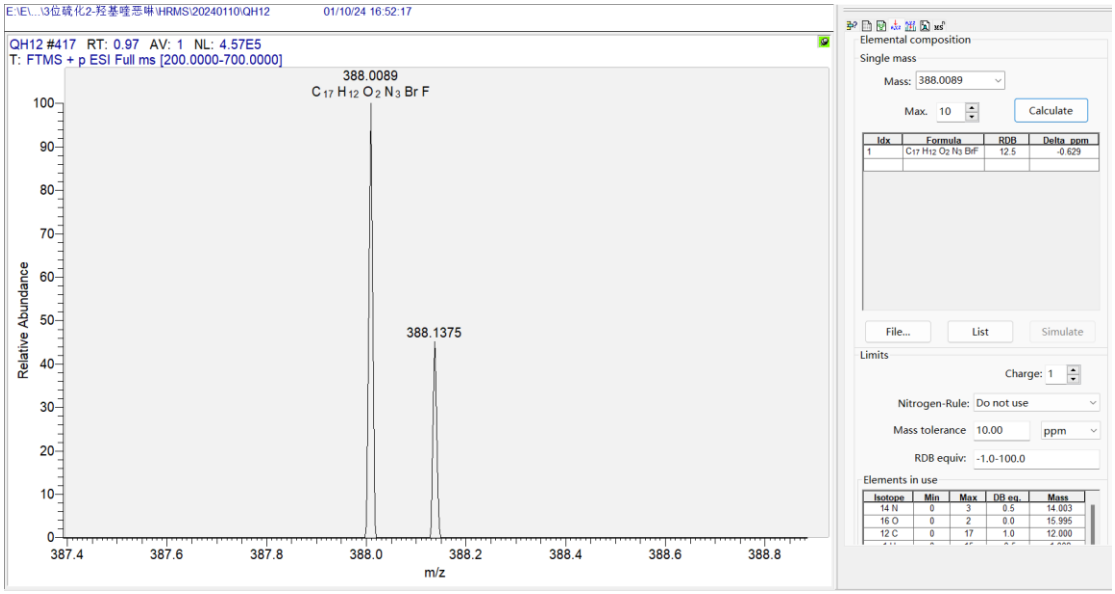


Figure S48. The HR-ESI-MS Spectrum of Compound **3l**

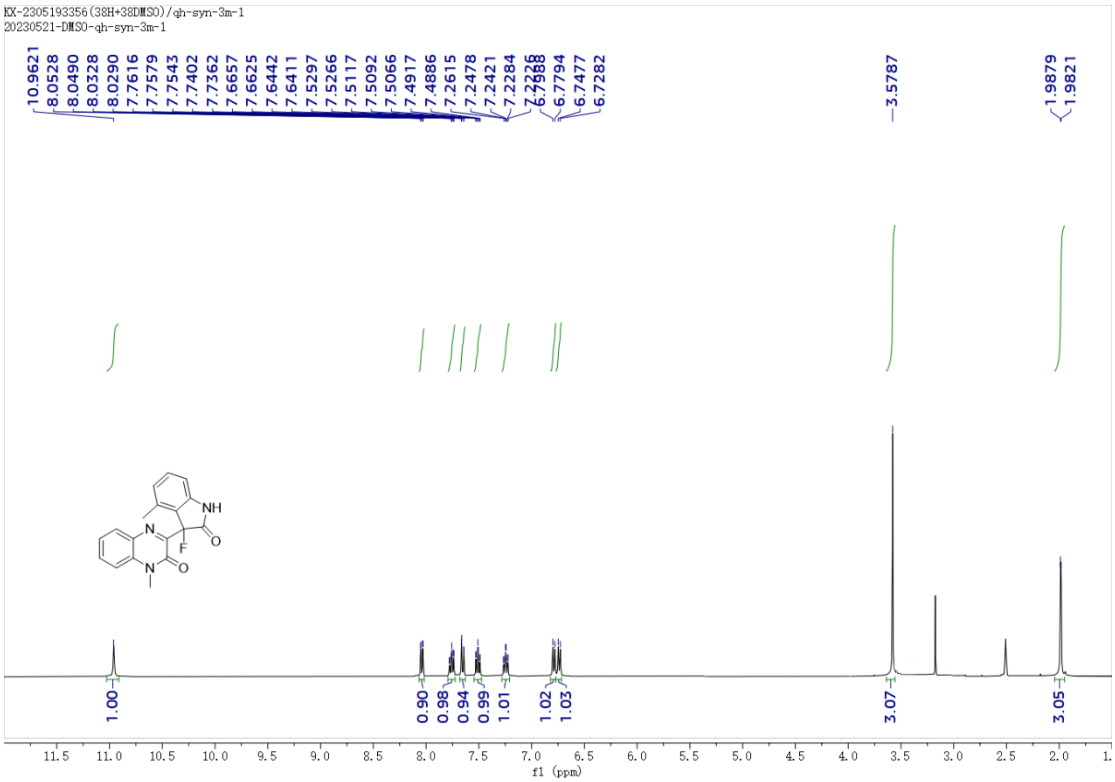


Figure S49. The ^{1}H NMR Spectrum of Compound **3m** in DMSO-d_6

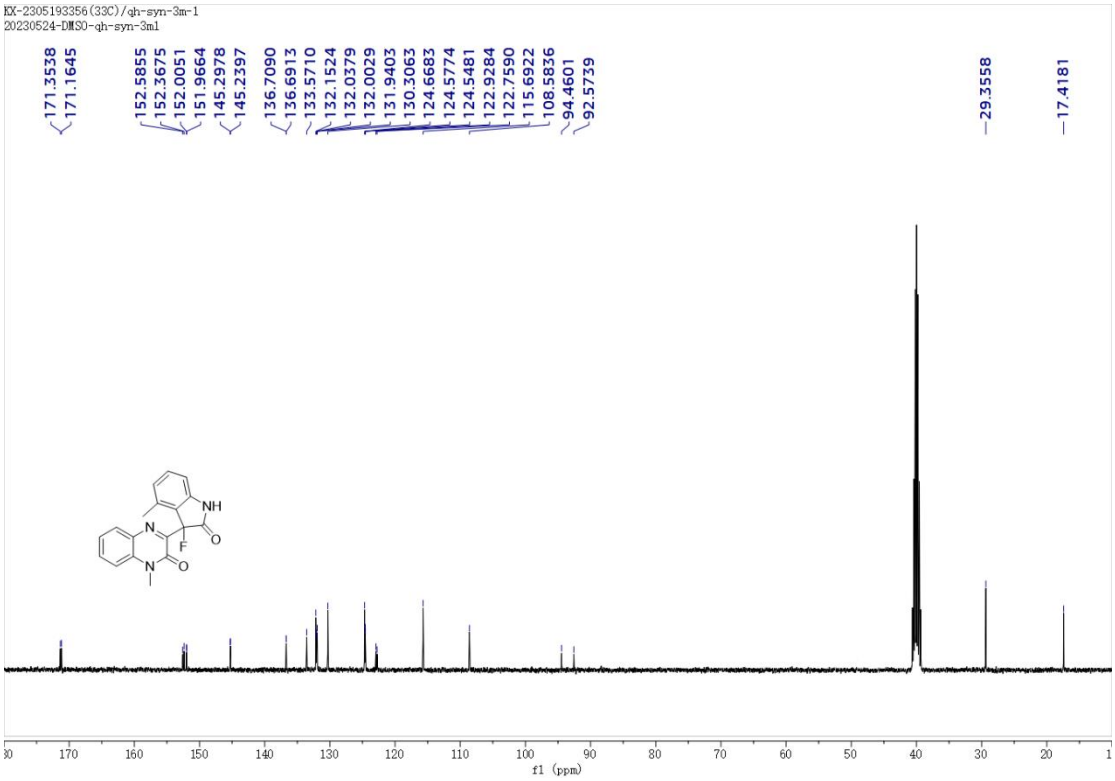


Figure S50. The ^{13}C NMR Spectrum of Compound **3m** in DMSO-d_6

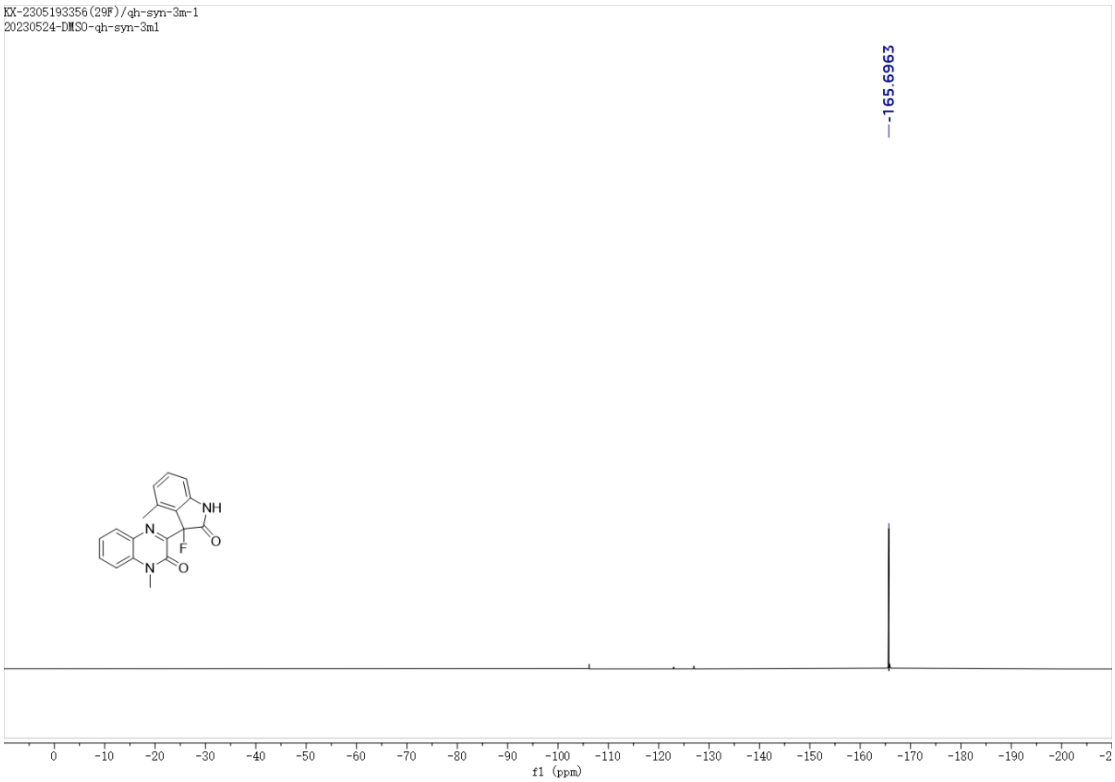


Figure S51. The ^{19}F NMR Spectrum of Compound **3m** in DMSO-d_6

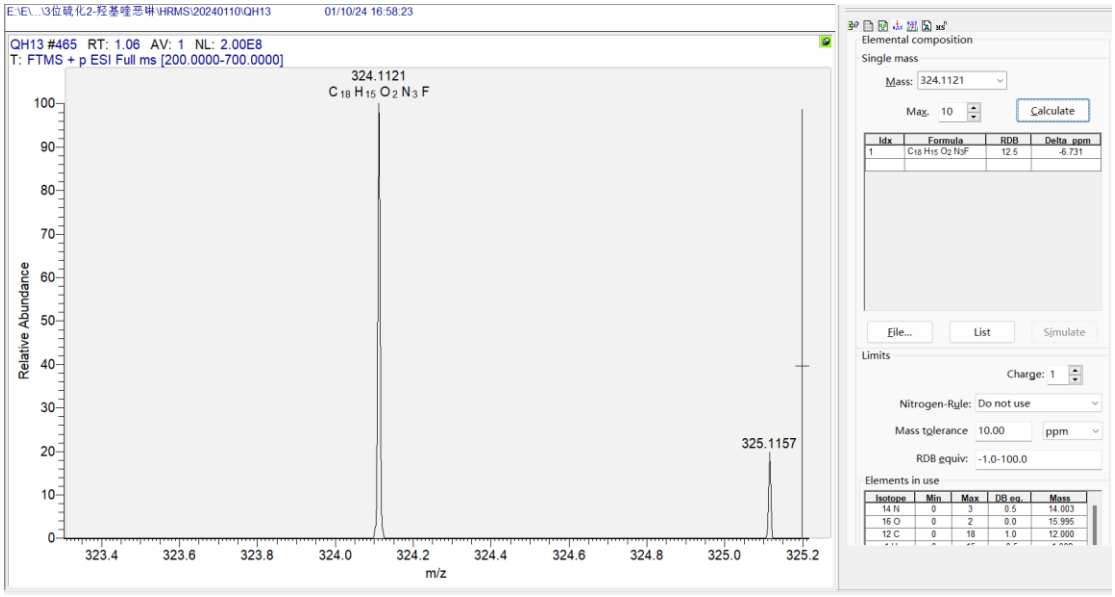


Figure S52. The HR-ESI-MS Spectrum of Compound **3m**

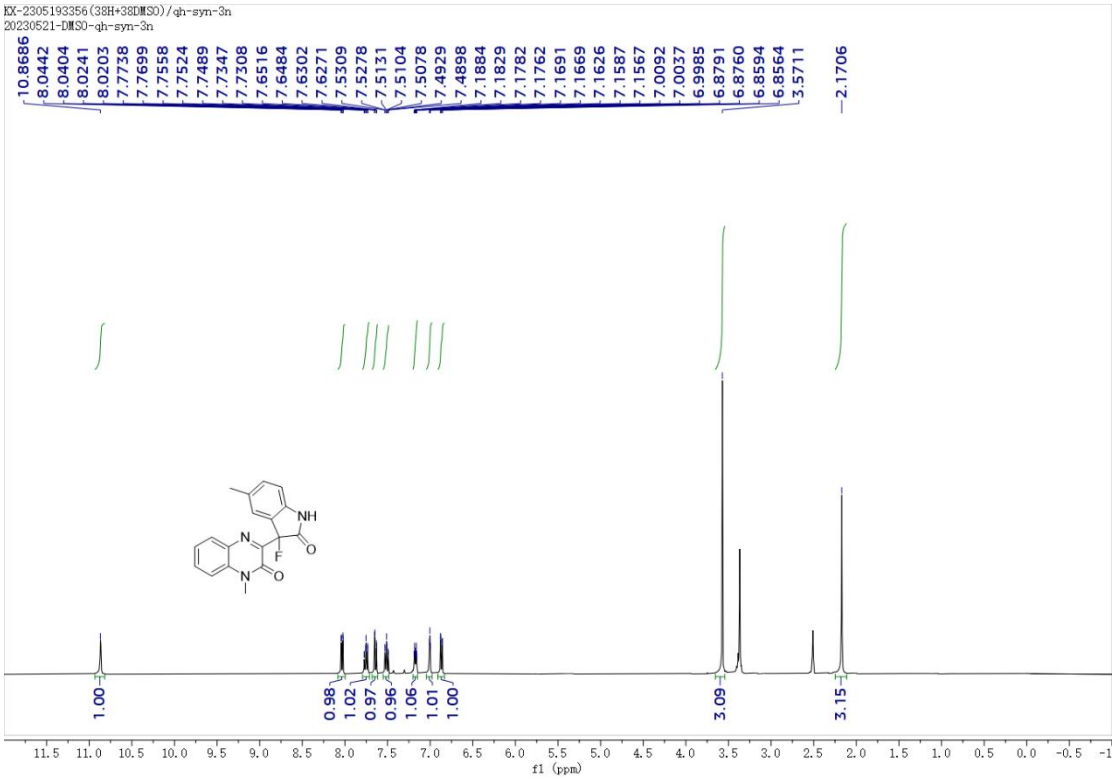


Figure S53. The ^{1}H NMR Spectrum of Compound **3n** in DMSO-d_6

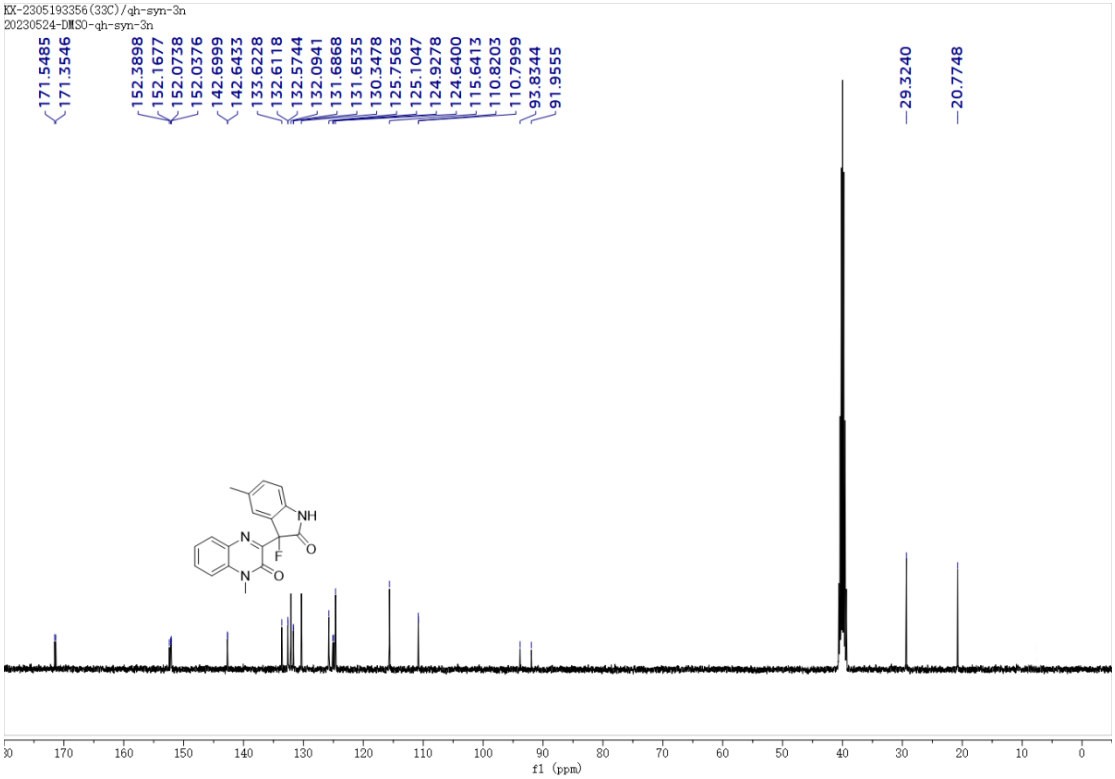


Figure S54 The ^{13}C NMR Spectrum of Compound **3n** in DMSO-d_6

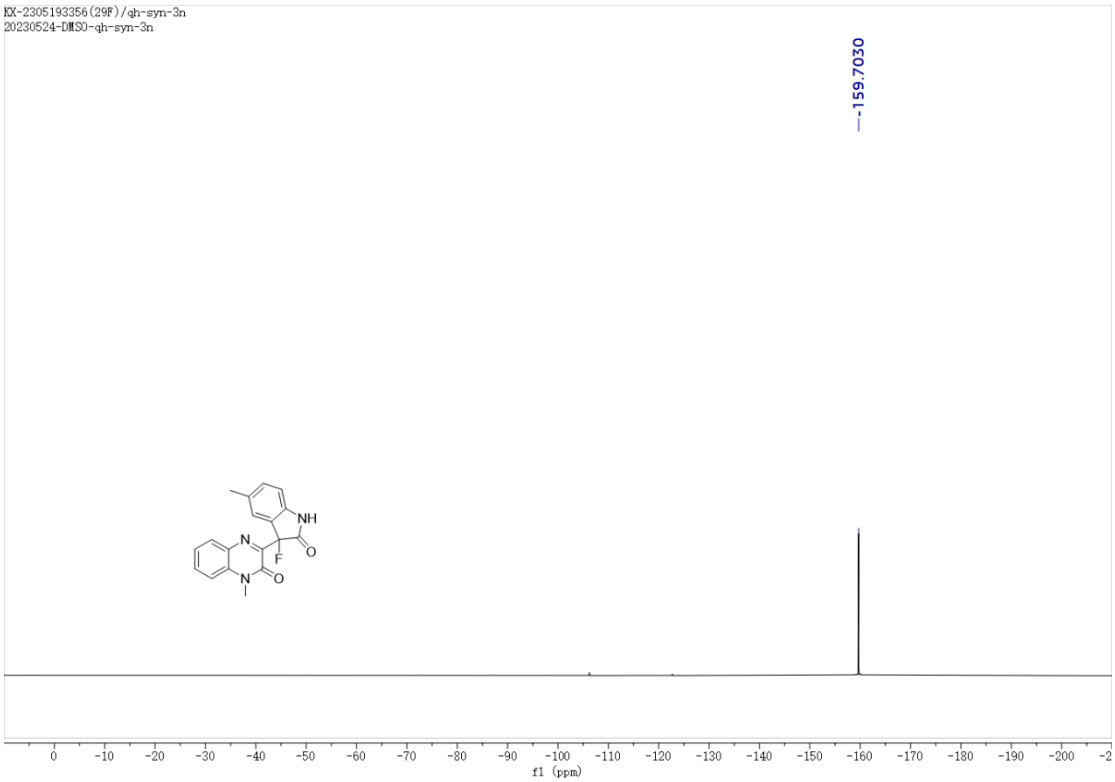


Figure S55. The ^{19}F NMR Spectrum of Compound **3n** in DMSO-d_6

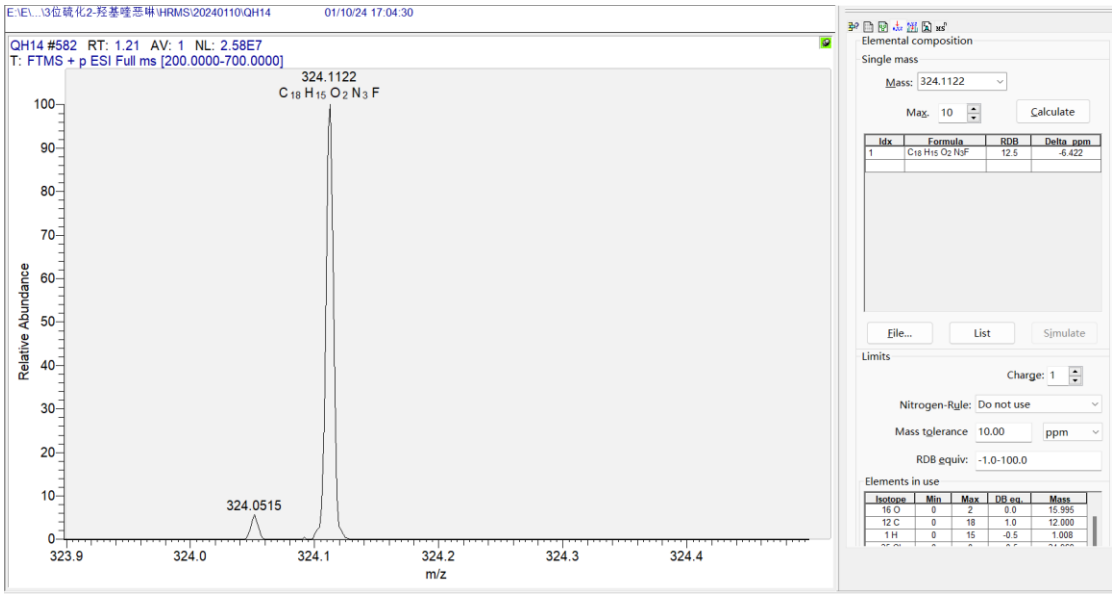


Figure S56. The HR-ESI-MS Spectrum of Compound **3n**

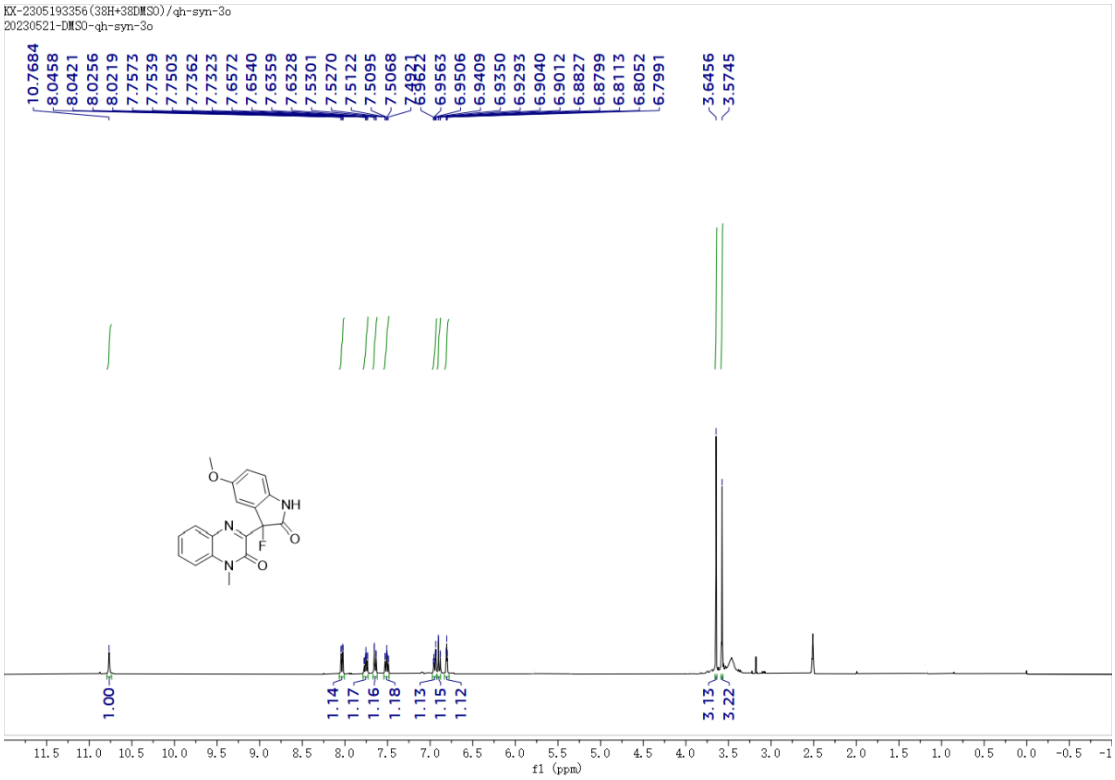


Figure S57. The ^{1}H NMR Spectrum of Compound **3o** in DMSO-d_6

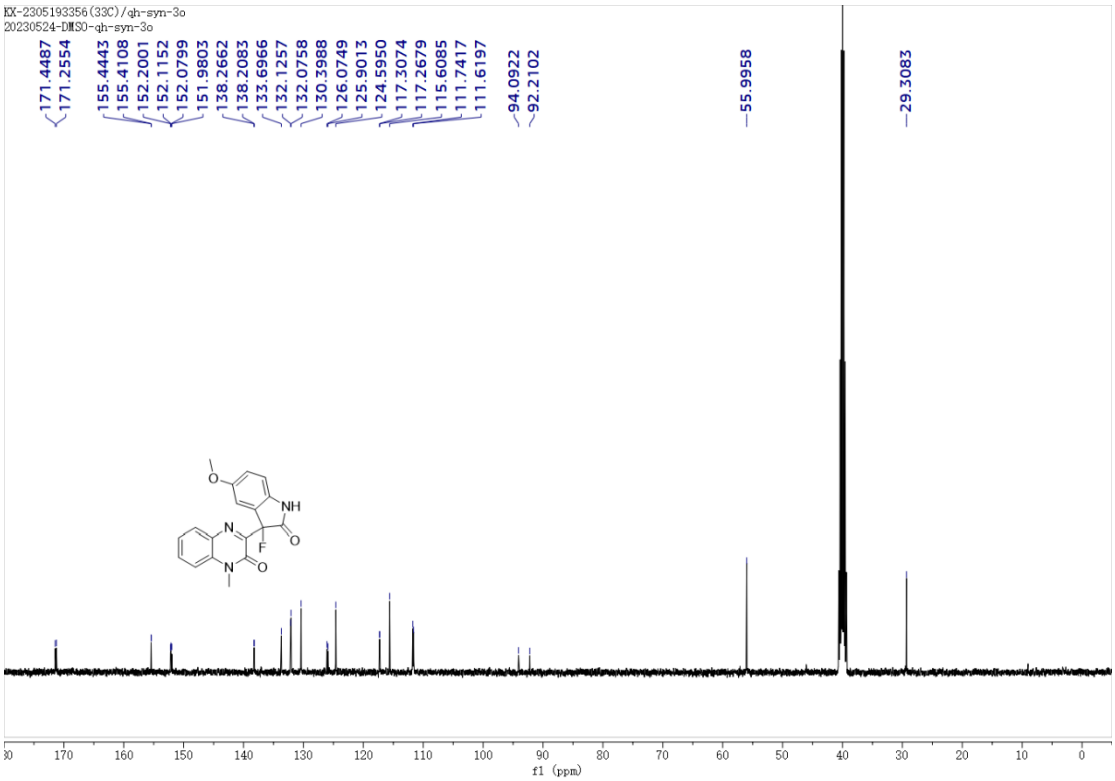


Figure S58. The ^{13}C NMR Spectrum of Compound **3o** in DMSO-d_6

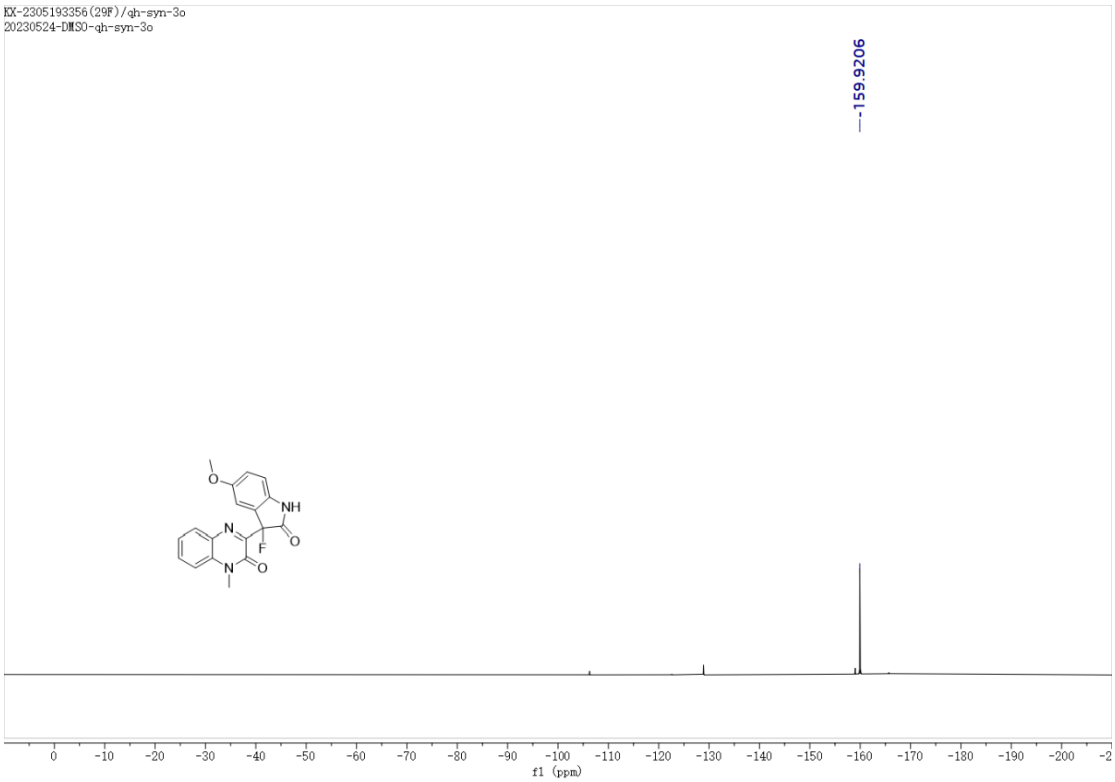


Figure S59. The ^{19}F NMR Spectrum of Compound **3o** in DMSO-d_6

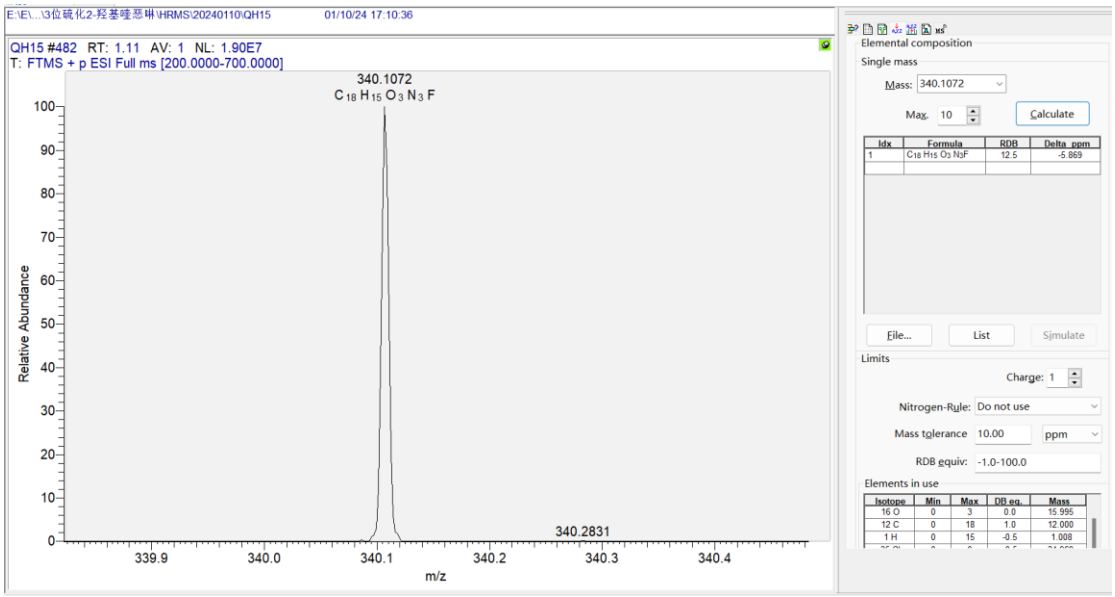


Figure S60. The HR-ESI-MS Spectrum of Compound **3o**

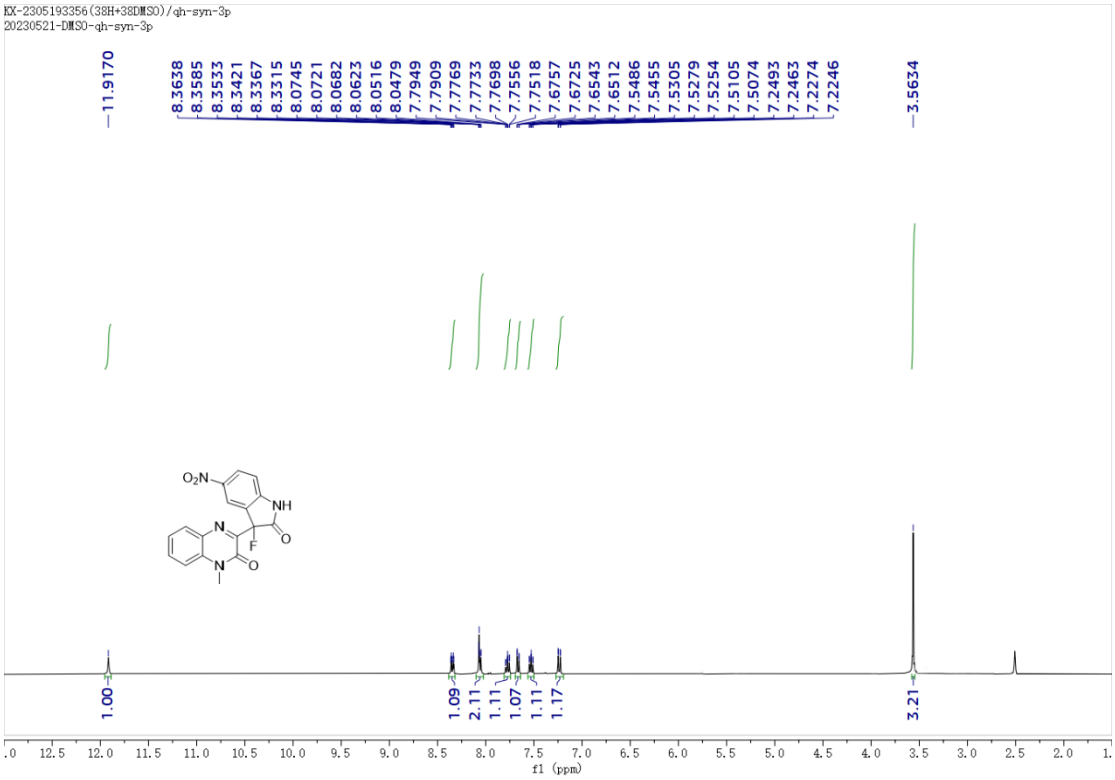


Figure S61. The ^{1}H NMR Spectrum of Compound **3p** in DMSO-d_6

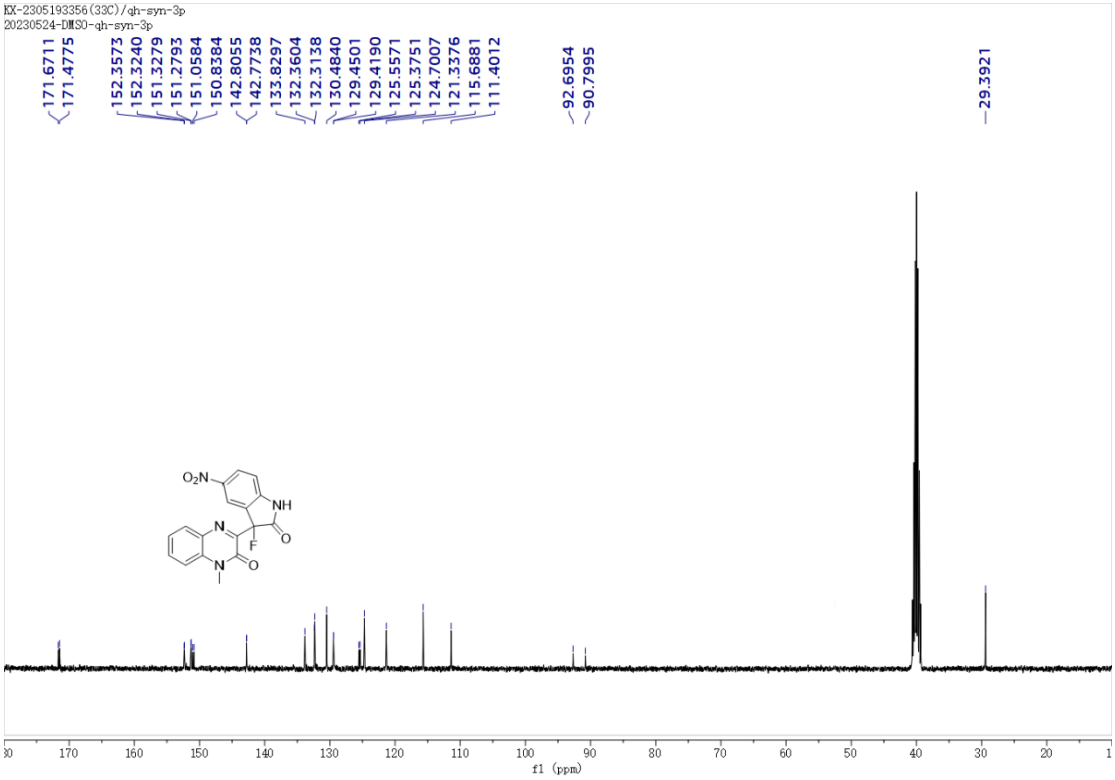


Figure S62. The ^{13}C NMR Spectrum of Compound **3p** in DMSO-d_6

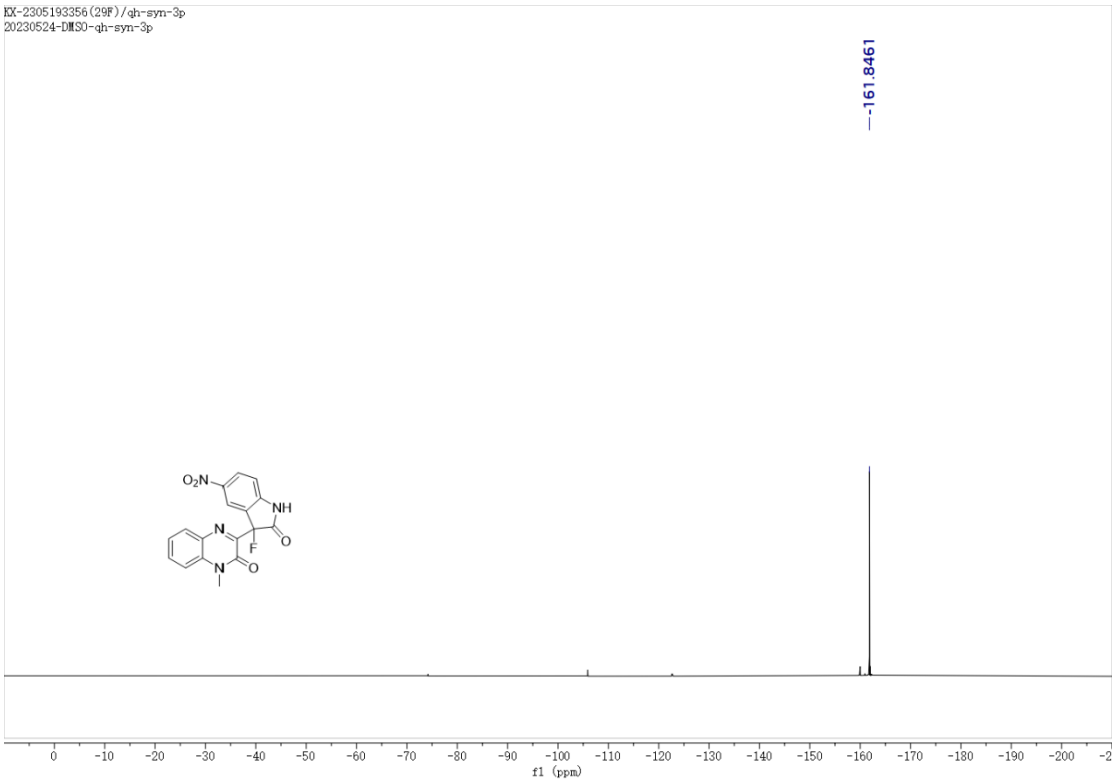


Figure S63 The ^{19}F NMR Spectrum of Compound **3p** in DMSO-d_6

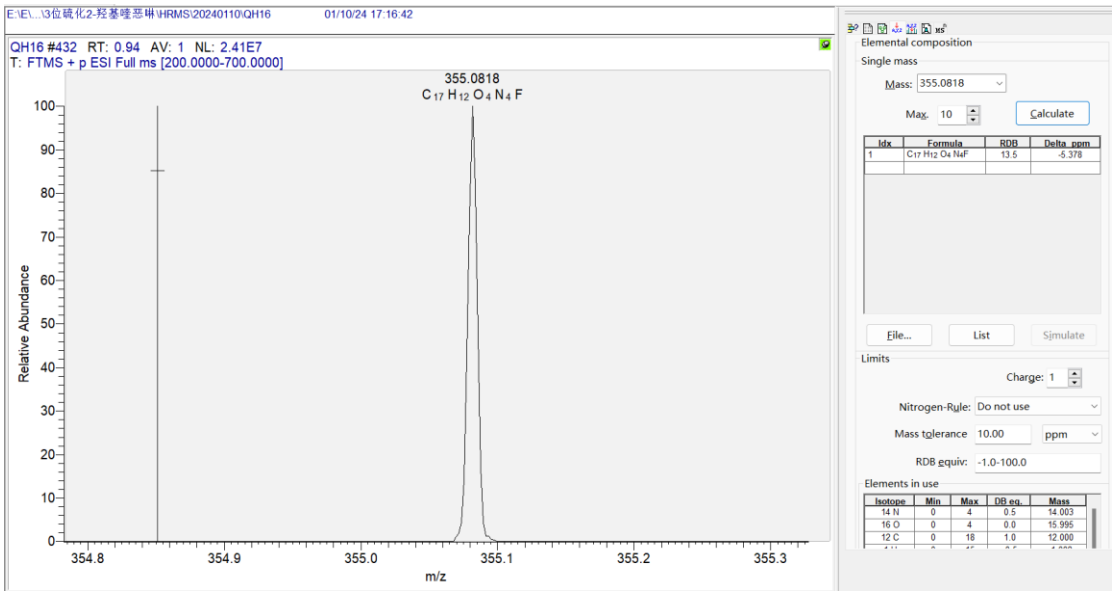


Figure S64. The HR-ESI-MS Spectrum of Compound **3p**

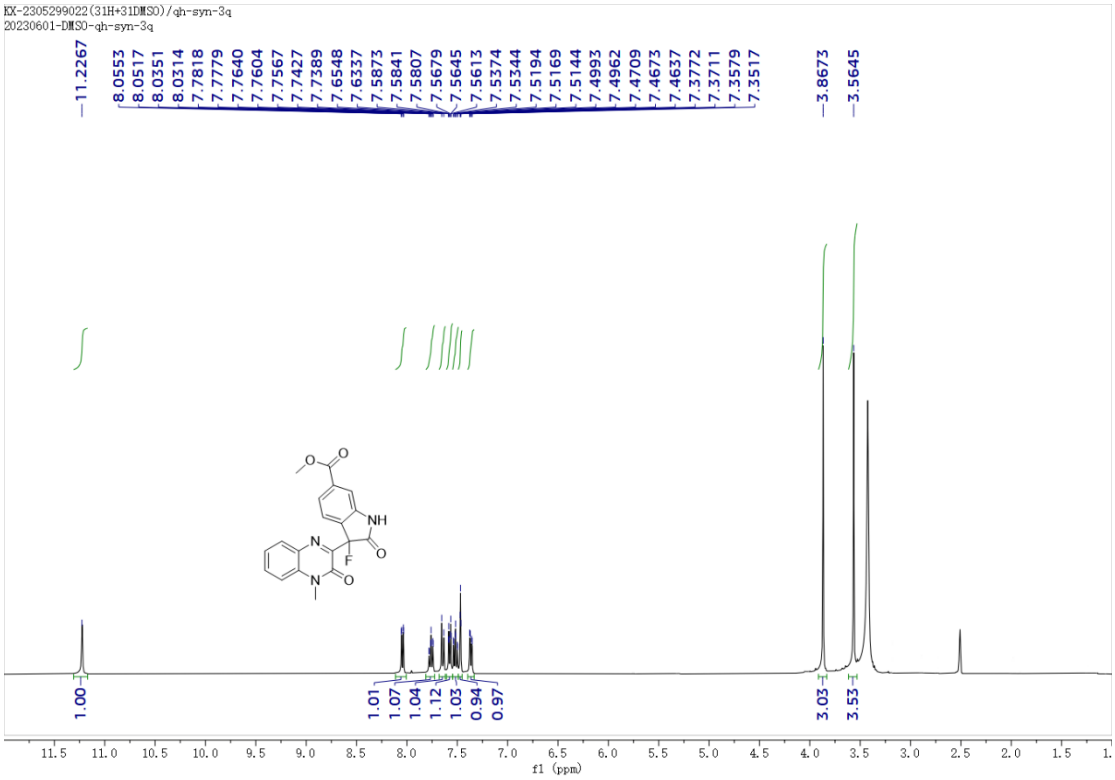


Figure S65 The ^{1}H NMR Spectrum of Compound **3q** in DMSO-d_6

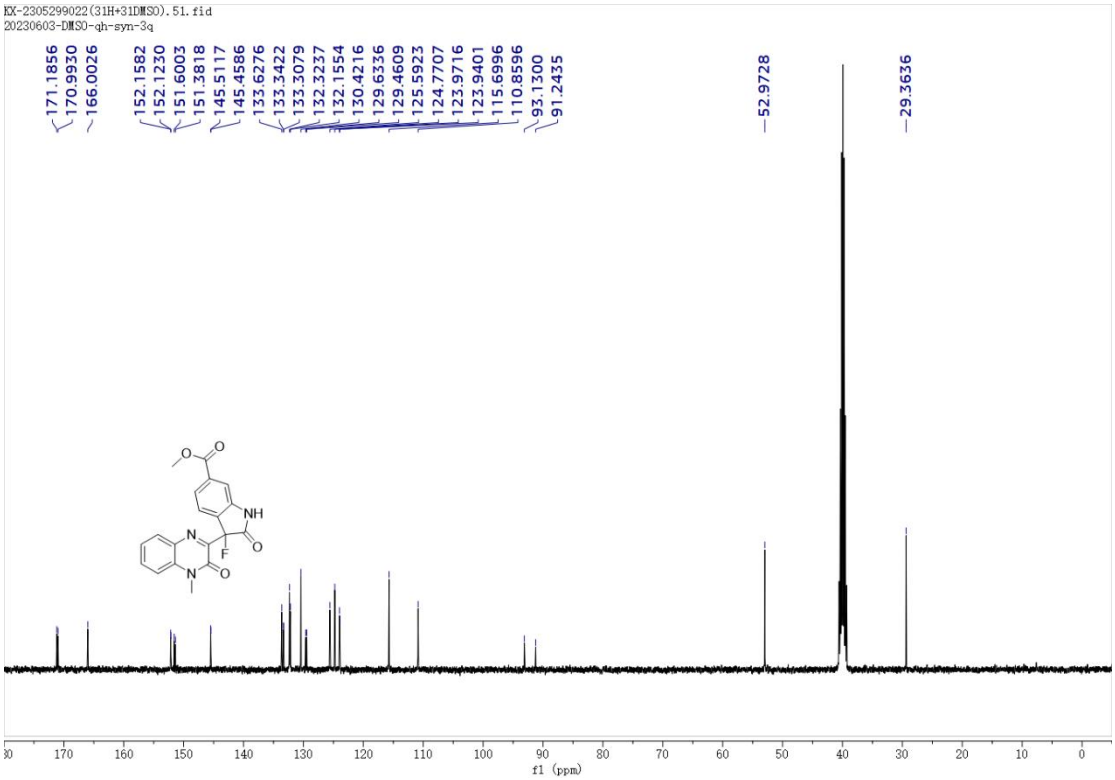


Figure S66 The ^{13}C NMR Spectrum of Compound **3q** in DMSO-d_6

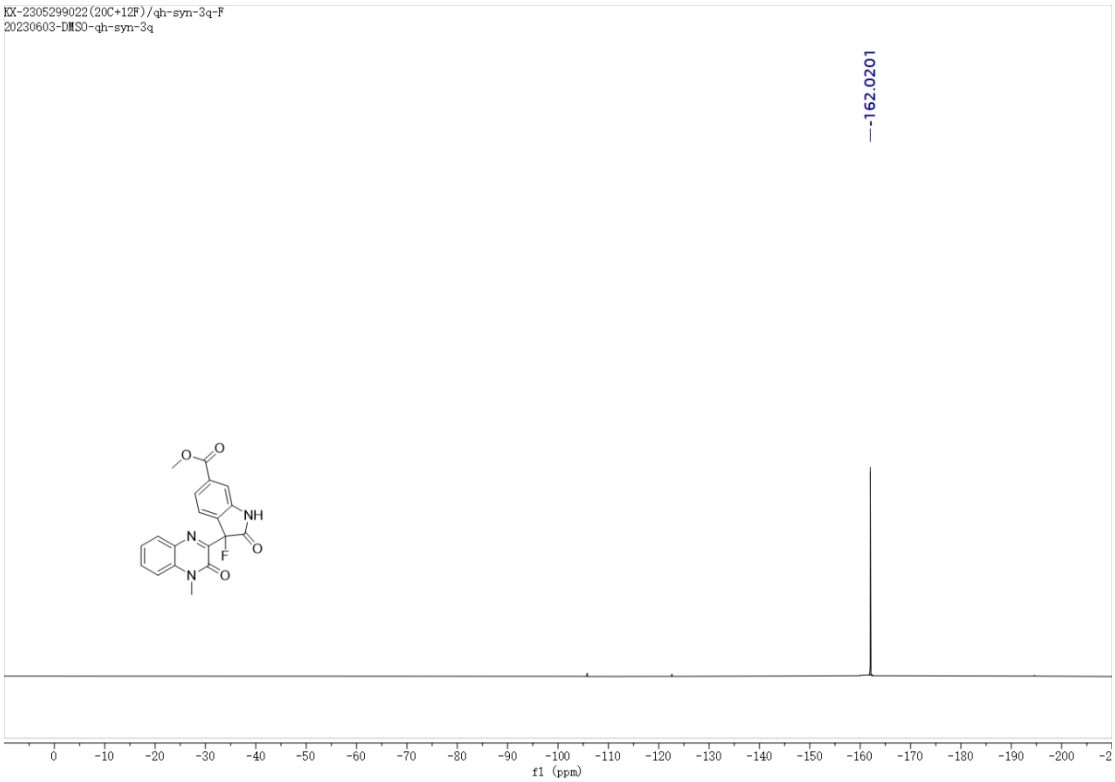


Figure S67 The ^{19}F NMR Spectrum of Compound **3q** in DMSO-d_6

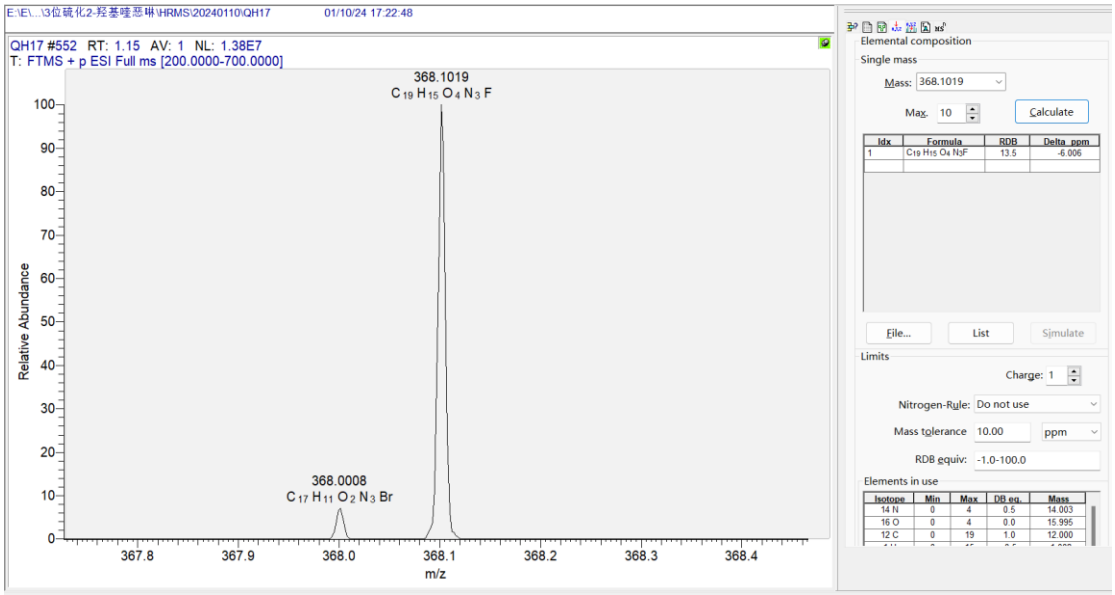


Figure S68. The HR-ESI-MS Spectrum of Compound **3q**

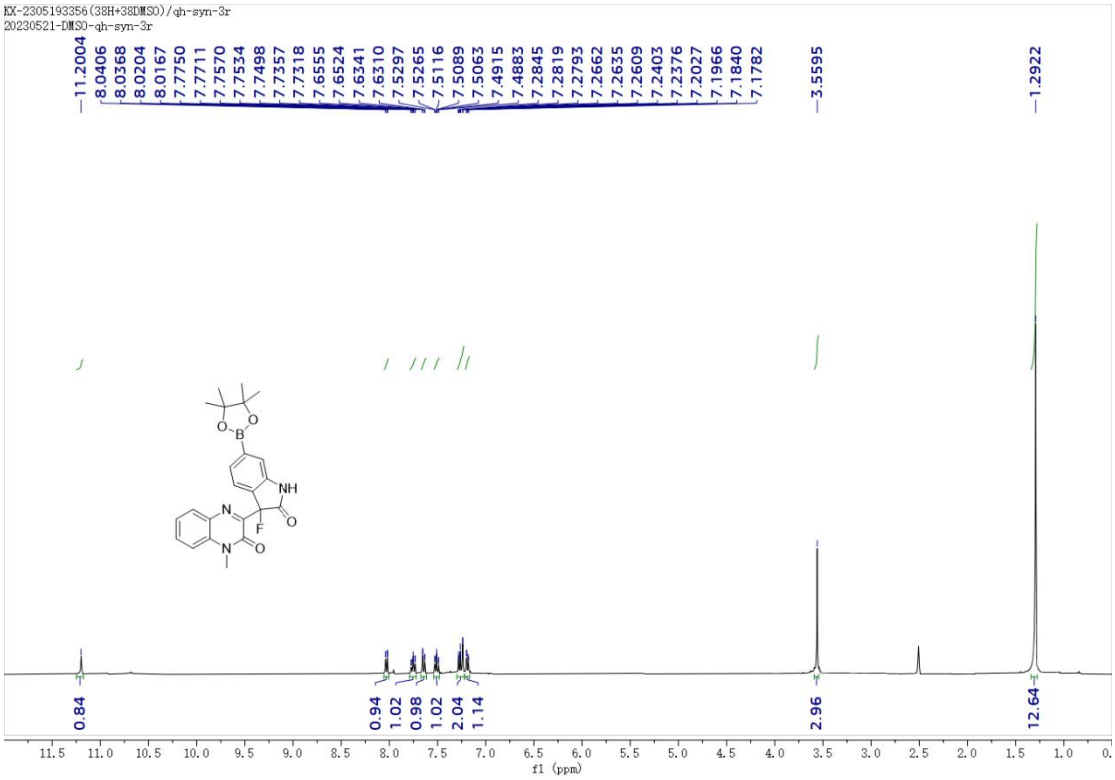


Figure S69 The ^{1}H NMR Spectrum of Compound **3r** in DMSO-d_6

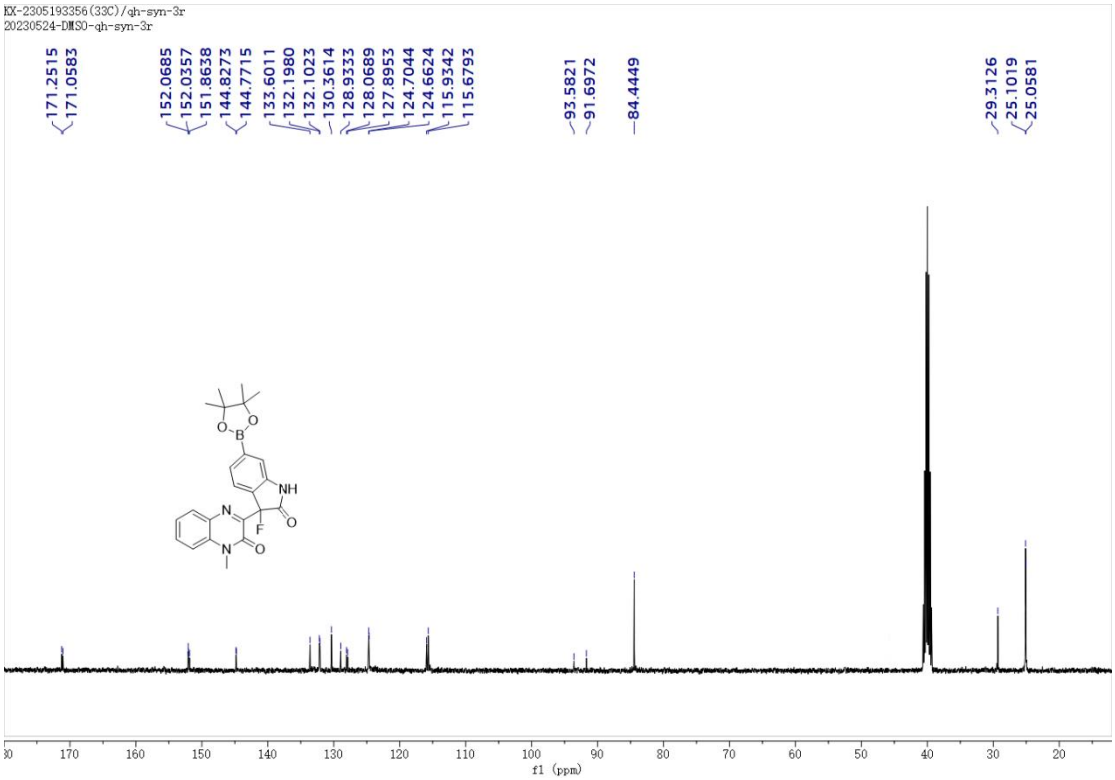


Figure S70 The ^{13}C NMR Spectrum of Compound **3r** in DMSO-d_6

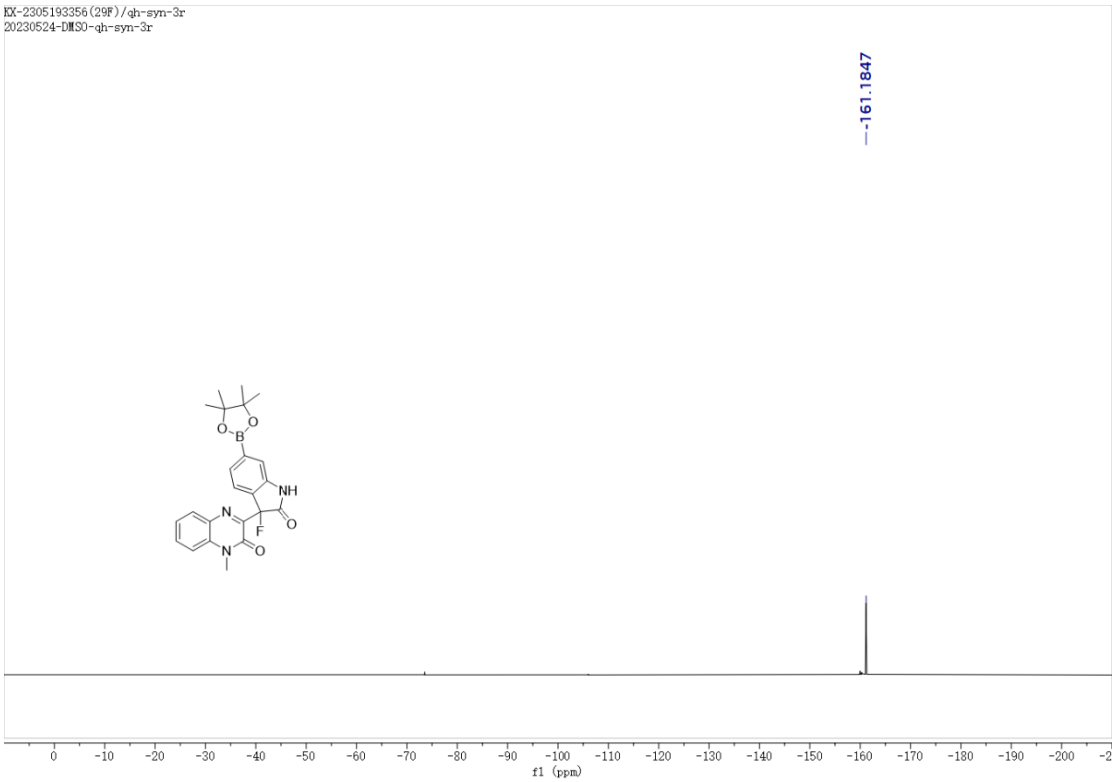


Figure S71 The ^{19}F NMR Spectrum of Compound **3r** in DMSO-d_6

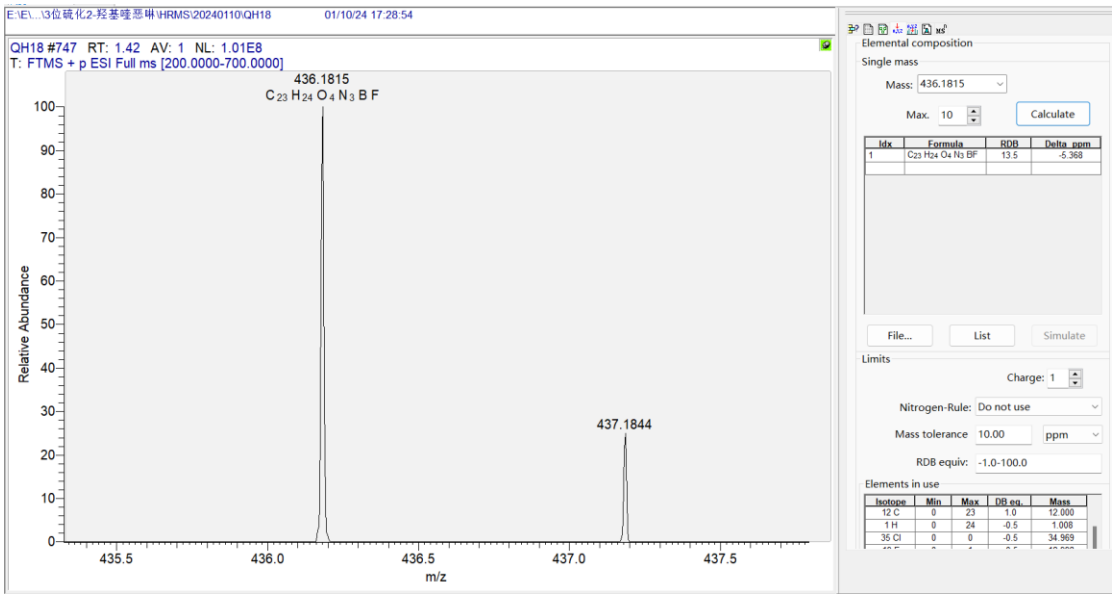


Figure S72. The HR-ESI-MS Spectrum of Compound **3r**

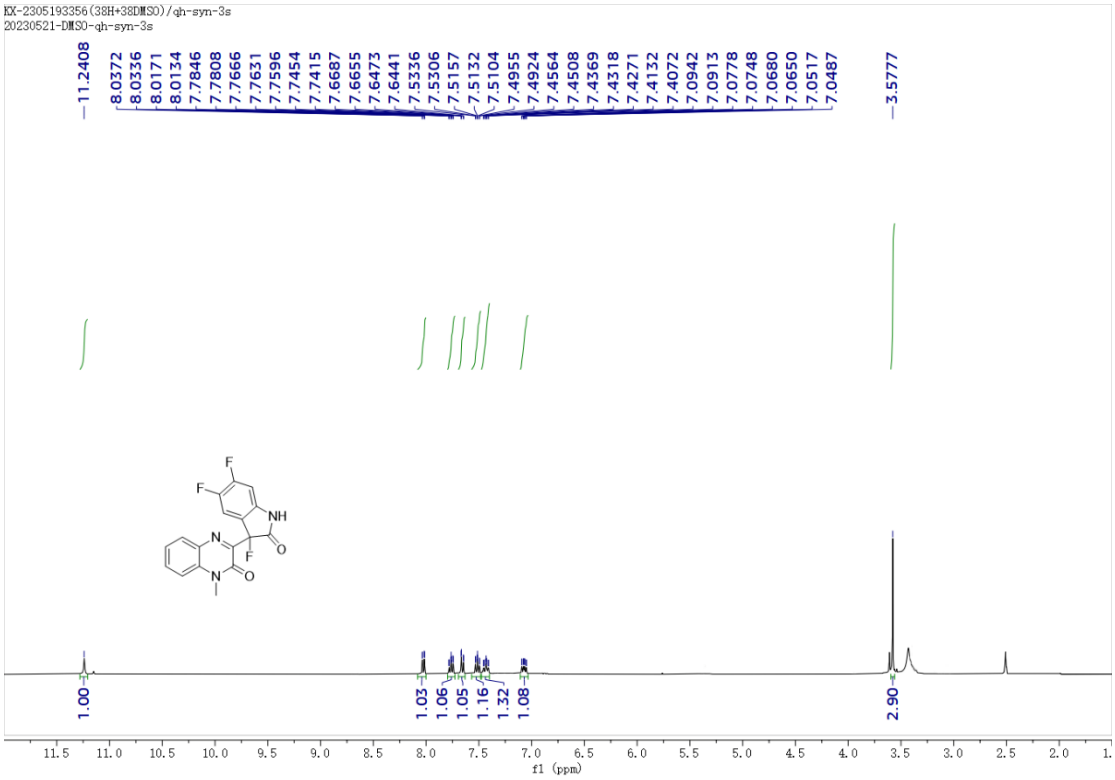


Figure S73 The ^{1}H NMR Spectrum of Compound **3s** in DMSO-d_6

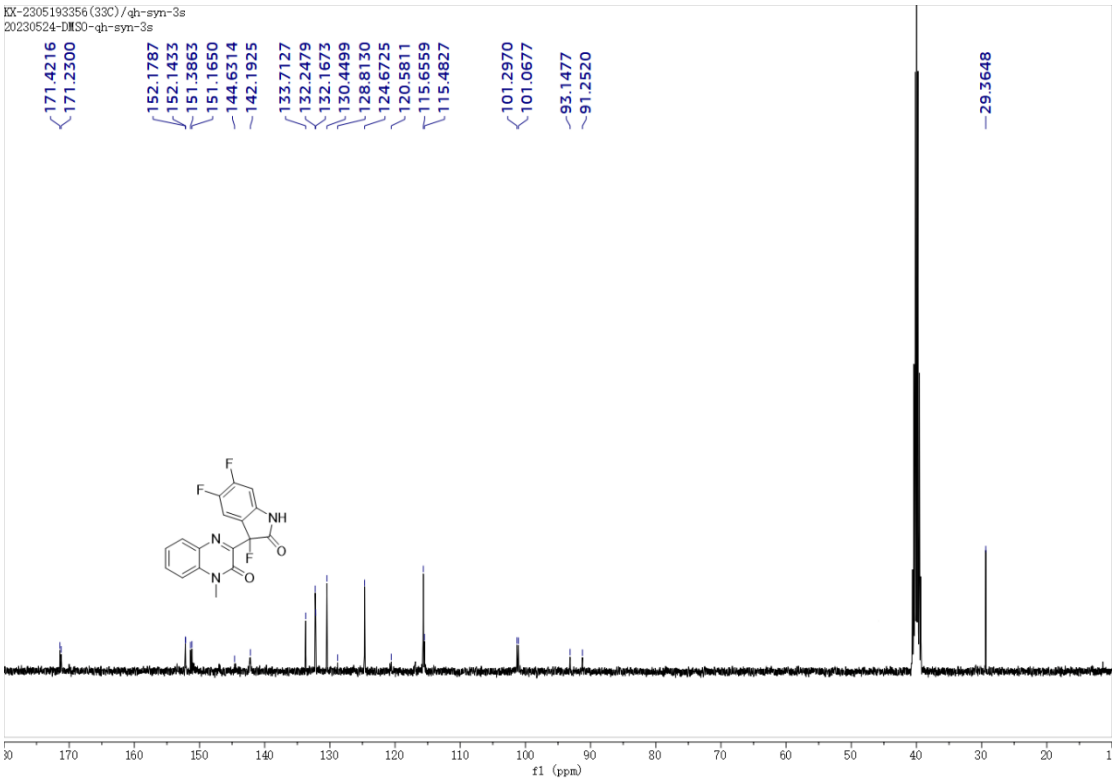


Figure S74 The ^{13}C NMR Spectrum of Compound **3s** in DMSO-d_6

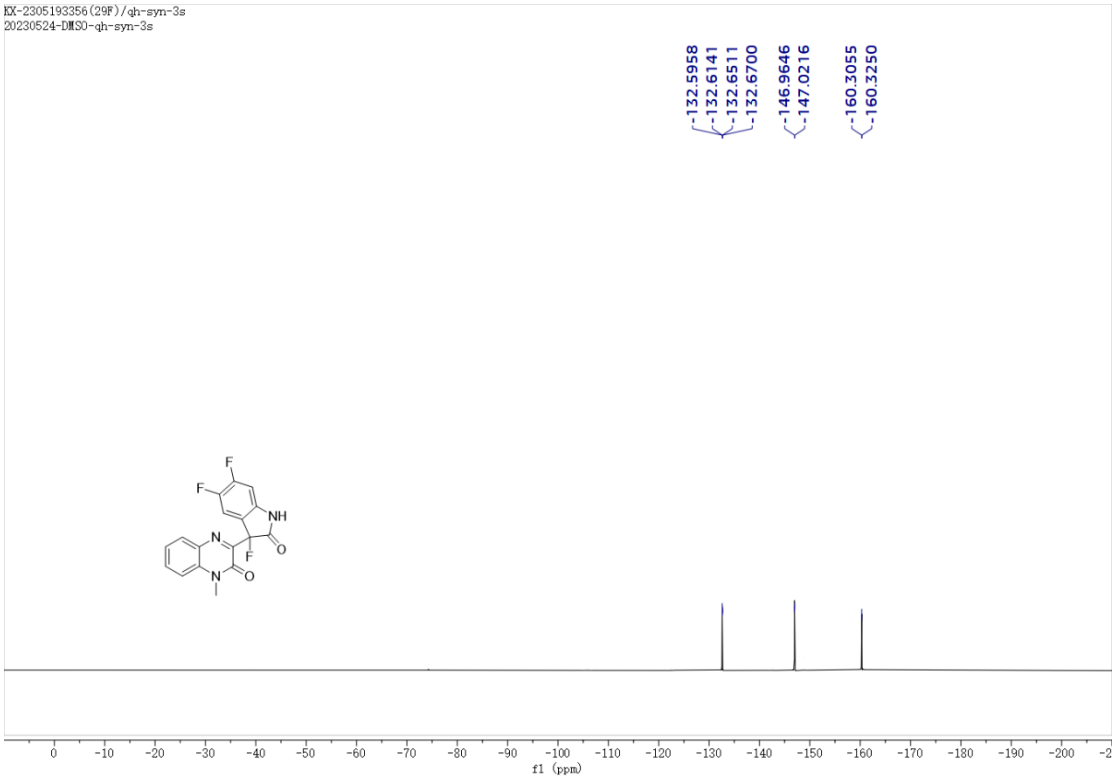


Figure S75 The ^{19}F NMR Spectrum of Compound **3s** in DMSO-d_6

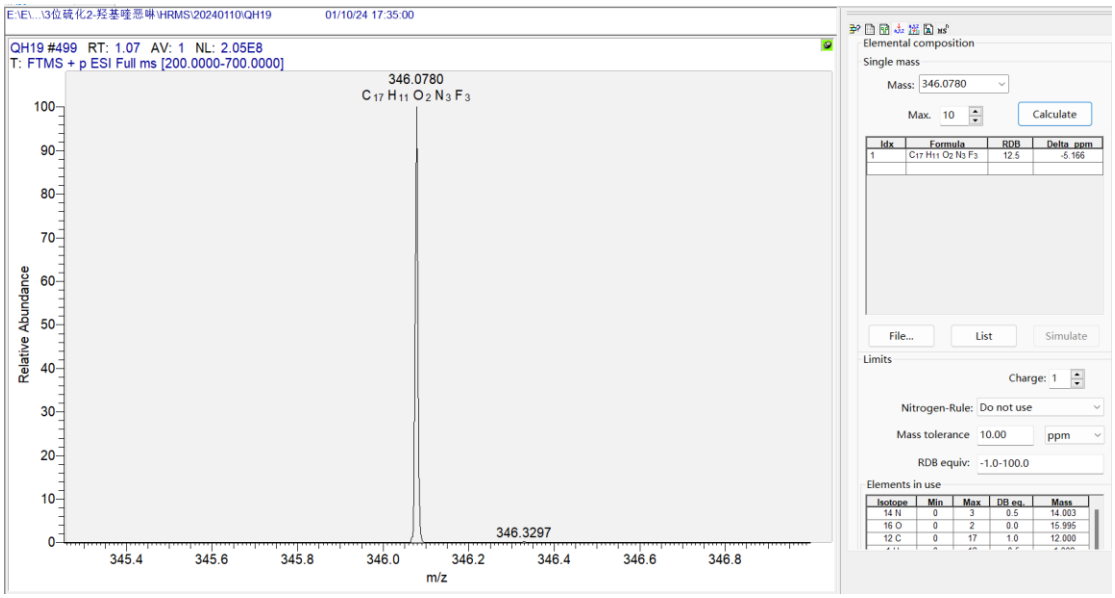


Figure S76. The HR-ESI-MS Spectrum of Compound **3s**

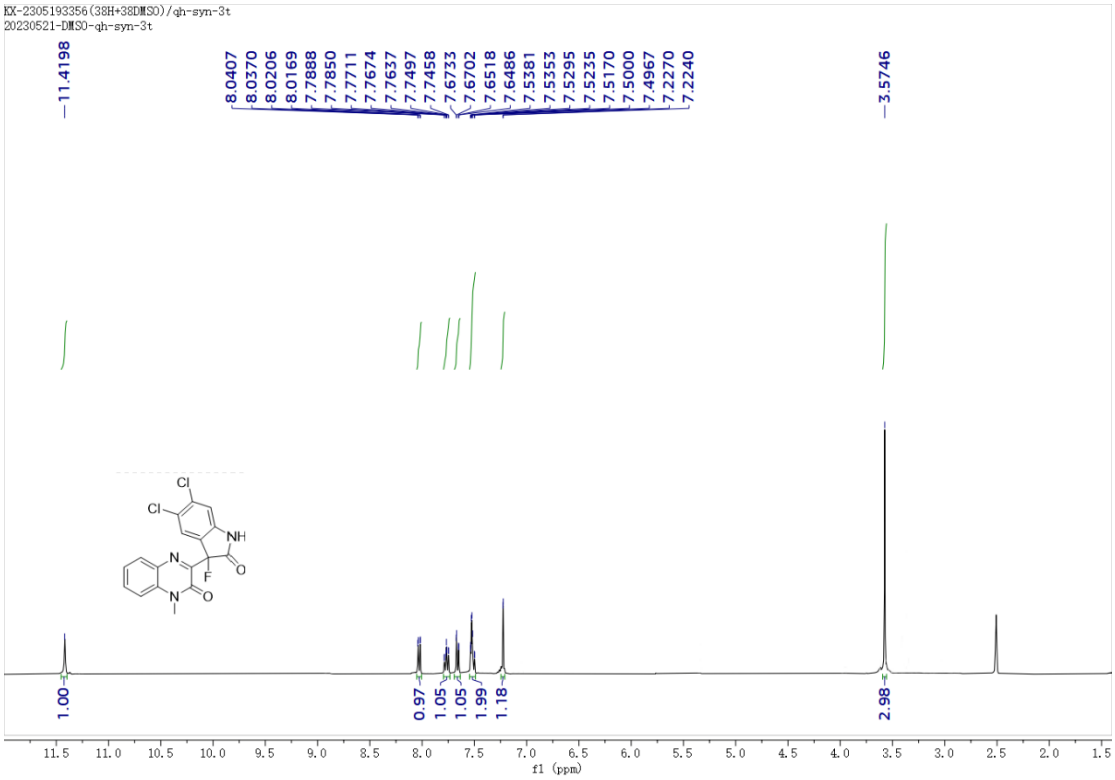


Figure S77 The ^{1}H NMR Spectrum of Compound **3t** in DMSO-d_6

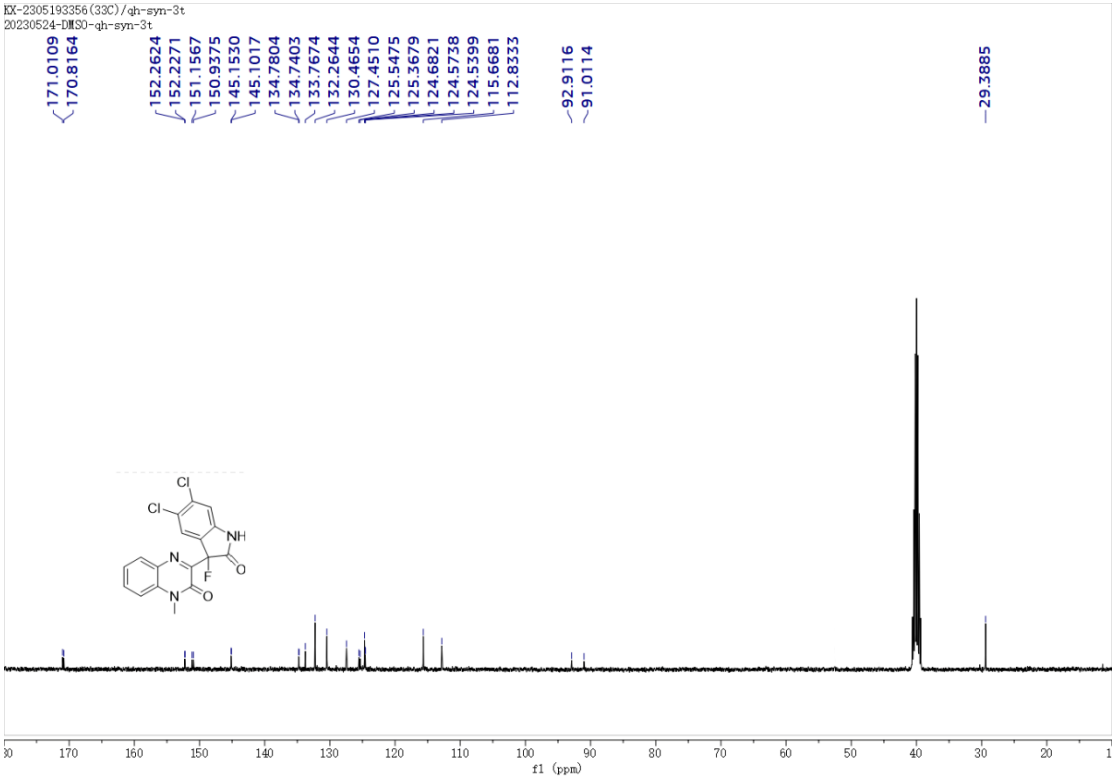


Figure S78 The ^{13}C NMR Spectrum of Compound **3t** in DMSO-d_6

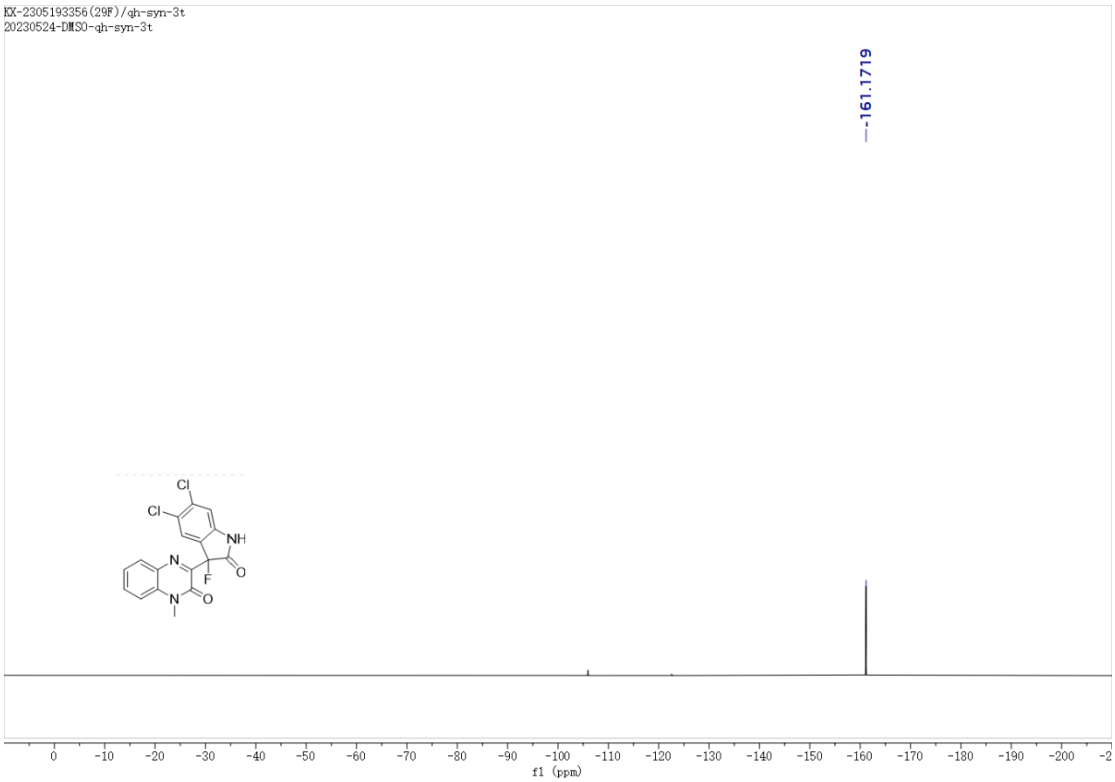


Figure S79 The ^{19}F NMR Spectrum of Compound **3t** in DMSO-d_6

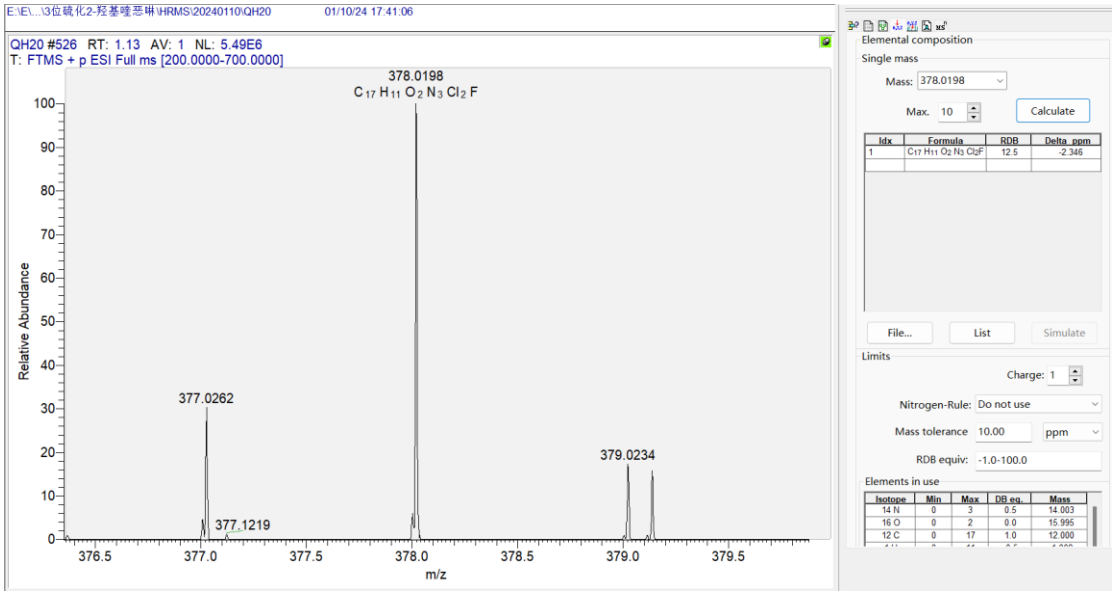


Figure S80. The HR-ESI-MS Spectrum of Compound **3t**

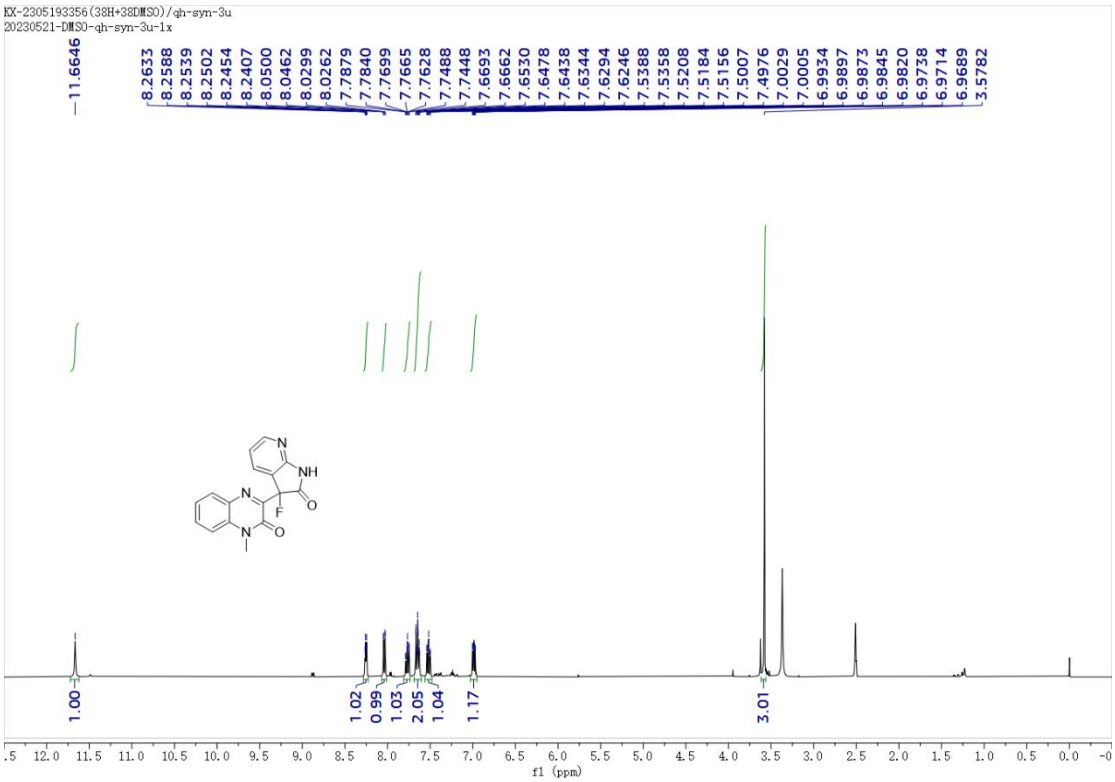


Figure S81 The ^{1}H NMR Spectrum of Compound **3u** in DMSO-d_6

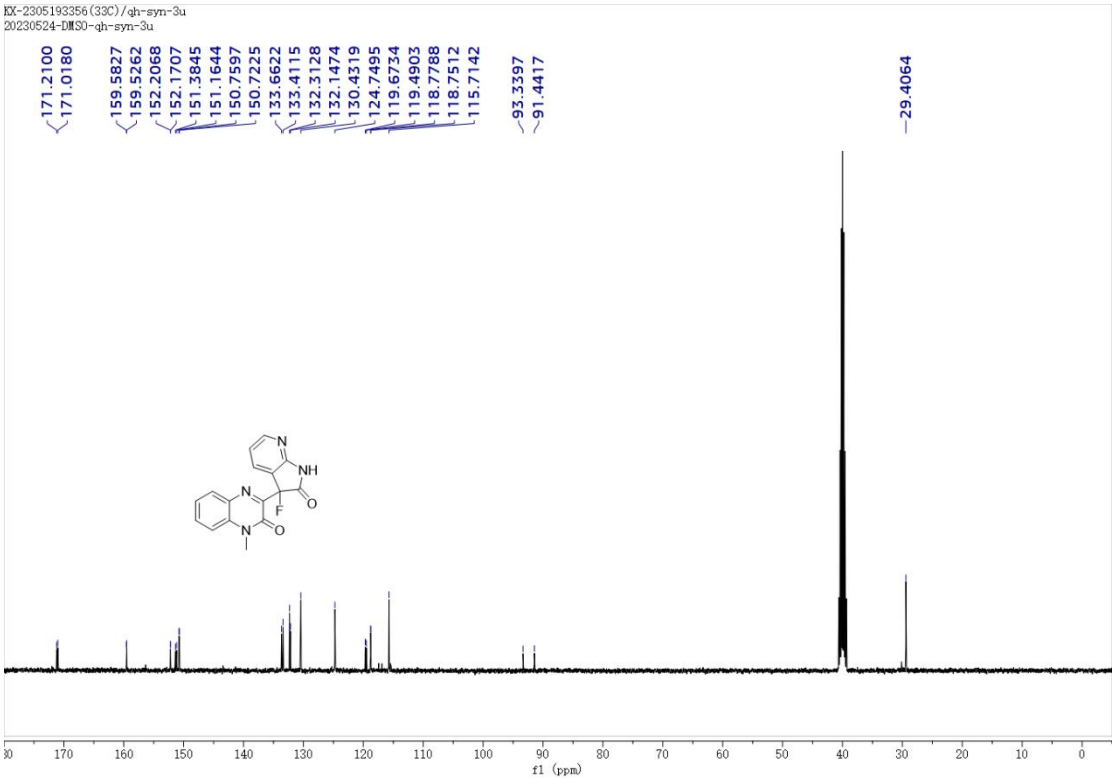


Figure S82 The ^{13}C NMR Spectrum of Compound **3u** in DMSO-d_6

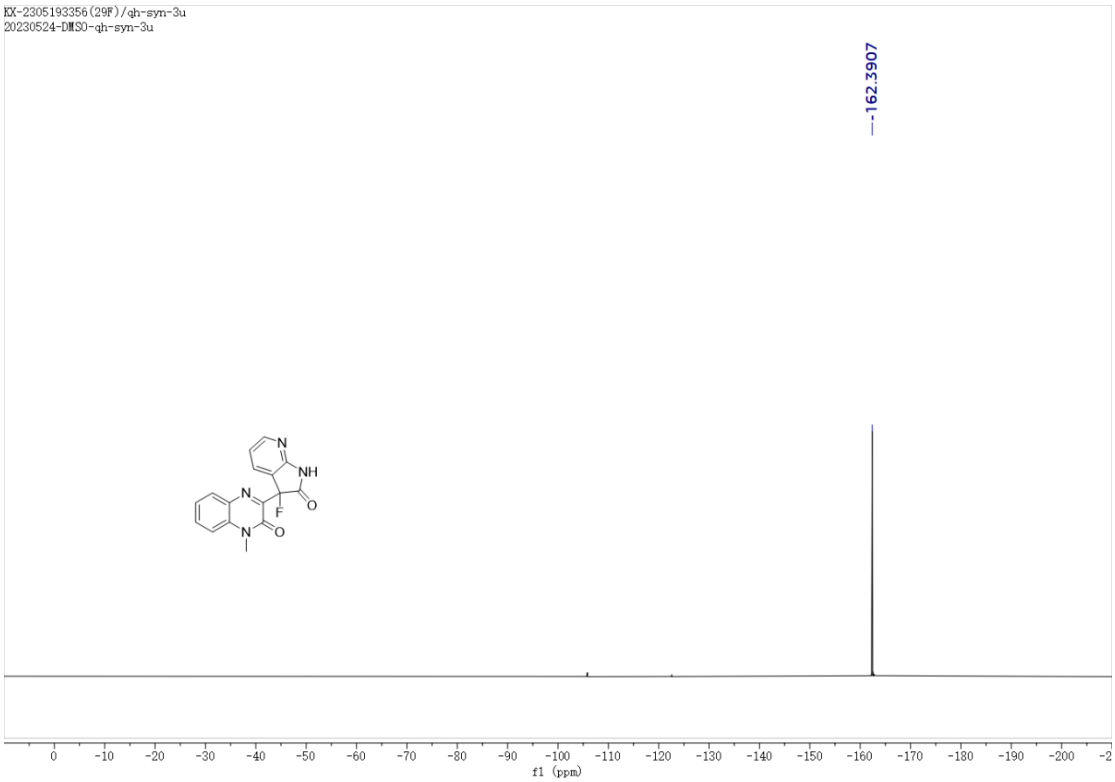


Figure S83 The ^{19}F NMR Spectrum of Compound **3u** in DMSO-d_6

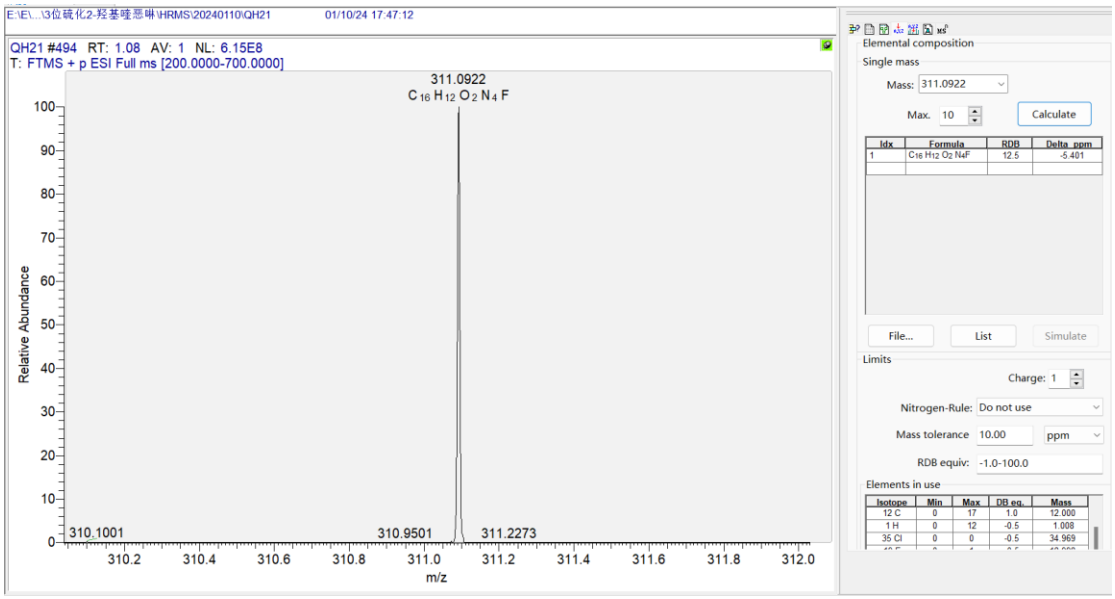


Figure S84. The HR-ESI-MS Spectrum of Compound **3u**

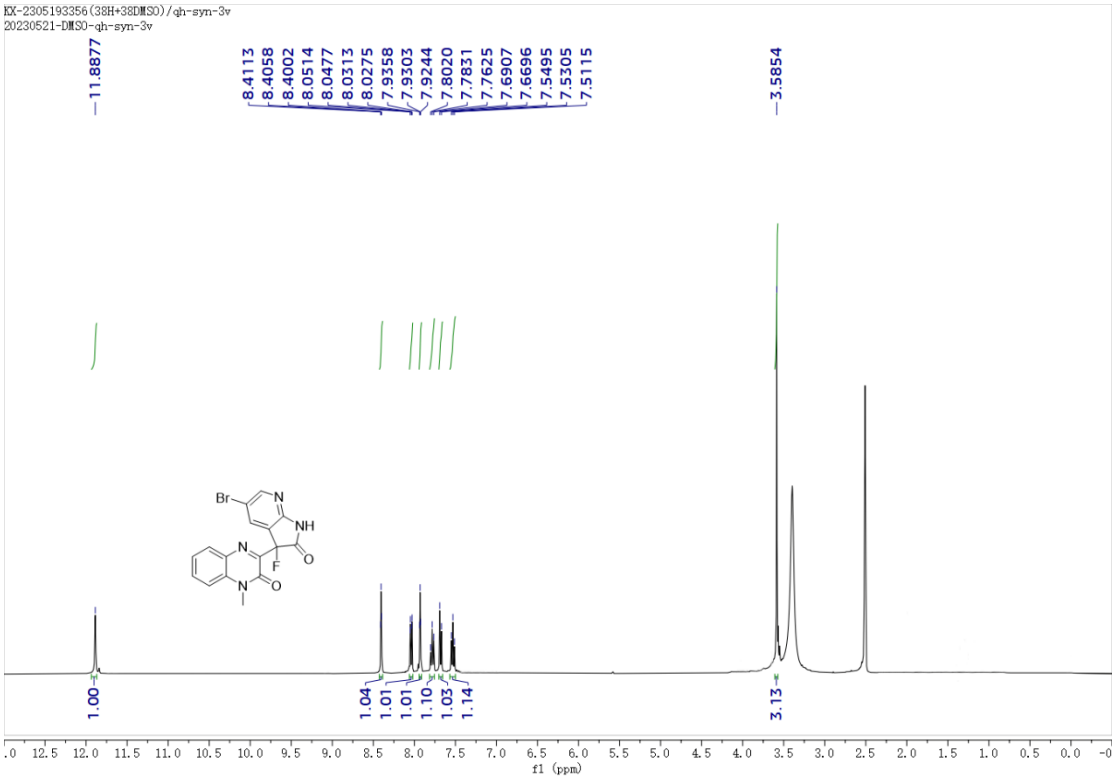


Figure S85 The ^{1}H NMR Spectrum of Compound **3v** in DMSO-d_6

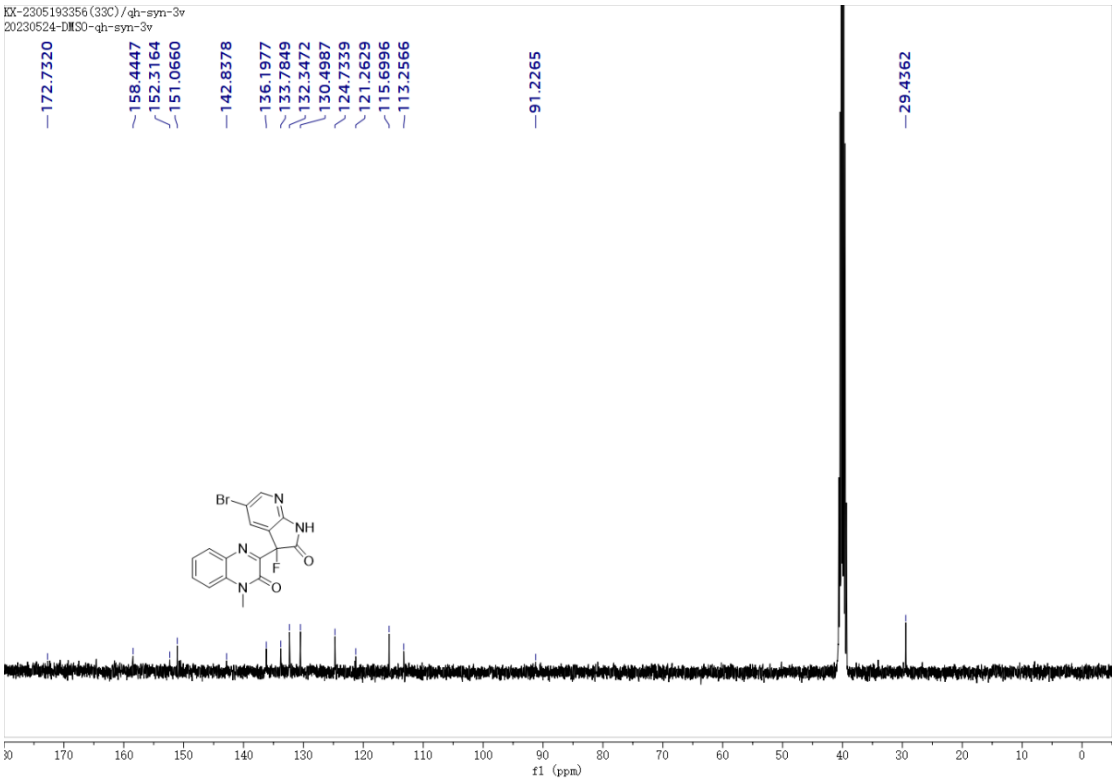


Figure S86 The ^{13}C NMR Spectrum of Compound **3v** in DMSO-d_6

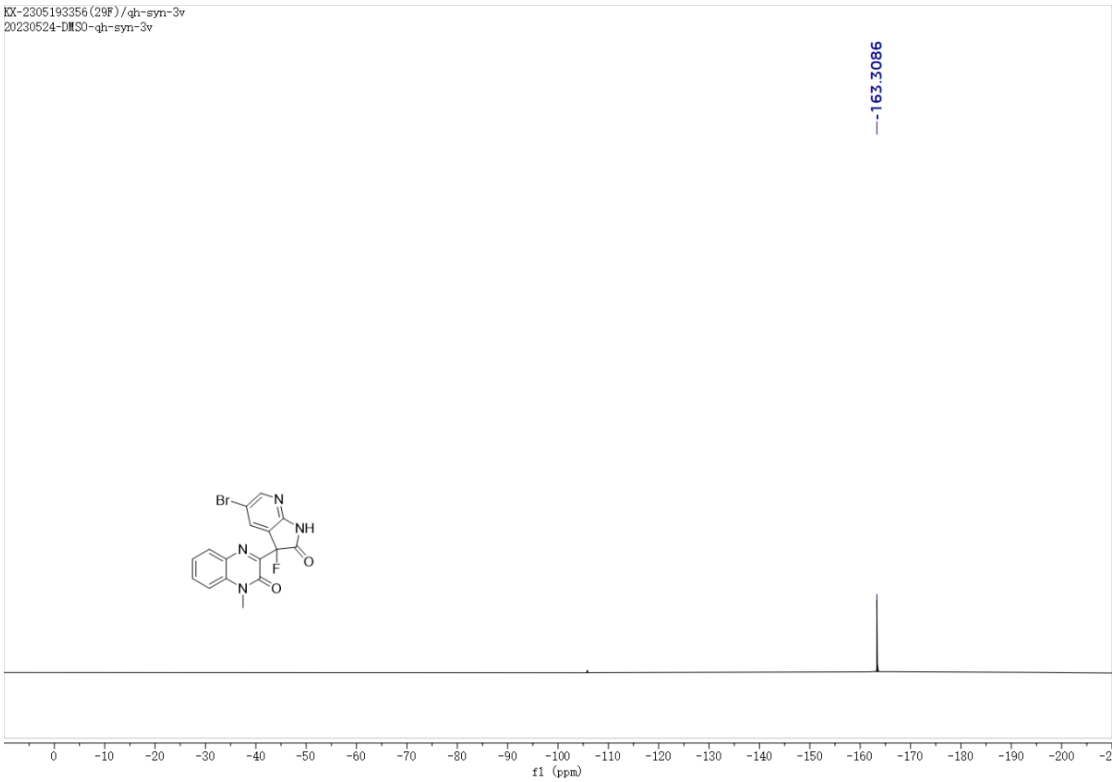


Figure S87 The ^{19}F NMR Spectrum of Compound **3v** in DMSO-d_6

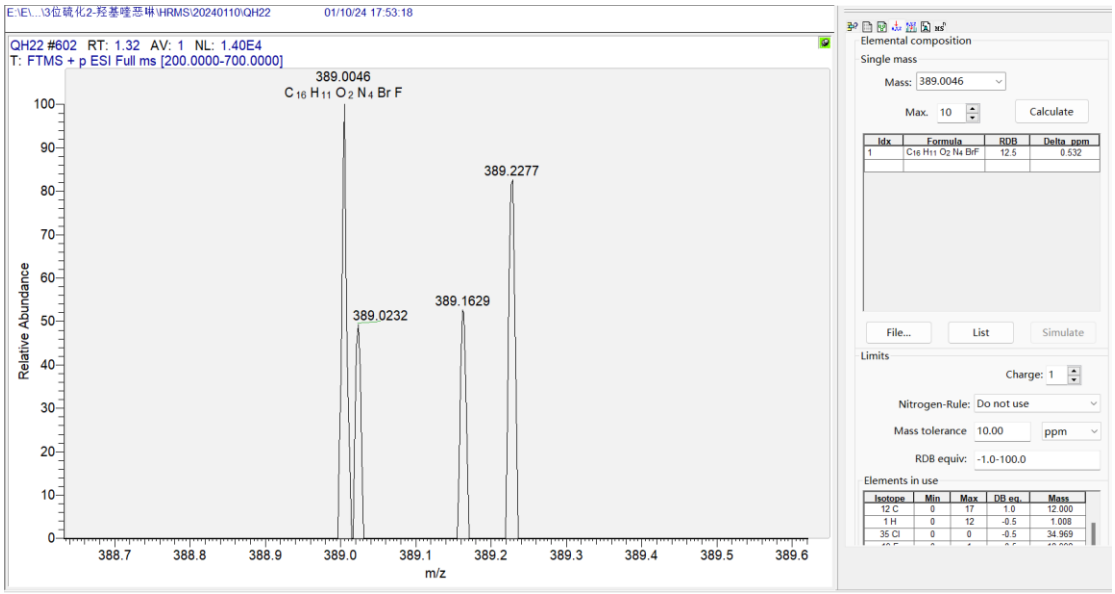


Figure S88. The HR-ESI-MS Spectrum of Compound **3v**

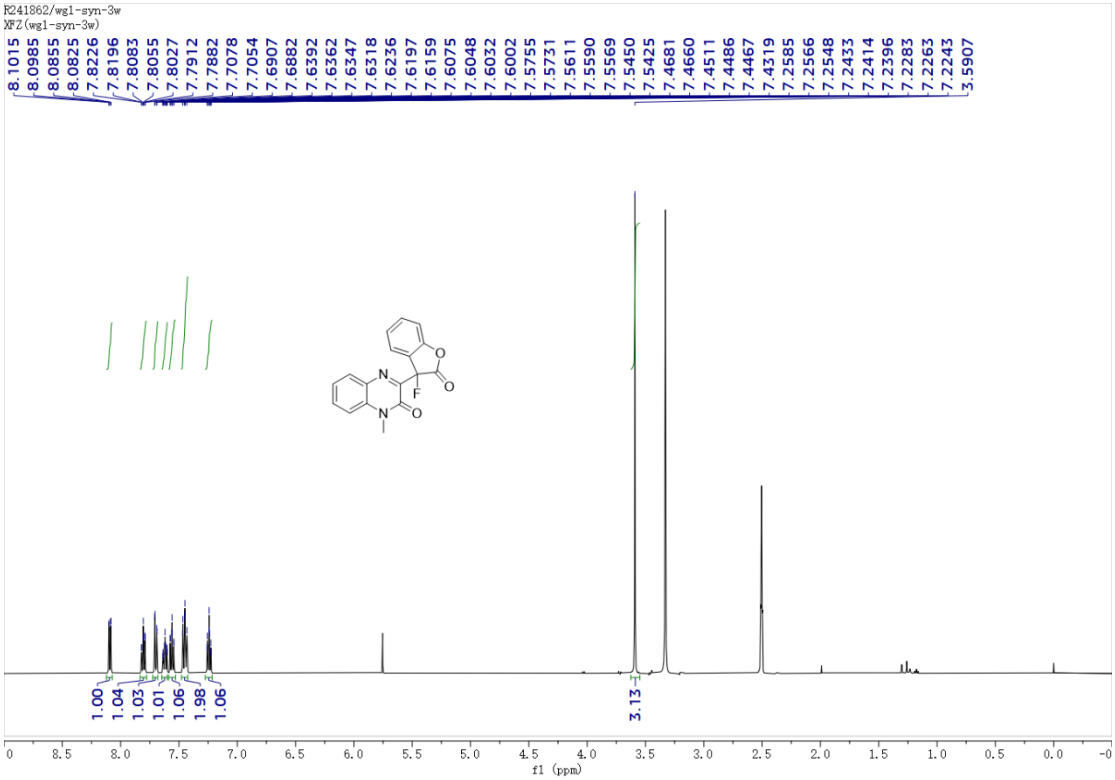


Figure S89 The ^{1}H NMR Spectrum of Compound **3w** in DMSO-d_6

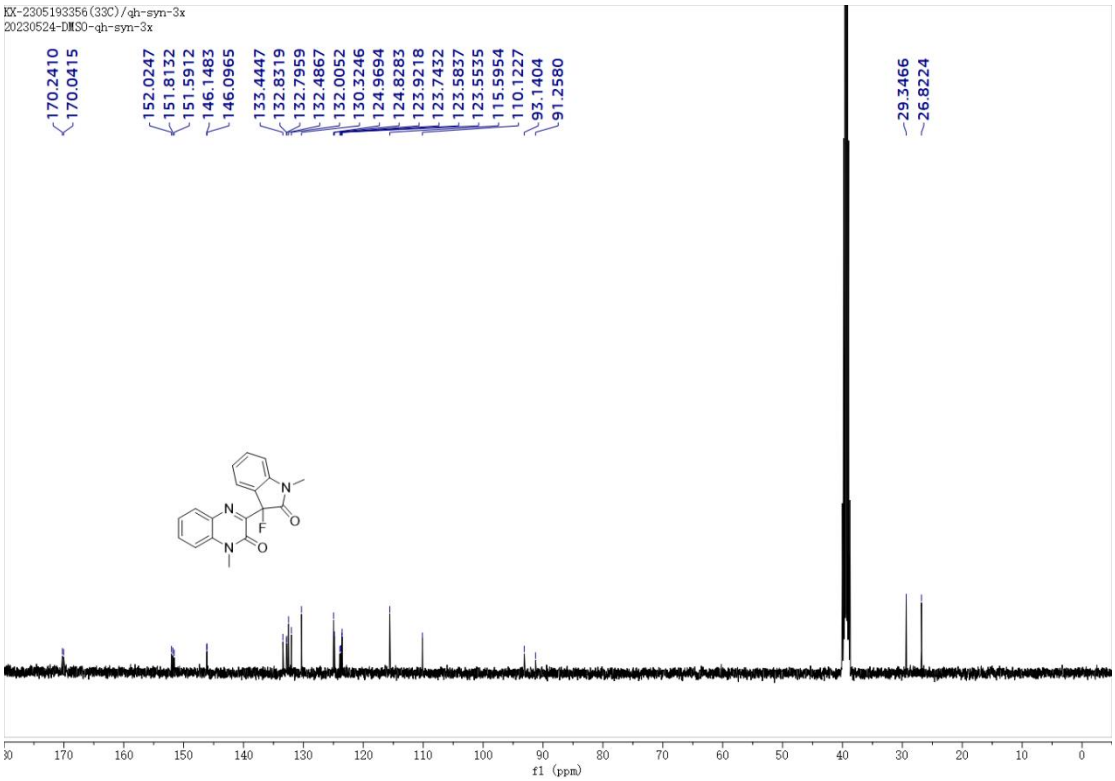


Figure S90 The ^{13}C NMR Spectrum of Compound **3w** in DMSO-d_6

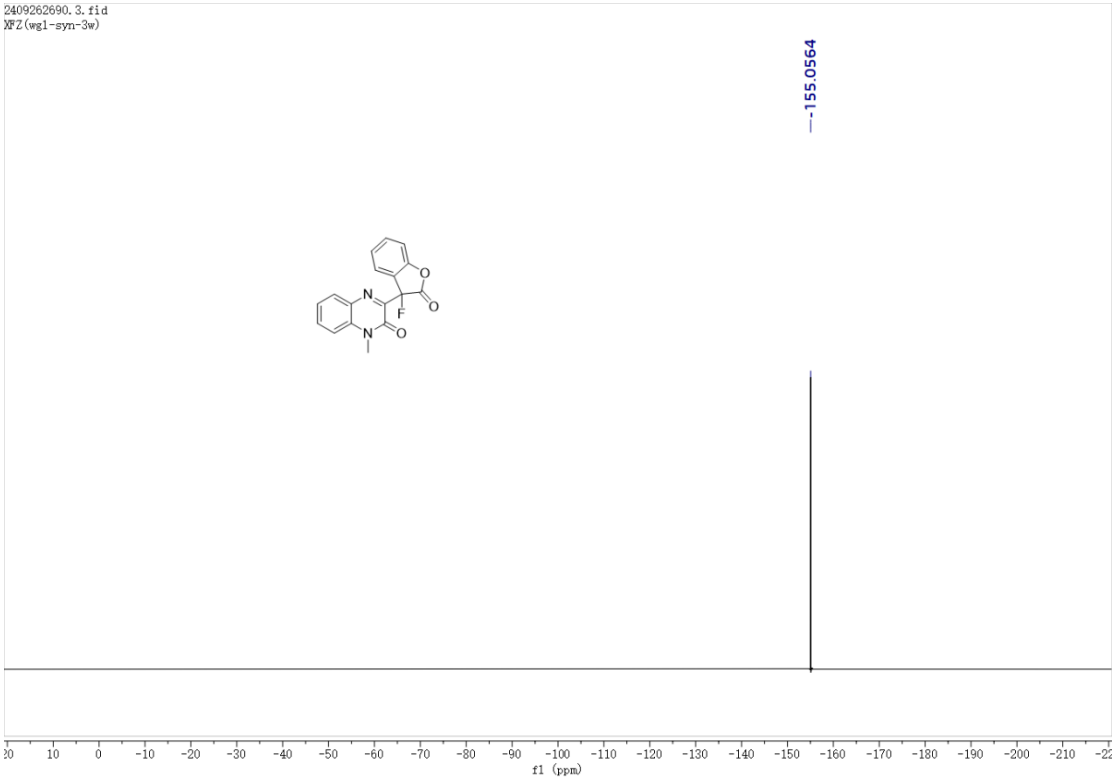


Figure S91 The ^{19}F NMR Spectrum of Compound **3w** in DMSO-d_6

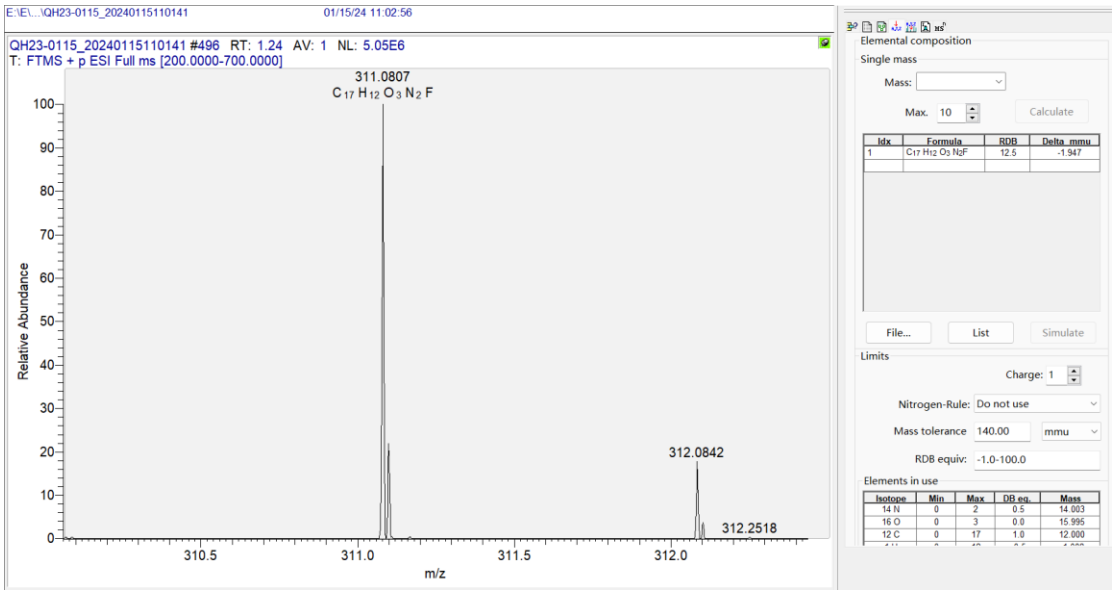


Figure S92. The HR-ESI-MS Spectrum of Compound **3w**

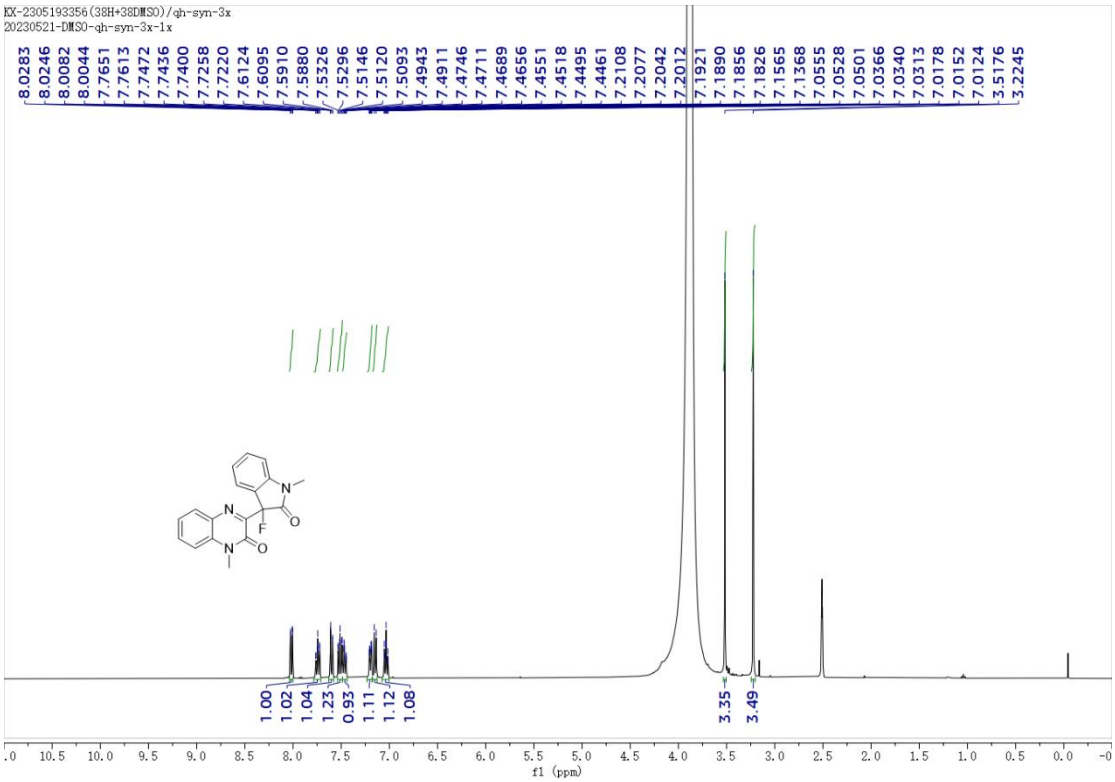


Figure S93 The ^{1}H NMR Spectrum of Compound **3x** in DMSO-d_6

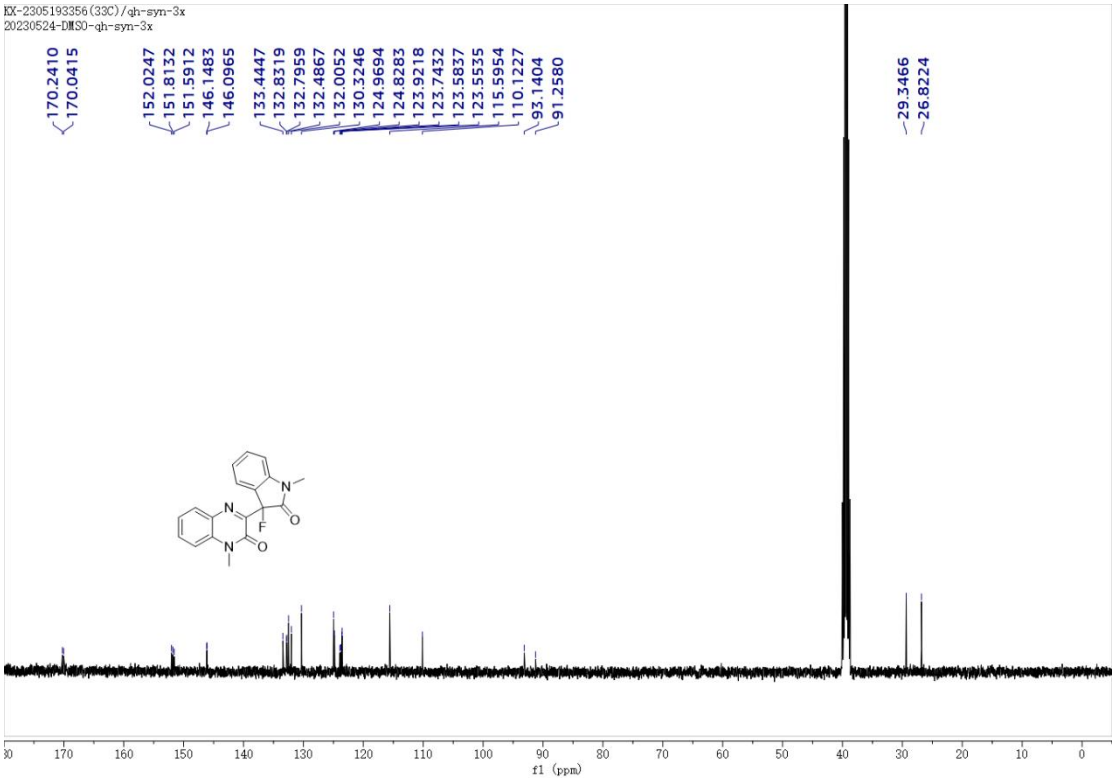


Figure S94 The ^{13}C NMR Spectrum of Compound **3x** in DMSO-d_6

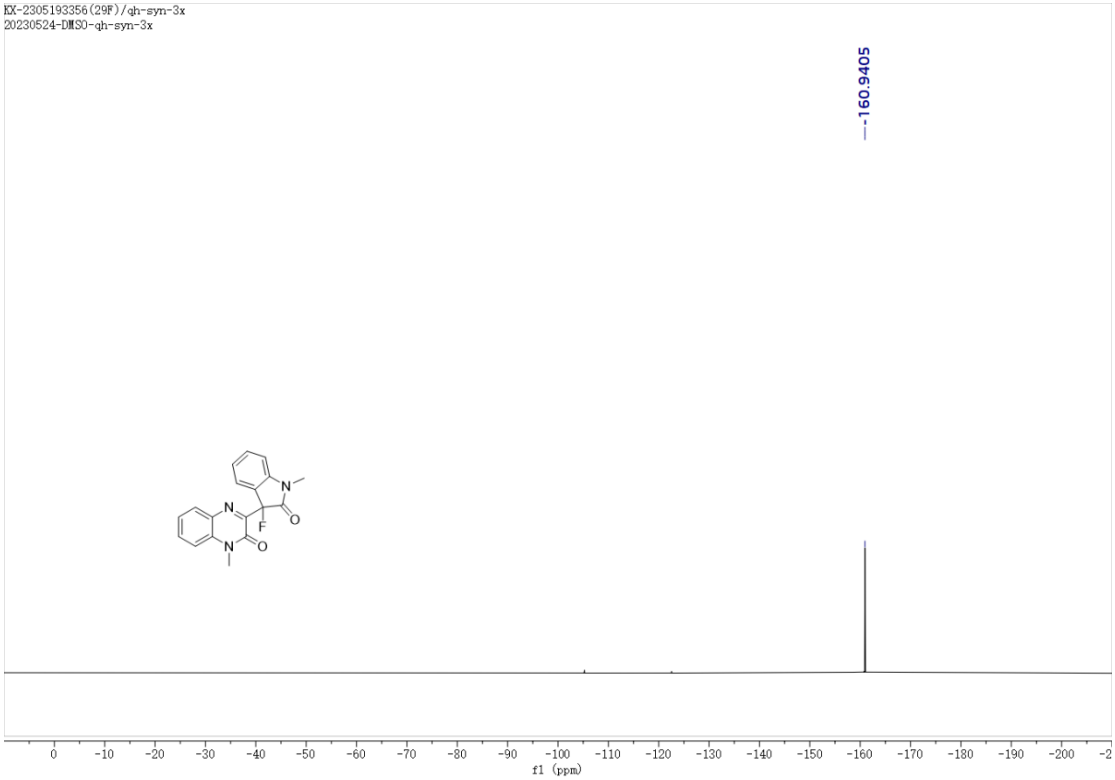


Figure S95 The ^{19}F NMR Spectrum of Compound **3x** in DMSO-d_6

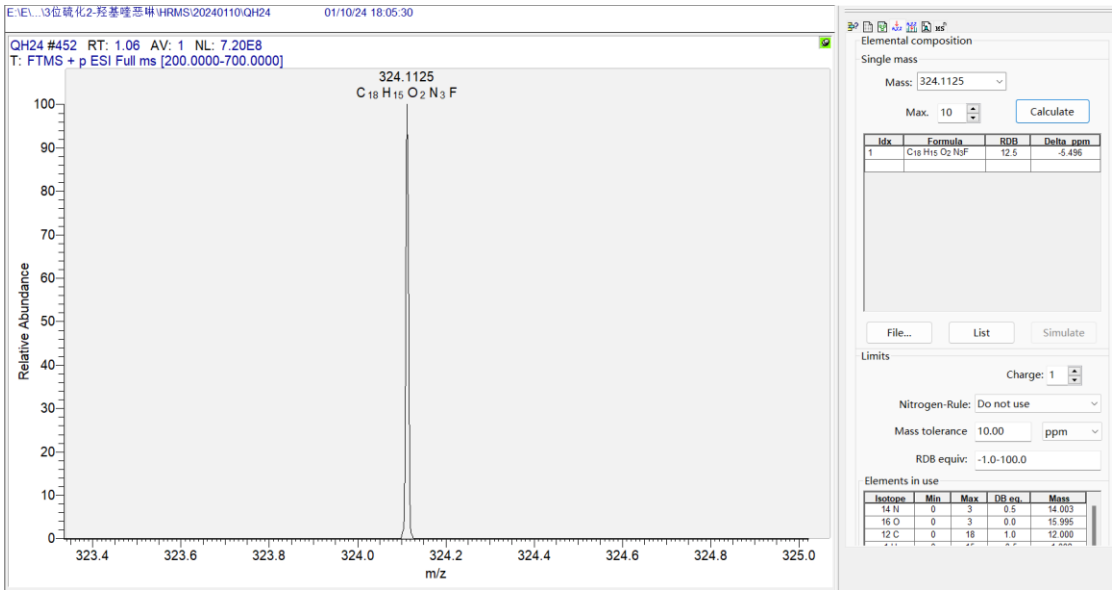


Figure S96. The HR-ESI-MS Spectrum of Compound **3x**

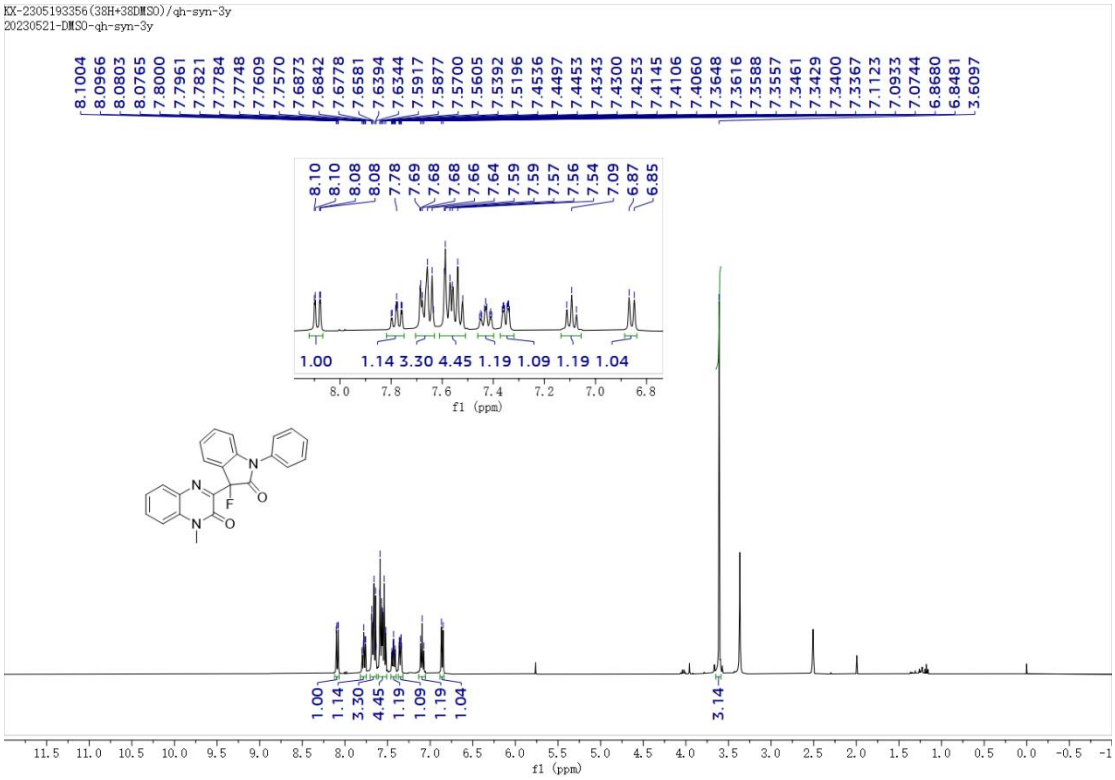


Figure S97 The ^{1}H NMR Spectrum of Compound **3y** in DMSO-d_6

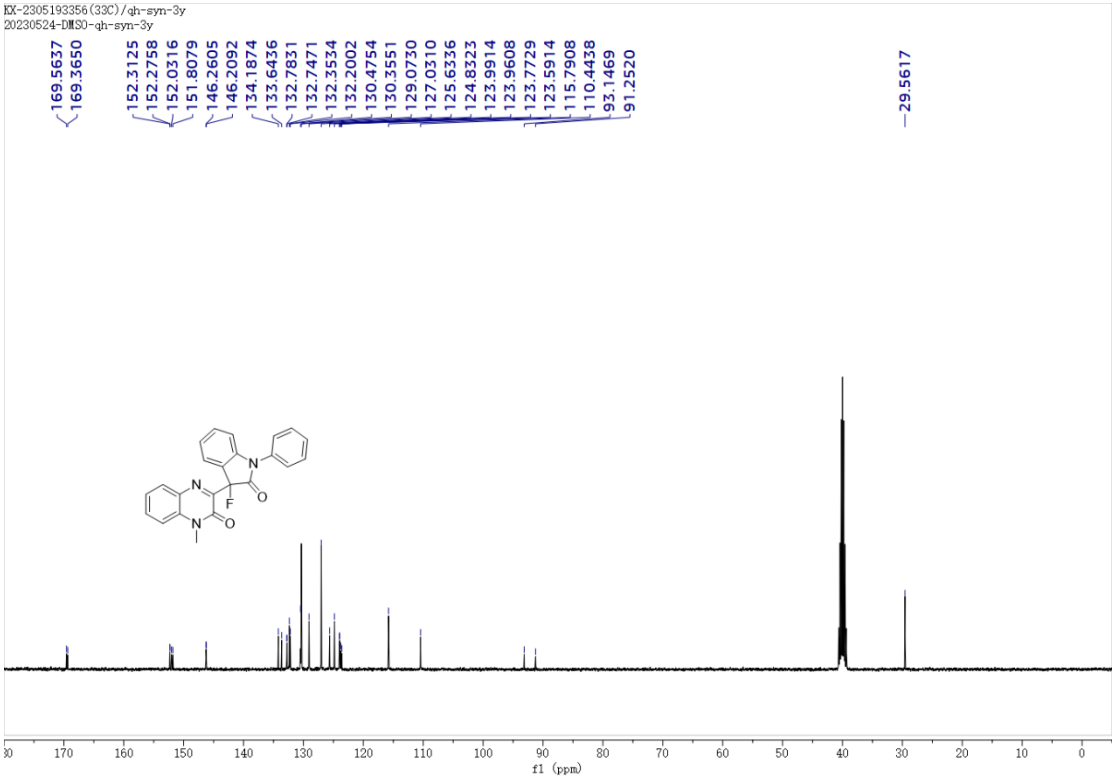


Figure S98 The ^{13}C NMR Spectrum of Compound **3y** in DMSO-d_6

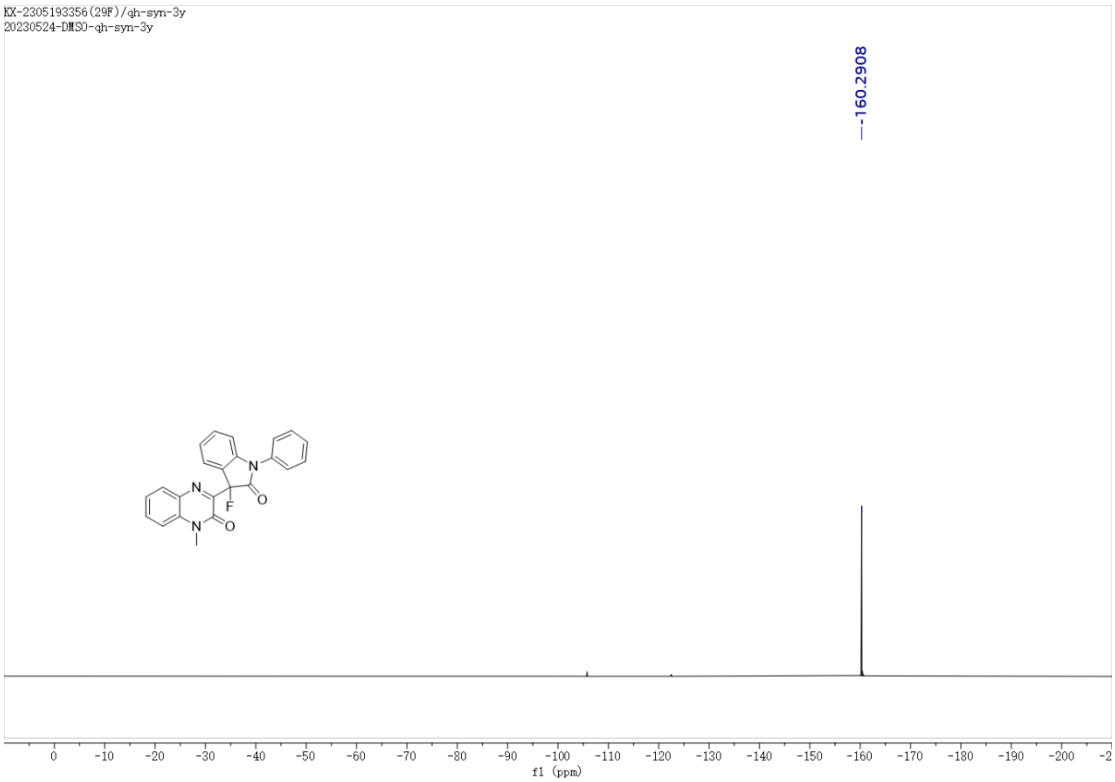


Figure S99 The ^{19}F NMR Spectrum of Compound **3y** in DMSO-d_6

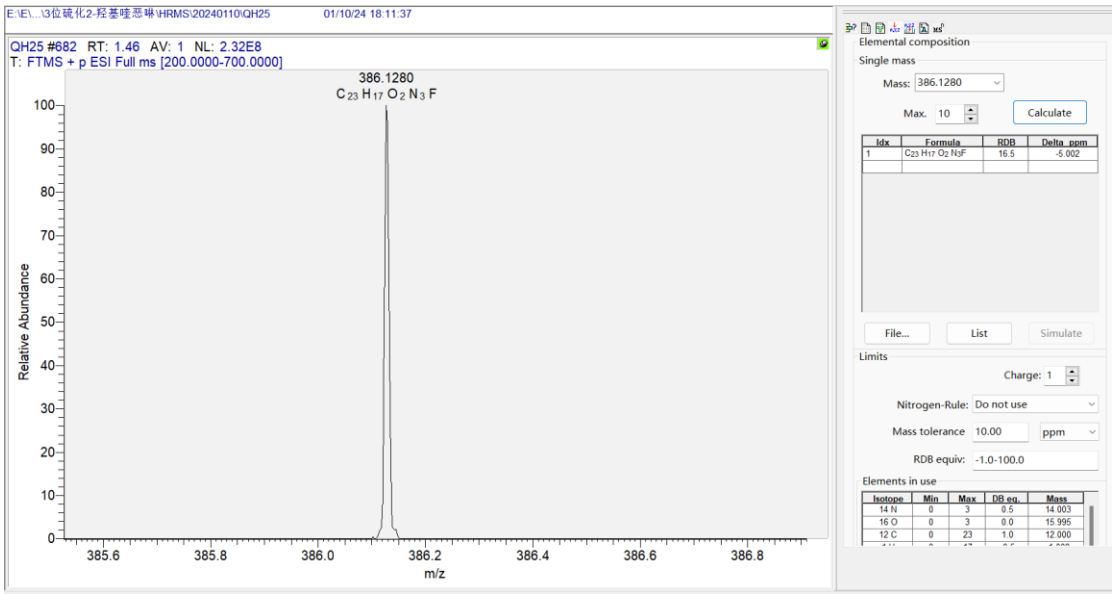


Figure S100. The HR-ESI-MS Spectrum of Compound **3y**

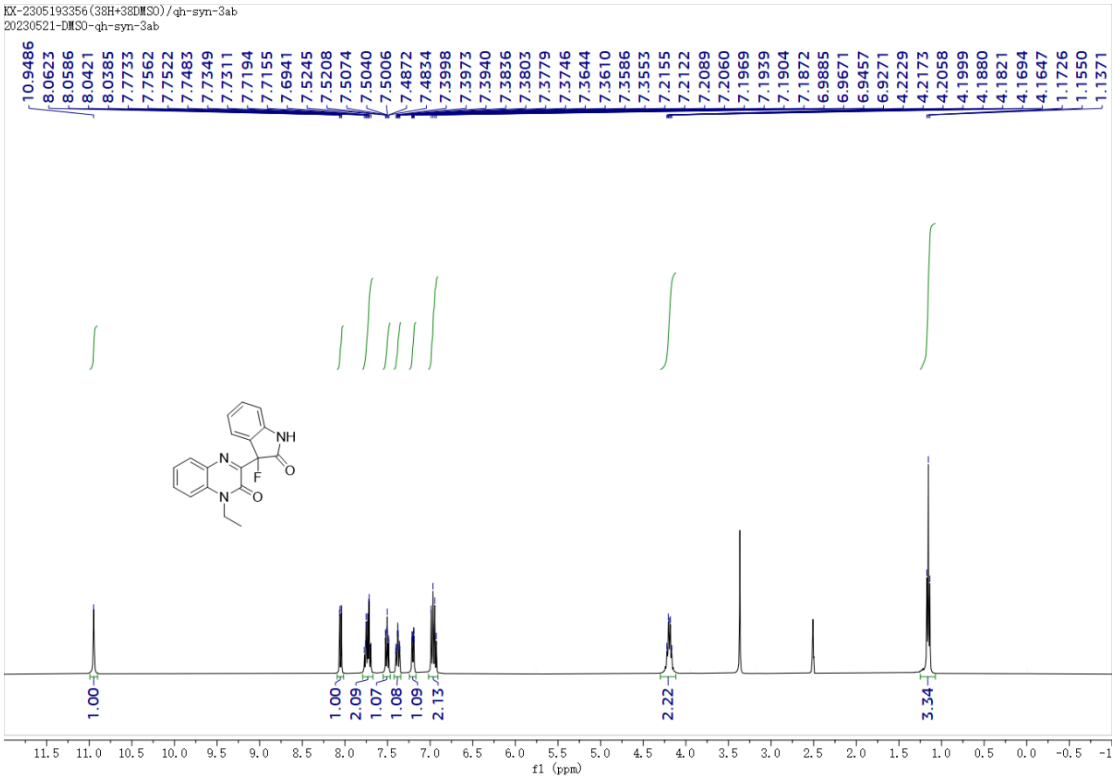


Figure S101 The ^{1}H NMR Spectrum of Compound **3ab** in DMSO-d_6

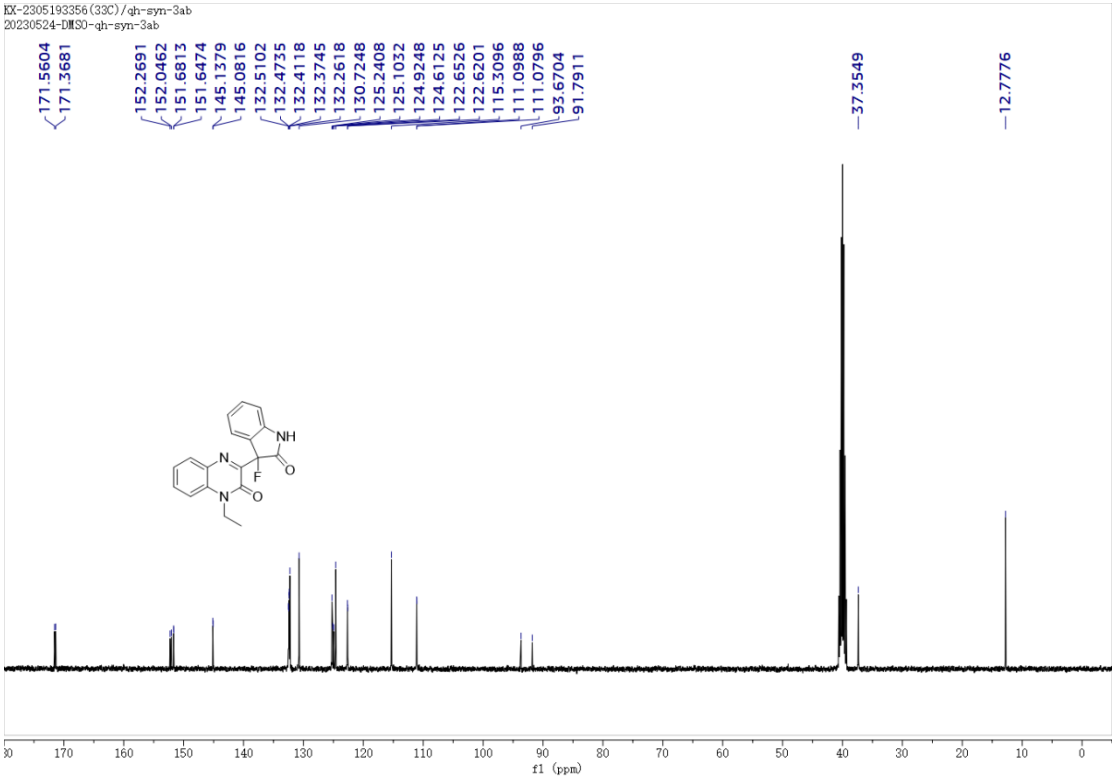


Figure S102 The ^{13}C NMR Spectrum of Compound **3ab** in DMSO-d_6

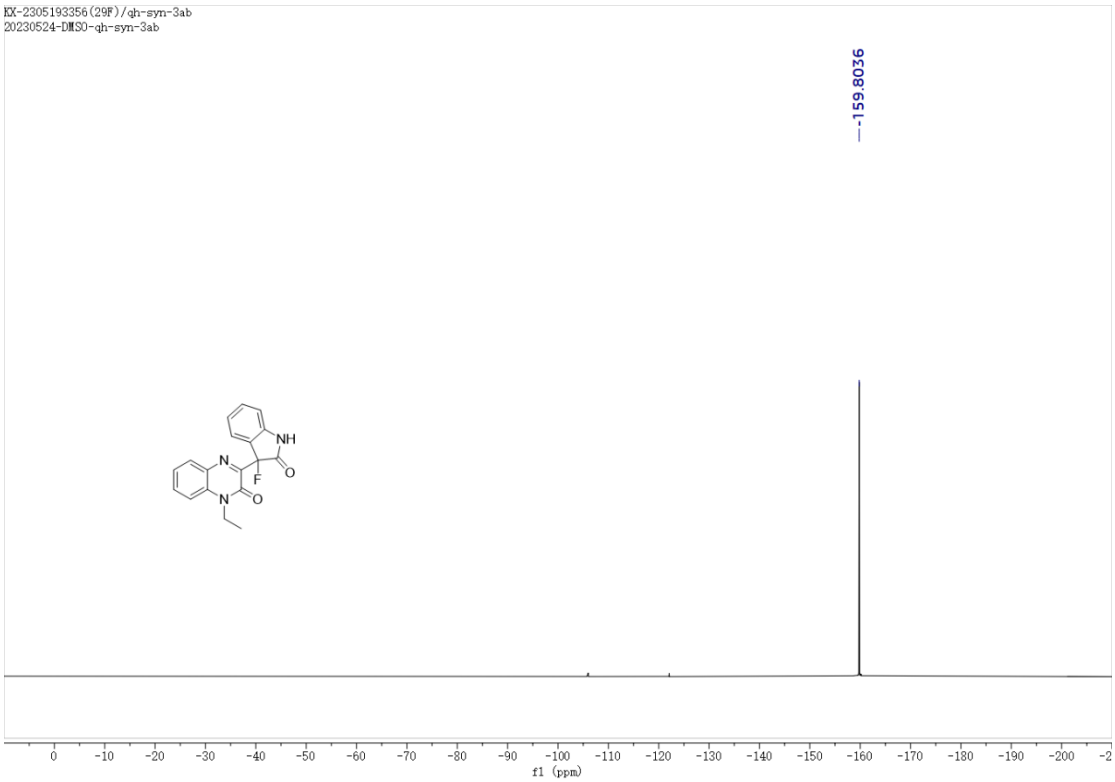


Figure S103 The ^{19}F NMR Spectrum of Compound **3ab** in DMSO-d_6

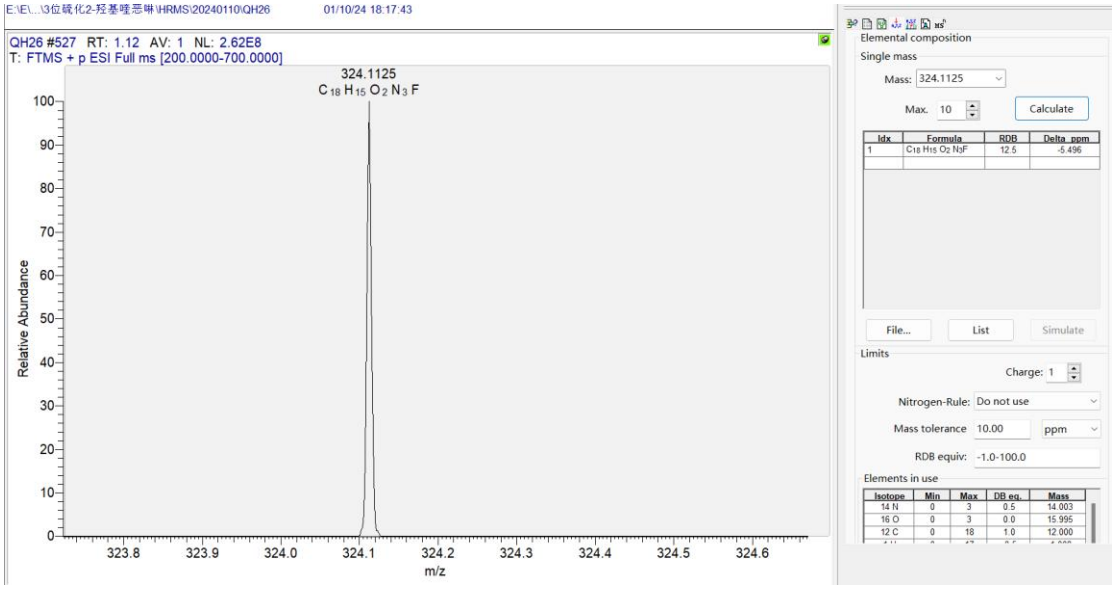


Figure S104. The HR-ESI-MS Spectrum of Compound **3ab**

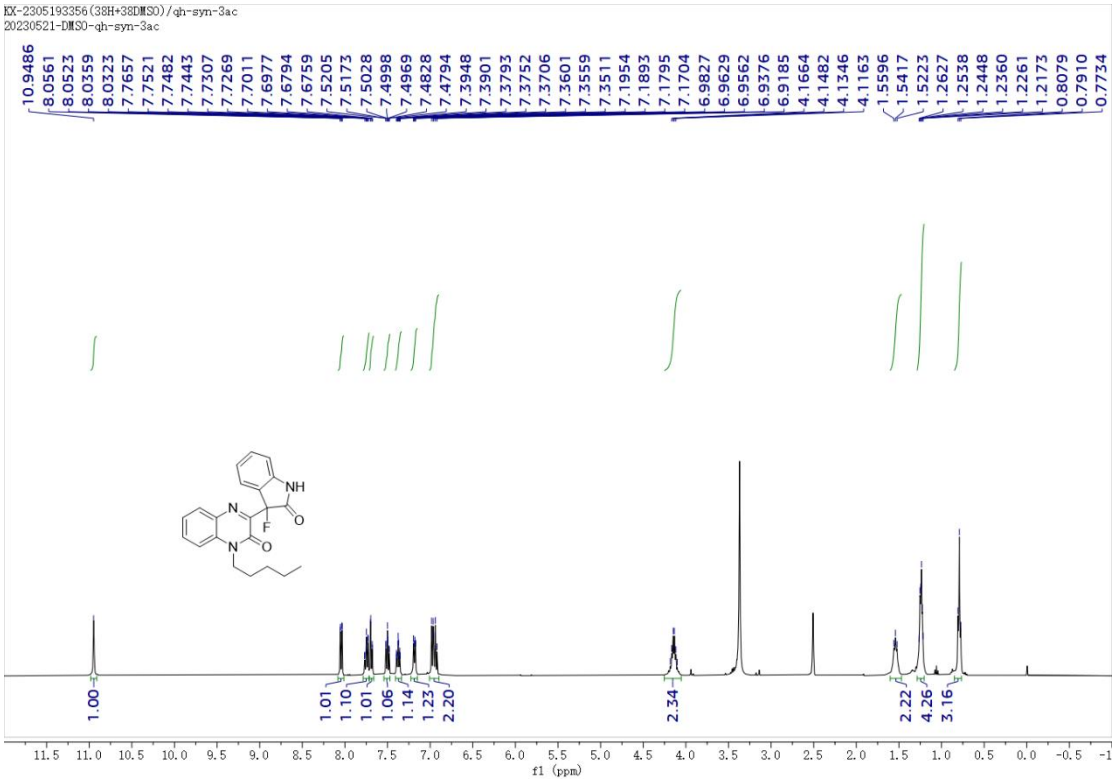


Figure S105 The ^{1}H NMR Spectrum of Compound **3ac** in DMSO-d_6

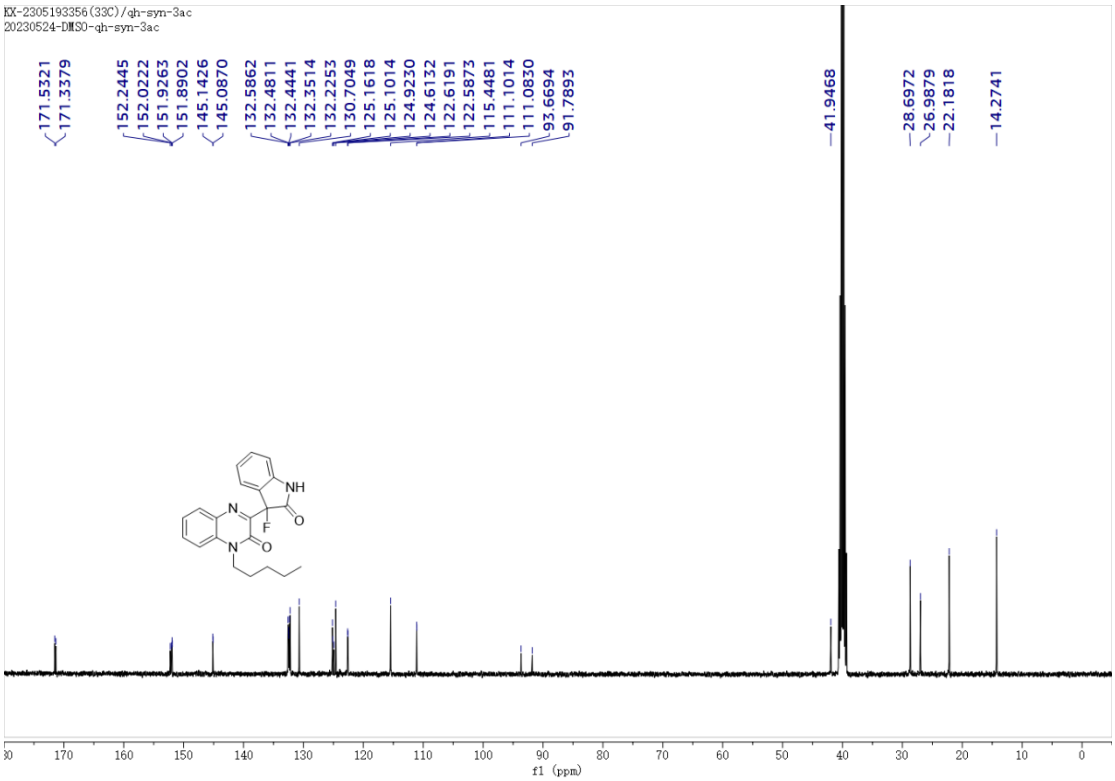


Figure S106 The ^{13}C NMR Spectrum of Compound **3ac** in DMSO-d_6

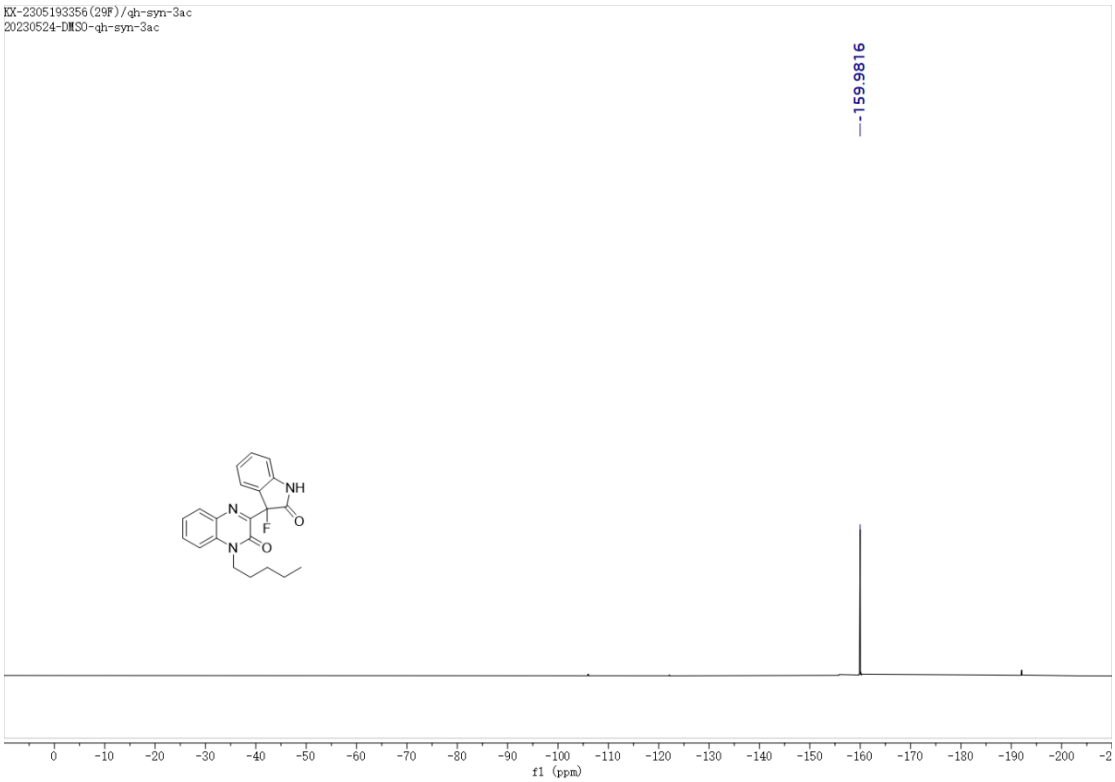


Figure S107 The ^{19}F NMR Spectrum of Compound **3ac** in DMSO-d_6

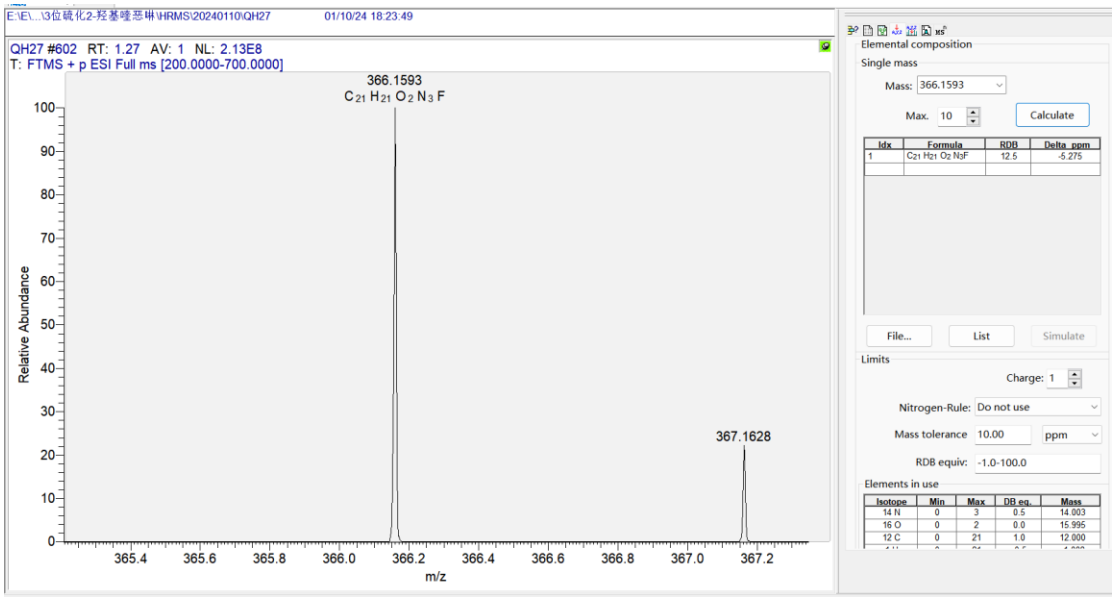


Figure S108. The HR-ESI-MS Spectrum of Compound **3ac**

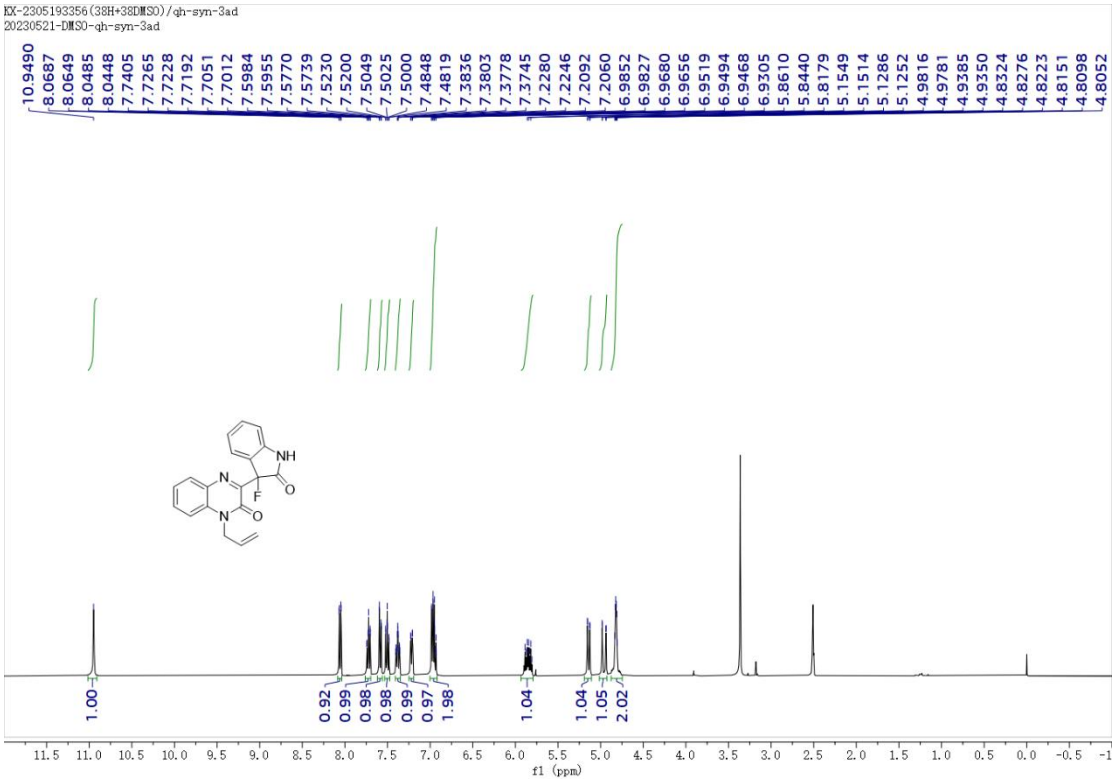


Figure S109 The ^{1}H NMR Spectrum of Compound **3ad** in DMSO-d_6

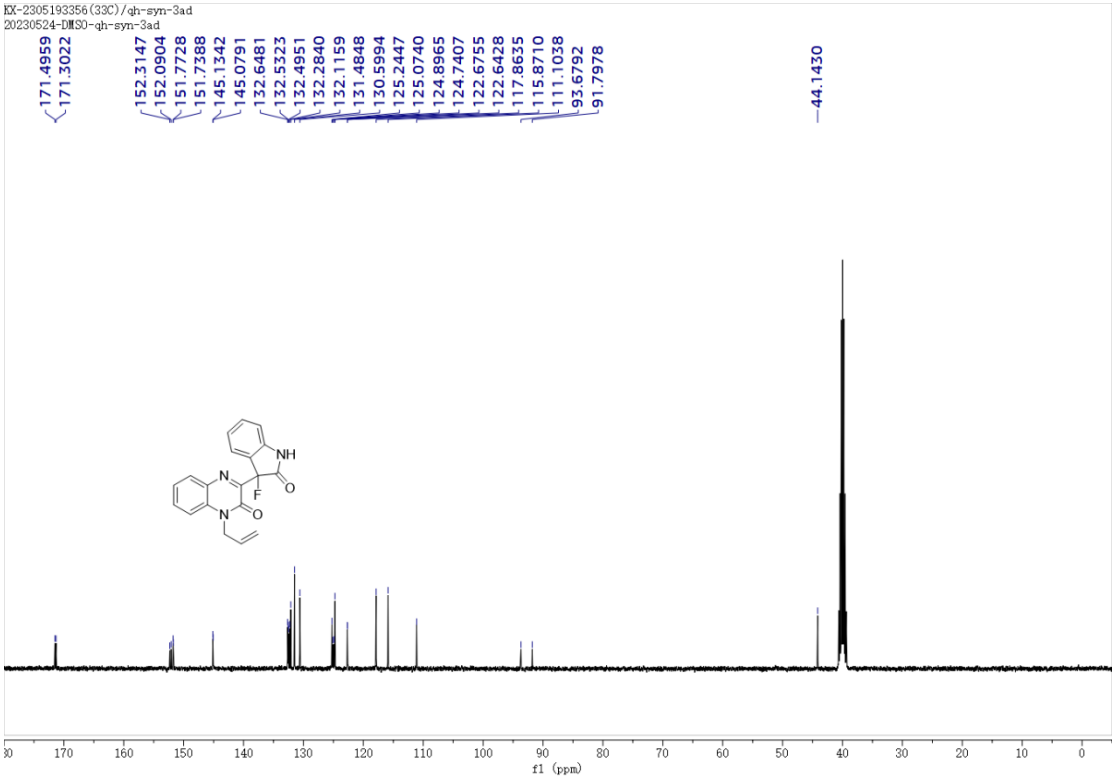


Figure S110 The ^{13}C NMR Spectrum of Compound **3ad** in DMSO-d_6

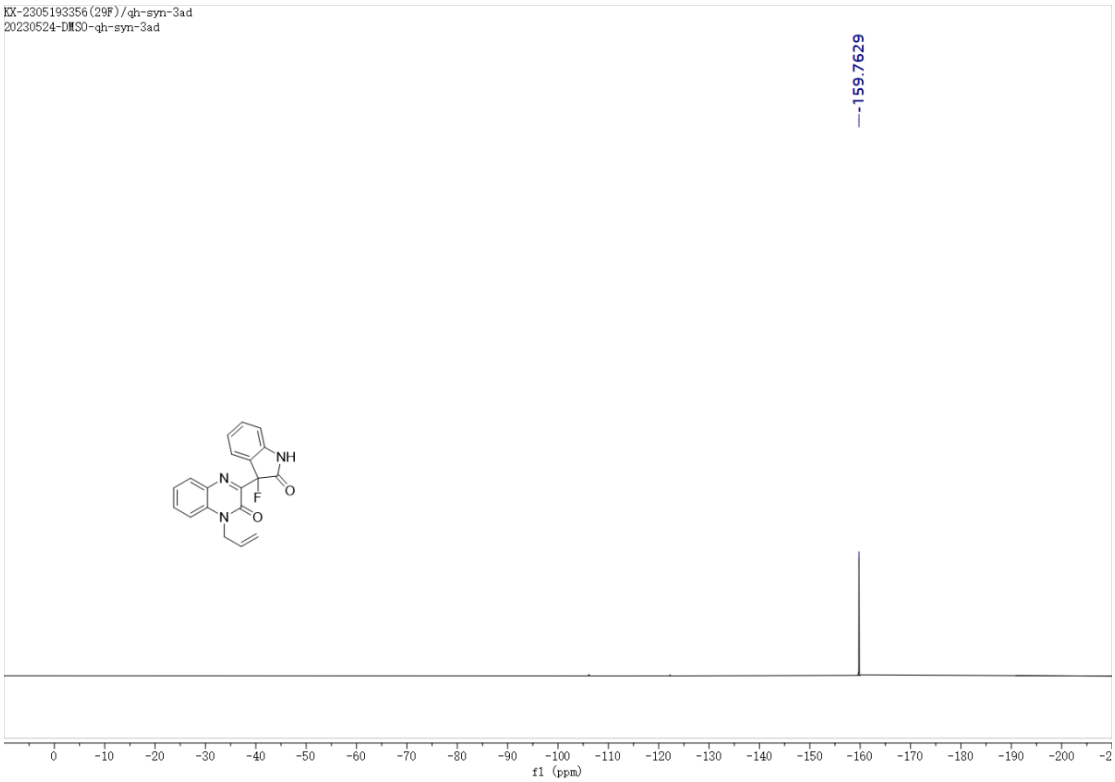


Figure S111 The ^{19}F NMR Spectrum of Compound **3ad** in DMSO-d_6

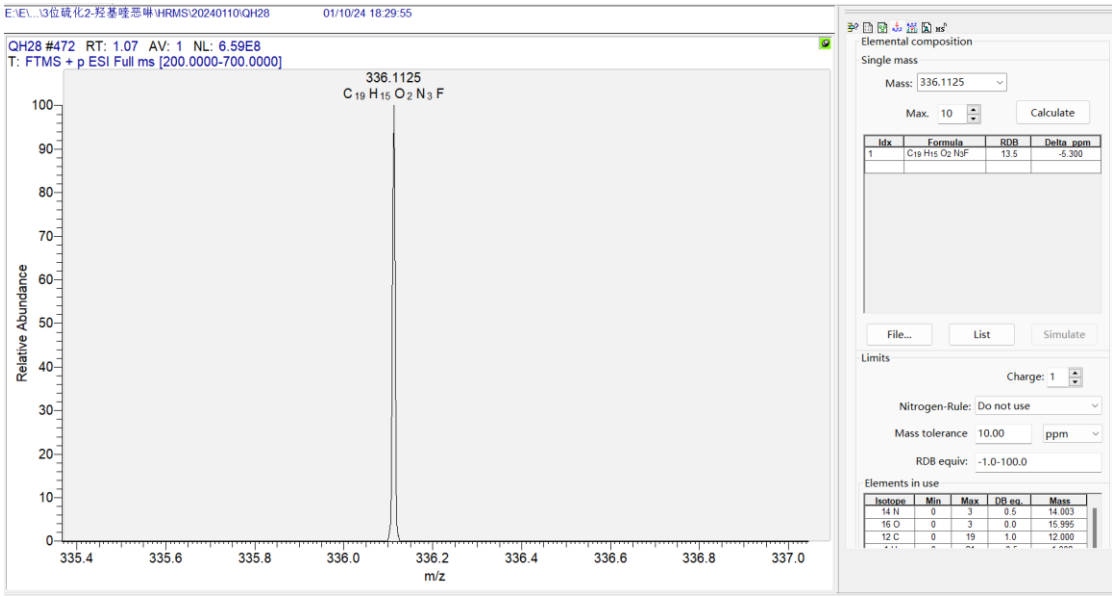


Figure S112. The HR-ESI-MS Spectrum of Compound **3ad**

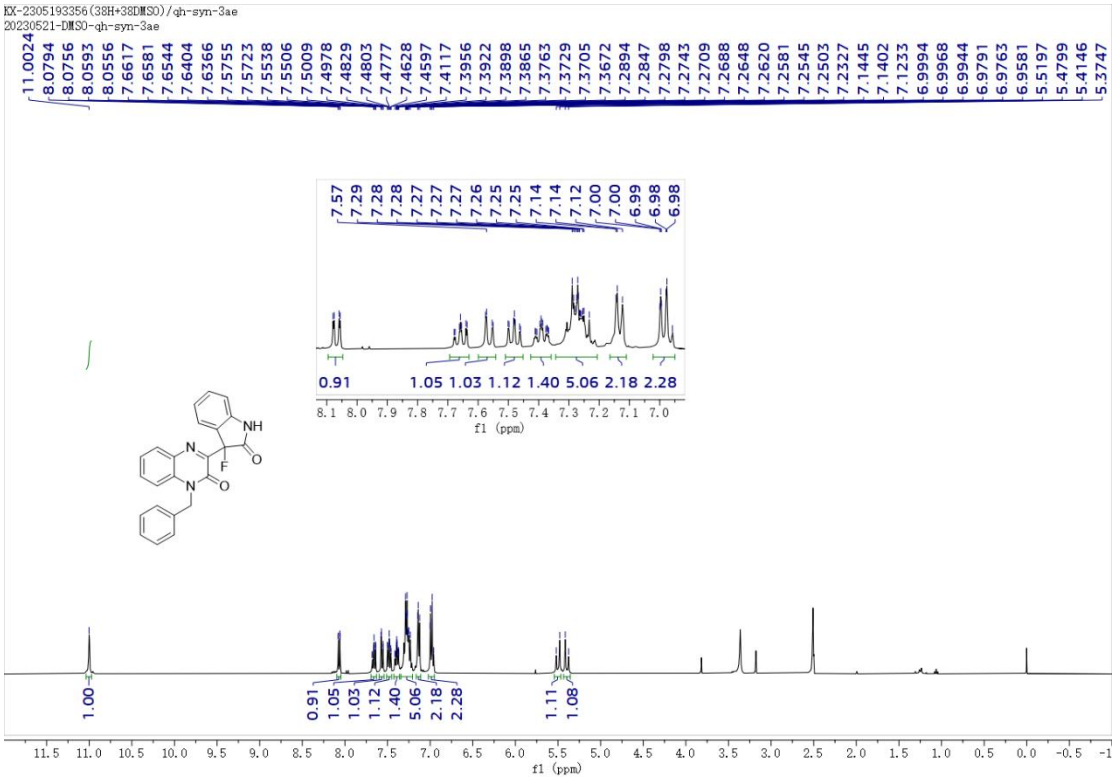


Figure S113 The ^{1}H NMR Spectrum of Compound **3ae** in DMSO-d_6

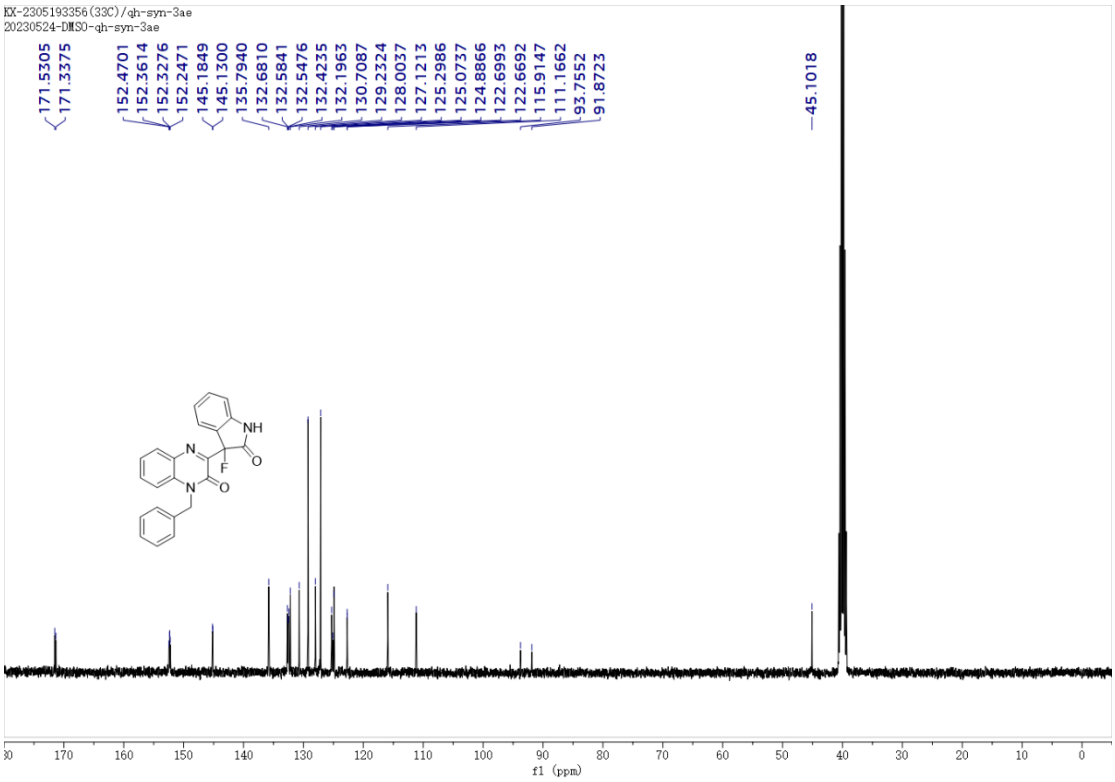


Figure S114 The ^{13}C NMR Spectrum of Compound **3ae** in DMSO-d_6

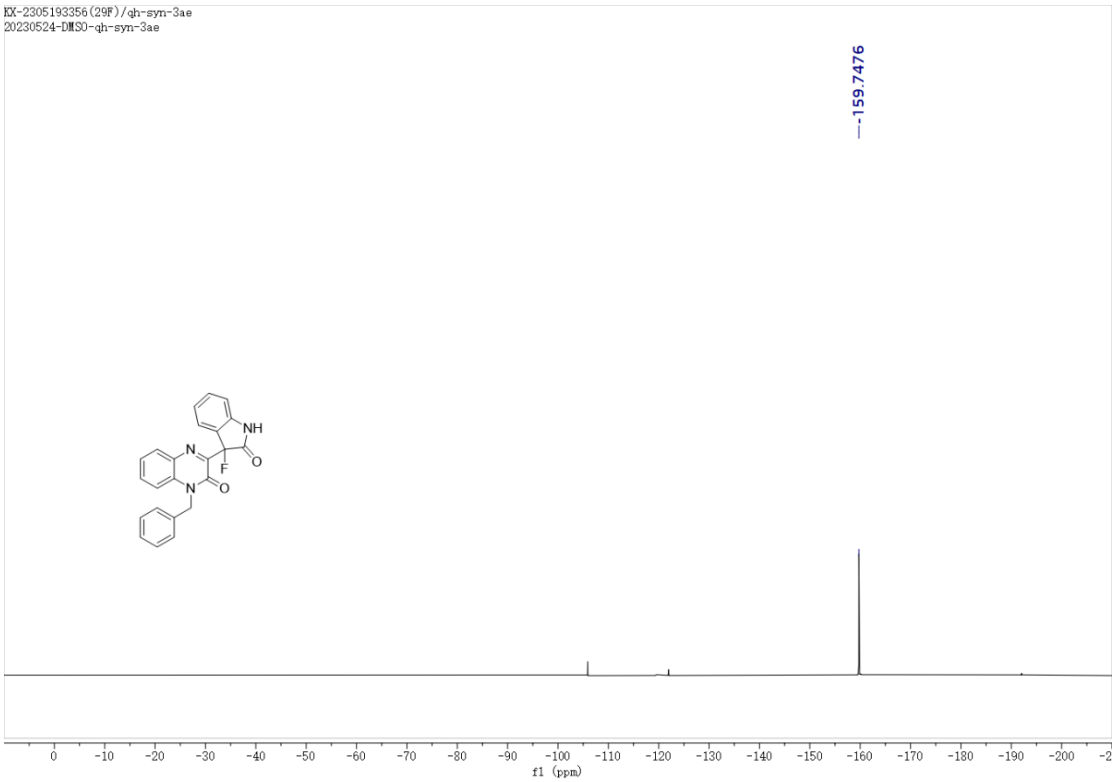


Figure S115 The ^{19}F NMR Spectrum of Compound **3ae** in DMSO-d_6

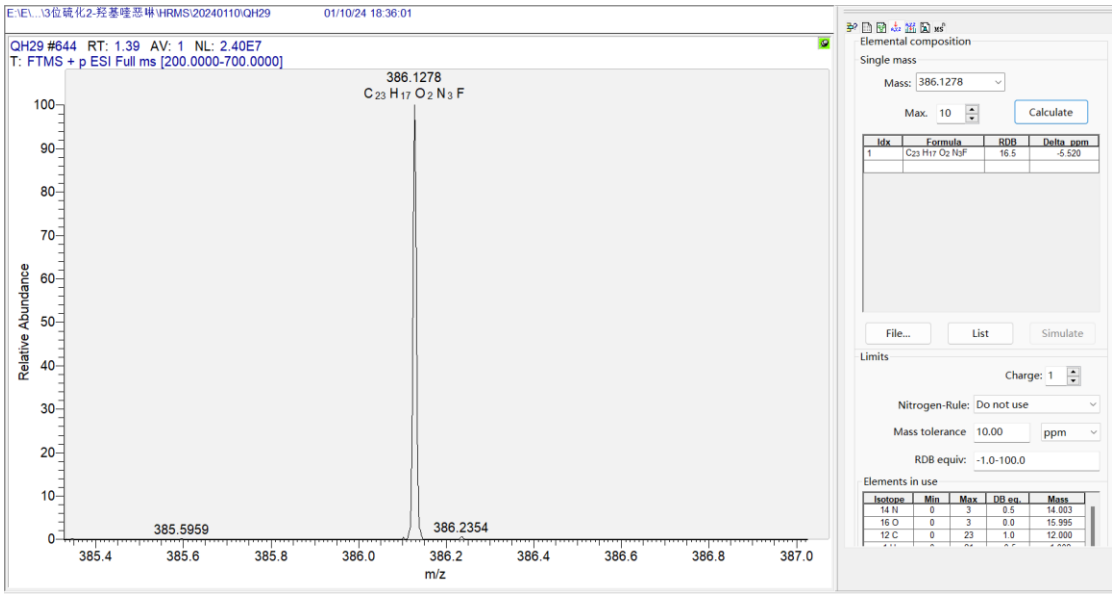


Figure S116. The HR-ESI-MS Spectrum of Compound **3ae**

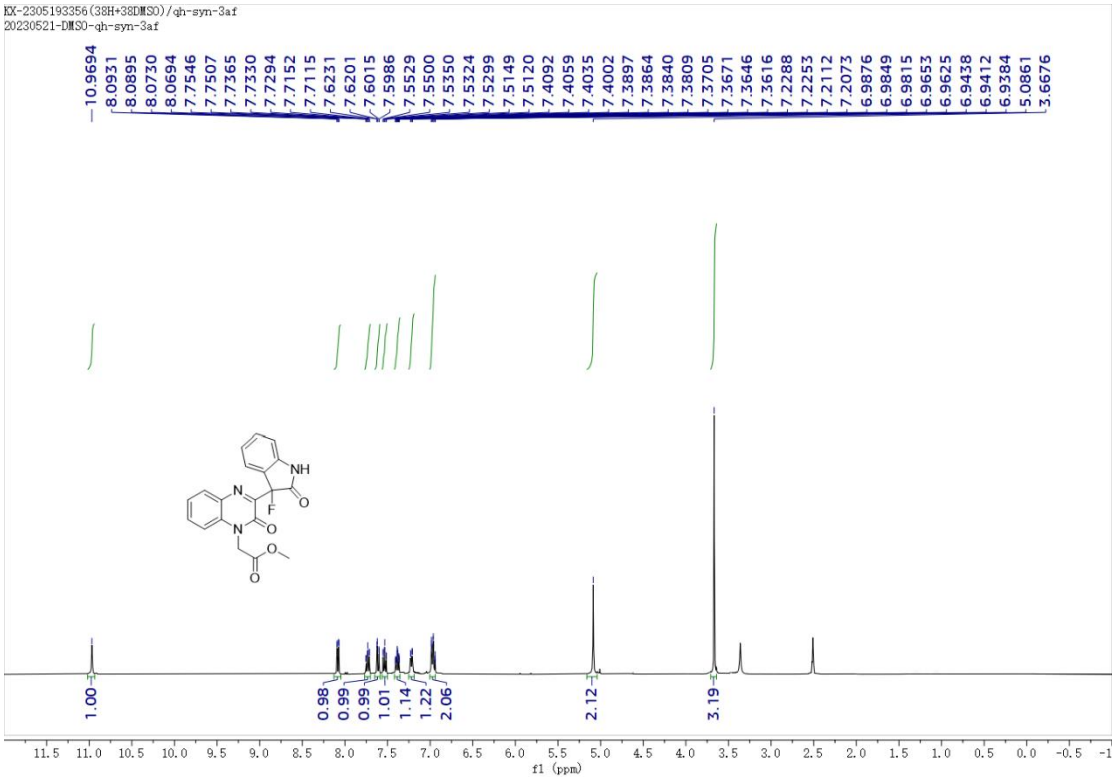


Figure S117 The ^{1}H NMR Spectrum of Compound **3af** in DMSO-d_6

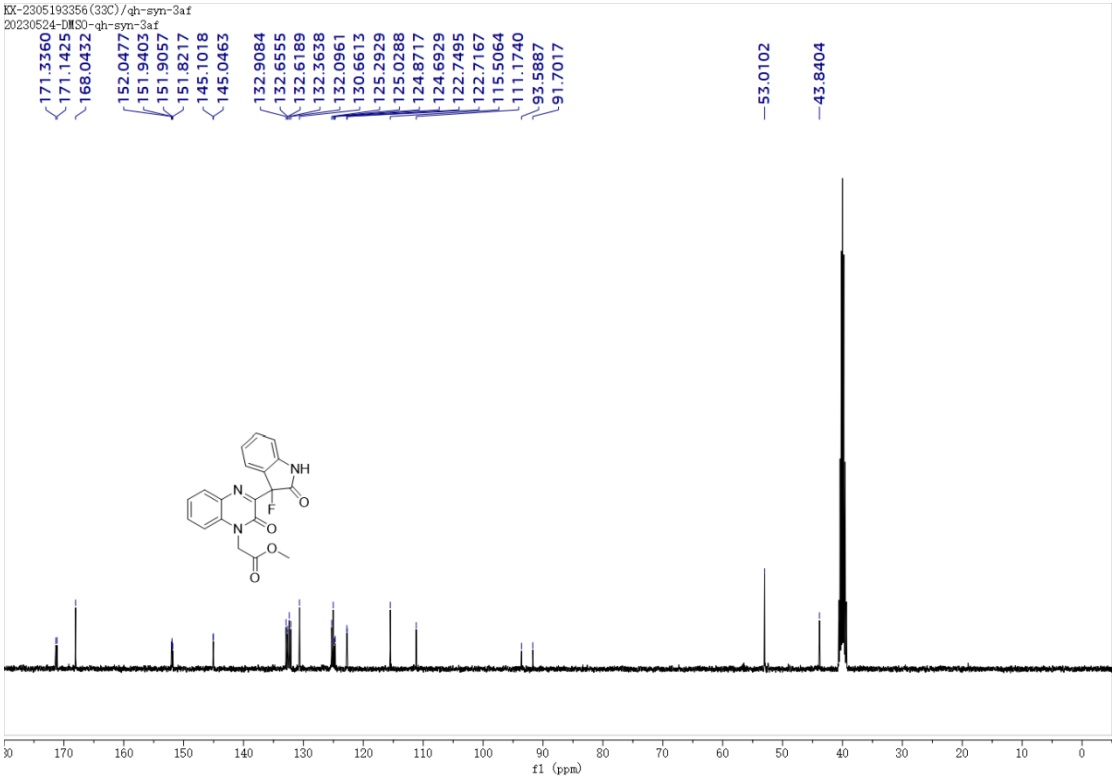


Figure S118 The ^{13}C NMR Spectrum of Compound **3af** in DMSO-d_6

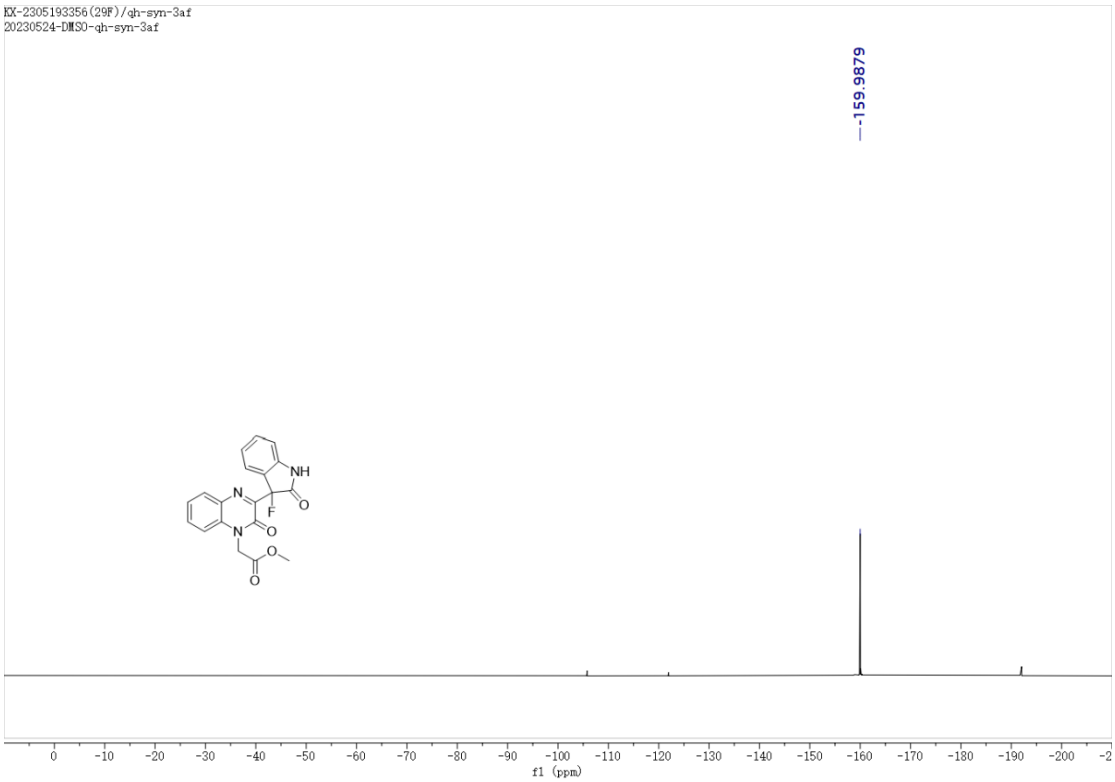


Figure S119 The ^{19}F NMR Spectrum of Compound **3af** in DMSO-d_6

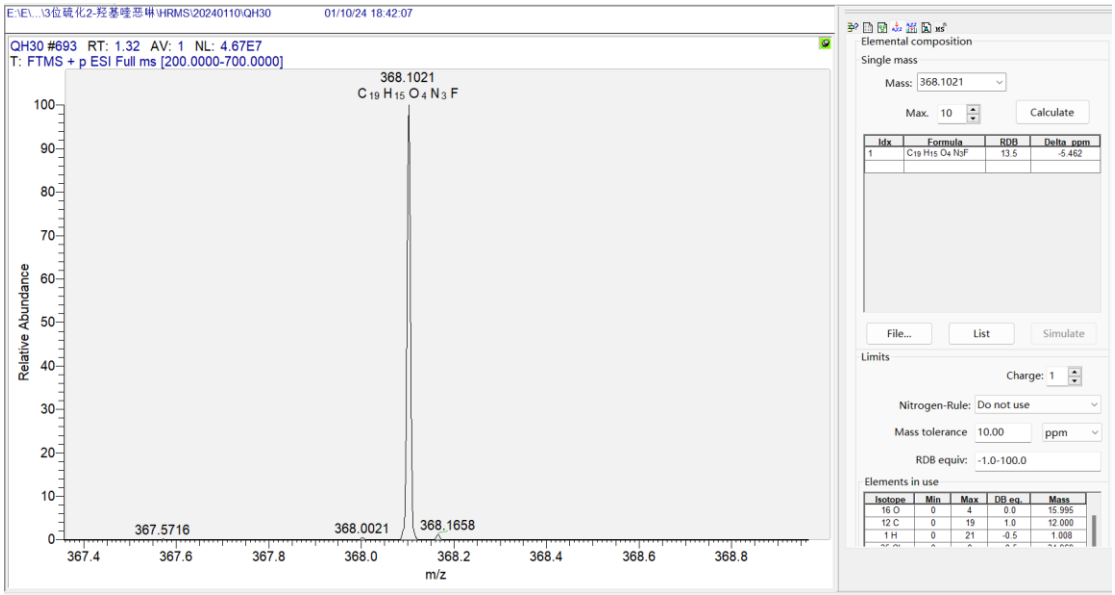


Figure S120. The HR-ESI-MS Spectrum of Compound **3af**

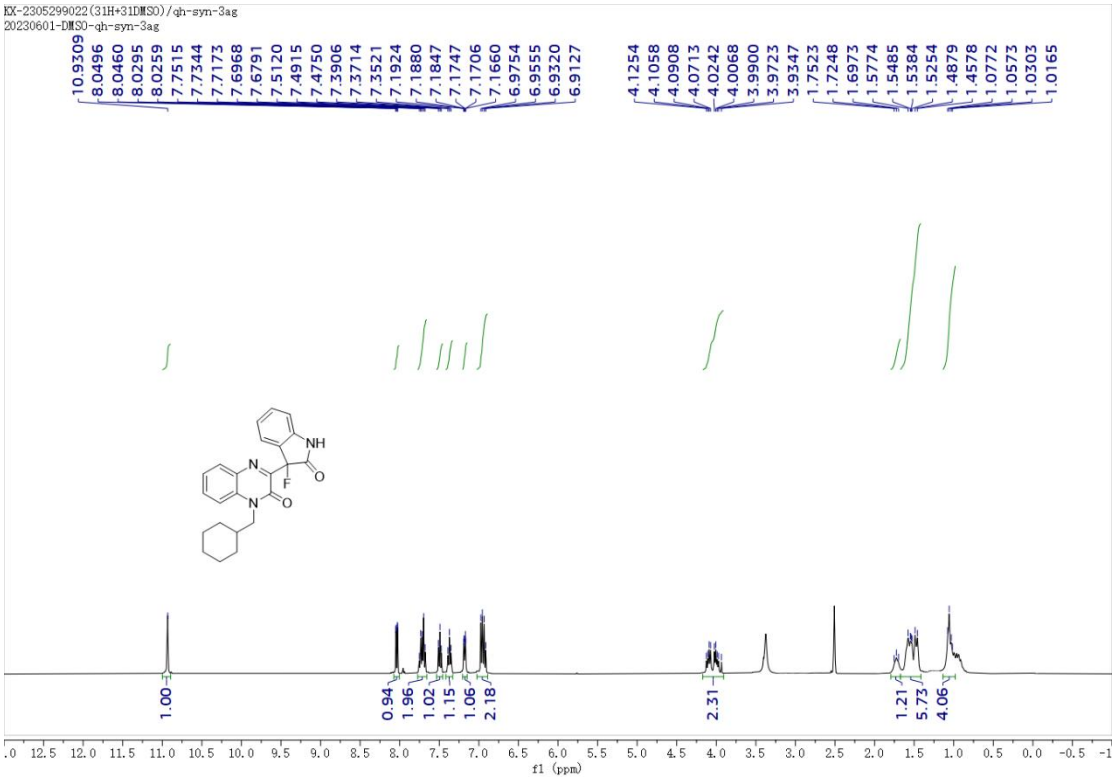


Figure S121 The ^{1}H NMR Spectrum of Compound **3ag** in DMSO-d_6

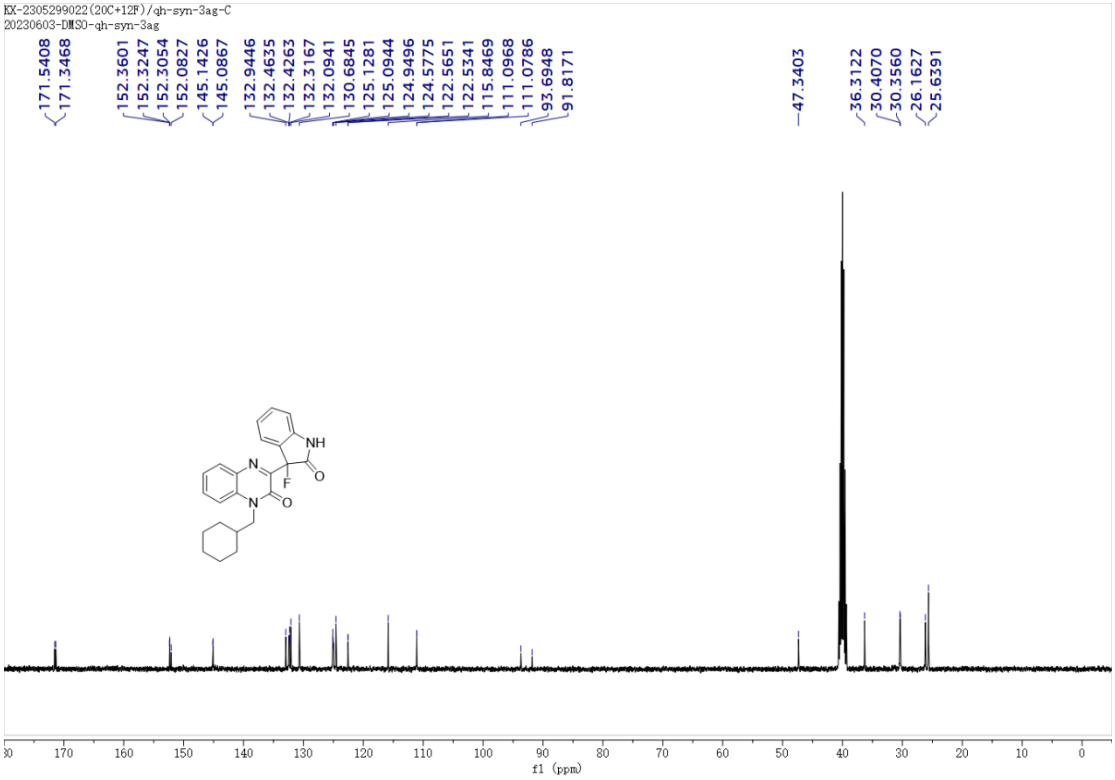


Figure S122 The ^{13}C NMR Spectrum of Compound **3ag** in DMSO-d_6

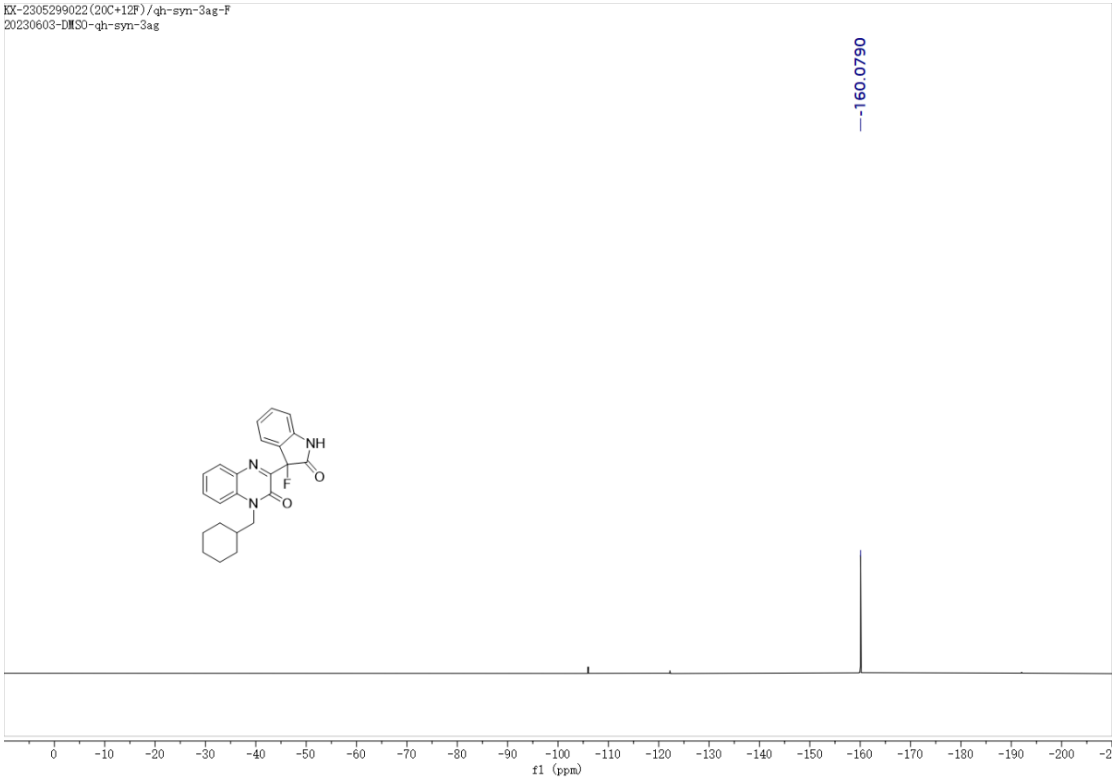


Figure S123 The ^{19}F NMR Spectrum of Compound **3ag** in DMSO-d_6

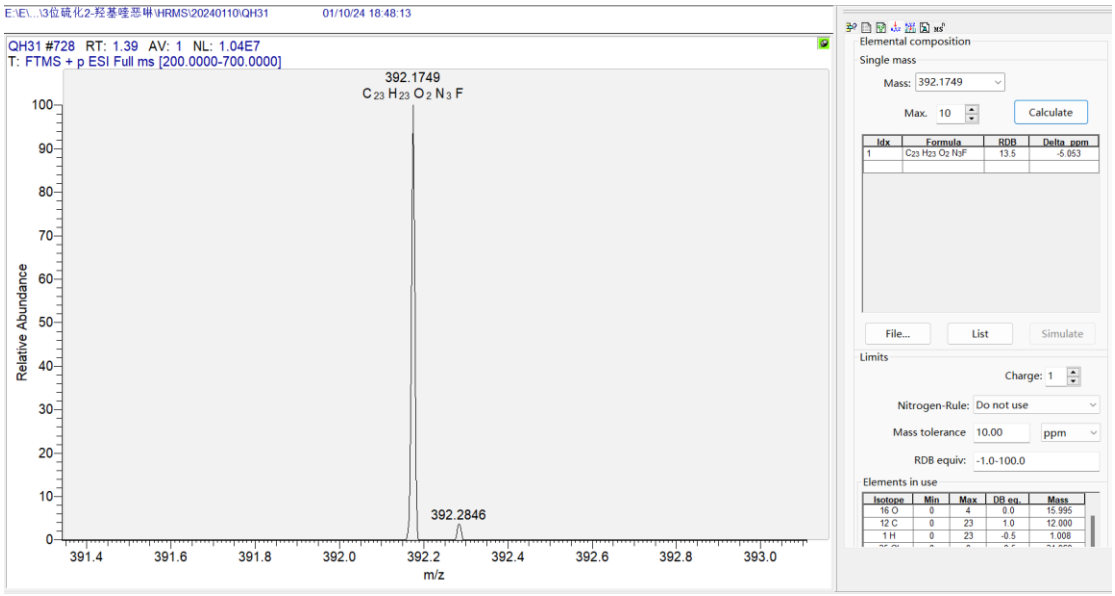


Figure S124. The HR-ESI-MS Spectrum of Compound **3ag**

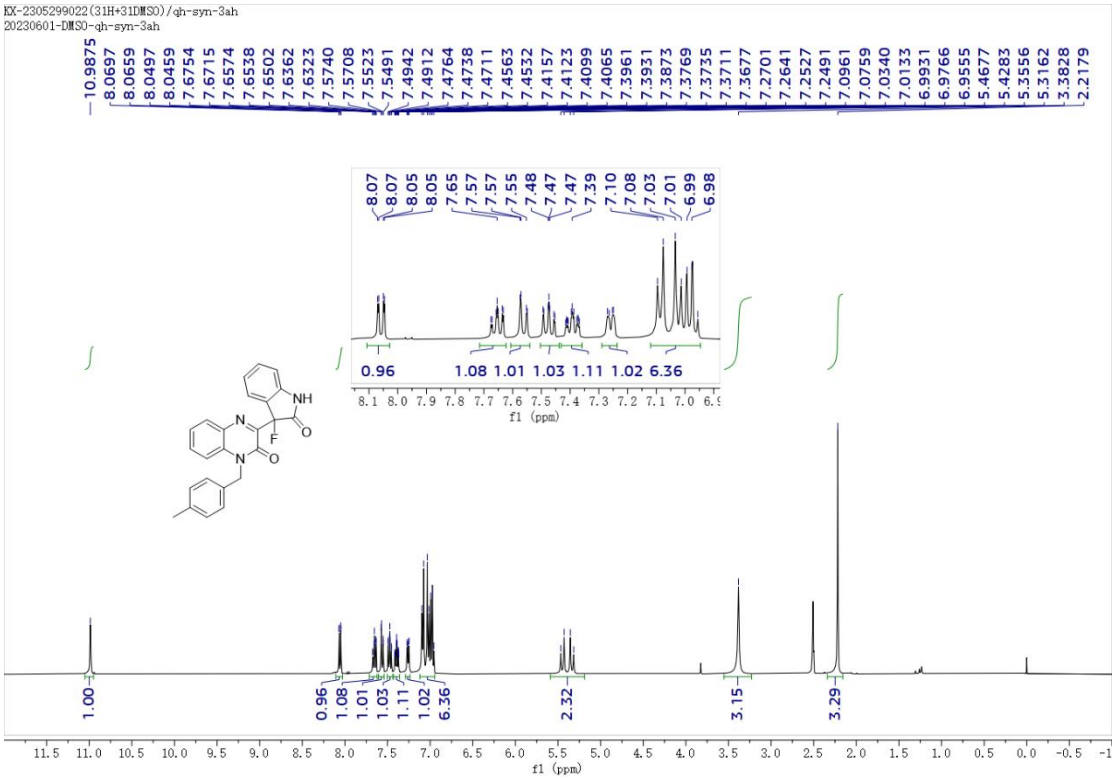


Figure S125 The ^{1}H NMR Spectrum of Compound **3ah** in DMSO-d_6

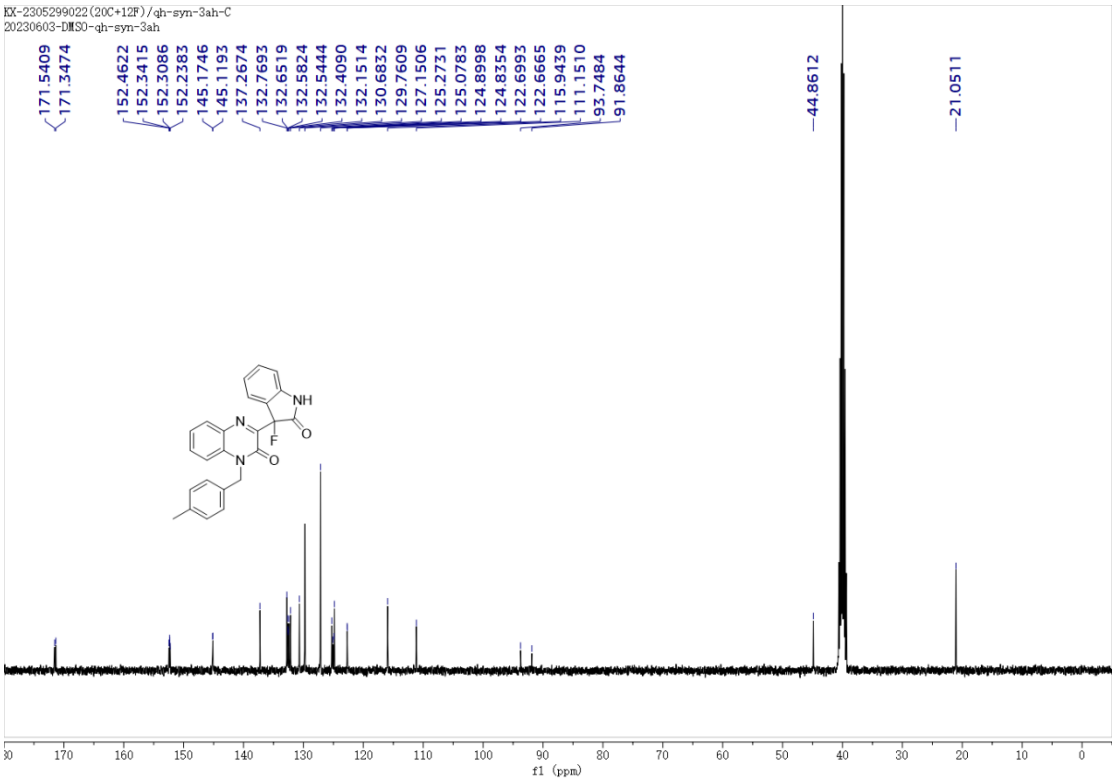


Figure S126 The ^{13}C NMR Spectrum of Compound **3ah** in DMSO-d_6

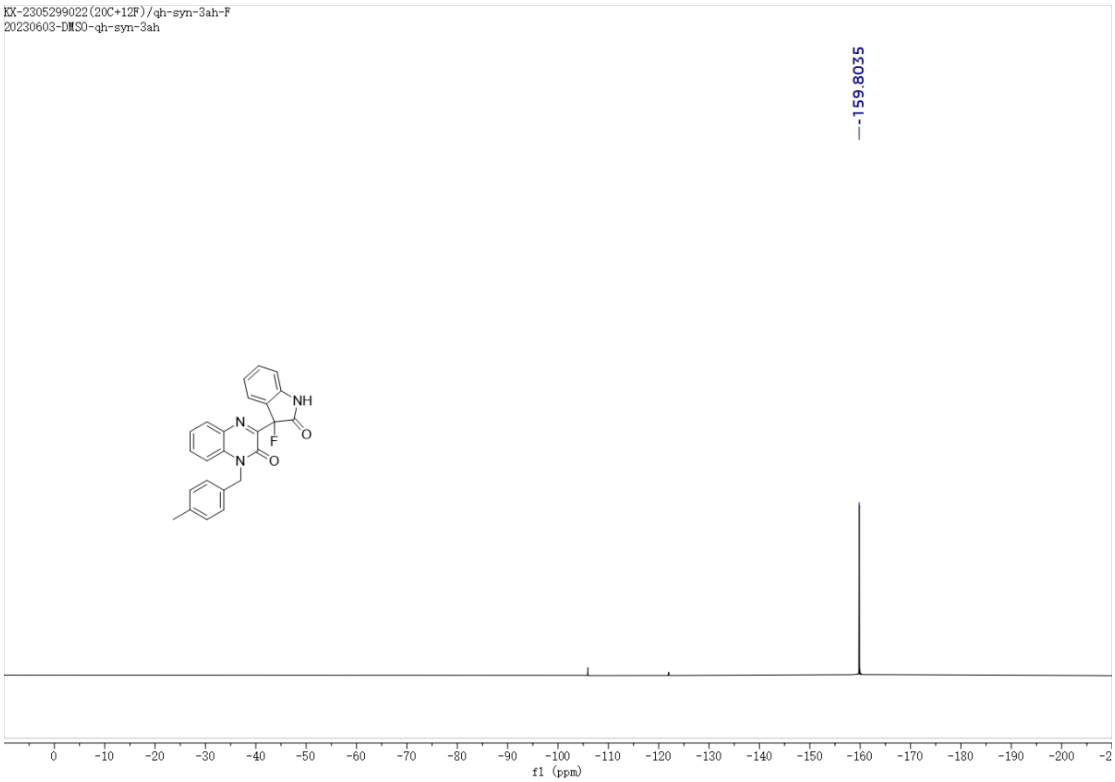


Figure S127 The ^{19}F NMR Spectrum of Compound **3ah** in DMSO-d_6

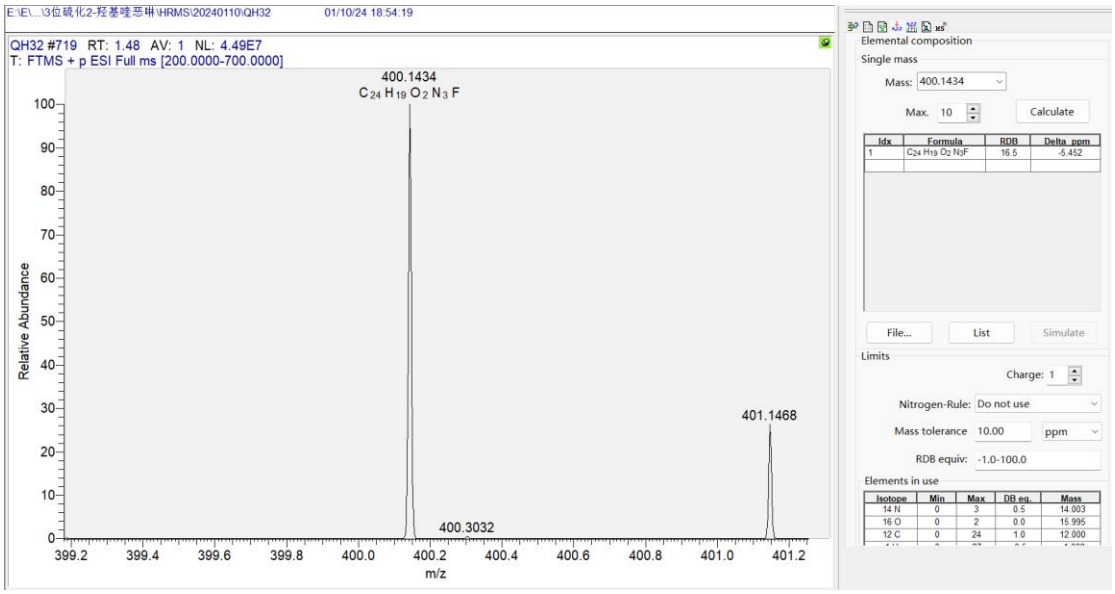


Figure S128. The HR-ESI-MS Spectrum of Compound **3ah**

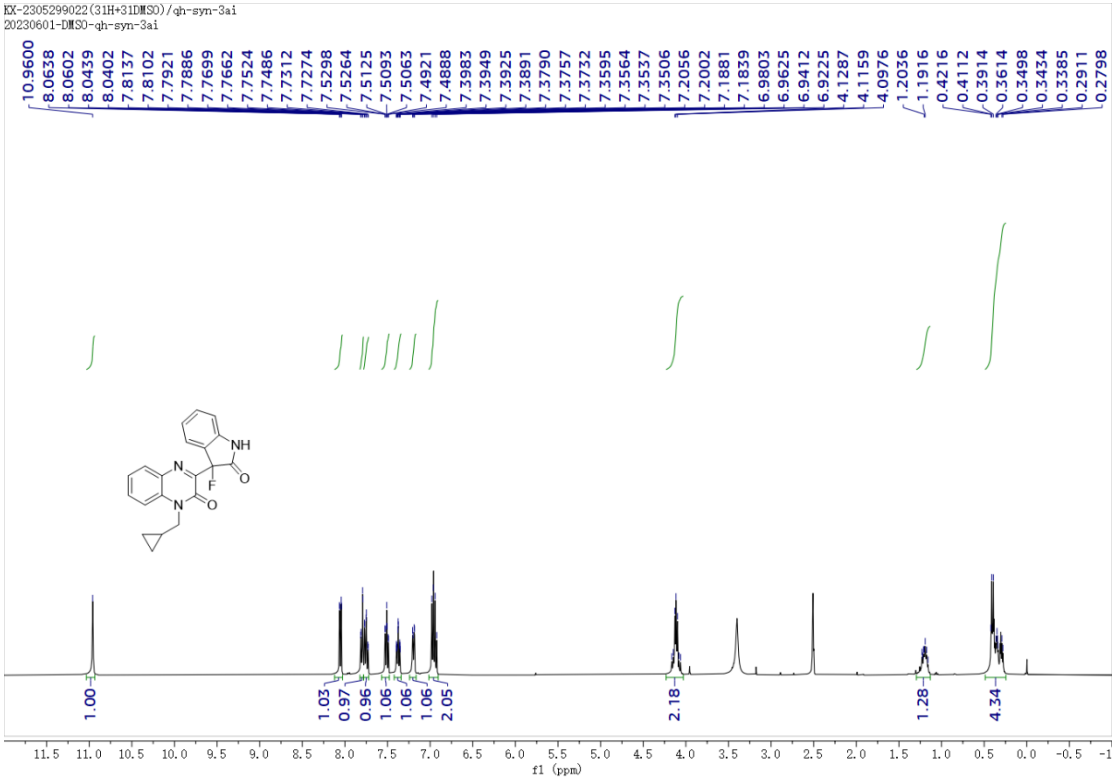


Figure S129 The ^{19}F NMR Spectrum of Compound **3ai** in DMSO-d_6

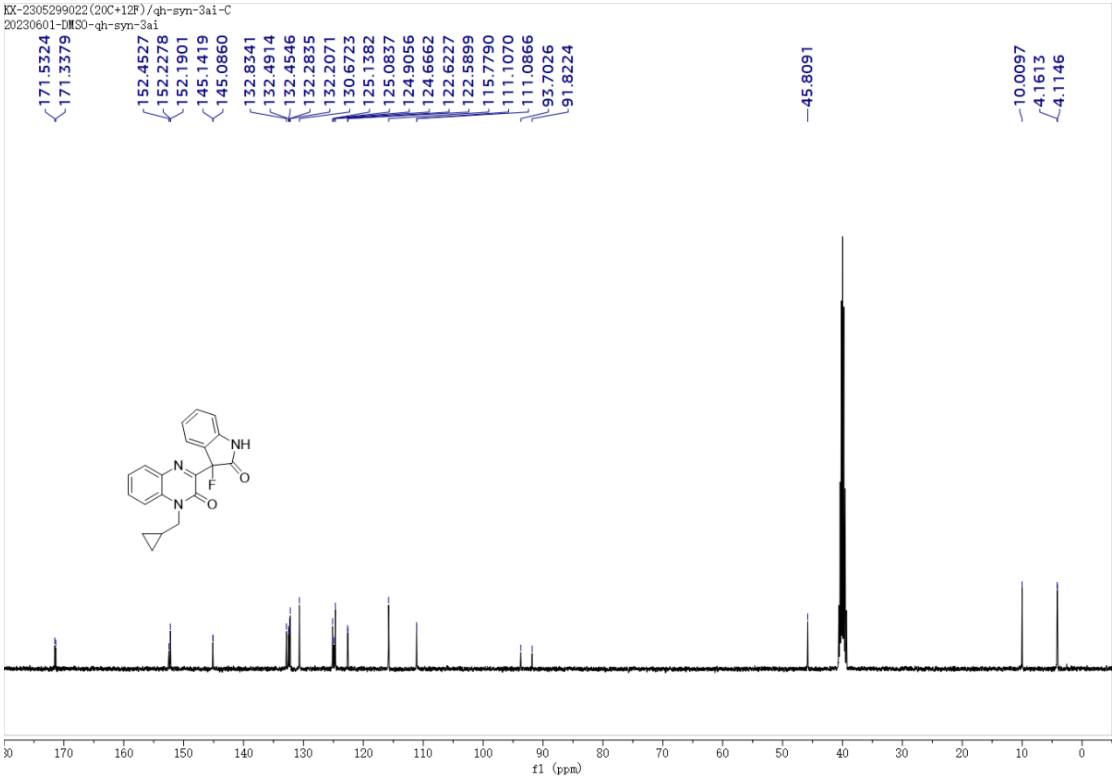


Figure S130 The ^{19}F NMR Spectrum of Compound **3ai** in DMSO-d_6

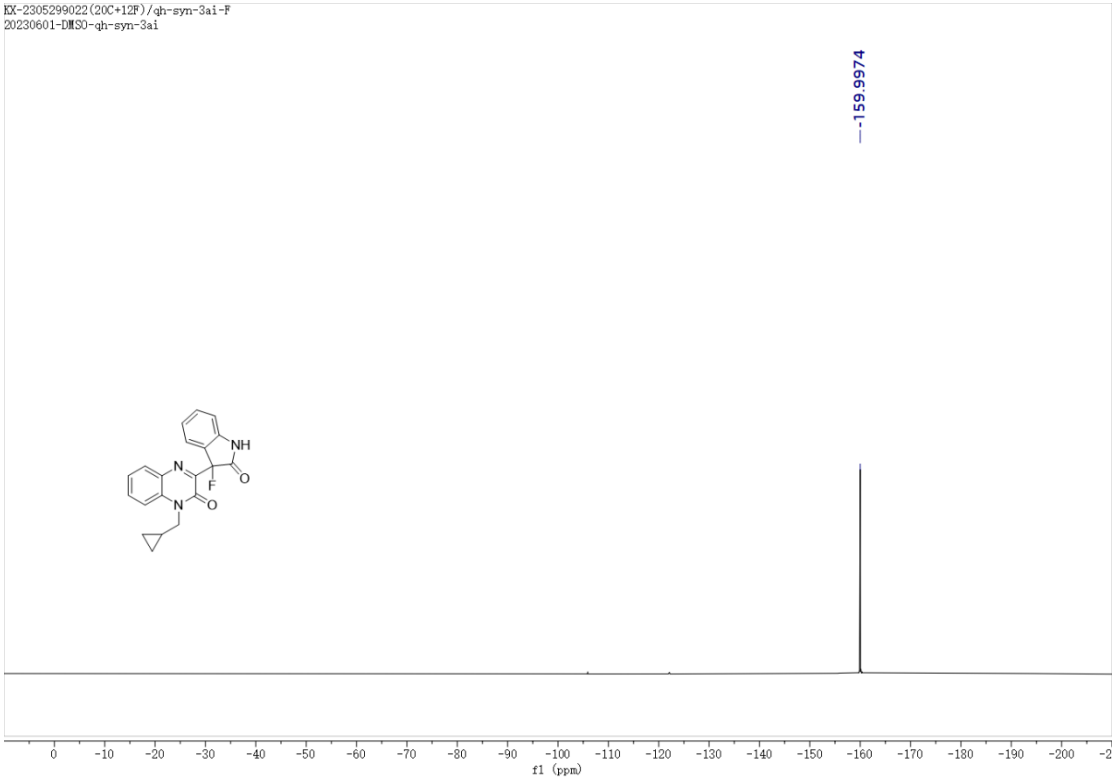


Figure S131 The ^{19}F NMR Spectrum of Compound **3ai** in DMSO-d_6

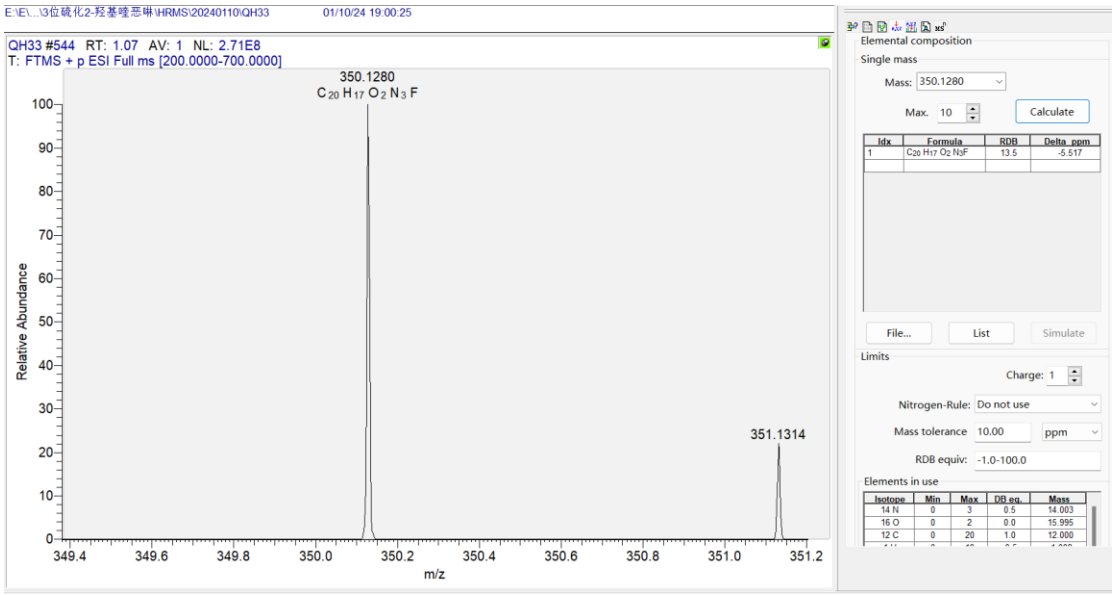


Figure S132. The HR-ESI-MS Spectrum of Compound **3ai**

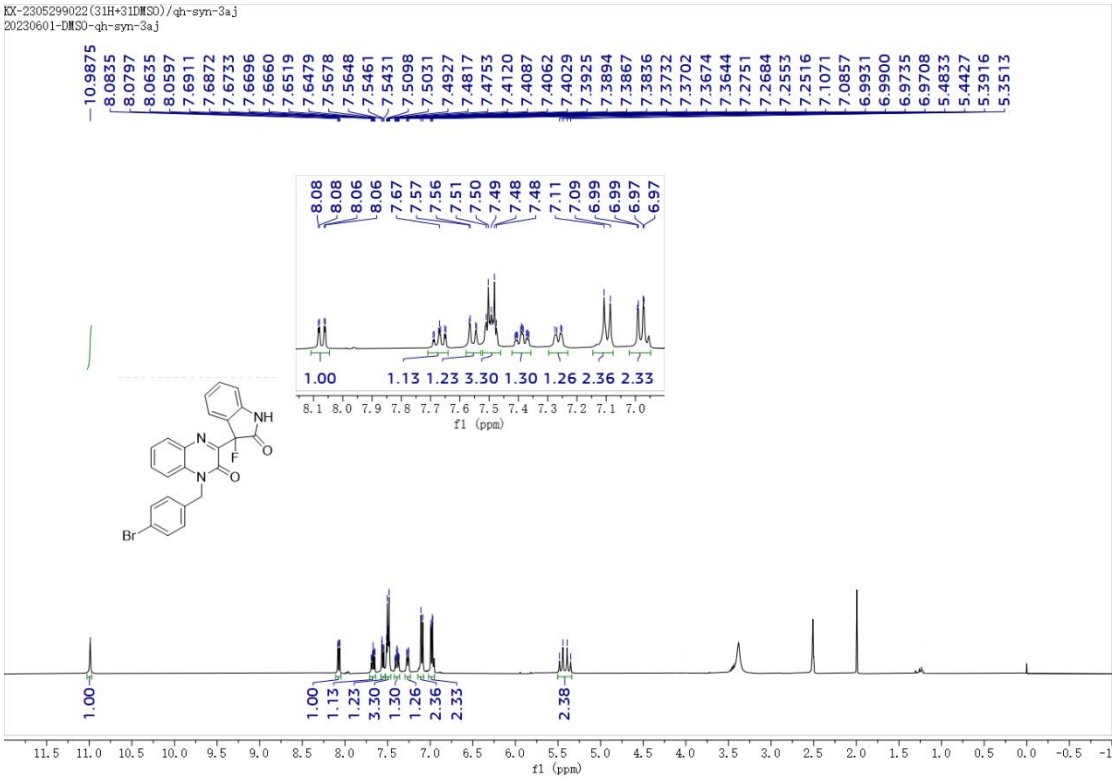


Figure S133 The ^{1}H NMR Spectrum of Compound **3aj** in DMSO-d_6

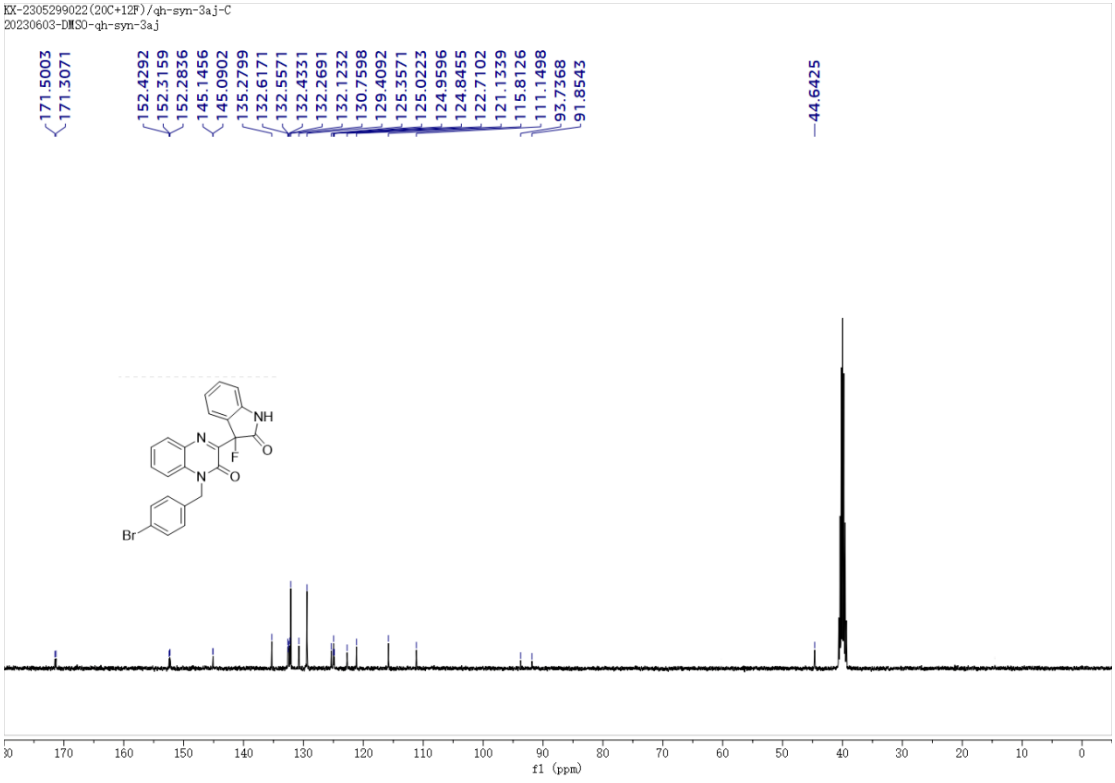


Figure S134 The ^{13}C NMR Spectrum of Compound **3aj** in DMSO-d_6

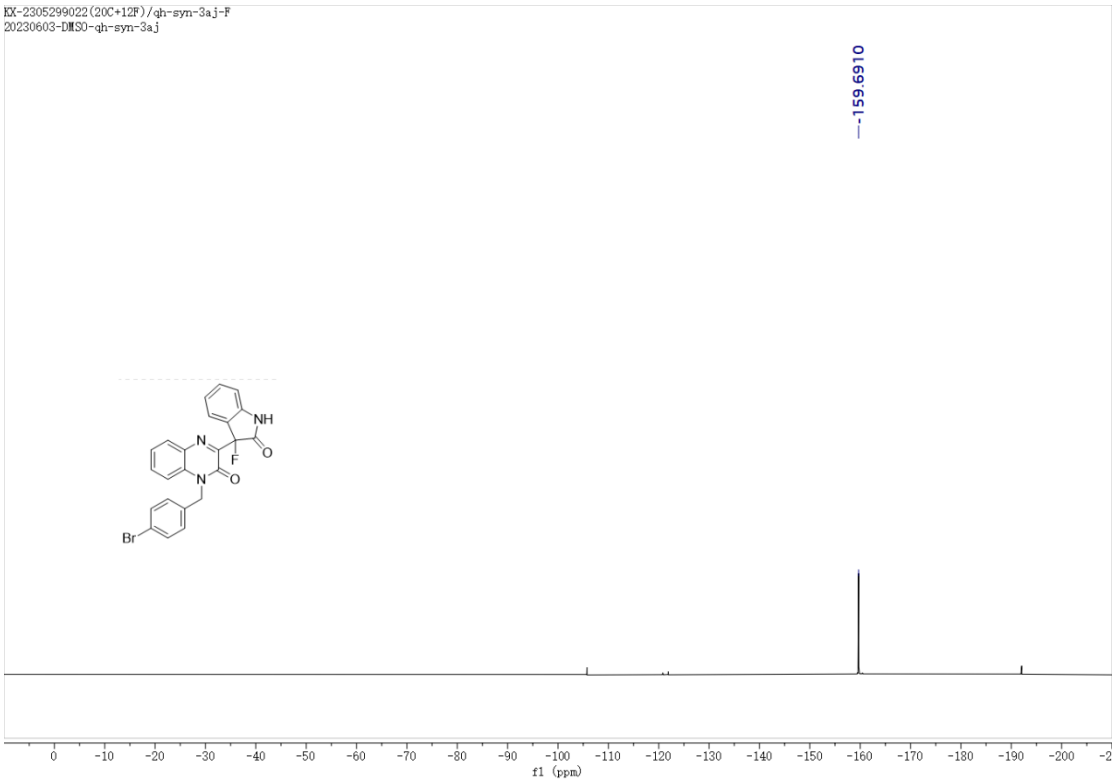


Figure S135 The ^{19}F NMR Spectrum of Compound **3aj** in DMSO-d_6

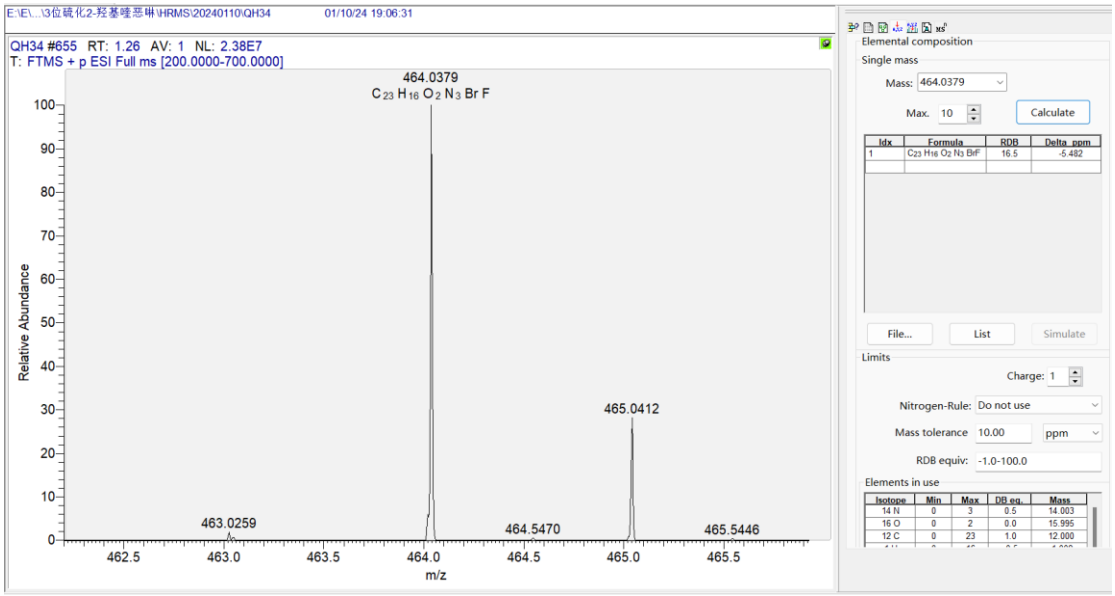


Figure S136. The HR-ESI-MS Spectrum of Compound **3aj**

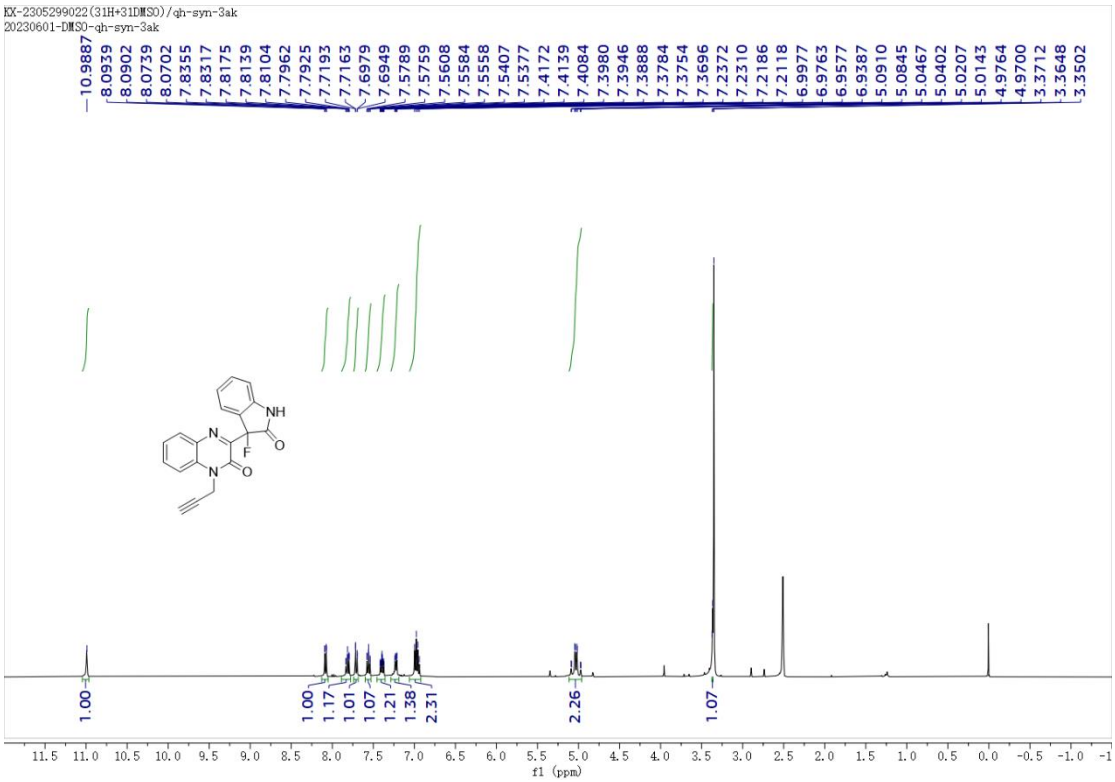


Figure S137 The ^{1}H NMR Spectrum of Compound **3ak** in DMSO-d_6

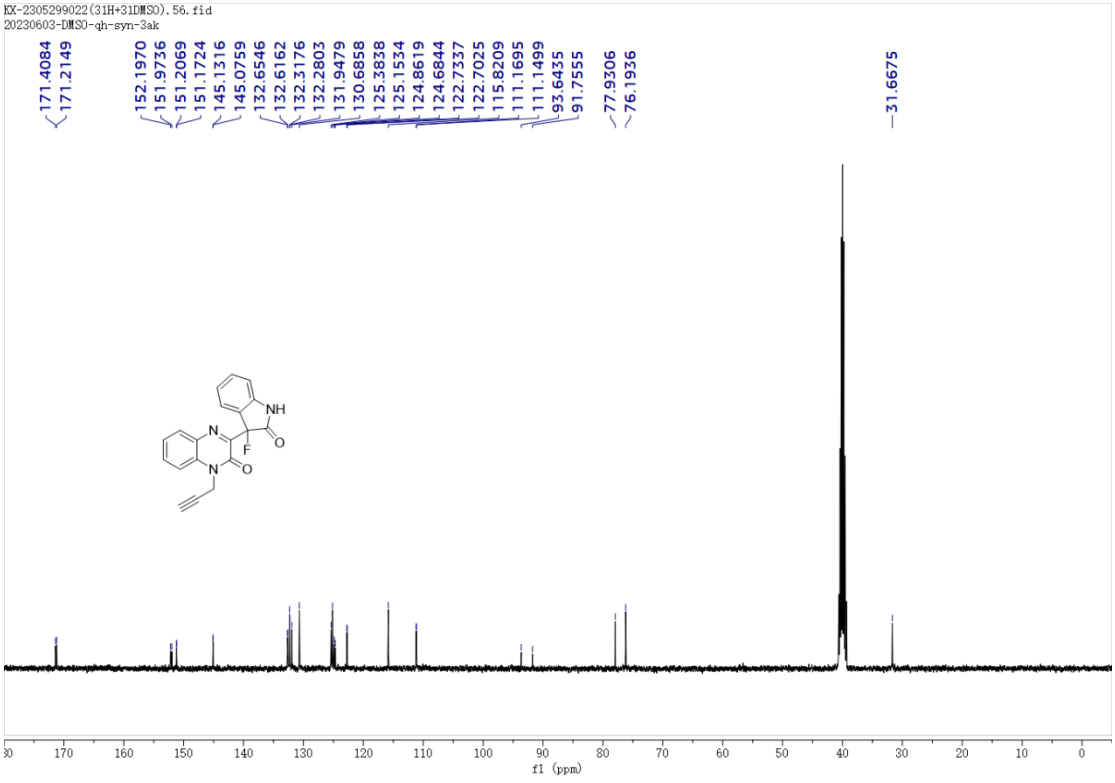


Figure S138 The ^{13}C NMR Spectrum of Compound **3ak** in DMSO-d_6

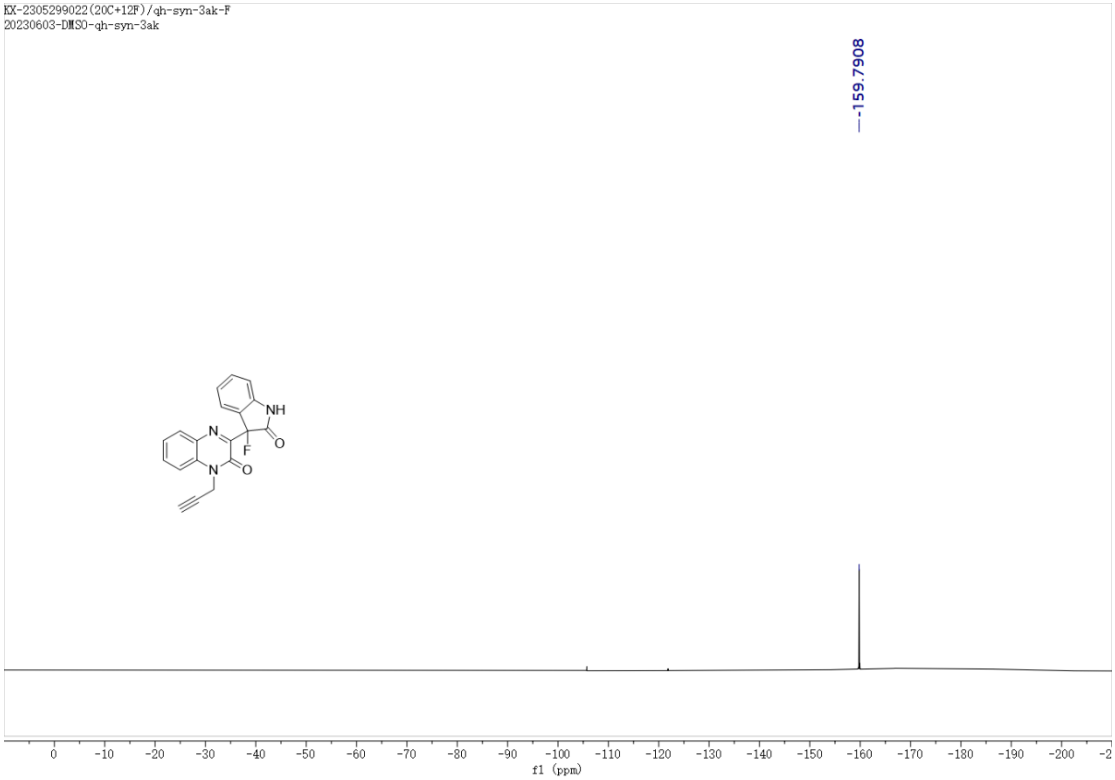


Figure S139 The ^{19}F NMR Spectrum of Compound **3ak** in DMSO-d_6

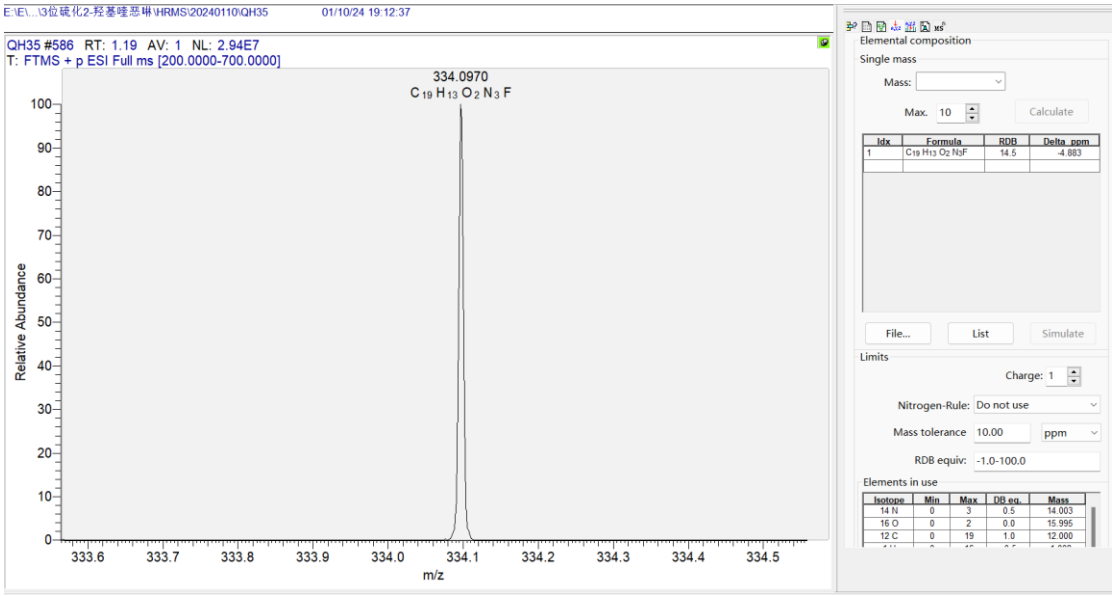


Figure S140. The HR-ESI-MS Spectrum of Compound **3ak**

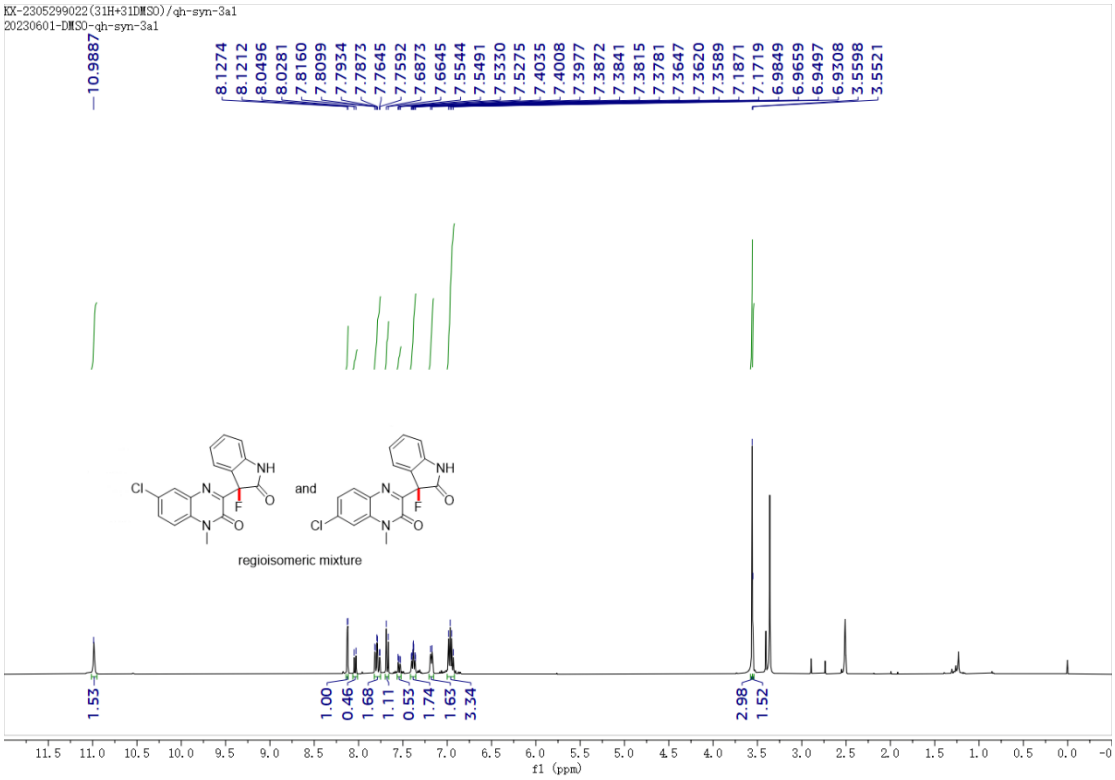


Figure S141 The ^{1}H NMR Spectrum of Compound **3al** in DMSO-d_6

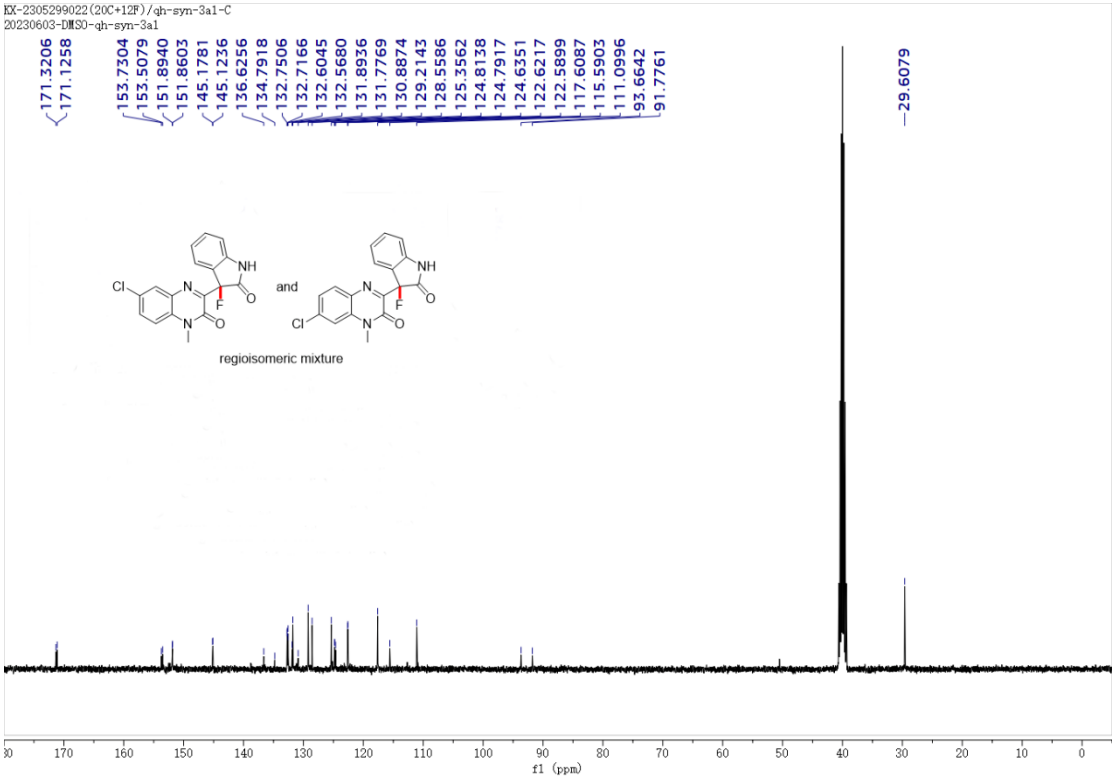


Figure S142 The ^{13}C NMR Spectrum of Compound **3al** in DMSO-d_6

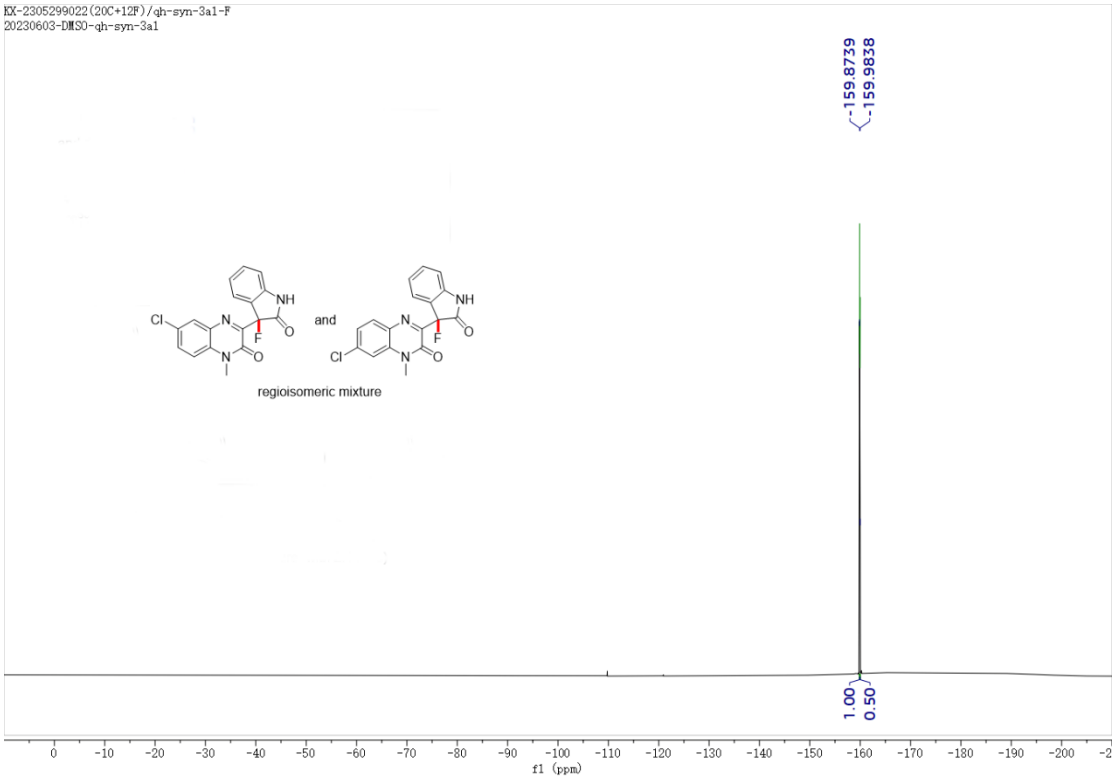


Figure S143 The ^{19}F NMR Spectrum of Compound **3al** in DMSO-d_6

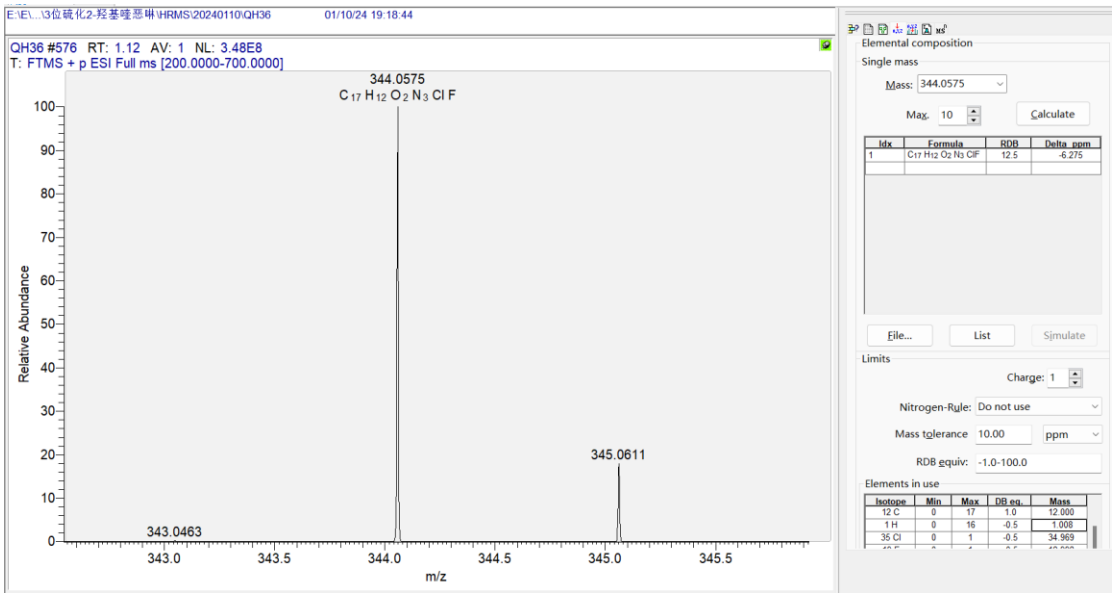


Figure S144. The HR-ESI-MS Spectrum of Compound **3al**

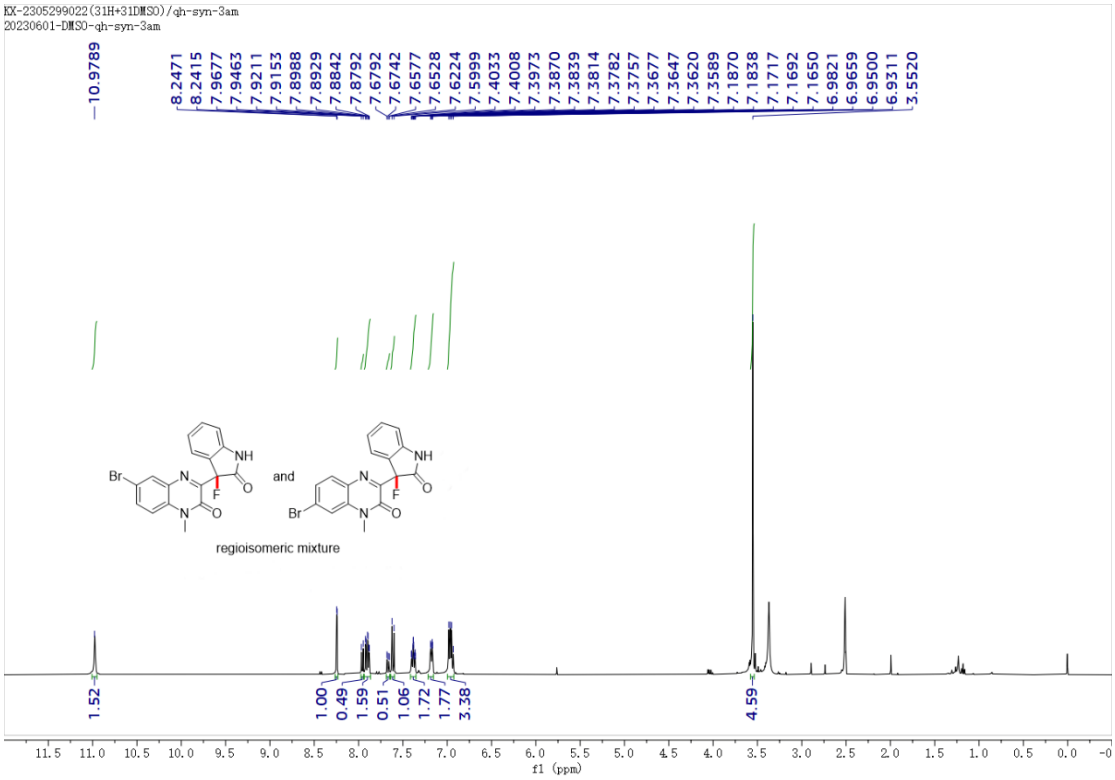


Figure S145 The ^{1}H NMR Spectrum of Compound **3am** in DMSO-d_6

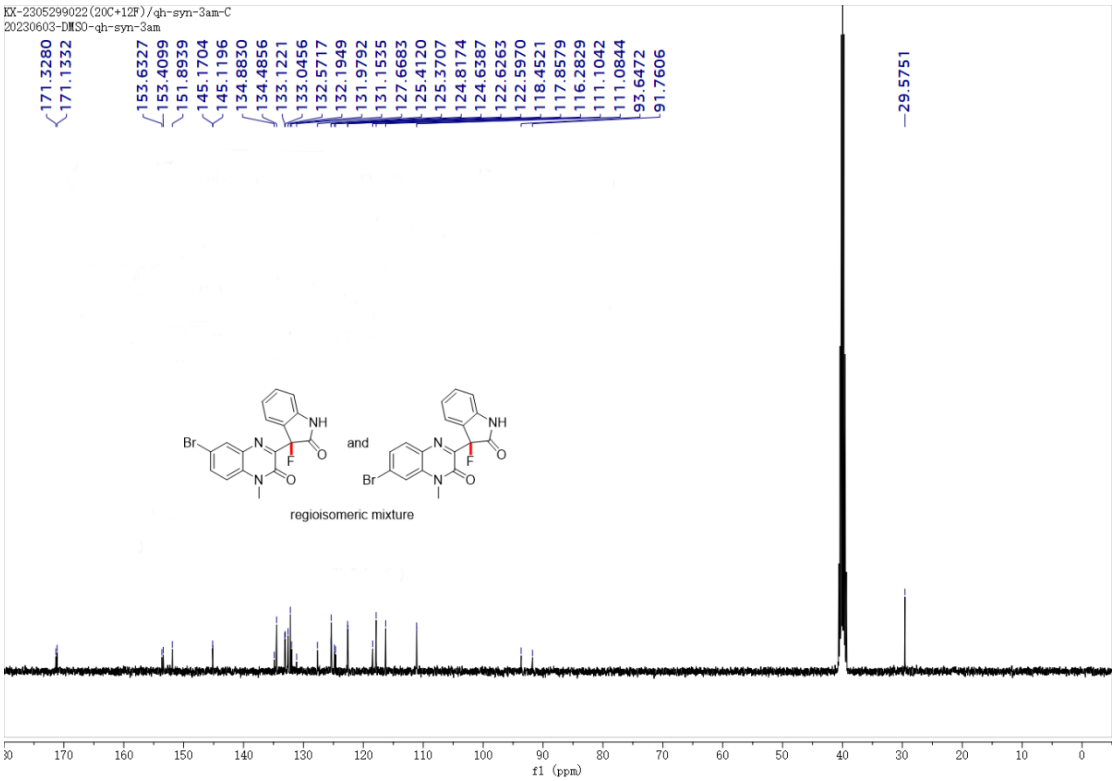


Figure S146 The ^{13}C NMR Spectrum of Compound **3am** in DMSO-d_6

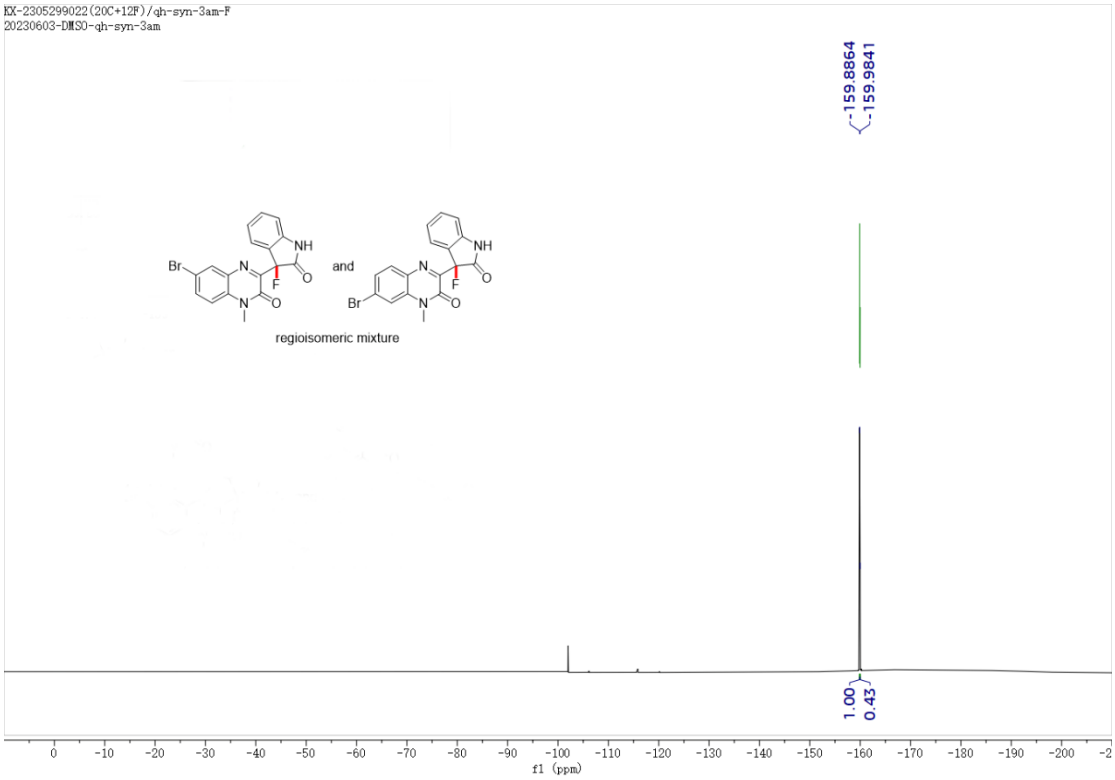


Figure S147 The ^{19}F NMR Spectrum of Compound **3am** in DMSO-d_6

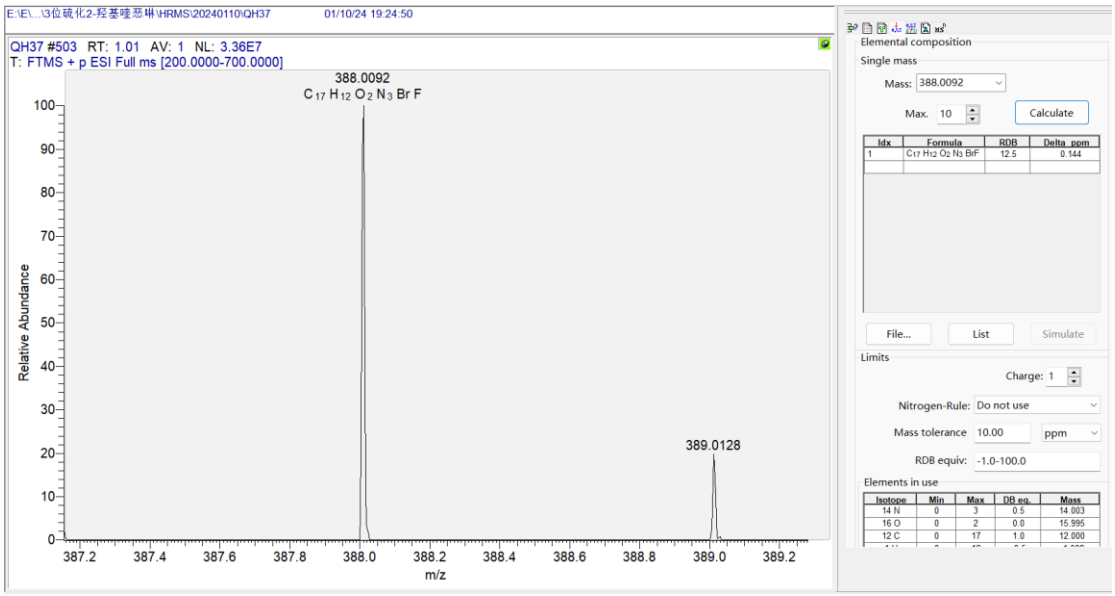


Figure S148. The HR-ESI-MS Spectrum of Compound **3am**

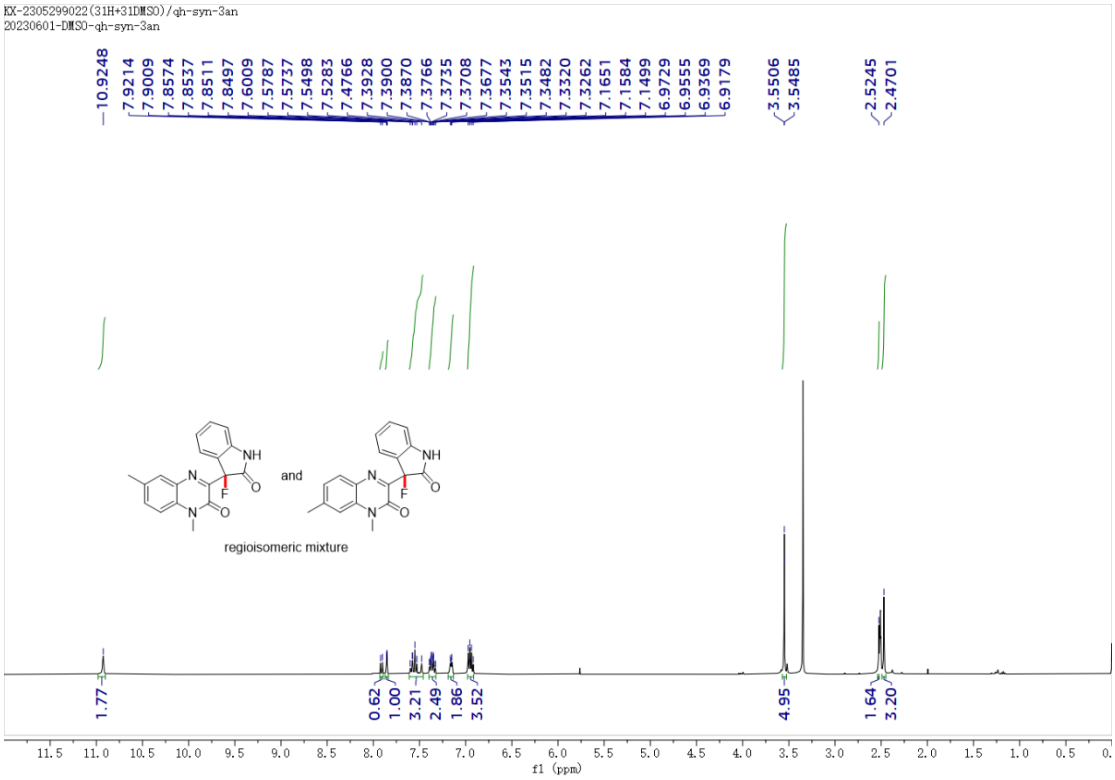


Figure S149 The ^{1}H NMR Spectrum of Compound **3an** in DMSO-d_6

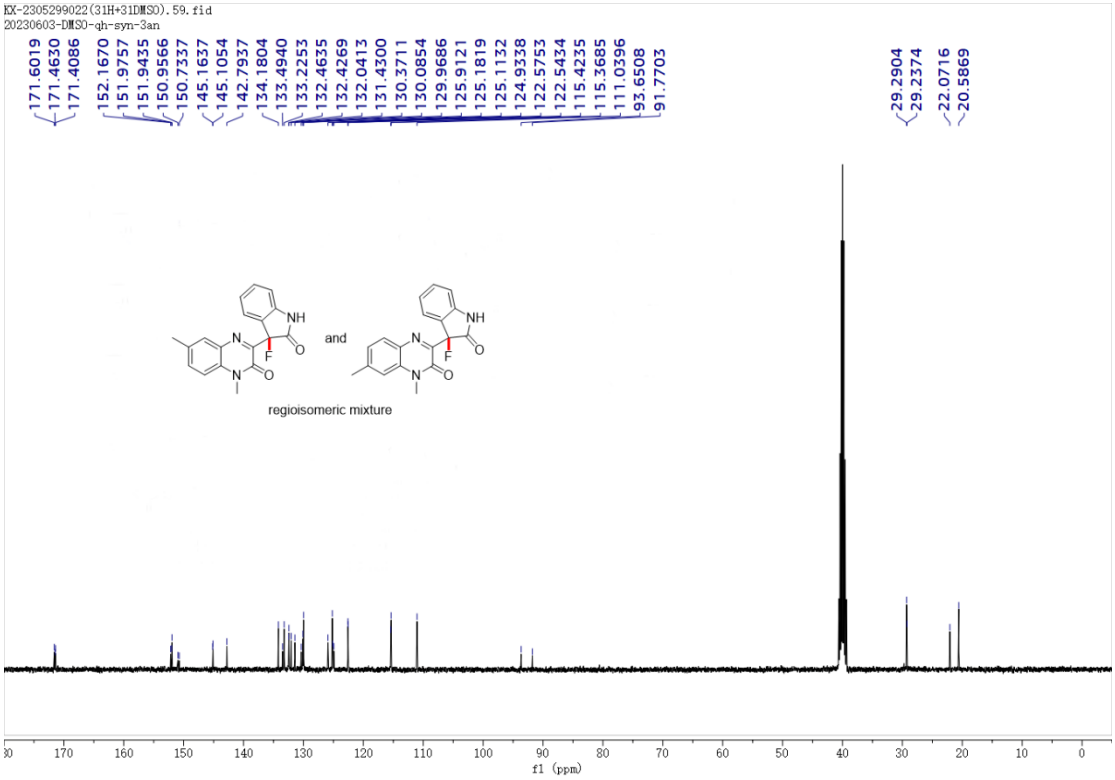


Figure S150 The ^{13}C NMR Spectrum of Compound **3an** in DMSO-d_6

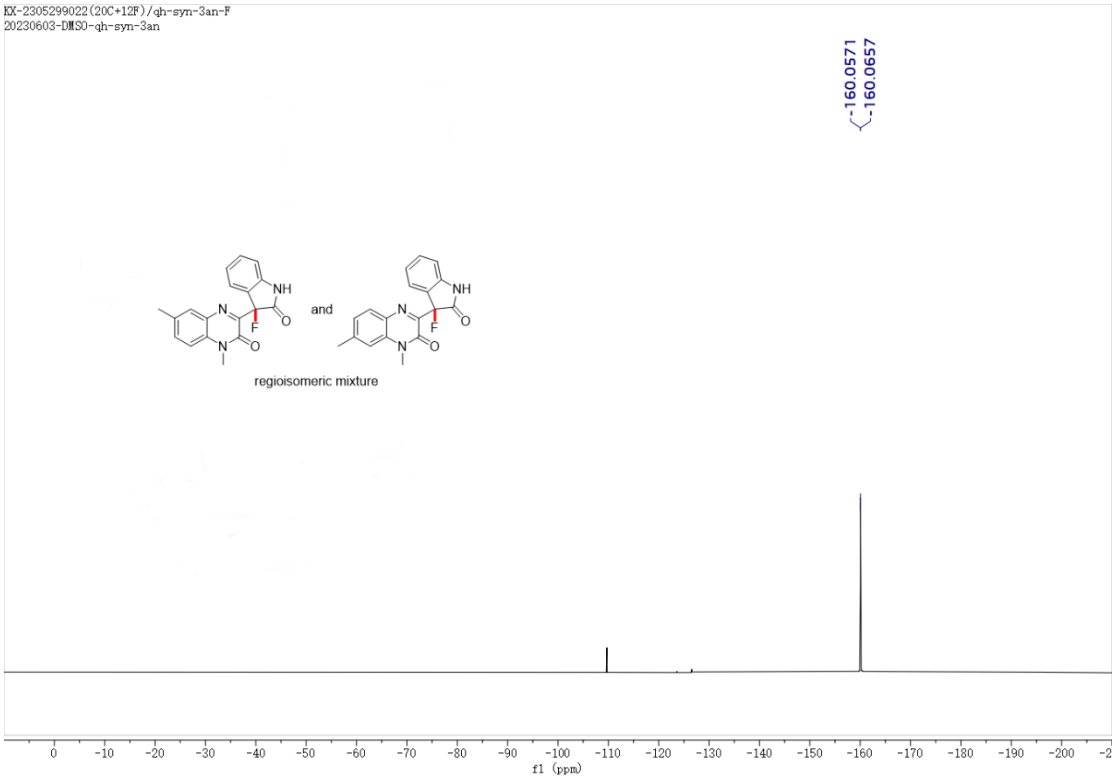


Figure S151 The ^{19}F NMR Spectrum of Compound **3an** in DMSO-d_6

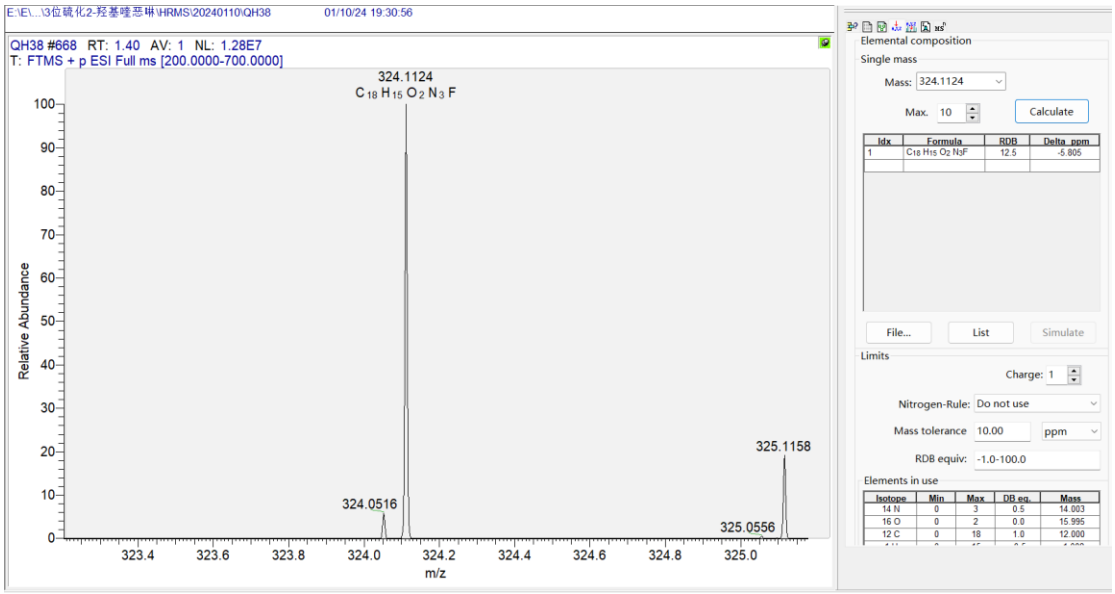


Figure S152. The HR-ESI-MS Spectrum of Compound **3an**

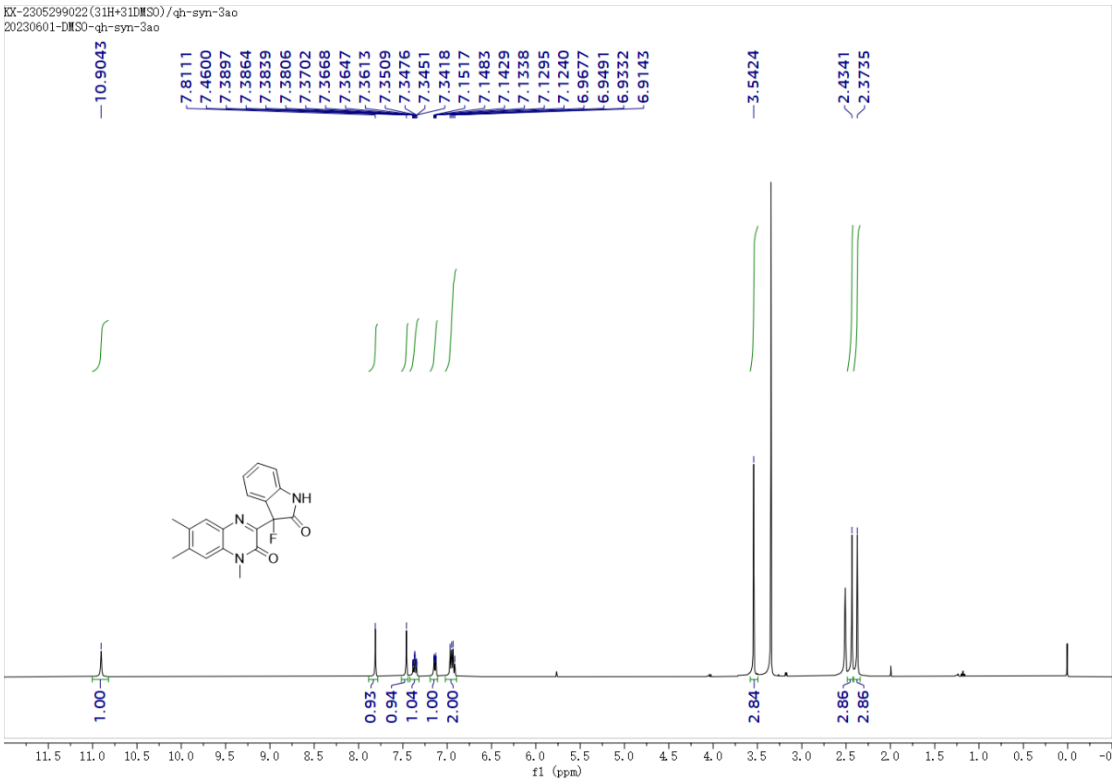


Figure S153 The ^{1}H NMR Spectrum of Compound **3ao** in DMSO-d_6

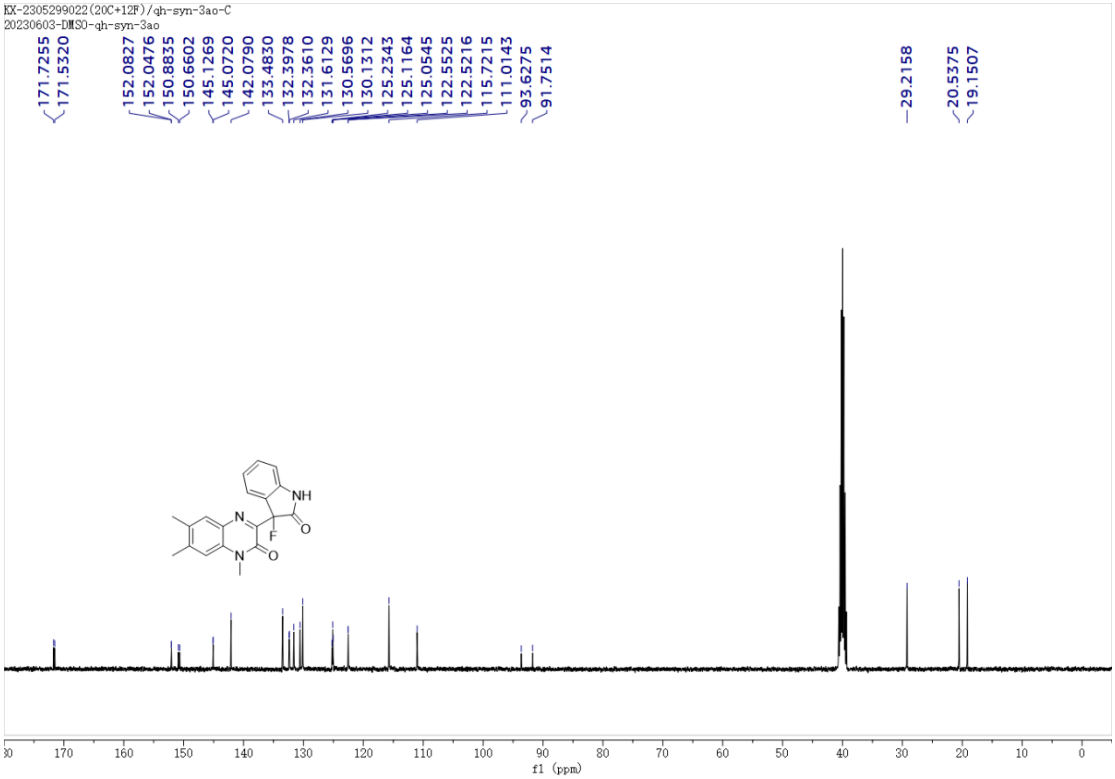


Figure S154 The ^{13}C NMR Spectrum of Compound **3ao** in DMSO-d_6

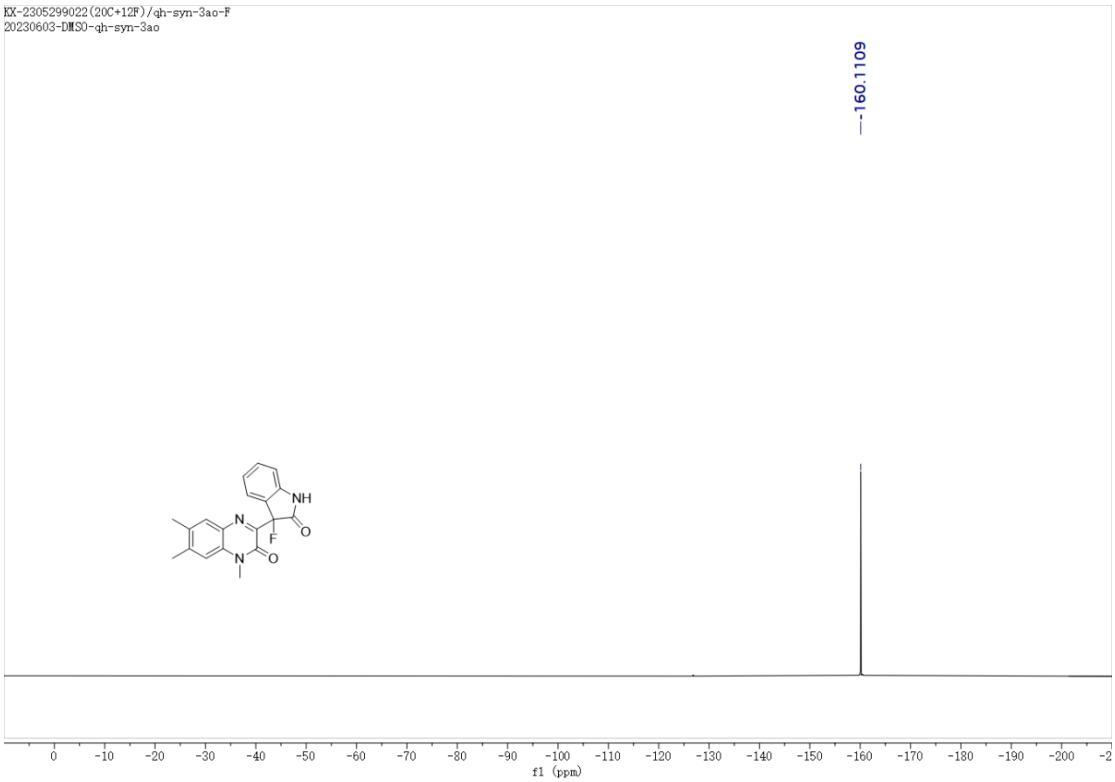


Figure S155 The ^{19}F NMR Spectrum of Compound **3ao** in DMSO-d_6

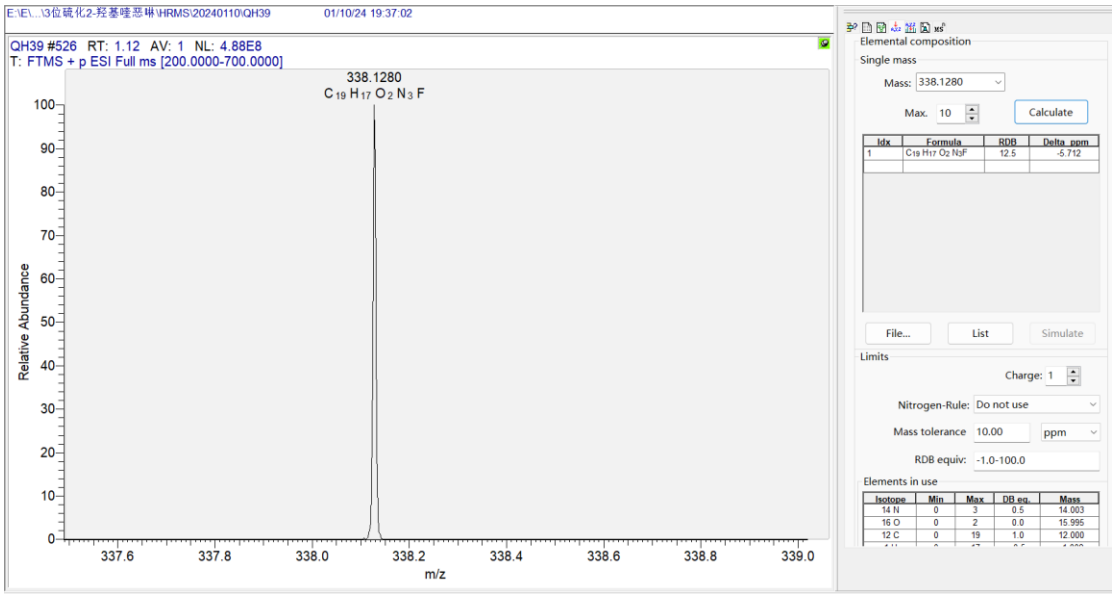


Figure S156. The HR-ESI-MS Spectrum of Compound **3ao**

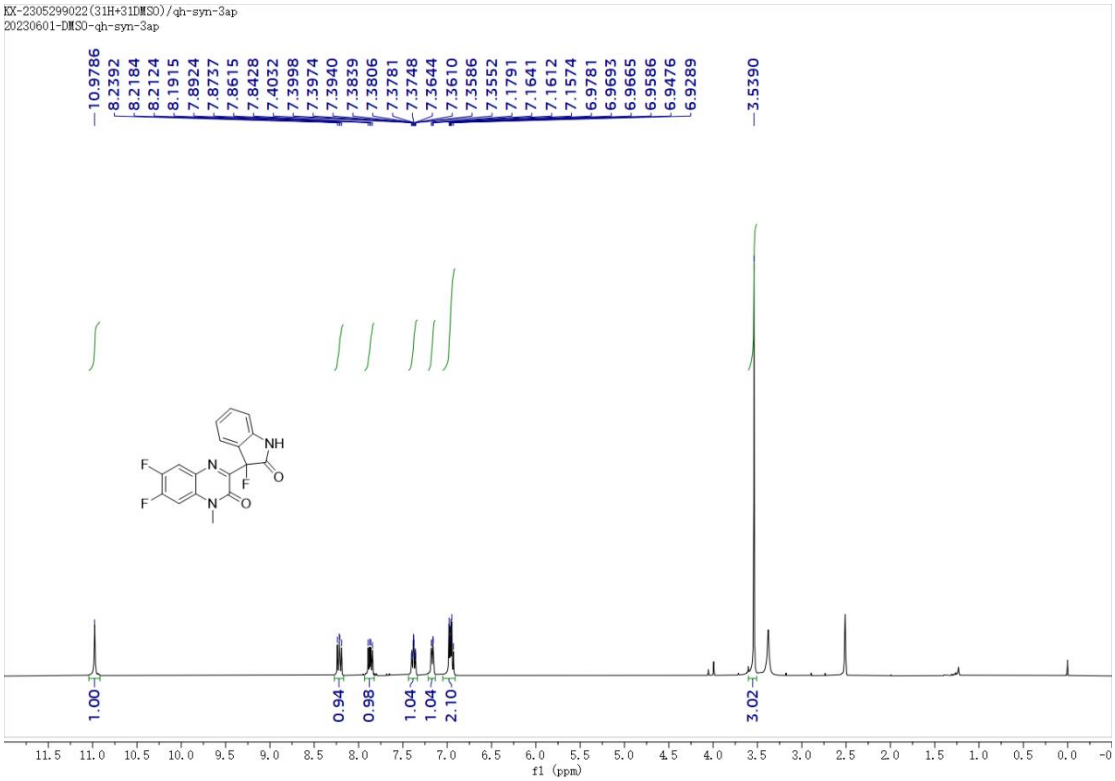


Figure S157 The ^{1}H NMR Spectrum of Compound **3ap** in DMSO-d_6

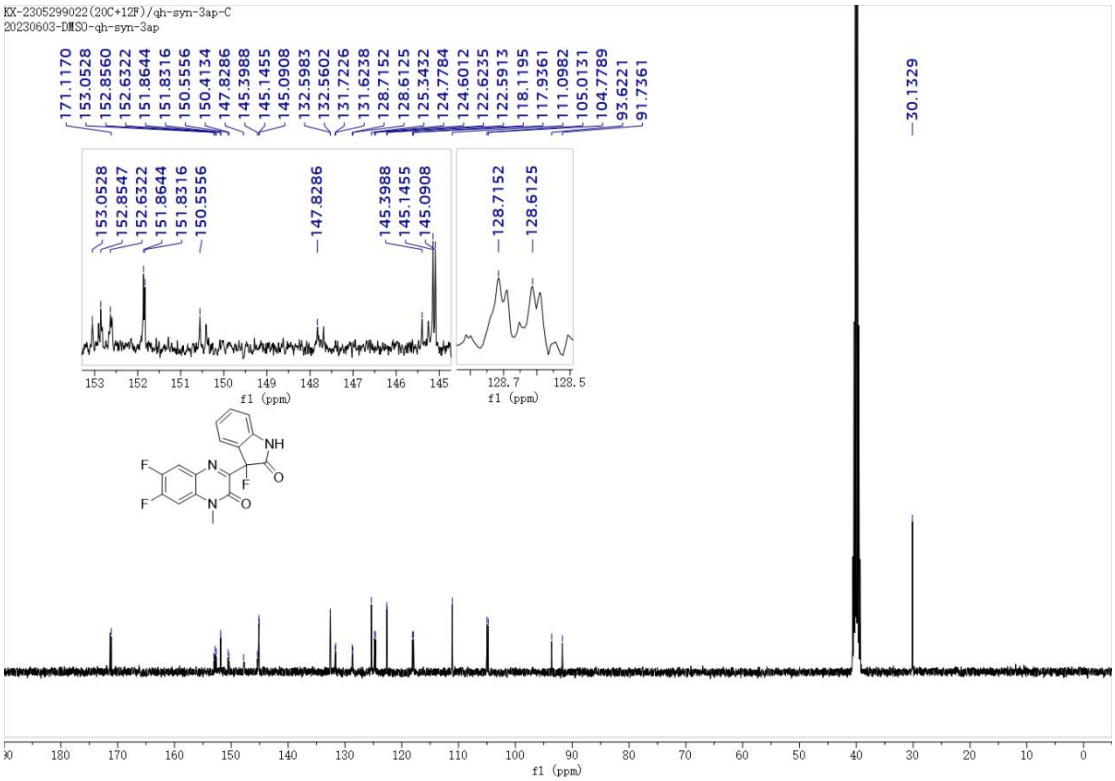


Figure S158 The ^{13}C NMR Spectrum of Compound **3ap** in DMSO-d_6

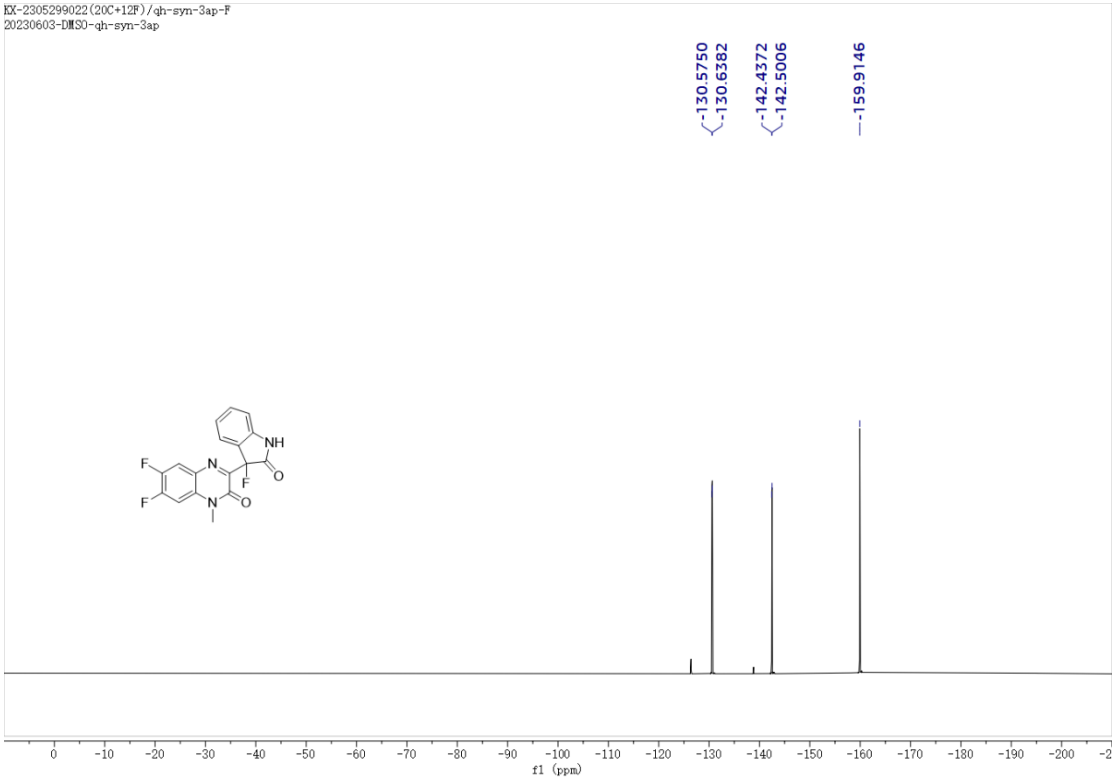


Figure S159 The ^{19}F NMR Spectrum of Compound **3ap** in DMSO-d_6

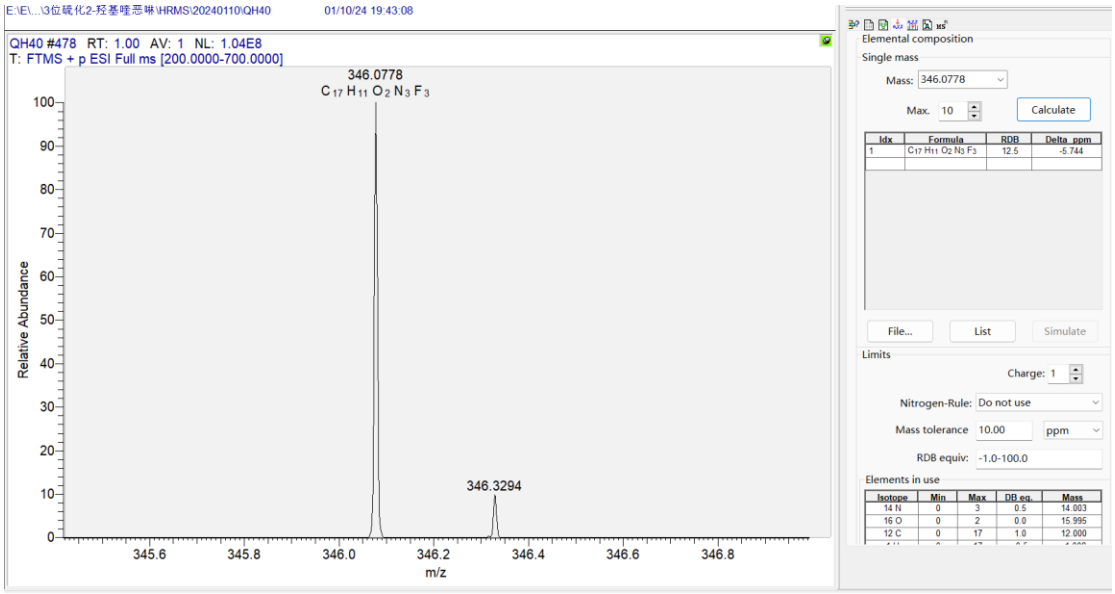


Figure S160. The HR-ESI-MS Spectrum of Compound **3ap**

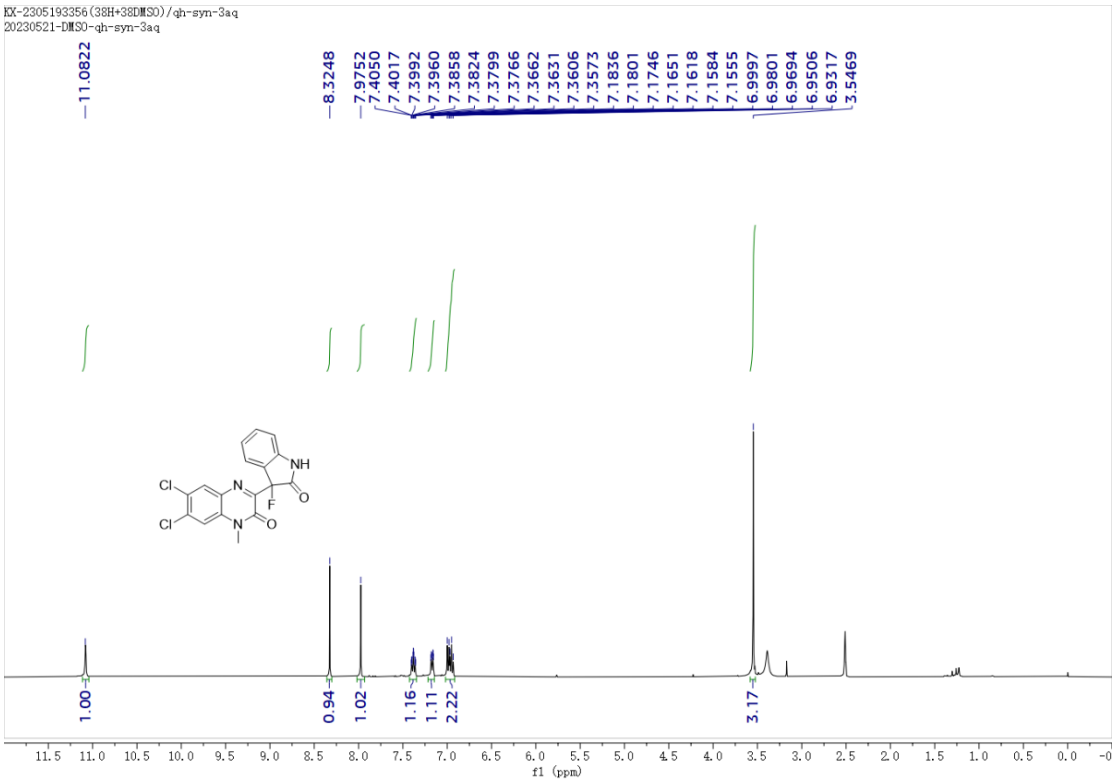


Figure S161 The ^{1}H NMR Spectrum of Compound **3aq** in DMSO-d_6

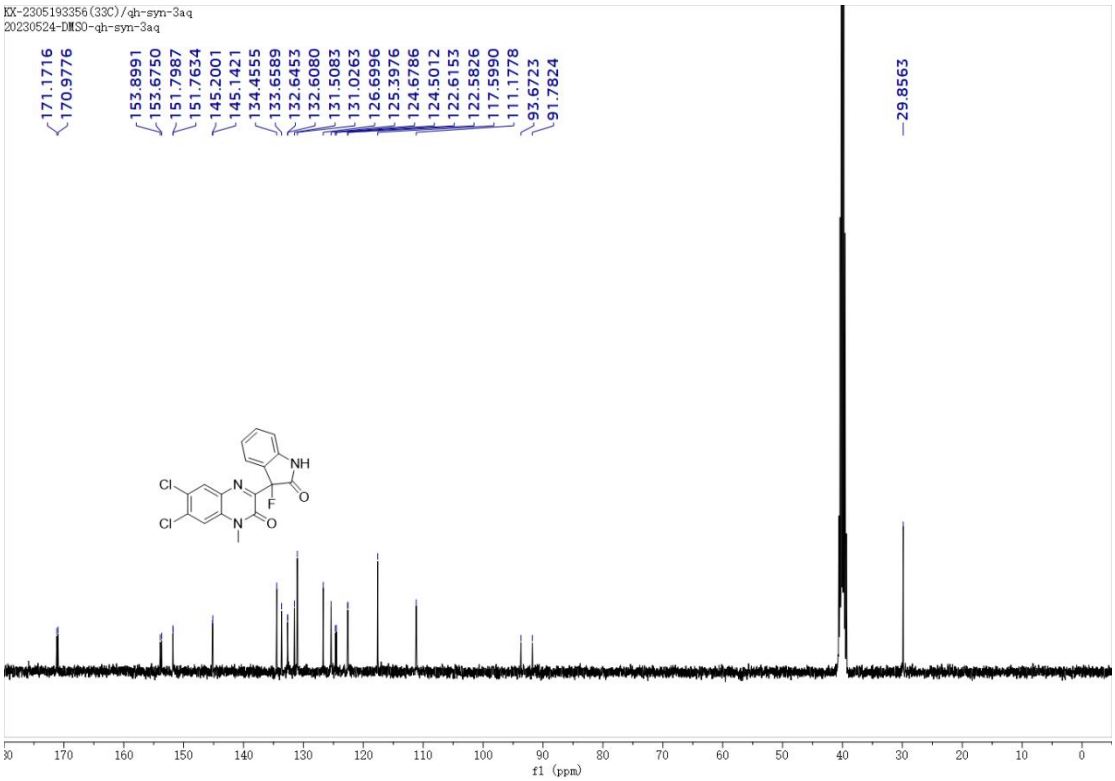


Figure S162 The ^{13}C NMR Spectrum of Compound **3aq** in DMSO-d_6

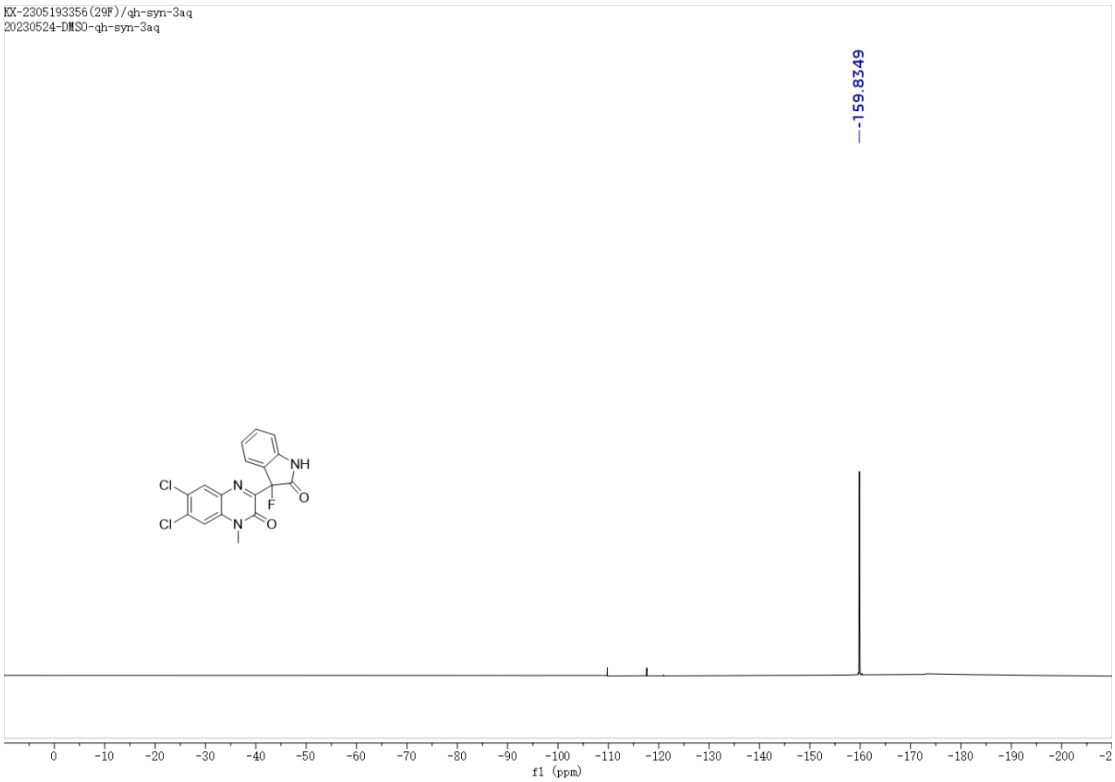


Figure S163 The ^{19}F NMR Spectrum of Compound **3aq** in DMSO-d_6

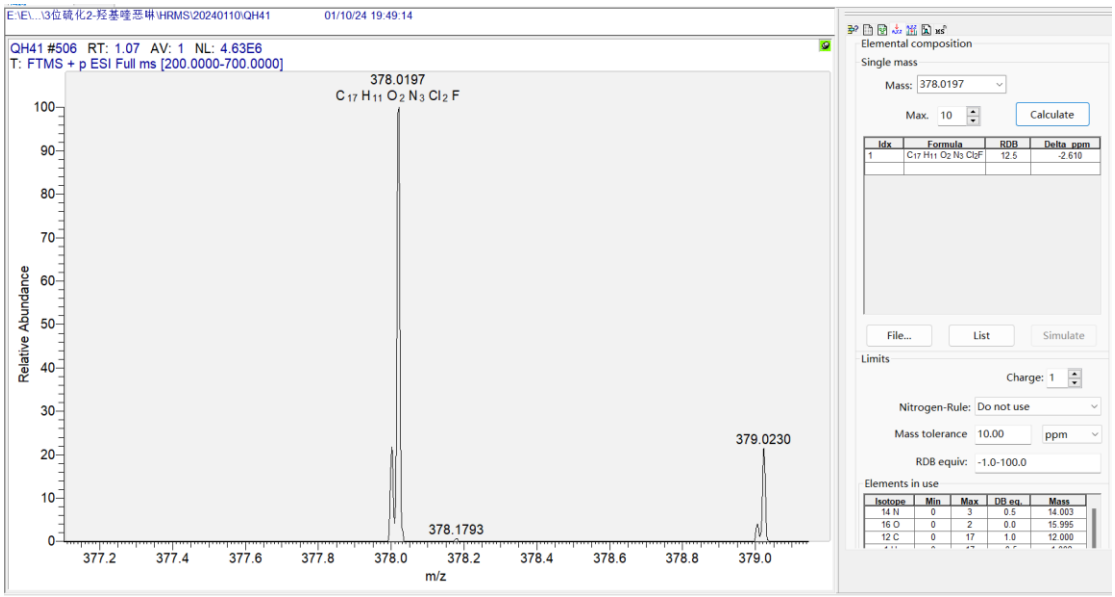


Figure S164. The HR-ESI-MS Spectrum of Compound **3aq**

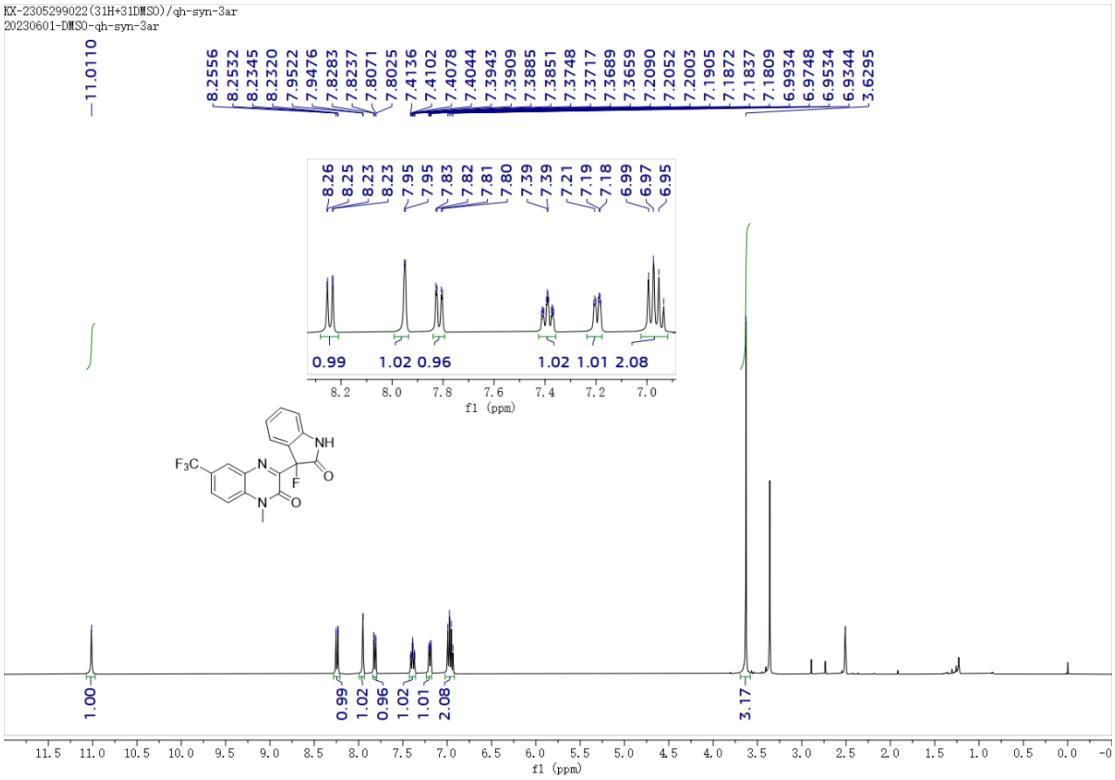


Figure S165 The ^{1}H NMR Spectrum of Compound **3ar** in DMSO-d_6

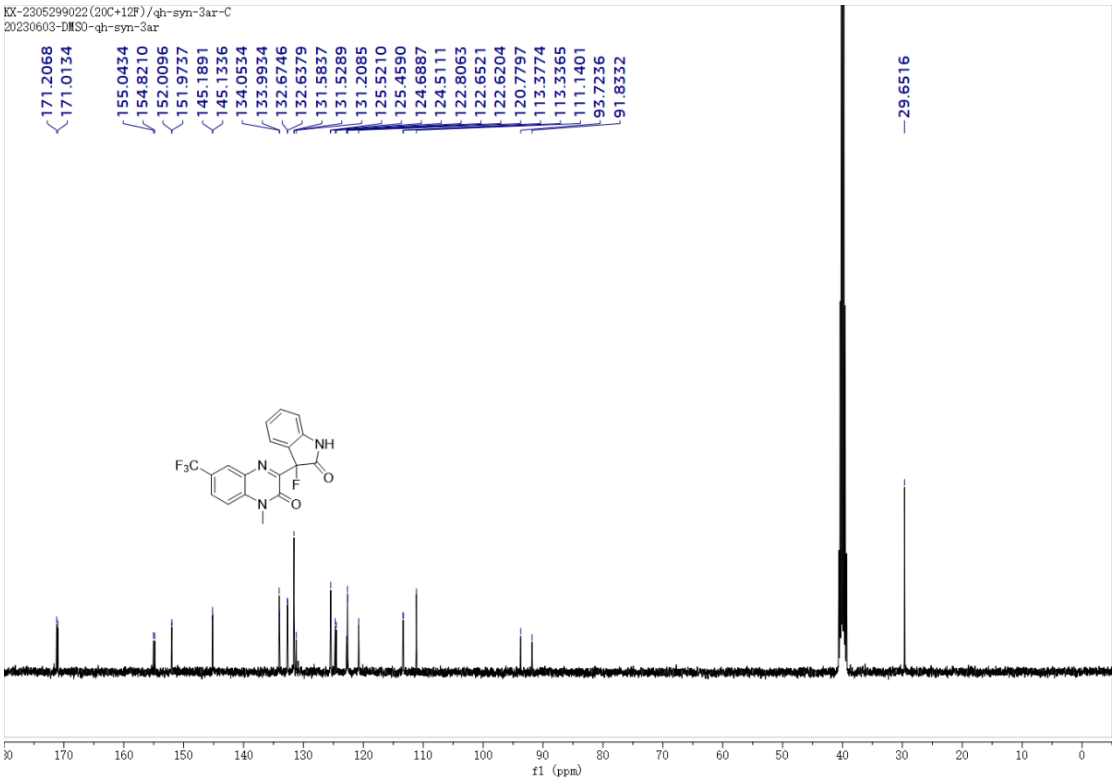


Figure S166 The ^{13}C NMR Spectrum of Compound **3ar** in DMSO-d_6

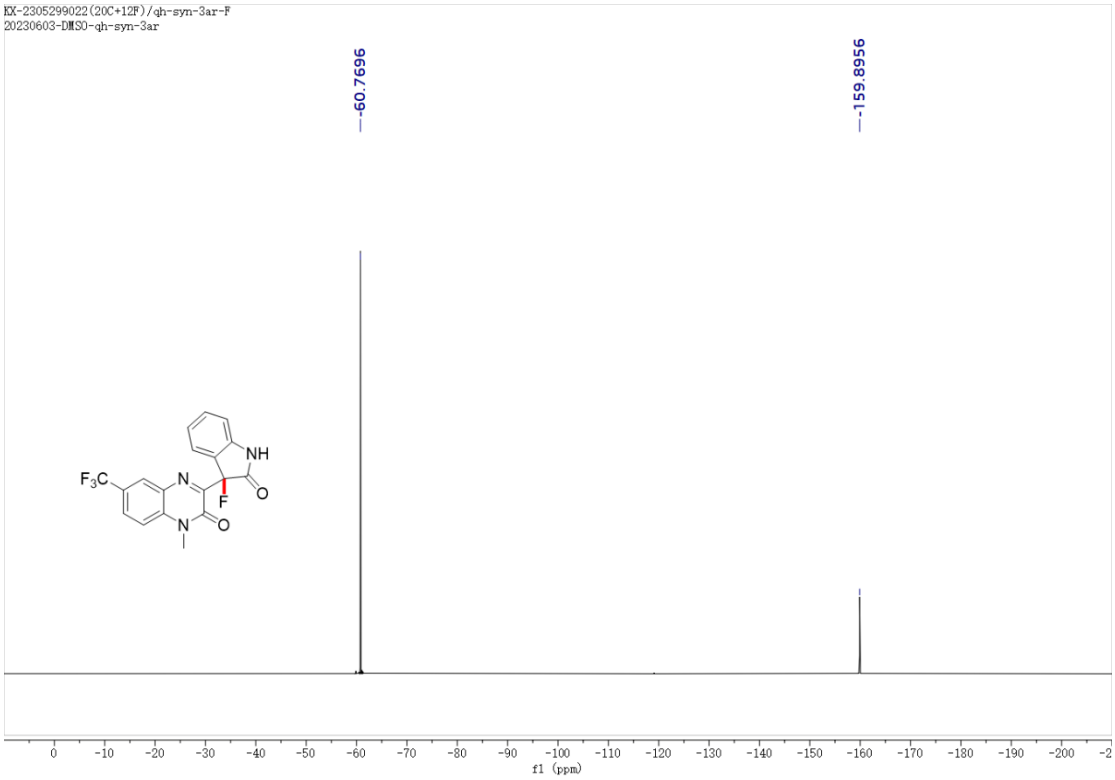


Figure S167 The ^{19}F NMR Spectrum of Compound **3ar** in DMSO-d_6

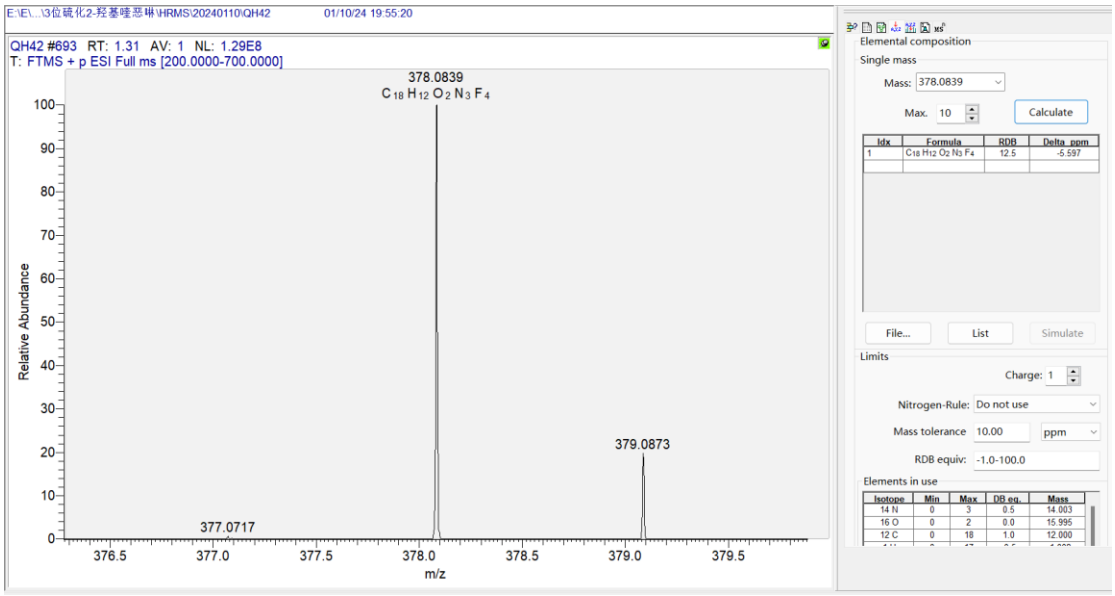


Figure S168 The HR-ESI-MS Spectrum of Compound **3ar**

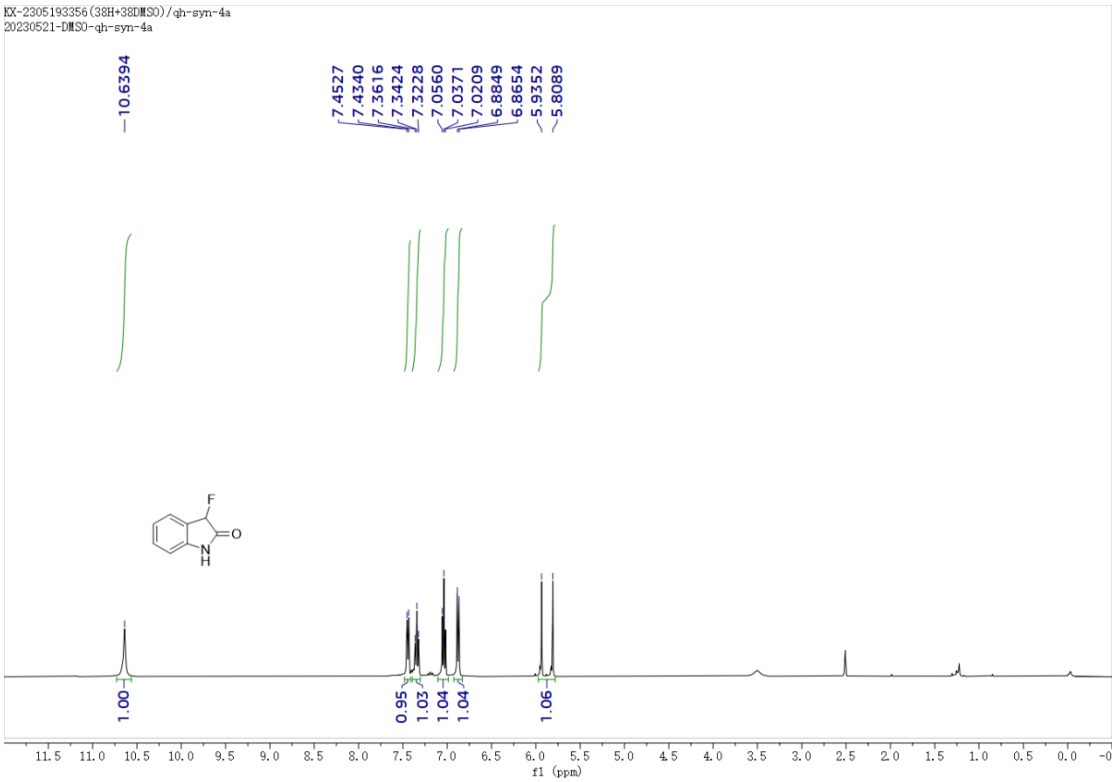


Figure S169 The ^{1}H NMR Spectrum of Compound **4a** in DMSO-d_6

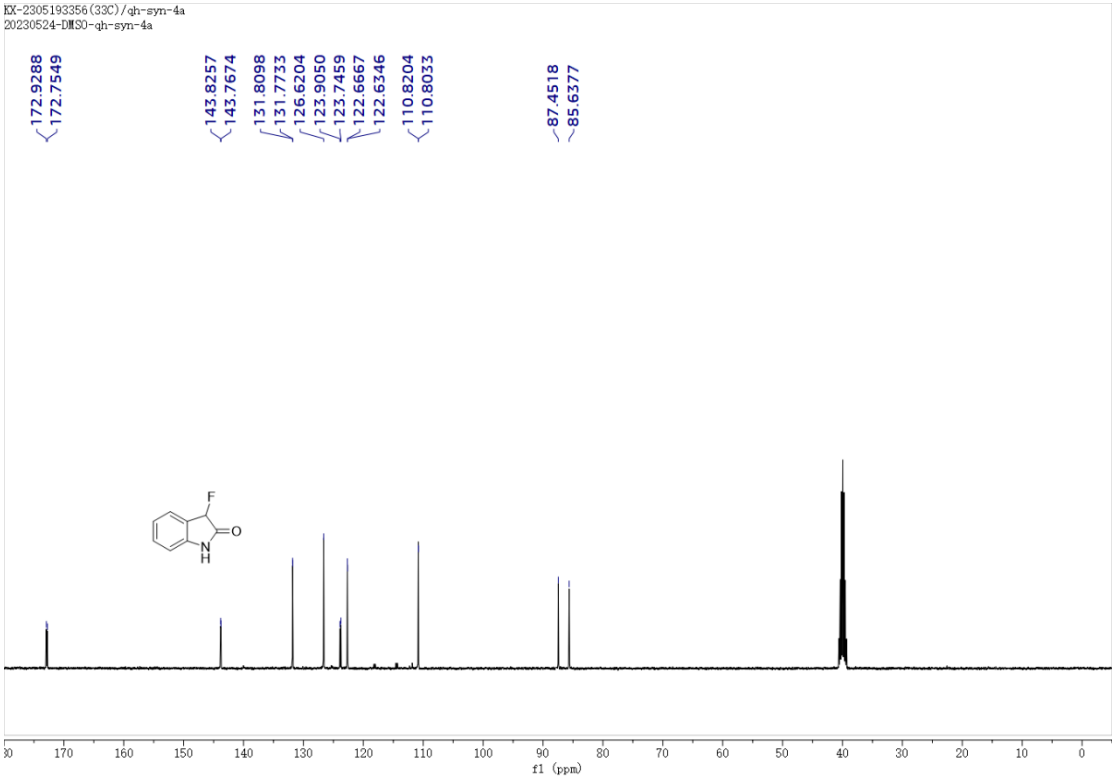


Figure S170 The ^{13}C NMR Spectrum of Compound **4a** in DMSO-d_6

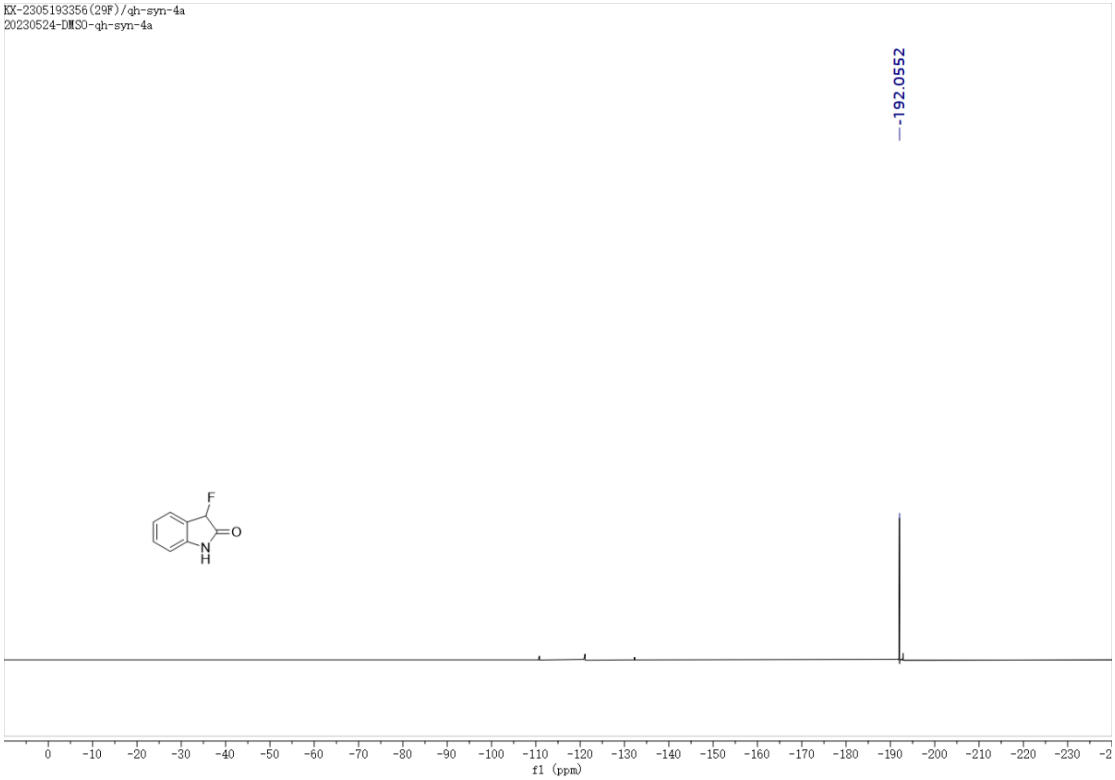


Figure S171 The ^{19}F NMR Spectrum of Compound **4a** in DMSO-d_6

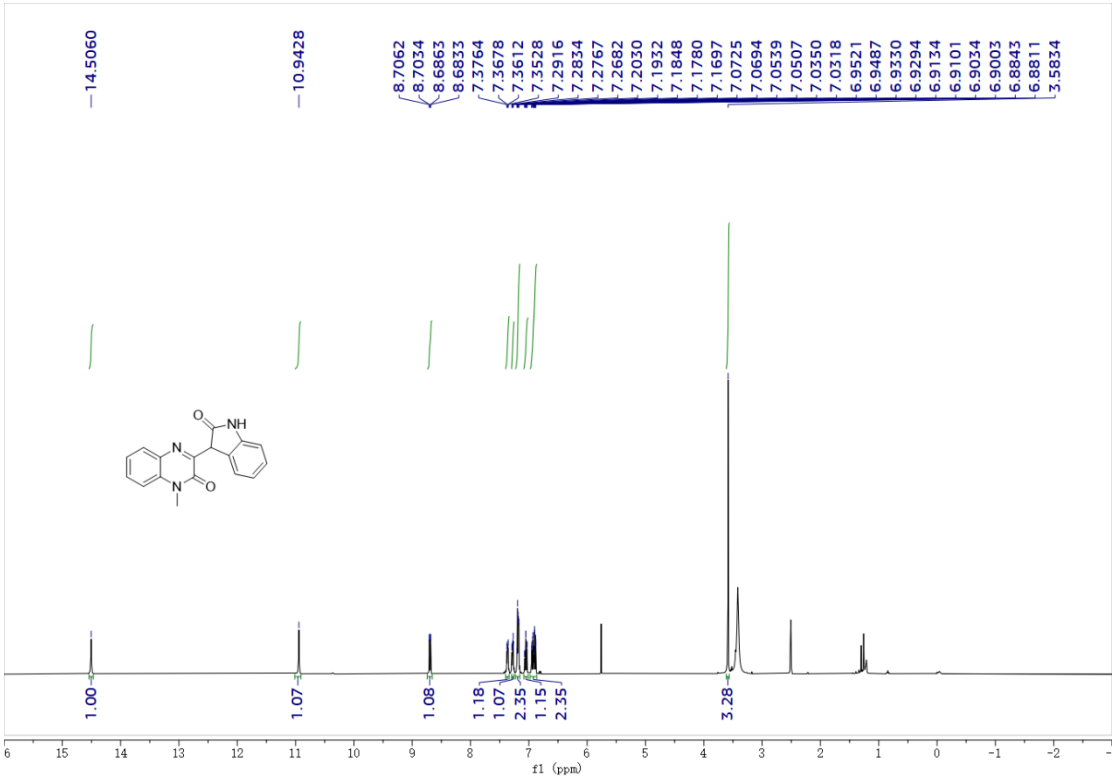


Figure S172 The ^{1}H NMR Spectrum of Compound **5a** in DMSO-d_6

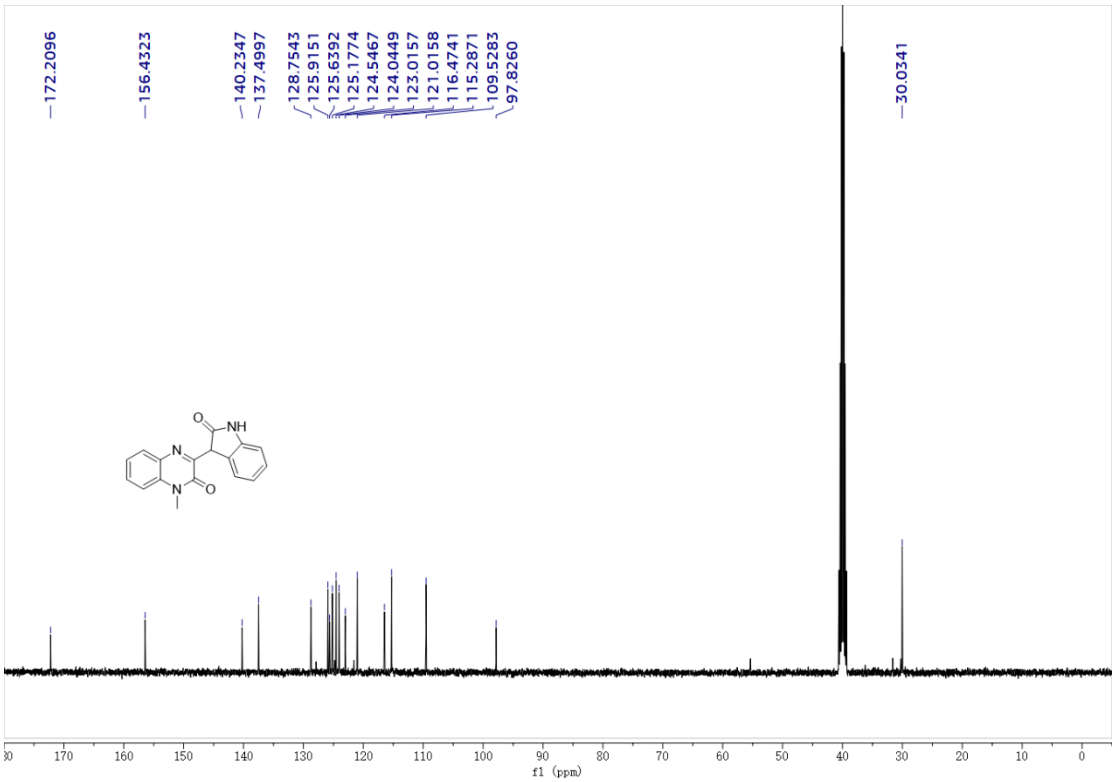


Figure S173 The ^{13}C NMR Spectrum of Compound **5a** in DMSO-d_6