Rhodium-Catalyzed C–H α-Fluoroalkenylation/annulation of *β*-ketosulfoxonium Ylides with 2,2-Difluorovinyl Tosylate/Oxadiazolones

Jia-Lin Song,[a,b] Zi-Feng Yang,[c] Sheng Fang,[a] Wang-Liang Chen,[a] Lian-Bao Ye*[a], Xiang Liu,*[c] and Bing Shu*[a, d]

[a]*School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China, E-mail: yelianbao@gdpu.edu.cn; shubing@gdpu.edu.cn.*

[b]*School of Chemistry, Sun Yat-sen University, Guangzhou, 510006, P. R. China.*

[c]*School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Zhongshan, 528458, P. R. China. E-mail: liux96@gdpu.edu.cn*

[d]*Guangdong Provincial Key Laboratory for Research and Evaluation of Pharmaceutical Preparations, Guangdong Pharmaceutical University, Guangzhou, 510006, P. R. China.*

Supporting Information

Table of content

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: 1,2-dichloroethane (CaH_2), Anhydrous 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), 1,4-dioxane, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

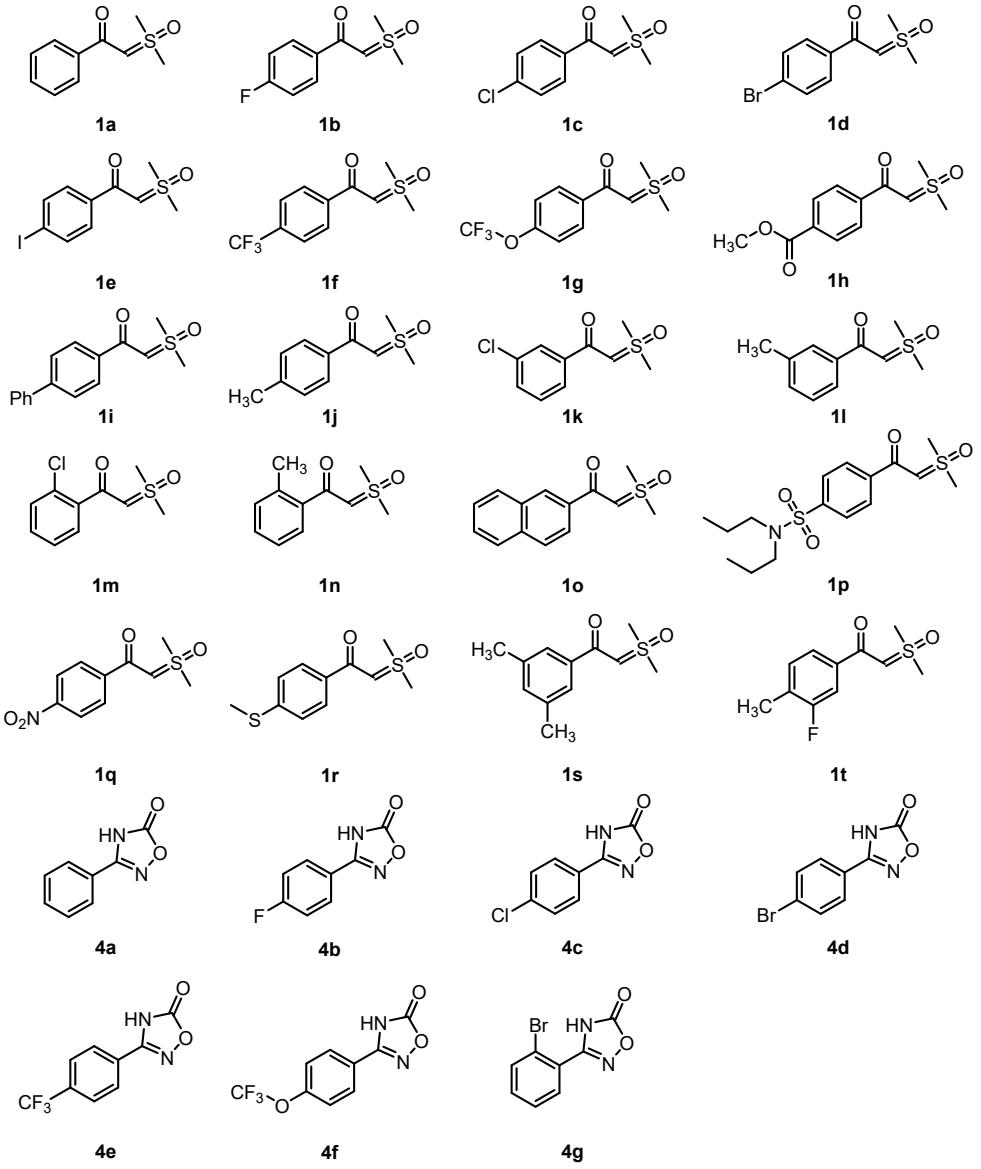
High-resolution mass spectra HRMS-ESI (Quadrupole) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

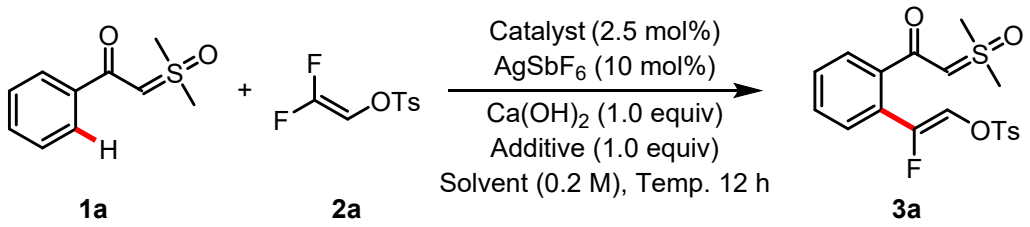
2. Preparation of starting materials

The substrates of *β*-ketosulfoxonium ylides **1**, fluorovinyls **2**, and oxadiazolones **4** were prepared accroding to the previous procedure[1-6]. All the characteristic data are consistent with the data reported before.



3. Optimization of Reaction Conditions

Table S1 Optimization of Reaction Conditions of **3a**



1a **2a** **3a**

Entry	Catalyst	Additive	Solvent	Temp. (°C)	Yield[b]
1	$[Cp^*RhCl_2]_2$	-	HFIP	60	20%
2	$[Cp^*IrCl_2]_2$	-	HFIP	60	ND[c]
3[d]	$[Ru(p\text{-}cym)Cl_2]_2$	-	HFIP	60	ND
4	$[Cp^*RhCl_2]_2$	$B(OH)_3$	HFIP	60	43%
5	$[Cp^*RhCl_2]_2$	HOAc	HFIP	60	35%
6	$[Cp^*RhCl_2]_2$	K_2CO_3	HFIP	60	41%
7	$[Cp^*RhCl_2]_2$	CsOPiv	HFIP	60	33%
8	$[Cp^*RhCl_2]_2$	Cs_2CO_3	HFIP	60	27%
9	$[Cp^*RhCl_2]_2$	KOAc	HFIP	60	70%
10	$[Cp^*RhCl_2]_2$	KOAc	DCE	60	62%
11	$[Cp^*RhCl_2]_2$	KOAc	DMF	60	trace
12	$[Cp^*RhCl_2]_2$	KOAc	MeOH	60	trace
13	$[Cp^*RhCl_2]_2$	KOAc	1,4-dioxane	60	trace
14	$[Cp^*RhCl_2]_2$	KOAc	H_2O/HFIP (0.2 ml/0.8ml)	60	37%
15	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	78%
16[e]	**$[Cp^*RhCl_2]_2$**	**KOAc**	**HFIP**	**70**	**90%**
17[f]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	trace
18[g]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	15%
19[h]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	61%
20[i]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	43%
21[j]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	trace
22[d]	$[Cp^*RhCl_2]_2$	KOAc	HFIP	70	35%
23	-	KOAc	HFIP	70	ND

[a]Reaction Conditons: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.5 mol%), $AgSbF_6$ (10 mol%), $Ca(OH)_2$ (1.0 eq), additives (1.0 equiv), solvent (0.2 M), Temp., 12 h.

[b]Isolated yield.

[c]ND: Not detected.

[d]No $AgSbF_6$.

[e]$Ca(OH)_2$ (1.5 eq).

[f]Under N_2 atmosphere.

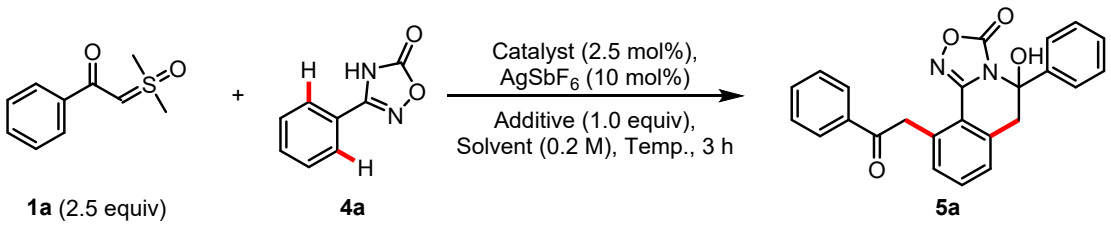
[g]Under O_2 atmosphere.

[h]$AgBF_4$ instead of $AgSbF_6$.

[i]Ag_2CO_3 instead of $AgSbF_6$.

[j]$Cu(OAc)_2$ instead of $AgSbF_6$

Table S2 Optimization of Reaction Conditions of **5a**



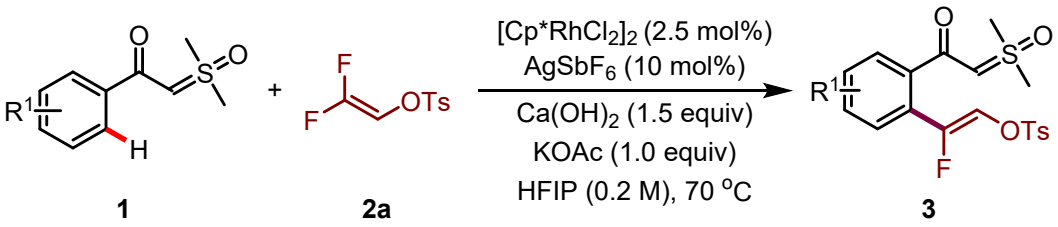
1a (2.5 equiv) **4a** **5a**

Entry	Catalyst	Additive	Solvent	Temp. (°C)	Yield[b]
1	$[Cp^*RhCl_2]_2$	——	DCE	100	33%
2	$[Cp^*IrCl_2]_2$	——	DCE	100	ND[c]
3[d]	$[Ru(p\text{-}cym)Cl_2]_2$	——	DCE	100	ND
4	$[Cp^*RhCl_2]_2$	$B(OH)_3$	DCE	100	16%
5	$[Cp^*RhCl_2]_2$	PivOH	DCE	100	43%
6	$[Cp^*RhCl_2]_2$	HOAc	DCE	100	50%
7	$[Cp^*RhCl_2]_2$	KOAc	DCE	100	59%
8	$[Cp^*RhCl_2]_2$	NaOAc	DCE	100	76%
9	$[Cp^*RhCl_2]_2$	Na_2CO_3	DCE	100	9%
10	**$[Cp^*RhCl_2]_2$**	**NaOAc**	**DCM**	**100**	**88%**
11	$[Cp^*RhCl_2]_2$	NaOAc	HFIP	100	trace
12	$[Cp^*RhCl_2]_2$	NaOAc	DMF	100	trace
13	$[Cp^*RhCl_2]_2$	NaOAc	NMP	100	trace
14	$[Cp^*RhCl_2]_2$	NaOAc	DCM	80	80%
15	**$[Cp^*RhCl_2]_2$**	NaOAc	DCM	120	72%
16	-	NaOAc	DCM	100	ND
17[d]	$[Cp^*RhCl_2]_2$	NaOAc	DCM	100	56%

[a]Reaction Conditons: **1a** (0.5 mmol, 2.5 equiv), **4a** (0.2 mmol), catalyst (2.5 mol%), $AgSbF_6$ (10 mol%), additive (1.0 equiv), solvent (0.2 M), Temp., 3 h. [b]Isolated yield. [c]ND: Not detected. [d]No $AgSbF_6$.

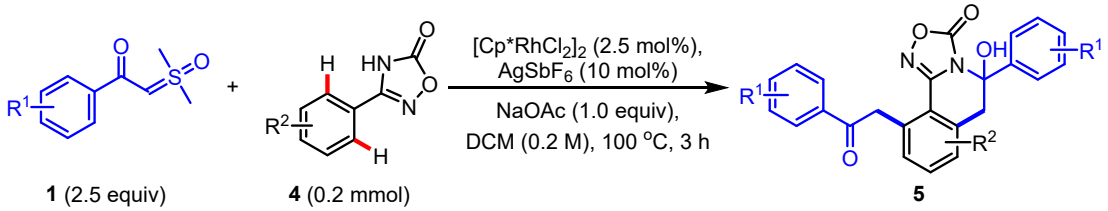
4. General procedure of products

(1) General procedure A



In an oven-dried Schlenk tube under air, a mixture of *β*-ketosulfoxonium ylides **1** (0.20 mmol, 1.0 equiv), 2,2-difluorovinyl tosylate **2a** (0.30 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $AgSbF_6$ (6.9 mg, 0.020 mmol, 10 mol%), $Ca(OH)_2$ (22.2 mg, 0.30 mmol, 1.5 equiv), KOAc (19.6 mg, 0.20 mmol, 1.0 equiv), and HFIP (1.0 mL, 0.20 M) was stirred at 70 °C for 4-12 h (heating mantle). Then the reaction mixture was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

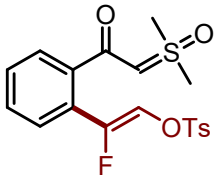
(2) General procedure B



In an oven-dried Schlenk tube under air, a mixture of*β*-ketosulfoxonium ylides **1** (0.50 mmol, 2.5 equiv), oxadiazolones **4** (0.20 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol, 2.5 mol%), $AgSbF_6$ (6.9 mg, 0.020 mmol, 10 mol%), NaOAc (16.4 mg, 0.20 mmol, 1.0 equiv), and DCM (1.0 mL, 0.20 M) was stirred at 100 °C for 3-20 h (heating mantle). Then the reaction mixture was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5**.

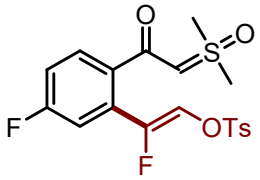
5. Characterization of products

(*Z*)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3a**)



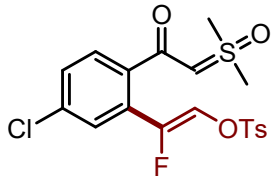
Following the general procedure A, the product **3a** was obtained in 90% yield (73.8 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.32 (m, 4H), 7.29 (t, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 18.8 Hz, 1H), 4.70 (s, 1H), 3.51 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.26, 151.39 (d, *J* = 258.0 Hz), 145.78, 141.16, 132.11, 130.18, 130.06, 128.96, 128.44 (d, *J* = 4.7 Hz), 128.20, 127.98, 125.89 (d, *J* = 22.4 Hz), 119.81 (d, *J* = 14.0 Hz), 72.22, 41.79, 21.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.18. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{20}FO_5S_2$ $[M+H]^+$ 411.0736; Found 411.0737.

(*Z*)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-fluorophenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3b**)



Following the general procedure A, the product **3b** was obtained in 71% yield (60.8 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.06 (t, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 9.2 Hz, 1H), 6.70 (d, *J* = 18.8 Hz, 1H), 4.66 (s, 1H), 3.52 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.28, 162.33 (d, *J* = 249.5 Hz), 149.71 (d, *J* = 259.4 Hz), 145.91, 137.22, 132.03, 130.20 (d, *J* = 8.5 Hz), 130.10, 128.19, 128.02 (d, *J* = 8.3 Hz), 120.65 (d, *J* = 13.5 Hz), 116.81 (d, *J* = 21.2 Hz), 115.15 (dd, *J* = 23.5, 5.6 Hz), 72.38, 41.87, 21.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.76, -118.03. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}F_2O_5S_2$ $[M+H]^+$ 429.0642; Found 429.0632.

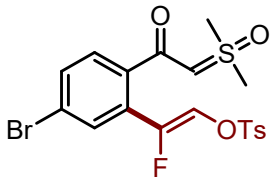
(*Z*)-2-(5-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)phenyl)-2-fluorovinyl 4-methylbenzenesu (**3c**)



Following the general procedure A, the product **3c** was obtained in 76%

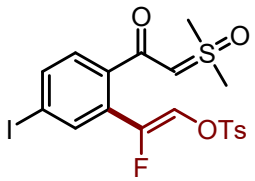
yield (67.5 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.32 (m, 4H), 7.28 (d, *J* = 1.9 Hz, 1H), 6.69 (d, *J* = 18.8 Hz, 1H), 4.68 (s, 1H), 3.52 (s, 6H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.12, 149.84 (d, *J* = 257.7 Hz), 146.01, 139.45, 134.85, 132.08, 130.19, 130.09, 129.57, 128.27, 128.20 (d, *J* = 5.3 Hz), 127.76 (d, *J* = 22.9 Hz), 120.71 (d, *J* = 13.5 Hz), 72.52, 41.93, 21.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.04. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}ClFO_5S_2$ $[M+H]^+$ 445.0346; Found 445.0347.

(*Z*)-2-(5-bromo-2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3d**)



Following the general procedure A, the product **3d** was obtained in 73% yield (71.4 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 18.8 Hz, 1H), 4.67 (s, 1H), 3.52 (s, 6H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.13, 149.73 (d, *J* = 257.8 Hz), 146.01, 139.90, 133.05, 132.07, 131.04 (d, *J* = 5.1 Hz), 130.20, 129.69, 128.27, 127.94 (d, *J* = 22.8 Hz), 122.83, 120.72 (d, *J* = 13.5 Hz), 72.49, 41.93, 21.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.10. ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.21, 149.67 (d, *J* = 258.1 Hz), 146.01, 140.44, 139.05, 136.87 (d, *J* = 5.0 Hz), 132.05, 130.20, 129.63, 128.27, 127.89 (d, *J* = 22.6 Hz), 120.60 (d, *J* = 13.5 Hz), 94.40, 72.54, 41.88, 21.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.80. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}BrFO_5S_2$ $[M+H]^+$ 488.9841; Found 488.9831.

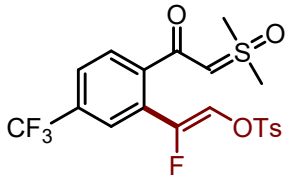
(*Z*)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-iodophenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3e**)



Following the general procedure A, the product **3e** was obtained in 65% yield (69.7 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 18.7 Hz, 1H),

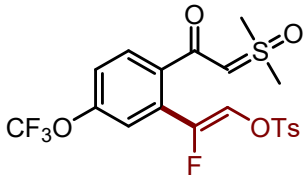
4.67 (s, 1H), 3.50 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.21, 149.67 (d, *J* = 258.1 Hz), 146.01, 140.44, 139.05, 136.87 (d, *J* = 5.0 Hz), 132.05, 130.20, 129.63, 128.27, 127.89 (d, *J* = 22.6 Hz), 120.60 (d, *J* = 13.5 Hz), 94.40, 72.54, 41.88, 21.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.09. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}FIO_5S_2$ $[M+H]^+$ 536.9702; Found 536.9699.

(*Z*)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-(trifluoromethyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3f**)



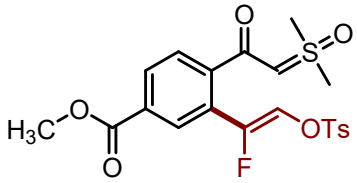
Following the general procedure A, the product **3f** was obtained in 70% yield (66.9 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58 (s, 1H), 7.55 (d, *J* = 5.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 18.9 Hz, 1H), 4.69 (s, 1H), 3.54 (s, 6H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.87, 149.56 (d, *J* = 257.0 Hz), 146.13, 144.17 (d, *J* = 1.5 Hz), 132.03, 131.19 (d, *J* = 33.1 Hz), 130.24, 128.71, 128.30, 126.93 (d, *J* = 18.2 Hz), 126.79, 125.11 (q, *J* = 9.0 Hz), 123.48 (q, *J* = 272.5 Hz), 121.06 (d, *J* = 13.3 Hz), 72.99, 41.97, 21.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88, -118.10. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{19}F_4O_5S_2$ $[M+H]^+$ 479.0610; Found 479.0604.

(*Z*)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-(trifluoromethoxy)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3g**)



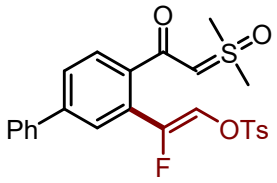
Following the general procedure A, the product **3g** was obtained in 82% yield (81.0 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.13 (s, 1H), 6.74 (d, *J* = 18.9 Hz, 1H), 4.69 (s, 1H), 3.52 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.99, 149.45 (d, *J* = 257.0 Hz), 149.17, 146.07, 139.57, 132.03, 130.20, 129.91, 128.28, 128.05 (d, *J* = 23.3 Hz), 122.09, 120.99 (d, *J* = 13.3 Hz), 120.54 (d, *J* = 5.2 Hz), 120.37 (d, *J* = 258.4 Hz), 72.82, 41.92, 21.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.83, -117.93. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{19}F_4O_6S_2$ $[M+H]^+$ 495.0559; Found 495.0555.

methyl (*Z*)-4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-3-(1-fluoro-2-(tosyloxy)vinyl)benzoate (**3h**)



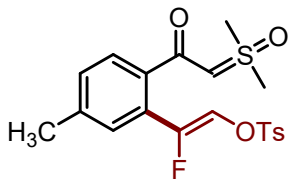
Following the general procedure A, the product **3h** was obtained in 75% yield (70.2 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 18.8 Hz, 1H), 4.71 (s, 1H), 3.92 (s, 3H), 3.54 (s, 6H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.14, 165.80, 150.25 (d, *J* = 257.6 Hz), 145.91, 144.93, 132.00, 131.05, 130.55, 130.11, 129.44 (d, *J* = 5.1 Hz), 128.22, 128.19, 126.33 (d, *J* = 23.0 Hz), 120.50 (d, *J* = 13.6 Hz), 72.71, 52.45, 41.81, 21.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.69. **HRMS (ESI)** *m/z* calcd. for $C_{21}H_{22}FO_7S_2$ $[M+H]^+$ 469.0791; Found 469.0790.

(*Z*)-2-(4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-[1,1'-biphenyl]-3-yl)-2-fluorovinyl 4-methylbenzenesulfonate (**3i**)



Following the general procedure A, the product **3i** was obtained in 49% yield (47.6 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.48 (s, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.67 (d, *J* = 18.7 Hz, 1H), 4.74 (s, 1H), 3.54 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.08, 151.41 (d, *J* = 258.3 Hz), 145.85, 142.20, 142.17, 139.84, 139.59, 132.26, 130.15, 129.06, 128.81, 128.33, 128.16, 127.28 (d, *J* = 5.0 Hz), 127.20, 126.61 (d, *J* = 22.3 Hz), 120.12 (d, *J* = 14.0 Hz), 72.18, 41.99, 21.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.09. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.76. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{24}FO_5S_2$ $[M+H]^+$ 487.1049; 487.1052.

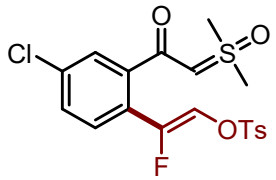
(Z)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-methylphenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3j**)



Following the general procedure A, the product **3j** was obtained in 81%

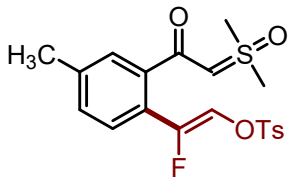
yield (68.7 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 1H), 6.57 (d, *J* = 18.7 Hz, 1H), 4.67 (s, 1H), 3.49 (s, 6H), 2.44 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.44, 151.75 (d, *J* = 258.5 Hz), 145.79, 139.26, 138.46, 132.28, 130.92, 130.11, 129.20 (d, *J* = 4.3 Hz), 128.29, 128.21, 125.94 (d, *J* = 22.1 Hz), 119.71 (d, *J* = 14.2 Hz), 71.96, 41.92, 21.83, 21.19. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.63. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{22}FO_5S_2$ $[M+H]^+$ 425.0892; Found 425.0896.

(Z)-2-(4-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3k**)



Following the general procedure A, the product **3l** was obtained in 68% yield (60.5 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.44 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 18.8 Hz, 1H), 4.66 (s, 1H), 3.51 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.55, 150.19 (d, *J* = 257.1 Hz), 145.93, 142.60, 136.20, 132.16, 130.16, 129.67 (d, *J* = 4.8 Hz), 129.05, 128.32, 128.28, 124.50 (d, *J* = 23.1 Hz), 120.31 (d, *J* = 13.8 Hz), 72.46, 41.97, 21.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.63. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}ClFO_5S_2$ $[M+H]^+$ 445.0345; Found 445.0347.

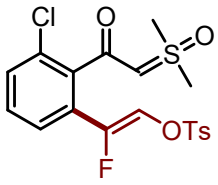
(Z)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-4-methylphenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3l**)



Following the general procedure A, the product **3m** was obtained in 52% yield (44.1 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 18.7 Hz, 1H), 4.66 (s, 1H), 3.51 (s, 6H), 2.44 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.58, 151.65 (d, *J* = 258.2 Hz), 145.77, 140.68, 132.29, 130.10, 129.69, 128.79, 128.52 (d, *J* = 4.6 Hz), 128.37, 128.31, 123.14 (d, *J* = 22.5 Hz), 119.48 (d, *J* = 14.4 Hz), 71.95, 41.96, 21.84, 21.35. ^{19}F

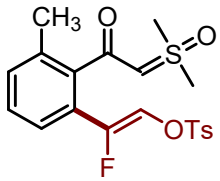
NMR (376 MHz, $CDCl_3$) δ -114.52. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{22}FO_5S_2$ $[M+H]^+$ 425.0892; Found 425.0896.

(Z)-2-(3-chloro-2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3m**)



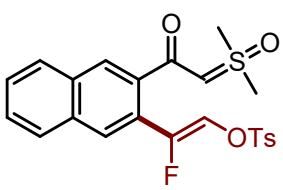
Following the general procedure A, the product **3n** was obtained in 66% yield (58.7 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 3H), 7.26 (dd, *J* = 9.8, 7.1 Hz, 2H), 6.94 (d, *J* = 19.3 Hz, 1H), 4.52 (s, 1H), 3.56 (s, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.12, 148.94 (d, *J* = 255.9 Hz), 145.97, 139.28, 132.07, 132.02, 131.16, 130.19, 129.05, 128.29, 127.78 (d, *J* = 23.6 Hz), 125.71 (d, *J* = 5.6 Hz), 121.21 (d, *J* = 13.3 Hz), 73.20, 42.07, 21.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.79. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{19}ClFO_5S_2$ $[M+H]^+$ 445.036; Found 445.0347.

(Z)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-3-methylphenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3n**)



Following the general procedure A, the product **3o** was obtained in 65% yield (55.1 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 6.7 Hz, 2H), 7.12 (d, *J* = 6.7 Hz, 1H), 6.68 (d, *J* = 19.0 Hz, 1H), 4.53 (s, 1H), 3.52 (s, 6H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.95, 151.08 (d, *J* = 257.6 Hz), 145.88, 140.78, 135.47, 132.22, 132.11, 130.14, 128.26, 127.94, 125.50 (d, *J* = 22.4 Hz), 125.07 (d, *J* = 4.9 Hz), 119.95 (d, *J* = 14.2 Hz), 73.21, 41.88, 21.82, 19.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.96. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{22}FO_5S_2$ $[M+H]^+$ 425.0892; Found 425.0896.

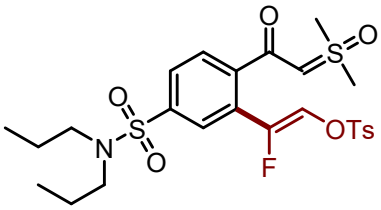
(Z)-2-(3-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)naphthalen-2-yl)-2-fluorovinyl 4-methylbenzenesulfonate (**3o**)



Following the general procedure A, the product **3p** was obtained in 50%

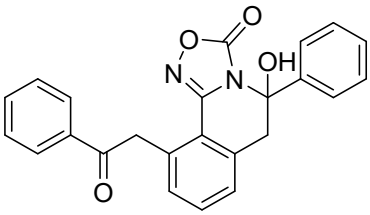
yield (46.0 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.74 (m, 3H), 7.52 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 18.5 Hz, 1H), 4.83 (s, 1H), 3.56 (s, 6H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.35, 152.06 (d, *J* = 257.8 Hz), 145.77, 137.63, 133.39, 132.73, 132.34, 130.12, 129.09, 128.85, 128.33, 128.16, 127.98, 127.67, 125.76, 124.02 (d, *J* = 22.3 Hz), 119.77 (d, *J* = 14.2 Hz), 71.92, 41.96, 21.83. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.81. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{22}FO_5S_2$ $[M+H]^+$ 461.0890; Found 461.0900.

(Z)-2-(2-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)-5-(N,N-dipropylsulfamoyl)phenyl)-2-fluorovinyl 4-methylbenzenesulfonate (**3p**)



Following the general procedure A, the product **3q** was obtained in 63% yield (72.2 mg, 0.20 mmol) as a brown solid after column chromatography (eluent = EA/PE : 1/1 v/v). RF (EA/PE, 3:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 18.9 Hz, 1H), 4.70 (s, 1H), 3.53 (s, 6H), 3.07 – 2.98 (m, 4H), 2.44 (s, 3H), 1.58 – 1.47 (m, 4H), 0.85 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.58, 149.30 (d, *J* = 257.2 Hz), 146.07, 144.26, 140.79, 131.88, 130.18, 128.84, 128.23, 128.18, 127.04 (d, *J* = 23.1 Hz), 126.53 (d, *J* = 5.2 Hz), 121.11 (d, *J* = 13.2 Hz), 73.17, 50.07, 41.82, 22.04, 21.77, 11.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.86. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{33}FNO_7S_3$ $[M+H]^+$ 574.1403; Found 574.1396.

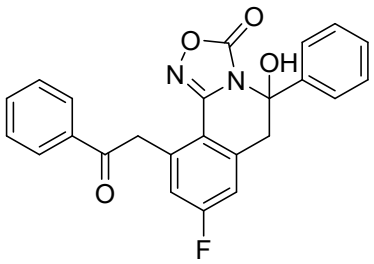
5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5a**)



Following the general procedure B, the product **5a** was obtained in 88% yield (70.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.30 (m,

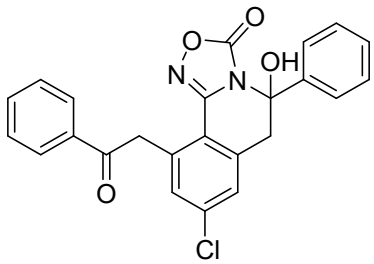
5H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 4.97 (d, *J* = 17.6 Hz, 1H), 4.74 (d, *J* = 17.6 Hz, 1H), 3.74 (d, *J* = 15.9 Hz, 1H), 3.45 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.87, 157.21, 154.61, 140.25, 137.04, 135.31, 134.46, 133.42, 132.57, 132.00, 129.40, 129.07, 128.82, 128.38, 128.35, 124.86, 119.72, 86.24, 45.70, 45.27. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{18}N_2O_4$ $[M+Na]^+$ 421.1165; Found 421.1165.

8-fluoro-5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5b**)



Following the general procedure B, the product **5b** was obtained in 73% yield (60.7 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.21. ^{1}H NMR (400 MHz, DMSO) δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.64 – 7.57 (m, 4H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.31 (d, *J* = 9.3 Hz, 2H), 4.96 (d, *J* = 17.9 Hz, 1H), 4.89 (d, *J* = 17.8 Hz, 1H), 4.57 (s, 1H), 3.68 (d, *J* = 16.4 Hz, 1H), 3.35 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 196.50, 163.79 (d, *J* = 250.8 Hz), 155.27, 154.34, 140.42, 139.24 (d, *J* = 12.3 Hz), 137.04, 133.79, 129.28, 128.73, 128.54, 128.46, 126.39, 119.09 (d, *J* = 22.3 Hz), 117.77 (d, *J* = 21.6 Hz), 116.54 (d, *J* = 2.8 Hz), 115.15 (d, *J* = 22.6 Hz), 84.92, 45.88, 45.60. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.96. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{17}FN_2O_4$ $[M+Na]^+$ 439.1070; Found 439.1075.

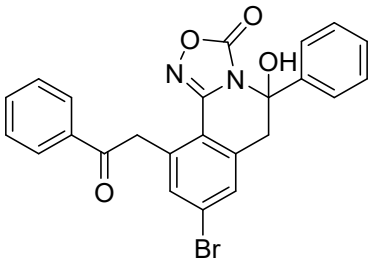
8-chloro-5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5c**)



Following the general procedure B, the product **5c** was obtained in 76% yield (65.6 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.26. ^{1}H NMR (400 MHz, DMSO) δ 8.12 – 8.04 (m, 2H), 7.96 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.63 – 7.57 (m, 4H), 7.57 – 7.49 (m, 3H), 7.43 – 7.33 (m, 3H), 4.94 (d, *J* = 17.8 Hz, 1H), 4.87 (d, *J* = 17.8 Hz, 1H), 4.56 (s, 1H), 3.67 (d, *J* = 16.4 Hz, 1H), 3.53 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (101

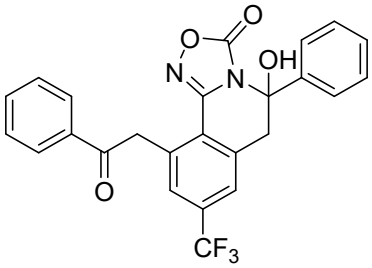
MHz, DMSO) δ 196.57, 155.20, 154.39, 140.35, 138.31, 137.85, 137.05, 136.73, 133.80, 131.75, 129.28, 128.74, 128.55, 128.46, 128.04, 126.42, 118.83, 84.97, 45.56, 45.36. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{17}ClN_2O_4$ $[M+Na]^+$ 455.0775; Found 455.0777.

8-bromo-5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5d**)



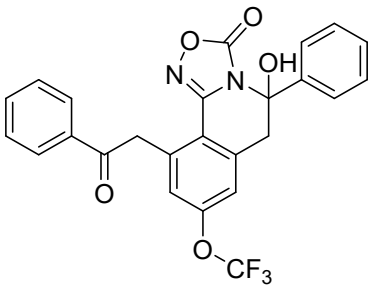
Following the general procedure B, the product **5d** was obtained in 79% yield (75.3 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.24. ^{1}H NMR (400 MHz, DMSO) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 1H), 7.71 – 7.67 (m, 3H), 7.64 – 7.59 (m, 3H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 4.94 (d, *J* = 17.8 Hz, 1H), 4.87 (d, *J* = 17.8 Hz, 1H), 4.57 (s, 1H), 3.68 (d, *J* = 16.4 Hz, 1H), 3.68 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 196.62, 155.21, 154.50, 140.35, 138.33, 137.83, 137.06, 136.57, 134.62, 133.99, 133.79, 130.95, 129.29, 128.46, 126.43, 125.82, 119.18, 84.98, 45.45, 45.30. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{17}BrN_2O_4$ $[M+Na]^+$ 499.0270; Found 499.0273.

5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-8-(trifluoromethyl)-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5e**)



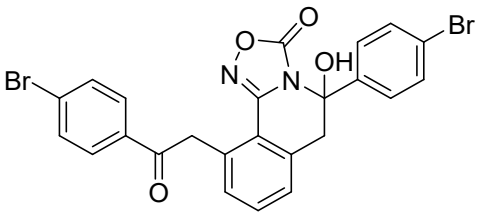
Following the general procedure B, the product **5e** was obtained in 82% yield (76.4 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.52 (s, 1H), 7.44 – 7.38 (m, 4H), 7.37 – 7.33 (m, 2H), 5.25 (s, 1H), 5.08 (d, *J* = 17.6 Hz, 1H), 4.82 (d, *J* = 17.6 Hz, 1H), 3.80 (d, *J* = 16.1 Hz, 1H), 3.55 (d, *J* = 16.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.83, 156.73, 153.77, 139.60, 136.60, 136.40, 135.29, 134.22 (q, *J* = 50.8 Hz), 133.62, 129.60, 129.16, 128.83, 128.60 (q, *J* = 3.6 Hz), 128.24, 125.04 (q, *J* = 3.8 Hz), 124.70, 123.06 (q, *J* = 273.2 Hz), 86.09, 45.67, 45.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.25. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{17}F_3N_2O_4$ $[M+Na]^+$ 489.1038; Found 489.1043.

5-hydroxy-10-(2-oxo-2-phenylethyl)-5-phenyl-8-(trifluoromethoxy)-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5f**)



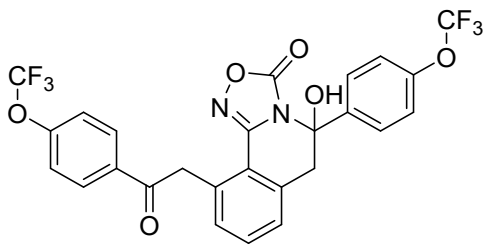
Following the general procedure B, the product **5f** was obtained in 81% yield (78.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.23 (m, 4H), 7.01 (s, 1H), 6.91 (s, 1H), 4.92 (d, *J* = 17.6 Hz, 1H), 4.66 (d, *J* = 17.6 Hz, 1H), 3.64 (d, *J* = 16.1 Hz, 1H), 3.38 (d, *J* = 16.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.89, 156.82, 153.76, 151.39, 139.69, 138.03, 136.80, 136.62, 133.57, 129.50, 129.09, 128.80, 128.25, 124.74, 123.43, 120.18 (q, *J* = 259.7 Hz), 119.49, 118.06, 85.91, 45.61, 45.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.38. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{17}F_3N_2O_5$ $[M+H]^+$ 483.1168; Found 483.1169.

5-(4-bromophenyl)-10-(2-(4-bromophenyl)-2-oxoethyl)-5-hydroxy-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5g**)



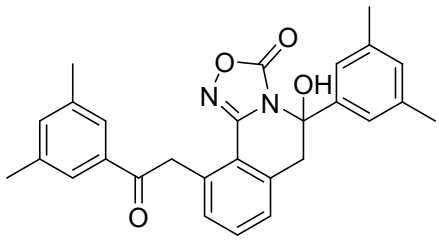
Following the general procedure B, the product **5g** was obtained in 67% yield (74.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 1H), 5.23 (s, 1H), 4.87 (d, *J* = 17.7 Hz, 1H), 4.58 (d, *J* = 17.7 Hz, 1H), 3.63 (d, *J* = 16.0 Hz, 1H), 3.32 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.83, 156.88, 154.33, 139.15, 135.58, 134.85, 134.08, 132.69, 132.15, 132.07, 132.03, 129.76, 128.57, 128.45, 126.64, 123.67, 119.51, 85.74, 45.54, 45.12. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{16}Br_2N_2O_4$ $[M+Na]^+$ 576.9375; Found 576.9370.

5-hydroxy-10-(2-oxo-2-(4-(trifluoromethoxy)phenyl)ethyl)-5-(4-(trifluoromethoxy)phenyl)-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5h**)



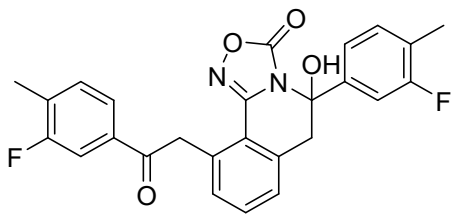
Following the general procedure B, the product **5h** was obtained in 68% yield (77.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.35 (s, 1H), 4.99 (d, *J* = 17.7 Hz, 1H), 4.66 (d, *J* = 17.7 Hz, 1H), 3.71 (d, *J* = 16.0 Hz, 1H), 3.41 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.39, 156.87, 154.35, 152.83, 149.78, 138.66, 135.08, 134.79, 134.08, 132.74, 132.06, 130.28, 128.50, 126.67, 121.17, 122.90 (d, *J* = 258.4 Hz), 120.52, 120.34 (d, *J* = 257.7 Hz), 119.49, 85.60, 45.65, 45.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.54, -57.76. **HRMS (ESI)** *m/z* calcd. for $C_{26}H_{16}F_6N_2O_6$ $[M+Na]^+$ 589.0811; Found 589.0813.

5-(3,5-dimethylphenyl)-10-(2-(3,5-dimethylphenyl)-2-oxoethyl)-5-hydroxy-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5i**)



Following the general procedure B, the product **5i** was obtained in 79% yield (71.7 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.23 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.95 – 6.89 (m, 3H), 5.11 (s, 1H), 5.00 (d, *J* = 17.6 Hz, 1H), 4.64 (d, *J* = 17.6 Hz, 1H), 3.68 (d, *J* = 15.9 Hz, 1H), 3.41 (d, *J* = 15.9 Hz, 1H), 2.39 (s, 6H), 2.28 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.83, 157.18, 154.69, 140.10, 138.60, 138.30, 137.07, 135.40, 134.97, 134.48, 132.36, 131.78, 130.96, 128.21, 126.02, 122.61, 119.73, 86.20, 45.72, 45.16, 21.42, 21.37. **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{26}N_2O_4$ $[M+Na]^+$ 477.1791; Found 477.1794.

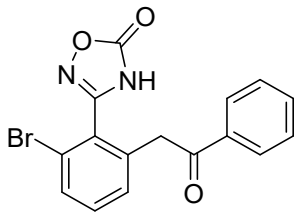
5-(3-fluoro-4-methylphenyl)-10-(2-(3-fluoro-4-methylphenyl)-2-oxoethyl)-5-hydroxy-5,6-dihydro-3H-[1,2,4]oxadiazolo[3,4-a]isoquinolin-3-one (**5j**)



Following the general procedure B, the product **5i** was obtained in 76% yield (70.2 mg, 0.20 mmol) as a

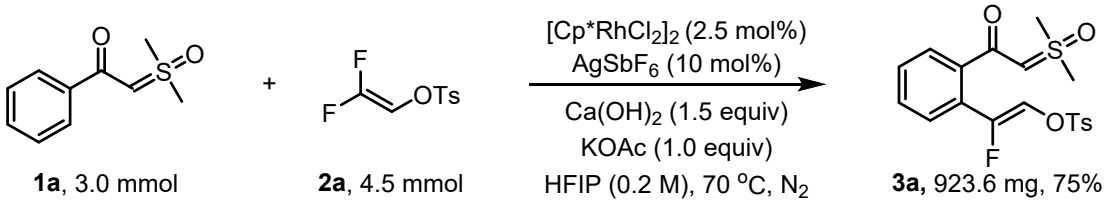
yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 10.2 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.04 (dd, *J* = 10.5, 1.0 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 4.88 (d, *J* = 17.6 Hz, 1H), 4.67 (d, *J* = 17.6 Hz, 1H), 3.67 (d, *J* = 16.0 Hz, 1H), 3.40 (d, *J* = 16.0 Hz, 1H), 2.36 (d, *J* = 0.8 Hz, 3H), 2.22 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.41, 161.33 (d, *J* = 246.2 Hz), 161.28 (d, *J* = 246.5 Hz), 156.92, 154.33, 139.80 (d, *J* = 6.4 Hz), 136.54 (d, *J* = 6.3 Hz), 134.97, 134.23, 132.57, 132.01, 131.98, 131.72 (d, *J* = 4.8 Hz), 131.14 (d, *J* = 17.4 Hz), 128.34, 126.19 (d, *J* = 17.6 Hz), 123.88 (d, *J* = 3.2 Hz), 120.17, 119.47, 114.64 (d, *J* = 23.3 Hz), 112.04 (d, *J* = 24.4 Hz), 85.48, 45.55, 45.12, 14.95 (d, *J* = 3.4 Hz), 14.31 (d, *J* = 3.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.38, -116.09. **HRMS (ESI)** *m/z* calcd. for $C_{26}H_{20}F_2N_2O_4$ $[M+H]^+$ 463.1469; Found 463.1470.

3-(2-bromo-6-(2-oxo-2-phenylethyl)phenyl)-1,2,4-oxadiazol-5(4H)-one (**5k**)



Following the general procedure B, the product **5k** was obtained in 73% yield (52.3 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = PE/EA 4:1, v/v). Rf (PE/EA 4:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.11 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.95, 164.20, 160.66, 141.67, 139.75, 137.94, 136.63, 135.93, 134.34, 132.83, 132.17, 129.96, 127.58, 47.29. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{11}BrN_2O_3$ $[M+Na]^+$ 380.9851; Found 380.9848.

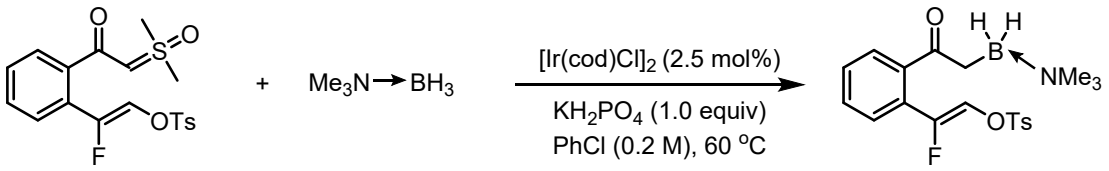
6. Gram-scale experiment



1a, 3.0 mmol **2a**, 4.5 mmol **3a,** 923.6 mg, 75%

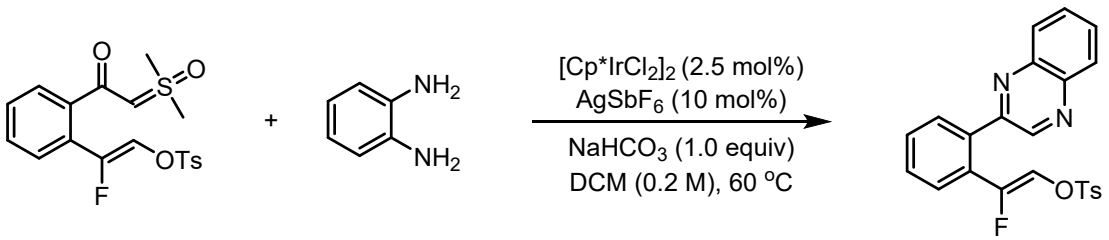
In an oven-dried Schlenk tube under air, a mixture of the substrate **1a** (3.0 mmol, 1.0 equiv), 2,2-difluorovinyl tosylate **2a** (6.0 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (0.075 mmol, 2.5 mol%), $AgSbF_6$ (0.3 mmol, 10 mol%), $Ca(OH)_2$ (4.5 mmol, 1.5 equiv) and HFIP (0.20 M) was stirred at 70 °C for 8 h. Then the reaction mixture was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product (EA : PE = 1:1) to give **3a** (923.6 mg, 75%).

7. Synthetic application of the product 3a



3a, 0.1 mmol 0.15 mmol **6**, 20.7 mg, 51%

In an oven-dried Schlenk tube under air, a mixture of the substrate **3a** (0.1 mmol, 1.0 equiv), trimethylamine-borane (10.9 mg, 0.15 mmol, 1.5 equiv), $[Ir(Cod)Cl]_2$ (1.7 mg, 0.0025 mmol, 2.5 mol%), KH_2PO_4 (13.6 mg, 0.1 mmol, 1.0 equiv), and PhCl (0.5 mL) was stirred at 60 °C for 6h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **6**, 20.7 mg, 51%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.25 (d, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 18.3 Hz, 1H), 2.59 (s, 2H), 2.56 (s, 9H), 2.44 (s, 3H), 2.29 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.39, 152.00 (d, *J* = 259.3 Hz), 145.58, 141.55, 132.26, 129.99, 129.63, 129.00 (d, *J* = 4.1 Hz), 128.75, 128.24, 127.12, 126.17 (d, *J* = 22.3 Hz), 119.62 (d, *J* = 14.1 Hz), 52.11, 49.62, 21.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.30. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{22}FO_5S_2$ $[M+H]^+$ 406.1659; Found 406.1662.



3a, 0.1 mmol 0,15 mmol **7**, 18.1 mg, 43%

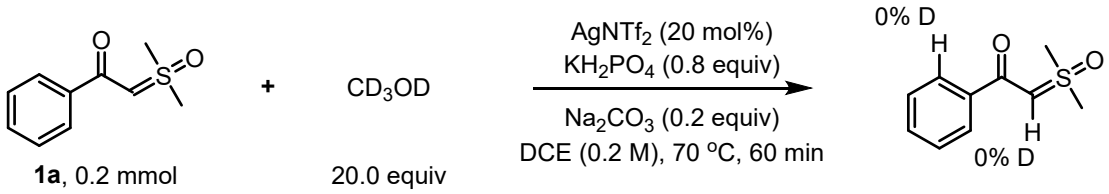
In an oven-dried Schlenk tube under air, a mixture of the substrate **3a** (0.1 mmol, 1.0 equiv),benzene-1,2-diamine (10.8 mg, 0.15 mmol, 1.5 equiv), $(Cp^*IrCl_2)_2$ (2.0 mg, 0.0025 mmol, 2.5 mol%), AgSbF6 (3.4 mg, 0.01 mmol, 10.0 mol%), $NaHCO_3$ (8.4 mg, 0.1 mmol, 1.0 equiv), and DCM (0.5 mL, 0.2 M) was stirred at 60 °C in the oil bath for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with

DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with anappropriate solvent to afford the pure product **7**, 18.1 mg, 43%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.25 (d, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 18.3 Hz, 1H), 2.59 (s, 2H), 2.56 (s, 9H), 2.44 (s, 3H), 2.29 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.96, 151.27 (d, *J* = 259.1 Hz), 145.75, 144.83 (d, *J* = 2.3 Hz), 141.95, 141.37, 136.69, 131.99, 131.21, 130.97, 130.41, 130.13, 129.98, 129.66, 129.64, 129.59 (d, *J* = 4.0 Hz), 129.25, 128.03, 127.81, 120.95 (d, *J* = 13.8 Hz), 21.82. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.25. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{18}FN_2O_3S$ $[M+H]^+$ 421.1022; Found 421.1018.

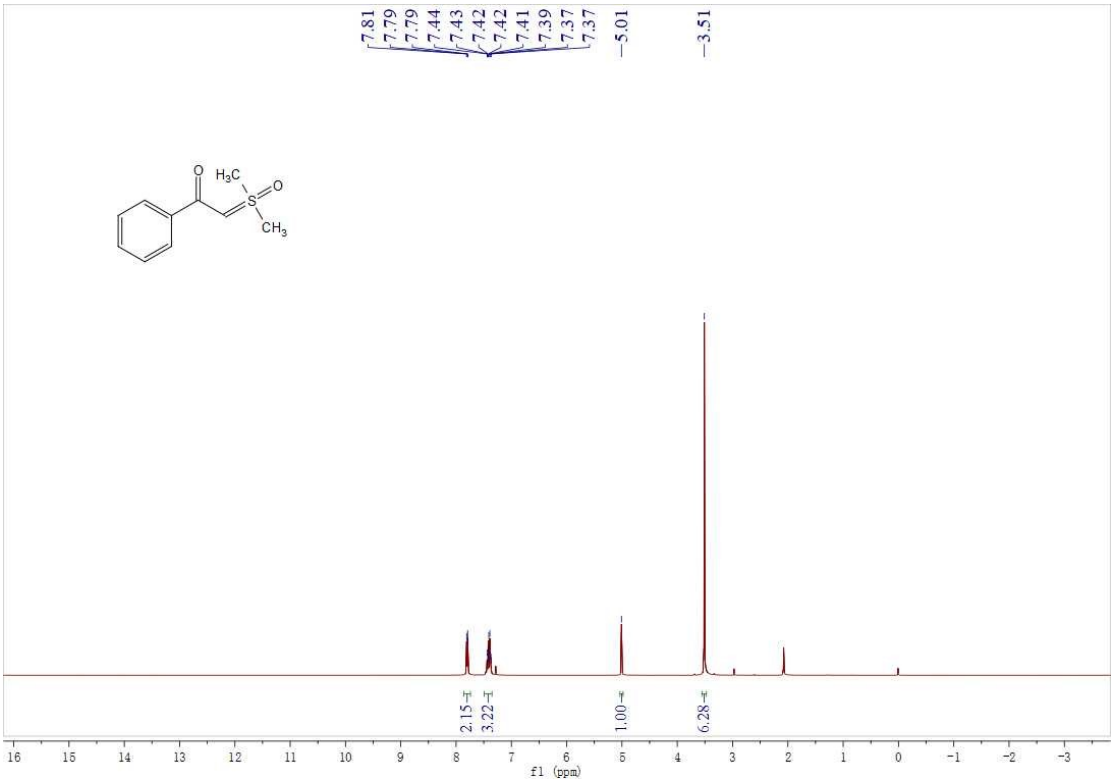
.

8. Mechanistic studies

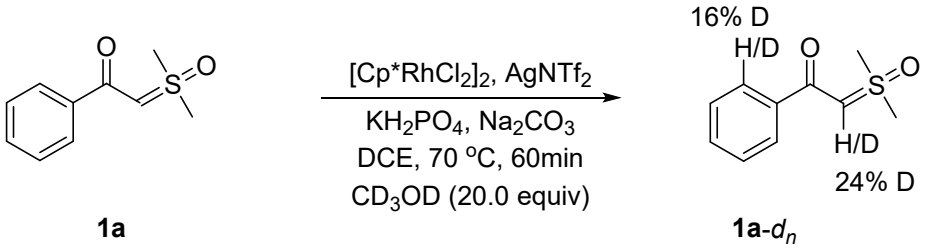
(1) Reversibility of C−H bond cleavage without Rh catalyst of 1a



To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ^6 -sulfanylidene)-1-phenylethan-1-one (**1a**, 39.2 mg, 0.20 mmol), [Cp*$RhCl_2$]$_2$ (3.1 mg, 0.0050 mmol), $AgNTf_2$ (15.6 mg, 20 mol%), KH_2PO_4 (21.8 mg, 0.16 mmol), Na_2CO_3 (4.2 mg, 0.040 mmol) CD_3OD (144 mg, 4.0 mmol) and DCE (1.0 mL). The resulting mixture was stirred at 70 °C for 60 min. Then it was cooled to room temperature, quenched with saturated brine (5.0 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using DCM/Mt (20:1) as eluent to afford **1a-*dn***, which was characterized by ^{1}H NMR spectroscopy. ^{1}H NMR analysis of **1a** revealed no deuteration at the 2-position of phenyl ring or the α-position of the carbonyl.

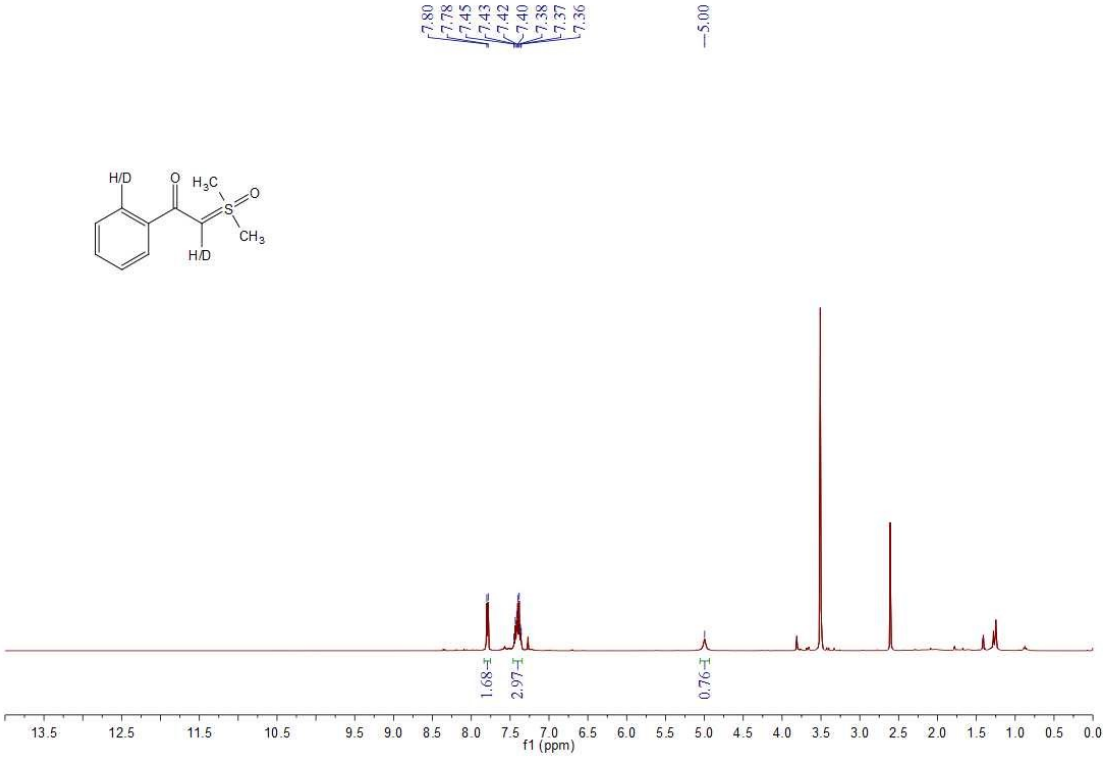


(2) Reversibility of C−H bond cleavage with Rh catalyst of 1a

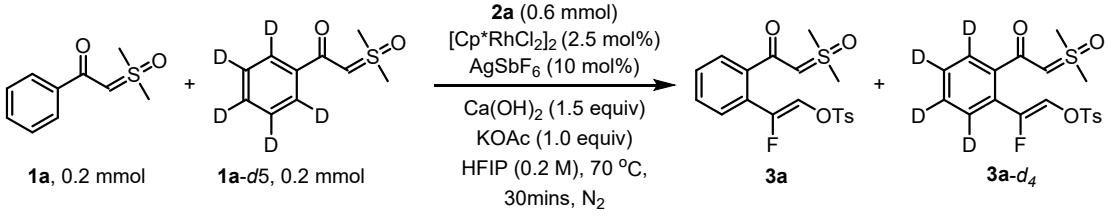


1a **1a-d_n**

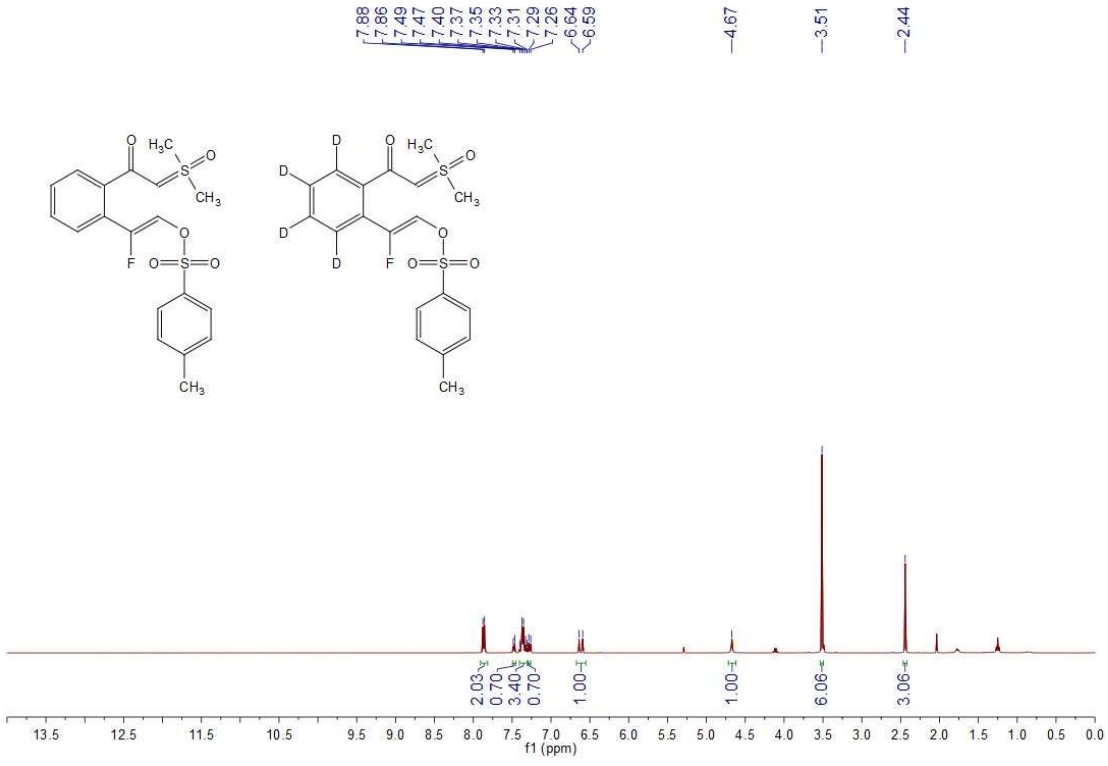
To a reaction tube equipped with a stir bar were charged with 2-(dimethyl(oxo)-λ^6 -sulfanylidene)-1-phenylethan-1-one (**1a**, 39.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol), $AgNTf_2$ (15.6 mg, 20 mol%), KH_2PO_4 (21.8 mg, 0.16 mmol), Na_2CO_3 (4.2 mg, 0.040 mmol) CD_3OD (144 mg, 4.0 mmol) and DCE (1.0 mL). The resulting mixture was stirred at 70 °C for 60 min. Afterwards, it was cooled to room temperature, quenched with saturated brine (5.0 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using DCM/Mt (20:1) as eluent to afford **1a-*dn***. ^{1}H NMR analysis revealed 16% deuteration at the *ortho*-position of phenyl ring and 24% deuteration at the α-position of the carbonyl unit.



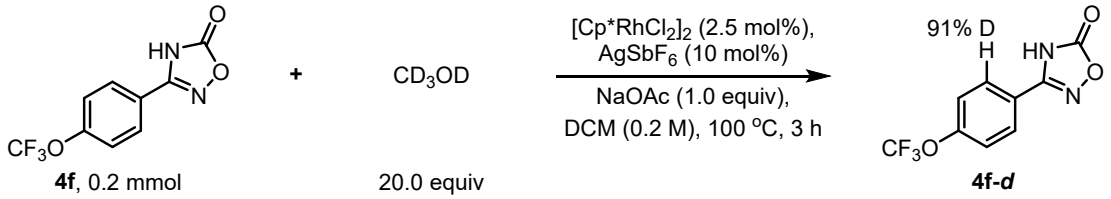
(3) An intermolecular KIE experiment of 3a



To a reaction tube equipped with a stir bar were added 2-(dimethyl(oxo)-λ^6 -sulfanylidene)-1-phenyl ethan-1-one (**1a**, 39.2 mg, 0.20 mmol), 2-(dimethyl(oxo)-λ^6 -sulfanylidene)-1-phenyl-d_5-ethan-1-one (**1a-*d*$_5$**, 40.2 mg, 0.20 mmol), 2,2-difluorovinyl tosylate (**2a**, 140.4mg, 0.60 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.001 mmol, 2.5 mol%), $AgSbF_6$ (13.72 mg, 0.04 mmol, 10 mol%), $Ca(OH)_2$ (44.4 mg, 0.60 mmol, 1.5 equiv), KOAc (39.2 mg, 0.40 mmol, 1.0 equiv) and HFIP (2 mL). The resulting mixture was then stirred at 70 °C for 30 min. Afterwards, cooled to room temperature, quenched with saturated brine (5.0 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using DCM/Mt (20:1) as eluent to afford a mixture of **3a** and **3a-*d*$_4$**. Upon analyzing the corresponding ^{1}H NMR spectrum, the intermolecular *KIE* (K_H/K_D) was determined as 2.3 (0.7/0.3).

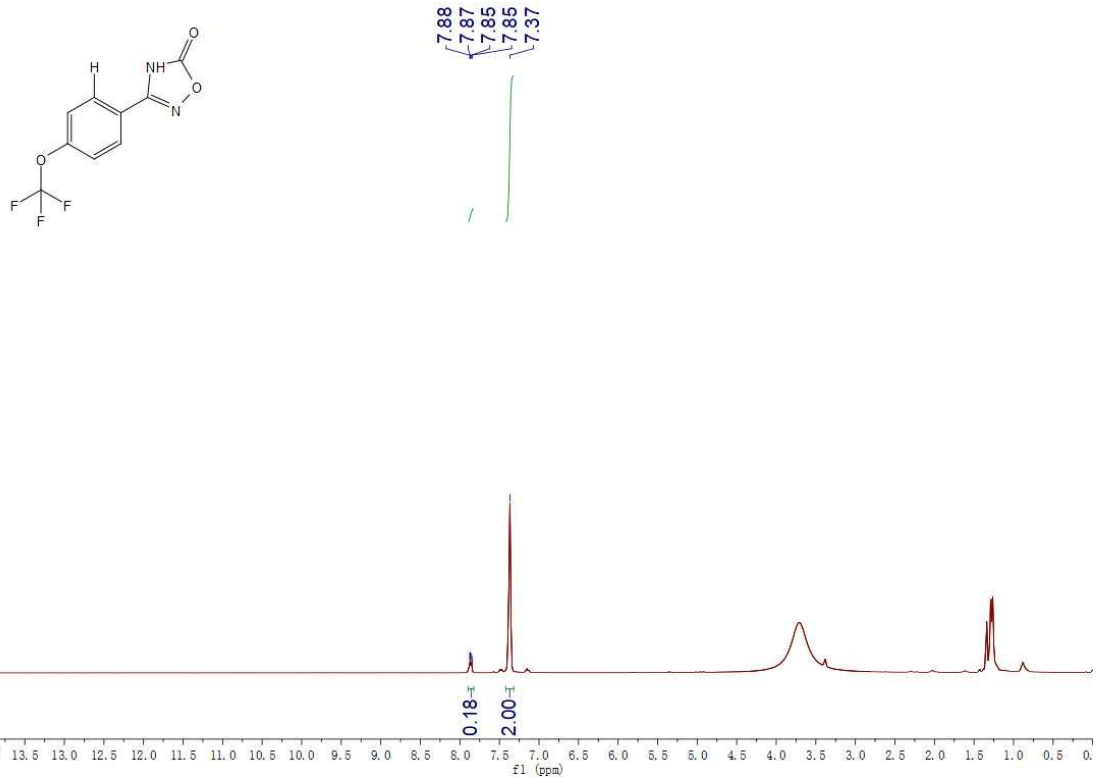


(4) Reversibility of C−H bond cleavage with Rh catalyst of 4f

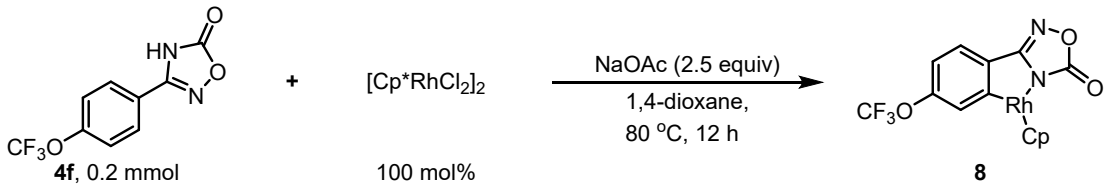


4f, 0.2 mmol　　20.0 equiv　　**4f-*d***

To a reaction tube equipped with a stir bar were charged with **4f**, 49.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.0050 mmol), $AgSbF_6$ (6.8 mg, 10 mol%), NaOAc (16.4 mg, 0.2 mmol), CD_3OD (144.3 mg, 4.0 mmol) and DCM (1.0 mL). The resulting mixture was stirred at 100 °C for 3 h. Then cooled to room temperature, quenched with saturated brine (5.0 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using PE/EA (2:1) as eluent to afford **4f-*d***. ^1H NMR analysis revealed 91% deuteration at the *ortho*-position of phenyl ring based on the double doublet at δ: 7.86.

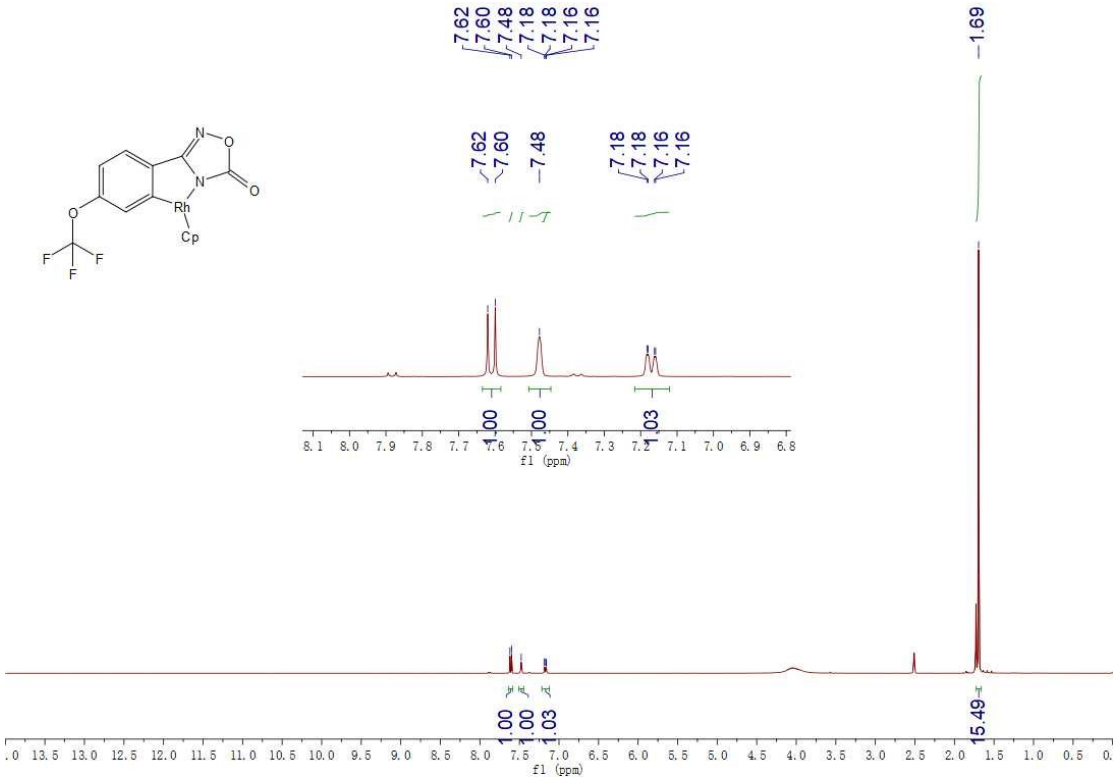


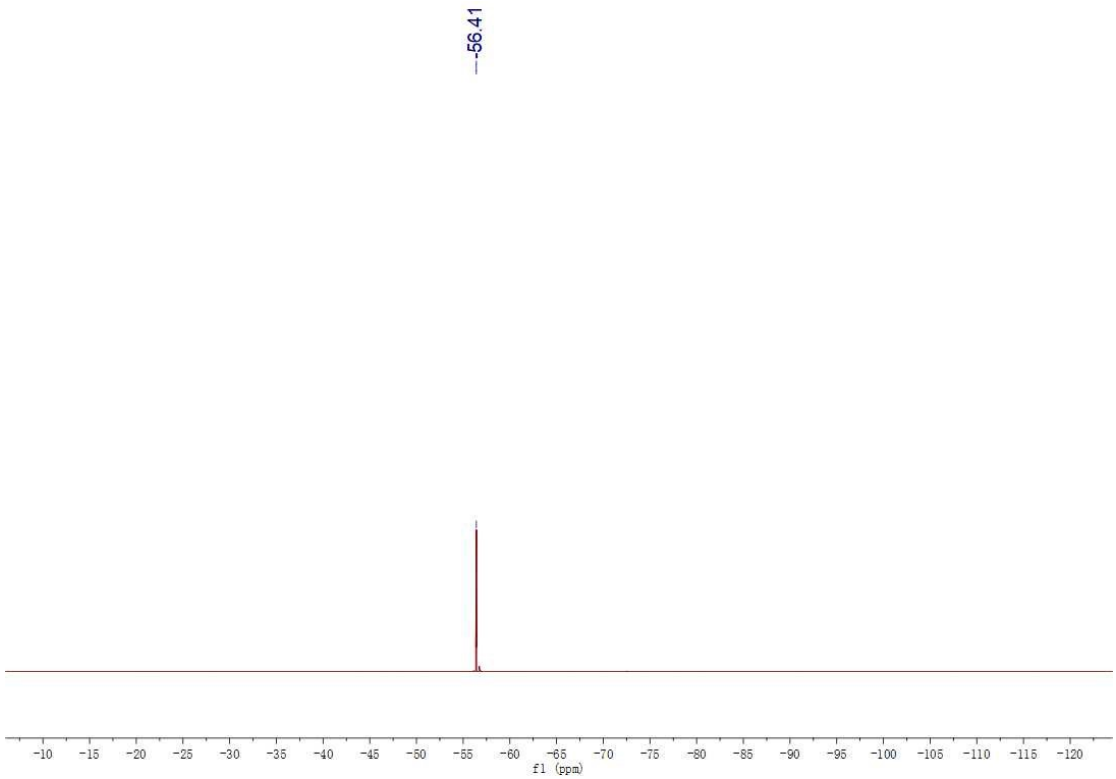
(5) Synthesis of Rh catalyst 8



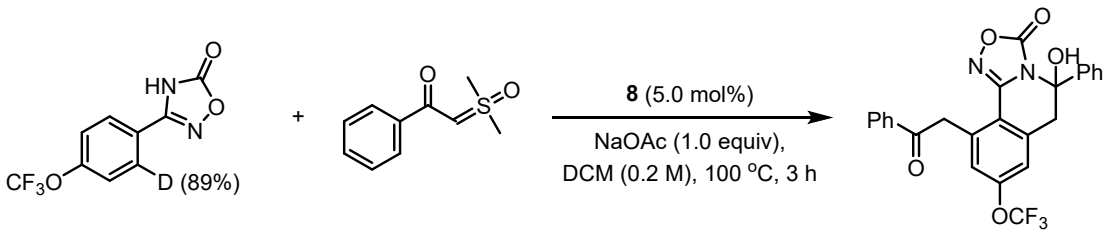
4f, 0.2 mmol 100 mol% **8**

According to the reported method[7], in an oven-dried Schlenk tube under air, a mixture of the substrates **4f** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.0 equiv), NaOAc (2.5 equiv), 1.4-dioxane (3 ml) was stirred at 80 °C for 12 h. The obtained yellow solution was cooled to room temperature, and then separated centrifugally. The solid was washed by 1,4-dioxane three times, dried to give **8** , yellow solid, yield 85%.





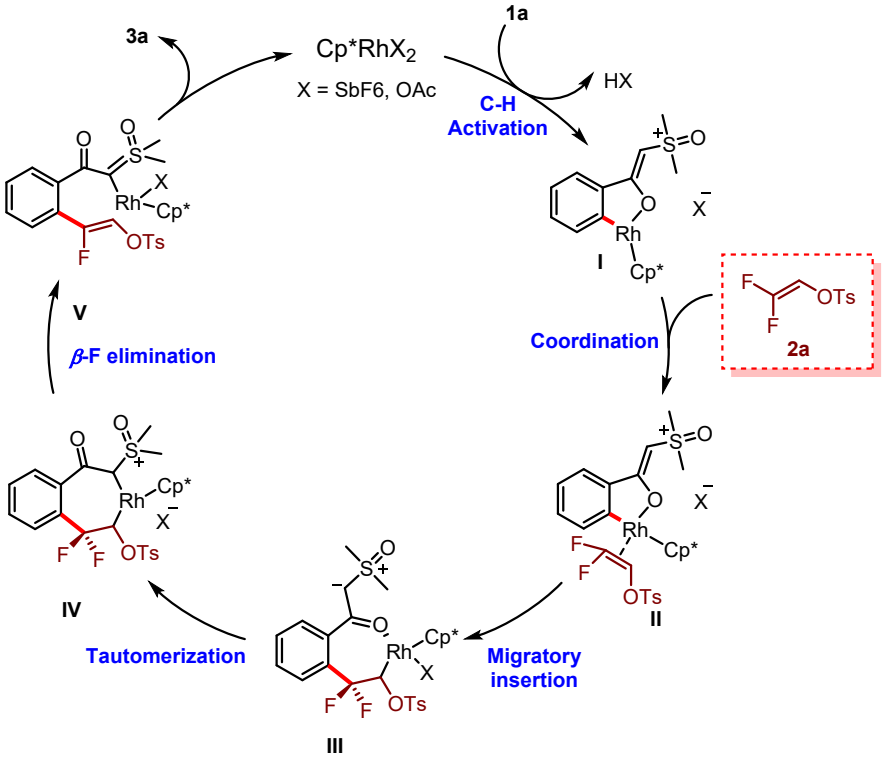
(5) Synthesis of 5h with Rh catalyst 8



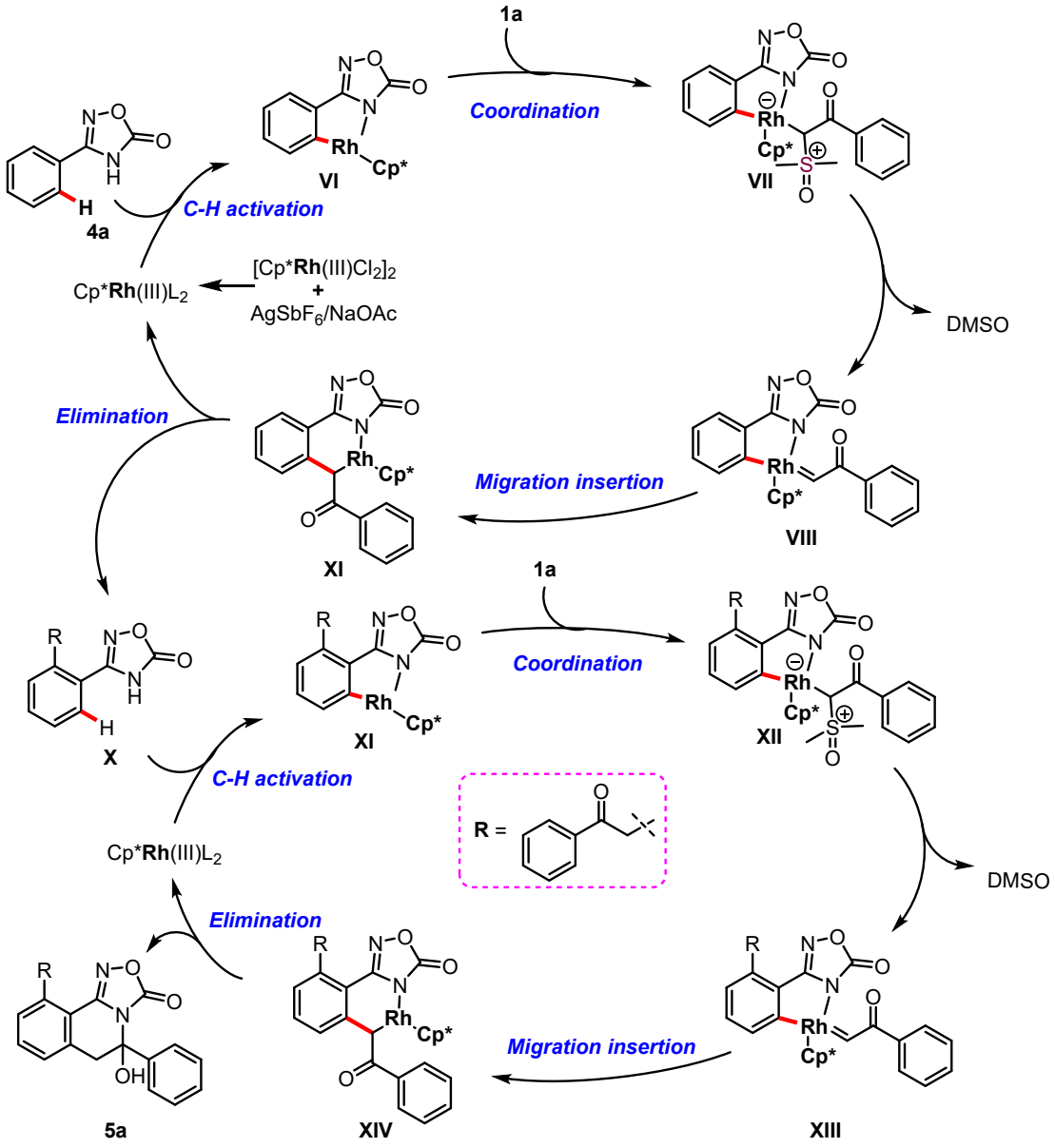
4f, 0.1 mmol **1a**, 2.5 mmol **5h**, 72%

In an oven-dried Schlenk tube under air, a mixture of the substrates **4f** (0.1 mmol, 1.0 equiv), **1a** (0.25 mmol, 2.5 equiv), **8** (5.0 mol%), NaOAc (1.0 equiv), and DCM (0.2 M) was stirred at 100 °C for 3 h. Then the reaction mixture was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5h** (72%).

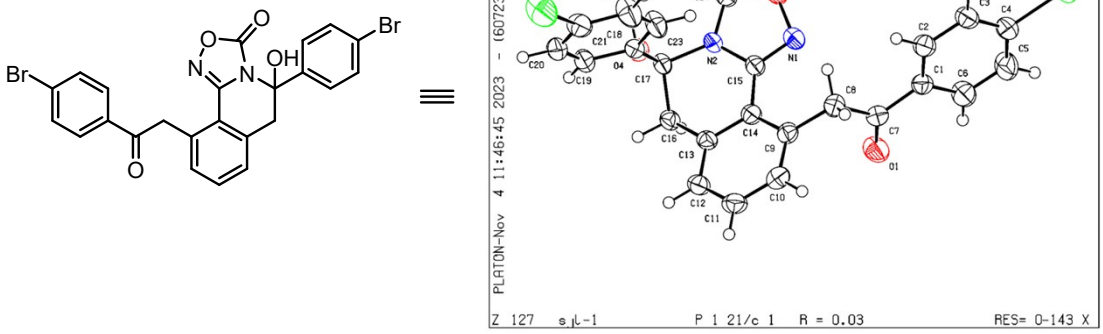
9. Scheme S1 Mechanistic Proposal of 3a



10. Scheme S2 Mechanistic Proposal of 5a



11. X-Ray crystal data for compound 5g



X-ray-quality crystal was obtained by slow diffusion of Petroleum ether into a dilute dichloromethane solution of **5g** at room temperature under air. Thermal ellipsoids drawn at the 50% probability level. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal was kept at 200.00(10) K during data collection.

Table 1 Crystal data and structure refinement for 5g.

Identification code	**5g**
Empirical formula	$C_{24}H_{16}Br_2N_2O_4$
Formula weight	556.21
Temperature/K	220.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.02870(10)
b/Å	20.8713(2)
c/Å	8.81380(10)
α/°	90
β/°	102.2430(10)
γ/°	90
Volume/Å^3	2342.19(4)
Z	4
ρ_{calc}g/cm^3	1.577
μ/mm^{-1}	4.667
F(000)	1104.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.134 to 148.604
Index ranges	-13 ≤ h ≤ 16, -25 ≤ k ≤ 25, -9 ≤ l ≤ 10
Reflections collected	12255
Independent reflections	4631 [R_{int} = 0.0227, R_{sigma} = 0.0211]
Data/restraints/parameters	4631/0/291
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0348, wR_2 = 0.0970

Final R indexes [all data] $R_1 = 0.0368$, $wR_2 = 0.0987$
Largest diff. peak/hole / e Å^{-3} 0.51/-0.61

Crystal structure determination of [5g]

Crystal Data for $C_{24}H_{16}Br_2N_2O_4$ (M = 556.21 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 13.02870(10) Å, b= 20.8713(2)Å, c = 8.81380(10) Å, β = 102.2430(10)°, V = 2342.19(4) Å^3, Z = 4, T = 220.00(10) K, μ(Cu Kα) = 4.667 mm^{-1}, *Dcalc* = 1.577 g/cm^3, 12255 reflections measured (8.134° ≤ 2Θ ≤ 148.604°), 4631 unique (R_{int} = 0.0227, R_{sigma} = 0.0211) which were used in all calculations. The final R_1 was 0.0348 (I >2σ(I)) and wR_2 was 0.0987 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5g. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	1358.4(2)	3363.0(2)	-2777.9(4)	60.99(13)
Br2	9668.4(3)	6575.5(2)	8063.3(5)	78.54(15)
O1	5344.6(14)	2401.4(8)	3176(2)	52.9(4)
O2	4305.3(12)	4322.9(8)	6039.2(18)	43.7(4)
O3	4680.3(12)	4900.4(8)	8269.3(19)	44.5(4)
O4	6516.9(12)	4283.5(7)	10162.8(16)	37.9(3)
N1	4884.1(14)	3903.1(9)	5224(2)	41.5(4)
N2	5877.8(12)	4218.0(8)	7460.0(18)	30.6(3)
C1	4266.1(16)	3037.6(10)	1253(2)	35.2(4)
C2	4098.4(17)	3625.4(11)	487(3)	40.7(5)
C3	3233.4(17)	3719.3(11)	-715(3)	42.4(5)
C4	2541.6(17)	3222.6(12)	-1130(3)	43.2(5)
C5	2678(2)	2636.5(13)	-395(3)	56.4(7)
C6	3547(2)	2546.9(12)	797(3)	49.5(6)
C7	5203.0(16)	2916.3(10)	2524(2)	34.8(4)
C8	5995.7(18)	3456.3(10)	2903(2)	36.6(4)
C9	6838.9(17)	3350.2(9)	4330(2)	33.6(4)
C10	7792.4(18)	3086.6(11)	4178(3)	40.7(5)
C11	8611.8(18)	3006.7(11)	5445(3)	42.6(5)
C12	8505.2(17)	3192.7(10)	6915(3)	37.4(4)
C13	7565.5(16)	3455.8(9)	7115(2)	31.4(4)
C14	6736.8(16)	3535.2(9)	5823(2)	31.5(4)
C15	5807.2(15)	3865.8(9)	6118(2)	31.3(4)
C16	7408.7(16)	3634.6(10)	8706(2)	32.8(4)
C17	6820.7(15)	4268.2(10)	8734(2)	30.7(4)
C18	7476.7(15)	4850.1(9)	8515(2)	31.2(4)
C19	8317.8(17)	5006.4(11)	9718(3)	39.1(5)
C20	8960.7(17)	5522.5(11)	9584(3)	44.2(5)
C21	8766.6(19)	5878.8(11)	8247(3)	47.6(6)
C22	7928(2)	5740.5(13)	7049(3)	57.7(7)
C23	7294.2(19)	5224.8(12)	7188(3)	46.8(6)
C24	4942.2(16)	4522.3(10)	7380(2)	35.5(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 5g. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	40.39(17)	60.9(2)	70.8(2)	-3.24(13)	-12.64(13)	0.50(11)
Br2	56.9(2)	48.5(2)	119.0(3)	19.57(16)	-6.51(19)	-22.38(13)
O1	48.2(10)	37.1(9)	66.6(11)	11.8(8)	-2.9(8)	-4.2(7)
O2	29.9(7)	54.2(10)	42.9(8)	-4.0(7)	-1.4(6)	9.7(7)
O3	40.4(8)	44.2(9)	49.0(9)	-3.2(7)	9.8(7)	10.0(7)
O4	39.2(8)	43.3(8)	31.6(7)	2.7(6)	8.7(6)	2.8(6)
N1	33.6(9)	47.9(11)	39.7(9)	-4.4(8)	0.4(7)	7.1(8)
N2	24.3(8)	33.0(8)	32.3(8)	-0.5(6)	1.1(6)	0.7(6)
C1	32.7(10)	33.5(10)	39.4(10)	-1.7(8)	7.6(8)	1.5(8)
C2	34.7(11)	33.3(11)	51.7(13)	0.1(9)	3.7(9)	-1.9(8)
C3	34.0(11)	37.5(11)	52.9(13)	2.9(9)	3.2(9)	1.6(9)
C4	30.9(11)	45.2(12)	50.7(12)	-4.4(10)	2.5(9)	1.5(9)
C5	47.9(14)	42.8(13)	70.3(16)	0.0(12)	-6.1(12)	-13.7(11)
C6	46.3(13)	36.0(12)	61.3(14)	6.0(10)	0.0(11)	-7.3(10)
C7	35.7(11)	32.7(10)	37.0(10)	-0.9(8)	9.8(8)	2.5(8)
C8	41.6(11)	33.9(11)	33.2(10)	0.0(8)	5.9(9)	-2.7(8)
C9	36.7(11)	27.1(9)	36.0(10)	0.4(7)	5.5(8)	-2.9(8)
C10	43.9(12)	36.2(11)	43.5(11)	-5.0(9)	12.7(9)	-0.2(9)
C11	34.8(11)	38.3(11)	55.7(13)	-1.7(10)	11.6(9)	6.2(9)
C12	32.2(10)	33.5(10)	44.5(11)	3.4(9)	3.7(8)	3.5(8)
C13	29.5(10)	24.8(9)	38.3(10)	3.4(7)	3.5(8)	0.0(7)
C14	30.4(10)	27.4(9)	35.8(10)	1.2(7)	5.1(8)	-1.5(7)
C15	29.4(9)	31.2(10)	31.2(9)	2.3(7)	2.1(7)	-0.3(8)
C16	33.2(10)	30.1(10)	32.6(9)	4.2(7)	1.4(8)	1.6(8)
C17	27.4(9)	34.2(10)	28.0(9)	2.0(7)	-0.1(7)	-0.2(8)
C18	28.3(9)	29.5(9)	34.1(9)	-0.8(7)	3.0(7)	2.4(7)
C19	34.8(11)	40.7(11)	37.5(10)	1.1(9)	-1.8(8)	0.2(9)
C20	32.8(11)	39.6(12)	54.5(13)	-7.3(10)	-3.4(9)	-1.2(9)
C21	37.0(11)	32.1(11)	70.1(15)	4.6(10)	3.1(11)	-5.6(9)
C22	54.1(15)	48.2(14)	61.7(15)	21.3(12)	-8.3(12)	-13.6(12)
C23	42.4(12)	45.1(13)	45.5(12)	11.2(10)	-7.2(10)	-8.1(10)
C24	29.4(10)	37.4(11)	38.0(10)	2.4(8)	3.2(8)	3.0(8)

Table 4 Bond Lengths for 5g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C4	1.903(2)	C7	C8	1.517(3)
Br2	C21	1.898(2)	C8	C9	1.500(3)
O1	C7	1.214(3)	C9	C10	1.391(3)
O2	N1	1.443(2)	C9	C14	1.405(3)
O2	C24	1.358(3)	C10	C11	1.382(3)
O3	C24	1.211(3)	C11	C12	1.387(3)
O4	C17	1.398(2)	C12	C13	1.387(3)
N1	C15	1.293(3)	C13	C14	1.403(3)
N2	C15	1.379(3)	C13	C16	1.506(3)
N2	C17	1.482(2)	C14	C15	1.464(3)
N2	C24	1.363(3)	C16	C17	1.531(3)

Table 4 Bond Lengths for 5g.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.395(3)	C17	C18	1.521(3)
C1	C6	1.389(3)	C18	C19	1.393(3)
C1	C7	1.493(3)	C18	C23	1.385(3)
C2	C3	1.387(3)	C19	C20	1.385(3)
C3	C4	1.371(3)	C20	C21	1.370(4)
C4	C5	1.378(4)	C21	C22	1.380(3)
C5	C6	1.385(3)	C22	C23	1.378(3)

Table 5 Bond Angles for 5g.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	O2	N1	109.41(15)	C14	C13	C16	119.57(18)
C15	N1	O2	104.47(16)	C9	C14	C15	122.82(18)
C15	N2	C17	125.55(16)	C13	C14	C9	121.23(19)
C24	N2	C15	107.93(16)	C13	C14	C15	115.77(18)
C24	N2	C17	126.49(17)	N1	C15	N2	112.02(18)
C2	C1	C7	122.09(19)	N1	C15	C14	128.16(18)
C6	C1	C2	118.8(2)	N2	C15	C14	119.74(17)
C6	C1	C7	119.08(19)	C13	C16	C17	113.34(16)
C3	C2	C1	120.8(2)	O4	C17	N2	109.67(16)
C4	C3	C2	118.6(2)	O4	C17	C16	105.81(15)
C3	C4	Br1	117.86(18)	O4	C17	C18	111.74(16)
C3	C4	C5	122.3(2)	N2	C17	C16	105.31(15)
C5	C4	Br1	119.88(18)	N2	C17	C18	110.97(15)
C4	C5	C6	118.7(2)	C18	C17	C16	113.02(16)
C5	C6	C1	120.8(2)	C19	C18	C17	117.57(18)
O1	C7	C1	121.5(2)	C23	C18	C17	123.91(18)
O1	C7	C8	121.67(19)	C23	C18	C19	118.5(2)
C1	C7	C8	116.72(18)	C20	C19	C18	120.6(2)
C9	C8	C7	114.74(17)	C21	C20	C19	119.4(2)
C10	C9	C8	119.23(19)	C20	C21	Br2	118.97(18)
C10	C9	C14	117.56(19)	C20	C21	C22	121.1(2)
C14	C9	C8	123.13(19)	C22	C21	Br2	119.93(19)
C11	C10	C9	121.5(2)	C23	C22	C21	119.2(2)
C10	C11	C12	120.5(2)	C22	C23	C18	121.2(2)
C13	C12	C11	119.7(2)	O2	C24	N2	106.07(17)
C12	C13	C14	119.44(19)	O3	C24	O2	123.99(19)
C12	C13	C16	120.95(18)	O3	C24	N2	129.94(19)

Table 6 Torsion Angles for 5g.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C4	C5	C6	179.8(2)	C12	C13	C14	C9	0.3(3)
Br2	C21	C22	C23	178.6(2)	C12	C13	C14	C15	-174.99(18)
O1	C7	C8	C9	-11.4(3)	C12	C13	C16	C17	139.48(19)
O2	N1	C15	N2	0.9(2)	C13	C14	C15	N1	-166.8(2)

Table 6 Torsion Angles for 5g.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	N1	C15	C14	-175.81(19)	C13	C14	C15	N2	16.7(3)
O4	C17	C18	C19	49.4(2)	C13	C16	C17	O4	165.78(16)
O4	C17	C18	C23	-131.4(2)	C13	C16	C17	N2	49.7(2)
N1	O2	C24	O3	176.8(2)	C13	C16	C17	C18	-71.6(2)
N1	O2	C24	N2	-2.8(2)	C14	C9	C10	C11	0.1(3)
N2	C17	C18	C19	172.18(17)	C14	C13	C16	C17	-42.8(2)
N2	C17	C18	C23	-8.7(3)	C15	N2	C17	O4	-142.63(18)
C1	C2	C3	C4	0.4(4)	C15	N2	C17	C16	-29.2(2)
C1	C7	C8	C9	171.60(18)	C15	N2	C17	C18	93.4(2)
C2	C1	C6	C5	0.1(4)	C15	N2	C24	O2	3.3(2)
C2	C1	C7	O1	-179.5(2)	C15	N2	C24	O3	-176.3(2)
C2	C1	C7	C8	-2.5(3)	C16	C13	C14	C9	-177.44(18)
C2	C3	C4	Br1	179.82(18)	C16	C13	C14	C15	7.2(3)
C2	C3	C4	C5	0.0(4)	C16	C17	C18	C19	-69.8(2)
C3	C4	C5	C6	-0.3(4)	C16	C17	C18	C23	109.3(2)
C4	C5	C6	C1	0.3(4)	C17	N2	C15	N1	179.02(18)
C6	C1	C2	C3	-0.4(3)	C17	N2	C15	C14	-4.0(3)
C6	C1	C7	O1	-0.7(3)	C17	N2	C24	O2	-178.44(17)
C6	C1	C7	C8	176.3(2)	C17	N2	C24	O3	2.1(4)
C7	C1	C2	C3	178.4(2)	C17	C18	C19	C20	178.7(2)
C7	C1	C6	C5	-178.8(2)	C17	C18	C23	C22	-178.9(2)
C7	C8	C9	C10	94.4(2)	C18	C19	C20	C21	-0.4(4)
C7	C8	C9	C14	-89.0(2)	C19	C18	C23	C22	0.2(4)
C8	C9	C10	C11	176.9(2)	C19	C20	C21	Br2	-178.89(18)
C8	C9	C14	C13	-176.78(18)	C19	C20	C21	C22	1.5(4)
C8	C9	C14	C15	-1.8(3)	C20	C21	C22	C23	-1.7(4)
C9	C10	C11	C12	-0.4(4)	C21	C22	C23	C18	0.9(4)
C9	C14	C15	N1	18.0(3)	C23	C18	C19	C20	-0.5(3)
C9	C14	C15	N2	-158.50(19)	C24	O2	N1	C15	1.2(2)
C10	C9	C14	C13	-0.1(3)	C24	N2	C15	N1	-2.7(2)
C10	C9	C14	C15	174.85(19)	C24	N2	C15	C14	174.34(18)
C10	C11	C12	C13	0.6(3)	C24	N2	C17	O4	39.4(3)
C11	C12	C13	C14	-0.5(3)	C24	N2	C17	C16	152.79(19)
C11	C12	C13	C16	177.21(19)	C24	N2	C17	C18	-84.6(2)

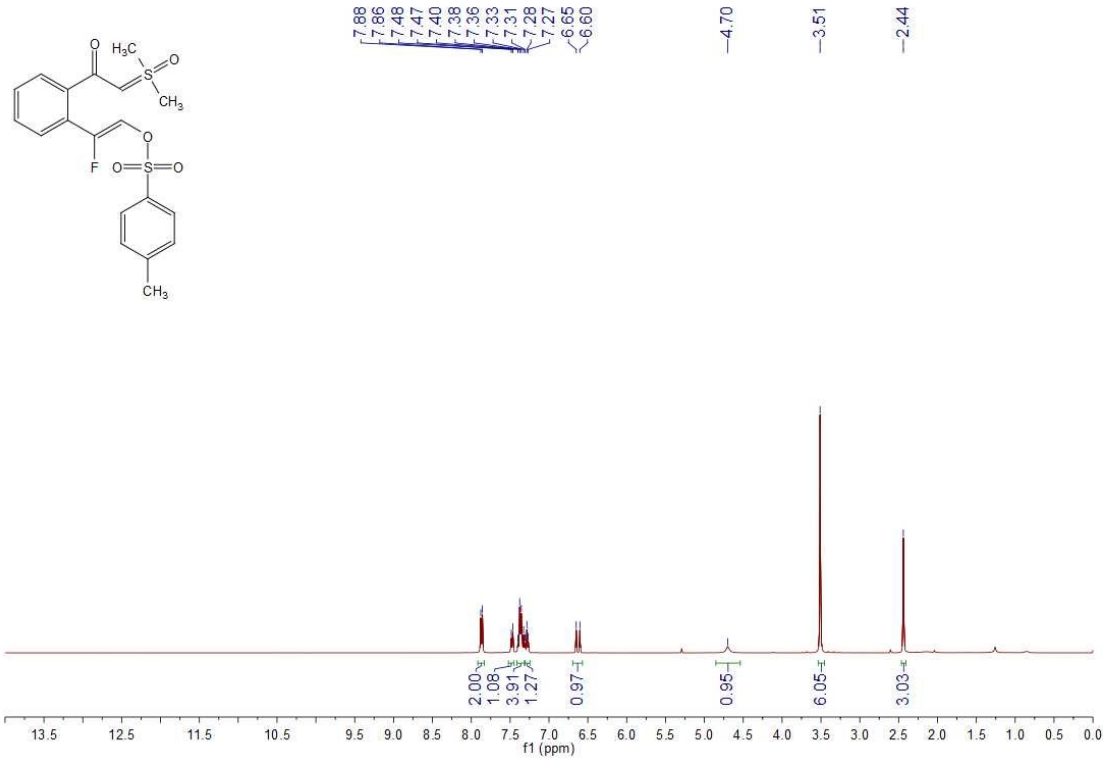
Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 5g.

Atom	*x*	*y*	*z*	U(eq)
H4	6221.55	4634.51	10258.3	57
H2	4582.48	3965.58	792.7	49
H3	3122.64	4119.09	-1239.37	51
H5	2185.64	2300.57	-701.05	68
H6	3652.69	2144.53	1310.78	59
H8A	6332.1	3519.47	2007.44	44
H8B	5616.11	3856.02	3039.75	44
H10	7882.42	2958.49	3180.44	49
H11	9253.2	2822.98	5308.68	51

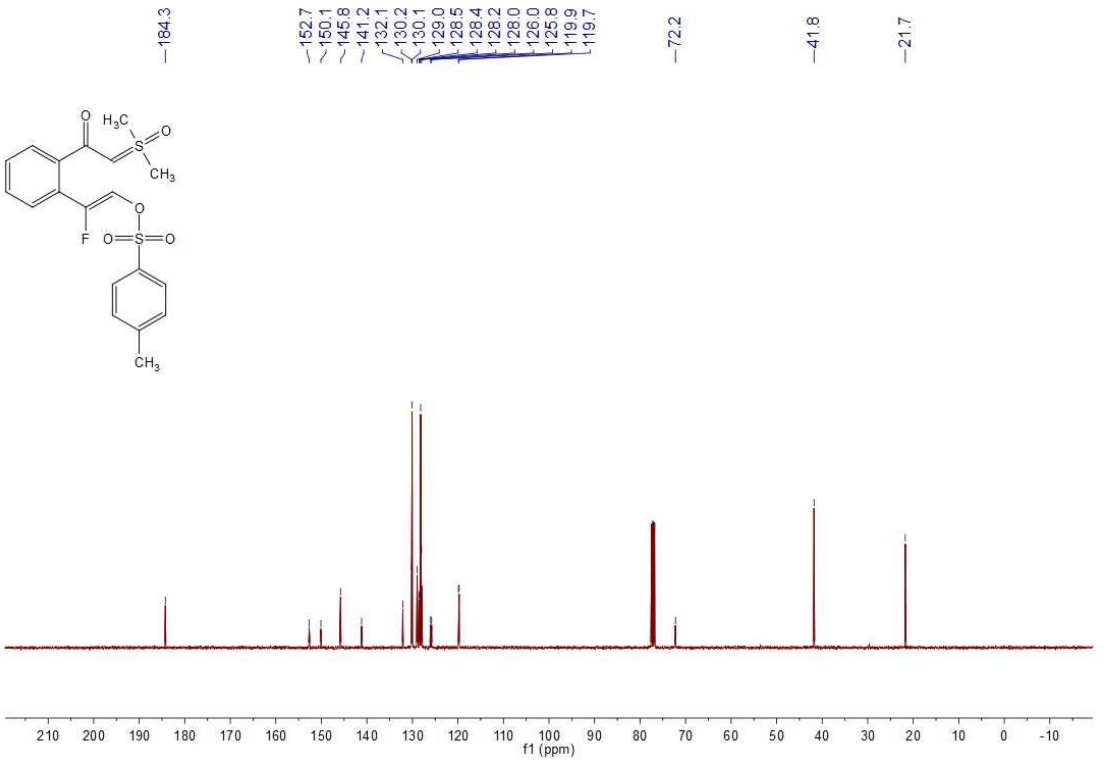
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5g.

Atom	*x*	*y*	*z*	U(eq)
H12	9073.35	3140	7780.49	45
H16A	8103.65	3666.95	9422.16	39
H16B	7011.32	3288.83	9093.09	39
H19	8451.78	4756.62	10640.15	47
H20	9531.02	5628.65	10410.62	53
H22	7789.26	5997.6	6138.79	69
H23	6721.82	5124.51	6359.33	56

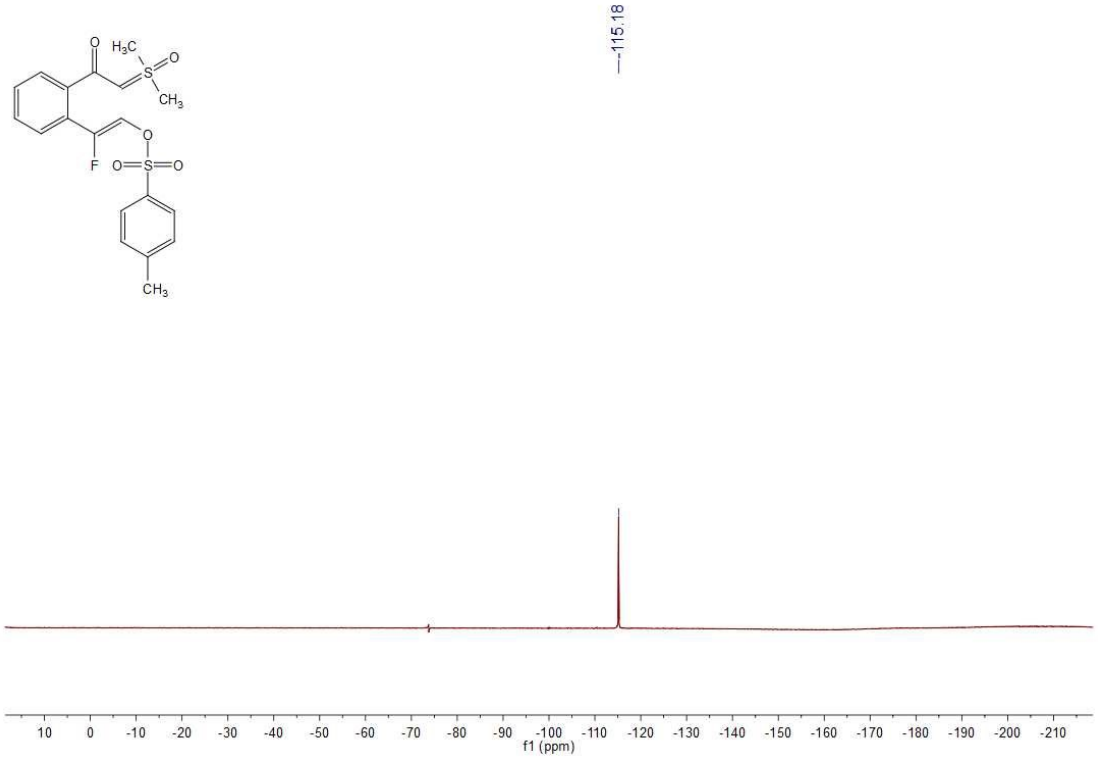
12. NMR Spectra for New Compounds



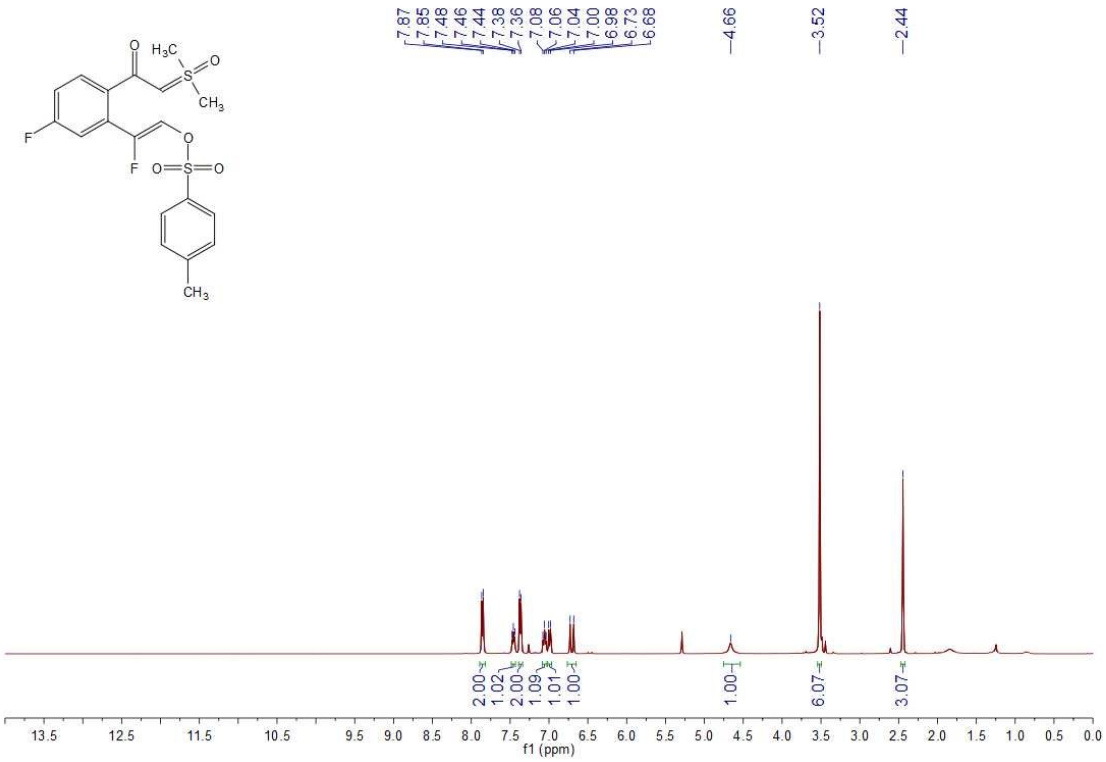
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



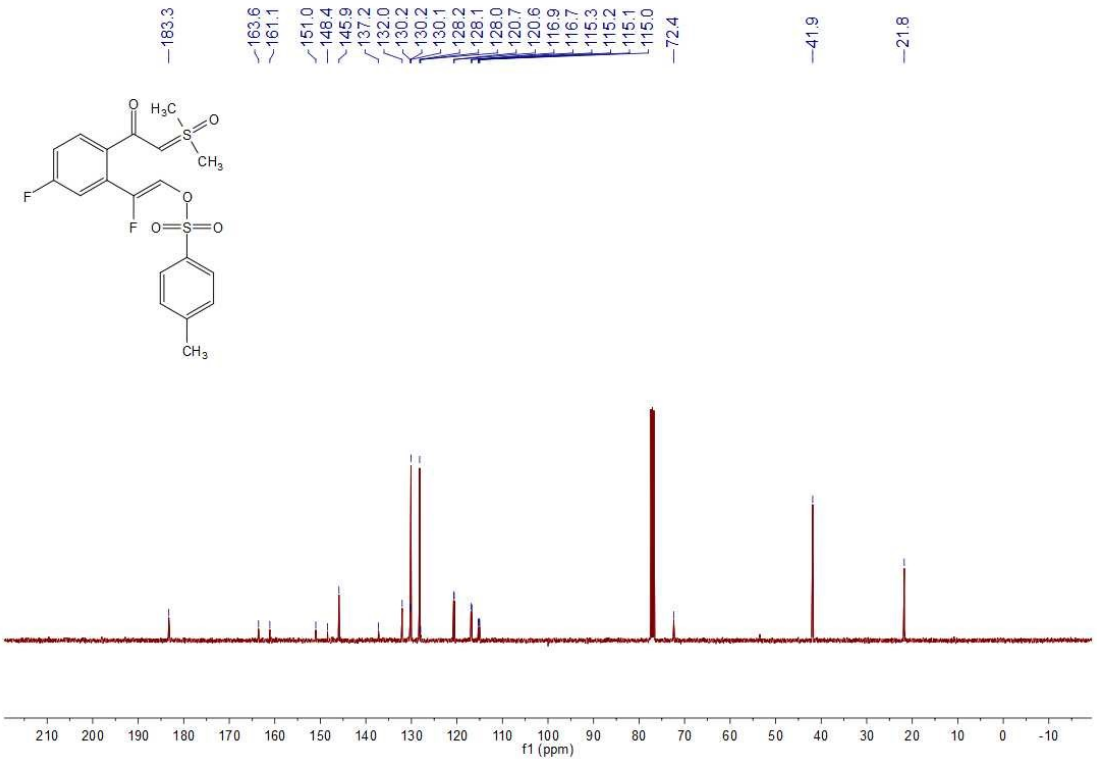
^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$)



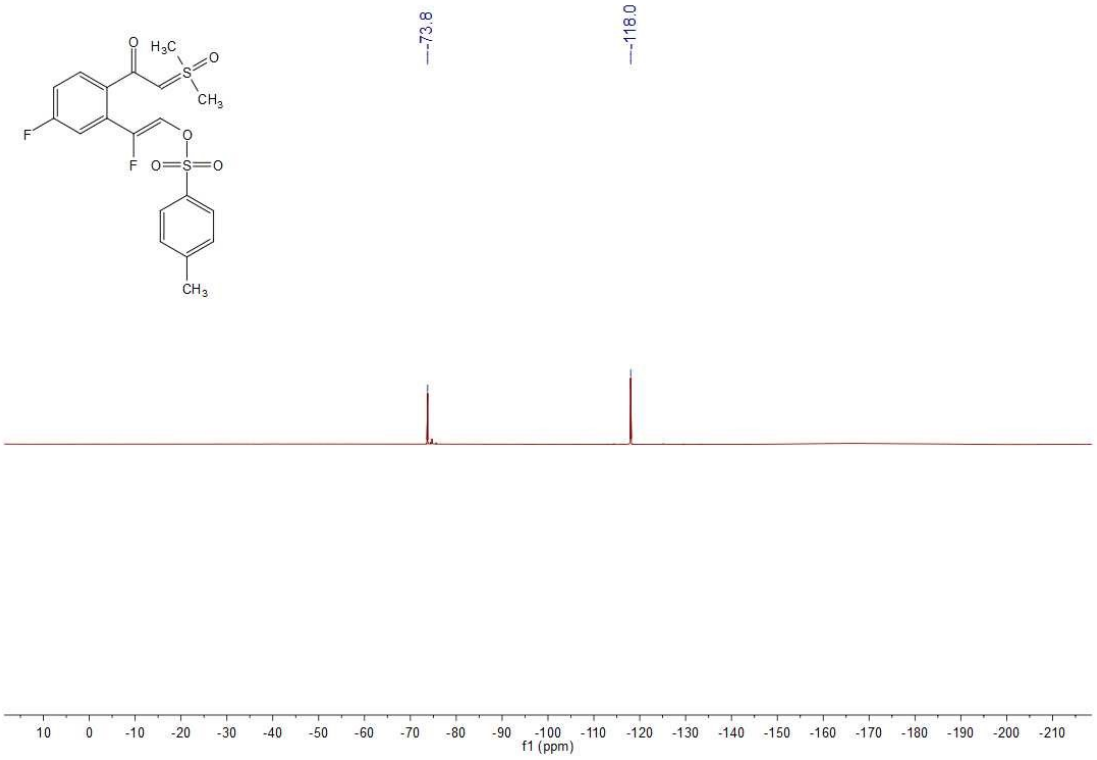
^{19}F NMR spectrum of **3a** (376 MHz, $CDCl_3$)



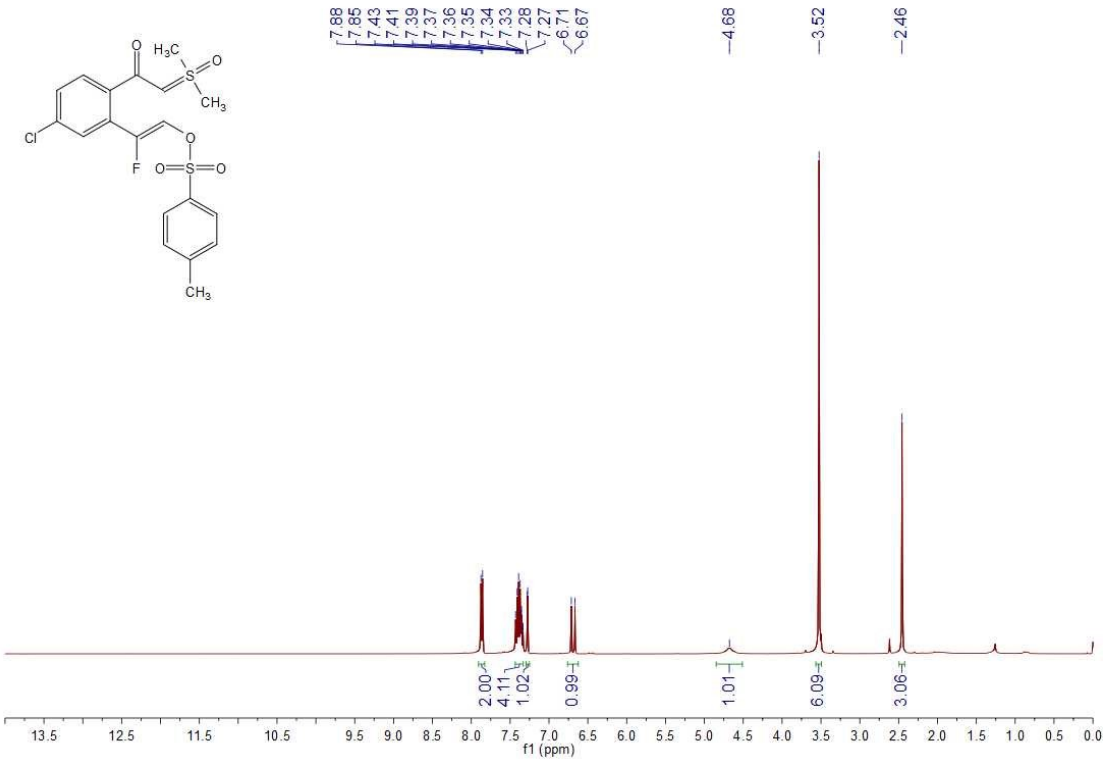
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



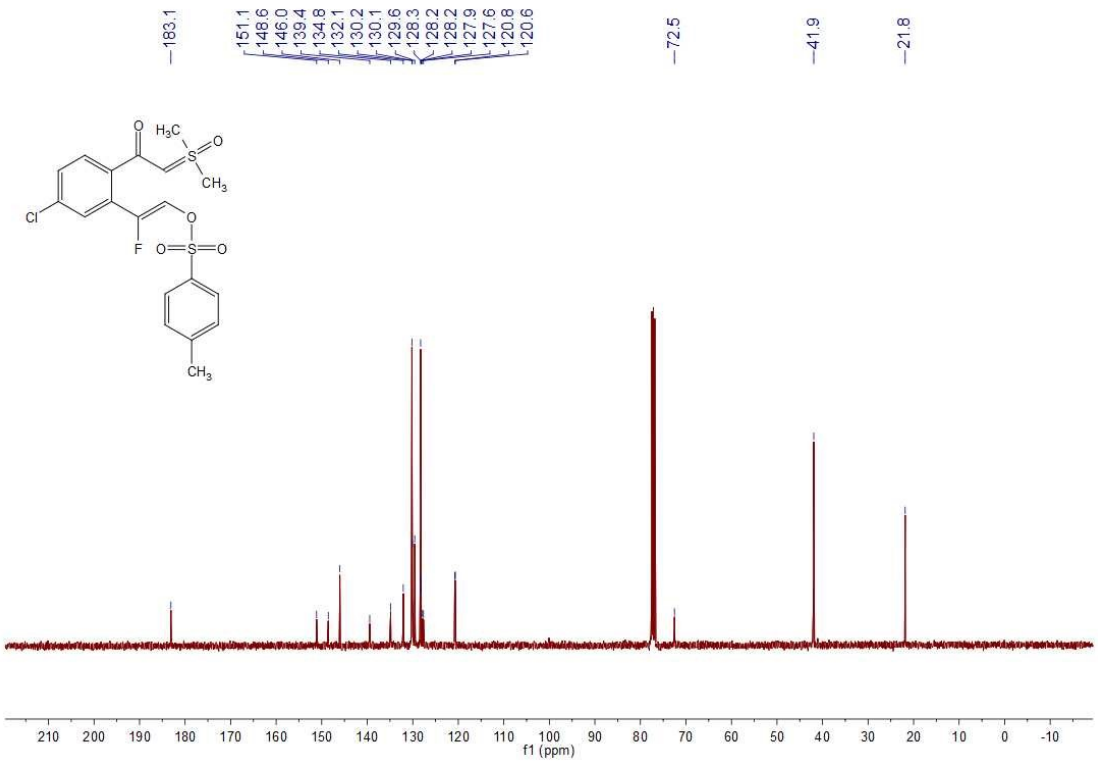
^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$)



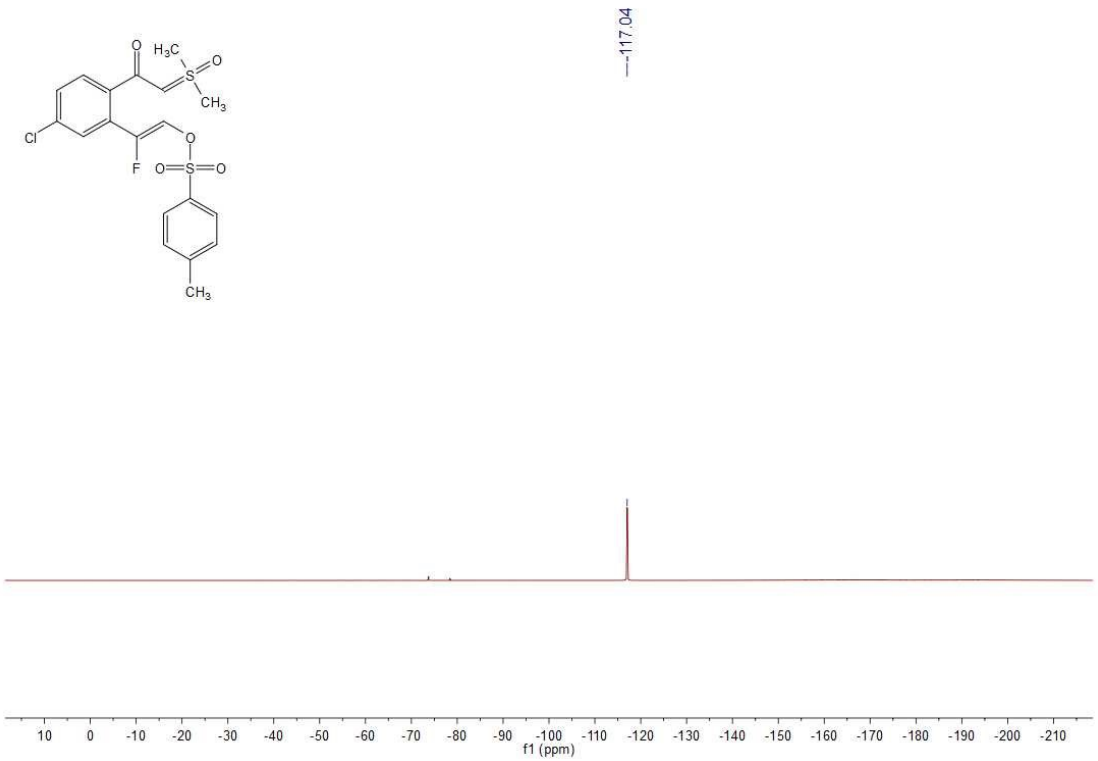
^{19}F NMR spectrum of **3b** (376 MHz, $CDCl_3$)



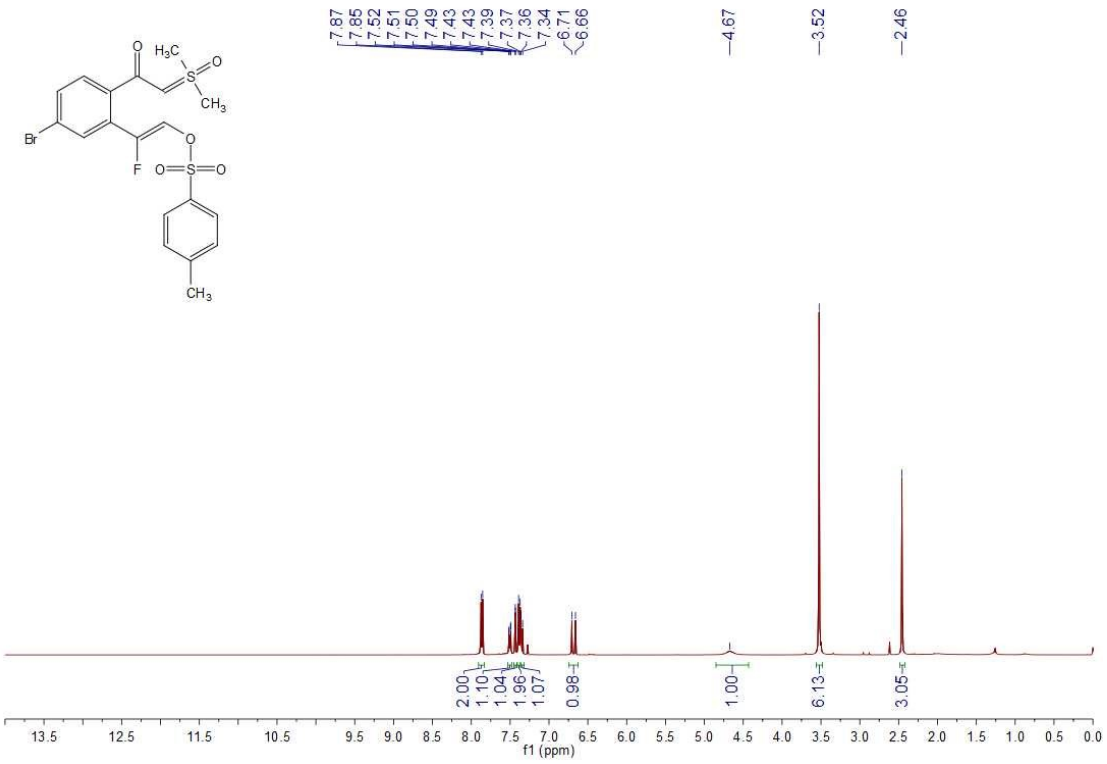
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



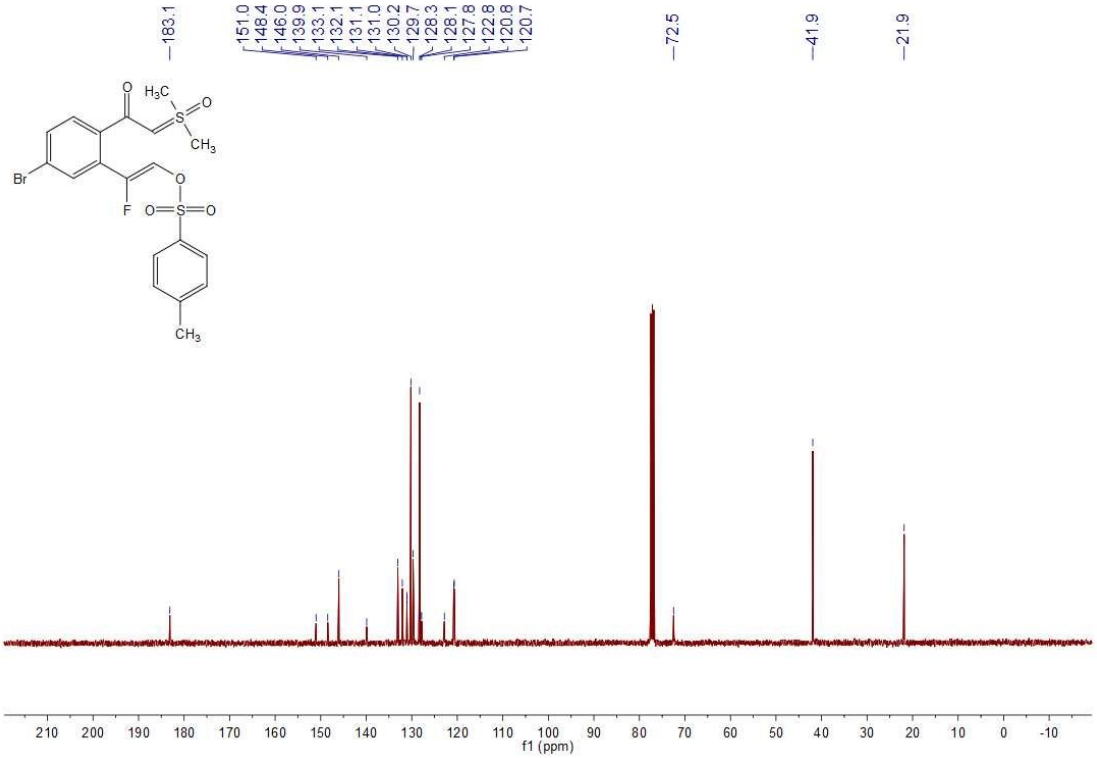
^{13}C NMR spectrum of **3c** (101 MHz, $CDCl_3$)



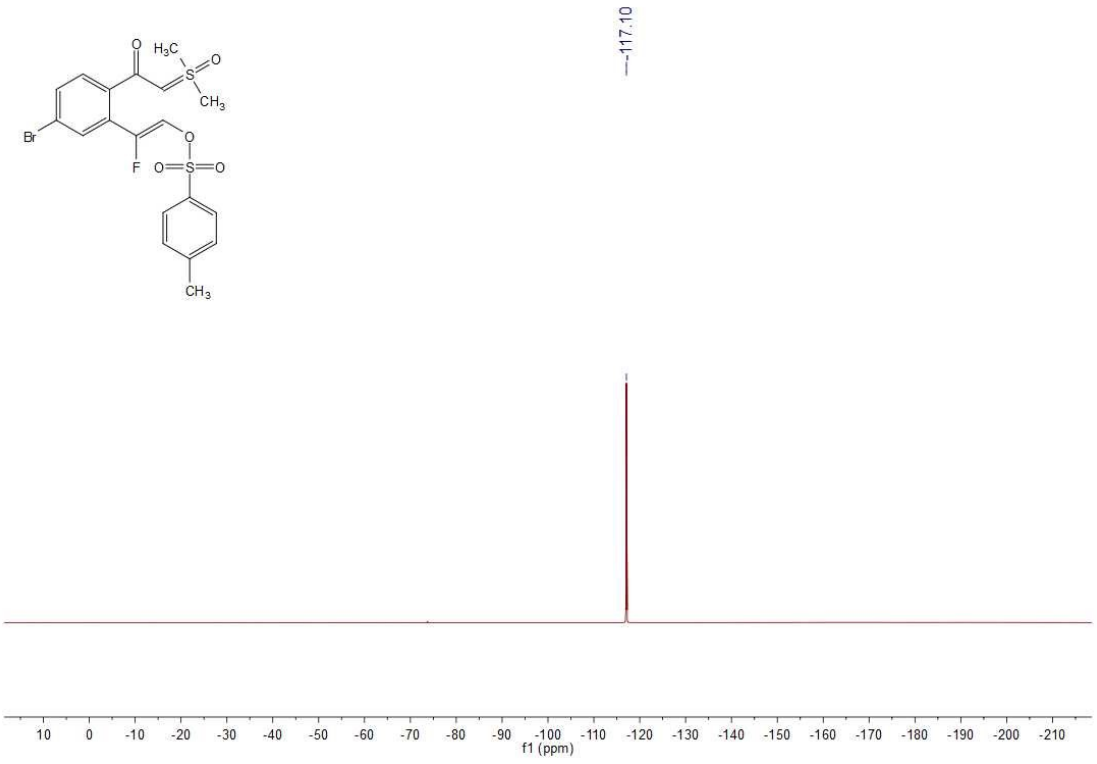
^{19}F NMR spectrum of **3c** (376 MHz, $CDCl_3$)



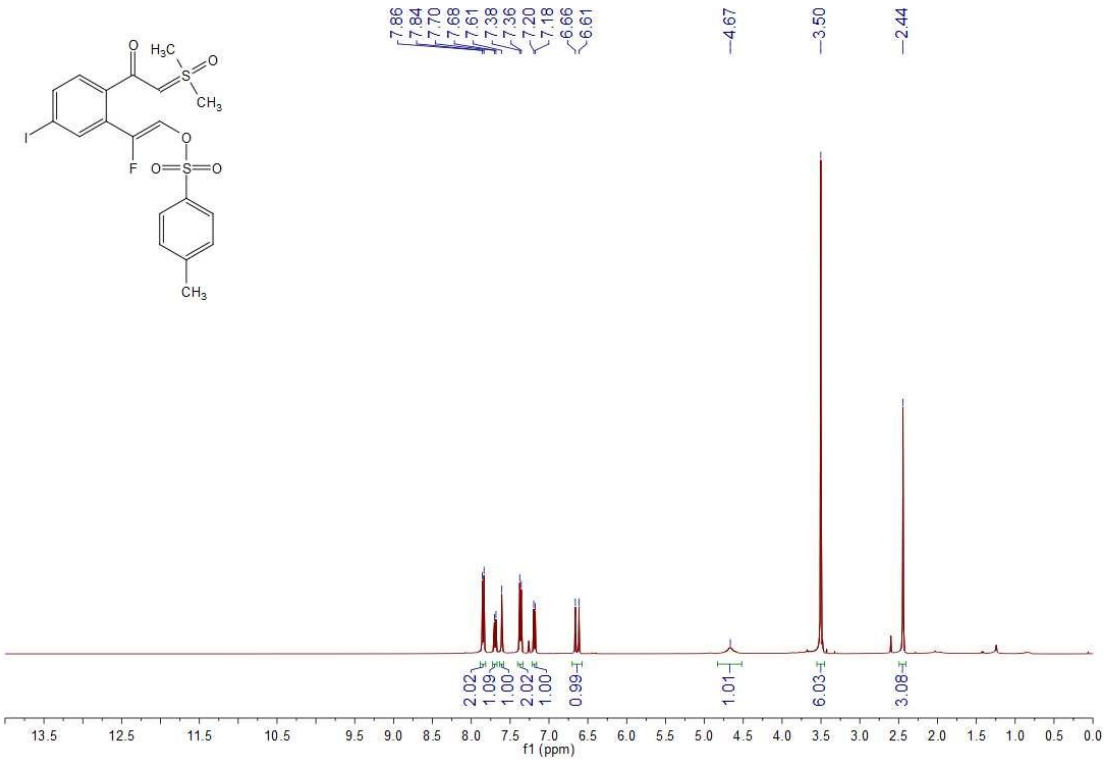
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



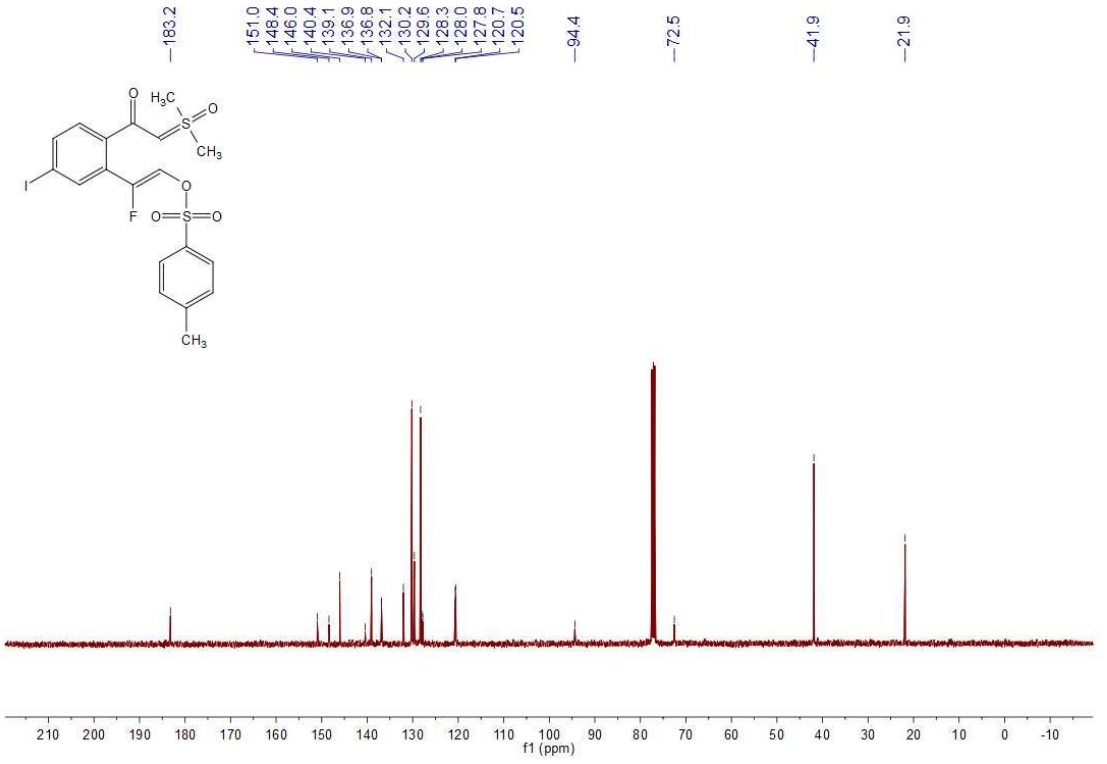
^{13}C NMR spectrum of **3d** (101 MHz, $CDCl_3$)



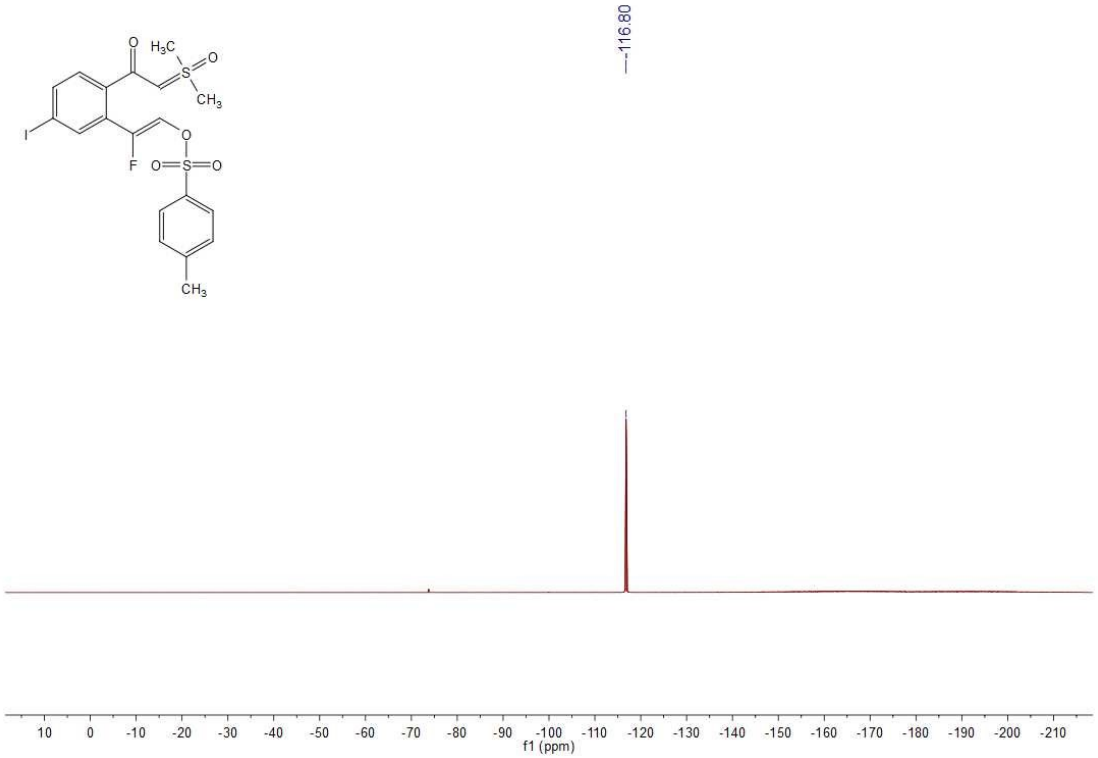
^{19}F NMR spectrum of **3d** (376 MHz, $CDCl_3$)



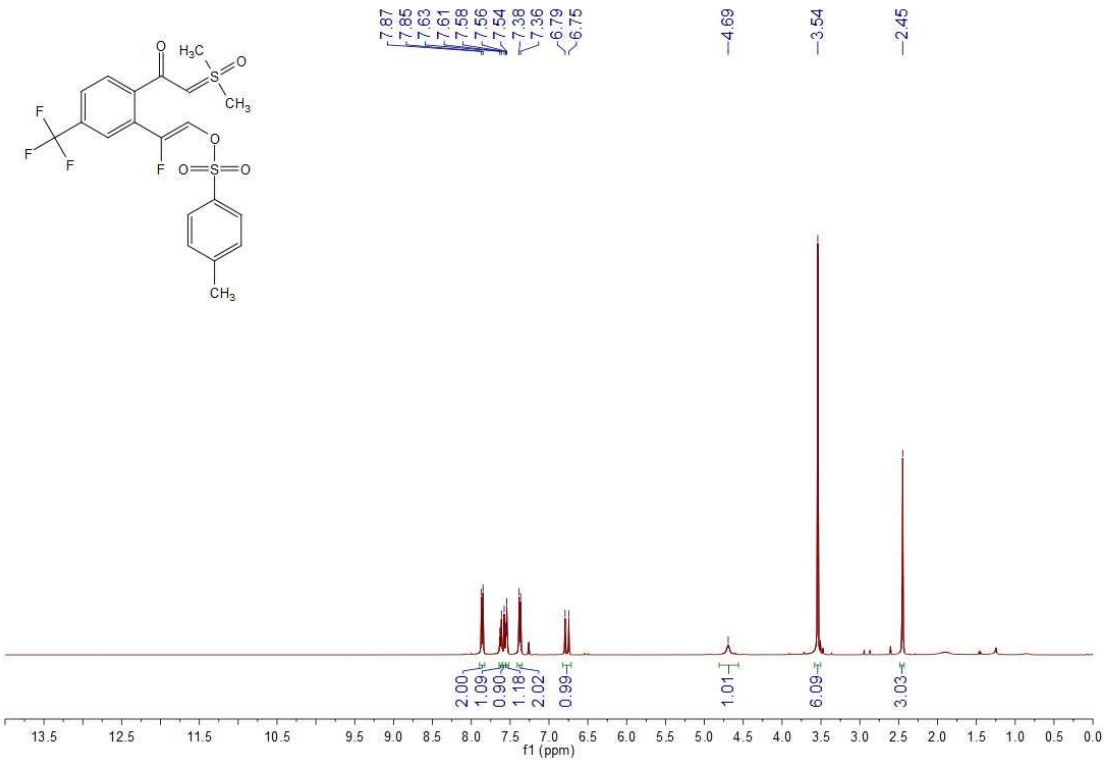
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



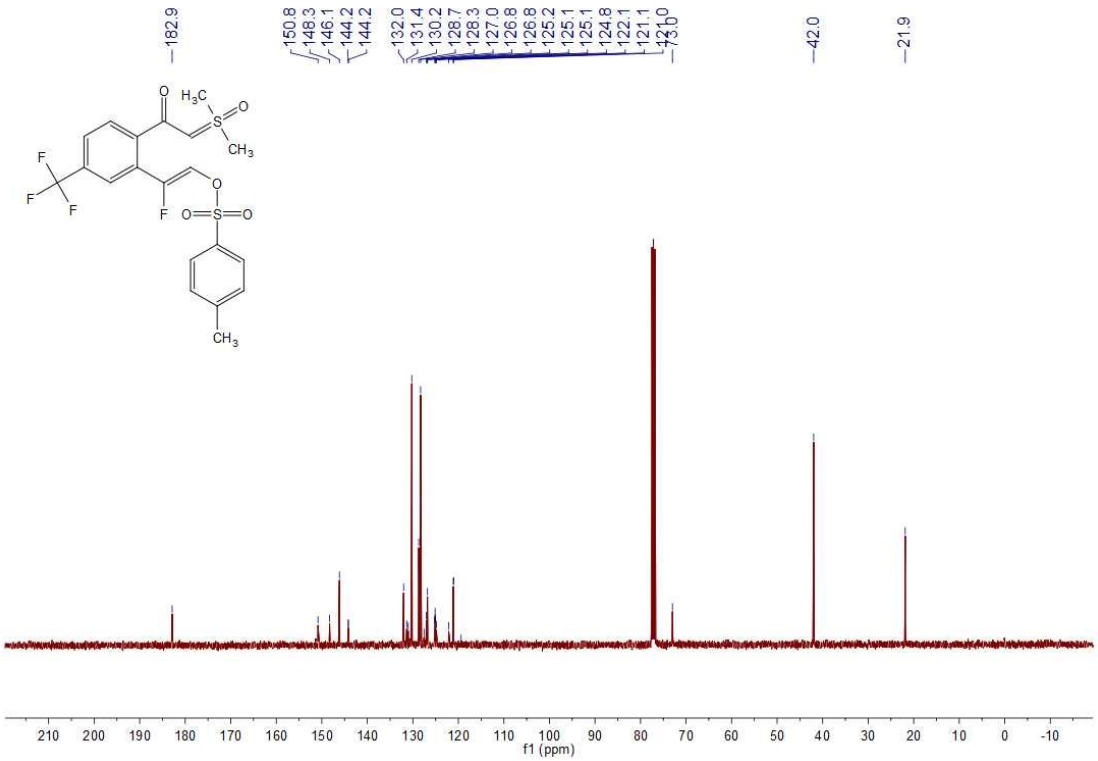
^{13}C NMR spectrum of **3e** (101 MHz, $CDCl_3$)



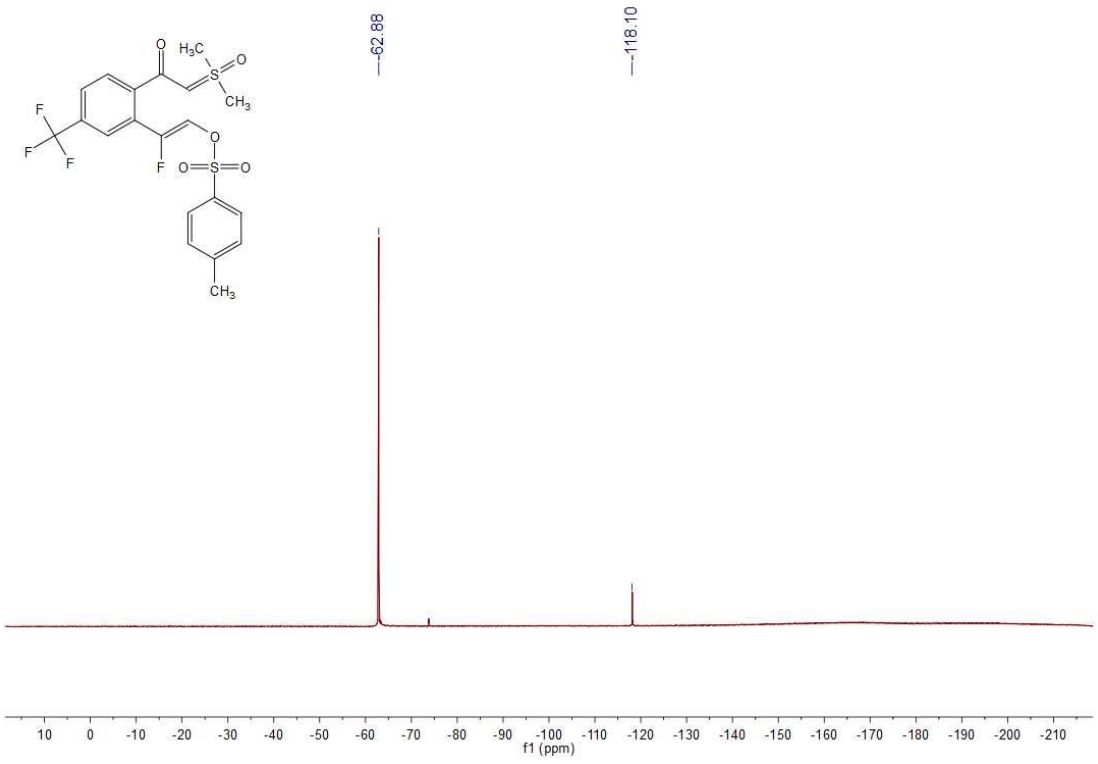
^{19}F NMR spectrum of **3e** (376 MHz, $CDCl_3$)



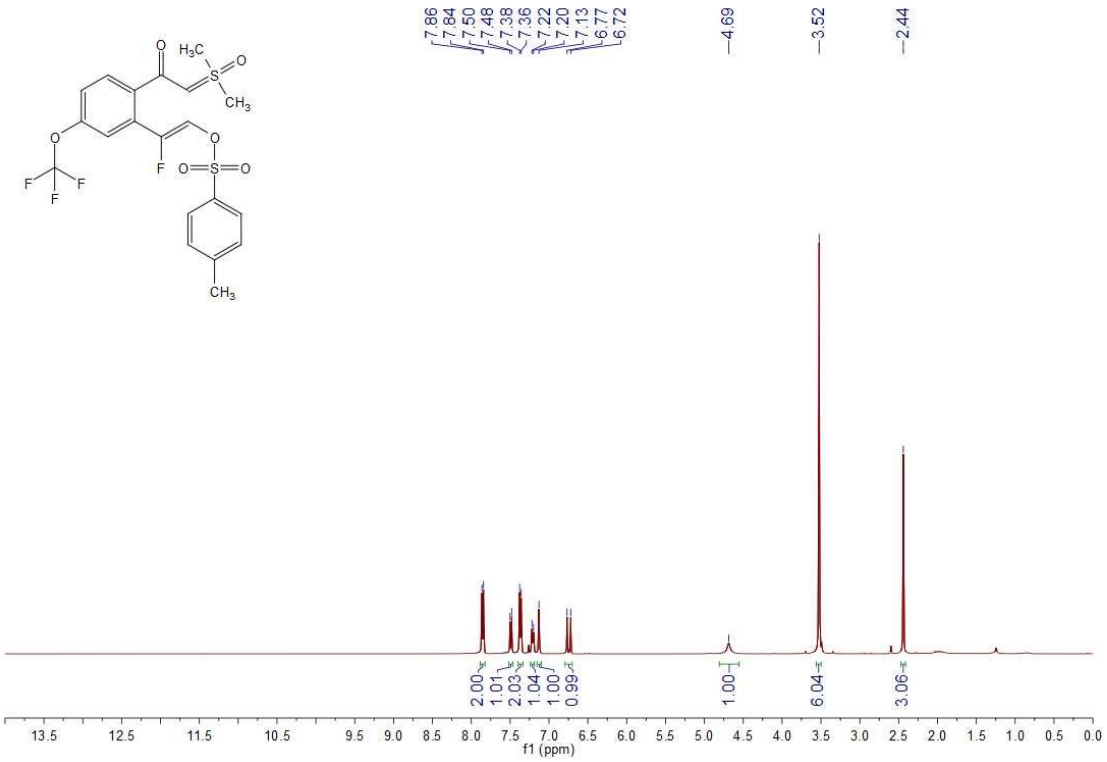
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



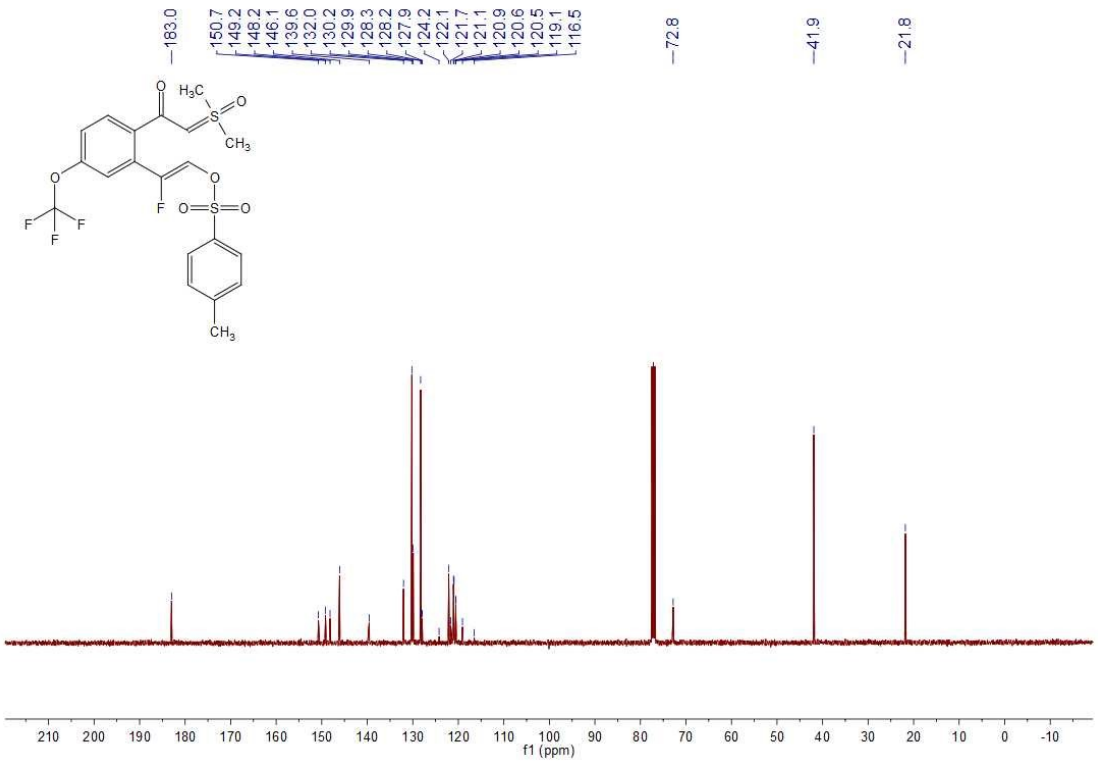
^{13}C NMR spectrum of **3f** (101 MHz, $CDCl_3$)



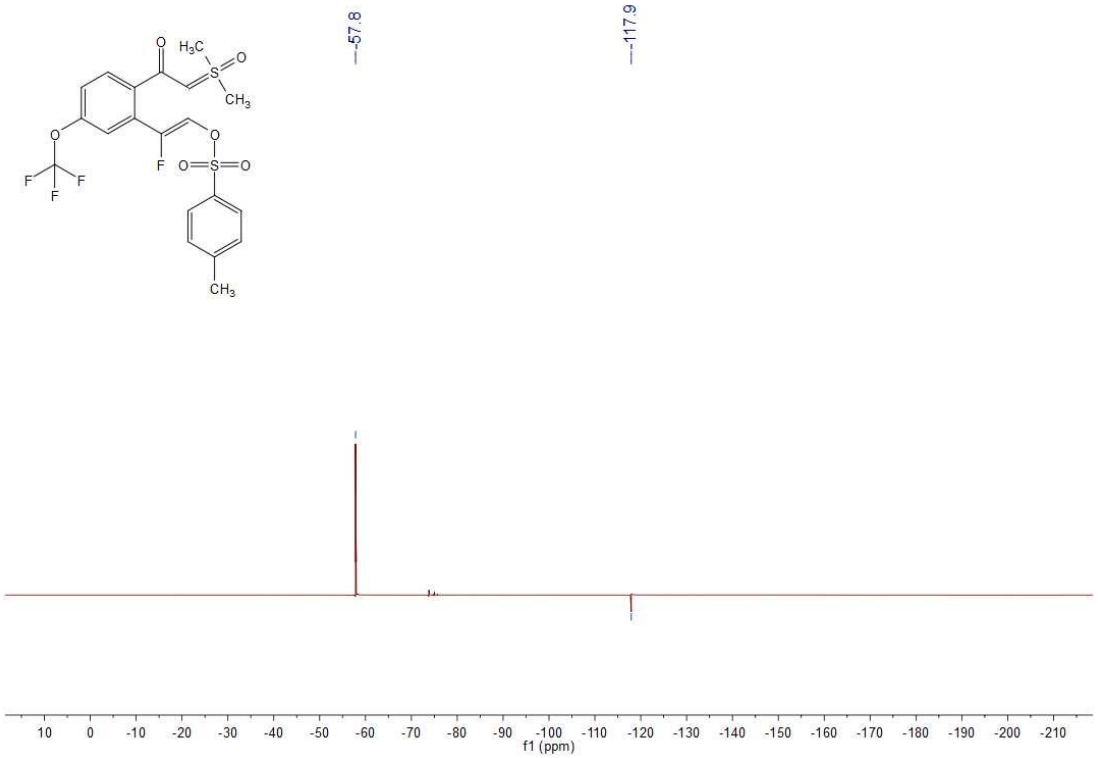
^{19}F NMR spectrum of **3f** (376 MHz, $CDCl_3$)



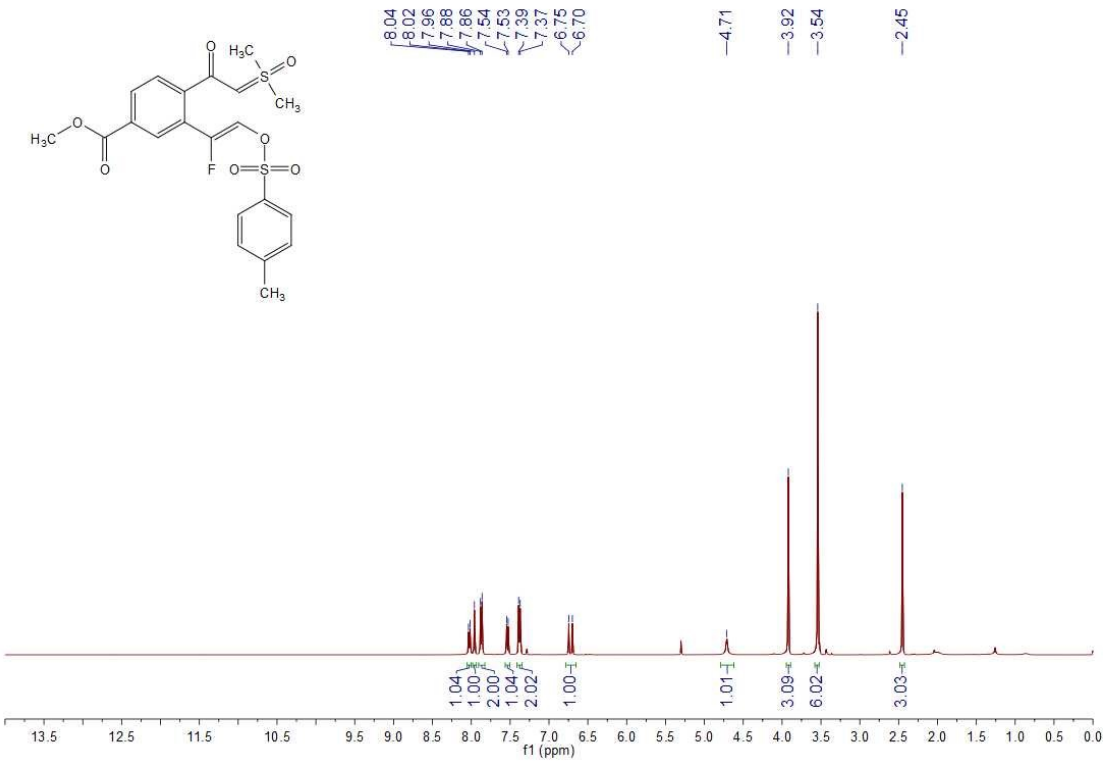
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



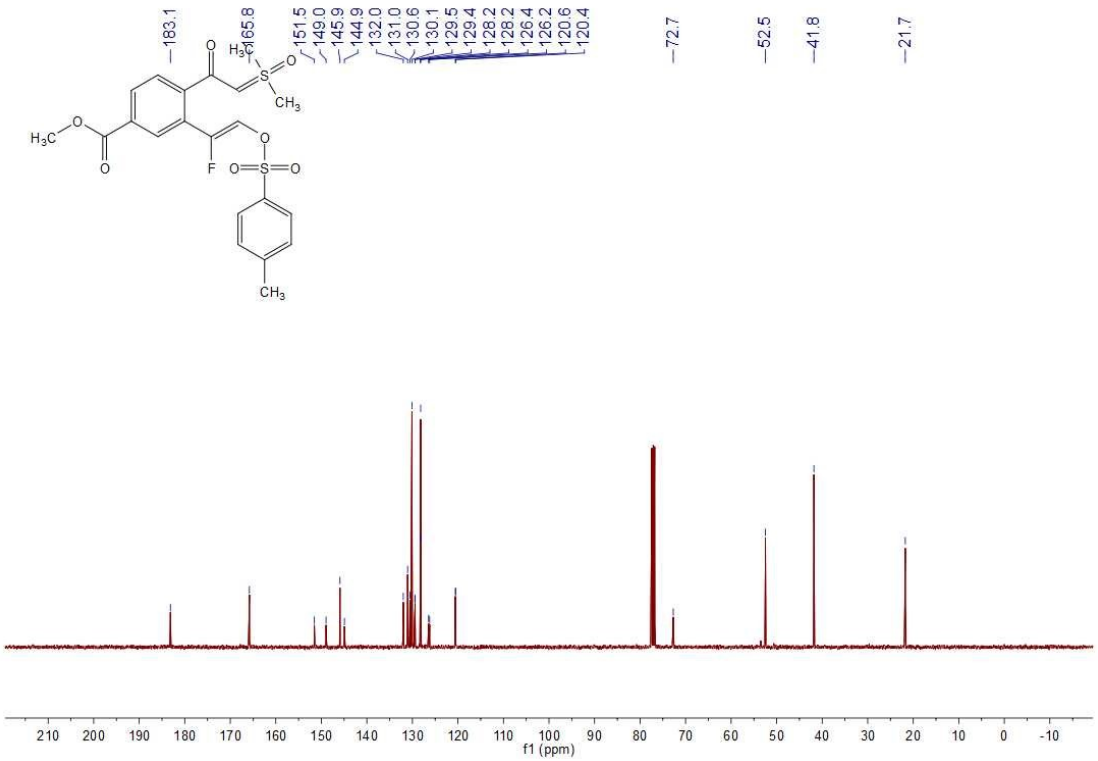
^{13}C NMR spectrum of **3g** (101 MHz, $CDCl_3$)



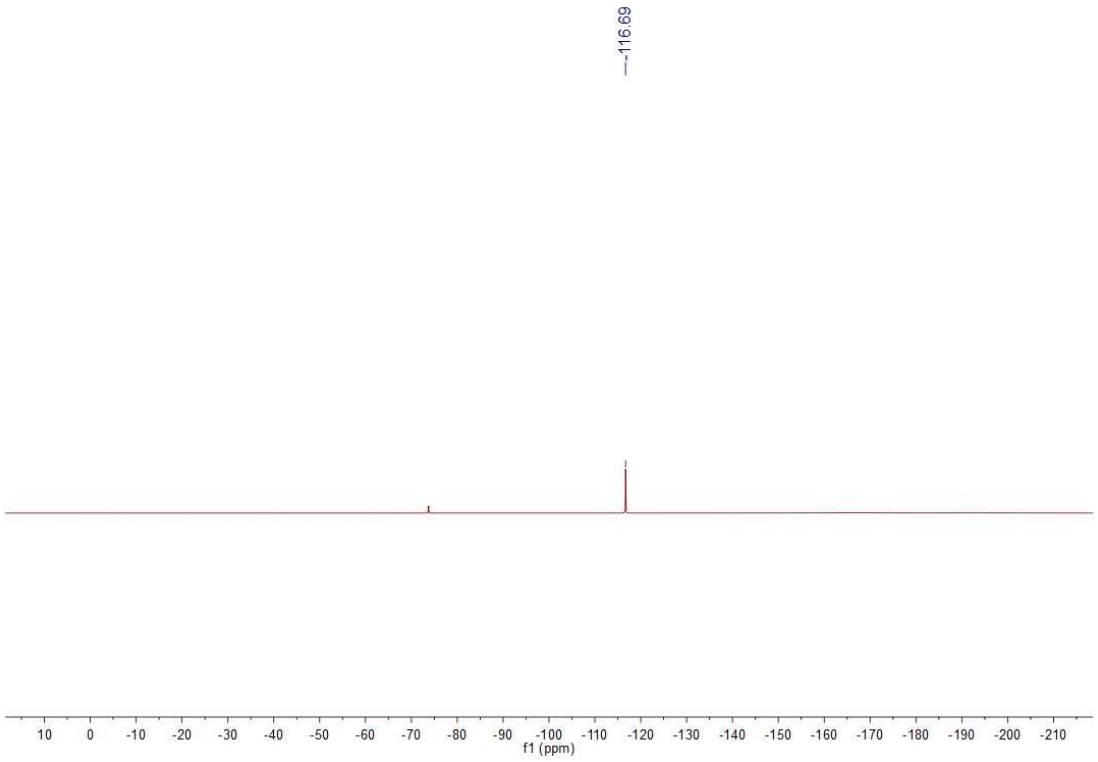
^{19}F NMR spectrum of **3g** (376 MHz, $CDCl_3$)



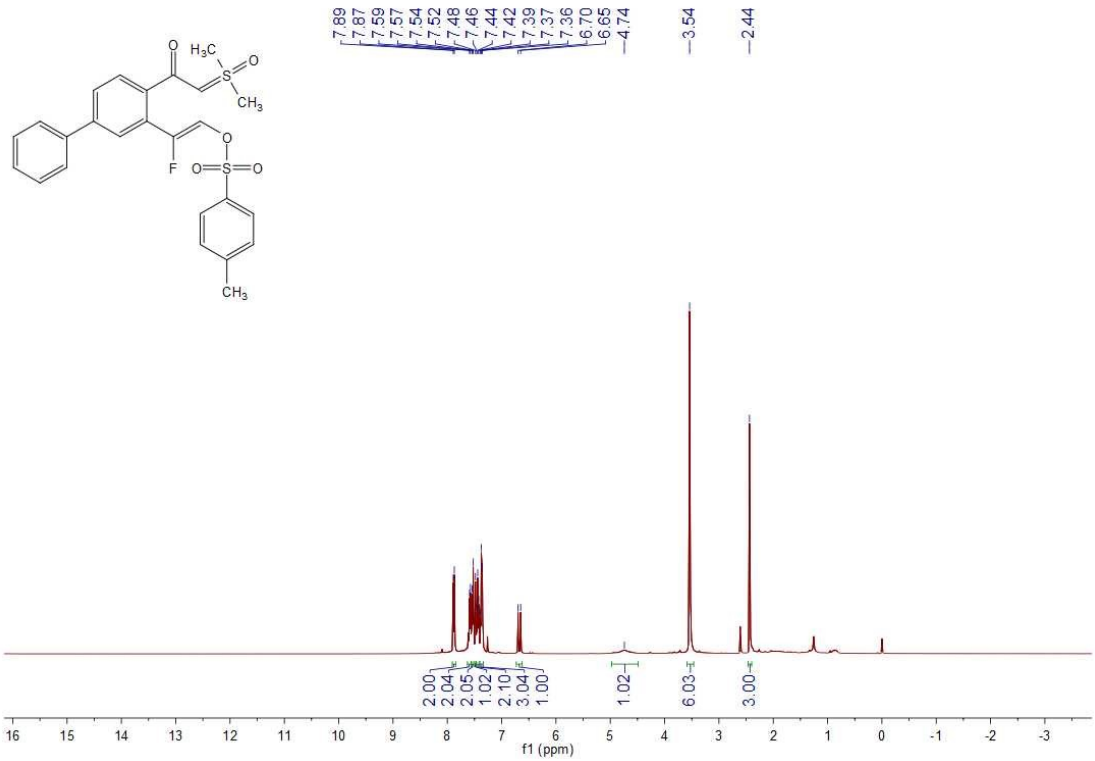
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



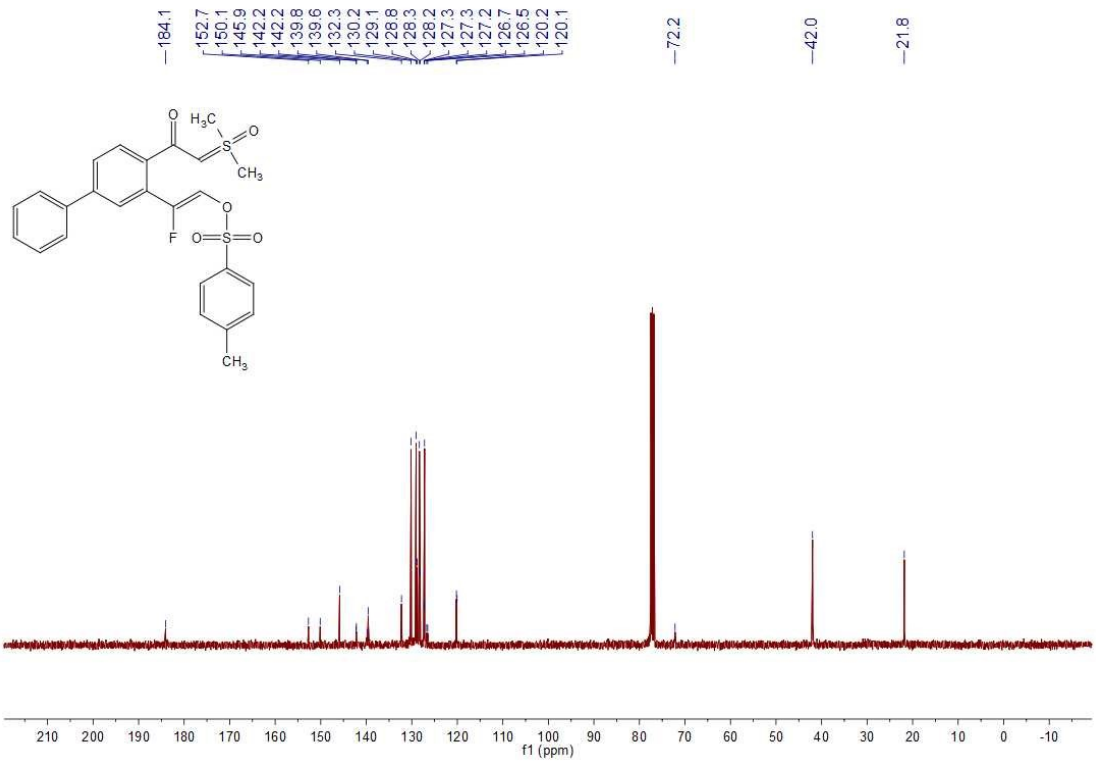
^{13}C NMR spectrum of **3h** (101 MHz, $CDCl_3$)



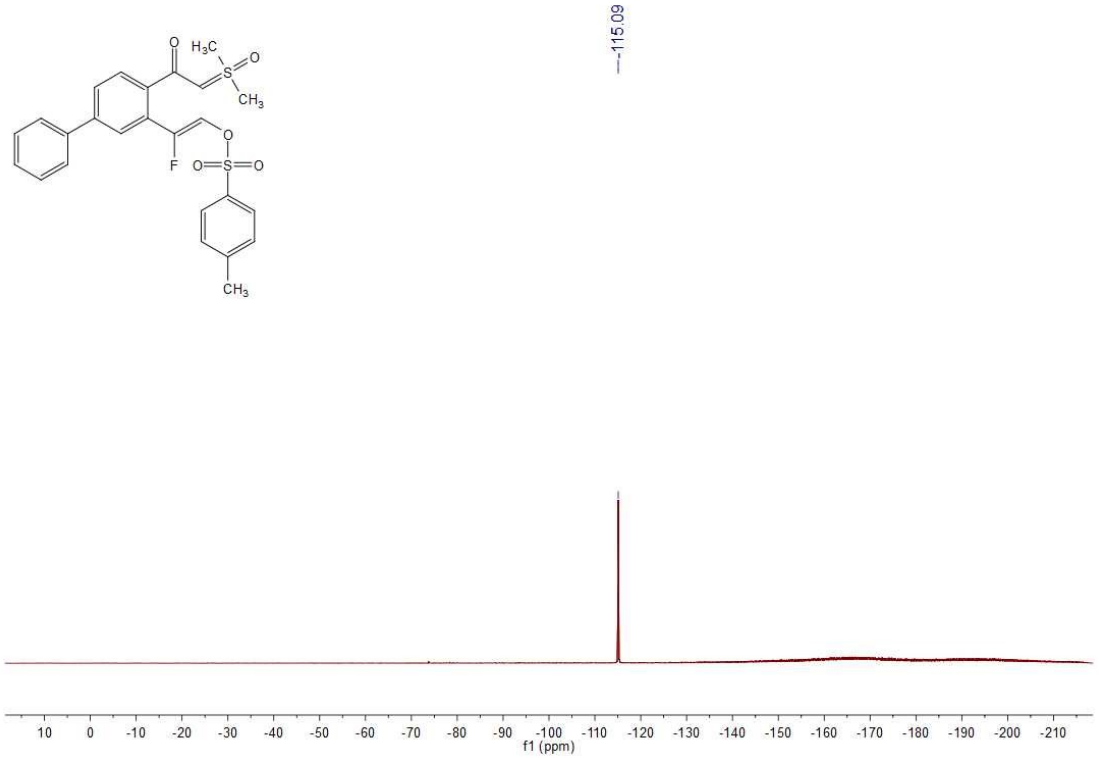
^{19}F NMR spectrum of **3h** (376 MHz, $CDCl_3$)



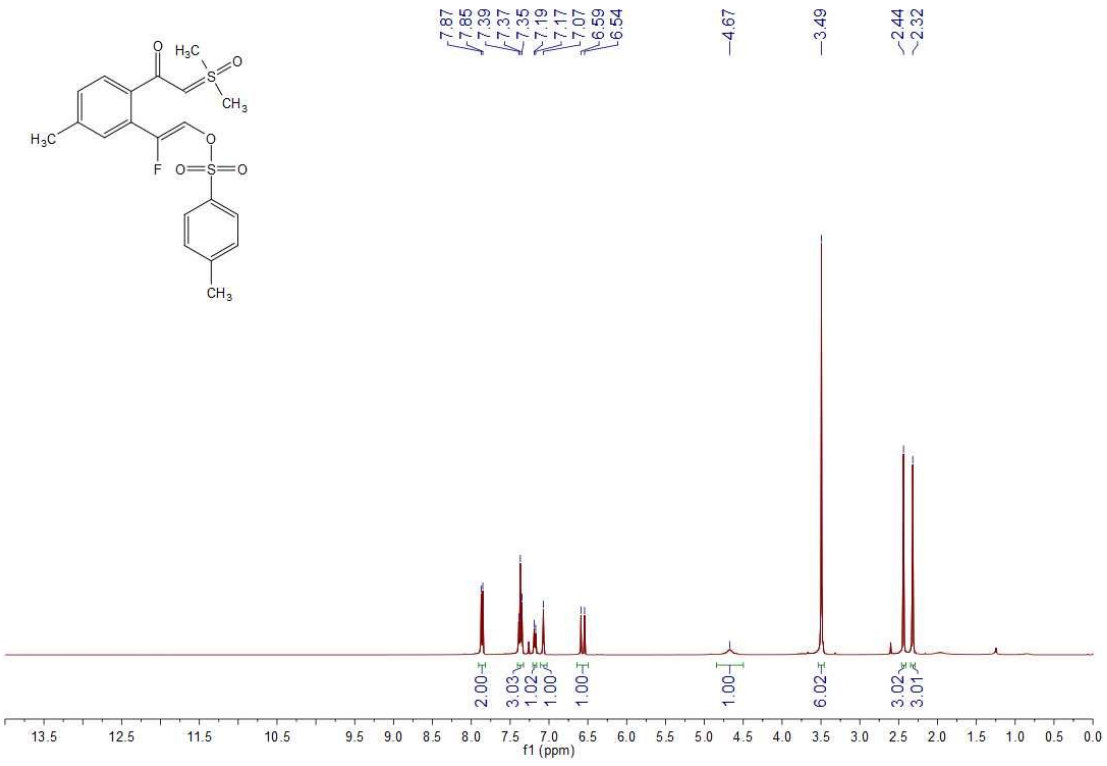
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



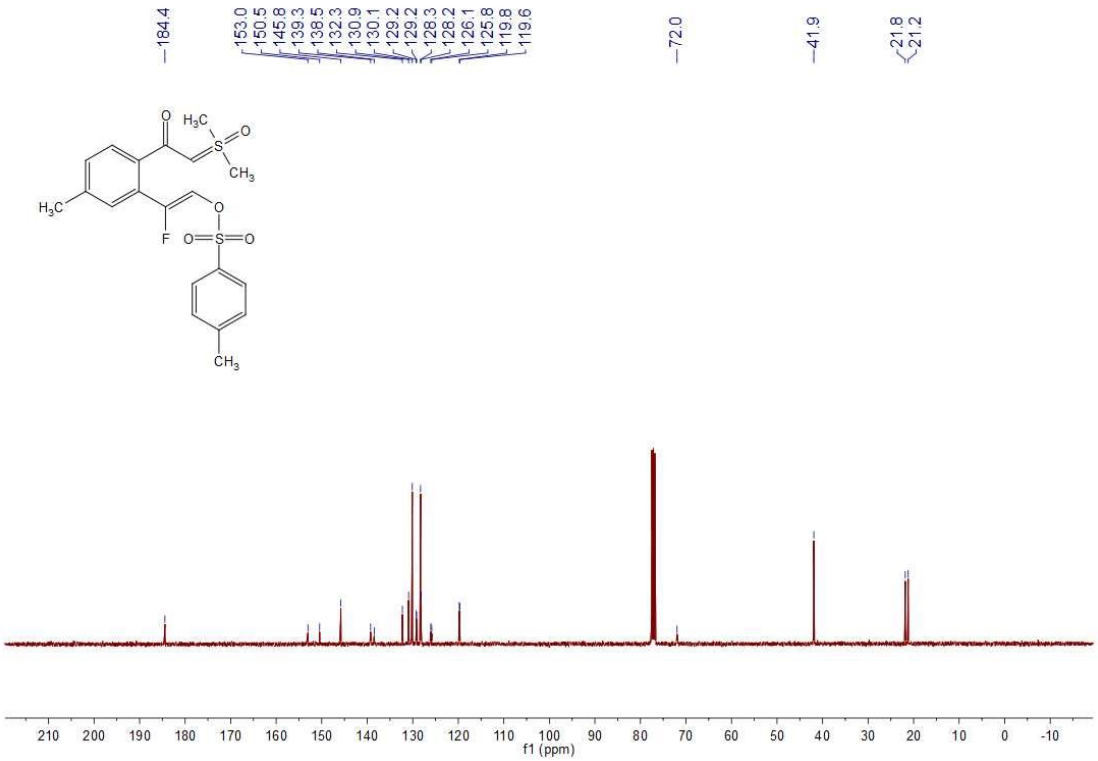
^{13}C NMR spectrum of **3i** (101 MHz, $CDCl_3$)



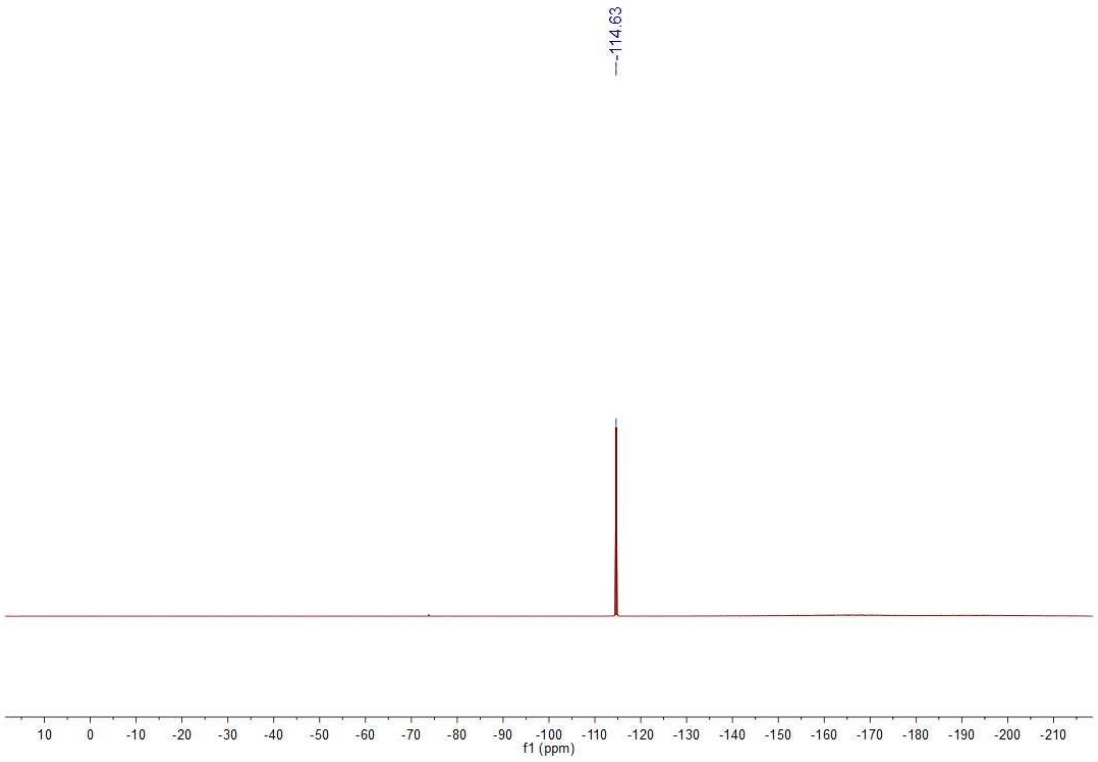
^{19}F NMR spectrum of **3i** (376 MHz, $CDCl_3$)



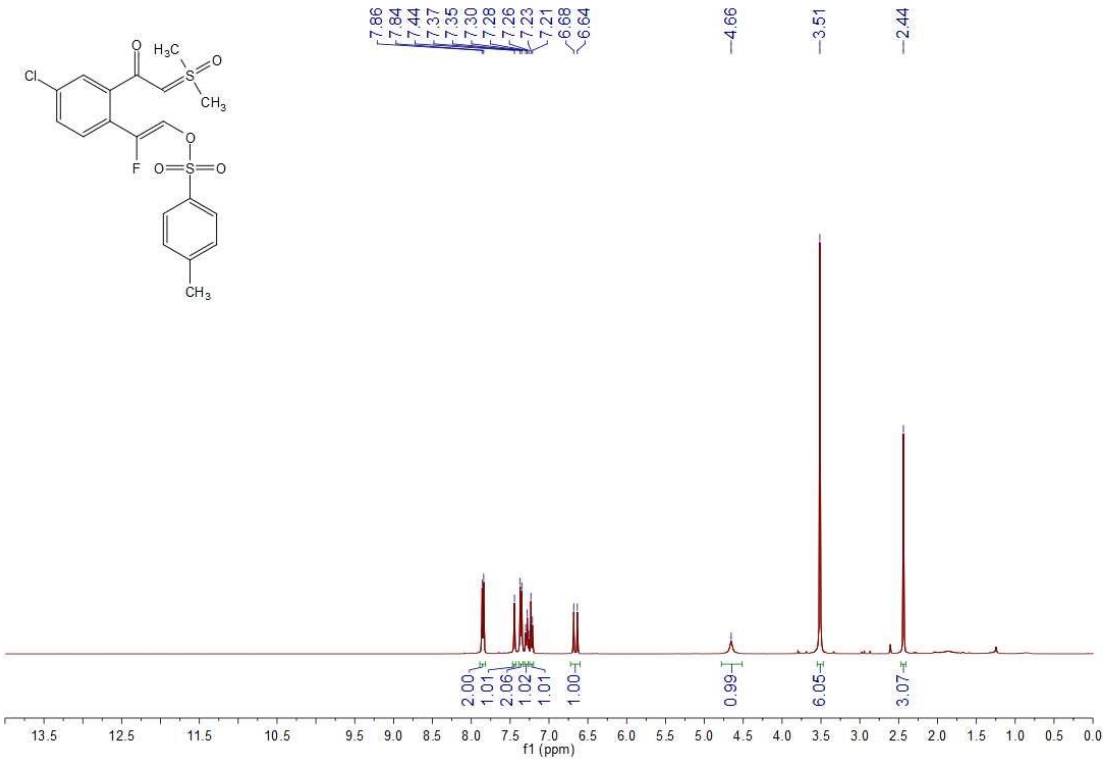
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



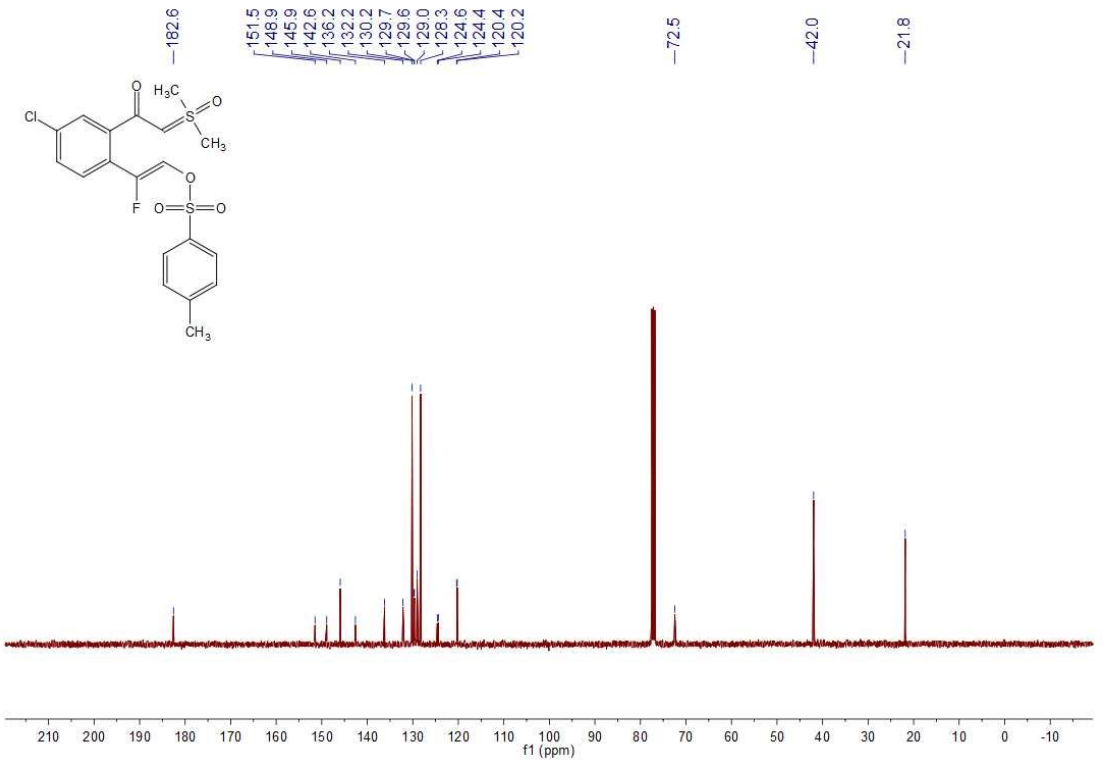
^{13}C NMR spectrum of **3j** (101 MHz, $CDCl_3$)



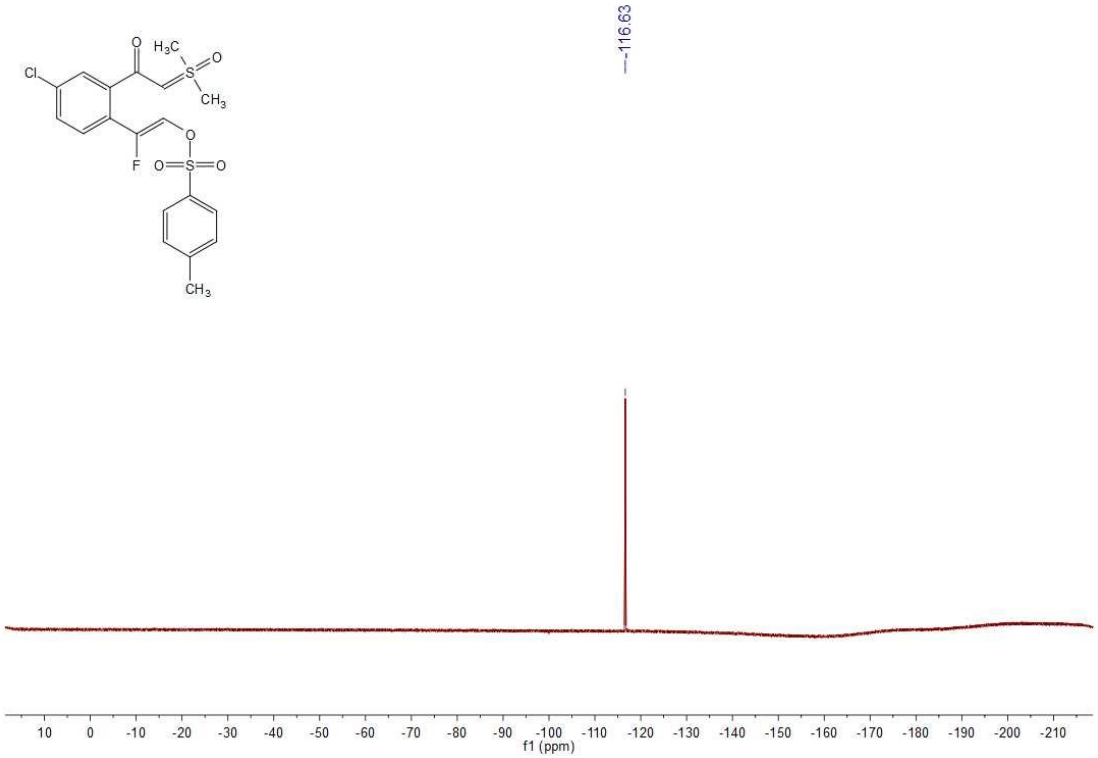
^{19}F NMR spectrum of **3j** (376 MHz, $CDCl_3$)



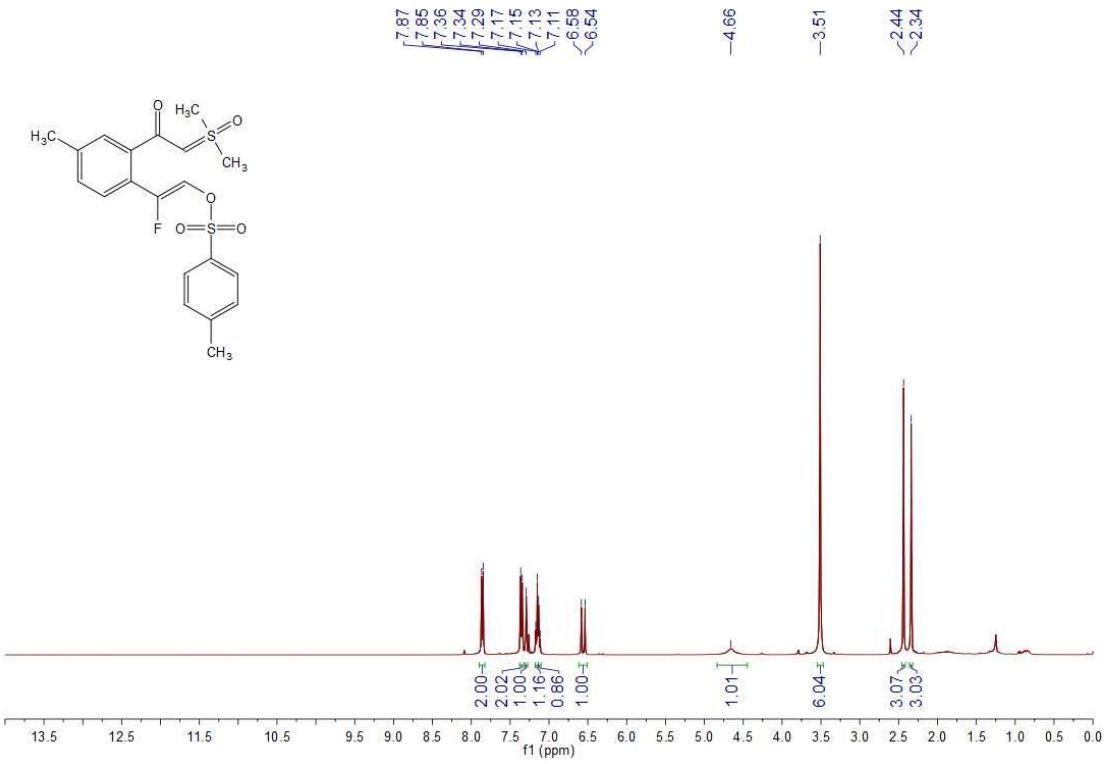
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



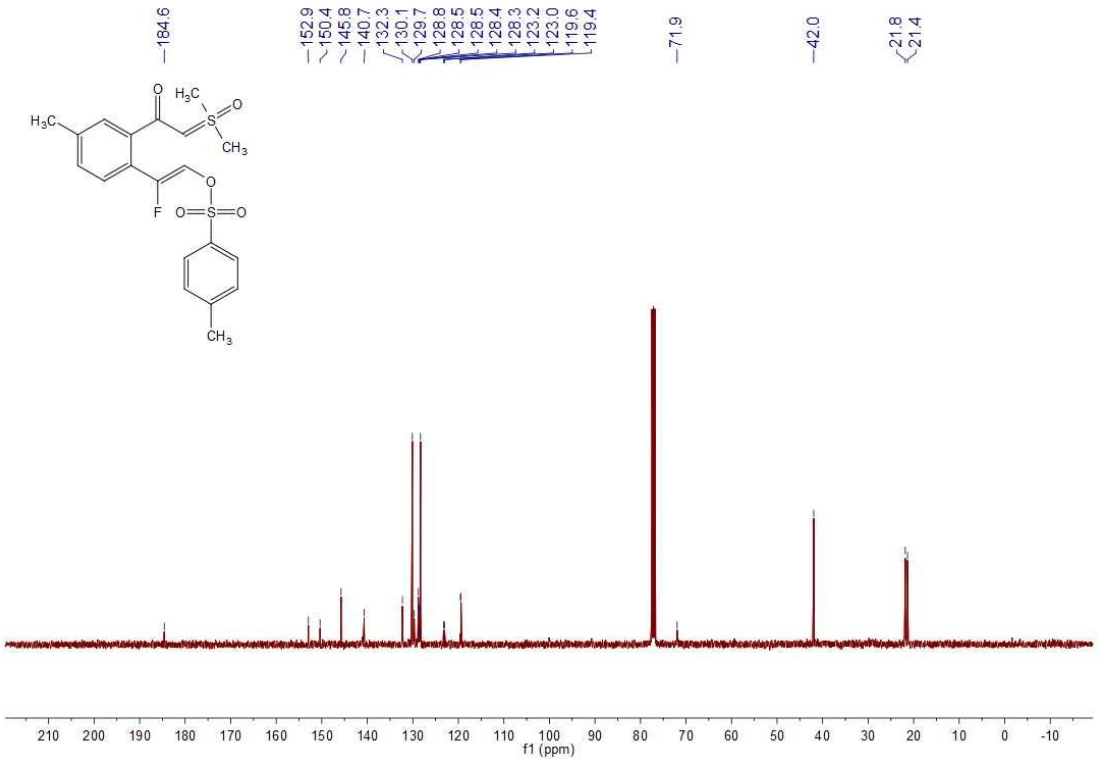
^{13}C NMR spectrum of **3k** (101 MHz, $CDCl_3$)



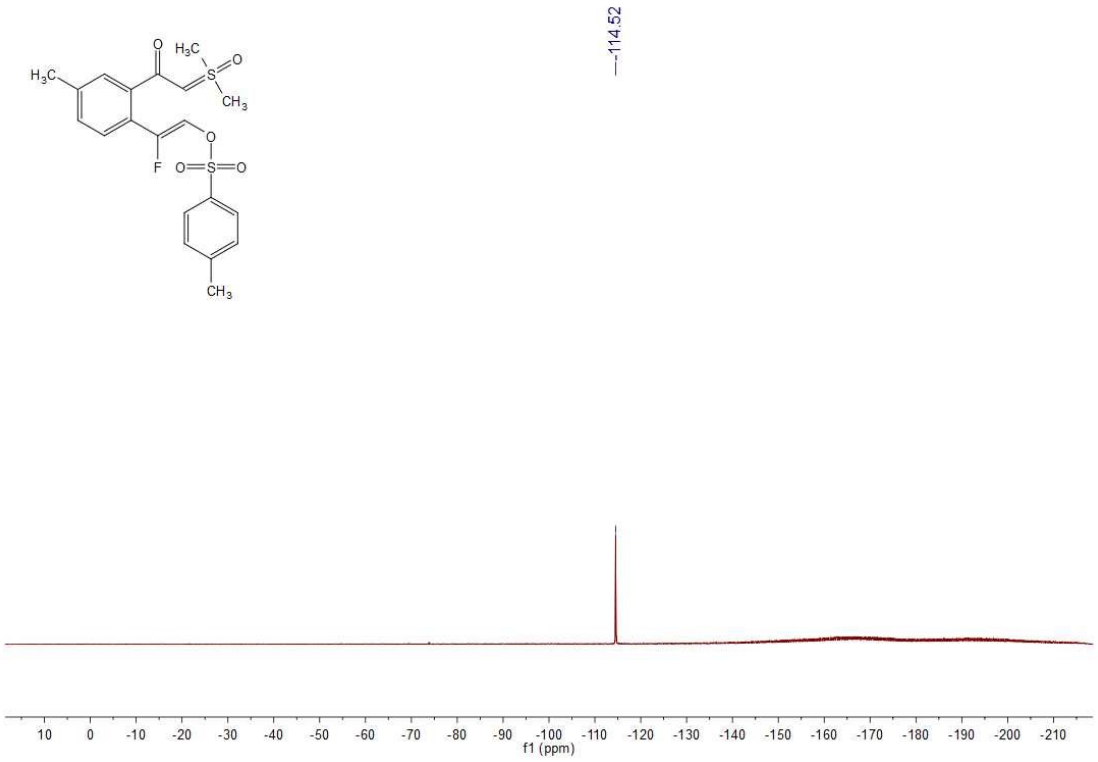
^{19}F NMR spectrum of **3k** (376 MHz, $CDCl_3$)



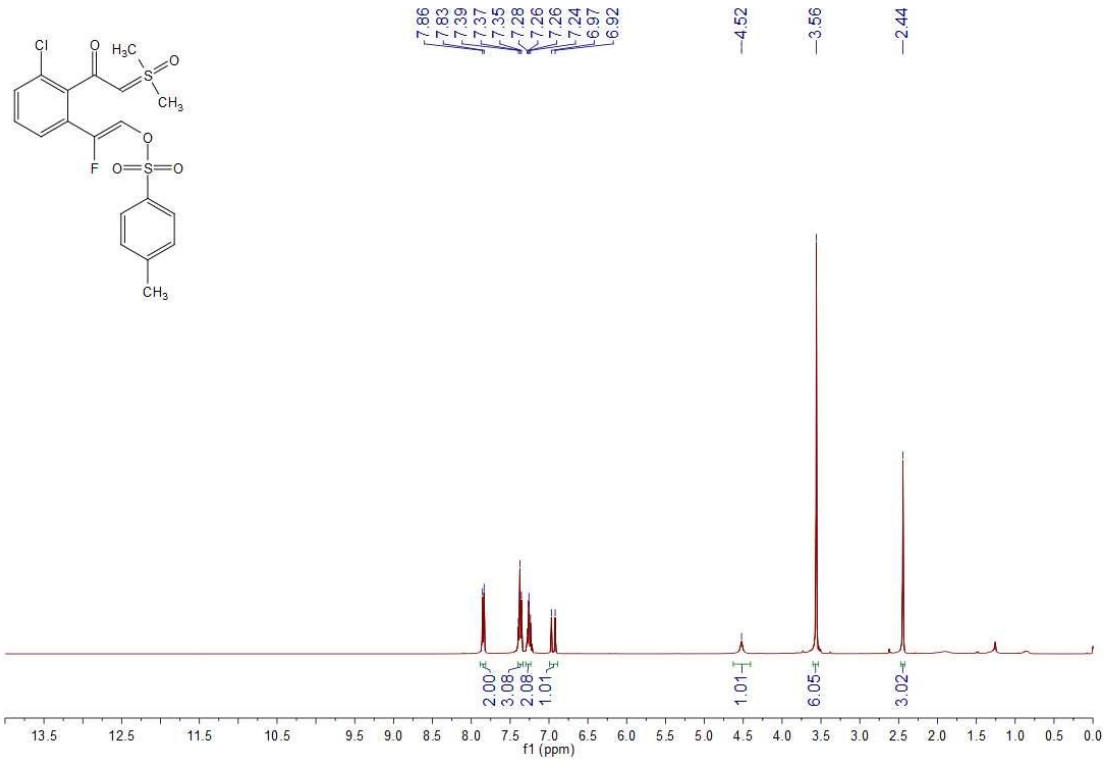
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



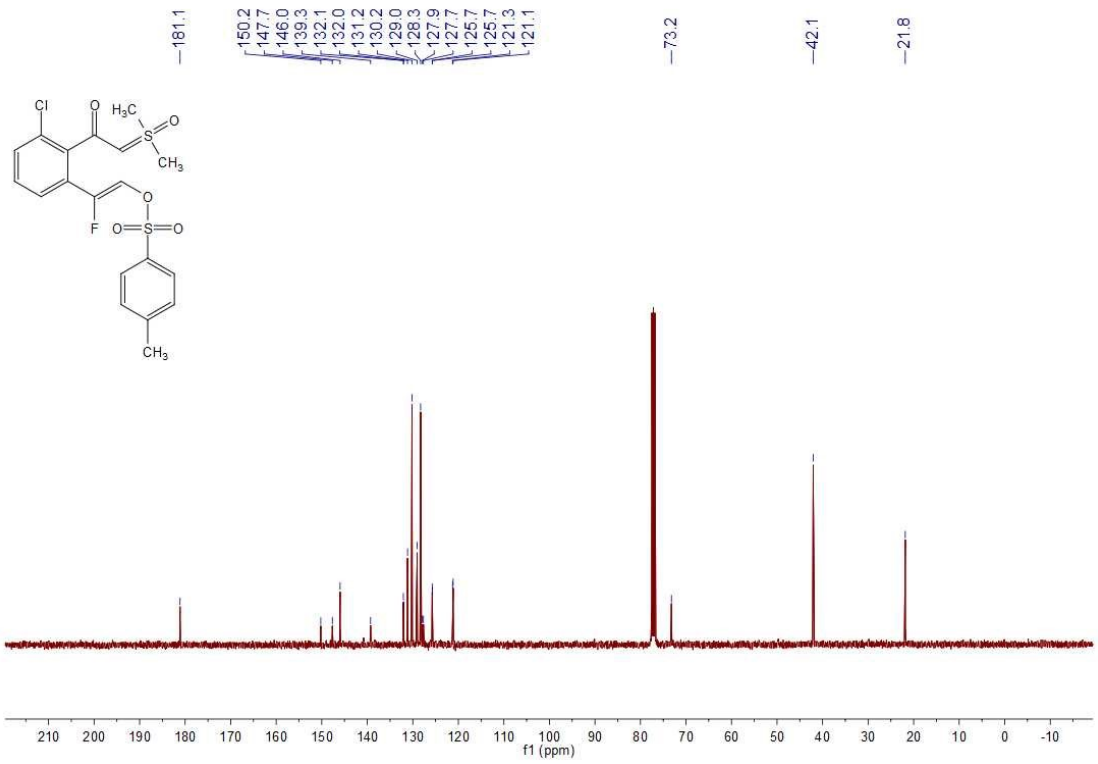
^{13}C NMR spectrum of **3l** (101 MHz, $CDCl_3$)



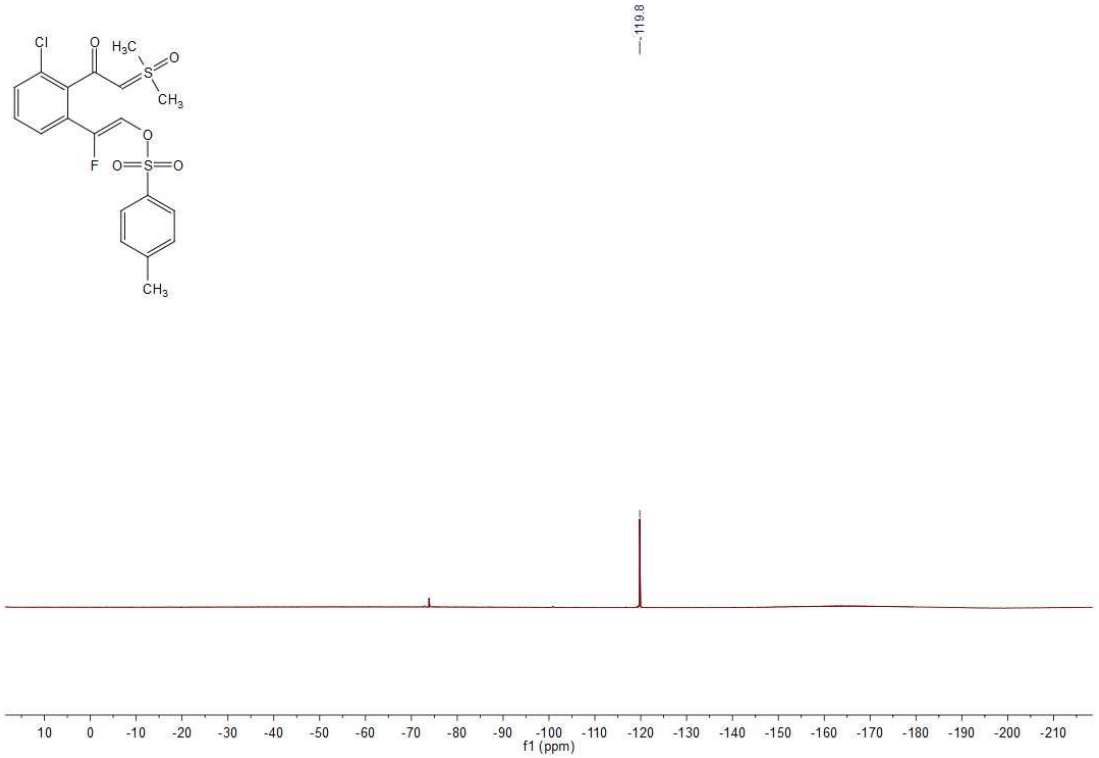
^{19}F NMR spectrum of **3l** (376 MHz, $CDCl_3$)



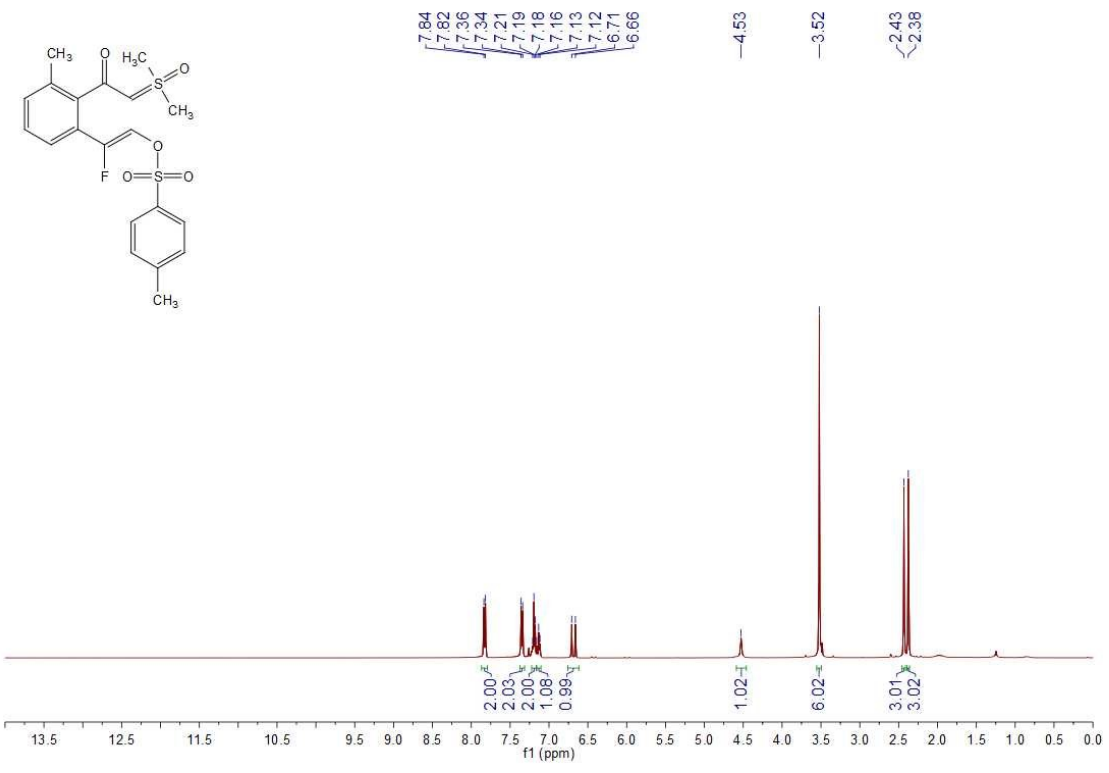
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



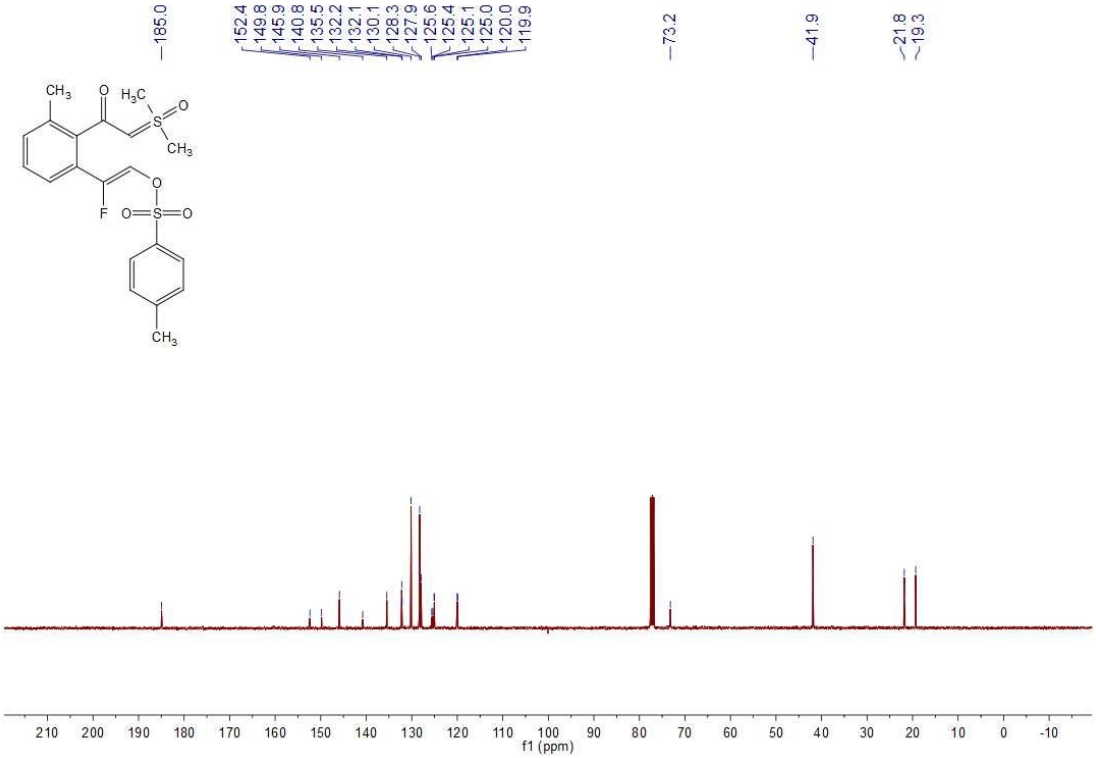
^{13}C NMR spectrum of **3m** (101 MHz, $CDCl_3$)



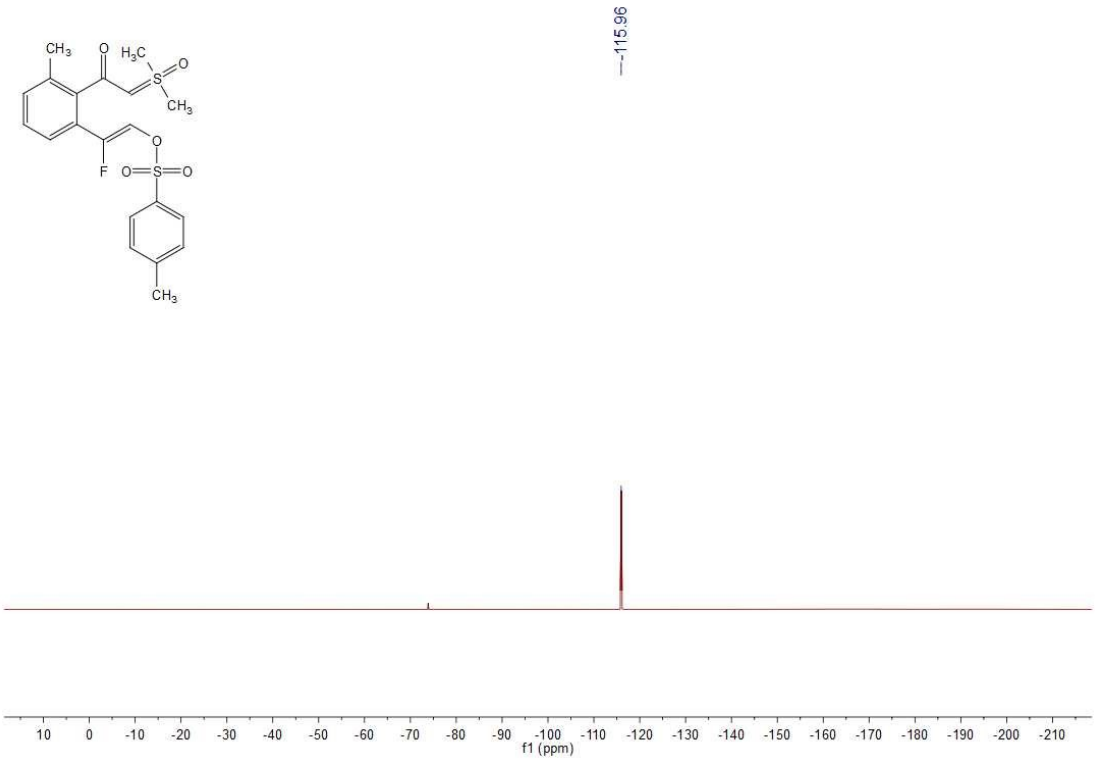
^{19}F NMR spectrum of **3m** (376 MHz, $CDCl_3$)



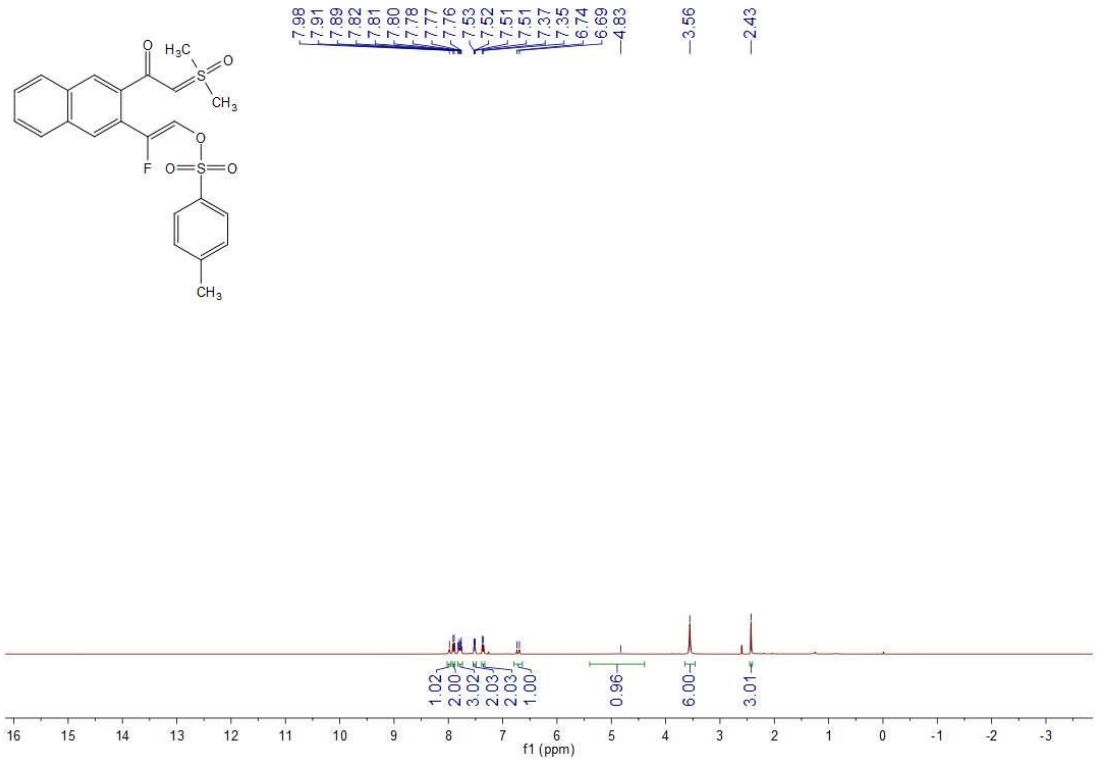
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



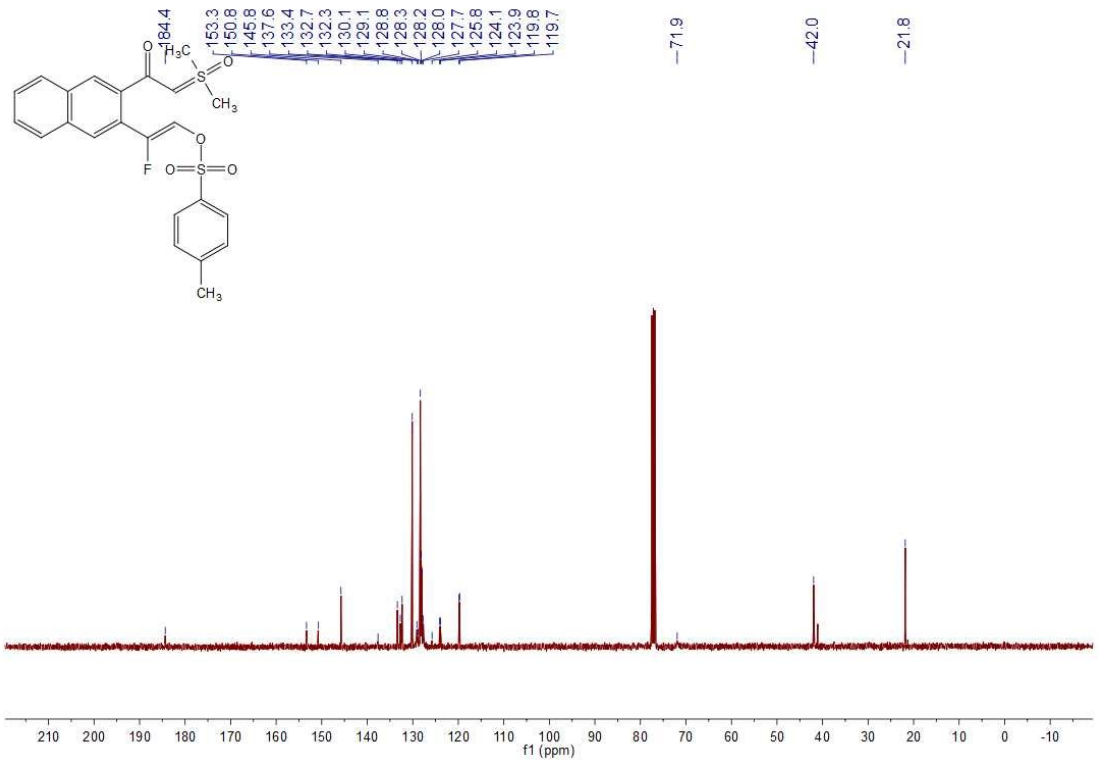
^{13}C NMR spectrum of **3n** (101 MHz, $CDCl_3$)



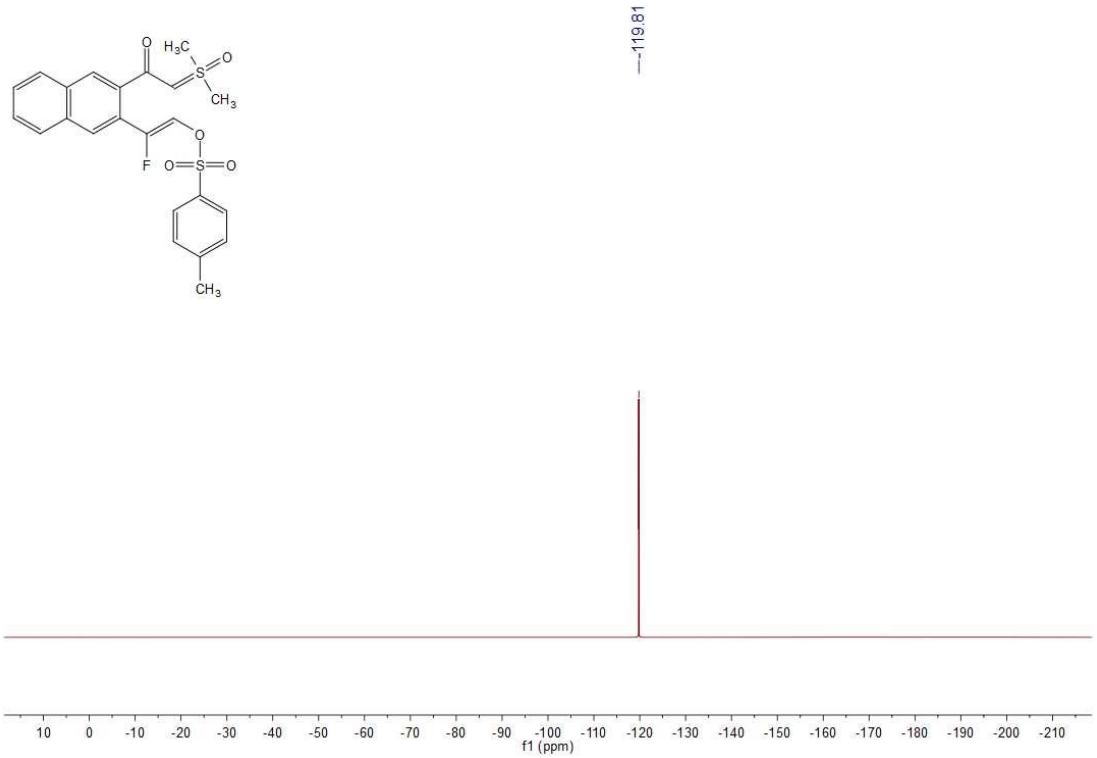
^{19}F NMR spectrum of **3n** (376 MHz, $CDCl_3$)



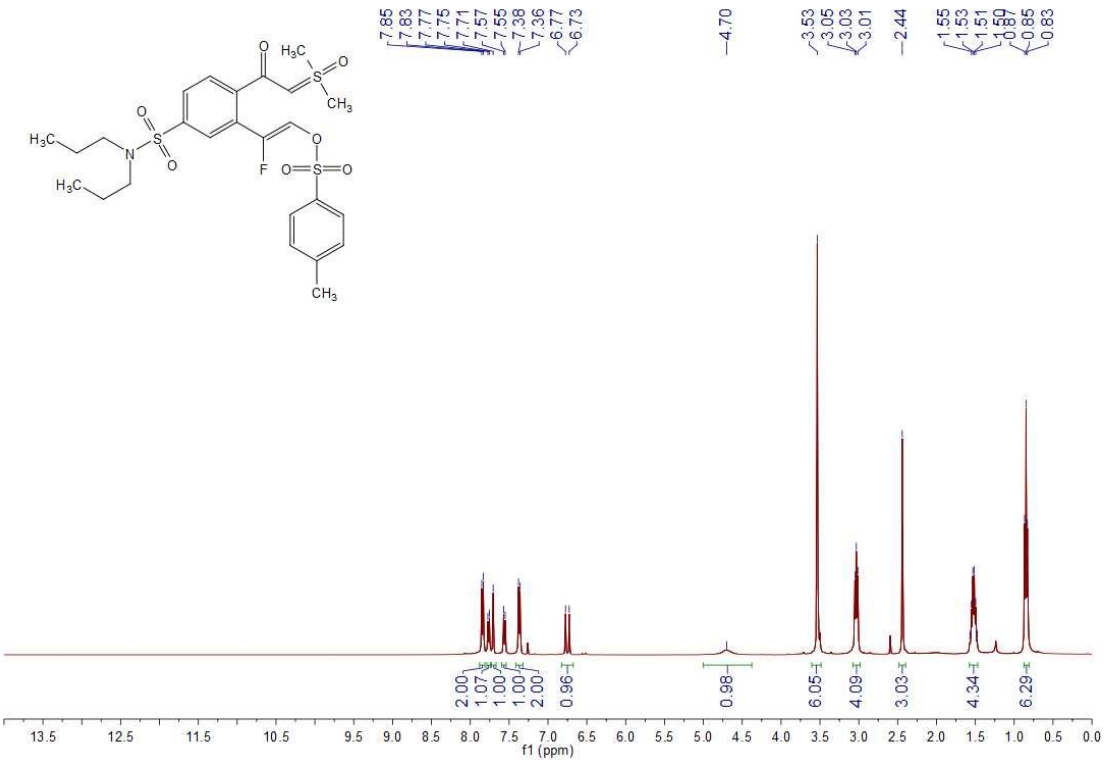
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



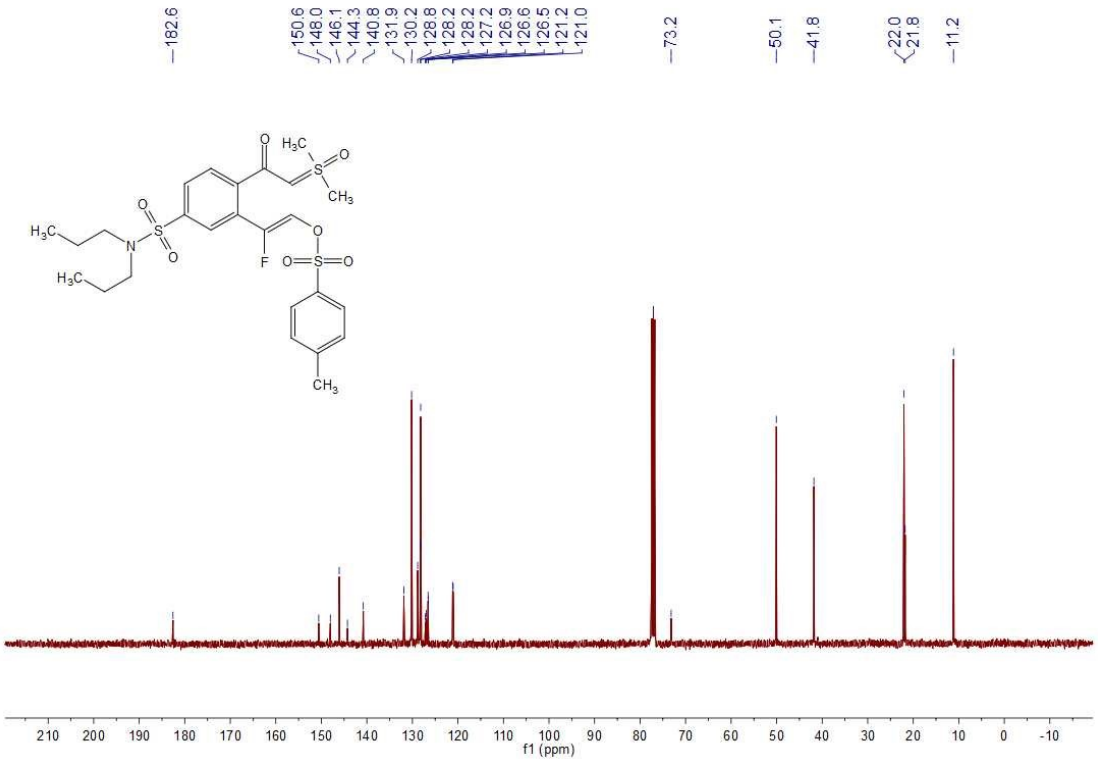
^{13}C NMR spectrum of **3o** (101 MHz, $CDCl_3$)



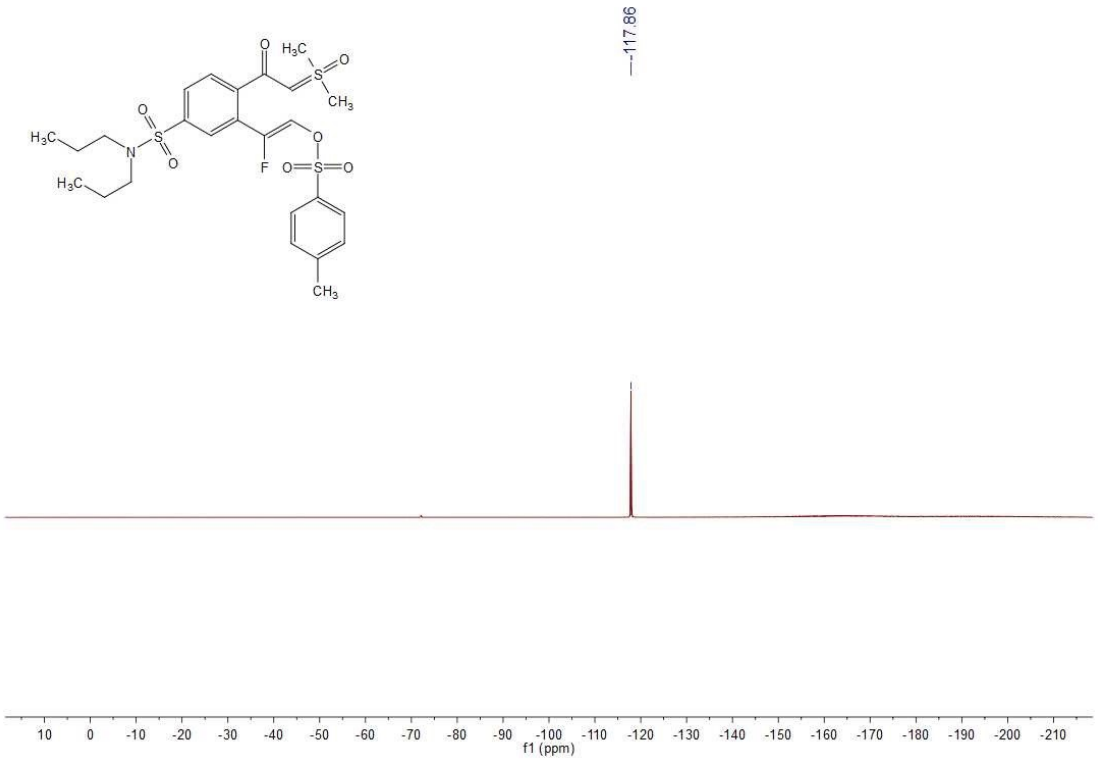
^{19}F NMR spectrum of **3o** (376 MHz, $CDCl_3$)



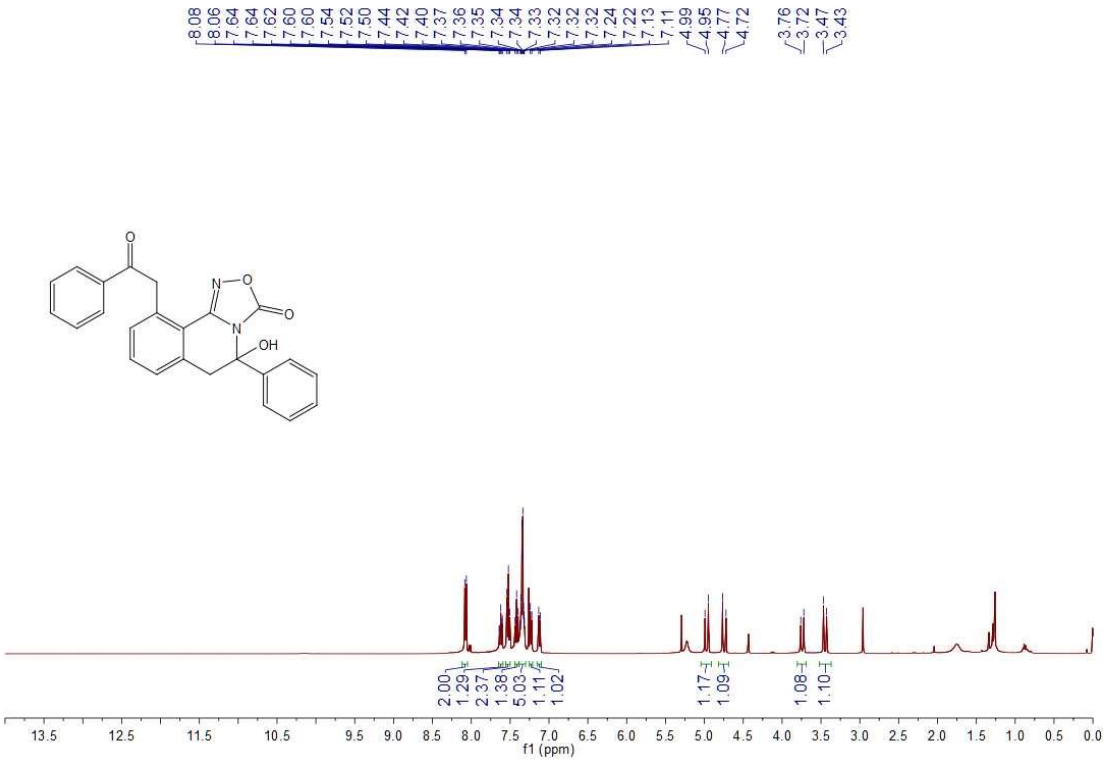
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



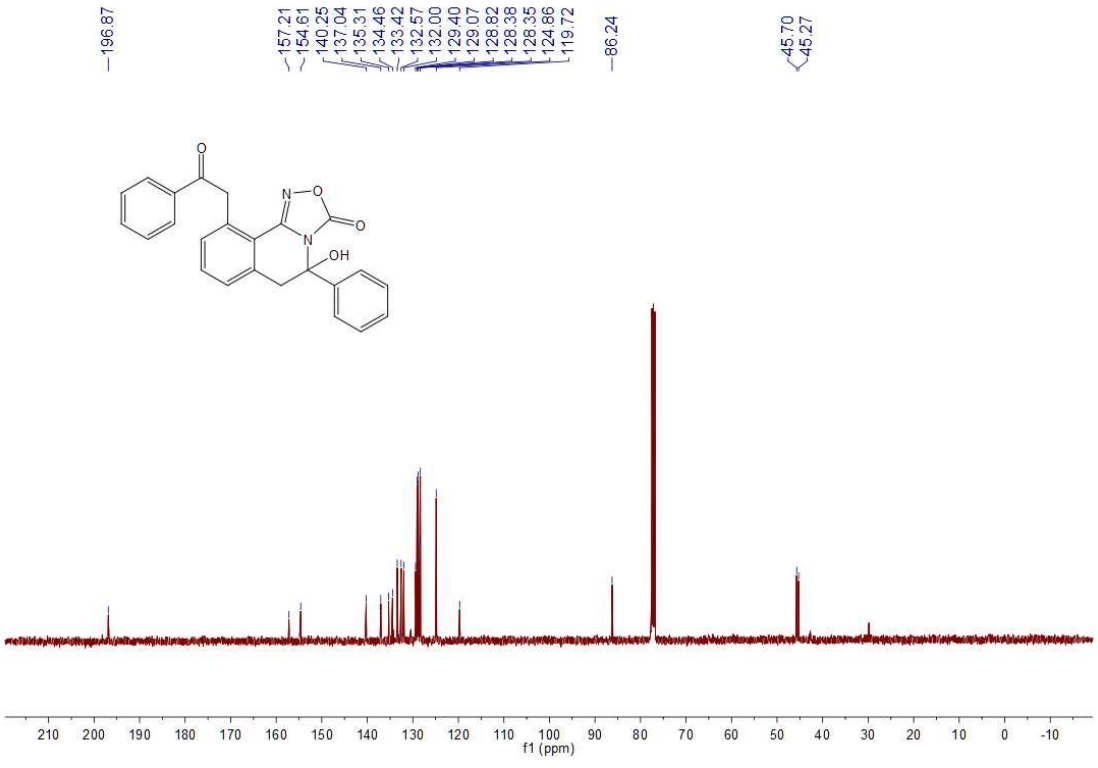
^{13}C NMR spectrum of **3p** (101 MHz, $CDCl_3$)



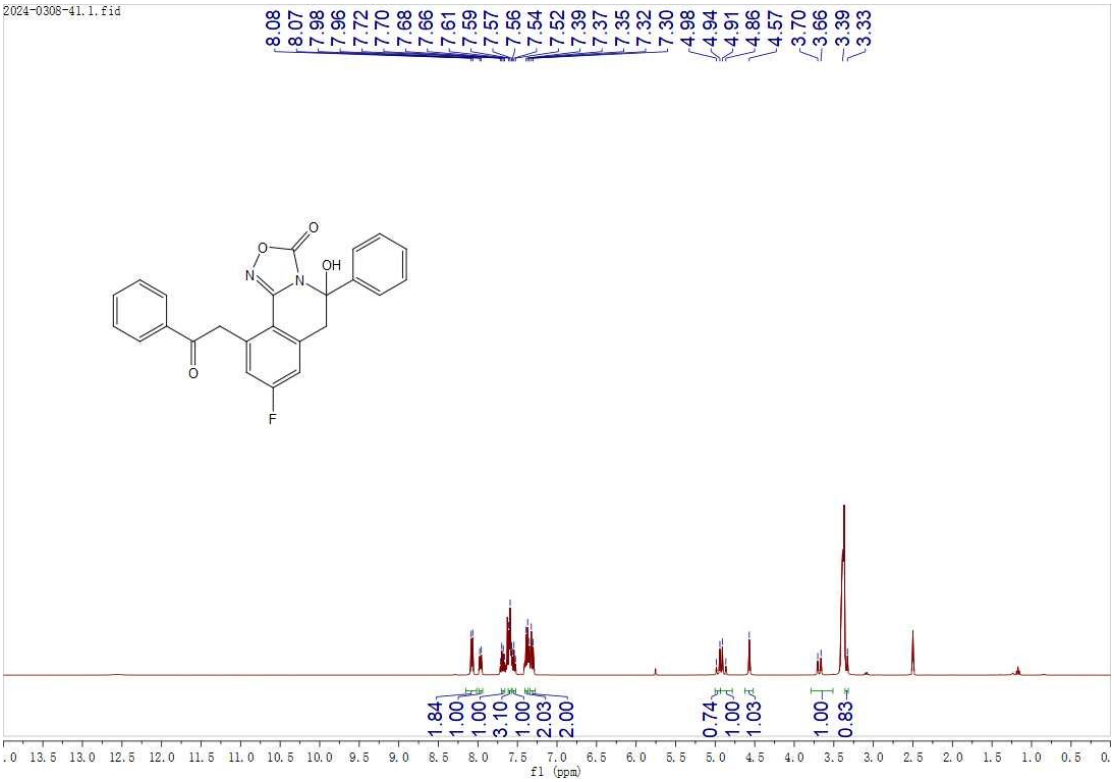
^{19}F NMR spectrum of **3p** (376 MHz, $CDCl_3$)



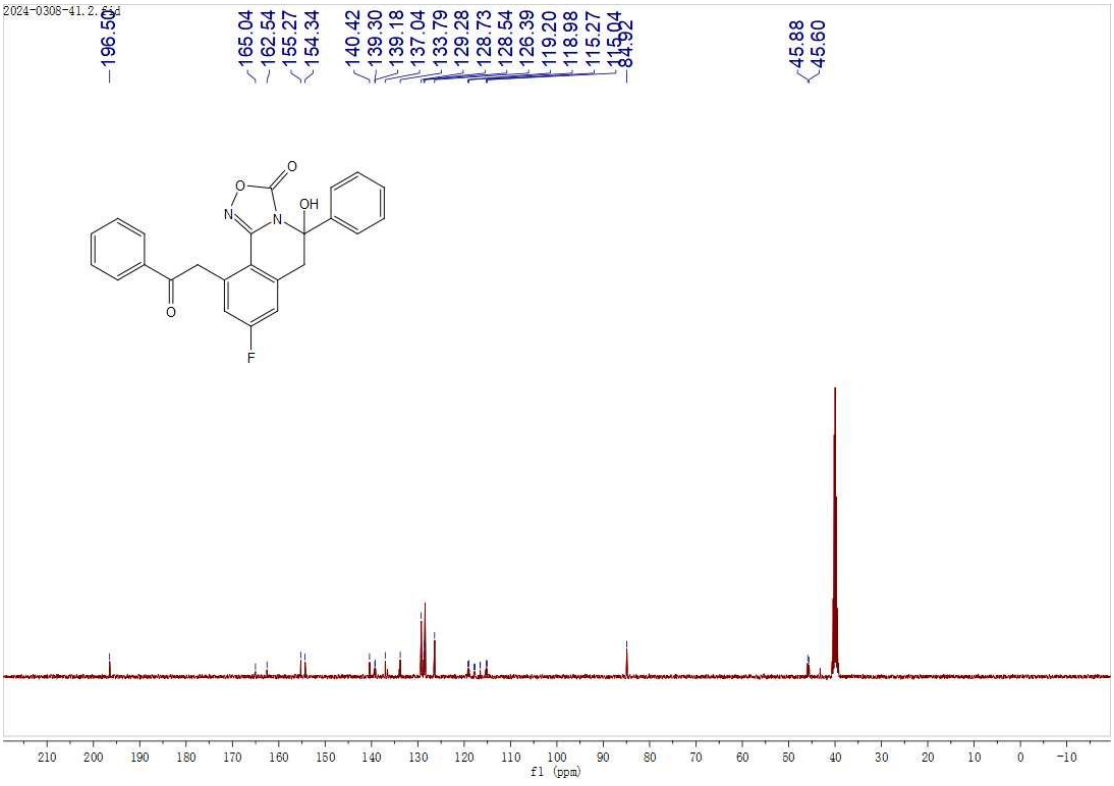
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



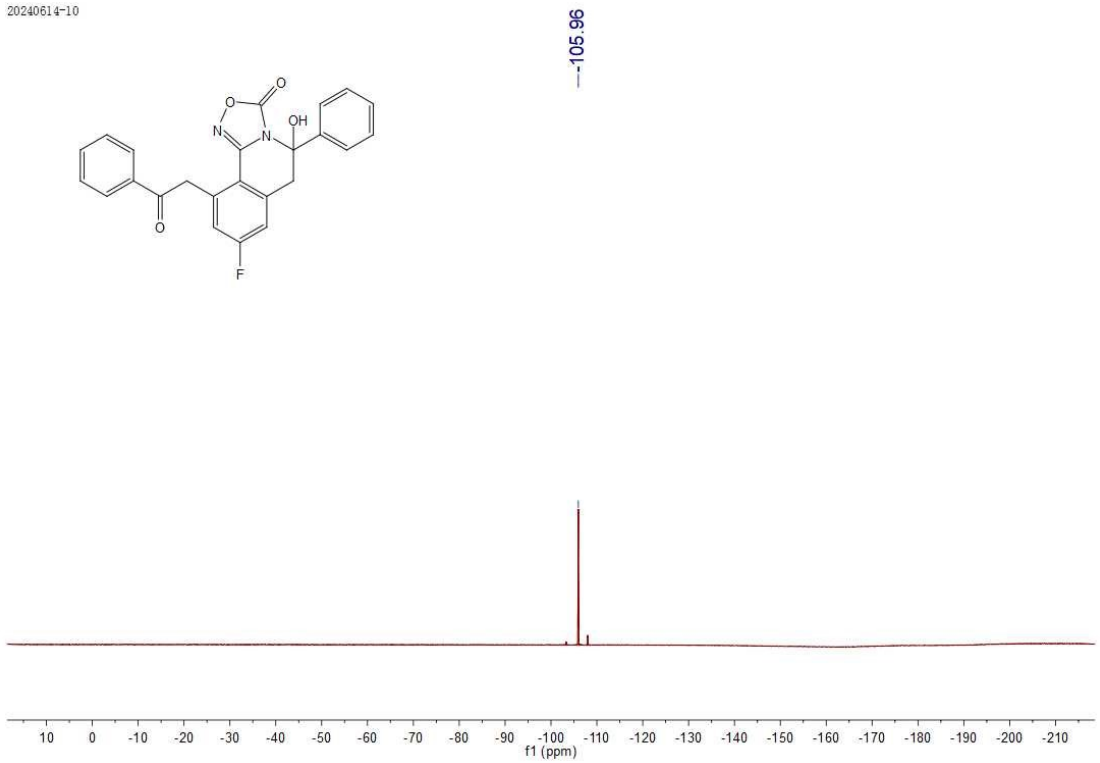
^{13}C NMR spectrum of **5a** (101 MHz, $CDCl_3$)



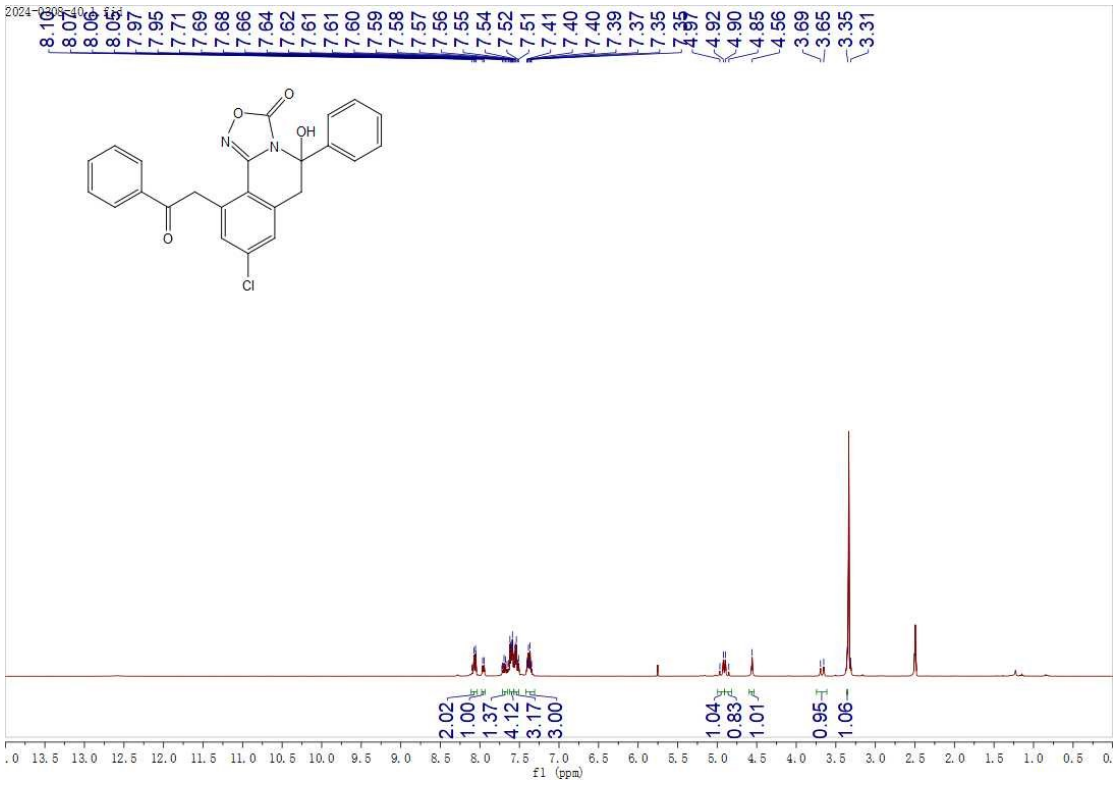
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



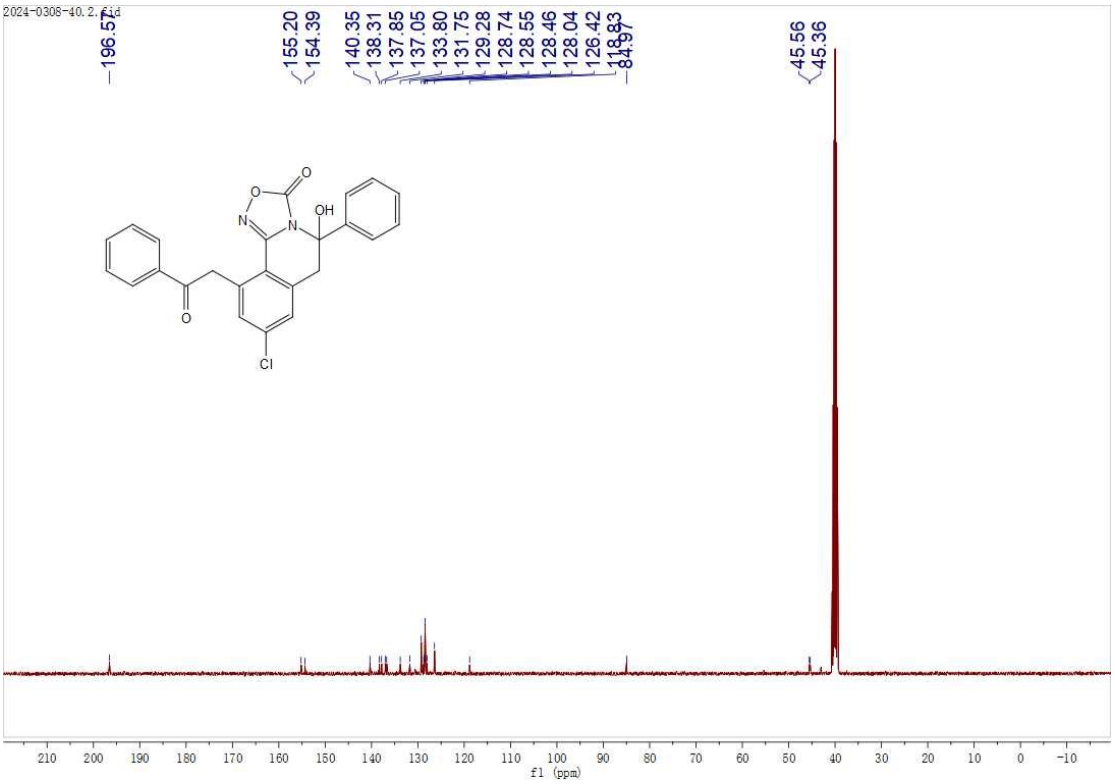
^{13}C NMR spectrum of **5b** (101 MHz, $CDCl_3$)



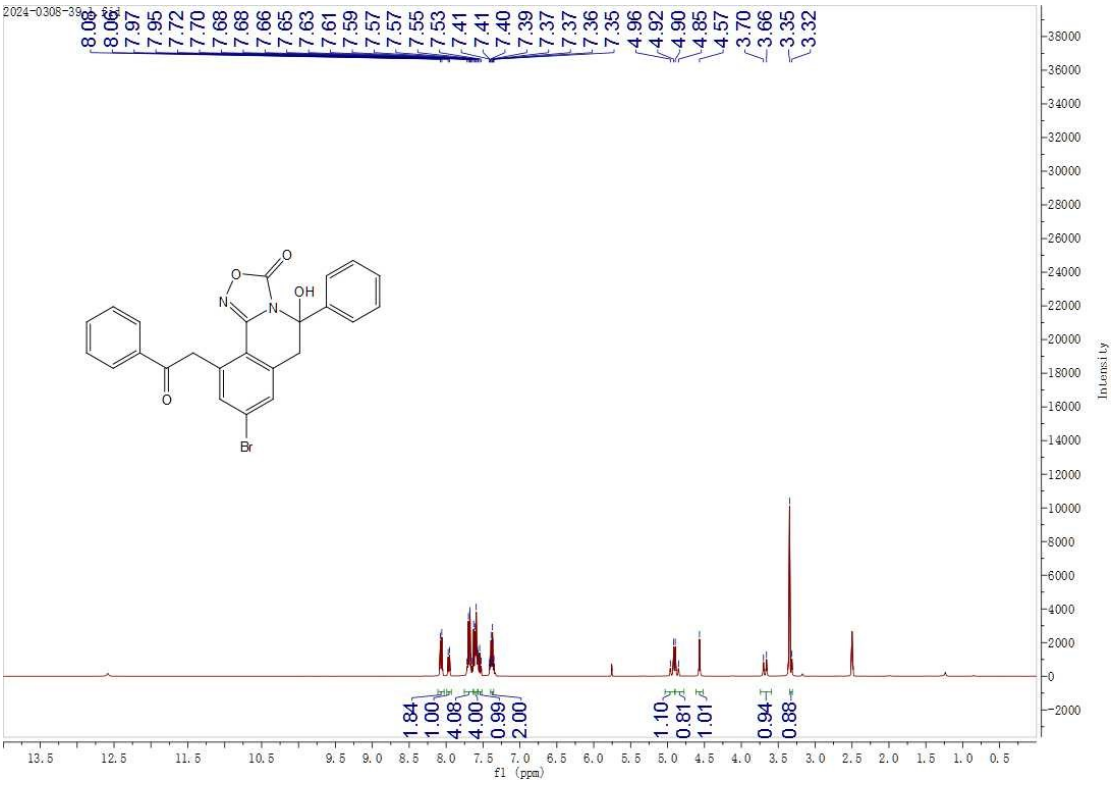
^{19}F NMR spectrum of **5b** (376 MHz, $CDCl_3$)



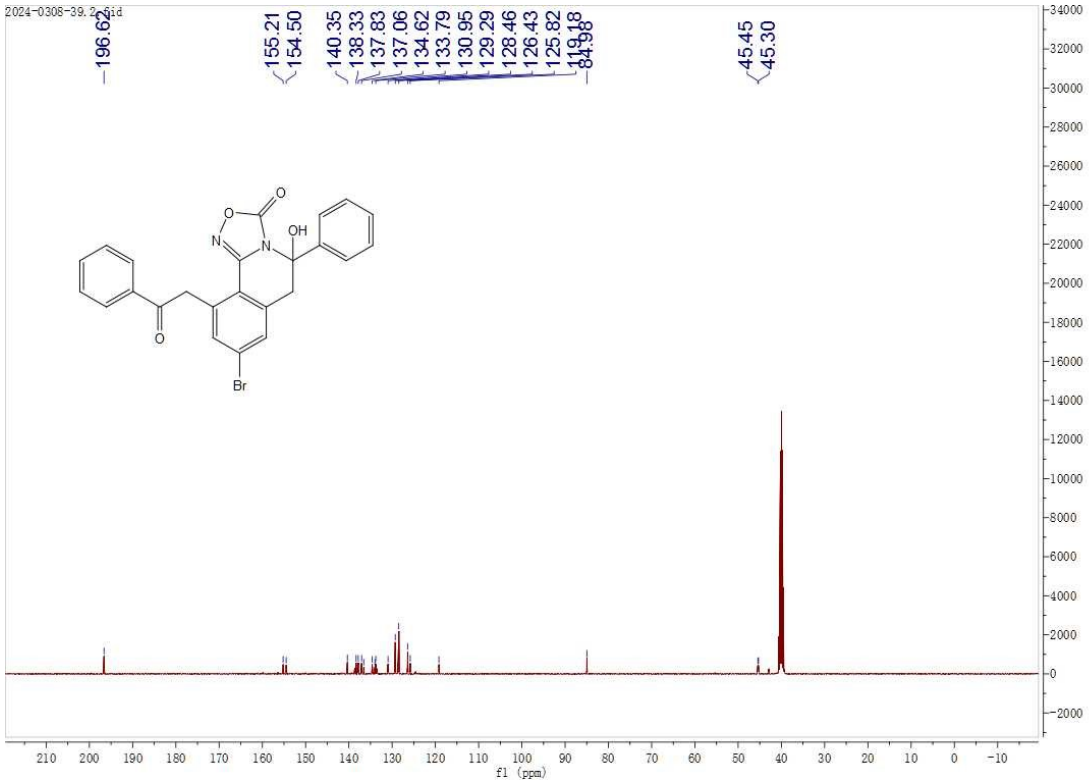
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



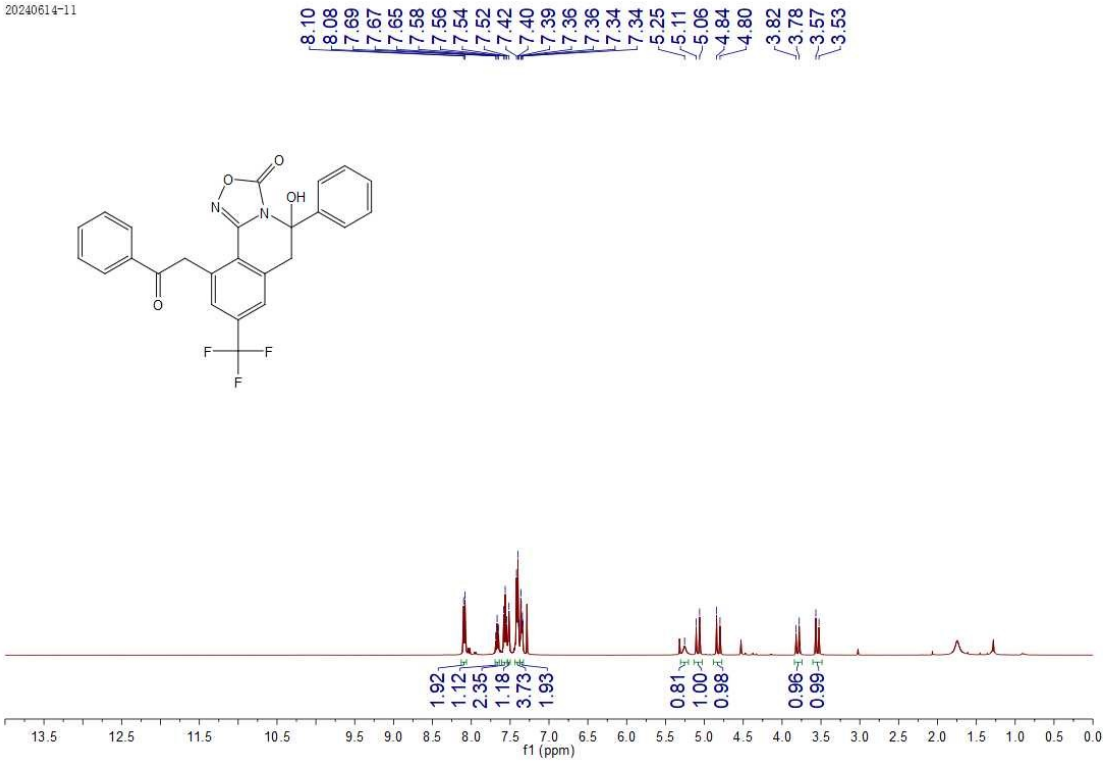
^{13}C NMR spectrum of **5c** (101 MHz, $CDCl_3$)



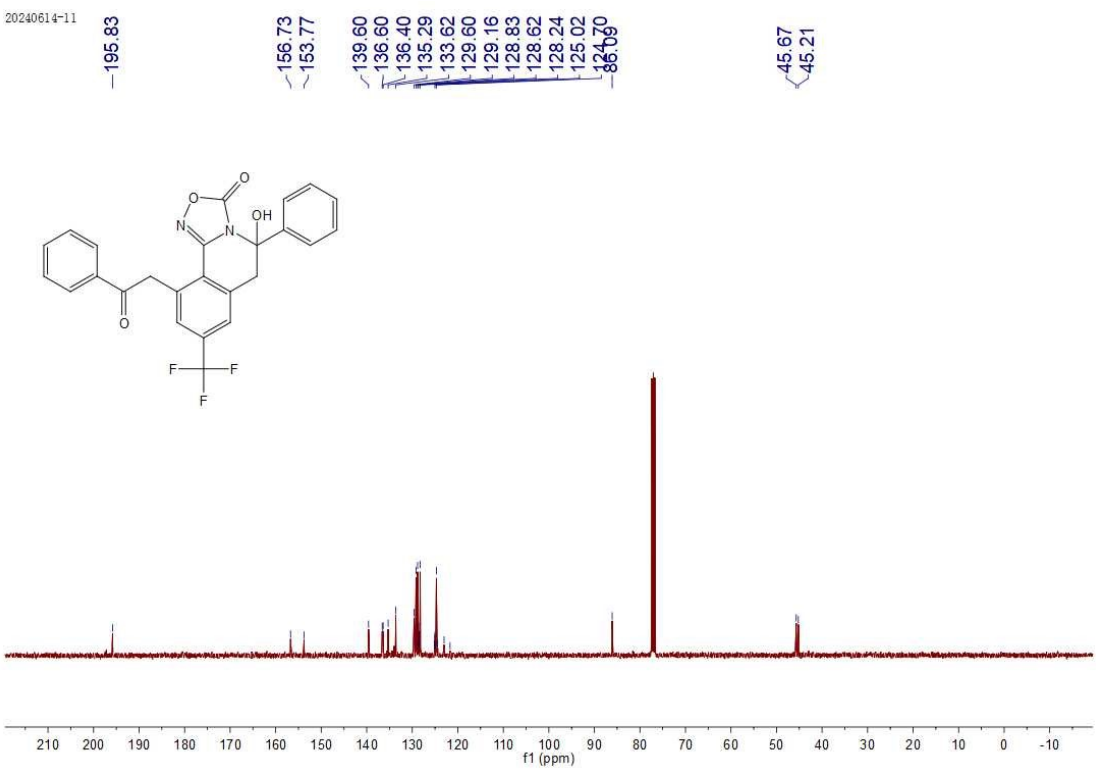
^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



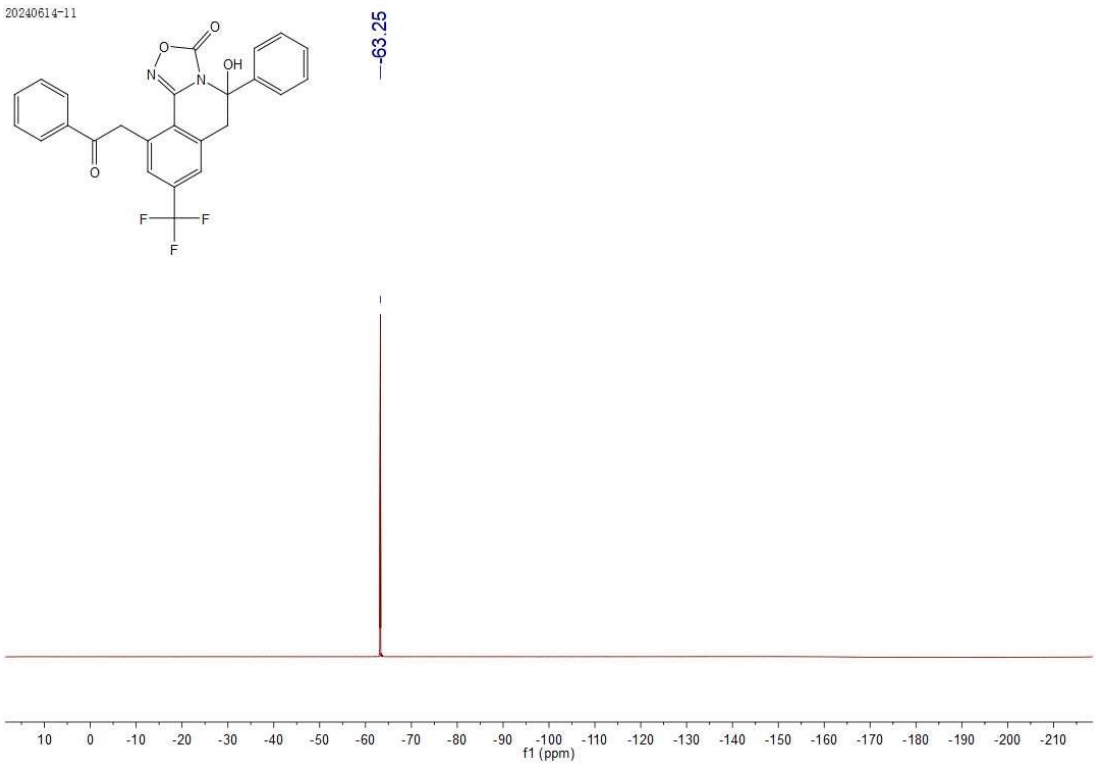
^{13}C NMR spectrum of **5d** (101 MHz, $CDCl_3$)



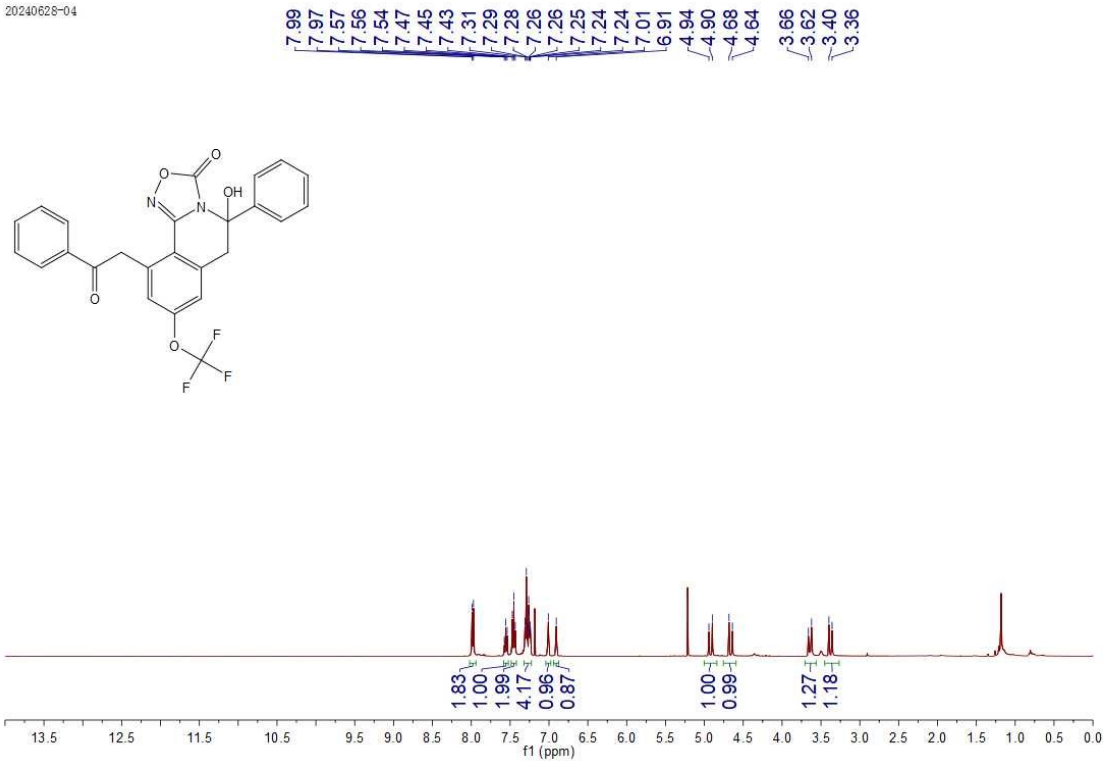
^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)



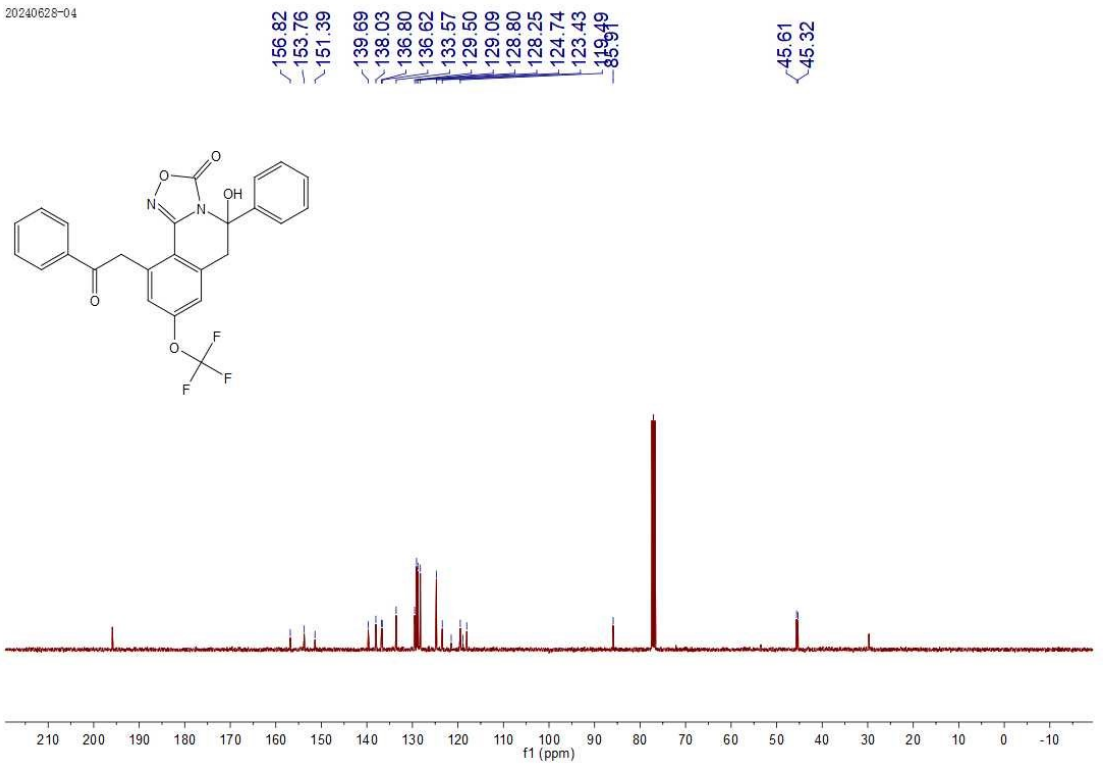
^{13}C NMR spectrum of **5e** (101 MHz, $CDCl_3$)



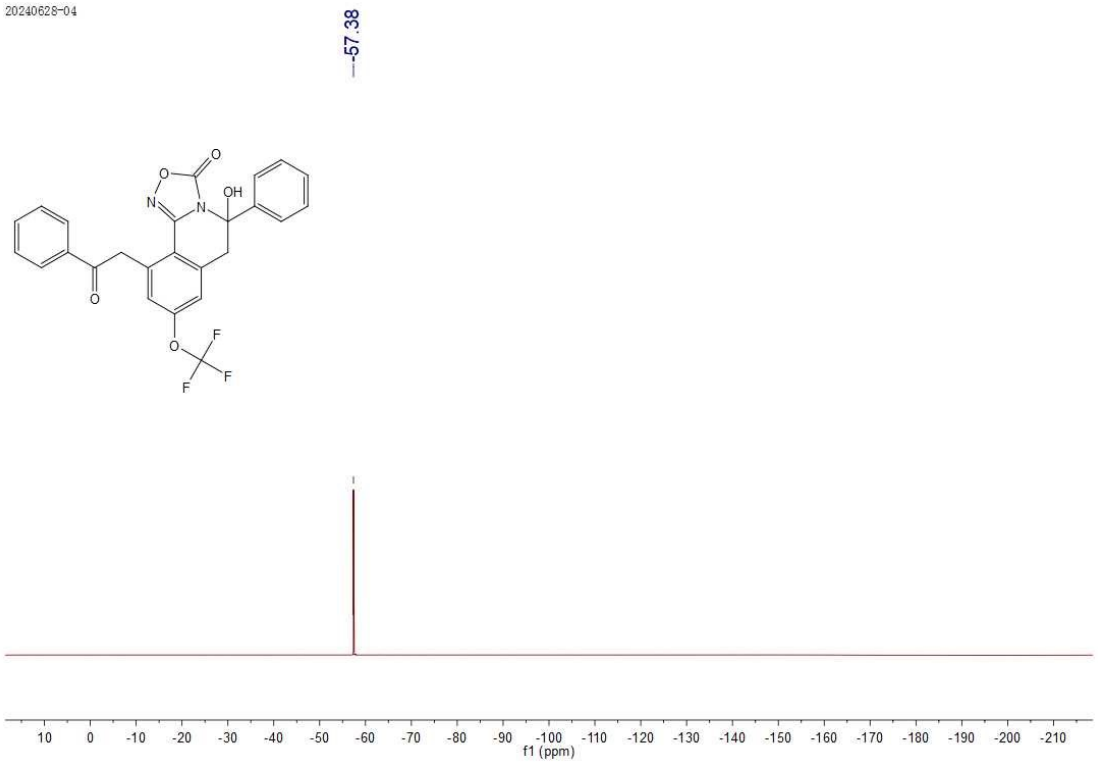
^{19}F NMR spectrum of **5e** (376 MHz, $CDCl_3$)



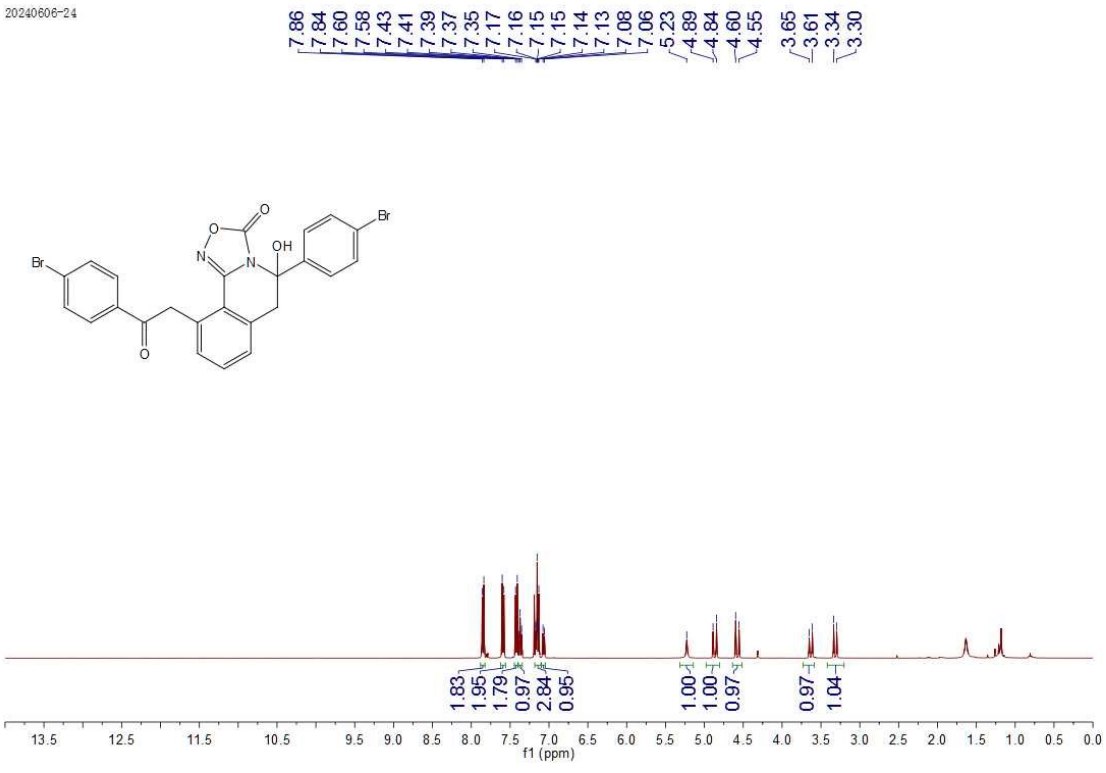
^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)



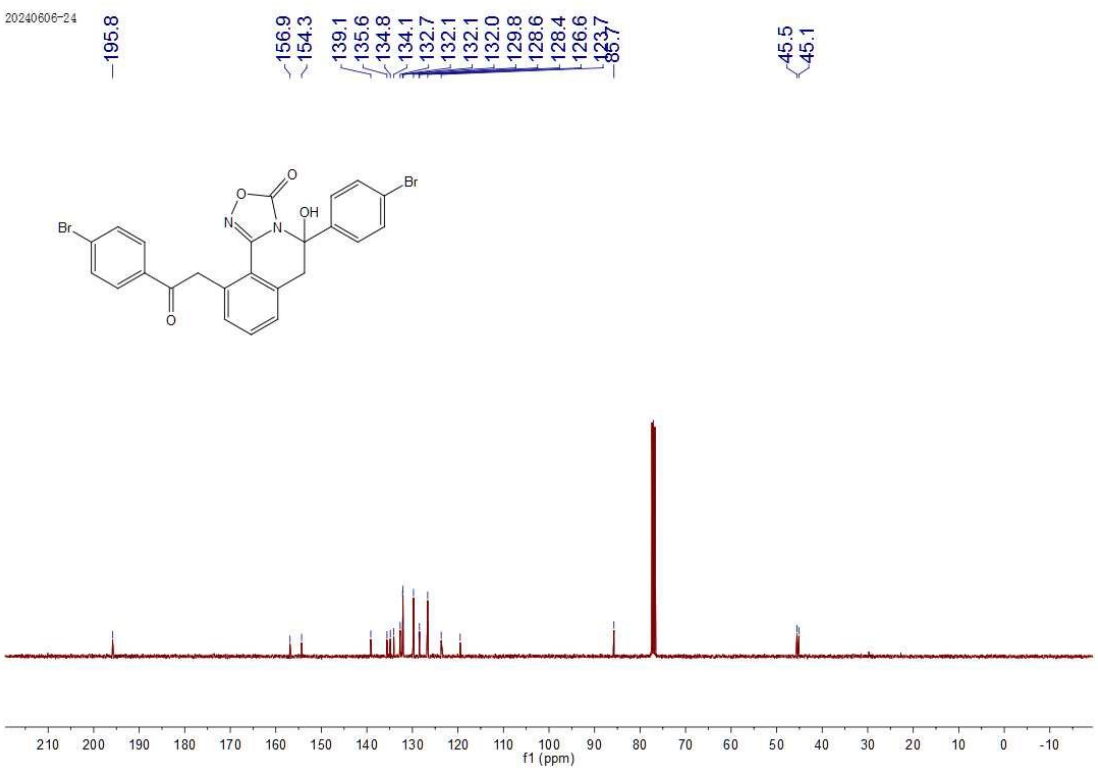
^{13}C NMR spectrum of **5f** (101 MHz, $CDCl_3$)



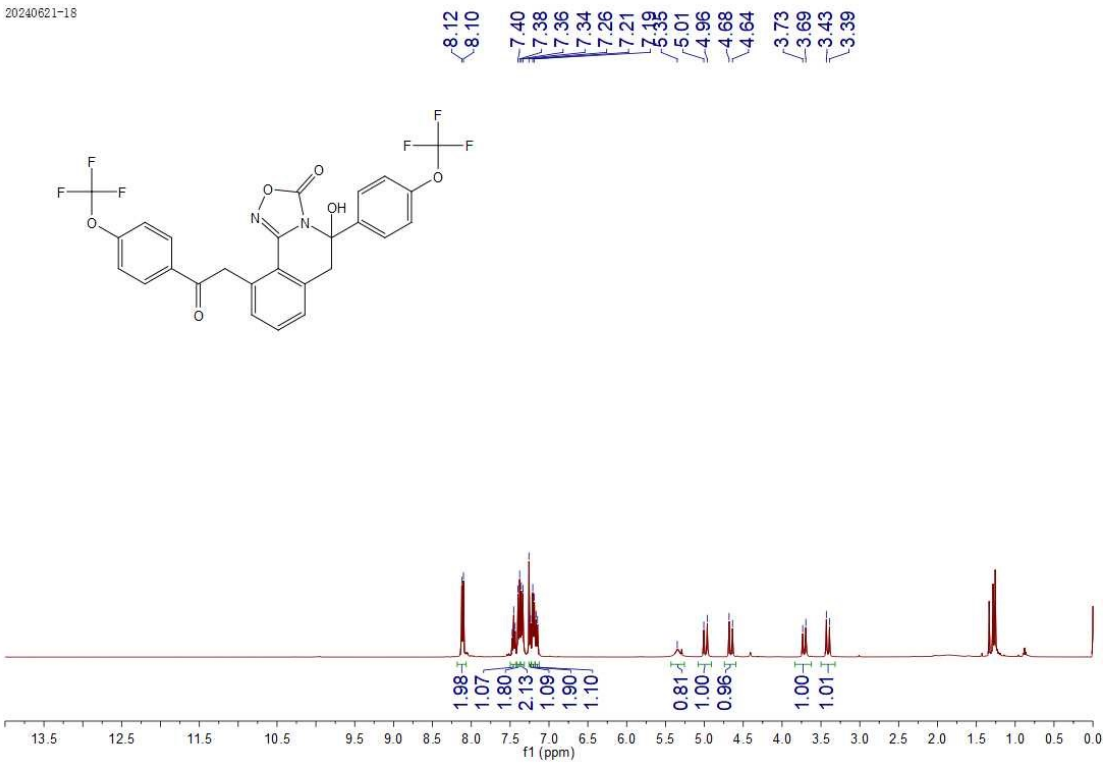
^{19}F NMR spectrum of **5f** (376 MHz, $CDCl_3$)



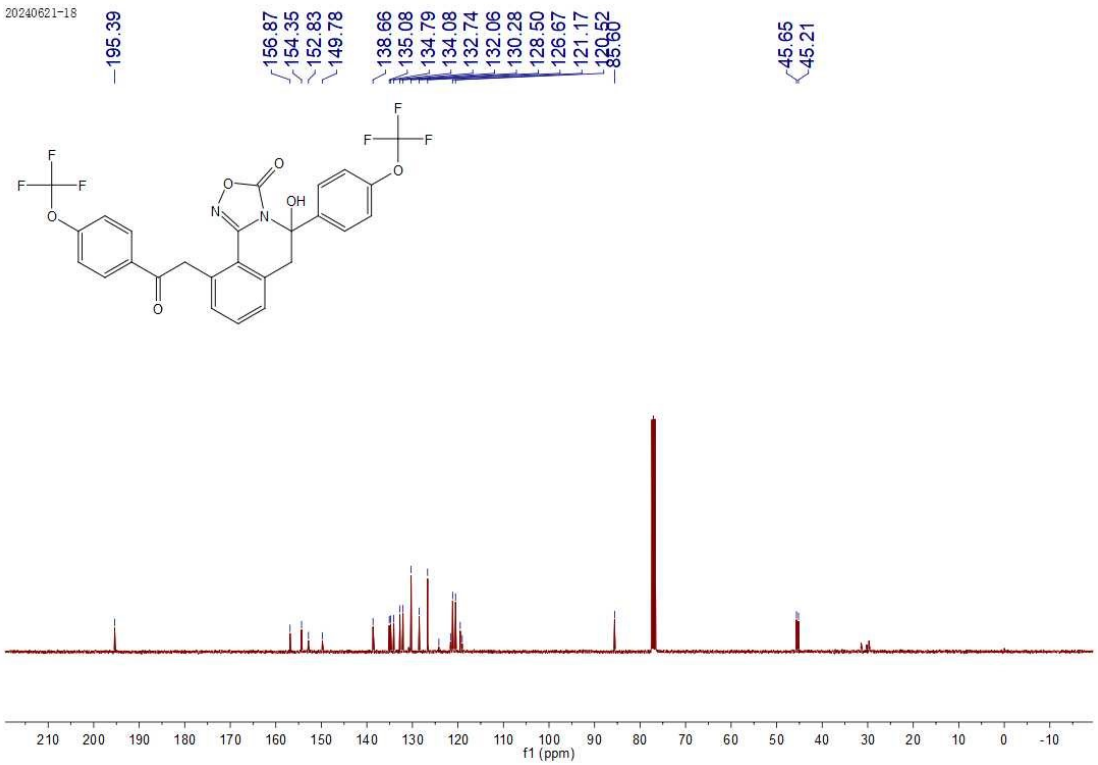
^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)



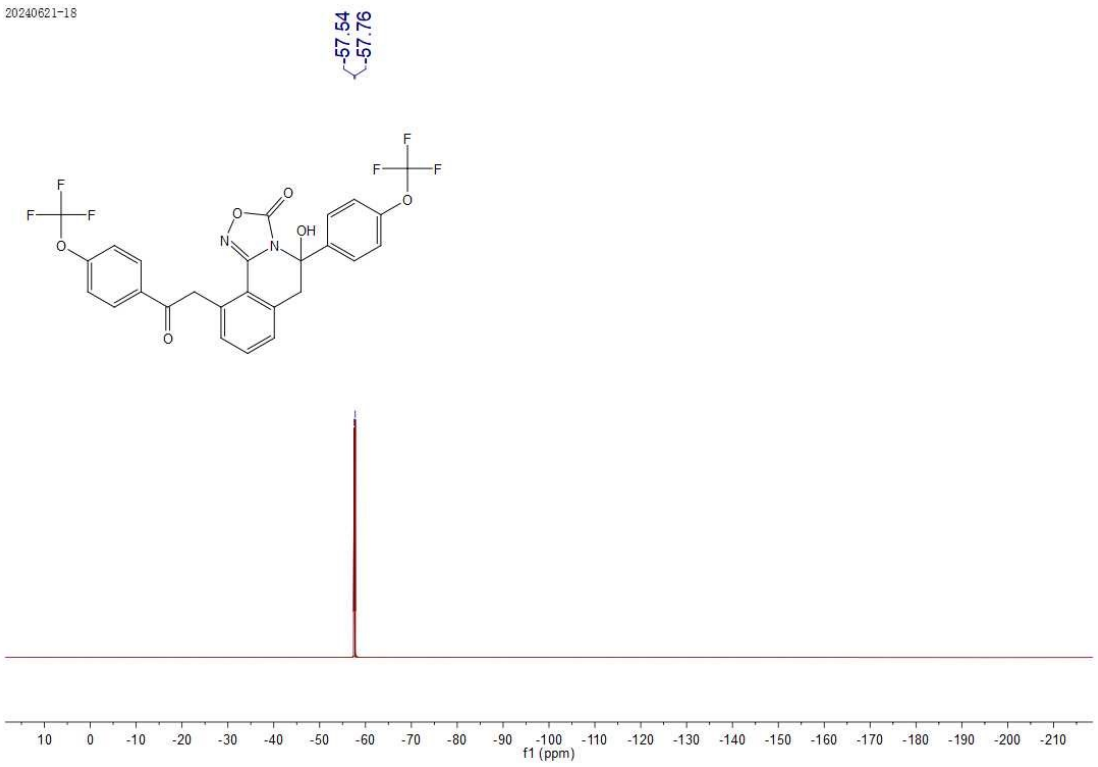
^{13}C NMR spectrum of **5g** (101 MHz, $CDCl_3$)



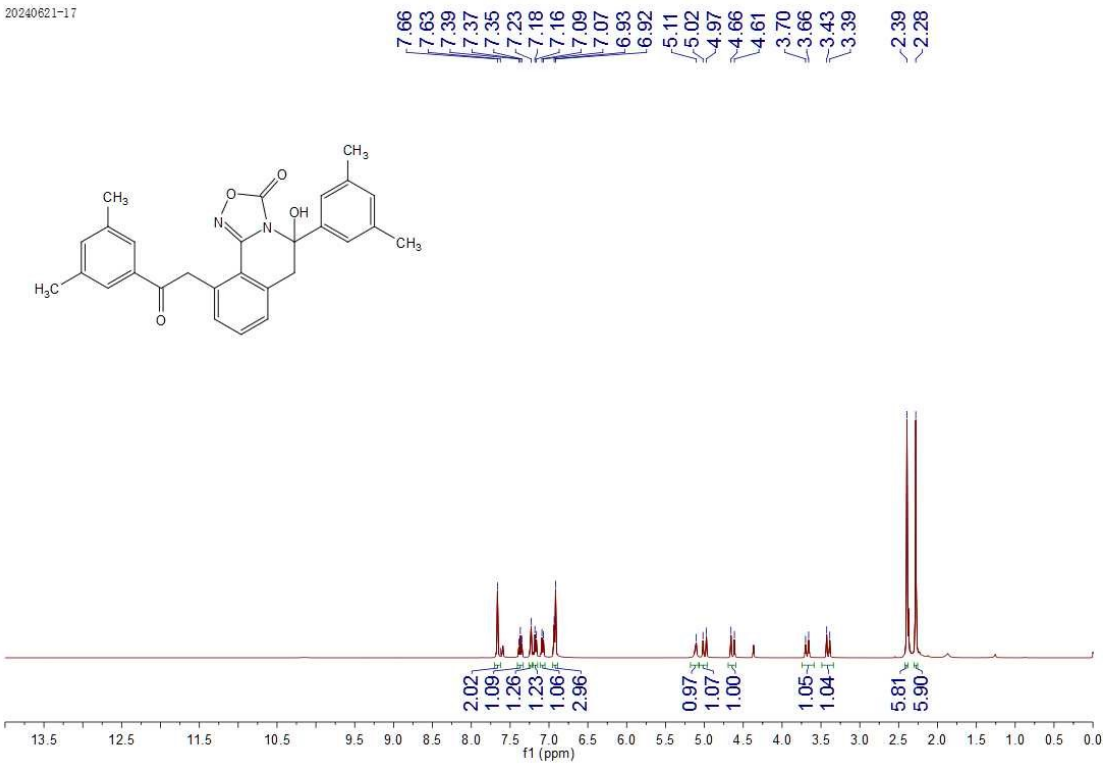
^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)



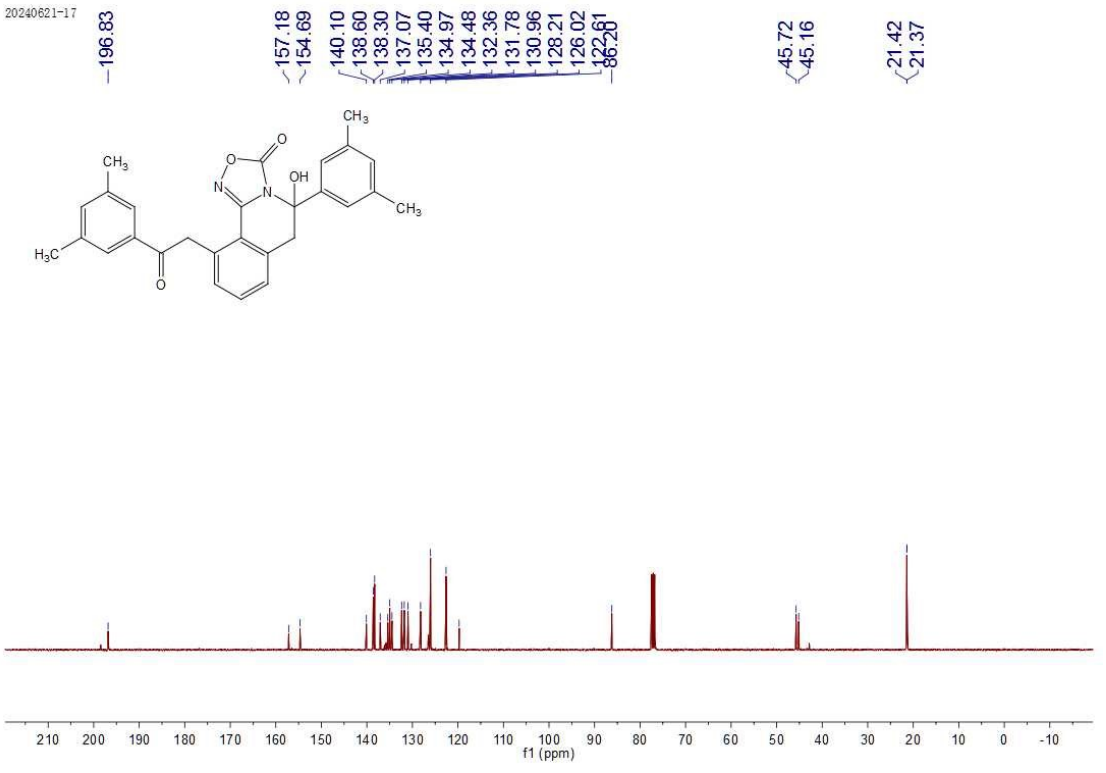
^{13}C NMR spectrum of **5h** (101 MHz, $CDCl_3$)



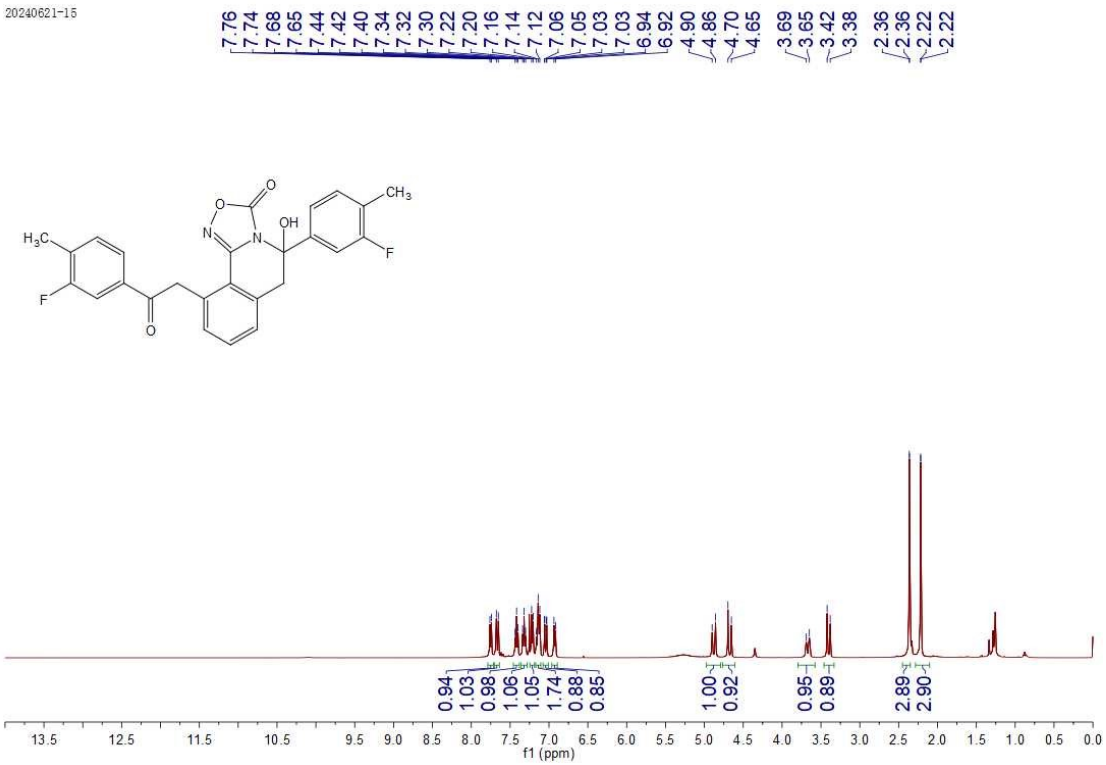
^{19}F NMR spectrum of **5h** (376 MHz, $CDCl_3$)



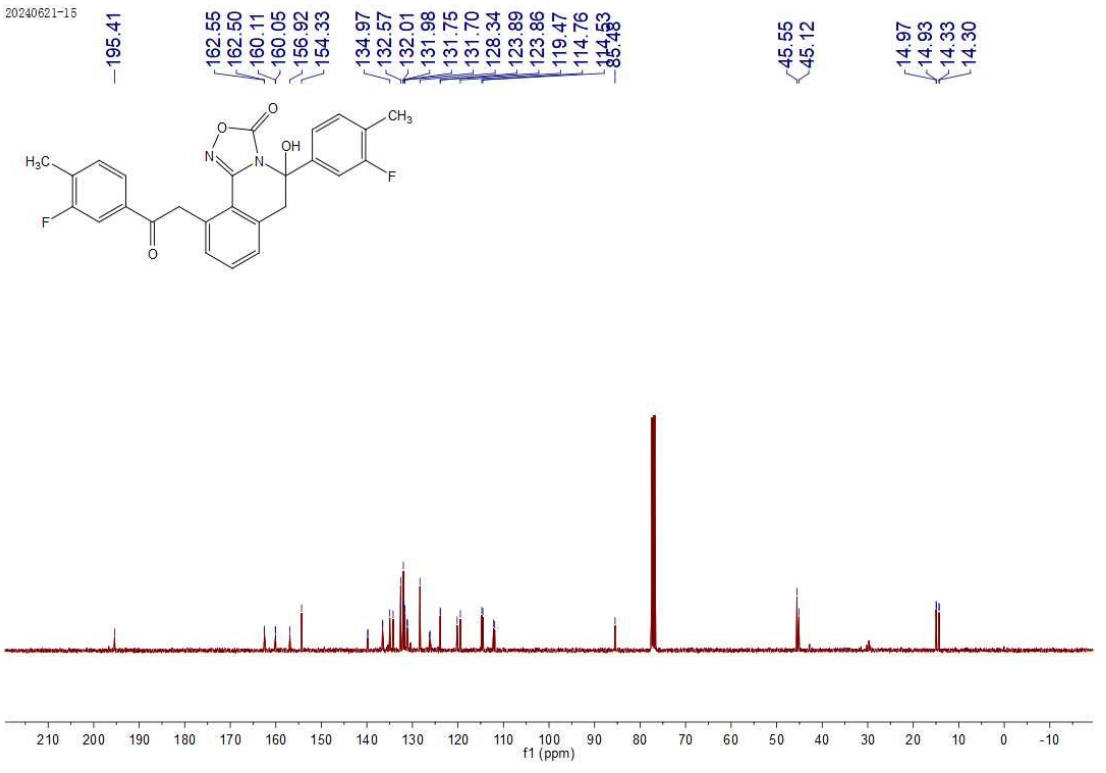
^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)



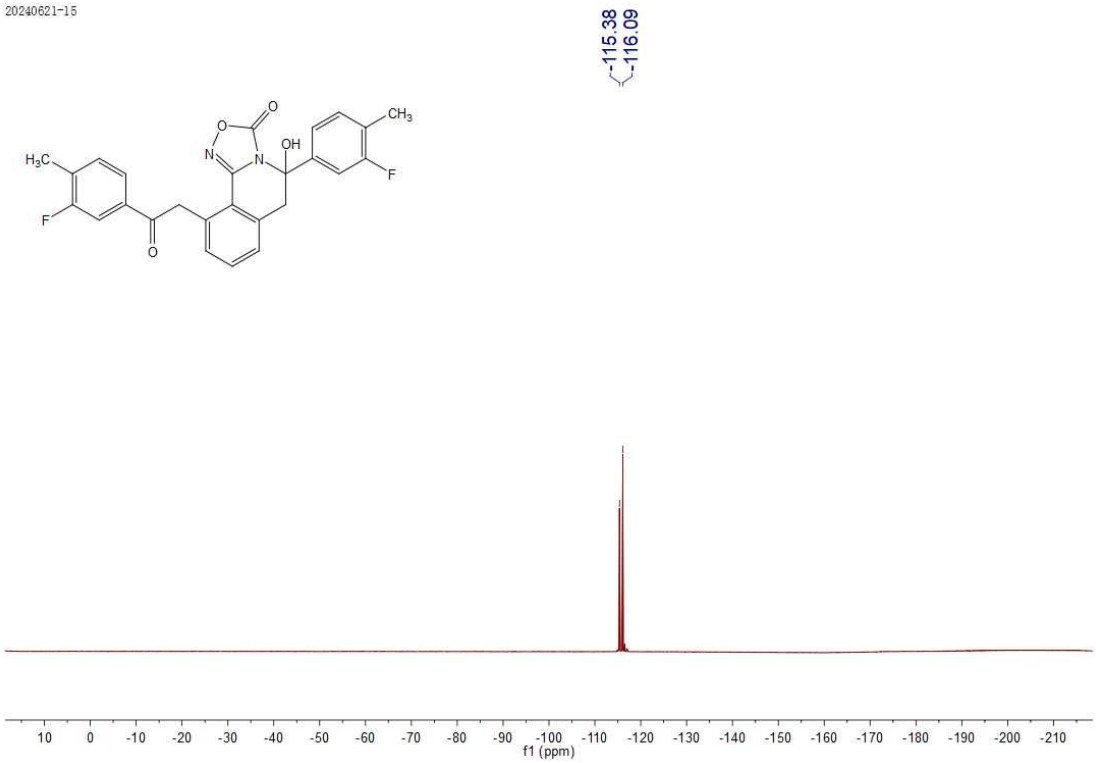
^{13}C NMR spectrum of **5i** (101 MHz, $CDCl_3$)



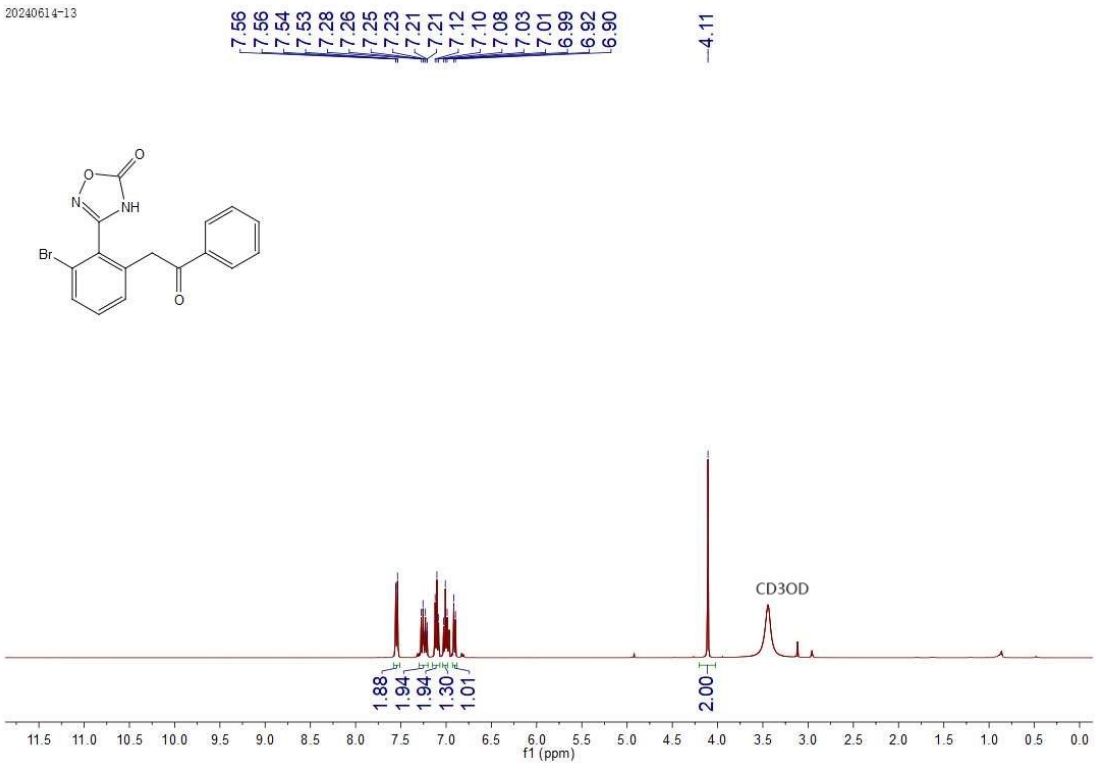
^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)



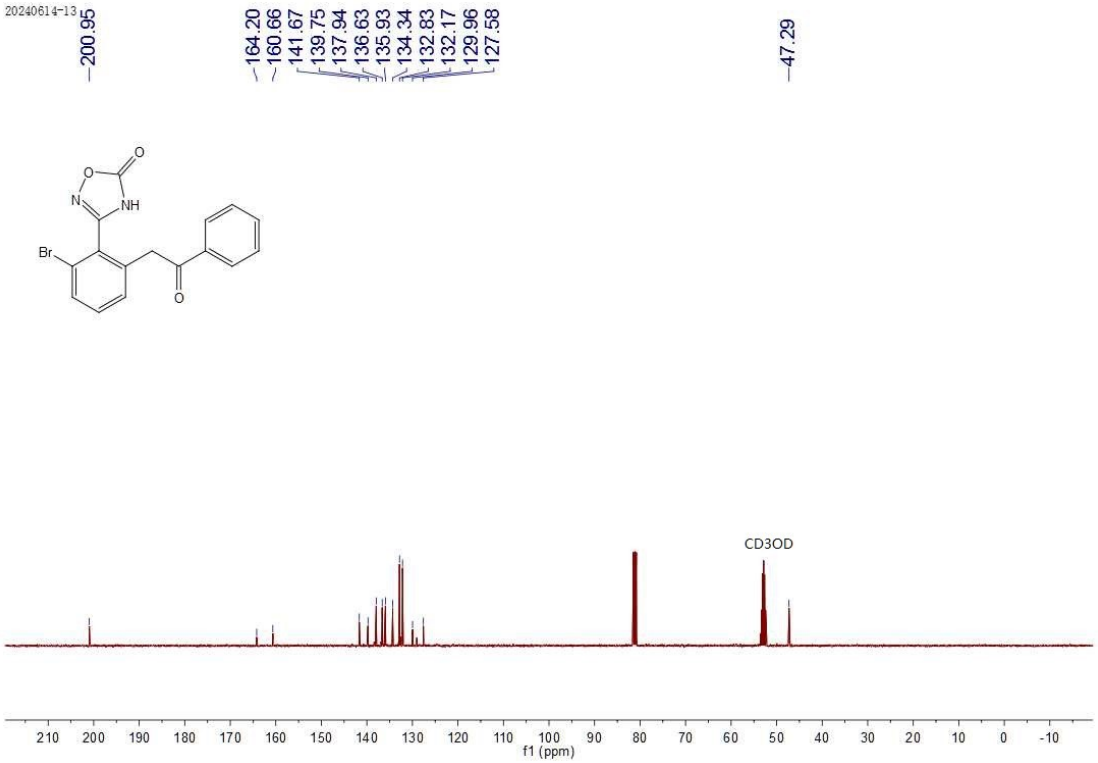
^{13}C NMR spectrum of **5j** (101 MHz, $CDCl_3$)



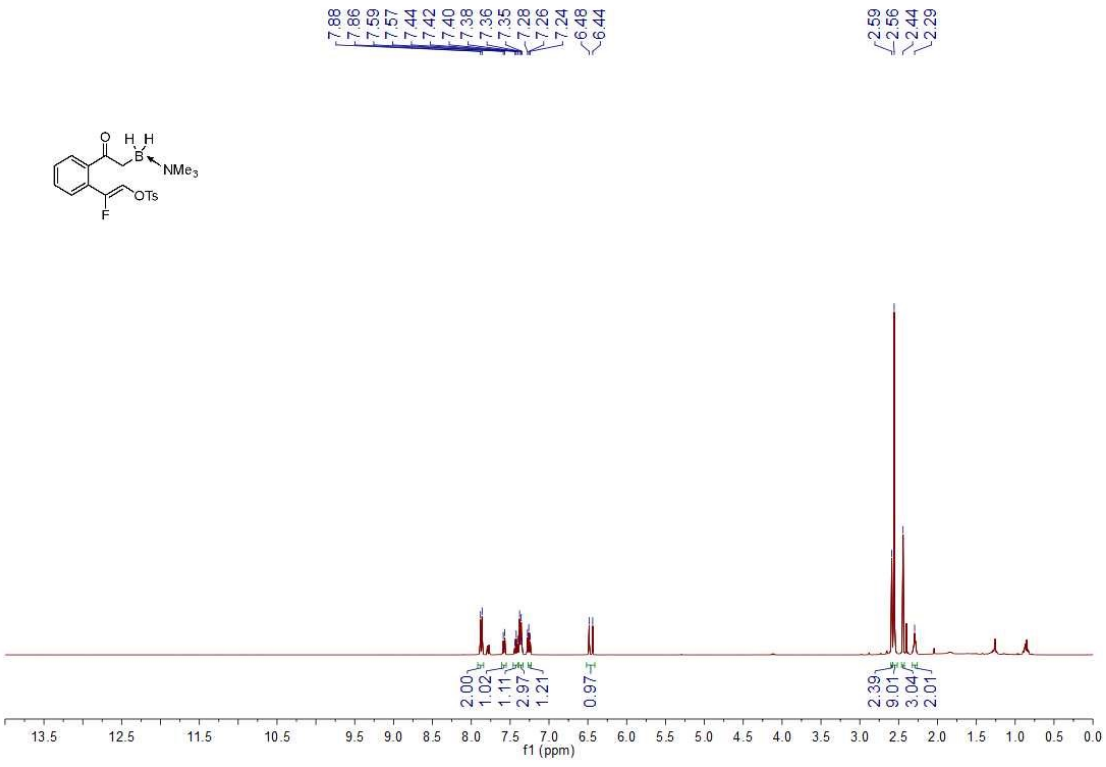
^{19}F NMR spectrum of **5j** (376 MHz, $CDCl_3$)



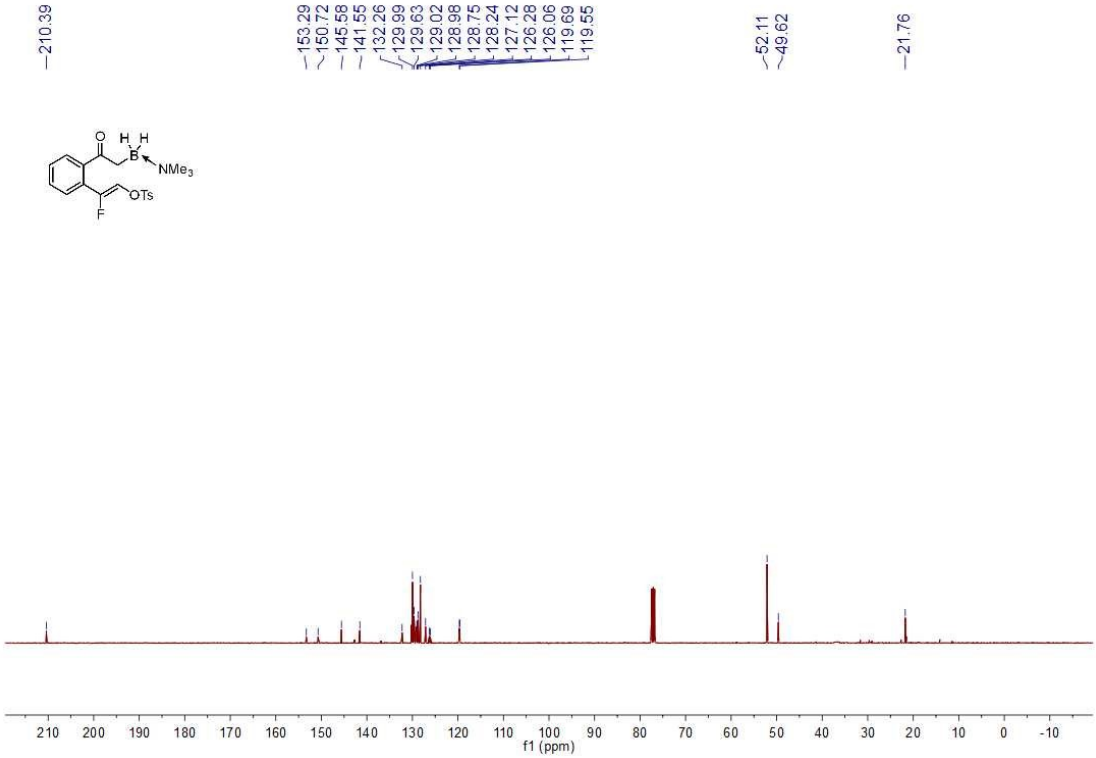
^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$)



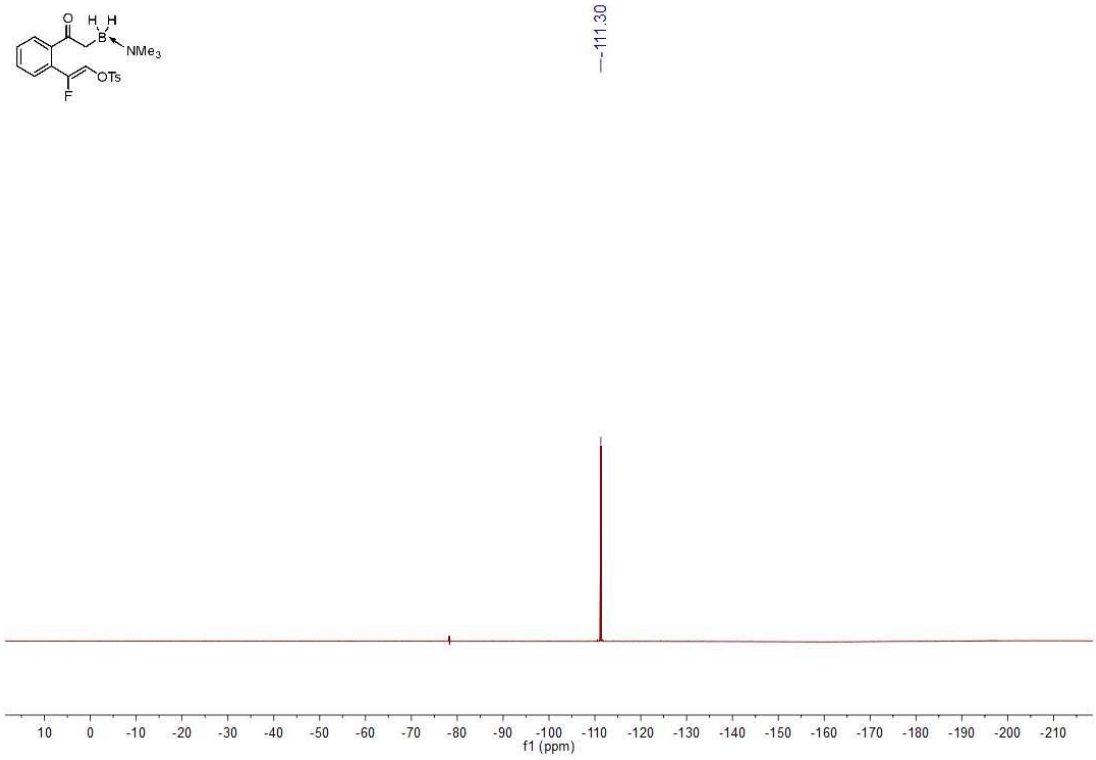
^{13}C NMR spectrum of **5k** (101 MHz, $CDCl_3$)



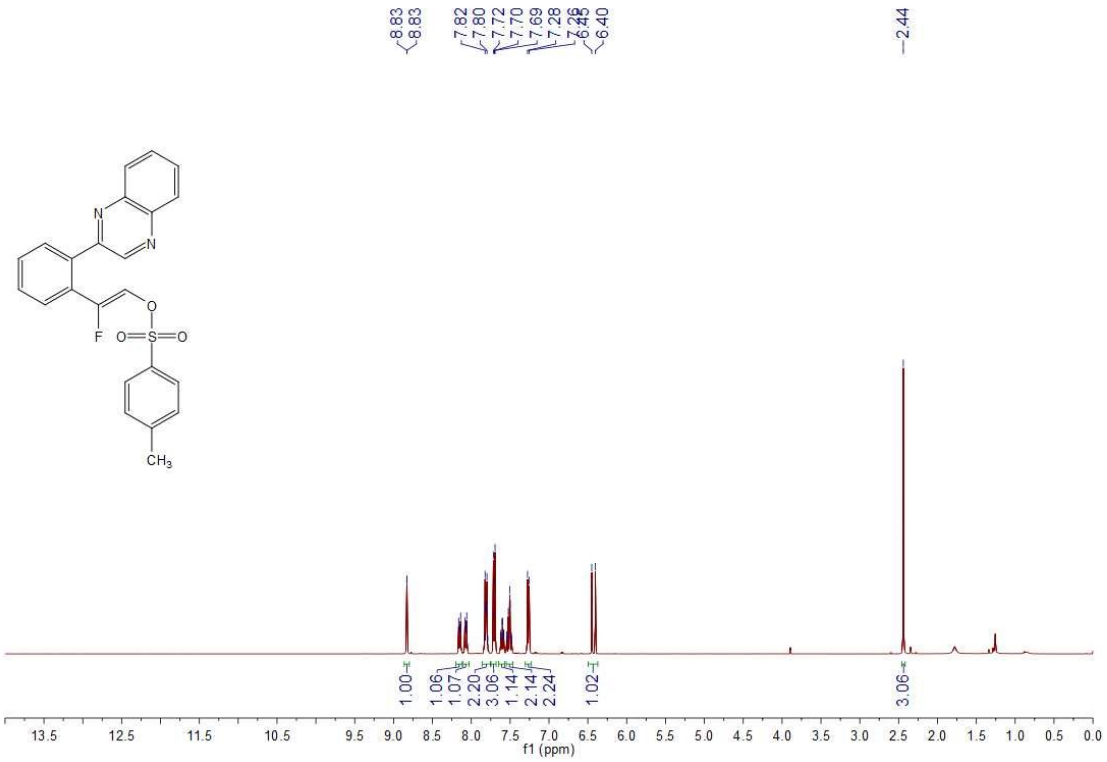
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



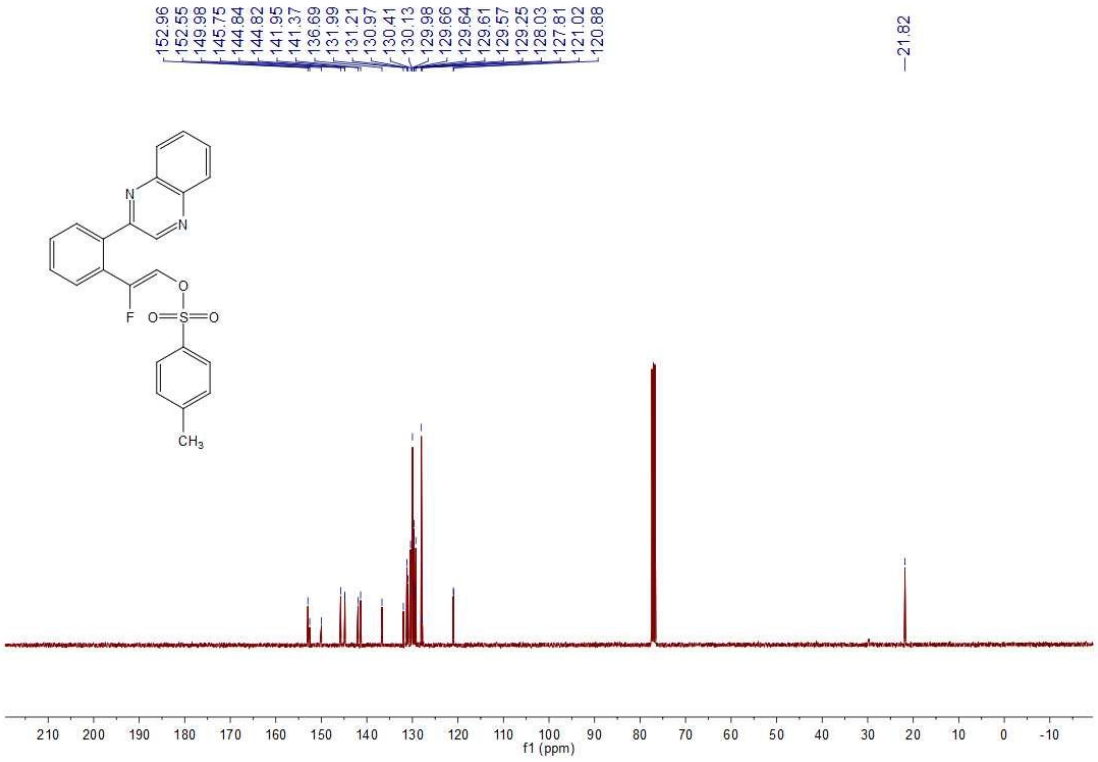
^{13}C NMR spectrum of **6** (101 MHz, $CDCl_3$)



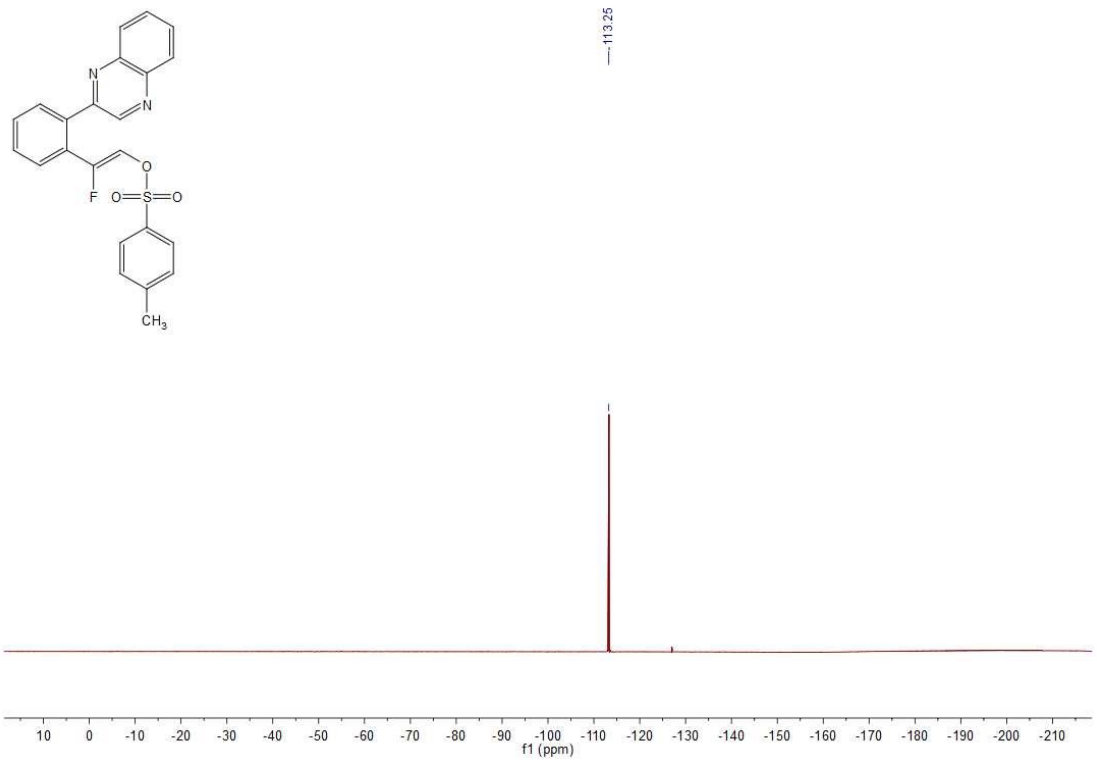
^{19}F NMR spectrum of **6** (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **7** (101 MHz, $CDCl_3$)



^{19}F NMR spectrum of **7** (376 MHz, $CDCl_3$)

13. References

1. S. S. Zhang, H. Xie, B. Shu, T. Che, X. T. Wang, D. M. Peng, F. Yang and L. Y. Zhang, *Chemical Communications*, 2020, **56**, 423-426.
2. B. Shu, X. T. Wang, Z. X. Shen, T. Che, M. Zhong, J. L. Song, H. J. Kang, H. Xie, L. Y. Zhang and S. S. Zhang, *Organic Chemistry Frontiers*, 2020, **7**, 1802-1808.
3. X. T. Wang, J. L. Song, M. Zhong, H. J. Kang, H. Xie, T. Che, B. Shu, D. M. Peng, L. Y. Zhang and S. S. Zhang, *European Journal of Organic Chemistry*, 2020, **2020**, 3635-3639.
4. Y. C. Zheng, B. Shu, Y. F. Zeng, S. Y. Chen, J. L. Song, Y. Z. Liu, L. Xiao, X. G. Liu, X. X. Zhang and S. S. Zhang, *Organic Chemistry Frontiers*, 2022, **9**, 5185-5190.
5. W. L. Chen, J. L. Song, S. Fang, J. B. Li, S. S. Zhang and B. Shu, *Chem Commun (Camb)*, 2024, **60**, 6560-6563.
6. J. Q. Wu, S. S. Zhang, H. Gao, Z. Qi, C. J. Zhou, W. W. Ji, Y. Liu, Y. Chen, Q. Li, X. Li and H. Wang, *J Am Chem Soc*, 2017, **139**, 3537-3545.
7. X. Yu, K. Chen, Q. Wang, S. Guo, S. Zha and J. Zhu, *Angewandte Chemie-International Edition*, 2017, **56**, 5222-5226.