Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bond Energy Enabled Amines Distinguishing: Chemo-, Regioselective 1,3-Diamination of (Trifluoromethyl)alkenes with Different Amines by Two C(sp^3)-F Bonds Cleavage

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A. General information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. HRMS was carried out on a high-resolution mass spectrometer (Agilent 6210 ESI/TOF MS or Thermo Q Exactive Plus). TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on Bruker APEX-II CCD Diffractometer.

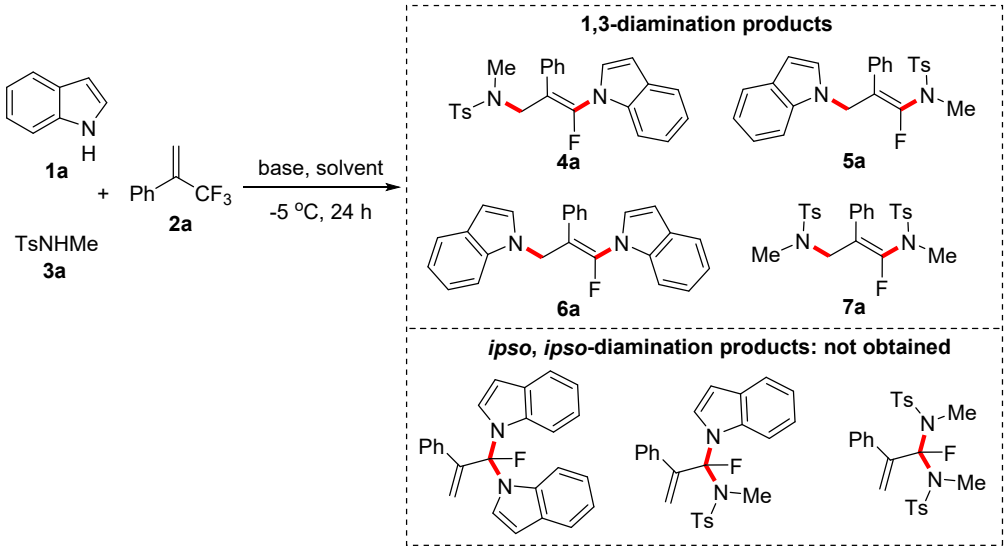
Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; 1,2-dichloroethane (DCE) was distilled from calcium hydride; acetonitrile (CH_3CN) was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF_{254}) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath or ethanol bath temperatures. All the indole derivatives (**1a**-**1l**) were purchased and used directly. The (trifluoromethyl)alkenes **2** were synthesized according to the reported methods.[1] All the used sulfonylamides (**1m**, **1n**, **3a**, **3b**, **3c**, **8a** and **8b**) were known compounds, among which **3a** and **3c** were purchased and used directly, while **1m**[2a], **1n**[2a], **3b**[2a], **8a**[2b] and 8**b**[2b] were synthesized according reported methods.

References

(1) Xia, P.-J.; Ye, Z.-P.; Hu, Y.-Z.; Song, D.; Xiang, H.-Y.; Chen, X.-Q.; Yang, H. *Org. Lett*. **2019**, *21*, 2658−2662.

(2) (a) Wang H.-P.; Sun, S.; Cheng, J. *Org. Lett.* **2017***, 19,* 5844−5847. (b) Feng, J.; Liu, S.; Tian, X.; Fan, S.; Huang, J.; Li, L. CN 107540726[A]. 2018.

B. Optimization of the Reaction Conditions.

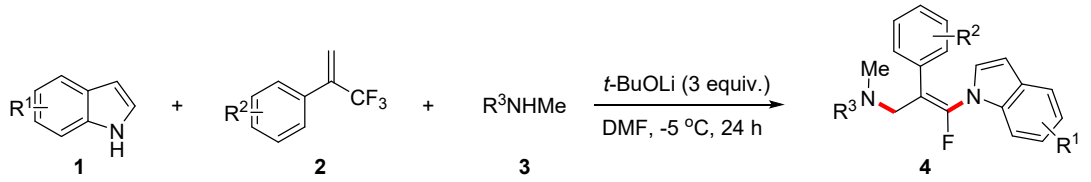


entry	base	solvent	NMR yield of **4a**/**5a**/**6a**/**7a**	yield of **4a** (%)[b]
1	Cs_2CO_3	DMF	30/0/21/22	30 (*Z*/*E* = 7:1)
2	Cs_2CO_3	1.4-dioxane	0/0/0/0	0
3	Cs_2CO_3	MeCN	0/0/0/0	0
4	Cs_2CO_3	DCE	0/0/0/0	0
5	Cs_2CO_3	toluene	0/0/0/0	0
6	Cs_2CO_3	EtOH	0/0/0/0	0
7	K_2CO_3	DMF	16/0/0/34	15 (*Z*/*E* = 7:1)
8	Li_2CO_3	DMF	0/0/0/0	0
9	*t*-BuOK	DMF	5/0/50/27	-
10	*t*-BuONa	DMF	2/0/39/27	-
11	*t*-BuOLi	DMF	75/0/16/10	75 (*Z*/*E* = 7:1)
12	Et_3N	DMF	0/0/0/0	0
13	DBU	DMF	0/0/0/0	0
14	DABCO	DMF	0/0/0/0	0
15	-	DMF	0/0/0/0	0
16[c]	*t*-BuOLi	DMF	60/0/23/19	60 (*Z*/*E* = 4:1)
17[d]	*t*-BuOLi	DMF	35/0/37/28	35 (*Z*/*E* = 8:1)

Product **5a** and all the *ipso*, *ipso*-diamination products were not obtained under all these conditions.

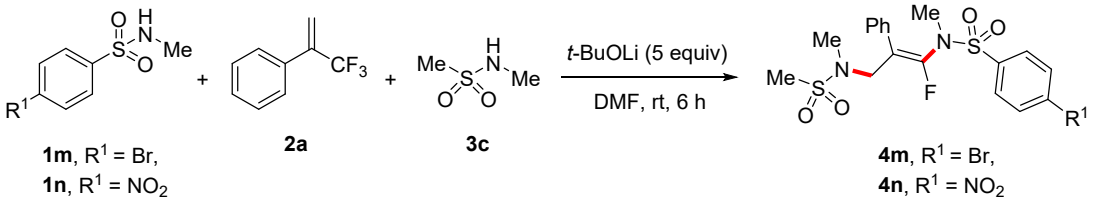
C. General Procedure for 1,3-Diamination of (Trifluoromethyl)alkenes 2.

1) The Distinguishing between Indole Derivatives 1 and Sulfonamide 3.



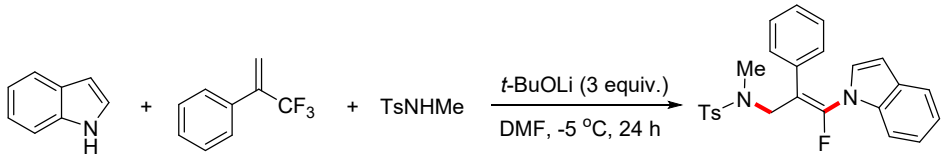
A 25 mL oven-dried Schlenk tube charged with a magnetic stirring bar, (trifluoromethyl)alkenes **2** (0.4 mmol) was added to the suspension of *t*-BuOLi (0.6 mmol), indole derivatives **1** (0.22 mmol), sulfonamides **3** (0.2 mmol) and DMF (4 mL) at -5 °C. The reaction mixture was vigorously stirred at -5 °C for 24 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **4**.

2) The Distinguishing between Arylsulfonamides and Alkylsulfonamide.



t-BuOLi (5 equiv) was added to the solution of *N*-methylsulfonamide **1m** or **1n** (0.2 mmol), (trifluoromethyl)alkene **2a** (4 equiv) in DMF (4 mL). Then *N*-methylmethanesulfonamide **3c** (5 equiv) was added by portions to the mixture within 20 minutes. The reaction mixture was vigorously stirred at room temperature for 6 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **4m**/**4n**.

3) Gram-Scale Reaction of Indole 1a, (Trifluoromethyl)alkene 2a, and Sulfonamide 3a.

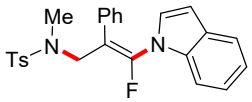


1a **2a** **3a** **4a**, 1.233 g
71%, Z/E = 7/1

A 250 mL oven-dried Schlenk tube charged with a magnetic stirring bar, (trifluoromethyl)alkene **2a** (1376 mg, 8 mmol) was added to the suspension of *t*-BuOLi (960 mg, 12 mmol), indole **1a** (514.8 mg, 4.4 mmol), sulfonamide **3a** (740 mg, 4 mmol) and DMF (80 mL) at -5 °C. The reaction mixture was vigorously stirred at -5 °C for 24 h. Then the mixture was stopped stirring, added water (150 mL), extracted with EtOAc (150 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) provided the product **4a** (1.233 g, 71% yield, Z/E = 7/1).

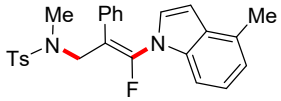
D. Analysis Data for the Products

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4a)



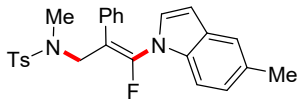
65.2 mg, 75% yield, *Z*/*E* = 7:1; eluent with petroleum ether/ethyl acetate = 10:1; white solid, mp: 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.36–7.39 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.17–7.27 (m, 5H), 7.07–7.09 (m, 2H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 4.39 (d, *J* = 2.8 Hz, 2H), 2.80 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8 (d, $^1J_{F\text{-}C}$ = 264.0 Hz), 143.6, 135.6 (d, $^3J_{F\text{-}C}$ = 3.7 Hz), 134.2, 133.4 (d, $^3J_{F\text{-}C}$ = 3.2 Hz), 129.8, 128.8, 128.6, 128.2 (d, $^3J_{F\text{-}C}$ = 3.1 Hz), 128.0, 127.7, 127.3 (d, $^4J_{F\text{-}C}$ = 2.1 Hz), 123.4, 121.7, 121.2, 111.4 (d, $^3J_{F\text{-}C}$ = 3.0 Hz), 109.3 (d, $^2J_{F\text{-}C}$ = 24.0 Hz), 105.9 (d, $^4J_{F\text{-}C}$ = 1.2 Hz), 48.3 (d, $^3J_{F\text{-}C}$ = 2.6 Hz), 34.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 1F); IR (KBr): 3056, 2927, 1692, 1456, 1341, 744 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{23}FN_2O_2S$+H, 435.1543; found, 435.1547.

(*Z*)-*N*-(3-Fluoro-3-(4-Methyl-1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4b)



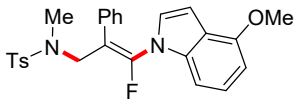
65.5 mg, 73% yield, *Z*/*E* = 13:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 3.2 Hz, 1H), 7.11–7.19 (m, 6H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 4.27 (s, 2H), 2.67 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.9 (d, $^{1}J_{F\text{-}C}$ = 266.7 Hz), 144.1, 135.6 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 133.8 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 133.7, 130.4, 128.7, 128.5 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 128.4, 128.2, 128.1, 128.0, 127.9, 123.6, 122.1, 112.1 (d, $^{2}J_{F\text{-}C}$ = 25.4 Hz), 108.8, 104.5, 49.0, 35.0, 21.5, 18.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -86.9 (s, 1F); IR (KBr): 3049, 2926, 1692, 1443, 1340, 749 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_2S$+H, 449.1699; found, 449.1698.

(*Z*)-*N*-(3-Fluoro-3-(5-Methyl-1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4c)



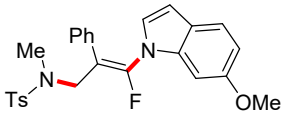
53.8 mg, 60% yield, *Z*/*E* = 16:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.27–7.31 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 4.5 Hz, 3H), 7.02–7.03 (m, 3H), 6.66 (d, *J* = 3.5 Hz, 1H), 6.33 (d, *J* = 3.0 Hz, 1H), 4.32 (s, 2H), 2.73 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0 (d, $^{1}J_{F\text{-}C}$ = 263.4 Hz), 143.6, 134.1, 133.9 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 133.4 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 131.2, 129.8, 129.1, 128.6, 128.2 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 127.9, 127.7, 127.4 (d, $^{4}J_{F\text{-}C}$ = 1.8 Hz), 124.9, 120.9, 111.1 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 108.7 (d, $^{2}J_{F\text{-}C}$ = 24.2 Hz), 105.6, 48.3 (d, $^{3}J_{F\text{-}C}$ = 2.6 Hz), 34.1, 21.6, 21.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.7 (s, 1F); IR (KBr): 3037, 2925, 1691, 1466, 1340, 744 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_2S$+H, 449.1699; found, 449.1696.

(*Z*)-*N*-(3-Fluoro-3-(4-Methoxy-1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4d)



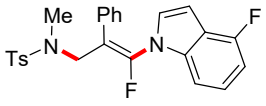
55.8 mg, 60% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.16 (d, *J* = 5.2 Hz, 3H), 7.05–7.06 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 4.35 (s, 2H), 3.94 (s, 3H), 2.77 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 147.9 (d, $^{1}J_{F\text{-}C}$ = 265.8 Hz), 143.7, 137.0 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 134.1, 133.3 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 129.8, 128.7, 128.2 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 128.0, 127.7, 125.9 (d, $^{4}J_{F\text{-}C}$ = 2.1 Hz), 124.4, 119.3, 109.5 (d, $^{2}J_{F\text{-}C}$ = 24.0 Hz), 104.6, 103.1, 101.8, 55.5, 48.36, 34.2, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.6 (s, 1F); IR (KBr): 3055, 2929, 1691, 1454, 1338, 741 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_3S$+H, 465.1648; found, 465.1651.

(*Z*)-*N*-(3-Fluoro-3-(5-Methoxy-1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4e)



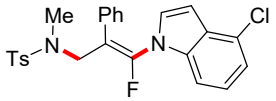
61.3 mg, 66% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 3.2 Hz, 1H), 7.15 (s, 5H), 6.75 (s, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.50 (d, *J* = 2.8 Hz, 1H), 4.28 (s, 2H), 3.69 (s, 3H), 2.66 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.0, 146.7 (d, $^{1}J_{F\text{-}C}$ = 266.4 Hz), 144.1, 136.4 (d, $^{3}J_{F\text{-}C}$ = 3.4 Hz), 133.9 (d, $^{3}J_{F\text{-}C}$ = 3.4 Hz), 133.6, 130.4, 128.7, 128.5 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 128.2, 127.9, 127.0 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 122.3, 121.8, 111.6 (d, $^{2}J_{F\text{-}C}$ = 25.6 Hz), 111.5, 106.0, 95.0, 55.7, 49.0, 35.0, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -86.8 (s, 1F); IR (KBr): 3057, 2933, 1691, 1452, 1341, 742 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_3S$+H, 465.1648; found, 465.1650.

(*Z*)-*N*-(3-Fluoro-3-(4-Fluoro-1*H*-Indol-1-yl)-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide(4f)



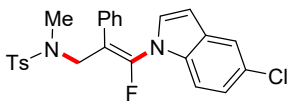
52.5 mg, 58% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; light yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 3.2 Hz, 1H), 7.11–7.21 (m, 7H), 6.88–6.93 (m, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 4.28 (s, 2H), 2.67 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.6 (d, $^{1}J_{F\text{-}C}$ = 245.7 Hz), 146.1 (d, $^{1}J_{F\text{-}C}$ = 266.9 Hz), 144.1, 138.3 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 138.1 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 133.7, 133.5 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 130.4, 129.3 (d, $^{4}J_{F\text{-}C}$ = 2.8 Hz), 128.7, 128.4–128.5 (m), 127.8, 124.5 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 117.2 (d, $^{2}J_{F\text{-}C}$ = 22.9 Hz), 113.3 (d, $^{2}J_{F\text{-}C}$ = 24.6 Hz), 107.9, 106.9 (d, *J* = 18.7 Hz), 101.3, 49.0, 35.1, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -87.7 (s, 1F), -121.9 – -121.9 (m, 1F).; IR (KBr): 3054, 2928, 1695, 1453, 1338, 746 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}F_2N_2O_2S$+H, 453.1448; found, 453.1439.

(*Z*)-*N*-(3-(4-Chloro-1*H*-Indol-1-yl)-3-Fluoro-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide(4g)



52.5 mg, 56% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 3H), 7.34 (d, *J* = 6.4 Hz, 1H), 7.13–7.17 (m, 7H), 6.60 (s, 1H), 4.28 (s, 2H), 2.67 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.0 (d, $^{1}J_{F\text{-}C}$ = 265.1 Hz), 144.1, 136.5 (d, $^{3}J_{F\text{-}C}$ = 3.5 Hz), 133.7, 133.4 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 130.4, 130.0 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 128.7, 128.5, 128.4, 127.8, 126.9, 125.3, 124.6, 121.5, 113.5 (d, $^{2}J_{F\text{-}C}$ = 24.4 Hz), 110.5, 103.7, 49.0, 35.1, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -87.6 (s, 1F); IR (KBr): 3037, 2926, 1690, 1439, 1338, 751 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}FClN_2O_2S$+H, 469.1153; found, 469.1150.

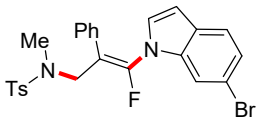
(*Z*)-*N*-(3-(5-Chloro-1*H*-Indol-1-yl)-3-Fluoro-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide(4h)



54.4 mg, 58% yield, *Z*/*E* = 21:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.59 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H),

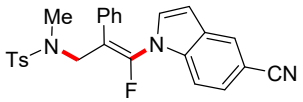
7.38 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.10–7.17 (m, 6H), 6.56 (d, J = 2.4 Hz, 1H), 4.27 (s, 2H), 2.67 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.1 (d, $^{1}J_{F\text{-}C}$ = 266.8 Hz), 144.1, 134.2 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 133.7, 133.5 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 130.4, 129.8, 128.7, 128.4 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 128.4, 128.0, 127.8, 126.4, 123.4, 120.7, 112.9 (d, $^{2}J_{F\text{-}C}$ = 24.6 Hz), 112.8, 105.6, 49.0, 35.1, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -87.4 (s, 1F); IR (KBr): 3057, 2925, 1692, 1453, 1339, 744 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}FClN_2O_2S$+H, 469.1153; found, 469.1151.

(*Z*)-*N*-(3-(5-Bromo-1*H*-Indol-1-yl)-3-Fluoro-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide(4i)



77.0 mg, 75% yield, Z/E = 18:1; eluent with petroleum ether/ethyl acetate = 10:1; yellow oil; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.68 (d, J = 7.5 Hz, 2H), 7.54 (s, 1H), 7.45–7.47 (m, 3H), 7.36 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.11–7.17 (m, 5H), 6.59 (s, 1H), 4.27 (s, 2H), 2.65 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 145.9 (d, $^{1}J_{F\text{-}C}$ = 266.7 Hz), 144.1, 136.3 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 133.7, 133.6 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 130.4, 129.7 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 128.7, 128.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 128.4, 127.8, 127.6, 124.8, 123.0, 116.3, 114.2, 113.0 (d, $^{2}J_{F\text{-}C}$ = 24.7 Hz), 106.1, 49.0, 35.2, 21.5; ^{19}F NMR (471 MHz, DMSO-d_6) δ -87.8 (s, 1F); IR (KBr): 3059, 2932, 1700, 1462, 1188, 938 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}BrFN_2O_2S$+H, 513.0648; found, 513.0652.

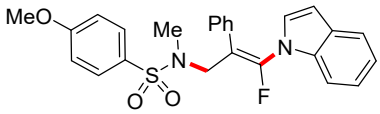
(*Z*)-*N*-(3-(5-Cyano-1*H*-Indol-1-yl)-3-Fluoro-2-Phenylallyl)-*N*,4-Dimethylbenzenesulfonamide (4j)



62.5 mg, 68% yield, Z/E = 8:1; eluent with petroleum ether/ethyl acetate = 6:1; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.88 (m, 8H), 6.53–7.19 (m, 6H), 4.35 (d, J = 2.8 Hz, 2H), 2.75 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3 (d, $^{1}J_{F\text{-}C}$ = 266.0 Hz), 143.8, 137.3 (d, $^{3}J_{F\text{-}C}$ = 3.4 Hz), 134.1, 132.7 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 129.9, 128.9, 128.6, 128.5, 128.1, 127.7, 126.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 120.0, 112.3 (d, $^{4}J_{F\text{-}C}$ = 2.0 Hz), 111.7 (d, J = 22.9 Hz), 106.2, 105.2, 48.4 (d, $^{3}J_{F\text{-}C}$

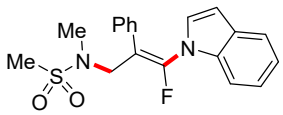
= 2.9 Hz), 34.7, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.7 (s, 1F); IR (KBr): 3038, 2919, 1639, 1461, 1159, 745 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{22}FN_3O_2S$+H, 460.1490; found, 460.1481.

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-Phenylallyl)-4-Methoxy-*N*-Methylbenzenesulfonamide (4k)



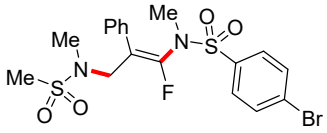
64.9 mg, 72% yield, *Z*/*E* = 23:1; eluent with petroleum ether/ethyl acetate = 6:1; white solid, mp: 177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.15–7.26 (m, 5H), 7.05–7.07 (m, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 6.76 (d, *J* = 3.2 Hz, 1H), 6.46 (d, *J* = 3.6 Hz, 1H), 4.36 (d, *J* = 2.8 Hz, 2H), 3.89 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 147.8 (d, $^1J_{F\text{-}C}$ = 265.6 Hz), 135.6 (d, $^3J_{F\text{-}C}$ = 3.9 Hz), 133.4 (d, $^3J_{F\text{-}C}$ = 3.1 Hz), 129.8, 128.8, 128.7, 128.6, 128.2 (d, $^3J_{F\text{-}C}$ = 3.2 Hz), 128.0, 127.3, 123.4, 121.7, 121.2, 114.4, 111.4 (d, $^3J_{F\text{-}C}$ = 2.9 Hz), 109.4 (d, $^2J_{F\text{-}C}$ = 24.0 Hz), 105.9, 55.7, 48.3, 34.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 1F); IR (KBr): 3060, 2936, 1691, 1459, 1336, 744 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{23}FN_2O_3S$+H, 451.1492; found, 451.1490.

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-Phenylallyl)-*N*-Methylmethanesulfonamide (4l)



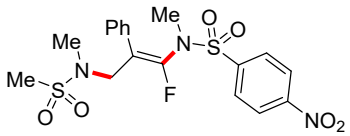
31.5 mg, 44% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.4 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.28–7.30 (m, 1H), 7.18–7.23 (m, 4H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.47 (d, *J* = 3.2 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 2H), 2.97 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9 (d, $^1J_{F\text{-}C}$ = 265.5 Hz), 135.7 (d, $^3J_{F\text{-}C}$ = 3.8 Hz), 133.5 (d, $^3J_{F\text{-}C}$ = 3.5 Hz), 128.8, 128.8, 128.3 (d, $^3J_{F\text{-}C}$ = 3.2 Hz), 128.3, 127.3, 123.5, 121.8, 121.2, 111.4 (d, $^3J_{F\text{-}C}$ = 3.2 Hz), 109.4 (d, $^2J_{F\text{-}C}$ = 24.5 Hz), 106.0, 48.1, 36.6, 33.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.2 (s, 1F); IR (KBr): 3045, 2930, 1692, 1451, 1320, 754 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{19}H_{19}FN_2O_2S$+H, 359.1224; found, 359.1217.

(*Z*)-4-Bromo-*N*-(1-Fluoro-3-(*N*-Methylmethylsulfonamido)-2-Phenylprop-1-en-1-yl)-*N*-Methylbenzenesulfonamide (4m)



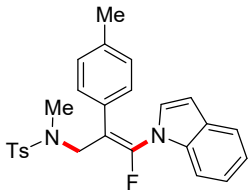
78.6 mg, 80% yield, *Z*/*E* = 8:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.63 (m, 2H), 7.56–7.58 (m, 2H), 7.36–7.44 (m, 5H), 4.33 (d, *J* = 2.8 Hz, 2H), 2.86 (s, 3H), 2.81 (d, *J* = 2.0 Hz, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (d, $^{1}J_{F\text{-}C}$ = 279.4 Hz), 137.1, 133.7 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 132.5, 129.5 (d, $^{4}J_{F\text{-}C}$ = 1.8 Hz), 128.9, 128.8, 128.7, 128.7, 116.5 (d, $^{2}J_{F\text{-}C}$ = 27.9 Hz), 48.6 (d, $^{4}J_{F\text{-}C}$ = 2.3 Hz), 37.0 (d, $^{4}J_{F\text{-}C}$ = 3.0 Hz), 36.2, 33.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.6 (s, 1F); IR (KBr): 3049, 2960, 1692, 1459, 1336, 742 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{18}H_{20}BrFN_2O_4S_2$+H, 491.0105; found, 491.0101.

(*Z*)-*N*-(1-Fluoro-3-(*N*-Methylmethylsulfonamido)-2-Phenylprop-1-en-1-yl)-*N*-Methyl-4-Nitrobenzenesulfonamide (4n)



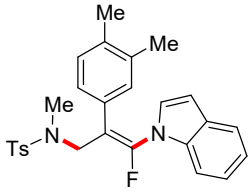
73.2 mg, 80% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 6:1; white solid, mp: 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.36–7.42 (m, 5H), 4.33 (d, *J* = 2.4 Hz, 2H), 2.87 (d, *J* = 2.0 Hz, 3H), 2.85 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.5 (d, $^{1}J_{F\text{-}C}$ = 277.0 Hz), 143.7, 133.4 (d, $^{3}J_{F\text{-}C}$ = 3.1 Hz), 129.2 (d, $^{4}J_{F\text{-}C}$ = 1.8 Hz), 129.0, 128.8, 128.6 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 124.4, 117.1 (d, $^{2}J_{F\text{-}C}$ = 27.2 Hz), 48.6 (d, $^{4}J_{F\text{-}C}$ = 2.1 Hz), 36.9 (d, $^{3}J_{F\text{-}C}$ = 3.9 Hz), 36.5, 33.9 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -91.8 (s, 1F); IR (KBr): 3090, 2934, 1695, 1459, 1341, 771 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{18}H_{20}FN_3O_6S_2$+H, 458.0850; found, 458.0846.

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-(*p*-Tolyl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4o)



62.8 mg, 70% yield, *Z*/*E* = 17:1; eluent with petroleum ether/ethyl acetate = 10:1; red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.14–7.23 (m, 2H), 6.89–6.94 (m, 4H), 6.72 (d, *J* = 3.2 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 4.31 (d, *J* = 2.4 Hz, 2H), 2.73 (s, 3H), 2.42 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (d, $^{1}J_{F\text{-}C}$ = 263.4 Hz), 143.6, 137.8, 135.7 (d, $^{3}J_{F\text{-}C}$ = 3.8 Hz), 134.2, 130.2 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 129.8, 129.4, 128.8, 128.0 (d, $^{3}J_{F\text{-}C}$ = 3.1 Hz), 127.7, 127.4 (d, $^{4}J_{F\text{-}C}$ = 2.2 Hz), 123.4, 121.7, 121.1, 111.4 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 109.3 (d, $^{2}J_{F\text{-}C}$ = 23.8 Hz), 105.8, 48.6 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 34.2, 21.6, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.0 (s, 1F); IR (KBr): 3048, 2925, 1693, 1456, 1341, 745 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_2S$+H, 449.1699; found, 449.1692.

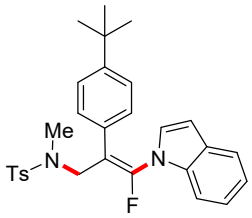
(*Z*)-*N*-(2-(3,4-Dimethylphenyl)-3-Fluoro-3-(1*H*-Indol-1-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4p)



62.9 mg, 68% yield, *Z*/*E* = 9:1; eluent with petroleum ether/ethyl acetate = 10:1; light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.19–7.29 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 6.72–6.77 (m, 2H), 6.46 (d, *J* = 3.2 Hz, 1H), 4.35 (s, 2H), 2.79 (s, 3H), 2.47 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (d, $^{1}J_{F\text{-}C}$ = 262.9 Hz), 143.5, 136.7, 136.4, 135.8 (d, $^{3}J_{F\text{-}C}$ = 3.7 Hz), 134.3, 130.5 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 129.8, 129.8, 129.2 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 128.8, 127.7, 127.5, 125.5 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 123.4, 121.6, 121.1, 111.5 (d, $^{3}J_{F\text{-}C}$ = 3.1 Hz), 109.3 (d, $^{2}J_{F\text{-}C}$ = 23.4 Hz), 105.7 (d, $^{4}J_{F\text{-}C}$ = 1.1 Hz), 48.3 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 34.1, 21.7, 19.8, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.2 (s, 1F); IR (KBr): 3047, 2926, 1689, 1456, 1341, 750 cm^{-1}; HRMS

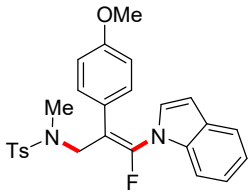
(ESI, m/z): $[M+H]^+$ Calcd. For $C_{27}H_{27}FN_2O_2S$+H, 463.1856; found, 463.1850.

(*Z*)-*N*-(2-(4-(*t*ert-Butyl)phenyl)-3-Fluoro-3-(1*H*-Indol-1-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4q)



68.7 mg, 70% yield, *Z*/*E* = 18:1; eluent with petroleum ether/ethyl acetate = 10:1; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.28–7.32 (m, 3H), 7.12–7.21 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 3.2 Hz, 1H), 6.43 (d, *J* = 3,2 Hz, 1H), 4.32 (s, 2H), 2.74 (s, 3H), 2.43 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 147.6 (d, $^1J_{F\text{-}C}$ = 263.4 Hz), 143.6, 135.7 (d, $^3J_{F\text{-}C}$ = 3.6 Hz), 134.0, 130.0 (d, $^3J_{F\text{-}C}$ = 3.1 Hz), 129.8, 128.8, 127.7, 127.7, 127.5 (d, $^3J_{F\text{-}C}$ = 3.1 Hz), 125.5, 123.4, 121.7, 121.1, 111.4 (d, $^3J_{F\text{-}C}$ = 2.9 Hz), 109.0 (d, $^2J_{F\text{-}C}$ = 23.7 Hz), 105.8 (d, $^4J_{F\text{-}C}$ = 1.2 Hz), 48.1 (d, $^3J_{F\text{-}C}$ = 2.9 Hz), 34.6, 34.1, 31.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.7 (s, 1F); IR (KBr): 3052, 2961, 1688, 1458, 1344, 746 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{29}H_{31}FN_2O_2S$+H, 491.2169; found, 491.2165.

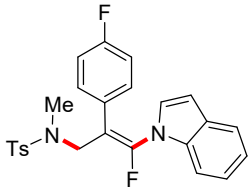
(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-(4-Methoxyphenyl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4r)



57.6 mg, 62% yield, *Z*/*E* = 25:1; eluent with petroleum ether/ethyl acetate = 10:1; brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.33–7.36 (m, 3H), 7.17–7.26 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 3.2 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 3.6 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 2H), 3.74 (s, 3H), 2.78 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.2 (d, $^1J_{F\text{-}C}$ = 262.9 Hz), 143.6, 135.6 (d, $^3J_{F\text{-}C}$ = 3.8 Hz), 134.1, 129.8, 129.4 (d, $^3J_{F\text{-}C}$ = 3.2 Hz), 128.8, 127.7, 127.4 (d, $^4J_{F\text{-}C}$ = 2.1 Hz), 125.3 (d, $^3J_{F\text{-}C}$ = 3.2

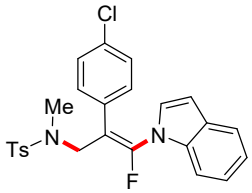
Hz), 123.4, 121.7, 121.2, 114.1, 111.4 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 109.0 (d, $^{2}J_{F\text{-}C}$ = 24.0 Hz), 105.9 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 55.2, 48.1 (d, $^{3}J_{F\text{-}C}$ = 2.7 Hz), 34.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.6 (s, 1F); IR (KBr): 3057, 2928, 1693, 1456, 1340, 743 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{25}FN_2O_3S$+H, 465.1648; found, 465.1649.

(*Z*)-*N*-(3-Fluoro-2-(4-Fluorophenyl)-3-(1*H*-Indol-1-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4s)



56.2 mg, 62% yield, *Z*/*E* = 21:1; eluent with petroleum ether/ethyl acetate = 10:1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.33–7.36 (m, 3H), 7.18–7.26 (m, 2H), 7.03–7.07 (m, 2H), 6.83–6.88 (m, 2H), 6.78 (d, *J* = 3.6 Hz, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 2H), 2.79 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, $^{1}J_{F\text{-}C}$ = 246.6 Hz), 147.8 (d, $^{1}J_{F\text{-}C}$ = 263.4 Hz), 143.8, 135.5 (d, $^{3}J_{F\text{-}C}$ = 3.7 Hz), 134.0, 130.0 (d, $^{3}J_{F\text{-}C}$ = 3.1 Hz), 129.9 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 129.9, 128.8, 127.6, 127.1 (d, $^{4}J_{F\text{-}C}$ = 2.0 Hz), 123.6, 121.9, 121.3, 115.7 (d, $^{1}J_{F\text{-}C}$ = 21.6 Hz), 111.3 (d, $^{3}J_{F\text{-}C}$ = 2.8 Hz), 108.6 (d, $^{2}J_{F\text{-}C}$ = 24.8 Hz), 106.2 (d, $^{4}J_{F\text{-}C}$ = 1.2 Hz), 48.4 (d, $^{3}J_{F\text{-}C}$ = 2.4 Hz), 34.3, 21.6; ^{19}F NMR (376 MHz, DMSO-d_6) δ -87.0 (s, 1F), -114.0 – -113.6(m, 1F); IR (KBr): 3057, 2928, 1694, 1456, 1342, 745 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}F_2N_2O_2S$+H, 453.1448; found, 453.1451.

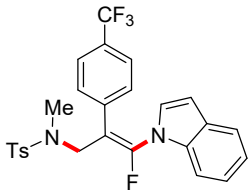
(*Z*)-*N*-(2-(4-Cchlorophenyl)-3-Fluoro-3-(1*H*-Indol-1-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4t)



56.3 mg, 60% yield, *Z*/*E* = 26:1; eluent with petroleum ether/ethyl acetate = 10:1; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 3H), 7.21–7.29 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 3.6 Hz,

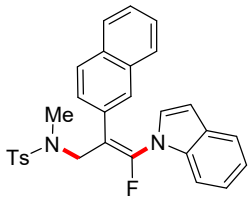
1H), 6.50 (d, J = 3.6 Hz, 1H), 4.34 (d, J = 2.8 Hz, 2H), 2.79 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9 (d, $^1J_{F\text{-}C}$ = 263.4 Hz), 143.8, 135.5 (d, $^3J_{F\text{-}C}$ = 3.7 Hz), 134.0, 133.9, 131.8 (d, $^3J_{F\text{-}C}$ = 3.4 Hz), 129.8, 129.5 (d, $^3J_{F\text{-}C}$ = 3.1 Hz), 128.9, 128.8, 127.6, 127.1 (d, $^4J_{F\text{-}C}$ = 1.9 Hz), 123.6, 122.0, 121.3, 111.3 (d, $^3J_{F\text{-}C}$ = 2.9 Hz), 108.4 (d, $^2J_{F\text{-}C}$ = 24.9 Hz), 106.3 (d, $^4J_{F\text{-}C}$ = 1.2 Hz), 48.2 (d, $^3J_{F\text{-}C}$ = 2.6 Hz), 34.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.6 (s, 1F); IR (KBr): 3056, 2928, 1692, 1455, 1342, 746 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{25}H_{22}ClFN_2O_2S$+H, 469.1153; found, 469.1151.

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-(4-(Trifluoromethyl)phenyl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4u)



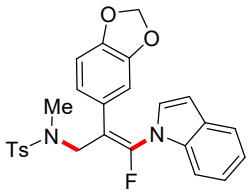
61.3 mg, 61% yield, Z/E > 30:1; eluent with petroleum ether/ethyl acetate = 10:1; yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.4 Hz, 3H), 7.45 (d, J = 8.0 Hz, 2H), 7.33–7.38 (m, 3H), 7.28 (d, J = 3.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 3.2 Hz, 1H), 4.32 (s, 2H), 2.71 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.4 (d, $^1J_{F\text{-}C}$ = 266.5 Hz), 144.1, 138.3 (d, $^4J_{F\text{-}C}$ = 2.1 Hz), 135.6 (d, $^3J_{F\text{-}C}$ = 3.7 Hz), 133.7, 130.4, 129.4 (d, $^3J_{F\text{-}C}$ = 2.8 Hz), 128.7, 128.6 (d, $^3J_{F\text{-}C}$ = 2.6 Hz), 128.5 (q, $^2J_{F\text{-}C}$ = 31.6 Hz), 127.8, 125.5 (d, $^3J_{F\text{-}C}$ = 3.7 Hz), 124.4 (q, $^2J_{F\text{-}C}$ = 270.6 Hz), 123.7, 122.1, 121.5, 111.3, 111.1 (d, $^2J_{F\text{-}C}$ = 24.9 Hz), 106.4, 48.9 (d, $^3J_{F\text{-}C}$ = 2.6 Hz), 35.0, 21.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.2 (s, 3F), -85.5 (s, 1F); IR (KBr): 3059, 2928, 1690, 1456, 1330, 746 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{22}F_4N_2O_2S$+H, 503.1416; found, 503.1413.

(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-(Naphthalen-2-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4v)



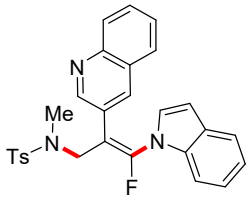
58.2 mg, 60% yield, *Z*/*E* = 17:1; eluent with petroleum ether/ethyl acetate = 10:1; brown solid, mp: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.68 (s, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 4.8 Hz, 3H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.18–7.25 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 4.50 (s, 2H), 2.85 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2 (d, $^{1}J_{F\text{-}C}$ = 264.0 Hz), 143.5, 135.6 (d, $^{3}J_{F\text{-}C}$ = 3.7 Hz), 134.2, 133.3, 132.7, 130.8 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 129.7, 128.9, 128.3, 127.6 (d, $^{3}J_{F\text{-}C}$ = 3.9 Hz), 127.6, 127.5, 126.4, 126.3, 125.7 (d, $^{4}J_{F\text{-}C}$ = 2.2 Hz), 123.5, 121.8, 121.2, 111.5 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 109.0 (d, $^{2}J_{F\text{-}C}$ = 24.0 Hz), 106.1 (d, $^{4}J_{F\text{-}C}$ = 1.2 Hz), 48.4 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 34.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.3 (s, 1F); IR (KBr): 3055, 2925, 1689, 1456, 1340, 744 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{29}H_{25}FN_2O_2S$+H, 485.1699; found, 485.1693.

(*Z*)-*N*-(2-(Benzo[*d*][1,3]dioxol-5-yl)-3-Fluoro-3-(1*H*-Indol-1-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4w)



59.3 mg, 62% yield *Z*/*E* = 12:1; eluent with petroleum ether/ethyl acetate = 6:1; brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.29–7.32 (m, 3H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.77 (d, *J* = 3.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 6.43–6.46 (m, 2H), 5.83 (s, 2H), 4.25 (s, 2H), 2.75 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 147.5 (d, $^{1}J_{F\text{-}C}$ = 265.4 Hz), 147.3, 143.7, 135.6 (d, $^{3}J_{F\text{-}C}$ = 3.6 Hz), 134.1, 129.8, 128.8, 127.6, 127.3 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 126.9 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 123.5, 122.1 (d, $^{3}J_{F\text{-}C}$ = 3.4 Hz), 121.7, 121.2, 111.3 (d, $^{3}J_{F\text{-}C}$ = 3.0 Hz), 109.0 (d, $^{2}J_{F\text{-}C}$ = 24.7 Hz), 108.5, 108.5 (d, $^{3}J_{F\text{-}C}$ = 3.3 Hz), 106.0, 101.2, 48.5 (d, $^{4}J_{F\text{-}C}$ = 2.6 Hz), 34.2, 21.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ -89.2 (s, 1F); IR (KBr): 3059, 2900, 1693, 1451, 1340, 746 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{26}H_{23}FN_2O_4S$+H, 479.1441; found, 479.1446.

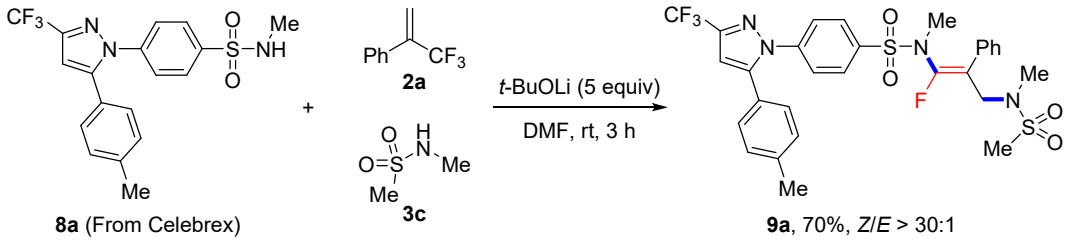
(*Z*)-*N*-(3-Fluoro-3-(1*H*-Indol-1-yl)-2-(Quinolin-3-yl)allyl)-*N*,4-Dimethylbenzenesulfonamide (4x)



56.3 mg, 58% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 6:1; yellow solid, mp: 143–144 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.42 (s, 1H), 8.23 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.67–7.72 (m, 3H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.38– 7.43 (m, 4H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 4.43 (s, 2H), 2.77 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 147.5 (d, $^{1}J_{F\text{-}C}$ = 267.6 Hz), 146.9, 144.1, 135.6 (d, $^{3}J_{F\text{-}C}$ = 3.9 Hz), 135.6 (d, $^{3}J_{F\text{-}C}$ = 3.8 Hz), 133.9, 130.4, 129.0, 128.7 (d, $^{3}J_{F\text{-}C}$ = 2.9 Hz), 128.6, 128.5, 127.7, 127.4, 127.3 (d, $^{3}J_{F\text{-}C}$ = 3.7 Hz), 123.8, 122.1, 121.5, 111.3, 109.7 (d, $^{2}J_{F\text{-}C}$ = 27.4 Hz), 106.5, 48.9, 35.2, 21.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -85.2 (s, 1F); IR (KBr): 3052, 2937, 1692, 1460, 1328, 741 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. For $C_{28}H_{24}FN_3O_2S$+H, 486.1652; found, 486.1660.

E. Late-stage Functionalization of Drug Molecules

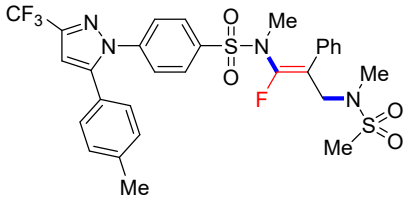
The Synthesis of 9a



t-BuOLi (5 equiv) was added to the solution of *N*-methylsulfonamide **8a** (0.2 mmol), (trifluoromethyl)alkene **2a** (4 equiv) and DMF (4 mL). Then *N*-methylmethanesulfonamide **3c** (5 equiv) was added by portions to the mixture within 20 minutes. The reaction mixture was vigorously stirred at room temperature for 3 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate =3:1) provided the

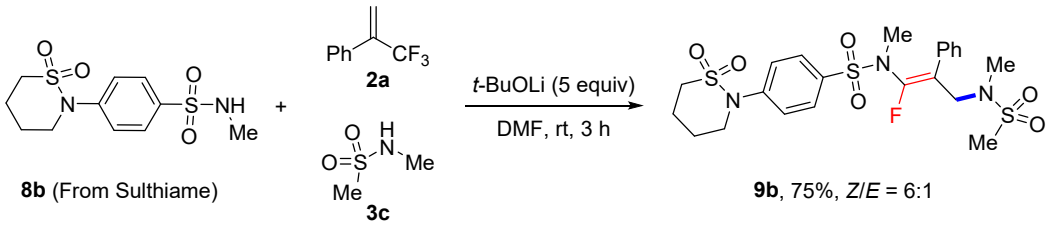
product **9a** in 70% isolated yield.

(*Z*)-*N*-(1-Fluoro-3-(*N*-Methylmethylsulfonamido)-2-Phenylprop-1-en-1-yl)-*N*-Methyl-4-(5-(*p*-Tolyl)-3-(Trifluoromethyl)-1*H*-Pyrazol-1-yl)benzenesulfonamide (9a)



89.1 mg, 70% yield, *Z*/*E* > 30:1; eluent with petroleum ether/ethyl acetate = 3:1; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.37–7.45 (m, 6H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 4.31 (d, *J* = 2.0 Hz, 2H), 2.84 (s, 3H), 2.77 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1 (d, $^{1}J_{F\text{-}C}$ = 279.4 Hz), 145.4, 144.6 (q, $^{2}J_{F\text{-}C}$ = 30.8 Hz), 143.2, 140.0, 137.2, 133.7 (d, $^{3}J_{F\text{-}C}$ = 3.2 Hz), 129.9, 129.1 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 129.0, 128.8, 128.7 (d, $^{4}J_{F\text{-}C}$ = 1.2 Hz), 128.7, 125.8, 125.5, 120.9 (q, $^{1}J_{F\text{-}C}$ = 265.9 Hz), 116.6 (d, *J* = 27.7 Hz), 106.6, 48.6 (d, $^{3}J_{F\text{-}C}$ = 1.8 Hz), 37.0, 36.2, 33.8, 21.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5 (d, *J* = 3.8 Hz, 3F), -91.8 (s, 1F); IR (KBr): 3054, 2939, 1704, 1474, 1118 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{29}H_{28}F_4N_4O_4S_2$+H, 637.1561; found, 637.1552.

The Synthesis of 9b

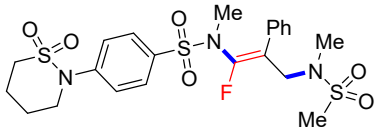


8b (From Sulthiame) + **2a** + **3c**; *t*-BuOLi (5 equiv), DMF, rt, 3 h → **9b**, 75%, *Z*/*E* = 6:1

t-BuOLi (5 equiv) was added to the solution of *N*-methylsulfonamide **8b** (0.2 mmol), (trifluoromethyl)alkene **2a** (4 equiv) and DMF (4 mL). Then *N*-methylmethanesulfonamide **3c** (5 equiv.) was added by portions to the mixture within 20 minutes. The reaction mixture was vigorously stirred at room temperature for 3 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 2:1) provided the

product **9b** in 75% isolated yield.

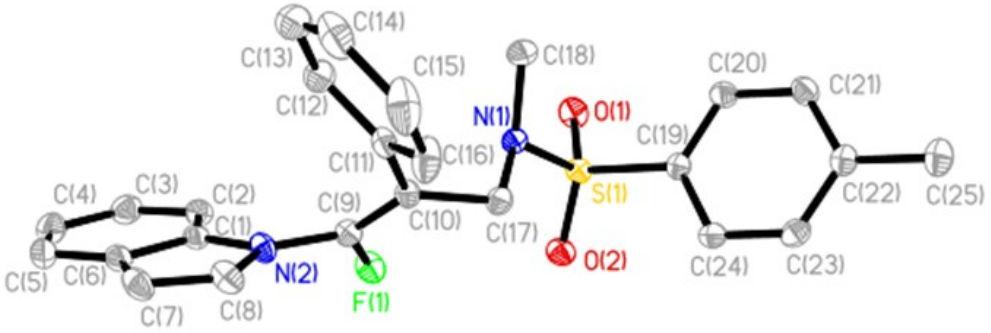
(*Z*)-4-(1,1-Dioxido-1,2-Thiazinan-2-yl)-*N*-(1-Fluoro-3-(*N*-Methylmethylsulfonamido)-2-Phenylprop-1-en-1-yl)-*N*-Methylbenzenesulfonamide (9b)



81.8 mg, 75% yield, *Z*/*E* = 6:1; eluent with petroleum ether/ethyl acetate = 2:1; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.70 (m, 2H), 7.34–7.42 (m, 7H), 4.33 (s, 2H), 3.81 (s, 2H), 3.22 (s, 2H), 2.85 (d, *J* = 2.8 Hz, 3H), 2.78 (s, 3H), 2.39 (s, 3H), 2.32–2.37 (m, 2H), 1.93 (d, *J* = 3.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (d, $^{1}J_{F\text{-}C}$ = 279.7 Hz), 145.2, 135.6, 133.7 (d, $^{3}J_{F\text{-}C}$ = 2.7 Hz), 128.9, 128.9, 128.7, 128.7, 126.3, 116.2 (d, $^{2}J_{F\text{-}C}$ = 28.0 Hz), 53.0, 51.0, 48.6 (d, $^{3}J_{F\text{-}C}$ = 2.1 Hz), 36.9, 36.2, 33.7, 24.4, 24.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.9 (s, 1F); IR (KBr): 3043, 2931, 1475, 1369, 1158 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{22}H_{28}FN_3O_6S_3$+H, 546.1197; found, 546.1186.

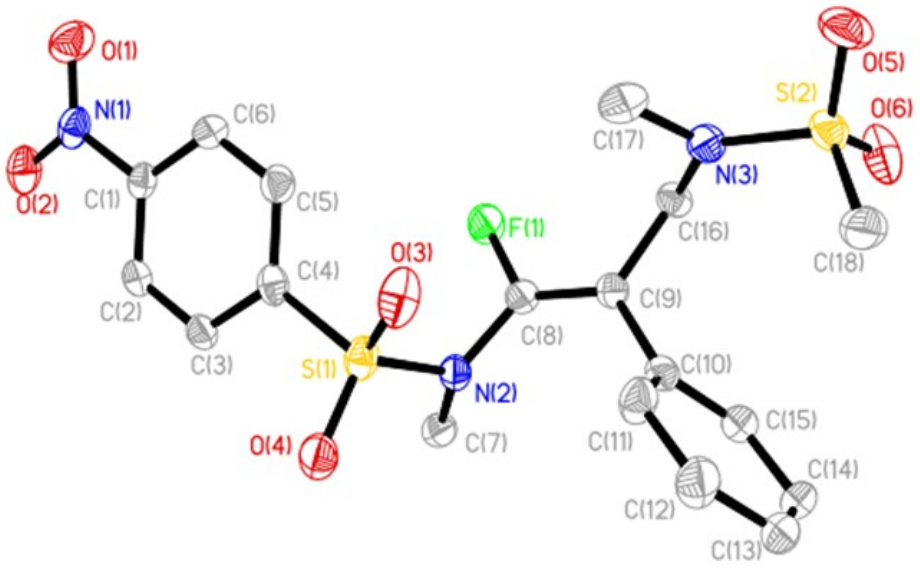
F. X-ray Crystallographic Data

The X-ray crystallographic structures for **4a**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2036948.



Empirical formula	$C_{25}H_{24}FN_2O_2S$
Formula weight	434.51
Temperature	170 K
Crystal system, Space group	Triclinic, P -1
Unit cell dimensions	a = 10.5052(14) Å alpha = 96.383(5) deg. b = 10.7663(14) Å beta = 108.432(5) deg. c = 11.1339(15) Å gamma = 110.430(4) deg.
Volume	1084.2(3) $Å^3$
Z	2
ρ_{calc}g/cm3	1.331
μ/mm 1	0.183 mm^{1}
F(000)	456.0
Crystal size	0.16 × 0.11 × 0.08 mm^3
Radiation	MoK\a (λ = 0.71073)
Theta range for data collection	2.237 to 26.329 deg.
Index ranges	-13 ≤ h ≤ 13, -13≤ k ≤12, -13 ≤ l ≤ 13
Reflections collected	12498
Independent reflections	3563 [R_{int} = 0.0309, R_{sigma} = 0.0360]
Data/restraints/parameters	3563/0/282
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0952
Final R indexes [all data]	R_1 = 0.0563, wR_2 = 0.1042

The X-ray crystallographic structures for **4n**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2036972.

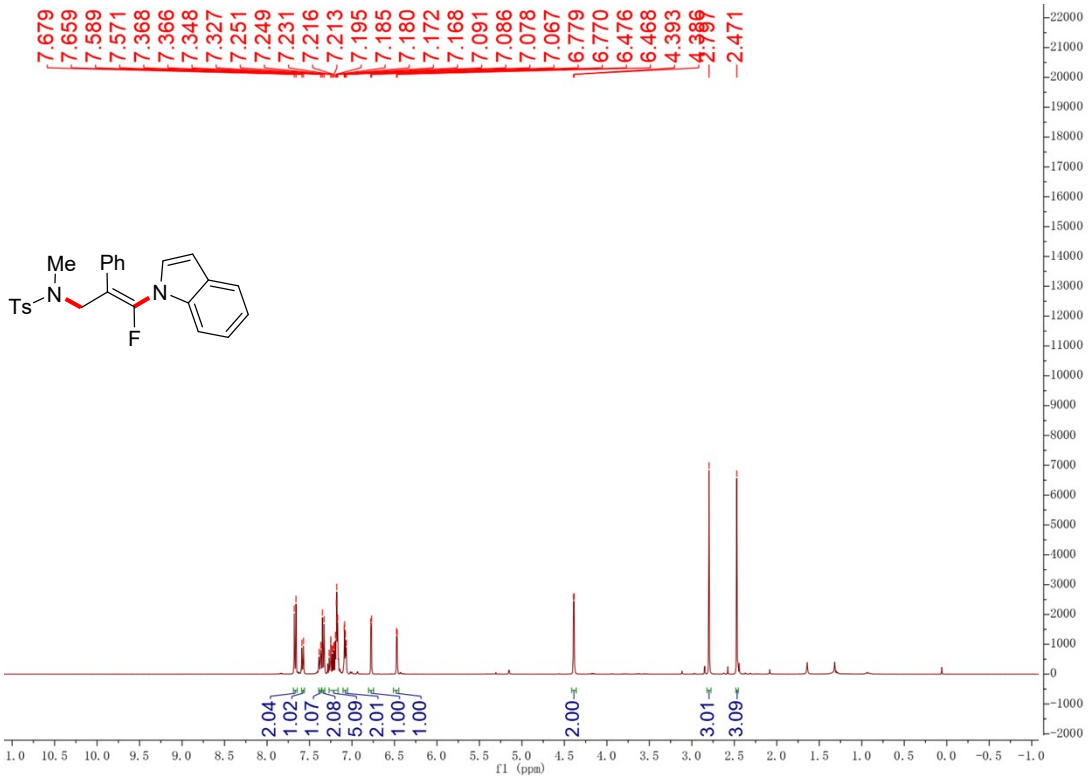


Empirical formula	$C_{18}H_{20}FN_3O_6S_2$
Formula weight	457.49
Temperature	170 K
Crystal system, Space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 6.3919(6) Å alpha = 90 deg. b = 13.7713(13) Å beta = 94.388(3) deg. c = 23.551(2) Å gamma = 90 deg.
Volume	2067.0(3) $Å^3$
Z	4
ρ_{calc}g/cm3	1.470
μ/mm 1	0.307 mm^{1}
F(000)	952
Crystal size	0.19 × 0.12 × 0.05 mm^3
Radiation	MoK\a (λ = 0.71073)
Theta range for data collection	2.994 to 26.123 deg.
Index ranges	-7 ≤ h ≤ 7, -17 ≤ k ≤ 17, -29 ≤ l ≤ 28
Reflections collected	22873
Independent reflections	4207 [R_{int} = 0.0687, R_{sigma} = 0.0526]
Data/restraints/parameters	4207/0/274
Goodness-of-fit on F^2	1.056

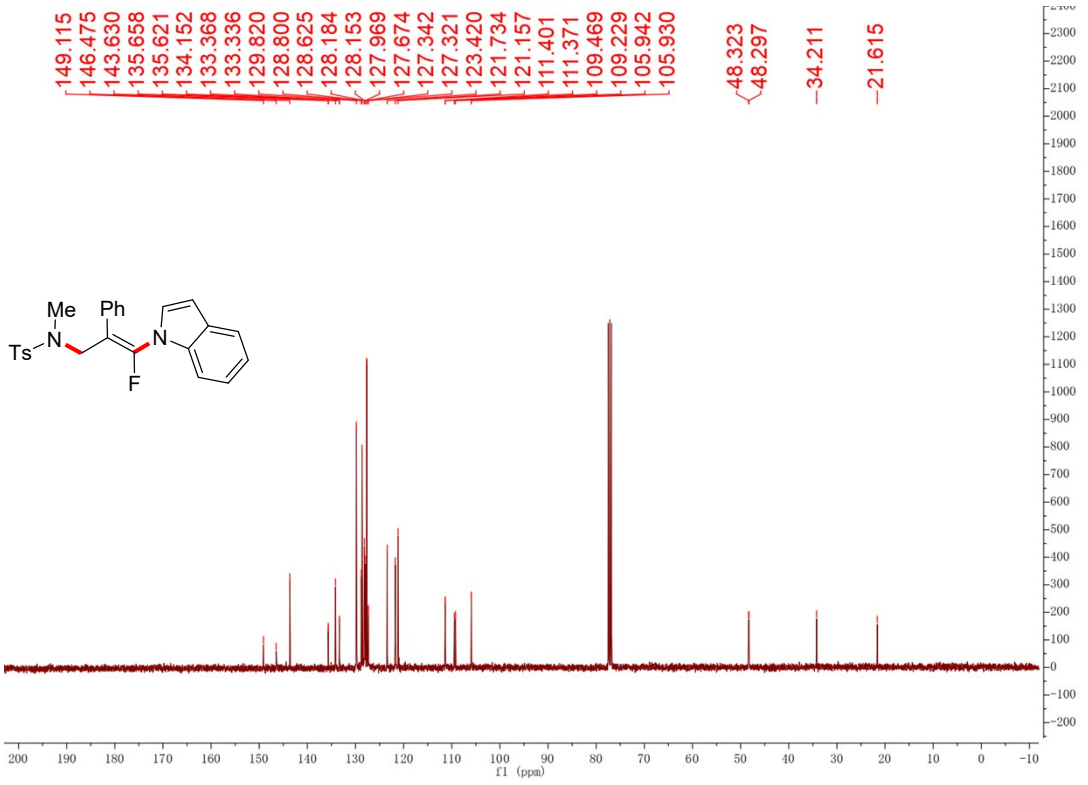
Final R indexes [I>=2σ (I)]	R_1 = 0.0757, wR_2 = 0.2276
Final R indexes [all data]	R_1 = 0.1071, wR_2 = 0.2505

G. NMR Spectra of New Compounds

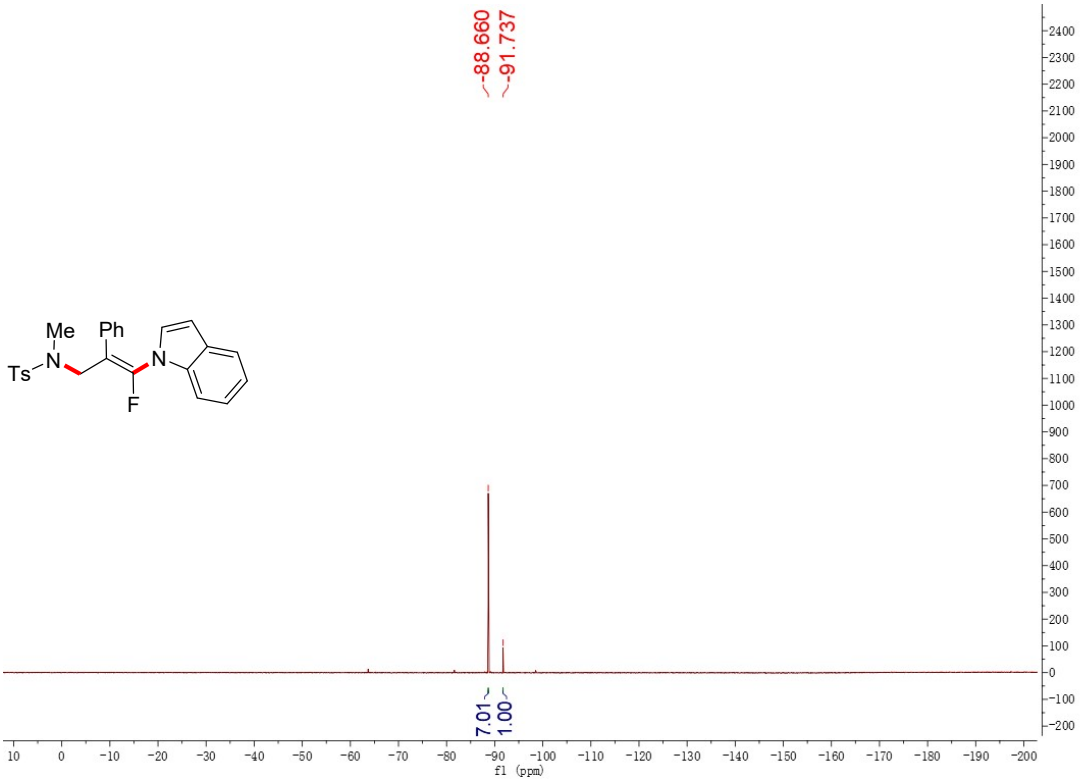
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4a



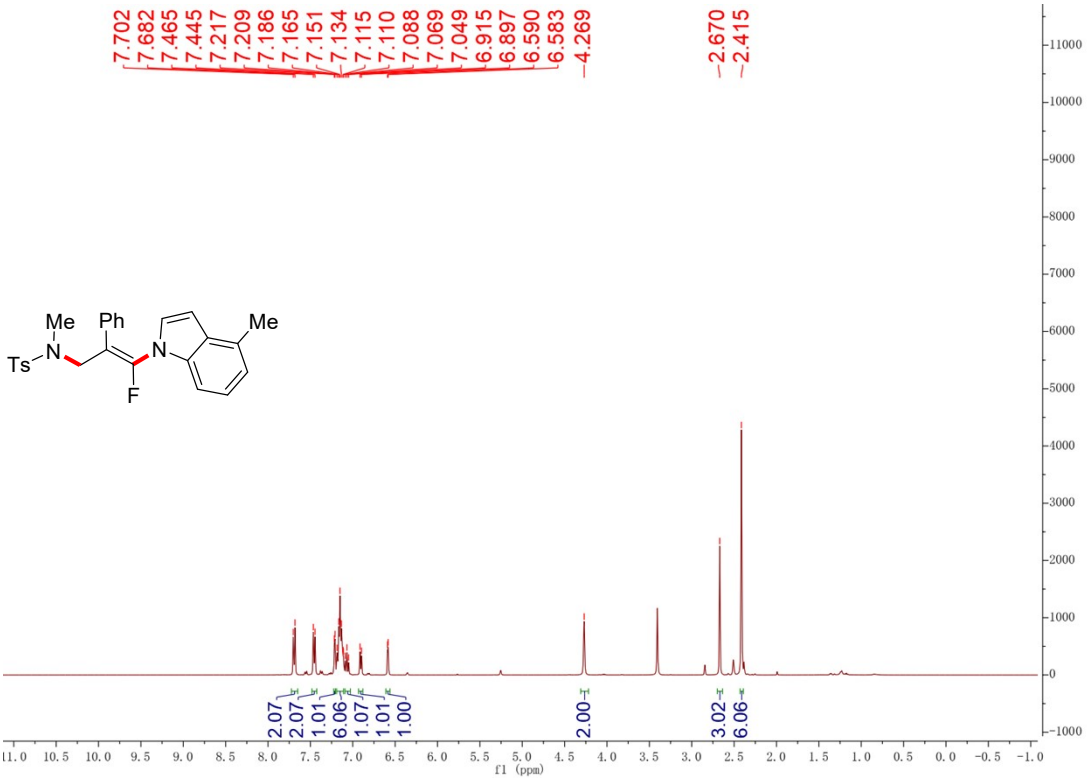
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4a



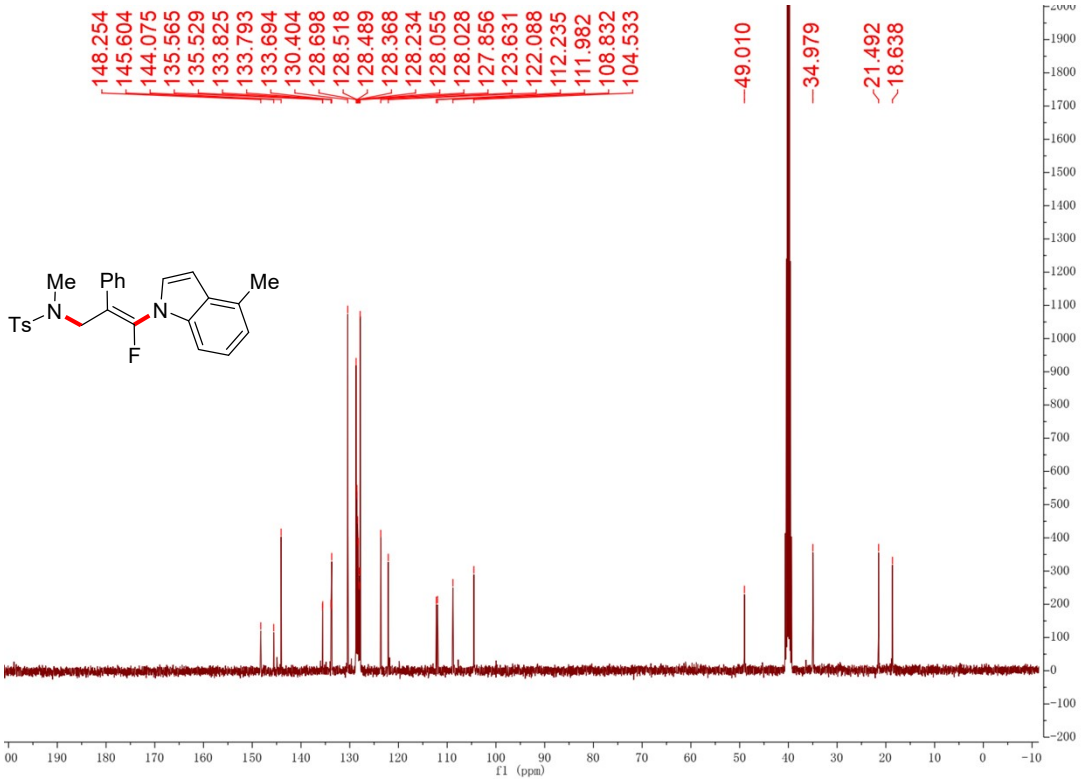
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4a



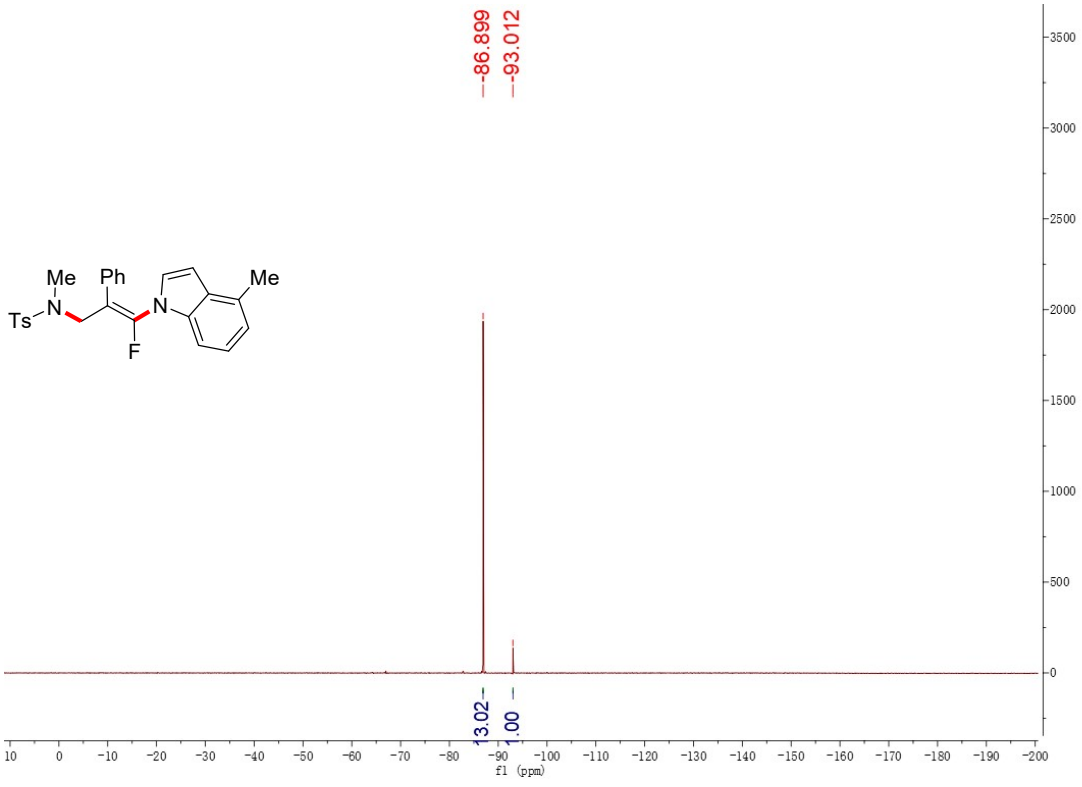
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4b



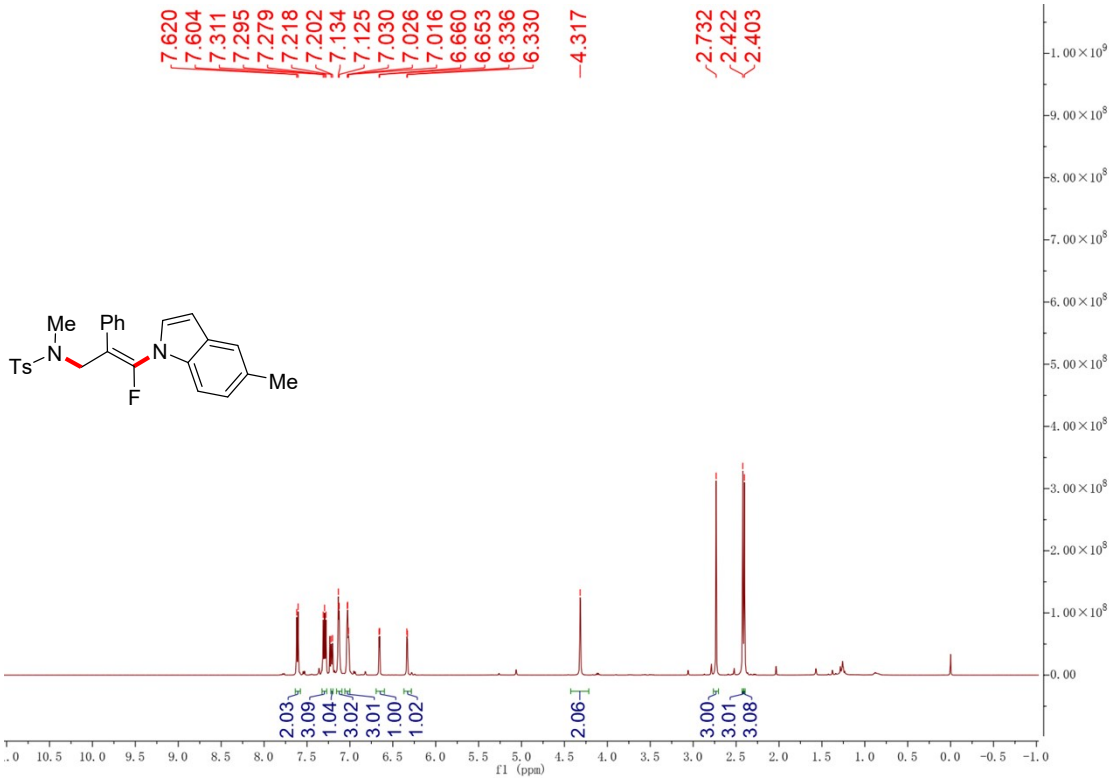
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4b



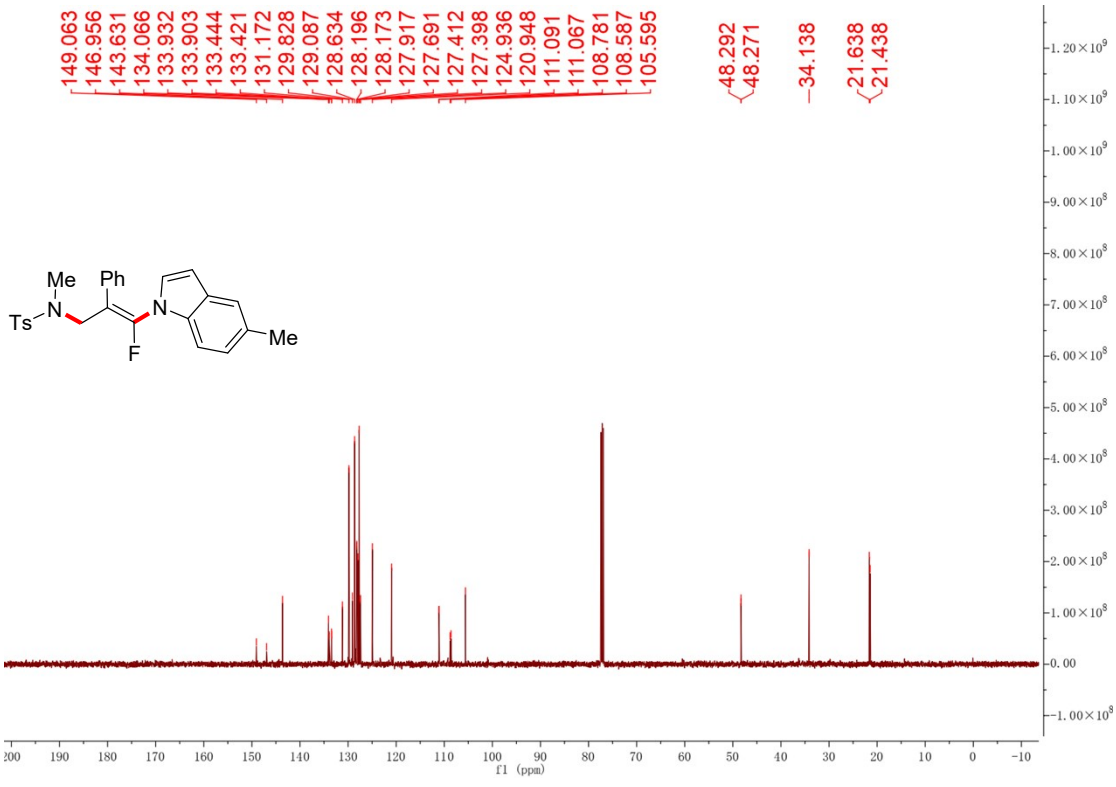
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4b



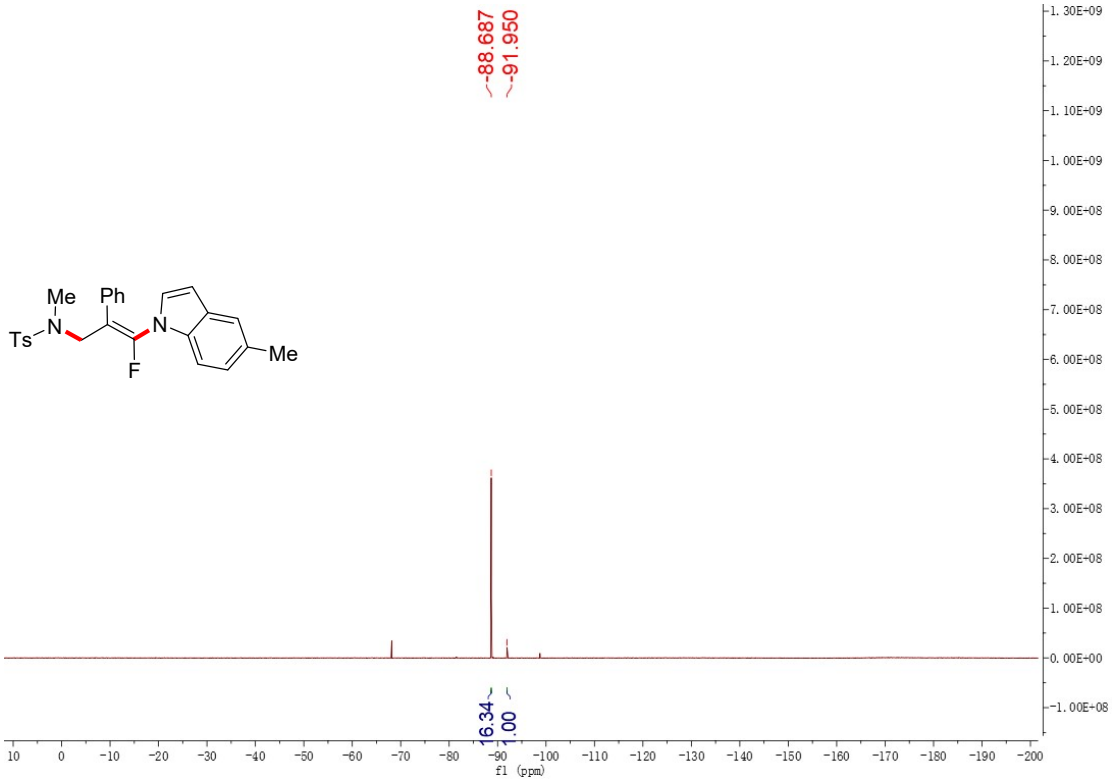
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 4c



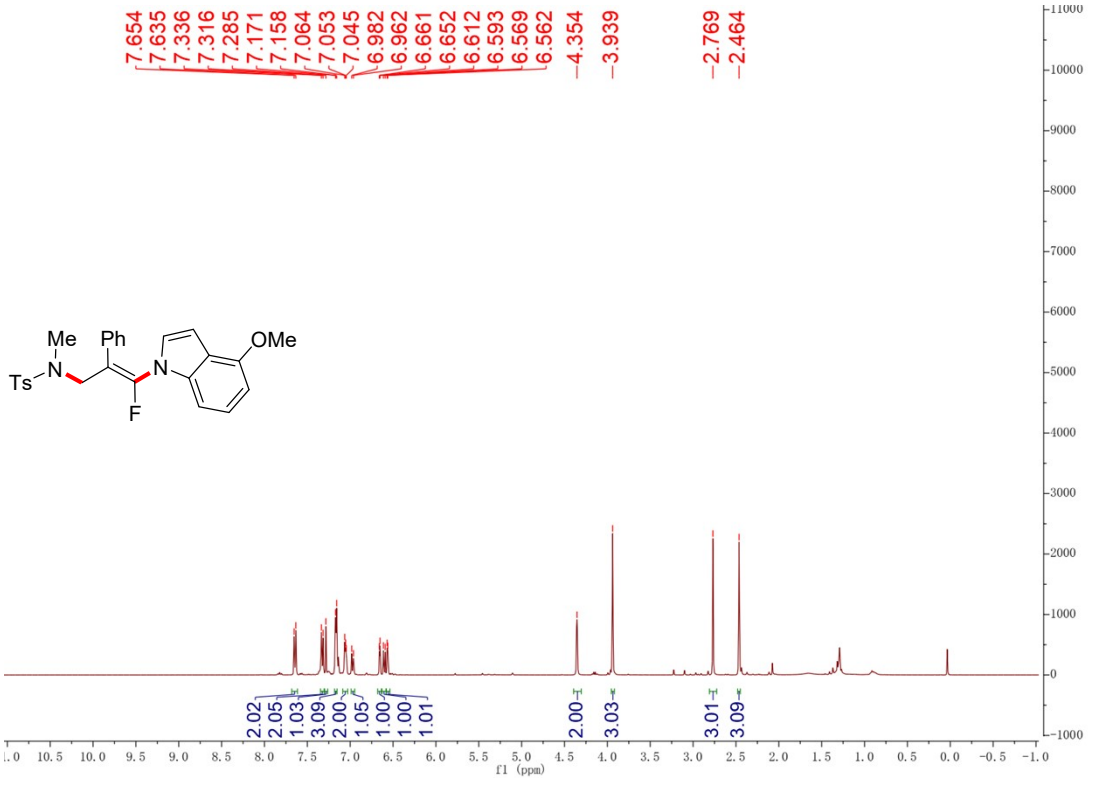
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 4c



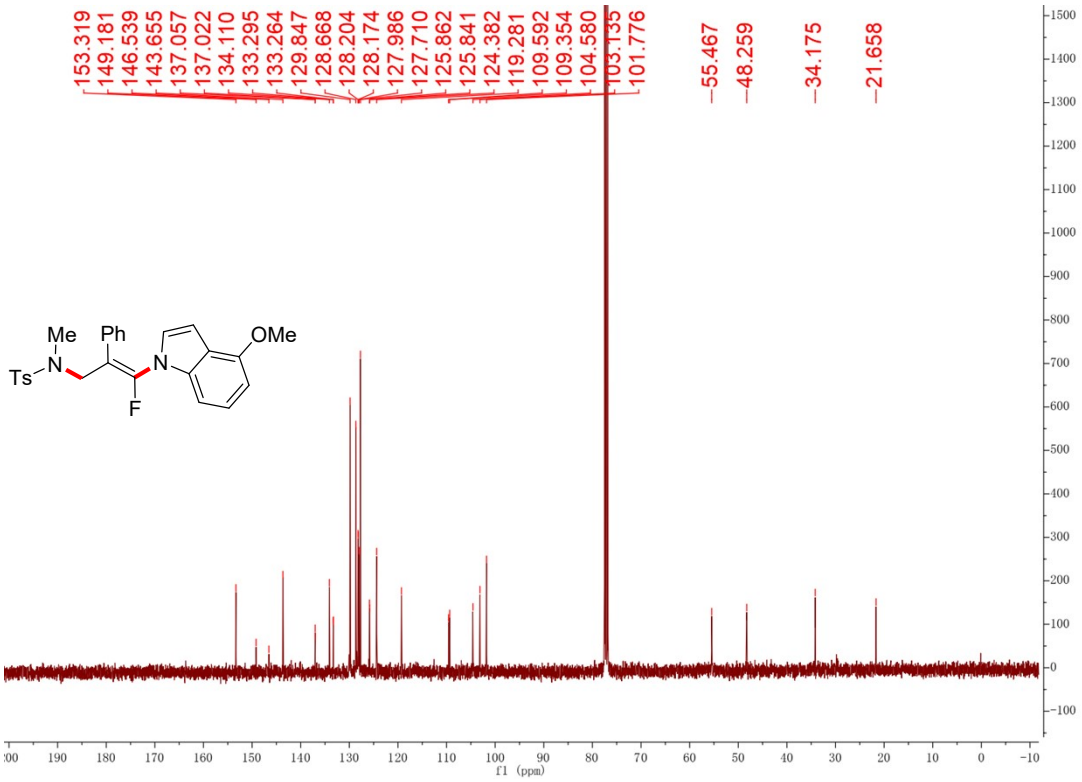
^{19}F NMR (471 MHz, $CDCl_3$) spectrum for 4c



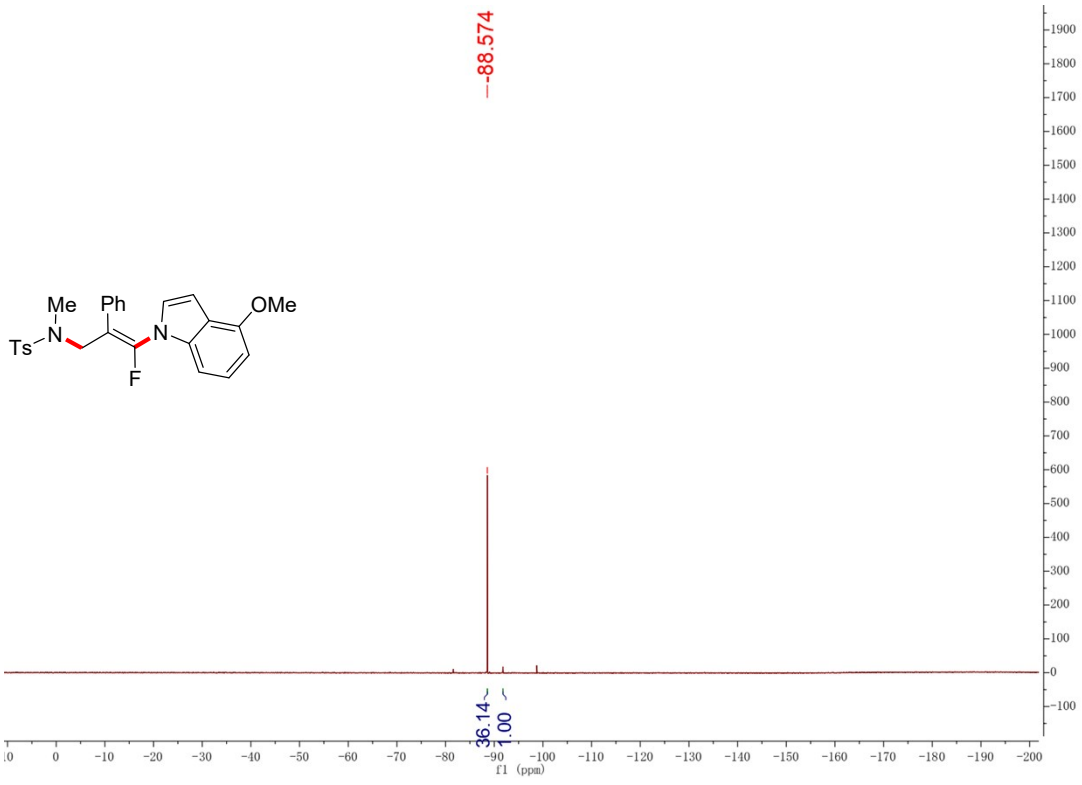
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4d



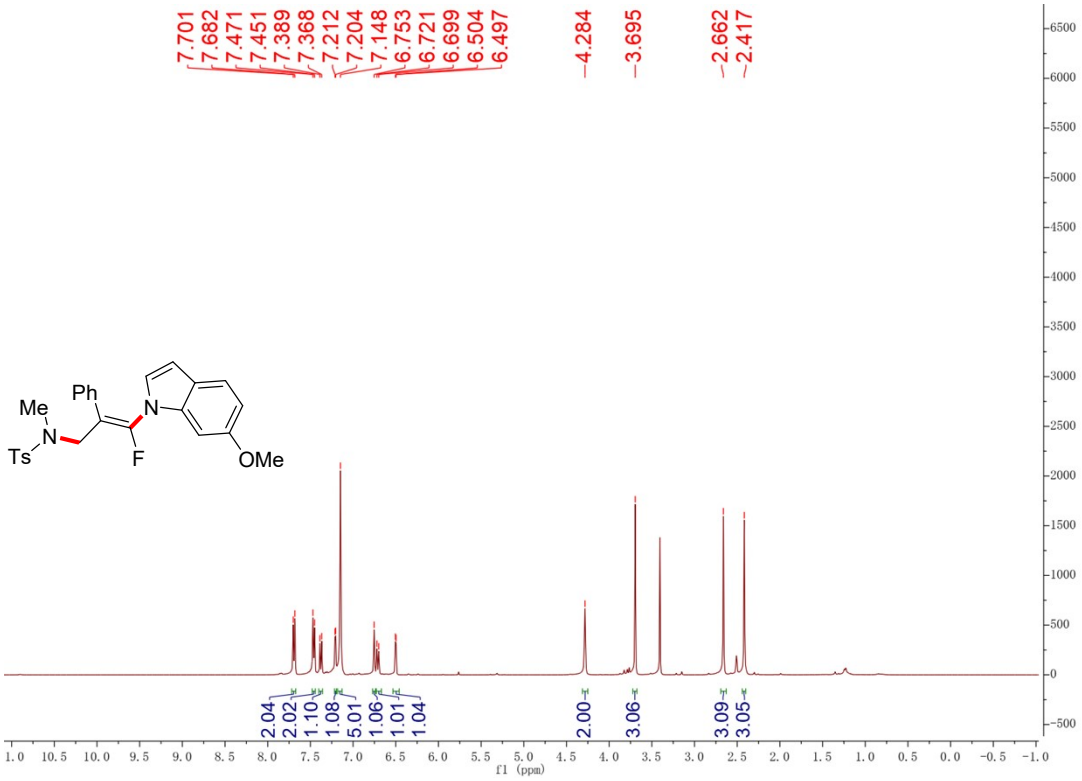
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4d



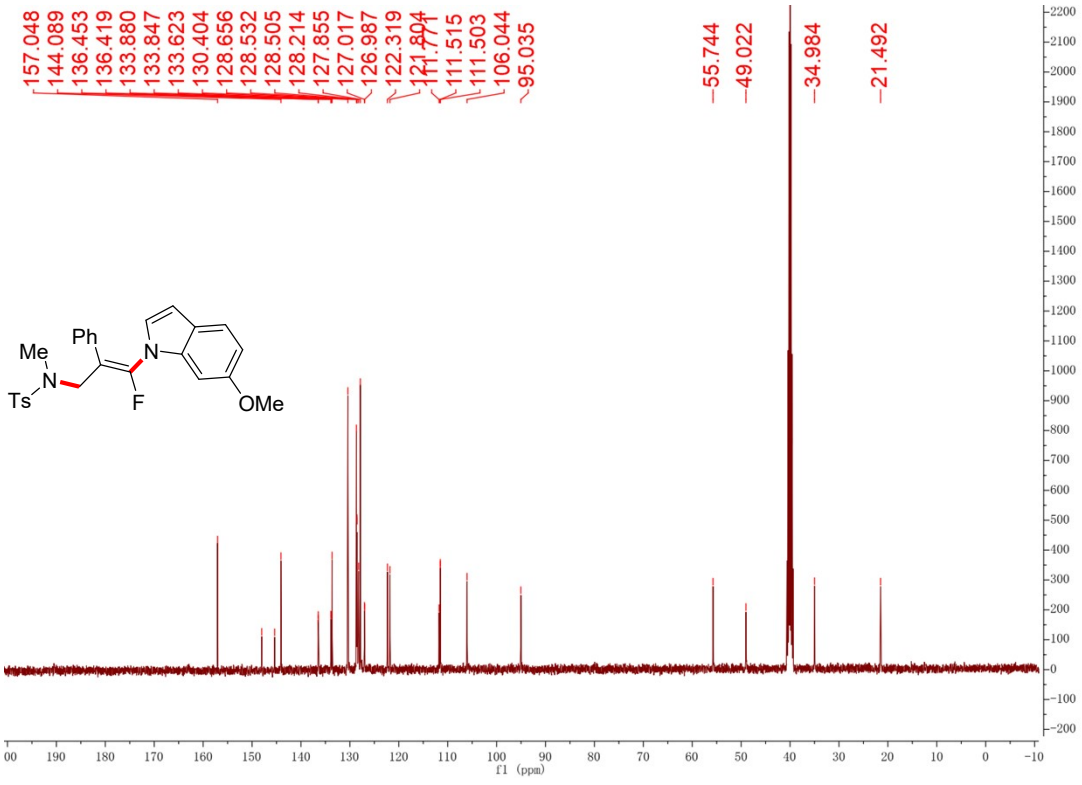
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4d



^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4e

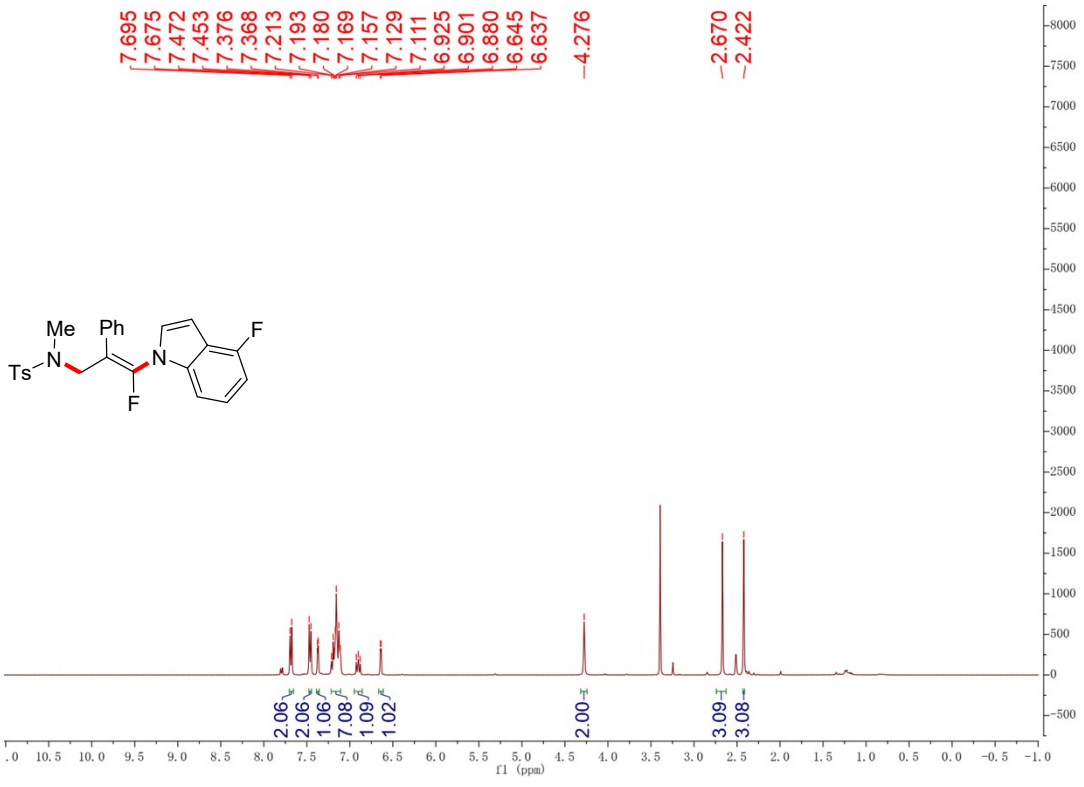


^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4e

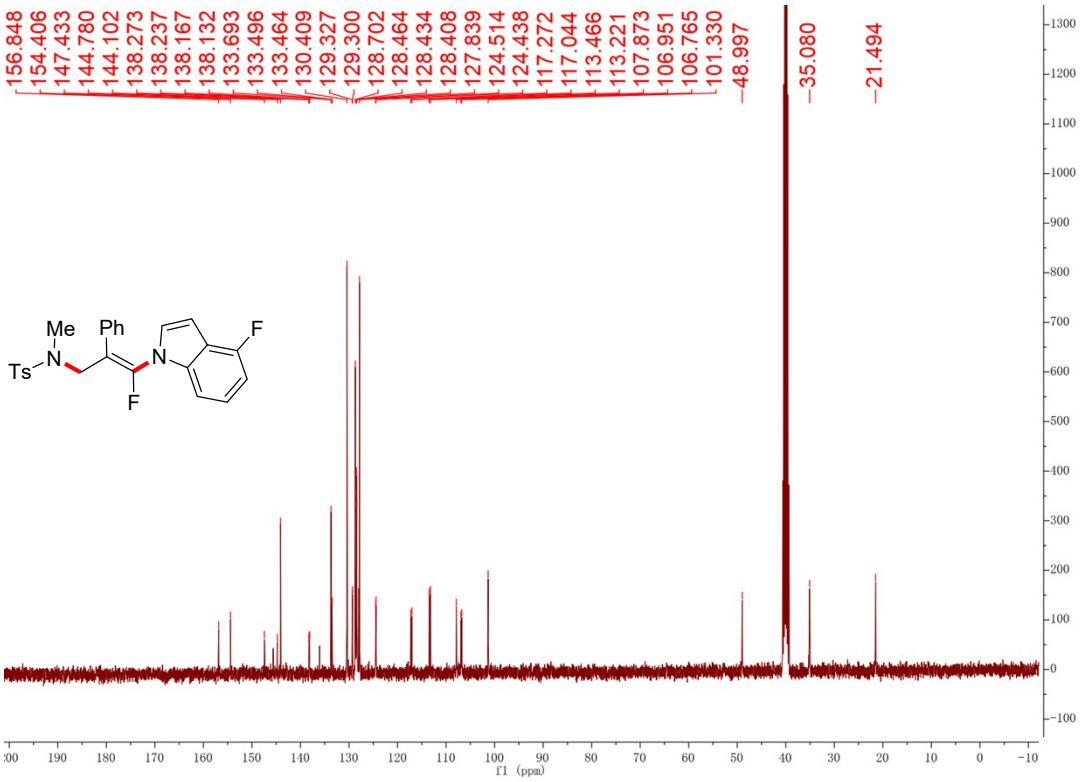


^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4e

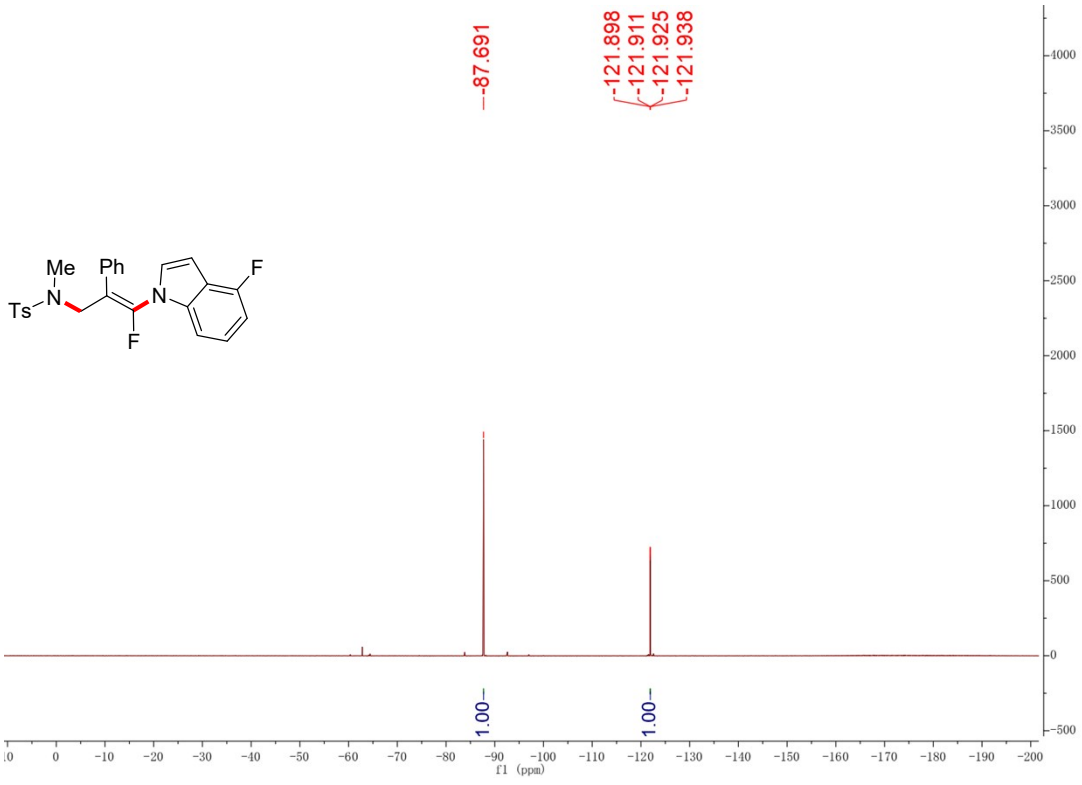
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4f



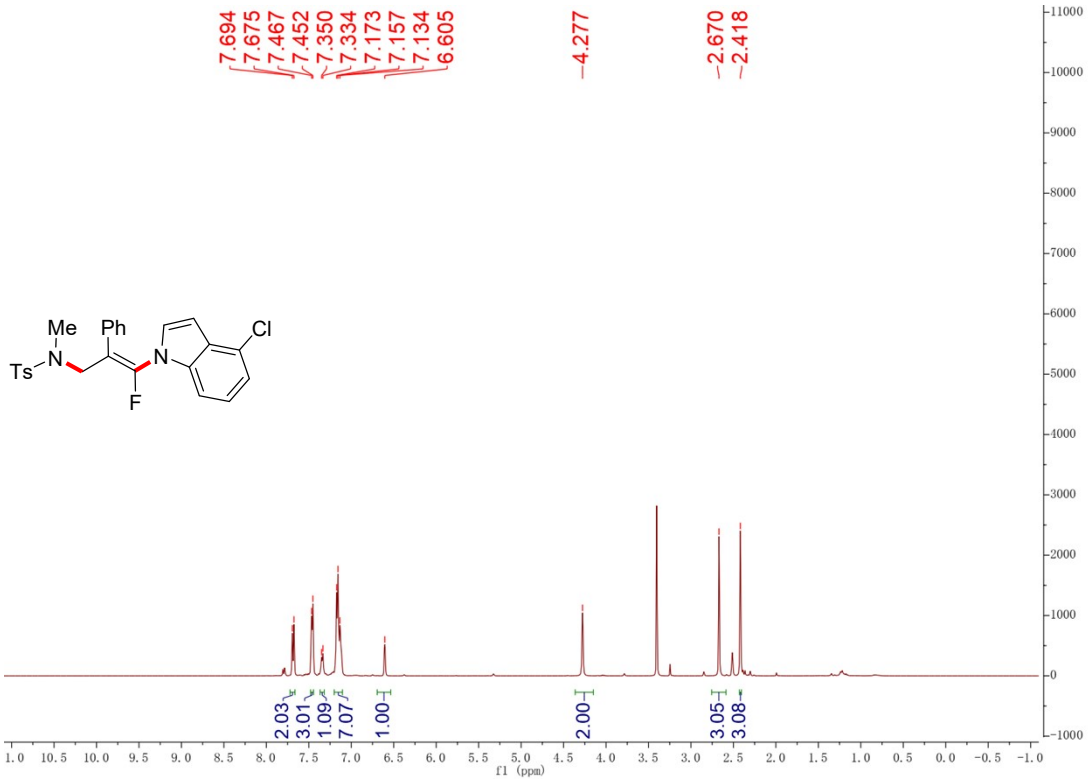
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4f



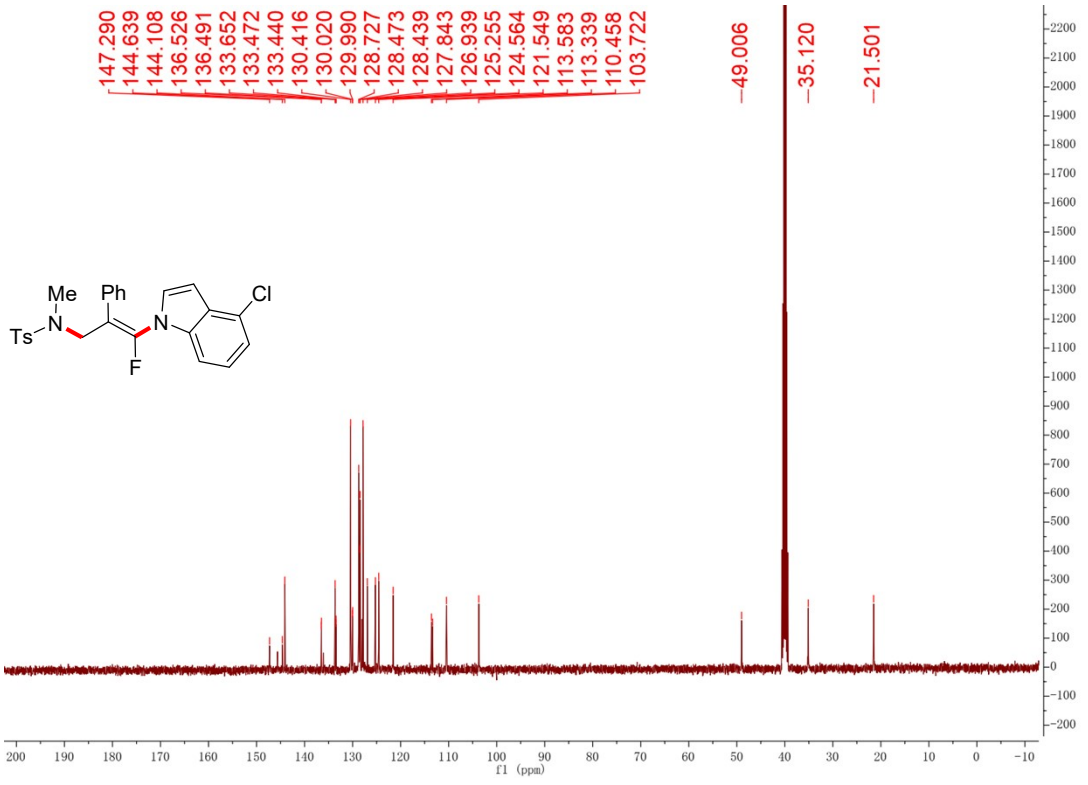
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4f



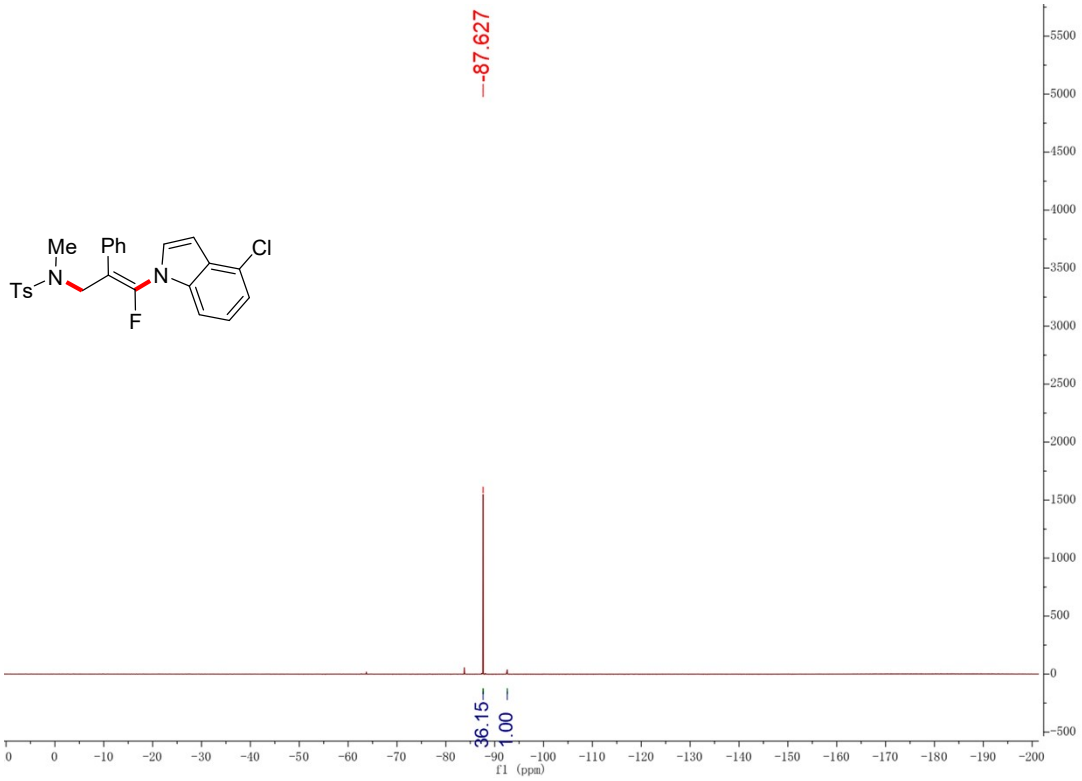
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4g



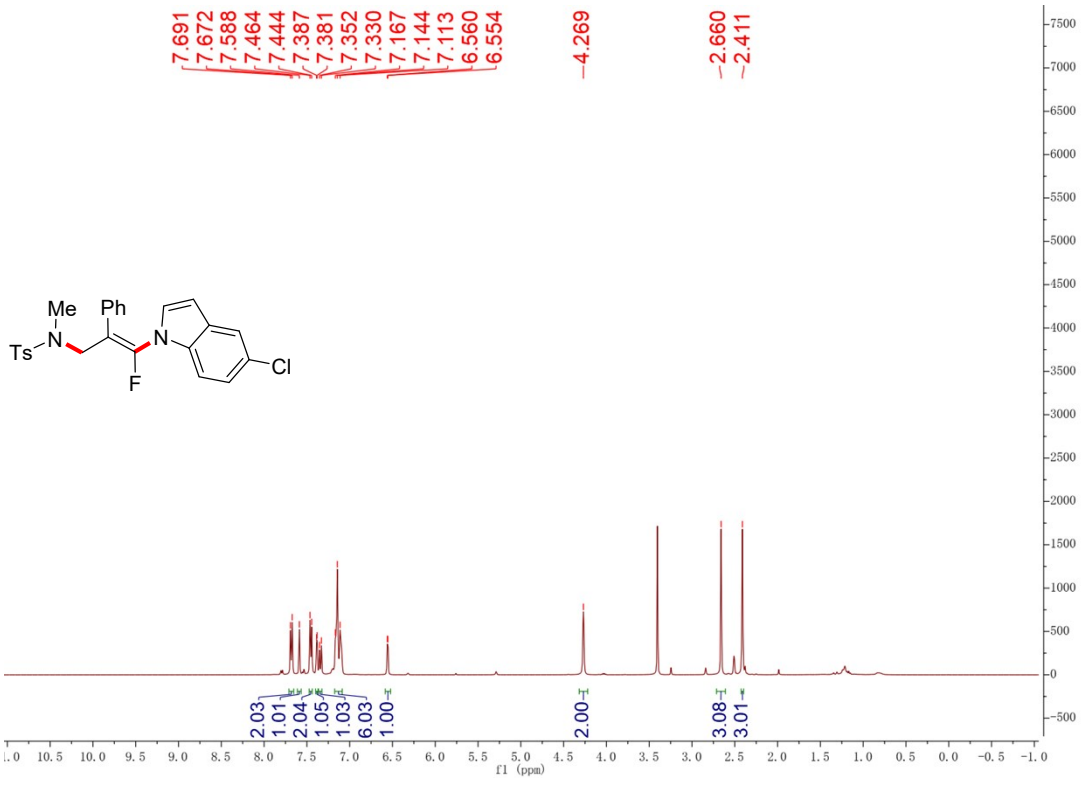
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4g



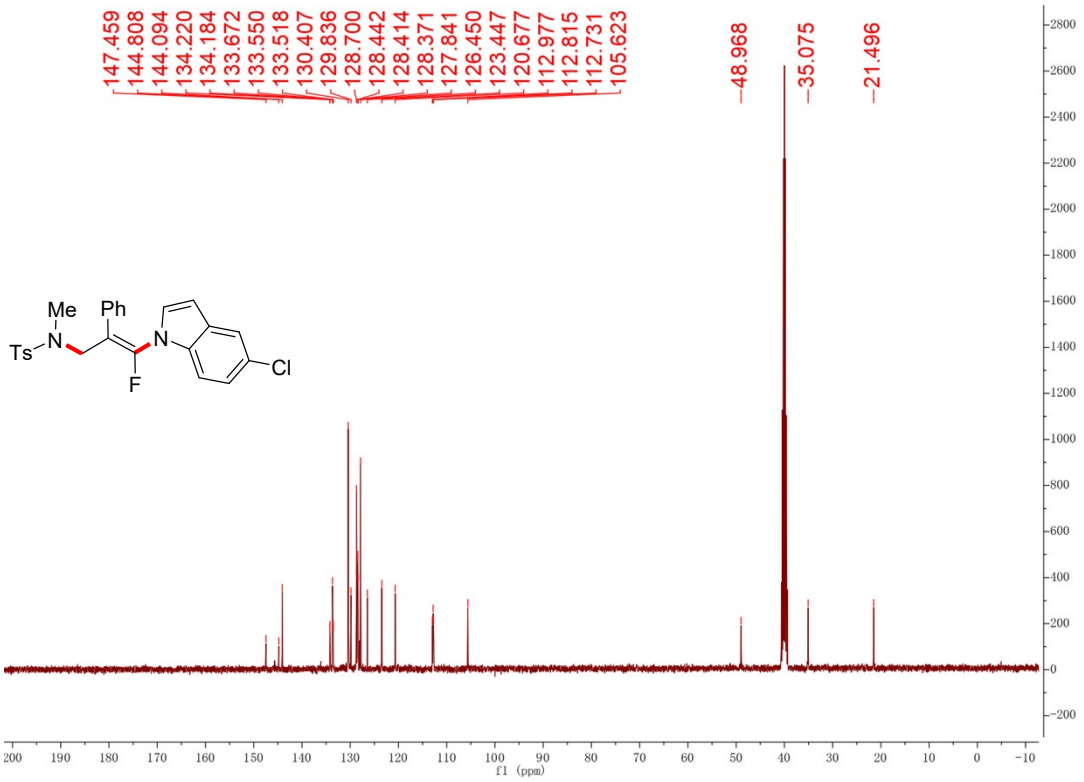
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4g



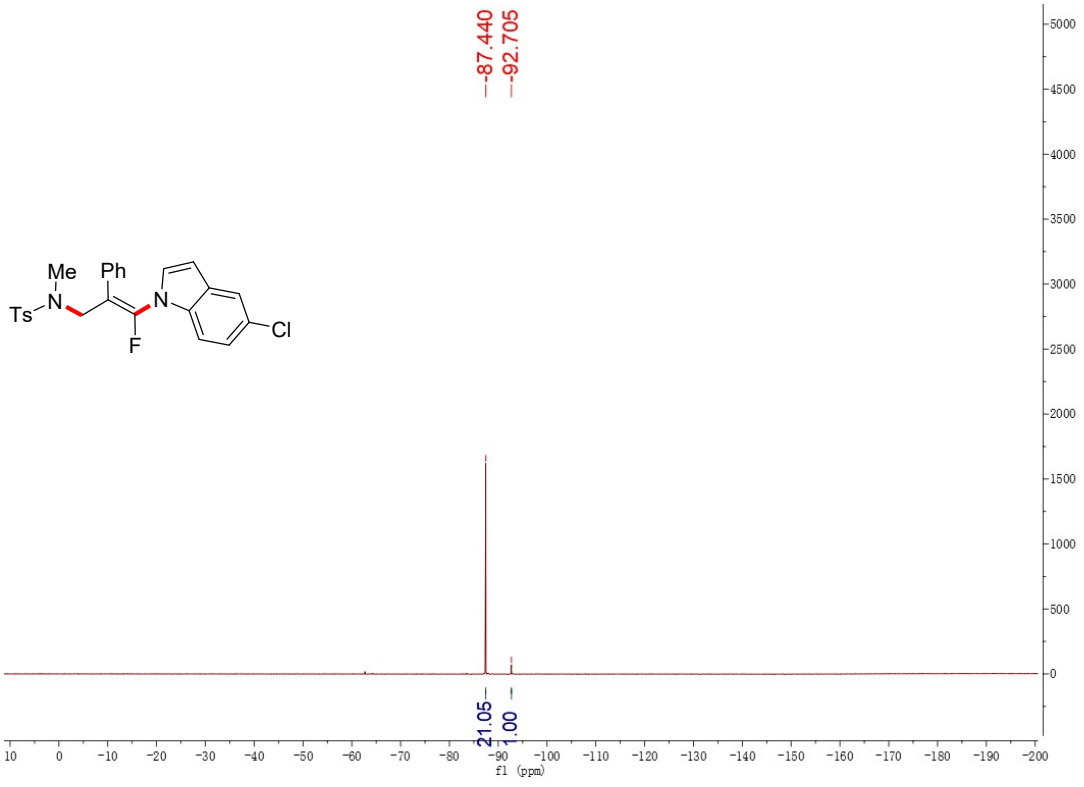
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4h



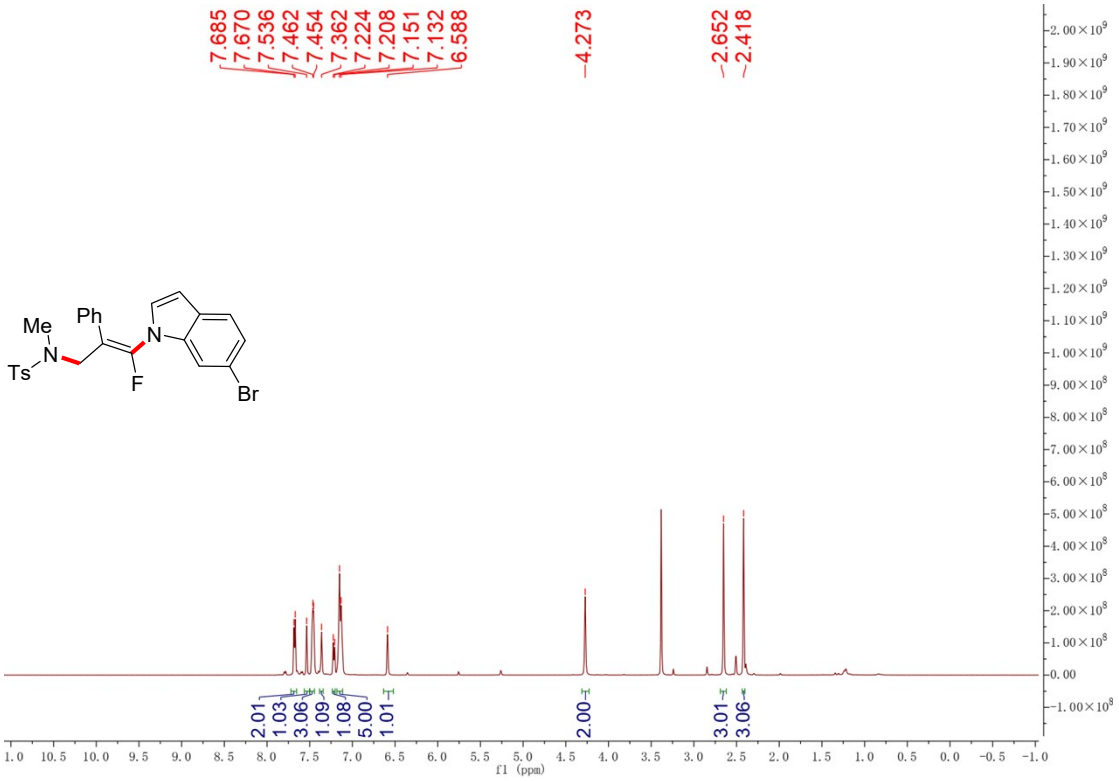
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4h



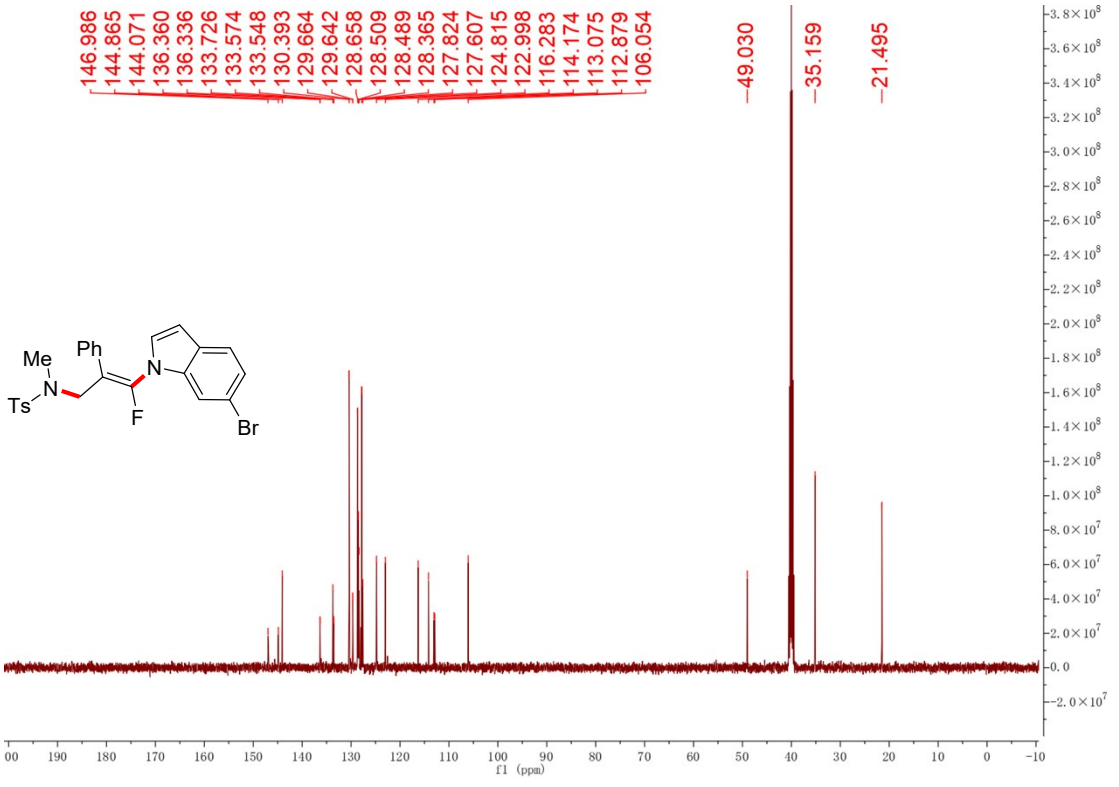
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4h



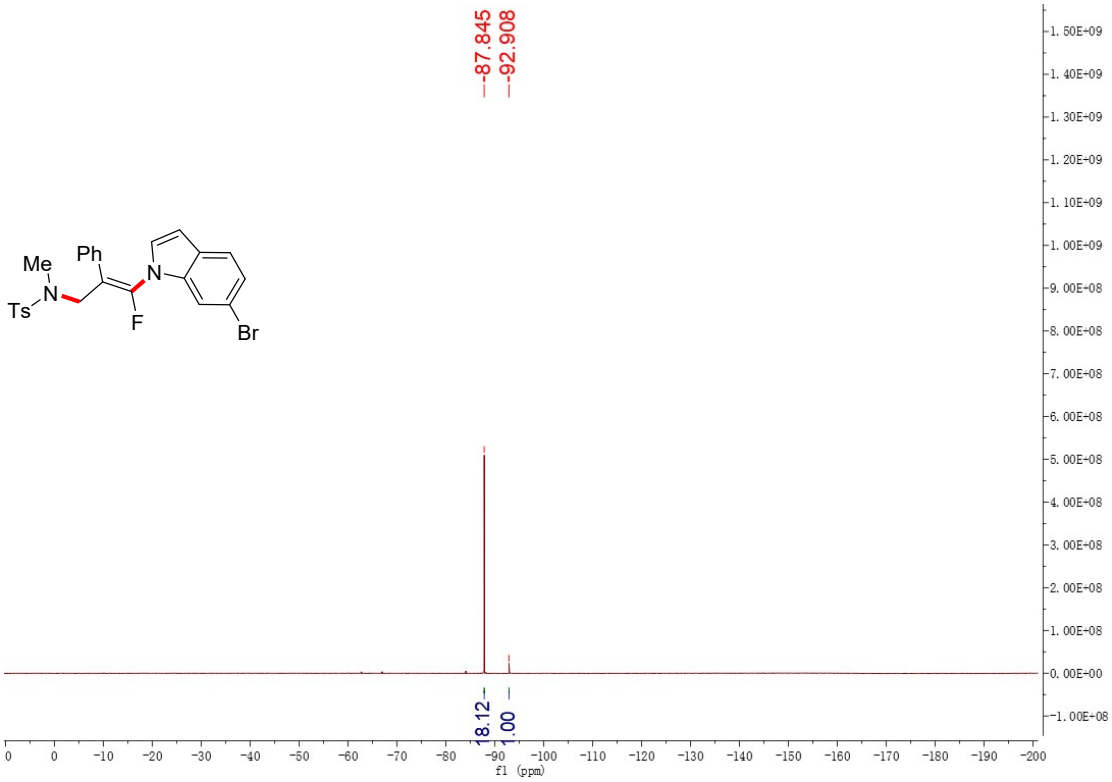
^{1}H NMR (500 MHz, DMSO-d_6) spectrum for 4i



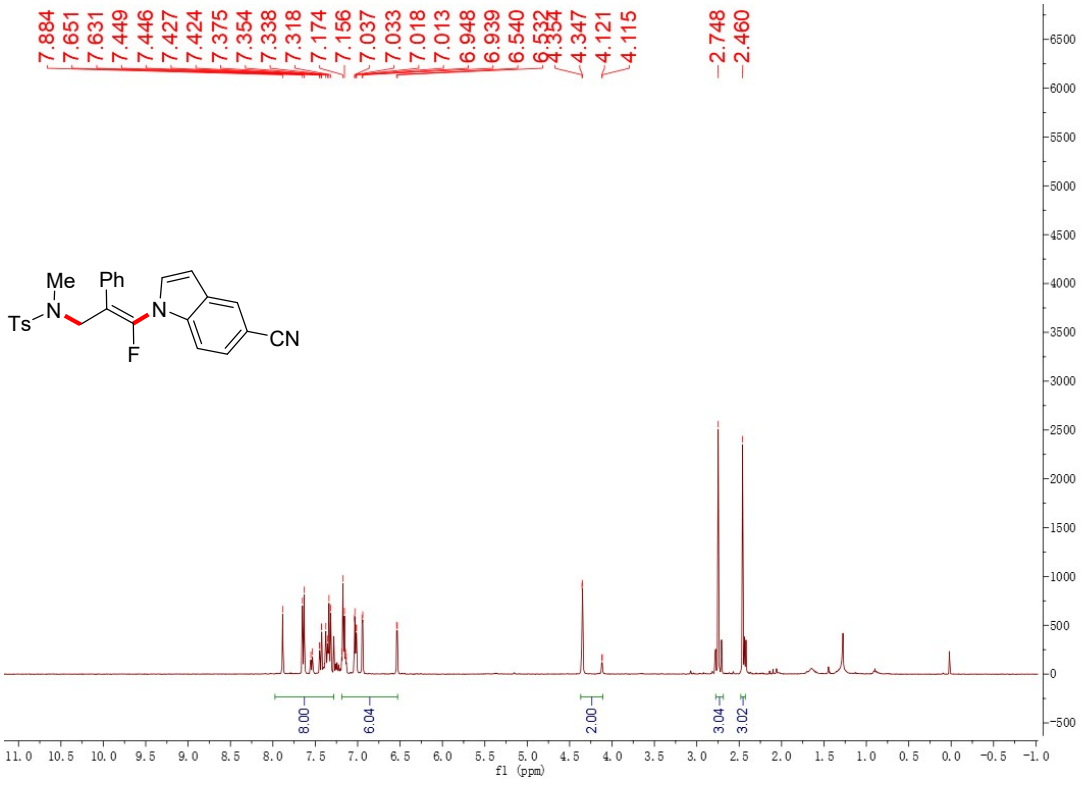
^{13}C NMR (126 MHz, DMSO-d_6) spectrum for 4i



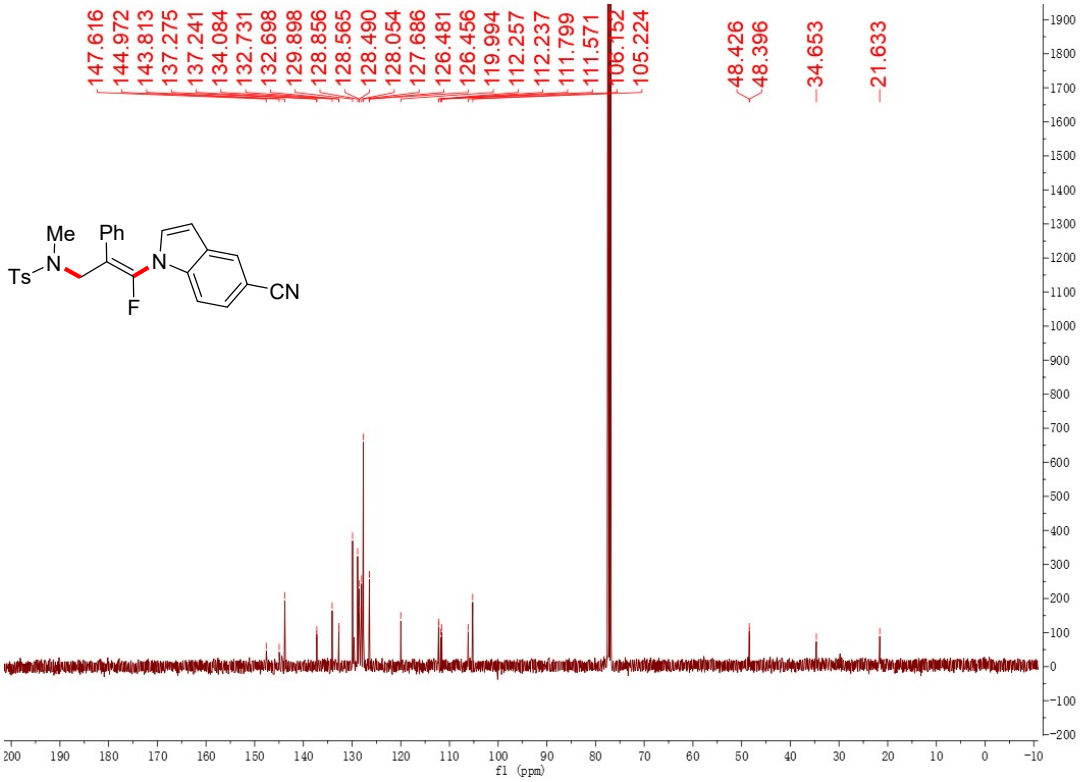
^{19}F NMR (471MHz, DMSO-d_6) spectrum for 4i



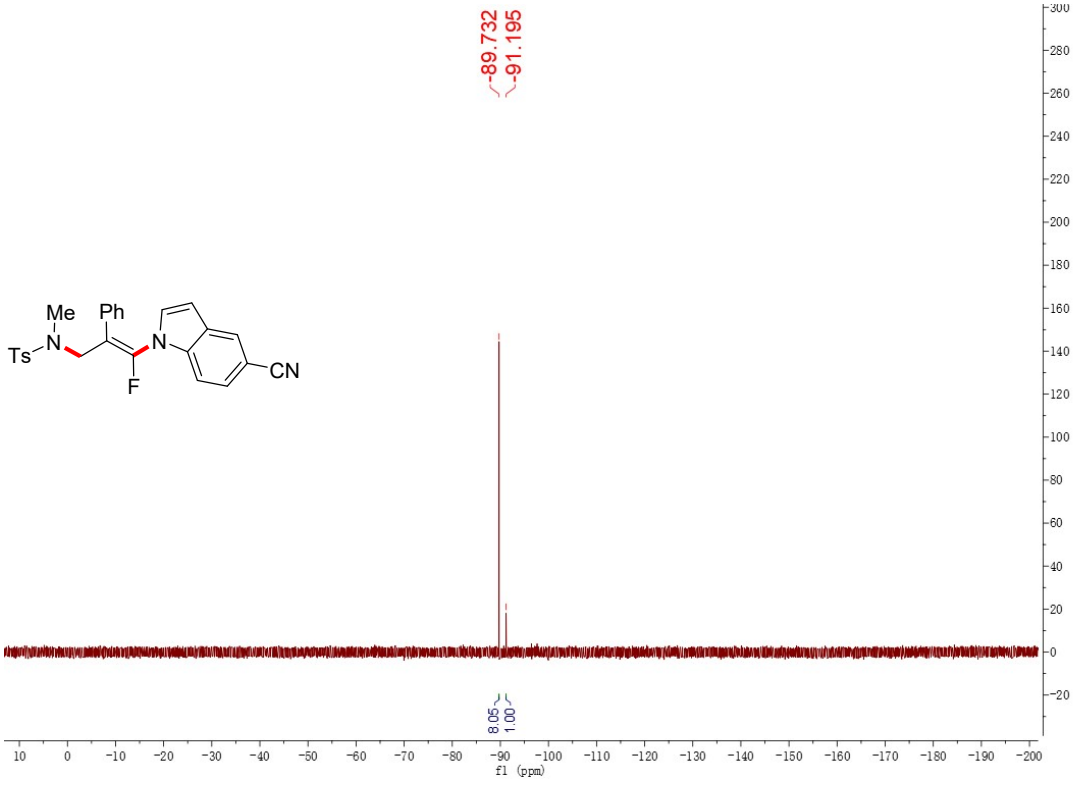
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4j



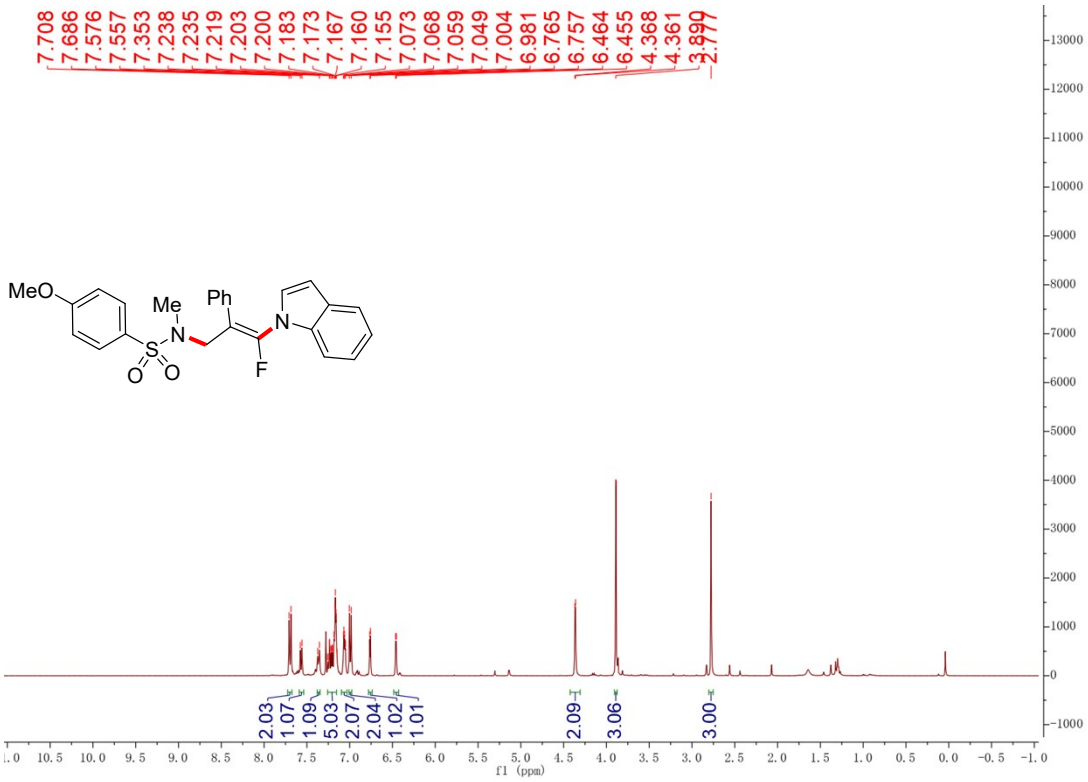
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4j



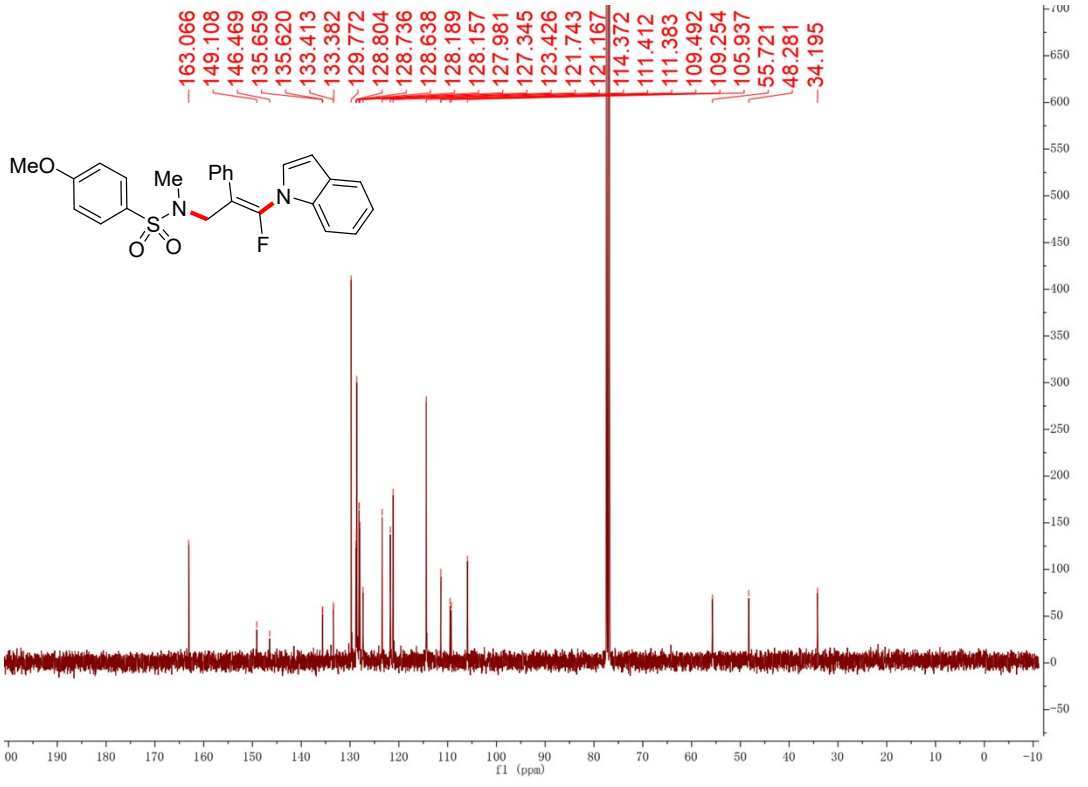
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4j



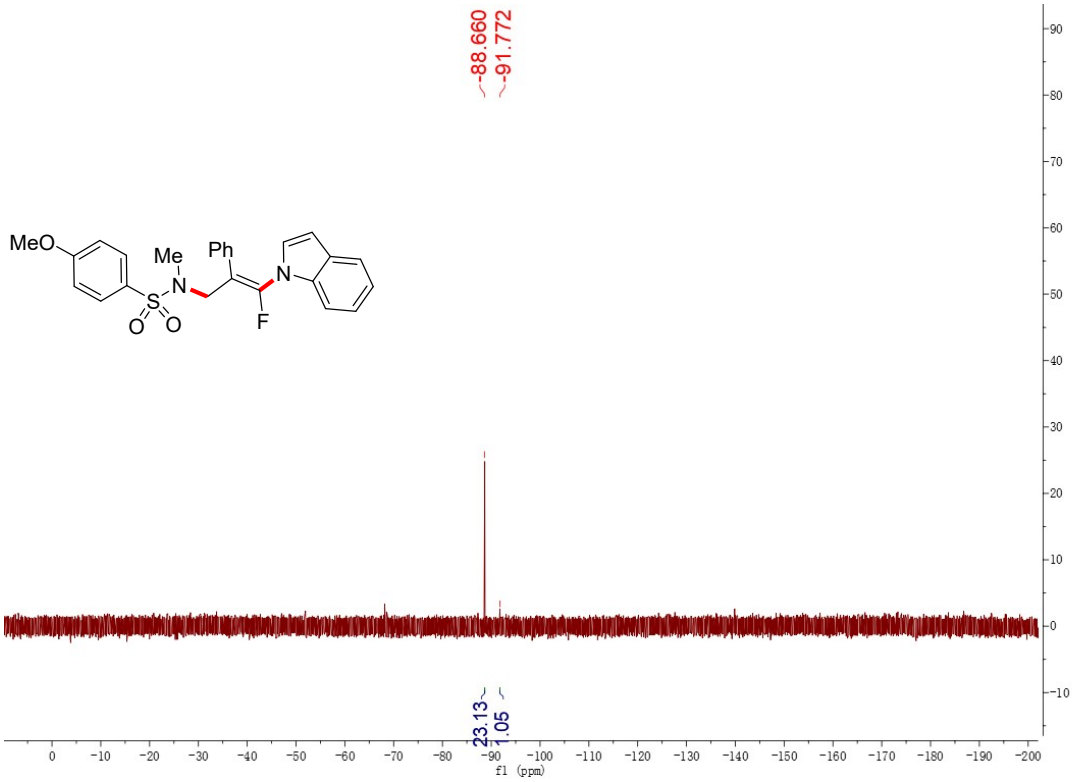
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4k



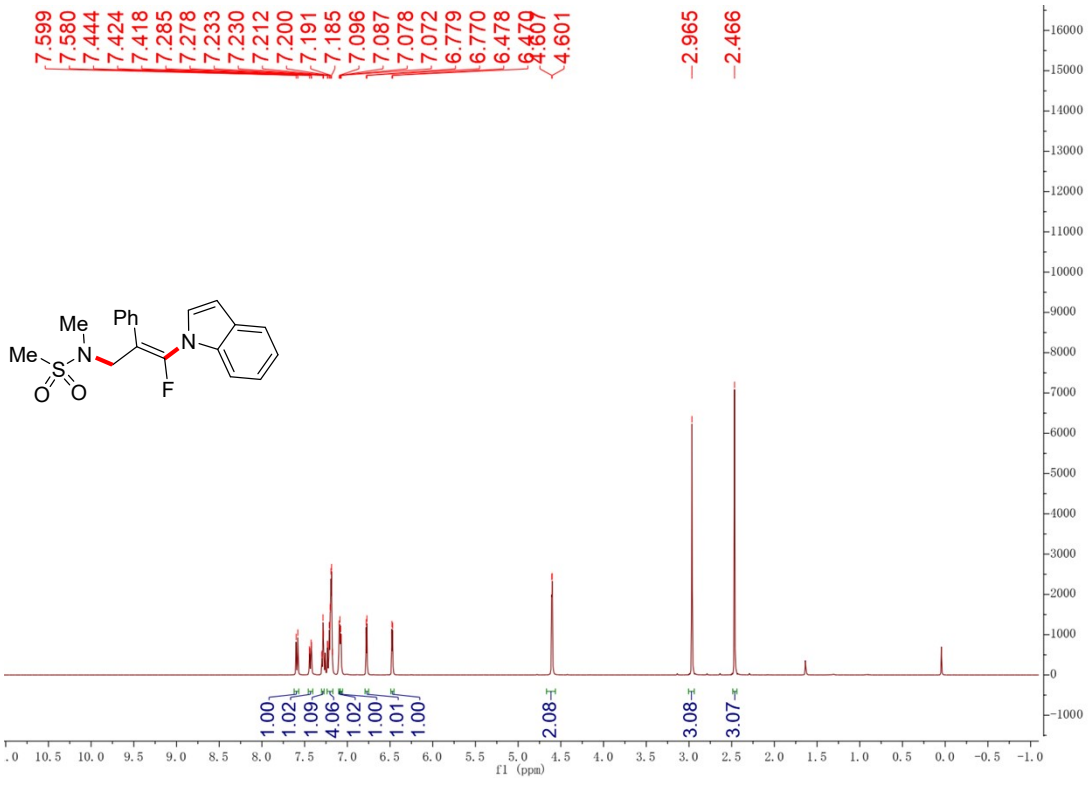
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4k



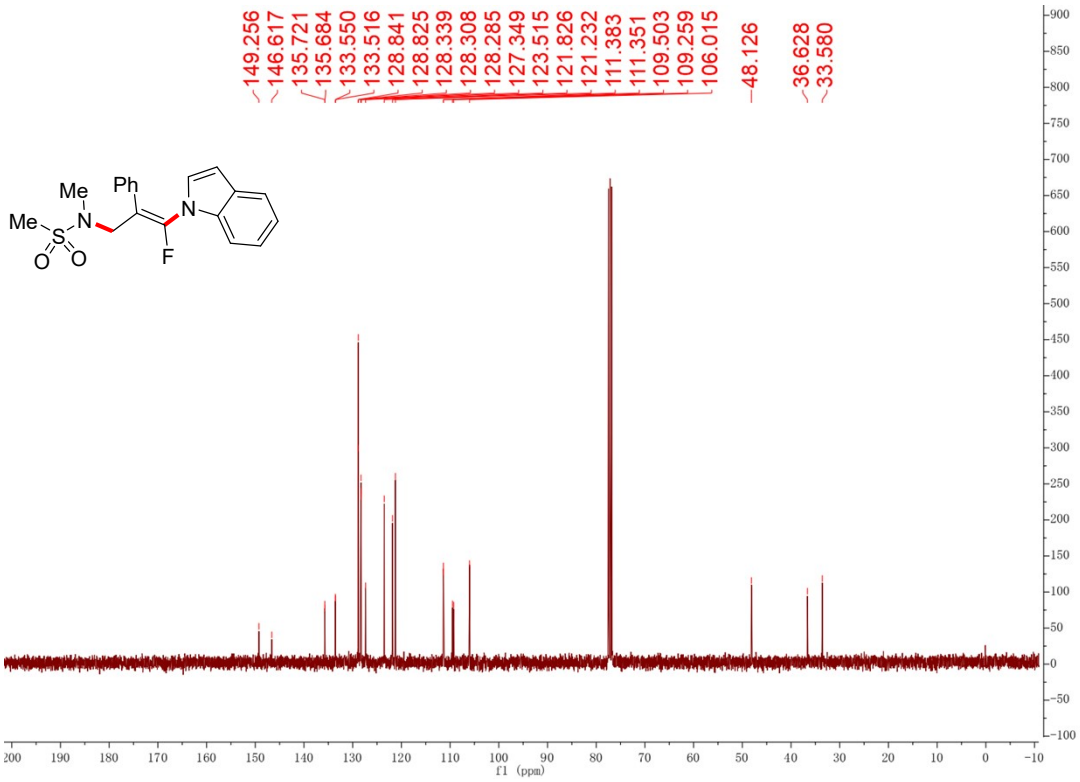
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4k



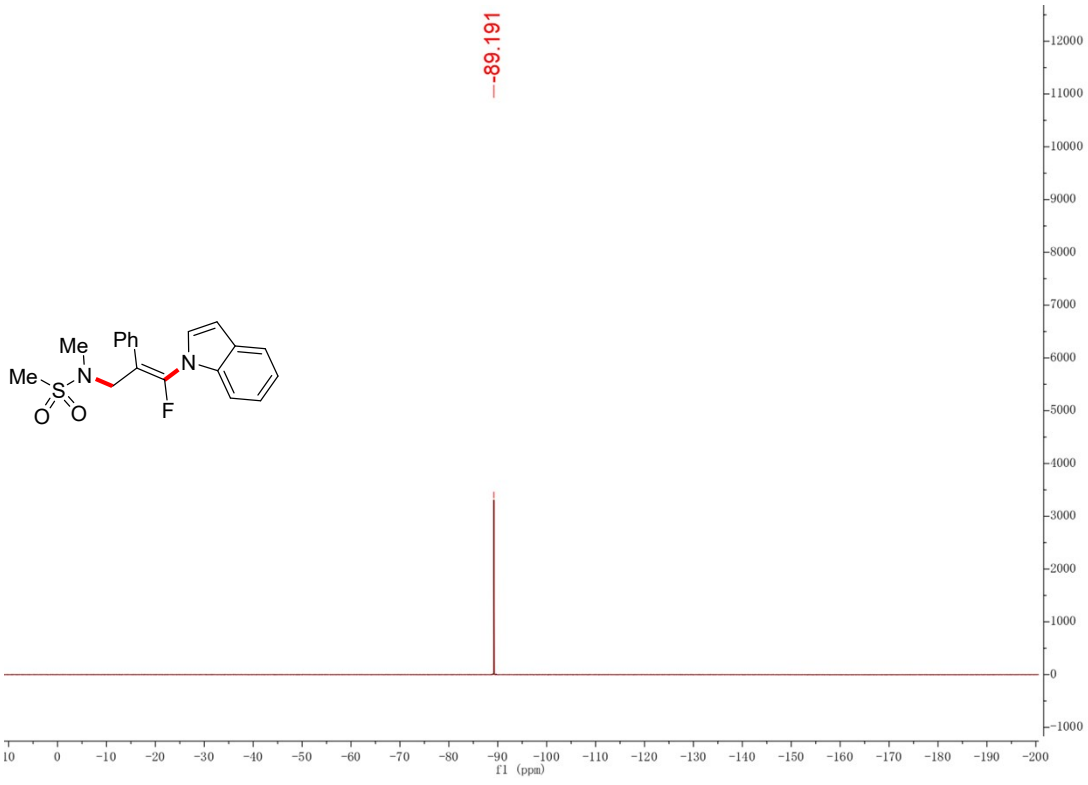
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4l



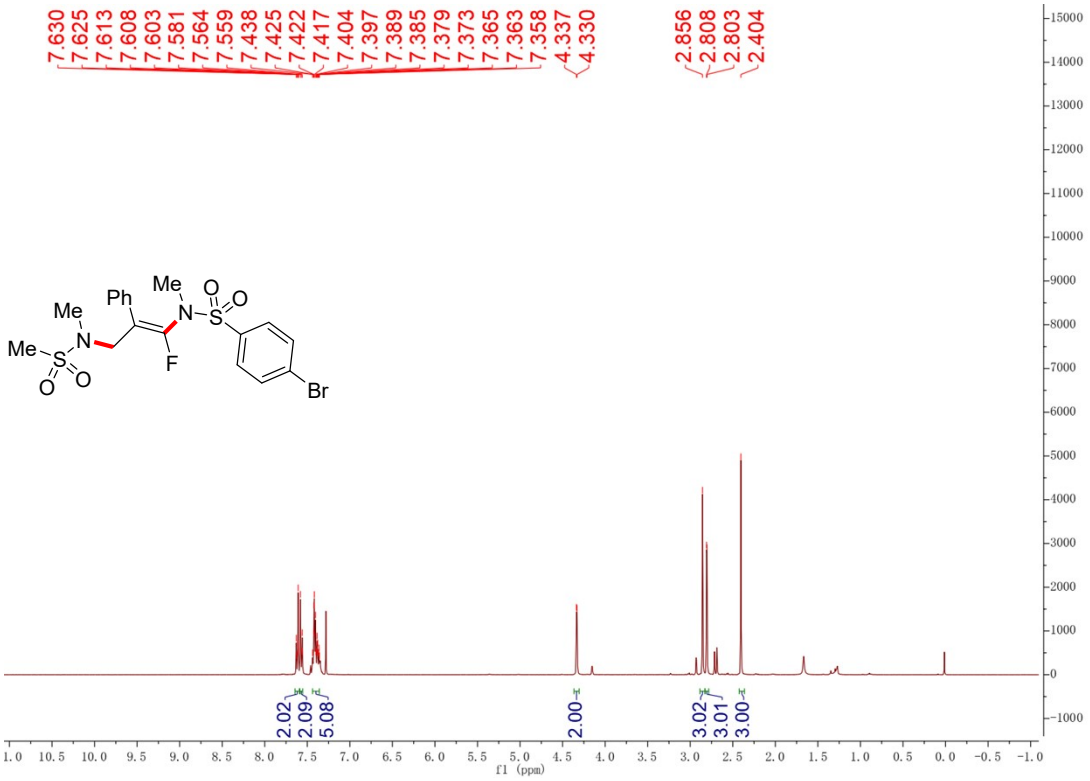
^{13}C NMR (100 MHz, $CDCl_3$) spectrum for 4l



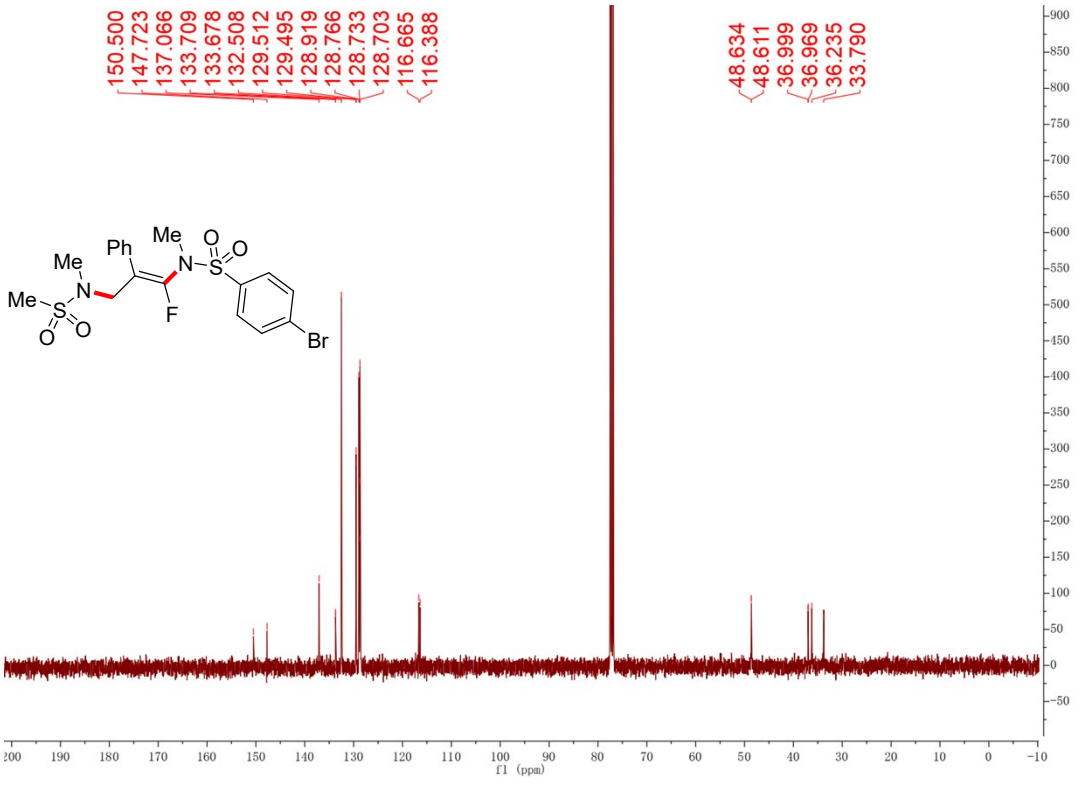
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4l



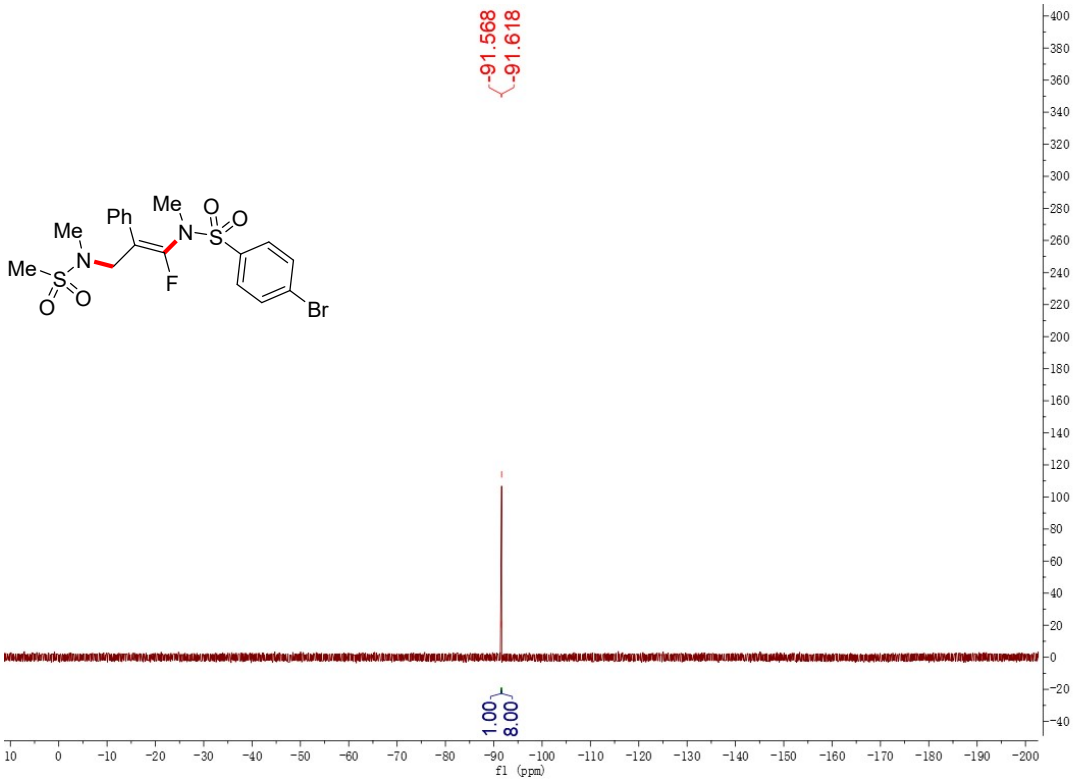
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4m



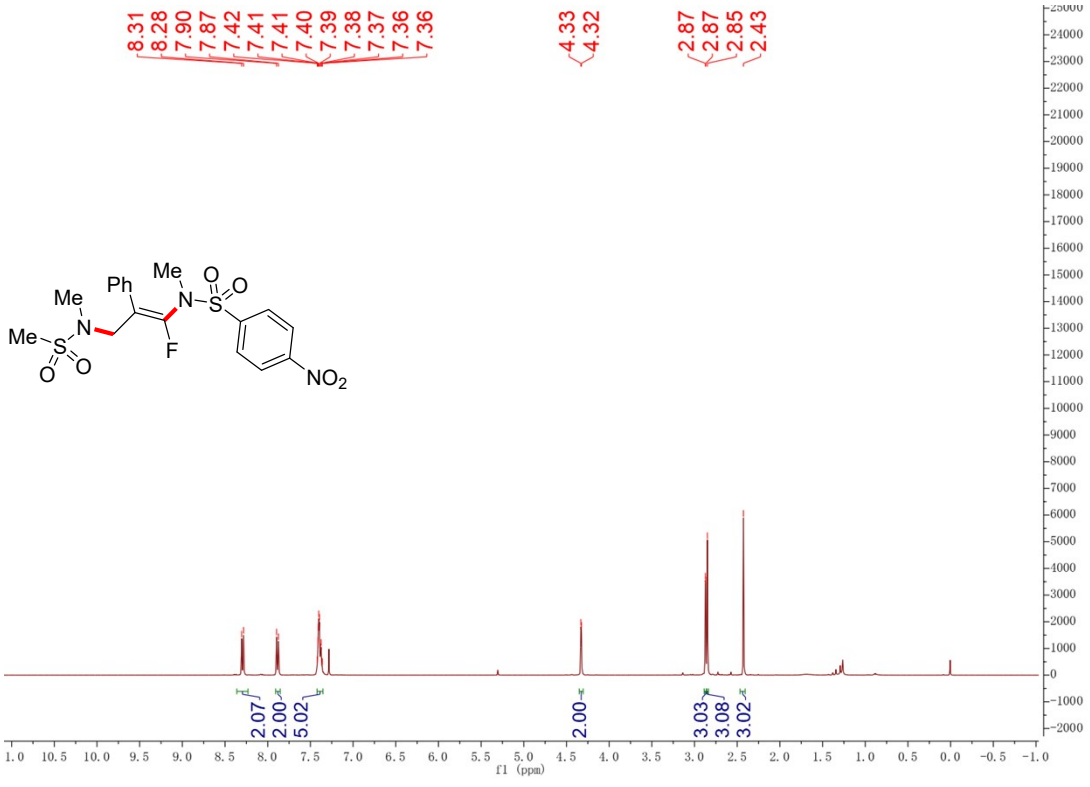
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4m



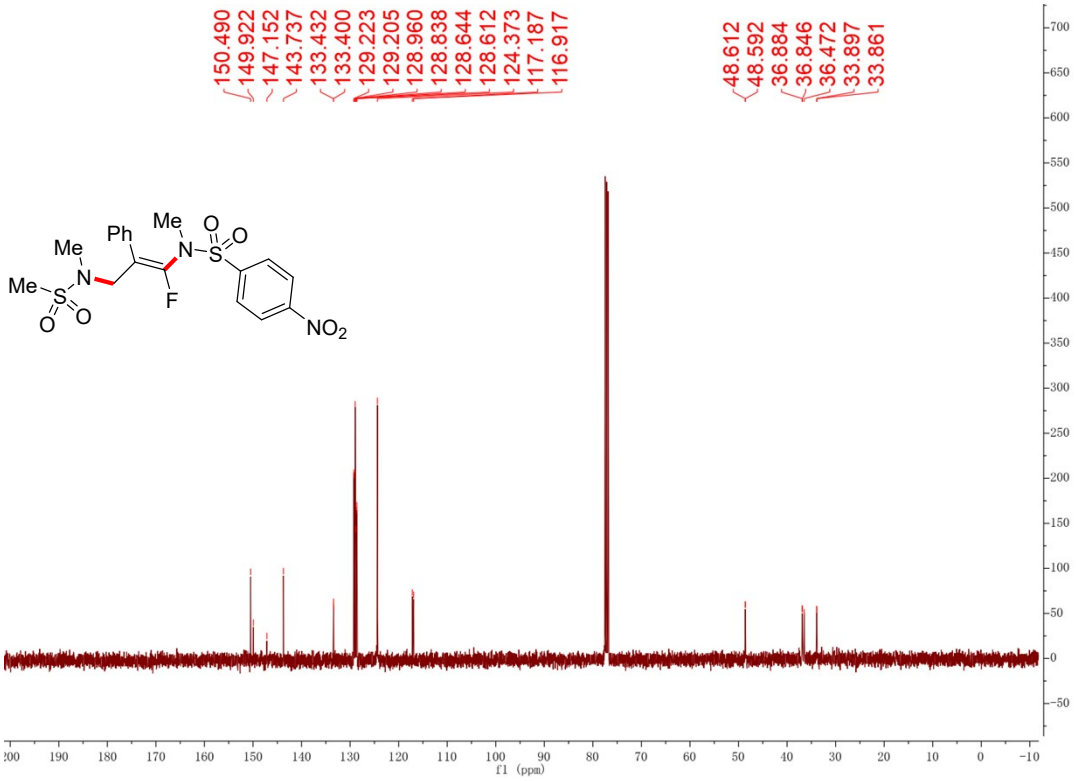
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4m



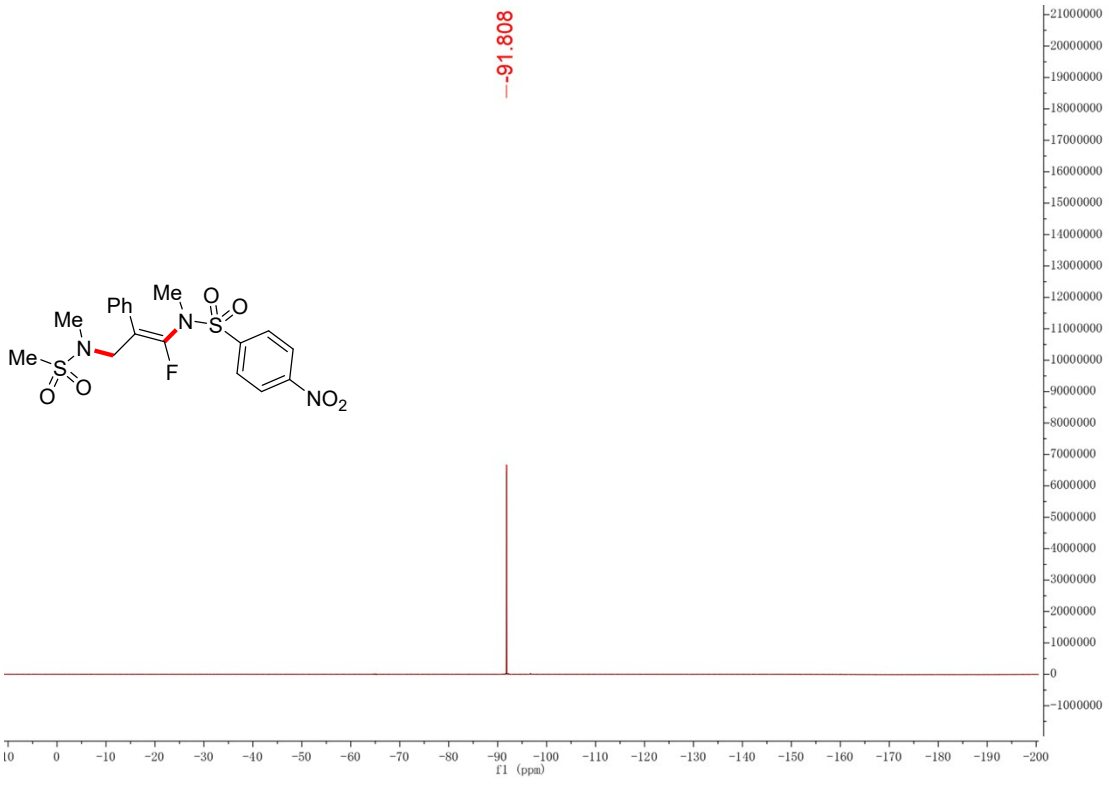
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4n



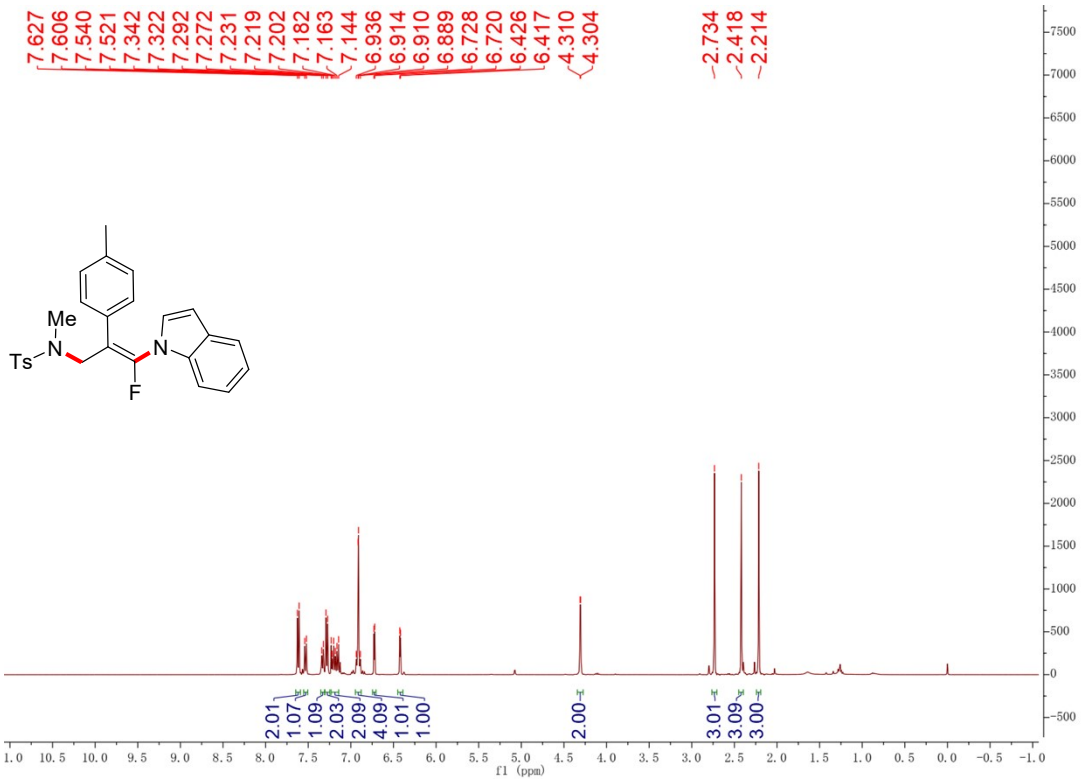
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4n



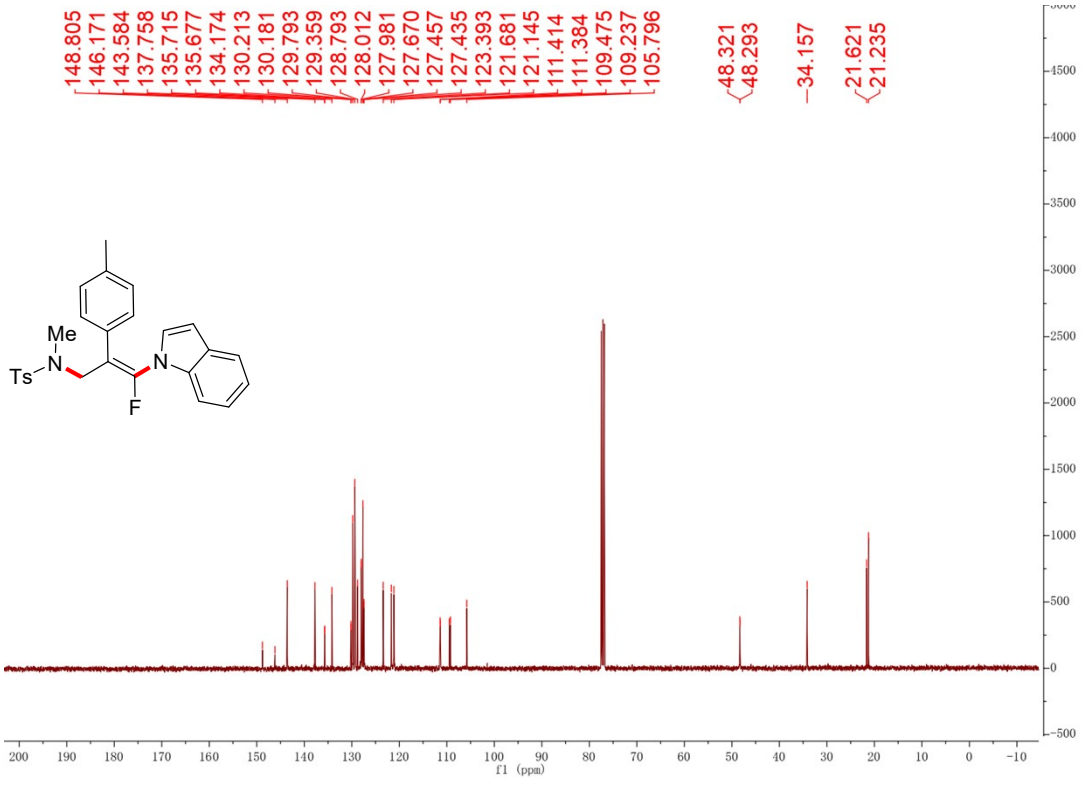
^{19}F NMR (471 MHz, $CDCl_3$) spectrum for 4n



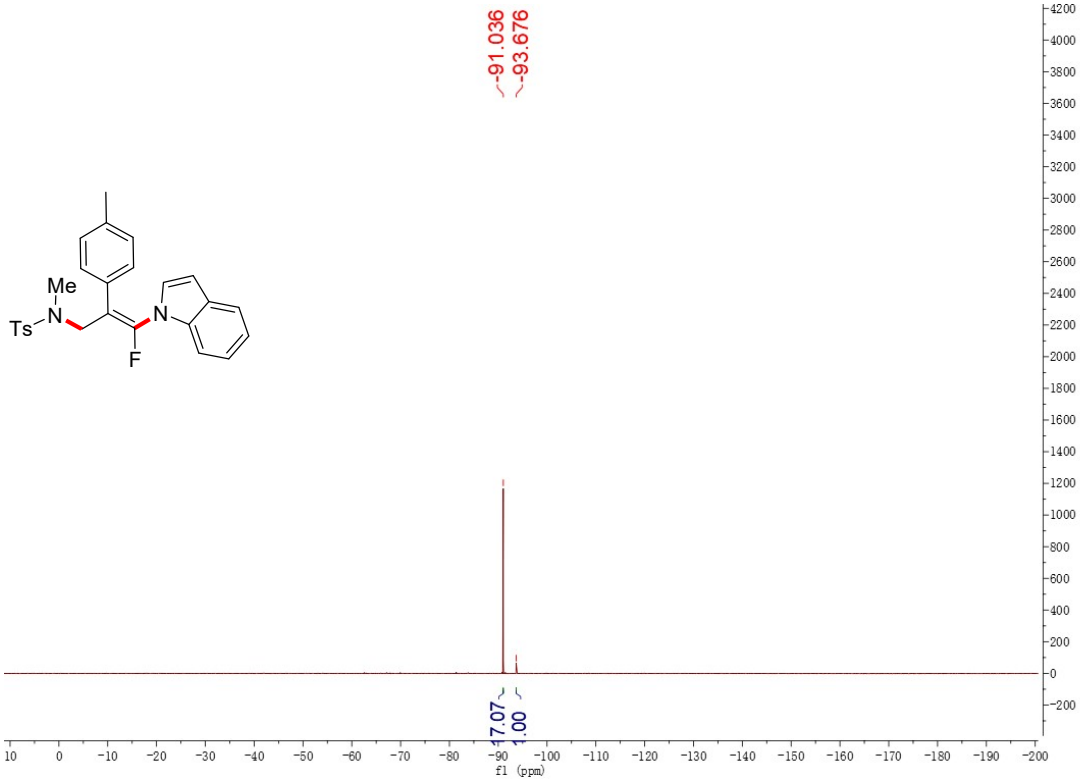
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4o



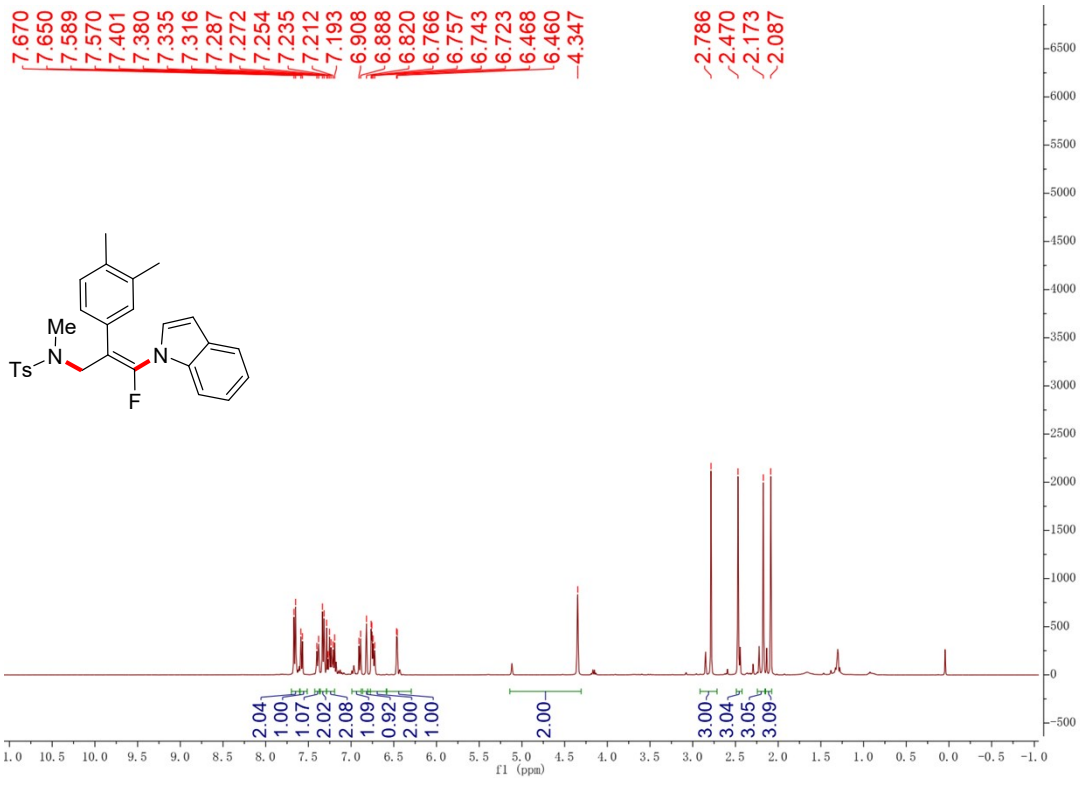
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4o



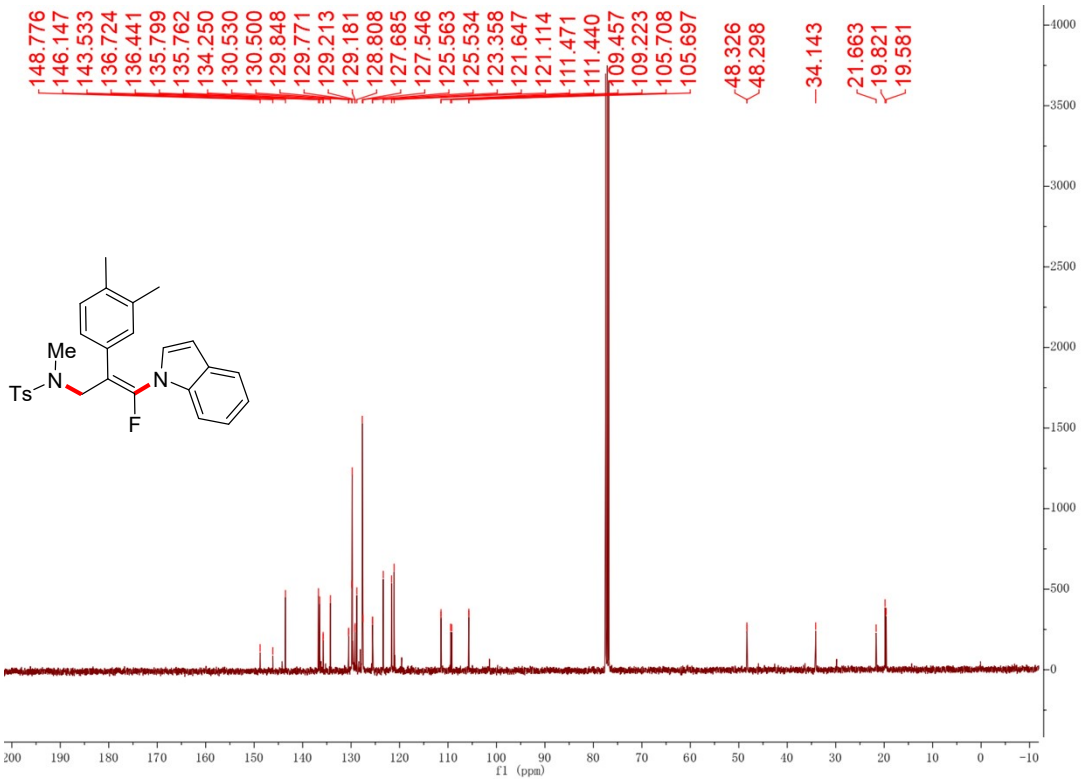
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4o



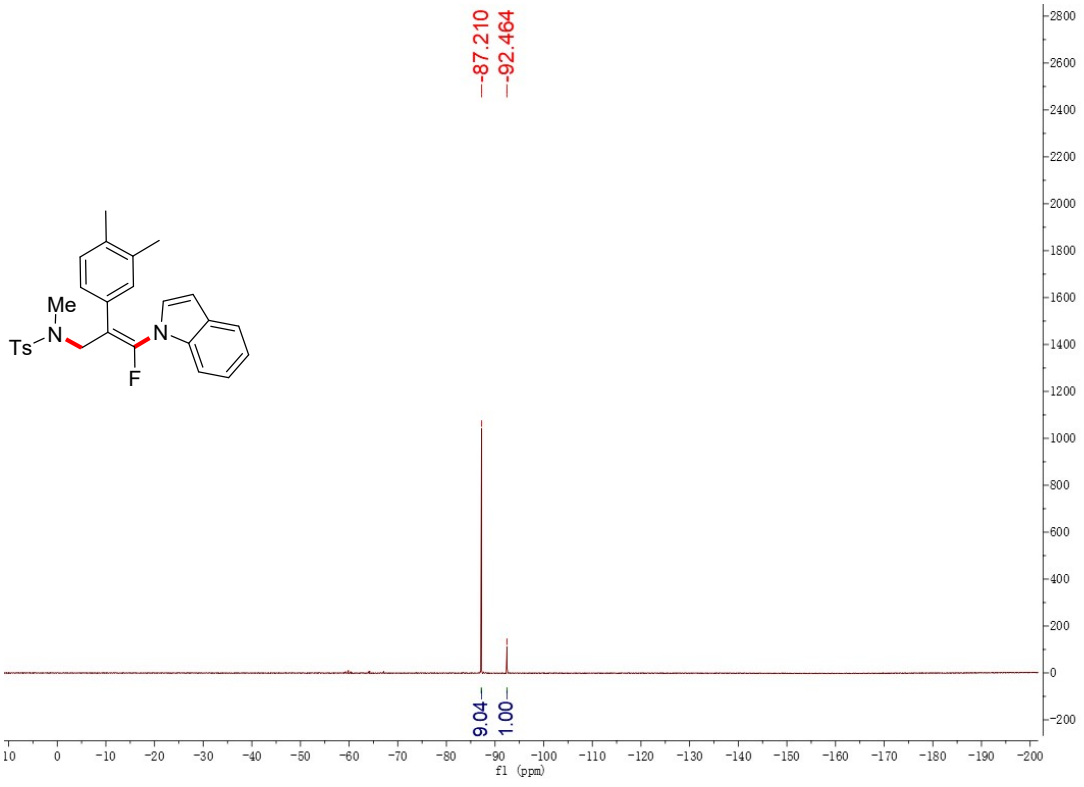
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4p



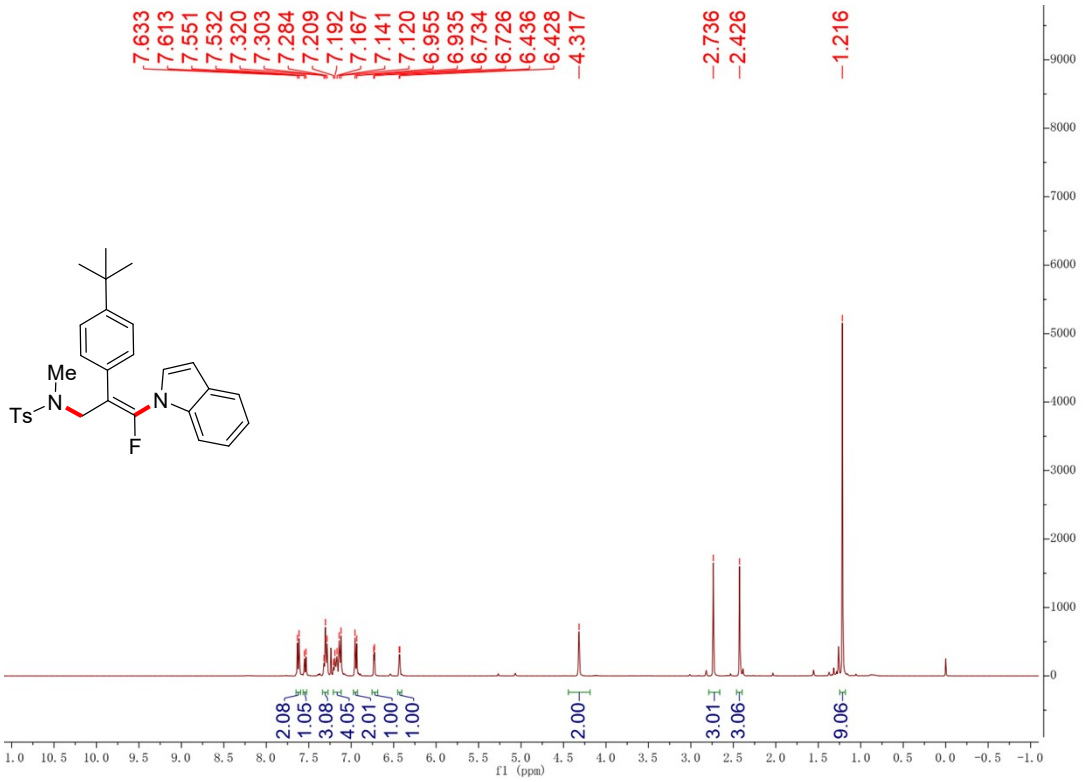
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4p



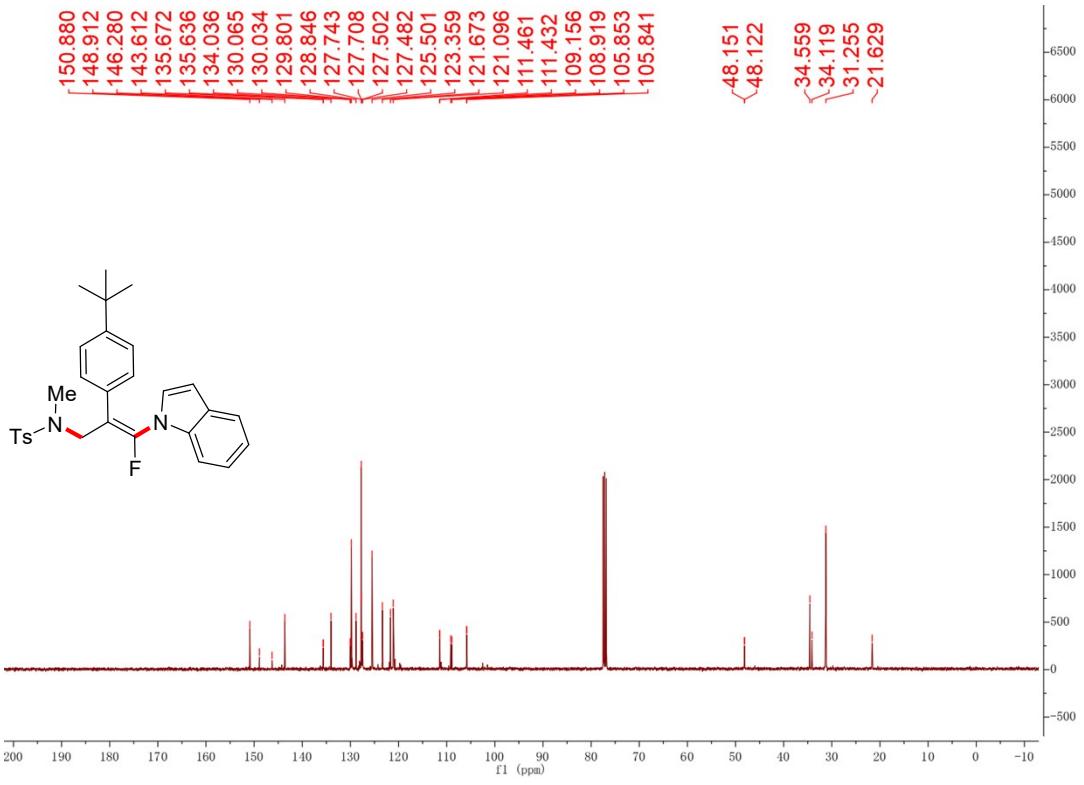
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4p



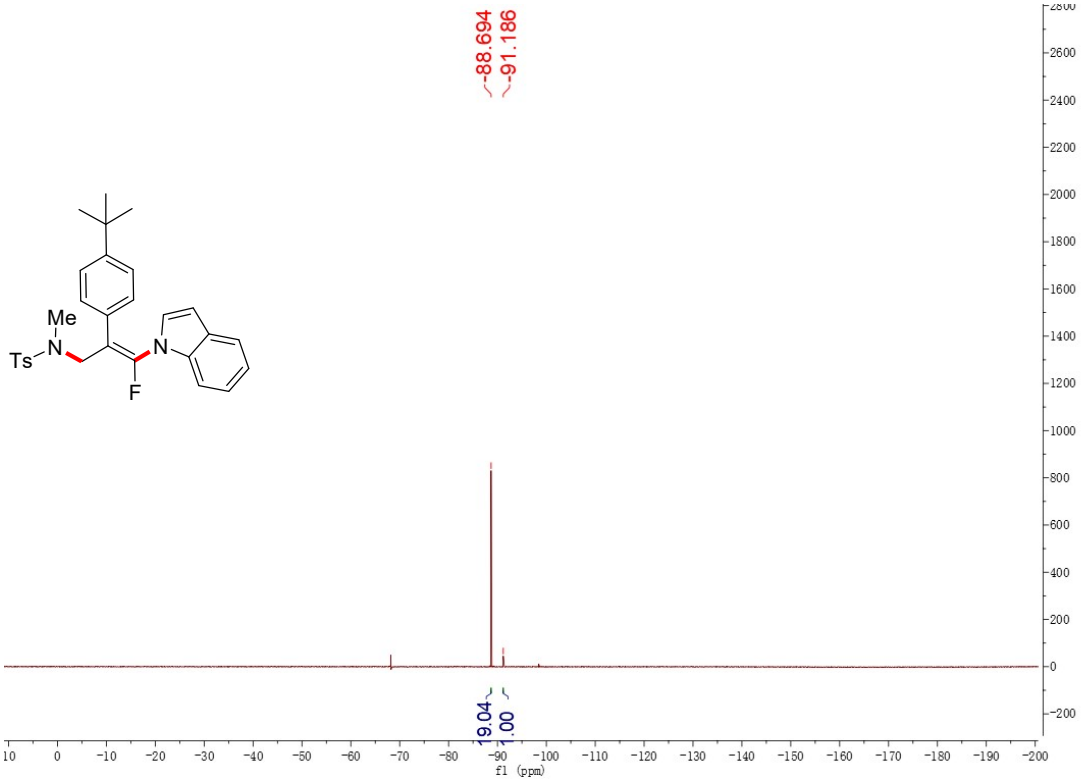
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4q



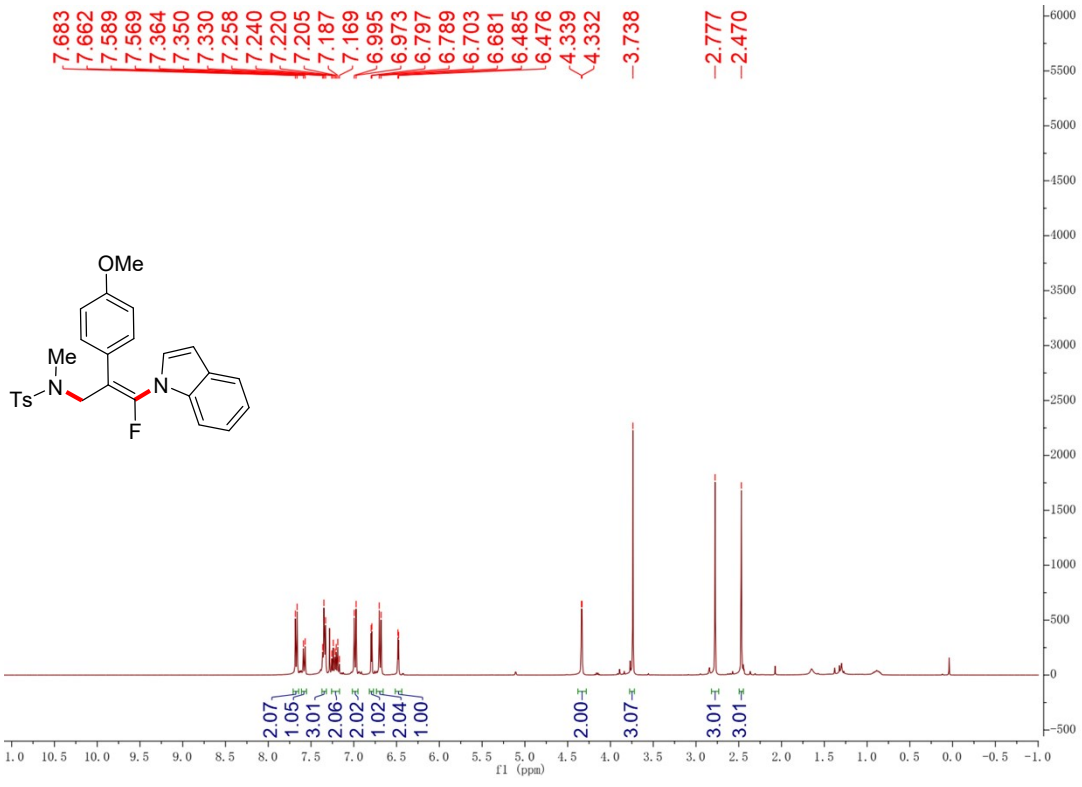
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4q



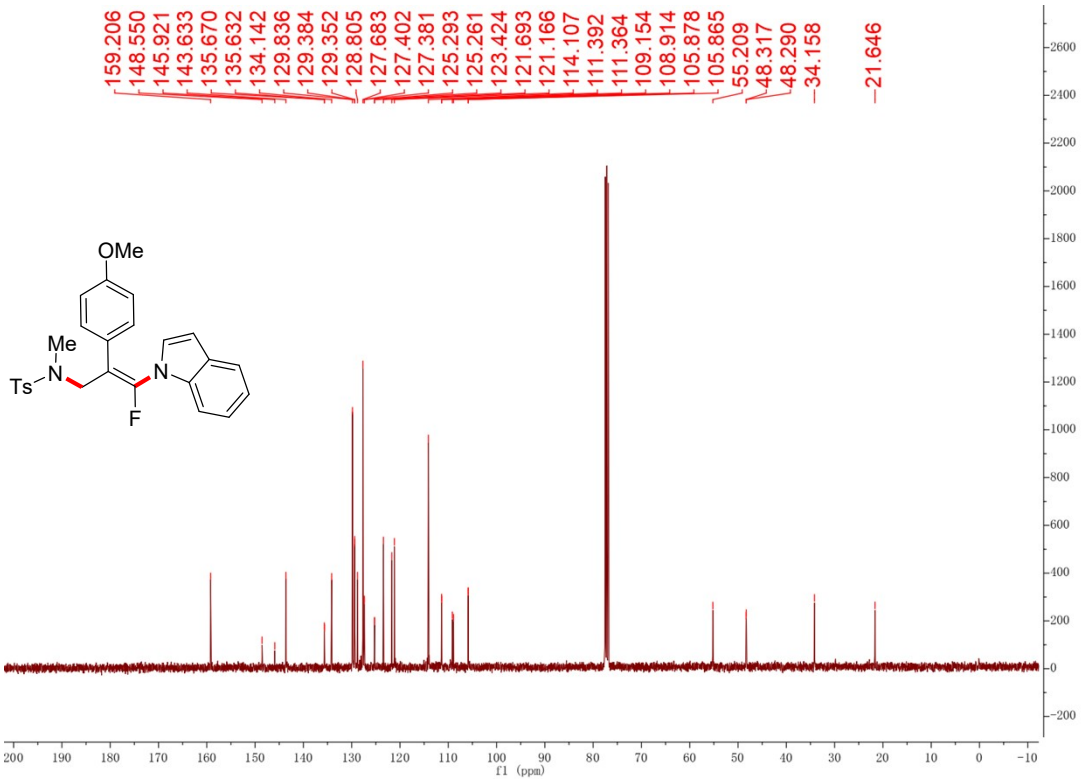
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4q



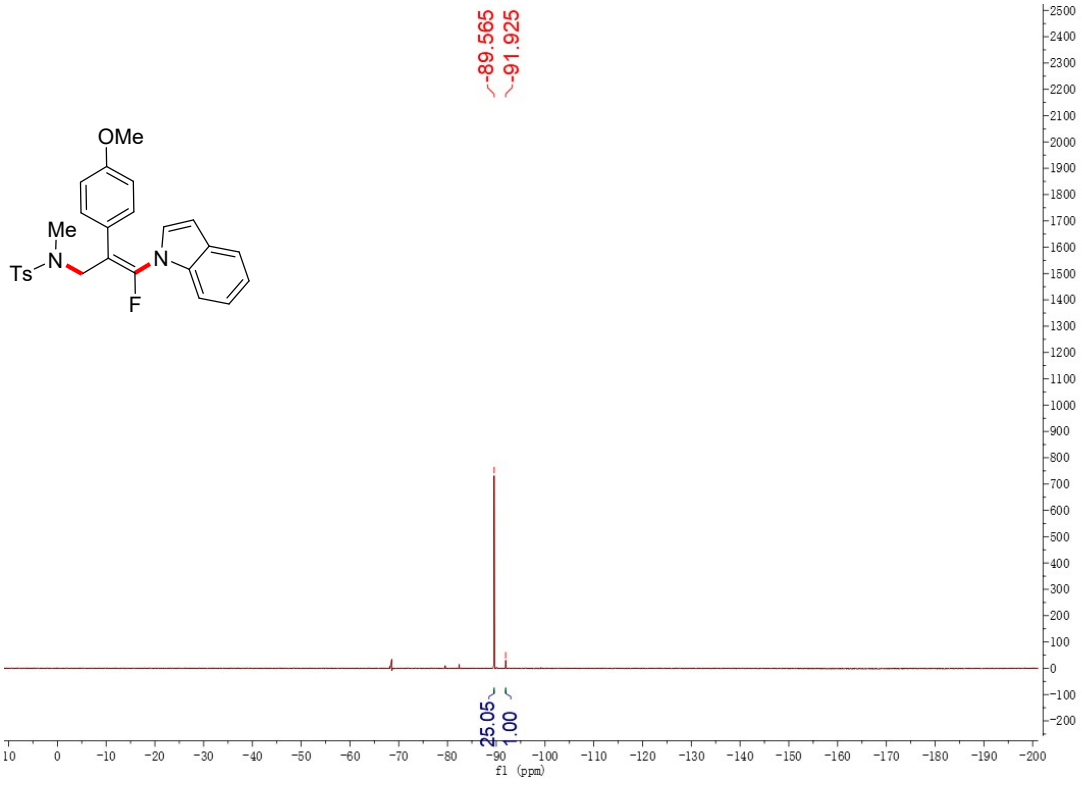
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4r



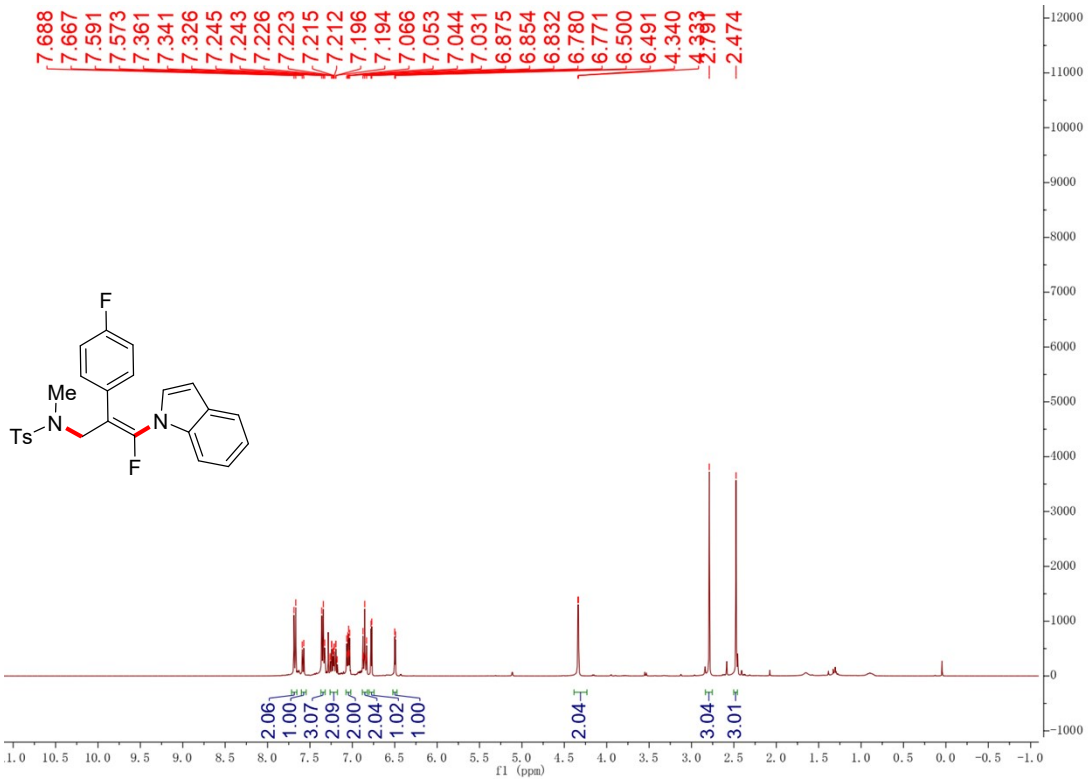
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4r



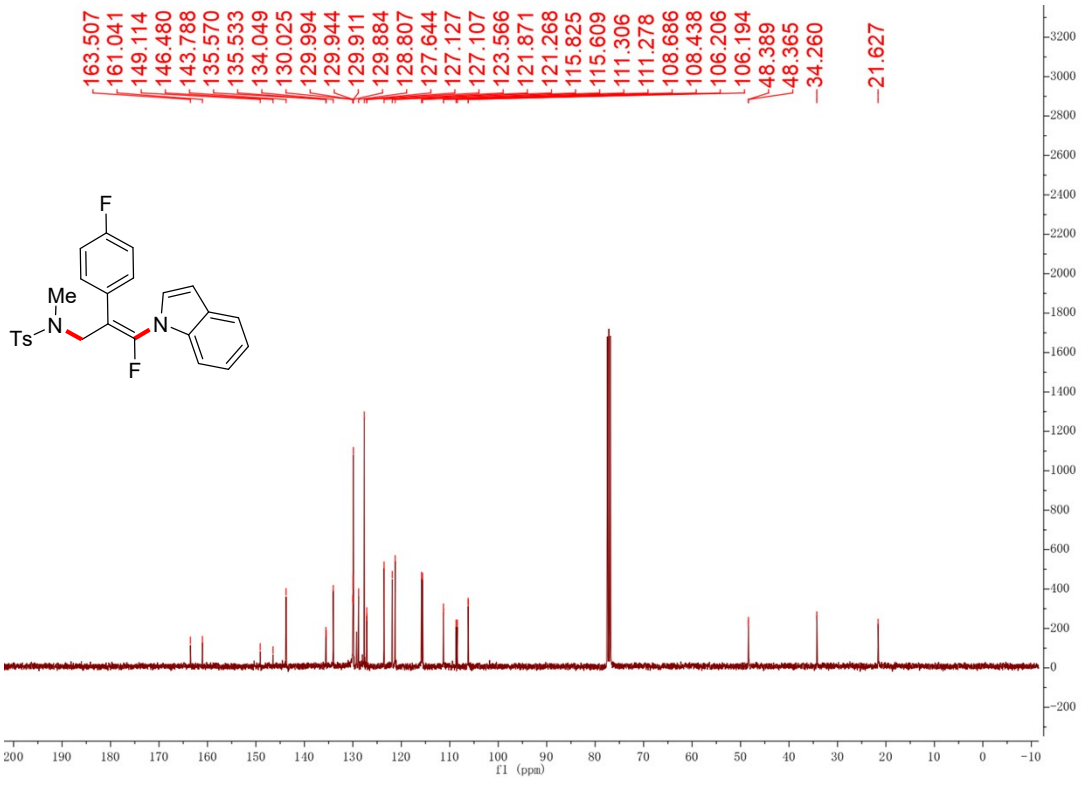
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4r



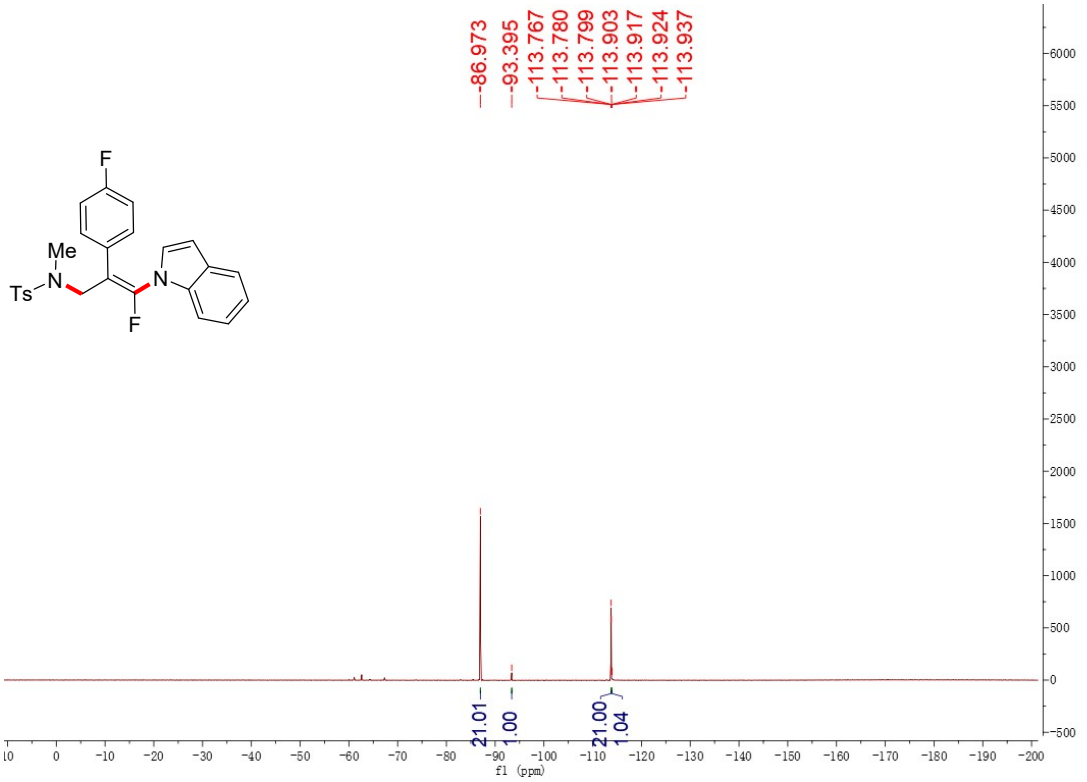
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4s



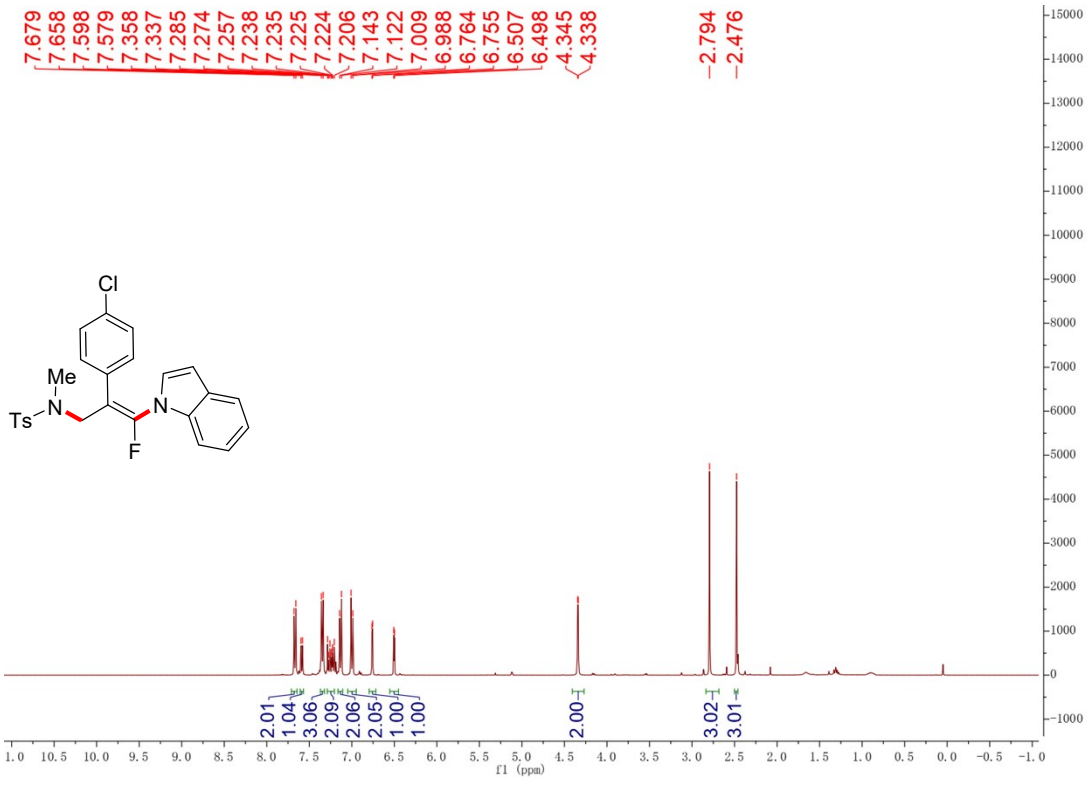
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4s



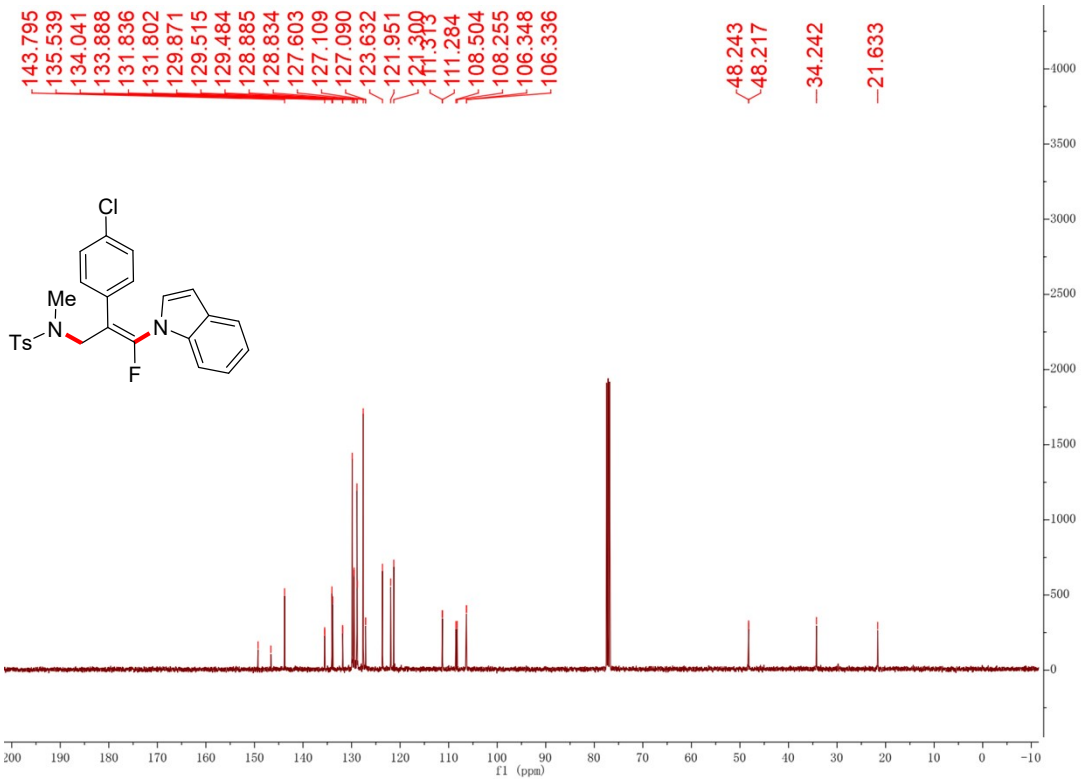
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4s



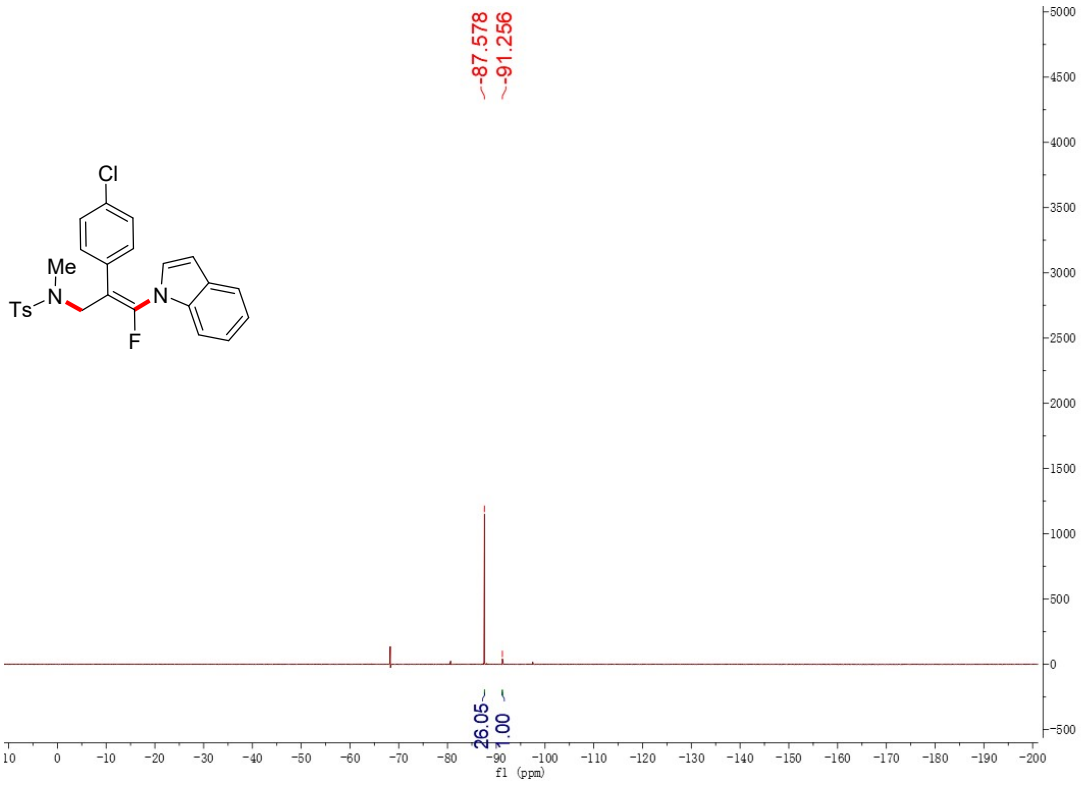
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4t



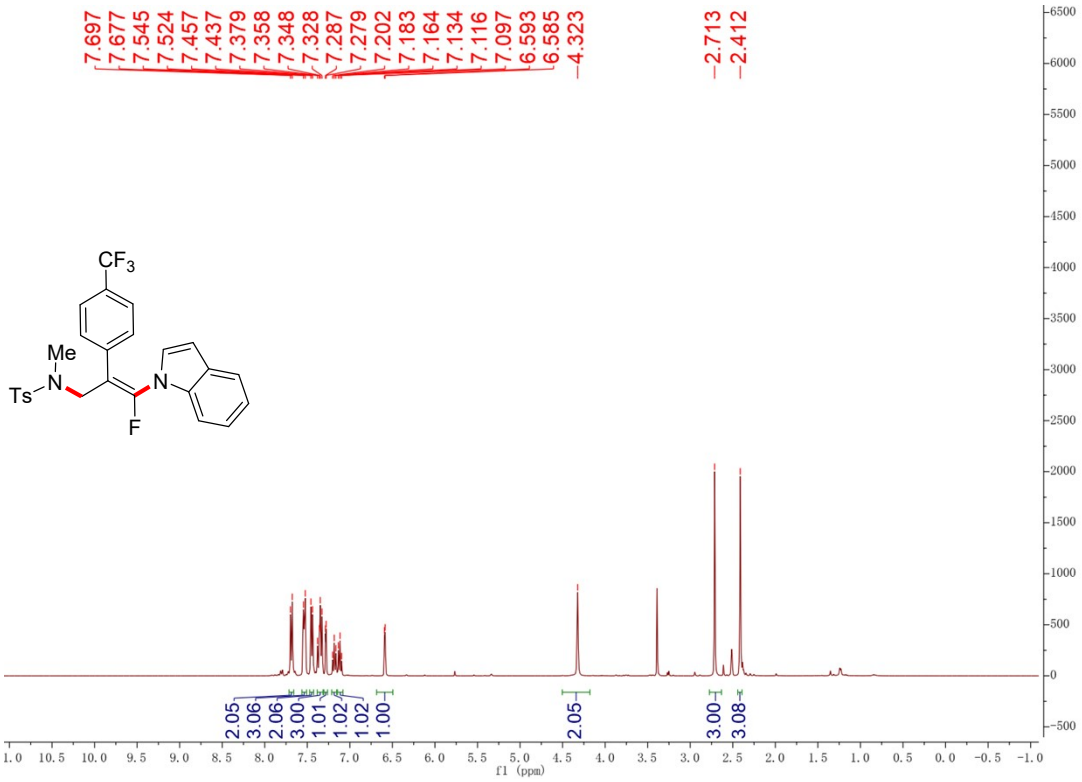
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4t



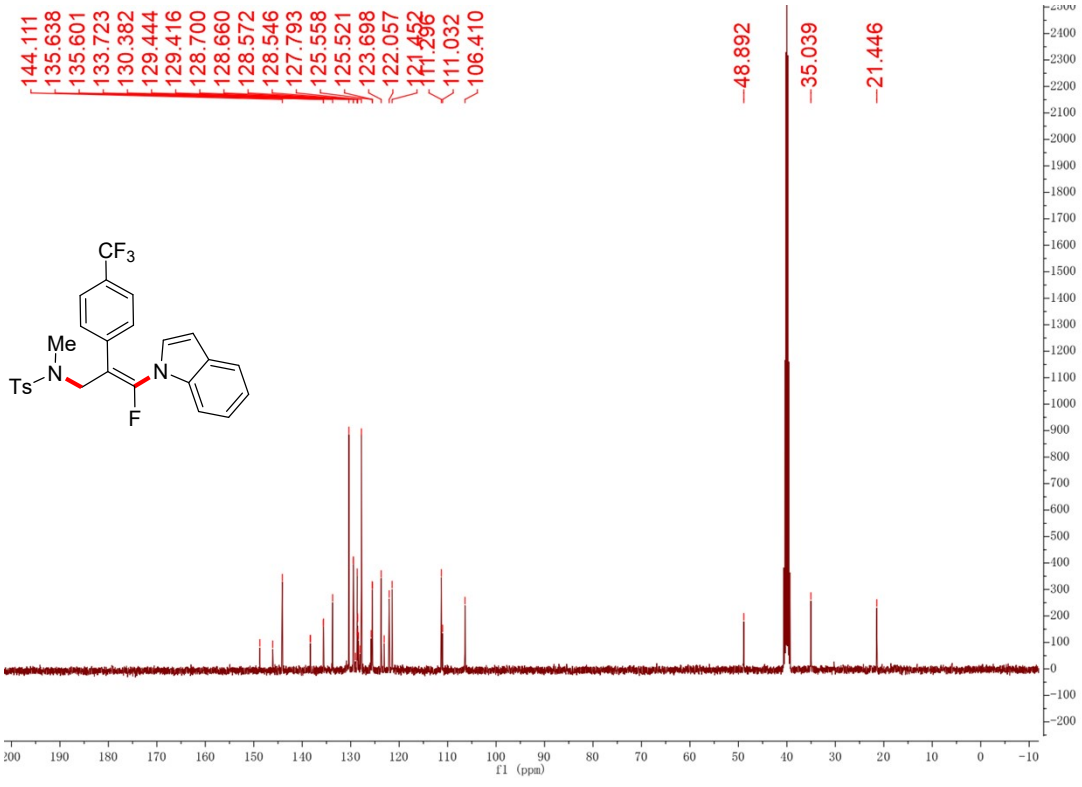
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4t



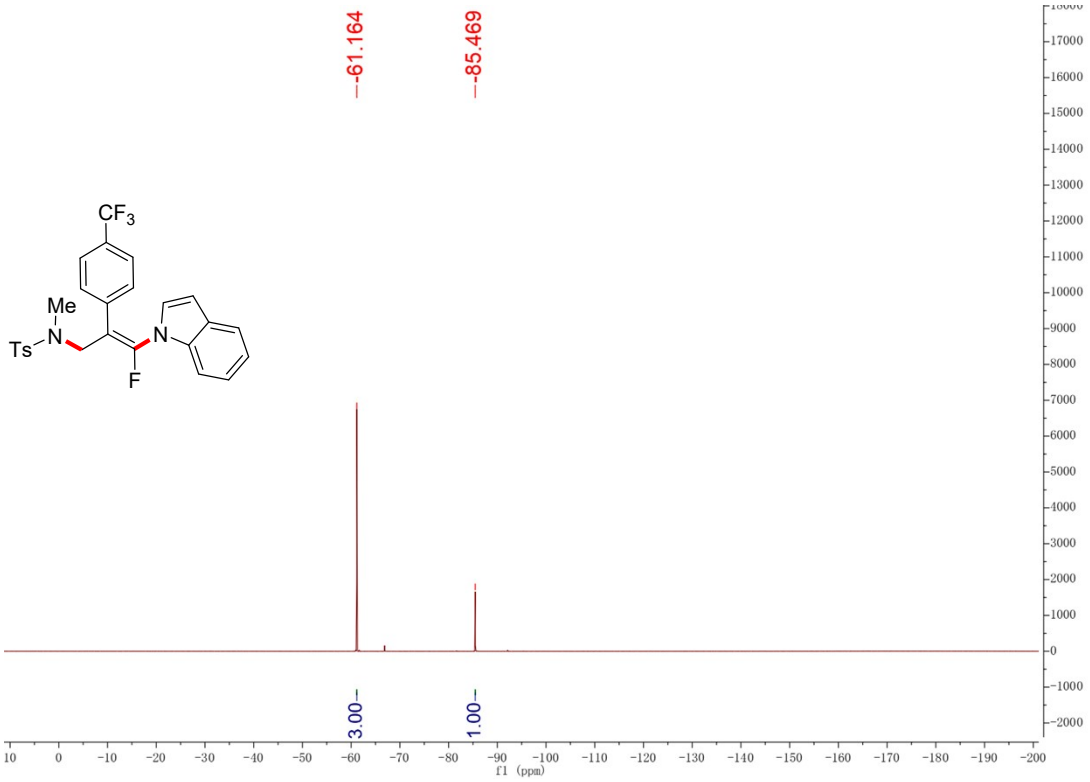
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4u



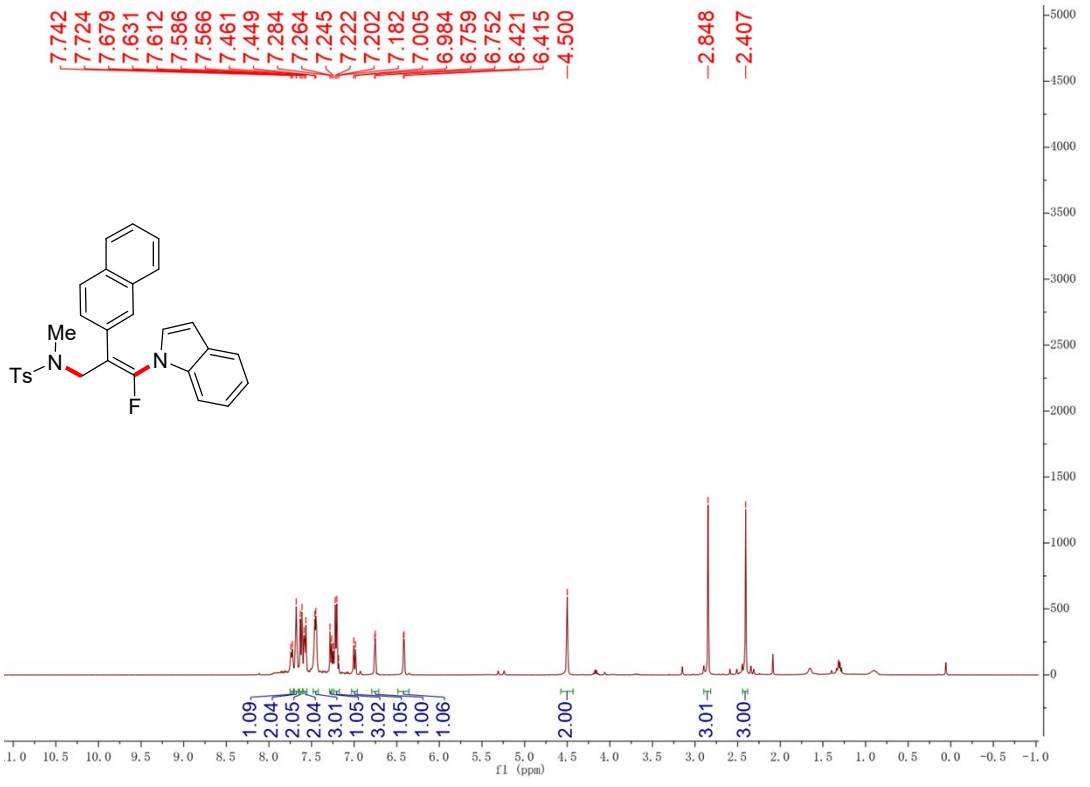
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4u



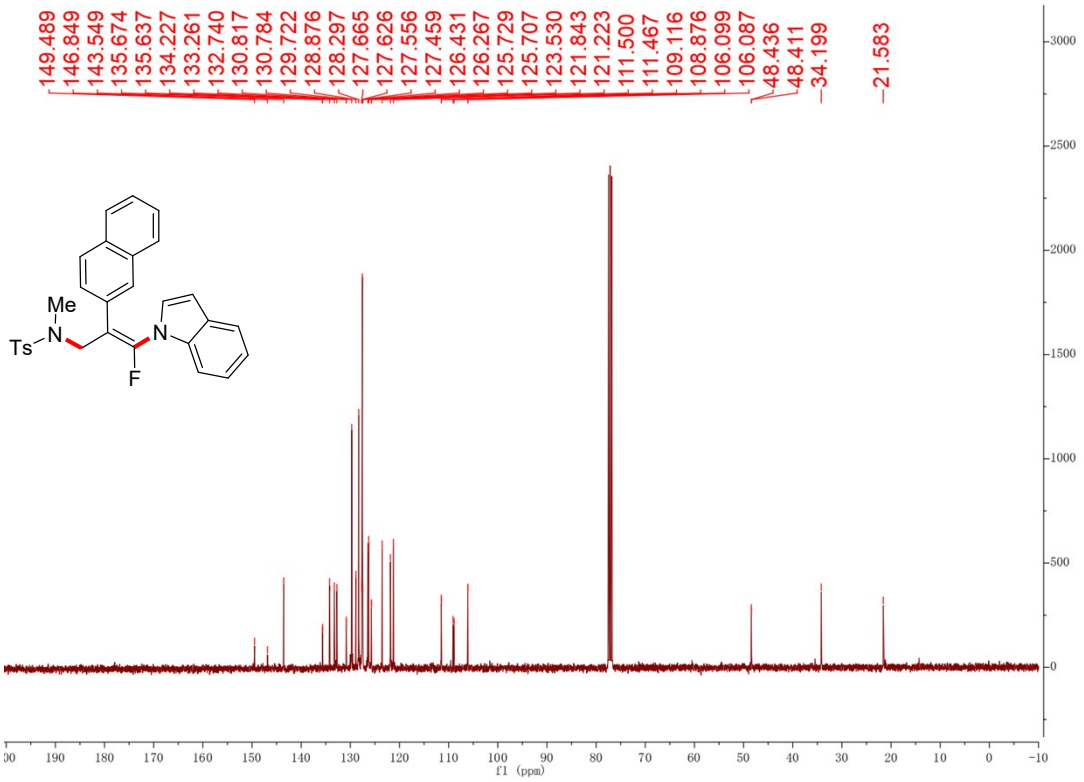
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4u



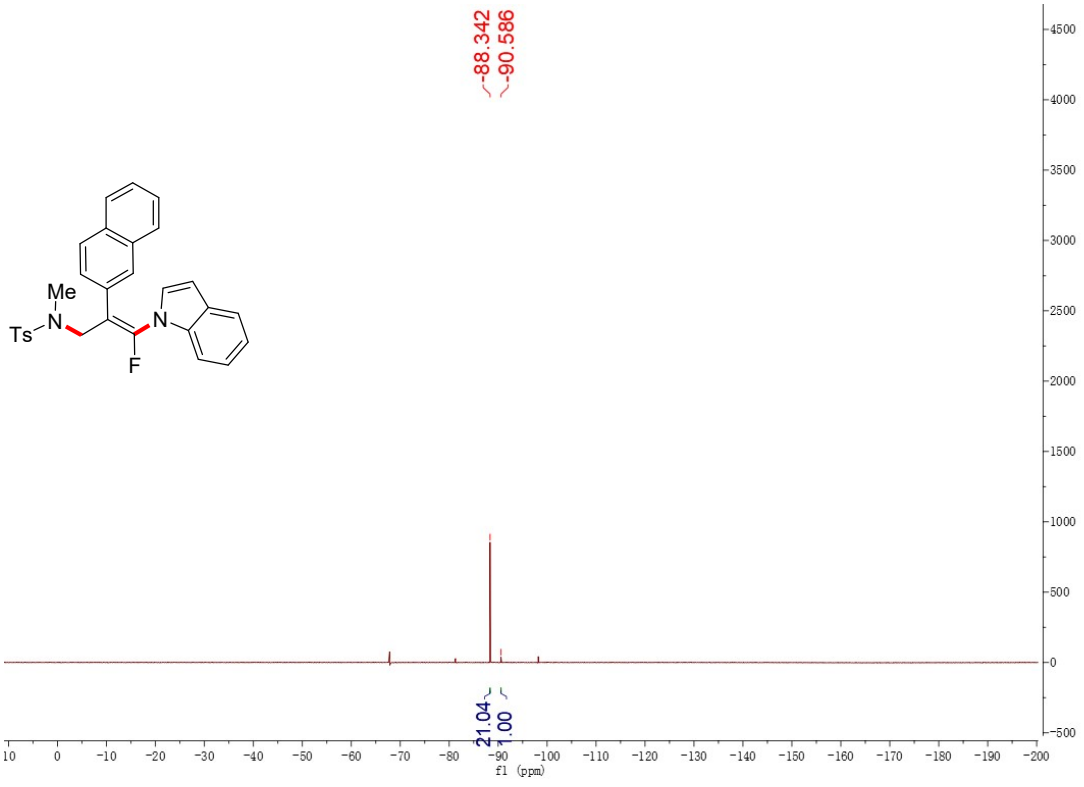
^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 4v



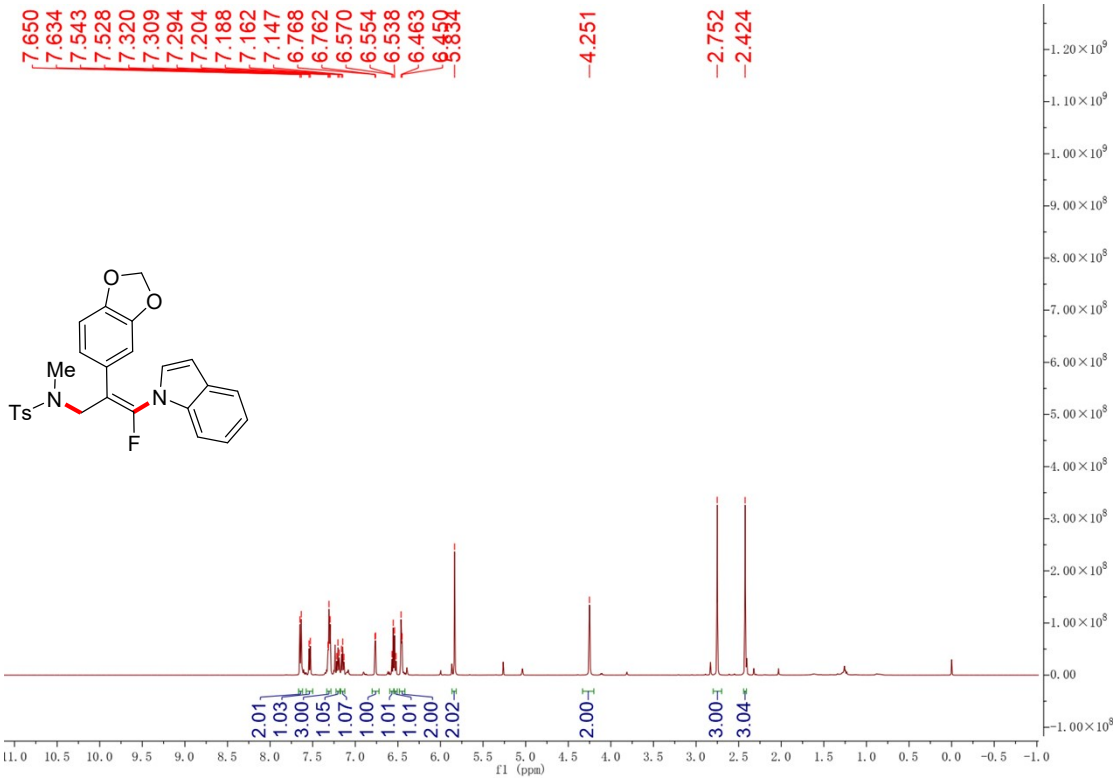
^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 4v



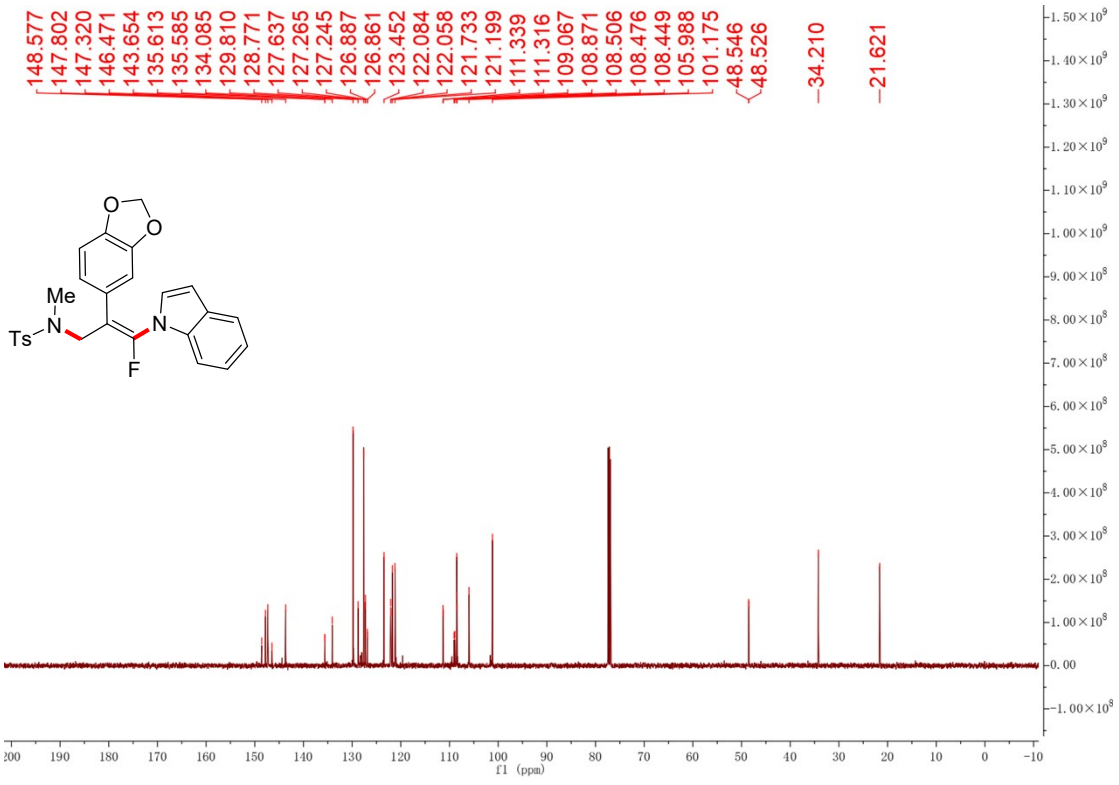
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 4v



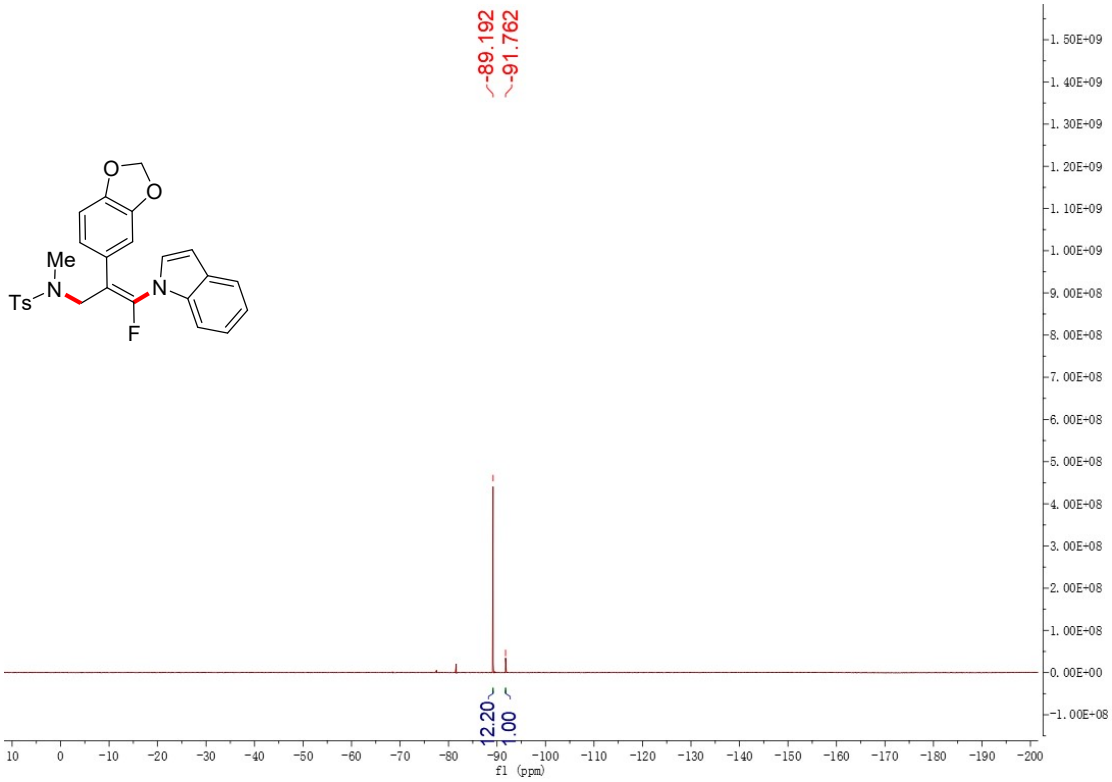
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 4w



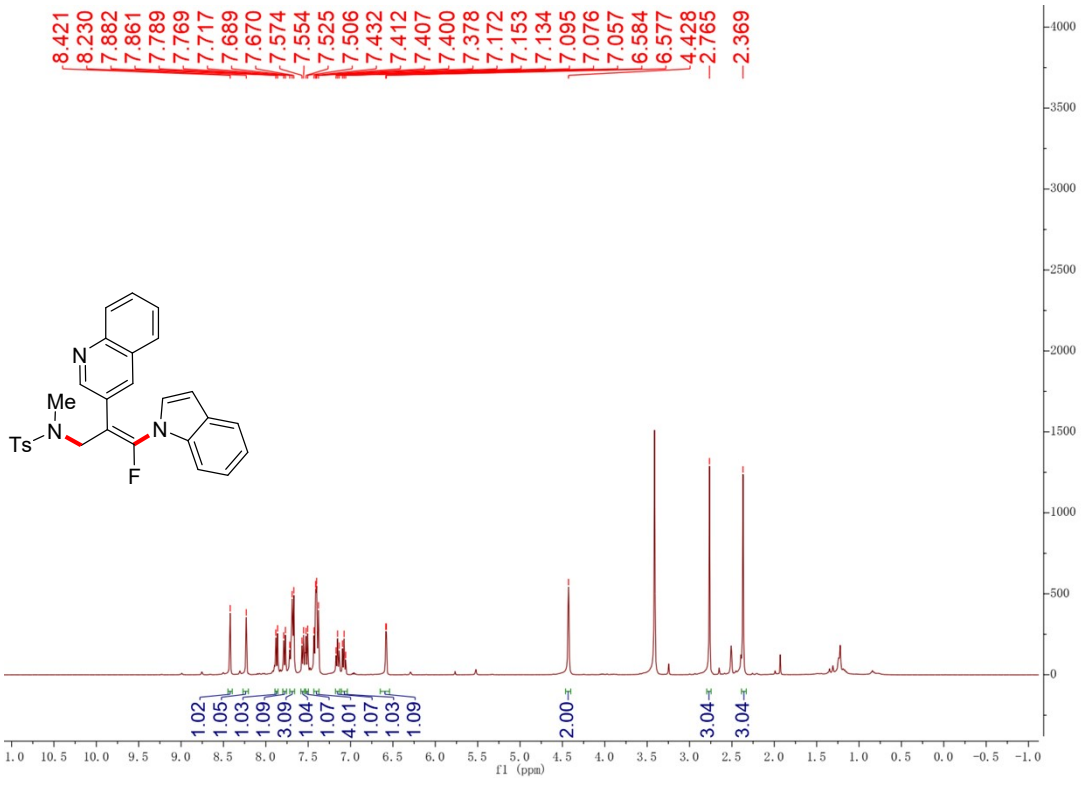
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 4w



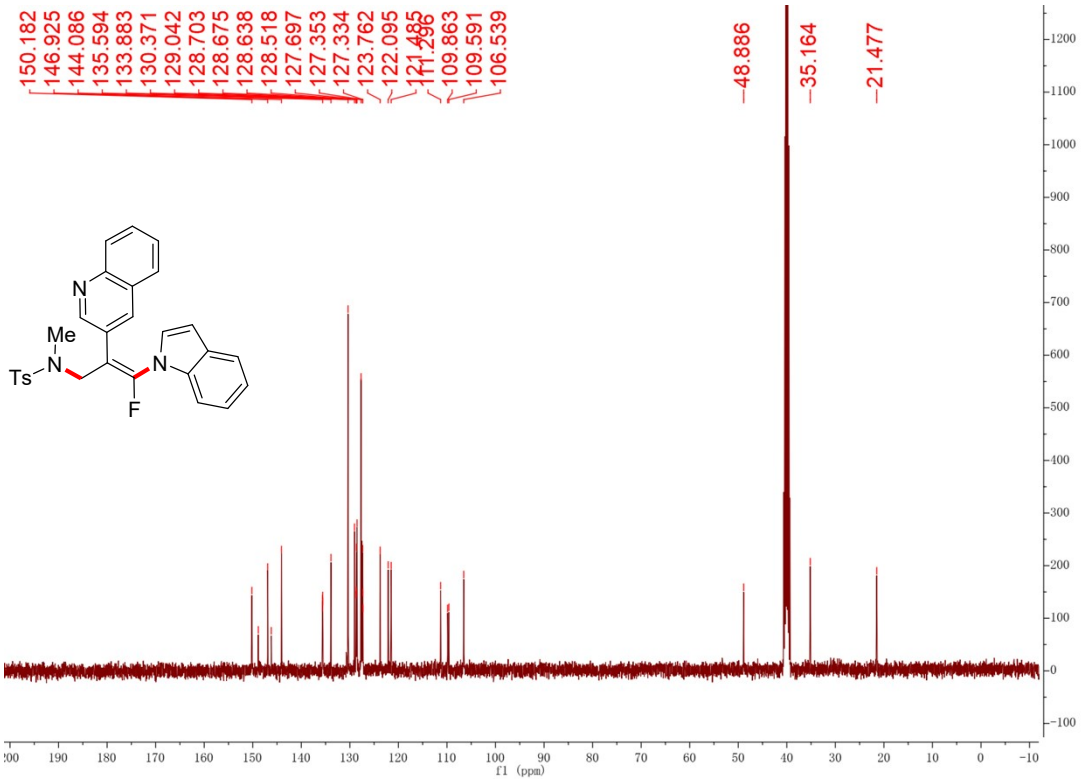
^{19}F NMR (471 MHz, $CDCl_3$) spectrum for 4w



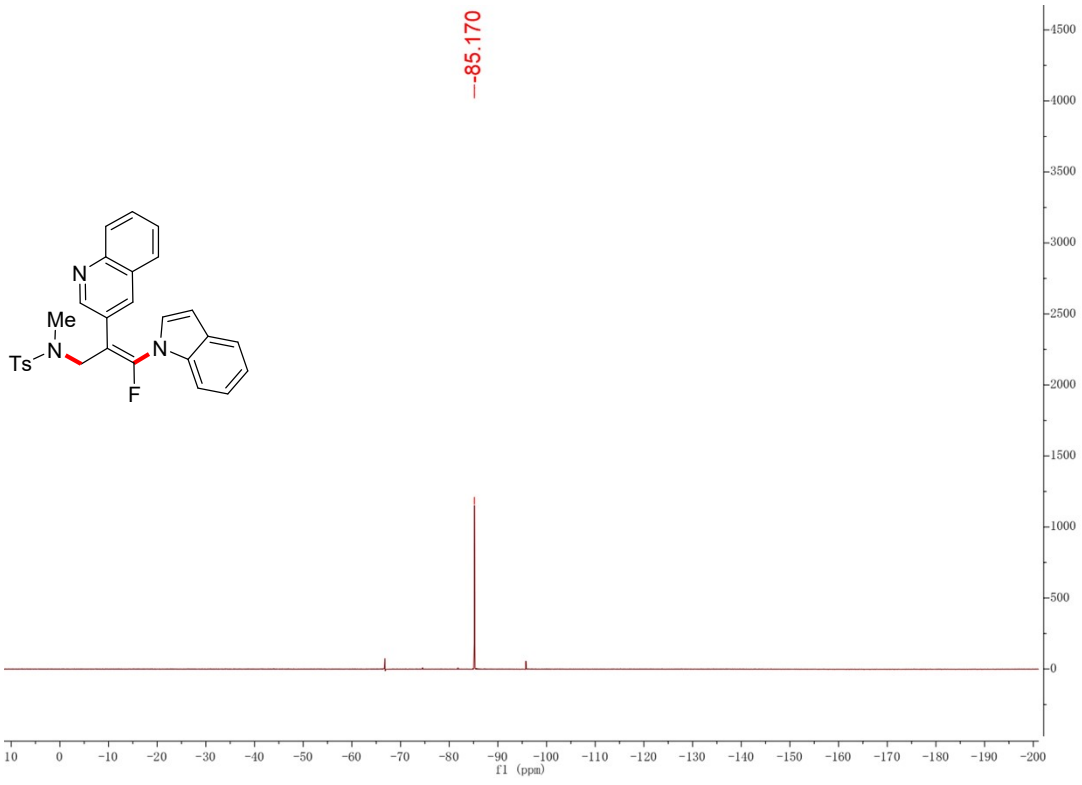
^{1}H NMR (400 MHz, DMSO-d_6) spectrum for 4x



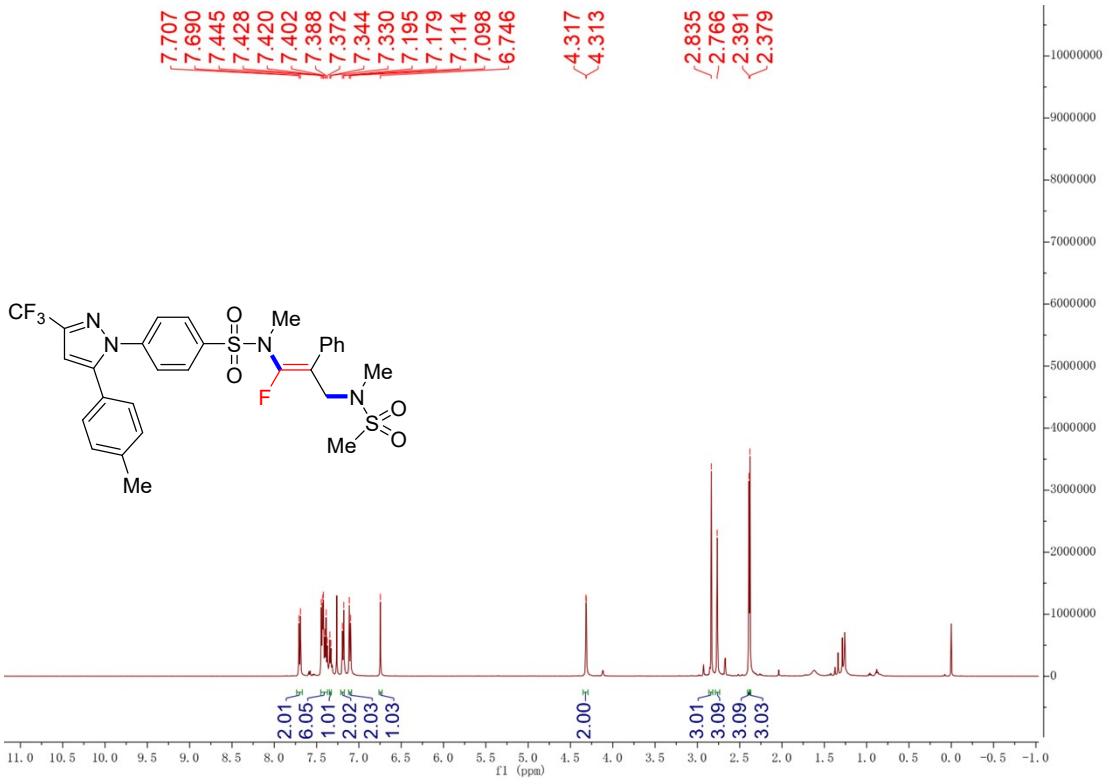
^{13}C NMR (101 MHz, DMSO-d_6) spectrum for 4x



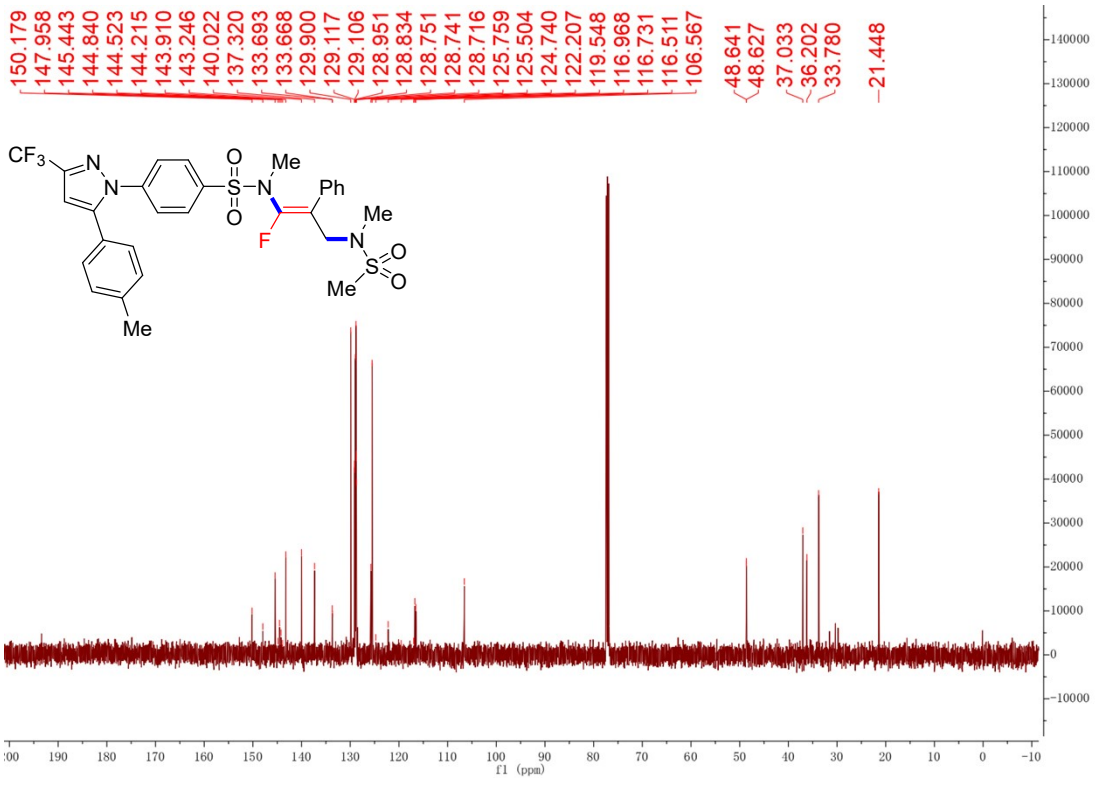
^{19}F NMR (376 MHz, DMSO-d_6) spectrum for 4x



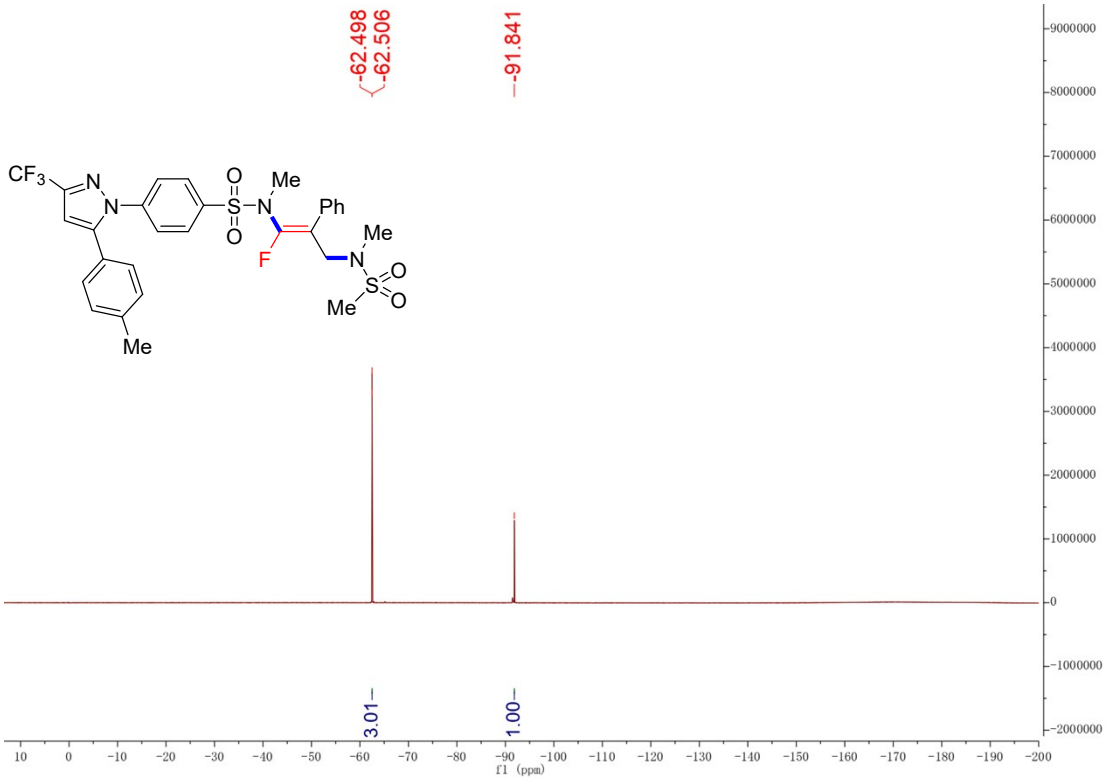
^{1}H NMR (500 MHz, $CDCl_3$) spectrum for 9a



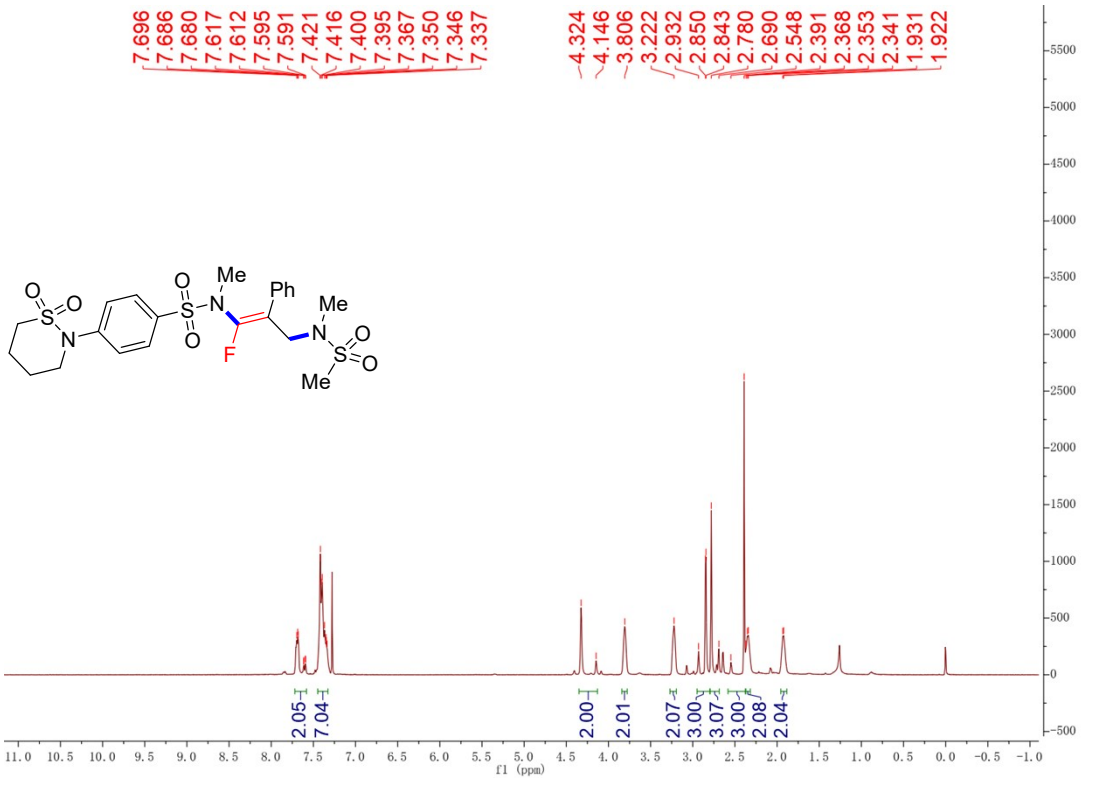
^{13}C NMR (126 MHz, $CDCl_3$) spectrum for 9a



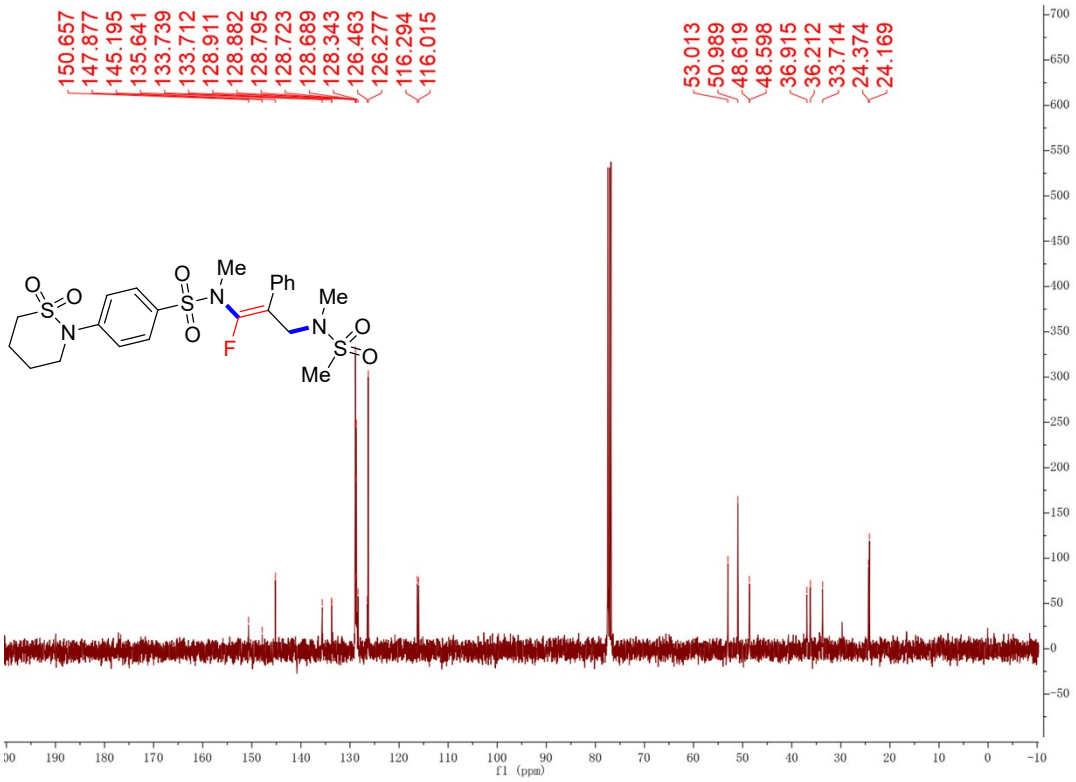
^{19}F NMR (471 MHz, $CDCl_3$) spectrum for 9a



^{1}H NMR (400 MHz, $CDCl_3$) spectrum for 9b



^{13}C NMR (101 MHz, $CDCl_3$) spectrum for 9b



^{19}F NMR (376 MHz, $CDCl_3$) spectrum for 9b