Supporting Information

Divergent Ritter-Type Amination *via* Photoredox Catalytic Four-component Radical-Polar Crossover Reactions

Sheng-Qiang Guo[a], Hui-Qing Yang[c], Ai-Lian Wang[a], Yu-Zhen Jiang[a], Guo-Qiang Xu[a], Yong-Chun Luo[a, b]*, Zhao-Xu Chen[c] and Peng-Fei Xu[a, b]*

[a]State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P.R. China.

[b]State Key Laboratory of Veterinary Etiological Biology, College of Veterinary Medicine, Lanzhou University, 730000, P. R. China

[c]Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical En gineering, Nanjing University, Nanjing 210023, P. R. China

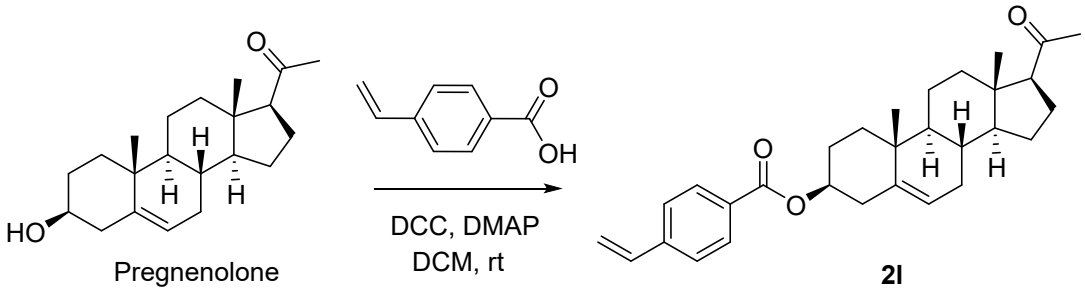
Corresponding author: xupf@lzu.edu.cn, luoych@lzu.edu.cn

Contents

1. General Information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). ^{19}F NMR spectra were recorded at 376 MHz on Bruker DPX-400 using the spectrometer reference. The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet, dt = doublet of triplet, ddd = doublet of doublets of doublets), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

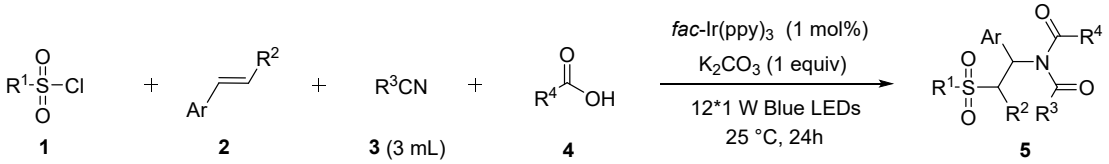
2. Preparation of Substrate 2l

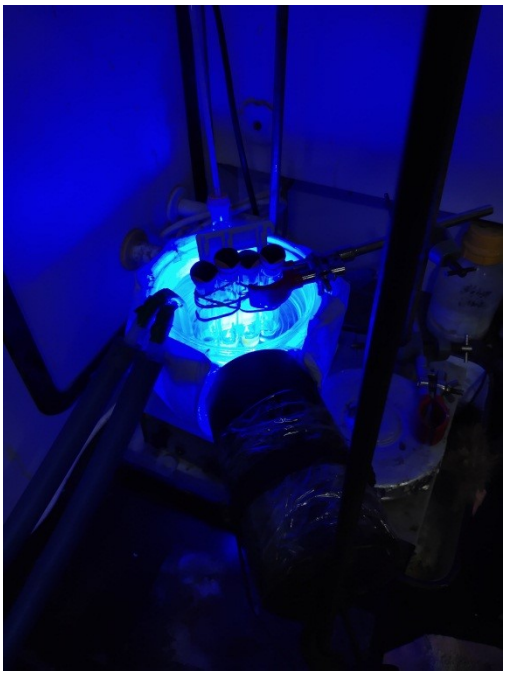


A 25 mL round flask equipped with a Teflon-coated magnetic stir bar was charged with pregnenolone (0.5 mmol, 1 equiv., 0.158 g), 4-Vinylbenzoic acid (1.5 mmol, 3 equiv., 0.23 g), N,N'-dicyclohexylcarbodiimide (DCC, 1.5 mmol, 3 equiv., 0.31 g), 4-dimethylaminopyridine (DMAP, 1.5 mmol, 3 equiv., 184 mg) and CH_2Cl_2 (10 mL) solvent. The reaction mixture was stirred at room temperature overnight. The reaction mixture was washed with H_2O (10 mL) and extracted 3 times with CH_2Cl_2. The organic fraction was dried with anhydrous Na_2SO_4, then concentrated under vacuum and purified by column chromatography on silica gel to afford the product **2l** as a white solid (0.217 g, 97% yield).

3. General Procedures for the Synthesis of Products

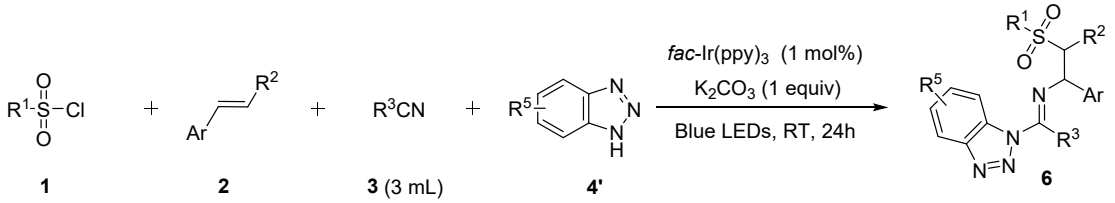
Procedure A: General procedures for synthesis of *β*-sulfonyl imide 5

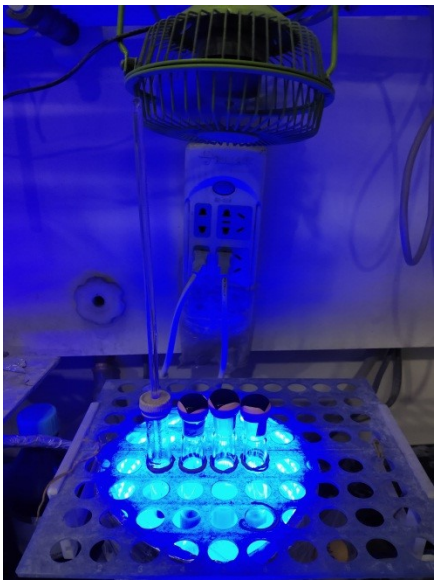




To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and carboxylic acid **4** (0.2 mmol). Dry nitrile **3** (3.0 mL) was added, after which the alkene **2** (0.2 mmol) and sulfonyl halide **1** (0.25 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25℃ for 24h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1), which furnished the title compounds as described.

Procedure B: General procedures for synthesis of *β*-sulfonyl imine 6



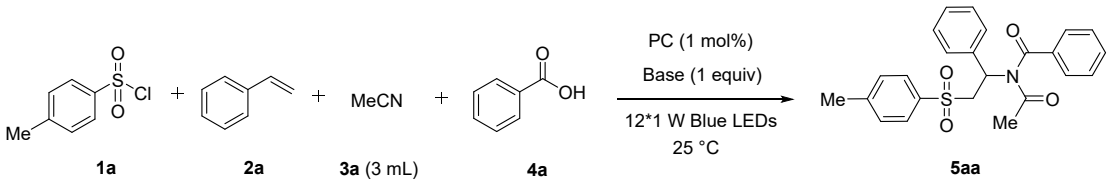


To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and benzotriazole **4'** (0.2 mmol). Dry nitrile **3** (3.0 mL) was added, after which the alkene **1** (0.2 mmol) and sulfonyl halide **2** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 24h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1), which furnished the title compounds as described.

4. Initial Studies and the Reaction Optimization

Optimization A: Optimization of reaction conditions for synthesis of *β*-sulfonyl imide 5

Table S1: Initial Studies and the Reaction Optimization[a]



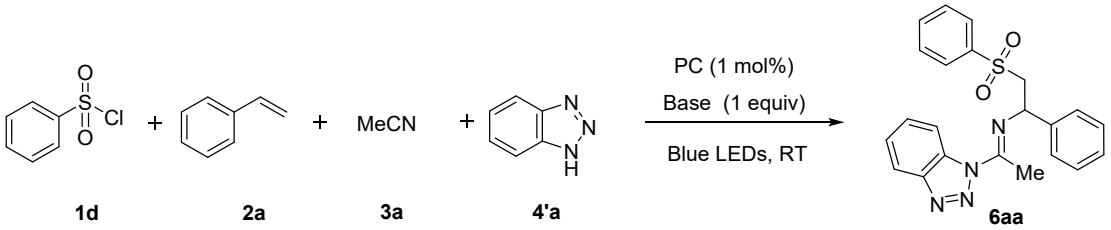
Entry	PC	1a/2a/4a/Base	Base	Solvent	Time(h)	Yield(%)[b]
1[c]	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	24	45
2[c]	-	1/1/1/1	K_2CO_3	CH_3CN	24	nr
3[c,d]	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	24	nr
4[c]	*fac*-Ir(ppy)$_3$	1/1/1/1	-	CH_3CN	24	nr
5[c]	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	DCM	24	nr
6[c,e]	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	24	60
7	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	24	81
8	$[Ir(ppy)_2(dtbpy)](PF_6)$	1/1/1/1	K_2CO_3	CH_3CN	24	25
9	EY	1/1/1/1	K_2CO_3	CH_3CN	24	nr
10	$[Ru(bpy)_3]Cl_2$	1/1/1/1	K_2CO_3	CH_3CN	24	nr
11	4CzIPN	1/1/1/1	K_2CO_3	CH_3CN	24	trace
12	*fac*-Ir(ppy)$_3$	1/1/1/1	Na_2CO_3	CH_3CN	24	50
13	*fac*-Ir(ppy)$_3$	1/1/1/1	Cs_2CO_3	CH_3CN	24	29
14	*fac*-Ir(ppy)$_3$	1/1/1/1	$NaHCO_3$	CH_3CN	24	16
15	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	2 mL CH_3CN	24	68
16	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	4 mL CH_3CN	24	70

17	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	18	54
18	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	24	81
19	*fac*-Ir(ppy)$_3$	1/1/1/1	K_2CO_3	CH_3CN	30	78
20	***fac*-Ir(ppy)$_3$**	**1.25/1/1/1**	**K_2CO_3**	**CH_3CN**	**24**	**90**
21	*fac*-Ir(ppy)$_3$	1/1.25/1/1	K_2CO_3	CH_3CN	24	81
22	*fac*-Ir(ppy)$_3$	1/1/1.25/1	K_2CO_3	CH_3CN	24	79
23	*fac*-Ir(ppy)$_3$	1/1/1/1.25	K_2CO_3	CH_3CN	24	77
24	*fac*-Ir(ppy)$_3$	1.5/1/1/1	K_2CO_3	CH_3CN	24	87
25	*fac*-Ir(ppy)$_3$	2.0/1/1/1	K_2CO_3	CH_3CN	24	86

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **4a** (0.2 mmol), PC (1 mol%), Base (1.0 eq.), Solvent (3 mL), N_2 atmosphere, a 12*1 W blue LED strip, 25 °C; [b] Isolated yield; [c] The reaction was performed in an 8 W blue light-emitting diode (LED) strip, the temperature is 32 °C; [d] The reaction was performed in the dark; [e] The temperature is 25 °C;

Optimization B: Optimization of reaction conditions for synthesis of *β*-sulfonyl imine 6

Table S2: Initial Studies and the Reaction Optimization[a]



1d **2a** **3a** **4'a** **6aa**

Entry	PC	Base	Solvent	Time(h)	Yield(%)[b]
1	*fac*-Ir(ppy)$_3$	LiO^{t}Bu	CH_3CN	24	50
2	-	LiO^{t}Bu	CH_3CN	24	nr
3[c]	*fac*-Ir(ppy)$_3$	LiO^{t}Bu	CH_3CN	24	nr
4	*fac*-Ir(ppy)$_3$	-	CH_3CN	24	47

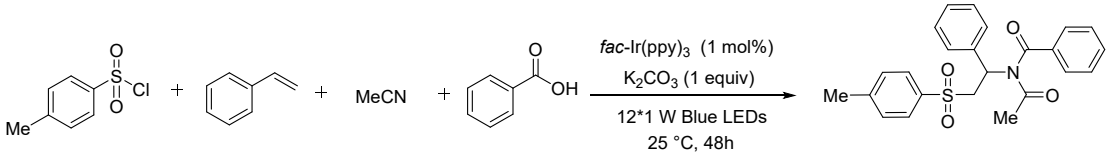
5	*fac*-Ir(ppy)$_3$	LiO^{t}Bu	DCM	24	nr
6	[Ir(ppy)$_2$dtbpy)](PF$_6$)	LiO^{t}Bu	CH_3CN	24	nr
7	[Ru(bpy)$_3$](PF$_6$)$_2$	LiO^{t}Bu	CH_3CN	24	nr
8	4CzIPN	LiO^{t}Bu	CH_3CN	24	nr
9	*fac*-Ir(ppy)$_3$	2,6-lutidine	CH_3CN	24	35
10	*fac*-Ir(ppy)$_3$	DMAP	CH_3CN	24	31
11	*fac*-Ir(ppy)$_3$	Pyridine	CH_3CN	24	41
12	*fac*-Ir(ppy)$_3$	Et_3N	CH_3CN	24	trace
13	*fac*-Ir(ppy)$_3$	DIPEA	CH_3CN	24	trace
14	*fac*-Ir(ppy)$_3$	DABCO	CH_3CN	24	44
15	*fac*-Ir(ppy)$_3$	DBU	CH_3CN	24	13
16	*fac*-Ir(ppy)$_3$	KO^{t}Bu	CH_3CN	24	56
17	*fac*-Ir(ppy)$_3$	Cs_2CO_3	CH_3CN	24	54
18	*fac*-Ir(ppy)$_3$	$NaHCO_3$	CH_3CN	24	68
19	*fac*-Ir(ppy)$_3$	Na_2CO_3	CH_3CN	24	83
20	***fac-Ir(ppy)$_3$***	**K_2CO_3**	**CH_3CN**	**24**	**94**
21	*fac*-Ir(ppy)$_3$	K_2HPO_4	CH_3CN	24	41
22[d]	*fac*-Ir(ppy)$_3$	K_2CO_3	DCM	24	27
23[d]	*fac*-Ir(ppy)$_3$	K_2CO_3	DCE	24	36
24[d]	*fac*-Ir(ppy)$_3$	K_2CO_3	Toluene	24	trace
25[d]	*fac*-Ir(ppy)$_3$	K_2CO_3	THF	24	nr
26	*fac*-Ir(ppy)$_3$	K_2CO_3	CH_3CN	6	68

27	*fac*-Ir(ppy)$_3$	K_2CO_3	CH_3CN	12	77
28	*fac*-Ir(ppy)$_3$	K_2CO_3	CH_3CN	18	84

[a] Reaction conditions: **1d** (0.2 mmol), **2a** (0.2 mmol), **4'a** (0.2 mmol), PC (1 mol%), Base (0.2 mmol), Solvent (3 mL), N_2 atmosphere, an 8 W blue light-emitting diode (LED) strip, room temperature; [b] Isolated yield. [c] The reaction was performed in the dark; [d] CH_3CN (2 mmol).

5. Gram-Scale Reaction

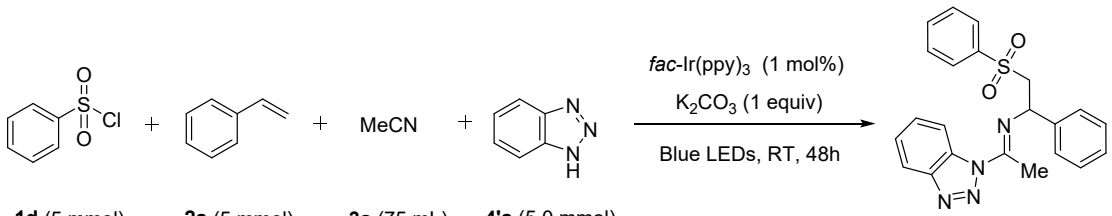
Reaction A: Gram-scale reaction for synthesis of *β*-sulfonyl imide 5aa



1a (6.25 mmol) 1.19g | **2a** (5.0 mmol) 0.52g | **3a** (75 mL) | **4a** (5 mmol) 0.61g | **5aa** 1.656g 79% yield

To an oven-dried 150 mL flask equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.05 mmol), K_2CO_3 (5.0 mmol), and benzoic acid **4a** (5.0 mmol). Dry acetonitrile **3a** (75.0 mL) was added, after which the styrene **2a** (5.0 mmol) and tosyl chloride **1a** (6.25 mmol) were added respectively at 25 °C. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25 °C for 24h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the desired product **5aa** (yield 64%, 1.348g). The resulting mixture was stirred at 25 °C for 48h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the desired product **5aa** (yield 79%, 1.656g).

Reaction B: Gram-scale reaction for synthesis of *β*-sulfonyl imine 6aa



1d (5 mmol) 0.88g | **2a** (5 mmol) 0.52g | **3a** (75 mL) | **4'a** (5.0 mmol) 0.60g | **6aa** 1.721g 85% yield

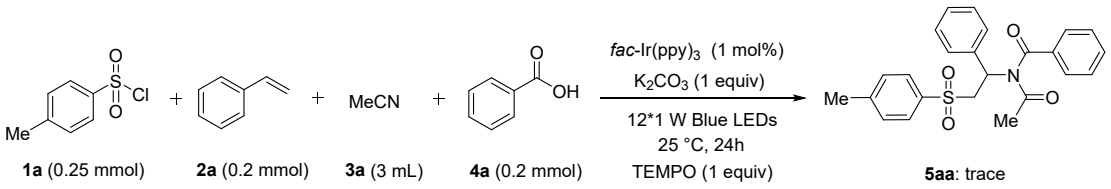
To an oven-dried 150 mL flask equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.05 mmol), K_2CO_3 (5.0 mmol), and benzotriazole **4'a** (5.0 mmol). Dry acetonitrile **3a** (75.0 mL) was added, after which the styrene **2a** (5.0 mmol) and sulfonyl halide **1d** (5.0 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by

three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 24h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the desired product **6aa** (yield 51%, 1.031g). The resulting mixture was stirred at room temperature for 48h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the desired product **6aa** (yield 85%, 1.721g).

6. Mechanistic Investigations

6.1 Radical inhibition experiments

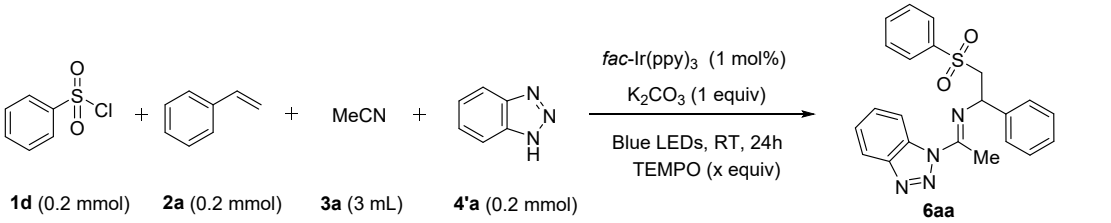
Experiment A: Radical inhibition experiment for synthesis of *β*-sulfonyl imide



1a (0.25 mmol) **2a** (0.2 mmol) **3a** (3 mL) **4a** (0.2 mmol) **5aa**: trace

In the model reaction of **1a**, **2a**, **3a** and **4a** in the presence of *fac*-Ir(ppy)$_3$ (1 mol%), the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the reaction mixture, the reaction mixture was irradiated under a 12*1 W blue LEDs for 24 hours, the desired product **5aa** was completely inhibited in the presence of 1 equivalents of TEMPO, suggesting that the reaction might involve a radical process.

Experiment B: Radical inhibition experiment for synthesis of *β*-sulfonyl imine



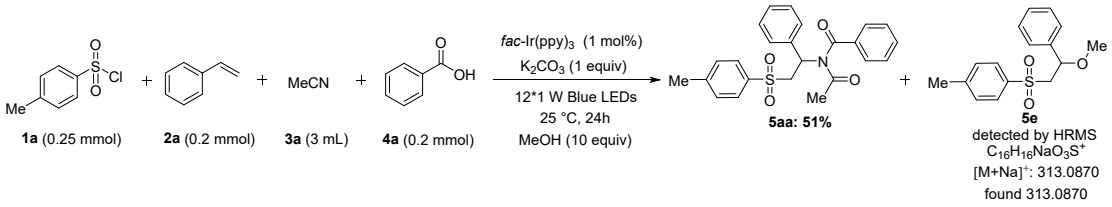
1d (0.2 mmol) **2a** (0.2 mmol) **3a** (3 mL) **4'a** (0.2 mmol) **6aa**

TEMPO (1.0 equiv) 21% yield
TEMPO (2.0 equiv) 0% yield

In the model reaction of **1d**, **2a**, **3a** and **4'a** in the presence of *fac*-Ir(ppy)$_3$ (1 mol%), the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the reaction mixture, the reaction mixture was irradiated under an 8 W blue LEDs for 24 hours, the desired product **6aa** decreased to 21% and 0% yield sharply, suggesting that the reaction might involve a radical process.

6.2 Carbenium ion trapping experiments

Experiment A: Carbenium ion trapping experiment for synthesis of *β*-sulfonyl imide



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), and K_2CO_3 (0.2 mmol). Dry acetonitrile (3.0 mL) was added, after which the styrene **2a** (0.2 mmol), MeOH (2.0 mmol), benzoic acid **4a** (0.2 mmol) and tosyl chloride **1a** (0.25 mmol) were added respectively at 25°C. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25 °C for 24h.

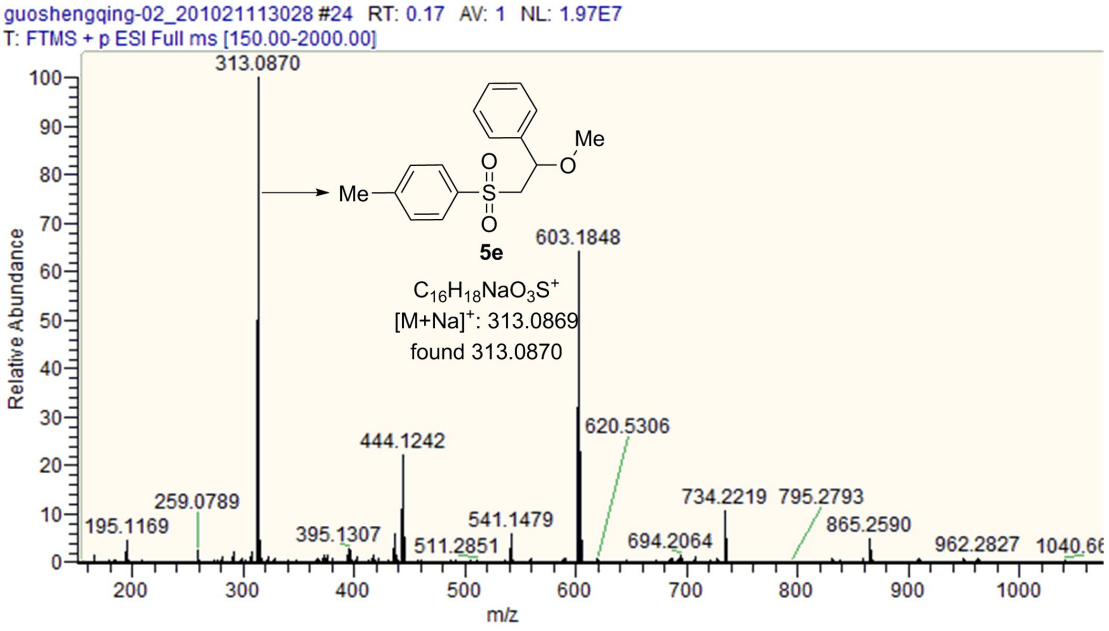
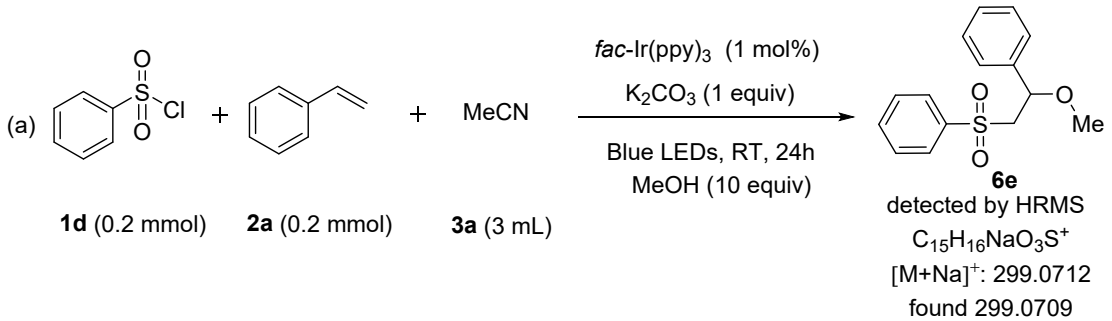


Figure S1. HRMS of the mixture (d).

Experiment B: Carbenium ion trapping experiment for synthesis of *β*-sulfonyl imine



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), and K_2CO_3 (0.2 mmol). Dry acetonitrile **3a** (3.0 mL) was added, after which the alkene **2a** (0.2 mmol), MeOH (2.0 mmol) and sulfonyl halide **1d** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of

freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 24h.

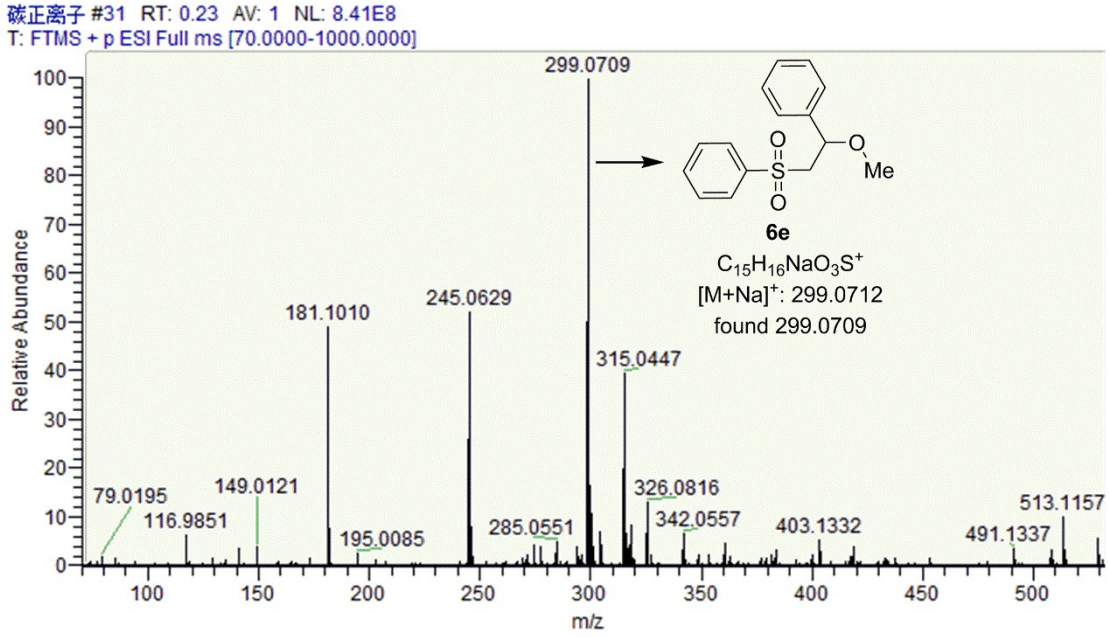
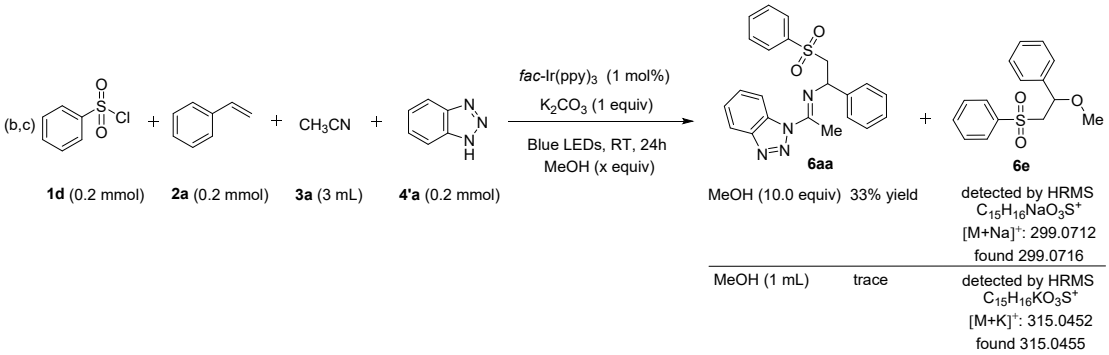


Figure S2. HRMS of the mixture (a).



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and benzotriazole **4'a** (0.2 mmol). Dry acetonitrile **3a** (3.0 mL) was added, after which the alkene **2a** (0.2 mmol), MeOH and sulfonyl halide **1d** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 24h. The desired product **6aa** decreased to 33% yield and trace sharply.

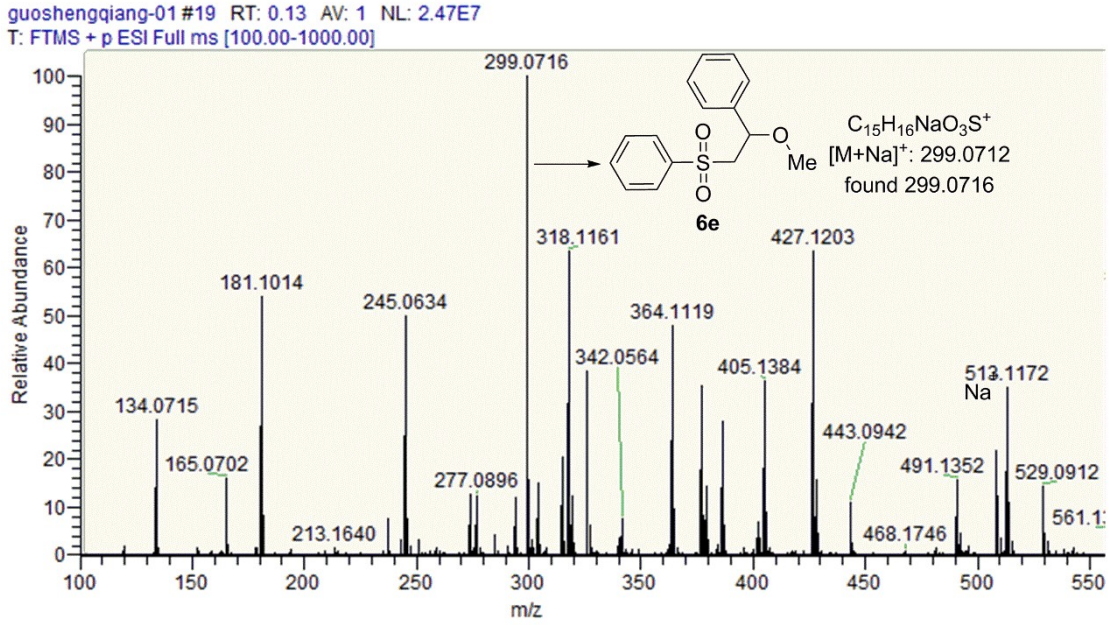


Figure S3. HRMS of the mixture (b).

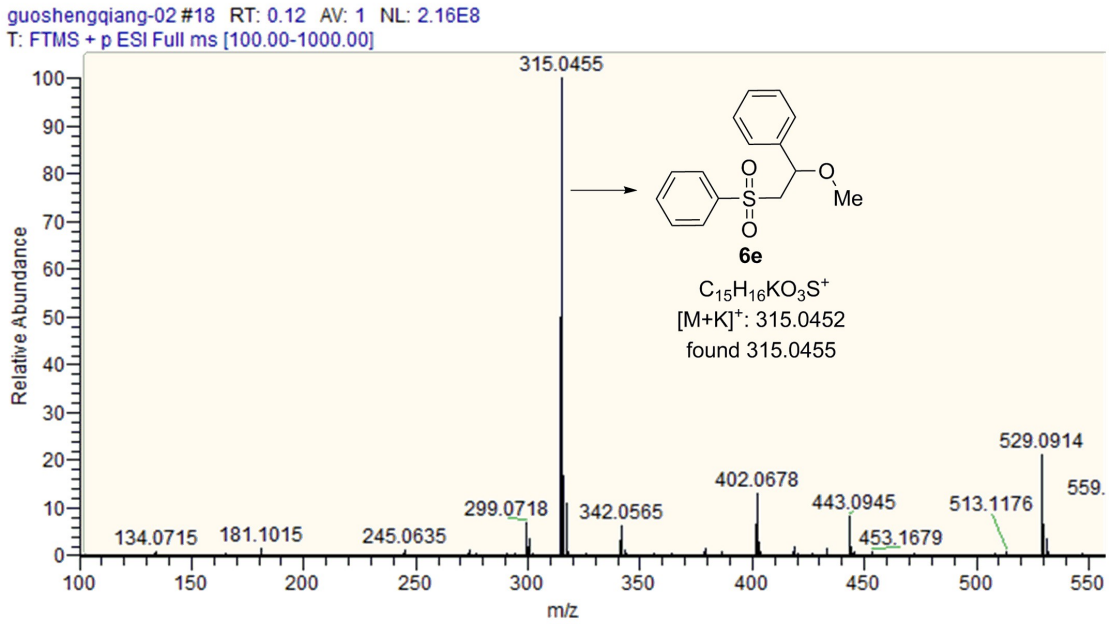
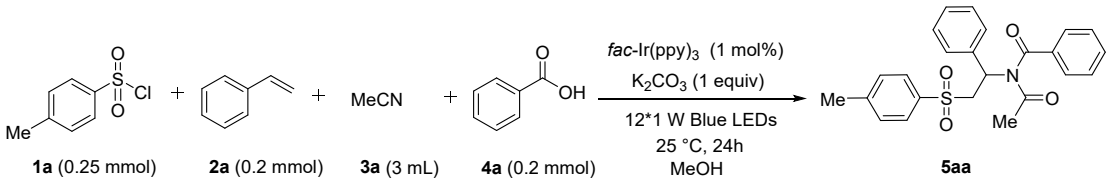


Figure S4. HRMS of the mixture (c).

6.3 Three-component competition reaction with adding different amounts of MeOH for synthesis of *β*-sulfonyl imide

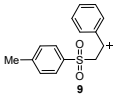


To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$

(0.002 mmol), and K_2CO_3 (0.2 mmol). Dry acetonitrile (3.0 mL) was added, after which the styrene (0.2 mmol), MeOH and tosyl chloride (0.25 mmol) were added respectively at 25 °C. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25 °C for 24h.

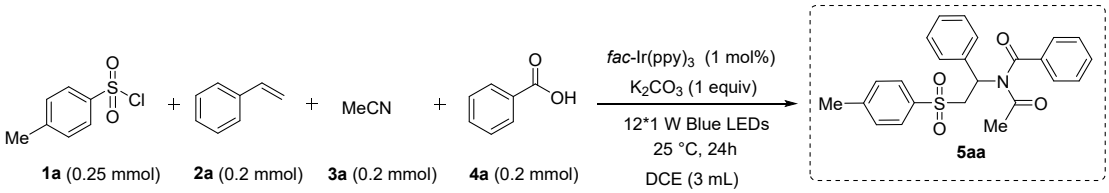
We were very interested that this four-component reaction was so efficient, thus we set up a series of three-component competitive carbenium ion trapping experiments. In standard conditions II, the *fac*-Ir(ppy)$_3$ (0.002 mmol) was added, the maximum amount of carbocation **9** (Figure 3. Plausible mechanism) that can be produced is $2*10^{-3}$mmol, so we set it as 1 equivalent. With the increase of the amount of MeOH, the yield of the target product **5aa** decreased gradually. When the amount of MeOH was more than MeCN, although the yield of the target product **5aa** decreased significantly, the four-component target could still be obtained at a certain yield (**Table S2, Entry 5,6,7**). Therefore, the four-component reaction tendency was obvious when (3ml) MeCN was used as the solvent.

Table S3: Three-component competition reaction with adding different amounts of MeOH.

Entry	CH_3CN	PhCOOH		MeOH	Yield(%)[a]
1	2.85*10^{4}eq.	100 eq.	1 eq.	-	90
2	2.85*10^{4}eq.	100 eq.	1 eq.	2 mmol (1*10^{3}eq)	51
3	2.85*10^{4}eq.	100 eq.	1 eq.	0.5 mL (1.23*10^{4}eq)	16
4	2.85*10^{4}eq.	100 eq.	1 eq.	1.0 mL (2.46*10^{4}eq)	14
5	2.85*10^{4}eq.	100 eq.	1 eq.	1.5 mL (3.69*10^{4}eq)	11
6	2.85*10^{4}eq.	100 eq.	1 eq.	3.0 mL (7.38*10^{4}eq)	8
7	1.43*10^{4}eq. (1.5 mL)	100 eq.	1 eq.	1.5 mL (3.69*10^{4}eq)	7

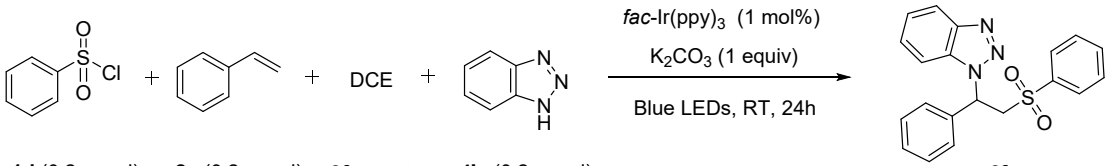
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **4a** (0.2 mmol), PC (1 mol%), Base (1.0 eq.), Solvent MeCN (3 mL), MeOH, 12*1 W blue LED strip, 25℃ for 24 h and under N_2 atmosphere; [b] **5aa** Isolated yield;

6.4 Evaluation of the stoichiometry of the MeCN for synthesis of *β*-sulfonyl imide



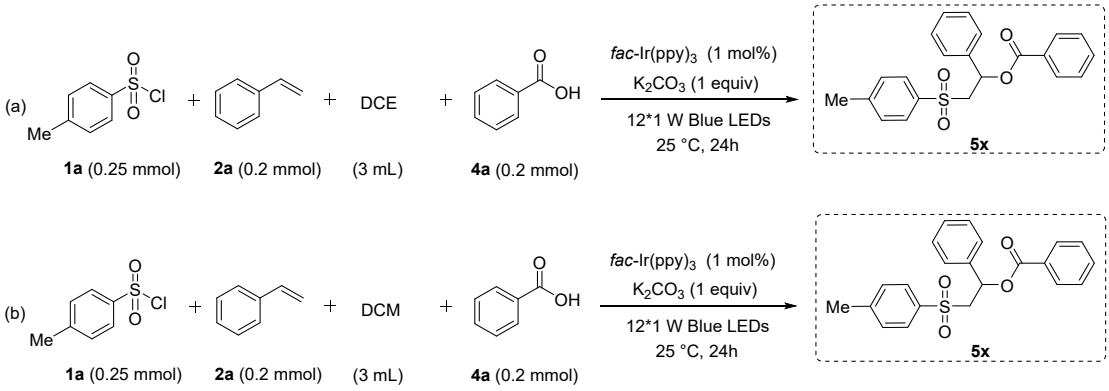
To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), and K_2CO_3 (0.2 mmol). Dry 1,2-Dichloroethane (3.0 mL) was added, after which the styrene (0.2 mmol), MeCN (0.2 mmol) and tosyl chloride (0.25 mmol) were added respectively at 25 °C. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25 °C for 24h. The target compound **5aa** was not obtained in this condition. Therefore, the solvent amount of MeCN is essential for the four-component reaction.

6.5 Three-component reaction with change CH_3CN to DCE (Variations from the reaction conditions for synthesis of *β*-sulfonyl imine)



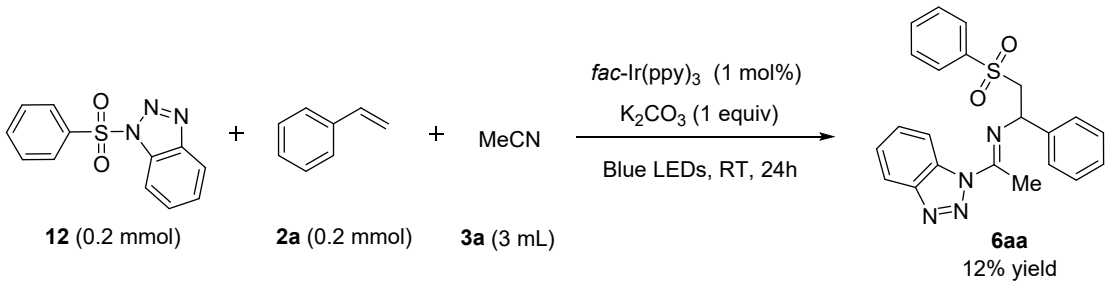
To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and benzotriazole (0.2 mmol). Dry dichloroethane **3f** (3.0 mL) was added, after which the alkene **2a** (0.2 mmol) and sulfonyl halide **1d** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at at room temperature for 24h. Then, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the three-component product **6f** (yield 13%).

6.6 Three-component reaction with change CH_3CN to DCE, DCM (Variations from the reaction conditions for synthesis of *β*-sulfonyl imide)



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and benzotriazole (0.2 mmol). Dry dichloroethane or dichloromethane (3.0 mL) was added, after which the alkene (0.2 mmol) and sulfonyl halide (0.2 mmol) were added respectively at 25 °C.. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 12*1 W blue LED strip. The resulting mixture was stirred at 25 °C. for 24h. The target three-component compound **5x** was not obtained in this condition.

6.7 Subjection of 1-(benzenesulfonyl)benzotriazole to the reaction conditions for synthesis of *β*-sulfonyl imine

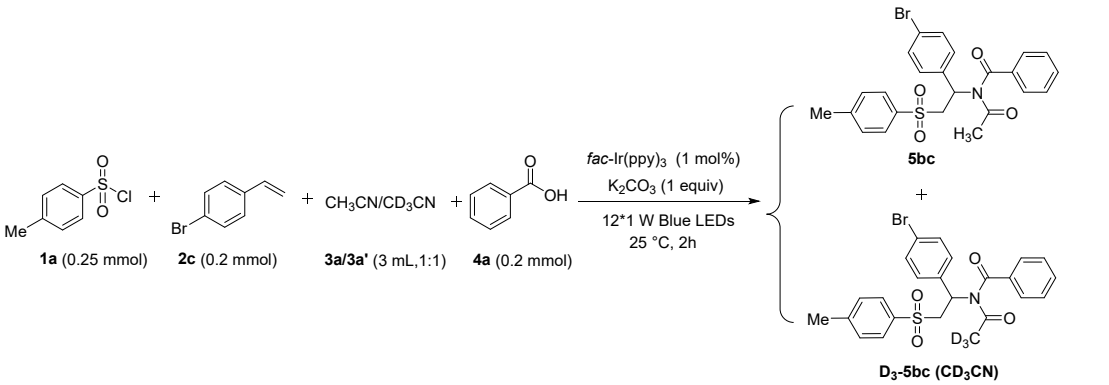


12 (0.2 mmol) **2a** (0.2 mmol) **3a** (3 mL) **6aa** 12% yield

To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added *fac*-Ir(ppy)$_3$ (0.002 mmol), K_2CO_3 (0.2 mmol), and 1-(benzenesulfonyl)benzotriazole **12** (0.2 mmol). Dry acetonitrile **3a** (3.0 mL) was added, after which the alkene **2a** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with an 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 24h. Then, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the desired product **6aa** (yield 12%).

6.8 Isotope labeling reaction

Reaction A: Isotope labeling reaction for synthesis of *β*-sulfonyl imide



1a (0.25 mmol) **2c** (0.2 mmol) **3a/3a'** (3 mL,1:1) **4a** (0.2 mmol)

Combined yield: 54%, **5bc/D$_3$-5bc (CD$_3$CN)** = 1:1

The deuterium-labeling experiment was conducted by using the co-solvent of CH_3CN and CD_3CN (3 mL, 1:1) instead of CH_3CN (3mL). As shown in Figure S5, the ratio of **5bc** and **D$_3$-5bc(CD$_3$CN)** was about 1/1.

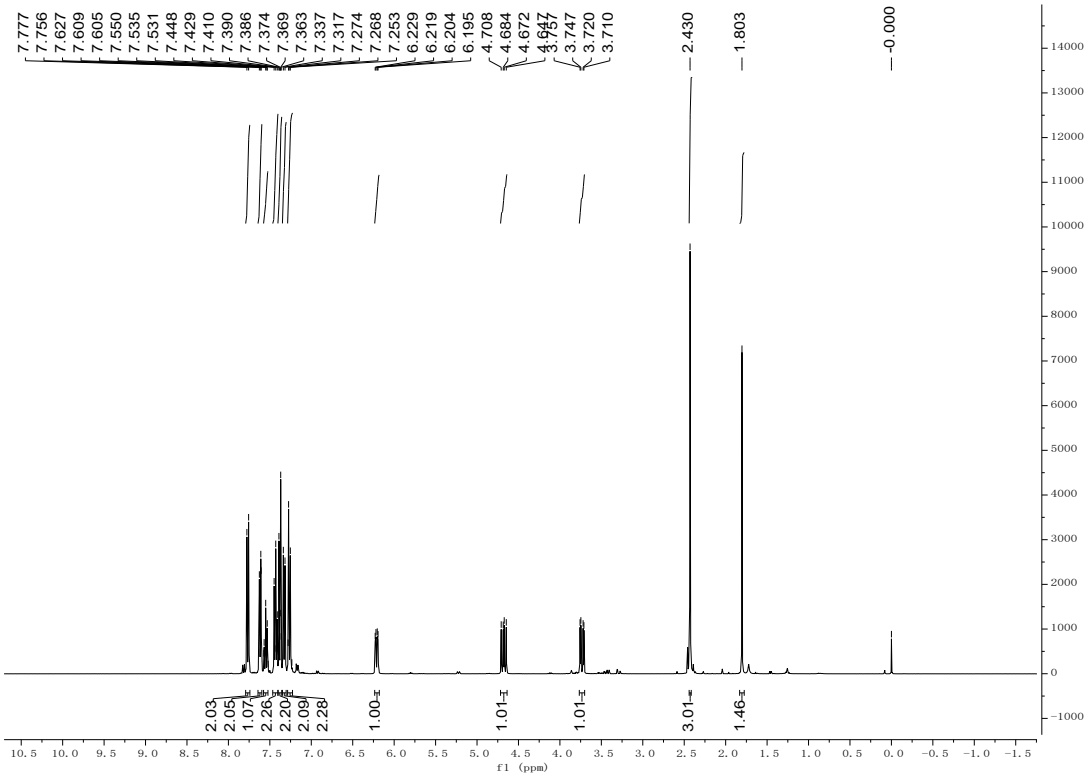
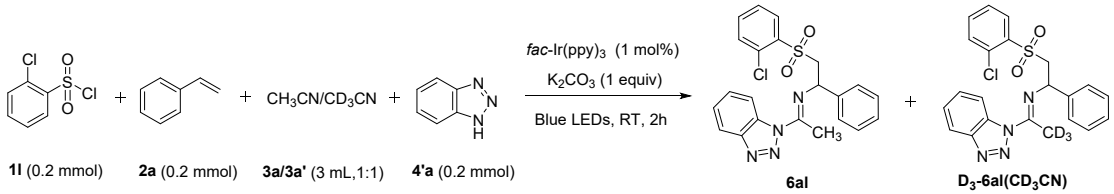


Figure S5. ^{1}H NMR for the products of isotope labeling reaction.

Reaction B: Isotope labeling reaction for synthesis of *β*-sulfonyl imine



Combined yield: 54%, **6al/D_3-6al(CD_3CN)=** 1:1

The deuterium-labeling experiment was conducted by using the co-solvent of CH_3CN and CD_3CN (3 mL, 1:1) instead of CH_3CN (3mL). As shown in Figure S6, the ratio of **6al** and **D_3-6al(CD_3CN)** was about 1/1.

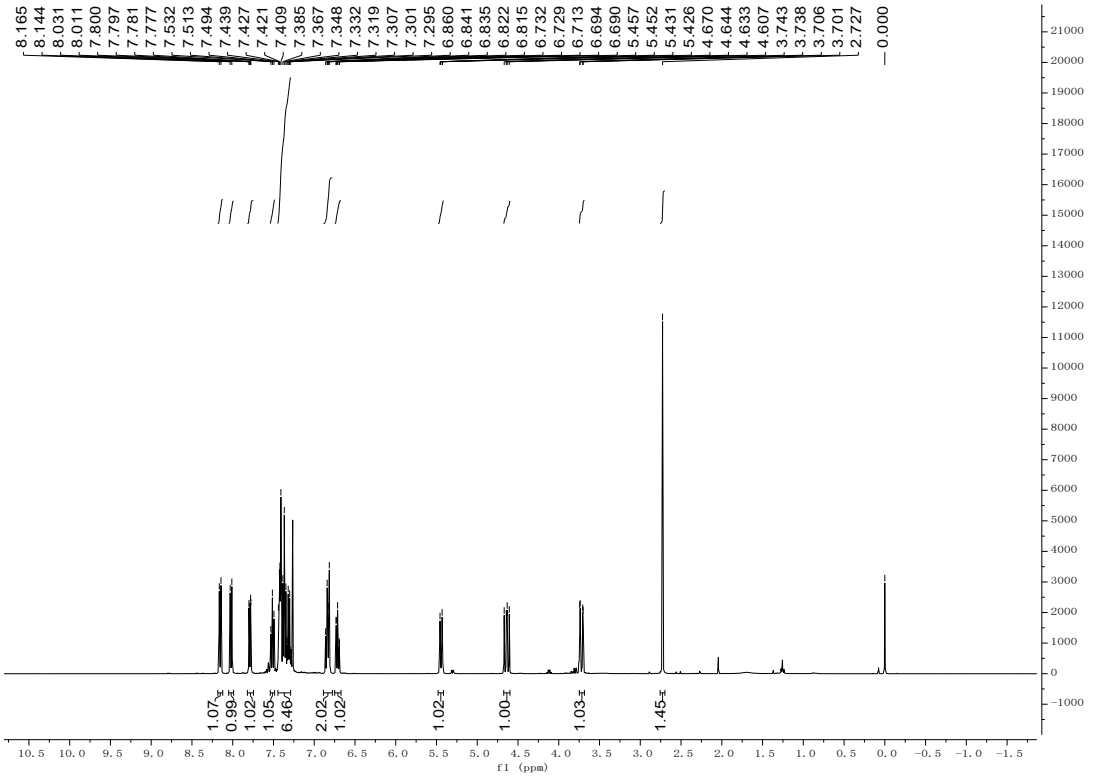
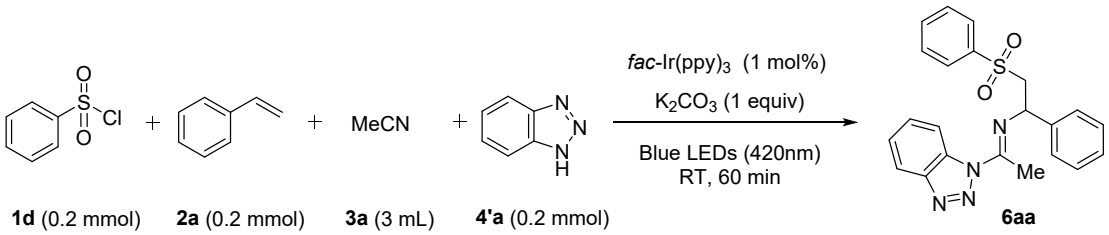


Figure S6. ^{1}H NMR for the products of isotope labeling reaction.

6.9 Measurement of quantum yield



1d (0.2 mmol) **2a** (0.2 mmol) **3a** (3 mL) **4'a** (0.2 mmol) **6aa**

0.67% yield

According to the procedure of related literature[1-2] and our previous studies[3], the photon flux of the LED was determined by standard ferrioxalate actinometry. Determination of the reaction quantum yield at 420 nm and quantum yield measurement was performed in an oven-dried 20 mL quartz vial with a magnetic stirring bar. K_2CO_3 (0.2 mmol), *fac*-Ir(ppy)$_3$ (0.002 mmol), benzotriazole **4a** (0.2 mmol) and dry acetonitrile **3a** (3.0 mL) was added, after which the alkene **2a** (0.2 mmol) and sulfonyl halide **1d** (0.2 mmol) were added respectively at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then irradiated in Parallel Light Reactor (WP-TEC-1020) for for 3600 s (1 h). The reaction mixture was concentrated under reduced pressure, and the resulting mixture was rapid filtered by flash column chromatography on silica gel. The crude yield of the product **6aa** was determined by ^{1}H NMR based on a toluene standard and the final yield was 0.67% ($1.34*10^{-6}$ mol). The reaction quantum yield (Φ) was determined using eq 2, where the photon flux is $2.38*10^{-9}$ E s^{-1} (determined by our previous studies as described[3a]), t is the reaction time (3600 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq 1 (A >3 indicating that the fraction of light absorbed is >0.999).

$f = 1 - 10^{-A(420\ nm)}$ (eq 1)

Φ = Mole number for product/Mole number for absorption of photons

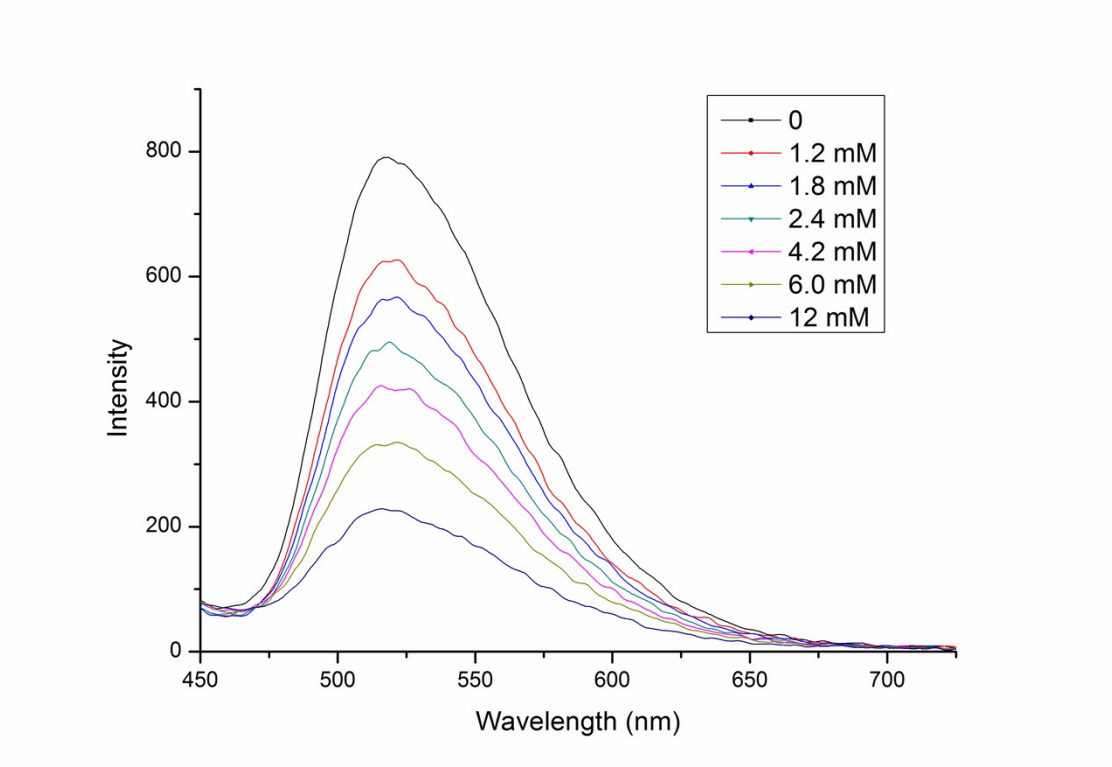
$$\Phi = \frac{Mol\ product}{flux * t * f} = \frac{1.34 \times 10^{-6}}{2.38 \times 10^{-9} \times 3600 \times 1} = 0.156 \quad \text{(eq 2)}$$

We calculated the quantum yield (Φ) of the model reaction to be 0.156. This result shows that the reaction does not support the radical chain growth process.

7. Stern-Volmer Fluorescence Quenching Experiments

Experiment A: Stern-Volmer fluorescence quenching experiment for synthesis of β-sulfonyl imide

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 0.6 mM solution of *fac*-Ir(ppy)$_3$ in dry CH_3CN added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 385 nm and fluorescence was measured from 450 nm to 725 nm. Control experiments showed that the excited state photocatalyst was mainly quenched by Tosyl chloride **1a**.



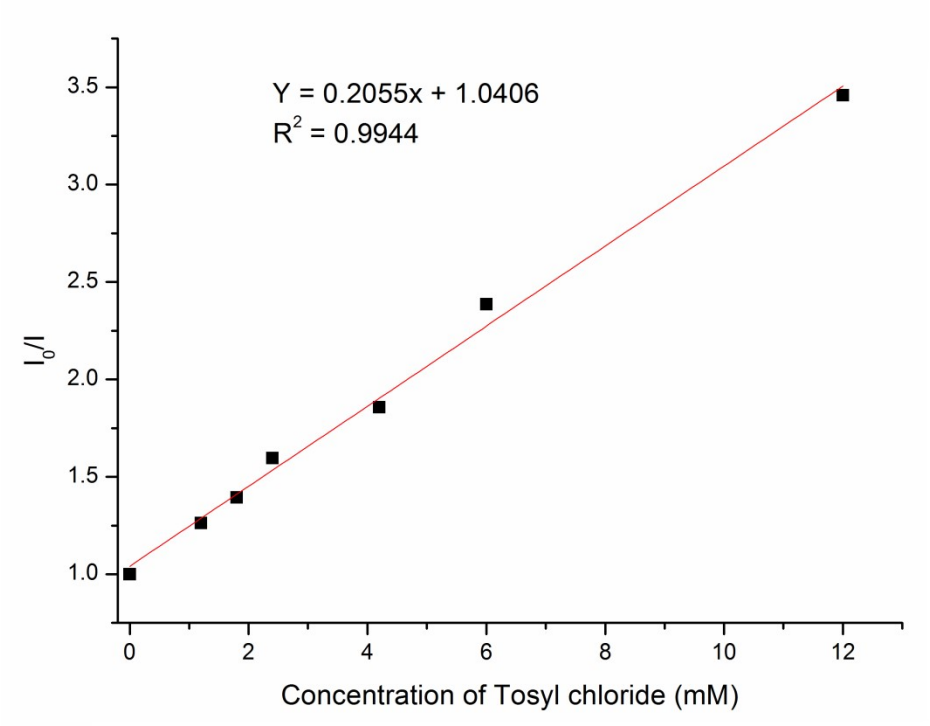


Figure S7-S8. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable TsCl.

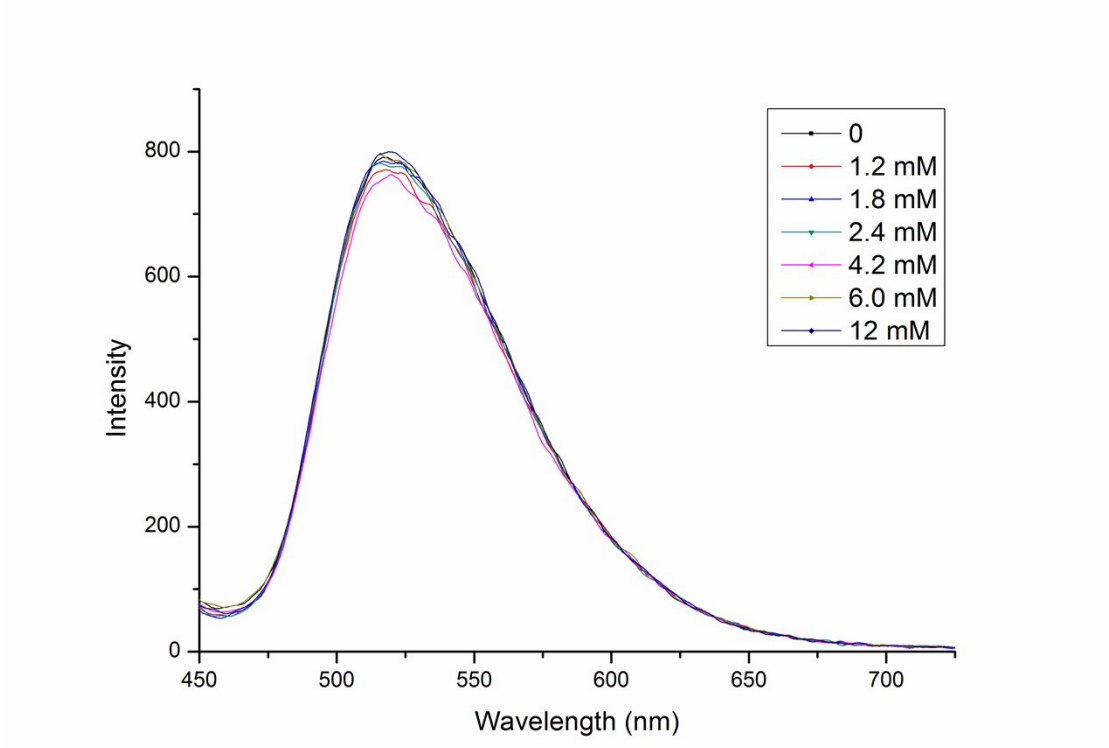


Figure S9. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable Styrene.

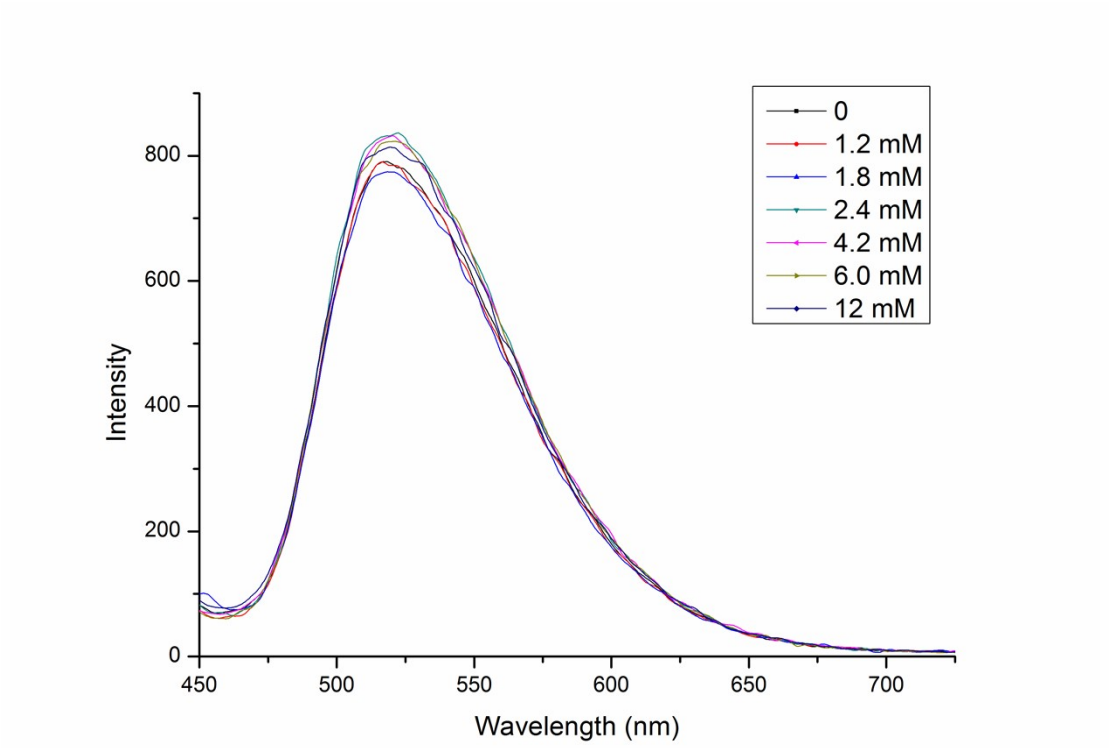


Figure S10. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable Benzoic acid.

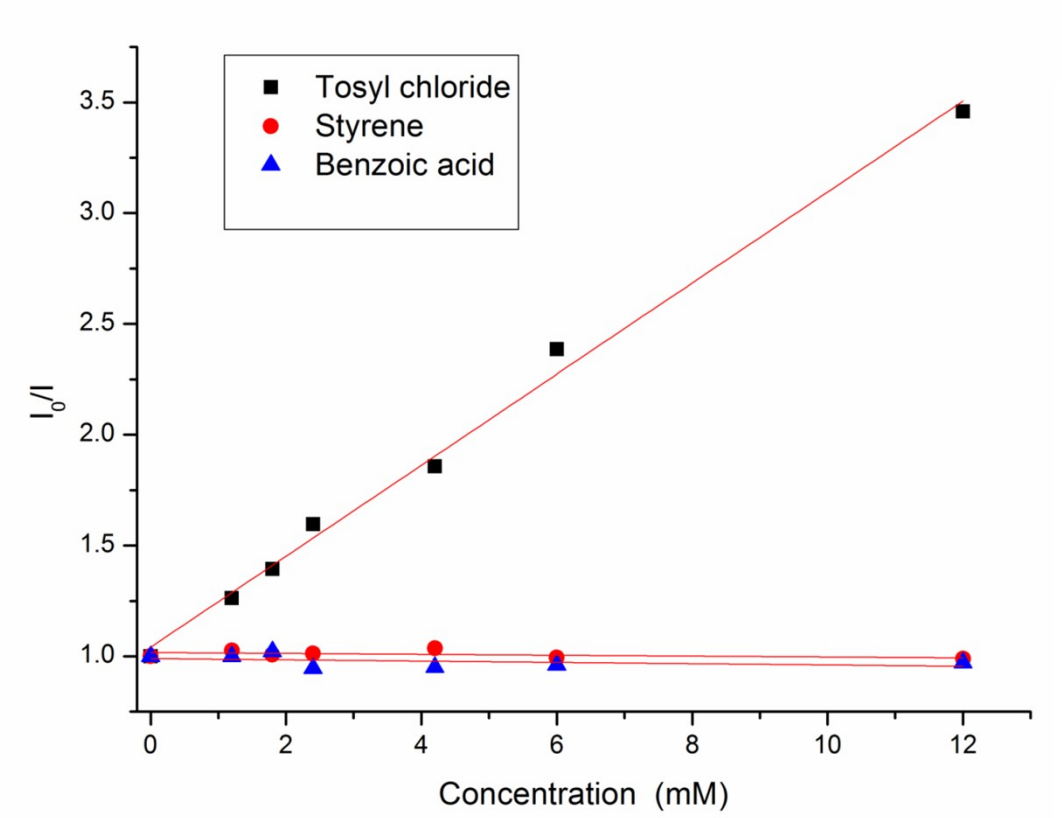


Figure S11. Stern-Volmer plots of *fac*-Ir(ppy)$_3$ with different quenchers.

Experiment B: Stern-Volmer fluorescence quenching experiment for synthesis of *β*-sulfonyl imine

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 0.4 mM solution of *fac*-Ir(ppy)$_3$ in dry CH_3CN added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solutions were irradiated at 385 nm and fluorescence was measured from 420 nm to 700 nm. Control experiments showed that the excited state photocatalyst was mainly quenched by Benzenesulfonyl chloride **1d**.

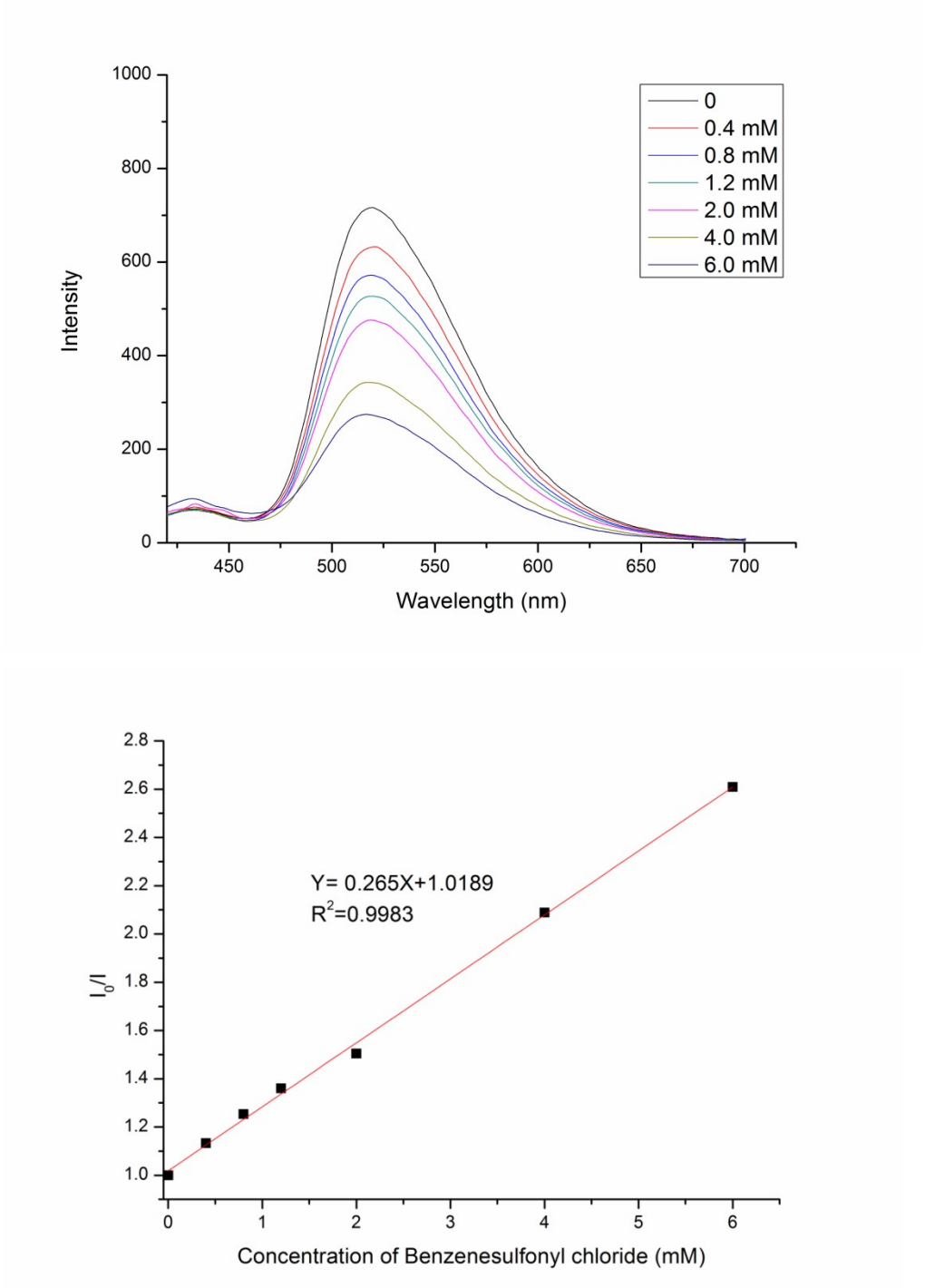


Figure S12-S13. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and

variable Benzenesulfonyl chloride.

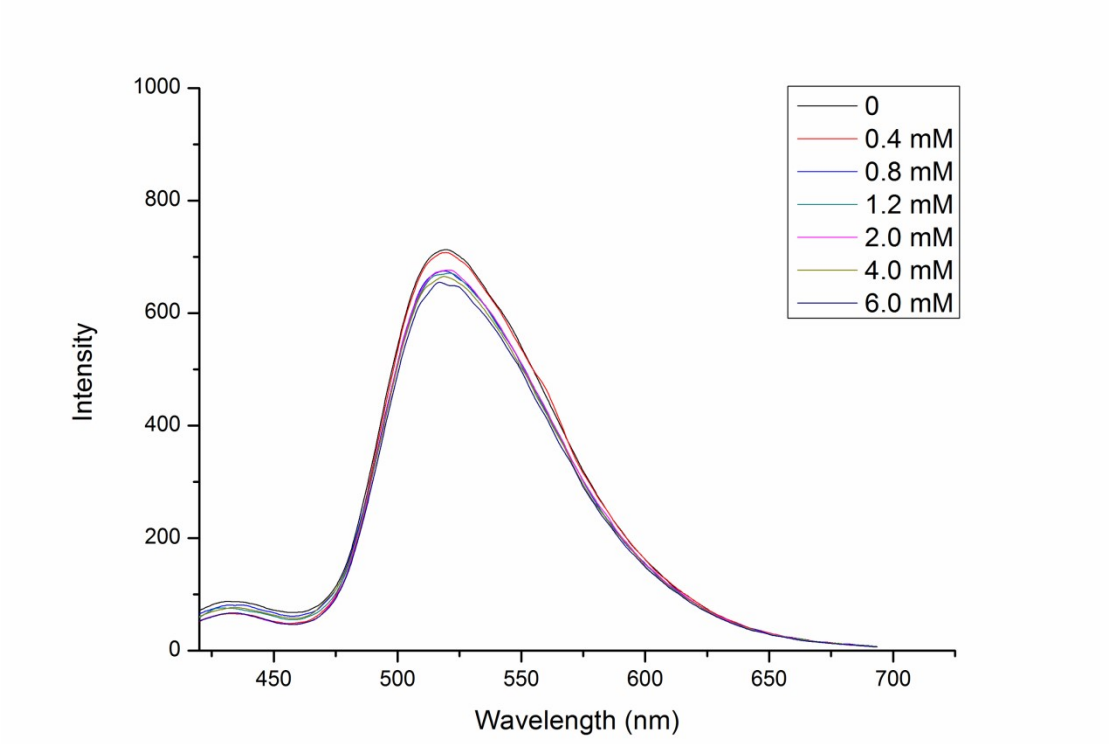


Figure S14. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable Styrene.

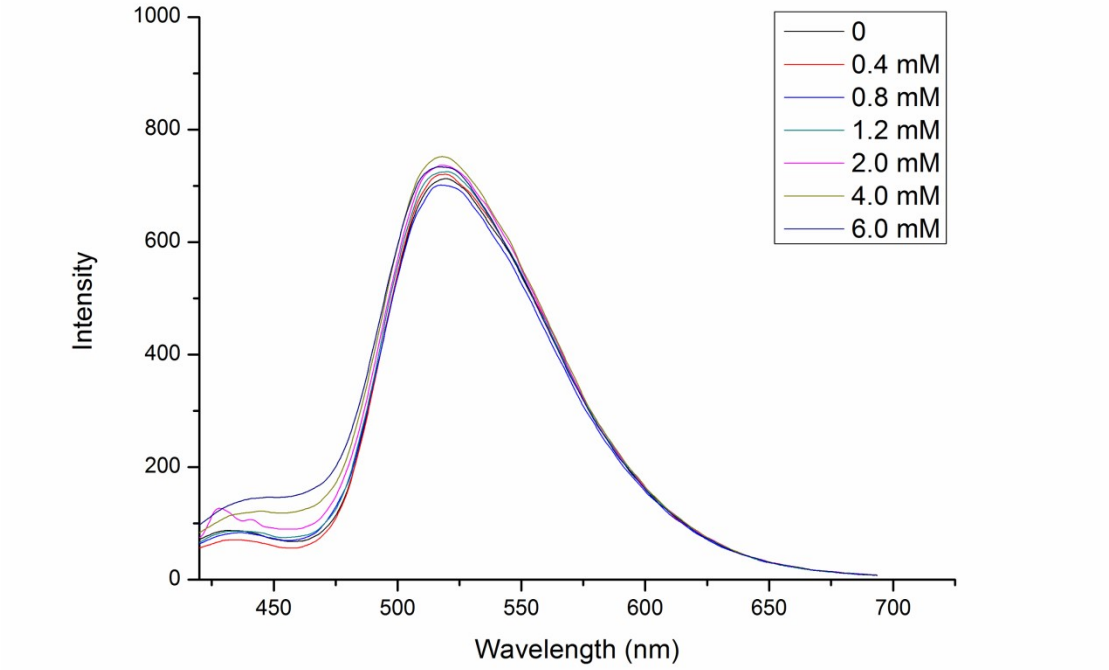


Figure S15. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable Benztriazole.

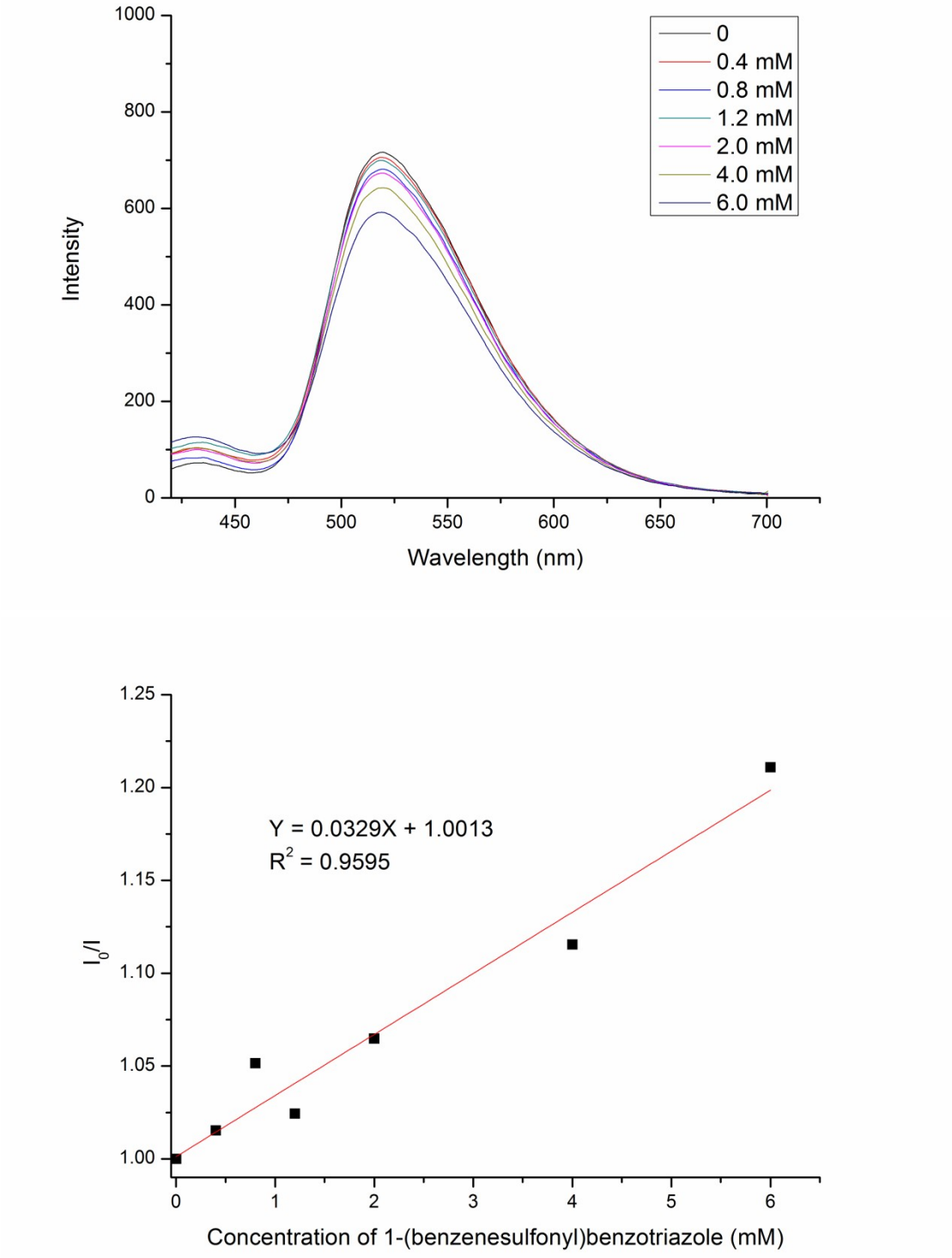


Figure S16-S17. Fluorescence quenching experiments date with *fac*-Ir(ppy)$_3$ and variable 1-(benzenesulfonyl)benzotriazole.

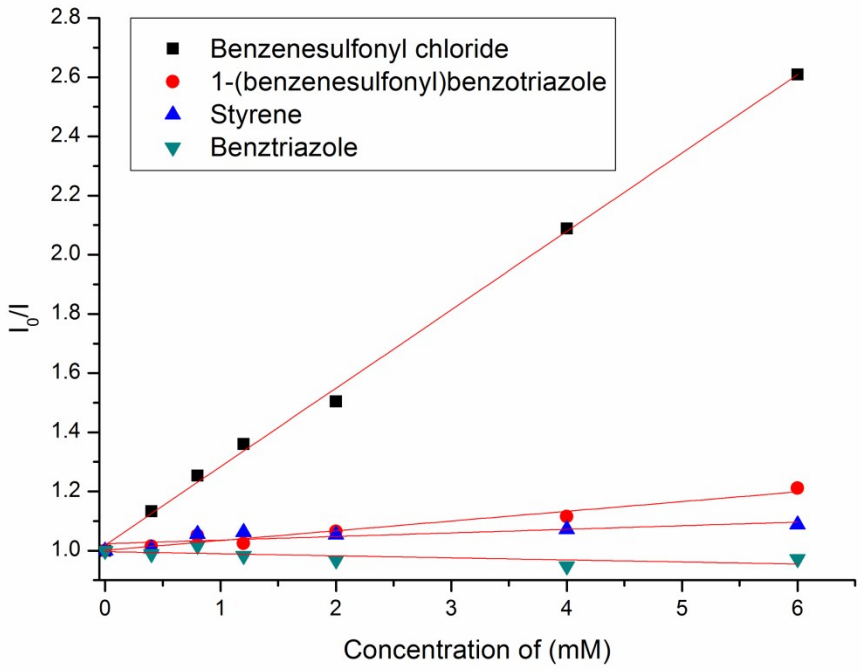


Figure S18. Stern-Volmer plots of *fac*-Ir(ppy)$_3$ with different quenchers.

Table S4: The Stern-Volmer quenching constant of different quenchers.

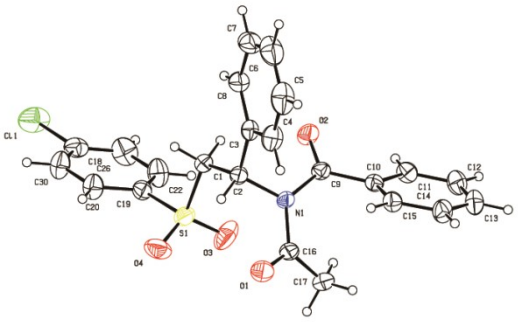
Benzenesulfonyl chloride	1-(benzenesulfonyl)benzotriazole
0.2650 mM^{-1}	0.0329 mM^{-1}

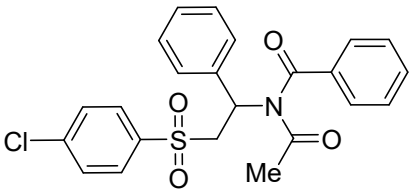
8. X-Ray Crystallographic Data

Data A: X-Ray crystallographic datas of *β*-sulfonyl imides

8.1 X-Ray crystallographic data of product 5ab

The crystal structure **5ab** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 2073712**.





Bond precision:	C-C = 0.0035 A	Wavelength=1.54184	
Cell:	a=12.7213(3)	b=10.0584(3)	c=17.2909(5)
	alpha=90	beta=106.273(3)	gamma=90
Temperature:	292 K		
	Calculated	Reported	
Volume	2123.84(11)	2123.83(10)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H20 Cl N O4 S	C23 H20 Cl N O4 S	
Sum formula	C23 H20 Cl N O4 S	C23 H20 Cl N O4 S	
Mr	441.91	441.91	
Dx,g cm-3	1.382	1.382	
Z	4	4	
Mu (mm-1)	2.765	2.765	
F000	920.0	920.0	
F000’	925.28		
h,k,lmax	15,11,20	15,11,20	
Nref	3753	3741	
Tmin,Tmax	0.793,0.871	0.812,1.000	
Tmin’	0.738		

Correction method= # Reported T Limits: Tmin=0.812 Tmax=1.000

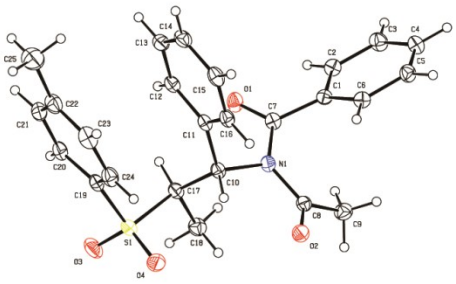
AbsCorr = MULTI-SCAN

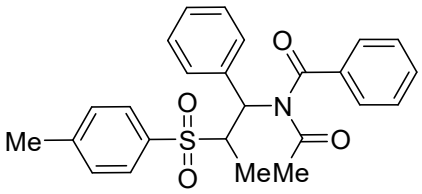
Data completeness= 0.997	Theta(max)= 66.600
R(reflections)= 0.0397(3133)	wR2(reflections)= 0.1139(3741)
S = 1.048	Npar= 273

Displacement ellipsoids are drawn at 30% probability level.

8.2 X-Ray crystallographic data of product 5bi

The crystal structure **5bi** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 2073716**.





Bond precision:	C-C = 0.0022 A	Wavelength=1.54184	
Cell:	a=19.8661(3)	b=9.09317(15)	c=25.7813(4)
	alpha=90	beta=109.6714(18)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	4385.48(13)	4385.48(13)	
Space group	I 2/a	I 1 2/a 1	
Hall group	-I 2ya	-I 2ya	
Moiety formula	C25 H25 N O4 S	C25 H25 N O4 S	
Sum formula	C25 H25 N O4 S	C25 H25 N O4 S	
Mr	435.52	435.52	
Dx,g cm-3	1.319	1.319	
Z	8	8	
Mu (mm-1)	1.573	1.573	
F000	1840.0	1840.0	
F000’	1847.89		
h,k,lmax	24,11,32	24,11,32	
Nref	4584	4342	
Tmin,Tmax	0.802,0.896	0.075,1.000	
Tmin’	0.802		

Correction method= # Reported T Limits: Tmin=0.075 Tmax=1.000

AbsCorr = MULTI-SCAN

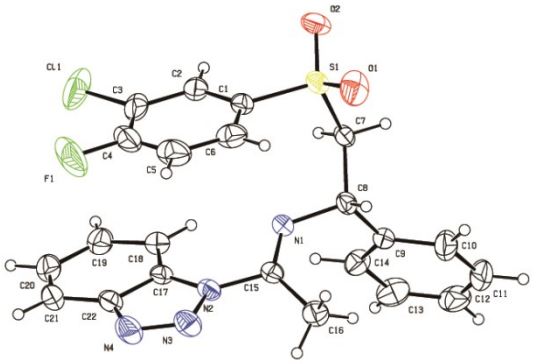
Data completeness= 0.947	Theta(max)= 75.911
R(reflections)= 0.0446(3926)	wR2(reflections)= 0.1279(4342)
S = 1.063	Npar= 283

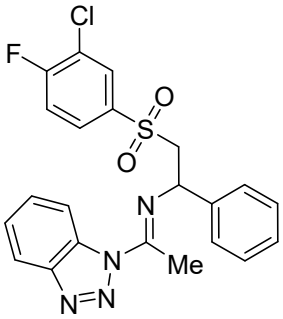
Displacement ellipsoids are drawn at 30% probability level.

Data B: X-Ray crystallographic datas of *β*-sulfonyl imines

8.3 X-Ray crystallographic data of product 6am

The crystal structure **6am** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 2073620**.





Bond precision:	C-C = 0.0045 A	Wavelength=1.54184	
Cell:	a=7.17026(19)	b=21.7971(5)	c=13.6848(4)
	alpha=90	beta=98.637(3)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2114.55(10)	2114.56(10)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C22 H18 Cl F N4 O2 S	C22 H18 Cl F N4 O2 S	
Sum formula	C22 H18 Cl F N4 O2 S	C22 H19 Cl F N4 O2 S	
Mr	456.91	457.92	
Dx,g cm-3	1.435	1.438	
Z	4	4	
Mu (mm-1)	2.837	2.837	
F000	944.0	948.0	
F000’	949.42		
h,k,lmax	8,25,16	8,25,16	
Nref	3744	3737	
Tmin,Tmax	0.630,0.711	0.687,1.000	
Tmin’	0.572		

Correction method= # Reported T Limits: Tmin=0.687 Tmax=1.000

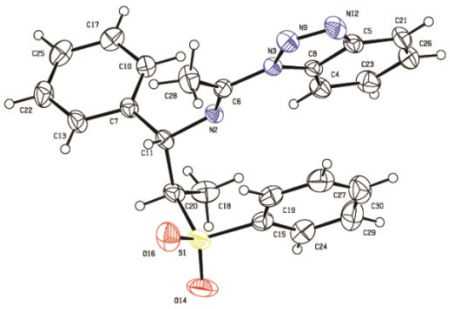
AbsCorr = MULTI-SCAN

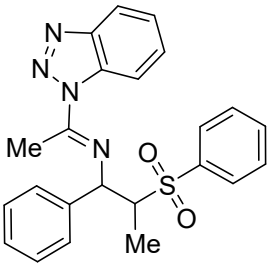
Data completeness= 0.998	Theta(max)= 66.592
R(reflections)= 0.0545(3148)	wR2(reflections)= 0.1552(3737)
S = 1.040	Npar= 281

Displacement ellipsoids are drawn at 30% probability level.

8.4 X-Ray crystallographic data of product 6bj

The crystal structure **6bj** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 2073707**.





Bond precision:	C-C = 0.0031 A	Wavelength=1.54184	
Cell:	a=8.65981(14)	b=17.7339(2)	c=27.7046(4)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	4254.66(10)	4254.66(11)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C23 H22 N4 O2 S	C23 H22 N4 O2 S	
Sum formula	C23 H22 N4 O2 S	C23 H22 N4 O2 S	
Mr	418.51	418.50	
Dx,g cm-3	1.307	1.307	
Z	8	8	
Mu (mm-1)	1.570	1.570	
F000	1760.0	1760.0	
F000’	1767.45		
h,k,lmax	10,21,32	10,21,32	
Nref	3768	3766	
Tmin,Tmax	0.754,0.828	0.315,1.000	
Tmin’	0.754		

Correction method= # Reported T Limits: Tmin=0.315 Tmax=1.000

AbsCorr = MULTI-SCAN

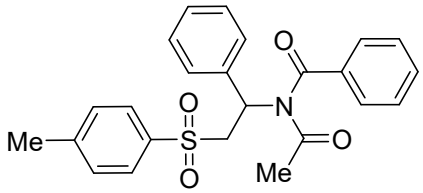
Data completeness= 0.999	Theta(max)= 66.595
R(reflections)= 0.0411(3091)	wR2(reflections)= 0.1142(3766)
S = 1.037	Npar= 274

Displacement ellipsoids are drawn at 30% probability level.

9. Characterization of Products

Data A: Characterization of Products *β*-Sulfonyl Imides

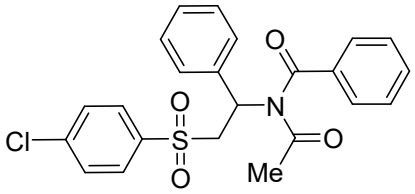
N-acetyl-N-(1-phenyl-2-tosylethyl)benzamide (5aa)



5aa

White solid; 75.5 mg, 90% yield; mp 142-144 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.56 – 7.50 (m, 1H), 7.44 – 7.31 (m, 6H), 7.30 – 7.19 (m, 3H), 6.26 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.81 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.73 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.42 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.8, 144.9, 137.6, 136.5, 136.0, 132. 8, 129.9, 128.8, 128.7, 128.5, 128.2, 128.1, 127.8, 56.7, 53.7, 28.3, 21.6; HRMS (ESI) for $C_{24}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 444.1240, found 444.1237.

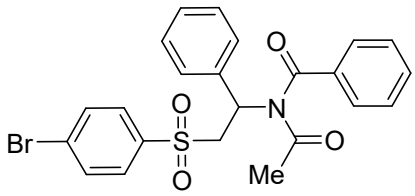
N-acetyl-N-(2-((4-chlorophenyl)sulfonyl)-1-phenylethyl)benzamide (5ab)



5ab

White solid; 70.7 mg, 80% yield; mp 98-100 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 2H), 7.62 – 7.57 (m, 2H), 7.55 – 7.48 (m, 3H), 7.44 – 7.35 (m, 4H), 7.30 – 7.22 (m, 3H), 6.26 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.81 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.78 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 140.6, 137.4, 137.3, 136.4, 132.9, 129.7, 129.6, 128.9, 128.8, 128.6, 128.3, 127.9, 56.9, 53.7, 28.2; HRMS (ESI) for $C_{23}H_{20}ClNNaO_4S$ $[M+Na]^+$ calcd 464.0694, found 464.0691.

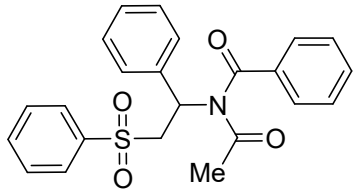
N-acetyl-N-(2-((4-bromophenyl)sulfonyl)-1-phenylethyl)benzamide (5ac)



5ac

White solid; 75.1 mg, 77% yield; mp 168-170 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.70 – 7.65 (m, 2H), 7.62 – 7.57 (m, 2H), 7.57 – 7.51 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.30 – 7.22 (m, 3H), 6.26 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.81 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.78 (dd, *J* = 14.8, 3.6 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.8, 138.0, 137.3, 136.4, 132.9, 132.6, 129.8, 129.3, 128.9, 128.8, 128.6, 128.3, 127.9, 56.9, 53.6, 28.3; HRMS (ESI) for $C_{23}H_{20}BrNNaO_4S$ $[M+Na]^+$ calcd 508.0189, found 508.0187.

N-acetyl-N-(1-phenyl-2-(phenylsulfonyl)ethyl)benzamide (5ad)

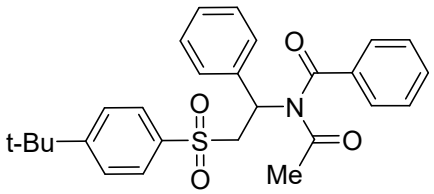


5ad

Colourless oil; 73.6 mg, 90% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.90 (m, 2H), 7.67 – 7.58 (m, 3H), 7.57 – 7.48 (m, 3H), 7.44 – 7.35 (m, 4H), 7.31 – 7.20 (m, 3H), 6.30 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.84 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.77 (dd, *J* = 14.8, 3.2 Hz, 1H), 1.81 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.8, 139.0, 137.5, 136.5, 133.9, 132.8, 129.3, 128.8, 128.7, 128.5, 128.2, 128.1, 127.8, 56.7, 53.6, 28.3; HRMS (ESI) for

$C_{23}H_{22}NO_4S$ $[M+H]^+$ calcd 408.1264, found 408.1260.

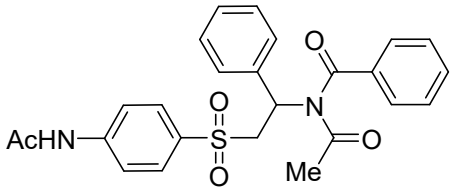
N-acetyl-N-(2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylethyl)benzamide (5ae)



5ae

Colourless oil; 88.1 mg, 95% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.50 (m, 3H), 7.44 – 7.35 (m, 4H), 7.28 – 7.20 (m, 3H), 6.30 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.78 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.77 (dd, *J* = 14.8, 3.6 Hz, 1H), 1.81 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.8, 157.7, 137.6, 136.6, 136.1, 132.8, 128.8, 128.7, 128.5, 128.1, 128.0, 127.9, 126.3, 56.9, 53.9, 35.2, 31.0, 28.2; HRMS (ESI) for $C_{27}H_{29}NNaO_4S$ $[M+Na]^+$ calcd 486.1710, found 486.1707.

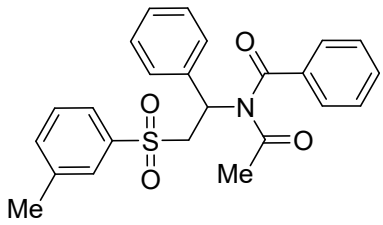
N-(2-((4-acetamidophenyl)sulfonyl)-1-phenylethyl)-N-acetylbenzamide (5af)



5af

White solid; 67.5 mg, 73% yield; mp 172-174 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.44 – 7.33 (m, 4H), 7.31 – 7.19 (m, 3H), 6.29 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.78 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.76 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.14 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.9, 169.1, 143.3, 137.4, 136.4, 133.2, 132.9, 129.4, 128.9, 128.8, 128.6, 128.3, 127.8, 119.4, 57.0, 53.7, 28.3, 24.6; HRMS (ESI) for $C_{25}H_{24}N_2NaO_5S$ $[M+Na]^+$ calcd 487.1298, found 487.1294.

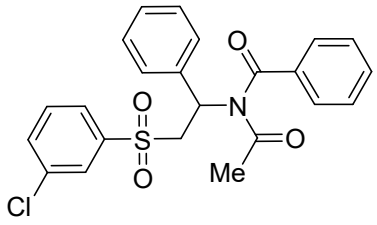
N-acetyl-N-(1-phenyl-2-(m-tolylsulfonyl)ethyl)benzamide (5ag)



5ag

Colourless oil; 81.6 mg, 97% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 2H), 7.63 – 7.59 (m, 2H), 7.55 – 7.50 (m, 1H), 7.44 – 7.36 (m, 6H), 7.31 – 7.21 (m, 3H), 6.29 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.78 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.76 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.41 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 139.5, 138.9, 137.6, 136.5, 134.6, 132.8, 129.1, 128.8, 128.7, 128.5, 128.4, 128.1, 127.8, 125.2, 56.8, 53.8, 28.2, 21.2; HRMS (ESI) for $C_{24}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 444.1240, found 444.1237.

N-acetyl-N-(2-((3-chlorophenyl)sulfonyl)-1-phenylethyl)benzamide (5ah)

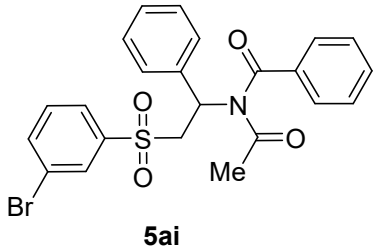


5ah

Colourless oil; 72.5 mg, 82% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.56 – 7.46 (m, 2H), 7.44 – 7.35 (m, 4H), 7.30 – 7.22 (m, 3H), 6.30 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.80 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.81 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 140.8, 137.2, 136.4, 135.5, 134.0, 132.9, 130.6,

128.9, 128.8, 128.6, 128.4, 128.3, 127.9, 126.3, 57.0, 53.7, 28.2; HRMS (ESI) for $C_{23}H_{20}ClNNaO_4S$ $[M+Na]^+$ calcd 464.0694, found 464.0689.

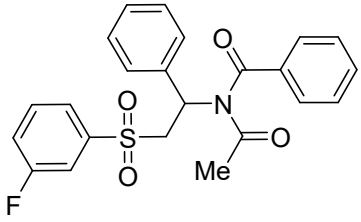
N-acetyl-N-(2-((3-bromophenyl)sulfonyl)-1-phenylethyl)benzamide (5ai)



5ai

Colourless oil; 88.0 mg, 90% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.72 (m, 1H), 7.62 – 7.57 (m, 2H), 7.56 – 7.50 (m, 1H), 7.44 – 7.35 (m, 5H), 7.31 – 7.22 (m, 3H), 6.30 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.80 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.82 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.8, 140.9, 137.1, 136.9, 136.3, 132.9, 131.0, 130.8, 128.9, 128.7, 128.5, 128.3, 127.9, 126.7, 123.2, 56.9, 53.6, 28.2; HRMS (ESI) for $C_{23}H_{20}BrNNaO_4S$ $[M+Na]^+$ calcd 508.0189, found 508.0185.

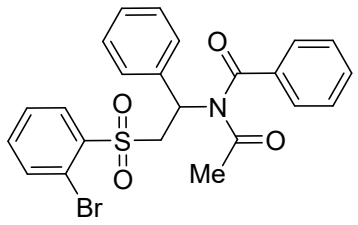
N-acetyl-N-(2-((3-fluorophenyl)sulfonyl)-1-phenylethyl)benzamide (5aj)



5aj

White solid; 84.1 mg, 99% yield; mp 96-98 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.70 (m, 1H), 7.64 – 7.58 (m, 3H), 7.57 – 7.50 (m, 2H), 7.45 – 7.36 (m, 4H), 7.35 – 7.22 (m, 3H), 6.29 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.81 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.81 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 162.4(d, *J* = 253.5 Hz), 141.1(d, *J* = 6.1 Hz), 137.3, 136.4, 132.9, 131.2(d, *J* = 7.1 Hz), 128.9, 128.8, 128.6, 128.3, 127.9, 124.0(d, *J* = 4.0 Hz), 121.2(d, *J* = 21.2 Hz), 115.5(d, *J* = 24.2 Hz), 56.9, 53.6, 28.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.80. HRMS (ESI) for $C_{23}H_{20}FNNaO_4S$ $[M+Na]^+$ calcd 448.0989, found 448.0984.

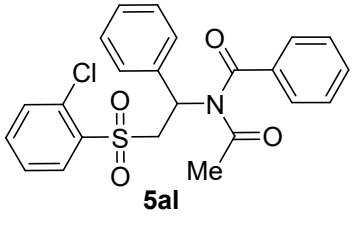
N-acetyl-N-(2-((2-bromophenyl)sulfonyl)-1-phenylethyl)benzamide (5ak)



5ak

Colourless oil; 96.1 mg, 99% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.05 (m, 1H), 7.76 – 7.71 (m, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.37 (m, 7H), 7.31 – 7.21 (m, 3H), 6.24 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.95 (dd, *J* = 14.8, 9.6 Hz, 1H), 4.32 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.8, 138.2, 137.4, 136.4, 135.4, 134.8, 132.8, 132.3, 128.9, 128.8, 128.6, 128.2, 128.0, 127.8, 121.0, 54.8, 54.0, 28.1; HRMS (ESI) for $C_{23}H_{20}BrNNaO_4S$ $[M+Na]^+$ calcd 508.0189, found 508.0180.

N-acetyl-N-(2-((2-chlorophenyl)sulfonyl)-1-phenylethyl)benzamide (5al)

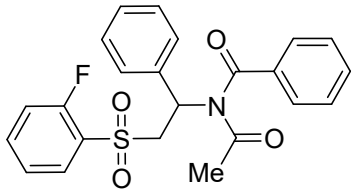


5al

Colourless oil; 82.2 mg, 93% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.03 (m, 1H), 7.63 – 7.58 (m, 2H), 7.58 – 7.50 (m, 3H), 7.47 – 7.37 (m, 5H), 7.30 – 7.19 (m, 3H), 6.24 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.95 (dd, *J* = 14.8, 10.0 Hz, 1H), 4.26 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.8, 137.3, 136.4, 136.3, 134.9,

132.9, 132.8, 131.9, 131.8, 128.8, 128.7, 128.6, 128.2, 127.8, 127.4, 55.2, 53.9, 28.1. HRMS (ESI) for $C_{23}H_{21}ClNO_4S$ $[M+H]^+$ calcd 442.0874, found 442.0872.

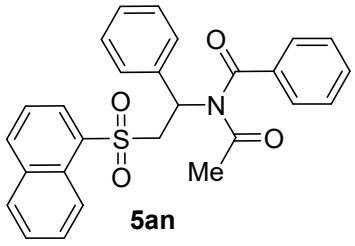
N-acetyl-N-(2-((2-fluorophenyl)sulfonyl)-1-phenylethyl)benzamide (5am)



5am

Colourless oil; 79.7 mg, 94% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 1H), 7.67 – 7.56 (m, 3H), 7.56 – 7.49 (m, 1H), 7.43 – 7.37 (m, 4H), 7.34 – 7.18 (m, 5H), 6.25 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.93 (dd, *J* = 14.8, 10.0 Hz, 1H), 4.08 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.8, 159.5 (d, *J* = 256.5 Hz), 137.3, 136.4, 136.3, 132.9, 130.8, 128.8, 128.7, 128.6, 128.2, 127.8, 126.8 (d, *J* = 15.2 Hz), 124.7 (d, *J* = 3.0 Hz), 117.1 (d, *J* = 21.2 Hz), 56.5, 53.7, 28.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.30. HRMS (ESI) for $C_{23}H_{21}FNO_4S$ $[M+H]^+$ calcd 426.1170, found 426.1168.

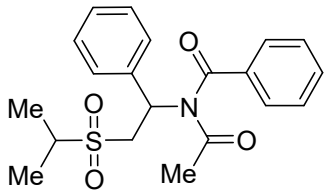
N-acetyl-N-(2-(naphthalen-1-ylsulfonyl)-1-phenylethyl)benzamide (5an)



5an

Pale yellow solid; 77.6 mg, 85% yield; mp 132-134 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.77 – 8.72 (m, 1H), 8.29 – 8.24 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.63 – 7.48 (m, 5H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.22 – 7.12 (m, 3H), 6.33 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.95 (dd, *J* = 14.4, 9.6 Hz, 1H), 4.01 (dd, *J* = 14.8, 4.0 Hz, 1H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 137.5, 136.4, 135.4, 134.1, 134.0, 132.8, 131.0, 129.3, 128.9, 128.8, 128.7, 128.7, 128.4, 128.1, 127.7, 127.0, 124.3, 123.9, 56.6, 54.1, 28.2; HRMS (ESI) for $C_{27}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 480.1240, found 480.1233.

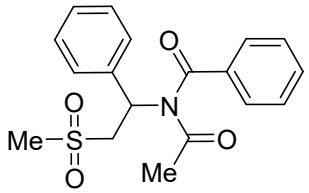
N-acetyl-N-(2-(isopropylsulfonyl)-1-phenylethyl)benzamide (5ao)



5ao

Colourless oil; 67.4 mg, 90% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.43 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 6.36 (dd, *J* = 10.8, 3.2 Hz, 1H), 4.60 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.61 (dd, *J* = 14.0, 3.6 Hz, 1H), 3.24 – 3.14 (m, 1H), 1.86 (s, 3H), 1.42 – 1.36 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.9, 137.7, 136.4, 132.7, 128.8, 128.6, 128.3, 127.8, 53.7, 53.3, 49.8, 28.1, 15.6, 14.7; HRMS (ESI) for $C_{20}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 396.1240, found 396.1233.

N-acetyl-N-(2-(methylsulfonyl)-1-phenylethyl)benzamide (5ap)

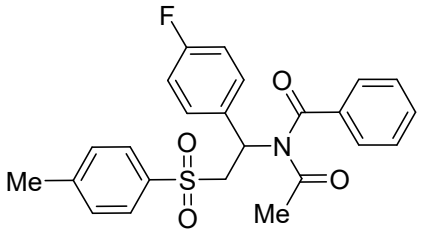


5ap

Colourless oil; 61.8 mg, 89% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.57 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 7.43 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 6.37 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.61 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.76 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.96 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.9, 137.2, 136.2, 132.9, 128.8, 128.7,

128.6, 128.4, 127.8, 55.3, 53.6, 41.2, 28.0; HRMS (ESI) for $C_{18}H_{19}NNaO_4S$ $[M+Na]^+$ calcd 368.0927, found 368.0922.

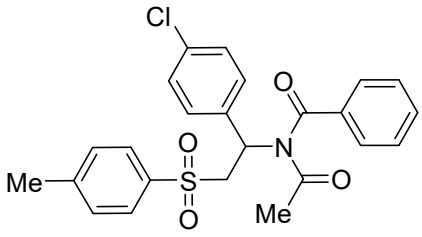
N-acetyl-N-(1-(4-fluorophenyl)-2-tosylethyl)benzamide (5ba)



5ba

Colourless oil; 65.6 mg, 75% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.46 – 7.31 (m, 6H), 6.97 – 6.90 (m, 2H), 6.24 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.72 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.73 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.43 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.8, 162.3(d, *J* = 248.5 Hz), 145.0, 136.3(d, *J* = 28.3 Hz), 133.5(d, *J* = 3.0 Hz), 132.9, 130.0(d, *J* = 8.1 Hz), 129.9, 128.8, 128.7, 128.2, 115.4(d, *J* = 21.2 Hz), 57.0, 53.3, 28.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.32. HRMS (ESI) for $C_{24}H_{22}FNNaO_4S$ $[M+Na]^+$ calcd 462.1146, found 462.1139.

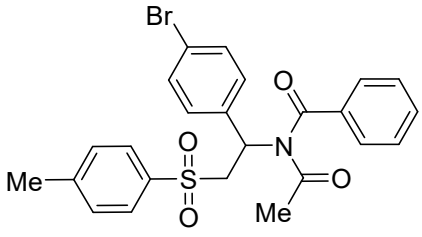
N-acetyl-N-(1-(4-chlorophenyl)-2-tosylethyl)benzamide (5bb)



5bb

Colourless oil; 66.6 mg, 73% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.60 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.40 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 4H), 7.25 – 7.20 (m, 2H), 6.23 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.69 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.73 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.43 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.7, 145.0, 136.3, 136.1, 136.0, 134.1, 133.0, 129.9, 129.5, 128.9, 128.8, 128.6, 128.1, 56.8, 53.3, 28.3, 21.6; HRMS (ESI) for $C_{24}H_{22}ClNNaO_4S$ $[M+Na]^+$ calcd 478.0850, found 478.0845.

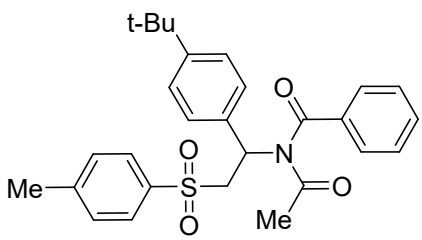
N-acetyl-N-(1-(4-bromophenyl)-2-tosylethyl)benzamide (5bc)



5bc

Colourless oil; 77.6 mg, 78% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.58 – 7.52 (m, 1H), 7.46 – 7.36 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 3H), 6.21 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.67 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.72 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.43 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.7, 145.0, 136.6, 136.3, 136.1, 133.0, 131.6, 129.9, 129.8, 128.9, 128.8, 128.2, 122.3, 56.8, 53.4, 28.3, 21.6; HRMS (ESI) for $C_{24}H_{22}BrNNaO_4S$ $[M+Na]^+$ calcd 522.0345, found 522.0336.

N-acetyl-N-(1-(4-(tert-butyl)phenyl)-2-tosylethyl)benzamide (5bd)

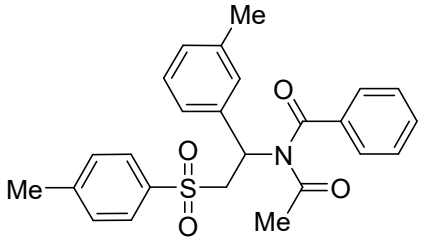


5bd

Colourless oil; 75.4 mg, 79% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.56 – 7.50 (m, 1H), 7.45 – 7.38 (m, 2H), 7.34 – 7.23 (m, 6H), 6.21 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.79 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.74 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.42 (s, 3H), 1.83 (s, 3H), 1.24 (s, 9H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 174.2, 173.8, 151.0, 144.8, 136.6, 136.1, 134.6, 132.7, 129.8, 128.8, 128.7, 128.2, 127.5, 125.4, 56.9, 53.6, 34.4, 31.1, 28.4, 21.6; HRMS (ESI) for $C_{28}H_{31}NNaO_4S$ $[M+Na]^+$ calcd 500.1866, found 500.1859.

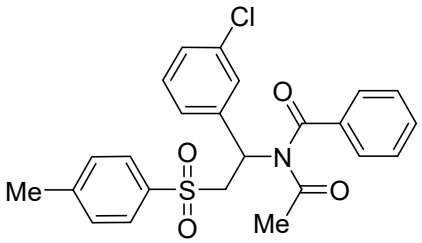
N-acetyl-N-(1-(m-tolyl)-2-tosylethyl)benzamide (5be)



5be

Colourless oil; 77.7 mg, 89% yield; reaction time 24h; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.56 – 7.50 (m, 1H), 7.45 – 7.38 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.03 (d, *J* = 6.4 Hz, 1H), 6.22 (dd, *J* = 10.4, 3.2 Hz, 1H), 4.79 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.73 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.43 (s, 3H), 2.27 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.8, 144.8, 138.2, 137.6, 136.6, 136.1, 132.7, 129.9, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 124.9, 56.8, 53.8, 28.3, 21.6, 21.4; HRMS (ESI) for $C_{25}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 458.1397, found 458.1389.

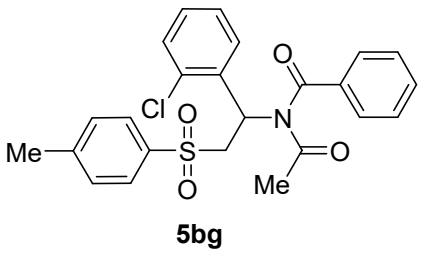
N-acetyl-N-(1-(3-chlorophenyl)-2-tosylethyl)benzamide (5bf)



5bf

Pale yellow solid; 55.5 mg, 61% yield; mp 100-102 °C; reaction time 24h; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.62 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 7.22 – 7.17 (m, 2H), 6.22 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.68 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.74 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.43 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.6, 145.0, 139.5, 136.3, 136.0, 134.4, 132.9, 129.9, 129.7, 128.9, 128.8, 128.3, 128.2, 128.1, 126.2, 56.7, 53.4, 28.3, 21.6; HRMS (ESI) for $C_{24}H_{22}ClNNaO_4S$ $[M+Na]^+$ calcd 478.0850, found 478.0841.

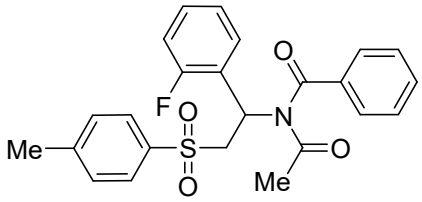
N-acetyl-N-(1-(2-chlorophenyl)-2-tosylethyl)benzamide (5bg)



5bg

Colourless oil; 73.5 mg, 81% yield; reaction time 24h; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.60 – 7.50 (m, 2H), 7.44– 7.38 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.20 – 7.14 (m, 2H), 6.50 (dd, *J* = 9.2, 4.8Hz, 1H), 4.47 (dd, *J* = 14.8, 9.2 Hz, 1H), 3.82 (dd, *J* = 14.8, 4.8 Hz, 1H), 2.43 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 173.0, 144.9, 136.2, 135.9, 134.5, 133.2, 133.0, 130.3, 129.8, 129.7, 129.5, 128.9, 128.8, 128.3, 126.8, 55.8, 51.9, 27.6, 21.6; HRMS (ESI) for $C_{24}H_{22}ClNNaO_4S$ $[M+Na]^+$ calcd 478.0850, found 478.0844.

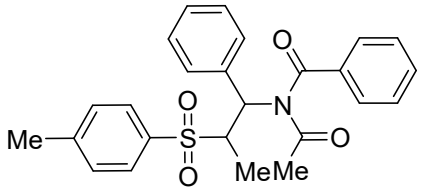
N-acetyl-N-(1-(2-fluorophenyl)-2-tosylethyl)benzamide (5bh)



5bh

White solid; 66.4 mg, 75% yield; mp 144-146 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.56 – 7.50 (m, 1H), 7.47 – 7.39 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.08 – 7.02 (m, 1H), 7.01– 6.94 (m, 1H), 6.44 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.58 (dd, *J* = 14.8, 9.6 Hz, 1H), 3.83 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.43 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.3, 160.0(d, *J* = 249.5 Hz), 144.9, 136.3, 135.9, 132.9, 130.0(d, *J* = 8.5 Hz), 129.8, 129.7(d, *J* = 3.0 Hz), 128.8, 128.7, 128.3, 124.2(d, *J* = 13.1 Hz), 124.0(d, *J* = 3.0 Hz), 115.5(d, *J* = 22.2 Hz), 56.1, 48.4, 27.6, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.06. HRMS (ESI) for $C_{24}H_{22}FNNaO_4S$ $[M+Na]^+$ calcd 462.1146, found 462.1138.

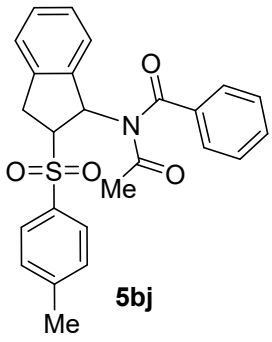
N-acetyl-N-(1-phenyl-2-tosylpropyl)benzamide (5bi)



5bi

White solid; 77.4 mg, 89% yield; mp 116-117 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.40 (m, 3H), 7.36 – 7.28 (m, 4H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.11 – 7.00 (m, 5H), 6.11 (d, *J* = 9.6 Hz, 1H), 4.75 – 4.65 (m, 1H), 2.33 (s, 3H), 1.60 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.5, 144.0, 136.3, 136.2, 135.4, 133.1, 129.2, 129.1, 128.9, 128.6, 128.5, 128.0, 127.8, 61.8, 59.6, 27.2, 21.4, 12.2; HRMS (ESI) for $C_{25}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 458.1397, found 458.1389.

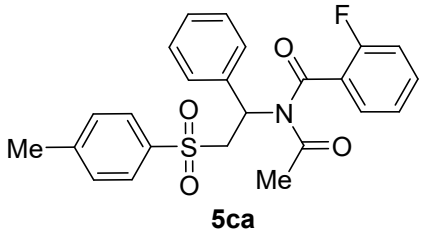
N-acetyl-N-(2-tosyl-2,3-dihydro-1H-inden-1-yl)benzamide (5bj)



5bj

Colourless oil; 51.9 mg, 60% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.62 (m, 2H), 7.61 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.22 (m, 4H), 6.43 (d, *J* = 6.8 Hz, 1H), 4.80 – 4.73 (m, 1H), 3.52 – 3.32 (m, 2H), 2.33 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 173.5, 145.0, 139.4, 139.0, 135.7, 134.4, 133.0, 129.9, 129.0, 128.9, 128.9, 128.5, 127.5, 124.6, 122.3, 67.6, 62.4, 32.6, 27.7, 21.5; HRMS (ESI) for $C_{25}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 456.1240, found 456.1231.

N-acetyl-2-fluoro-N-(1-phenyl-2-tosylethyl)benzamide (5ca)

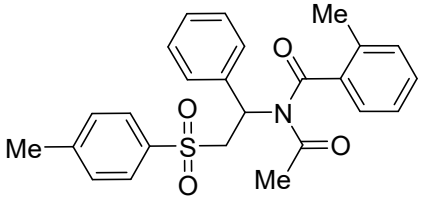


5ca

White solid; 68.7 mg, 78% yield; mp 127-129 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.44 (m, 2H), 7.38 – 7.31 (m, 4H), 7.30 – 7.16 (m, 4H), 7.13 – 7.03 (m, 1H), 6.22 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.70 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.81 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.42 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 168.5, 159.2 (d, *J* = 254.5 Hz), 144.9, 137.2, 136.0, 133.8 (d, *J* = 8.1 Hz), 130.1 (d, *J* = 1.0 Hz), 129.9, 128.4, 128.1, 128.0, 127.7,

124.9 (d, J = 13.1 Hz), 124.7 (d, J = 3.1 Hz), 116.3 (d, J = 21.2 Hz), 56.8, 53.7, 27.1, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.80. HRMS (ESI) for $C_{24}H_{22}FNNaO_4S$ $[M+Na]^+$ calcd 462.1146, found 462.1146.

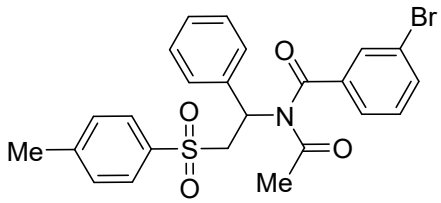
N-acetyl-2-methyl-N-(1-phenyl-2-tosylethyl)benzamide (5cb)



5cb

Pale yellow oil; 50.5 mg, 58% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, J = 8.4 Hz, 2H), 7.40 – 7.31 (m, 5H), 7.29 – 7.21 (m, 4H), 7.15 (d, J = 4.0 Hz, 2H), 6.29 (dd, J = 10.8, 3.6 Hz, 1H), 4.84 (dd, J = 14.0, 11.2 Hz, 1H), 3.71 (dd, J = 14.8, 3.6 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.1, 144.9, 137.7, 137.1, 136.4, 136.2, 131.4, 131.2, 129.9, 128.5, 128.2, 128.1, 128.0, 127.6, 125.9, 56.6, 53.3, 27.8, 21.6, 19.5; HRMS (ESI) for $C_{25}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 458.1397, found 458.1397.

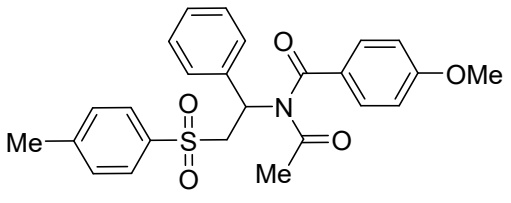
N-acetyl-3-bromo-N-(1-phenyl-2-tosylethyl)benzamide (5cc)



5cc

Colourless oil; 92.9 mg, 93% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 3H), 7.68 – 7.63 (m, 1H), 7.58 – 7.53 (m, 1H), 7.38 – 7.33 (m, 4H), 7.32 – 7.25 (m, 4H), 6.22 (dd, J = 10.8, 3.2 Hz, 1H), 4.79 (dd, J = 14.8, 10.8 Hz, 1H), 3.69 (dd, J = 14.4, 3.2 Hz, 1H), 2.44 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 172.3, 145.0, 138.3, 137.4, 136.0, 135.6, 131.6, 130.3, 129.9, 128.6, 128.3, 128.2, 127.7, 127.3, 123.0, 56.6, 54.0, 28.4, 21.6; HRMS (ESI) for $C_{24}H_{22}BrNNaO_4S$ $[M+Na]^+$ calcd 522.0345, found 522.0347.

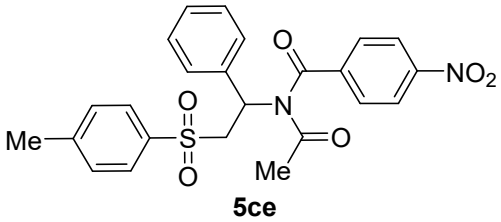
N-acetyl-4-methoxy-N-(1-phenyl-2-tosylethyl)benzamide (5cd)



5cd

Colourless oil; 54.0 mg, 60% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, J = 8.0 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.39 – 7.29 (m, 4H), 7.28 – 7.20 (m, 3H), 6.93 – 6.84 (m, 2H), 6.23 (dd, J = 10.0, 3.6 Hz, 1H), 4.76 (dd, J = 14.8, 10.0 Hz, 1H), 3.83 (s, 3H), 3.76 (dd, J = 14.8, 3.6 Hz, 1H), 2.42 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.3, 163.5, 144.8, 137.7, 136.2, 131.4, 129.8, 128.7, 128.5, 128.2, 128.0, 127.9, 114.1, 57.1, 55.5, 53.9, 28.0, 21.6; HRMS (ESI) for $C_{25}H_{25}NNaO_5S$ $[M+Na]^+$ calcd 474.1346, found 474.1345.

N-acetyl-4-nitro-N-(1-phenyl-2-tosylethyl)benzamide (5ce)

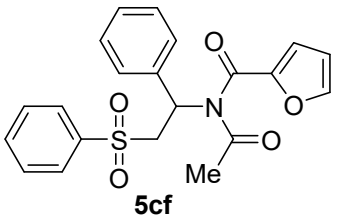


5ce

Colourless oil; 39.2 mg, 42% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.38 – 7.26 (m, 7H), 6.19 (dd, J = 11.2, 2.8 Hz, 1H), 4.77 (dd, J = 14.8, 11.2 Hz, 1H), 3.65 (dd, J = 14.4, 3.2 Hz, 1H), 2.45 (s, 3H), 2.00

(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 171.9, 149.7, 145.2, 141.9, 137.2, 136.0, 130.0, 129.6, 128.8, 128.4, 128.0, 127.5, 123.9, 56.3, 54.4, 28.0, 21.6; HRMS (ESI) for $C_{24}H_{22}N_2NaO_6S$ $[M+Na]^+$ calcd 489.1091, found 489.1089.

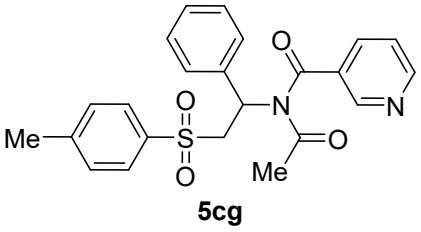
N-acetyl-N-(1-phenyl-2-tosylethyl)furan-2-carboxamide (5cf)



5cf

Colourless oil; 62.6 mg, 76% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 1H), 7.37 – 7.29 (m, 4H), 7.28 – 7.16 (m, 4H), 6.57 – 6.49 (m, 1H), 6.15 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.67 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.79 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.42 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 162.5, 148.2, 146.4, 144.8, 137.3, 136.1, 129.8, 128.4, 128.1, 128.0, 127.6, 119.6, 112.9, 77.3, 57.2, 53.9, 26.2, 21.6; HRMS (ESI) for $C_{22}H_{21}NNaO_5S$ $[M+Na]^+$ calcd 434.1033, found 434.1033.

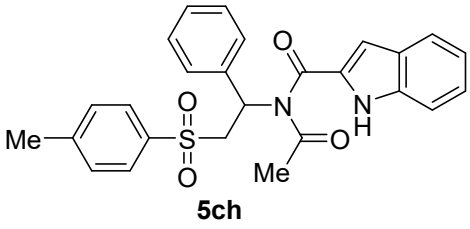
N-acetyl-N-(1-phenyl-2-tosylethyl)nicotinamide (5cg)



5cg

Pale yellow solid; 74.7 mg, 88% yield; mp 153-155 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, *J* = 2.0 Hz, 1H), 8.77 – 8.73 (m, 1H), 8.04 – 7.98 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.33 (m, 5H), 7.32 – 7.24 (m, 3H), 6.22 (dd, *J* = 10.8, 3.2 Hz, 1H), 4.78 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.69 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.44 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 171.9, 153.0, 149.5, 145.1, 137.3, 136.1, 136.0, 132.4, 130.0, 128.7, 128.3, 128.1, 127.6, 123.5, 56.5, 54.2, 28.3, 21.6; HRMS (ESI) for $C_{23}H_{23}N_2O_4S$ $[M+H]^+$ calcd 423.1373, found 423.1374.

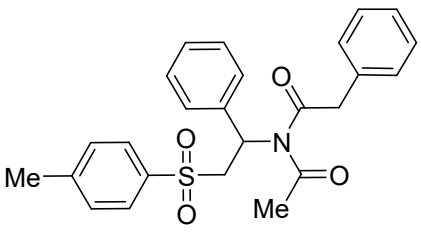
N-acetyl-N-(1-phenyl-2-tosylethyl)-1H-indole-2-carboxamide (5ch)



5ch

Yellow solid; 61.8 mg, 67% yield; mp 182-184 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.42 – 7.36 (m, 1H), 7.33 – 7.23 (m, 8H), 7.11 (s, 1H), 5.50 – 5.42 (m, 1H), 3.77 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.52 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 161.8, 145.3, 139.0, 137.8, 135.5, 133.3, 130.1, 129.0, 128.2, 128.0, 127.4, 127.1, 126.1, 123.7, 121.9, 115.7, 113.9, 60.0, 49.6, 26.4, 21.6; HRMS (ESI) for $C_{26}H_{24}N_2NaO_4S$ $[M+Na]^+$ calcd 483.1349, found 483.1351.

N-acetyl-2-phenyl-N-(1-phenyl-2-tosylethyl)acetamide (5ci)

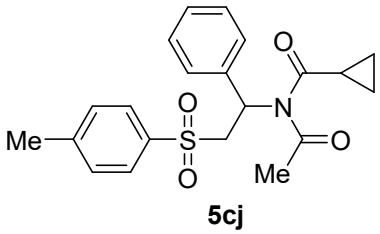


5ci

Colourless oil; 47.6 mg, 55% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.22 (m, 6H), 7.17 – 7.10 (m, 4H), 5.82 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.48 (dd, *J* = 14.8, 9.2 Hz, 1H), 4.08 (q, *J* = 16.2 Hz, 2H), 3.78 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 173.9, 145.1, 137.2, 136.4, 133.9, 130.0,

129.6, 128.6, 128.5, 127.9, 127.8, 127.0, 126.3, 57.1, 54.6, 45.0, 26.6, 21.6; HRMS (ESI) for $C_{25}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 458.1397, found 458.1395.

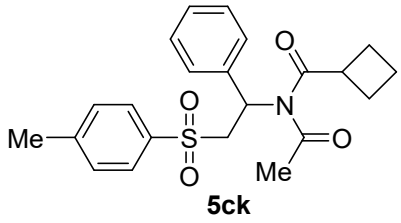
N-acetyl-N-(1-phenyl-2-tosylethyl)cyclopropanecarboxamide (5cj)



5cj

Colourless oil; 68.4 mg, 89% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.23 (m, 5H), 6.06 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.59 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.77 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 2.15 – 2.06 (m, 1H), 1.26 – 1.20 (m, 1H), 1.15 – 1.08 (m, 1H), 1.07 – 0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 173.4, 144.9, 137.7, 136.4, 129.9, 128.6, 128.0, 127.8, 126.8, 56.9, 54.0, 26.8, 21.6, 17.1, 11.6, 11.2; HRMS (ESI) for $C_{21}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 408.1240, found 408.1239.

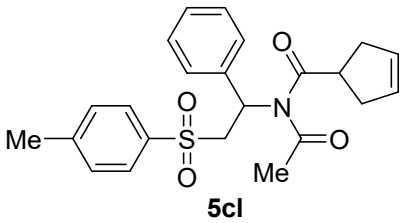
N-acetyl-N-(1-phenyl-2-tosylethyl)cyclobutanecarboxamide (5ck)



5ck

Colourless oil; 52.4 mg, 66% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 5.72 (dd, *J* = 9.2, 4.0 Hz, 1H), 4.46 (dd, *J* = 14.8, 9.2 Hz, 1H), 3.80 (dd, *J* = 14.8, 4.0 Hz, 1H), 3.69 – 3.57 (m, 1H), 2.44 (s, 3H), 2.42 – 2.33 (s, 4H), 2.22– 2.08 (m, 3H), 1.99 – 1.87 (m, 1H), 1.85 – 1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 173.8, 145.0, 137.6, 136.4, 129.9, 128.6, 127.8, 127.7, 126.2, 57.5, 53.9, 41.3, 26.8, 26.1, 25.0, 21.6, 17.5; HRMS (ESI) for $C_{22}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 422.1397, found 422.1397.

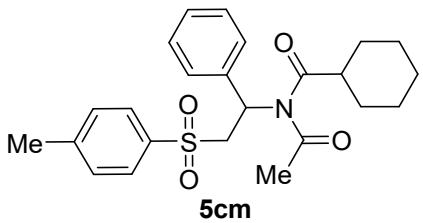
N-acetyl-N-(1-phenyl-2-tosylethyl)cyclopent-3-ene-1-carboxamide (5cl)



5cl

Colourless oil; 53.8 mg, 65% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.20 (m, 5H), 5.85 (dd, *J* = 8.8, 3.6 Hz, 1H), 5.66 – 5.60 (m, 1H), 5.58 – 5.50 (m, 1H), 4.48 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.81 (dd, *J* = 14.8, 4.0 Hz, 1H), 3.71 – 3.60 (m, 1H), 2.74 – 2.50 (m, 3H), 2.45 (s, 3H), 2.44 (s, 3H), 2.41 – 2.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.7, 174.0, 145.0, 137.5, 136.3, 129.9, 129.0, 128.6, 128.1, 127.9, 126.4, 57.5, 54.2, 44.1, 37.9, 37.4, 26.7, 21.6; HRMS (ESI) for $C_{23}H_{25}NNaO_4S$ $[M+Na]^+$ calcd 434.1397, found 434.1395.

N-acetyl-N-(1-phenyl-2-tosylethyl)cyclohexanecarboxamide (5cm)

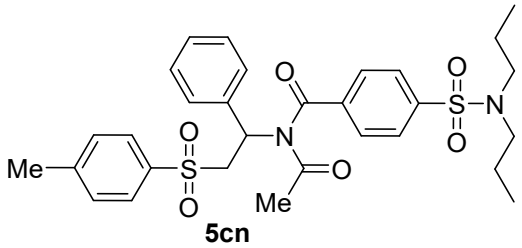


5cm

White solid; 59.6 mg,70% yield; mp 125-127 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.20 (m, 5H), 5.81 (dd, *J* = 8.8, 4.0 Hz, 1H), 4.43 (dd, *J* = 14.8, 8.8 Hz, 1H), 3.85 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.89 – 2.79 (m, 1H), 2.44 (s, 3H), 2.42 (s, 3H),1.84 – 1.71 (m, 2H), 1.69 – 1.58 (m, 3H), 1.44 – 1.32 (m, 1H), 1.27 – 1.15 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9,

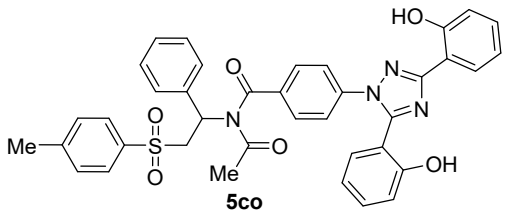
174.0, 145.0, 137.7, 136.4, 129.9, 128.6, 128.0, 127.9, 126.6, 57.8, 54.0, 46.0, 29.7, 29.1, 26.5, 25.6, 25.5, 25.3, 21.6; HRMS (ESI) for $C_{24}H_{29}NNaO_4S$ $[M+Na]^+$ calcd 450.1710, found 450.1709.

N-acetyl-4-(N,N-dipropylsulfamoyl)-N-(1-phenyl-2-tosylethyl)benzamide (5cn)



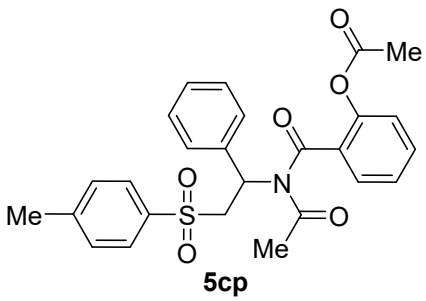
Colourless oil; 60.5 mg, 52% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.32 – 7.24 (m, 3H), 6.23 (dd, *J* = 10.8, 2.8 Hz, 1H), 4.80 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.66 (dd, *J* = 14.8, 3.2 Hz, 1H), 3.12 – 3.03 (m, 4H), 2.45 (s, 3H), 1.88 (s, 3H), 1.60 – 1.49 (M, 4H), 0.90 – 0.83 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.5, 145.1, 143.8, 139.8, 137.4, 136.0, 130.0, 129.2, 128.6, 128.3, 128.1, 127.6, 127.4, 56.4, 54.1, 50.0, 28.4, 22.0, 21.6, 11.1; HRMS (ESI) for $C_{30}H_{36}N_2NaO_6S_2$ $[M+Na]^+$ calcd 607.1907, found 607.1909.

N-acetyl-4-(3,5-bis(2-hydroxyphenyl)-1H-1,2,4-triazol-1-yl)-N-(1-phenyl-2-tosylethyl)benzamide (5co)



White solid; 47.4 mg, 44% yield; mp 116-118 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.10 (s, 1H), 9.56 (s, 1H), 8.16 – 8.09 (m, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.34 (m, 6H), 7.34 – 7.26 (m, 3H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.94 – 6.90 (m, 1H), 6.71 – 6.63 (m, 1H), 6.26 (dd, *J* = 10.8, 2.8 Hz, 1H), 4.81 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.69 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.45 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.4, 159.7, 157.8, 156.5, 152.2, 145.2, 141.1, 137.8, 137.4, 136.1, 133.2, 131.9, 130.3, 130.0, 128.7, 128.4, 128.1, 127.7, 127.6, 126.3, 119.9, 119.1, 118.4, 117.2, 113.1, 109.8, 56.6, 54.3, 28.4, 21.7; HRMS (ESI) for $C_{38}H_{33}N_4O_6S$ $[M+H]^+$ calcd 673.2115, found 673.2114.

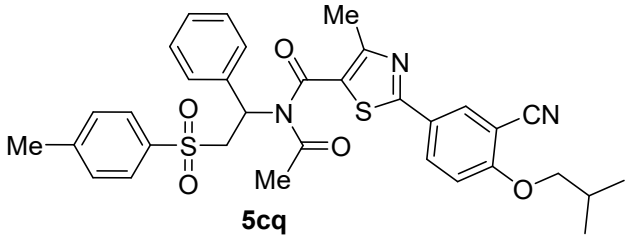
2-(acetyl(1-phenyl-2-tosylethyl)carbamoyl)phenyl acetate (5cp)



Colourless oil; 56.4 mg, 59% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.38 – 7.31 (m, 4H), 7.30 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 6.29 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.72 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.73 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.43 (s, 3H), 2.17 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 169.7, 169.0, 148.3, 144.9, 137.7, 136.1, 132.8, 129.9, 129.6, 129.3, 128.4, 128.2, 128.1, 127.9, 126.0, 123.6, 56.5, 53.3, 27.7, 21.6, 20.7; HRMS (ESI) for $C_{26}H_{25}NNaO_6S$ $[M+Na]^+$ calcd 502.1295, found 502.1292.

N-acetyl-2-(3-cyano-4-isobutoxyphenyl)-4-methyl-N-(1-phenyl-2-tosylethyl)thiazole-5-

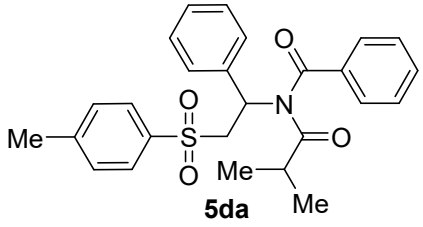
carboxamide (5cq)



5cq

White solid; 86.3 mg, 70% yield; mp 138-140 °C; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 2.4Hz, 1H), 8.05 – 7.99 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.31 – 7.24 (m, 3H), 7.01 (d, *J* = 9.2 Hz, 1H), 6.17 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.69 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.90 (d, *J* = 6.4 Hz, 2H), 3.76 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.54 (s, 3H), 2.44 (s, 3H), 2.25 – 2.15 (m, 1H), 2.13 (s, 3H), 1.09 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 168.0, 166.3, 162.6, 159.6, 145.0, 136.9, 136.0, 132.6, 132.0, 129.9, 128.6, 128.4, 128.1, 127.9, 127.8, 125.3, 115.2, 112.6, 102.9, 75.6, 57.0, 54.3, 28.0, 26.9, 21.6, 18.9, 17.1; HRMS (ESI) for $C_{33}H_{33}N_3NaO_5S_2$ $[M+Na]^+$ calcd 638.1754, found 638.1754.

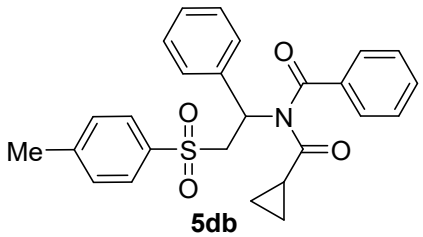
N-isobutyryl-N-(1-phenyl-2-tosylethyl)benzamide (5da)



5da

Colourless oil; 31.7 mg, 35% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.71 (m, 4H), 7.57 – 7.51 (m, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.20 (m, 3H), 6.22 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.78 (dd, *J* = 14.8, 9.6 Hz, 1H), 3.82 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.41 (s, 3H), 2.19 – 2.09 (m, 1H), 0.70 (d, *J* = 6.4 Hz, 3H), 0.52 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.4, 173.7, 144.8, 137.6, 136.6, 136.0, 132.8, 129.9, 129.2, 128.9, 128.5, 128.4, 128.3, 128.2, 57.6, 54.3, 38.9, 21.6, 19.2, 18.4; HRMS (ESI) for $C_{26}H_{28}NO_4S$ $[M+H]^+$ calcd 450.1734, found 450.1731.

N-(cyclopropanecarbonyl)-N-(1-phenyl-2-tosylethyl)benzamide (5db)

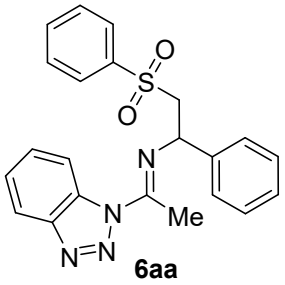


5db

Colourless oil; 67.1 mg, 75% yield; reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.60 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.36 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.20 (m, 3H), 6.30 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.82 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.77 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.41 (s, 3H), 1.15 – 1.08 (m, 1H), 1.00 – 0.86 (m, 2H), 0.61 – 0.52 (m, 1H), 0.41– 0.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 173.4, 144.8, 137.9, 136.8, 136.2, 132.4, 129.8, 129.1, 128.5, 128.4, 128.3, 128.0, 127.9, 57.0, 53.8, 21.6, 21.0, 12.9, 12.3; HRMS (ESI) for $C_{26}H_{26}NO_4S$ $[M+H]^+$ calcd 448.1577, found 448.1575.

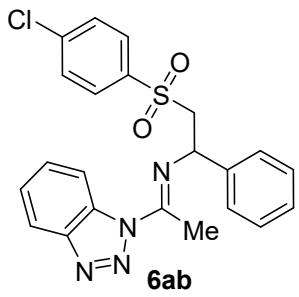
Data B: Characterization of products *β*-sulfonyl Imines

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6aa)



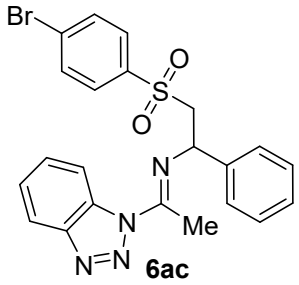
White solid; 75.9 mg, 94% yield, mp 180-182 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.03 (m, 2H), 7.73 – 7.70 (m, 2H), 7.46 – 7.27 (m, 7H), 7.07 – 7.01 (m, 3H), 5.47 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.66 (dd, *J* = 10.4, 2.0 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 146.5, 140.1, 140.0, 132.9, 131.1, 129.1, 128.7, 128.6, 128.2, 127.4, 126.6, 125.0, 119.5, 115.7, 64.4, 59.3, 15.1. HRMS (ESI) for $C_{22}H_{21}N_4O_2S$ $[M+H]^+$ calcd 405.1380, found 405.1378.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((4-chlorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ab)



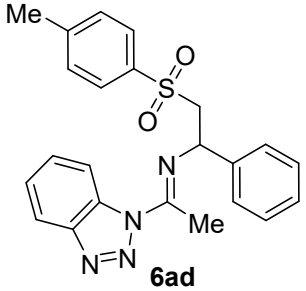
Pale yellow solid; 68.4 mg, 78% yield, mp 154-156 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.03 (m, 1H), 7.97 – 7.90 (m, 1H), 7.63 – 7.58 (m, 2H), 7.47 – 7.41 (m, 2H), 7.39 – 7.27 (m, 6H), 5.48 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.05 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.66 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.5, 140.0, 139.8, 138.7, 130.9, 129.2, 129.0, 128.9, 128.8, 128.3, 126.6, 125.3, 119.8, 115.3, 64.4, 59.4, 15.2. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0987.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((4-bromophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ac)



White solid; 71.2 mg, 74% yield, mp 211-212 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.03 (m, 1H), 7.95 – 7.89 (m, 1H), 7.55 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.39 – 7.25 (m, 5H), 7.18 – 7.11 (m, 2H), 5.48 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.05 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.66 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.5, 139.8, 139.2, 132.0, 130.8, 129.2, 129.0, 128.9, 128.6, 128.4, 126.6, 125.4, 119.8, 115.3, 64.4, 59.4, 15.2. HRMS (ESI) for $C_{22}H_{20}BrN_4O_2S$ $[M+H]^+$ calcd 483.0485, found 483.0485.

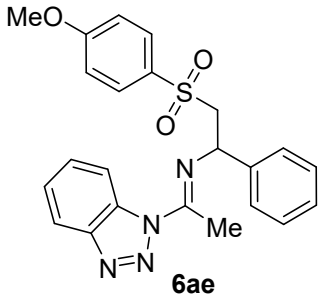
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-tosylethyl)ethan-1-imine (6ad)



Pale yellow solid; 59.8 mg, 72% yield, mp 152-154 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 1H), 7.98 – 7.91 (m, 1H), 7.60 – 7.52 (m, 2H), 7.47 – 7.27 (m, 7H), 6.81 – 6.73 (m, 2H), 5.46 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.04 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.63 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.79 (s, 3H), 1.85 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 146.4, 144.3, 140.2, 137.0, 131.0,

129.2, 129.1, 128.6, 128.2, 127.5, 126.6, 125.0, 119.5, 115.9, 64.4, 59.5, 21.0, 15.1. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 419.1534.

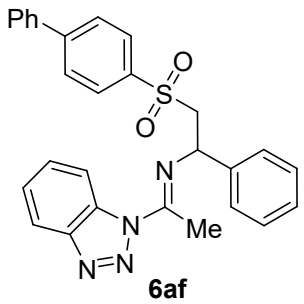
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((4-methoxyphenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ae)



6ae

Pale yellow solid; 29.1 mg, 62% yield, mp 146-148 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 1H), 7.99 – 7.93 (m, 1H), 7.64 – 7.56 (m, 2H), 7.47 – 7.39 (m, 2H), 7.39 – 7.28 (m, 5H), 6.49 – 6.36 (m, 2H), 5.45 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.02 (dd, *J* = 14.4, 10.4 Hz, 1H), 3.63 (dd, *J* = 14.4, 2.4 Hz, 1H), 3.41 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 155.4, 146.5, 140.2, 131.4, 131.0, 129.6, 129.2, 128.7, 128.2, 126.6, 125.1, 119.4, 115.8, 113.8, 64.6, 59.6, 55.2, 15.2 HRMS (ESI) for $C_{23}H_{23}N_4O_3S$ $[M+H]^+$ calcd 435.1485, found 435.1483.

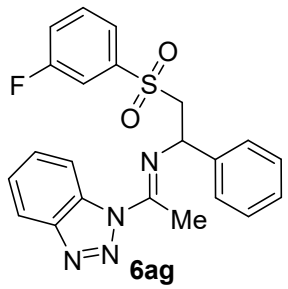
(E)-N-(2-([1,1'-biphenyl]-4-ylsulfonyl)-1-phenylethyl)-1-(1H-benzo[d][1,2,3]triazol-1-yl)ethan-1-imine (6af)



6af

Pale yellow solid; 70.4 mg, 73% yield, mp 154-156 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.40 – 7.31 (m, 8H), 7.30 – 7.19 (m, 4H), 7.11 – 7.08 (m, 2H), 5.52 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.11 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.70 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 146.4, 146.1, 140.1, 138.5, 138.2, 130.9, 129.2, 128.7, 128.6, 128.5, 128.3, 128.0, 127.2, 127.1, 126.7, 125.1, 119.5, 115.5, 64.4, 59.5, 15.2. HRMS (ESI) for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$ calcd 481.1693, found 481.1689.

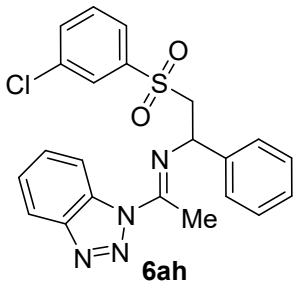
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((3-fluorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ag)



6ag

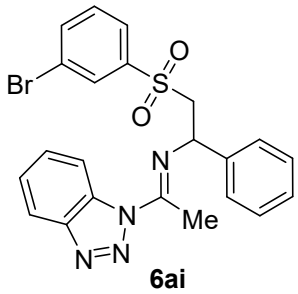
Pale yellow solid; 77.4 mg, 92% yield, mp 164-166 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.01 (m, 2H), 7.53 – 7.26 (m, 9H), 7.02 – 6.95 (m, 1H), 6.73 – 6.64 (m, 1H), 5.48 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.67 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 253.5 Hz), 155.8, 146.5, 142.1 (d, *J* = 6.1 Hz), 139.8, 131.0, 130.4 (d, *J* = 7.1 Hz), 129.2, 128.9, 128.4, 126.7, 125.2, 123.2 (d, *J* = 4.0 Hz), 120.2 (d, *J* = 22.2 Hz), 119.6, 115.4, 115.0 (d, *J* = 24.2 Hz), 64.3, 59.3, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.28. HRMS (ESI) for $C_{22}H_{20}FN_4O_2S$ $[M+H]^+$ calcd 423.1286, found 423.1284.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((3-chlorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ah)



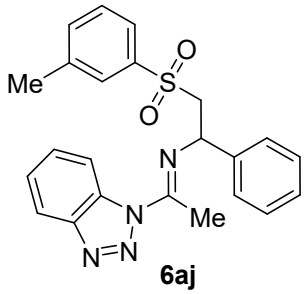
Pale yellow solid; 73.1 mg, 84% yield, mp 148-150 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.02 (m, 1H), 7.97 – 7.94 (m, 1H), 7.68 – 7.66 (m, 1H), 7.58 – 7.55 (m, 1H), 7.50 – 7.40 (m, 2H), 7.39 – 7.28 (m, 5H), 6.95 – 6.90 (m, 2H), 5.47 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.08 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.67 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.81 (S, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.5, 141.8, 139.7, 135.2, 133.1, 131.0, 129.8, 129.2, 128.9, 128.4, 127.7, 126.7, 125.5, 125.2, 119.7, 115.3, 64.4, 59.4, 15.2. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0988.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((3-bromophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ai)



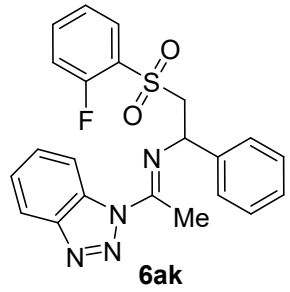
Pale yellow solid; 88.3 mg, 92% yield, mp 152-154 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.99 – 7.90 (m, 1H), 7.83 – 7.81 (m, 1H), 7.63 – 7.60 (m, 1H), 7.50 – 7.40 (m, 2H), 7.39 – 7.28 (m, 5H), 7.08 – 7.05 (m, 1H), 6.88 – 6.84 (m, 1H), 5.47 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.08 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.68 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.5, 141.9, 139.7, 136.0, 131.0, 130.5, 130.0, 129.2, 129.0, 128.4, 126.6, 125.9, 125.1, 123.0, 119.6, 115.3, 64.4, 59.4, 15.1. HRMS (ESI) for $C_{22}H_{20}BrN_4O_2S$ $[M+H]^+$ calcd 483.0485, found 483.0484.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(m-tolylsulfonyl)ethyl)ethan-1-imine (6aj)



White solid; 62.5 mg, 75% yield, mp 169-171 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.98 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.40 – 7.27 (m, 5H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.46 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.65 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.79 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 146.5, 140.1, 139.8, 139.2, 133.7, 131.0, 129.1, 128.7, 128.6, 128.2, 127.8, 126.6, 125.0, 124.6, 119.5, 115.7, 64.4, 59.4, 20.7, 15.1. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 419.1532.

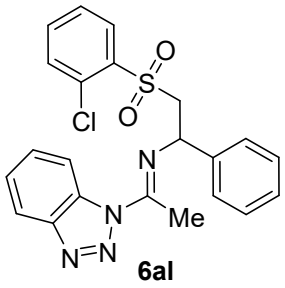
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((2-fluorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6ak)



Pale yellow solid; 60.7 mg, 72% yield, mp 148-150 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 1H), 8.05 – 7.01 (m, 1H), 7.65 – 7.60 (m, 1H), 7.54 – 7.48 (m, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.86 – 6.79 (m, 1H), 6.76 – 6.71 (m, 1H), 6.55 – 6.49 (m, 1H), 5.48 – 5.43 (m, 1H), 4.33 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.74 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0(d, J = 255.5 Hz), 155.5, 146.4, 139.6, 134.9(d, J = 9.1), 131.0, 129.2, 128.8, 128.4, 128.0(d, J

= 15.2), 126.6, 125.1, 123.9(d, J = 3.0), 119.5, 116.7 (d, J = 21.2) 115.5, 63.3 (d, J = 3.0), 59.4, 15.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.69. HRMS (ESI) for $C_{22}H_{20}FN_4O_2S$ $[M+H]^+$ calcd 423.1286, found 423.1283.

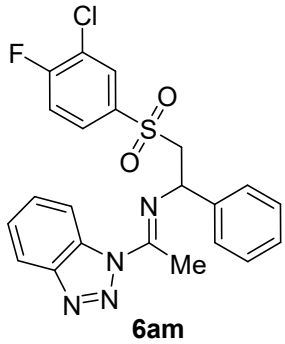
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((2-chlorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6al)



6al

White solid; 80.7 mg, 92% yield, mp 171-173 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.14 (m, 1H), 8.03 – 8.00 (m, 1H), 7.80 – 7.77 (m, 1H), 7.54 – 7.49 (m, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.30 (m, 1H), 6.86 – 6.80 (m, 2H), 6.73 – 6.68 (m, 1H), 5.45 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.64 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.72 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 146.4, 139.6, 137.6, 133.3, 132.2, 131.4, 130.9, 130.0, 129.2, 128.7, 128.4, 126.6, 126.5, 125.1, 119.4, 115.6, 61.9, 59.5, 15.0. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0987.

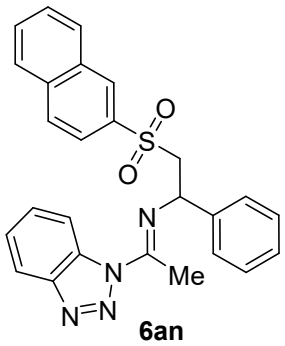
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-((3-chloro-4-fluorophenyl)sulfonyl)-1-phenylethyl)ethan-1-imine (6am)



6am

Yellow solid; 62.5 mg, 69% yield, mp 179-181 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.05 (m, 1H), 7.94 – 7.85 (m, 1H), 7.74 – 7.71 (m, 1H), 7.58– 7.53 (m, 1H), 7.48 – 7.42 (m, 2H),7.39 – 7.27 (m, 5H), 6.73 (t, *J* = 8.4 Hz, 1H), 5.48 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.06 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.68 (dd, *J* = 14.8, 2.8 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7(d, J = 259.6 Hz), 156.1, 146.6, 139.5, 137.3, 130.8, 130.7 (d, J = 1.0 Hz), 129.2, 128.9, 128.5, 128.0 (d, J = 8.1 Hz), 126.7, 125.4, 122.5 (d, J = 19.2 Hz), 119.9, 116.8(d, J = 22.2 Hz), 115.0, 64.6, 59.5, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.77. HRMS (ESI) for $C_{22}H_{19}ClFN_4O_2S$ $[M+H]^+$ calcd 457.0896, found 457.0892.

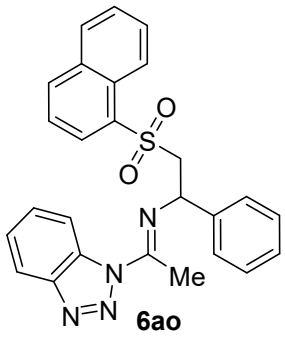
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(naphthalen-2-ylsulfonyl)-1-phenylethyl)ethan-1-imine (6an)



6an

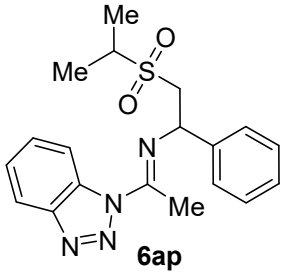
White amorphous solid; 63.1 mg, 70% yield, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 1.8 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.70 – 7.65 (m, 2H), 7.54 – 7.45 (m, 2H), 7.40 – 7.25 (m, 8H), 7.17 – 7.12 (m, 1H), 7.08 – 7.03 (m, 1H), 5.52 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.15 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.72 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 146.1, 140.1, 136.8, 134.6, 131.6, 130.5, 129.4, 129.1, 128.8, 128.5, 128.3, 128.2, 127.5, 127.4, 126.6, 124.8, 122.1, 119.2, 115.2, 64.5, 59.5, 15.1. HRMS (ESI) for $C_{26}H_{23}N_4O_2S$ $[M+H]^+$ calcd 455.1536, found 455.1533.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(naphthalen-1-ylsulfonyl)-1-phenylethyl)ethan-1-imine (6ao)



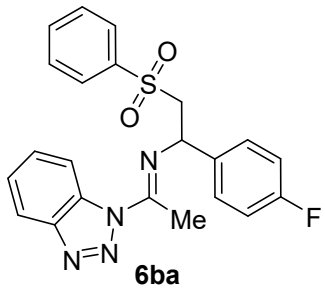
Yellow solid; 56.1 mg, 62% yield, mp 138-140 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.8 Hz, 1H), 8.07 – 8.05 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.42 – 7.24 (m, 10H), 7.06 – 6.97 (m, 2H), 5.47 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.36 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.79 (dd, *J* = 14.4, 1.6 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 146.3, 140.1, 134.8, 134.4, 133.9, 130.7, 129.6, 129.1, 129.0, 128.8, 128.6, 128.5, 128.2, 126.6, 126.5, 124.7, 123.6, 123.4, 119.2, 114.9, 64.0, 59.5, 15.0. HRMS (ESI) for $C_{26}H_{23}N_4O_2S$ $[M+H]^+$ calcd 455.1536, found 455.1532.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(isopropylsulfonyl)-1-phenylethyl)ethan-1-imine (6ap)



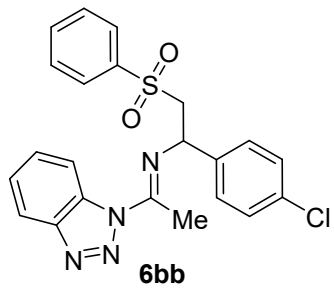
White solid; 30.1 mg, 41% yield, mp 100-102 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 – 8.60 (m, 1H), 8.11 – 8.08 (m, 1H), 7.65 – 7.60 (m, 1H), 7.49 – 7.44 (m, 3H), 7.41 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 5.52 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.89 (dd, *J* = 14.0, 9.6 Hz, 1H), 3.39 (dd, *J* = 14.4, 3.2 Hz, 1H), 3.02 – 2.95 (m, 1H), 2.85 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 146.7, 140.6, 131.3, 129.2, 129.1, 128.3, 126.8, 125.2, 119.8, 115.5, 58.7, 57.6, 54.3, 15.6, 15.4, 14.4. HRMS (ESI) for $C_{19}H_{23}N_4O_2S$ $[M+H]^+$ calcd 371.1536, found 371.1534.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(4-fluorophenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6ba)



White solid; 66.7 mg, 79% yield, mp 77-79 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.98 (m, 2H), 7.75 – 7.68 (m, 2H), 7.47 – 7.39 (m, 2H), 7.39 – 7.33 (m, 2H), 7.11 – 6.99 (m, 5H), 5.47 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.02 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.63 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 248.5 Hz), 155.7, 146.5, 139.9, 135.9(d, J = 4.0 Hz), 133.0, 131.0, 128.8, 128.7, 128.3(d, J = 8.1 Hz), 127.4, 125.1, 119.6, 116.2, 116.0, 115.6, 64.4, 58.6, 15.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.19. HRMS (ESI) for $C_{22}H_{20}FN_4O_2S$ $[M+H]^+$ calcd 423.1286, found 423.1283.

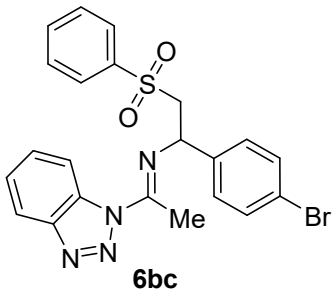
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(4-chlorophenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bb)



Pale yellow solid; 54.6 mg, 62% yield, mp 108-110 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.98 (m, 2H), 7.74 – 7.67 (m, 2H), 7.47 – 7.38 (m, 2H), 7.34 – 7.28 (m, 4H), 7.12 – 7.00 (m, 3H), 5.46 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.01 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.63 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.5, 139.9, 138.6, 134.1, 133.0, 131.0, 129.3, 128.9, 128.7, 128.0, 127.4, 125.1, 119.6,

115.6, 64.2, 58.6, 15.1. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0988.

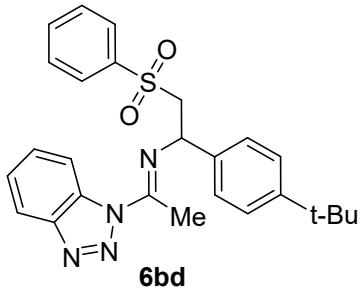
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(4-bromophenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bc)



6bc

Yellow solid; 70.2 mg, 73% yield, mp 125-127 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.97 (m, 2H), 7.73 – 7.66 (m, 2H), 7.50 – 7.39 (m, 4H), 7.28 – 7.24 (m, 2H), 7.13 – 7.00 (m, 3H), 5.44 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.01 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.62 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 146.5, 139.9, 139.1, 133.0, 132.3, 131.0, 128.9, 128.7, 128.4, 127.4, 125.1, 122.2, 119.6, 115.6, 64.1, 58.7, 15.2. HRMS (ESI) for $C_{22}H_{20}BrN_4O_2S$ $[M+H]^+$ calcd 483.0485, found 483.0483.

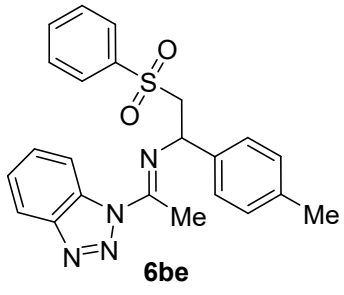
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(4-(tert-butyl)phenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bd)



6bd

Yellow solid; 54.6 mg, 59% yield, mp 133-135 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.02 (m, 2H), 7.72 – 7.68 (m, 2H), 7.46 – 7.38 (m, 2H), 7.37 – 7.27 (m, 4H), 7.07 – 6.97 (m, 3H), 5.45 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.05 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.66 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.79 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 151.3, 146.5, 140.1, 137.0, 132.8, 131.1, 128.7, 128.6, 127.4, 126.3, 126.0, 125.0, 119.5, 115.8, 64.3, 59.0, 34.6, 31.2, 15.1. HRMS (ESI) for $C_{26}H_{29}N_4O_2S$ $[M+H]^+$ calcd 461.2006, found 461.2003.

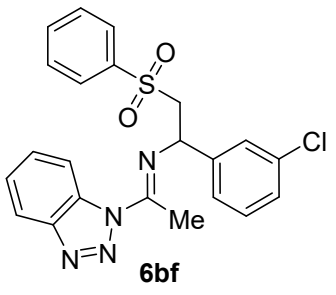
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(phenylsulfonyl)-1-(p-tolyl)ethyl)ethan-1-imine (6be)



6be

Pale yellow solid; 45.8 mg, 55% yield, mp 118-120 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.73 – 7.67 (m, 2H), 7.47 – 7.37 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 – 6.96 (m, 3H), 5.43 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.06 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.64 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 146.4, 139.9, 138.1, 137.0, 132.8, 131.0, 129.8, 128.6, 127.4, 126.5, 125.0, 119.4, 115.7, 64.3, 59.0, 21.1, 15.10. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 419.1532.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(3-chlorophenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bf)

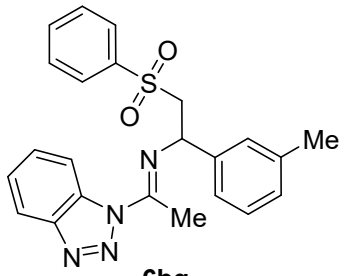


6bf

White solid; 34.8 mg, 40% yield, mp 176-178 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.99 (m, 2H), 7.74 – 7.69 (m, 2H), 7.49 – 7.39 (m, 2H), 7.36 – 7.34 (m, 1H),

7.30 – 7.26 (m, 4H), 7.13 – 7.02 (m, 3H), 5.46 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.02 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.64 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 146.6, 142.0, 139.9, 135.0, 133.1, 131.1, 130.5, 128.9, 128.8, 128.5, 127.4, 126.9, 125.2, 124.9, 119.61, 115.6, 64.2, 58.8, 15.2. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0988.

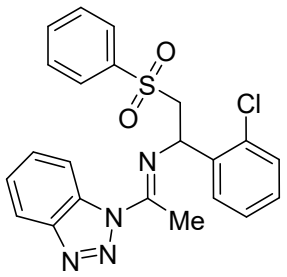
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(phenylsulfonyl)-1-(m-tolyl)ethyl)ethan-1-imine (6bg)



6bg

White solid; 61.3 mg, 73% yield, mp 163-165 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m 2H), 7.74 – 7.68 (m, 2H), 7.49 – 7.37 (m, 2H), 7.25 – 7.14 (m, 3H), 7.12 – 6.96 (m, 4H), 5.43 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.07 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.65 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.79 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 146.4, 140.0, 139.9, 138.9, 132.9, 131.0, 129.0, 128.9, 128.7, 128.6, 127.4, 127.3, 125.0, 123.7, 119.4, 115.7, 64.3, 59.3, 21.4, 15.2. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 419.1533.

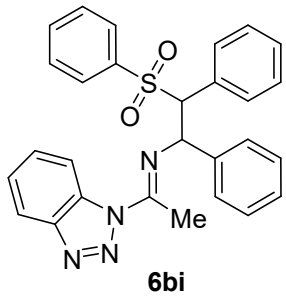
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-(2-chlorophenyl)-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bh)



6bh

Yellow solid; 63.1 mg, 72% yield, mp 99-101 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 1H), 8.08– 8.05 (m, 1H), 7.81 – 7.72 (m, 2H), 7.54 – 7.35 (m, 4H), 7.26 – 7.18 (m, 2H), 7.17 – 7.06 (m, 3H), 5.88 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.95 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.71 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 146.5, 140.0, 137.6, 133.1, 131.9, 131.1, 130.0, 129.3, 129.0, 128.8, 128.5, 127.6, 127.5, 125.1, 119.5, 115.7, 62.4, 55.8, 15.5. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0987.

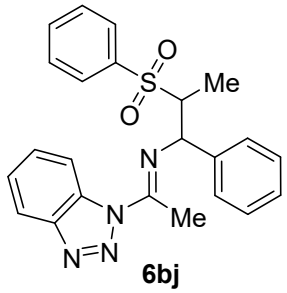
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1,2-diphenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6bi)



6bi

White solid; 22.7 mg, 24% yield, mp 185-187 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.48 (m, 3H), 7.46 – 7.40 (m, 2H), 7.32 – 7.19 (m, 11H), 7.17 – 7.12 (m, 2H), 6.15 (d, *J* = 4.4 Hz, 1H), 4.57 (d, *J* = 4.4 Hz, 1H), 2.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 146.7, 139.9, 138.6, 133.3, 131.7, 131.3, 130.2, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.7, 125.0, 119.7, 115.8, 62.3, 15.6. HRMS (ESI) for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$ calcd 481.1693, found 481.1690.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)propyl)ethan-1-imine (6bj)

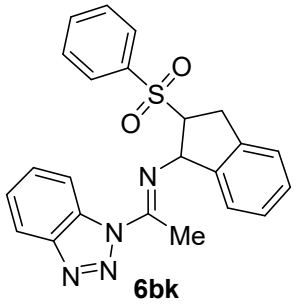


6bj

Pale yellow solid; 64.2 mg, 77% yield, mp 169-171 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.15 (m, 1H), 8.12

– 8.06 (m, 1H), 7.78 – 7.72 (m, 2H), 7.53 – 7.40 (m, 2H), 7.34 – 7.25 (m, 5H), 7.20 – 7.15 (m, 3H), 5.81 (d, *J* = 2.0 Hz, 1H), 3.60 – 3.52 (m, 1H), 2.75 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 146.6, 139.9, 137.9, 133.2, 131.1, 129.0, 128.9, 128.8, 128.6, 127.9, 126.9, 125.1, 119.6, 115.4, 67.6, 60.8, 15.5, 9.3. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 405.1533.

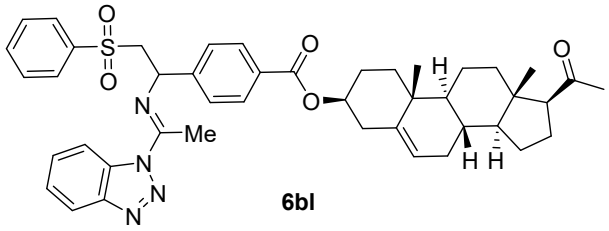
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-(2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)ethan-1-imine (6bk)



6bk

Pale yellow solid; 39.3 mg, 47% yield, mp 200-202 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 2H), 7.91 – 7.85 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25– 7.16 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 1H), 5.73 (d, *J* = 7.6 Hz, 1H), 4.38 – 4.30 (m, 1H), 3.71 (dd, *J* = 16.4, 10.0 Hz, 1H), 3.46 (dd, *J* = 16.4, 8.8 Hz, 1H), 2.88 (s, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 146.5, 140.3, 138.8, 138.4, 133.4, 131.1, 129.0, 128.8, 128.7, 128.2, 127.6, 125.2, 125.0, 123.6, 119.5, 115.9, 71.5, 64.8, 31.6, 15.2. HRMS (ESI) for $C_{23}H_{21}N_4O_2S$ $[M+H]^+$ calcd 417.1380, found 417.1377.

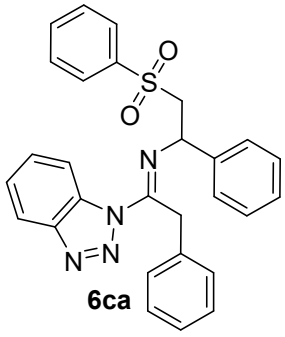
(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-4-(1-(((E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)ethylidene)amino)-2-(phenylsulfonyl)ethyl)benzoate (6bl)



6bl

Pale yellow amorphous solid; 44.8 mg, 30% yield, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 4H), 7.73 – 7.71 (m, 2H), 7.48 – 7.42 (m, 4H), 7.10 – 7.04 (m, 3H), 5.54 (dd, *J* = 10.0, 2.8 Hz, 1H), 5.41 (d, *J* = 4.8 Hz, 1H), 4.89 – 4.80 (m, 1H), 4.04 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.65 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.80 (s, 3H), 2.56 – 2.52 (m, 1H), 2.45 – 2.43 (m, 2H), 2.20 – 2.16 (m, 1H), 2.14 (s, 3H), 2.07 – 1.90 (m, 4H), 1.74 – 1.58 (m, 6H), 1.53 – 1.45 (m, 3H), 1.26 – 1.16 (m, 3H), 1.05 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 165.3, 156.1, 146.5, 144.8, 139.9, 139.5, 133.1, 131.0, 130.8, 130.4, 128.9, 128.8, 127.4, 126.7, 125.2, 122.6, 119.6, 115.6, 77.3, 74.7, 64.0, 63.6, 59.1, 56.8, 49.8, 44.0, 38.7, 38.1, 37.0, 36.6, 31.8, 31.7, 31.5, 27.8, 24.5, 22.8, 21.0, 19.3, 15.2, 13.2. HRMS (ESI) for $C_{44}H_{51}N_4NaO_5S$ $[M+Na]^+$ calcd 769.3394, found 769.3394.

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-2-phenyl-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6ca)

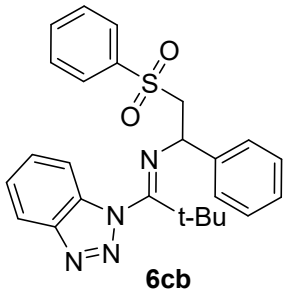


6ca

Yellow solid; 53.8 mg, 56% yield, mp 134-136 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 7.99 (m, 2H), 7.70 – 7.64 (m, 2H), 7.49 – 7.38 (m, 2H), 7.24 (d, *J* = 1.6 Hz, 5H), 7.25 – 7.20 (m, 5H), 7.13 – 7.04 (m, 8H),5.64 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.88 – 4.68 (m, 2H), 4.03 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.64 (dd, *J* = 14.4, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 146.6, 140.1, 140.0, 134.2, 132.9, 131.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 127.4, 126.9,

126.7, 125.1, 119.5, 115.7, 64.4, 59.2, 34.3. HRMS (ESI) for $C_{28}H_{25}N_4O_2S$ $[M+H]^+$ calcd 481.1693, found 481.1690.

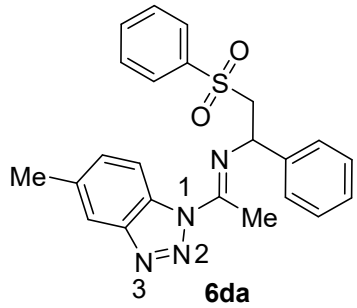
(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-2,2-dimethyl-N-(1-phenyl-2-(phenylsulfonyl)ethyl)propan-1-imine (6cb)



6cb

White solid; 21.4 mg, 24% yield, mp 92-94 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 7.42 – 7.28 (s, 2H), 7.23 – 7.10 (m, 4H), 6.88 – 6.79 (m, 2H), 4.23 (br s, 1H), 3.88 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.31 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 144.3, 140.2, 133.5, 133.0, 129.2, 128.7, 128.0, 127.9, 126.6, 124.1, 119.7, 63.7, 59.4, 41.0, 27.8. HRMS (ESI) for $C_{25}H_{27}N_4O_2S$ $[M+H]^+$ calcd 447.1849, found 447.1846.

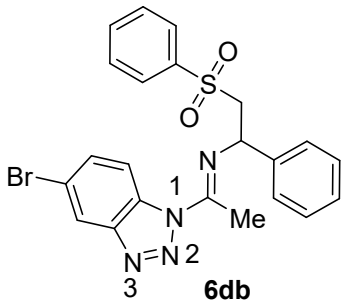
(E)-1-(5-methyl-1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6da, N1/N3 = 1/1**)**



6da

White amorphous solid; 44.3 mg, 53% yield, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.80 (br s, 1H), 7.76 – 7.68 (m, 5H), 7.38 – 7.27 (m, 10H), 7.26 – 7.21 (m, 2H), 7.11 – 7.00 (m, 6H), 5.49 – 5.42 (m, 2H), 4.11 – 4.01 (m, 2H), 3.70 – 3.61 (m, 2H), 2.77 (d, *J* = 3.0 Hz, 6H), 2.53 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 155.5, 147.1, 145.1, 140.3, 140.2, 140.1, 140.0, 139.3, 135.1, 132.9, 132.8, 131.5, 130.7, 129.5, 129.2, 128.7, 128.6, 128.2, 127.5, 127.1, 126.7, 126.6, 118.9, 118.5, 115.2, 115.1, 64.5, 64.4, 59.3, 59.2, 22.3, 21.4, 15.2, 15.0. HRMS (ESI) for $C_{23}H_{23}N_4O_2S$ $[M+H]^+$ calcd 419.1536, found 419.1535.

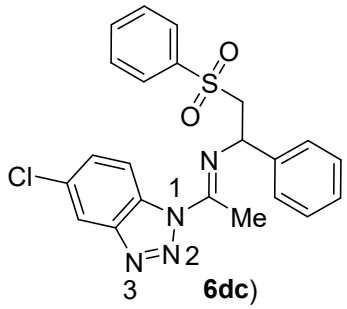
(E)-1-(5-bromo-1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6db, N1/N3 = 1/1**)**



6db

Pale yellow solid; 59.8 mg, 62% yield, mp 148-150 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.17 (m, 1H), 8.12 – 8.07 (m, 1H), 8.00 – 7.94 (m, 1H), 7.93 – 7.89 (m, 1H), 7.76 – 7.69 (m, 4H), 7.55 – 7.49 (m, 2H), 7.38 – 7.27 (m, 10H), 7.17 – 7.06 (m, 5H), 7.06 – 7.00 (m, 1H), 5.51 – 5.44 (m, 2H), 4.14 – 4.00 (m, 2H), 3.69 – 7.60 (m, 2H), 2.79 (d, *J* = 3.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 155.4, 147.5, 145.2, 140.2, 140.1, 139.8, 139.7, 133.1, 132.9, 132.1, 131.9, 130.1, 129.3, 129.2, 128.8, 128.7, 128.4, 127.5, 127.4, 126.6, 123.3, 122.2, 120.5, 118.6, 118.2, 116.9, 64.2, 59.4, 59.3, 15.2, 15.1. HRMS (ESI) for $C_{22}H_{20}BrN_4O_2S$ $[M+H]^+$ calcd 483.0485, found 483.0483.

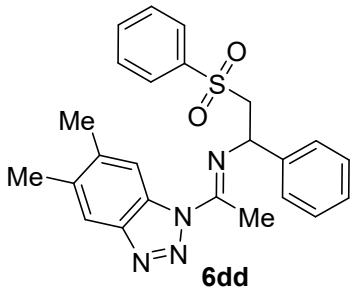
(E)-1-(5-chloro-1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6dc, N1/N3 = 1/1**)**



6dc)

Yellow solid; 47.0 mg, 54% yield, mp 147-149 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 8.01 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.76 – 7.69 (m, 4H), 7.43 – 7.38 (m, 1H), 7.37 – 7.27 (m, 11H), 7.17 – 7.00 (m, 6H), 5.51 – 5.44 (m, 2H), 4.13 – 4.00 (m, 2H), 3.68 – 3.61 (m, 2H), 2.80 (d, *J* = 3.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 155.4, 147.1, 144.9, 140.2, 140.1, 139.8, 139.7, 135.1, 133.0, 132.9, 131.5, 130.7, 129.8, 129.5, 129.3, 129.2, 128.8, 128.7, 128.4, 127.5, 127.4, 126.6, 126.2, 120.3, 118.9, 116.6, 115.5, 64.2, 59.4, 59.3, 15.2, 15.1. HRMS (ESI) for $C_{22}H_{20}ClN_4O_2S$ $[M+H]^+$ calcd 439.0990, found 439.0987.

(E)-1-(5,6-dimethyl-1H-benzo[d][1,2,3]triazol-1-yl)-N-(1-phenyl-2-(phenylsulfonyl)ethyl)ethan-1-imine (6dd)



6dd

Yellow solid; 42.7 mg, 50% yield, mp 192-194 °C, reaction time 24h; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.69 (m, 4H), 7.39 – 7.25 (m, 5H), 7.10 – 7.01 (m, 3H), 5.45 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.07 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.67 (dd, *J* = 14.8, 2.4 Hz, 1H), 2.75 (s, 2H), 2.40 (d, *J* = 12.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 145.7, 140.3, 140.1, 138.9, 134.7, 132.9, 130.1, 129.1, 128.6, 128.2, 127.5, 126.6, 118.7, 115.3, 64.6, 59.2, 21.2, 20.4, 15.1. HRMS (ESI) for $C_{24}H_{25}N_4O_2S$ $[M+H]^+$ calcd 439.1693, found 439.1690.

10. Computational Experiment

10.1 Calculation details

All the calculations were performed with the Gaussian 16 program package[S1] using the default conditions implemented in it. For geometry optimization and frequency analysis we adopted the B3LYP[S2]-D3BJ[S3] with the def2-SVP[S4,5] basis set. Intrinsic reaction coordinate

(IRC)[S6] calculations were performed to confirm the connectivity between the transition states and local minima. Optimized minima and transition states were proved by vibrational analysis to have no and one proper imaginary frequency, respectively. To refine the calculated energy, single point calculations were performed using the larger basis set def2-TZVP[S4,5] based on these optimized structures. Solvent effect was modeled in these optimization and single point calculations by employing SMD continuum solvation model[S7], taking acetonitrile as the solvent for each reaction.

TS means the structures of transition state, and Int means corresponding intermediate.

Ir^{III}

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.421364

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1541.4731148 a.u.

C	-1.31046300	-2.57287200	0.58140300
C	0.41694600	-2.16243900	2.22059600
C	0.11503800	-3.37694800	2.84321700
C	-0.90324300	-4.19990400	2.34082400
C	-1.61160800	-3.79533700	1.21071400
C	-2.03239500	-2.10018400	-0.60952600
C	-2.20190400	-0.36004000	-2.17133700
C	-3.23381700	-0.99556400	-2.85376300
C	-3.67498400	-2.23600500	-2.38094700
C	-3.07239700	-2.78883000	-1.25515700
H	1.21258400	-1.53995800	2.63724400
H	0.67635500	-3.68744100	3.72978900
H	-2.40444600	-4.43775700	0.82003000
H	-1.82065500	0.61008900	-2.49514900
H	-3.67833300	-0.52514900	-3.73210000
H	-3.40609500	-3.75299700	-0.87269300
N	-1.61922600	-0.89543400	-1.08822100
C	2.88371500	0.14910700	0.59228500
C	4.09020200	0.49652500	1.22867000
C	4.08193300	1.30918400	2.36093200
C	2.85817400	1.77807600	2.85959000
C	1.65822500	1.43514500	2.23011500
C	2.83976900	-0.70744600	-0.60265100
C	3.95853300	-1.25979200	-1.24808000
C	3.78475100	-2.05515800	-2.37662400
C	2.49132500	-2.29404800	-2.85290800
C	1.42269300	-1.72007600	-2.17251300
H	5.02055200	1.57561700	2.85303500
H	0.71978200	1.81339600	2.64271100

H	4.95924900	-1.06242500	-0.86456800
H	4.65164400	-2.48678500	-2.88212600
H	0.39241800	-1.87446800	-2.49927200
C	-0.80452800	2.81467100	-0.59760300
C	0.79203100	2.10045400	-2.15895800
C	0.75879900	3.31497000	-2.83551500
C	-0.09612800	4.31456200	-2.35974900
C	-0.87951000	4.06334900	-1.23754100
C	-1.57767300	2.41695000	0.58930100
C	-2.08375800	0.70794600	2.22114100
C	-2.98852100	1.57119600	2.84557000
C	-3.19669700	2.86505600	2.34701600
C	-2.49028900	3.28280300	1.22054900
H	1.44094300	1.28600000	-2.48663200
H	-0.15111600	5.28354700	-2.86127200
H	-1.94009900	-0.29342800	2.63400800
H	-3.90409500	3.54072900	2.83402600
H	-2.65319600	4.29079000	0.83280200
Ir	0.00028600	0.00009300	0.04120400
H	-3.53921400	1.23439900	3.72925300
H	2.30930700	-2.91334600	-3.73254600
H	5.04423700	0.13003900	0.84245700
H	2.84239400	2.41766800	3.74741600
H	1.39072500	3.46865800	-3.71156400
H	-1.55095400	4.83181800	-0.85500800
C	-0.28079700	-1.71720100	1.07887800
H	-4.48337500	-2.76856500	-2.88737300
H	-1.14159400	-5.14866500	2.82792000
C	-1.34845100	1.09617600	1.08247800
N	0.03407300	1.85787500	-1.07917300
N	1.59162100	-0.95045300	-1.08695800
C	1.62597300	0.61186100	1.08581600

Ir^{IV}

Charge: 1

Spin Multiplicity: 2

Thermal correction to Gibbs Free Energy (a.u.): 0.420354

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1541.2908881 a.u.

C	2.40954800	1.57912000	-0.56778600
C	2.25045300	-0.29557500	-2.11186900
C	3.43241800	0.11906000	-2.72522800
C	4.11183800	1.25630300	-2.26456600
C	3.60512200	1.97891600	-1.18670100
C	1.83297500	2.27726200	0.58559300

C	0.04665000	2.30010100	2.11243100
C	0.52553100	3.44103100	2.74307500
C	1.71246300	4.01204900	2.26704000
C	2.36623600	3.42993900	1.18753200
H	1.72973000	-1.17766000	-2.48725300
H	3.83065900	-0.44429000	-3.57261000
H	4.15010300	2.85505000	-0.83093400
H	-0.87687800	1.81451800	2.43364400
H	-0.02034100	3.87293600	3.58259600
H	3.28701100	3.86640900	0.80282500
N	0.68571500	1.73350000	1.07751400
C	0.16312800	-2.87608800	-0.56713700
C	-0.08783400	-4.11131100	-1.18644700
C	-0.96748600	-4.18902500	-2.26392100
C	-1.61352700	-3.03230400	-2.72414700
C	-1.38184300	-1.80136200	-2.11079900
C	1.05585900	-2.72555900	0.58637000
C	1.78802700	-3.76339400	1.18818400
C	2.61920300	-3.48791300	2.26746500
C	2.71728200	-2.17453400	2.74376600
C	1.96814000	-1.18963900	2.11323000
H	-1.15437900	-5.15071800	-2.74570900
H	-1.88560500	-0.90936500	-2.48596400
H	1.70612100	-4.77901500	0.80333200
H	3.19360500	-4.29024200	2.73537000
H	2.00892000	-0.14711000	2.43452900
C	-2.88839700	0.44816200	0.58697900
C	-2.01305200	-1.10876100	2.11416500
C	-3.24010100	-1.26505900	2.74556800
C	-4.32889200	-0.52372700	2.26974500
C	-4.15280800	0.33329500	1.18981000
C	-2.57311300	1.29596400	-0.56713600
C	-0.87070400	2.09637900	-2.11176700
C	-1.82153700	2.91177600	-2.72517900
C	-3.14612200	2.93049700	-2.26436300
C	-3.51794000	2.13022200	-1.18637600
H	-1.13014500	-1.66485800	2.43509400
H	-5.31055300	-0.61983600	2.73847400
H	0.15363800	2.08703400	-2.48707100
H	-3.88593900	3.57278100	-2.74607500
H	-4.54932200	2.16317300	-0.83087200
Ir	-0.00010600	0.00031600	-0.05894700
H	-1.53343800	3.53841400	-3.57272200
H	3.36417800	-1.91750600	3.58327200

H	0.39901400	-5.02125900	-0.83121600
H	-2.30059600	-3.09567500	-3.57145900
H	-3.34022900	-1.95333900	3.58554500
H	-4.99177400	0.91172000	0.80525800
C	1.70332600	0.43155600	-1.03904000
H	2.12060700	4.91033600	2.73512200
H	5.03837600	1.57494400	-2.74611400
C	-1.22615000	1.25920800	-1.03858500
N	-1.84313900	-0.27259900	1.07862500
N	1.15810800	-1.46004100	1.07818100
C	-0.47859000	-1.69105300	-1.03797500

Int1

Charge: 0

Spin Multiplicity: 2

Thermal correction to Gibbs Free Energy (a.u.): 0.185916

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1090.2701688 a.u.

S	2.49189000	-0.40137500	0.14012000
O	2.69359500	-0.89409600	1.53405300
O	3.64825000	0.14938300	-0.63059300
C	-0.79528900	2.77166100	0.22464500
C	1.21992500	0.88149900	0.19741000
C	1.11973300	1.77255800	-0.87328400
C	0.32706600	0.89683900	1.27044000
C	-0.68276900	1.86094900	1.28029600
C	0.10233000	2.72865300	-0.84820400
H	1.82937300	1.72479700	-1.70068100
H	0.42764500	0.17471400	2.08096700
H	-1.38943900	1.89290400	2.11216500
H	0.01038300	3.44145500	-1.67083300
H	-1.59422700	3.51662200	0.23405200
C	-3.60888500	0.14313500	-0.08412000
C	-1.34584300	-1.53362300	-0.24396800
C	-2.21874200	-1.59742400	0.86032500
C	-1.63486000	-0.61194800	-1.27190600
C	-2.75186800	0.21515200	-1.19076200
C	-3.33839300	-0.76783700	0.94119900
H	-2.00374000	-2.30460400	1.66578000
H	-0.97417500	-0.53557800	-2.13712900
H	-2.95477800	0.92955500	-1.99223000
H	-4.00033600	-0.83005900	1.80853300
H	-4.48190100	0.79751800	-0.02318200
C	-0.16817200	-2.40603700	-0.26739500

H	-0.07765100	-3.08276000	0.58954500
C	0.80574400	-2.42517600	-1.19976900
H	0.78582800	-1.78659300	-2.08728700
H	1.63814900	-3.12868500	-1.11873500

TS1

Charge: 0

Spin Multiplicity: 2

Thermal correction to Gibbs Free Energy (a.u.): 0.188758

Imaginary frequencies: -210.9836

Calculation of single point energy based on the optimized structure, E = -1090.2695364 a.u.

S	2.38333900	-0.43613900	0.09806300
O	2.69107300	-0.90783700	1.47533300
O	3.48931700	0.02616900	-0.78754800
C	-0.79868400	2.82911600	0.34434900
C	1.18391800	0.90172600	0.23506400
C	1.08115600	1.82503500	-0.80799300
C	0.31369000	0.91518400	1.32755300
C	-0.68291100	1.89212600	1.37688700
C	0.08342900	2.79977500	-0.74197100
H	1.77404300	1.77994200	-1.64978300
H	0.41837500	0.17449100	2.12107200
H	-1.37526900	1.91612400	2.22131400
H	-0.00850600	3.53603100	-1.54383400
H	-1.58528700	3.58626300	0.38446600
C	-3.63755100	0.00276700	-0.22592300
C	-1.26651400	-1.53054500	-0.24667200
C	-2.24063100	-1.70719100	0.76400100
C	-1.52040600	-0.57251400	-1.25763200
C	-2.68786800	0.18293700	-1.24217900
C	-3.40936000	-0.94900700	0.77511200
H	-2.05697200	-2.44226500	1.55182900
H	-0.79020900	-0.41142800	-2.05183400
H	-2.86077400	0.92585400	-2.02444400
H	-4.14544200	-1.09548100	1.56942700
H	-4.55063300	0.60280500	-0.21623200
C	-0.04224900	-2.30273800	-0.18437500
H	0.03093100	-3.01378800	0.64473300
C	1.06732400	-2.13895800	-0.99026500
H	1.02464300	-1.55556300	-1.91389800
H	1.88850200	-2.85770700	-0.91983900

Int2

Charge: 0

Spin Multiplicity: 2

Thermal correction to Gibbs Free Energy (a.u.): 0.191480

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1090.2874165 a.u.

S	2.22396000	-0.67224700	0.05467400
O	2.44269200	-1.24396700	1.39820700
O	3.38398100	-0.38265000	-0.81202600
C	-0.38862200	3.04384400	0.41631600
C	1.24911200	0.82051600	0.23062100
C	1.27280000	1.76612500	-0.79730500
C	0.43592200	0.96997200	1.35625200
C	-0.38966700	2.09280300	1.44245200
C	0.44480700	2.88588500	-0.69701500
H	1.92552600	1.62176000	-1.65980100
H	0.44690400	0.21466000	2.14275400
H	-1.03877500	2.22242700	2.31126500
H	0.44822400	3.63590000	-1.49121900
H	-1.04140000	3.91726400	0.48532300
C	-3.76929000	0.04813600	-0.29064200
C	-1.33707700	-1.41214600	-0.22918700
C	-2.40557600	-1.71006000	0.66838100
C	-1.54658500	-0.36353900	-1.17341500
C	-2.73829400	0.34959600	-1.19459600
C	-3.59316800	-0.99096900	0.63718000
H	-2.26772300	-2.51137900	1.39894300
H	-0.75934900	-0.10362600	-1.88151800
H	-2.86957700	1.15598400	-1.92052400
H	-4.39263800	-1.23335600	1.34204400
H	-4.70181200	0.61697400	-0.30996400
C	-0.12028700	-2.13607800	-0.12634300
H	-0.05251400	-2.90607900	0.64613200
C	1.11335200	-1.83139600	-0.87351200
H	0.96850800	-1.35256500	-1.85145700
H	1.77330100	-2.70518900	-0.99133000

Int3

Charge: 1

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.194247

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1090.1109757 a.u.

S	2.22988800	-0.45226100	0.13341900
O	2.39004000	-1.08149800	1.45089000
O	3.39933400	-0.03939800	-0.65123300

C	-0.81197600	2.91147100	0.38077800
C	1.07192800	0.89614400	0.25561400
C	1.03229100	1.84513400	-0.77059800
C	0.19760900	0.93374100	1.34621400
C	-0.75154100	1.95517200	1.40021700
C	0.07919100	2.86154000	-0.69712700
H	1.72964100	1.78651200	-1.60775600
H	0.25833300	0.17824000	2.13006700
H	-1.44732200	2.00069200	2.24050300
H	0.03016000	3.61441900	-1.48656100
H	-1.56152100	3.70478800	0.42669300
C	-3.52944600	-0.15035300	-0.20103300
C	-1.12052400	-1.54722700	-0.36329800
C	-2.11225400	-1.91949900	0.60432800
C	-1.40019800	-0.48167400	-1.28284900
C	-2.58991000	0.20840500	-1.18747100
C	-3.29754700	-1.21613800	0.68629900
H	-1.89346700	-2.73996200	1.29085100
H	-0.67665200	-0.21780500	-2.05368000
H	-2.80742700	1.02971400	-1.87137800
H	-4.04725700	-1.47664100	1.43487000
H	-4.46577300	0.40860700	-0.13002200
C	0.12749600	-2.15659900	-0.27729000
H	0.24431400	-2.95757200	0.45980700
C	1.33286800	-1.71299900	-0.96170400
H	1.18091100	-1.18945400	-1.91272200
H	2.09495300	-2.50090400	-1.04511500

Int4

Charge: 1

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.229113

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1222.9406884 a.u.

S	0.94608200	-2.17195800	0.33526100
O	0.91552300	-2.35077500	1.79436300
O	1.27351400	-3.29650600	-0.55059900
C	3.45671900	1.46642700	-0.71824200
C	1.97601100	-0.77273700	-0.06577000
C	2.42129900	-0.61972800	-1.38219700
C	2.26210000	0.16095800	0.93434600
C	3.00949300	1.28979500	0.59551600
C	3.16968200	0.51372700	-1.70252100
H	2.18290900	-1.36924900	-2.13853200

H	1.90051800	0.00789800	1.95151400
H	3.23859600	2.03471700	1.36025900
H	3.52729900	0.65428400	-2.72469000
H	4.03557900	2.35559000	-0.97829200
C	-0.13971100	3.48682300	0.09650700
C	-0.92898300	0.82984600	0.40937800
C	-1.09122500	1.76182200	1.48006800
C	-0.39617600	1.27844700	-0.83837700
C	-0.00120100	2.59404500	-0.98197400
C	-0.68867800	3.07565200	1.32236600
H	-1.50859400	1.41020200	2.42583900
H	-0.30041800	0.58595300	-1.67423700
H	0.41798800	2.94261400	-1.92682300
H	-0.79093900	3.78869900	2.14203600
H	0.18095700	4.52441100	-0.02490500
C	-1.20116400	-0.51803400	0.66870200
H	-1.58200500	-0.76957500	1.66120900
C	-0.77723000	-1.63540400	-0.17452200
H	-0.71017900	-1.41834800	-1.24692900
H	-1.35872800	-2.54770200	0.01279100
N	-3.64980800	-0.78866600	0.01668500
C	-4.67696200	-0.50714400	-0.43808100
C	-5.96723200	-0.16042300	-1.00715300
H	-6.76233000	-0.72931800	-0.50178700
H	-6.15453200	0.91619700	-0.87571100
H	-5.97751200	-0.40056400	-2.08111000

TS2

Charge: 1

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.232926

Imaginary frequencies: -110.2864

Calculation of single point energy based on the optimized structure, E = -1222.938925 a.u.

S	0.88745700	-2.15942200	0.34080700
O	0.83734100	-2.31044200	1.80376900
O	1.24564200	-3.29799900	-0.51605900
C	3.41400900	1.46497500	-0.72787200
C	1.91854000	-0.76243000	-0.06714600
C	2.37364500	-0.62198700	-1.38143100
C	2.20402400	0.17706400	0.92722400
C	2.95842300	1.30001200	0.58454600
C	3.12833100	0.50605100	-1.70643900
H	2.13812400	-1.37718400	-2.13303900
H	1.83494400	0.03302800	1.94289200

H	3.18603600	2.04998300	1.34479900
H	3.49276500	0.63723700	-2.72748600
H	3.99817200	2.34971400	-0.99121300
C	-0.10249500	3.44094200	0.12500200
C	-0.97639900	0.80593600	0.40293300
C	-1.06661900	1.70981000	1.49612300
C	-0.47061600	1.26162900	-0.84539400
C	-0.03534500	2.56941000	-0.97472300
C	-0.62054100	3.01519000	1.35688400
H	-1.46451800	1.35155700	2.44781000
H	-0.42323800	0.58591200	-1.69943600
H	0.36376500	2.92243400	-1.92682500
H	-0.66832100	3.70712200	2.19962100
H	0.25108100	4.46916500	0.01696200
C	-1.30509700	-0.55200800	0.63623200
H	-1.62054800	-0.81391600	1.64772400
C	-0.82426200	-1.66578800	-0.19971300
H	-0.75502900	-1.44563300	-1.27116400
H	-1.38964200	-2.59114700	-0.02699400
N	-3.43500800	-0.70609400	0.02762000
C	-4.45521200	-0.44014600	-0.44858100
C	-5.73623800	-0.11335600	-1.04264500
H	-6.53186400	-0.69032900	-0.54737100
H	-5.93547500	0.96217000	-0.91938200
H	-5.71927500	-0.36100500	-2.11483500

Int5

Charge: 1

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.238864

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1222.9648133 a.u.

S	0.45659800	-2.05863000	0.48679800
O	0.32716000	-1.90641500	1.94889000
O	0.74873600	-3.37953900	-0.09551100
C	3.59059600	0.87658900	-1.02579300
C	1.68628100	-0.90375900	-0.10499500
C	2.07689500	-0.96646600	-1.44611200
C	2.24071800	0.01180300	0.78923400
C	3.20154900	0.90845500	0.31682800
C	3.03238100	-0.05937500	-1.90504400
H	1.64181800	-1.70809400	-2.11854500
H	1.91441100	0.02426900	1.82884800
H	3.64101000	1.63832200	0.99993800

H	3.34601500	-0.08572300	-2.95088400
H	4.33685800	1.58564600	-1.39166000
C	0.51632800	3.30823700	0.31117100
C	-0.97804400	0.94830300	0.40067100
C	-0.65469200	1.61705400	1.58562700
C	-0.55908600	1.46444600	-0.83312500
C	0.18805200	2.64195900	-0.87521000
C	0.09312600	2.79665500	1.54037300
H	-0.97706800	1.20417900	2.54421200
H	-0.80637300	0.94431600	-1.76138100
H	0.52259700	3.03746500	-1.83676200
H	0.35046000	3.31198600	2.46857300
H	1.10826200	4.22588200	0.27560400
C	-1.75644300	-0.35374600	0.47413700
H	-1.91405200	-0.62956200	1.52641600
C	-1.12358800	-1.54654300	-0.25301800
H	-0.95009900	-1.35628700	-1.32079800
H	-1.74905300	-2.44506400	-0.14398800
N	-3.07361800	-0.16298900	-0.07863600
C	-4.10710800	0.00676500	-0.55048700
C	-5.39808400	0.21761600	-1.14290700
H	-6.13392900	-0.42926100	-0.63949100
H	-5.67898100	1.27574000	-1.01976600
H	-5.34256500	-0.03515000	-2.21376300

CH_3CN

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.021968

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -132.8252303 a.u.

N	0.00000000	0.00000000	1.43660300
C	0.00000000	0.00000000	0.27747000
C	0.00000000	0.00000000	-1.17693200
H	0.00000000	1.03440900	-1.55314800
H	0.89582500	-0.51720500	-1.55314800
H	-0.89582500	-0.51720500	-1.55314800

Int6

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.323609

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1618.5623462 a.u.

S	0.41642500	-1.73795000	-1.90020900
O	0.92990300	-0.98166100	-3.05573400
O	-0.11488600	-3.10247200	-2.08842600
N	-0.85176000	-1.33701600	1.14791900
N	1.43949400	1.74686400	2.06016800
N	0.27697400	1.76846600	1.40727200
N	2.41025700	2.39192900	1.42596600
C	1.68644800	-1.79743600	-0.64178200
C	0.49180000	2.48132500	0.26420700
C	-2.96190800	0.62792200	0.89808500
C	-0.91999600	-0.72624300	-1.20449500
C	3.37370200	-0.68211300	0.65320600
C	0.20240400	3.54845000	-1.86071300
C	2.39838900	-0.63201600	-0.34379000
C	1.57230000	3.93466100	-1.85478000
C	3.63408500	-1.88485500	1.31923700
C	-4.17630200	-1.15087500	-0.22536600
C	1.93022600	-3.00654500	0.01355800
C	2.41238200	3.61203800	-0.79777900
C	-1.67415200	-1.35473700	-0.02936300
C	2.91819400	-3.04395800	1.00034100
C	-0.19441500	-1.18992900	2.07951900
C	-4.16080200	1.32112200	1.08305300
C	-2.97334400	-0.61146900	0.24331600
C	-5.37143100	-0.44947600	-0.04154000
C	1.86131000	2.87540200	0.27403900
C	-5.36529300	0.78613000	0.61293600
C	-0.35542700	2.82825500	-0.81316200
C	0.63339800	-1.00227500	3.23015400
H	-2.01846600	1.04882400	1.25883800
H	-0.50375300	0.25846500	-0.95656800
H	-1.61238200	-0.62219900	-2.05221700
H	-0.42119100	3.83013300	-2.71352100
H	2.19006100	0.30074700	-0.87022800
H	1.96462200	4.50022100	-2.70428300
H	-4.17642600	-2.11800100	-0.73419200
H	1.35092700	-3.89332800	-0.24669600
H	3.46369700	3.91140000	-0.79416400
H	-1.88474500	-2.41051800	-0.25414600
H	3.12546900	-3.97990000	1.52395600
H	-4.15240000	2.28611900	1.59559400
H	-6.30988600	-0.87328800	-0.40686700
H	-6.30064700	1.33190900	0.75923400
H	-1.40888300	2.53989400	-0.82287300

H	1.36464800	-1.82283600	3.28551300
H	-0.00141400	-0.98926300	4.13014400
H	1.14609400	-0.02260500	3.09655600
H	3.91020800	0.22945000	0.91963700
H	4.39736300	-1.91693200	2.10033600

TS3

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.322641

Imaginary frequencies: -110.7792

Calculation of single point energy based on the optimized structure, E = -1618.5589579 a.u.

S	0.05112400	-2.29456000	-1.48433300
O	0.36235600	-2.11551800	-2.91401600
O	-0.51776600	-3.57168100	-1.00772500
N	-0.93964300	-0.87795000	1.36050900
N	2.19728700	1.50003400	1.71473000
N	0.95168700	1.41298600	1.25195000
N	2.97294000	2.26236800	0.96496600
C	1.53115600	-1.94982700	-0.54172400
C	0.89299700	2.16780300	0.11555900
C	-3.06087800	0.98509700	0.96267500
C	-1.13871000	-0.98522200	-1.07256700
C	3.57369700	-0.71531100	-0.27785000
C	0.16079600	3.28147200	-1.87459000
C	2.41499400	-0.97234900	-1.01007400
C	1.46768200	3.80793500	-2.06666500
C	3.83408800	-1.42897200	0.89713600
C	-4.26340700	-0.76678900	-0.20125600
C	1.77855200	-2.67892300	0.62311100
C	2.49398900	3.53790000	-1.17188100
C	-1.83338100	-1.15602000	0.28269100
C	2.94205600	-2.40705900	1.34708600
C	-0.16948300	-0.49280600	2.13666900
C	-4.21960800	1.76832100	0.97191000
C	-3.08000500	-0.28409000	0.37390300
C	-5.41734500	0.01924900	-0.19363400
C	2.19773700	2.71007400	-0.06772800
C	-5.39782600	1.28949000	0.39288500
C	-0.14748400	2.46810600	-0.79184100
C	0.59625700	-0.41733700	3.35948200
H	-2.14744600	1.37082600	1.41795700
H	-0.63203900	-0.01835400	-1.18064400
H	-1.88825500	-1.08913600	-1.87006900

H	-0.62070500	3.53035300	-2.59745000
H	2.19951500	-0.42594700	-1.92954400
H	1.65952600	4.44331500	-2.93535100
H	-4.27856800	-1.76065000	-0.65601500
H	1.07055900	-3.44042800	0.95265900
H	3.49689200	3.94921700	-1.31205600
H	-2.12891000	-2.21156700	0.38034700
H	3.15121000	-2.96243600	2.26400200
H	-4.19684000	2.75783400	1.43449700
H	-6.33665900	-0.36463600	-0.64227900
H	-6.30184300	1.90316300	0.40140300
H	-1.15905700	2.08701800	-0.64840300
H	0.58418700	-1.41040800	3.83407100
H	0.11683600	0.32419200	4.01820900
H	1.61736500	-0.07682100	3.13415200
H	4.26919700	0.05353200	-0.61722400
H	4.73919000	-1.21503600	1.47012500

Product 6

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.329115

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1618.6043951 a.u.

S	2.97279000	-1.58261800	-0.40726400
O	3.56433000	-1.98821600	-1.69805900
O	3.34563300	-2.31285500	0.82119700
N	0.65633500	-0.24461000	1.28753100
N	-0.55316800	0.87203200	-1.33054300
N	-0.90644300	0.99851000	-0.02341900
N	-1.58750500	1.05767900	-2.07524300
C	3.33979600	0.15668000	-0.17018300
C	-2.24091000	1.29514100	0.07452900
C	-1.93172100	-1.85218200	1.60707900
C	1.18086600	-1.70574100	-0.63137200
C	3.48507400	2.38346800	-1.06162800
C	-4.44804000	1.73598900	0.81771100
C	3.19330100	1.03078500	-1.25042900
C	-4.89643800	1.76135300	-0.52925500
C	3.93366900	2.83712000	0.18422900
C	-1.72334700	-2.03025900	-0.79036500
C	3.78835700	0.59044700	1.07729100
C	-4.02477200	1.55467900	-1.58839400
C	0.36384100	-1.53222600	0.64708400

C	4.09016300	1.94310000	1.24899100
C	0.08627000	0.85077400	1.02081400
C	-3.30648000	-2.06793500	1.51033500
C	-1.12499800	-1.81714400	0.45746300
C	-3.10249100	-2.24582000	-0.88902400
C	-2.67413800	1.31825100	-1.27069000
C	-3.89942700	-2.26030900	0.25730900
C	-3.12026800	1.50064500	1.14948100
C	0.41451800	2.12939700	1.72321300
H	-1.47517800	-1.69354700	2.58759400
H	0.91521700	-0.97874300	-1.40949000
H	1.06703800	-2.72460300	-1.02967700
H	-5.17407100	1.89977900	1.61745400
H	2.85720300	0.66323100	-2.22149600
H	-5.95440400	1.94562000	-0.72879800
H	-1.12810900	-2.00816400	-1.70318300
H	3.88346700	-0.12365700	1.89577000
H	-4.36114200	1.56547800	-2.62658300
H	0.74654700	-2.28454200	1.35397400
H	4.44192500	2.30090100	2.21929100
H	-3.91895900	-2.08203500	2.41530200
H	-3.55400400	-2.39495300	-1.87296100
H	-4.97725500	-2.42079500	0.17671300
H	-2.78159700	1.46678200	2.18497000
H	1.13177000	1.94436700	2.53114000
H	-0.49784000	2.59091700	2.13377700
H	0.84300100	2.84206900	0.99982400
H	3.36781400	3.08376800	-1.89166700
H	4.16276000	3.89602400	0.32574800

Int7

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.331065

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1643.5434352 a.u.

S	0.53058400	1.79820800	-1.82618700
O	-0.22286500	1.37352200	-3.02057900
O	1.53161600	2.87967200	-1.93485900
N	1.74231000	0.83088600	1.11293500
C	-0.64261400	2.24439600	-0.55133700
C	2.83147800	-1.85144500	0.51198700
C	1.38124300	0.31258900	-1.22792000
C	-2.70827600	1.80892800	0.59357800

C	-1.80509700	1.48124400	-0.41778400
C	-2.45090900	2.89549800	1.43677200
C	4.69061800	-0.51876600	-0.30678900
C	-0.36970600	3.33486300	0.27733100
C	2.41828800	0.56557500	-0.12906900
C	-1.28967400	3.65983900	1.27732000
C	1.06123900	0.83819400	2.04170300
C	3.68118600	-2.95333400	0.62996800
C	3.34111300	-0.63108900	0.04415200
C	5.53486700	-1.62760000	-0.19140100
C	5.03186200	-2.84432800	0.27821600
C	0.22827100	0.87682600	3.19917300
H	1.77305800	-1.92809400	0.77846500
H	0.61619900	-0.40677500	-0.89289500
H	1.89450900	-0.05070700	-2.12963800
H	-1.99635700	0.64265800	-1.08695600
H	5.07964800	0.43579100	-0.66965100
H	0.54649300	3.91030200	0.13851800
H	3.00705600	1.46031800	-0.37427900
H	-1.09630500	4.50971900	1.93561000
H	3.28641900	-3.90415200	0.99648400
H	6.58879200	-1.53749600	-0.46540500
H	5.69297900	-3.70953400	0.37118800
H	-0.15892200	1.89870500	3.33111200
H	0.81795200	0.57298700	4.07864100
H	-0.61418600	0.15302800	3.01674700
C	-2.22297700	-2.23554500	-1.04368700
C	-3.18688200	-2.70075600	-1.94266800
C	-4.53006000	-2.77178300	-1.55488800
C	-4.90276200	-2.37784600	-0.26431800
C	-3.93530100	-1.91438800	0.63132400
C	-2.58778600	-1.83503000	0.25007900
H	-1.17272800	-2.17148400	-1.33399300
H	-2.89208200	-3.00845600	-2.94959900
H	-5.28525400	-3.13371700	-2.25763400
H	-5.95098700	-2.43221300	0.04201500
H	-4.20325100	-1.60055500	1.64183400
C	-1.54376800	-1.30040200	1.22501000
O	-0.36196100	-1.19183500	0.79714000
O	-1.94568600	-0.98402800	2.37170800
H	-3.16132100	3.14809500	2.22742000
H	-3.61217700	1.21156000	0.72267700

TS4

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.330410

Imaginary frequencies: -145.4978

Calculation of single point energy based on the optimized structure, E = -1643.5415836 a.u.

S	-0.39888700	1.81112500	1.86580000
O	0.28475700	1.33782800	3.08386200
O	-1.34315500	2.94470500	1.94651300
N	-1.61142500	0.98525600	-1.11605200
C	0.84623300	2.20152400	0.64243000
C	-2.82396100	-1.67135000	-0.63076800
C	-1.31038900	0.37960100	1.22439700
C	2.95751500	1.69857700	-0.38539300
C	1.99418100	1.40749200	0.58029800
C	2.76956000	2.77455100	-1.25978800
C	-4.61574800	-0.30849400	0.27741800
C	0.64302400	3.28296000	-0.21724800
C	-2.30971300	0.70215500	0.10953100
C	1.61912600	3.56605400	-1.17581600
C	-0.83097500	0.84608600	-1.96683000
C	-3.71550200	-2.73637200	-0.77709700
C	-3.27720400	-0.45291900	-0.10372600
C	-5.50301000	-1.37971900	0.13313200
C	-5.05461600	-2.59376100	-0.39504800
C	-0.10098000	1.03863800	-3.19446100
H	-1.77577700	-1.77675800	-0.92354800
H	-0.57606400	-0.37116100	0.90047300
H	-1.85782800	0.02916700	2.11104800
H	2.12744600	0.57376800	1.27023100
H	-4.96339400	0.64307600	0.68723800
H	-0.26370000	3.88362400	-0.13532700
H	-2.87266300	1.60501200	0.38240200
H	1.47927700	4.40651000	-1.85927800
H	-3.36217800	-3.68454000	-1.18988500
H	-6.54782400	-1.26220500	0.43076700
H	-5.74899900	-3.42969900	-0.51057900
H	-0.07233400	2.11630000	-3.41853500
H	-0.63989600	0.50435000	-3.99436500
H	0.90574500	0.59209500	-3.08882700
C	1.67039400	-2.45505800	0.82022200
C	2.39641300	-3.14822700	1.79287500
C	3.77332300	-3.34248700	1.63400200
C	4.41929200	-2.84446000	0.49629900
C	3.68975800	-2.15417900	-0.47475200

C	2.31089800	-1.94829100	-0.32013800
H	0.59695700	-2.29825900	0.93730500
H	1.88816600	-3.53812300	2.67880600
H	4.34228800	-3.88193500	2.39580400
H	5.49460500	-2.99517900	0.36839000
H	4.17267000	-1.75698500	-1.36937600
C	1.54442200	-1.16406400	-1.37596900
O	0.31686700	-0.93630500	-1.12397600
O	2.16708200	-0.78361900	-2.38653500
H	3.52589800	2.99610100	-2.01638700
H	3.85311100	1.07963700	-0.45712400

Int8

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.336427

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1643.5721301 a.u.

S	0.14510000	-2.14327200	-1.60997500
O	0.47822700	-1.83608700	-3.01608700
O	-0.37070100	-3.48376500	-1.26254200
N	-1.18647000	-1.37686500	1.42285300
C	1.61966300	-1.84062300	-0.63777300
C	-3.07340900	0.86529000	0.96551700
C	-1.08949500	-0.91350000	-1.11114600
C	3.67209800	-0.63086100	-0.32274000
C	2.50572100	-0.84387200	-1.05814400
C	3.94220700	-1.41309100	0.80522000
C	-4.26008200	-0.67704700	-0.46269200
C	1.87423100	-2.63277600	0.48275500
C	-1.88846200	-1.26888100	0.15471200
C	3.04899000	-2.41143000	1.20613400
C	-0.28929200	-0.60783400	1.86828600
C	-4.18957500	1.70850800	0.97576700
C	-3.09646000	-0.33606800	0.24366000
C	-5.37434600	0.16525900	-0.45593700
C	-5.34240000	1.36380800	0.26455000
C	0.30536700	-0.79986100	3.22776400
H	-2.18561500	1.15545700	1.52675200
H	-0.58618200	0.05797500	-1.08798100
H	-1.76961800	-0.93311200	-1.97592400
H	2.28535600	-0.25131500	-1.94714700
H	-4.29012400	-1.61515600	-1.02376300
H	1.16216600	-3.40396000	0.77798800

H	-2.28826600	-2.27393000	-0.04281100
H	3.26495700	-3.02062700	2.08659100
H	-4.15480600	2.64062200	1.54539900
H	-6.27252100	-0.11882900	-1.01019400
H	-6.21365000	2.02345100	0.27490000
H	-0.25037900	-1.60244600	3.72735500
H	0.23809400	0.12630900	3.81774400
H	1.36756700	-1.06682400	3.15762600
C	0.23171700	2.66846700	-0.55099400
C	0.36294100	3.69049800	-1.49246000
C	1.58822100	4.34673200	-1.65036600
C	2.68510100	3.98840900	-0.85732100
C	2.55703000	2.97440700	0.09043100
C	1.33191000	2.30400800	0.24299000
H	-0.72622700	2.16492600	-0.42289900
H	-0.49520400	3.97549900	-2.10529500
H	1.68903300	5.14221400	-2.39285500
H	3.64149800	4.50168300	-0.98049600
H	3.40195600	2.68253300	0.71609000
C	1.26216400	1.22016900	1.25672300
O	0.11675000	0.48436500	1.10332600
O	2.10534700	1.00012000	2.08789200
H	4.85541100	-1.23961400	1.37905200
H	4.37023800	0.15021500	-0.63081800

Product 5

Charge: 0

Spin Multiplicity: 1

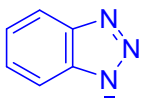
Thermal correction to Gibbs Free Energy (a.u.): 0.334745

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1643.594268 a.u.

S	-2.25142600	-0.44719300	0.87773400
O	0.85635500	-0.39517300	2.86101800
O	0.87505300	-0.24302100	-1.68631900
O	-1.58800000	-1.75808200	0.71179600
O	-2.53866100	0.04394800	2.23931700
N	0.92994700	-0.17945400	0.59661500
C	-1.28931800	0.81924100	0.01236800
C	0.07726200	1.03036700	0.66429100
C	0.83664800	2.24044300	0.14461500
C	1.97129900	2.65128200	0.86357000
C	2.73770600	3.73282100	0.42810500
C	2.37666600	4.42337100	-0.73510600
C	1.24750500	4.02271000	-1.45296900

C	0.48229300	2.93428100	-1.01779200
C	1.44777500	-0.54756900	-0.65363000
C	2.78675000	-1.20553300	-0.68168500
C	3.06041100	-2.13701700	-1.69559700
C	4.32355400	-2.71980600	-1.78574300
C	5.32959000	-2.35369500	-0.88254200
C	5.06891400	-1.40445500	0.11066100
C	3.79850000	-0.83428600	0.21714500
C	1.08191500	-0.92055900	1.78828300
C	1.43676700	-2.38477700	1.69759200
C	-6.13942800	-0.52198500	-1.50148600
C	-3.78411000	-0.48502000	-0.04893300
C	-4.84615900	0.32275500	0.36455400
C	-3.87505700	-1.31575000	-1.16909200
C	-5.06592500	-1.32769000	-1.89828400
C	-6.03189100	0.29897300	-0.37340300
H	-1.21303900	0.49587000	-1.03123600
H	-1.89563000	1.73225400	0.08419500
H	-0.08274100	1.18032800	1.73900600
H	2.25102500	2.11386400	1.77341200
H	3.61698300	4.04101300	0.99939200
H	2.97436700	5.27143100	-1.07849600
H	0.95930900	4.55500400	-2.36296500
H	-0.38945500	2.63156900	-1.59919700
H	2.27066700	-2.40564700	-2.39986200
H	4.52857700	-3.45900600	-2.56367700
H	6.32146100	-2.80613300	-0.95811900
H	5.85798700	-1.10518800	0.80437800
H	3.59906900	-0.08601300	0.98642300
H	1.28176800	-2.82008500	0.70548300
H	0.79662800	-2.90100000	2.42677500
H	2.48266700	-2.53825100	2.00028300
H	-4.74344600	0.95011300	1.25145300
H	-3.02967300	-1.94298900	-1.45690300
H	-5.15722200	-1.97090300	-2.77642800
H	-6.87500200	0.92115400	-0.06466800
H	-7.06908100	-0.53612100	-2.07534100



Charge: -1

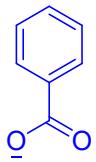
Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.063526

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -395.5810794 a.u.

N	2.36589600	0.00001600	0.00001900
N	1.63096200	-1.11242700	-0.00027500
N	1.63114500	1.11237700	-0.00007600
C	0.32778900	-0.71330200	-0.00006600
C	-2.07121400	-0.71167900	0.00008700
C	-2.07124600	0.71168200	0.00017400
C	-0.88624100	1.43663600	0.00013800
C	0.32766200	0.71330400	0.00001500
C	-0.88625800	-1.43661800	-0.00003200
H	-3.02889200	-1.23998900	0.00009700
H	-3.02886900	1.24006500	0.00025600
H	-0.89065700	2.53035500	0.00019700
H	-0.89056400	-2.53033500	-0.00012400



Charge: -1

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.070799

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -420.5563943 a.u.

C	0.43676800	-1.20563900	-0.01842400
C	1.83511300	-1.21034600	-0.02141100
C	2.53922000	-0.00000200	-0.00000100
C	1.83511400	1.21034500	0.02141000
C	0.43677000	1.20564400	0.01842600
C	-0.27980900	0.00000300	0.00000100
H	-0.13694000	-2.13498400	-0.03101800
H	2.38112300	-2.15823100	-0.03973200
H	3.63277700	-0.00000400	-0.00000200
H	2.38112700	2.15822700	0.03972900
H	-0.13693700	2.13498800	0.03102100
C	-1.82638900	0.00000100	0.00000000
O	-2.37386500	-1.12629100	0.04891400
O	-2.37386800	1.12628800	-0.04891600

N-acetyl-N-((1S,2R)-1-phenyl-2-tosylpropyl)benzamide (5bi(1S,2R))

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.388384

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1722.2708448 a.u.

S	2.19948500	2.16594300	-0.05539700
O	-1.71718200	0.35843900	-1.96264600
O	-1.89894000	2.20157700	2.15412600
O	2.79677200	3.10130100	-1.03201200
O	2.10687700	2.57121700	1.36495200
N	-1.71621600	0.99828400	0.23001600
C	-3.49309100	-0.49552300	-0.64629300
C	-4.38517200	-0.71165800	-1.70896900
C	-5.49639100	-1.53355000	-1.52992300
C	-5.70752500	-2.16625600	-0.29809200
C	-4.80644700	-1.97456800	0.75437200
C	-3.70373300	-1.13534000	0.58575200
C	-2.27809800	0.32993600	-0.88232000
C	-2.44103200	1.76345700	1.15481000
C	-3.88156700	2.09495700	0.84000900
C	-0.24422200	0.93237100	0.39124300
C	0.18778900	-0.51955900	0.50779700
C	0.57422700	-1.29424300	-0.59373600
C	0.93330100	-2.63430700	-0.42624000
C	0.90160200	-3.22032500	0.84257600
C	0.50664800	-2.45744600	1.94639900
C	0.15354000	-1.11716600	1.77696000
C	0.49102100	1.79570800	-0.65182600
C	-0.17868400	3.14424600	-0.89571700
C	3.11928100	0.63900600	-0.14665300
C	3.56927800	0.19195400	-1.39018900
C	4.23712100	-1.03036000	-1.46438600
C	4.46605000	-1.80250100	-0.31336000
C	4.02602300	-1.30778300	0.92732200
C	3.35248900	-0.09246500	1.01943200
C	5.13521800	-3.14618500	-0.39937100
H	-4.20234500	-0.22024700	-2.66648900
H	-6.20011400	-1.68637000	-2.35146700
H	-6.57585800	-2.81540200	-0.16091100
H	-4.96257200	-2.48111100	1.70955700
H	-2.99380000	-0.99260000	1.40241700
H	-4.55046700	1.36751900	1.32259700
H	-4.10377400	2.11150000	-0.23408100
H	-4.08605100	3.08216800	1.27620200

H	-0.07665900	1.41121100	1.36251600
H	0.60660400	-0.85343600	-1.58947500
H	1.24574200	-3.22138300	-1.29319700
H	1.18796900	-4.26710200	0.97123900
H	0.48204500	-2.90478300	2.94317200
H	-0.14528800	-0.51769000	2.64064100
H	0.64133500	1.27065200	-1.60306100
H	-0.33399100	3.68868300	0.04746100
H	-1.15392000	2.98224500	-1.37397200
H	0.43501800	3.76172100	-1.56406500
H	3.39408300	0.78711600	-2.28802400
H	4.58550400	-1.39458000	-2.43396300
H	4.20419600	-1.89263000	1.83314400
H	2.99649100	0.28455100	1.97824800
H	5.62092100	-3.29645200	-1.37429200
H	4.39158600	-3.95115800	-0.26479500
H	5.88912500	-3.27017600	0.39387600

N-acetyl-N-((1R,2R)-1-phenyl-2-tosylpropyl)benzamide (5bi(1R,2R))

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.387191

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1722.2586909 a.u.

S	2.56354100	0.99364400	-1.52549500
O	-1.39387700	-1.08275200	-1.76716200
O	-1.53332600	2.80515100	0.55228700
O	2.86866000	0.91144000	-2.96958300
O	3.31708500	1.96654900	-0.70738700
N	-1.41879100	0.73921300	-0.38994200
C	-3.36063500	-0.80947400	-0.47737100
C	-4.22946700	-1.47566600	-1.35616800
C	-5.46780300	-1.92802400	-0.90318200
C	-5.83302800	-1.74416400	0.43636700
C	-4.95792800	-1.10624100	1.32139000
C	-3.72587700	-0.63234100	0.86660800
C	-2.01463400	-0.40141600	-0.97001900
C	-2.09388200	1.93466700	-0.08313900
C	-3.48383900	2.15553600	-0.63919300
C	0.05642700	0.66853400	-0.22682300
C	0.75056200	1.35142500	-1.42531000
C	0.56164100	2.84167000	-1.68658000
C	2.77490200	-0.63057500	-0.81126300
C	2.44427700	-1.75540600	-1.57069400

C	2.55522000	-3.01817500	-0.98771900
C	2.99972900	-3.16995600	0.33659500
C	3.34181700	-2.01792300	1.06743500
C	3.23150600	-0.74844400	0.50452900
C	3.11978200	-4.53030300	0.96719700
H	-3.92830500	-1.62233900	-2.39515900
H	-6.15088200	-2.42898500	-1.59309600
H	-6.80141800	-2.10471200	0.79190200
H	-5.23521300	-0.97715300	2.37011300
H	-3.04117100	-0.13996700	1.55965400
H	-4.24060600	1.91742100	0.12197900
H	-3.70102200	1.57181600	-1.54131000
H	-3.56152500	3.22833600	-0.86388800
H	0.39671300	0.79661600	-2.30556200
H	0.81008700	3.46830000	-0.82346200
H	-0.48509600	3.03271800	-1.96026300
H	1.18142600	3.14484800	-2.54394200
H	2.10028900	-1.64524500	-2.60042800
H	2.29344000	-3.90390300	-1.57168500
H	3.69574300	-2.11895800	2.09665800
H	3.48961400	0.14412000	1.07434000
H	2.75715400	-5.32179100	0.29595700
H	2.54483400	-4.57985600	1.90642600
H	4.16964300	-4.75081500	1.22363800
C	0.48221600	0.95280600	1.20545300
C	0.06842500	0.02101200	2.17123400
C	0.44109400	0.15712500	3.50946600
C	1.24979100	1.22903400	3.90233200
C	1.67251300	2.15619500	2.94555100
C	1.28737700	2.02330900	1.60790400
H	-0.54683300	-0.82922200	1.86464900
H	0.10898300	-0.58068800	4.24422500
H	1.55199700	1.33787100	4.94700400
H	2.30786700	2.99548400	3.24003500
H	1.64485600	2.74717000	0.88078400
H	0.26484900	-0.39621600	-0.37387800

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-((1S,2R)-1-phenyl-2-(phenylsulfonyl)propyl)ethan-1-imine (6bj(1S,2R))

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.355497

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1657.9536839 a.u.

S	0.92871700	2.72458100	0.12716400
N	0.63517300	-0.52277000	0.28162600
N	-1.26644500	-1.48428200	1.08236200
C	-1.71187600	-1.34713400	-1.44589300
C	-3.26350000	-2.00129800	0.34436400
C	0.04128300	-0.97832100	1.30593300
C	3.06587700	-0.81805200	0.00824600
C	-1.98824700	-1.57917900	-0.09039700
N	-2.06083600	-1.82230000	2.13976700
C	2.86488600	-1.94347900	-0.80224900
C	1.92607100	0.12376400	0.37384600
N	-3.23285400	-2.12924200	1.71962900
C	4.35856600	-0.53552900	0.47374400
O	1.12728000	3.88170200	-0.77124100
C	-0.80468600	2.26446900	0.04238400
O	1.29012100	2.85176400	1.55640500
C	3.94024000	-2.77002400	-1.14414600
C	1.60909000	1.09399400	-2.02196200
C	-1.44186700	1.82119200	1.20360100
C	1.94278900	1.35318200	-0.56334200
C	-4.31643200	-2.20118700	-0.56376600
C	5.43336100	-1.35925000	0.13062600
C	-2.76308000	-1.54953300	-2.33457600
C	-1.49224200	2.40000800	-1.16701500
C	5.22707100	-2.48025700	-0.68112500
C	-4.04683900	-1.96676400	-1.90572200
C	-2.79210500	1.47346700	1.14237300
C	0.49292800	-1.01475300	2.73510000
C	-2.84192900	2.04323400	-1.21608000
C	-3.48805700	1.57657700	-0.06675200
H	-0.73176400	-1.01486400	-1.77428200
H	1.86121500	-2.17608800	-1.16141600
H	2.13138600	0.51176800	1.38273200
H	4.52142300	0.33670900	1.11294700
H	3.76940700	-3.64588500	-1.77536700
H	0.60135200	0.67514600	-2.14028600
H	2.32982700	0.37350800	-2.43582900
H	1.68246900	2.02295600	-2.60319200
H	-0.88006200	1.74286400	2.13462800
H	2.93444300	1.82737000	-0.47738600
H	-5.29971200	-2.52294400	-0.21616900
H	6.43450100	-1.12900800	0.50394000
H	-2.59388100	-1.37486300	-3.39977500
H	-0.98341600	2.78107800	-2.05294800

H	6.06636900	-3.12765900	-0.94733700
H	-4.83549600	-2.10525800	-2.64865900
H	-3.29745100	1.10607100	2.03797600
H	1.54780300	-0.73279400	2.81659000
H	0.35647500	-2.02267000	3.15066800
H	-0.11565200	-0.32635300	3.34104700
H	-3.39017200	2.12949100	-2.15668000
H	-4.54082300	1.28980400	-0.11397700

(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-((1R,2R)-1-phenyl-2-(phenylsulfonyl)propyl)ethan-1-imine (6bj(1R,2R))

Charge: 0

Spin Multiplicity: 1

Thermal correction to Gibbs Free Energy (a.u.): 0.354576

Imaginary frequencies: 0

Calculation of single point energy based on the optimized structure, E = -1657.9479665 a.u.

S	-0.74381800	-2.03522900	1.56339400
C	-2.57389700	1.33697700	-0.12534000
C	-3.57179800	1.38379600	-1.10609500
C	-1.65400500	0.12869000	-0.02091900
C	-2.43357000	2.41438000	0.76244000
O	-1.48464800	-3.20841100	2.07500200
C	-0.05215900	-2.50237300	-0.02680600
O	0.34648700	-1.48199300	2.39512000
C	-4.42430900	2.48930200	-1.19774600
C	-3.38818500	-1.22044200	1.28018000
C	1.29318800	-2.23525200	-0.28282800
C	-1.97248800	-0.66908800	1.25947600
C	-3.28318000	3.51882600	0.67081600
C	-0.87039600	-3.13908500	-0.96432300
C	-4.28218700	3.55889900	-0.30929000
C	1.82832300	-2.59627900	-1.52102300
C	-0.32576200	-3.48696900	-2.20275400
C	1.01868900	-3.21428200	-2.48033700
H	-3.68249700	0.54706000	-1.80052100
H	-1.65181400	2.38724800	1.52499200
H	-5.20015800	2.51415800	-1.96721400
H	-3.59932900	-1.82075700	0.38192400
H	-4.10133900	-0.38375100	1.30686000
H	-3.55199400	-1.84496900	2.16676800
H	1.89991700	-1.73917900	0.47452800
H	-1.77553500	-0.04088000	2.14183600
H	-3.16592600	4.35317600	1.36708700
H	-1.91464300	-3.35715600	-0.73416500

H	-4.94674000	4.42365800	-0.38009800
H	2.87796000	-2.38651100	-1.73838900
H	-0.95285300	-3.97604300	-2.95153700
H	1.43840300	-3.48723700	-3.45143500
H	-1.87484100	-0.52964400	-0.87506500
N	-0.26756200	0.56044400	-0.00831300
N	1.73263000	1.10718800	-0.95928500
C	2.33131100	0.94572900	1.53497400
C	3.75303600	1.68107000	-0.33544100
C	0.37485900	0.71590600	-1.09258400
C	2.51888700	1.21725700	0.17067400
N	2.45336200	1.47484200	-2.05880700
N	3.63800300	1.81482600	-1.70551600
C	4.84819400	1.91476000	0.51350700
C	3.42644700	1.17975400	2.36166400
C	4.66332500	1.66211600	1.86628800
C	-0.08053800	0.52497600	-2.50781800
H	1.39519700	0.54004900	1.90990500
H	5.79810100	2.27424400	0.11382900
H	3.33083000	0.97807500	3.43151100
H	5.48623100	1.82798000	2.56530000
H	-1.09379900	0.11307400	-2.54146900
H	0.60670500	-0.14793600	-3.03872400
H	-0.07325700	1.48911200	-3.03806600

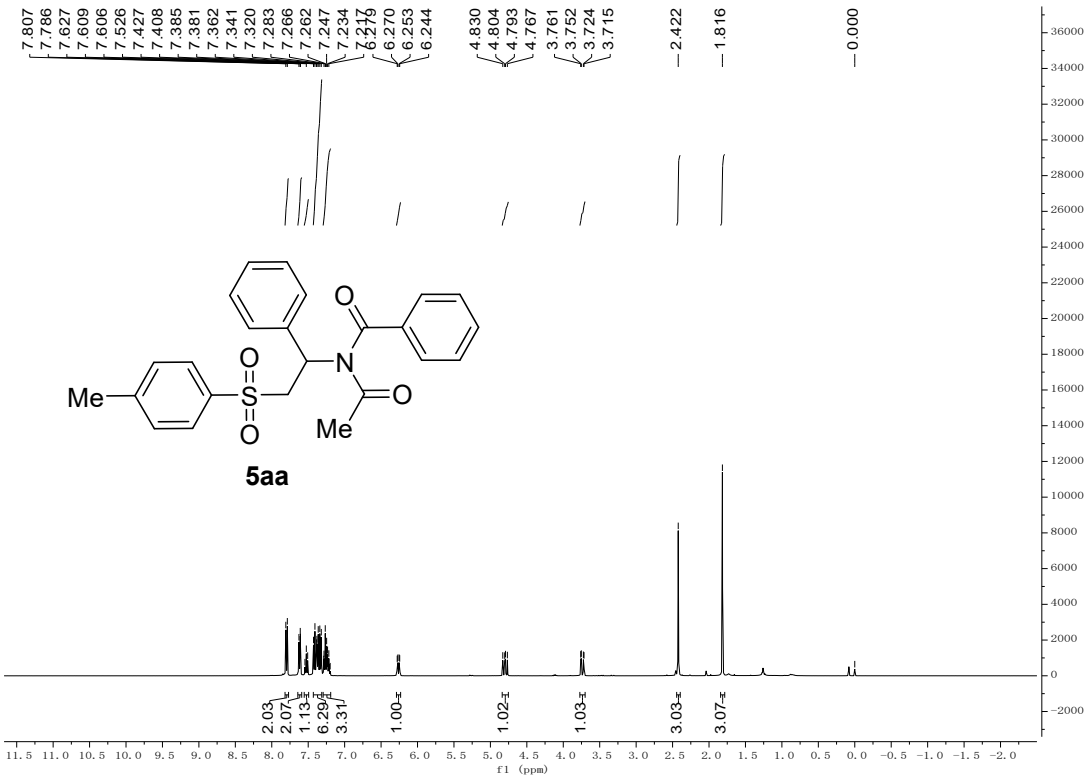
The free energy of **N-acetyl-N-((1S,2R)-1-phenyl-2-tosylpropyl)benzamide (5bi(1S,2R))** is lower 6.9 kcal/mol than **N-acetyl-N-((1R,2R)-1-phenyl-2-tosylpropyl)benzamide (5bi(1R,2R)).**

The free energy of **(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-((1S,2R)-1-phenyl-2-(phenylsulfonyl)propyl)ethan-1-imine (6bj(1S,2R))** is lower 3.0 kcal/mol than **(E)-1-(1H-benzo[d][1,2,3]triazol-1-yl)-N-((1R,2R)-1-phenyl-2-(phenylsulfonyl)propyl)ethan-1-imine (6bj(1R,2R)).**

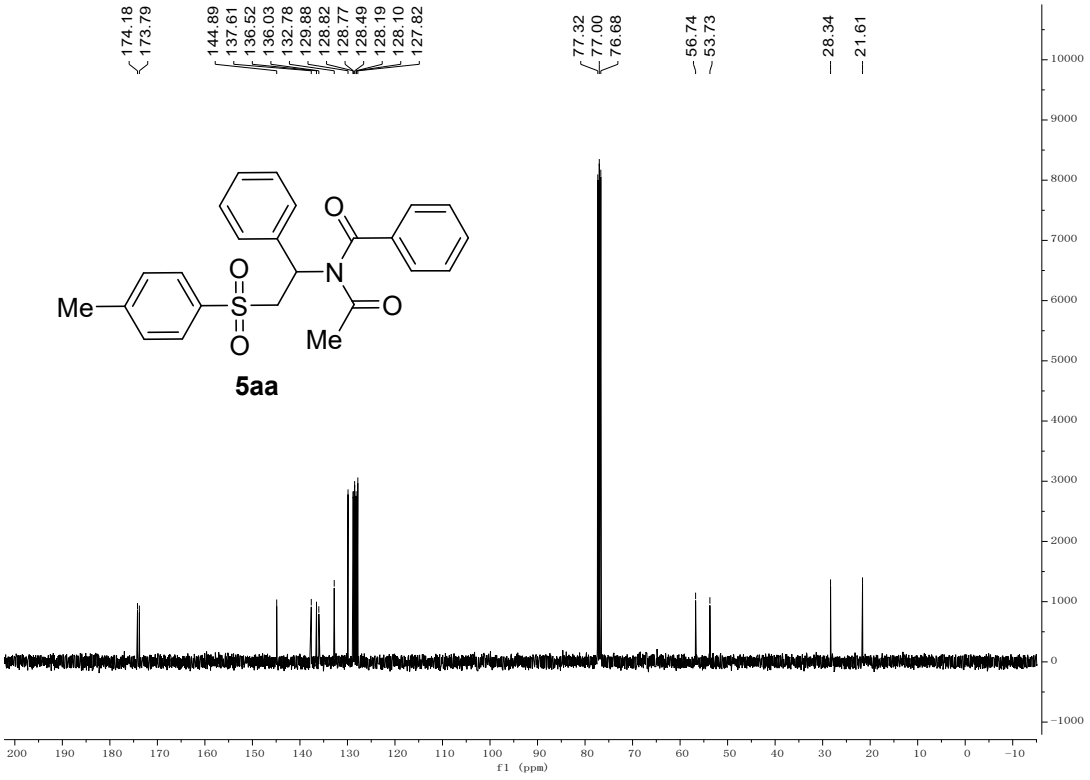
11. NMR Spectra of Compounds

Spectra A: NMR Spectra of Compounds *β*-Sulfonyl Imides

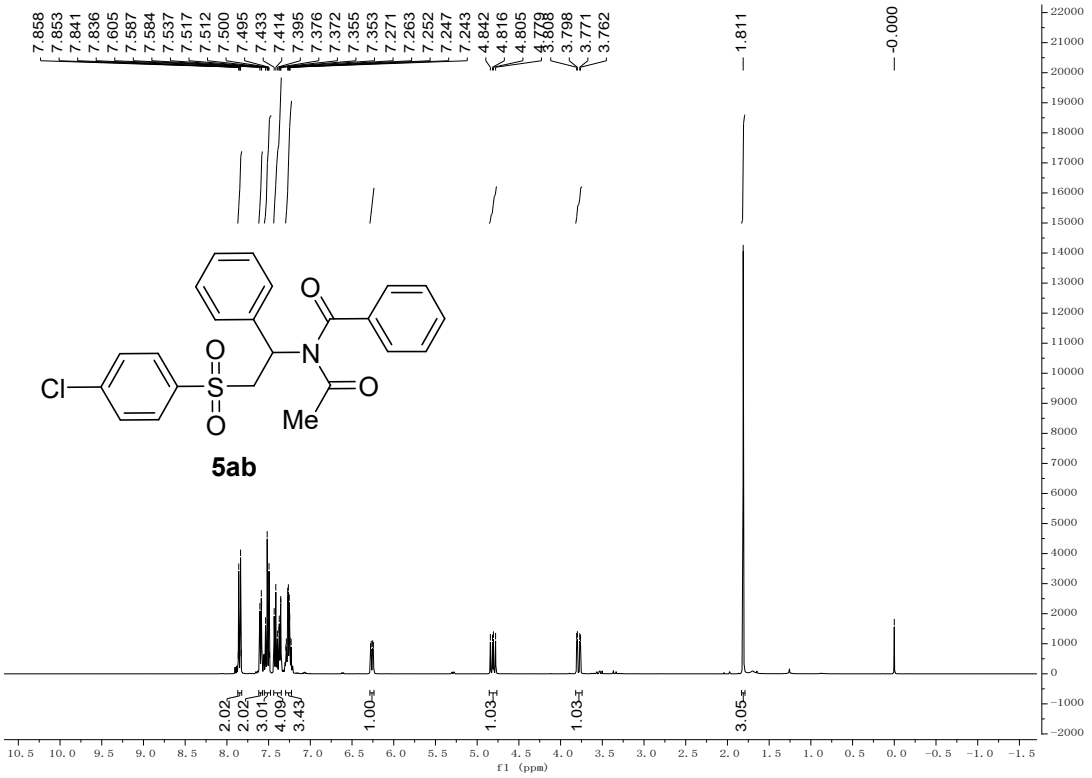
^{1}H NMR of **5aa** in $CDCl_3$



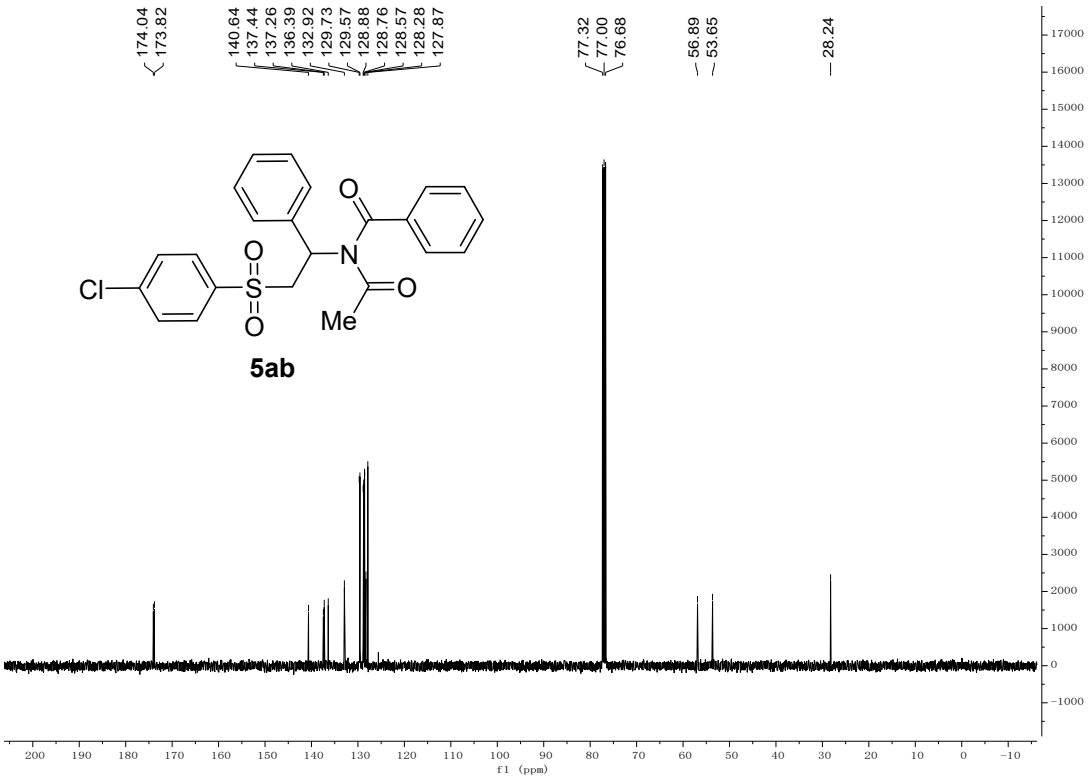
^{13}C NMR of **5aa** in $CDCl_3$



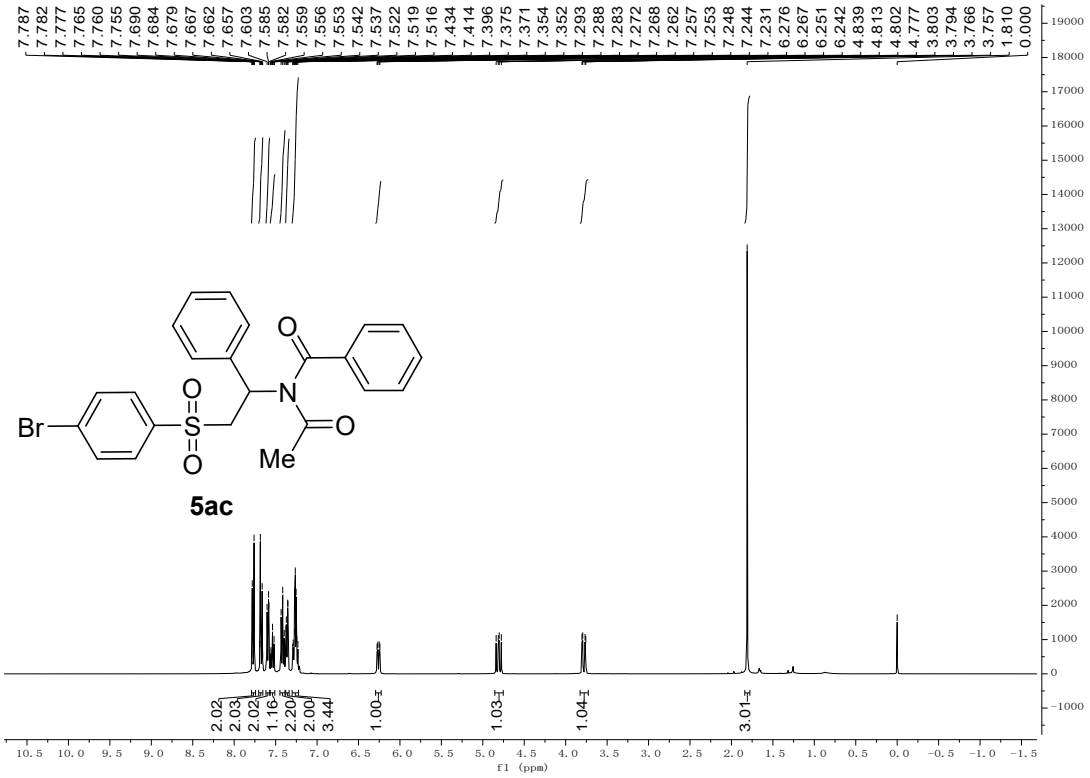
^{1}H NMR of **5ab** in $CDCl_3$



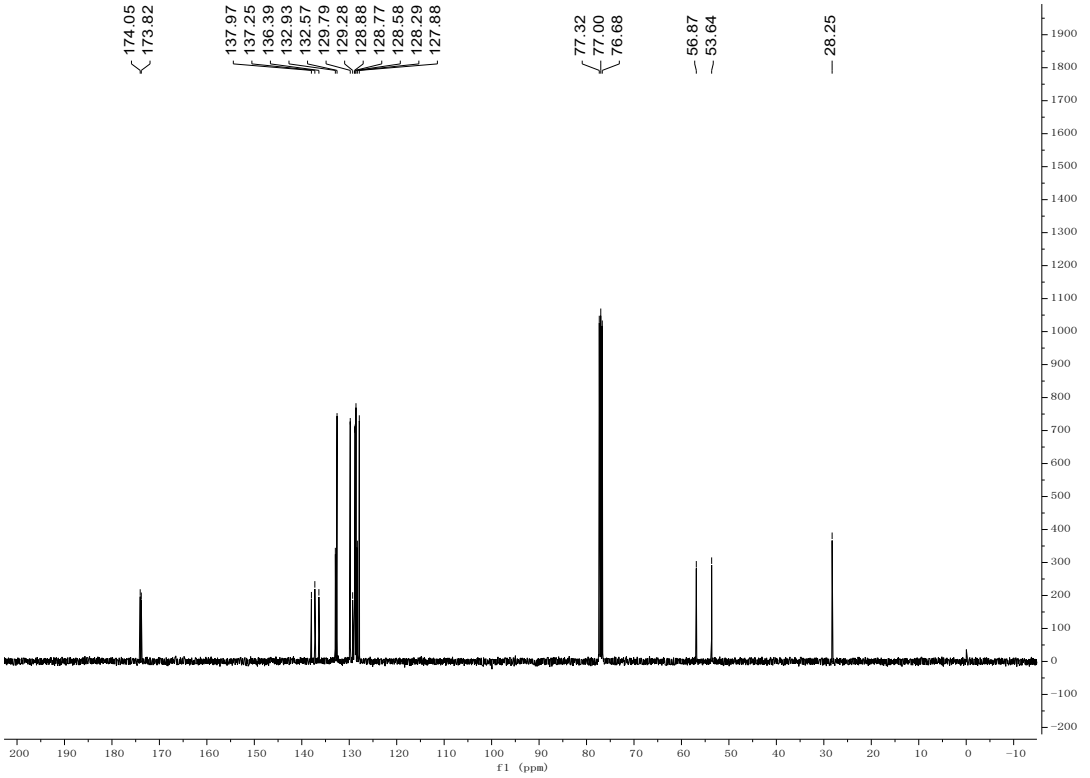
^{13}C NMR of **5ab** in $CDCl_3$



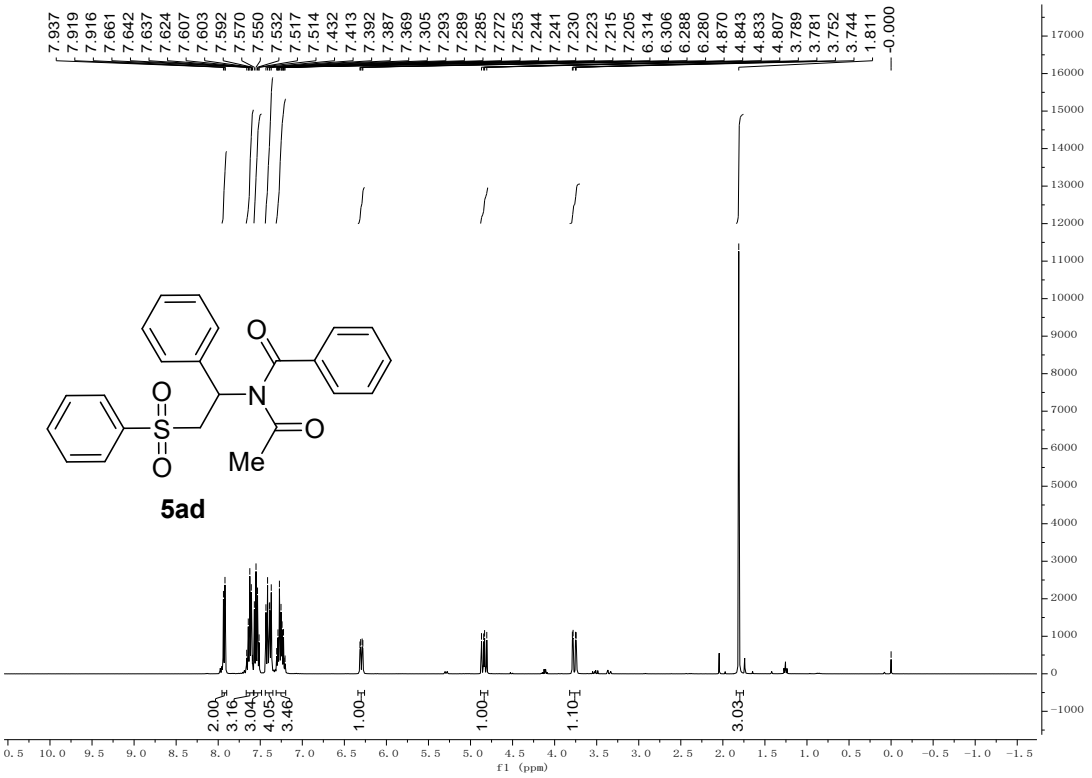
^{1}H NMR of **5ac** in $CDCl_3$



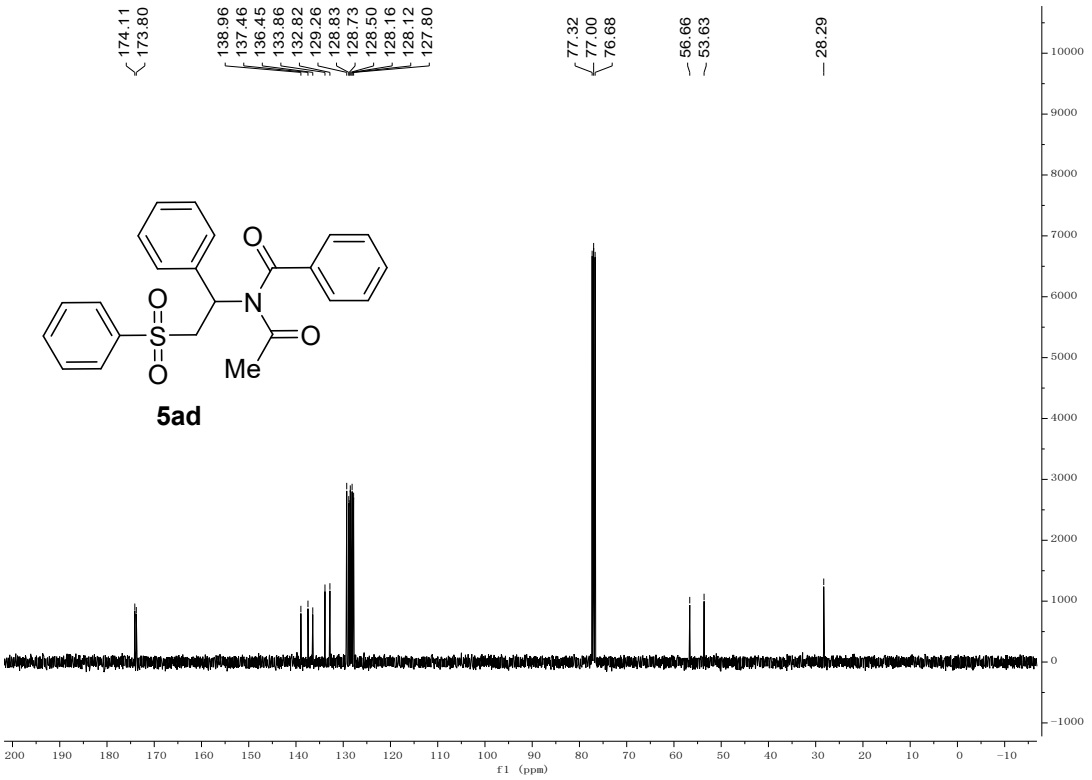
^{13}C NMR of **5ac** in $CDCl_3$



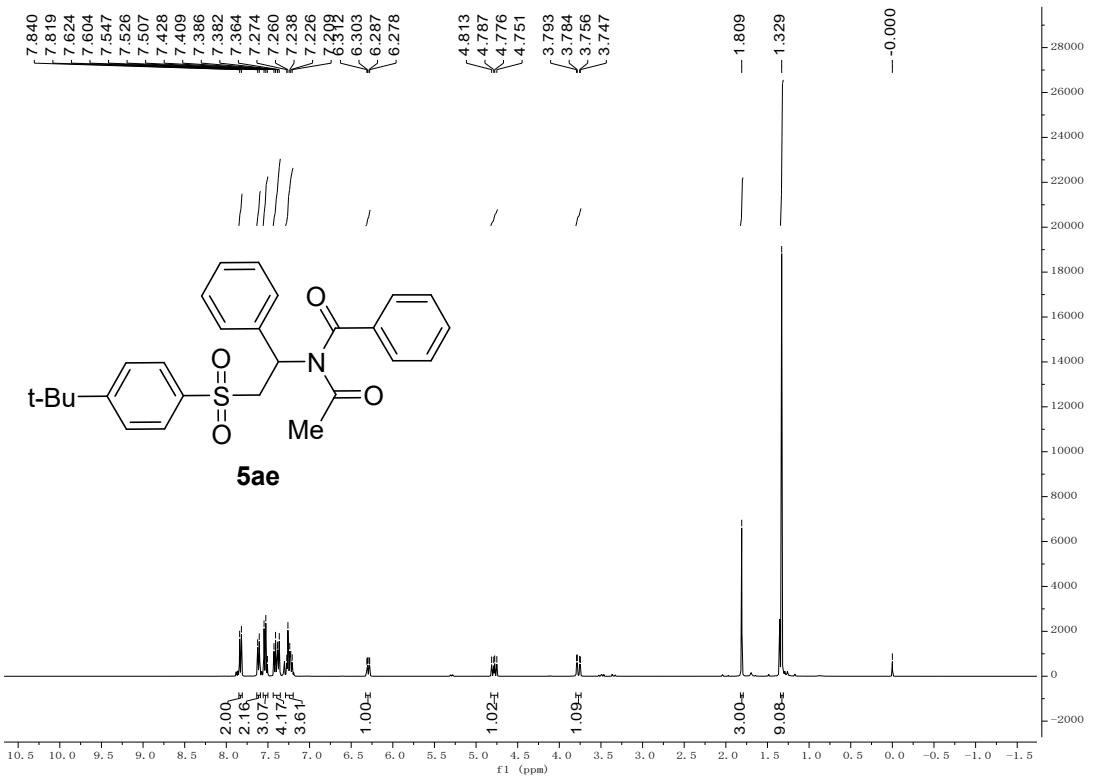
^{1}H NMR of **5ad** in $CDCl_3$



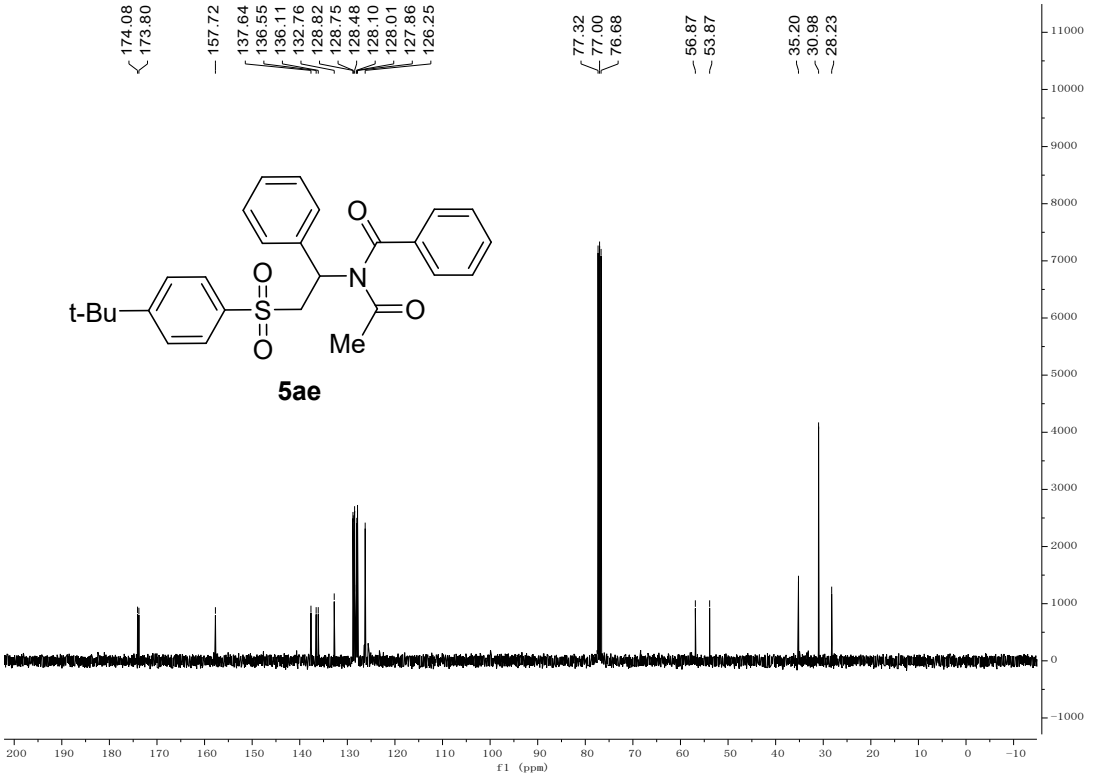
^{13}C NMR of **5ad** in $CDCl_3$



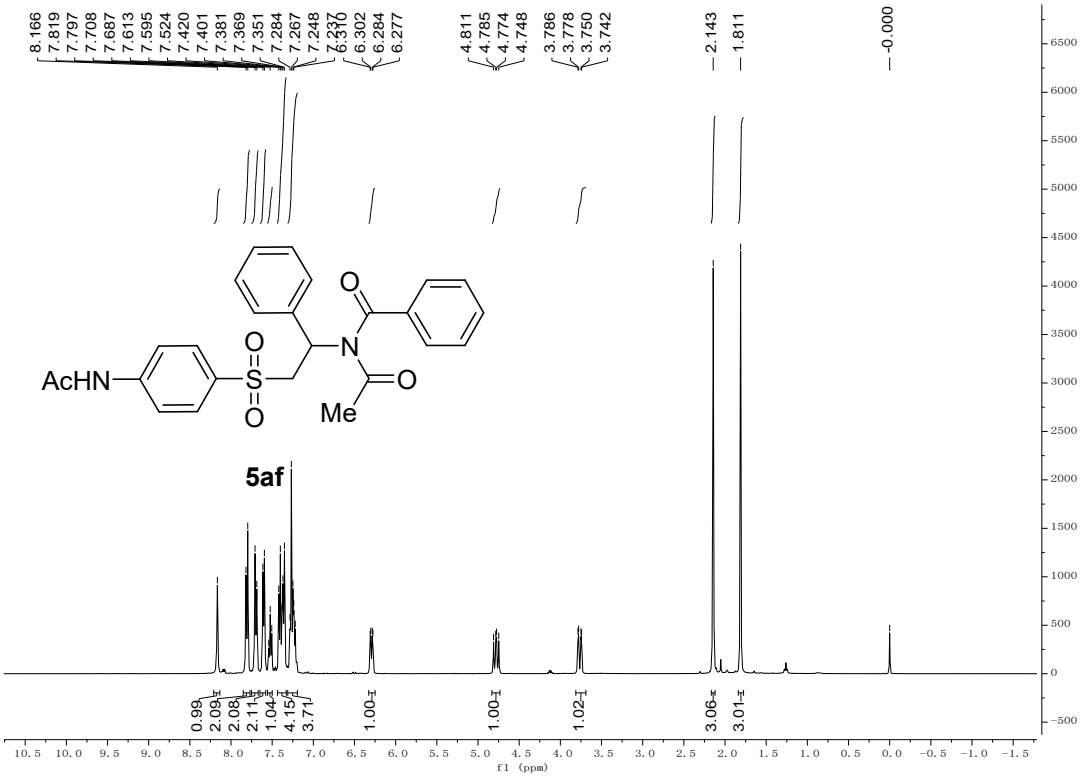
^{1}H NMR of **5ae** in $CDCl_3$



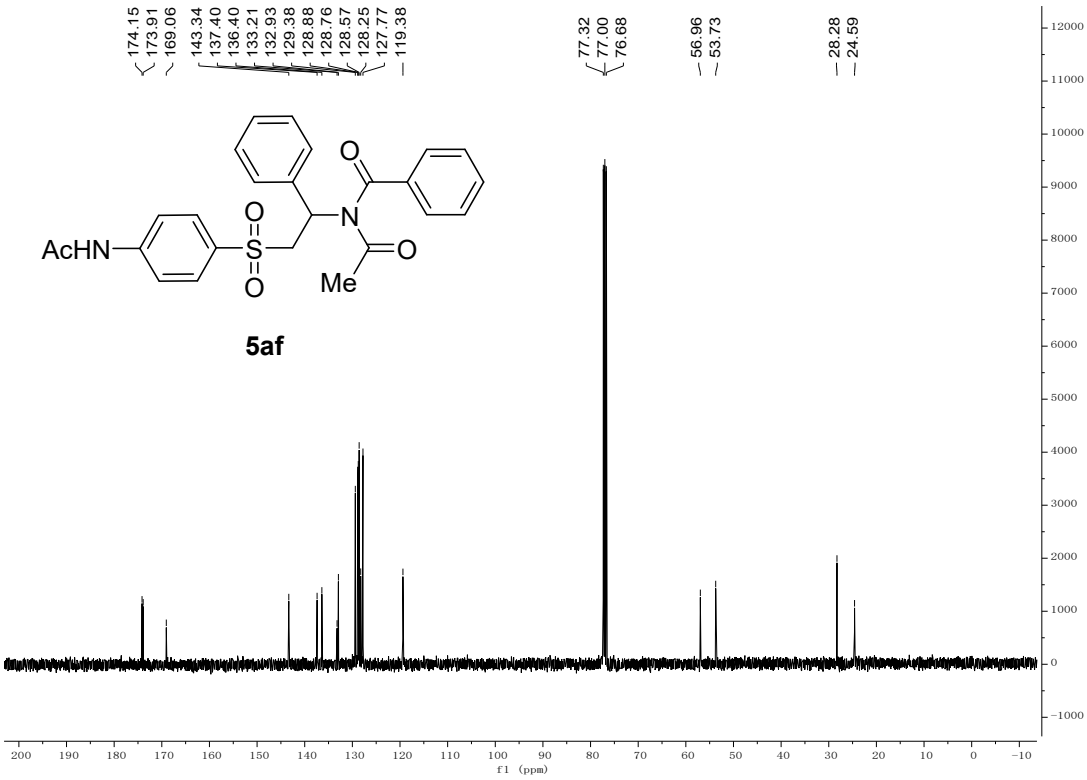
^{13}C NMR of **5ae** in $CDCl_3$



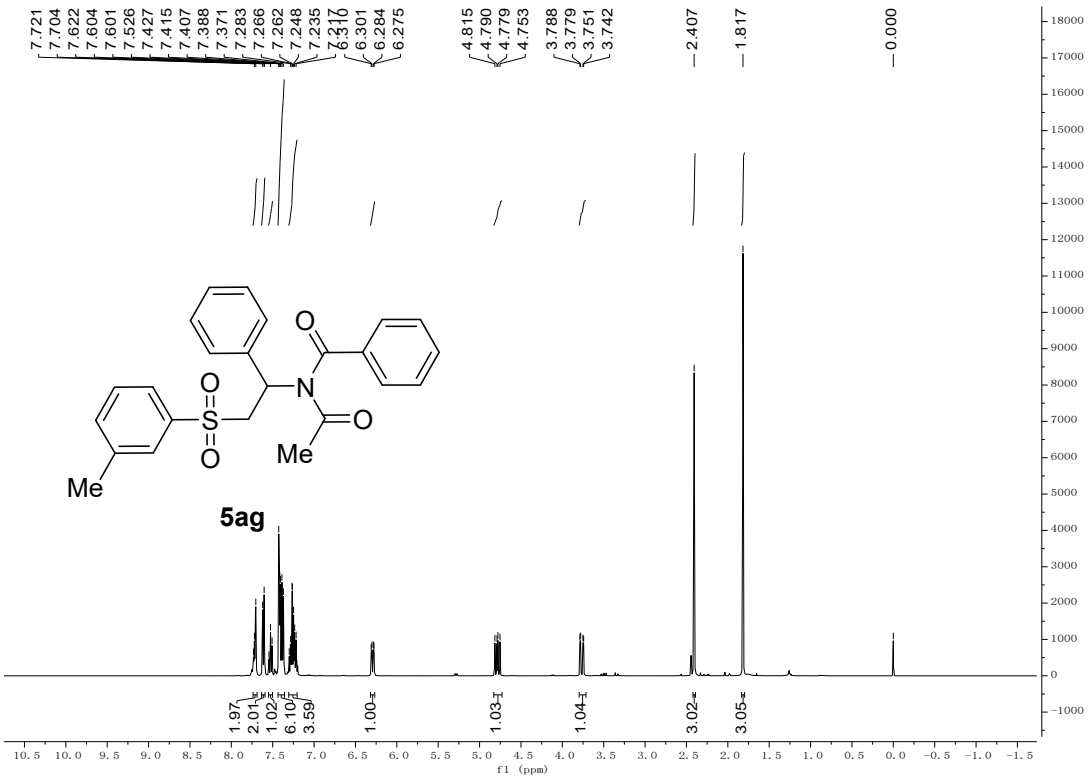
^{1}H NMR of **5af** in $CDCl_3$



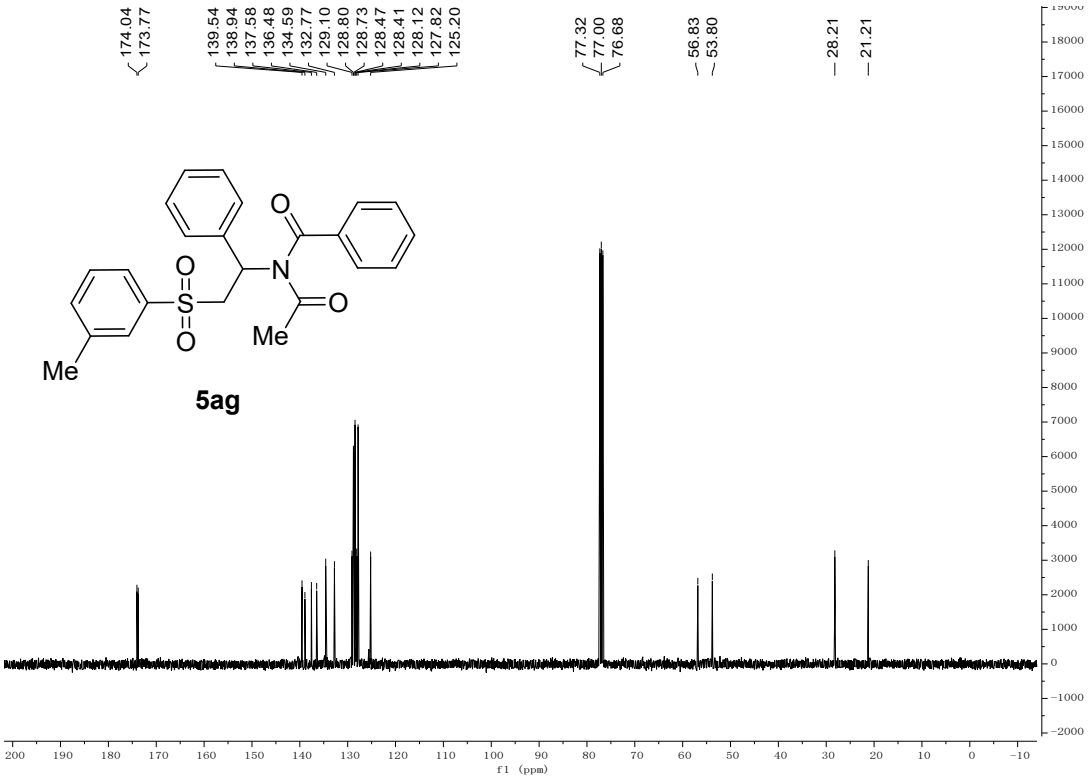
^{13}C NMR of **5af** in $CDCl_3$



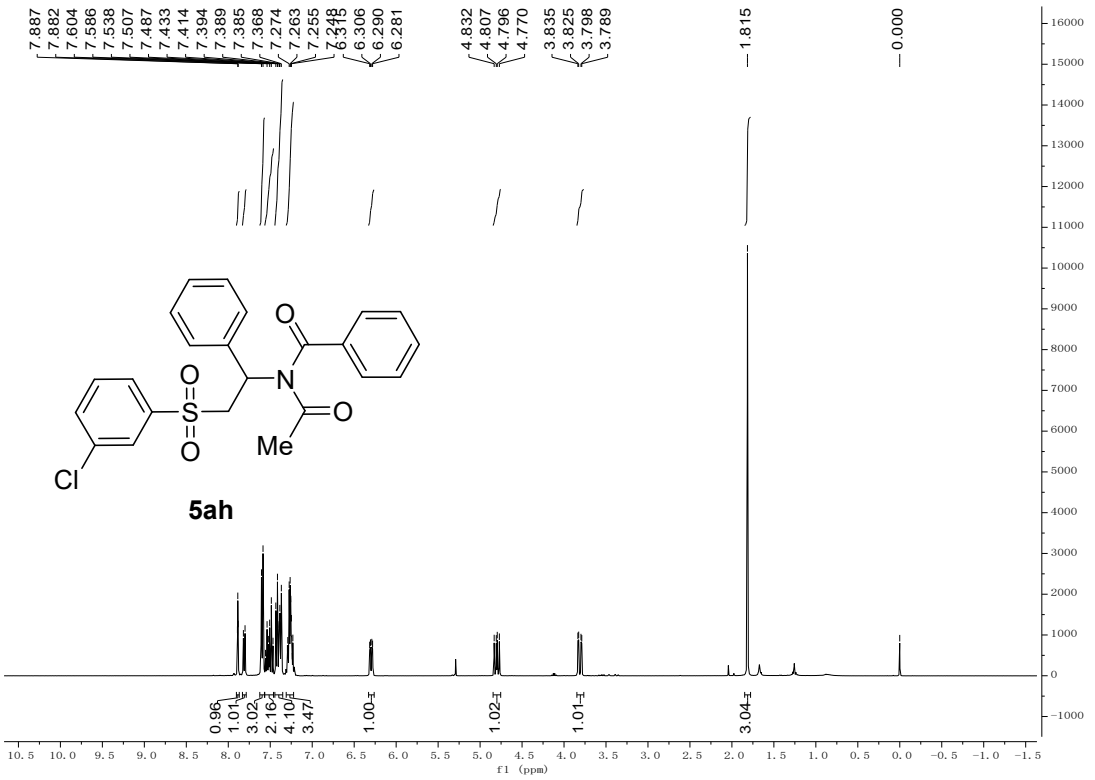
^{1}H NMR of **5ag** in $CDCl_3$



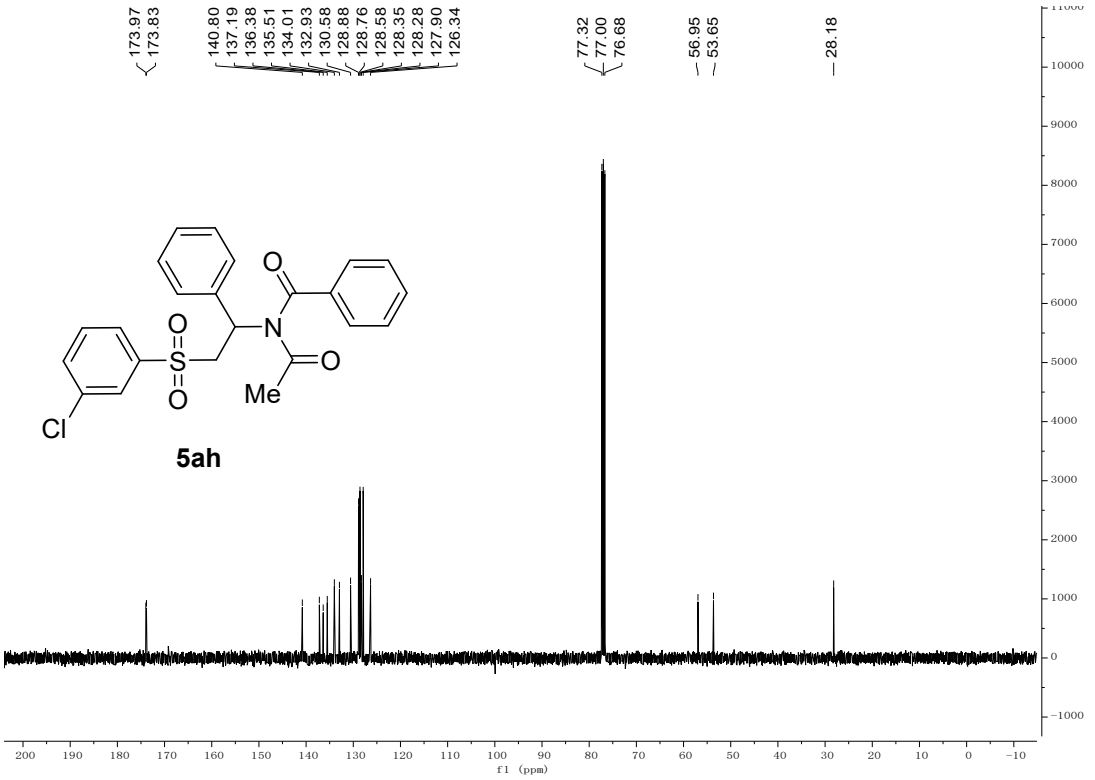
^{13}C NMR of **5ag** in $CDCl_3$



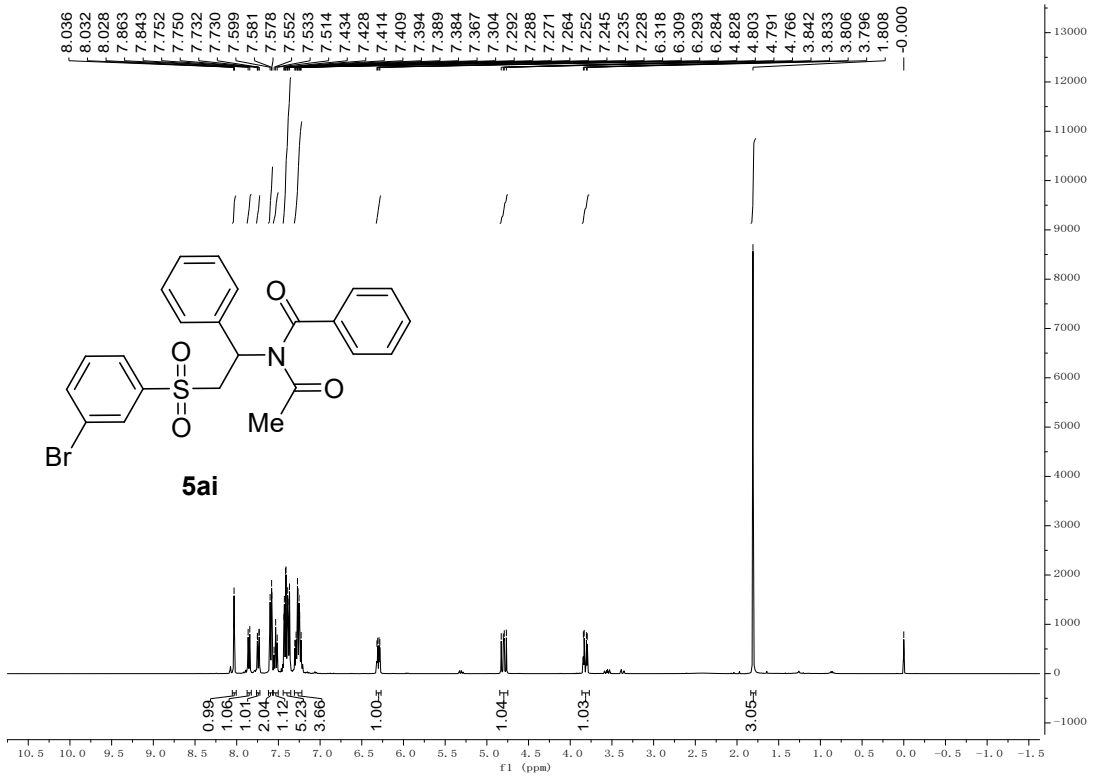
^{1}H NMR of **5ah** in $CDCl_3$



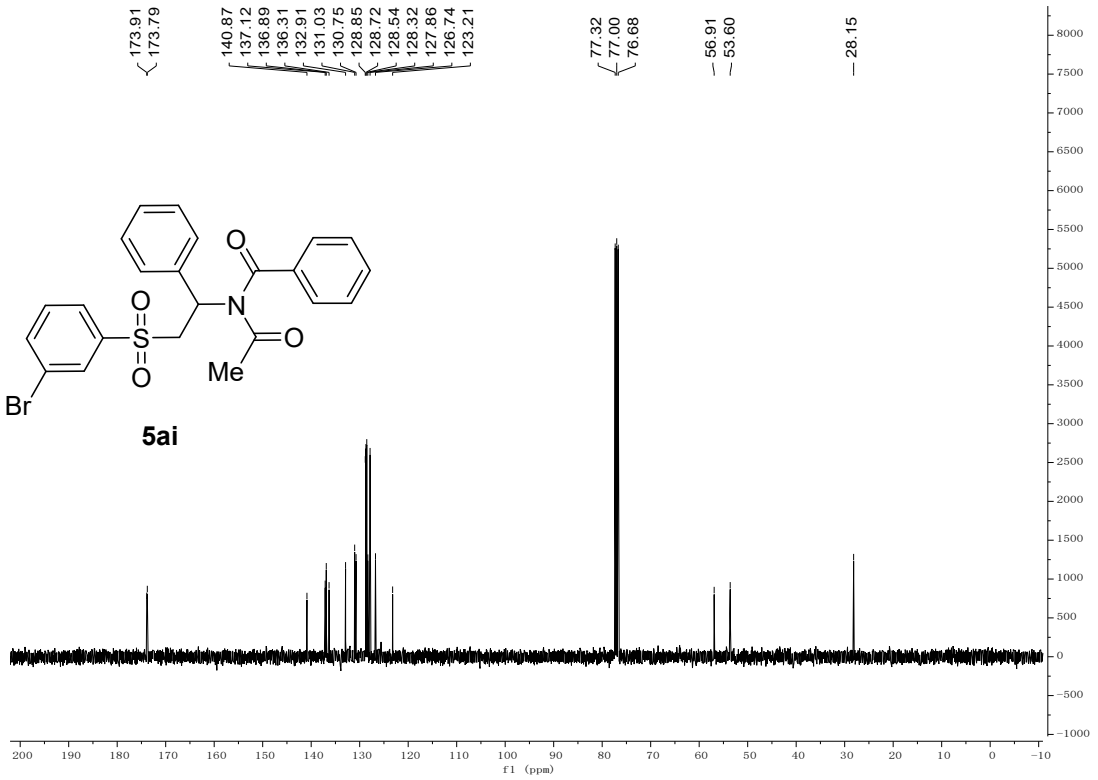
^{13}C NMR of **5ah** in $CDCl_3$



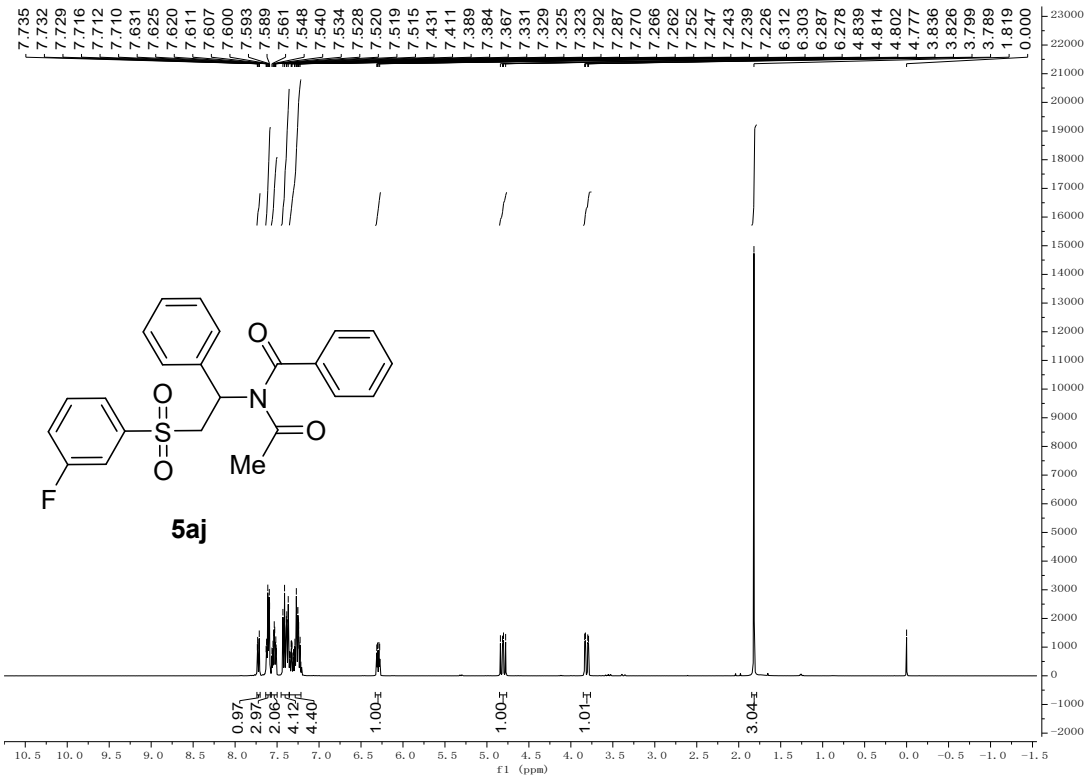
^{1}H NMR of **5ai** in $CDCl_3$



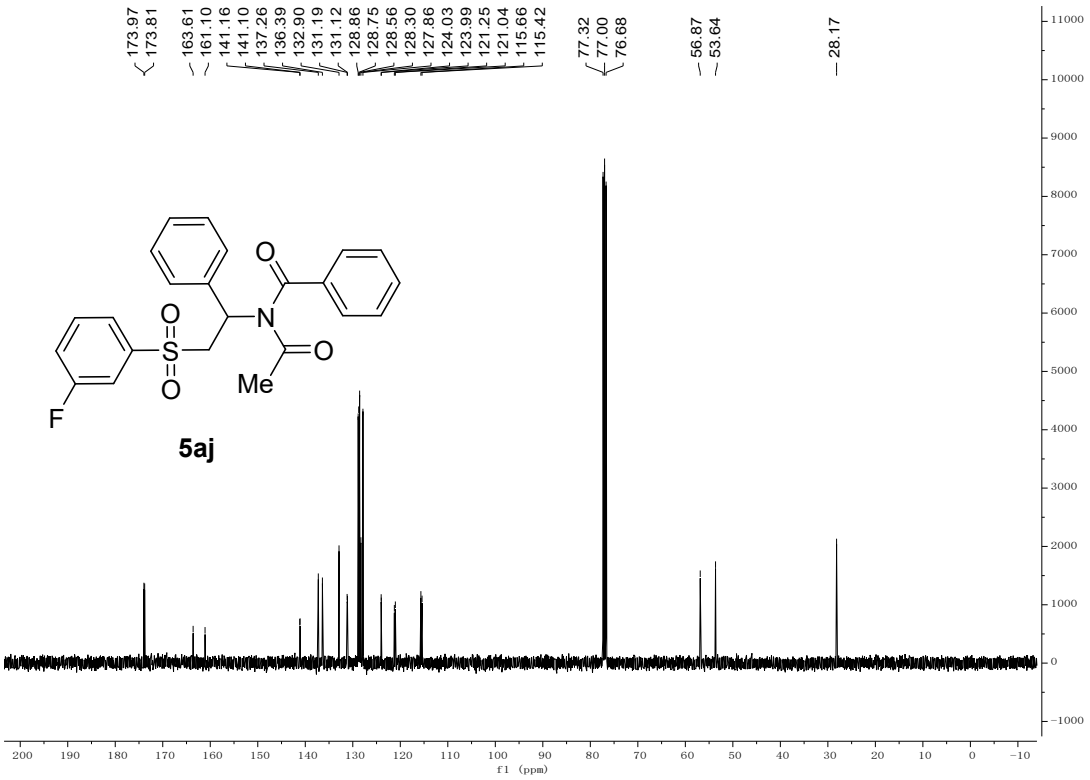
^{13}C NMR of **5ai** in $CDCl_3$



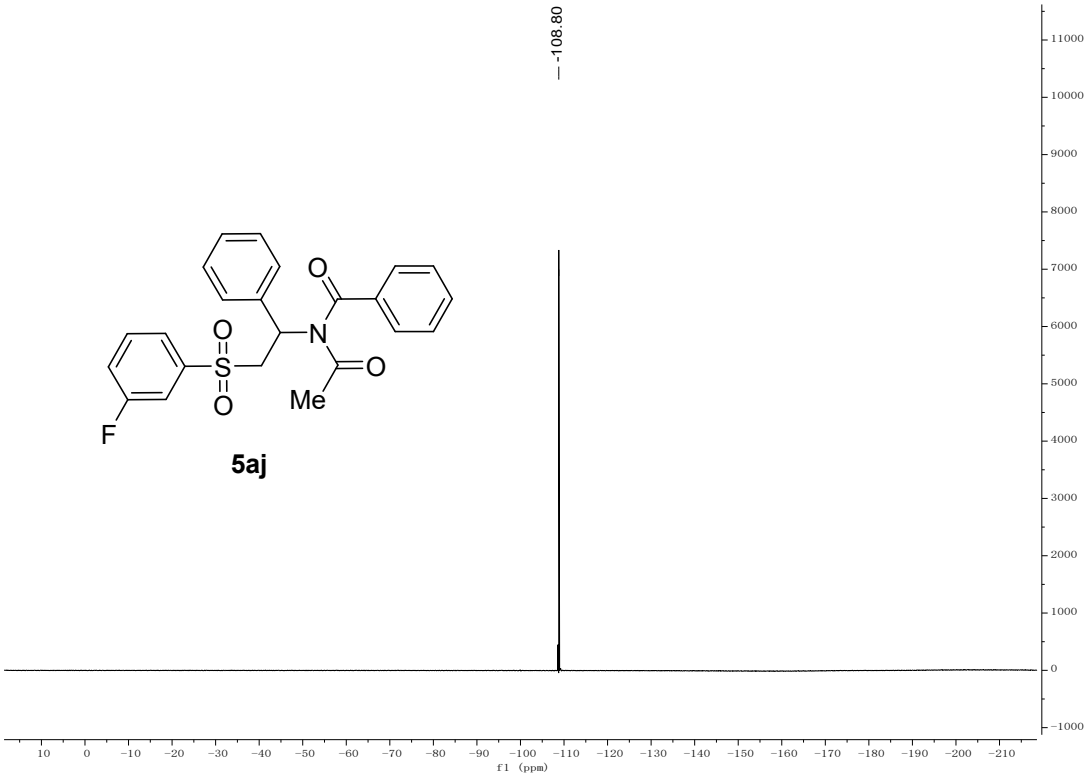
^{1}H NMR of **5aj** in $CDCl_3$



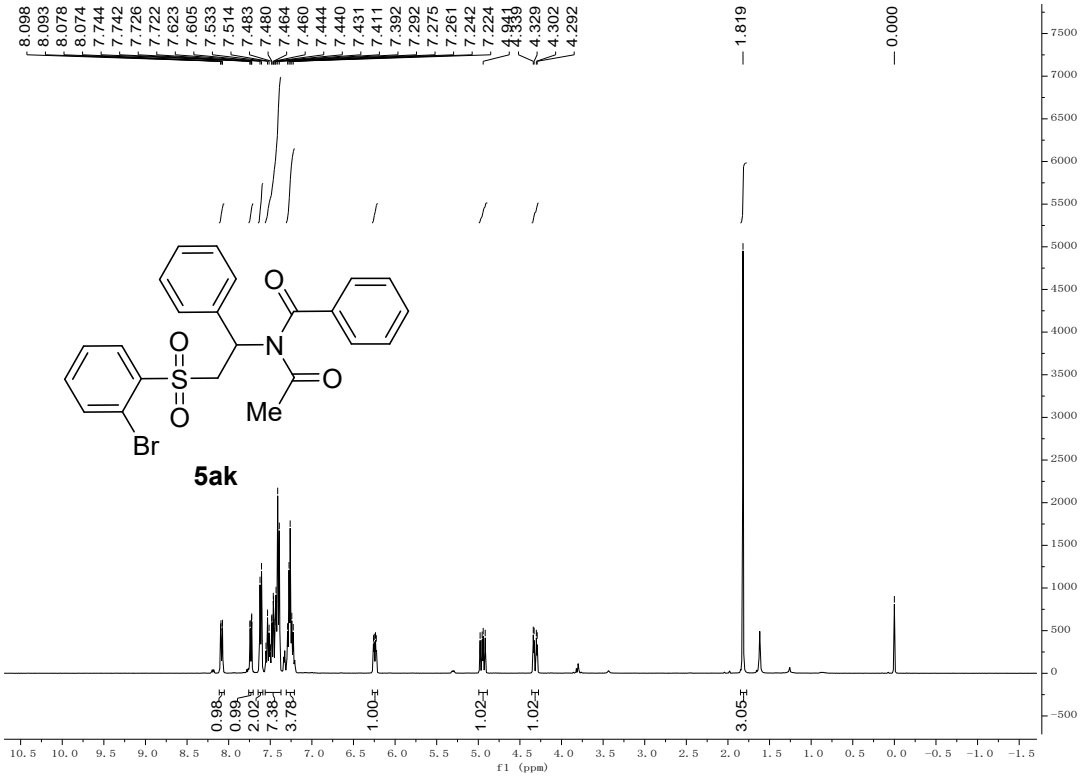
^{13}C NMR of **5aj** in $CDCl_3$



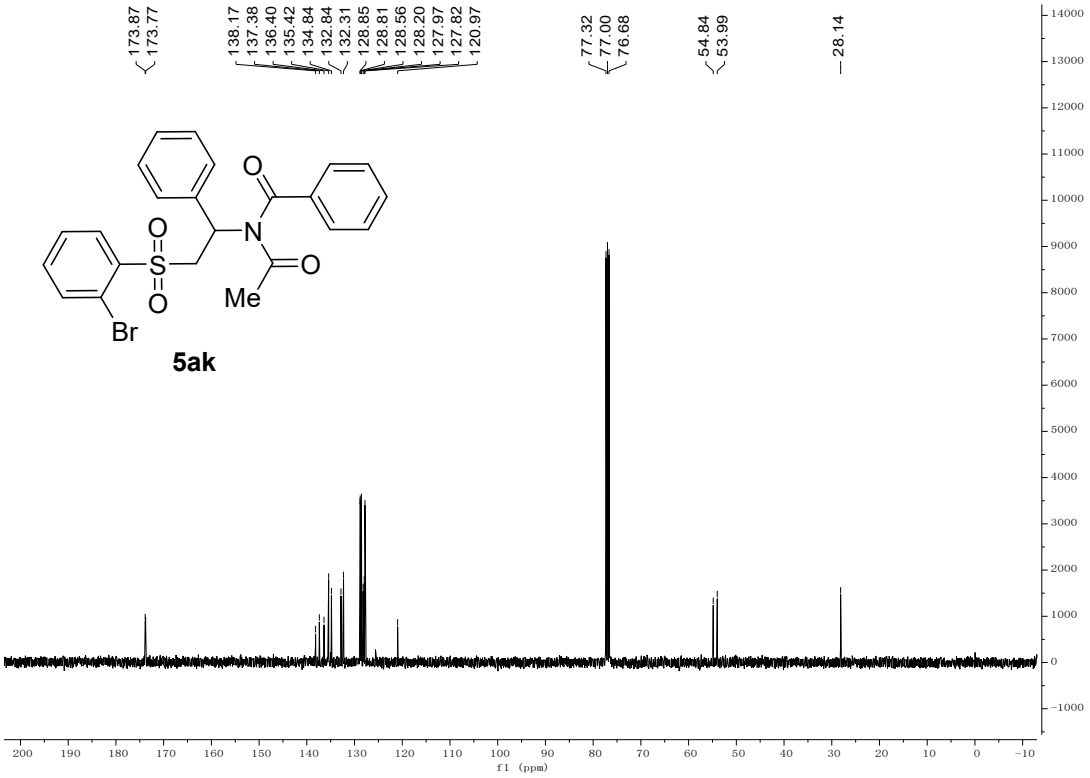
^{19}F NMR spectra of **5aj** in $CDCl_3$



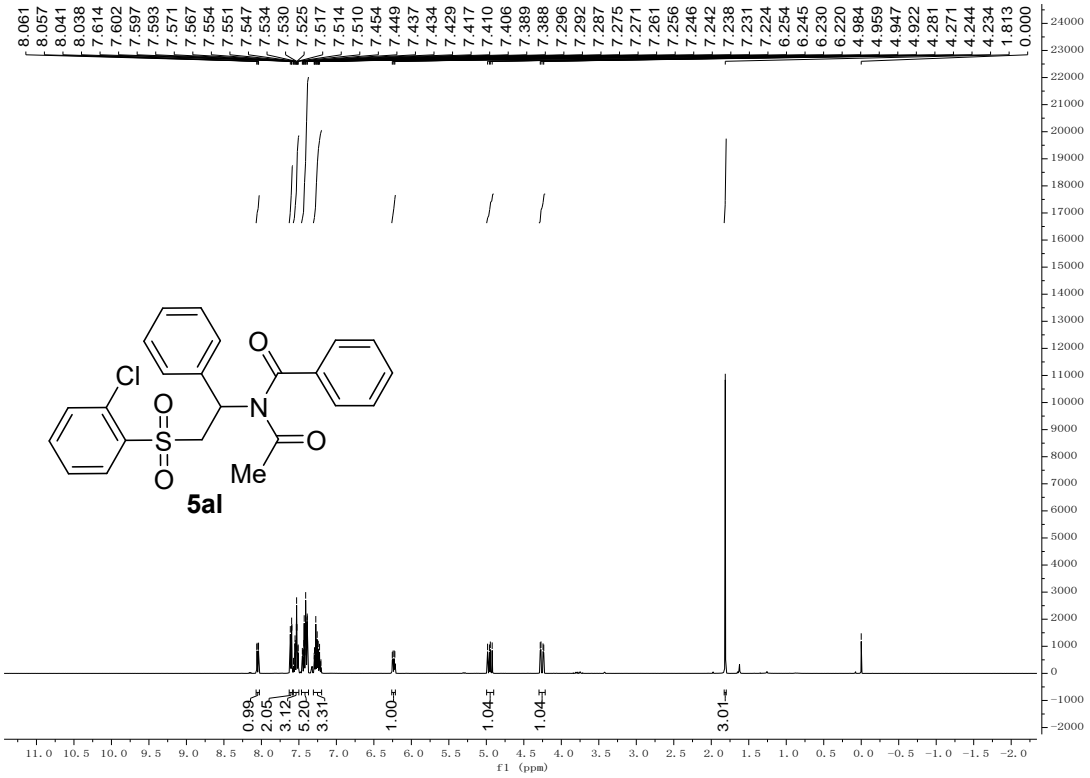
^{1}H NMR of **5ak** in $CDCl_3$



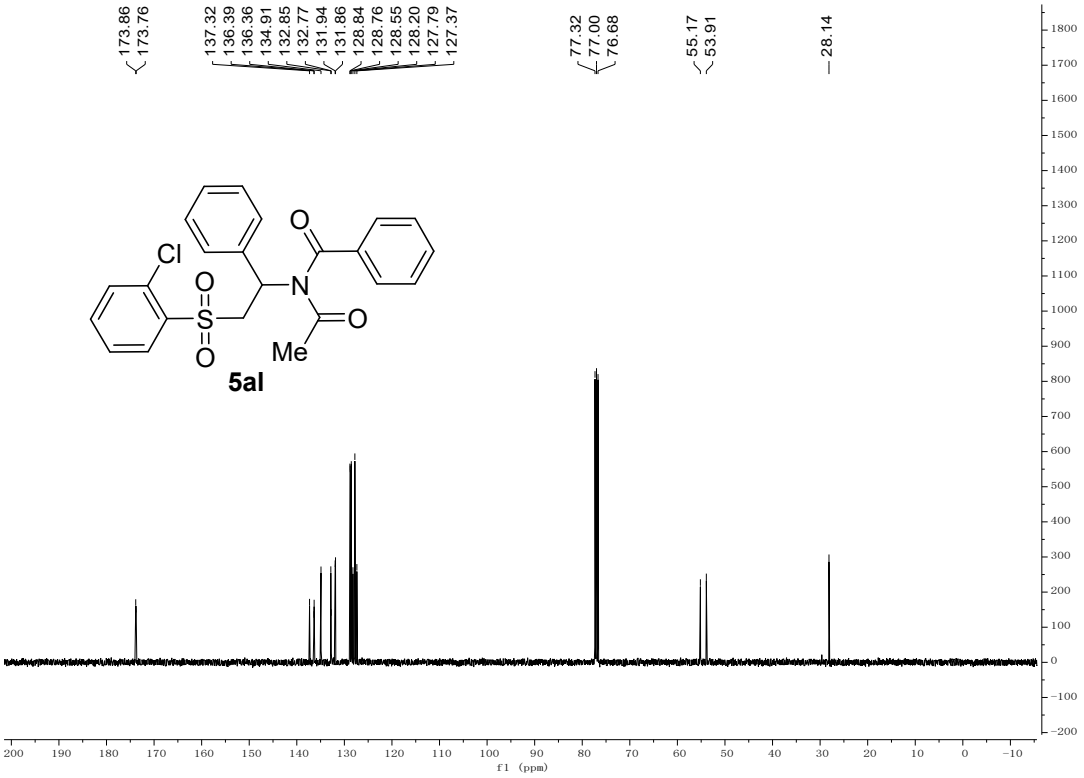
^{13}C NMR of **5ak** in $CDCl_3$



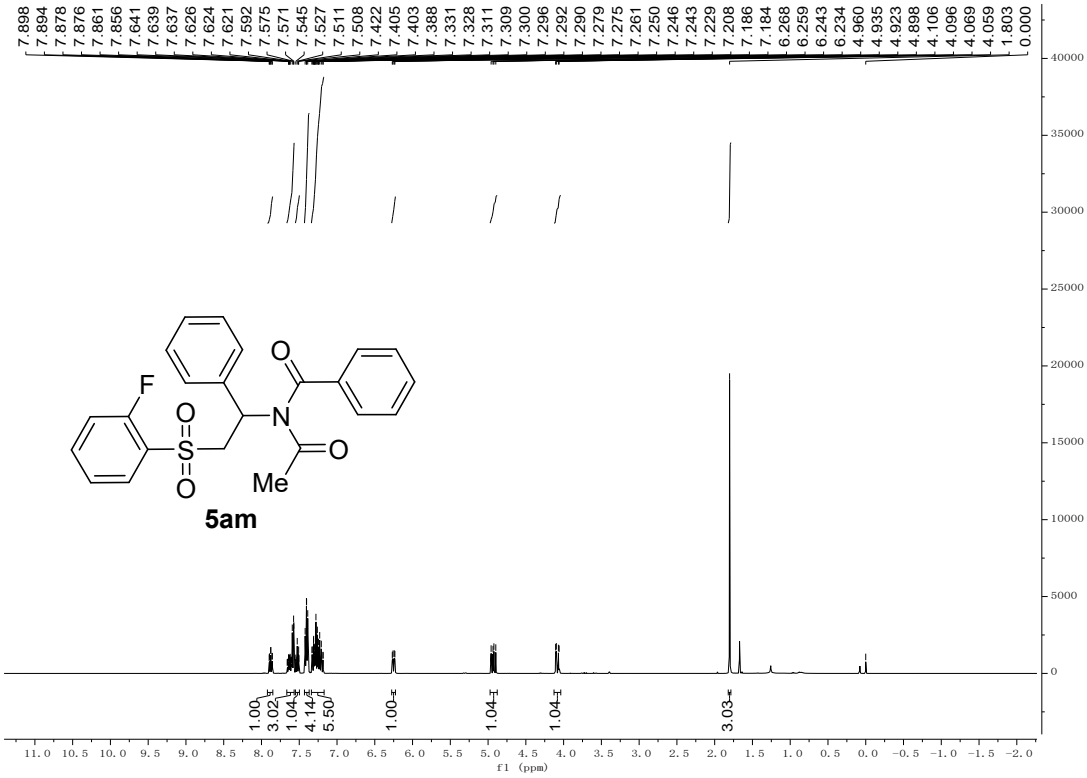
^{1}H NMR of **5al** in $CDCl_3$



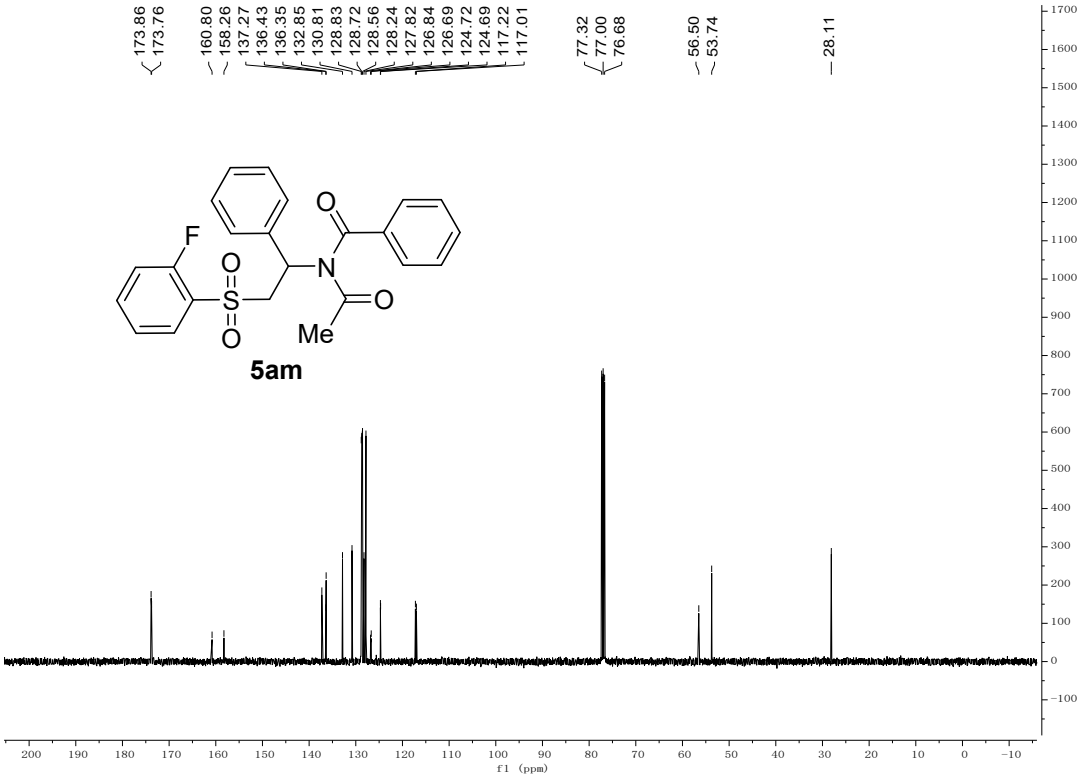
^{13}C NMR of **5al** in $CDCl_3$



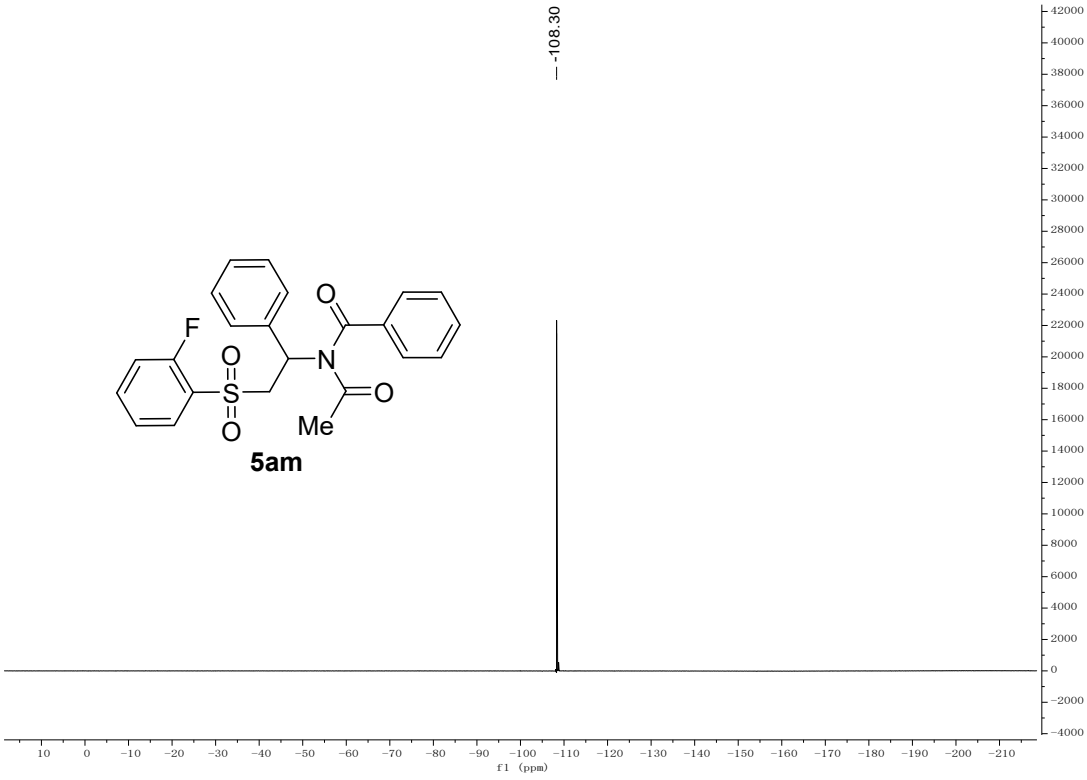
^{1}H NMR of **5am** in $CDCl_3$



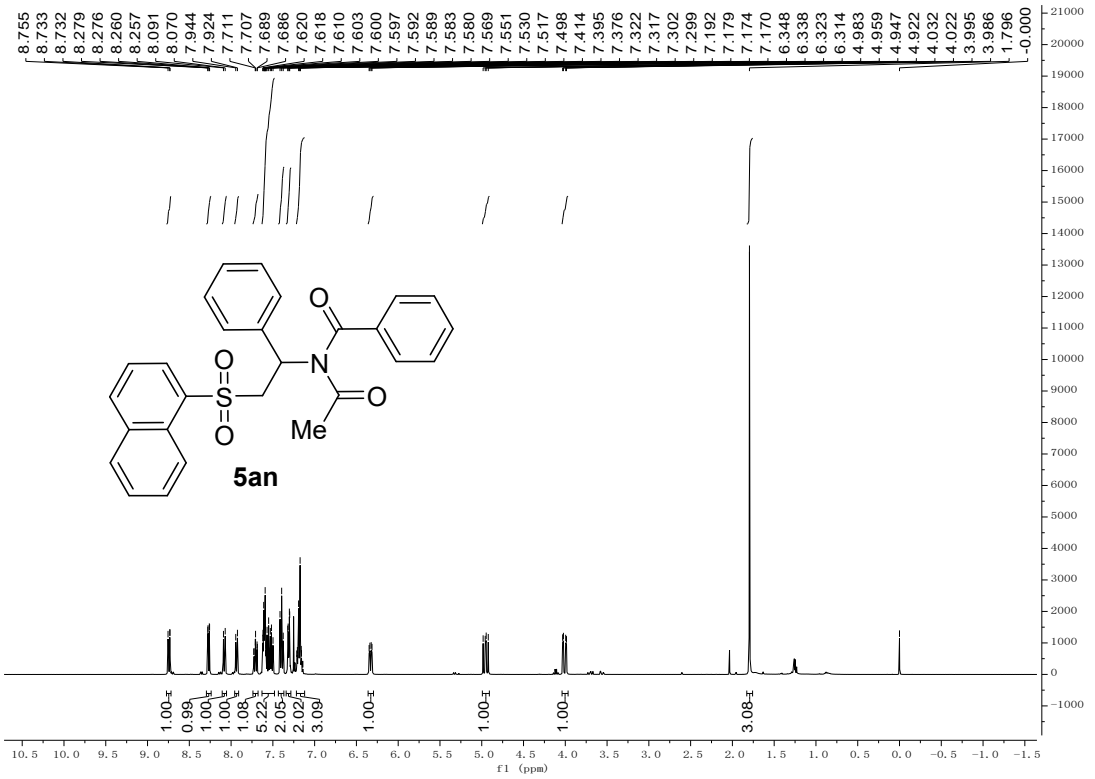
^{13}C NMR of **5am** in $CDCl_3$



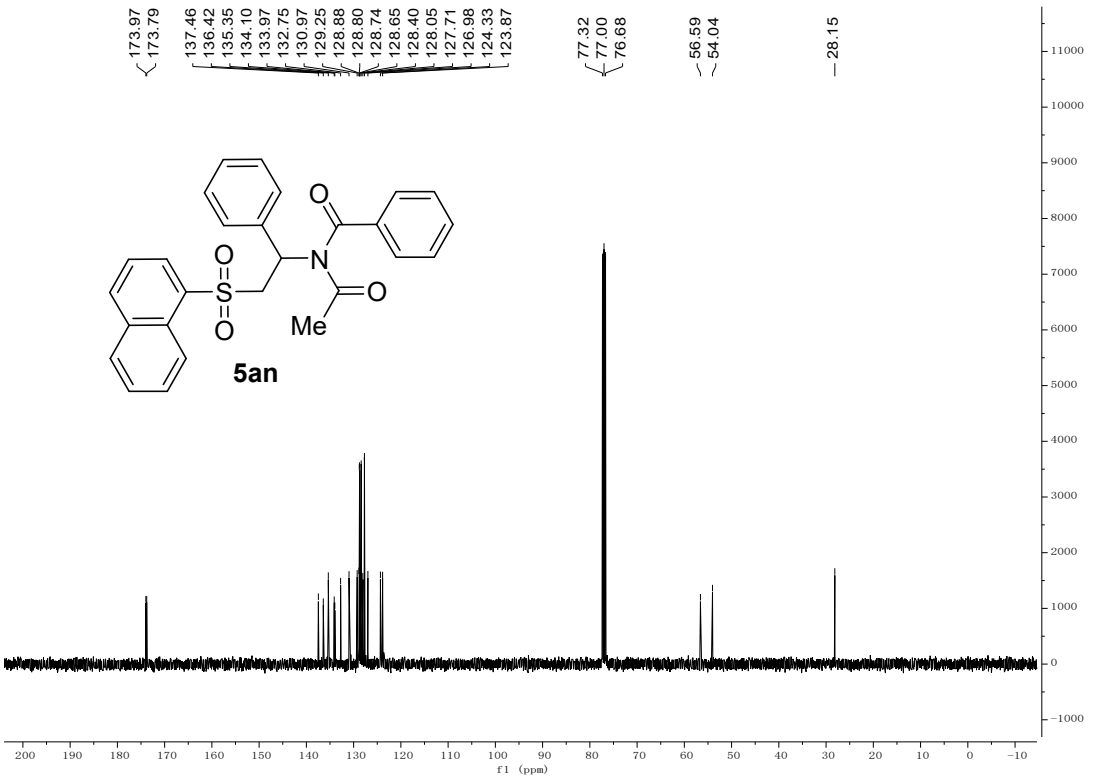
^{19}F NMR spectra of **5am** in $CDCl_3$



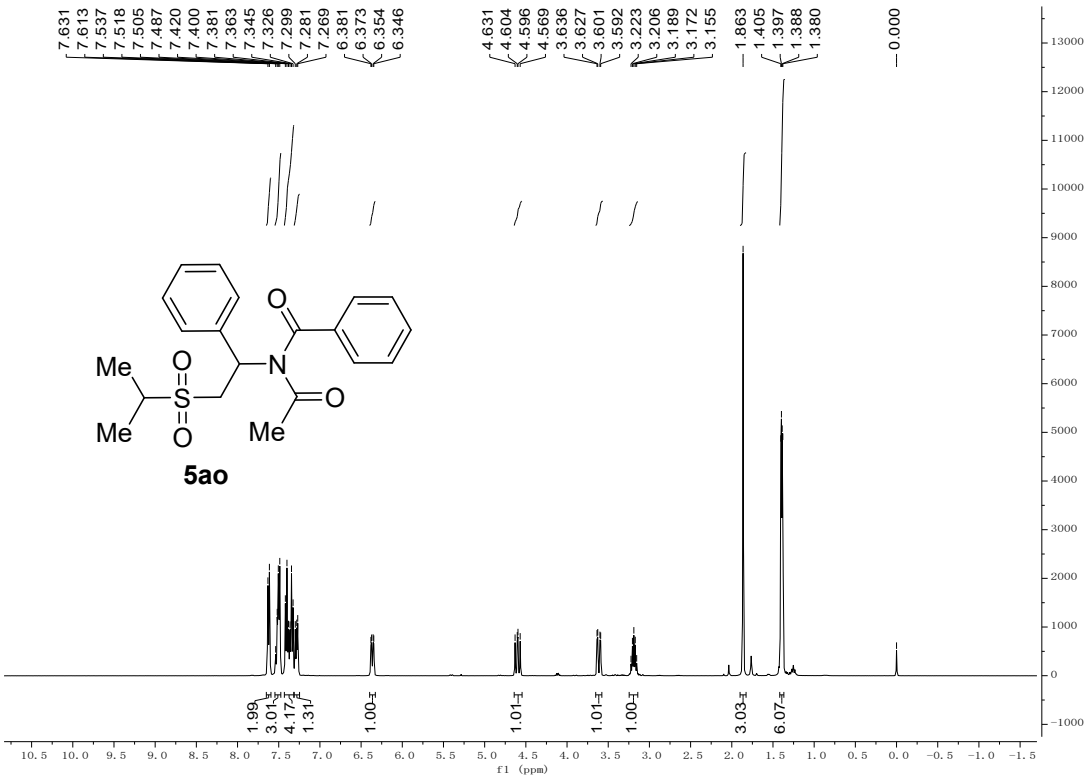
^{1}H NMR of **5an** in $CDCl_3$



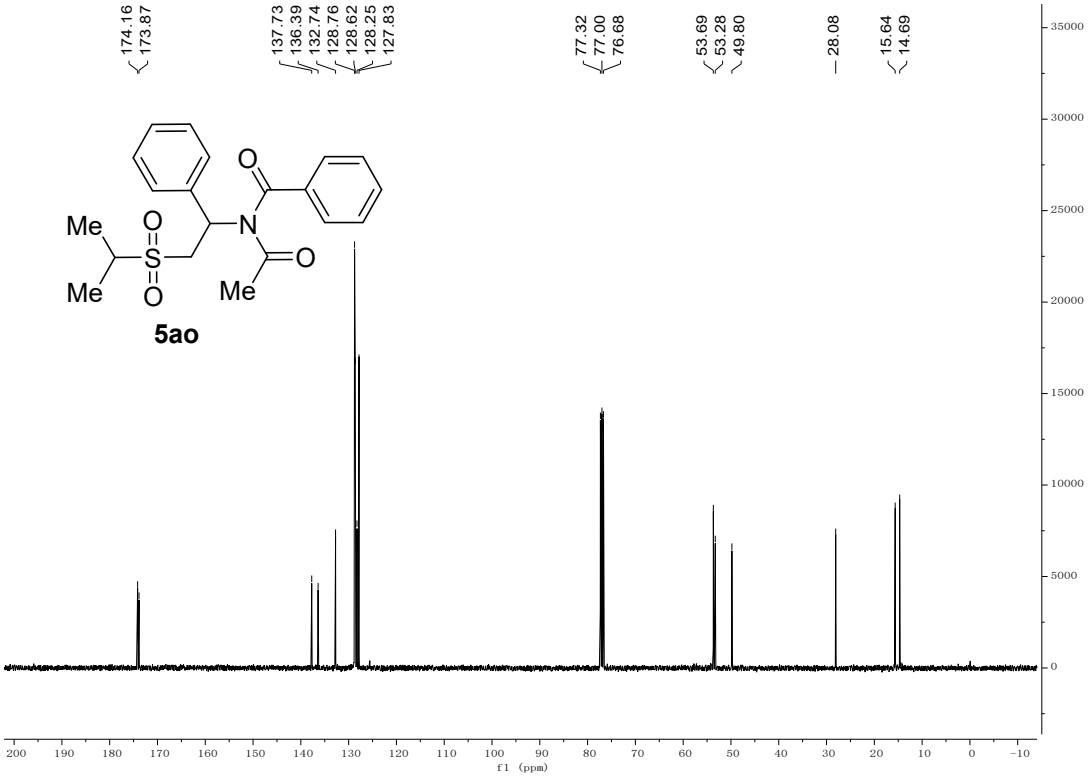
^{13}C NMR of **5an** in $CDCl_3$



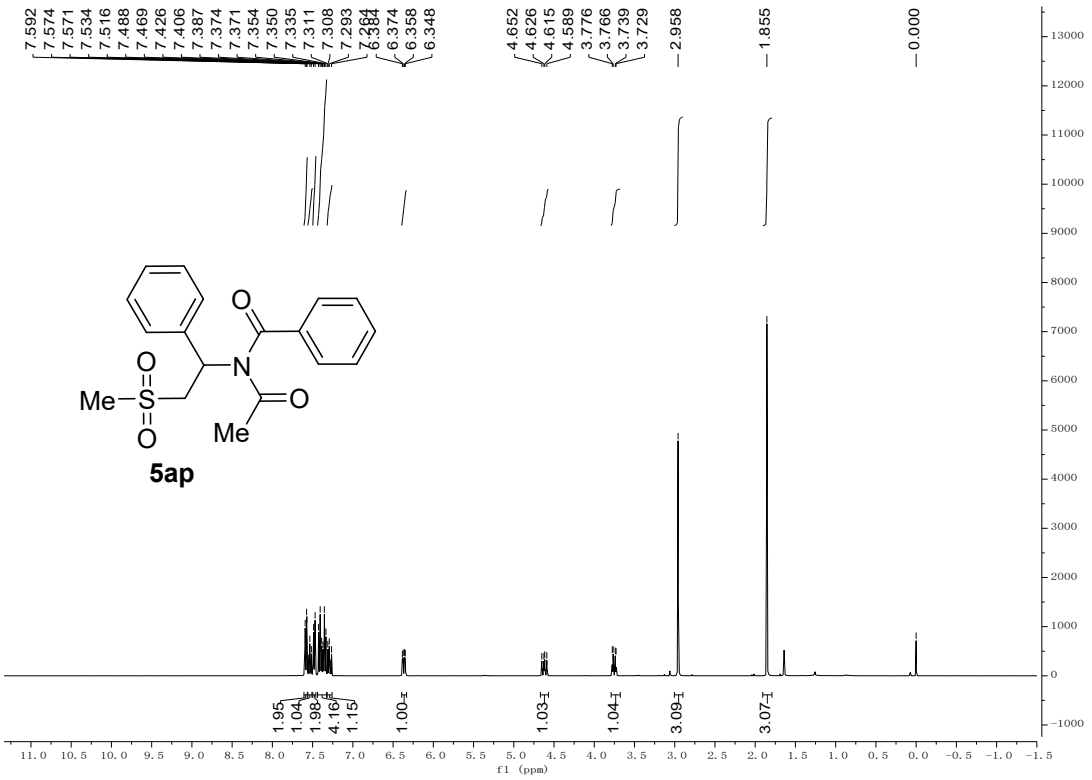
^{1}H NMR of **5ao** in $CDCl_3$



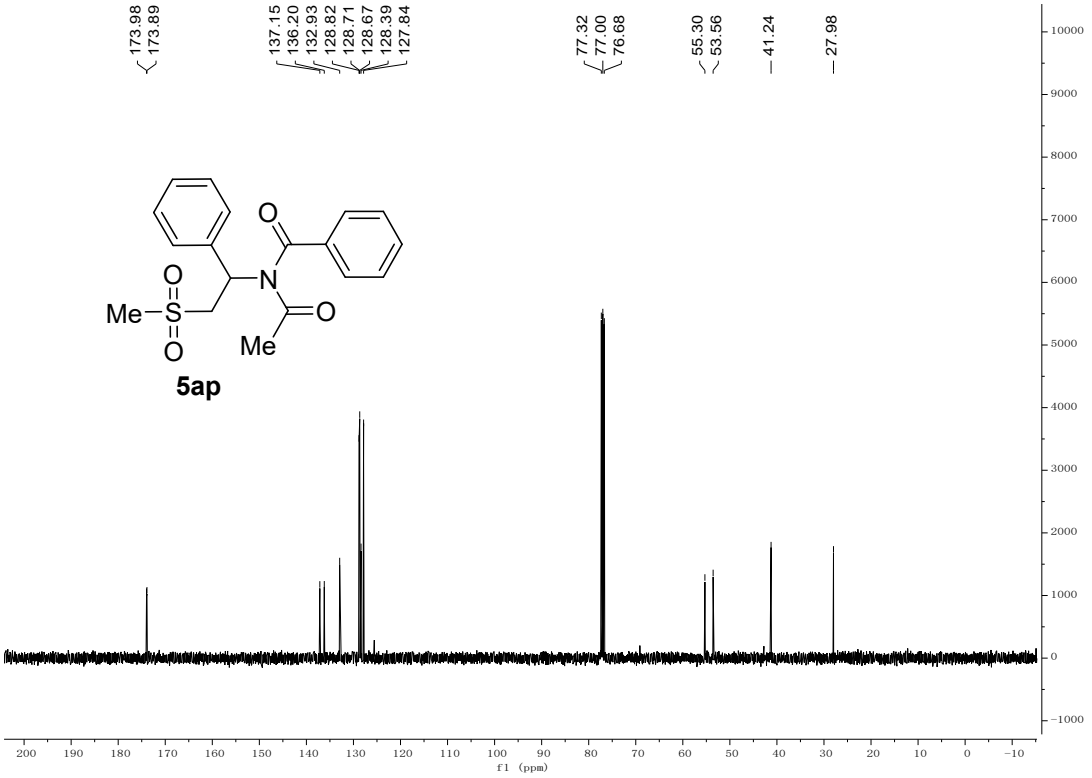
^{13}C NMR of **5ao** in $CDCl_3$



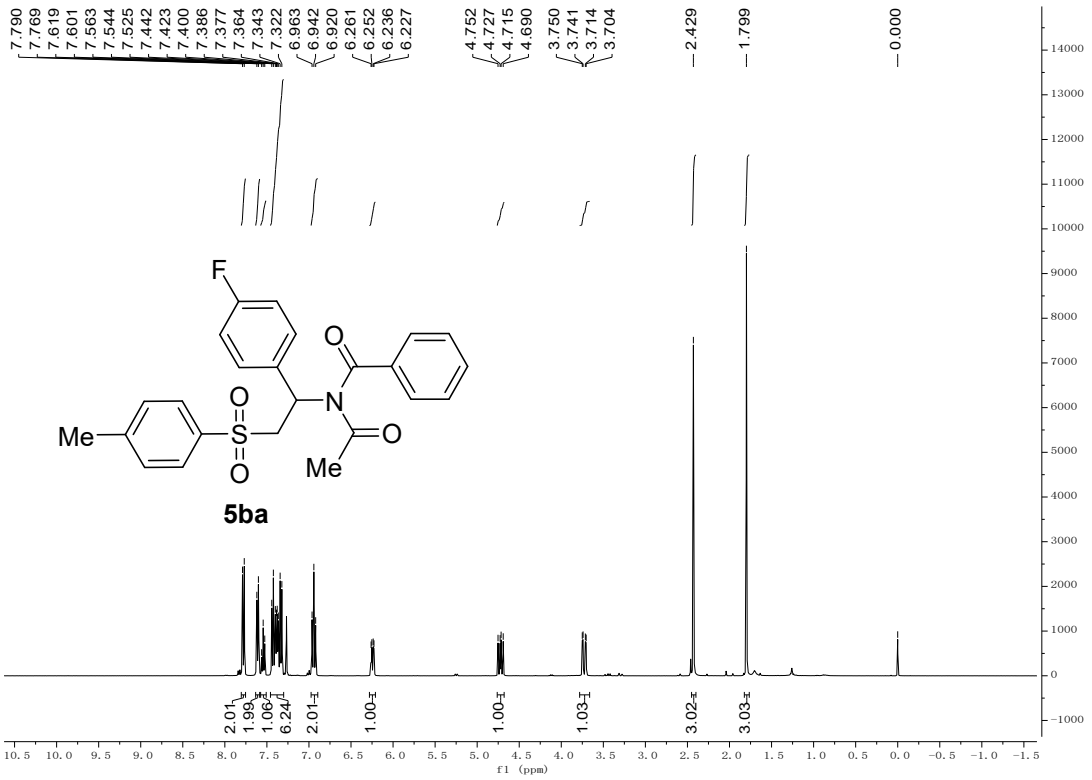
^{1}H NMR of **5ap** in $CDCl_3$



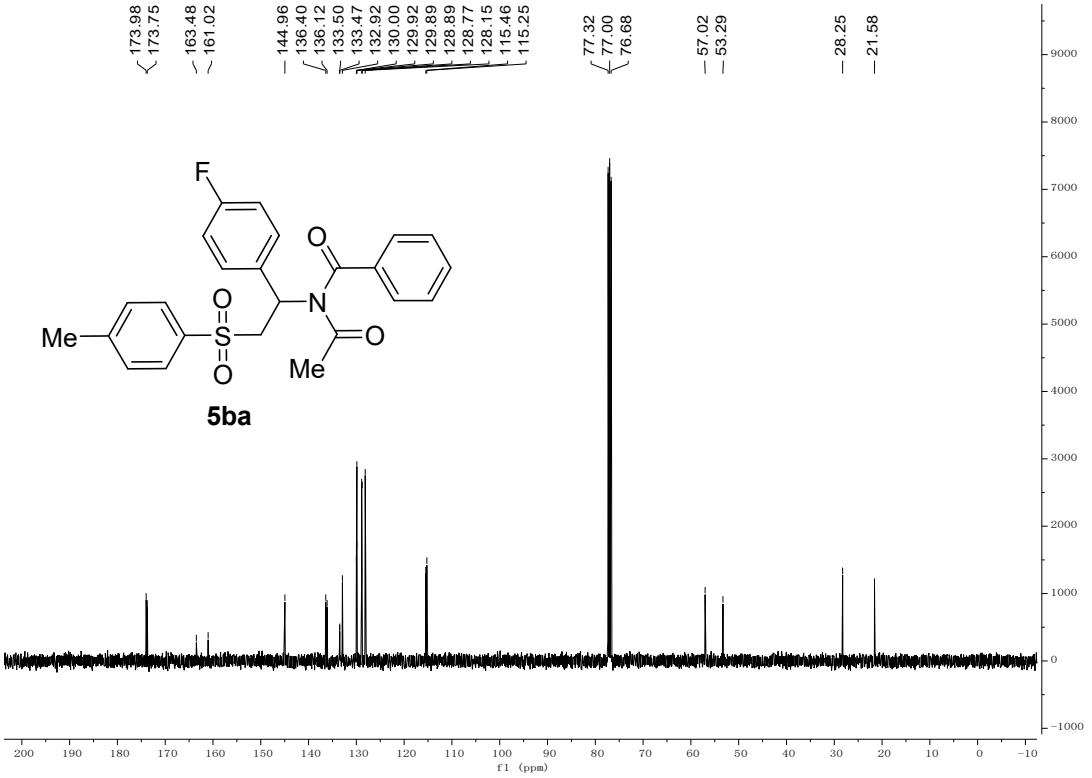
^{13}C NMR of **5ap** in $CDCl_3$



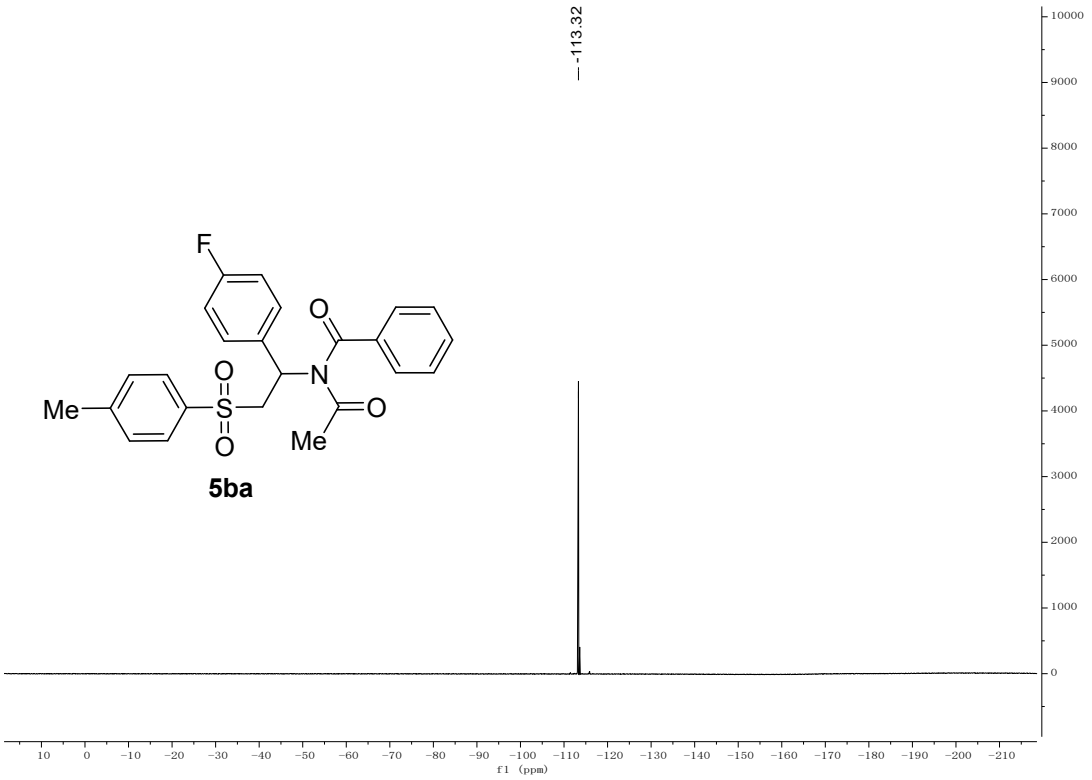
^{1}H NMR of **5ba** in $CDCl_3$



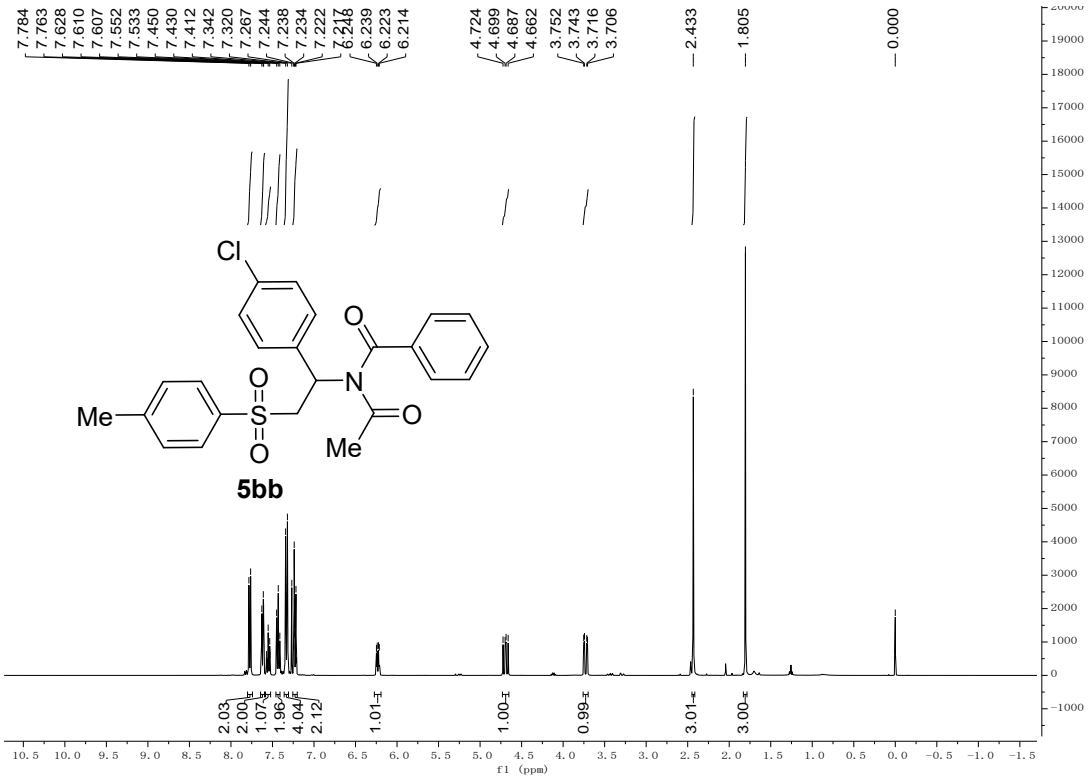
^{13}C NMR of **5ba** in $CDCl_3$



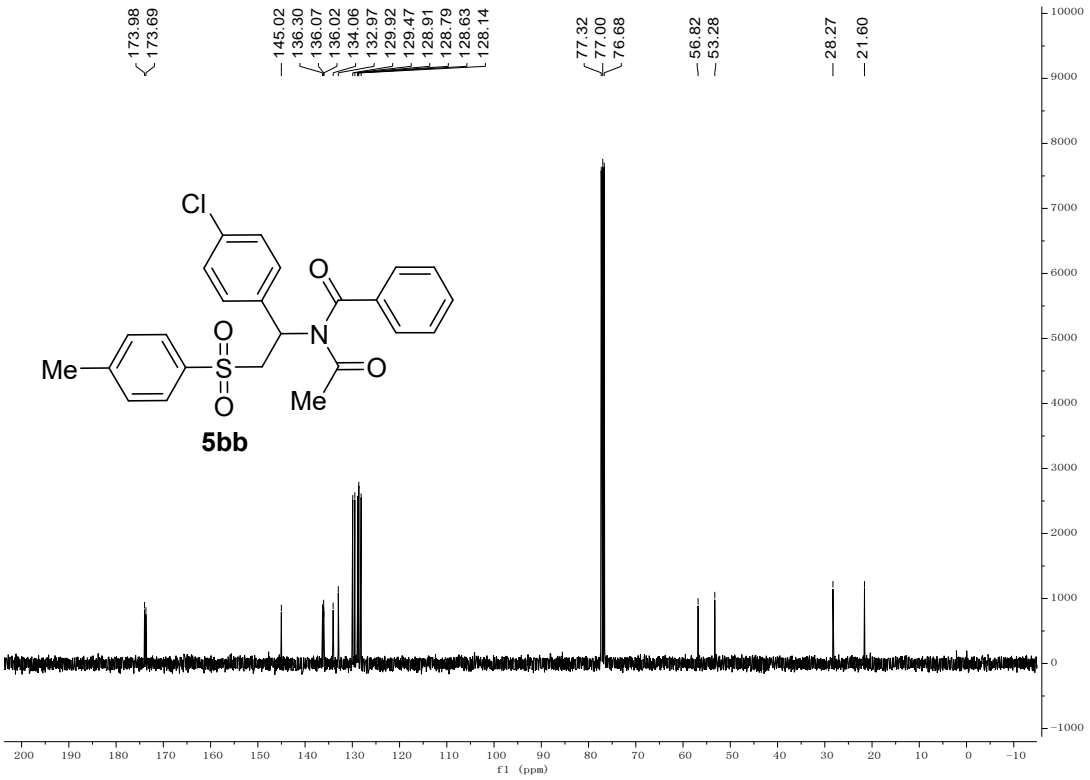
^{19}F NMR spectra of **5ba** in $CDCl_3$



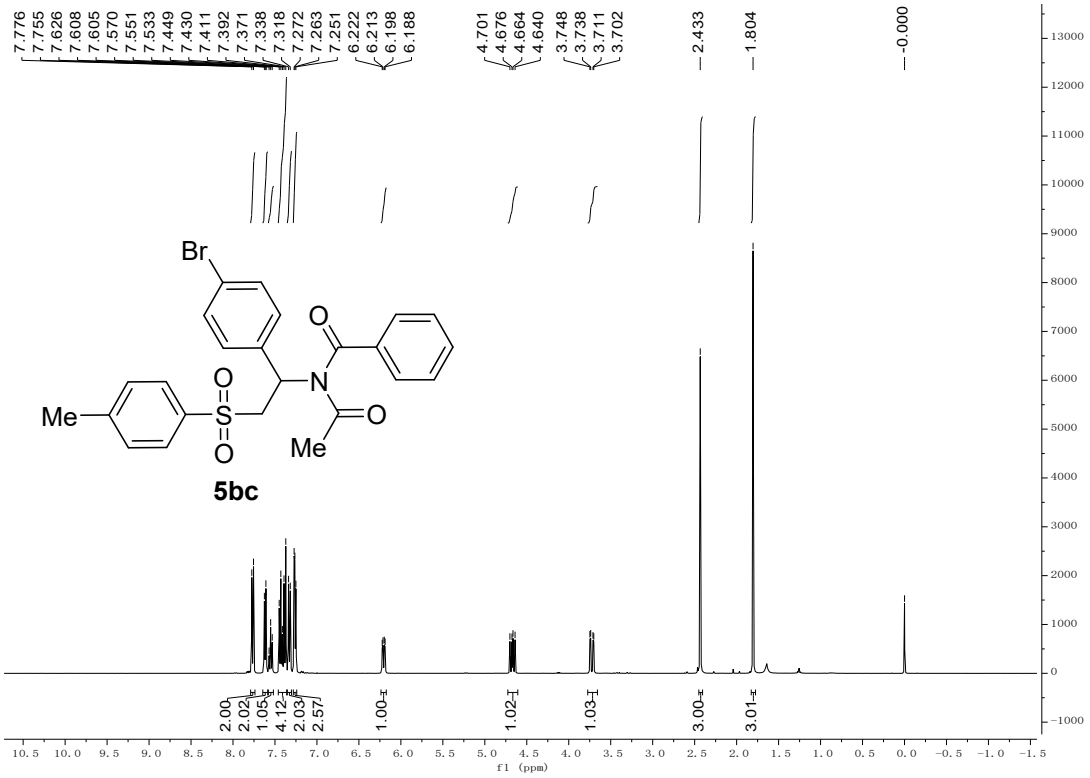
^{1}H NMR of **5bb** in $CDCl_3$



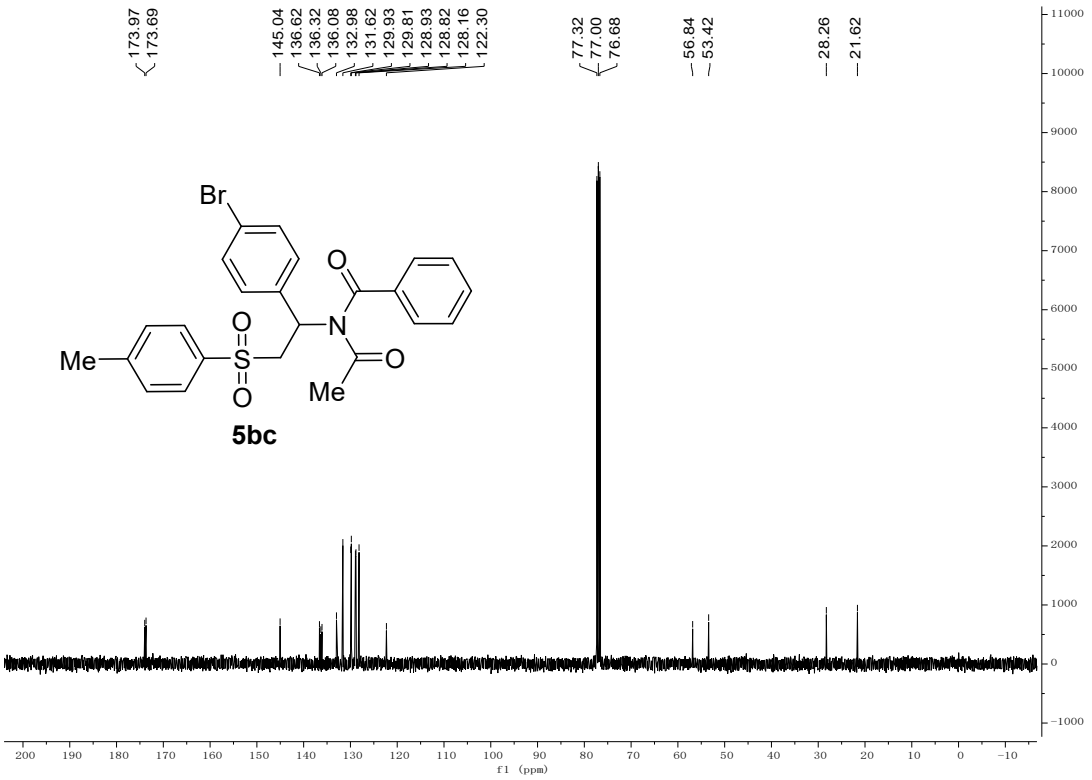
^{13}C NMR of **5bb** in $CDCl_3$



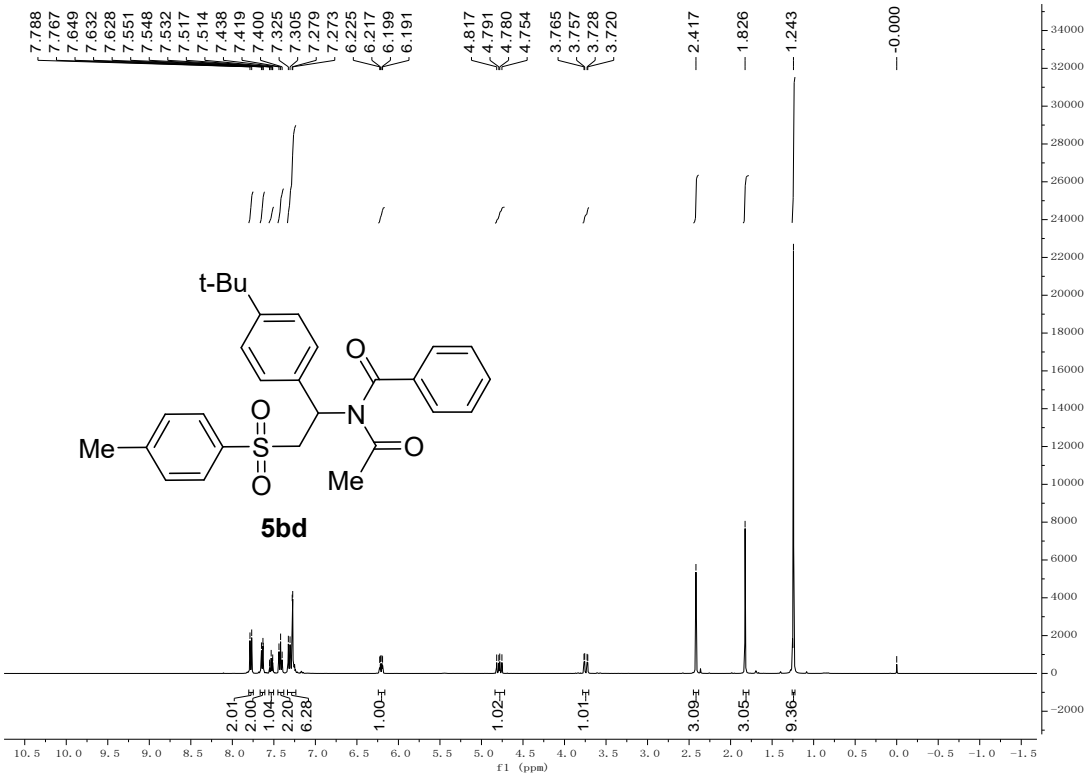
^{1}H NMR of **5bc** in $CDCl_3$



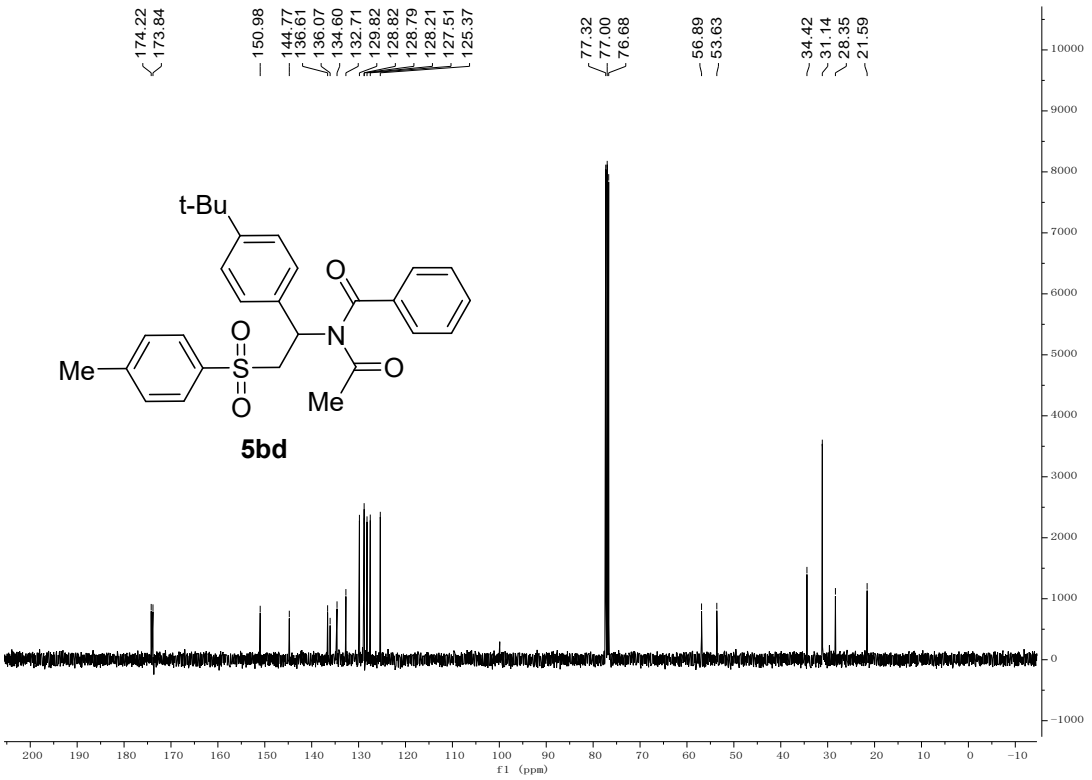
^{13}C NMR of **5bc** in $CDCl_3$



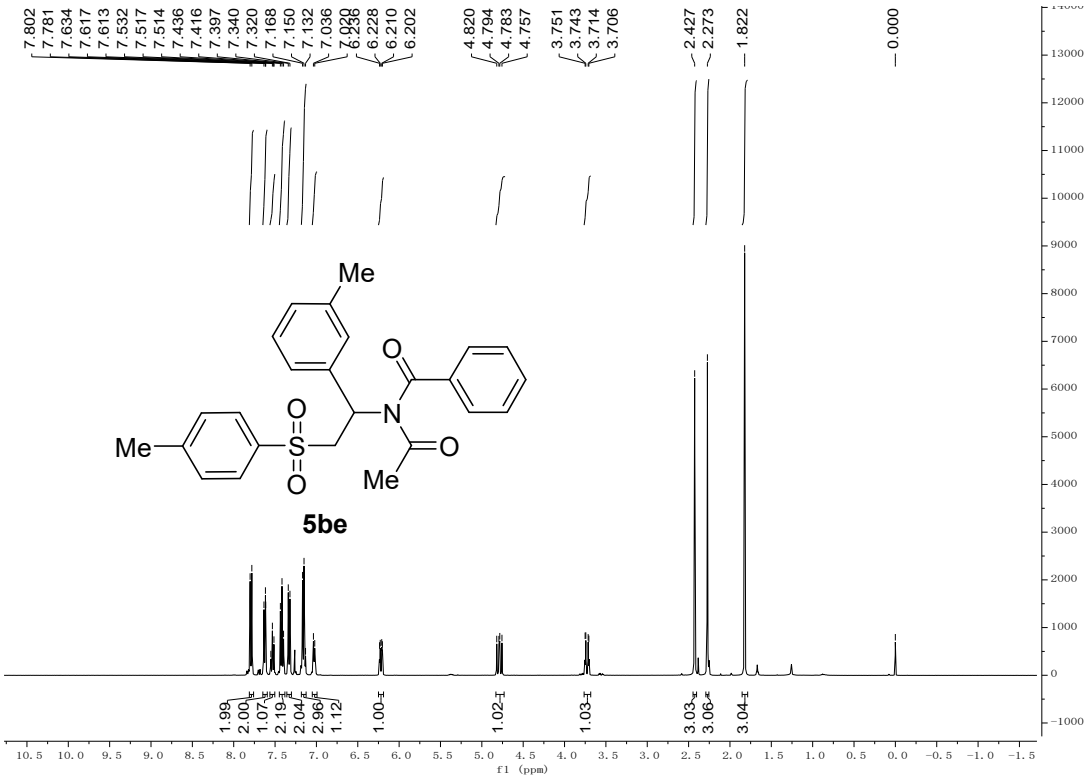
^{1}H NMR of **5bd** in $CDCl_3$



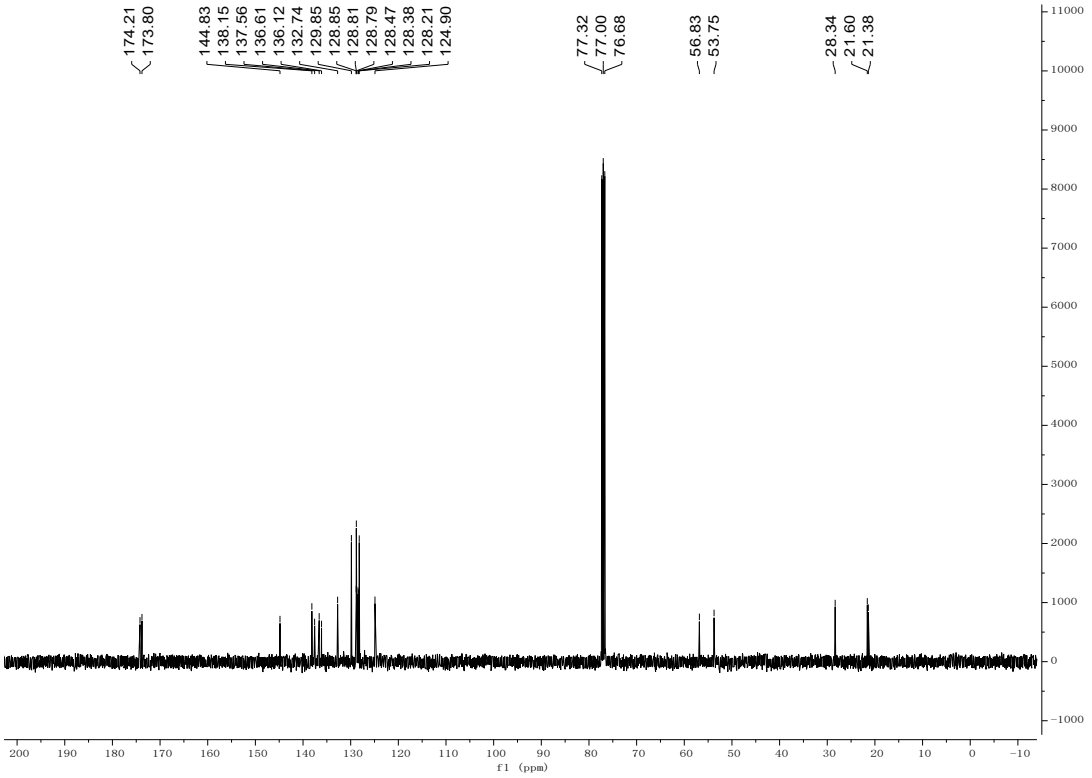
^{13}C NMR of **5bd** in $CDCl_3$



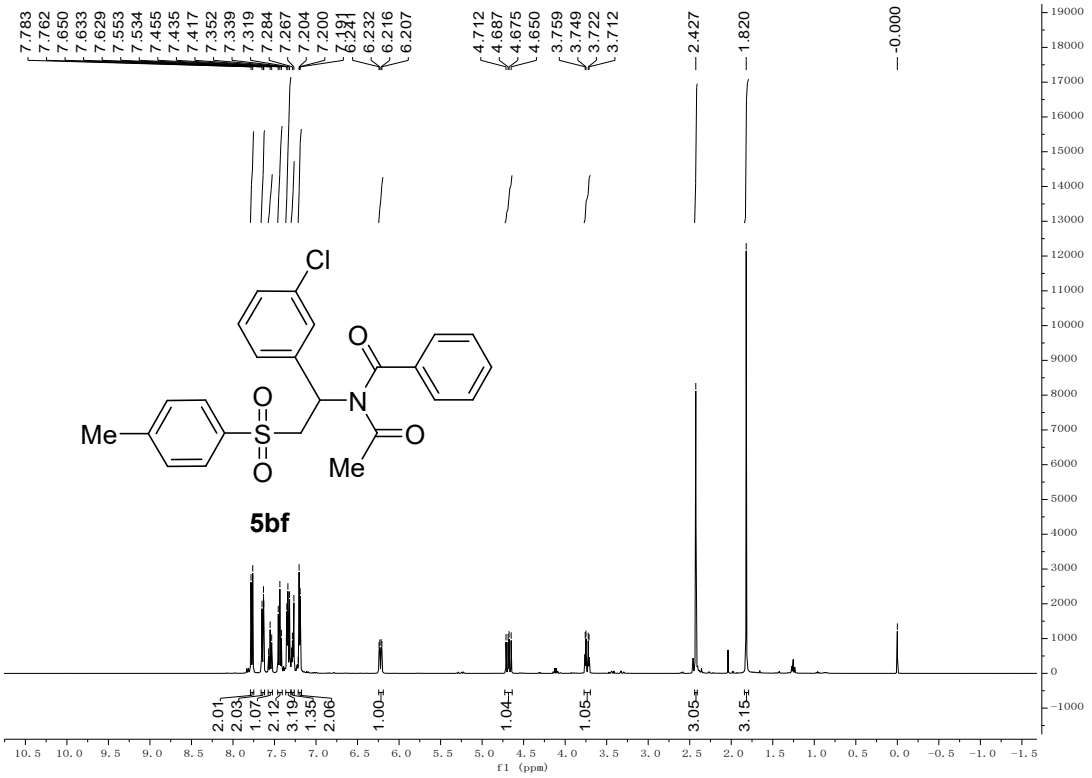
^{1}H NMR of **5be** in $CDCl_3$



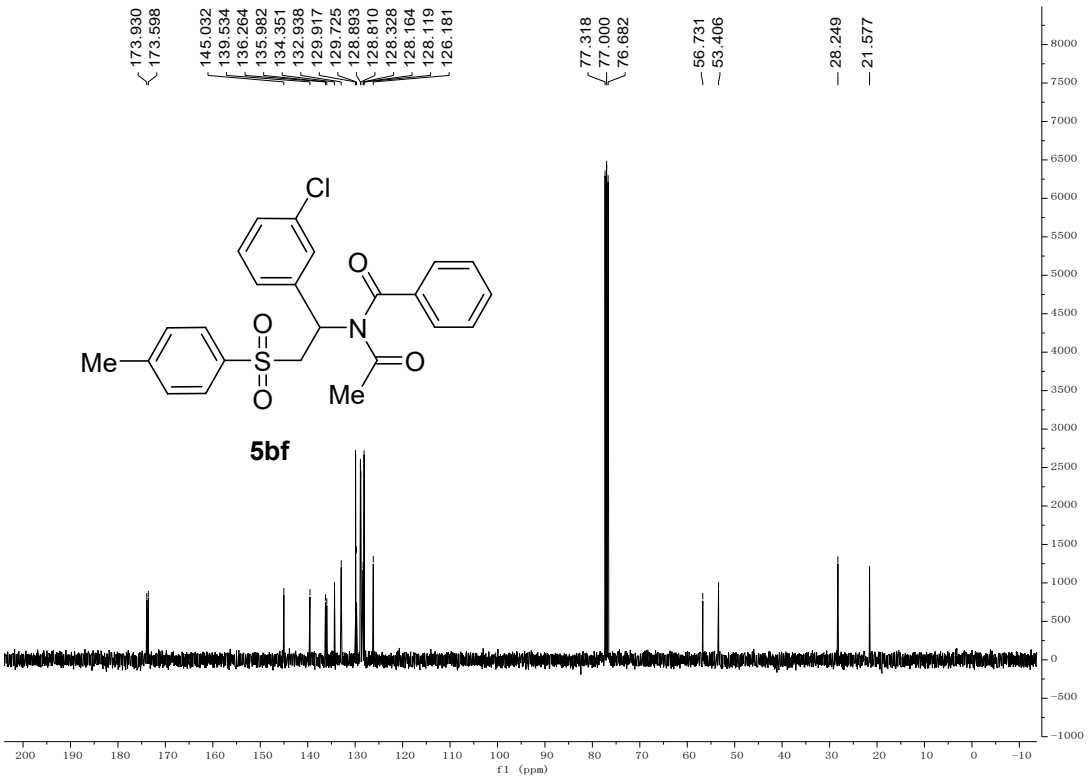
^{13}C NMR of **5be** in $CDCl_3$



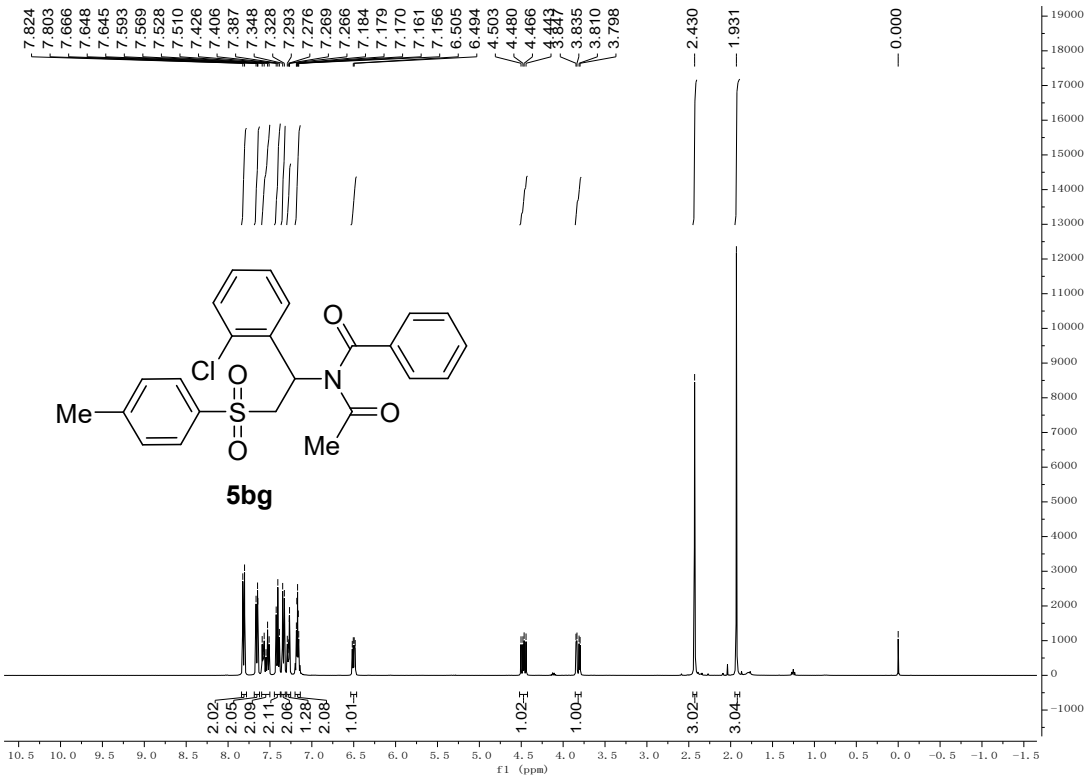
^{1}H NMR of **5bf** in $CDCl_3$



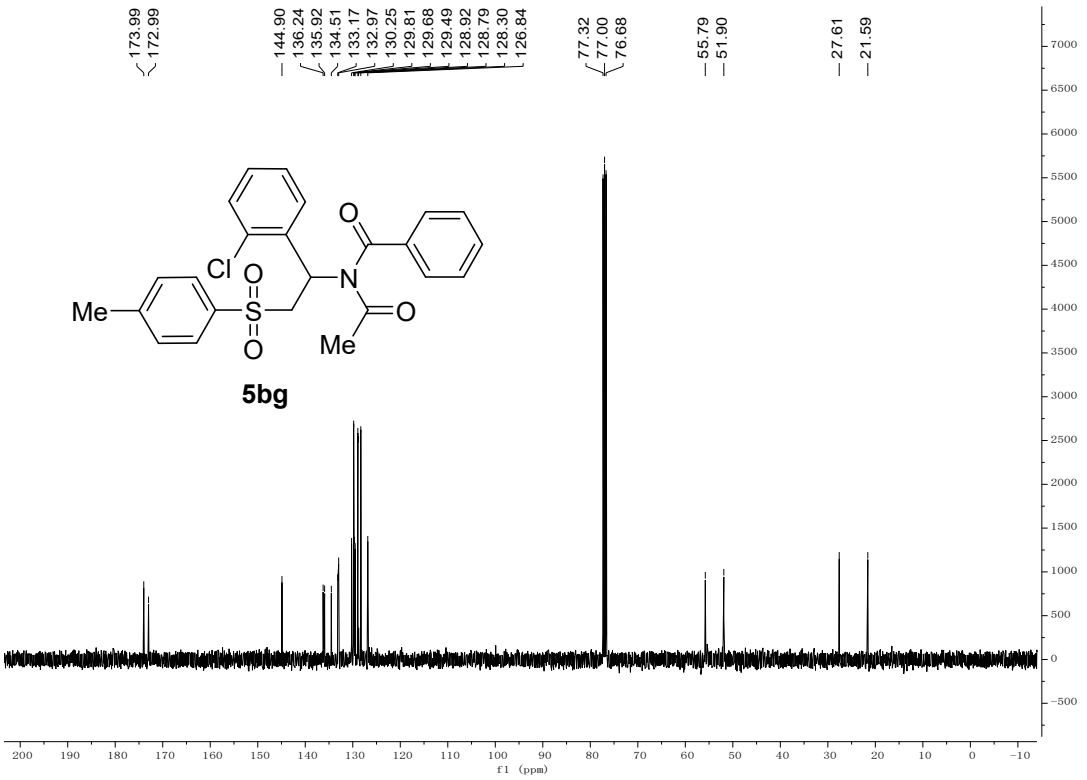
^{13}C NMR of **5bf** in $CDCl_3$



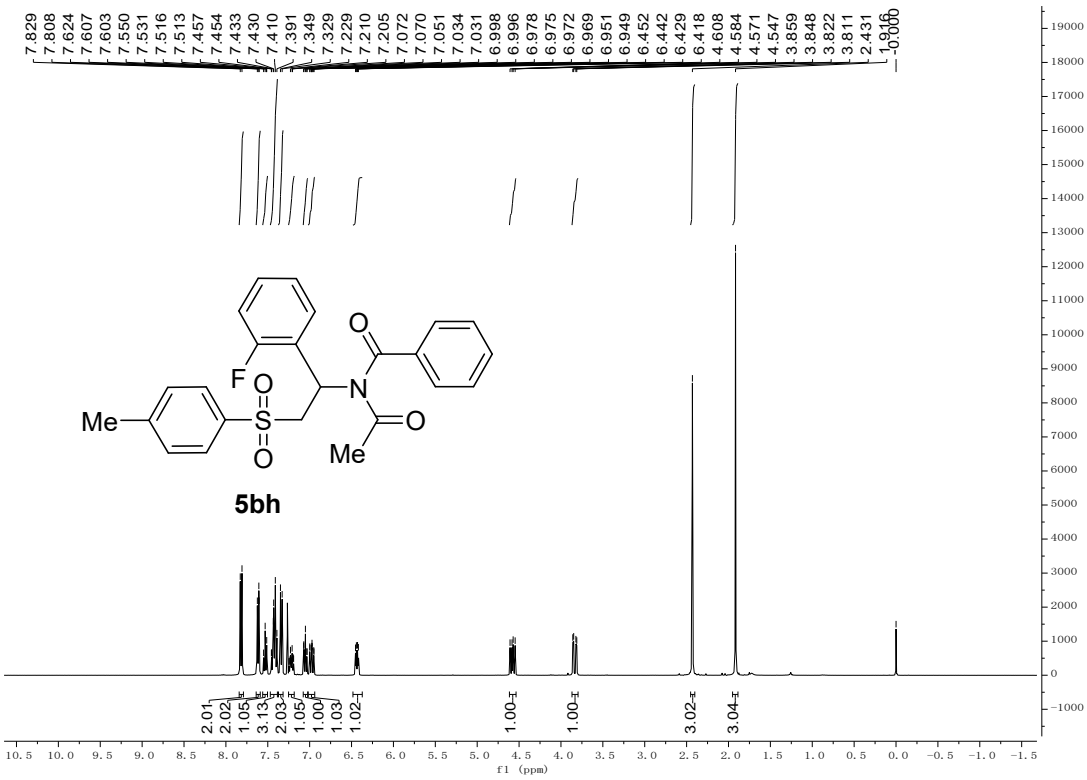
^{1}H NMR of **5bg** in $CDCl_3$



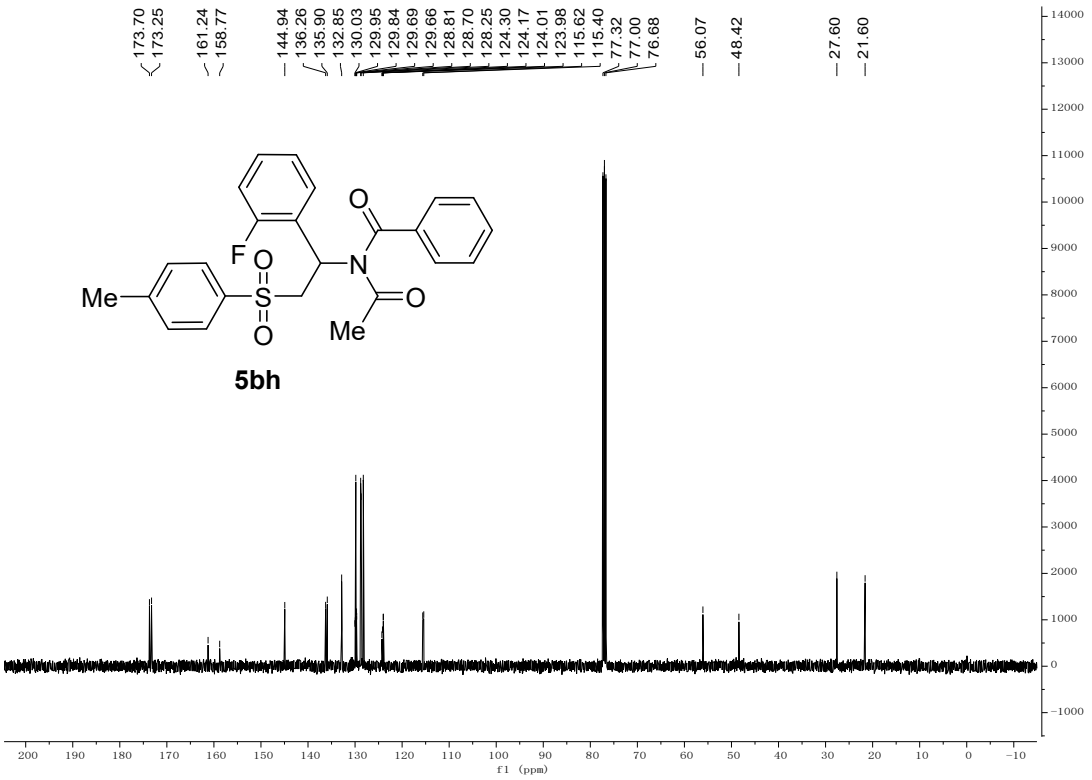
^{13}C NMR of **5bg** in $CDCl_3$



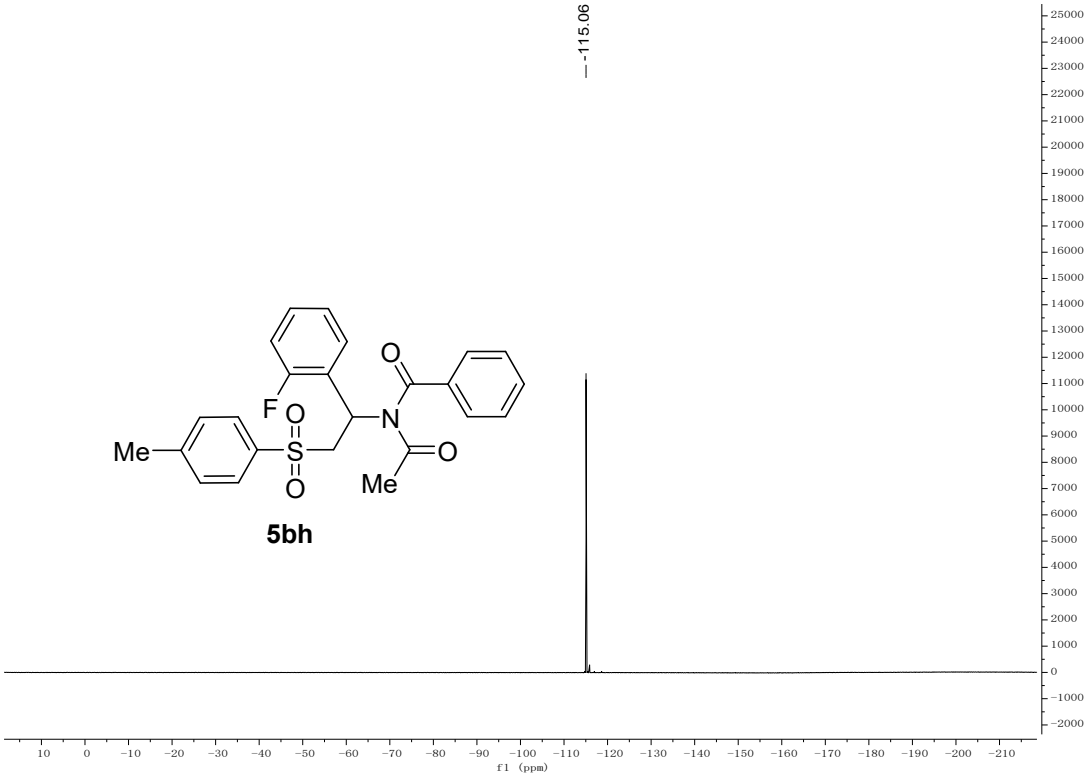
^{1}H NMR of **5bh** in $CDCl_3$



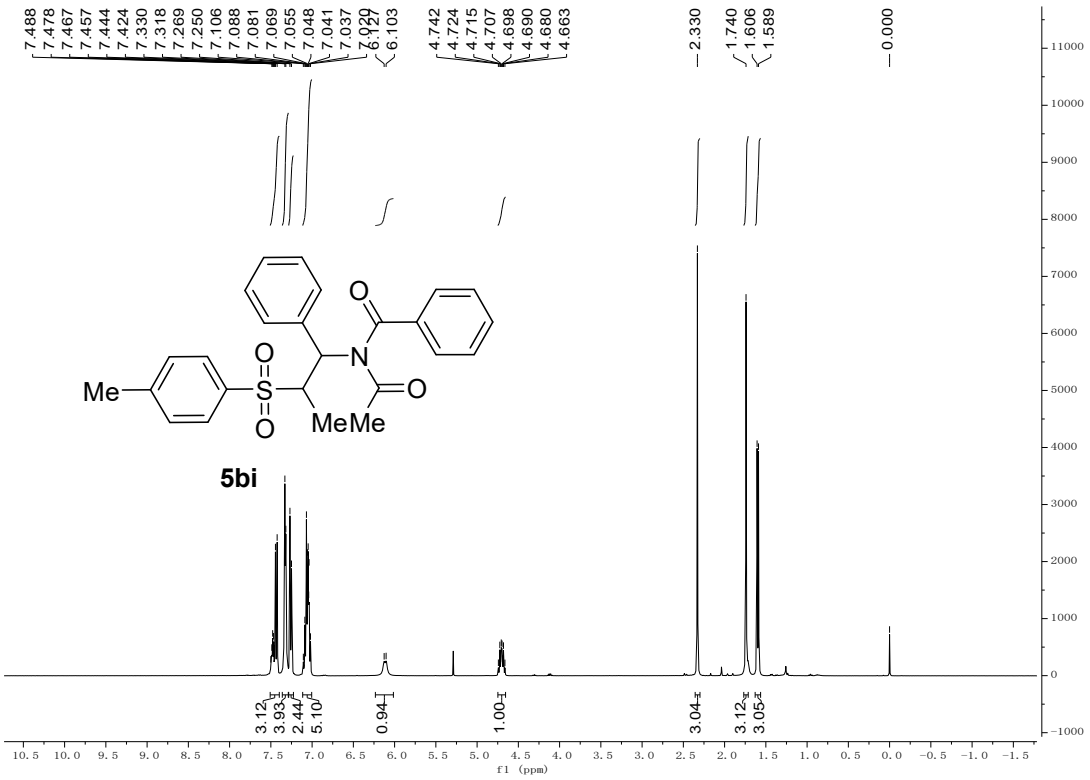
^{13}C NMR of **5bh** in $CDCl_3$



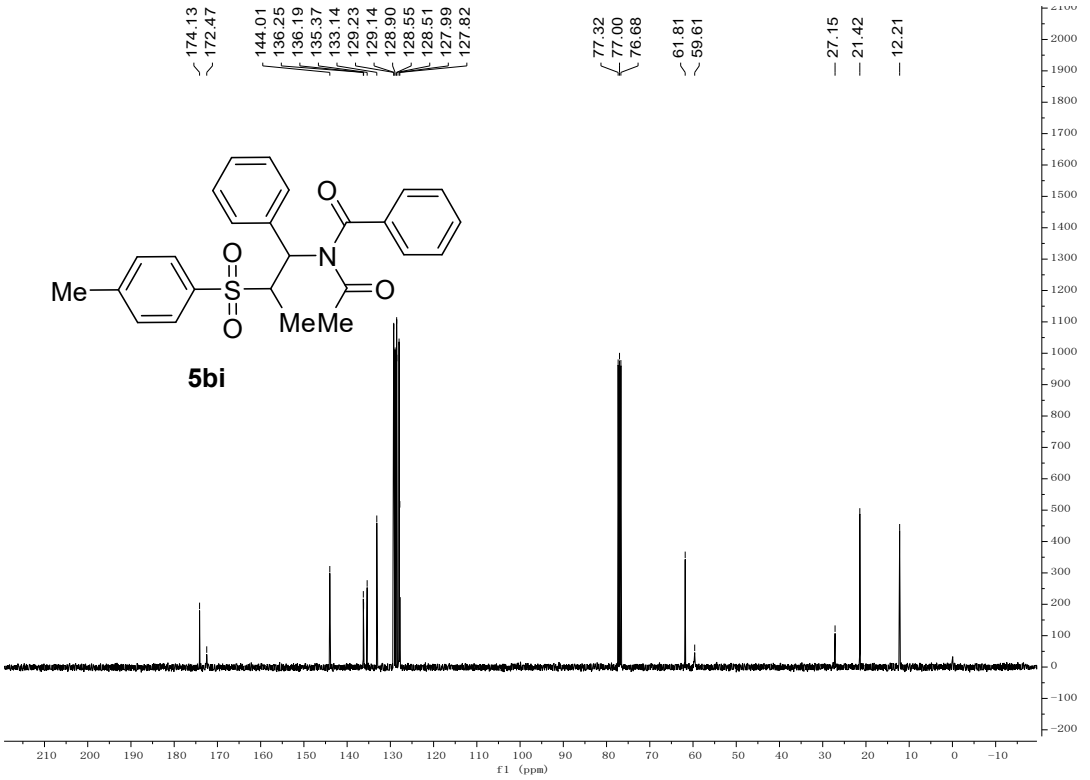
^{19}F NMR spectra of **5bh** in $CDCl_3$



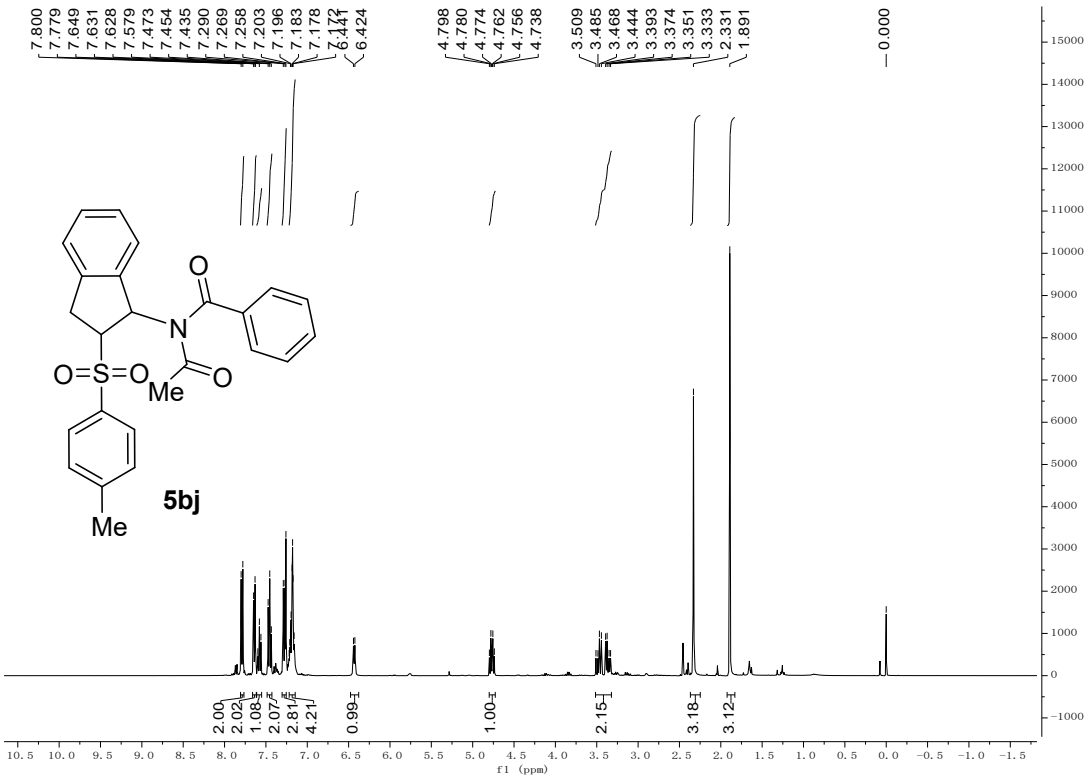
^{1}H NMR of **5bi** in $CDCl_3$



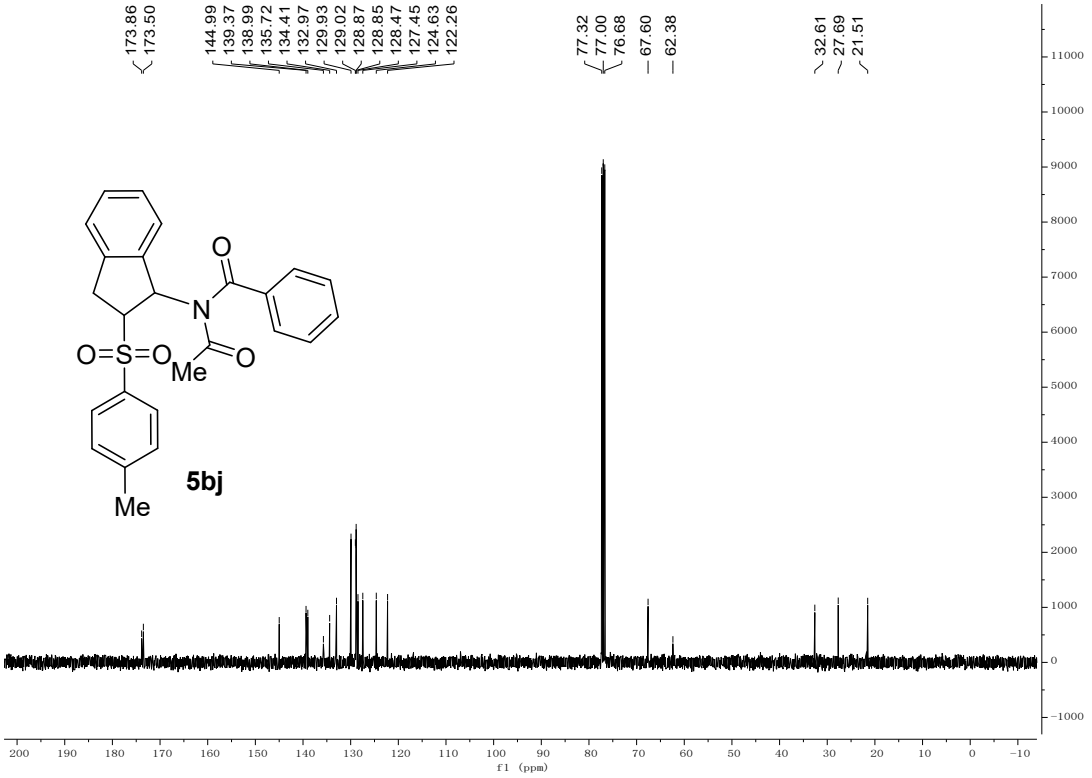
^{13}C NMR of **5bi** in $CDCl_3$



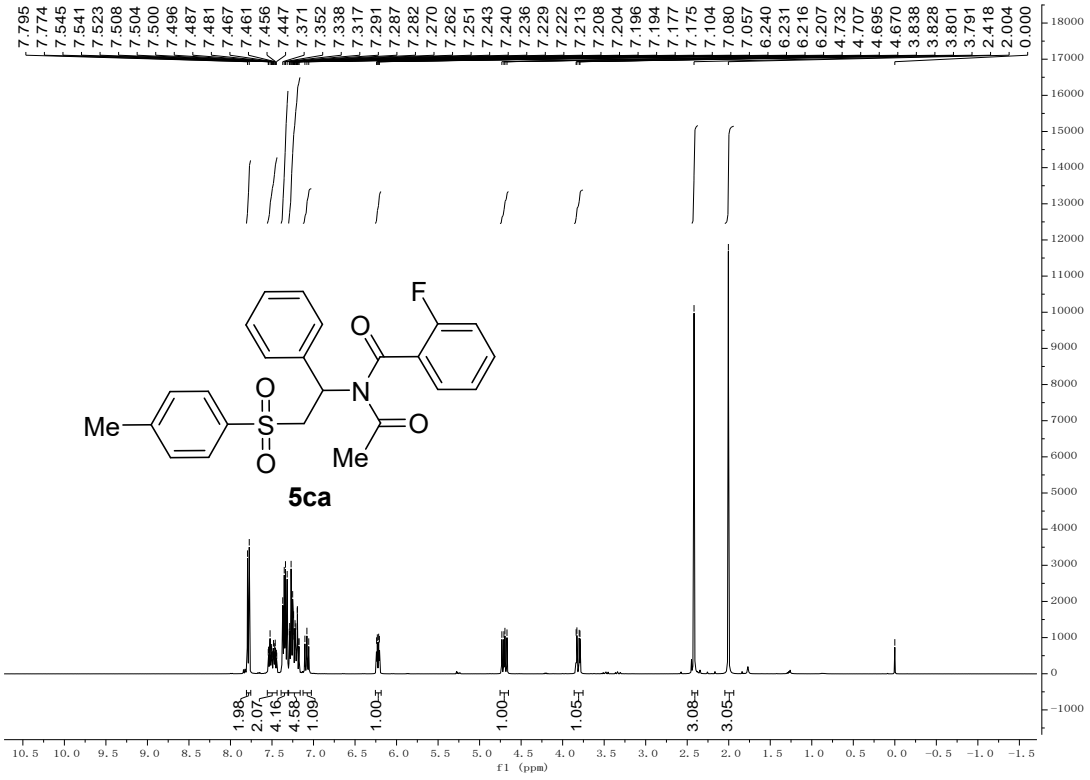
^{1}H NMR of **5bj** in $CDCl_3$



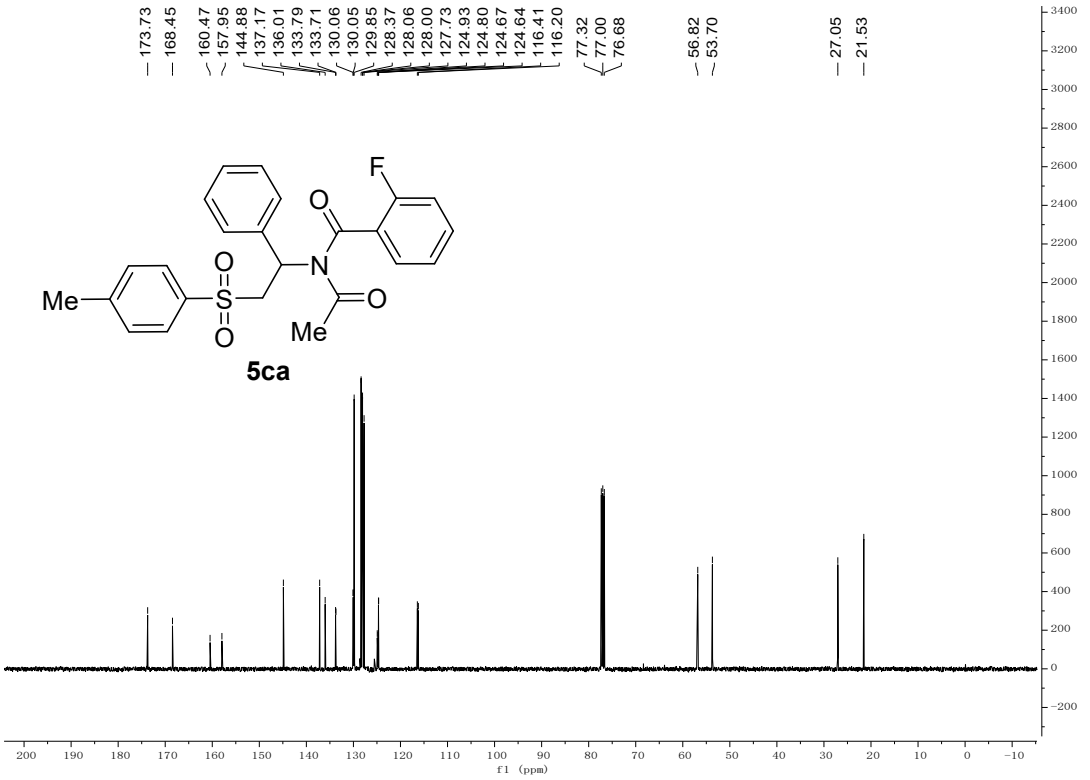
^{13}C NMR of **5bj** in $CDCl_3$



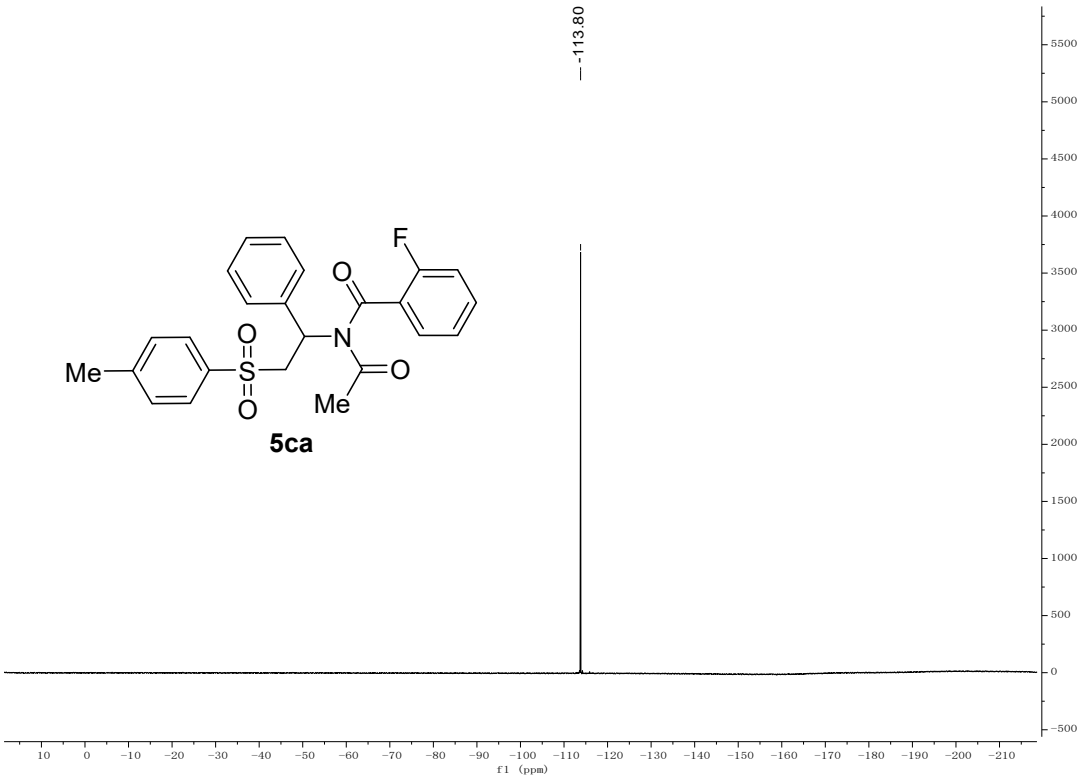
^{1}H NMR of **5ca** in $CDCl_3$



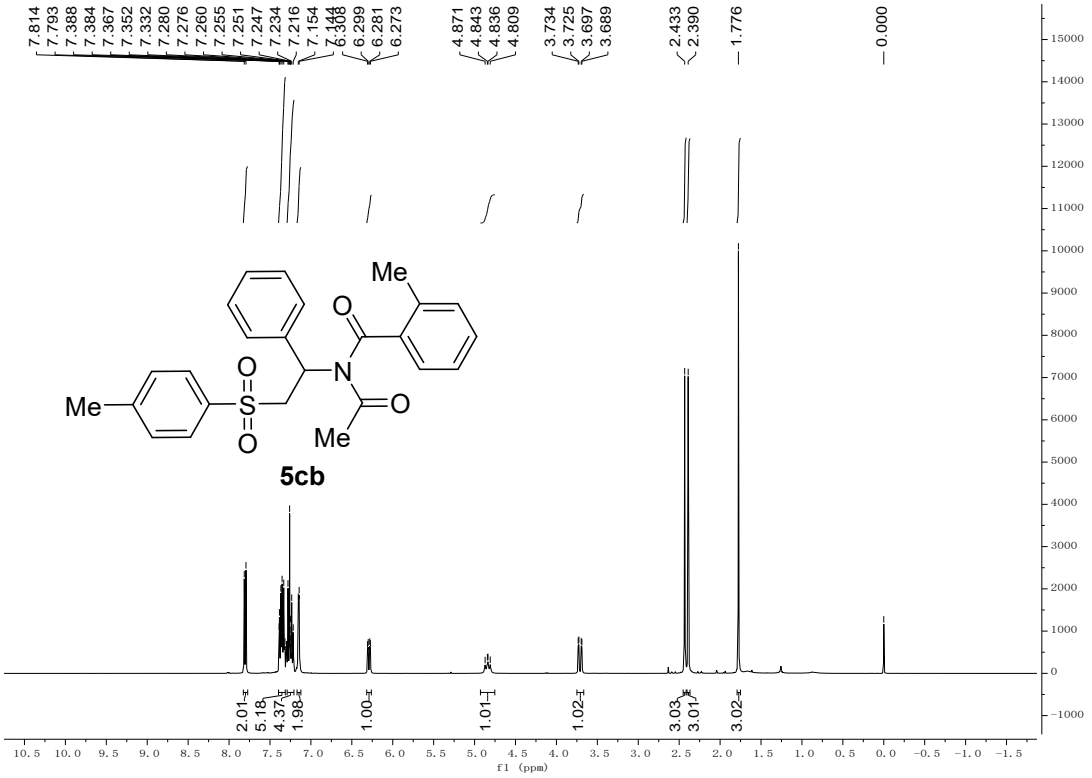
^{13}C NMR of **5ca** in $CDCl_3$



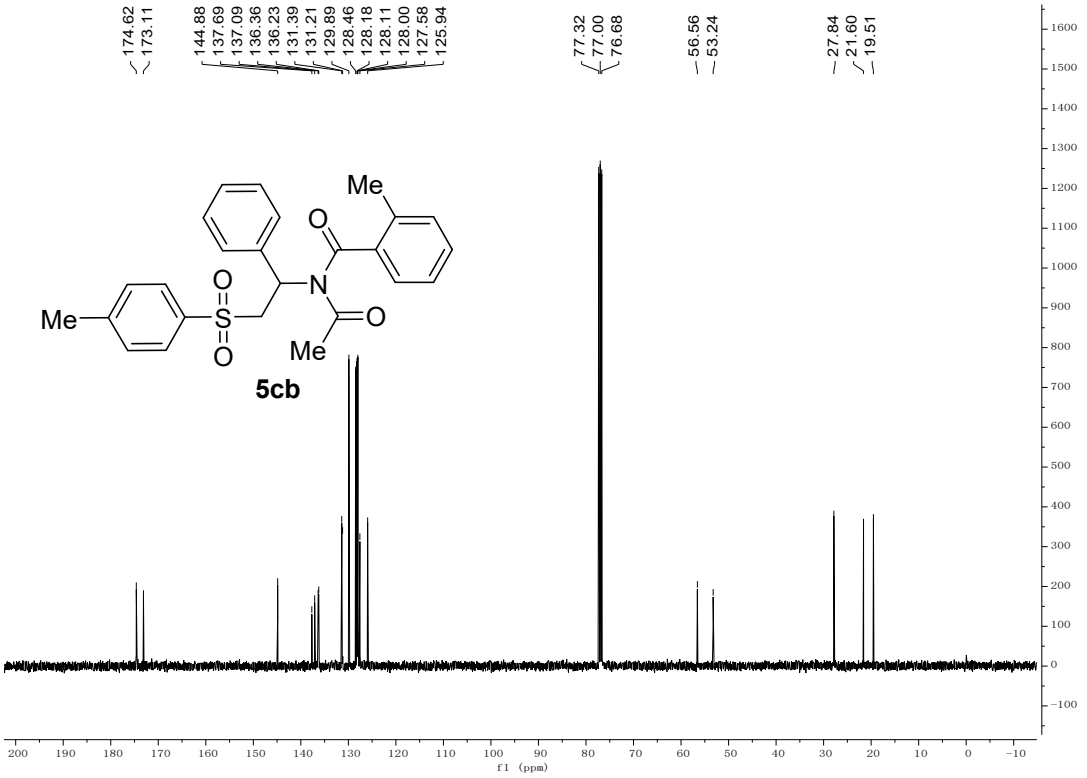
^{19}F NMR spectra of **5ca** in $CDCl_3$



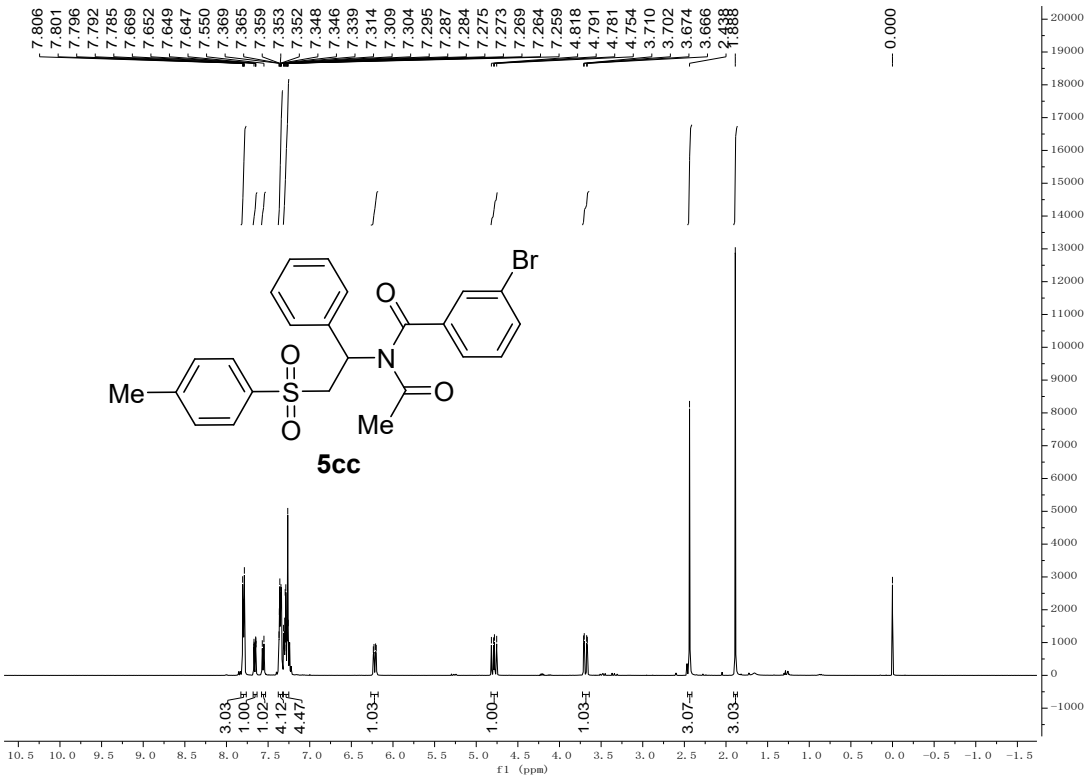
^{1}H NMR of **5cb** in $CDCl_3$



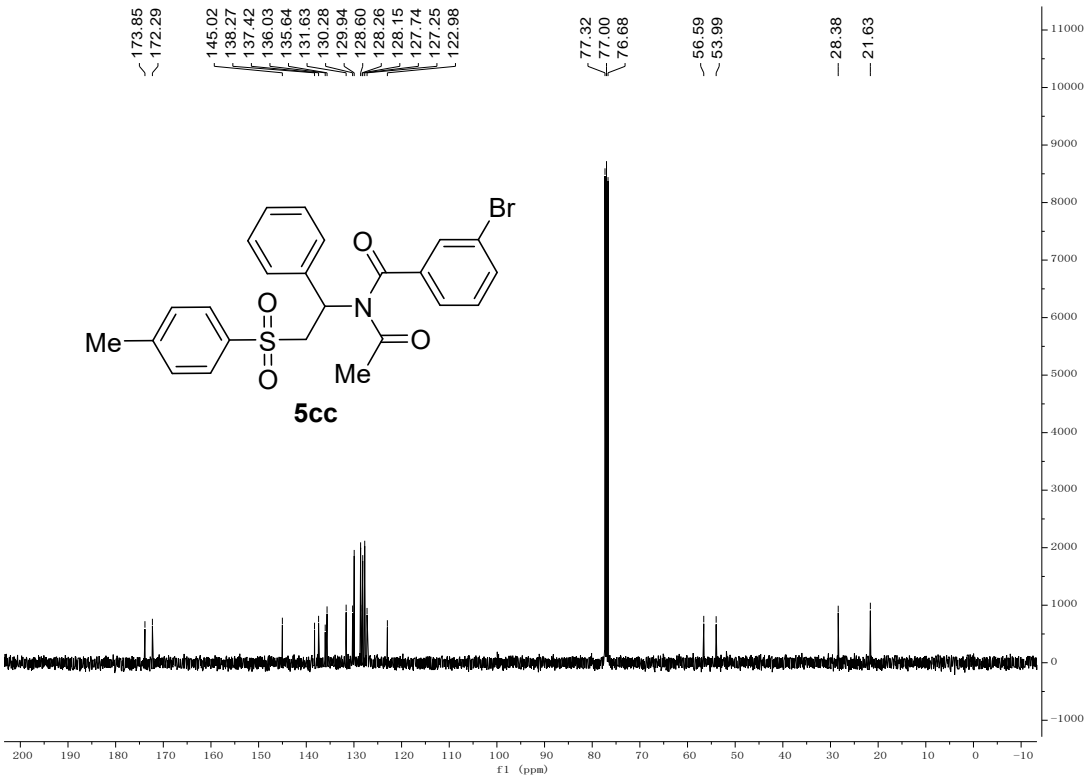
^{13}C NMR of **5cb** in $CDCl_3$



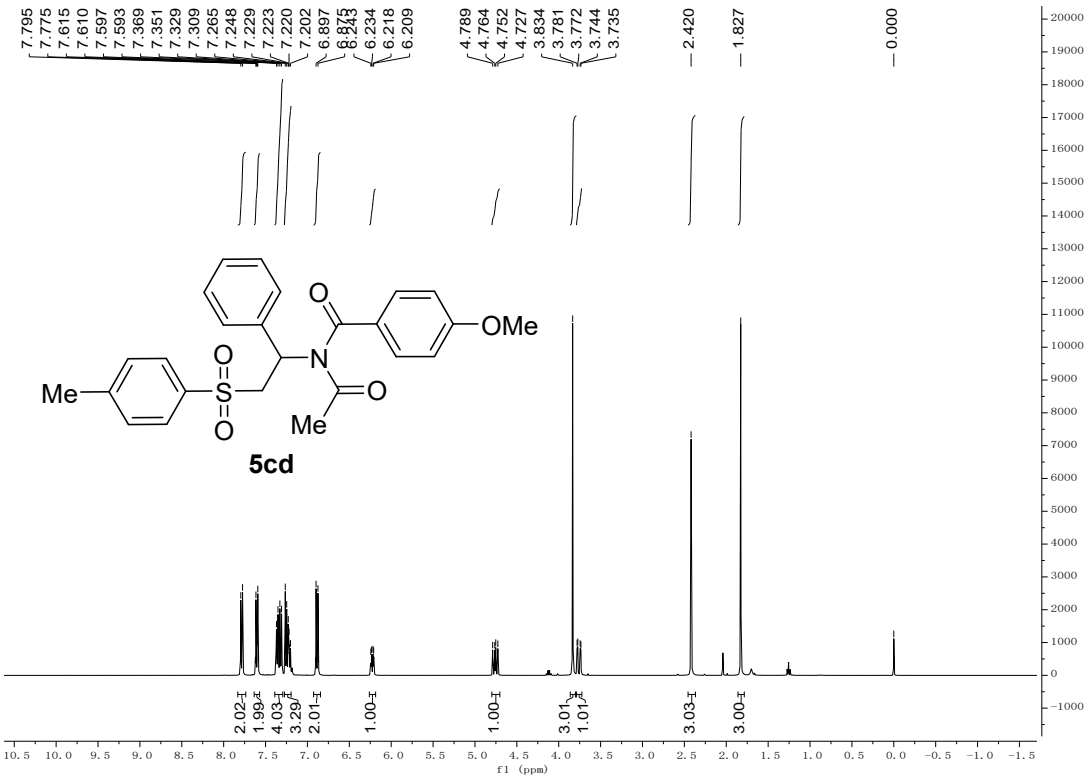
^{1}H NMR of **5cc** in $CDCl_3$



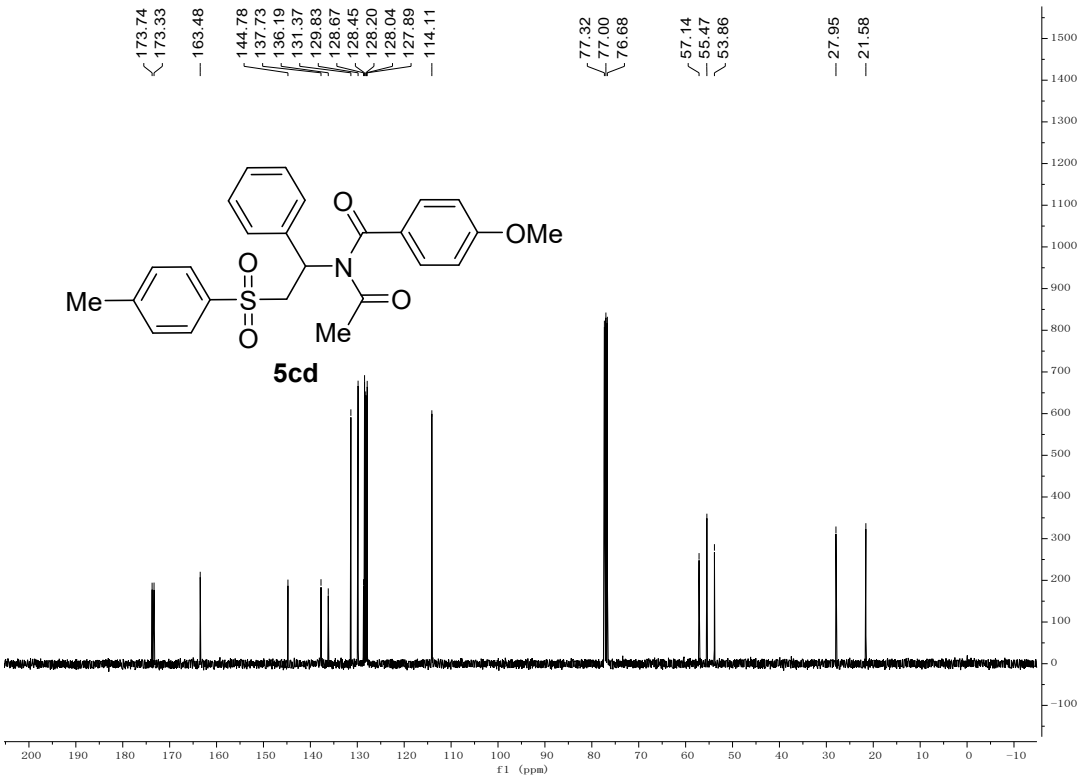
^{13}C NMR of **5cc** in $CDCl_3$



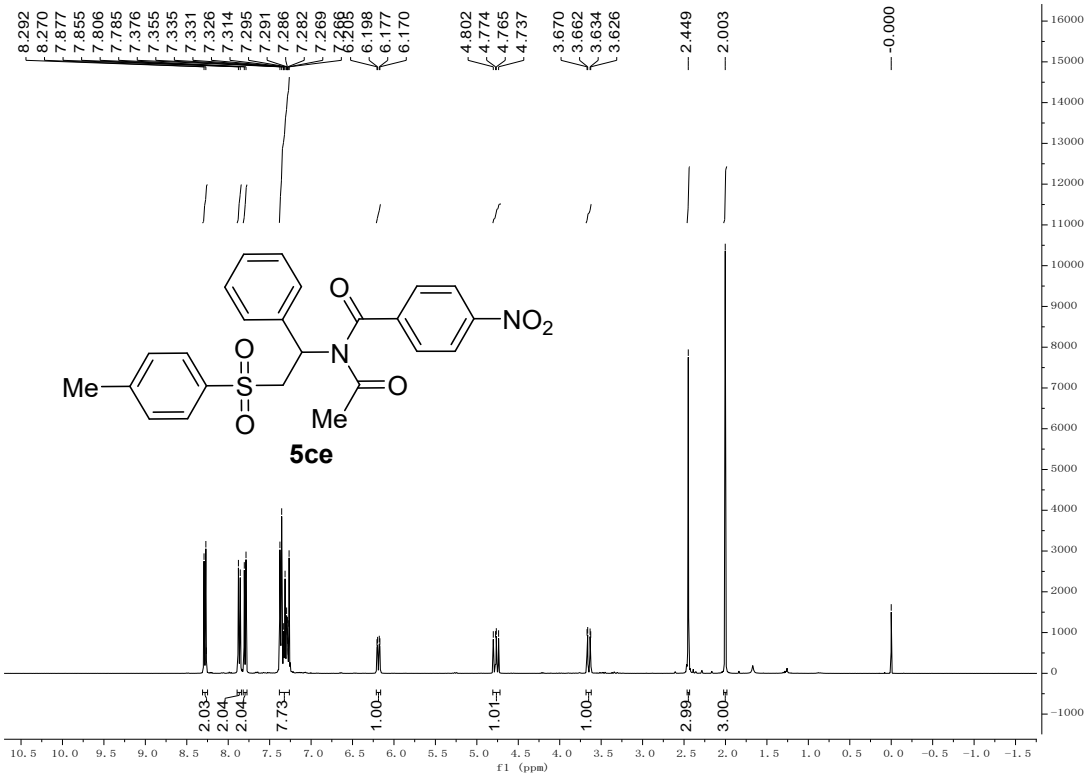
^{1}H NMR of **5cd** in $CDCl_3$



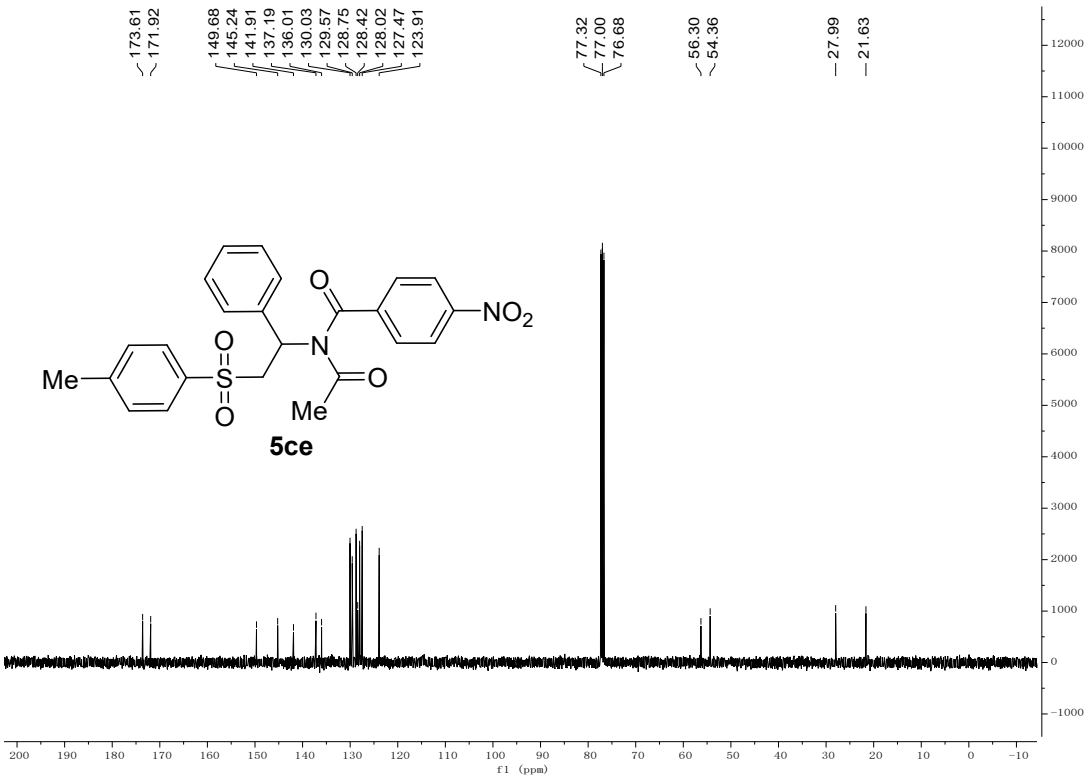
^{13}C NMR of **5cd** in $CDCl_3$



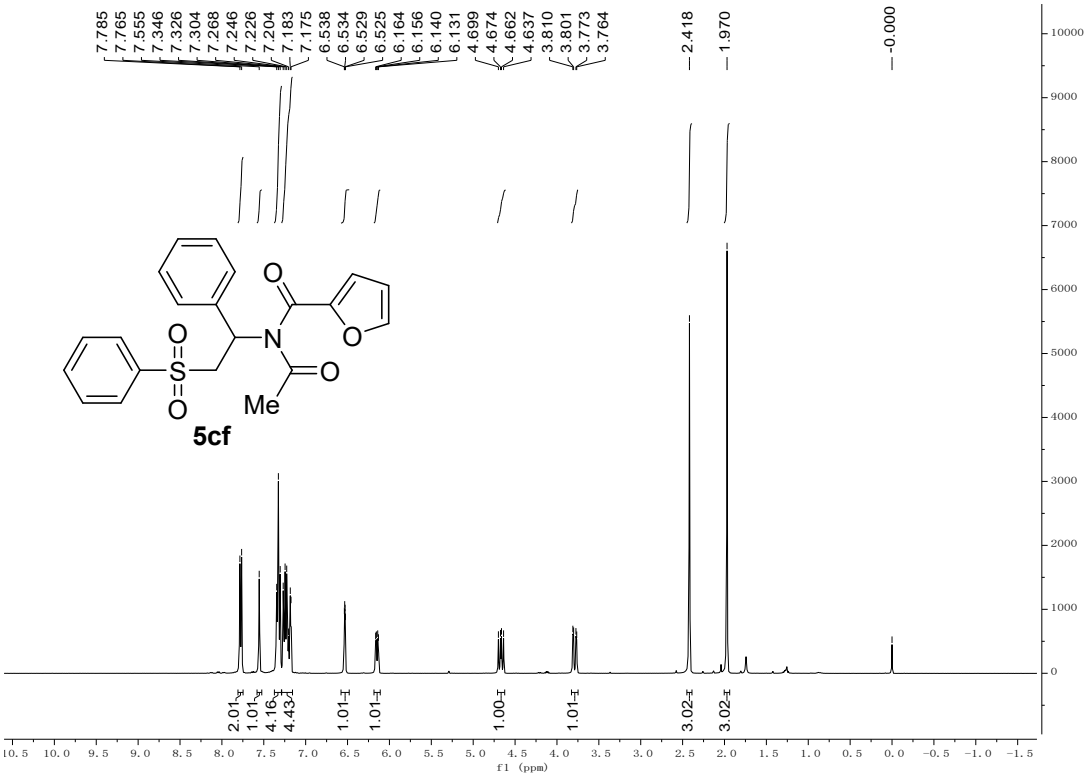
^{1}H NMR of **5ce** in $CDCl_3$



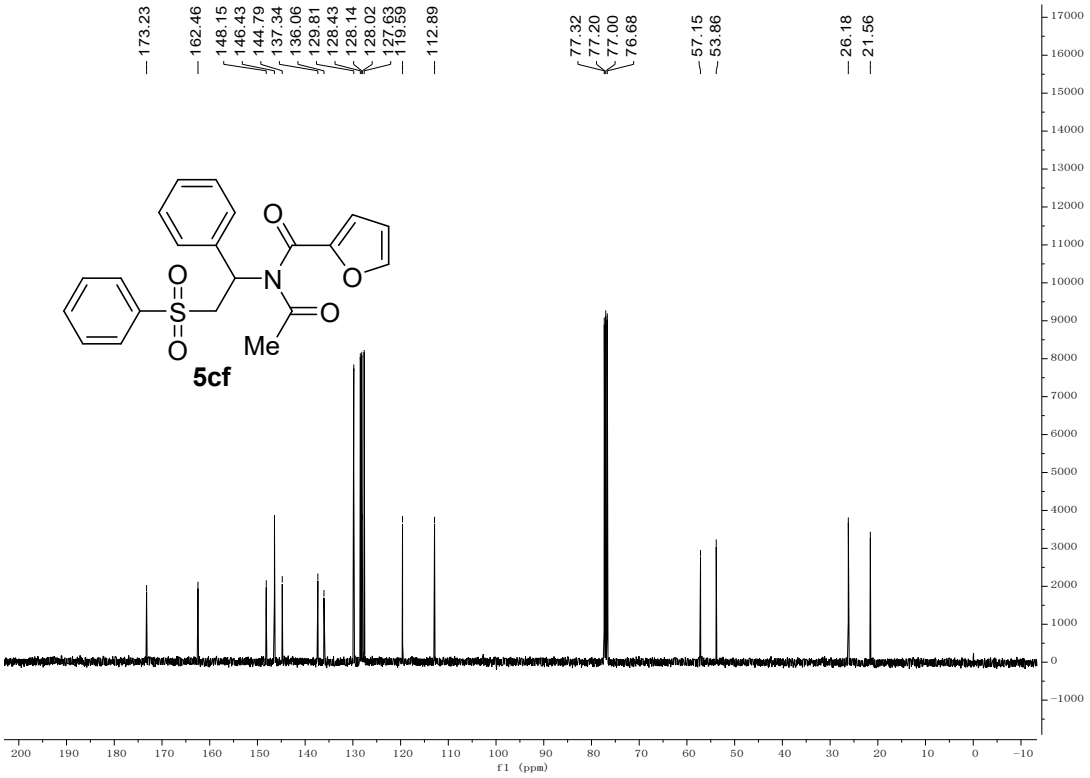
^{13}C NMR of **5ce** in $CDCl_3$



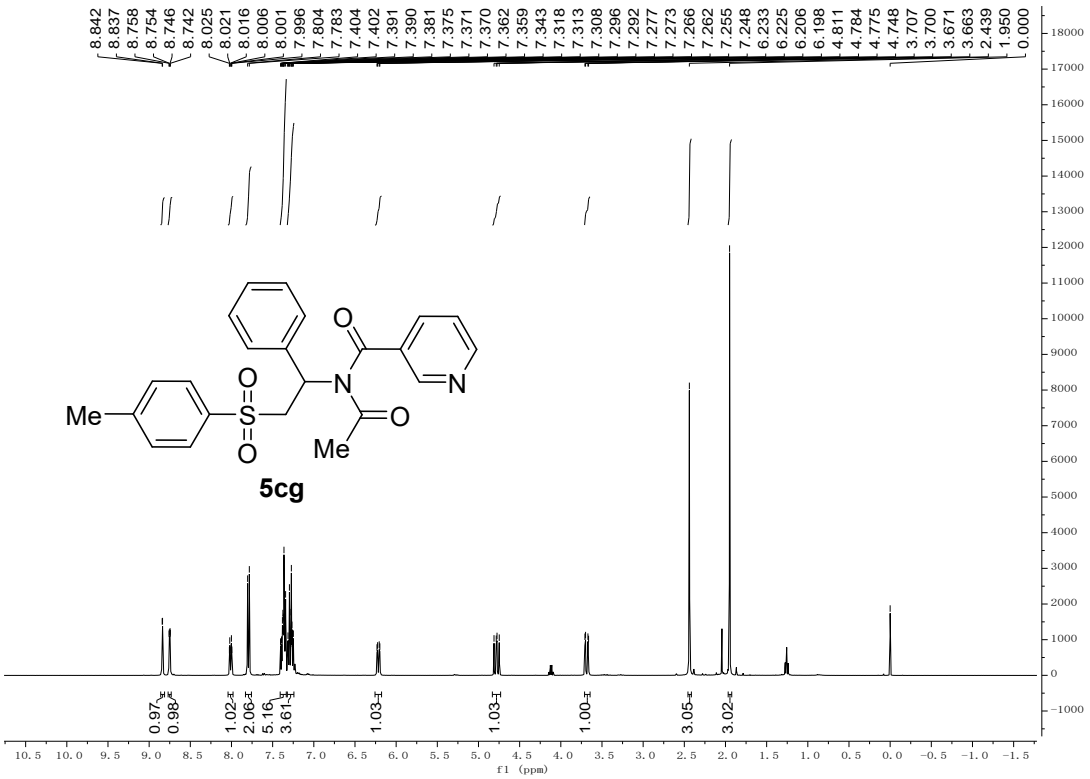
^{1}H NMR of **5cf** in $CDCl_3$



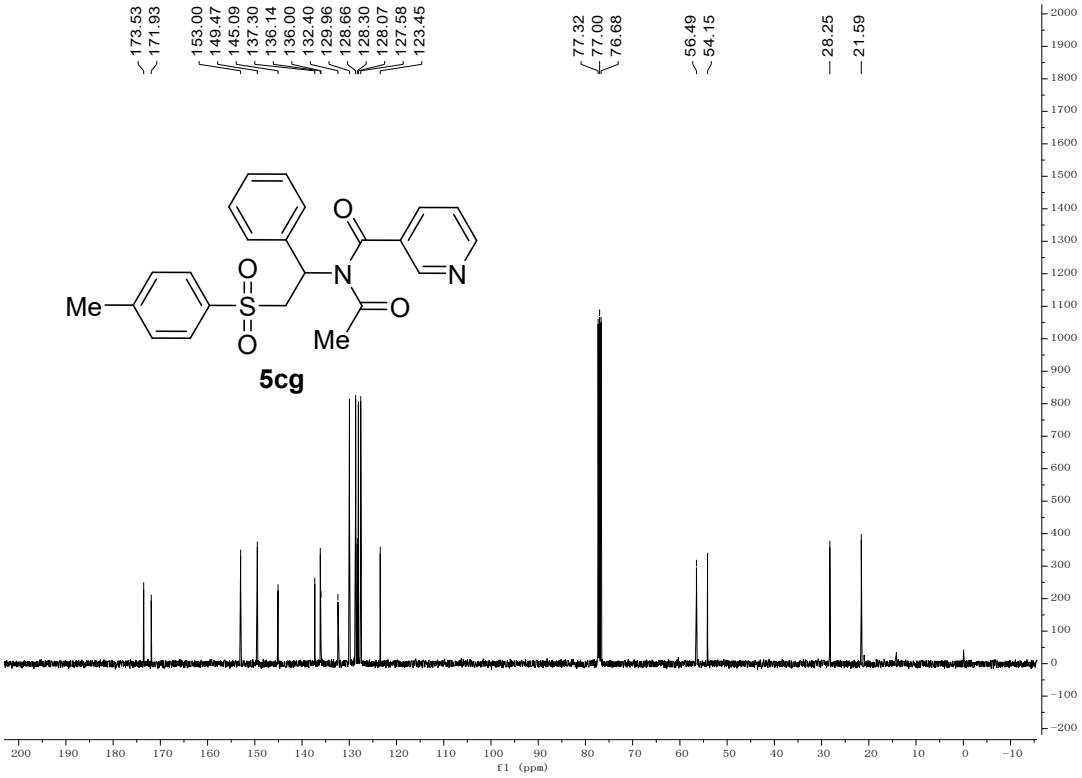
^{13}C NMR of **5cf** in $CDCl_3$



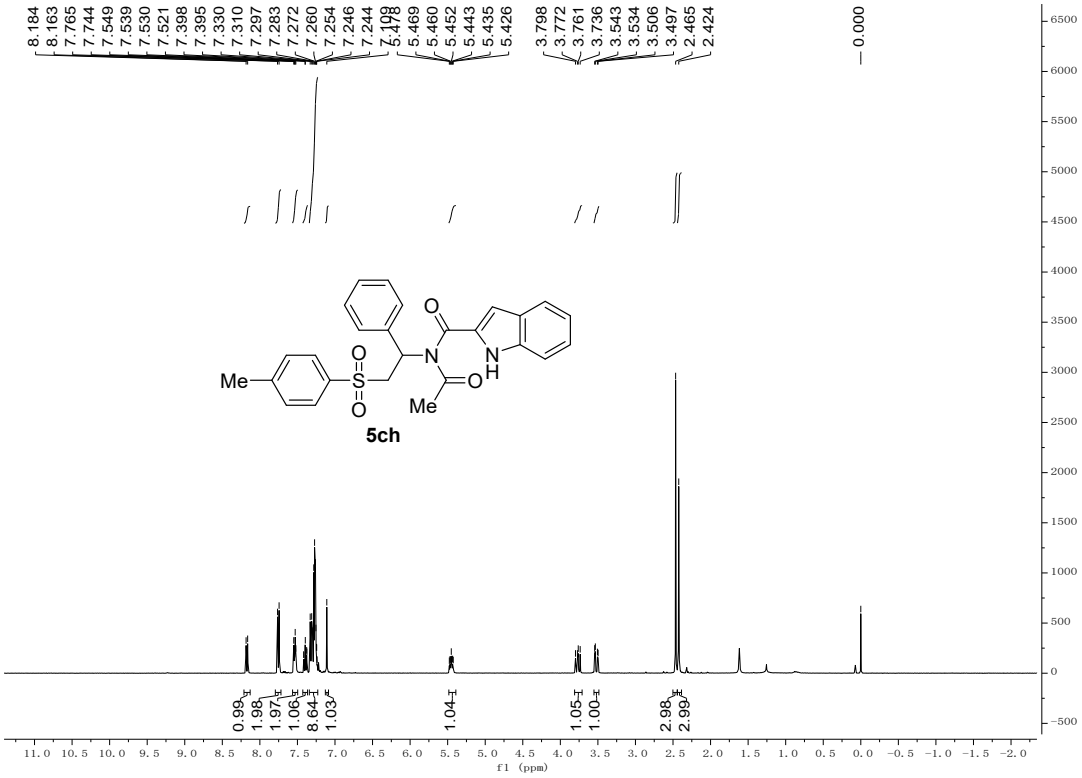
^{1}H NMR of **5cg** in $CDCl_3$



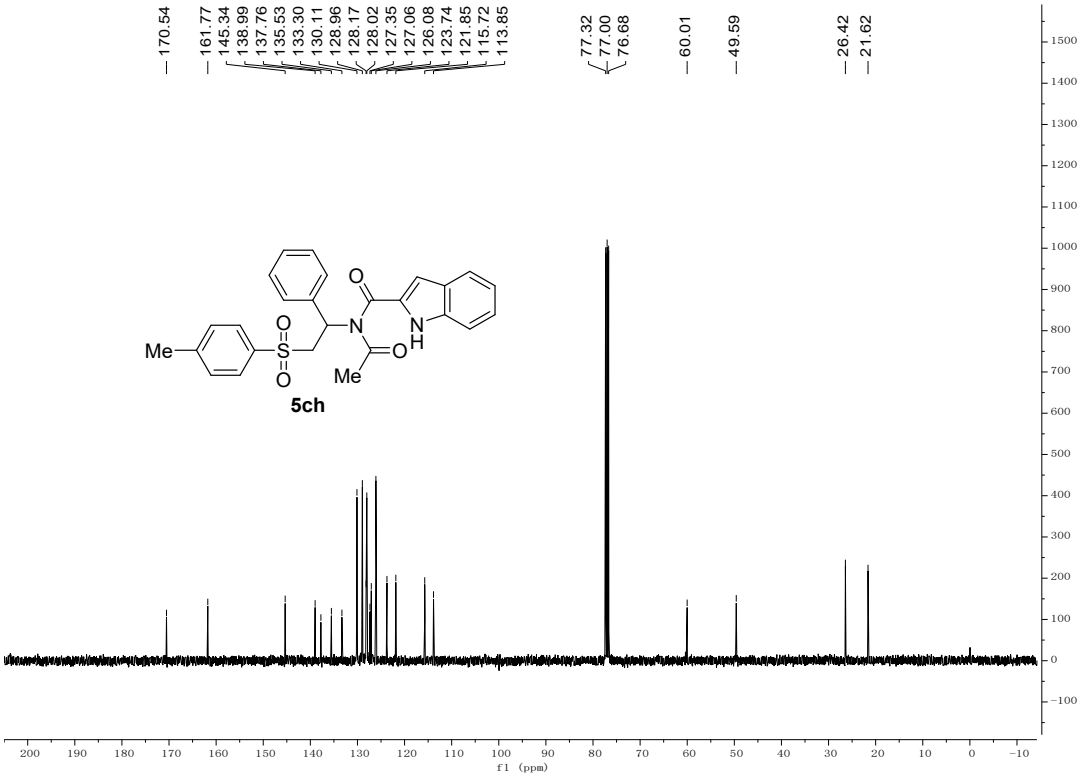
^{13}C NMR of **5cg** in $CDCl_3$



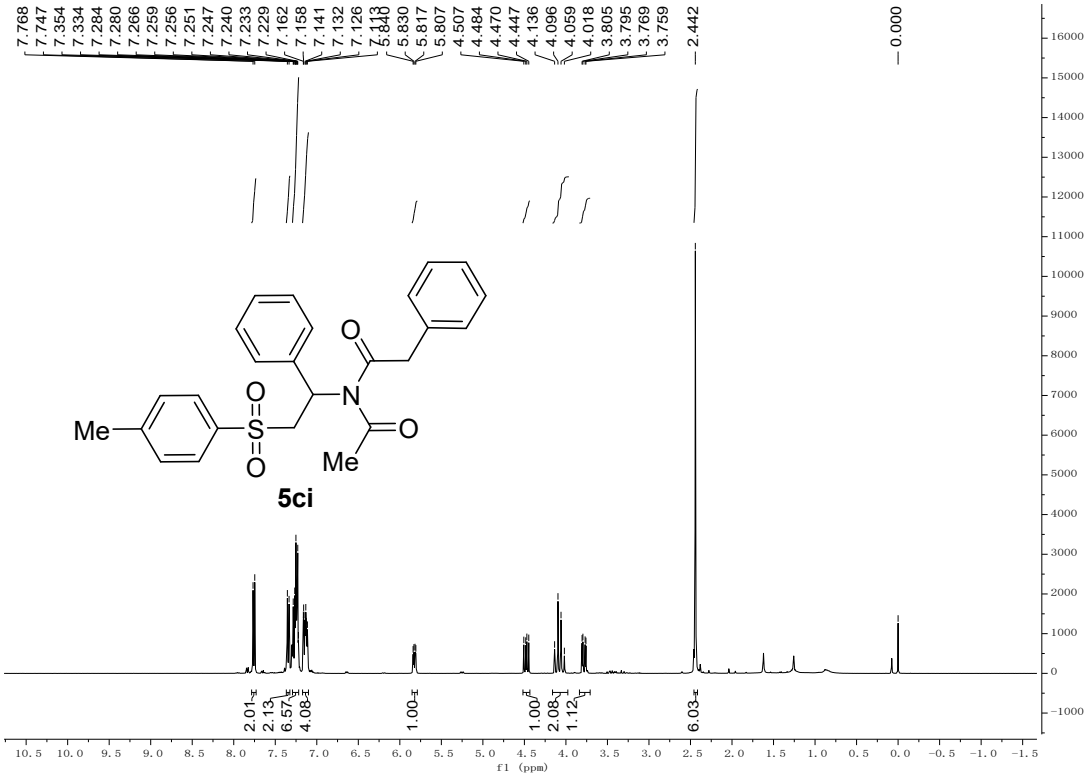
^{1}H NMR of **5ch** in $CDCl_3$



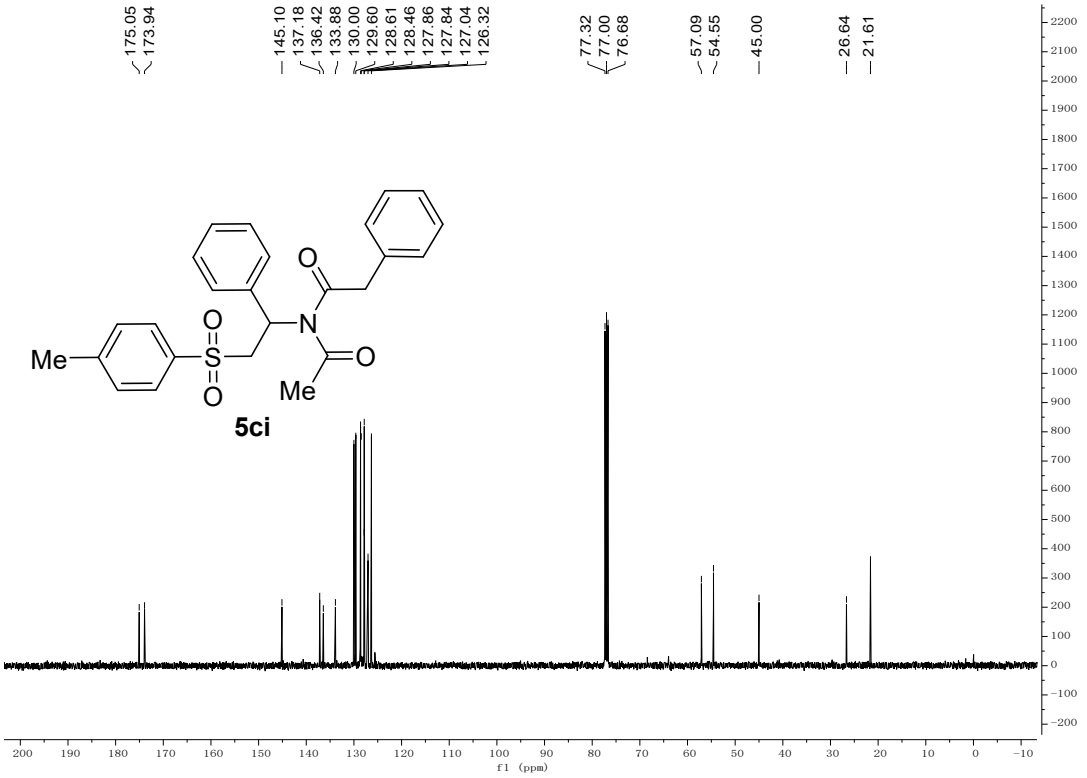
^{13}C NMR of **5ch** in $CDCl_3$



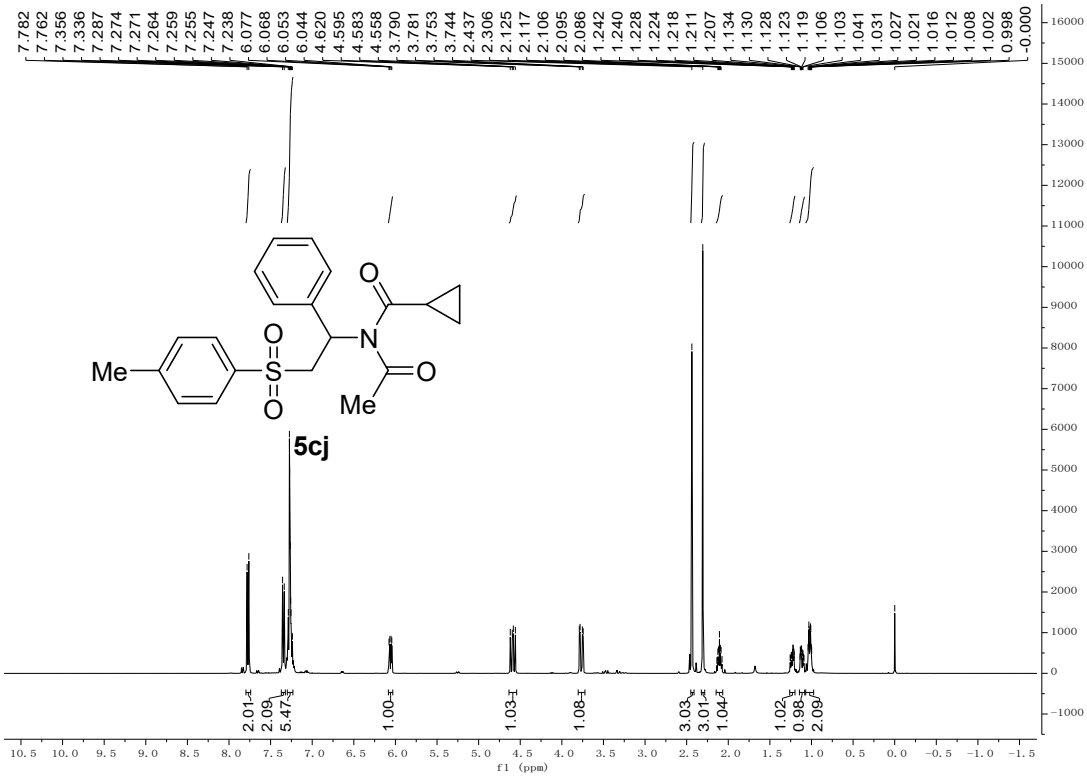
^{1}H NMR of **5ci** in $CDCl_3$



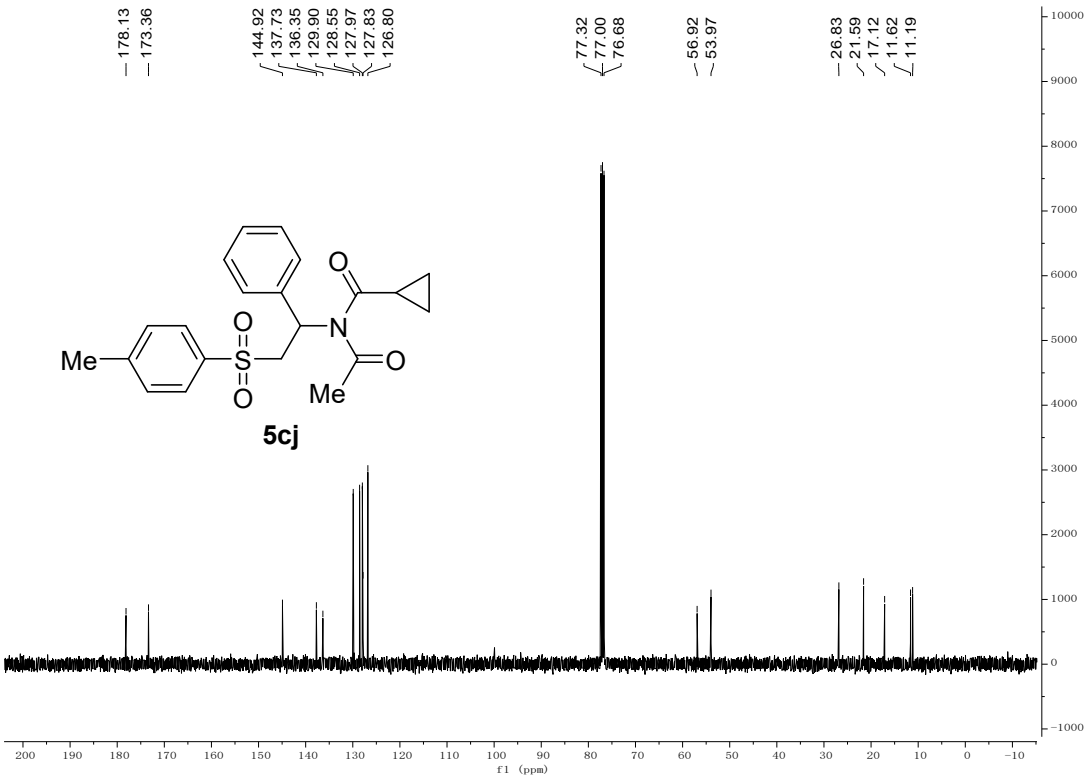
^{13}C NMR of **5ci** in $CDCl_3$



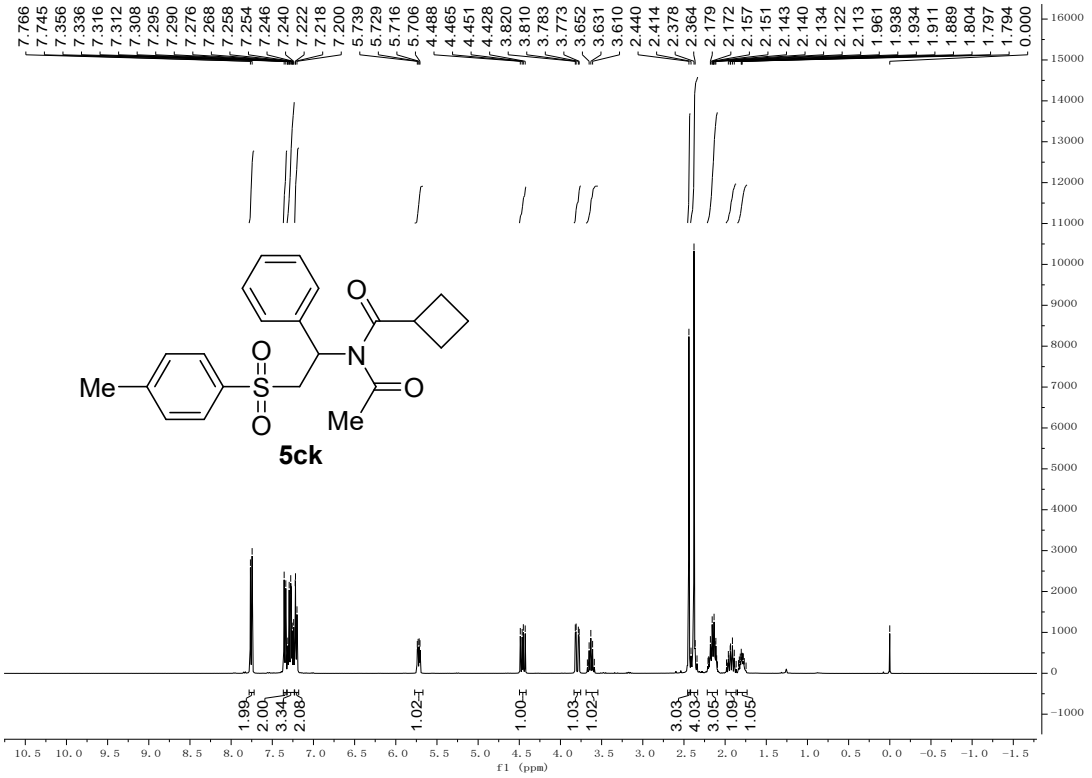
^{1}H NMR of **5cj** in $CDCl_3$



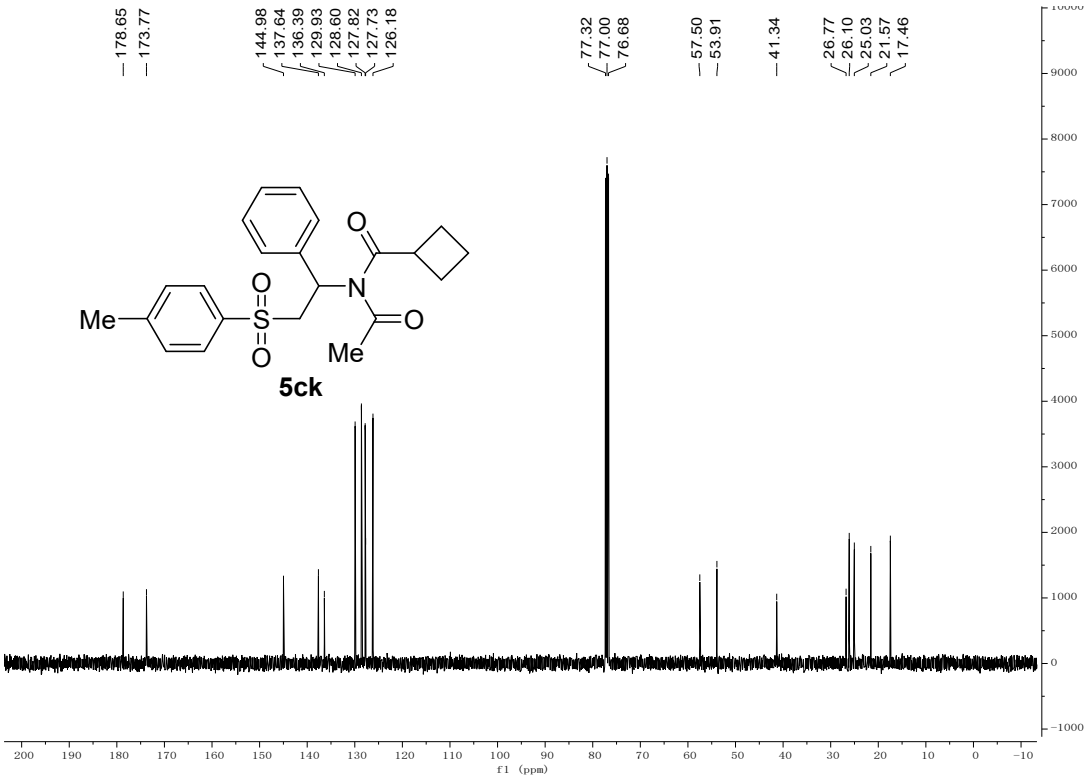
^{13}C NMR of **5cj** in $CDCl_3$



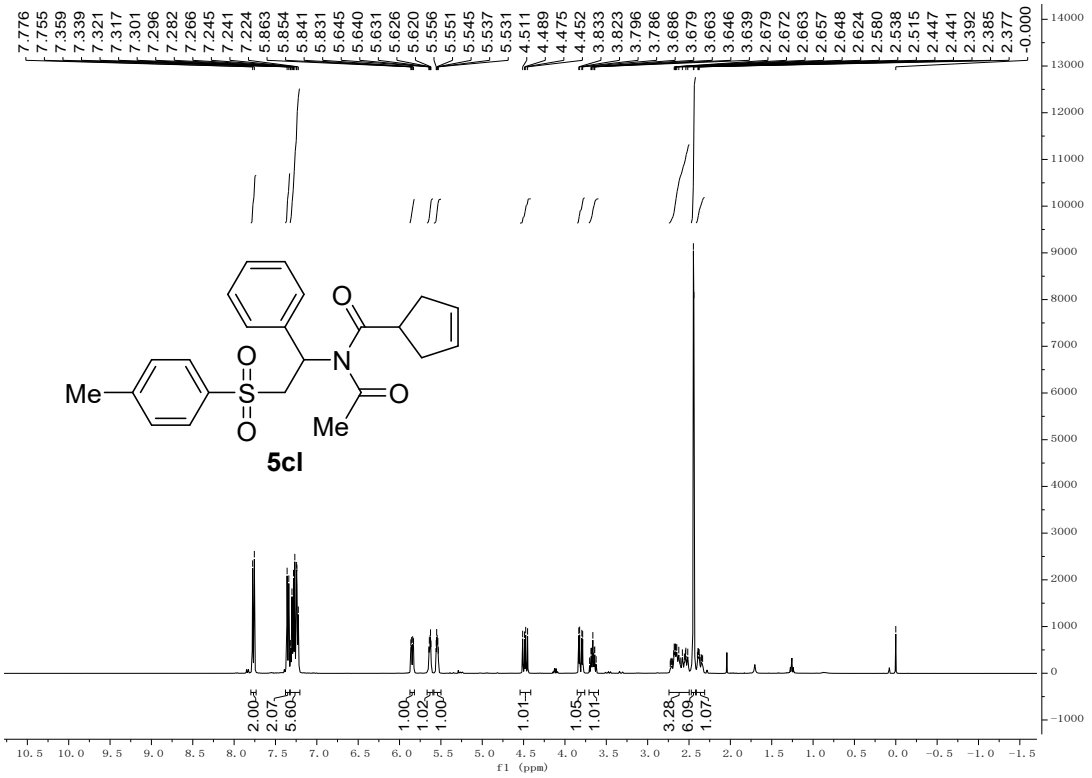
^{1}H NMR of **5ck** in $CDCl_3$



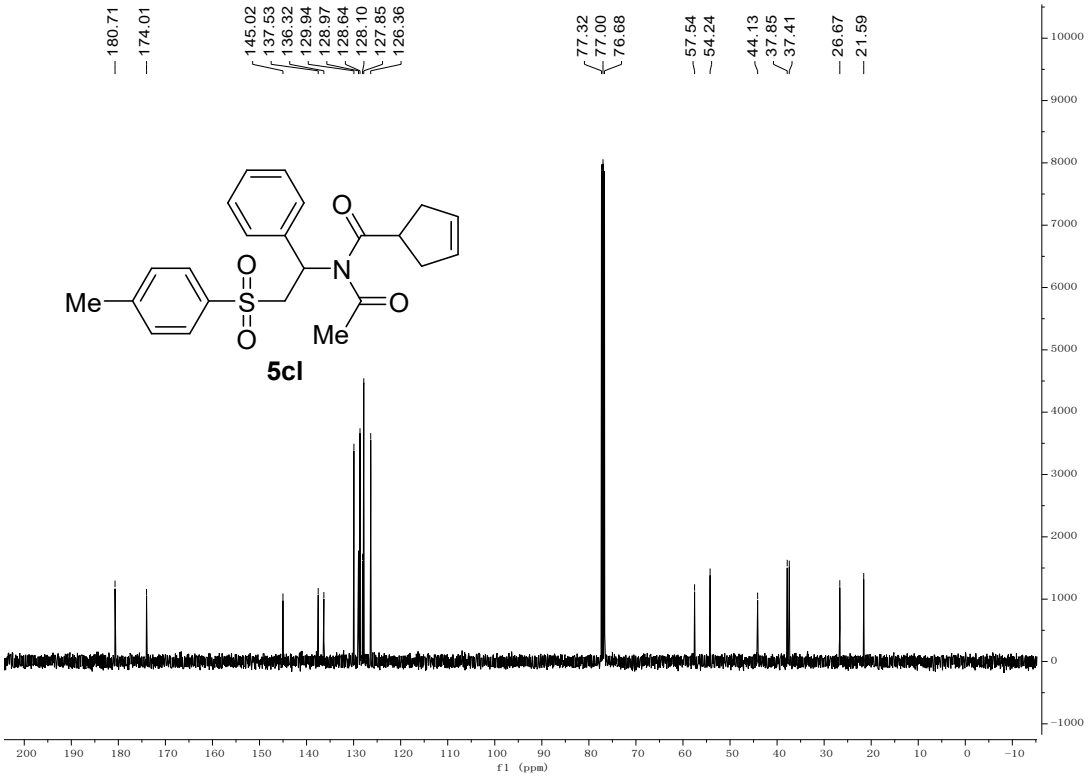
^{13}C NMR of **5ck** in $CDCl_3$



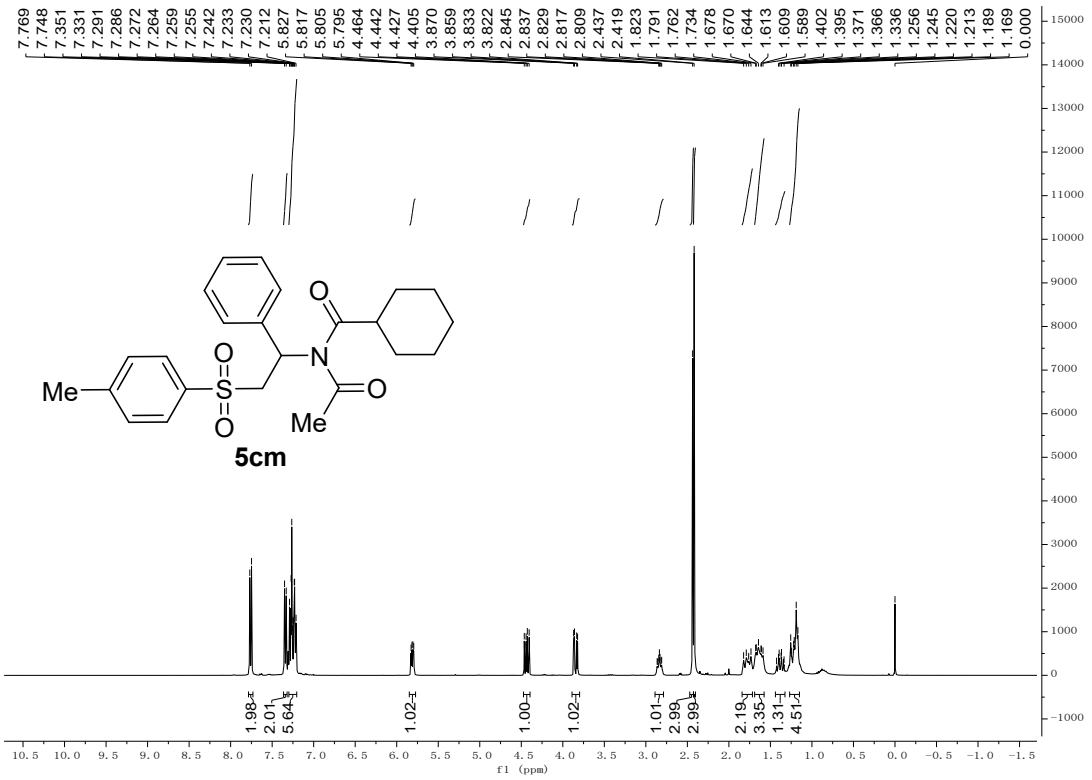
^{1}H NMR of **5cl** in $CDCl_3$



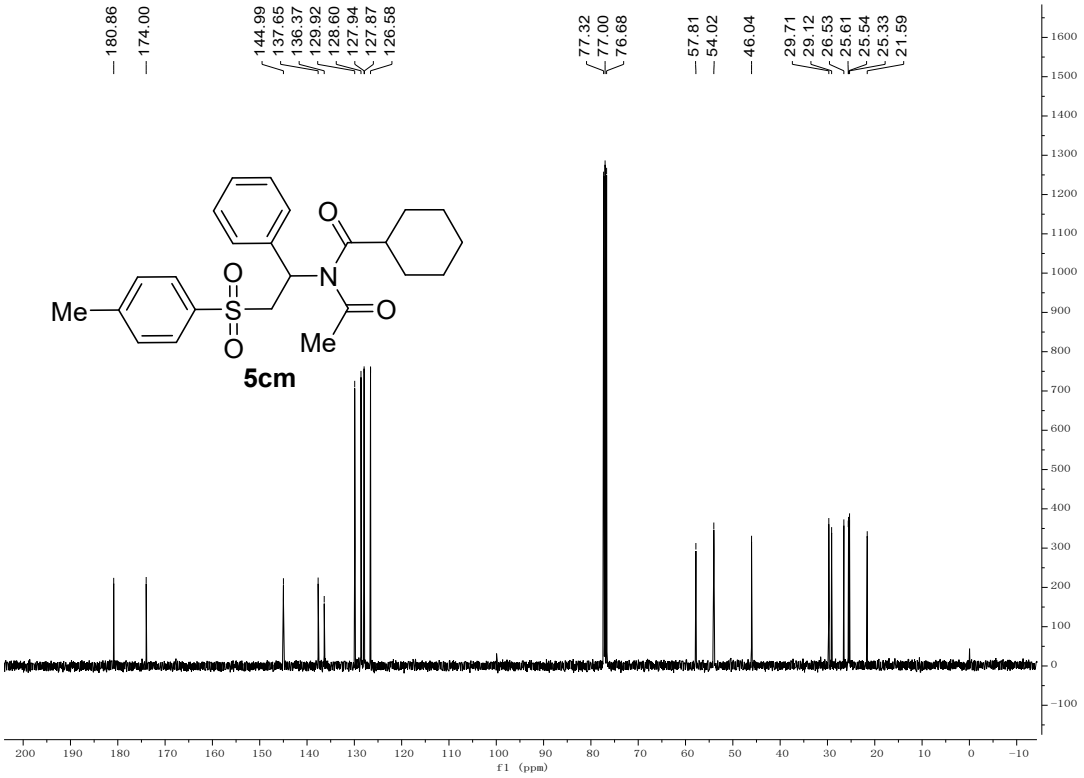
^{13}C NMR of **5cl** in $CDCl_3$



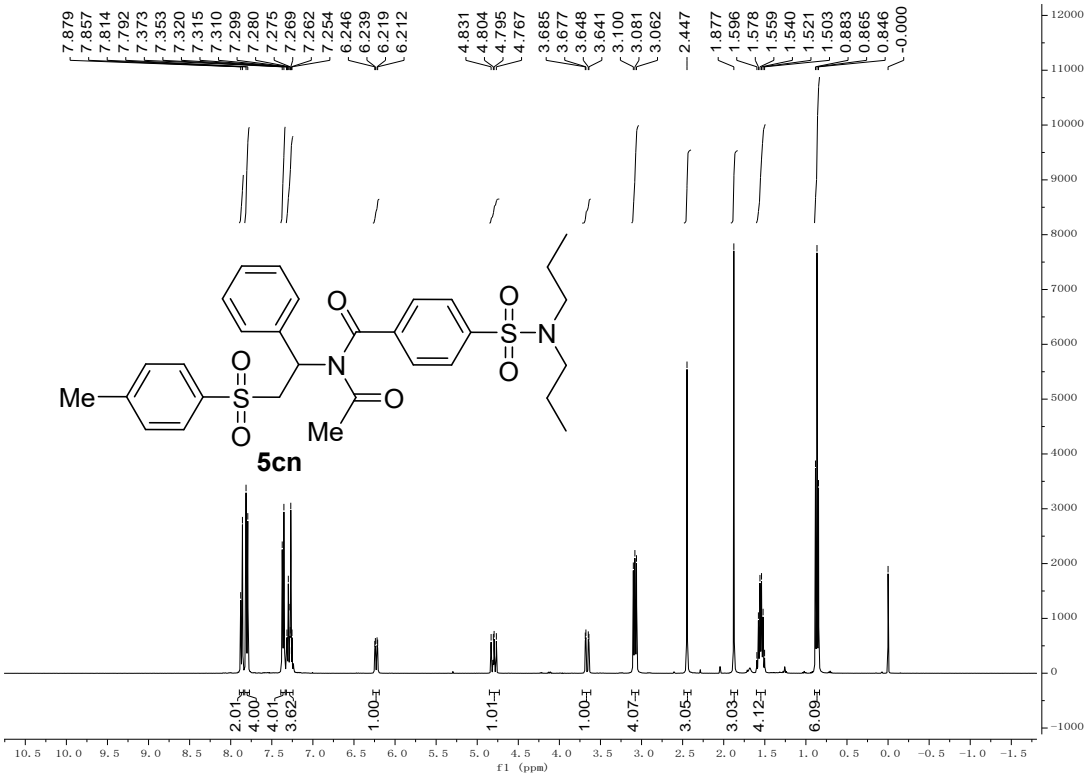
^{1}H NMR of **5cm** in $CDCl_3$



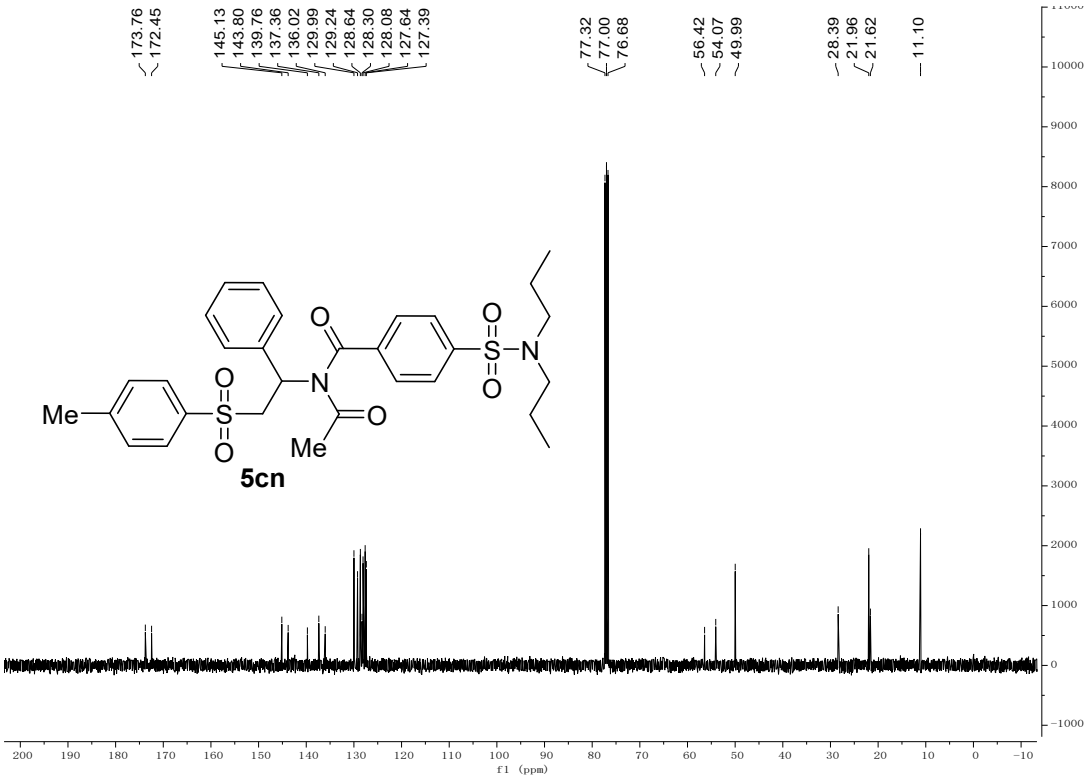
^{13}C NMR of **5cm** in $CDCl_3$



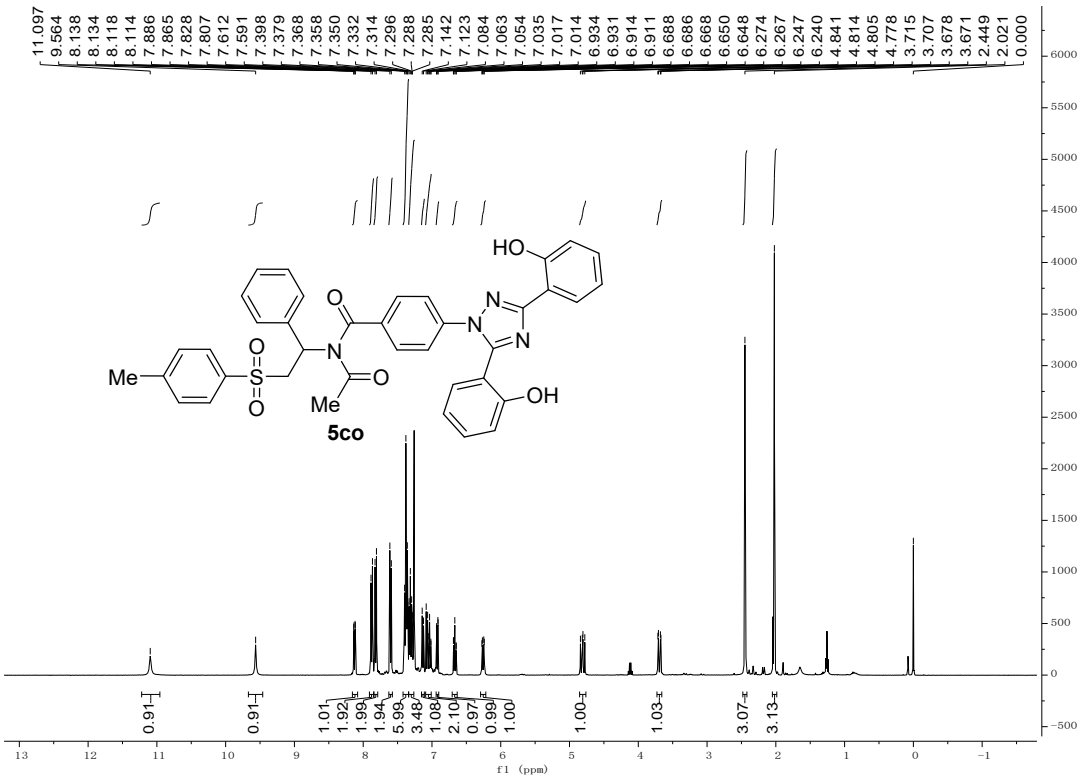
^{1}H NMR of **5cn** in $CDCl_3$



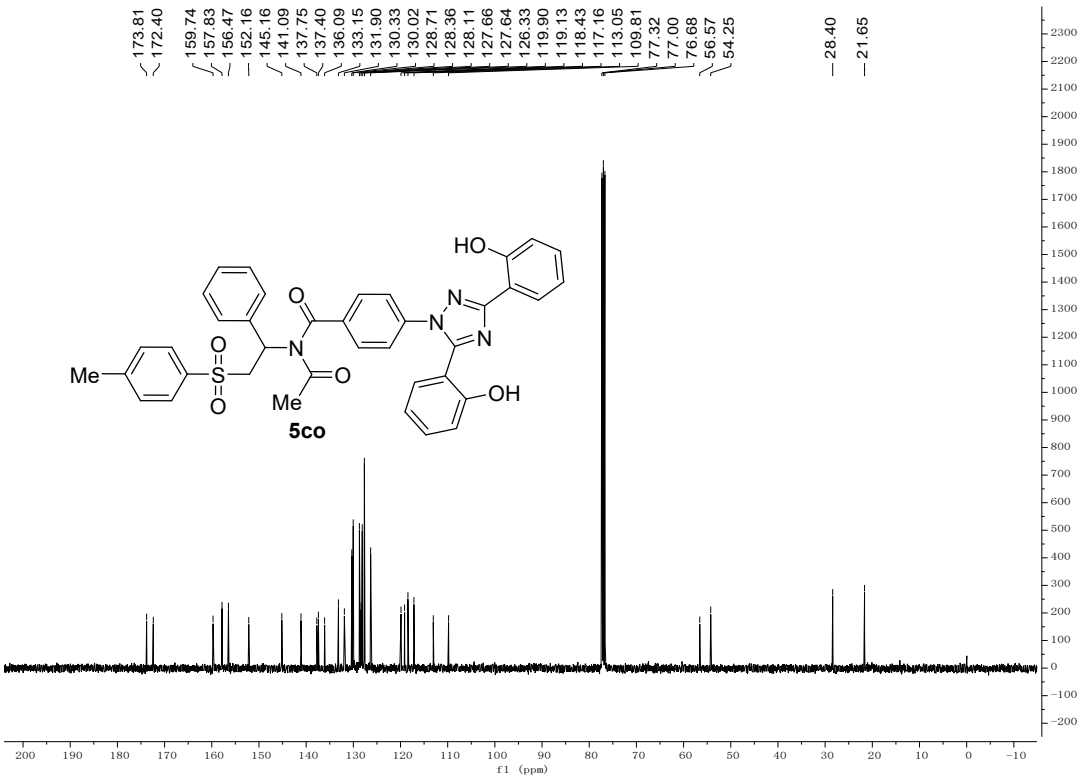
^{13}C NMR of **5cn** in $CDCl_3$



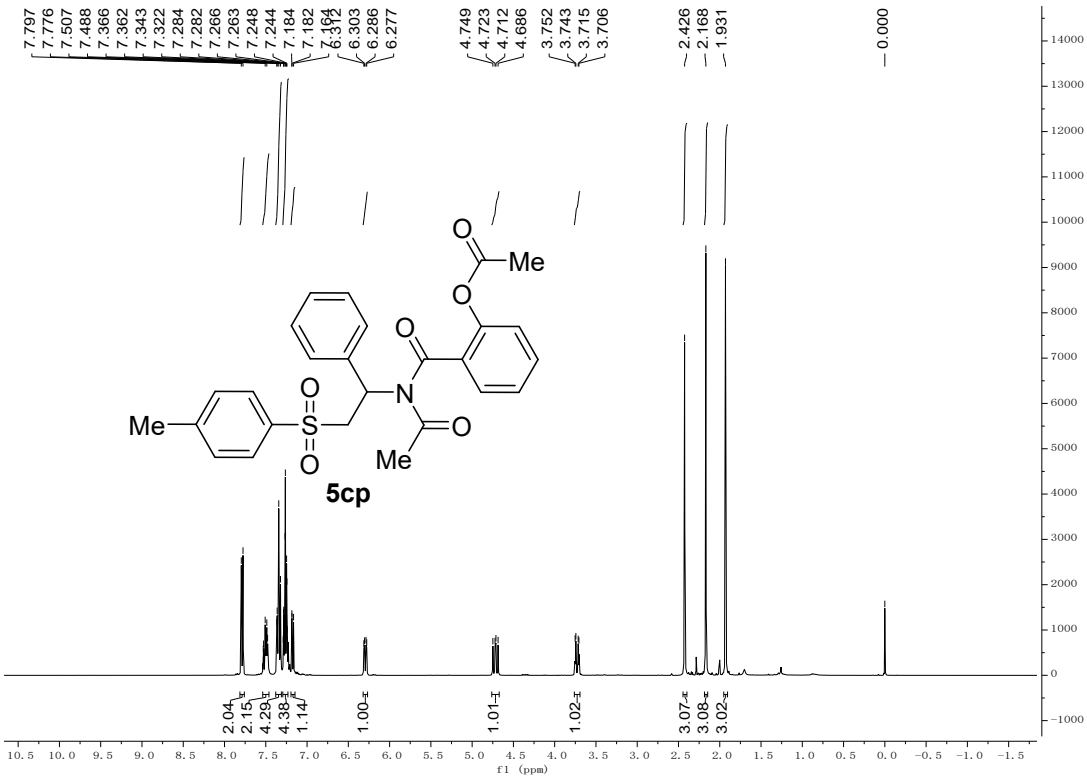
^{1}H NMR of **5co** in $CDCl_3$



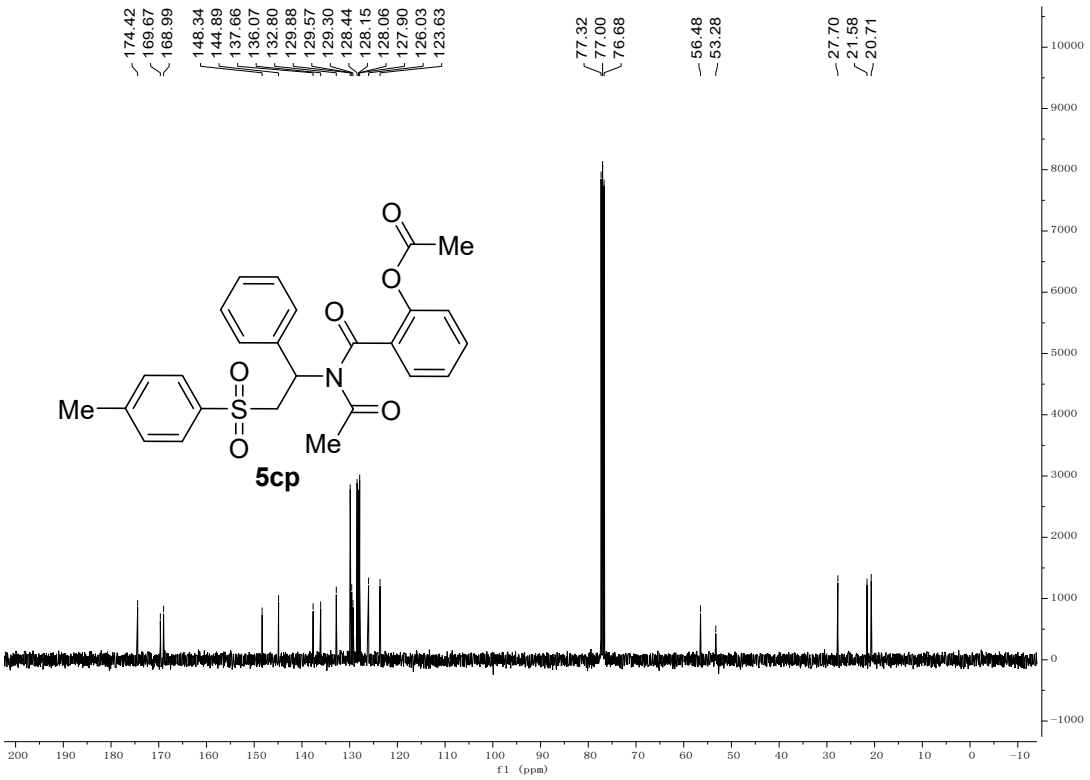
^{13}C NMR of **5co** in $CDCl_3$



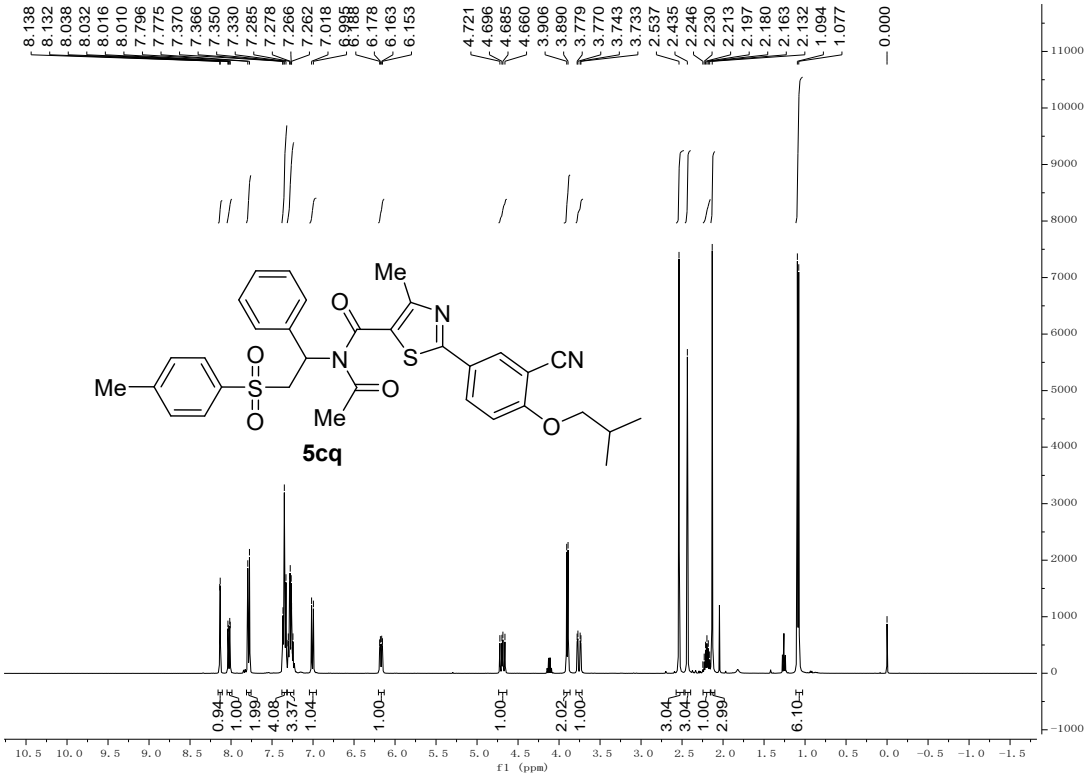
^{1}H NMR of **5cp** in $CDCl_3$



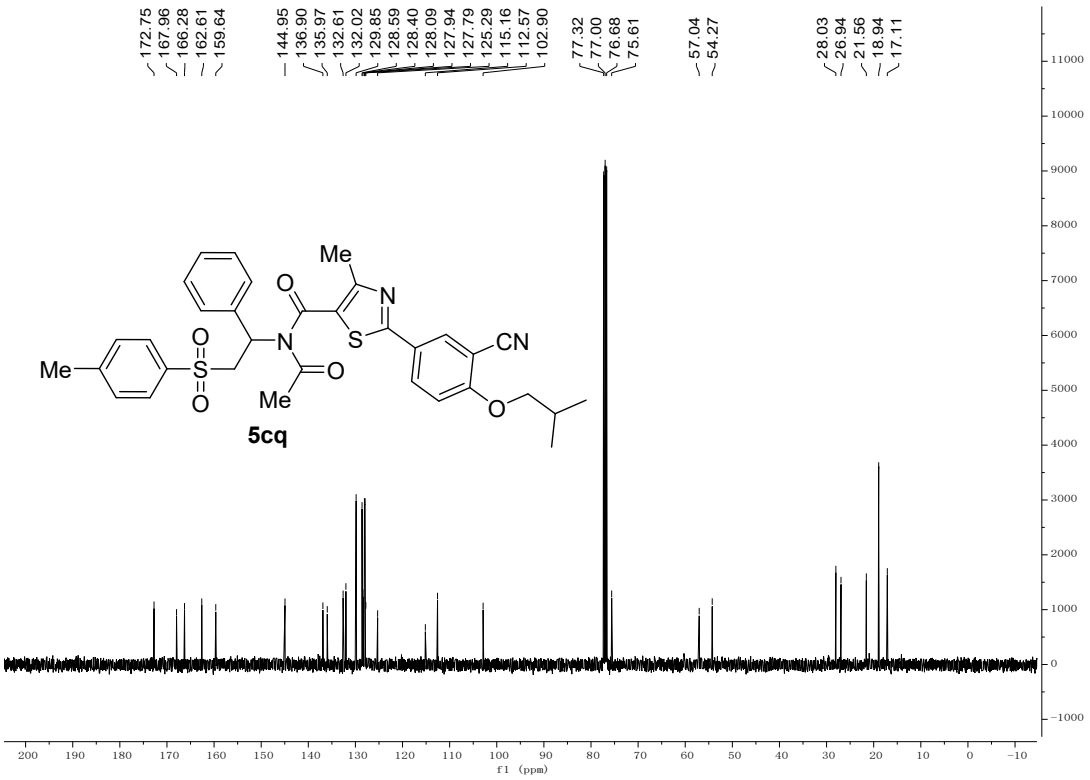
^{13}C NMR of **5cp** in $CDCl_3$



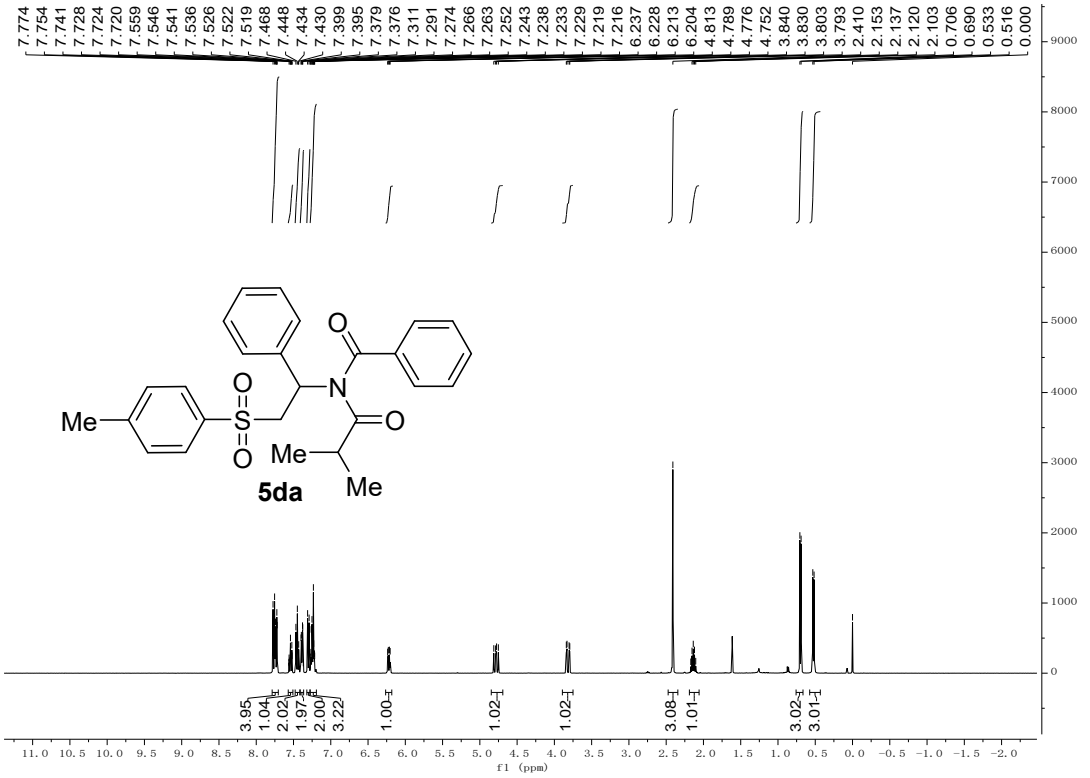
^{1}H NMR of **5cq** in $CDCl_3$



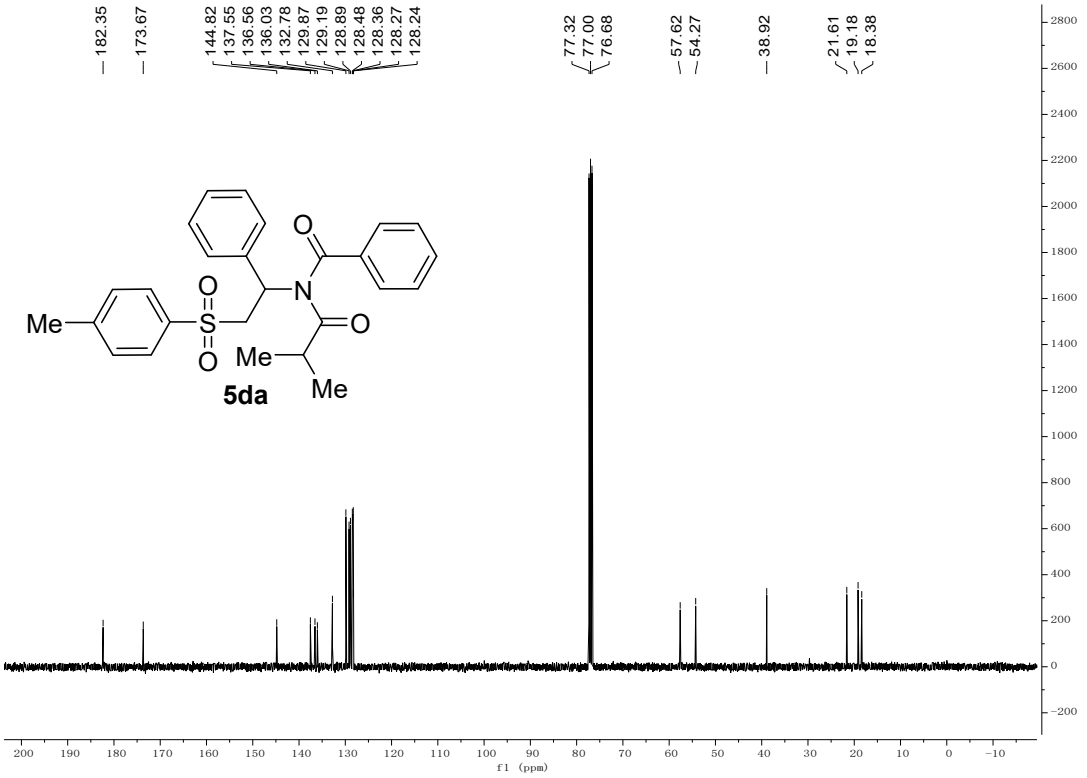
^{13}C NMR of **5cq** in $CDCl_3$



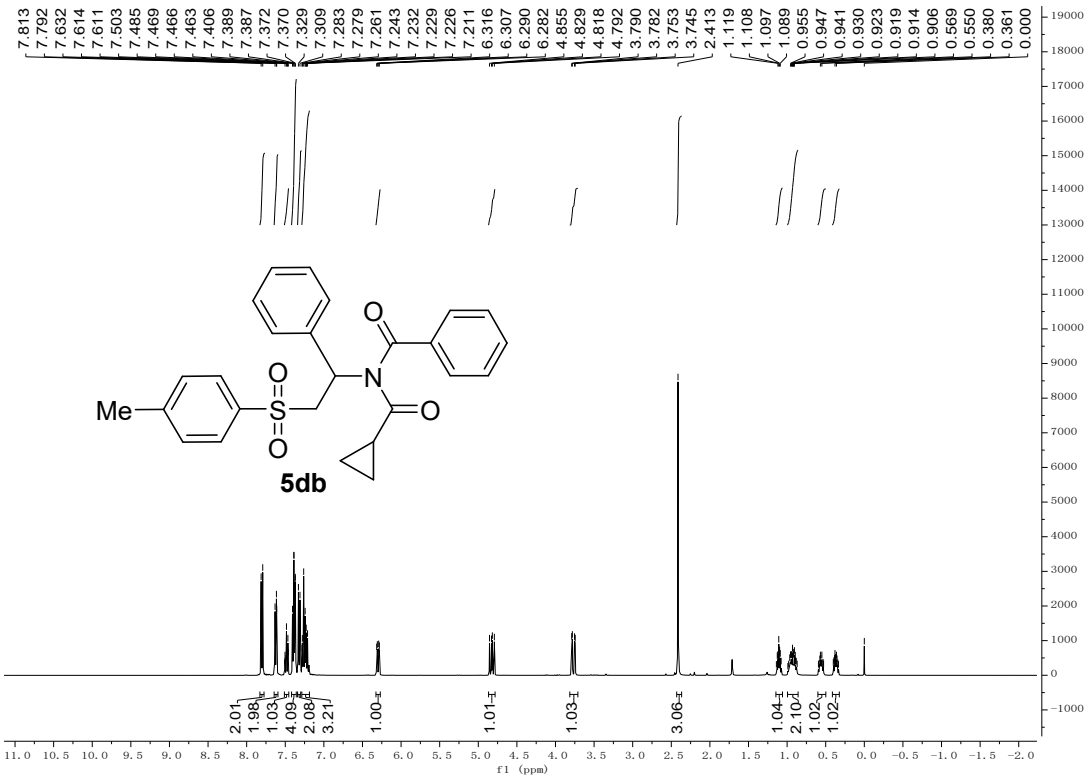
^{1}H NMR of **5da** in $CDCl_3$



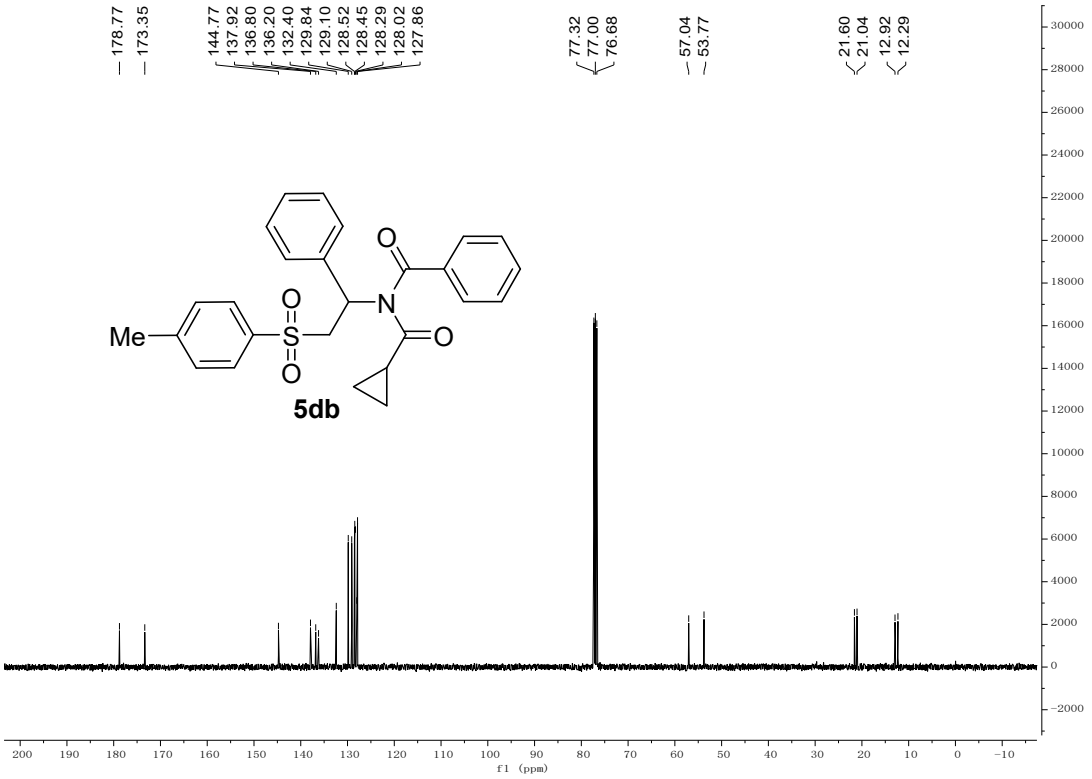
^{13}C NMR of **5da** in $CDCl_3$



^{1}H NMR of **5db** in $CDCl_3$

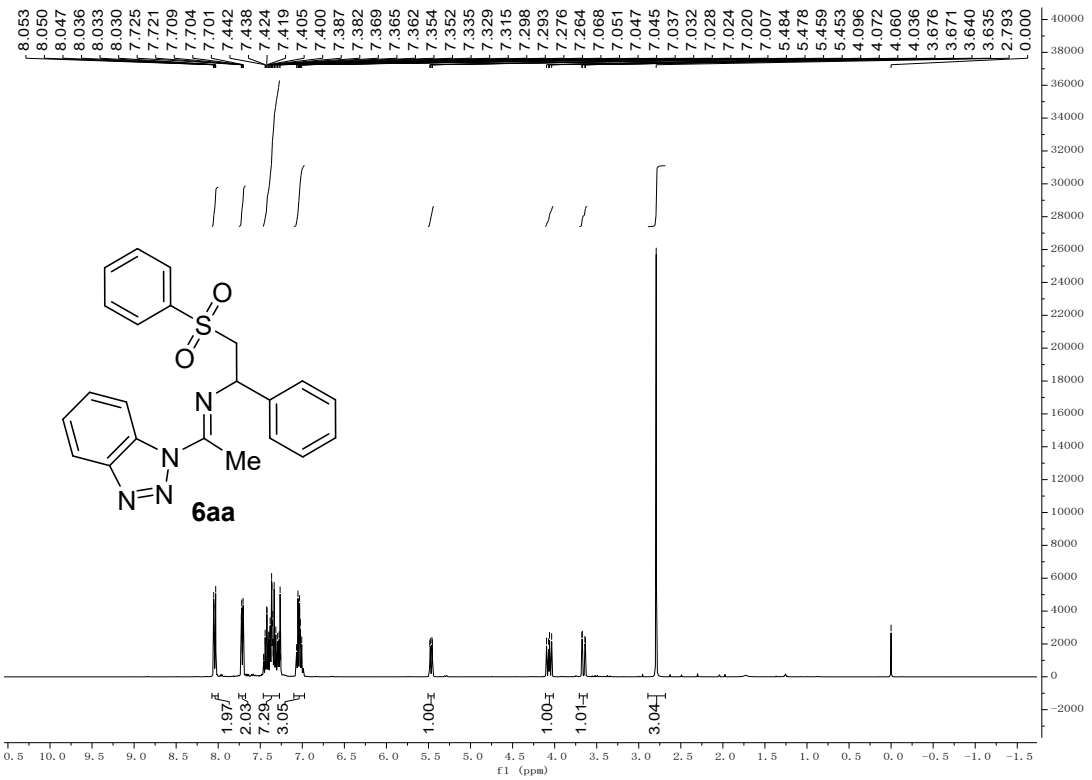


^{13}C NMR of **5db** in $CDCl_3$

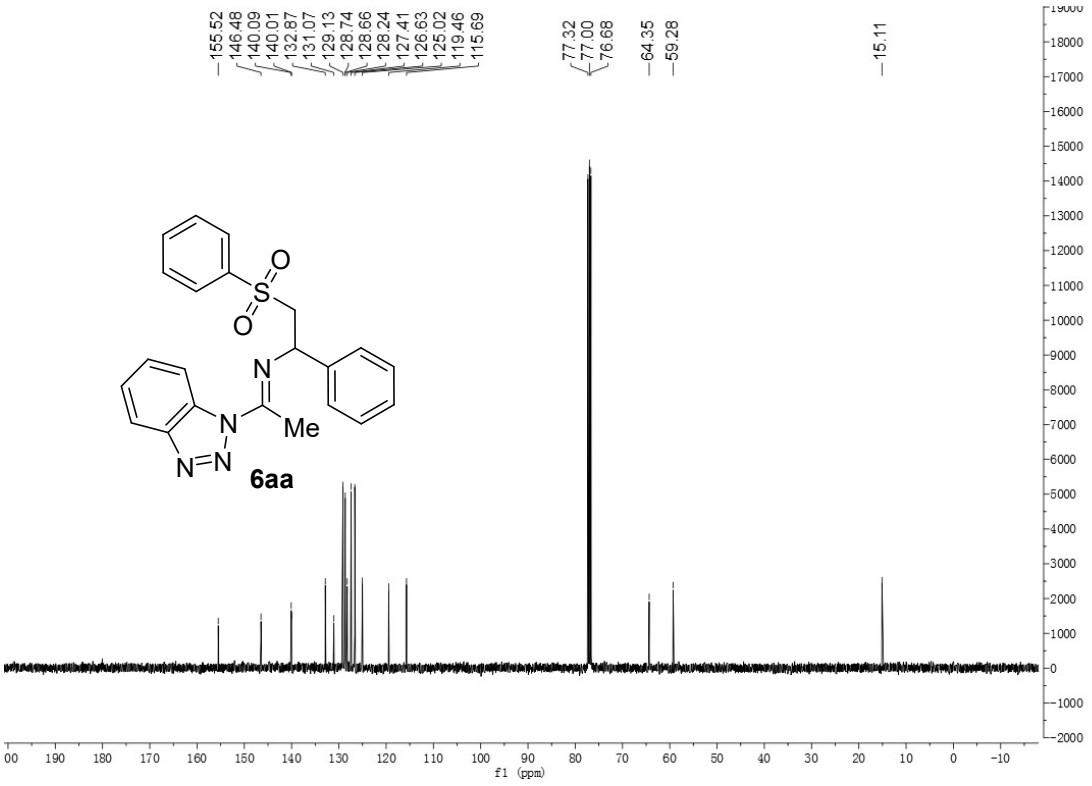


Spectra B: NMR Spectra of Compounds *β*-Sulfonyl Imines

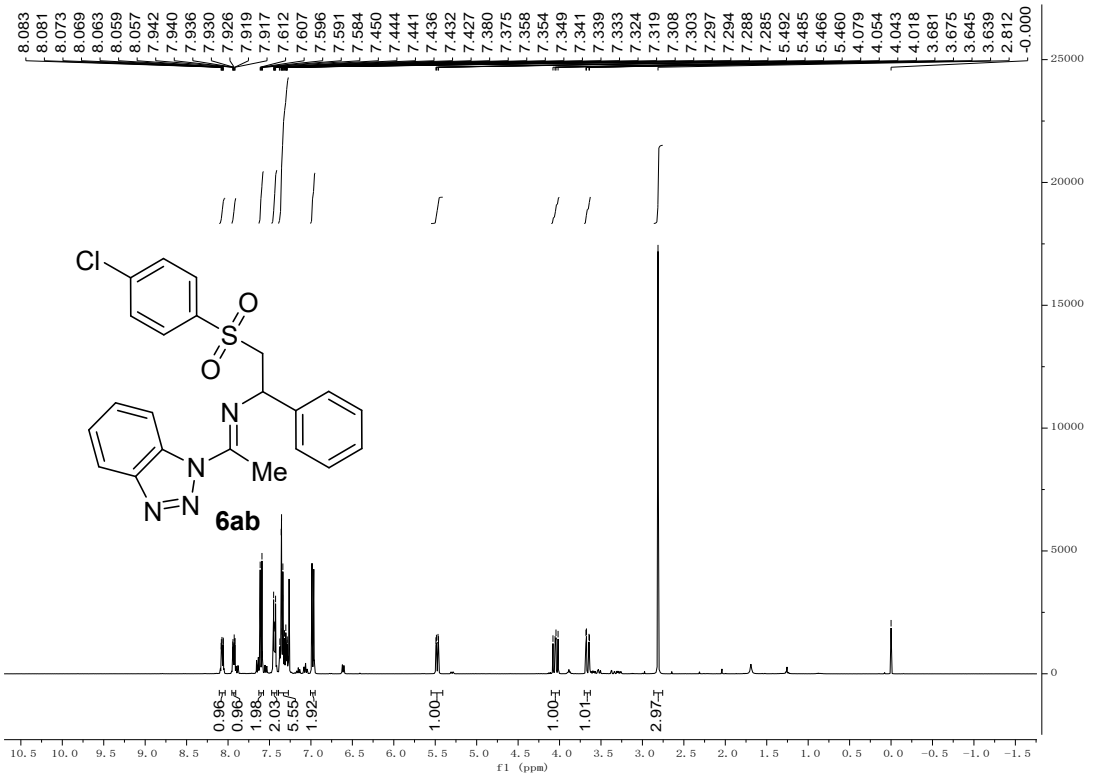
^{1}H NMR of **6aa** in $CDCl_3$



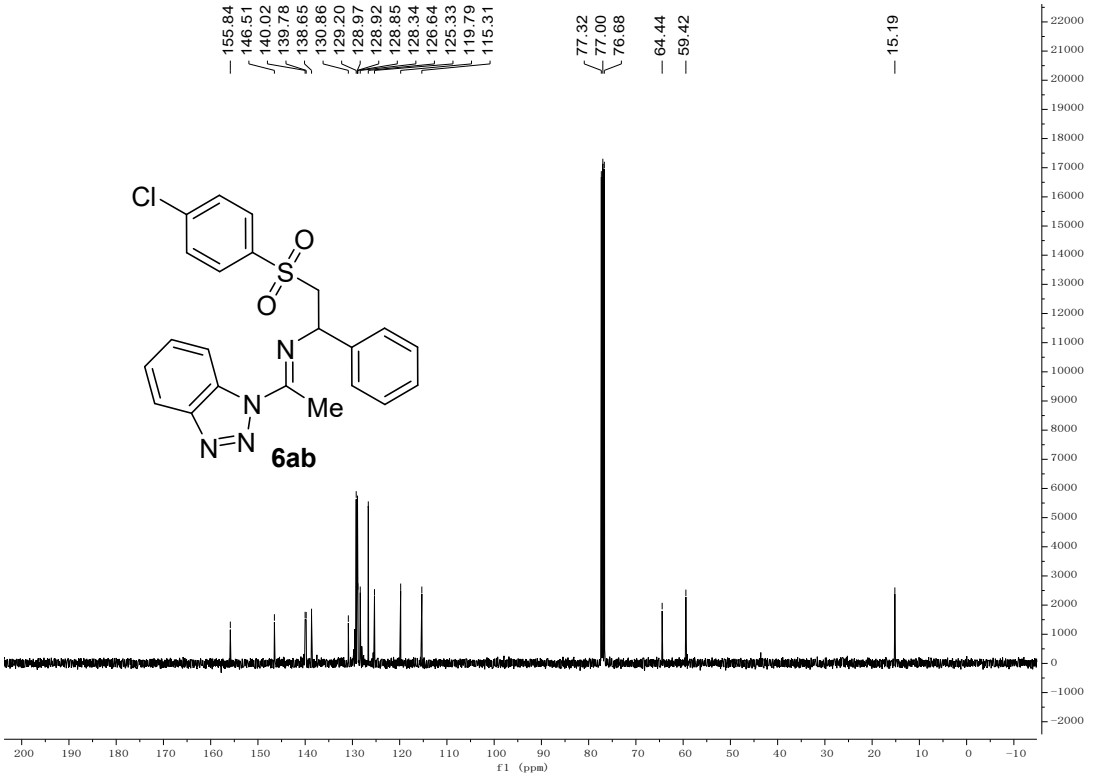
^{13}C NMR of **6aa** in $CDCl_3$



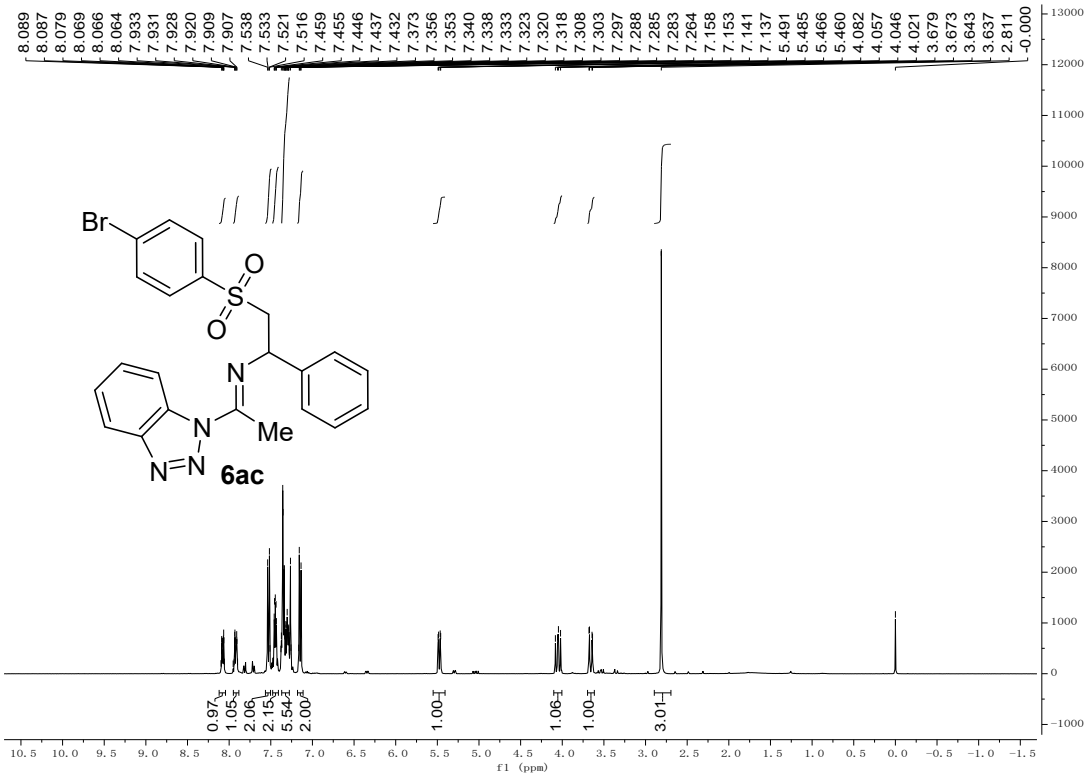
^{1}H NMR of **6ab** in $CDCl_3$



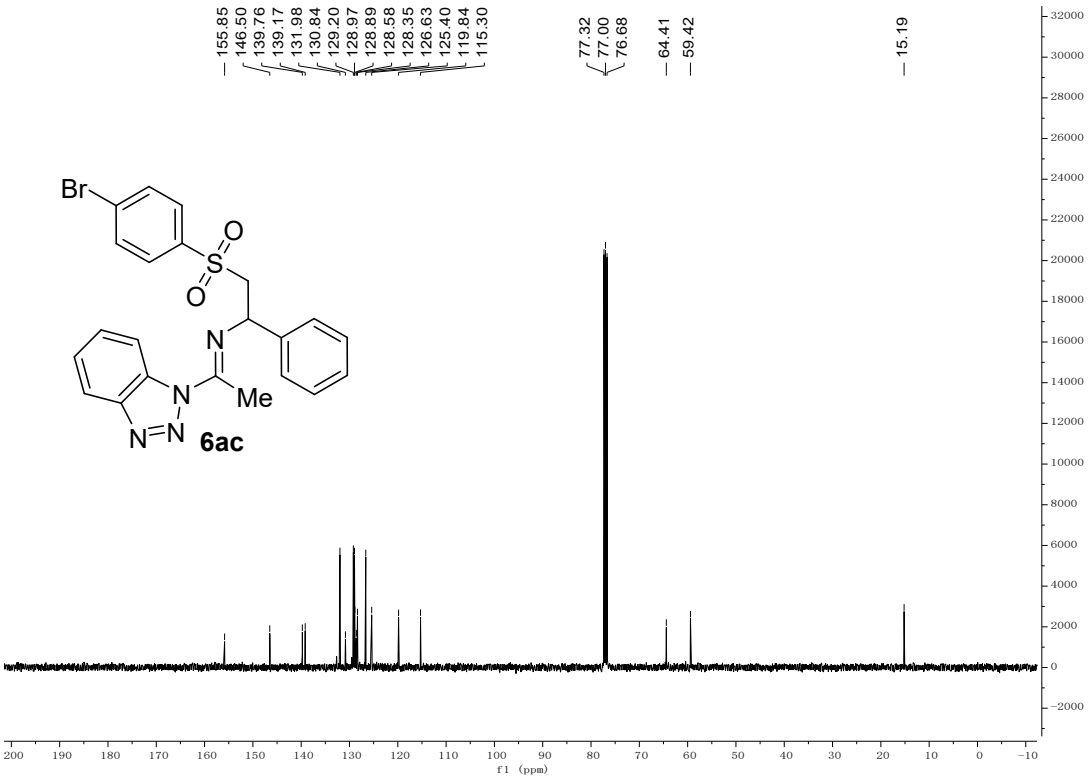
^{13}C NMR of **6ab** in $CDCl_3$



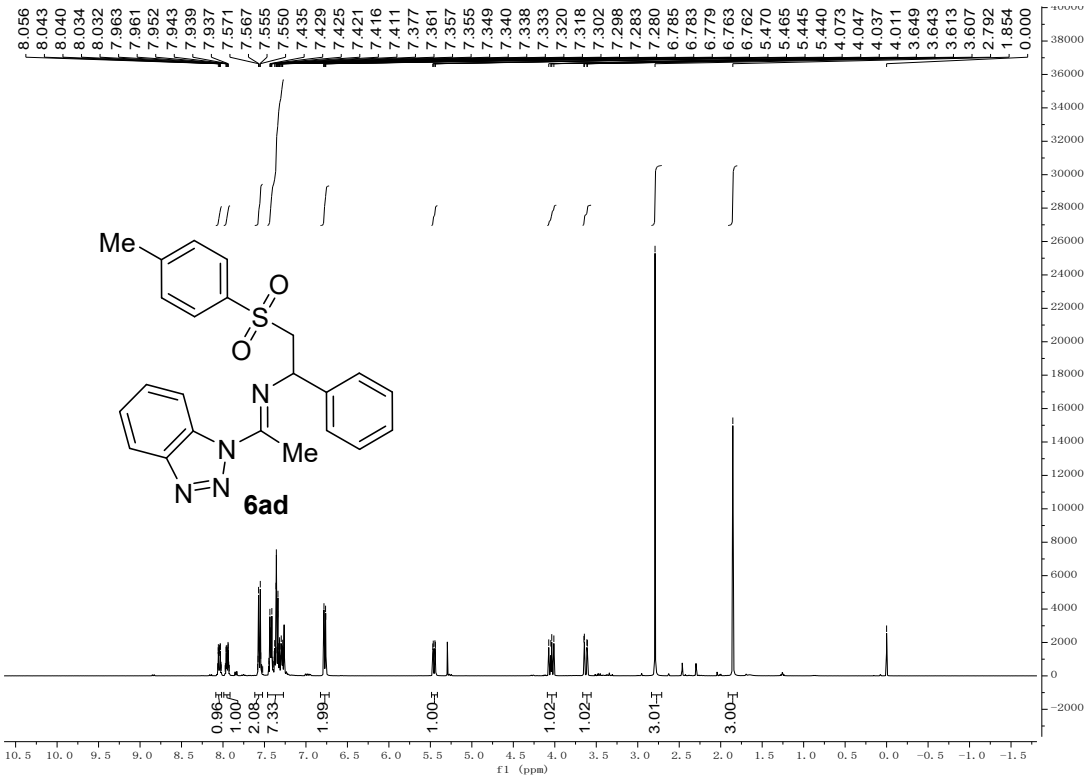
^{1}H NMR of **6ac** in $CDCl_3$



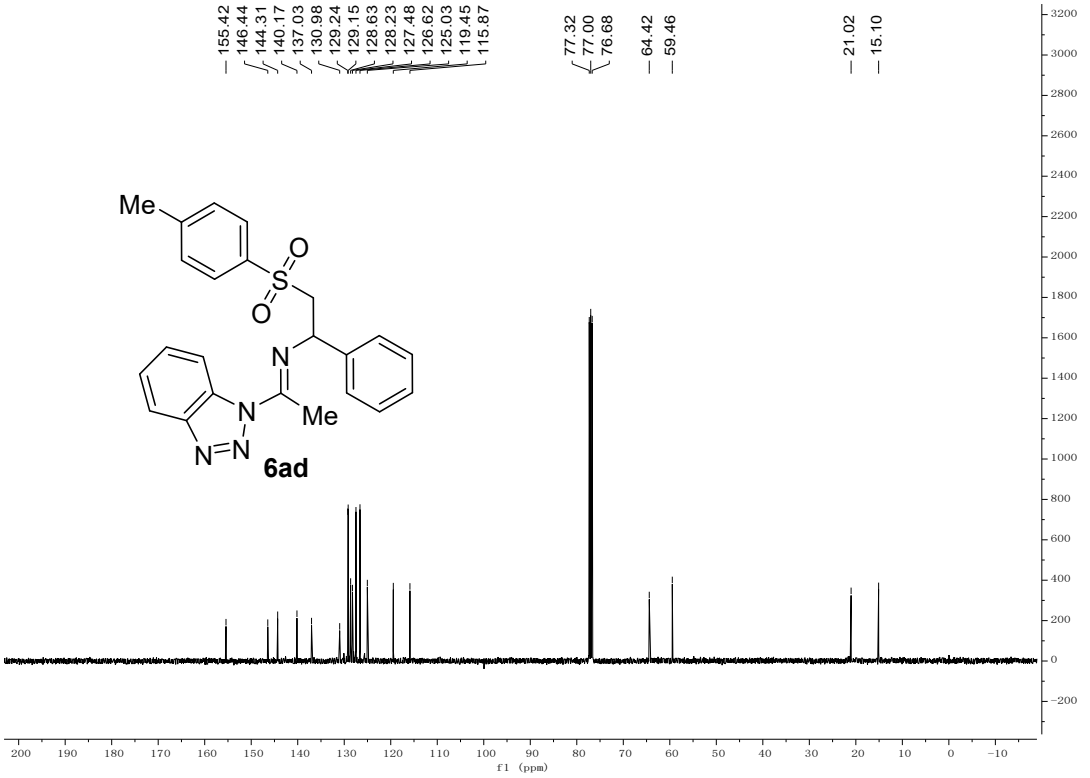
^{13}C NMR of **6ac** in $CDCl_3$



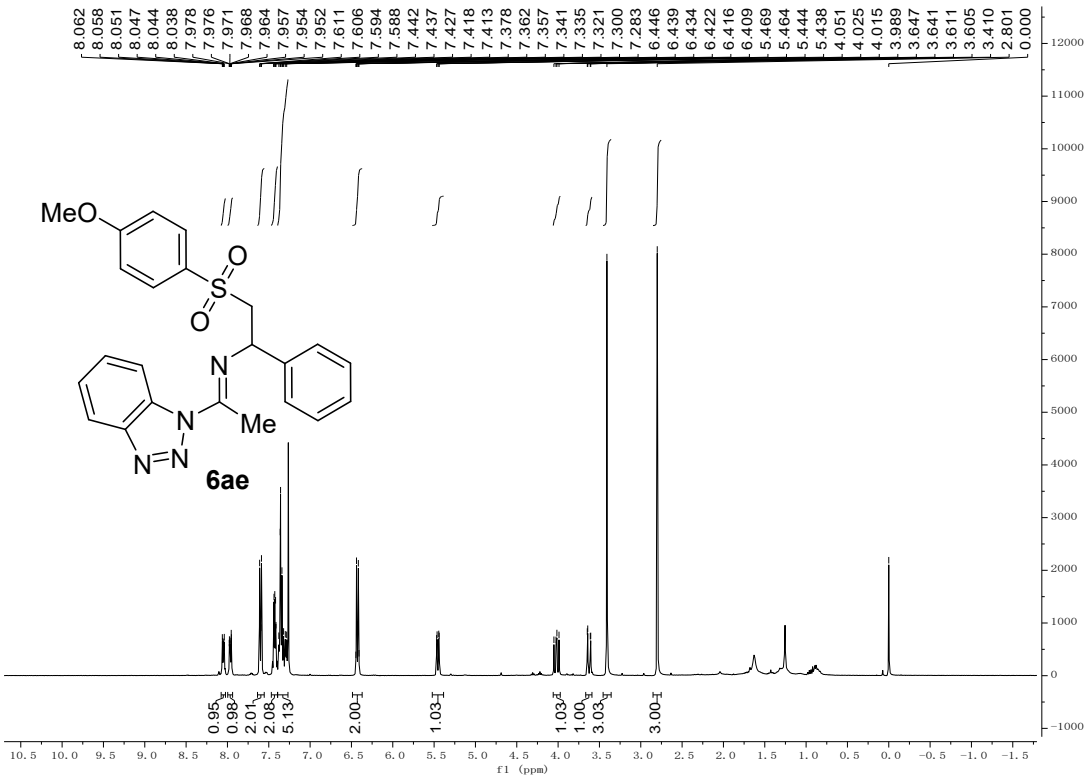
^{1}H NMR of **6ad** in $CDCl_3$



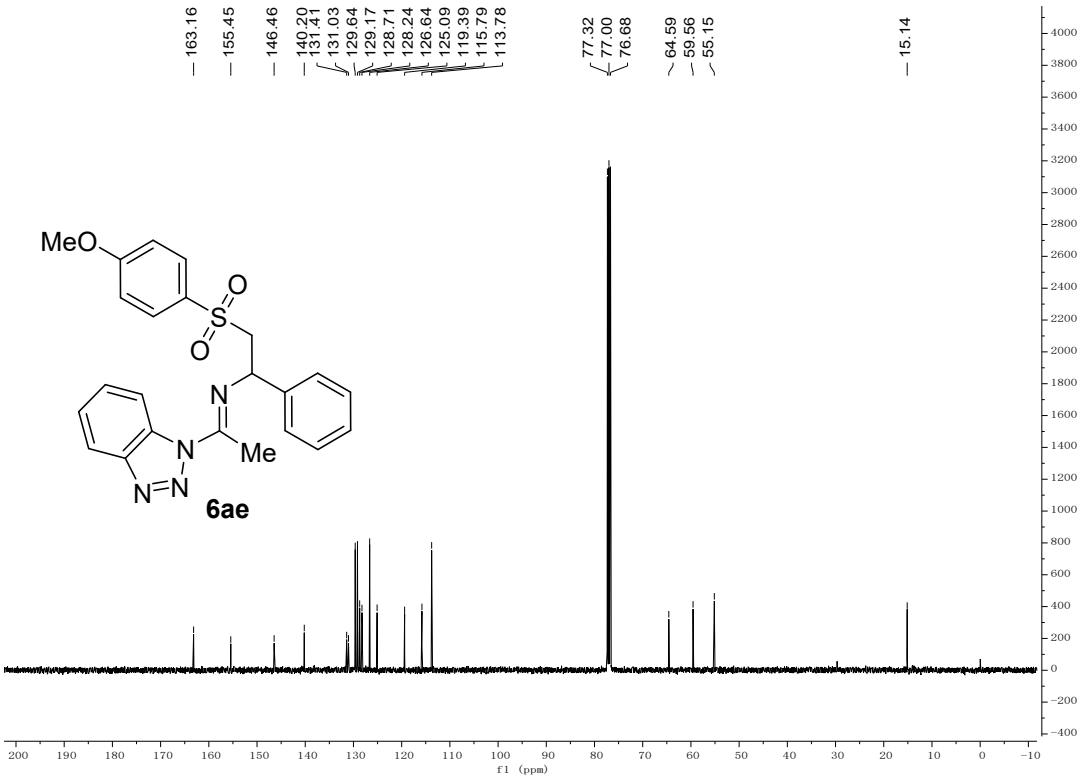
^{13}C NMR of **6ad** in $CDCl_3$



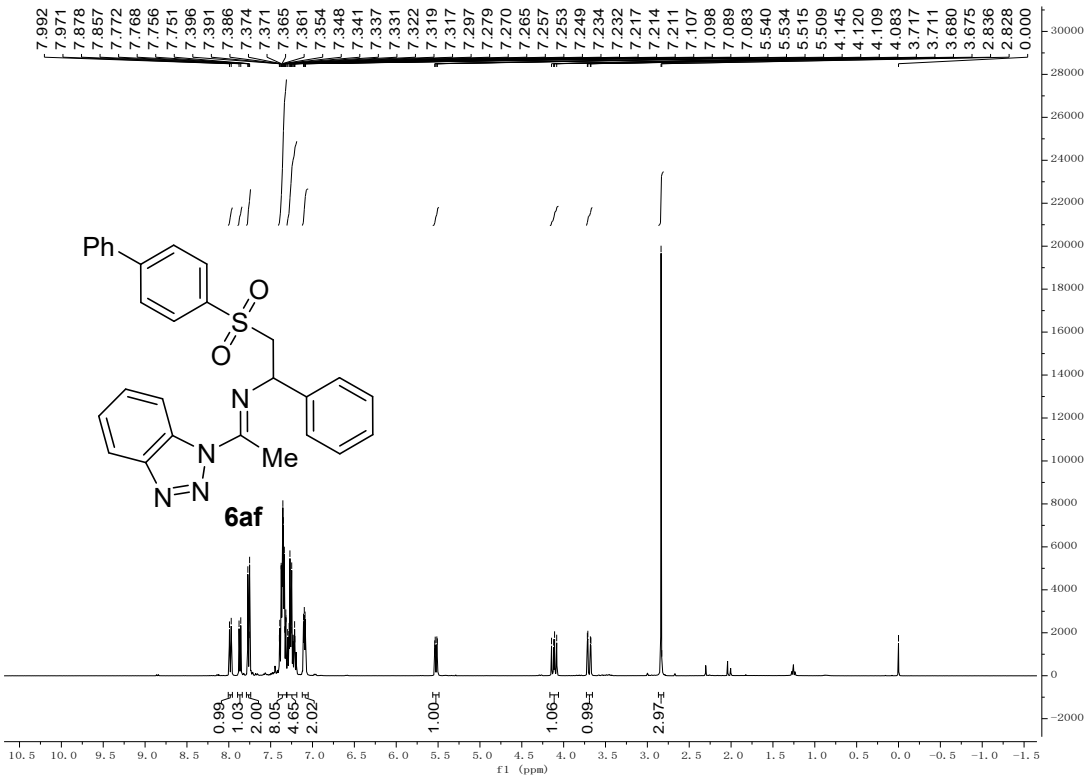
^{1}H NMR of **6ae** in $CDCl_3$



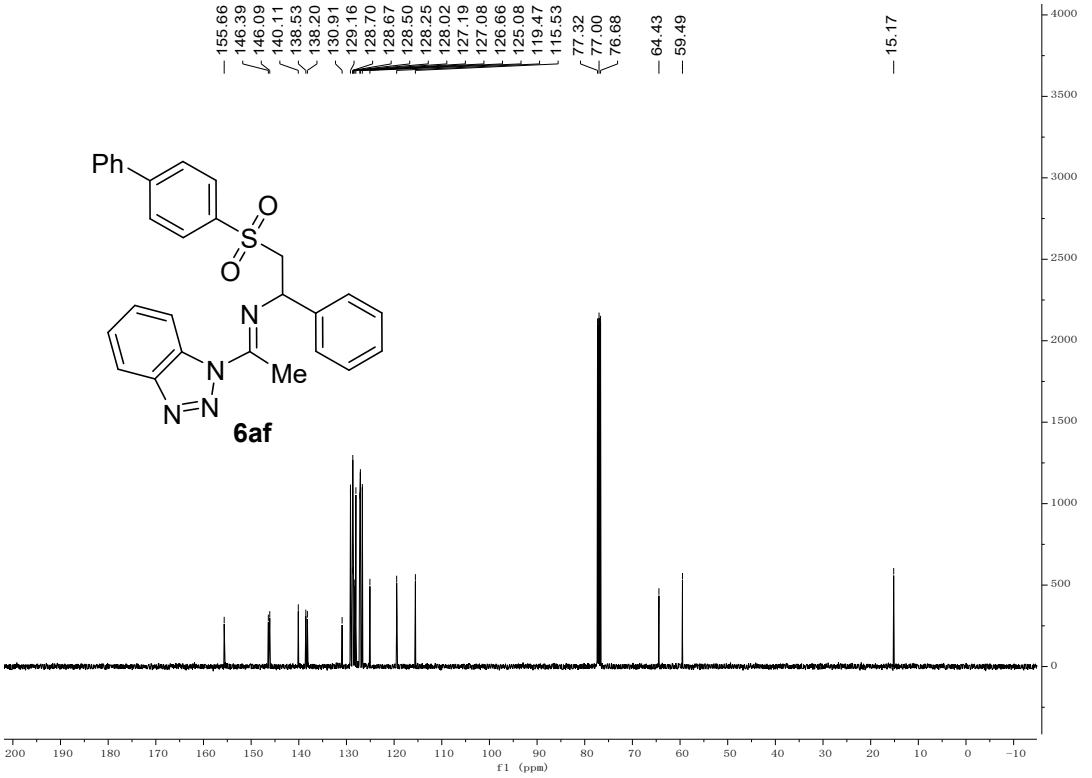
^{13}C NMR of **6ae** in $CDCl_3$



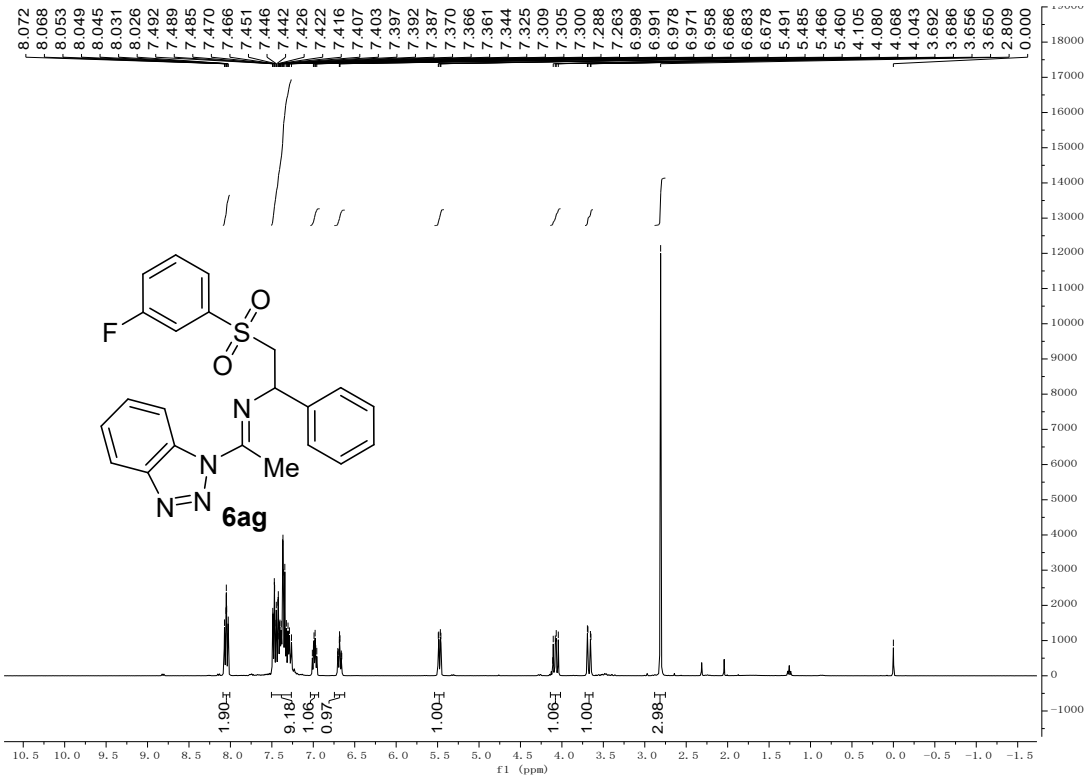
^{1}H NMR of **6af** in $CDCl_3$



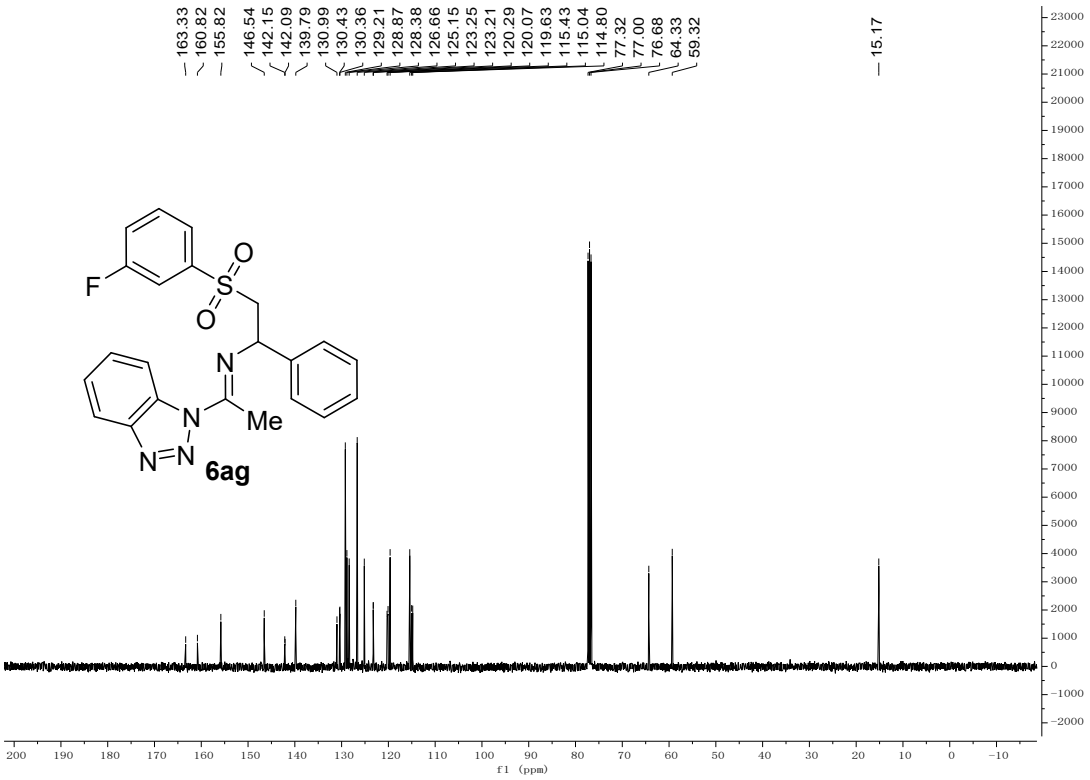
^{13}C NMR of **6af** in $CDCl_3$



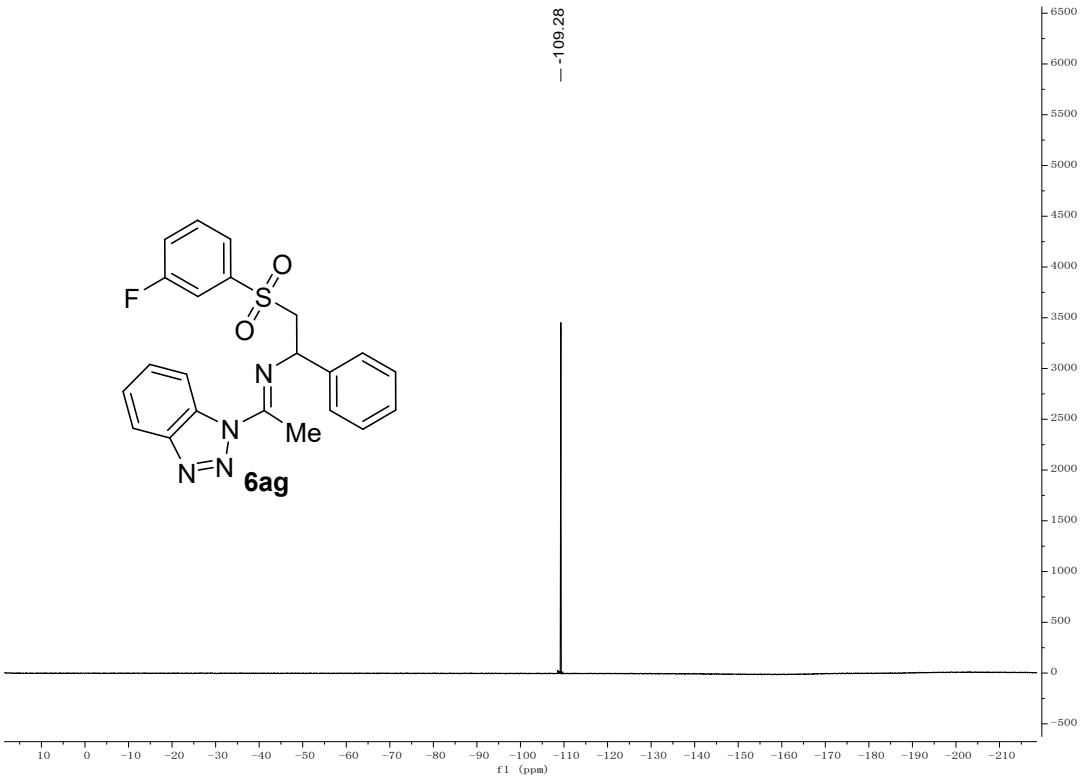
^{1}H NMR of **6ag** in $CDCl_3$



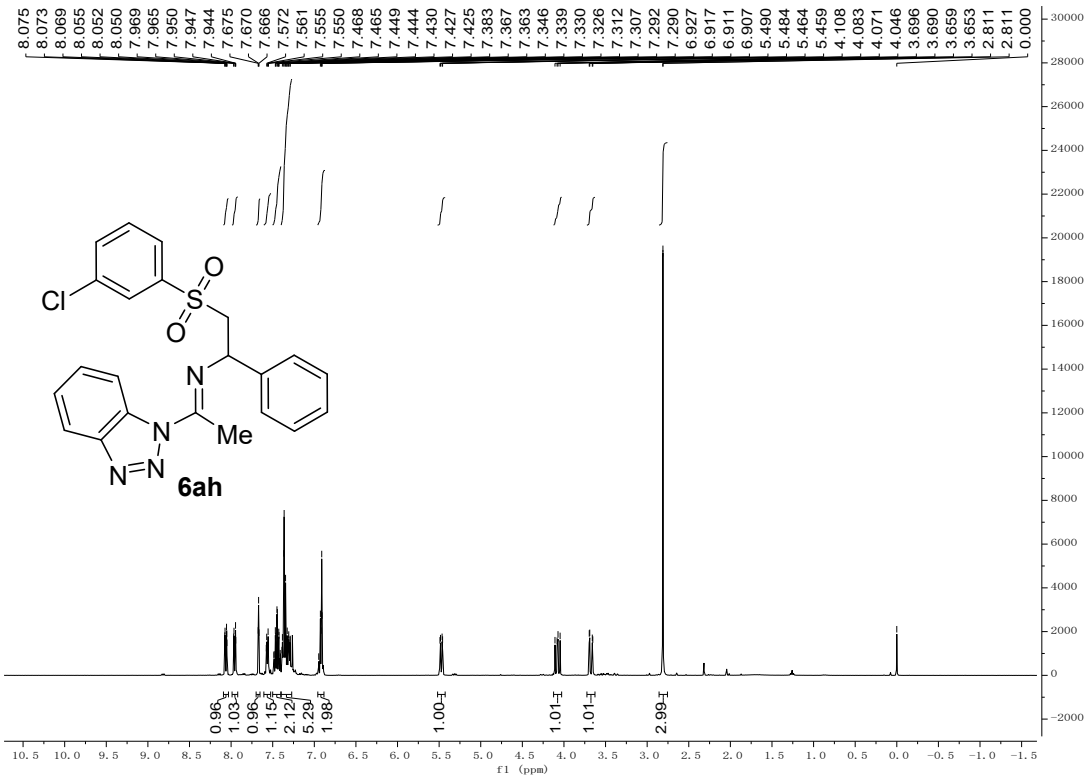
^{13}C NMR of **6ag** in $CDCl_3$



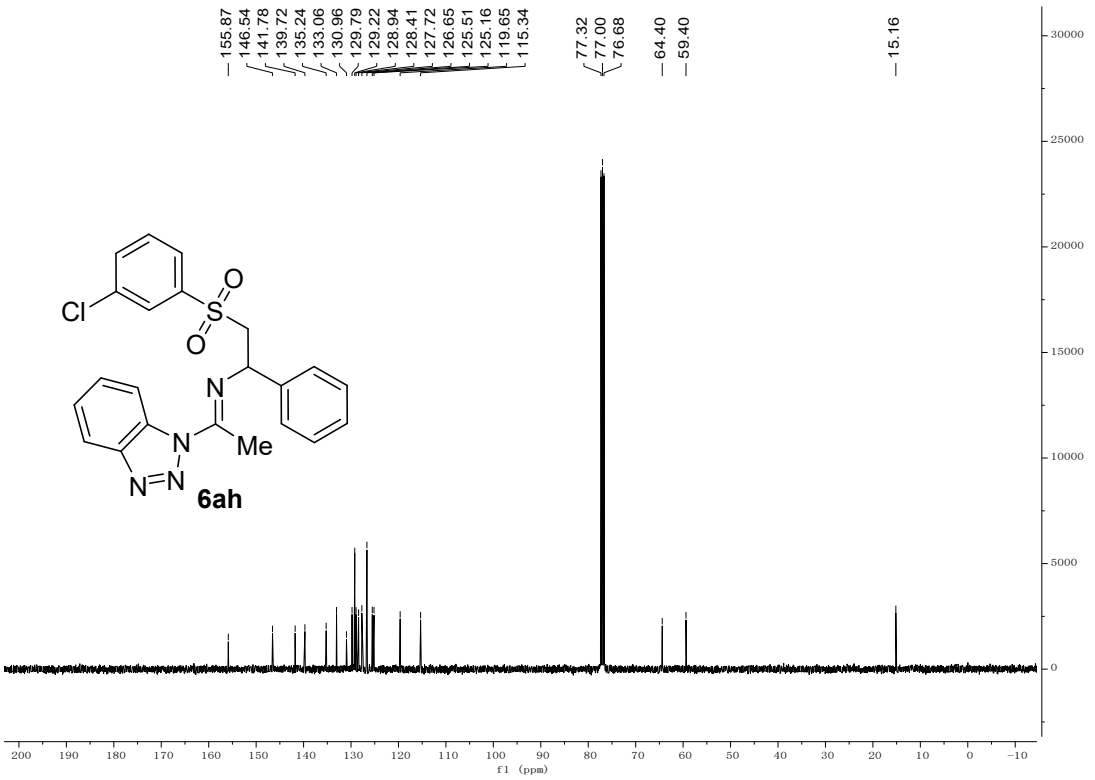
^{19}F NMR spectra of **6ag** in $CDCl_3$



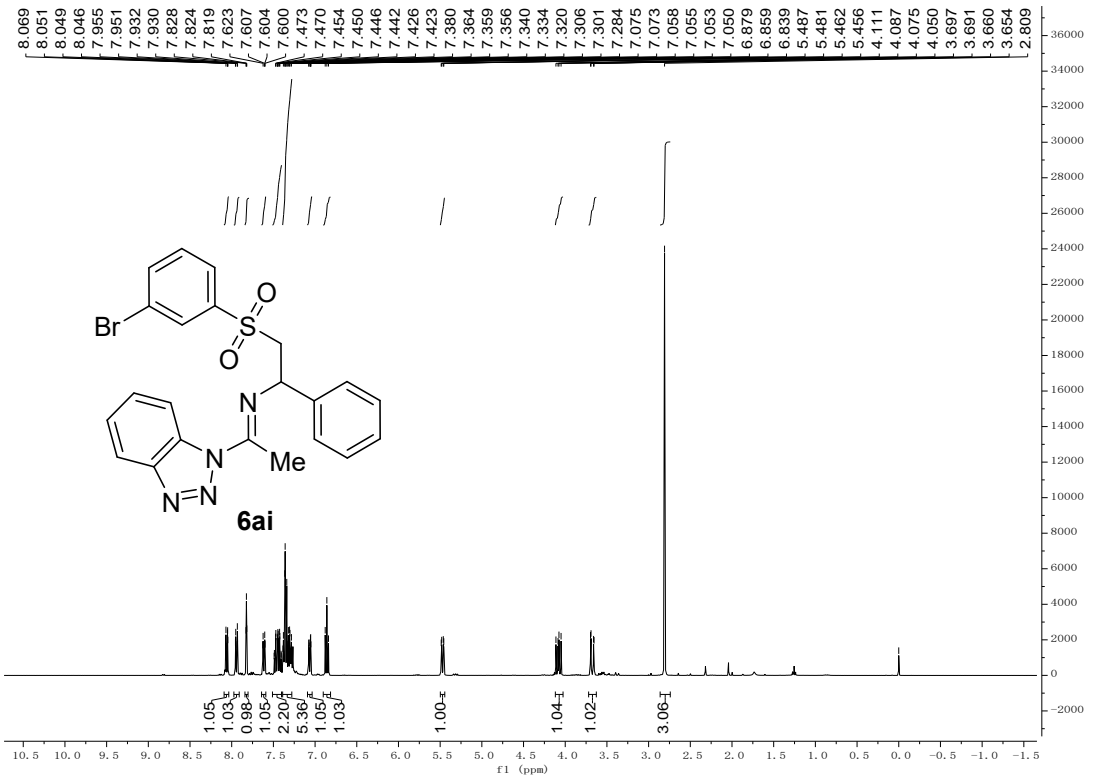
^{1}H NMR of **6ah** in $CDCl_3$



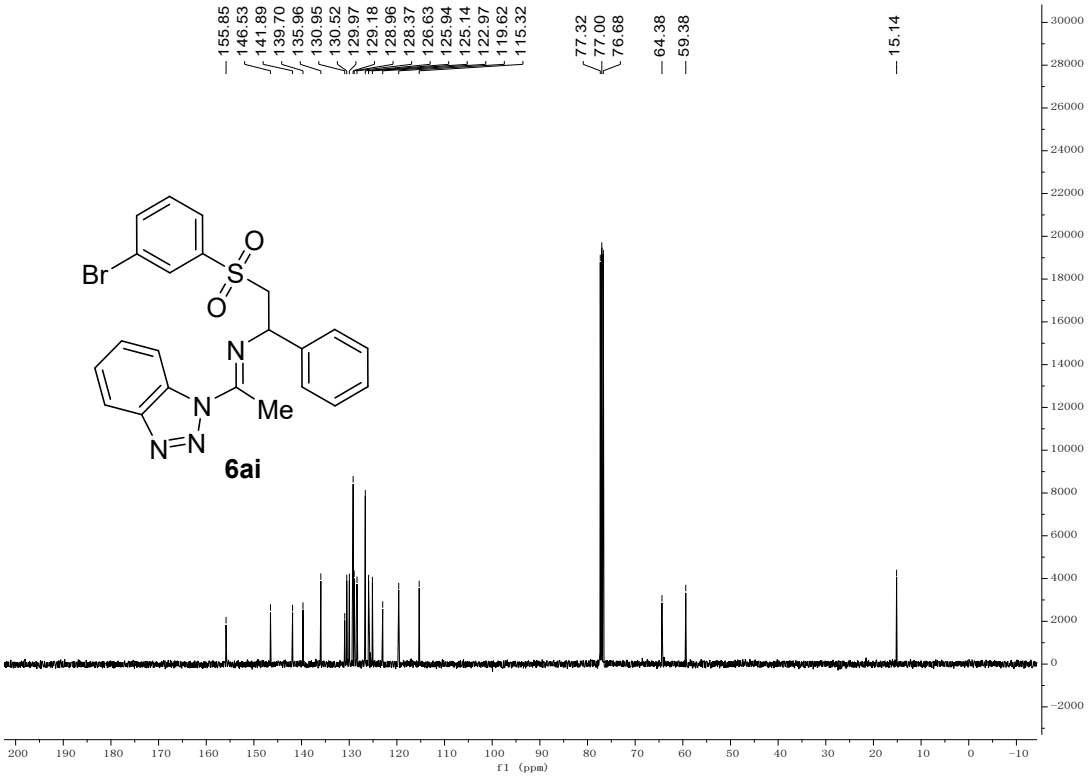
^{13}C NMR of **6ah** in $CDCl_3$



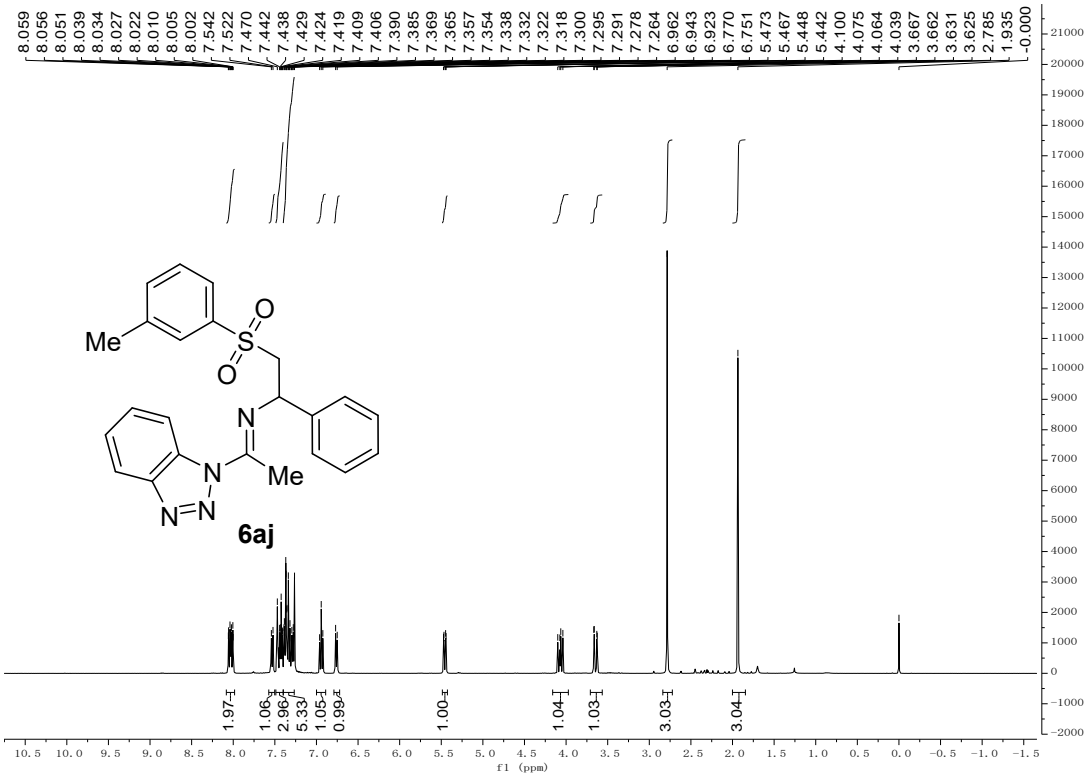
^{1}H NMR of **6ai** in $CDCl_3$



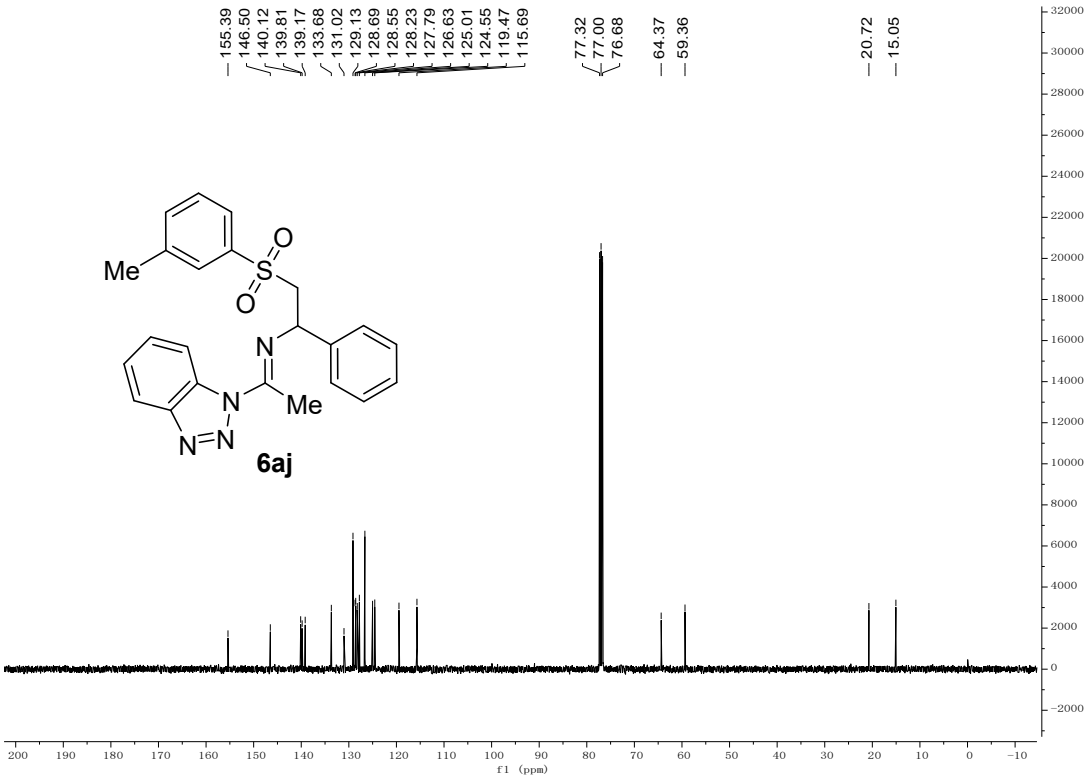
^{13}C NMR of **6ai** in $CDCl_3$



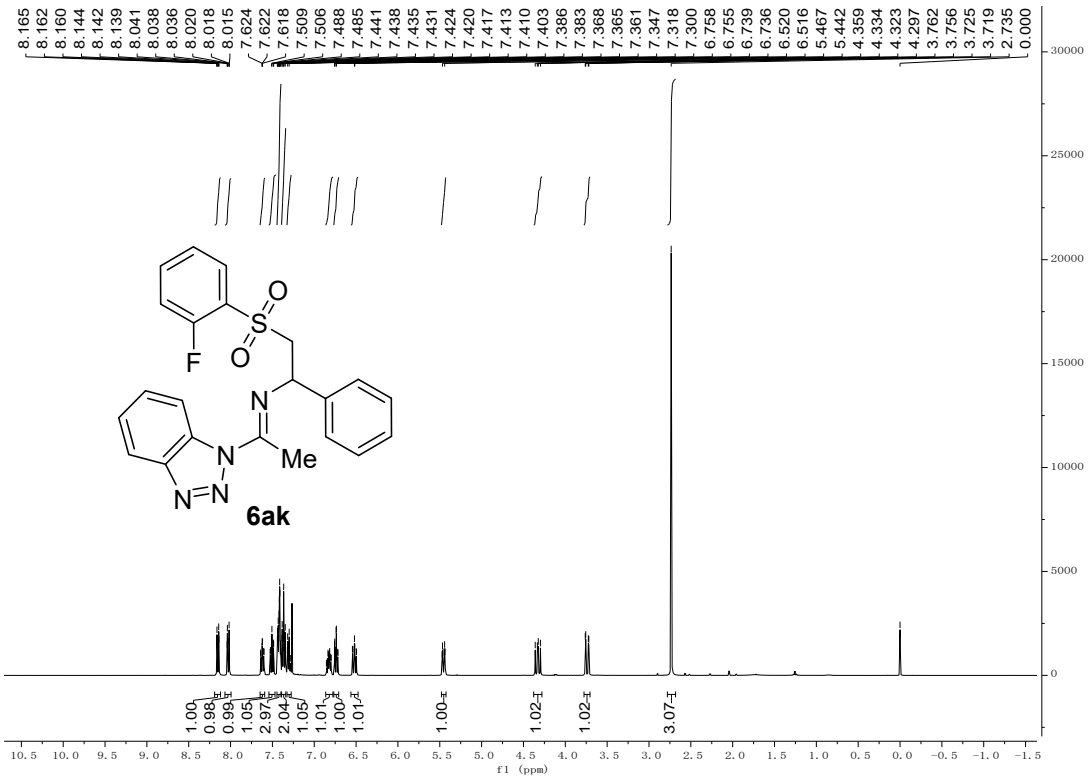
^{1}H NMR of **6aj** in $CDCl_3$



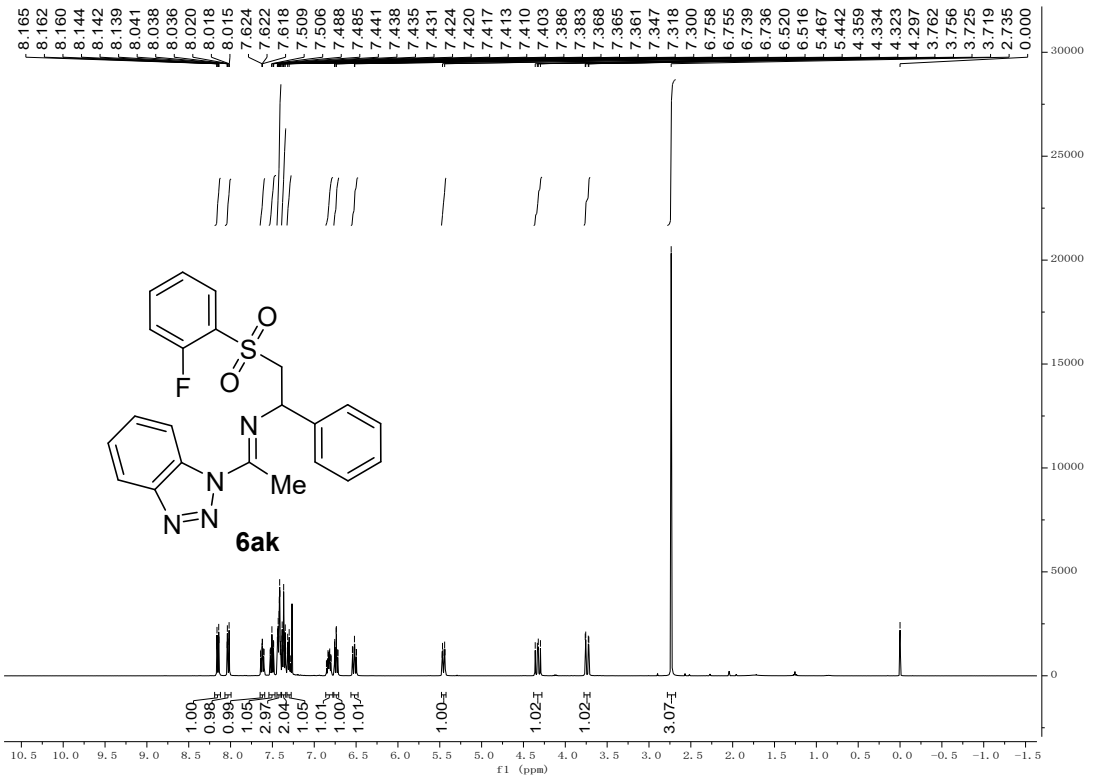
^{13}C NMR of **6aj** in $CDCl_3$



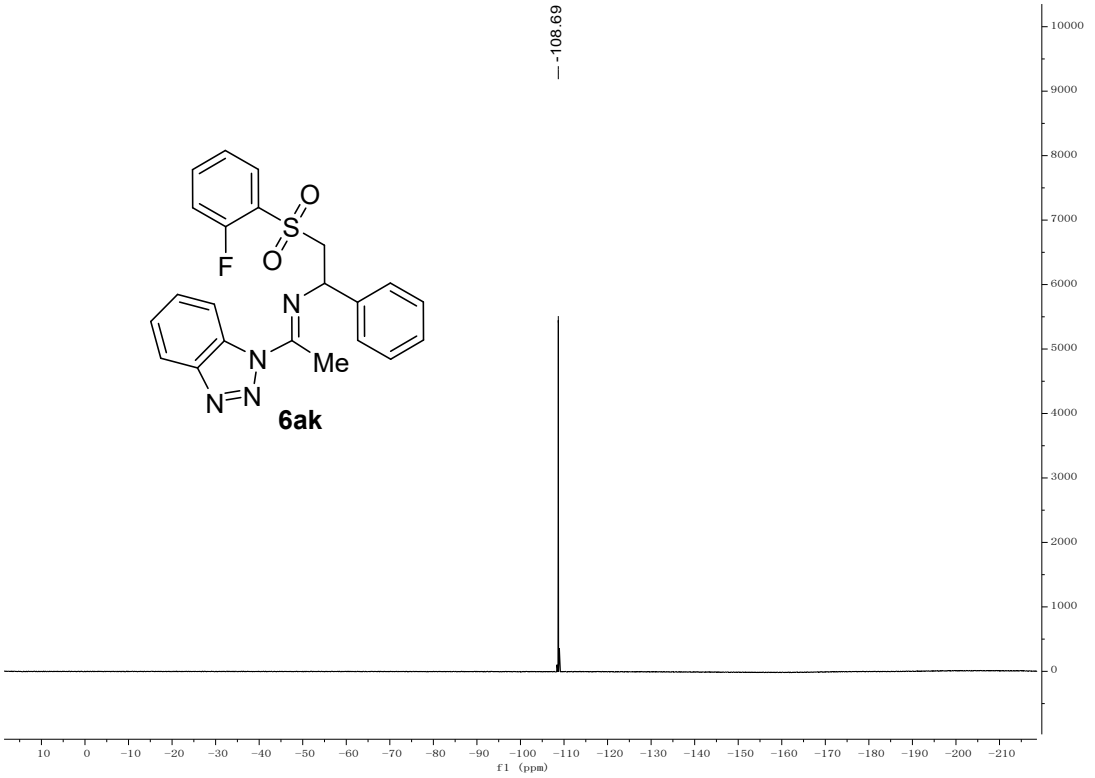
^{1}H NMR of **6ak** in $CDCl_3$



^{13}C NMR of **6ak** in $CDCl_3$

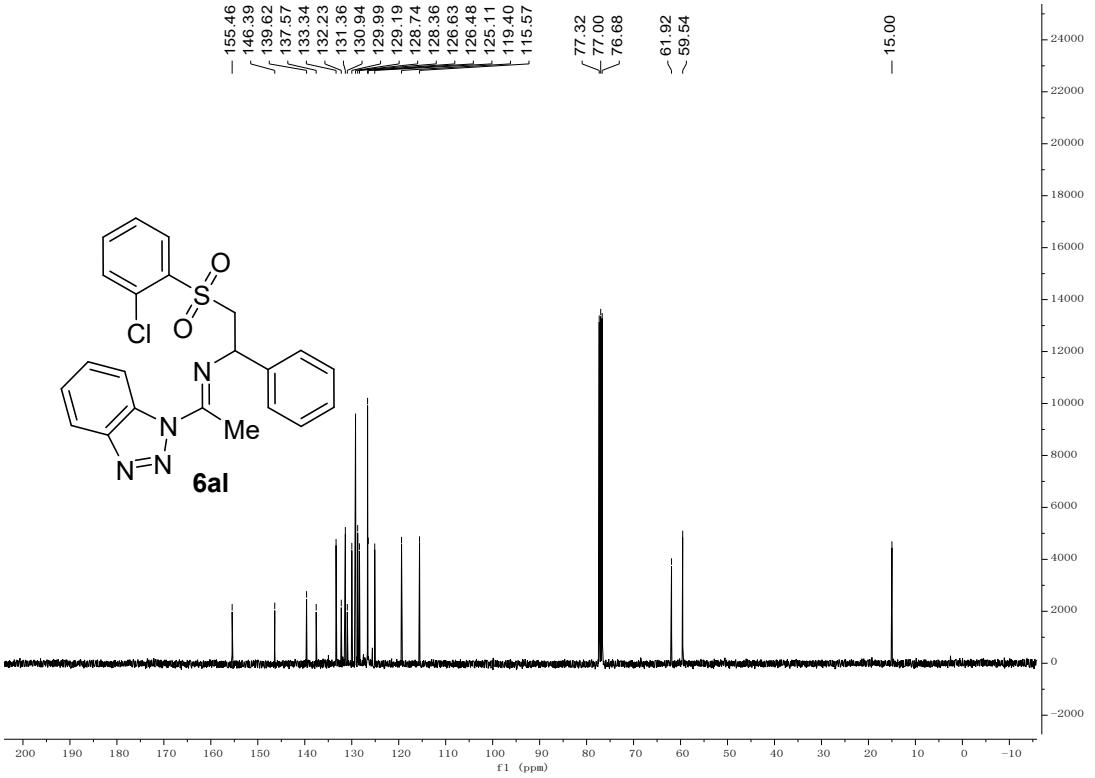


^{19}F NMR spectra of **6ak** in $CDCl_3$

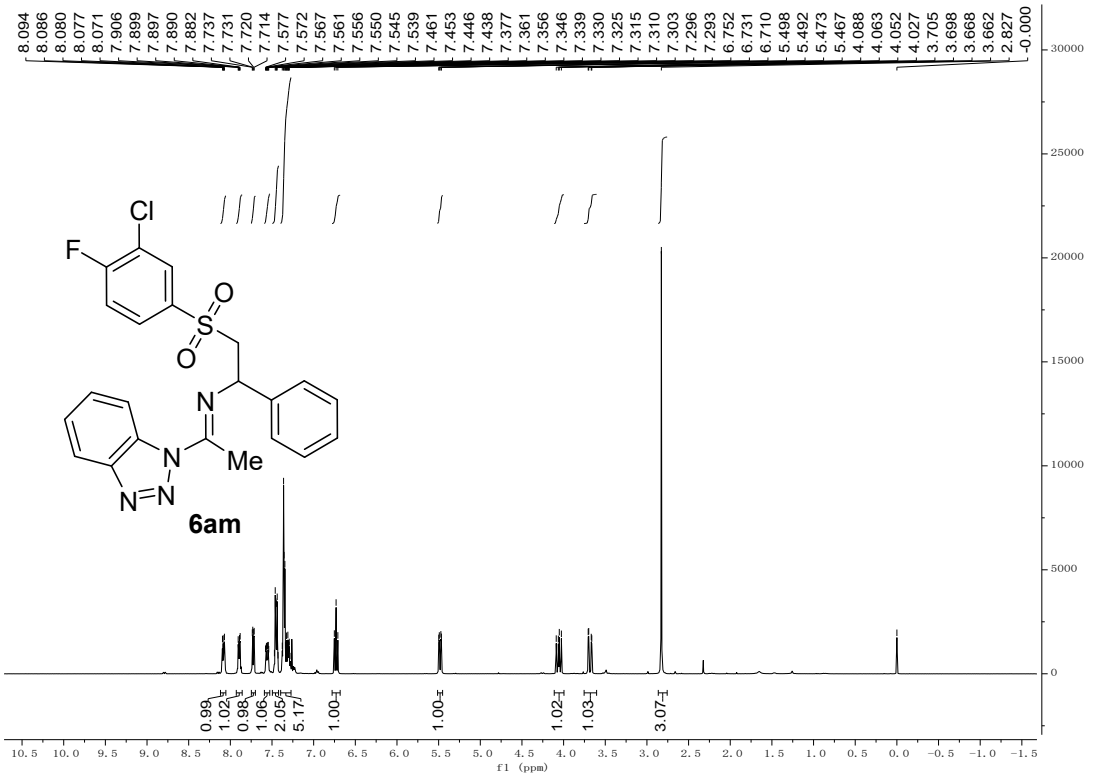


^{1}H NMR of **6al** in $CDCl_3$

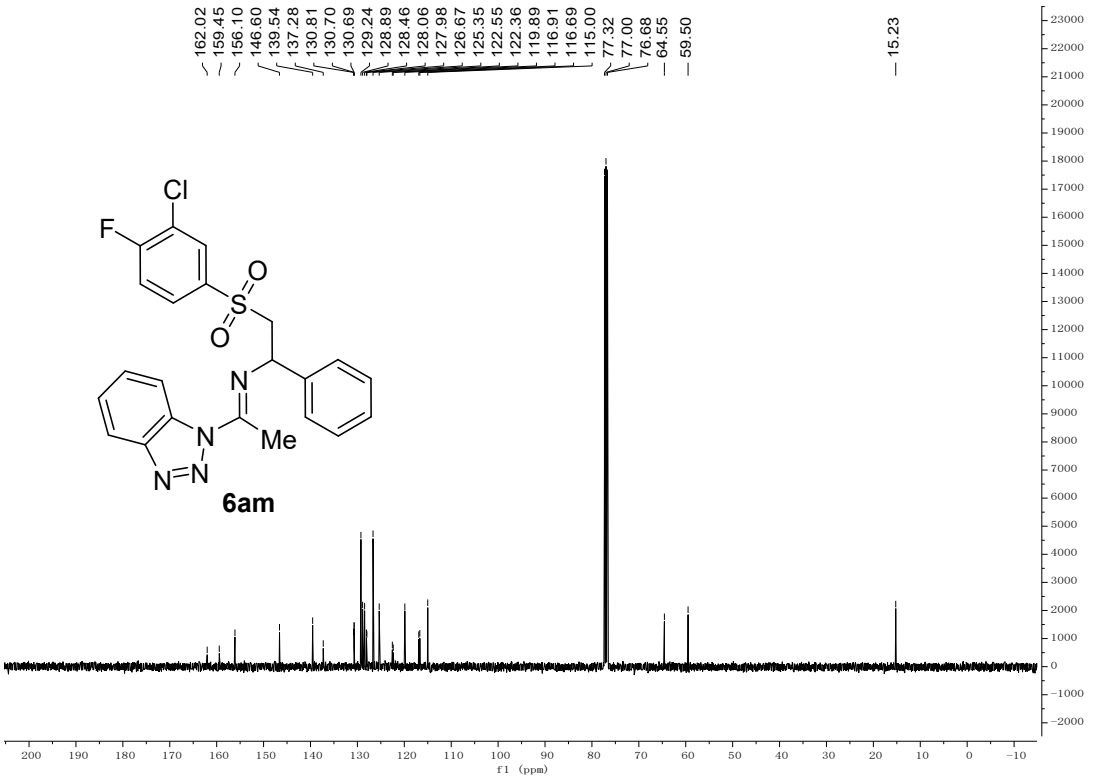
^{13}C NMR of **6al** in $CDCl_3$



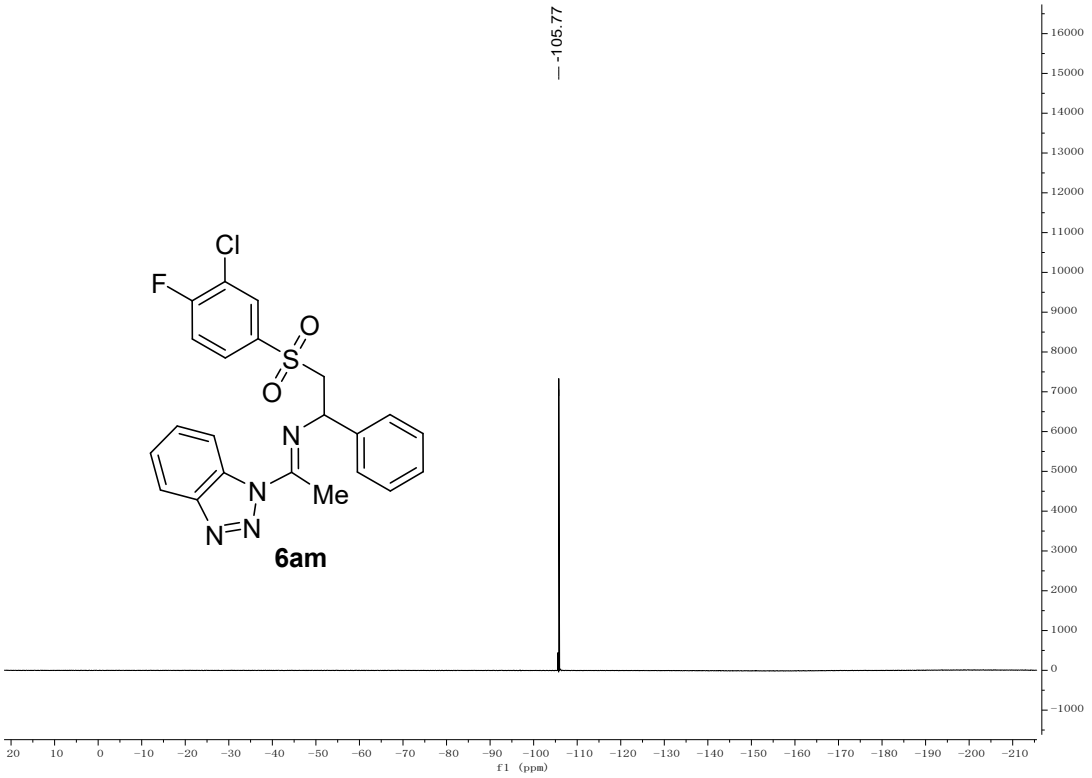
^{1}H NMR of **6am** in $CDCl_3$



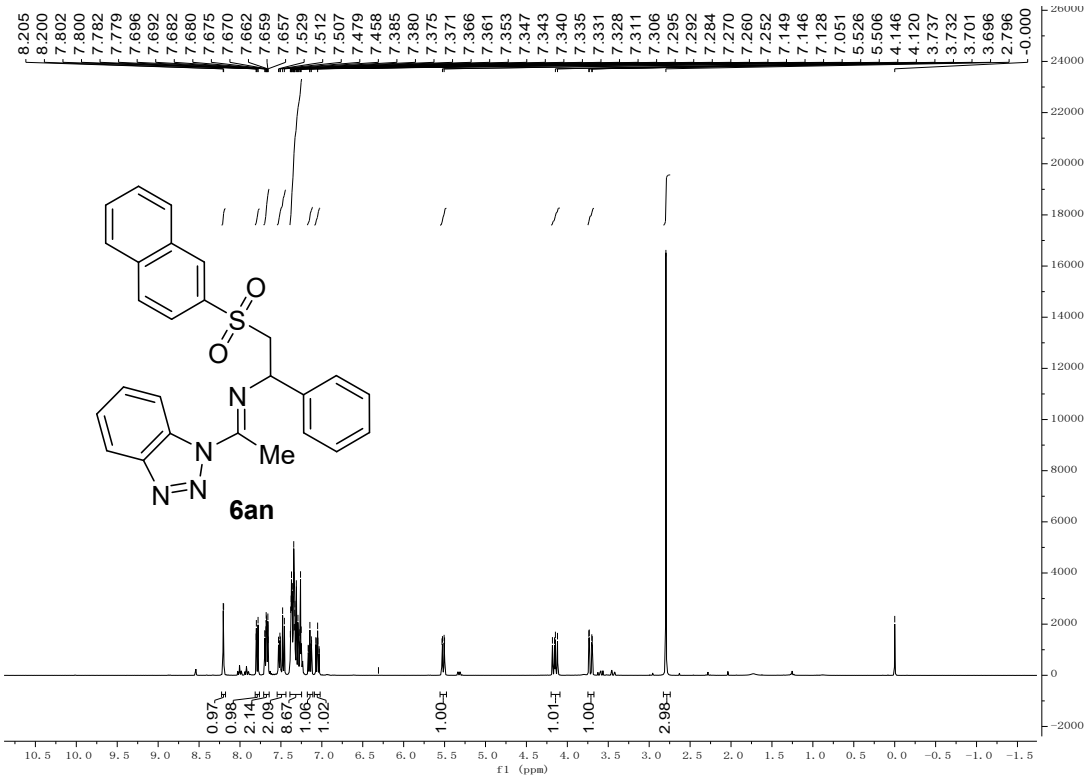
^{13}C NMR of **6am** in $CDCl_3$



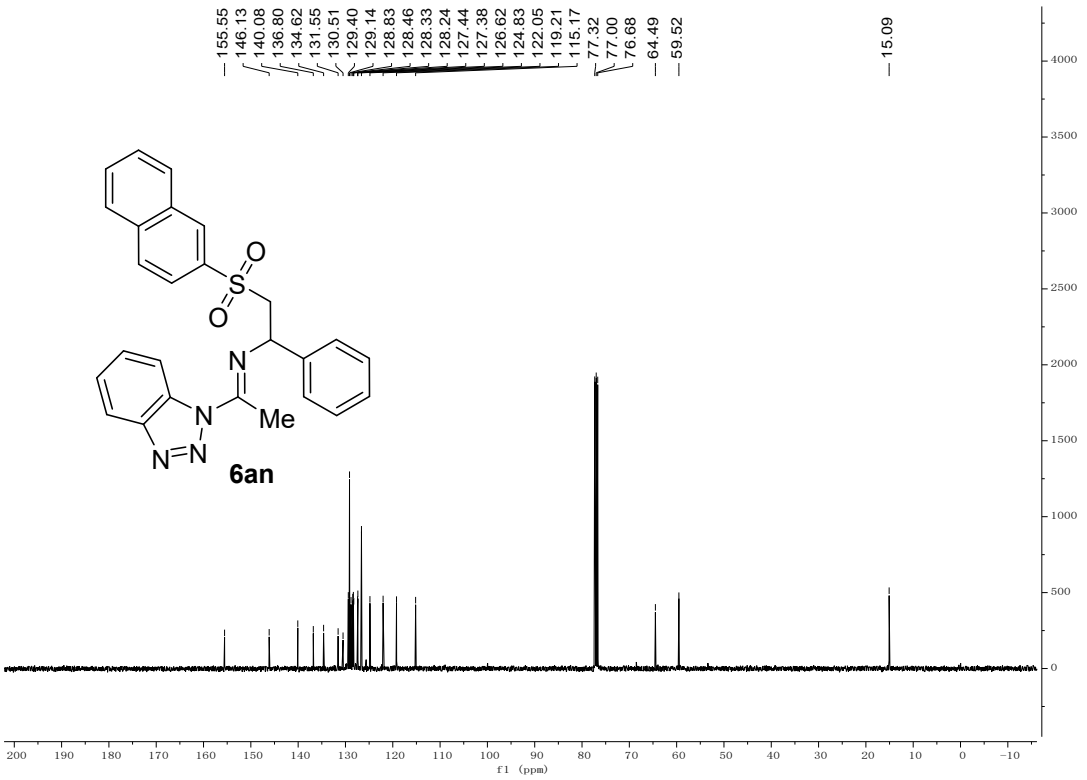
^{19}F NMR spectra of **6am** in $CDCl_3$



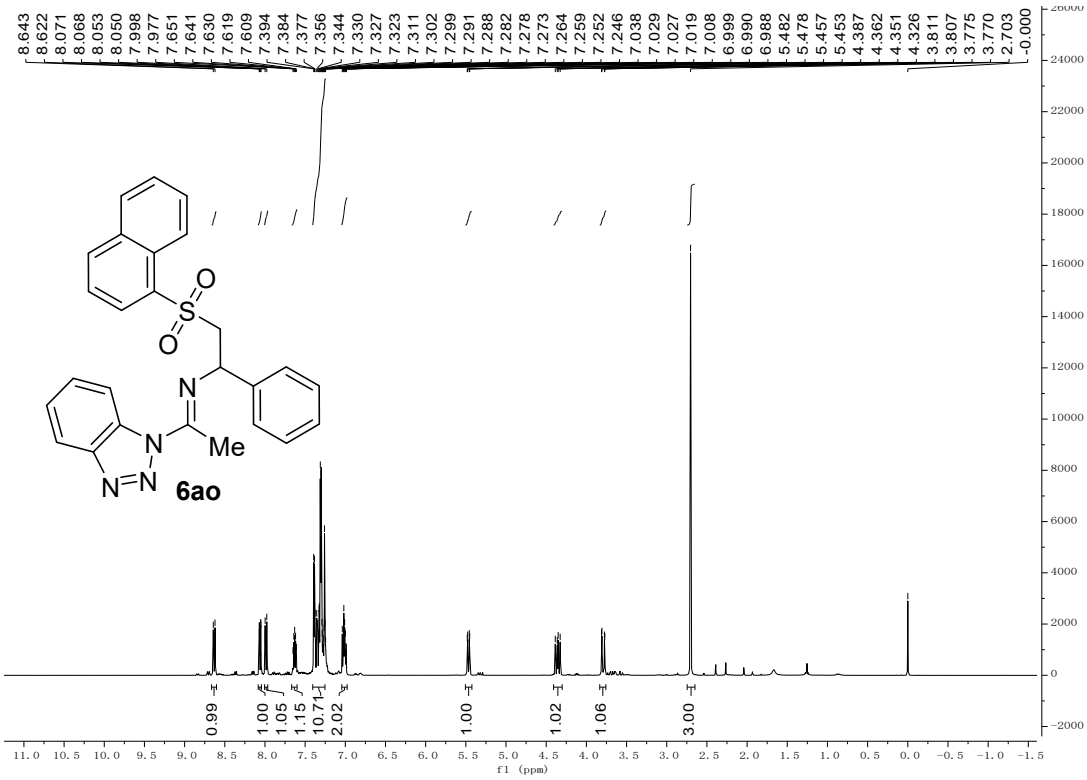
^{1}H NMR of **6an** in $CDCl_3$



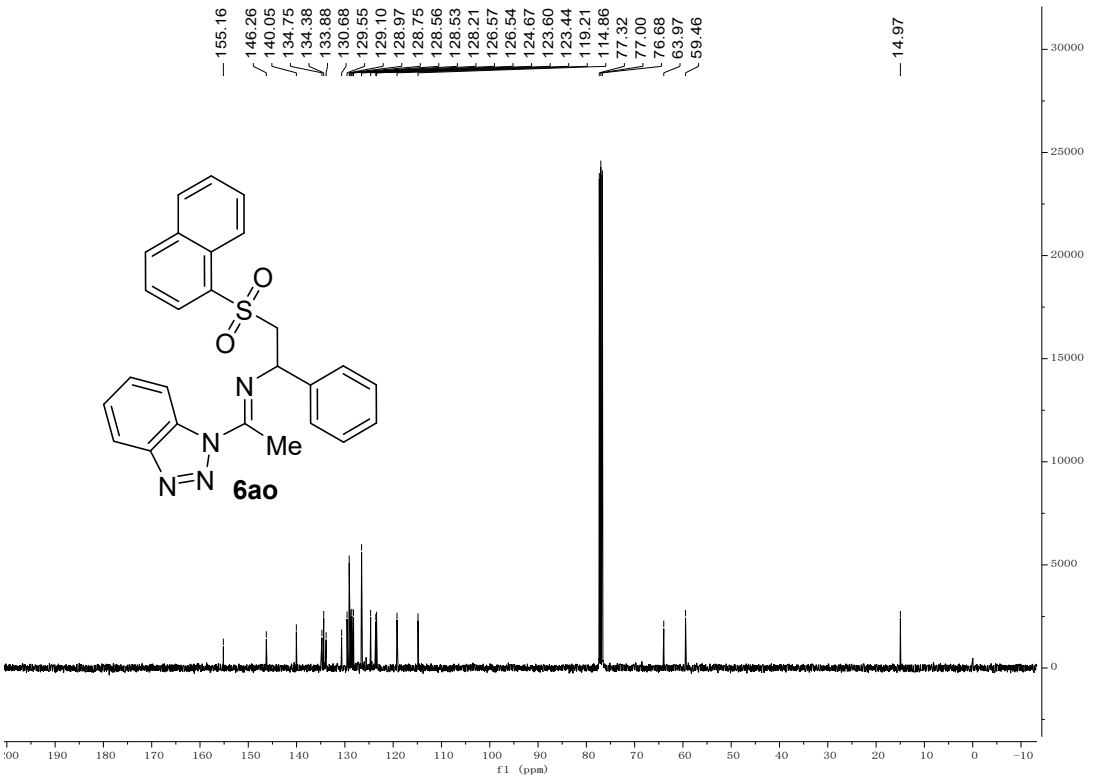
^{13}C NMR of **6an** in $CDCl_3$



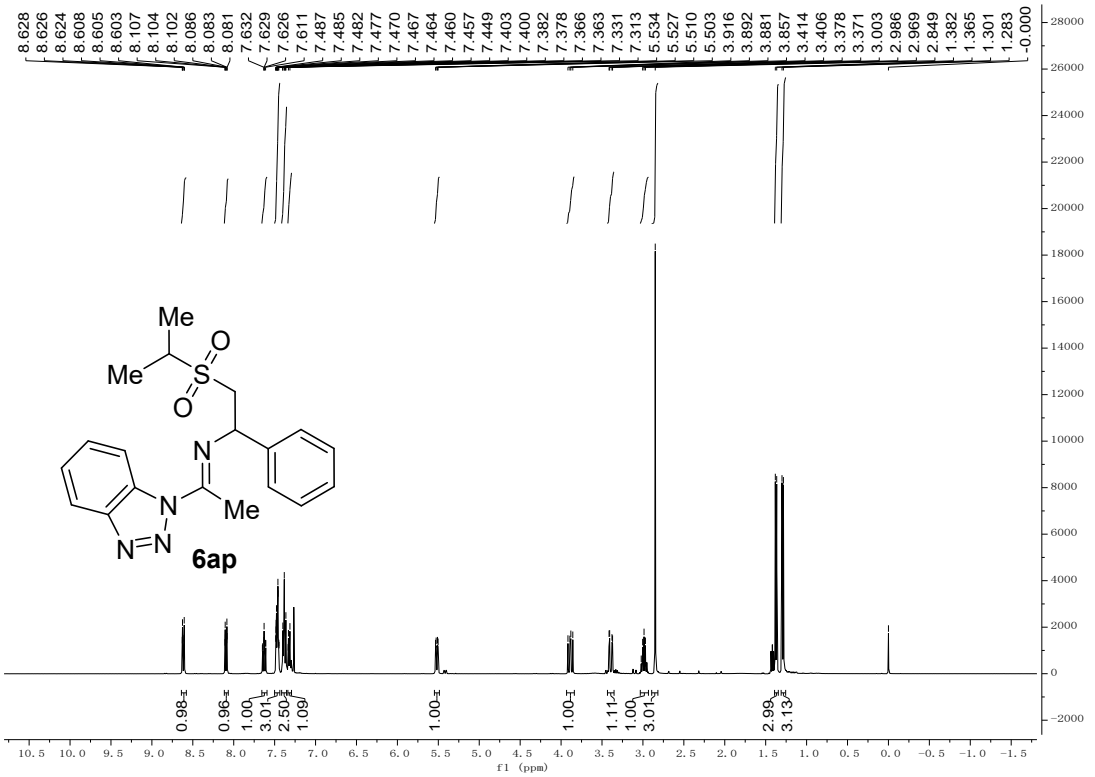
^{1}H NMR of **6ao** in $CDCl_3$



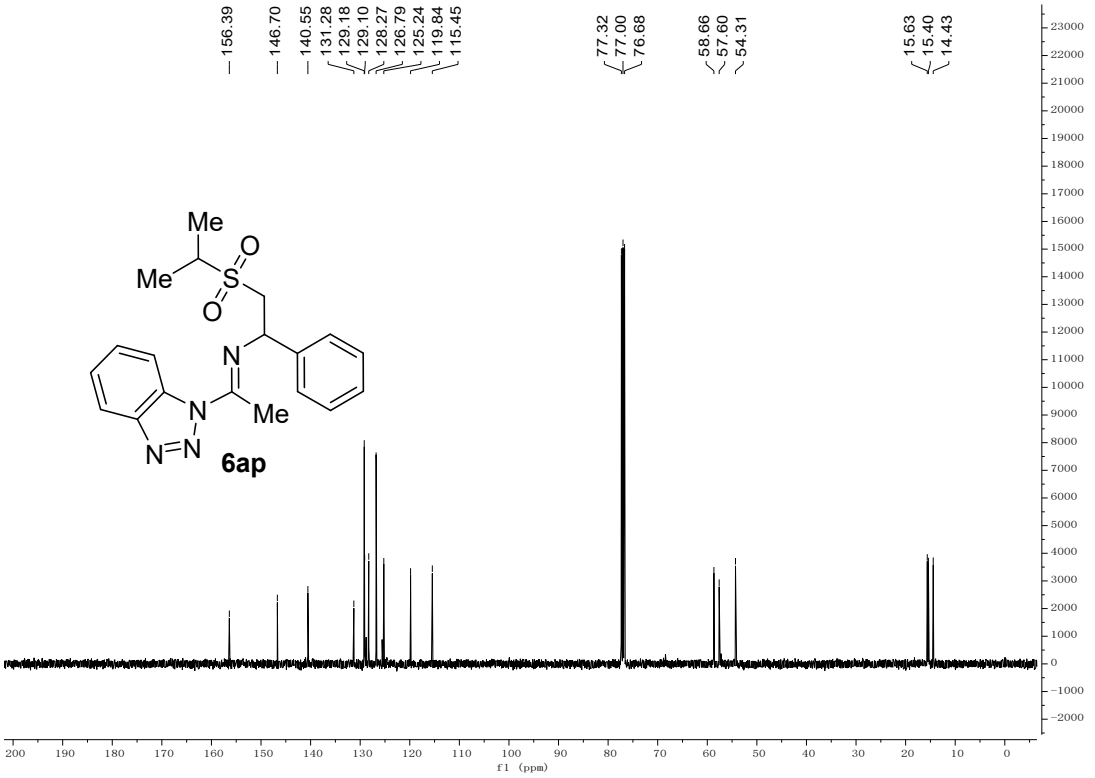
^{13}C NMR of **6ao** in $CDCl_3$



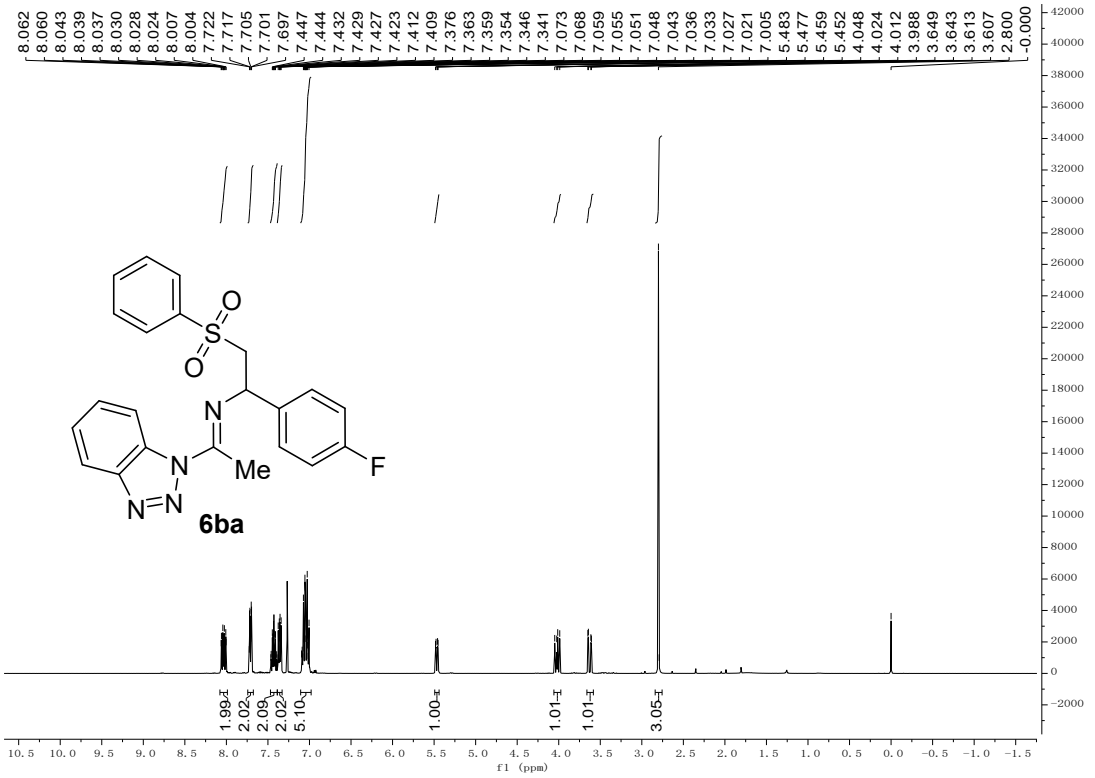
^{1}H NMR of **6ap** in $CDCl_3$



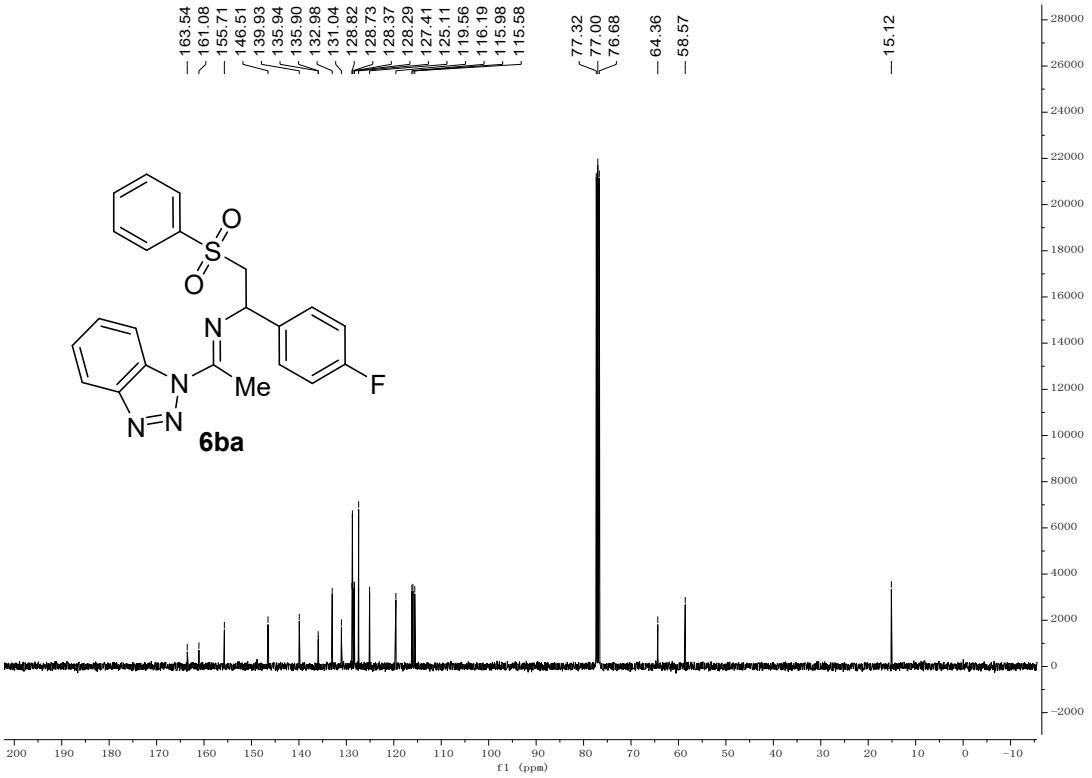
^{13}C NMR of **6ap** in $CDCl_3$



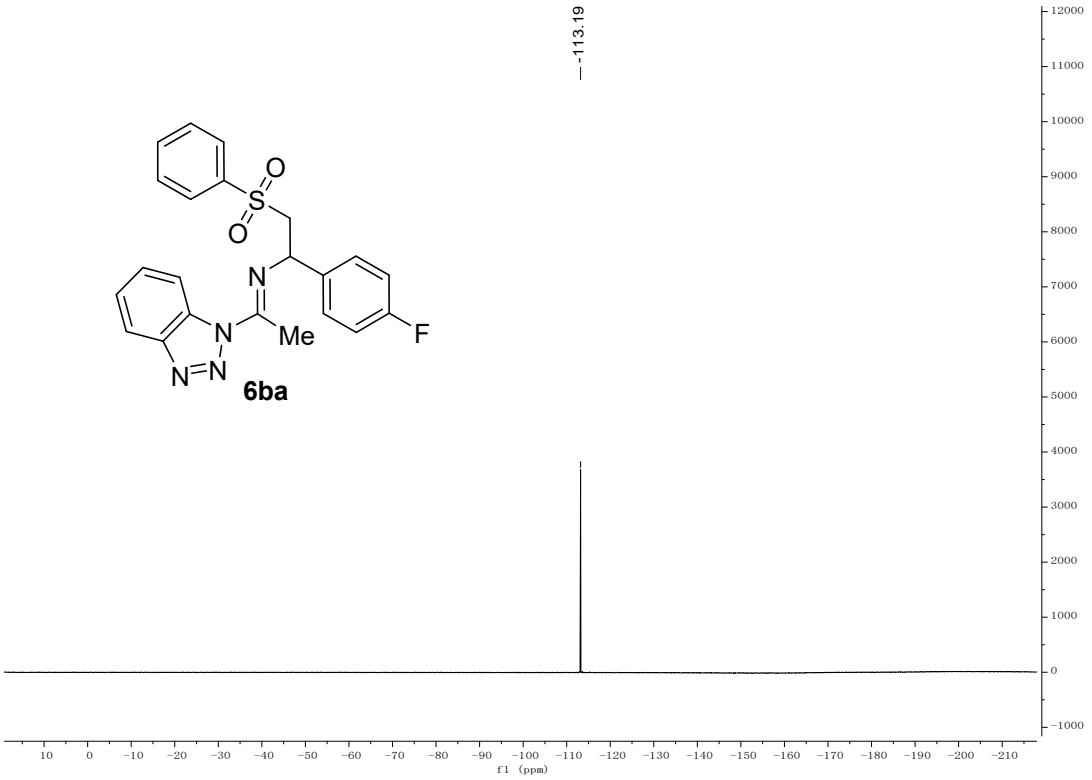
^{1}H NMR of **6ba** in $CDCl_3$



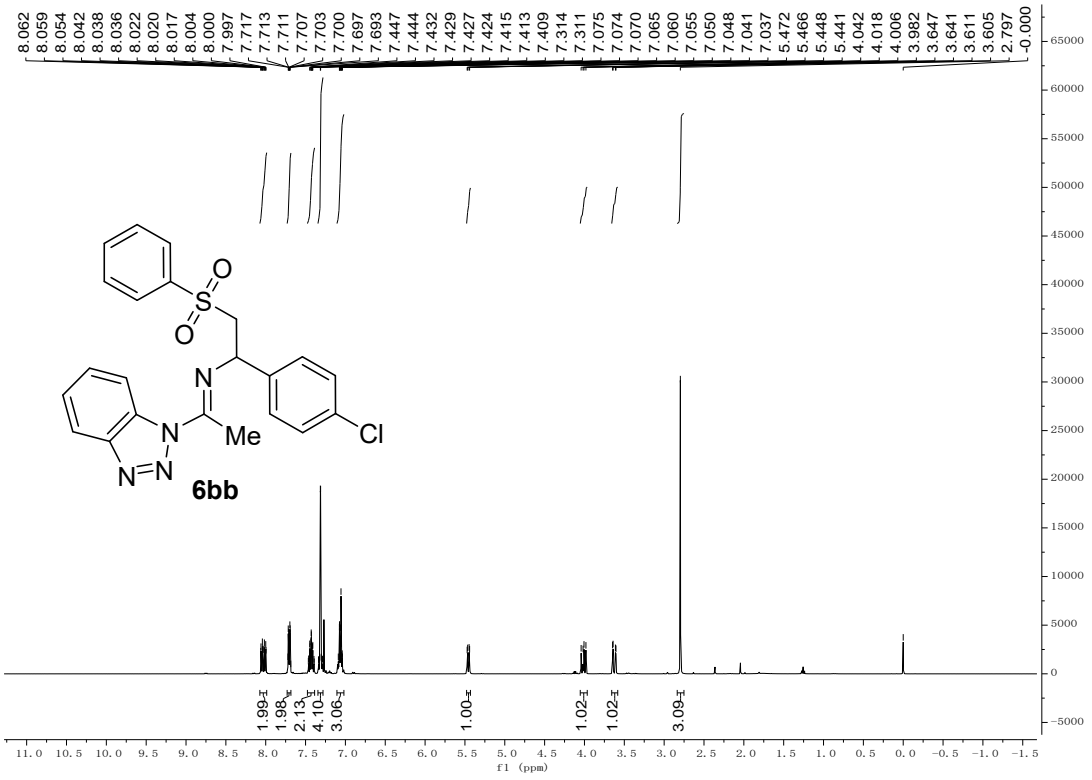
^{13}C NMR of **6ba** in $CDCl_3$



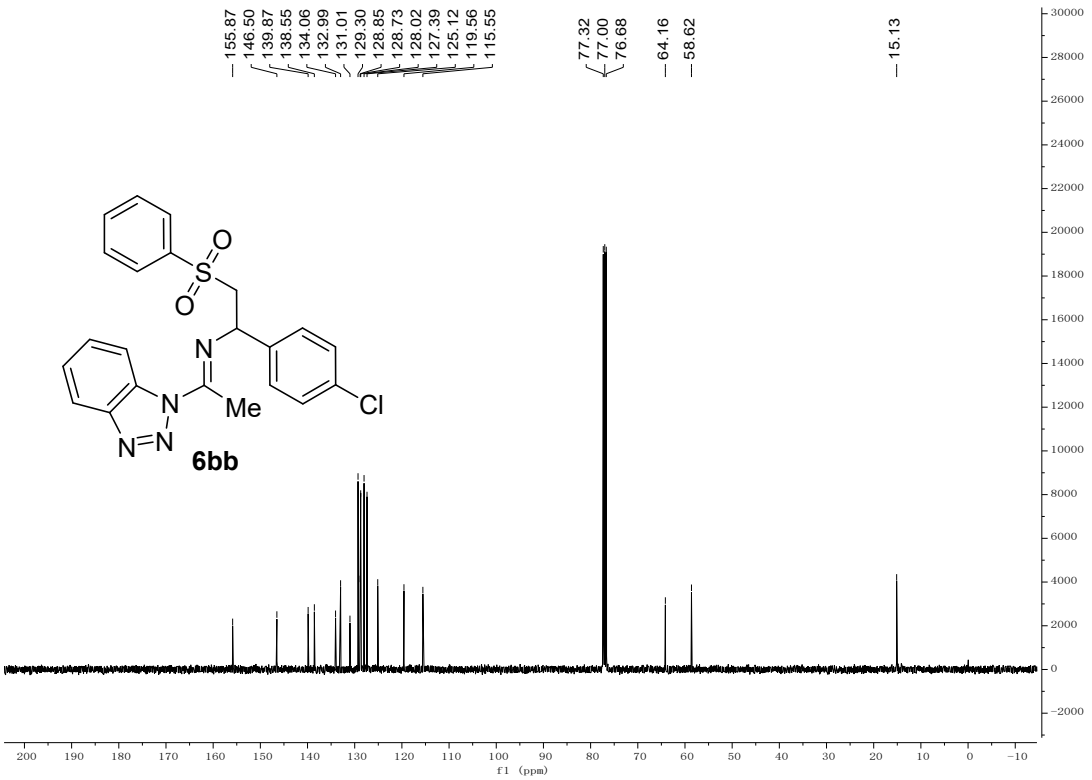
^{19}F NMR spectra of **6ba** in $CDCl_3$



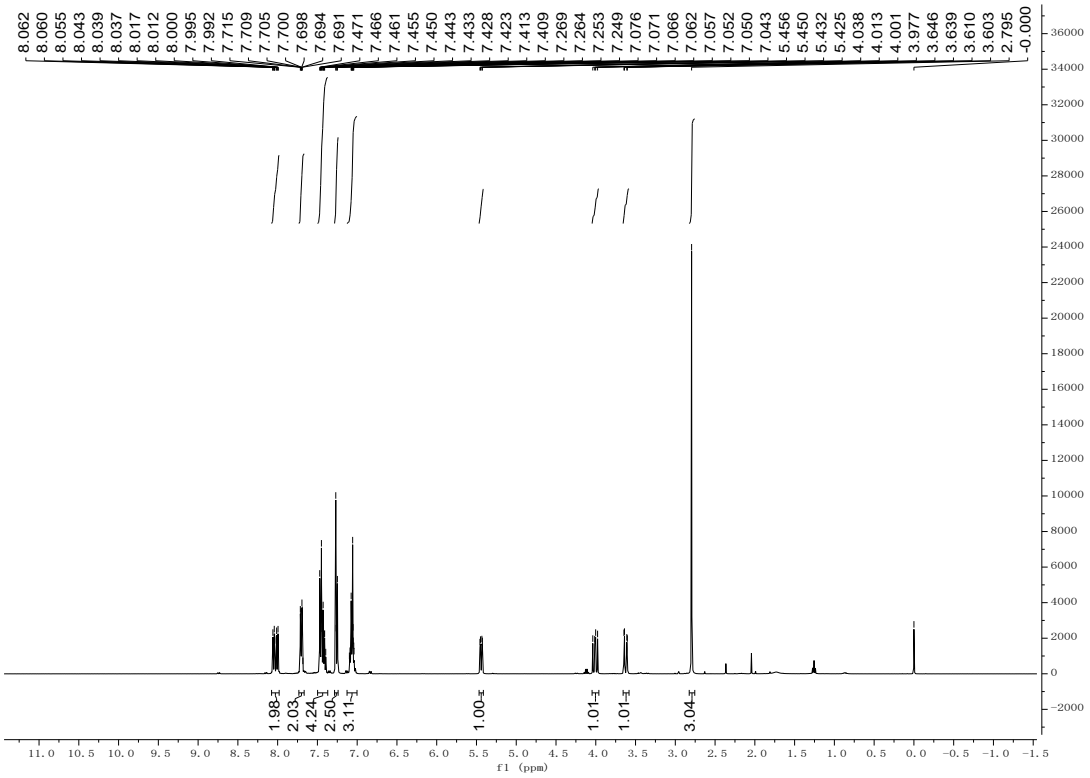
^{1}H NMR of **6bb** in $CDCl_3$



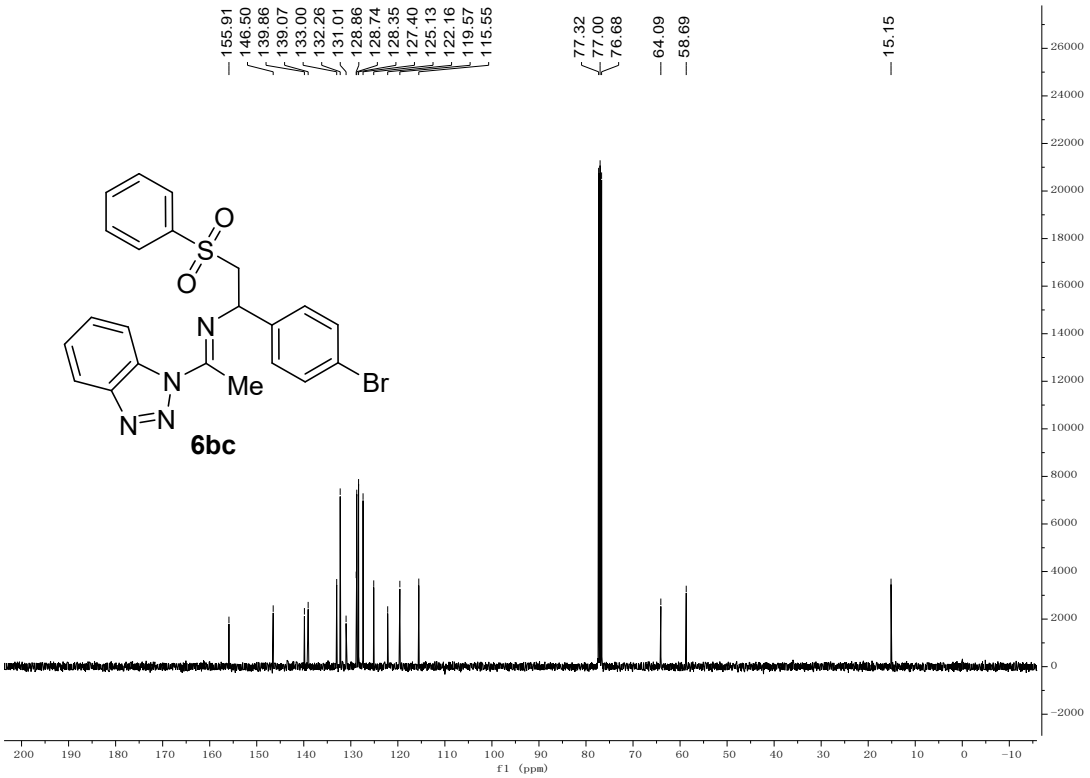
^{13}C NMR of **6bb** in $CDCl_3$



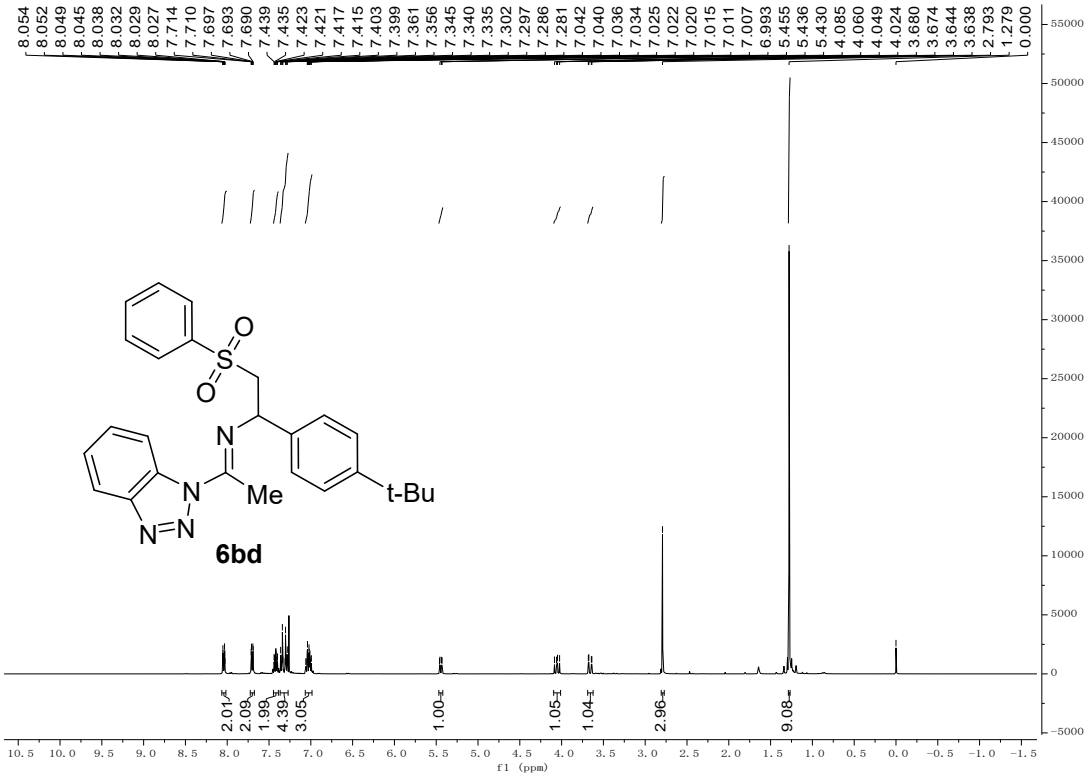
^{1}H NMR of **6bc** in $CDCl_3$



^{13}C NMR of **6bc** in $CDCl_3$



^{1}H NMR of **6bd** in $CDCl_3$



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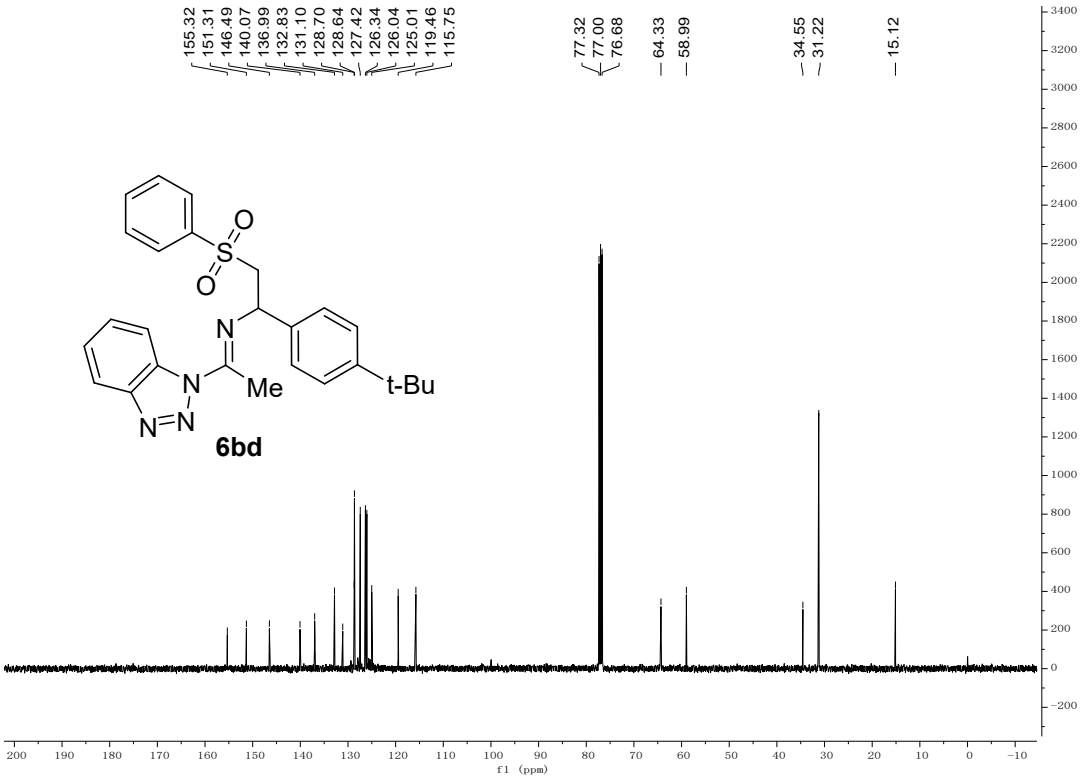
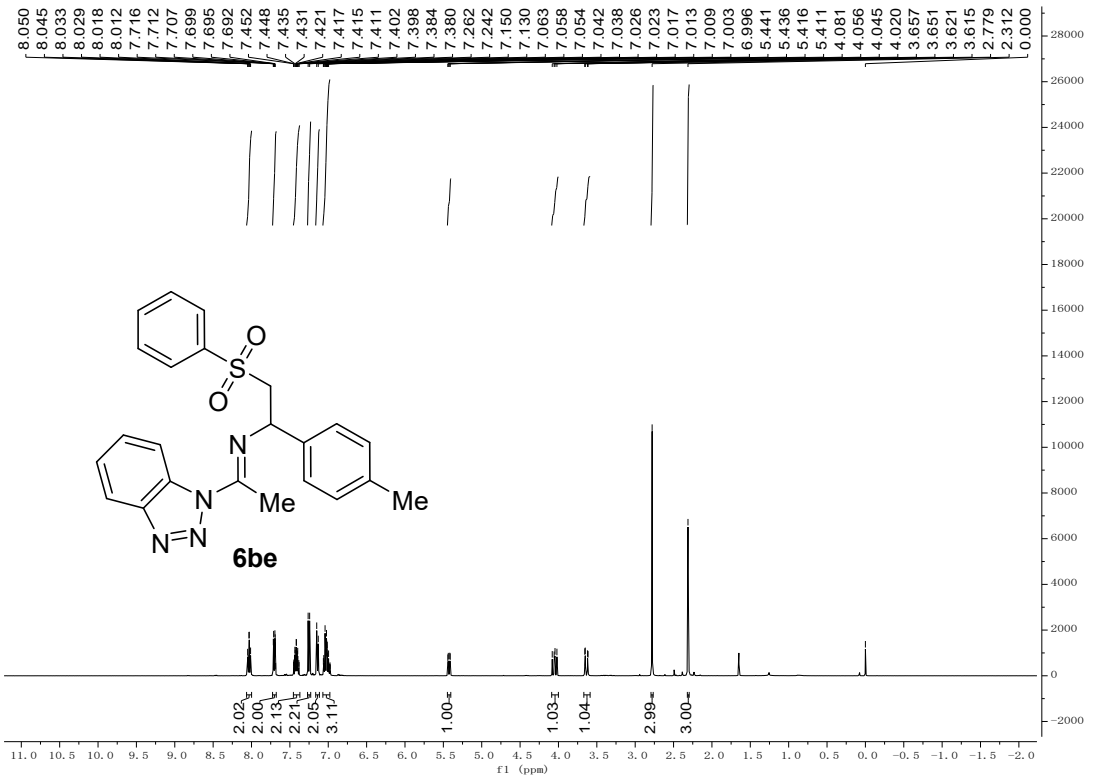


^{1}H NMR of **6be** in $CDCl_3$



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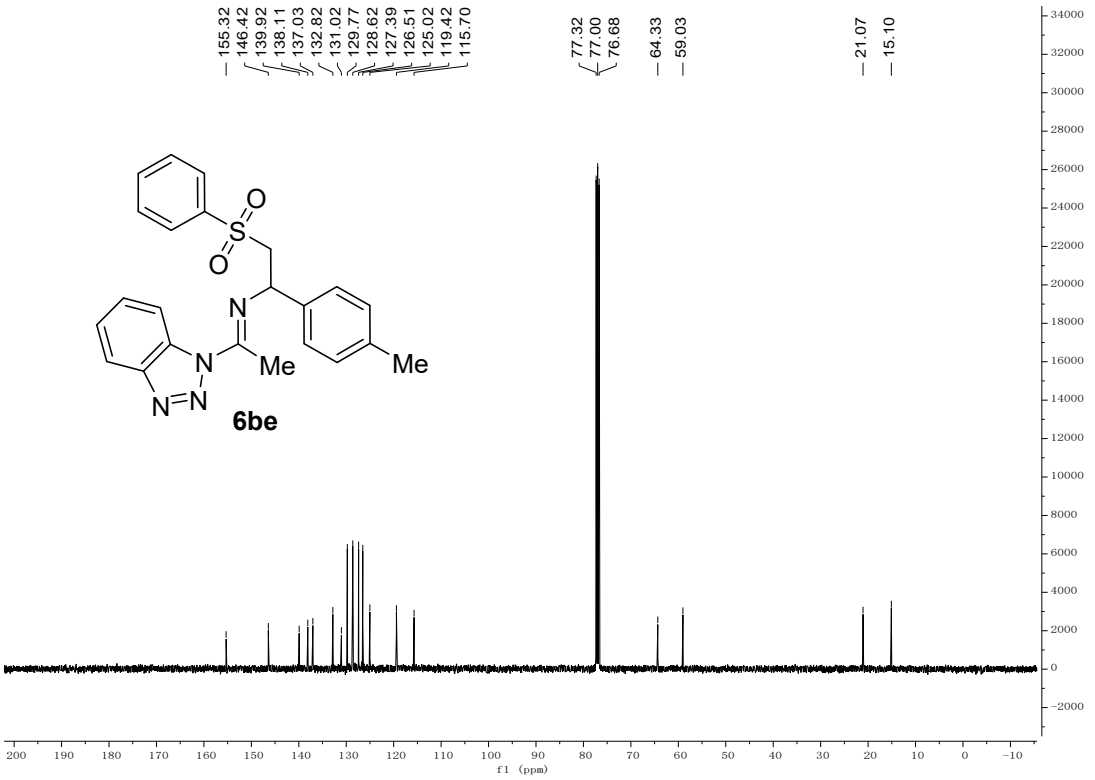
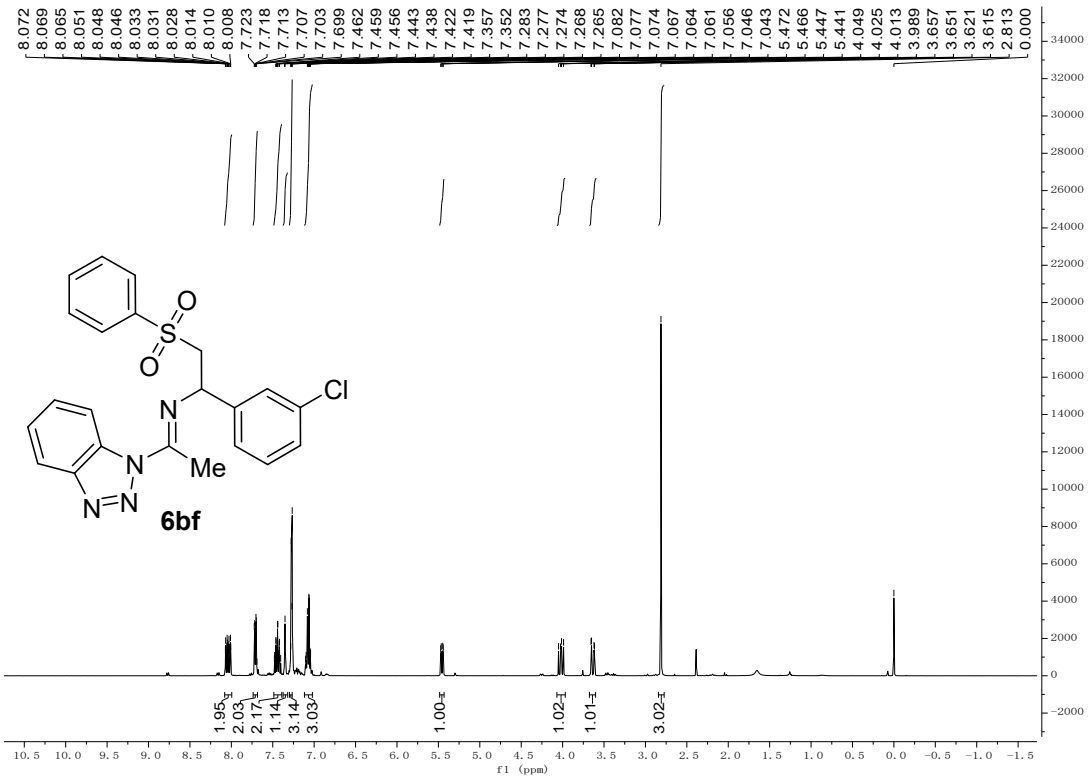


^{1}H NMR of **6bf** in $CDCl_3$



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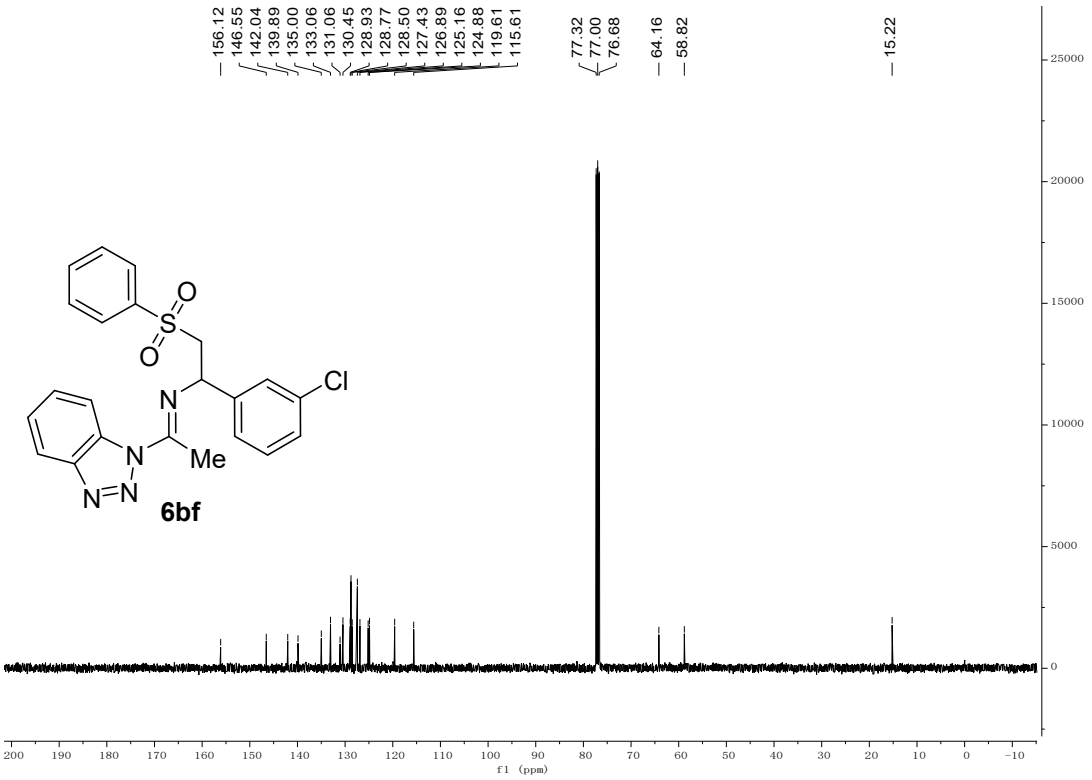

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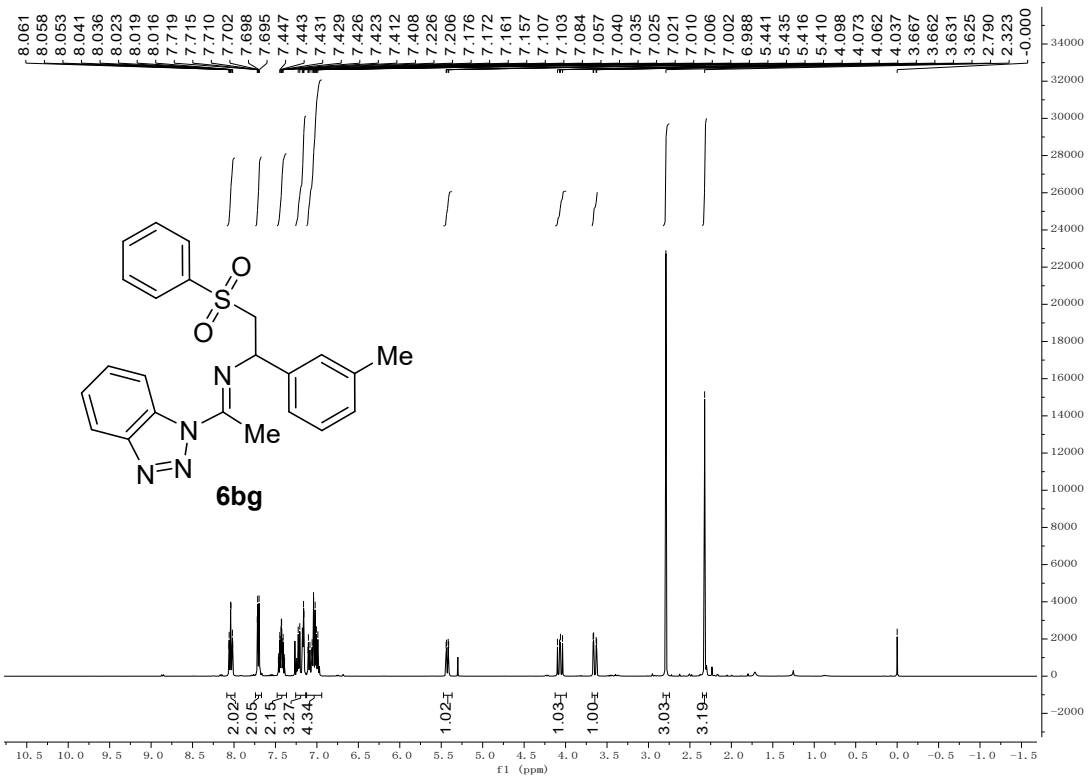

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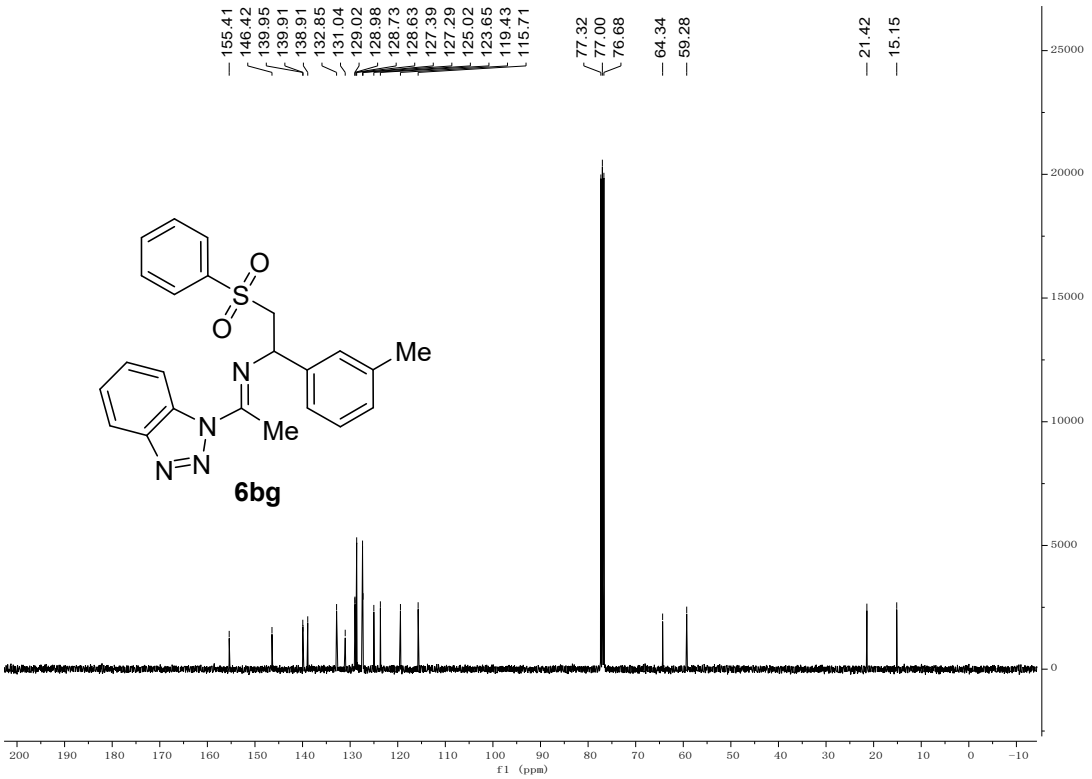
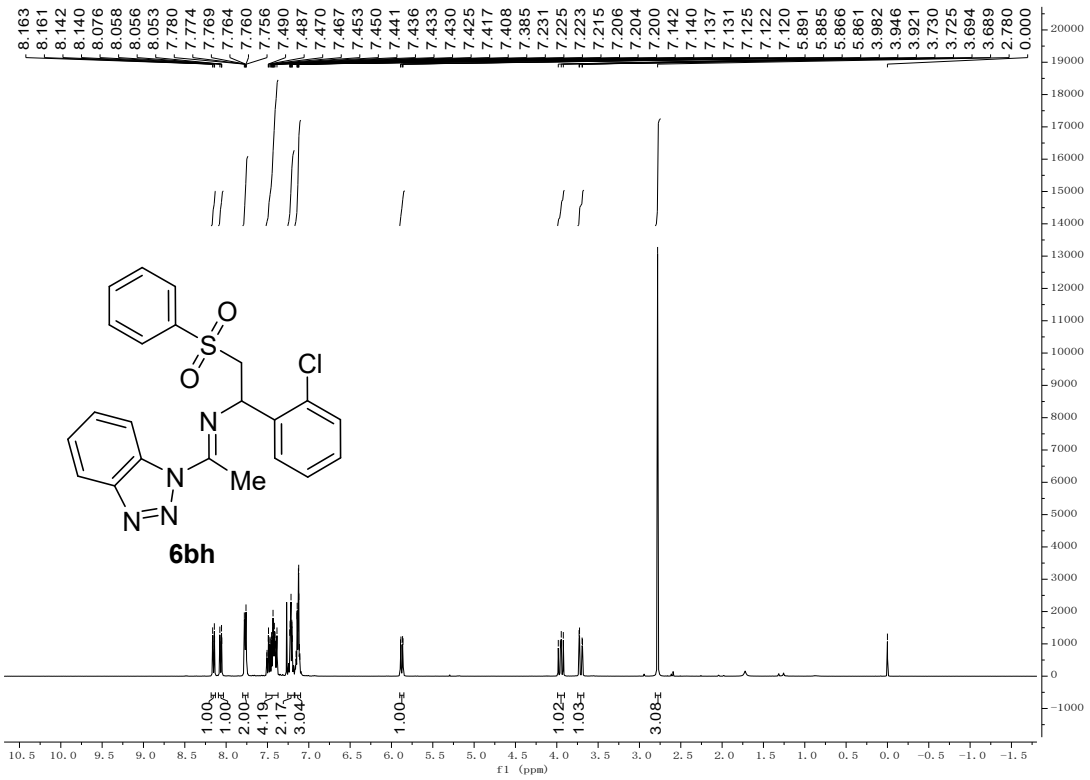


^{1}H NMR of **6bh** in $CDCl_3$



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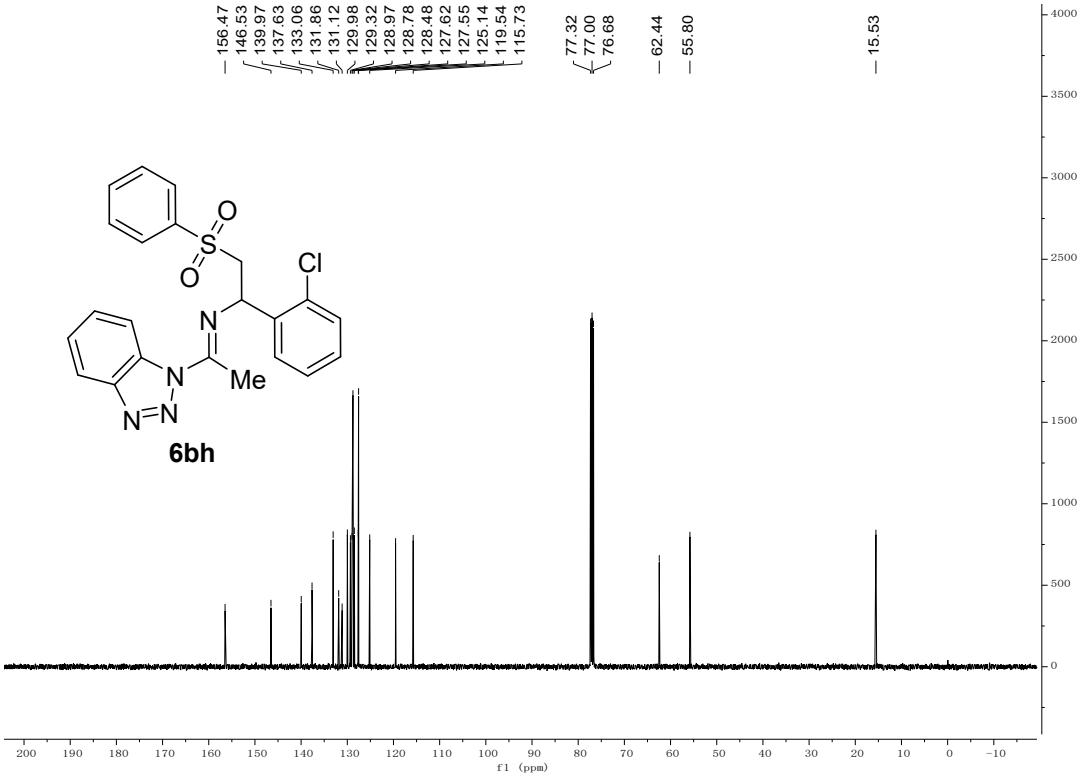

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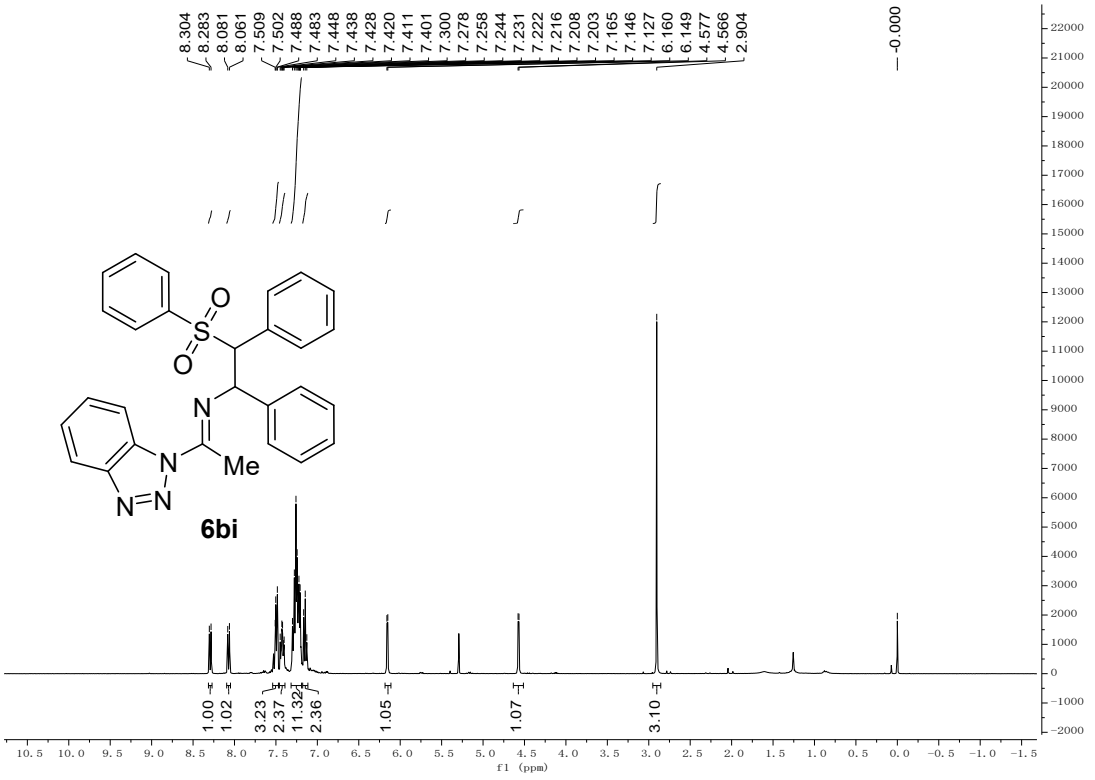
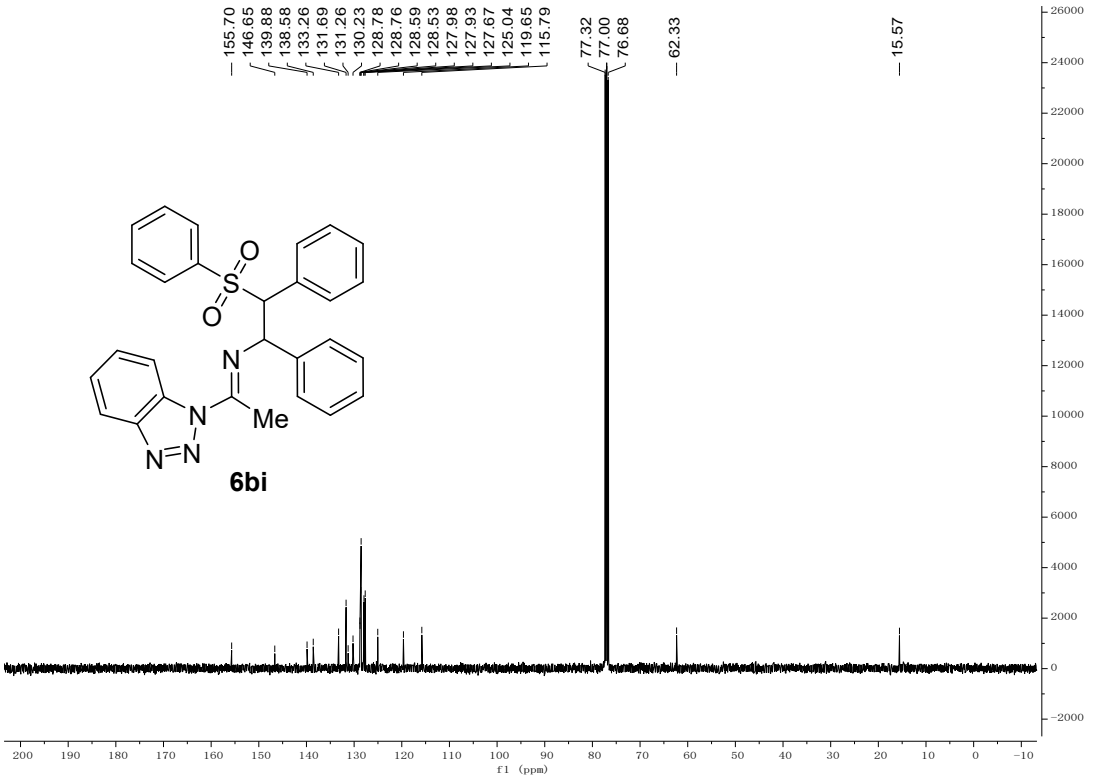


^{13}C NMR of **6bi** in $CDCl_3$



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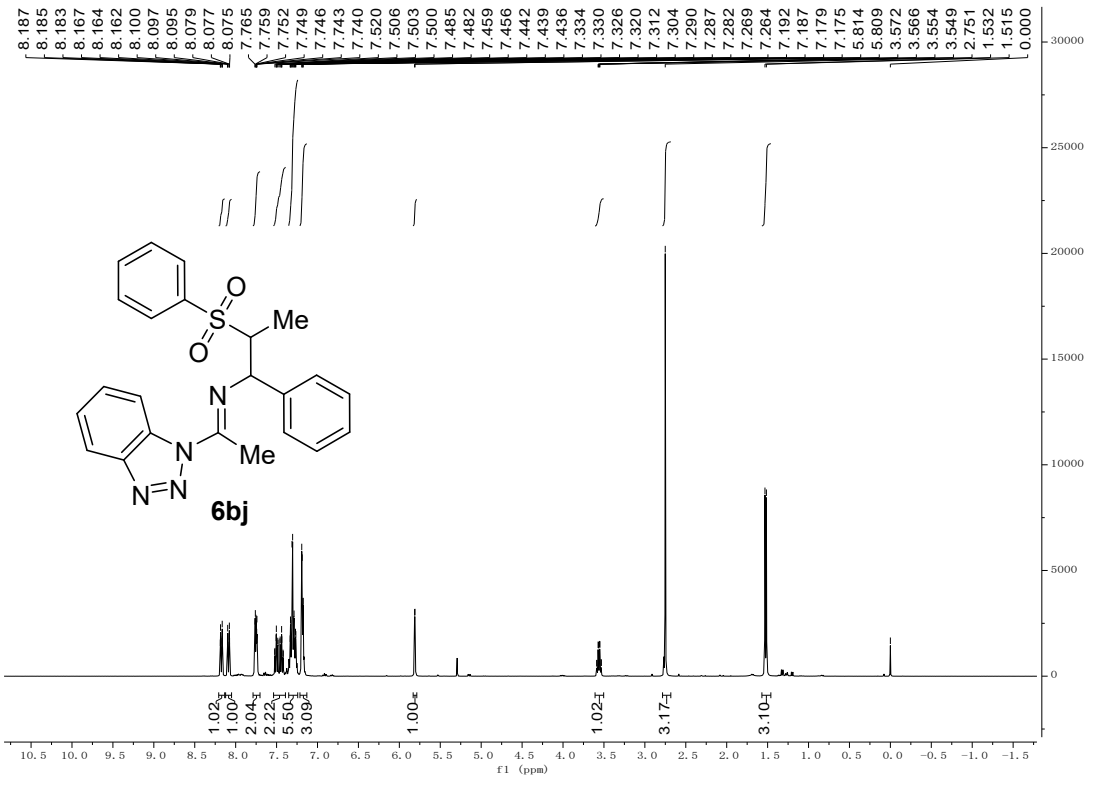

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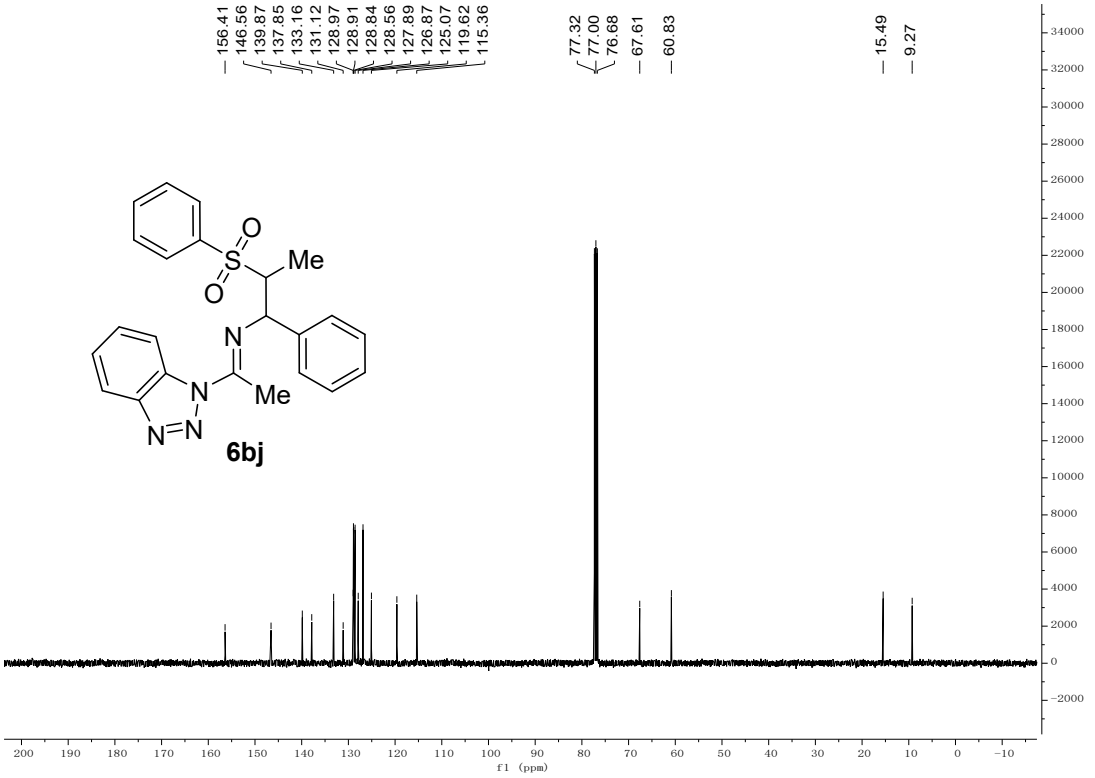
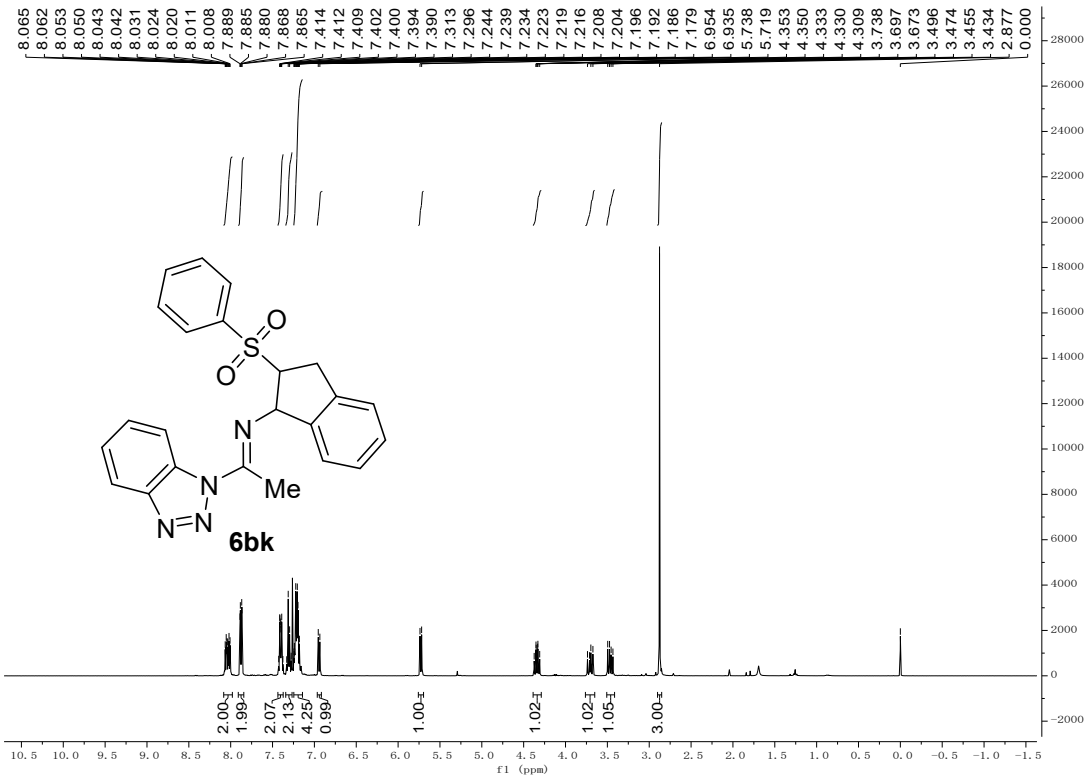


^{1}H NMR of **6bk** in $CDCl_3$



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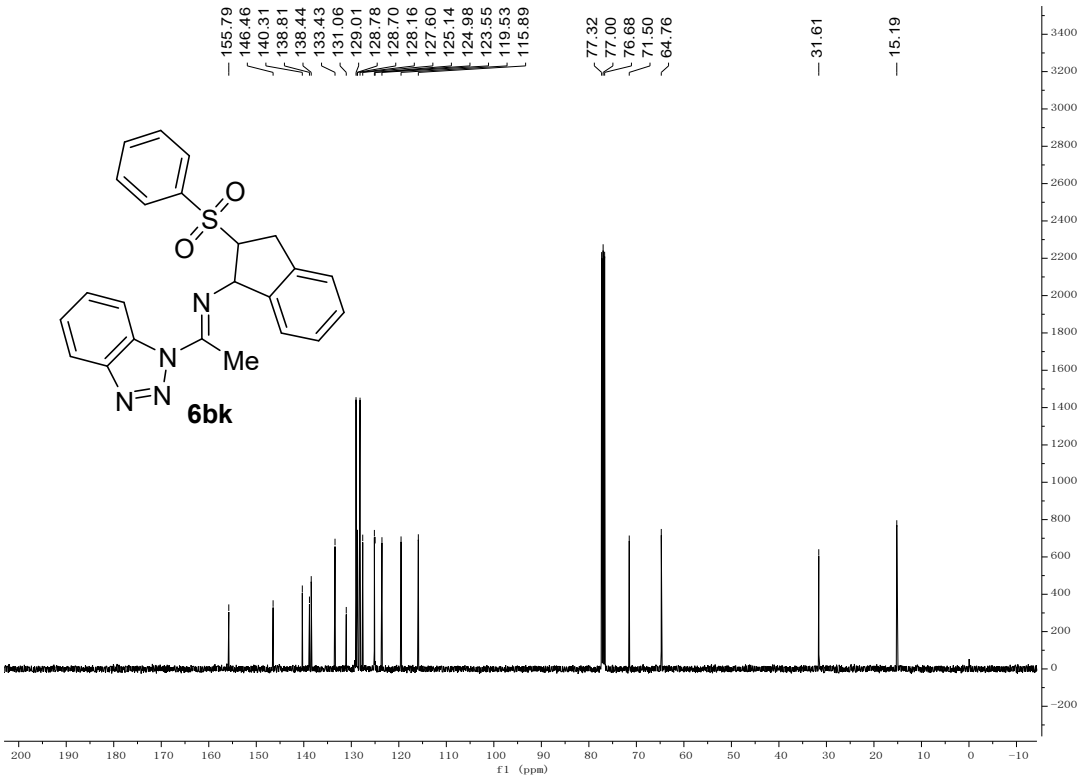

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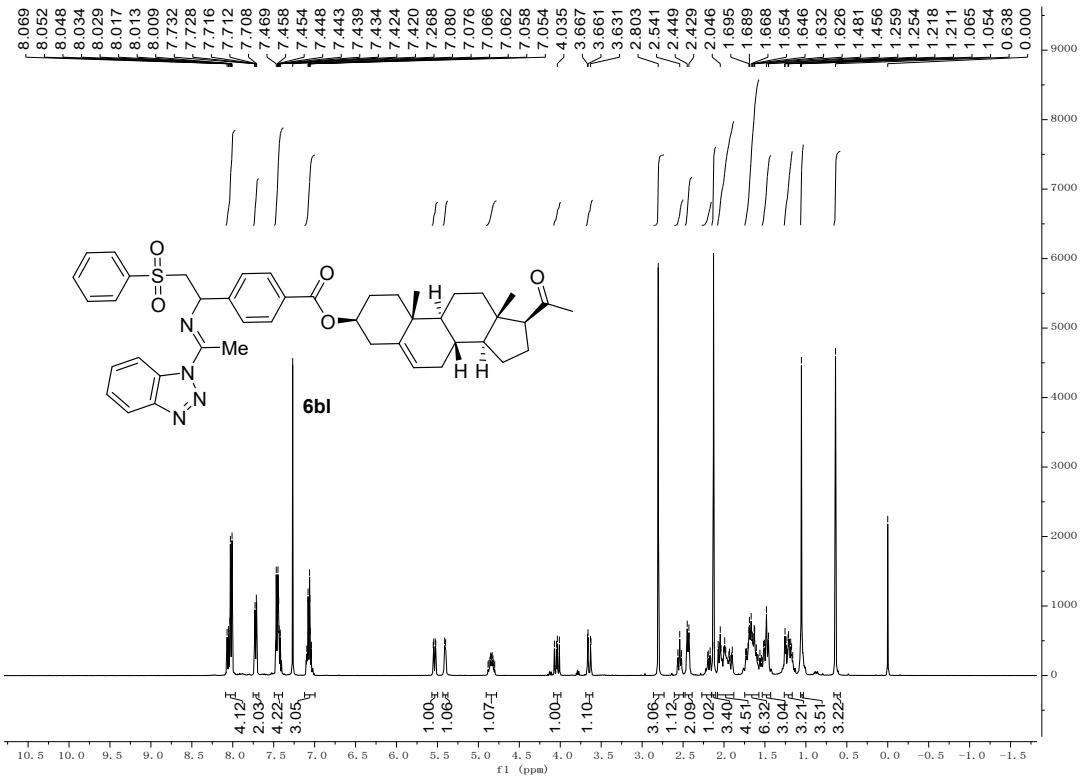

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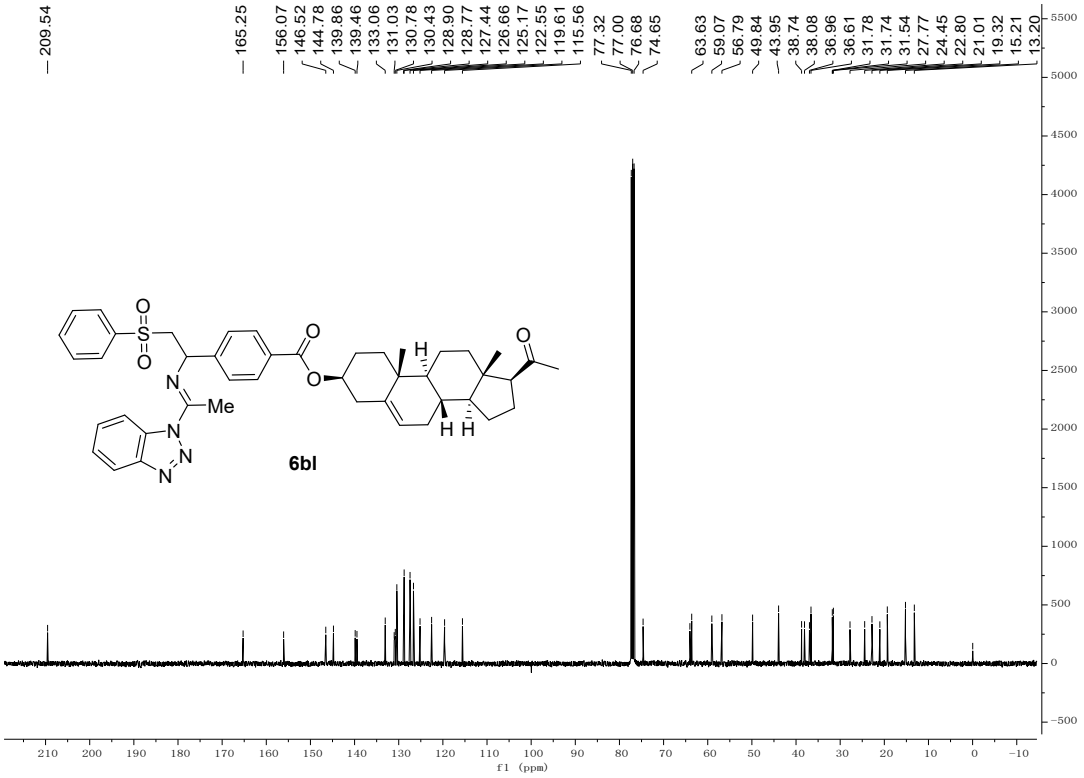
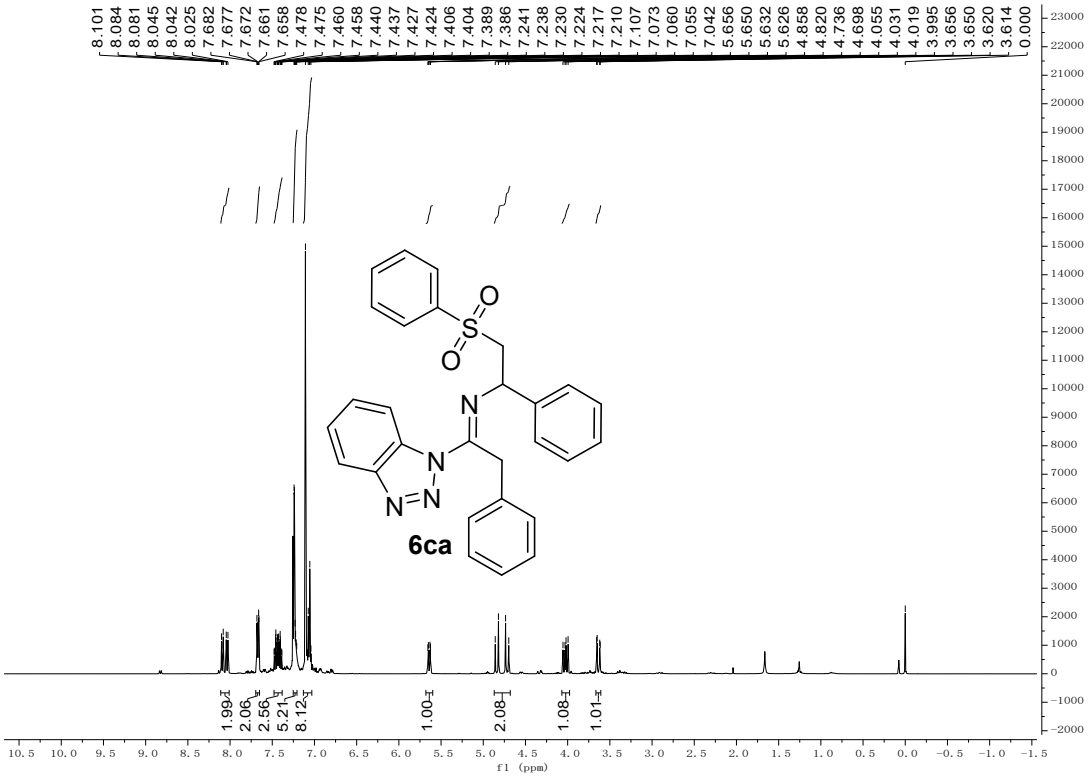


^{1}H NMR of **6ca** in $CDCl_3$



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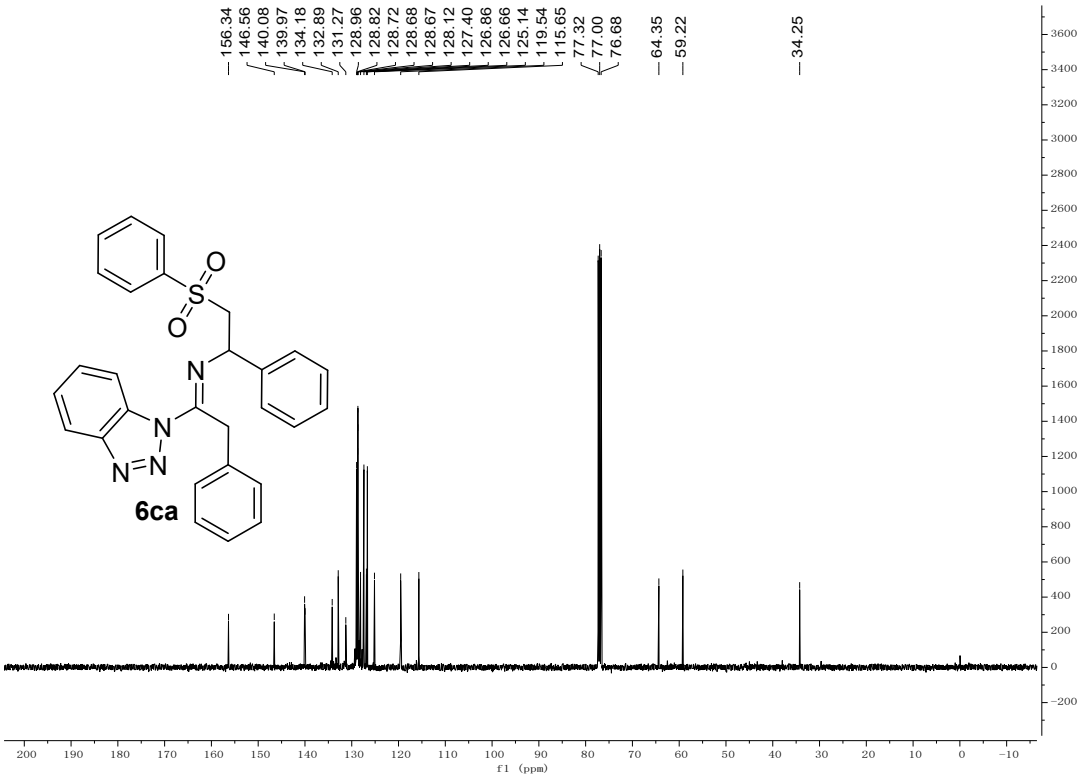
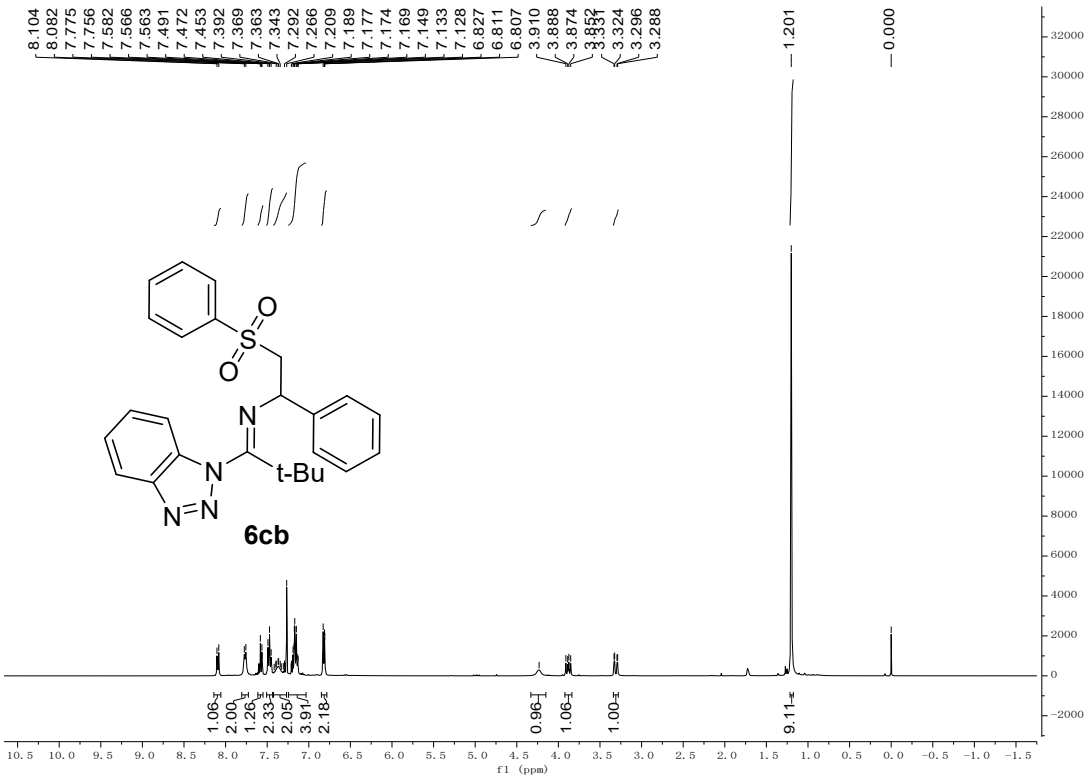
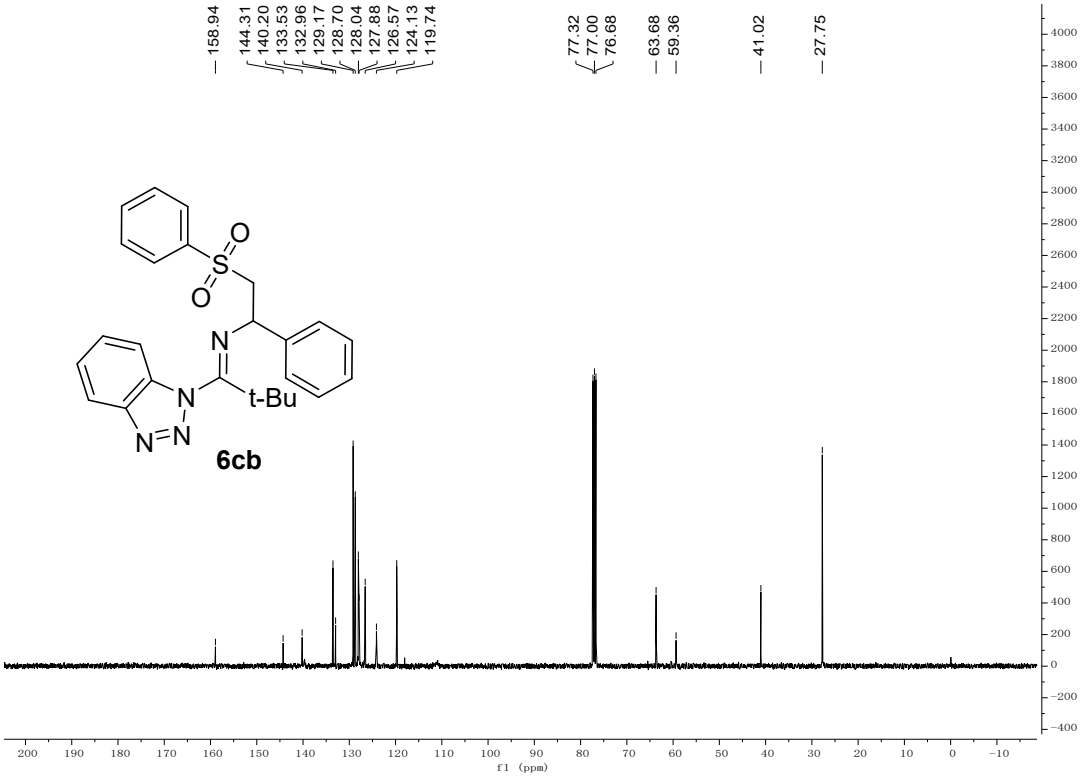


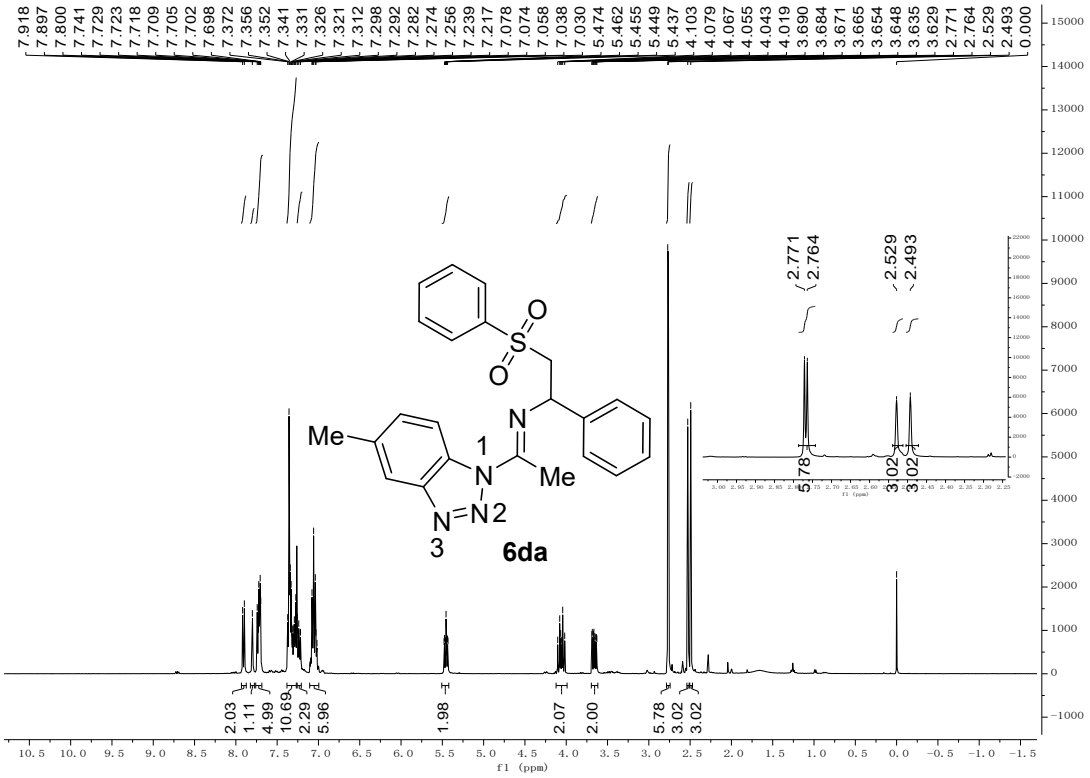
^{1}H NMR of **6cb** in $CDCl_3$



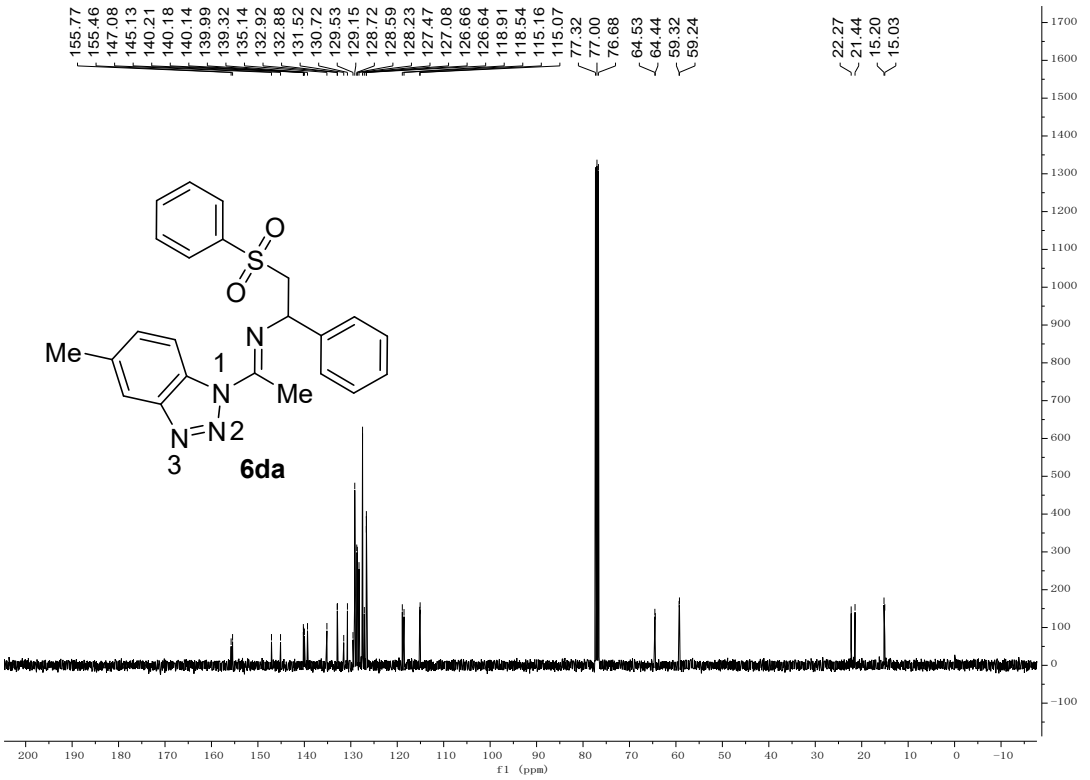
^{13}C NMR of **6cb** in $CDCl_3$



^{1}H NMR of **6da** in $CDCl_3$



^{13}C NMR of **6da** in $CDCl_3$



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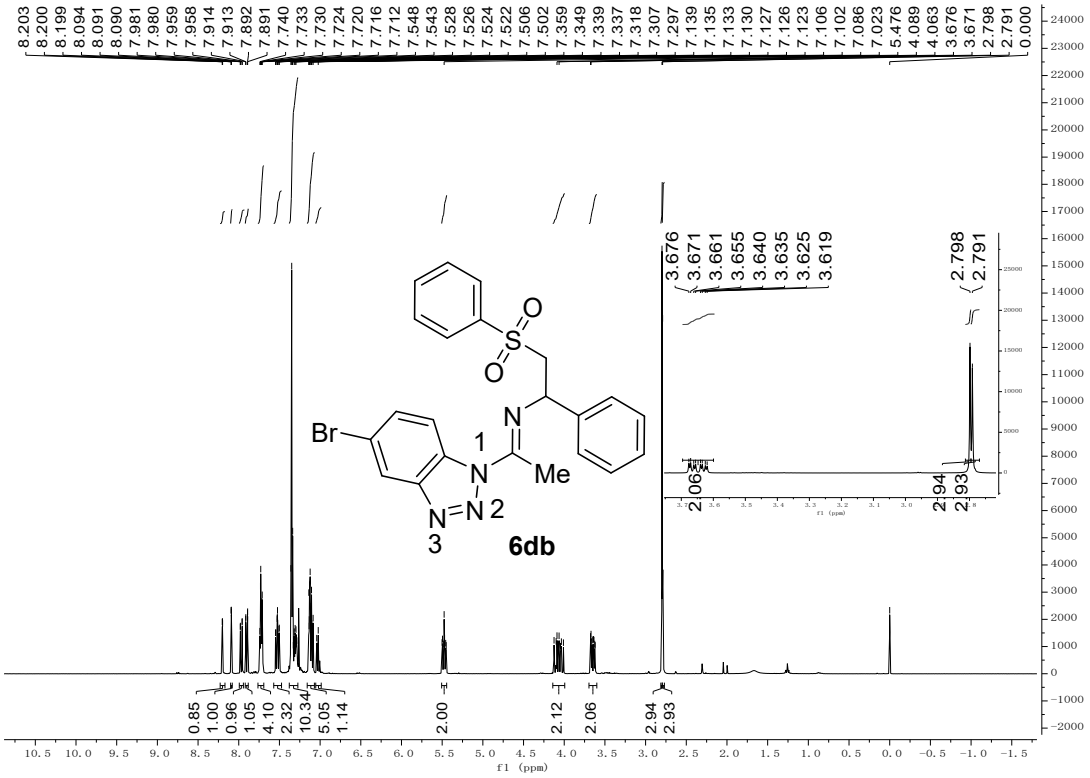

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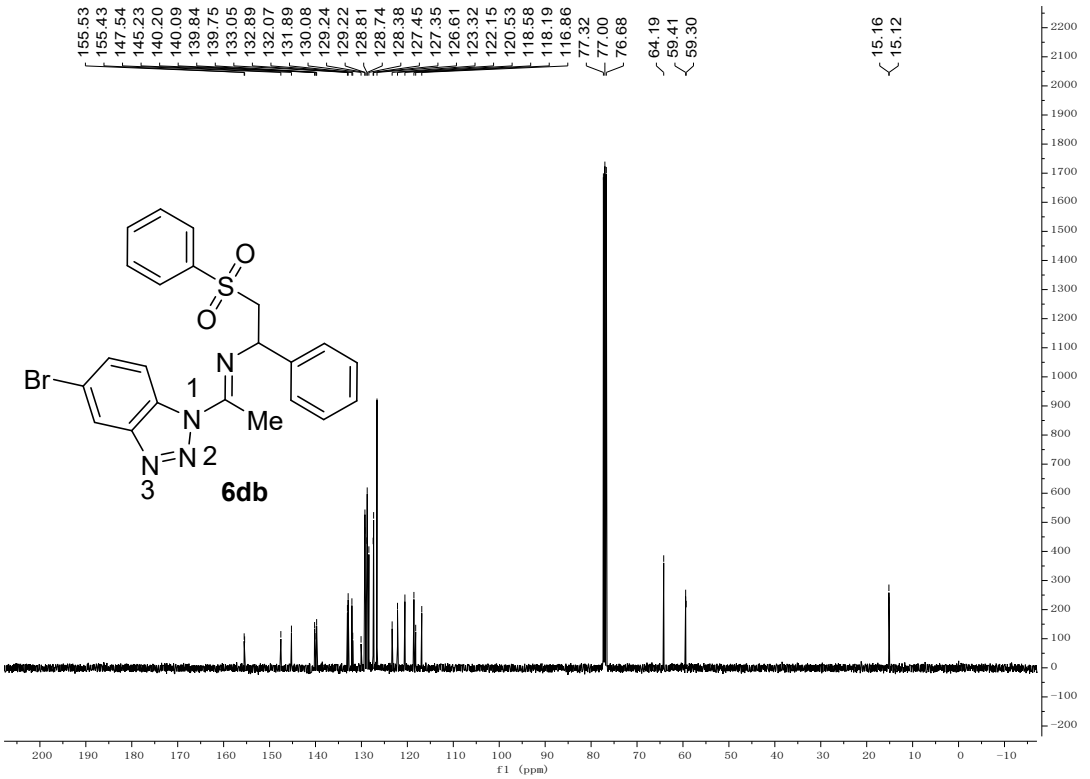
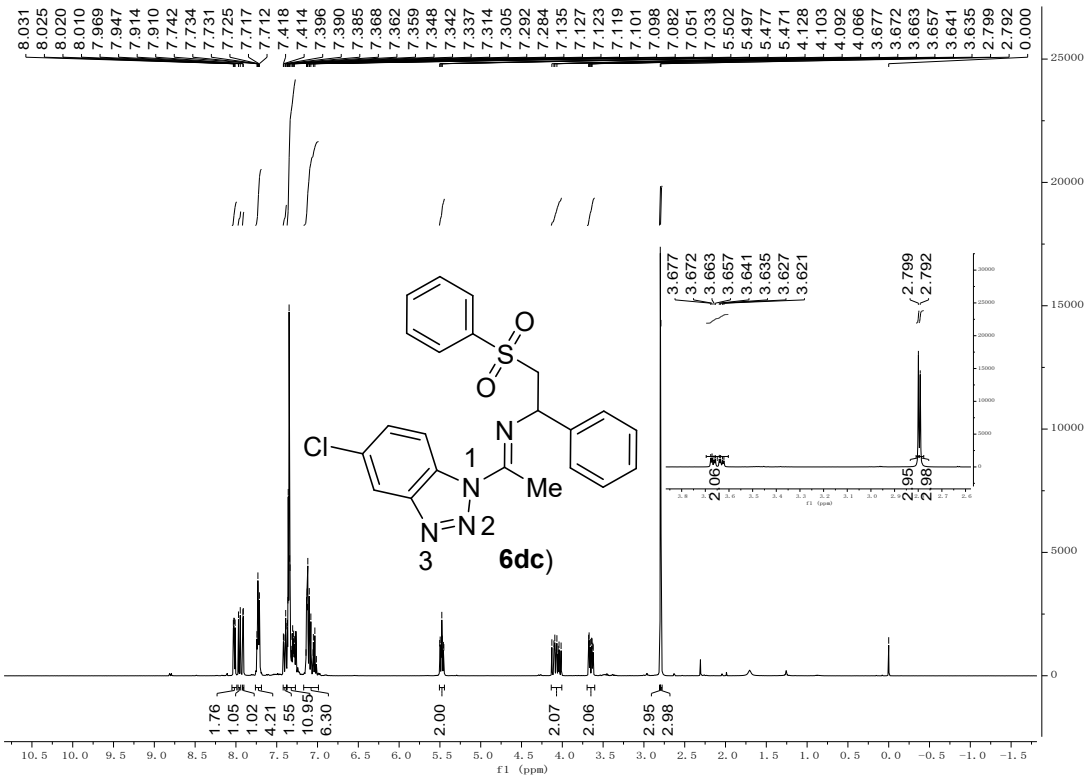
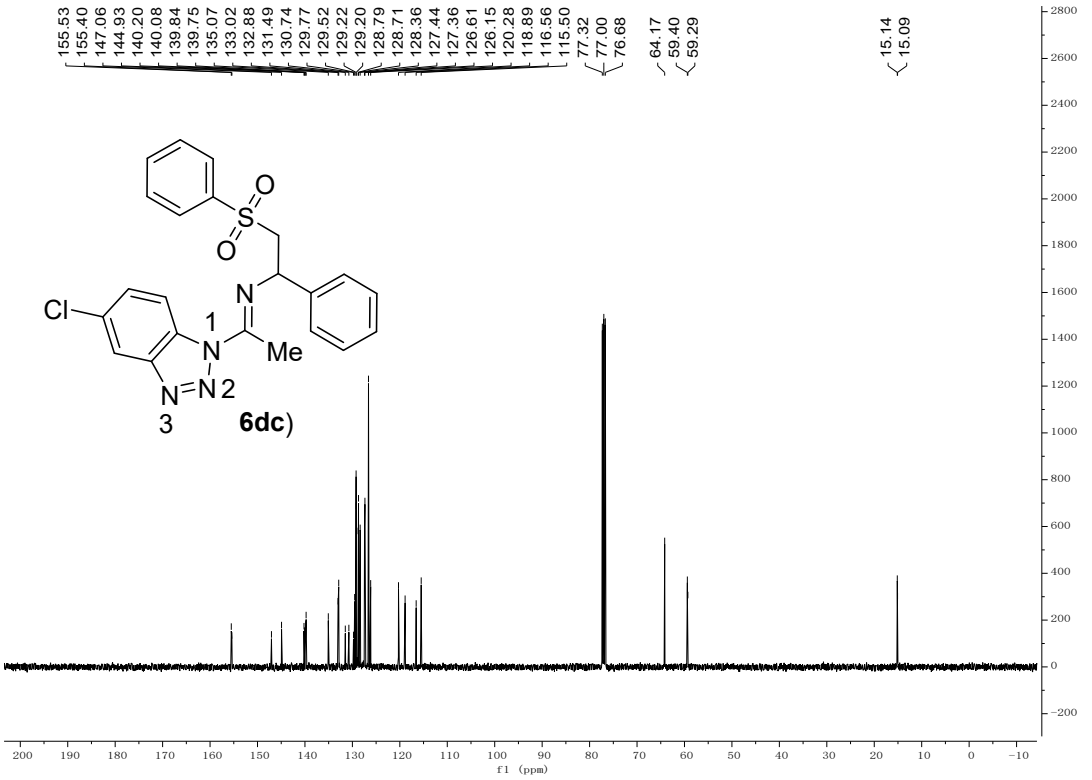


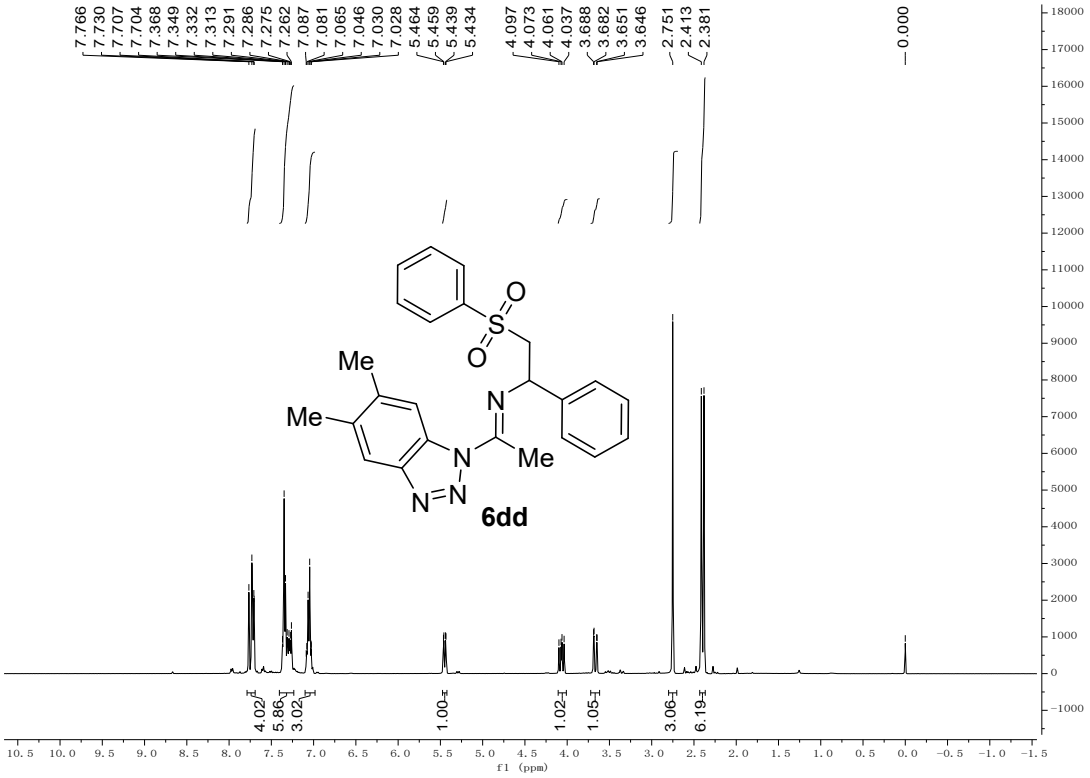
^{1}H NMR of **6dc** in $CDCl_3$



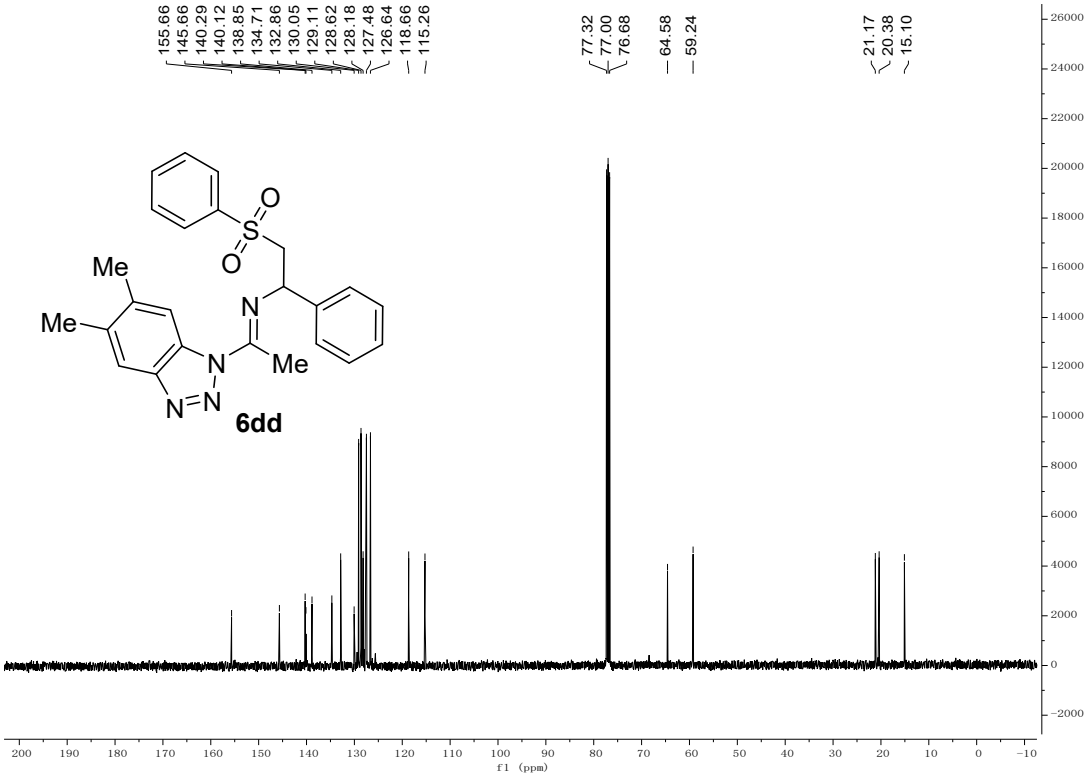
^{13}C NMR of **6dc** in $CDCl_3$



^{1}H NMR of **6dd** in $CDCl_3$



^{13}C NMR of **6dd** in $CDCl_3$



12. References

(S1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; D., Williams-Young, Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.

(S2) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627.

(S3) Goerigk, L.; Hansen, A.; Bauer, C.; Ehrlich, S.; Najibi A.; Grimme, S. A look at the density functional theory zoo with the advanced GMTKN55 database for general main group thermochemistry, kinetics and noncovalent interactions. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32184-32215.

(S4) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

(S5) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

(S6) Fukui, K. The path of chemical reactions: The IRC approach. *Acc. Chem. Res.* **1981**, *14*, 363-368.

(S7) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.