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Supporting Information

Organophotoredox catalytic four-component radical-polar crossover cascade reactions for the stereoselective synthesis of *β*-amido sulfones

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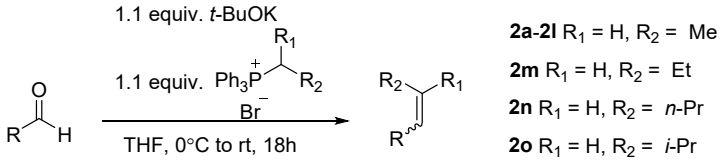
1. General Information

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).

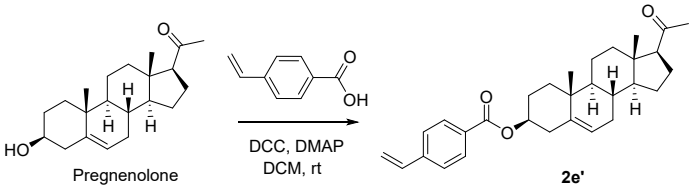
2. Synthesis of Starting Materials

Synthesis of internal alkenes[S1,S2]

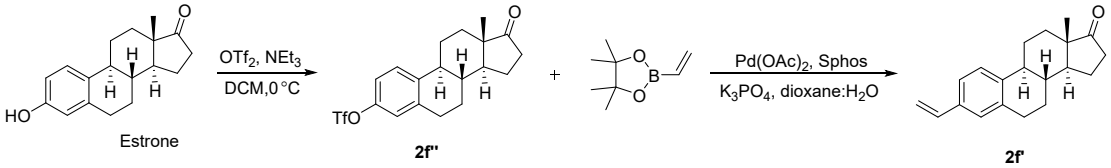


Potassium *tert*-butoxide (0.618g, 5.5 mmol) was added to a suspension of the corresponding phosphonium salt (5.5 mmol) in THF (6.5 mL) at 0 °C. After this, the resulting reaction mixture was stirred for 30 min at room temperature. Then, the appropriate aldehyde (5 mmol) was added and stirred for 18 h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with diethyl ether. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude residues were purified by silica gel flash column chromatography (10% Et_2O/pentane) affording the corresponding alkenes **2**. (Substrates **2a-2o** were obtained as a mixture of E- and Z-isomers).

Synthesis of terminal alkenes[S3]

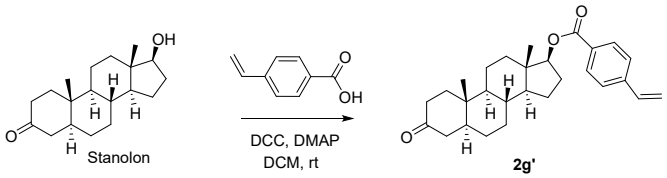


A 25 mL round flask equipped with a Teflon-coated magnetic stir bar was charged with pregnenolone (0.5 mmol, 1 equiv., 0.158 g), 4-Vinylbenzoic acid (1.5 mmol, 3 equiv., 0.23 g), N,N'-dicyclohexylcarbodiimide (DCC, 1.5 mmol, 3 equiv., 0.31 g), 4-dimethylaminopyridine (DMAP, 1.5 mmol, 3 equiv., 184 mg) 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 **2e'** as a white solid (0.217 g, 97% yield).



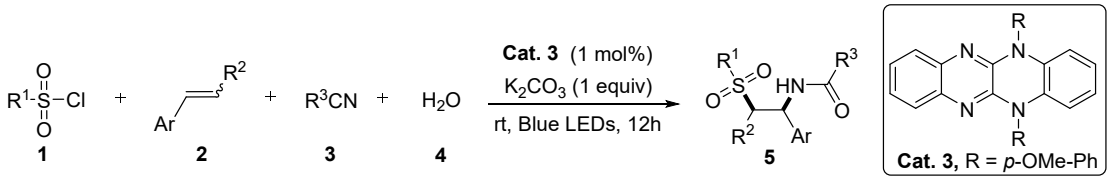
An oven dried 50 mL flask was charged with Estrone (5.0 mmol, 1.0 eq.), triethylamine (10 mmol, 2.0 eq.) and dry dichloromethane (25 ml) under argon. The mixture was cooled to 0 °C and triflic anhydride (5.5 mmol, 1.1 eq.) was added dropwise via syringe. The reaction mixture was stirred for 2 h at 0 °C before it was poured into an aqueous saturated solution of $NaHCO_3$. The biphasic mixture was extracted with dichloromethane (3*30 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed in vacuo. The crude material was purified by column chromatography to afford 3-(trifluoromethanesulfonyl)estrone **2f''** as a

colourless solid (65% yield). A Schlenk flask was charged with 3-(trifluoromethanesulfonyl)estrone **2f''** (500 mg, 1.24 mmol, 1.0 eq.), SPhos (59 mg, 0.14 mmol, 0.1 eq.), K_3PO_4 (792 mg, 3.73 mmol, 3.0 eq.), 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (0.42 ml, 2.48 mmol, 2.0 eq.), 1,4-dioxane (7.5 ml) and water (1.2 ml). The reaction vessel was sealed with a septum, evacuated and refilled with argon (cycle 3 times). $Pd(OAc)_2$ (14 mg, 0.06 mmol, 5 mol%) was added under a flow of argon and the reaction mixture was heated to 80 °C and stirred for 22 h. The reaction mixture was allowed to cool to ambient temperature and was subsequently diluted with ethyl acetate (10 ml). The mixture was filtered through a plug of silica. The organic phase was washed with brine (20 ml), dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (PE:EA = 10:1) and the product **2f'** was obtained as a colourless solid (91% yield).

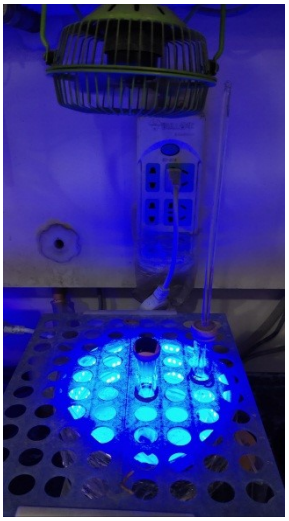


A 25 mL round flask equipped with a Teflon-coated magnetic stir bar was charged with pregnenolone (0.5 mmol, 1 equiv., 0.145 g), 4-Vinylbenzoic acid (1.5 mmol, 3 equiv., 0.23 g), N,N'-dicyclohexylcarbodiimide (DCC, 1.5 mmol, 3 equiv., 0.31 g), 4-dimethylaminopyridine (DMAP, 1.5 mmol, 3 equiv., 184 mg) 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 **2g'** as pale yellow solid (0.178 g, 85% yield).

3. General Procedures for the Synthesis of *β*-Amido Sulfones

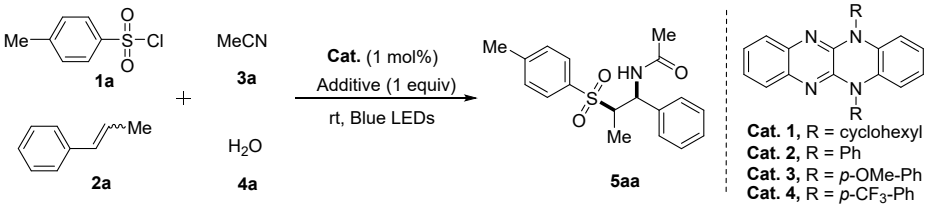


To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added photocatalyst **Cat. 3** (0.002 mmol) and K_2CO_3 (0.2 mmol). Dry nitrile **3** (4.0 mL) was added, after which the sulfonyl halide **1** (0.3 mmol), alkene **2** (0.2 mmol) and H_2O **4** (0.2 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 8 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at room temperature for 12h. 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 = 1:1), which furnished the title compounds **5** as described.



4. Initial Studies and the Reaction Optimization

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



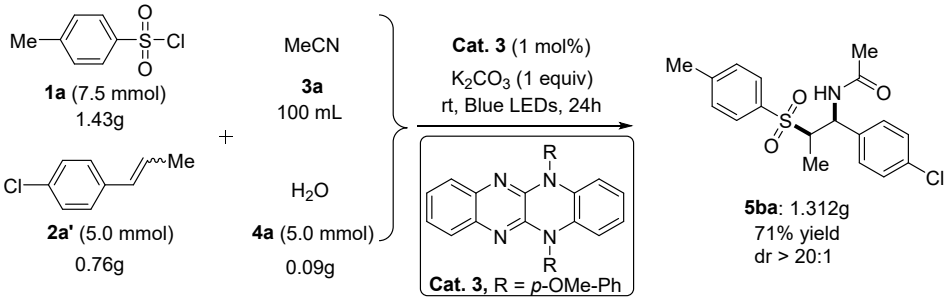
Entry	PC	1a/2a/4a	Additive	Solvent (3a)	Time(h)	Yield(%)[b]
1	*fac*-Ir(ppy)$_3$	1/1/3	K_2CO_3	2 mL	12	43
2	[Ru(bpy)$_3$]Cl$_2$	1/1/3	K_2CO_3	2 mL	12	Nr
3	Cat. 1	1/1/3	K_2CO_3	2 mL	12	49
4	Cat. 2	1/1/3	K_2CO_3	2 mL	12	43
5	Cat. 3	1/1/3	K_2CO_3	2 mL	12	51
6	Cat. 4	1/1/3	K_2CO_3	2 mL	12	41
7	Cat. 3	1/1/3	-	2 mL	12	16
8	-	1/1/3	K_2CO_3	2 mL	12	Nr
9[c]	Cat. 3	1/1/3	K_2CO_3	2 mL	12	Nr
10	Cat. 3	1/1/3	TFA	2 mL	12	Nr
11	Cat. 3	1/1/3	Na_2CO_3	2 mL	12	34
12	Cat. 3	1/1/3	Cs_2CO_3	2 mL	12	50
13	Cat. 3	1/1/3	$NaHCO_3$	2 mL	12	36

14	Cat. 3	1/1/3	DMAP	2 mL	12	Nr
15	Cat. 3	1.25/1/3	K_2CO_3	2 mL	12	51
16	Cat. 3	1.5/1/3	K_2CO_3	2 mL	12	54
17	Cat. 3	1.75/1/3	K_2CO_3	2 mL	12	51
18	Cat. 3	1.5/1/2	K_2CO_3	2 mL	12	61
19	Cat. 3	1.5/1/1	K_2CO_3	2 mL	12	71
20	Cat. 3	1/1.5/1	K_2CO_3	2 mL	12	63
21	Cat. 3	1.5/1/1	K_2CO_3	1.5 mL	12	63
22	Cat. 3	1.5/1/1	K_2CO_3	2.5 mL	12	73
23	Cat. 3	1.5/1/1	K_2CO_3	3 mL	12	76
24	Cat. 3	1.5/1/1	K_2CO_3	3.5 mL	12	79
25	**Cat. 3**	**1.5/1/1**	**K_2CO_3**	**4 mL**	**12**	**84**
26	Cat. 3	1.5/1/1	K_2CO_3	4.5 mL	12	83
27	Cat. 3	1.5/1/1	K_2CO_3	4 mL	6	63
28	Cat. 3	1.5/1/1	K_2CO_3	4 mL	9	78

[a] Unless otherwise noted, reaction conditions are as follows: **1a** (0.3 mmol), **2a** (0.2 mmol, E- and Z-alkene mixtures), **4a** (0.2 mmol), PC (1 mol%), additive (1.0 eq.), solvent **3a** (4 mL), N_2 atmosphere, an 8 W blue LED strip, room temperature for 12 h; The diastereomeric ratio determined by ^1H NMR analysis of products; dr > 20:1. [b] Isolated yield; [c] The reaction was performed in the dark.

5. Gram-Scale Reaction

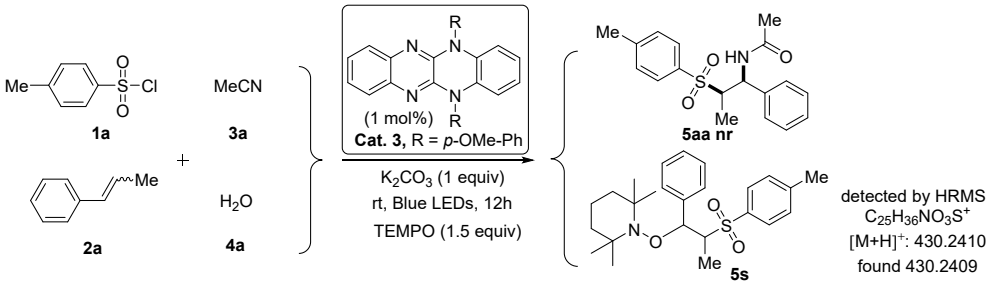
Gram-scale reaction for synthesis of *β*-amido sulfone 5ba



To an oven-dried 150 mL flask equipped with a magnetic stirring bar was added photocatalyst **Cat. 3** (0.05 mmol) and K_2CO_3 (5.0 mmol). Dry acetonitrile **3a** (100 mL) was added, after which the tosyl chloride **1a** (7.5 mmol), alkene **2a'** (5.0 mmol) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h. 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 = 1:1) to afford the desired product **5ba** (yield 54%, dr > 20:1, 0.998g). 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 = 1:1) to afford the desired product **5ba** (yield 71%, dr > 20:1, 1.312g).

6. Mechanistic Investigations

6.1 Radical inhibition experiments Radical inhibition experiment for synthesis of *β*-amido sulfone



In the model reaction of **1a**, **2a**, **3a** and **4a** in the presence of photocatalyst **Cat. 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 8 W blue LEDs for 12 hours, the desired product **5aa** was completely inhibited in the presence of 1.5 equivalents of TEMPO. The adduct **5s** of TEMPO and benzyl radical was detected by HRMS (ESI): calcd for $C_{25}H_{36}NO_3S^+$ $[M+H]^+$ 430.2410, found 430.2409 (Figure S1), suggesting that the reaction might involve a radical process.

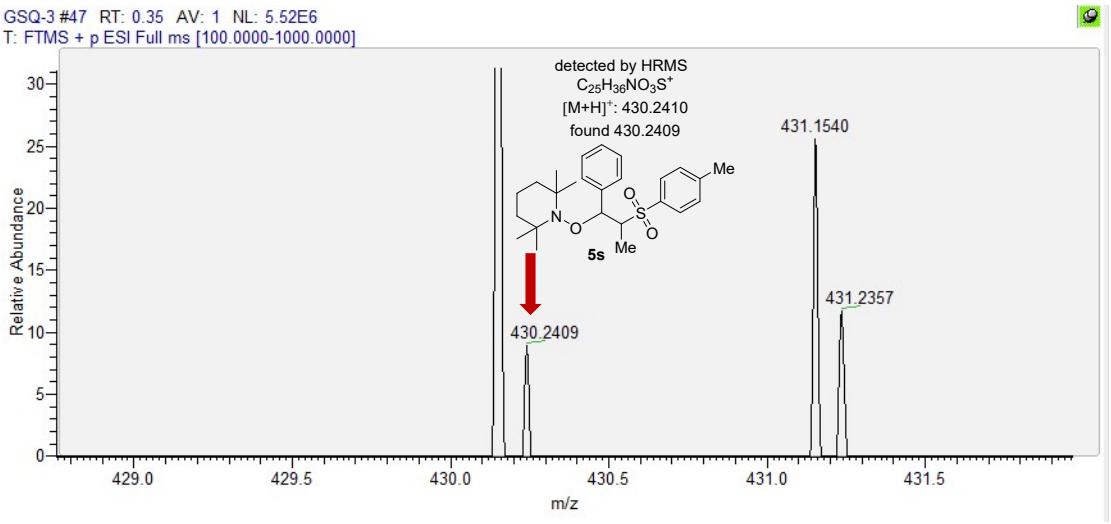
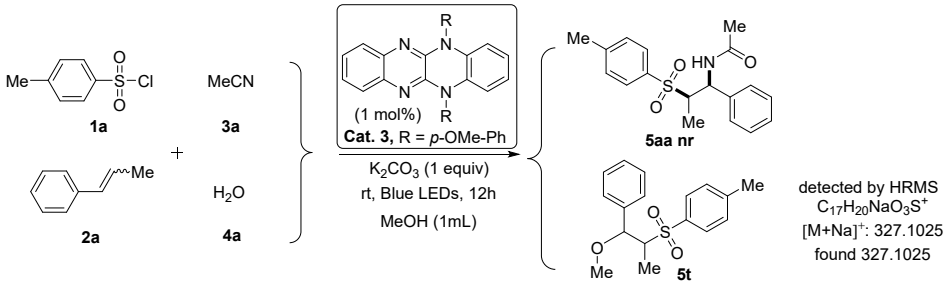


Figure S1. HRMS (ESI) spectra of the mixture (a).

6.2 Carbenium ion trapping experiments for synthesis of *β*-amido sulfone



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%), and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol), the alkene **2a** (0.2 mmol), MeOH (1.0 mL) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h.

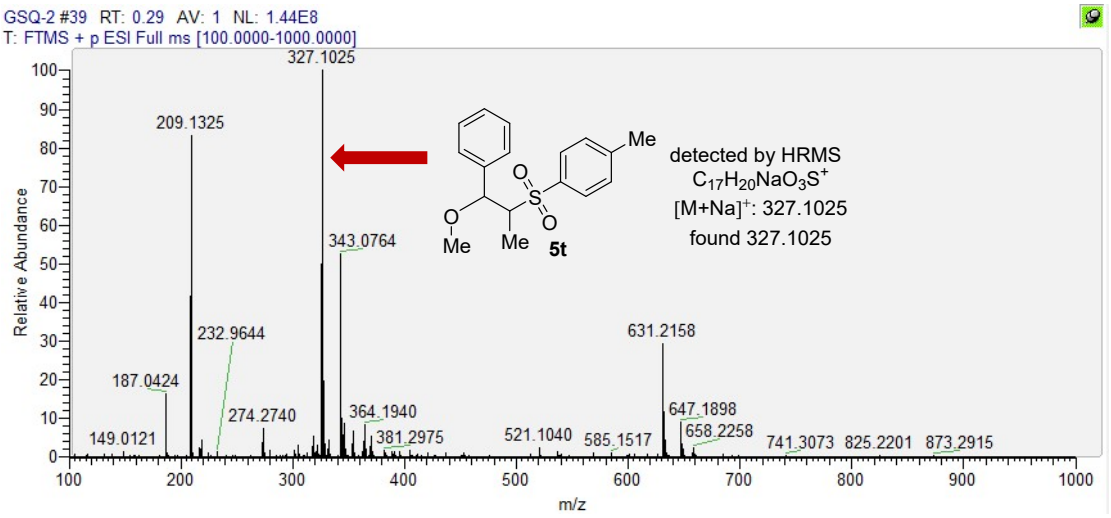
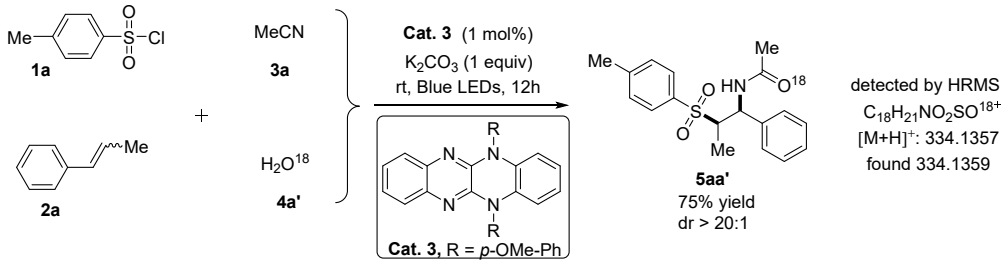


Figure S2. HRMS (ESI) spectra of the mixture (b).

6.3 Isotope labeling reaction

Reaction A: ^{18}O labeling experiment



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%), and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol), the alkene **2a** (0.2 mmol) and H_2O^{18} **4a'** (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 LED strip. The resulting mixture was stirred at room temperature for 12h.

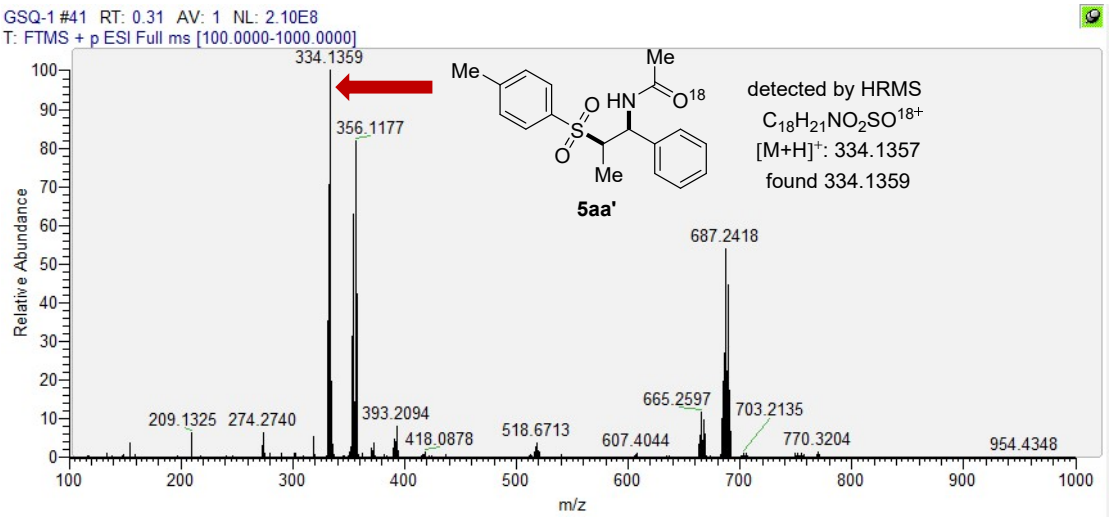
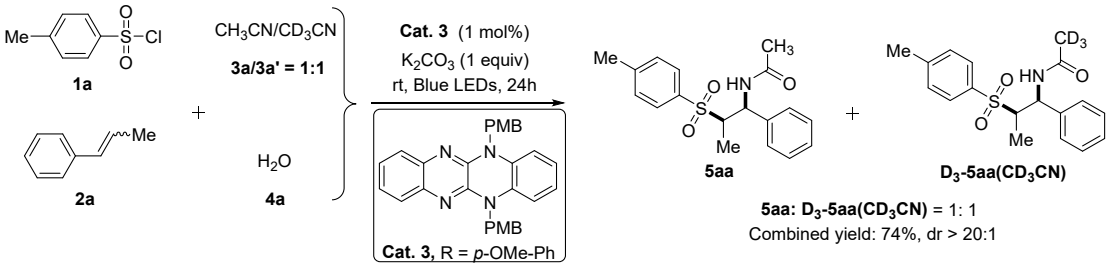


Figure S3. HRMS (ESI) spectra of the mixture (c).

Reaction B: CD_3CN labeling experiment



The deuterium-labeling experiment was conducted by using the co-solvent of CH_3CN and CD_3CN (4 mL, 1:1) instead of CH_3CN (4mL). As shown in **Figure S4**, the ratio of **5aa** and **D_3-5aa(CD_3CN)** was about 1/1.

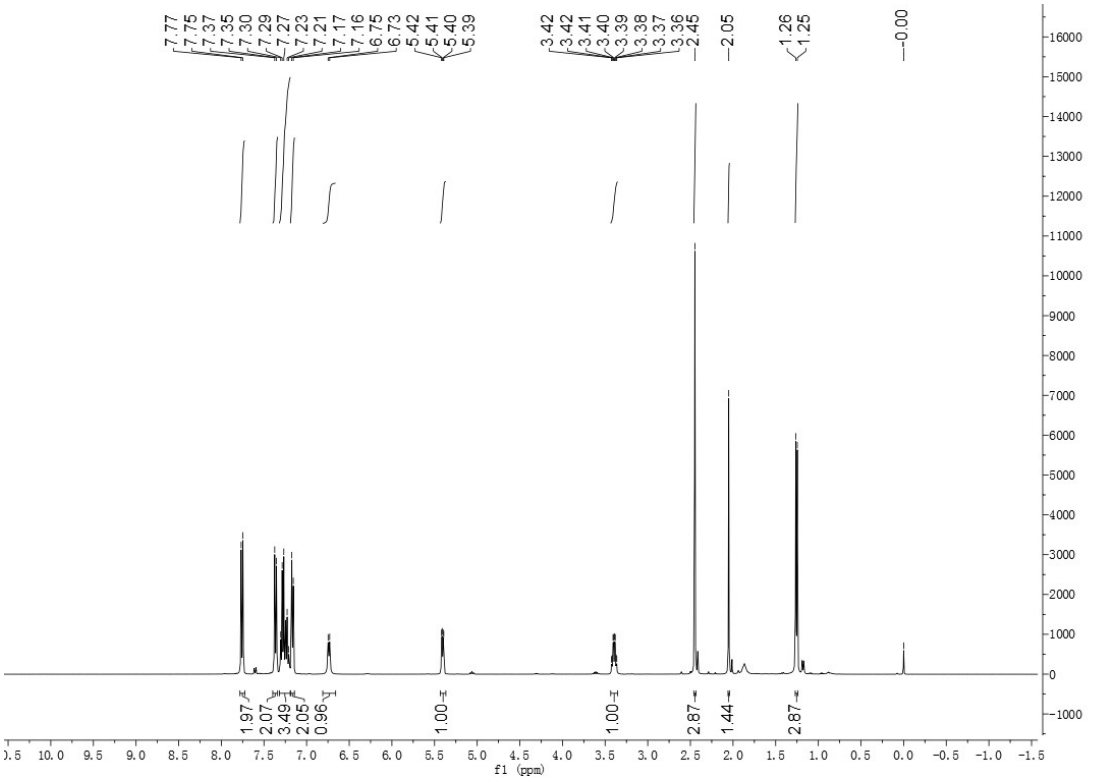
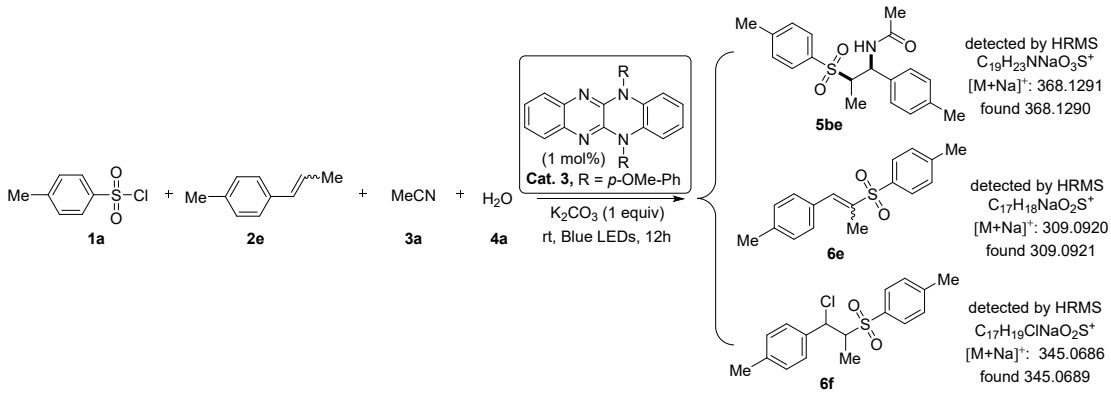


Figure S4. ^{1}H NMR for the products of isotope labeling reaction.

6.4 Exploration of by-products

Reaction A:



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%), and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol), the alkene **2e** (0.2 mmol) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h.

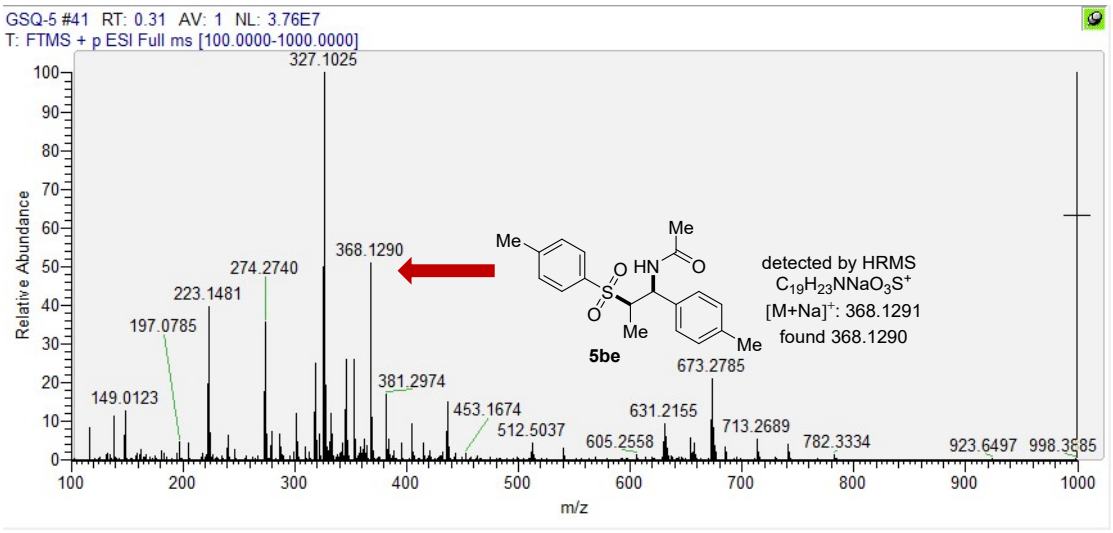


Figure S5. HRMS (ESI) spectra of the mixture (d1).

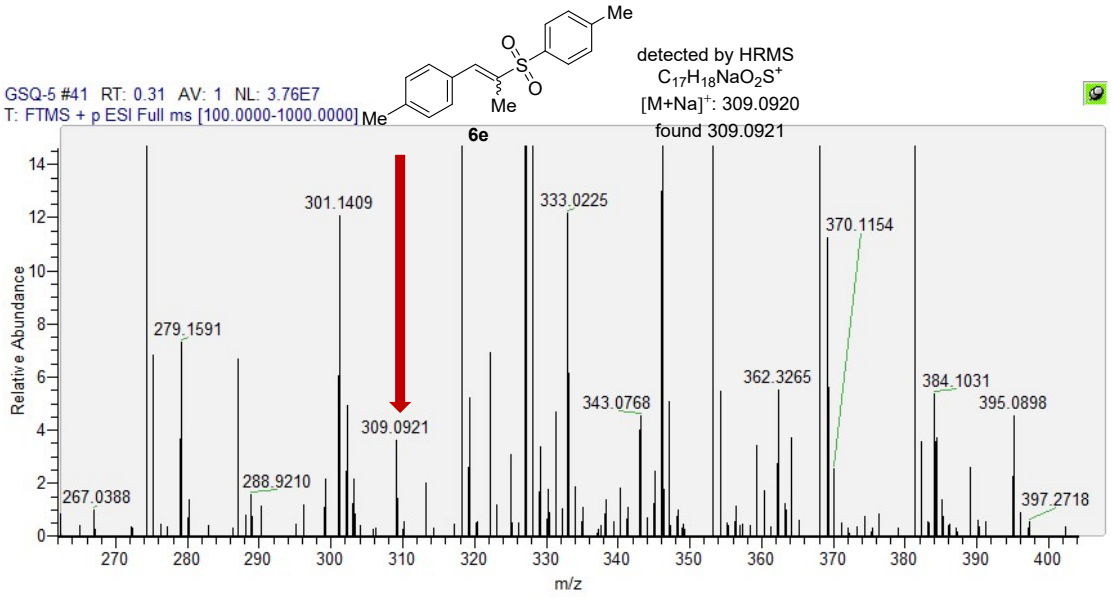


Figure S6. HRMS (ESI) spectra of the mixture (d2).

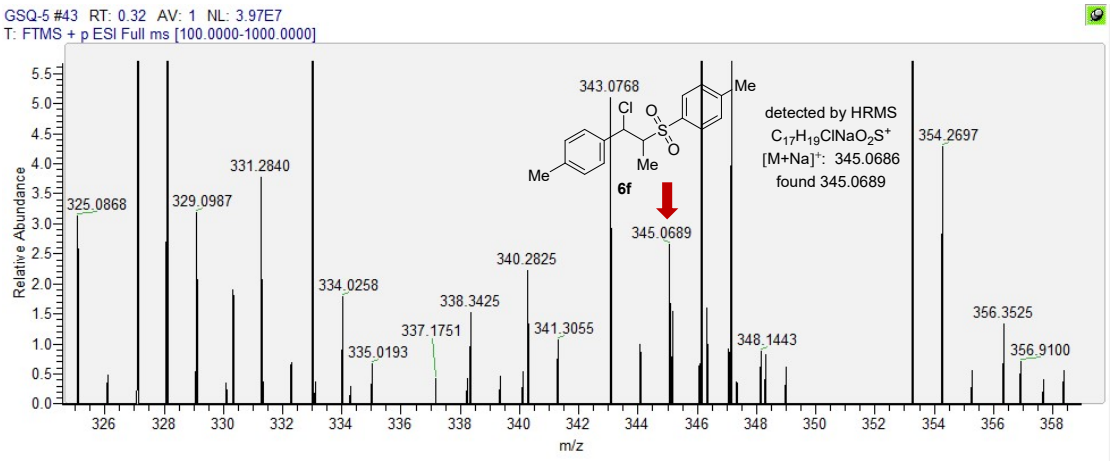
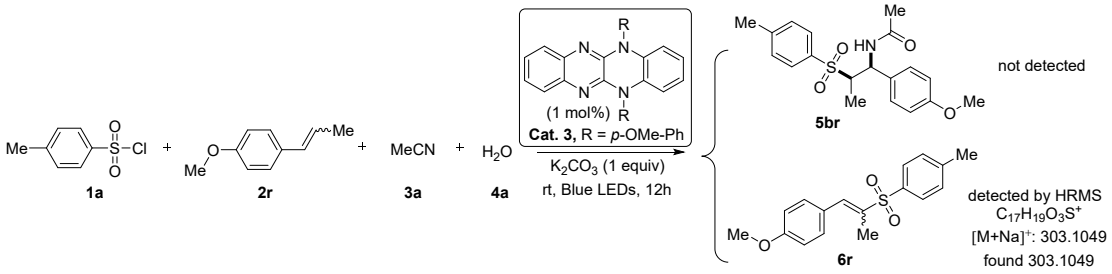


Figure S7. HRMS (ESI) spectra of the mixture (d3).

Reaction B:



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%), and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol) , the alkene **2r** (0.2 mmol) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h.

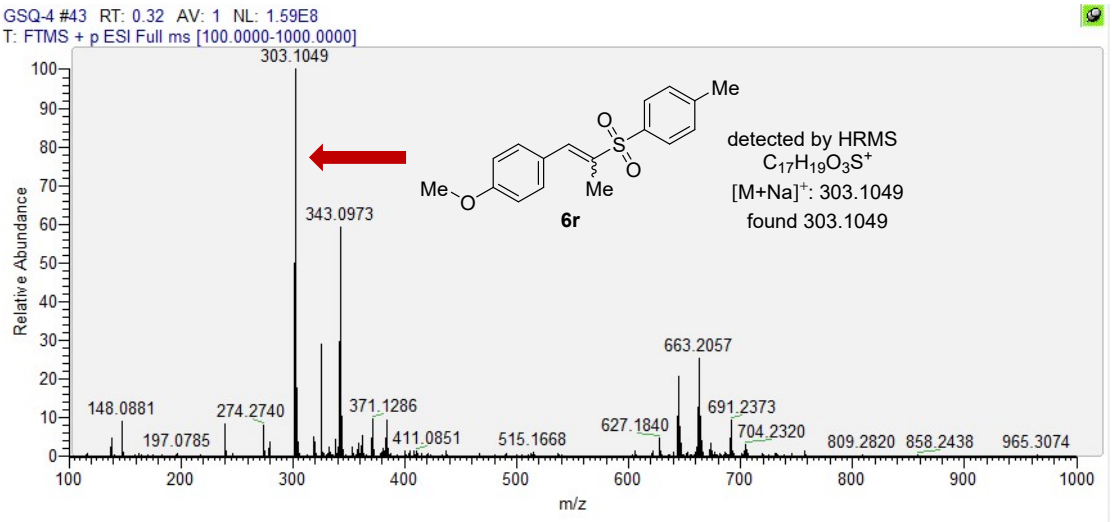
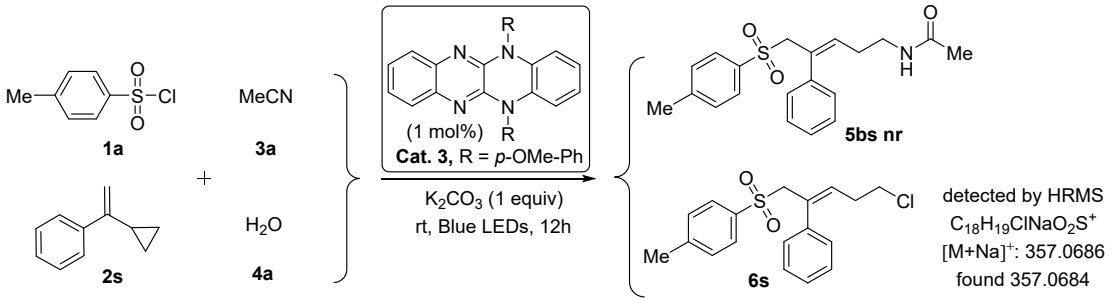


Figure S8. HRMS (ESI) spectra of the mixture (e).

6.5 Radical-clock experiment

Reaction A:



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%),

and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol) , the alkene **2s** (0.2 mmol) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h. Unfortunately, we did not detect the ring-opening product **5bs** of the four-component radical clock experiment. However, the ring-opening product **6s** of ATRA addition reaction of sulfonyl chloride **1a** with alkene **2s** was detected by high resolution mass spectrometry (HRMS).

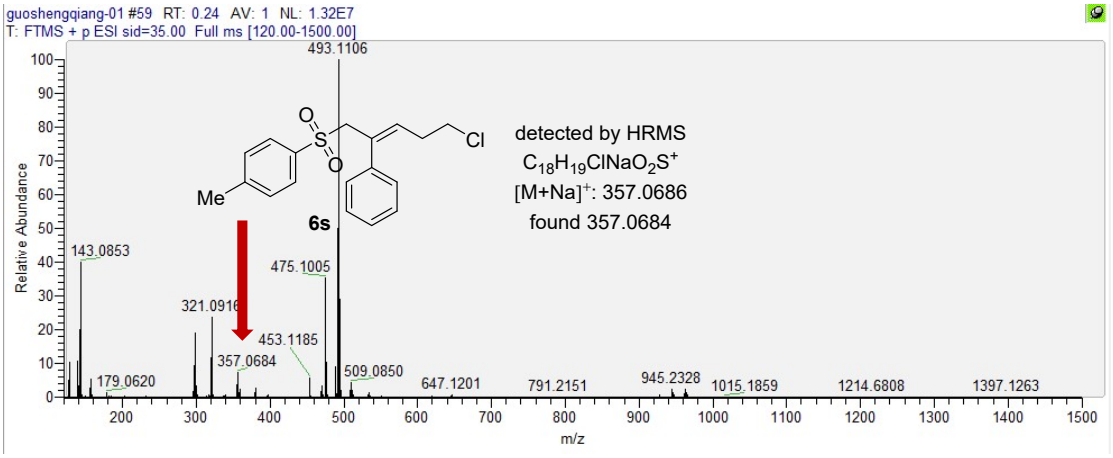
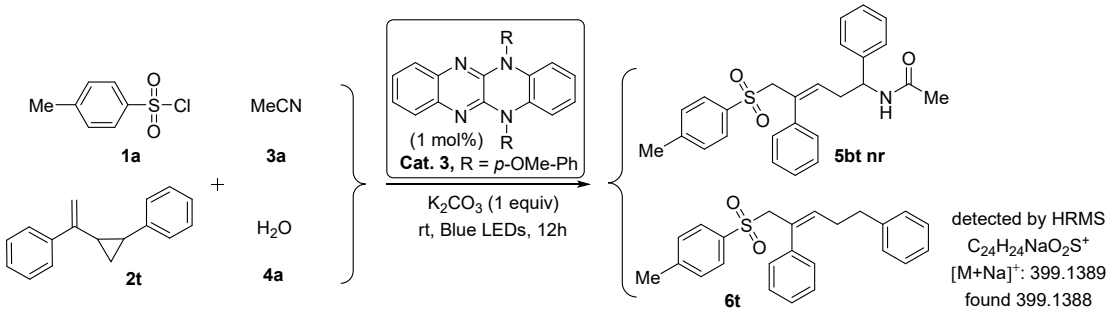


Figure S9. HRMS (ESI) spectra of the mixture (f).

Reaction B:



To an oven-dried 10 mL tube equipped with a magnetic stirring bar was added **Cat. 3** (1 mol%), and K_2CO_3 (0.2 mmol). Dry acetonitrile (4.0 mL) was added, after which tosyl chloride **1a** (0.3 mmol), the alkene **2t** (0.2 mmol) and H_2O **4a** (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 LED strip. The resulting mixture was stirred at room temperature for 12h. Unfortunately, we did not detect the ring-opening product **5bt** of the four-component radical clock experiment. However, the ring-opening product **6t** of hydrosulfonylation reaction of sulfonyl chloride **1a** with alkene **2t** was detected by high resolution mass spectrometry (HRMS).

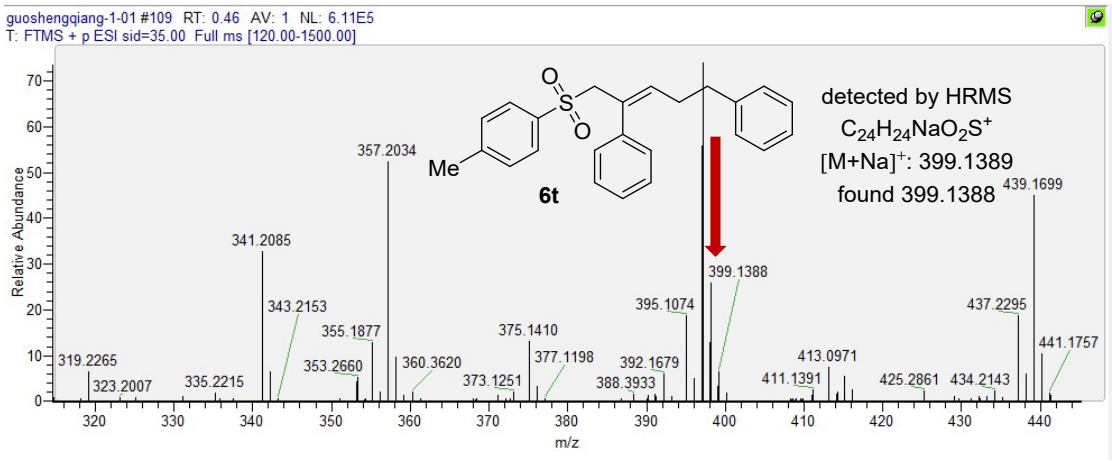
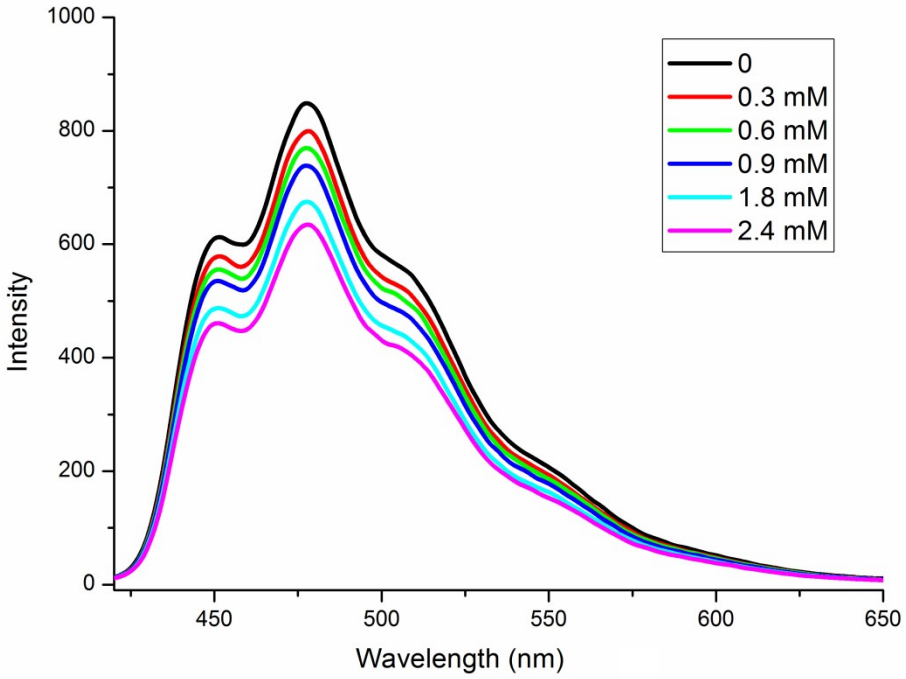


Figure S10. HRMS (ESI) spectra of the mixture (g).

7. Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiment for synthesis of *β*-amido sulfone

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solution of 0.6 mM solution of **Cat. 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 390 nm and fluorescence was measured from 420 nm to 650 nm. Control experiments showed that the excited state photocatalyst was mainly quenched by Tosyl chloride **1a**.



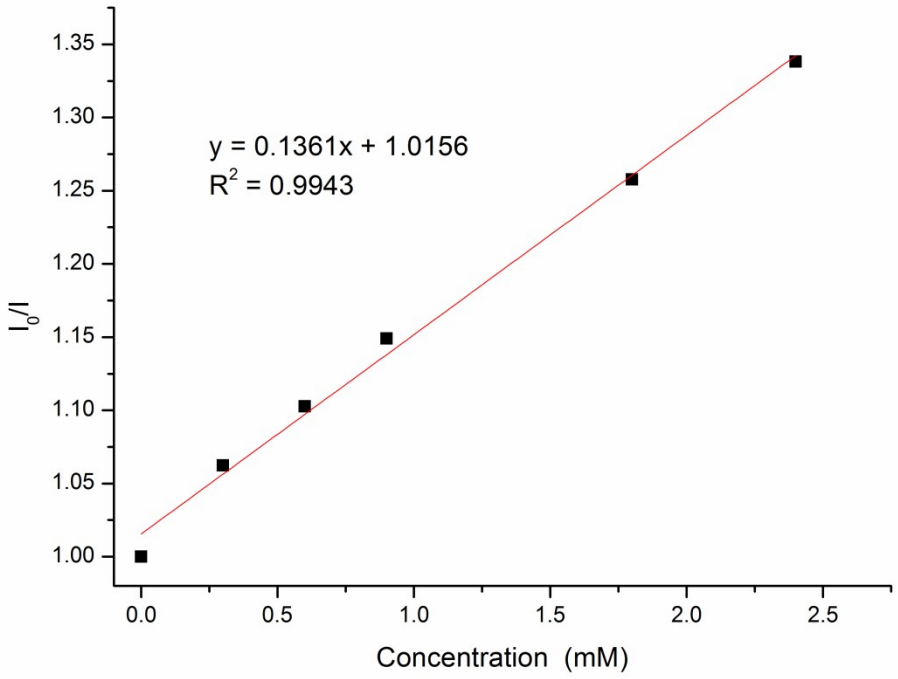


Figure S11-S12. Fluorescence quenching experiments date with **Cat. 3** and variable TsCl.

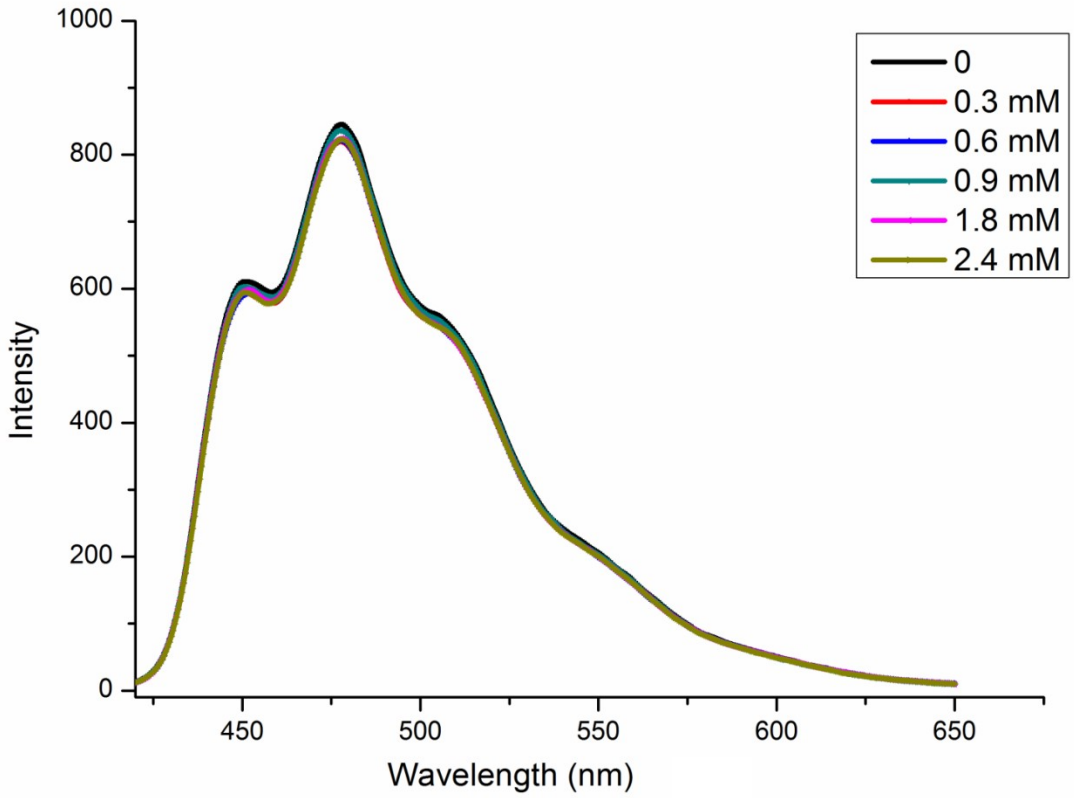


Figure S13. Fluorescence quenching experiments date with **Cat. 3** and variable H_2O.

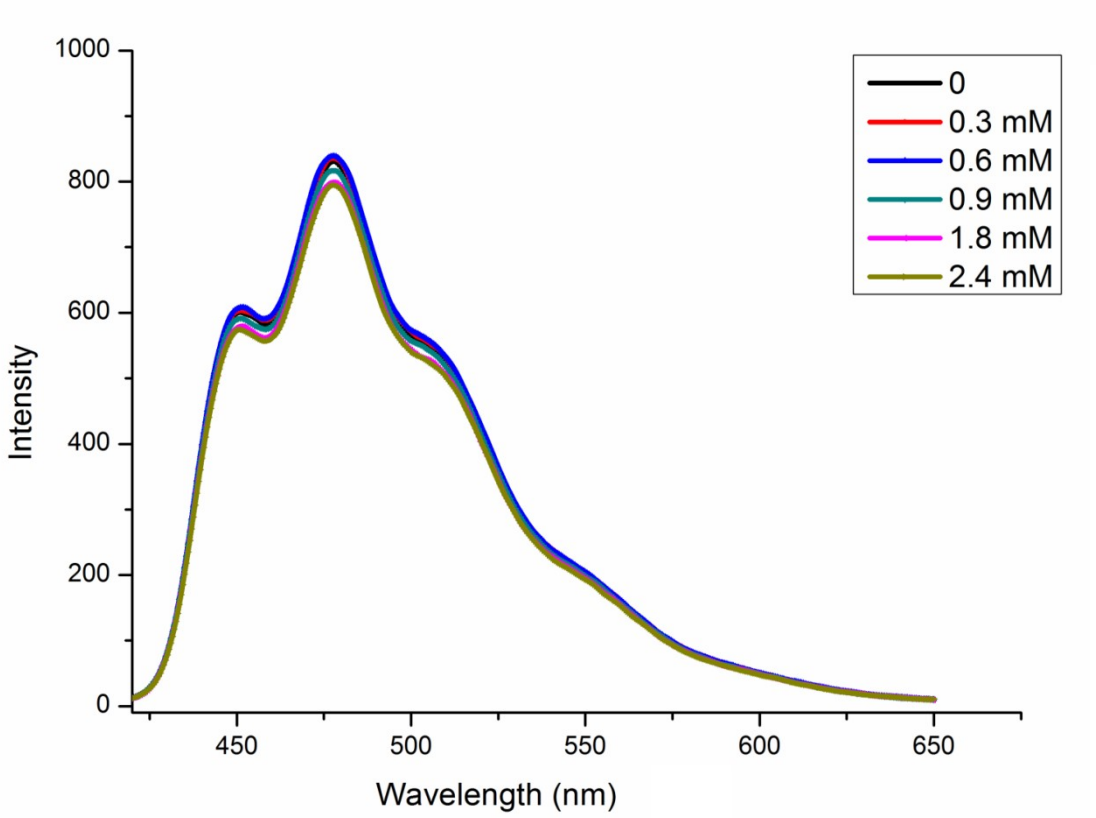


Figure S14. Fluorescence quenching experiments date with **Cat. 3** and variable *β*-Methylstyrene.

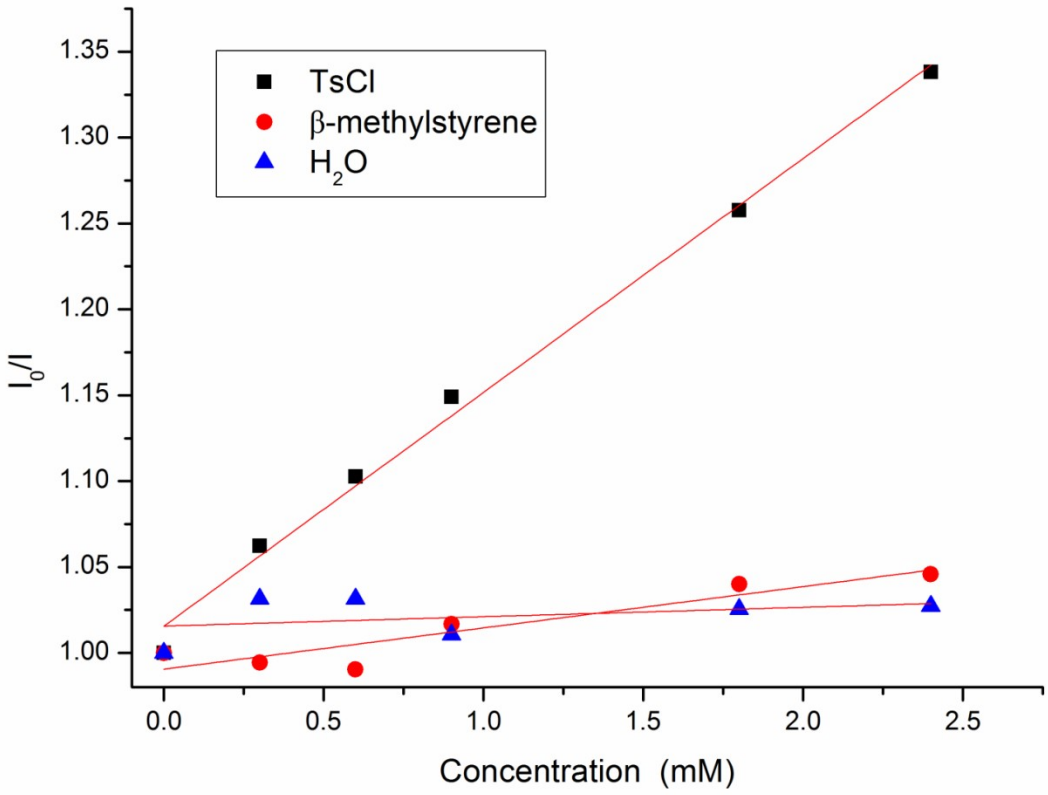
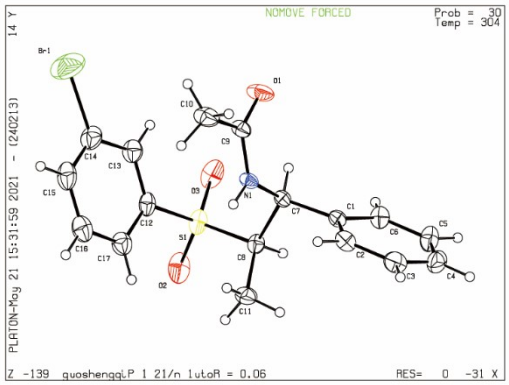


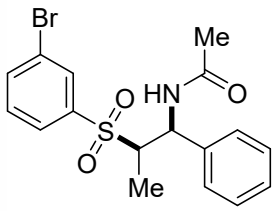
Figure S15. Stern-Volmer plots of **Cat. 3** with different quenchers.

8. X-Ray Crystallographic Data

X-Ray crystallographic datas of *β*-amido sulfone 5aj

The crystal structure **5aj** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 2127126.**





5aj

Bond precision:	C-C = 0.0039 A	Wavelength=0.71073	
Cell:	a=11.1683(5)	b=9.4026(4)	c=16.7625(9)
	alpha=90	beta=95.079(5)	gamma=90
Temperature:	304 K		
	Calculated	Reported	
Volume	1753.34(14)	1753.34(14)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C17 H18 Br N O3 S	C17 H18 Br N O3 S	
Sum formula	C17 H18 Br N O3 S	C17 H18 Br N O3 S	
Mr	396.28	396.29	
Dx,g cm-3	1.501	1.501	
Z	4	4	
Mu (mm-1)	2.477	2.477	
F000	808.0	808.0	
F000’	807.67		
h,k,lmax	16,13,24	15,12,21	
Nref	5573	4500	
Tmin,Tmax	0.812,0.884	0.852,1.000	
Tmin’	0.743		

Correction method= # Reported T Limits: Tmin=0.852 Tmax=1.000

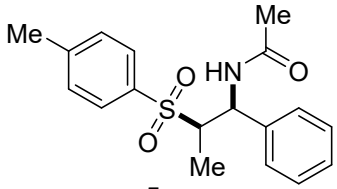
AbsCorr = MULTI-SCAN

Data completeness= 0.807	Theta(max)= 30.983
R(reflections)= 0.0563(3001)	wR2(reflections)= 0.1262(4500)
S = 1.025	Npar= 210

Displacement ellipsoids are drawn at 30% probability level.

9. Characterization of Products

Characterization of Products *β*-amido sulfones

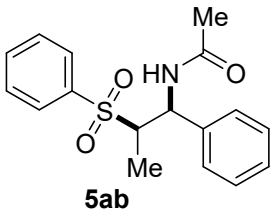


5aa

N-(1-phenyl-2-tosylpropyl)acetamide (5aa)

White solid; 55.9 mg, 84% yield, dr > 20:1; mp 158-159 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.20 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.73 (d, *J* = 6.0 Hz, 1H), 5.44 – 5.35 (m, 1H), 3.44 – 3.34 (m, 1H), 2.45 (s, 3H), 2.06 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 145.2, 138.1, 134.4, 130.0, 128.6, 128.5, 127.7, 126.5, 63.4, 52.5, 23.3, 21.6, 8.6. HRMS (ESI) for $C_{18}H_{22}NO_3S^+$ $[M+H]^+$ calcd 332.1315, found 332.1317.

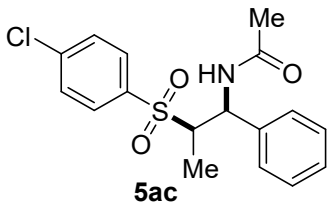


5ab

N-(1-phenyl-2-(phenylsulfonyl)propyl)acetamide (5ab)

Off-white solid; 48.7 mg, 77% yield, dr = 17:1; mp 146-148 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.84 (m, 2H), 7.70– 7.64 (m, 1H), 7.60 – 7.53 (m, 2H), 7.32 – 7.14 (m, 5H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.47 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.48 – 3.37 (m, 1H), 2.04 (s, 4H), 1.27 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 138.1, 137.6, 134.0, 129.3, 128.7, 128.6, 127.7, 126.5, 63.4, 52.4, 23.3, 8.8. HRMS (ESI) for $C_{17}H_{20}NO_3S^+$ $[M+H]^+$ calcd 318.1158, found 318.1159.

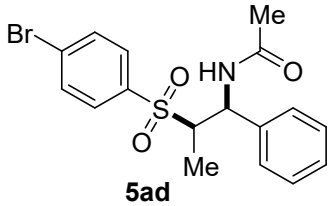


5ac

N-(2-((4-chlorophenyl)sulfonyl)-1-phenylpropyl)acetamide (5ac)

White solid; 49.1 mg, 70% yield, dr > 20:1; mp 160-161 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 2H), 7.56 – 7.50 (m, 2H), 7.33 – 7.21 (m, 3H), 7.19 – 7.14 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.50 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.47 – 3.37 (m, 1H), 2.03 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 140.9, 137.9, 136.0, 130.2, 129.6, 128.7, 127.9, 126.5, 63.6, 52.2, 23.3, 8.9. HRMS (ESI) for $C_{17}H_{19}ClNO_3S^+$ $[M+H]^+$ calcd 352.0769, found 352.0771.

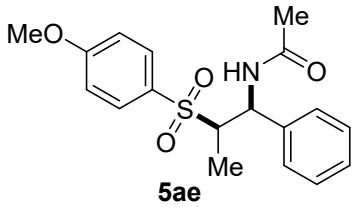


5ad

N-(2-((4-bromophenyl)sulfonyl)-1-phenylpropyl)acetamide (5ad)

Pale yellow solid; 54.8 mg, 69% yield, dr > 20:1; mp 171-172 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.67 (m, 4H), 7.32 – 7.22 (m, 3H), 7.19 – 7.14 (m, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.49 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.48 – 3.39 (m, 1H), 2.04 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 137.9, 136.6, 132.6, 130.2, 129.5, 128.7, 127.9, 126.5, 63.6, 52.3, 23.3, 8.9. HRMS (ESI) for $C_{17}H_{19}BrNO_3S^+$ $[M+H]^+$ calcd 396.0264, found 396.0267.

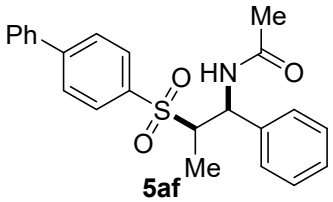


5ae

N-(2-((4-methoxyphenyl)sulfonyl)-1-phenylpropyl)acetamide (5ae)

Yellow solid; 57.6 mg, 83% yield, dr > 20:1; mp 152-153 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.77 (m, 2H), 7.32 – 7.20 (m, 3H), 7.19 – 7.14 (m, 2H), 7.06 – 6.99 (m, 2H), 6.71 (d, *J* = 7.2 Hz, 1H), 5.40 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.88 (s, 3H), 3.42 – 3.32 (m, 1H), 2.06 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 164.0, 138.2, 130.9, 128.8, 128.6, 127.7, 126.5, 114.5, 63.5, 55.7, 52.6, 23.3, 8.6. HRMS (ESI) for $C_{18}H_{22}NO_4S^+$ $[M+H]^+$ calcd 348.1264, found 348.1265.

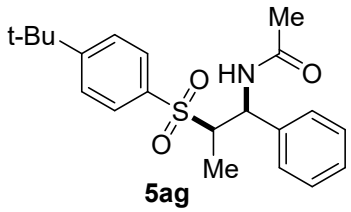


5af

N-(2-([1,1'-biphenyl]-4-ylsulfonyl)-1-phenylpropyl)acetamide (5af)

Pale yellow oil; 67.3 mg, 85% yield, dr > 20:1; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.79 – 7.74 (m, 2H), 7.63 – 7.58 (m, 2H), 7.51 – 7.40 (m, 3H), 7.33 – 7.17 (m, 5H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.51 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.52 – 3.43 (m, 1H), 2.06 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 146.9, 138.9, 138.0, 136.0, 129.2, 129.1, 128.7, 128.6, 127.9, 127.8, 127.4, 126.6, 63.5, 52.5, 23.3, 8.9. HRMS (ESI) for $C_{23}H_{24}NO_3S^+$ $[M+H]^+$ calcd 394.1471, found 394.1473.

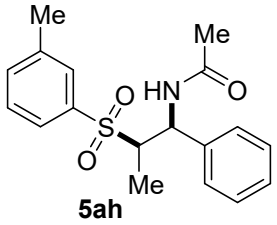


5ag

N-(2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylpropyl)acetamide (5ag)

Pale yellow solid; 65.8 mg, 88% yield, dr > 20:1; mp 144-145 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 2H), 7.59 – 7.53 (m, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 6.75 (d, *J* = 7.2 Hz, 1H), 5.49 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.46 – 3.36 (m, 1H), 2.04 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 158.0, 138.1, 134.5, 128.5, 127.7, 126.5, 126.3, 63.3, 52.5, 35.2, 31.0, 23.3, 8.9. HRMS (ESI) for $C_{21}H_{28}NO_3S^+$ $[M+H]^+$ calcd 374.1784, found 374.1786.

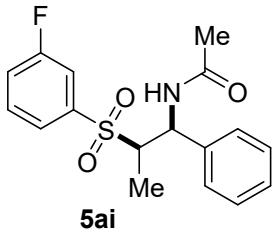


5ah

N-(1-phenyl-2-(m-tolylsulfonyl)propyl)acetamide (5ah)

Yellow solid; 46.6 mg, 70% yield, dr > 20:1; mp 129-130 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H), 7.49 – 7.43 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.45 (dd, *J* = 7.6, 3.2 Hz, 1H), 3.46 – 3.38 (m, 1H), 2.44 (s, 3H), 2.04 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 139.6, 138.1, 137.4, 134.8, 129.1, 128.9, 128.5, 127.7, 126.5, 125.8, 63.4, 52.5, 23.3, 21.3, 8.9. HRMS (ESI) for $C_{18}H_{22}NO_3S^+$ $[M+H]^+$ calcd 332.1315, found 332.1316.

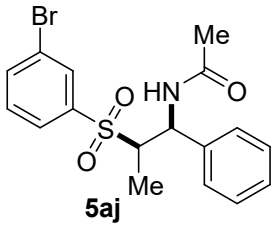


5ai

N-(2-((3-fluorophenyl)sulfonyl)-1-phenylpropyl)acetamide (5ai)

White solid; 47.0 mg, 70% yield, dr > 20:1; mp 170-172 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.65 (m, 1H), 7.61 – 7.52 (m, 2H), 7.41 – 7.35 (m, 1H), 7.33 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 6.60 (d, *J* = 7.6 Hz, 1H), 5.48 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.52 – 3.43 (m, 1H), 2.08 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 162.4(d, J = 254.5 Hz), 139.8(d, J = 7.1 Hz), 137.6, 131.2(d, J = 7.1 Hz), 128.7, 128.0, 126.6, 124.6(d, J = 4.0 Hz), 121.4(d, J = 21.2 Hz), 116.0(d, J = 24.2 Hz), 63.6, 52.6, 23.4, 9.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.62. HRMS (ESI) for $C_{17}H_{19}FNO_3S^+$ $[M+H]^+$ calcd 336.1064, found 336.1064.

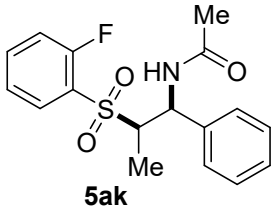


5aj

N-(2-((3-bromophenyl)sulfonyl)-1-phenylpropyl)acetamide (5aj)

White solid; 55.1 mg, 70% yield, dr > 20:1; mp 167-168 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (t, *J* = 1.6 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.34 – 7.23 (m, 3H), 7.22 – 7.17 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.51 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.52 – 3.43 (m, 1H), 2.06 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 139.6, 137.6, 137.1, 131.5, 130.7, 128.7, 128.0, 127.3, 126.7, 123.3, 63.7, 52.5, 23.4, 9.4. HRMS (ESI) for $C_{17}H_{19}BrNO_3S^+$ $[M+H]^+$ calcd 396.0264, found 396.0267.

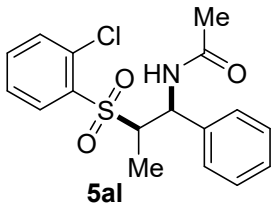


5ak

N-(2-((2-fluorophenyl)sulfonyl)-1-phenylpropyl)acetamide (5ak)

Yellow solid; 47.1 mg, 70% yield, dr = 14:1; mp 156-157 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 1H), 7.69 – 7.60 (m, 1H), 7.35 – 7.18 (m, 7H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.43 (dd, *J* = 7.6, 3.6 Hz, 1H), 3.85 – 3.75 (m, 1H), 2.03 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 159.4 (d, J = 255.5 Hz), 137.7, 136.5 (d, J = 8.1 Hz), 131.2, 128.6, 127.9, 126.6, 125.7 (d, J = 15.2 Hz), 124.9 (d, J = 3.0 Hz), 117.1 (d, J = 21.2 Hz), 62.9(d, J = 3.0 Hz), 52.5, 23.2, 8.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.58. HRMS (ESI) for $C_{17}H_{19}FNO_3S^+$ $[M+H]^+$ calcd 336.1064, found 336.1064.

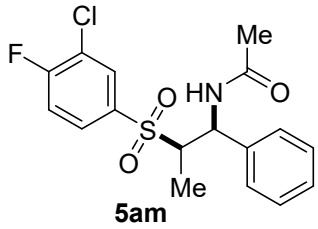


5al

N-(2-((2-chlorophenyl)sulfonyl)-1-phenylpropyl)acetamide (5al)

Pale yellow oil; 53.2 mg, 76% yield, dr > 20:1; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 1H), 7.59 – 7.54 (m, 2H), 7.46 – 7.39 (m, 1H), 7.32 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 6.70 (d, *J* = 7.6 Hz, 1H), 5.33 (dd, *J* = 7.6, 4.0 Hz, 1H), 4.19 – 4.09 (m, 1H), 2.05 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 137.7, 135.2, 135.1, 132.4, 132.2, 132.0, 128.6, 127.9, 127.6, 126.6, 61.1, 52.6, 23.2, 8.2. HRMS (ESI) for $C_{17}H_{19}ClNO_3S^+$ $[M+H]^+$ calcd 352.0769, found 352.0770.

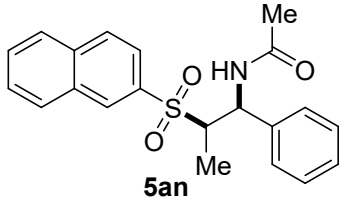


5am

N-(2-((3-chloro-4-fluorophenyl)sulfonyl)-1-phenylpropyl)acetamide (5am)

White solid; 50.0 mg, 68% yield, dr > 20:1; mp 144-145 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.86 (m, 1H), 7.78 – 7.72 (m, 1H), 7.32 – 7.23 (m, 4H), 7.20 – 7.15 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.58 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.53 – 3.44 (m, 1H), 2.01 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 161.3(d, J = 260.6 Hz), 137.8, 134.7(d, J = 4.0 Hz), 131.7, 129.4(d, J = 9.1 Hz), 128.6, 128.0, 126.6, 122.7(d, J = 19.2 Hz), 117.5(d, J = 23.2 Hz), 64.0, 52.0, 23.2, 9.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.95. HRMS (ESI) for $C_{17}H_{18}ClFNO_3S^+$ $[M+H]^+$ calcd 370.0674, found 370.0676.

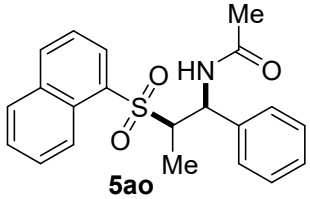


5an

N-(2-(naphthalen-2-ylsulfonyl)-1-phenylpropyl)acetamide (5an)

Pale yellow solid; 68.1 mg, 92% yield, dr > 20:1; mp 112-113 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 1.6 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.71 – 7.59 (m, 2H), 7.29 – 7.14 (m, 5H), 6.78 (d, *J* = 7.6 Hz, 1H), 5.54 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.56 – 3.47 (m, 1H), 2.00 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 138.1, 135.3, 134.4, 132.1, 130.9, 129.5, 129.4, 128.5, 127.9, 127.8, 127.7, 126.5, 122.9, 63.5, 52.5, 23.3, 9.0. HRMS (ESI) for $C_{21}H_{22}NO_3S^+$ $[M+H]^+$ calcd 368.1315, found 368.1317.

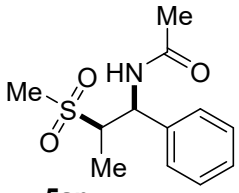


5ao

N-(2-(naphthalen-1-ylsulfonyl)-1-phenylpropyl)acetamide (5ao)

Yellow solid; 58.3 mg, 79% yield, dr = 14:1; mp 170-171 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 8.8 Hz, 1H), 8.25 – 8.19 (m, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.67 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.24 – 7.14 (m, 3H), 7.08 – 6.99 (m, 2H), 6.77 (d, *J* = 7.2 Hz, 1H), 5.33 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.82 – 3.73 (m, 1H), 2.08 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 138.0, 135.6, 134.2, 132.2, 131.7, 129.5, 128.9, 128.7, 128.5, 127.7, 127.1, 126.4, 124.4, 123.6, 62.5, 52.6, 23.3, 8.5. HRMS (ESI) for $C_{21}H_{22}NO_3S^+$ $[M+H]^+$ calcd 368.1315, found 368.1315.



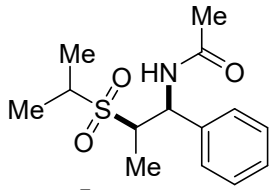
5ap

N-(2-(methylsulfonyl)-1-phenylpropyl)acetamide (5ap)

Pale yellow solid; 26.2 mg, 51% yield, dr = 6:1; mp 138-140 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 1H), 5.61 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.46 – 3.37 (m, 1H), 2.60 (s, 3H), 2.05 (s, 3H), 1.41 (d, *J* = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 137.0, 128.8, 128.2, 127.1, 63.3, 52.6, 38.8, 23.3, 10.6.

HRMS (ESI) for $C_{12}H_{18}NO_3S^+$ $[M+H]^+$ calcd 256.1002, found 256.1001.

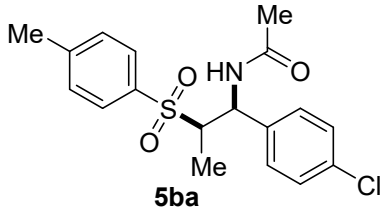


5aq

N-(2-(isopropylsulfonyl)-1-phenylpropyl)acetamide (5aq)

White solid; 24.3 mg, 43% yield, dr = 5:1; mp 124-126 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.25 (s, 3H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.63 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.35 – 3.23 (m, 1H), 2.05 (s, 3H), 1.44 – 1.35 (m, 6H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 137.9, 128.7, 127.9, 126.6, 57.0, 52.1, 51.0, 23.2, 15.4, 14.7, 8.3. HRMS (ESI) for $C_{14}H_{22}NO_3S^+$ $[M+H]^+$ calcd 284.1315, found 284.1316.

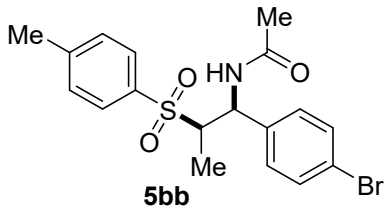


5ba

N-(1-(4-chlorophenyl)-2-tosylpropyl)acetamide (5ba)

Yellow solid; 66.4 mg, 91% yield, dr > 20:1; mp 72-74 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.16 – 7.09 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 5.37 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.40 – 3.32 (m, 1H), 2.45 (s, 3H), 2.04 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.3, 136.7, 134.4, 133.5, 130.0, 128.7, 128.6, 128.0, 63.1, 52.3, 23.2, 21.6, 9.0. HRMS (ESI) for $C_{18}H_{21}ClNO_3S^+$ $[M+H]^+$ calcd 366.0925, found 366.0927.

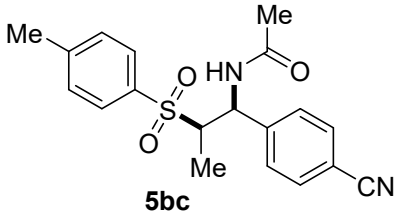


5bb

N-(1-(4-bromophenyl)-2-tosylpropyl)acetamide (5bb)

Pale yellow solid; 69.8 mg, 85% yield, dr > 20:1; mp 79-80 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.32 (m, 4H), 7.11 – 7.03 (m, 2H), 6.86 (d, *J* = 6.8 Hz, 1H), 5.33 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.40 – 3.31 (m, 1H), 2.45 (s, 3H), 2.05 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.3, 137.2, 134.4, 131.6, 130.0, 128.6, 128.4, 121.7, 63.0, 52.5, 23.3, 21.6, 9.0. HRMS (ESI) for $C_{18}H_{21}BrNO_3S^+$ $[M+H]^+$ calcd 410.0420, found 410.0422.

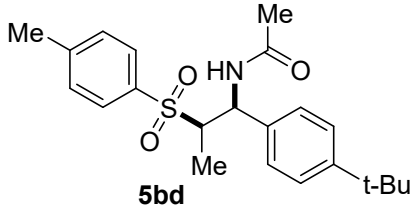


5bc

N-(1-(4-cyanophenyl)-2-tosylpropyl)acetamide (5bc)

Pale yellow oil; 69.2 mg, 97% yield, dr > 20:1; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.05 (d, *J* = 6.8 Hz, 1H), 5.47 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.44 – 3.33 (m, 1H), 2.46 (s, 3H), 2.07 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 145.6, 143.7, 134.1, 132.3, 130.1, 128.5, 127.6, 118.4, 111.5, 62.6, 52.7, 23.1, 21.6, 9.1. HRMS (ESI) for $C_{19}H_{21}N_2O_3S^+$ $[M+H]^+$ calcd 357.1267, found 357.1268.

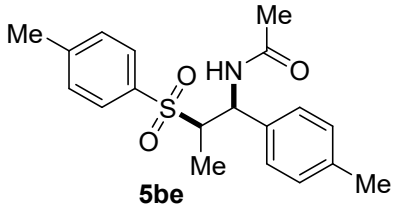


5bd

N-(1-(4-(tert-butyl)phenyl)-2-tosylpropyl)acetamide (5bd)

Yellow solid; 42.8 mg, 55% yield, dr > 20:1; mp 147-148 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.10 – 7.06 (m, 2H), 6.61 (d, *J* = 7.2 Hz, 1H), 5.37 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.45 – 3.37 (m, 1H), 2.44 (s, 3H), 2.05 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.6, 145.0, 134.9, 134.6, 129.9, 128.7, 126.2, 125.5, 63.5, 52.3, 34.4, 31.2, 23.4, 21.6, 8.8. HRMS (ESI) for $C_{22}H_{30}NO_3S^+$ $[M+H]^+$ calcd 388.1941, found 388.1941.

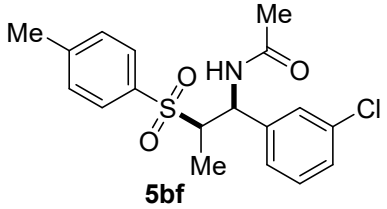


5be

N-(1-(p-tolyl)-2-tosylpropyl)acetamide (5be)

Pale yellow solid; 19.2 mg, 28% yield, dr > 20:1; mp 65-67 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.12 – 7.04 (m, 4H), 6.67 (d, *J* = 2.4 Hz, 1H), 5.33 (dd, *J* = 7.2, 2.8 Hz, 1H), 3.44 – 3.33 (m, 1H), 2.45 (s, 3H), 2.30 (s, 3H), 2.06 (s, 3H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 145.1, 137.5, 134.9, 134.6, 130.0, 129.2, 128.6, 126.5, 63.4, 52.6, 23.4, 21.6, 21.0, 8.9. HRMS (ESI) for $C_{19}H_{24}NO_3S^+$ $[M+H]^+$ calcd 346.1471, found 346.1473.

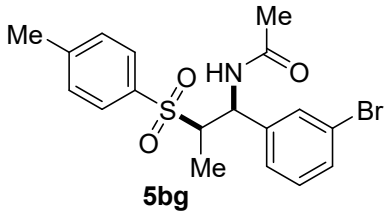


5bf

N-(1-(3-chlorophenyl)-2-tosylpropyl)acetamide (5bf)

Yellow solid; 71.9 mg, 98% yield, dr > 20:1; mp 149-150 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.15 (s, 1H), 7.10 – 7.05 (m, 1H), 6.83 (d, *J* = 6.8 Hz, 1H), 5.38 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.42 – 3.31 (m, 1H), 2.45 (s, 3H), 2.05 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 145.3, 140.4, 134.5, 134.2, 130.0, 129.8, 128.6, 127.9, 126.7, 124.8, 63.1, 52.2, 23.2, 21.6, 8.7. HRMS (ESI) for $C_{18}H_{21}ClNO_3S^+$ $[M+H]^+$ calcd 366.0925, found 366.0927.

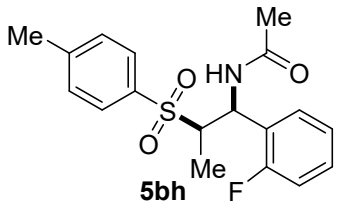


5bg

N-(1-(3-bromophenyl)-2-tosylpropyl)acetamide (5bg)

Pale yellow solid; 78.3 mg, 96% yield, dr > 20:1; mp 164-165 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 3H), 7.30 (s, 1H), 7.20 – 7.10 (m, 2H), 6.75 (d, *J* = 6.8 Hz, 1H), 5.34 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.40 – 3.31 (m, 1H), 2.46 (s, 3H), 2.07 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.4, 140.6, 134.3, 130.9, 130.1, 130.0, 129.6, 128.6, 125.3, 122.7, 63.0, 52.3, 23.3, 21.7, 8.8. HRMS (ESI) for $C_{18}H_{21}BrNO_3S^+$ $[M+H]^+$ calcd 410.0420, found 410.0421.

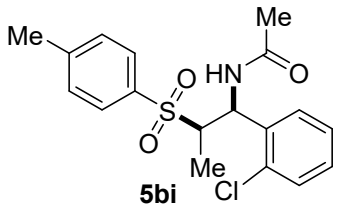


5bh

N-(1-(2-fluorophenyl)-2-tosylpropyl)acetamide (5bh)

Pale yellow solid; 58.2 mg, 84% yield, dr > 20:1; mp 167-168 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.17 (m, 2H), 7.12 – 7.05 (m, 1H), 6.98 – 6.90 (m, 1H), 6.68 (d, *J* = 6.8 Hz, 1H), 5.58 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.56 – 3.45 (m, 1H), 2.45 (s, 3H), 2.06 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 159.7 (d, J = 246.4 Hz), 145.1, 134.3, 129.9, 129.5 (d, J = 8.1 Hz), 128.6, 128.40 (d, J = 3.0 Hz), 125.5 (d, J = 13.1 Hz), 124.3 (d, J = 4.0 Hz), 115.6 (d, J = 21.2 Hz), 61.3, 47.7, 23.2, 21.6, 8.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.46. HRMS (ESI) for $C_{18}H_{21}FNO_3S^+$ $[M+H]^+$ calcd 350.1211, found 350.1211.

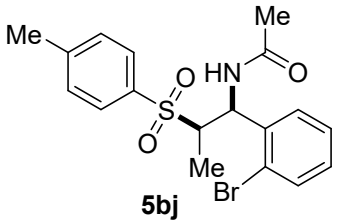


5bi

N-(1-(2-chlorophenyl)-2-tosylpropyl)acetamide (5bi)

Off-white solid; 40.7 mg, 56% yield, dr > 20:1; mp 201-203 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.13 (m, 4H), 6.64 (d, *J* = 6.0 Hz, 1H), 5.50 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.62 – 3.54 (m, 1H), 2.46 (s, 3H), 2.09 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 145.4, 135.8, 133.9, 131.9, 130.0, 129.9, 128.9, 128.8, 127.9, 126.9, 59.4, 49.9, 23.2, 21.7, 6.8. HRMS (ESI) for $C_{18}H_{21}ClNO_3S^+$ $[M+H]^+$ calcd 366.0925, found 366.0927.

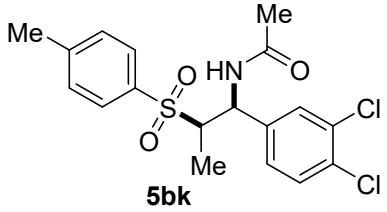


5bj

N-(1-(2-bromophenyl)-2-tosylpropyl)acetamide (5bj)

White solid; 70.9 mg, 86% yield, dr > 20:1; mp 204-205 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.13 – 7.04 (m, 1H), 6.80 (d, *J* = 5.6 Hz, 1H), 5.48 (dd, *J* = 6.0, 3.2 Hz, 1H), 3.62 – 3.54 (m, 1H), 2.45 (s, 3H), 2.08 (s, 3H), 1.27 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 145.3, 137.4, 133.8, 133.3, 129.9, 129.2, 128.9, 128.2, 127.5, 122.0, 59.3, 51.9, 23.1, 21.7, 6.6. HRMS (ESI) for $C_{18}H_{21}BrNO_3S^+$ $[M+H]^+$ calcd 410.0420, found 410.0422.

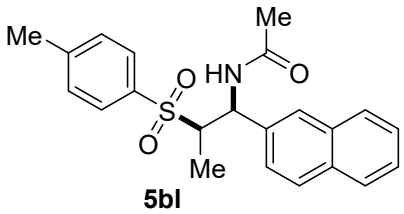


5bk

N-(1-(3,4-dichlorophenyl)-2-tosylpropyl)acetamide (5bk)

Pale yellow solid; 79.0 mg, 99% yield, dr > 20:1; mp 112-114 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 – 7.26 (m, 1H), 7.09 – 7.03 (m, 1H), 6.89 (d, *J* = 6.8 Hz, 1H), 5.32 (dd, *J* = 6.8, 3.6 Hz, 1H), 3.40 – 3.31 (m, 1H), 2.46 (s, 3H), 2.07 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 145.5, 138.5, 134.2, 132.7, 131.9, 130.5, 130.1, 128.8, 128.5, 126.2, 62.8, 52.2, 23.2, 21.6, 9.2. HRMS (ESI) for $C_{18}H_{20}Cl_2NO_3S^+$ $[M+H]^+$ calcd 400.0535, found 400.0537.

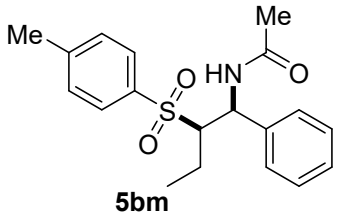


5bl

N-(1-(naphthalen-2-yl)-2-tosylpropyl)acetamide (5bl)

Yellow solid; 28.5 mg, 37% yield, dr > 20:1; mp 146-148 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.71 (m, 5H), 7.62 (s, 1H), 7.48 – 7.41 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 5.55 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.54 – 3.46 (m, 1H), 2.43 (s, 3H), 2.10 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 145.2, 135.5, 134.5, 133.1, 132.8, 130.0, 128.7, 128.5, 127.8, 127.6, 126.3, 126.1, 125.5, 124.3, 63.2, 52.8, 23.4, 21.6, 8.8. HRMS (ESI) for $C_{22}H_{24}NO_3S^+$ $[M+H]^+$ calcd 382.1471, found 382.1472.

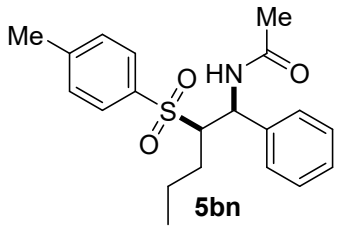


5bm

N-(1-phenyl-2-tosylbutyl)acetamide (5bm)

Yellow solid; 55.6 mg, 81% yield, dr > 20:1; mp 144-145 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.24 (m, 4H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.44 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.31 – 3.25 (m, 1H), 2.43 (s, 3H), 2.07 (s, 3H), 1.94 – 1.84 (m, 1H), 1.73 – 1.60 (m, 1H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 145.0, 137.4, 135.2, 129.9, 128.4, 127.7, 126.9, 70.2, 51.9, 23.3, 21.6, 18.2, 12.8. HRMS (ESI) for $C_{19}H_{24}NO_3S^+$ $[M+H]^+$ calcd 346.1471, found 346.1475.

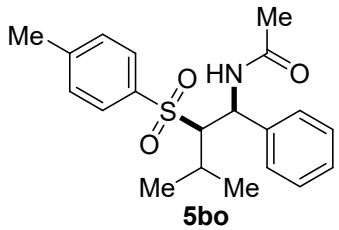


5bn

N-(1-phenyl-2-tosylpentyl)acetamide (5bn)

Yellow solid; 37.0 mg, 52% yield, dr > 20:1; mp 122-123 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 3H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.38 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.36 – 3.29 (m, 1H), 2.45 (s, 3H), 2.09 (s, 3H), 1.87 – 1.77 (m, 1H), 1.64 – 1.53 (m, 1H), 1.36 – 1.19 (m, 2H), 0.69 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 145.1, 137.4, 135.1, 129.9, 128.5, 127.8, 126.8, 68.1, 52.2, 26.5, 23.4, 21.6, 21.2, 13.5. HRMS (ESI) for $C_{20}H_{26}NO_3S^+$ $[M+H]^+$ calcd 360.1628, found 360.1629.

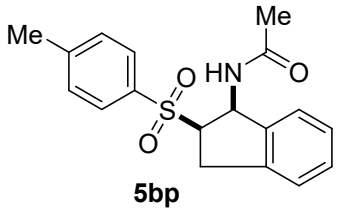


5bo

N-(3-methyl-1-phenyl-2-tosylbutyl)acetamide (5bo)

Yellow solid; 29.5 mg, 41% yield; mp 185-186 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.21 (m, 5H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.54 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.47 (t, *J* = 4.4 Hz, 1H), 2.43 (s, 3H), 2.37 – 2.27 (m, 1H), 2.09 (s, 3H), 1.16 – 1.09 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 144.6, 138.2, 137.1, 129.8, 128.5, 128.0, 127.7, 127.2, 73.3, 52.2, 27.3, 23.5, 21.8, 21.6, 21.4. HRMS (ESI) for $C_{20}H_{26}NO_3S^+$ $[M+H]^+$ calcd 360.1628, found 360.1629.

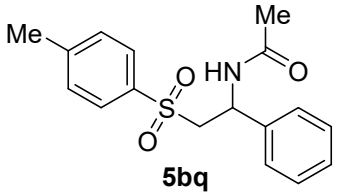


5bp

N-(2-tosyl-2,3-dihydro-1H-inden-1-yl)acetamide (5bp)

Yellow brown solid; 21.2 mg, 32% yield, dr > 20:1; mp 165-166 °C; reaction time 12h;

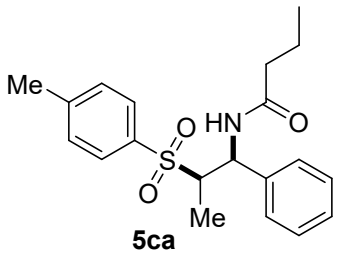
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.09 (m, 4H), 6.03 (d, *J* = 8.4 Hz, 1H), 5.73 (t, *J* = 8.4 Hz, 1H), 4.01 – 3.91 (m, 1H), 3.37– 3.21 (m, 2H), 2.44 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 145.0, 140.7, 138.0, 134.5, 129.9, 129.1, 128.5, 127.6, 124.5, 123.8, 69.3, 55.5, 31.6, 23.0, 21.6. HRMS (ESI) for $C_{18}H_{20}NO_3S^+$ $[M+H]^+$ calcd 330.1158, found 330.1159.



N-(1-phenyl-2-tosylethyl)acetamide (5bq)

Pale yellow solid; 44.0 mg, 70% yield; mp 113-115 °C; reaction time 12h;

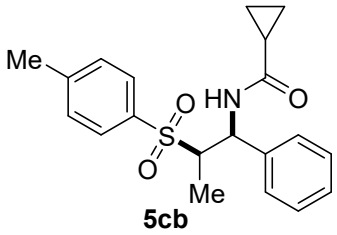
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.18 – 7.14 (m, 2H), 6.87 (d, *J* = 7.2 Hz, 1H), 5.34 – 5.26 (m, 1H), 3.74 (dd, *J* = 14.8, 9.6 Hz, 1H), 3.43 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.42 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 145.0, 139.3, 135.8, 129.9, 128.7, 128.0, 127.8, 126.2, 60.2, 49.3, 23.1, 21.6. HRMS (ESI) for $C_{17}H_{20}NO_3S^+$ $[M+H]^+$ calcd 318.1158, found 318.1159.



N-(1-phenyl-2-tosylpropyl)butyramide (5ca)

Pale yellow solid; 35.4 mg, 49% yield; mp 144-145 °C; reaction time 12h;

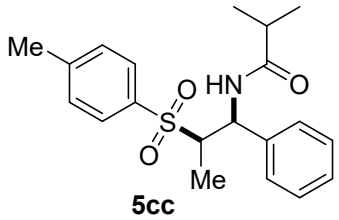
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.20 (m, 3H), 7.19 – 7.13 (m, 2H), 6.69 (d, *J* = 6.8 Hz, 1H), 5.37 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.43 – 3.33 (m, 1H), 2.45 (s, 3H), 2.30 – 2.22 (m, 2H), 1.76 – 1.64 (m, 2H), 1.26 (d, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.2, 138.2, 134.5, 130.0, 128.6, 128.5, 127.7, 126.5, 63.3, 52.5, 38.6, 21.6, 19.0, 13.8, 8.7. HRMS (ESI) for $C_{20}H_{26}NO_3S^+$ $[M+H]^+$ calcd 360.1628, found 360.1629.



N-(1-phenyl-2-tosylpropyl)cyclopropanecarboxamide (5cb)

White solid; 33.6 mg, 47% yield, dr = 12:1; mp 206-208 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.22 (m, 3H), 7.21 – 7.16 (m, 2H), 6.82 (d, *J* = 6.8 Hz, 1H), 5.33 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.45 – 3.36 (m, 1H), 2.45 (s, 3H), 1.56 – 1.47 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.02 – 0.90 (m, 2H), 0.85 – 0.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 145.2, 138.2, 134.5, 130.0, 128.7, 128.5, 127.7, 126.5, 63.5, 52.9, 21.7, 14.8, 8.8, 7.4. HRMS (ESI) for $C_{20}H_{24}NO_3S^+$ $[M+H]^+$ calcd 358.1471, found 358.1472.

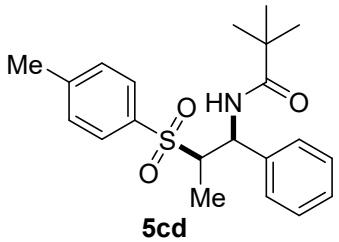


5cc

N-(1-phenyl-2-tosylpropyl)isobutyramide (5cc)

White solid; 39.5 mg, 55% yield, dr > 20:1; mp 198-200 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.20 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 1H), 5.33 (dd, *J* = 6.8, 2.8 Hz, 1H), 3.43 – 3.34(m, 1H), 2.54 – 2.47 (m, 1H), 2.45 (s, 3H), 1.29 – 1.18 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 145.2, 138.2, 134.5, 130.0, 128.6, 128.5, 127.7, 126.4, 63.3, 52.4, 35.6, 21.6, 19.4, 19.4, 8.6. HRMS (ESI) for $C_{20}H_{26}NO_3S^+$ $[M+H]^+$ calcd 360.1628, found 360.1629.

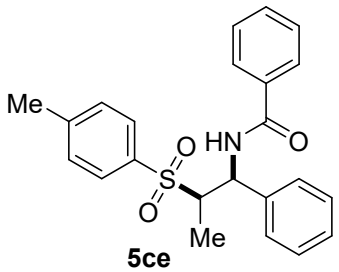


5cd

N-(1-phenyl-2-tosylpropyl)pivalamide (5cd)

Pale yellow solid; 46.5 mg, 62% yield, dr > 20:1; mp 139-140 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 6.0 Hz, 1H), 5.27 (dd, *J* = 6.4, 2.8 Hz, 1H), 3.42 – 3.34 (m, 1H), 2.45 (s, 3H), 1.29 (s, 9H), 1.26 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 145.2, 138.1, 134.5, 130.0, 128.6, 128.5, 127.6, 126.3, 63.2, 52.6, 38.8, 27.4, 21.6, 8.7. HRMS (ESI) for $C_{21}H_{28}NO_3S^+$ $[M+H]^+$ calcd 374.1784, found 374.1785.

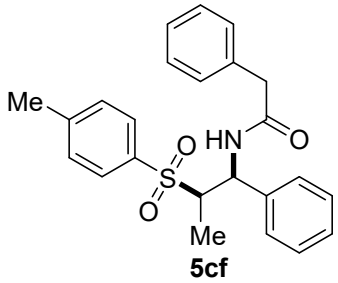


5ce

N-(1-phenyl-2-tosylpropyl)benzamide (5ce)

White solid; 39.5 mg, 50% yield, dr > 20:1; mp 162-164 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.43 (m, 4H), 7.36 – 7.28 (m, 4H), 7.27 – 7.21 (m, 3H), 5.48 (dd, *J* = 6.8, 3.2 Hz, 1H), 3.53 – 3.45 (m, 1H), 2.41 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.3, 137.8, 134.3, 133.9, 131.8, 130.1, 128.6, 128.5, 127.8, 127.1, 126.5, 63.3, 53.4, 21.6, 8.7. HRMS (ESI) for $C_{23}H_{24}NO_3S^+$ $[M+H]^+$ calcd 394.1471, found 394.1473.

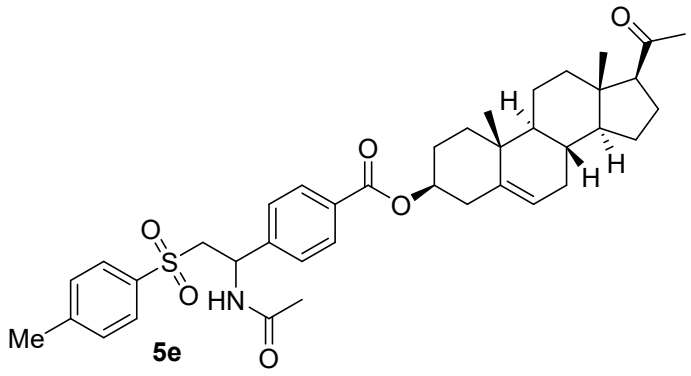


5cf

2-phenyl-N-(1-phenyl-2-tosylpropyl)acetamide (5cf)

Yellow solid; 35.2 mg, 43% yield, dr > 20:1; mp 160-162 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.38 – 7.31 (m, 5H), 7.28 – 7.20 (m, 3H), 6.99 (d, *J* = 6.4 Hz, 2H), 6.51 (d, *J* = 7.6 Hz, 1H), 5.34 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.63 (s, 2H), 3.33 – 3.22 (m, 1H), 2.45 (s, 3H), 1.08 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 145.1, 138.0, 134.6, 134.4, 129.9, 129.5, 129.1, 128.7, 128.6, 127.7, 127.5, 126.2, 63.4, 52.1, 43.9, 21.6, 7.9. HRMS (ESI) for $C_{24}H_{26}NO_3S^+$ $[M+H]^+$ calcd 408.1628, found 408.1628.

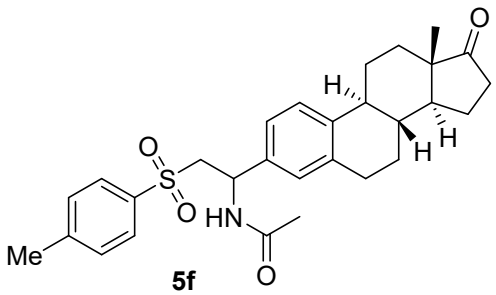


5e

(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-acetamido-2-tosylethyl)benzoate (5e)

White solid; 60.6 mg, 46% yield; mp 226-228 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.90 (m, 1H), 5.41 (d, *J* = 4.0 Hz, 1H), 5.39 – 5.31 (m, 1H), 4.88 – 4.77 (m, 1H), 3.73 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.46 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.45 (s, 1H), 2.43 (s, 3H), 2.25 – 2.15 (m, 1H), 2.13 (s, 3H), 2.09 – 2.03 (m, 1H), 2.01 – 1.96 (m, 4H), 1.95 – 1.84 (m, 2H), 1.76 – 1.56 (m, 5H), 1.53 – 1.42 (m, 3H), 1.32 – 1.12 (m, 4H), 1.10 – 1.00 (m, 4H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 169.7, 165.3, 145.2, 143.9, 139.5, 135.7, 130.3, 130.0, 129.9, 128.0, 126.2, 122.5, 74.5, 63.6, 59.9, 56.8, 49.8, 49.2, 43.9, 38.7, 38.1, 37.0, 36.6, 31.8, 31.7, 31.5, 27.8, 24.4, 23.1, 22.8, 21.6, 21.0, 19.3, 13.2. HRMS (ESI) for $C_{39}H_{50}NO_6S^+$ $[M+H]^+$ calcd 660.3353, found 660.3354.

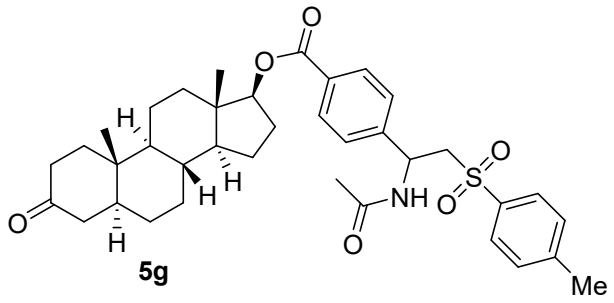


5f

N-(1-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-tosylethyl)acetamide (5f)

Pale yellow solid; 23.7 mg, 24% yield; mp 148-150 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.53 – 6.65 (m, 1H), 5.26 – 5.17 (m, 1H), 3.71 (dd, *J* = 14.8, 8.8 Hz, 1H), 3.46 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.85 – 2.74 (m, 2H), 2.55 – 2.46 (m, 1H), 2.44 (s, 3H), 2.39 – 2.31 (m, 1H), 2.27 – 2.01 (m, 4H), 1.97 (s, 3H), 1.66 – 1.32 (m, 7H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 144.8, 139.5, 136.9, 136.4, 135.9, 129.8, 128.0, 126.9, 125.8, 123.5, 60.2, 50.4, 49.1, 49.0, 47.9, 44.2, 38.0, 35.8, 31.5, 29.3, 26.3, 25.6, 23.2, 21.7, 21.5, 13.8. HRMS (ESI) for $C_{29}H_{36}NO_4S^+$ $[M+H]^+$ calcd 494.2360, found 494.2361.



5g

(5S,8R,9S,10S,13S,14S,17S)-10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl 4-(1-acetamido-2-tosylethyl)benzoate (5g)

Yellow solid; 105.1 mg, 83% yield; mp 138-140 °C; reaction time 12h;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.86 (dd, *J* = 6.8, 2.0 Hz, 1H), 5.37 – 5.29 (m, 1H), 4.85 – 4.78 (m, 1H), 3.77 – 3.67 (m, 1H), 3.51 – 3.41 (m, 1H), 2.43 (s, 3H), 2.40 – 2.22 (m, 4H), 2.13 – 2.06 (m, 1H), 2.01 (s, 3H), 1.83 – 1.65 (m, 4H), 1.64 – 1.45 (m, 4H), 1.44 – 1.29 (m, 5H), 1.29 – 1.07 (m, 3H), 1.03 (s, 3H), 0.92 (s, 3H), 0.84 – 0.72 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9, 169.7, 165.8, 145.3, 143.8, 135.7, 130.3, 130.0, 128.0, 126.2, 83.3, 59.8, 53.7, 50.6, 49.3, 46.6, 44.6, 43.0, 38.4, 38.1, 36.9, 35.7, 35.2, 31.2, 28.7, 27.7, 23.6, 23.2, 21.6, 20.9, 12.3, 11.4. HRMS (ESI) for $C_{37}H_{48}NO_6S^+$ $[M+H]^+$ calcd 634. 3197, found 634. 3199.

10. Computational Experiment

Calculation details

All the calculations were performed with the Gaussian 16 program package[S4] using the default conditions implemented in it. For geometry optimization and frequency analysis we adopted the B3LYP[S5]-D3BJ[S6] with the def2-SVP[S7,8] basis set. Intrinsic reaction coordinate (IRC)[S9] 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[S7,8] based on these optimized structures. Solvent effect was modeled in these optimization and single point calculations by employing SMD continuum solvation model[S10], taking acetonitrile as the solvent for each reaction.

TS means the structures of transition state, and Int means corresponding intermediate.
PC
Charge: 0
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.383567
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1450.3884852 a.u.

C	0.70485400	5.34278200	0.02049000
C	-0.70498400	5.34276300	0.02040300
C	-1.40572500	4.14303000	0.02607800
C	-0.71298700	2.91353300	0.03201500
C	0.71291800	2.91355200	0.03211200
C	1.40562500	4.14306700	0.02625700
N	-1.40426400	1.72724500	0.03910400
C	-0.72986700	0.61109100	0.04581800
C	0.72986100	0.61110900	0.04597900
N	1.40422500	1.72728200	0.03933100
N	-1.40095900	-0.59740800	0.05797300
C	-0.70832400	-1.82347700	0.06141800
C	0.70837200	-1.82346300	0.06165100
N	1.40098200	-0.59738200	0.05827500
C	-1.39341000	-3.04468500	0.06489800
C	-0.69682100	-4.25744500	0.06897900
C	0.69690800	-4.25743200	0.06936200
C	1.39347700	-3.04466100	0.06557200
C	2.83660600	-0.58597400	0.08199800
C	-2.83657800	-0.58604800	0.08180400
C	3.51518900	-0.58200900	1.30696600
C	4.90485000	-0.58294200	1.33374600
C	5.63882300	-0.58547100	0.13214900
C	4.95641900	-0.58888700	-1.09612200
C	3.55858700	-0.58836700	-1.11059000
C	-3.51504100	-0.58400700	1.30684100
C	-4.90470500	-0.58509700	1.33375700
C	-5.63878900	-0.58579700	0.13223200
C	-4.95649900	-0.58723100	-1.09611400
C	-3.55867300	-0.58663500	-1.11071800
O	6.98388200	-0.58552700	0.25544700
C	7.78354400	-0.58620100	-0.91568000
O	-6.98383700	-0.58611400	0.25565800
C	-7.78362200	-0.58552700	-0.91538600
H	1.24837200	6.29081300	0.01632200
H	-1.24852700	6.29078000	0.01616700
H	-2.49806900	4.11991100	0.02658600
H	2.49796900	4.11997500	0.02691000
H	-2.48257300	-3.04281400	0.06450200

H	-1.25441900	-5.19654800	0.07176700
H	1.25451900	-5.19652600	0.07250000
H	2.48264000	-3.04276500	0.06572700
H	2.94487700	-0.58094300	2.23812900
H	5.45005800	-0.58052600	2.27975500
H	5.49957900	-0.59110700	-2.04064300
H	3.02330700	-0.59213900	-2.06238800
H	-2.94464200	-0.58432400	2.23795200
H	-5.44981800	-0.58418400	2.27982300
H	-5.49975200	-0.58798900	-2.04058300
H	-3.02348000	-0.58892800	-2.06256800
H	8.82851900	-0.58460900	-0.57819800
H	7.60498700	-1.48584600	-1.52924400
H	7.60293200	0.31139400	-1.53157100
H	-8.82856100	-0.58472500	-0.57779000
H	-7.60338700	0.31293100	-1.53012800
H	-7.60481900	-1.48431200	-1.53013700

$PC^{\cdot+}$
Charge: 1
Spin Multiplicity: 2
Thermal correction to Gibbs Free Energy (a.u.): 0.383039
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1450.2125465 a.u.

C	0.71191400	5.29502600	0.03786500
C	-0.71202500	5.29501100	0.03795100
C	-1.41858400	4.11213200	0.03952300
C	-0.72202800	2.87478200	0.04204900
C	0.72196600	2.87479700	0.04197700
C	1.41849700	4.11216100	0.03936000
N	-1.40472100	1.70877400	0.04689000
C	-0.72315700	0.58755100	0.05341700
C	0.72314400	0.58756600	0.05340000
N	1.40468400	1.70880400	0.04679100
N	-1.40015600	-0.61531000	0.06605500
C	-0.71639900	-1.81680000	0.07974800
C	0.71644000	-1.81678400	0.07982600
N	1.40017000	-0.61527900	0.06610600
C	-1.40767900	-3.04677800	0.09578200
C	-0.70567700	-4.23778700	0.11165100
C	0.70577000	-4.23776900	0.11180100
C	1.40774700	-3.04674500	0.09603400
C	2.84491200	-0.59470200	0.08010800
C	-2.84489900	-0.59476900	0.08007200
C	3.52030900	-0.56983700	1.30448900
C	4.90890300	-0.55501300	1.31819700
C	5.63384000	-0.56152100	0.11012100
C	4.94367300	-0.58525100	-1.11451600
C	3.54708400	-0.60039800	-1.12211600
C	-3.52028800	-0.57064800	1.30447100
C	-4.90888300	-0.55586800	1.31819900
C	-5.63382600	-0.56167600	0.11012400
C	-4.94366600	-0.58465500	-1.11453300
C	-3.54707800	-0.59976300	-1.12215200
O	6.97610300	-0.54465400	0.22371900
C	7.77135000	-0.54486900	-0.95248200
O	-6.97608800	-0.54490800	0.22374300
C	-7.77135100	-0.54460200	-0.95244700
H	1.24532000	6.24814400	0.03717100
H	-1.24545100	6.24811800	0.03732200
H	-2.50985600	4.09052300	0.04025900
H	2.50976900	4.09057500	0.03997600
H	-2.49592600	-3.04509100	0.09536300
H	-1.25099900	-5.18323900	0.12371200
H	1.25111200	-5.18320900	0.12400000
H	2.49599400	-3.04502900	0.09582200
H	2.95460100	-0.56499100	2.23795000
H	5.46007600	-0.53689800	2.26019100
H	5.47999500	-0.59112300	-2.06263900

H	3.00306600	-0.61878000	-2.06833500
H	-2.95457400	-0.56633400	2.23793100
H	-5.46005000	-0.53831700	2.26020700
H	-5.47999600	-0.58997700	-2.06265600
H	-3.00306500	-0.61757900	-2.06838400
H	8.81707000	-0.52717400	-0.61864800
H	7.60041100	-1.45213000	-1.55622300
H	7.57537300	0.34572200	-1.57317900
H	-8.81706800	-0.52717700	-0.61859000
H	-7.57547100	0.34632200	-1.57269700
H	-7.60033000	-1.45154200	-1.55664800

Int1
Charge: 0
Spin Multiplicity: 2
Thermal correction to Gibbs Free Energy (a.u.): 0.213179
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1129.6062593 a.u.

S	-2.41242600	-0.13000500	-0.54385200
O	-3.58049000	0.18868300	0.33423400
O	-2.58567800	-0.18127000	-2.02623600
C	1.34260300	-1.49033700	-0.10655900
C	1.84213900	-0.93655700	1.09287000
C	3.01866600	-0.18657500	1.09731300
C	3.73540900	0.02236200	-0.08599700
C	3.26903100	-0.53822400	-1.28007200
C	2.09268200	-1.28501200	-1.28673500
C	0.10518800	-2.26528900	-0.21868100
C	-0.92876100	-2.42017300	0.64620400
C	-1.11863900	-1.85922800	2.02210000
C	-1.12244600	1.08474000	-0.18931400
C	-0.12745400	1.30119400	-1.14465900
C	0.91123000	2.18125800	-0.83547100
C	0.95076000	2.81163700	0.41265600
C	-0.05305800	2.57490600	1.35852700
C	-1.10141600	1.70009300	1.06471500
H	1.32226500	-1.10201200	2.03405100
H	3.38215000	0.23597700	2.03735700
H	4.65496300	0.61258000	-0.07570900
H	3.82341800	-0.38883400	-2.20998800
H	1.72829100	-1.71524300	-2.22320400
H	-0.00877900	-2.76712800	-1.18553000
H	-1.73237500	-3.08002200	0.30005100
H	-0.67981400	-0.85944200	2.14255600
H	-0.65368900	-2.51319500	2.78258000
H	-2.19037200	-1.79645300	2.26247100
H	-0.16939600	0.79420100	-2.10881400
H	1.77304100	3.48983300	0.65185600
H	-0.02126900	3.07253000	2.33041300
H	-1.89413700	1.50422400	1.78763900
H	1.69825600	2.36498000	-1.56945300

TS1
Charge: 0
Spin Multiplicity: 2
Thermal correction to Gibbs Free Energy (a.u.): 0.216037
Imaginary frequencies: -246.4530
Calculation of single point energy based on the optimized structure, E = -1129.6037591 a.u.

S	-2.32414000	-0.18546700	-0.43549500
O	-3.49383200	0.21301500	0.40090500
O	-2.51950800	-0.45027500	-1.88674800
C	1.25933300	-1.45821800	-0.03273800
C	1.65932400	-0.79582500	1.15627000
C	2.90344300	-0.17704400	1.24382700
C	3.79554800	-0.20689100	0.16411200
C	3.43134400	-0.87591200	-1.01189600
C	2.18809600	-1.49174200	-1.10684300
C	-0.02906000	-2.07198800	-0.25221800
C	-1.20341800	-2.04135100	0.50936000

C	-1.35222400	-1.68757500	1.96437600
C	-1.06765800	1.09479100	-0.27226400
C	-0.09792300	1.21483600	-1.27056900
C	0.95211600	2.11552500	-1.08148700
C	1.02359500	2.87355000	0.09228400
C	0.03948700	2.74589400	1.07916000
C	-1.01557500	1.84738500	0.90426400
H	0.99393200	-0.75725200	2.01457100
H	3.18220800	0.33731400	2.16682000
H	4.76849300	0.28432700	0.24050400
H	4.12090000	-0.91011400	-1.85903900
H	1.90165900	-1.99986500	-2.03109000
H	-0.13529000	-2.54478900	-1.23334900
H	-1.98688400	-2.70543100	0.12581500
H	-0.94733100	-0.69730400	2.21361700
H	-0.82048600	-2.42756500	2.58724100
H	-2.41301800	-1.70125800	2.24874000
H	-0.16677900	0.60938500	-2.17482600
H	1.85293600	3.56940500	0.23921300
H	0.09425000	3.34614200	1.99028400
H	-1.79190200	1.73183000	1.66201000
H	1.72170400	2.21812100	-1.84968600

Int2
Charge: 0
Spin Multiplicity: 2
Thermal correction to Gibbs Free Energy (a.u.): 0.217910
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1129.6173155 a.u.

S	-2.14783900	-0.52446400	-0.40492100
O	-3.40387900	-0.30755100	0.34502000
O	-2.21474100	-0.94148600	-1.82097800
C	1.39377800	-1.33410300	0.03713900
C	1.63002100	-0.34433800	1.03772800
C	2.86240200	0.28868800	1.14270600
C	3.91365100	-0.03283700	0.27093800
C	3.71183300	-1.00863100	-0.71803600
C	2.48407700	-1.64588400	-0.83327300
C	0.16042600	-2.00532400	-0.17983100
C	-1.14946200	-1.83422200	0.50025300
C	-1.22682300	-1.59249500	2.00528000
C	-1.16569700	0.97120800	-0.31237800
C	-0.23813300	1.23169800	-1.32443500
C	0.57507100	2.36090200	-1.21607600
C	0.45160500	3.20982300	-0.11056800
C	-0.49519900	2.94463000	0.88513700
C	-1.31652600	1.81899700	0.78823400
H	0.83391800	-0.05470600	1.71775300
H	3.00721100	1.05142900	1.91199100
H	4.87827300	0.47231800	0.35973000
H	4.52283100	-1.26681400	-1.40389400
H	2.33088400	-2.39856000	-1.61091900
H	0.14059600	-2.68737800	-1.03347300
H	-1.77994000	-2.70116600	0.24274500
H	-0.89807900	-0.58894700	2.30317900
H	-0.59256900	-2.32718300	2.52399000
H	-2.26292700	-1.72132300	2.34542500
H	-0.15532400	0.55518900	-2.17539700
H	1.09520000	4.08875400	-0.02689900
H	-0.59643700	3.61751500	1.73963000
H	-2.06562400	1.60027000	1.55039300
H	1.31022800	2.57564700	-1.99476400

Int3
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.221281
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1129.442019 a.u.

S	-2.16241900	-0.25256800	-0.46885800
O	-3.38332000	0.10534400	0.26604500
O	-2.23207700	-0.71493800	-1.86210400
C	1.16162700	-1.49270100	0.11017100
C	1.51824000	-0.64957500	1.21412500
C	2.76795200	-0.06719700	1.25798200
C	3.69849300	-0.31774200	0.23154700
C	3.39077600	-1.16728100	-0.84405600
C	2.14291100	-1.75541200	-0.90517300
C	-0.11977000	-1.98795700	-0.12984500
C	-1.38789500	-1.70961400	0.54301900
C	-1.49445700	-1.40581500	2.02794100
C	-0.96829800	1.06242800	-0.33692800
C	0.02647200	1.15614600	-1.31625500
C	1.01167300	2.13287600	-1.17086600
C	0.98969900	2.99309100	-0.06738900
C	-0.02285200	2.89364400	0.89278000
C	-1.01647200	1.92127400	0.76546400
H	0.80685600	-0.45667700	2.01139600
H	3.03771800	0.58839600	2.08714400
H	4.68287800	0.15458400	0.27636500
H	4.12947000	-1.35121400	-1.62560800
H	1.86950700	-2.40265600	-1.74066300
H	-0.22164500	-2.58509400	-1.04149700
H	-2.11230400	-2.48388800	0.24465300
H	-1.09863500	-0.42174300	2.30754500
H	-0.95023200	-2.17481800	2.59603400
H	-2.55282000	-1.43936500	2.31628100
H	0.02990700	0.47542100	-2.16788400
H	1.76811000	3.75141100	0.04330900
H	-0.04103700	3.57500400	1.74588300
H	-1.81471700	1.83257300	1.50333000
H	1.80024400	2.21891900	-1.92118700

Int4
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.258120
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1262.2776549 a.u.

S	0.15811900	-2.05206400	-0.16770700
O	-0.36344500	-3.36132200	0.25250900
O	1.28117500	-1.96592400	-1.11467100
N	-1.62598700	2.03204500	1.39998900
C	2.21446300	0.66712200	0.53247500
C	3.35416400	-0.15430000	0.24801300
C	4.44770800	0.39300800	-0.39274200
C	4.44044700	1.75428200	-0.75206900
C	3.33942400	2.58423000	-0.47554300
C	2.23578700	2.05279800	0.16201300
C	1.04752000	0.17902200	1.11311600
C	0.74695600	-1.21182400	1.44817200
C	-2.71539100	2.35580100	1.17684600
C	-4.08168500	2.76019900	0.89374300
C	-0.30345000	-1.39258800	2.53188000
C	-1.18336600	-1.04287000	-0.76742300
C	-0.88442600	0.01856400	-1.62801600
C	-1.93493600	0.81472800	-2.08706500
C	-3.24854700	0.54009400	-1.69240500
C	-3.52542200	-0.52960800	-0.83393000
C	-2.48846700	-1.33675900	-0.36270100
H	3.35904400	-1.20393700	0.53809100
H	5.32074900	-0.22214800	-0.61640800
H	5.31439500	2.17655000	-1.25442500
H	3.36128800	3.63565000	-0.76628300
H	1.35907700	2.66596500	0.38062400
H	0.23234900	0.89579100	1.27638800
H	1.64508100	-1.82205400	1.62750500
H	-4.73923000	1.87844900	0.90162500

H	-4.13088100	3.23562300	-0.09709800
H	-4.42625000	3.47597800	1.65537500
H	-1.22332900	-0.83667900	2.29904500
H	0.09809300	-1.00906900	3.48187100
H	-0.53770300	-2.45780900	2.65687800
H	0.14355600	0.21043300	-1.93692900
H	-4.06581300	1.16572600	-2.05748100
H	-4.55342600	-0.73998900	-0.53175000
H	-2.68591900	-2.18083500	0.29892500
H	-1.72557200	1.64762600	-2.76144400

TS2
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.260695
Imaginary frequencies: -91.6071
Calculation of single point energy based on the optimized structure, E = -1262.2698002 a.u.

S	1.10442800	-1.96427200	0.35287600
O	1.66198300	-3.05033800	-0.47121100
O	0.73728500	-2.21279300	1.76071900
N	-0.08141100	1.44615500	-0.53114400
C	-2.51770700	-0.05439400	0.21140200
C	-3.39134400	-0.63457900	-0.74990600
C	-4.72755500	-0.27042500	-0.77413200
C	-5.21317500	0.67744100	0.14198800
C	-4.36816800	1.25869500	1.09908400
C	-3.03223300	0.89378300	1.14023700
C	-1.14789400	-0.39116300	0.31780400
C	-0.45626000	-1.43673400	-0.48686300
C	0.41758400	2.48549800	-0.62214500
C	1.05475600	3.78193500	-0.74241500
C	-0.24506900	-1.19498900	-1.98147000
C	2.21253400	-0.56500500	0.29955200
C	2.29788000	0.26839500	1.41809800
C	3.12631700	1.38996800	1.35533300
C	3.85147200	1.66143300	0.19019500
C	3.77083000	0.80345100	-0.91270200
C	2.95251100	-0.32617600	-0.86277900
H	-3.02130700	-1.38235500	-1.45102500
H	-5.40448100	-0.72149700	-1.50177100
H	-6.26802500	0.96104900	0.11194000
H	-4.76301500	1.98890300	1.80764300
H	-2.35469100	1.33452200	1.87475200
H	-0.65727600	-0.05090900	1.23147900
H	-1.05685800	-2.35774700	-0.35136600
H	1.81332300	3.74616500	-1.53853100
H	1.54217800	4.03938000	0.20966000
H	0.30139900	4.54567300	-0.98759200
H	0.45266700	-0.36503200	-2.14578000
H	-1.19665300	-0.94186400	-2.46604700
H	0.15017600	-2.11016700	-2.43977200
H	1.72491400	0.03894100	2.31730600
H	4.49074900	2.54601700	0.14312500
H	4.35095100	1.01194400	-1.81424300
H	2.89026700	-1.01059900	-1.70962200
H	3.20369500	2.05510300	2.21809400

Int5
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.264985
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1262.2967429 a.u.

S	-1.13814800	-1.80400400	-0.41035300
O	-1.60606900	-2.96239400	0.37133800
O	-0.83601700	-1.95770800	-1.84783000
N	0.39114600	1.14568000	-0.00055200
C	2.56830100	0.10271900	-0.19198500
C	3.37264400	-0.88854700	0.38210900

C	4.75519300	-0.69929100	0.48187500
C	5.34352200	0.47662200	0.01274100
C	4.54259500	1.46679400	-0.56593000
C	3.16383700	1.27967300	-0.67042400
C	1.05794900	-0.07557600	-0.37158800
C	0.43009700	-1.25457500	0.38992400
C	-0.15605400	2.10720900	0.30696300
C	-0.85465400	3.29967600	0.69099300
C	0.28115700	-1.07892200	1.89157800
C	-2.32397000	-0.47596800	-0.22892700
C	-2.52034000	0.40341200	-1.29804000
C	-3.42731000	1.45373100	-1.14454600
C	-4.12428100	1.60816300	0.05895200
C	-3.92822200	0.70884000	1.11282700
C	-3.02672100	-0.34866200	0.97339300
H	2.94201500	-1.81798800	0.75449700
H	5.37074700	-1.48054800	0.93371500
H	6.42315400	0.62223300	0.09571600
H	4.99249200	2.38861100	-0.94193200
H	2.54973100	2.05668300	-1.13177300
H	0.84882000	-0.20437100	-1.44682600
H	1.04164800	-2.13905200	0.15682200
H	-1.74280800	3.01013900	1.27439100
H	-1.16249100	3.84159300	-0.21675600
H	-0.18424300	3.92616500	1.30042200
H	-0.39401100	-0.24930200	2.14541200
H	1.26414000	-0.86777200	2.33664700
H	-0.11004600	-2.00173200	2.33862900
H	-1.97017100	0.26405800	-2.22940900
H	-4.83022300	2.43376500	0.17482000
H	-4.48371200	0.82616100	2.04576500
H	-2.87708300	-1.06698100	1.78014900
H	-3.59139100	2.15167900	-1.96833800

Int6
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.303615
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1415.2603259 a.u.

S	-1.63107900	-1.89744200	-0.58540000
O	-2.28526800	-3.07938300	0.00448400
O	-1.28604600	-1.88640000	-2.02167500
N	0.19466500	0.77376700	0.29847100
C	2.22044300	-0.53076700	0.06069300
C	2.76883200	-0.06863300	1.26359700
C	4.14467400	-0.17557800	1.48963700
C	4.97461600	-0.74655400	0.51916400
C	4.42528800	-1.21157600	-0.68026600
C	3.05098100	-1.10357100	-0.91095700
C	0.72901600	-0.44984500	-0.22217100
C	-0.04187200	-1.66955500	0.32400900
C	-0.16020300	1.82082800	0.61337000
C	-0.69881500	3.04779700	1.13041100
C	-0.21559900	-1.72830400	1.83015400
C	-2.63317600	-0.45425800	-0.24553500
C	-2.67792500	0.57191300	-1.19383200
C	-3.43098800	1.71312600	-0.91178200
C	-4.12389600	1.81424300	0.29961800
C	-4.08085400	0.77079000	1.23102100
C	-3.33685900	-0.37966400	0.96063200
H	2.12998300	0.38804900	2.02195800
H	4.56801500	0.19280400	2.42670700
H	6.04992300	-0.82342700	0.69535900
H	5.06908700	-1.65177500	-1.44505600
H	2.62117000	-1.45557800	-1.85187400
H	0.57980900	-0.40301400	-1.31118600
H	0.49900300	-2.55701200	-0.04167600
H	-1.32670400	2.81153000	2.00376900

H	-1.30223000	3.52743900	0.34687200
H	0.13208800	3.70730900	1.41980900
H	-0.73668600	-0.84216700	2.22061700
H	0.77148600	-1.78997400	2.31056800
H	-0.78469700	-2.62595200	2.10469200
H	-2.12837700	0.47558200	-2.13098300
H	-4.70636100	2.71225800	0.51817100
H	-4.63363000	0.84915800	2.16967200
H	-3.30758400	-1.20715300	1.67058000
H	-3.47537600	2.52570700	-1.64016600
O	1.02482600	3.13488200	-1.25700800
H	1.10770300	4.09961500	-1.21718000
H	1.95377400	2.81936600	-1.17553500
O	3.62685000	2.26099100	-0.94004600
H	3.79250000	1.44175200	-1.43512300
H	3.73682900	1.98511000	-0.01552100

TS3
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.309586
Imaginary frequencies: -199.9486
Calculation of single point energy based on the optimized structure, E = -1415.2480395 a.u.

S	-1.60745000	-1.84469200	-0.63296700
O	-2.26331600	-3.06503800	-0.12612900
O	-1.26717200	-1.73837500	-2.06736500
N	0.15731700	0.77249100	0.47486800
C	2.21254400	-0.48413800	0.12127500
C	2.76948300	-0.02316000	1.32091100
C	4.14961700	-0.10938000	1.53152000
C	4.97820200	-0.66124800	0.54943700
C	4.42149800	-1.13115600	-0.64527200
C	3.04326700	-1.04220400	-0.85979300
C	0.72053700	-0.39786500	-0.15928100
C	-0.02083500	-1.67027700	0.28740300
C	0.02944100	1.94175700	0.33504600
C	-0.51057300	3.18982100	0.85546100
C	-0.19655000	-1.83799800	1.78517100
C	-2.62006400	-0.43180700	-0.20252800
C	-2.67536500	0.65082100	-1.08466900
C	-3.44365800	1.76277200	-0.73546000
C	-4.14144600	1.78010600	0.47742100
C	-4.08747400	0.68130800	1.34205500
C	-3.32828400	-0.44087900	1.00281100
H	2.13076800	0.42053800	2.08713500
H	4.57726200	0.26016500	2.46635200
H	6.05666200	-0.72150400	0.71275200
H	5.06321900	-1.55874900	-1.41908500
H	2.60954900	-1.39420900	-1.79909600
H	0.58492500	-0.28065700	-1.24485400
H	0.52396700	-2.52617000	-0.14237300
H	-1.04945700	2.96104200	1.78641800
H	-1.20502500	3.62909700	0.12434800
H	0.30672500	3.89947900	1.05248500
H	-0.72704100	-0.98361300	2.22945500
H	0.79201700	-1.91414000	2.26150500
H	-0.75264600	-2.75965200	2.00087900
H	-2.11931400	0.62102700	-2.02237800
H	-4.73717700	2.65491700	0.74835200
H	-4.64428800	0.69388700	2.28155600
H	-3.29115000	-1.31107000	1.65937300
H	-3.49715400	2.61791000	-1.41276500
O	0.86626400	2.48750900	-1.31551100
H	0.69355300	3.42272100	-1.52936400
H	1.87011200	2.40890200	-1.19668700
O	3.43799400	2.27766300	-0.97929300
H	3.78457600	1.48268000	-1.42144000
H	3.65568600	2.13210800	-0.04184000

Int7
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.312918
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1415.2536514 a.u.

S	-1.55099500	-1.70292600	-0.75899600
O	-2.14663000	-3.01282100	-0.42428200
O	-1.21653500	-1.39909200	-2.16767700
N	0.13329700	0.84951500	0.50145300
C	2.23673700	-0.40963700	0.21514600
C	2.74380000	0.10434800	1.41526800
C	4.11060800	0.01216600	1.70272100
C	4.98635400	-0.59062100	0.79581300
C	4.48740500	-1.11471800	-0.40324300
C	3.11885700	-1.02930000	-0.69049300
C	0.76644700	-0.28057500	-0.15620000
C	0.01511800	-1.58010100	0.19682900
C	0.20216600	2.01211400	0.02564800
C	-0.47961400	3.20933900	0.59330400
C	-0.20117900	-1.83639000	1.67749900
C	-2.66195400	-0.42494300	-0.17240500
C	-2.77548400	0.75931500	-0.90449500
C	-3.64209500	1.75285900	-0.44603400
C	-4.37825800	1.55457900	0.72764800
C	-4.26333100	0.35674300	1.44142800
C	-3.40671200	-0.64958700	0.98854900
H	2.07015100	0.59699000	2.11783100
H	4.49307200	0.42472900	2.63920700
H	6.05435700	-0.64847700	1.01659600
H	5.16253400	-1.58386500	-1.12234100
H	2.73034500	-1.43957100	-1.62658700
H	0.71993400	-0.17478300	-1.25211600
H	0.55527300	-2.42220400	-0.26634200
H	-1.07962600	2.91417300	1.46120800
H	-1.13821800	3.66549400	-0.16433000
H	0.26463400	3.96548800	0.89262100
H	-0.73946700	-1.00598900	2.15345200
H	0.77567700	-1.94037300	2.17319700
H	-0.76013400	-2.76960000	1.82874400
H	-2.18928300	0.89552900	-1.81390800
H	-5.05204000	2.33691300	1.08500800
H	-4.84870000	0.20036600	2.35030000
H	-3.32281100	-1.59591500	1.52406400
H	-3.74330800	2.68464500	-1.00683800
O	0.95877000	2.27483100	-1.12935400
H	0.72166300	3.14385200	-1.51108900
H	2.39713300	2.03902300	-1.24155100
O	3.42560800	1.86069300	-1.36892600
H	3.56699200	0.87354900	-1.29660500
H	3.92177300	2.27778600	-0.62673200

Int8
Charge: 0
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.278988
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1338.3636584 a.u.

S	1.14926300	-1.76402300	0.60390000
O	1.55610600	-3.09503300	0.10433600
O	0.94836600	-1.57409700	2.05777100
N	-0.28746300	1.08553300	-0.28219100
C	-2.50766300	0.03988800	0.00496600
C	-3.01470400	0.76817500	-1.07925800
C	-4.38808400	0.78031700	-1.34564600
C	-5.27045900	0.06466900	-0.53110200
C	-4.77111600	-0.66297900	0.55518400
C	-3.39958100	-0.67377200	0.81980900
C	-1.01347000	-0.01852800	0.30451700

C	-0.44161400	-1.35562200	-0.22052400
C	-0.04237600	2.14802900	0.37369700
C	-0.41889900	2.51805400	1.77533800
C	-0.33671900	-1.47879600	-1.73055300
C	2.37814800	-0.57678700	0.06130000
C	2.66431700	0.51935300	0.87770300
C	3.59872400	1.45918000	0.44102600
C	4.23942000	1.28938100	-0.79170200
C	3.95833100	0.17366300	-1.58780200
C	3.02517900	-0.77475600	-1.16111300
H	-2.32749500	1.33201500	-1.71198700
H	-4.76950300	1.35368300	-2.19467200
H	-6.34355400	0.07654800	-0.73813600
H	-5.45368400	-1.21951800	1.20267400
H	-3.01311700	-1.23937400	1.67251900
H	-0.90758000	-0.05641100	1.40053800
H	-1.05070200	-2.17718500	0.19079200
H	-1.09242300	3.38981700	1.74994600
H	0.48379000	2.81708900	2.33015000
H	-0.91918600	1.69962700	2.30436000
H	0.27598900	-0.67203900	-2.15403300
H	-1.34401800	-1.40562700	-2.16746800
H	0.08860100	-2.45125400	-2.01303700
H	2.14987100	0.63447900	1.83200300
H	4.96794800	2.02916500	-1.13206900
H	4.47045900	0.03754300	-2.54306200
H	2.80583100	-1.65632700	-1.76445900
H	3.82566800	2.32728500	1.06367700
O	0.66128000	3.12961000	-0.22405100
H	0.89451300	2.80547400	-1.11427600

TS4
Charge: 0
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.274191
Imaginary frequencies: -1918.8199
Calculation of single point energy based on the optimized structure, E = -1338.3154412 a.u.

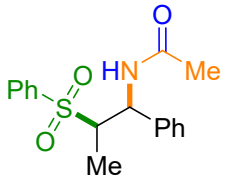
S	1.11911300	-1.75932500	0.58386900
O	1.50406800	-3.09138000	0.07126700
O	0.91269900	-1.57943500	2.03786600
N	-0.32307700	1.12968700	-0.21862700
C	-2.54038900	0.05424300	0.02886100
C	-3.06401300	0.83290700	-1.01045300
C	-4.44019200	0.84572700	-1.26286000
C	-5.30733200	0.08090400	-0.47739600
C	-4.79058800	-0.69673000	0.56539300
C	-3.41642000	-0.70897400	0.81521500
C	-1.04138500	-0.00279900	0.31018000
C	-0.46276200	-1.32272100	-0.24273500
C	0.04438300	2.23130000	0.39048400
C	-0.12638700	2.62462700	1.81356900
C	-0.35001600	-1.40635900	-1.75546100
C	2.36979000	-0.58817100	0.05796900
C	2.68018200	0.48808900	0.89200800
C	3.64527000	1.40605300	0.47600200
C	4.29253600	1.23425600	-0.75265600
C	3.98490100	0.13949600	-1.56762100
C	3.02072700	-0.78697700	-1.16265500
H	-2.38981700	1.43704900	-1.62008200
H	-4.83530000	1.45846700	-2.07732800
H	-6.38252500	0.09318400	-0.67302700
H	-5.46162700	-1.29189400	1.19010800
H	-3.01610200	-1.31461300	1.63339800
H	-0.91393500	-0.03859400	1.40402300
H	-1.07839000	-2.15297500	0.13957600
H	-0.86713200	3.43838600	1.87426100
H	0.82650800	3.01318400	2.20151100
H	-0.46805700	1.78551000	2.43334100
H	0.29137600	-0.61139200	-2.15975900

H	-1.35149100	-1.29368000	-2.19720800
H	0.05037700	-2.38274300	-2.05973900
H	2.16425900	0.60328100	1.84542000
H	5.04597100	1.95654600	-1.07579100
H	4.50094300	0.00180300	-2.52052000
H	2.78265300	-1.65393800	-1.77987900
H	3.89238100	2.25795700	1.11331400
O	0.62120300	2.98151800	-0.48944200
H	0.27202700	1.90100100	-1.14773300

TS2′
Charge: 1
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.259754
Imaginary frequencies: -107.0739
Calculation of single point energy based on the optimized structure, E = -1262.2668555 a.u.

S	-1.48908100	0.92809000	-1.09647600
O	-2.13200200	0.89423200	-2.42192400
O	-1.35928400	2.22417000	-0.40987900
N	0.63961400	1.13014700	1.51569100
C	2.23063500	-0.66463900	-0.04669800
C	3.20458000	0.00689000	-0.83716900
C	4.54843800	-0.27401000	-0.65653900
C	4.94413000	-1.21650000	0.30802700
C	3.99824500	-1.88429900	1.10017000
C	2.65079600	-1.60890200	0.93126000
C	0.84208600	-0.43863900	-0.18823300
C	0.23042700	0.23942600	-1.35206700
C	0.73651300	2.28389600	1.56772300
C	0.81806500	3.72818500	1.61132500
C	0.19428800	-0.80889300	-2.48770500
C	-2.33100600	-0.23148200	-0.03023400
C	-2.44948900	0.05441500	1.33250300
C	-3.10915100	-0.86390800	2.15218000
C	-3.63533200	-2.04015700	1.60786500
C	-3.51703500	-2.30416400	0.23844900
C	-2.86623000	-1.39421300	-0.59611900
H	2.89766400	0.74202400	-1.58191600
H	5.30125500	0.23640100	-1.25982200
H	6.00710400	-1.43032900	0.44428300
H	4.32385800	-2.61173900	1.84575100
H	1.89619700	-2.10862300	1.54194400
H	0.18172500	-1.06142900	0.42111700
H	0.78582600	1.13342700	-1.67100500
H	0.04474600	4.13839800	0.94418900
H	1.81189600	4.05954900	1.27430100
H	0.64455600	4.08502000	2.63796600
H	-0.29774000	-1.73759100	-2.16523900
H	1.22208000	-1.04135600	-2.79692600
H	-0.35590700	-0.37996600	-3.33477100
H	-2.03649000	0.97720500	1.73772300
H	-4.14848700	-2.75519000	2.25518600
H	-3.94051600	-3.21784700	-0.18413200
H	-2.78440100	-1.57701600	-1.66819100
H	-3.21483300	-0.65666100	3.21930500

N-((1S,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide

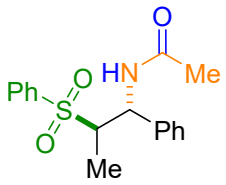


Product
Charge: 0

Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.281064
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1338.3868328 a.u.

S	1.17752300	-1.64637800	0.71800700
O	1.57117300	-3.02601600	0.36311800
O	0.97370000	-1.29662800	2.14086000
N	-0.30615500	1.13280000	-0.21686000
C	-2.52974400	0.01908600	-0.03192000
C	-3.02766200	0.74231900	-1.12239900
C	-4.39293700	0.71464100	-1.42739000
C	-5.27416800	-0.03550700	-0.64368100
C	-4.78326500	-0.75749000	0.45033400
C	-3.42016000	-0.72884500	0.75294300
C	-1.04218200	0.00243900	0.30880800
C	-0.41389500	-1.32871300	-0.14994900
C	-0.06009400	2.32069100	0.41093900
C	-0.53033100	2.44614300	1.84344900
C	-0.28807500	-1.53472800	-1.65101300
C	2.41485800	-0.53629200	0.04752100
C	2.70622100	0.64543100	0.73230000
C	3.66623400	1.50994800	0.20509500
C	4.32550700	1.18320200	-0.98505000
C	4.03632600	-0.01399400	-1.64914600
C	3.07832100	-0.88891000	-1.13130700
H	-2.34632600	1.33682600	-1.73405900
H	-4.76809400	1.28425400	-2.28152100
H	-6.34087200	-0.05483200	-0.88061000
H	-5.46619300	-1.34021100	1.07379900
H	-3.03985400	-1.29012300	1.61131900
H	-0.95450800	0.01354600	1.40148800
H	-1.00712600	-2.14730900	0.28776100
H	-1.61648500	2.28367900	1.92249500
H	-0.28348200	3.45244500	2.20335700
H	-0.03523000	1.69965200	2.48451200
H	0.34204600	-0.77087000	-2.13006400
H	-1.28843100	-1.48785600	-2.10633100
H	0.14007400	-2.52283800	-1.86675100
H	2.18281100	0.88108200	1.65879300
H	5.07454900	1.86438900	-1.39588800
H	4.56213900	-0.27151300	-2.57136300
H	2.85437200	-1.83310600	-1.62894300
H	3.89718600	2.44242400	0.72455800
O	0.53079400	3.22458700	-0.16832200
H	0.00108400	1.10074300	-1.18510600

N-((1R,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide



Product′
Charge: 0
Spin Multiplicity: 1
Thermal correction to Gibbs Free Energy (a.u.): 0.281534
Imaginary frequencies: 0
Calculation of single point energy based on the optimized structure, E = -1338.3767798 a.u.

S	1.51606100	0.71748200	1.31055400
O	2.10173900	0.45715300	2.64191300
O	1.46091800	2.11595000	0.83716500
N	-0.42237800	0.72578700	-1.09976000
C	-2.22750900	-0.64281700	-0.09726700
C	-3.14381000	-0.26842900	0.89413000
C	-4.49732500	-0.60598700	0.77816000

C	-4.95272700	-1.32292900	-0.33048300
C	-4.04433200	-1.70482700	-1.32454700
C	-2.69536900	-1.36752400	-1.20528900
C	-0.74237700	-0.26804600	-0.07657200
C	-0.20297600	0.03043100	1.33706300
C	-0.78070300	2.03839800	-1.24042000
C	-1.56288200	2.69804400	-0.13016300
C	-0.25140300	-1.19665800	2.23992700
C	2.44376700	-0.24452500	0.11362700
C	2.71790800	0.30917700	-1.13952100
C	3.45263100	-0.44181900	-2.06000900
C	3.90191400	-1.72292200	-1.72160100
C	3.63288300	-2.25635500	-0.45620000
C	2.90626000	-1.51349600	0.47698500
H	-2.81402600	0.29215300	1.77023900
H	-5.19665900	-0.30369100	1.56167600
H	-6.00958200	-1.58631300	-0.41977100
H	-4.38808200	-2.27072500	-2.19414300
H	-1.98940500	-1.66562300	-1.98537100
H	-0.20095500	-1.16366600	-0.41301200
H	-0.73287400	0.87339100	1.80568700
H	-0.87179300	2.92878800	0.69429100
H	-2.36917000	2.06367400	0.25851900
H	-1.98185600	3.63679300	-0.51435500
H	0.29001800	-2.04258100	1.79018300
H	-1.29433400	-1.50744500	2.38807800
H	0.18659300	-0.97316000	3.22025100
H	2.36289700	1.31091100	-1.38234500
H	4.47325300	-2.30733700	-2.44674900
H	3.99685200	-3.25135700	-0.19046000
H	2.70963500	-1.90837200	1.47450900
H	3.67711500	-0.02290300	-3.04355400
O	-0.43453400	2.65743600	-2.24122700
H	0.10336900	0.37463100	-1.89392800

The free energy of product N-((1S,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide is lower 6.6 kcal/mol than product' N-((1R,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide.

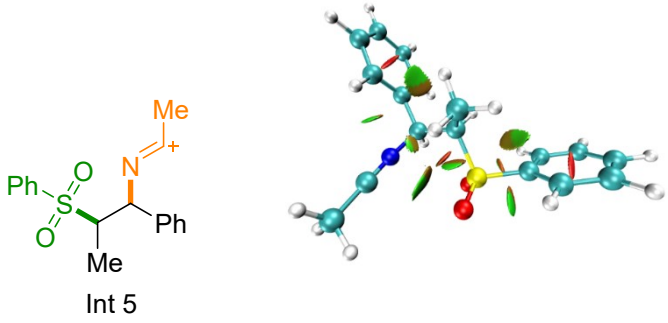


Figure S16. NCI (non-covalent interaction) plots for intermediate of Int 5 ((1S,2R)-N-ethylidyne-1-phenyl-2-(phenylsulfonyl)propan-1-aminium)).
Blue, green and red regions represent strong electrostatic interactions, more dispersive attraction and repulsion interactions.

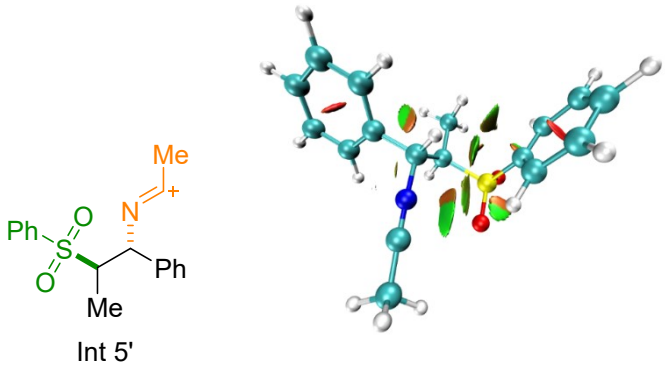


Figure S17. NCI (non-covalent interaction) plots for intermediate of Int 5' ((1R,2R)-N-ethylidyne-1-phenyl-2-(phenylsulfonyl)propan-1-aminium)).
Blue, green and red regions represent strong electrostatic interactions, more dispersive attraction and repulsion interactions.

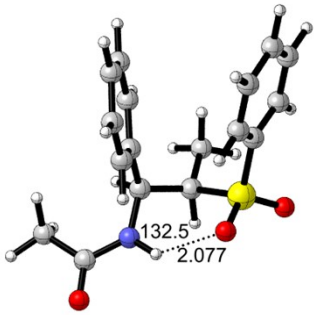


Figure S18. Ball-and-stick models of N-((1S,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide

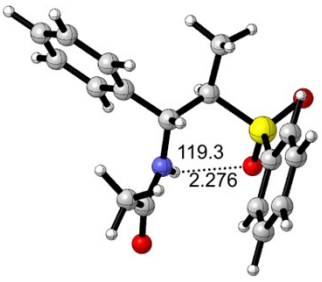
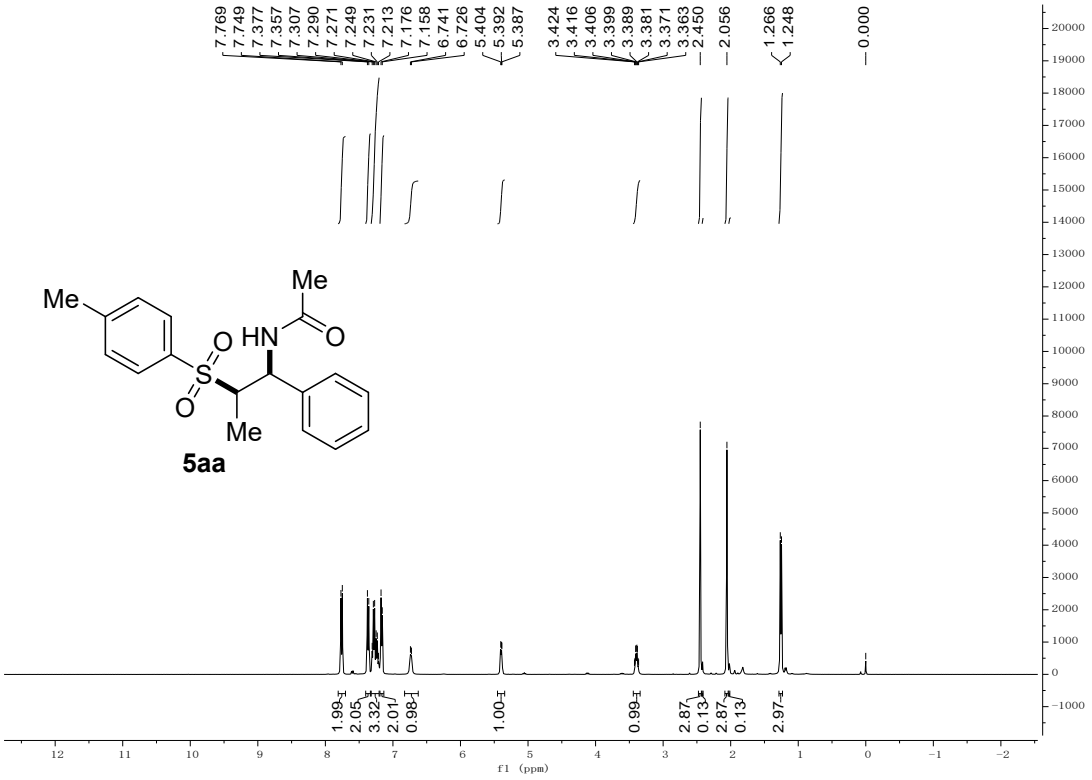


Figure S19. Ball-and-stick models of N-((1R,2R)-1-phenyl-2-(phenylsulfonyl)propyl)acetamide

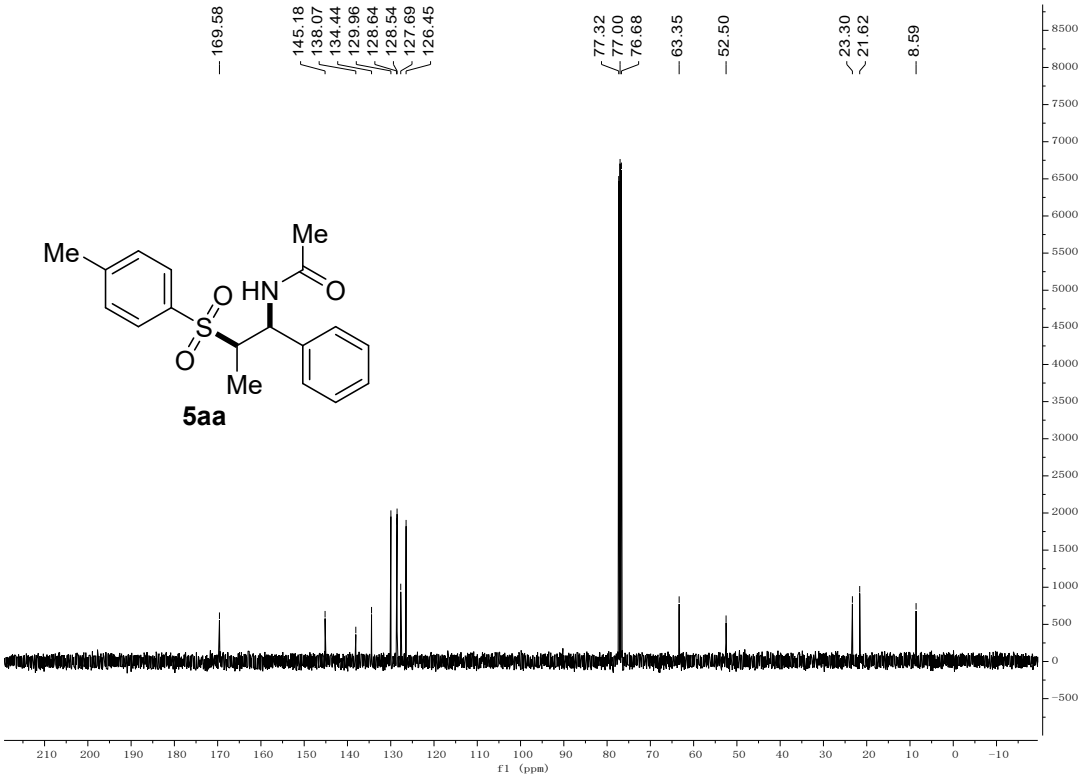
11. NMR Spectra of Compounds

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

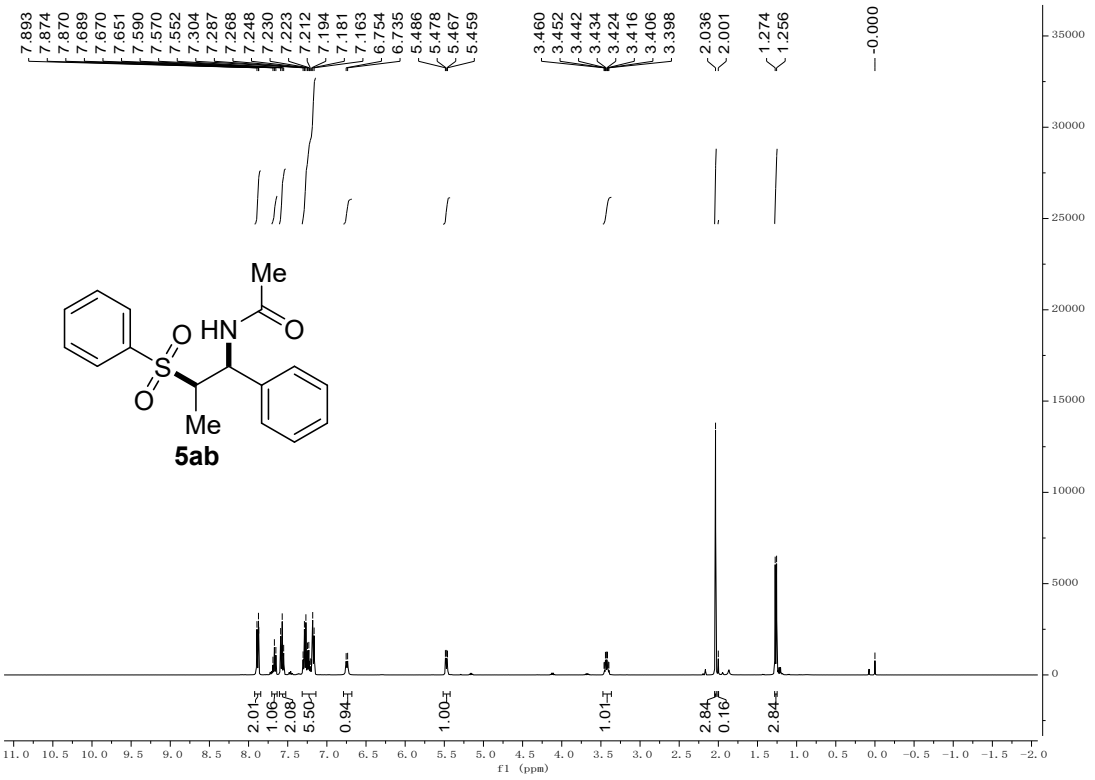
^{1}H NMR of **5aa** in $CDCl_3$



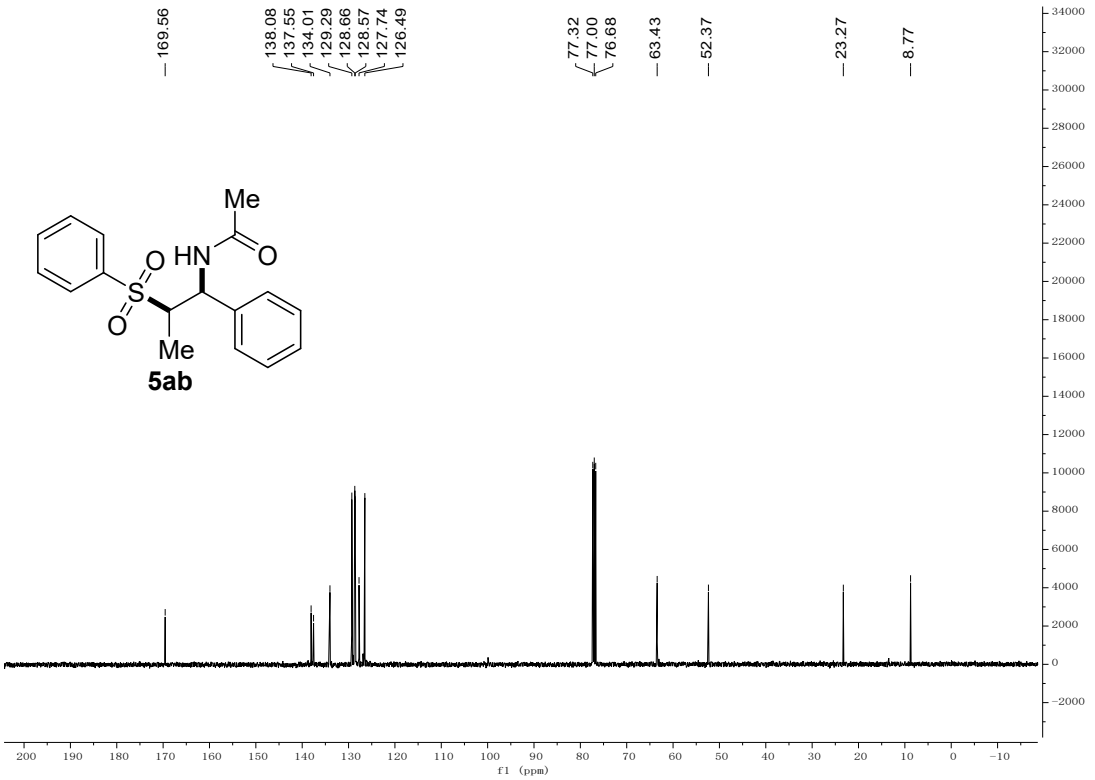
^{13}C NMR of **5aa** in $CDCl_3$



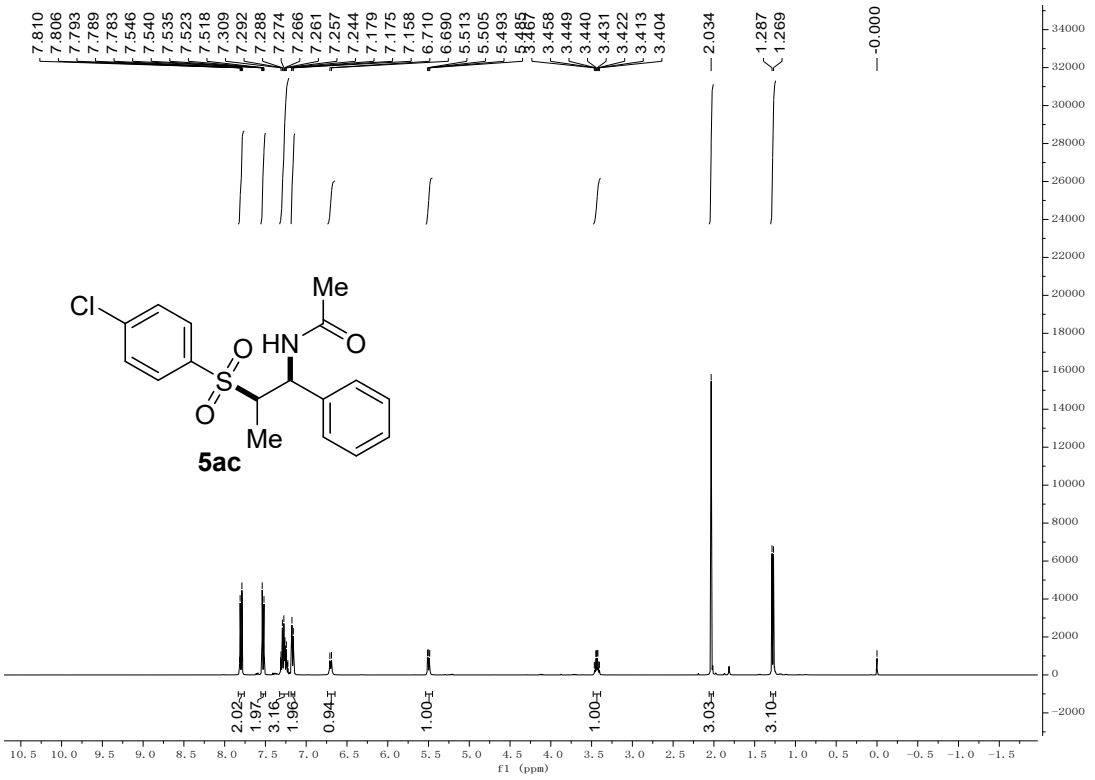
^{1}H NMR of **5ab** in $CDCl_3$



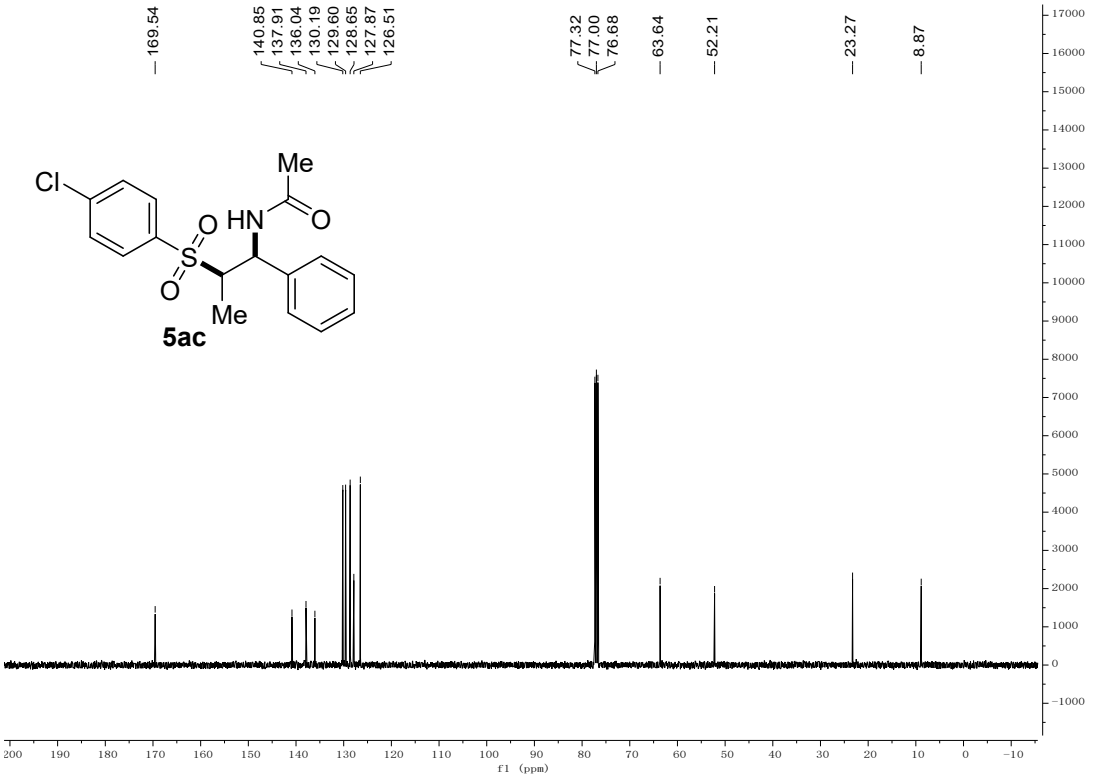
^{13}C NMR of **5ab** in $CDCl_3$



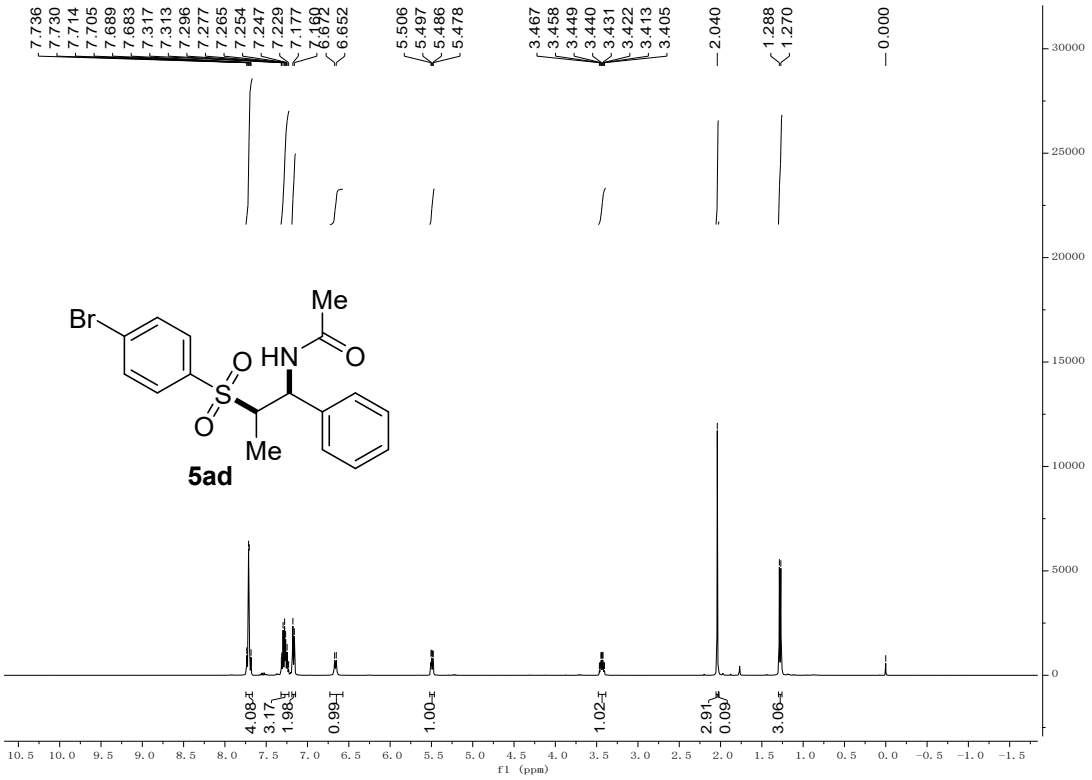
^{1}H NMR of **5ac** in $CDCl_3$



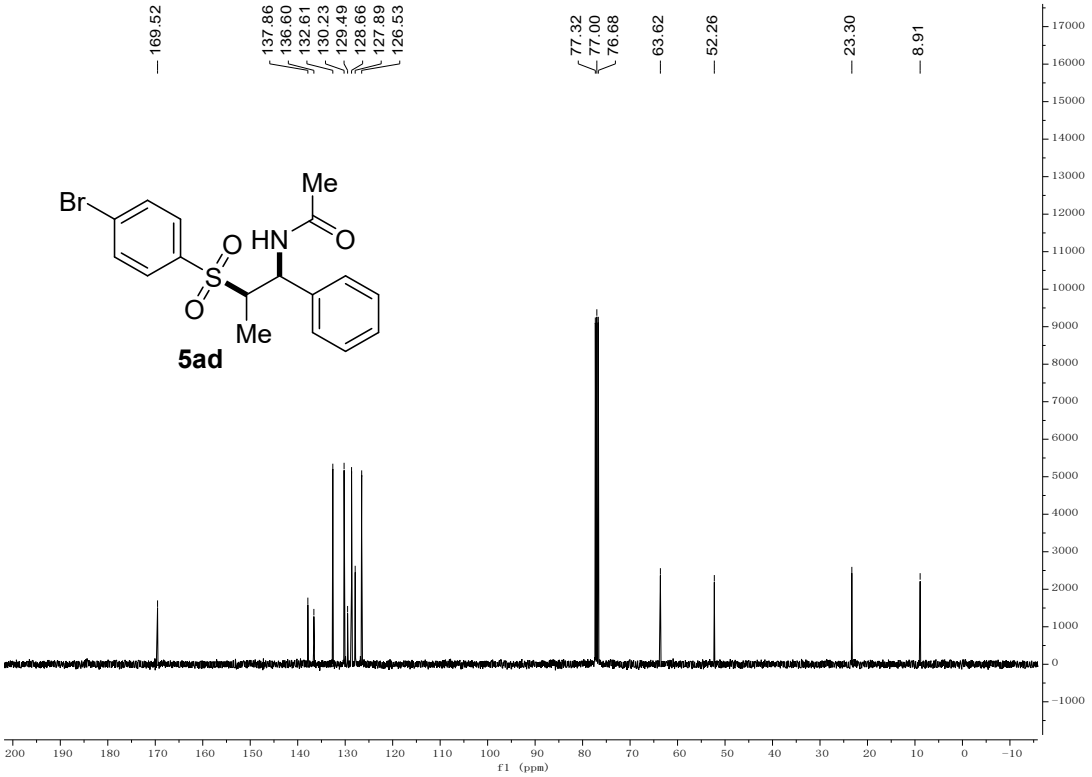
^{13}C NMR of **5ac** in $CDCl_3$



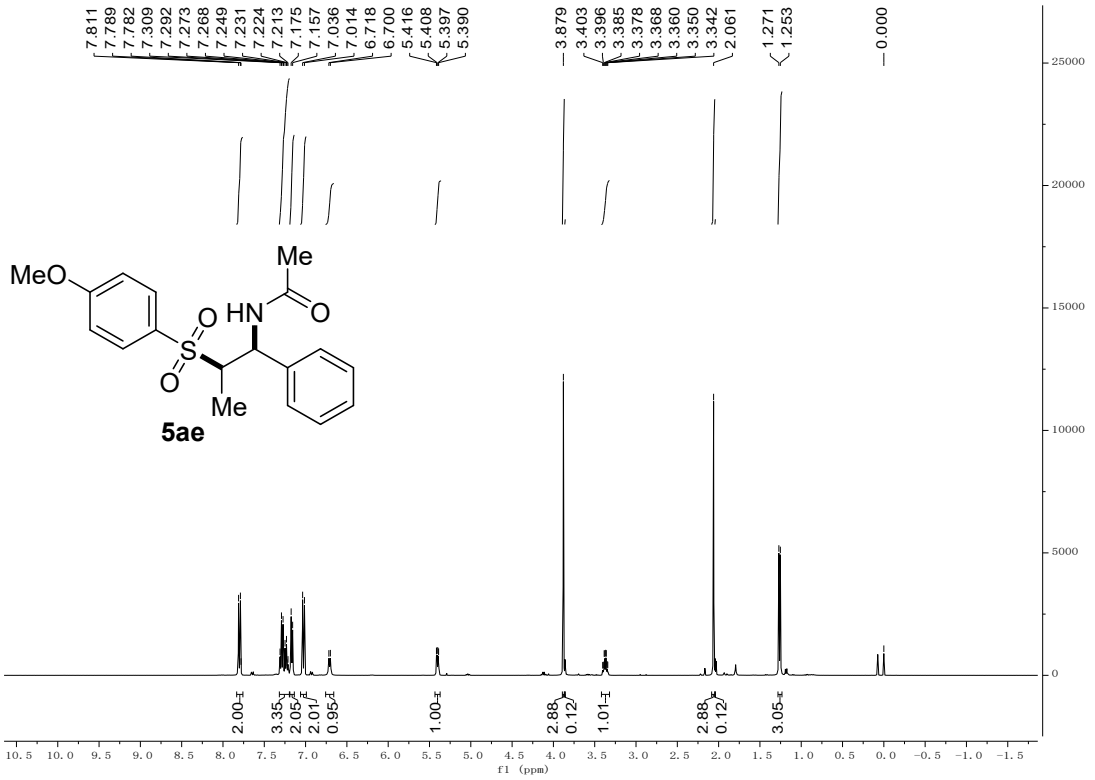
^{1}H NMR of **5ad** in $CDCl_3$



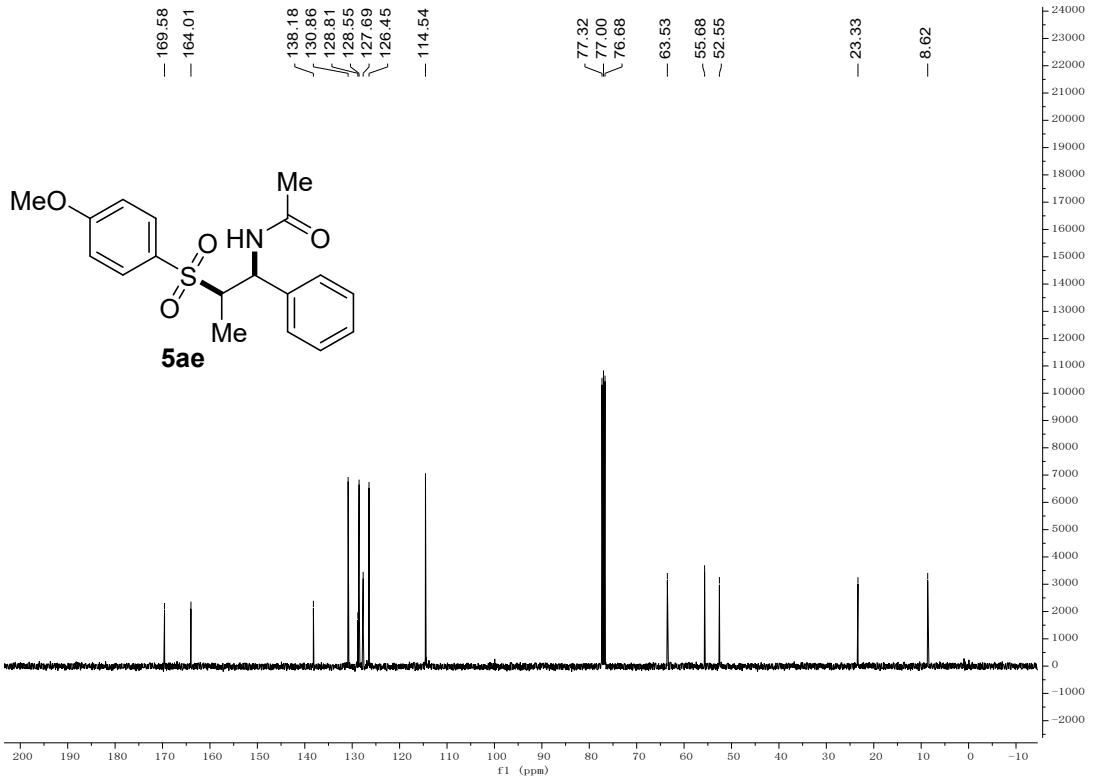
^{13}C NMR of **5ad** in $CDCl_3$



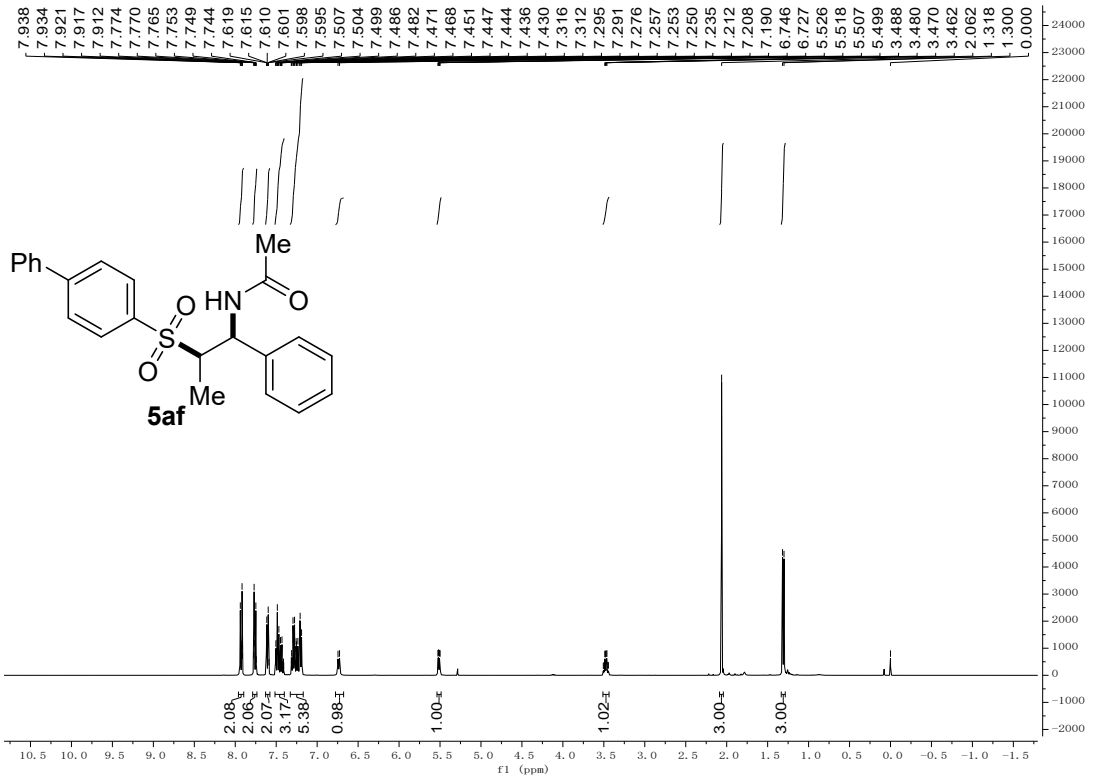
^{1}H NMR of **5ae** in $CDCl_3$



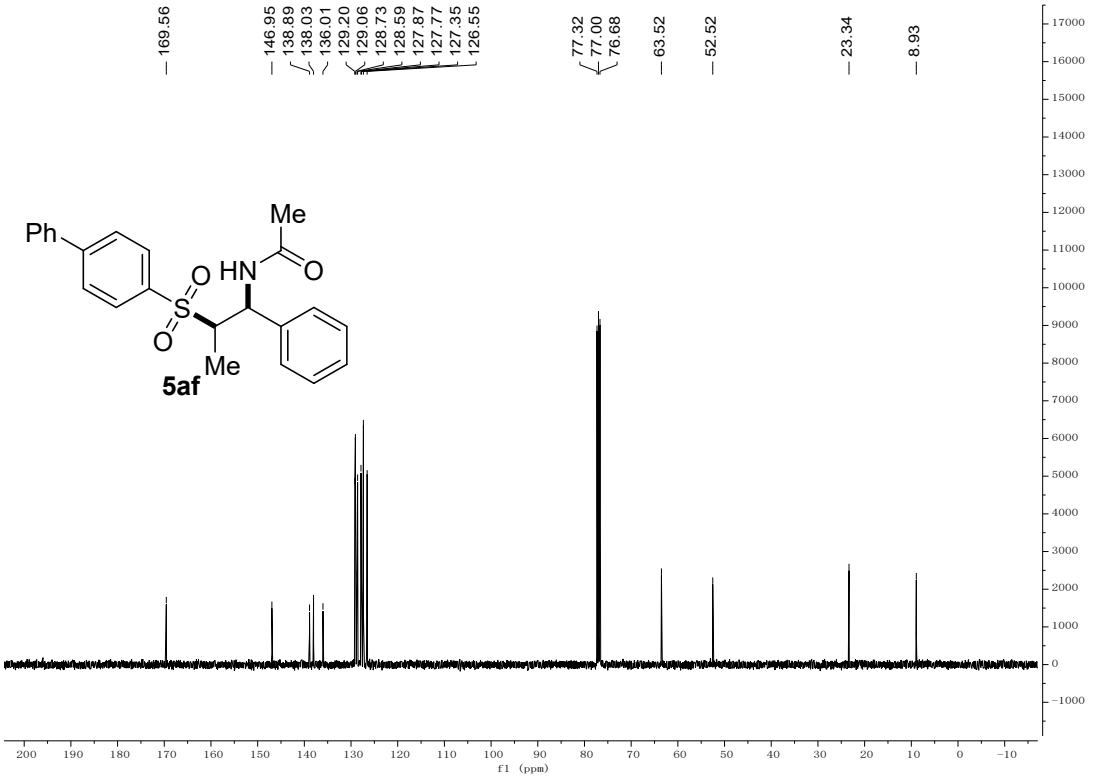
^{13}C NMR of **5ae** in $CDCl_3$



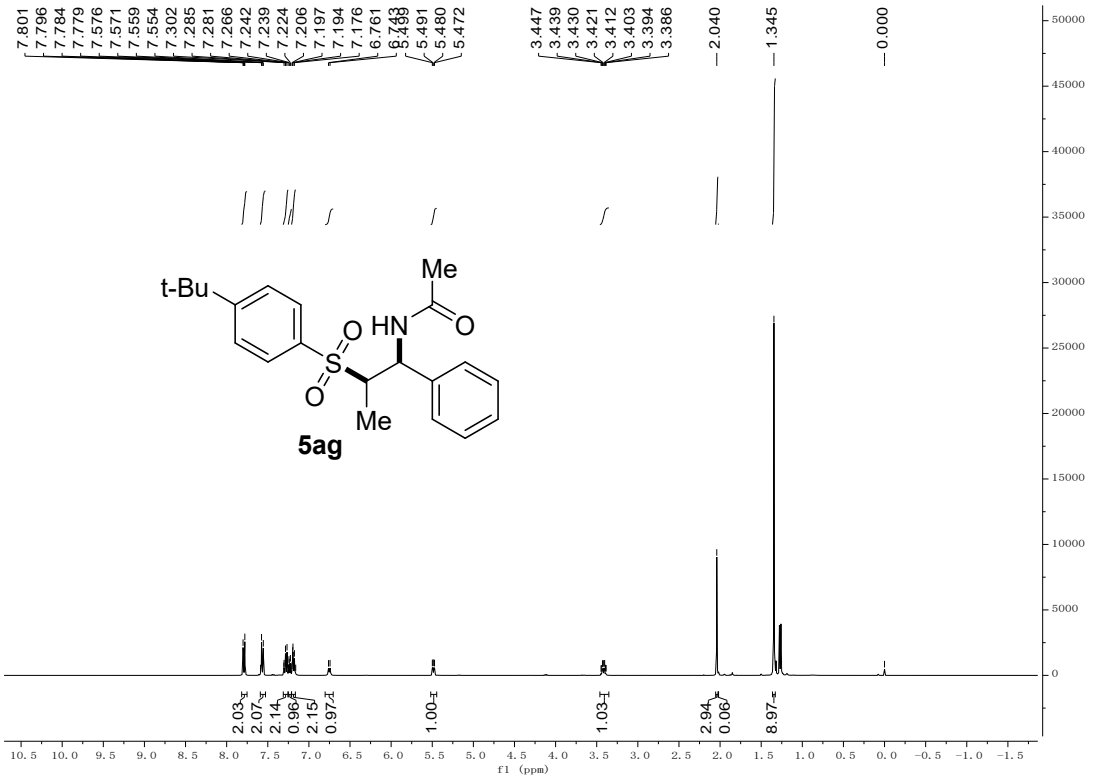
^{1}H NMR of **5af** in $CDCl_3$



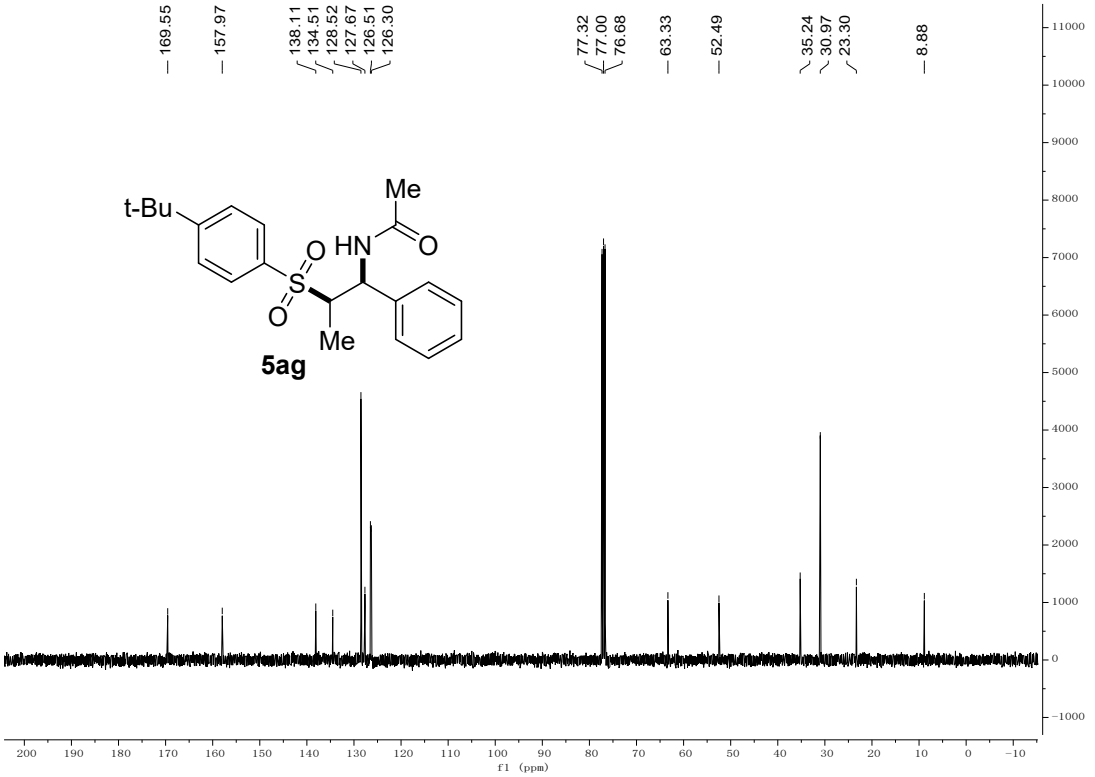
^{13}C NMR of **5af** in $CDCl_3$



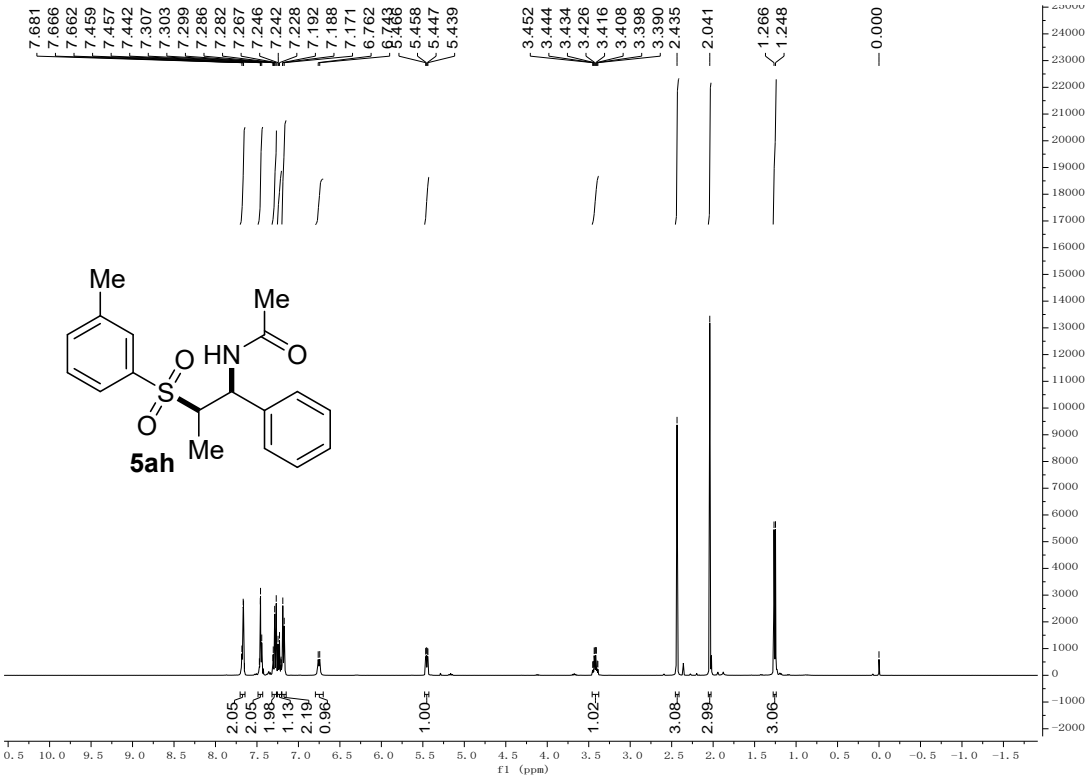
^{1}H NMR of **5ag** in $CDCl_3$



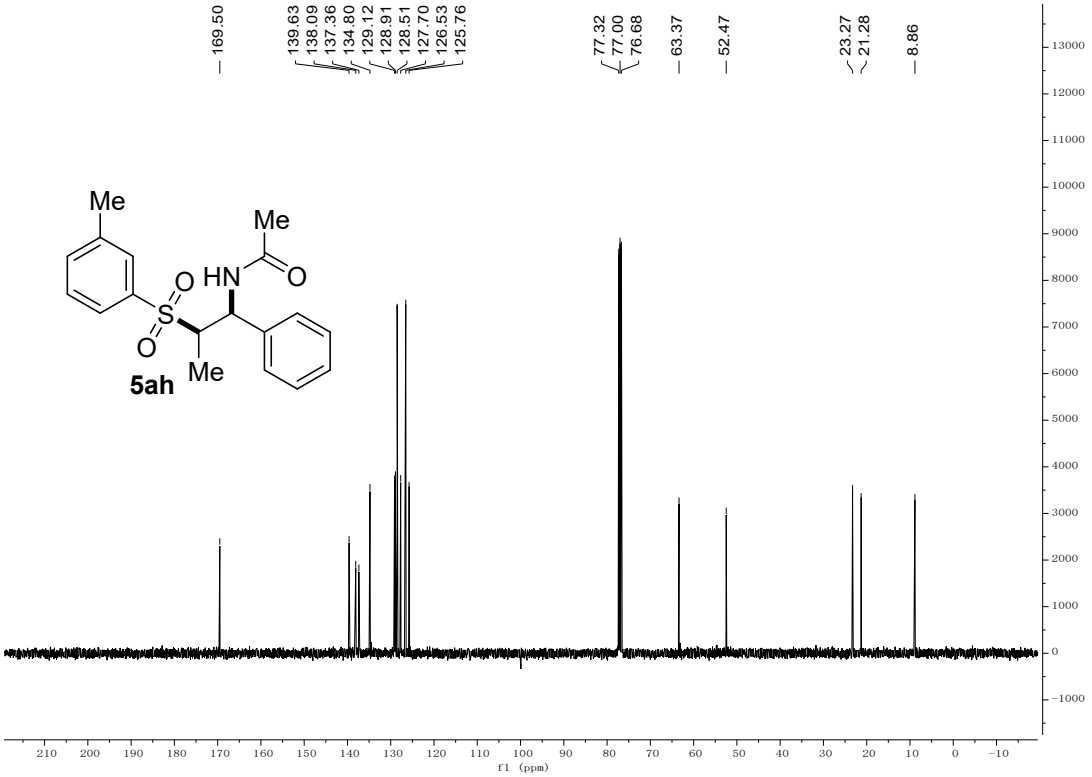
^{13}C NMR of **5ag** in $CDCl_3$



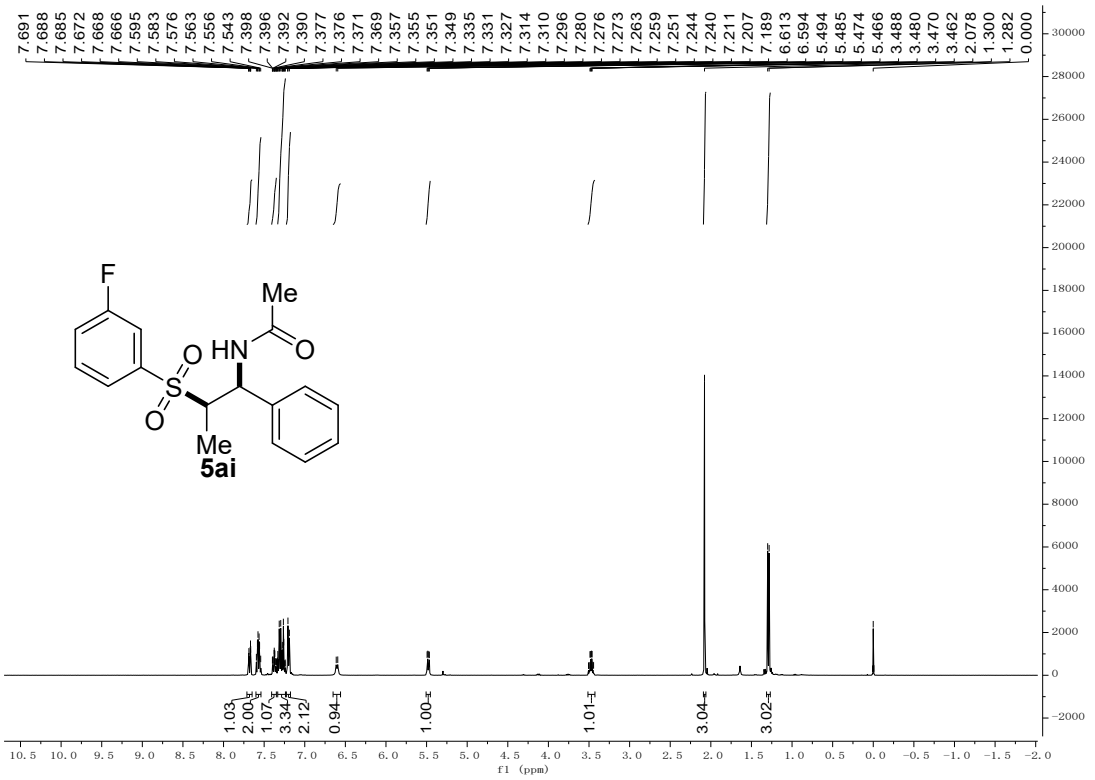
^{1}H NMR of **5ah** in $CDCl_3$



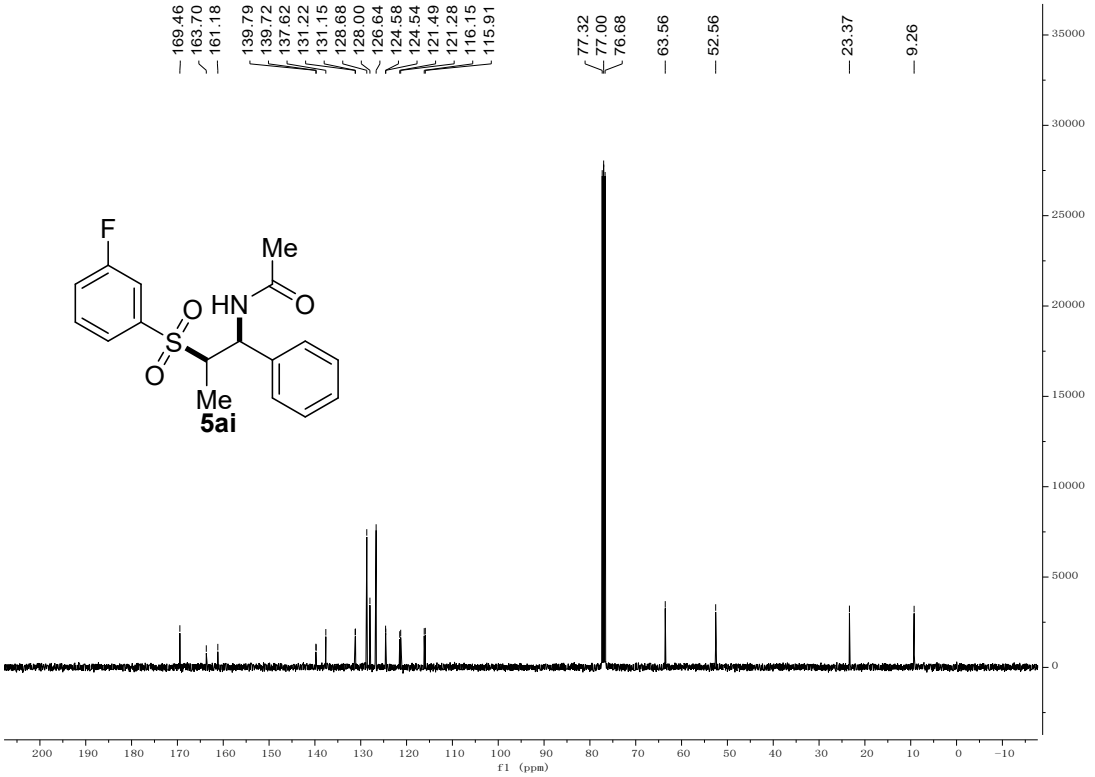
^{13}C NMR of **5ah** in $CDCl_3$



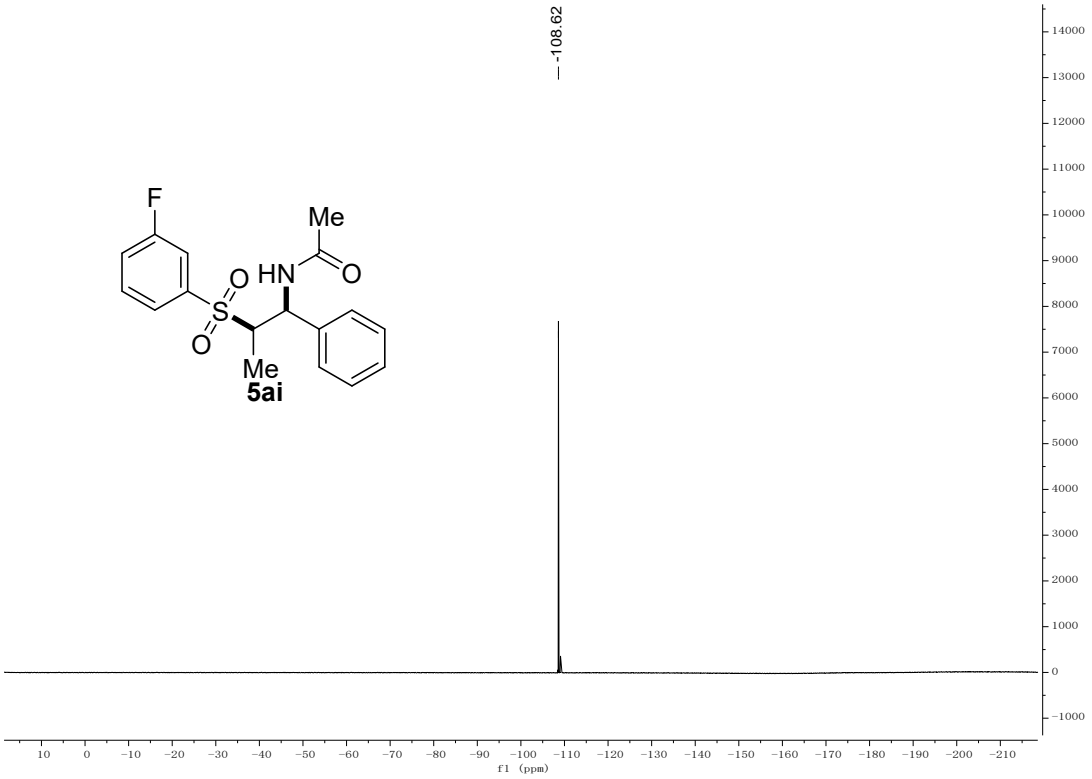
^{1}H NMR of **5ai** in $CDCl_3$



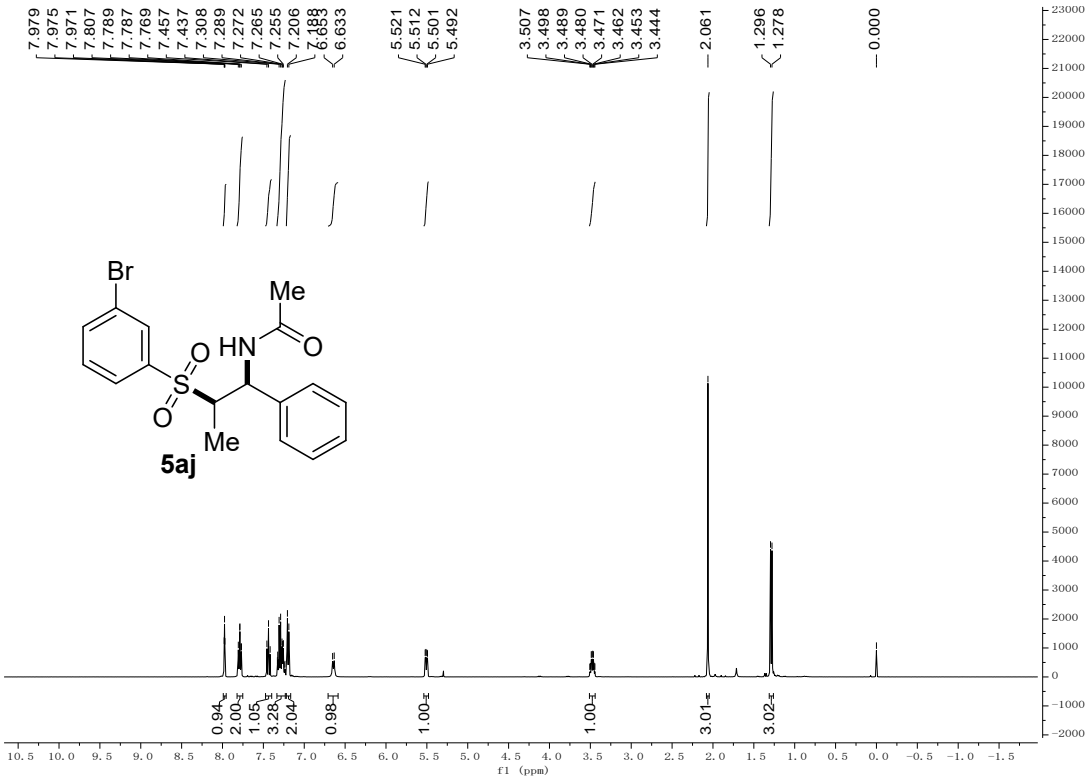
^{13}C NMR of **5ai** in $CDCl_3$



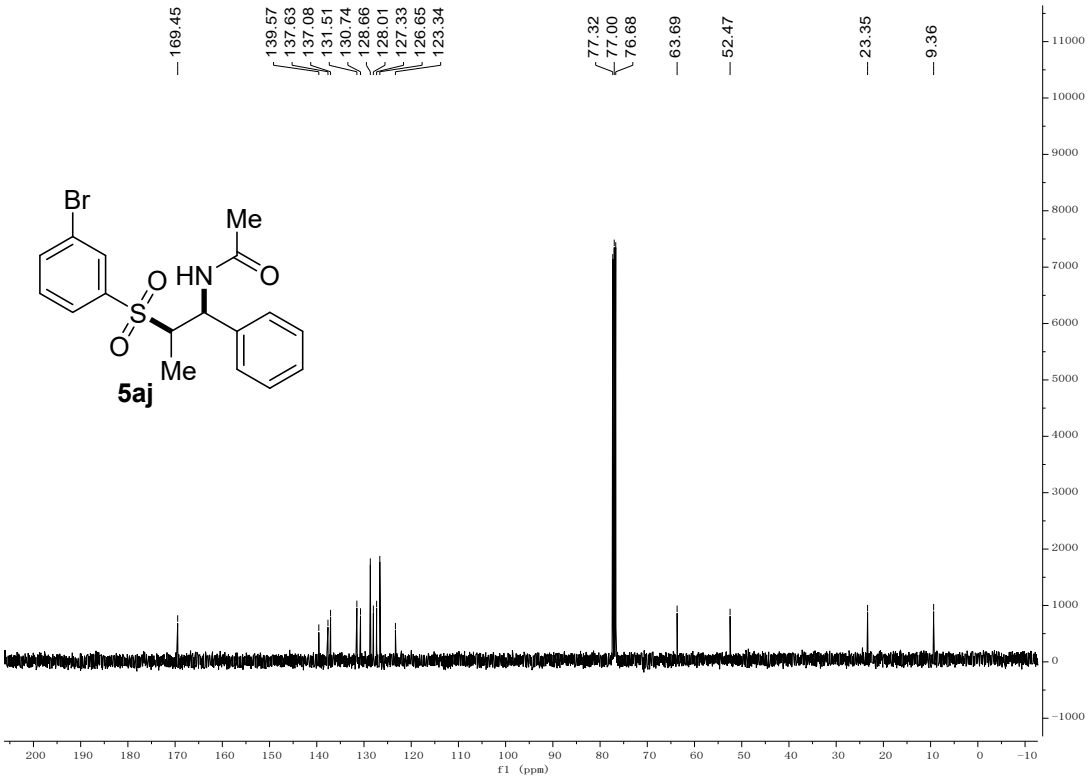
^{19}F NMR spectra of **5ai** in $CDCl_3$



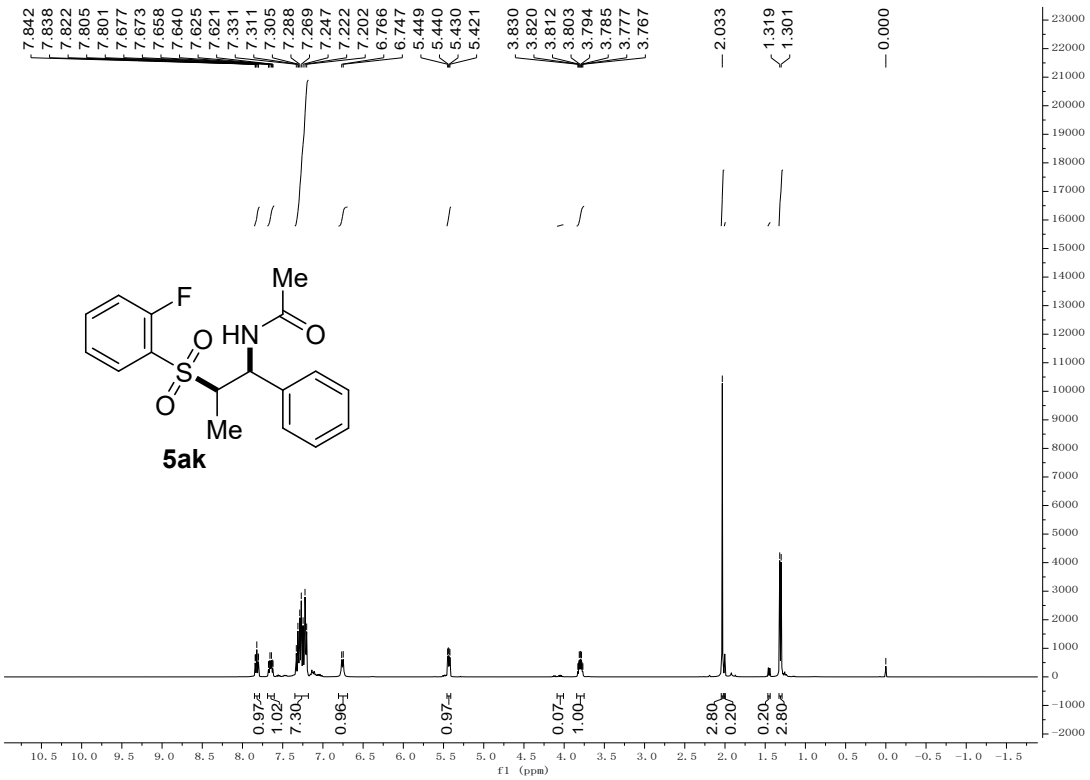
^{1}H NMR of **5aj** in $CDCl_3$



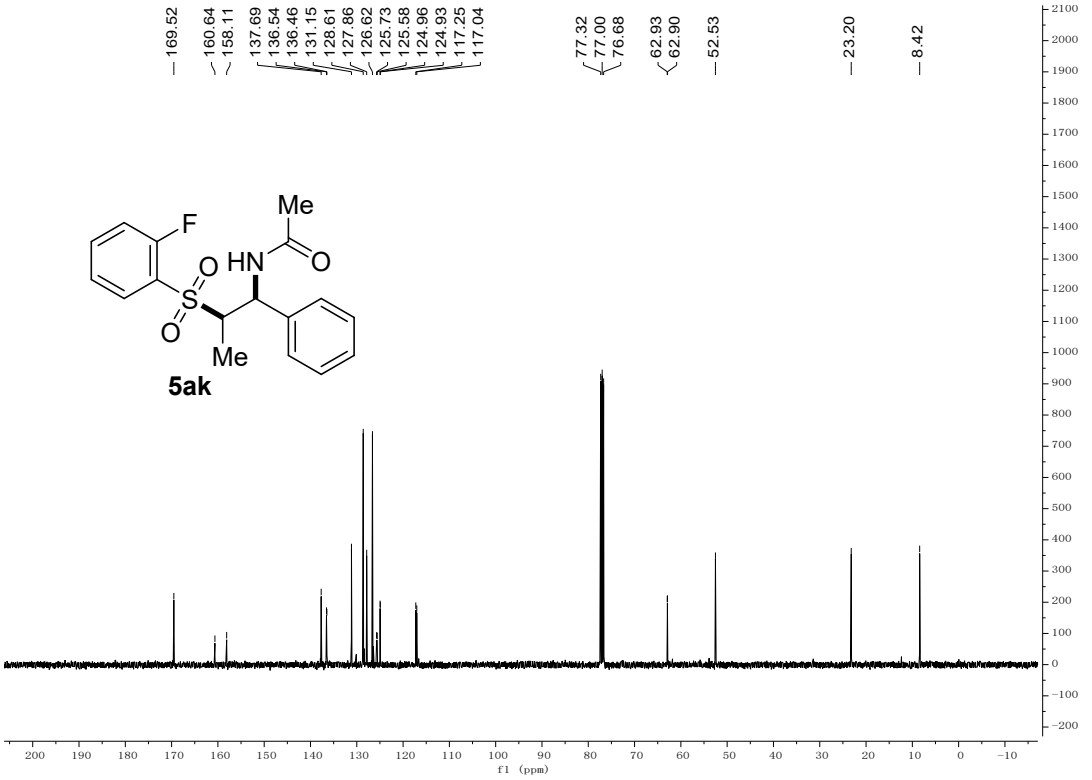
^{13}C NMR of **5aj** in $CDCl_3$



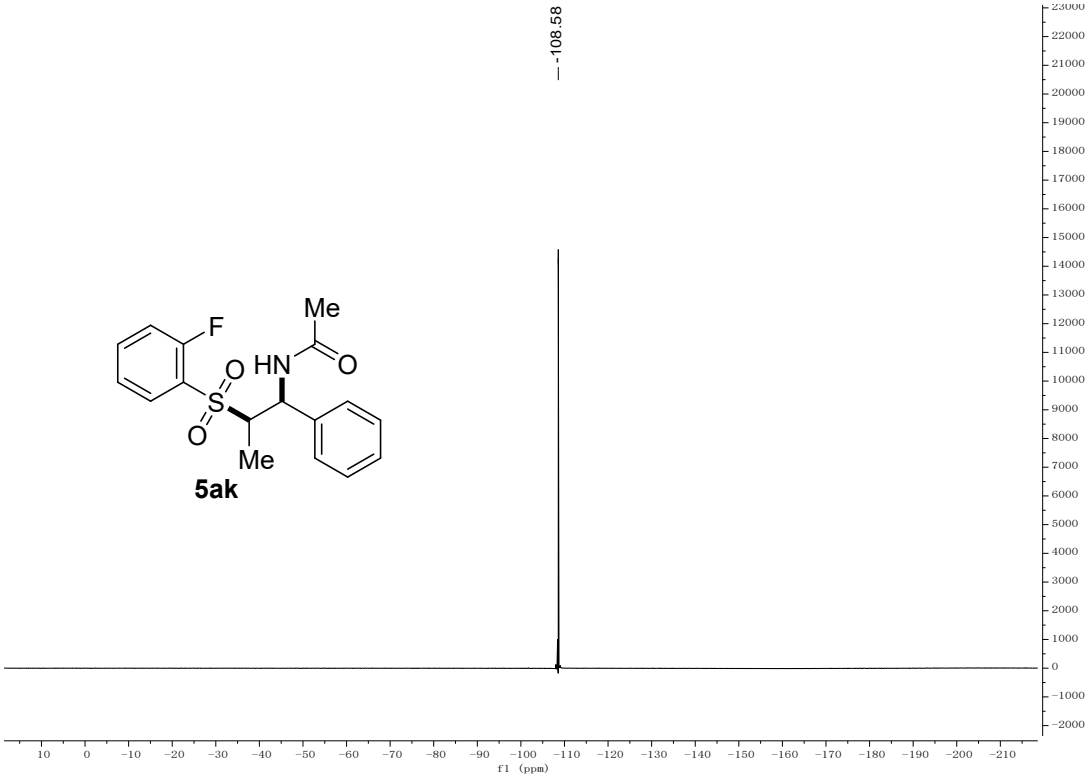
^{1}H NMR of **5ak** in $CDCl_3$



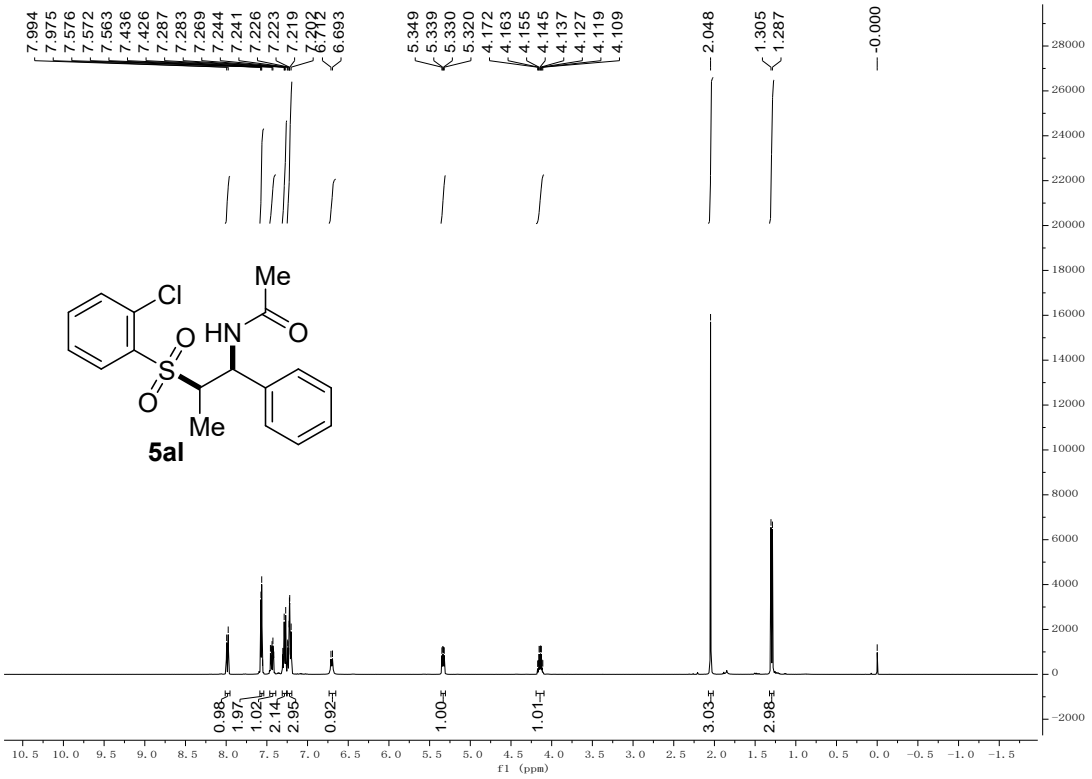
^{13}C NMR of **5ak** in $CDCl_3$



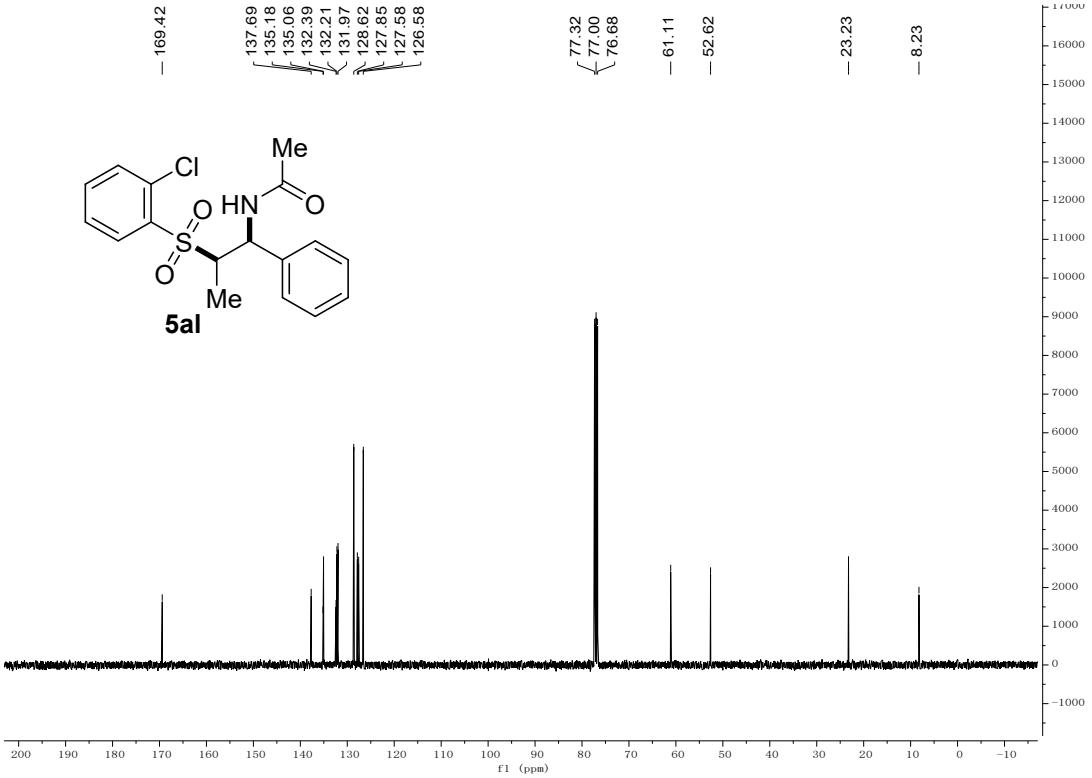
^{19}F NMR spectra of **5ak** in $CDCl_3$



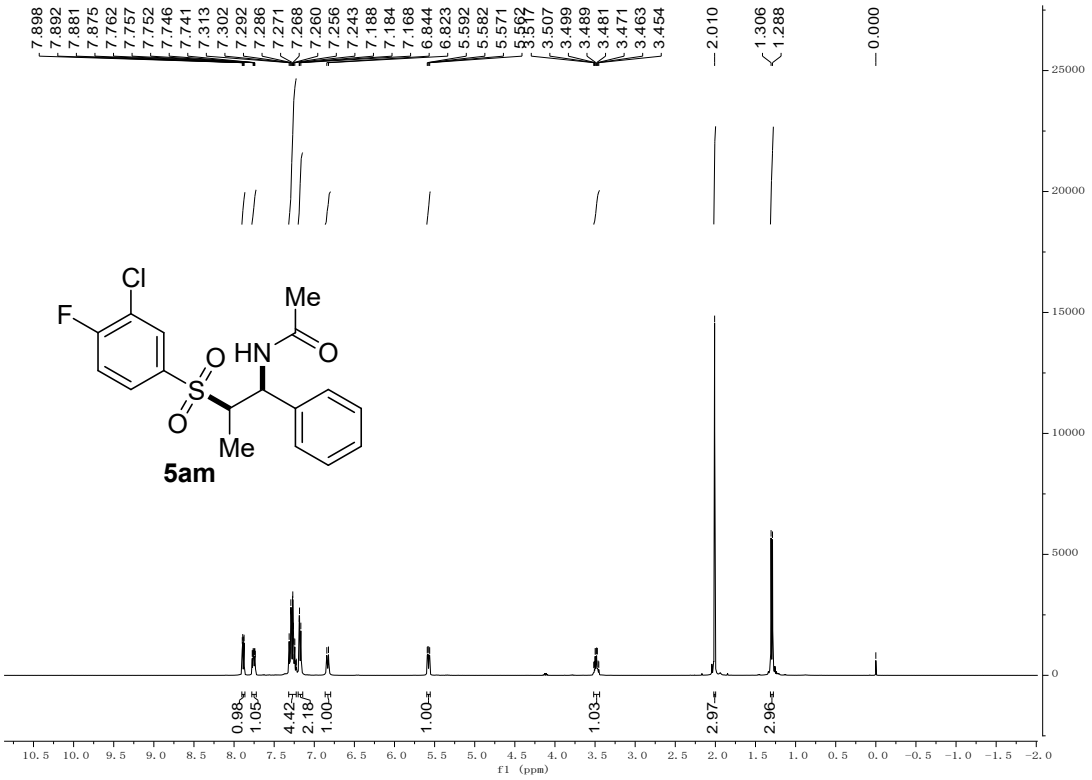
^{1}H NMR of **5al** in $CDCl_3$



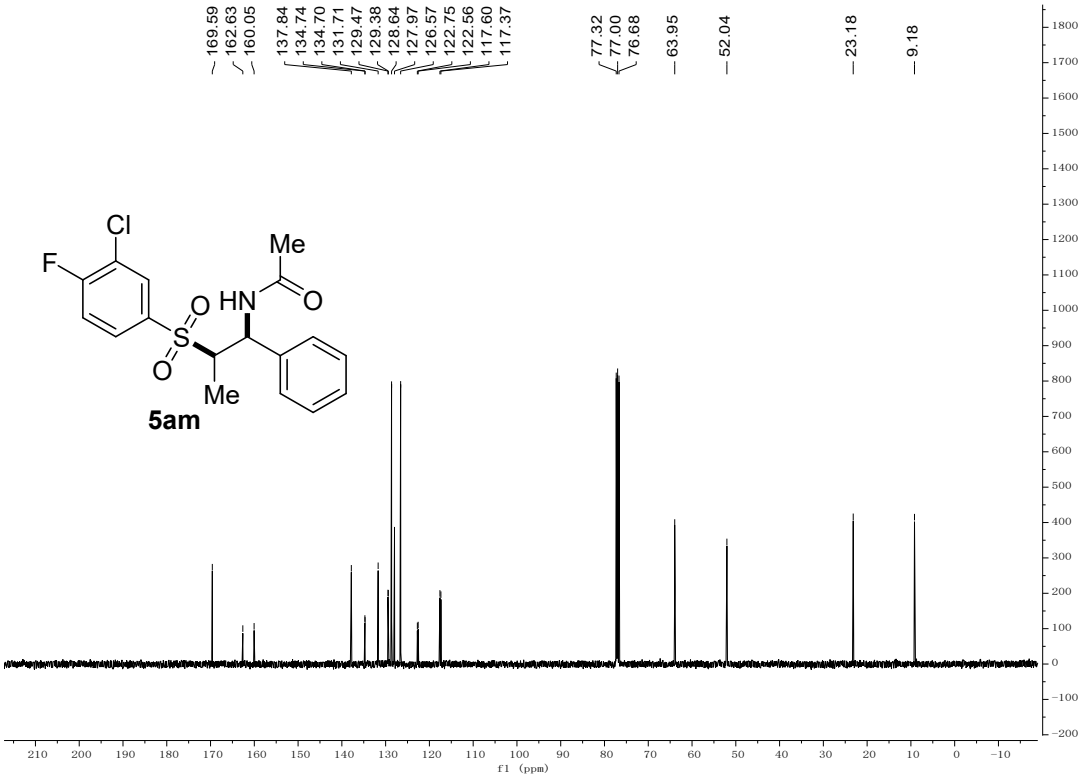
^{13}C NMR of **5al** in $CDCl_3$



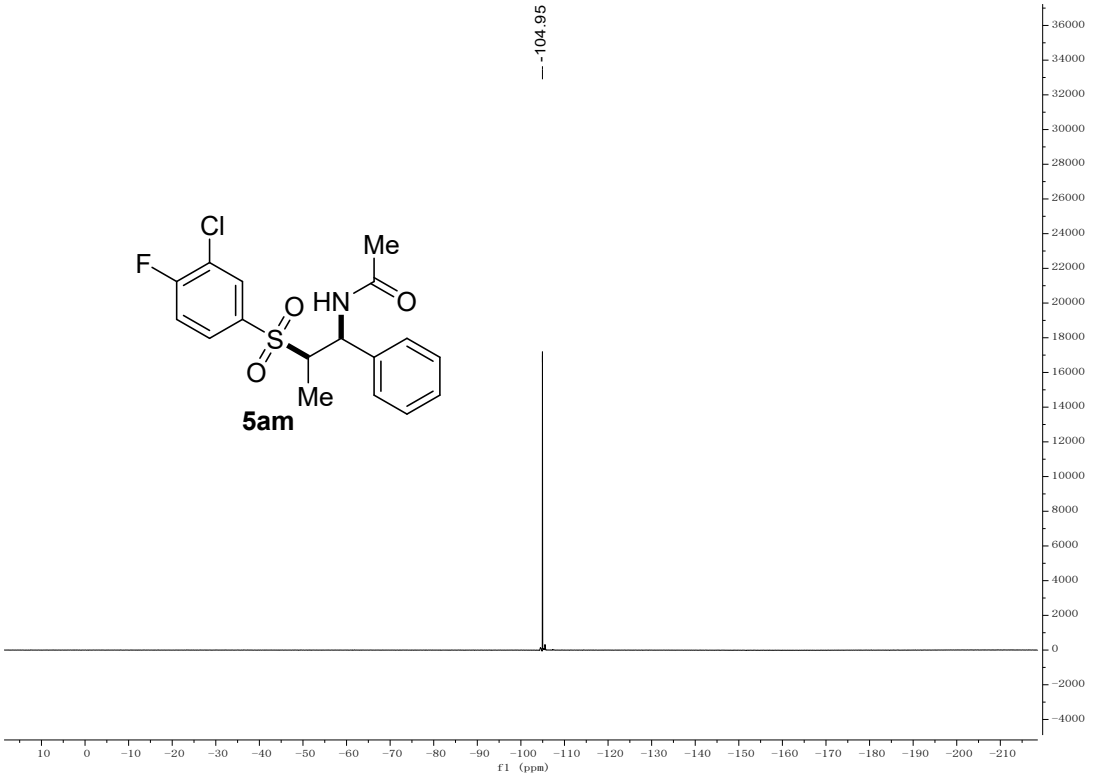
^{1}H NMR of **5am** in $CDCl_3$



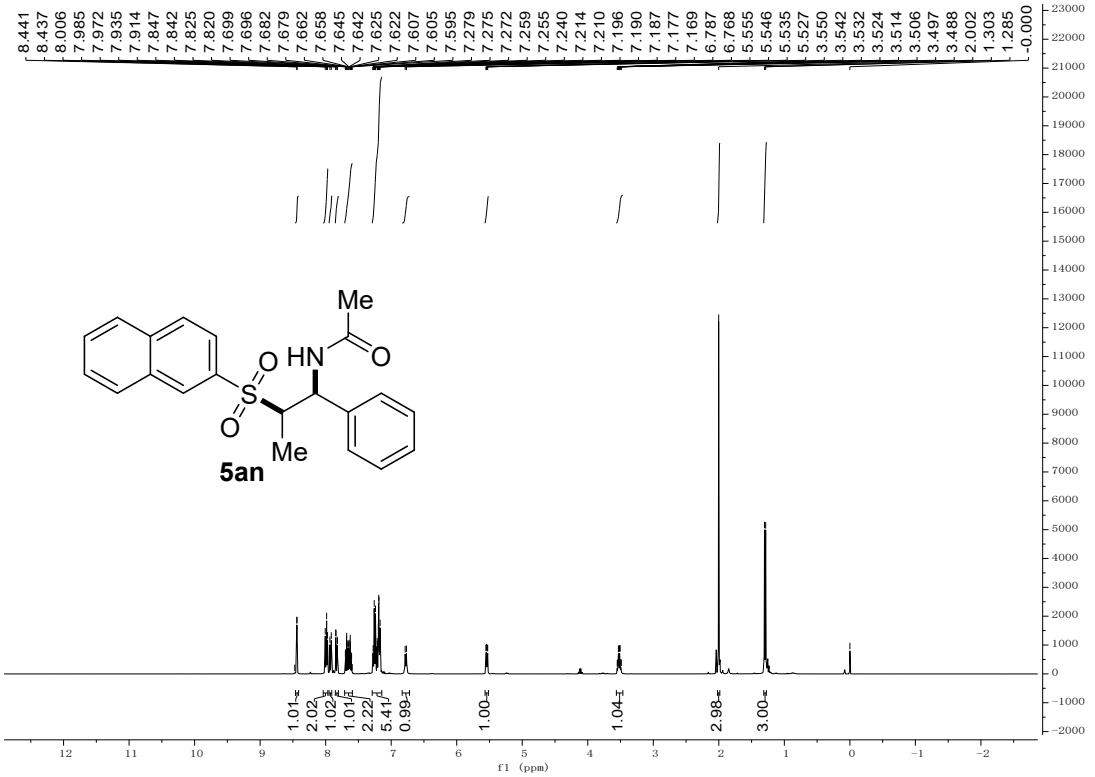
^{13}C NMR of **5am** in $CDCl_3$



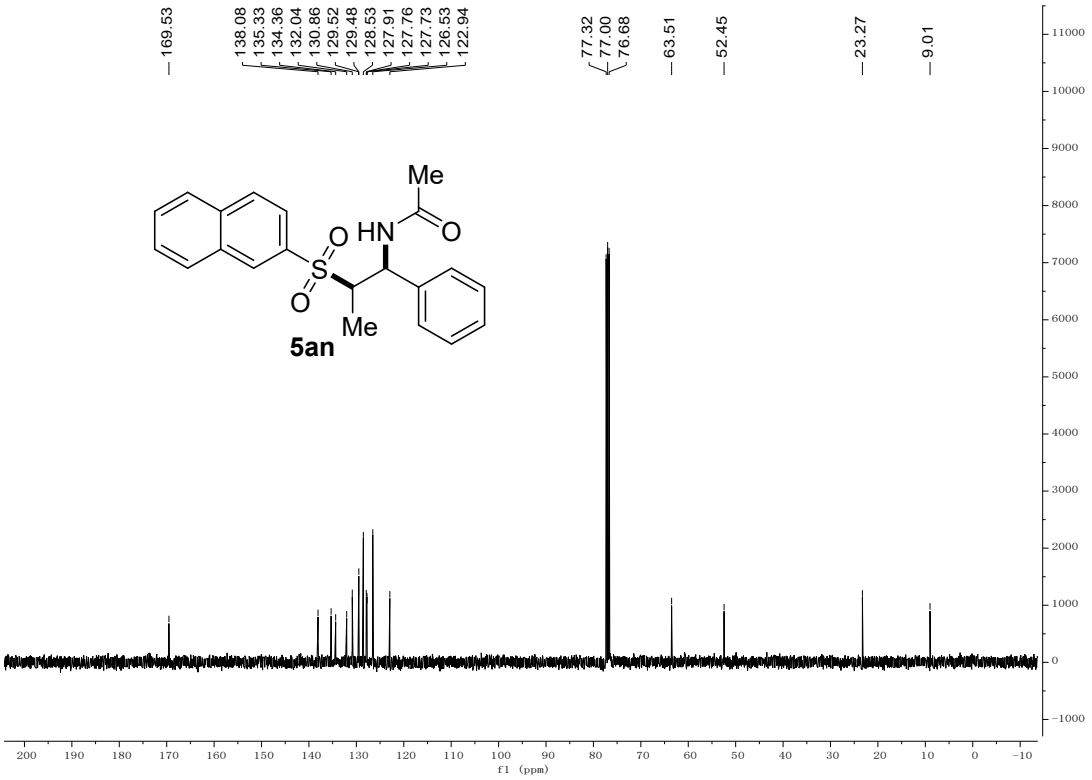
^{19}F NMR spectra of **5ak** in $CDCl_3$



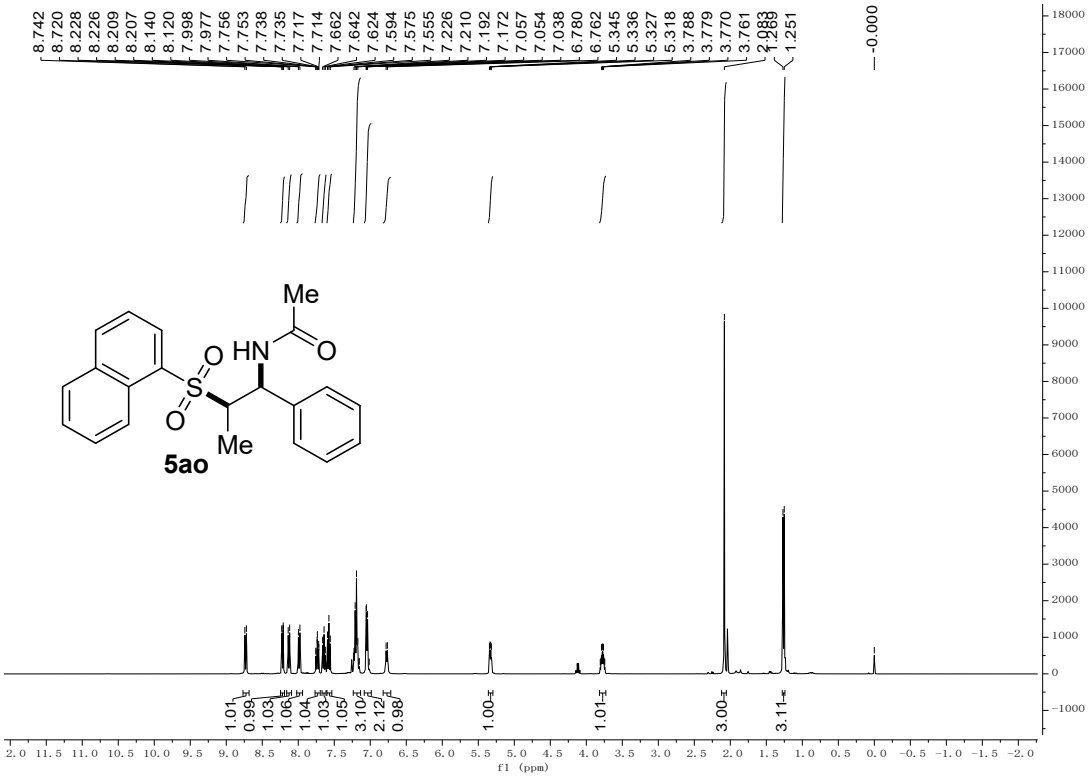
^{1}H NMR of **5an** in $CDCl_3$



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



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



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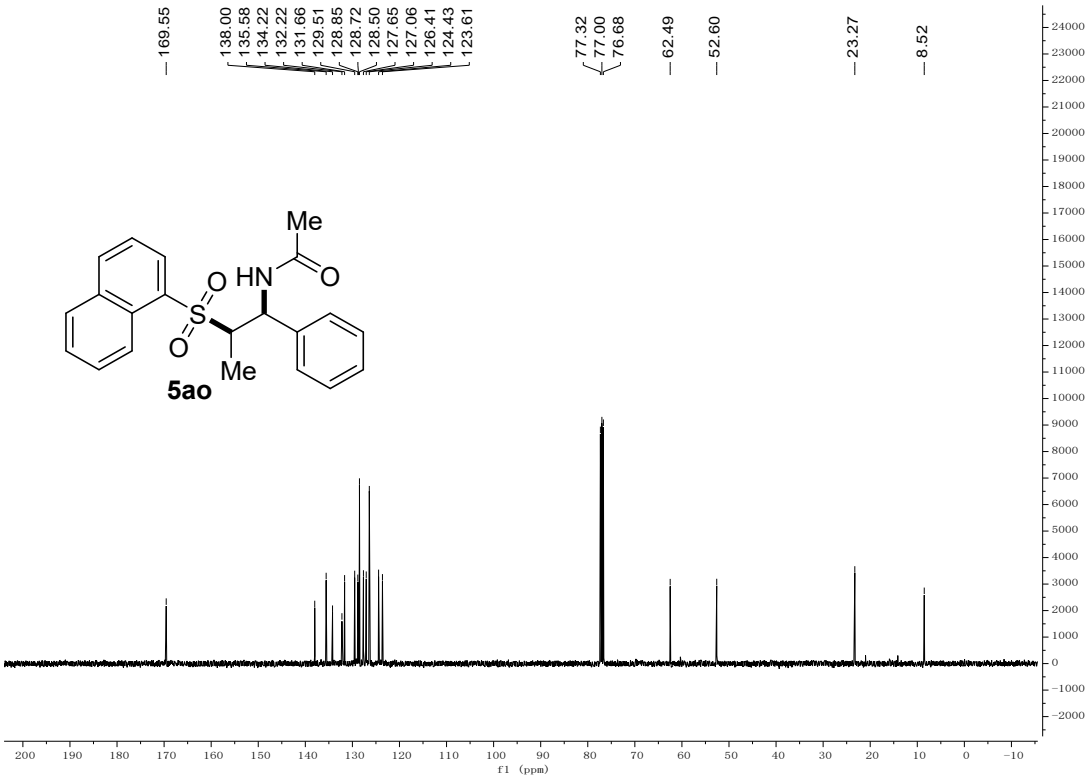

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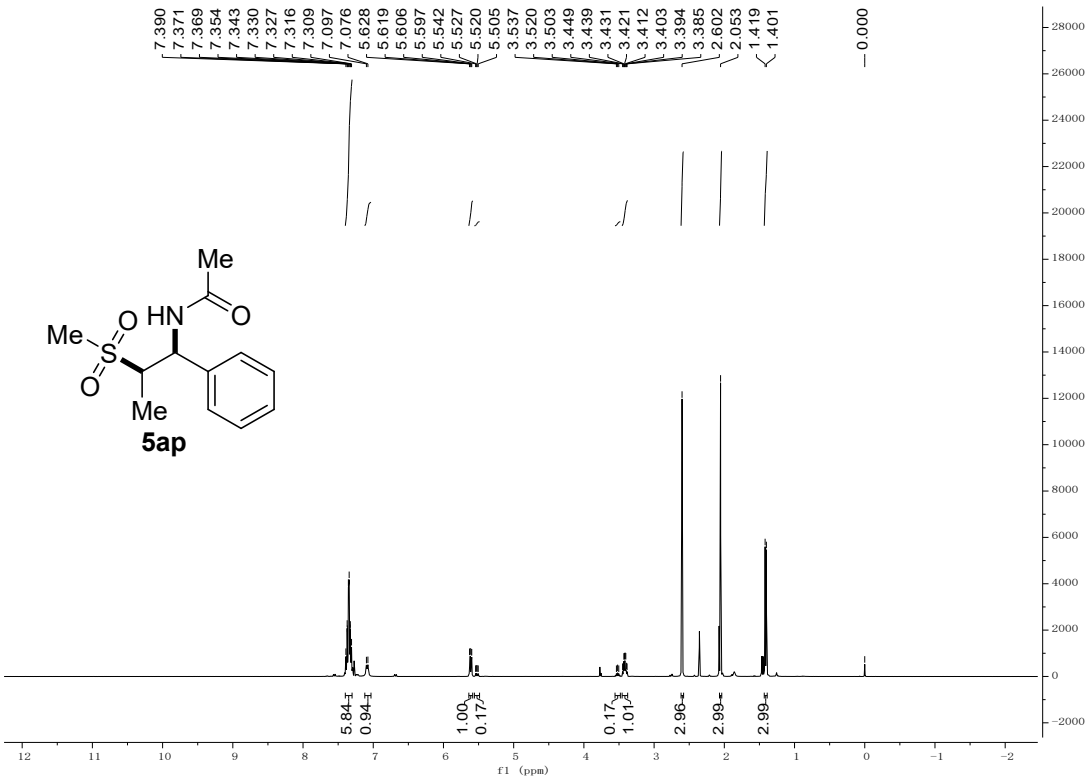
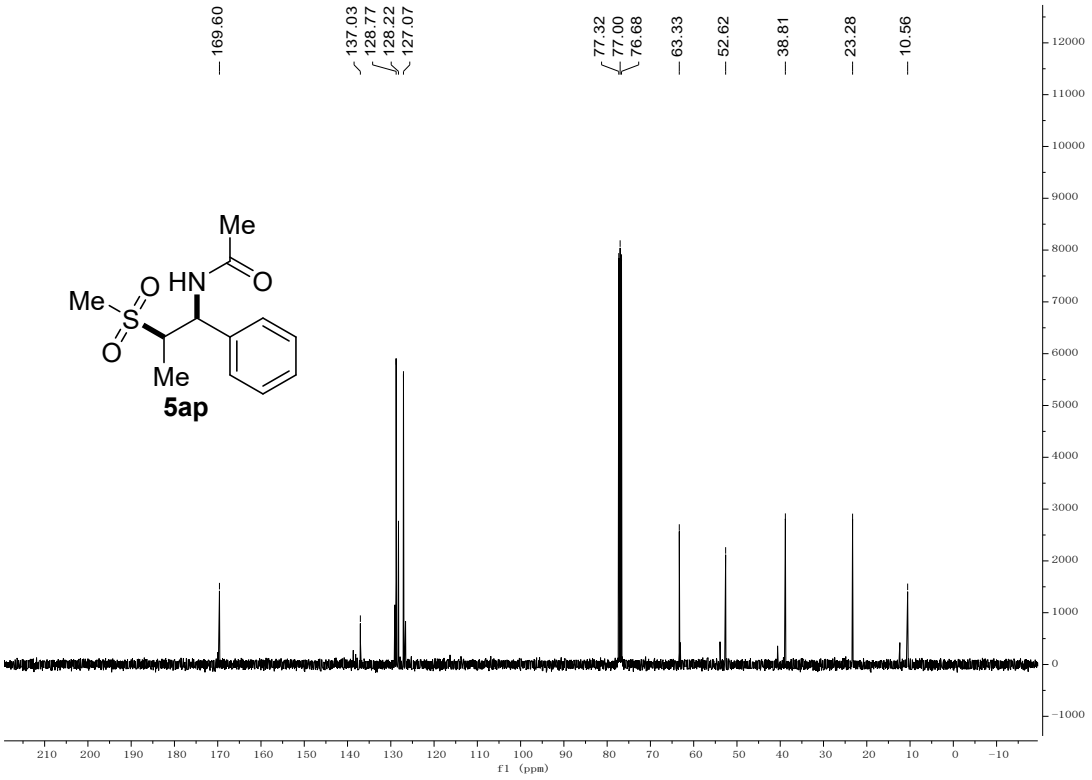
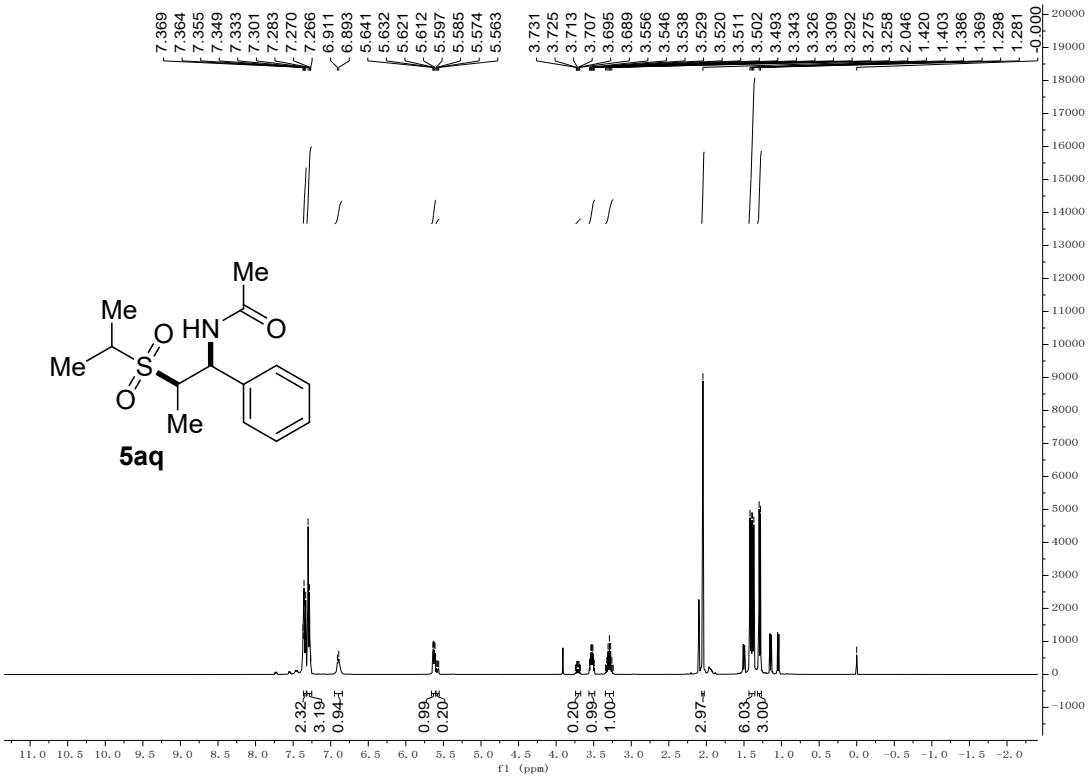


^{13}C NMR of **5ap** in $CDCl_3$



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



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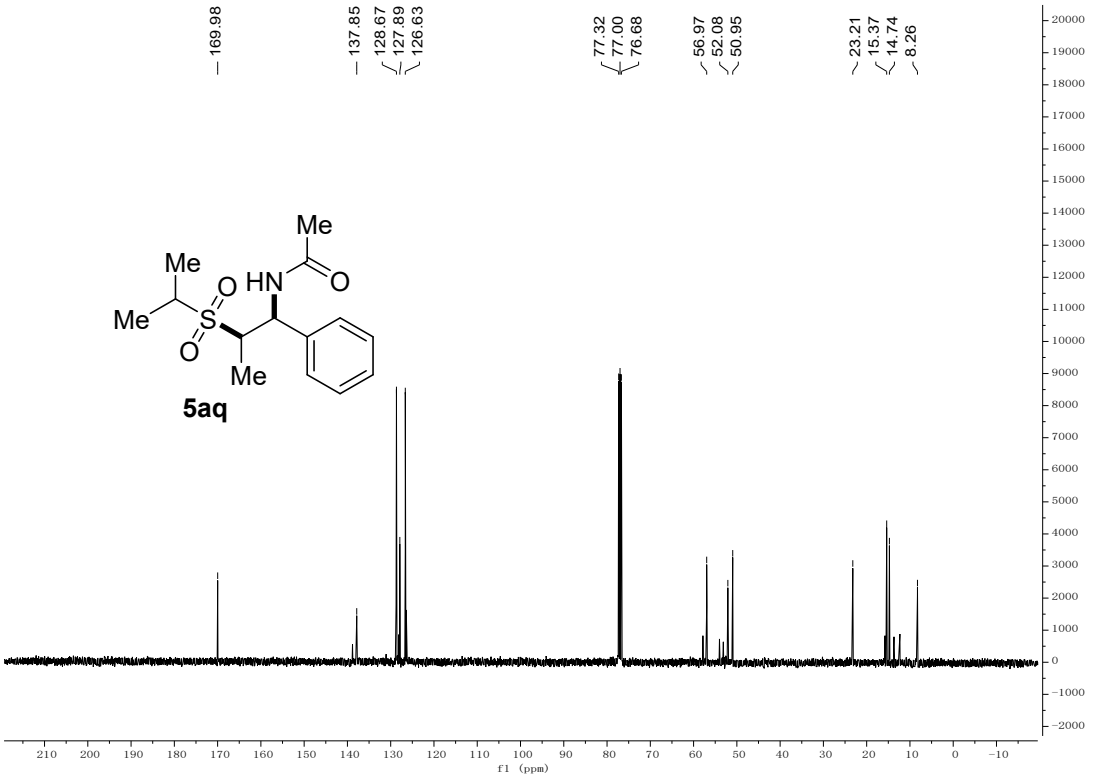
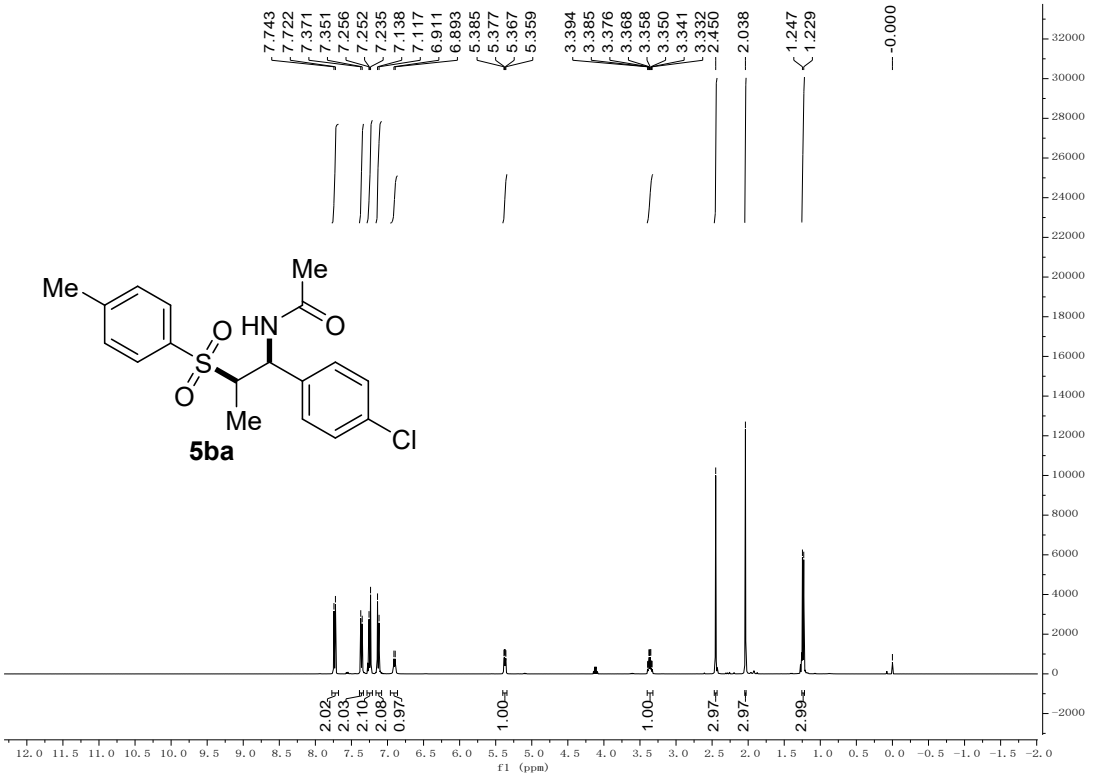
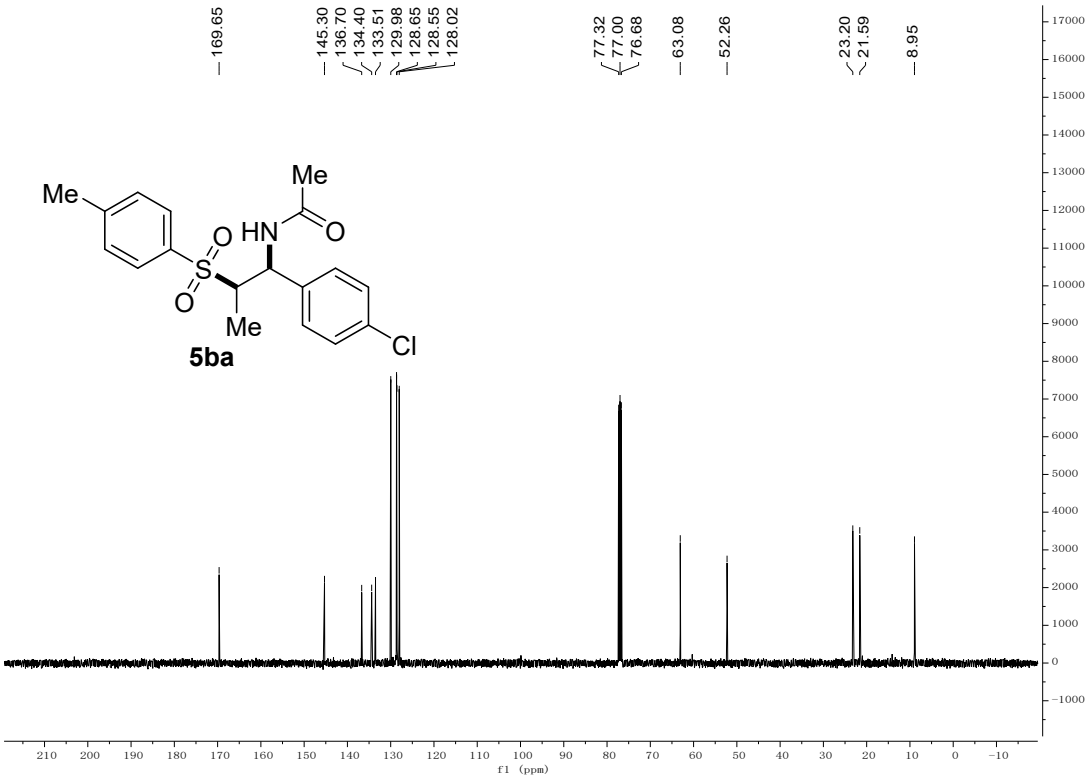


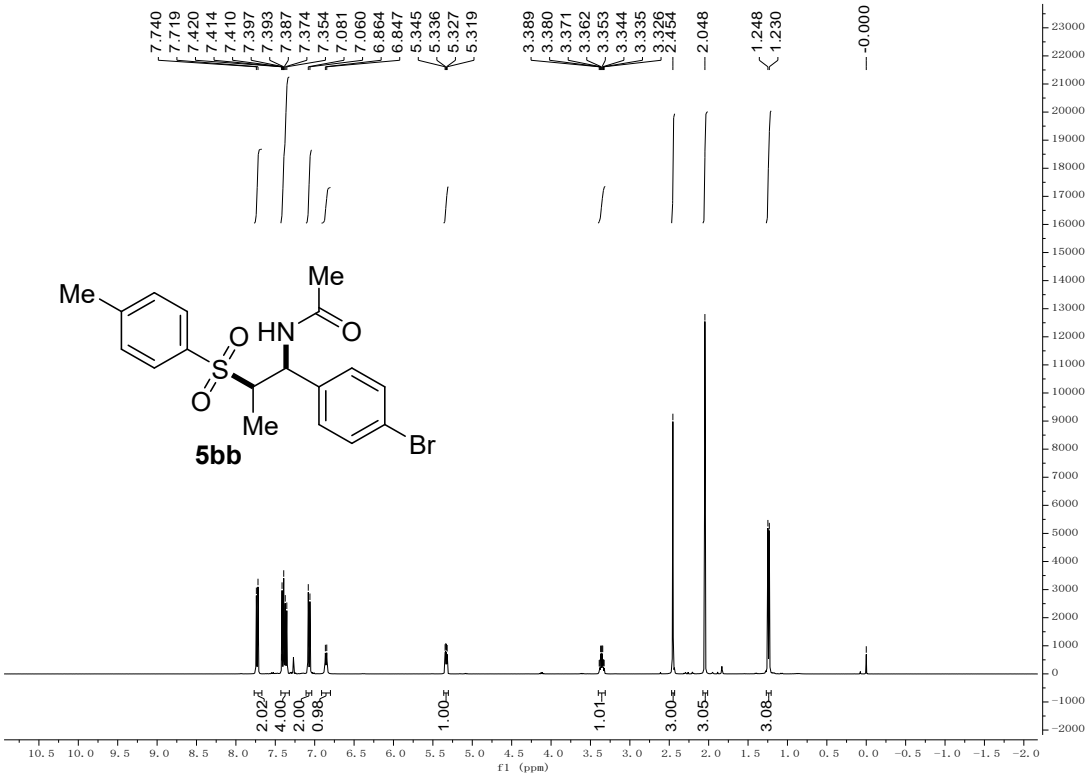
^{1}H NMR of **5ba** in $CDCl_3$



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



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



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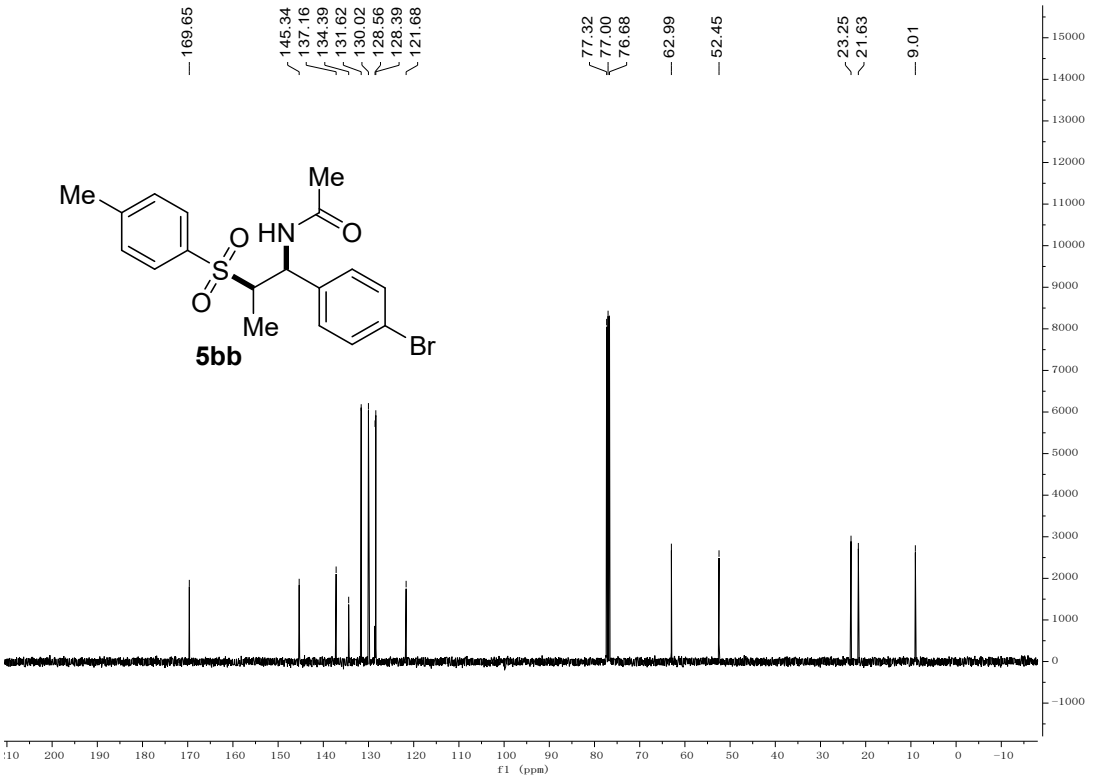
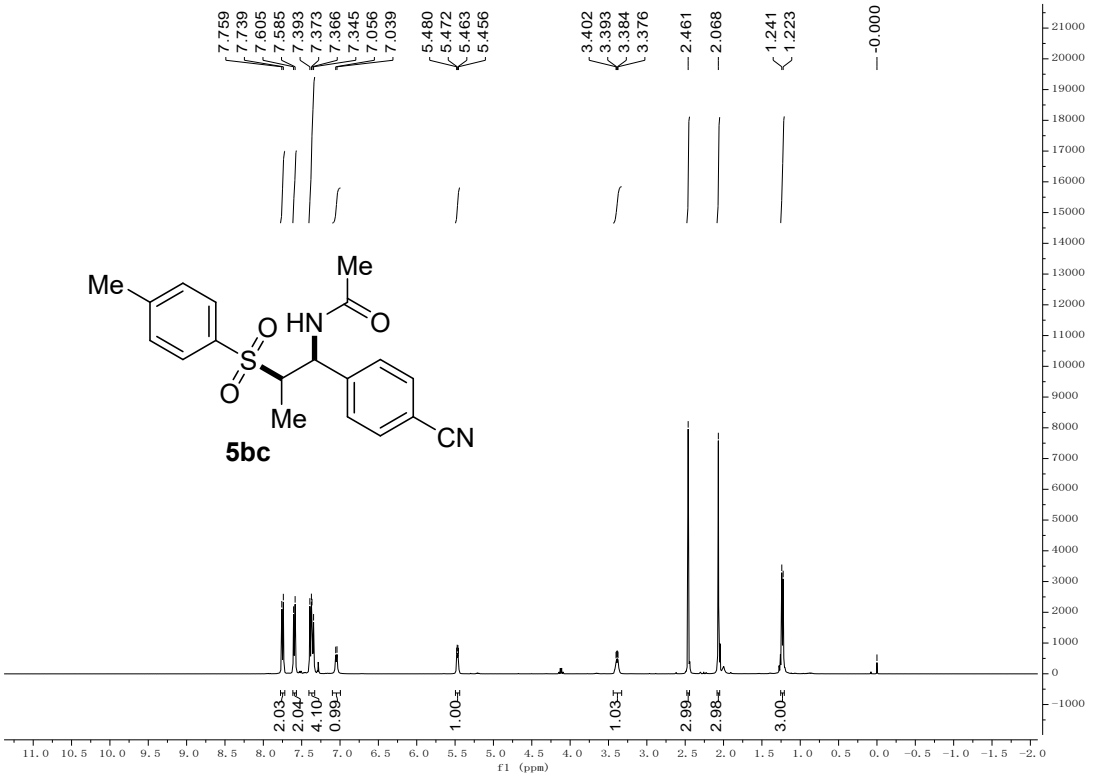
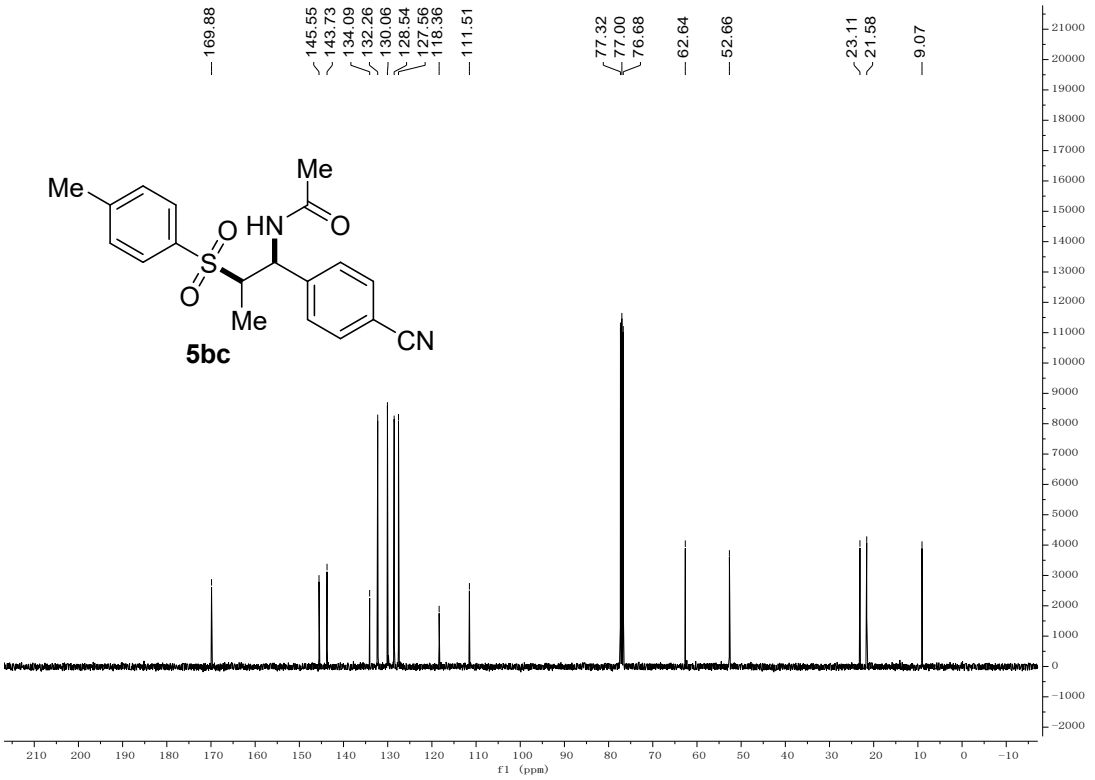


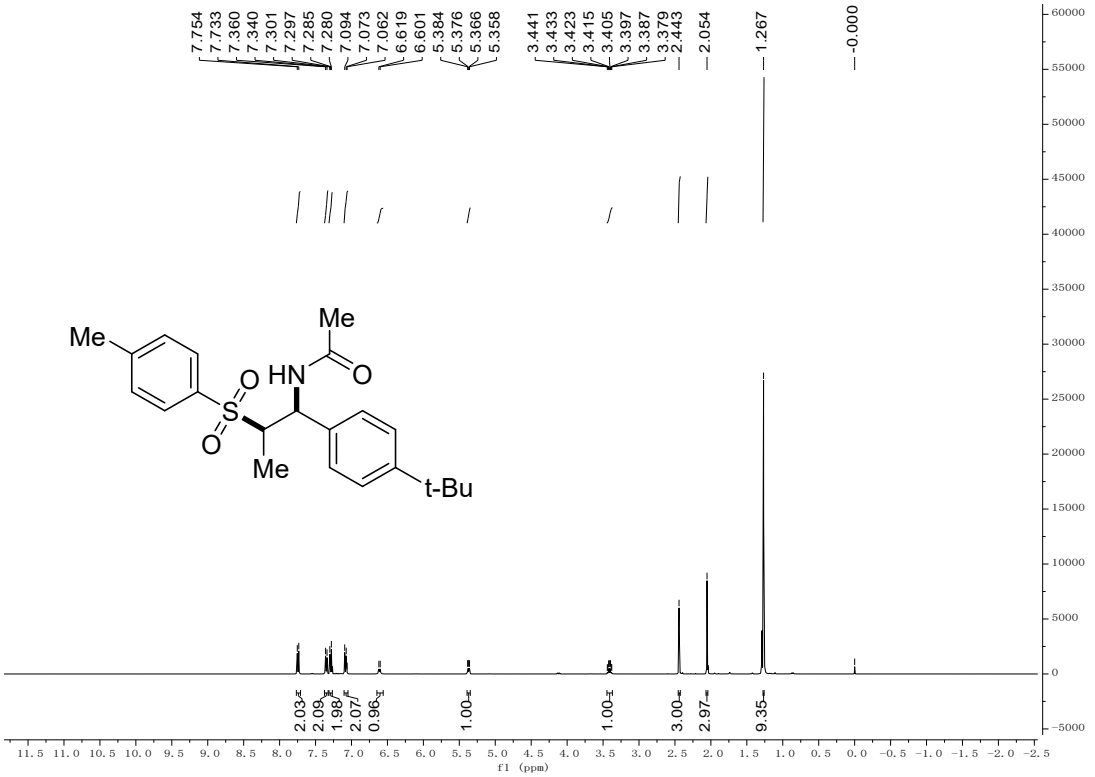
^{1}H NMR of **5bc** in $CDCl_3$



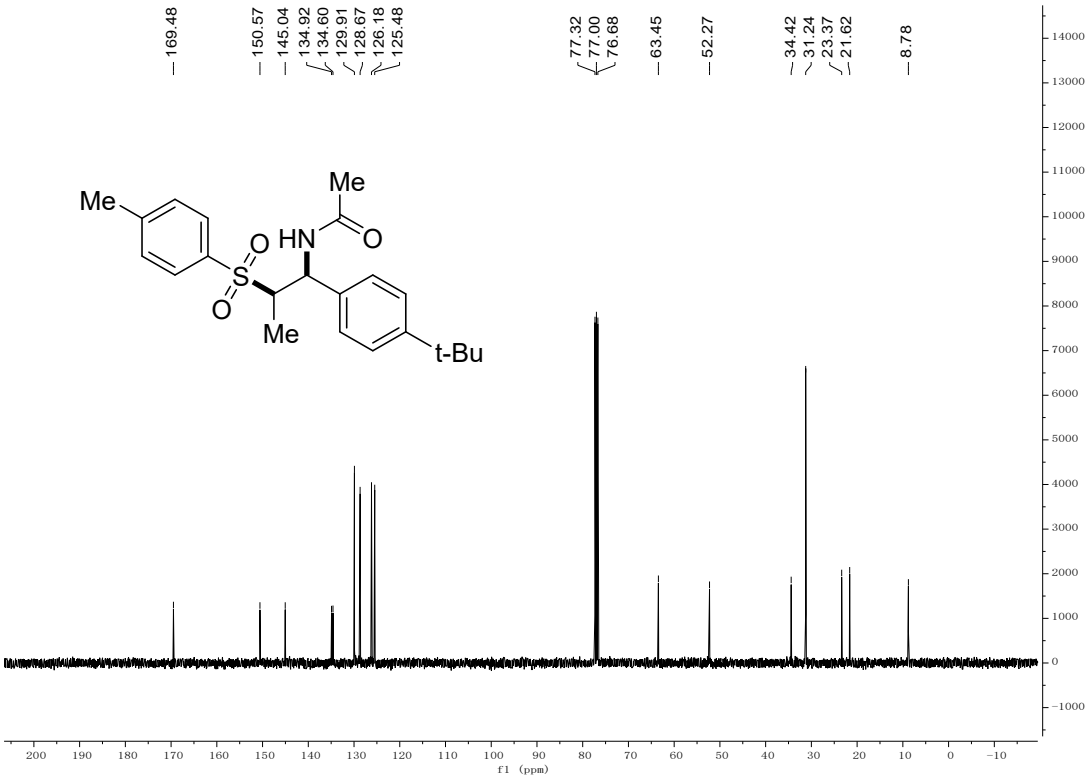
^{13}C NMR of **5bc** in $CDCl_3$



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



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



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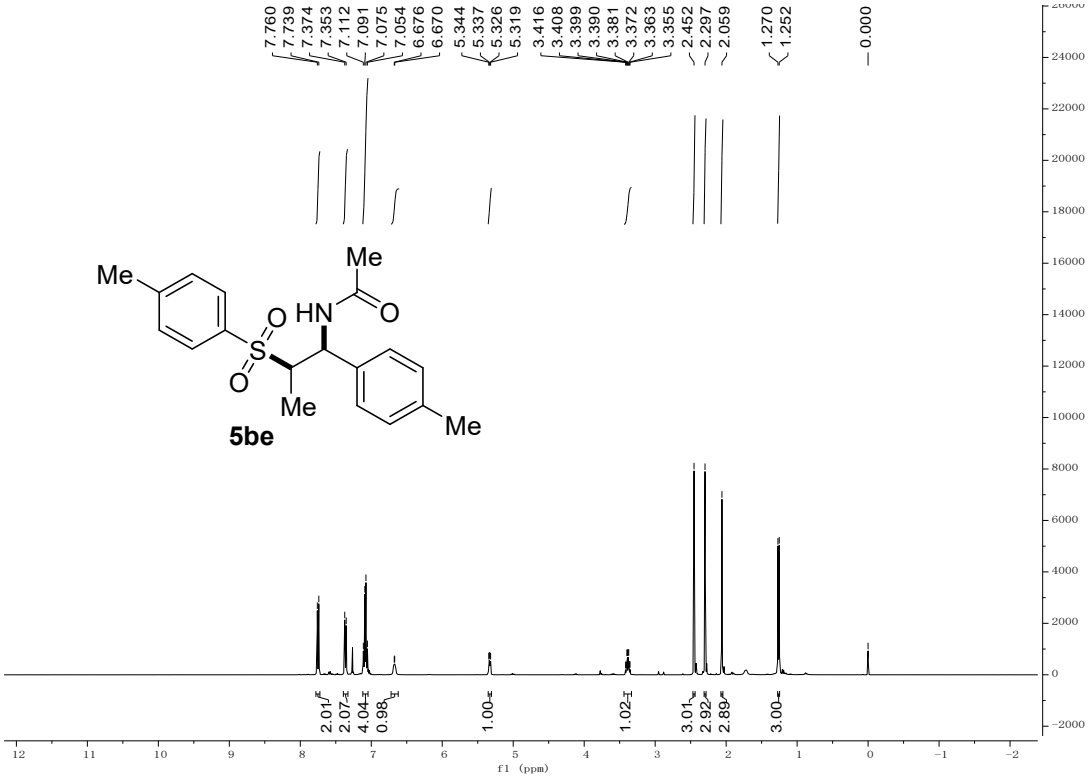

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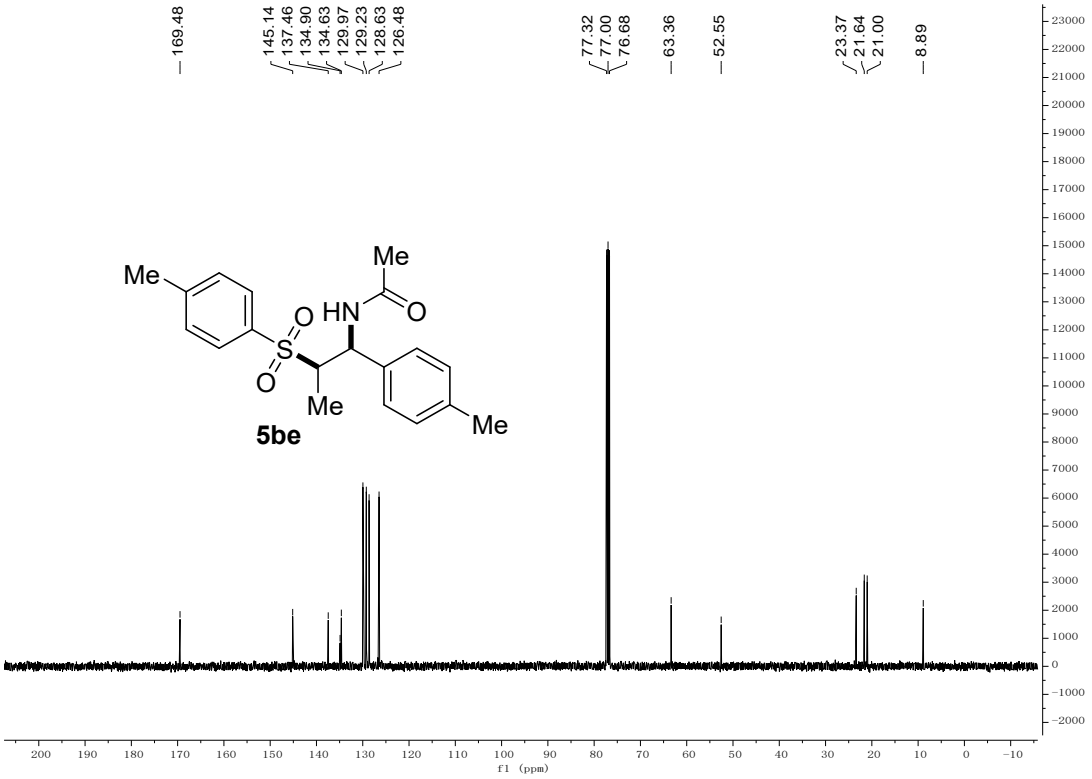

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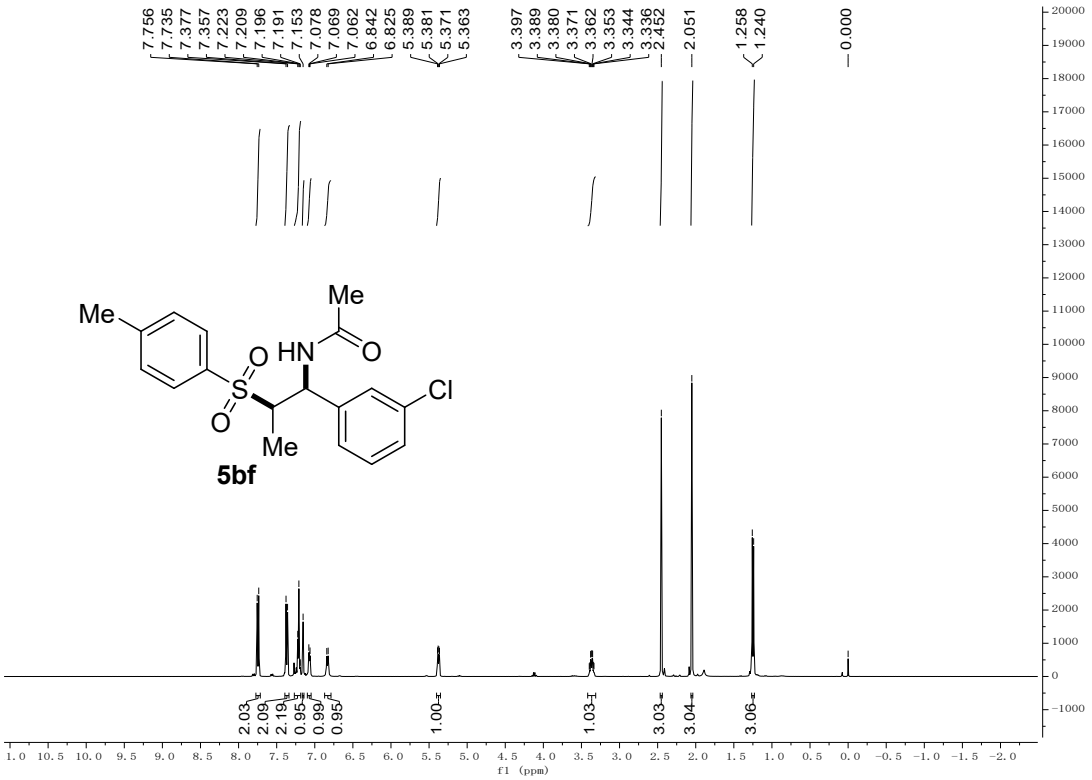

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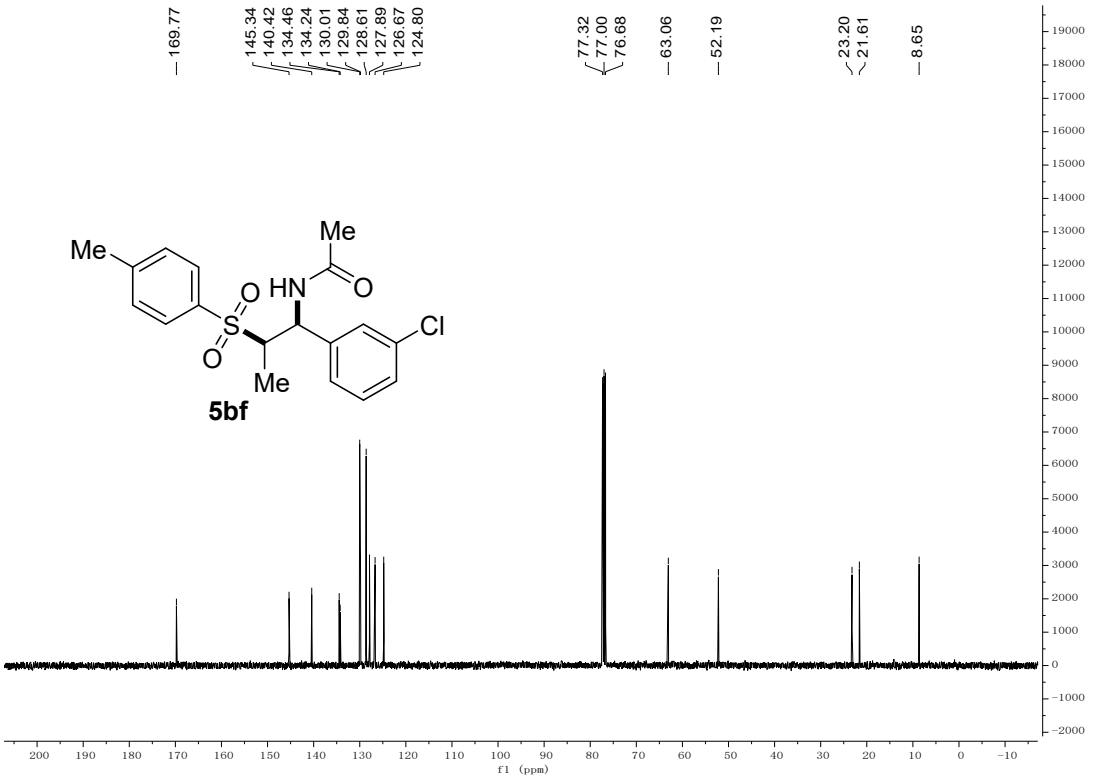
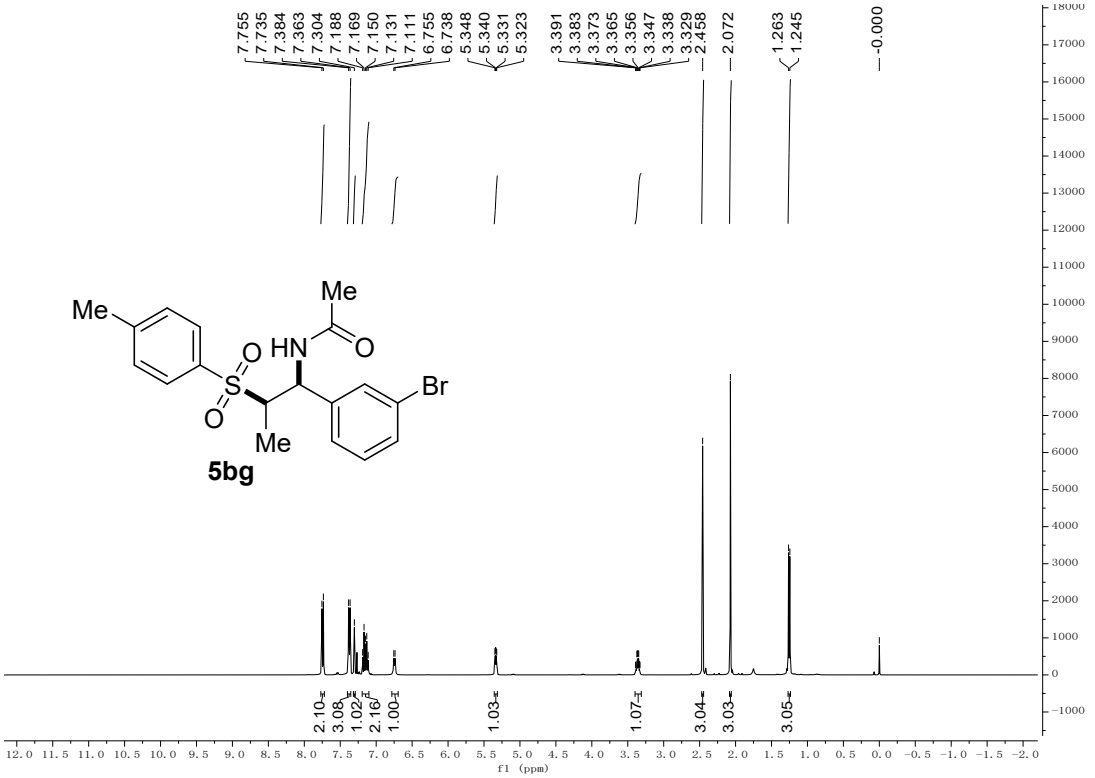
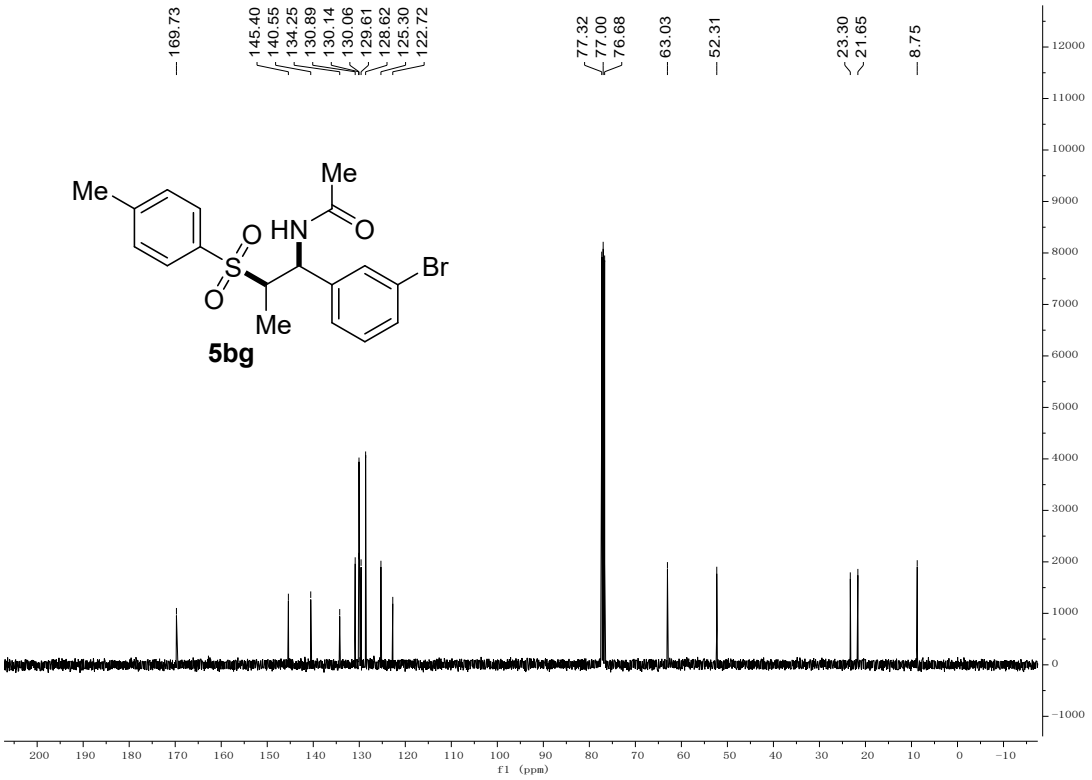


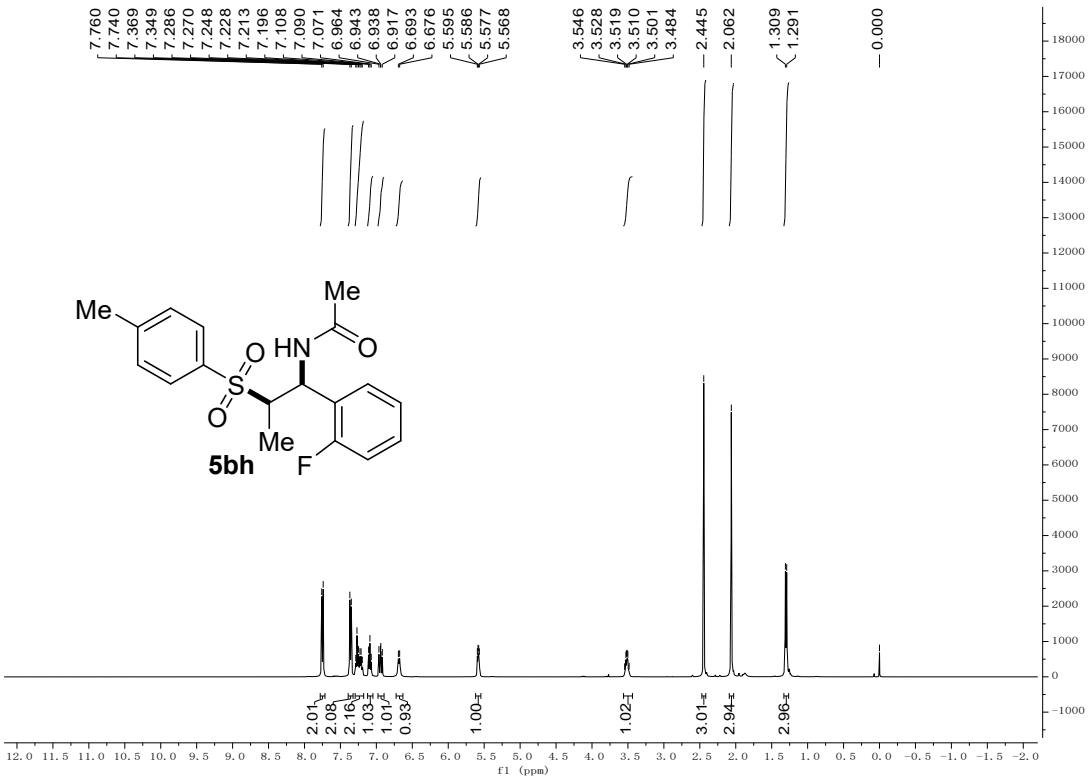
^{1}H NMR of **5bg** in $CDCl_3$



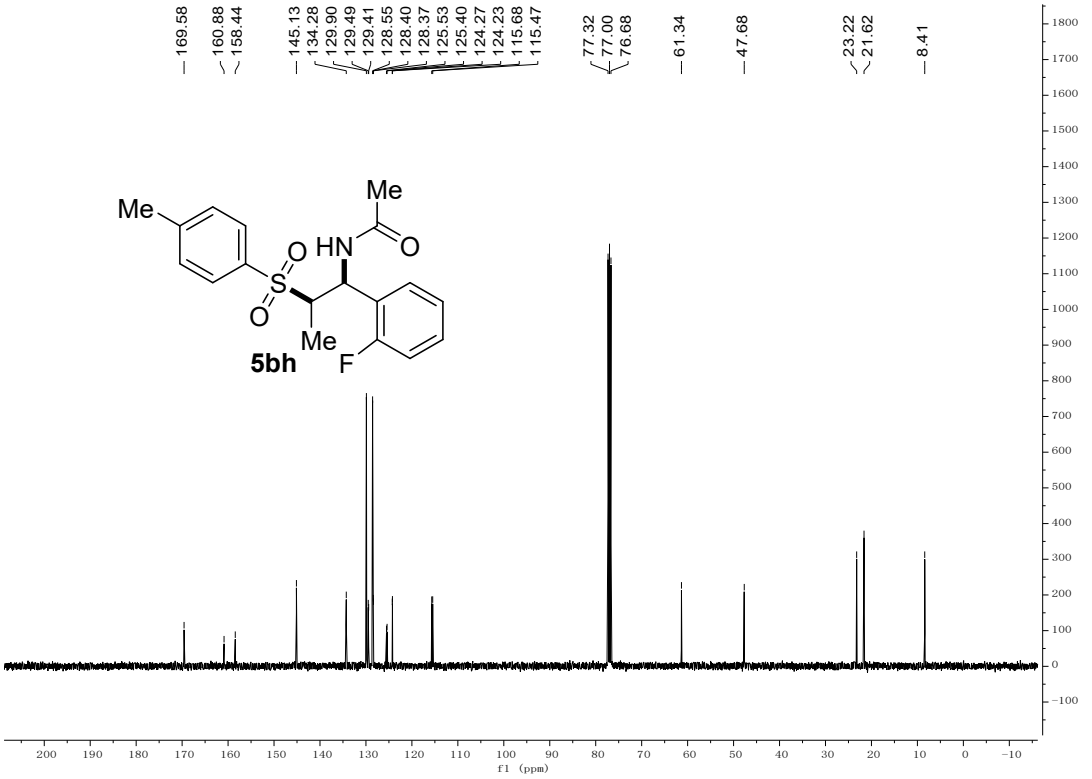
^{13}C NMR of **5bg** in $CDCl_3$



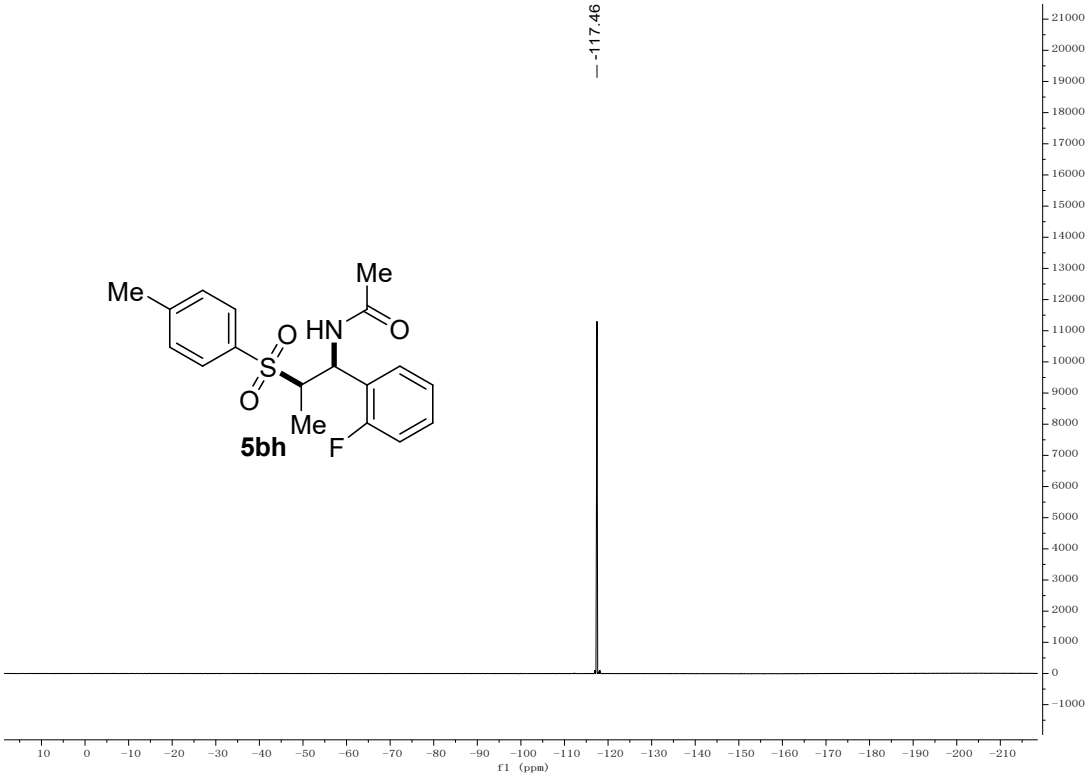
^{1}H NMR of **5bh** in $CDCl_3$



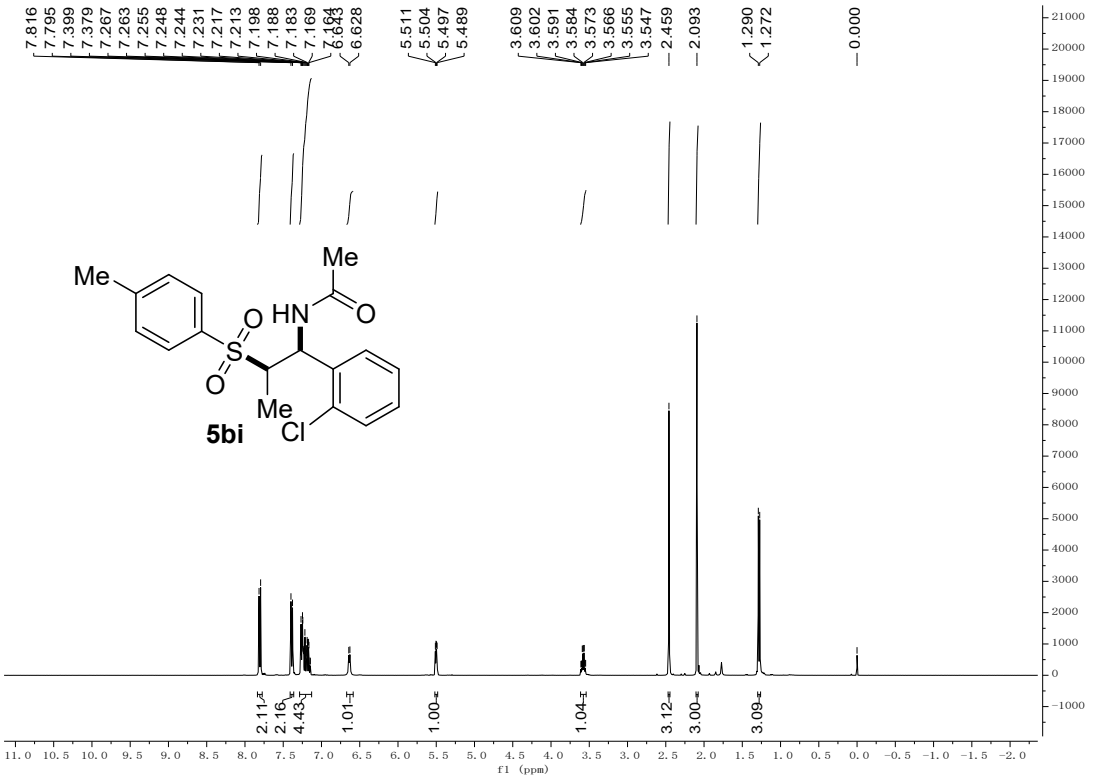
^{13}C NMR of **5bh** in $CDCl_3$



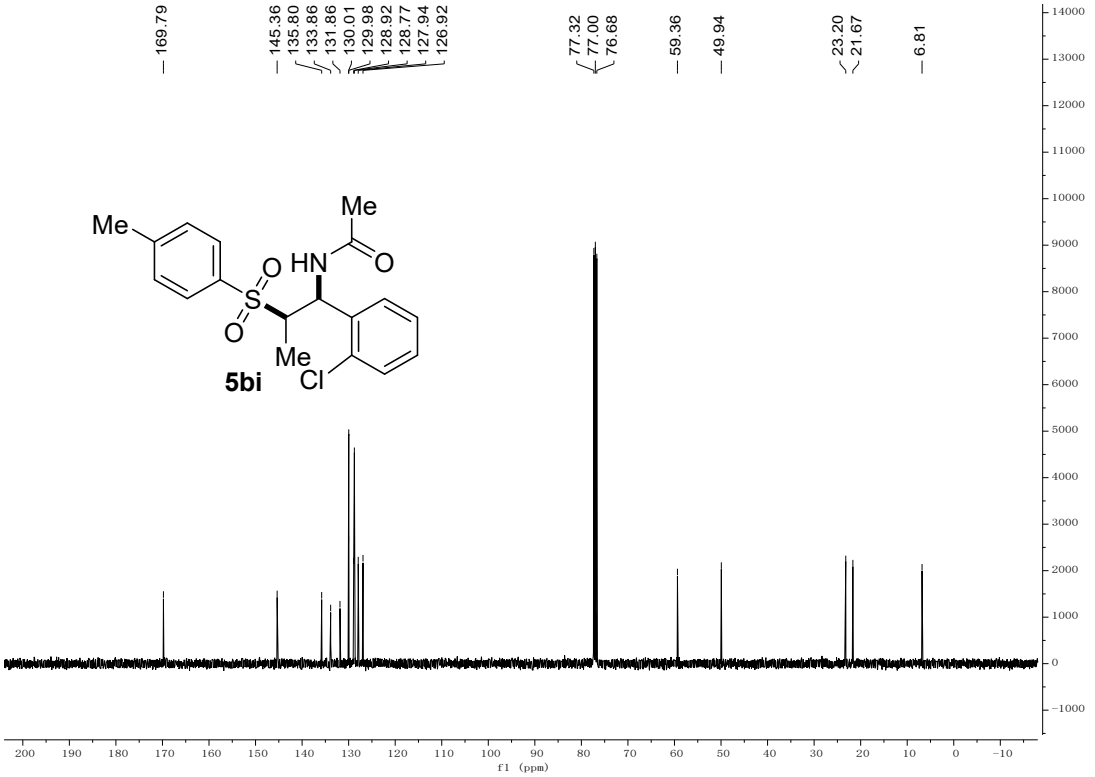
^{19}F NMR spectra of **5bh** in $CDCl_3$



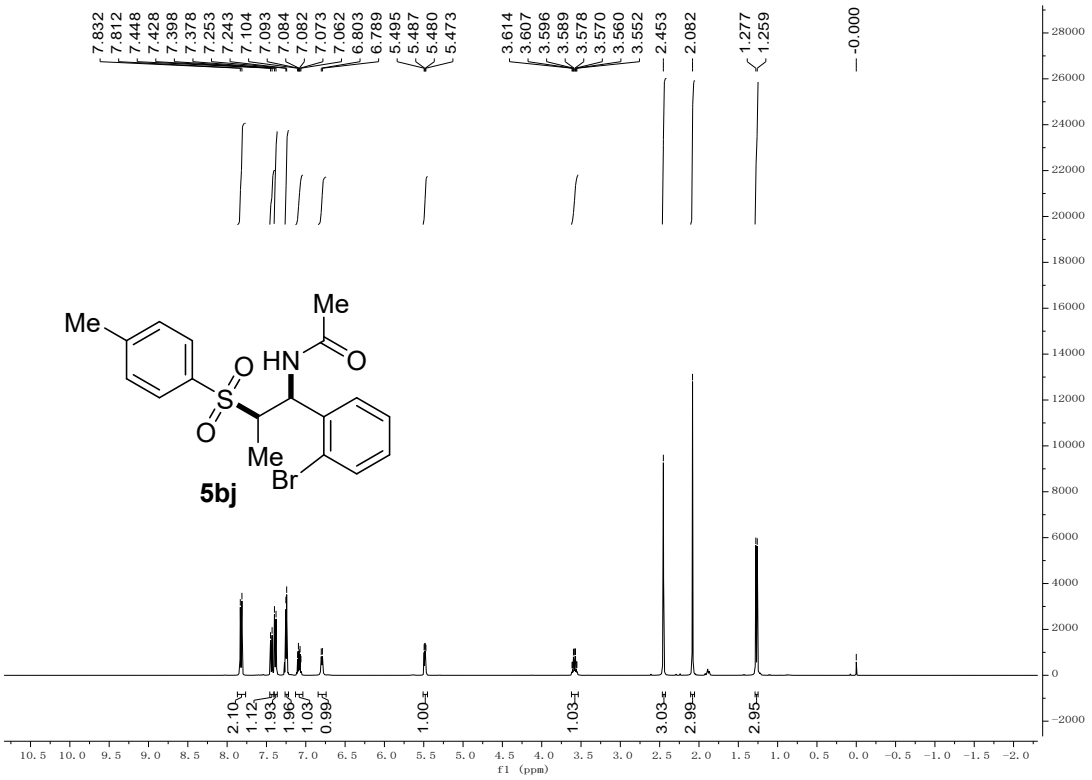
^{1}H NMR of **5bi** in $CDCl_3$



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



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



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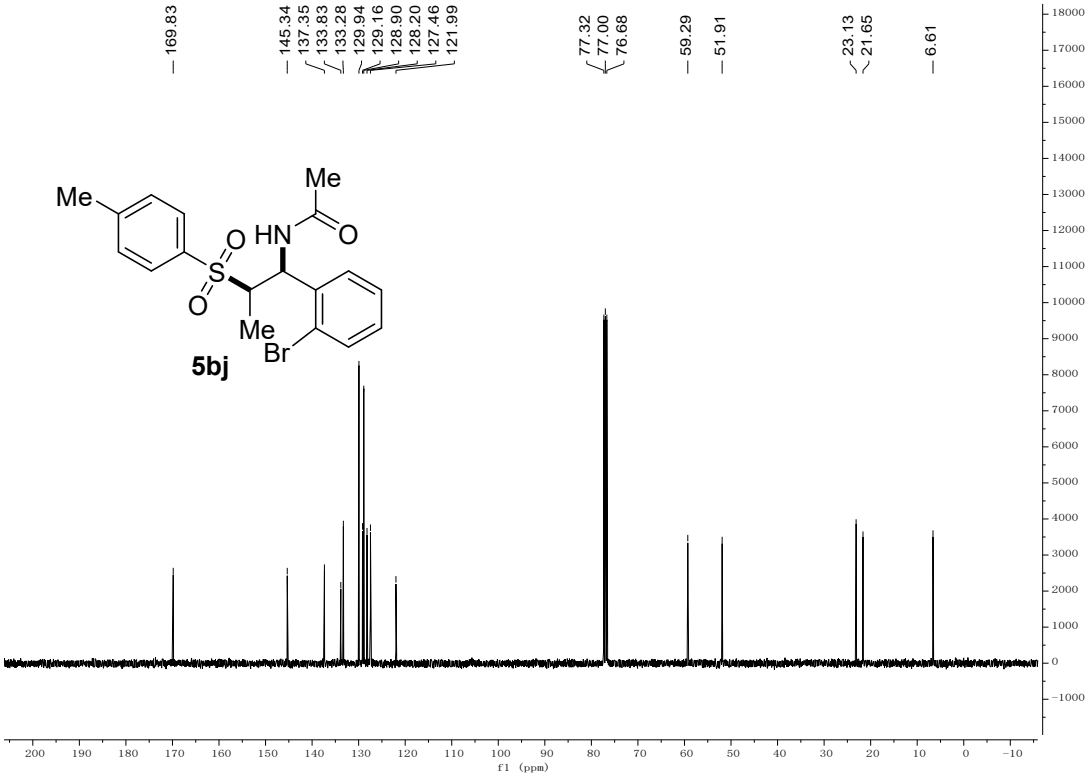
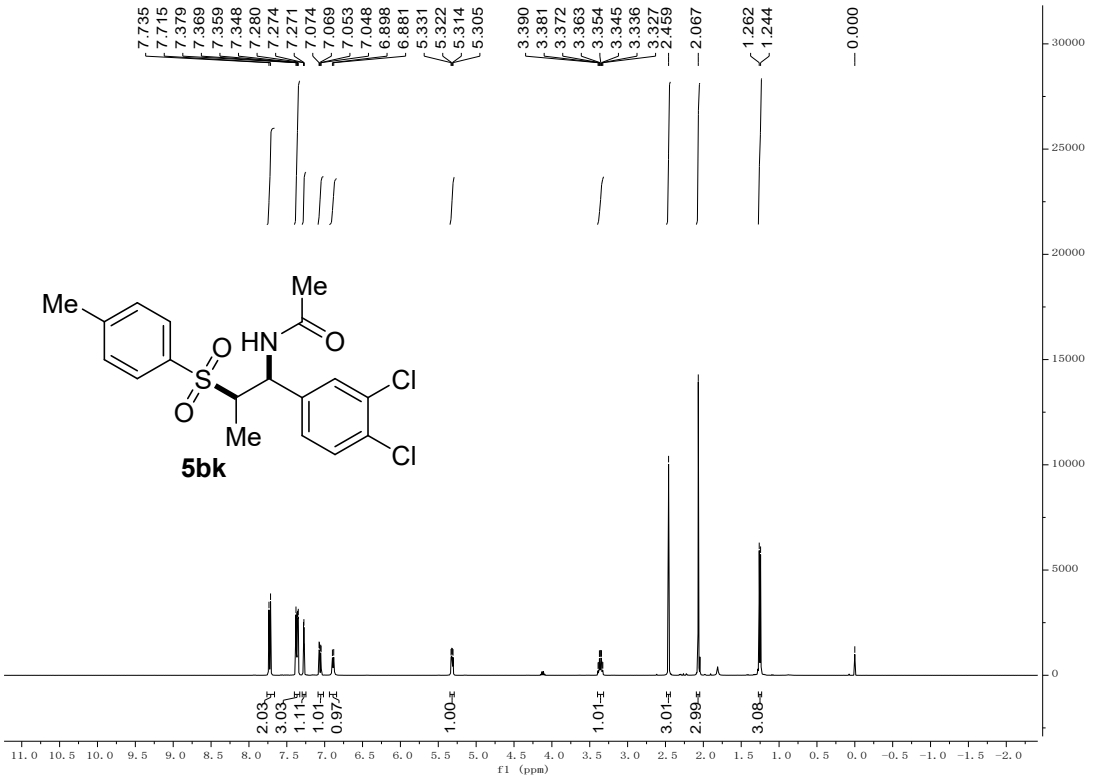


^{1}H NMR of **5bk** in $CDCl_3$



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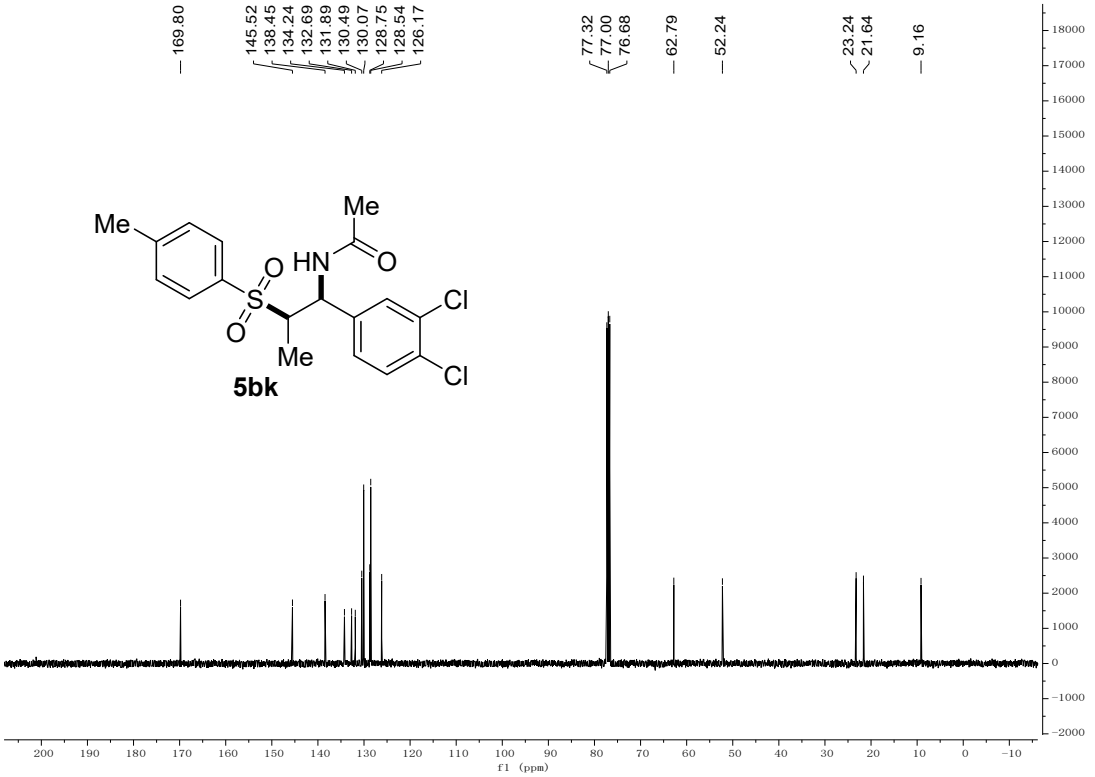
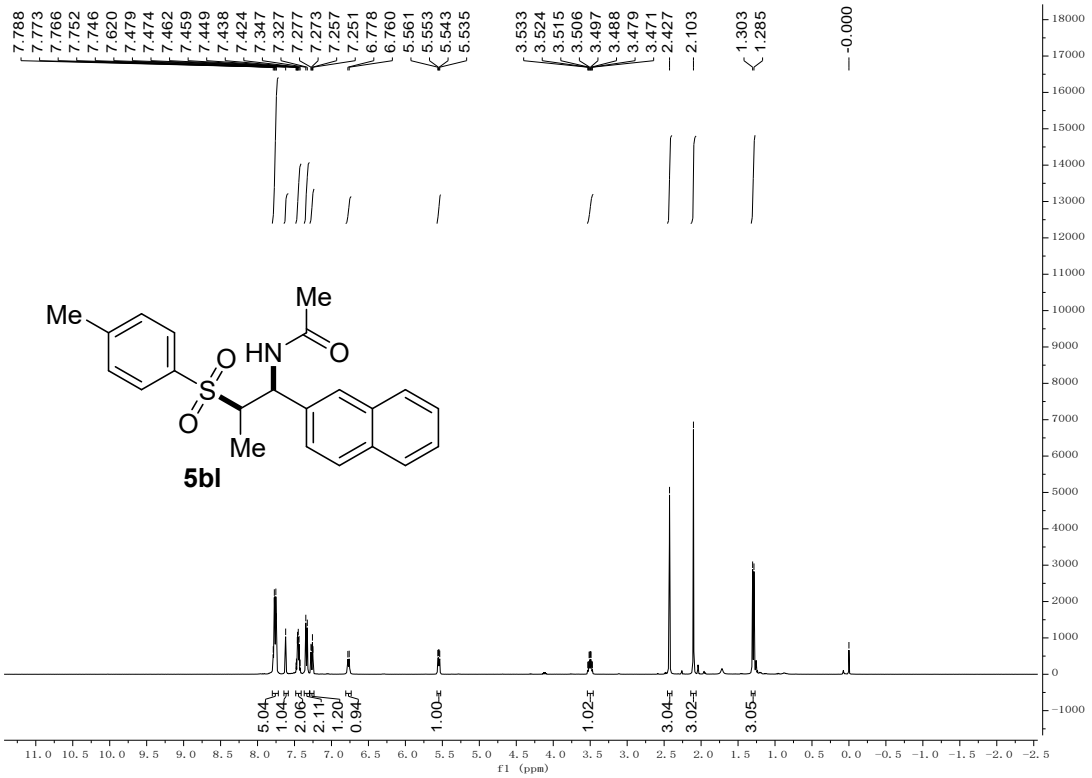


^{1}H NMR of **5bl** in $CDCl_3$



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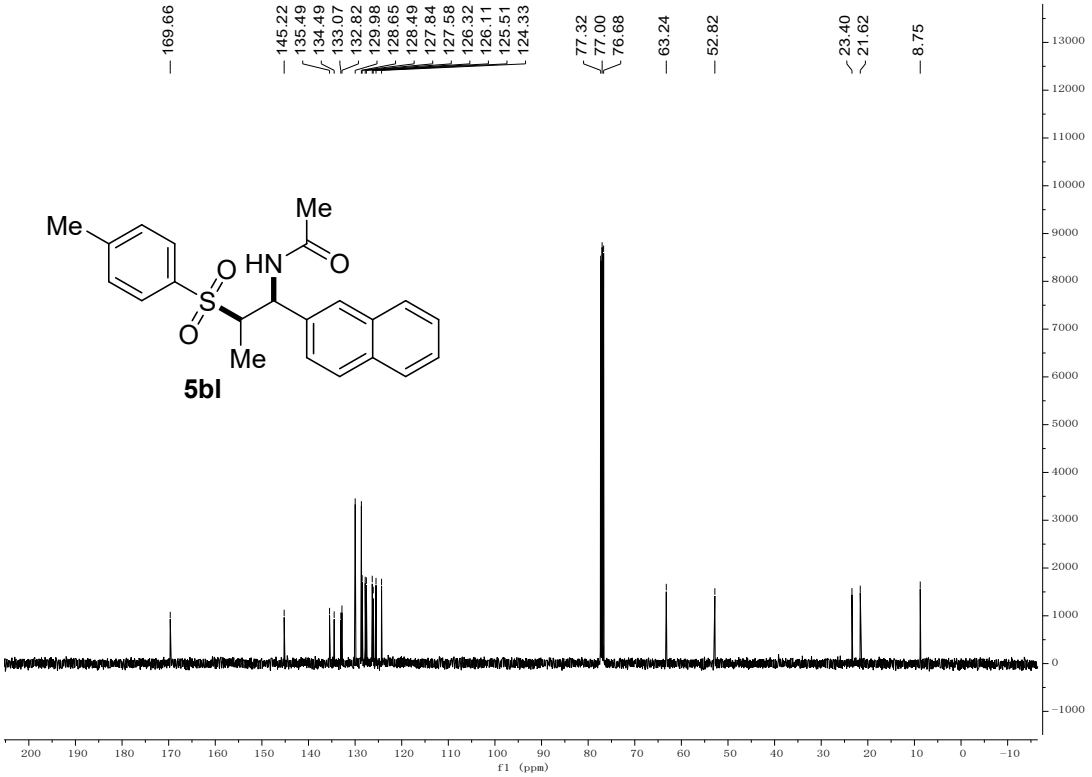
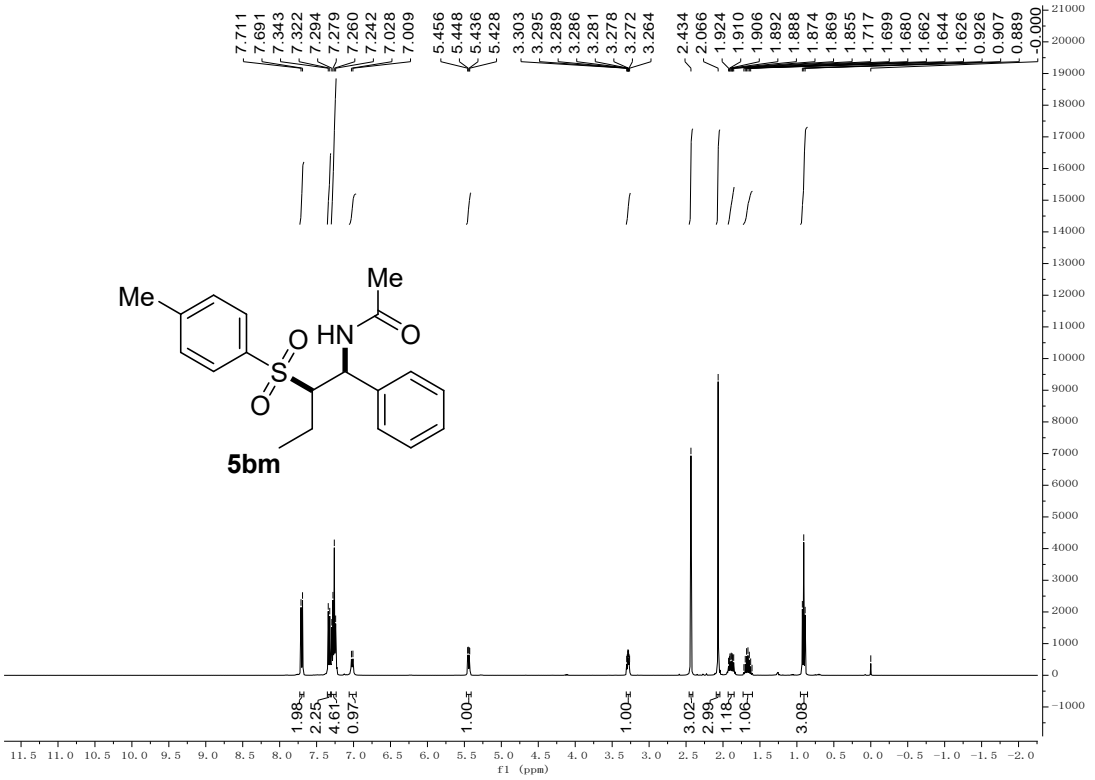
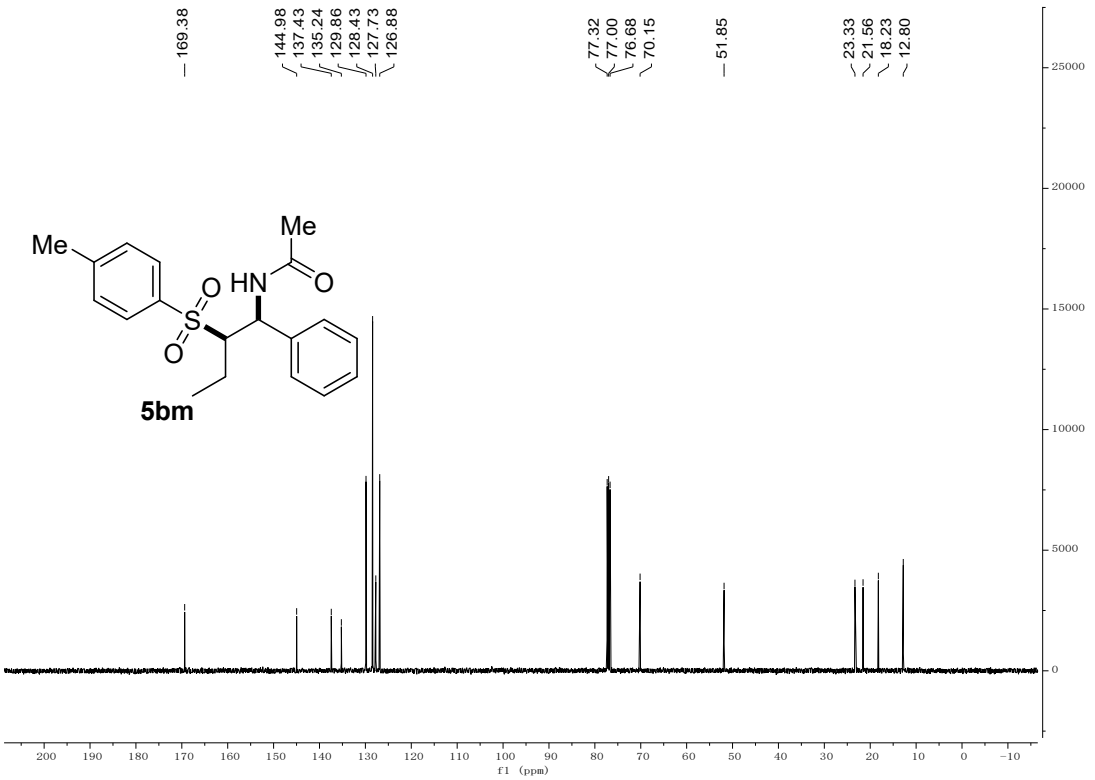


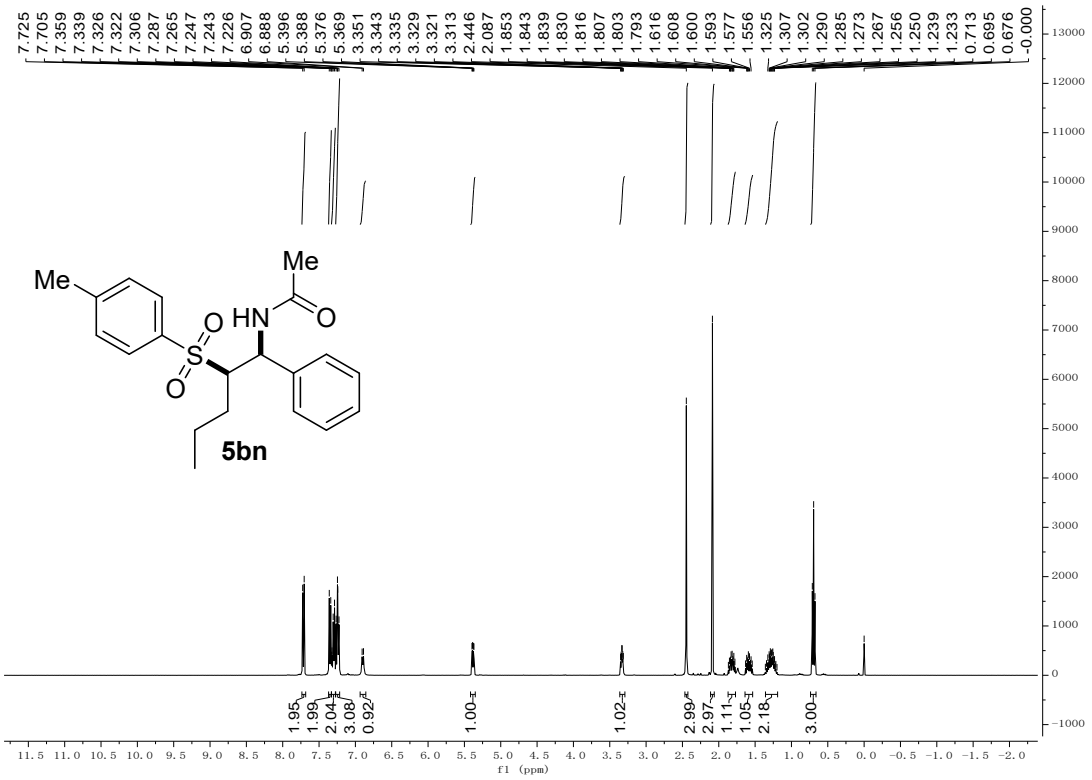
^{1}H NMR of **5bm** in $CDCl_3$



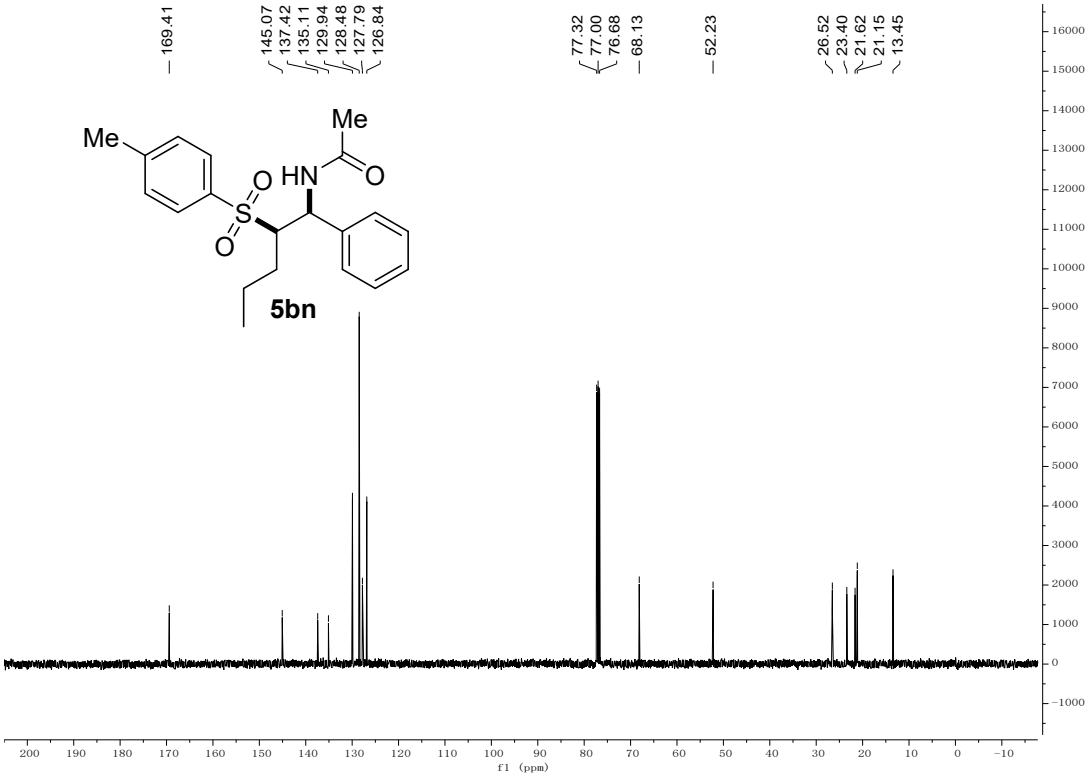
^{13}C NMR of **5bm** in $CDCl_3$



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



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



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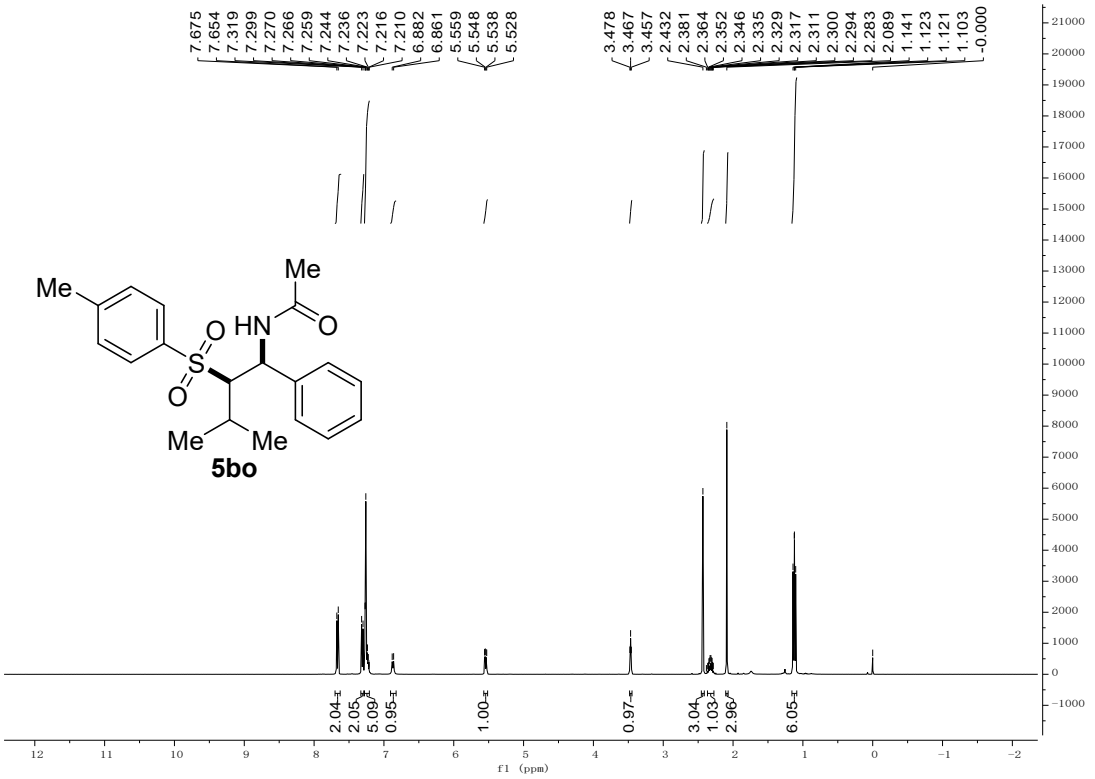
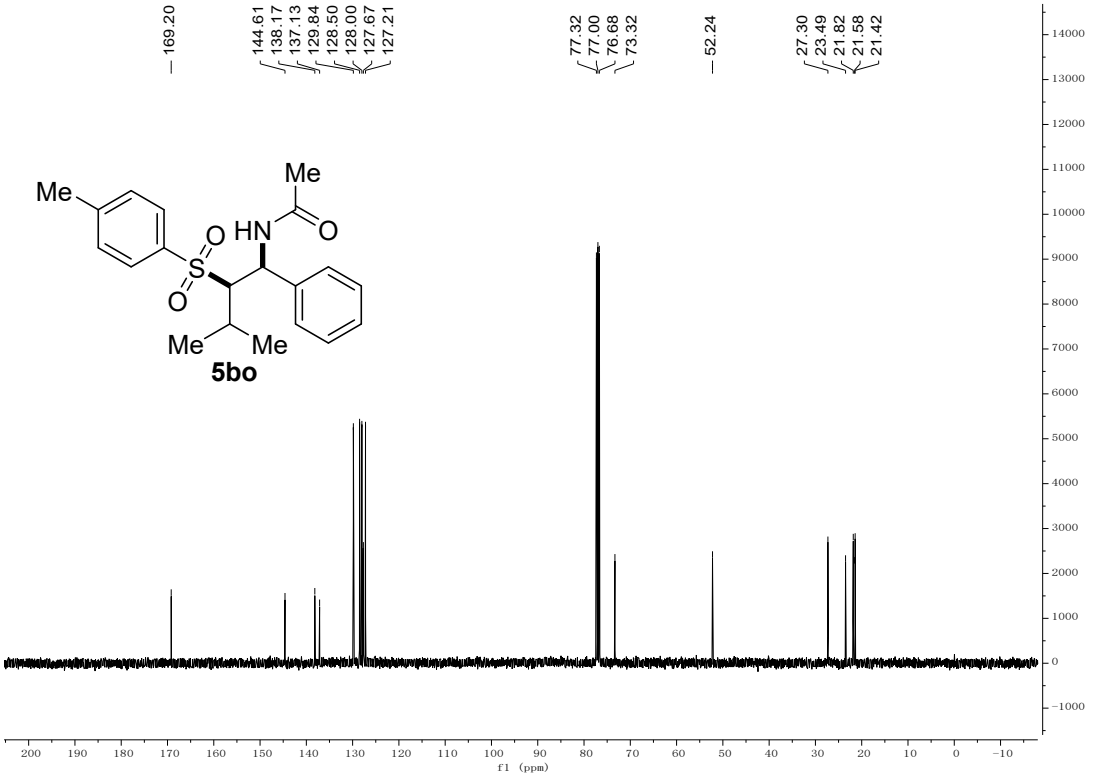
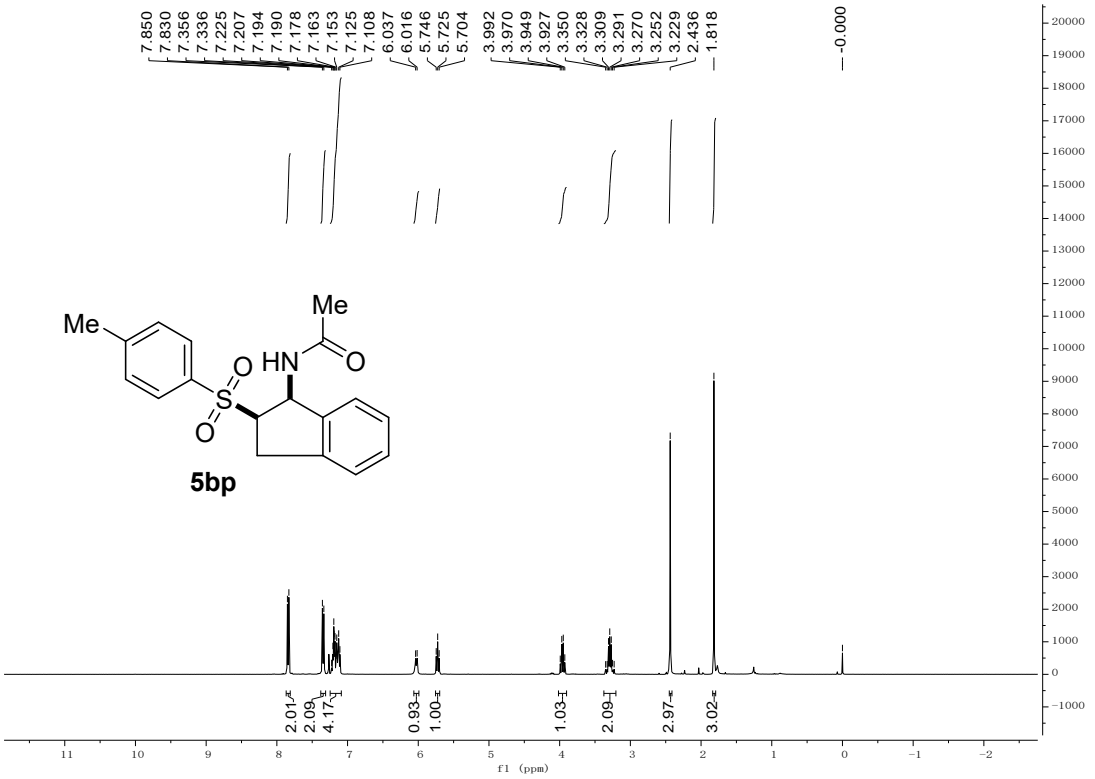


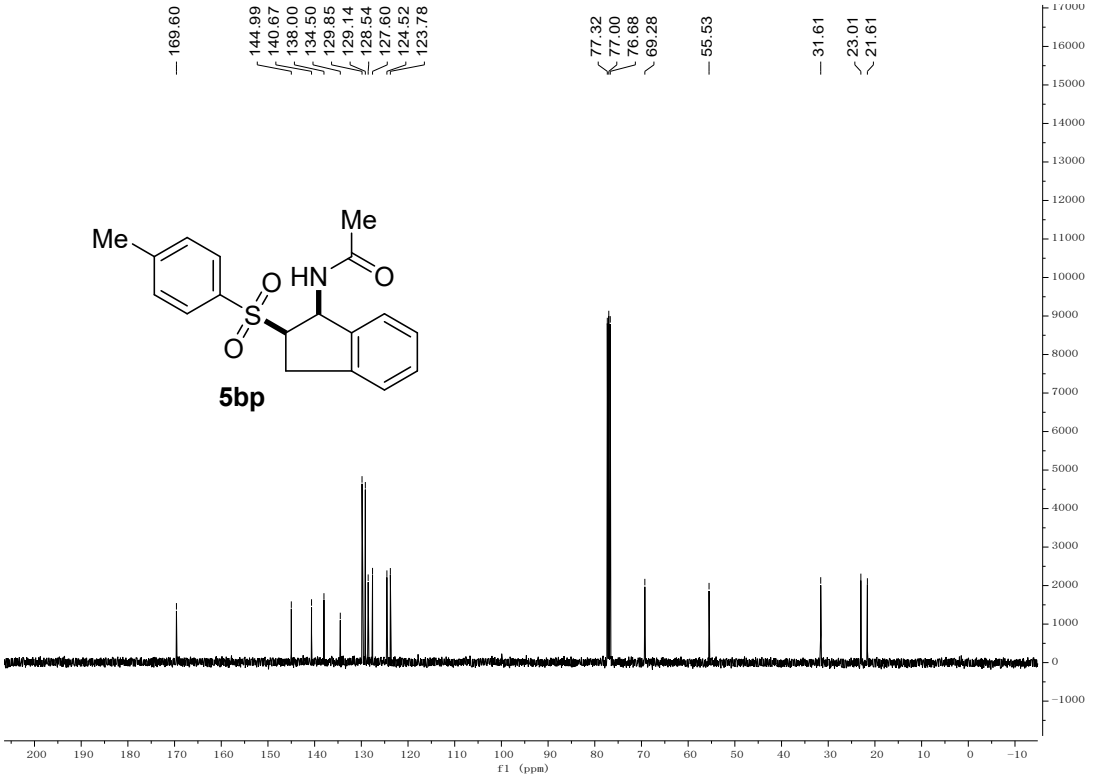
^{13}C NMR of **5bo** in $CDCl_3$



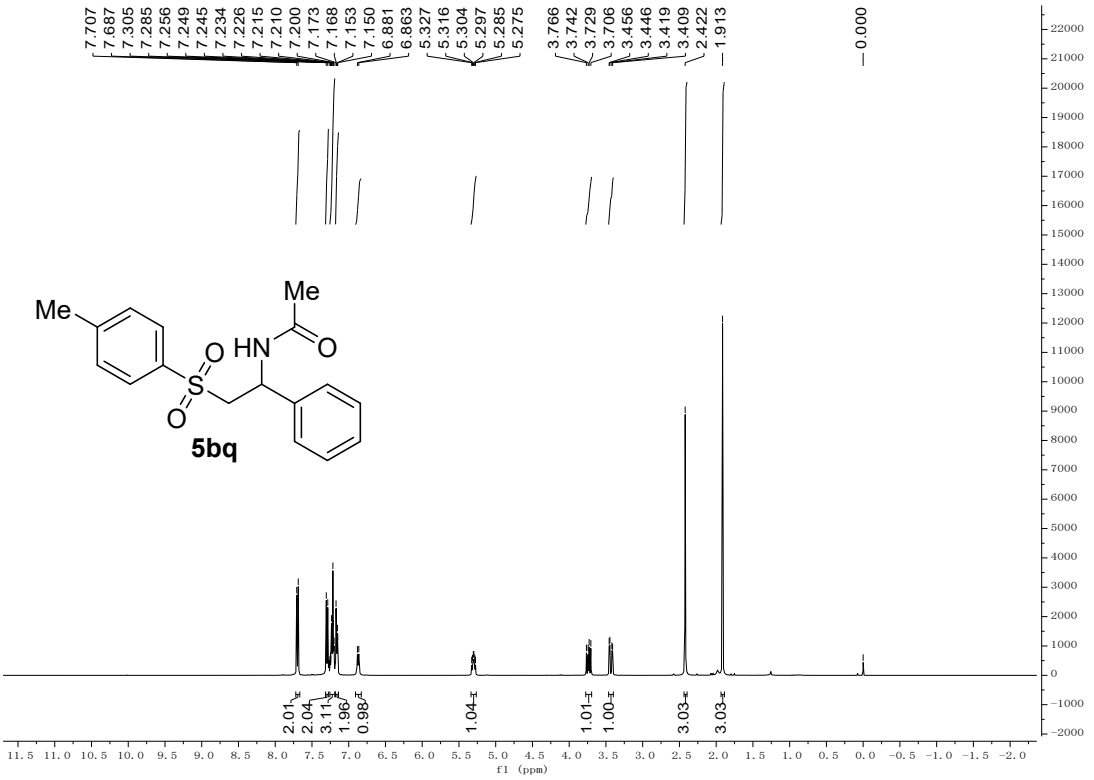
^{1}H NMR of **5bp** in $CDCl_3$



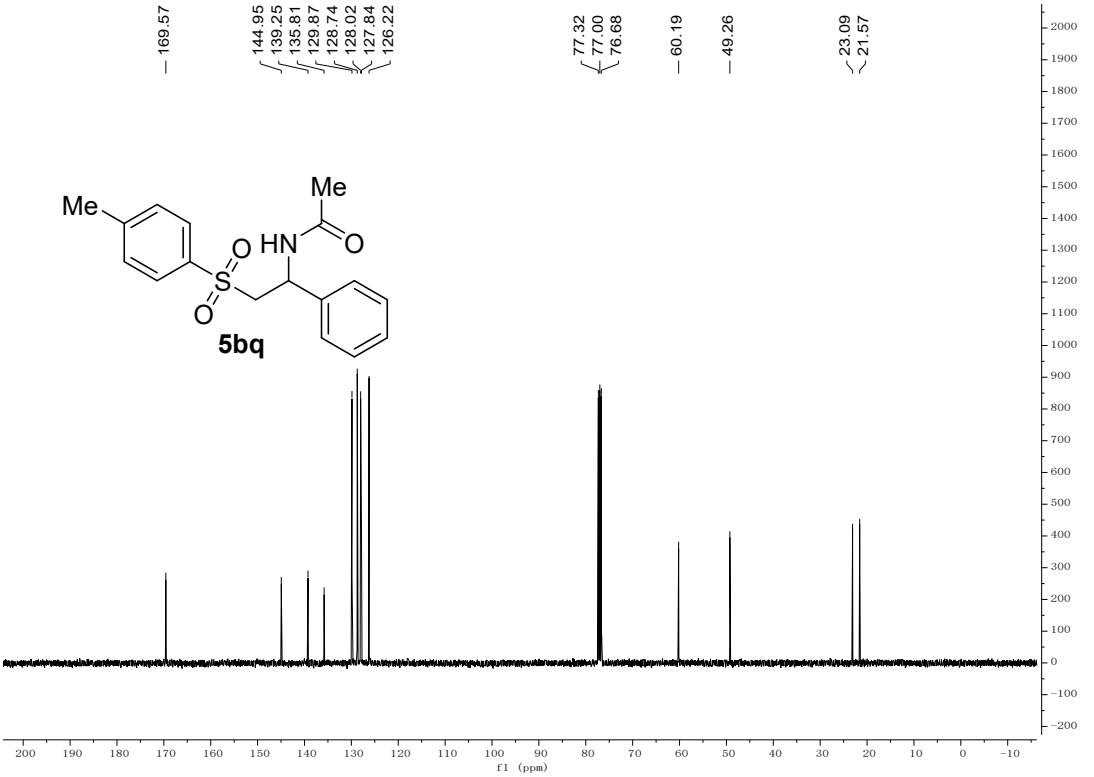
^{13}C NMR of **5bp** in $CDCl_3$



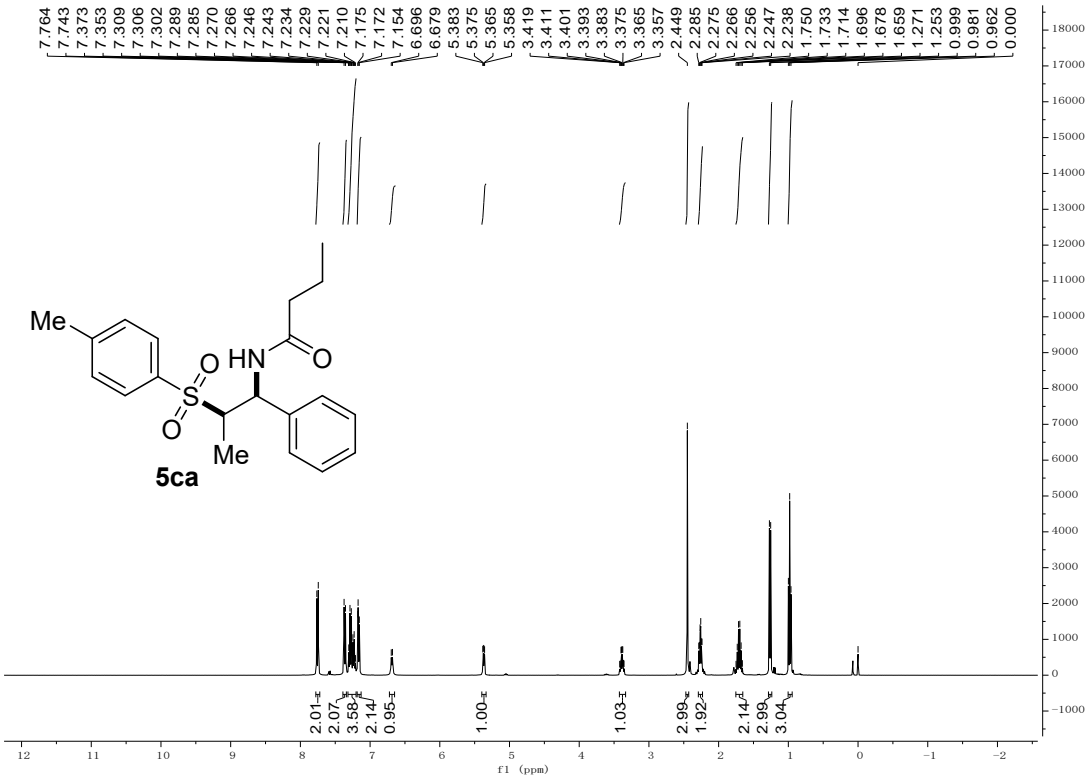
^{1}H NMR of **5bq** in $CDCl_3$



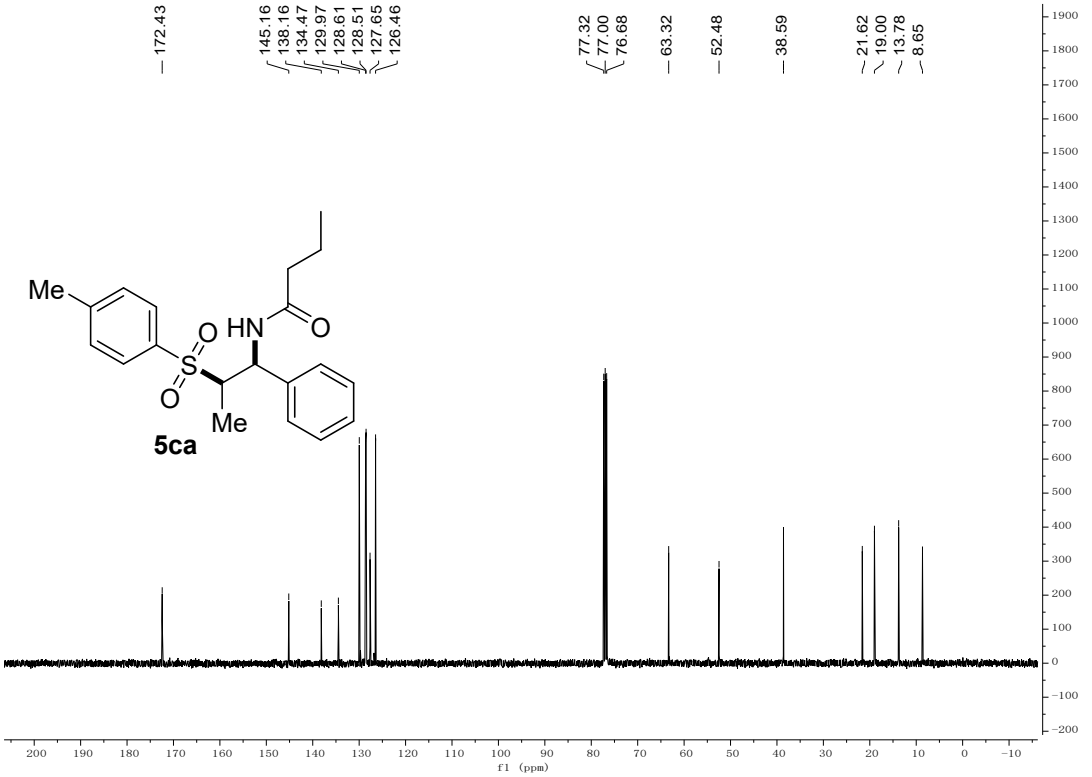
^{13}C NMR of **5bq** in $CDCl_3$



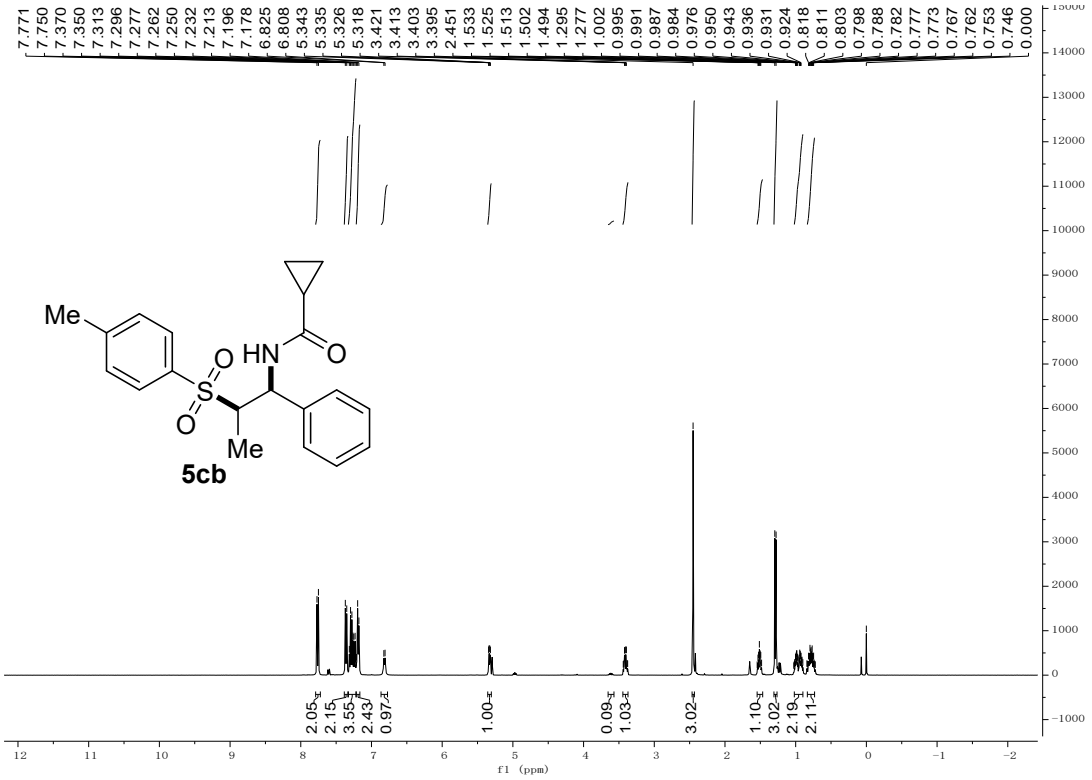
^{1}H NMR of **5ca** in $CDCl_3$



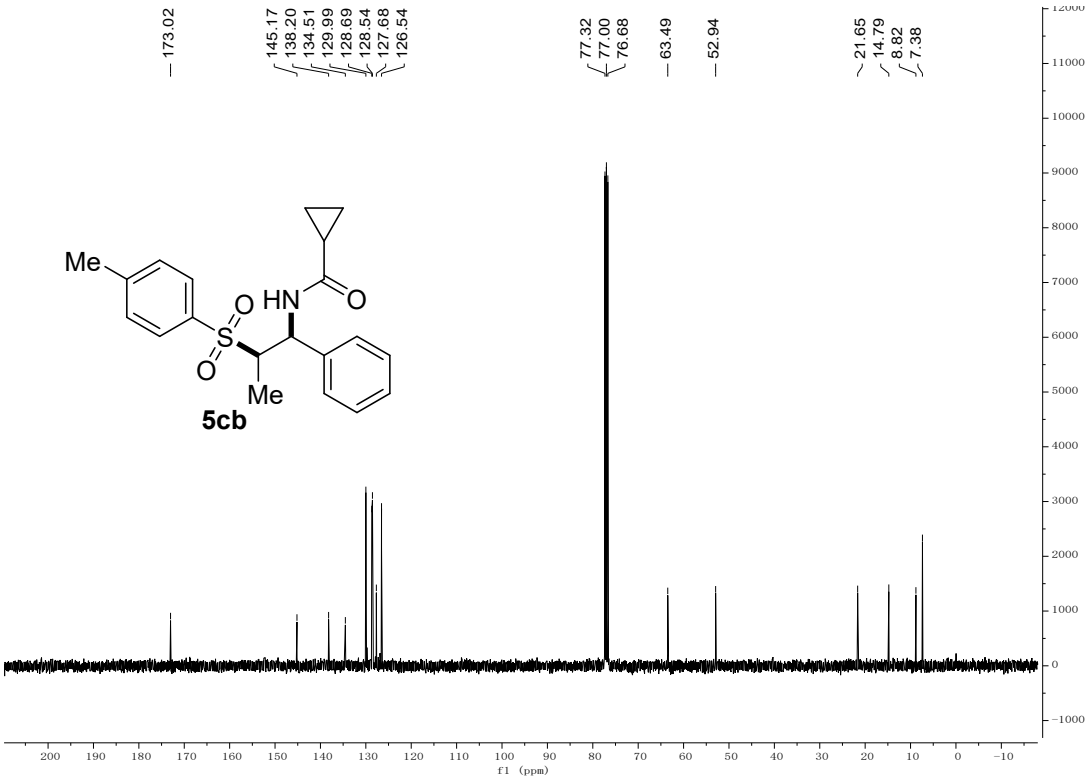
^{13}C NMR of **5ca** in $CDCl_3$



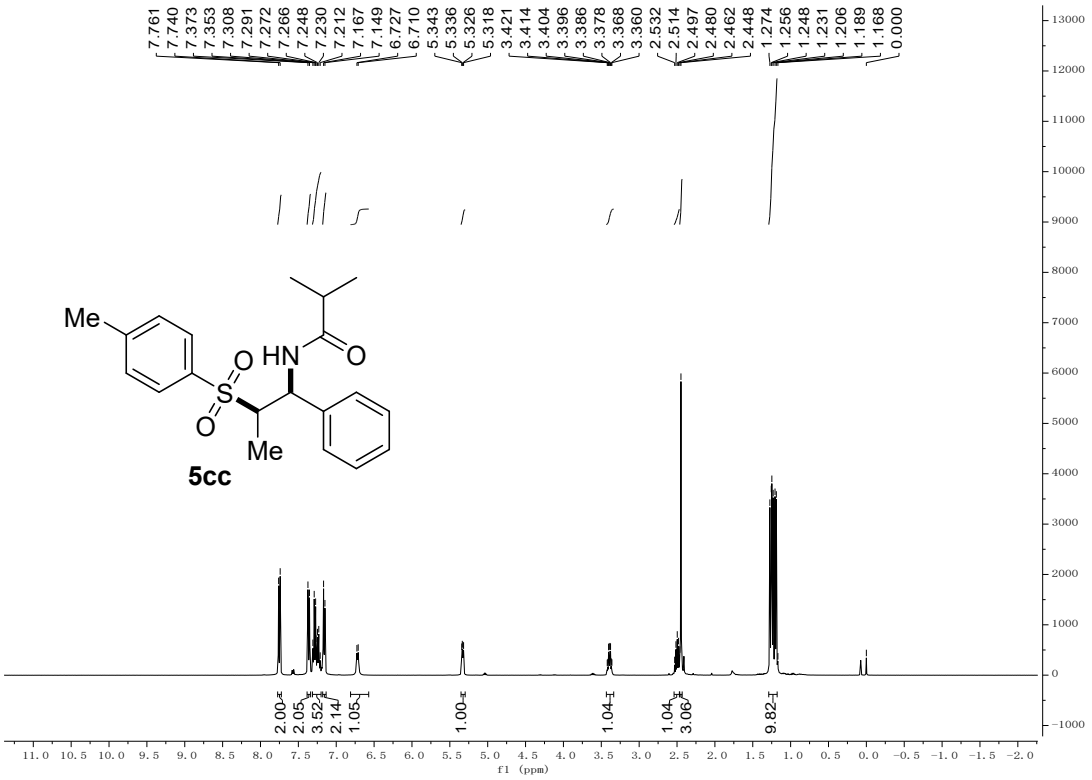
^{1}H NMR of **5cb** in $CDCl_3$



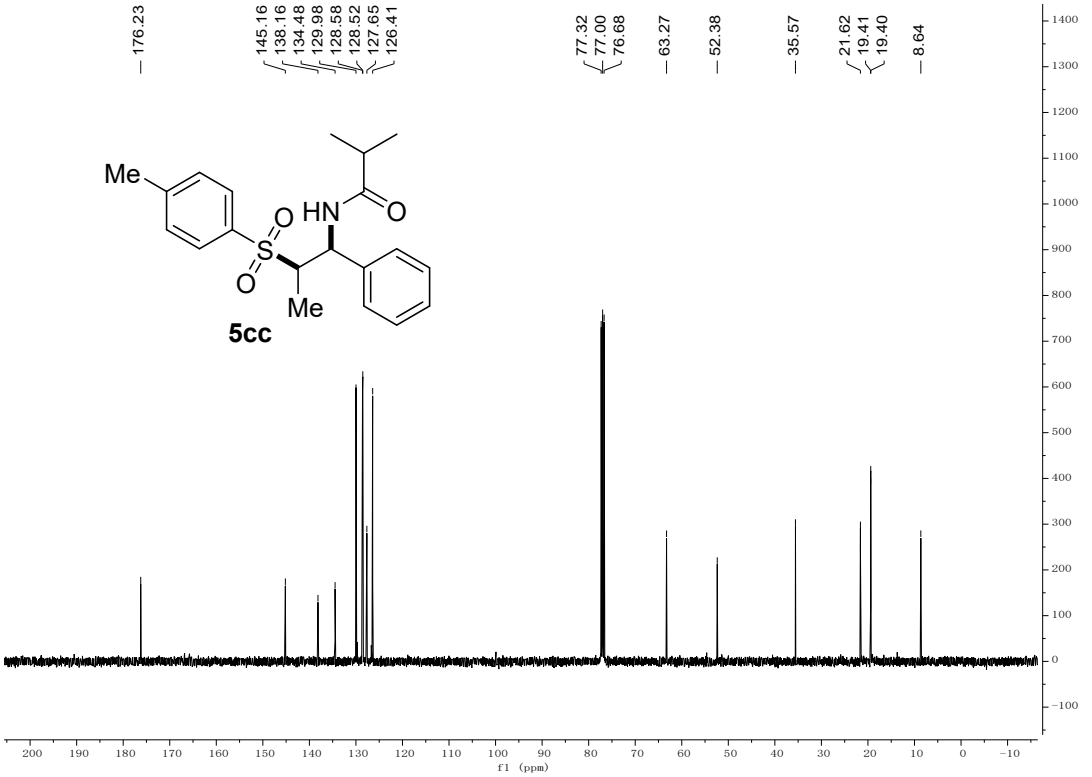
^{13}C NMR of **5cb** in $CDCl_3$



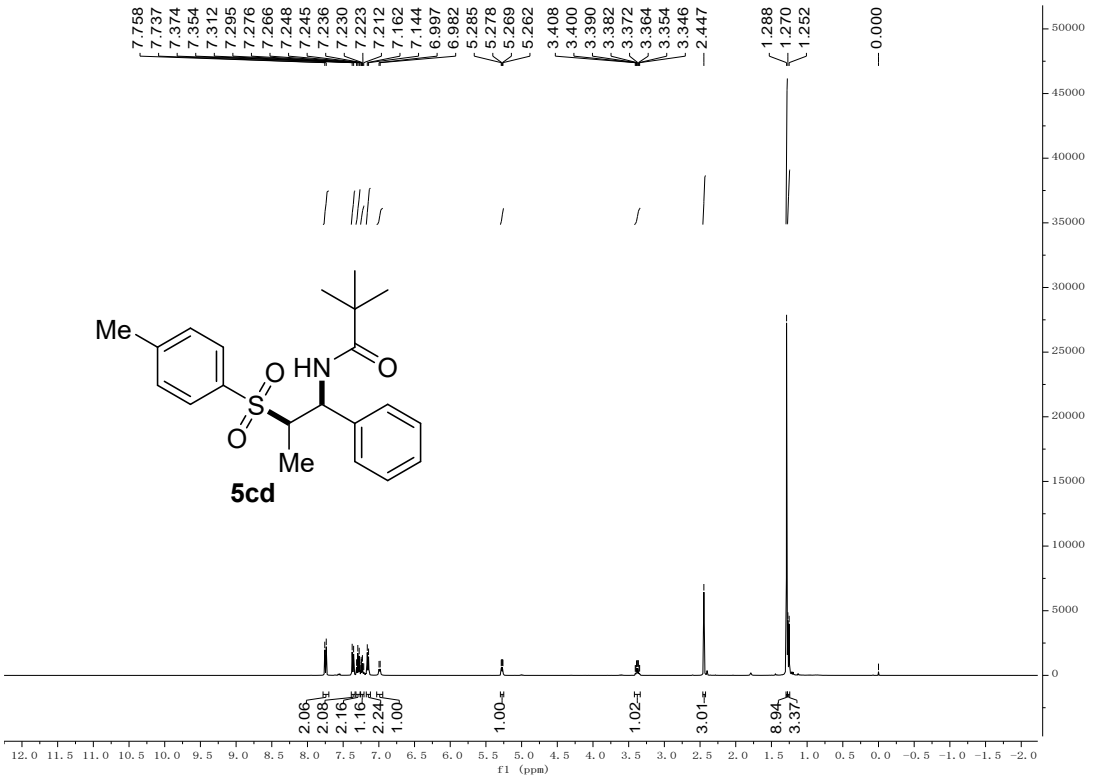
^{1}H NMR of **5cc** in $CDCl_3$



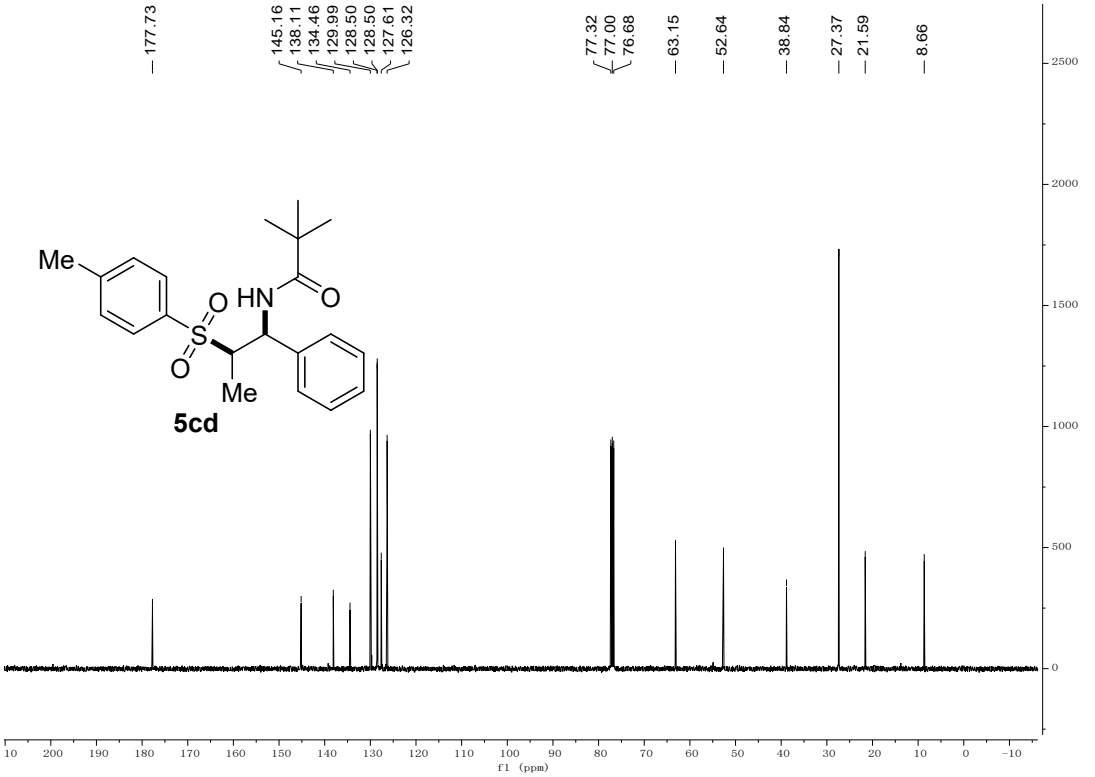
^{13}C NMR of **5cc** in $CDCl_3$



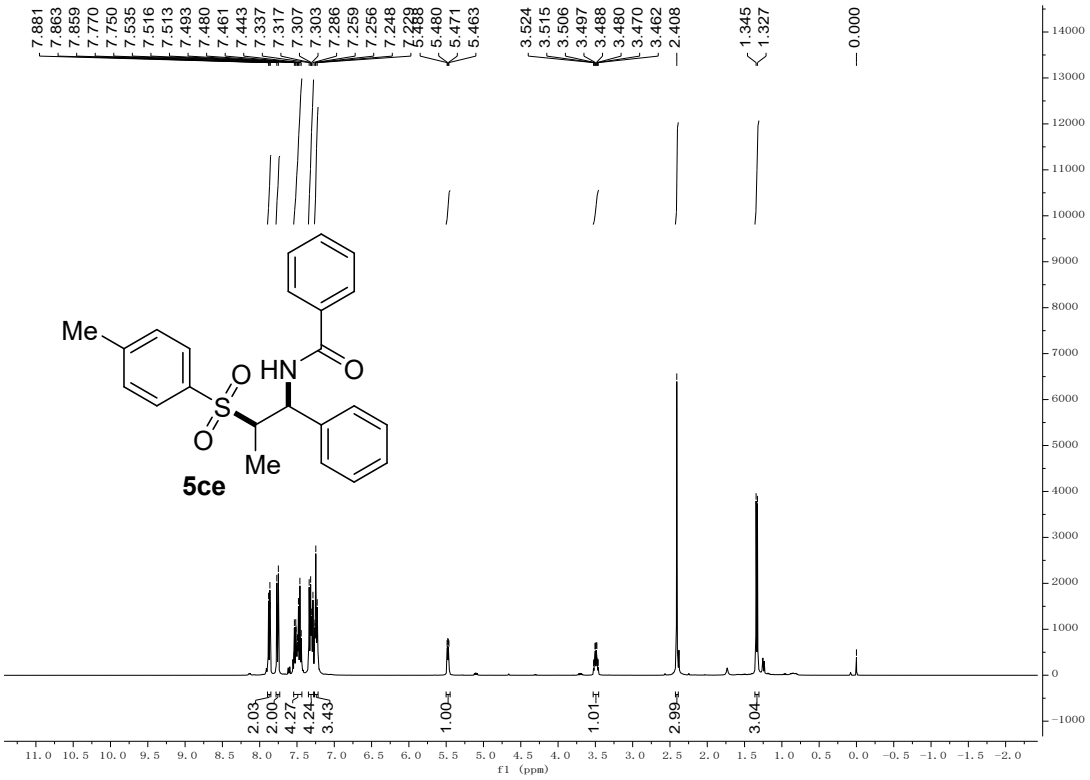
^{1}H NMR of **5cd** in $CDCl_3$



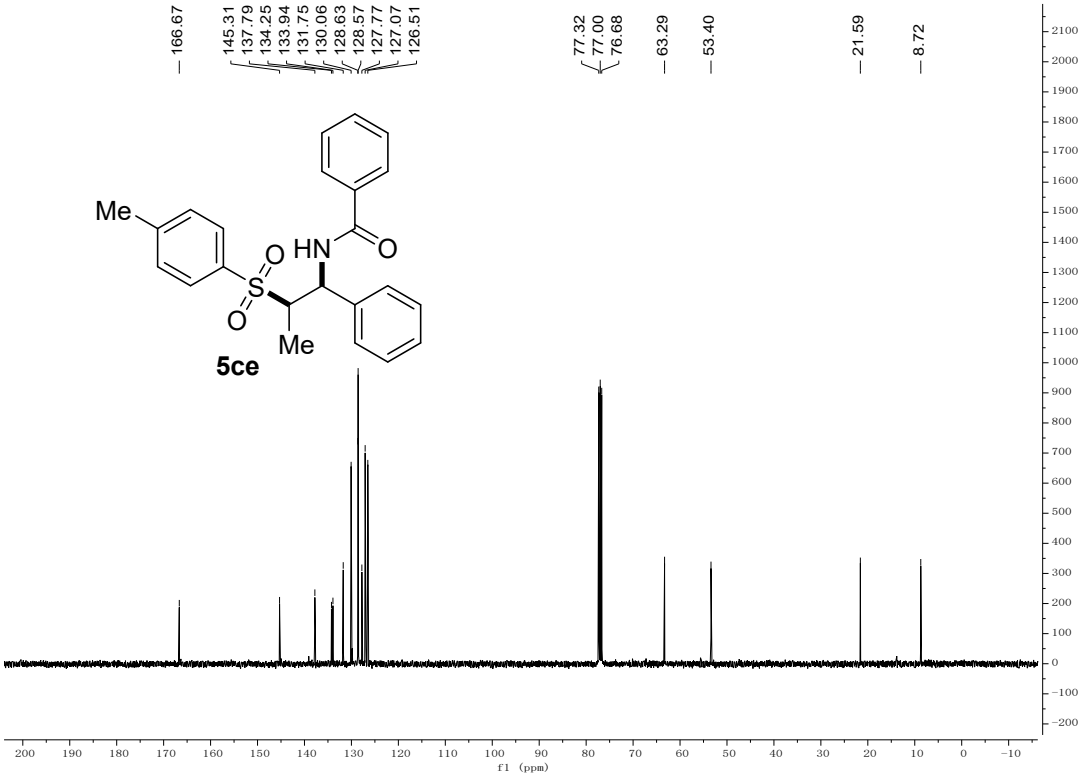
^{13}C NMR of **5cd** in $CDCl_3$



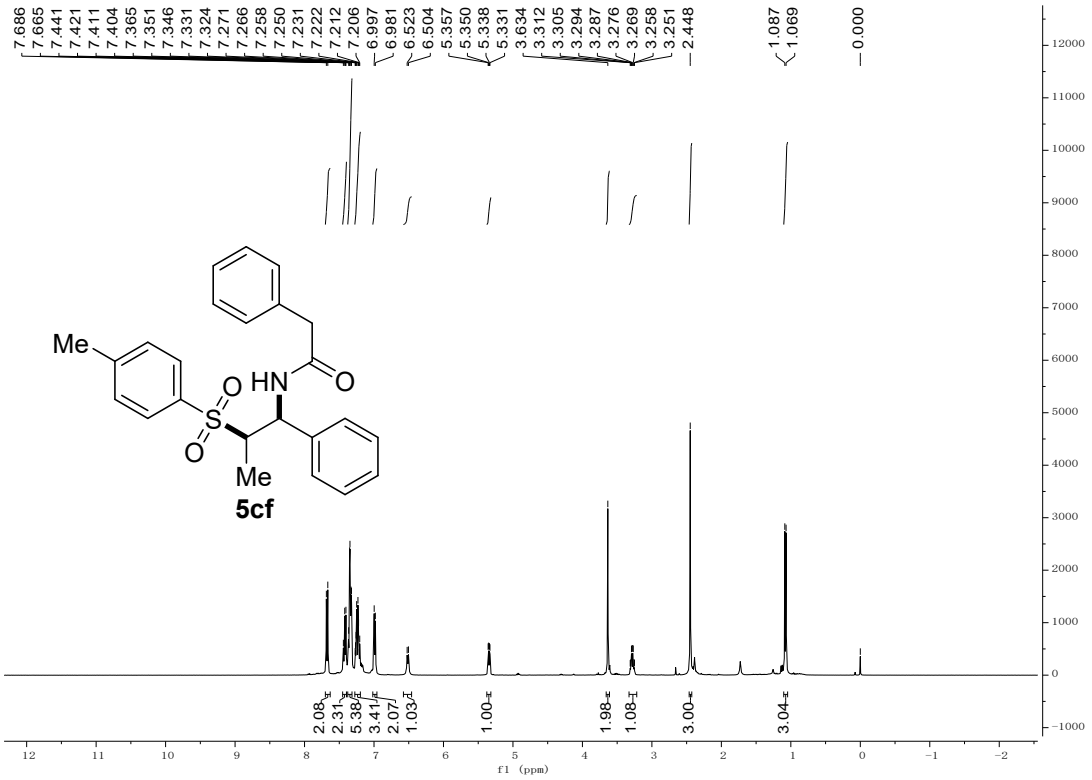
^{1}H NMR of **5ce** in $CDCl_3$



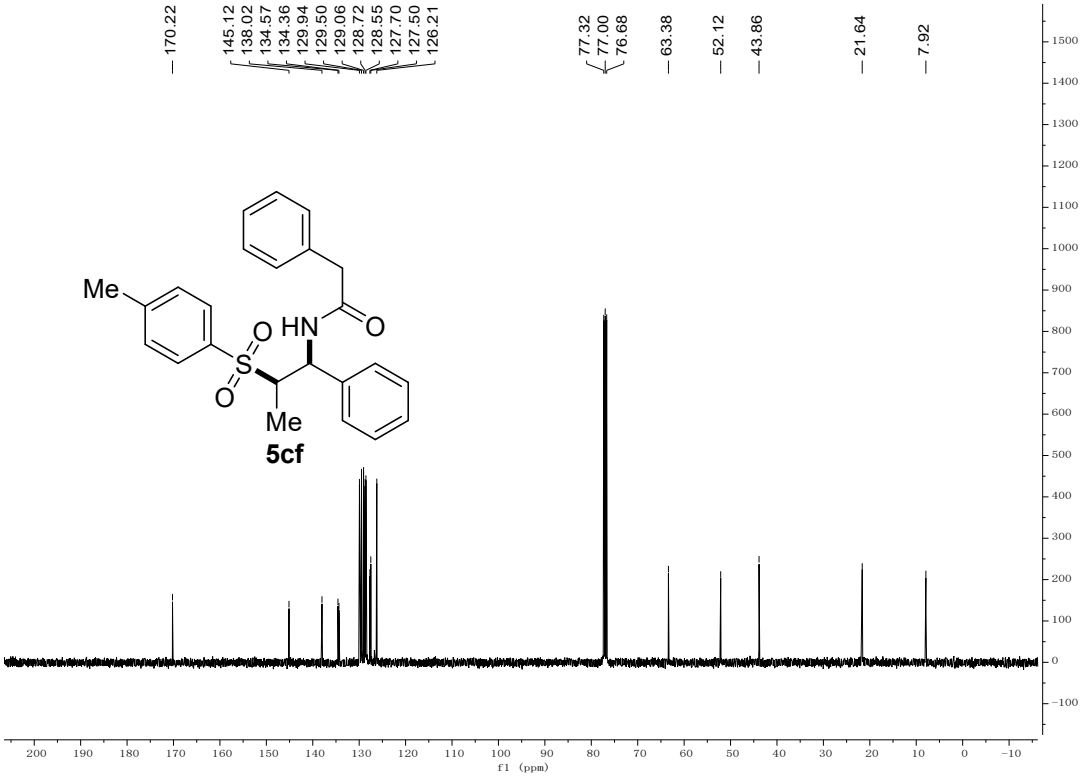
^{13}C NMR of **5ce** in $CDCl_3$



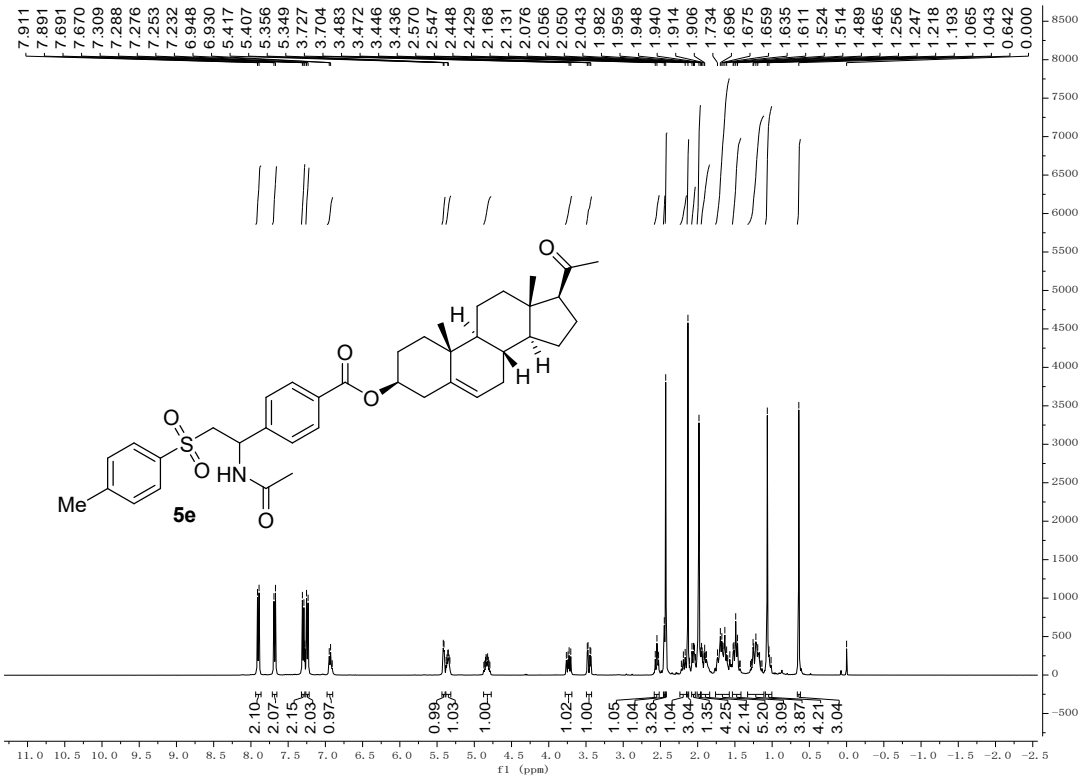
^{1}H NMR of **5cf** in $CDCl_3$



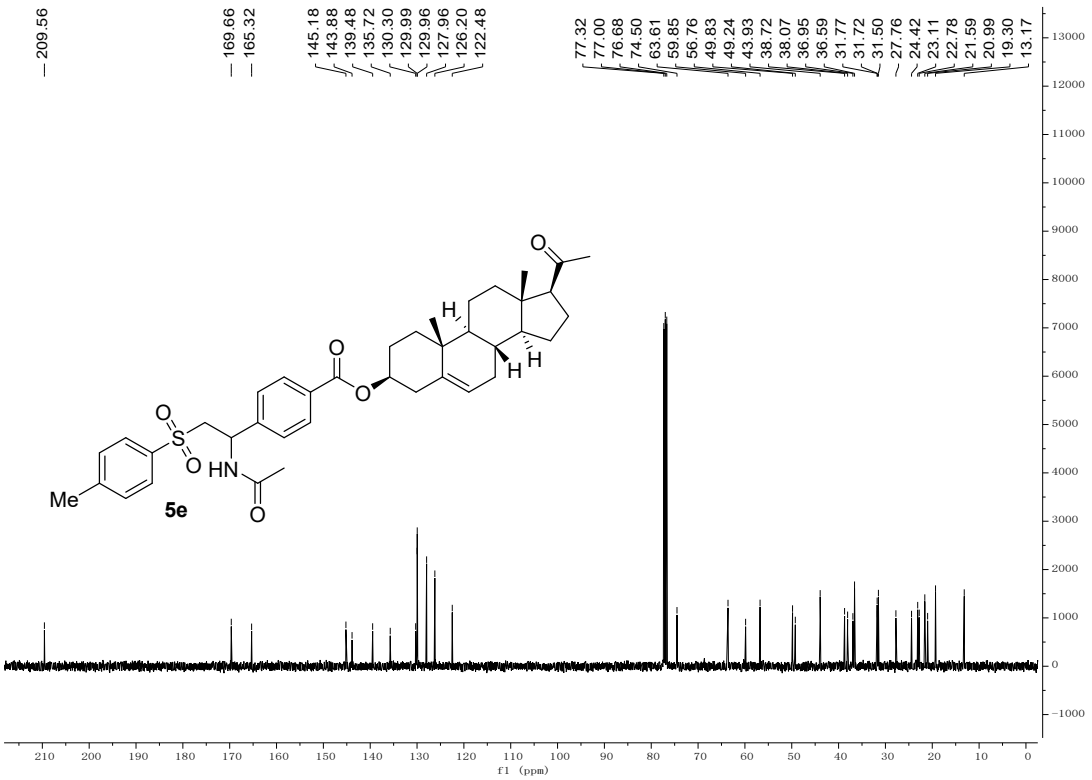
^{13}C NMR of **5cf** in $CDCl_3$



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



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



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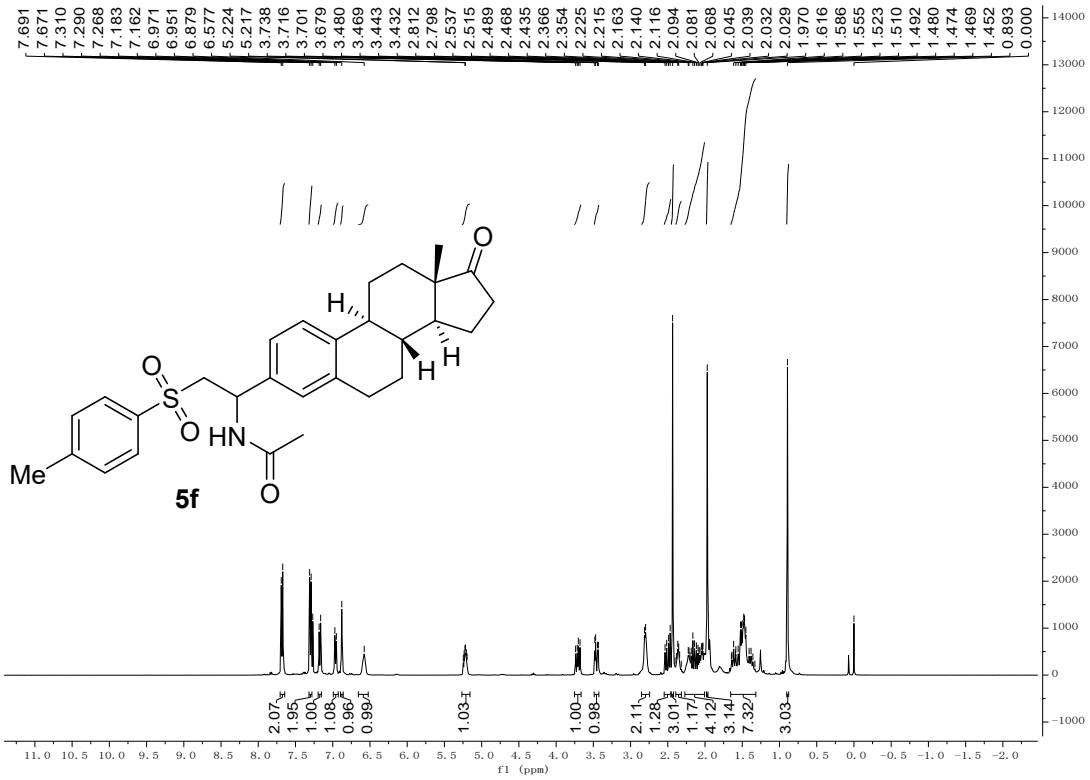

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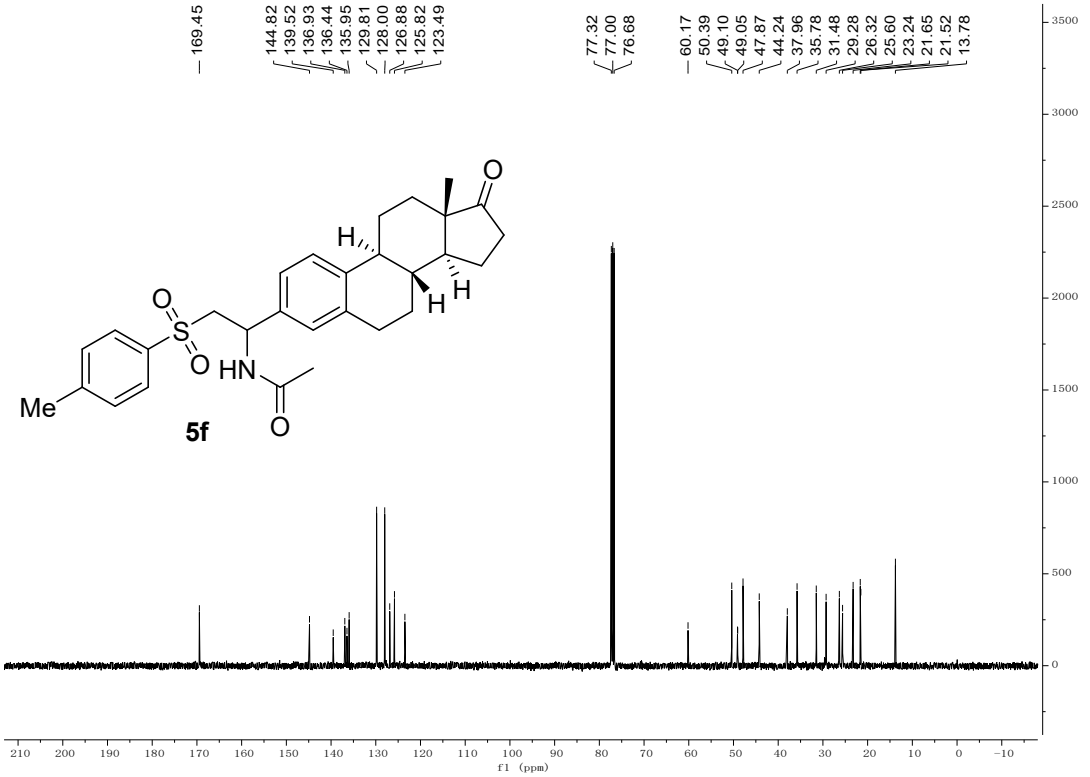
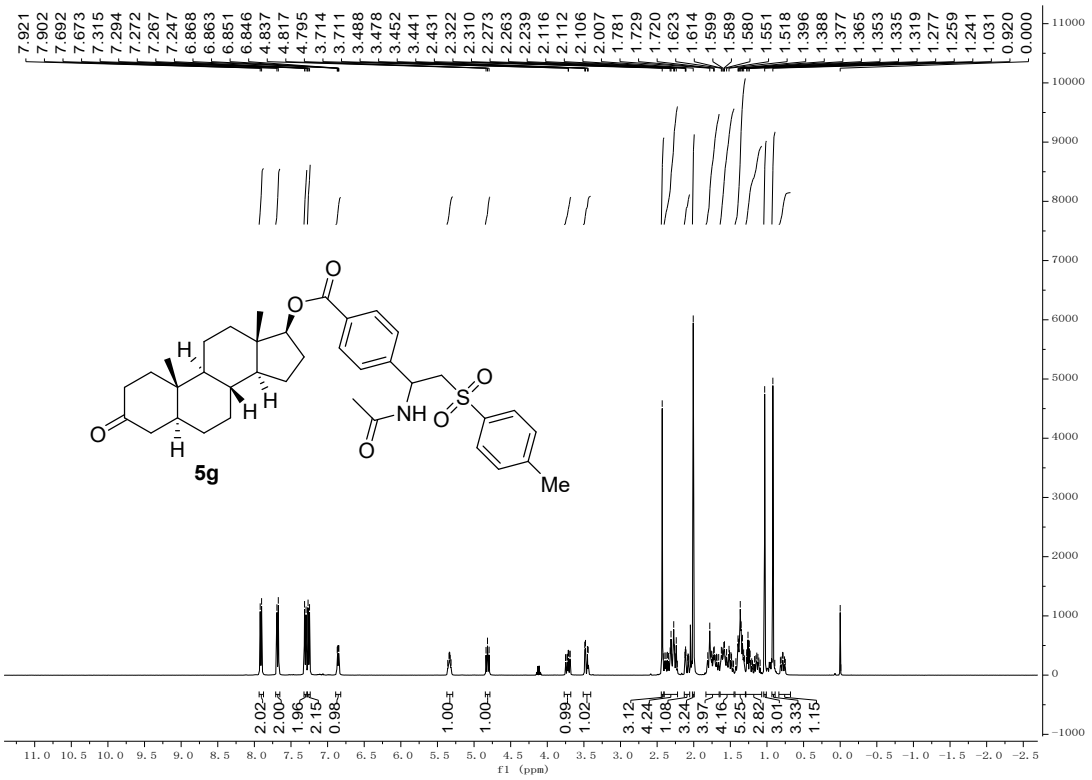
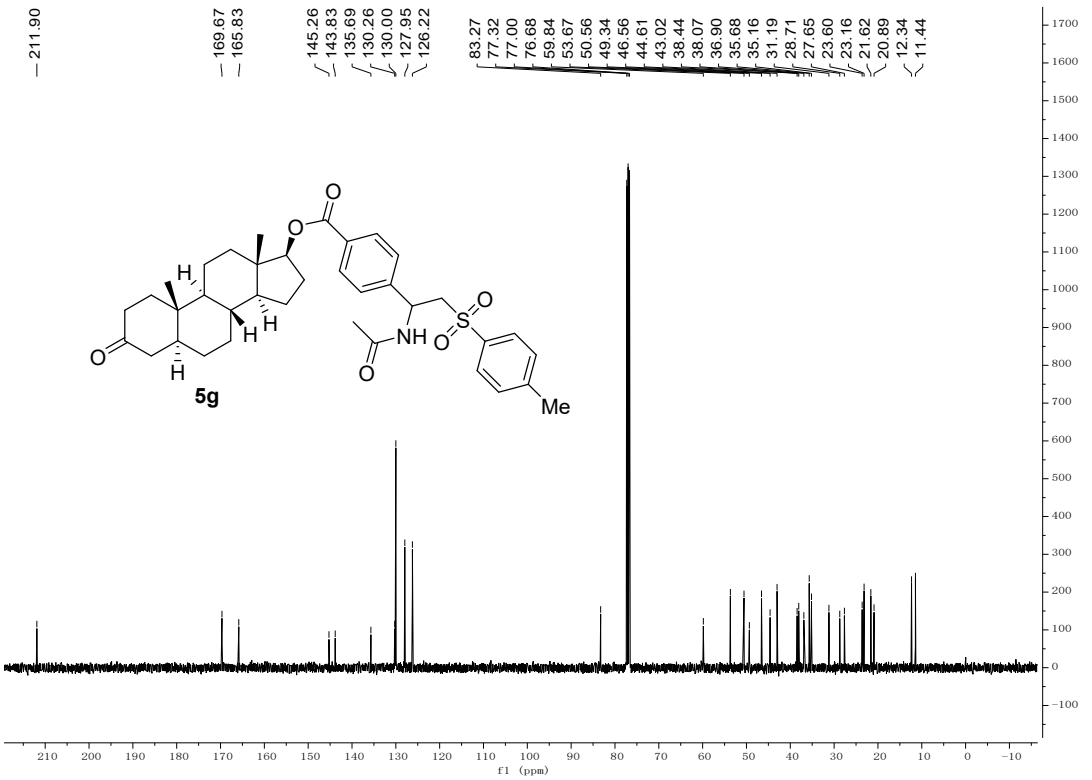


^{1}H NMR of **5g** in $CDCl_3$



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



12. References

(S1) Gesmundo, N. J.; Grandjean, J.-M. M.; and Nicewicz, D. A. Amide and Amine Nucleophiles in Polar Radical Crossover Cycloadditions: Synthesis of γ-Lactams and Pyrrolidines. *Org. Lett*., **2015**, *17*, 1316-1319.

(S2) Hoyo, A. M. del; Herraiz, A. G.; and Suero, M. G. A Stereoconvergent Cyclopropanation Reaction of Styrenes. *Angew. Chem*, *Int. Ed*., **2017**, *56*, 1610-1613.

(S3) Fang, J.; Hu, Q.; Dong, W.-L.; Xu, G.-Q.; Hu, X.-Q.; Luo, Y. -C. and Xu, P.-F. Photoredox-Catalyzed Hydrocarboxymethylation of Alkenes. *CCS Chemistry*, **2021**, *3*, 95-104.

(S4) 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**.

(S5) 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.

(S6) 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.

(S7) 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.

(S8) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

(S9) Fukui, K. The path of chemical reactions: The IRC approach. *Acc. Chem. Res.* **1981**, *14*, 363-368.

(S10) 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.