Visible-Light-Induced Radical 1,3-Hydrosulfonylation of Allylketones with Sulfonyl Chlorides

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1. General Methods

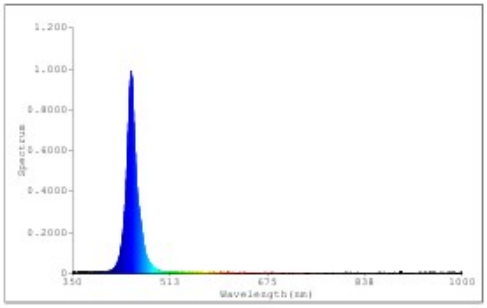
Unless otherwise noted, all commercially available reagents were used without further purification. Solvents for chromatography and reaction were purchased from commercial suppliers and used without any purification. NMR spectra were recorded for ^{1}H-NMR at 400 MHz or 600 MHz and ^{13}C-NMR at 101 MHz or 151 MHz and ^{19}F-NMR at 376 MHz. Tetramethylsilane (TMS) was served as internal standard (δ=0) or the $CDCl_3$ (δ=7.26), and chemical shits data were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and coupling constant(s) in Hz for ^{1}H-NMR. For 13C NMR, TMS (δ=0) or $CDCl_3$ (δ=7.26) was used as internal standard and spectra were obtained with complete proton decoupling. High-resolution mass spectra (HRMS) was recorded a ThermoFisher Scientific Q Exactive Focus LC-MS with ESI mode unless otherwise stated.

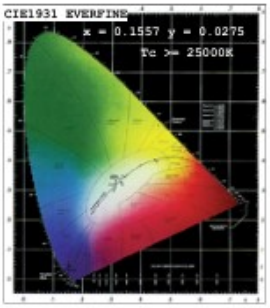
The visible light irradiation was performed with 20 W LED lamp (445-450 nm, DT) which purchased from Xuzhou Ai Jia electronic technology Co.LTD. The blue LED'S energy peak wavelength is 448 nm, the peak width at half-height is 16.0 nm. The reaction tube is made by borosilicate glass and the distance from the lamp is about 2.0 cm. The reaction was cooled by three fan and the internal temperature was determined to be 28-30 °C.

Test report

EVERFINE LEDspec Test Report 1 Of 2

Spectrum Test Report





Color Parameters:

Chromaticity Coordinate(2Deg):x=0.1557 y=0.0275/u'=0.2062 v'=0.0820 duv=-2.128

Tc=100000K Dominant WL:Ld=454.0nm Purity=98.1%

Ratio:R=1.7% G=18.0% B=80.3% Peak WL:Lp=448.4nm HWL:15.8nm

Render Index:Ra=-53.9

R1 =6.71	R2 =-38.09	R3 =-161.36	R4 =-105.20	R5 =17.54
R6 =-44.24	R7 =-59.84	R8 =-46.78	R9 =-219.51	R10=-222.91
R11=-128.48	R12=-105.69	R13=-8.80	R14=-36.39	R15=21.61

TM30 Parameters: Rf = 0.0, Rg:25.4

Photo Parameters:

Flux = 1.333 lm Eff. : 21.94 lm/W Fe = 36.34 mW

Electrical parameters:

VF = 3.036 V IF = 20.00 mA P = 60.74 mW

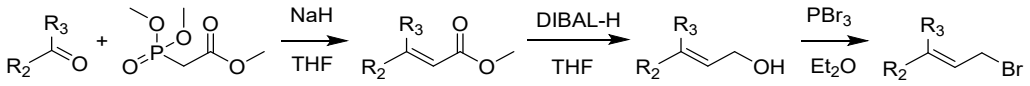
IR = 0 uA (VR = 5.000 V)

LEVEL:**[OUT] WHITE:OUT

Status: T=600.00ms Ip=8631 (13%) [HAAS1200_V1_USB] V2.00.289

2. Experimental Procedures

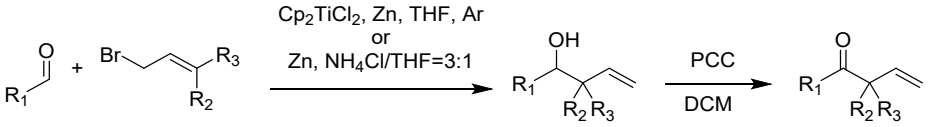
2.1 Synthesis of Allylketones



Step 1: To a suspension of NaH (60% dispersion in mineral oil, 1.2 equiv) in anhydrous THF (0.2 M) was added triethyl phosphonoacetate (1.0 equiv). The bubbling mixture stirred for one hour, then ketone derivative (1.5 equiv) was added. The reaction stirred for four more hours, then was diluted with Et_2O and rinsed with saturated aqueous $NaHCO_3$. The organic layer was rinsed with brine, dried over Na_2SO_4, and concentrated in vacuo. The product was isolated by flash chromatography (0-10% ethyl acetate/hexanes gradient) as a clear oil.

Step 2: To a solution of product in step 1 (1.0 equiv) in anhydrous THF (0.1 M) at -78°C was added DIBAL-H (2.5 equiv) slowly. The reaction was allowed to warm to room temperature over three hours. The reaction was worked up at room temperature by adding 4 mL H_2O, 4 mL 15% aqueous NaOH, and 10 mL H_2O waiting 5 minutes between each addition. The resulting suspension was carefully dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was obtained as a clear oil.

Step 3: To a solution of pyridine (0.39 equiv) and phosphorus tribromide (0.4 equiv) in ether (1M) on an ice and water bath was added the product in step 2 (1.0 equiv) in ether (6M) by syringe over 20 minutes. The reaction was warmed up to room temperature and stirred for three hours. After cooling to 0°C, the reaction was quenched with H_2O (50 mL). The organic portion was rinsed with a further 50 mL of water, dried over Na_2SO_4, and concentrated in vacuo. Filtration through a short plug of silica with hexanes followed by concentration in vacuo of the filtrate afforded the intermediate bromide as a yellow oil.[1]

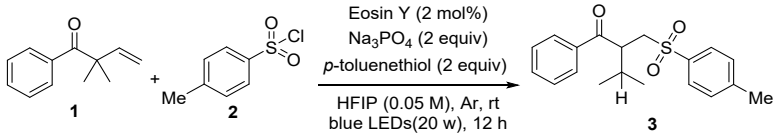


Following the reported procedure[2]: To a solution of Cp_2TiCl_2 (1mol%) and activated Zinc powder (2.4 equiv.) in anhydrous THF (0.25 M), a solution of aldehyde (1.0 equiv.) and allyl bromide (2.4 equiv.) in anhydrous THF (0.25 mL) was added dropwise at room temperature under Ar atmosphere. The reaction mixture was stirred overnight. Then, the mixture was diluted with saturated aqueous NH_4Cl and EA. The aqueous layer was extracted with EA three times and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as an eluent to afford the alcohols. TLC plate was visualized with $KMnO_4$ solution.

Or A round-bottomed flask charged with a solution of the 3,3-dimethylallylbromide (1.5 equiv) or its analogue and the aldehyde (1.0 equiv) in saturated ammonium chloride was cooled to 0 °C in ice bath. The activated zinc powder (2.0 equiv) was added to the solution slowly. After stirring for an additional 30 min at 0 °C, the ice bath was removed, and the resulting suspension was stirred overnight. Then the Zn powder was filtered and 1 N hydrochloride solution was added to the filtrate at 0 °C. The THF layer was separated from the aqueous layer, extracted with EA 3 times. The combined organic layers were washed with brine, dried with Na_2SO_4, filtered and concentrated

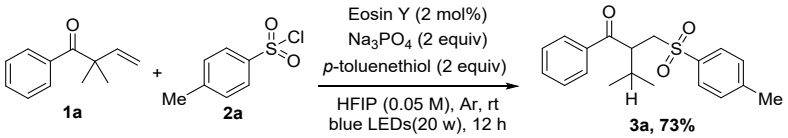
in vacuo. The crude product was was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as an eluent to afford the alcohols[3].

2.2 General Procedure for the Synthesis of Products 3



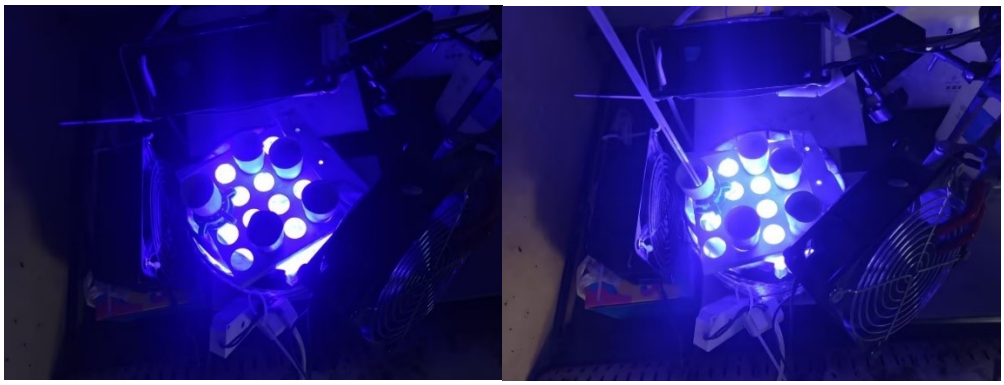
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1** (0.2 mmol, 1.0 equiv), sulfonyl chlorides **2** (0.3 mmol, 1.5 equiv), Na_3PO_4 (0.4 mmol, 2.0 equiv), *p*-toluenethiol (0.4 mmol, 2.0 equiv), Eosin Y (2 mol%), HFIP (4 ml, 0.05 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Then the reaction mixture was diluted with EA and solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (10:1 to 2:1, v:v) as the eluent.

2.3 Scale-up Experiment

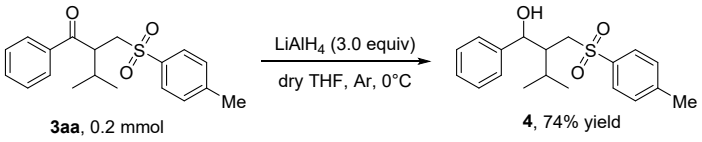


An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1** (2 mmol, 1.0 equiv), sulfonyl chlorides **2** (3 mmol, 1.5 equiv), Na_3PO_4 (4 mmol, 2.0 equiv), *p*-toluenethiol (4 mmol, 2.0 equiv), Eosin Y (2 mol%), HFIP (40 mL, 0.05 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Then the reaction mixture was diluted with EA and solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (10:1, v:v) as the eluent afford the pure product **3aa** as white solid (964 mg, 73%).

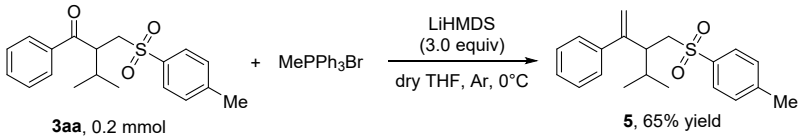
2.4 Reaction setup



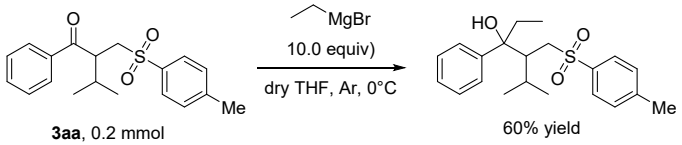
2.5 Derivatization of 3aa



To cold (0℃) solution of **3aa** (0.2 mmol, 1.0 equiv), in dry THF at Ar atmosphere was added $LiAlH_4$ (2.5 M in dry THF, 0.24 mL, 3.0 equiv) dropwise. After added the $LiAlH_4$, the mixture was stirred in the same temperature for another 2 h and the **3aa** was completely consumed by TLC detection. Then the mixture was worked up at 0 ℃ by adding 0.023 mL water, 0.069 mL 15% aqueous NaOH and 0.023 mL water waiting 5 minutes between each addition. The resulting suspension was carefully dried over $MgSO_4$, filtered, concentrated in vacuo and purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (6:1) as the eluent to afford the pure product **4** as white solid (49.1 mg, 74%).



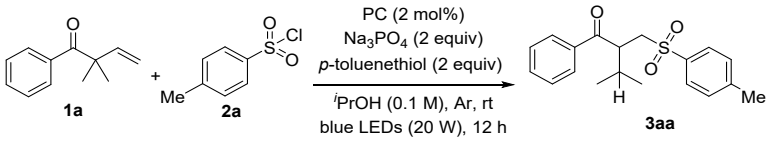
To cold (0℃) solution of **3aa** (0.2 mmol, 1.0 equiv) and $MePPh_3Br$ (144.2 mg, 0.4 mmol, 2.0 equiv) in dry THF at Ar atmosphere was added LiHMDS (1.0 M in dry THF, 0.60 mL, 3.0 equiv). The mixture was stirred in the same temperature for 3 h and the start material **3aa** was completely consumed by TLC detection. Then the reaction solution was quenched by water, diluted by EA (20 mL), washed with saturated brine, dried over $MgSO_4$, filtered, concentrated in vacuo and purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (10:1) as the eluent to afford the pure product **5** as colorless oil (42.6 mg, 65%).



To cold (0℃) solution of **3aa** (0.2 mmol, 1.0 equiv) in dry THF at Ar atmosphere was added EtMgBr (2.0 M in dry THF, 1.0 mL, 10.0 equiv). The mixture was stirred at room temperature for 6 h and the start material **3aa** was completely consumed by TLC detection. Then the reaction solution was quenched by water, diluted by EA (20 mL), washed with saturated brine, dried over $MgSO_4$, filtered, concentrated in vacuo and purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (4:1) as the eluent to afford the pure product **6** as colorless oil (43.2 mg, 60%).

3. Optimization of the Reaction Conditions

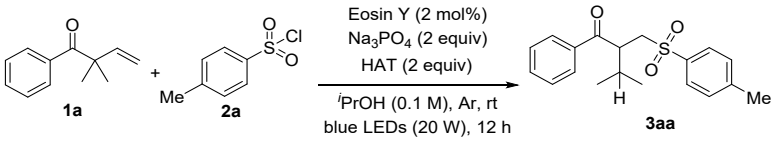
3.1 Evaluation of Photocatalyst (PC)



Entry	PC	Yield
1	Eosin Y	57%
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	42%
3	$Ir[(dtbbpy)(ppy)_2]PF_6$	38%
4	fac-$Ir(ppy)_3$	9%
5	$Ru(bpy)_3PF_6$	12%
6	$Ru(bpy)_3Cl_2\,6H_2O$	20%
7	Mes-Acr-ClO_4	15%
8	4CzIPN	40%
9	Rodamine B	8%
10	AQ	0%
11	PQ	0%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), PC (2mol%), ^{i}PrOH (2 mL), Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

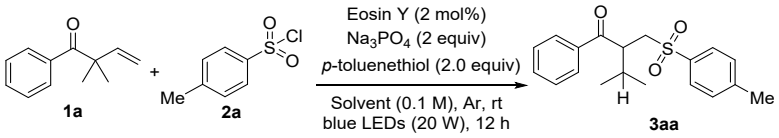
3.2 Evaluation of Hydrogen Atom Transfer (HAT)



Entry	HAT	Yield
1	p-Toluenethiol	57%
2	HE	0%
3	1,2-Ethanedithiol	30%
4	Butanethiol	34%
5	Ph_2MeSiH	0%
6	Et_3SiH	0%
7	$tBuMe_2SiOH$	0%
8	TTMSS	0%
9	4-Methoxybenzenethiol	57%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), ^{i}PrOH (2 mL), Na_3PO_4 (2.0 equiv). HAT (2.0 equiv). Ar atmosphere, room temperature.

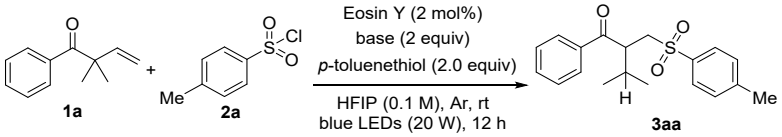
3.3 Evaluation of Solvent



Entry	Solvent	Yield
1	HFIP	75%
2	MeOH	24%
3	EtOH	15%
4	MeCN	0%
5	THF	10%
6	Acetone	8%
7	DMSO	16%
8	TFE	61%
9	1,4-dioxane	0%
10	Toluene	0%
11	DCM	10%
12	DMC	13%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), Solvent (2 mL), Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

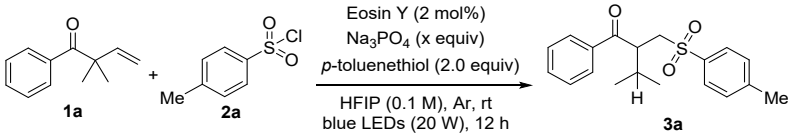
3.4 Evaluation of Base



Entry	Additive	Yield
1	Na_2HPO_4	59%
2	NaH_2PO_4	5%
3	K_3PO_4	70%
4	K_2HPO_4	68%
5	KH_2PO_4	5%
6	Na_2CO_3	68%
7	$NaHCO_3$	64%
8	K_2CO_3	59%
9	$KHCO_3$	60%
10	Cs_2CO_3	48%
11	DMAP	51%
12	Et_3N	43%
13	DCHA	36%
14	Prydine	62%
15	2,6-lutidine	32%
16	DBU	50%
17	DIPA	51%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP (2 mL), base (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

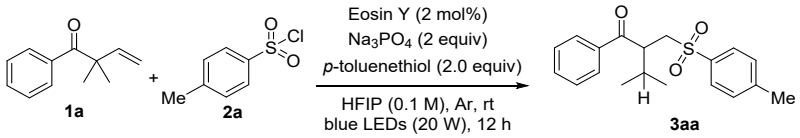
3.5 Evaluation of the Equivalent of Base



Entry	Na_3PO_4(x equiv)	Yield
1	1	65%
2	2	75%
3	3	78%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP (2 mL), Na_3PO_4 (x equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

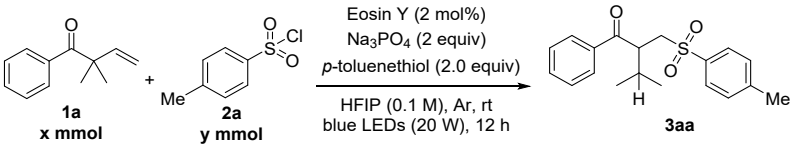
3.6 Evaluation of the Equivalent of *p*-toluenethiol



Entry	p-Toluenethiol (x equiv)	Yield
1	0.2	5%
2	1	39%
3	2	75%
4	3	70%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP (2 mL), Na_3PO_4 (2.0 equiv). *p*-toluenethiol (x equiv). Ar atmosphere, room temperature.

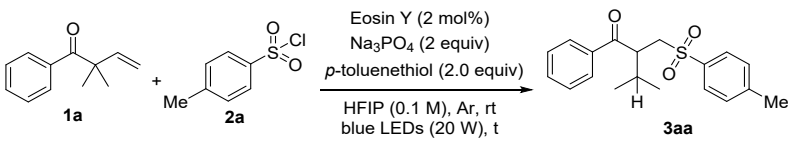
3.7 Evaluation of the ratio of 1:2



Entry	1 (x mmol)	2 (y mmol)	Yield
1	0.1 mmol	0.1 mmol	74%
2	0.1 mmol	0.15 mmol	75%
3	0.1 mmol	0.2 mmol	75%
4	0.15 mmol	0.1 mmol	75%

Reaction Conditions: **1a** (x mmol), **2a** (y mmol), Eosin Y (2 mol%), HFIP (2 mL), Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

3.8 Evaluation of the Reaction Time

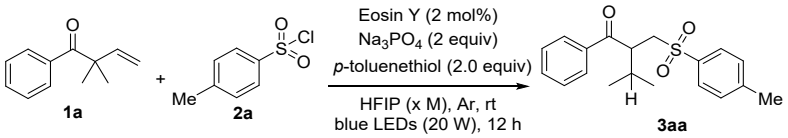


Entry	Time	Yield

1	6 h	73%
2	12 h	75%
3	18 h	70%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP (2 mL), Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

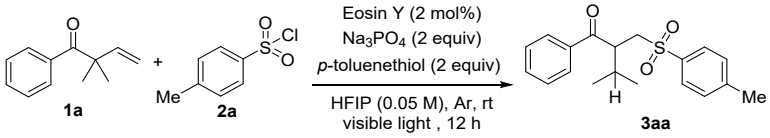
3.9 Evaluation of the concentration of Substrates 1



Entry	x M	Yield
1	0.05	89%
2	0.1	75%
3	0.2	65%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP, Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

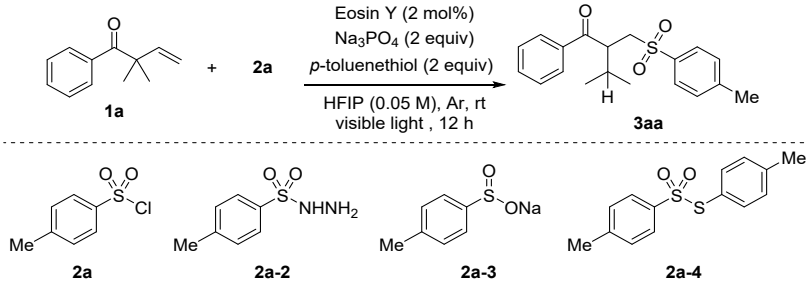
3.10 Evaluation of the wavelength of the LEDs and light intensity



Entry	wavelength	light intensity	Yield
1	535 nm	100%	86%
2	450 nm	100%	89%
3	450 nm	75%	85%
4	450 nm	50%	80%
5	405 nm	100%	64%
6	385 nm	100%	36%

Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Eosin Y (2 mol%), HFIP, Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

3.11 Evaluation of the sulfonyl radical precursors



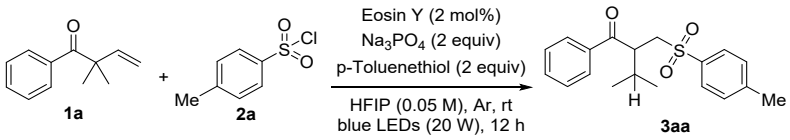
Entry	sulfonyl radical precursors	Yield
1	2a	89%

2	2a-2	7%
3	2a-3	42%
4	2a-4	82%

Reaction Conditions: **1a** (0.2 mmol), sulfonyl radical precursors (0.3 mmol), Eosin Y (2 mol%), HFIP, Na_3PO_4 (2.0 equiv). *p*-toluenethiol (2.0 equiv). Ar atmosphere, room temperature.

4. Mechanistic Studies

4.1 Control experiments

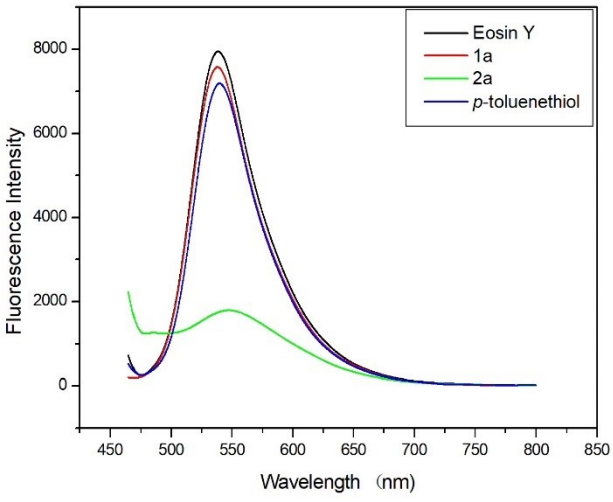


Entry	Deviation	Yield
1	No PC	0%
2	Under Dark	0%
3	No base	0%
4	No p-Toluenethiol	0%
5	In air	0%

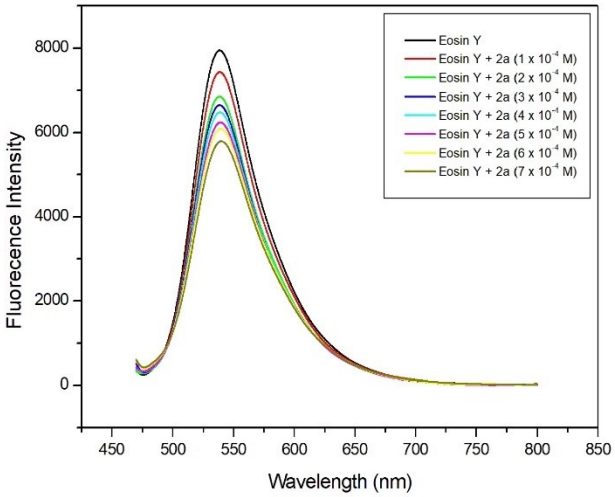
Reaction Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol).

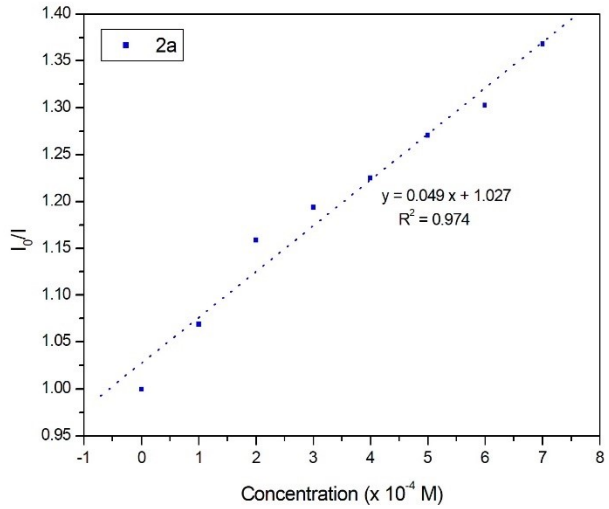
4.2 Luminescence quenching experiments

Fluorescence spectra was collected on Lumina for all experiments. A series of solutions of Eosin Y (1×10^{-5} M) and Eosin Y (1×10^{-5} M) with different quenchers (1a, 2a or *p*-toluenethiol of 5×10^{-3} M) in quartz cuvettes were prepared freshly. Then each sample was excited at 425 nm and emission intensity at 539 nm was measured. As showed in the spectra, the substrate of sulfonyl chloride (2a) quenched the excited state of Eosin Y most.



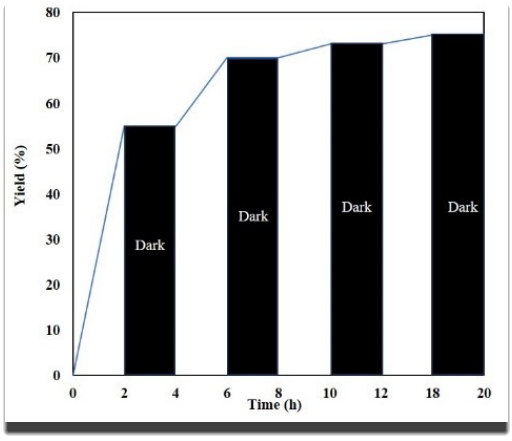
In the HFIP solution of Eosin Y (1×10^{-5} M, 3 mL), a solution (0.01 M) of sulfonyl chloride (2a) was successively added in a gradient of 30 μL and uniformly stirred. The mixture was excited at 425 nm and fluorescence intensity of 0 μL, 30.0 μL, 60 μL, 90 μL, 120 μL, 150 μL, 180 μL, 210 μL for 2a was recorded. Plots were derived according to the Stern–Volmer equation.



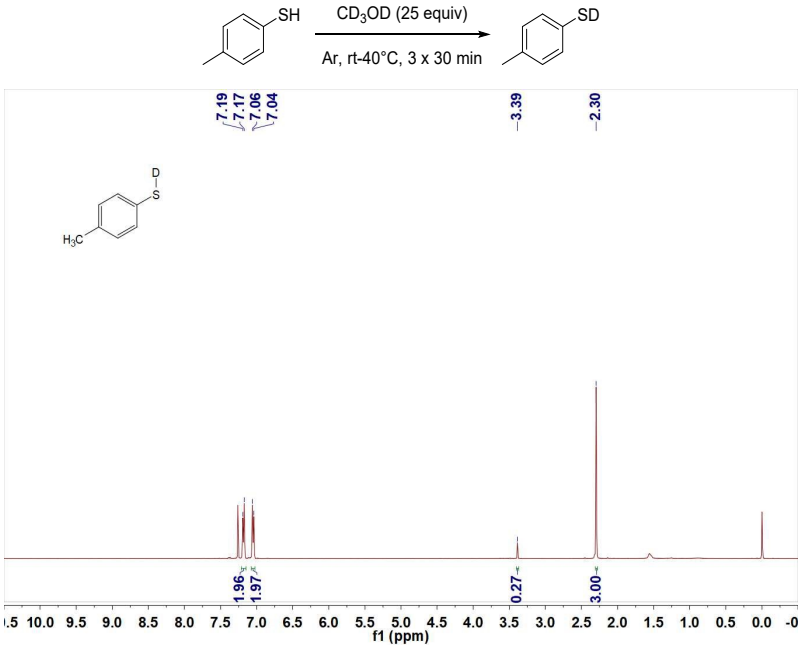


4.3 Light on-off experiment

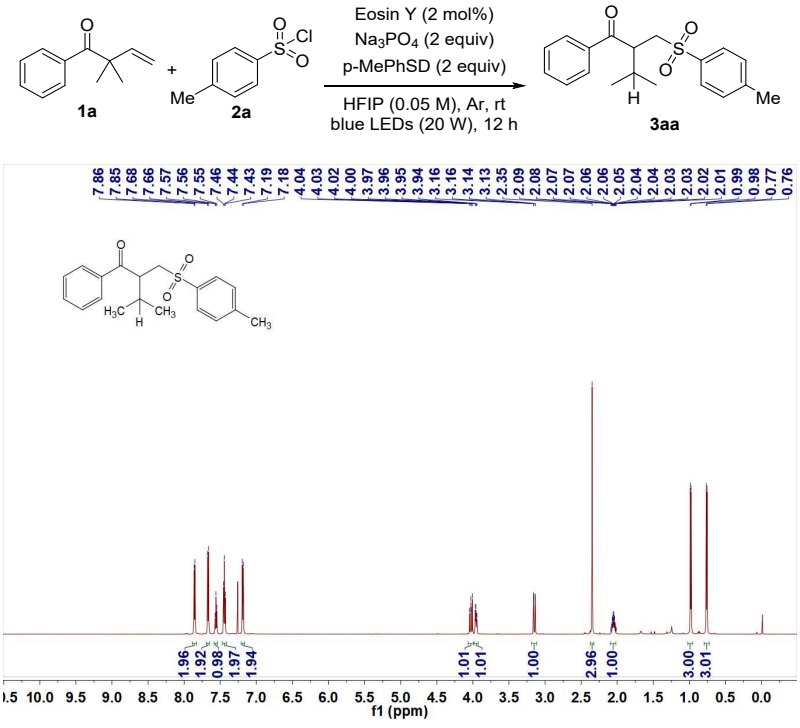
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1** (2 mmol, 1.0 equiv), sulfonyl chlorides **2** (3 mmol, 1.5 equiv), Na_3PO_4 (4 mmol, 2.0 equiv), *p*-toluenethiol (4 mmol, 2.0 equiv), Eosin Y (2 mol%), HFIP (40 mL, 0.05 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for indicated time. The corresponding yield was determined by ^{1}H NMR analysis.



4.4 Deuteration reaction using p-MePhSD

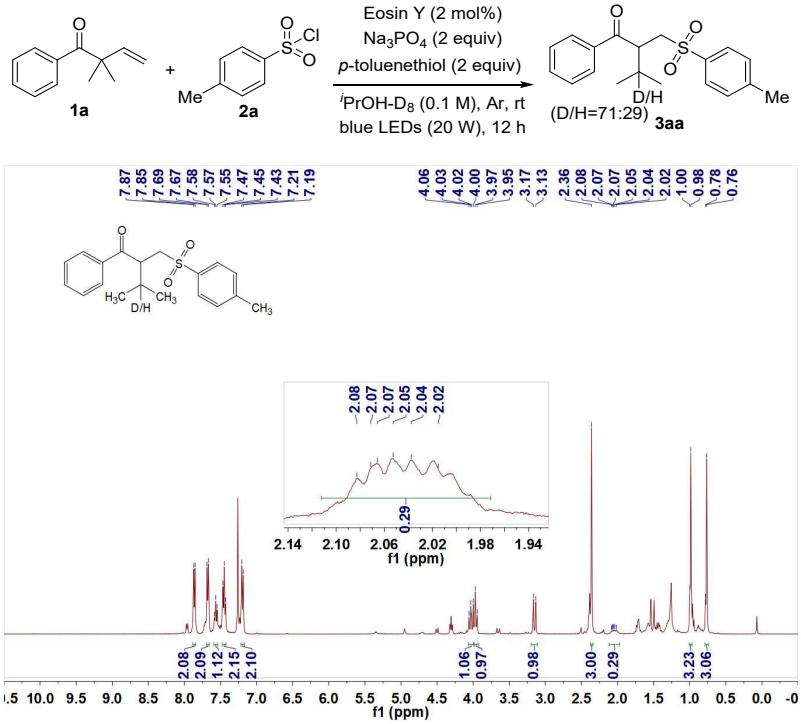


The experiment was carried out in a 12 mL screw cap equipped with a Teflon-coated magnetic stirring bar. The tube was charged with *p*-toluenethiol (248 mg, 2.0 mmol). The atmosphere was removed and filled with argon. Next, methanol-d4 (2.0 mL, 1.78 g, 50 mmol, 25 equiv.) was added via syringe under counter current argon flow. The vial was closed and stirred vigorously for 5 minutes, then the solvent was evaporated in vacuo and under slight heating (50 °C) over ca. 30 minutes. This process was repeated three more times, after which the resulting white solid (73% deuterium incorporation) was used in the next step[4].



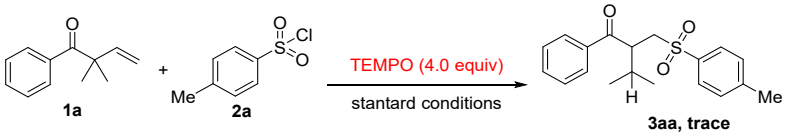
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1a** (0.1 mmol, 1.0 equiv), sulfonyl chlorides **2a** (0.15 mmol, 1.5 equiv), Na_3PO_4 (0.2 mmol, 2.0 equiv), p-MePhSD (0.2 mmol, 2.0 equiv), Eosin Y (2 mol%), HFIP (2 ml, 0.05 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Then the reaction mixture was diluted with EA and solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (8:1, v:v) as the eluent to obtain the product **3aa** (29.4 mg, 80%yield). The deuterium exchange of product 3aa was 0%.

4.5 Deuteration reaction using ^{i}PrOH-D_8 as solvent



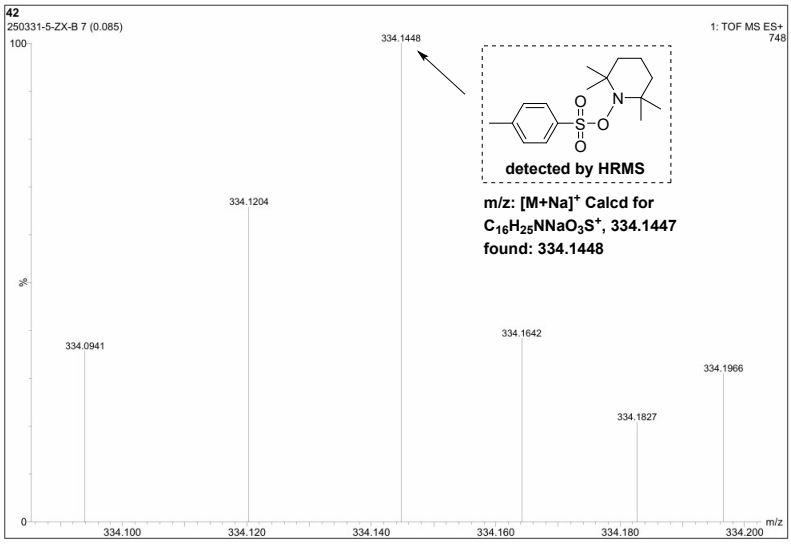
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1a** (0.1 mmol, 1.0 equiv), sulfonyl chlorides **2a** (0.15 mmol, 1.5 equiv), Na_3PO_4 (0.2 mmol, 2.0 equiv), *p*-toluenethiol (0.2 mmol, 2.0 equiv), Eosin Y (2 mol%), ^{i}PrOH-D_8 (1 ml, 0.1 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Then the reaction mixture was diluted with EA and solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (8:1, v:v) as the eluent to obtain the product **[D]-3aa** (15.7 mg, 47%yield, 71% deuterium incorporation).

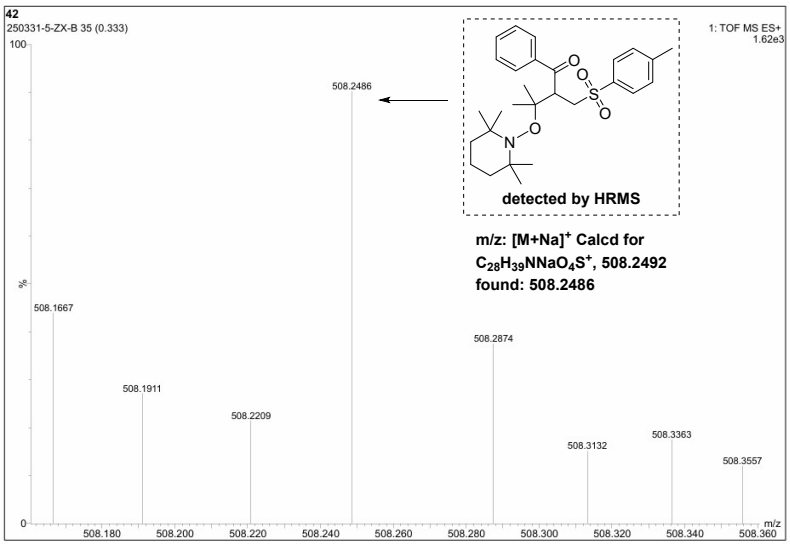
4.6 Radical capture experiments

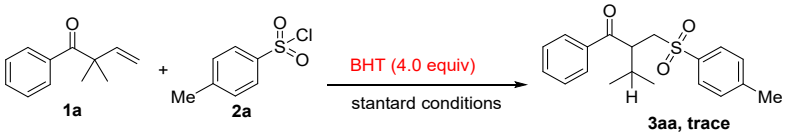


An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1a** (0.1

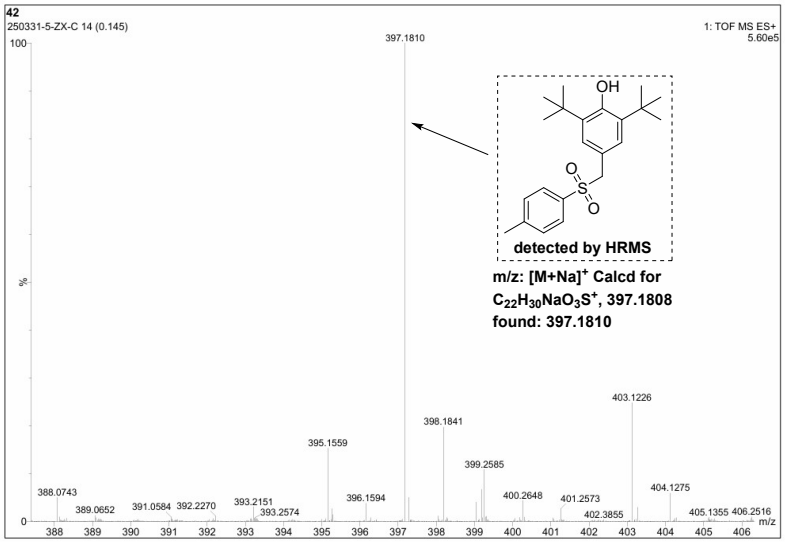
mmol, 1.0 equiv), sulfonyl chlorides **2a** (0.15 mmol, 1.5 equiv), Na_3PO_4 (0.2 mmol, 2.0 equiv), *p*-toluenethiol (0.2 mmol, 2.0 equiv), Eosin Y (2 mol%), 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO) (4.0 equiv) and HFIP (2 mL, 0.05 M) in Ar atmosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Furthermore, the reaction mixture was analyzed by HRMS.

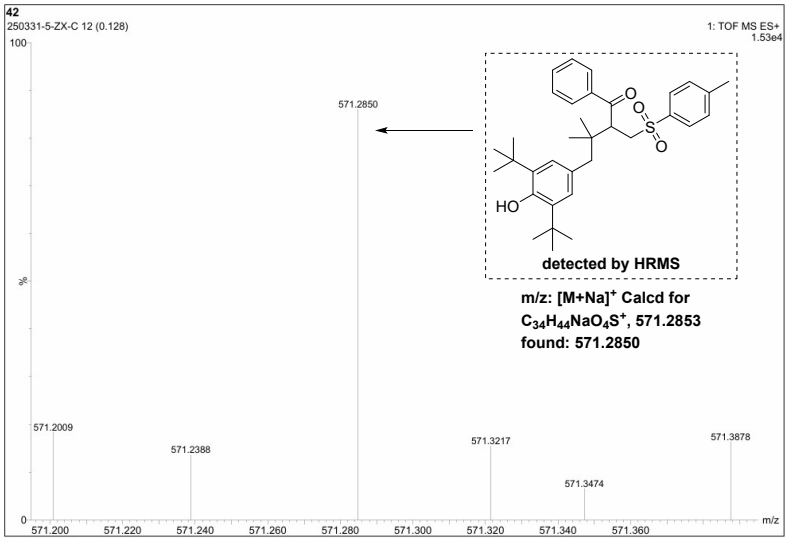


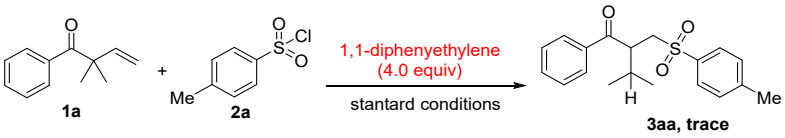




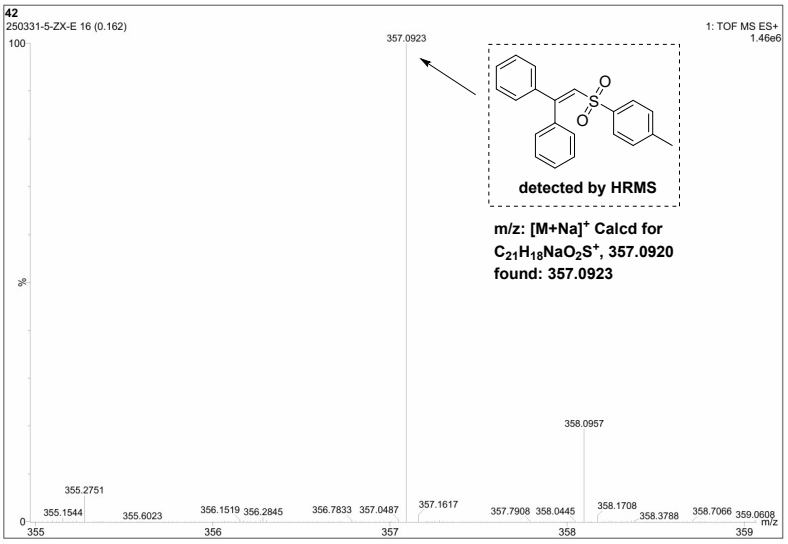
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1a** (0.1 mmol, 1.0 equiv), sulfonyl chlorides **2a** (0.15 mmol, 1.5 equiv), Na_3PO_4 (0.2 mmol, 2.0 equiv), *p*-toluenethiol (0.2 mmol, 2.0 equiv), Eosin Y (2 mol%), 2,6-di-tert-butyl-4-methylphenol (BHT) (4.0 equiv) and HFIP (2 mL, 0.05 M) in Ar atmosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Furthermore, the reaction mixture was analyzed by HRMS.

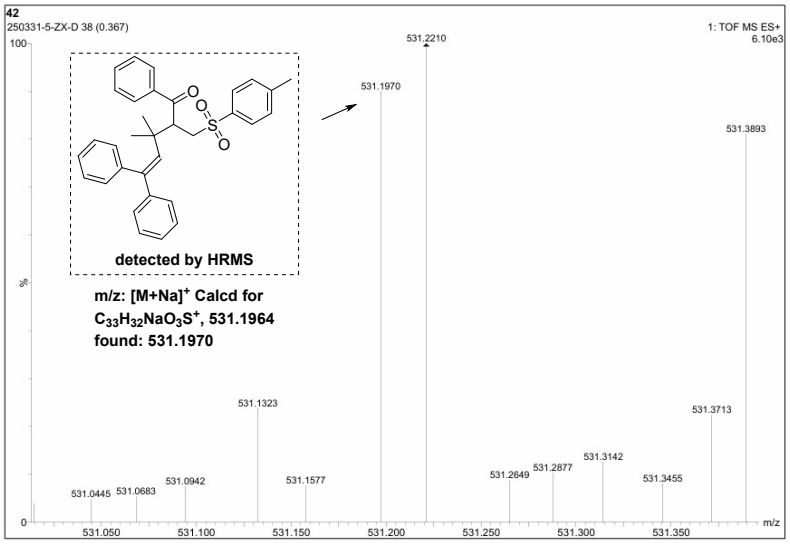






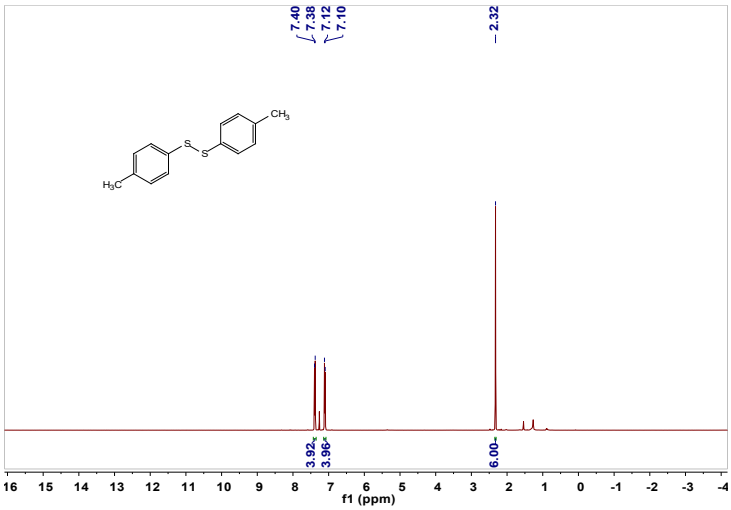
An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1a** (0.1 mmol, 1.0 equiv), sulfonyl chlorides **2a** (0.15 mmol, 1.5 equiv), Na_3PO_4 (0.2 mmol, 2.0 equiv), *p*-toluenethiol (0.2 mmol, 2.0 equiv), Eosin Y (2 mol%), 1,1-diphenyethylene (4.0 equiv) and HFIP (2 mL, 0.05 M) in Ar atmosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Furthermore, the reaction mixture was analyzed by HRMS.

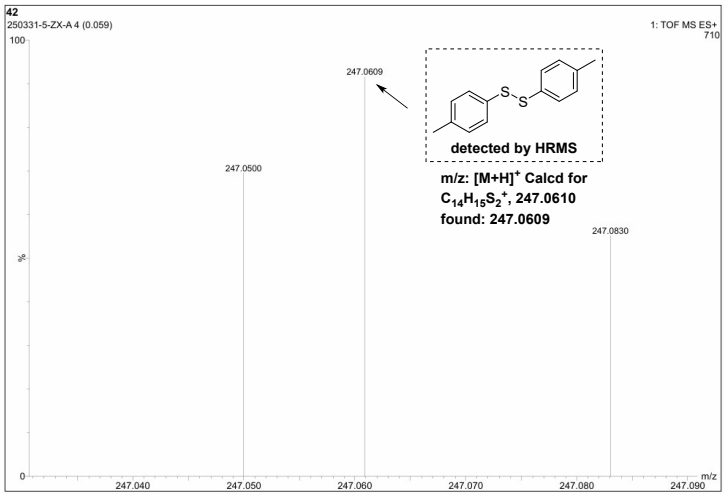




4.7 Detection of disulfide

An oven-dried screw cap reaction tube installed a magnetic stirrer was added reagent **1** (2 mmol, 1.0 equiv), sulfonyl chlorides **2** (3 mmol, 1.5 equiv), Na_3PO_4 (4 mmol, 2.0 equiv), *p*-toluenethiol (4 mmol, 2.0 equiv), Eosin Y (2 mol%), HFIP (40 mL, 0.05 M) in Ar atomosphere. The tube was irradiated by 20 w blue LEDs and stirred at room temperature for 12 h. Then the reaction mixture was diluted with EA and solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether:ethyl acetate (100:1, v:v) as the eluent afford the pure disulfide in 10% yield.

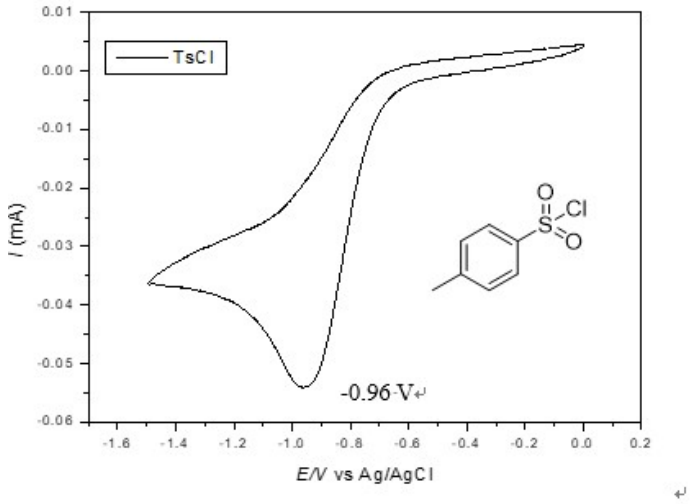




4.8 Electrochemical Measurements

Cyclic Voltammetry was performed using CH Instruments using a glassy carbon working electrode, a silver/silver chloride electrode and a platinum wire counter electrode in a 40 mL electrolyte of Bu_4NPF_6 (0.1 M) in degassed MeCN. The potential was scanned at a scan rate 100 mV.

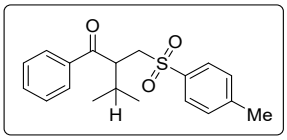
Cyclic voltammograms of sulfonyl chloride (2a, 1.5 mM) in MeCN



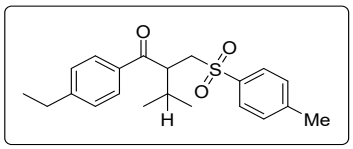
5. Supplementary References

1. Comito, R. J., Fineli, F. G., D, MacMillan, W. C. *J. Am. Chem. Soc*. **2013**, *135*, 9358-9361.
2. Chen, G., Zhang, X., Zeng, Z., W., Peng, W., Liang, Q., Liu, J. *ChemistrySelect* **2017**, *2*, 1979-1982.
3. Zhang, G.-Y., Lv, S-S., Shoberu, A., Zou, J.-P. *J. Org. Chem.* **2017**, *82*, 9801-9807.
4. Vos, D. D., Cunha, A. V., Jei, B. B., Maes, B. U. W. *ACS Catal,* **2024**, *14*, 12282-12296.

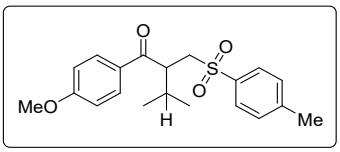
6. Product Characterization



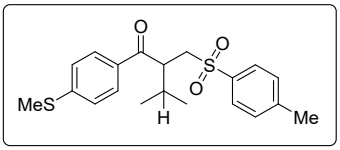
3-Methyl-1-phenyl-2-(tosylmethyl)butan-1-one (**3aa**). The product (89% yield, 58.7 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.02 (dd, *J* = 13.1, 10.5 Hz, 1H), 3.95 (dd, *J* = 10.2, 4.0 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 2.34 (s, 3H), 2.09 – 2.00 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 144.7, 136.5, 136.2, 133.3, 129.8, 128.7, 128.5, 128.2, 54.4, 46.1, 30.8, 21.6, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}O_3S$: 331.1362, Found 331.1364.



1-(4-Ethylphenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ba**). The product (68% yield, 48.7 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.03 (dd, *J* = 13.5, 10.2 Hz, 1H), 3.94 (dd, *J* = 10.0, 3.8 Hz, 1H), 2.72 (q, *J* = 7.5 Hz, 2H), 2.36 (s, 3H), 2.11 – 2.02 (m, 1H), 1.27 (t, *J* = 7.6 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 150.4, 144.7, 136.3, 134.2, 129.8, 128.7, 128.2, 128.2, 54.5, 46.0, 30.9, 29.0, 21.7, 20.8, 18.4, 15.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{27}O_3S$: 359.1675, Found 359.1671.

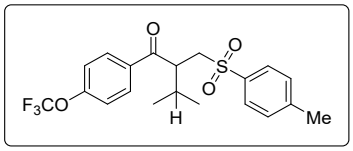


1-(4-Methoxyphenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ca**). The product (71% yield, 51.1 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 1H), 4.01 (dd, *J* = 13.9, 10.0 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.86 (s, 3H), 3.13 (d, *J* = 13.8 Hz, 1H), 2.34 (s, 3H), 2.07 – 1.99 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 163.9, 144.6, 136.6, 130.8, 129.8, 129.8, 128.3, 113.9, 55.6, 54.8, 45.9, 31.1, 21.6, 20.7, 18.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_4S$: 361.1468, Found 361.1466.

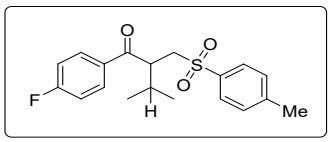


3-Methyl-1-(4-(methylthio)phenyl)-2-(tosylmethyl)butan-1-one (**3da**). The product (65%yield, 49.0 mg) was purified with column chromatography (PE:EA=5:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H),

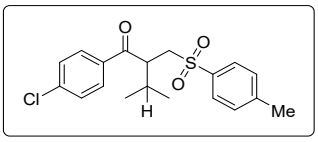
7.19 (d, *J* = 8.0 Hz, 2H), 4.00 (dd, *J* = 13.8, 10.1 Hz, 1H), 3.88 (dd, *J* = 9.9, 4.3 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 2.51 (s, 3H), 2.35 (s, 3H), 2.08 – 1.96 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.3, 146.4, 144.7, 136.3, 132.9, 129.8, 128.9, 128.2, 125.0, 54.6, 45.8, 31.1, 21.7, 20.7, 18.5, 14.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_3S_2$: 377.1240, Found 377.1246.



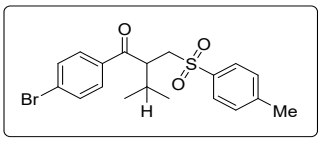
3-Methyl-2-(tosylmethyl)-1-(4-(trifluoromethoxy)phenyl)butan-1-one (**3ea**). The product (92%yield, 76.2 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.02 – 3.96 (m, 1H), 3.92 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.16 (d, *J* = 13.4 Hz, 1H), 2.37 (s, 3H), 2.07 – 1.99 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.2, 152.9, 144.9, 136.2, 134.9, 130.6, 129.9, 128.2, 120.5, 120.4 (q, *J* = 260 Hz), 54.7, 46.1, 31.0, 21.7, 20.8, 18.5. **^{19}F NMR** (376 MHz, CDCl3) δ -57.60. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{22}F_3O_4S$: 415.1185, Found 415.1189.



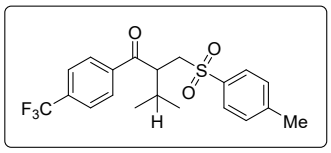
1-(4-Fluorophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3fa**). The product (68%yield, 47.3 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 8.2 Hz, 2H), 3.99 (dd, *J* = 13.6, 10.2 Hz, 1H), 3.91 (dd, *J* = 10.3, 3.3 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.36 (s, 3H), 2.07 – 1.99 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 166.0 (d, *J* = 256.2 Hz), 144.8, 136.6, 133.3 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 9.3 Hz), 129.9, 128.2, 115.8 (d, *J* = 22.0 Hz), 54.8, 46.1, 31.0, 21.6, 20.7, 18.6. **^{19}F NMR** (376 MHz, CDCl3) δ -104.83. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{22}FO_3S$: 349.1268, Found 349.1265.



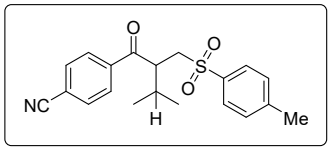
1-(4-Chlorophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ga**). The product (78%yield, 56.8 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.99 (dd, *J* = 13.5, 10.2 Hz, 1H), 3.90 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 2.38 (s, 3H), 2.06 – 1.98 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 144.9, 139.9, 136.3, 135.1, 129.9, 129.9, 129.1, 128.2, 54.7, 46.1, 31.0, 21.7, 20.7, 18.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{22}ClO_3S$: 365.0973, Found 365.0971.



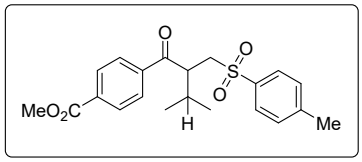
1-(4-Bromophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ha**). The product (76%yield, 62.0 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 3.98 (dd, *J* = 13.6, 10.3 Hz, 1H), 3.88 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H), 2.06 – 1.97 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.7, 144.9, 136.3, 135.5, 132.0, 130.0, 129.9, 128.6, 128.2, 54.7, 46.0, 31.0, 21.7, 20.7, 18.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{22}BrO_3S$: 409.0468, Found 409.0464.



3-Methyl-2-(tosylmethyl)-1-(4-(trifluoromethyl)phenyl)butan-1-one (**3ia**). The product (73%yield, 58.1 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.02 – 3.94 (m, 2H), 3.18 (d, *J* = 11.8 Hz, 1H), 2.37 (s, 3H), 2.07 – 1.99 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 145.0, 139.5, 136.3, 134.6 (q, J = 32.8 Hz), 129.9, 128.9, 128.2, 125.8 (q, J = 3.5 Hz), 123.7 (q, J = 273.7 Hz), 54.8, 46.3, 30.9, 21.6, 20.7, 18.5. **^{19}F NMR** (376 MHz, CDCl3) δ -63.13. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{22}F_3O_3S$: 399.1236, Found 399.1238.

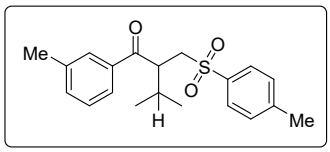


4-(3-Methyl-2-(tosylmethyl)butanoyl)benzonitrile (**3ja**). The product (78%yield, 55.4 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.24 (s, 2H), 3.97 – 3.90 (m, 2H), 3.19 – 3.12 (m, 1H), 2.38 (s, 3H), 2.04 – 1.96 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 145.1, 140.0, 136.3, 132.7, 130.0, 129.0, 128.1, 118.0, 116.6, 54.9, 46.3, 30.9, 21.7, 20.7, 18.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{22}NO_3S$: 356.1315, Found 356.1311.

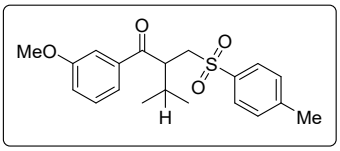


Methyl 4-(3-methyl-2-(tosylmethyl)butanoyl)benzoate (**3ka**). The product (99%yield, 76.8 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.02 – 3.94 (m, 2H), 3.93 (s, 3H), 3.16 (d, *J* = 12.6 Hz, 1H), 2.34 (s, 3H), 2.06 – 1.98 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ

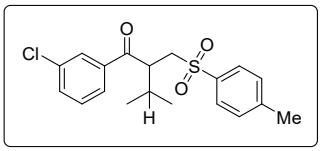
199.1, 166.2, 144.9, 139.8, 136.1, 134.0, 129.9, 128.3, 128.1, 54.4, 52.6, 46.4, 30.8, 21.7, 20.7, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{25}O_5S$: 389.1417, Found 389.1415.



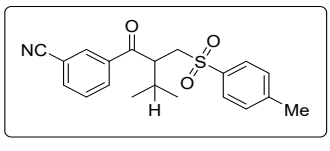
3-Methyl-1-(m-tolyl)-2-(tosylmethyl)butan-1-one (**3la**). The product (60%yield, 41.3 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.67 (m, 2H), 7.67 – 7.64 (m, 2H), 7.36 (t, *J* = 5.8 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.19 (d, *J* = 8.1 Hz,2H), 4.05 – 3.99 (m, 1H), 3.94 (dd, *J* = 10.1, 4.3 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.09 – 2.01 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.5, 144.7, 138.5, 136.6, 136.3, 134.1, 129.8, 128.9, 128.5, 128.2, 125.7, 54.3, 46.1, 30.8, 21.6, 21.5, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_3S$: 345.1519, Found 345.1521.



1-(3-Methoxyphenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ma**). The product (78% yield, 56.2 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.00 (dd, *J* = 13.6, 10.3 Hz, 1H), 3.90 (dd, *J* = 10.1, 3.7 Hz, 1H), 3.83 (s, 3H), 3.14 (d, *J* = 13.7 Hz, 1H), 2.35 (s, 3H), 2.10 – 2.00 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 159.9, 144.7, 137.9, 136.2, 129.8, 129.7, 128.2, 121.0, 119.7, 112.8, 55.5, 54.4, 46.3, 30.9, 21.6, 20.7, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_4S$: 361.1468, Found 361.1460.

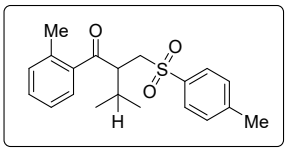


1-(3-Chlorophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3na**). The product (88% yield, 64.2 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.98 (dd, *J* = 13.7, 10.3 Hz, 1H), 3.87 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.16 (d, *J* = 13.7 Hz, 1H), 2.36 (s, 3H), 2.08 – 1.96 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.3, 144.9, 138.2, 136.1, 135.1, 133.2, 130.0, 129.9, 128.5, 128.2, 126.6, 54.6, 46.3, 30.8, 21.6, 20.7, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{22}ClO_3S$: 365.0973, Found 365.0977.

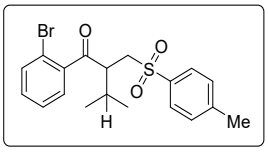


3-(3-Methyl-2-(tosylmethyl)butanoyl)benzonitrile (**3oa**). The product (76% yield, 54.0 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz,

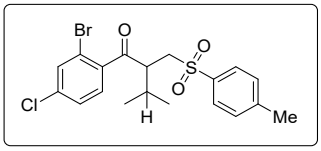
Chloroform-*d*) δ 8.16 (d, *J* = 6.6 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.98 (dd, *J* = 13.2, 10.5 Hz, 1H), 3.91 (dd, *J* = 10.6, 4.5 Hz, 1H), 2.41 (s, 3H), 2.07 – 1.99 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.0, 145.1, 137.6, 136.2, 136.1, 132.4, 132.1, 130.0, 129.8, 128.1, 117.9, 113.4, 54.8, 46.1, 30.9, 21.7, 20.7, 18.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{22}NO_3S$: 356.1315, Found 356.1318.



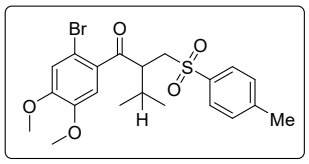
3-Methyl-1-(o-tolyl)-2-(tosylmethyl)butan-1-one (**3pa**). The product (68% yield, 46.8 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 7.8 Hz, 3H), 7.35 – 7.31 (m, 1H), 7.25 – 7.22 (m, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.00 (dd, *J* = 13.9, 9.8 Hz, 1H), 3.86 – 3.83 (m, 1H), 3.04 (dd, *J* = 13.9, 1.2 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.03 – 1.92 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.4, 144.7, 138.8, 137.4, 136.7, 132.0, 131.6, 129.9, 128.8, 128.0, 125.9, 53.5, 48.7, 30.2, 21.7, 21.1, 20.8, 18.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_3S$: 345.1519, Found 345.1516.



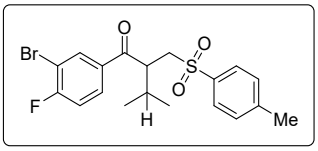
1-(2-Bromophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3qa**). The product (99% yield, 80.8 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.70 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.31—7.27 (m, 1H), 4.04 (dd, *J* = 13.9, 9.6 Hz, 1H), 3.88—3.84 (m, 1H), 3.06 (dd, *J* = 13.9, 1.6 Hz, 1H), 2.41 (s, 3H), 2.13—2.05 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.7, 144.9, 140.0, 136.8, 134.3, 132.1, 130.0, 129.6, 128.0, 127.5, 120.2, 52.8, 50.0, 29.3, 21.7, 20.7, 17.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{22}BrO_3S$: 409.0468, Found 409.0474.



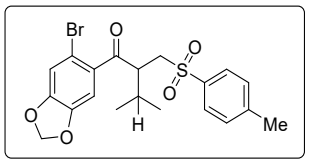
1-(2-Bromo-4-chlorophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ra**). The product (98% yield, 86.6 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.38 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.00 (dd, *J* = 13.9, 9.8 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.06 (d, *J* = 13.8 Hz, 1H), 2.42 (s, 3H), 2.10 – 2.02 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 145.0, 138.4, 137.6, 136.8, 134.1, 130.6, 130.1, 127.9, 127.8, 121.0, 53.2, 49.9, 29.5, 21.7, 20.7, 17.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{21}BrClO_3S$: 443.0078, Found 443.0072.



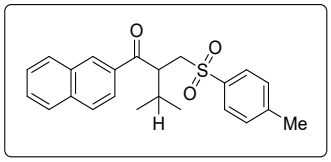
1-(2-Bromo-4,5-dimethoxyphenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3sa**). The product (24% yield, 22.5 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.34 (s, 1H), 7.32 (s, 1H), 7.06 (s, 1H), 4.02 (dd, *J* = 13.5, 9.9 Hz, 1H), 3.95 – 3.94 (m, 4H), 3.92 (s, 3H), 3.08 (d, *J* = 13.6 Hz, 1H), 2.43 (s, 3H), 2.11 – 2.06 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 151.6, 148.2, 144.9, 136.9, 132.0, 130.0, 128.0, 116.9, 112.9, 111.8, 56.5, 53.8, 49.4, 30.2, 21.8, 20.7, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{26}BrO_5S$: 469.0679, Found 469.0675.



1-(3-Bromo-4-fluorophenyl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ta**). The product (69% yield, 58.8 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.26 (m, 1H), 4.05 (dd, *J* = 13.7, 10.3 Hz, 1H), 3.93 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.25 (d, *J* = 13.7 Hz, 1H), 2.47 (s, 3H), 2.14 – 2.06 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1, 162.2 (d, *J* = 257.1 Hz), 145.0, 136.2, 134.4, 134.3 (d *J* = 3.5 Hz), 129.9, 129.7 (d, *J* = 8.6 Hz), 128.2, 116.7 (d, *J* = 23.0 Hz), 110.0 (d, *J* = 21.6 Hz), 54.8, 46.0, 31.0, 21.7, 20.7, 18.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{21}BrFO_3S$: 427.0373, Found 427.0375.

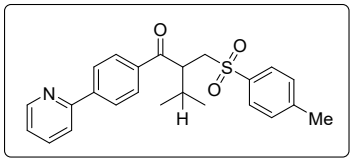


1-(6-Bromobenzo[d][1,3]dioxol-5-yl)-3-methyl-2-(tosylmethyl)butan-1-one (**3ua**). The product (99% yield, 89.5 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (s, 1H), 7.03 (s, 1H), 6.04 (d, *J* = 2.5 Hz, 2H), 3.99 (dd, *J* = 14.0, 9.7 Hz, 1H), 3.78 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.04 (d, *J* = 14.0 Hz, 1H), 2.41 (s, 3H), 2.10 – 2.02 (m, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.5, 150.5, 147.4, 144.9, 136.8, 133.1, 130.0, 128.0, 114.4, 112.6, 109.6, 102.6, 53.2, 49.6, 29.7, 21.7, 20.7, 17.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{22}BrO_5S$: 453.0366, Found 453.0368.

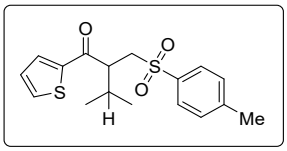


3-Methyl-1-(naphthalen-2-yl)-2-(tosylmethyl)butan-1-one (**3va**). The product (39% yield, 29.6 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91–7.86(m, 3H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.63–7.5 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.14–4.05 (m, 2H), 3.22 (d, *J* = 12.4 Hz, 1H), 2.29 (s,

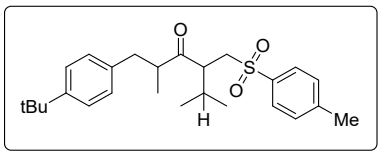
3H), 2.15–2.08 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.4, 144.8, 136.3, 135.8, 134.0, 132.6, 130.2, 129.8, 129.8, 128.8, 128.6, 128.3, 127.8, 127.0, 124.2, 54.7, 46.3, 31.2, 21.6, 20.8, 18.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{23}H_{25}O_3S$: 381.1519, Found 381.1521.



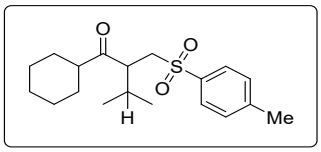
3-Methyl-1-(4-(pyridin-2-yl)phenyl)-2-(tosylmethyl)butan-1-one (**3wa**). The product (76% yield, 61.9 mg) was purified with column chromatography (PE:EA=3:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 3.7 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.04 (dd, *J* = 13.4, 10.1 Hz, 1H), 3.97 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.17 (d, *J* = 13.3 Hz, 1H), 2.33 (s, 3H), 2.10 – 2.02 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 156.0, 150.0, 144.8, 143.8, 137.0, 136.6, 136.2, 129.8, 128.9, 128.2, 127.1, 123.1, 121.1, 54.5, 46.3, 31.0, 21.6, 20.7, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{24}H_{26}NO_3S$: 408.1628, Found 408.1625.



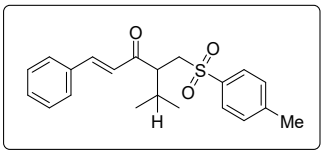
3-Methyl-1-(thiophen-2-yl)-2-(tosylmethyl)butan-1-one (**3xa**). The product (45% yield, 30.2 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.64 (m, 4H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 3.9 Hz, 1H), 3.96 (dd, *J* = 13.8, 10.4 Hz, 1H), 3.70 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.14 (d, *J* = 14.1 Hz, 1H), 2.37 (s, 3H), 2.13 – 2.05 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.1, 144.8, 144.3, 136.0, 134.4, 132.5, 129.8, 128.3, 128.3, 54.8, 48.2, 31.7, 21.7, 20.7, 18.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{21}O_3S_2$: 337.0927, Found 337.0925.



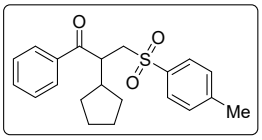
1-(4-(tert-Butyl)phenyl)-2,5-dimethyl-4-(tosylmethyl)hexan-3-one (**3ya**). The product (64% yield, 54.8 mg, dr = 1.25:1) was purified with column chromatography (PE:EA=10:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.78 (m, 2H), 7.38 – 7.26 (m, 4H), 7.16 – 7.09 (m, 2H), 3.87 – 3.78 (m, 1H), 3.32 – 3.29 (m, 0.51H), 3.14 – 3.10 (m, 0.42H), 3.08 – 2.80 (m, 3H), 2.61 – 2.57 (m, 0.30H), 2.46 (s, 3H), 2.37 – 2.31 (m, 0.54H), 2.21 – 2.13 (m, 0.49H), 1.78 – 1.71 (m, 0.40H), 1.34 (s, 5H), 1.29 (s, 4H), 1.17 (d, *J* = 6.7 Hz, 1.23H), 1.02 (d, *J* = 6.7 Hz, 1.71H), 1.00 (d, *J* = 6.8 Hz, 1.81H), 0.86 (d, *J* = 6.8 Hz, 1.25H), 0.75 (d, *J* = 6.9 Hz, 1.81H), 0.22 (d, *J* = 6.9 Hz, 1.17H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.1, 211.1, 149.2, 149.1, 144.8, 144.7, 137.1, 136.9, 136.8, 136.5, 130.0, 129.9, 129.0, 128.9, 128.1, 128.0, 125.4, 125.2, 52.4, 51.3, 50.2, 49.6, 48.0, 47.4, 38.5, 38.1, 34.5, 34.4, 31.7, 31.5, 31.4, 29.2, 28.0, 21.7, 21.2, 21.0, 18.1, 17.7, 16.8, 15.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{26}H_{37}O_3S$: 429.2458, Found 429.2456.



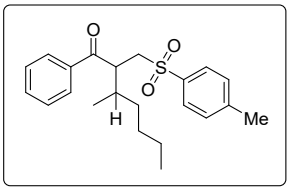
1-Cyclohexyl-3-methyl-2-(tosylmethyl)butan-1-one (**3za**). The product (57% yield, 38.3 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.82 (dd, *J* = 14.0, 9.4 Hz, 1H), 3.22 (dd, *J* = 8.8, 2.6 Hz, 1H), 2.87 (d, *J* = 13.9 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.43 (s, 3H), 2.15 – 2.07 (m, 1H), 1.91 (d, *J* = 12.3 Hz, 1H), 1.82 – 1.74 (m, 2H), 1.67 – 1.63 (m, 2H), 1.49 – 1.38 (m, H), 1.31 – 1.11 (m, 4H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.67 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.9, 144.7, 136.9, 129.9, 128.1, 52.3, 50.3, 49.4, 29.6, 29.2, 28.0, 26.2, 25.9, 25.5, 21.7, 21.1, 17.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{29}O_3S$: 337.1832, Found 337.1837.



(*E*)-5-Methyl-1-phenyl-4-(tosylmethyl)hex-1-en-3-one (**3aaa**). The product (37% yield, 26.3 mg) was purified with column chromatography (PE:EA=6:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.55 –7.52 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.42 – 7.39 (m, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 3.94 (dd, *J* = 14.1, 9.8 Hz, 1H), 3.37 – 3.32 (m, 1H), 3.07 (dd, *J* = 14.0, 1.6 Hz, 1H), 2.34 (s, 3H), 2.11 – 2.03 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.5, 144.9, 143.4, 136.4, 134.4, 130.8, 129.9, 129.1, 128.6, 128.3, 125.4, 54.4, 50.0, 30.7, 21.7, 20.6, 18.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{25}O_3S$: 357.1519, Found 357.1515.

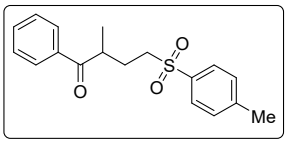


2-cyclopentyl-1-phenyl-3-tosylpropan-1-one (**3aba**). The product (49.8 mg, 70%) was purified with column chromatography (PE:EA=6:1) as colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 6.9 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.08 – 3.97 (m, 2H), 3.23 (d, *J* = 12.6 Hz, 1H), 2.35 (s, 3H), 2.08 – 1.98 (m, 1H), 1.73 – 1.51 (m, 4H), 1.48 – 1.43 (m, 2H), 1.21 – 1.10 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 144.8, 137.0, 136.2, 133.4, 129.8, 128.6, 128.6, 128.2, 77.2, 57.1, 44.3, 43.4, 30.7, 30.0, 25.3, 24.6, 21.7. **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{25}O_3S$: 357.1519, Found 357.1518.

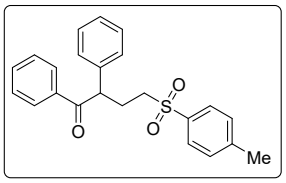


3-Methyl-1-phenyl-2-(tosylmethyl)heptan-1-one (**3aca**). The product (67% yield, 49.8 mg, dr = 1.3 : 1) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.19 (dd, *J* = 7.6, 4.4 Hz, 2H), 4.09 – 3.97 (m, 2H), 3.17 – 3.05 (m, 1H), 2.35 (s,

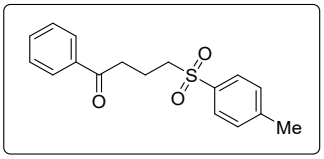
3H), 1.88 – 1.81 (m, 1H), 1.37 – 0.98 (m, 7H), 0.96 – 0.92 (m, 2H), 0.88 – 0.85 (m, 2H), 0.78 – 0.67 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.4, 198.7, 144.7, 136.8, 136.3, 136.0, 133.3, 129.8, 129.8, 128.7, 128.7, 128.4, 128.4, 128.3, 128.2, 54.9, 53.0, 45.7, 44.5, 36.0, 35.1, 34.9, 32.0, 31.7, 29.5, 29.2, 22.8, 22.6, 21.6, 17.7, 15.1, 14.0, 14.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{22}H_{29}O_3S$: 373.1832, Found 373.1830.



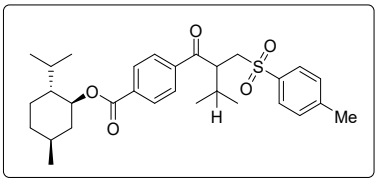
2-methyl-1-phenyl-4-tosylbutan-1-one (**3ada'**). The product (73% yield, 46.1 mg) was purified with column chromatography (PE:EA=8:1) as colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.73 – 3.65 (m, 1H), 3.19 – 3.02 (m, 2H), 2.43 (s, 3H), 2.24 – 2.14 (m, 1H), 1.98 – 1.89 (m, 1H), 1.19 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 144.8, 142.0, 136.2, 135.9, 133.4, 130.0, 129.9, 128.4, 128.1, 54.0, 39.2, 26.0, 21.8, 18.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{21}O_3S$: 317.1206, Found 317.1209.



1,2-diphenyl-4-tosylbutan-1-one (**3aea'**). The product (53% yield, 40.1 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.32 – 7.21 (m, 5H), 4.82 (t, *J* = 7.4 Hz, 1H), 3.18 – 3.01 (m, 2H), 2.52 – 2.47 (m, 1H), 2.45 (s, 3H), 2.34 – 2.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 144.8, 138.0, 136.1, 133.3, 130.0, 129.4, 128.9, 128.6, 128.3, 128.1, 127.7, 54.0, 51.6, 27.0, 21.7. .**HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{23}H_{23}O_3S$: 379.1362, Found 379.1365.

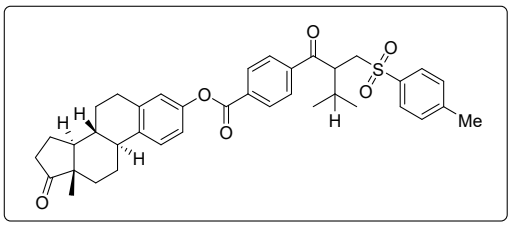


1-Phenyl-4-tosylbutan-1-one (**3afa'**). The product (90% yield, 54.4 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 3.24 – 3.20 (m, 2H), 3.18 – 3.14 (m, 2H), 2.43 (s, 3H), 2.18 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 144.8, 136.5, 136.1, 133.4, 130.0, 128.7, 128.1, 128.0, 55.3, 36.3, 21.7, 17.5. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{17}H_{19}O_3S$: 303.1049, Found 303.1047.

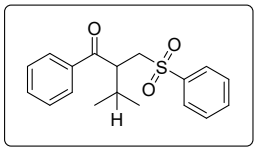


(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-(3-methyl-2-(tosylmethyl)butanoyl)benzoate

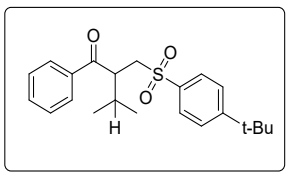
(**3aha**). The product (91% yield, 93.2 mg, dr = 1:1) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.98 – 7.95 (m, 2H), 7.73 – 7.70 (m, 2H), 7.26 – 7.24 (m, 2H), 4.99 (td, *J* = 10.9, 4.4 Hz, 1H), 4.06 – 3.96 (m, 2H), 3.20 (d, *J* = 12.4 Hz, 1H), 2.39 (d, 3H), 2.19 – 2.14 (m, 1H), 2.10 – 2.02 (m, 1H), 2.01 – 1.92 (m, 1H), 1.80 – 1.74 (m, 2H), 1.64 – 1.55 (m, 2H), 1.34 – 1.29 (m, 1H), 1.20 – 1.11 (m, 2H), 1.00 (dd, *J* = 6.9, 2.5 Hz, 3H), 0.96 (dd, *J* = 6.7, 3.9 Hz, 6H), 0.83 (d, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 165.2, 144.8, 139.8, 139.7, 136.3, 136.2, 134.8, 129.9, 128.3, 128.2, 128.1, 75.6, 54.6, 54.6, 47.3, 46.4, 46.4, 41.0, 34.3, 31.6, 31.5, 30.9, 30.8, 26.7, 23.7, 22.7, 22.1, 21.6, 21.6, 20.8, 20.7, 20.6, 18.5, 18.4, 16.6, 14.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{30}H_{41}O_5S$: 513.2669, Found 513.2678.



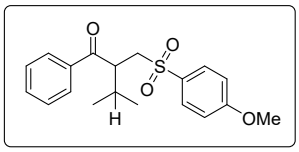
(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-(3-methyl-2-(tosylmethyl)butanoyl)benzoate (**3aia**). The product (84% yield, 105.3 mg) was purified with column chromatography (PE:EA=2:1) as a red oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28 (s, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.99 (s, 1H), 4.06 – 3.99 (m, 2H), 3.21 (d, *J* = 11.8 Hz, 1H), 2.99 – 2.95 (m, 2H), 2.53 (dd, *J* = 18.9, 8.8 Hz, 1H), 2.47 – 2.43 (m, 1H), 2.41 (s, 3H), 2.37 – 2.31 (m, 1H), 2.21 – 2.14 (m, 1H), 2.12 – 2.09 (m, 1H), 2.09 – 2.04 (m, 2H), 2.01 – 1.97 (m, 1H), 1.71 – 1.61 (m, 3H), 1.57 – 1.47 (m, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94 (s, 3H), 0.82 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.7, 199.2, 164.5, 148.7, 144.9, 140.4, 138.3, 137.8, 136.2, 133.6, 130.4, 129.9, 128.5, 128.1, 126.6, 121.6, 118.7, 77.4, 54.6, 50.5, 48.0, 46.4, 44.2, 38.1, 35.9, 31.6, 30.9, 29.5, 26.4, 25.9, 21.7, 20.7, 18.5, 13.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{38}H_{43}O_6S$: 627.2775, Found 627.2766.



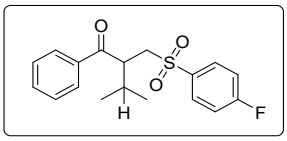
3-Methyl-1-phenyl-2-((phenylsulfonyl)methyl)butan-1-one (**3ab**). The product (76% yield, 48.0 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.47 – 7.41 (m, 4H), 4.06 (dd, *J* = 13.3, 10.1 Hz, 1H), 3.99 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.17 (d, *J* = 13.3 Hz, 1H), 2.13 – 2.02 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 139.3, 136.6, 133.8, 133.4, 129.3, 128.8, 128.5, 128.2, 54.3, 46.1, 30.9, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{21}O_3S$: 317.1206, Found 317.1204.



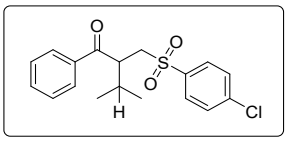
2-(((4-(tert-Butyl)phenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ac**). The product (43% yield, 32.0 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 4.04 (dd, *J* = 12.9, 10.3 Hz, 1H), 3.98 (dd, *J* = 10.2, 4.1 Hz, 1H), 3.15 (d, *J* = 13.0 Hz, 1H), 2.10 – 2.00 (m, 1H), 1.26 (s, 9H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 157.7, 136.4, 136.0, 133.4, 128.7, 128.5, 128.2, 126.2, 54.3, 46.0, 35.3, 31.1, 30.9, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{22}H_{29}O_3S$: 373.1832, Found 373.1830.



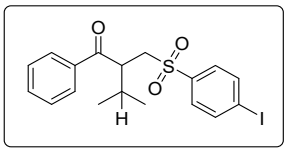
2-(((4-Methoxyphenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ad**). The product (84% yield, 58.1 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.02 (dd, *J* = 13.5, 10.1 Hz, 1H), 3.95 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.79 (s, 3H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.05 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.3, 163.8, 136.5, 133.4, 130.4, 128.7, 128.5, 114.4, 55.7, 54.6, 46.2, 30.9, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{23}O_4S$: 347.1312, Found 347.1316.



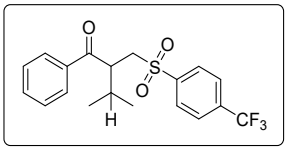
2-(((4-Fluorophenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ae**). The product (52% yield, 34.7 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.80 (dd, *J* = 8.6, 5.1 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 2H), 4.05 (dd, *J* = 13.4, 10.3 Hz, 1H), 3.98 (dd, *J* = 10.3, 4.1 Hz, 1H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.12 – 2.04 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 165.9 (d, *J* = 257.4 Hz), 136.4, 135.3 (d, *J* = 3.1 Hz), 133.6, 131.2 (d, *J* = 9.7 Hz), 128.9, 128.5, 116.5 (d, *J* = 22.8 Hz), 76.8, 54.4, 46.2, 30.9, 20.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{20}FO_3S$: 335.1112, Found 335.1116.



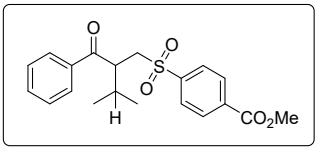
2-(((4-Chlorophenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3af**). The product (78% yield, 54.6 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.05 (dd, *J* = 13.6, 10.3 Hz, 1H), 3.97 (dd, *J* = 10.3, 4.2 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 140.6, 137.7, 136.4, 133.6, 129.8, 129.5, 128.9, 128.5, 54.5, 46.2, 30.9, 20.9, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{20}ClO_3S$: 351.0816, Found 351.0818.



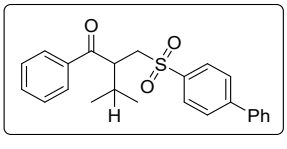
2-(((4-Iodophenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ag**). The product (82% yield, 72.5 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.45 (m, 4H), 4.04 (dd, *J* = 13.7, 10.3 Hz, 1H), 3.95 (dd, *J* = 10.2, 4.4 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.11 – 2.04 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 138.8, 138.5, 136.3, 133.6, 129.6, 128.8, 128.5, 101.9, 54.4, 46.1, 30.9, 20.9, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{20}IO_3S$: 443.0172, Found 443.0178.



3-Methyl-1-phenyl-2-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)butan-1-one (**3ah**). The product (52% yield, 39.9 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.09 (dd, *J* = 13.8, 10.4 Hz, 1H), 3.99 (dd, *J* = 10.4, 4.2 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 142.6, 136.1, 135.5 (q, *J* = 33.2 Hz), 133.7, 129.0, 128.9, 128.4, 126.3 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 274 Hz), 54.2, 46.1, 30.9, 20.9, 18.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.31. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{20}F_3O_3S$: 385.1080, Found 385.1086.

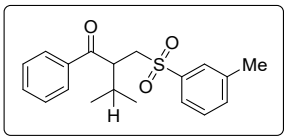


Methyl 4-((2-benzoyl-3-methylbutyl)sulfonyl)benzoate (**3ai**). The product (61% yield, 45.6 mg) was purified with column chromatography (PE:EA=6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.89 – 7.84 (m, 4H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.08 (dd, *J* = 13.8, 10.2 Hz, 1H), 3.98 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.94 (s, 3H), 3.19 (d, *J* = 13.6 Hz, 1H), 2.12 – 2.04 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 165.5, 143.1, 136.3, 134.9, 133.6, 130.4, 128.9, 128.5, 128.3, 54.2, 52.8, 46.1, 30.9, 20.8, 18.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{23}O_5S$: 375.1261, Found 375.1265.

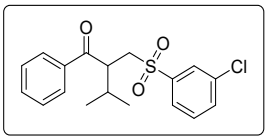


2-(([1,1'-Biphenyl]-4-ylsulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3aj**). The product (91% yield, 71.3 mg) was purified with column chromatography (PE:EA=6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 8.0 Hz, 4H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.40 (m, 5H), 4.10 (dd, *J* = 13.5, 10.3 Hz, 1H), 4.02 (dd, *J* = 10.1,

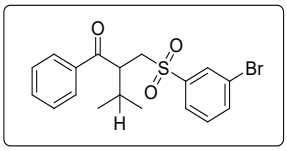
4.3 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 146.7, 139.2, 137.6, 136.4, 133.4, 129.1, 128.8, 128.8, 128.7, 128.5, 127.8, 127.5, 54.5, 46.1, 30.9, 20.9, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{24}H_{25}O_3S$: 393.1519, Found 393.1517.



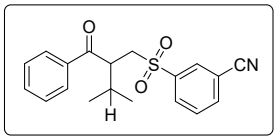
3-Methyl-1-phenyl-2-((m-tolylsulfonyl)methyl)butan-1-one (**3ak**). The product (88% yield, 58.1 mg) was purified with column chromatography (PE:EA=6:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.62 – 7.60 (m, 1H), 7.57 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 4.5 Hz, 2H), 4.06 – 3.97 (m, 2H), 3.15 (d, *J* = 12.2 Hz, 1H), 2.24 (s, 3H), 2.10 – 2.02 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 139.6, 139.0, 136.5, 134.5, 133.4, 129.2, 128.8, 128.6, 128.5, 125.4, 54.3, 46.1, 30.9, 21.2, 20.8, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{23}O_3S$: 331.1362, Found 331.1366.



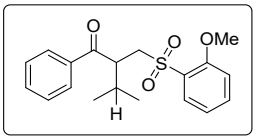
2-(((3-Chlorophenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3al**). The product (89% yield, 62.3 mg) was purified with column chromatography (PE:EA=6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.4 Hz, 2H), 7.78 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.38 (t, *J* = 7.9 Hz, 1H), 4.06 (dd, *J* = 13.4, 10.2 Hz, 1H), 3.99 (dd, *J* = 10.4, 4.2 Hz, 1H), 3.17 (d, *J* = 13.4 Hz, 1H), 2.14 – 2.03 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.1, 140.9, 136.3, 135.6, 134.0, 133.6, 130.6, 128.9, 128.5, 128.4, 126.4, 54.3, 46.1, 30.9, 20.9, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{20}ClO_3S$: 351.0816, Found 351.0818.



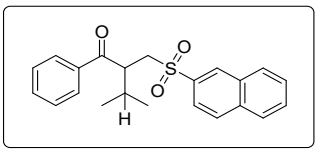
2-(((3-Bromophenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3am**). The product (70% yield, 55.2 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 4.06 (dd, *J* = 13.3, 10.4 Hz, 1H), 3.98 (dd, *J* = 10.4, 4.1 Hz, 1H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.13 – 2.03 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.0, 141.0, 136.9, 136.3, 133.6, 131.3, 130.8, 129.0, 128.5, 126.8, 123.3, 54.3, 46.1, 30.9, 20.9, 18.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{18}H_{20}BrO_3S$: 395.0311, Found 395.0315.



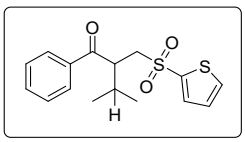
3-((2-Benzoyl-3-methylbutyl)sulfonyl)benzonitrile (**3an**). The product (39% yield, 26.6 mg) was purified with column chromatography (PE:EA=6:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.08 (dd, *J* = 13.6, 10.5 Hz, 1H), 4.00 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 141.0, 136.9, 136.0, 134.0, 132.3, 132.0, 130.3, 129.1, 128.4, 116.8, 113.8, 54.3, 46.3, 30.9, 20.9, 18.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{20}NO_3S$: 342.1158, Found 342.1156.



2-(((2-Methoxyphenyl)sulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ao**). The product (34% yield, 23.5 mg) was purified with column chromatography (PE:EA=6:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 4.30 (dd, *J* = 14.1, 10.0 Hz, 1H), 4.00 (s, 3H), 3.85 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.41 (d, *J* = 14.1 Hz, 1H), 2.06 – 1.98 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.8, 157.7, 136.8, 135.8, 133.2, 130.7, 128.6, 128.4, 126.5, 120.4, 112.3, 56.4, 52.8, 46.3, 31.1, 20.7, 18.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{23}O_4S$: 347.1312, Found 347.1314.

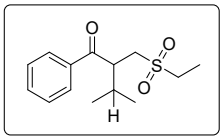


3-Methyl-2-((naphthalen-2-ylsulfonyl)methyl)-1-phenylbutan-1-one (**3ap**). The product (86% yield, 62.9 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.74 (m, 4H), 7.64 – 7.60 (m, 1H), 7.55 – 7.47 (m, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 4.12 (dd, *J* = 13.7, 10.3 Hz, 1H), 4.02 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.25 (d, *J* = 13.5 Hz, 1H), 2.12 – 2.01 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.2, 136.4, 136.0, 135.4, 133.4, 132.1, 130.3, 129.7, 129.4, 129.3, 128.7, 128.4, 128.0, 127.7, 122.9, 54.5, 46.2, 31.0, 20.9, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{22}H_{23}O_3S$: 367.1362, Found 367.1368.

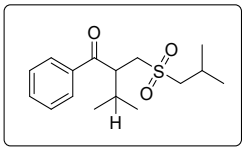


3-Methyl-1-phenyl-2-((thiophen-2-ylsulfonyl)methyl)butan-1-one (**3aq**). The product (34% yield, 21.9 mg) was purified with column chromatography (PE:EA=5:1) as a colorless oil. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 4.7 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 6.99 (t, *J* = 4.0 Hz, 1H), 4.18 (dd, *J* = 13.9, 10.2 Hz, 1H), 4.00 (dd, *J* = 10.3, 3.8 Hz, 1H), 3.26 (d, *J* = 14.2 Hz, 1H), 2.12 – 2.07 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.9, 140.2, 136.4, 134.5, 134.3, 133.5, 128.8, 128.5, 127.9, 55.5, 46.7, 30.8, 20.8, 18.2. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{16}H_{19}O_3S_2$: 323.0770,

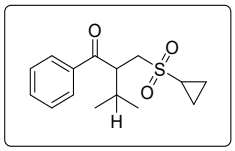
Found 323.0760.



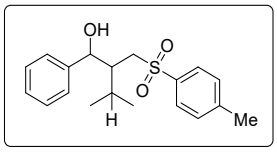
2-((Ethylsulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3ar**). The product (76% yield, 40.7 mg) was purified with column chromatography (PE:EA=5:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.05 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.94 (dd, *J* = 13.8, 10.4 Hz, 1H), 2.97 (d, *J* = 13.7 Hz, 1H), 2.94 – 2.84 (m, 2H), 2.19 – 2.11 (m, 1H), 1.37 (t, *J* = 7.4 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 136.6, 133.7, 129.0, 128.7, 49.8, 48.7, 46.3, 30.8, 20.9, 18.3, 6.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{14}H_{21}O_3S$: 269.1206, Found 269.1200.



2-((Isobutylsulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3as**). The product (52% yield, 30.8 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.04 (dd, *J* = 10.4, 4.3 Hz, 1H), 3.92 (dd, *J* = 13.7, 10.3 Hz, 1H), 2.98 (d, *J* = 13.6 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.39 – 2.29 (m, 1H), 2.18 – 2.07 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3 H), 1.03 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.5, 136.7, 133.5, 129.0, 128.6, 61.8, 52.0, 46.0, 30.8, 23.8, 23.0, 22.8, 20.9, 18.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{16}H_{25}O_3S$: 297.1519, Found 297.1517.

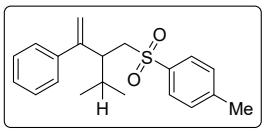


2-((Cyclopropylsulfonyl)methyl)-3-methyl-1-phenylbutan-1-one (**3at**). The product (71% yield, 39.8 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.06 – 3.98 (m, 2H), 3.11 – 3.04 (m, 1H), 2.28 – 2.22 (m, 1H), 2.17 – 2.10 (m, 1H), 1.20 – 1.09 (m, 2H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.99 – 0.83 (m, 2H), 0.81 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.1, 136.6, 133.6, 129.0, 128.5, 51.7, 46.3, 30.8, 30.5, 20.9, 18.2, 5.6, 4.8. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{15}H_{21}O_3S$: 281.1206, Found 281.1208.

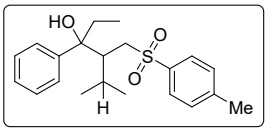


3-Methyl-1-phenyl-2-(tosylmethyl)butan-1-ol (**4**). The product (74% yield, 49.1 mg) was purified with column chromatography (PE:EA=8:1) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.33 (m, 4H), 7.32 – 7.25 (m, 1H), 5.27 (d, *J* = 4.3 Hz, 1H), 3.53 (dd, *J* = 14.5, 8.6 Hz, 1H), 3.05 (dd, *J* = 14.5, 2.9 Hz, 1H), 2.49 (s, 3H), 2.30 – 2.25 (m, 1H), 1.87 – 1.76 (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 144.7, 142.7, 136.9, 130.0, 128.4, 128.0, 127.3, 126.0, 74.4, 53.3, 45.3, 26.4, 21.9, 21.7, 18.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{19}H_{25}O_3S$: 333.1519, Found 333.1517.



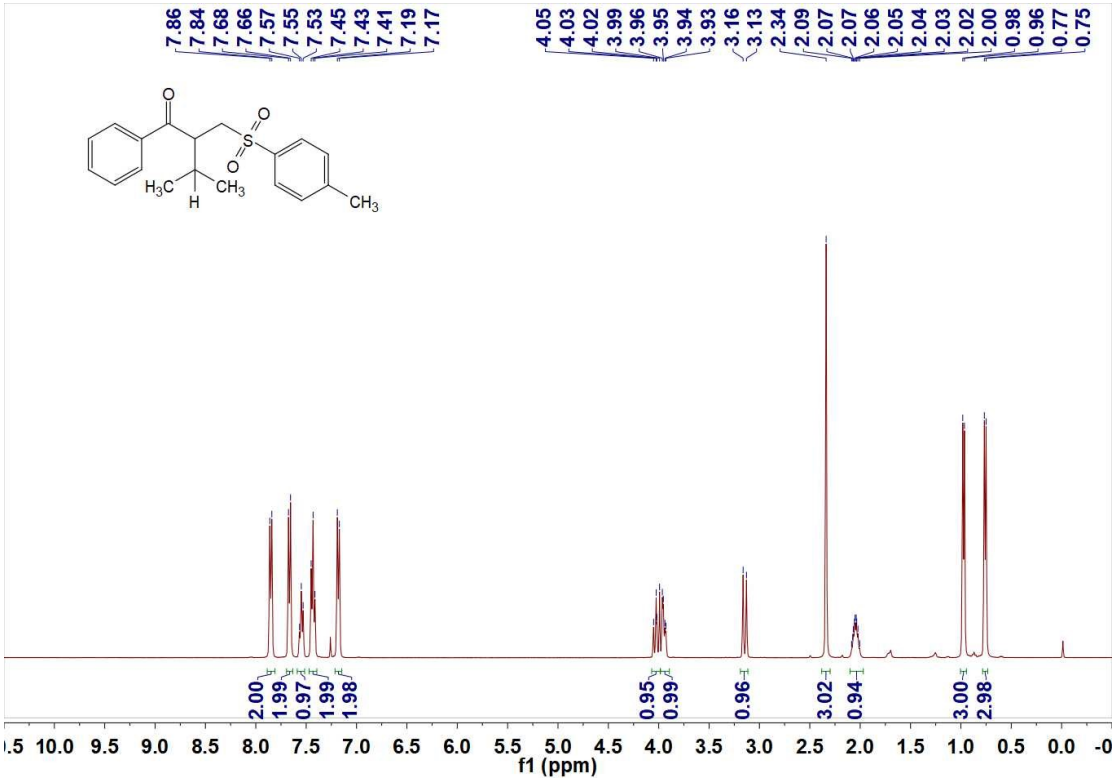
1-((2-isopropyl-3-phenylbut-3-en-1-yl)sulfonyl)-4-methylbenzene (**5**). The product (65% yield, 42.6 mg) was purified with column chromatography (PE:EA=8:1) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.24 (m, 7H), 5.22 (s, 1H), 4.86 (s, 1H), 3.47 (dd, *J* = 14.6, 9.2 Hz, 1H), 3.31 (dd, *J* = 14.6, 3.0 Hz, 1H), 3.11 – 3.07 (m, 1H), 2.42 (s, 3H), 1.86 – 1.76 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.5, 144.6, 142.5, 137.1, 129.8, 128.4, 128.2, 127.6, 126.9, 114.7, 57.4, 45.0, 31.5, 21.7, 20.2, 19.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{20}H_{25}O_2S$: 329.1570, Found 329.1566.



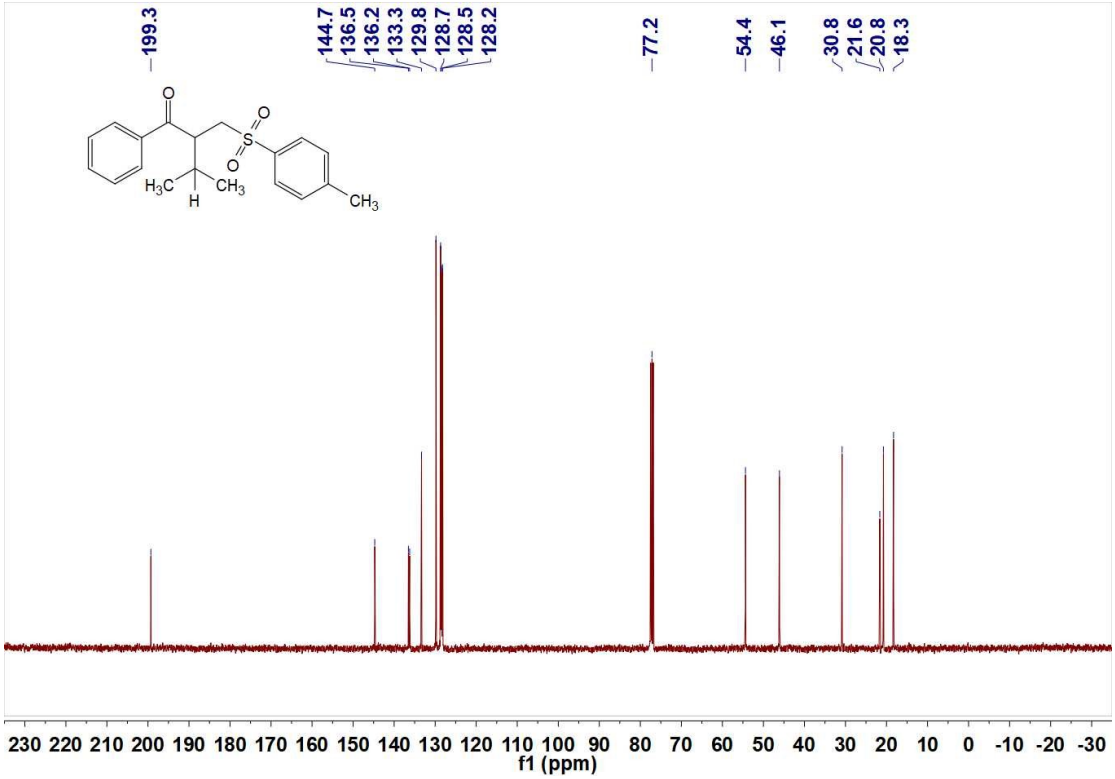
5-methyl-3-phenyl-4-(tosylmethyl)hexan-3-ol (**6**). The product (60% yield, 43.2 mg) was purified with column chromatography (PE:EA=4:1) as white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 4H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.22 (m, 1H), 3.58 (dd, *J* = 15.2, 5.0 Hz, 1H), 2.96 (dd, *J* = 15.2, 3.4 Hz, 1H), 2.51 – 2.48 (m, 1H), 2.47 (s, 3H), 2.41 – 2.39 (m, 1H), 2.14 – 1.95 (m, 2H), 1.76 – 1.66 (m, 1H), 0.74 (d, *J* = 7.0 Hz, 3H), 0.70 (t, *J* = 7.3 Hz, 3H), 0.40 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 143.9, 137.7, 130.1, 128.3, 128.1, 126.8, 126.0, 79.6, 53.2, 48.1, 34.1, 27.9, 23.3, 21.8, 17.5, 7.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd. For $C_{21}H_{29}O_3S$: 361.1832, Found 361.1834.

7. NMR Spectra of Products

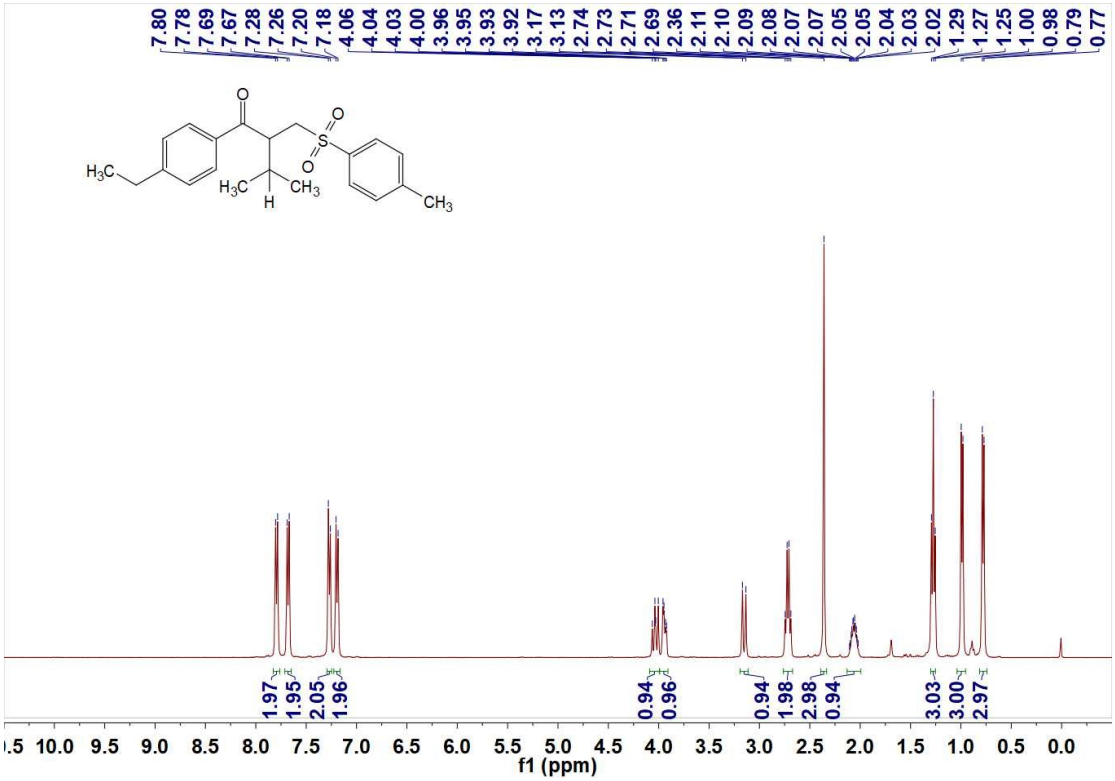
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



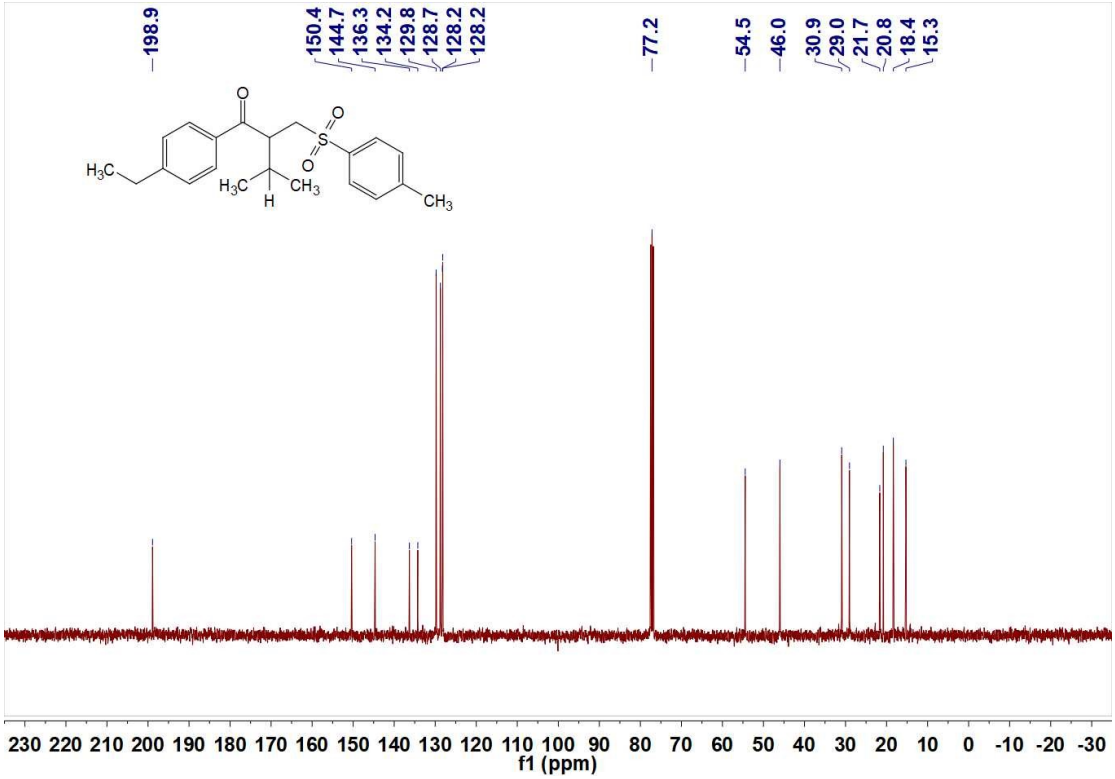
^{13}C NMR of **3aa** (101 MHz, $CDCl_3$, 77.16)



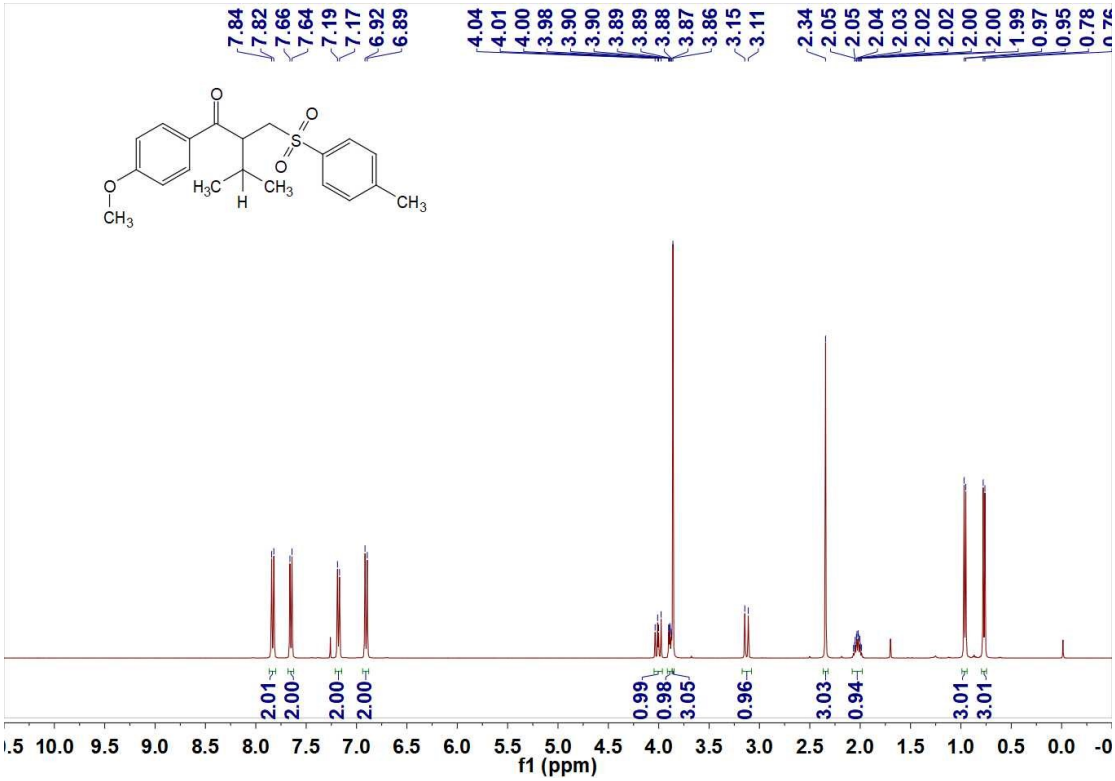
^{1}H NMR of **3ba** (400 MHz, $CDCl_3$)



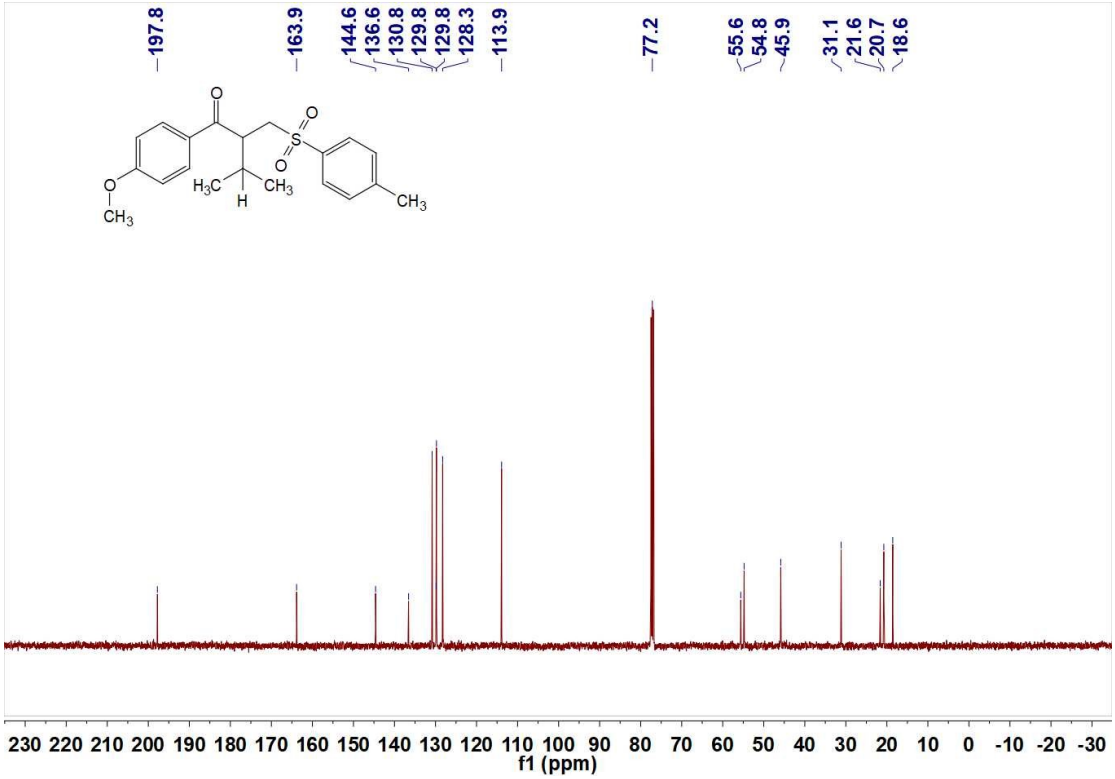
^{13}C NMR of **3ba** (101 MHz, $CDCl_3$, 77.16)



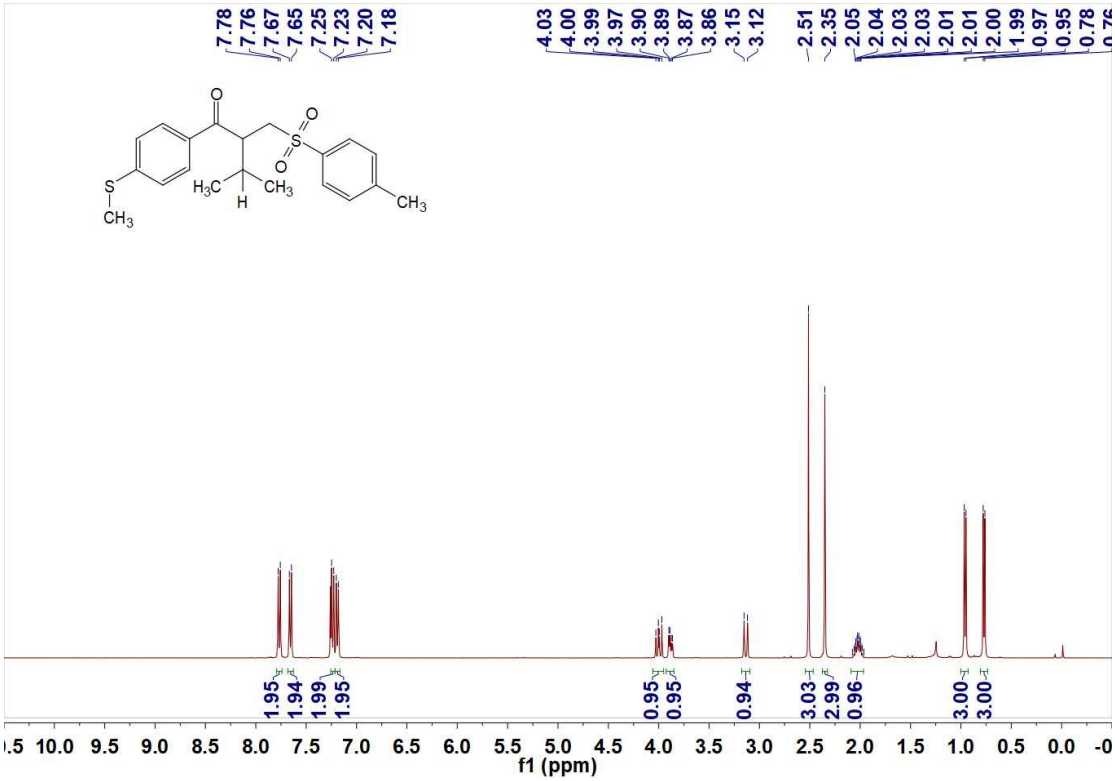
^{1}H NMR of **3ca** (400 MHz, $CDCl_3$)



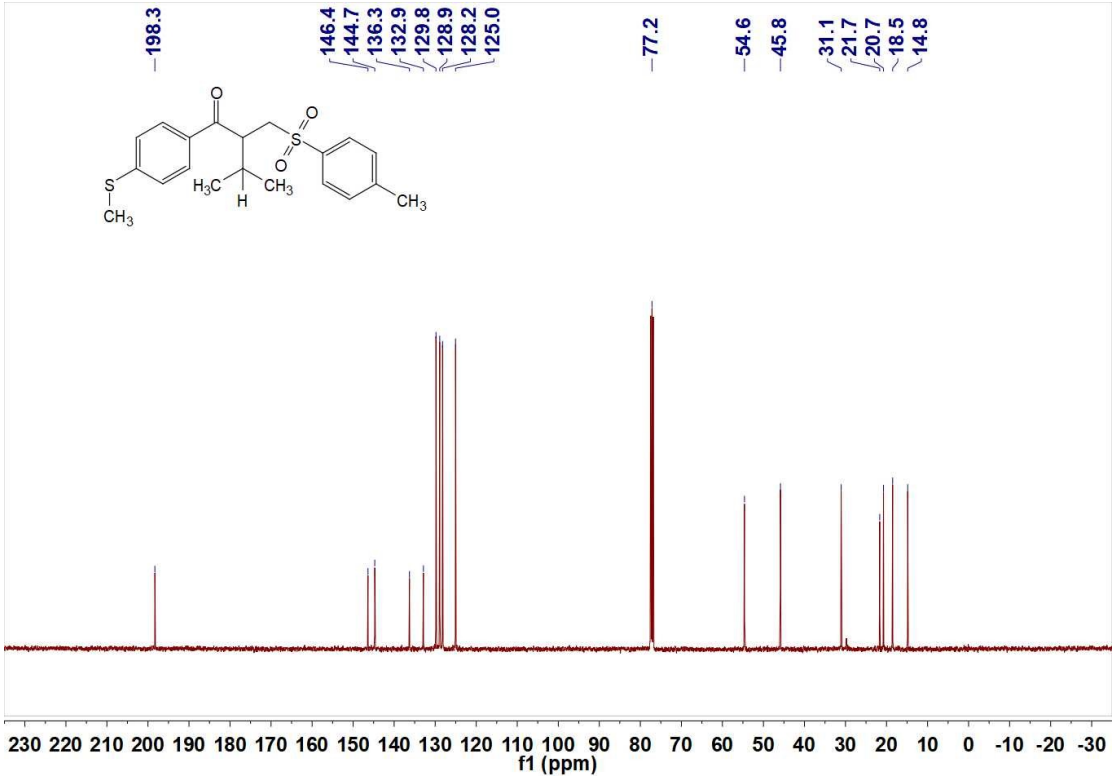
^{13}C NMR of **3ca** (101 MHz, $CDCl_3$, 77.16)



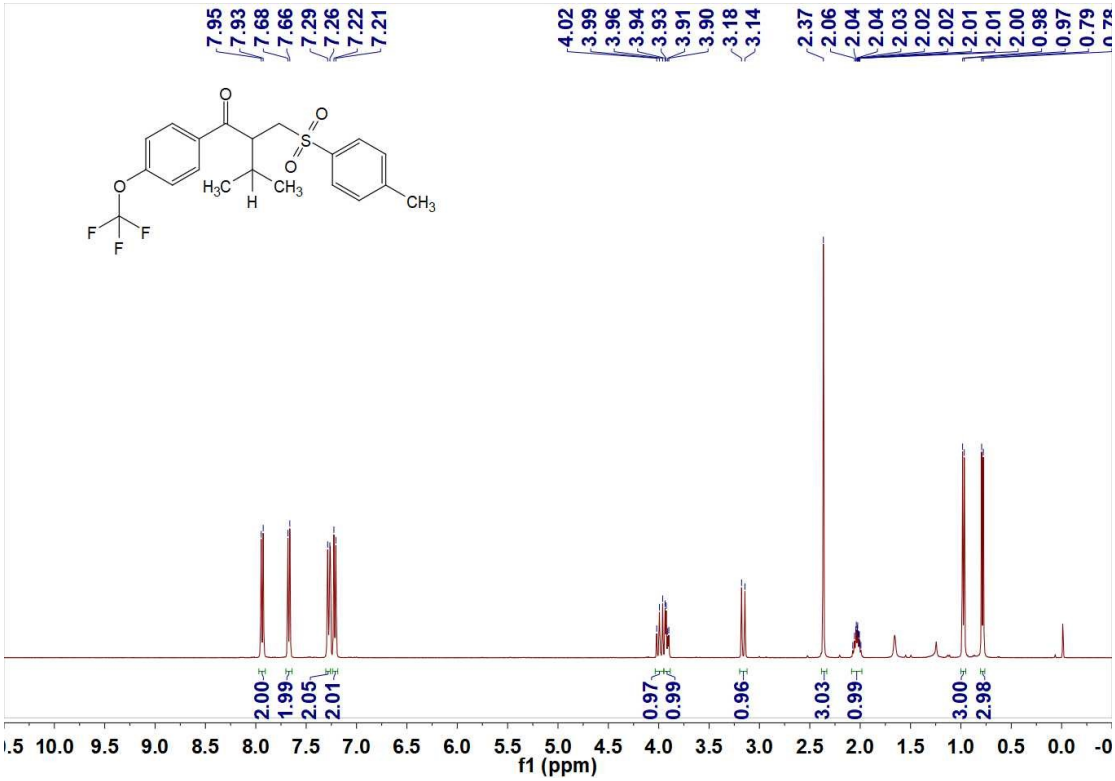
^{1}H NMR of **3da** (400 MHz, $CDCl_3$)



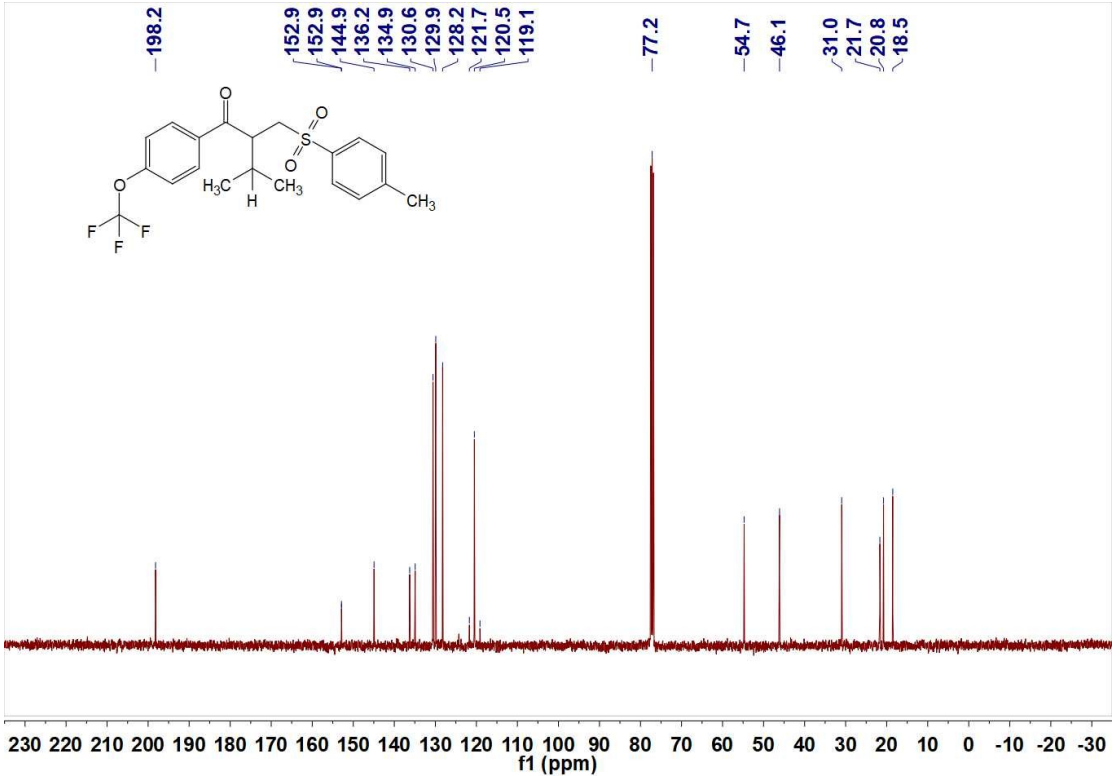
^{13}C NMR of **3da** (101 MHz, $CDCl_3$, 77.16)



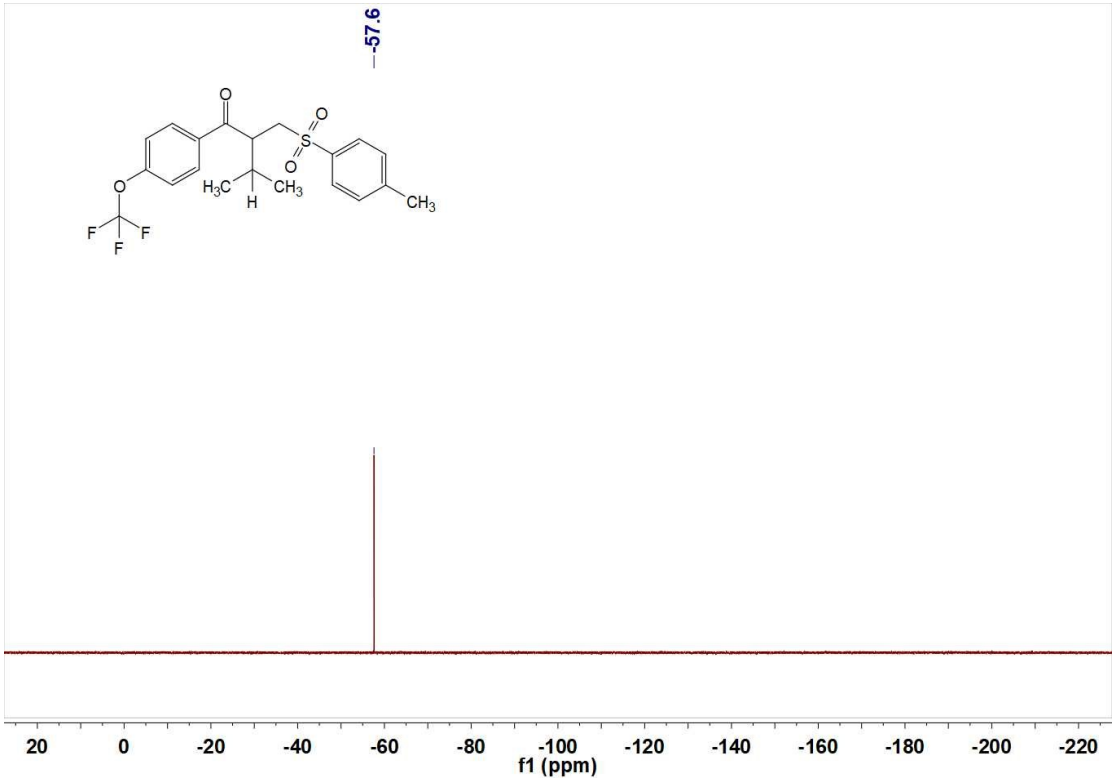
^{1}H NMR of **3ea** (400 MHz, $CDCl_3$)



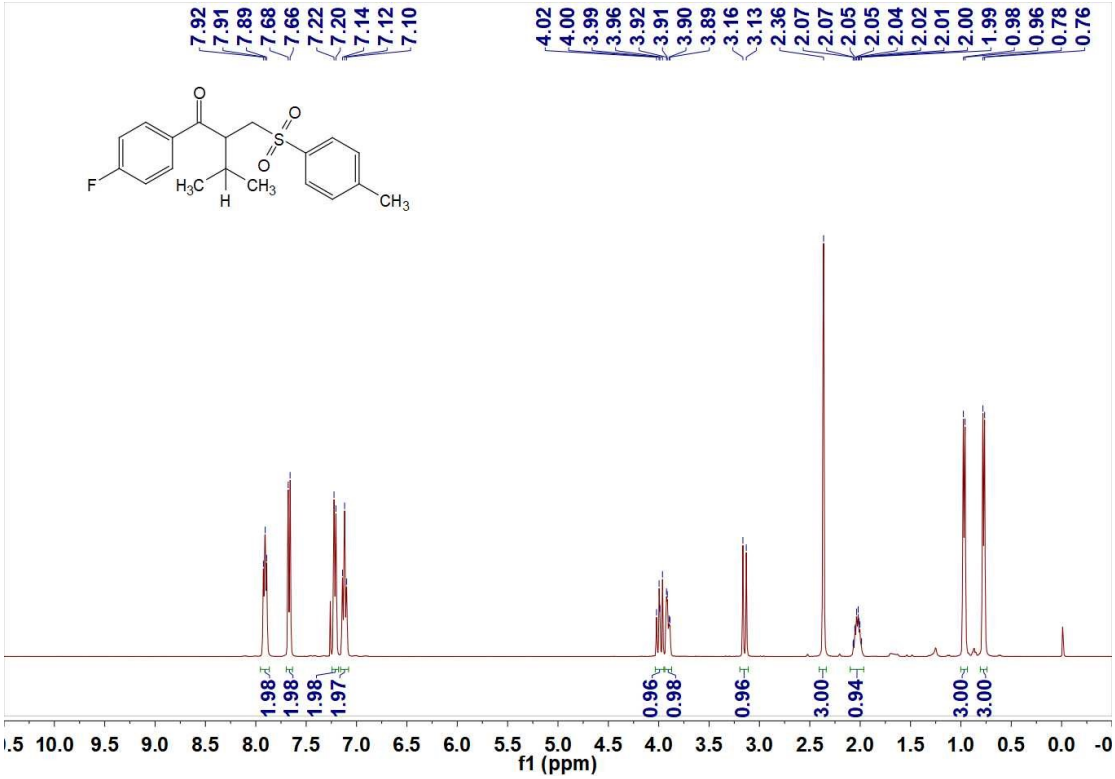
^{13}C NMR of **3ea** (101 MHz, $CDCl_3$, 77.16)



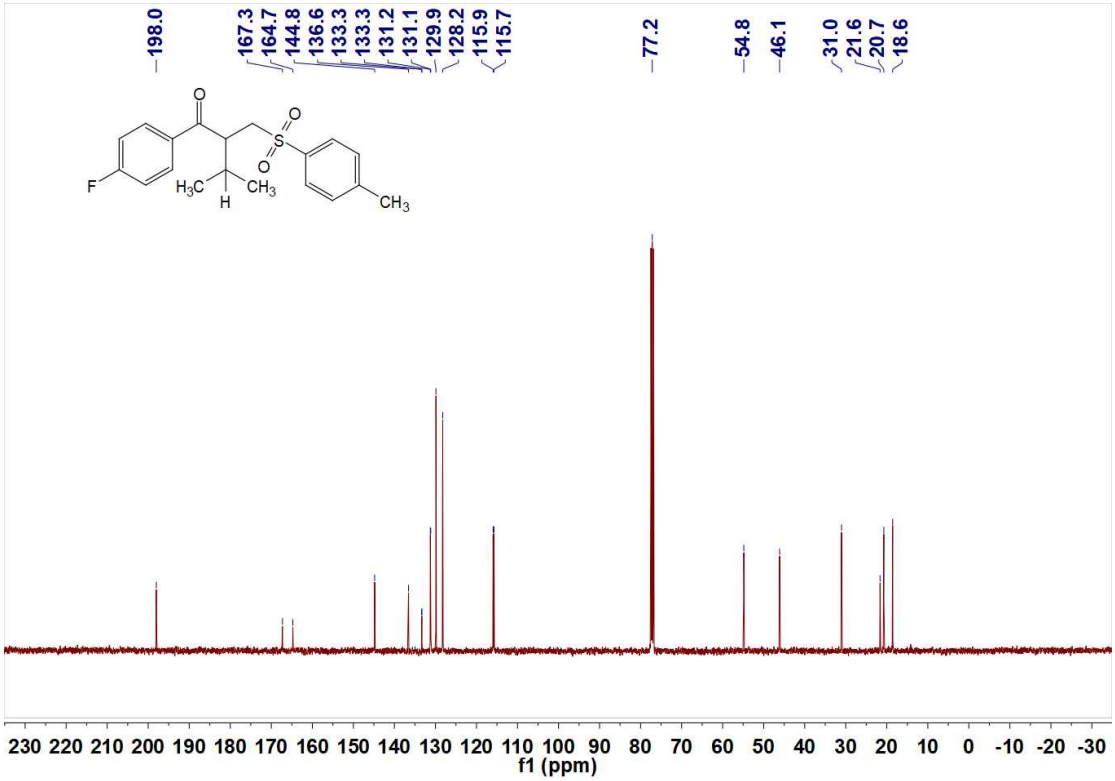
^{19}F NMR of **3ea** (376 MHz, $CDCl_3$)



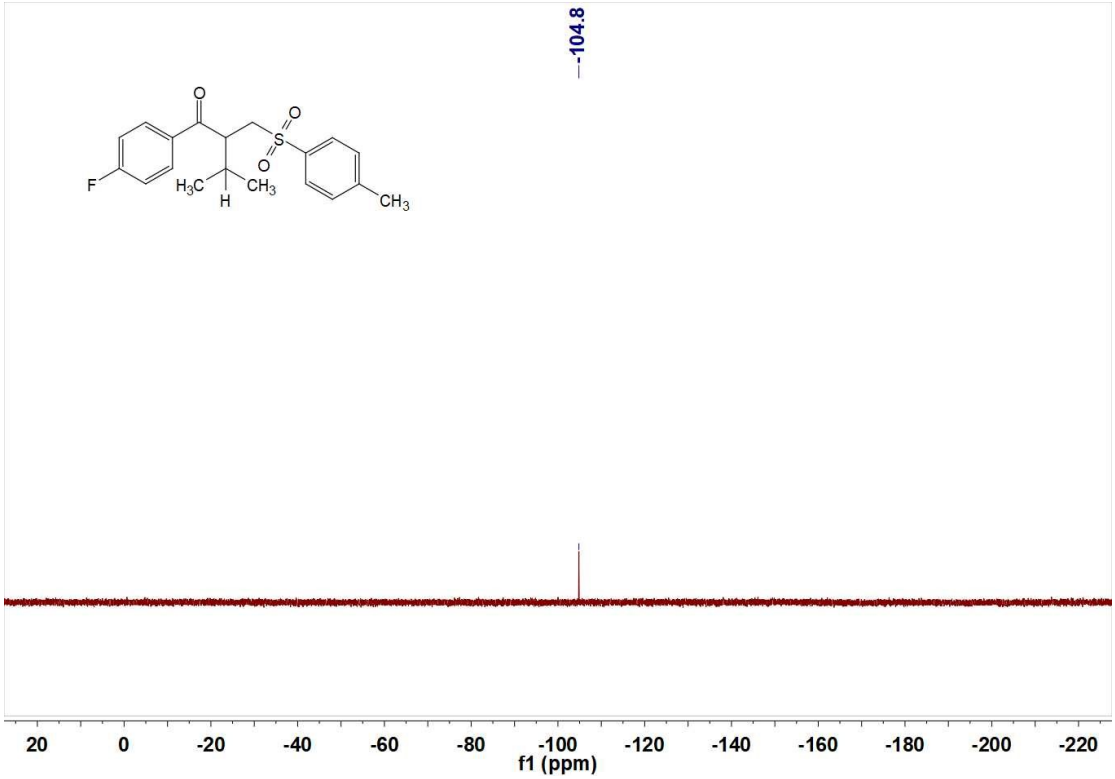
^{1}H NMR of **3fa** (400 MHz, $CDCl_3$)



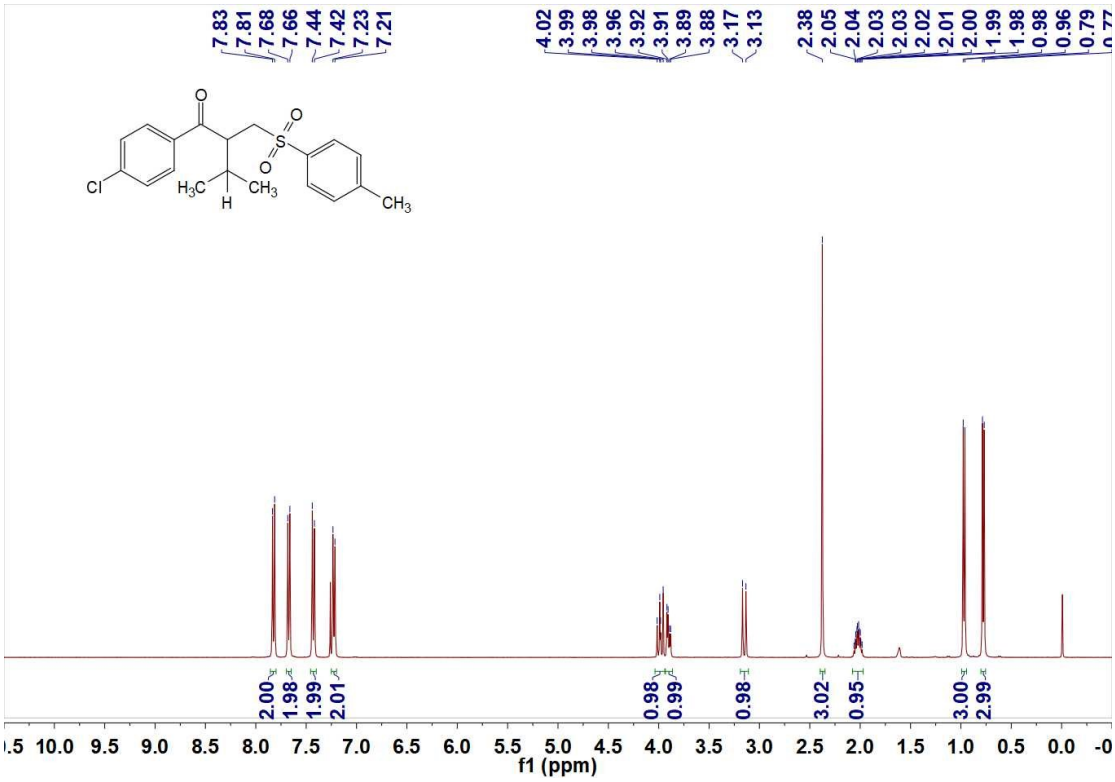
^{13}C NMR of **3fa** (101 MHz, $CDCl_3$, 77.16)



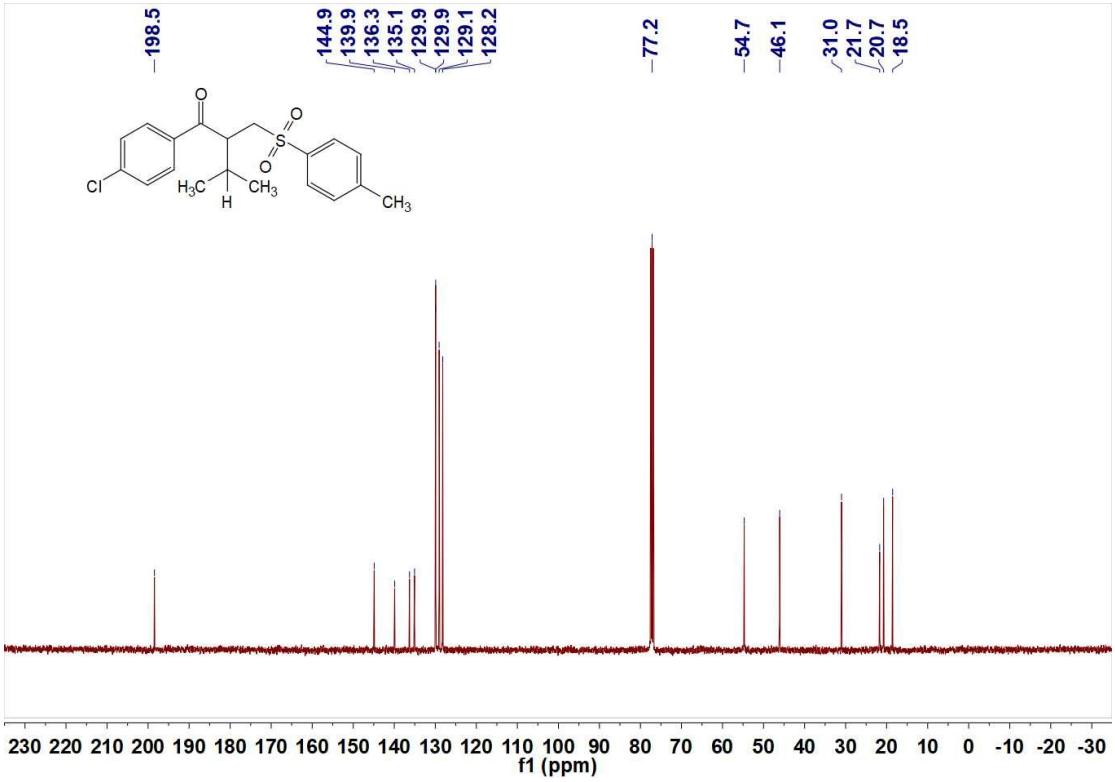
^{19}F NMR of **3fa** (376 MHz, $CDCl_3$)



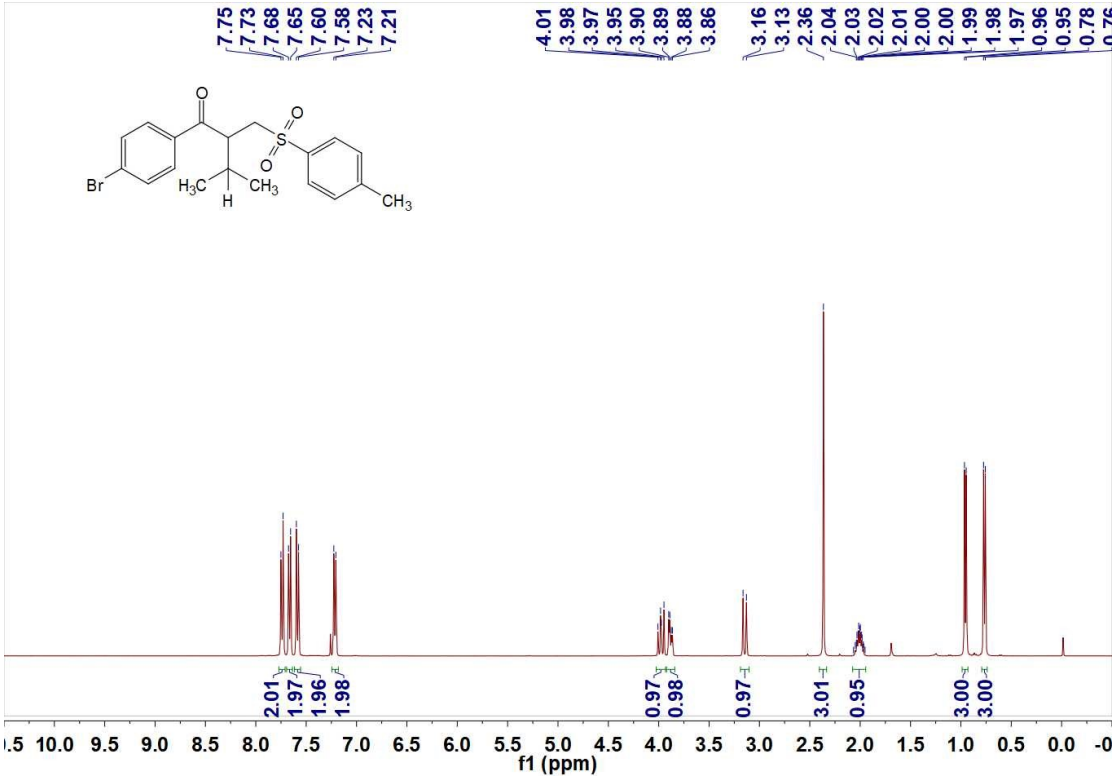
^{1}H NMR of **3ga** (400 MHz, $CDCl_3$)



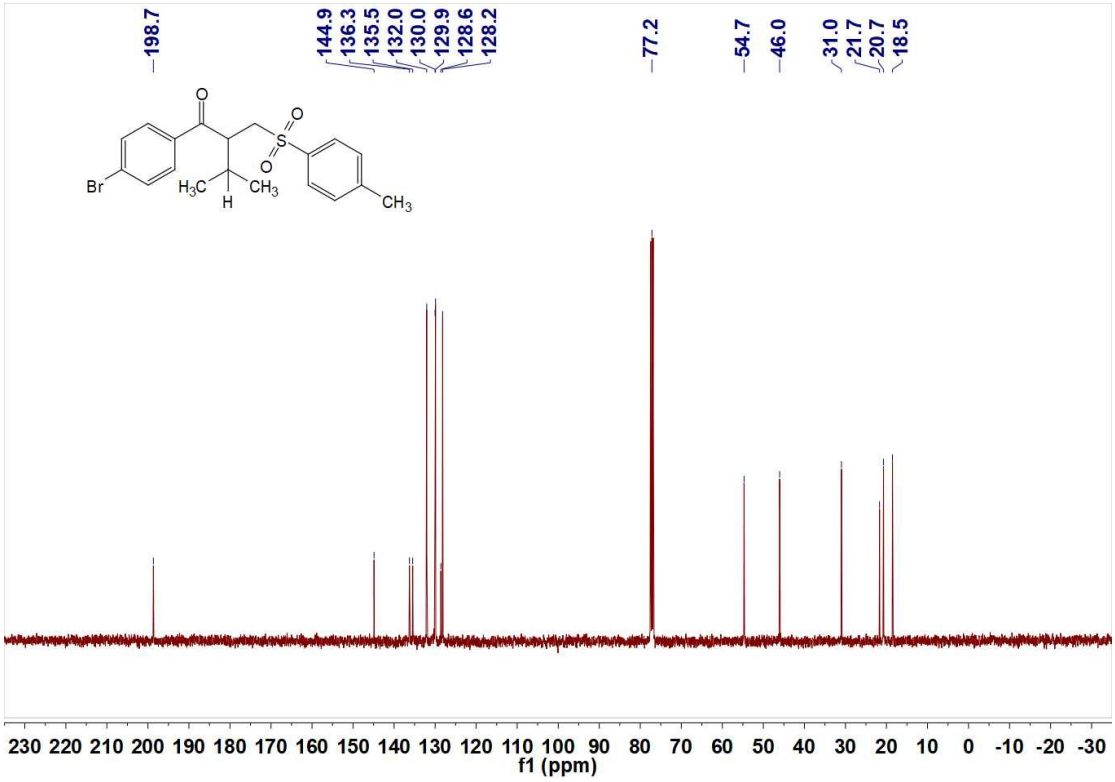
^{13}C NMR of **3ga** (101 MHz, $CDCl_3$, 77.16)



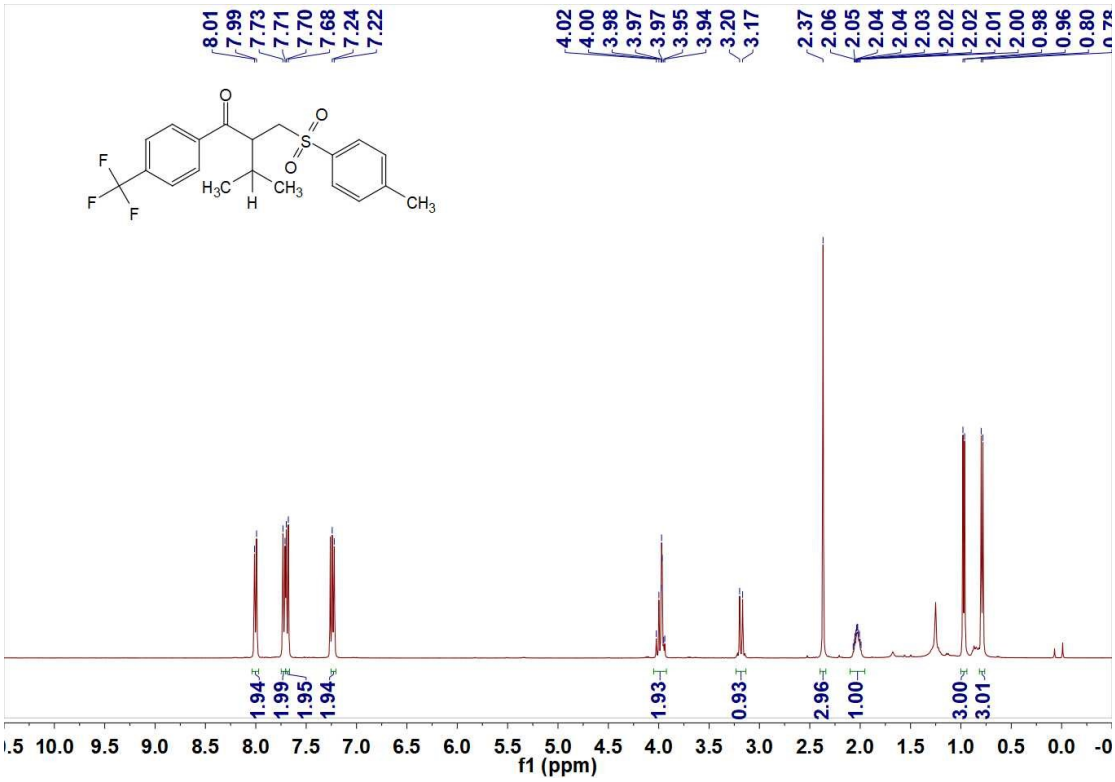
^{1}H NMR of **3ha** (101 MHz, $CDCl_3$, 77.16)



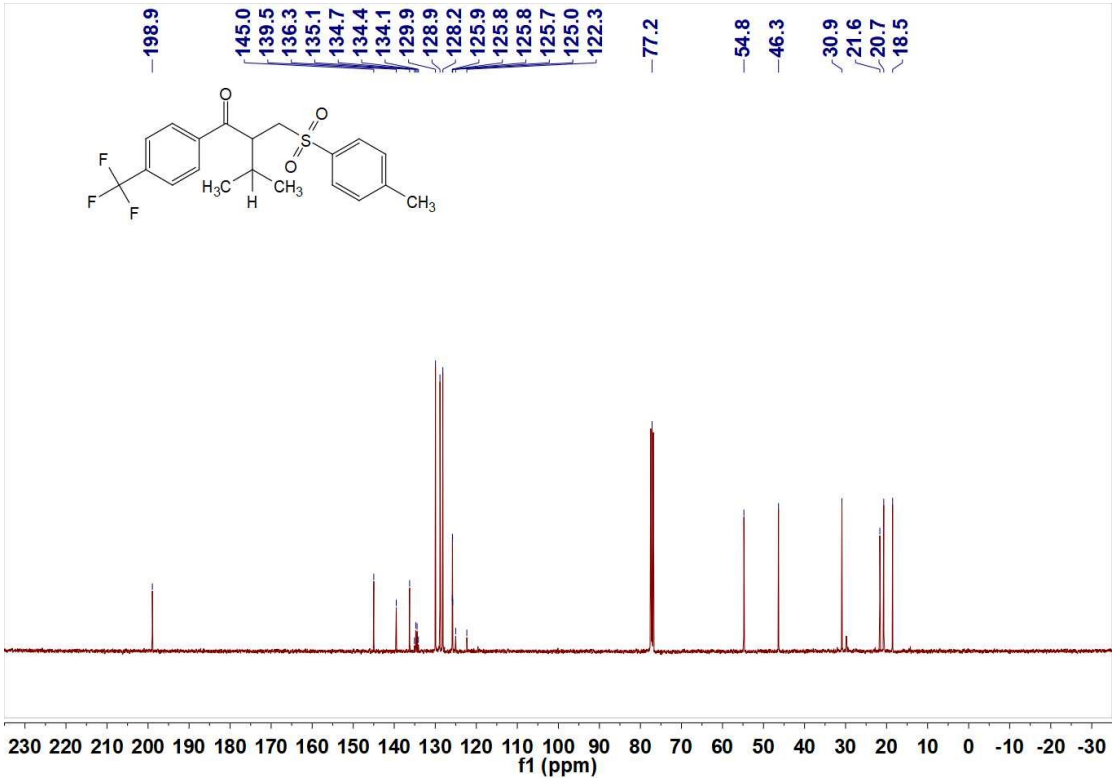
^{13}C NMR of **3ha** (101 MHz, $CDCl_3$, 77.16)



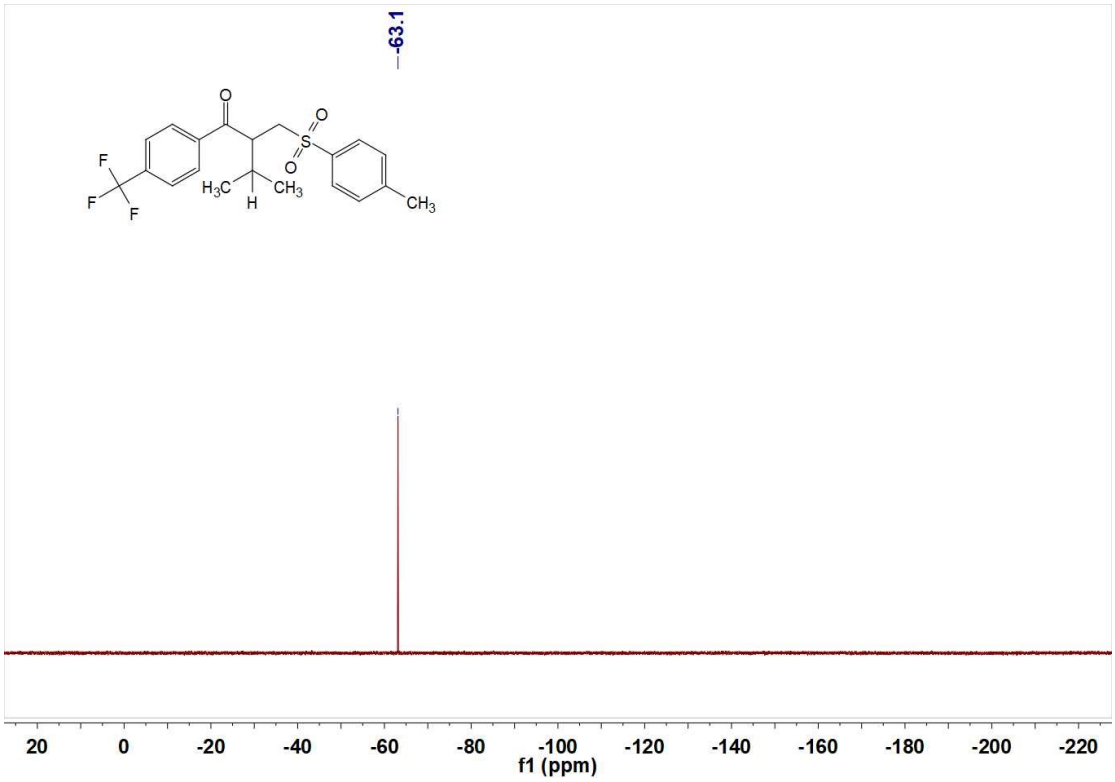
^{1}H NMR of **3ia** (400 MHz, $CDCl_3$)



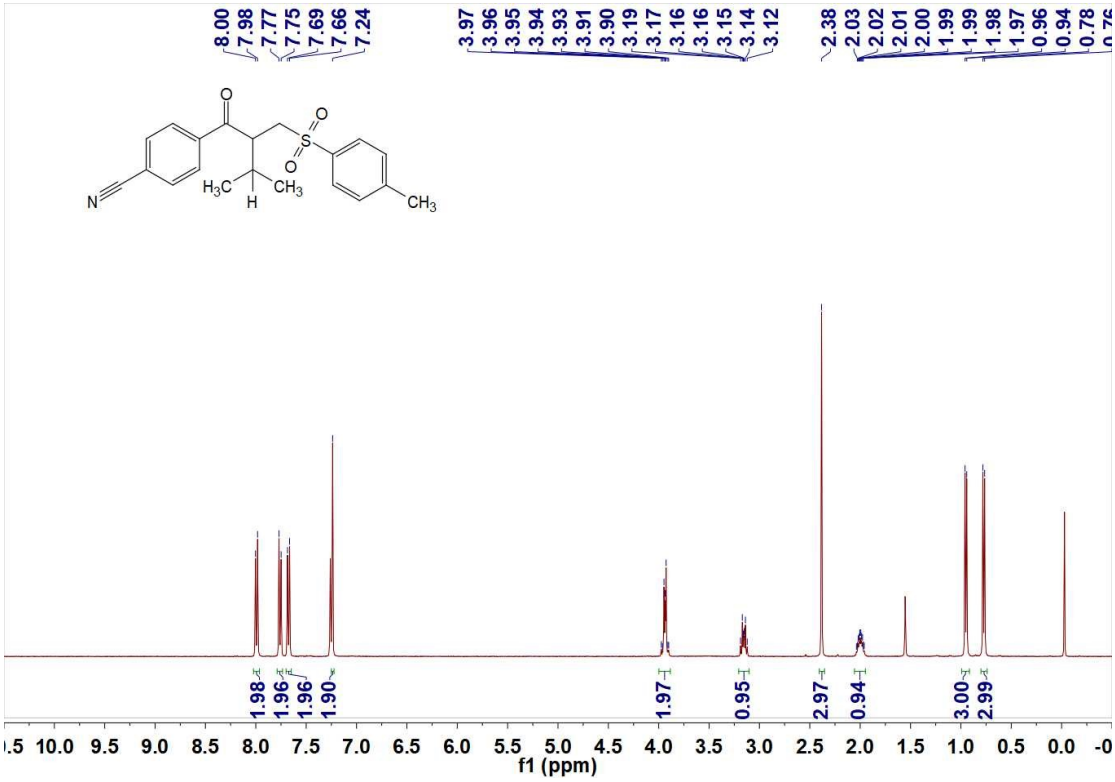
^{13}C NMR of **3ia** (101 MHz, $CDCl_3$, 77.16)



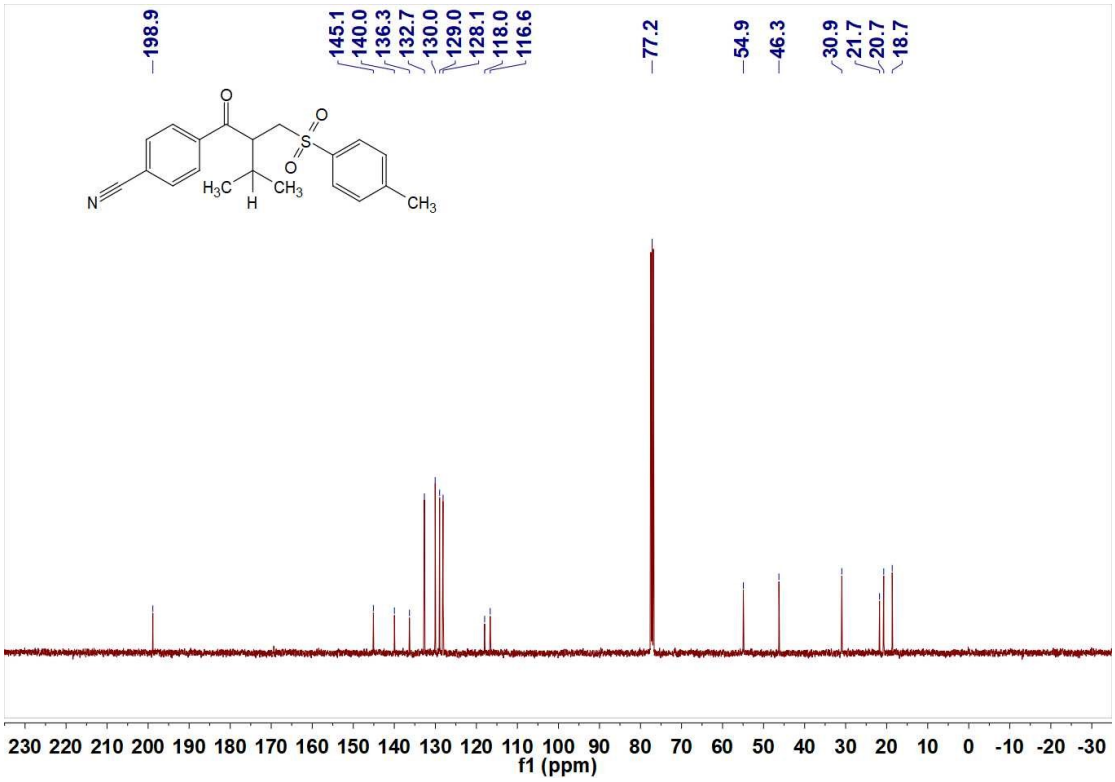
^{19}F NMR of **3ia** (376 MHz, $CDCl_3$)



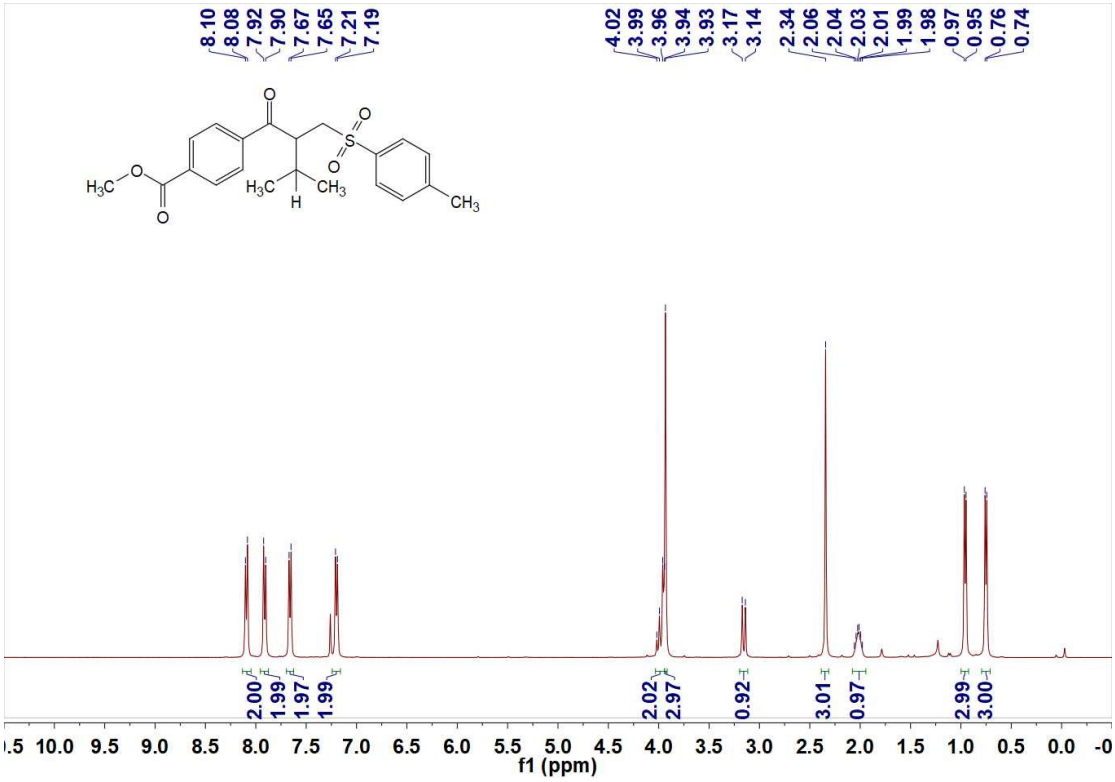
^{1}H NMR of **3ja** (400 MHz, $CDCl_3$)



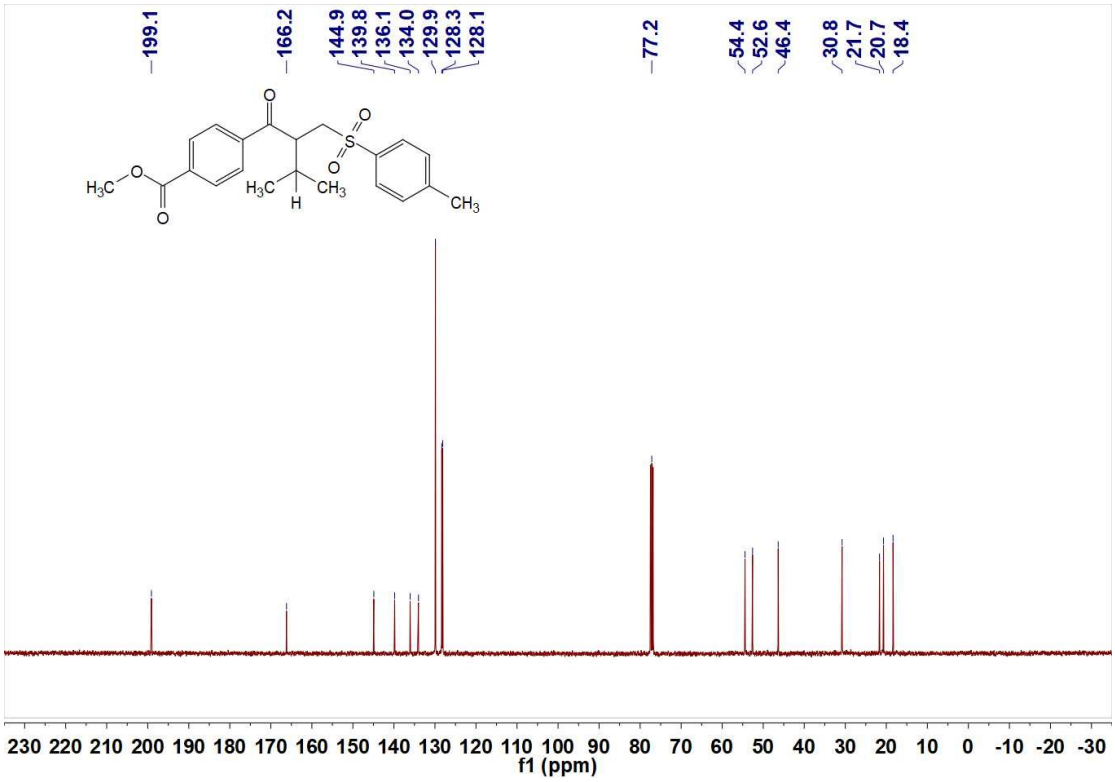
^{13}C NMR of **3ja** (101 MHz, $CDCl_3$, 77.16)



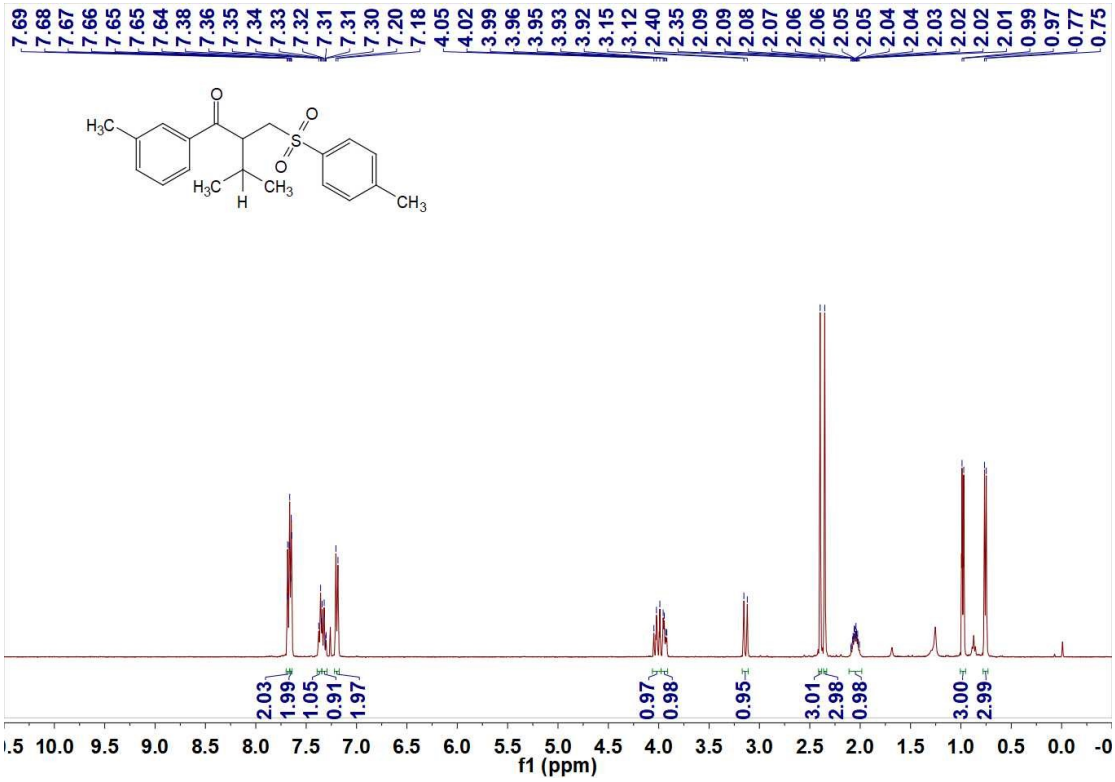
^{1}H NMR of **3ka** (400 MHz, $CDCl_3$)



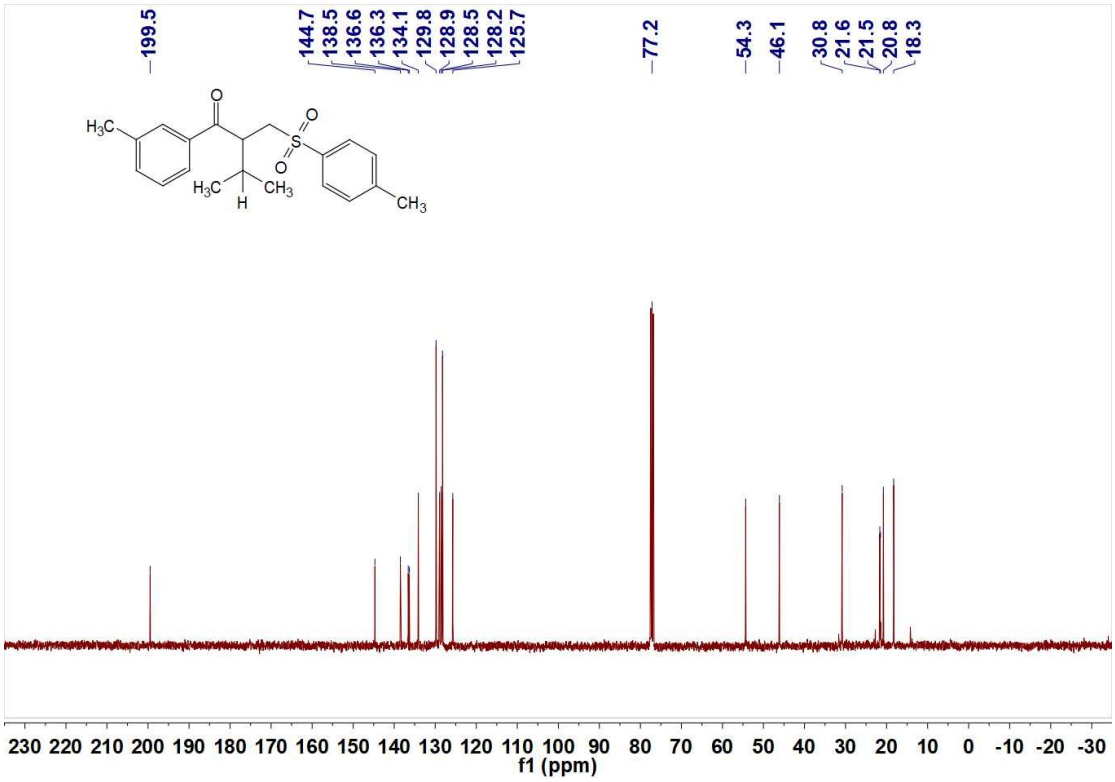
^{13}C NMR of **3ka** (101 MHz, $CDCl_3$, 77.16)



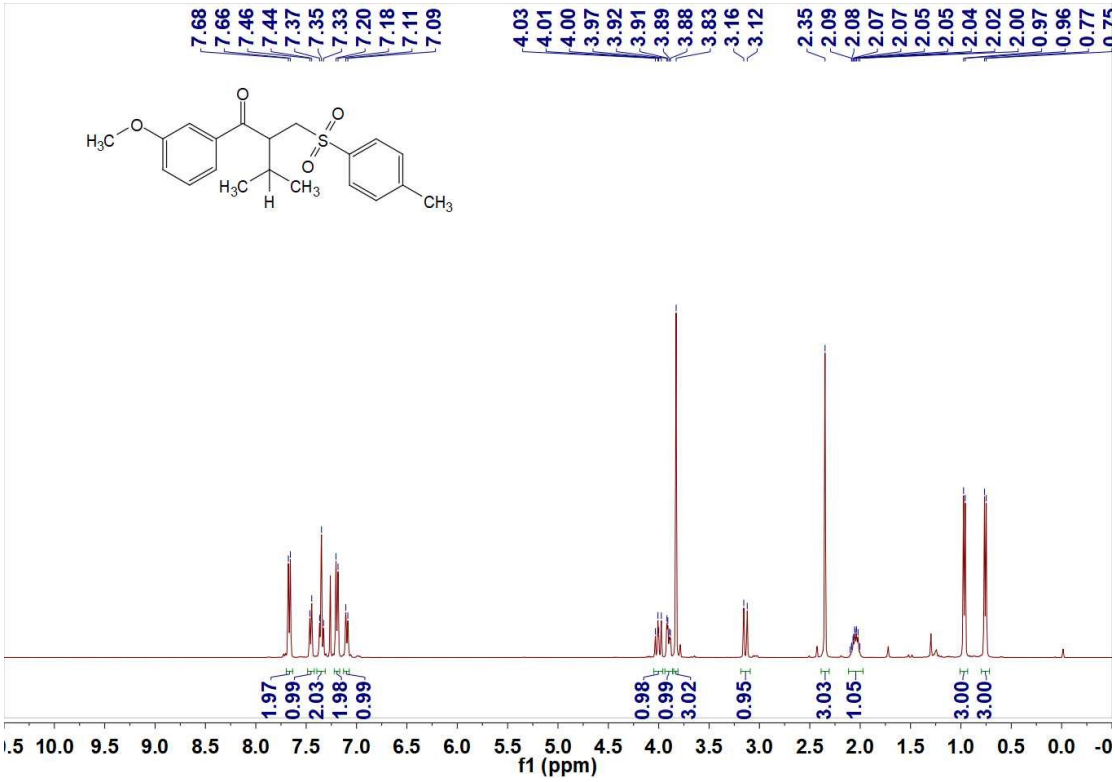
^{1}H NMR of **3la** (400 MHz, $CDCl_3$)



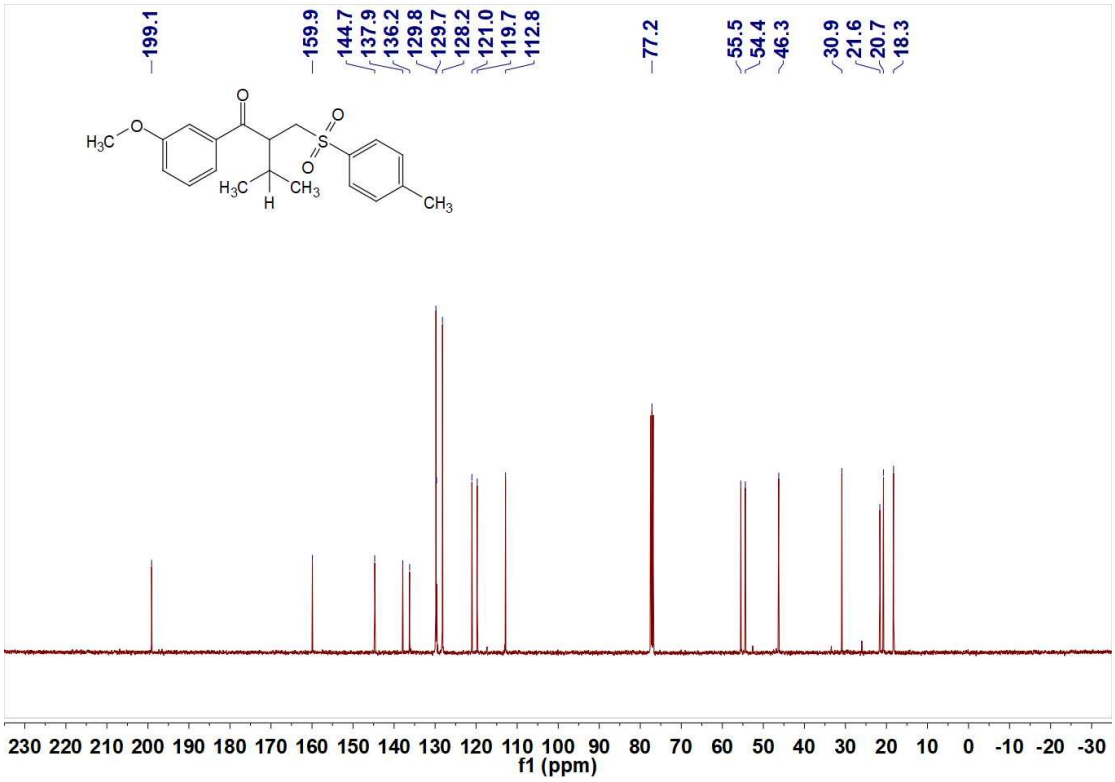
^{13}C NMR of **3la** (101 MHz, $CDCl_3$, 77.16)



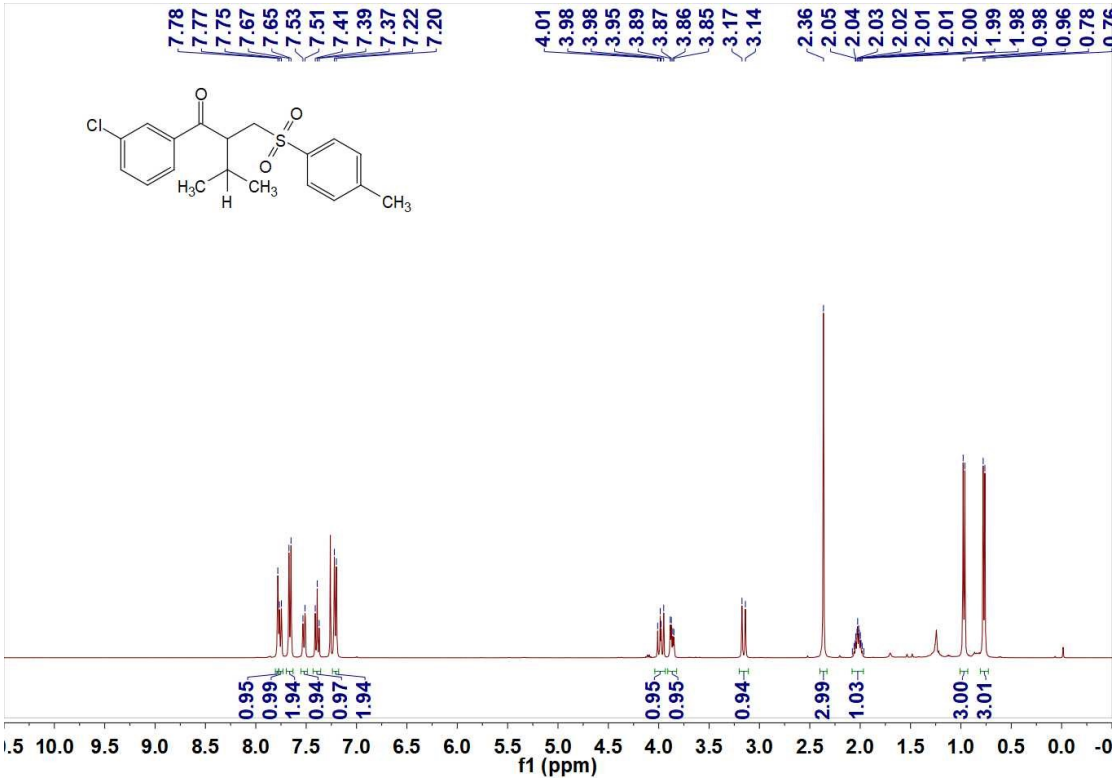
^{1}H NMR of **3ma** (400 MHz, $CDCl_3$)



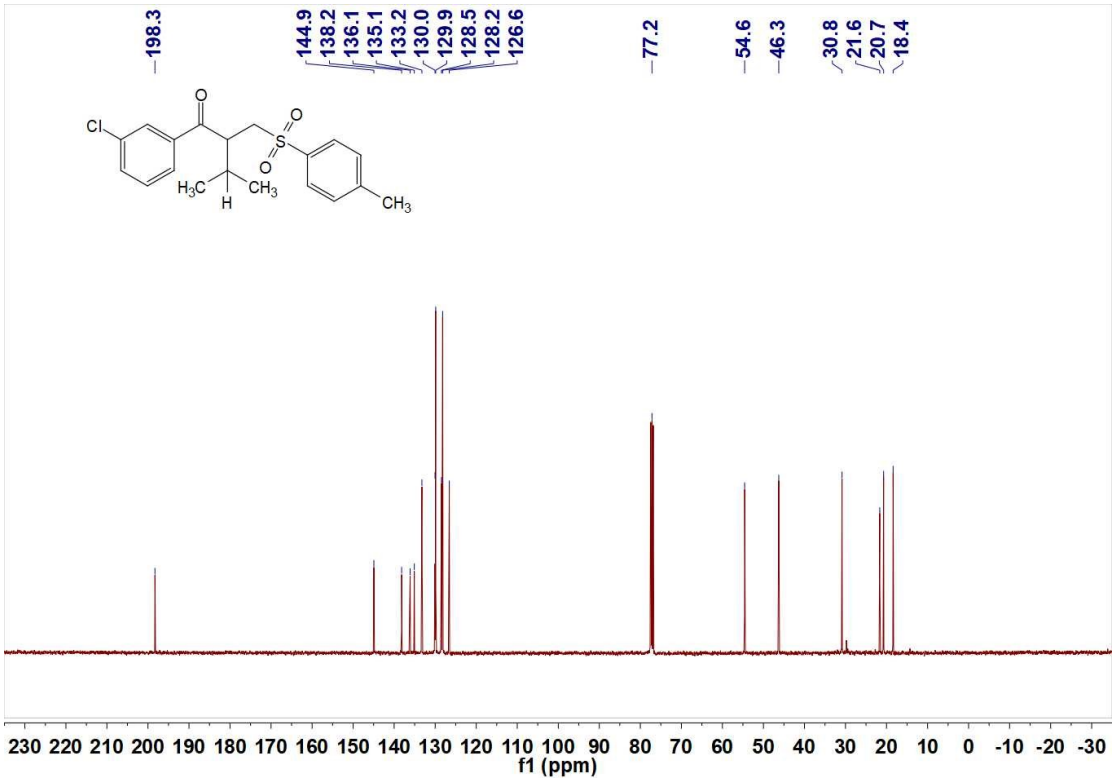
^{13}C NMR of **3ma** (101 MHz, $CDCl_3$, 77.16)



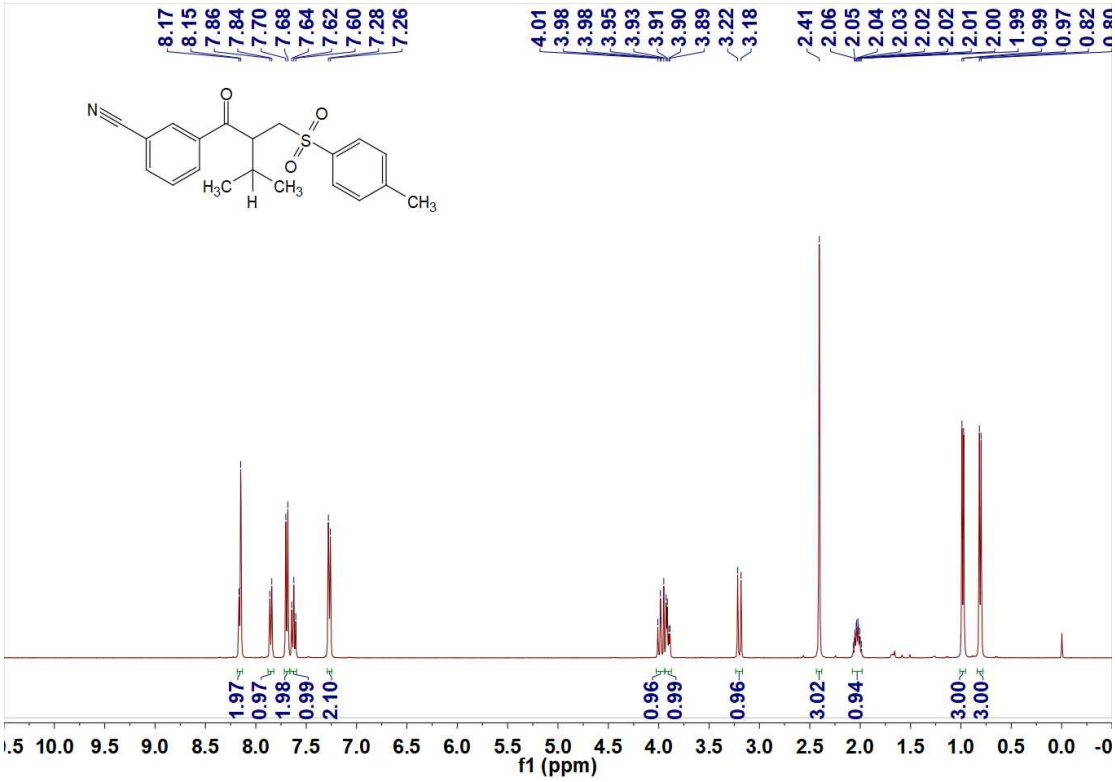
^{1}H NMR of **3na** (400 MHz, $CDCl_3$)



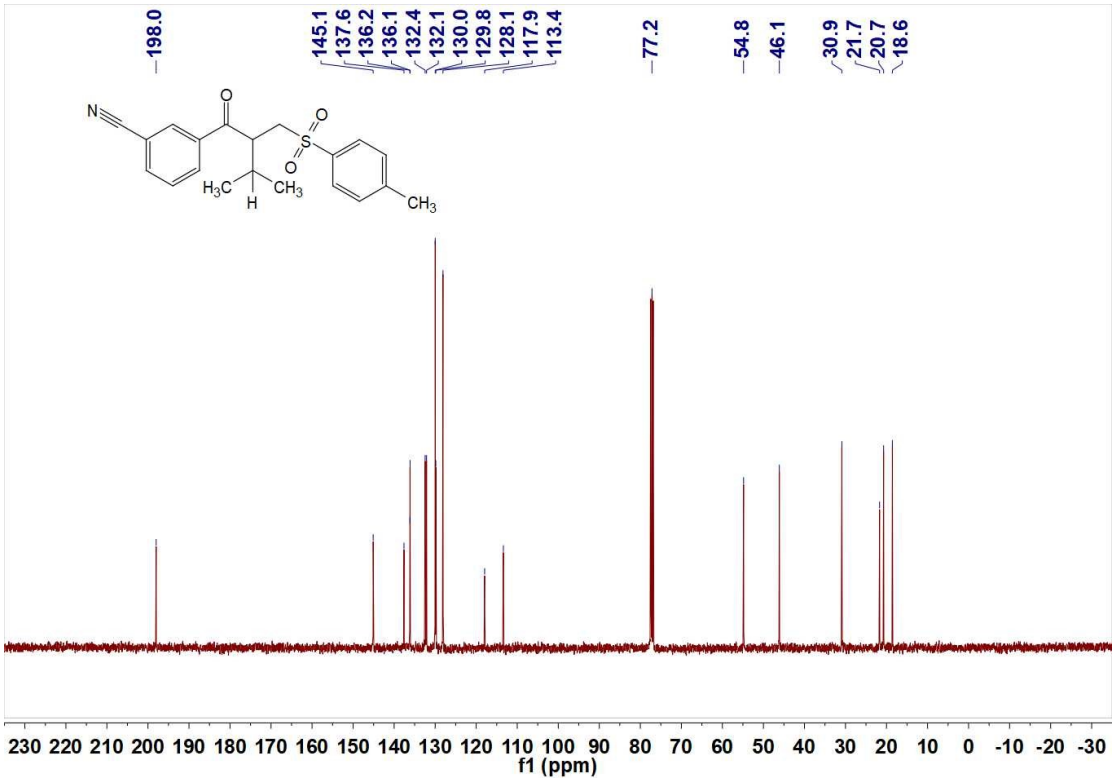
^{13}C NMR of **3na** (101 MHz, $CDCl_3$, 77.16)



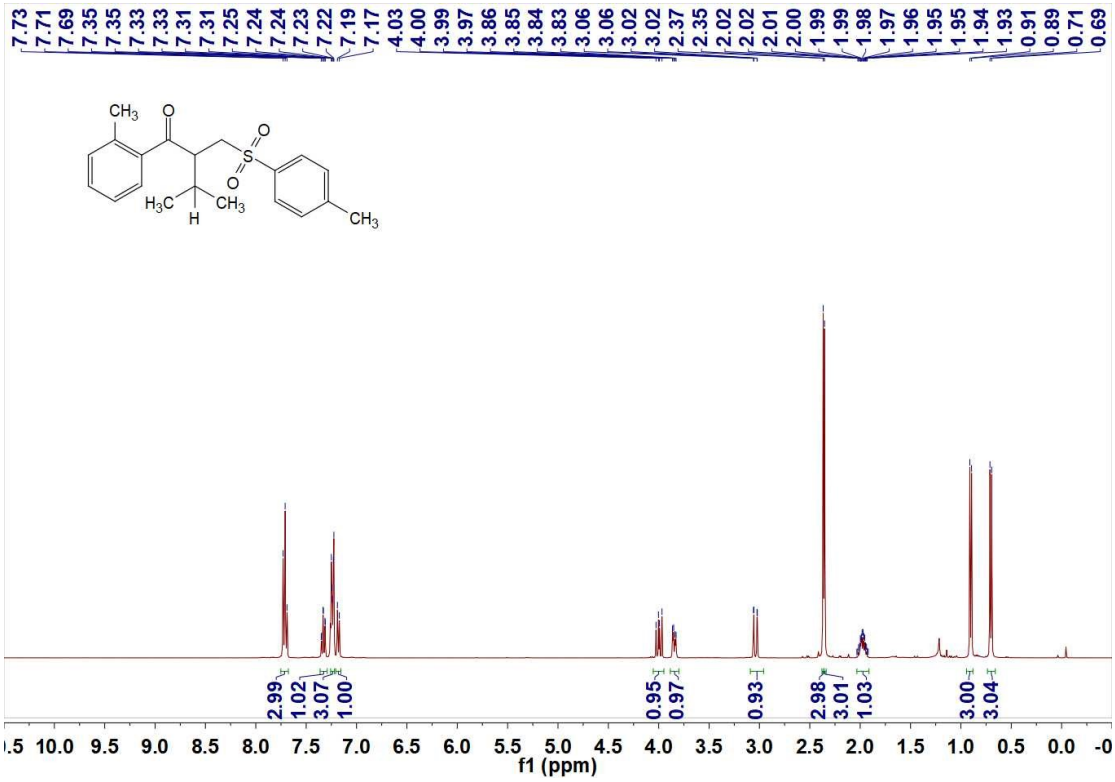
^{1}H NMR of **3oa** (400 MHz, $CDCl_3$)



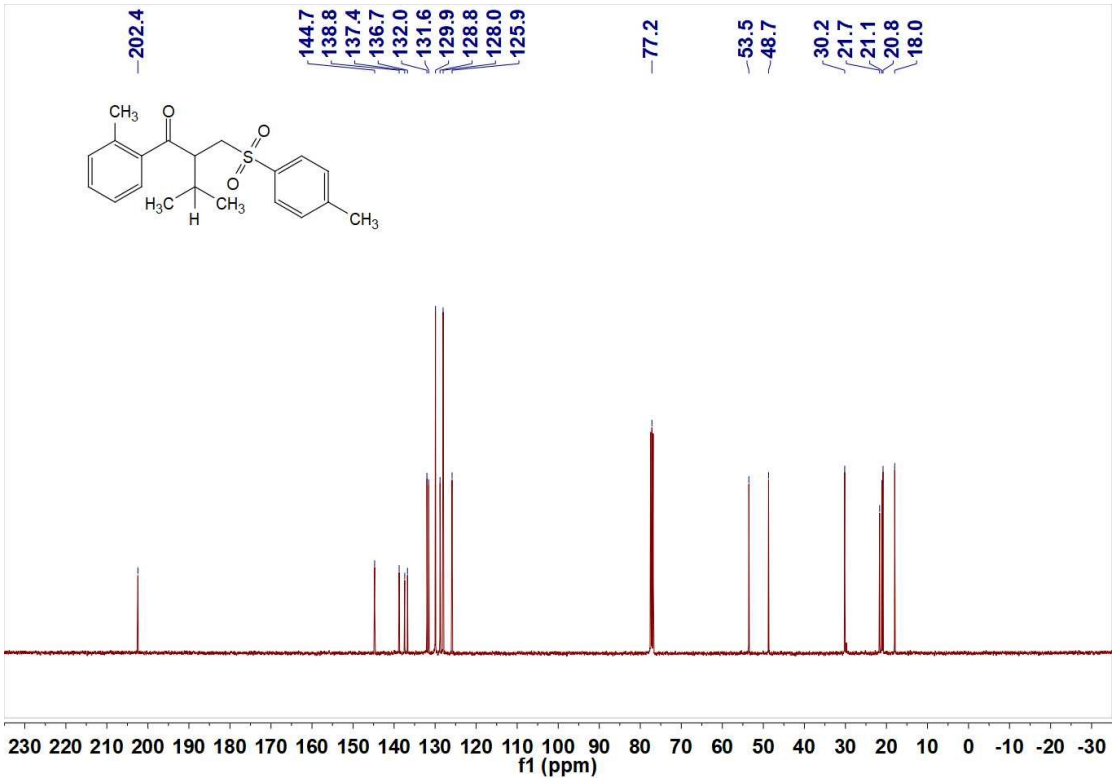
^{13}C NMR of **3oa** (101 MHz, $CDCl_3$, 77.16)



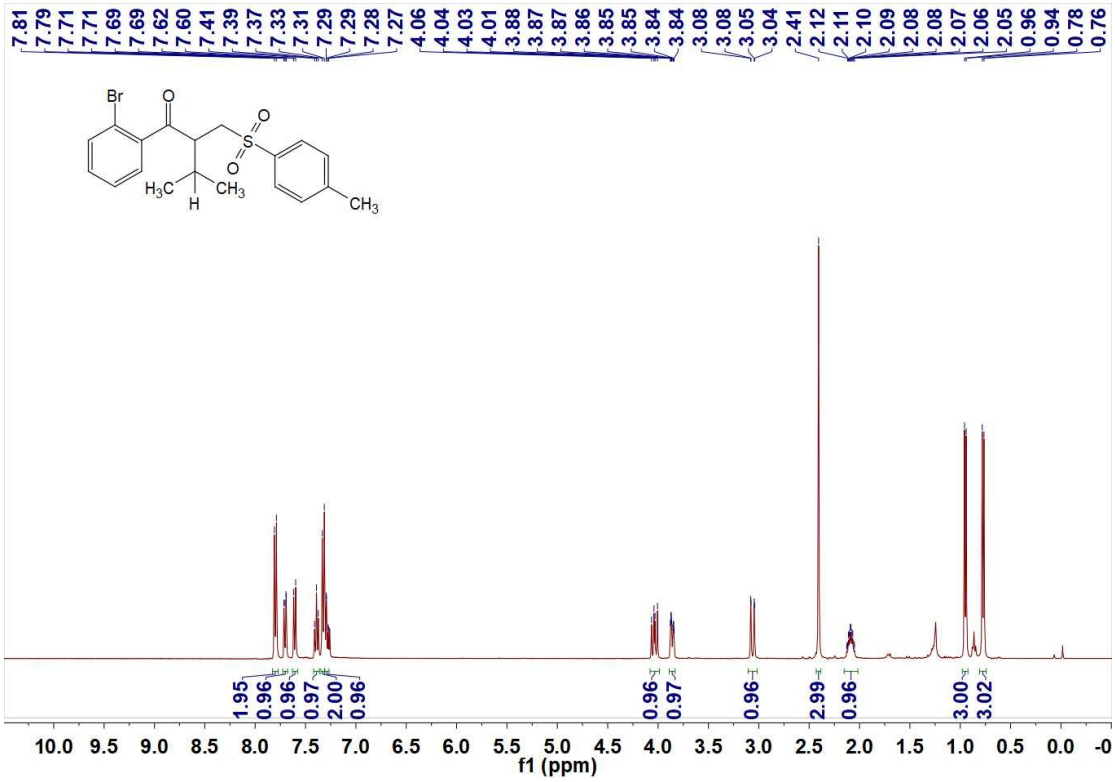
^{1}H NMR of **3pa** (400 MHz, $CDCl_3$)



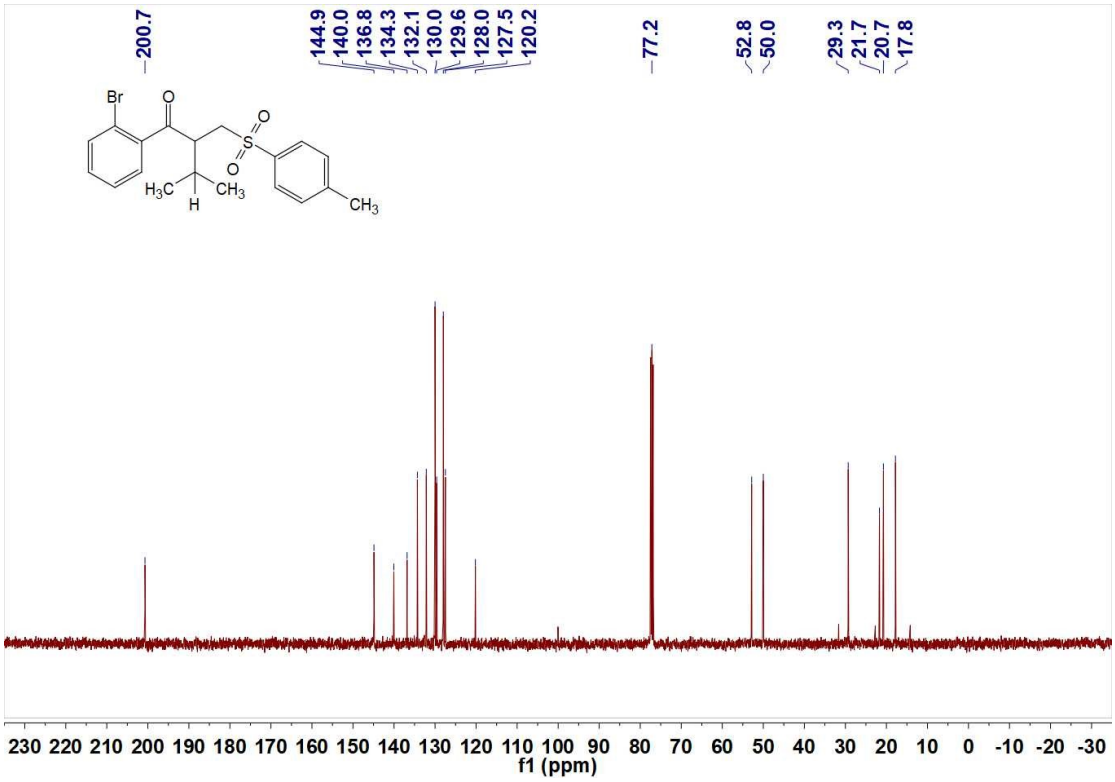
^{13}C NMR of **3pa** (101 MHz, $CDCl_3$, 77.16)



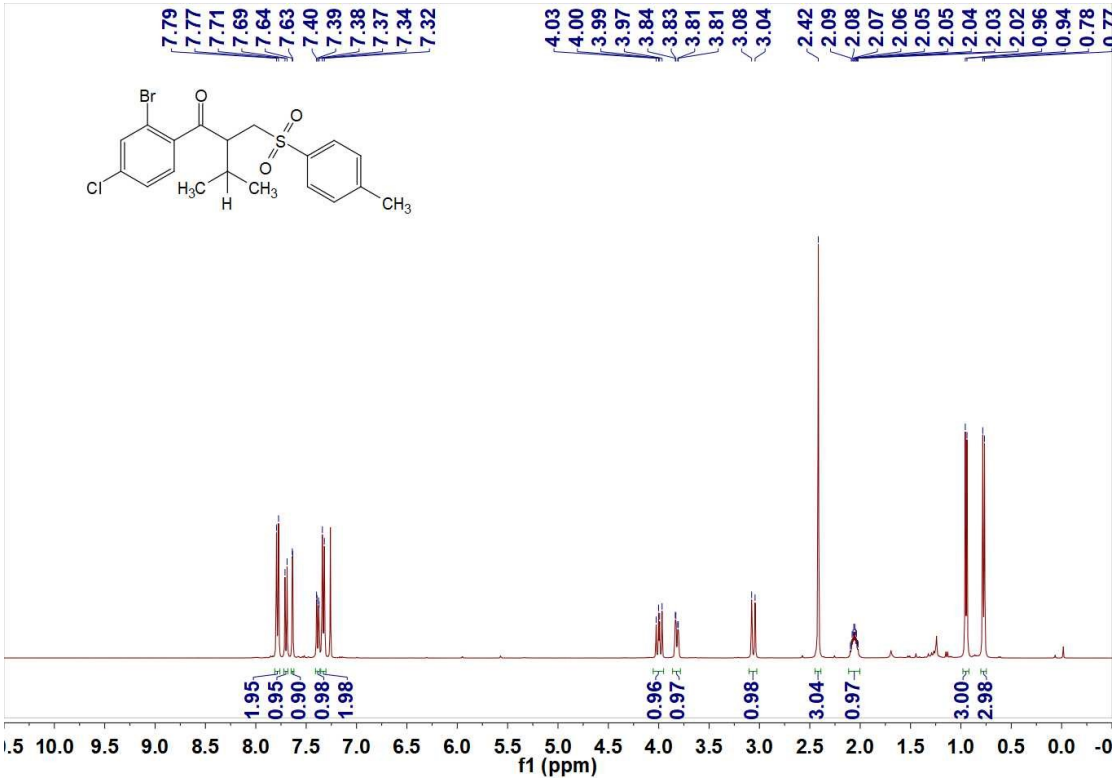
^{1}H NMR of **3qa** (400 MHz, $CDCl_3$)



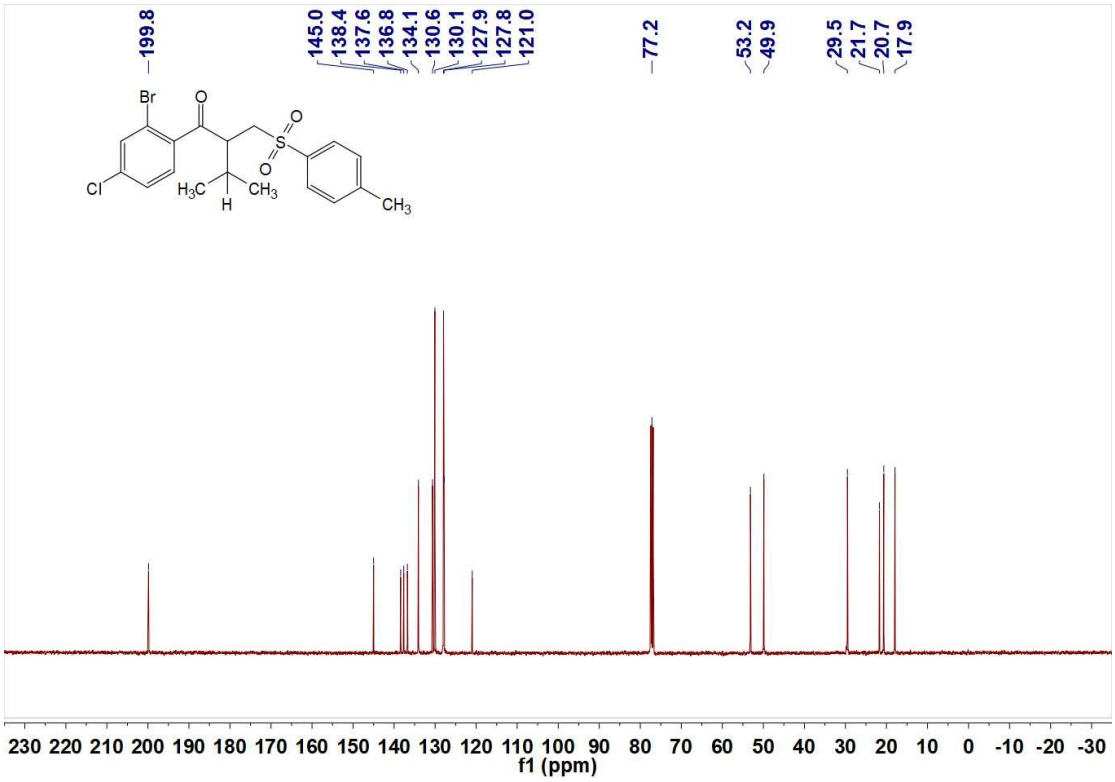
^{13}C NMR of **3qa** (101 MHz, $CDCl_3$, 77.16)



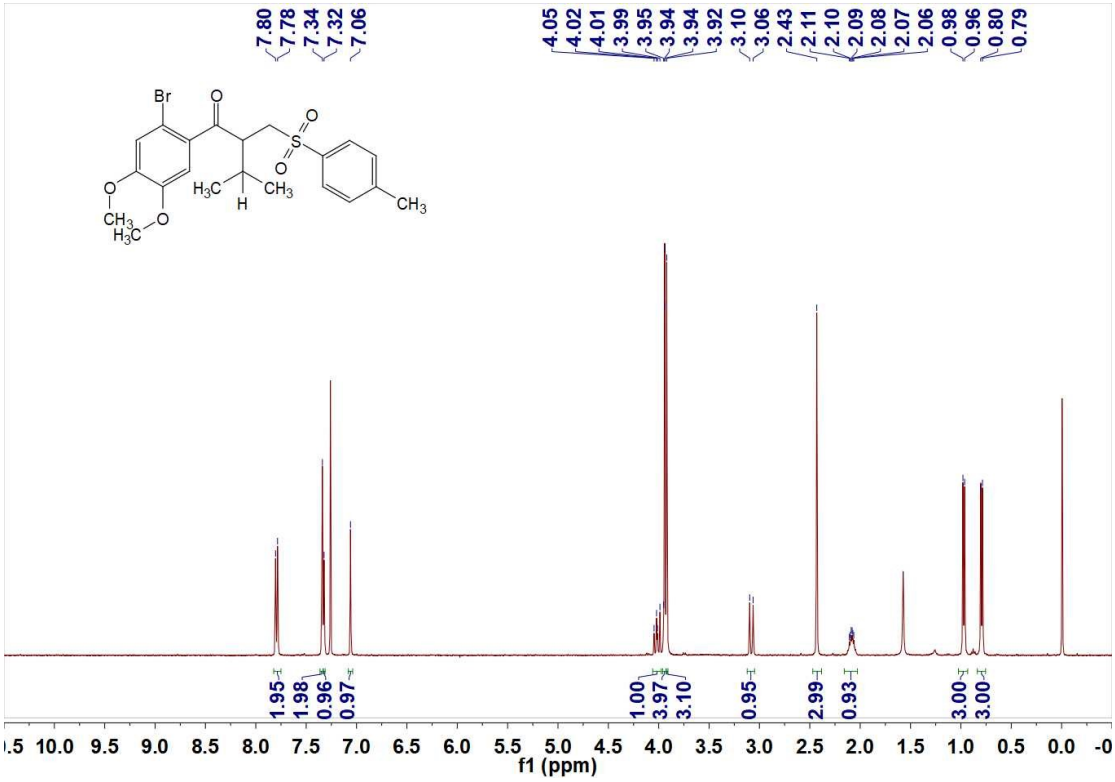
^{1}H NMR of **3ra** (400 MHz, $CDCl_3$)



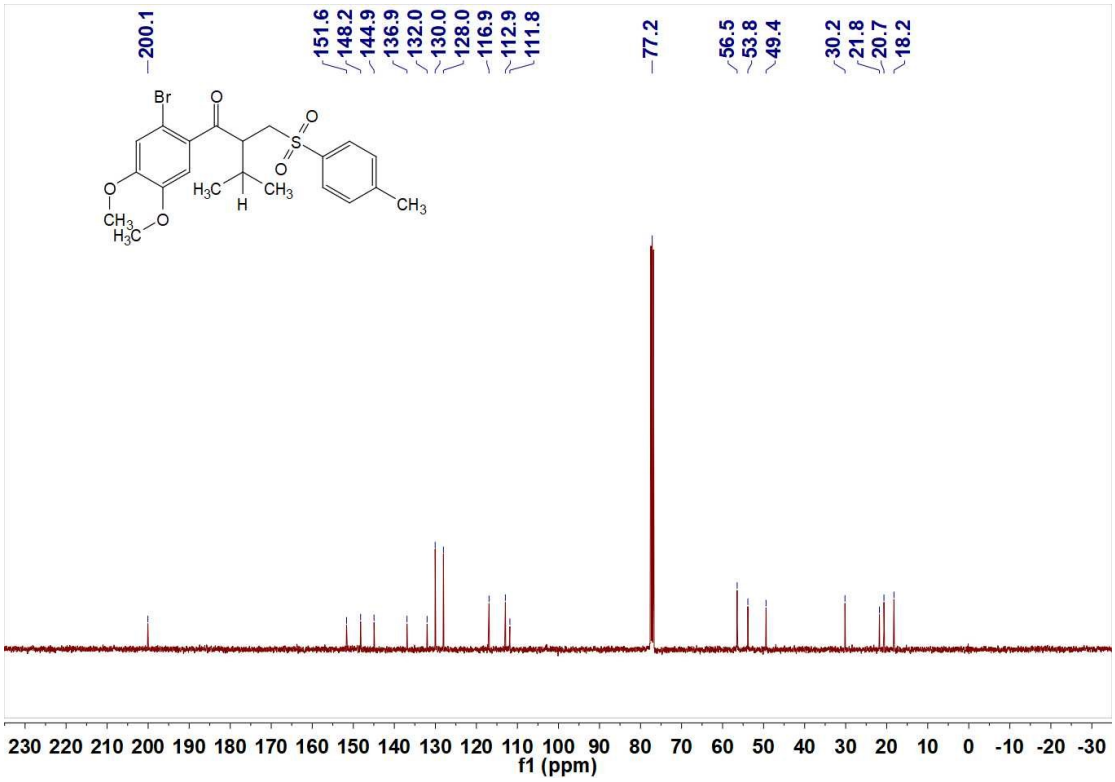
^{13}C NMR of **3ra** (101 MHz, $CDCl_3$, 77.16)



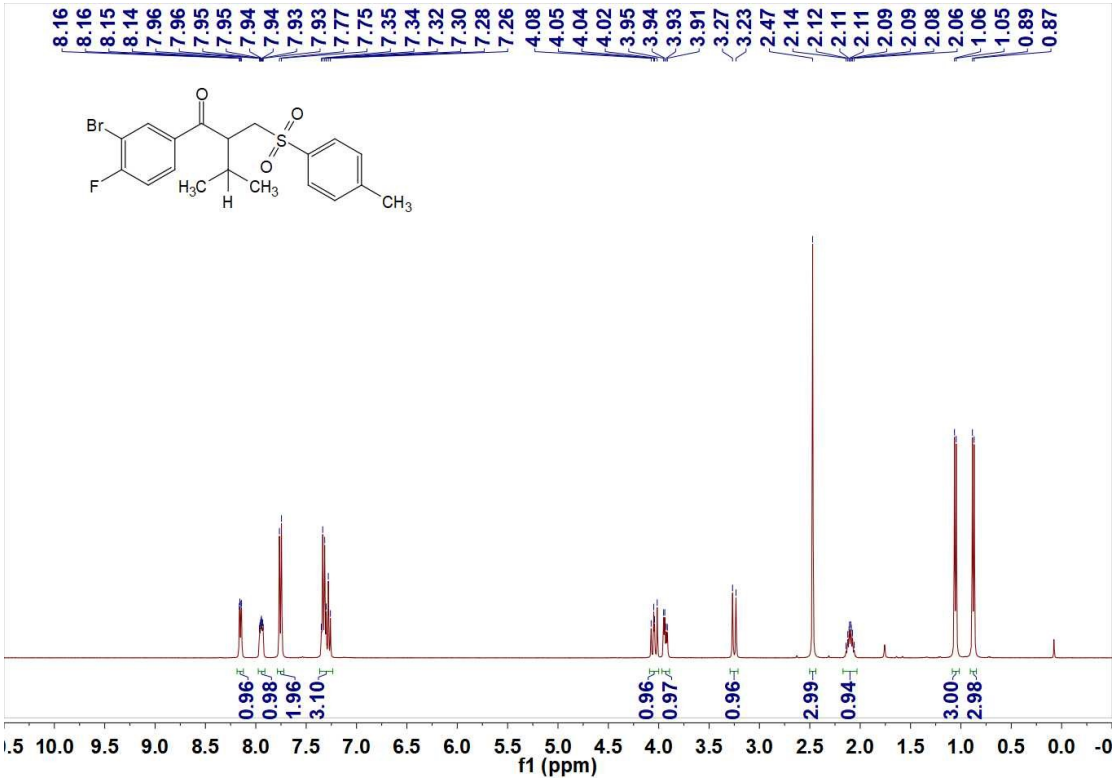
^{1}H NMR of **3sa** (400 MHz, $CDCl_3$)



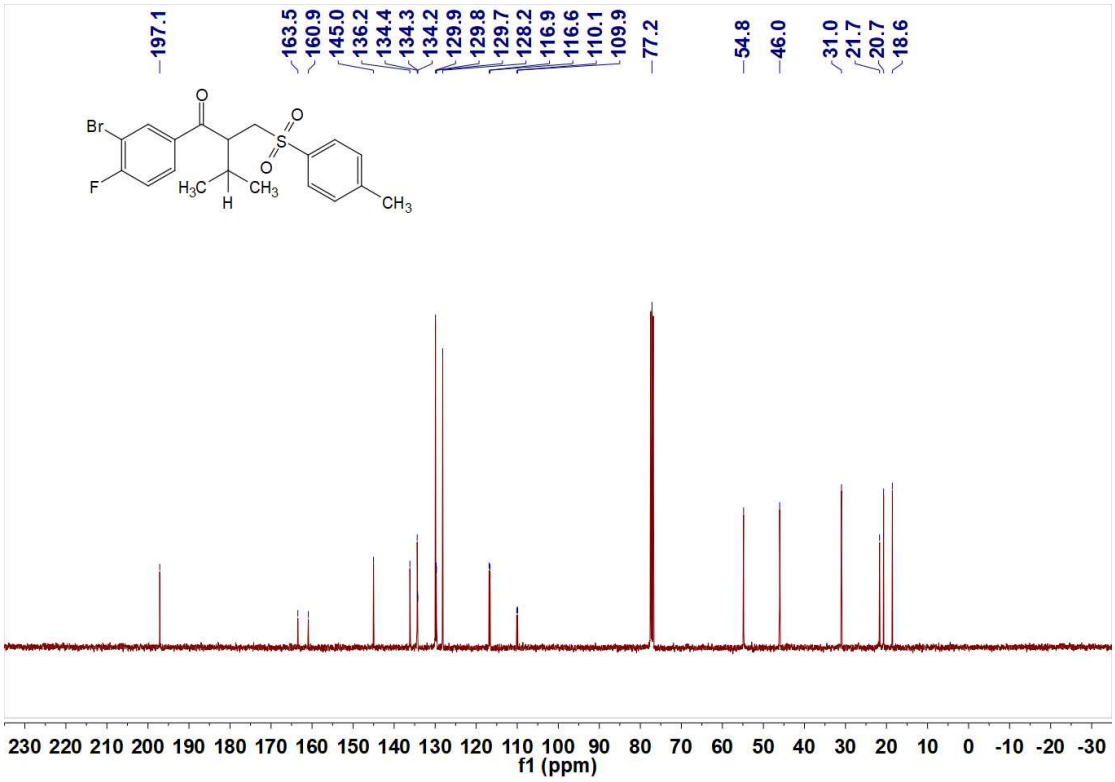
^{13}C NMR of **3sa** (101 MHz, $CDCl_3$, 77.16)



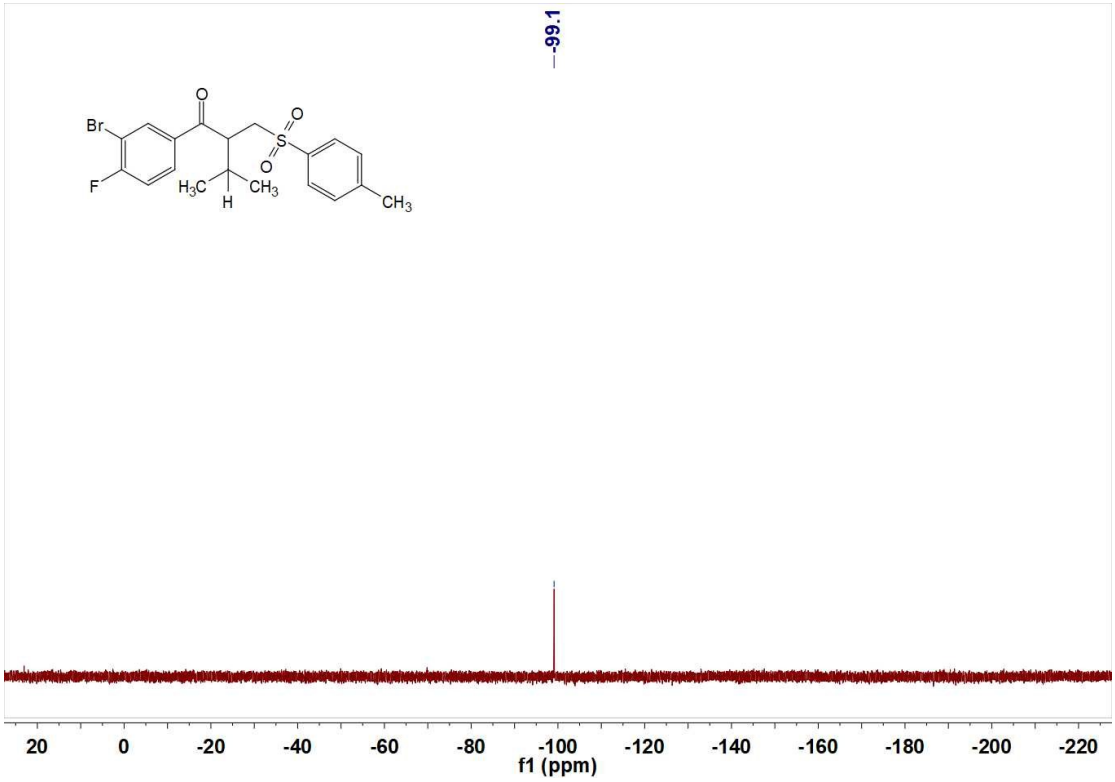
^{1}H NMR of **3ta** (400 MHz, $CDCl_3$)



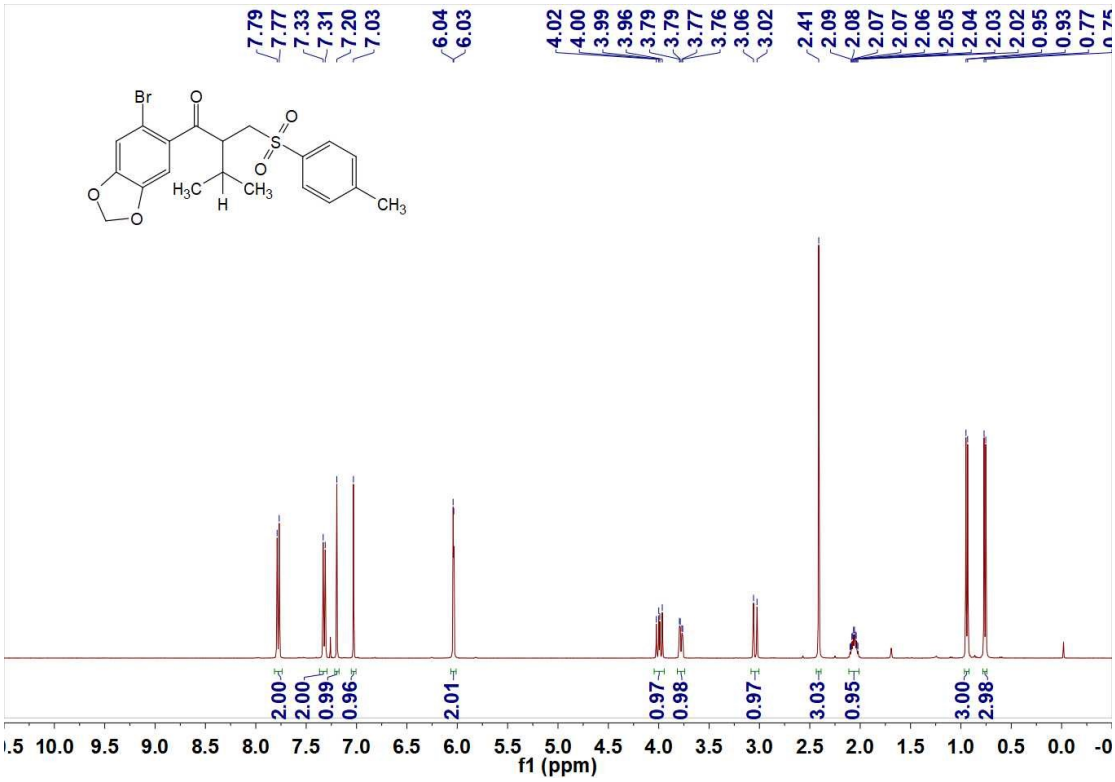
^{13}C NMR of **3ta** (101 MHz, $CDCl_3$, 77.16)



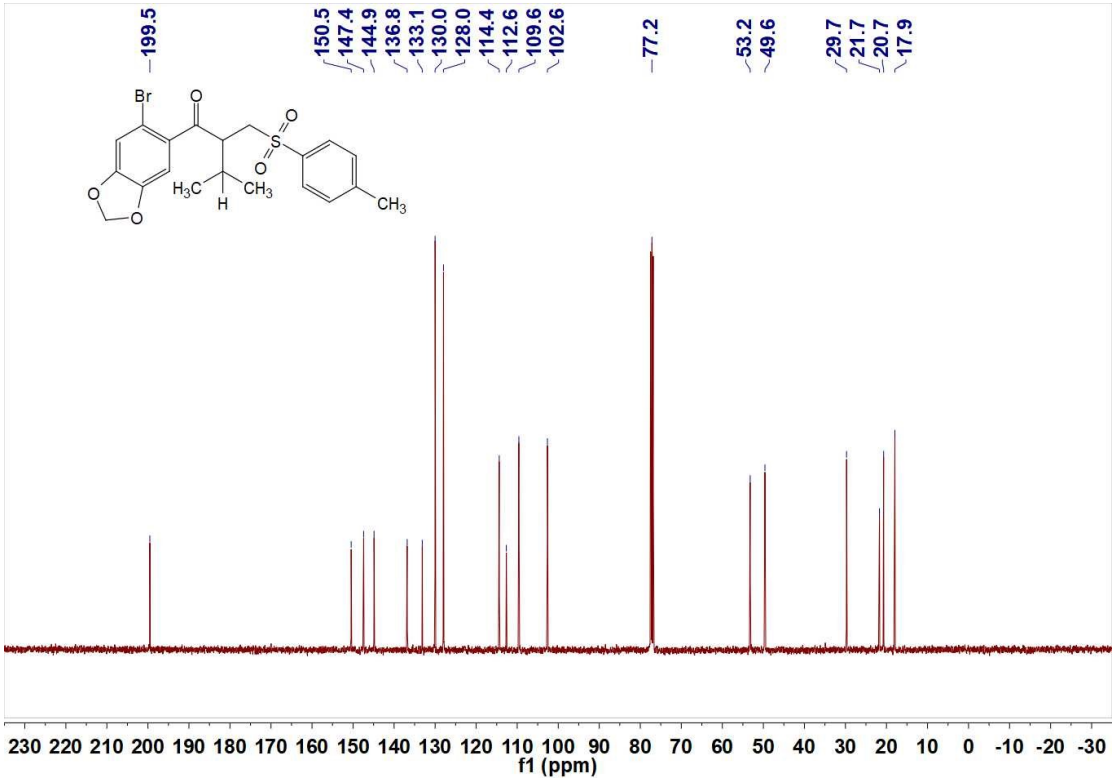
^{19}F NMR of **3ta** (376 MHz, $CDCl_3$)



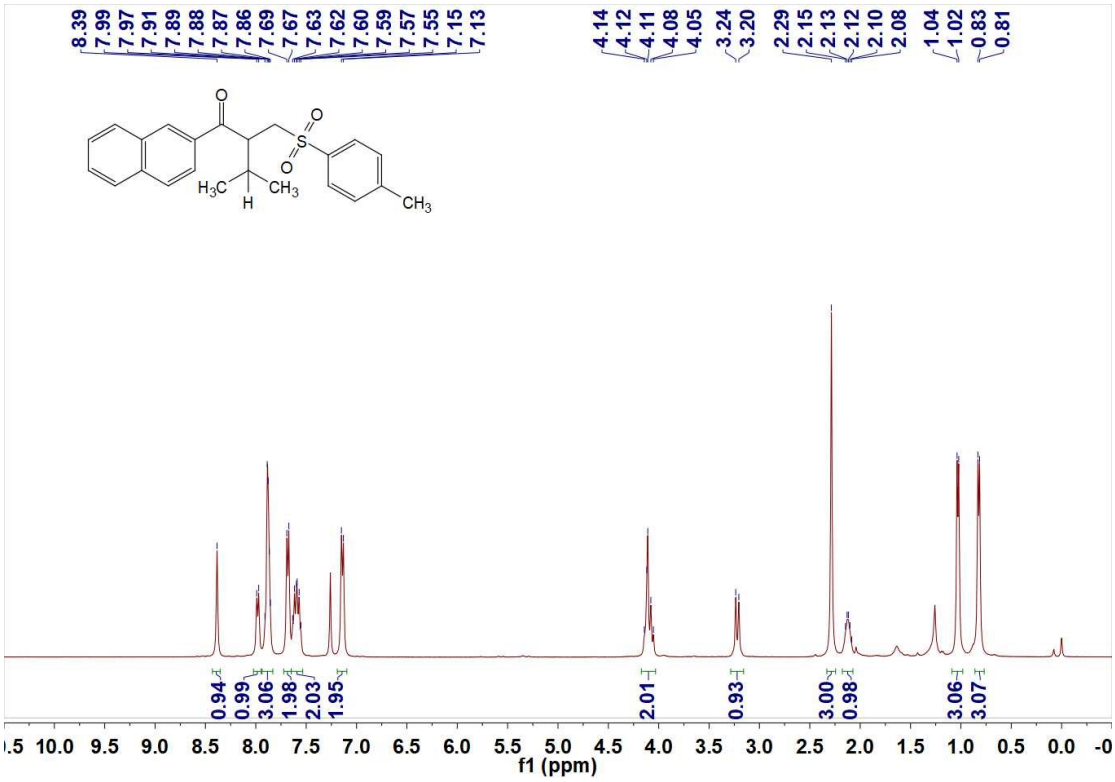
^{1}H NMR of **3ua** (400 MHz, $CDCl_3$)



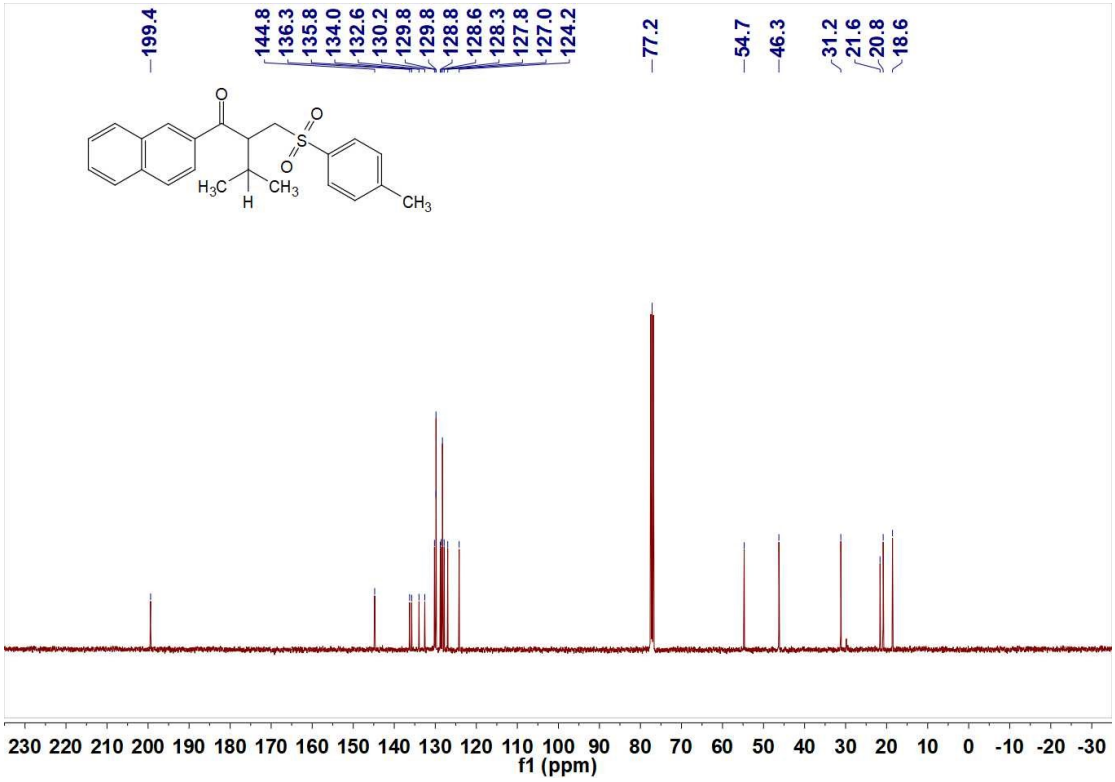
^{13}C NMR of **3ua** (101 MHz, $CDCl_3$, 77.16)



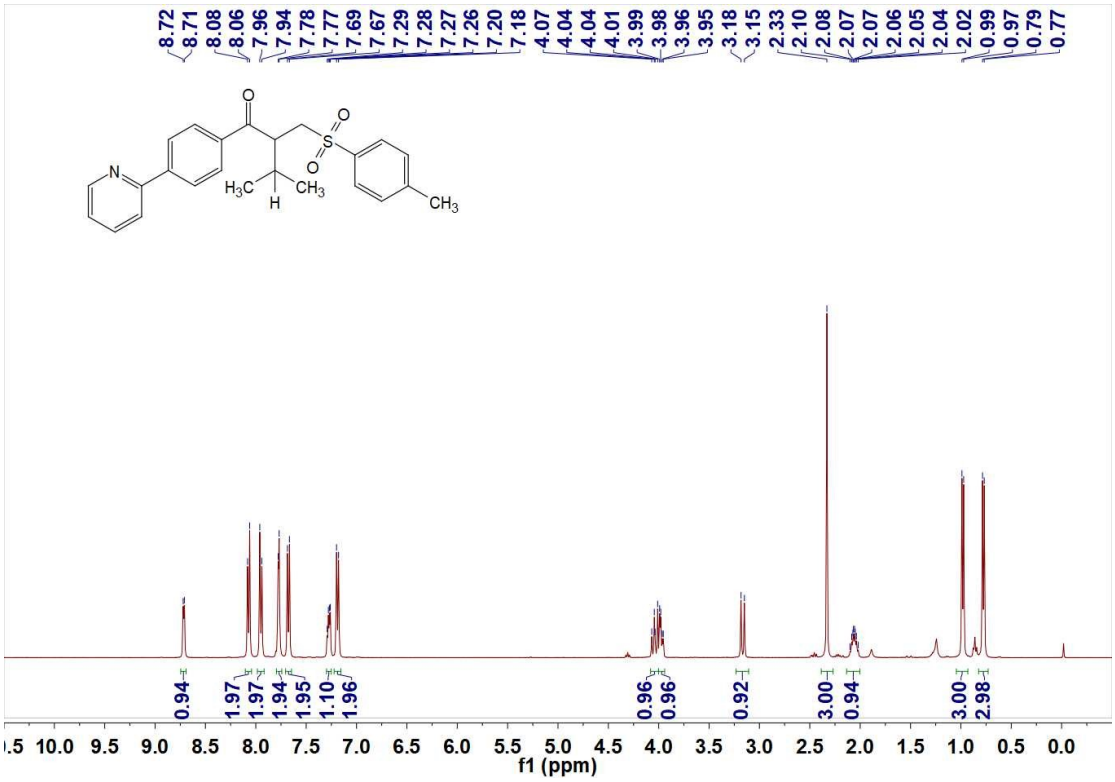
^{1}H NMR of **3va** (400 MHz, $CDCl_3$)



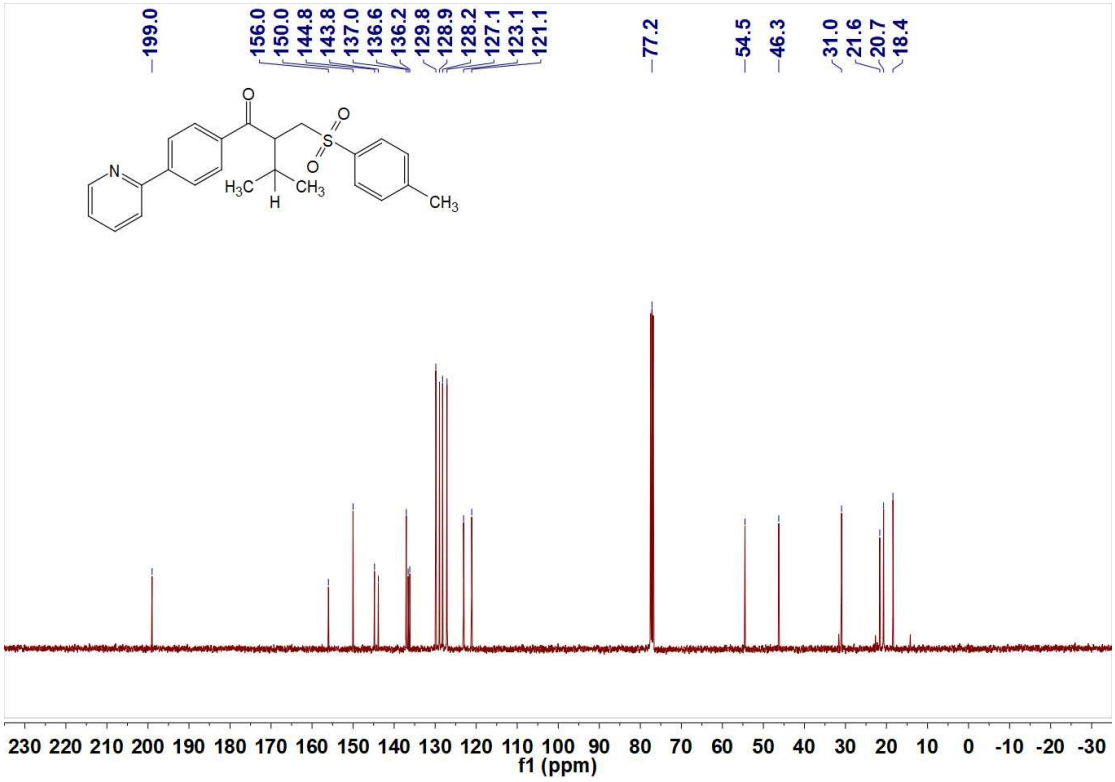
^{13}C NMR of **3va** (101 MHz, $CDCl_3$, 77.16)



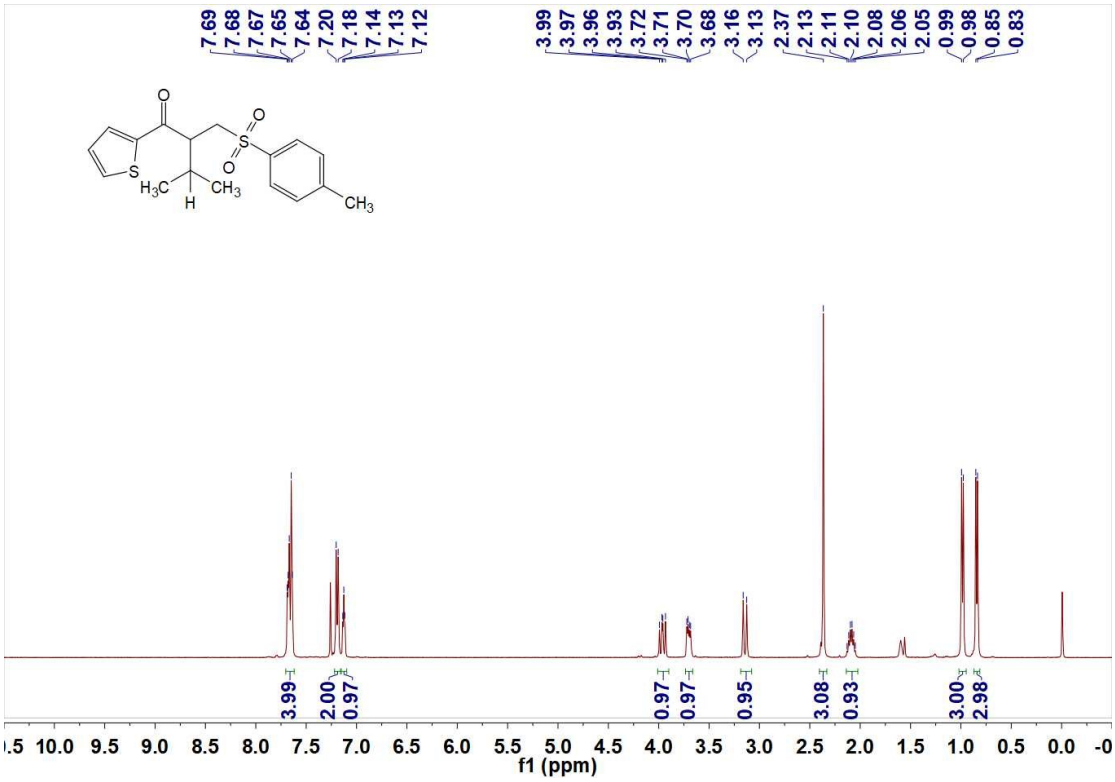
^{1}H NMR of **3wa** (400 MHz, $CDCl_3$)



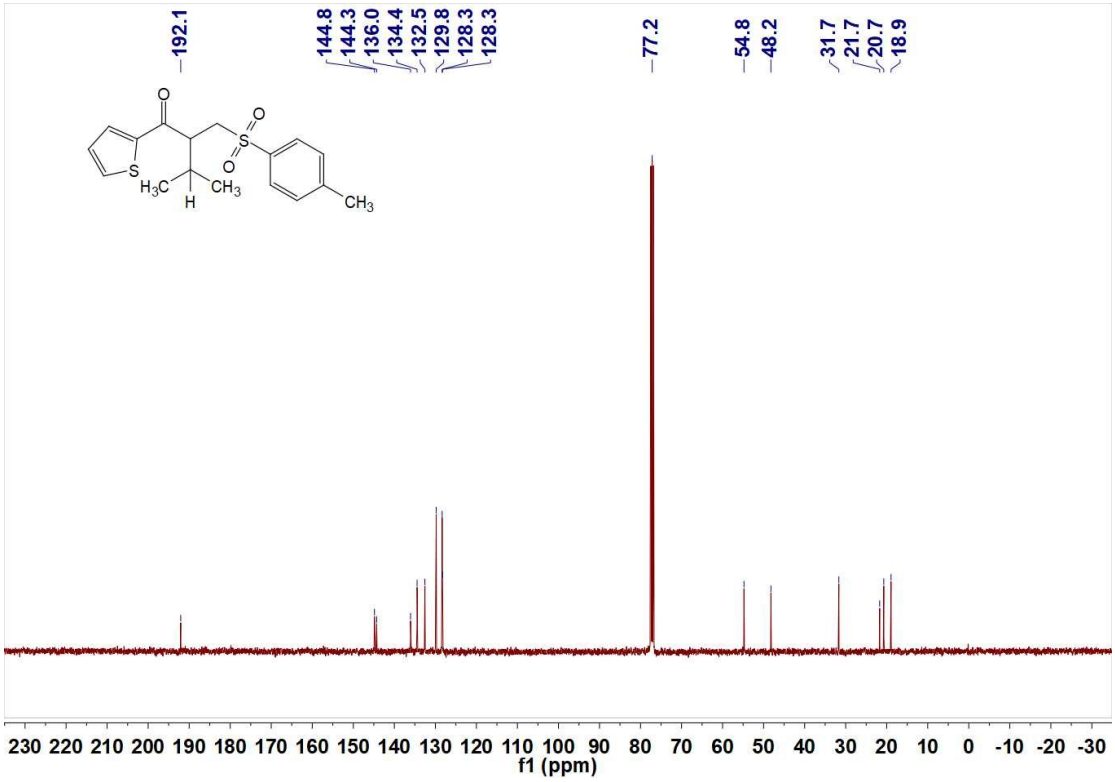
^{13}C NMR of **3wa** (101 MHz, $CDCl_3$, 77.16)



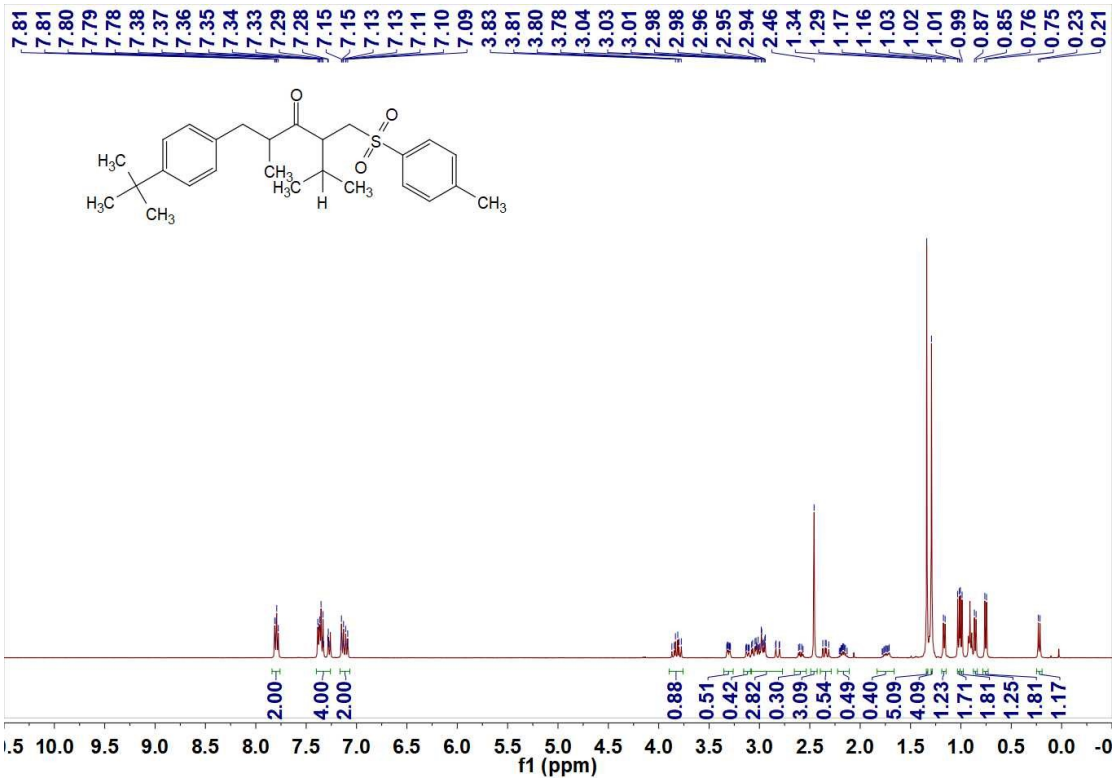
^{1}H NMR of **3xa** (400 MHz, $CDCl_3$)



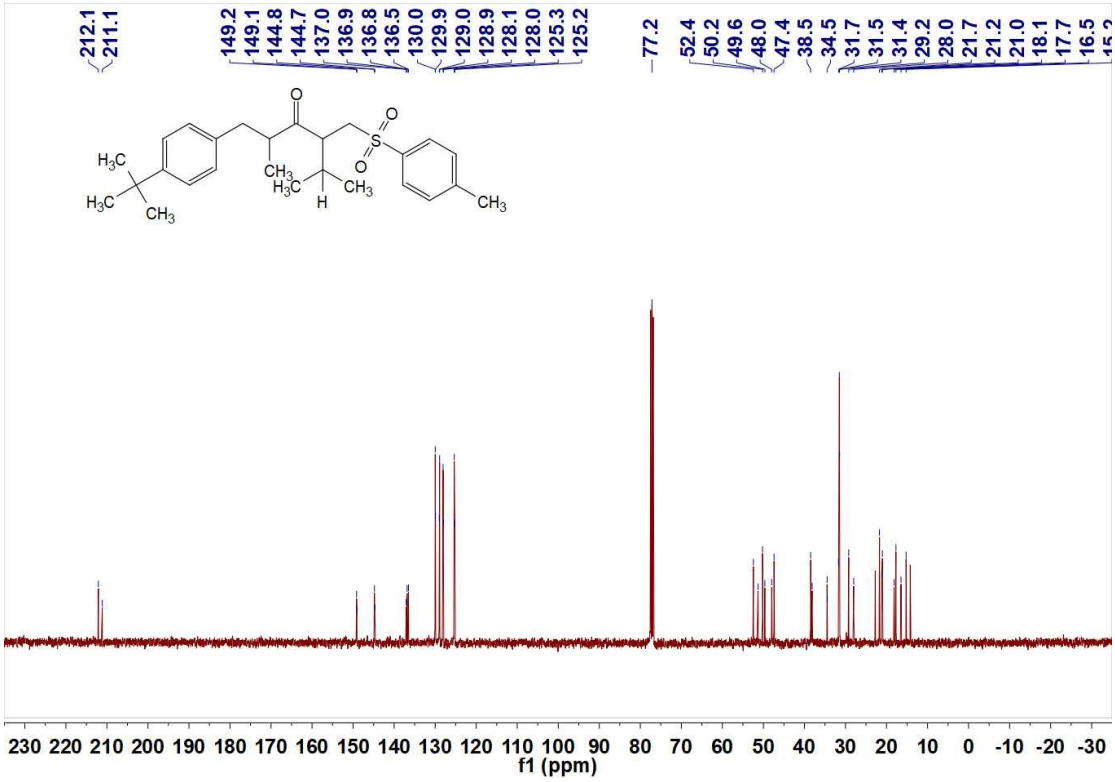
^{13}C NMR of **3xa** (101 MHz, $CDCl_3$, 77.16)



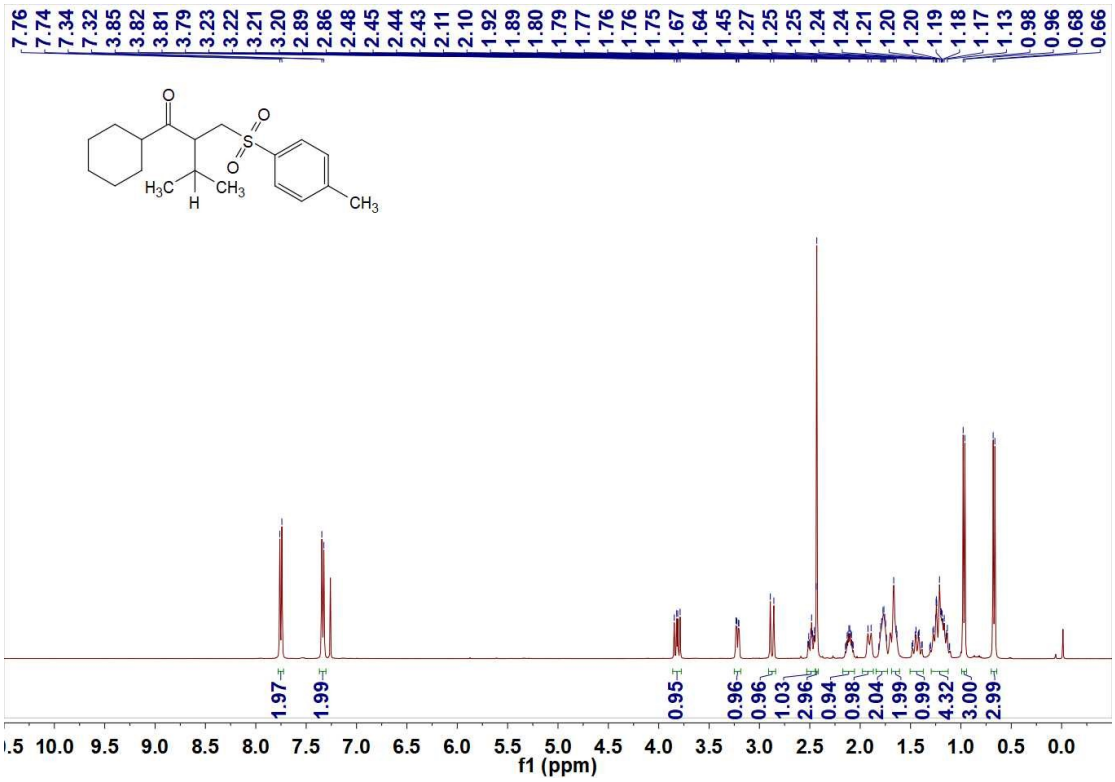
^{1}H NMR of **3ya** (400 MHz, $CDCl_3$)



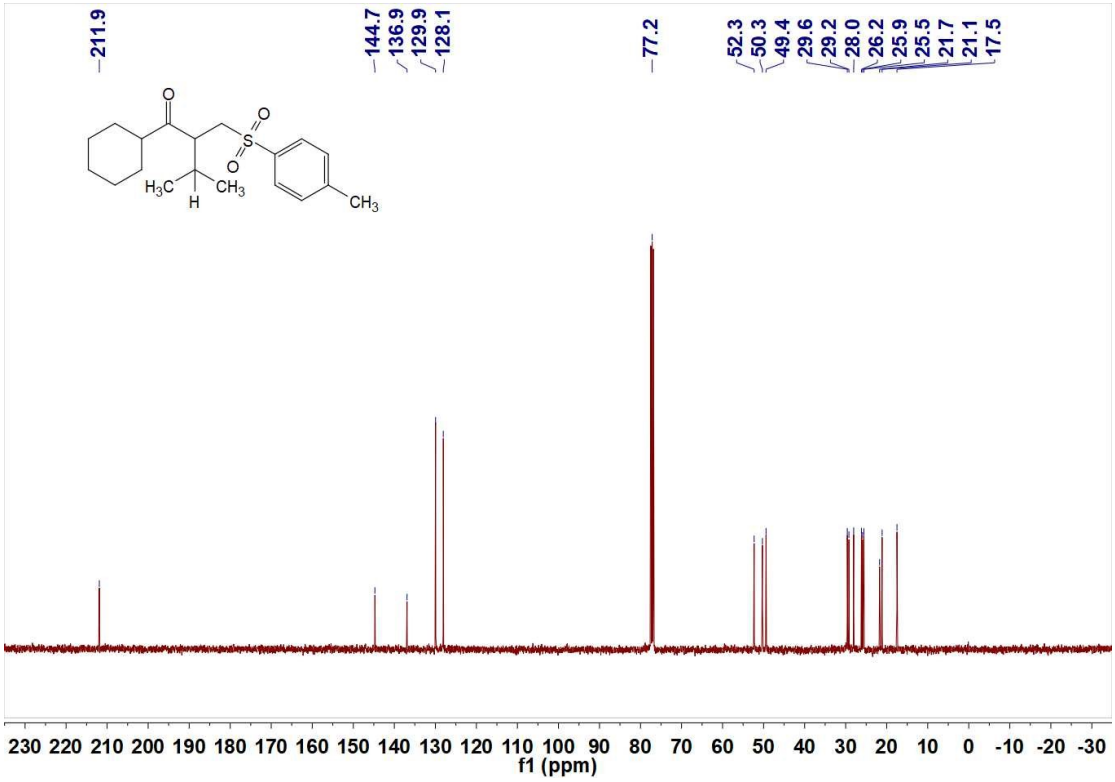
^{13}C NMR of **3ya** (101 MHz, $CDCl_3$, 77.16)



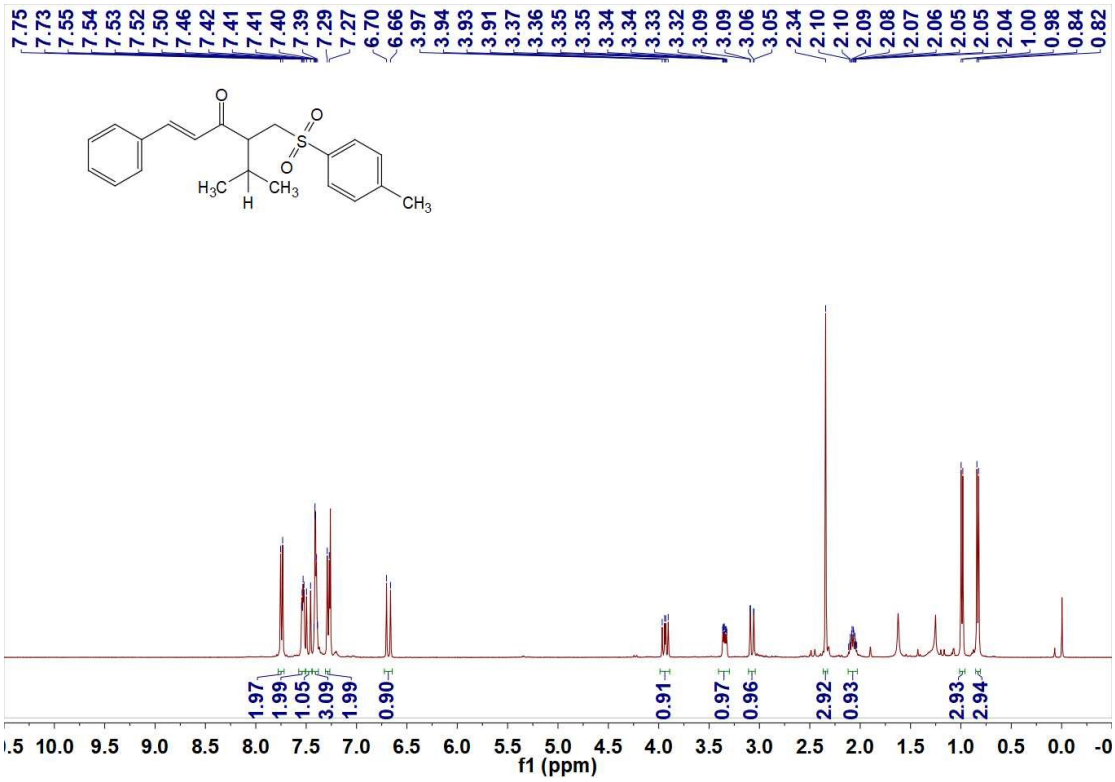
^{13}C NMR of **3za** (400 MHz, $CDCl_3$)



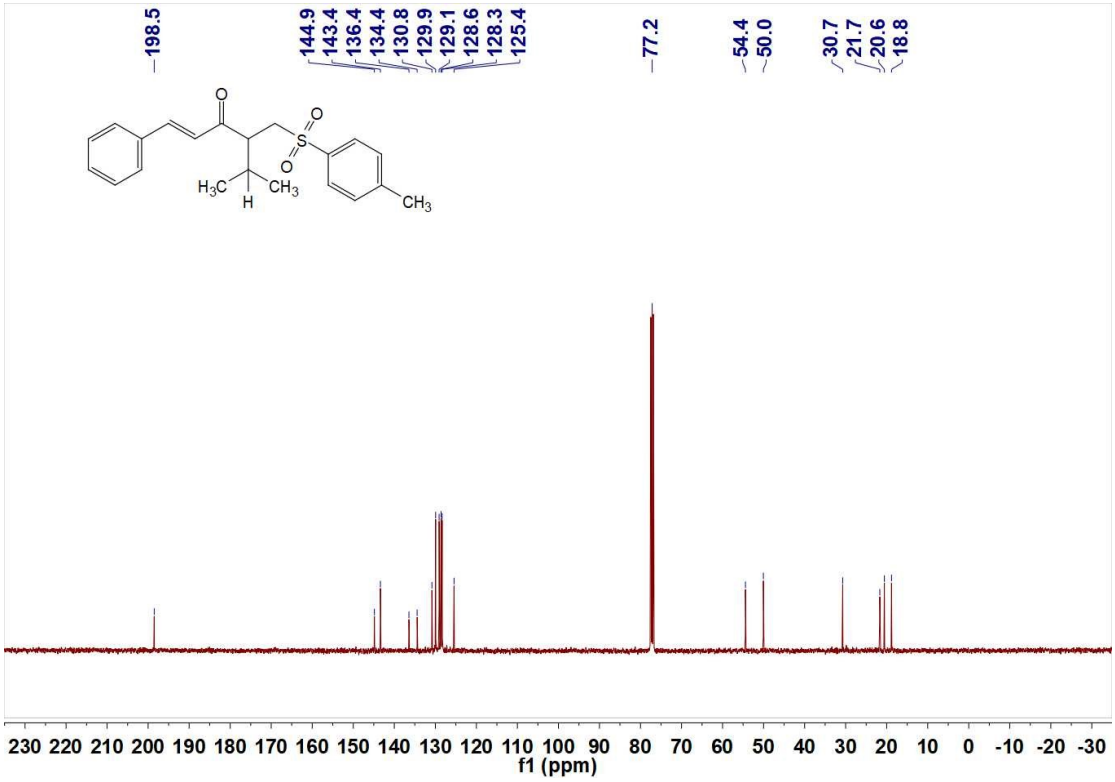
^{13}C NMR of **3za** (101 MHz, $CDCl_3$, 77.16)



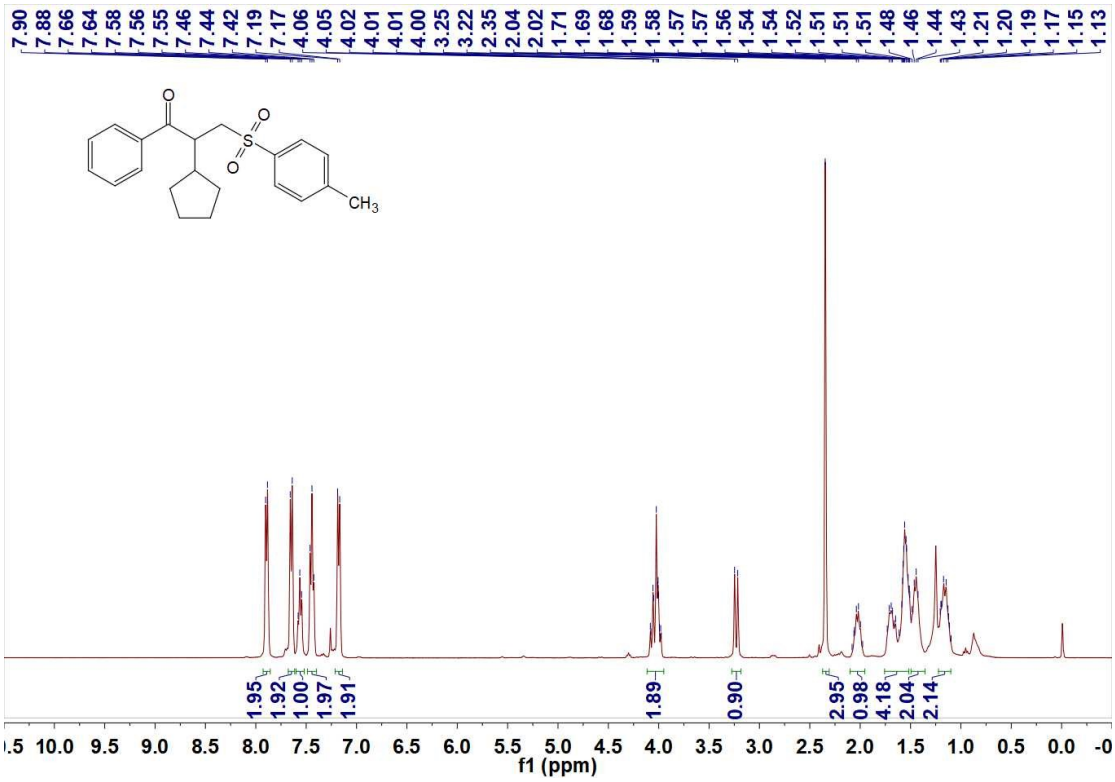
^{1}H NMR of **3aaa** (400 MHz, $CDCl_3$)



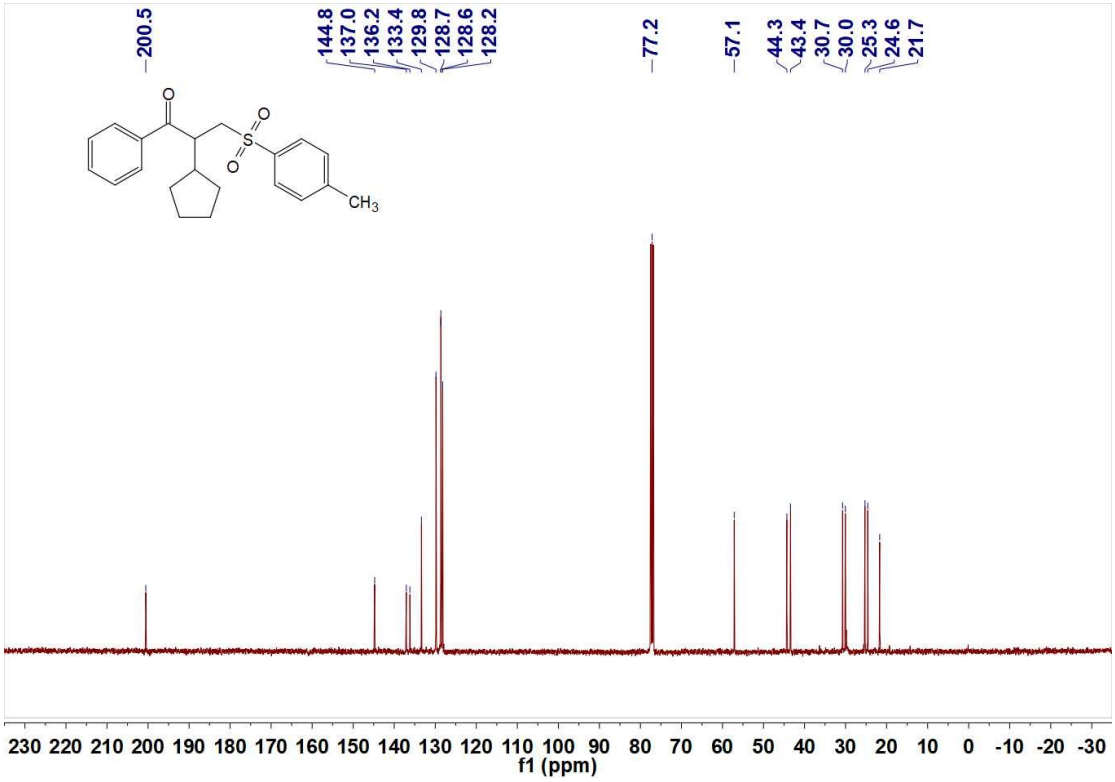
^{13}C NMR of **3aaa** (101 MHz, $CDCl_3$, 77.16)



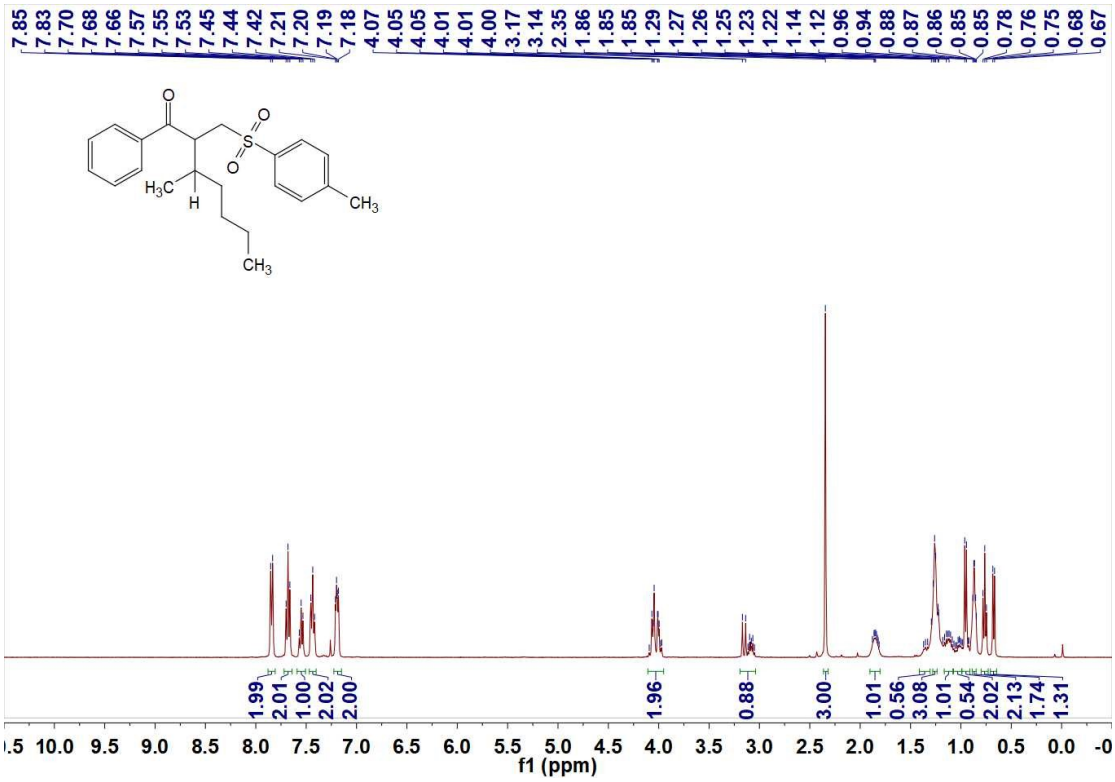
^{1}H NMR of **3aba** (400 MHz, $CDCl_3$)



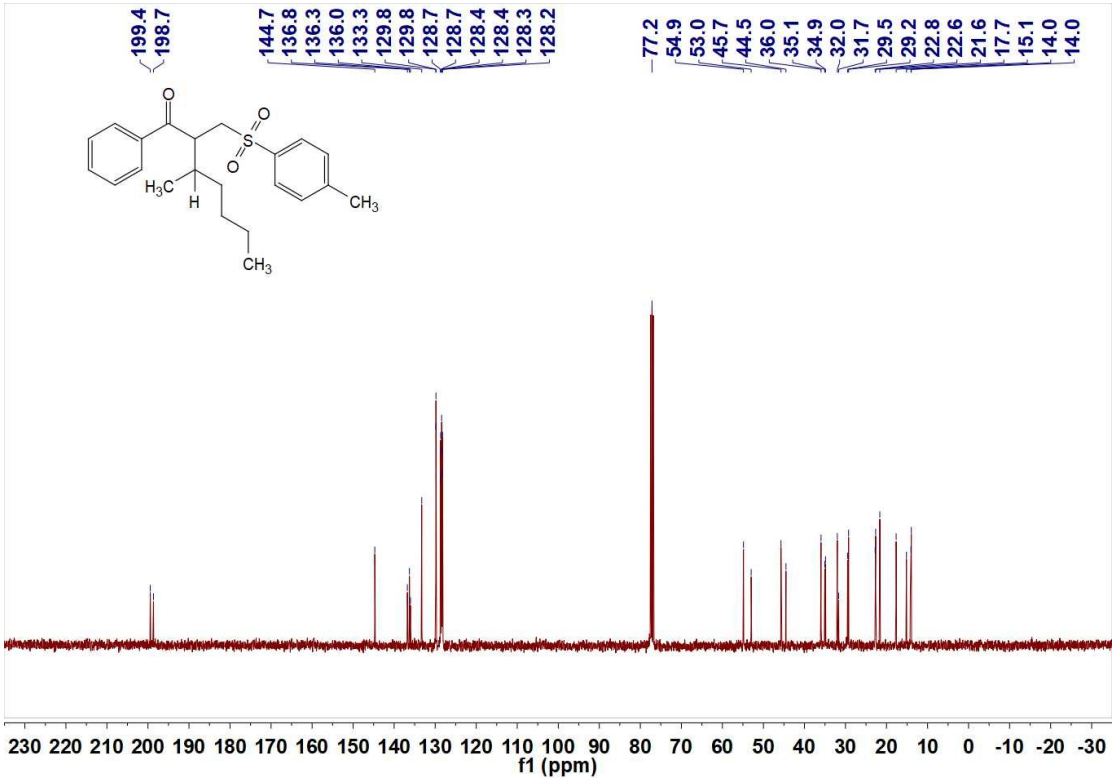
^{13}C NMR of **3aba** (101 MHz, $CDCl_3$, 77.16)



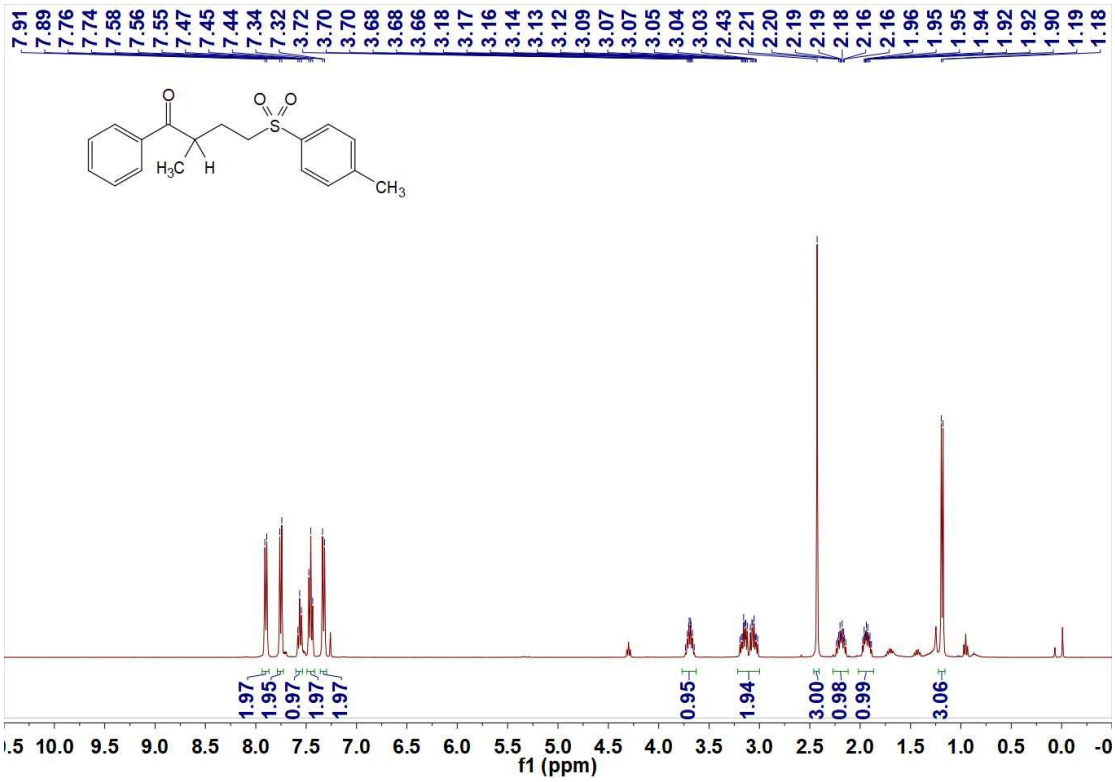
^{1}H NMR of **3aca** (400 MHz, $CDCl_3$)



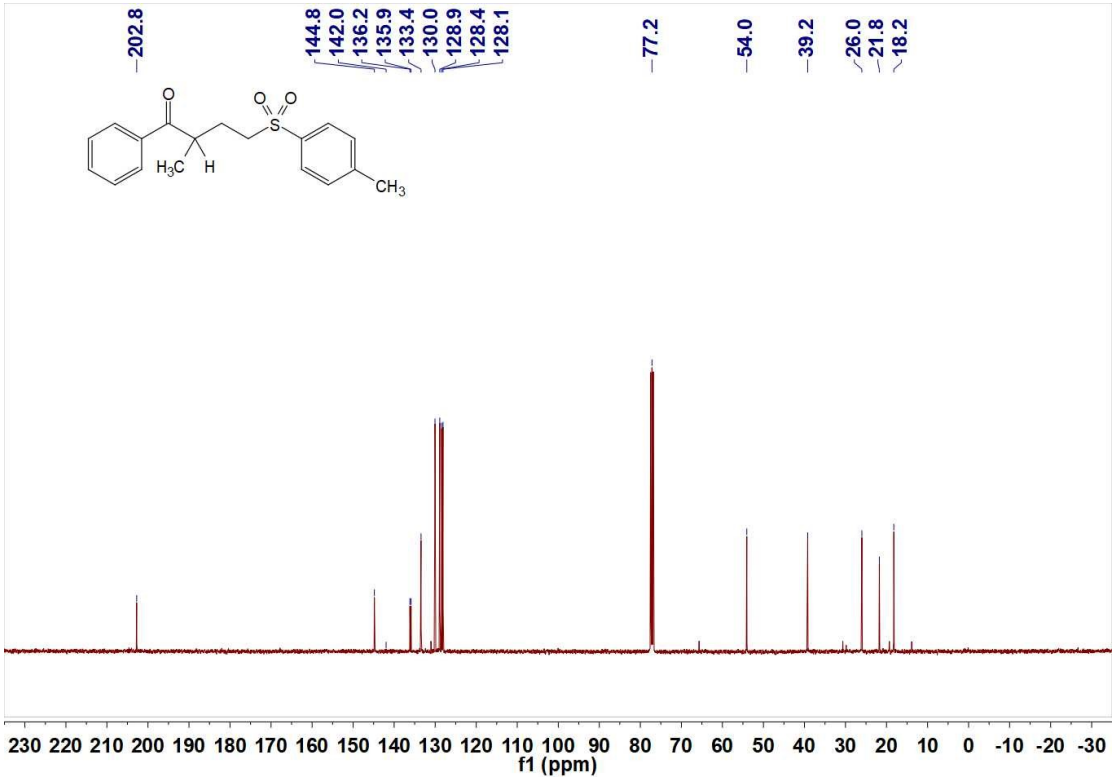
^{13}C NMR of **3aca** (101 MHz, $CDCl_3$, 77.16)



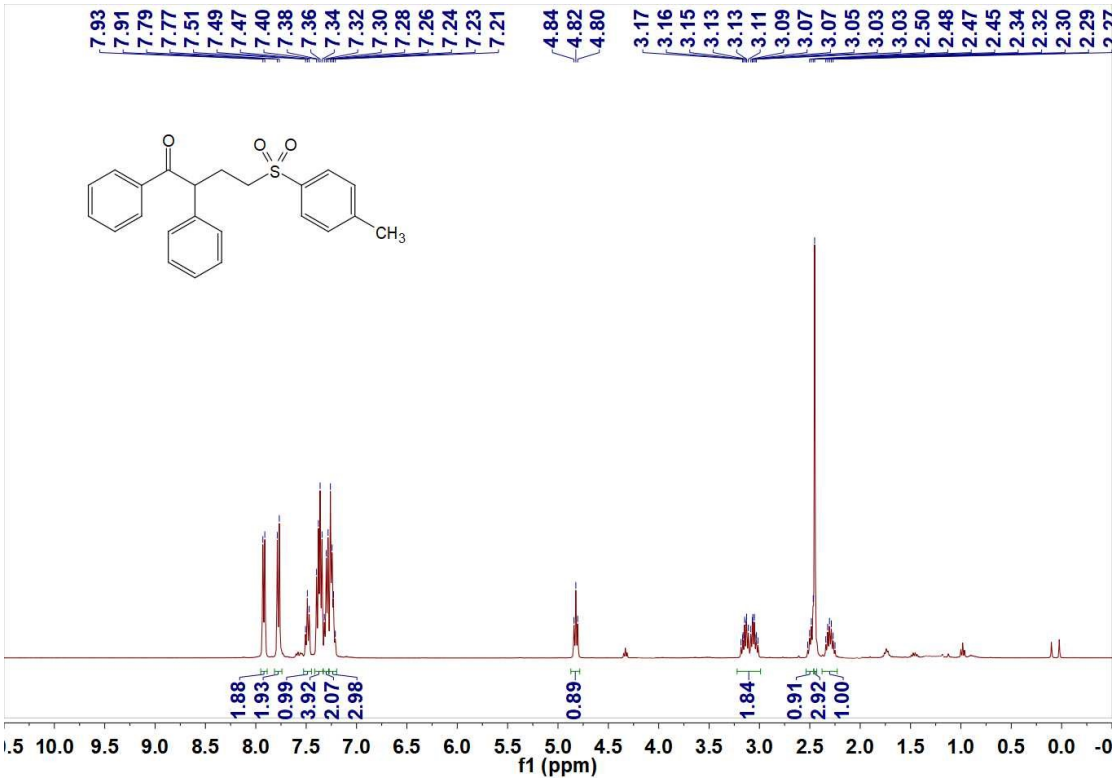
^{1}H NMR of **3ada'** (400 MHz, $CDCl_3$)



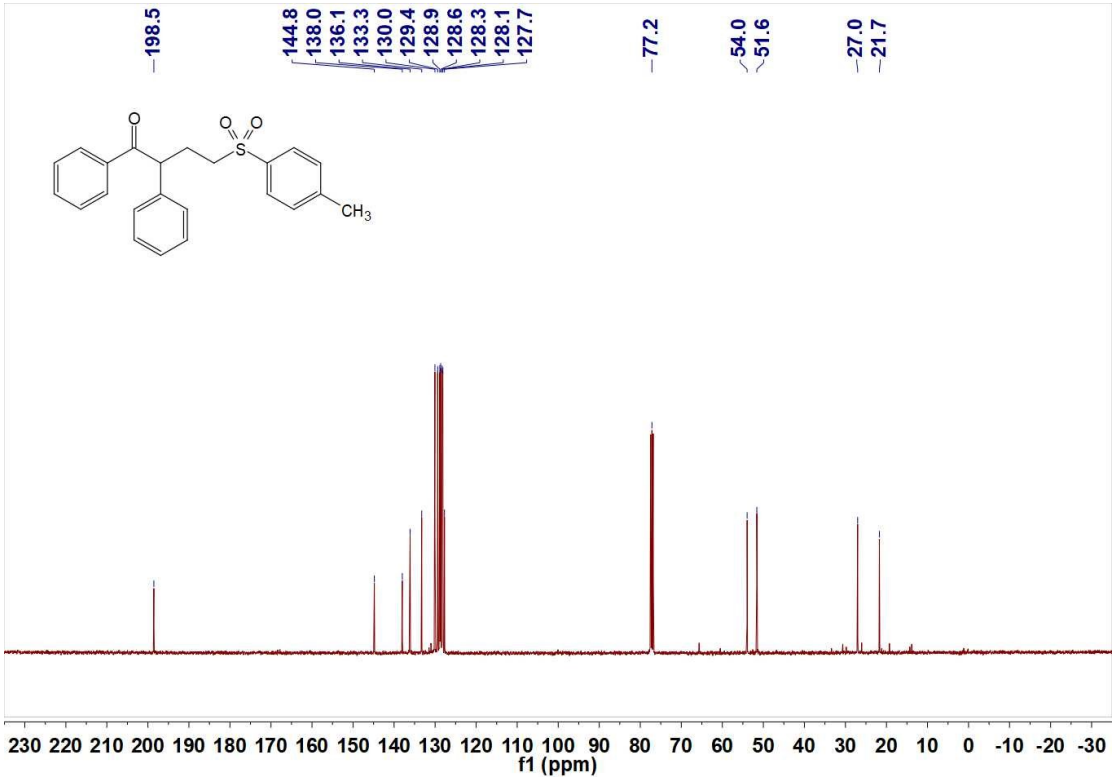
^{13}C NMR of **3ada'** ($CDCl_3$, 77.16)



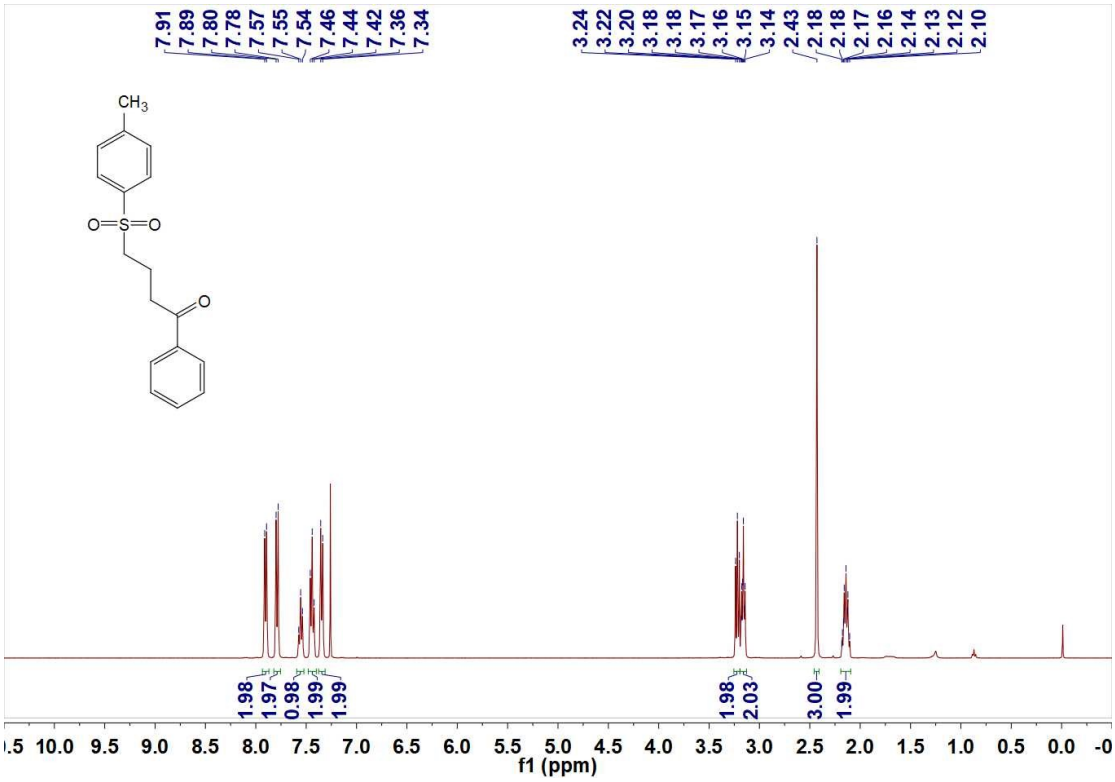
^{1}H NMR of **3aea'** (400 MHz, $CDCl_3$)



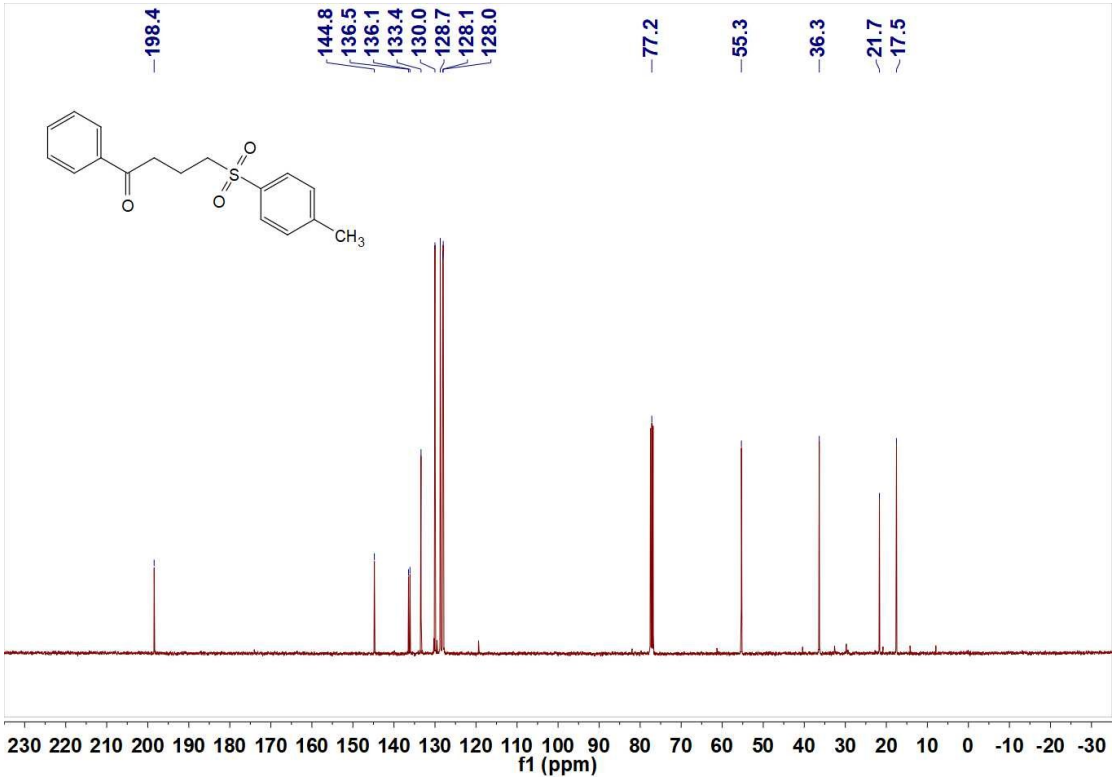
^{13}C NMR of **3aea'** (101 MHz, $CDCl_3$, 77.16)



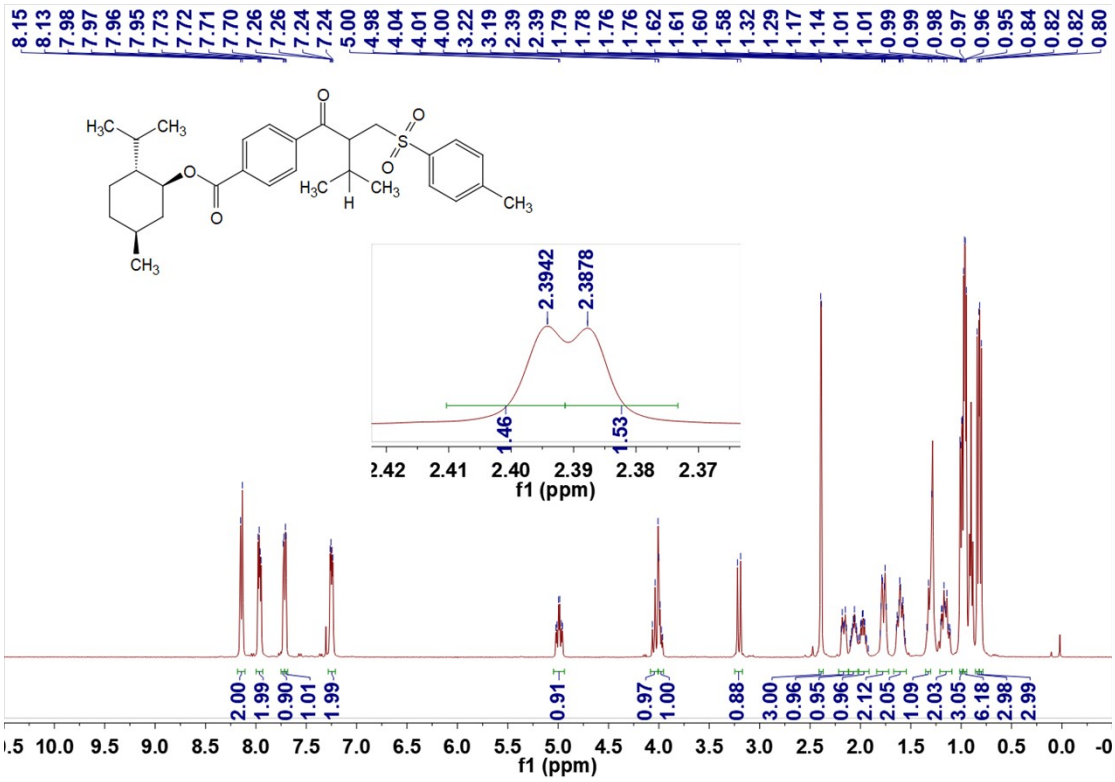
^{1}H NMR of **3afa'** (400 MHz, $CDCl_3$)



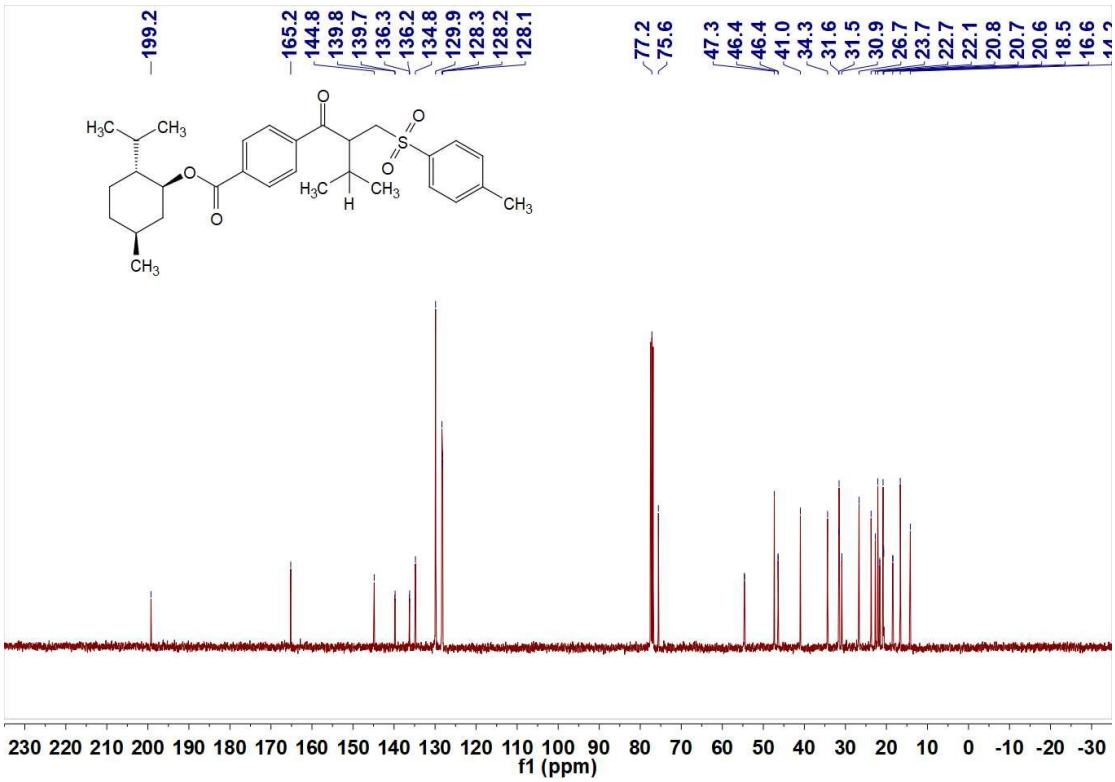
^{13}C NMR of **3afa'** (101 MHz, $CDCl_3$, 77.16)



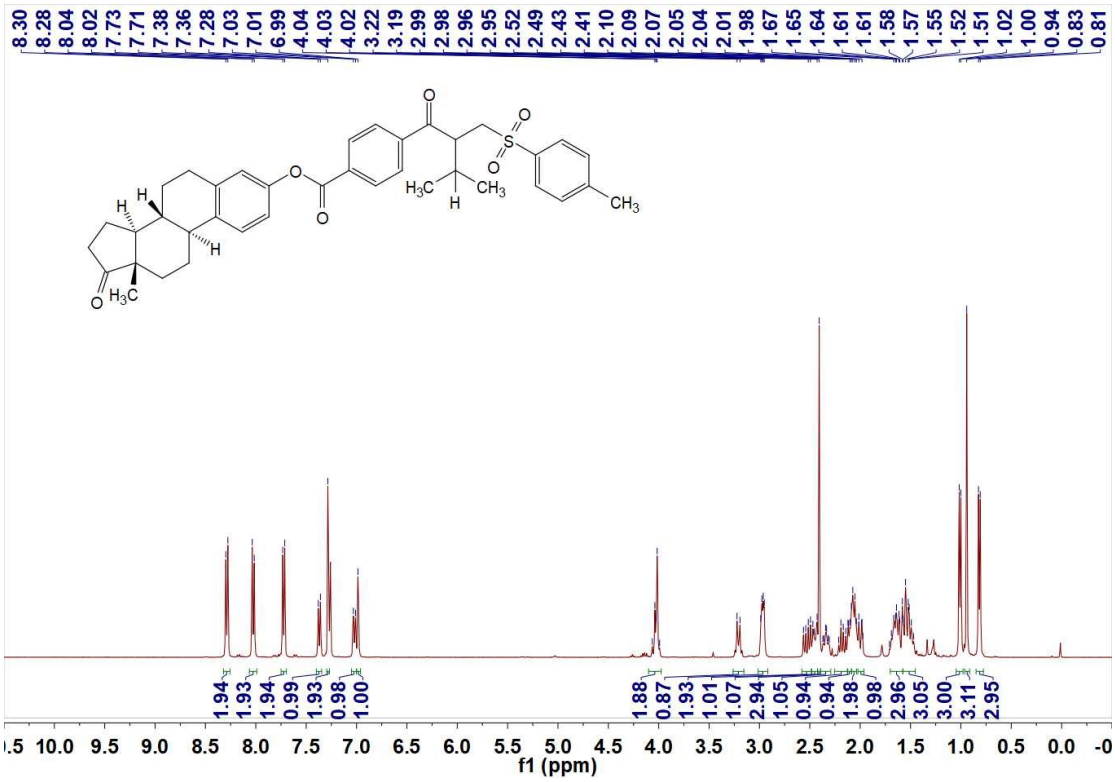
^{1}H NMR of **3aha** (400 MHz, $CDCl_3$)



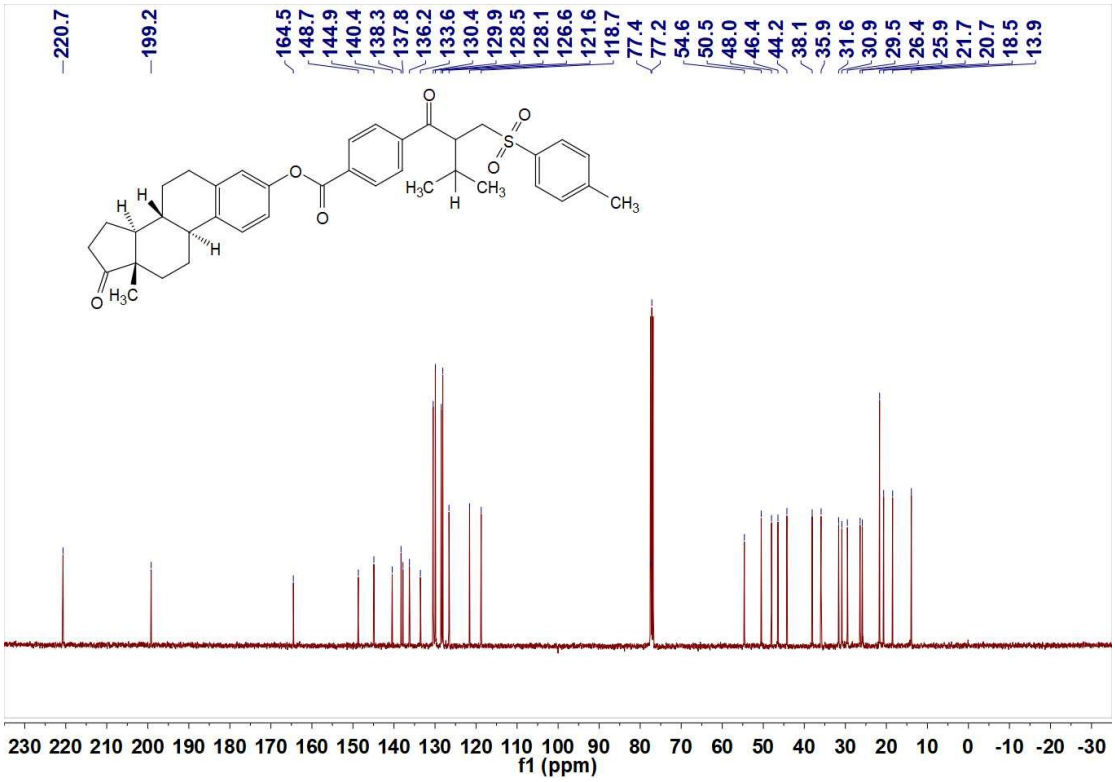
^{13}C NMR of **3aha** (101 MHz, $CDCl_3$, 77.16)



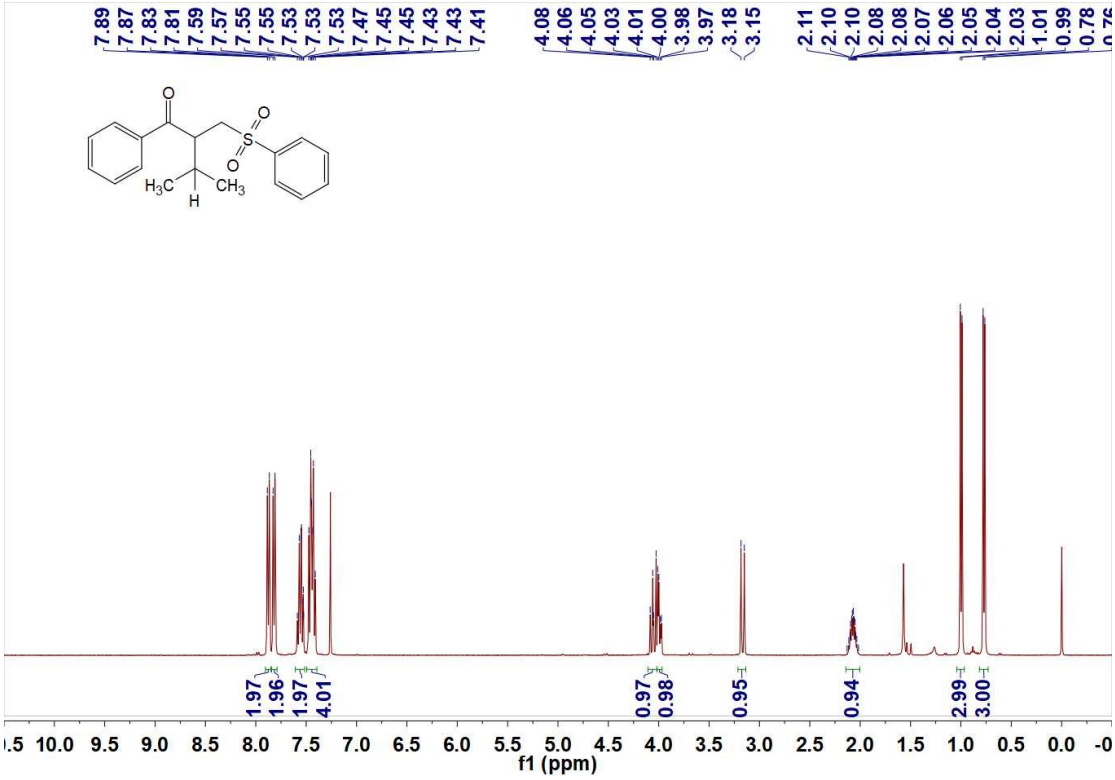
^{1}H NMR of **3aia** (400 MHz, $CDCl_3$)



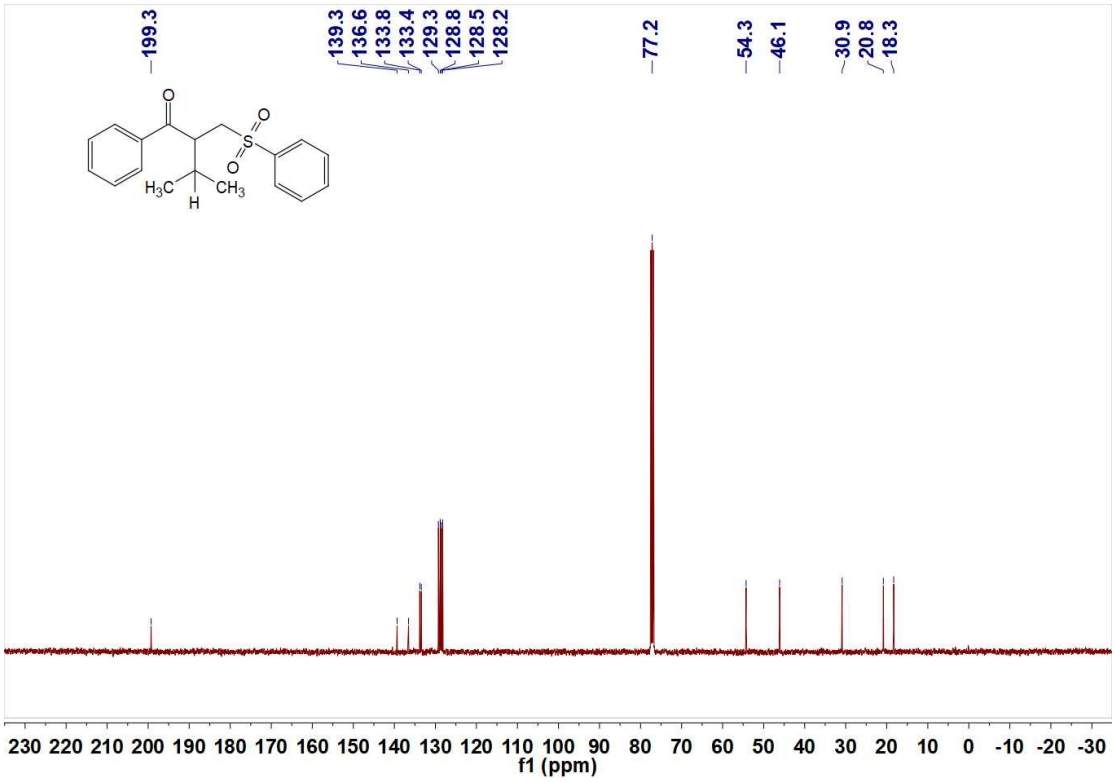
^{13}C NMR of **3aia** (101 MHz, $CDCl_3$, 77.16)



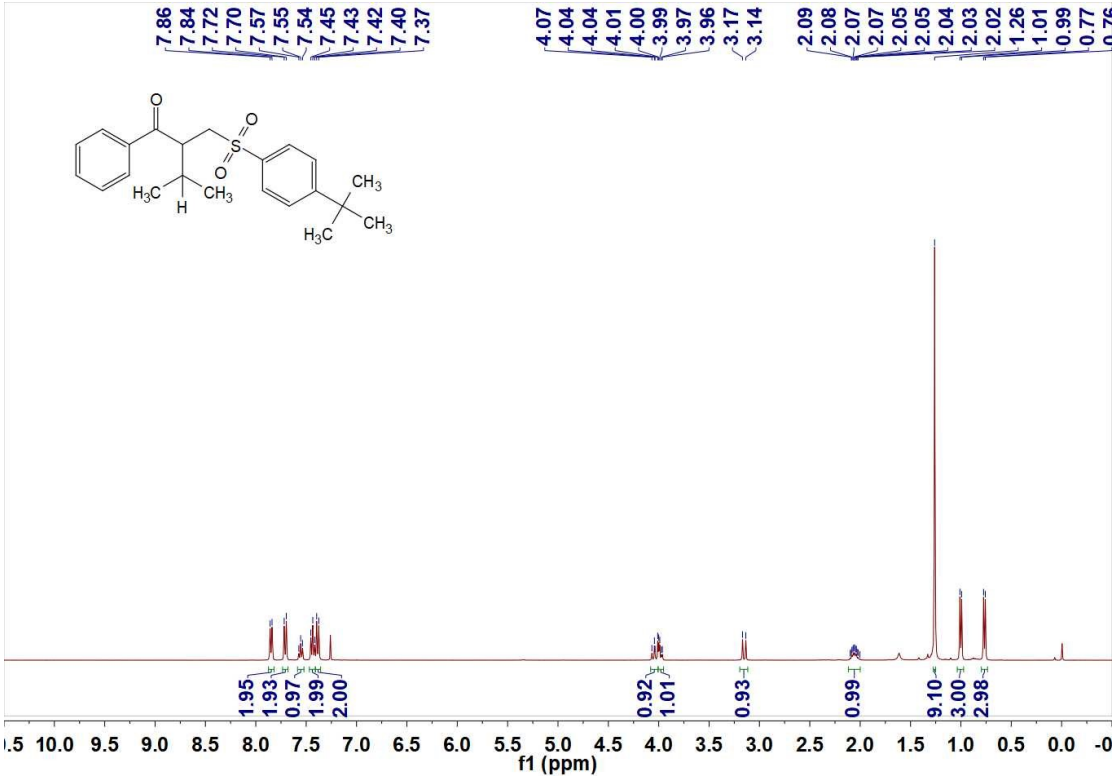
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



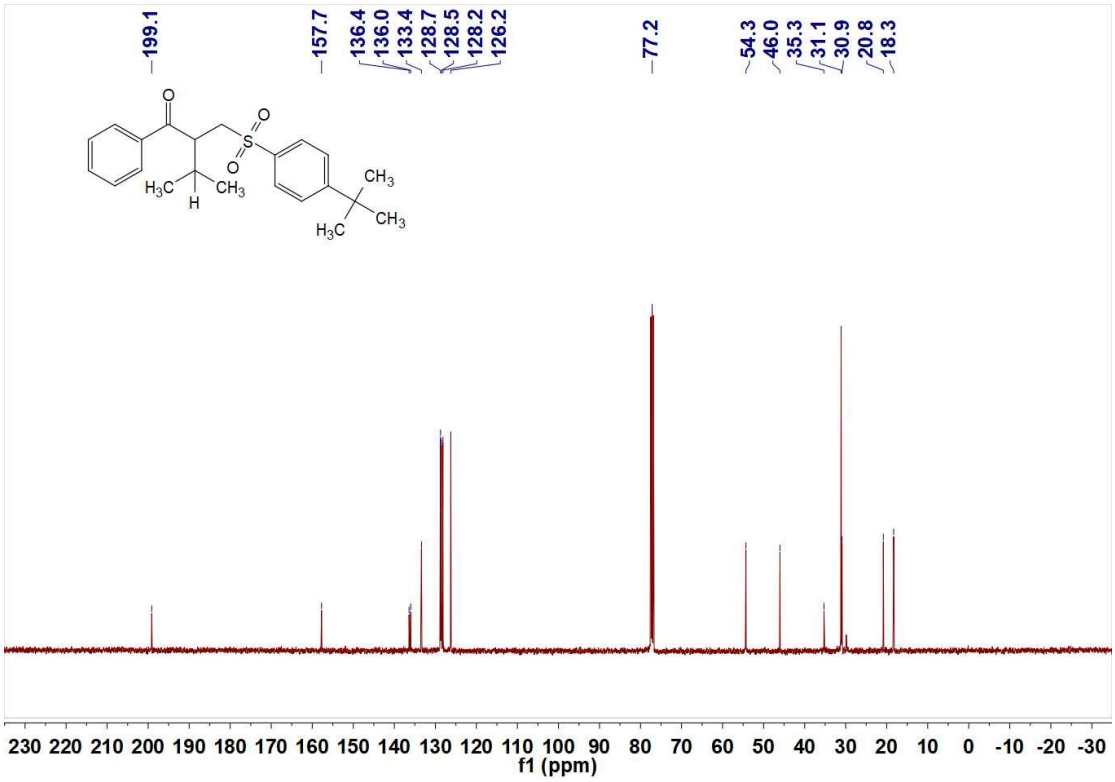
^{13}C NMR of **3ab** (101 MHz, $CDCl_3$, 77.16)



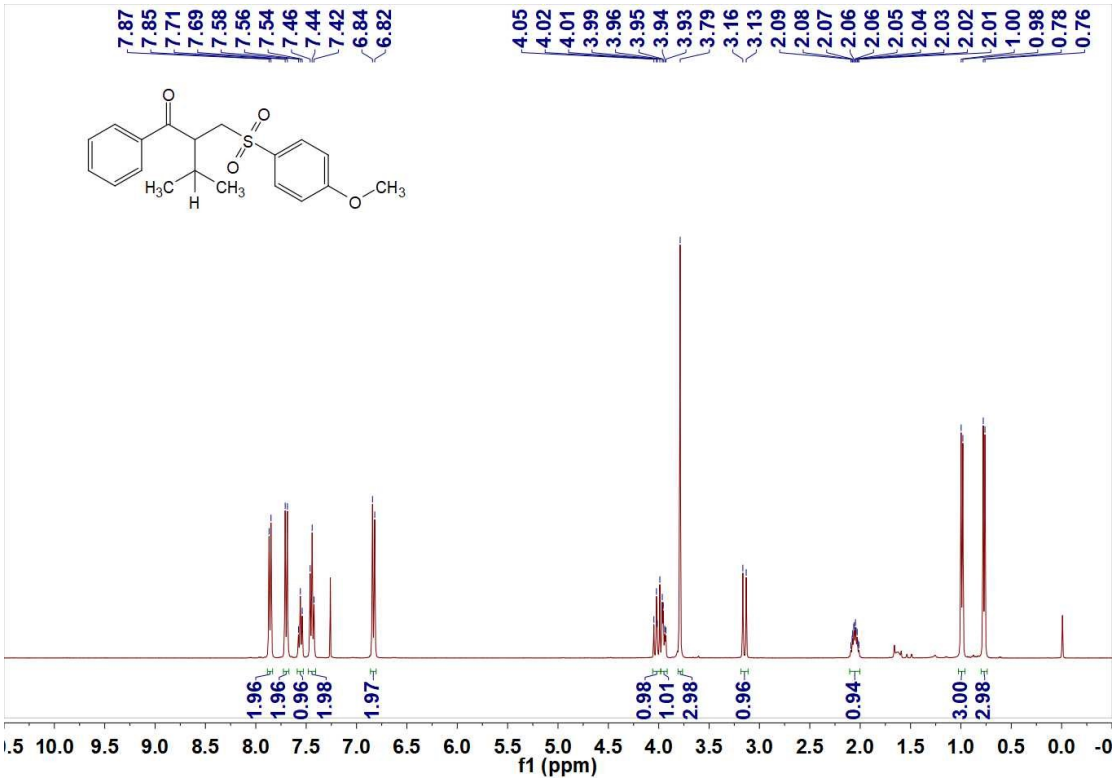
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



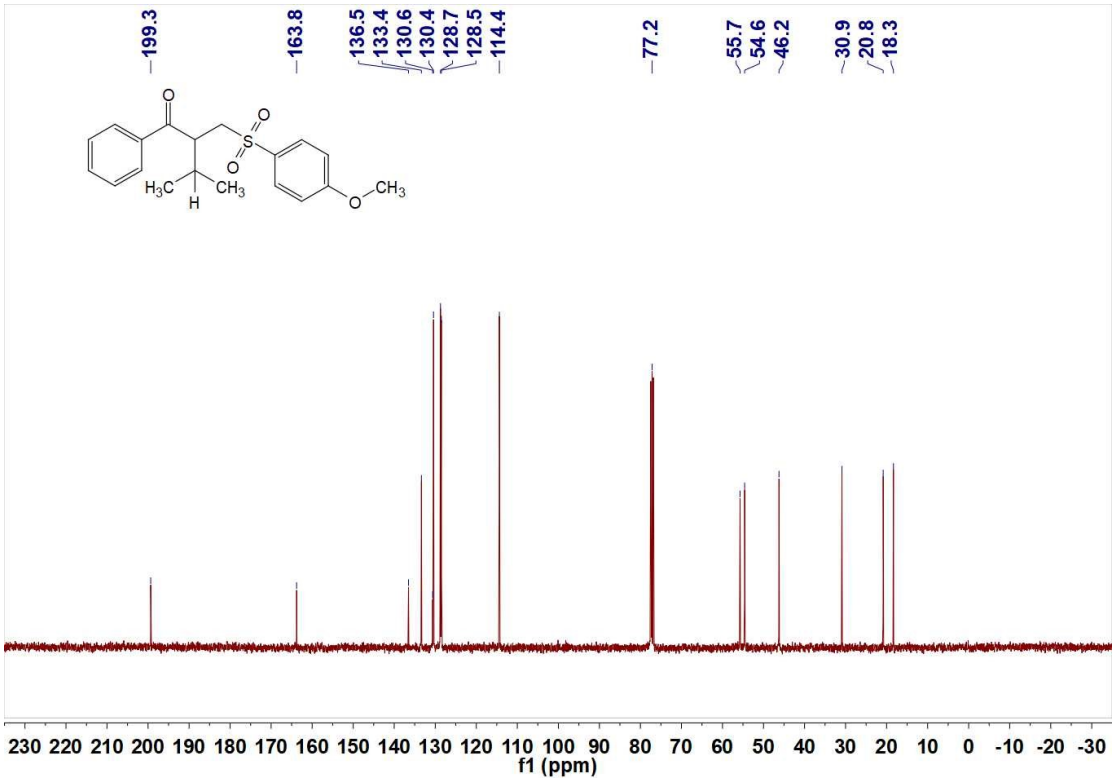
^{13}C NMR of **3ac** (101 MHz, $CDCl_3$, 77.16)



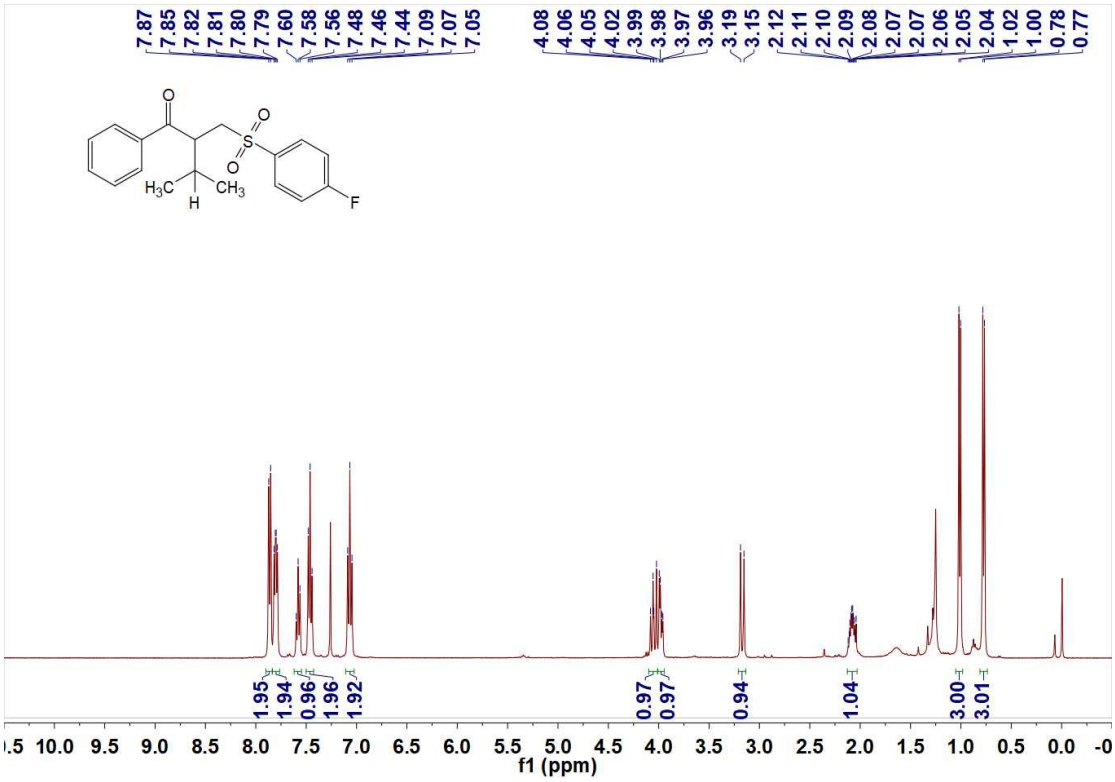
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$)



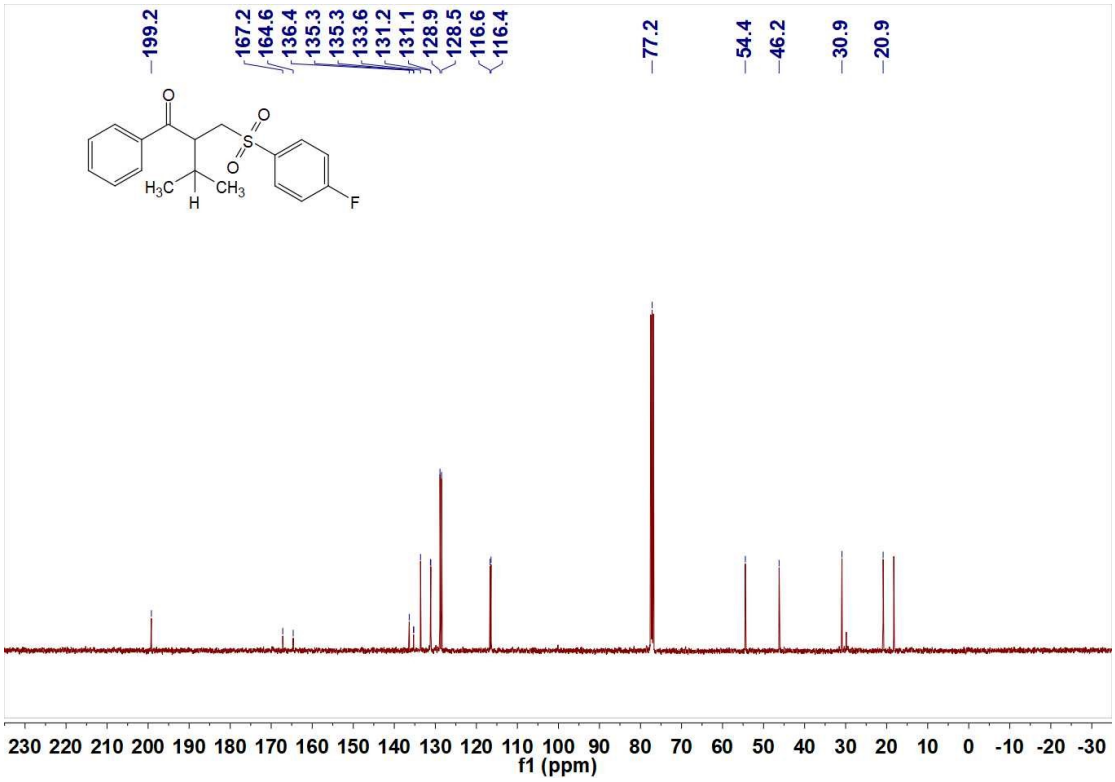
^{13}C NMR of **3ad** (101 MHz, $CDCl_3$, 77.16)



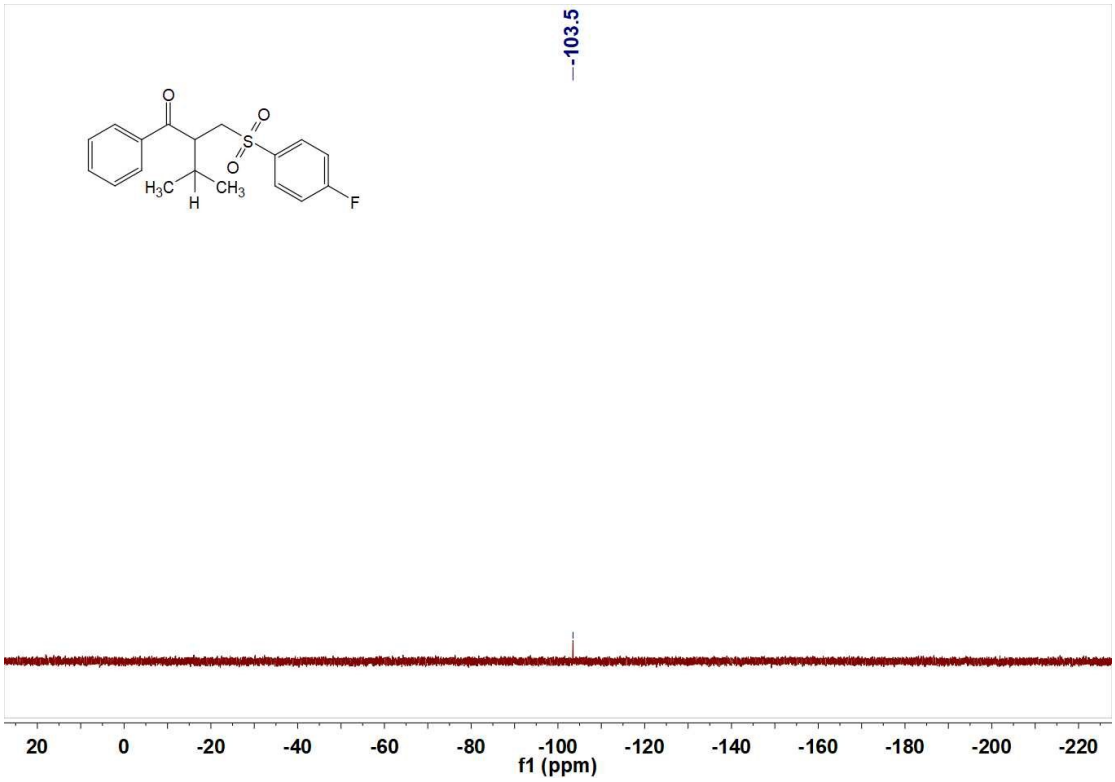
^{1}H NMR of **3ae** (400 MHz, $CDCl_3$)



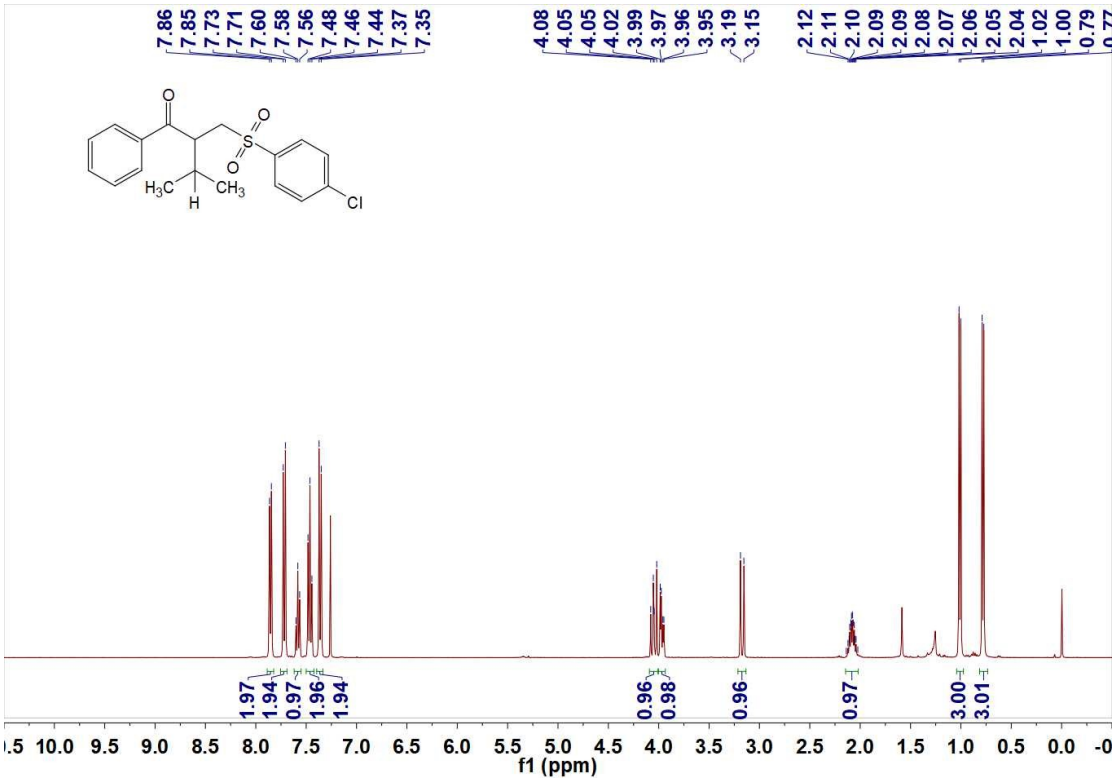
^{13}C NMR of **3ae** (101 MHz, $CDCl_3$, 77.16)



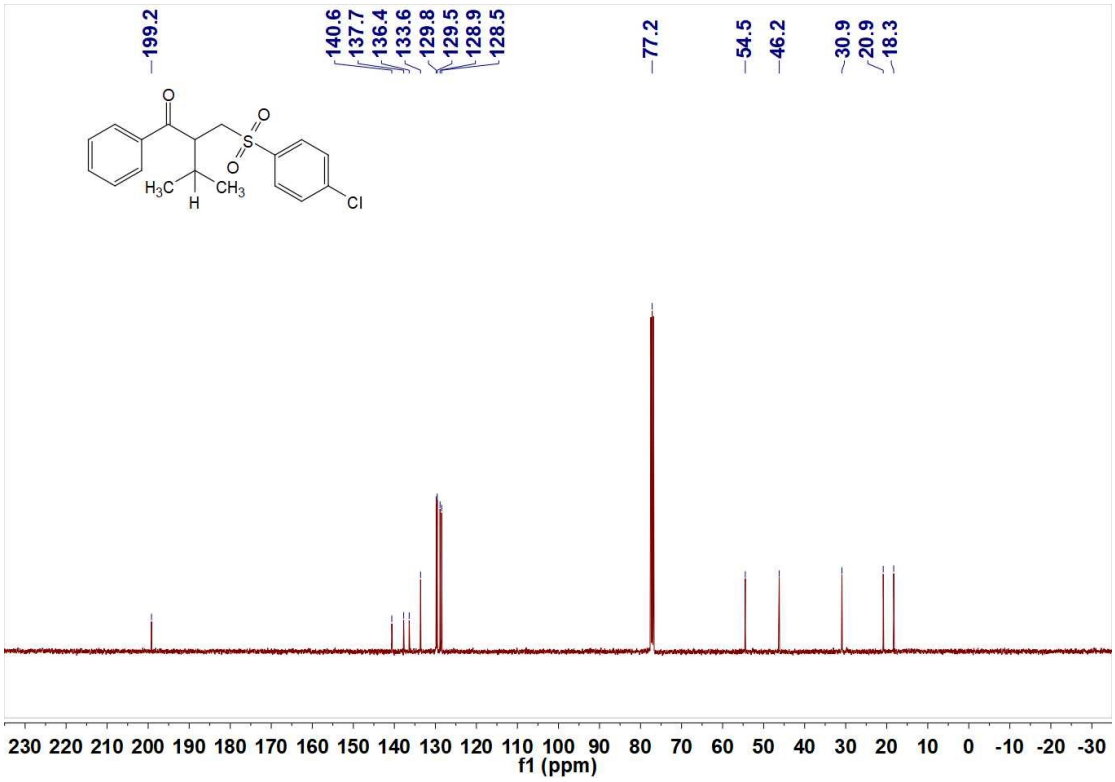
^{19}F NMR of **3ae** (376 MHz, $CDCl_3$)



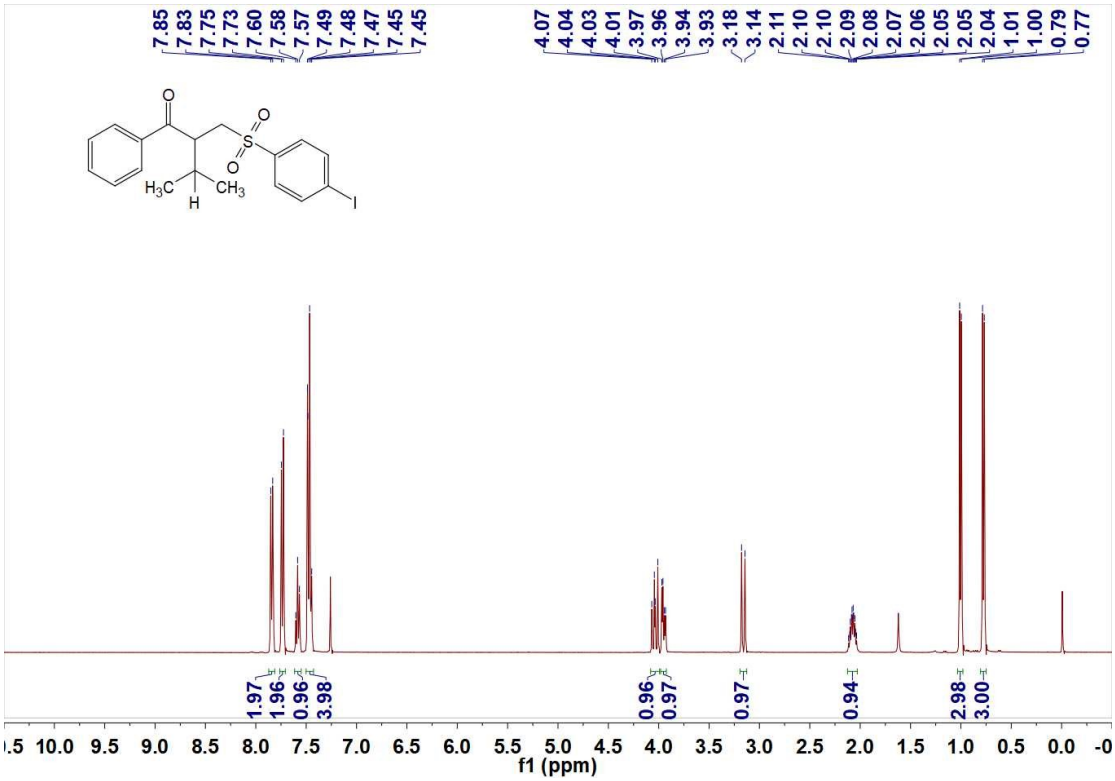
^{1}H NMR of **3af** (400 MHz, $CDCl_3$)



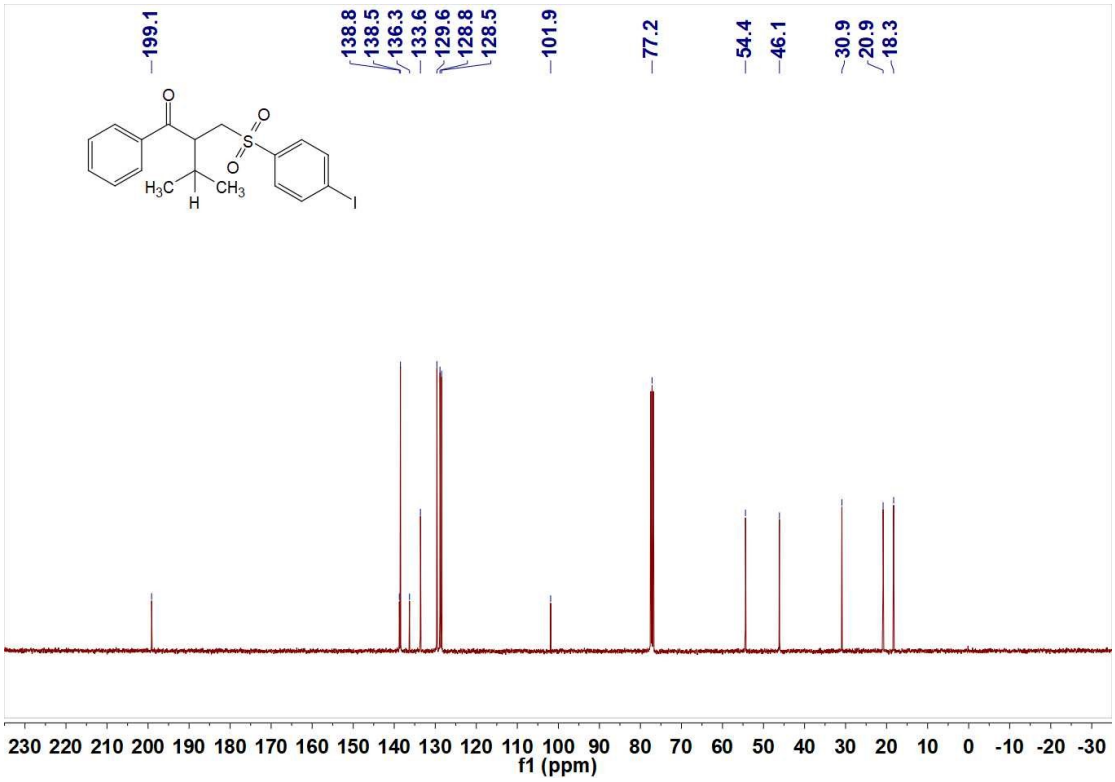
^{13}C NMR of **3af** (101 MHz, $CDCl_3$, 77.16)



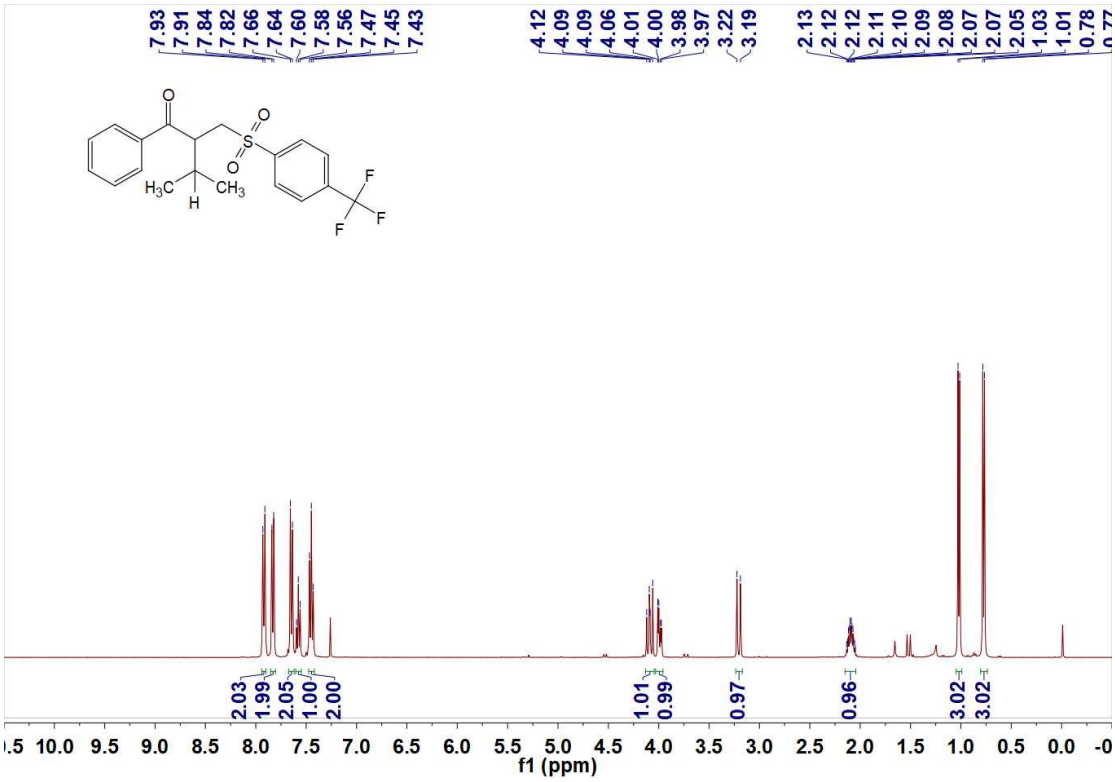
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$)



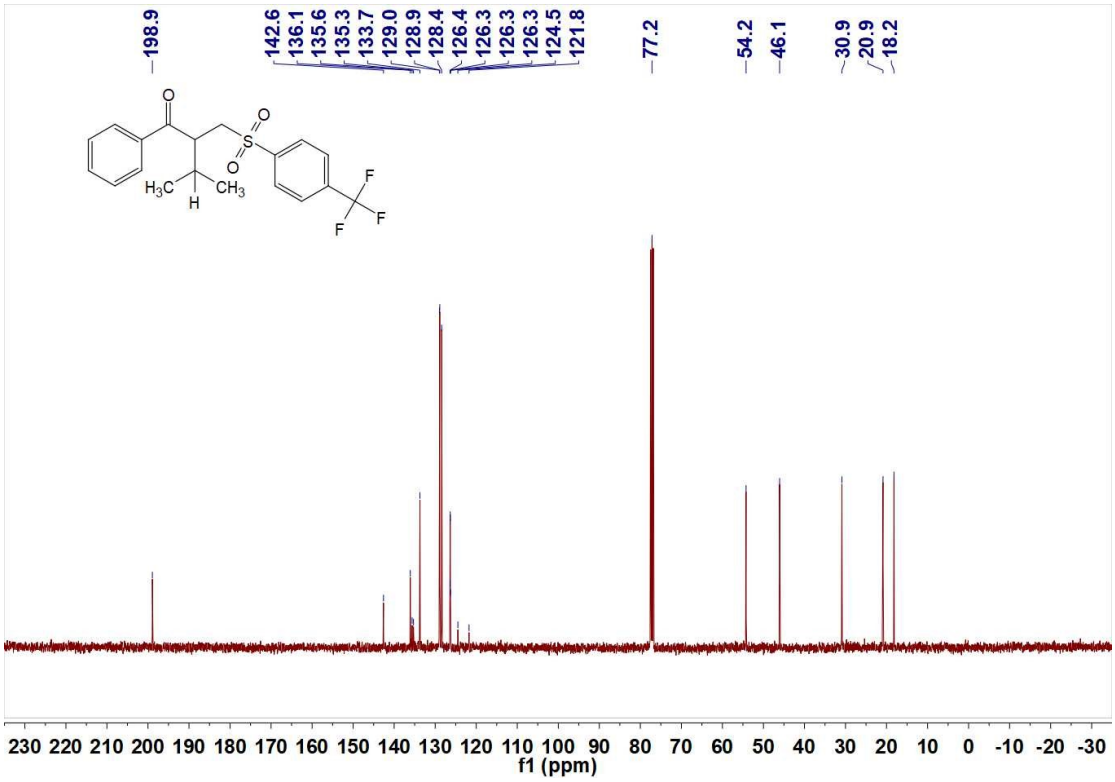
^{13}C NMR of **3ag** (101 MHz, $CDCl_3$, 77.16)



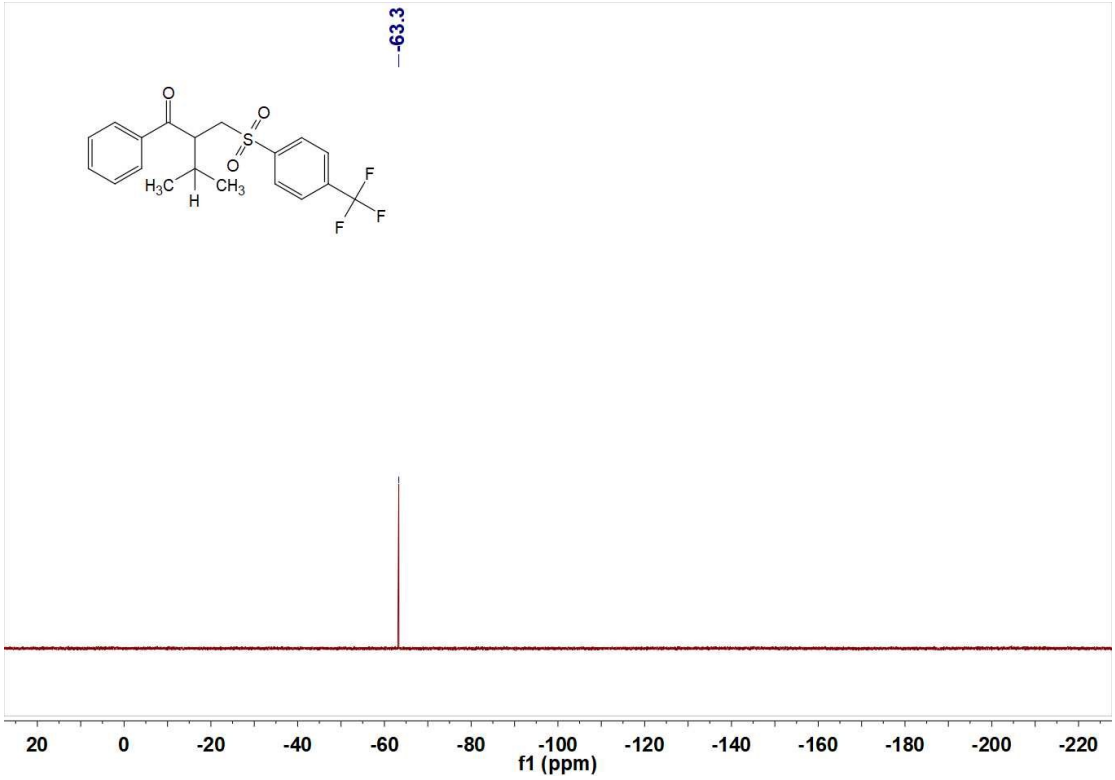
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



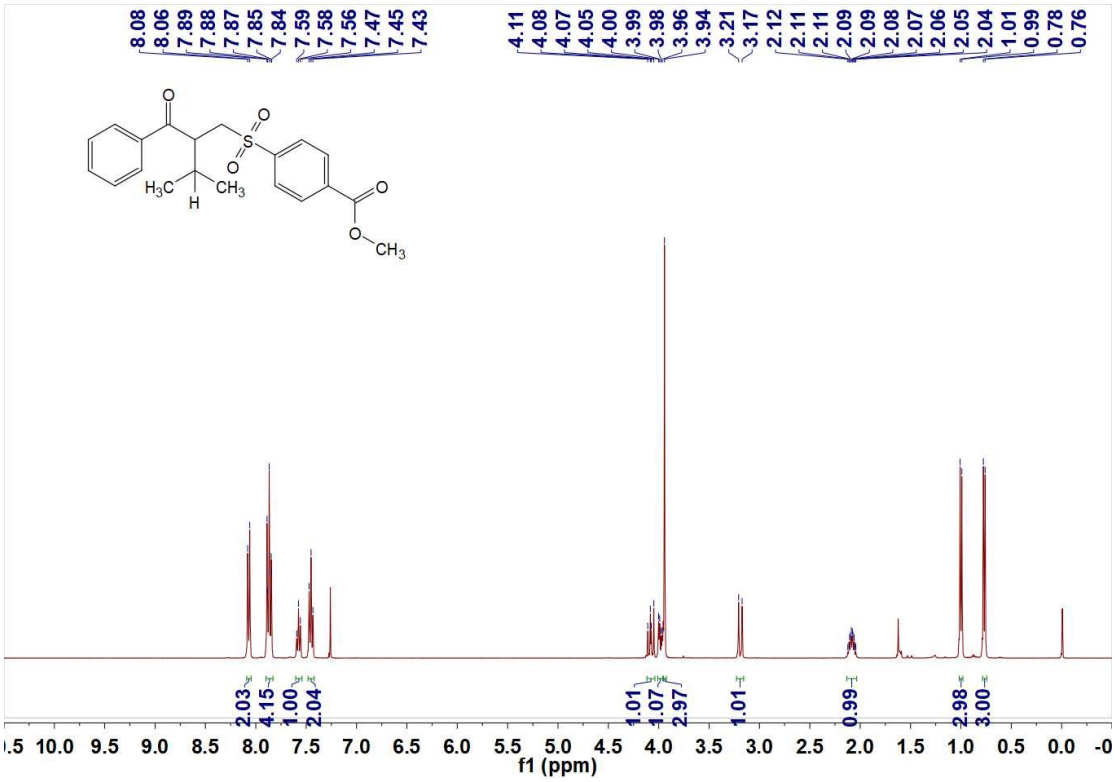
^{13}C NMR of **3ah** (101 MHz, $CDCl_3$, 77.16)



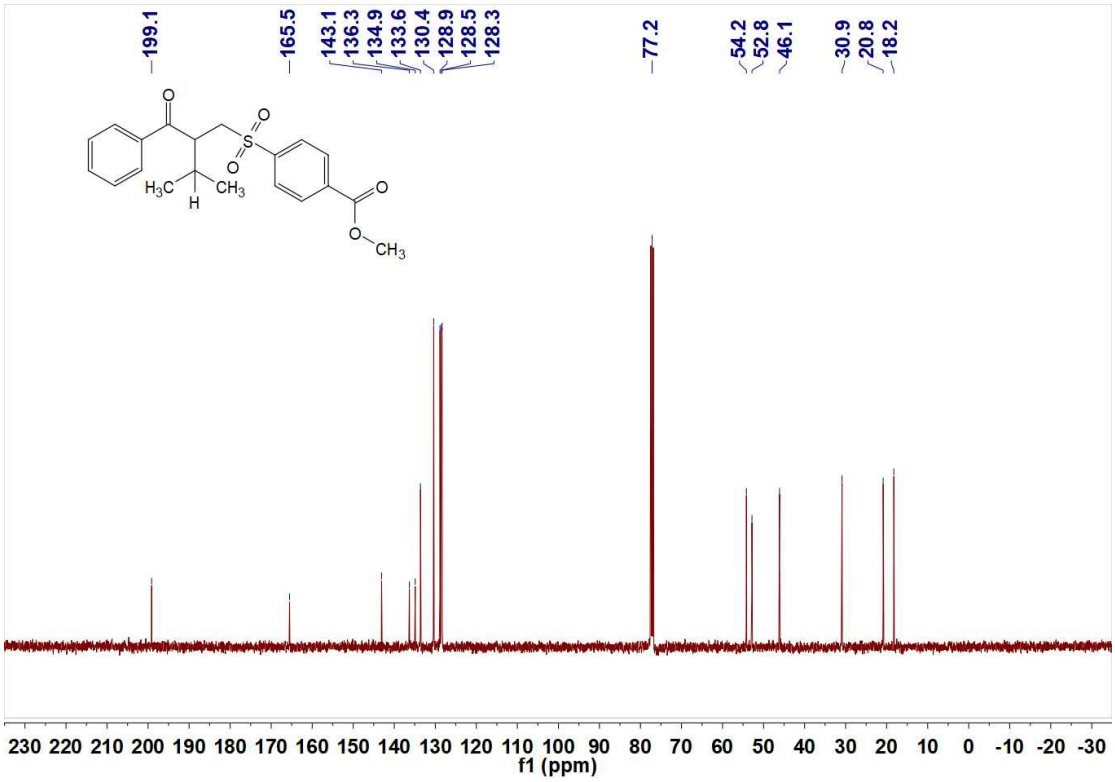
^{19}F NMR of **3ah** (376 MHz, $CDCl_3$)



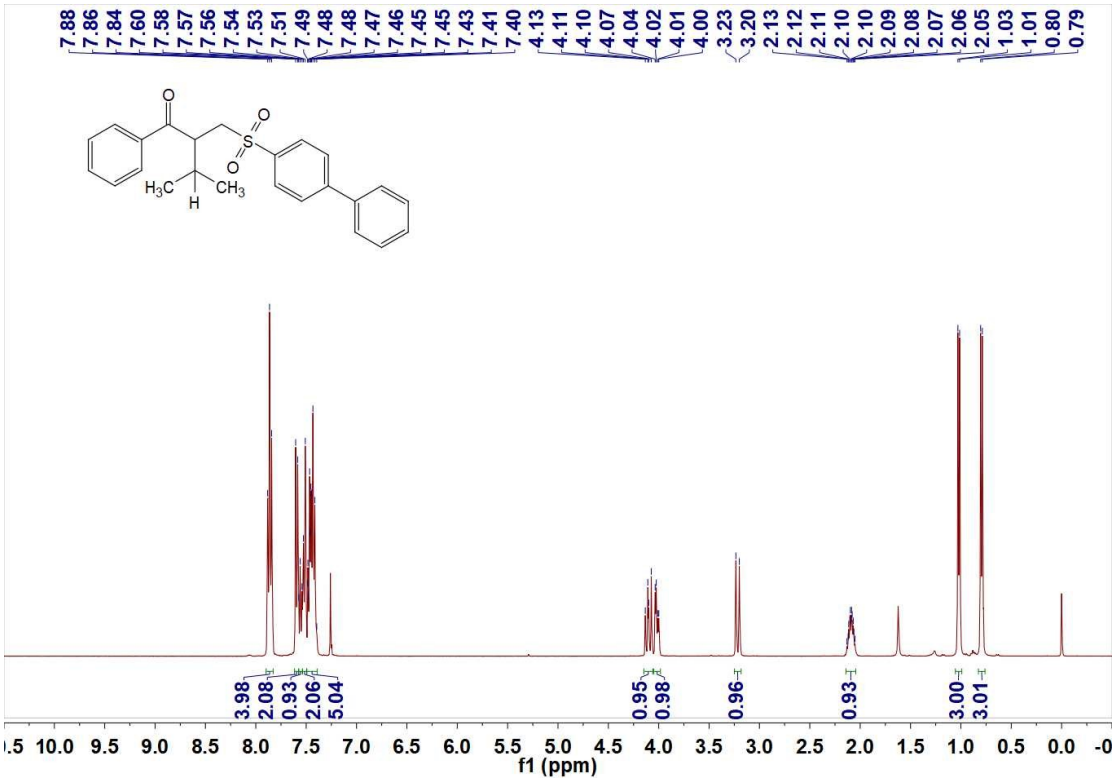
^{1}H NMR of **3ai** (400 MHz, $CDCl_3$)



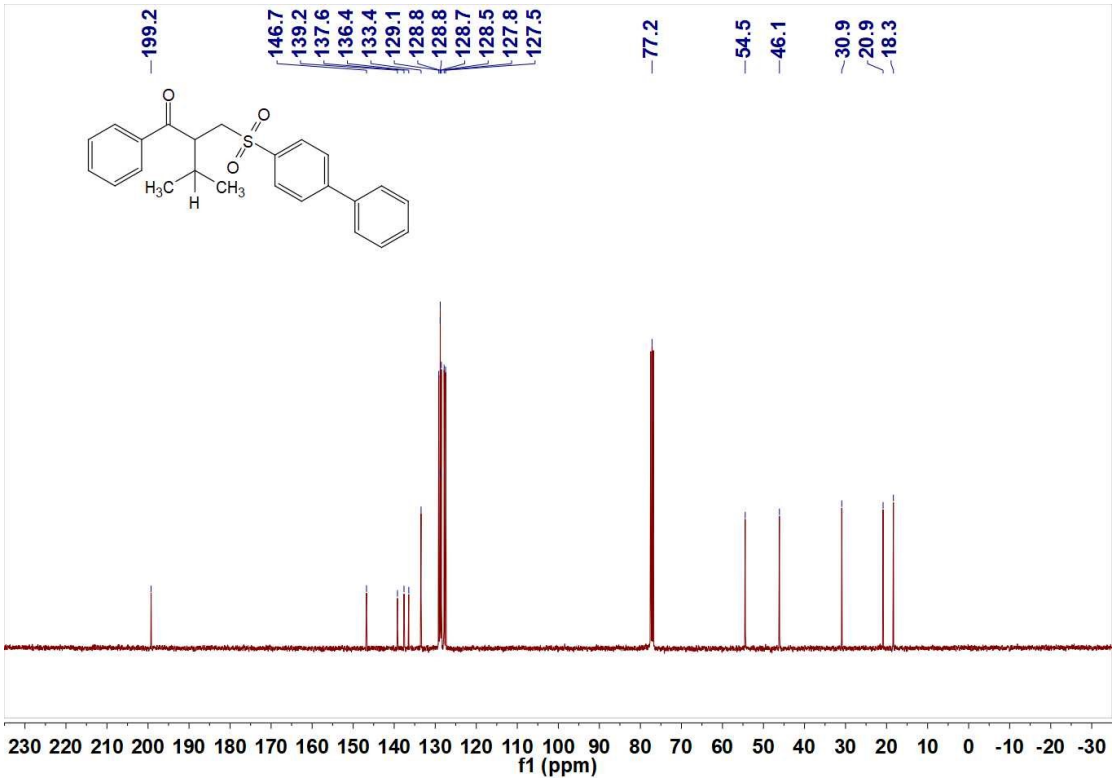
^{13}C NMR of **3ai** (101 MHz, $CDCl_3$, 77.16)



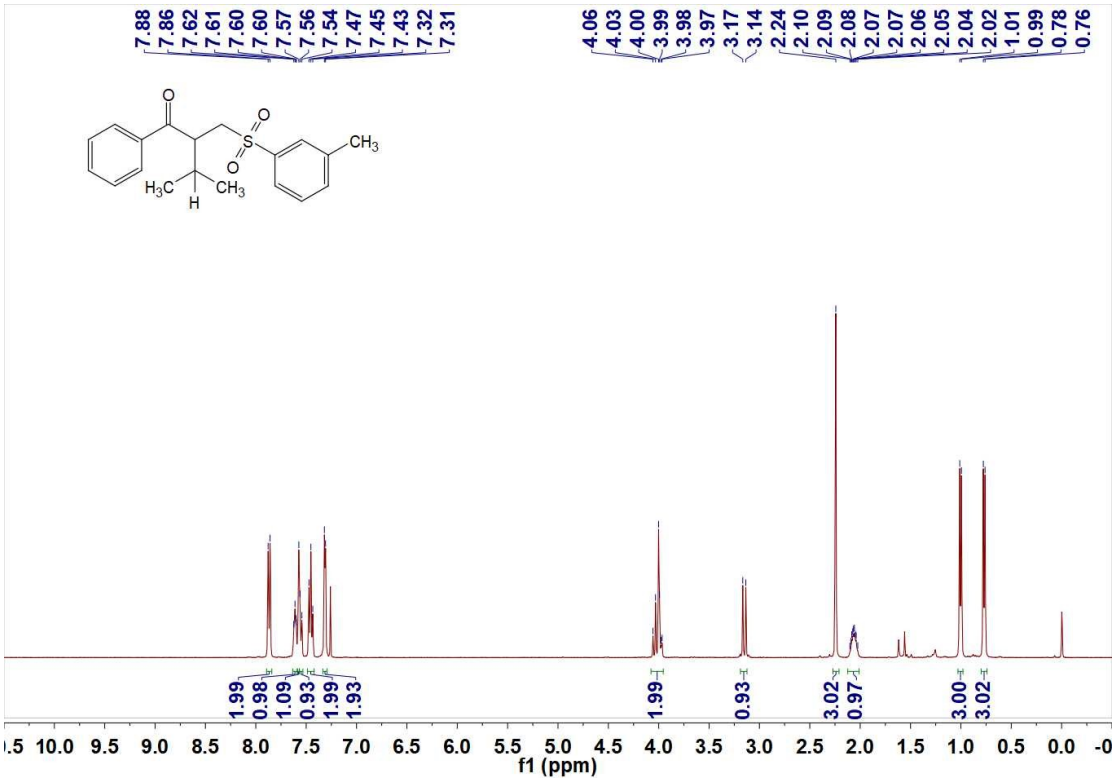
^{1}H NMR of **3aj** (400 MHz, $CDCl_3$)



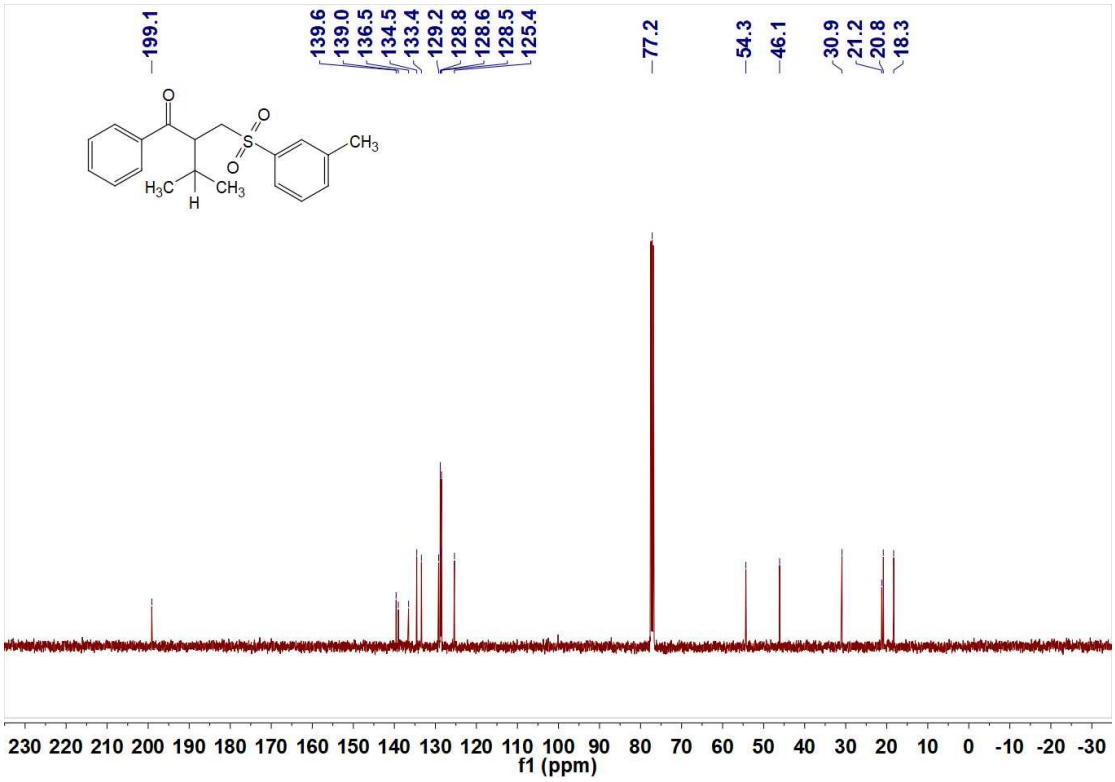
^{13}C NMR of **3aj** (101 MHz, $CDCl_3$, 77.16)



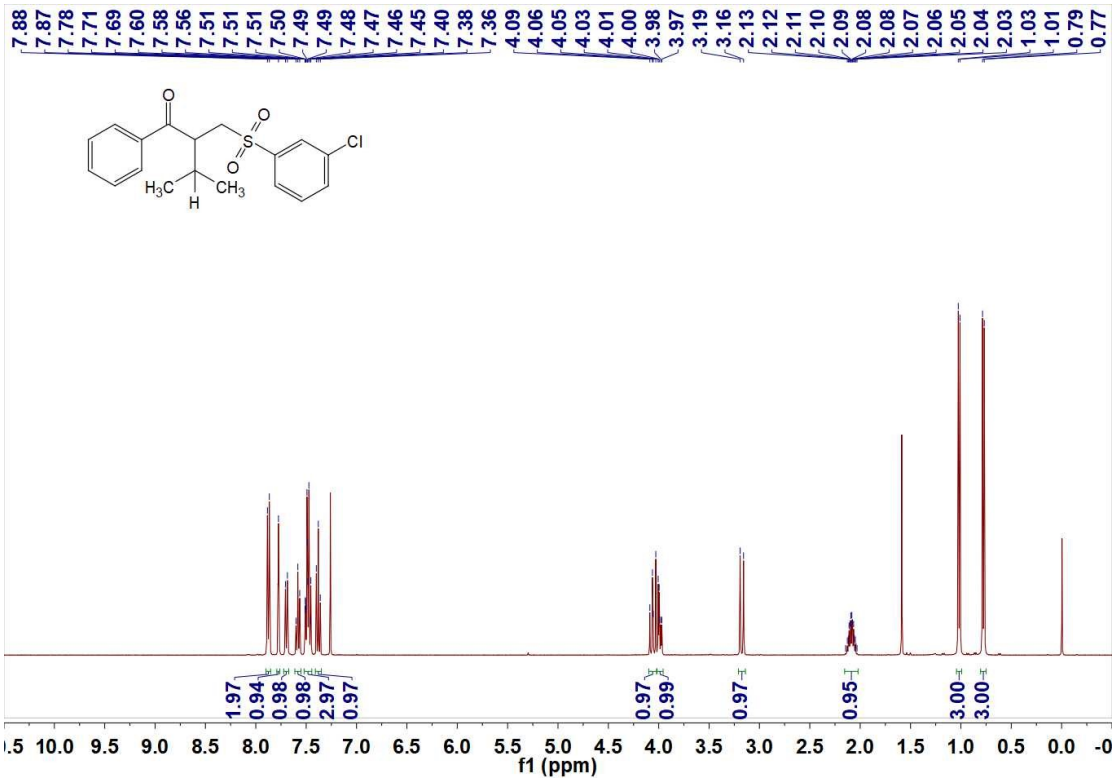
^{1}H NMR of **3ak** (400 MHz, $CDCl_3$)



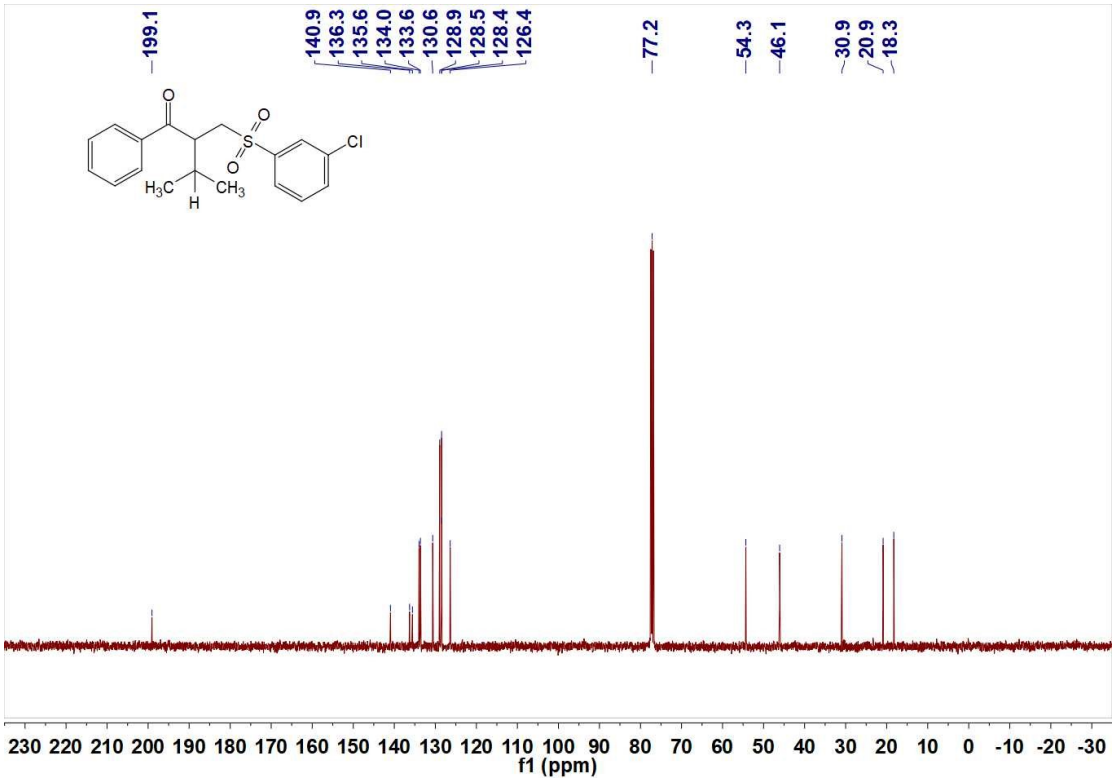
^{13}C NMR of **3ak** (101 MHz, $CDCl_3$, 77.16)



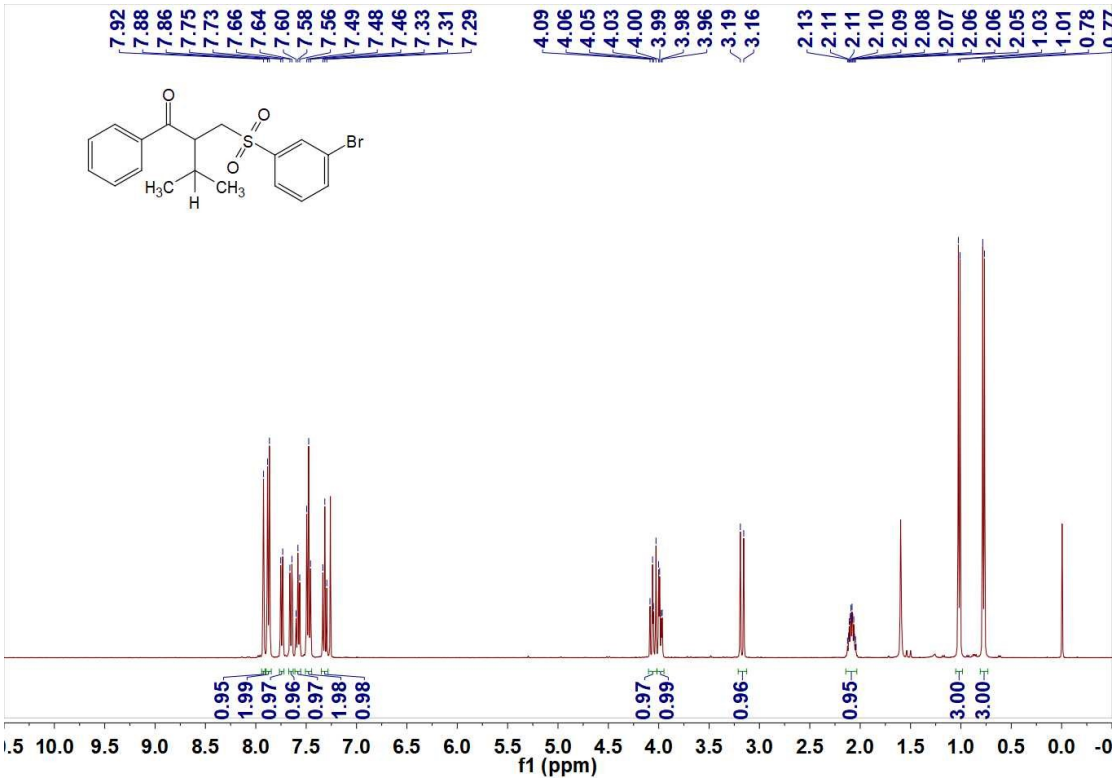
^{1}H NMR of **3al** (400 MHz, $CDCl_3$)



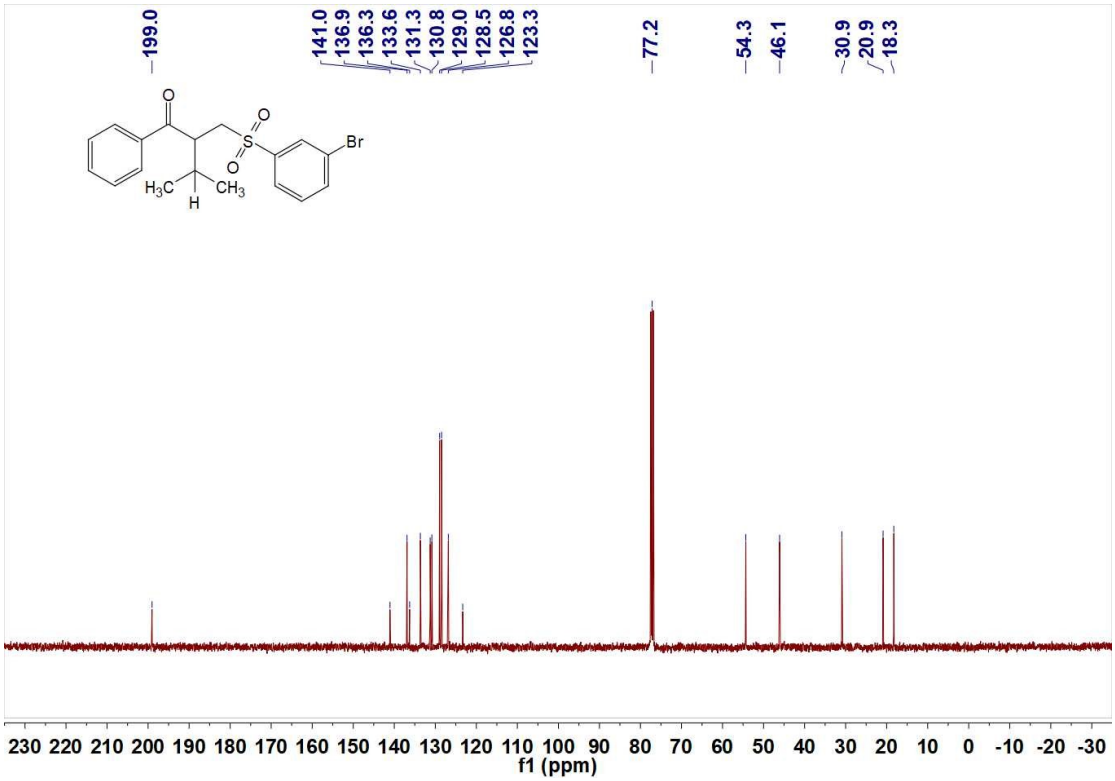
^{13}C NMR of **3al** (101 MHz, $CDCl_3$, 77.16)



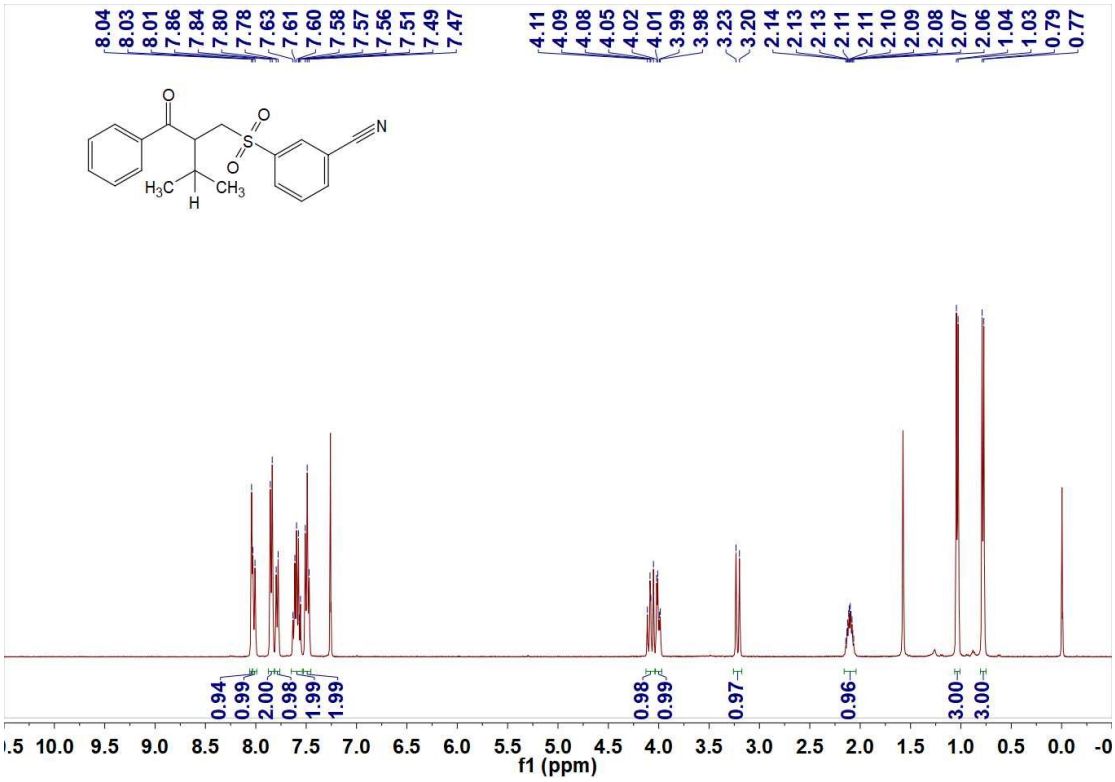
^{1}H NMR of **3am** (400 MHz, $CDCl_3$)



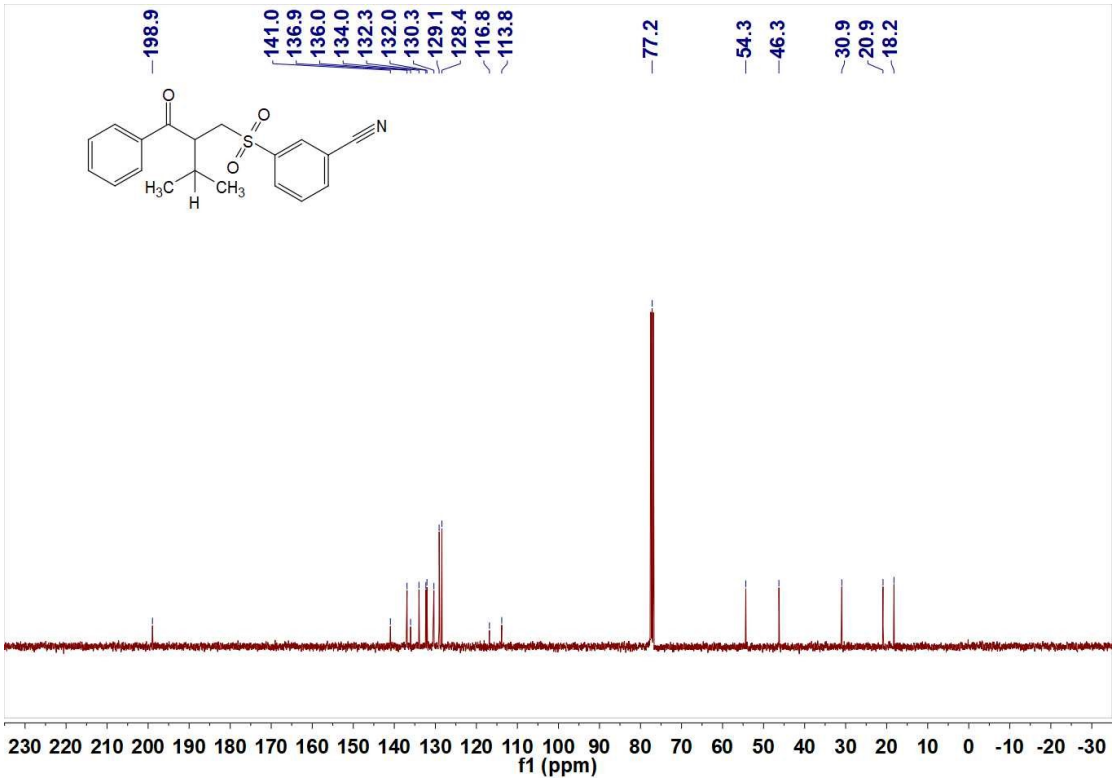
^{13}C NMR of **3am** (101 MHz, $CDCl_3$, 77.16)



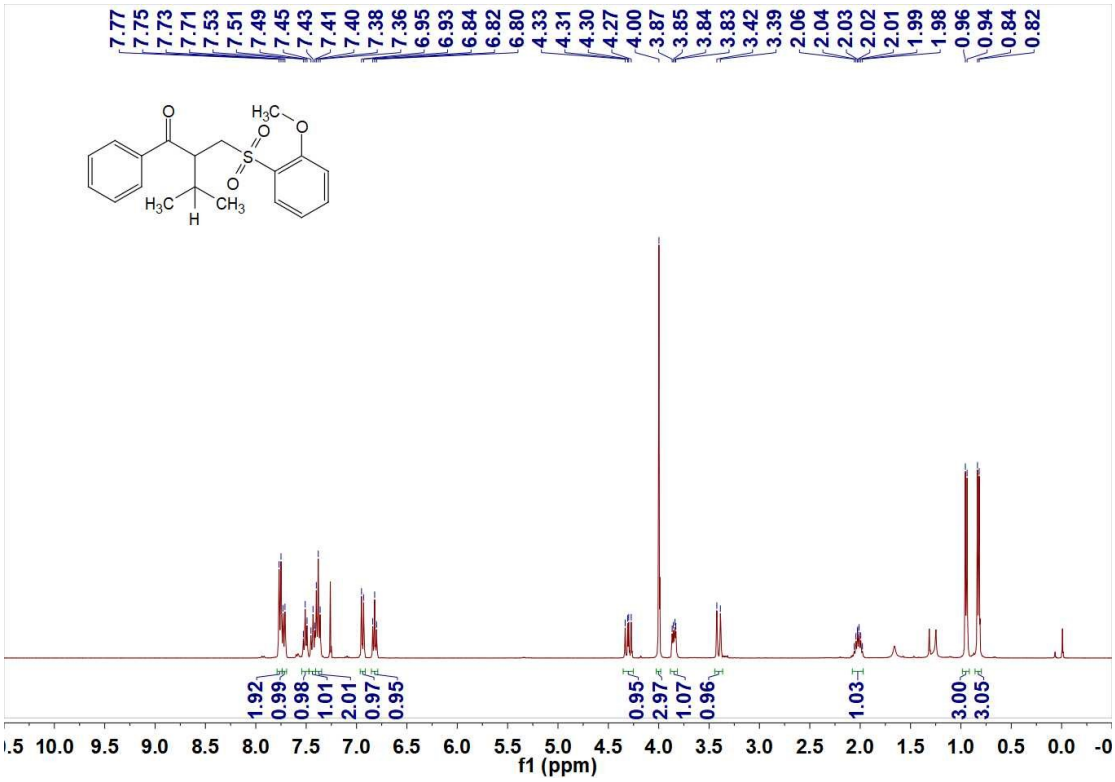
^{1}H NMR of **3an**



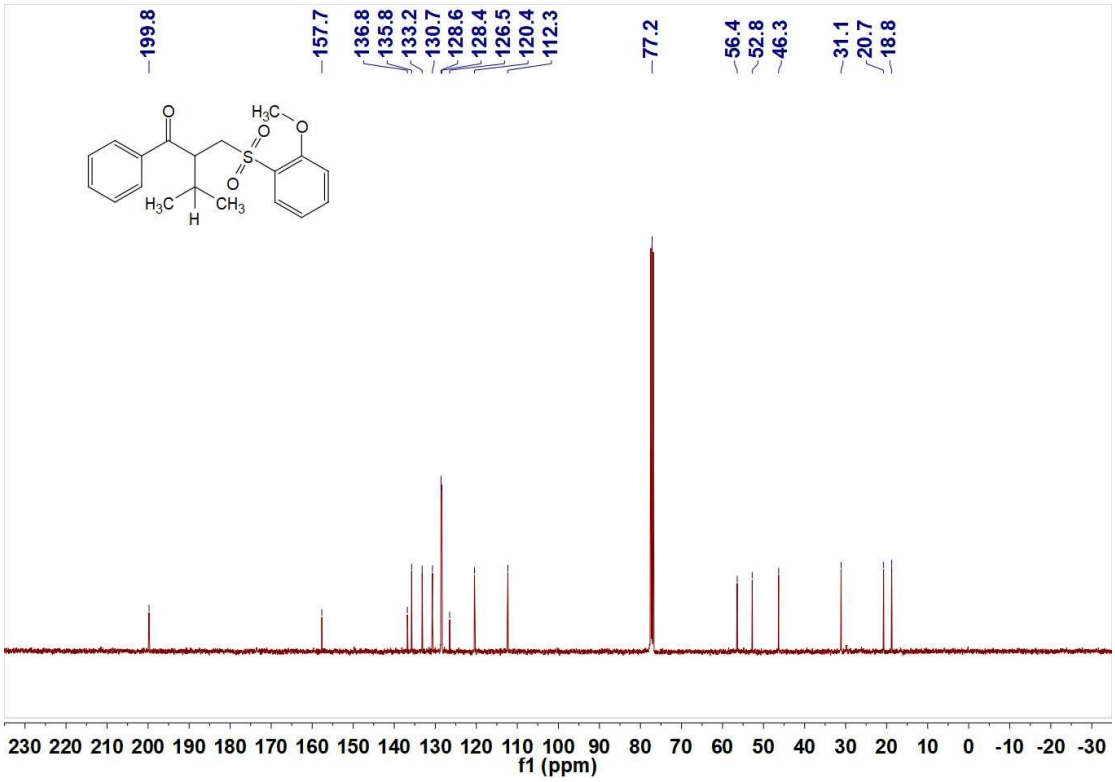
^{13}C NMR of **3an** (101 MHz, $CDCl_3$, 77.16)



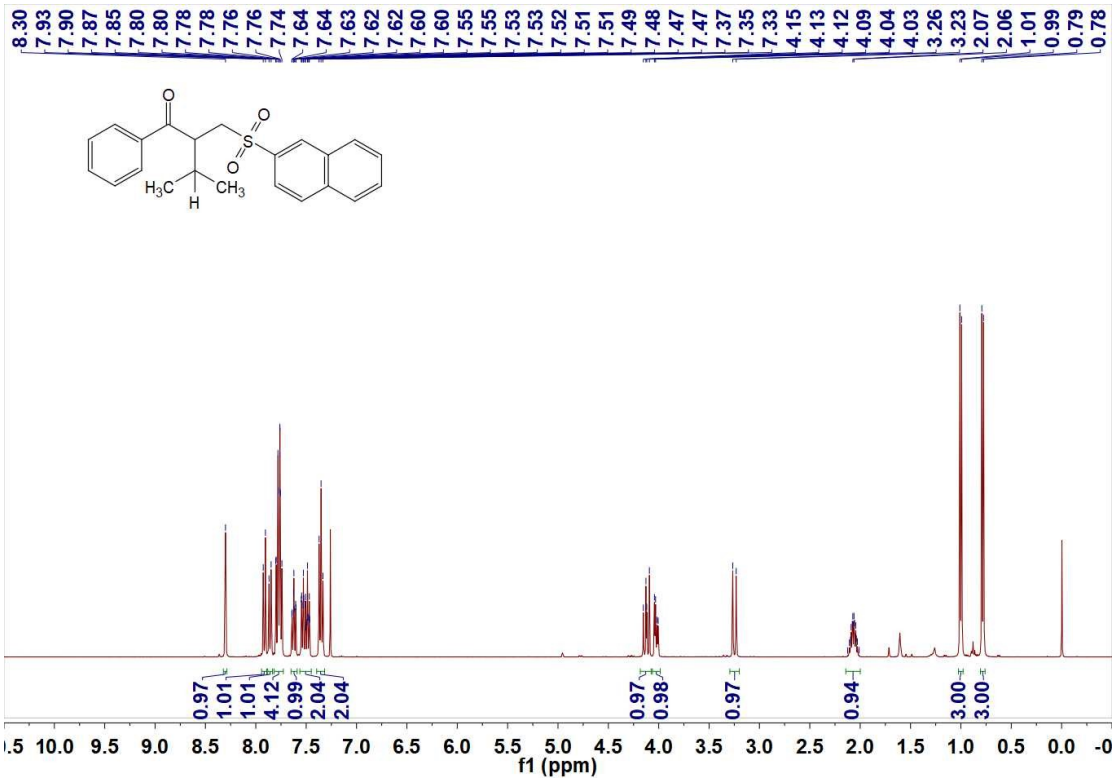
^{1}H NMR of **3ao**(400 MHz, $CDCl_3$)



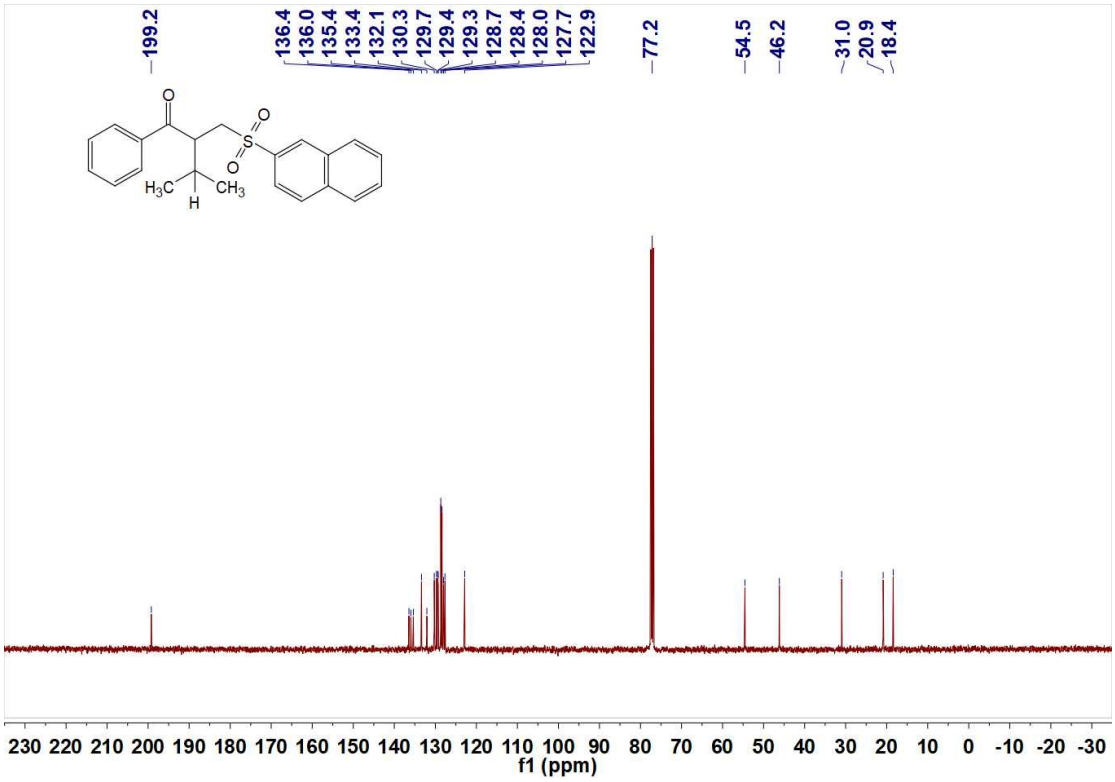
^{13}C NMR of **3ao** (101 MHz, $CDCl_3$, 77.16)



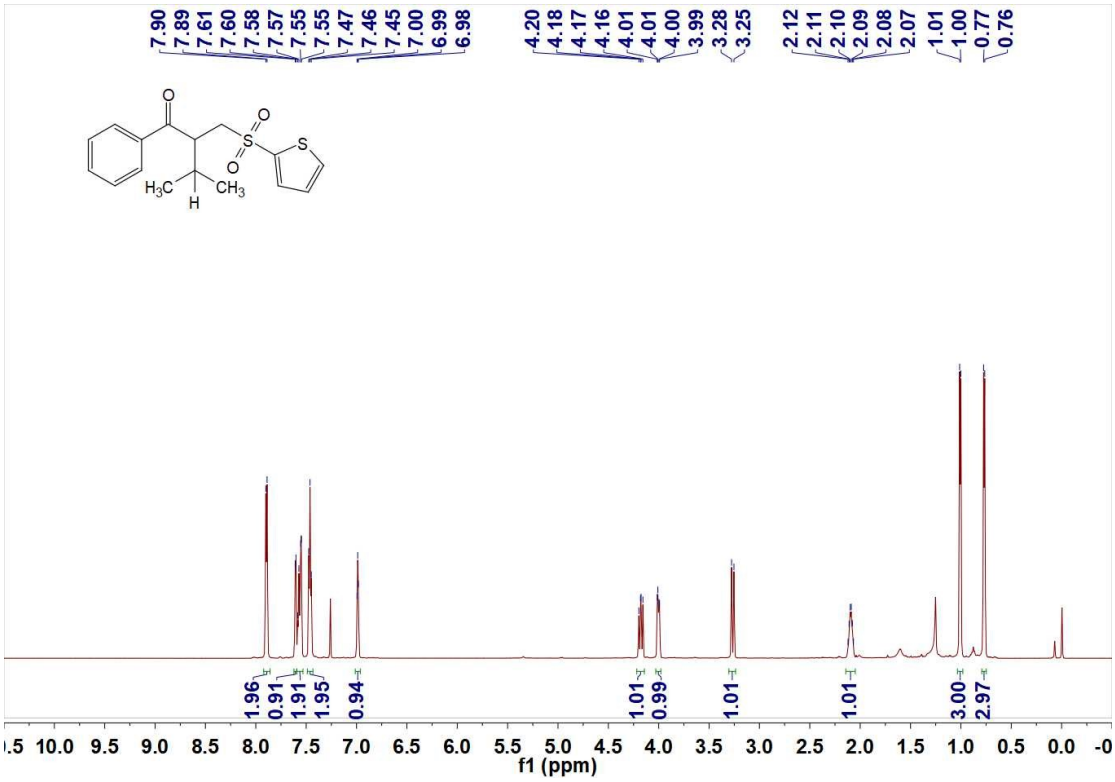
^{1}H NMR of **3ap** (400 MHz, $CDCl_3$)



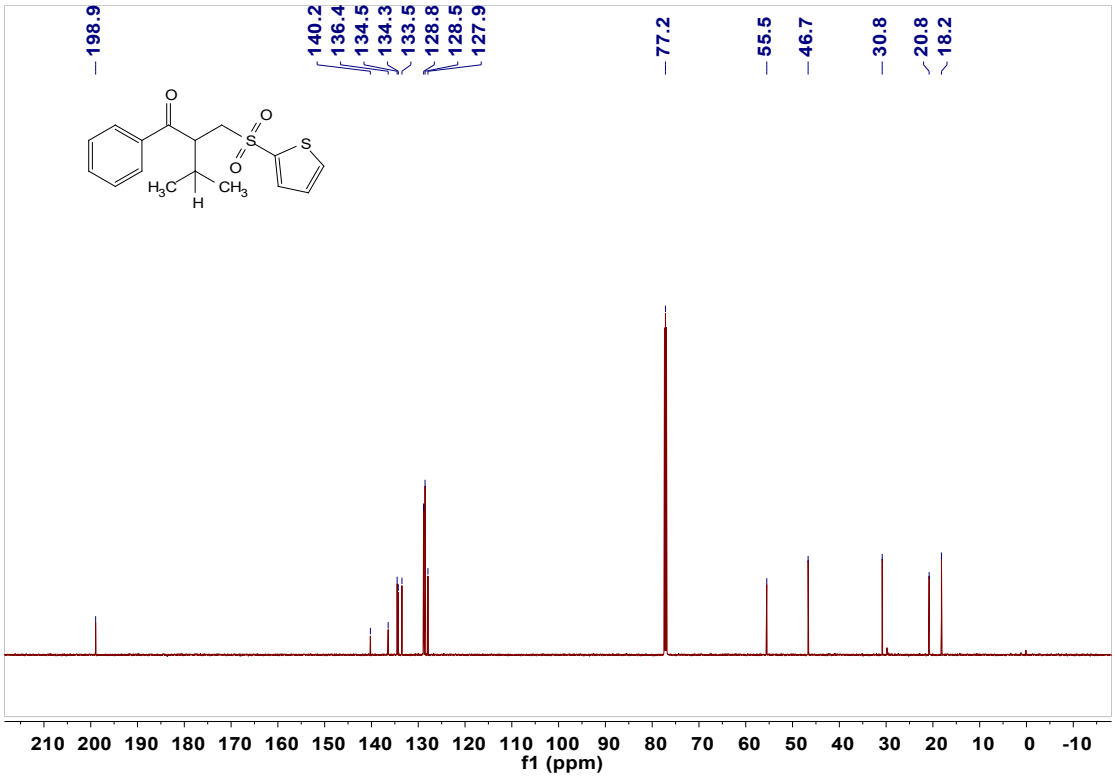
^{13}C NMR of **3ap** (101 MHz, $CDCl_3$, 77.16)



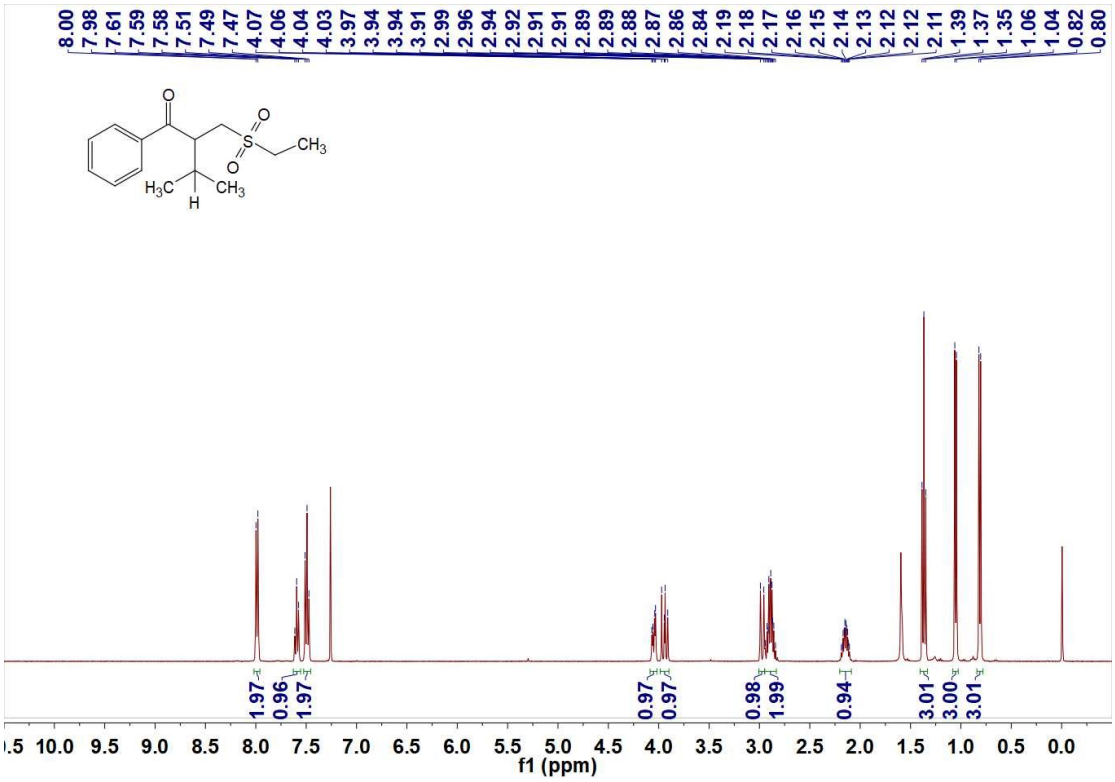
^{1}H NMR of **3aq** (600 MHz, $CDCl_3$)



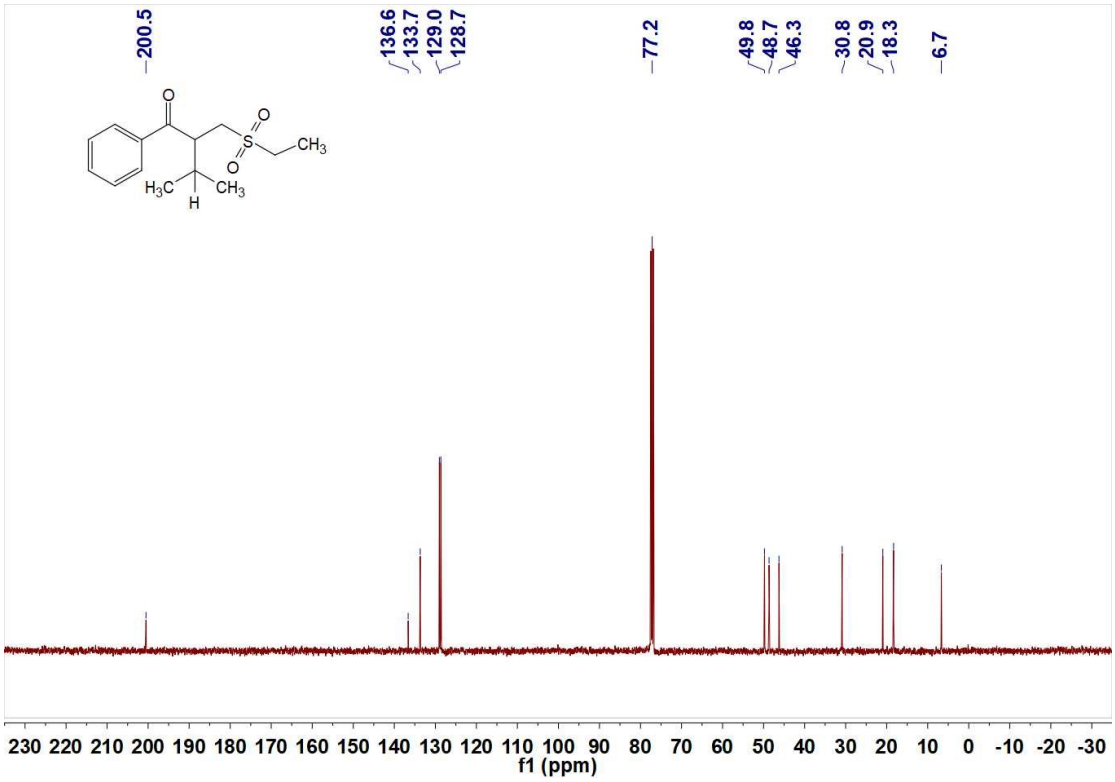
^{13}C NMR of **3aq** (151 MHz, $CDCl_3$, 77.16)



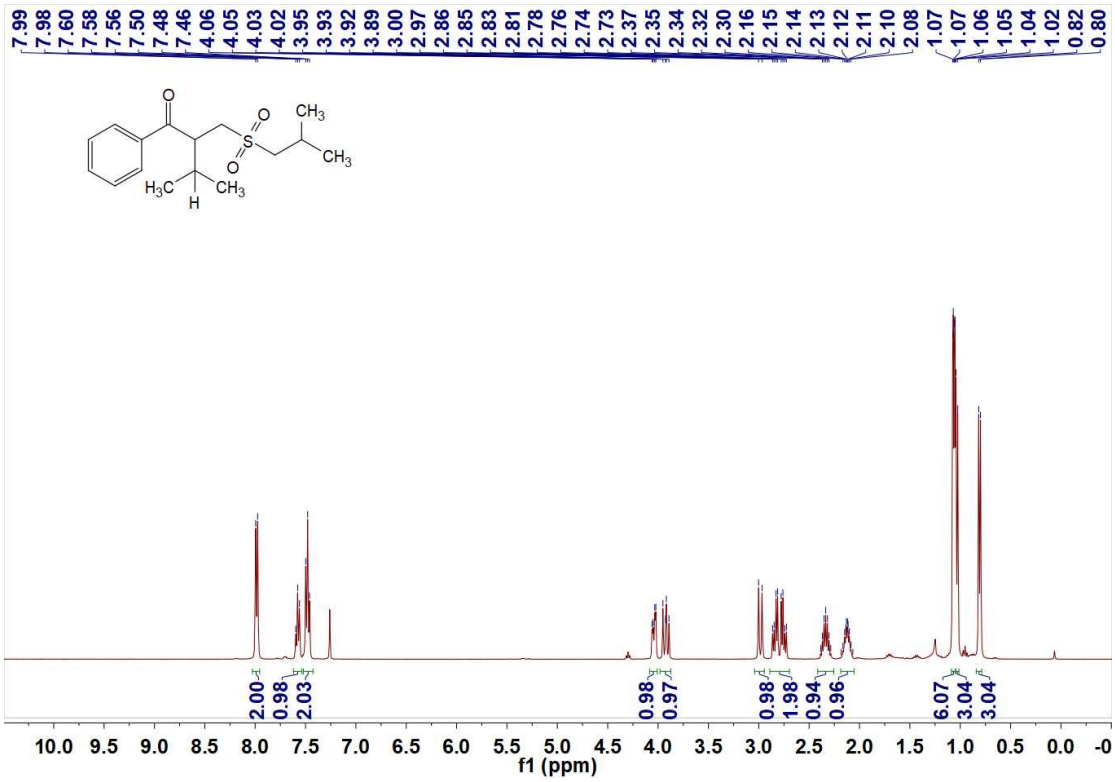
^{1}H NMR of **3ar** (400 MHz, $CDCl_3$)



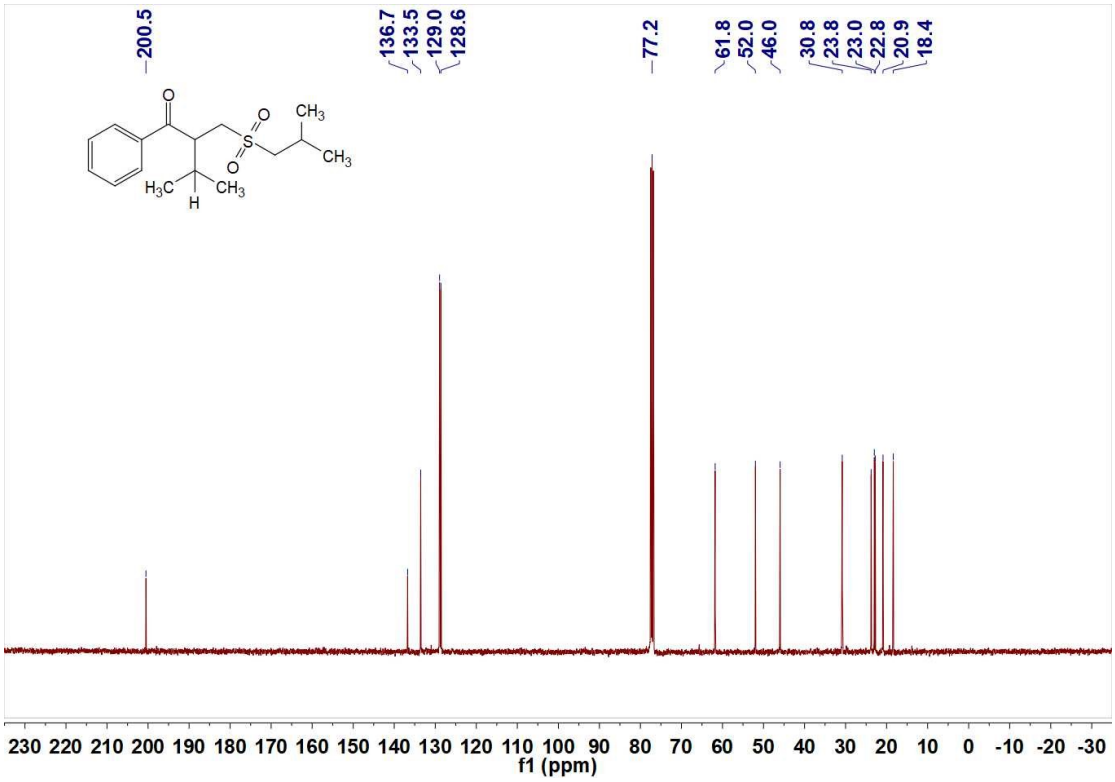
^{13}C NMR of **3ar** (101 MHz, $CDCl_3$, 77.16)



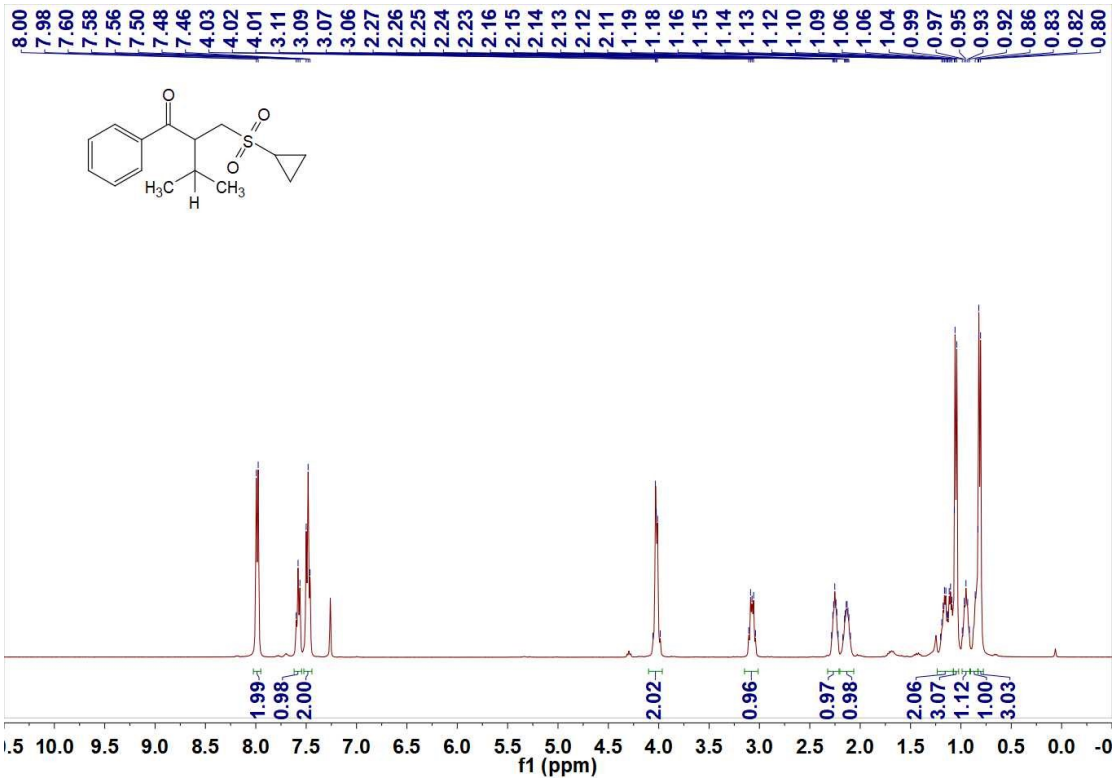
^{1}H NMR of **3as** (400 MHz, $CDCl_3$)



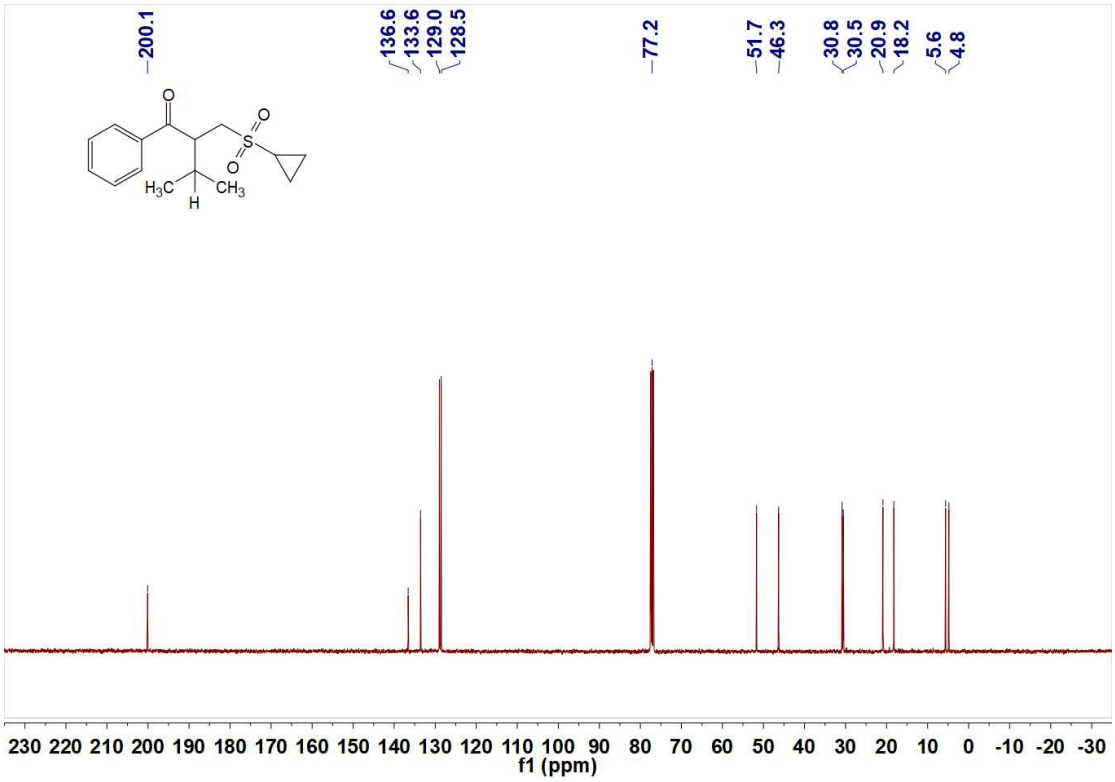
^{13}C NMR of **3as** (101 MHz, $CDCl_3$, 77.16)



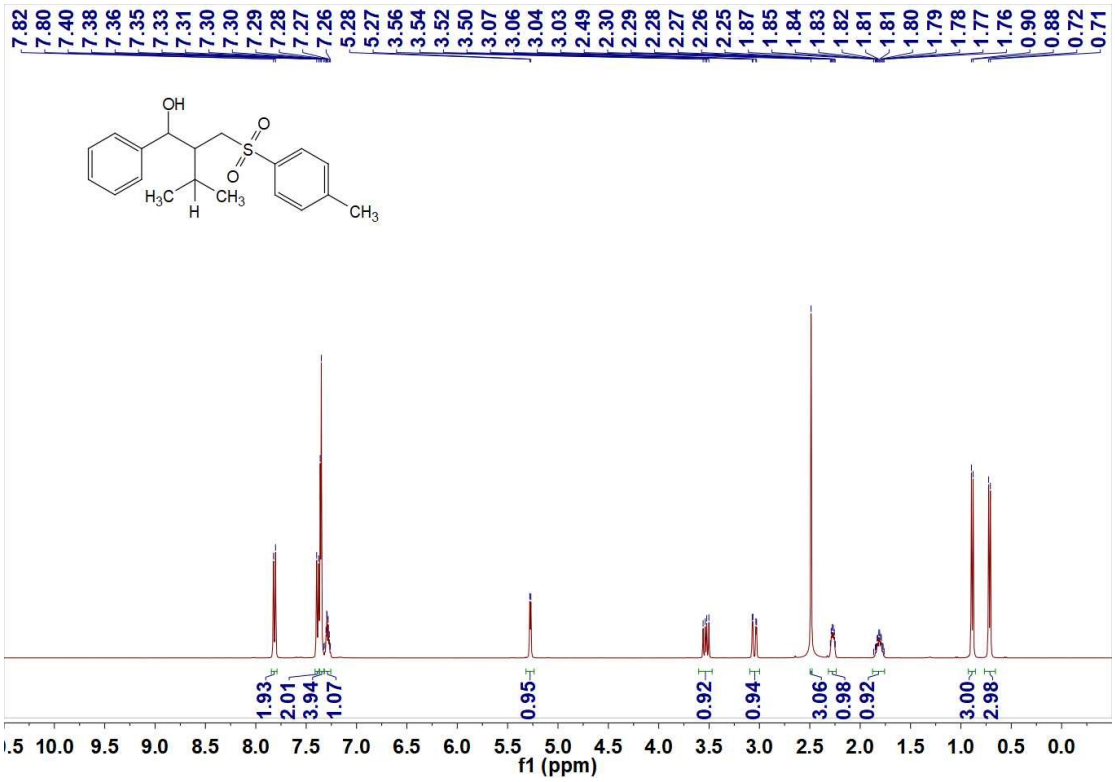
^{1}H NMR of **3at** (400 MHz, $CDCl_3$)



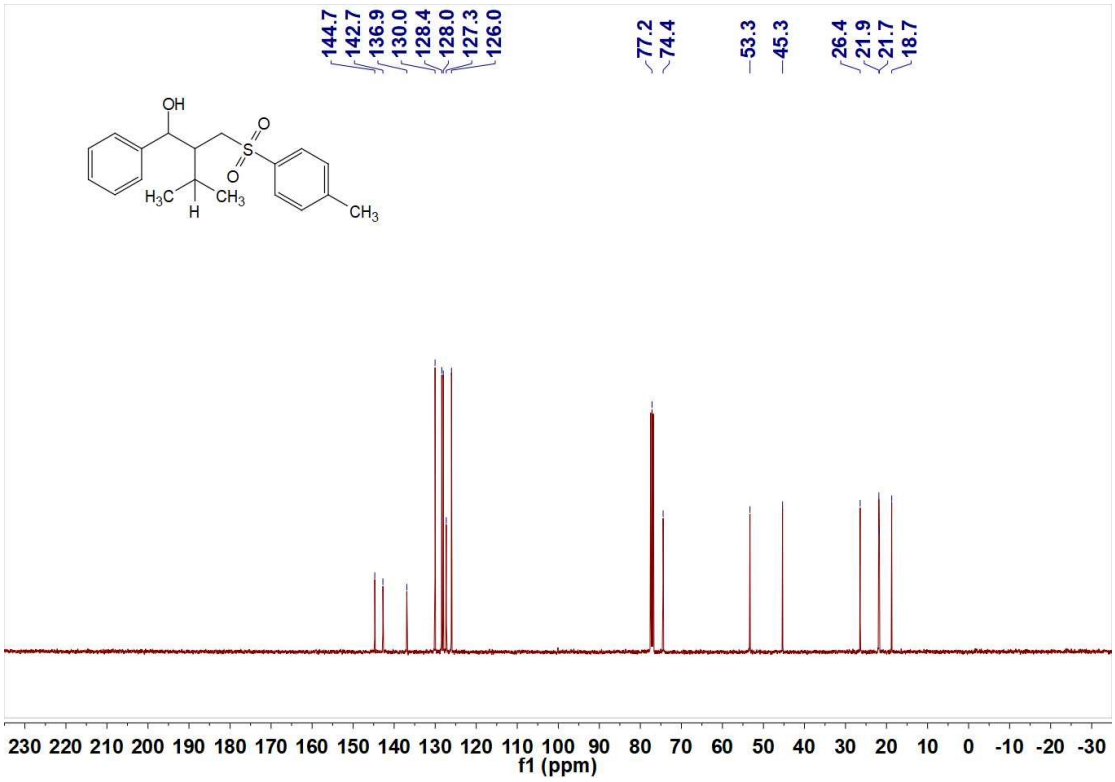
^{13}C NMR of **3at** (101 MHz, $CDCl_3$, 77.16)



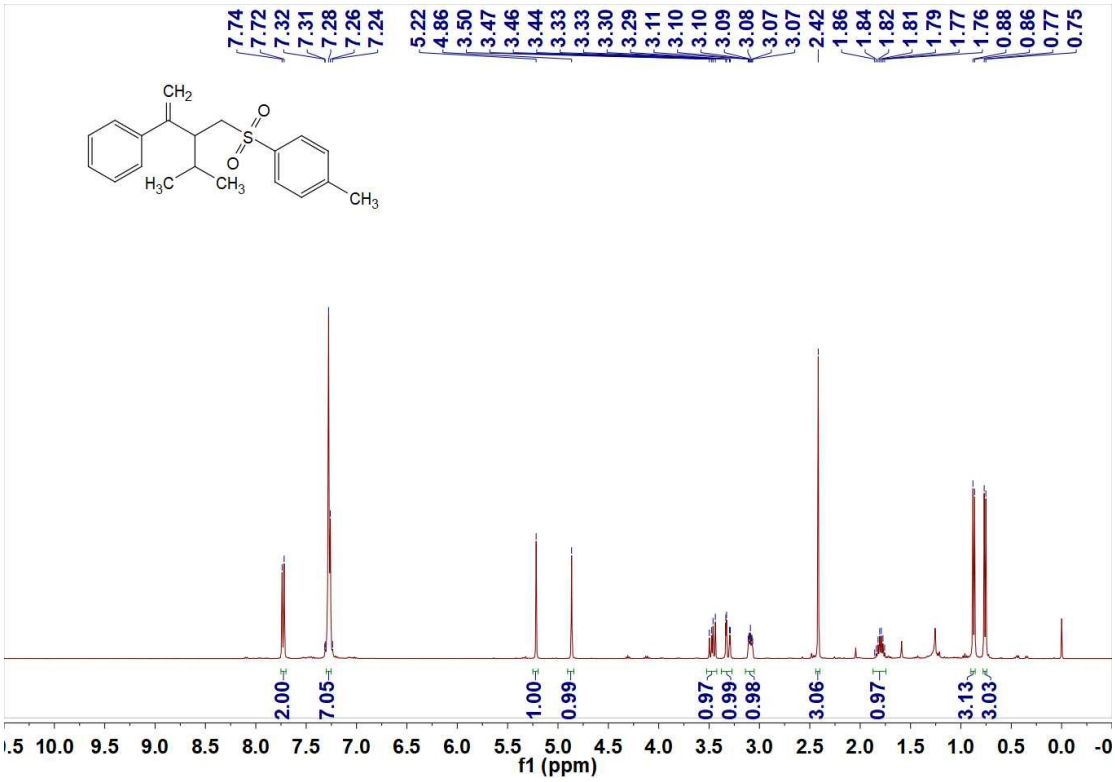
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



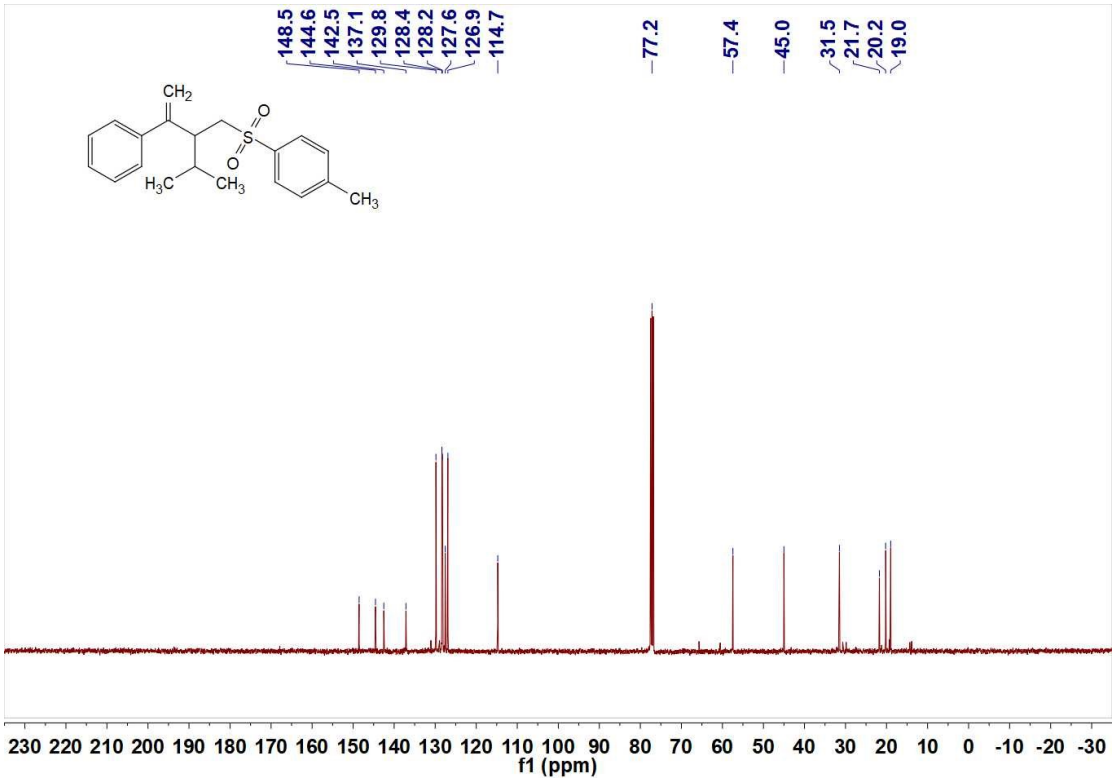
^{13}C NMR of **4** (101 MHz, $CDCl_3$, 77.16)



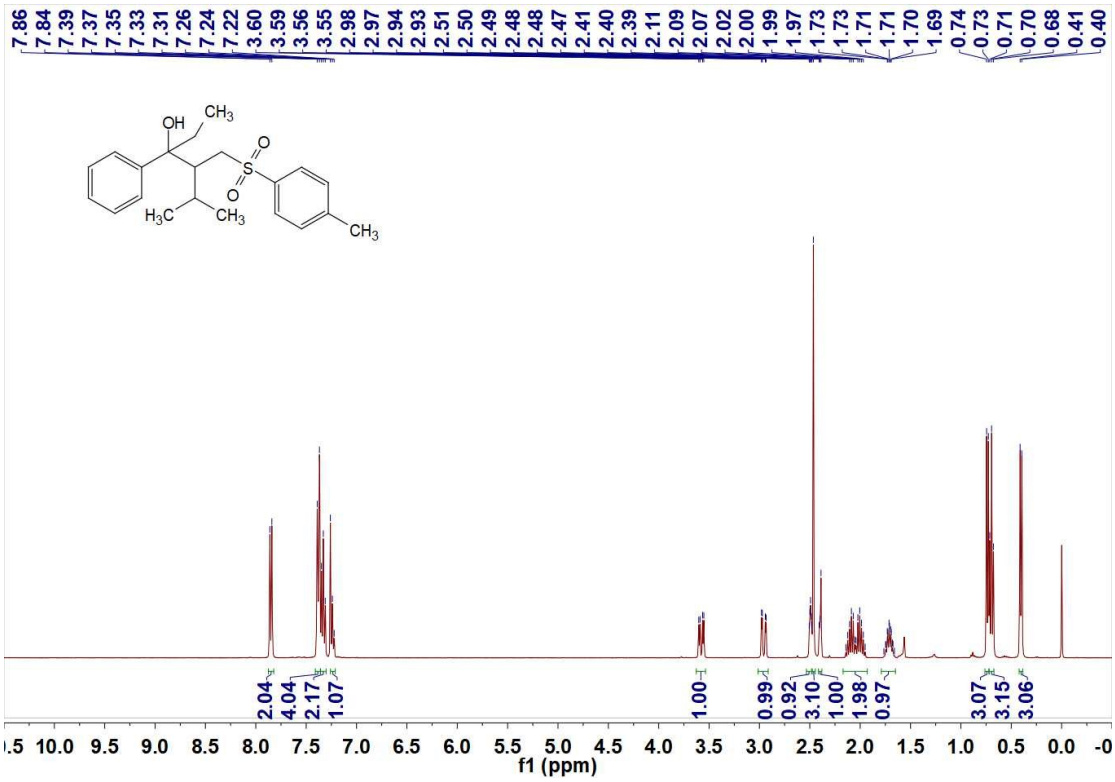
^{1}H NMR of **5** (400 MHz, $CDCl_3$)



^{13}C NMR of **5** (101 MHz, $CDCl_3$, 77.16)



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



^{13}C NMR of **6** (101 MHz, $CDCl_3$, 77.16)