Supplementary Information

Stereoselective synthesis of allylic sulfones via palladium-catalyzed hydrosulfonylation of cyclopropenes

Suliang Wang,[‡a] Xuening Li,[‡a] Jian Song*[a,b] and Xianjie Fang*[a]

*E-mail: fangxj@hznu.edu.cn

[a]Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Zhejiang Key Laboratory of Organosilicon Material Technology, College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, 2318 Yuhangtang Road, Hangzhou 311121, China

[b]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

[‡]These authors contributed equally: Suliang Wang, Xuening Li

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1. General Information

All regents used were purchased commercially without further purification. $Pd(dba)_2$ was purchased from Energy Chemical. Solvent was purified using solvent purification system (Vigor YJC-7). The air and moisture sensitive manipulations were carried out with standard Schlenk technique or in a nitrogen-filled glovebox (Vigor).

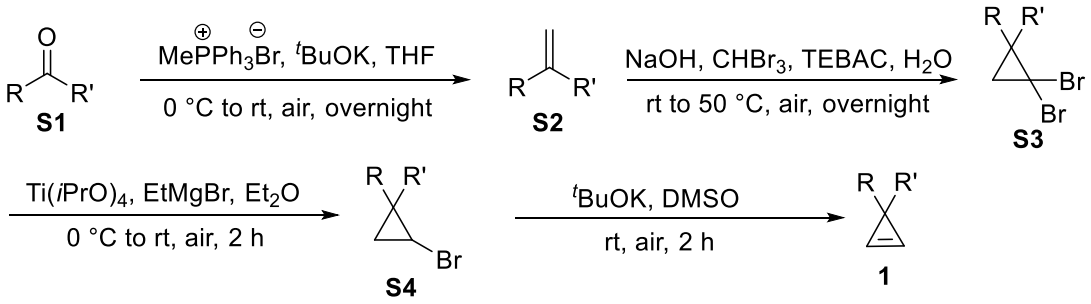
NMR spectrum: The NMR spectra were recorded on a Bruker 400 MHz or 500 MHz instrument and chemical shifts are reported in ppm relative to the residual deuterated solvents. Chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (δ H = 7.26 ppm or 0.00 ppm, and δ C = 77.16 ppm. Coupling constants (*J*) are reported in Hz and apparent splitting patterns are designated using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Mass spectroscopy: High resolution mass spectra (HRMS) were measured on electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer.

Chromatography: Column chromatography was performed using 300-400 mesh silica gels.

2. Preparation of Substrates

General procedure A[1-6]:



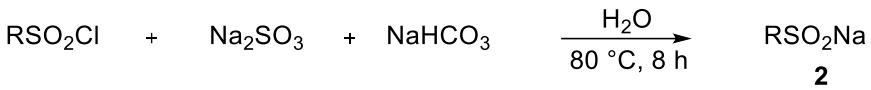
S1 to S2: Wittig reactions were performed to synthesized different alkenes **S2** from corresponding ketones **S1** when unsaturated compounds **S2** cannot be purchased commercially. To a stirred solution of **S1** (1.0 equiv.) in THF (0.5 M) at 0 ^{o}C was added methyltriphenylphosphonium bromide (1.5 equiv.). The mixture was further stirred for 5 minutes at the same temperature and then ^{t}BuOK (2.0 equiv.) was added in three portions. The reaction mixture was allowed to warm to room temperature and stirred overnight. After the reaction, saturated NH_4Cl aqueous solution was added slowly and extracted with ethyl acetate for three times. The combined organic layers was dried over anhydrous Na_2SO_4. After evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to obtain alkene **S2.**

S2 to S3: To a round-bottomed flask equipped with a magnetic stirring bar was added **S2** (1.0 equiv.), TEBAC (0.02 equiv.) and $CHBr_3$ (1.5 equiv.) at room temperature. After stirring for 10 minutes, NaOH aqueous solution (15.0 equiv., 25 M) was added through a dropper at the same temperature. The reaction mixture was then transferred to a preheated oil bath at 50 ^{o}C and stirred overnight. After the reaction, the dark viscous mixture was quenched with saturated NH_4Cl aqueous solution and extracted with dichloromethane for three times. Combine all organic phases, dried over anhydrous Na_2SO_4 and remove the solvent under vacuum. The residue was then purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to obtain **S3.**

S3 to S4: In an oven-dried three-necked round-bottomed flask equipped with a stirring bar, **S3** (1.0 equiv.) and Ti(^{i}PrO)$_4$ (5.0 mol%) were dissolved in Et_2O (0.5 M) at room temperature under argon atmosphere. The mixture was then cooled down to 0 ^{o}C, followed by slow addition of EtMgBr (3 M in Et_2O, 1.2 equiv.). After 2 hours, the reaction was quenched by addition of saturated NH_4Cl aqueous solution. The mixture was extracted with ethyl acetate for three times and organic layers were combined, followed by the addition of excess of anhydrous Na_2SO_4. The crude product was then purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) toobtain **S4**.

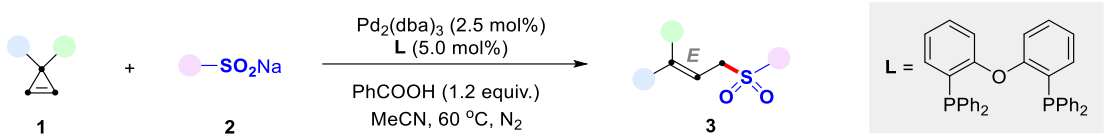
S4 to 1: To a stirred solution of **S4** (1.0 equiv.) in DMSO (0.5 M), ^{t}BuOK (1.5 equiv.) was added in three portions at room temperature. After 2 hours, saturated NH_4Cl aqueous solution was added to quench the reaction. The mixture was then extracted with ethyl acetate for three times and organic phases were combined. After drying over anhydrous Na_2SO_4, the solvent was then removed under reduced pressure, followed by the purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to obtain desired cyclopropene **1**.

General procedure B[7]:



Add sulfonyl chloride, sodium sulfinate, sodium bicarbonate and water successively to a 50 mL round-bottomed flask. Then the whole system was placed in a pan of oil at 80 ^{o}C for 8 h. After the reaction, the round-bottom flask was cooled to room temperature by air, anhydrous ethanol was added to the flask, and then the anhydrous ethanol was removed by steam under a water bath heated at 70 ^{o}C, and then anhydrous ethanol was added to the flask, and the mixture was pumped and filtered to collect the filtrate. The solvent was removed by vacuum distillation and white solid was obtained. The product was further purified by recrystallization.

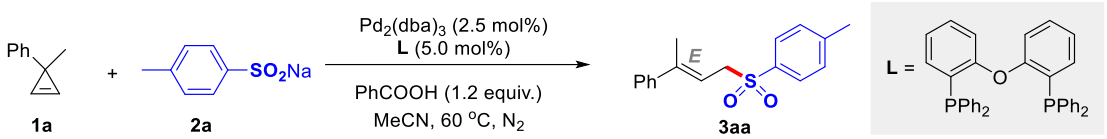
3. General Procedure



1 2 3

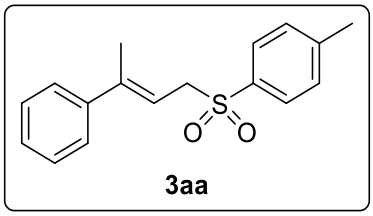
In a N_2-filled glovebox, $Pd_2(dba)_3$ (2.5 mol%), **L1** (5.0 mol%), and MeCN (2.0 mL) were added to an oven-dried 4 mL screw-cap vial. The resulting mixture was stirred for 1-2 minutes, and then **1** (0.3 mmol, 1.5 equiv.), **2** (0.2 mmol, 1.0 equiv.) and PhCOOH (0.24 mmol, 1.2 equiv.) were added successively. The vial was taken out of the glovebox and heated at 60 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **3**.

4. Scale-up Experiment



In a N_2-filled glovebox, $Pd_2(dba)_3$ (2.5 mol%), **L1** (5 mol%), and MeCN (100 mL) were added to an oven-dried 350 mL screw-cap vial. The resulting mixture was stirred for 1-2 minutes, and then **1a** (15 mmol, 1.5 equiv.), **2a** (10 mmol, 1.0 equiv.) and PhCOOH (12 mmol, 1.2 equiv.) were added successively. The vial was taken out of the glovebox and heated at 60 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **3aa** (2.63g, 92% yield, *E*/*Z* > 20/1).

5. Data for Products



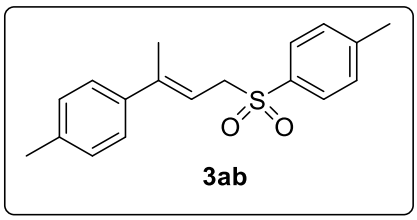
(*E*)-1-methyl-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3aa)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3aa** was obtained as white solid (56.2 mg, 98% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.65 (m, 2H), 7.28-7.17 (m, 7H), 5.69-5.59 (m, 1H), 3.91 (d, *J* = 8.1 Hz, 2H), 2.36 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.4, 142.3, 135.7, 129.7, 128.6, 128.4, 127.9, 125.9, 113.4, 56.8, 21.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{18}O_2S]^+$ 309.0920, found 309.0920.



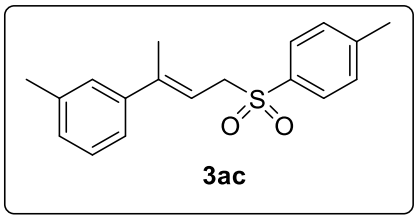
(*E*)-1-methyl-4-((3-(p-tolyl)but-2-en-1-yl)sulfonyl)benzene (3ab)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ab** was obtained as white solid (51.0 mg, 85% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.73-5.66 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.2, 139.4, 137.8, 135.6, 129.7, 129.1, 128.6, 125.7, 112.6, 56.8, 21.7, 21.1, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{20}O_2S]^+$ 323.1076, found 323.1074.



3ac

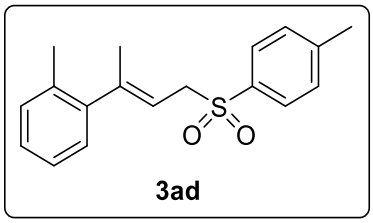
(*E*)-1-methyl-3-(4-tosylbut-2-en-2-yl)benzene (3ac)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ac** was obtained as yellow solid (51.0 ng, 85% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.68 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24-6.97 (m, 4H), 5.77-5.63 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.5, 142.3, 138.0, 135.7, 129.7, 128.7, 128.6, 128.3, 126.7, 123.0, 113.2, 56.8, 21.7, 21.5, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{20}O_2S]^+$ 323.1076, found 323.1080.



3ad

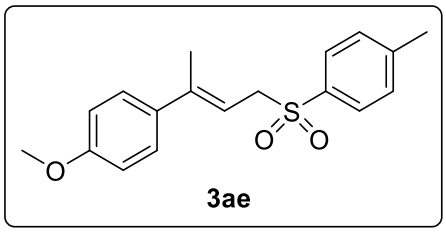
(*E*)-1-methyl-2-(4-tosylbut-2-en-2-yl)benzene (3ad)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ad** was obtained as yellow solid (49.0 mg, 82% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21-7.05 (m, 3H), 7.00-6.88 (m, 1H), 5.33-5.244 (m, 1H), 3.99 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.15 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.8, 143.8, 136.0, 134.4, 130.2, 129.8, 128.5, 127.6, 127.3, 125.7, 115.1, 56.3, 21.7, 19.7, 18.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{20}O_2S]^+$ 323.1076, found 323.1078.



3ae

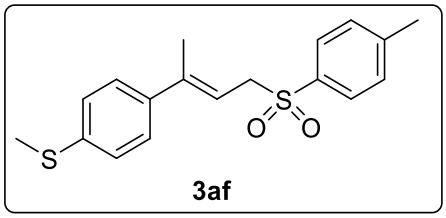
(*E*)-1-methoxy-4-(4-tosylbut-2-en-2-yl)benzene (3ae)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ae** was obtained as yellow solid (55.0 mg, 87% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, CDCl3) δ 7.88-7.64 (m, 2H), 7.44-7.12 (m, 4H), 6.87-6.80 (m, 2H), 5.72-5.54 (m, 1H), 3.98 (d, *J* = 8.2 Hz, 2H), 3.81 (s, 3H), 2.44 (s, 3H), 1.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 144.7, 143.7, 135.7, 134.6, 129.7, 128.6, 127.0, 113.7, 113.6, 111.7, 56.8, 55.3, 21.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{20}O_3S]^+$ 339.1025, found 339.1024.



3af

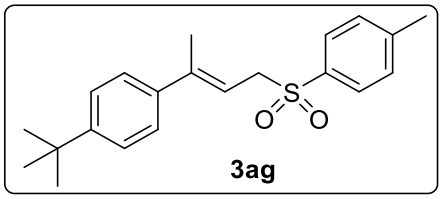
(*E*)-methyl(4-(4-tosylbut-2-en-2-yl)phenyl)sulfane (3af)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3af** was obtained as white solid (53.5 mg, 81% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25-7.16 (m, 4H), 5.74-5.66 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H), 2.44 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.6, 138.8, 138.4, 135.7, 129.7, 128.5, 126.2, 112.8, 56.8, 21.7, 15.9, 15.7.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{20}BrO_2S_2]^+$ 355.0797, found 355.0798.



3ag

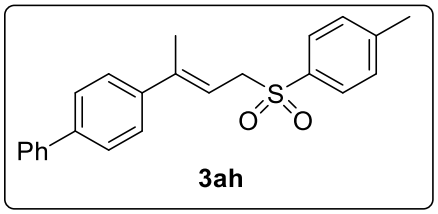
(*E*)-1-(tert-butyl)-4-(4-tosylbut-2-en-2-yl)benzene (3ag)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ag** was obtained as white solid (49.0 mg, 72% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.44-7.14 (m, 6H), 5.78-5.63 (m, 1H), 3.99 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 1.68 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 144.7, 144.1, 139.3, 135.7, 129.7, 128.6, 125.6, 125.3, 112.7, 56.8, 34.6, 31.3, 21.7, 15.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{21}H_{26}O_2S]^+$ 365.1546, found 365.1547.



3ah

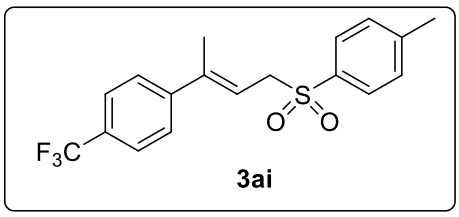
(*E*)-4-(4-tosylbut-2-en-2-yl)-1,1'-biphenyl (3ah)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ah** was obtained as white solid (28.3 mg, 39% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.64-7.52 (m, 4H), 7.51-7.29 (m, 7H), 5.83-5.72 (m, 1H), 4.02 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.9, 141.1, 140.7, 140.5, 135.7, 129.8, 128.9, 128.6, 127.5, 127.1, 127.0, 126.3, 113.4, 56.8, 21.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{23}H_{22}O_2S]^+$ 385.1233, found 385.1128.



3ai

(*E*)-1-methyl-4-((3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)sulfonyl)benzene (3ai)

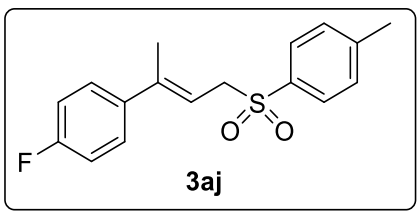
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ai** was obtained as yellow solid (58.0 mg, 82% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.63 (m, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.29 (dd, *J* = 18.2, 8.0 Hz, 4H), 5.76-5.62 (m, 1H), 3.93 (d, *J* = 8.1 Hz, 2H), 2.38 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.0, 143.3, 135.7, 129.8, 128.5, 126.2, 125.4, 125.4, 125.4, 115.5, 56.6, 21.7, 16.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.54.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{18}H_{17}F_3O_2S]^+$ 377.0794, found 377.0794.



3aj

(*E*)-1-fluoro-4-(4-tosylbut-2-en-2-yl)benzene (3aj)

According to the general procedure, the product was purified through column

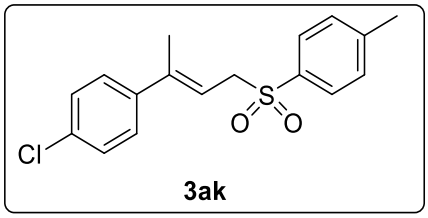
chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3aj** was obtained as white solid (50.0 mg, 82% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.69 (m, 2H), 7.38-7.19 (m, 4H), 7.08-6.90 (m, 2H), 5.71-5.62 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.4, 138.3, 135.7, 129.8, 128.5, 127.5, 127.4, 115.35, 115.1, 113.3, 56.7, 21.7, 16.2.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.33.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}FO_2S]^+$ 327.0825, found 327.0823.



3ak

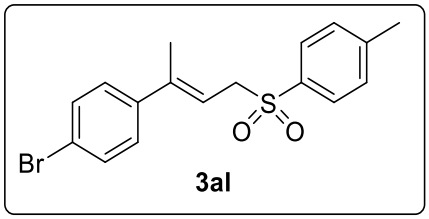
(*E*)-1-chloro-4-(4-tosylbut-2-en-2-yl)benzene (3ak)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ak** was obtained as white solid (57.0 mg, 89% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.69 (m, 2H), 7.40-7.16 (m, 6H), 5.76-5.64 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.3, 140.6, 135.7, 133.7, 129.8, 128.5, 128.5, 127.2, 113.9, 56.7, 21.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}ClO_2S]^+$ 343.0530, found 343.0531.



3al

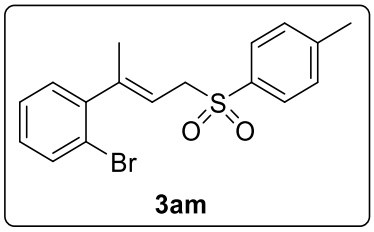
(*E*)-1-bromo-4-(4-tosylbut-2-en-2-yl)benzene (3al)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3al** was obtained as white solid (58.0 mg, 80% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.66 (m, 2H), 7.50-7.39 (m, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.21-7.10 (m, 2H), 5.77-5.65 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 143.3, 141.1, 135.7, 131.5, 129.8, 128.5, 127.5, 121.9, 114.0, 56.7, 21.7, 15.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}BrO_2S]^+$ 387.0025, found 387.0020.



3am

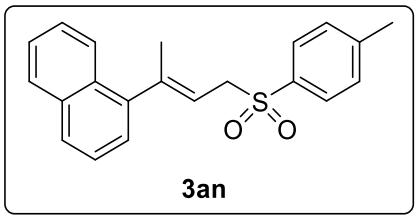
(*E*)-1-bromo-2-(4-tosylbut-2-en-2-yl)benzene (3am)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3am** was obtained as yellow solid (65.0 mg, 89% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.76 (m, 2H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 1H), 7.17-7.09 (m, 1H), 7.04 (dd, *J* = 7.5, 1.8 Hz, 1H), 5.43-5.30 (m, 1H), 3.99 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 144.8, 144.6, 135.9, 132.8, 129.8, 129.6, 128.9, 128.6, 127.4, 121.5, 116.7, 56.2, 21.7, 17.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{17}BrO_2S]^+$ 387.0025, found 387.0026.



3an

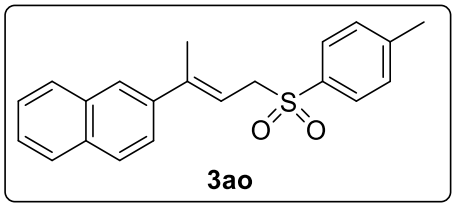
(*E*)-1-(4-tosylbut-2-en-2-yl)naphthalene (3an)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3an** was obtained as white solid (59.0 mg, 89% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.72 (m, 4H), 7.66-7.60 (m, 1H), 7.51-7.34 (m, 5H), 7.14 (dd, *J* = 7.1, 1.3 Hz, 1H), 5.53-5.42 (m, 1H), 4.09 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.7, 142.1, 136.0, 133.6, 130.6, 129.9, 128.6, 128.4, 127.7, 126.0, 125.9, 125.5, 125.4, 124.6, 116.4, 56.5, 21.7, 19.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{21}H_{20}O_2S]^+$ 359.1076, found 359.1073.



3ao

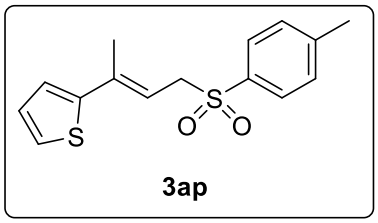
(*E*)-2-(4-tosylbut-2-en-2-yl)naphthalene (3ao)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ao** was obtained as white solid (59.0 mg, 89% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.65 (m, 6H), 7.52-7.40 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.94-5.81 (m, 1H), 4.05 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.2, 139.4, 135.7, 133.2, 133.0, 129.8, 128.6, 128.2, 128.0, 127.6, 126.4, 126.2, 124.2, 124.0, 113.9, 56.9, 21.7, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{21}H_{20}O_2S]^+$ 359.1076, found 359.1075.



3ap

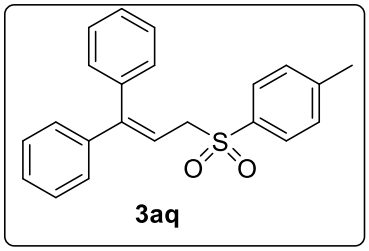
(*E*)-2-(4-tosylbut-2-en-2-yl)thiophene (3ap)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ap** was obtained as white solid (42.0 mg, 72% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.71 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.06-6.93 (m, 2H), 5.88-5.78 (m, 1H), 3.97 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 144.8, 137.7, 135.6, 129.8, 128.6, 127.5, 125.0, 124.1, 111.5, 56.6, 21.7, 15.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{15}H_{16}O_2S_2]^+$ 315.0484, found 315.0488.



3aq

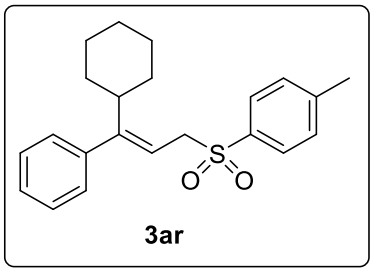
(3-tosylprop-1-ene-1,1-diyl)dibenzene (3aq)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3aq** was obtained as white solid (68 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.58 (m, 2H), 7.40-7.06 (m, 10H), 6.80-6.58 (m, 2H), 6.13 (t, *J* = 7.9 Hz, 1H), 3.90 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 144.7, 140.9, 137.8, 135.7, 129.7, 129.3, 128.5, 128.3, 128.3, 128.3, 127.8, 127.5, 114.2, 77.4, 77.1, 76.7, 57.6, 21.7.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{22}H_{20}O_2S]^+$ 371.1076, found 371.1080.



3ar

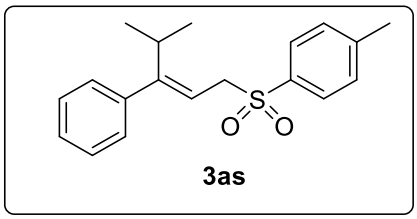
(*E*)-1-((3-cyclohexyl-3-phenylallyl)sulfonyl)-4-methylbenzene (3ar)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ar** was obtained as yellow solid (37 mg, 52% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.58 (m, 2H), 7.45-7.09 (m, 5H), 6.60-6.38 (m, 2H), 5.68-5.39 (m, 1H), 3.60 (d, *J* = 7.7 Hz, 2H), 2.49 (s, 3H), 2.16-1.96 (m, 1H), 1.82-1.51 (m, 5H), 1.28-0.98 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 144.5, 139.0, 135.6, 129.5, 128.8, 128.0, 128.0, 127.0, 111.4, 57.0, 46.5, 31.8, 26.4, 26.1, 21.7.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{22}H_{26}O_2S]^+$ 377.1546, found 377.1547.



3as

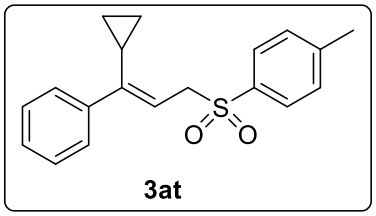
(*E*)-1-methyl-4-((4-methyl-3-phenylpent-2-en-1-yl)sulfonyl)benzene (3as)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3as** was obtained as yellow solid (50,0 mg, 80% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.57 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24-7.11 (m, 3H), 6.55-6.45 (m, 2H), 5.59-5.47 (m, 1H), 3.60 (d, *J* = 7.7 Hz, 2H), 2.48 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 144.6, 138.6, 135.6, 129.5, 128.8, 128.1, 128.0, 127.1, 111.2, 57.0, 36.5, 21.7, 21.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{19}H_{22}O_2S]^+$ 337.1233, found 337.1236.



3at

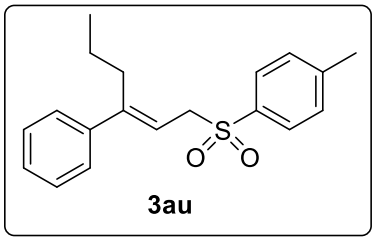
(*E*)-1-((3-cyclopropyl-3-phenylallyl)sulfonyl)-4-methylbenzene (3at)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3at** was obtained as white solid (49.0 mg, 79% yield, *E/Z* = 1.5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.64 (m, 2H), 7.56-7.46 (m, 3H), 7.32-7.00 (m, 15H), 6.56-6.43 (m, 3H), 5.61-5.52 (m, 1H), 5.47-5.36 (m, 2H), 4.10 (d, *J* = 8.0 Hz, 2H), 3.53 (d, *J* = 7.8 Hz, 3H), 2.43-2.26 (m, 8H), 1.55-1.40 (m, 2H), 1.26-1.10 (m, 2H), 0.62-0.45 (m, 5H), 0.32-0.18 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 149.7, 144.7, 144.5, 140.7, 137.4, 135.9, 135.8, 129.7, 129.6, 128.6, 128.3, 128.0, 127.9, 127.4, 127.4, 127.3, 116.4, 110.9, 57.0, 56.6, 21.69, 18.7, 11.3, 6.5, 5.6.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{19}H_{20}O_2S]^+$ 335.1076, found 335.1077.



3au

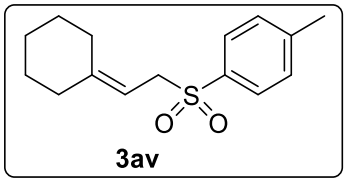
(*E*)-1-methyl-4-((3-phenylhex-2-en-1-yl)sulfonyl)benzene (3au)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3au** was obtained as white solid (53.0 mg, 84% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.72 (m, 2H), 7.40-7.15 (m, 7H), 5.60 (t, *J* = 8.0 Hz, 1H), 4.00 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 3H), 2.20-2.07 (m, 2H), 1.15-0.94 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 144.8, 141.6, 135.7, 129.7, 129.6, 128.6, 128.4, 128.20, 127.7, 127.7, 126.5, 113.9, 56.6, 31.8, 21.7, 21.332, 13.8.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{19}H_{22}O_2S]^+$ 337.1233, found 337.1235.



3av

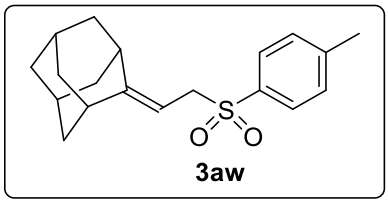
1-((2-cyclohexylideneethyl)sulfonyl)-4-methylbenzene (3av)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3av** was obtained as white solid (32 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.13 (t, *J* = 8.0 Hz, 1H), 3.79 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.07 (t, *J* = 5.6 Hz, 2H), 1.86-1.74 (m, 2H), 1.52-1.36 (m, 4H), 1.17 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 144.4, 135.7, 129.5, 128.7, 107.3, 55.3, 37.2, 28.8, 28.1, 27.0, 26.3, 21.7.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{15}H_{120}O_2S]^+$ 287.1076, found 287.1076.



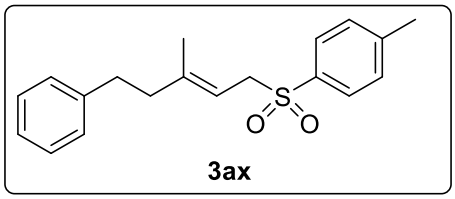
(5R,7R,E)-2-(2-tosylethylidene)adamantane (3aw)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3aw** was obtained as white solid (47.0 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.08 (t, *J* = 8.0 Hz, 1H), 3.80 (d, *J* = 8.0 Hz, 2H), 2.61-2.28 (m, 5H), 1.85-1.56 (m, 9H), 1.22 (d, *J* = 12.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 144.4, 135.8, 129.5, 128.7, 102.5, 54.9, 40.7, 39.4, 38.3, 36.8, 32.6, 28.1, 21.6.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{19}H_{24}O_2S]^+$ 339.1389, found 339.1392.



(*E*)-1-methyl-4-((3-methyl-5-phenylpent-2-en-1-yl)sulfonyl)benzene (3ax)

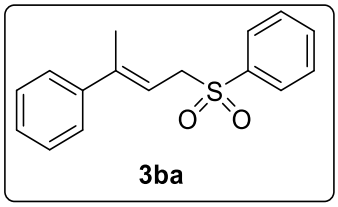
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ax** was obtained as white solid (42.0 mg, 76% yield, *E/Z* = 2/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.62 (m, 3H), 7.39-6.98 (m, 11H), 5.30-5.09 (m, 1.5H), 3.78 (d, *J* = 8.0 Hz, 2H), 3.59 (d, *J* = 7.9 Hz, 1H), 2.76-2.58 (m, 2H), 2.53-2.37 (m, 5H), 2.30 (dd, *J* = 9.7, 6.5 Hz, 2H), 2.07 (dd, *J* = 9.2, 6.7 Hz, 1H), 1.77 (d, *J* = 1.4 Hz, 1.5H), 1.39 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.1, 144.6, 144.5, 141.5, 141.4, 135.9, 135.7, 129.7, 129.6, 128.6, 128.5, 128.4, 128.3, 128.3, 126.1, 126.0, 111.7, 111.0, 56.1, 55.7,

41.5, 34.1, 33.9, 33.7, 23.7, 21.7, 21.7, 16.4.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{19}H_{22}O_2S]^+$ 337.1233, found 337.1234.



3ba

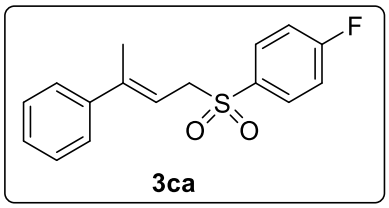
(*E*)-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ba)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ba** was obtained as white solid (53.0 mg, 96% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.83 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.37-7.22 (m, 5H), 5.77-5.68 (m, 1H), 4.01 (d, *J* = 8.2 Hz, 2H), 1.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.2, 138.6, 133.8, 129.1, 128.6, 128.4, 128.0, 125.8, 113.2, 56.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{16}O_2S]^+$ 295.0763, found 295.0761.



3ca

(*E*)-1-fluoro-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ca)

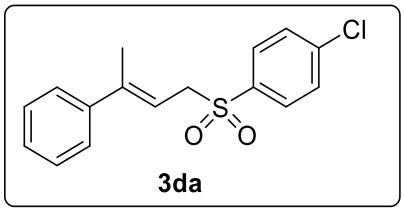
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ca** was obtained as white solid (54.0 mg 93% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.74 (m, 2H), 7.48-7.03 (m, 7H), 5.82-5.62 (m, 1H), 4.01 (d, *J* = 8.1 Hz, 2H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 164.6, 144.8, 142.0, 134.6, 134.6, 131.5, 131.4, 128.5, 128.1, 125.8, 116.5, 116.3, 113.1, 56.8, 16.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -103.33.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}FO_2S]^+$ 313.0669, found 313.0666.



3da

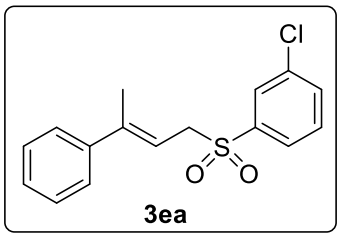
(*E*)-1-chloro-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3da)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3da** was obtained as white solid (54.0 mg, 88% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.40-7.22 (m, 5H), 5.80-5.65 (m, 1H), 4.02 (d, *J* = 8.1 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 142.0, 140.6, 137.1, 130.1, 129.4, 128.5, 128.1, 125.8, 112.9, 56.8, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}ClO_2S]^+$ 329.0373, found 329.0373.



3ea

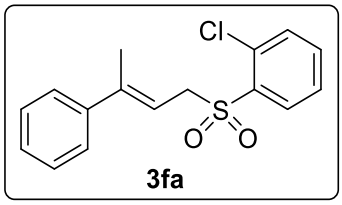
(*E*)-1-chloro-3-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ea)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ea** was obtained as white solid (55.0 mg, 90% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.37-7.23 (m, 5H), 5.78-5.62 (m, 1H), 4.02 (d, *J* = 8.1 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.1, 140.3, 135.5, 133.9, 130.4, 128.7, 128.5, 128.08, 126.7, 125.9, 112.8, 56.7, 16.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}ClO_2S]^+$ 329.0373, found 329.0372.



3fa

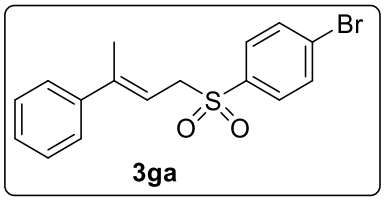
(*E*)-1-chloro-2-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3fa)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3fa** was obtained as white solid (53.0 mg, 87% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 3.6 Hz, 2H), 7.48-7.39 (m, 1H), 7.33- 7.18 (m, 5H), 5.80-5.61 (m, 1H), 4.35 (d, *J* = 8.0 Hz, 2H), 1.91 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.2, 136.4, 134.8, 132.7, 132.4, 131.9, 128.3, 127.94, 127.4, 125.9, 112.6, 54.6, 16.4.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}ClO_2S]^+$ 329.0373, found 329.0374.



3ga

(*E*)-1-bromo-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ga)

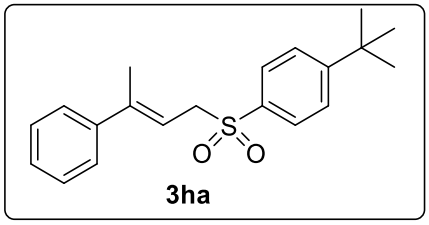
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ga** was

obtained as white solid (58.0 mg, 83% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.58 (m, 4H), 7.35-7.24 (m, 5H), 5.75-5.66 (m, 1H), 4.01 (d, *J* = 8.2 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 142.0, 137.6, 132.4, 130.1, 129.2, 128.5, 128.1, 125.8, 112.9, 56.7, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}BrO_2S]^+$ 372.9868, found 372.9867.



3ha

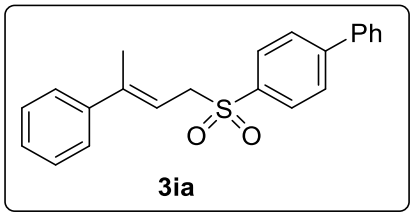
(*E*)-1-(tert-butyl)-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ha)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ha** was obtained as white solid (58.0 mg, 88% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.74 (m, 2H), 7.59-7.48 (m, 2H), 7.40-7.21 (m, 5H), 5.83-5.64 (m, 1.5 Hz, 1H), 3.99 (d, *J* = 8.1 Hz, 2H), 1.69 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 144.5, 142.3, 135.6, 128.4, 128.4, 127.9, 126.1, 125.9, 113.5, 56.8, 35.3, 31.1, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{20}H_{24}O_2S]^+$ 351.1389, found 351.1390.



3ia

(*E*)-4-((3-phenylbut-2-en-1-yl)sulfonyl)-1,1'-biphenyl (3ia)

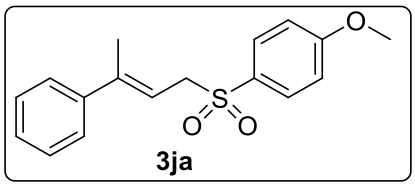
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ia** was

obtained as white solid (51.0 mg, 73% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 6.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.52-7.41 (m, 3H), 7.36-7.23 (m, 5H), 5.86-5.68 (m, 1H), 4.05 (d, *J* = 8.1 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 144.7, 142.2, 139.1, 137.2, 129.1, 129.1, 128.8, 128.44, 128.0, 127.7, 127.4, 125.9, 113.3, 56.9, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{22}H_{20}O_2S]^+$ 371.1076, found 371.1075.



3ja

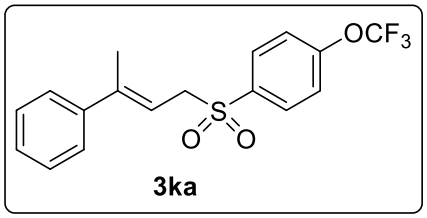
(*E*)-1-methoxy-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3ja)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ja** was obtained as white solid (60.0 mg, 99% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.37-7.24 (m, 5H), 6.99 (d, *J* = 8.9 Hz, 2H), 5.78-5.68 (m, 1H), 3.99 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 144.3, 142.3, 130.7, 130.2, 128.4, 127.9, 125.9, 114.3, 113.6, 56.9, 55.7, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{18}O_3S]^+$ 325.0869, found 325.0870.



3ka

(*E*)-1-((3-phenylbut-2-en-1-yl)sulfonyl)-4-(trifluoromethoxy)benzene (3ak)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ka** was

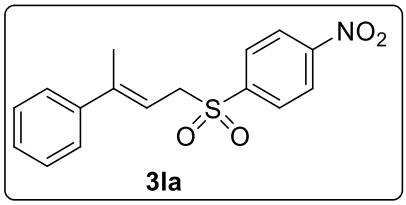
obtained as white solid (58.0 mg, 82% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.87 (m, 2H), 7.45-7.14 (m, 7H), 5.81-5.64 (m, 1H), 4.03 (d, *J* = 8.1 Hz, 2H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 145.0, 141.9, 136.8, 130.9, 128.5, 128.1, 125.8, 121.49, 120.9, 118.9, 112.8, 56.8, 16.0.

^{19}F NMR (471 MHz, $CDCl_3$) δ -57.69.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{15}F_3O_3S]^+$ 379.0586, found 379.0584.



3la

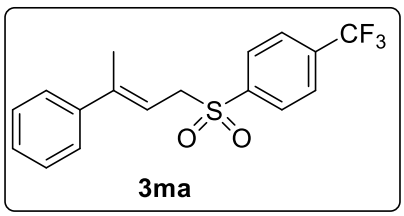
(*E*)-1-nitro-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzene (3la)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3la** was obtained as white solid (39.3 mg, 62% yield, *E/Z* > 20/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.28-7.17 (m, 5H), 5.63 (t, *J* = 8.2 Hz, 1H), 4.01 (d, *J* = 8.1 Hz, 2H), 1.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 145.6, 144.4, 141.6, 130.1, 128.6, 128.3, 125.8, 124.2, 112.1, 56.7, 16.3.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{16}H_{15}NO_4S]^+$ 340.0614, found 340.0617.



3ma

(*E*)-1-((3-phenylbut-2-en-1-yl)sulfonyl)-4-(trifluoromethyl)benzene (3ma)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ma** was

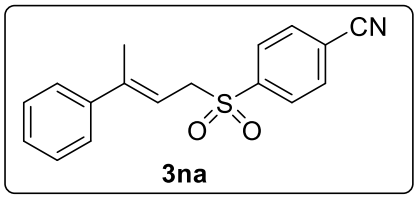
obtained as white solid (65.0 mg, 96% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.41-7.21 (m, 5H), 5.76-5.67 (m, 1H), 4.05 (d, *J* = 8.1 Hz, 2H), 1.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 142.2, 141.9, 129.3, 128.5, 128.2, 126.3, 126.3, 126.2, 126.2, 125.8, 112.5, 56.7, 16.1.

^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{15}F_3O_2S]^+$ 363.0637, found 363.0635.



3na

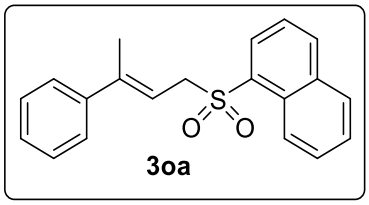
(*E*)-4-((3-phenylbut-2-en-1-yl)sulfonyl)benzonitrile (3na)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3na** was obtained as white solid (32.0 mg, 58% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.39-7.23 (m, 5H), 5.74-5.66 (m, 1H), 4.06 (d, *J* = 8.1 Hz, 2H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.8, 141.7, 132.8, 129.4, 128.6, 128.3, 125.8, 117.6, 117.1, 112.2, 56.6, 16.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{15}NO_2S]^+$ 320.0716, found 320.0712.



3oa

(*E*)-1-((3-phenylbut-2-en-1-yl)sulfonyl)naphthalene (3oa)

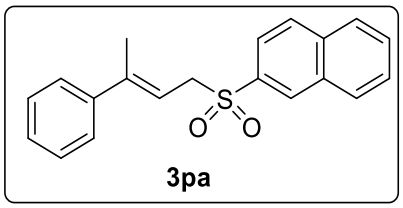
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3oa** was

obtained as yellow solid (58.0 mg, 90% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.79-7.51 (m, 3H), 7.34-7.08 (m, 5H), 5.74-5.53 (m, 1H), 4.21 (d, *J* = 8.1 Hz, 2H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.2, 135.3, 134.2, 133.8, 131.4, 129.2, 129.2, 128.8, 128.3, 127.8, 127.0, 125.8, 124.4, 124.2, 113.3, 56.3, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{20}H_{18}O_2S]^+$ 345.0920, found 345.0921.



3pa

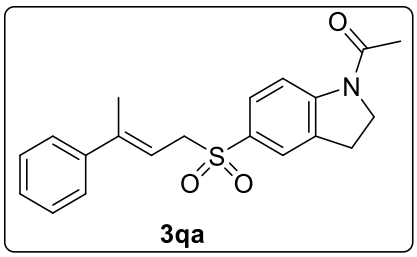
(*E*)-2-((3-phenylbut-2-en-1-yl)sulfonyl)naphthalene (3pa)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3pa** was obtained as white solid (47.0 mg, 73% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.10-7.82 (m, 4H), 7.74-7.51 (m, 2H), 7.36-7.18 (m, 5H), 5.76 (t, *J* = 8.1 Hz, 1H), 4.09 (d, *J* = 8.1 Hz, 2H), 1.65 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.2, 135.6, 135.3, 132.2, 130.5, 129.4, 129.3, 129.3, 128.4, 128.0, 127.9, 127.7, 125.9, 123.2, 113.3, 56.9, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{20}H_{18}O_2S]^+$ 345.0920, found 345.0919.



3qa

(*E*)-1-(5-((3-phenylbut-2-en-1-yl)sulfonyl)indolin-1-yl)ethan-1-one (3qa)

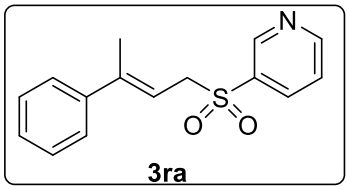
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 3/1). **3qa** was

obtained as yellow solid (58.0 mg, 81% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.81-7.59 (m, 2H), 7.38-7.22 (m, 5H), 5.80-5.62 (m, 1H), 4.14 (t, *J* = 8.6 Hz, 2H), 3.99 (d, *J* = 8.1 Hz, 2H), 3.21 (t, *J* = 8.6 Hz, 2H), 2.26 (s, 3H), 1.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 147.5, 144.4, 142.3, 133.5, 132.9, 132.2, 130.1, 129.3, 128.4, 127.9, 125.8, 124.9, 116.6, 113.5, 56.9, 49.2, 27.4, 24.4, 16.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{20}H_{21}NO_3S]^+$ 378.1134, found 378.1131.



3ra

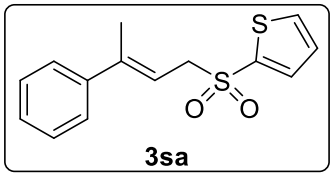
(*E*)-3-((3-phenylbut-2-en-1-yl)sulfonyl)pyridine (3ra)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ra** was obtained as yellow solid (41.0 mg, 76% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.3 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.40-7.19 (m, 5H), 5.84-5.63 (m, 1H), 4.07 (d, *J* = 8.1 Hz, 2H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 149.5, 145.4, 141.8, 136.4, 135.0, 128.5, 128.2, 125.82, 123.7, 112.4, 57.0, 16.2.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{15}H_{15}NO_2S]^+$ 296.0716, found 296.0717.



3sa

(*E*)-2-((3-phenylbut-2-en-1-yl)sulfonyl)thiophene (3sa)

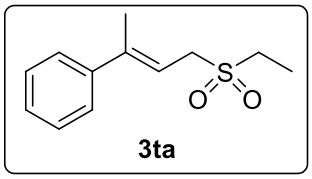
According to the general procedure, the product was purified through column

chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3sa** was obtained as white solid (45 mg, 81% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.51 (m, 2H), 7.38-7.21 (m, 5H), 7.19-7.09 (m, 1H), 5.87-5.71 (m, 1.5 Hz, 1H), 4.11 (d, *J* = 8.1 Hz, 2H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 142.1, 139.3, 134.6, 134.5, 128.4, 128.0, 127.9, 126.0, 113.2, 57.8, 16.0.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{14}H_{14}O_2S_2]^+$ 301.0327, found 301.0328.



3ta

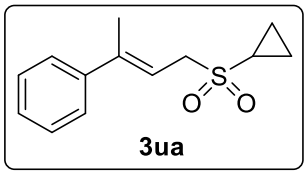
(*E*)-(4-(ethylsulfonyl)but-2-en-2-yl)benzene (3ta)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ta** was obtained as white solid (38.0 mg, 79% yield, *E/Z* > 20/1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.21 (m, 5H), 5.96-5.64 (m, 1H), 3.84 (d, *J* = 8.0 Hz, 2H), 2.93 (q, *J* = 7.5 Hz, 2H), 2.10 (s, 3H), 1.34 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.0, 128.5, 128.1, 126.0, 113.1, 52.9, 46.1, 16.7, 6.5.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{12}H_{16}O_2S]^+$ 247.0763, found 247.0763.



3ua

(*E*)-(4-(cyclopropylsulfonyl)but-2-en-2-yl)benzene (3ua)

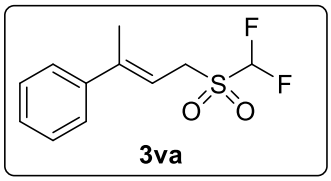
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3ua** was

obtained as yellow solid (39.0 mg, 83% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.21 (m, 5H), 5.96-5.86 (m, 1H), 3.98 (d, *J* = 8.1 Hz, 2H), 2.90-2.38 (m, 1H), 2.18 (s, 3H), 1.31-1.24 (m, 2H), 1.07-0.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 142.1, 128.5, 128.0, 126.0, 113.3, 54.4, 28.8, 16.7, 4.7.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{13}H_{16}O_2S]^+$ 259.0763, found 259.0765.



3va

(*E*)-(4-((difluoromethyl)sulfonyl)but-2-en-2-yl)benzene (3va)

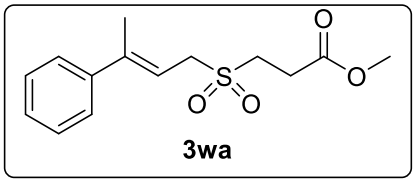
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3va** was obtained as yellow solid (46.0 mg, 94% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.28 (m, 5H), 6.18 (t, *J* = 52.8 Hz, 1H), 5.86-5.72 (m, 1H), 4.12 (d, *J* = 8.0 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 141.8, 128.5, 128.3, 126.0, 117.8, 115.0, 112.1, 108.8, 49.2, 16.9.

^{19}F NMR (471 MHz, $CDCl_3$) δ -122.99.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{11}H_{12}F_2O_2S]^+$ 269.0418, found 269.0418.



3wa

methyl (*E*)-2-((3-phenylbut-2-en-1-yl)sulfonyl)acetate (3wa)

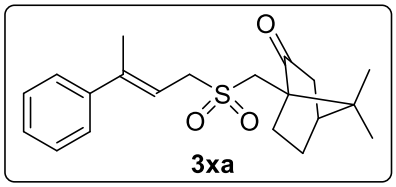
According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 3/1). **3wa** was

obtained as yellow solid (32.0 mg, 59% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.25 (m, 5H), 5.95-5.76 (m, 1H), 3.97 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 3.32 (t, *J* = 7.5 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 144.9, 141.9, 128.5, 128.2, 126.0, 112.5, 54.34, 52.5, 47.1, 26.5, 16.8.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{14}H_{18}O_4S]^+$ 305.0818, found 305.0807.



3xa

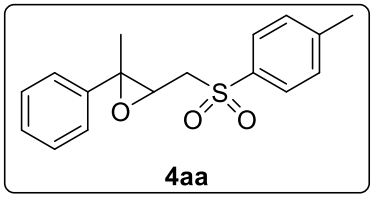
(E)-7,7-dimethyl-1-(((3-phenylbut-2-en-1-yl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (3xa)

According to the general procedure, the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **3xa** was obtained as yellow solid (57.0 mg, 86% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.09 (m, 5H), 6.03-5.87 (m, 1H), 4.31 (dd, *J* = 14.2, 8.3 Hz, 1H), 4.03 (dd, *J* = 14.2, 7.6 Hz, 1H), 3.46 (d, *J* = 14.9 Hz, 1H), 2.78 (d, *J* = 14.9 Hz, 1H), 2.49-2.30 (m, 2H), 2.19 (s, 3H), 2.16-1.85 (m, 4H), 1.53-1.41 (m, 1H), 1.06 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 142.3, 128.4, 127.9, 126.0, 113.4, 59.2, 56.5, 49.9, 48.7, 42.7, 42.6, 27.1, 25.5, 19.8, 19.7, 16.8.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{20}H_{26}O_3S]^+$ 369.1492, found 369.1495.



4aa

2-methyl-2-phenyl-3-(tosylmethyl)oxirane (4aa)

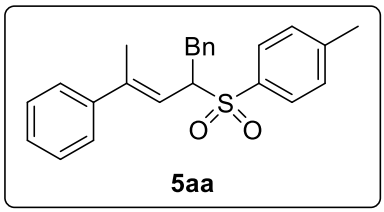
According to literature procedure[8], Fill a mixture of 3aa (0.1 mmol, 28.6 mg), m-

CPBA (0.2 mmol, 52.9 mg), $NaHCO_3$ (0.3 mmol, 25.2 mg), DCM (2 mL). Stir the resulting mixture at room temperature overnight. the product was purified through column chromatography on silica gel (petroleum ether/ethyl acetate, 100/0 to 5/1). **4aa** was obtained as white solid (25.7 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.39-6.99 (m, 7H), 3.53-3.29 (m, 2H), 3.14 (t, *J* = 6.0 Hz, 1H), 2.40 (s, 3H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.8, 135.2, 129.1, 127.4, 127.3, 126.8, 124.0, 59.45, 58.2, 55.5, 20.7, 16.9.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{18}O_3S]^+$ 325.0864, found 325.0869.



5aa

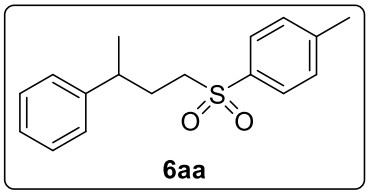
(*E*)-(2-tosylpent-3-ene-1,4-diyl)dibenzene (5aa)

According to literature procedure[9],**3aa** (57.2 mg, 0.2 mmol) was dissolved in 2 mL THF. The solution was cooling to -78 ^{o}C. ^{n}BuLi (1 equiv, 1.6 M in hexane, 0.2 mmol) was added to the mixture under N_2 atmosphere and stirred for 1 h. Benzyl bromide (34.2 mg, 0.2 mmol 1 equiv) was added to the mixture and the reaction was stirred at 0 °C for 2 h. The reaction was warmed to room temperature and quenched by 2 mL saturated NH_4Cl solution. After extraction with EtOAc, the organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent of the filtrate was removed under vacuum. The crude product was purified by flash column chromatography on silica gel with PE/EA to provide **5aa** as white solid (53.5 mg, 71% yield, *E/Z* > 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.71 (m, 2H), 7.32-7.11 (m, 12H), 5.63-5.48 (m, 1H), 4.18-4.03 (m, 1H), 3.76-3.57 (m, 1H), 3.04-2.87 (m, 1H), 2.43 (s, 3H), 1.26 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.0, 142.5, 137.0, 134.9, 129.6, 129.2, 129.2, 128.5, 128.3, 127.7, 126.8, 125.8, 119.8, 67.0, 34.1, 21.7, 16.1.

HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{24}H_{24}O_2S]^+$ 399.1389, found 399.1392.



6aa

1-methyl-4-((3-phenylbutyl)sulfonyl)benzene (6aa)

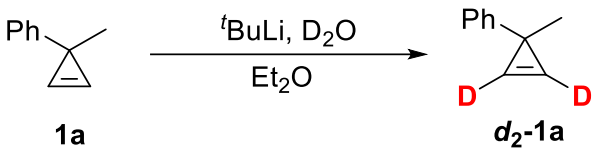
According to literature procedure[10], Fill a mixture of 3aa (0.1 mmol, 28.6 mg), 10 wt% Pd/C (0.01 mmol, 10.6 mg), methanol (3 mL) and ethyl acetate (1.5 mL) with a H_2 balloon. Stir the resulting mixture at room temperature overnight. Then, the reaction mixture was filtered, and concentrated under vacuum to afford 6aa as white solid (25.7 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 2H), 7.29-7.10 (m, 5H), 7.02-6.97 (m, 2H), 2.98-2.74 (m, 2H), 2.71-2.60 (m, 1H), 2.37 (s, 3H), 2.03-1.77 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 3H).

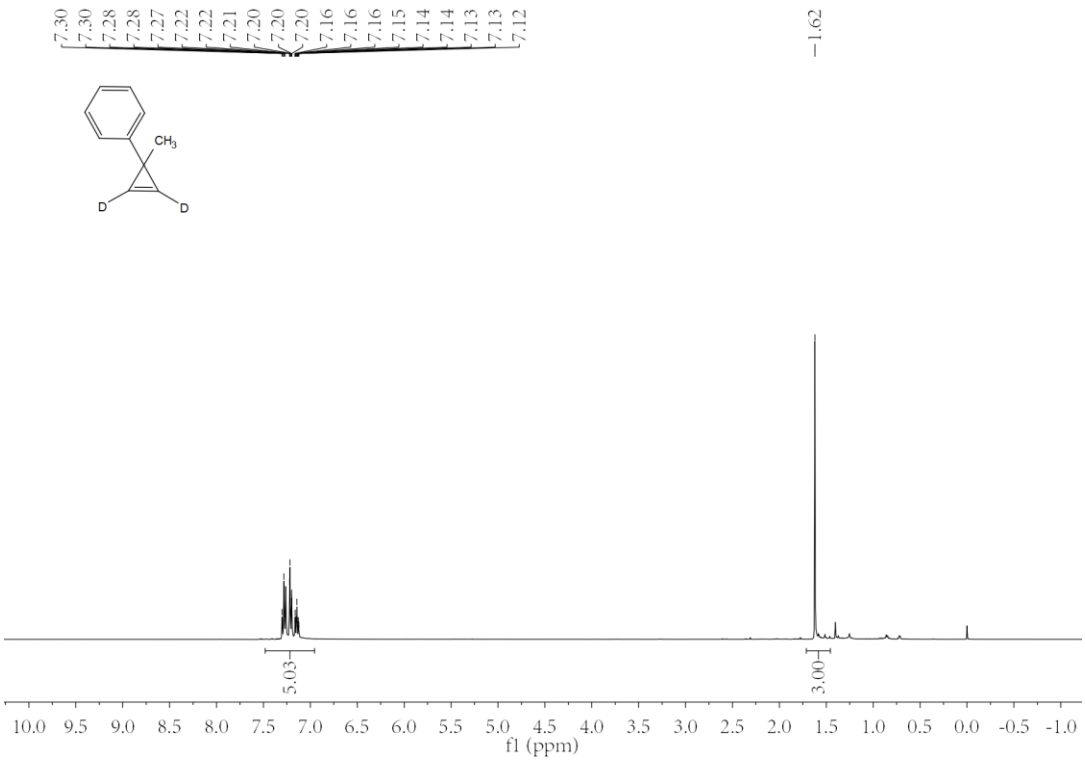
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 143.6, 135.1, 128.8, 127.7, 127.0, 125.8, 125.6, 53.7, 37.8, 29.5, 21.3, 20.6.

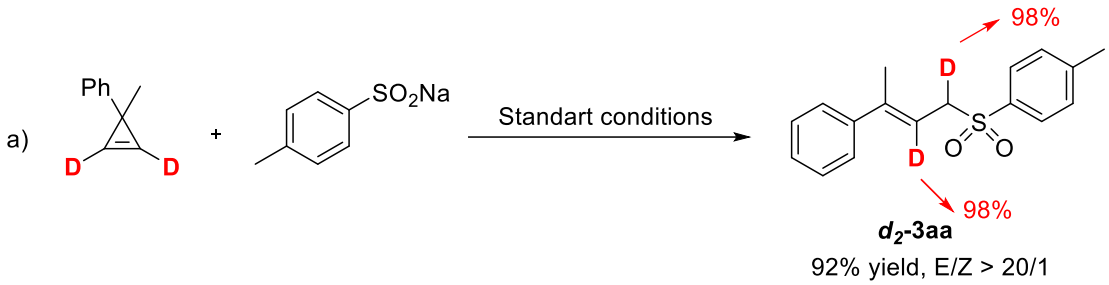
HRMS-ESI (m/z): $[M+Na]^+$ calcd for $[C_{17}H_{20}O_2S]^+$ 311.1076, found 311.1079.

6. Deuterium Reactions

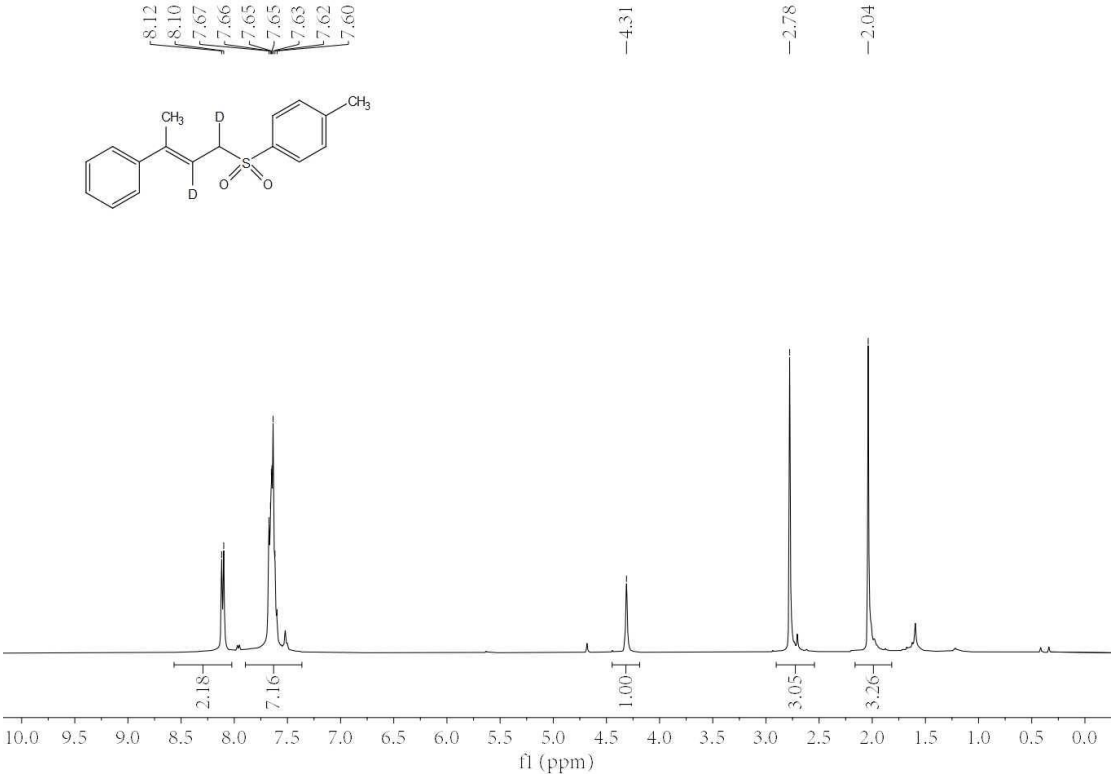


The substrate ***d*₂-1a** was synthesized based on the reported literature.[11] To a stirring solution of cyclopropene **1a** (258 mg, 1.98 mmol, 1.0 equiv.) in dry Et_2O (7 mL) at -78 °C was added dropwise a solution of ^{t}BuLi (2.91 mL of 1.7M solution in Pentane, 4.95 mmol, 2.5 equiv.). The yellow solution was stirred for 30 min at -78 °C and 30 min at 0 °C, where it turned deep red. The mixture was again cooled to -78 °C and was quenched with dry CD_3OD (402 µL, 9.90 mmol, 5.0 equiv.), which led to complete discoloration. The reaction was warmed to room temperature, diluted with D_2O (5 mL) and extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with water (5 mL), brine (5 mL), dried with $MgSO_4$, filtered and concentrated under vacuum. Purification by flash chromatography (Eluent: Pentane) afforded ***d*₂-1a** as a colorless liquid (155 mg, 59% yield, 98.5% D). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48-6.95 (m, 5H), 1.62 (s, 3H).



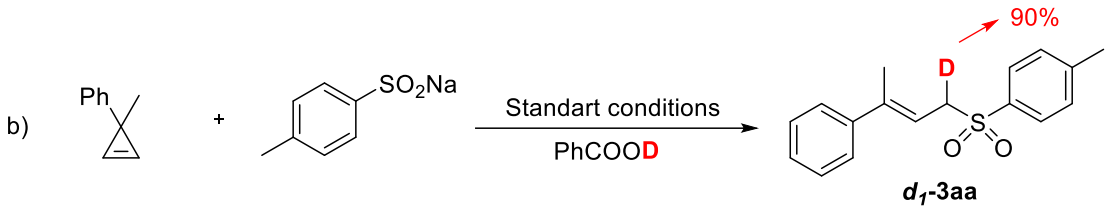


^{1}H NMR of ***d*$_2$-3aa** (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.9 Hz, 2H), 7.90-7.36 (m, 7H), 4.31 (s, 1H), 2.78 (s, 3H), 2.04 (s, 3H).

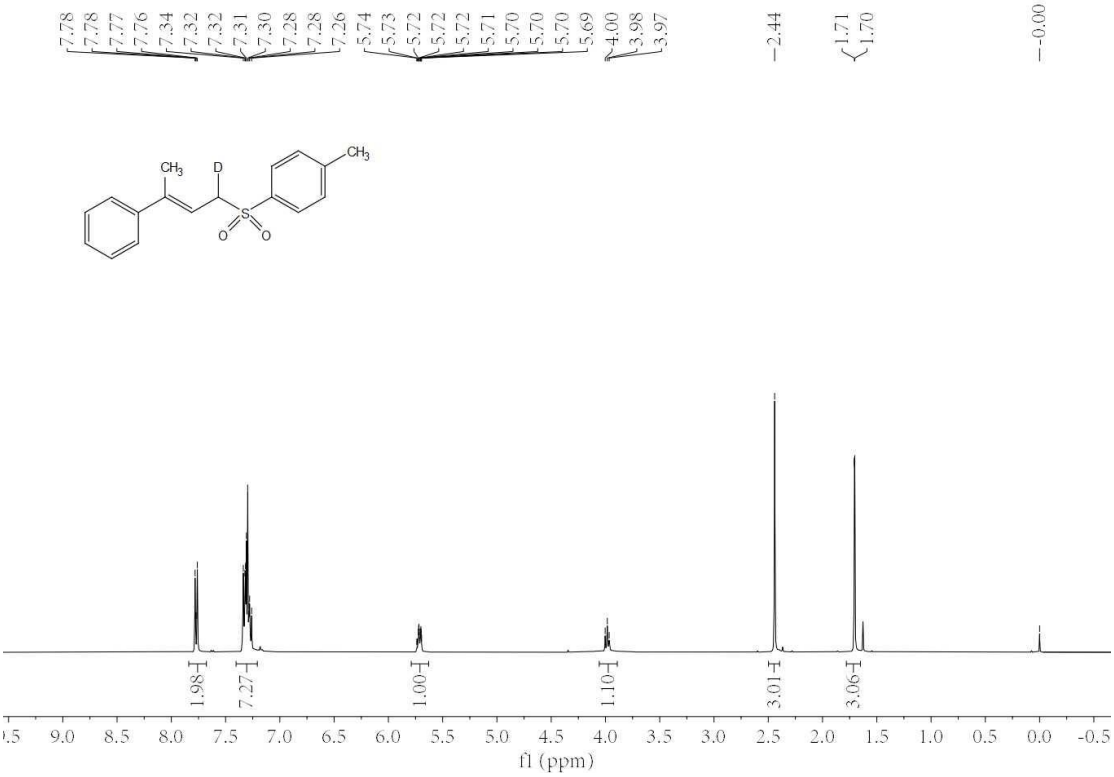
b)



***d*$_1$-3aa**

90% yield, E/Z > 20/1

^{1}H NMR of ***d*$_1$-3aa** (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.40-7.21 (m, 7H), 5.79-5.63 (m, 1H), 3.98 (t, *J* = 7.4 Hz, 1H), 2.44 (s, 3H), 1.70 (d, *J* = 1.4 Hz, 3H).

7. Proposed Mechanism

The proposed mechanism is shown in Figure S1 based on the results presented above and previous studies[12]. The reaction initiates with Pd(0) species, which undergoes oxidative addition with PhCOOH to give an intermediate **II**. Intermediate **II** subsequently undergoes ligand exchange with R-SO_2Na **2** to give Pd(II) species **III**. The palladium cyclopropane complex **IV** was gave by hydropalladation of cyclopropene **1** with species **III**. This pivotal intermediate **IV** undergoes β-carbon elimination, it forms the ring-opening π-allylpalladium intermediate **V**. The lone pair of electrons on the sulfur atom attacks π-allylpalladium complexes provides the target product **3** and regenerates the Pd catalyst.

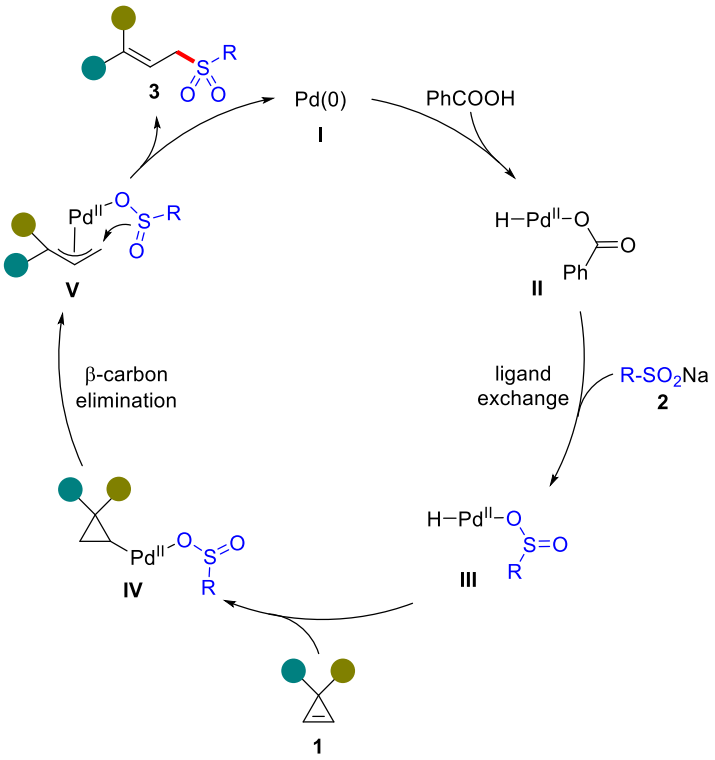
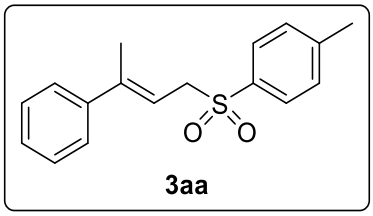


Figure S1 Proposed Mechanism

8. X-ray Structure of Compound 3aa



Single crystal of **3aa** (CCDC 2405802) was obtained by recrystallization from ethyl acetate. X-ray crystallographic data were collected using a Bruker APEX-II CCD diffractometer, equipped with a sealed tube Cu-Kα radiation (λ=1.54178 Å) at low temperature or at ambient temperature under liquid N_2 flow. The crystal structure was solved with the Superflip, structure solution program using Charge Flipping and refined by direct methods using SHELXL-2018/3 and with full−matrix least squares on F^2 using SHELXL-2018/3. All the non−hydrogen atoms were refined anisotropically.

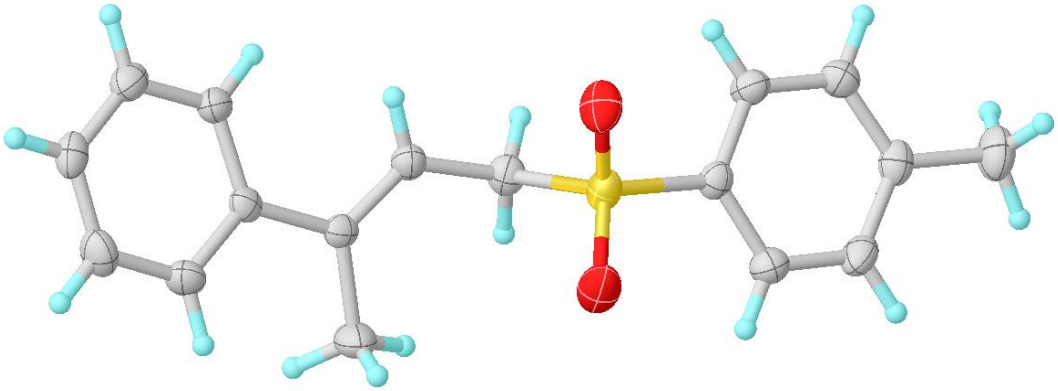


Table S1 Crystal data and structure refinement for 3aa.

Identification code	mo240831b
Empirical formula	$C_{17}H_{18}O_2S$
Formula weight	286.37
Temperature/K	304.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.6166(2)
b/Å	7.9642(3)
c/Å	33.1774(9)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	1484.08(9)
Z	4
ρ_{calc}g/cm^3	1.282
μ/mm^{-1}	0.217
F(000)	608.0
Crystal size/mm^3	0.1 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.094 to 61.046
Index ranges	-8 ⩽ h ⩽ 7, -9 ⩽ k ⩽ 11, -47 ⩽ l ⩽ 33
Reflections collected	21439
Independent reflections	4411 [R_{int} = 0.0668, R_{sigma} = 0.0567]
Data/restraints/parameters	4411/0/183
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1318
Final R indexes [all data]	R_1 = 0.0853, wR_2 = 0.1434
Largest diff. peak/hole / e Å^{-3}	0.40/-0.23
Flack parameter	0.06(4)

9. References

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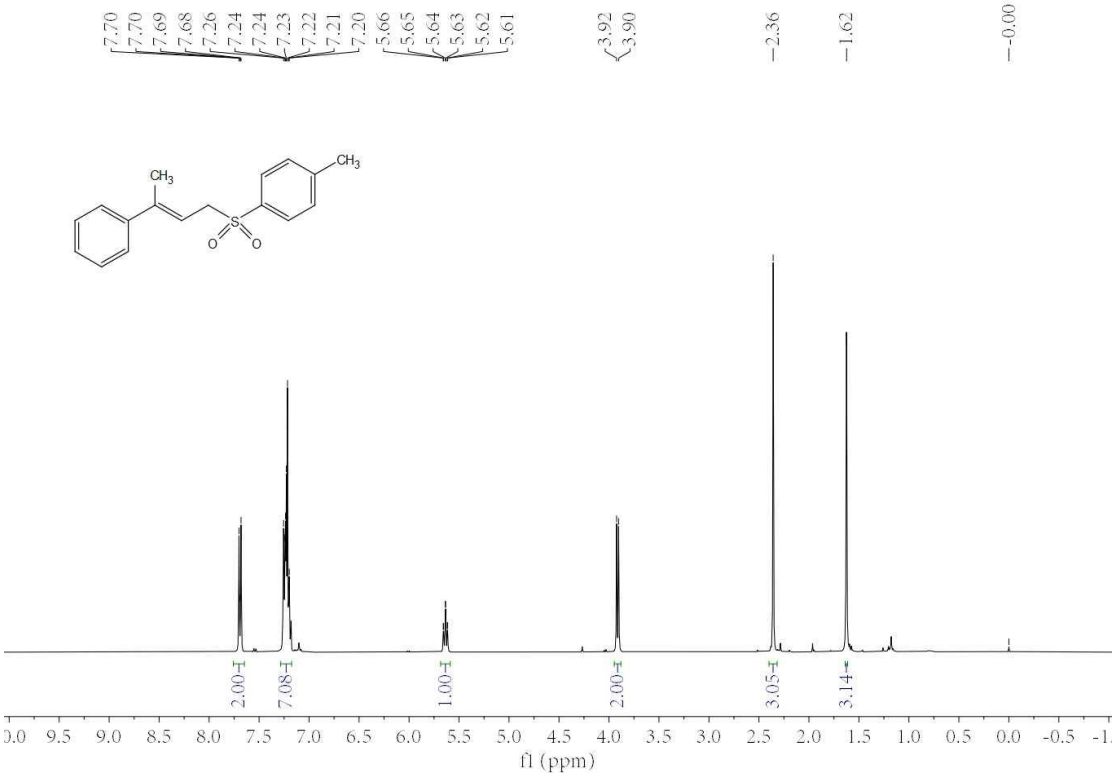
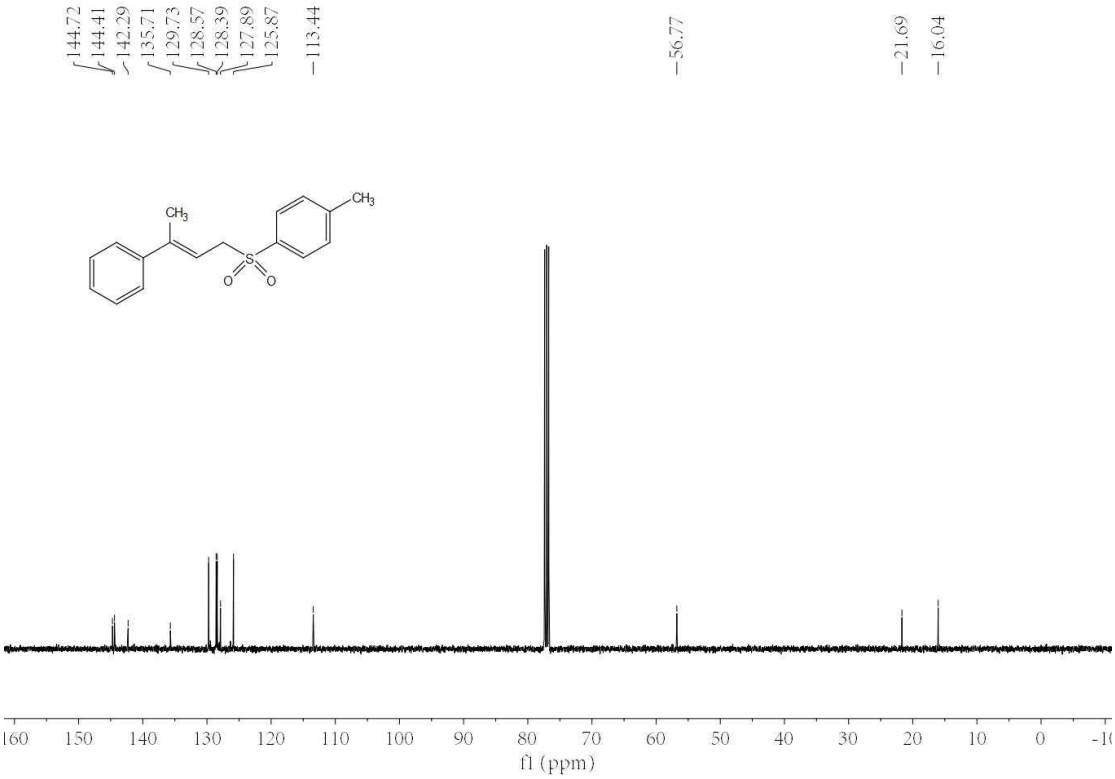
10. NMR Spectra

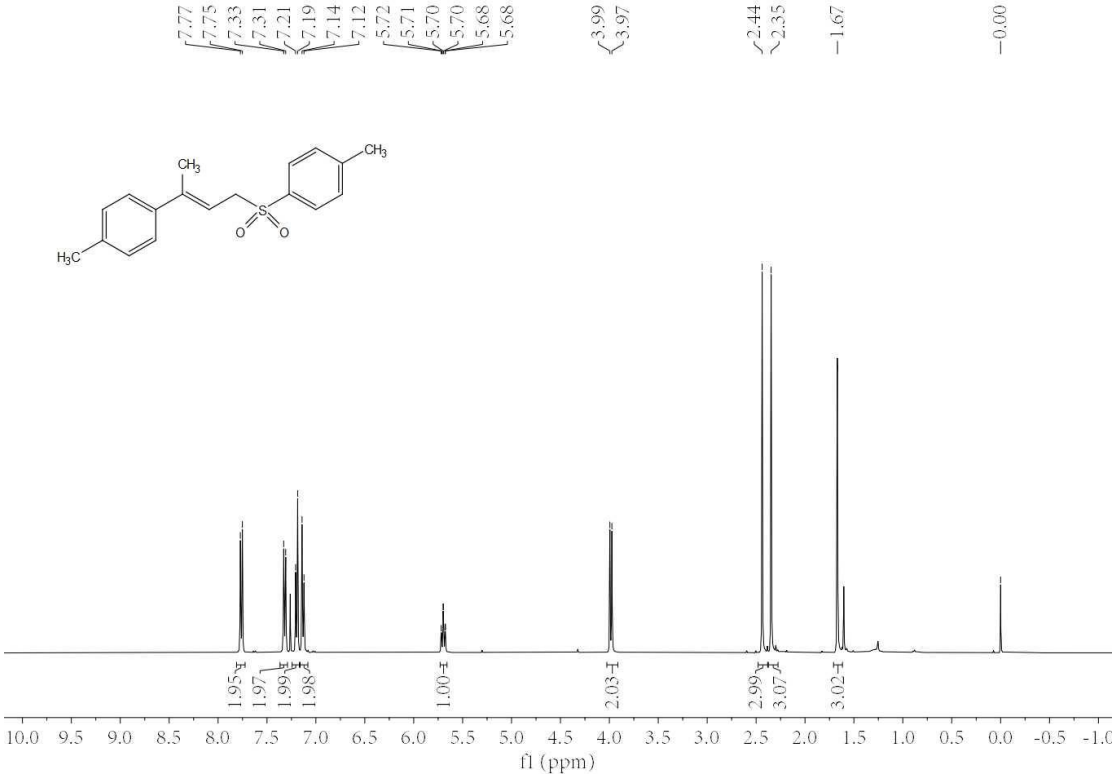
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



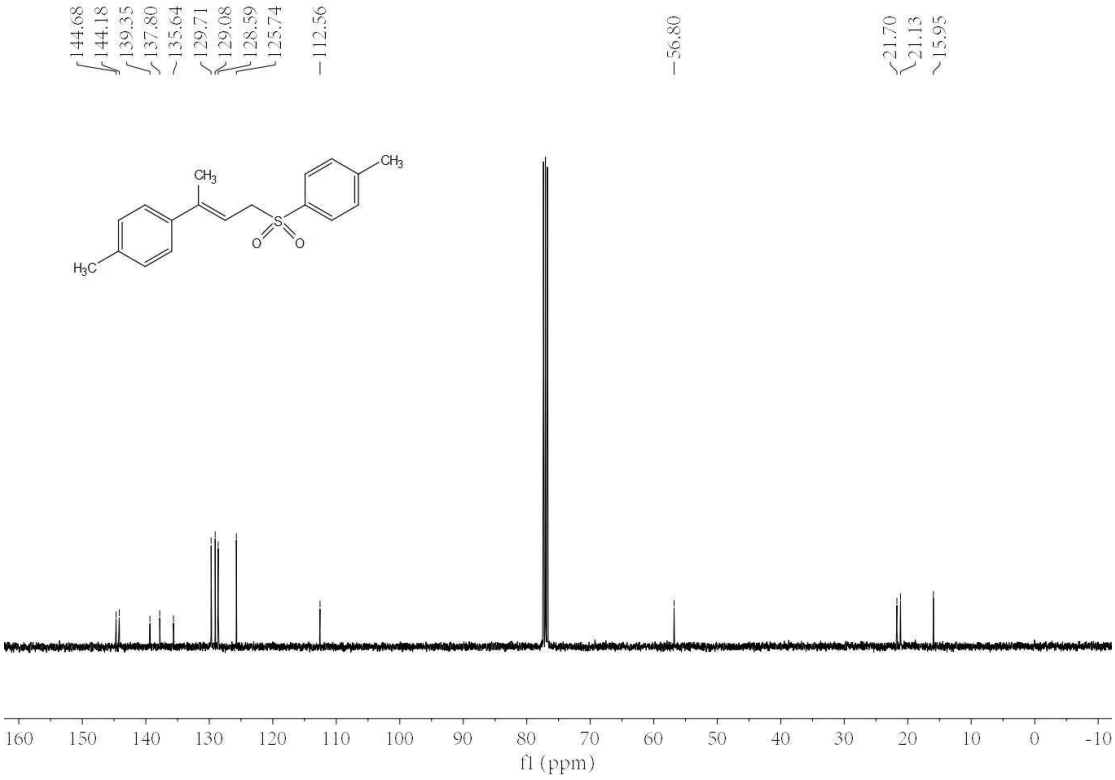
^{13}C NMR of **3aa** (100 MHz, $CDCl_3$)



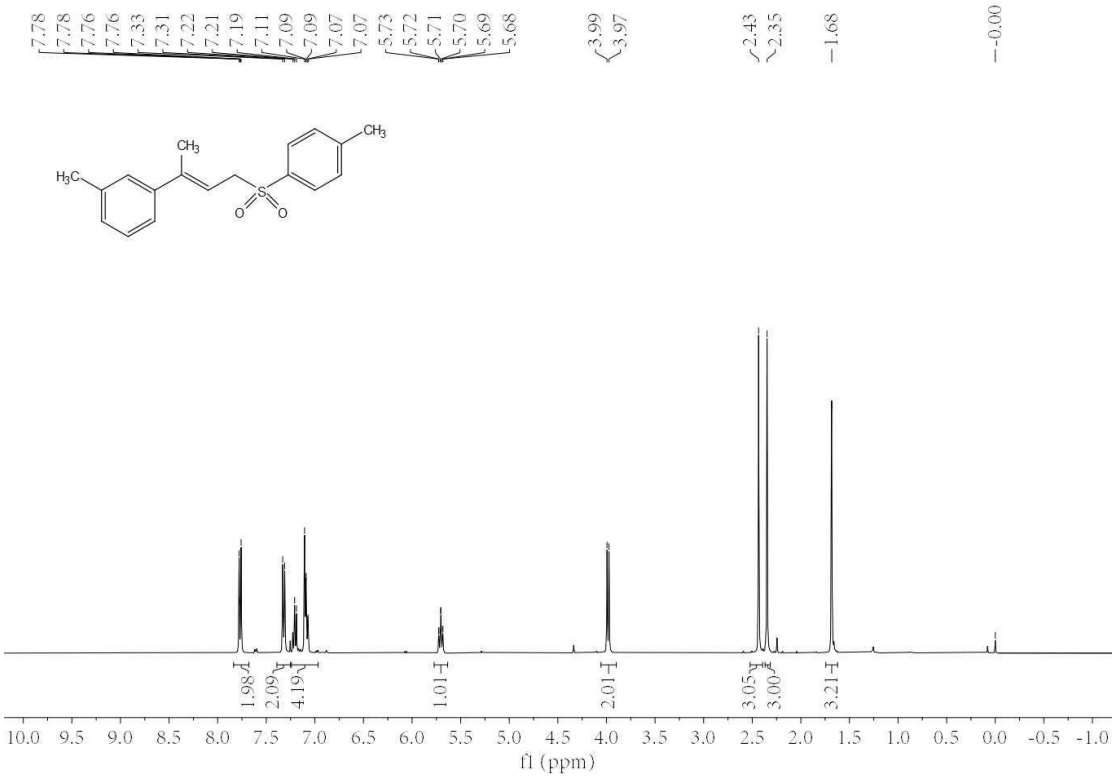
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



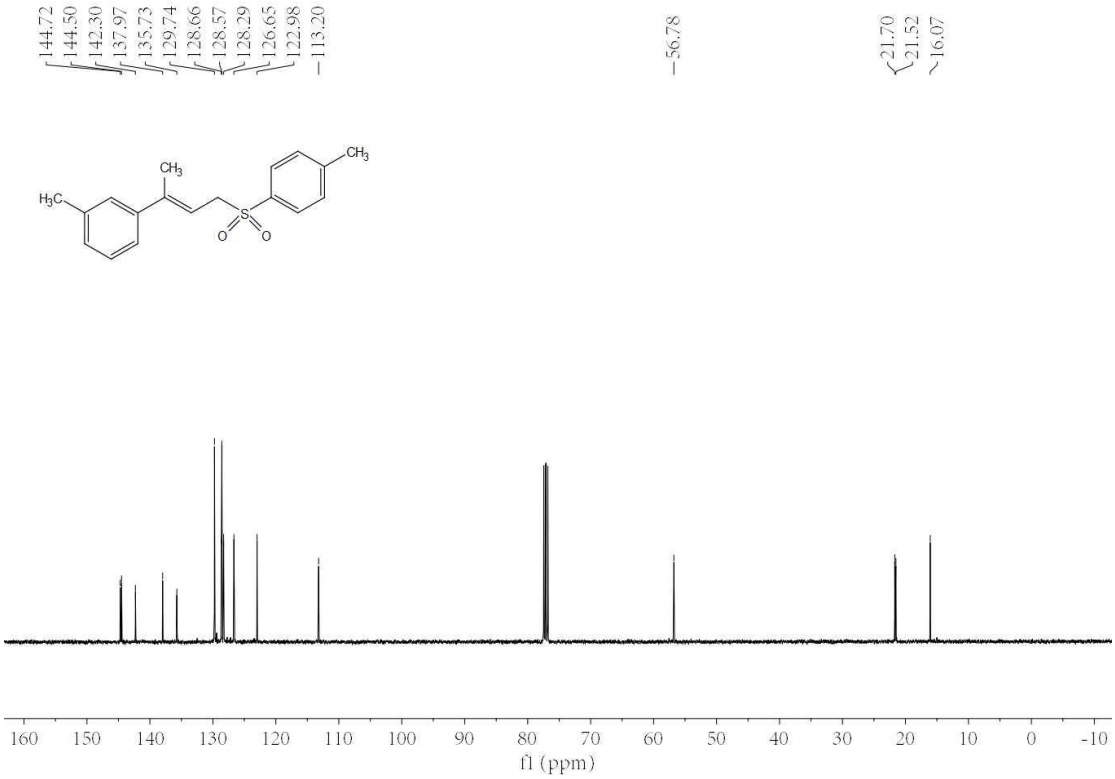
^{13}C NMR of **3ab** (100 MHz, $CDCl_3$)



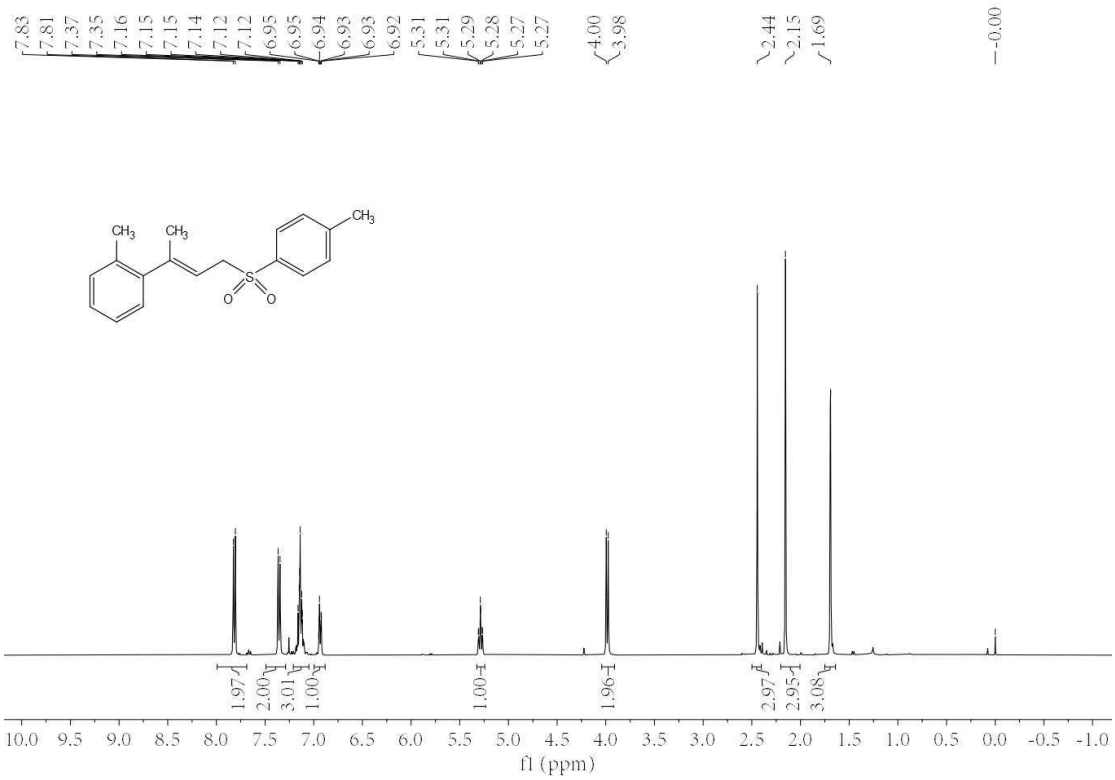
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



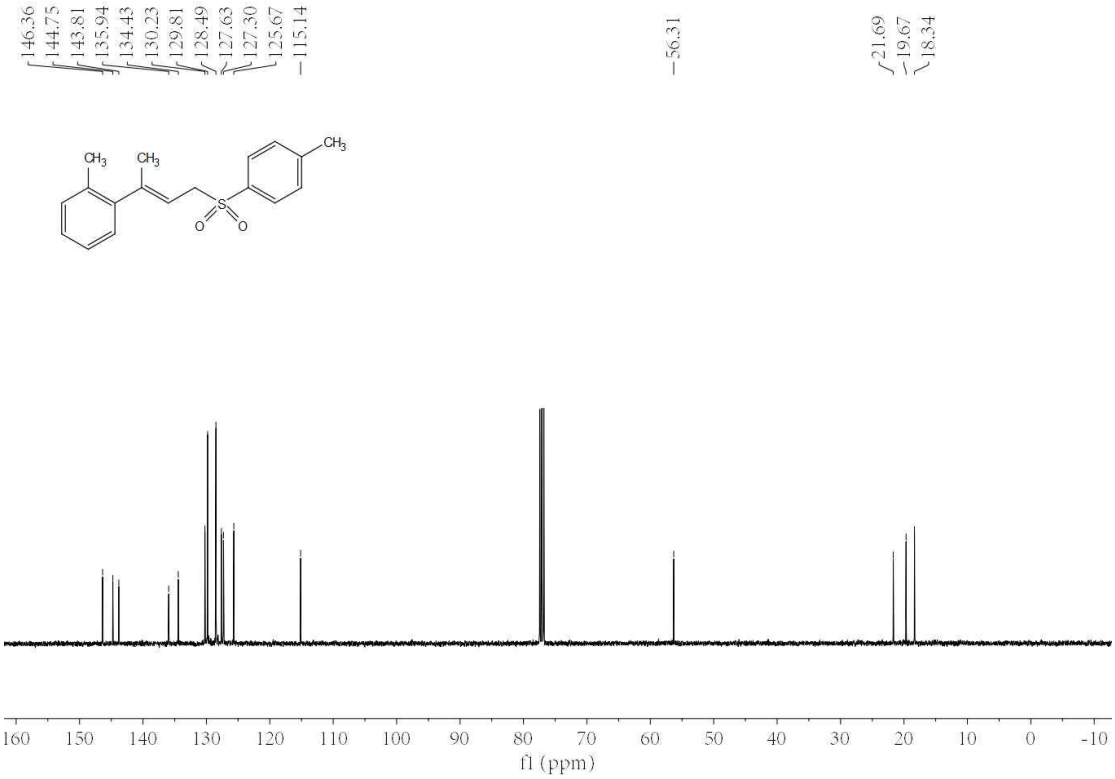
^{13}C NMR of **3ac** (100 MHz, $CDCl_3$)



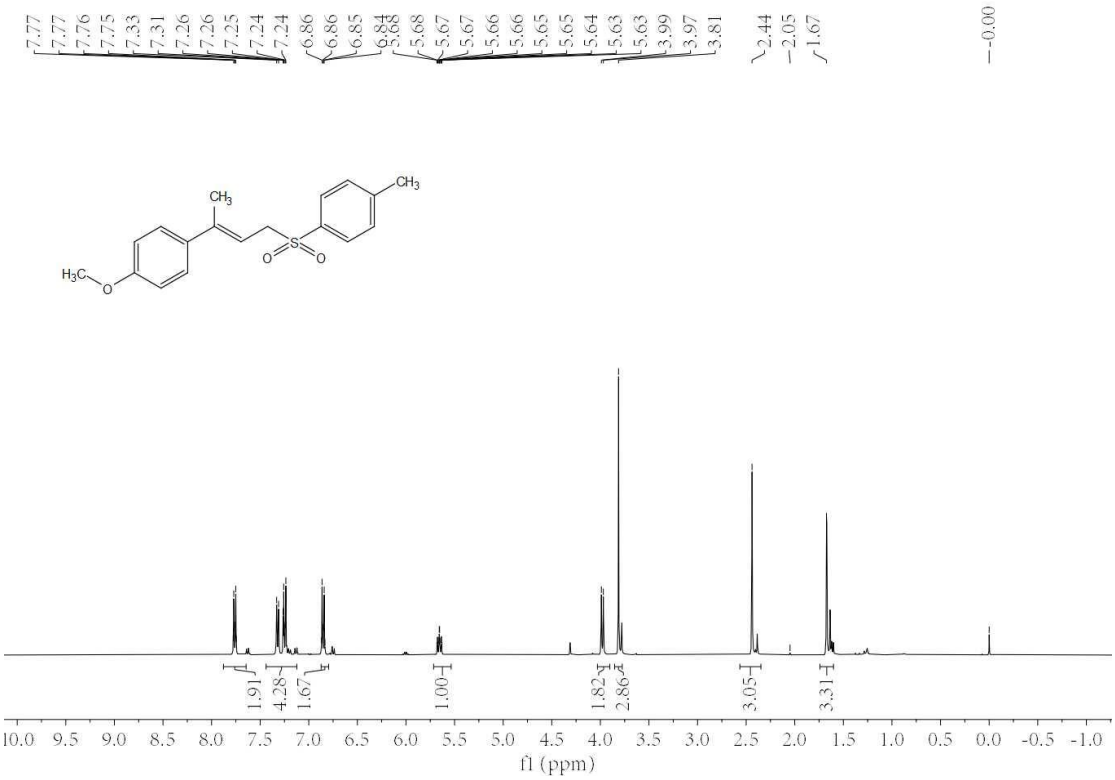
^{1}H NMR of **3ad** (400 MHz, $CDCl_3$)



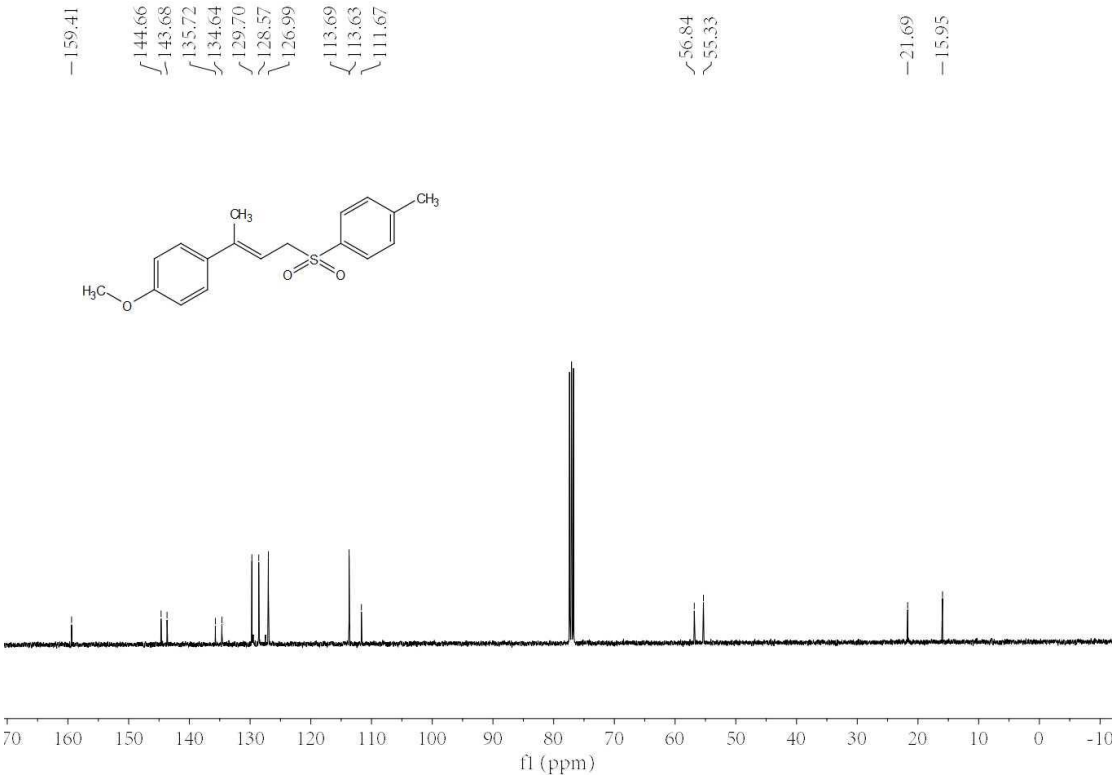
^{13}C NMR of **3ad** (100 MHz, $CDCl_3$)



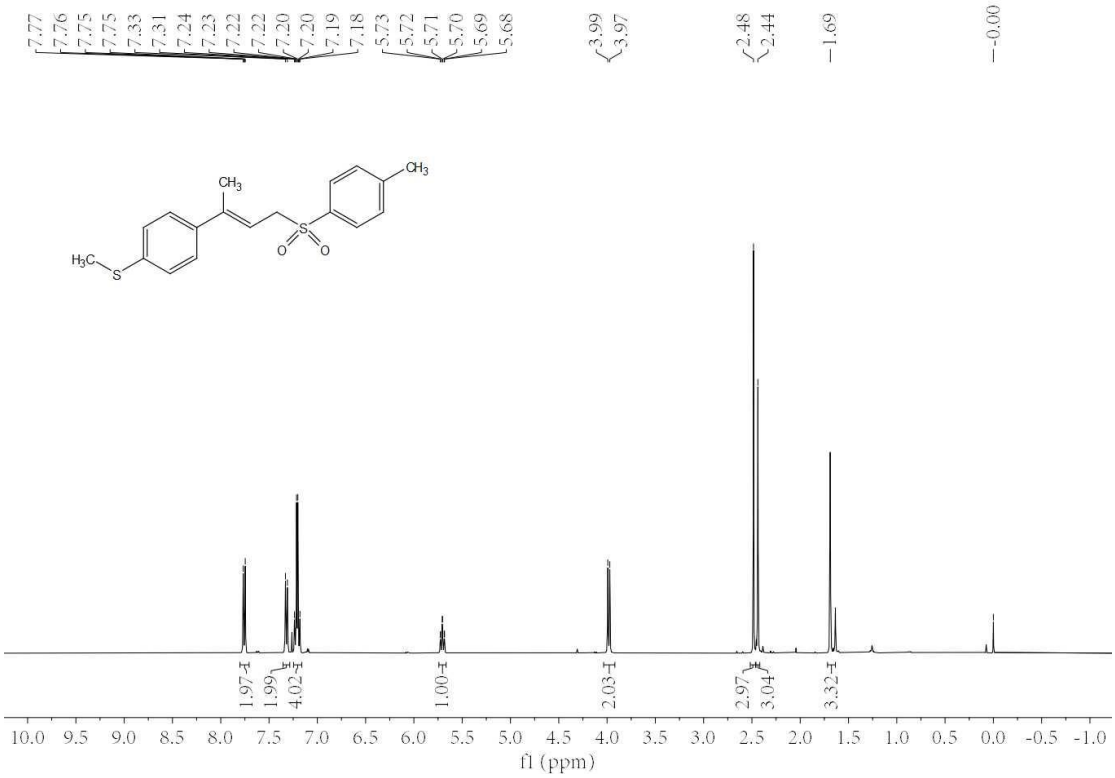
^{1}H NMR of 3ae (400 MHz, $CDCl_3$)



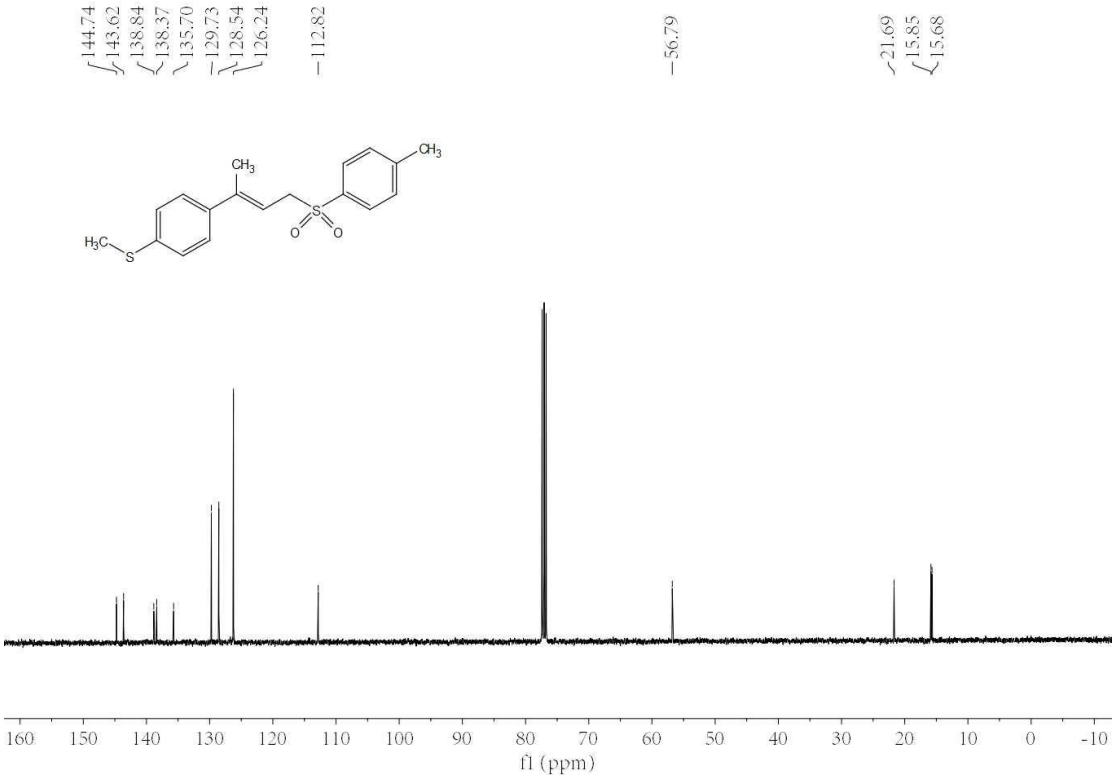
^{13}C NMR of **3ae** (100 MHz, $CDCl_3$)



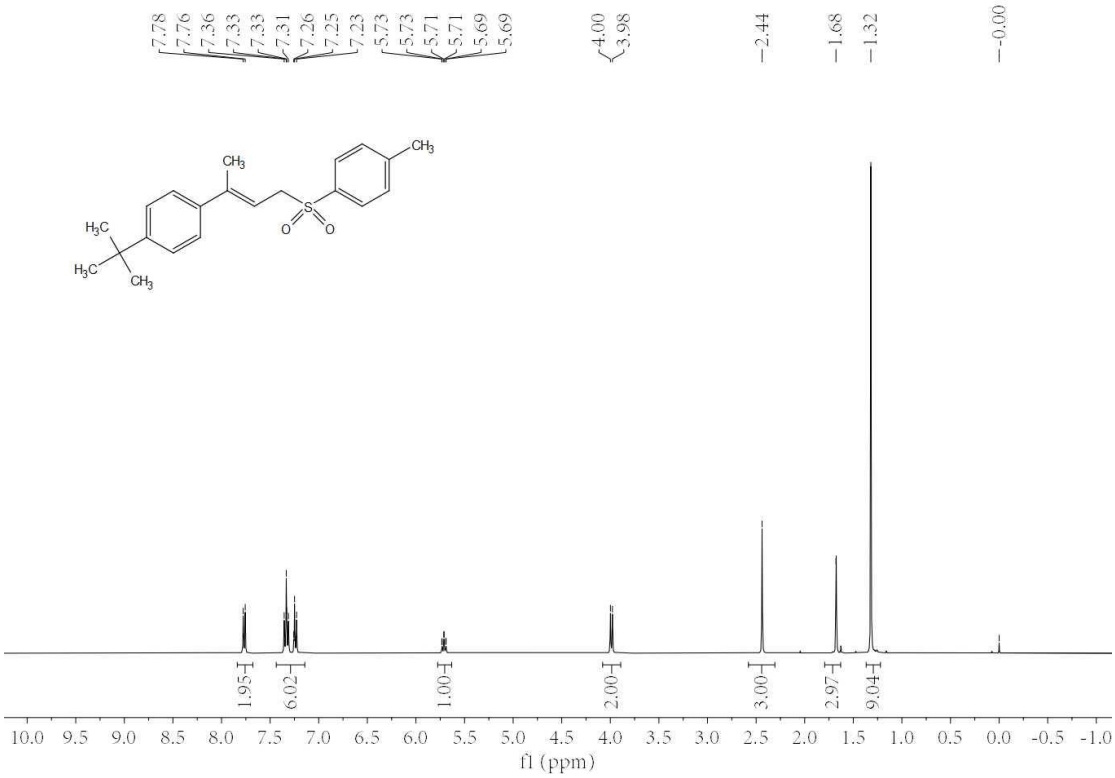
^{1}H NMR of **3af** (400 MHz, $CDCl_3$)



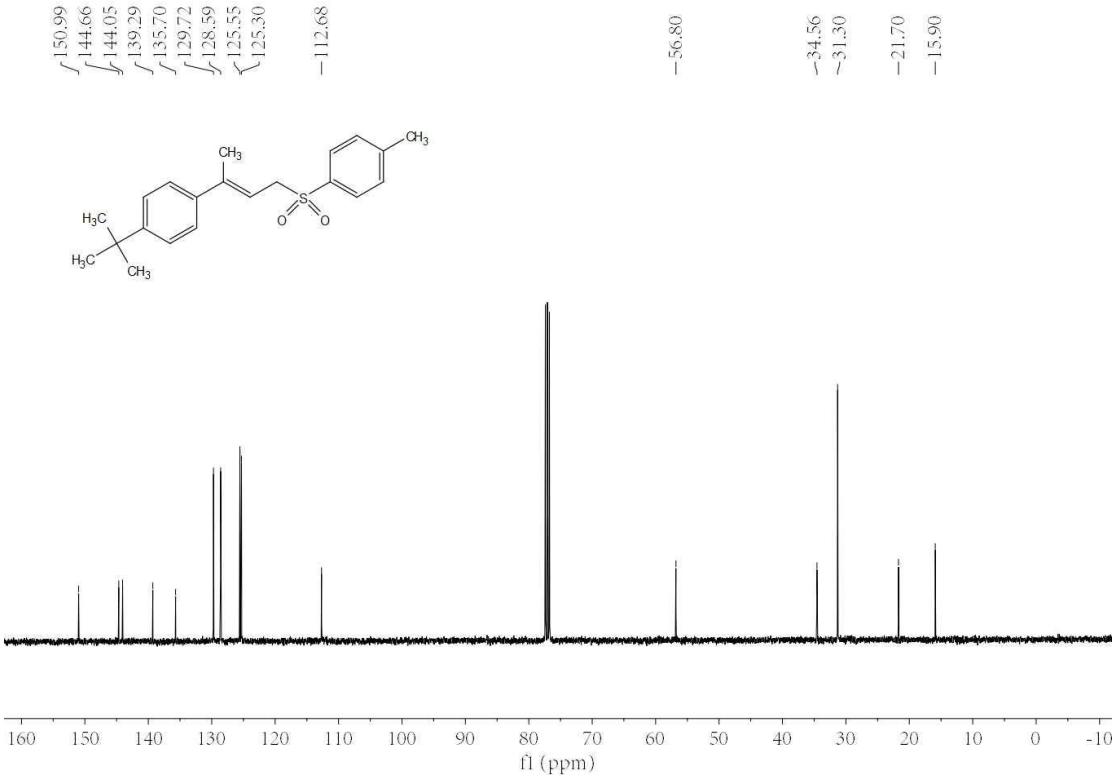
^{13}C NMR of **3af** (100 MHz, $CDCl_3$)



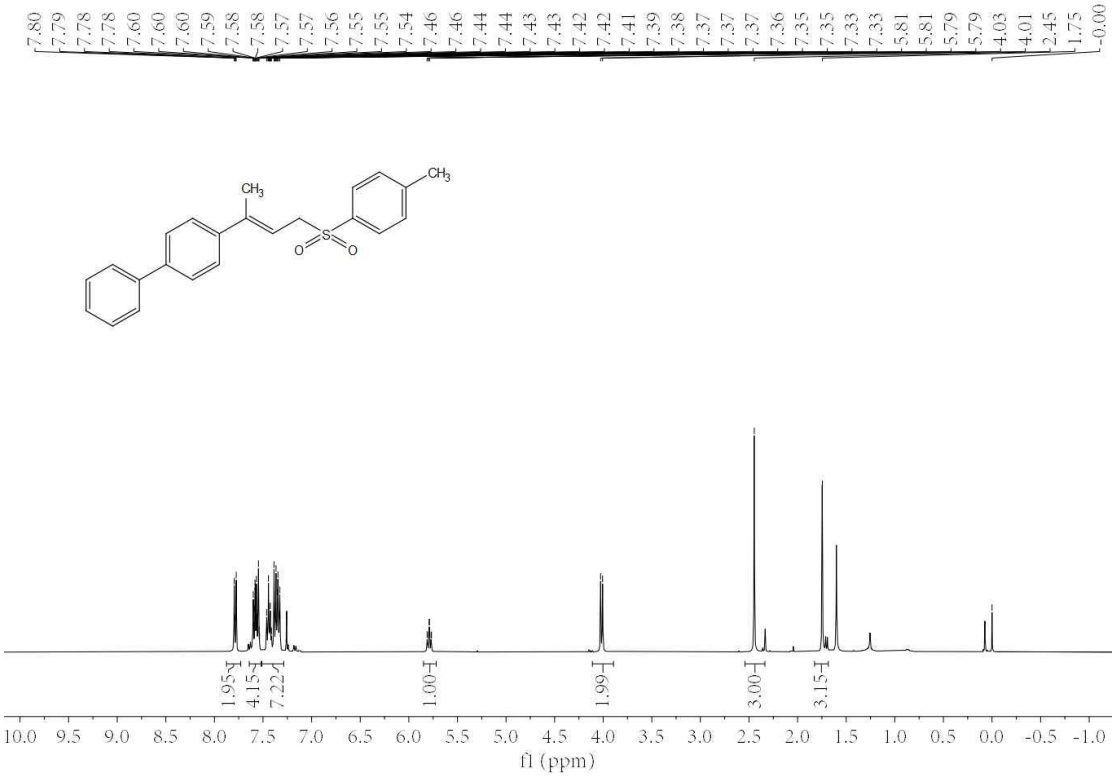
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$)



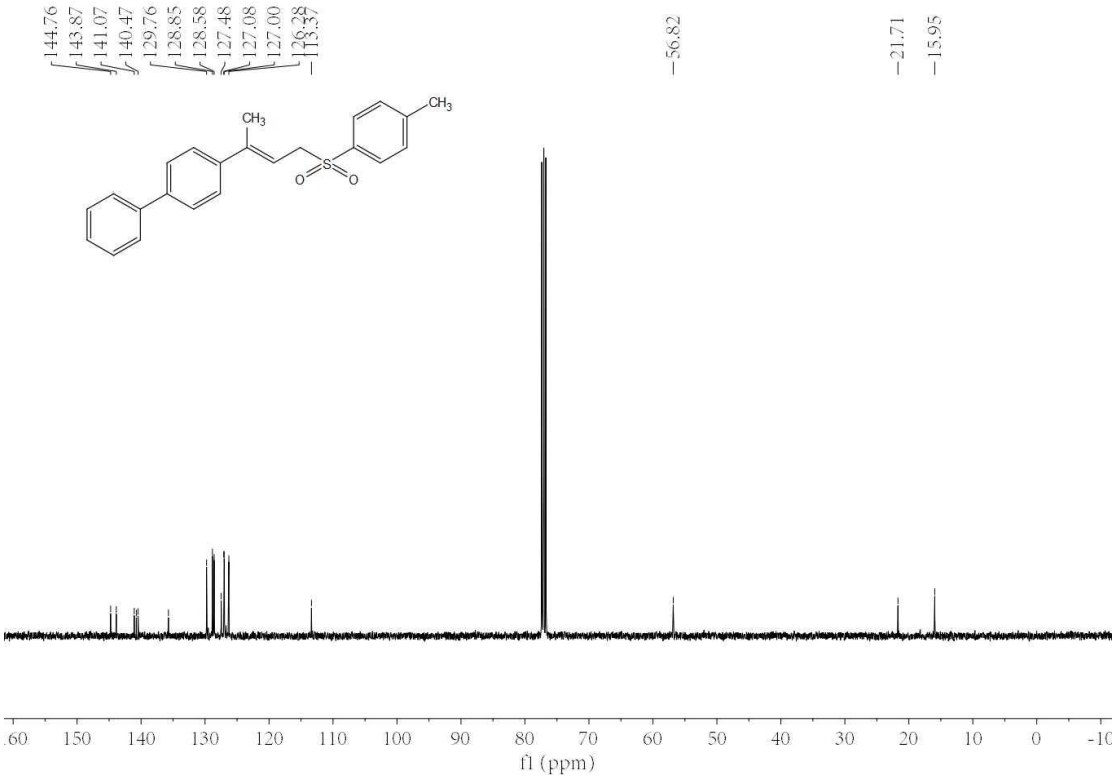
^{13}C NMR of **3ag** (100 MHz, $CDCl_3$)



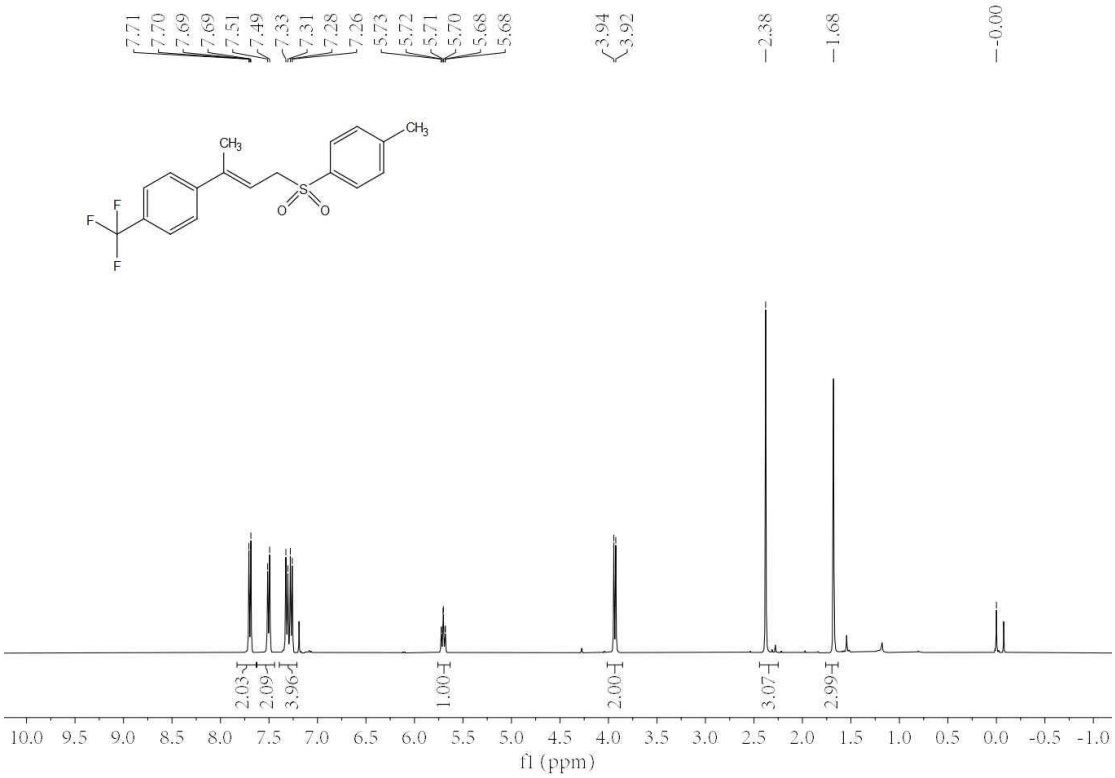
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



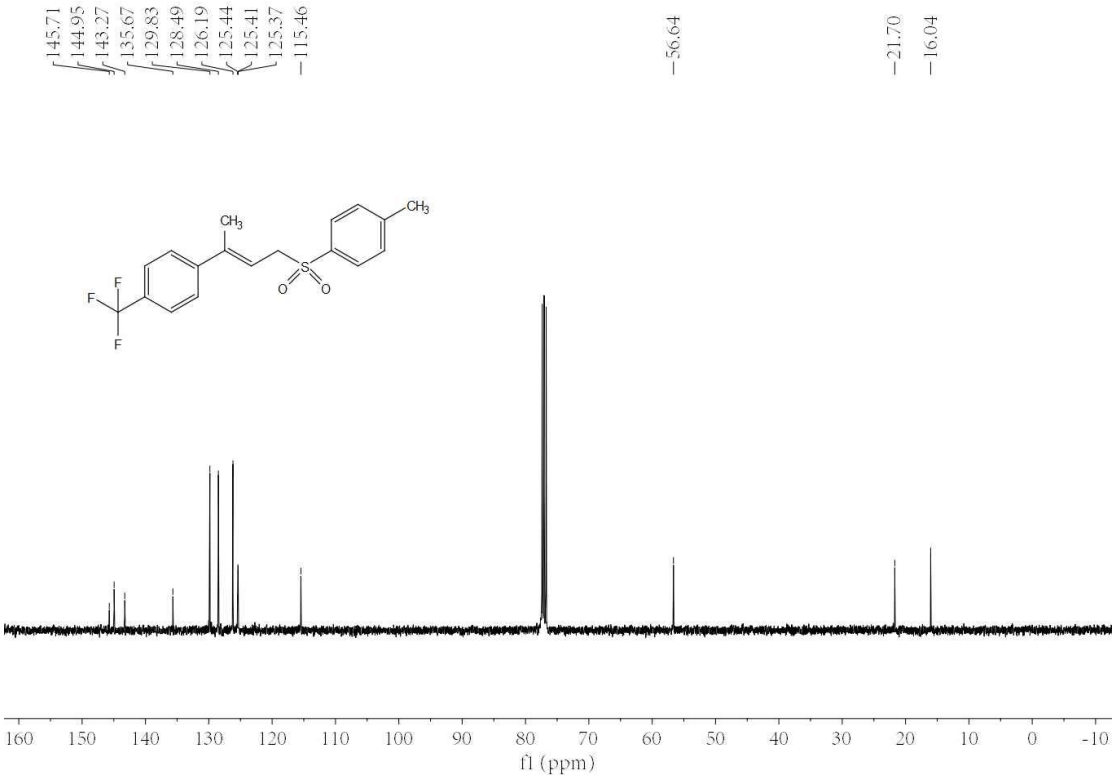
^{13}C NMR of **3ah** (100 MHz, $CDCl_3$)



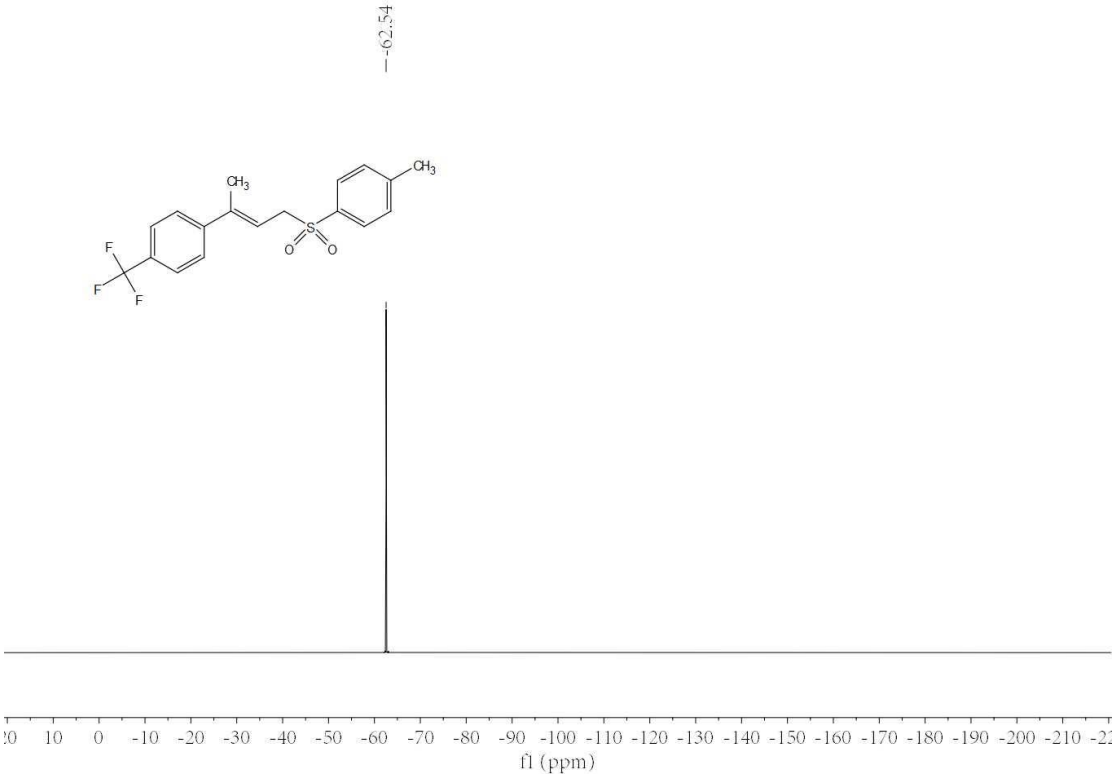
^{1}H NMR of **3ai** (400 MHz, $CDCl_3$)



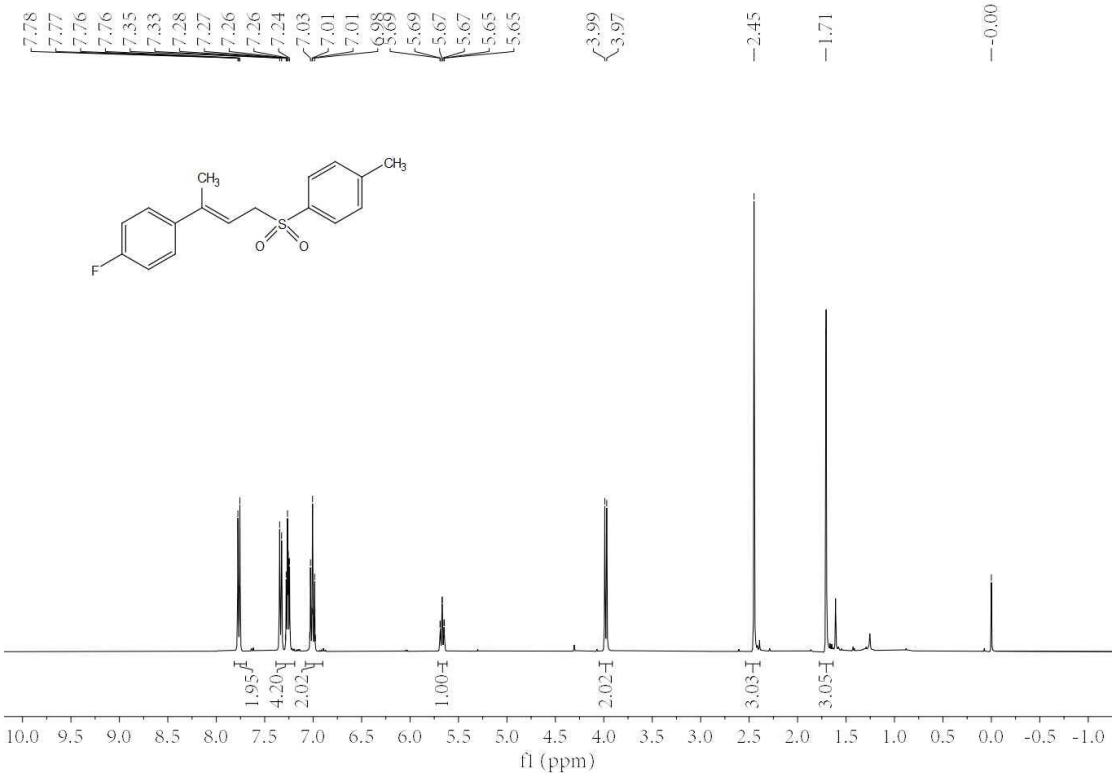
^{13}C NMR of **3ai** (100 MHz, $CDCl_3$)



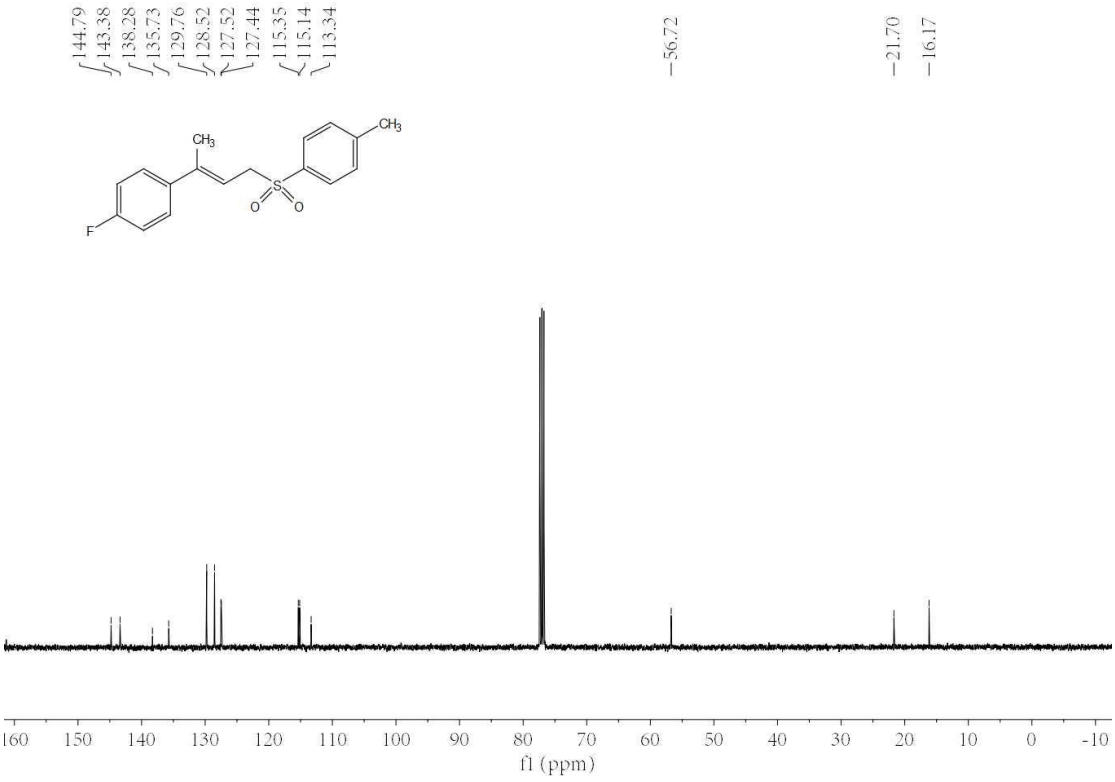
^{19}F NMR of **3ai** (471 MHz, $CDCl_3$)



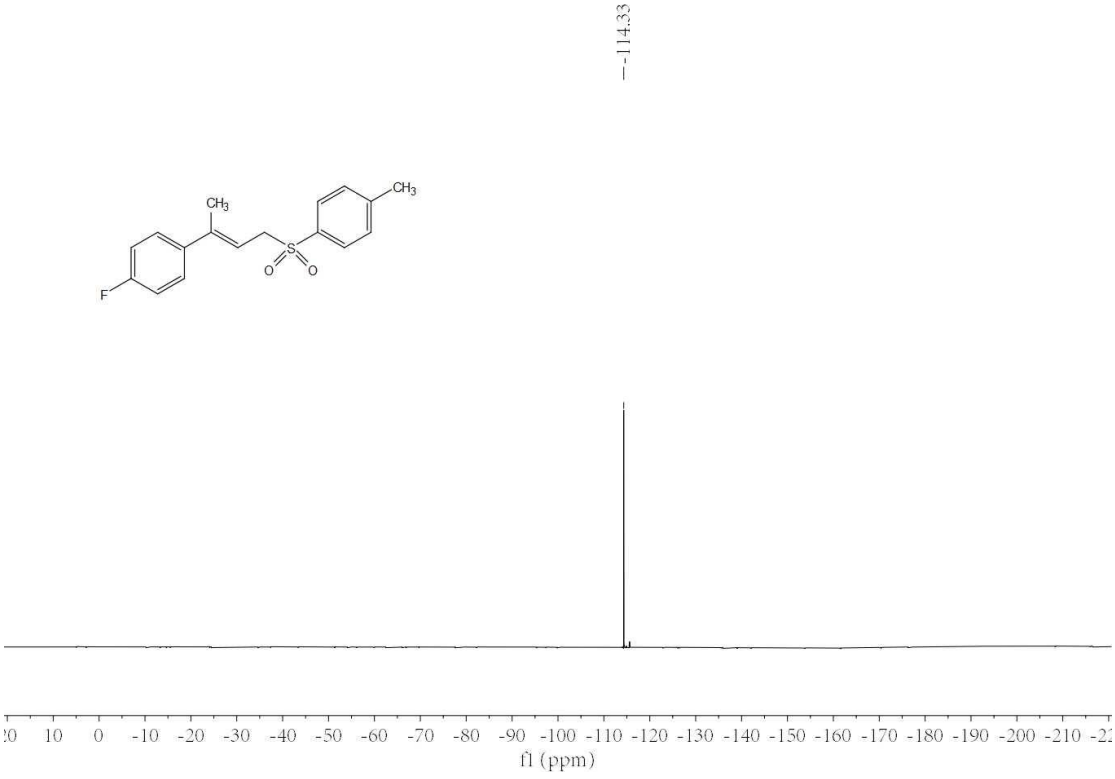
^{1}H NMR of **3aj** (400 MHz, $CDCl_3$)



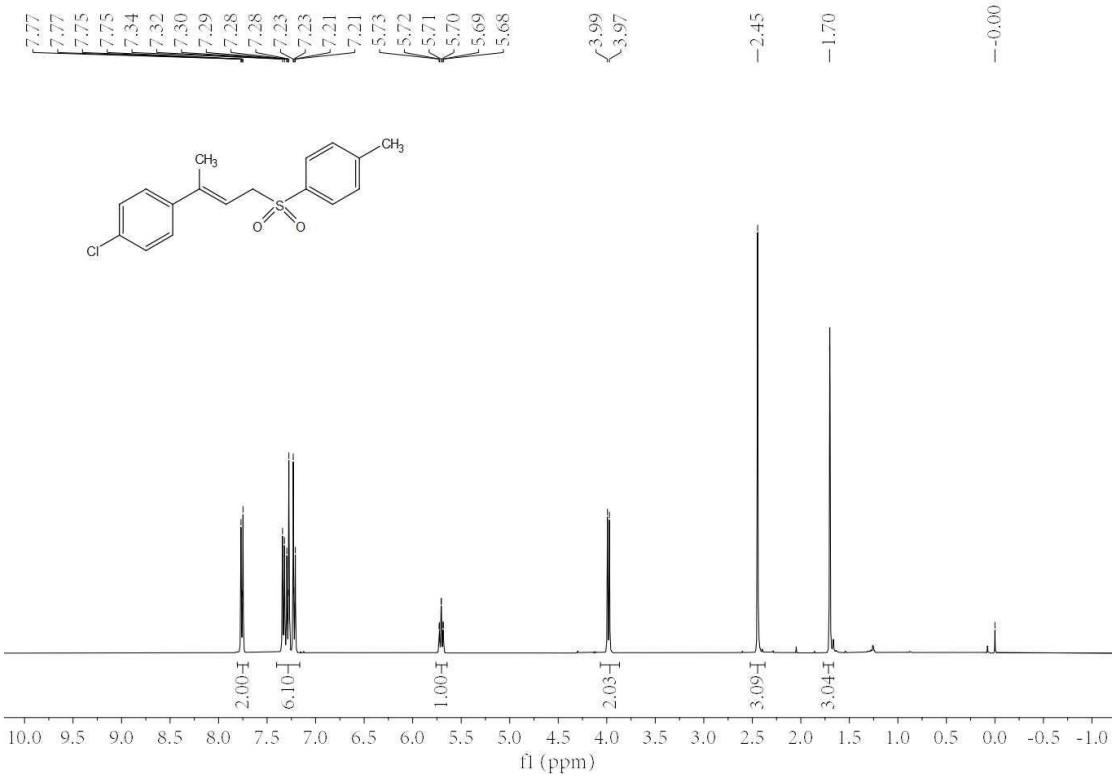
^{13}C NMR of **3aj** (100 MHz, $CDCl_3$)



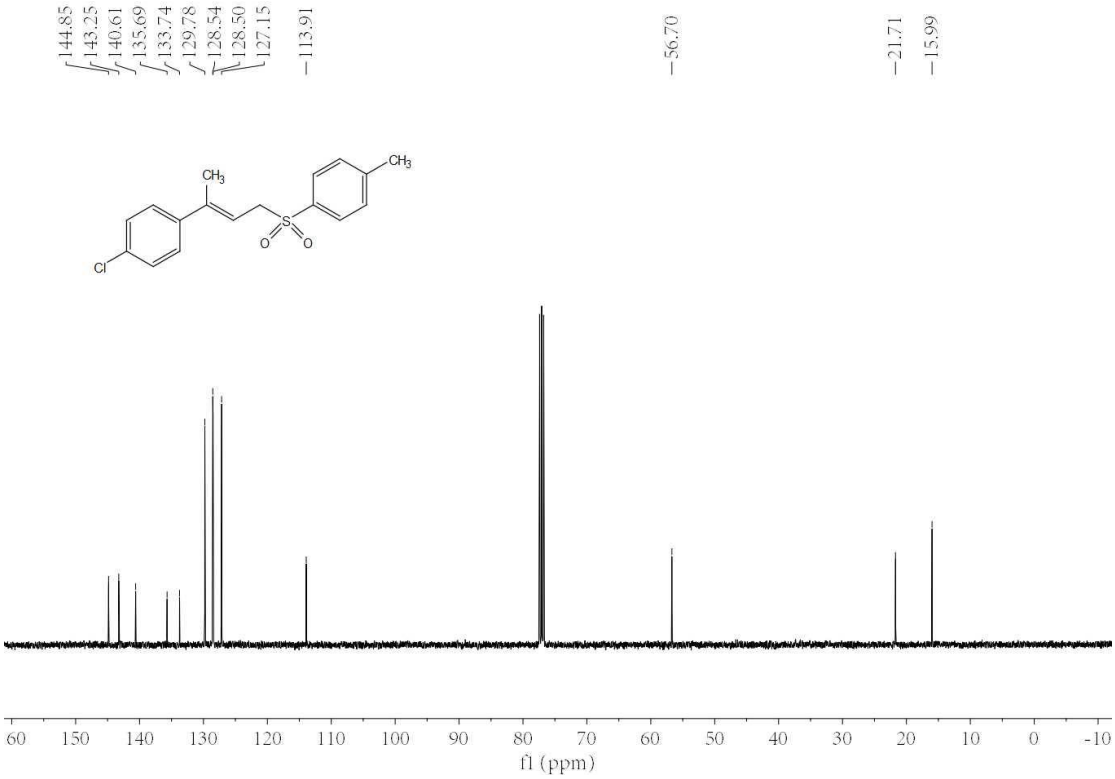
^{19}F NMR of **3aj** (471 MHz, $CDCl_3$)



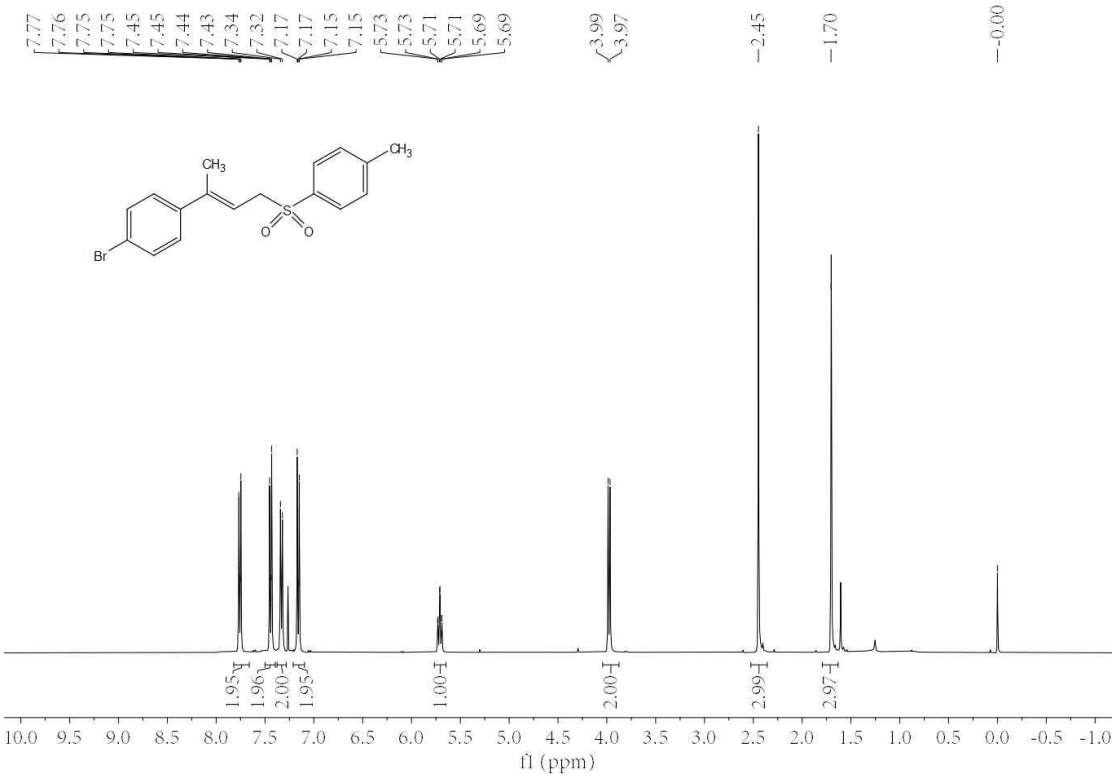
^{1}H NMR of **3ak** (400 MHz, $CDCl_3$)



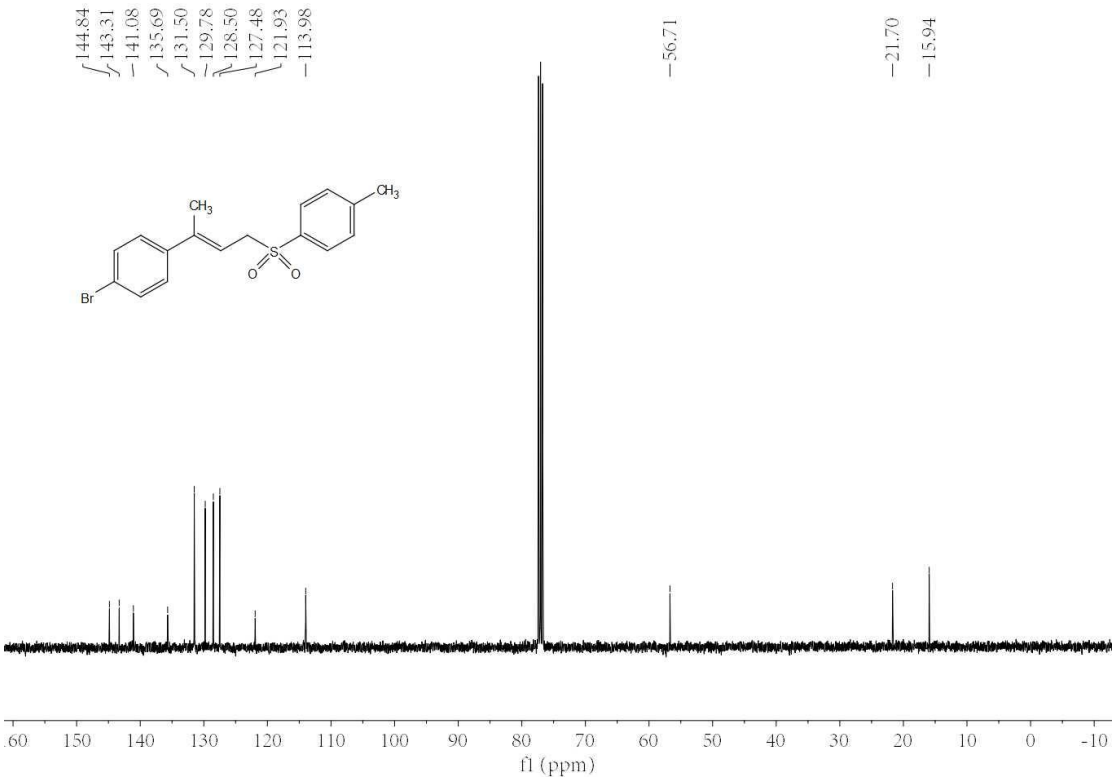
^{13}C NMR of **3ak** (100 MHz, $CDCl_3$)



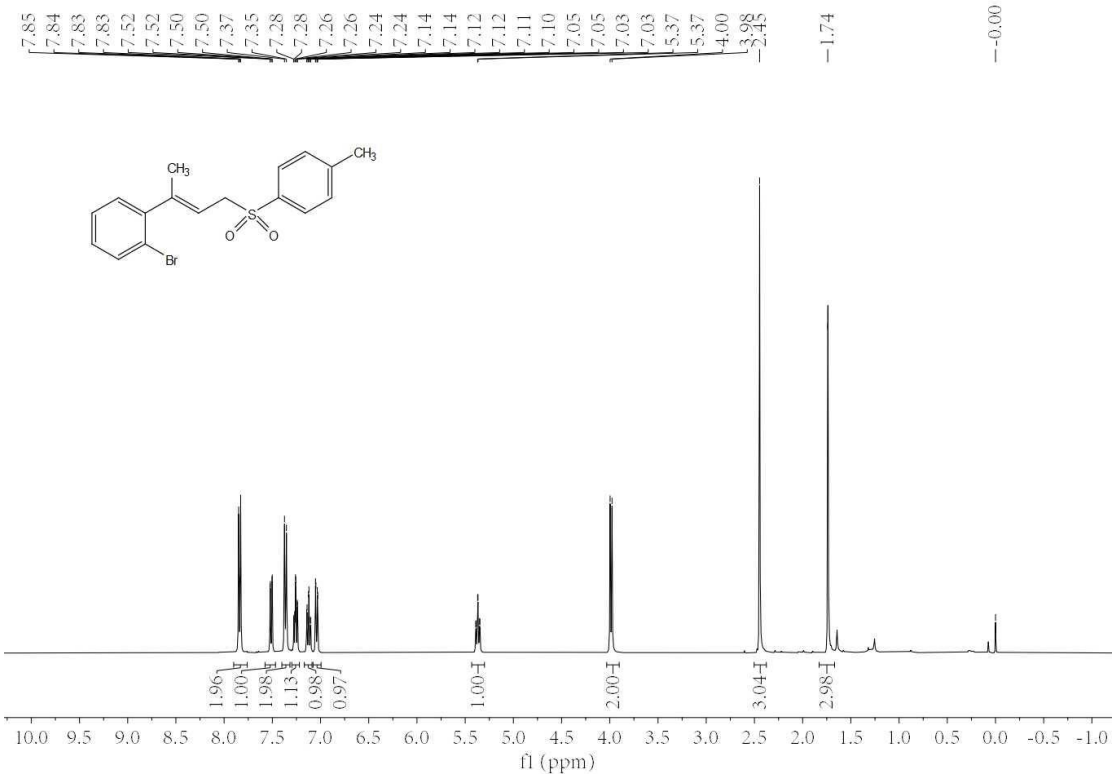
^{1}H NMR of **3al** (400 MHz, $CDCl_3$)



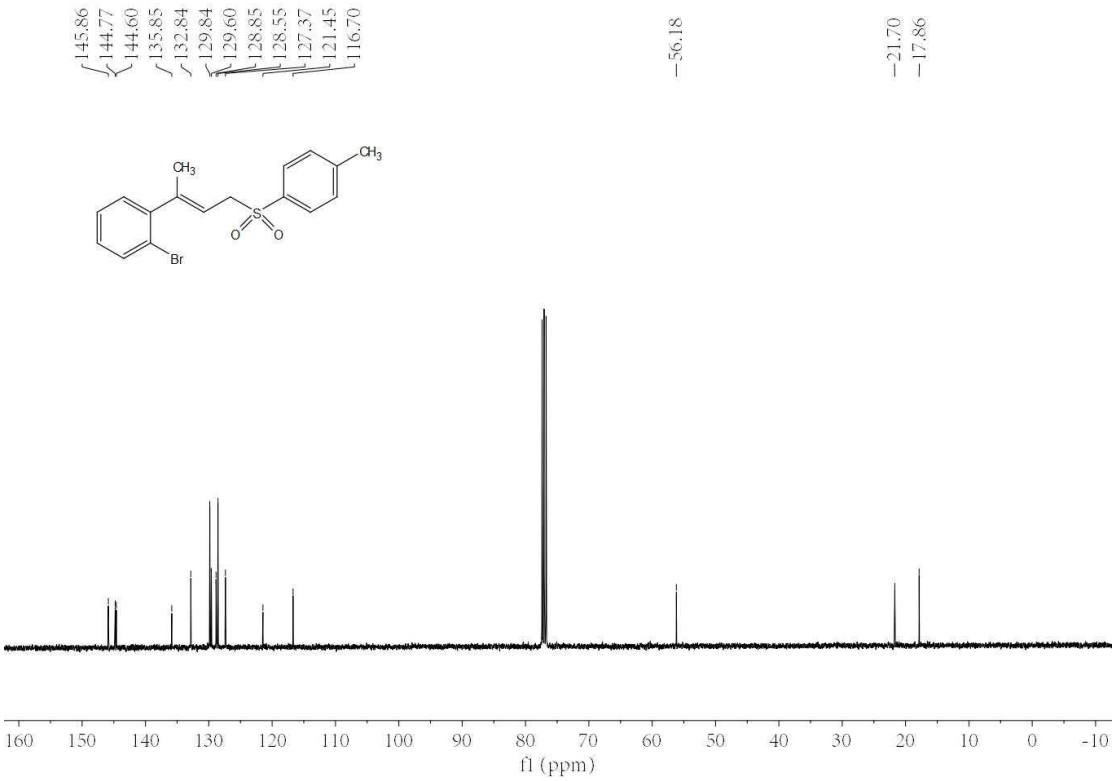
^{13}C NMR of **3al** (100 MHz, $CDCl_3$)



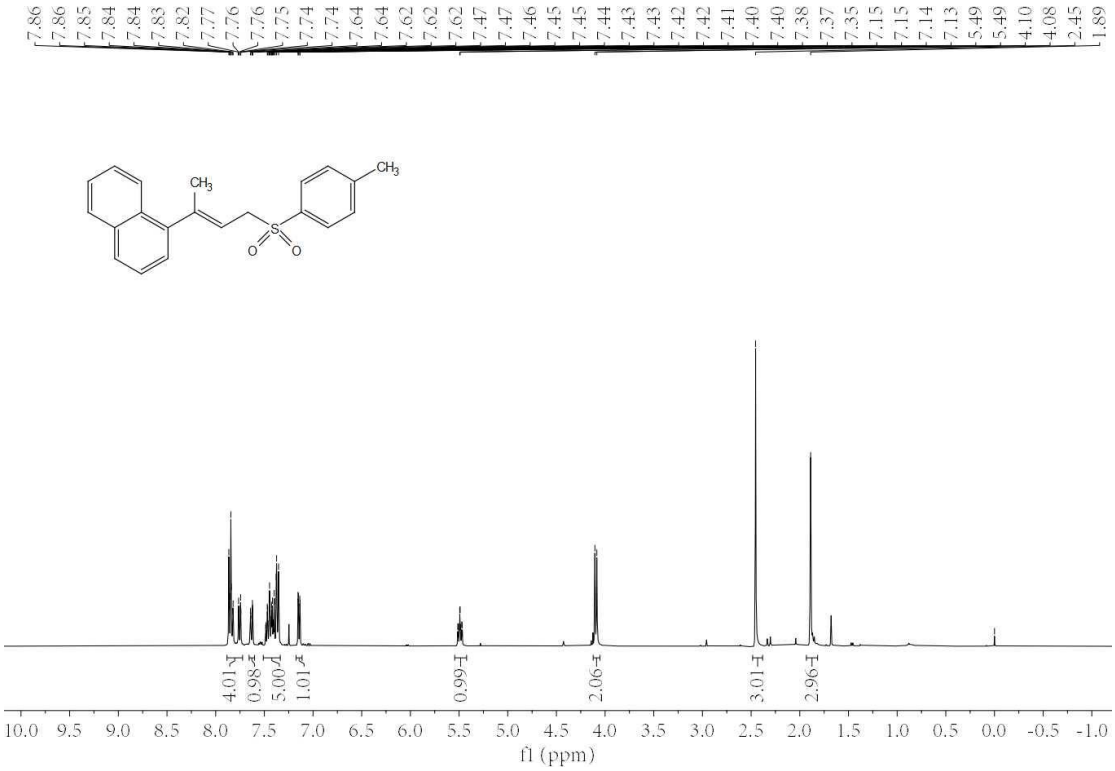
^{1}H NMR of **3am** (400 MHz, $CDCl_3$)



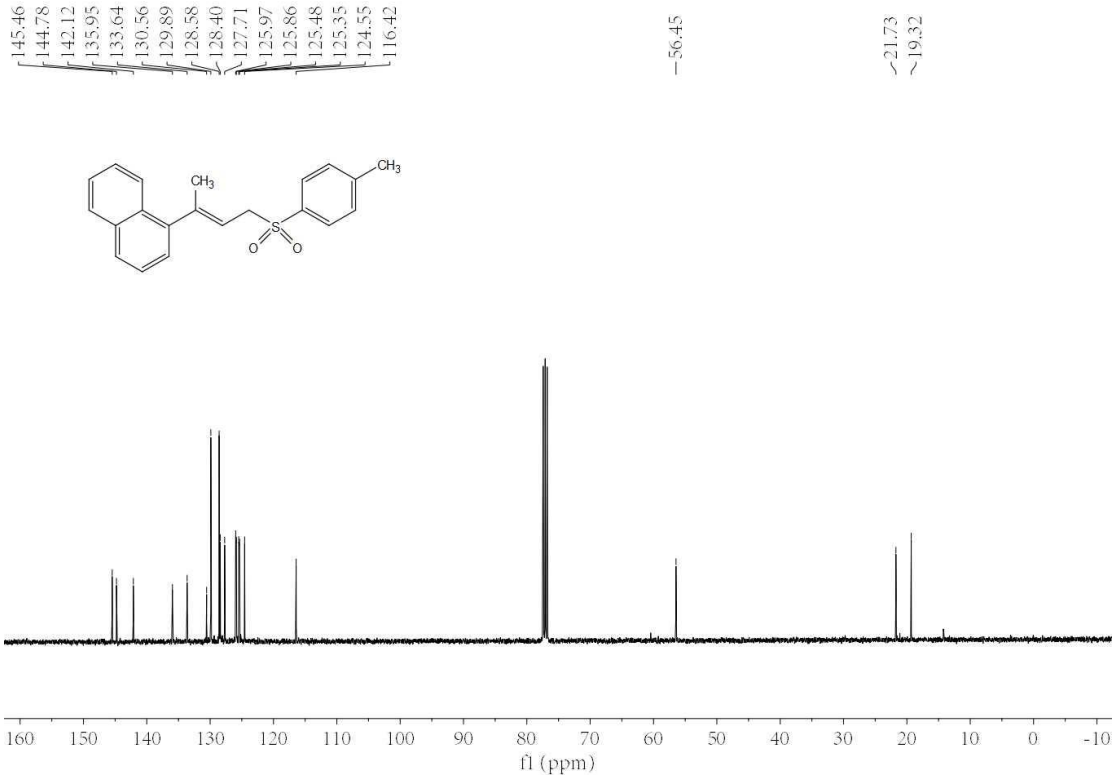
^{13}C NMR of **3am** (100 MHz, $CDCl_3$)



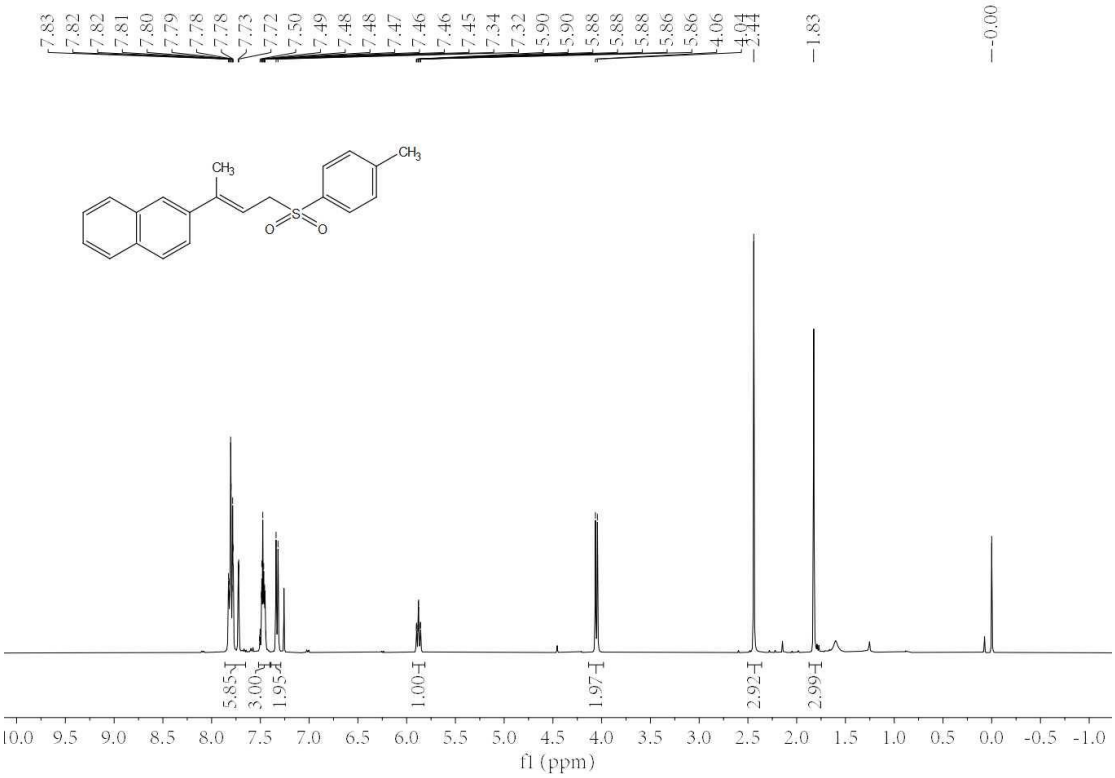
^{1}H NMR of **3an** (400 MHz, $CDCl_3$)



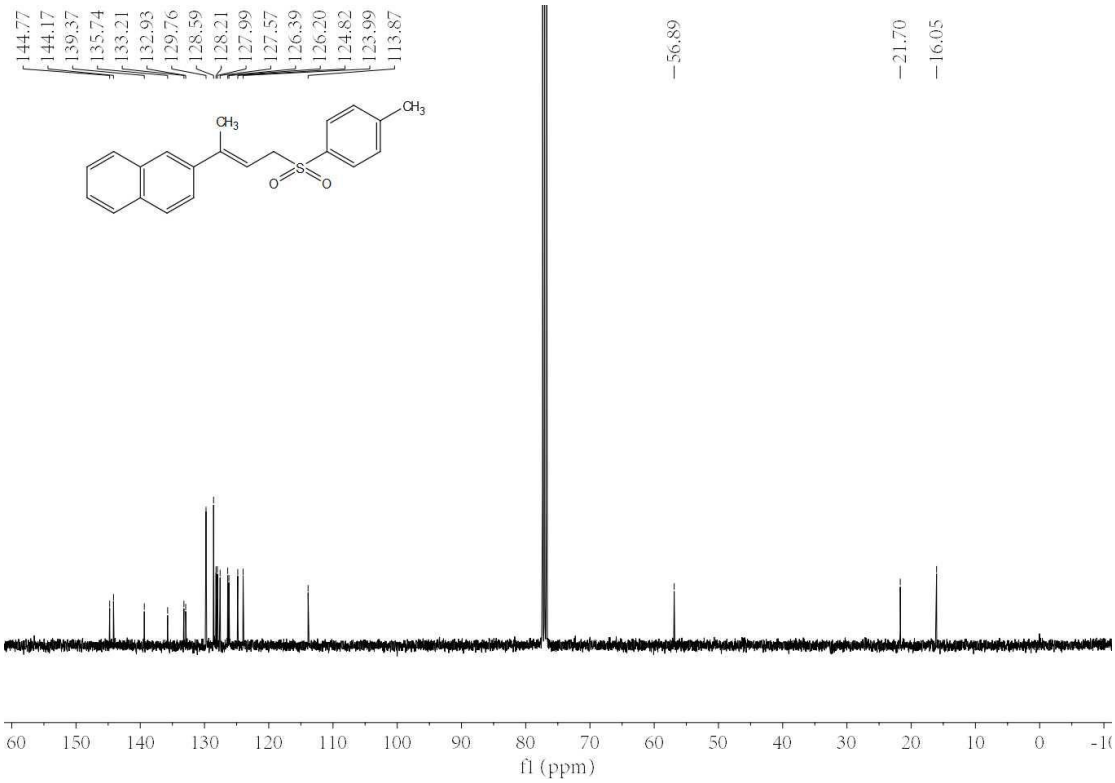
^{13}C NMR of **3an** (100 MHz, $CDCl_3$)



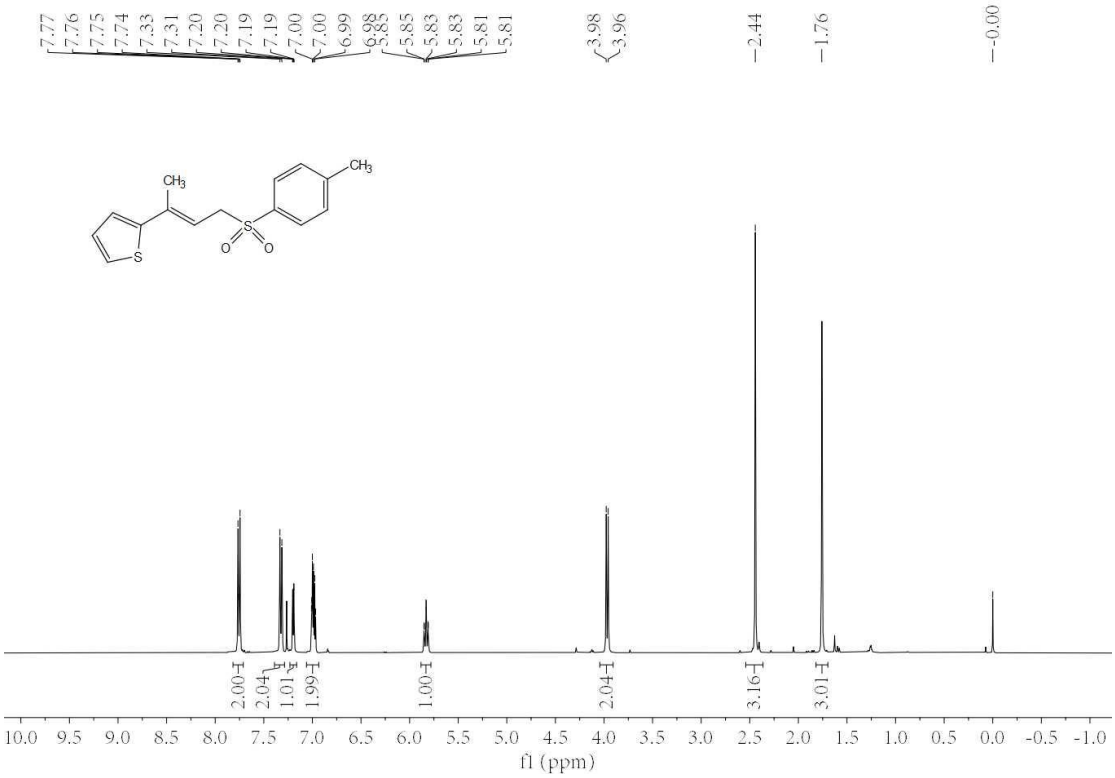
^{1}H NMR of **3ao** (400 MHz, $CDCl_3$)



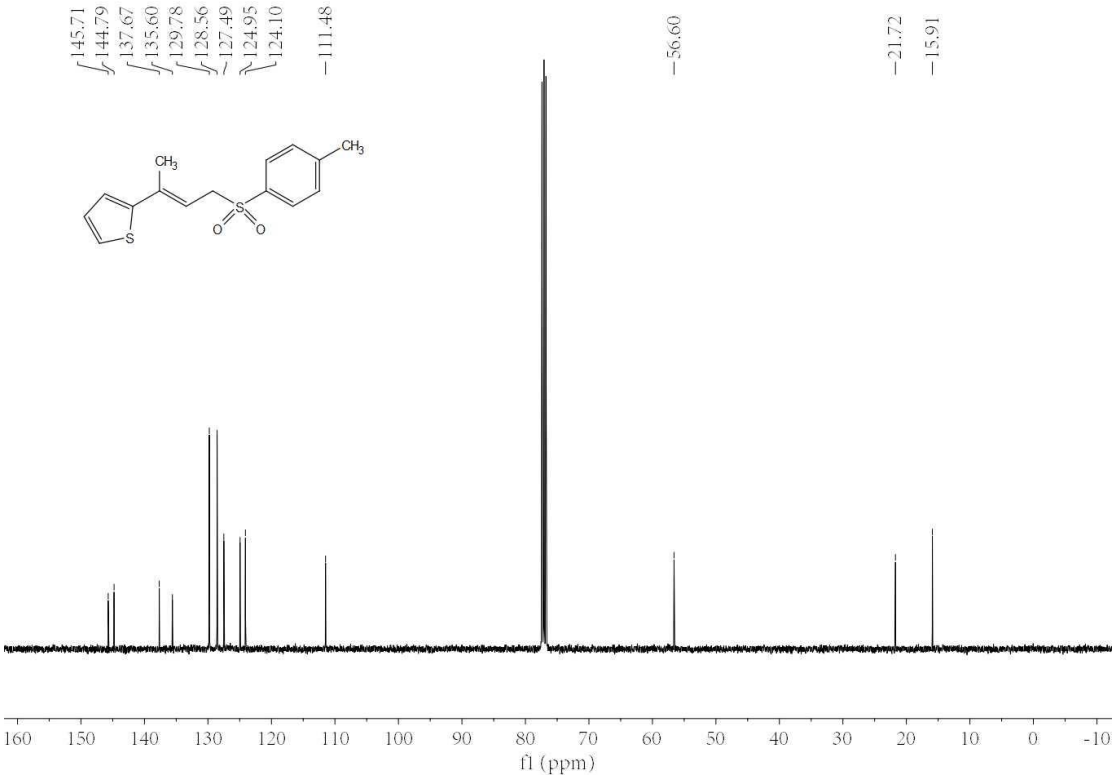
^{13}C NMR of **3ao** (100 MHz, $CDCl_3$)



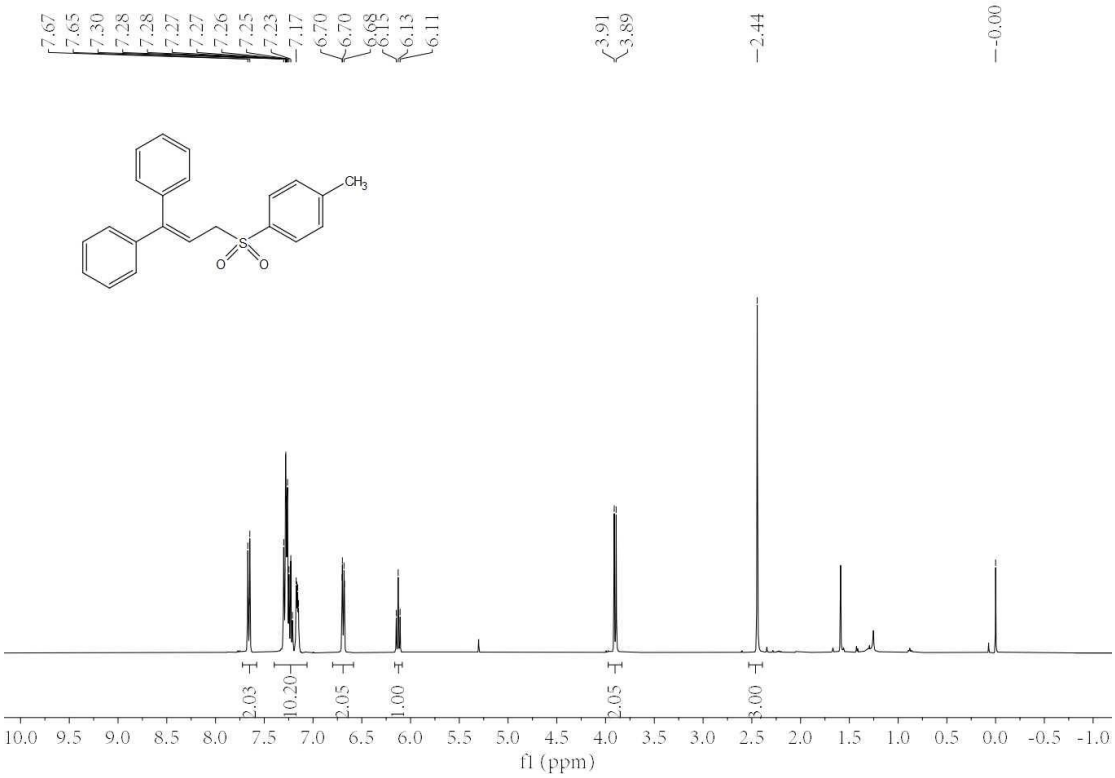
^{1}H NMR of **3ap** (400 MHz, $CDCl_3$)



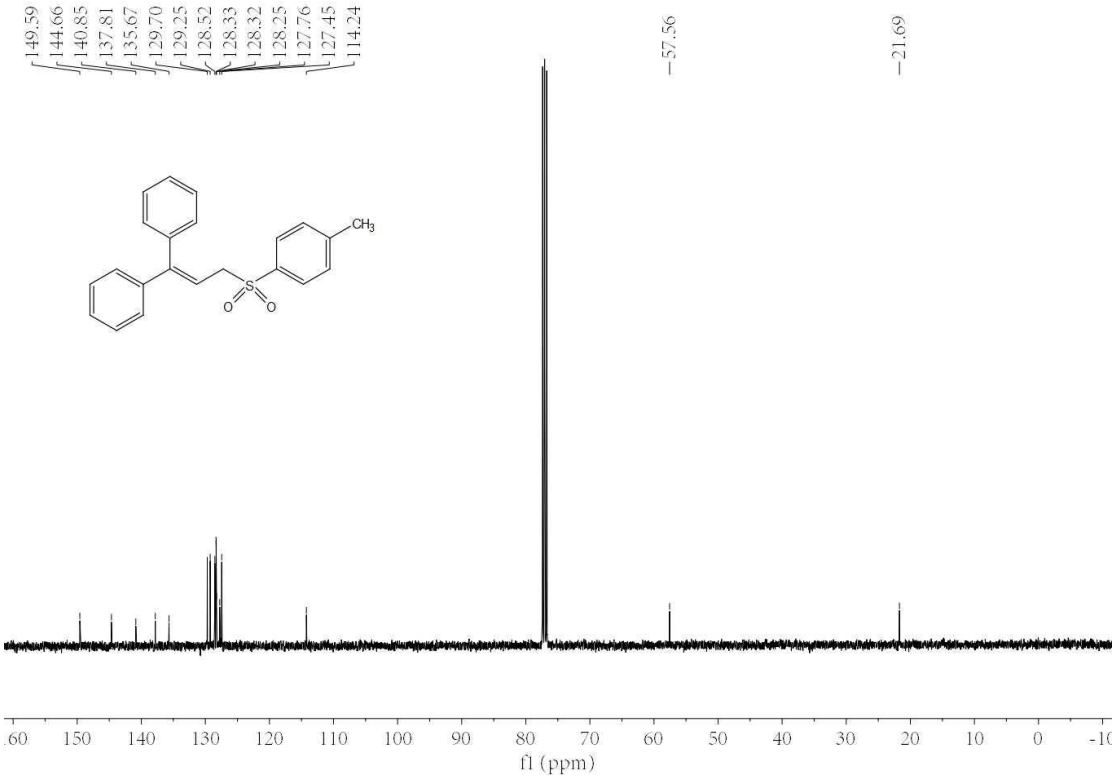
^{13}C NMR of **3ap** (100 MHz, $CDCl_3$)



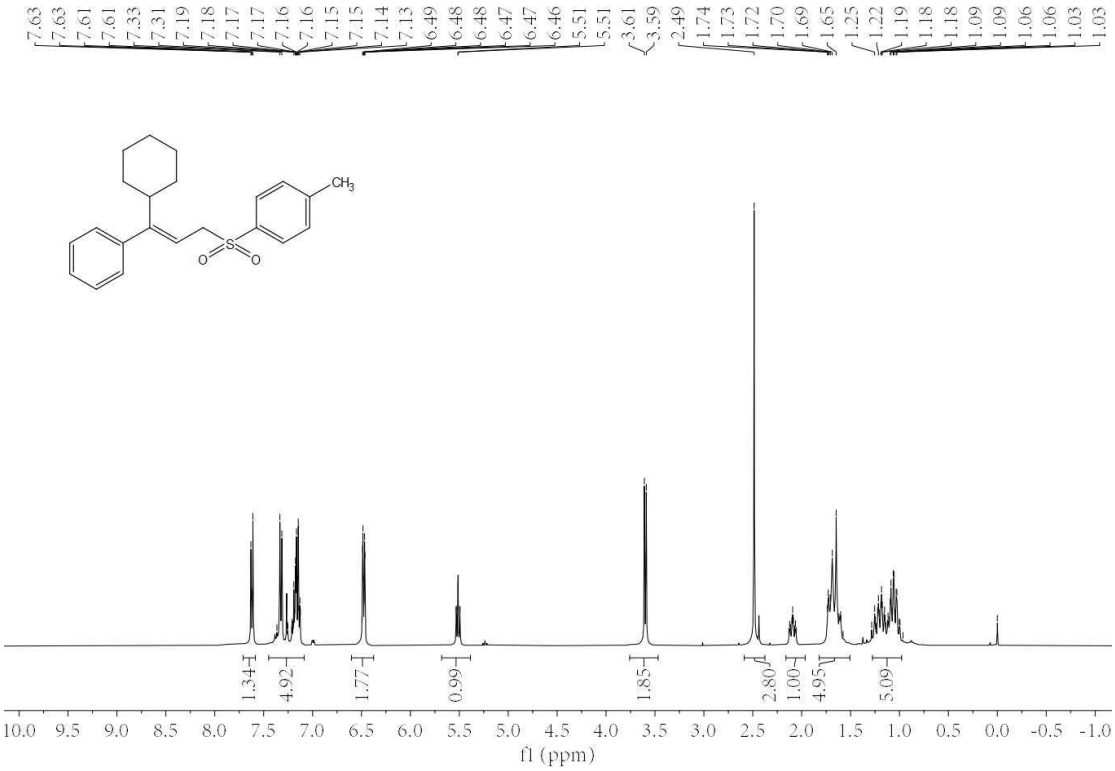
^{1}H NMR of **3aq** (400 MHz, $CDCl_3$)



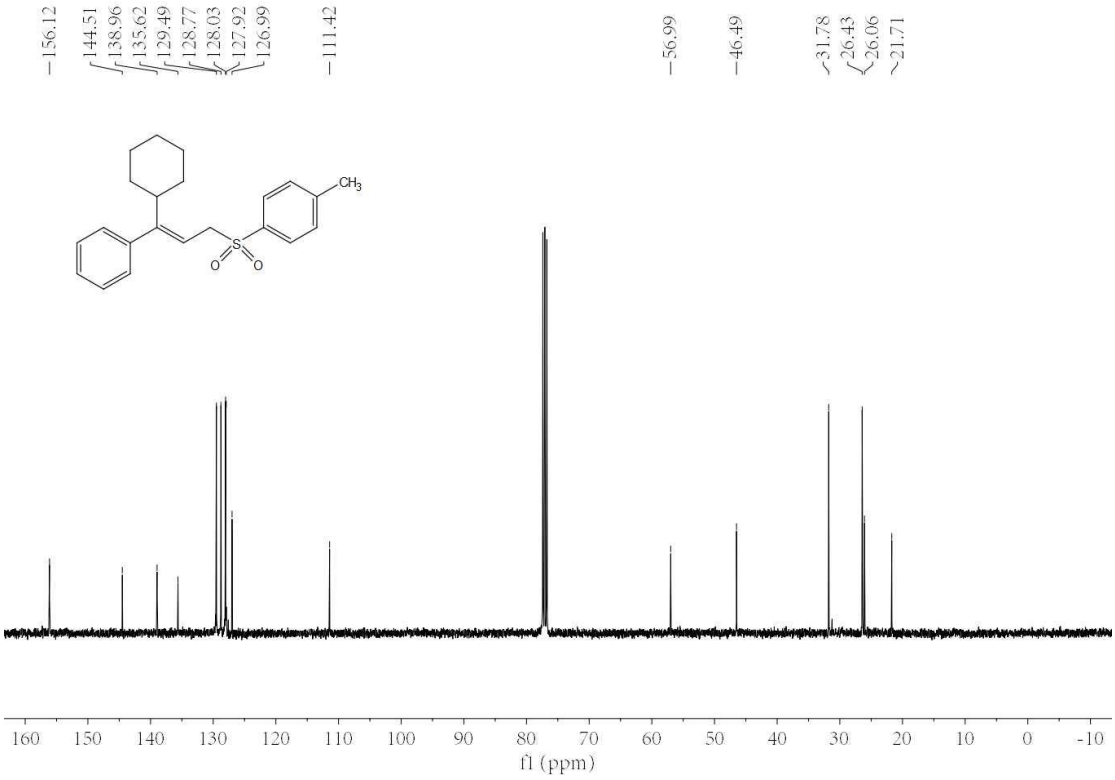
^{13}C NMR of **3aq** (100 MHz, $CDCl_3$)



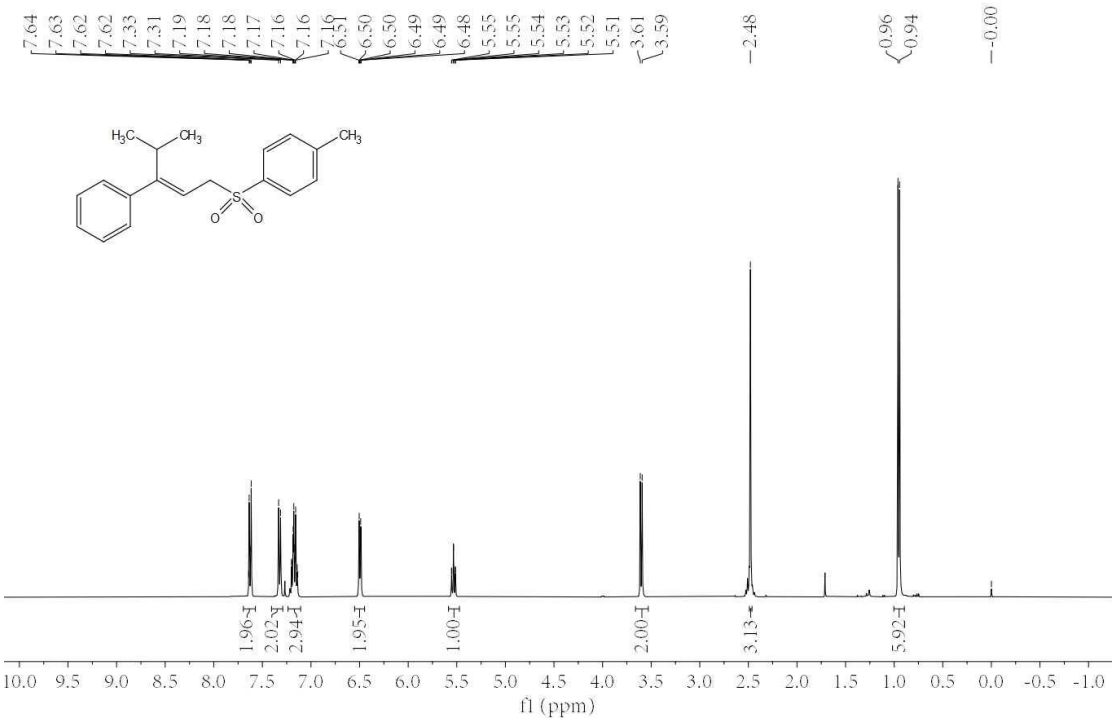
^{1}H NMR of **3ar** (400 MHz, $CDCl_3$)



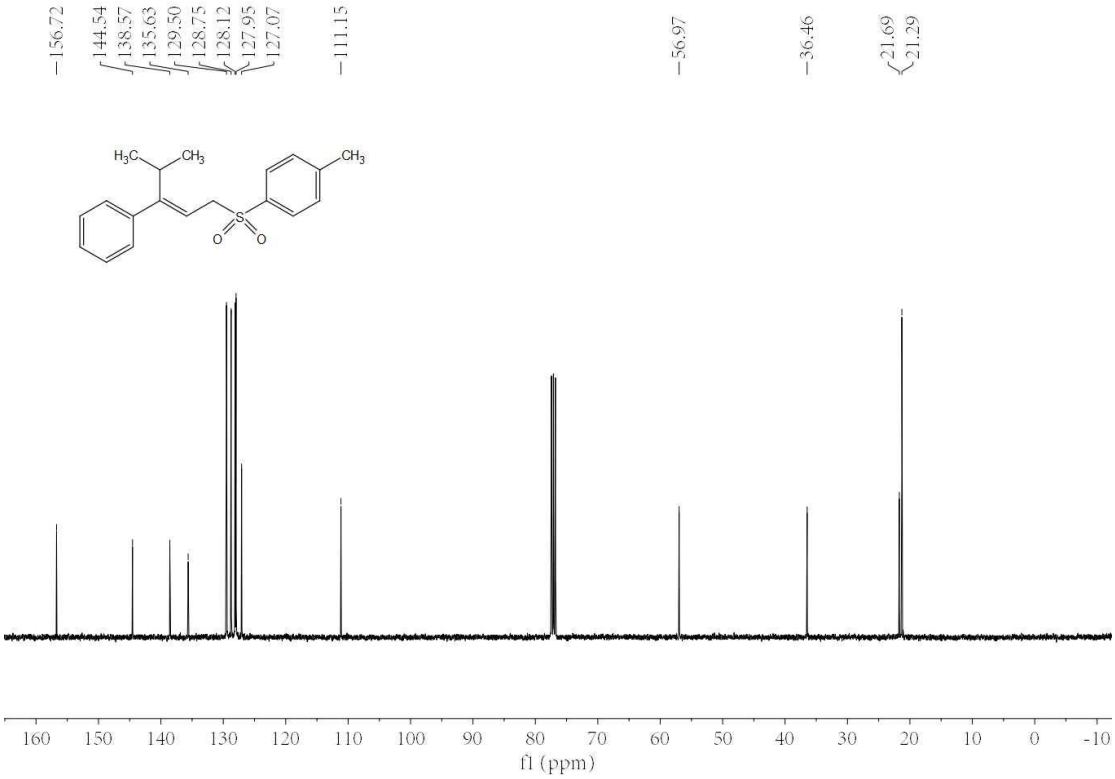
^{13}C NMR of **3ar** (100 MHz, $CDCl_3$)



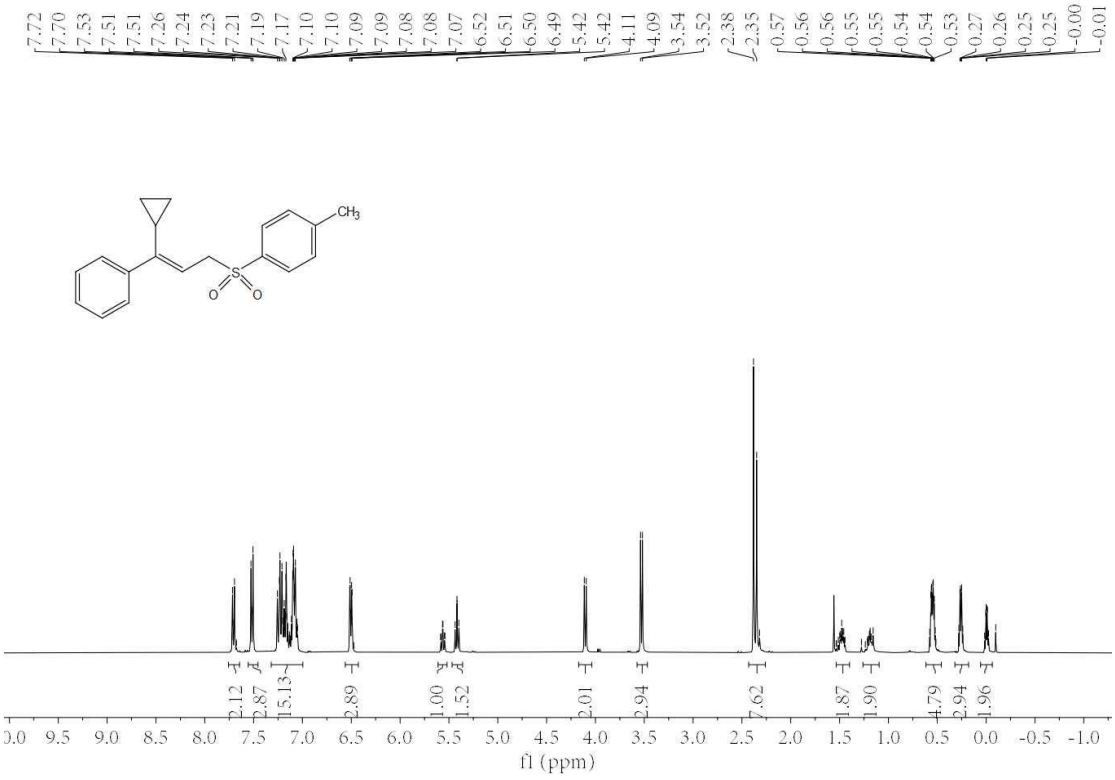
^{1}H NMR of **3as** (400 MHz, $CDCl_3$)



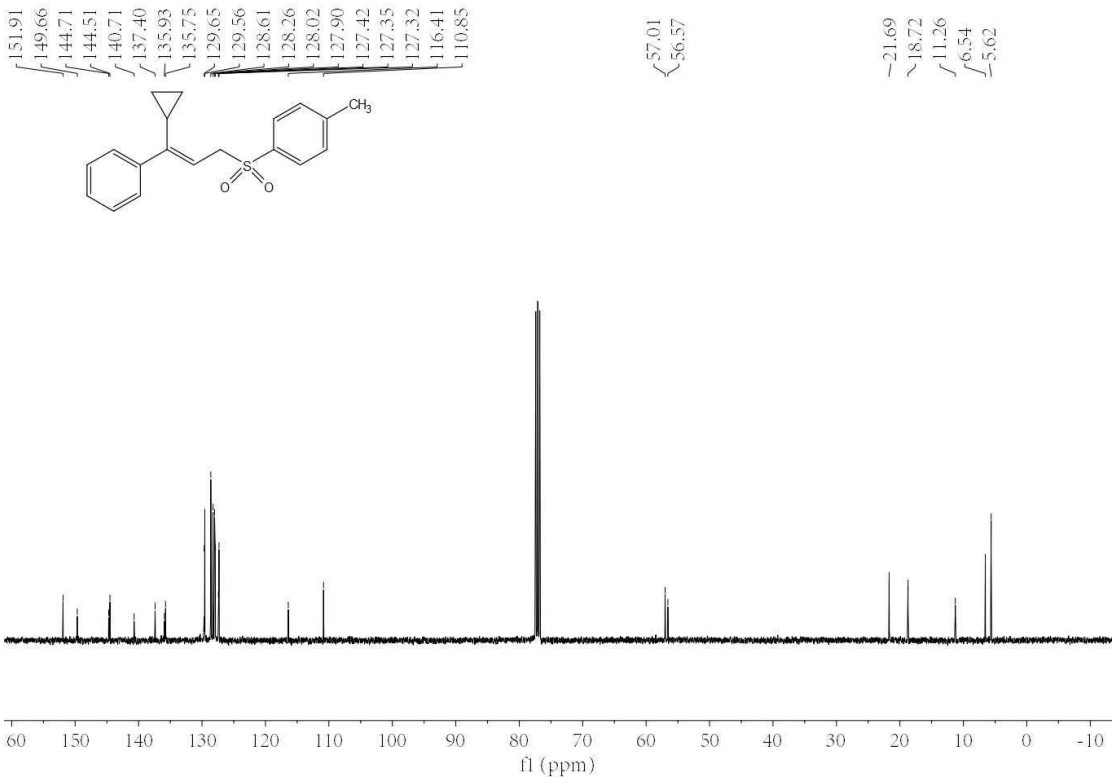
^{13}C NMR of **3as** (100 MHz, $CDCl_3$)



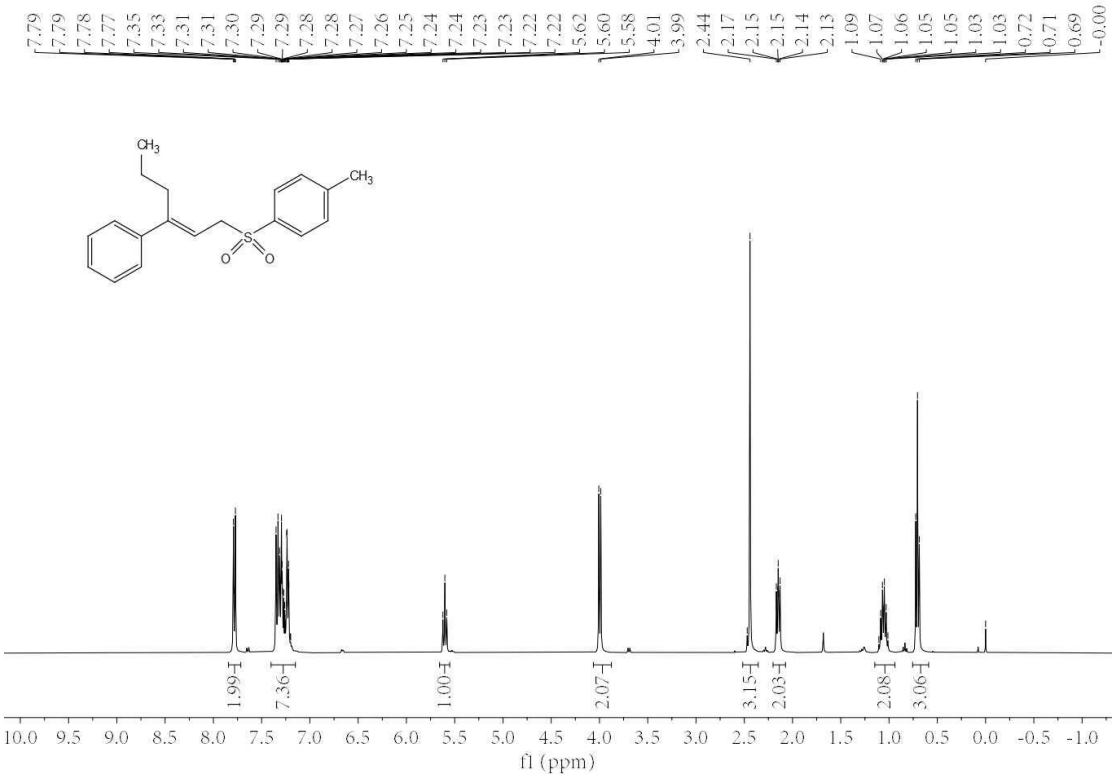
^{1}H NMR of **3at** (400 MHz, $CDCl_3$)



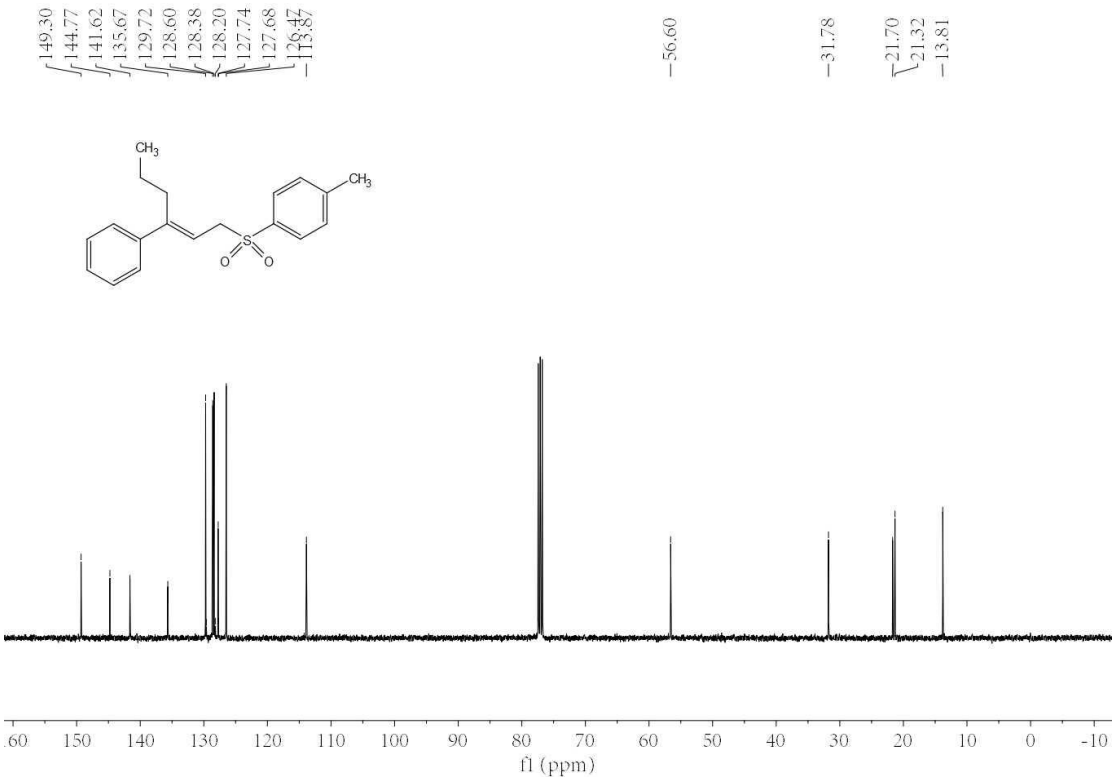
^{13}C NMR of **3at** (100 MHz, $CDCl_3$)



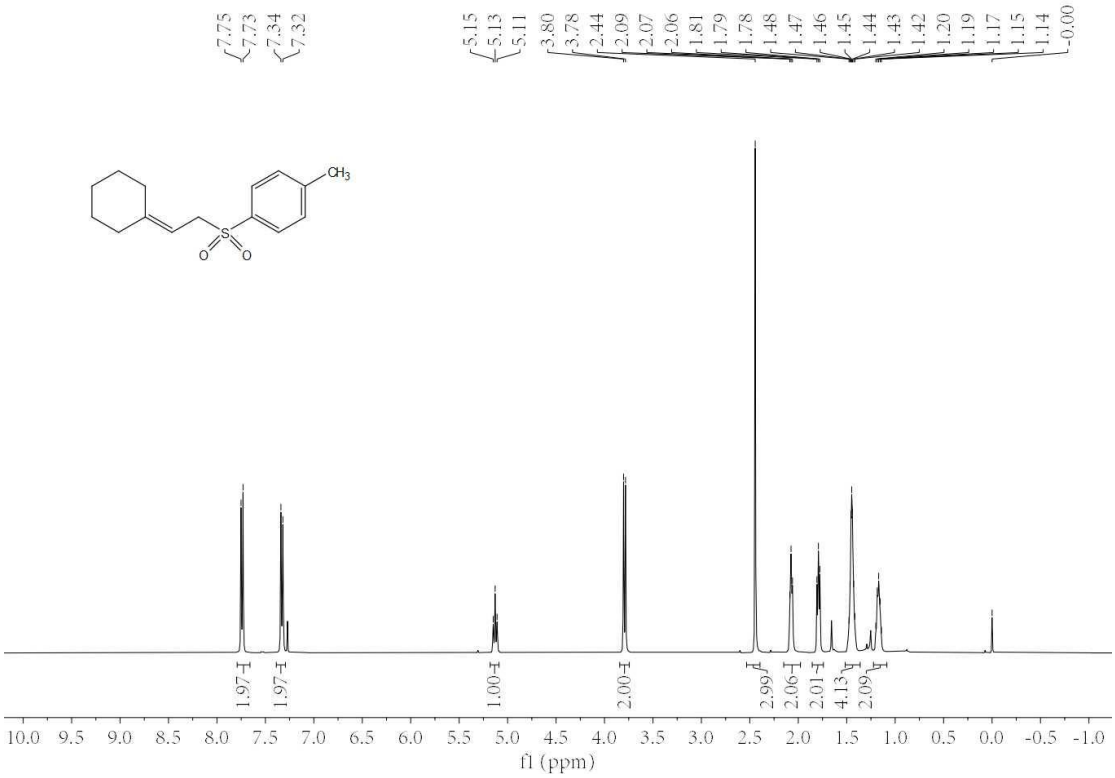
^{1}H NMR of **3au** (400 MHz, $CDCl_3$)



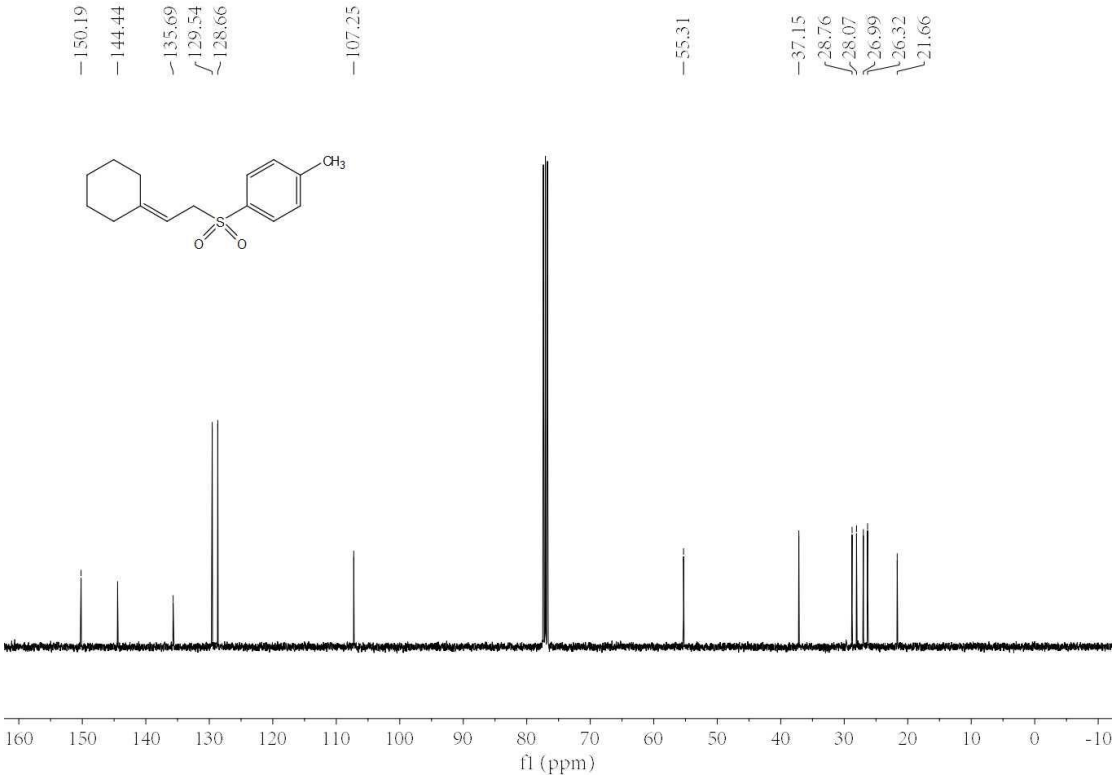
^{13}C NMR of **3au** (100 MHz, $CDCl_3$)



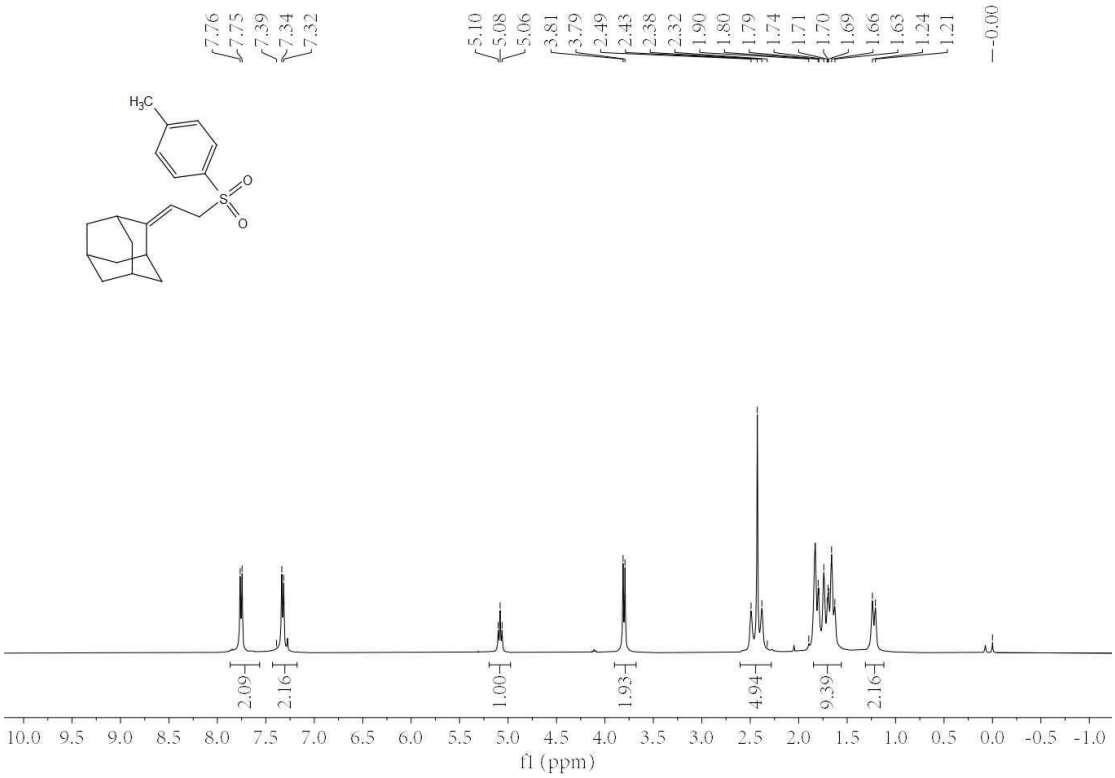
^{1}H NMR of **3av** (400 MHz, $CDCl_3$)



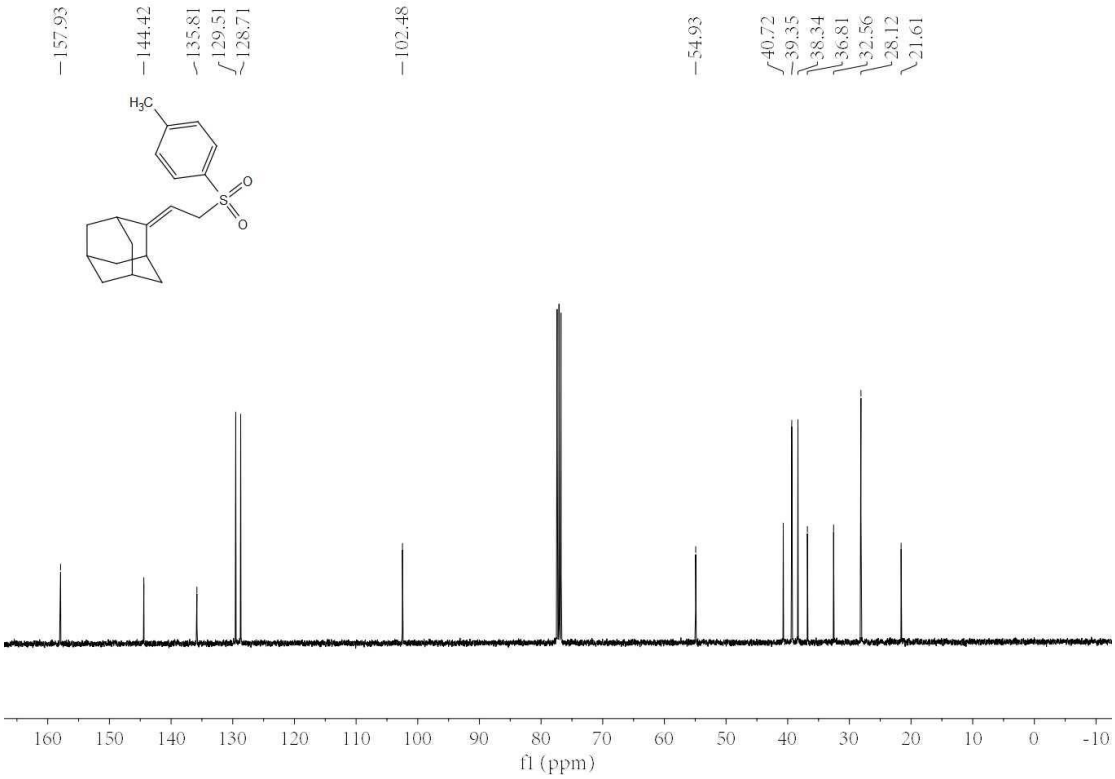
^{13}C NMR of **3av** (100 MHz, $CDCl_3$)



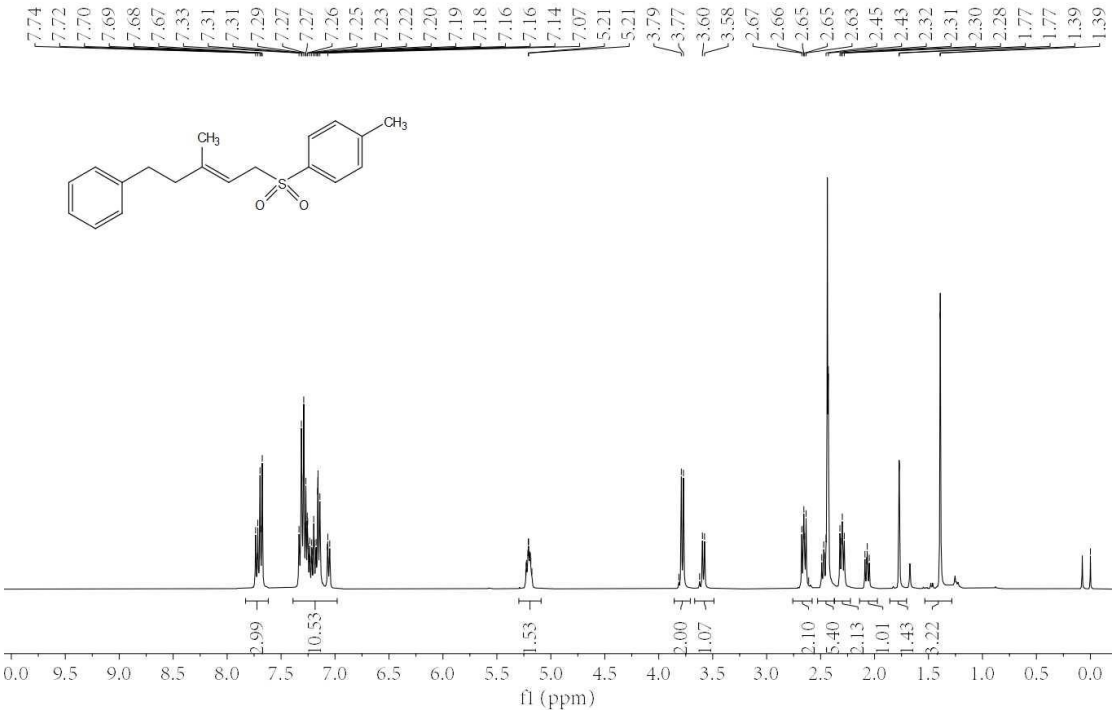
^{1}H NMR of **3aw** (400 MHz, $CDCl_3$)



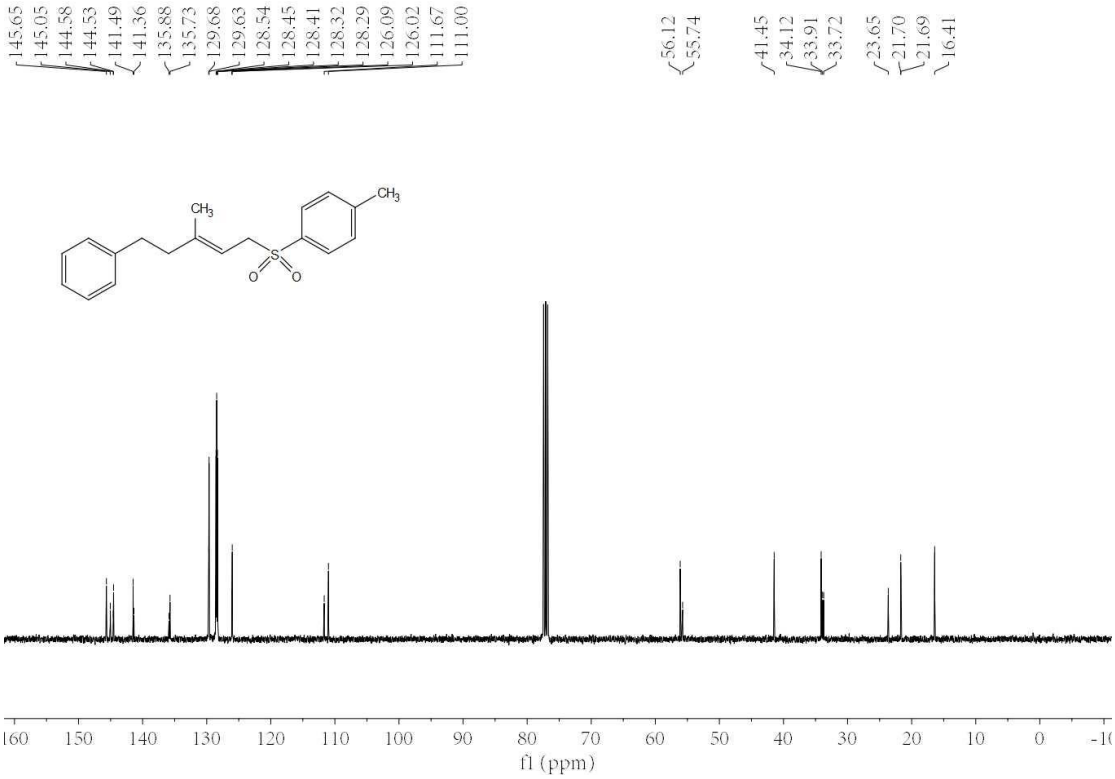
^{13}C NMR of **3aw** (100 MHz, $CDCl_3$)



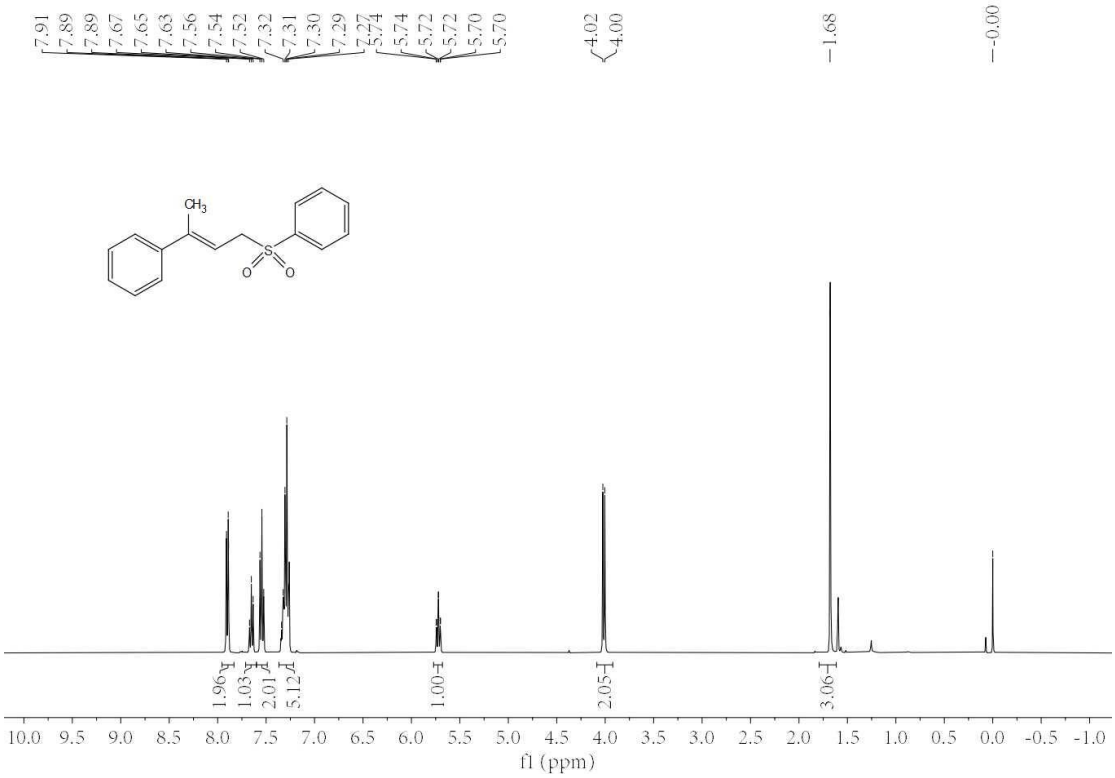
^{1}H NMR of **3ax** (400 MHz, $CDCl_3$)



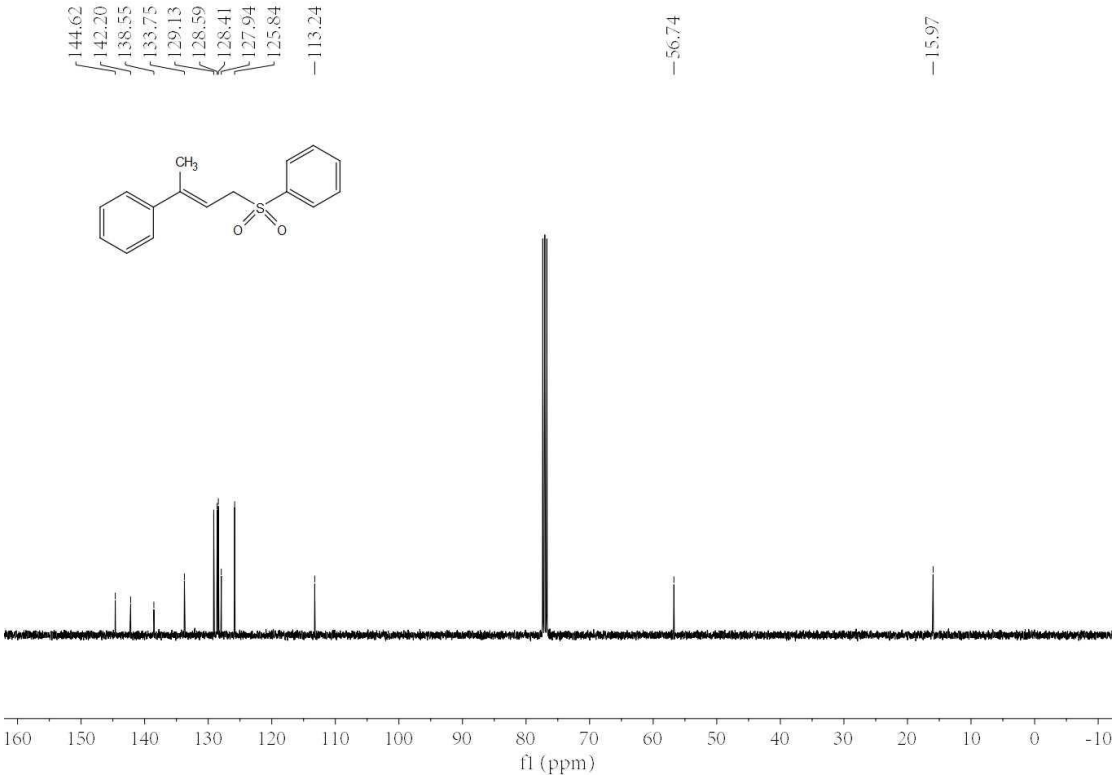
^{13}C NMR of **3ax** (100 MHz, $CDCl_3$)



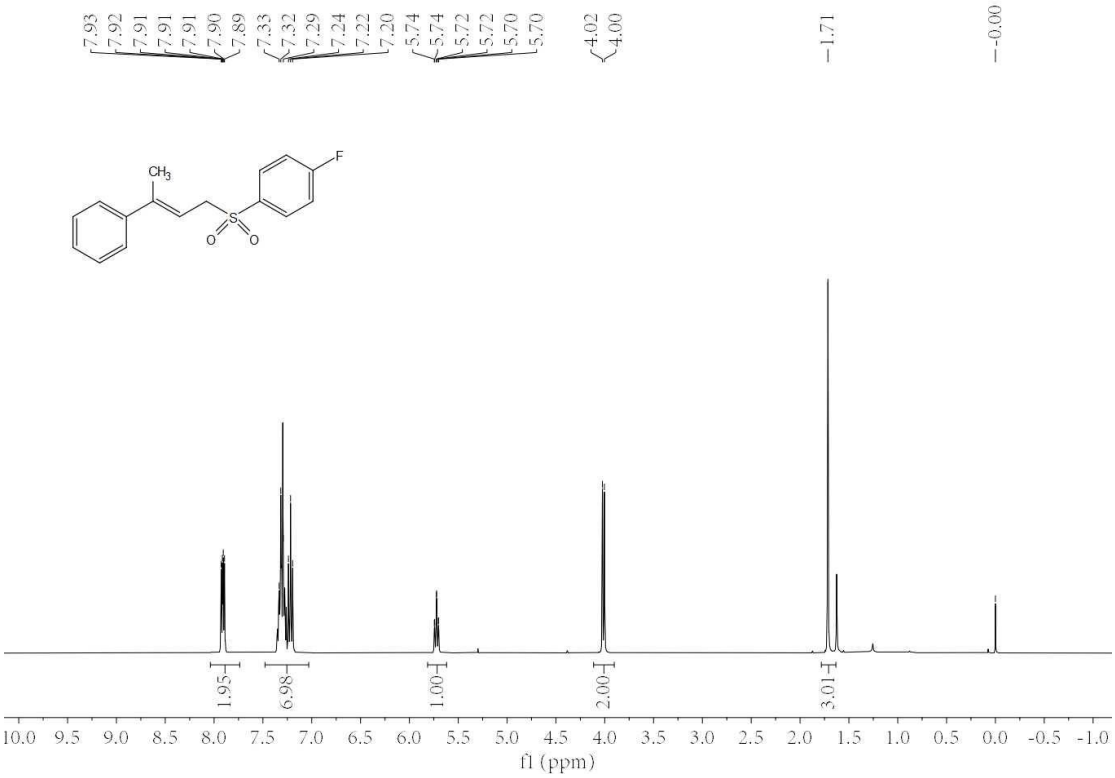
^{1}H NMR of **3ba** (400 MHz, $CDCl_3$)



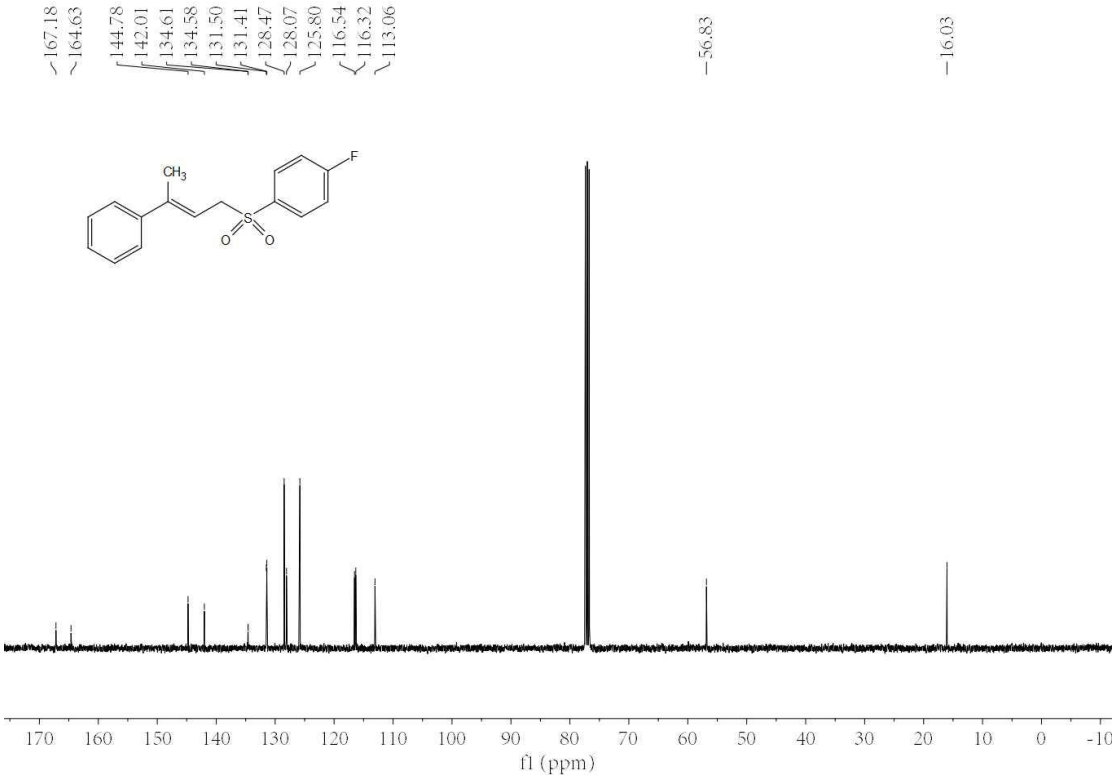
^{13}C NMR of **3ba** (100 MHz, $CDCl_3$)



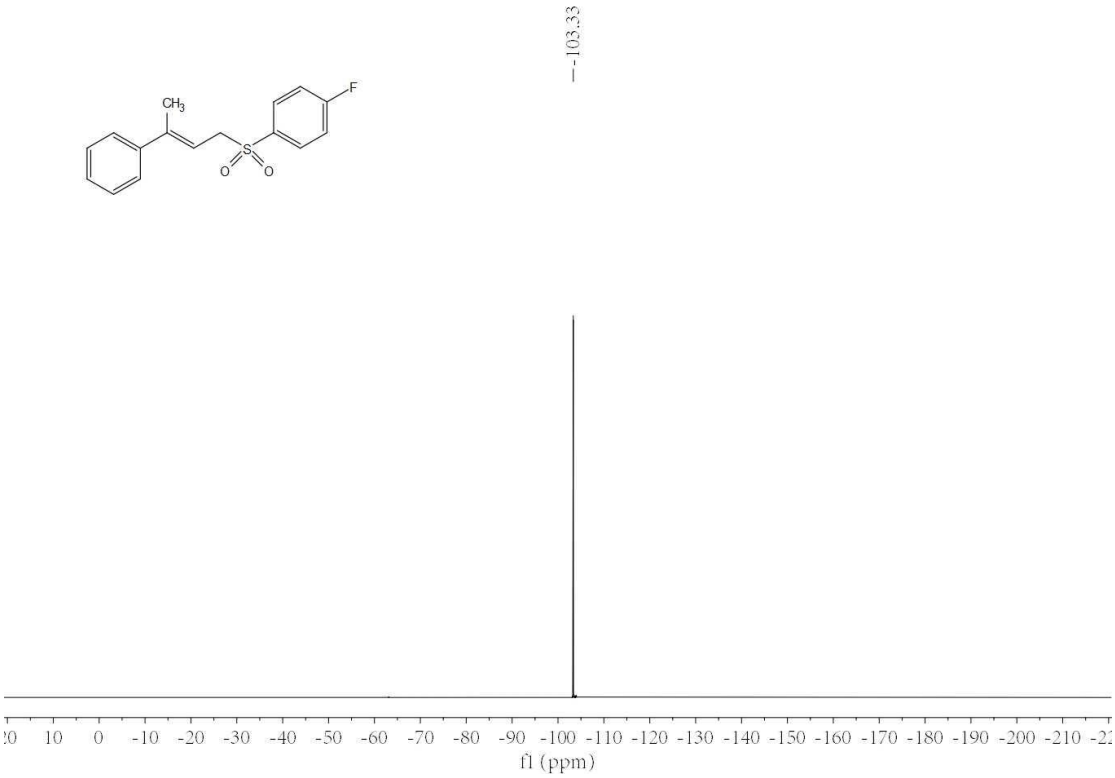
^{1}H NMR of **3ca** (400 MHz, $CDCl_3$)



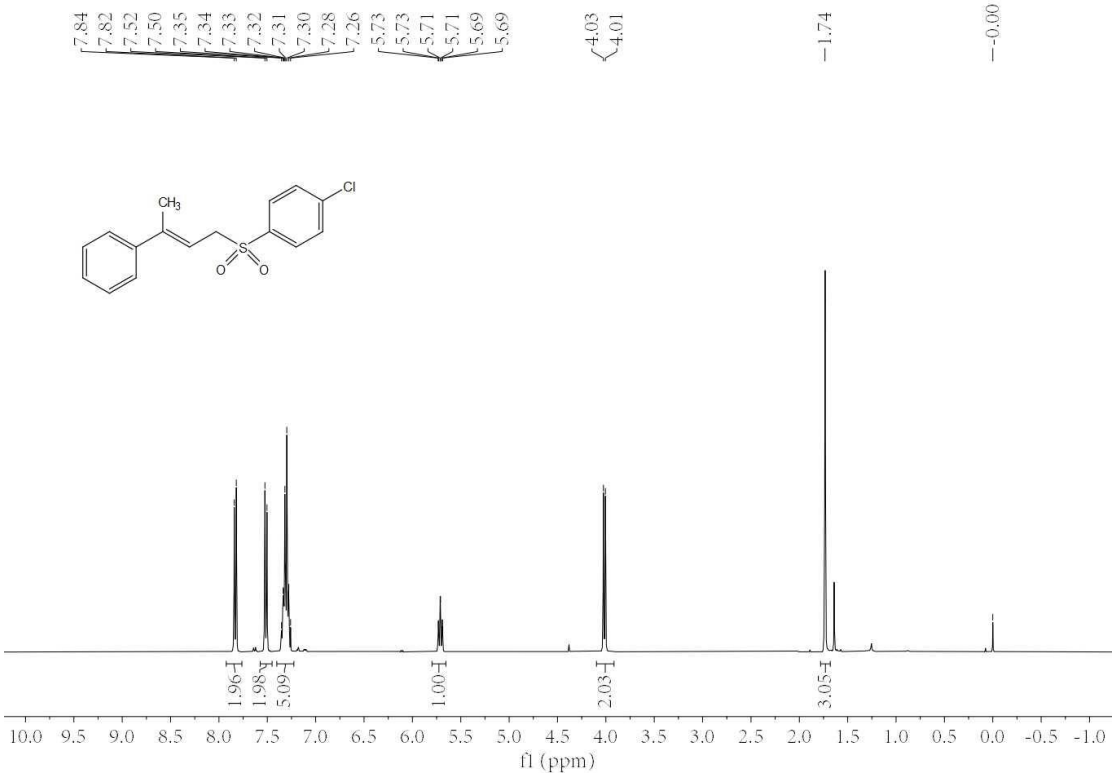
^{13}C NMR of **3ca** (100 MHz, $CDCl_3$)



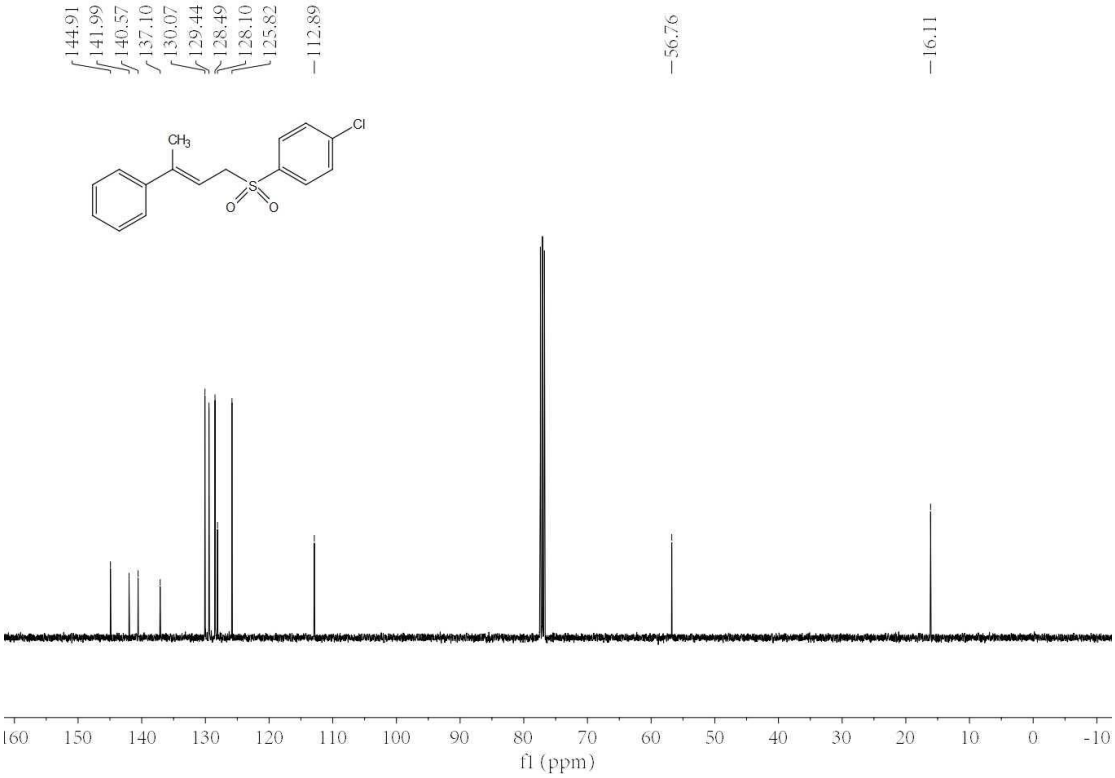
^{19}F NMR of **3ca** (471 MHz, $CDCl_3$)



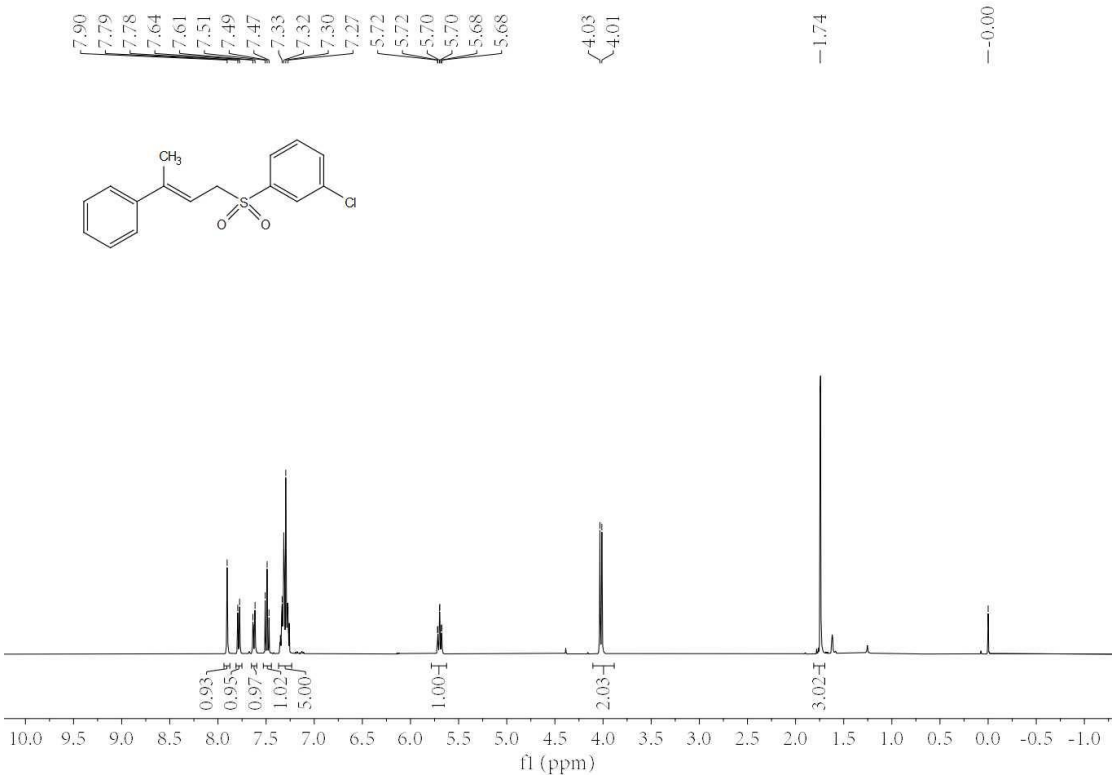
^{1}H NMR of **3da** (400 MHz, $CDCl_3$)



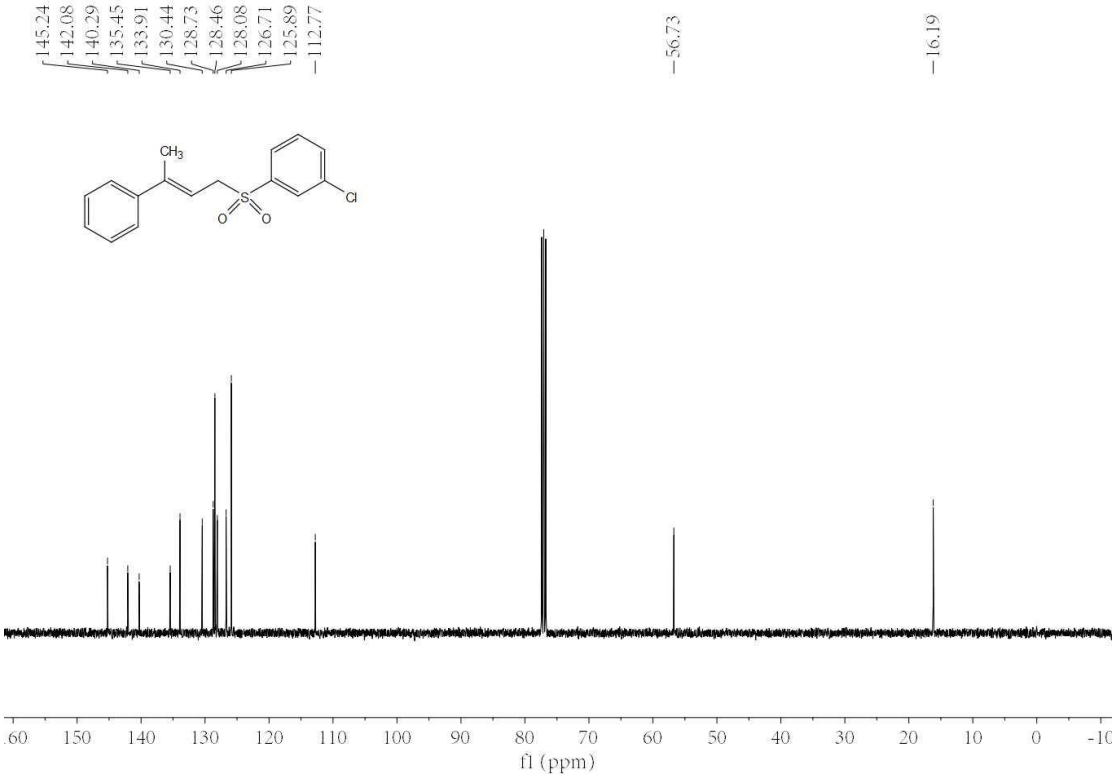
^{13}C NMR of **3da** (100 MHz, $CDCl_3$)



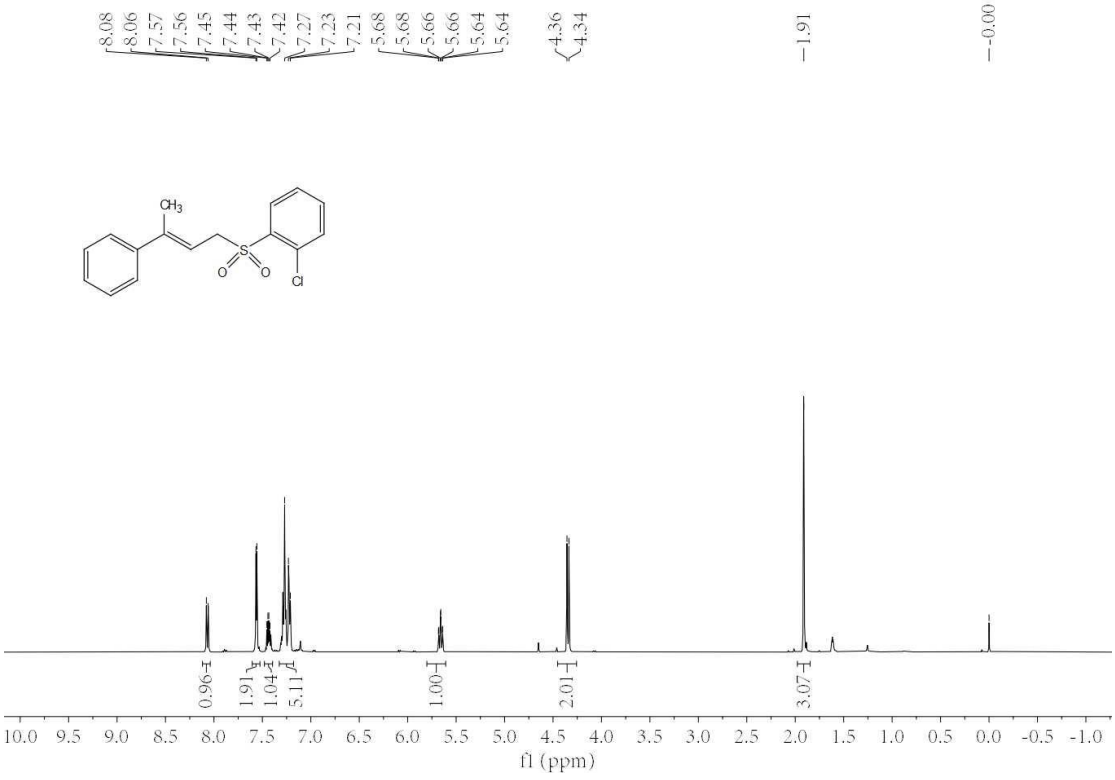
^{1}H NMR of **3ea** (400 MHz, $CDCl_3$)



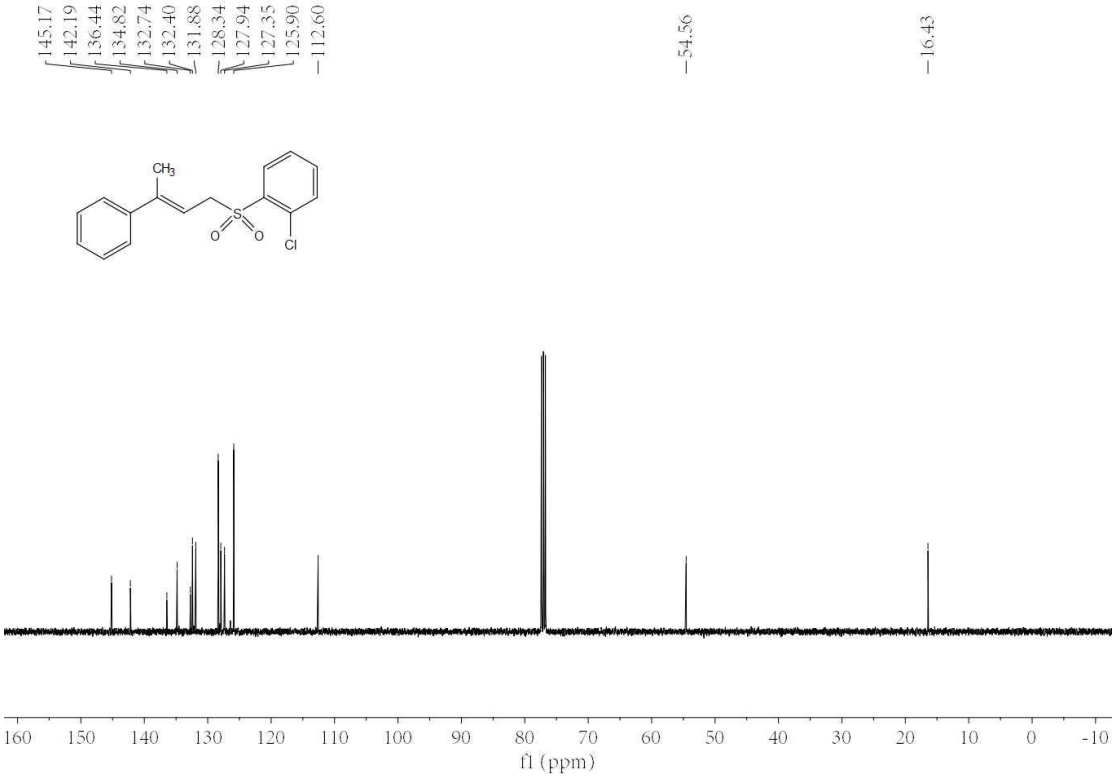
^{13}C NMR of **3ea** (100 MHz, $CDCl_3$)



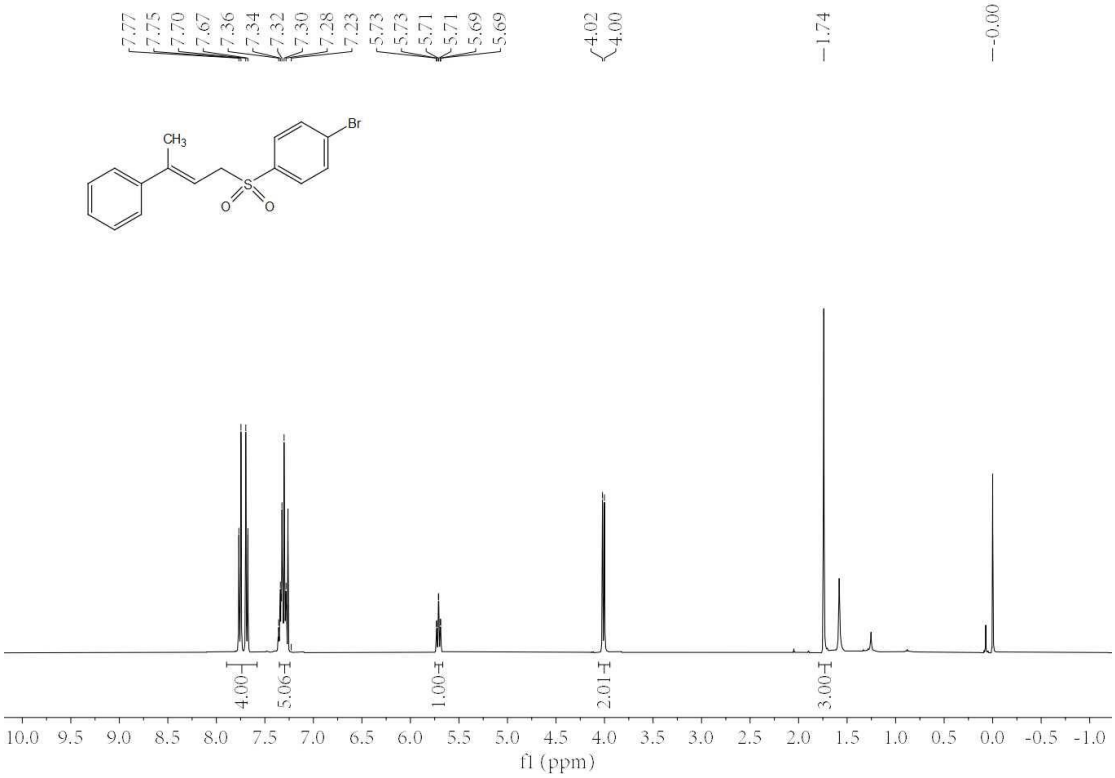
^{1}H NMR of **3fa** (400 MHz, $CDCl_3$)



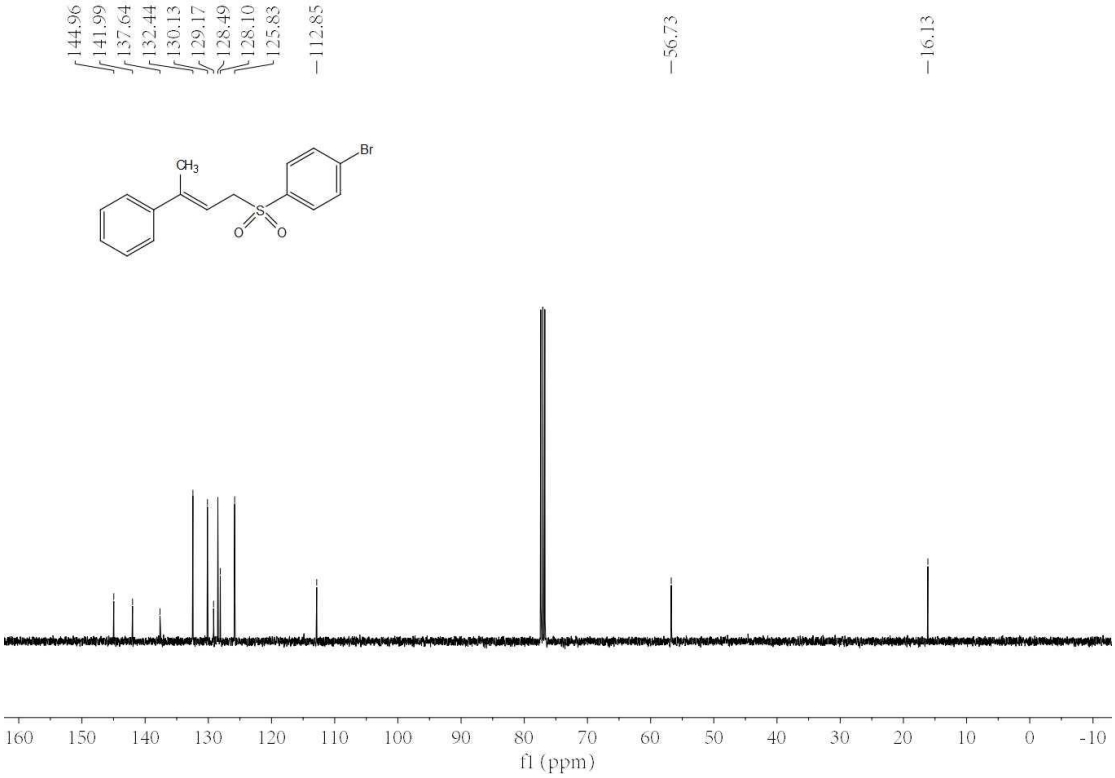
^{13}C NMR of **3fa** (100 MHz, $CDCl_3$)



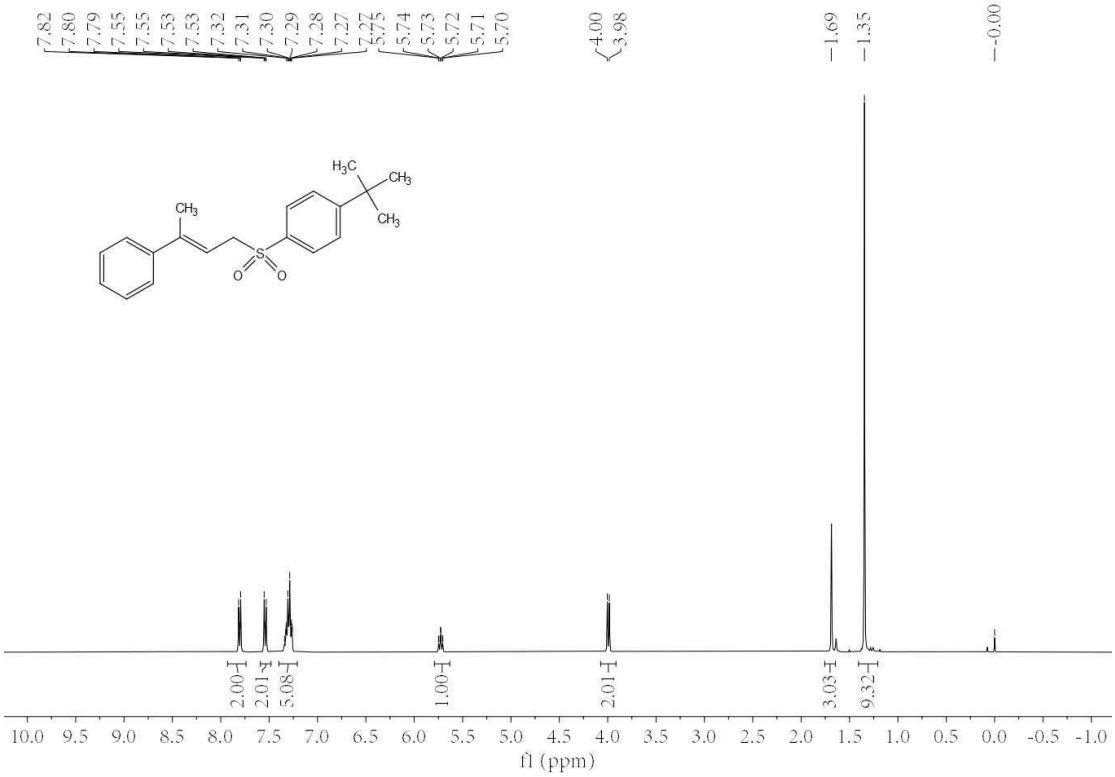
^{1}H NMR of **3ga** (400 MHz, $CDCl_3$)



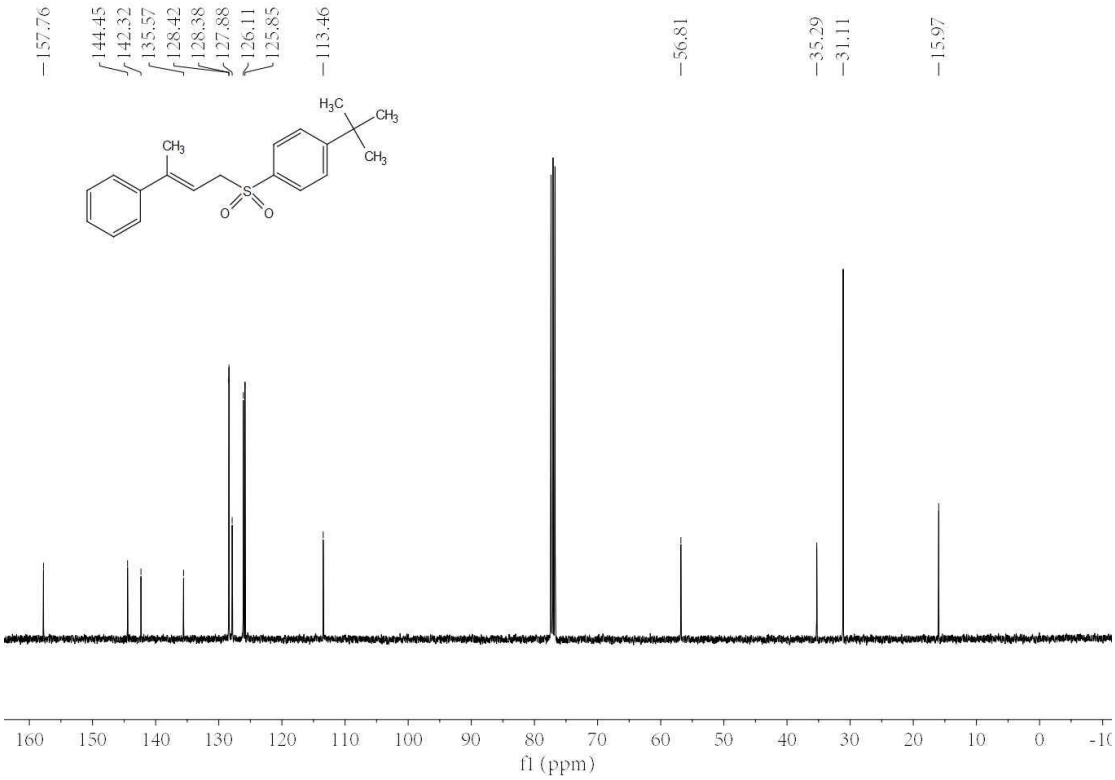
^{13}C NMR of **3ga** (100 MHz, $CDCl_3$)



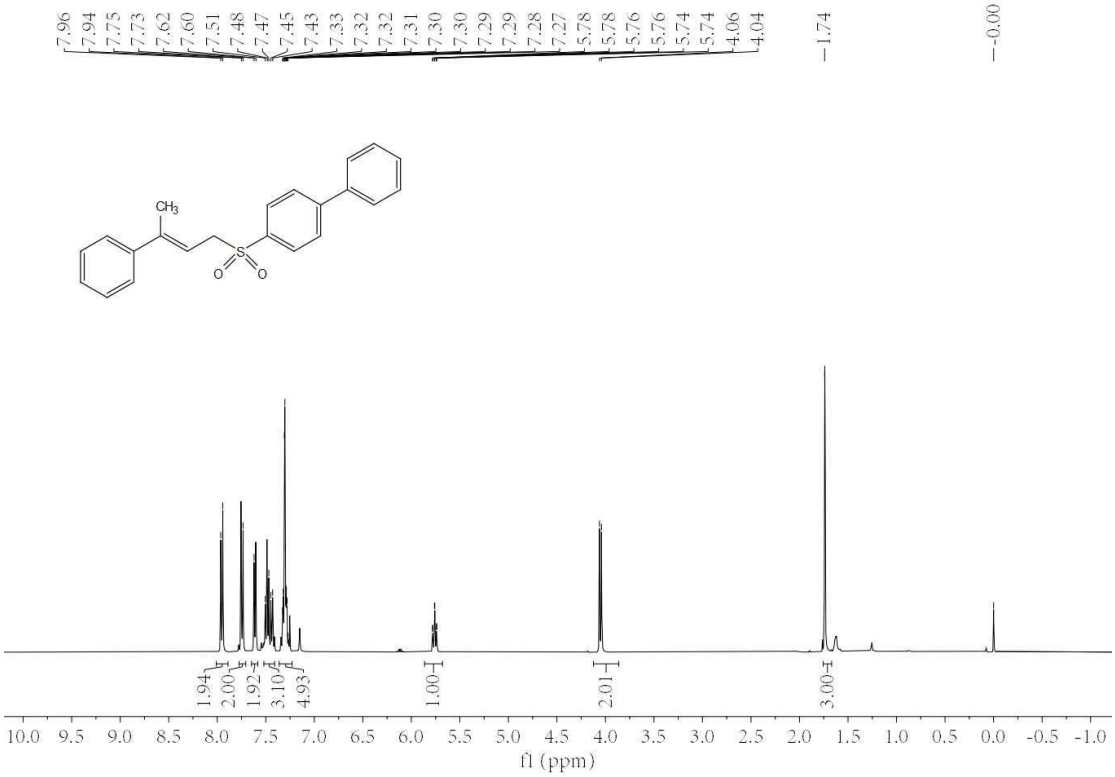
^{1}H NMR of **3ha** (400 MHz, $CDCl_3$)



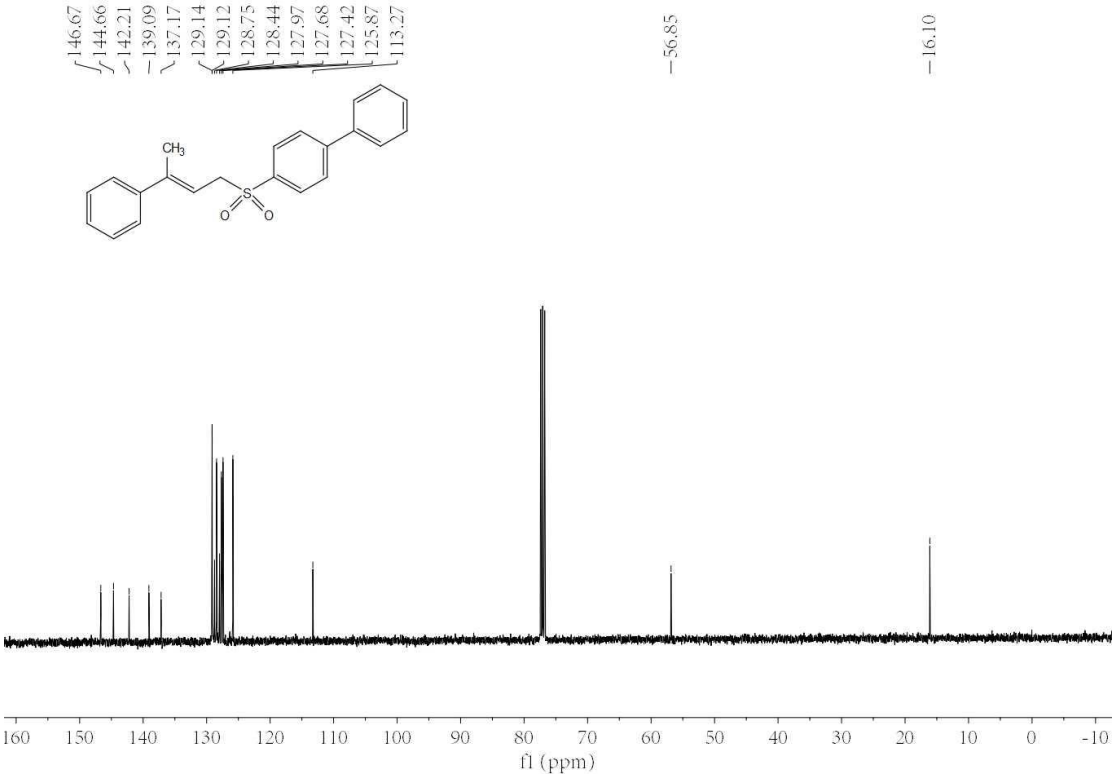
^{13}C NMR of **3ha** (100 MHz, $CDCl_3$)



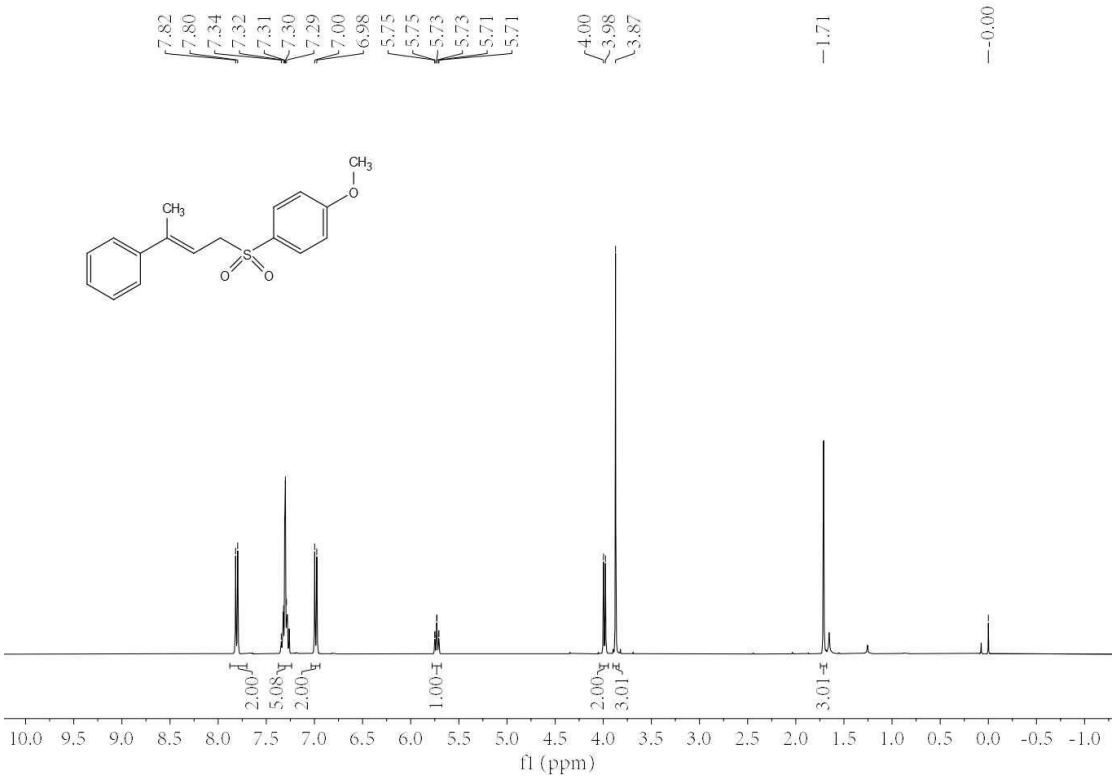
^{1}H NMR of **3ia** (400 MHz, $CDCl_3$)



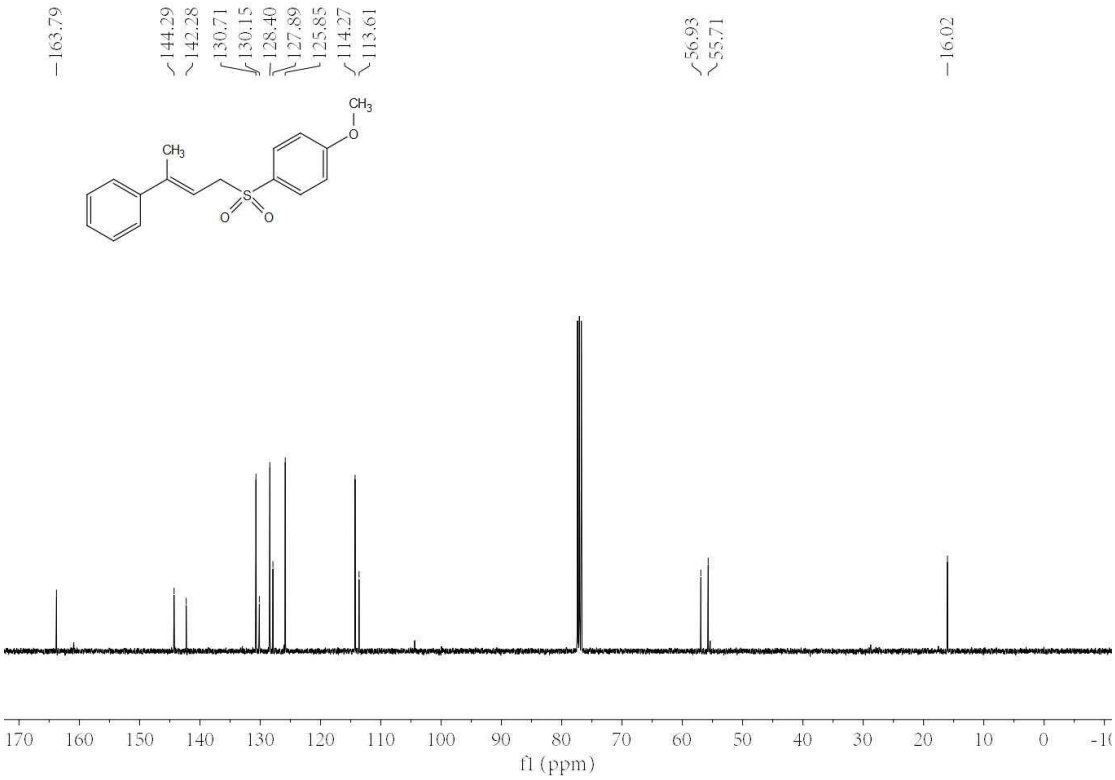
^{13}C NMR of **3ia** (100 MHz, $CDCl_3$)



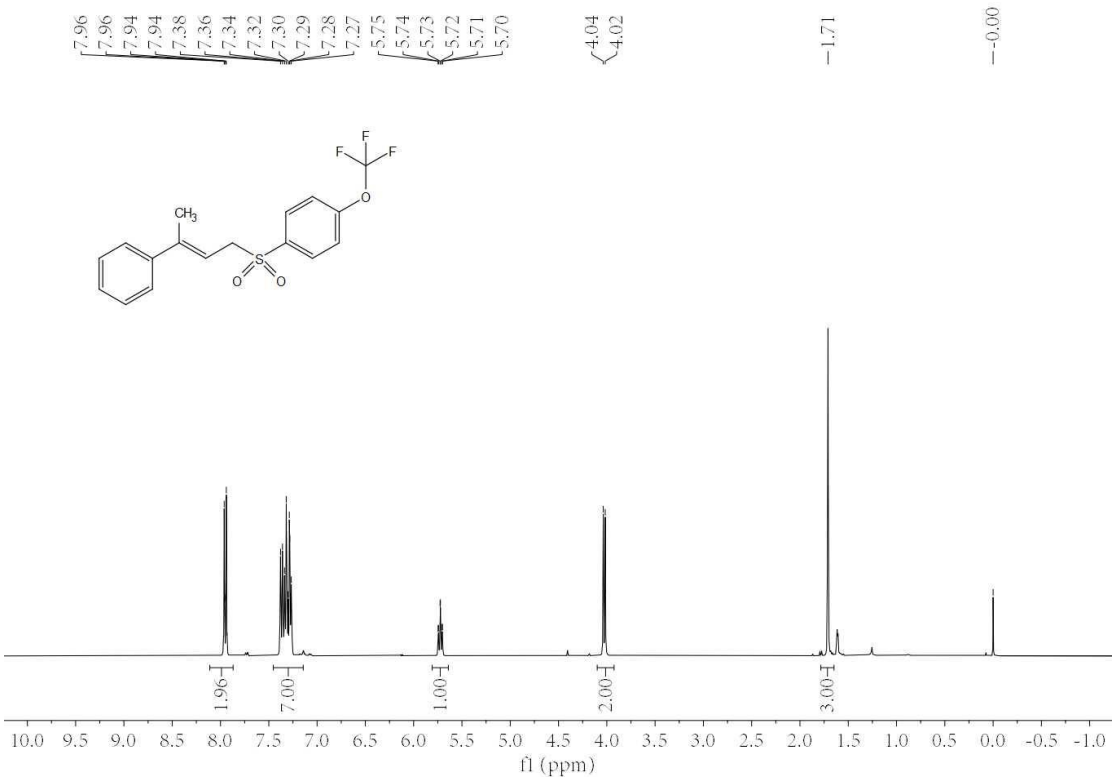
^{1}H NMR of **3ja** (400 MHz, $CDCl_3$)



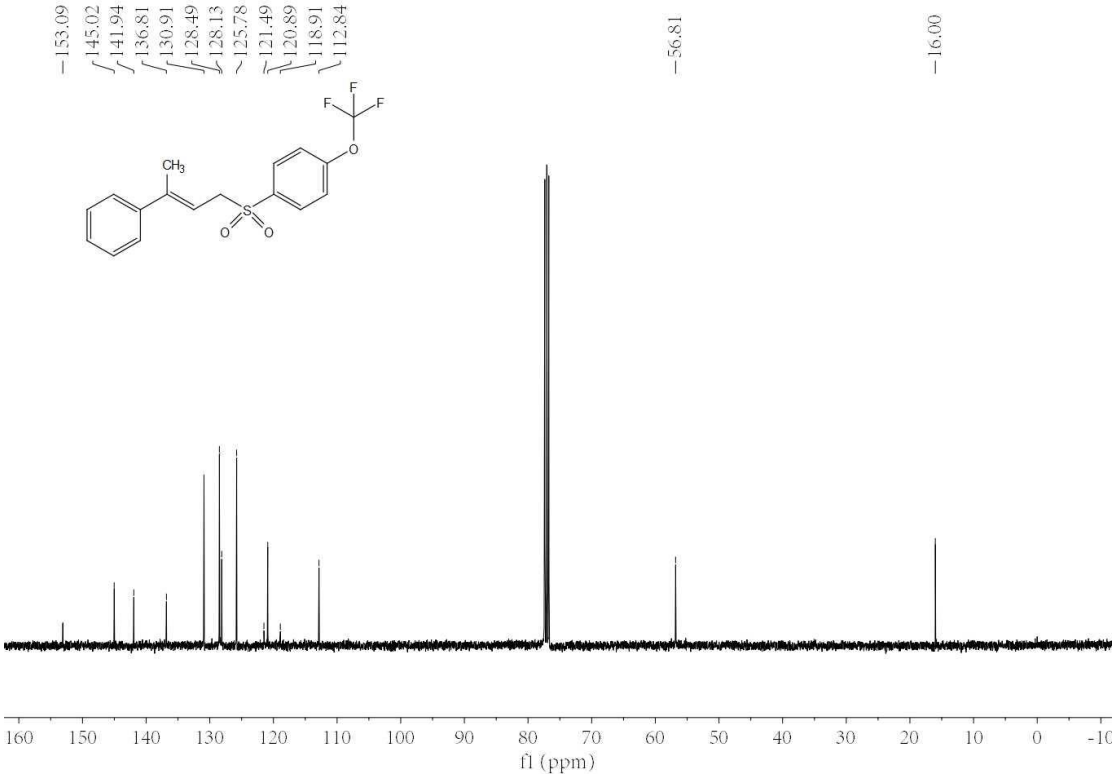
^{13}C NMR of **3ja** (100 MHz, $CDCl_3$)



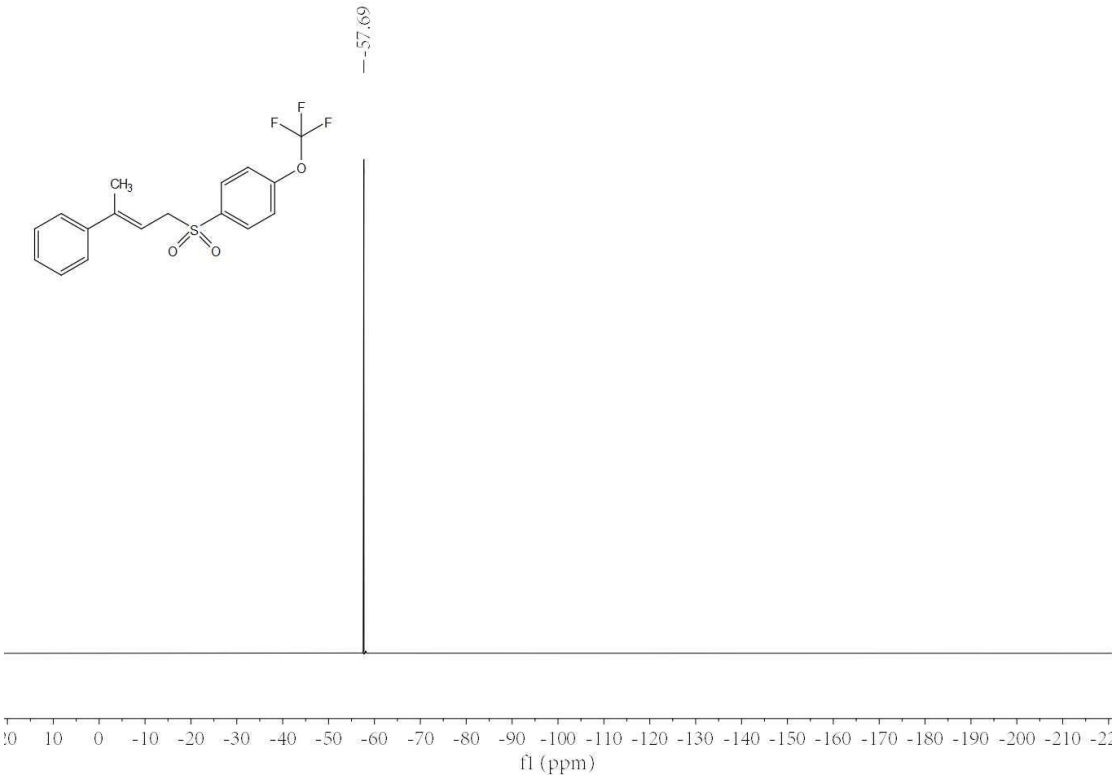
^{1}H NMR of **3ka** (400 MHz, $CDCl_3$)



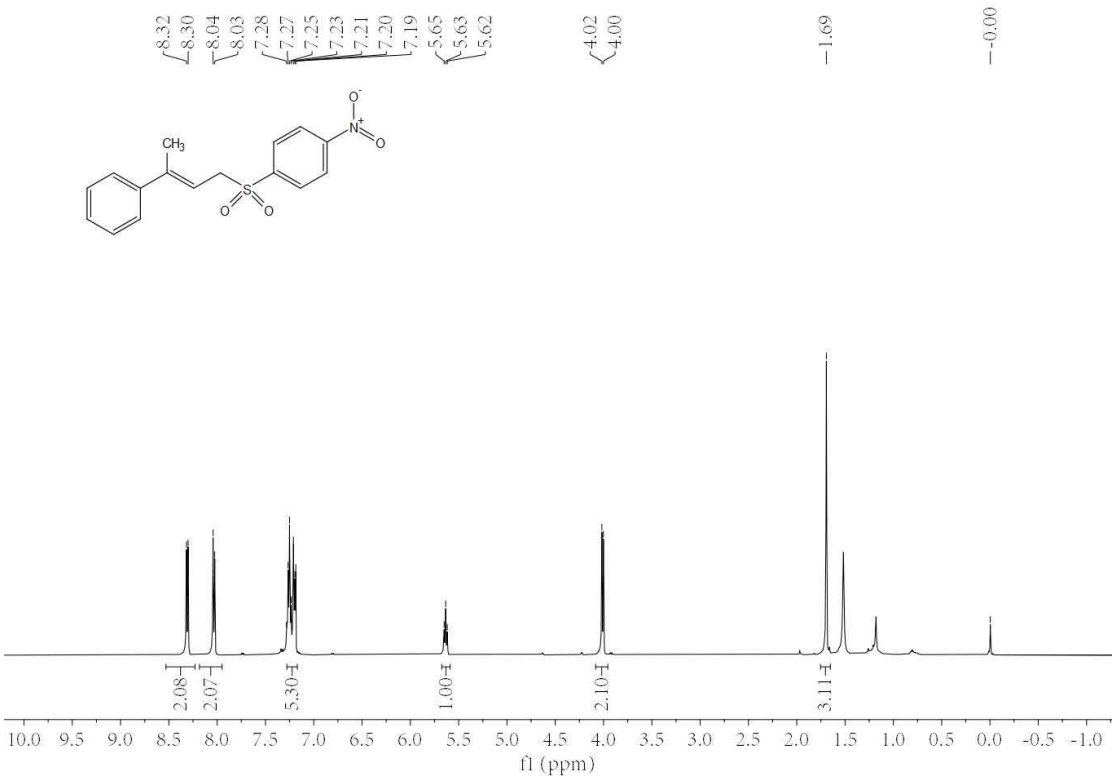
^{13}C NMR of **3ka** (100 MHz, $CDCl_3$)



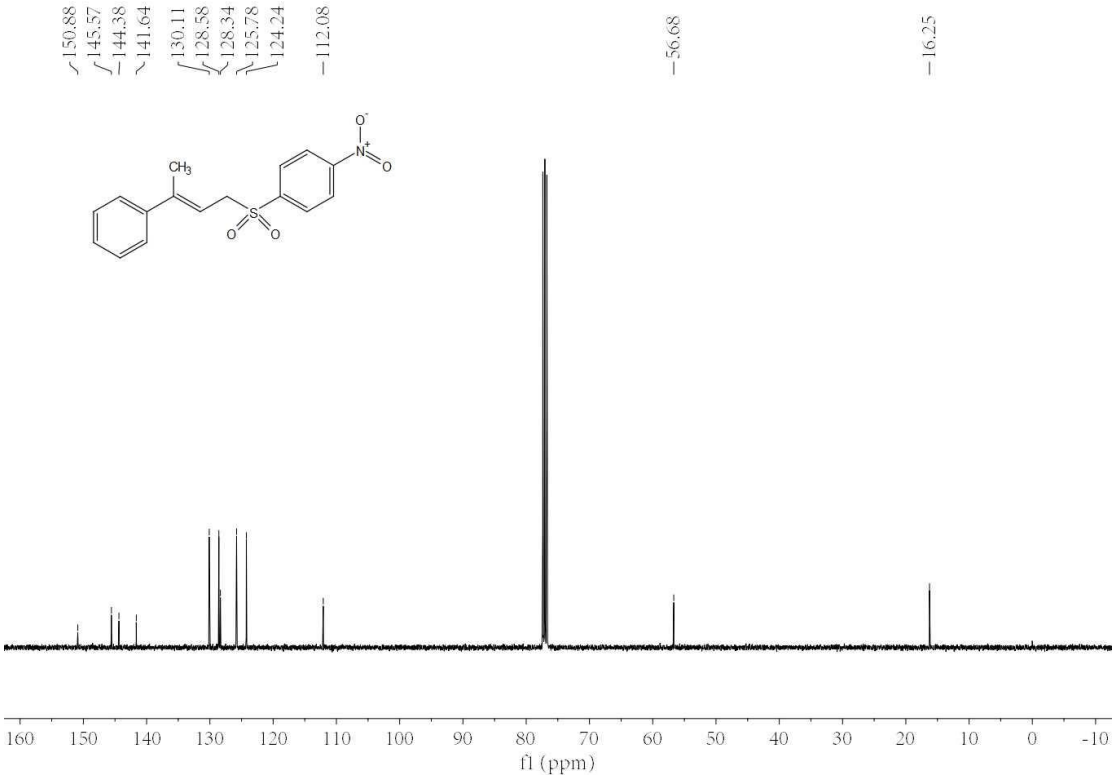
^{19}F NMR of **3ka** (471 MHz, $CDCl_3$)



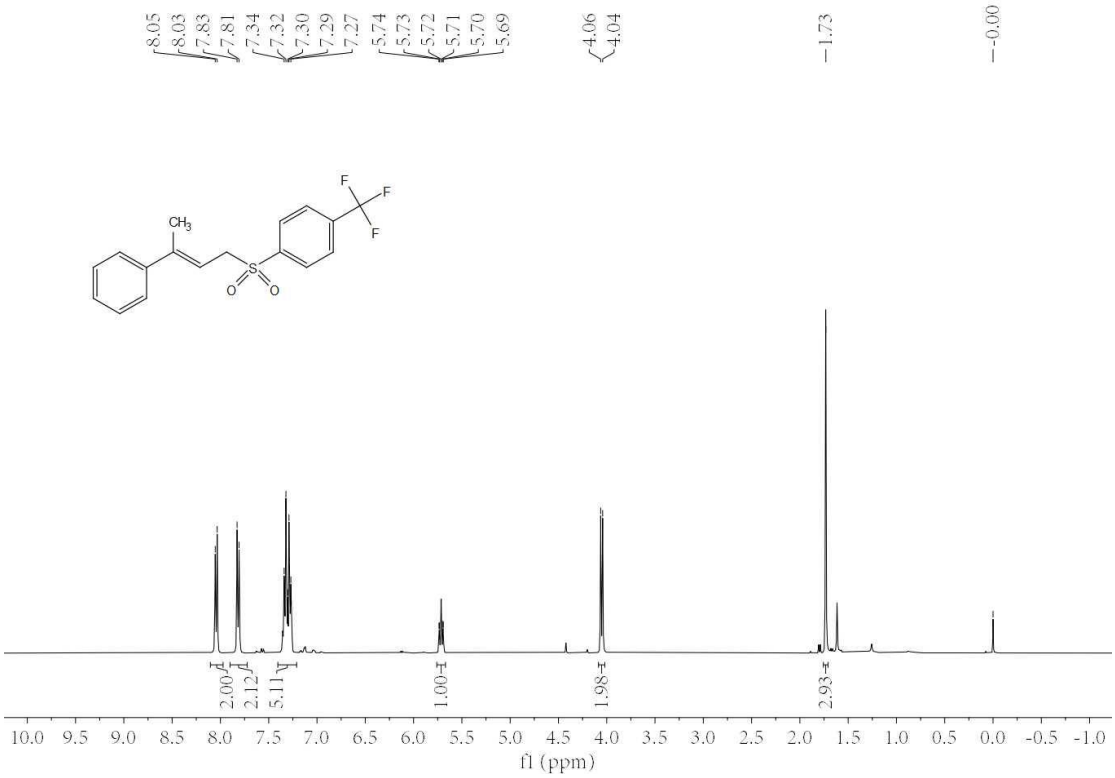
^{1}H NMR of **3la** (500 MHz, $CDCl_3$)



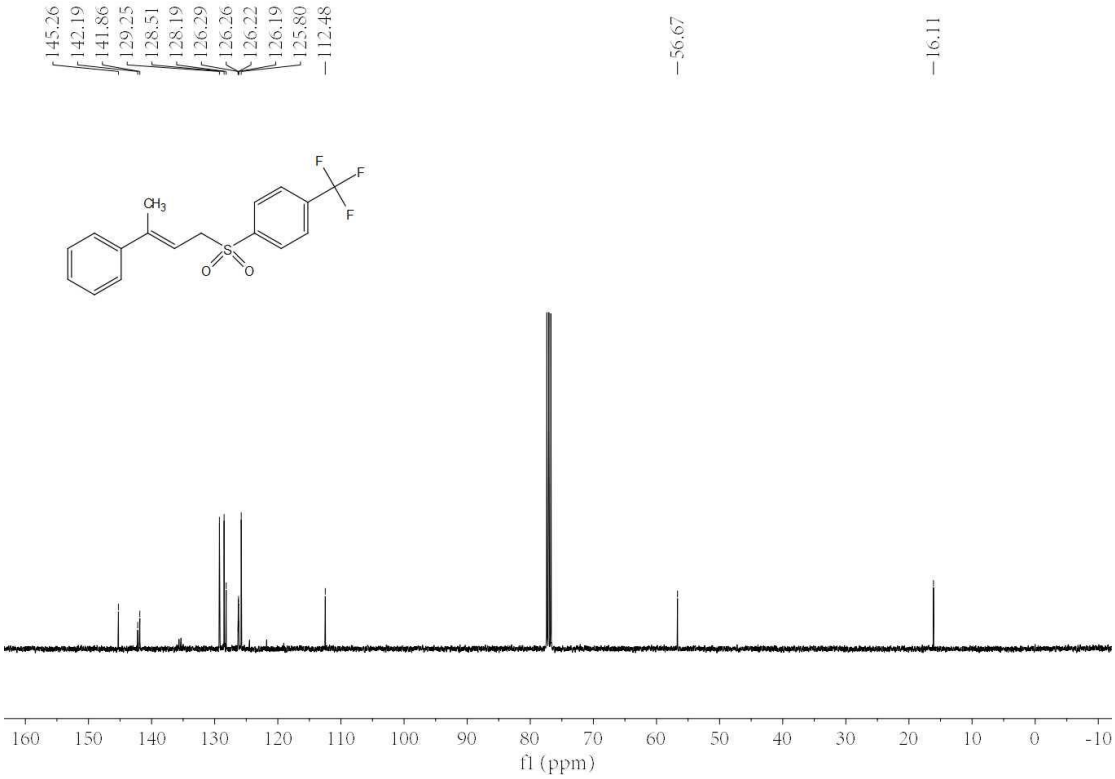
^{13}C NMR of **3la** (100 MHz, $CDCl_3$)



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

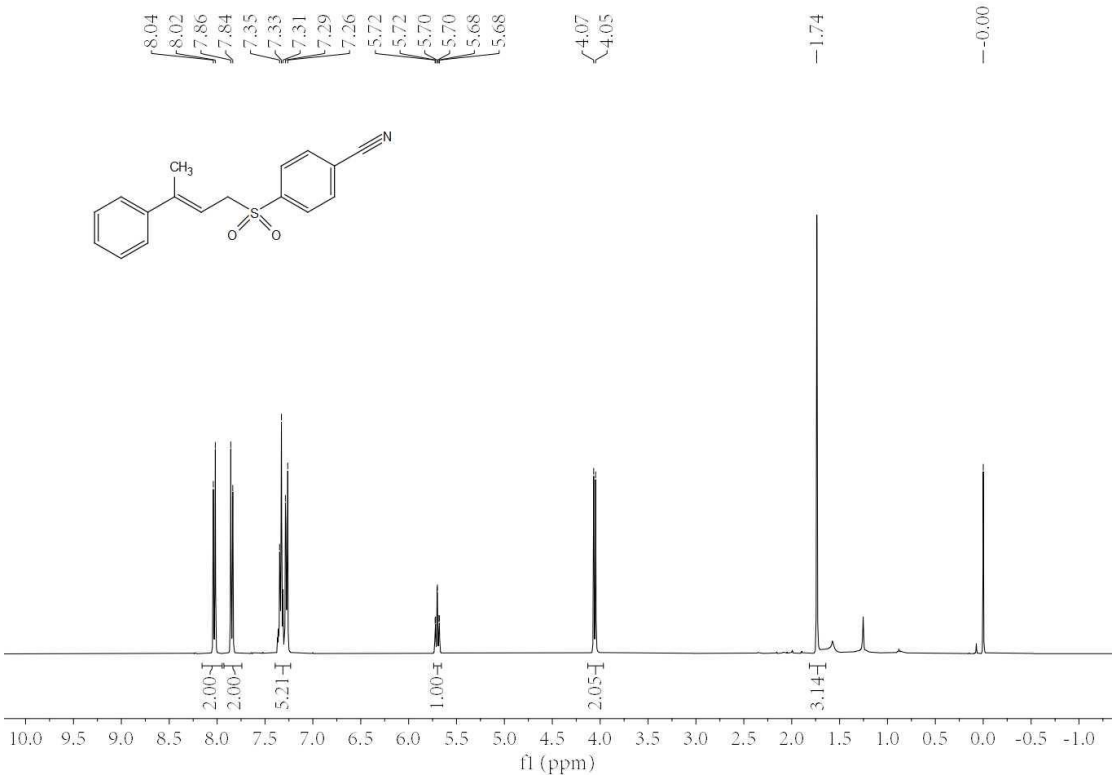


^{13}C NMR of **3ma** (100 MHz, $CDCl_3$)

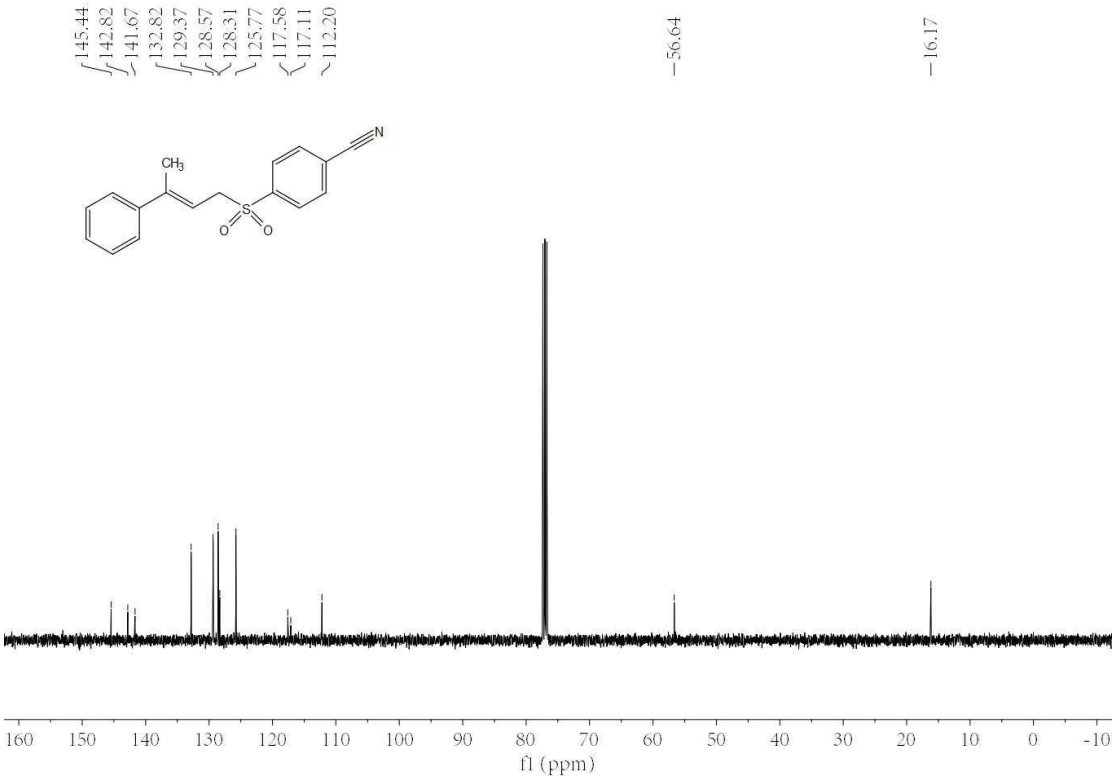


^{19}F NMR of **3ma** (471 MHz, $CDCl_3$)

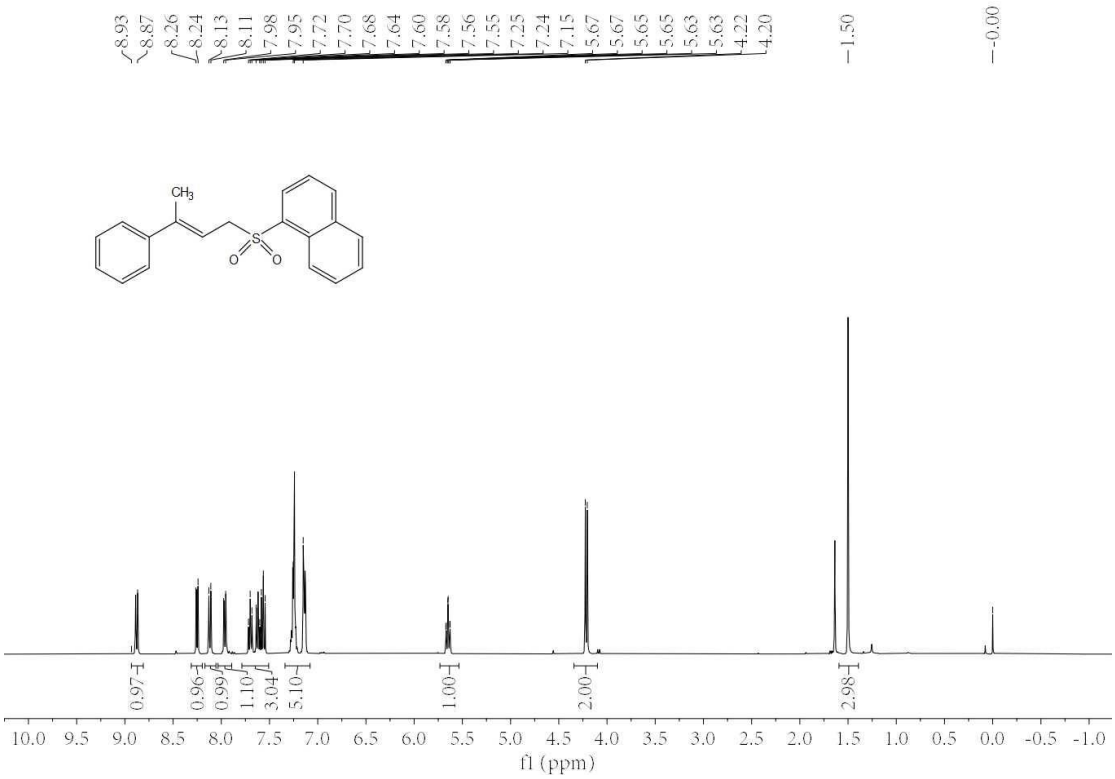
^{1}H NMR of **3na** (400 MHz, $CDCl_3$)



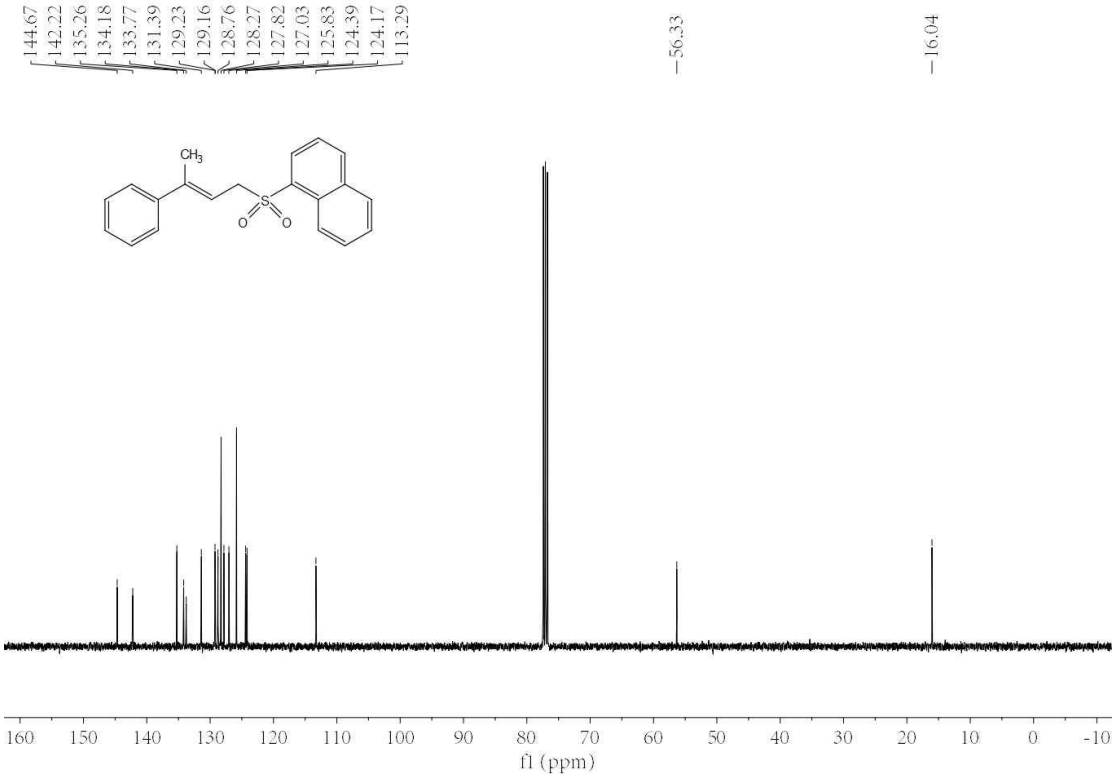
^{13}C NMR of **3na** (100 MHz, $CDCl_3$)



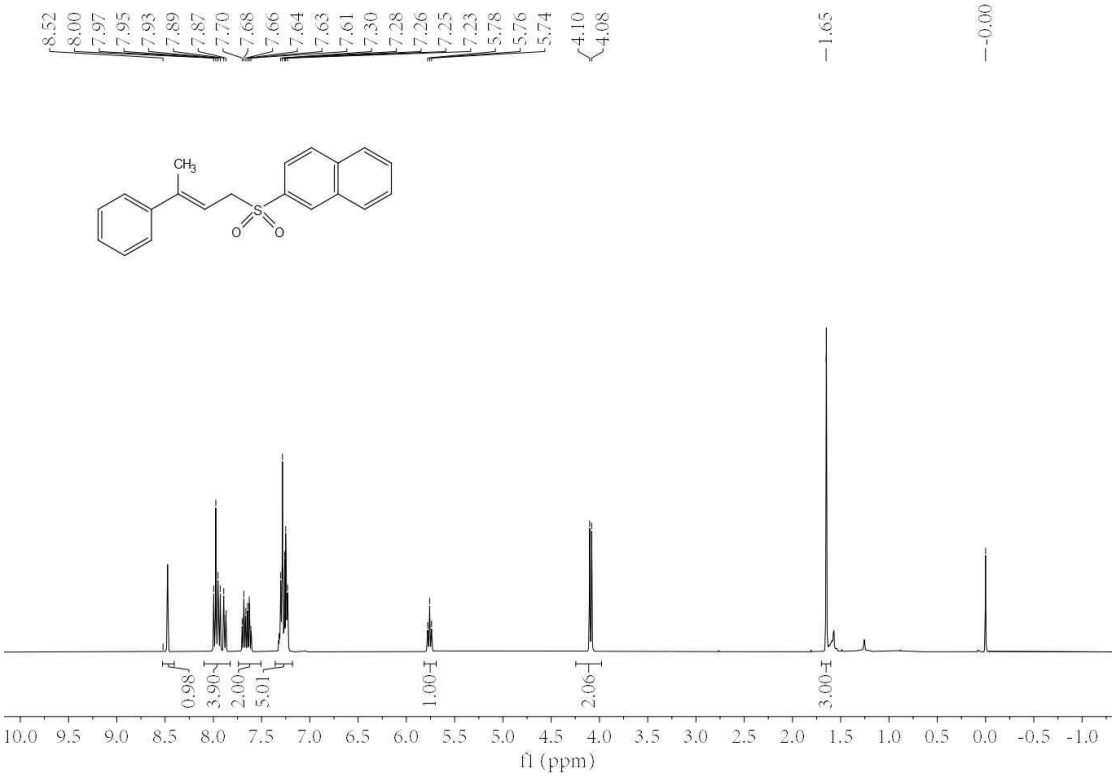
^{1}H NMR of **3oa** (400 MHz, $CDCl_3$)



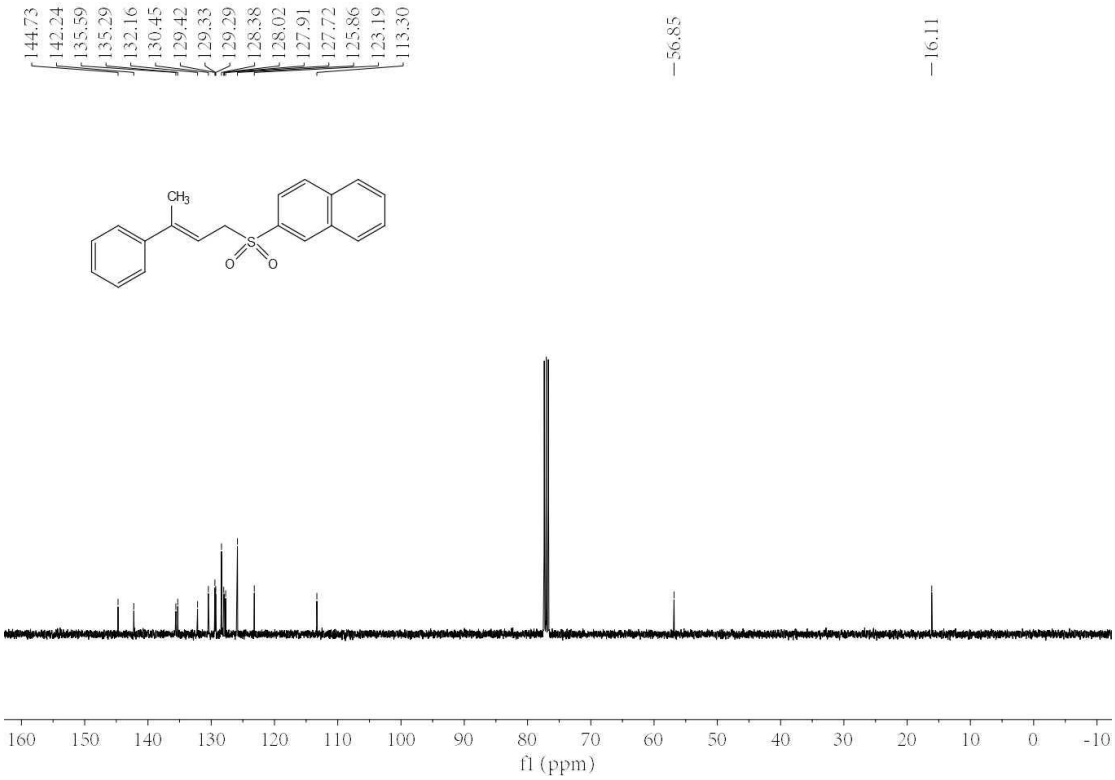
^{13}C NMR of **3oa** (100 MHz, $CDCl_3$)



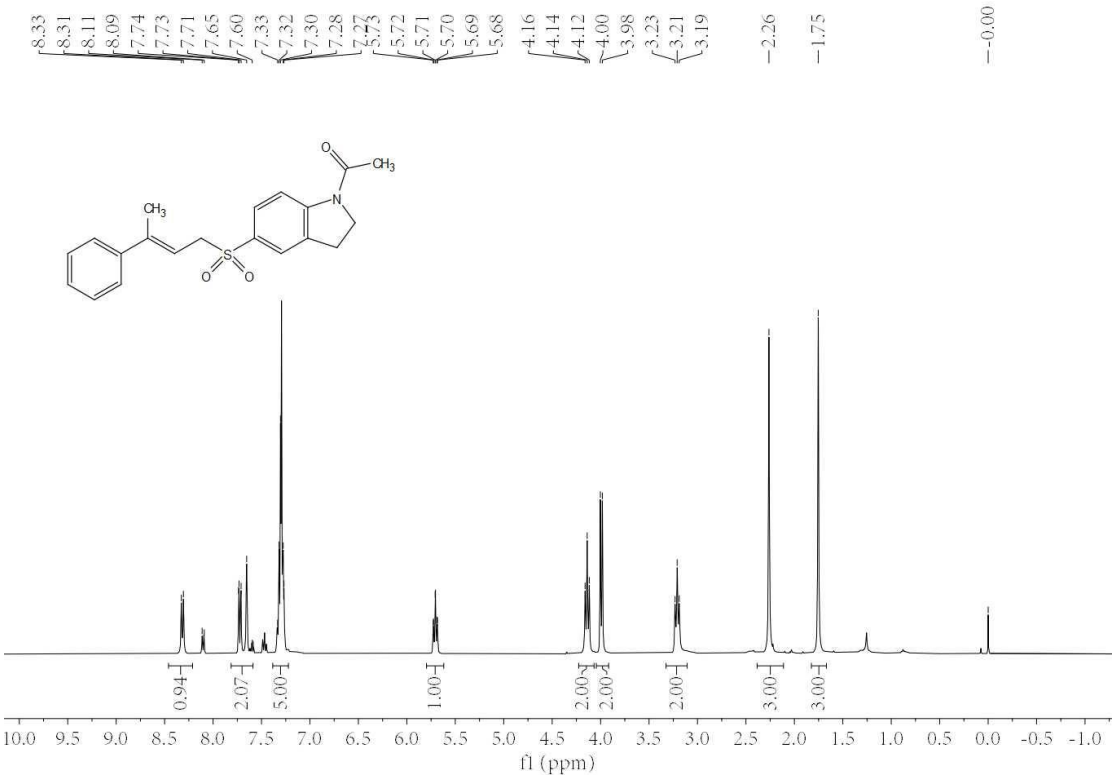
^{1}H NMR of **3pa** (400 MHz, $CDCl_3$)



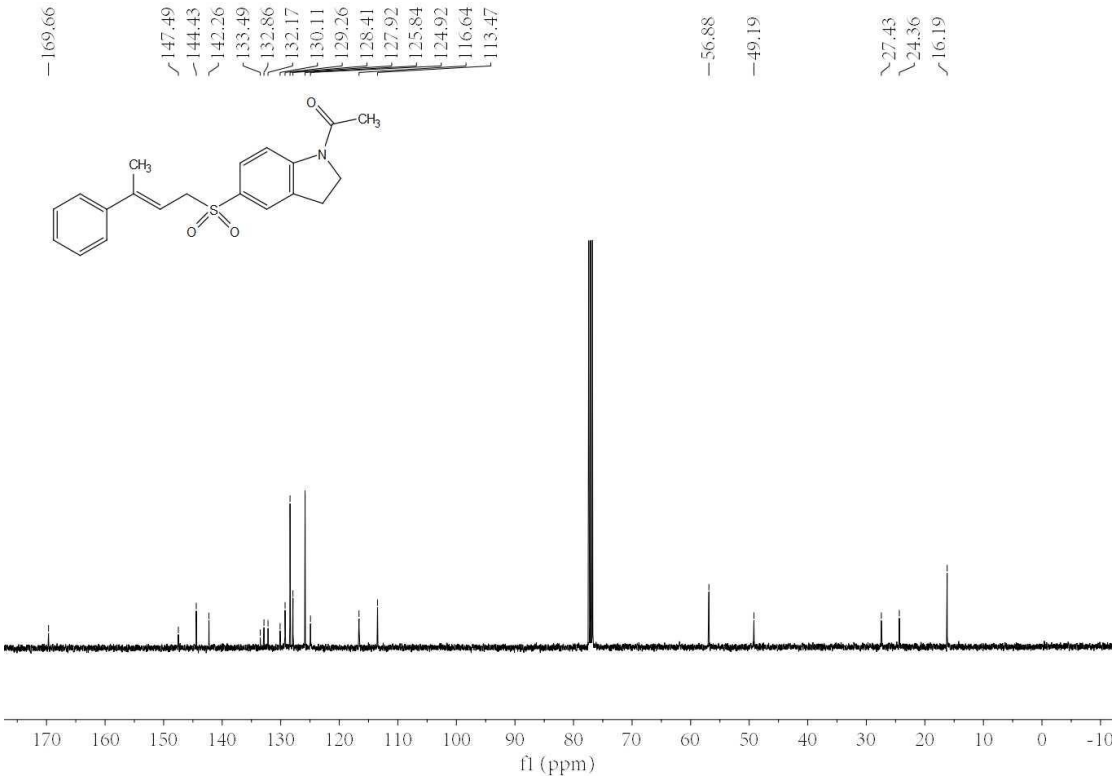
^{13}C NMR of **3pa** (100 MHz, $CDCl_3$)



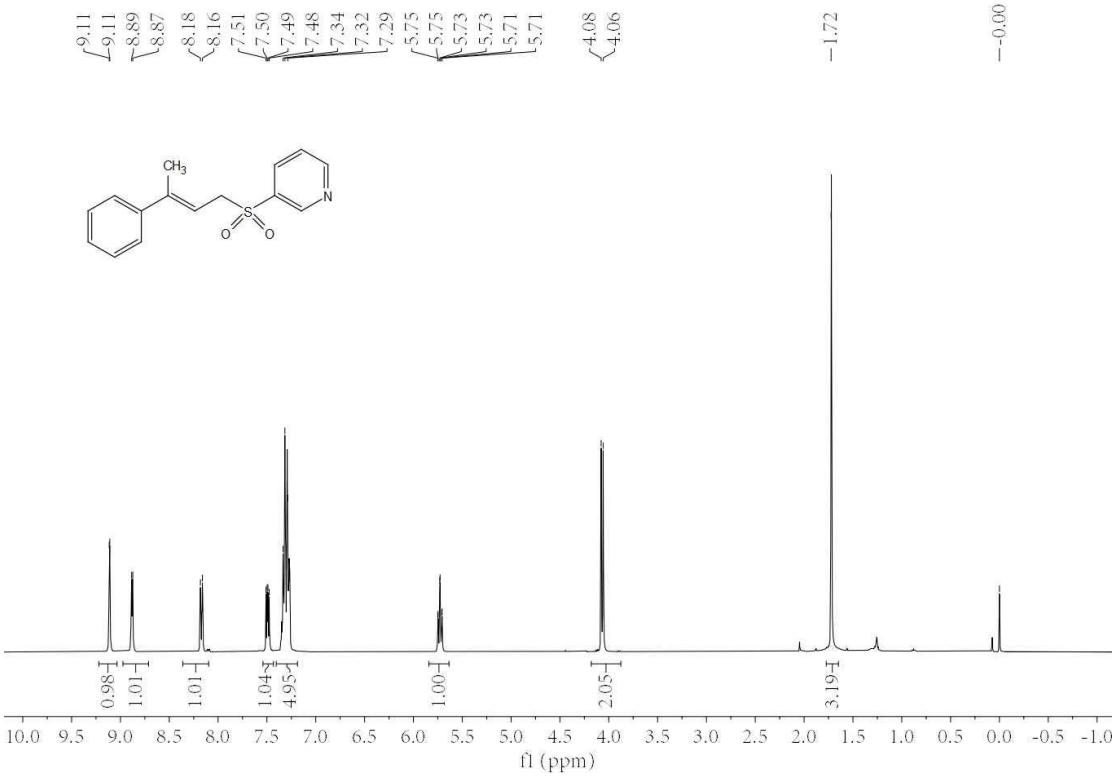
^{1}H NMR of **3qa** (400 MHz, $CDCl_3$)



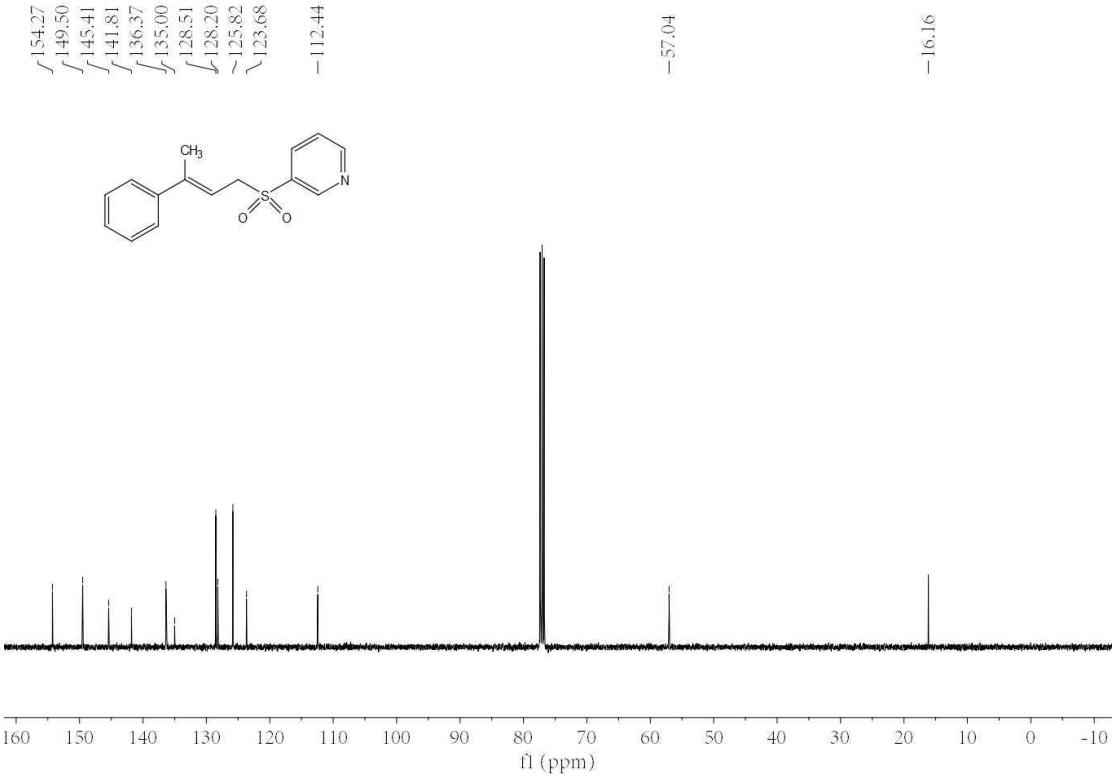
^{13}C NMR of **3qa** (100 MHz, $CDCl_3$)



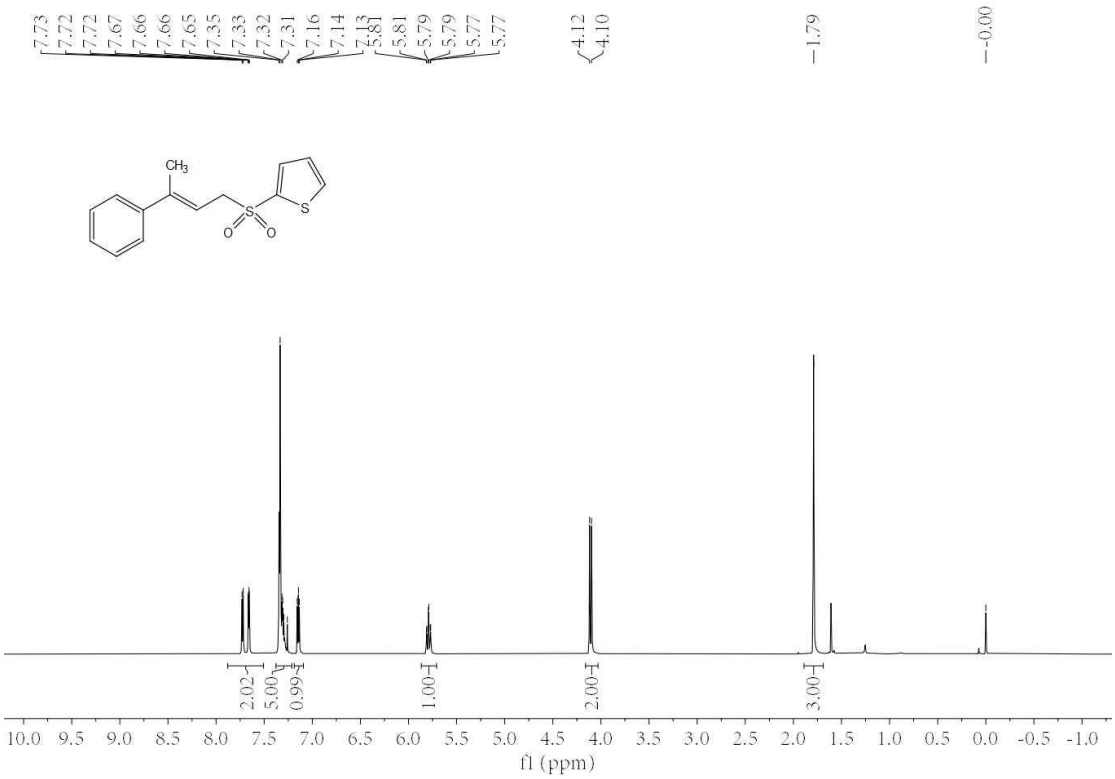
^{1}H NMR of **3ra** (400 MHz, $CDCl_3$)



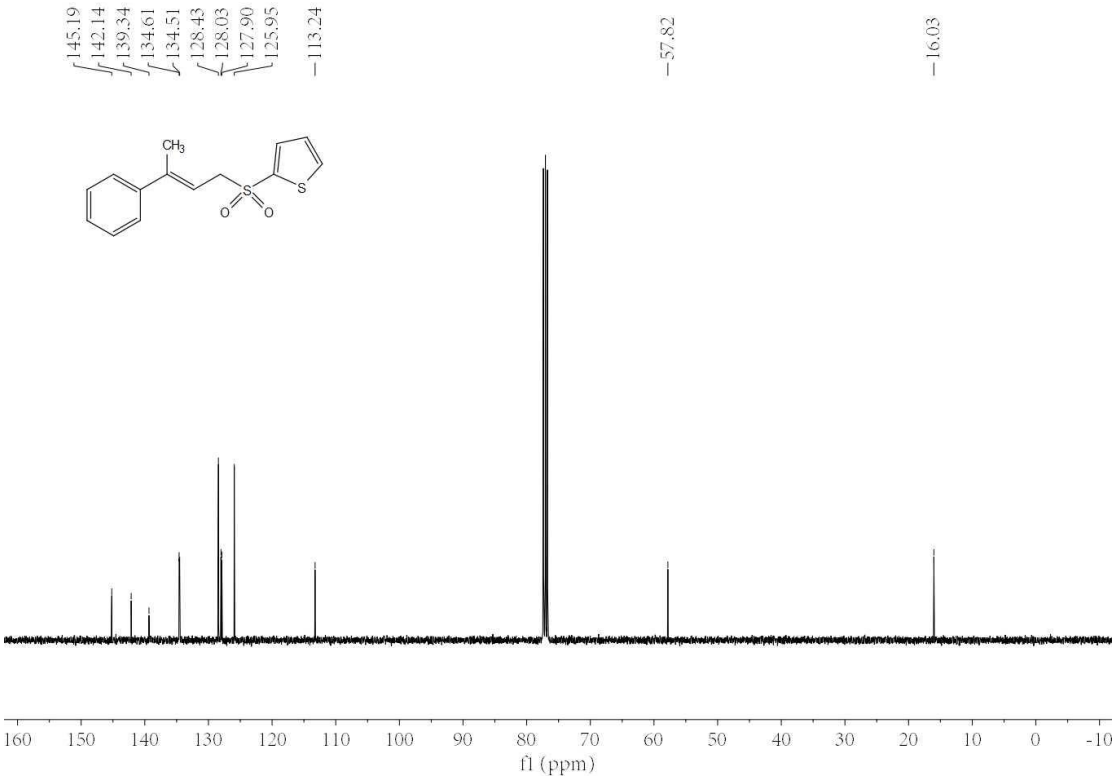
^{13}C NMR of **3ra** (100 MHz, $CDCl_3$)



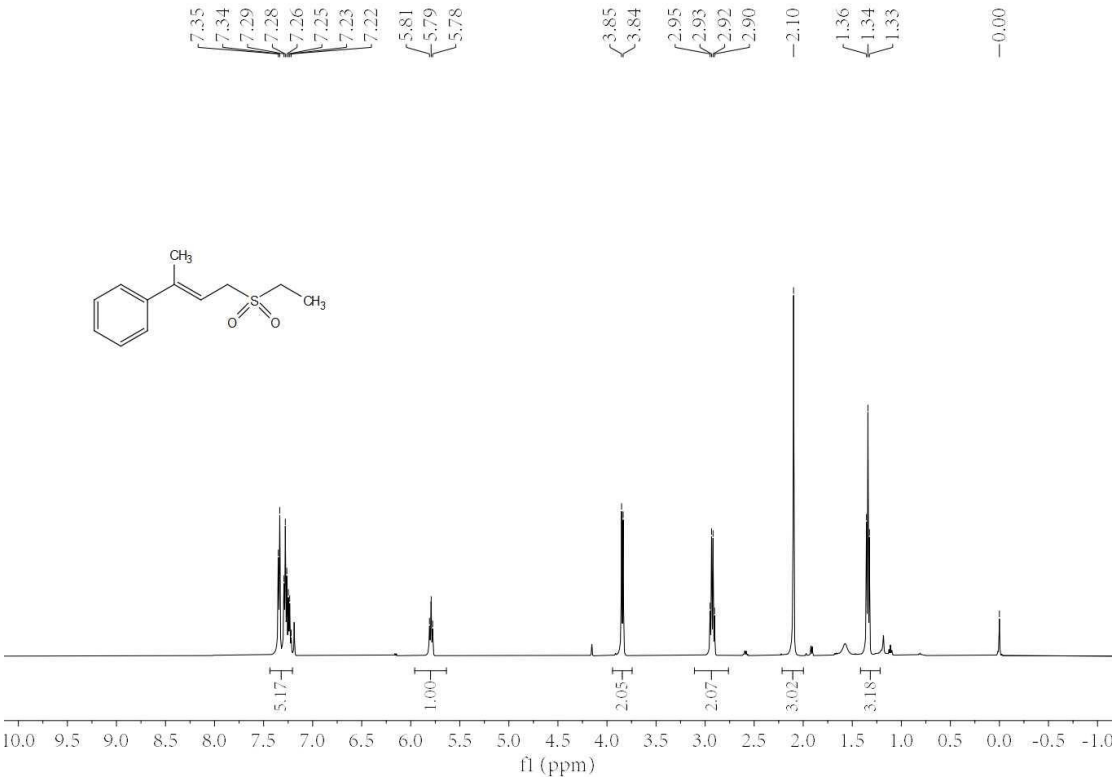
^{1}H NMR of **3sa** (400 MHz, $CDCl_3$)



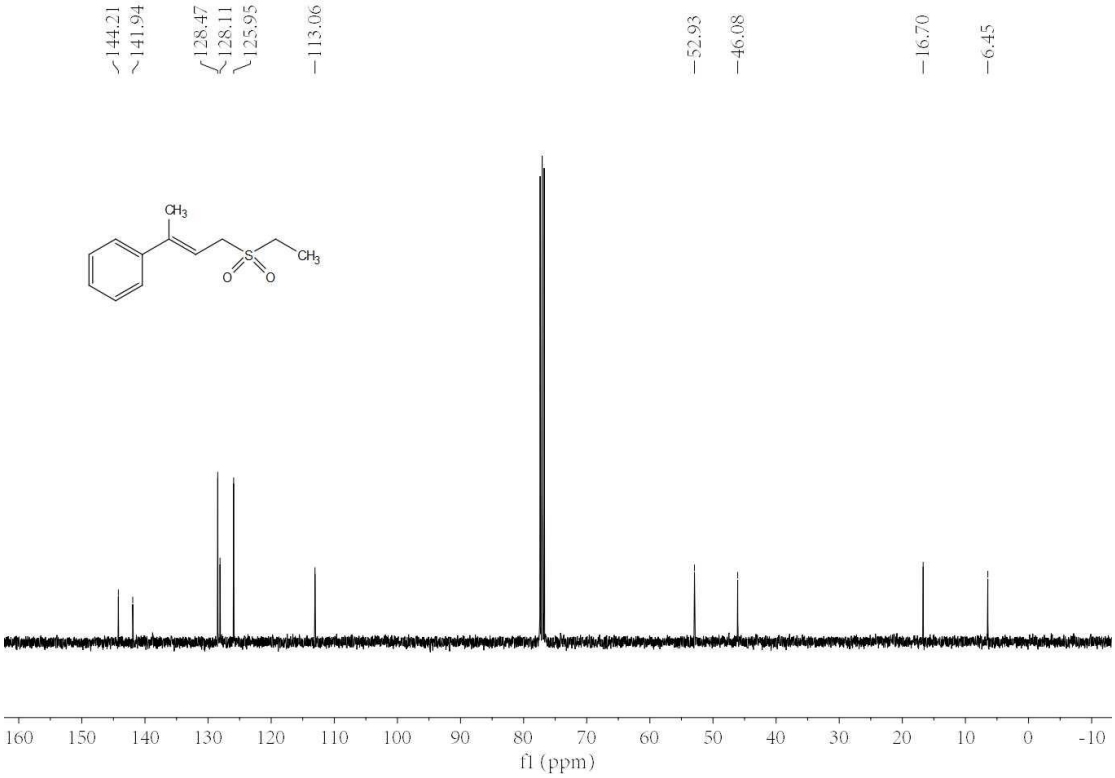
^{13}C NMR of **3sa** (100 MHz, $CDCl_3$)



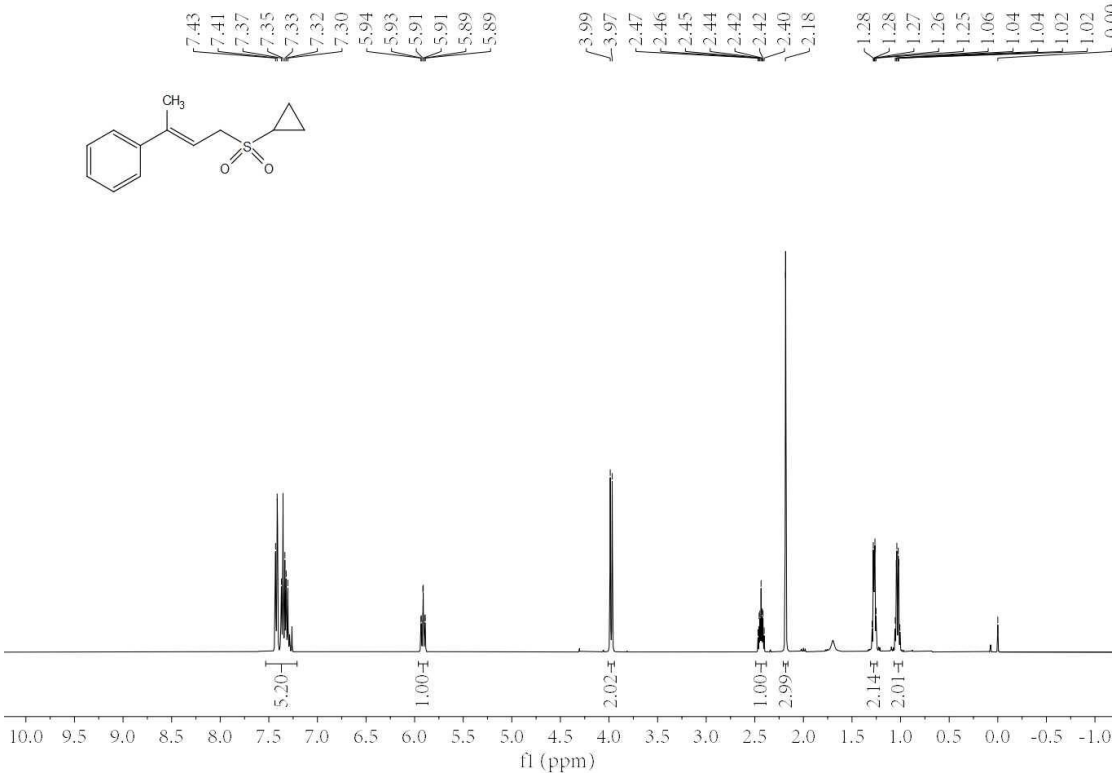
^{1}H NMR of **3ta** (500 MHz, $CDCl_3$)



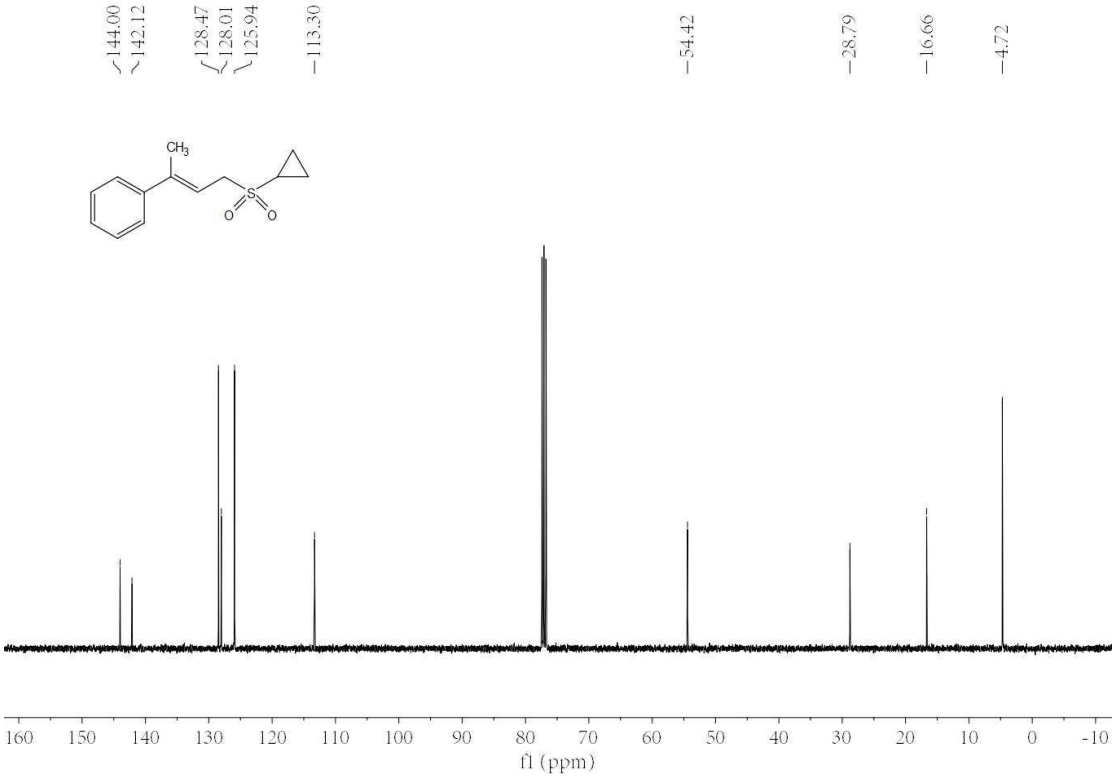
^{13}C NMR of **3ta** (100 MHz, $CDCl_3$)



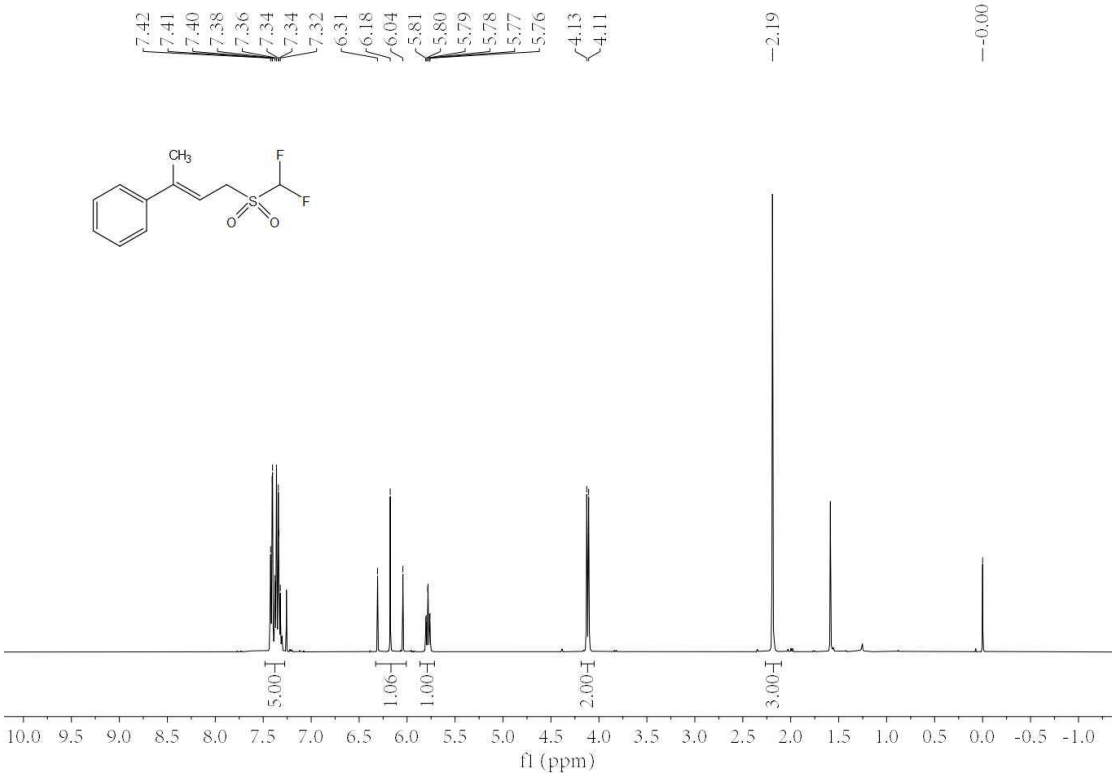
^{1}H NMR of **3ua** (400 MHz, $CDCl_3$)



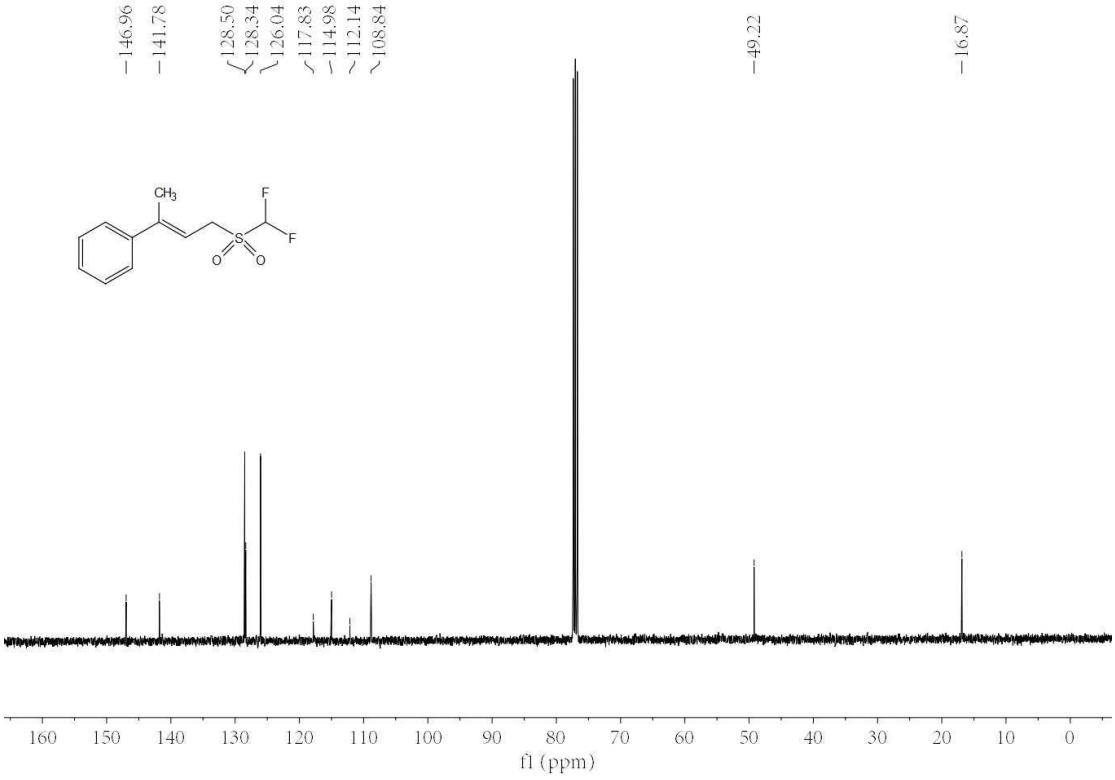
^{13}C NMR of **3ua** (100 MHz, $CDCl_3$)



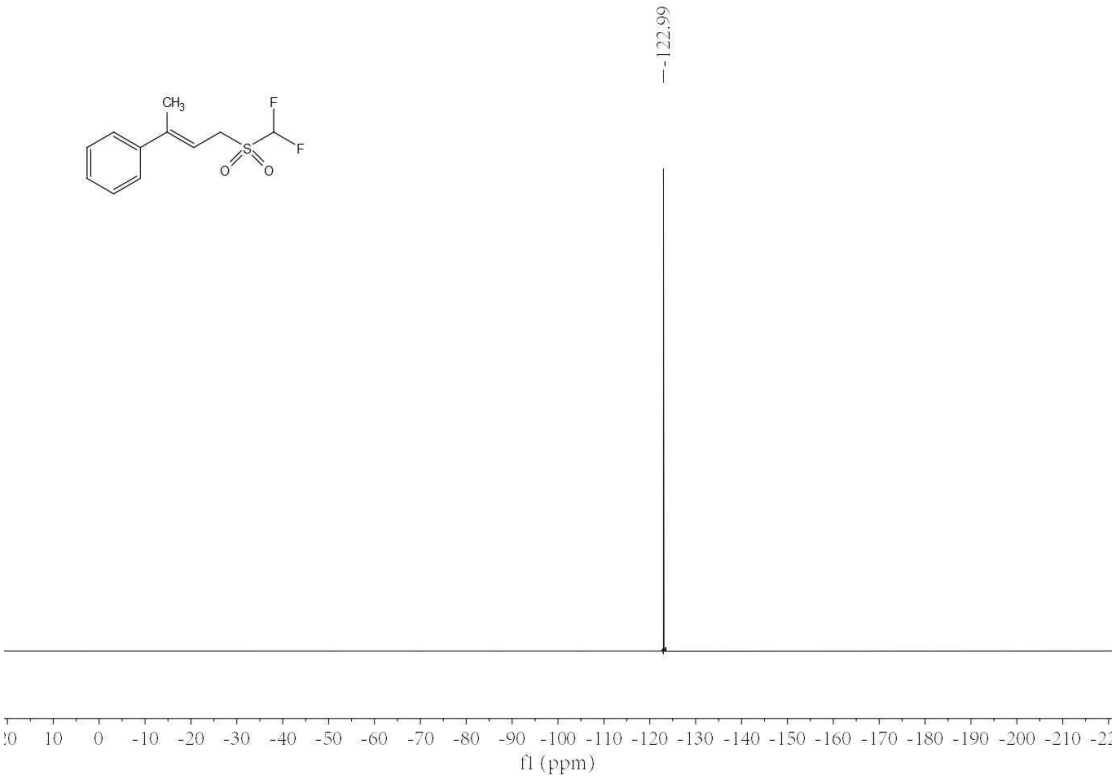
^{1}H NMR of **3va** (400 MHz, $CDCl_3$)



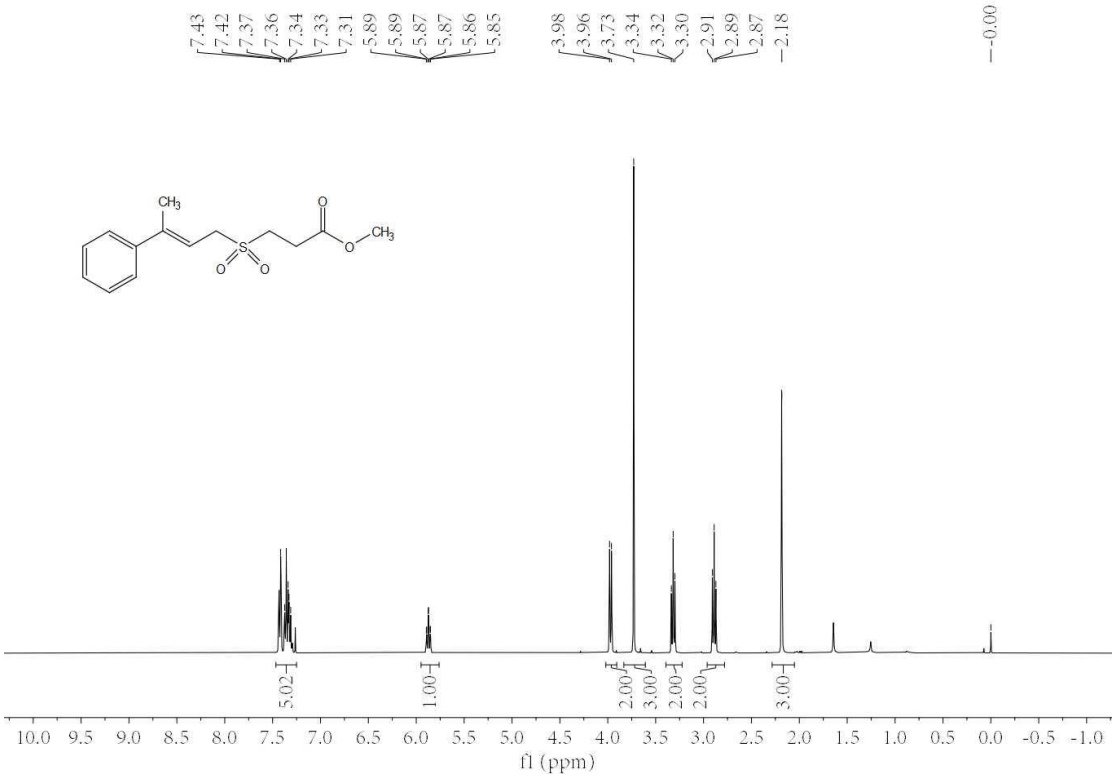
^{13}C NMR of **3va** (100 MHz, $CDCl_3$)



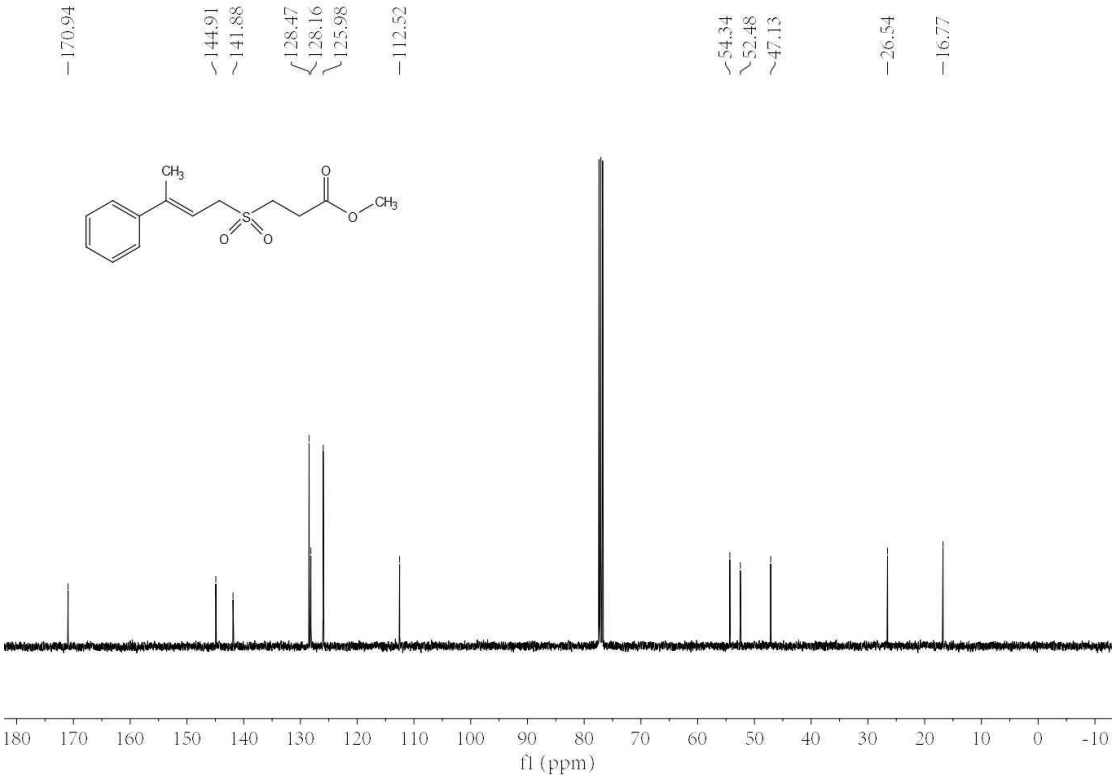
^{19}F NMR of **3va** (471 MHz, $CDCl_3$)



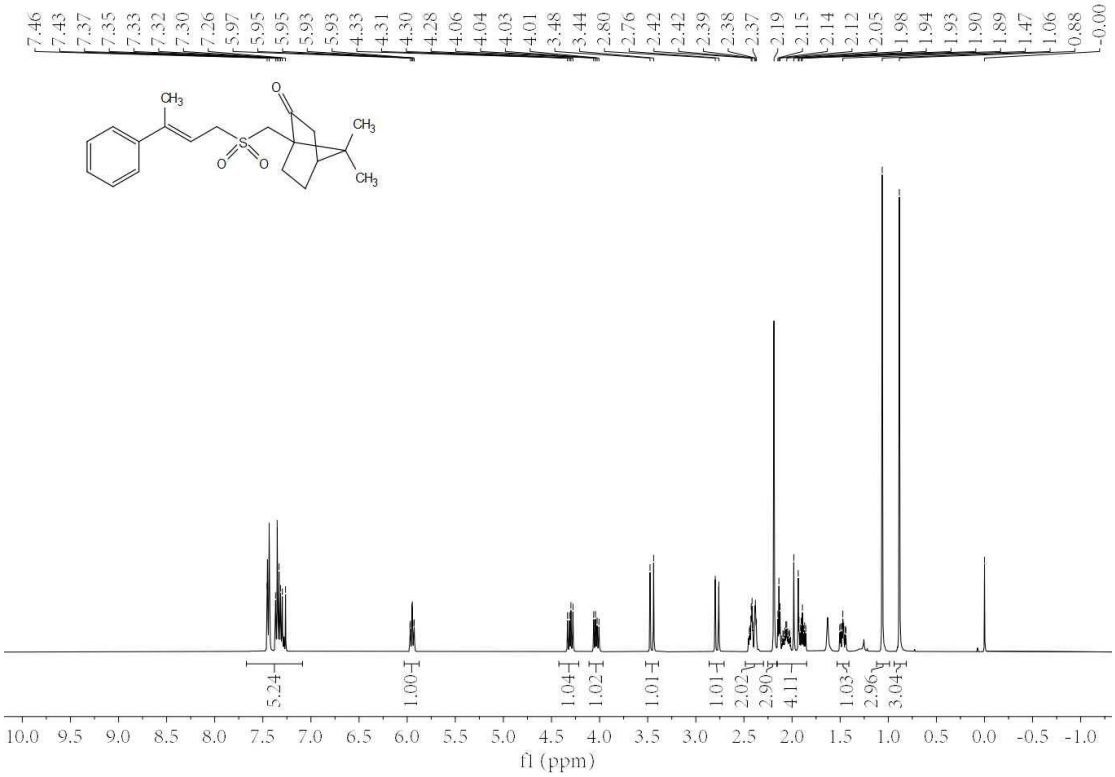
^{1}H NMR of **3wa** (400 MHz, $CDCl_3$)



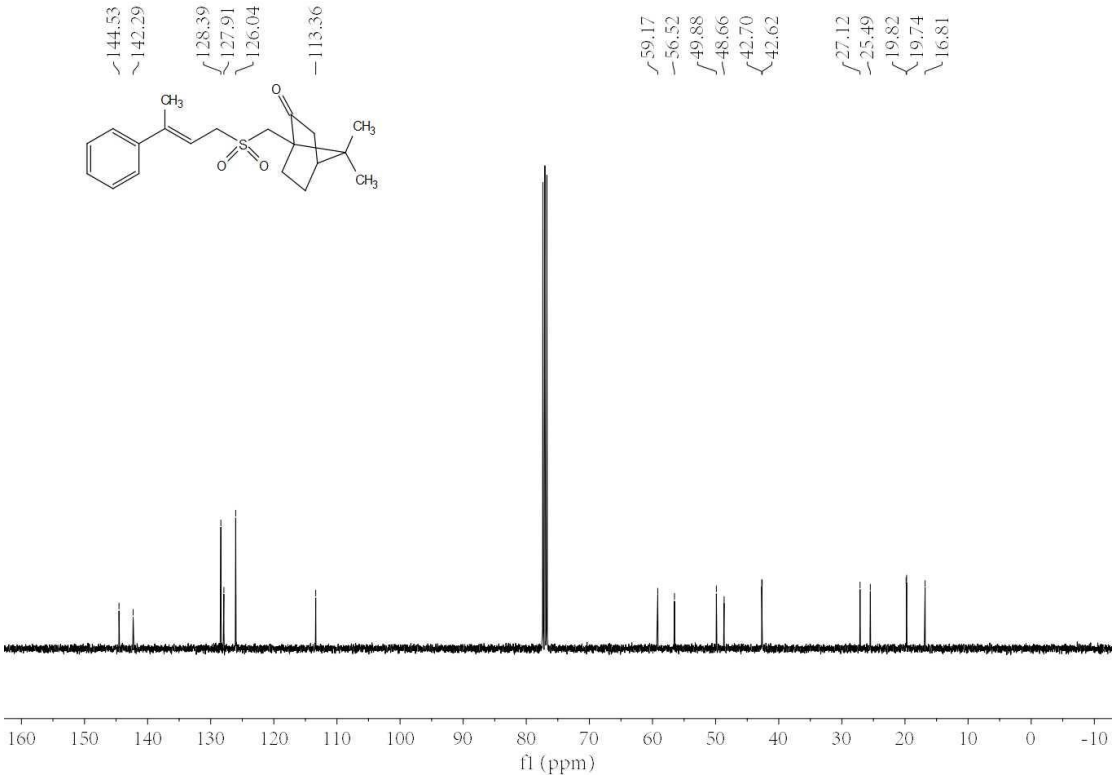
^{13}C NMR of **3wa** (100 MHz, $CDCl_3$)



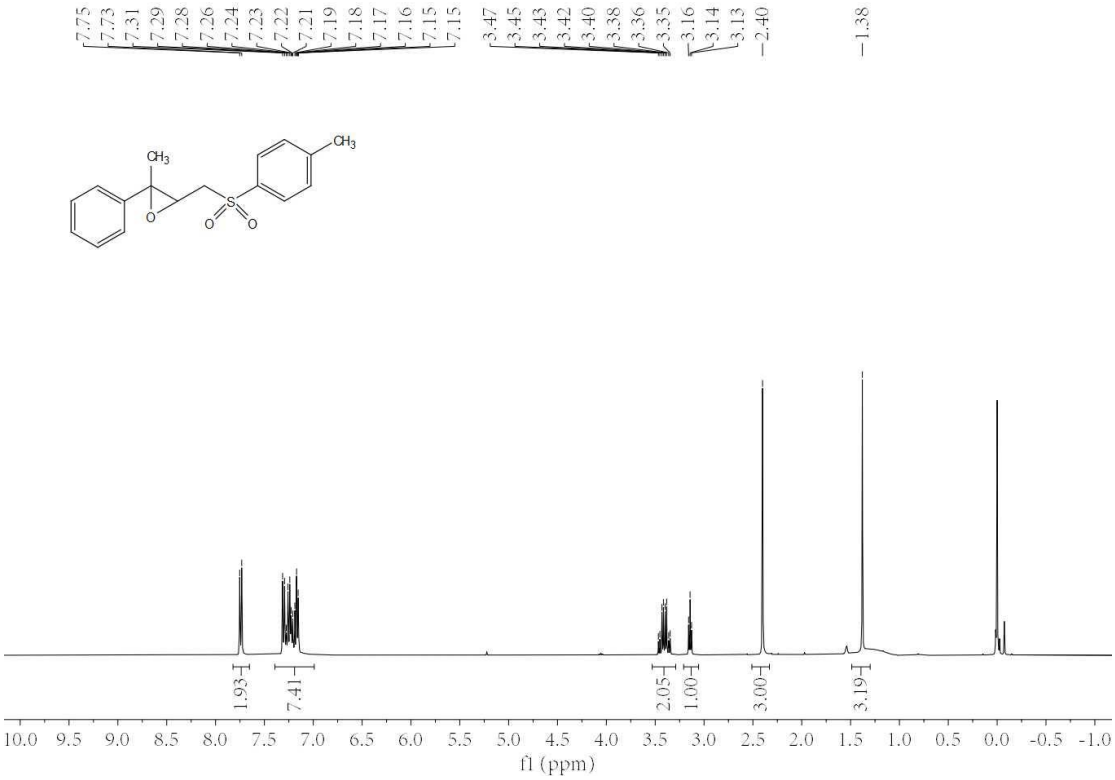
^{1}H NMR of **3xa** (400 MHz, $CDCl_3$)



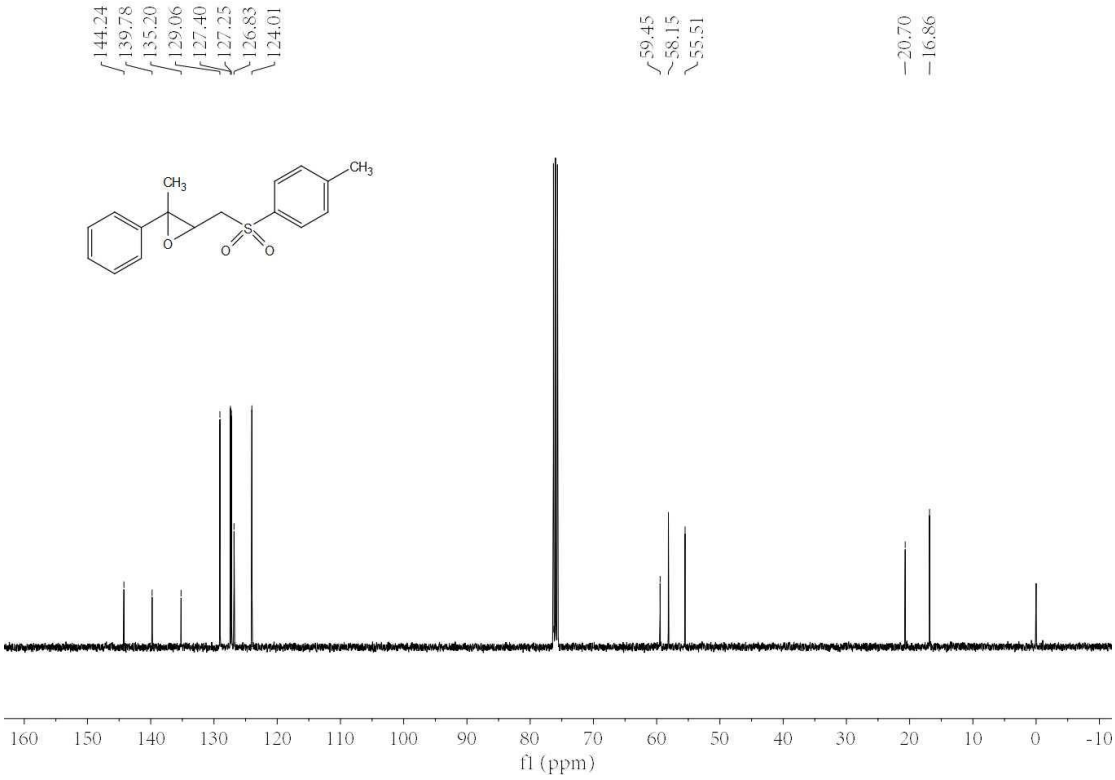
^{13}C NMR of **3xa** (100 MHz, $CDCl_3$)



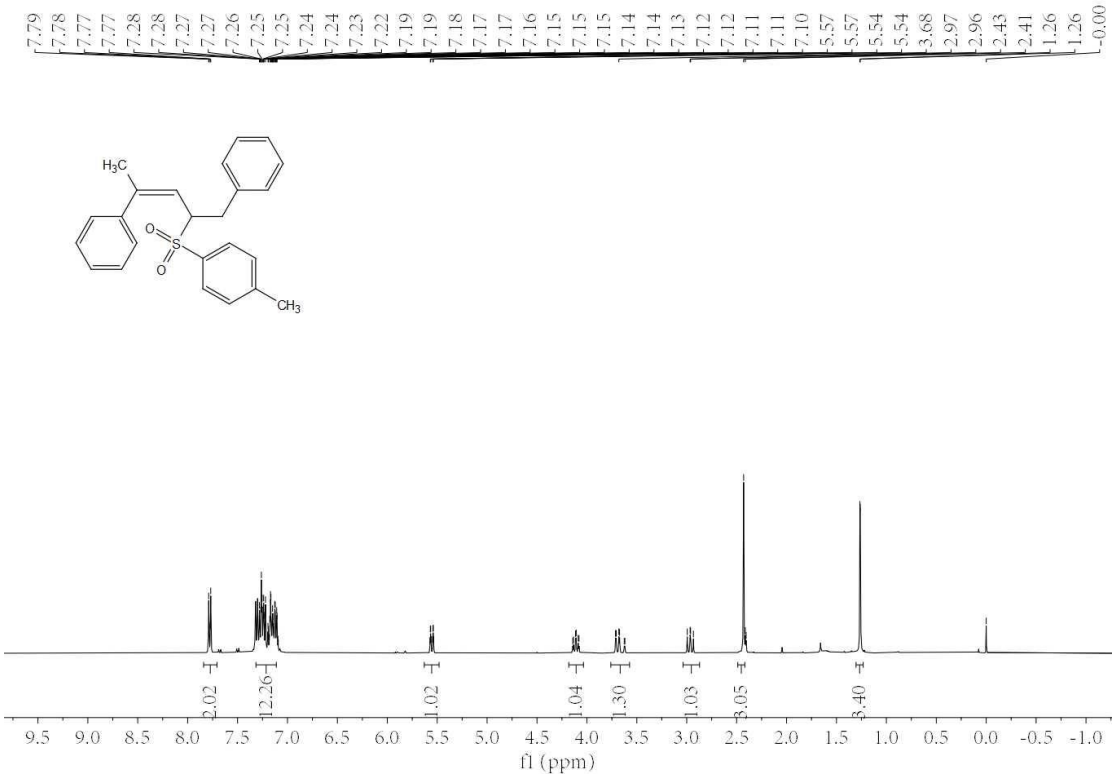
^{1}H NMR of **4aa** (400 MHz, $CDCl_3$)



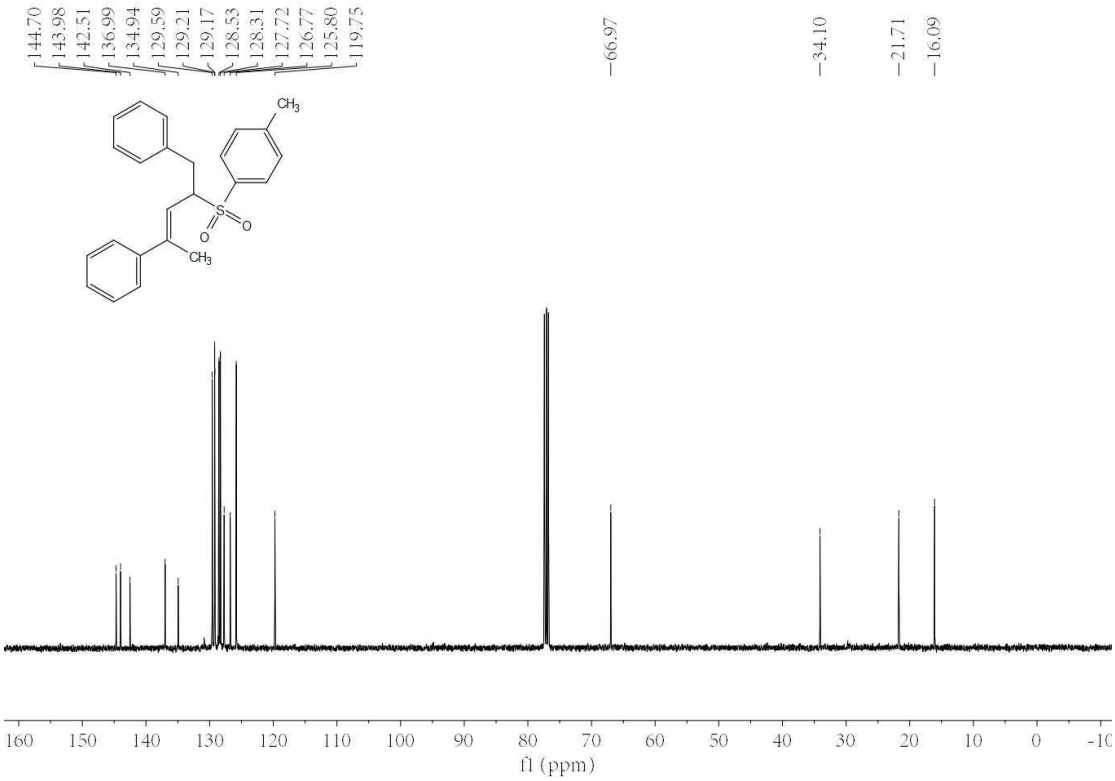
^{13}C NMR of **4aa** (100 MHz, $CDCl_3$)



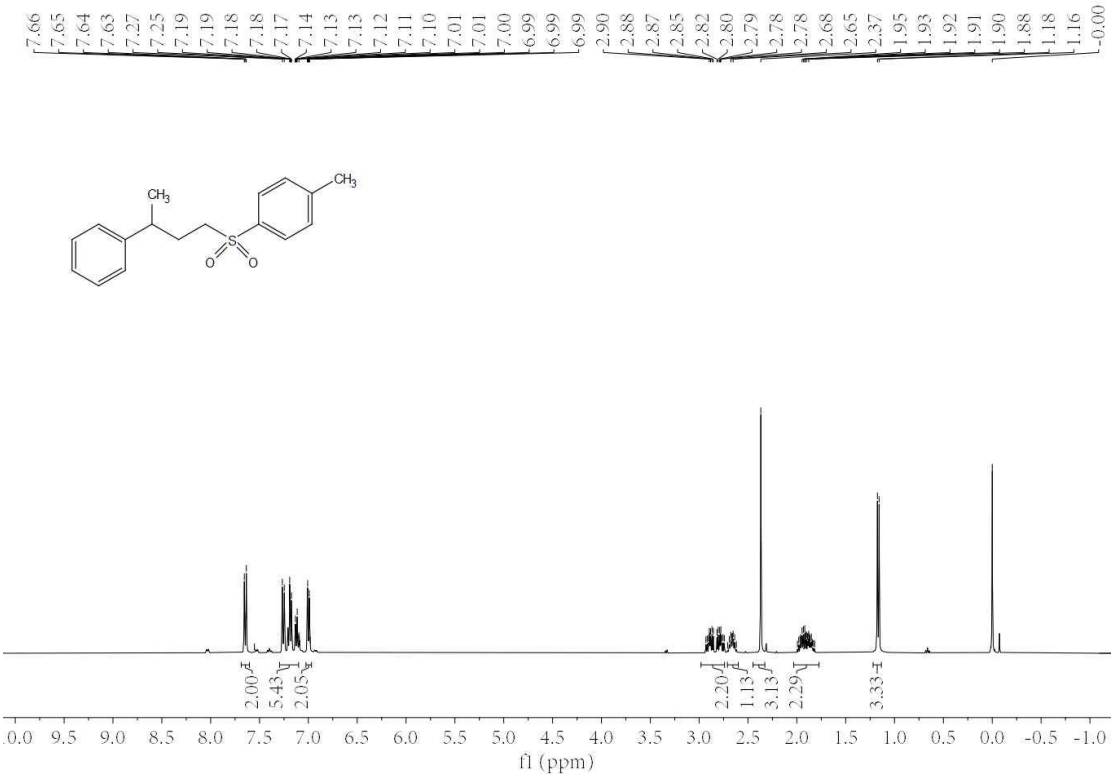
^{1}H NMR of **5aa** (400 MHz, $CDCl_3$)



^{13}C NMR of **5aa** (100 MHz, $CDCl_3$)



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



^{13}C NMR of **6aa** (100 MHz, $CDCl_3$)