Copper-Catalyzed Enantioselective Sulfonylation from Sulfur Dioxide: Generation of Tertiary Propargylic Sulfones

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Supporting Information

Table of Content

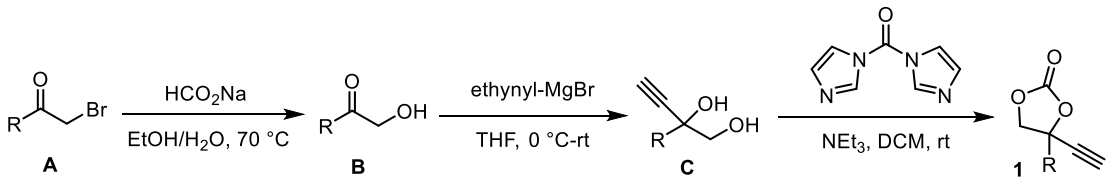
1 Supplementary Notes

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or I_2. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. Electrospray–ionisation HRMS data were acquired on a Q–TOF mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF. The enantiomeric excess values were determined by chiral HPLC with a Shimadzu instrument and a Daicel CHIRALCEL and CHIRALPAK column.

2. The substrates involved in the reactions and their synthesis

2.1 General procedure for the preparation of cyclic carbonates

The propargylic cyclic carbonates **1** are known compounds, which were prepared according to literatures. [1]

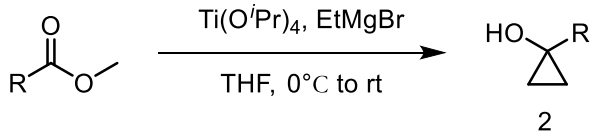


To a mixture of HCOONa (204 mmol), EtOH (80 mL), and H_2O (40 mL) was added compound **A** (30 mmol). The mixture was then stirred for 12 h at 70 ℃ in oil bath. After concentrated under vacuum, the residue was added EtOAc (100 mL) and H_2O (50 mL). The aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and then concentrated under vacuum to give the crude **B**.

To the solution of **B** in THF (50 mL) was dropwisely added ethynylmagnesium bromide (0.5 M in THF, 180 mL) at 0 ℃ with ice-water bath. The mixture was then stirred for 12 h at room temperature. After quenched with NH_4Cl (sat.), the aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to give the crude **C**.

To the solution of **C** in DCM (40 mL) was added sequentially Et_3N (30 mmol) and 1,1'- carbonyldiimidazole (30 mmol). The resulted mixture was stirred for 12 h at room temperature. After concentrated under vacuum, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give the substrate**1**.

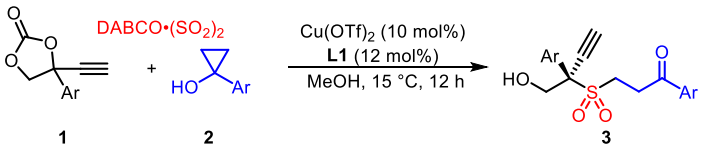
2.2 General procedure for the preparation of cyclopropanol 2.[2]



2

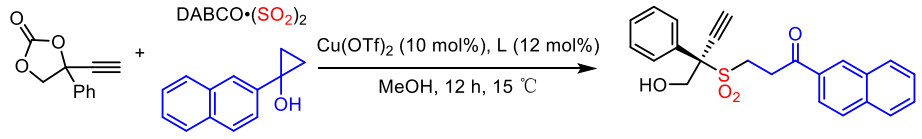
Ethyl magnesium bromide (1.0 M in THF, 17.5 mmol, 3.5 equiv) in THF was added dropwisely over 30 min at -10 °C to a solution of ester (5.0 mmol, 1.0 equiv) and titanium isopropoxide (7.0 mmol, 1.4 equiv) in THF (20 mL, 0.25 M). The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with water, and the precipitated solid was removed by filtration. The filtrate was extracted with ethyl acetate, washed with water, and dried over Na_2SO_4. Followed by filtration and concentration, the residue was purified by column chromatography to afford cyclopropanol **2**.

3. General procedure for the reaction of propargylic cyclic carbonates 1, cyclopropanols 2, and DABCO·$(SO_2)_2$

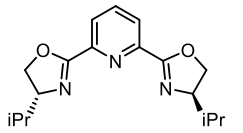


In a screw-capped vial, $Cu(OTf)_2$ (3.6 mg, 10 mol %) and **L1** (4 mg, 12 mol %) were combined with MeOH (2 mL). The resultant solution was stirred for 30 min at room temperature. Propargylic cyclic carbonate **1** (0.1 mmol, 1.0 equiv), cyclopropanol **2** (0.15 mmol, 1.5 equiv), and DABCO.$(SO_2)_2$ (36.0 mg, 0.15 mmol, 1.5 equiv) were added under N_2 atmosphere. The mixture was stirred at 15 °C for 12 h. Then the mixture was purified directly by flash column chromatography (*n*-Hexane/EtOAc (v/v): 3/1 - 8/1) to provide the desired product **3**.

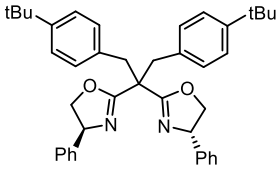
4. Optimization of the ligands



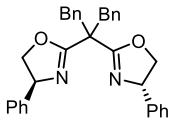
1a 2a 3a



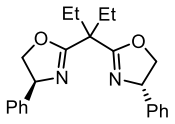
17% yield, 56:44 er



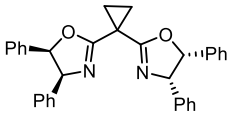
rac



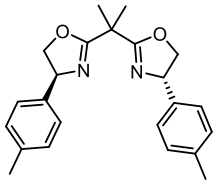
11% yield, 54:46 er



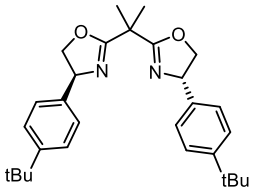
5% yield, 56:44 er



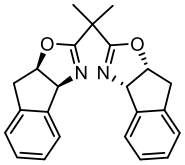
30% yield, 60:40 er



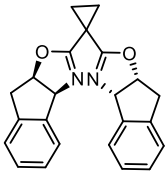
rac



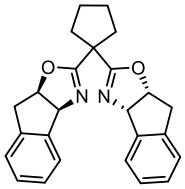
17% yield, 63:27 er



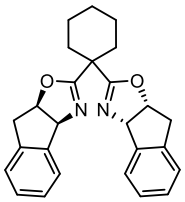
45% yield, 64:36 er



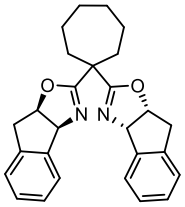
32% yeld, 58:42 er



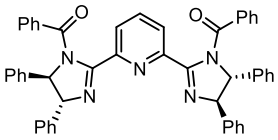
24% yieid, 64:36 er



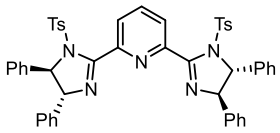
14% yield, 69:31 er



23% yield, 67:33 er



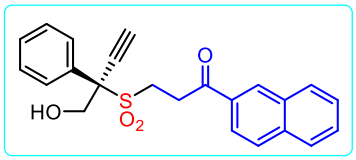
73% yield, 65:35 er



61% yield, 57:43 er

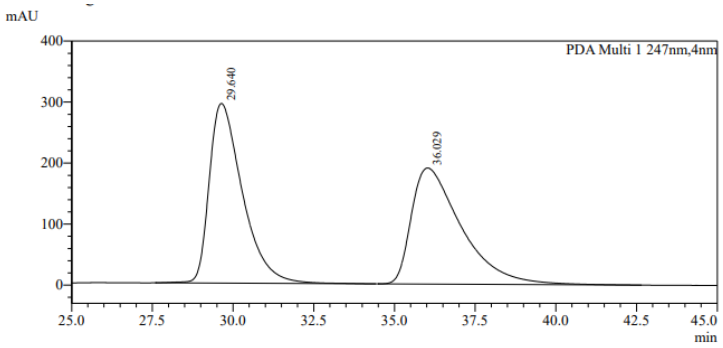
5. Characterization of all products and HPLC chromatograph

(R)-3-((1-hydroxy-2-phenylbut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3a)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 82% yield, 95:5 er. $[\alpha]_D^{25}$= -11.5 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.42 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.91 – 7.81 (m, 4H), 7.59 (dt, *J* = 14.3, 6.9 Hz, 2H), 7.50 – 7.42 (m, 3H), 4.80 (dd, *J* = 11.9, 6.8 Hz, 1H), 4.22 (dd, *J* = 11.9, 7.3 Hz, 1H), 3.91 – 3.81 (m, 1H), 3.70 – 3.43 (m, 3H), 3.09 (s, 1H), 2.76 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 135.9, 133.1, 132.4, 130.4, 130.1, 129.7, 128.9, 127.8, 127.1, 123.5, 81.5, 71.9, 65.6, 45.3, 30.4; HRMS (ESI) for $C_{23}H_{20}O_4S$ $[M+Na]^+$ calcd. 415.1293, found: 415.0984.

HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 30.565 min (major), t_R = 39.384 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
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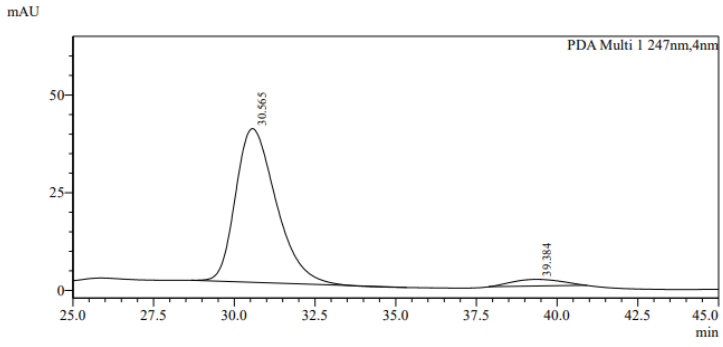
2	36.029	20537291	190298	49.309

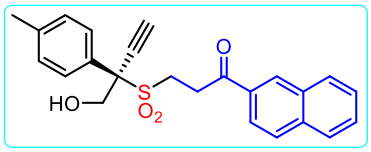


<Peak Table>

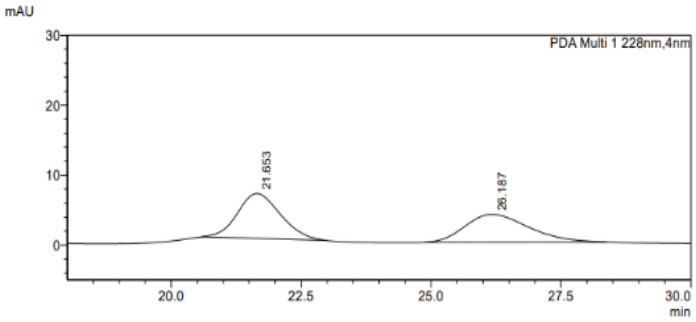
PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	30.565	3453461	39329	94.938
2	39.384	184149	1713	5.062

(R)-3-((1-hydroxy-2-(p-tolyl)but-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3b)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 77% yield, 93.5:6.5 er. $[\alpha]_D^{25}$= 88.2 (c = 0.24, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.41 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.87 (dd, *J* = 8.3, 4.0 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.59 (dt, *J* = 14.4, 7.0 Hz, 2H), 7.25 (s, 2H), 4.77 (dd, *J* = 11.7, 6.0 Hz, 1H), 4.20 (dd, *J* = 11.7, 6.4 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.65 – 3.44 (m, 3H), 3.07 (s, 1H), 2.79 (t, *J* = 6.5 Hz, 1H), 2.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.7, 140.2, 135.9, 133.1, 132.4, 130.1, 129.7, 128.9, 128.7, 127.8, 127.3, 127.0, 123.5, 81.3, 77.5, 71.7, 65.6, 45.2, 30.4, 21.2; HRMS (ESI) for $C_{24}H_{22}O_4S$ $[M+Na]^+$ calcd. 429.1239, found: 429.1136. HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 227 nm, t_R = 21.712 min (major), t_R = 26.270 min (minor).



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PDA Ch1 228nm

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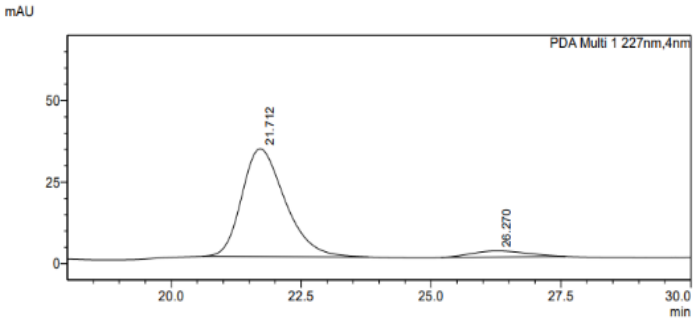
1	21.653	370755	6432	52.160
2	26.187	340051	3979	47.840

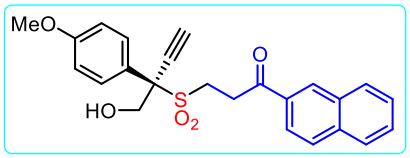


<Peak Table>

PDA Ch1 227nm

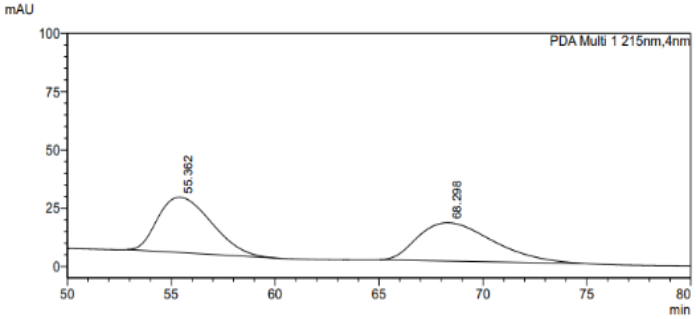
Peak#	Ret. Time	Area	Height	Aera%
1	21.712	1912918	33022	93.278
2	26.270	137847	1859	6.722

(R)-3-((1-hydroxy-2-(4-methoxyphenyl)but-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3c)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 66% yield, 90:10 er. $[\alpha]_D^{25}$= -12.7 (c = 0.2, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.41 (s, 1H), 7.96 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.89 – 7.86 (m, 2H), 7.79 – 7.71 (m, 2H), 7.64 – 7.55 (m, 2H), 7.00 – 6.92 (m, 2H), 4.75 (dd, *J* = 11.8, 6.9 Hz, 1H), 4.19 (dd, *J* = 11.9, 7.2 Hz, 1H), 3.86 – 3.77 (m, 4H), 3.69 – 3.53 (m, 2H), 3.52 – 3.42 (m, 1H), 3.07 (s, 1H), 2.76 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.7, 160.8, 135.9, 133.1, 132.4, 130.2, 129.7, 128.9, 128.7, 127.8, 127.0, 123.5, 122.0, 114.4, 81.2, 71.4, 65.6, 55.4, 45.1, 30.4; HRMS (ESI) for $C_{24}H_{22}O_5S$ $[M+Na]^+$ calcd. 445.1188, found: 445.1084.

HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 215 nm, t_R = 55.996 min (major), t_R = 70.721 min (minor).



<Peak Table>

PDA Ch1 215nm

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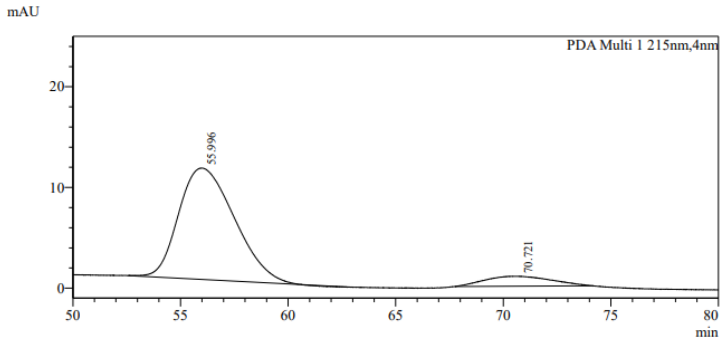
1	55.362	4275313	23725	50.826
2	68.298	4136397	16407	49.174

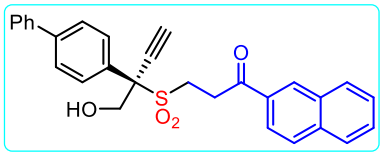


<Peak Table>

PDA Ch1 215nm

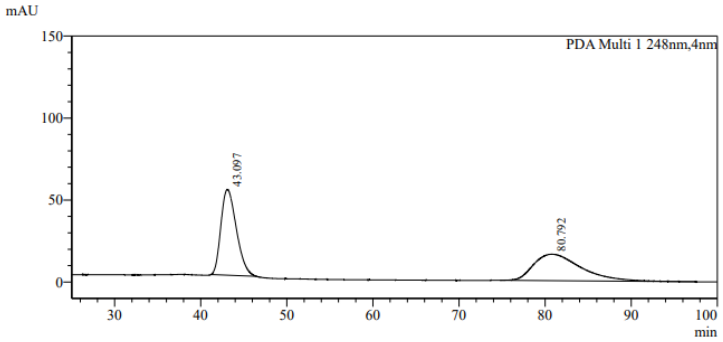
Peak#	Ret. Time	Area	Height	Aera%
1	55.996	1991024	11059	90.362
2	70.721	212351	989	9.638

(R)-3-((2-([1,1'-biphenyl]-4-yl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3d)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 80% yield, 93:7 er. $[\alpha]_D^{25}$= 7.4 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.39 (s, 1H), 7.96 – 7.83 (m, 6H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.51 (m, 4H), 7.40 (m, 3H), 4.82 (dd, *J* = 11.7, 6.5 Hz, 1H), 4.27 (dd, *J* = 11.6, 6.9 Hz, 1H), 3.89 (m, 1H), 3.65 (m, 2H), 3.54 – 3.41 (m, 1H), 3.12 (s, 1H), 2.85 (t, *J* = 6.3 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 142.8, 139.8, 135.9, 133.1, 132.4, 130.1, 129.7, 129.3, 128.8, 127.9, 127.6, 127.1, 123.5, 81.5, 71.8, 65.6, 45.5, 30.5; HRMS (ESI) for $C_{29}H_{24}O_4S$ $[M+Na]^+$ calcd. 491.1395, found: 491.1284.

HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 42.417 min (major), t_R = 80.940 min (minor).



<Peak Table>

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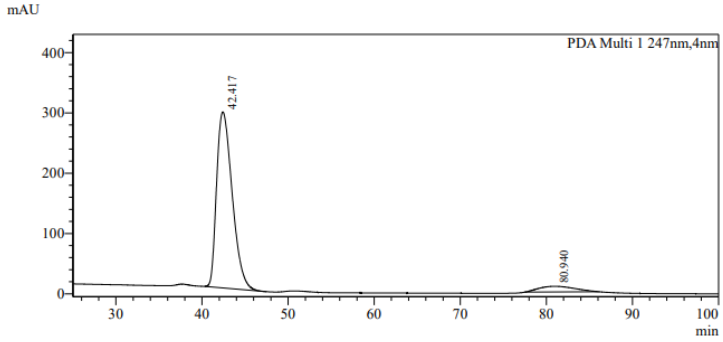
1	43.097	6536979	52288	51.252
2	80.792	6217699	16143	48.748



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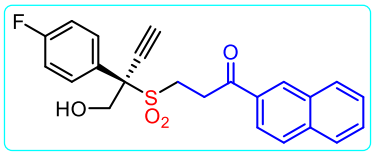
PDA Ch1 247nm

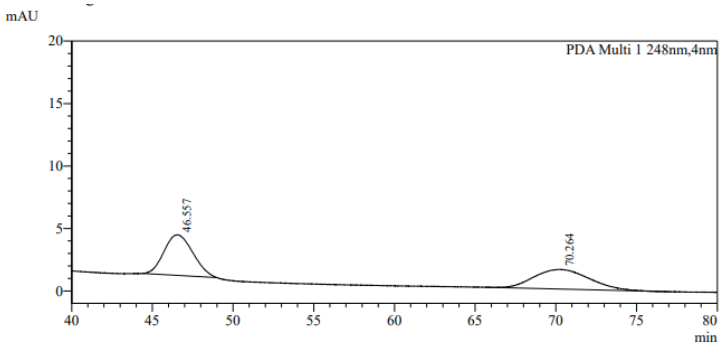
Peak#	Ret. Time	Area	Height	Aera%
1	42.417	36729547	291701	93.113
2	80.940	2716679	9368	6.887

(R)-3-((2-(4-fluorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3e)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 75% yield, 90:10 er. $[\alpha]_D^{25}$= -7.1 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.44 (s, 1H), 8.00 – 7.93 (m, 2H), 7.90 – 7.81 (m, 4H), 7.60 (dt, *J* = 21.2, 6.9 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 4.74 (dd, *J* = 11.9, 7.0 Hz, 1H), 4.19 (dd, *J* = 11.9, 7.0 Hz, 1H), 3.94 – 3.85 (m, 1H), 3.72 – 3.51 (m, 3H), 3.10 (s, 1H), 2.84 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 162.3 (d, *J* = 250.0 Hz), 135.9, 133.1, 132.4, 130.9 (d, *J* = 8.0 Hz), 130.2, 129.7, 129.0, 128.8, 127.8, 127.1, 126.1 (d, *J* = 3.0 Hz), 123.5, 116.0 (d, *J* = 25.0 Hz), 81.7, 77.2, 71.3, 65.8, 45.5, 30.3; HRMS (ESI) for $C_{23}H_{19}FO_4S$ $[M+Na]^+$ calcd. 433.0988, found: 433.0881.

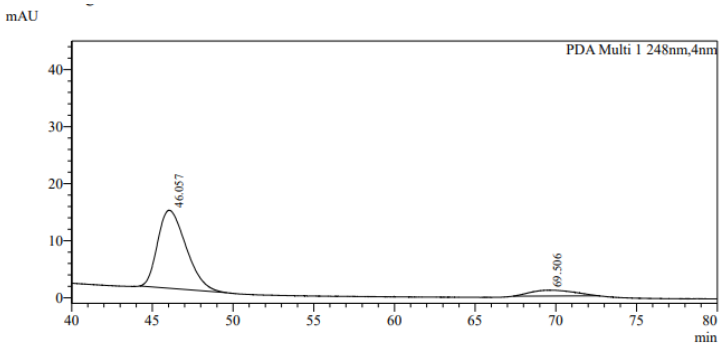
HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 70:30, flow rate = 0.7 mL/min, wave length = 248 nm, t_R = 46.057 min (major), t_R = 69.506 min (minor).



<Peak Table>

PDA Ch1 248nm

Peak#	Ret. Time	Area	Height	Aera%
1	46.557	404243	3246	51.858
2	70.264	375281	1574	48.142

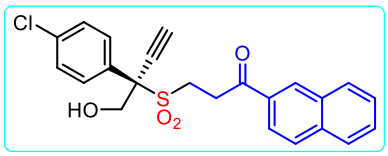


<Peak Table>

PDA Ch1 248nm

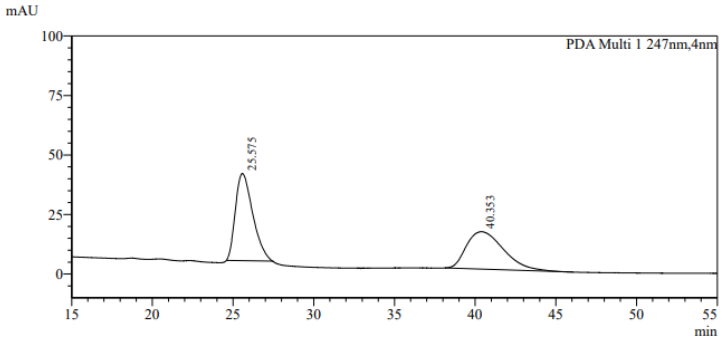
Peak#	Ret. Time	Area	Height	Aera%
1	46.057	1676353	13670	89.766
2	69.506	191109	1021	10.234

(R)-3-((2-(4-chlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3f)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 80% yield, 93:7 er. $[\alpha]_D^{25}$= -6.4 (c = 0.2, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.92 – 7.84 (m, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.59 (ddd, *J* = 14.9, 13.9, 6.9 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.19 (d, *J* = 11.8 Hz, 1H), 3.93 – 3.84 (m, 1H), 3.70 – 3.49 (m, 3H), 3.11 (s, 1H), 2.91 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 136.4, 135.9, 133.1, 132.4, 130.3, 130.2, 129.7, 129.2, 129.0, 128.9, 128.8, 127.8, 127.1, 123.5, 81.8, 71.4, 65.7, 45.6, 30.3; HRMS (ESI) for $C_{23}H_{19}ClO_4S$ $[M+Na]^+$ calcd. 449.0693, found: 449.0580.

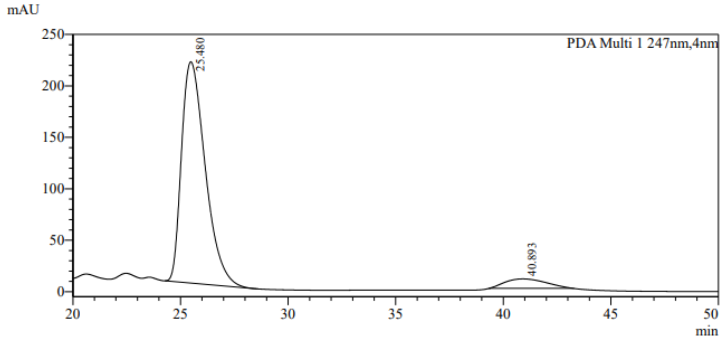
HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 25.480 min (major), t_R = 40.893 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	25.575	2740585	36613	51.918
2	40.353	2538116	15722	48.082

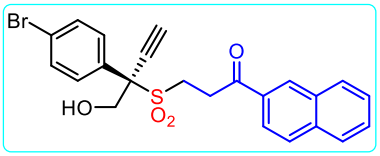


<Peak Table>

PDA Ch1 247nm

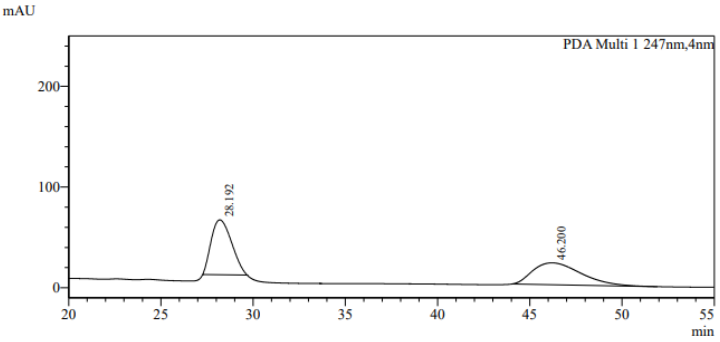
Peak#	Ret. Time	Area	Height	Aera%
1	25.480	16532222	215068	93.071
2	40.893	1230772	9216	6.929

(R)-3-((2-(4-bromophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3g)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 56% yield, 94:6 er. $[\alpha]_D^{25}$ = -10.5 (c = 0.4, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.44 (s, 1H), 7.97 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.74 – 7.68 (m, 2H), 7.64 – 7.55 (m, 4H), 4.72 (dd, *J* = 11.9, 6.9 Hz, 1H), 4.19 (dd, *J* = 11.9, 7.0 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.72 – 3.50 (m, 3H), 3.10 (s, 1H), 2.86 (t, *J* = 7.1 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.5, 135.9, 133.0, 132.4, 132.1, 130.5, 130.2, 129.7, 129.4, 129.0, 128.8, 127.8, 127.1, 124.7, 123.5, 81.8, 71.5, 65.7, 45.6, 30.3; HRMS (ESI) for $C_{23}H_{19}BrO_4S$ $[M+Na]^+$ calcd. 493.0187, found: 493.0080.

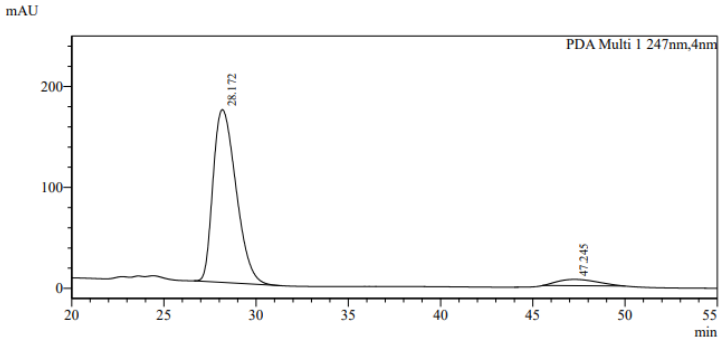
HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 28.172 min (major), t_R = 47.245 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	28.192	4196505	54485	51.258
2	46.200	3990520	21772	48.742

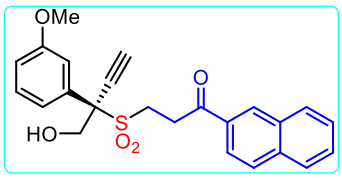


<Peak Table>

PDA Ch1 247nm

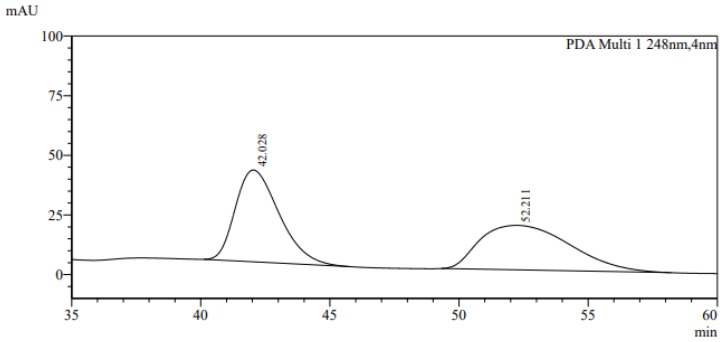
Peak#	Ret. Time	Area	Height	Aera%
1	28.172	14896825	171252	94.003
2	47.245	950430	6274	5.997

(R)-3-((1-hydroxy-2-(3-methoxyphenyl)but-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3h)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 65% yield, 92:8 er. $[\alpha]_D^{25}$= -6.7 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.40 (s, 1H), 7.97 – 7.91 (m, 2H), 7.87 – 7.84 (m, 2H), 7.58 (ddd, *J* = 15.0, 13.8, 6.9 Hz, 2H), 7.45 – 7.34 (m, 3H), 6.96 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.75 (dd, *J* = 11.8, 5.9 Hz, 1H), 4.20 (dd, *J* = 11.8, 6.1 Hz, 1H), 3.86 – 3.79 (m, 4H), 3.66 – 3.45 (m, 3H), 3.09 (s, 1H), 2.94 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.7, 159.8, 135.8, 133.1, 132.4, 131.8, 130.2, 130.0, 129.7, 128.9, 128.7, 127.8, 127.0, 123.5, 121.0, 115.1, 81.5, 71.9, 65.7, 55.4, 45.5, 30.4; HRMS (ESI) for $C_{24}H_{22}O_5S$ $[M+Na]^+$ calcd. 445.1188, found: 445.1084.

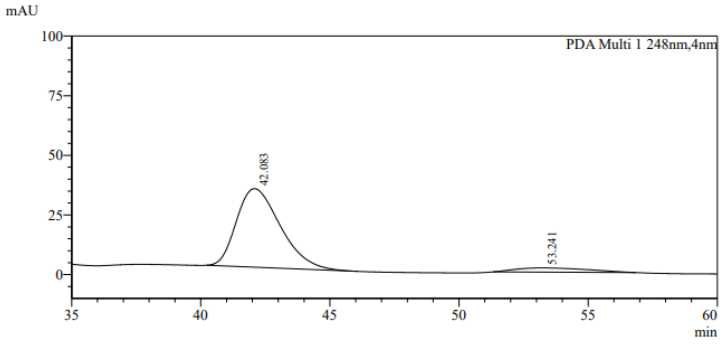
HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 248 nm, t_R = 42.083 min (major), t_R = 53.241 min (minor).



<Peak Table>

PDA Ch1 248nm

Peak#	Ret. Time	Area	Height	Aera%
1	42.028	4544700	38455	49.959
2	52.211	4552090	18645	50.041

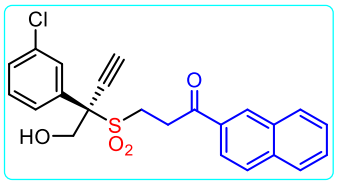


<Peak Table>

PDA Ch1 248nm

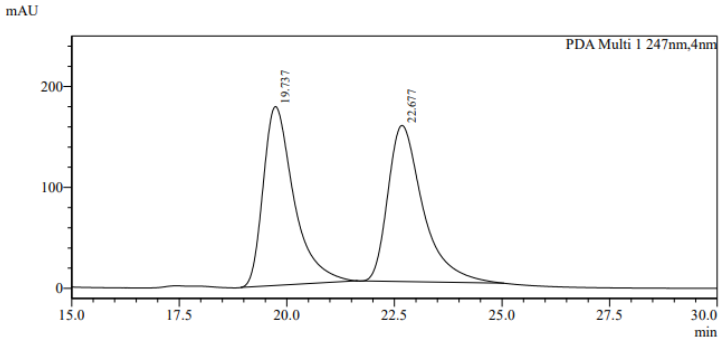
Peak#	Ret. Time	Area	Height	Aera%
1	42.083	3903259	32920	91.996
2	53.241	339597	1735	8.004

(R)-3-((2-(3-chlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3i)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 60% yield, 92.5:7.5 er. $[\alpha]_D^{25}$= -6.8 (c = 0.19, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 7.99 – 7.92 (m, 2H), 7.88 – 7.85 (m, 3H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.52 (m, 2H), 7.46 – 7.33 (m, 2H), 4.72 (d, *J* = 11.8 Hz, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.75 – 3.51 (m, 3H), 3.13 (s, 1H), 3.05 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 135.9, 135.0, 133.0, 132.4, 130.4, 130.1, 129.7, 129.1, 128.7, 127.8, 127.0, 123.5, 82.0, 76.9, 71.5, 65.8, 45.8, 30.3; HRMS (ESI) for $C_{23}H_{19}ClO_4S$ $[M+Na]^+$ calcd. 449.0693, found: 449.0582.

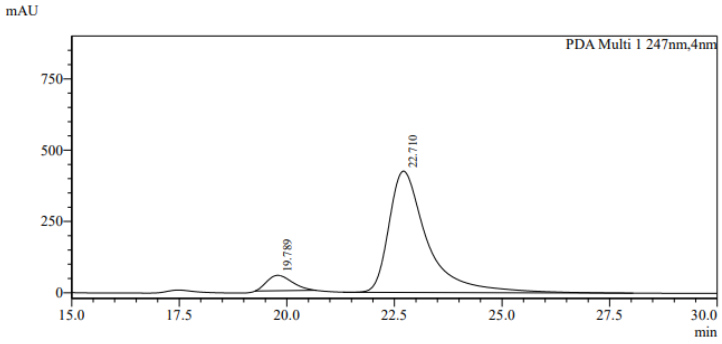
HPLC analysis: CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 19.789 min (minor), t_R = 22.710 min (major).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	19.737	8822615	177290	50.088
2	22.677	8791574	154762	49.912

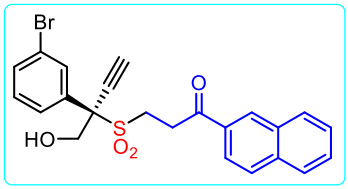


<Peak Table>

PDA Ch1 247nm

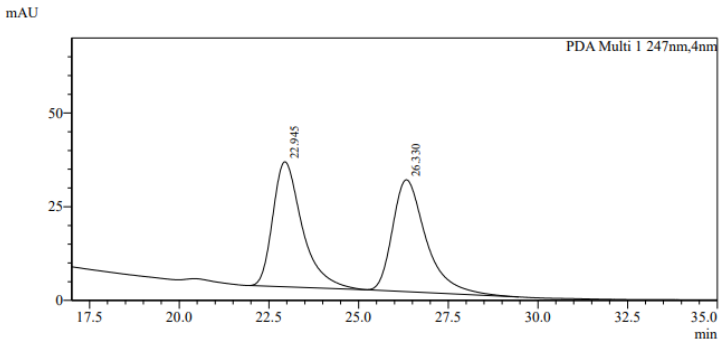
Peak#	Ret. Time	Area	Height	Aera%
1	19.789	2204560	54097	7.705
2	22.710	26406777	425171	92.295

(R)-3-((2-(3-bromophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3j)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 65% yield, 92.5:7.5 er. $[\alpha]_D^{25}$= 9.2 (c = 0.5, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.42 (s, 1H), 8.01 – 7.92 (m, 3H), 7.86 (dd, *J* = 8.1, 6.1 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 3.90 (td, *J* = 10.9, 2.3 Hz, 1H), 3.73 – 3.60 (m, 2H), 3.59 – 3.46 (m, 1H), 3.13 (s, 1H), 3.04 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 135.9, 133.1, 132.6, 132.4, 132.0, 130.3, 129.7, 129.0, 128.7, 127.8, 127.5, 127.1, 123.5, 123.0, 82.1, 71.5, 65.8, 45.8, 30.3; HRMS (ESI) for $C_{23}H_{19}BrO_4S$ $[M+Na]^+$ calcd. 493.0187, found: 493.0081.

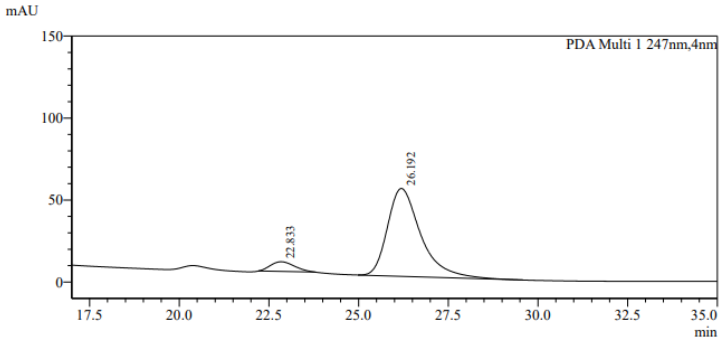
HPLC analysis: CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 22.833 min (minor), t_R = 26.192 min (major).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	22.945	1906744	33357	49.524
2	26.330	1943436	29822	50.476

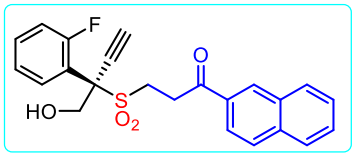


<Peak Table>

PDA Ch1 247nm

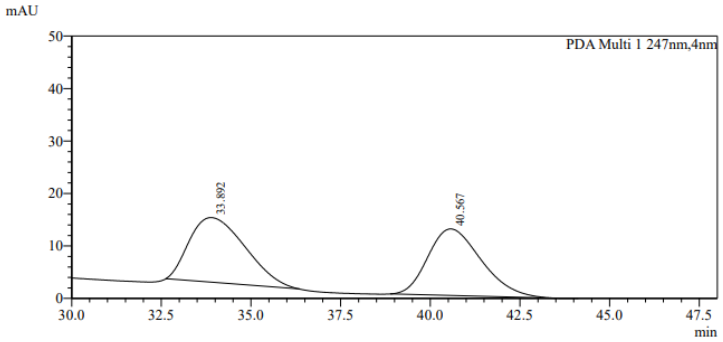
Peak#	Ret. Time	Area	Height	Aera%
1	22.833	276882	5919	7.386
2	26.192	3471702	53563	92.614

(R)-3-((2-(2-fluorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3k)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid 38% yield, 91:9 er. $[\alpha]_D^{25}$= -6.9 (c = 0.16, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.46 (s, 1H), 8.00 – 7.92 (m, 3H), 7.92 – 7.84 (m, 2H), 7.59 (dt, *J* = 21.1, 7.2 Hz, 2H), 7.49 – 7.40 (m, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 12.0, 8.5 Hz, 1H), 5.02 (d, *J* = 11.9 Hz, 1H), 4.42 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.99 – 3.88 (m, 1H), 3.79 – 3.57 (m, 3H), 3.09 (s, 1H), 2.84 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 161.3 (d, *J* = 251 Hz), 135.9, 133.1, 132.7 (d, *J* = 3 Hz), 132.4, 132.2, 132.1, 130.2, 129.7, 128.9, 128.7, 127.8, 127.1, 124.7 (d, *J* = 3 Hz), 123.5, 117.5, 117.5 (d, *J* = 11 Hz), 117.3, 81.3, 72.2 (d, *J* = 5 Hz), 64.1 (d, *J* = 13 Hz), 45.3, 30.3; HRMS (ESI) for $C_{23}H_{19}FO_4S$ $[M+Na]^+$ calcd. 433.0988, found: 433.0884.

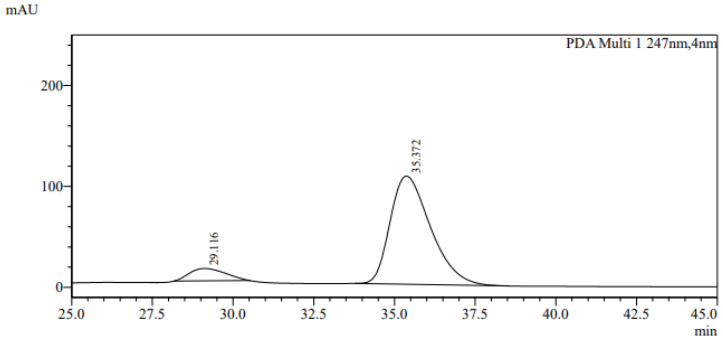
HPLC analysis: CHIRALPAK ID (Hexane/i-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 29.116 min (minor), t_R = 35.372 min (major).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	33.892	1336425	12302	50.464
2	40.567	1311874	12681	49.536

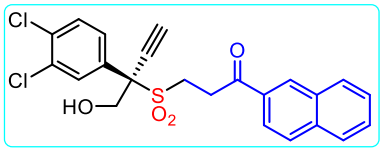


<Peak Table>

PDA Ch1 247nm

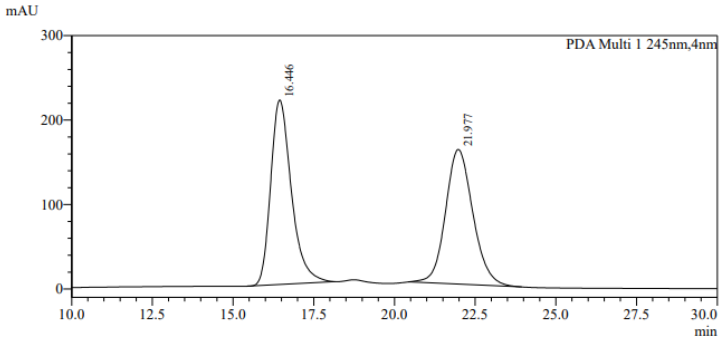
Peak#	Ret. Time	Area	Height	Aera%
1	29.116	950942	12273	9.210
2	35.372	9374576	107163	90.790

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3l)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 80% yield, 92:8 er. $[\alpha]_D^{25}$= -5.8 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.46 (s, 1H), 8.00 – 7.94 (m, 3H), 7.92 – 7.85 (m, 2H), 7.68 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.76 – 3.55 (m, 3H), 3.13 (s, 1H), 2.91 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.5, 135.9, 134.7, 133.3, 133.0, 132.4, 131.0, 130.8, 130.5, 130.2, 129.7, 129.0, 128.8, 128.1, 127.8, 127.1, 123. 5, 82.2, 71.1, 65.8, 45.9, 30.3; HRMS (ESI) for $C_{23}H_{18}Cl_2O_4S$ $[M+Na]^+$ calcd. 483.0303, found: 483.0195.

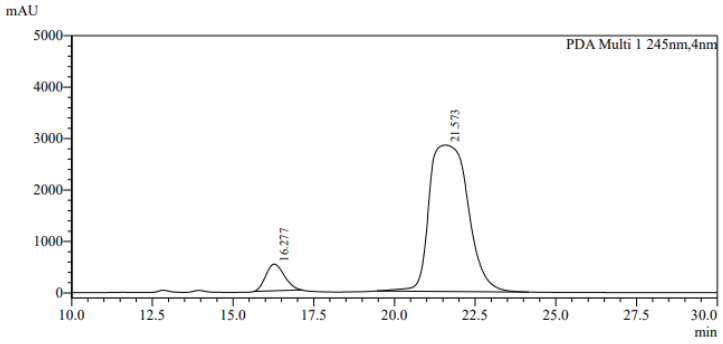
HPLC analysis: CHIRALPAK OZ-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 245 nm, t_R = 16.277 min (minor), t_R = 21.573 min (major).



<Peak Table>

PDA Ch1 245nm

Peak#	Ret. Time	Area	Height	Aera%
1	16.446	9754295	218494	50.899
2	21.977	9409613	159437	49.101

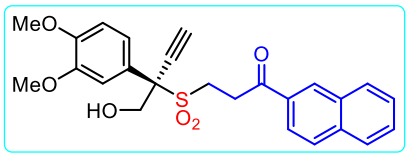


<Peak Table>

PDA Ch1 245nm

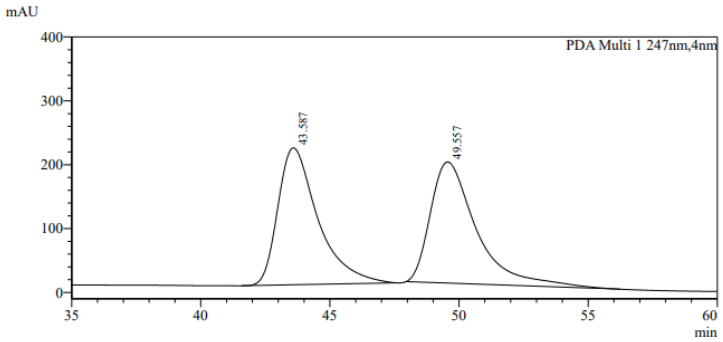
Peak#	Ret. Time	Area	Height	Aera%
1	16.277	20730899	518981	7.987
2	21.573	238839519	2845219	92.013

(R)-3-((2-(3,4-dimethoxyphenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3m)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 68% yield, 86.5:13.5 er. $[\alpha]_D^{25}$= -14.1 (c = 0.13, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.42 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.93 – 7.85 (m, 2H), 7.66 – 7.54 (m, 2H), 7.41 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.74 (dd, *J* = 11.7, 4.9 Hz, 1H), 4.21 (dd, *J* = 11.8, 5.2 Hz, 1H), 3.93 (s, 3H), 3.89 – 3.81 (m, 4H), 3.65 – 3.47 (m, 3H), 3.08 (s, 1H), 2.74 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 150.4, 149.1, 135.9, 133.1, 132.4, 130.2, 129.7, 128.9, 128.7, 127.8, 127.1, 123.5, 122.3, 121.7, 111.7, 111.1, 81.3, 71.7, 65.7, 56.0, 45.2, 30.4; HRMS (ESI) for $C_{25}H_{24}O_6S$ $[M+Na]^+$ calcd. 475.1294, found: 475.1182.

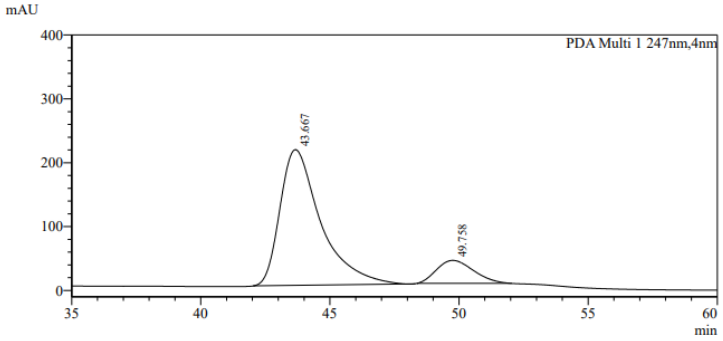
CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 0.7 mL/min, wave length = 247 nm, t_R = 43.667 min (major), t_R = 49.758 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	43.587	23170888	214477	49.620
2	49.557	23525778	189657	50.380

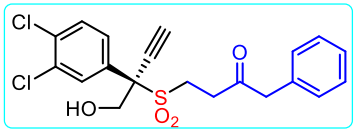


<Peak Table>

PDA Ch1 247nm

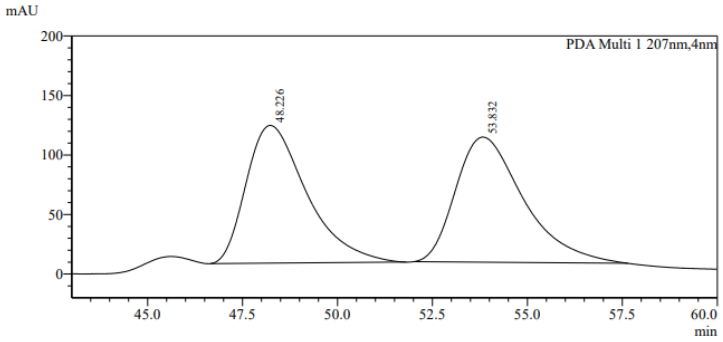
Peak#	Ret. Time	Area	Height	Aera%
1	43.667	23285040	212508	86.661
2	49.758	3583946	35956	13.339

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-phenylbutan-2-one (3n)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 80% yield, 92:8 er. $[\alpha]_D^{25}$= -19.1 (c = 0.6, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.85 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.20 – 7.15 (m, 2H), 4.57 (dd, *J* = 11.8, 6.8 Hz, 1H), 4.08 (dd, *J* = 11.8, 6.4 Hz, 1H), 3.73 (s, 2H), 3.69 – 3.60 (m, 1H), 3.48 – 3.38 (m, 1H), 3.03 (s, 1H), 3.00 – 2.96 (m, 1H), 2.94 – 2.84 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 204.2, 134.6, 133.2, 133.1, 130.9, 130.7, 130.4, 129.4, 129.0, 128.0, 127.5, 82.1, 70.9, 65.7, 50.0, 47.8, 45.6, 33.7, 33.2; HRMS (ESI) for $C_{20}H_{18}Cl_2O_4S$ $[M+Na]^+$ calcd. 447.0303, found: 447.0146.

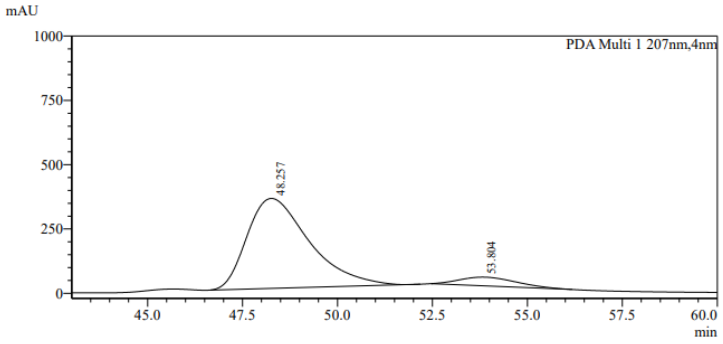
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 48.257 min (major), t_R = 53.804 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	48.226	12840528	115746	49.515
2	53.832	13092174	105172	50.485

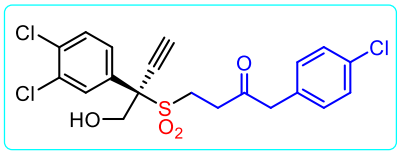


<Peak Table>

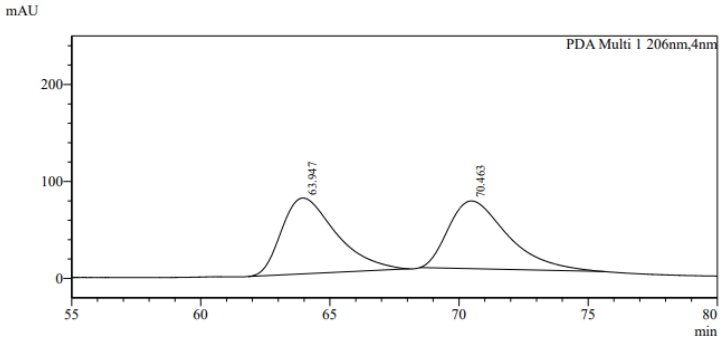
PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	48.257	39913766	349673	91.873
2	53.804	3530714	33386	8.127

(R)-1-(4-chlorophenyl)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)butan-2-one (3o)



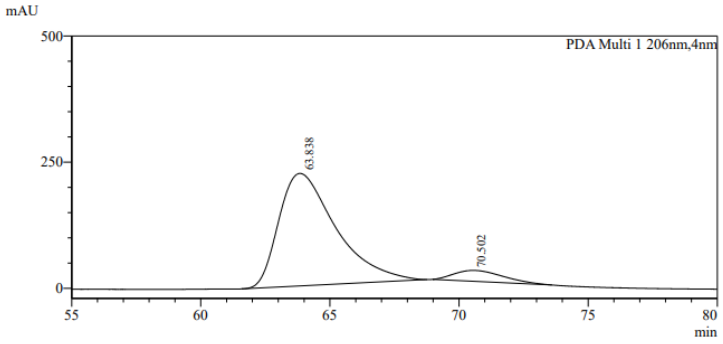
Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 82% yield, 93:7 er. $[\alpha]_D^{25}$= -9.7 (c = 0.69, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.09 (m, 2H), 4.58 (d, *J* = 10.5 Hz, 1H), 4.09 (d, *J* = 10.9 Hz, 1H), 3.74 – 3.64 (m, 3H), 3.52 – 3.41 (m, 1H), 3.06 – 2.89 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 203.6, 134.7, 133.5, 133.3, 131.5, 130.9, 130.8, 130.7, 130.3, 129.1, 128.0, 82.1, 71.0, 65.7, 49.1, 49.0, 47.8, 45.5, 33.9, 33.3; HRMS (ESI) for $C_{20}H_{17}Cl_3O_4S$ $[M+Na]^+$ calcd. 480.9913, found: 480.9803. CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 68.838 min (major), t_R = 70.502 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	63.947	11497572	78250	50.762
2	70.463	11152212	69869	49.238

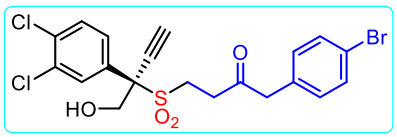


<Peak Table>

PDA Ch1 206nm

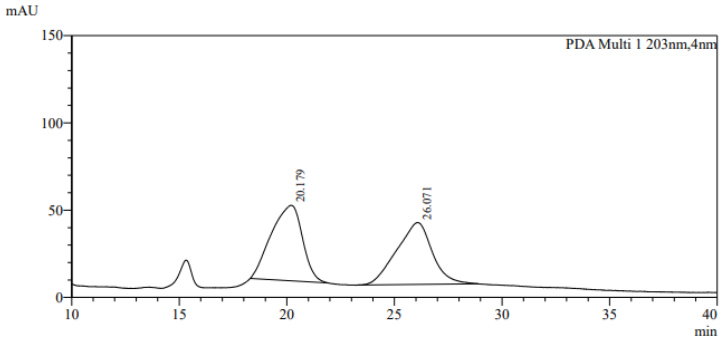
Peak#	Ret. Time	Area	Height	Aera%
1	63.838	34346409	223056	92.331
2	70.502	2852893	21354	7.669

(R)-1-(4-bromophenyl)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)butan-2-one (3p)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 65% yield, 91:9 er. $[\alpha]_D^{25}$= 5.4 (c = 0.17, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 3H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.10 (d, *J* = 11.8 Hz, 1H), 3.73 (s, 2H), 3.69 – 3.62 (m, 1H), 3.51 – 3.39 (m, 1H), 3.26 (t, *J* = 7.0 Hz, 1H), 3.06 (s, 1H), 3.01 – 2.98 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 203.4, 134.7, 133.3, 132.0, 131.2, 130.9, 130.7, 130.3, 128.0, 121.6, 82.1, 71.0, 65.8, 49.2, 47.9, 45.5, 33.9, 33.3; HRMS (ESI) for $C_{20}H_{17}BrCl_2O_4S$ $[M+H]^+$ calcd. 502.9408, found: 502.0252.

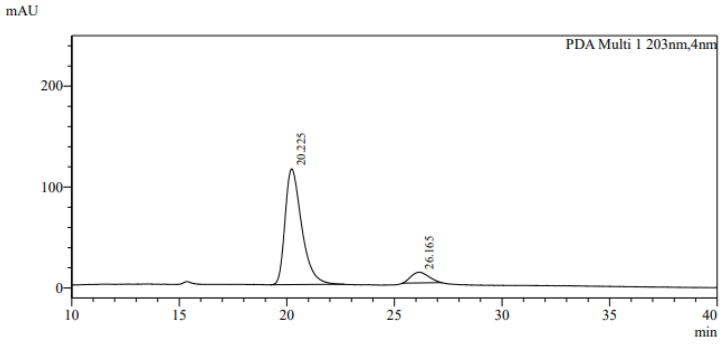
CHIRALPAK AY-H (Hexane/i-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 203 nm, t_R = 20.225 min (major), t_R = 26.165 min (minor).



<Peak Table>

PDA Ch1 203nm

Peak#	Ret. Time	Area	Height	Aera%
1	20.179	4367166	43235	51.605
2	26.071	4095465	35499	48.395

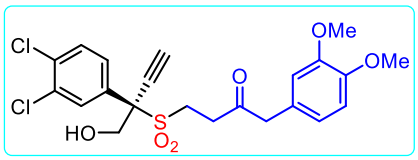


<Peak Table>

PDA Ch1 203nm

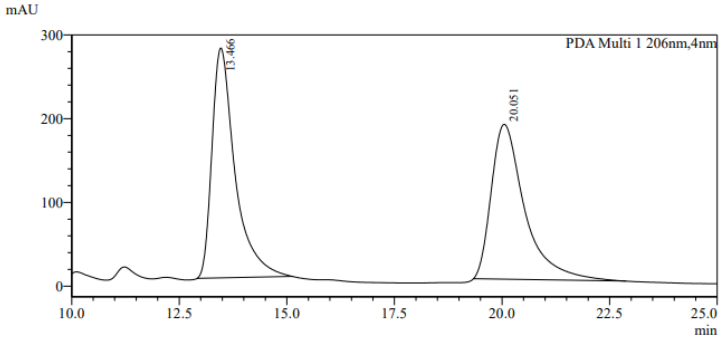
Peak#	Ret. Time	Area	Height	Aera%
1	20.225	6164126	114791	91.087
2	26.165	603205	10556	8.913

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(3,4-dimethoxyphenyl)butan-2-one (3q)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 76% yield, 90.5:9.5 er. $[\alpha]_D^{25}$= -15.2 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (d, *J* = 2.2 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.72 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 4.59 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.10 (dd, *J* = 11.9, 6.7 Hz, 1H), 3.86 (d, *J* = 4.0 Hz, 6H), 3.68 – 3.63 (m, 3H), 3.47 – 3.38 (m, 1H), 3.05 (s, 1H), 3.02 – 2.81 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 204.5, 149.2, 148.4, 134.6, 133.2, 130.9, 130.7, 130.4, 128.0, 125.6, 121.7, 112.3, 111.5, 82.1, 70.9, 65.7, 55.9, 49.6, 45.5, 32.9; HRMS (ESI) for $C_{22}H_{22}Cl_2O_6S$ $[M+Na]^+$ calcd. 507.0514, found: 507.0407.

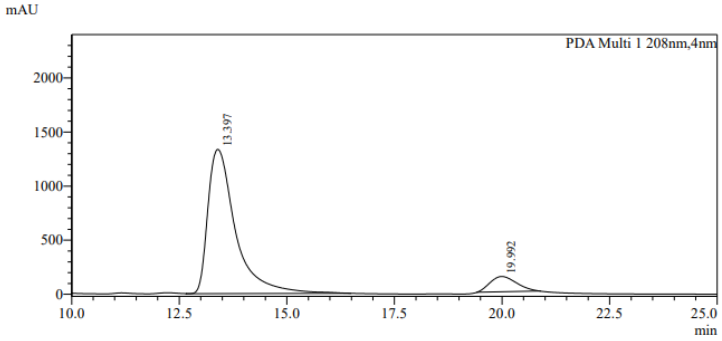
CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 13.397 min (major), t_R = 19.992 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	13.466	10230610	274268	50.587
2	20.051	9993133	184855	49.413

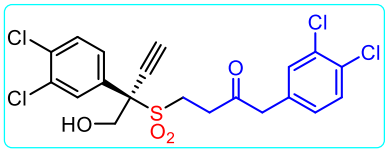


<Peak Table>

PDA Ch1 208nm

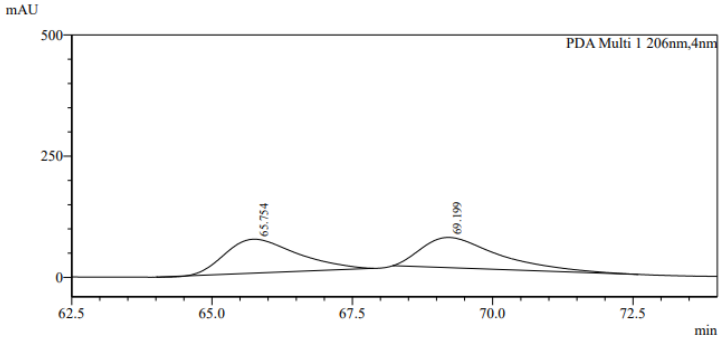
Peak#	Ret. Time	Area	Height	Aera%
1	13.397	59494239	1332736	90.685
2	19.992	6110835	141583	9.315

(R)-1-(3,4-dichlorophenyl)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)butan-2-one (3r)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1); white solid, 48% yield, 90:10 er. $[\alpha]_D^{25}$= -10.9 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.87 (d, *J* = 2.2 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.01 (dd, *J* = 8.2, 1.9 Hz, 1H), 4.60 (d, *J* = 11.7 Hz, 1H), 4.11 (d, *J* = 11.7 Hz, 1H), 3.74 – 3.68 (m, 3H), 3.53 – 3.44 (m, 1H), 3.08 (s, 1H), 3.04 – 2.92 (m, 2H), 2.81 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 202.87 (s), 134.7, 133.3, 133.1, 132.8, 131.7, 131.4, 130.9, 130.7, 130.2, 128.9, 128.0, 82.2, 71.1, 65.8, 48.5, 47.9, 45.6, 34.1, 33.5; HRMS (ESI) for $C_{20}H_{16}Cl_4O_4S$ $[M+Na]^+$ calcd. 514.9523, found: 514.9418.

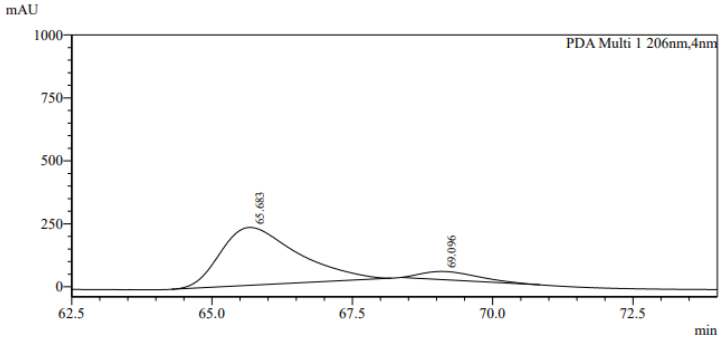
CHIRALPAK AD-3 (Hexane/i-PrOH) = 70:30, flow rate = 0.2 mL/min, wave length = 206 nm, t_R = 65.683 min (major), t_R = 69.096 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	65.754	6265851	70047	51.090
2	69.199	5998468	62277	48.910

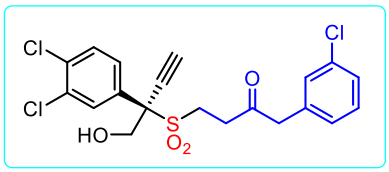


<Peak Table>

PDA Ch1 206nm

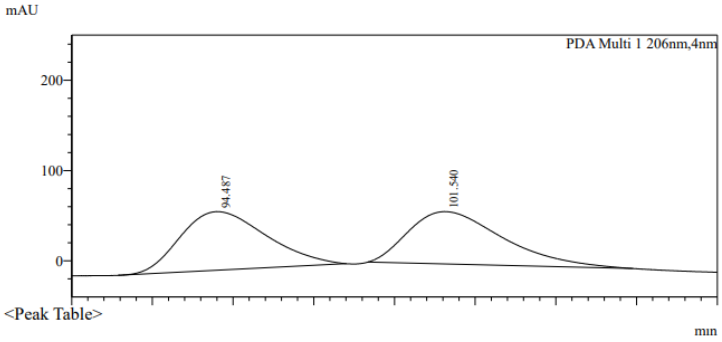
Peak#	Ret. Time	Area	Height	Aera%
1	65.683	21993957	229981	90.493
2	69.096	2310599	32293	9.507

(R)-1-(3-chlorophenyl)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)butan-2-one (3s)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 80% yield, 94:6 er. $[\alpha]_D^{25}$= -16.6 (c = 0.8, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (s, 1H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 2H), 7.18 (s, 1H), 7.06 (d, *J* = 3.1 Hz, 1H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.10 (d, *J* = 11.3 Hz, 1H), 3.75 – 3.65 (m, 3H), 3.53 – 3.40 (m, 1H), 3.07 – 2.86 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 203.3, 134.9, 134.7, 133.3, 130.9, 130.7, 130.3, 130.1, 129.6, 128.0, 127.7, 127.7, 82.2, 71.0, 65.8, 49.3, 45.5, 33.4; HRMS (ESI) for $C_{20}H_{17}Cl_3O_4S$ $[M+Na]^+$ calcd. 480.9913, found: 480.9803.

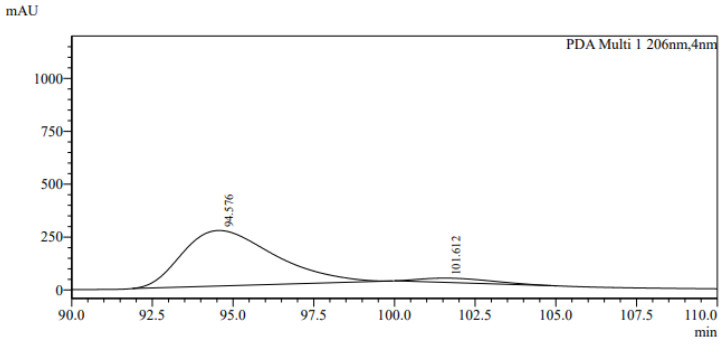
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 0.6 mL/min, wave length = 206 nm, t_R = 94.576 min (major), t_R = 101.612 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	94.487	12028009	64972	50.404
2	101.540	11835126	57979	49.596

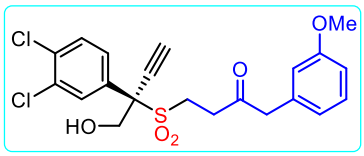


<Peak Table>

PDA Ch1 206nm

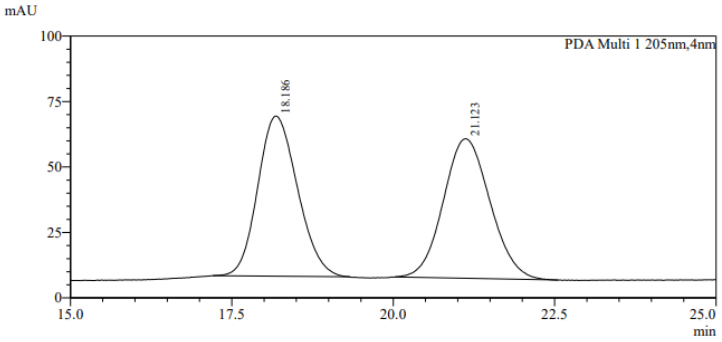
Peak#	Ret. Time	Area	Height	Aera%
1	94.576	52198110	262277	94.172
2	101.612	3230279	20351	5.828

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(3-methoxyphenyl)butan-2-one (3t)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 71% yield, 88:12 er. $[\alpha]_D^{25}$= -11.0 (c = 0.46, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (d, *J* = 2.2 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.82 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.79 – 6.69 (m, 2H), 4.58 (dd, *J* = 11.7, 5.0 Hz, 1H), 4.09 (dd, *J* = 11.7, 4.4 Hz, 1H), 3.79 (s, 3H), 3.71 – 3.61 (m, 3H), 3.47 – 3.37 (m, 1H), 3.04 (s, 1H), 3.02 – 2.83 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 204.1, 160.0, 134.6, 134.6, 133.2, 130.9, 130.7, 130.4, 130.0, 128.0, 121.7, 115.1, 112.9, 82.1, 76.5, 70.9, 65.7, 55.3, 50.1, 45.5, 33.1; HRMS (ESI) for $C_{21}H_{20}Cl_2O_5S$ $[M+Na]^+$ calcd. 477.0408, found: 477.0304.

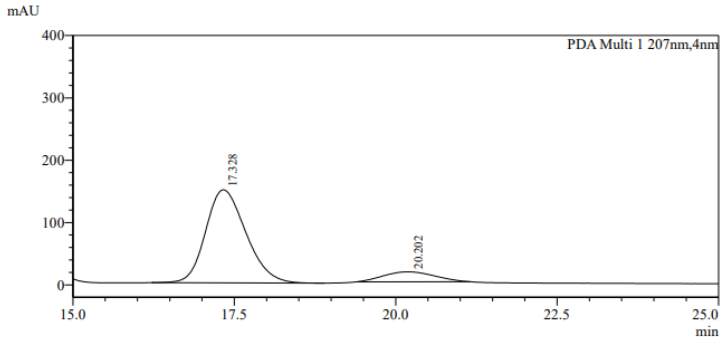
CHIRALPAK OD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 17.328 min (major), t_R = 20.202 min (minor).



<Peak Table>

PDA Ch1 205nm

Peak#	Ret. Time	Area	Height	Aera%
1	18.186	2623405	61172	49.391
2	21.123	2688141	53332	50.609

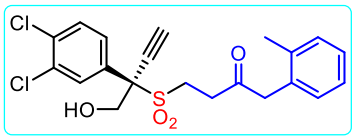


<Peak Table>

PDA Ch1 207nm

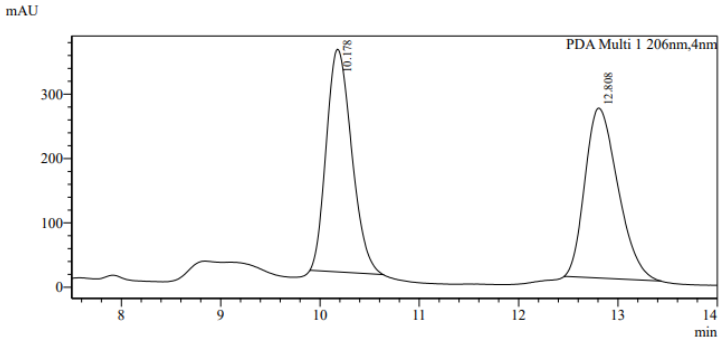
Peak#	Ret. Time	Area	Height	Aera%
1	17.328	6483417	149213	88.028
2	20.202	881734	15994	11.972

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(o-tolyl)butan-2-one (3u)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 74% yield, 88:12 er. $[\alpha]_D^{25}$= -15.7 (c = 0.33, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.09 (m, 4H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.08 (d, *J* = 11.8 Hz, 1H), 3.75 (s, 2H), 3.71 – 3.64 (m, 1H), 3.49 – 3.41 (m, 1H), 3.03 (s, 1H), 3.00 – 2.84 (m, 3H), 2.22 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 204.2, 136.9, 134.6, 133.2, 132.0, 130.9, 130.7, 130.4, 128.0, 127.8, 126.5, 82.1, 65.8, 48.2, 45.6, 33.2, 19.7; HRMS (ESI) for $C_{21}H_{20}Cl_2O_4S$ $[M+Na]^+$ calcd. 461.0459, found: 461.0350.

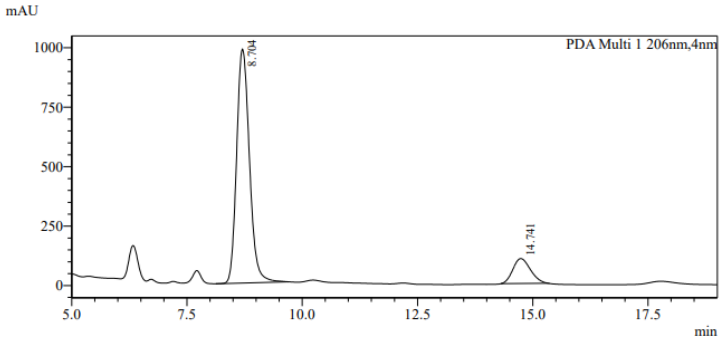
CHIRALPAK IF (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 8.704 min (major), t_R = 14.741 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	10.178	6159433	345931	50.216
2	12.808	6106452	264016	49.784

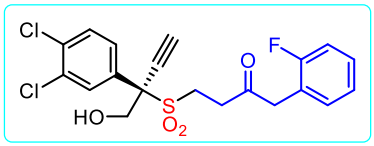


<Peak Table>

PDA Ch1 206nm

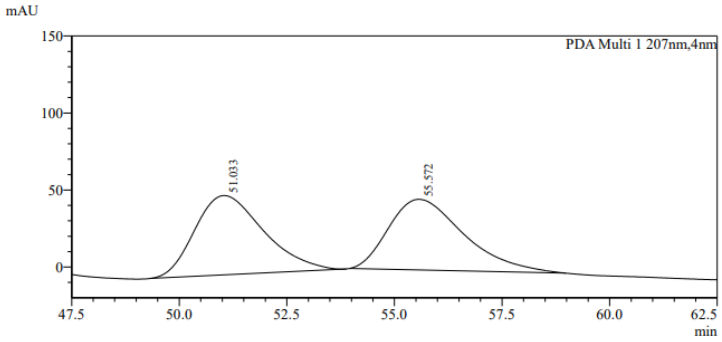
Peak#	Ret. Time	Area	Height	Aera%
1	8.704	19023365	983650	87.263
2	14.741	2776760	104874	12.737

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(2-fluorophenyl)butan-2-one (3v)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 83% yield, 94:6 er. $[\alpha]_D^{25}$= -13.4 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.86 (d, *J* = 1.5 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.20 – 7.01 (m, 4H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.08 (d, *J* = 11.6 Hz, 1H), 3.77 (s, 2H), 3.72 – 3.64 (m, 1H), 3.55 – 3.44 (m, 1H), 3.06 – 2.97 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 202.9, 160.9 (d, *J* = 245.9 Hz), 134.6, 133.3, 131.7, 131.6, 130.9, 130.7, 130.4, 129.6, 129.5, 128.0, 124.5, 124.5, 120.6 (d, *J* = 16.1 Hz), 115.7, 115.5, 82.1, 76.4, 71.0, 65.8, 45.5, 43.1, 43.1, 33.3; HRMS (ESI) for $C_{20}H_{17}Cl_2FO_4S$ $[M+Na]^+$ calcd. 465.0209, found: 465.0303.

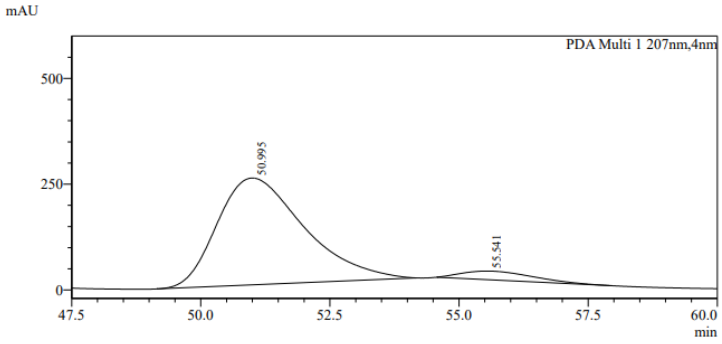
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 50.995 min (major), t_R = 55.541 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	51.033	5727370	51562	50.730
2	55.572	5562510	45844	49.270

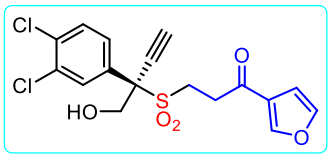


<Peak Table>

PDA Ch1 207nm

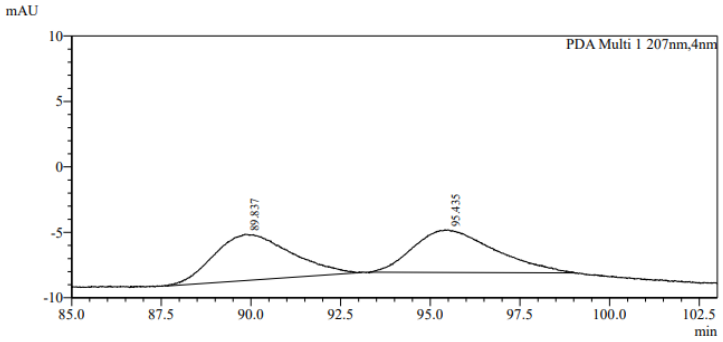
Peak#	Ret. Time	Area	Height	Aera%
1	50.995	29570216	252517	93.755
2	55.541	1969702	20216	6.245

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(furan-3-yl)propan-1-one (3w)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 45% yield, 90:10 er. $[\alpha]_D^{25}$= 55.6 (c = 0.15, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.08 (s, 1H), 7.91 (d, *J* = 1.9 Hz, 1H), 7.64 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.53 – 7.44 (m, 2H), 6.76 (s, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 3.91 – 3.81 (m, 1H), 3.66 – 3.53 (m, 1H), 3.38 – 3.19 (m, 2H), 3.11 (s, 1H), 2.88 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 190.2, 147.8, 144.6, 134.7, 133.3, 131.0, 130.7, 130.4, 128.1, 126.8, 108.4, 82.2, 71.1, 65.8, 45.4, 31.5; HRMS (ESI) for $C_{17}H_{14}Cl_2O_5S$ $[M+Na]^+$ calcd. 422.9939, found: 422.9834.

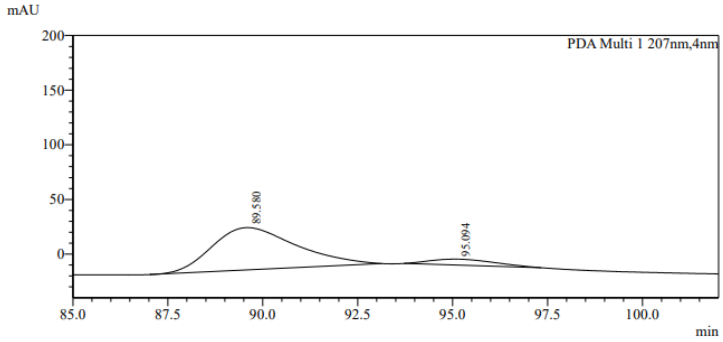
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 89.580 min (major), t_R = 95.094 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	89.837	523829	3539	50.460
2	95.435	514268	3256	49.540

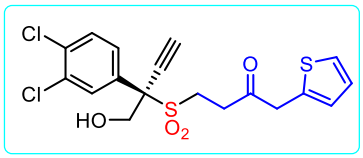


<Peak Table>

PDA Ch1 207nm

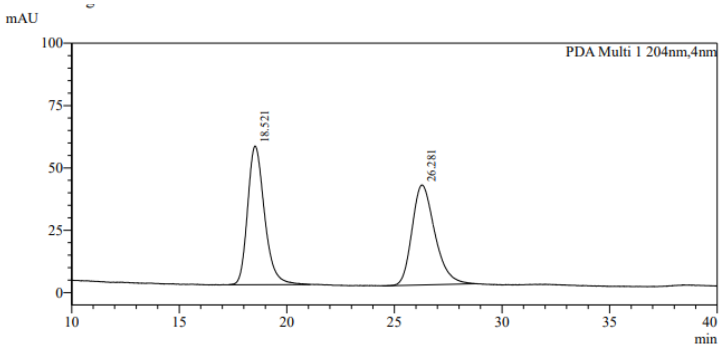
Peak#	Ret. Time	Area	Height	Aera%
1	89.580	5967861	38750	90.281
2	95.094	642448	5437	9.719

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(thiophen-2-yl)butan-2-one (3x)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 49% yield, 91.5:8.5 er. $[\alpha]_D^{25}$= -16.1 (c = 0.2, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.87 (d, *J* = 2.2 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 4.2 Hz, 1H), 7.00 – 6.97 (m, 1H), 6.90 (dd, *J* = 9.7, 3.0 Hz, 1H), 4.60 (dd, *J* = 11.7, 5.3 Hz, 1H), 4.11 (dd, *J* = 11.8, 4.7 Hz, 1H), 3.94 (s, 2H), 3.73 – 3.63 (m, 1H), 3.51 – 3.41 (m, 1H), 3.27 (t, *J* = 7.1 Hz, 1H), 3.05 – 2.95 (m, 2H), 2.81 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 202.8, 134.7, 134.0, 133.3, 130.9, 130.7, 130.3, 128.0, 127.4, 127.3, 125.6, 82.1, 71.0, 65.8, 47.8, 45.5, 43.6, 43.5, 33.5, 33.0; HRMS (ESI) for $C_{18}H_{16}Cl_2O_4S_2$ $[M+Na]^+$ calcd. 452.9867, found: 452.9760.

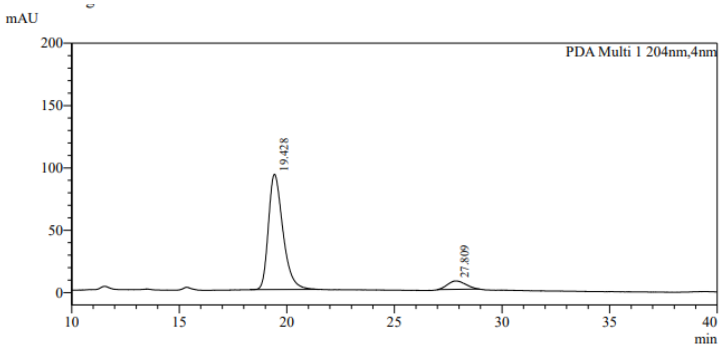
CHIRALPAK AY-H (Hexane/i-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 204 nm, t_R = 19.428 min (major), t_R = 27.809 min (minor).



<Peak Table>

PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Aera%
1	18.521	3043800	55642	50.749
2	26.281	2953940	40096	49.251

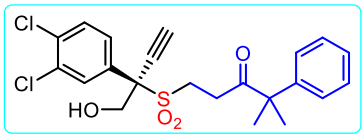


<Peak Table>

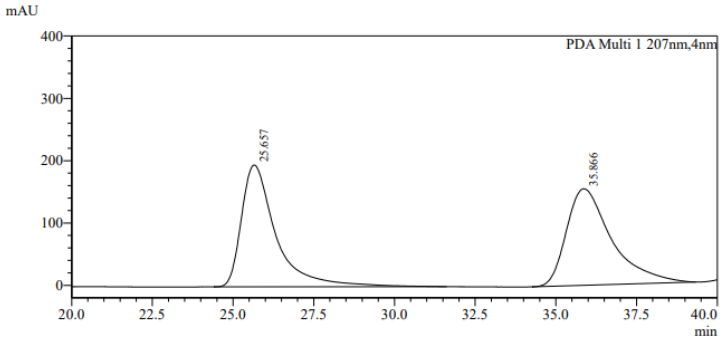
PDA Ch1 204nm

Peak#	Ret. Time	Area	Height	Aera%
1	19.428	4339947	92450	91.637
2	27.809	396070	6758	8.363

(R)-1-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-4-methyl-4-phenylpentan-3-one (3y)



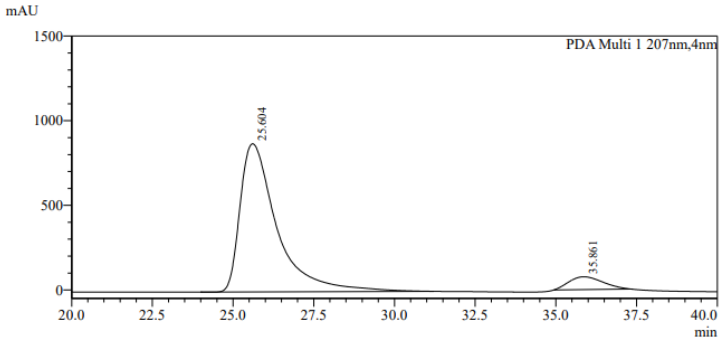
Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). colorless oil, 85% yield, 92:8 er. $[\alpha]_D^{25}$= -17.9 (c = 0.6, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.83 (d, *J* = 2.2 Hz, 1H), 7.56 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.19 (m, 2H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.07 (d, *J* = 11.8 Hz, 1H), 3.60 – 3.47 (m, 1H), 3.42 – 3.31 (m, 1H), 2.99 (s, 1H), 2.93 (s, 1H), 2.82 – 2.70 (m, 1H), 2.69 – 2.59 (m, 1H), 1.49 (d, *J* = 5.1 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 209.2, 142.9, 134.5, 133.2, 130.9, 130.7, 130.5, 129.0, 128.0, 127.4, 126.0, 82.0, 76.5, 70.8, 65.7, 52.2, 46.1, 29.5, 25.3, 25.2; HRMS (ESI) for $C_{22}H_{22}Cl_2O_4S$ $[M+Na]^+$ calcd. 475.0616, found: 475.0514. CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 25.604 min (major), t_R = 35.861 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	25.657	14585654	195281	49.234
2	35.866	15039555	154861	50.766

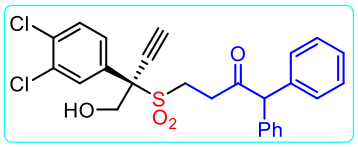


<Peak Table>

PDA Ch1 207nm

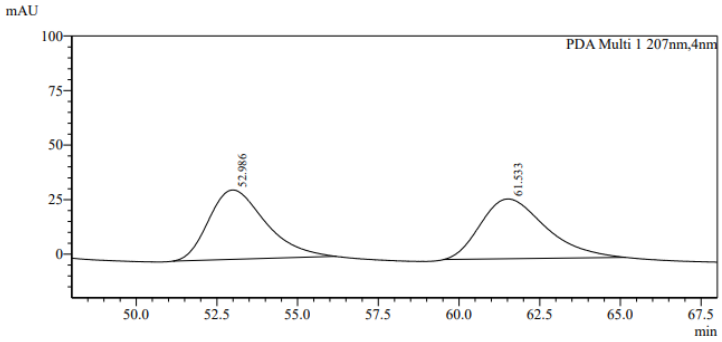
Peak#	Ret. Time	Area	Height	Aera%
1	25.604	69750502	875457	92.630
2	35.861	5549856	75630	7.370

(R)-4-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1,1-diphenylbutan-2-one (3z)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). colorless oil, 57% yield, 94.5:5.5 er. $[\alpha]_D^{25}$= -12.1 (c = 0.36, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.85 (d, *J* = 2.3 Hz, 1H), 7.58 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.21 – 7.17 (m, 4H), 5.13 (s, 1H), 4.56 (dd, *J* = 11.8, 5.6 Hz, 1H), 4.07 (dd, *J* = 11.8, 5.2 Hz, 1H), 3.72 – 3.61 (m, 1H), 3.52 – 3.41 (m, 1H), 3.13 – 2.96 (m, 3H), 2.83 (s, 1H) ; **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 204.7, 137.4, 137.4, 134.6, 133.3, 130.9, 130.7, 130.4, 128.9, 128.0, 82.1, 76.4, 71.0, 65.7, 64.3, 45.8, 34.1; HRMS (ESI) for $C_{26}H_{22}Cl_2O_4S$ $[M+Na]^+$ calcd. 523.0616, found: 523.0510.

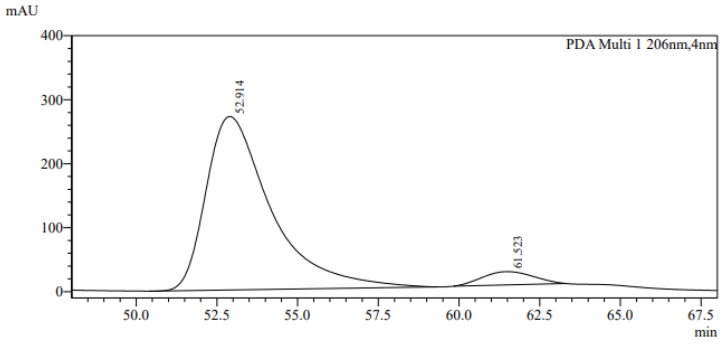
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 52.914 min (major), t_R = 61.523 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	52.986	3881693	31780	50.179
2	61.533	3853998	27413	49.821

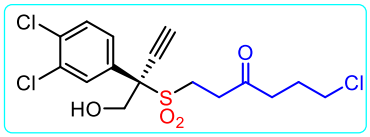


<Peak Table>

PDA Ch1 206nm

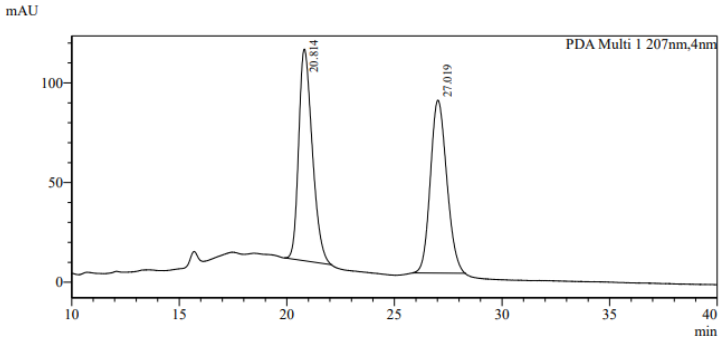
Peak#	Ret. Time	Area	Height	Aera%
1	52.914	38042947	271098	94.358
2	61.523	2274903	20736	5.642

(R)-6-chloro-1-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)hexan-3-one (3aa)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 80% yield, 87.5:12.5 er. $[\alpha]_D^{25}$= -17.9 (c = 0.4, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.88 (d, *J* = 2.0 Hz, 1H), 7.62 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 3.78 – 3.65 (m, 1H), 3.56 (t, *J* = 6.2 Hz, 2H), 3.53 – 3.44 (m, 1H), 3.11 (s, 1H), 3.07 – 2.89 (m, 3H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.11 – 2.04 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 205.4, 134.7, 133.3, 131.0, 130.7, 130.3, 128.0, 82.1, 76.5, 71.0, 65.8, 45.4, 44.1, 39.5, 33.8, 26.1; HRMS (ESI) for $C_{16}H_{17}Cl_3O_4S$ $[M+H]^+$ calcd. 410.9913, found: 410.9987.

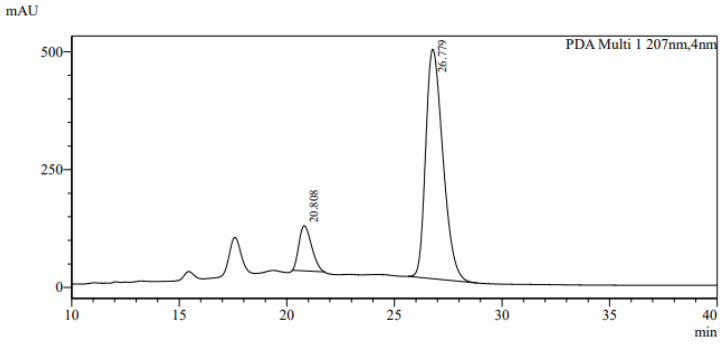
CHIRALPAK IG (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 20.808 min (minor), t_R = 26.779 min (major).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	20.814	4679293	106186	50.400
2	27.019	4605066	86705	49.600

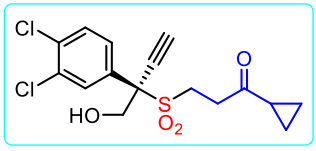


<Peak Table>

PDA Ch1 207nm

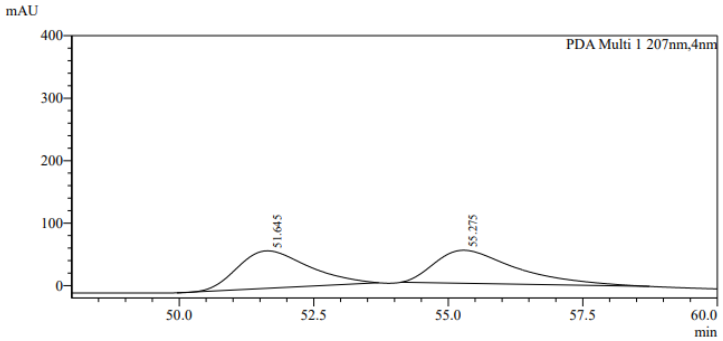
Peak#	Ret. Time	Area	Height	Aera%
1	20.808	3928133	95922	12.652
2	26.779	27120341	487037	87.348

(R)-1-cyclopropyl-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)propan-1-one (3ab)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 57% yield, 91:9 er. $[\alpha]_D^{25}$= -23.8 (c = 0.5, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.88 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 4.60 (dd, *J* = 11.8, 5.0 Hz, 1H), 4.11 (dd, *J* = 11.7, 4.7 Hz, 1H), 3.79 – 3.66 (m, 1H), 3.51 – 3.40 (m, 1H), 3.20 – 3.01 (m, 4H), 2.00 – 1.91 (m, 1H), 1.10 – 1.03 (m, 2H), 0.99 – 0.92 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 206.6, 134.6, 133.2, 131.0, 130.7, 130.5, 128.1, 82.06, 76.5, 71.0, 65.8, 45.4, 34.2, 20.9, 11.7, 11.6; HRMS (ESI) for $C_{16}H_{16}Cl_2O_4S$ $[M+Na]^+$ calcd. 397.0146, found: 397.0042.

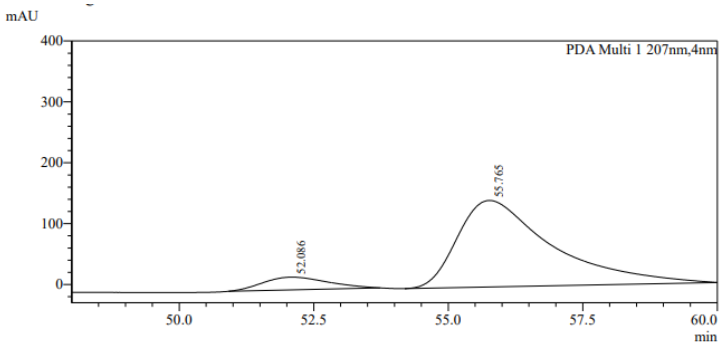
CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 0.7 mL/min, wave length = 207 nm, t_R = 52.086 min (minor), t_R = 55.765 min (major).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	51.645	5502104	59929	49.576
2	55.275	5596274	52819	50.424

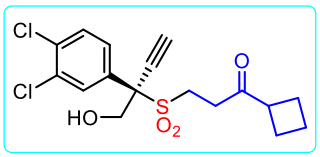


<Peak Table>

PDA Ch1 207nm

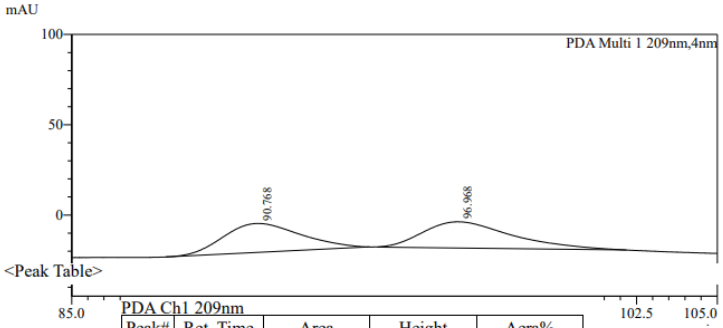
Peak#	Ret. Time	Area	Height	Aera%
1	52.086	1747789	20856	9.176
2	55.765	17299850	142000	90.824

(R)-1-cyclobutyl-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)propan-1-one (3ac)

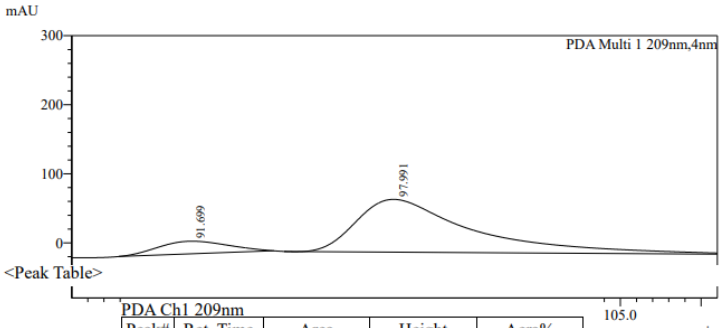


Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 80% yield, 87.5:12.5 er. $[\alpha]_D^{25}$= -5.8 (c = 0.19, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.89 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.62 (dd, *J* = 11.5, 4.3 Hz, 1H), 4.13 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.79 – 3.67 (m, 1H), 3.54 – 3.41 (m, 1H), 3.37 – 3.28 (m, 1H), 3.16 – 3.05 (m, 2H), 2.96 – 2.89 (m, 1H), 2.84 – 2.74 (m, 1H), 2.26 – 2.15 (m, 4H), 2.02 – 1.91 (m, 1H), 1.90 – 1.80 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 207.5, 134.6, 133.2, 131.0, 130.7, 130.5, 128.1, 82.0, 71.0, 65.8, 45.4, 45.4, 31.0, 24.5, 17.8, 8.6; HRMS (ESI) for $C_{17}H_{18}Cl_2O_4S$ $[M+H]^+$ calcd. 389.0303, found: 389.0376.

CHIRALPAK AD-H (Hexane/i-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 209 nm, t_R = 91.699 min (minor), t_R = 97.991 min (major).

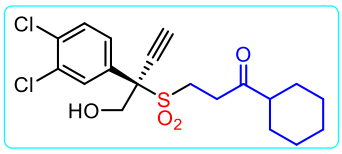


Peak#	Ret. Time	Area	Height	Aera%
1	90.768	2678209	16061	48.931
2	96.968	2795211	14535	51.069



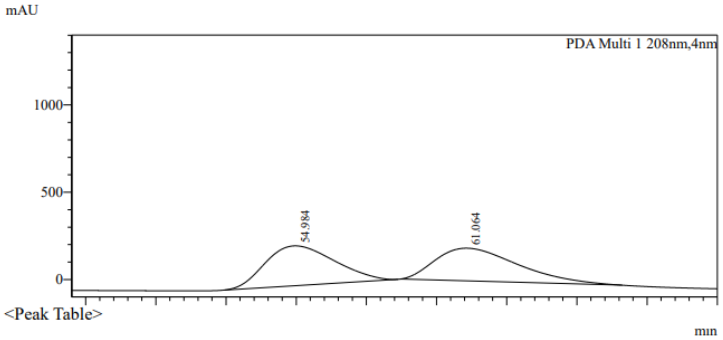
Peak#	Ret. Time	Area	Height	Aera%
1	91.699	2728379	18216	12.475
2	97.991	19142720	76484	87.525

(R)-1-cyclohexyl-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)propan-1-one (3ad)



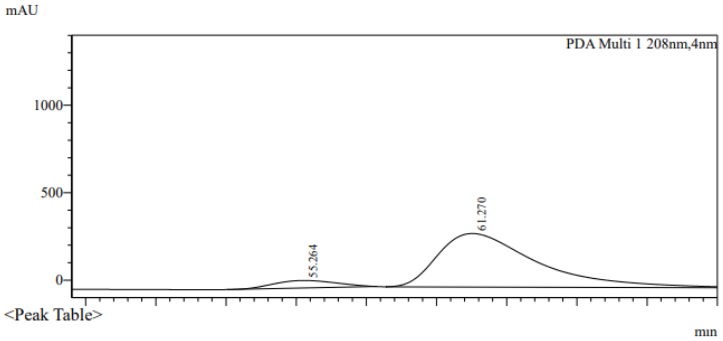
Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 83% yield, 92:8 er. $[\alpha]_D^{25}$= -18.9 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.89 (d, *J* = 2.3 Hz, 1H), 7.63 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.61 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.13 (dd, *J* = 11.9, 6.9 Hz, 1H), 3.73 – 3.62 (m, 1H), 3.50 – 3.39 (m, 1H), 3.11 (s, 1H), 3.07 – 2.96 (m, 2H), 2.94 – 2.84 (m, 1H), 2.43 – 2.33 (m, 1H), 1.89 – 1.73 (m, 5H), 1.71 – 1.61 (m, 1H), 1.36 – 1.19 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 209.7, 134.6, 133.2, 131.0, 130.7, 130.5, 128.1, 82.1, 76.5, 70.9, 65.8, 50.9, 45.4, 31.6, 28.4, 25.7, 25.5; HRMS (ESI) for $C_{19}H_{22}Cl_2O_4S$ $[M+Na]^+$ calcd. 439.0616, found: 439.0508.

CHIRALPAK AD-H (Hexane/i-PrOH) = 90:10, flow rate = 0.6 mL/min, wave length = 208 nm, t_R = 55.264 min (minor), t_R = 61.270 min (major).



PDA Ch1 208nm

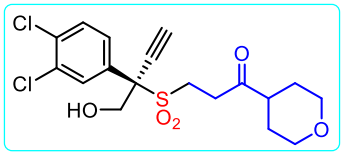
Peak#	Ret. Time	Area	Height	Aera%
1	54.984	39179838	227878	50.463
2	61.064	38461199	186932	49.537



PDA Ch1 208nm

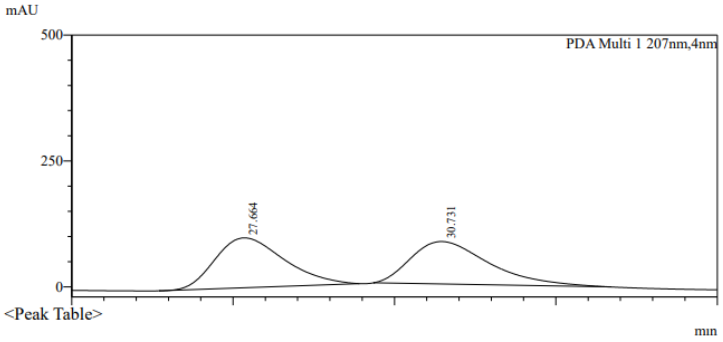
Peak#	Ret. Time	Area	Height	Aera%
1	55.264	6733398	43053	8.198
2	61.270	75401715	305986	91.802

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(tetrahydro-2H-pyran-4-yl)propan-1-one (3ae)



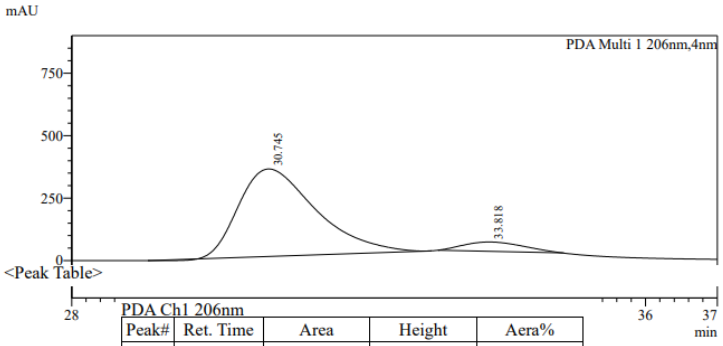
Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 81% yield, 92.5:7.5 er. $[\alpha]_D^{25}$= -20.3 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.89 (d, *J* = 2.3 Hz, 1H), 7.62 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.13 (d, *J* = 12.0 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.76 – 3.67 (m, 1H), 3.49 – 3.37 (m, 3H), 3.10 (s, 1H), 3.08 – 2.97 (m, 1H), 2.95 – 2.87 (m, 1H), 2.83 (s, 1H), 2.66 – 2.55 (m, 1H), 1.82 – 1.68 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 207.6, 134.7, 133.3, 131.0, 130.7, 130.3, 128.0, 82.1, 76.5, 71.0, 67.1, 65.8, 47.6, 45.4, 31.5, 28.0; HRMS (ESI) for $C_{18}H_{20}Cl_2O_5S$ $[M+Na]^+$ calcd. 441.0408, found: 441.0305.

CHIRALPAK AD-H (Hexane/i-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 30.745 min (major), t_R = 33.818 min (minor).



PDA Ch1 207nm

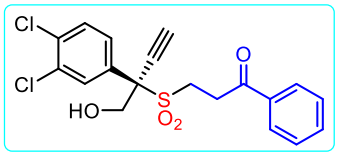
Peak#	Ret. Time	Area	Height	Aera%
1	27.664	7395817	99114	50.876
2	30.731	7141084	84407	49.124



PDA Ch1 206nm

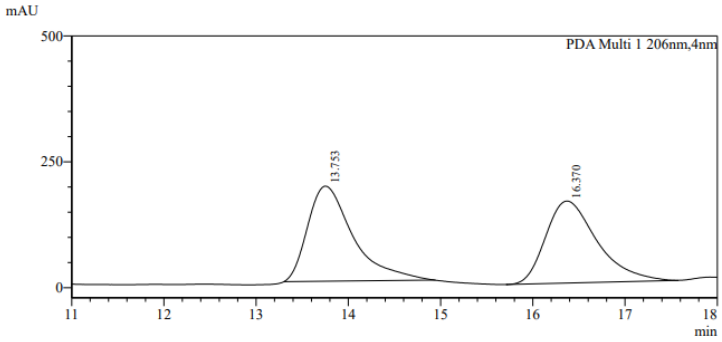
Peak#	Ret. Time	Area	Height	Aera%
1	30.745	26130146	350121	92.280
2	33.818	2185894	37292	7.720

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-phenylpropan-1-one (3af)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 76% yield, 91:9 er. $[\alpha]_D^{25}$= -11.9 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.97 – 7.91 (m, 3H), 7.66 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.54 – 7.45 (m, 3H), 4.66 (dd, *J* = 11.9, 7.1 Hz, 1H), 4.17 (dd, *J* = 11.9, 7.0 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.69 – 3.51 (m, 2H), 3.50 – 3.39 (m, 1H), 3.12 (s, 1H), 2.87 (t, *J* = 7.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 135.7, 134.7, 134.0, 133.3, 131.0, 130.7, 130.5, 128.9, 128.2, 128.1, 82.2, 71.0, 65.8, 45.8, 30.2; HRMS (ESI) for $C_{19}H_{16}Cl_2O_4S$ $[M+Na]^+$ calcd. 433.0146, found: 433.0041.

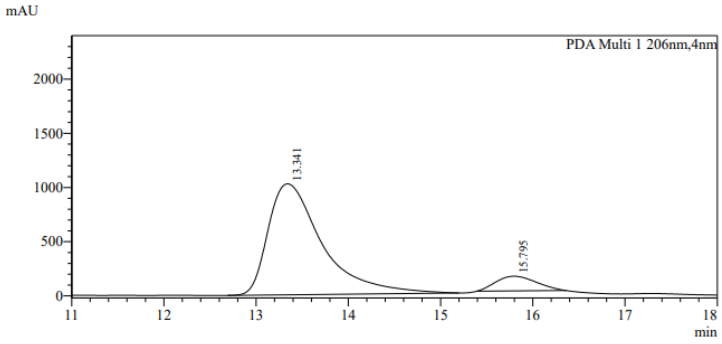
CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 206 nm, t_R = 13.341 min (major), t_R = 15.795 min (minor).



<Peak Table>

PDA Ch1 206nm

Peak#	Ret. Time	Area	Height	Aera%
1	13.753	6469316	188741	50.596
2	16.370	6316882	162917	49.404

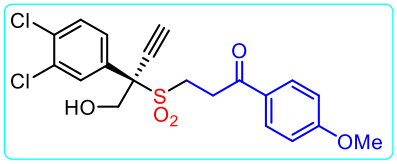


<Peak Table>

PDA Ch1 206nm

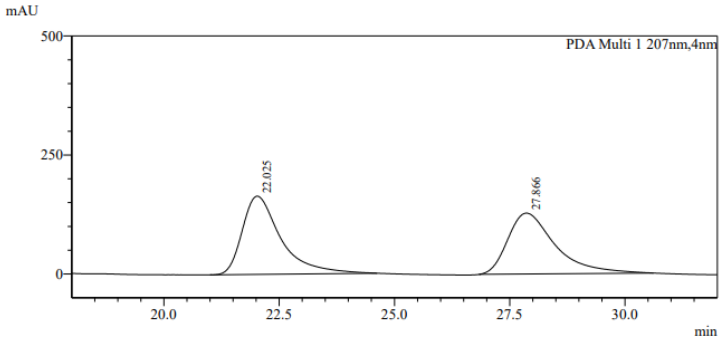
Peak#	Ret. Time	Area	Height	Aera%
1	13.341	41682519	1023535	90.977
2	15.795	4134150	135618	9.023

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(4-methoxyphenyl)propan-1-one (3ag)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 85% yield, 93:7 er. $[\alpha]_D^{25}$= -14.3 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.98 – 7.89 (m, 3H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.66 (dd, *J* = 11.6, 6.8 Hz, 1H), 4.16 (dd, *J* = 11.6, 6.9 Hz, 1H), 3.90 – 3.84 (m, 4H), 3.62 – 3.49 (m, 2H), 3.45 – 3.32 (m, 1H), 3.11 (s, 1H), 2.96 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 194.1, 164.1, 134.6, 133.3, 131.0, 130.7, 130.5, 128.8, 128.1, 114.0, 82.1, 71.0, 65.8, 55.6, 45.9, 29.7; HRMS (ESI) for $C_{20}H_{18}Cl_2O_5S$ $[M+Na]^+$ calcd. 463.0252, found: 463.0141.

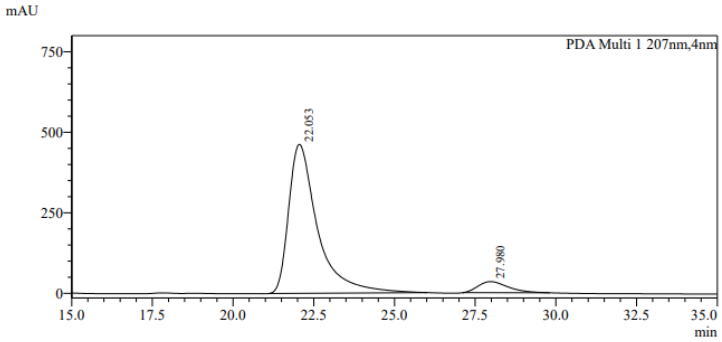
CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 22.053 min (major), t_R = 27.980 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	22.025	9598665	164475	51.213
2	27.866	9143937	127998	48.787

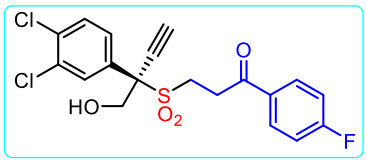


<Peak Table>

PDA Ch1 207nm

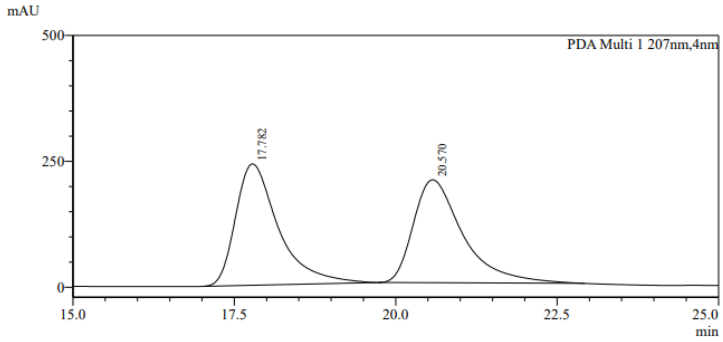
Peak#	Ret. Time	Area	Height	Aera%
1	22.053	28863250	462634	92.800
2	27.980	2239522	34484	7.200

(R)-3-((2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(4-fluorophenyl)propan-1-one (3ah)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 66% yield, 93:7 er. $[\alpha]_D^{25}$= -12.5 (c = 0.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.01 – 7.94 (m, 2H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.15 (t, *J* = 8.6 Hz, 2H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.16 (d, *J* = 11.9 Hz, 1H), 3.87 (ddd, *J* = 13.8, 9.6, 5.5 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.56 – 3.48 (m, 1H), 3.47 – 3.36 (m, 1H), 3.13 (s, 1H), 2.95 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 194.1, 166.2 (d, *J* = 255 Hz), 134.7, 133.3, 132.2 (d, *J* = 2 Hz), 131.0, 130.9, 130.8, 130.7, 130.4, 128.1, 116.2, 116.0, 82.2, 76.5, 71.1, 65.8, 45.8, 30.2; HRMS (ESI) for $C_{19}H_{15}Cl_2FO_4S$ $[M+H]^+$ calcd. 429.0052, found: 429.0126.

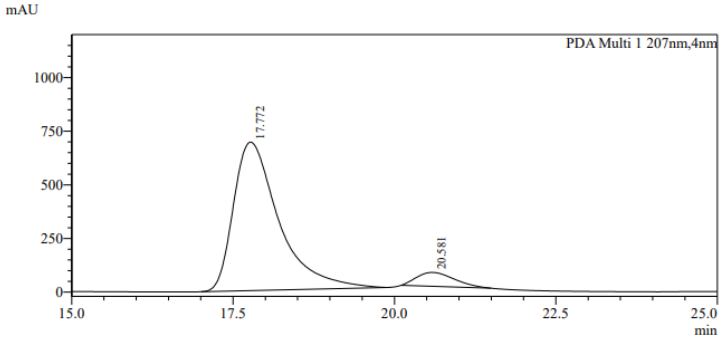
CHIRALPAK AD-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 207 nm, t_R = 17.772 min (major), t_R = 20.581 min (minor).



<Peak Table>

PDA Ch1 207nm

Peak#	Ret. Time	Area	Height	Aera%
1	17.782	11157426	241000	50.531
2	20.570	10923071	204338	49.469

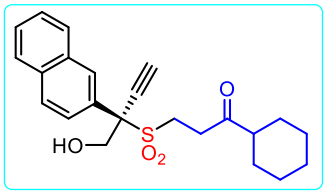


<Peak Table>

PDA Ch1 207nm

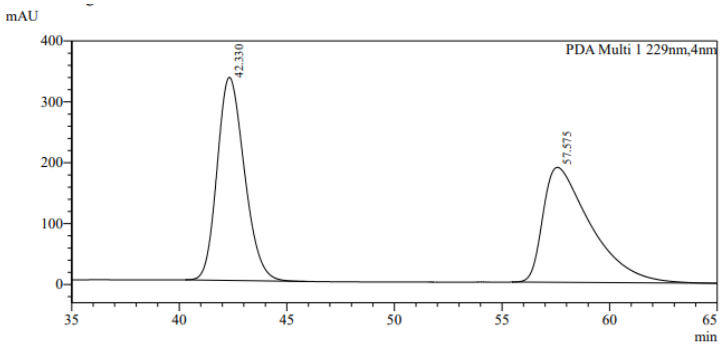
Peak#	Ret. Time	Area	Height	Aera%
1	17.772	33905827	691616	92.837
2	20.581	2616213	64275	7.163

(R)-1-cyclohexyl-3-((1-hydroxy-2-(naphthalen-2-yl)but-3-yn-2-yl)sulfonyl)propan-1-one (3ai)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 96% yield, 93:7 er. $[\alpha]_D^{25}$= -10.6 (c = 0.47, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.30 (s, 1H), 7.93 – 7.81 (m, 4H), 7.57 – 7.48 (m, 2H), 4.81 (d, *J* = 11.8 Hz, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 3.70 – 3.58 (m, 1H), 3.40 – 3.29 (m, 1H), 3.13 (s, 1H), 3.01 – 2.84 (m, 2H), 2.79 – 2.67 (m, 1H), 2.31 – 2.20 (m, 1H), 1.80 – 1.56 (m, 6H), 1.23 – 1.16 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 209.7, 133.6, 132.9, 129.3, 128.7, 128.7, 127.7, 127.6, 127.4, 126.8, 125.1, 81.6, 72.0, 65.6, 50.8, 45.0, 31.7, 28.3, 25.7, 25.5; HRMS (ESI) for $C_{23}H_{26}O_4S$ $[M+Na]^+$ calcd. 421.1552, found: 421.1449.

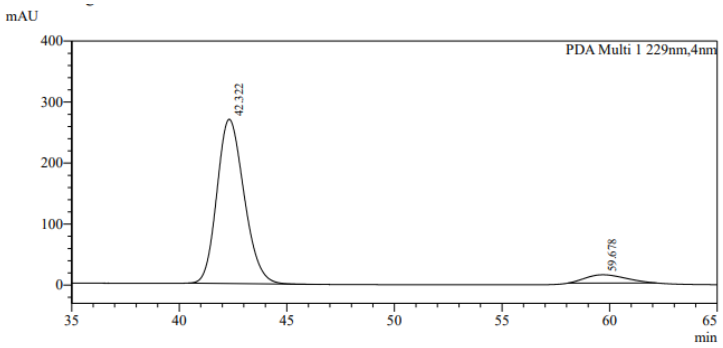
CHIRALPAK IG (Hexane/i-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 229 nm, t_R = 42.322 min (major), t_R = 59.678 min (minor).



<Peak Table>

PDA Ch1 229nm

Peak#	Ret. Time	Area	Height	Aera%
1	42.330	29390556	333487	50.216
2	57.575	29137429	188843	49.784

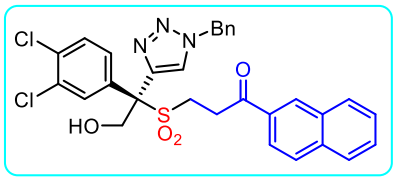


<Peak Table>

PDA Ch1 229nm

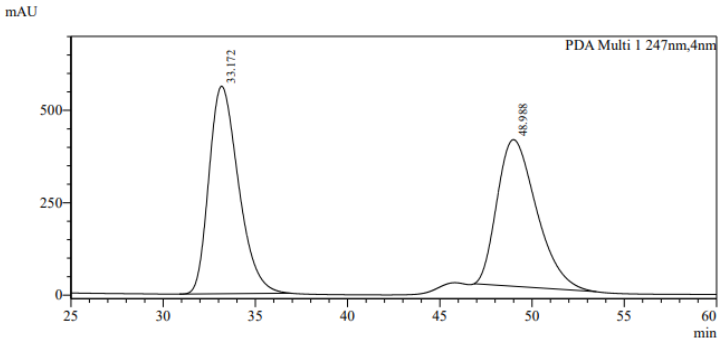
Peak#	Ret. Time	Area	Height	Aera%
1	42.322	23649971	269226	93.142
2	59.678	1741423	13520	6.858

(S)-3-((1-(1-benzyl-1H-1,2,3-triazol-4-yl)-1-(3,4-dichlorophenyl)-2-hydroxyethyl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3l-I)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). yellow solid, 65% yield, 85:15 er. $[\alpha]_D^{25}$= 13.9 (c = 0.2, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.43 (s, 1H), 8.00 – 7.93 (m, 3H), 7.90 – 7.85 (m, 2H), 7.64 – 7.55 (m, 2H), 7.45 (s, 1H), 7.41 – 7.29 (m, 7H), 5.66 (q, *J* = 14.8 Hz, 2H), 4.85 – 4.75 (m, 1H), 4.71 – 4.62 (m, 1H), 3.89 (t, *J* = 7.0 Hz, 1H), 3.75 – 3.64 (m, 1H), 3.63 – 3.50 (m, 2H), 3.39 – 3.28 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195. 5, 142.4, 135.8, 134.0, 133.9, 133.2, 133.0, 132.9, 132.4, 131.3, 130.6, 130.1, 129.7, 129.4, 129.2, 128.9, 128.7, 128.4, 128.0, 127.8, 127.0, 126.2, 123.5, 73.2, 66.0, 54.8, 47.8, 29.9. HRMS (ESI) for $C_{30}H_{25}Cl_2N_3O_4S$ $[M+Na]^+$ calcd. 616.0943, found: 616.0833.

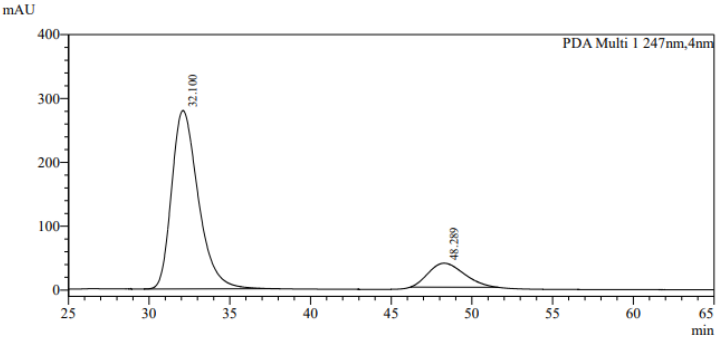
CHIRALPAK OZ-H (Hexane/i-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 32.100 min (major), t_R = 48.289 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	33.172	62679855	561650	51.474
2	48.988	59089972	396709	48.526

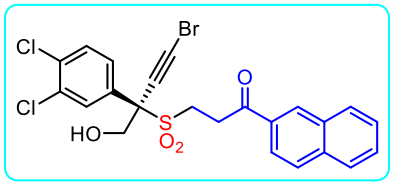


<Peak Table>

PDA Ch1 247nm

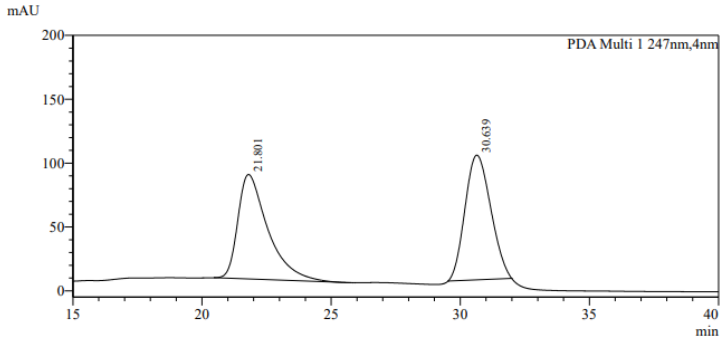
Peak#	Ret. Time	Area	Height	Aera%
1	32.100	32138365	279445	84.836
2	48.289	5744542	37433	15.164

(S)-3-((4-bromo-2-(3,4-dichlorophenyl)-1-hydroxybut-3-yn-2-yl)sulfonyl)-1-(naphthalen-2-yl)propan-1-one (3l-II)



Purification by flash chromatography (*n*-hexane/ethyl acetate = 4/1). white solid, 76% yield, 92:8 er. $[\alpha]_D^{25}$= 12.9 (c = 0.15, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) 8.45 (s, 1H), 8.00 – 7.93 (m, 2H), 7.88 (t, *J* = 8.0 Hz, 3H), 7.66 – 7.54 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.18 (d, *J* = 11.8 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.77 – 3.57 (m, 3H), 3.09 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) 195.6, 135.9, 134.7, 133.3, 133.0, 132.4, 130.9, 130.8, 130.7, 130.2, 129.7, 129.0, 128.8, 128.1, 127.8, 127.1, 123.5, 73.0, 72.1, 65.9, 54.5, 46.3, 30.5. HRMS (ESI) for $C_{23}H_{17}BrCl_2O_4S$ $[M+Na]^+$ calcd. 560.9408, found: 560.9312.

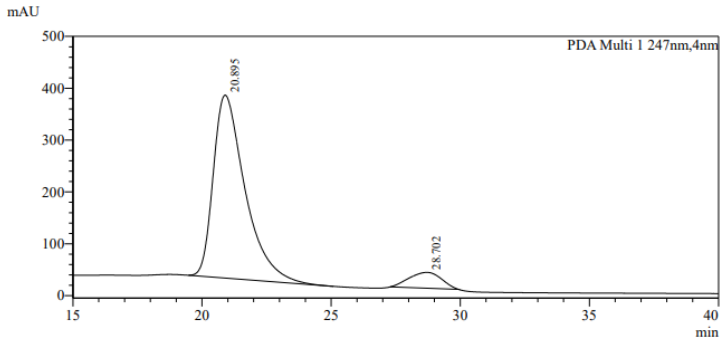
CHIRALPAK OD-H (Hexane/i-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 247 nm, t_R = 20.895 min (major), t_R = 28.702 min (minor).



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	21.801	6627468	81849	49.464
2	30.639	6771185	97621	50.536



<Peak Table>

PDA Ch1 247nm

Peak#	Ret. Time	Area	Height	Aera%
1	20.895	30207830	352709	91.923
2	28.702	2654348	30615	8.077

6. Crystal data and structural refinement for 3ai

The crystal structure of compound **3ai** has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2368900).

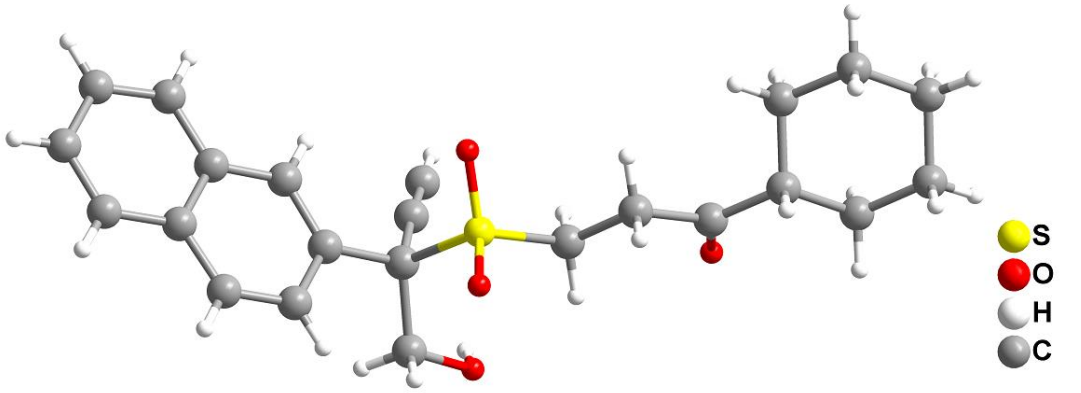


Table 1 Crystal data and structure refinement for **3ai.**

Identification code	3ai
Empirical formula	$C_{23}H_{26}O_4S$
Formula weight	398.50
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.2877(3)
b/Å	6.0439(2)
c/Å	15.4637(5)
α/°	90
β/°	105.7840(10)
γ/°	90
Volume/Å^3	1015.18(5)
Z	2
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	1.629
F(000)	424.0
Crystal size/mm^3	0.25 × 0.23 × 0.22
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.14 to 136.464

Index ranges	$-13 \le h \le 13$, $-6 \le k \le 7$, $-18 \le l \le 18$
Reflections collected	12360
Independent reflections	3428 [R_{int}= 0.0435, R_{sigma}= 0.0465]
Data/restraints/parameters	3428/1/254
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1= 0.0412, wR_2= 0.1056
Final R indexes [all data]	R_1= 0.0419, wR_2= 0.1063
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.43
Flack parameter	0.207(11)

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for **3ai**. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S001	2239.3(5)	6646.5(13)	5974.1(4)	37.4(2)
O2	1992(2)	4575(4)	6345.5(15)	49.7(5)
O4	4411(2)	9960(5)	5627.1(15)	59.0(6)
O3	1320(2)	8333(5)	5831.6(17)	62.5(6)
O1	2859(2)	5159(6)	3306.2(16)	72.0(8)
C19	3735(2)	6456(5)	8293.4(15)	33.8(5)
C14	3389(2)	8053(4)	7648.6(16)	32.3(5)
C18	3546(2)	6713(5)	9157.4(15)	34.8(5)
C10	3665(2)	7790(4)	6736.7(17)	34.7(5)
C20	3922(3)	5094(5)	9835.6(18)	43.1(6)
C17	2998(2)	8710(5)	9352.4(18)	38.2(6)
C11	4656(2)	6214(5)	6756.4(17)	38.9(6)
C15	2785(3)	9983(5)	7832.1(19)	40.1(6)
C22	3253(3)	7446(7)	10872(2)	56.2(9)
C16	2607(2)	10282(5)	8660.4(19)	41.9(6)
C5	801(3)	885(5)	2994(2)	47.8(7)
C6	962(3)	3260(5)	2704.2(18)	40.2(6)
C13	3975(3)	10084(5)	6396(2)	47.7(6)
C23	2872(3)	9017(6)	10232(2)	49.6(7)
C1	1283(3)	3272(6)	1805.3(19)	52.3(7)
C21	3770(3)	5460(7)	10675(2)	52.3(8)
C12	5457(3)	5009(6)	6721(2)	51.8(7)
C9	2611(3)	6114(7)	4953(2)	59.2(10)
C7	1897(3)	4503(6)	3420(2)	47.1(7)

C2	322(3)	2025(8)	1090.7(19)	62.4(10)
C4	-178(3)	-325(7)	2271(2)	61.4(9)
C8	1577(3)	4958(8)	4290(2)	63.6(10)
C3	124(4)	-285(8)	1366(3)	72.1(12)

Table 3 Anisotropic Displacement Parameters (Å2×103) for 1. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S001	35.3(3)	44.5(4)	32.8(3)	-4.0(3)	10.2(2)	-3.3(3)
O2	54.8(12)	47.6(12)	49.1(11)	-5.5(9)	18.5(9)	-16.5(10)
O4	63.7(13)	65.1(15)	55.3(12)	10.7(11)	28.4(10)	-10.1(12)
O3	45.8(12)	67.6(16)	64.6(14)	-5.1(12)	-1.1(10)	13.7(12)
O1	61.3(14)	102(2)	61.4(14)	-27.9(15)	32.2(12)	-35.9(15)
C19	34.3(10)	29.8(12)	36.5(11)	-2.7(11)	8.5(8)	1.4(10)
C14	31.2(11)	30.4(12)	34.0(11)	-2.5(9)	6.8(9)	-0.2(10)
C18	30.2(10)	37.1(12)	34.9(11)	-3.7(12)	5.2(8)	-2.0(11)
C10	35.5(12)	32.7(13)	35.6(12)	0.5(10)	9.6(10)	-1.0(10)
C20	40.9(13)	46.0(15)	39.9(13)	2.6(12)	6.8(11)	0.3(12)
C17	32.7(11)	42.6(15)	38.7(13)	-6.7(11)	8.5(10)	0.4(11)
C11	38.3(12)	41.3(16)	38.9(12)	-2.1(11)	13.3(10)	-5.6(11)
C15	42.9(13)	31.7(13)	43.4(13)	-1.6(11)	8.1(11)	4.3(11)
C22	49.9(16)	85(3)	36.8(14)	-6.3(14)	17.1(13)	-2.5(16)
C16	40.8(13)	36.7(14)	48.2(15)	-6.8(12)	12.2(11)	7.8(11)
C5	49.7(16)	51.4(17)	44.4(15)	1.4(12)	16.4(12)	-4.2(13)
C6	40.0(13)	47.6(16)	33.6(12)	-4.1(11)	11.1(10)	0.3(12)
C13	55.4(16)	40.3(15)	51.4(15)	4.4(13)	21.7(13)	-5.8(13)
C23	44.2(15)	62(2)	45.3(15)	-12.0(14)	16.6(12)	3.8(14)
C1	61.4(18)	61.0(19)	36.1(13)	2.2(13)	16.1(13)	-2.5(16)
C21	49.2(16)	70(2)	36.3(14)	8.9(14)	9.0(12)	-1.7(15)
C12	44.3(15)	51.0(17)	64.7(18)	0.6(15)	22.7(14)	6.0(14)
C9	55.3(16)	89(3)	37.7(14)	-18.5(15)	19.4(12)	-25.5(17)
C7	47.4(15)	54.7(18)	41.1(14)	-8.0(12)	15.5(12)	-10.6(13)
C2	54.0(16)	98(3)	33.3(13)	-11.3(17)	9.2(12)	8(2)
C4	62.7(19)	67(2)	61.5(19)	-21.8(17)	28.9(16)	-21.4(17)
C8	55.4(18)	96(3)	43.7(15)	-25.7(18)	21.2(14)	-34(2)
C3	72(2)	89(3)	64(2)	-40(2)	33.2(18)	-21(2)

Table 4 Bond Lengths for **3ai.**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**

S001	O2	1.436(2)	C17	C16	1.409(4)
S001	O3	1.428(2)	C17	C23	1.417(4)
S001	C10	1.851(3)	C11	C12	1.174(4)
S001	C9	1.770(3)	C15	C16	1.361(4)
O4	C13	1.407(4)	C22	C23	1.354(5)
O1	C7	1.214(4)	C22	C21	1.403(5)
C19	C14	1.366(4)	C5	C6	1.529(4)
C19	C18	1.418(3)	C5	C4	1.527(5)
C14	C10	1.533(3)	C6	C1	1.529(4)
C14	C15	1.418(4)	C6	C7	1.506(4)
C18	C20	1.413(4)	C1	C2	1.521(5)
C18	C17	1.425(4)	C9	C8	1.500(4)
C10	C11	1.463(4)	C7	C8	1.510(4)
C10	C13	1.557(4)	C2	C3	1.494(7)
C20	C21	1.373(4)	C4	C3	1.528(5)

Table 5 Bond Angles for **3ai.**

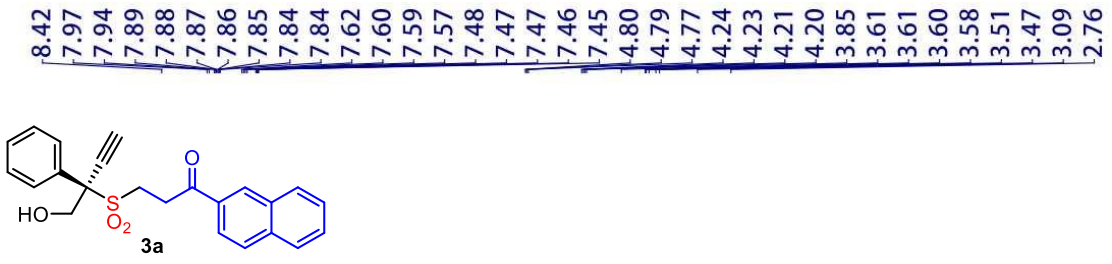
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O2	S001	C10	107.49(12)	C23	C17	C18	118.5(3)
O2	S001	C9	108.49(17)	C12	C11	C10	175.7(3)
O3	S001	O2	118.14(15)	C16	C15	C14	120.0(3)
O3	S001	C10	107.54(14)	C23	C22	C21	120.7(3)
O3	S001	C9	109.33(18)	C15	C16	C17	121.9(3)
C9	S001	C10	105.08(13)	C4	C5	C6	110.8(3)
C14	C19	C18	121.6(2)	C1	C6	C5	110.3(3)
C19	C14	C10	120.6(2)	C7	C6	C5	111.6(2)
C19	C14	C15	119.5(2)	C7	C6	C1	112.0(2)
C15	C14	C10	119.9(2)	O4	C13	C10	113.6(3)
C19	C18	C17	118.5(2)	C22	C23	C17	120.9(3)
C20	C18	C19	122.1(3)	C2	C1	C6	111.1(3)
C20	C18	C17	119.3(2)	C20	C21	C22	120.5(3)
C14	C10	S001	105.39(16)	C8	C9	S001	111.4(2)
C14	C10	C13	109.9(2)	O1	C7	C6	122.1(3)
C11	C10	S001	107.32(18)	O1	C7	C8	120.7(3)
C11	C10	C14	113.2(2)	C6	C7	C8	117.2(2)
C11	C10	C13	110.2(2)	C3	C2	C1	112.8(3)
C13	C10	S001	110.70(19)	C5	C4	C3	111.4(3)
C21	C20	C18	120.1(3)	C9	C8	C7	111.3(3)
C16	C17	C18	118.3(2)	C2	C3	C4	111.4(3)

C16	C17	C23	123.2(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3ai.**

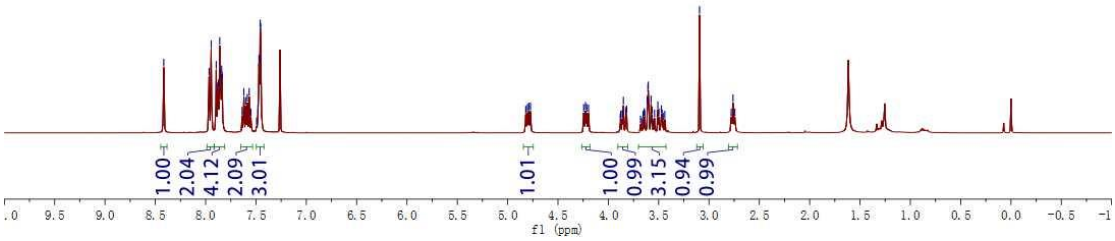
Atom	*x*	*y*	*z*	U(eq)
H4	5086.11	9353.8	5756.33	88
H19	4104.24	5169.18	8162.53	41
H20	4272.17	3779.01	9713.18	52
H15	2510.43	11043.3	7386.88	48
H22	3170.71	7685.21	11446.48	67
H16	2215.5	11561.26	8772.8	50
H5A	1578.5	103.6	3101.37	57
H5B	561.99	901.84	3550.53	57
H6	168.85	4014.72	2614.34	48
H13A	3241.36	10998.56	6260.96	57
H13B	4593.39	10803.5	6873.51	57
H23	2523.08	10316.43	10371.25	60
H1A	1331.56	4787.36	1611.54	63
H1B	2082.27	2589.21	1880.15	63
H21	4012.27	4383.44	11118.03	63
H12	6091.2	4053.6	6693.2	62
H9A	2787.03	7500.02	4696.97	71
H9B	3345.43	5202.75	5072.19	71
H2A	-451.91	2823.25	963.57	75
H2B	580.06	1977.8	541.71	75
H4A	-971.9	369.28	2208.45	74
H4B	-233.23	-1847.56	2454.93	74
H8A	843.16	5868.77	4170.41	76
H8B	1401	3571.36	4546.19	76
H3A	860.12	-1151.78	1407.58	86
H3B	-547.35	-954.13	912.22	86

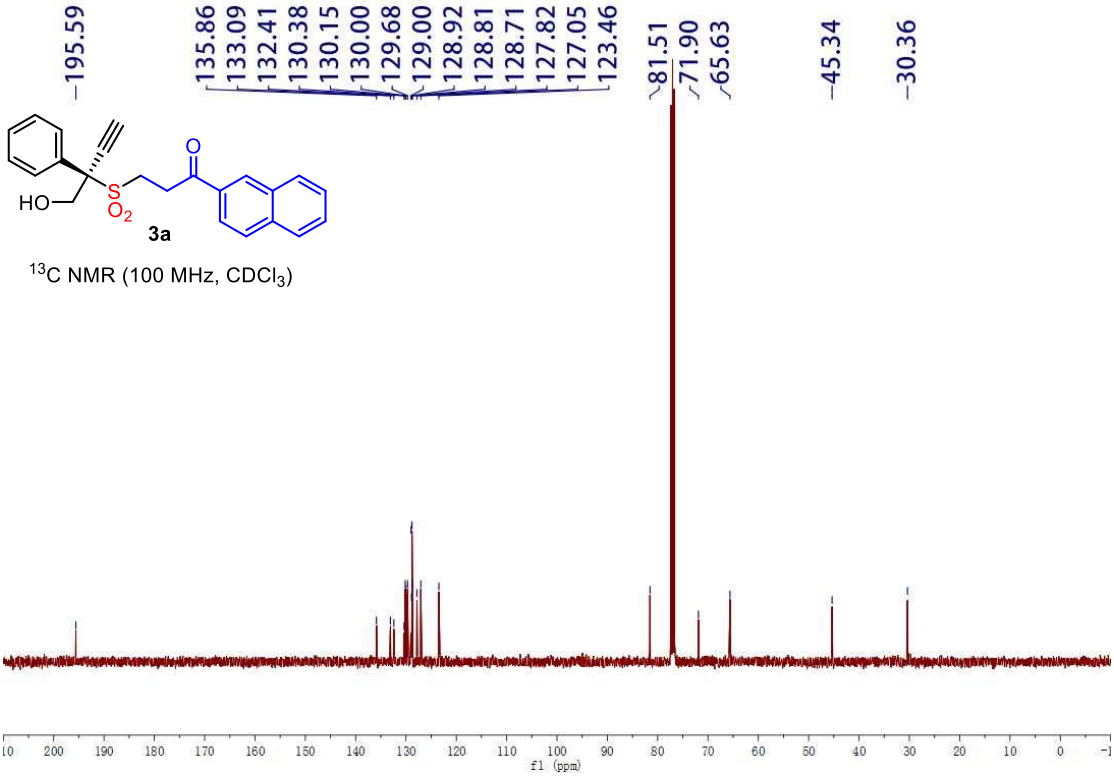
7. NMR spectra of compounds



3a

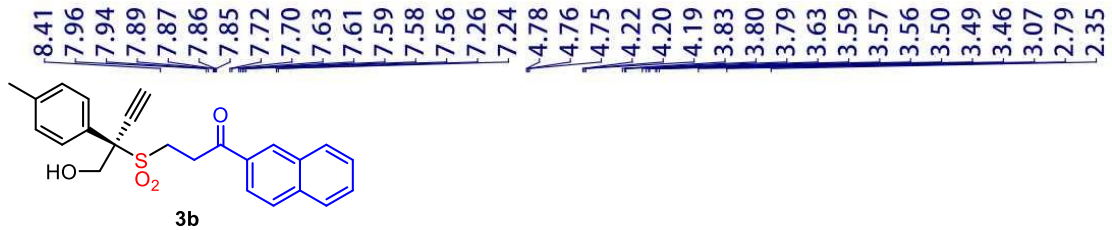
^{1}H NMR (400 MHz, $CDCl_3$)





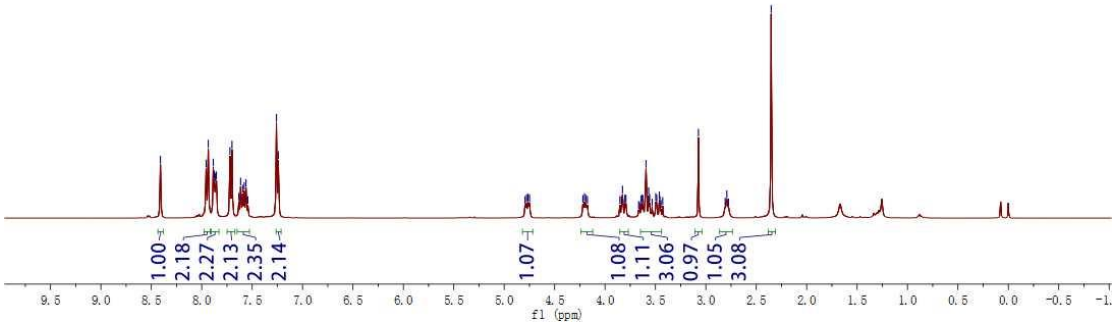
3a

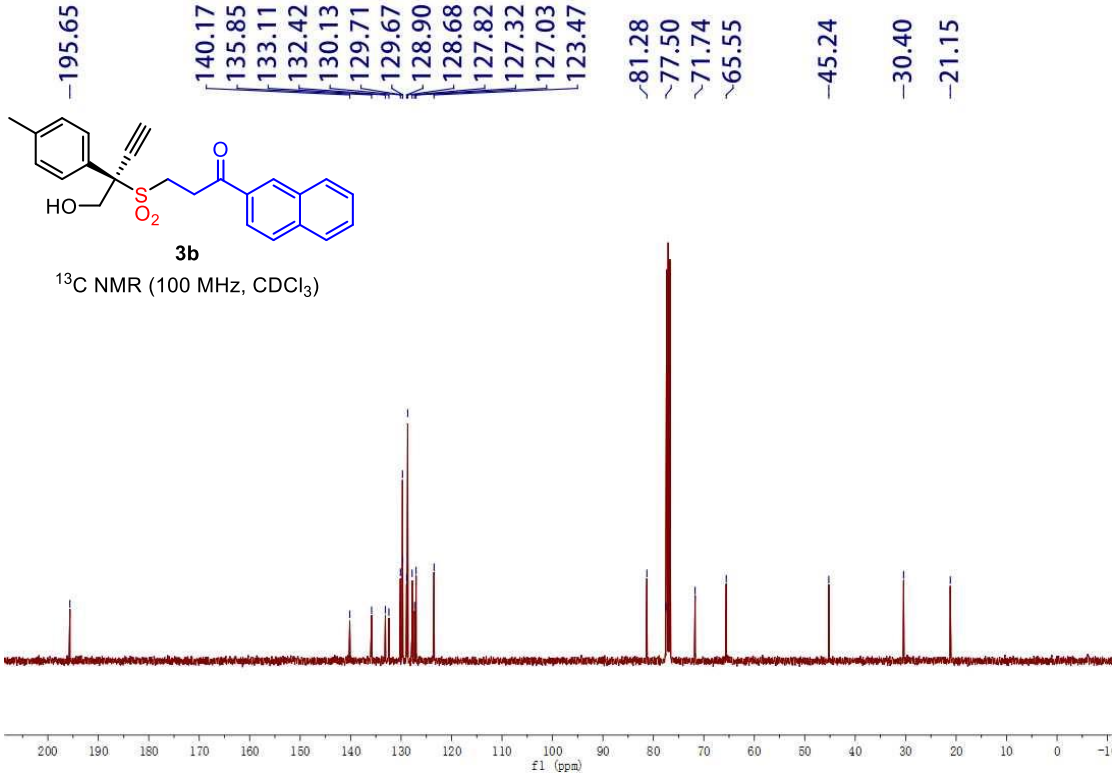
^{13}C NMR (100 MHz, $CDCl_3$)



3b

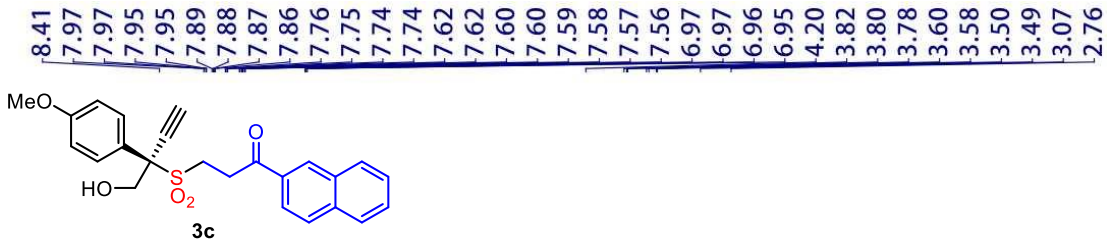
^{1}H NMR (400 MHz, $CDCl_3$)





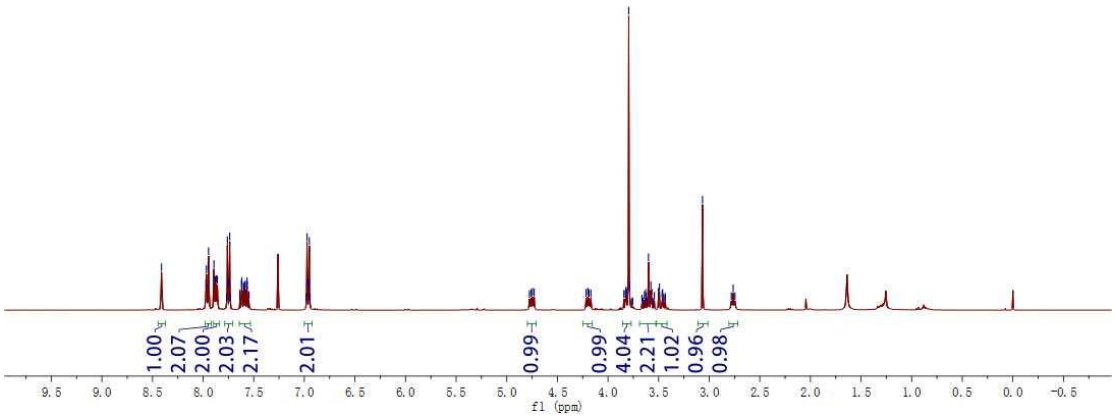
3b

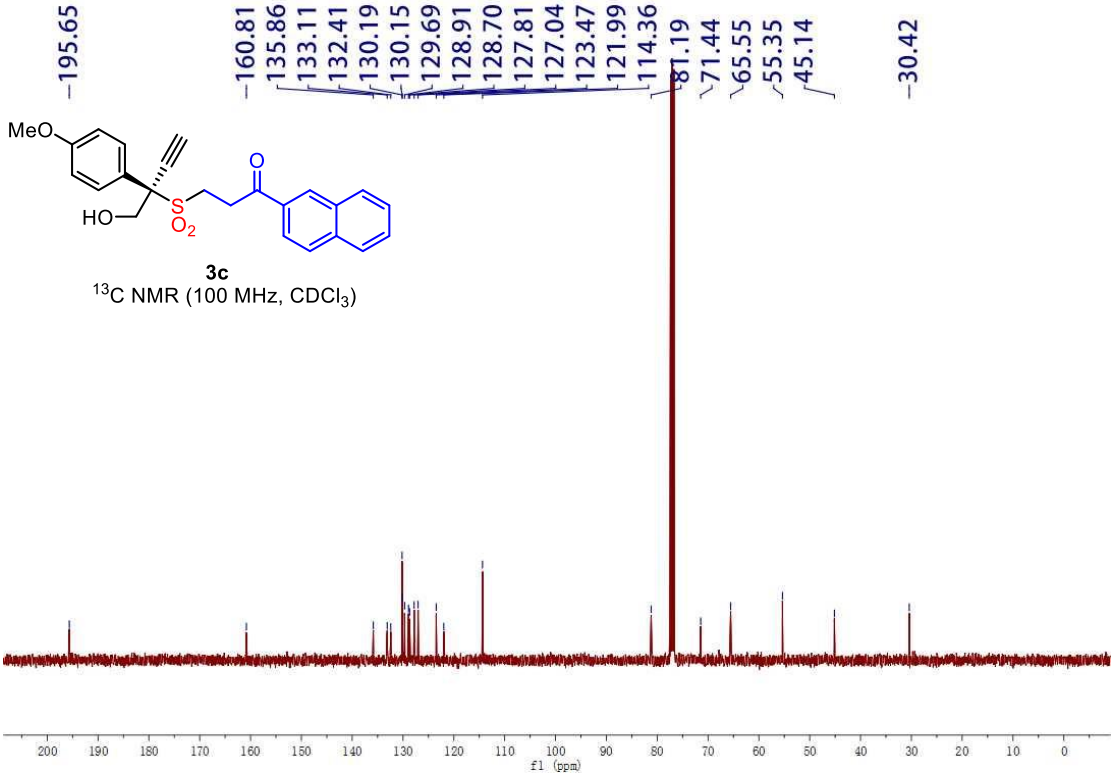
^{13}C NMR (100 MHz, $CDCl_3$)



3c

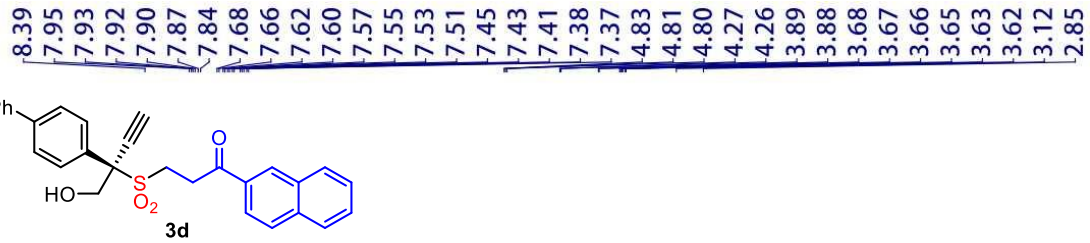
^{1}H NMR (400 MHz, $CDCl_3$)





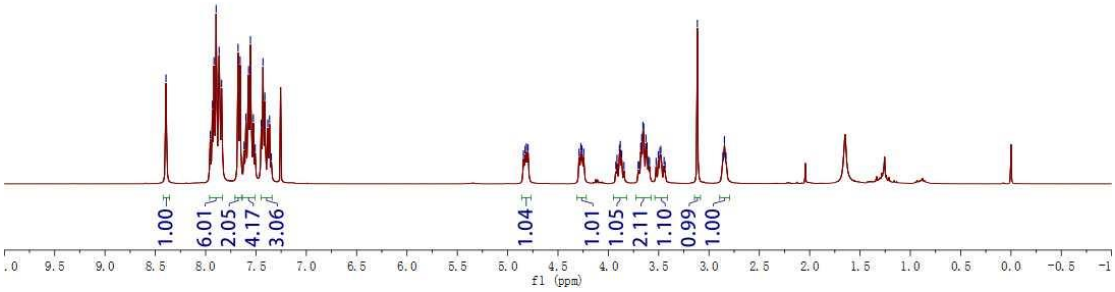
3c

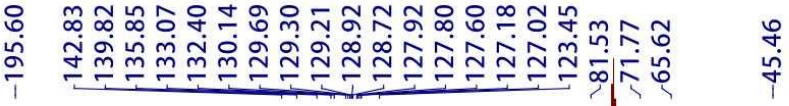
^{13}C NMR (100 MHz, $CDCl_3$)

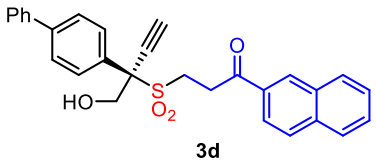


3d

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

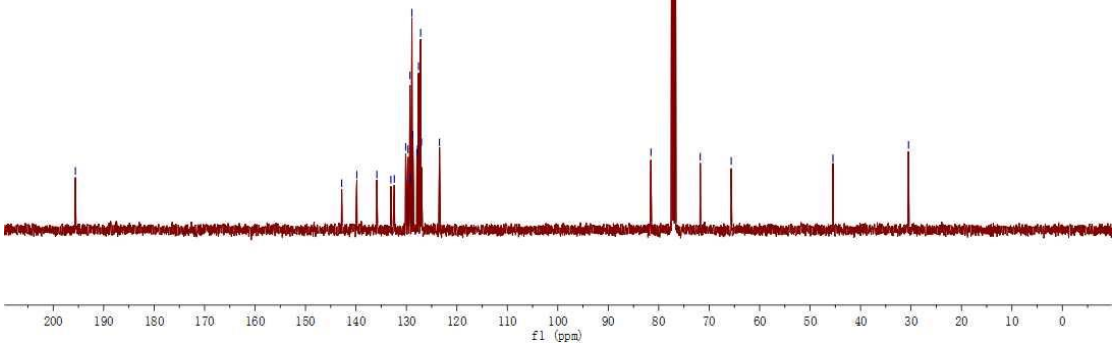


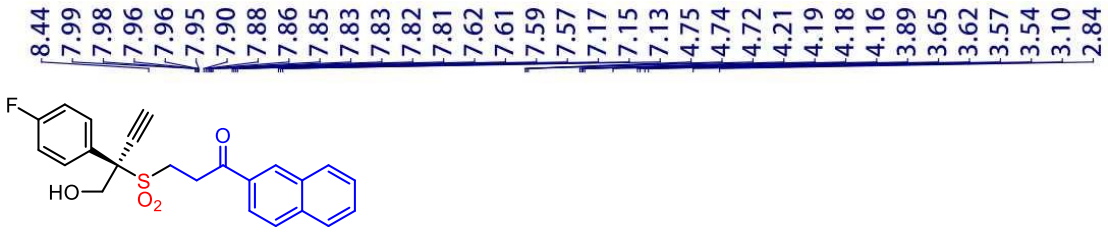




3d

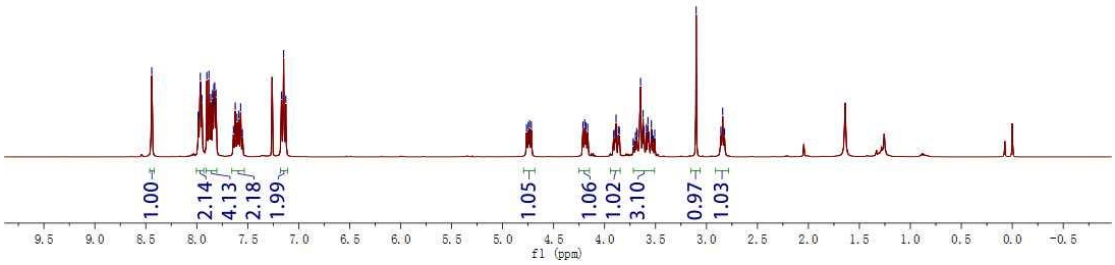
^{13}C NMR (100 MHz, $CDCl_3$)

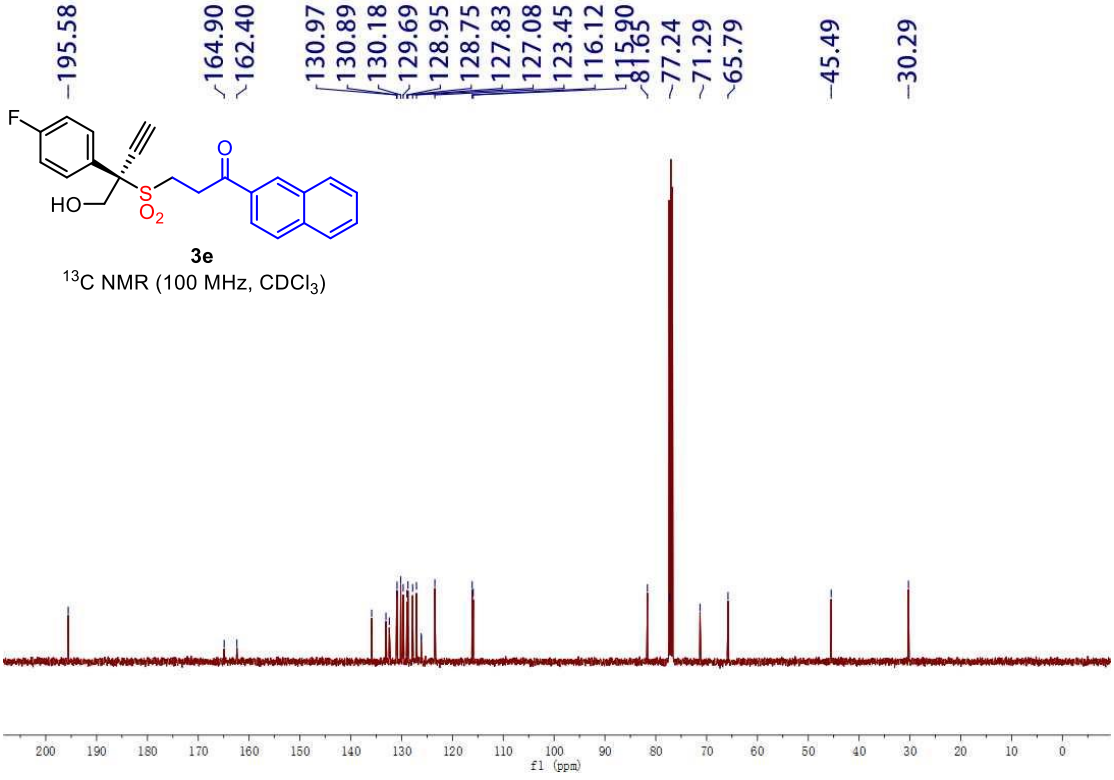




3e

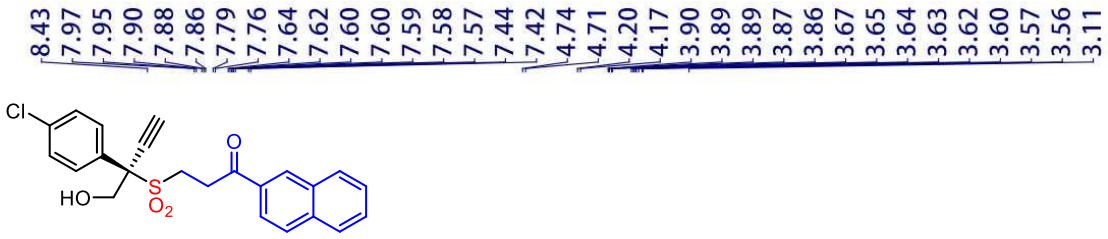
^{1}H NMR (400 MHz, $CDCl_3$)





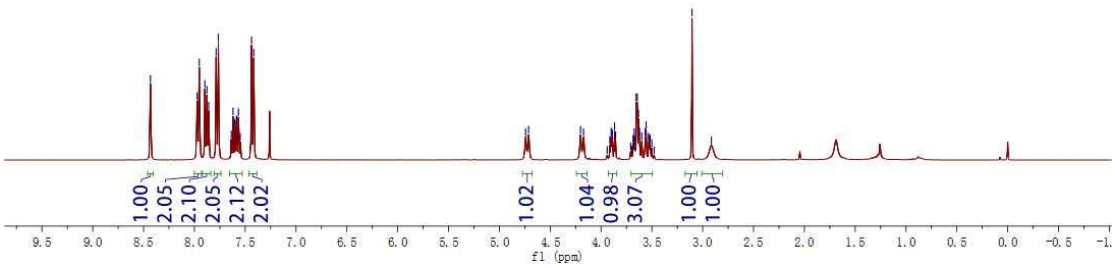
3e

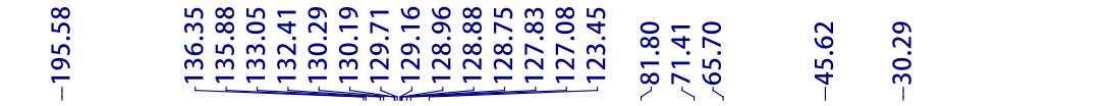
^{13}C NMR (100 MHz, $CDCl_3$)



3f

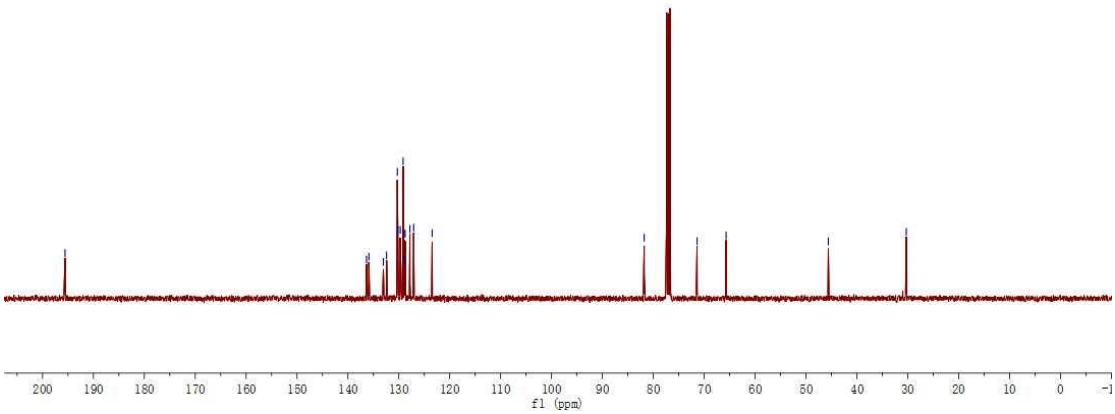
^{1}H NMR (400 MHz, $CDCl_3$)

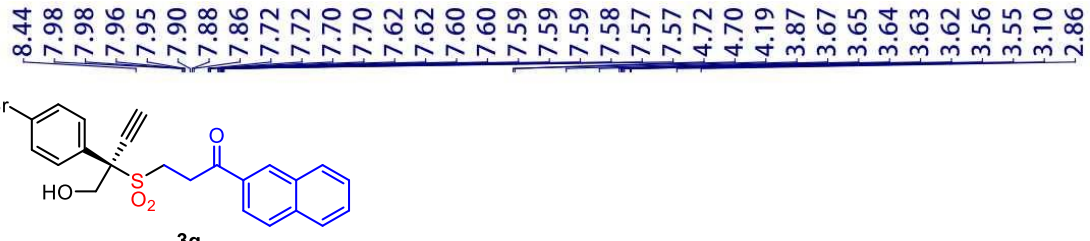




3f

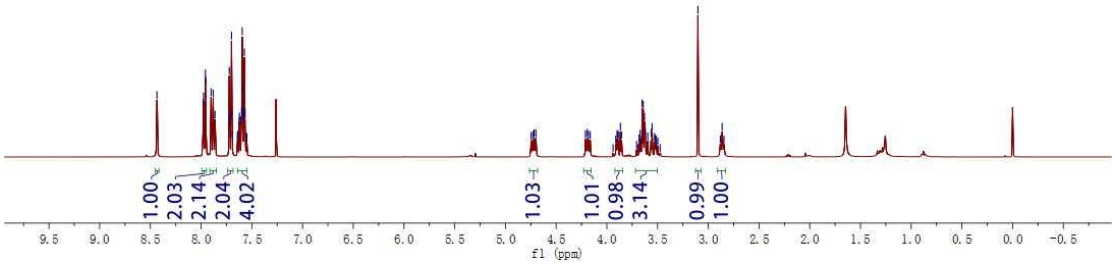
^{13}C NMR (100 MHz, $CDCl_3$)

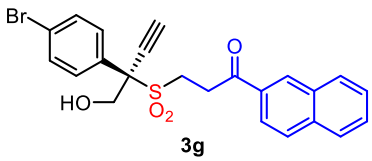




3g

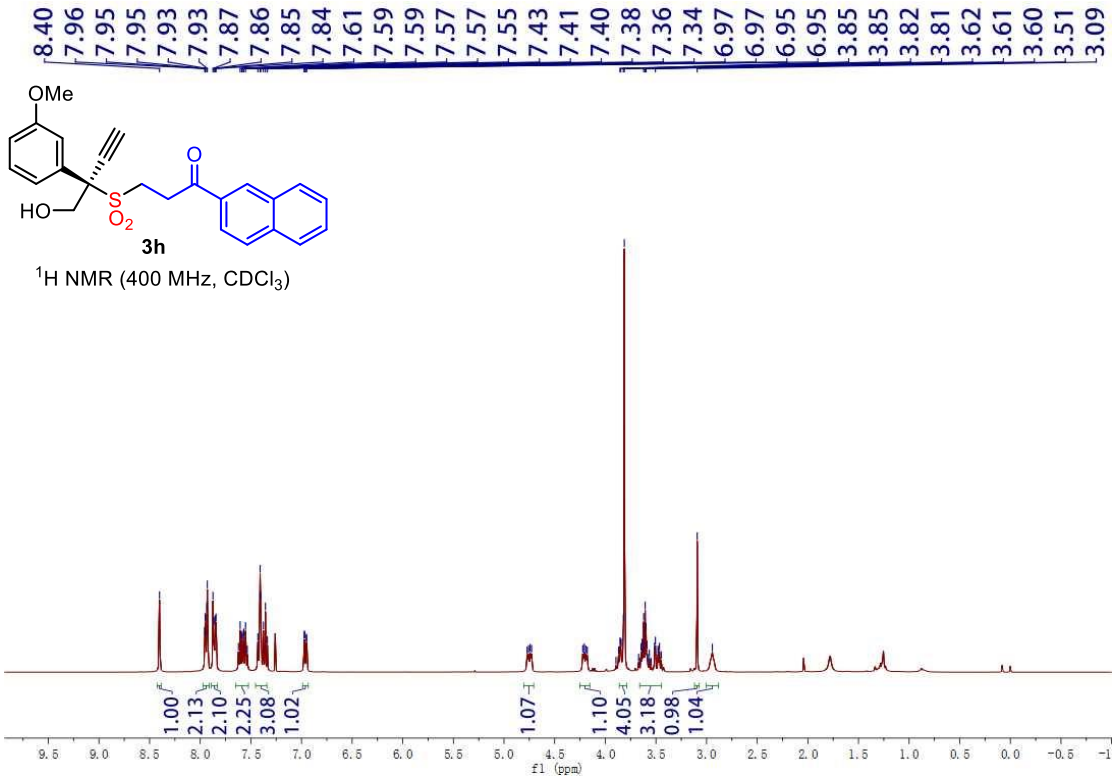
^{1}H NMR (400 MHz, $CDCl_3$)

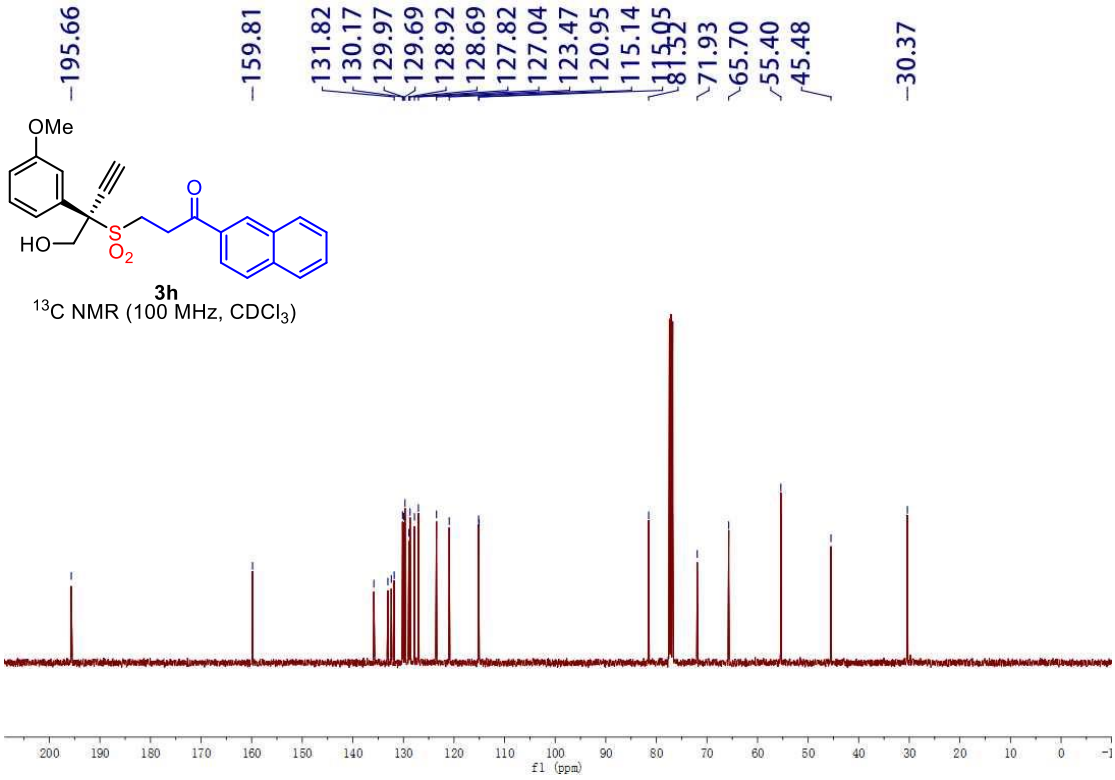


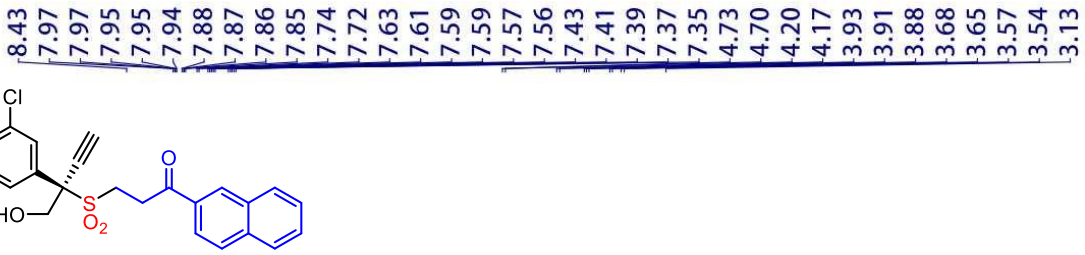


3g

^{13}C NMR (100 MHz, $CDCl_3$)

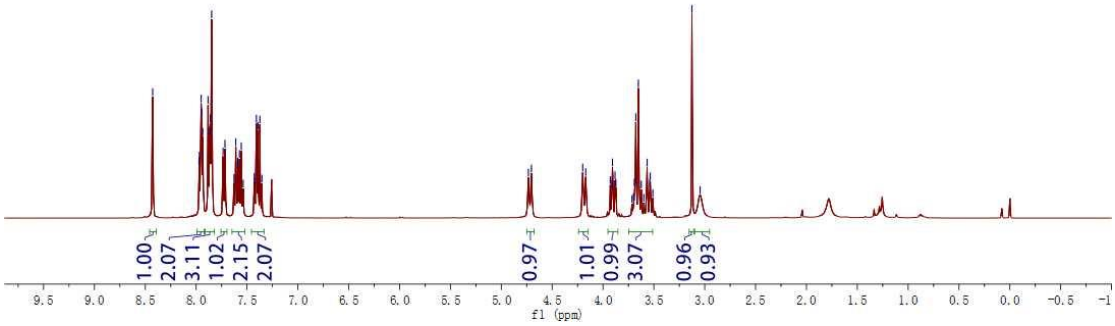

8.40
7.96
7.95
7.95
7.93
7.93
7.87
7.86
7.85
7.84
7.61
7.59
7.59
7.57
7.57
7.55
7.43
7.41
7.40
7.38
7.36
7.34
6.97
6.97
6.95
6.95
3.85
3.85
3.82
3.81
3.62
3.61
3.60
3.51
3.09
OMe
HO
S
O2
O
3h
1H NMR (400 MHz, CDCl3)
1.00
2.13
2.10
2.25
3.08
1.02
1.07
1.10
4.05
3.18
0.98
1.04
f1 (ppm)

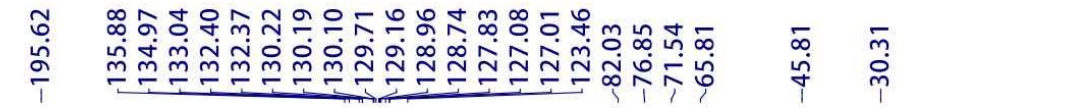

195.66
159.81
131.82
130.17
129.97
129.69
128.92
128.69
127.82
127.04
123.47
120.95
115.14
115.05
81.52
71.93
65.70
55.40
45.48
30.37
OMe
HO
S
O2
O
3h
13C NMR (100 MHz, CDCl3)
f1 (ppm)



3i

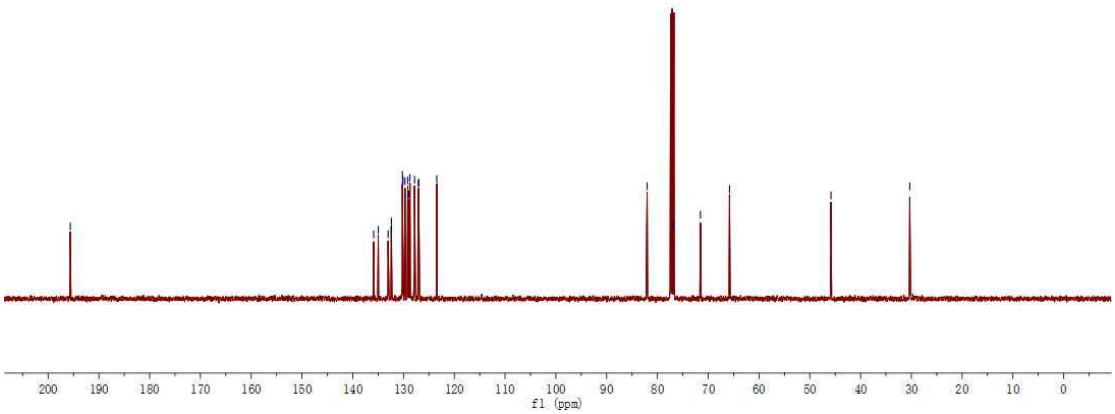
^{1}H NMR (400 MHz, $CDCl_3$)

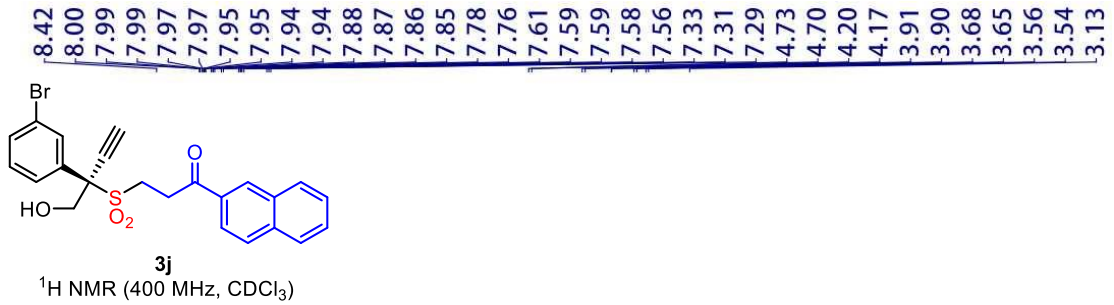




3i

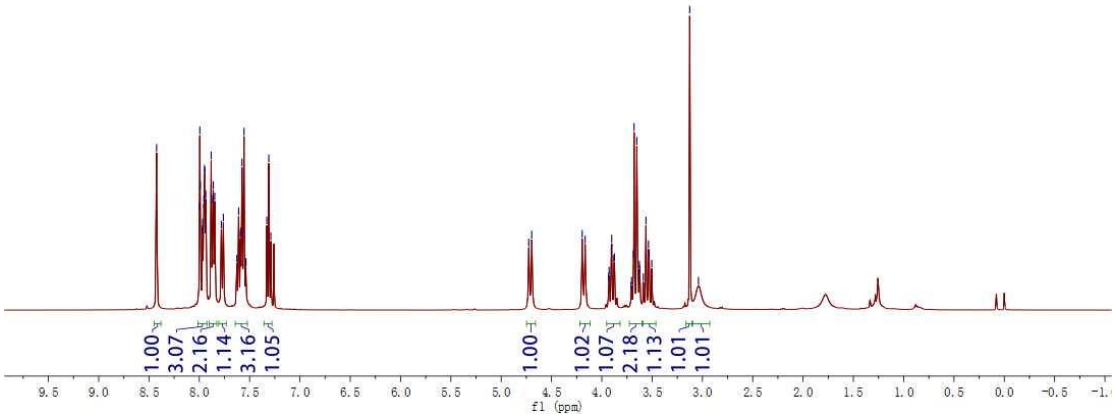
^{13}C NMR (100 MHz, $CDCl_3$)

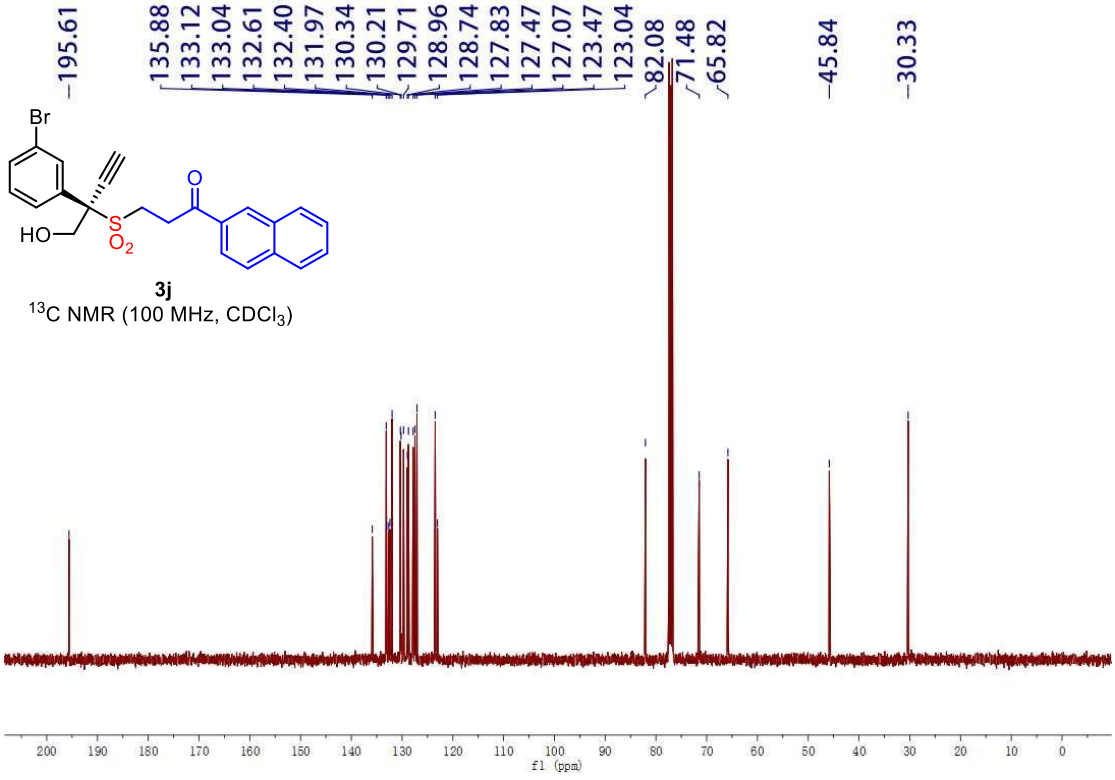




3j

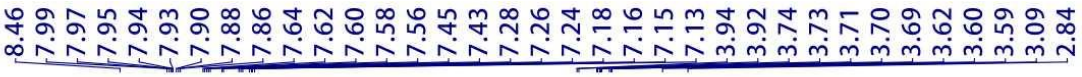
^{1}H NMR (400 MHz, $CDCl_3$)

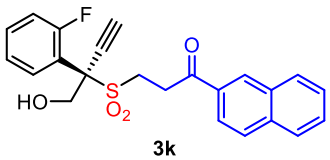




3j

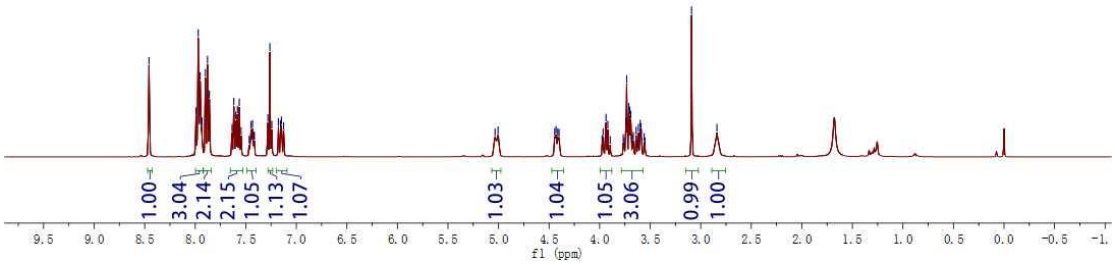
^{13}C NMR (100 MHz, $CDCl_3$)

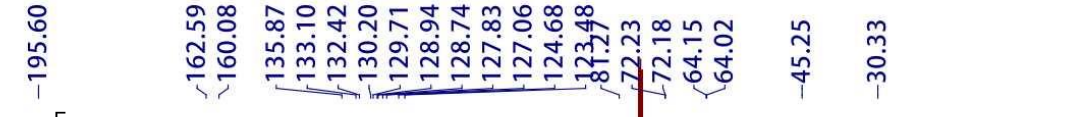


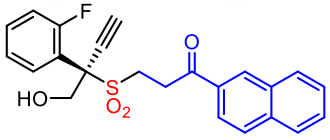


3k

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

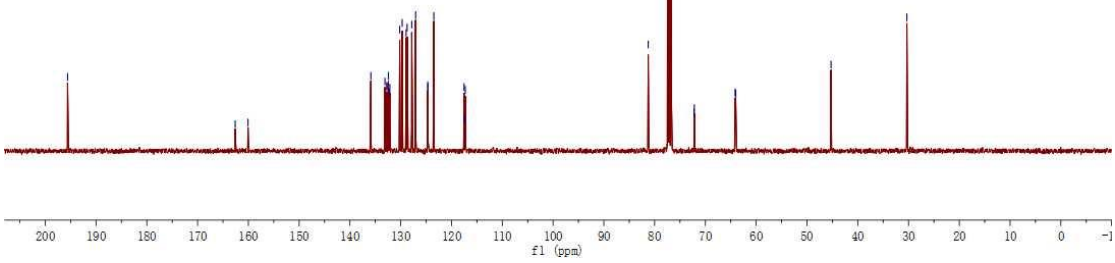


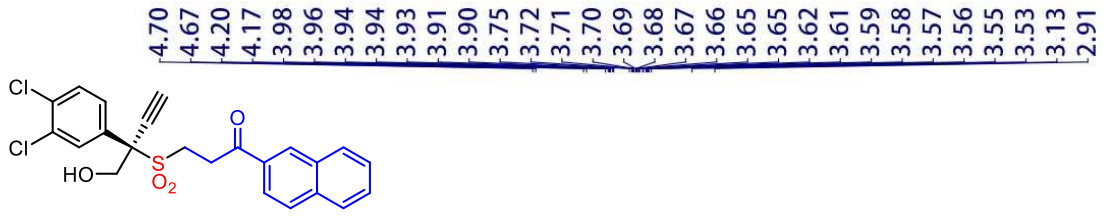




3k

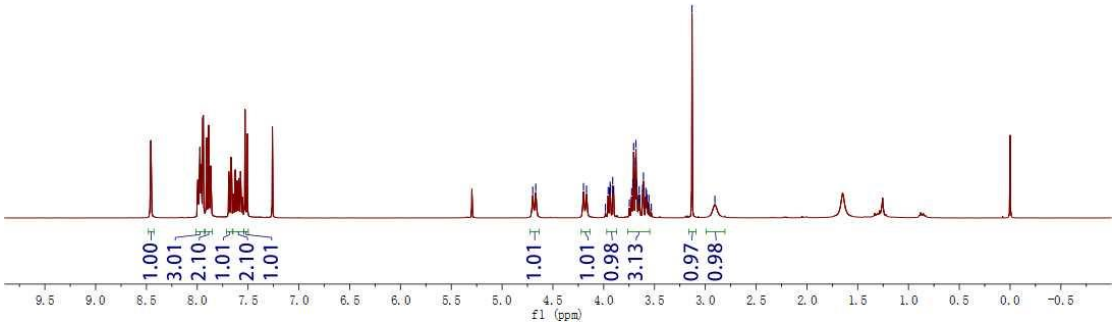
^{13}C NMR (100 MHz, $CDCl_3$)

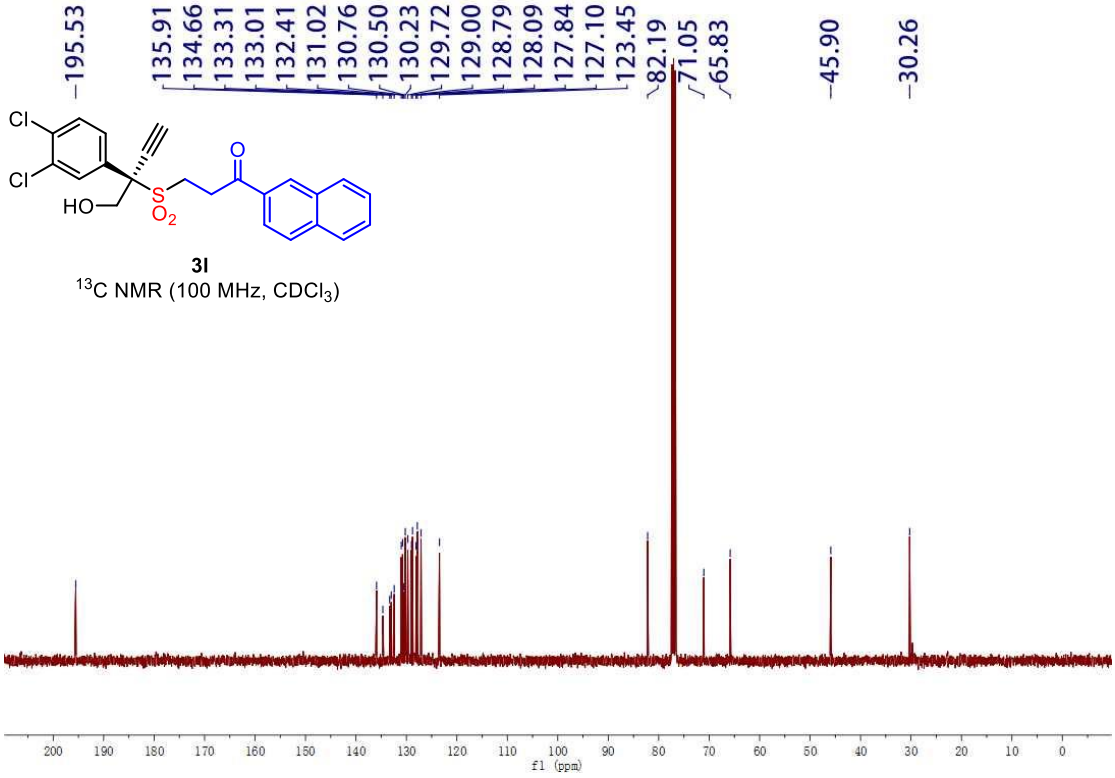




3l

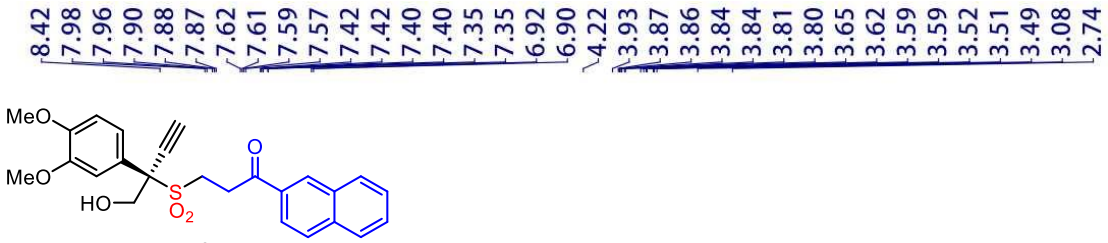
^{1}H NMR (400 MHz, $CDCl_3$)





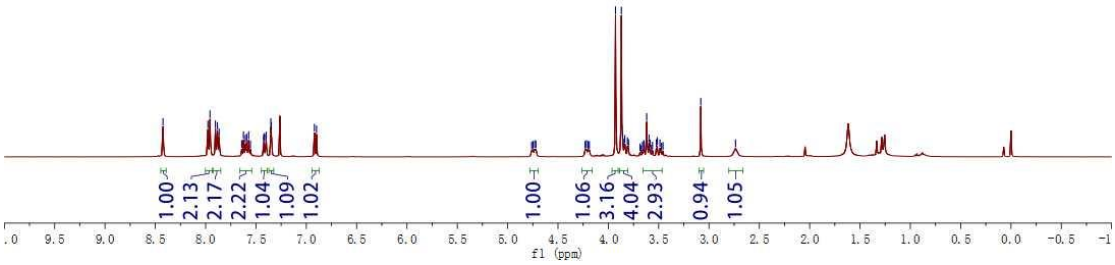
3l

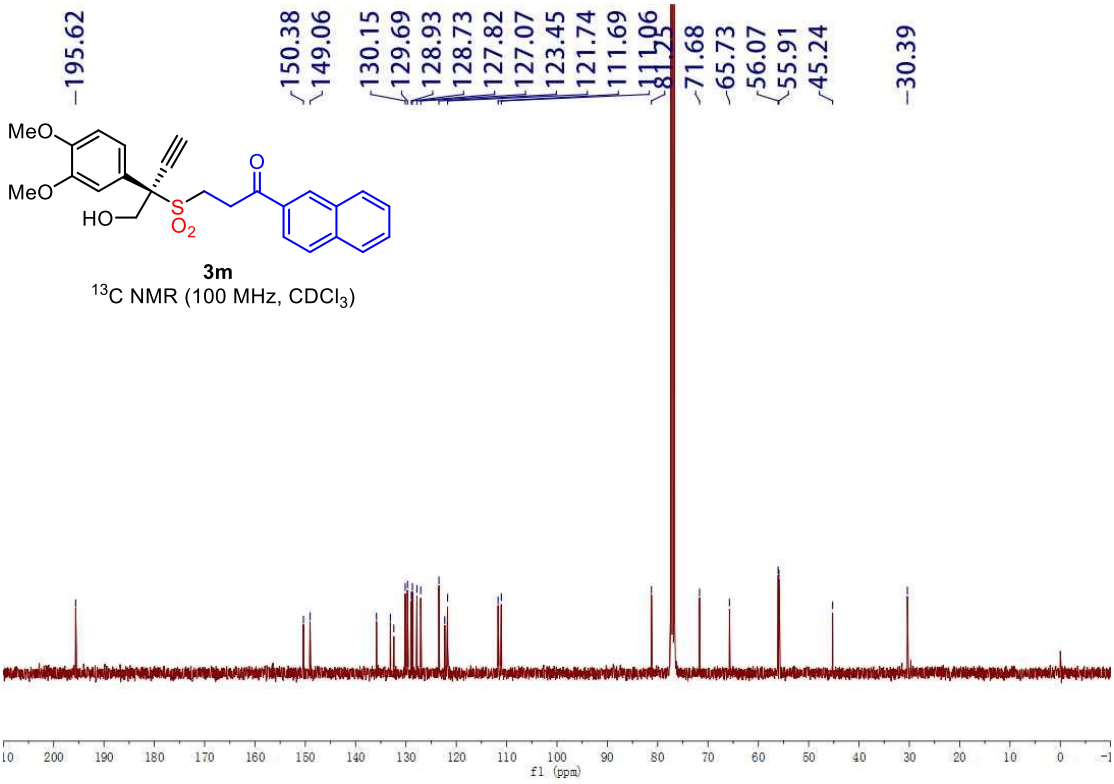
^{13}C NMR (100 MHz, $CDCl_3$)



3m

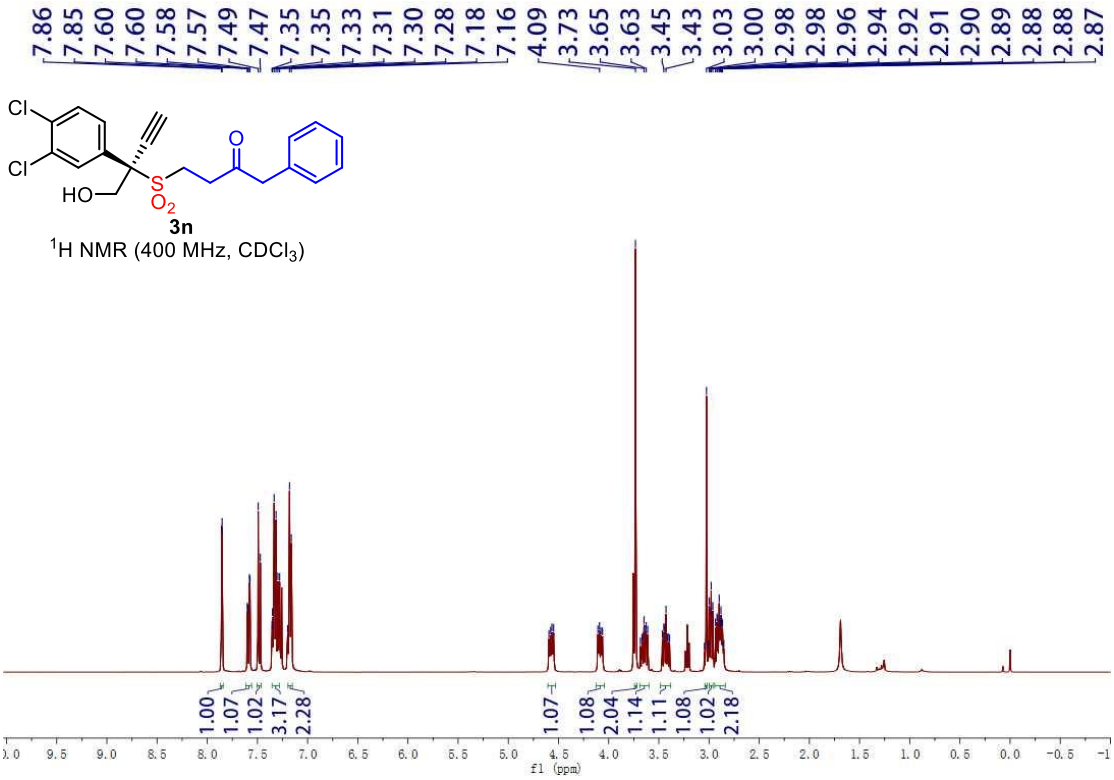
^{1}H NMR (400 MHz, $CDCl_3$)

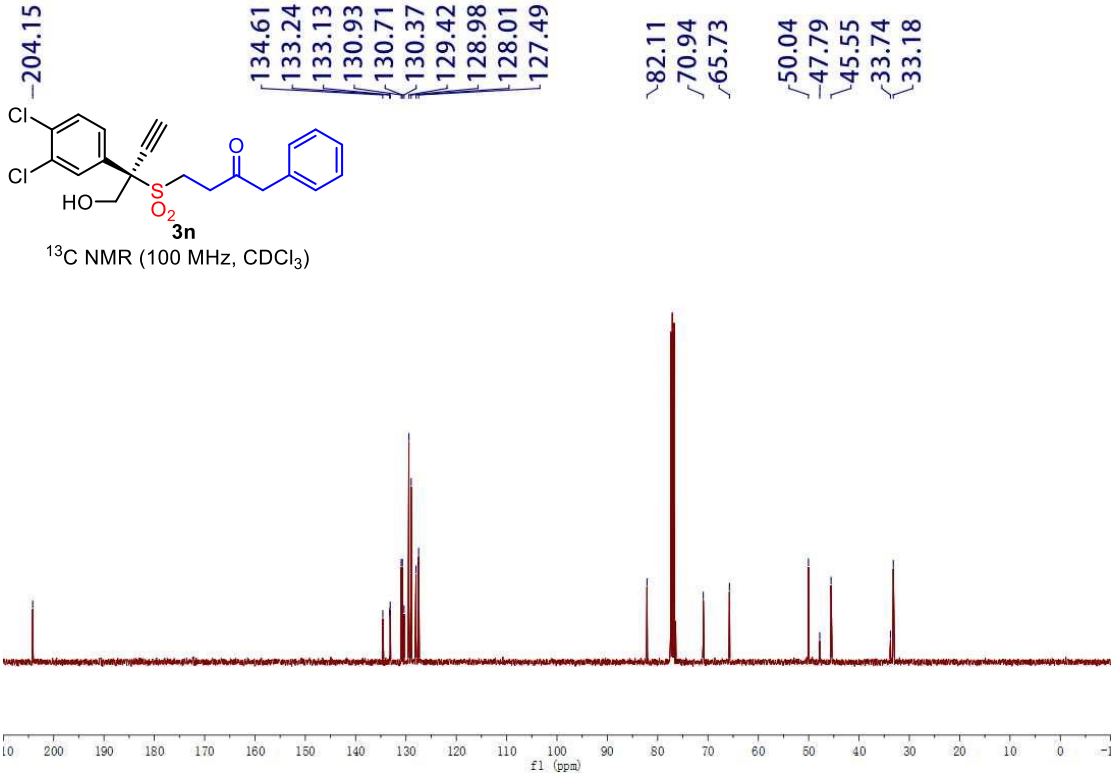


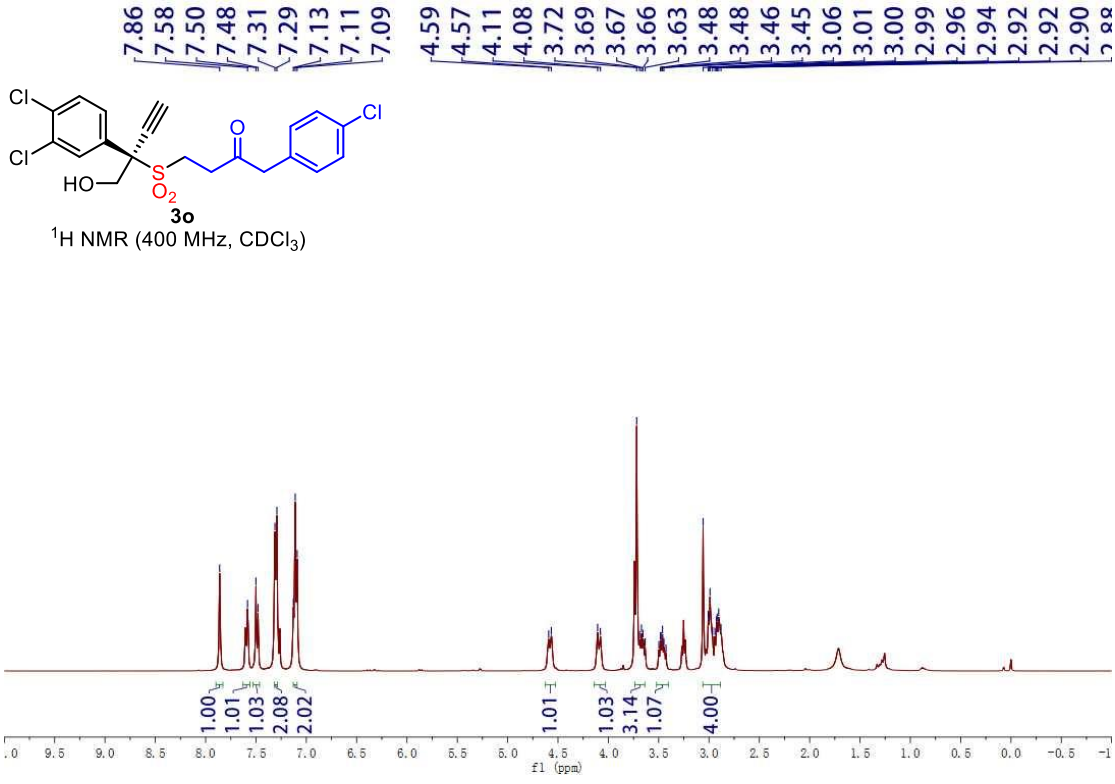


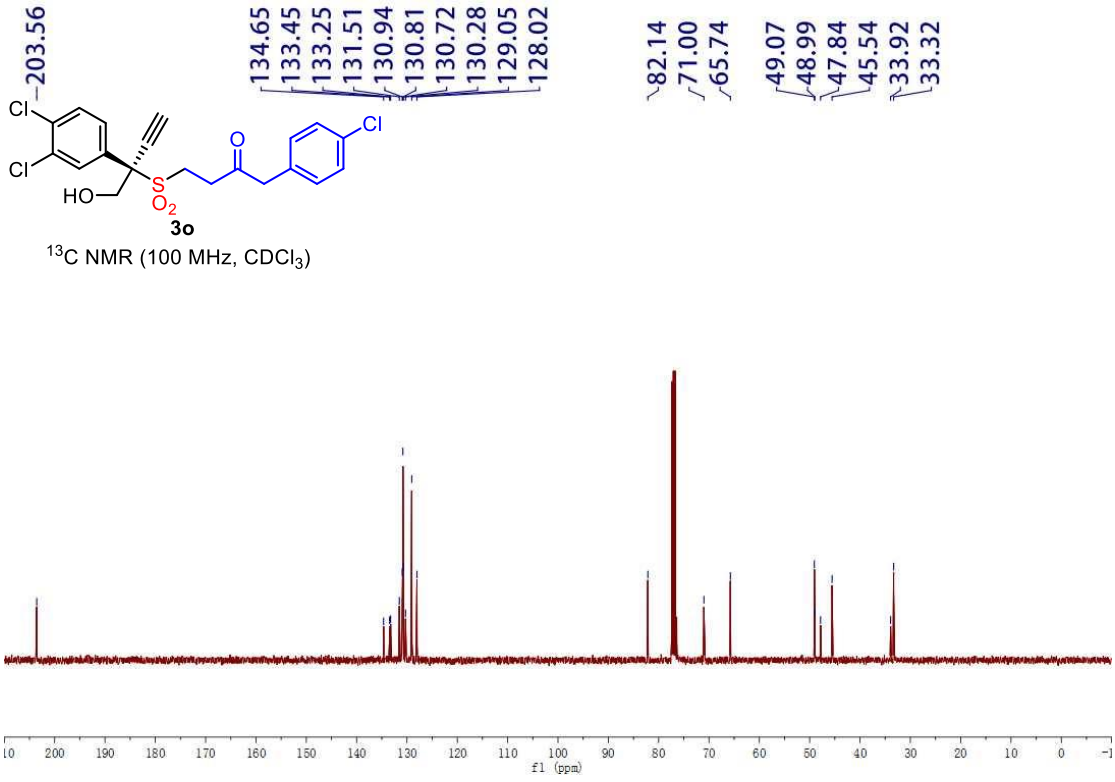
3m

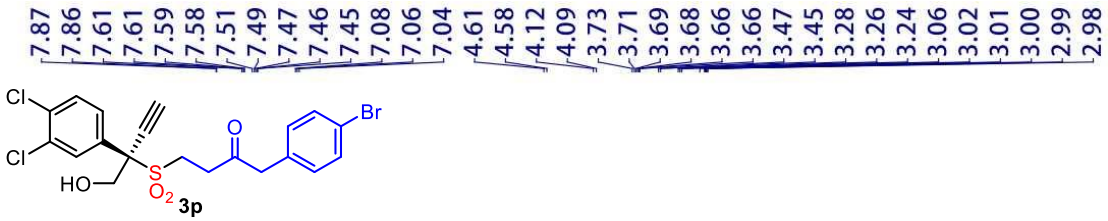
^{13}C NMR (100 MHz, $CDCl_3$)


7.86
7.85
7.60
7.60
7.58
7.57
7.49
7.47
7.35
7.35
7.33
7.31
7.30
7.28
7.18
7.16
4.09
3.73
3.65
3.63
3.45
3.43
3.03
3.00
2.98
2.98
2.96
2.94
2.92
2.91
2.90
2.89
2.88
2.88
2.87
Cl
Cl
HO
S
O2
O
3n
1H NMR (400 MHz, CDCl3)
1.00
1.07
1.02
3.17
2.28
1.07
1.08
2.04
1.14
1.11
1.08
1.02
2.18
f1 (ppm)


204.15
134.61
133.24
133.13
130.93
130.71
130.37
129.42
128.98
128.01
127.49
82.11
70.94
65.73
50.04
47.79
45.55
33.74
33.18
Cl
Cl
HO
S
O2
O
3n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

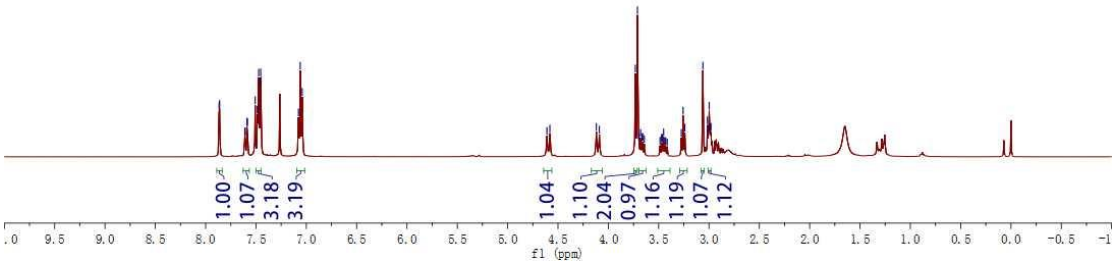

7.86
7.58
7.50
7.48
7.31
7.29
7.13
7.11
7.09
4.59
4.57
4.11
4.08
3.72
3.69
3.67
3.66
3.63
3.48
3.48
3.46
3.45
3.06
3.01
3.00
2.99
2.96
2.94
2.92
2.92
2.90
Cl
Cl
HO
S
O2
O
Cl
3o
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.03
2.08
2.02
1.01
1.03
3.14
1.07
4.00
f1 (ppm)

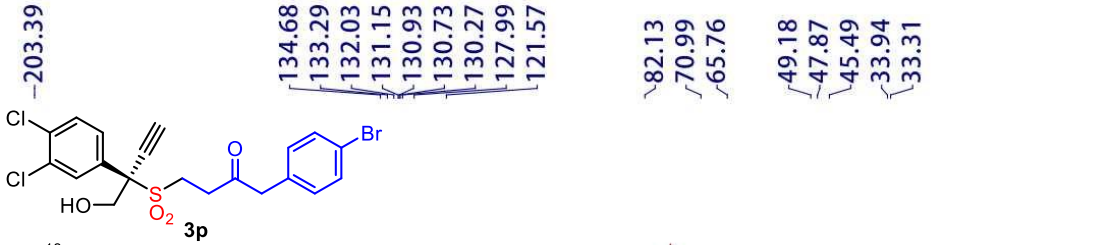

203.56
134.65
133.45
133.25
131.51
130.94
130.81
130.72
130.28
129.05
128.02
82.14
71.00
65.74
49.07
48.99
47.84
45.54
33.92
33.32
Cl
Cl
HO
S
O2
O
Cl
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)



3p

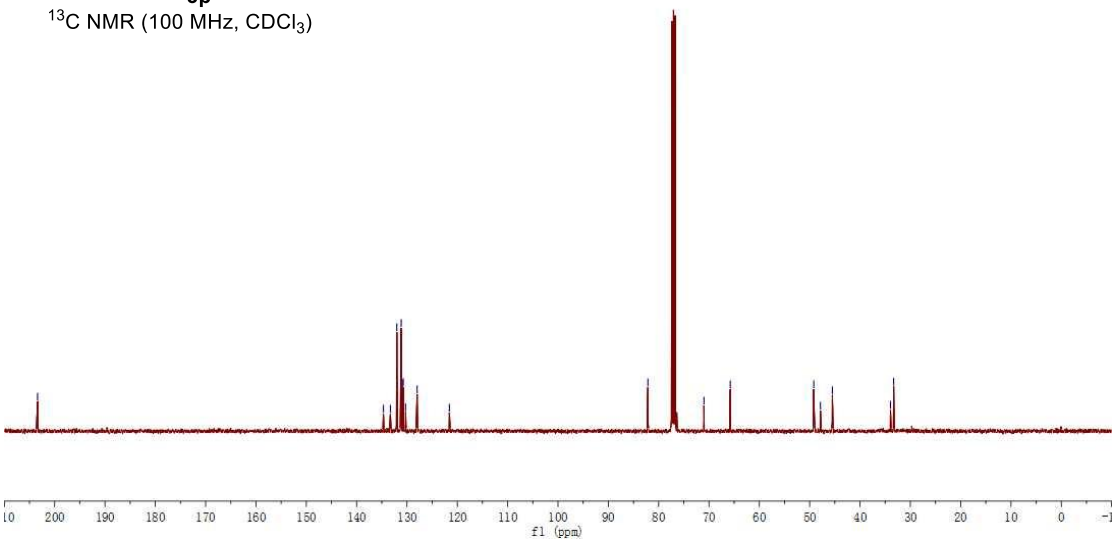
^{1}H NMR (400 MHz, $CDCl_3$)

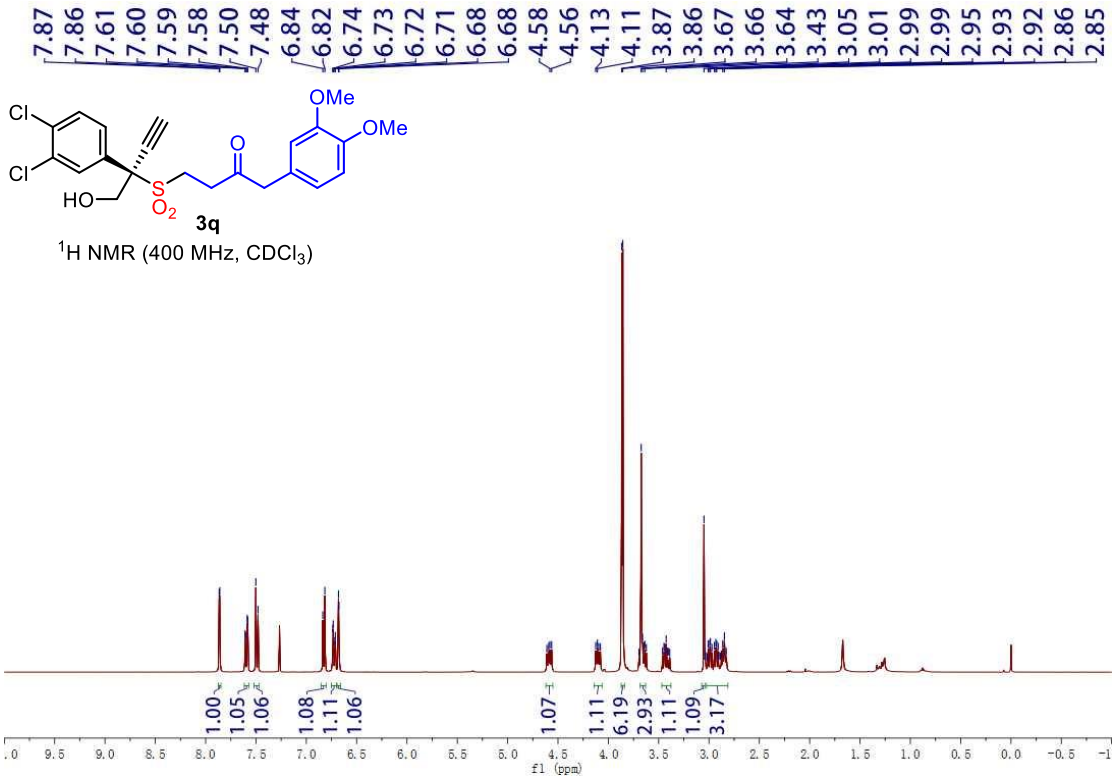


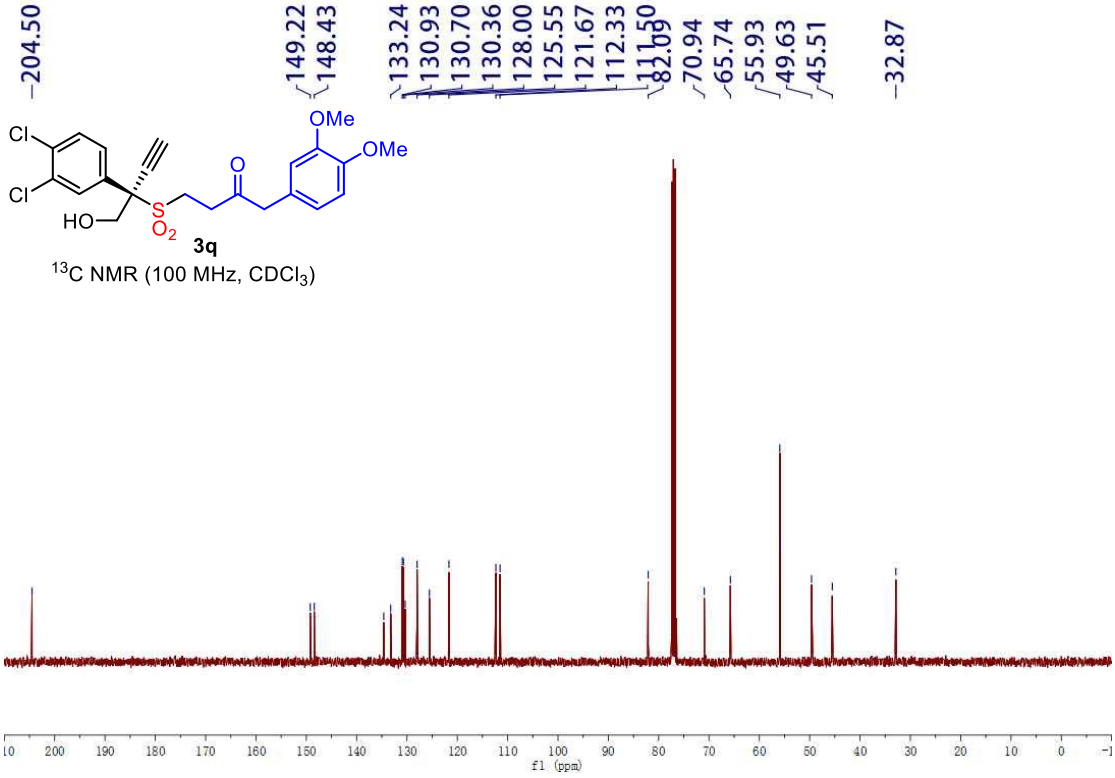


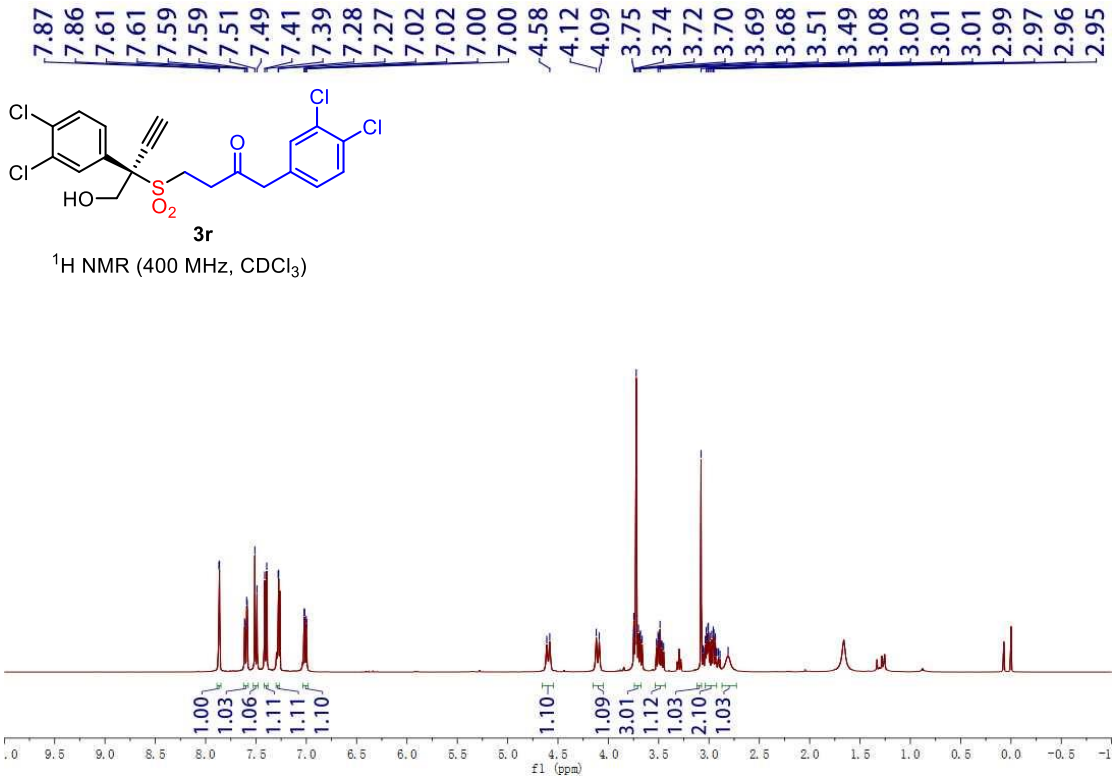
3p

^{13}C NMR (100 MHz, $CDCl_3$)



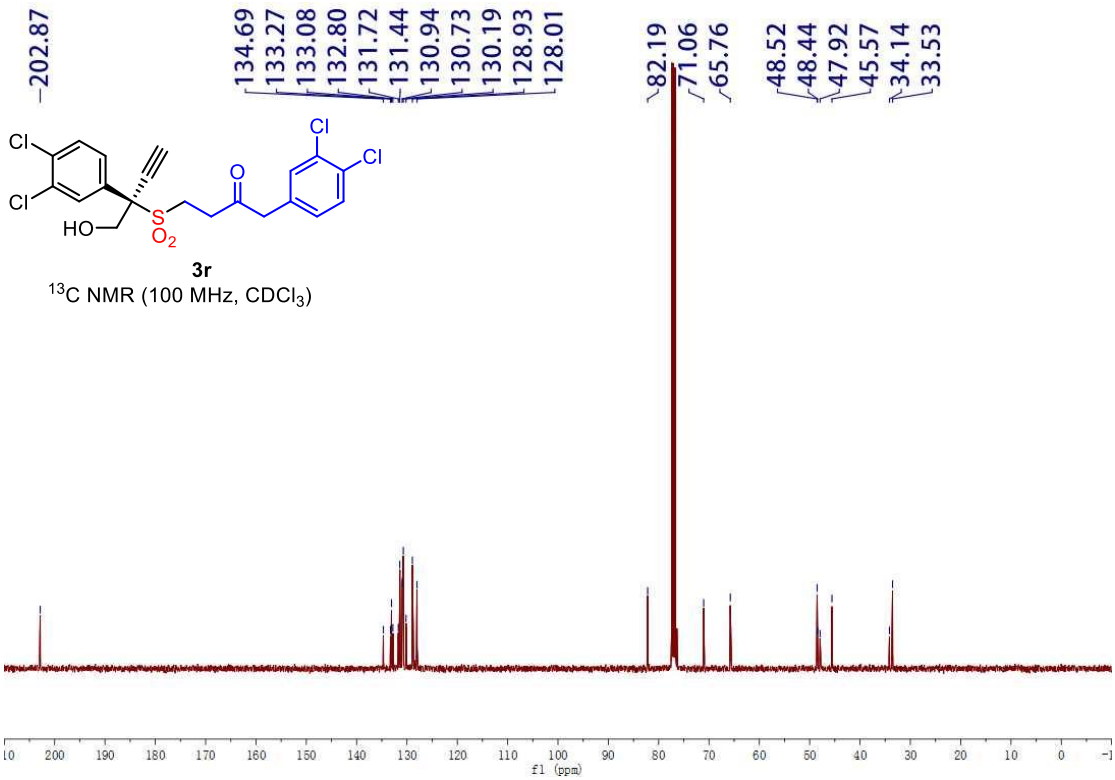

7.87
7.86
7.61
7.60
7.59
7.58
7.50
7.48
6.84
6.82
6.74
6.73
6.72
6.71
6.68
6.68
4.58
4.56
4.13
4.11
3.87
3.86
3.67
3.66
3.64
3.43
3.05
3.01
2.99
2.99
2.95
2.93
2.92
2.86
2.85
Cl
Cl
HO
S
O2
O
OMe
OMe
3q
1H NMR (400 MHz, CDCl3)
1.00
1.05
1.06
1.08
1.11
1.06
1.07
1.11
6.19
2.93
1.11
1.09
3.17
f1 (ppm)


204.50
149.22
148.43
133.24
130.93
130.70
130.36
128.00
125.55
121.67
112.33
111.50
82.09
70.94
65.74
55.93
49.63
45.51
32.87
Cl
Cl
HO
S
O2
O
OMe
OMe
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)



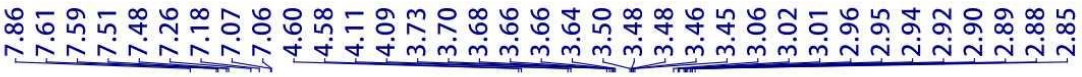
3r

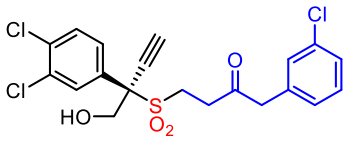
^{1}H NMR (400 MHz, $CDCl_3$)



3r

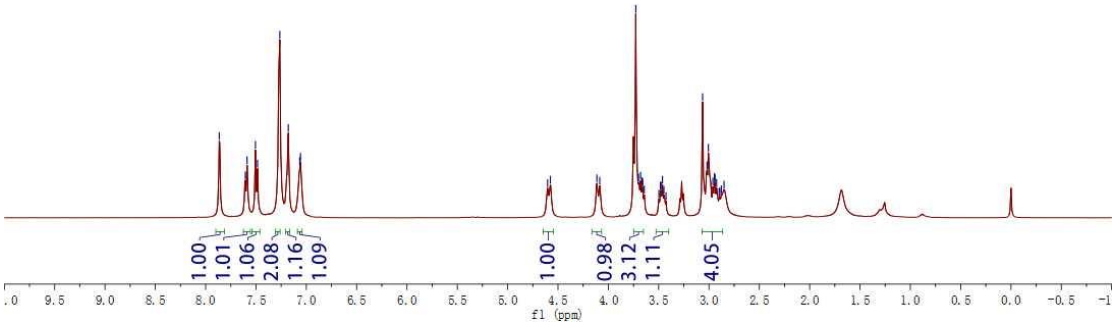
^{13}C NMR (100 MHz, $CDCl_3$)

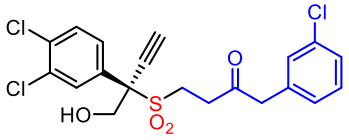




3s

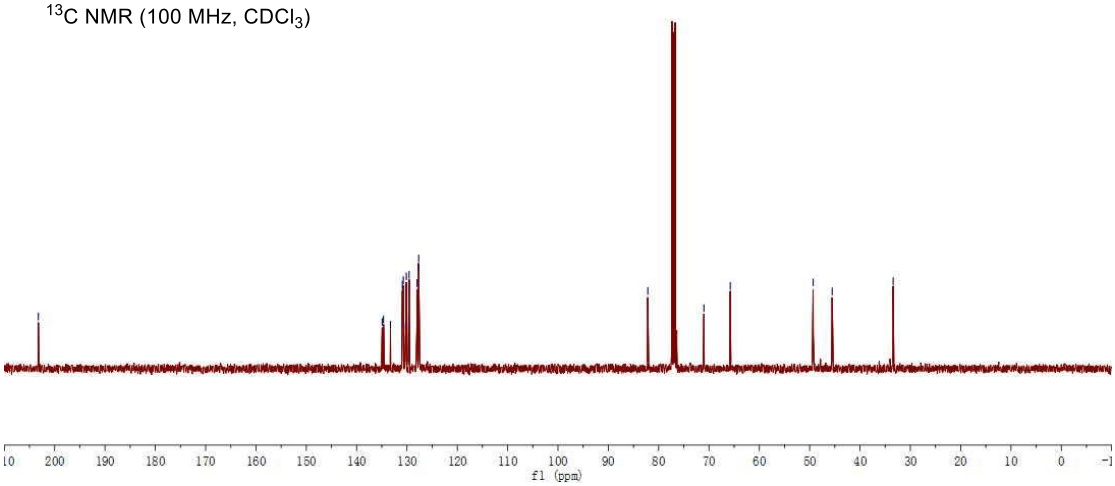
^{1}H NMR (400 MHz, $CDCl_3$)

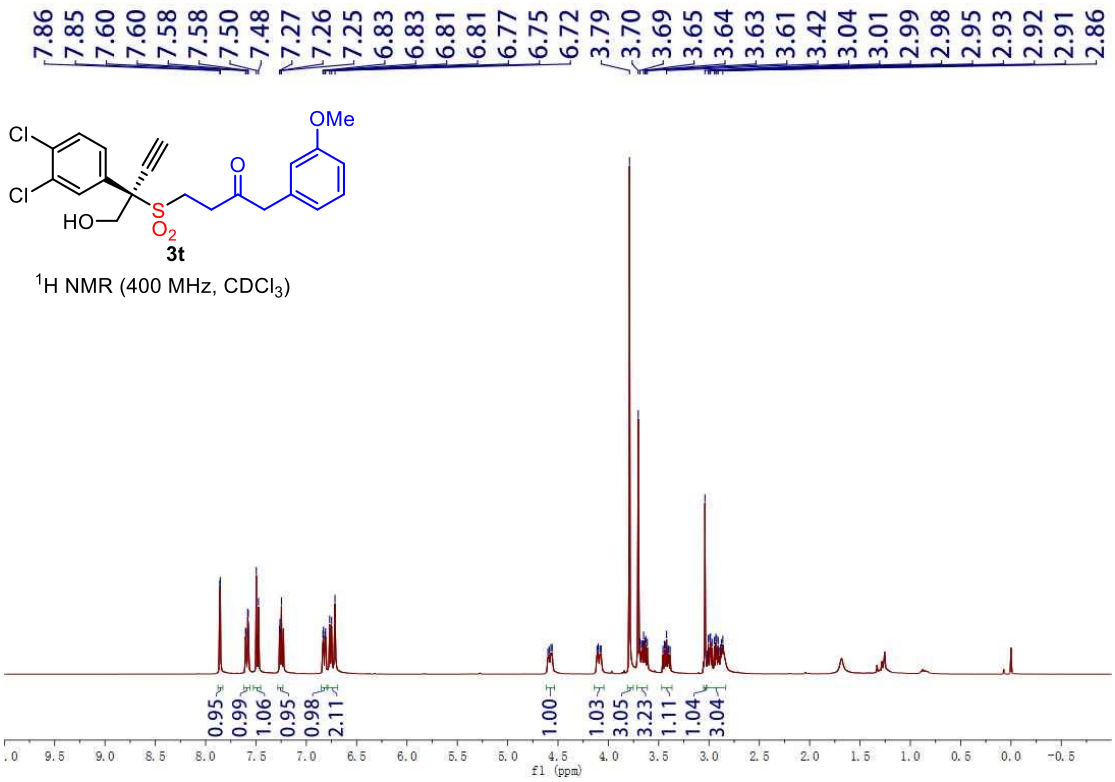




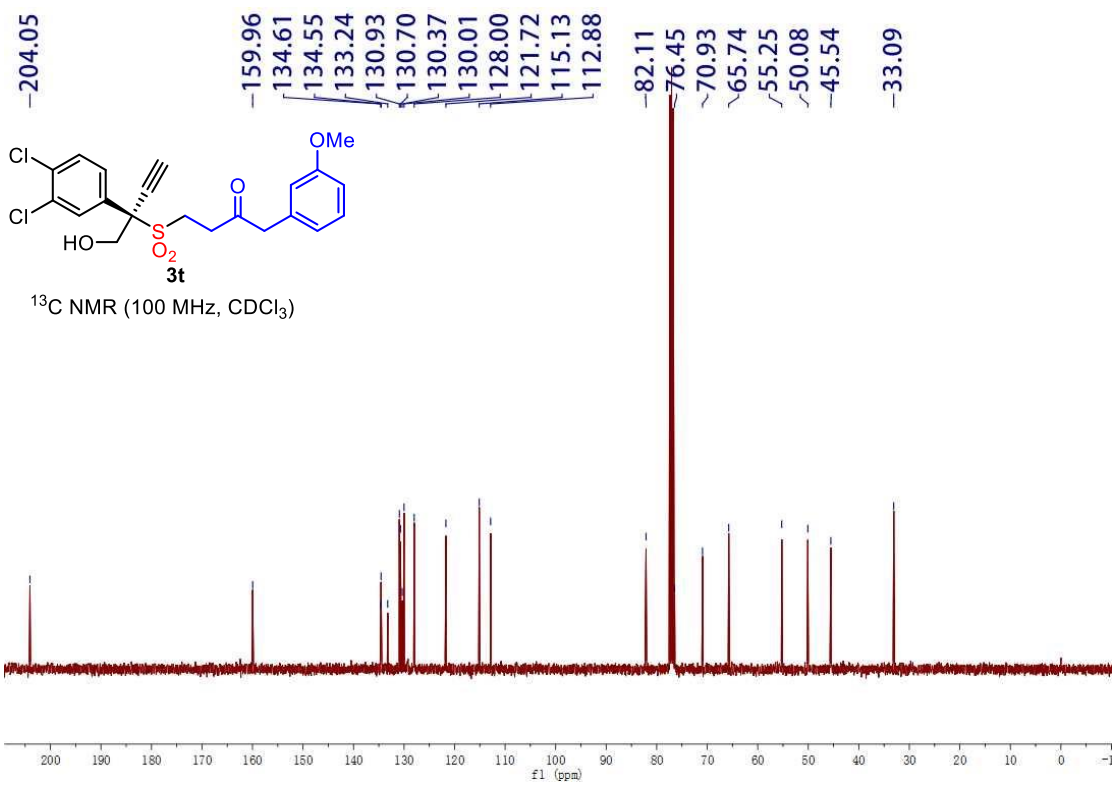
3s

^{13}C NMR (100 MHz, $CDCl_3$)

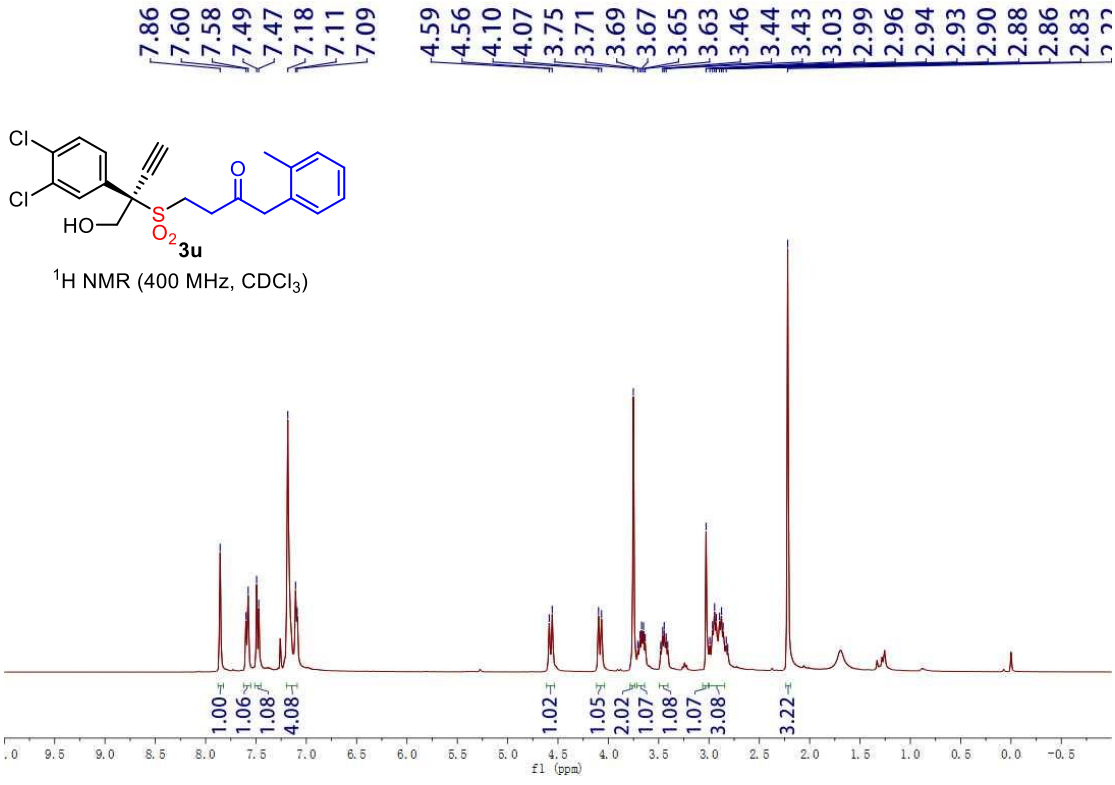




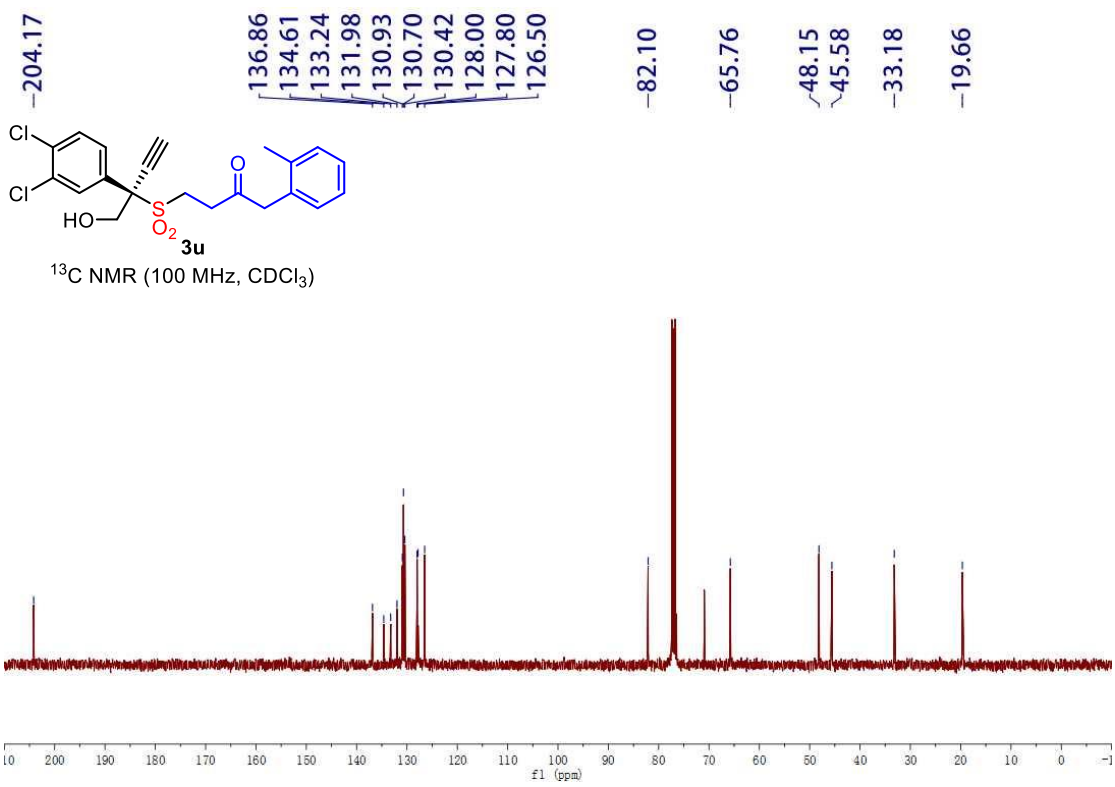
^{1}H NMR (400 MHz, $CDCl_3$)



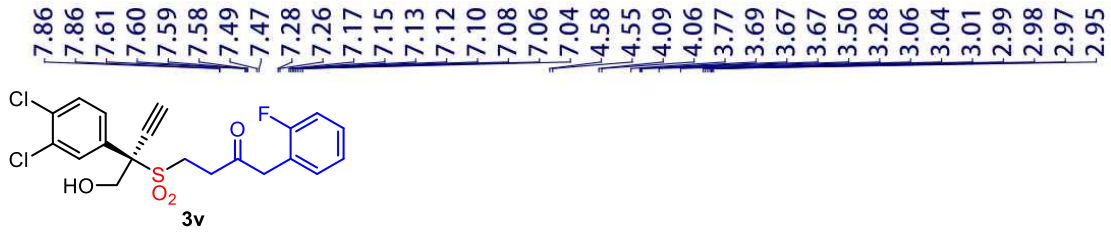
^{13}C NMR (100 MHz, $CDCl_3$)



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

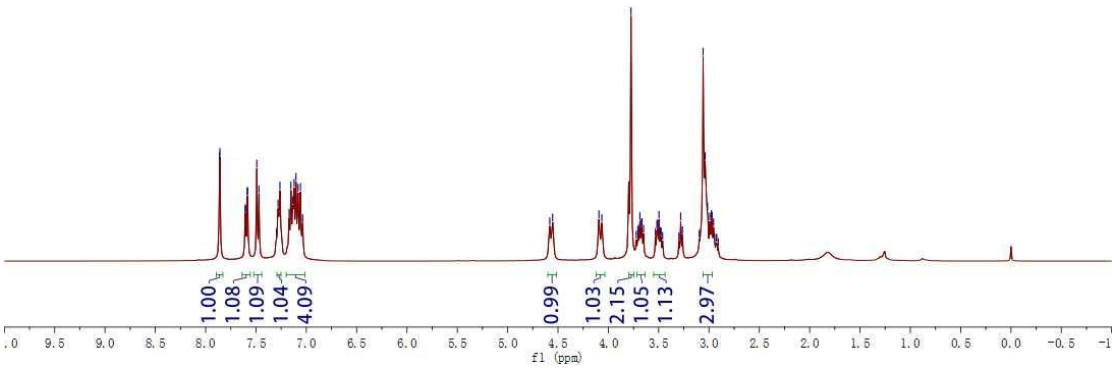


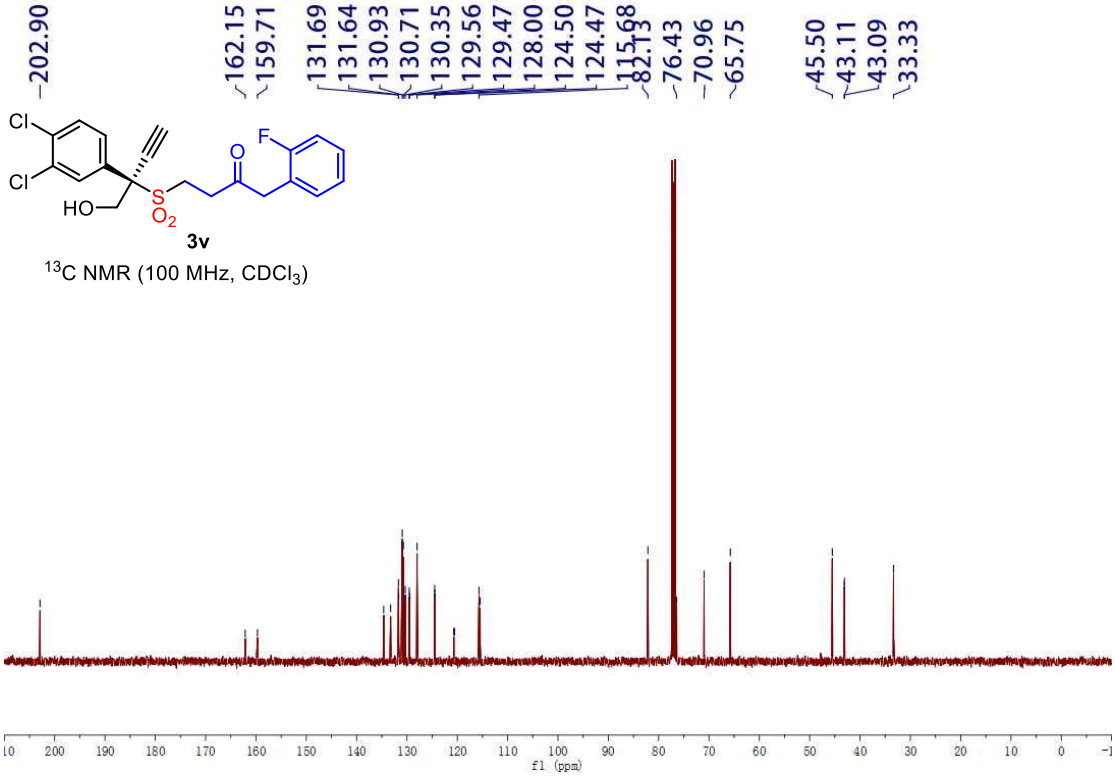
^{13}C NMR (100 MHz, $CDCl_3$)



3v

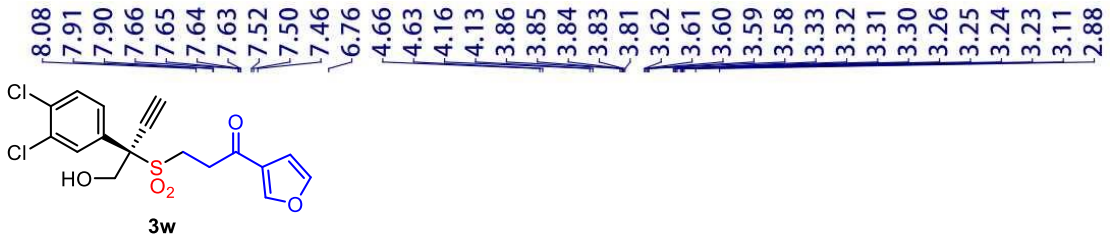
^{1}H NMR (400 MHz, $CDCl_3$)





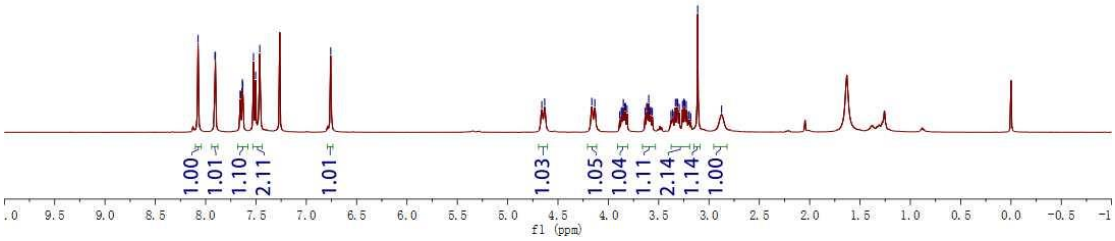
3v

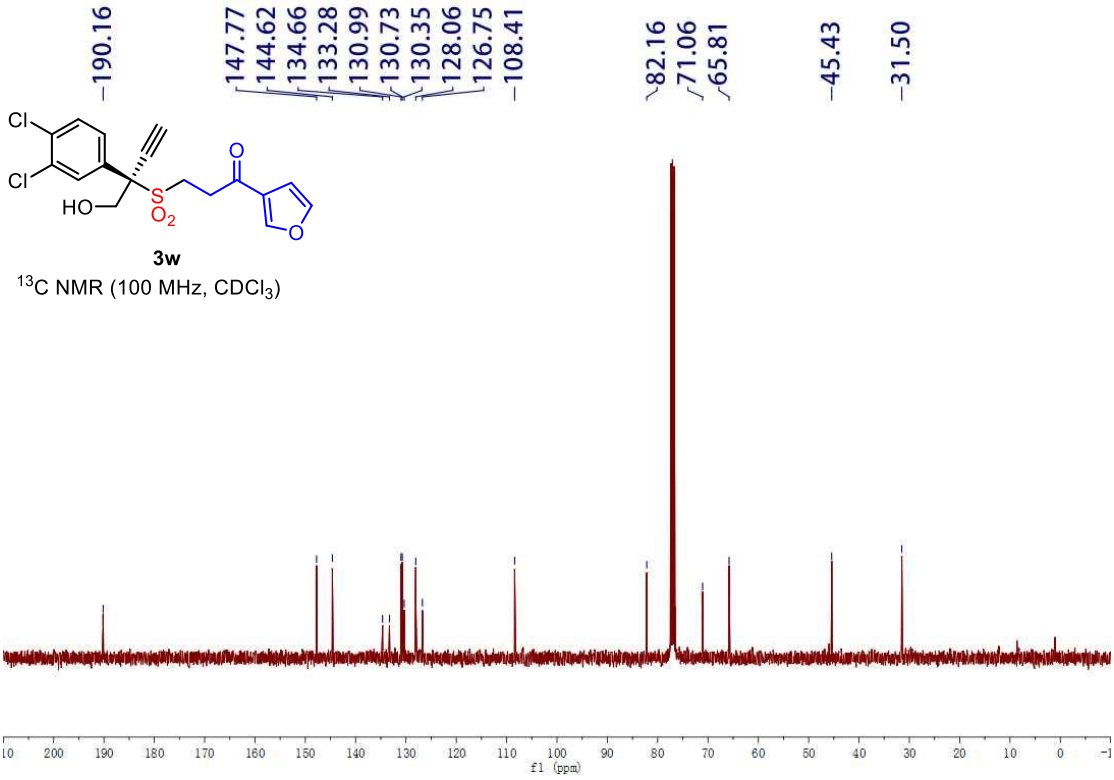
^{13}C NMR (100 MHz, $CDCl_3$)



3w

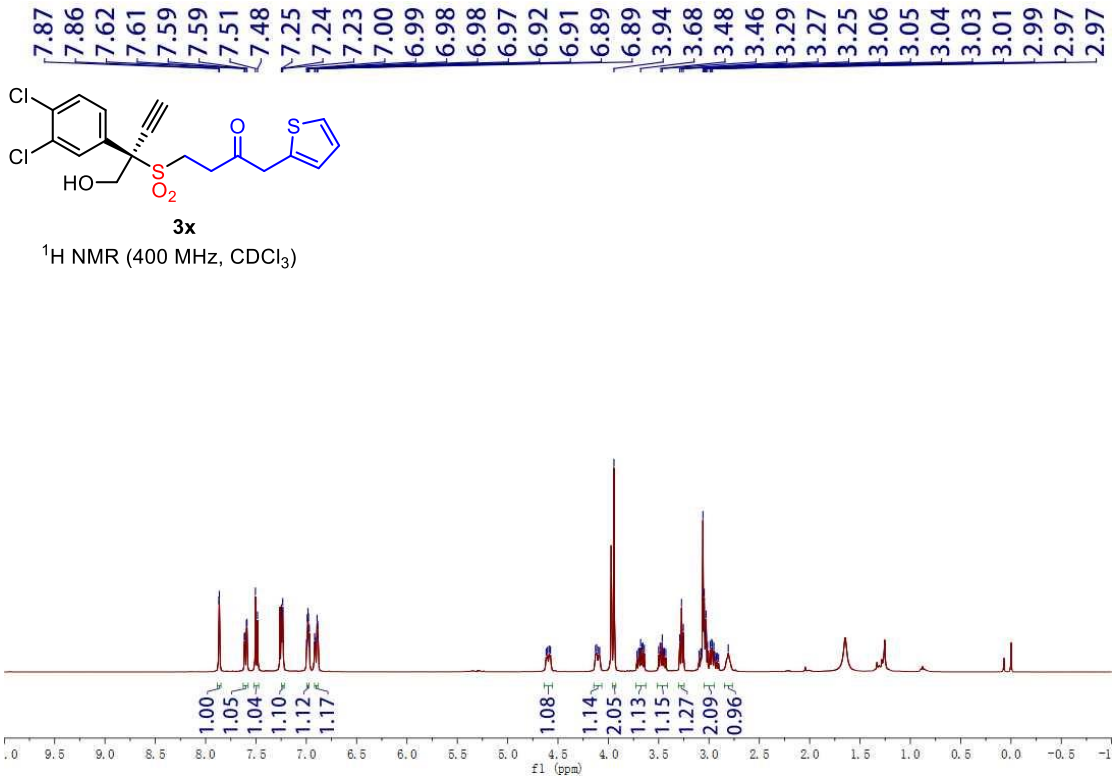
^{1}H NMR (400 MHz, $CDCl_3$)

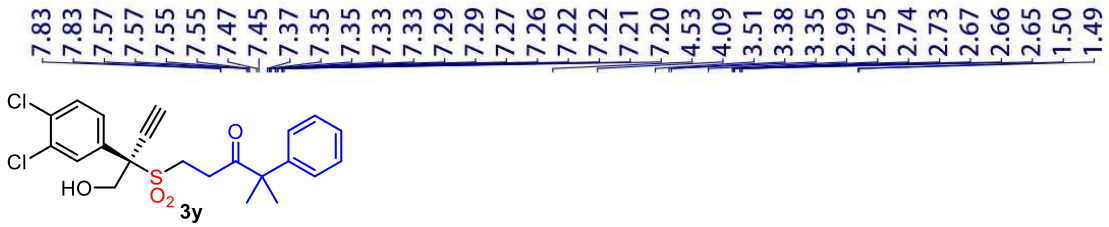




3w

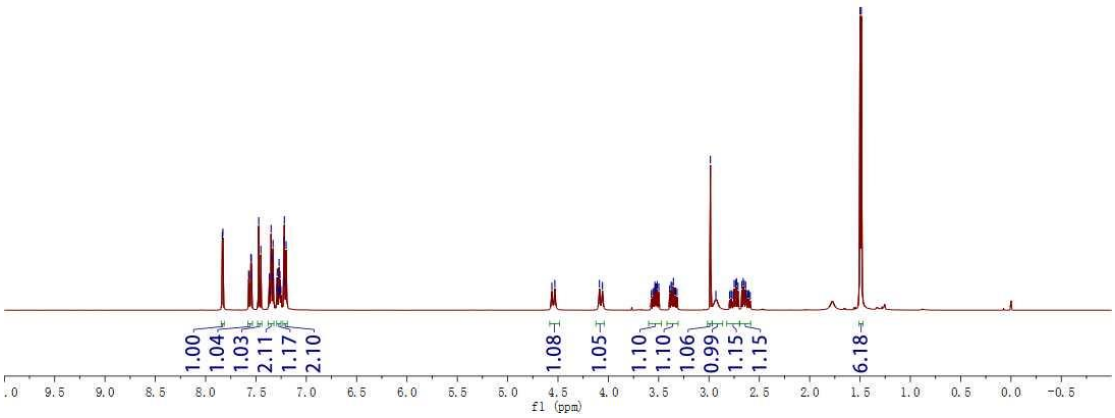
^{13}C NMR (100 MHz, $CDCl_3$)

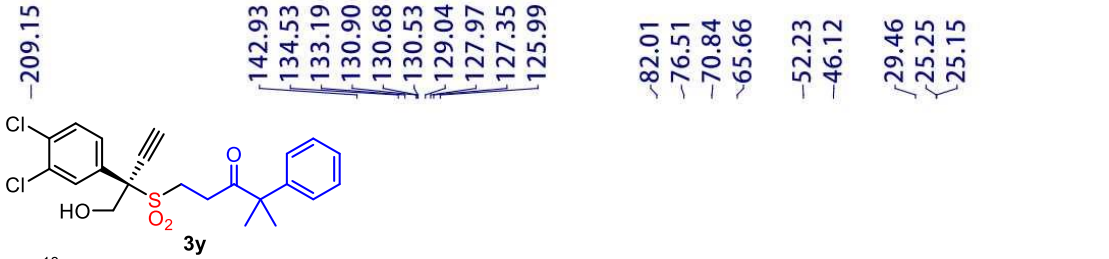

7.87
7.86
7.62
7.61
7.59
7.59
7.51
7.48
7.25
7.24
7.23
7.00
6.99
6.98
6.98
6.97
6.92
6.91
6.89
6.89
3.94
3.68
3.48
3.46
3.29
3.27
3.25
3.06
3.05
3.04
3.03
3.01
2.99
2.97
2.97
Cl
Cl
HO
S
O2
O
S
3x
1H NMR (400 MHz, CDCl3)
1.00
1.05
1.04
1.10
1.12
1.17
1.08
1.14
2.05
1.13
1.15
1.27
2.09
0.96
f1 (ppm)
202.75
134.66
133.97
133.28
130.93
130.72
130.33
127.99
127.38
127.30
125.63
82.14
70.97
65.76
47.84
45.54
43.60
43.53
33.52
32.95
Cl
Cl
HO
S
O2
O
S
3x
13C NMR (100 MHz, CDCl3)
f1 (ppm)



3y

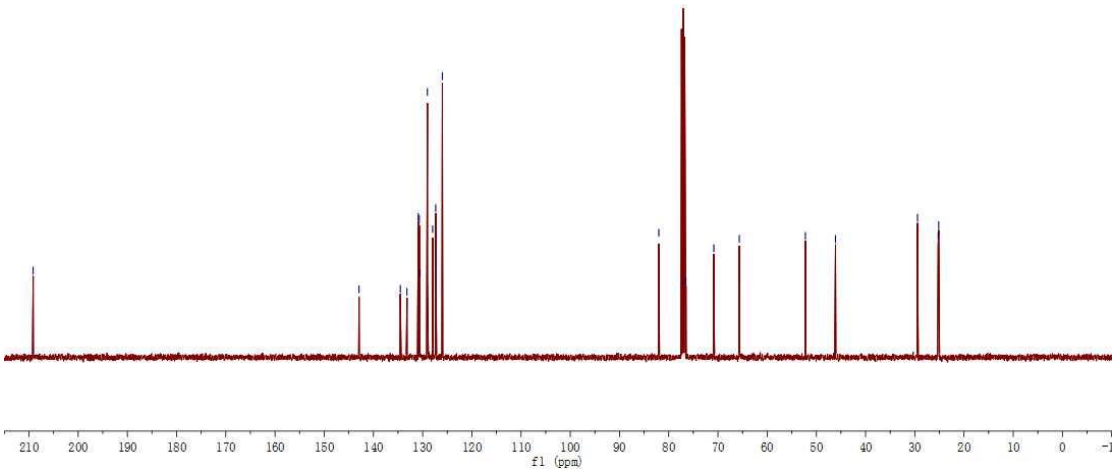
^{1}H NMR (400 MHz, $CDCl_3$)

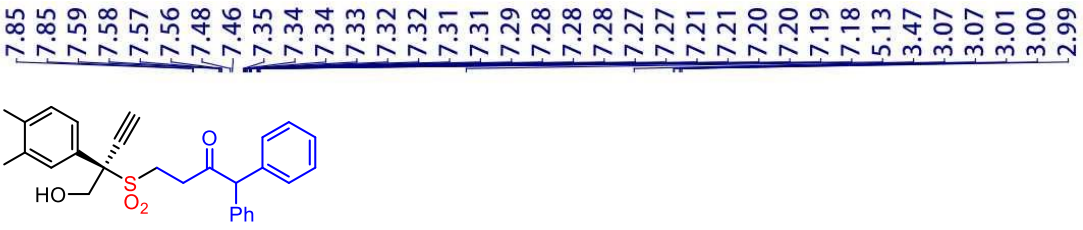




3y

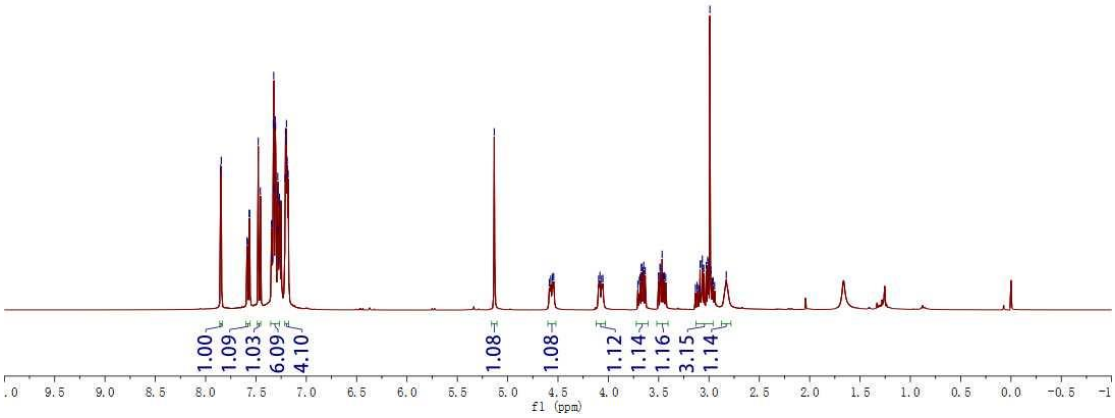
^{13}C NMR (100 MHz, $CDCl_3$)

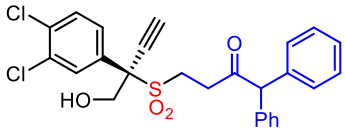




3z

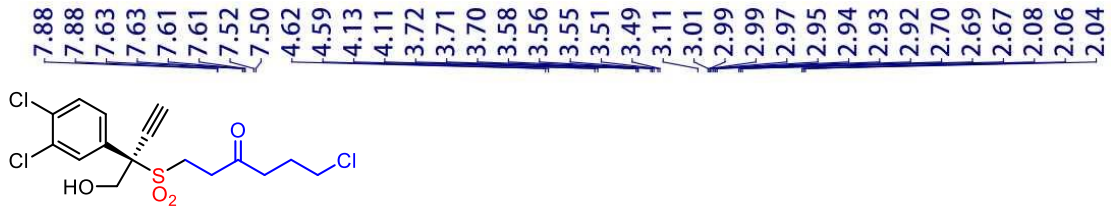
^{1}H NMR (400 MHz, $CDCl_3$)





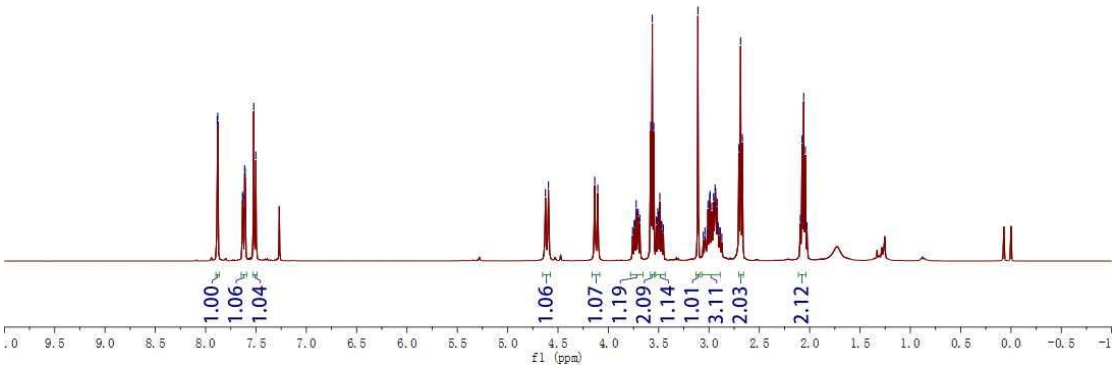
3z

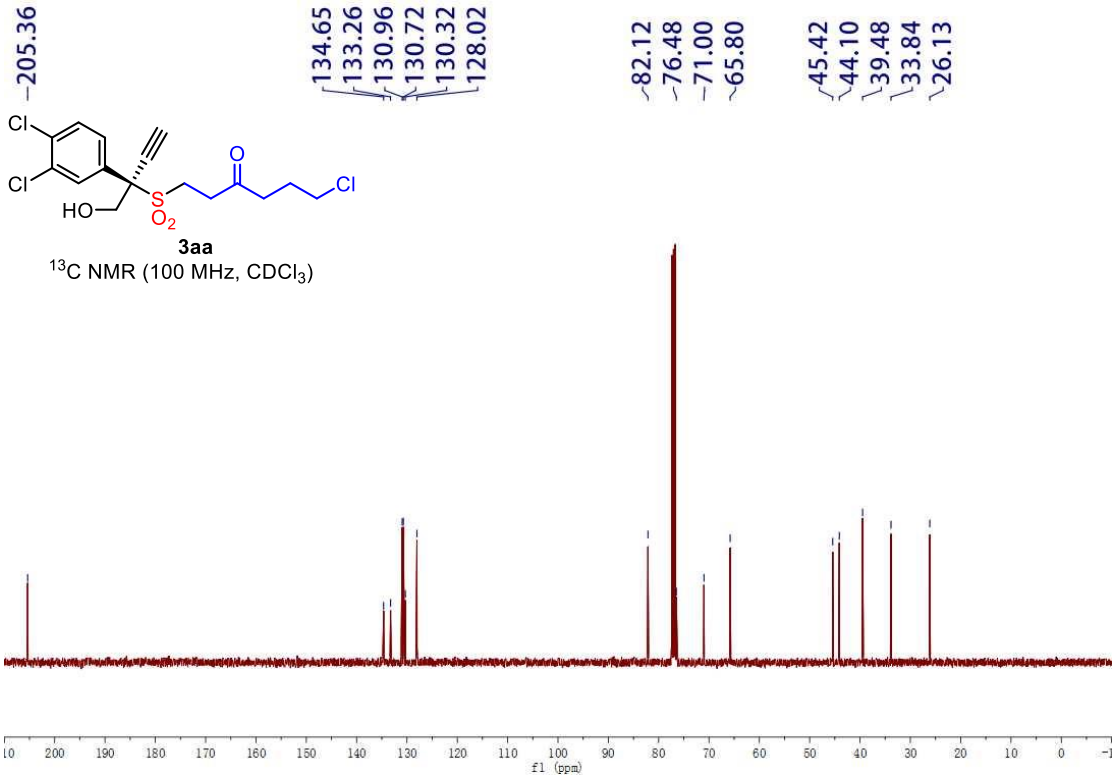
^{13}C NMR (100 MHz, $CDCl_3$)



3aa

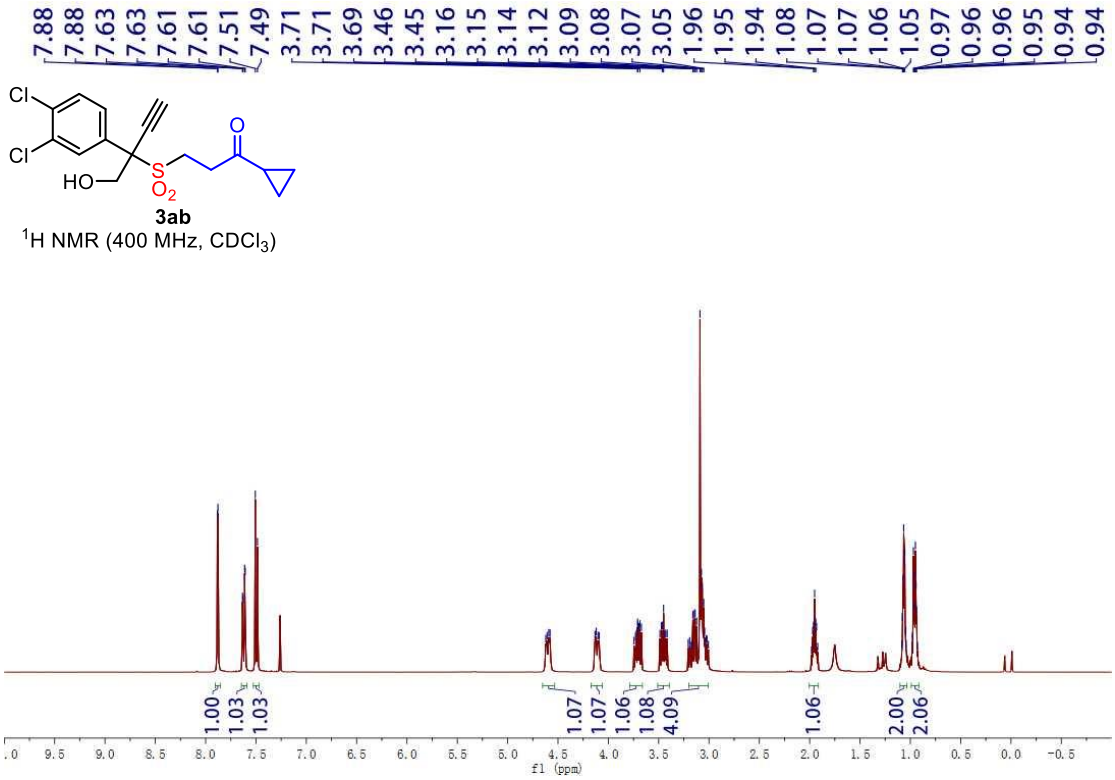
^{1}H NMR (400 MHz, $CDCl_3$)

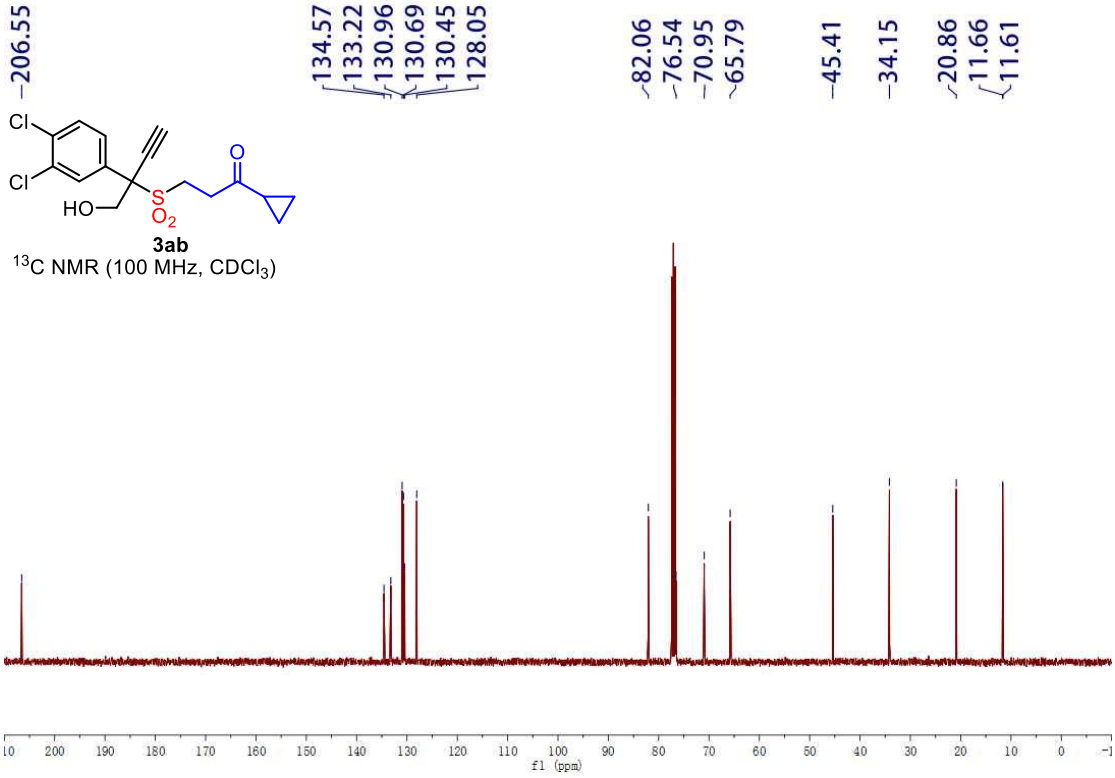


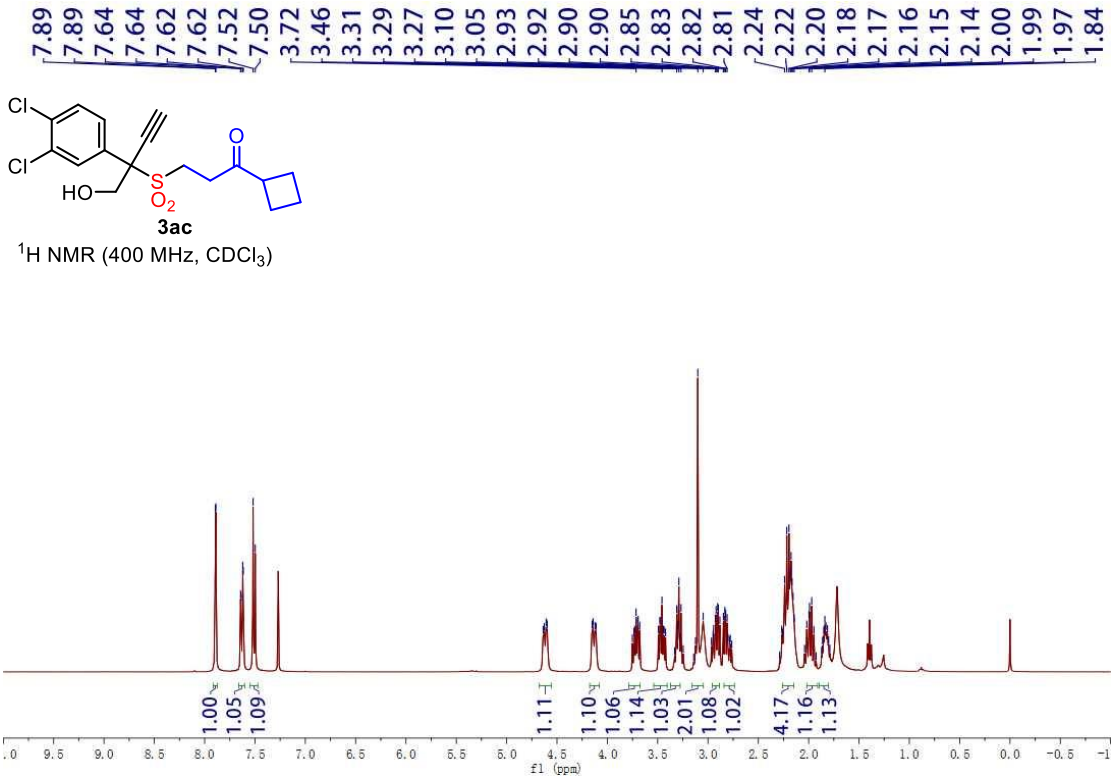


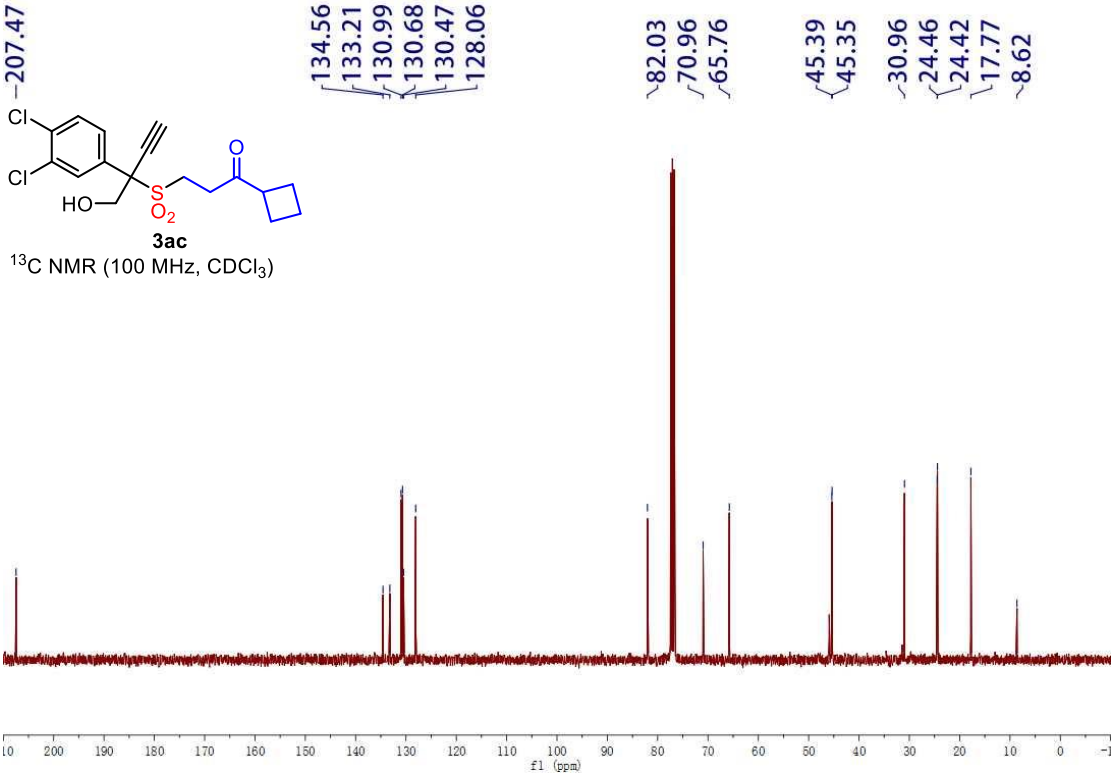
3aa

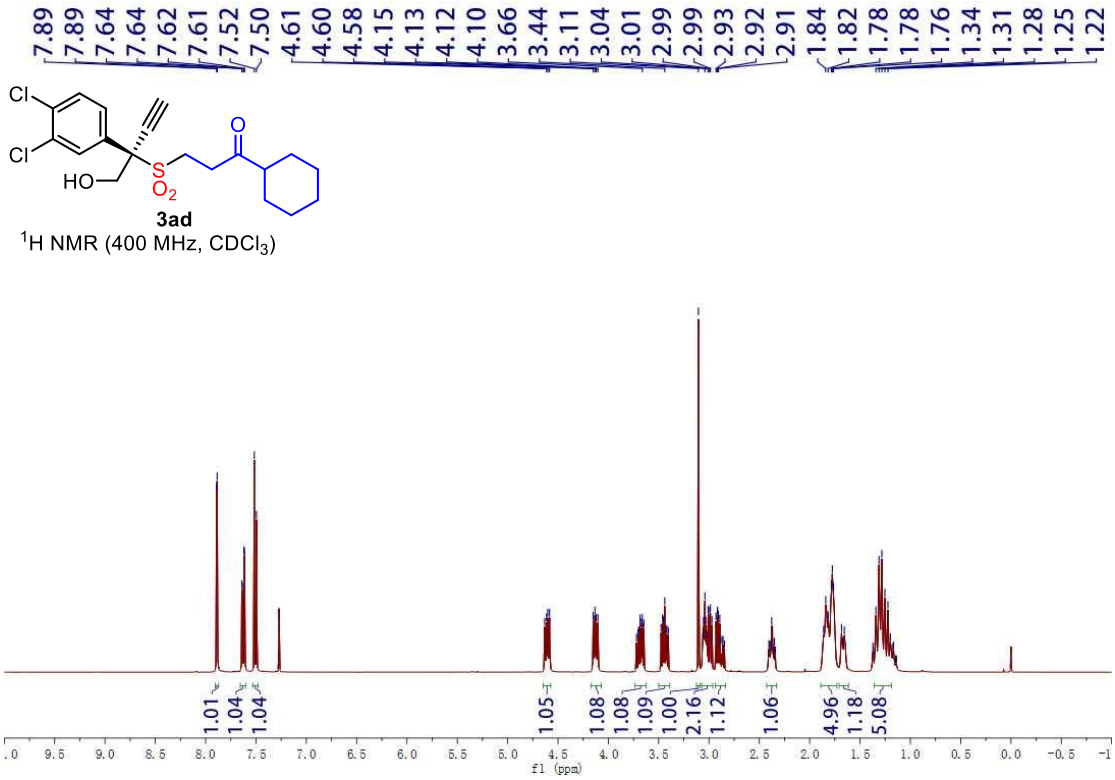
^{13}C NMR (100 MHz, $CDCl_3$)

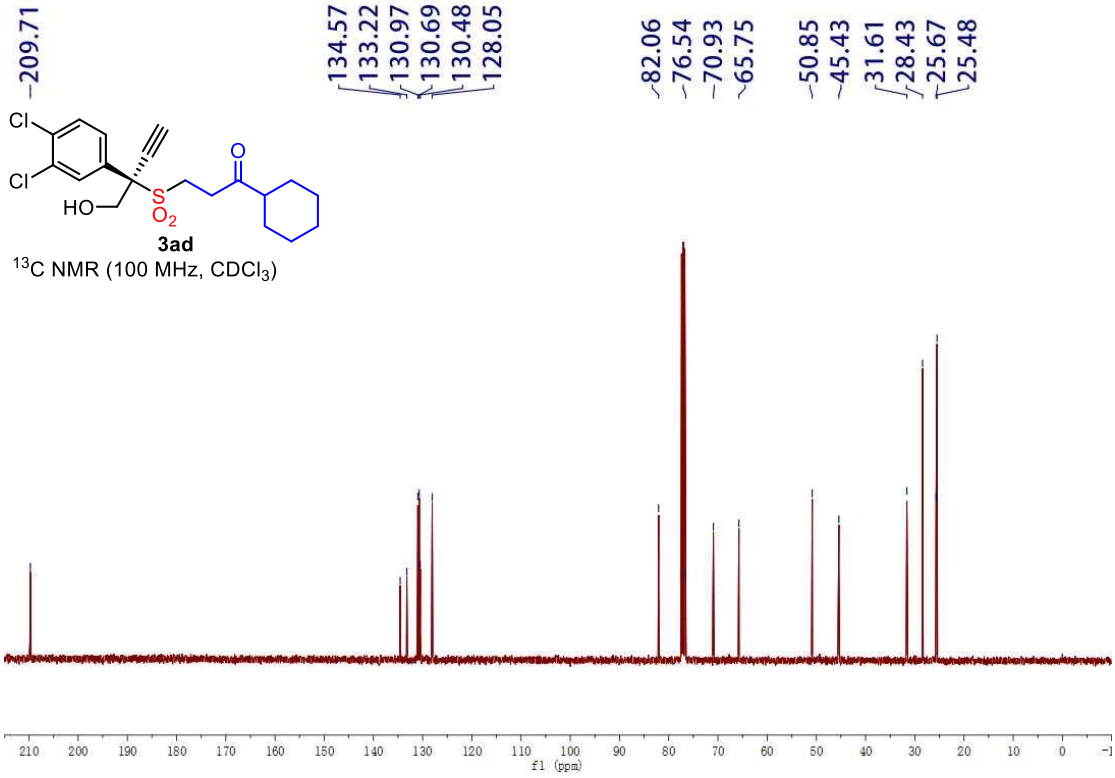

7.88
7.88
7.63
7.63
7.61
7.61
7.51
7.49
3.71
3.71
3.69
3.46
3.45
3.16
3.15
3.14
3.12
3.09
3.08
3.07
3.05
1.96
1.95
1.94
1.08
1.07
1.07
1.06
1.05
0.97
0.96
0.96
0.95
0.94
0.94
Cl
Cl
HO
S
O2
O
3ab
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.03
1.07
1.07
1.06
1.08
4.09
1.06
2.00
2.06
f1 (ppm)

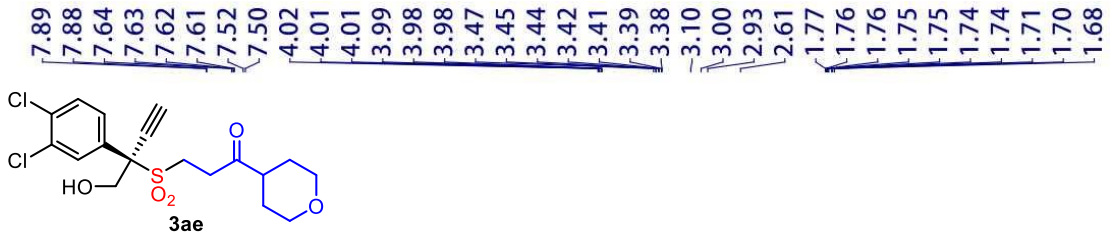

206.55
134.57
133.22
130.96
130.69
130.45
128.05
82.06
76.54
70.95
65.79
45.41
34.15
20.86
11.66
11.61
Cl
Cl
HO
S
O2
O
3ab
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.89
7.89
7.64
7.64
7.62
7.62
7.52
7.50
3.72
3.46
3.31
3.29
3.27
3.10
3.05
2.93
2.92
2.90
2.90
2.85
2.83
2.82
2.81
2.24
2.22
2.20
2.18
2.17
2.16
2.15
2.14
2.00
1.99
1.97
1.84
Cl
Cl
HO
S
O2
O
3ac
1H NMR (400 MHz, CDCl3)
1.00
1.05
1.09
1.11
1.10
1.06
1.14
1.03
2.01
1.08
1.02
4.17
1.16
1.13
f1 (ppm)


207.47
134.56
133.21
130.99
130.68
130.47
128.06
82.03
70.96
65.76
45.39
45.35
30.96
24.46
24.42
17.77
8.62
Cl
Cl
HO
S
O2
O
3ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)

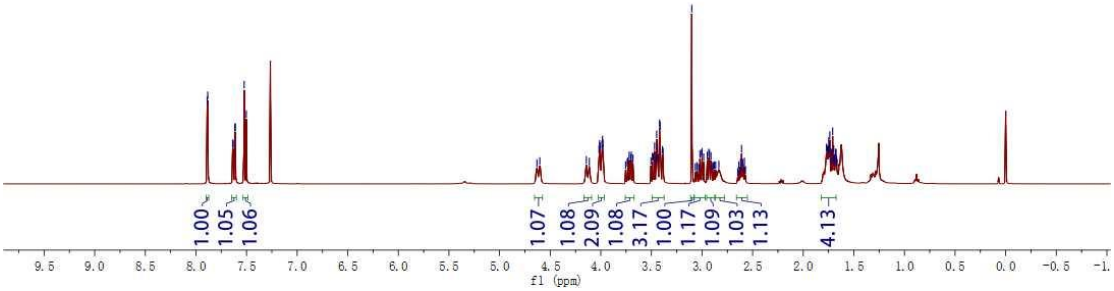

7.89
7.89
7.64
7.64
7.62
7.61
7.52
7.50
4.61
4.60
4.58
4.15
4.13
4.12
4.10
3.66
3.44
3.11
3.04
3.01
2.99
2.99
2.93
2.92
2.91
1.84
1.82
1.78
1.78
1.76
1.34
1.31
1.28
1.25
1.22
Cl
Cl
HO
S
O2
O
3ad
1H NMR (400 MHz, CDCl3)
1.01
1.04
1.04
1.05
1.08
1.08
1.09
1.00
2.16
1.12
1.06
4.96
1.18
5.08
f1 (ppm)

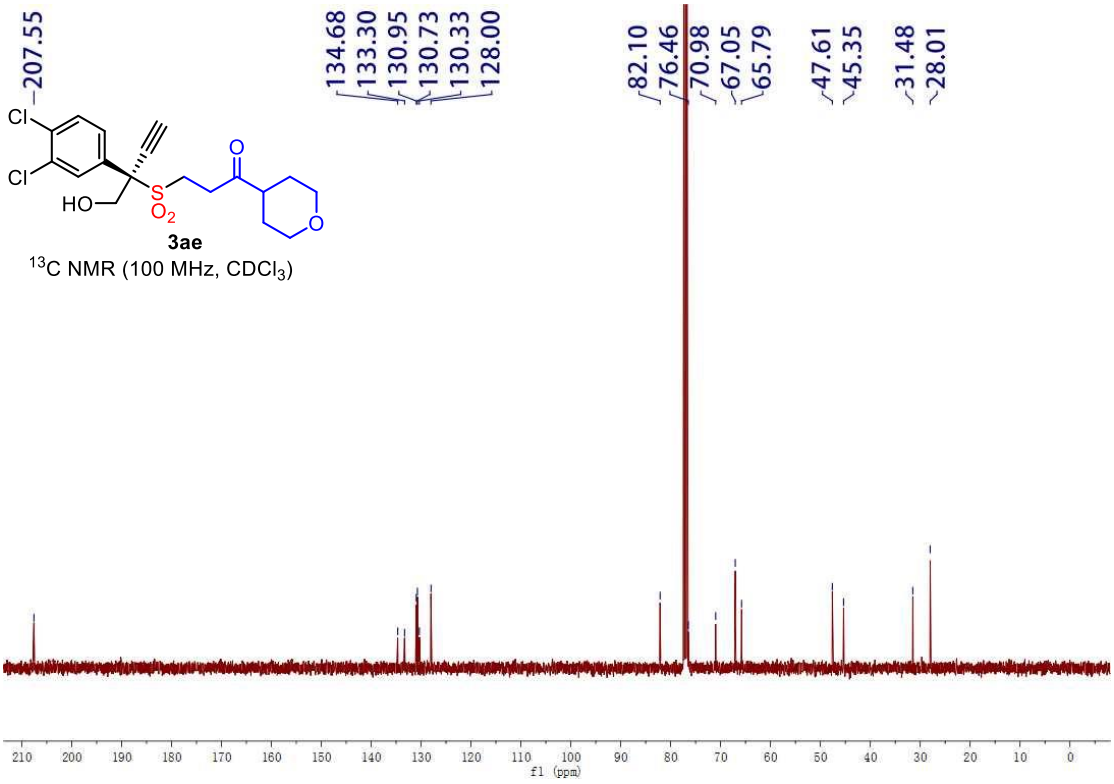

209.71
134.57
133.22
130.97
130.69
130.48
128.05
82.06
76.54
70.93
65.75
50.85
45.43
31.61
28.43
25.67
25.48
Cl
Cl
HO
S
O2
O
3ad
13C NMR (100 MHz, CDCl3)
f1 (ppm)



3ae

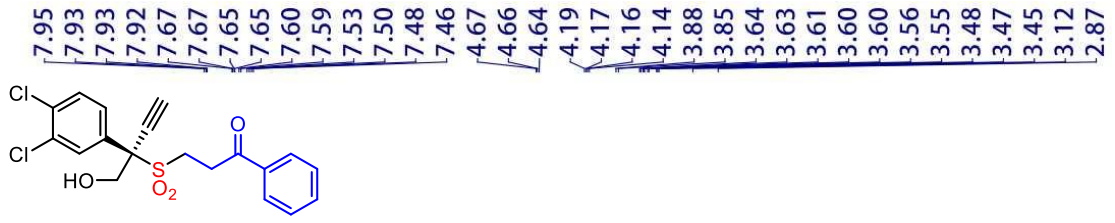
^{1}H NMR (400 MHz, $CDCl_3$)





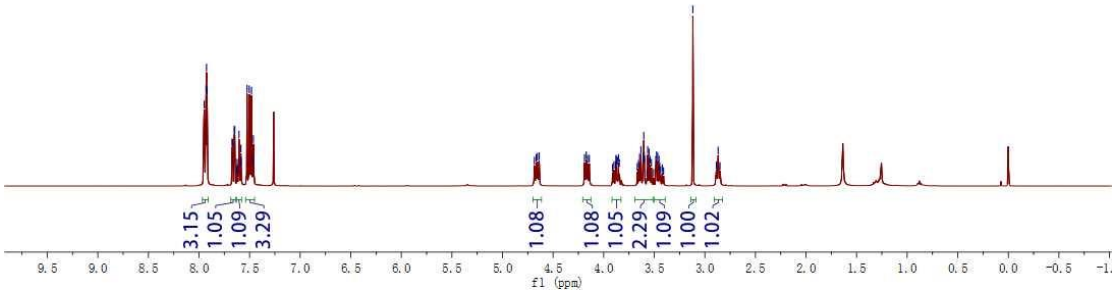
3ae

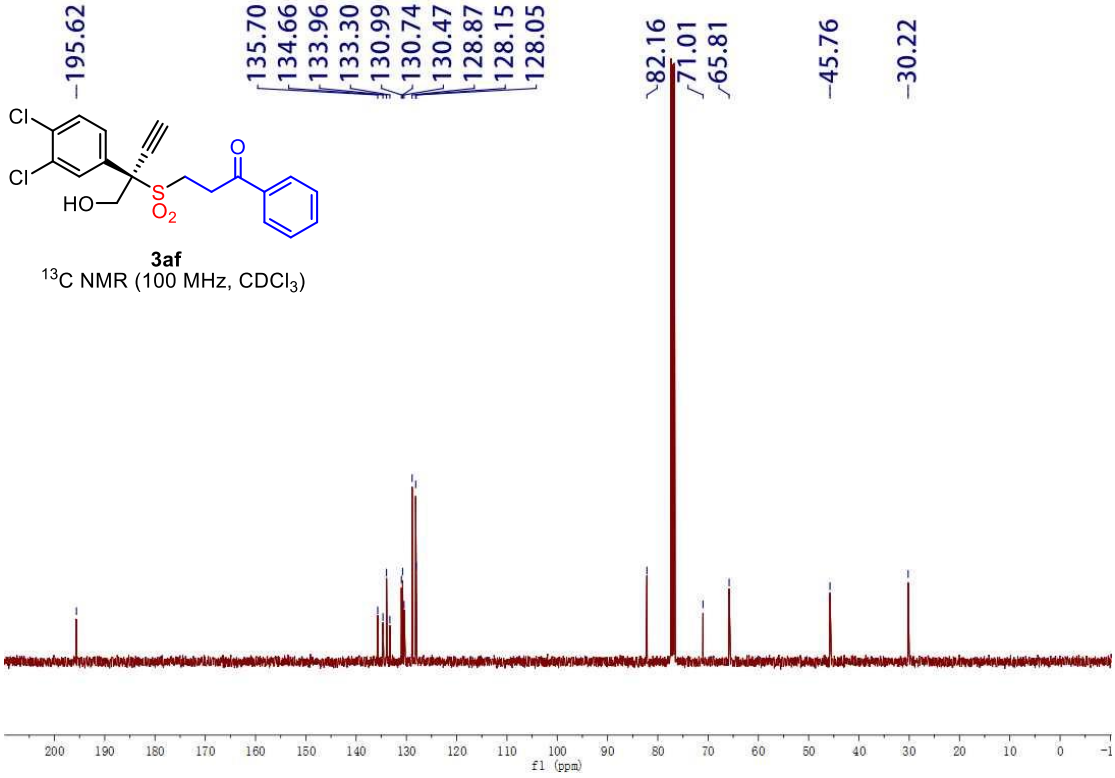
^{13}C NMR (100 MHz, $CDCl_3$)



3af

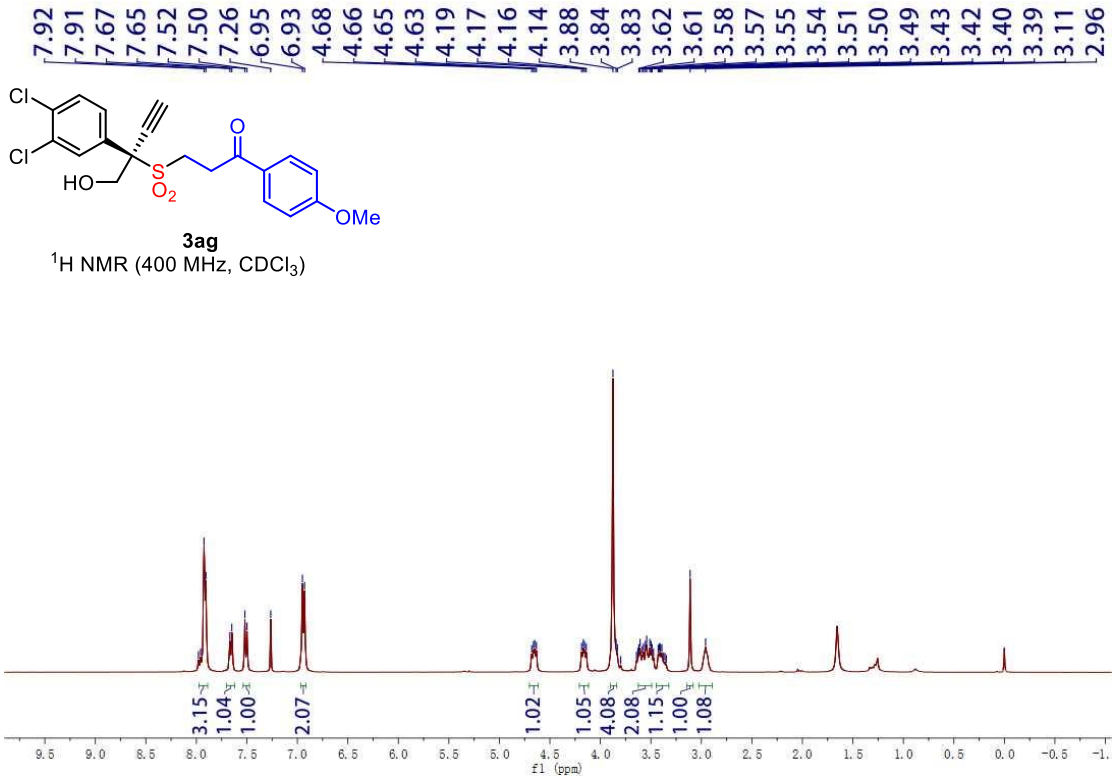
^{1}H NMR (400 MHz, $CDCl_3$)





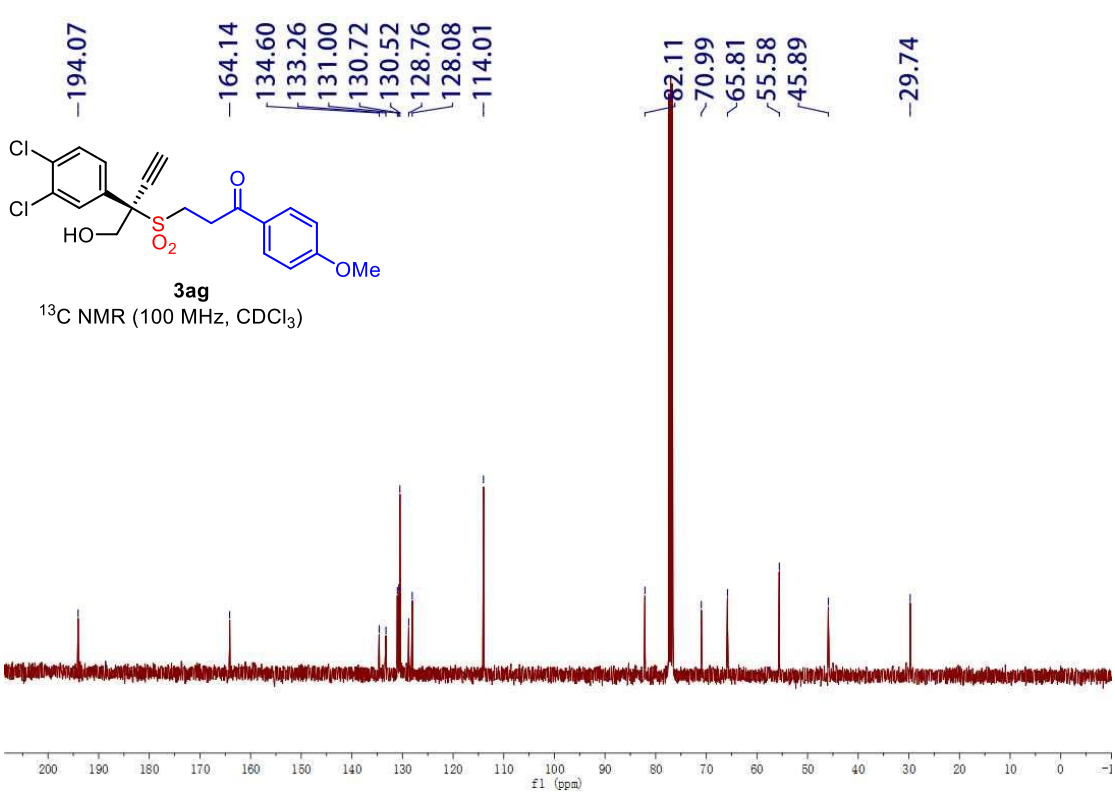
3af

^{13}C NMR (100 MHz, $CDCl_3$)



3ag

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

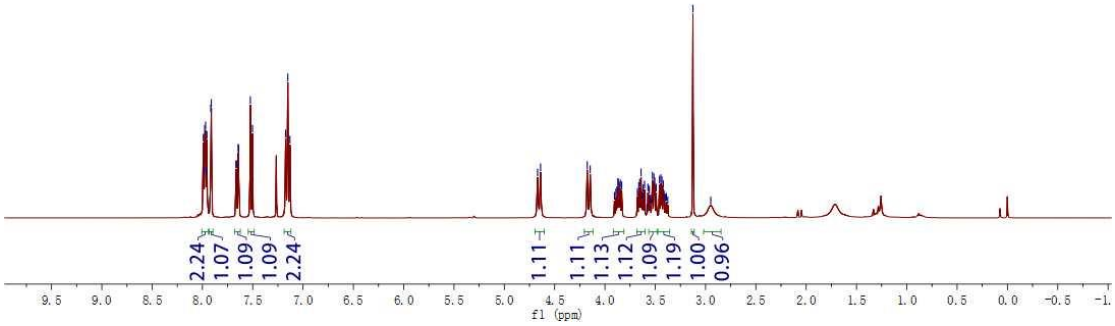


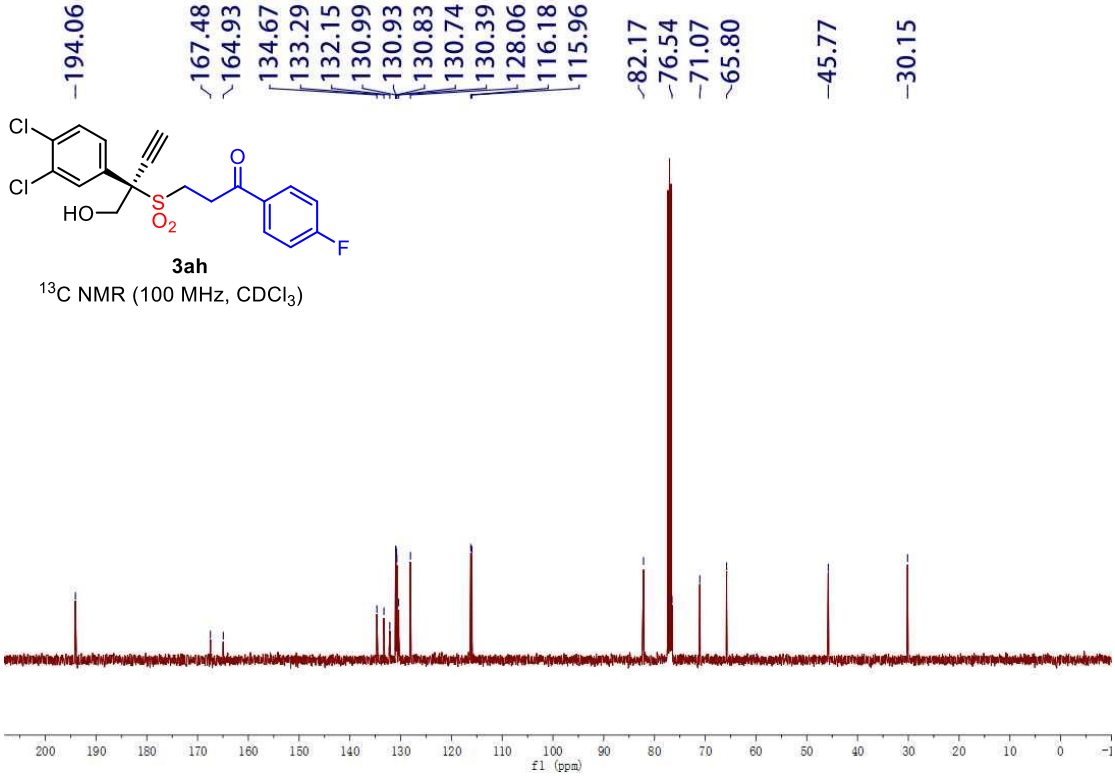
3ag

^{13}C NMR (100 MHz, $CDCl_3$)

3ah

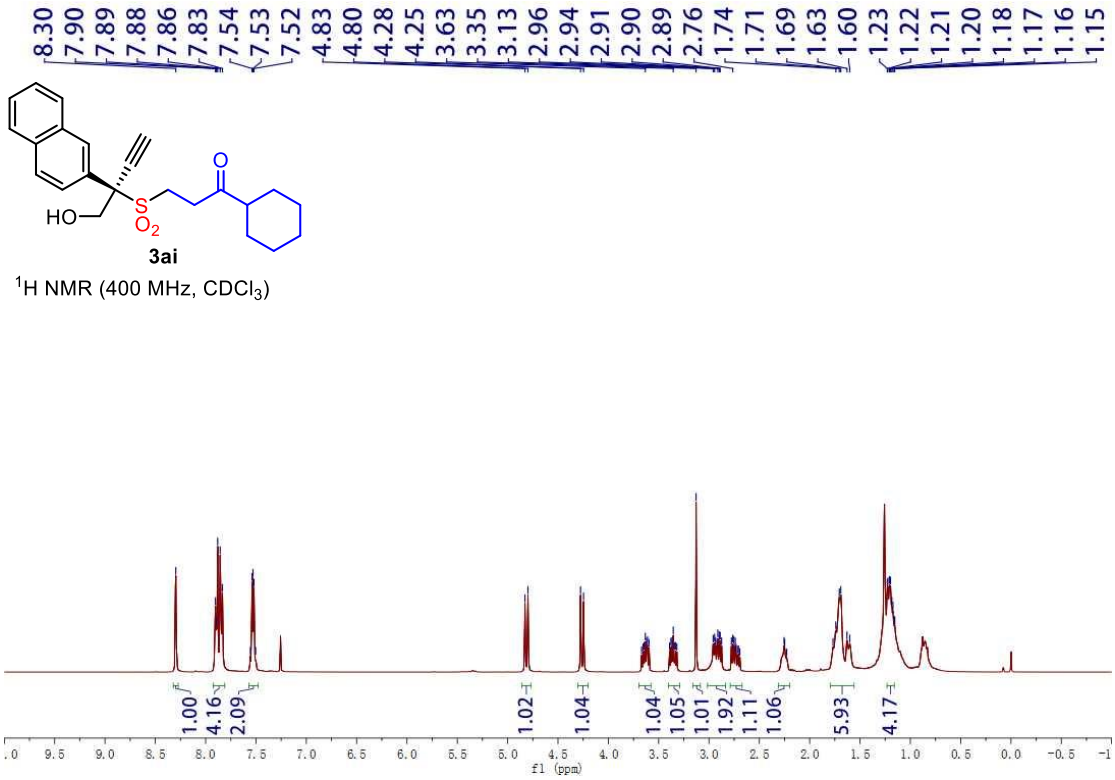
^{1}H NMR (400 MHz, $CDCl_3$)





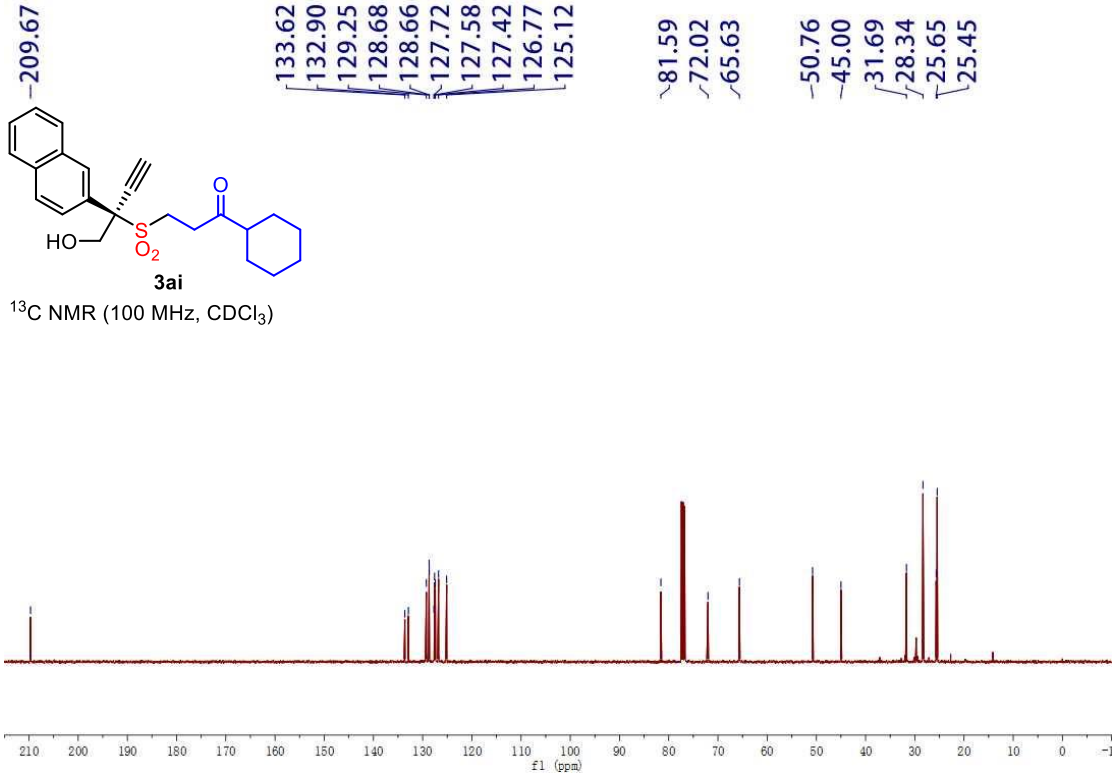
3ah

^{13}C NMR (100 MHz, $CDCl_3$)



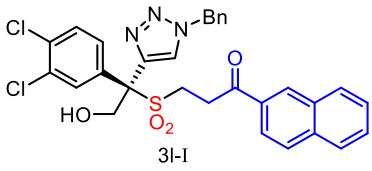
3ai

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



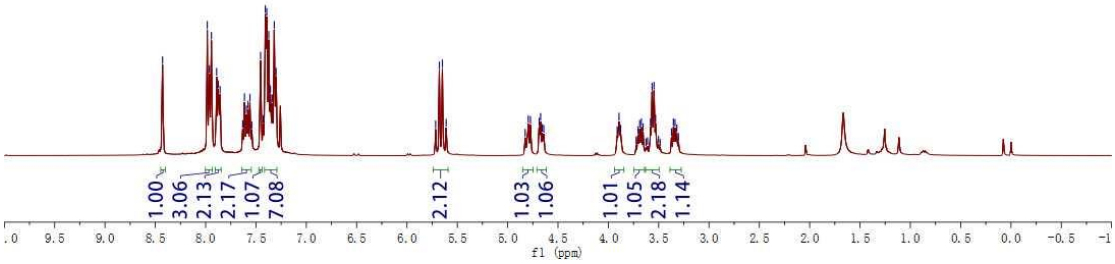
3ai

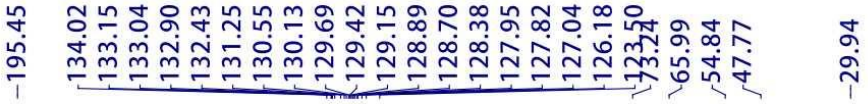
^{13}C NMR (100 MHz, $CDCl_3$)

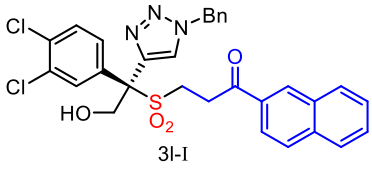


3l-I

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

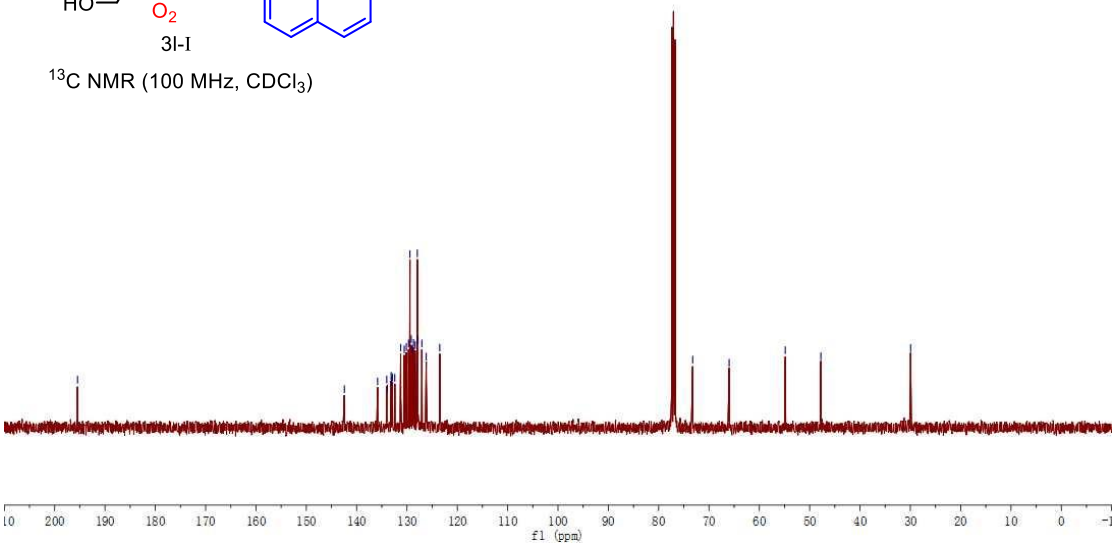


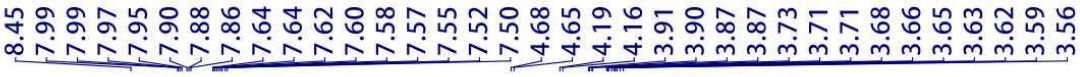


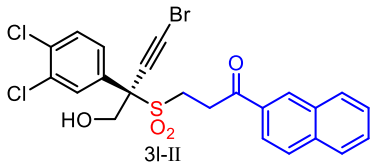


3l-I

^{13}C NMR (100 MHz, $CDCl_3$)

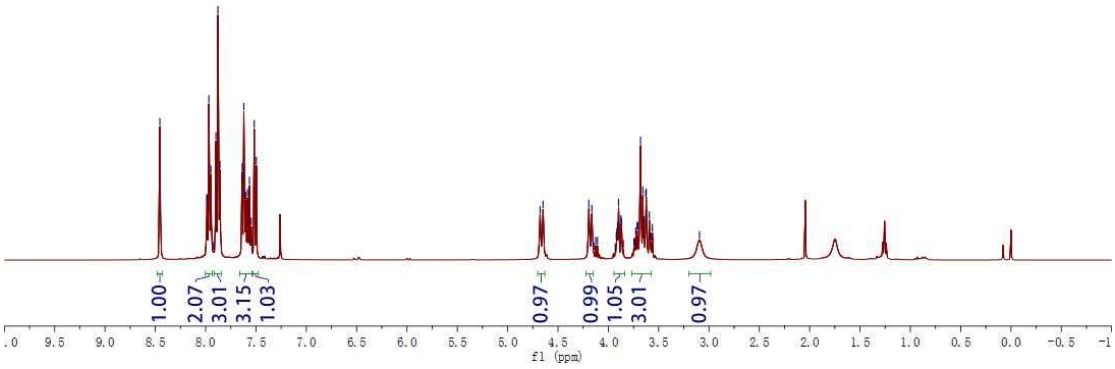


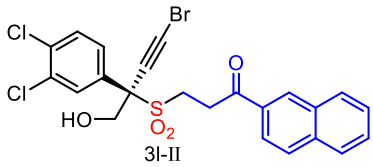




3l-II

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





3l-II

^{13}C NMR (100 MHz, $CDCl_3$)

8. References

(1) You, Y.; Li, T.-T.; Sun, T.-J.; Zhang, Y.-P.; Wang, Z.-H.; Zhao, J.-Q.; Yuan, W.-C. Enantioselective Construction of Vicinal Quaternary-Tetrasubstituted Carbon Stereocenters by Copper-Catalyzed Decarboxylative Propargylic Substitution. *Org. Lett.* **2022**, *24* (41), 7671–7676.
(2) Zhang, C.; Ye, S.; Wu, J. Asymmetric Sulfonylation from a Reaction of Cyclopropan-1-Ol, Sulfur Dioxide, and 1-(Alkynyl)Naphthalen-2-Ol. *Org. Lett.* **2024**, *26* (15), 3321–3325.