Organocatalytic Atropo- and *E/Z*-selective Michael Addition Reaction of Ynones with α-Amido Sulfones as Sulfone-type Nucleophile

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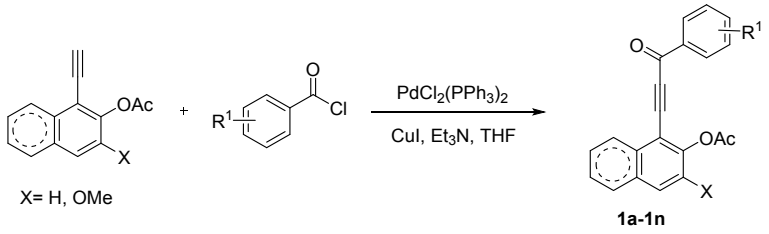
Supporting Information

I. General information

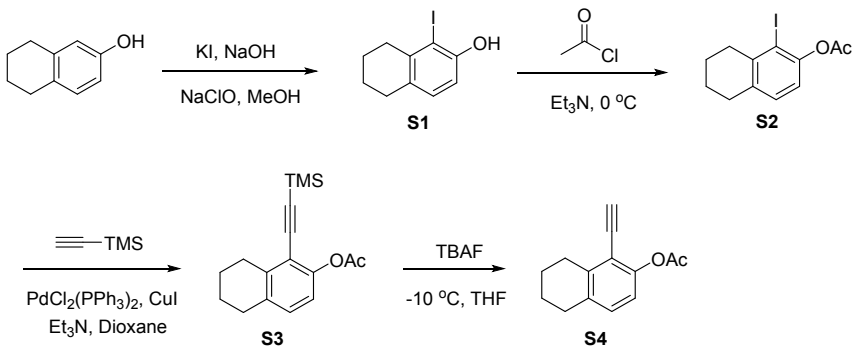
^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: $CDCl_3$ (^{1}H NMR δ 0.00, ^{13}C NMR δ 77.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6mm *Φ*×250mmL, DAICEL CHIRALCEL OD-H, 4.6mm *Φ*×250mmL. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Optical rotations were measured on a Rudolph Autopol I polarimeter and are reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL solvent). Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the synthesis of compounds 1a-1p

General procedure for the synthesis of compounds **1a-1n**:



A mixture of acyl chloride (1.2 equiv), $PdCl_2(PPh_3)_2$ (0.02 equiv) and Et_3N (1.2 equiv) in anhydrous THF were stirred for 10 min at 23 °C under argon. CuI (0.04 equiv) was then added and the reaction mixture was stirred for another 10 min. Terminal alkyne (1.0 equiv) was then added in one portion, the resulting mixture was stirred at 23 °C for 15 h. After the reaction was complete, ethyl acetate was added, and the resulting solution was washed with 0.1N HCl in a separatory funnel. After the layers were separated, the organic phase was dried over Na_2SO_4 and evaporated on a rotary evaporator to give the crude product, which was purified by flash chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the corresponding α, β-alkynic ketones **1a-1n**. The preparation of **1a-1n** was followed the literature procedure.



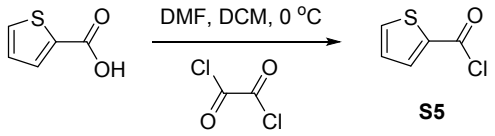
5,6,7,8-tetrahydronaphthalen-2-ol (5.0 g, 33.7 mmol) was dissolved in 100 mL of methanol. Potassium iodide (5.6 g, 33.7 mmol) and sodium hydroxide (1.35 g, 33.7 mmol) were added, and the solution was cooled to 0 °C.

Aqueous sodium hypochlorite (15 mL, 14.5% NaOCl) was added dropwise over 1 h at 0 – 3 °C. The resulting slurry was stirred for 8 h at 0 – 2 °C and treated with 95 mL of 10% aqueous $Na_2S_2O_3$. The mixture was neutralized using 5% aqueous HCl. Then ether (150 mL) was added. The organic layer was washed with brine (100 mL) and dried over Na_2SO_4. After filtration and rotary evaporation, this material was purified by flash chromatography (PE:EA = 20:1) to provide a white solid **S1** (6.0 g, 65%). The preparation of **S1** was followed the literature procedure.

Acetyl chloride (0.74 mL, 10.40 mmol) was added to a mixture of **S1** (1.9 g, 6.93 mmol) and Et_3N (1.95 mL, 13.86 mmol) in DCM (20 mL) at 0 °C. The mixture was then stirred at room temperature for about 30 min (determined by TLC), quenched with water and extracted with diethyl ether. The organic phase was separated, washed with water and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S2** (1.84 g, 84%). The preparation of **S2** was followed the literature procedure.

Dichlorobis(triphenylphosphine)palladium(II) (74.4 mg, 5 mol %) and copper(I) iodide (10.1 mg, 2.5 mol %) were added to a solution of **S2** (670 mg, 2.12 mmol) in 65 mL of dry 1,4-dioxane and 65 mL of dry triethylamine. Subsequently, (trimethylsilyl)acetylene (0.45 mL, 3.18 mmol) was added, and the mixture was refluxed for 8 h, at which time a further 1.5 equiv of (trimethylsilyl)acetylene (0.45 mL, 3.18 mmol), 2.5 mol % of dichlorobis(triphenylphosphine)palladium(II) (37.0 mg), and 2.5 mol % of copper(I) iodide (10.1 mg) were added. The mixture was refluxed for 16 h before water was added. The mixture was acidified with 10% HCl solution and extracted with ethyl acetate. The combined organic layers were washed with NaCl solution, dried (Na_2SO_4), and evaporated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA = 10:1) to afford **S3** (250 mg, 41%).

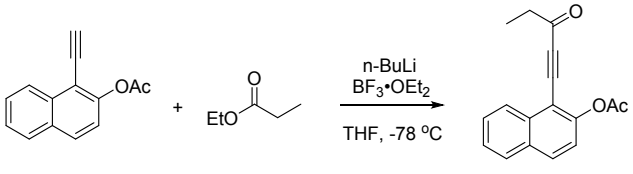
S3 was dissolved in 5 mL of THF and was cooled to -10 °C, followed by the addition of tetra-*n*butylammonium fluoride (0.44 mL of a 1.0 M solution in THF, 0.44 mmol). The reaction was stirred for 5 h at room temperature, NH_4Cl solution was added, and the mixture was extracted several times with ethyl acetate. The combined organic layers were washed with NaCl solution, dried (Na_2SO_4), concentrated under vacuum, and chromatographed (PE:EA = 10:1) to give acetylene **S4** (186.4 mg, 87%). The preparation of **S4** was followed the literature procedure.



S5

Aromatic carboxylic acid was dissolved in CH_2Cl_2 with dropping three drop DMF. 1.5 times the amount of oxalyl chloride was cautiously added into the reaction solution at 0 °C. After stirring at ambient temperature for 3 h, the reaction mixture was concentrated under reduced pressure to give the corresponding acid chloride **S5**. The preparation of **S5** was followed the literature procedure.

General procedure for the synthesis of compounds **1o**:



1o

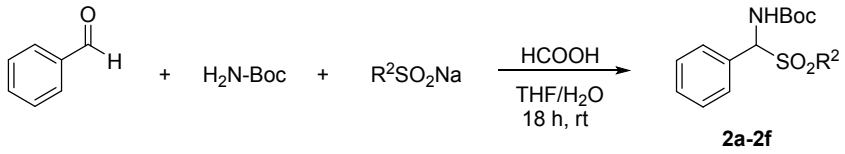
Terminal alkyne (100 mg, 0.476 mmol) was dissolved into THF (2 mL), and the solution was cooled to -78 ºC. To

the solution, n-Buli (0.19 mL, 0.476 mmol, 2.5 M in hexane) was added. After being stirred for 1 h at -78 ºC, ethyl propionate (27.6 uL, 0.476 mmol) and BF_3.OEt_2 (81.07 uL, 0.571 mmol) were added successively. The reaction was quenched by sat. NH_4Cl aq., and extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, and the solvent was removed under a reduced pressure. The residue was purified by column chromatography (SiO_2, eluent: hexane/EtOAc) to afford the desired ynones **1o**.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.78 (q, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 187.87, 168.79, 152.78, 133.96, 132.50, 131.04, 128.41, 128.23, 126.63, 125.60, 121.14, 110.14, 96.91, 83.63, 77.00, 38.91, 20.88, 8.21.

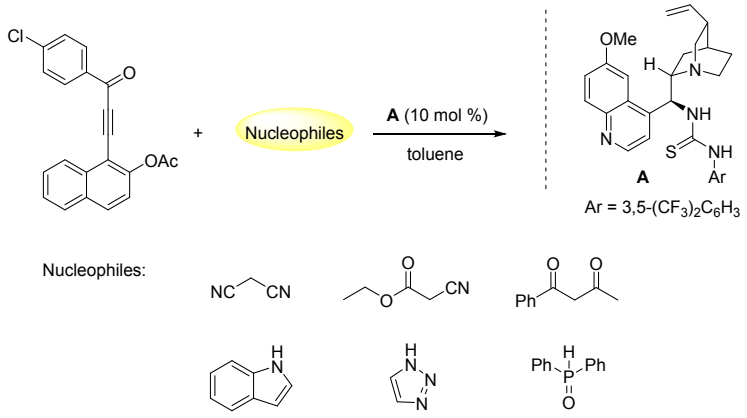
III. General procedure for the synthesis of compounds 2a-2f



A two-necked, round-bottomed flask is equipped with a magnetic stirring bar and fitted with a glass stopper and an argon inlet. The flask is flushed with argon and charged with tert-butyl carbamate (1.00 equiv) and 40 mL of tetrahydrofuran. Water, sodium benzenesulfinate (1.00 equiv), and freshly distilled benzaldehyde (1.02 equiv) are sequentially added in single portions, followed by formic acid. The reaction mixture is stirred for 18 h at room temperature under an argon atmosphere, during which time the desired product precipitates. The resulting white solid is filtered through a Büchner funnel (diameter 100 mm) and washed with distilled water. The solid is transferred to a single-necked, round-bottomed flask and is slurried in a mixture of hexane/dichloromethane (10/1 mL). The product **2a-2f** can be obtained by draining. The preparation of **2a-2f** was followed the literature procedure.

IV. Optimization of the reaction conditions

Scheme S1. Screening of nucleophiles[a]



[a] Reaction conditions: **1h** (0.1 mmol), **A** (10 mol %) and nucleophiles (0.1 mmol) in toluene (1.0 mL) at 25 ºC for 24 h.

Some other types of nucleophiles such as malononitrile, ethyl 2-cyanoacetate, 1-phenylbutane-1,3-dione, 1*H*-indole, 1*H*-1,2,3-triazole, diphenylphosphine oxide were tested under the optimized conditions, the reactions

proceeded sluggishly and no desired products were obtained.

Scheme S2. α-Amido sulfones as sulfone-type nucleophile

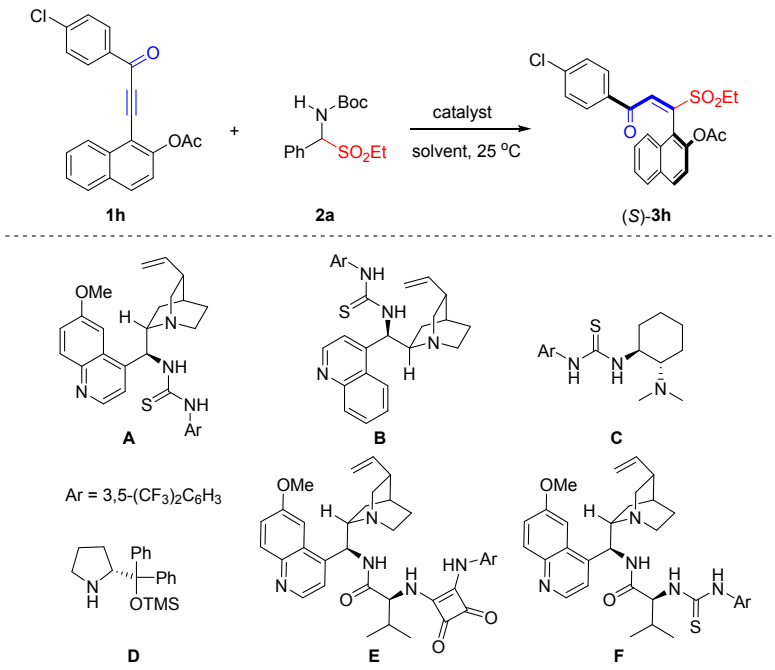


Table S1. Catalyst screening.[a]

entry	catalyst (10 mol %)	solvent	time(h)	temp(°C)	yield(%)[b]	*E*/*Z* ratio[c]	ee(%)[d]
1	**A**	toluene	72	25	63	>20:1	79
2	**B**	toluene	72	25	73	>20:1	-64
3	**C**	toluene	72	25	78	>20:1	52
4	**D**	toluene	72	25	<10	-	14
5	**E**	toluene	72	25	20	>20:1	96
6	**F**	toluene	72	25	70	>20:1	88
7	**F**	DCM	72	25	48	>20:1	88
8	**F**	THF	72	25	-	-	-
9	**F**	$PhCF_3$	72	25	50	>20:1	90
10	**F**	*m*-xylene	72	25	47	>20:1	87
11[e]	**F**	$PhCF_3$	72	25	98	>20:1	90
12[f]	**F**	$PhCF_3$	72	25	48	>20:1	87
13[g]	**F**	$PhCF_3$	72	25	45	>20:1	88
14[h]	**F**	$PhCF_3$	72	25	86	>20:1	90

[a] Reaction conditions: **1h** (0.1 mmol), catalyst (10 mol %) and **2a** (0.1 mmol) in solvent (1.0 mL) at 25 °C for 72 h, unless otherwise specified. [b] Isolated yield of *E*-**3h**. [c] Determined by ^{1}H NMR (400 MHz) analysis of the crude reaction mixture. [d] The ee value of *E* isomer. Determined by HPLC analysis. [e] **F** (20 mol %). [f] **F** (5 mol %). [g] $PhCF_3$ (0.75 mL). [h] $PhCF_3$ (1.5 mL).

Table S2. Solvent screening.[a]

entry	catalyst (10 mol %)	solvent	time(h)	temp(°C)	yield(%)[b]	*E/Z* ratio	ee(%)[c]
1	**E**	DCM	72	25	<5	>20:1	97
2	**E**	THF	72	25	<5	>20:1	88
3	**E**	CH_3CN	72	25	-	-	-
4	**E**	$PhCF_3$	72	25	42	>20:1	97
5	**E**	*m*-xylene	72	25	28	>20:1	96
6	**E**	EA	72	25	23	>20:1	97

[a] Reaction conditions: **1h** (0.1 mmol), **E** (10 mol %) and **2a** (0.1 mmol) in solvent (1.0 mL) at 25 °C for 72 h, unless otherwise specified. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S3. Catalyst loading screening.[a]

entry	catalyst **E** (mol %)	solvent	time(h)	temp(°C)	yield (%)[b]	*E/Z* ratio	ee (%)[c]
1	**5**	$PhCF_3$	72	25	15	>20:1	96
2	**20**	$PhCF_3$	72	25	48	>20:1	97

[a] Reaction conditions: **1h** (0.1 mmol), **E** and **2a** (0.1 mmol) in $PhCF_3$ (1.0 mL) at 25 °C for 72 h, unless otherwise specified. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S4. Concentration screening.[a]

entry	catalyst	CF_3Ph (mL)	time(h)	temp(°C)	yield (%)[b]	*E/Z* ratio	ee (%)[c]
1	**E**	0.75	72	25	27	>20:1	97
2	**E**	1.5	72	25	30	>20:1	97

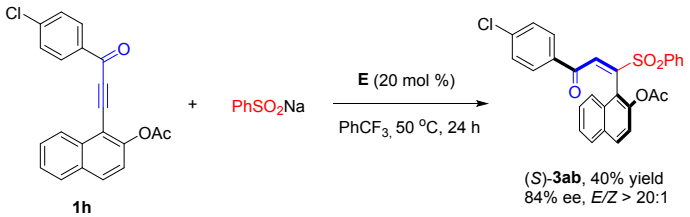
[a] Reaction conditions: **1h** (0.1 mmol), **E** (20 mol %) and **2a** (0.1 mmol) in $PhCF_3$ at 25 °C for 72 h, unless otherwise specified. [b] Isolated yield. [c] Determined by HPLC analysis.

Table S5. Temperature screening.[a]

entry	catalyst	solvent	time(h)	temp(°C)	yield (%)[b]	*E/Z* ratio	ee (%)[c]
1	**E**	CF_3Ph	24	40	27	>20:1	96
2	**E**	CF_3Ph	24	50	85	>20:1	97
3	**E**	CF_3Ph	24	70	64	>20:1	88

[a] Reaction conditions: **1h** (0.1 mmol), **E** (20 mol %) and **2a** (0.1 mmol) in $PhCF_3$ (1.0 mL) for 24 h, unless otherwise specified. [b] Isolated yield. [c] Determined by HPLC analysis.

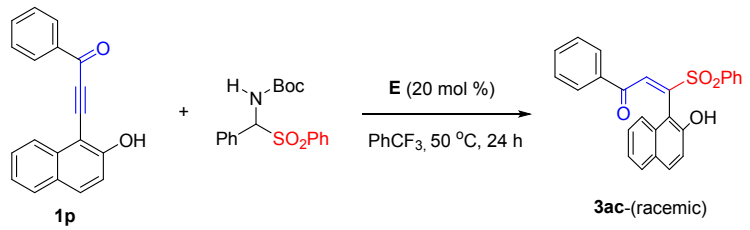
Scheme S3. $PhSO_2Na$ as sulfone-type nucleophiles



Reaction condition: **1h** (0.1 mmol), catalyst **E** (20 mol %) and $PhSO_2Na$ (0.1 mmol) in solvent (1.0 mL) at 50 °C

for 24 h.

Scheme S4. the free hydroxyl substrate was used in this reaction



Reaction condition: **1p** (0.1 mmol), catalyst **E** (20 mol %) and α-Amido sulfone (0.1 mmol) in solvent (1.0 mL) at 50 °C for 24 h.

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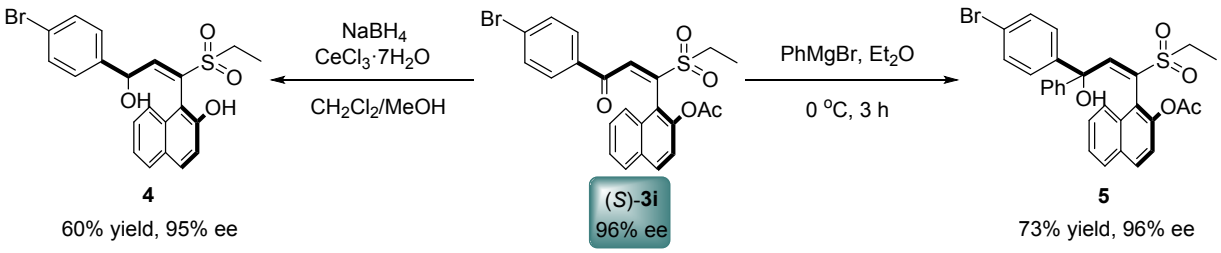
V. Synthetic transformations



To a solution of (*S*)-**3i** (30.0 mg, 0.0616 mmol) and Cerium chloride heptahydrate (27.5 mg, 0.123 mmol) in dry CH_2Cl_2/MeOH (v/v=1:1), $NaBH_4$ (7.0 mg, 0.185 mmol) was carefully added at room temperature over 5.0 min. The mixture was stirred for another 20 min until the starting material disappeared. Then, ice water (5 mL) was slowly added and stirred for 15 min. The mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were washed with saturated brine (15 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification of the residue *via* column chromatography (PE:EA=2:1) afforded the desired compound **4** as a white solid (16.5 mg, 60%).

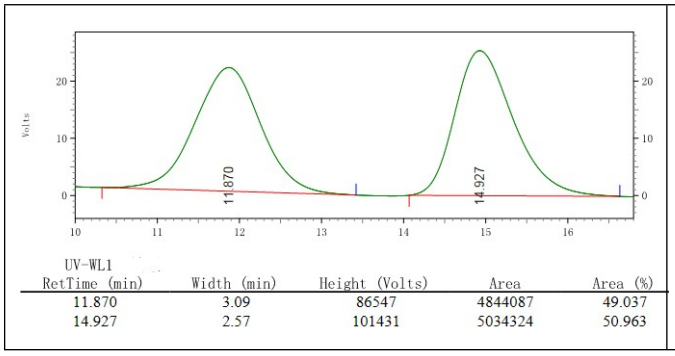
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.40 (t, J = 7.3 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 8.3 Hz, 2H), 7.27 – 7.21 (m, 2H), 6.83 (d, J = 8.3 Hz, 2H), 4.72 (d, J = 9.0 Hz, 1H), 3.05 (s, 1H), 2.86 (q, J = 7.4 Hz, 2H), 1.26 (d, J = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.86, 146.47, 138.36, 136.81, 132.81, 132.48, 131.68, 129.14, 128.66, 128.42, 127.58, 124.34, 123.74, 122.54, 119.37, 109.68, 70.33, 46.09, 5.70.

HRMS (ESI) m/z Calcd for $[C_{21}H_{19}BrNaO_4S, M + Na]^+$: 469.0080, Found: 469.0073.

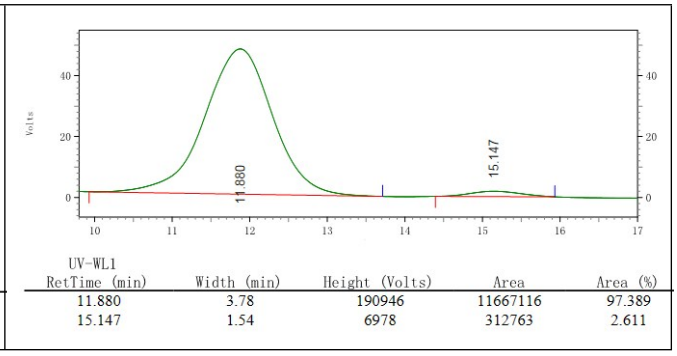
Optical Rotation: $[\alpha]_D^{25}$ = +94.0° (c = 0.35, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 11.880 min (major), t_R = 15.147 min (minor).



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.870	3.09	86547	4844087	49.037
14.927	2.57	101431	5034324	50.963



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.880	3.78	190946	11667116	97.389
15.147	1.54	6978	312763	2.611

Under argon atmosphere, (*S*)-**3i** (40 mg, 0.082 mmol), dehydrated diethyl ether 1.5 mL were charged in a flask and cooled to 0 °C. Phenyl magnesium bromide (1M in THF, 0.33 mL, 4.0 equiv) was added dropwise and stirred for 3 h at 0 °C, water (2 mL) was added and then filtered. The organic layer of the filtrate was dried over magnesium sulfate. Concentration and flash chromatography on a silica column (PE: EA=2:1) afforded compound **5** as a white solid (34.0 mg, 73%).

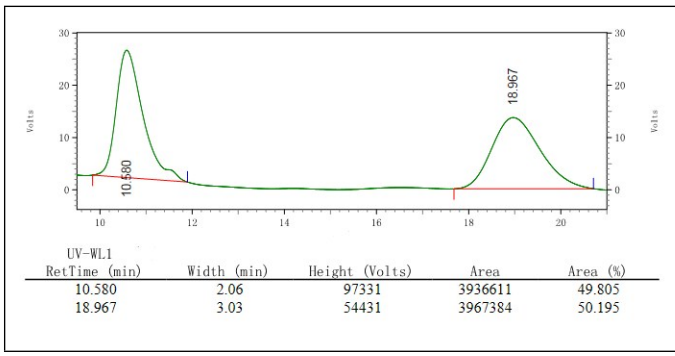
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.72 (t, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.22 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 11.0 Hz, 3H), 6.79 (d, *J* = 8.4 Hz, 2H), 2.86 (q, *J* = 7.2 Hz, 2H), 1.62 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.59, 152.95, 145.33, 141.43, 139.32, 137.56, 132.70, 131.83, 130.82, 128.54, 128.29, 128.05, 127.96, 127.75, 126.84, 126.32, 124.16, 123.61, 121.58, 118.97, 109.87, 82.69, 45.89, 20.99, 5.77.

HRMS (ESI) m/z Calcd for $[C_{29}H_{25}BrNaO_5S, M + Na]^+$: 587.0498, Found: 587.0492.

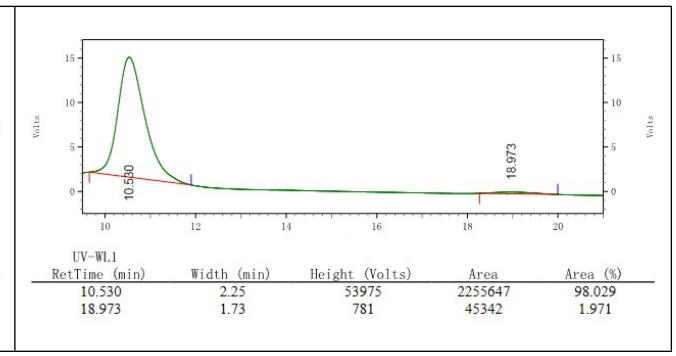
Optical Rotation: $[\alpha]_D^{25}$ = +68.8° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.530 min (major), t_R = 18.973 min (minor).



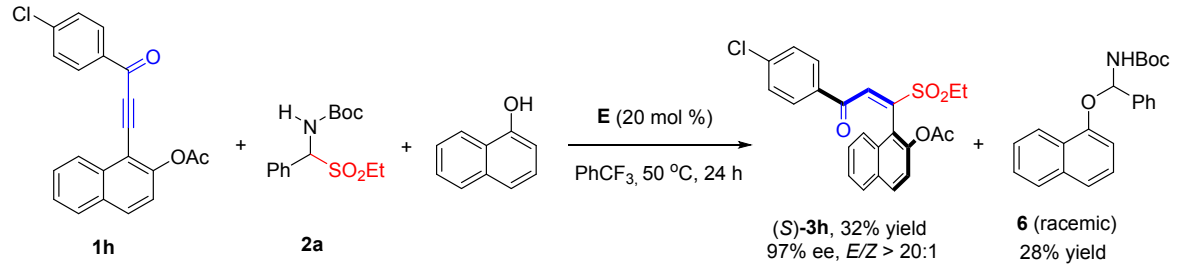
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.580	2.06	97331	3936611	49.805
18.967	3.03	54431	3967384	50.195



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.530	2.25	53975	2255647	98.029
18.973	1.73	781	45342	1.971

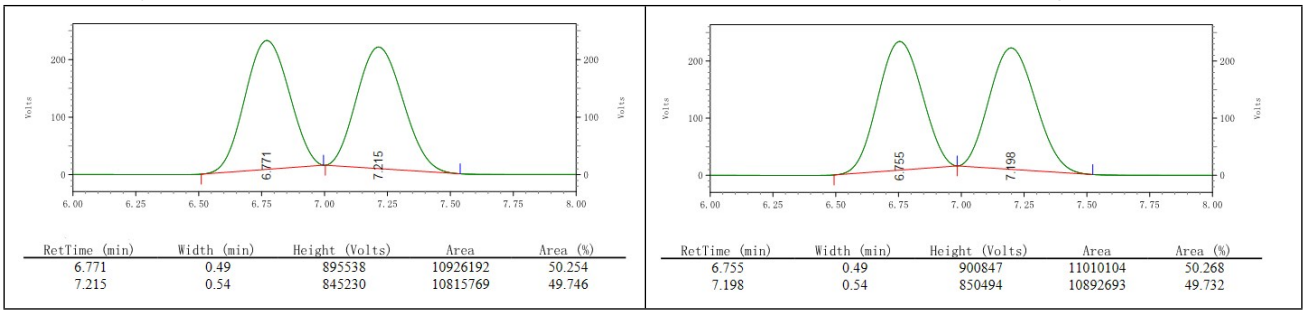


Reaction conditions: **1h** (0.1 mmol), **2a** (0.1 mmol), 1-Naphthol (0.1 mmol) and catalyst **E** (20 mol %) in solvent (1.0 mL) at 50 °C for 24 h. Purification of the residue *via* column chromatography (PE:EA=15:1) afforded the compound **6**.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.37 (d, J = 8.9 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.53 – 7.41 (m, 2H), 7.38-7.33 (m, 2H), 7.32 – 7.23 (m, 4H), 6.88 (d, J = 8.6 Hz, 1H), 6.45 (d, J = 9.2 Hz, 1H), 5.62 (d, J = 9.2 Hz, 1H), 1.44 (s, 9H).

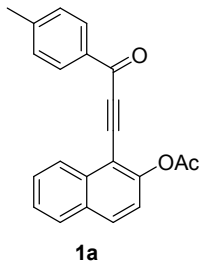
^{13}C NMR (150 MHz, $CDCl_3$): δ 157.65, 150.98, 139.56, 133.97, 128.58, 127.38, 127.23, 126.77, 126.49, 126.05, 125.74, 125.31, 122.97, 122.50, 119.96, 81.44, 52.42, 28.29.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm)



VI. Analytical data of compounds 1a-1p

1-(3-oxo-3-(p-tolyl)prop-1-yn-1-yl)naphthalen-2-yl acetate (1a)



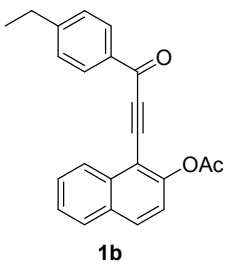
1a

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 7.7 Hz, 2H), 7.98 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 6.8 Hz, 3H), 2.46 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.27, 168.90, 152.76, 145.37, 134.67, 134.08, 132.39, 131.09, 129.71, 129.40, 128.44, 128.30, 126.68, 125.83, 121.21, 110.38, 96.32, 85.62, 21.83, 20.99.

HRMS (ESI) m/z Calcd for $[C_{22}H_{16}NaO_3, M + Na]^+$: 351.0992, Found: 351.0990.

1-(3-(4-ethylphenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1b)



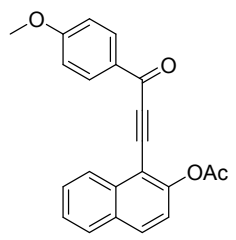
1b

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.34 (dd, J = 14.5, 8.5 Hz, 3H), 2.75 (q, J = 7.6 Hz, 2H), 2.46 (s, 3H), 1.28 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.27, 168.91, 152.73, 151.51, 134.80, 134.03, 132.38, 131.05, 129.80, 128.42, 128.28, 128.20, 126.65, 125.79, 121.19, 110.34, 96.32, 85.59, 29.08, 20.98, 15.12.

HRMS (ESI) m/z Calcd for $[C_{23}H_{18}NaO_3, M + Na]^+$: 365.1148, Found: 365.1142.

1-(3-oxo-3-(p-tolyl)prop-1-yn-1-yl)naphthalen-2-yl acetate (1c)



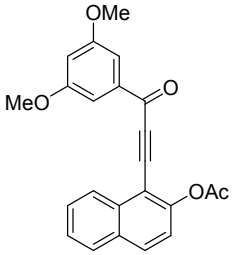
1c

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.3 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.20, 168.93, 164.55, 152.63, 134.00, 132.26, 131.96, 131.07, 130.30, 128.42, 128.25, 126.65, 125.81, 121.19, 113.94, 110.46, 96.26, 85.31, 55.61, 20.99.

HRMS (ESI) m/z Calcd for $[C_{22}H_{16}NaO_4, M + Na]^+$: 367.0941, Found: 367.0944.

1-(3-(3,5-dimethoxyphenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1d)



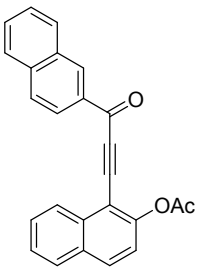
1d

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 1H), 6.73 (s, 1H), 3.87 (s, 6H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.21, 169.06, 160.94, 152.95, 138.89, 134.12, 132.56, 131.06, 128.48, 128.31, 126.69, 125.76, 121.26, 110.21, 107.29, 106.68, 96.23, 85.92, 55.66, 20.91.

HRMS (ESI) m/z Calcd for $[C_{23}H_{18}NaO_5, M + Na]^+$: 397.1046, Found: 397.1041.

1-(3-(naphthalen-2-yl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1e)



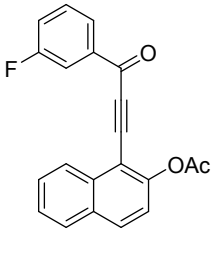
1e

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.98 – 7.81 (m, 4H), 7.60 (dp, *J* = 29.7, 7.6 Hz, 4H), 7.32 (d, *J* = 8.9 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.44, 168.93, 152.74, 136.10, 134.43, 134.01, 132.68, 132.47, 132.36, 131.04, 129.69, 129.06, 128.58, 128.43, 128.29, 127.89, 127.03, 126.66, 125.72, 123.80, 121.17, 110.30, 96.28, 86.09, 20.98.

HRMS (ESI) m/z Calcd for $[C_{25}H_{16}NaO_3, M + Na]^+$: 387.0992, Found: 387.0987.

1-(3-(3-fluorophenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1f)



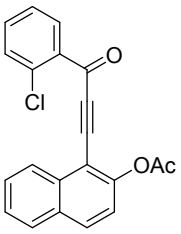
1f

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.99 (t, *J* = 10.3 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 2H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.19, 168.86, 162.73 (d, *J* = 247.0 Hz), 153.04, 138.95 (d, *J* = 6.0 Hz), 134.07, 132.86, 131.04, 130.4 (d, *J* = 7.0 Hz), 128.49 (d, *J* = 2.0 Hz), 126.78, 125.67, 125.20 (d, *J* = 3.0 Hz), 121.22 (d, *J* = 21.0 Hz), 121.12, 116.25, 116.03, 109.85, 95.83, 86.86, 20.94.

HRMS (ESI) m/z Calcd for $[C_{21}H_{13}FNaO_3, M + Na]^+$: 355.0741, Found: 355.0738.

1-(3-(2-chlorophenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1g)



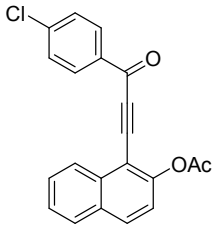
1g

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.59 – 7.46 (m, 3H), 7.45 – 7.39 (m, 1H), 7.30 (d, *J* = 8.9 Hz, 1H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.32, 168.90, 153.17, 135.79, 134.11, 133.47, 133.44, 132.86, 132.52, 131.54, 131.04, 128.44, 128.38, 126.78, 126.70, 125.71, 121.20, 110.10, 97.47, 87.12, 20.87.

HRMS (ESI) m/z Calcd for $[C_{21}H_{13}ClNaO_3, M + Na]^+$: 371.0445, Found: 371.0440.

1-(3-(4-chlorophenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1h)



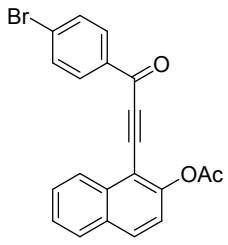
1h

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.23 (d, *J* = 8.1 Hz, 2H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.55 (dd, *J* = 22.6, 7.9 Hz, 3H), 7.34 (d, *J* = 8.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.17, 168.76, 152.93, 140.78, 135.28, 133.95, 132.72, 131.01, 130.79, 129.02, 128.48, 128.40, 126.72, 125.60, 121.17, 109.94, 95.82, 86.70, 20.95.

HRMS (ESI) m/z Calcd for $[C_{21}H_{13}ClNaO_3, M + Na]^+$: 371.0445, Found: 371.0441.

1-(3-(4-bromophenyl)-3-oxoprop-1-yn-1-yl)naphthalen-2-yl acetate (1i)



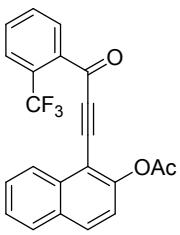
1i

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 3H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.44, 168.83, 152.95, 135.72, 133.99, 132.78, 132.05, 131.06, 130.91, 129.70, 128.53, 128.45, 126.78, 125.66, 121.21, 109.98, 95.81, 86.79, 21.01.

HRMS (ESI) m/z Calcd for $[C_{21}H_{13}BrNaO_3, M + Na]^+$: 414.9940, Found: 414.9936.

1-(3-oxo-3-(2-(trifluoromethyl)phenyl)prop-1-yn-1-yl)naphthalen-2-yl acetate (1j)



1j

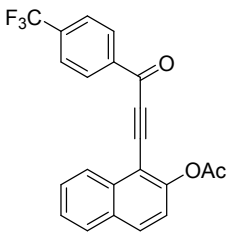
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (t, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.84 (t, *J* = 8.5 Hz, 2H), 7.76 – 7.64 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.10, 168.74, 153.27, 137.23, 134.01, 133.07, 132.15, 131.74, 130.99, 130.97 (q, *J* = 22.0 Hz), 128.45 (q, *J* = 3.0 Hz), 127.38 (q, *J* = 6.0 Hz),

127.30, 126.72, 126.17 (q, J = 58.0 Hz), 123.22 (q, J = 272.0 Hz), 121.16, 109.74, 97.21, 95.73, 87.46, 20.71.

HRMS (ESI) m/z Calcd for $[C_{22}H_{13}F_3NaO_3, M + Na]^+$: 405.0709, Found: 405.0702.

1-(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)naphthalen-2-yl acetate (1k)



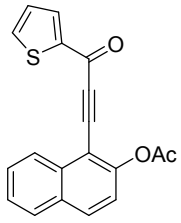
1k

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, J = 8.1 Hz, 2H), 8.35 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.9 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.31, 168.77, 153.18, 139.45, 135.31 (q, J = 33.0 Hz), 134.03, 133.02, 131.10, 129.80, 128.57 (q, J = 3.0 Hz), 126.84, 125.77 (q, J = 3.0 Hz), 125.72, 125.59, 123.49 (q, J = 271.0 Hz), 121.25, 109.81, 95.83, 87.63, 20.98.

HRMS (ESI) m/z Calcd for $[C_{22}H_{13}F_3NaO_3, M + Na]^+$: 405.0709, Found: 405.0701.

1-(3-oxo-3-(thiophen-2-yl)prop-1-yn-1-yl)naphthalen-2-yl acetate (1l)



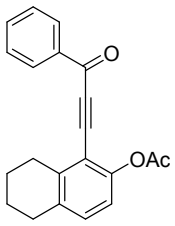
1l

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 3.4 Hz, 1H), 7.99 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 4.8 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.9 Hz, 1H), 7.25 – 7.20 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.29, 168.94, 152.86, 144.90, 135.42, 135.04, 133.98, 132.57, 131.06, 128.49, 128.39, 126.72, 125.72, 121.22, 110.07, 95.70, 94.21, 84.77, 21.02.

HRMS (ESI) m/z Calcd for $[C_{19}H_{12}NaO_3S, M + Na]^+$: 343.0399 , Found: 343.0394.

1-(3-oxo-3-phenylprop-1-yn-1-yl)-5,6,7,8-tetrahydronaphthalen-2-yl acetate (1m)



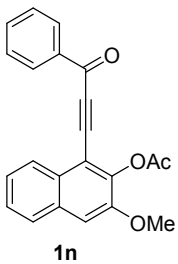
1m

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.5 Hz, 2H), 7.63 (t, J = 7.9 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 3.02 (t, J = 6.3 Hz, 2H), 2.77 (t, J = 6.2 Hz, 2H), 2.37 (s, 3H), 1.90 – 1.77 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.64, 169.28, 151.24, 142.45, 136.87, 135.56, 134.07, 132.49, 129.47, 128.58, 119.35, 113.90, 95.58, 86.89, 29.16, 28.41, 22.41, 20.87.

HRMS (ESI) m/z Calcd for $[C_{21}H_{18}NaO_3, M + Na]^+$: 341.1148, Found: 341.1143.

3-methoxy-1-(3-oxo-3-phenylprop-1-yn-1-yl)naphthalen-2-yl acetate (1n)



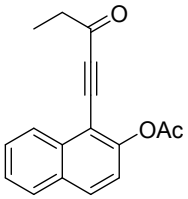
1n

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 7.5 Hz, 2H), 8.22 (d, J = 8.5 Hz, 1H), 7.71 (m, 1H), 7.60 (t, J = 7.1 Hz, 1H), 7.54 – 7.41 (m, 4H), 7.28 (s, 1H), 3.89 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.33, 168.14, 149.64, 144.75, 136.69, 134.11, 131.78, 129.36, 128.52, 127.02, 126.92, 125.68, 125.26, 111.65, 110.71, 95.51, 85.70, 55.88, 20.39.

HRMS (ESI) m/z Calcd for $[C_{22}H_{16}NaO_4, M + Na]^+$: 367.0941, Found: 367.0932.

1-(3-oxopent-1-yn-1-yl)naphthalen-2-yl acetate (1o)

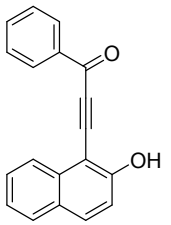


1o

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.78 (q, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 187.87, 168.79, 152.78, 133.96, 132.50, 131.04, 128.41, 128.23, 126.63, 125.60, 121.14, 110.14, 96.91, 83.63, 77.00, 38.91, 20.88, 8.21.

3-(2-hydroxynaphthalen-1-yl)-1-phenylprop-2-yn-1-one (1p)



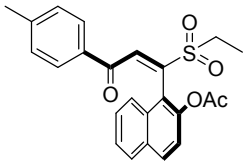
1P

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, *J* = 7.6 Hz, 2H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 178.12, 160.53, 136.72, 134.34, 134.09, 129.63, 128.83, 128.66, 128.38, 128.34, 124.58, 124.49, 117.42, 99.65, 99.10, 88.50.

VII. Analytical data of compounds (*S*)-3a-3aa, (*S*)-3ab, 3ac

(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-(p-tolyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3a)**



(*S*)-**3a**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.94 (q, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 2.28 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H).

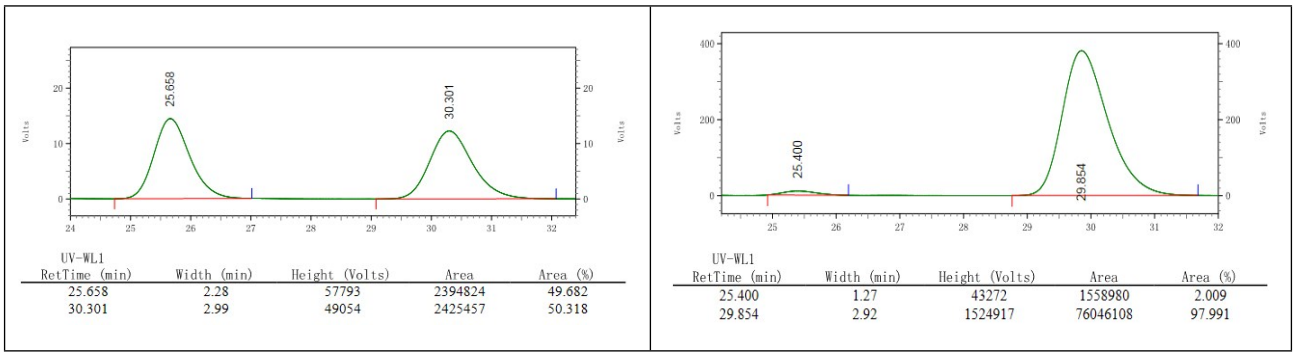
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.79, 168.29, 146.75, 145.27, 144.35, 138.62, 133.09, 132.17, 131.17, 131.03, 129.26, 128.81, 128.24, 127.22, 125.96, 125.28, 121.54, 117.51, 46.54, 21.65, 21.11, 5.93.

HRMS (ESI) m/z Calcd for $[C_{24}H_{22}NaO_5S, M + Na]^+$: 445.1080, Found: 445.1077.

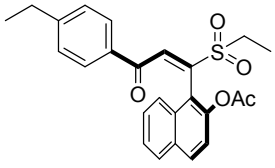
Optical Rotation: $[\alpha]_D^{25}$ = +58.8° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 25.400 min (minor), t_R = 29.854 min (major).

Physical properties: pale yellow solid; **Yield:** 99%, 41.8 mg.



(*E*)-1-(3-(4-ethylphenyl)-1-(ethylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3b)**



(*S*)-**3b**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 7.78 (t, *J* = 8.8 Hz, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H).

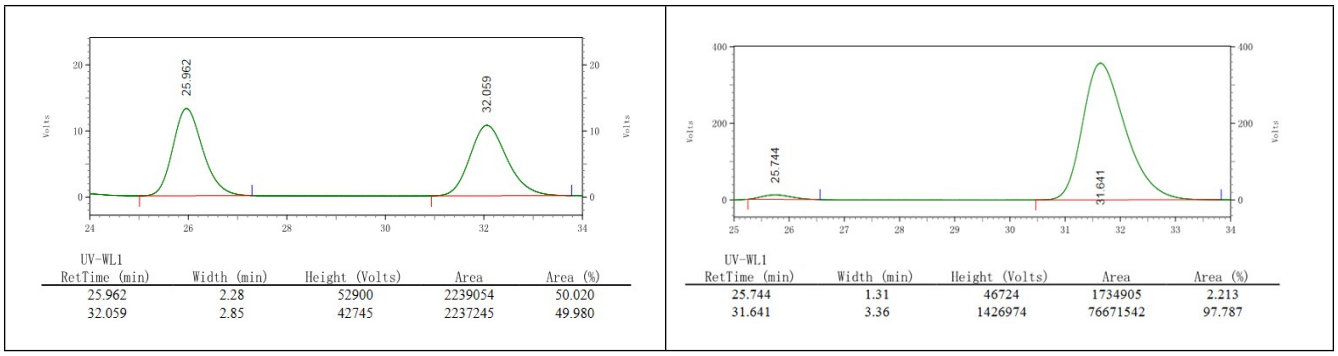
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.86, 168.33, 151.37, 146.79, 144.48, 138.60, 133.38, 132.21, 131.20, 128.95, 128.27, 128.10, 127.26, 125.99, 125.33, 121.57, 117.56, 94.54, 46.58, 28.92, 21.15, 14.93, 5.96.

HRMS (ESI) m/z Calcd for $[C_{25}H_{24}NaO_5S, M + Na]^+$: 459.1237, Found: 459.1233.

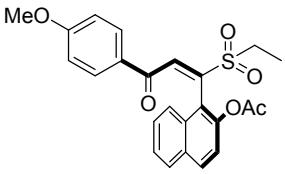
Optical Rotation: $[\alpha]_D^{25}$ = +61.4° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 25.744 min (minor), t_R = 31.641 min (major).

Physical properties: pale yellow solid; **Yield:** 90%, 39.2 mg.



(*E*)-1-(1-(ethylsulfonyl)-3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3c)**



(*S*)-**3c**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.89 – 7.83 (m, 3H), 7.83 – 7.76 (m, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.35 (d, J = 9.0 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.94 (q, J = 7.4 Hz, 2H), 2.29 (s, 3H), 1.34 (t, J = 7.4 Hz, 3H).

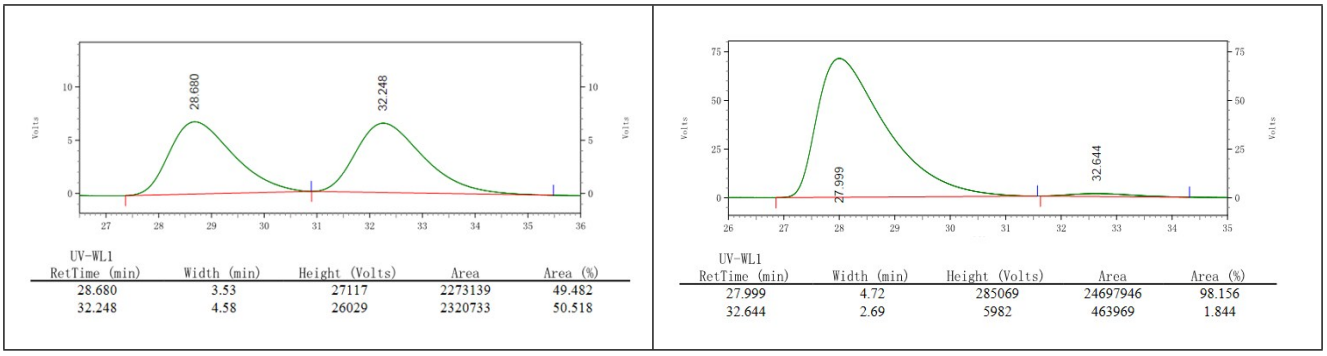
^{13}C NMR (100 MHz, $CDCl_3$): δ 187.63, 168.30, 164.25, 146.74, 143.86, 138.84, 132.17, 131.16, 131.12, 131.02, 128.62, 128.23, 127.18, 125.94, 125.33, 121.55, 117.56, 113.79, 55.40, 46.56, 21.13, 5.95.

HRMS (ESI) m/z Calcd for $[C_{24}H_{22}NaO_6S, M + Na]^+$: 461.1029, Found: 461.1022.

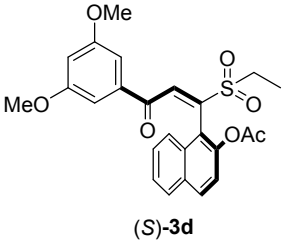
Optical Rotation: $[\alpha]_D^{25}$ = +46.4° (c = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 27.999 min (major), t_R = 32.644 min (minor).

Physical properties: pale yellow solid; **Yield:** 63%, 27.6 mg.



(*E*)-1-(3-(3,5-dimethoxyphenyl)-1-(ethylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3d)**



(*S*)-**3d**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.83 (t, J = 7.6 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 6.97 (d, J = 1.7 Hz, 2H), 6.59 (s, 1H), 3.75 (s, 6H), 2.95 (q, J = 7.4 Hz, 2H), 2.31 (s, 3H), 1.36 (t, J = 7.4 Hz, 3H).

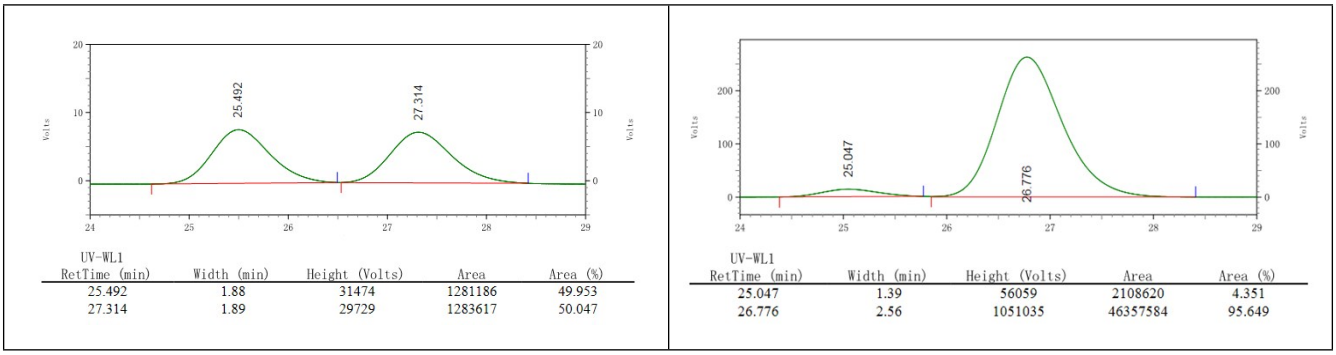
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.12, 168.45, 160.81, 146.85, 144.96, 138.38, 137.45, 132.24, 131.35, 131.13, 128.35, 127.39, 126.10, 125.34, 121.61, 117.51, 106.52, 106.43, 55.58, 46.63, 21.20, 6.00.

HRMS (ESI) m/z Calcd for $[C_{25}H_{24}NaO_7S, M + Na]^+$: 491.1135, Found: 491.1128.

Optical Rotation: $[\alpha]_D^{25}$ = +64.7° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 25.047 min (minor), t_R = 26.776 min (major).

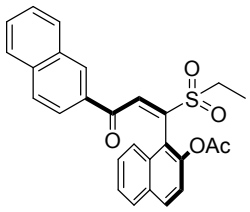
Physical properties: pale yellow solid; **Yield:** 82%, 38.4 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
25.492	1.88	31474	1281186	49.953
27.314	1.89	29729	1283617	50.047

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
25.047	1.39	56059	2108620	4.351
26.776	2.56	1051035	46357584	95.649

(*E*)-1-(1-(ethylsulfonyl)-3-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3e)**



(*S*)-**3e**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.42 (s, 1H), 7.91 (t, *J* = 8.2 Hz, 2H), 7.85 – 7.72 (m, 5H), 7.60 – 7.49 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 2.98 (q, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.37 (t, *J* = 7.4 Hz, 3H).

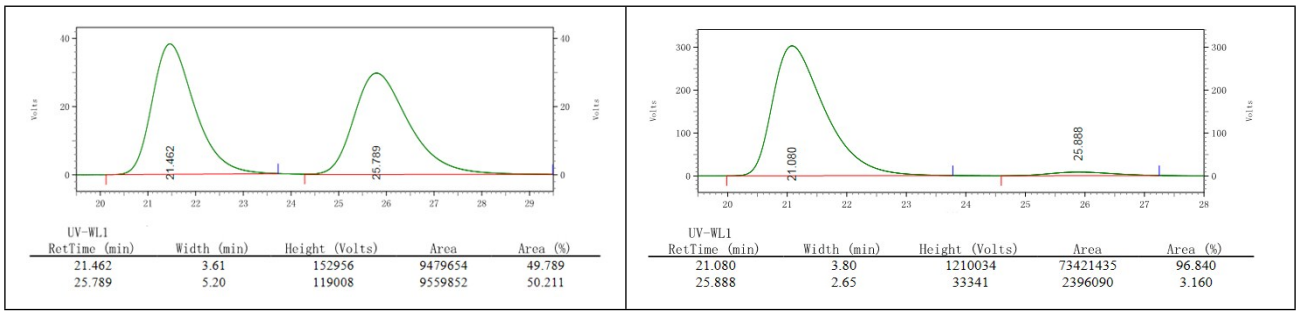
^{13}C NMR (100 MHz, $CDCl_3$): δ 189.36, 168.38, 146.87, 144.65, 138.60, 135.92, 132.95, 132.18, 132.05, 131.57, 131.31, 131.10, 129.55, 129.11, 128.71, 128.34, 127.81, 127.38, 127.01, 126.06, 125.30, 123.35, 121.64, 117.54, 46.67, 21.23, 5.98.

HRMS (ESI) m/z Calcd for $[C_{27}H_{22}NaO_5S, M + Na]^+$: 481.1080, Found: 481.1077.

Optical Rotation: $[\alpha]_D^{25}$ = +75.9° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 21.080 min (major), t_R = 25.888 min (minor).

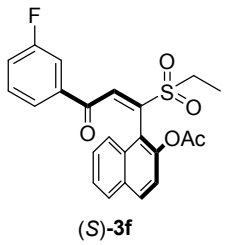
Physical properties: pale yellow solid; **Yield:** 98%, 44.9 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
21.462	3.61	152956	9479654	49.789
25.789	5.20	119008	9559852	50.211

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
21.080	3.80	1210034	73421435	96.840
25.888	2.65	33341	2396090	3.160

(*E*)-1-(1-(ethylsulfonyl)-3-(3-fluorophenyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3f)



(*S*)-**3f**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.91 – 7.77 (m, 3H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.19 (t, *J* = 8.2 Hz, 1H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H).

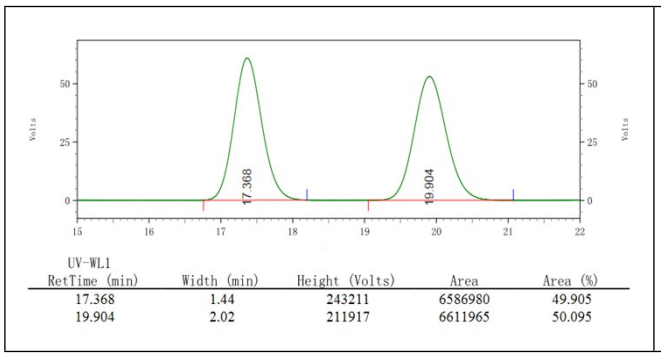
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.47, 168.31, 162.48 (d, *J* = 248.0 Hz), 146.80, 145.53, 137.78, 137.48(d, *J* = 7.0 Hz), 132.04, 131.46, 131.04, 130.28 (d, *J* = 9.0 Hz), 128.36, 127.44, 126.12, 125.13, 124.46 (d, *J* = 3.0 Hz), 121.57, 121.16 (d, *J* = 21.0 Hz), 117.25, 115.26 (d, *J* = 23.0 Hz), 46.61, 21.11, 5.90.

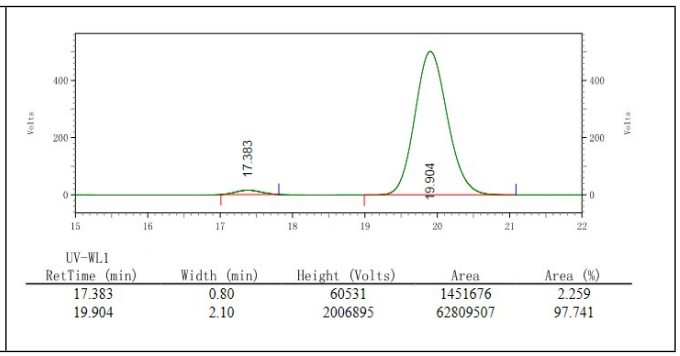
HRMS (ESI) m/z Calcd for $[C_{23}H_{19}FNaO_5S, M + Na]^+$: 449.0829, Found: 449.0821.

Optical Rotation: $[\alpha]_D^{25}$ = +89.0° (*c* = 1.00, $CHCl_3$).

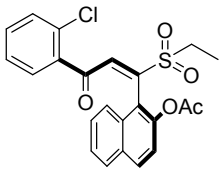
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 17.383 min (minor), t_R = 19.904 min (major).

Physical properties: pale yellow solid; **Yield:** 94%, 40.0 mg.





(*E*)-1-(3-(2-chlorophenyl)-1-(ethylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3g)



(*S*)-**3g**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.80 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.46 (dt, *J* = 21.1, 7.3 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 1H), 7.11 (s, 2H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 1H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H).

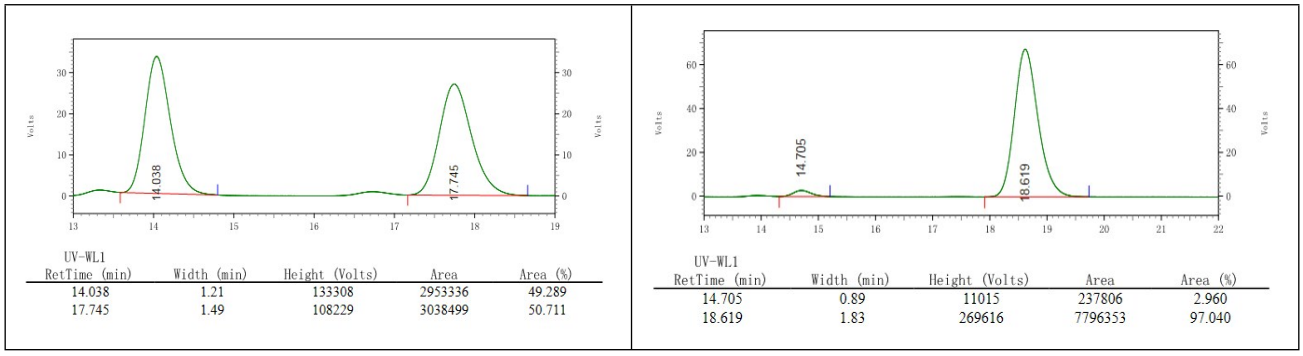
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.85, 168.45, 146.88, 142.75, 140.43, 136.73, 132.54, 132.09, 131.77, 131.26, 130.92, 129.72, 129.68, 128.05, 127.33, 126.41, 126.03, 125.28, 121.40, 117.35, 46.82, 21.17, 5.99.

HRMS (ESI) m/z Calcd for $[C_{23}H_{19}ClNaO_5S, M + Na]^+$: 465.0534, Found: 465.0528.

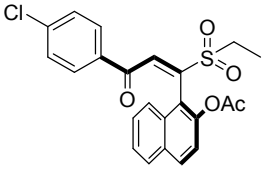
Optical Rotation: $[\alpha]_D^{25}$ = +35.8° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 14.705 min (minor), t_R = 18.619 min (major).

Physical properties: pale yellow solid; **Yield:** 72%, 31.8 mg.



(*E*)-1-(3-(4-chlorophenyl)-1-(ethylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3h)



(*S*)-**3h**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 8.6 Hz, 3H), 2.95 (q, *J* = 7.3 Hz, 2H), 2.30 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H).

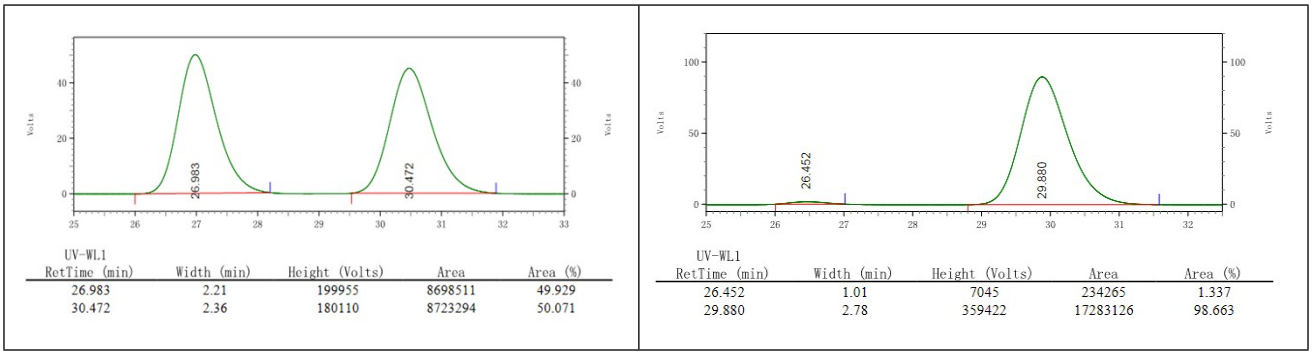
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.42, 168.32, 146.86, 145.45, 140.71, 137.82, 133.93, 132.12, 131.48, 131.13, 130.06, 128.95, 128.42, 127.46, 126.17, 125.21, 121.64, 117.39, 46.68, 21.18, 5.96.

HRMS (ESI) m/z Calcd for $[C_{23}H_{19}ClNaO_5S, M + Na]^+$: 465.0534, Found: 465.0525.

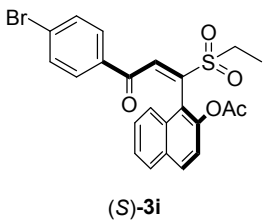
Optical Rotation: $[\alpha]_D^{25}$ = +58.5° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 26.452 min (minor), t_R = 29.880 min (major).

Physical properties: pale yellow solid; **Yield:** 85%, 37.6 mg.



(*E*)-1-(3-(4-bromophenyl)-1-(ethylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3i)



(*S*)-**3i**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.81 (t, *J* = 9.2 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.48 (d, *J* = 8.5 Hz, 3H), 7.34 (d, *J* = 9.0 Hz, 1H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 1.34 (t, *J* = 7.4 Hz, 3H).

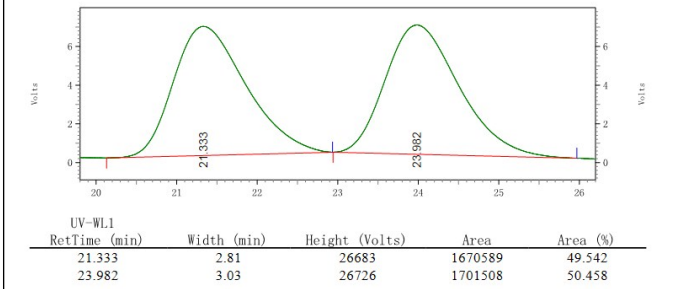
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.55, 168.26, 146.75, 145.35, 137.75, 134.21, 132.03, 131.86, 131.40, 131.02, 130.03, 129.47, 128.35, 127.39, 126.09, 125.13, 121.56, 117.29, 46.58, 21.12, 5.91.

HRMS (ESI) m/z Calcd for $[C_{23}H_{19}BrNaO_5S, M + Na]^+$: 509.0029, Found: 509.0020.

Optical Rotation: $[\alpha]_D^{25}$ = +67.2° (*c* = 1.00, $CHCl_3$).

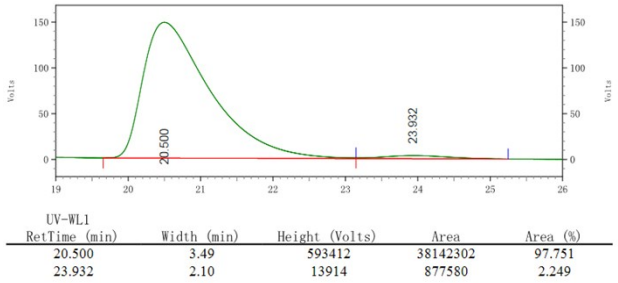
HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 20.500 min (major), t_R = 23.932 min (minor).

Physical properties: pale yellow solid; **Yield:** 95%, 46.1 mg.



UV-WL1

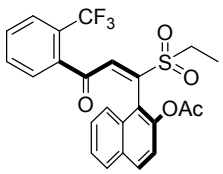
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
21.333	2.81	26683	1670589	49.542
23.982	3.03	26726	1701508	50.458



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
20.500	3.49	593412	38142302	97.751
23.932	2.10	13914	877580	2.249

(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-(2-(trifluoromethyl)phenyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3j)**



(*S*)-**3j**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.31 – 7.24 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 2.91 (q, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.31 (t, *J* = 7.4 Hz, 3H).

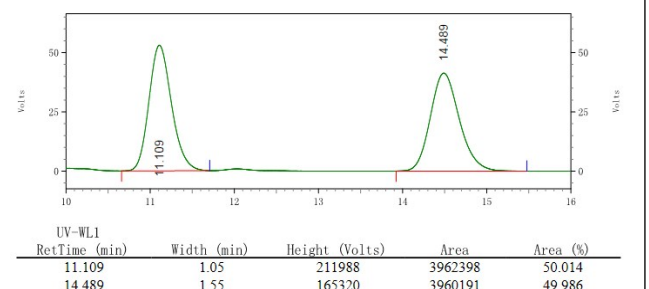
^{13}C NMR (100 MHz, $CDCl_3$): δ 192.19, 168.37, 146.83, 145.69, 138.79, 136.73, 131.82, 131.39, 131.05, 130.84, 130.68, 128.19, 127.99, 127.27 (q, *J* = 44.0 Hz), 126.72, 126.18 (q, *J* = 4.0 Hz), 126.06, 124.77, 123.19 (q, *J* = 272.0 Hz), 121.47, 116.97, 46.66, 21.01, 5.78.

HRMS (ESI) m/z Calcd for $[C_{24}H_{19}F_3NaO_5S, M + Na]^+$: 499.0798, Found: 499.0791.

Optical Rotation: $[\alpha]_D^{25}$ = +39.8° (*c* = 1.00, $CHCl_3$).

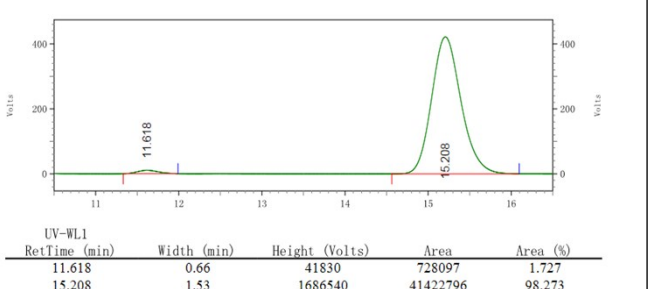
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 11.618 min (minor), t_R = 15.208 min (major).

Physical properties: pale yellow solid; **Yield:** 95%, 45.2 mg.



UV-WL1

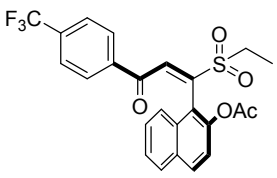
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.109	1.05	211988	3962398	50.014
14.489	1.55	165320	3960191	49.986



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.618	0.66	41830	728097	1.727
15.208	1.53	1686540	41422796	98.273

(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3k)**



(*S*)-**3k**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.88 (dd, *J* = 8.6, 5.2 Hz, 3H), 7.81 (t, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 2.97 (q, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H).

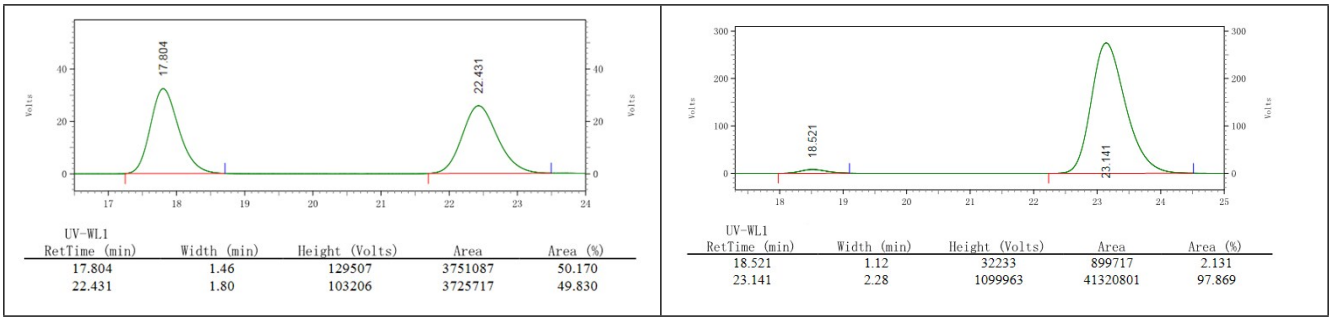
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.97, 168.34, 146.57 (q, *J* = 58.0 Hz), 138.22, 137.44, 134.97 (q, *J* = 33.0 Hz), 134.49, 132.05, 131.61, 131.09, 128.89, 128.44, 127.55, 126.22, 125.53 (q, *J* = 4.0 Hz), 125.14, 123.22 (q, *J* = 272.0 Hz), 121.61, 117.30, 46.69, 21.16, 5.94.

HRMS (ESI) m/z Calcd for[$C_{24}H_{19}F_3NaO_5S$, M + Na]$^+$: 499.0798, Found: 499.0789.

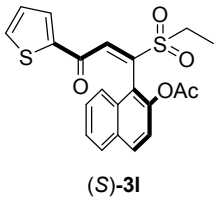
Optical Rotation: $[\alpha]_D^{25}$ = +47.4° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 18.521 min (minor), t_R = 23.141 min (major).

Physical properties: pale yellow solid; **Yield:** 98%, 46.6 mg.



(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3l)**



(*S*)-**3l**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.82 (dd, *J* = 16.2, 8.5 Hz, 3H), 7.65 (d, *J* = 3.7 Hz, 1H), 7.54 – 7.41 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.10 (s, 1H), 2.92 (q, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).

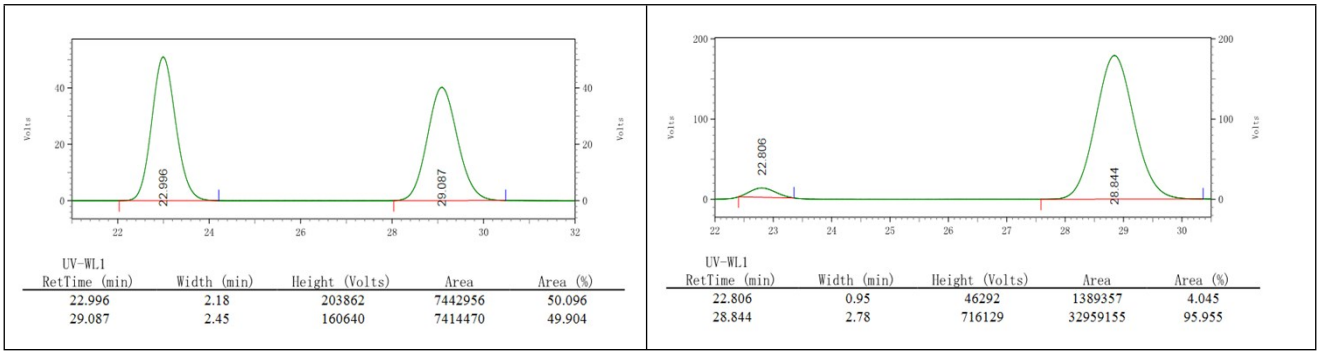
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.22, 168.39, 146.58, 146.24, 143.53, 136.01, 135.77, 133.66, 132.02, 131.22, 131.09, 128.41, 128.34, 127.37, 126.01, 124.90, 121.64, 117.70, 46.41, 21.09, 5.83.

HRMS (ESI) m/z Calcd for [$C_{21}H_{18}NaO_5S_2$, M + Na]$^+$: 437.0488, Found: 437.0479.

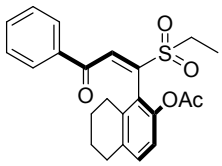
Optical Rotation: $[\alpha]_D^{25}$ = +89.0° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 22.806 min (minor), t_R = 28.844 min (major).

Physical properties: pale yellow solid; **Yield:** 68%, 28.1 mg.



(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-phenylprop-1-en-1-yl)-5,6,7,8-tetrahydronaphthalen-2-yl acetate (*S*)**-(3m)**


(*S*)-**3m**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.08 (dp, *J* = 14.5, 7.2 Hz, 2H), 2.87 (dt, *J* = 10.9, 5.6 Hz, 1H), 2.75 (t, *J* = 5.9 Hz, 2H), 2.68 – 2.57 (m, 1H), 2.13 (s, 3H), 1.73 (qt, *J* = 14.5, 6.6 Hz, 4H), 1.42 (t, *J* = 7.4 Hz, 3H).

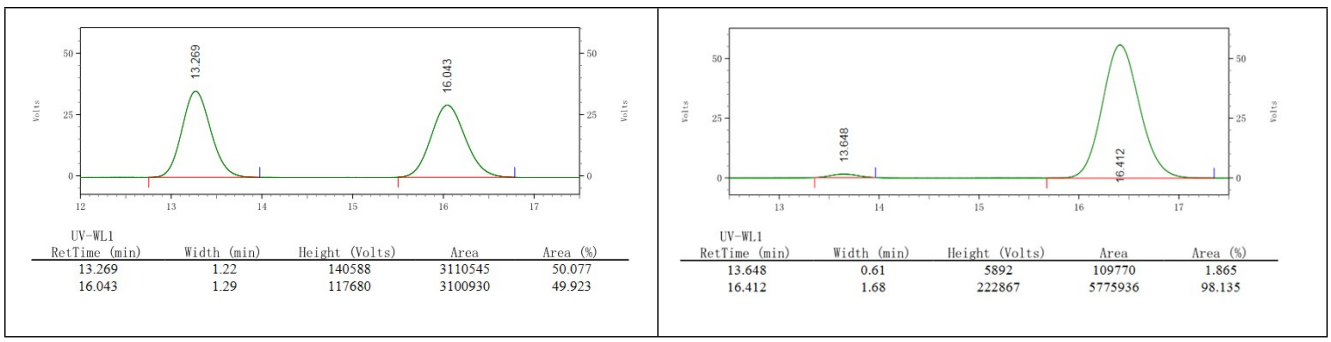
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.87, 168.08, 146.38, 145.53, 139.40, 136.90, 135.79, 135.24, 134.09, 131.35, 128.70, 128.59, 121.16, 119.60, 46.50, 29.14, 27.76, 22.27, 20.96, 6.15.

HRMS (ESI) m/z Calcd for $[C_{23}H_{24}NaO_5S, M + Na]^+$: 435.1237, Found: 435.1231.

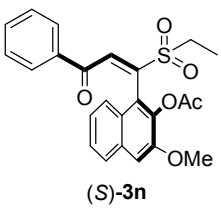
Optical Rotation: $[\alpha]_D^{25}$ = +27.5° (*c* = 0.40, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 13.648 min (minor), t_R = 16.412 min (major).

Physical properties: pale yellow solid; **Yield:** 65%, 26.8 mg.



(*E*)-1-(1-(ethylsulfonyl)-3-oxo-3-phenylprop-1-en-1-yl)-3-methoxynaphthalen-2-yl acetate (*S*)**-(3n)**


(*S*)-**3n**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 4H), 7.24 (s, 1H), 3.87 (s, 3H), 2.99 (th, *J* = 14.4, 7.4 Hz, 2H), 2.23 (s, 3H), 1.35 (t, *J* = 7.4 Hz, 3H).

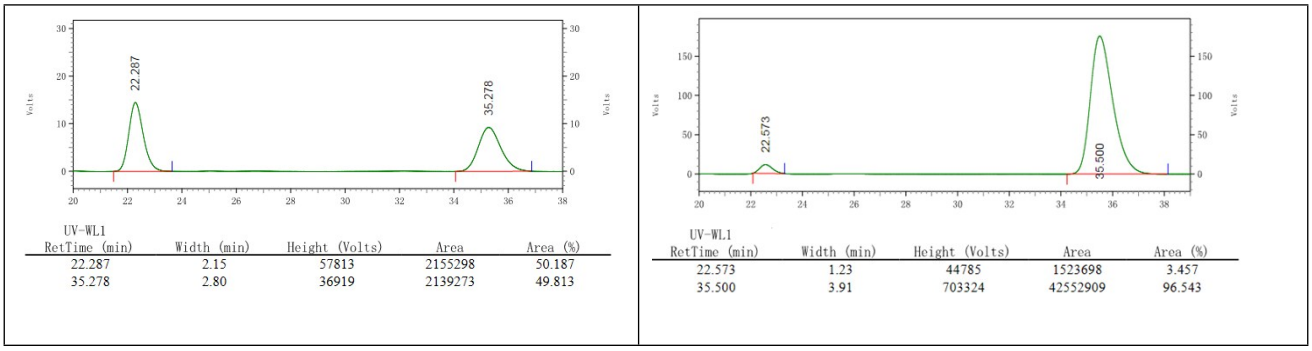
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.74, 167.32, 149.49, 145.29, 138.98, 137.82, 135.81, 133.99, 132.14, 128.66, 128.57, 127.22, 126.99, 126.56, 125.51, 124.96, 120.09, 109.59, 55.87, 46.41, 20.45, 5.95.

HRMS (ESI) m/z Calcd for $[C_{24}H_{22}NaO_6S, M + Na]^+$: 461.1029, Found: 461.1021.

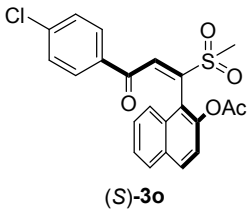
Optical Rotation: $[\alpha]_D^{25}$ = +27.6° (c = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 22.573 min (minor), t_R = 35.500 min (major).

Physical properties: pale yellow solid; **Yield:** 62%, 27.2 mg.



(*E*)-1-(3-(4-chlorophenyl)-1-(methylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3o)**



(*S*)-**3o**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.83 (dd, J = 11.8, 8.4 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.36 (dd, J = 8.8, 2.2 Hz, 3H), 2.83 (s, 3H), 2.30 (s, 3H).

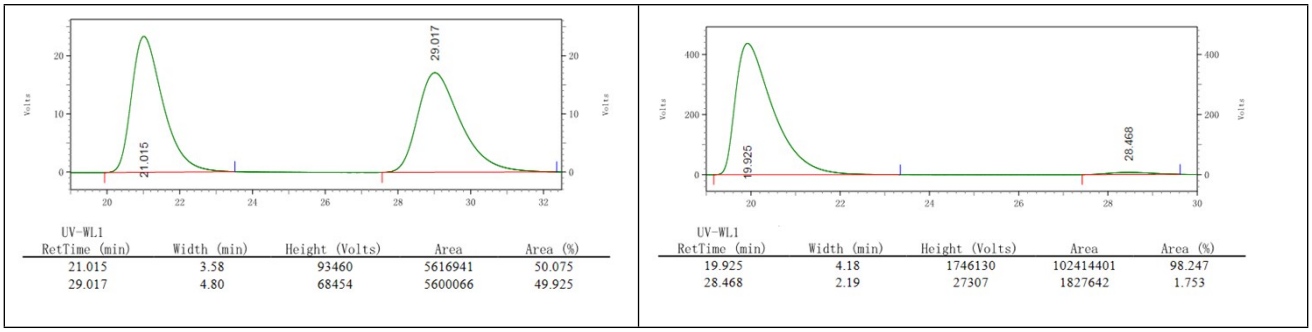
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.10, 168.47, 146.76, 146.61, 140.78, 136.19, 133.98, 131.97, 131.61, 131.19, 130.06, 129.02, 128.52, 127.69, 126.25, 125.00, 121.75, 117.46, 40.22, 21.16.

HRMS (ESI) m/z Calcd for $[C_{22}H_{17}ClNaO_5S, M + Na]^+$: 451.0377, Found: 451.0367.

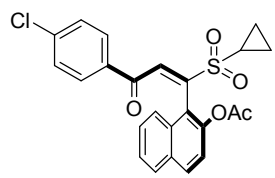
Optical Rotation: $[\alpha]_D^{25}$ = +84.2° (c = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 75:25, flow rate = 1 mL/min, wave length = 254 nm), t_R = 19.925 min (major), t_R = 28.468 min (minor).

Physical properties: pale yellow solid; **Yield:** 94%, 40.2 mg.



(*E*)-1-(3-(4-chlorophenyl)-1-(cyclopropylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3p)



(*S*)-**3p**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.87 (t, *J* = 8.1 Hz, 2H), 7.79 (dd, *J* = 11.6, 8.5 Hz, 3H), 7.48 (dt, *J* = 21.3, 7.0 Hz, 2H), 7.33 (dd, *J* = 8.7, 2.2 Hz, 3H), 2.29 (s, 3H), 2.21 (dt, *J* = 7.8, 3.2 Hz, 1H), 1.09 (dq, *J* = 11.6, 5.0 Hz, 1H), 0.99 (dt, *J* = 10.4, 5.2 Hz, 1H), 0.86 – 0.79 (m, 1H), 0.65 (dt, *J* = 14.5, 8.0 Hz, 1H).

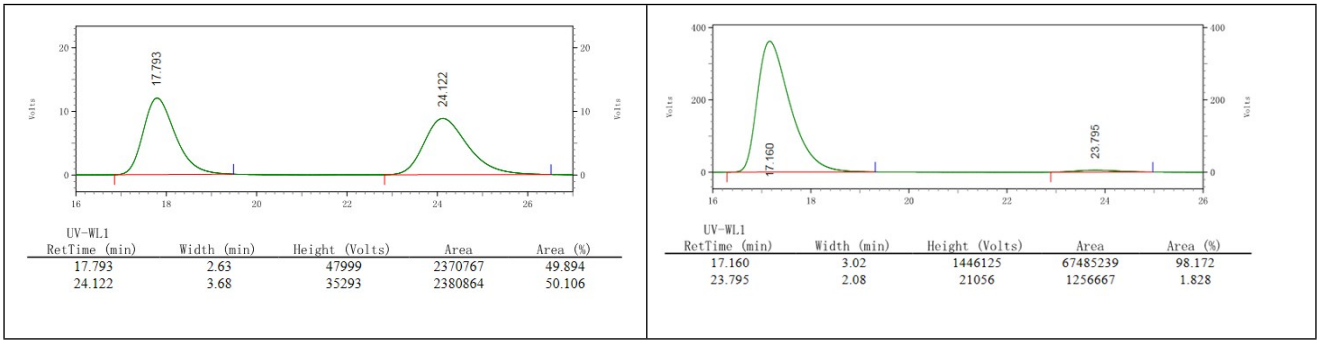
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.25, 168.52, 146.74, 146.39, 140.60, 135.72, 134.09, 132.14, 131.16, 130.96, 130.03, 128.93, 128.30, 127.16, 125.99, 125.28, 121.75, 117.91, 29.25, 21.17, 5.88.

HRMS (ESI) m/z Calcd for $[C_{24}H_{19}ClNaO_5S, M + Na]^+$: 477.0534, Found: 477.0525.

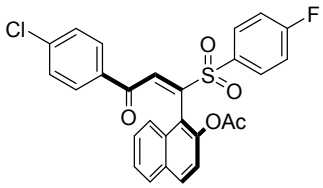
Optical Rotation: $[\alpha]_D^{25}$ = +68.6° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 75:25, flow rate = 1 mL/min, wave length = 254 nm), t_R = 17.160 min (major), t_R = 23.795 min (minor).

Physical properties: pale yellow solid; **Yield:** 99%, 45.0 mg.



(*E*)-1-(3-(4-chlorophenyl)-1-((4-fluorophenyl)sulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3q)



(*S*)-**3q**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.78 (dd, *J* = 11.3, 9.0 Hz, 3H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 3H), 7.22 (dd, *J* = 11.9, 6.4 Hz, 3H), 6.89 (t, *J* = 8.4 Hz, 2H), 2.20 (s, 3H).

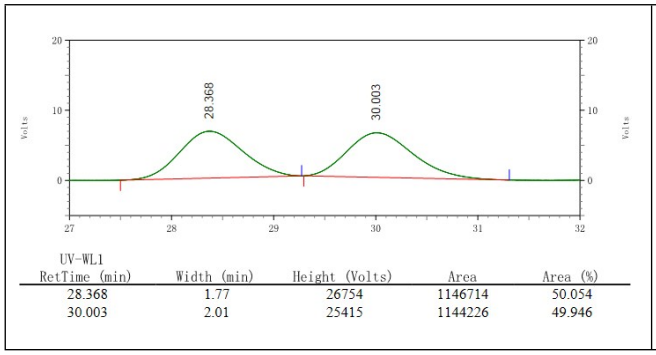
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.14, 168.26, 165.98 (d, *J* = 257.0 Hz), 147.17, 146.64, 140.60, 135.43, 134.00, 132.67 (d, *J* = 3.0 Hz), 132.16 (d, *J* = 10.0 Hz), 131.93, 131.19, 130.48, 130.00, 128.91, 127.89, 126.76, 125.67, 124.62, 121.43, 117.01, 116.06 (d, *J* = 22.0 Hz), 21.01.

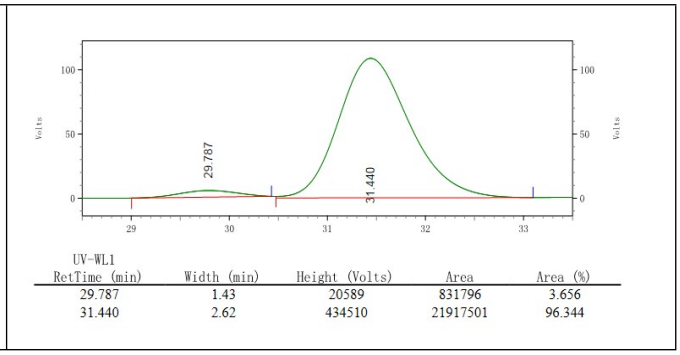
HRMS (ESI) m/z Calcd for $[C_{27}H_{18}ClFNaO_5S, M + Na]^+$: 531.0440, Found: 531.0432.

Optical Rotation: $[\alpha]_D^{25}$ = +31.8° (*c* = 1.00, $CHCl_3$).

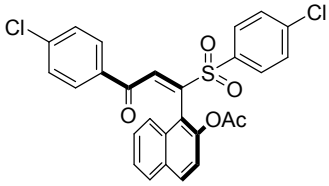
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1 mL/min, wave length = 254 nm), t_R = 29.787 min (minor), t_R = 31.440 min (major).

Physical properties: pale yellow solid; **Yield:** 44%, 22.2 mg.





(*E*)-1-(3-(4-chlorophenyl)-1-((4-chlorophenyl)sulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3r)


(*S*)-**3r**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 3H), 7.27 – 7.17 (m, 5H), 2.18 (s, 3H).

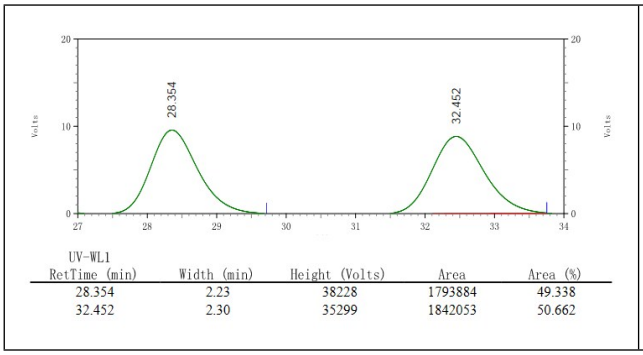
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.12, 168.20, 147.04, 146.67, 140.90, 140.64, 135.79, 135.25, 133.97, 131.94, 131.25, 130.67, 130.51, 130.00, 129.04, 128.92, 127.92, 126.82, 125.70, 124.67, 121.39, 116.90, 21.00.

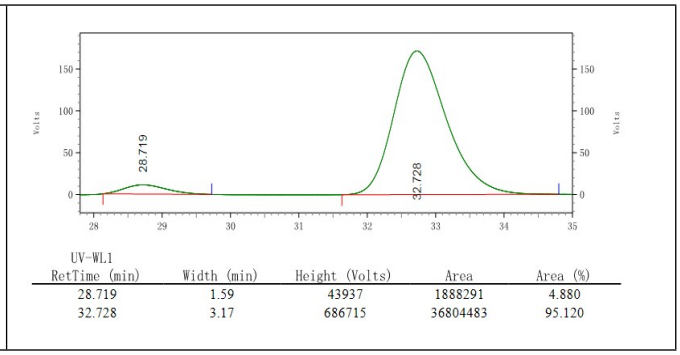
HRMS (ESI) m/z Calcd for $[C_{27}H_{18}Cl_2NaO_5S, M + Na]^+$: 547.0144, Found: 547.0135.

Optical Rotation: $[\alpha]_D^{25}$ = +34.0° (*c* = 1.00, $CHCl_3$).

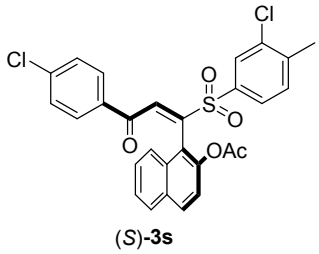
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1 mL/min, wave length = 254 nm), t_R = 28.719 min (minor), t_R = 32.728 min (major).

Physical properties: pale yellow solid; **Yield:** 45%, 23.6 mg.





(*E*)-1-(1-((3-chloro-4-methylphenyl)sulfonyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3s)


(*S*)-**3s**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.78 (t, *J* = 9.1 Hz, 3H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 1.5 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.9 Hz, 4H), 7.26 – 7.18 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 2.28 (s, 3H), 2.16 (s, 3H).

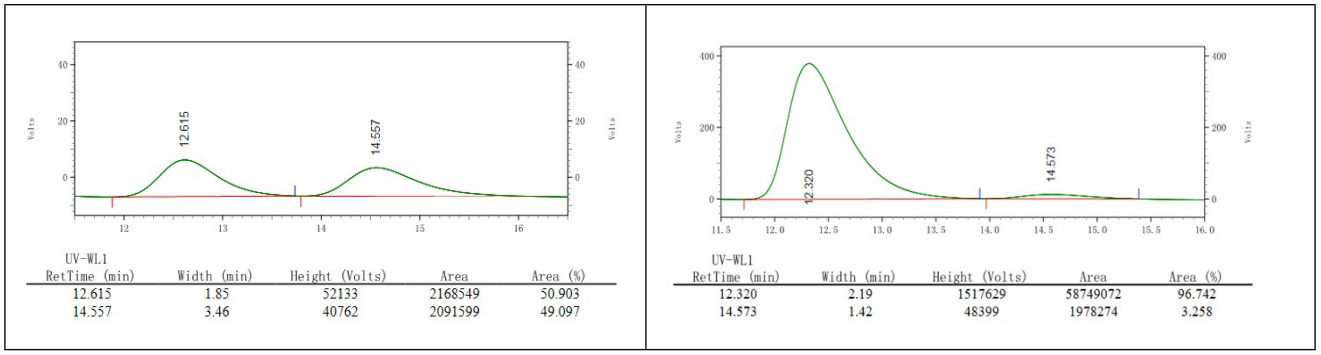
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.04, 168.03, 147.18, 146.58, 143.10, 140.55, 135.57, 135.50, 134.98, 133.99, 131.96, 131.16, 130.98, 130.50, 129.97, 129.48, 128.88, 127.83, 127.41, 126.59, 125.57, 124.84, 121.22, 116.91, 20.93, 20.16.

HRMS (ESI) m/z Calcd for $[C_{28}H_{20}Cl_2NaO_5S, M + Na]^+$: 561.0301, Found: 561.0298.

Optical Rotation: $[\alpha]_D^{25}$ = +36.1° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 75:25, flow rate = 1 mL/min, wave length = 254 nm), t_R = 12.320 min (major), t_R = 14.573 min (minor).

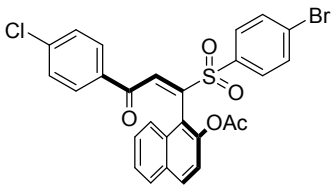
Physical properties: pale yellow solid; **Yield:** 89%, 47.8 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
12.615	1.85	52133	2168549	50.903
14.557	3.46	40762	2091599	49.097

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
12.320	2.19	1517629	58749072	96.742
14.573	1.42	48399	1978274	3.258

(*E*)-1-(1-((4-bromophenyl)sulfonyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3t)**



(*S*)-**3t**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 2.3 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 3H), 7.26 – 7.20 (m, 3H), 2.17 (s, 3H).

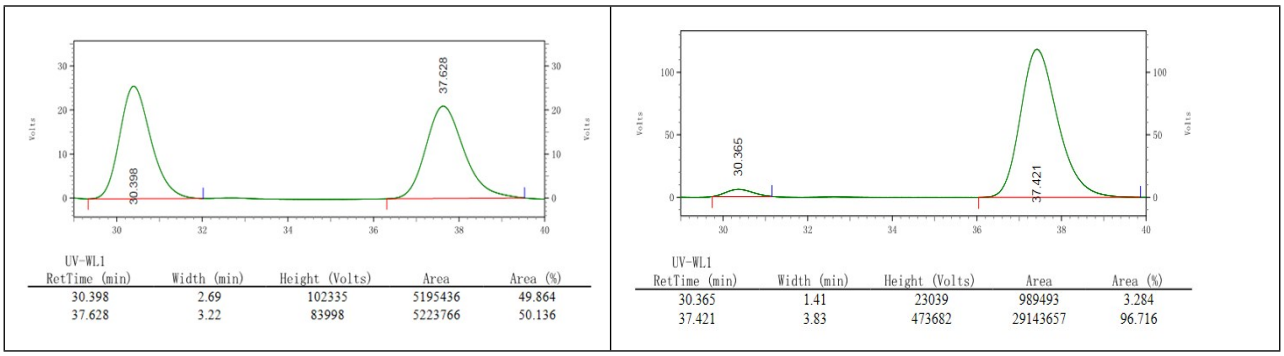
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.09, 168.16, 146.97, 146.64, 140.62, 135.84, 135.77, 133.93, 132.04, 131.92, 131.24, 130.68, 130.48, 129.99, 129.55, 128.90, 127.90, 126.82, 125.68, 124.64, 121.36, 116.84, 20.98.

HRMS (ESI) m/z Calcd for $[C_{27}H_{18}BrClNaO_5S, M + Na]^+$: 590.9639, Found: 590.9633.

Optical Rotation: $[\alpha]_D^{25}$ = +43.8° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1 mL/min, wave length = 254 nm), t_R = 30.365 min (minor), t_R = 37.421 min (major).

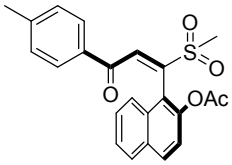
Physical properties: pale yellow solid; **Yield:** 79%, 44.8 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
30.398	2.69	102335	5195436	49.864
37.628	3.22	83998	5223766	50.136

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
30.365	1.41	23039	989493	3.284
37.421	3.83	473682	29143657	96.716

(*E*)-1-(1-(methylsulfonyl)-3-oxo-3-(p-tolyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3u)



(*S*)-**3u**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.83 (t, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.81 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H).

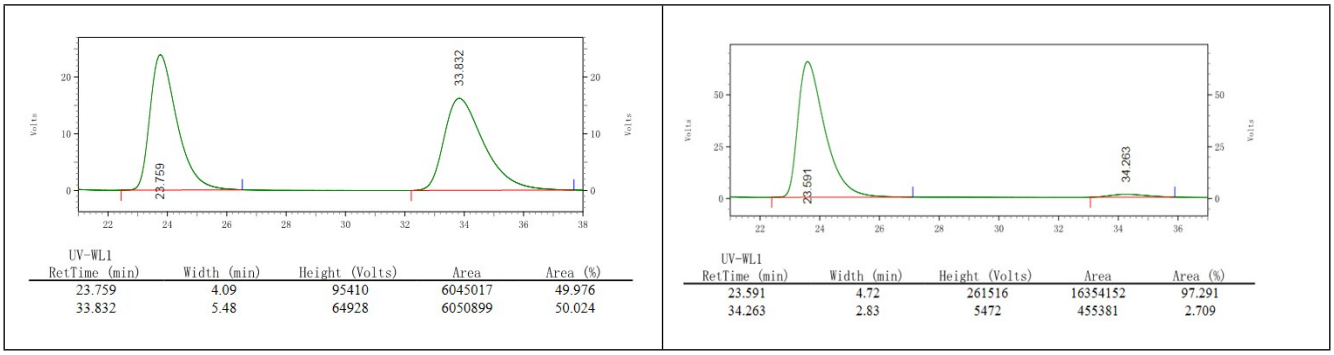
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.56, 168.45, 146.73, 145.64, 145.35, 136.98, 133.23, 132.06, 131.34, 131.15, 129.34, 128.86, 128.38, 127.49, 126.08, 125.14, 121.69, 117.64, 40.20, 21.72, 21.12.

HRMS (ESI) m/z Calcd for $[C_{23}H_{20}NaO_5S, M + Na]^+$: 431.0924, Found: 431.0917.

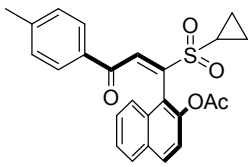
Optical Rotation: $[\alpha]_D^{25}$ = +47.7° (*c* = 0.45, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 23.591 min (major), t_R = 34.263 min (minor).

Physical properties: pale yellow solid; **Yield:** 77%, 31.4 mg.



(*E*)-1-(1-(cyclopropylsulfonyl)-3-oxo-3-(p-tolyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3v)



(*S*)-**3v**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.77 (t, *J* = 9.1 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 3H), 2.21 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.08 (dq, *J* = 11.7, 5.7 Hz, 1H), 0.97 (dq, *J* = 10.3, 5.1 Hz, 1H), 0.81 (dt, *J* = 14.1, 8.0 Hz, 1H), 0.63 (dt, *J* = 14.3, 7.9 Hz, 1H).

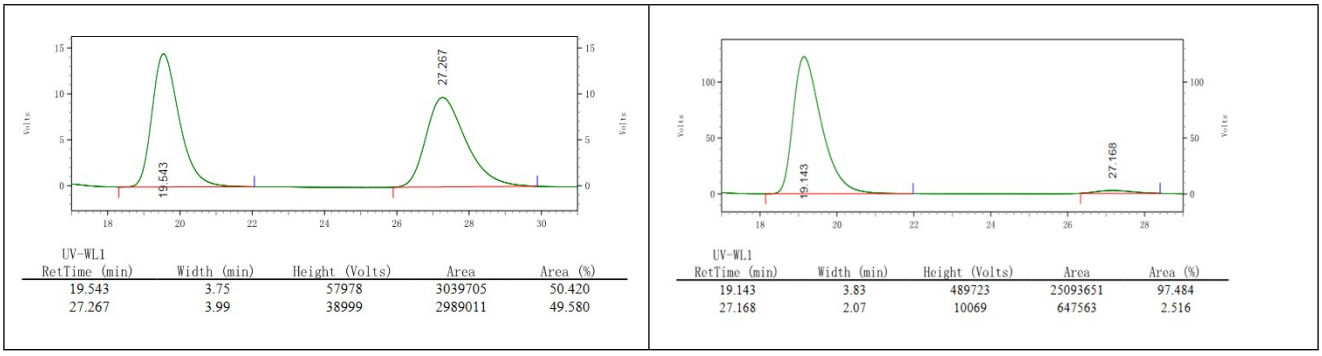
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.75, 168.50, 146.71, 145.42, 145.17, 136.46, 133.31, 132.22, 130.89, 129.26, 128.80, 128.15, 126.96, 125.83, 125.41, 121.67, 118.08, 29.22, 21.65, 21.12, 5.78, 5.68.

HRMS (ESI) m/z Calcd for $[C_{25}H_{22}NaO_5S, M + Na]^+$: 457.1080, Found: 457.1072.

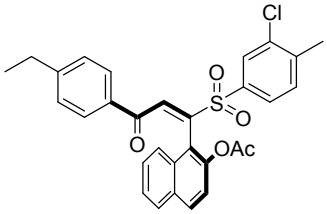
Optical Rotation: $[\alpha]_D^{25}$ = +50.0° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 19.143 min (major), t_R = 27.168 min (minor).

Physical properties: pale yellow solid; **Yield:** 85%, 36.9 mg.



(*E*)-1-(1-((3-chloro-4-methylphenyl)sulfonyl)-3-(4-ethylphenyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3w)



(*S*)-**3w**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.49 (s, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.04 (m, 5H), 6.93 (d, *J* = 8.0 Hz, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 2.06 (s, 3H), 1.10 (t, *J* = 7.6 Hz, 3H).

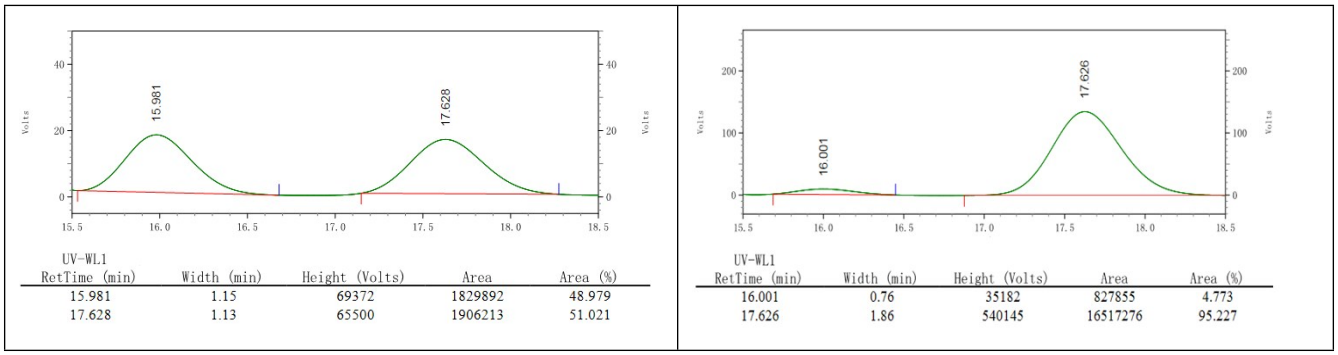
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.56, 168.08, 151.30, 146.60, 146.37, 142.95, 136.31, 135.71, 134.94, 133.51, 132.09, 130.95, 130.51, 129.48, 128.90, 128.09, 127.75, 127.40, 126.45, 125.47, 125.01, 121.21, 117.12, 28.90, 20.95, 20.15, 14.92.

HRMS (ESI) m/z Calcd for $[C_{30}H_{25}ClNaO_5S, M + Na]^+$: 555.1003, Found: 555.1009.

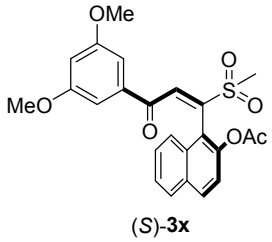
Optical Rotation: $[\alpha]_D^{25}$ = +23.6° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 16.001 min (minor), t_R = 17.626 min (major).

Physical properties: pale yellow solid; **Yield:** 93%, 49.5 mg.



(*E*)-1-(3-(3,5-dimethoxyphenyl)-1-(methylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(3x)



(*S*)-**3x**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 2H), 6.59 (t, *J* = 2.0 Hz, 1H), 3.72 (s, 6H), 2.82 (s, 3H), 2.29 (s, 3H).

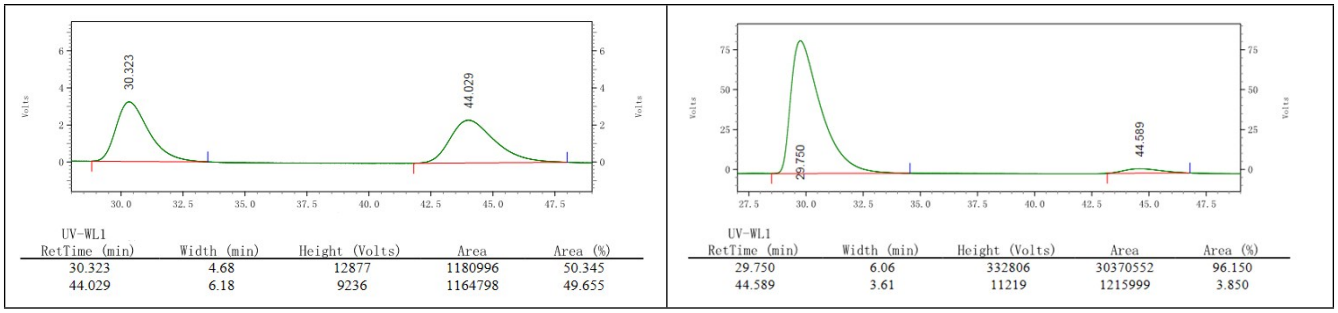
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.78, 168.41, 160.74, 146.68, 145.98, 137.40, 136.75, 132.01, 131.33, 131.07, 128.31, 127.47, 126.05, 125.13, 121.61, 117.51, 106.42, 106.27, 55.45, 40.16, 21.03.

HRMS (ESI) m/z Calcd for $[C_{24}H_{22}NaO_7S, M + Na]^+$: 477.0978, Found: 477.0971.

Optical Rotation: $[\alpha]_D^{25}$ = +71.7° (c = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 29.750 min (major), t_R = 44.589 min (minor).

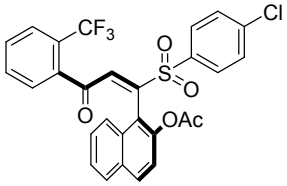
Physical properties: pale yellow solid; **Yield:** 75%, 34.0 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
30.323	4.68	12877	1180996	50.345
44.029	6.18	9236	1164798	49.655

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
29.750	6.06	332806	30370552	96.150
44.589	3.61	11219	1215999	3.850

(*E*)-1-(1-((4-chlorophenyl)sulfonyl)-3-oxo-3-(2-(trifluoromethyl)phenyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3y)**



(*S*)-**3y**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.44 (t, J = 8.0 Hz, 3H), 7.27 (dd, J = 17.1, 7.9 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.11 (t, J = 7.9 Hz, 2H), 6.90 (d, J = 7.4 Hz, 1H), 2.18 (s, 3H).

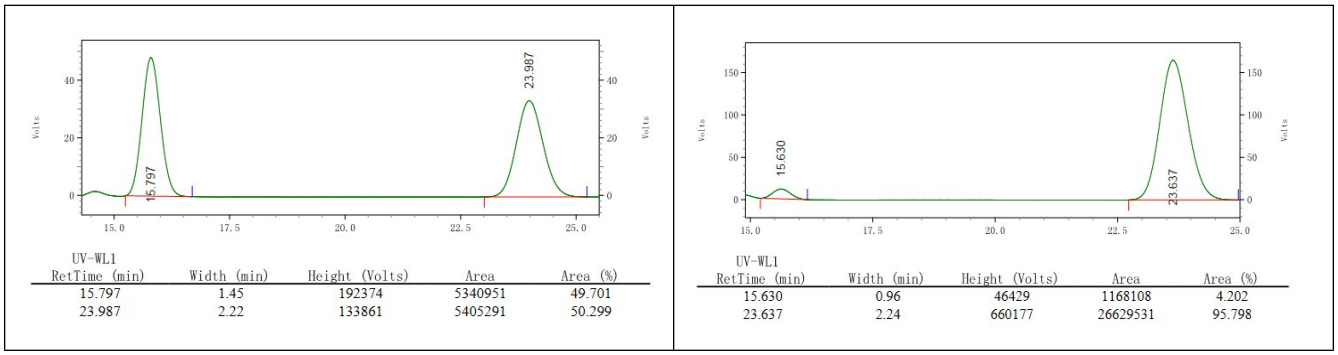
^{13}C NMR (100 MHz, $CDCl_3$): δ 192.13, 168.20, 147.42, 146.67, 140.96, 137.10, 136.77, 135.24, 131.75, 131.23, 131.01, 130.70, 130.62, 130.31, 129.09, 127.90, 127.75, 126.88, 126.84 (q, J = 33.0 Hz), 126.14 (q, J = 5.0 Hz), 125.67, 124.35, 123.18 (q, J = 273.0 Hz), 121.28, 116.46, 20.86.

HRMS (ESI) m/z Calcd for $[C_{28}H_{18}ClF_3NaO_5S, M + Na]^+$: 581.0408, Found: 581.0412.

Optical Rotation: $[\alpha]_D^{25}$ = +20.2° (c = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 85:15, flow rate = 1 mL/min, wave length = 254 nm), t_R = 15.630 min (minor), t_R = 23.637 min (major).

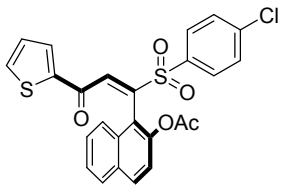
Physical properties: pale yellow solid; **Yield:** 61%, 34.0 mg.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
15.797	1.45	192374	5340951	49.701
23.987	2.22	133861	5405291	50.299

UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
15.630	0.96	46429	1168108	4.202
23.637	2.24	660177	26629531	95.798

(*E*)-1-(1-((4-chlorophenyl)sulfonyl)-3-oxo-3-(thiophen-2-yl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3z)**



(*S*)-**3z**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.89 (d, *J* = 3.4 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 4.6 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.16 – 7.11 (m, 1H), 2.18 (s, 3H).

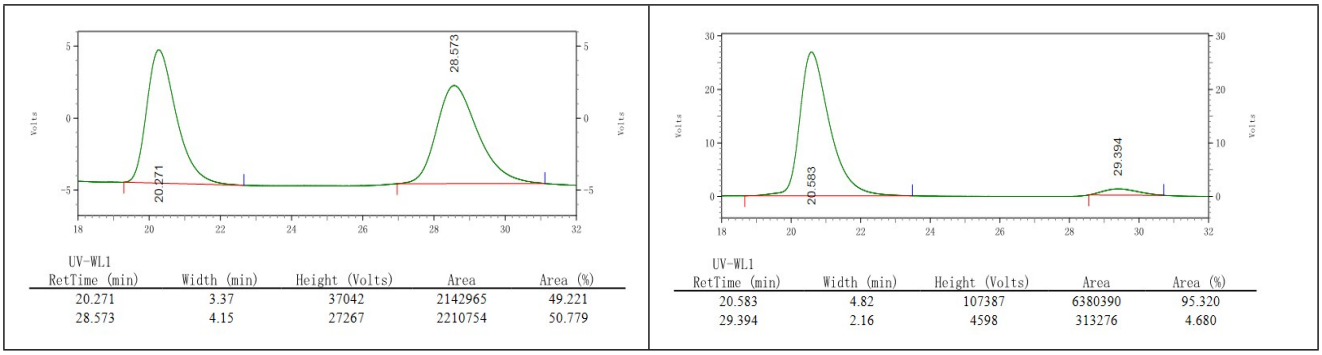
^{13}C NMR (100 MHz, $CDCl_3$): δ 180.03, 168.36, 147.99, 146.51, 143.77, 140.94, 136.00, 135.11, 133.78, 133.63, 131.94, 131.08, 130.76, 130.57, 129.02, 128.39, 127.98, 126.78, 125.62, 124.45, 121.50, 117.32, 21.04.

HRMS (ESI) m/z Calcd for $[C_{25}H_{17}ClNaO_5S_2, M + Na]^+$: 519.0098, Found: 519.0091.

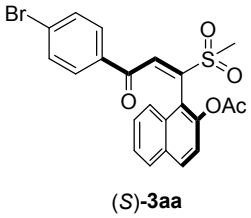
Optical Rotation: $[\alpha]_D^{25}$ = +60.0° (*c* = 0.55, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 20.583 min (major), t_R = 29.394 min (minor).

Physical properties: pale yellow solid; **Yield:** 58%, 28.8 mg.



(*E*)-1-(3-(4-bromophenyl)-1-(methylsulfonyl)-3-oxoprop-1-en-1-yl)naphthalen-2-yl acetate (*S*)**-(3aa)**



(*S*)-**3aa**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.52 (q, *J* = 6.9, 6.3 Hz, 4H), 7.35 (d, *J* = 9.0 Hz, 1H), 2.82 (s, 3H), 2.30 (s, 3H).

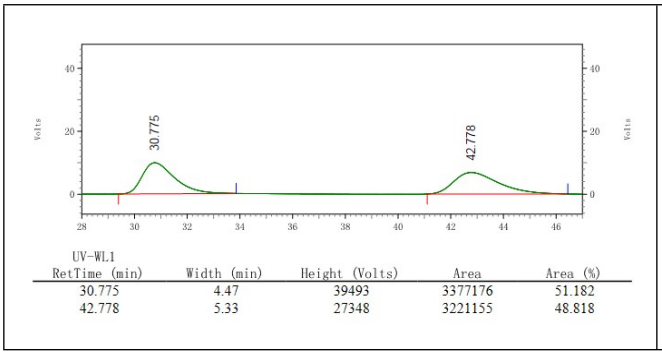
^{13}C NMR (100 MHz, $CDCl_3$): δ 188.29, 168.44, 146.74, 146.66, 136.11, 134.36, 131.98, 131.95, 131.59, 131.17, 130.08, 129.60, 128.50, 127.68, 126.23, 124.98, 121.73, 117.44, 40.20, 21.14.

HRMS (ESI) m/z Calcd for $[C_{22}H_{17}BrNaO_5S, M + Na]^+$: 494.9872, Found: 494.9868.

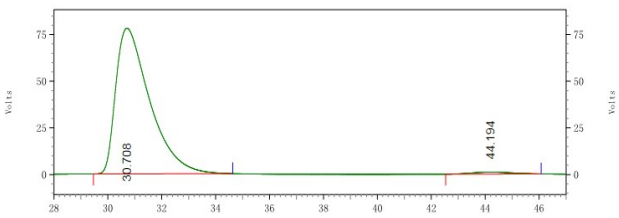
Optical Rotation: $[\alpha]_D^{25}$ = +75.7° (*c* = 1.00, $CHCl_3$).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 30.708 min (major), t_R = 44.194 min (minor).

Physical properties: pale yellow solid; **Yield:** 92%, 43.4 mg.

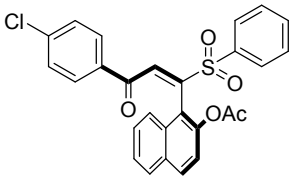


UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
30.775	4.47	39493	3377176	51.182
42.778	5.33	27348	3221155	48.818



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
30.708	5.17	312289	27368054	98.438
44.194	3.54	4119	434344	1.562

(*E*)-1-(3-(4-chlorophenyl)-3-oxo-1-(phenylsulfonyl)prop-1-en-1-yl)naphthalen-2-yl acetate (*S*)-(**3ab**)

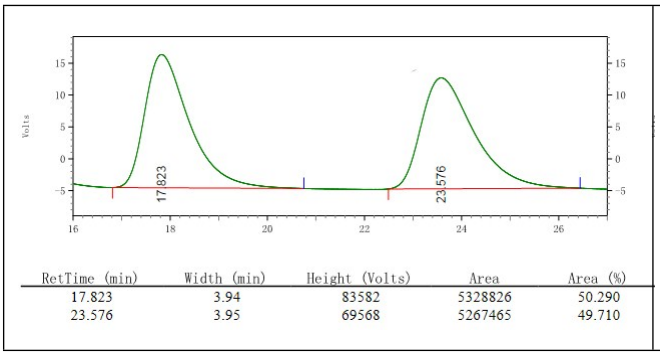


(*S*)-**3ab**

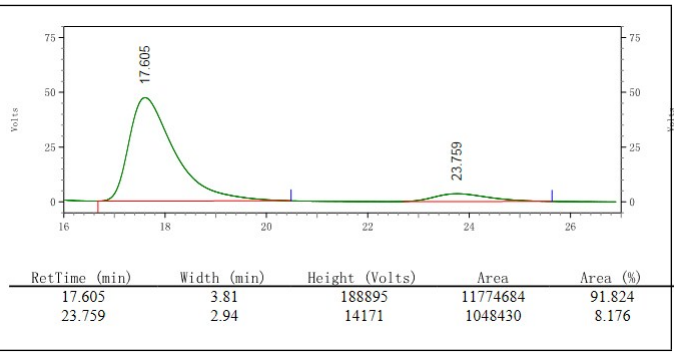
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.23 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 188.30, 168.23, 147.58, 146.70, 140.61, 136.95, 135.58, 134.16, 133.98, 132.15, 131.13, 130.56, 130.03, 129.31, 128.94, 128.85, 127.83, 126.72, 125.62, 124.88, 121.35, 117.22, 21.07.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wave length = 254 nm), t_R = 17.605 min (major), t_R = 23.759 min (minor).

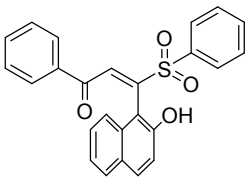


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
17.823	3.94	83582	5328826	50.290
23.576	3.95	69568	5267465	49.710



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
17.605	3.81	188895	11774684	91.824
23.759	2.94	14171	1048430	8.176

(*E*)-3-(2-hydroxynaphthalen-1-yl)-1-phenyl-3-(phenylsulfonyl)prop-2-en-1-one (3ac)

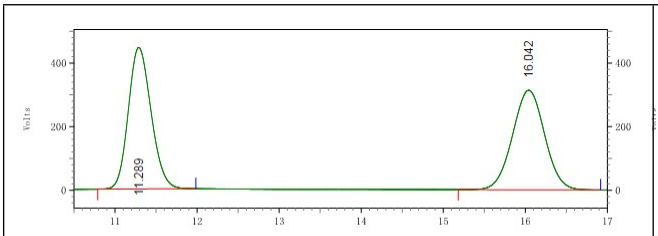


3ac

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 3H), 7.23 (t, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 191.14, 153.04, 146.12, 137.78, 135.91, 135.19, 134.23, 134.20, 132.56, 132.32, 129.03, 128.86, 128.71, 128.51, 128.38, 127.64, 126.67, 123.62, 123.47, 119.18, 110.22.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 75:25, flow rate = 1 mL/min, wave length = 254 nm).



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
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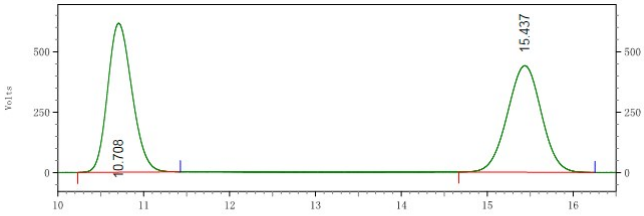
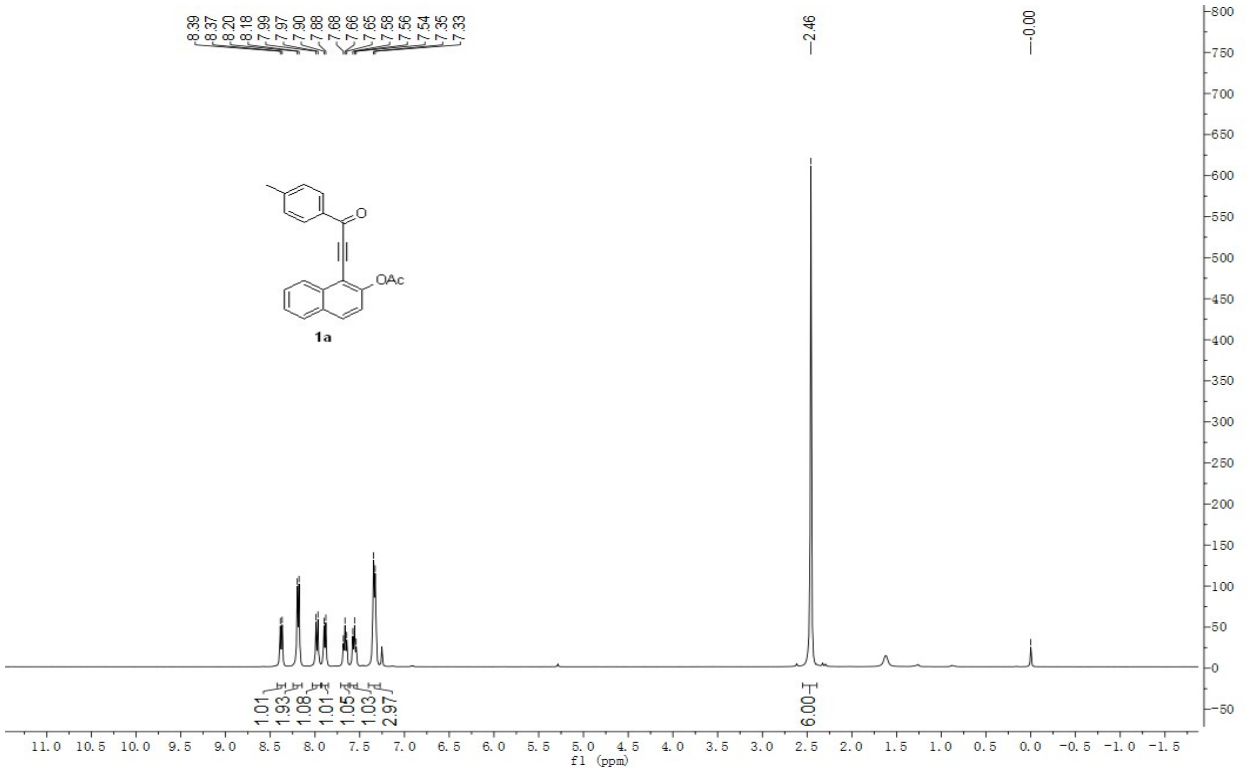
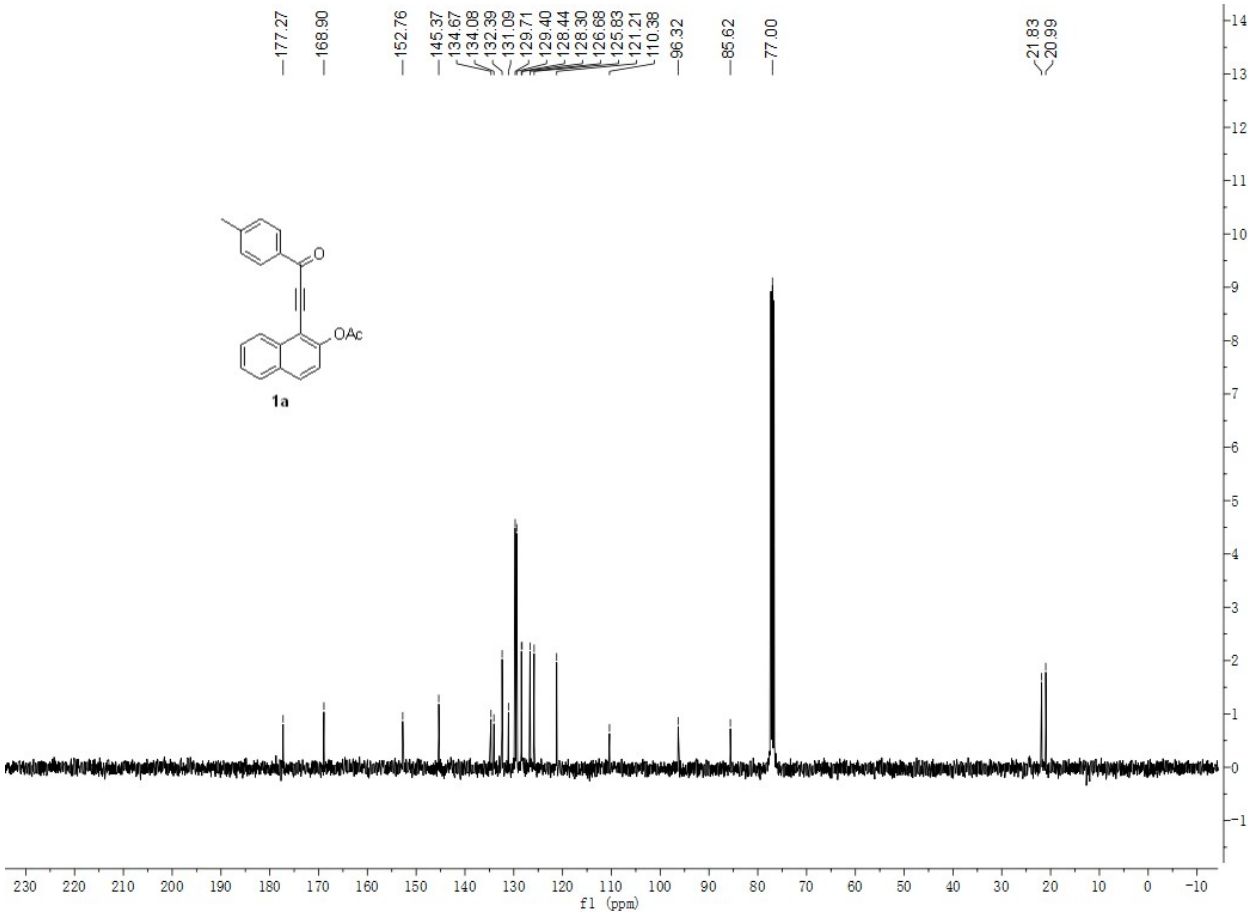
16.042	1.74	1252080	34077586	49.821

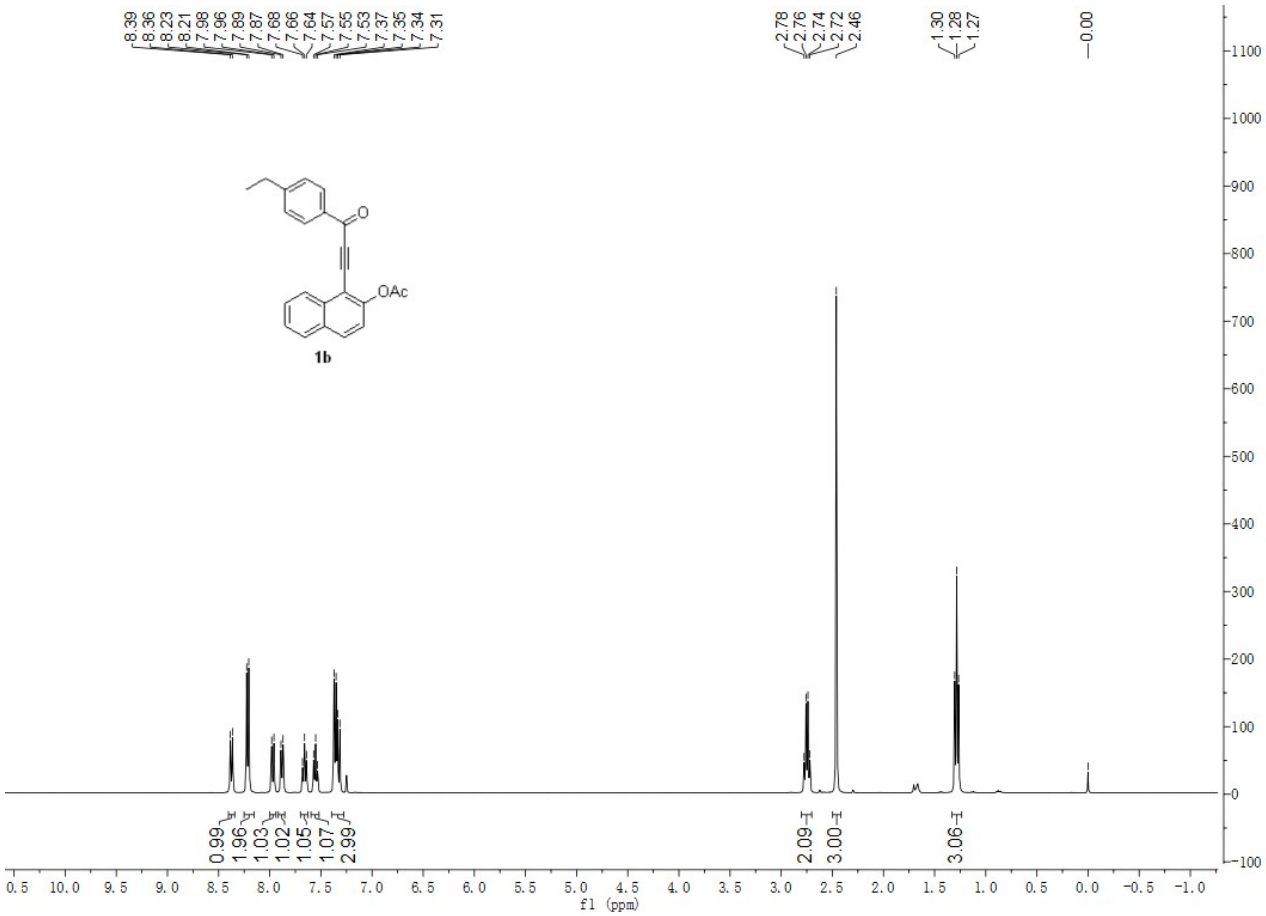


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.708	1.20	2461021	48452367	50.024
15.437	1.59	1760523	48404959	49.976

VIII. ^{1}H and ^{13}C NMR spectra 1a-1p, (*S*)-3a-3aa, (*S*)-3ab, 3ac, 4, 5, 6



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7.37
7.35
7.34
7.31
2.78
2.76
2.74
2.72
2.46
1.30
1.28
1.27
0.00
O
OAc
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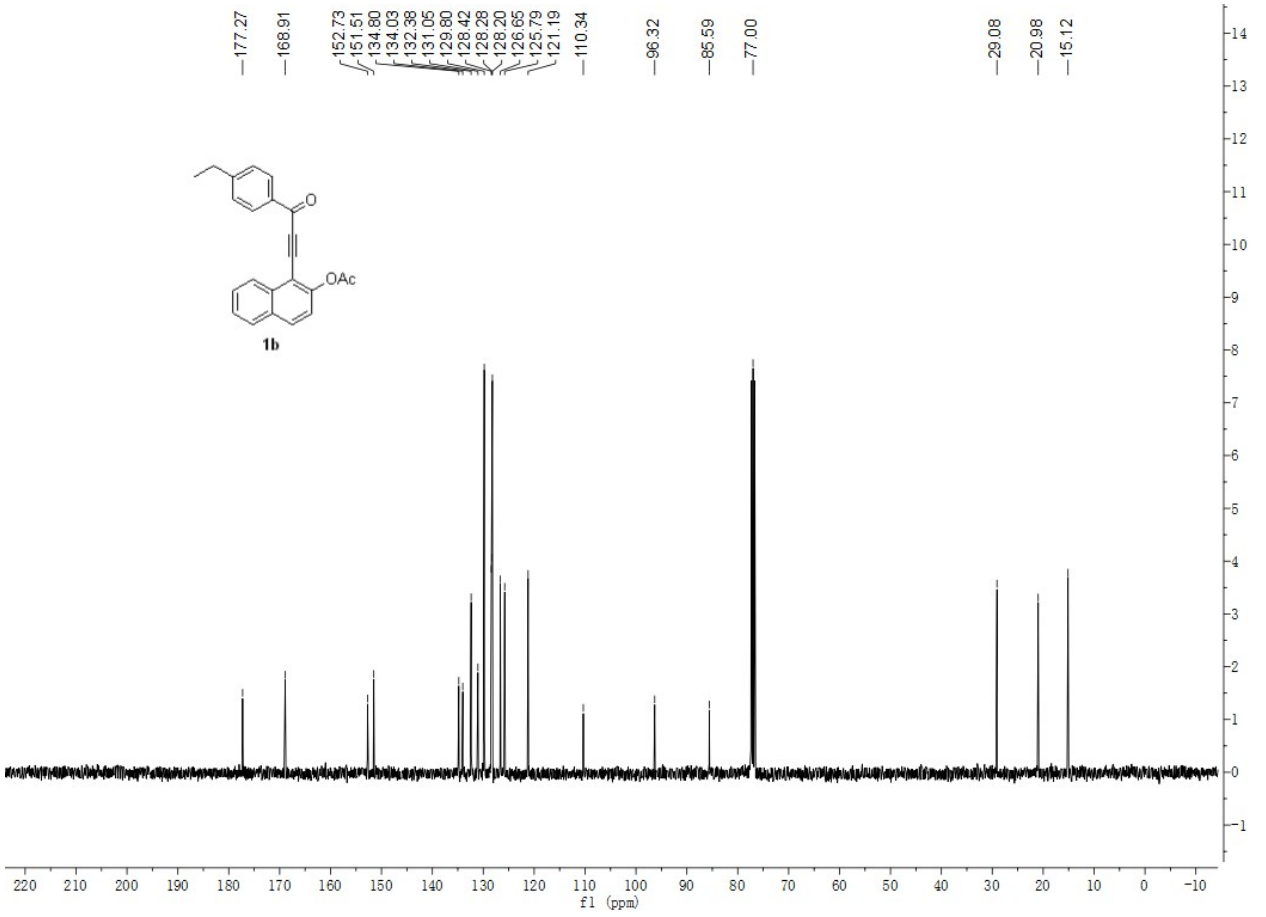
1.02
1.05
1.07
2.99
2.09
3.00
3.06
f1 (ppm)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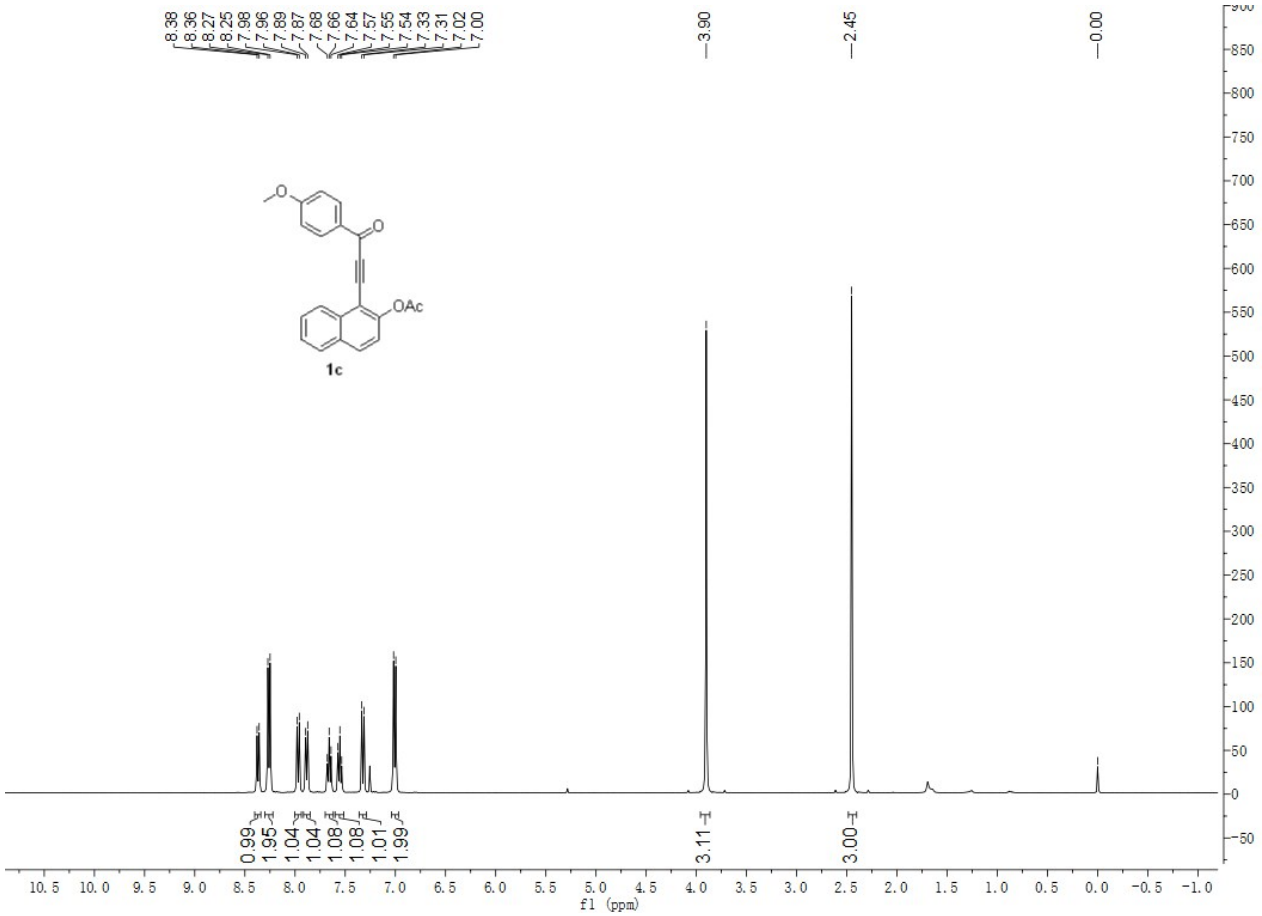
15.12
O
OAc
1b
f1 (ppm)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7.55
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7.33
7.31
7.02
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O
OAc
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1.08
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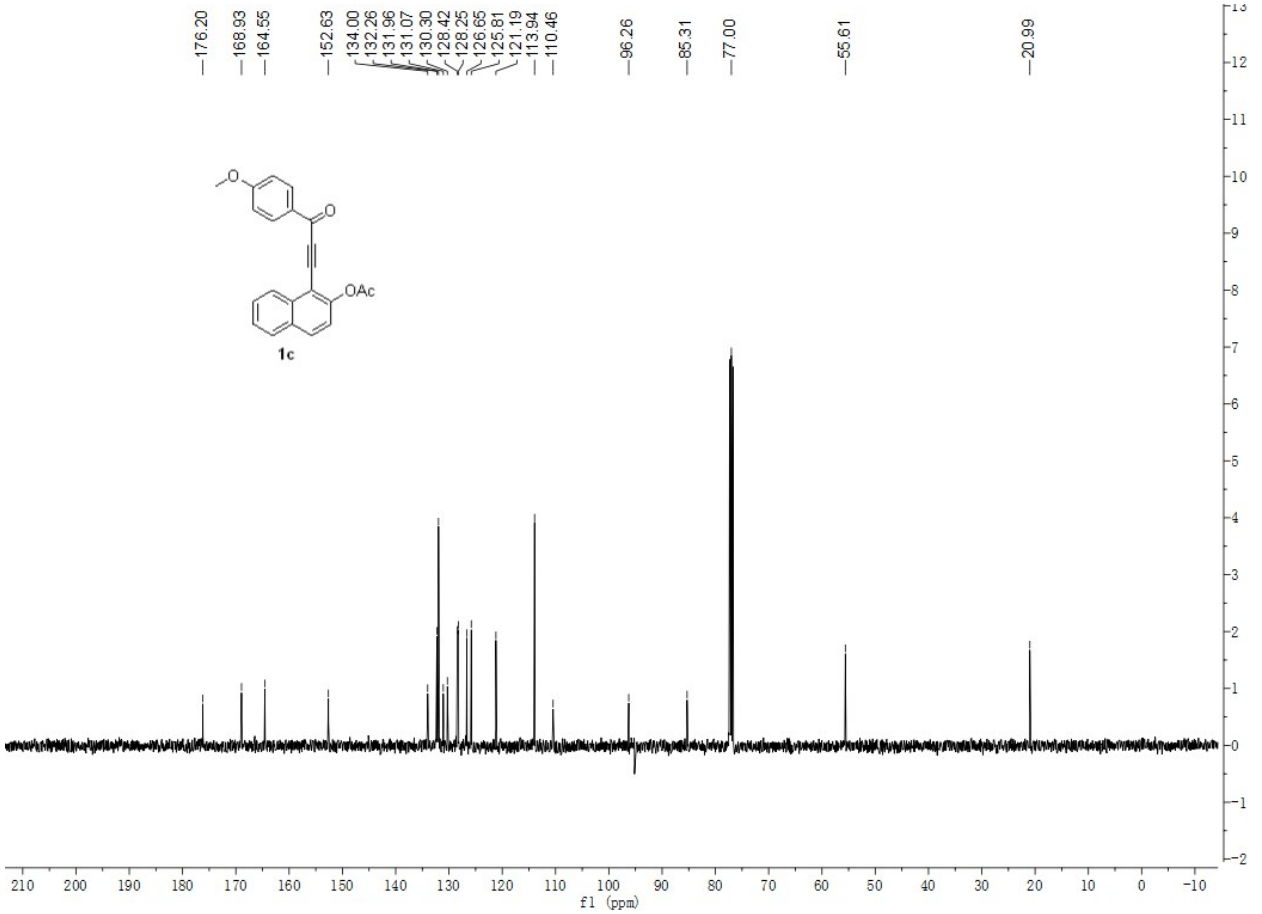
3.00
f1 (ppm)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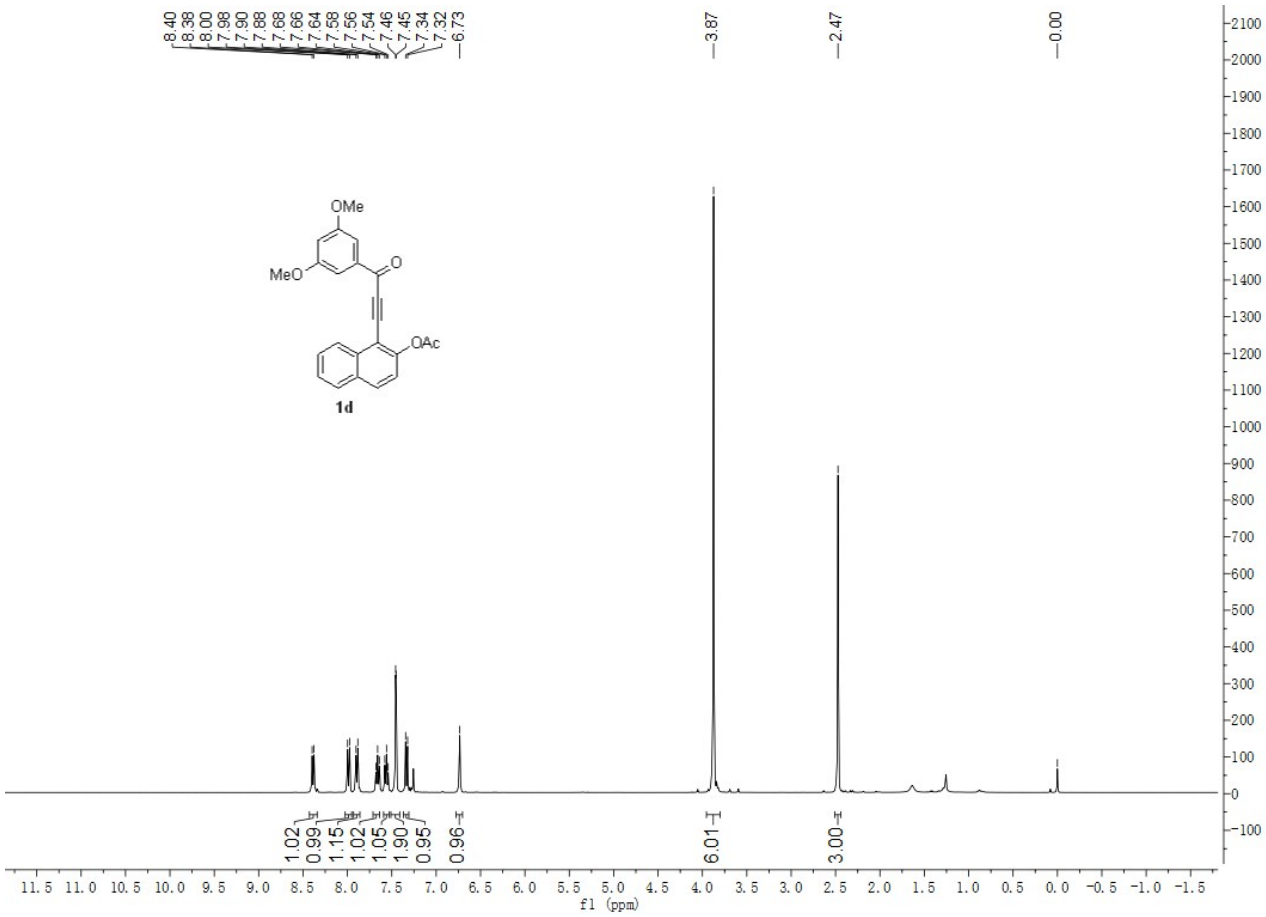
1c
f1 (ppm)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7.34
7.32
6.73
3.87
2.47
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MeO
O
OAc
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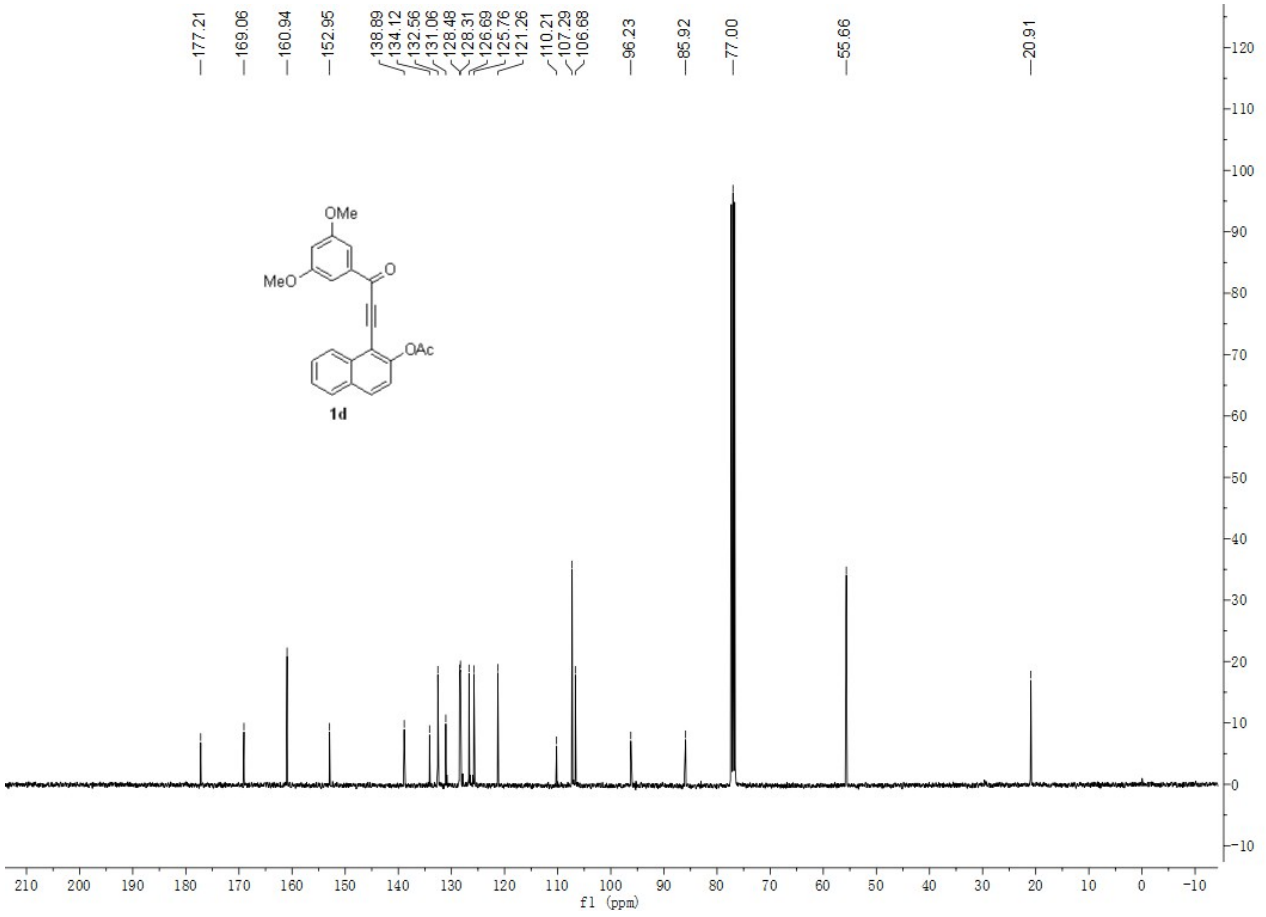
0.96
6.01
3.00
f1 (ppm)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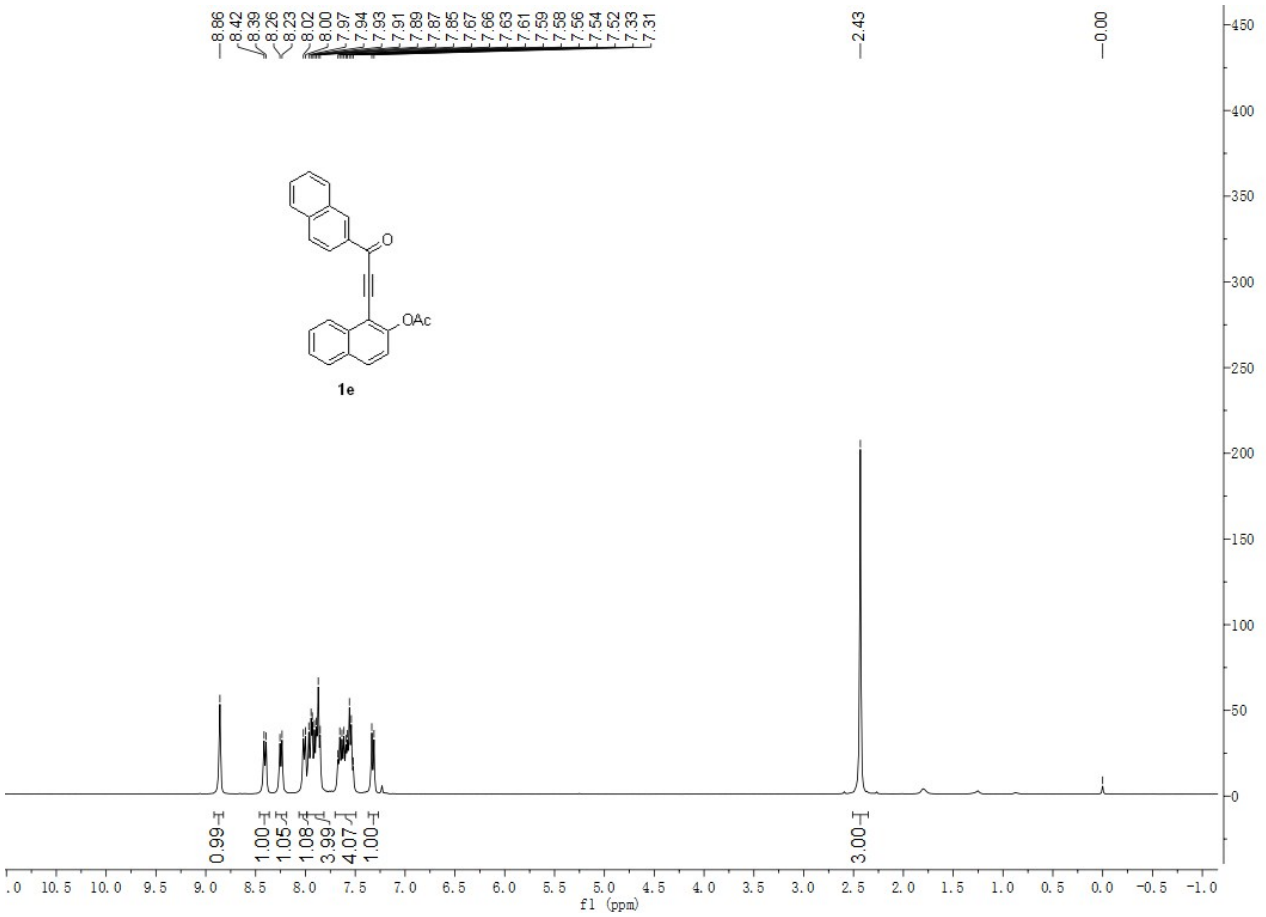
1d
f1 (ppm)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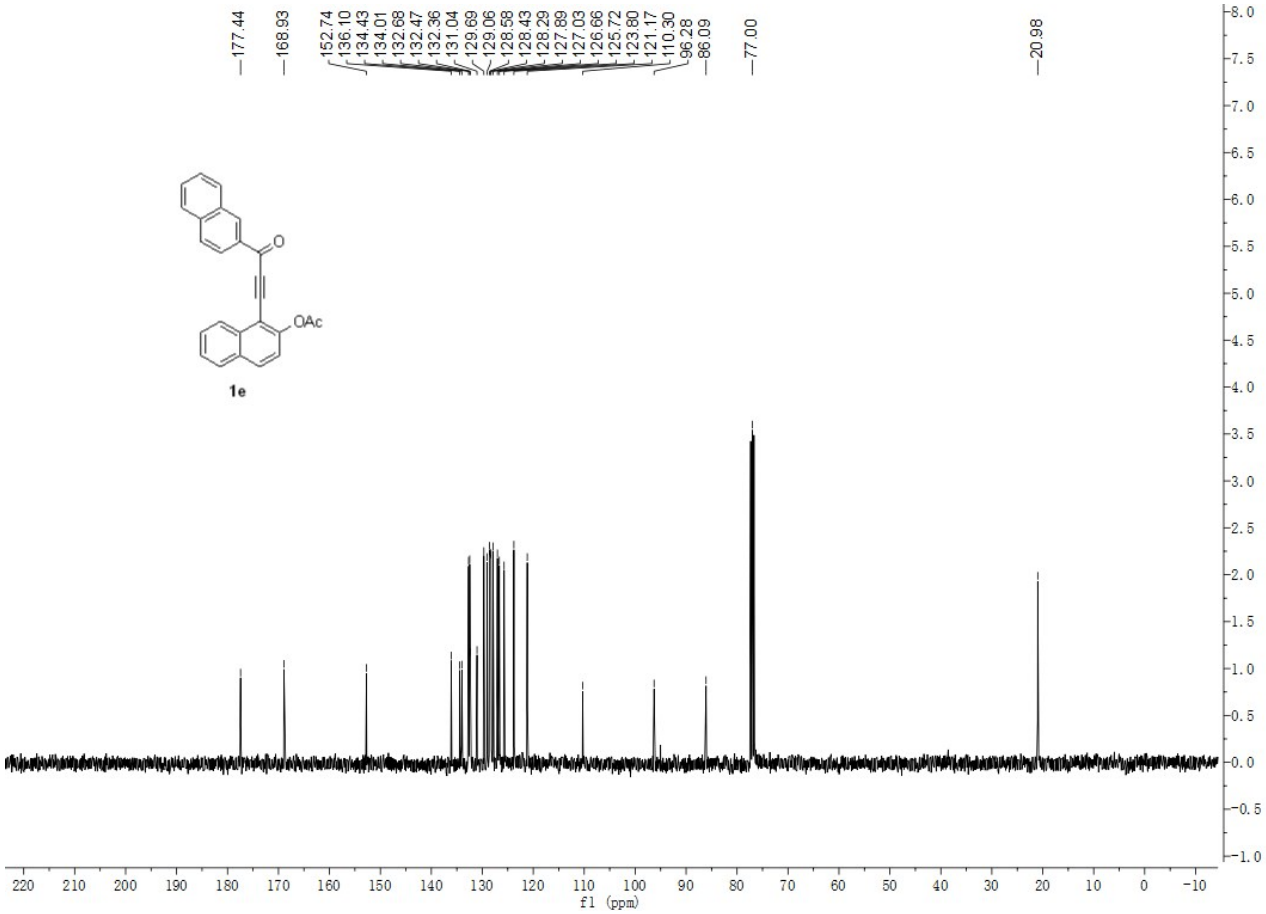
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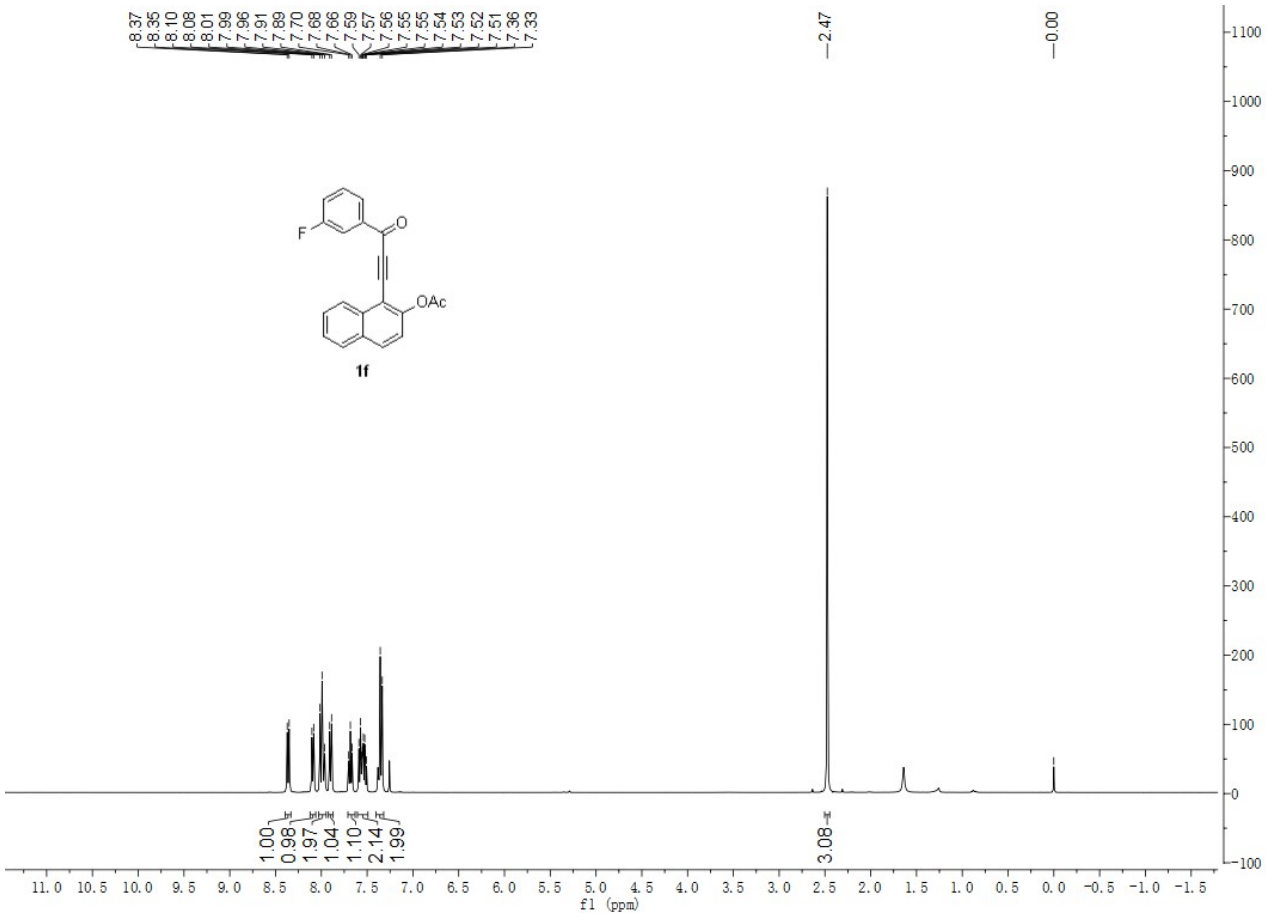
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7.51
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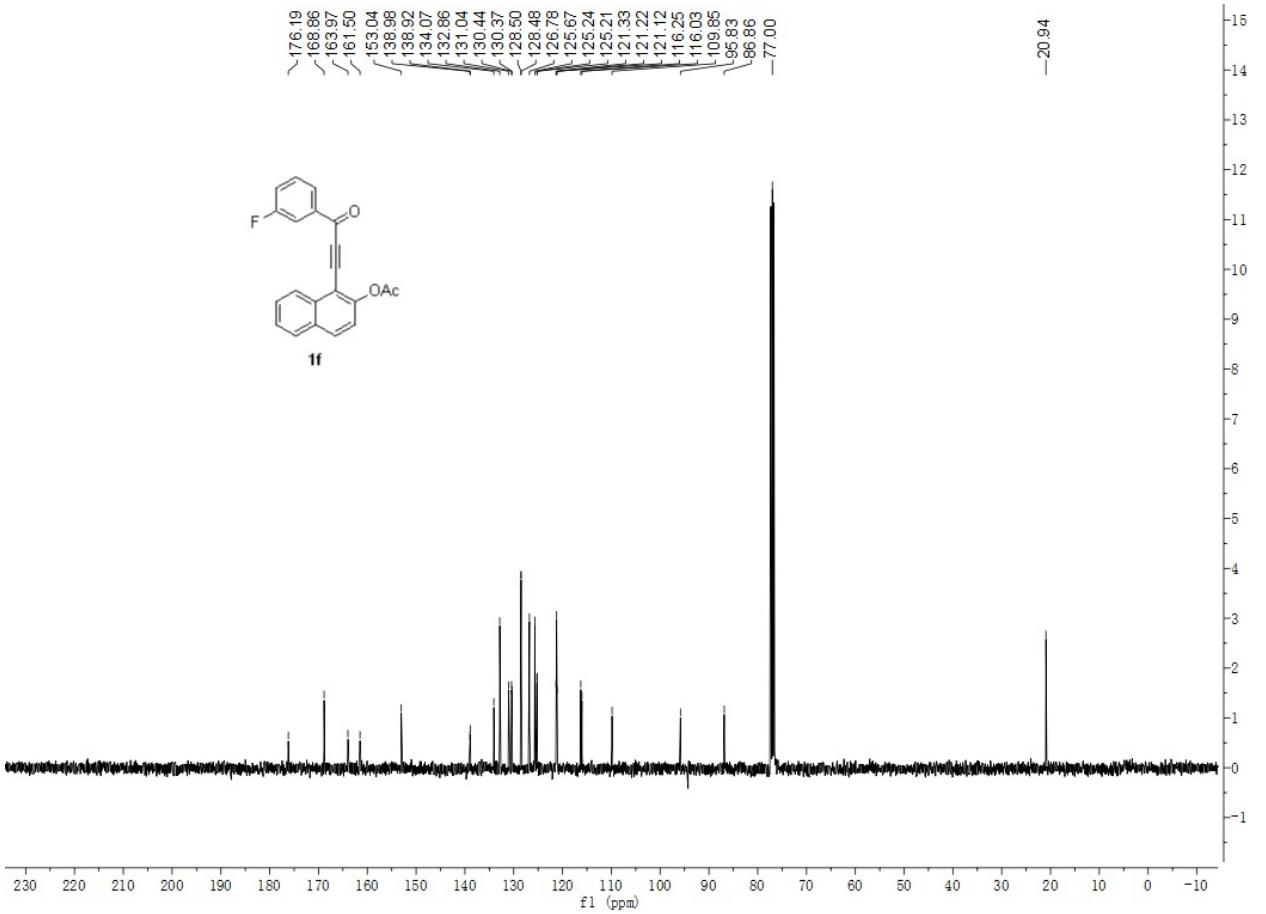
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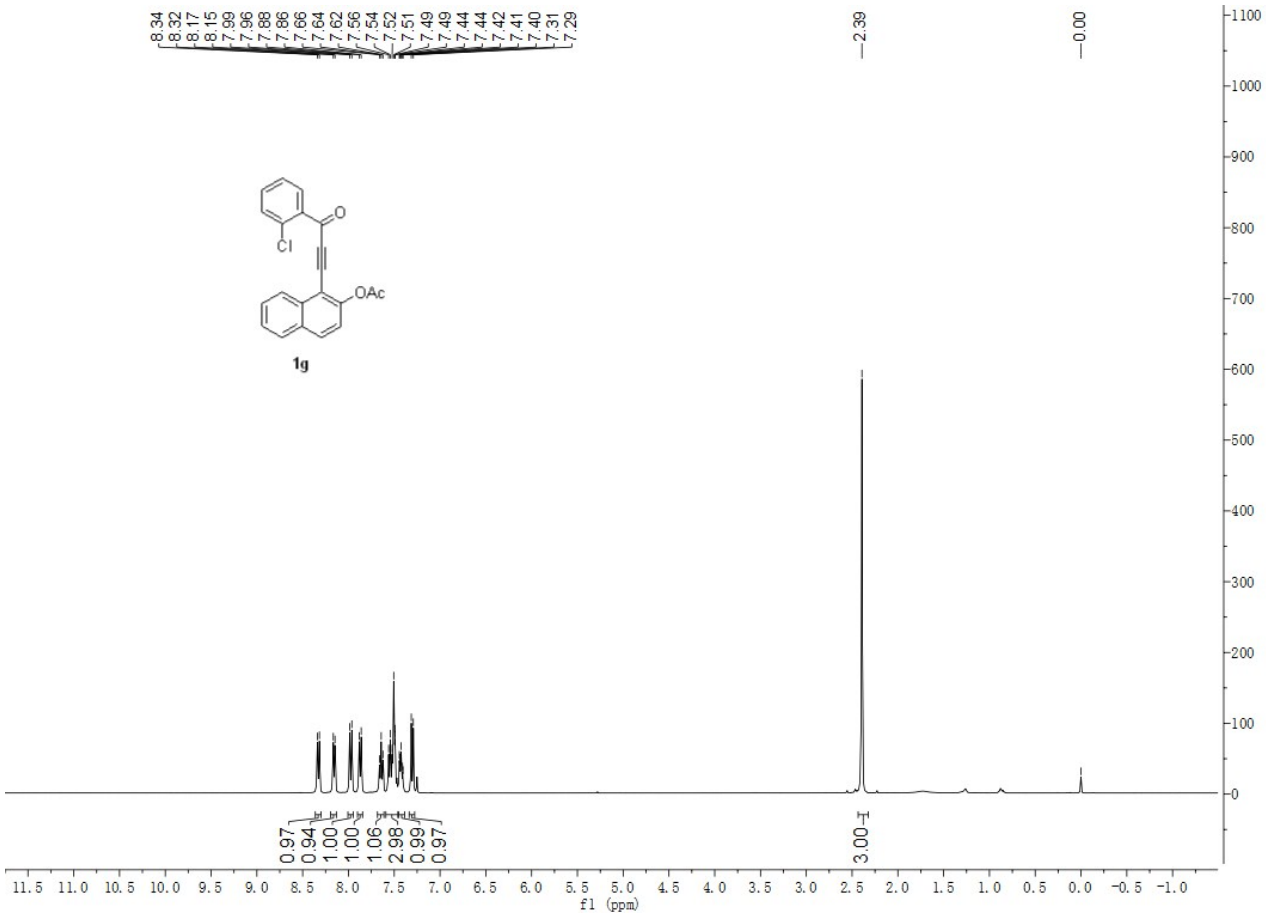
1f
f1 (ppm)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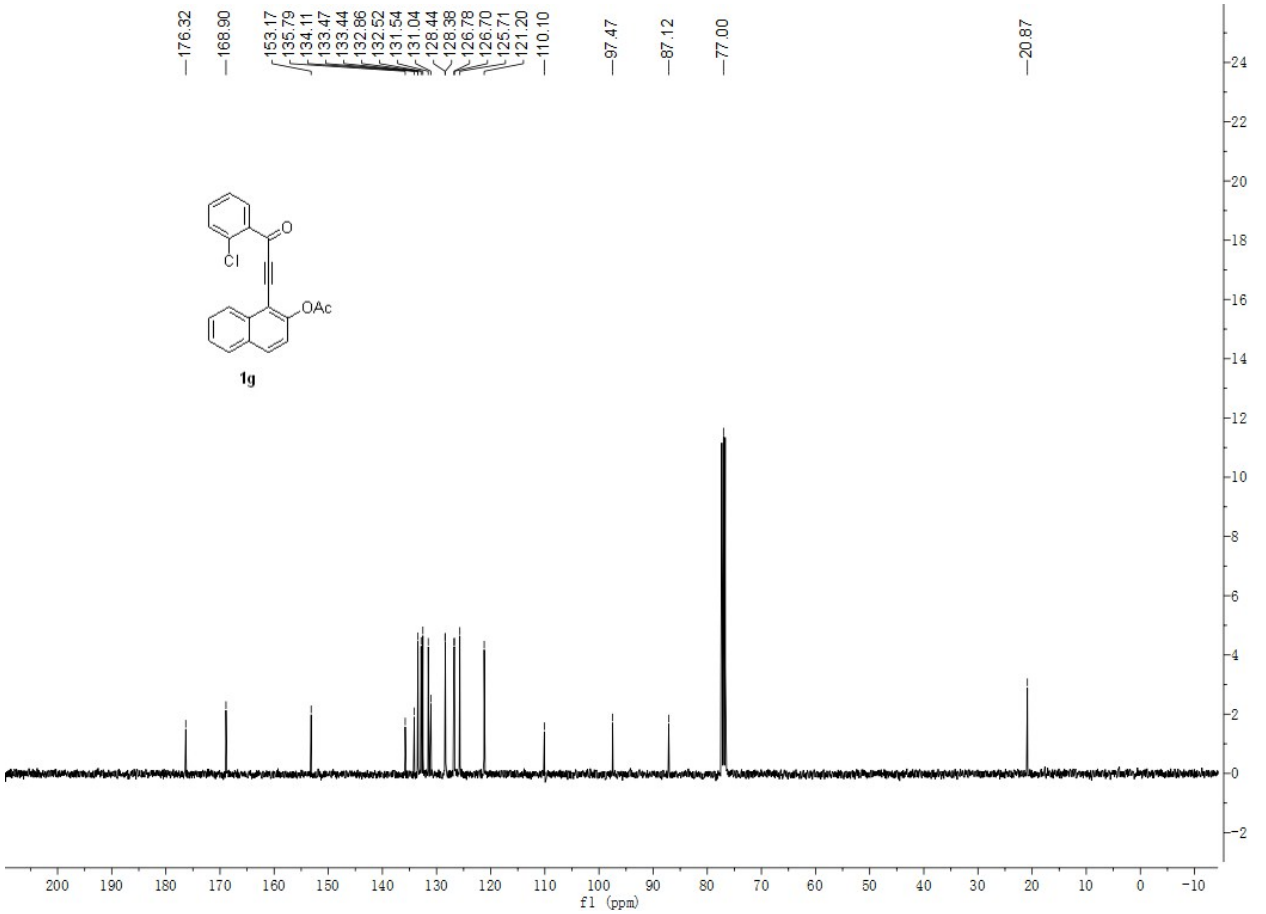
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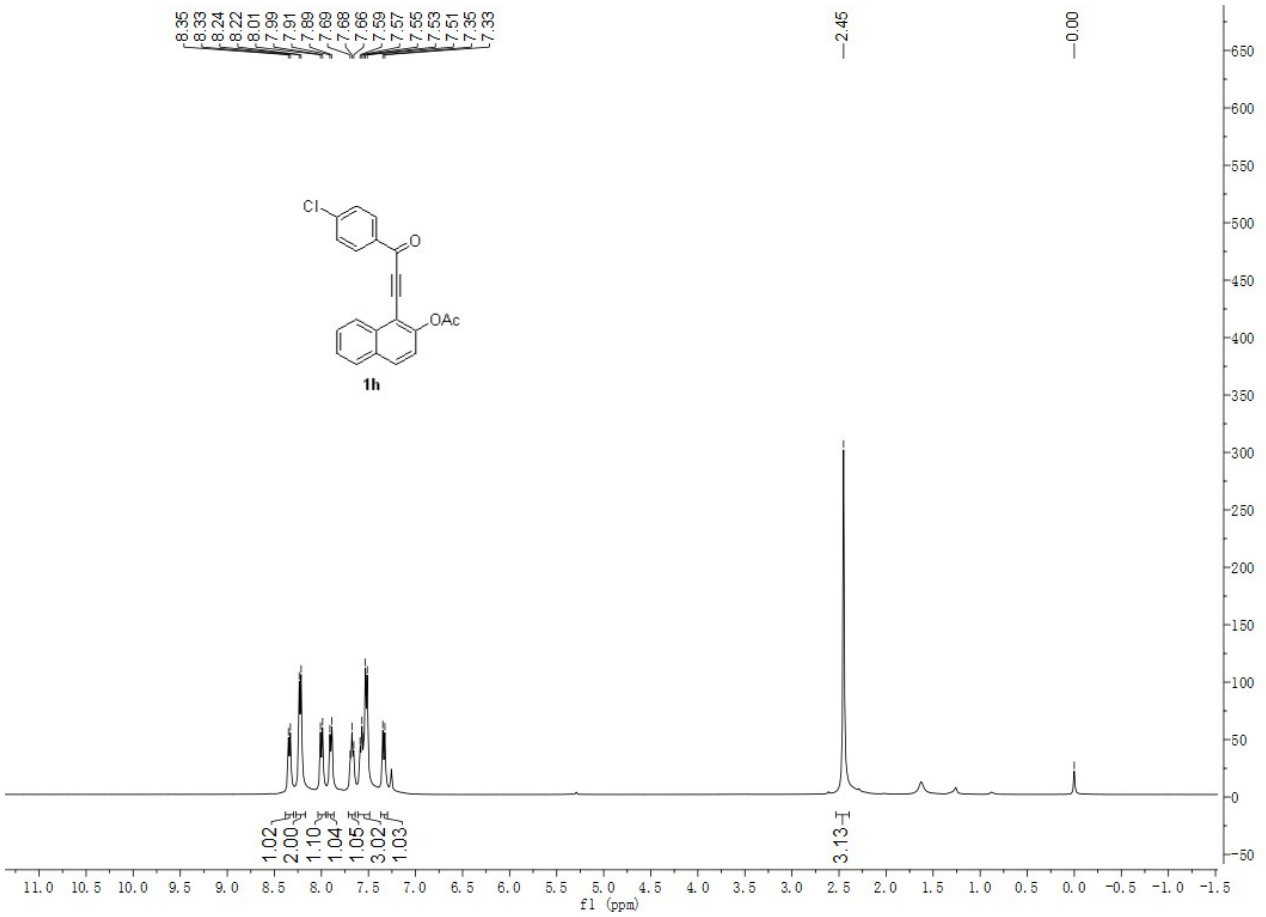
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7.51
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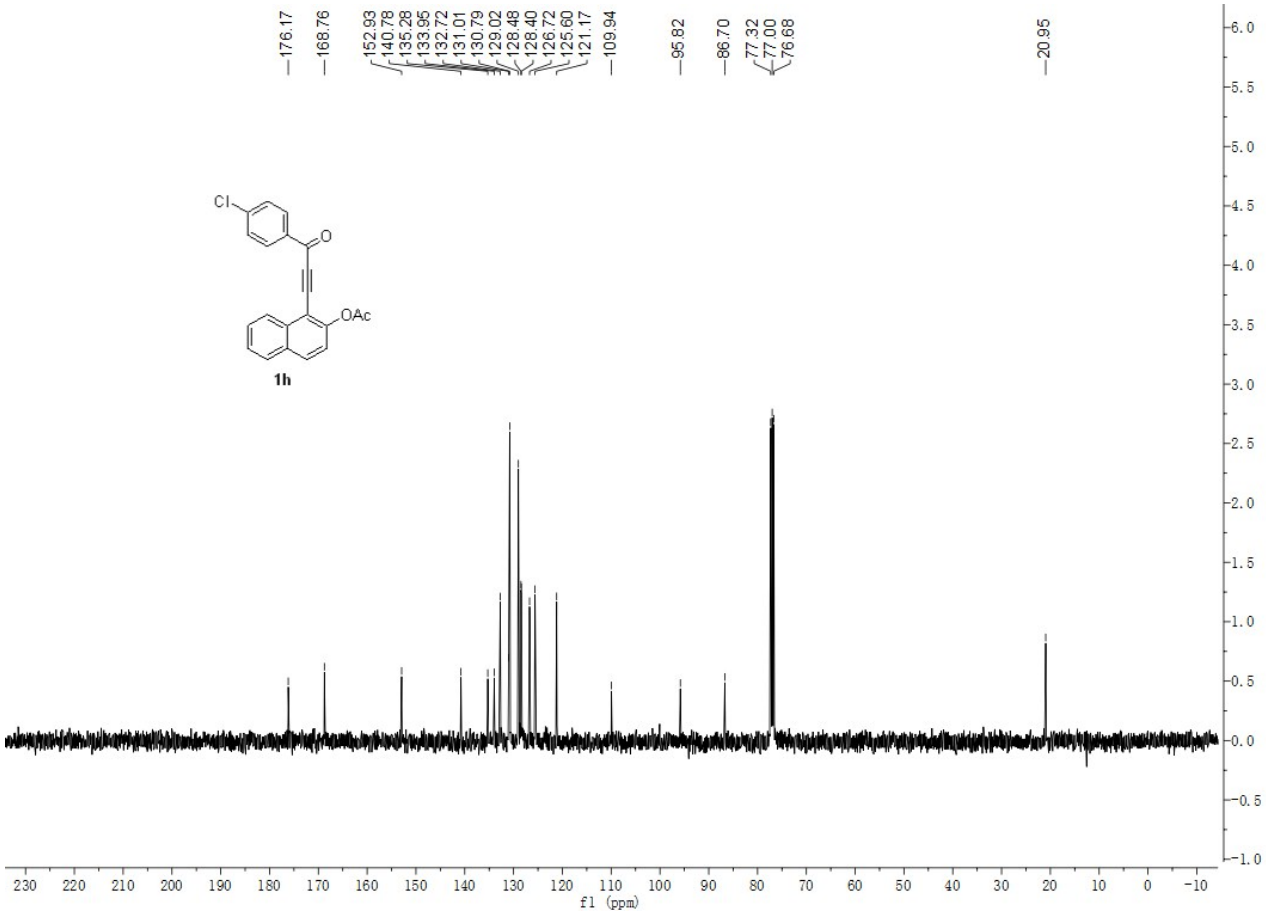
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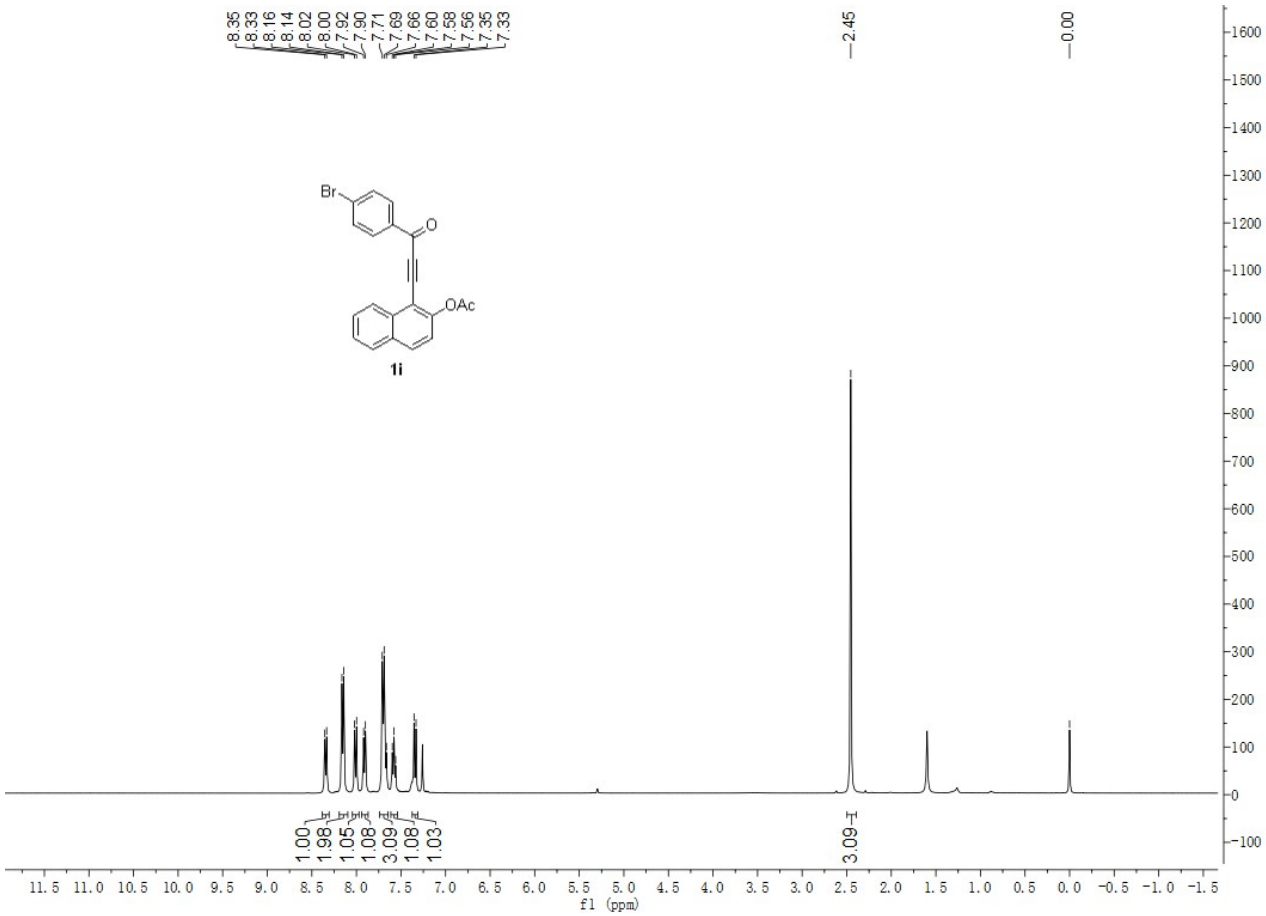
1h
f1 (ppm)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7.35
7.33
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3.09
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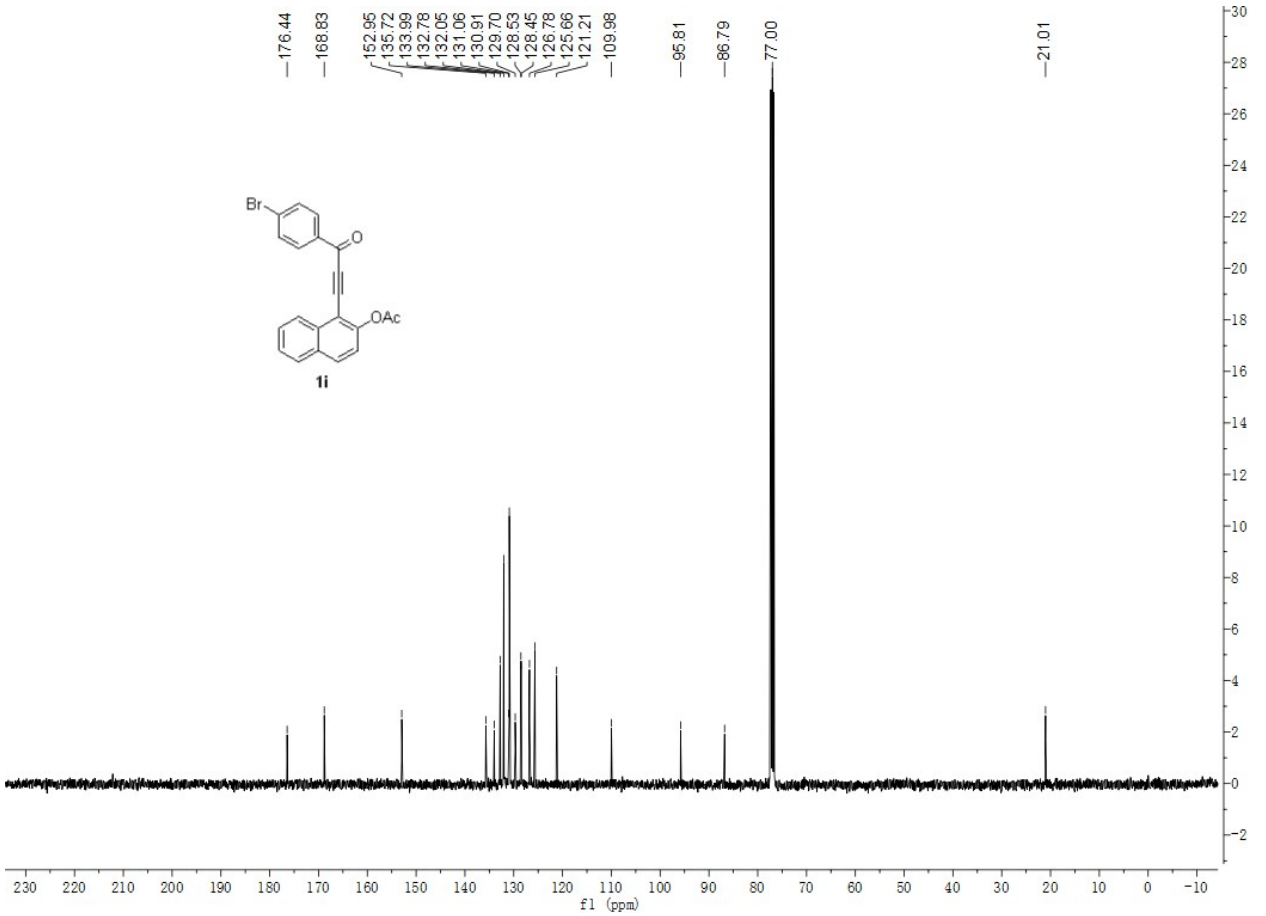
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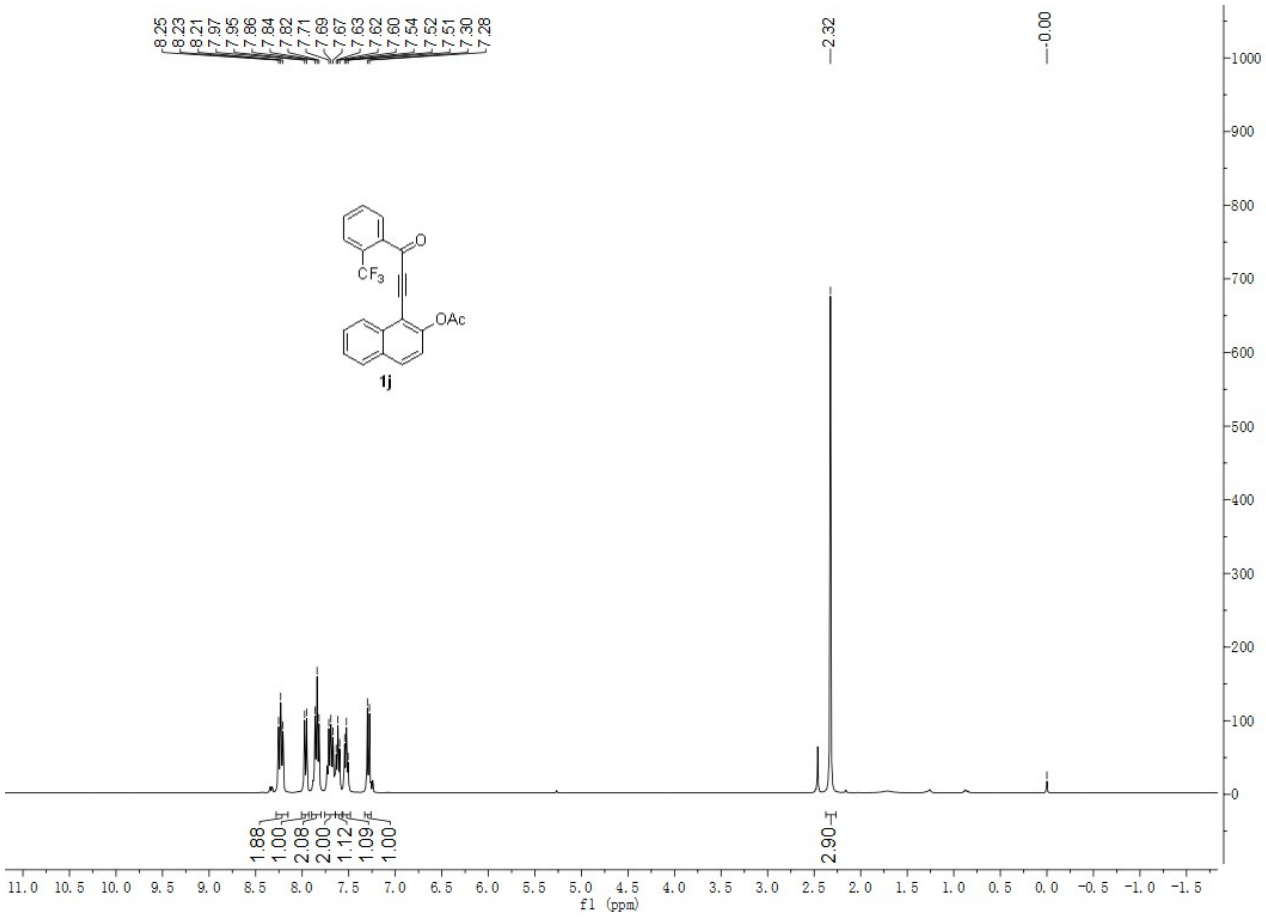
1i
f1 (ppm)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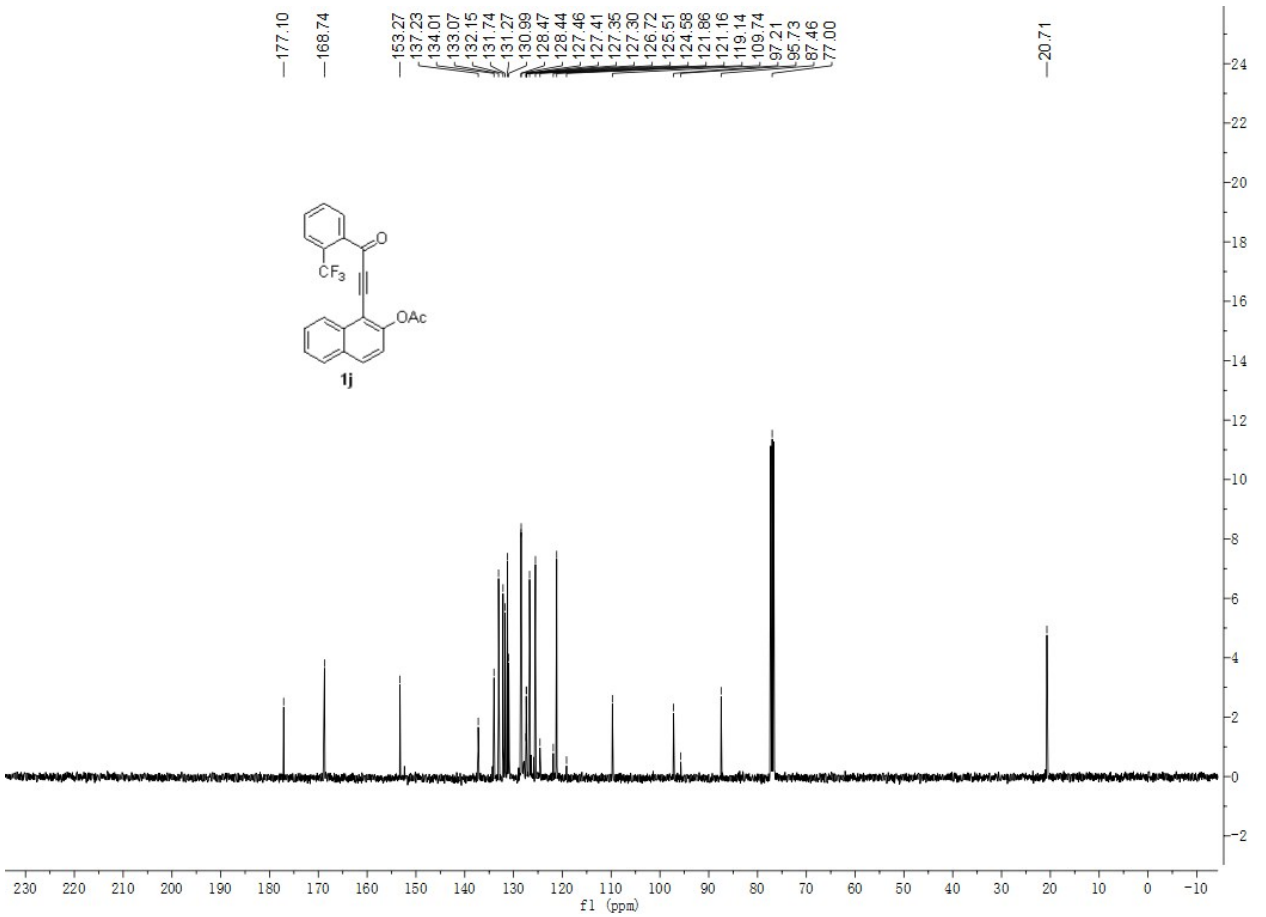
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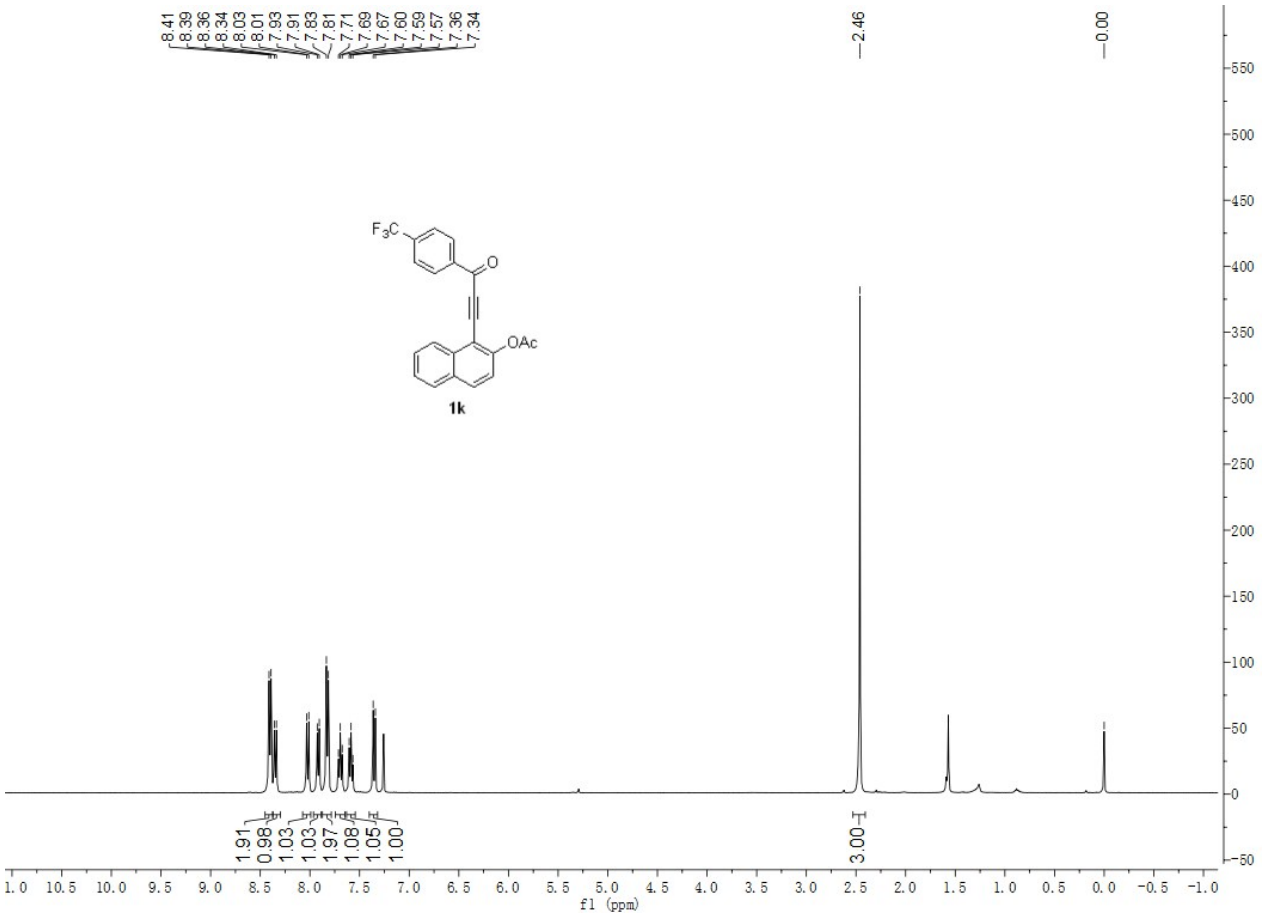
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7.57
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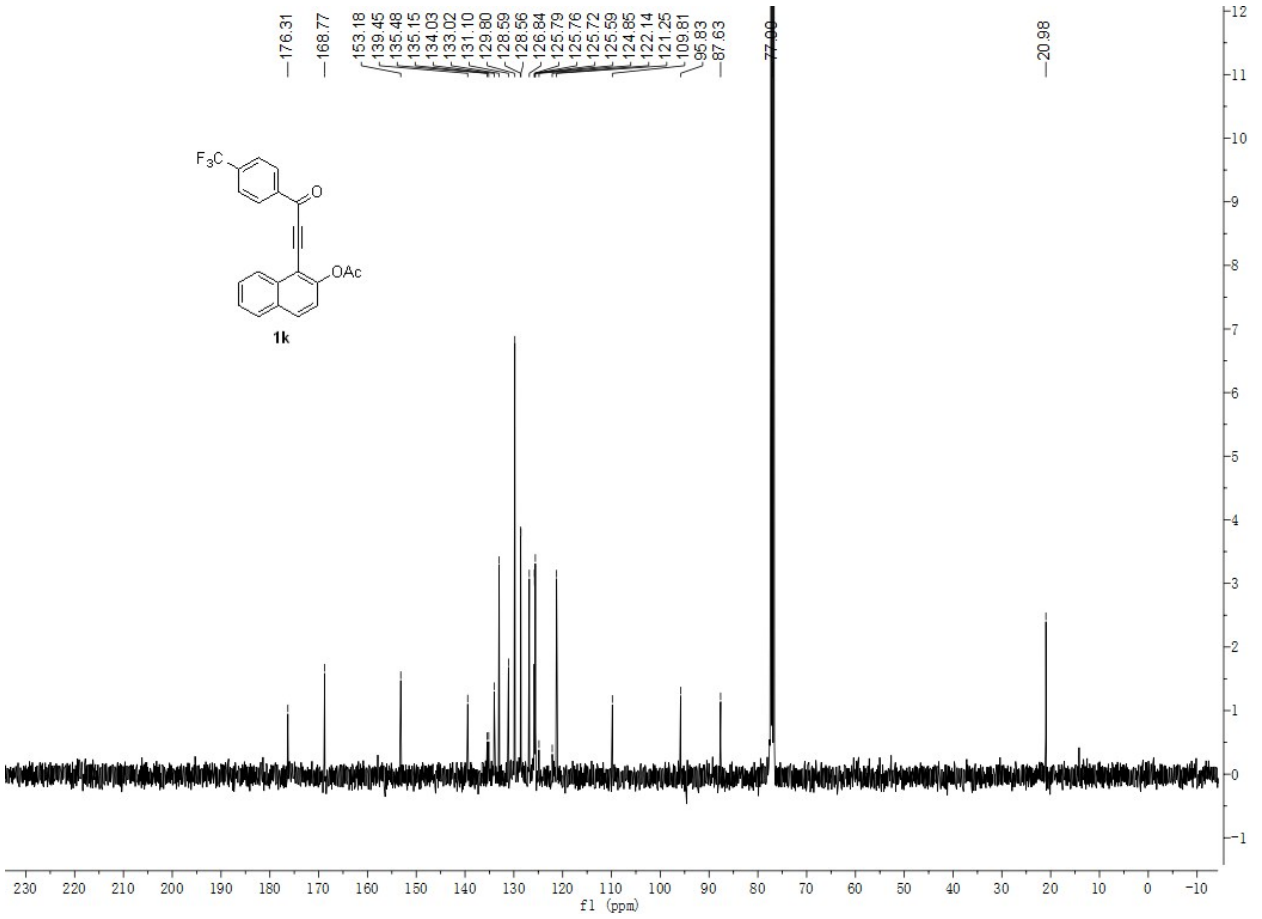
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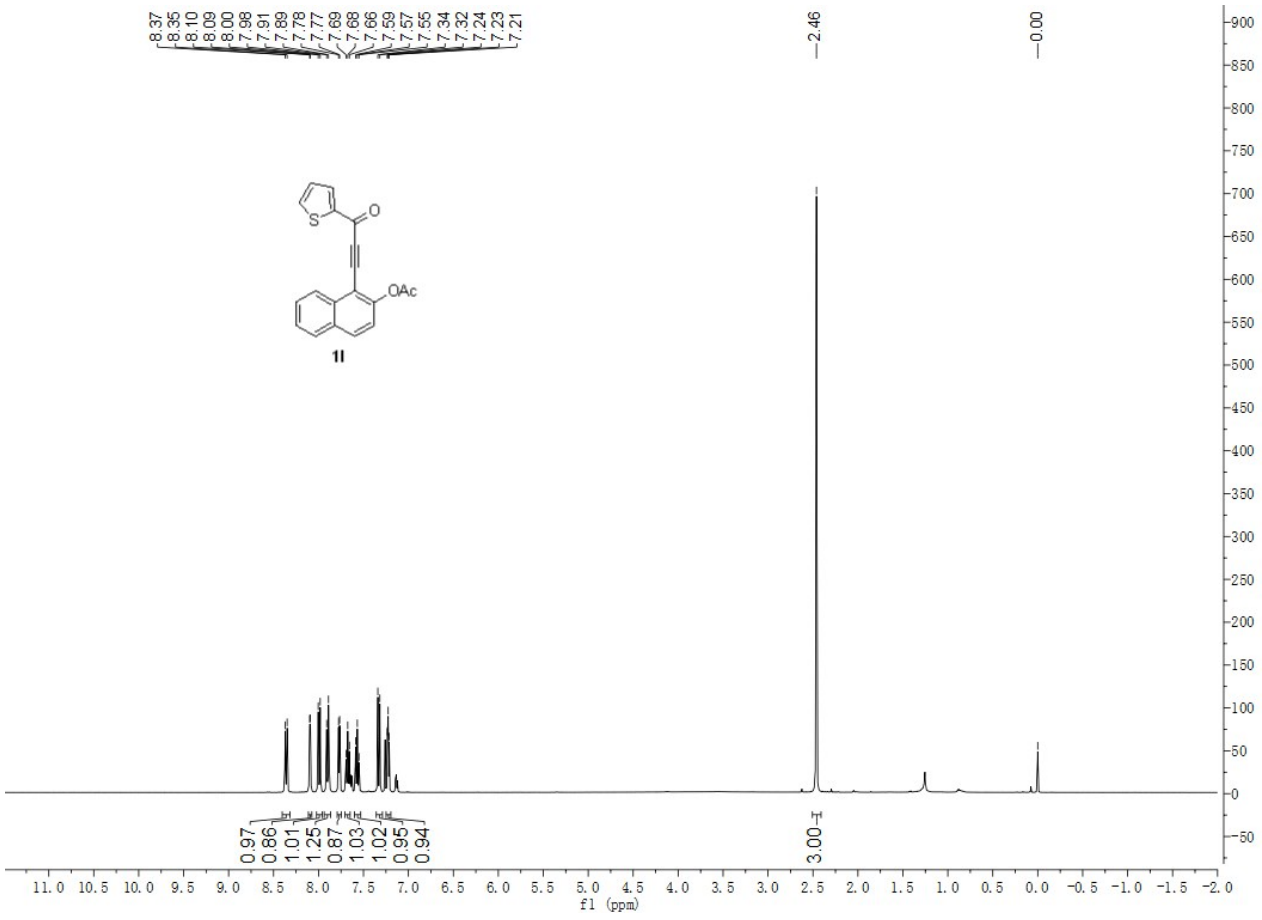
f1 (ppm)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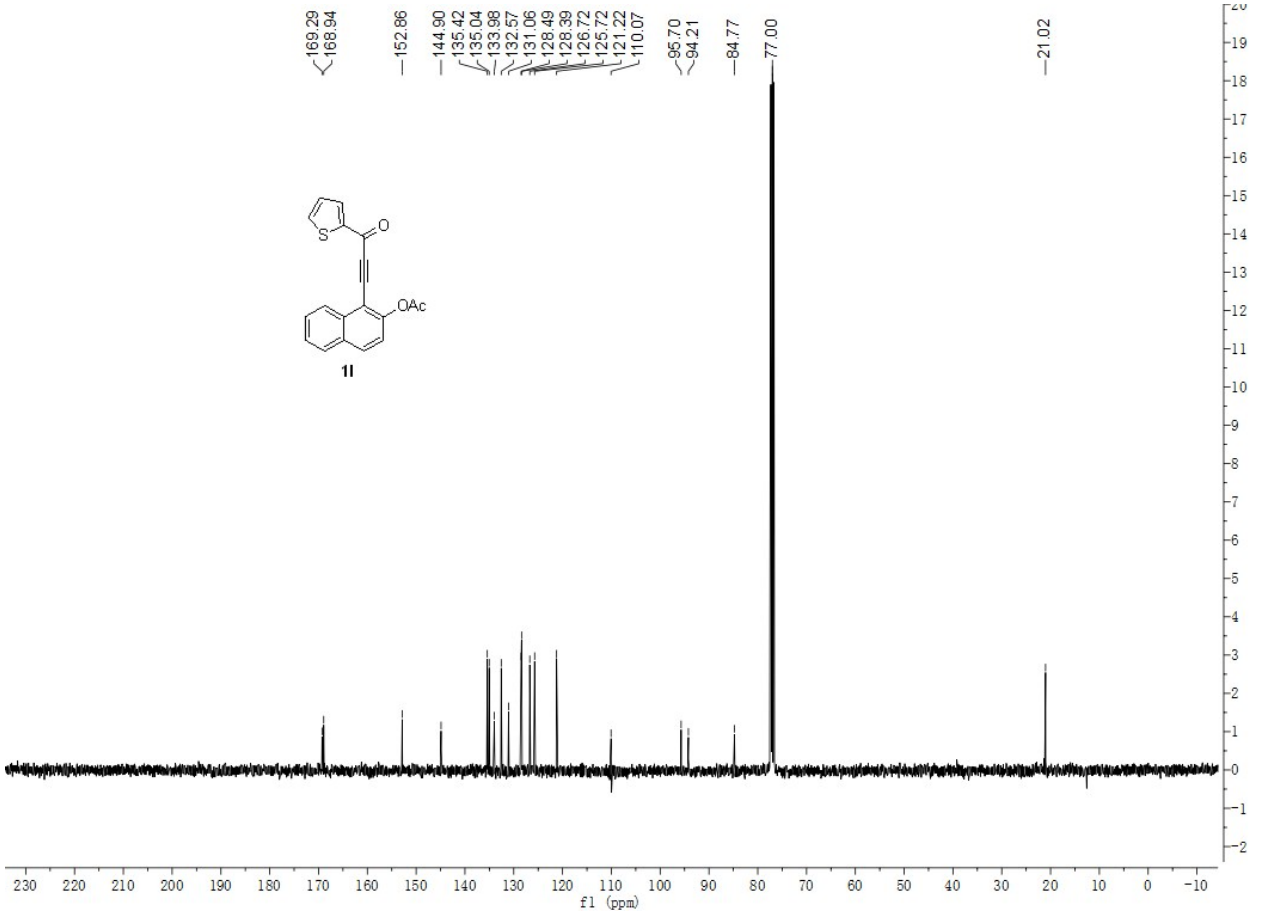
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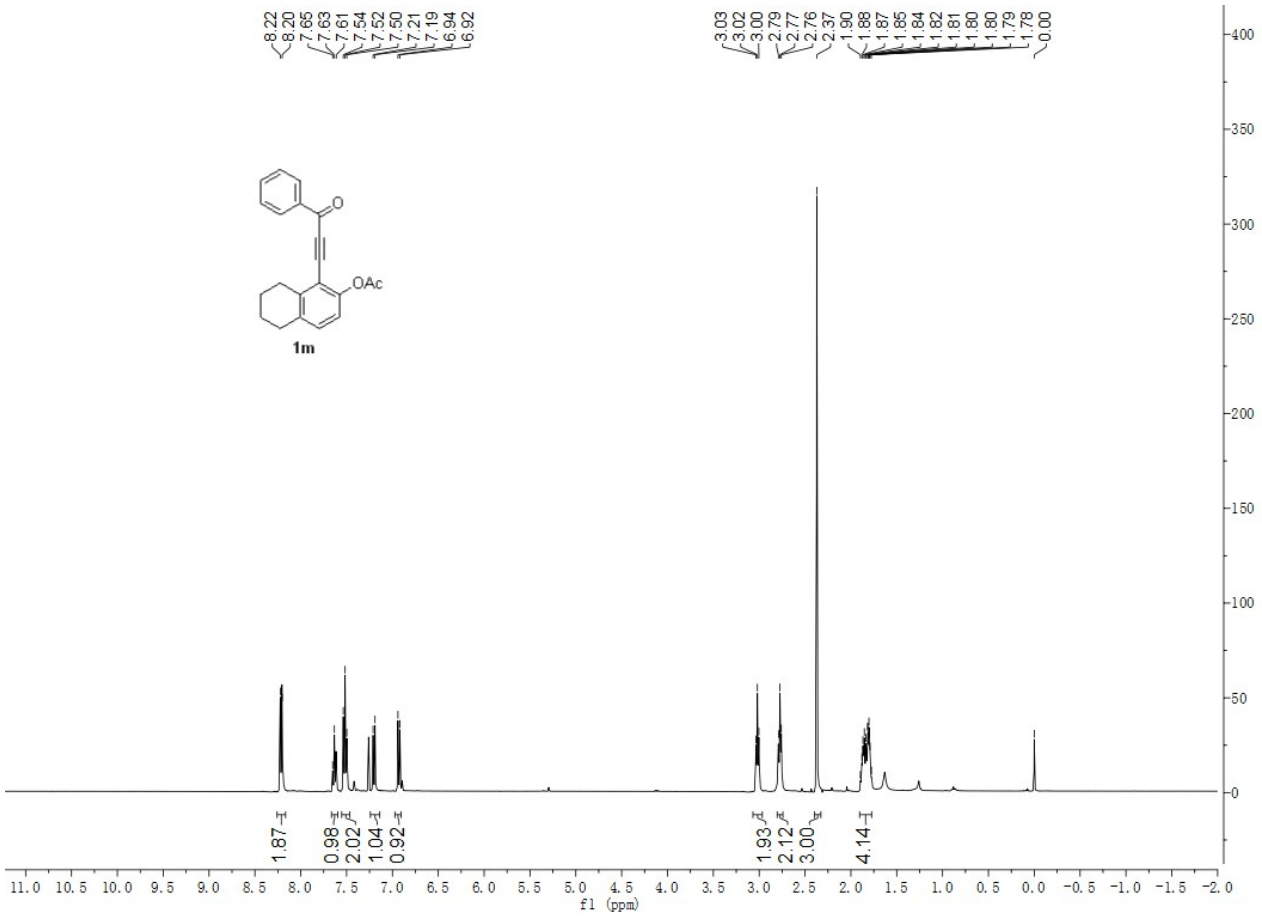
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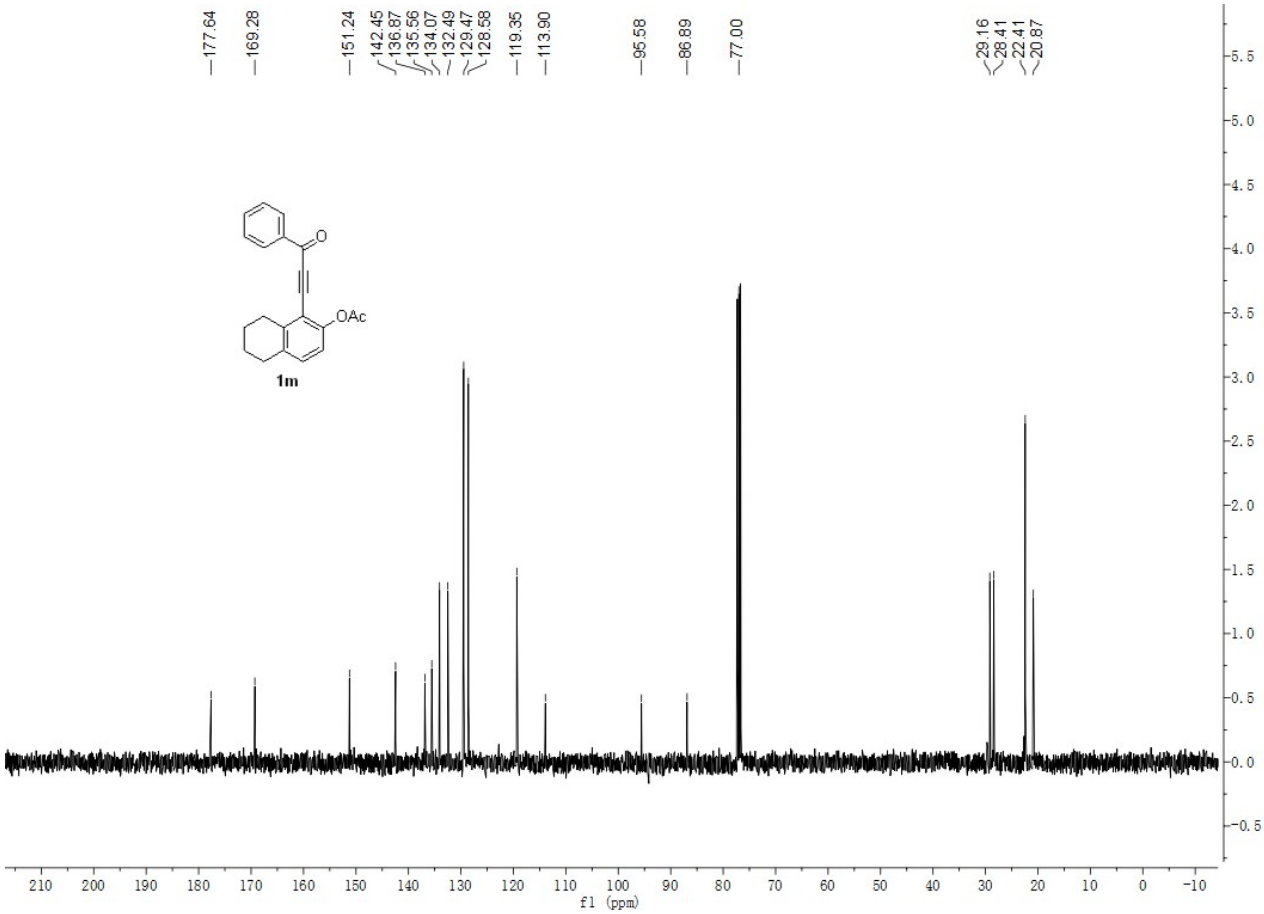
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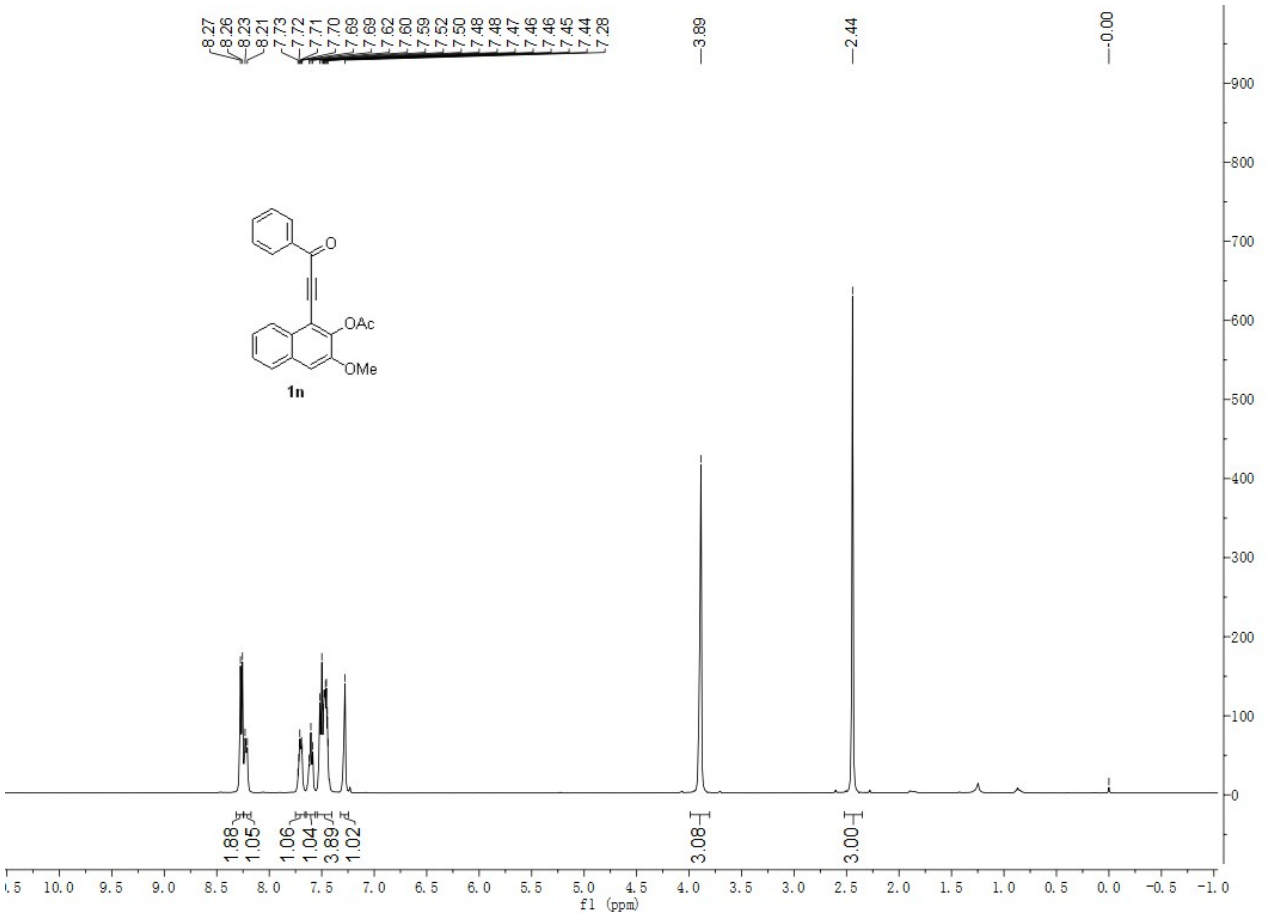
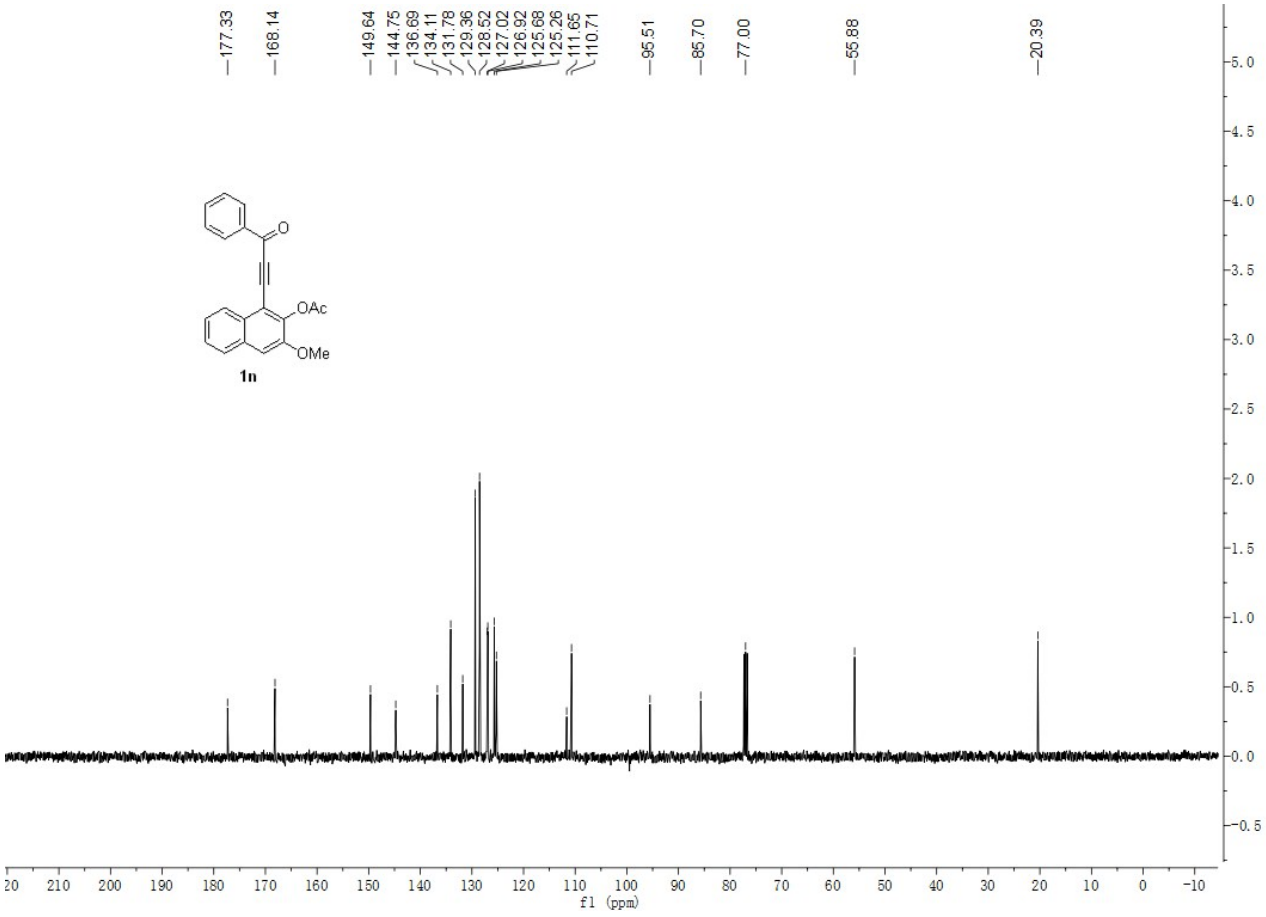
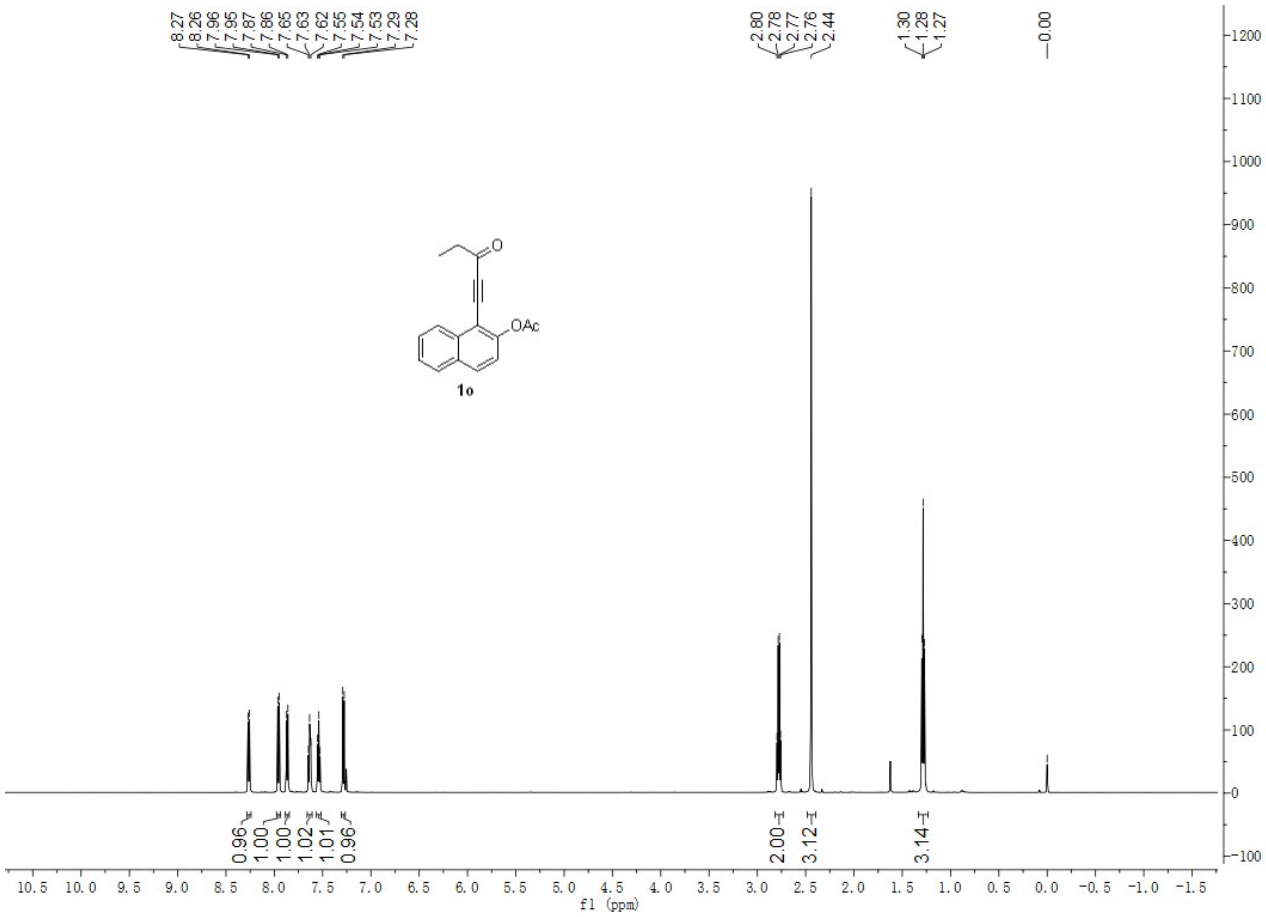
29.16
28.41
22.41
20.87
O
OAc
1m
f1 (ppm)


8.27
8.26
8.23
8.21
7.73
7.72
7.71
7.70
7.69
7.69
7.62
7.60
7.59
7.52
7.50
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.28
3.89
2.44
0.00
O
OAc
OMe
1n
1.88
1.05
1.06
1.04
3.89
1.02
3.08
3.00
f1 (ppm)


177.33
168.14
149.64
144.75
136.69
134.11
131.78
129.36
128.52
127.02
126.92
125.68
125.26
111.65
110.71
95.51
85.70
77.00
55.88
20.39
O
OAc
OMe
1n
f1 (ppm)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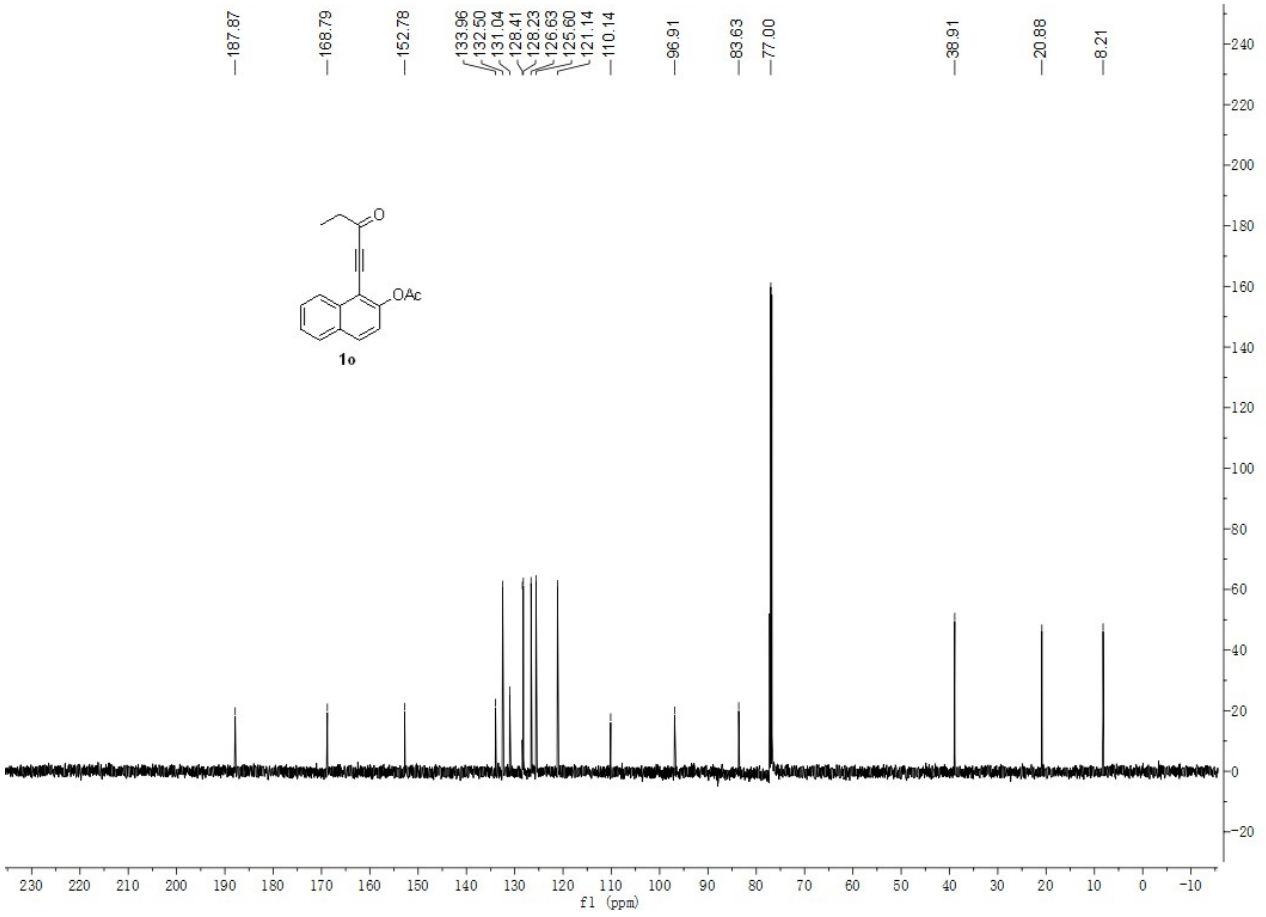
8.26
7.96
7.95
7.87
7.86
7.65
7.63
7.62
7.55
7.54
7.53
7.29
7.28
2.80
2.78
2.77
2.76
2.44
1.30
1.28
1.27
0.00
O
OAc
1o
0.96
1.00
1.00
1.02
1.01
0.96
2.00
3.12
3.14
f1 (ppm)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132.50
131.04
128.41
128.23
126.63
125.60
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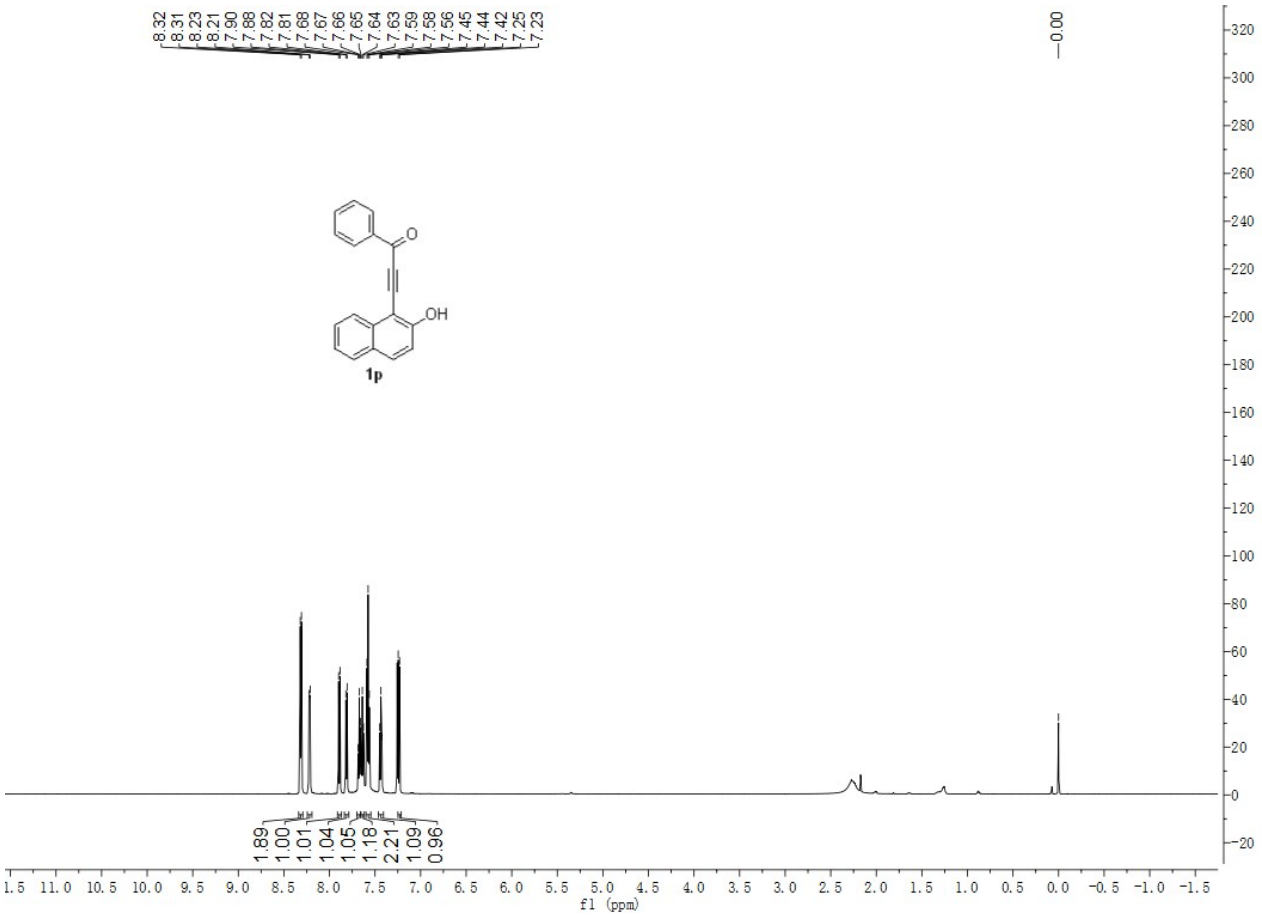
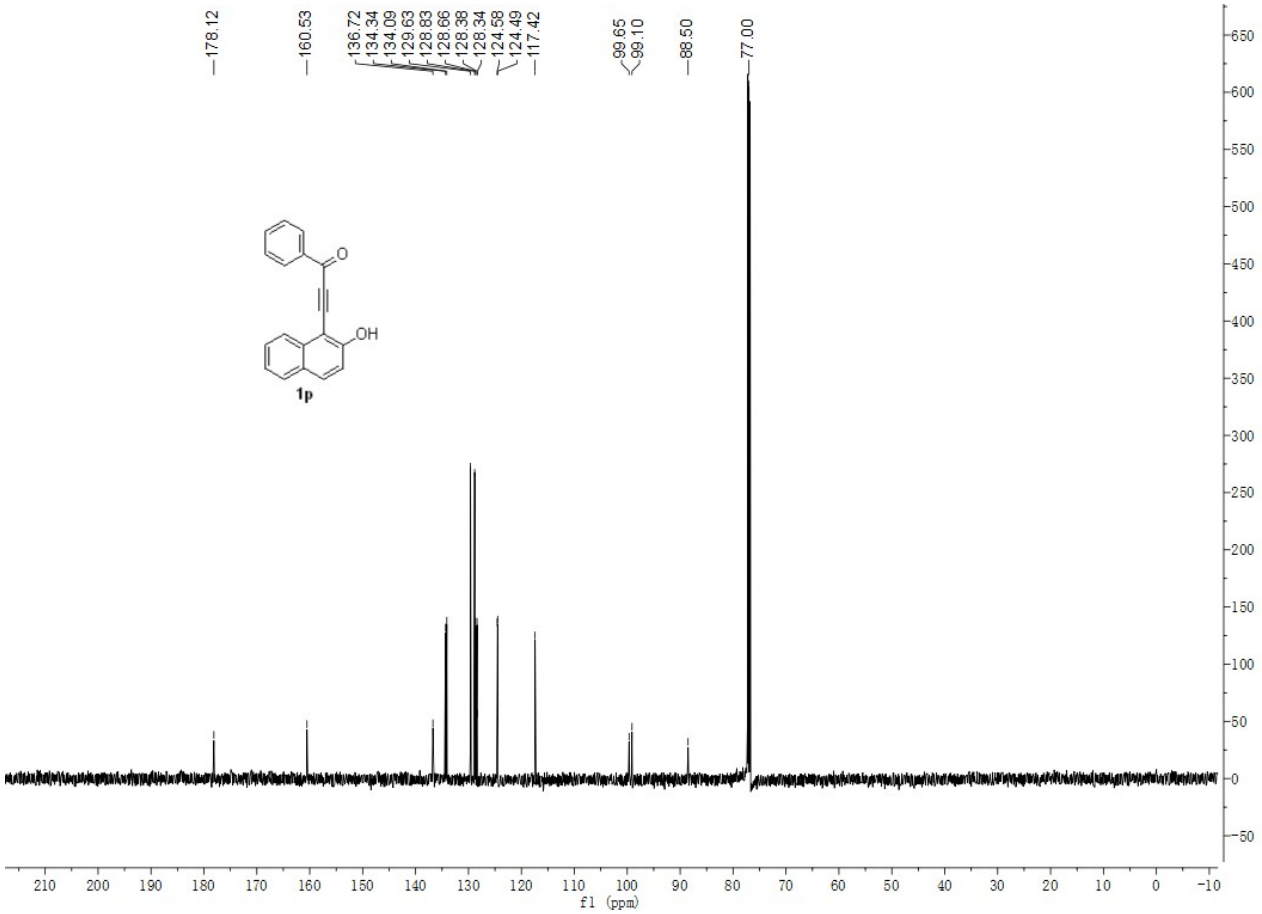
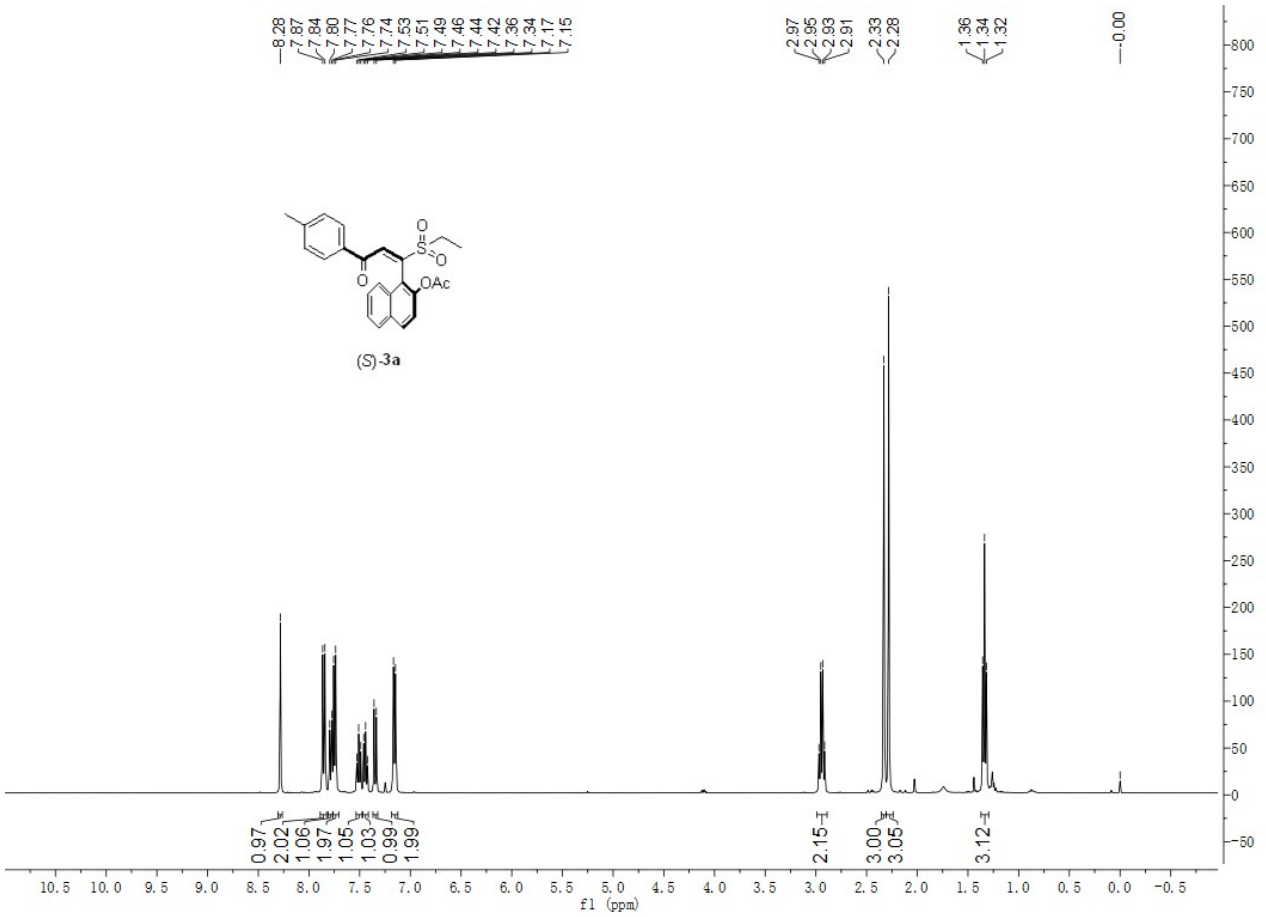
110.14
96.91
83.63
77.00
38.91
20.88
8.21
O
OAc
1o
f1 (ppm)


8.32
8.31
8.23
8.21
7.90
7.88
7.82
7.81
7.68
7.67
7.66
7.65
7.64
7.63
7.59
7.58
7.56
7.45
7.44
7.42
7.25
7.23
0.00
O
OH
1p
1.89
1.00
1.01
1.04
1.05
1.18
2.21
1.09
0.96
f1 (ppm)


178.12
160.53
136.72
134.34
134.09
129.63
128.83
128.66
128.38
128.34
124.58
124.49
117.42
99.65
99.10
88.50
77.00
O
OH
1p
f1 (ppm)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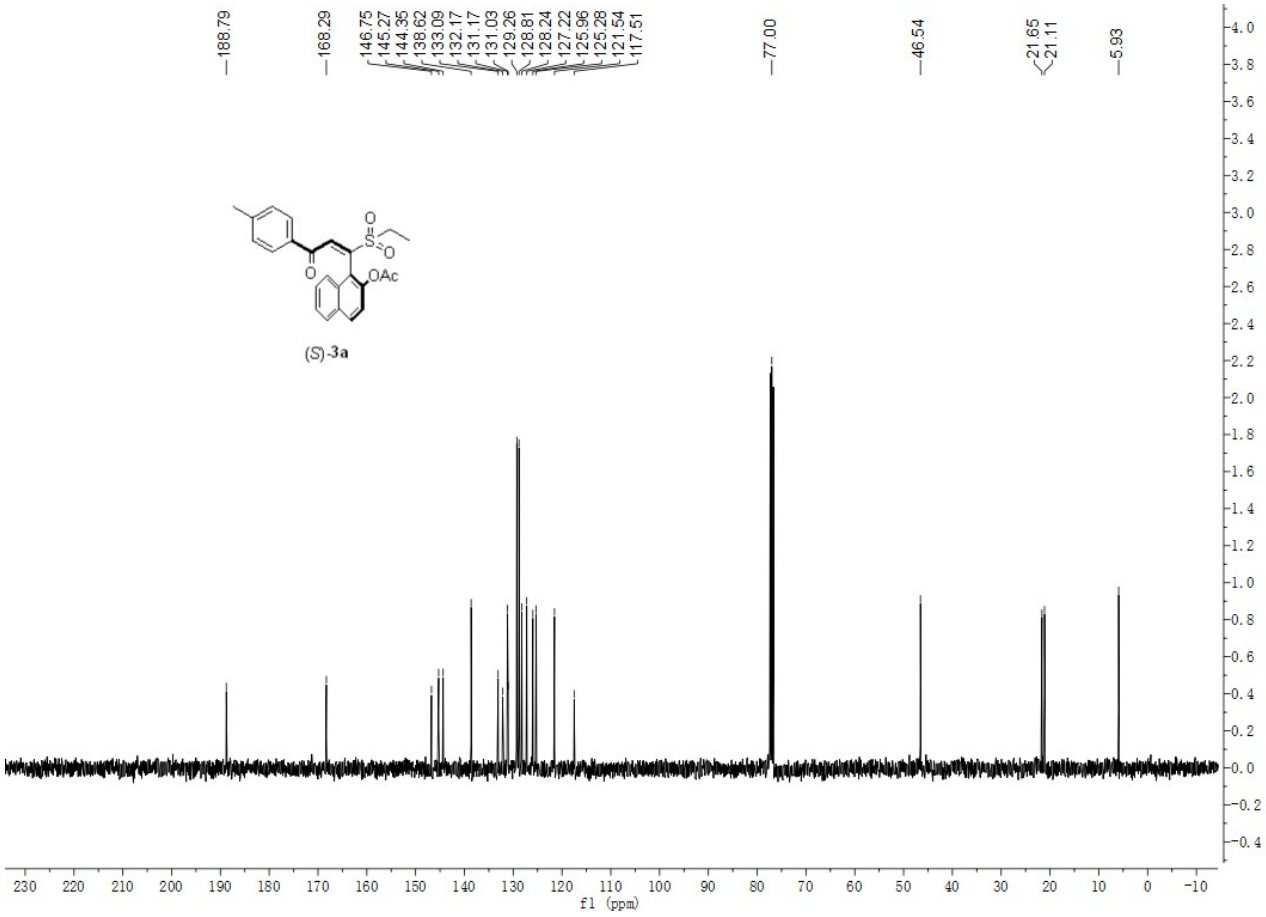
7.84
7.80
7.77
7.76
7.74
7.53
7.51
7.49
7.46
7.44
7.42
7.36
7.34
7.17
7.15
2.97
2.95
2.93
2.91
2.33
2.28
1.36
1.34
1.32
0.00
O
S
O
O
OAc
(S)-3a
0.97
2.02
1.06
1.97
1.05
1.03
0.99
1.99
2.15
3.00
3.05
3.12
f1 (ppm)


188.79
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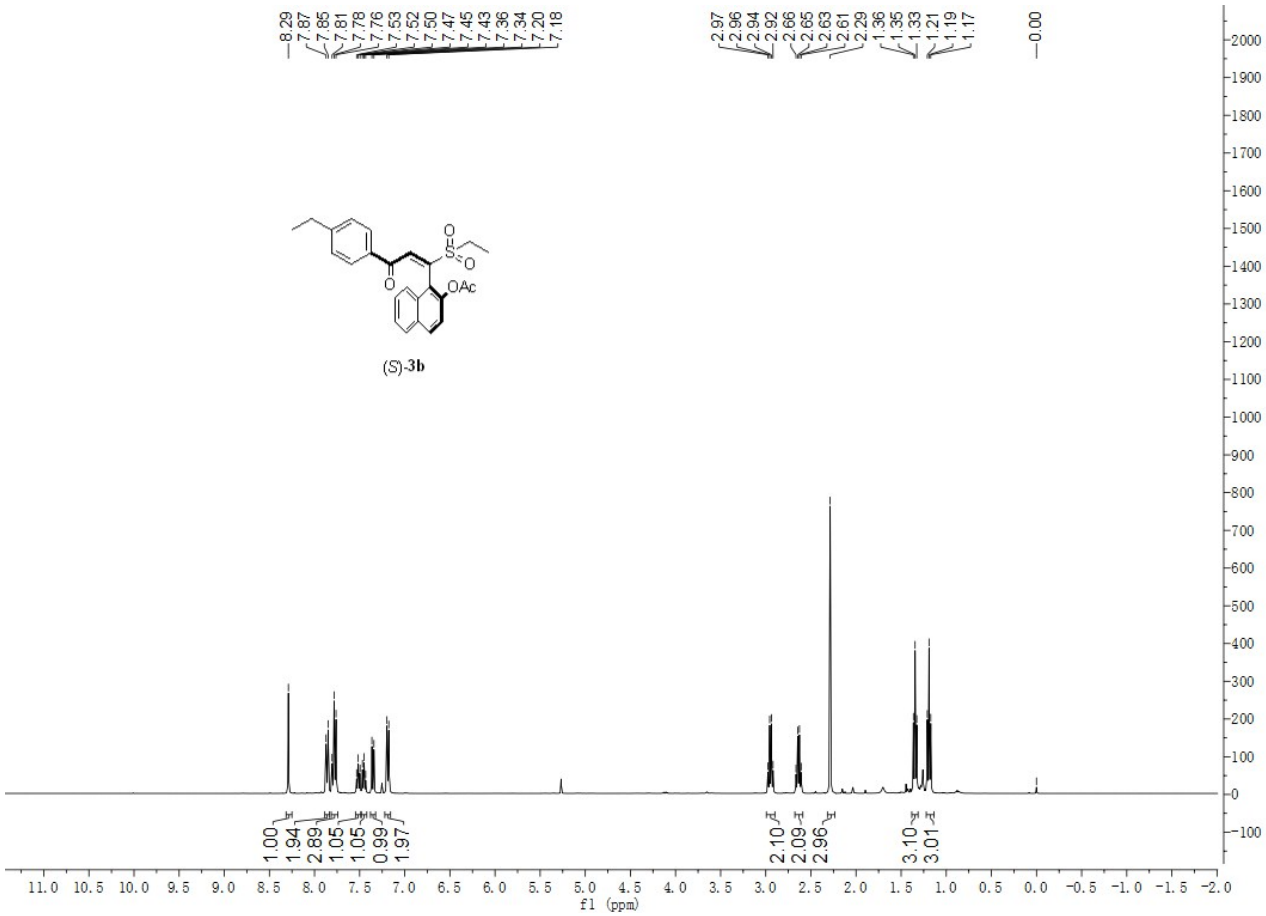
144.35
138.62
133.09
132.17
131.17
131.03
129.26
128.81
128.24
127.22
125.96
125.28
121.54
117.51
77.00
46.54
21.65
21.11
5.93
O
S
O
O
OAc
(S)-3a
f1 (ppm)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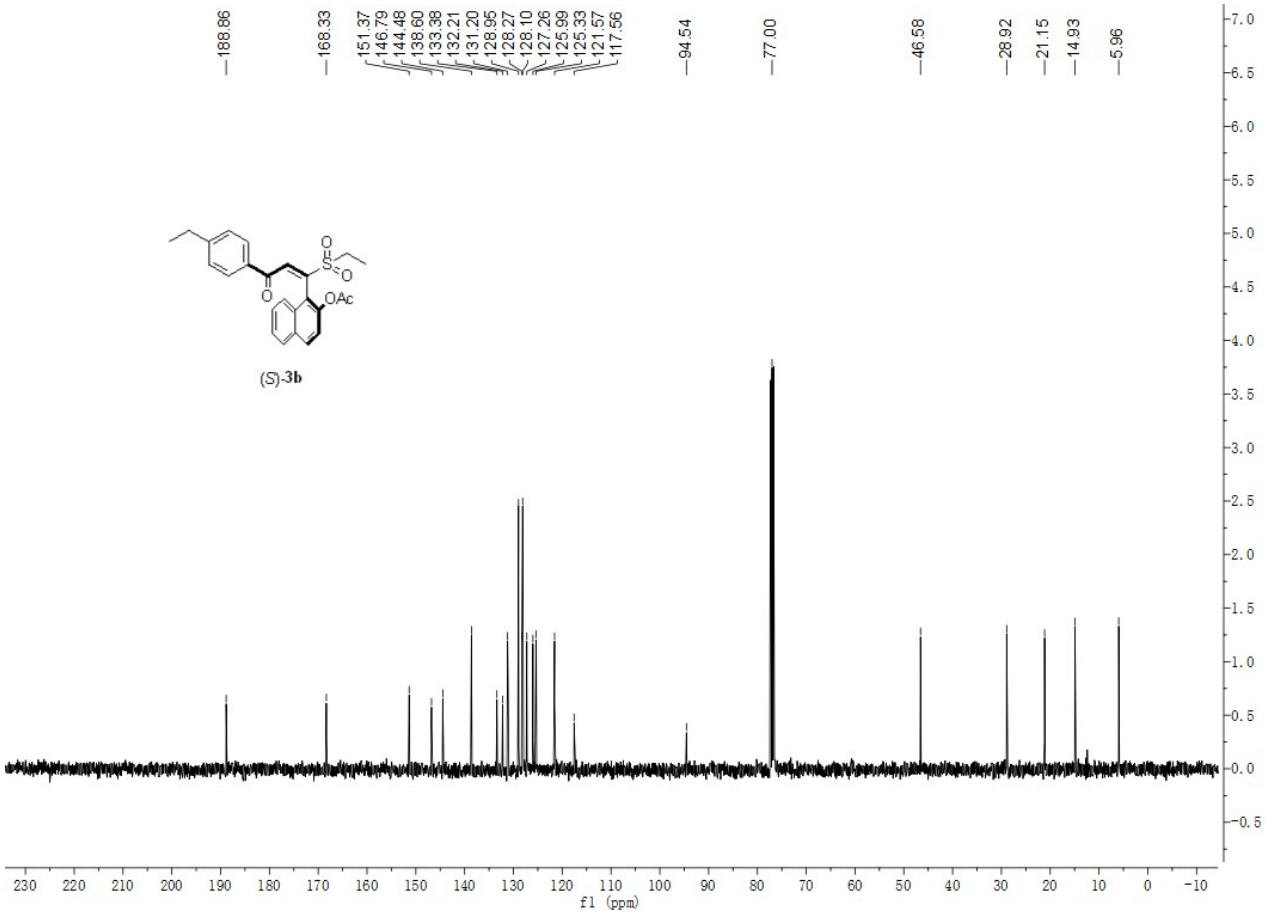
7.87
7.85
7.81
7.78
7.76
7.53
7.52
7.50
7.47
7.45
7.43
7.36
7.34
7.20
7.18
2.97
2.96
2.94
2.92
2.66
2.65
2.63
2.61
2.29
1.36
1.35
1.33
1.21
1.19
1.17
0.00
OAc
1.00
1.94
2.89
1.05
1.05
0.99
1.97
2.10
2.09
2.96
3.10
3.01
f1 (ppm)

(*S*)-**3b**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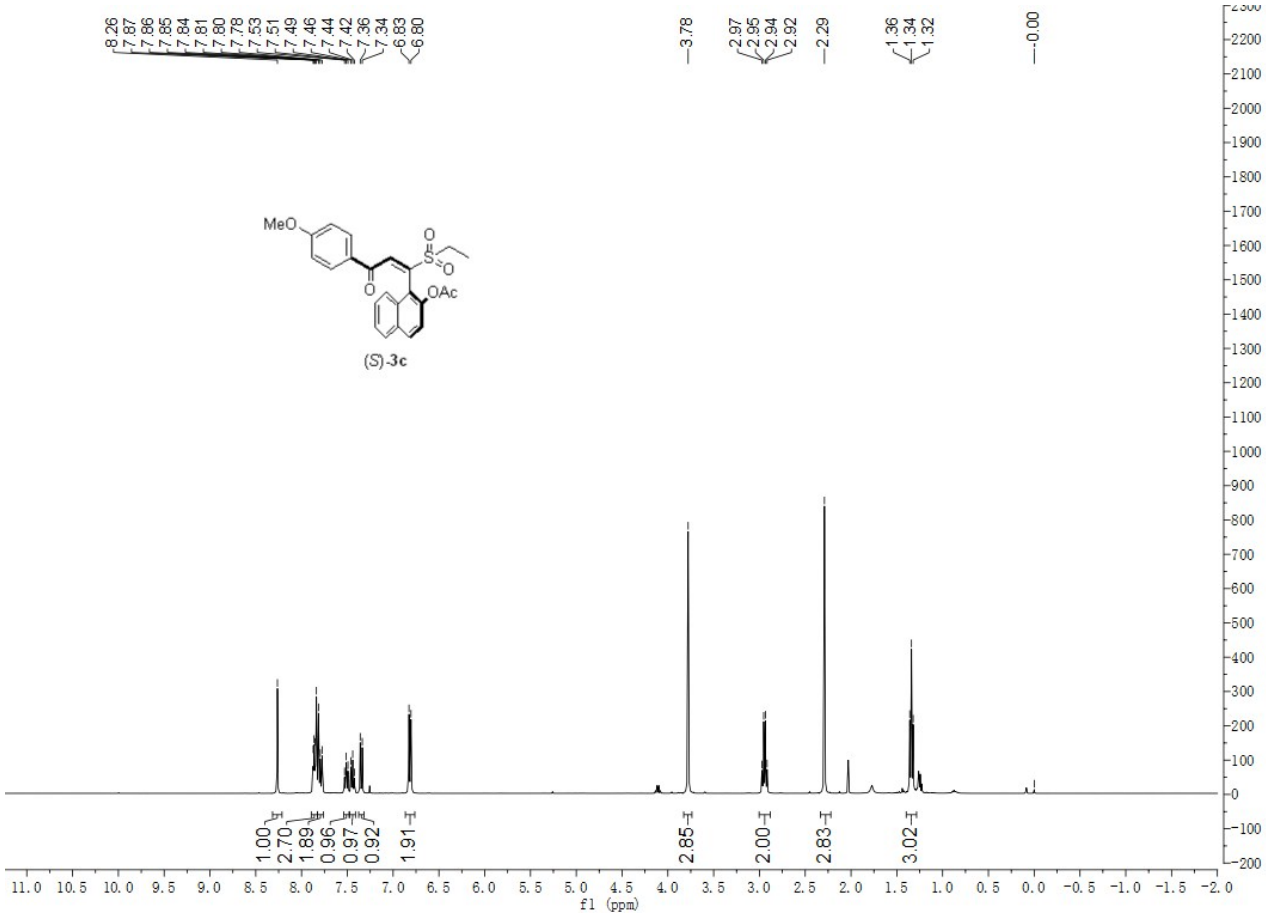
168.33
151.37
146.79
144.48
138.60
133.38
132.21
131.20
128.95
128.27
128.10
127.26
125.99
125.33
121.57
117.56
94.54
77.00
46.58
28.92
21.15
14.93
5.96
OAc
f1 (ppm)

(*S*)-**3b**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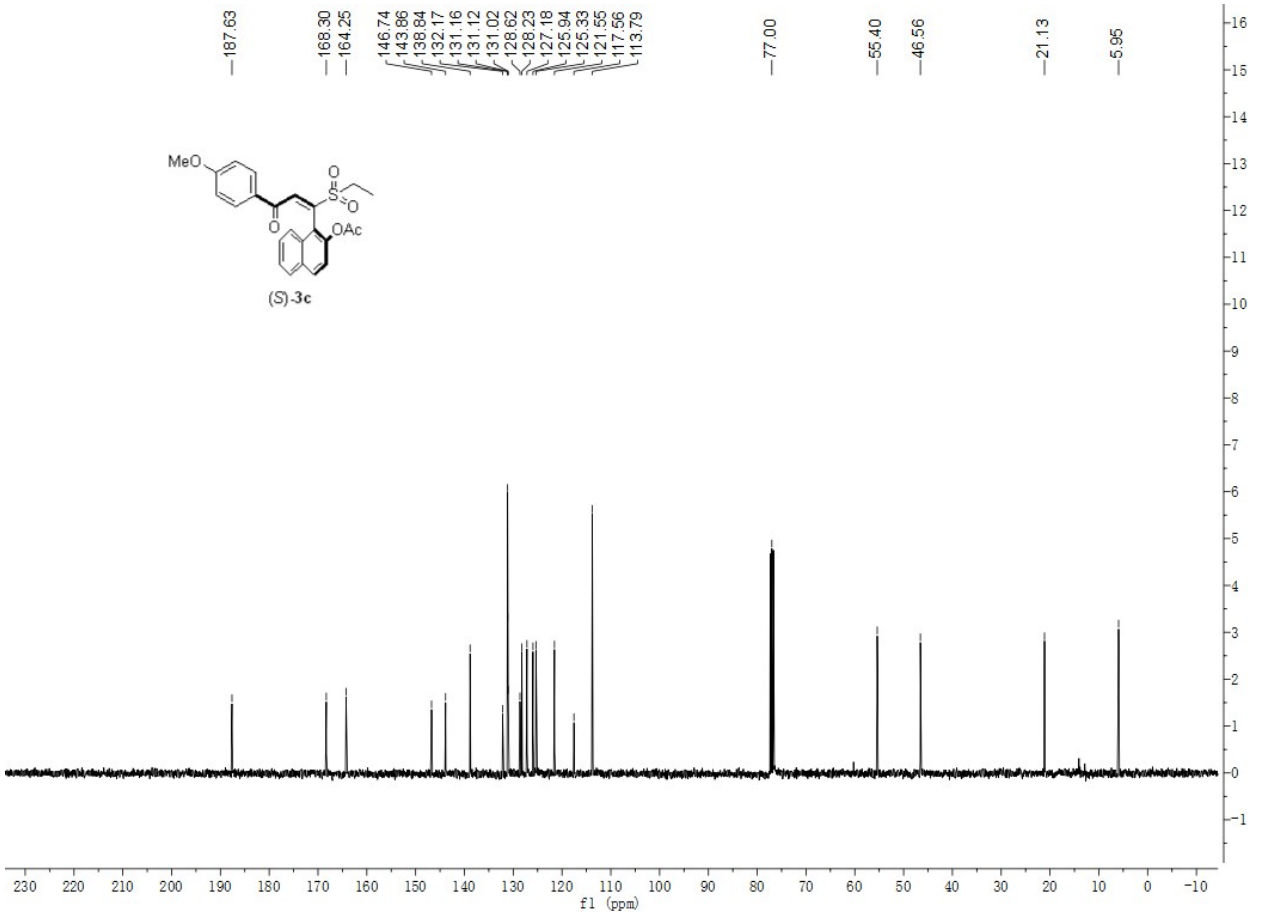
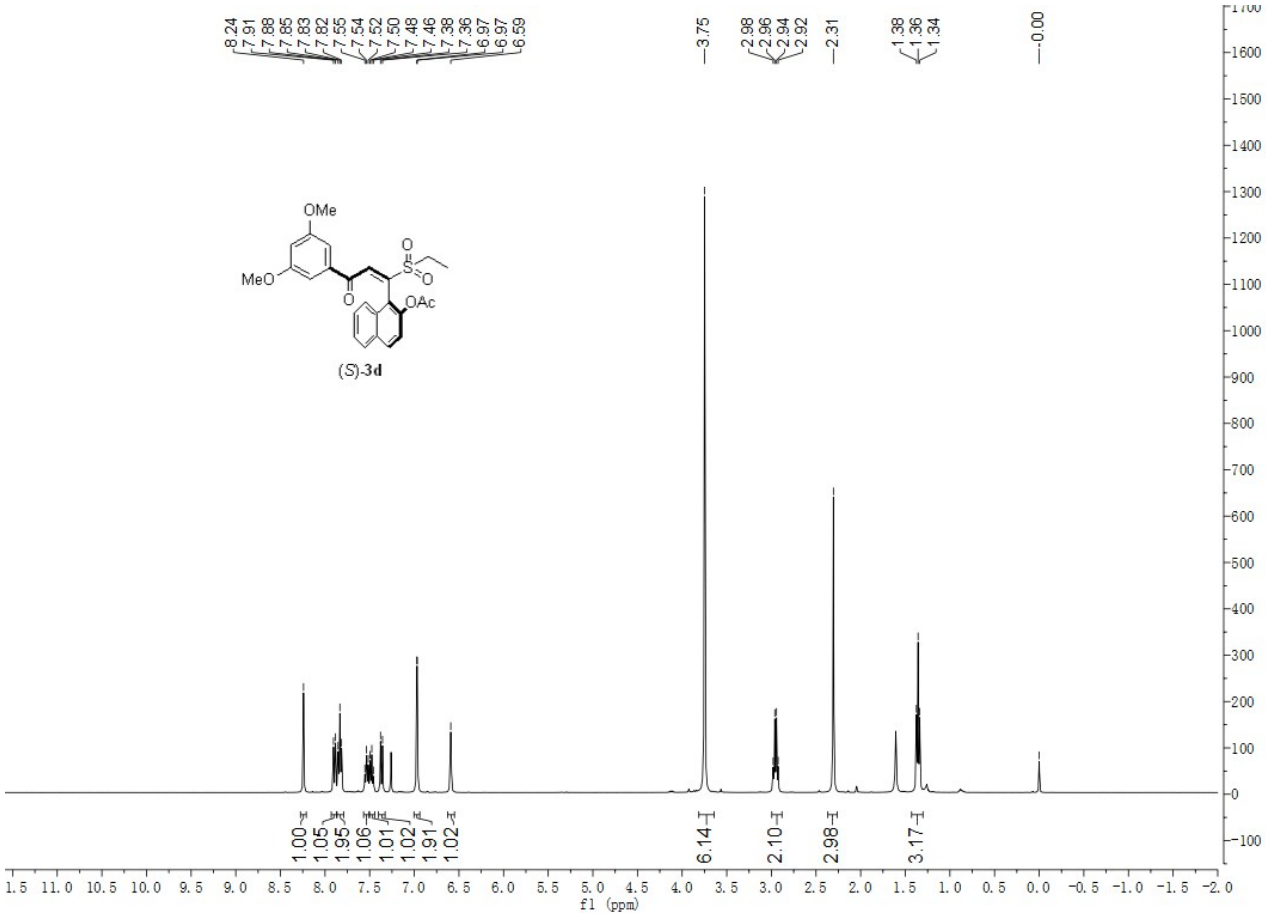
7.87
7.86
7.85
7.84
7.81
7.80
7.78
7.53
7.51
7.49
7.46
7.44
7.42
7.36
7.34
6.83
6.80
3.78
2.97
2.95
2.94
2.92
2.29
1.36
1.34
1.32
0.00
MeO
O
S
O
O
OAc
(S)-3c
1.00
2.70
1.89
0.96
0.97
0.92
1.91
2.85
2.00
2.83
3.02
f1 (ppm)


187.63
168.30
164.25
146.74
143.86
138.84
132.17
131.16
131.12
131.02
128.62
128.23
127.18
125.94
125.33
121.55
117.56
113.79
77.00
55.40
46.56
21.13
5.95
MeO
O
S
O
O
OAc
(S)-3c
f1 (ppm)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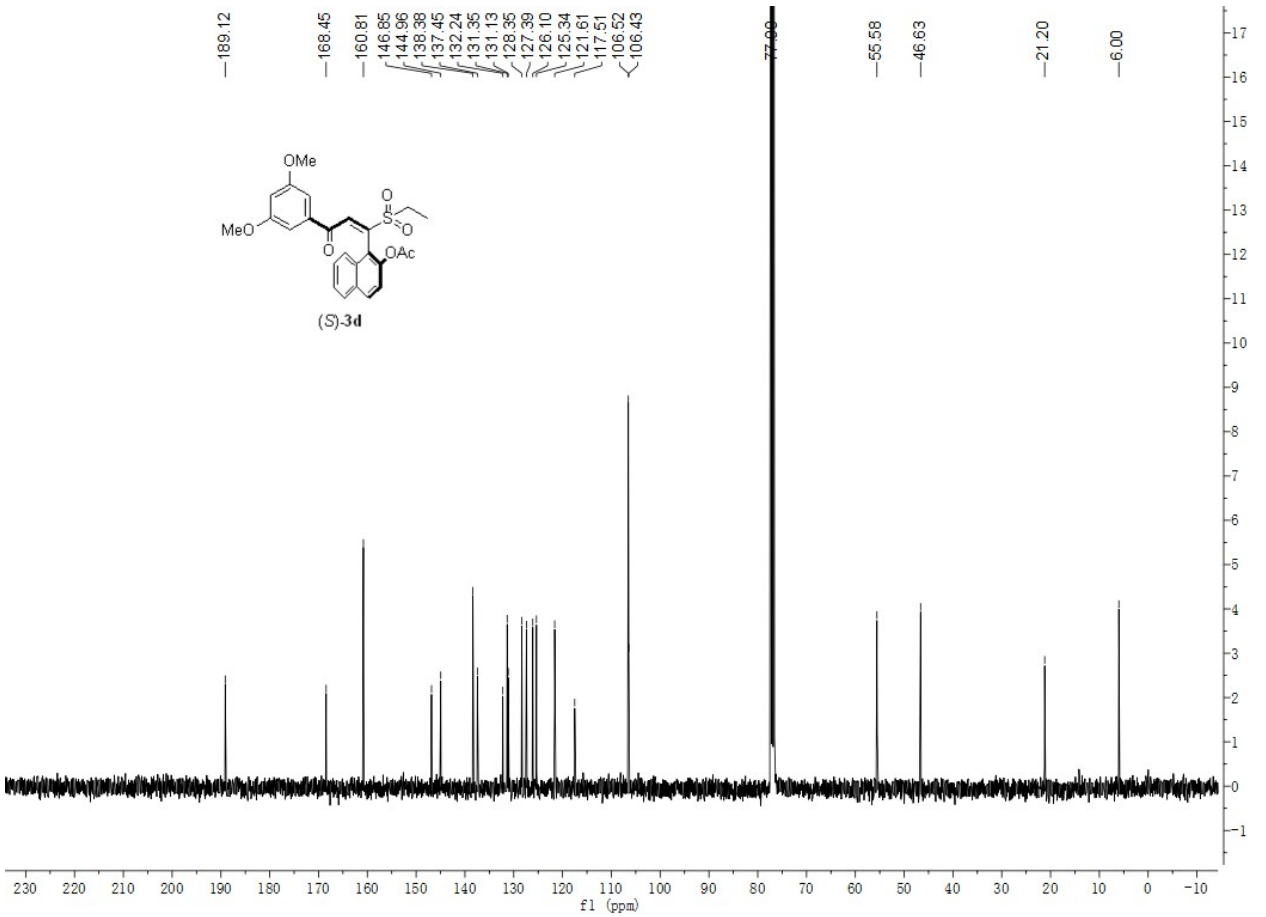
7.88
7.85
7.83
7.82
7.55
7.54
7.52
7.50
7.48
7.46
7.38
7.36
6.97
6.97
6.59
3.75
2.98
2.96
2.94
2.92
2.31
1.38
1.36
1.34
0.00
OMe
MeO
O
S
O
O
OAc
(S)-3d
1.00
1.05
1.95
1.06
1.01
1.02
1.91
1.02
6.14
2.10
2.98
3.17
f1 (ppm)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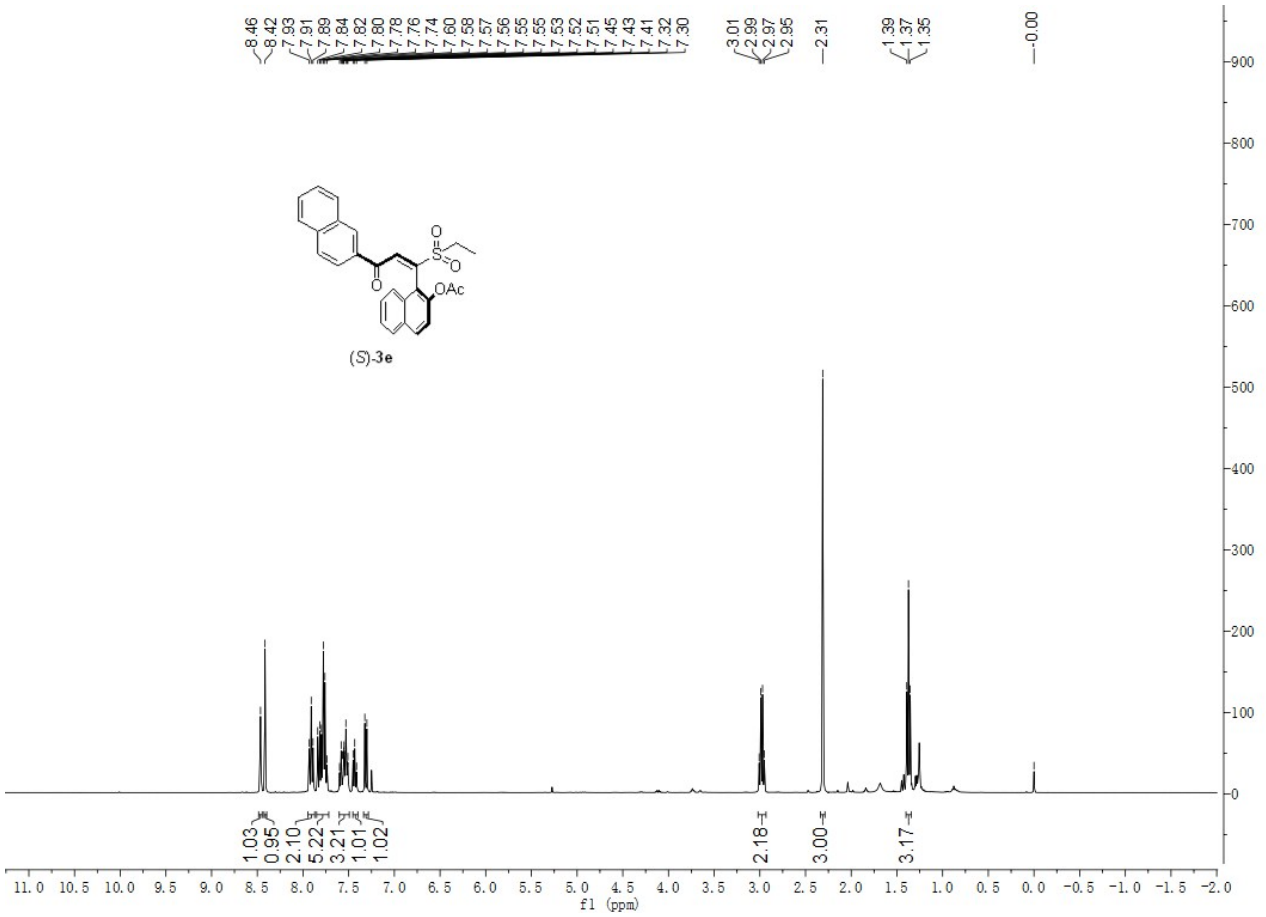
168.45
160.81
146.85
144.96
138.38
137.45
132.24
131.35
131.13
128.35
127.39
126.10
125.34
121.61
117.51
106.52
106.43
77.00
55.58
46.63
21.20
6.00
OMe
MeO
O
S
O
O
OAc
(S)-3d
f1 (ppm)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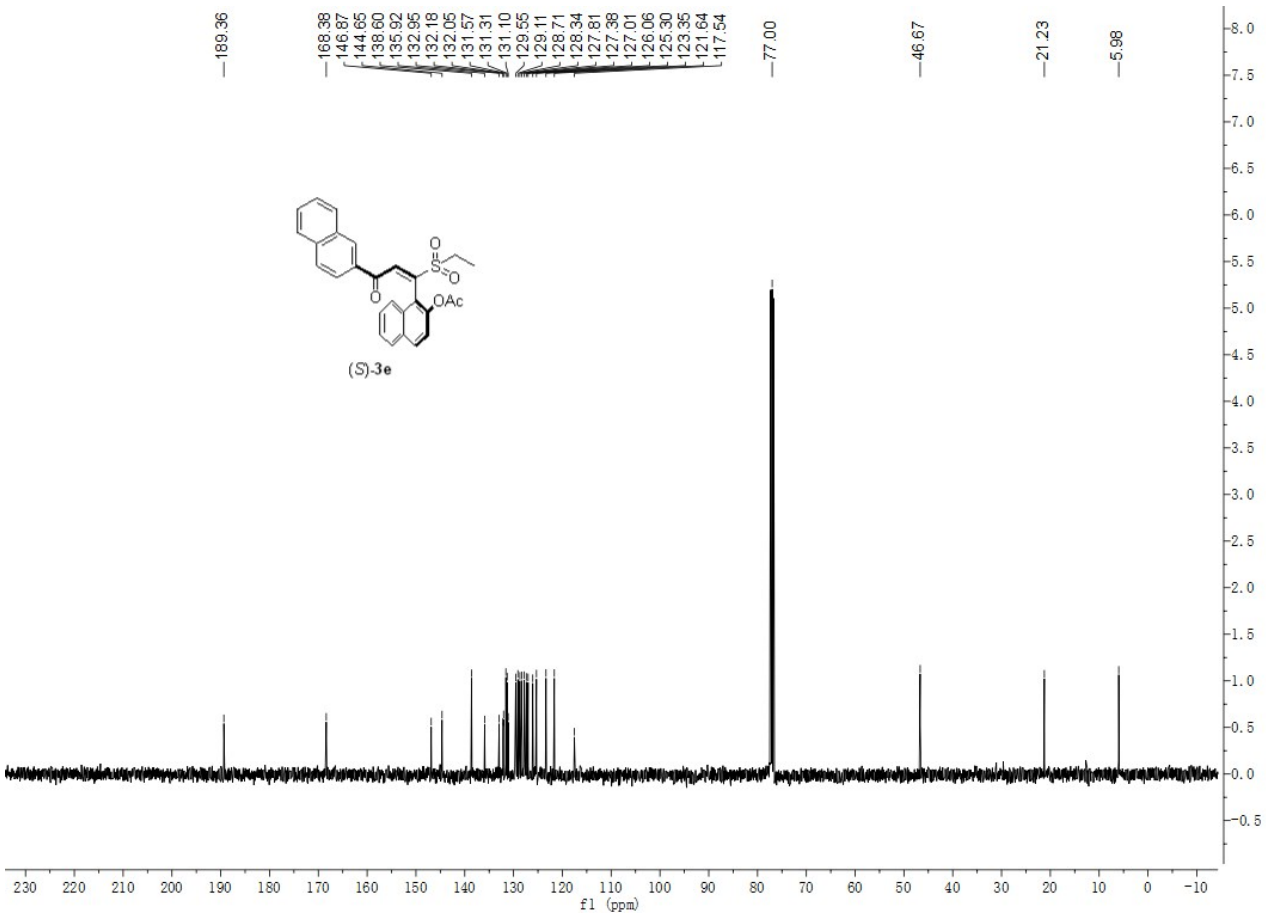
7.84
7.82
7.80
7.78
7.76
7.74
7.60
7.58
7.57
7.56
7.55
7.55
7.53
7.52
7.51
7.45
7.43
7.41
7.32
7.30
3.01
2.99
2.97
2.95
2.31
1.39
1.37
1.35
0.00
OAc
(S)-3e
1.03
0.95
2.10
5.22
3.21
1.01
1.02
2.18
3.00
3.17
f1 (ppm)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144.65
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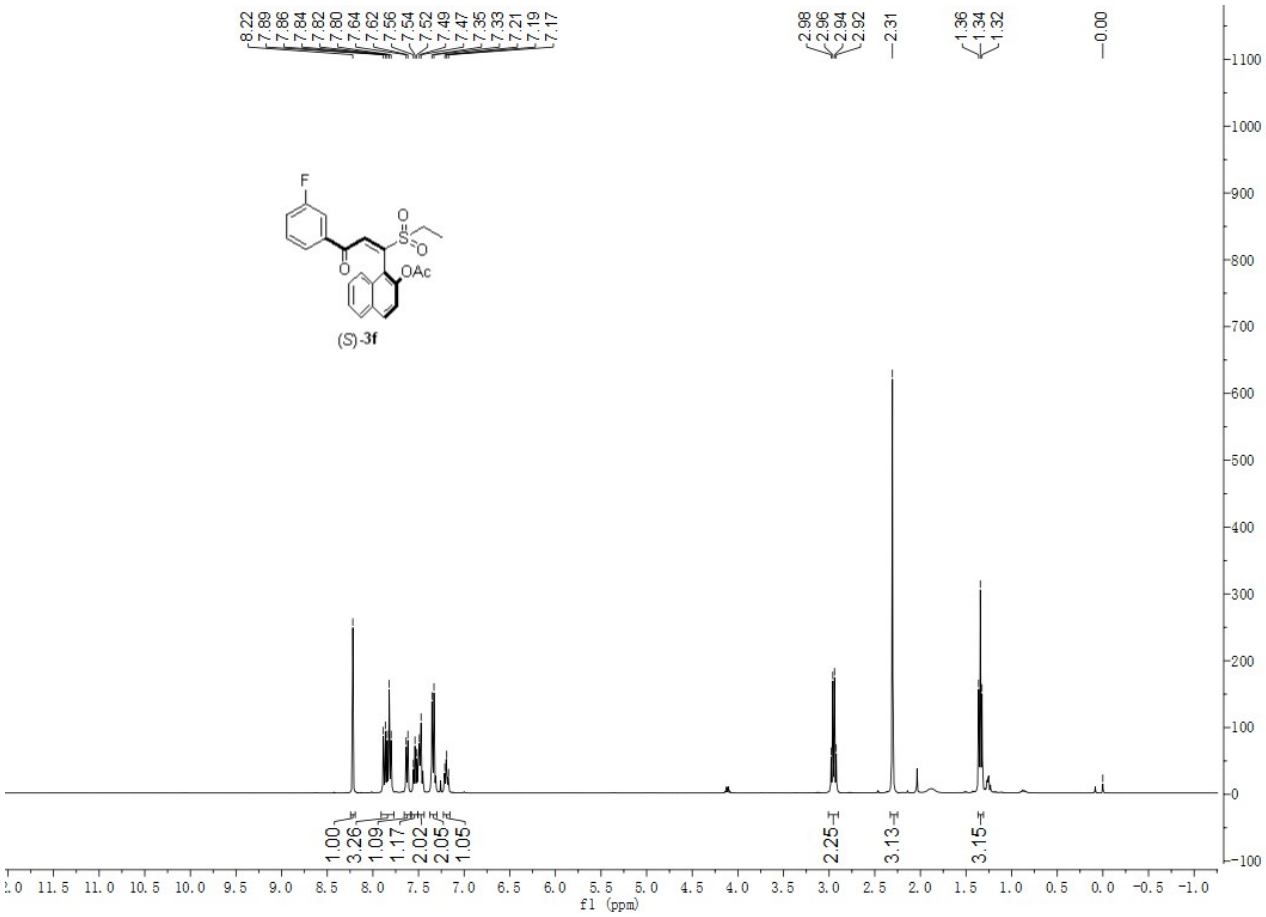
135.92
132.95
132.18
132.05
131.57
131.31
131.10
129.55
129.11
128.71
128.34
127.81
127.38
127.01
126.06
125.30
123.35
121.64
117.54
77.00
46.67
21.23
5.98
OAc
(S)-3e
f1 (ppm)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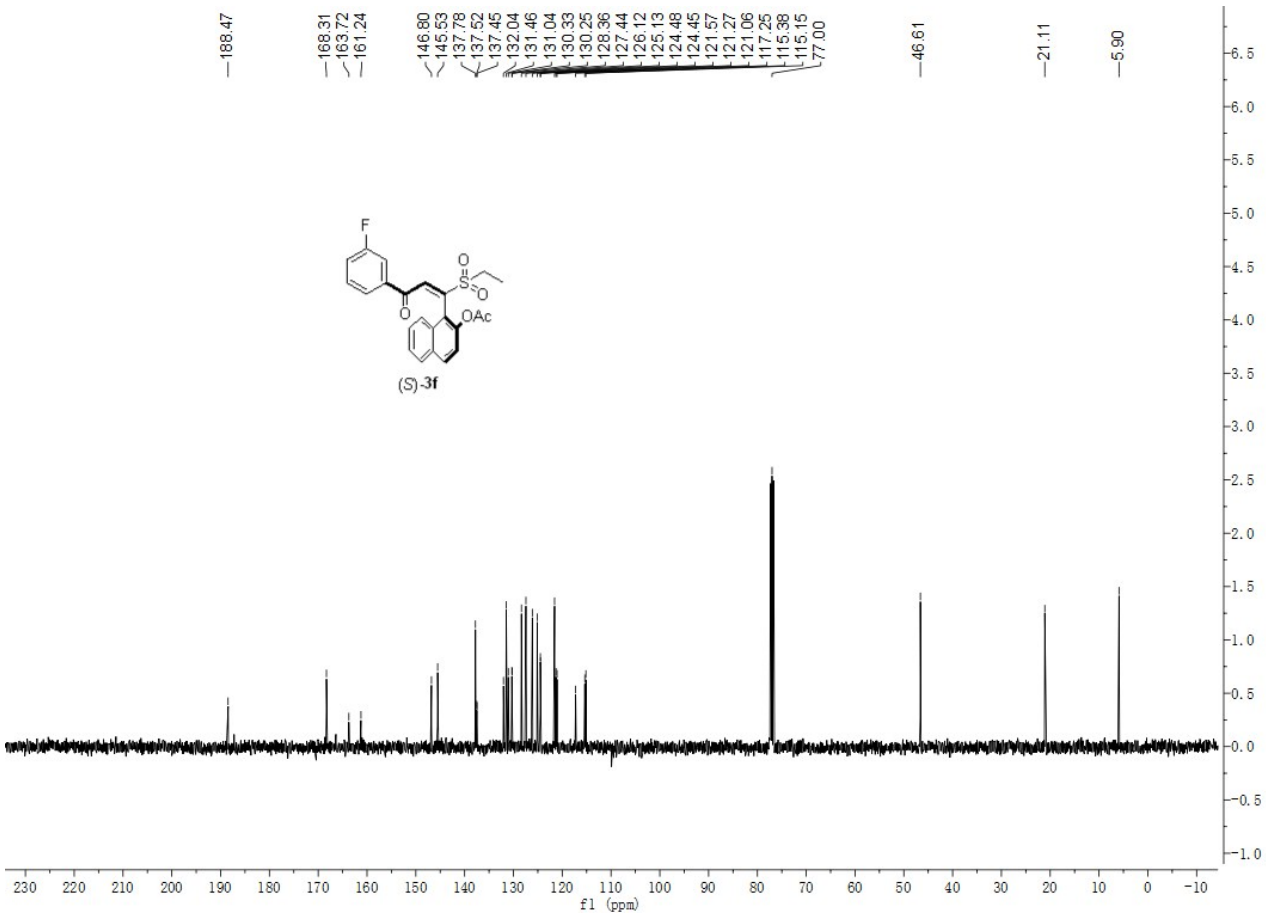
7.62
7.56
7.54
7.52
7.49
7.47
7.35
7.33
7.21
7.19
7.17
2.98
2.96
2.94
2.92
2.31
1.36
1.34
1.32
0.00
F
O
O
S
O
O
OAc
(S)-3f
1.00
3.26
1.09
1.17
2.02
2.05
1.05
2.25
3.13
3.15
f1 (ppm)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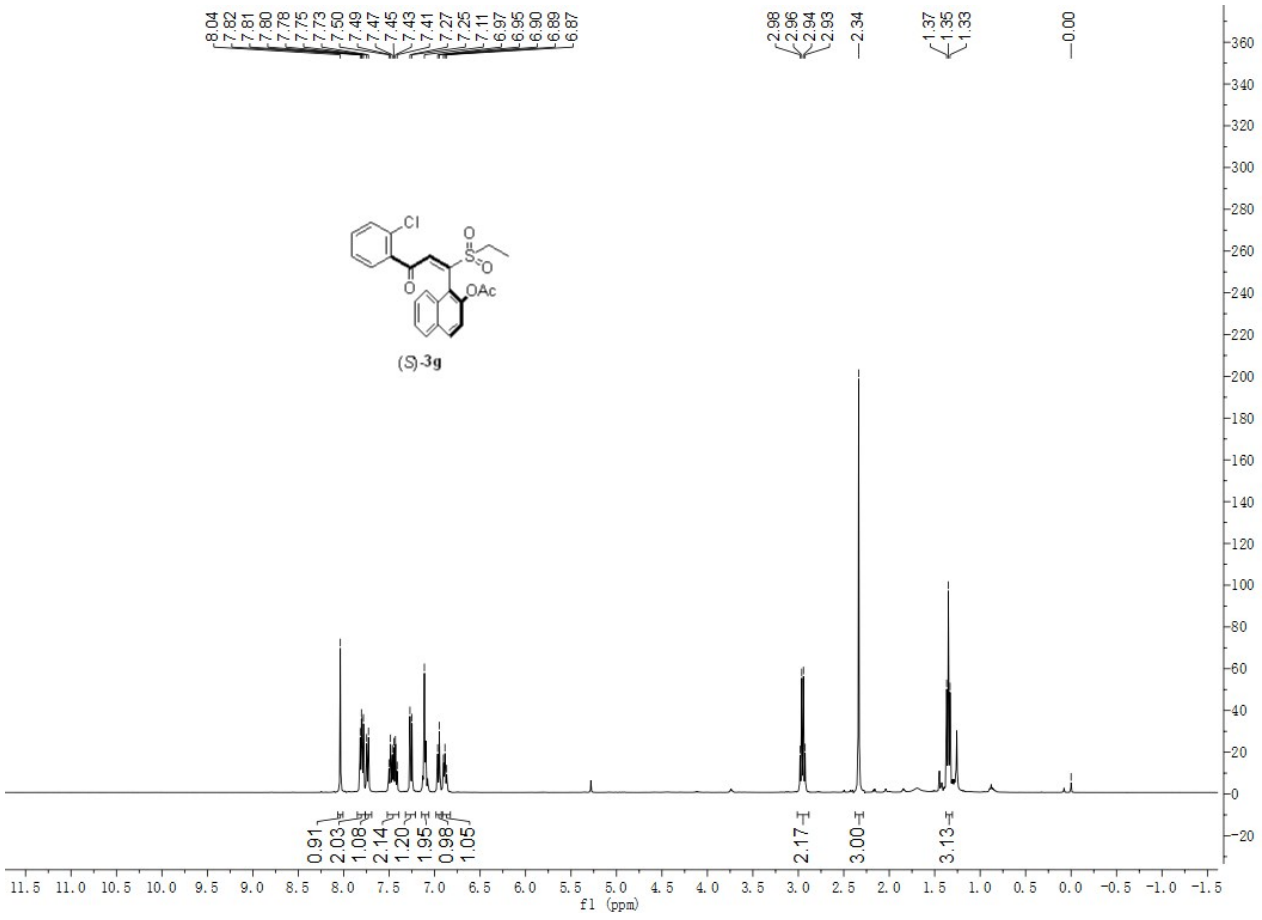
137.52
137.45
132.04
131.46
131.04
130.33
130.25
128.36
127.44
126.12
125.13
124.48
124.45
121.57
121.27
121.06
117.25
115.38
115.15
77.00
46.61
21.11
5.90
F
O
O
S
O
O
OAc
(S)-3f
f1 (ppm)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7.78
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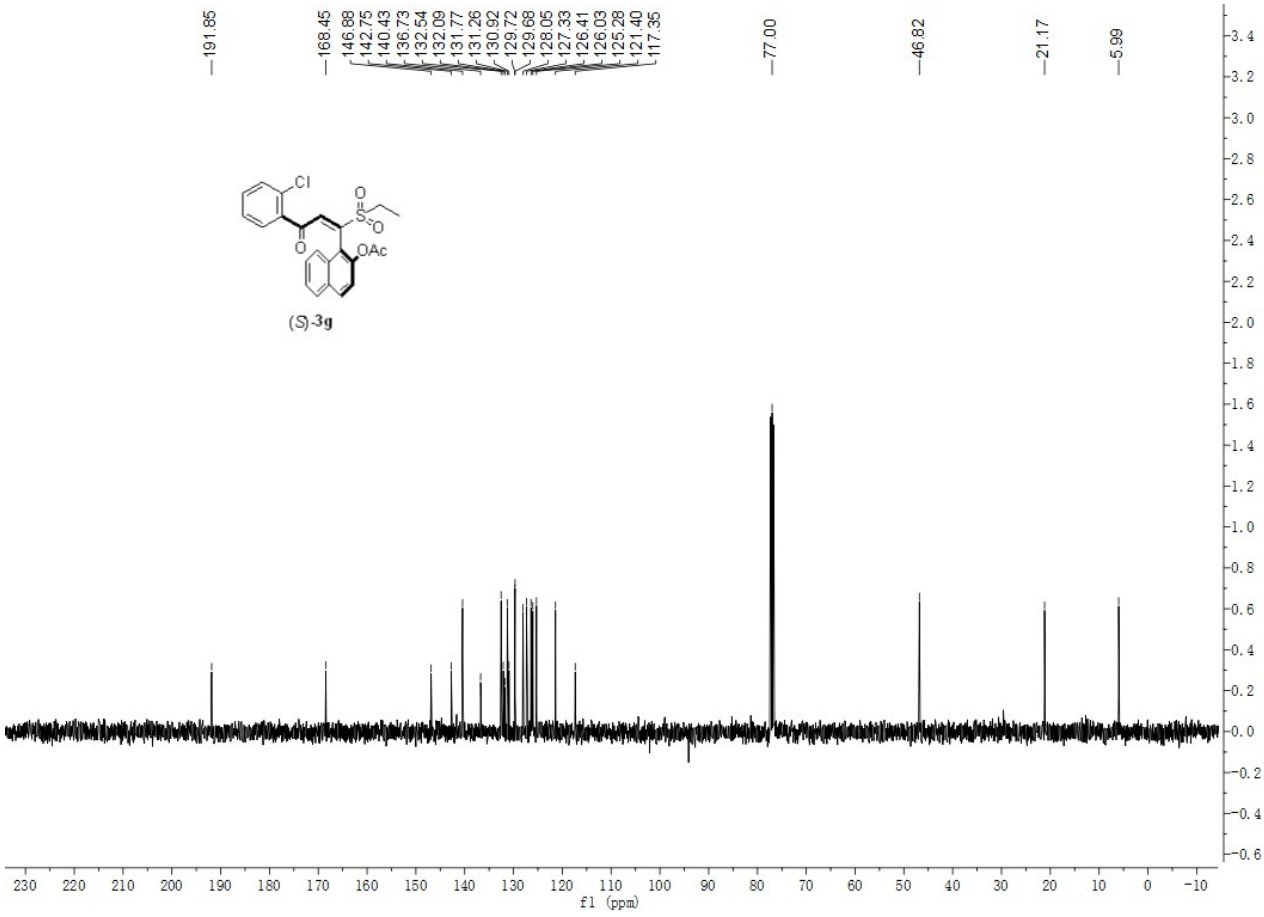
7.50
7.49
7.47
7.45
7.43
7.41
7.27
7.25
7.11
6.97
6.95
6.90
6.89
6.87
2.98
2.96
2.94
2.93
2.34
1.37
1.35
1.33
0.00
Cl
O
S
O
O
OAc
(S)-3g
0.91
2.03
1.08
2.14
1.20
1.95
0.98
1.05
2.17
3.00
3.13
f1 (ppm)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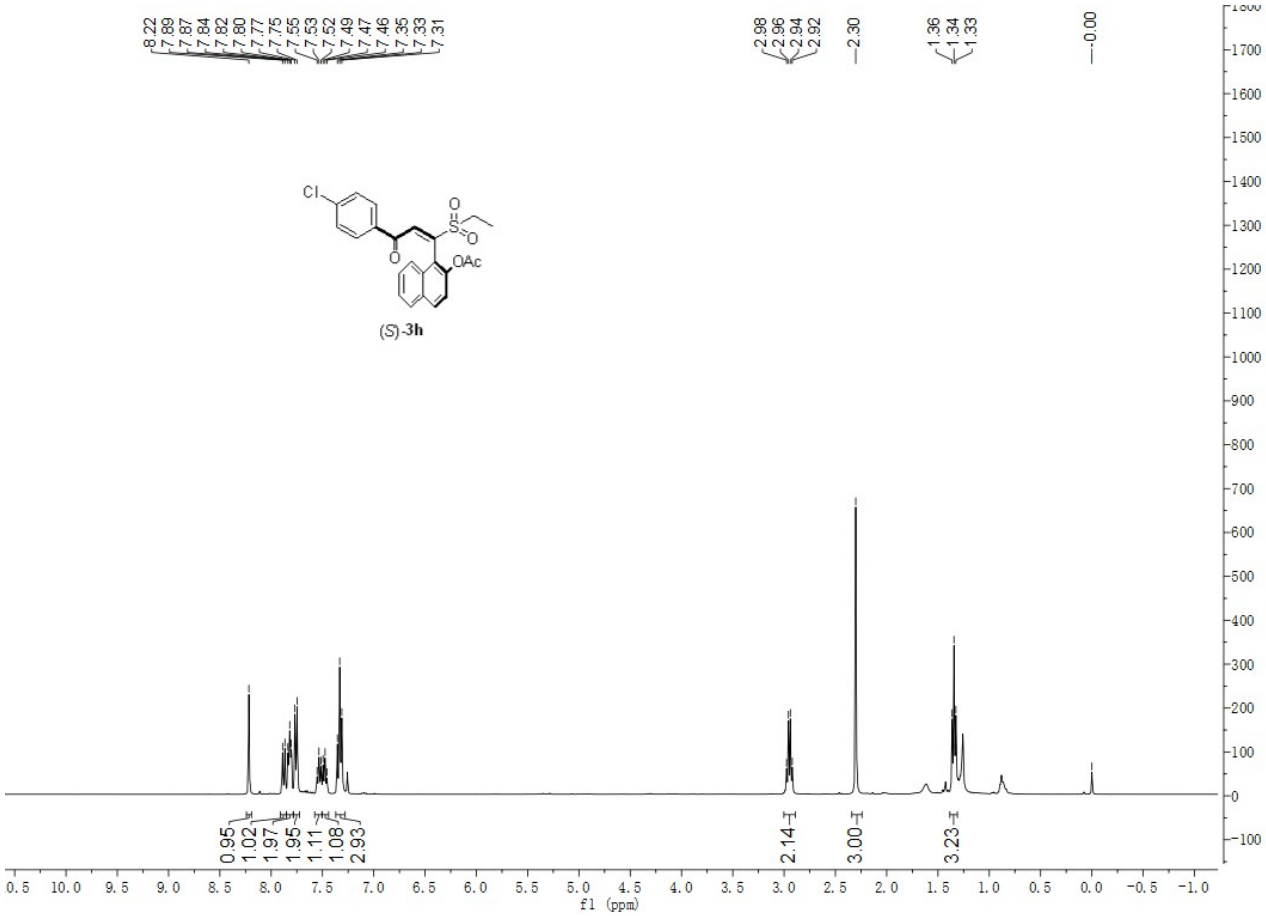
132.09
131.77
131.26
130.92
129.72
129.68
128.05
127.33
126.41
126.03
125.28
121.40
117.35
77.00
46.82
21.17
5.99
Cl
O
S
O
O
OAc
(S)-3g
f1 (ppm)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7.77
7.75
7.55
7.53
7.52
7.49
7.47
7.46
7.35
7.33
7.31
2.98
2.96
2.94
2.92
2.30
1.36
1.34
1.33
0.00
Cl
O
O
O
OAc
(S)-3h
0.95
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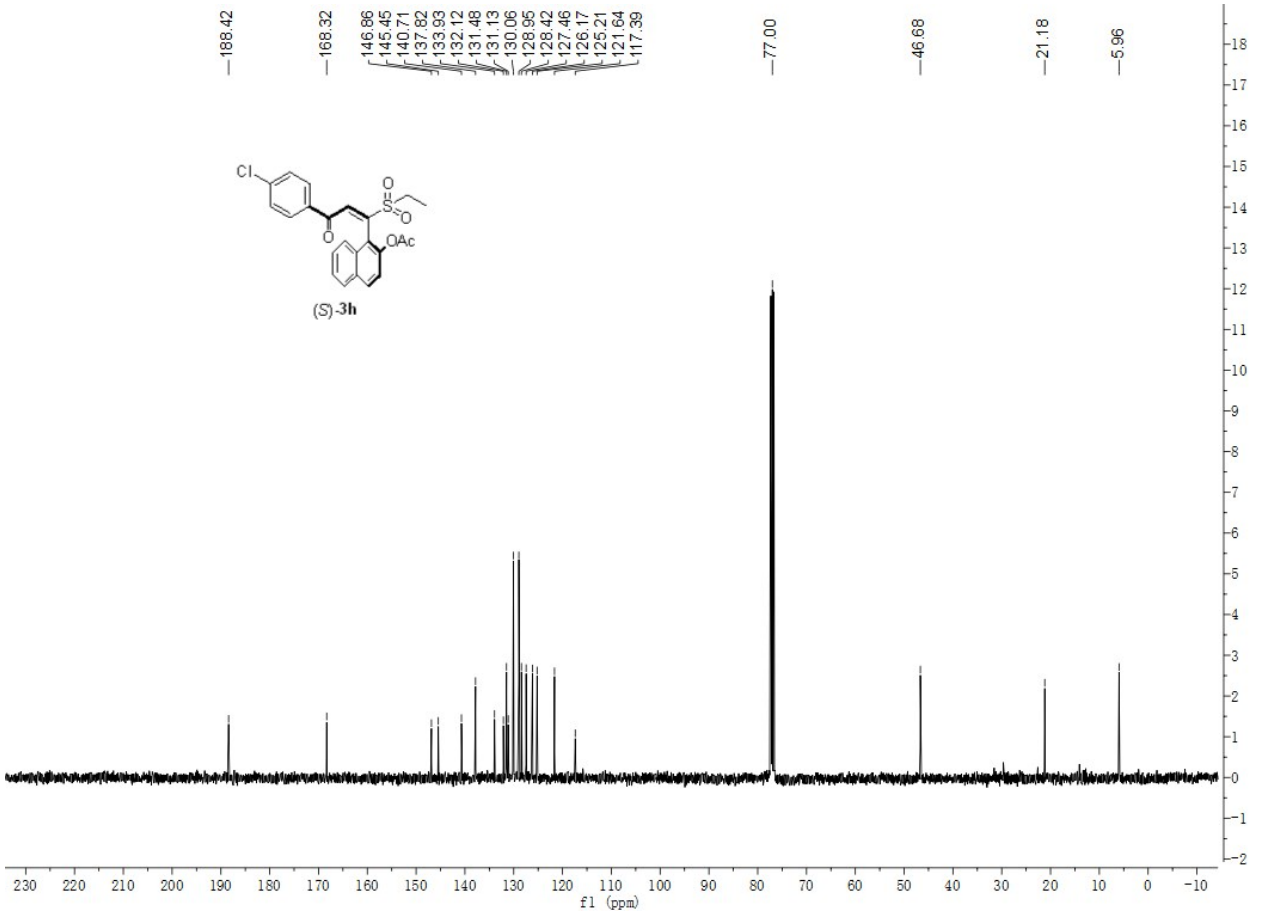
1.97
1.95
1.11
1.08
2.93
2.14
3.00
3.23
f1 (ppm)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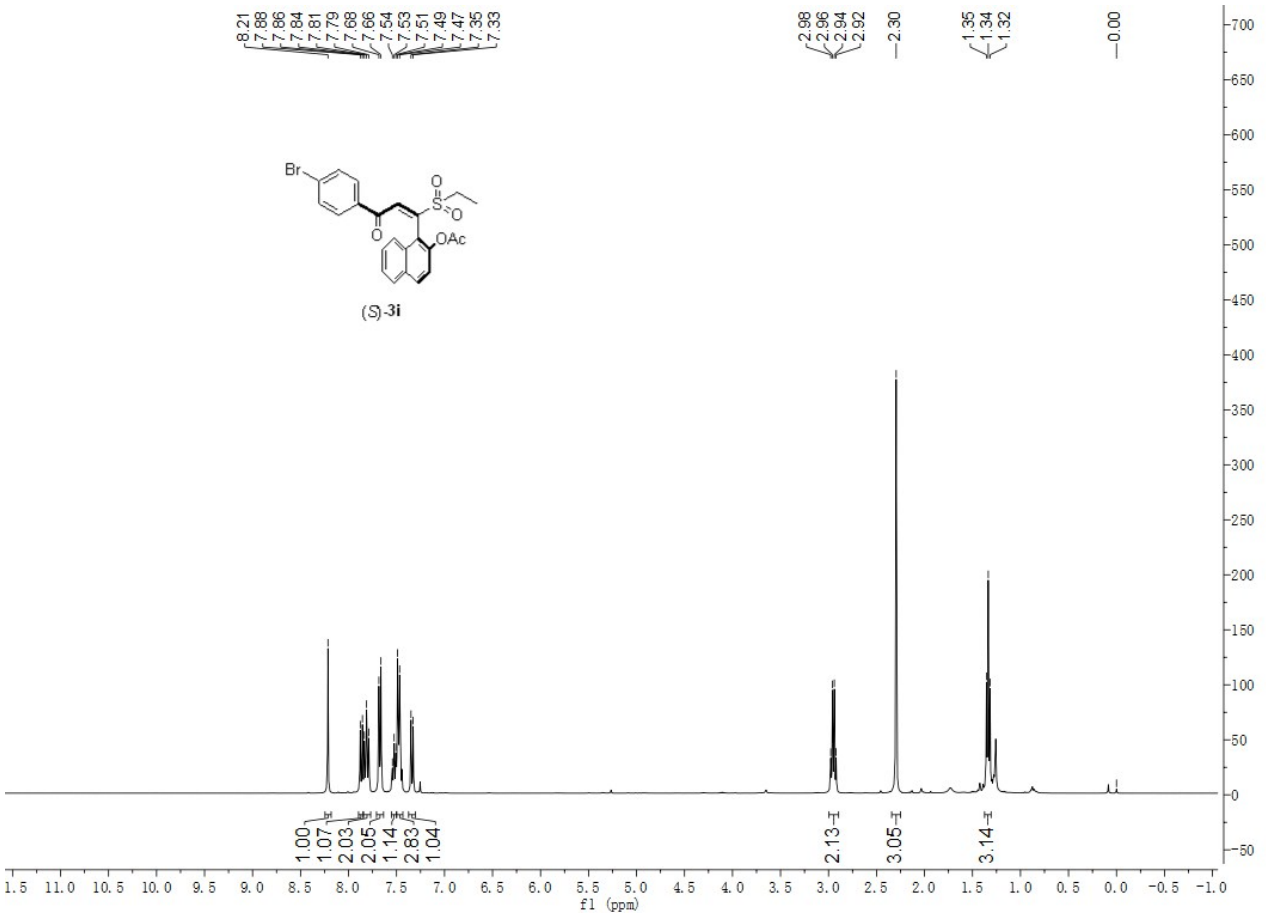
132.12
131.48
131.13
130.06
128.95
128.42
127.46
126.17
125.21
121.64
117.39
77.00
46.68
21.18
5.96
Cl
O
O
O
OAc
(S)-3h
f1 (ppm)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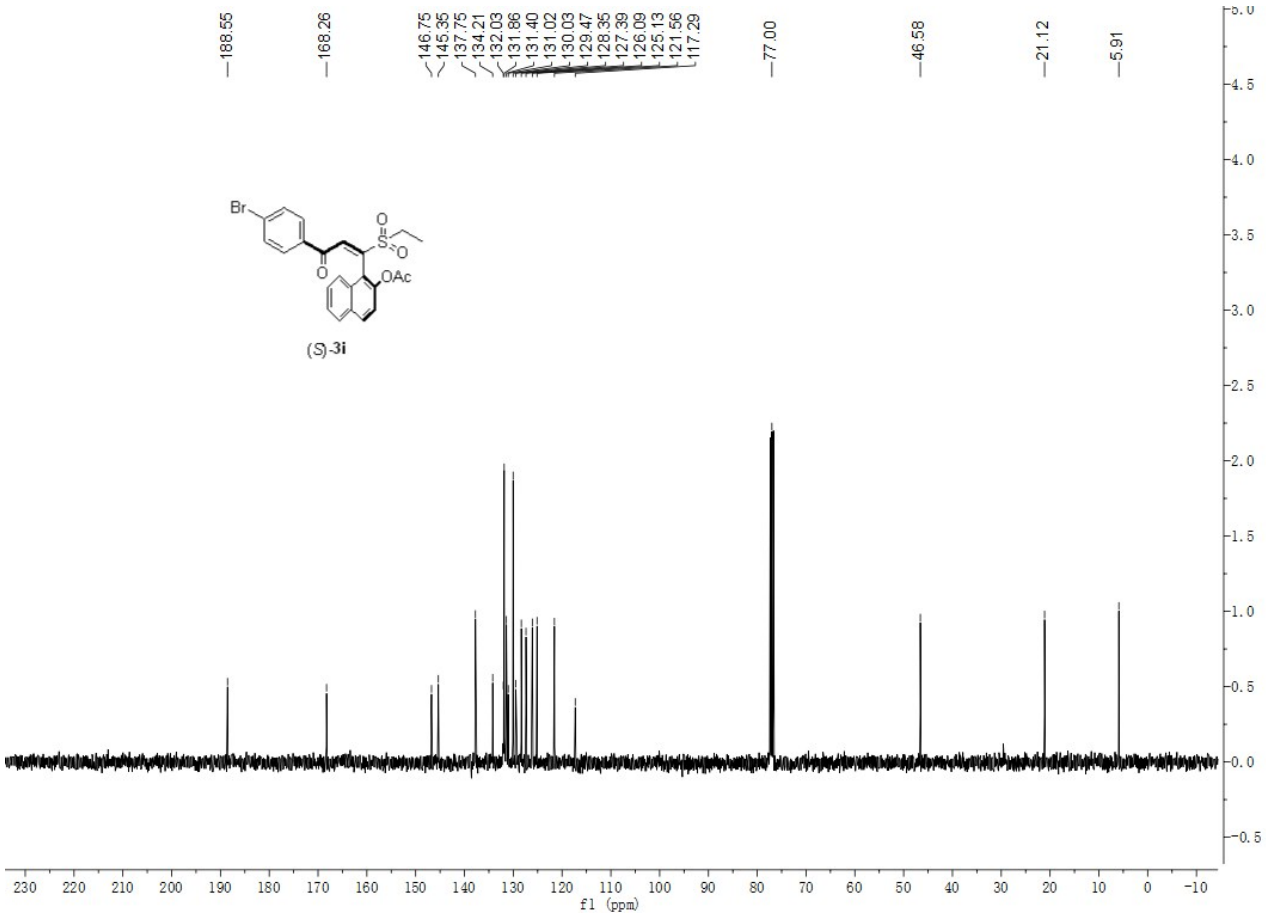
7.84
7.81
7.79
7.68
7.66
7.54
7.53
7.51
7.49
7.47
7.35
7.33
2.98
2.96
2.94
2.92
2.30
1.35
1.34
1.32
0.00
Br
O
S
O
O
OAc
(S)-3i
1.00
1.07
2.03
2.05
1.14
2.83
1.04
2.13
3.05
3.14
f1 (ppm)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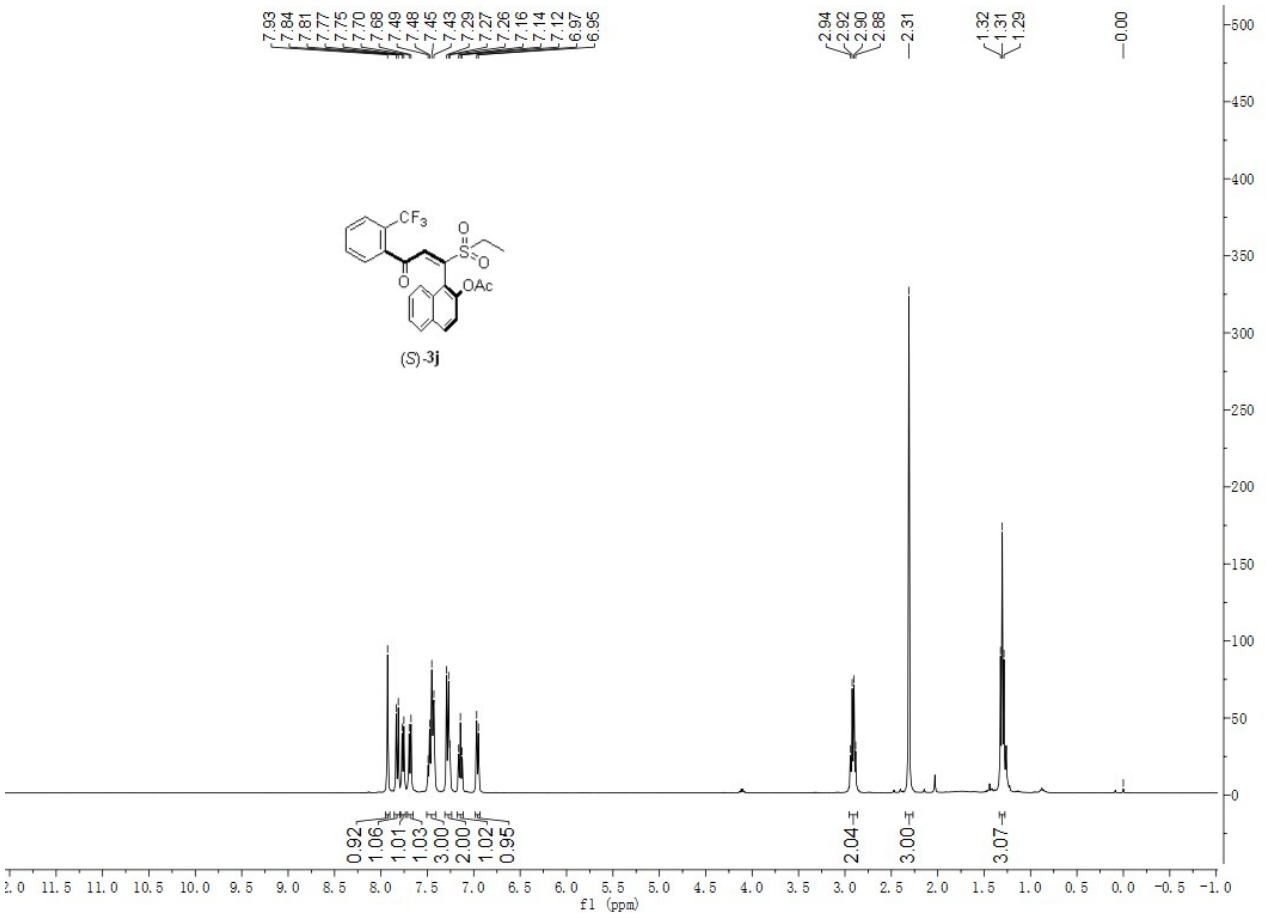
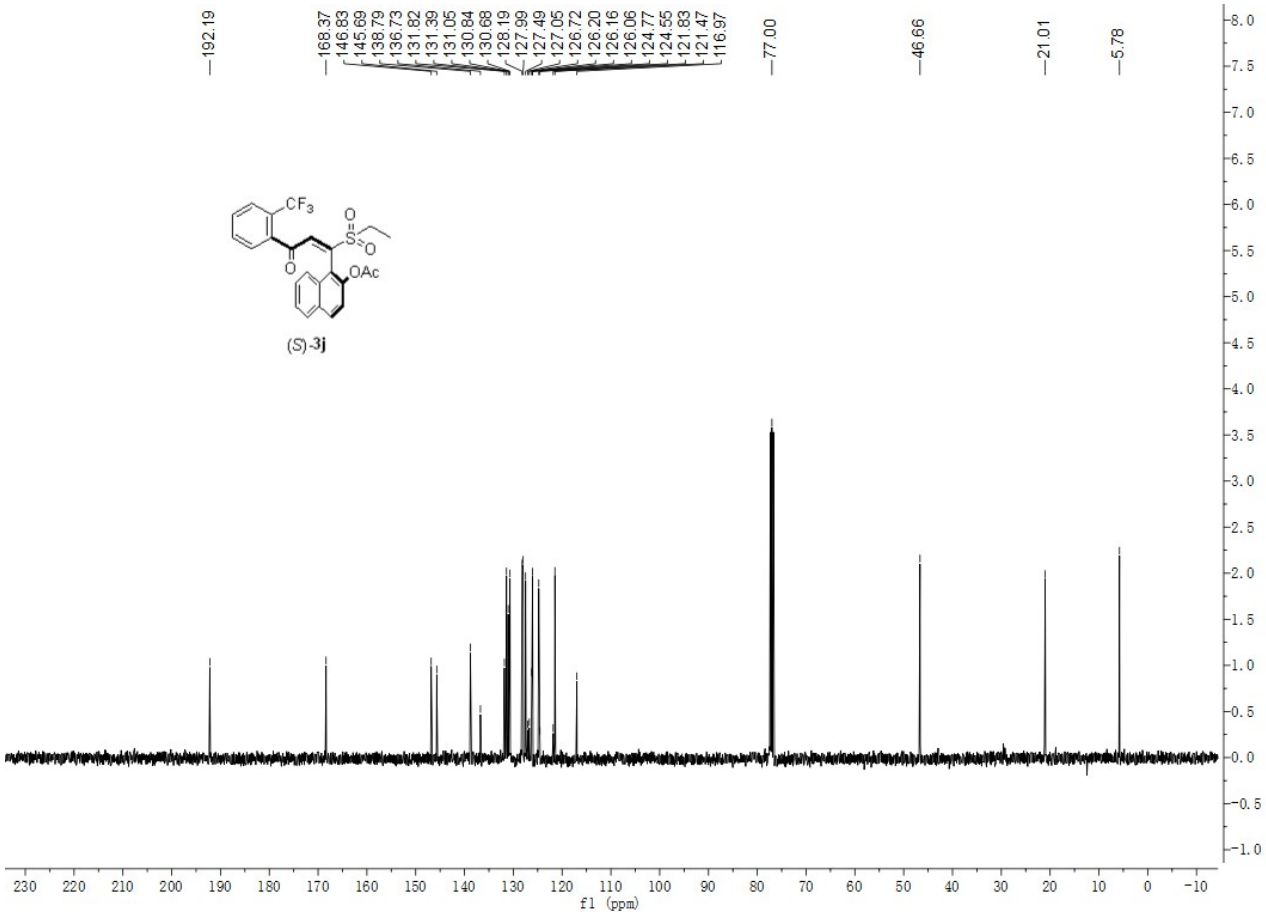
145.35
137.75
134.21
132.03
131.86
131.40
131.02
130.03
129.47
128.35
127.39
126.09
125.13
121.56
117.29
77.00
46.58
21.12
5.91
Br
O
S
O
O
OAc
(S)-3i
f1 (ppm)


7.93
7.84
7.81
7.77
7.75
7.70
7.68
7.49
7.48
7.45
7.43
7.29
7.27
7.26
7.16
7.14
7.12
6.97
6.95
2.94
2.92
2.90
2.88
2.31
1.32
1.31
1.29
0.00
CF3
O
S
O
O
OAc
(S)-3j
0.92
1.06
1.01
1.03
3.00
2.00
1.02
0.95
2.04
3.00
3.07
f1 (ppm)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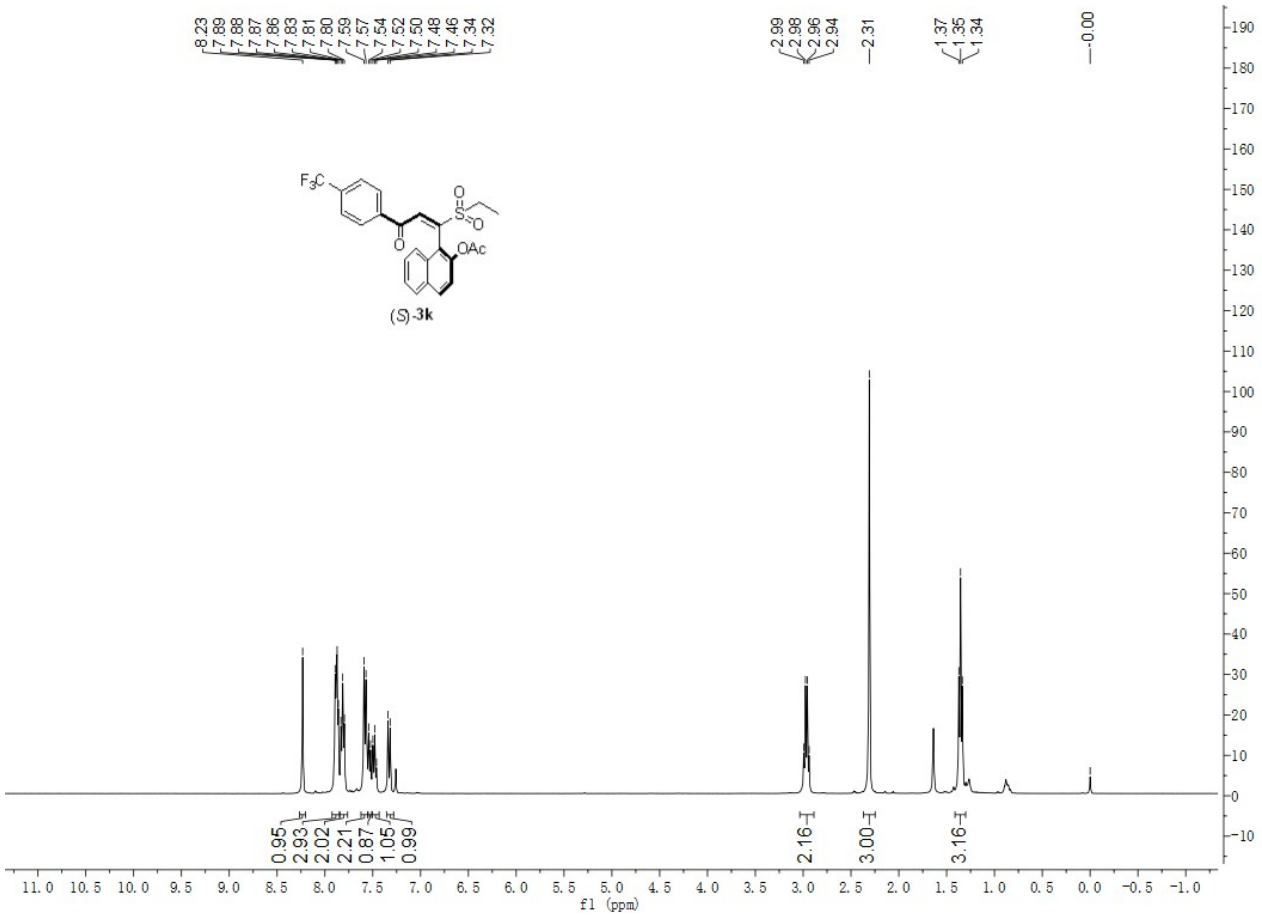
136.73
131.82
131.39
131.05
130.84
130.68
128.19
127.99
127.49
127.05
126.72
126.20
126.16
126.06
124.77
124.55
121.83
121.47
116.97
77.00
46.66
21.01
5.78
CF3
O
S
O
O
OAc
(S)-3j
f1 (ppm)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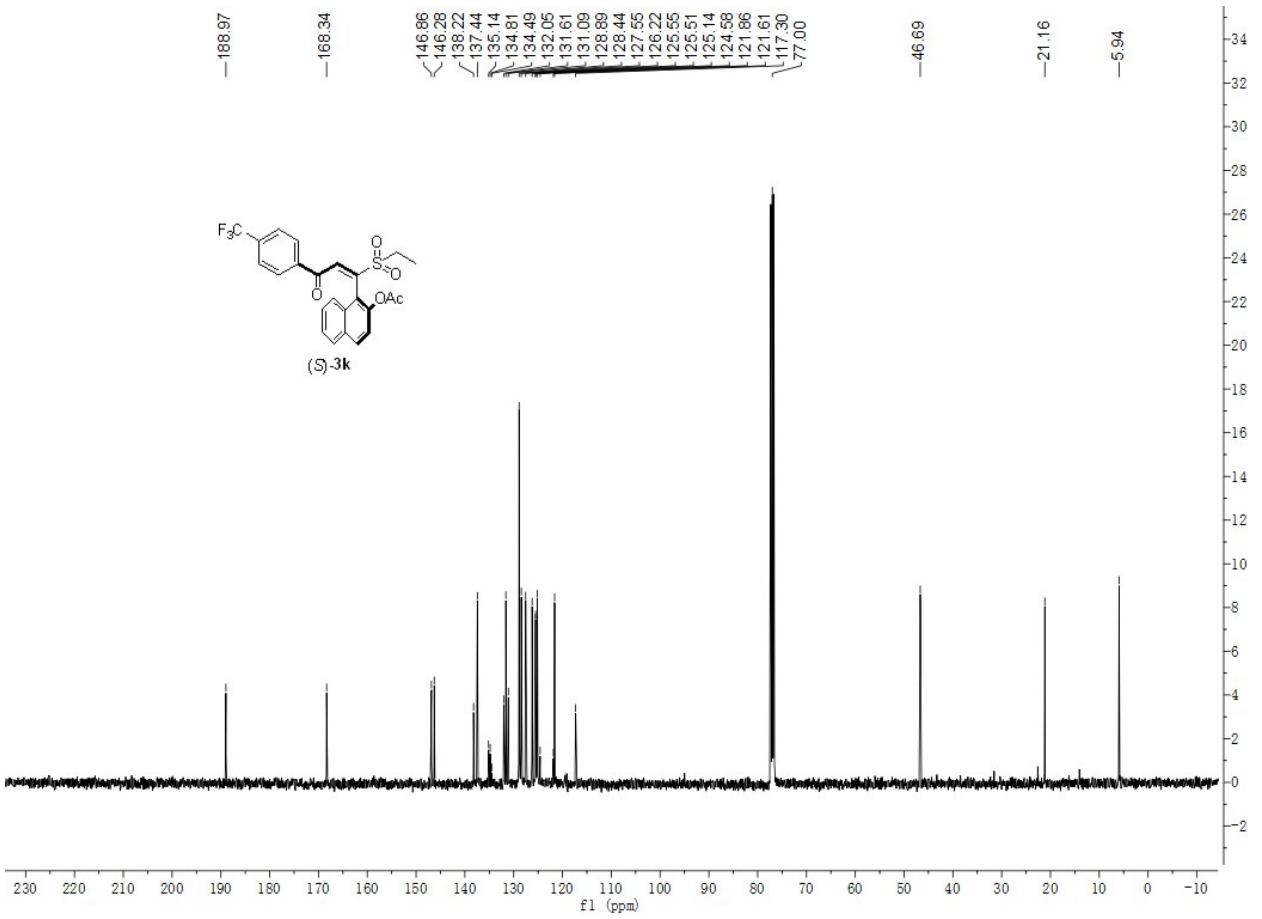
7.89
7.88
7.87
7.86
7.83
7.81
7.80
7.59
7.57
7.54
7.52
7.50
7.48
7.46
7.34
7.32
2.99
2.98
2.96
2.94
2.31
1.37
1.35
1.34
0.00
F3C
O
S
O
O
OAc
(S)-3k
0.95
2.93
2.02
2.21
0.87
1.05
0.99
2.16
3.00
3.16
f1 (ppm)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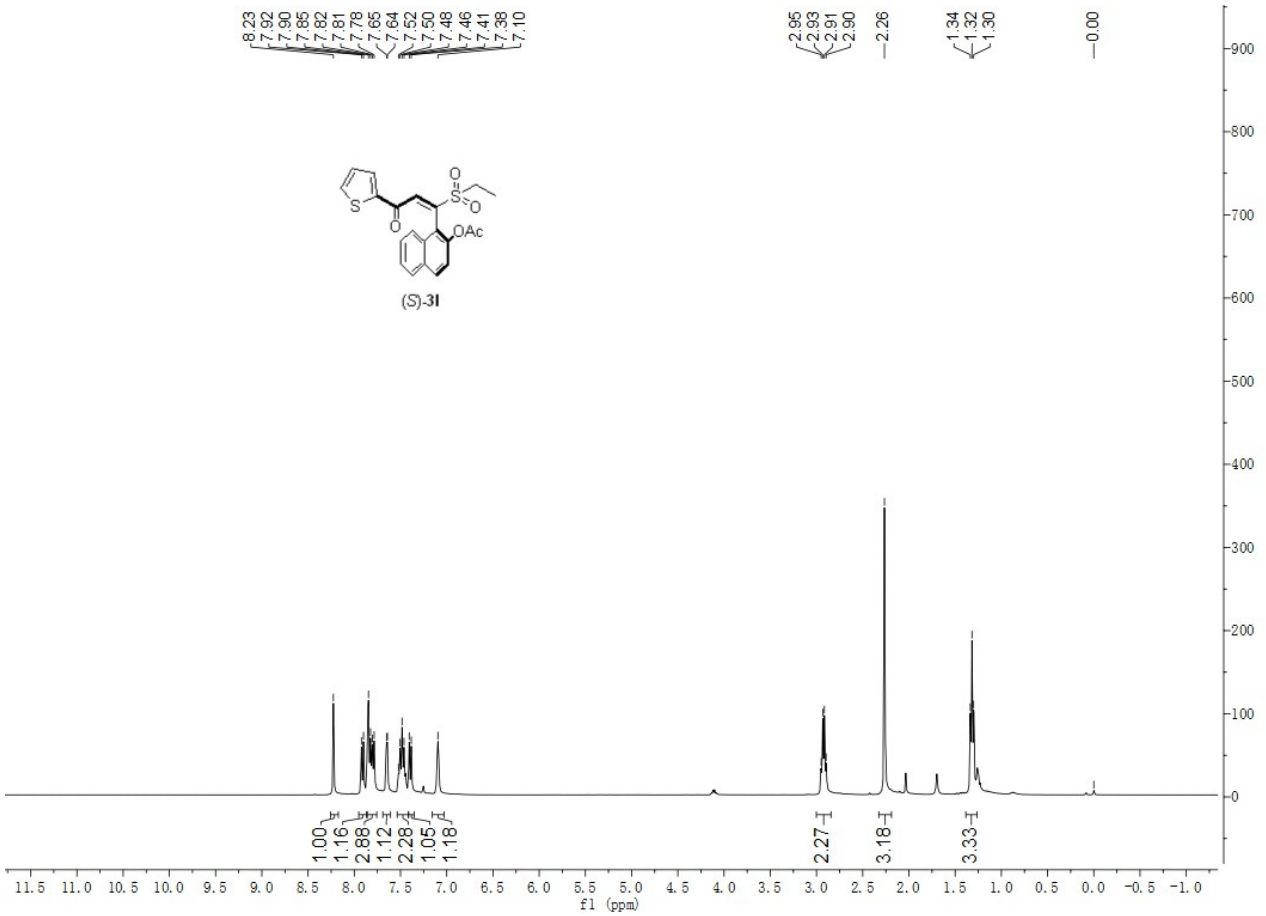
146.86
146.28
138.22
137.44
135.14
134.81
134.49
132.05
131.61
131.09
128.89
128.44
127.55
126.22
125.55
125.51
125.14
124.58
121.86
121.61
117.30
77.00
46.69
21.16
5.94
F3C
O
S
O
O
OAc
(S)-3k
f1 (ppm)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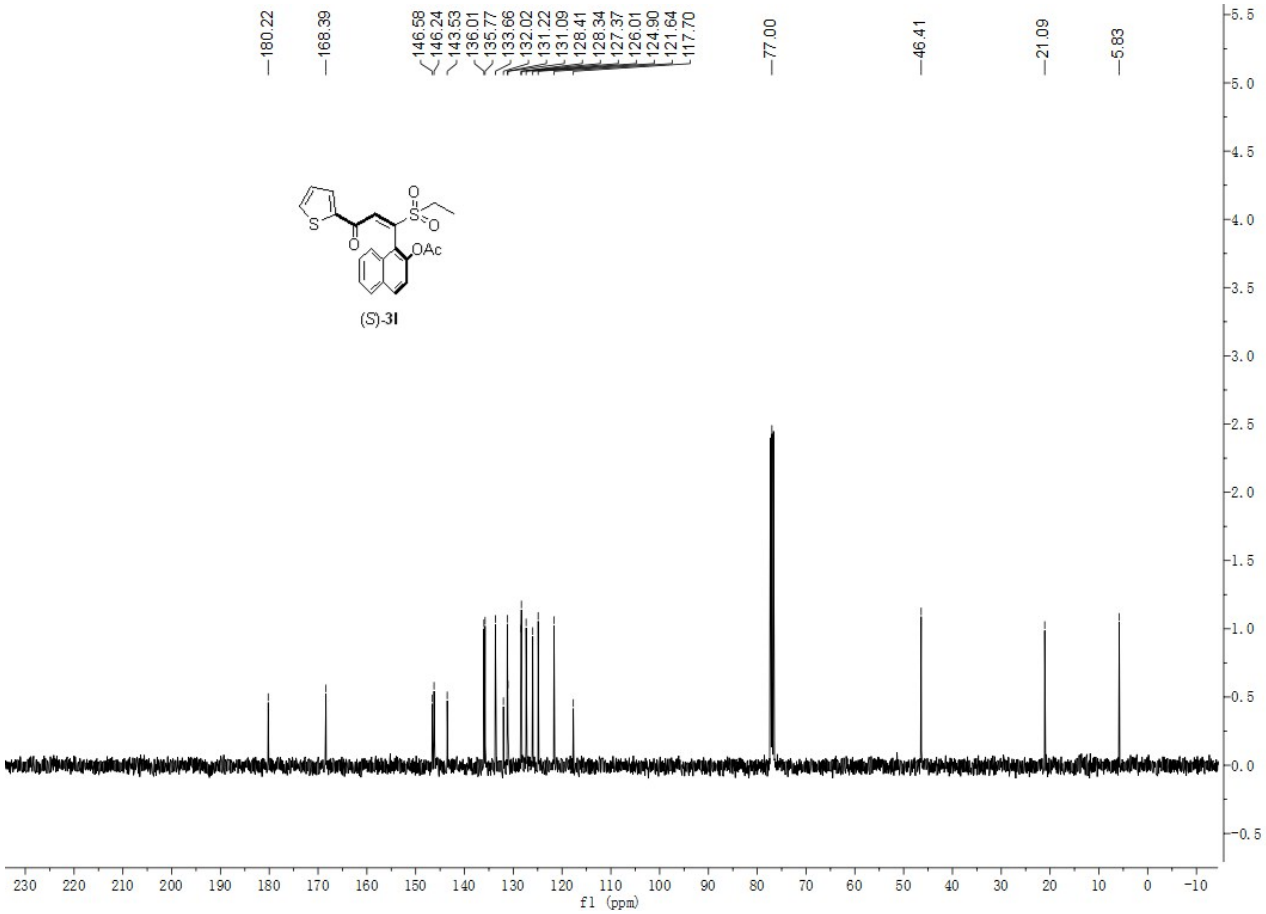
7.81
7.78
7.65
7.64
7.52
7.50
7.48
7.46
7.41
7.38
7.10
2.95
2.93
2.91
2.90
2.26
1.34
1.32
1.30
0.00
(S)-3l
1.00
1.16
2.88
1.12
2.28
1.05
1.18
2.27
3.18
3.33
f1 (ppm)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136.01
135.77
133.66
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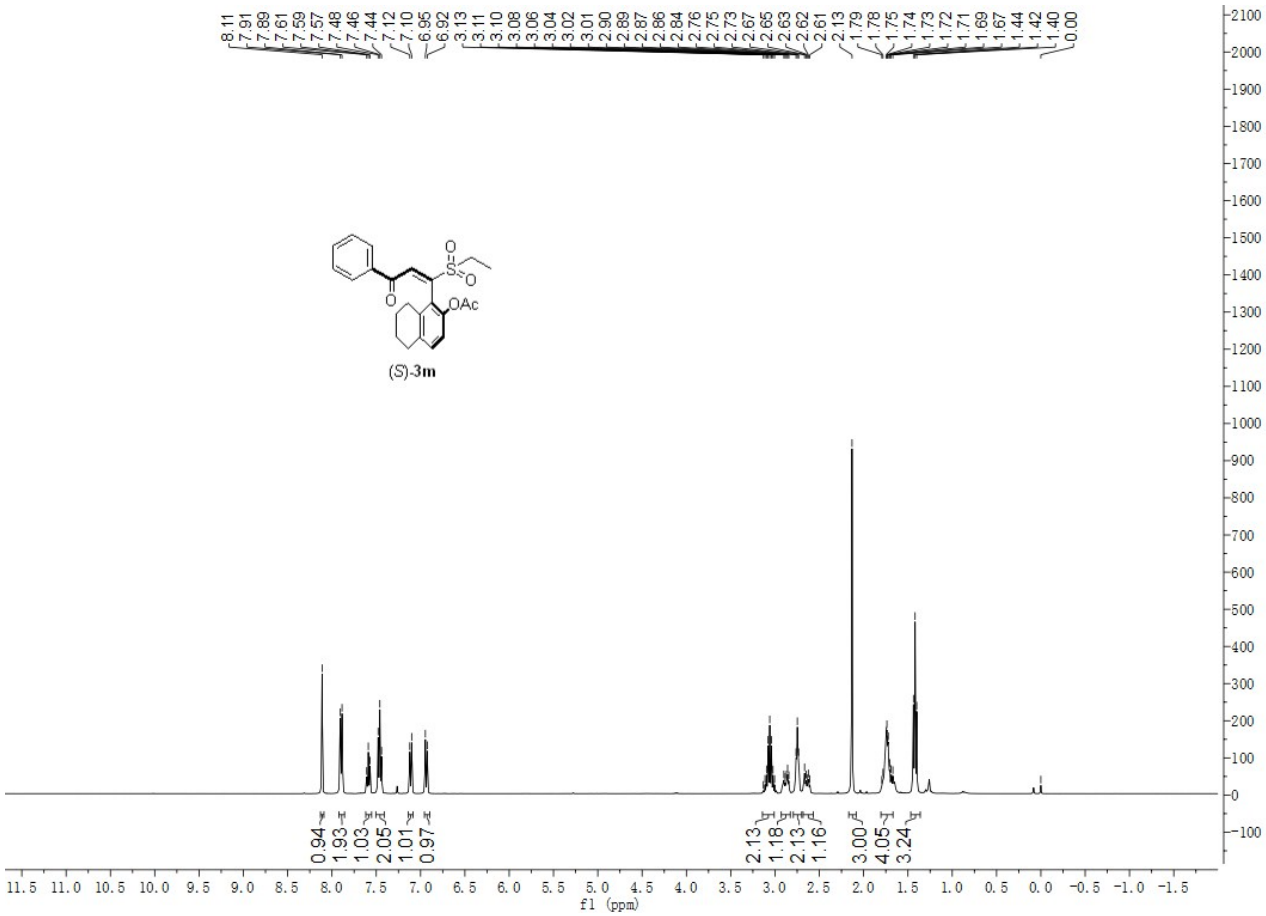
131.22
131.09
128.41
128.34
127.37
126.01
124.90
121.64
117.70
77.00
46.41
21.09
5.83
(S)-3l
f1 (ppm)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7.46
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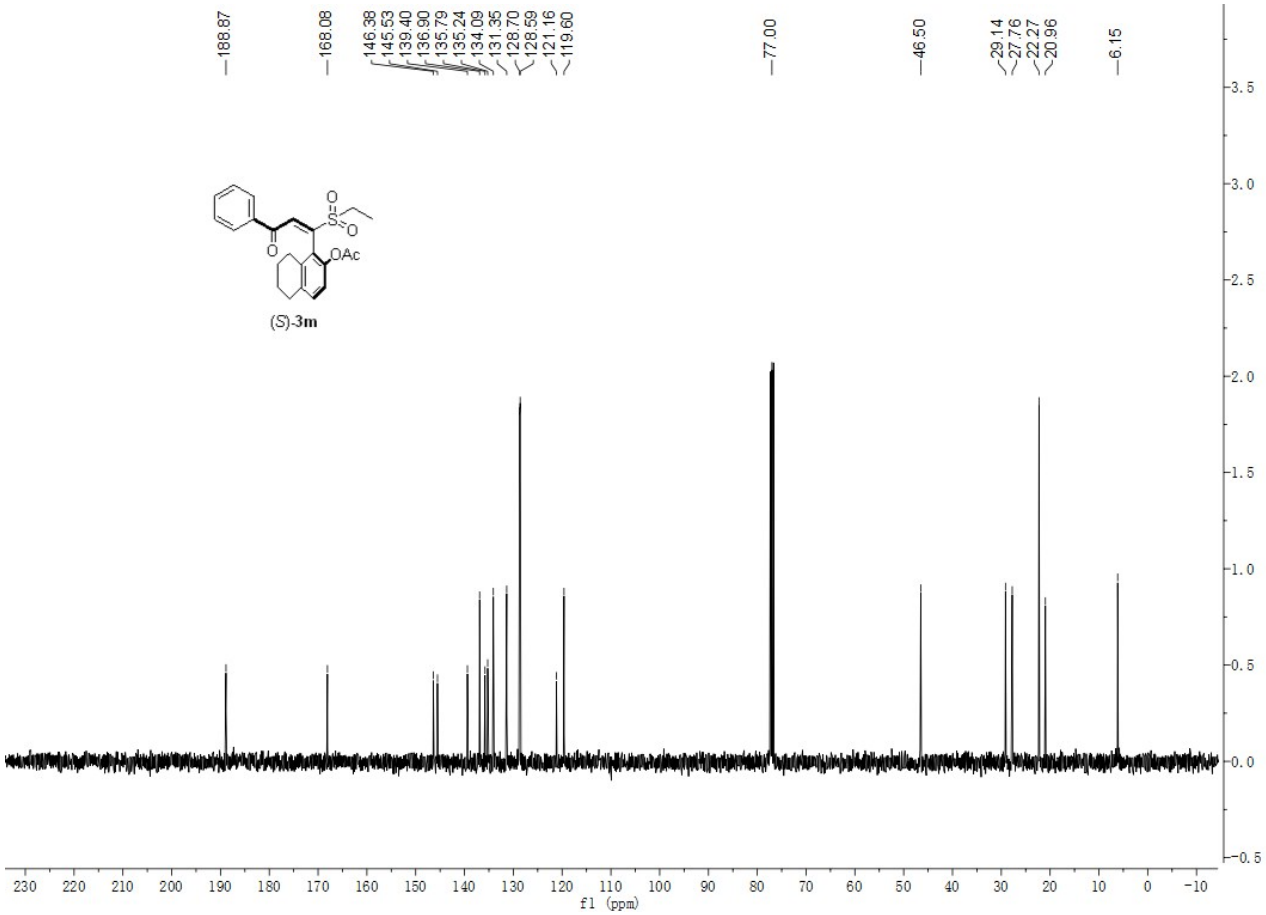
7.12
7.10
6.95
6.92
3.13
3.11
3.10
3.08
3.06
3.04
3.02
3.01
2.90
2.89
2.87
2.86
2.84
2.76
2.75
2.73
2.67
2.65
2.63
2.62
2.61
2.13
1.79
1.78
1.75
1.74
1.73
1.72
1.71
1.69
1.67
1.44
1.42
1.40
0.00
OAc
(S)-3m
0.94
1.93
1.03
2.05
1.01
0.97
2.13
1.18
2.13
1.16
3.00
4.05
3.24
f1 (ppm)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135.79
135.24
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131.35
128.70
128.59
121.16
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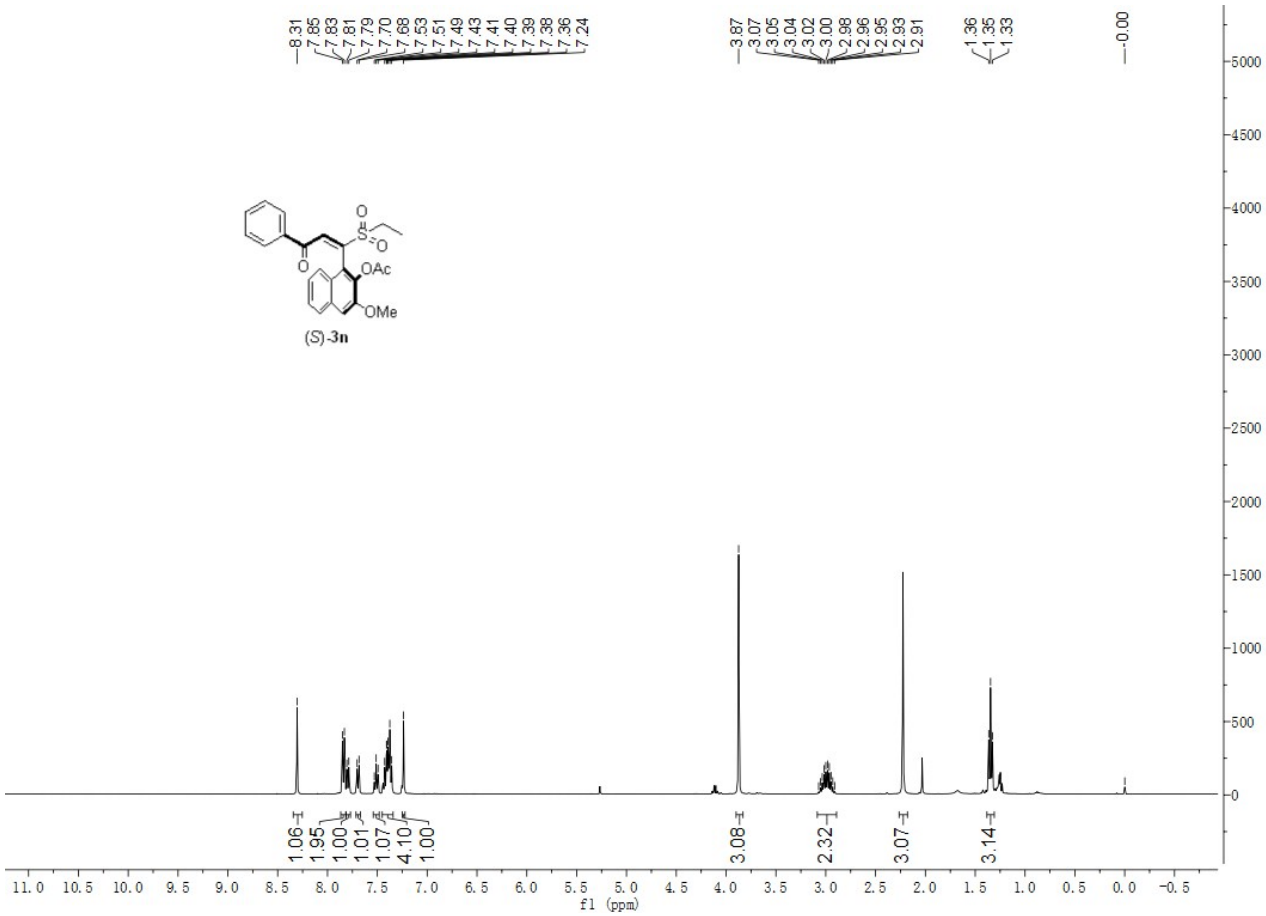
46.50
29.14
27.76
22.27
20.96
6.15
OAc
(S)-3m
f1 (ppm)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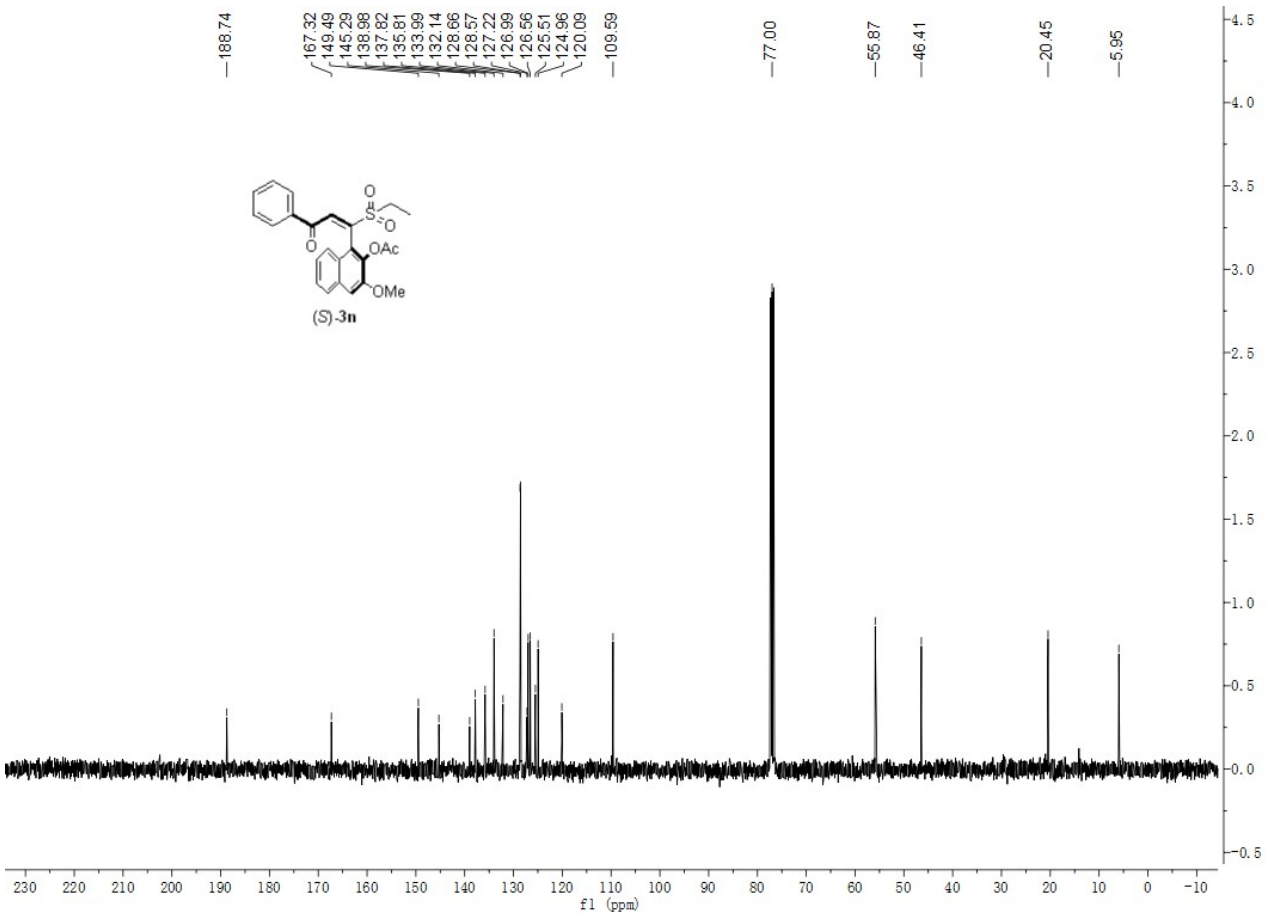
7.53
7.51
7.49
7.43
7.41
7.40
7.39
7.38
7.36
7.24
3.87
3.07
3.05
3.04
3.02
3.00
2.98
2.96
2.95
2.93
2.91
1.36
1.35
1.33
0.00
OAc
OMe
(S)-3n
1.06
1.95
1.00
1.01
1.07
4.10
1.00
3.08
2.32
3.07
3.14
f1 (ppm)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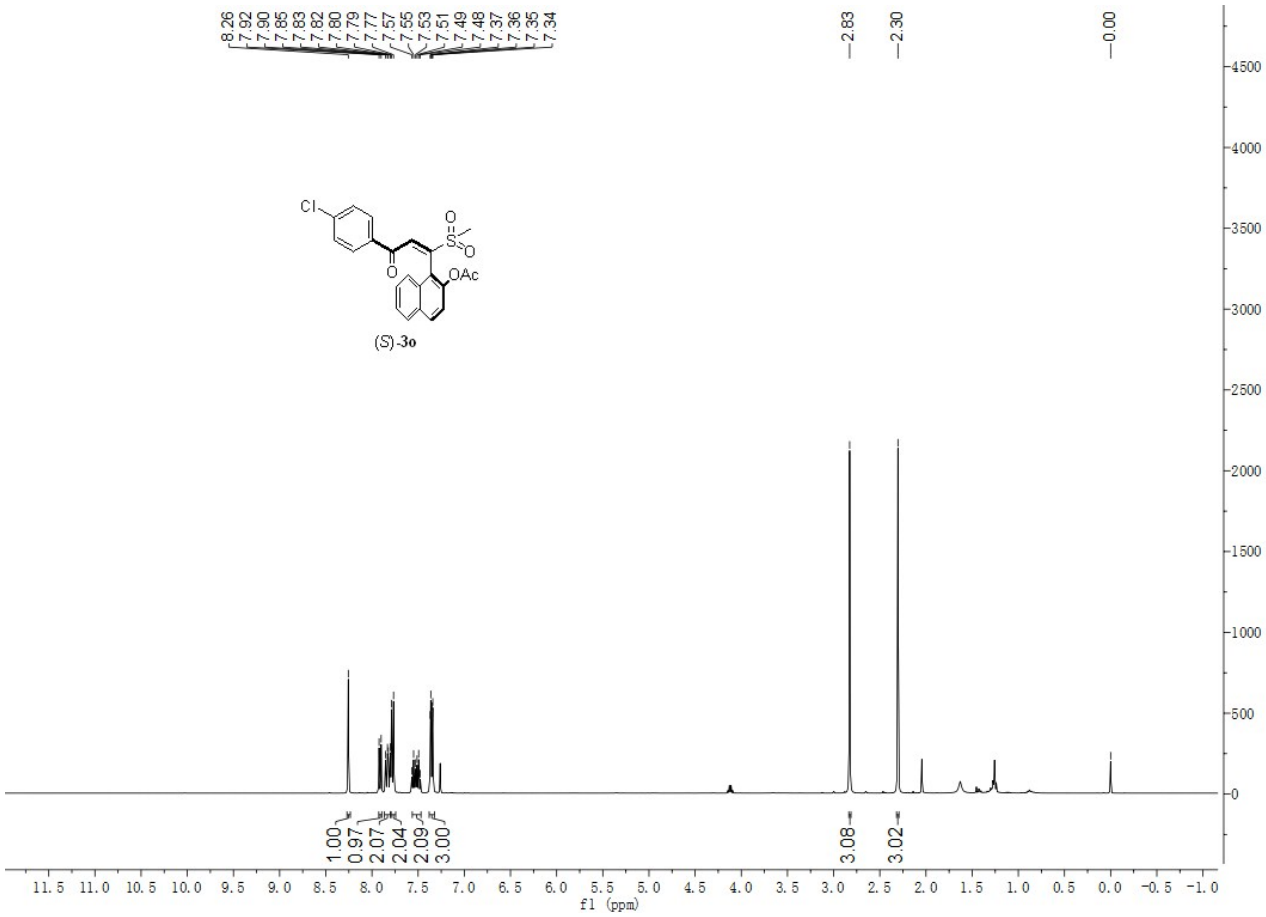
145.29
138.98
137.82
135.81
133.99
132.14
128.66
128.57
127.22
126.99
126.56
125.51
124.96
120.09
109.59
77.00
55.87
46.41
20.45
5.95
OAc
OMe
(S)-3n
f1 (ppm)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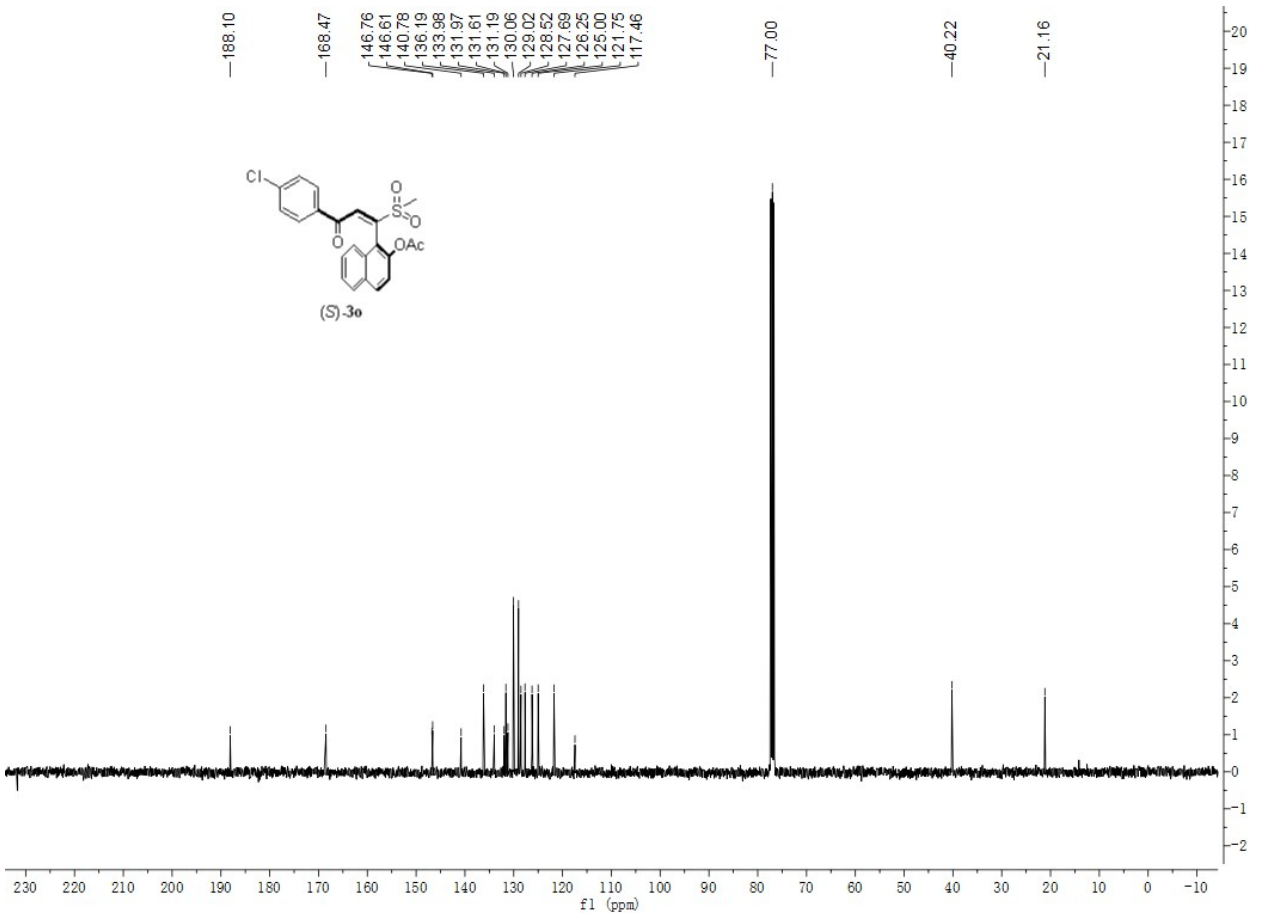
7.82
7.80
7.79
7.77
7.57
7.55
7.53
7.51
7.49
7.48
7.37
7.36
7.35
7.34
2.83
2.30
0.00
Cl
O
S
O
O
OAc
(S)-3o
1.00
0.97
2.07
2.04
2.09
3.00
3.08
3.02
f1 (ppm)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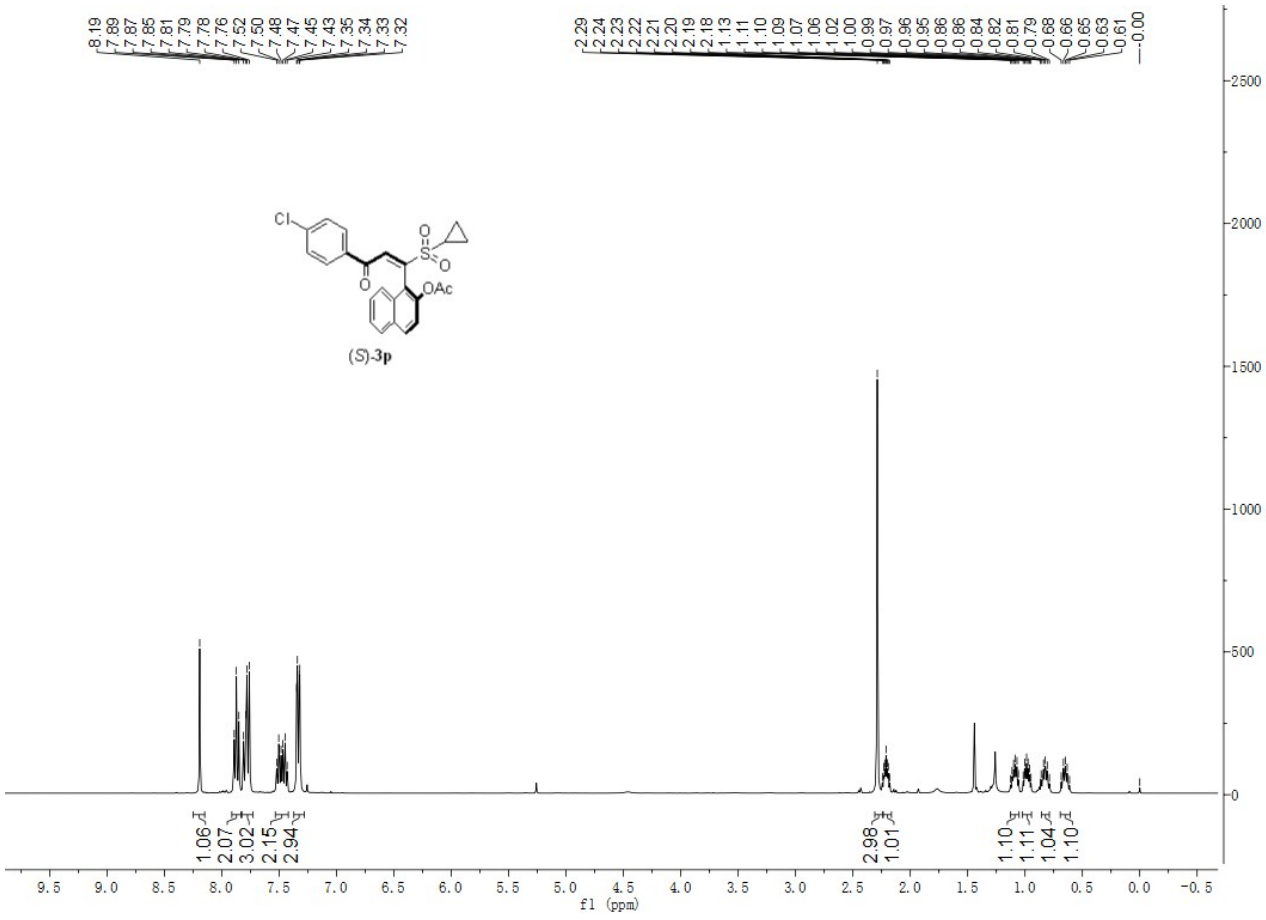
146.76
146.61
140.78
136.19
133.98
131.97
131.61
131.19
130.06
129.02
128.52
127.69
126.25
125.00
121.75
117.46
77.00
40.22
21.16
Cl
O
S
O
O
OAc
(S)-3o
f1 (ppm)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7.89
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7.79
7.78
7.76
7.52
7.50
7.48
7.47
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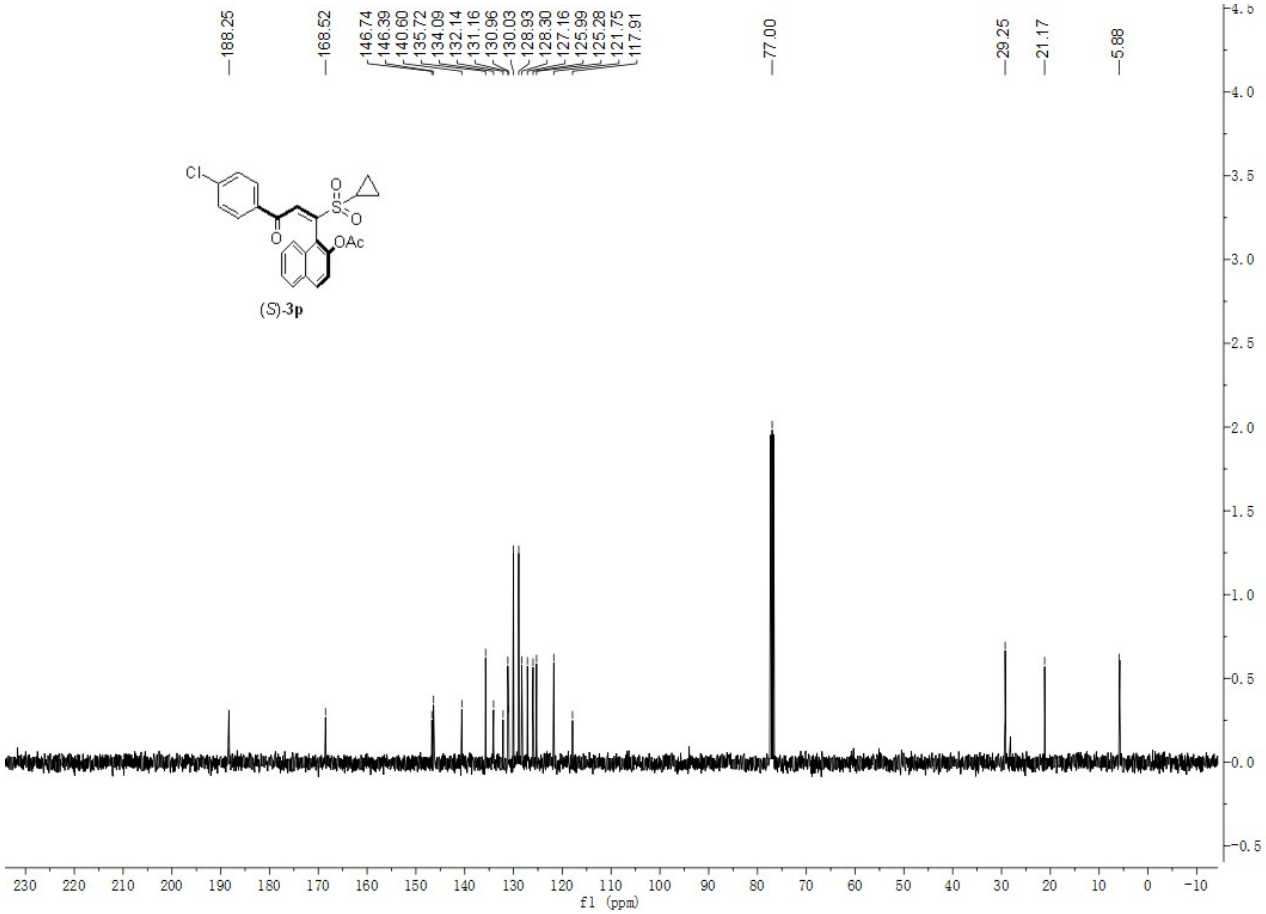
7.43
7.36
7.34
7.33
7.32
2.29
2.24
2.23
2.22
2.21
2.20
2.19
2.18
1.13
1.11
1.10
1.09
1.07
1.06
1.02
1.00
0.99
0.97
0.96
0.95
0.86
0.86
0.84
0.82
0.81
0.79
0.68
0.66
0.65
0.63
0.61
0.00
Cl
O
S
O
O
OAc
(S)-3p
1.06
2.07
3.02
2.15
2.94
2.98
1.01
1.10
1.11
1.04
1.10
f1 (ppm)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140.60
135.72
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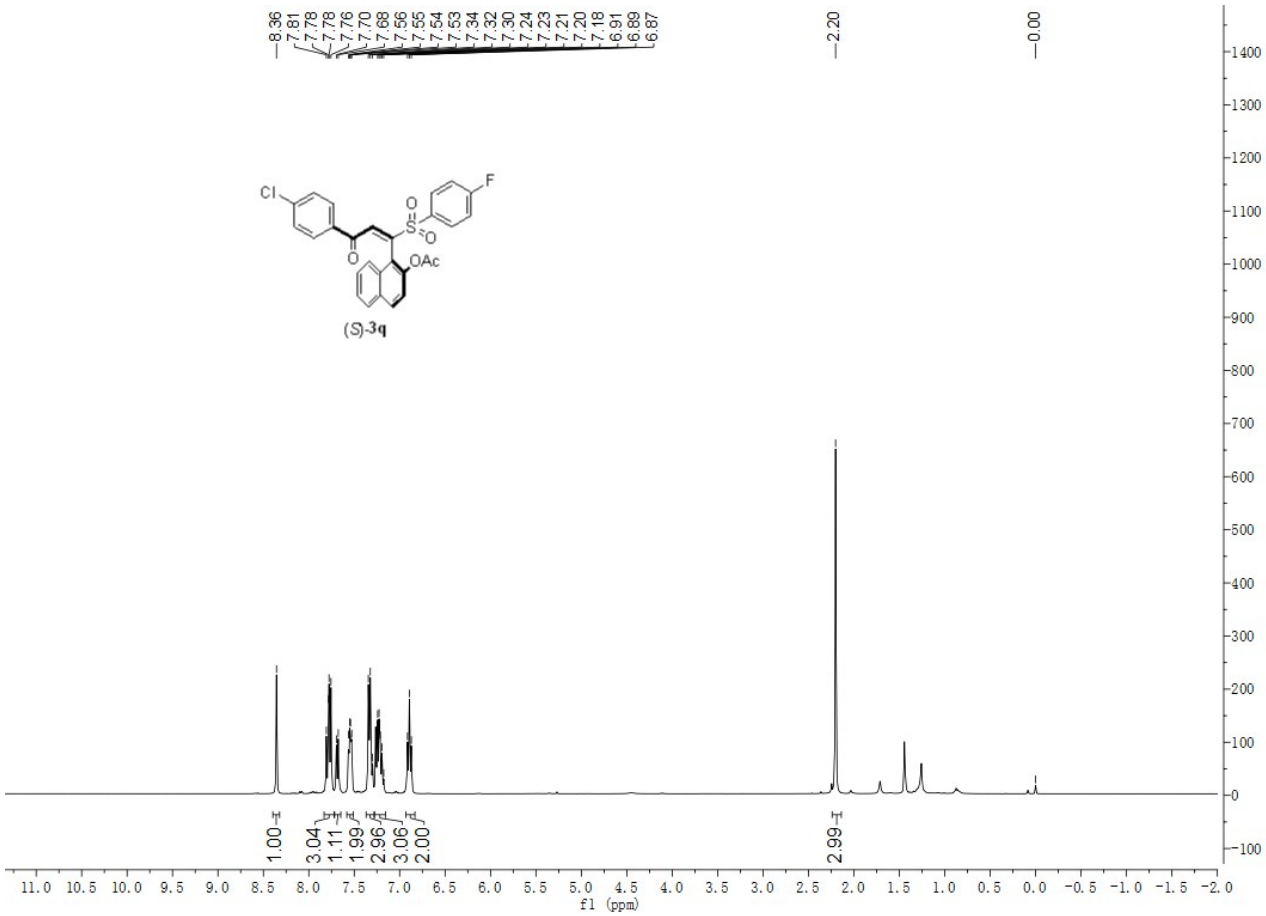
132.14
131.16
130.96
130.03
128.93
128.30
127.16
125.99
125.28
121.75
117.91
77.00
29.25
21.17
5.88
Cl
O
S
O
O
OAc
(S)-3p
f1 (ppm)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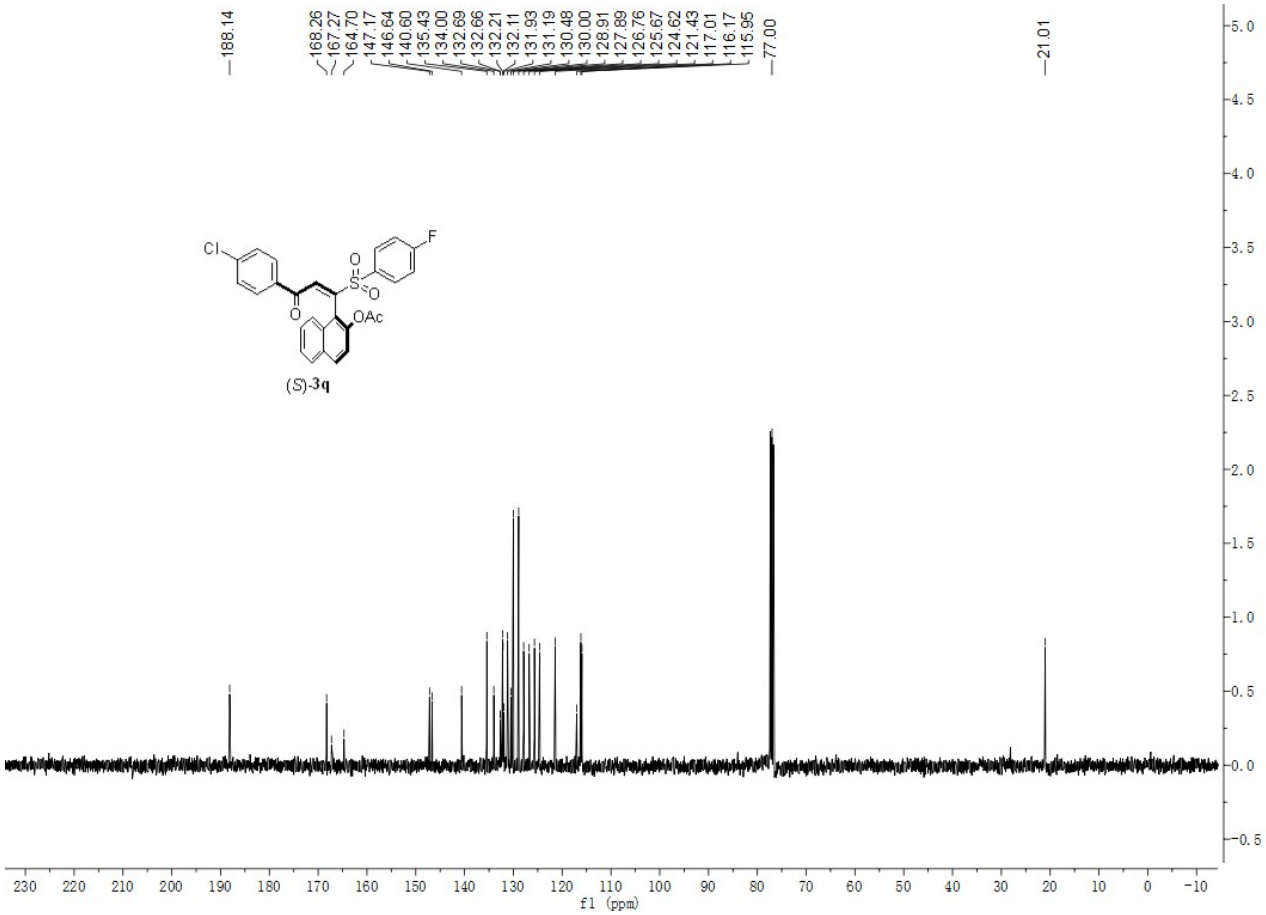
7.68
7.56
7.55
7.54
7.53
7.34
7.32
7.30
7.24
7.23
7.21
7.20
7.18
6.91
6.89
6.87
2.20
0.00
Cl
F
O
S
O
O
OAc
(S)-3q
1.00
3.04
1.11
1.99
2.96
3.06
2.00
2.99
f1 (ppm)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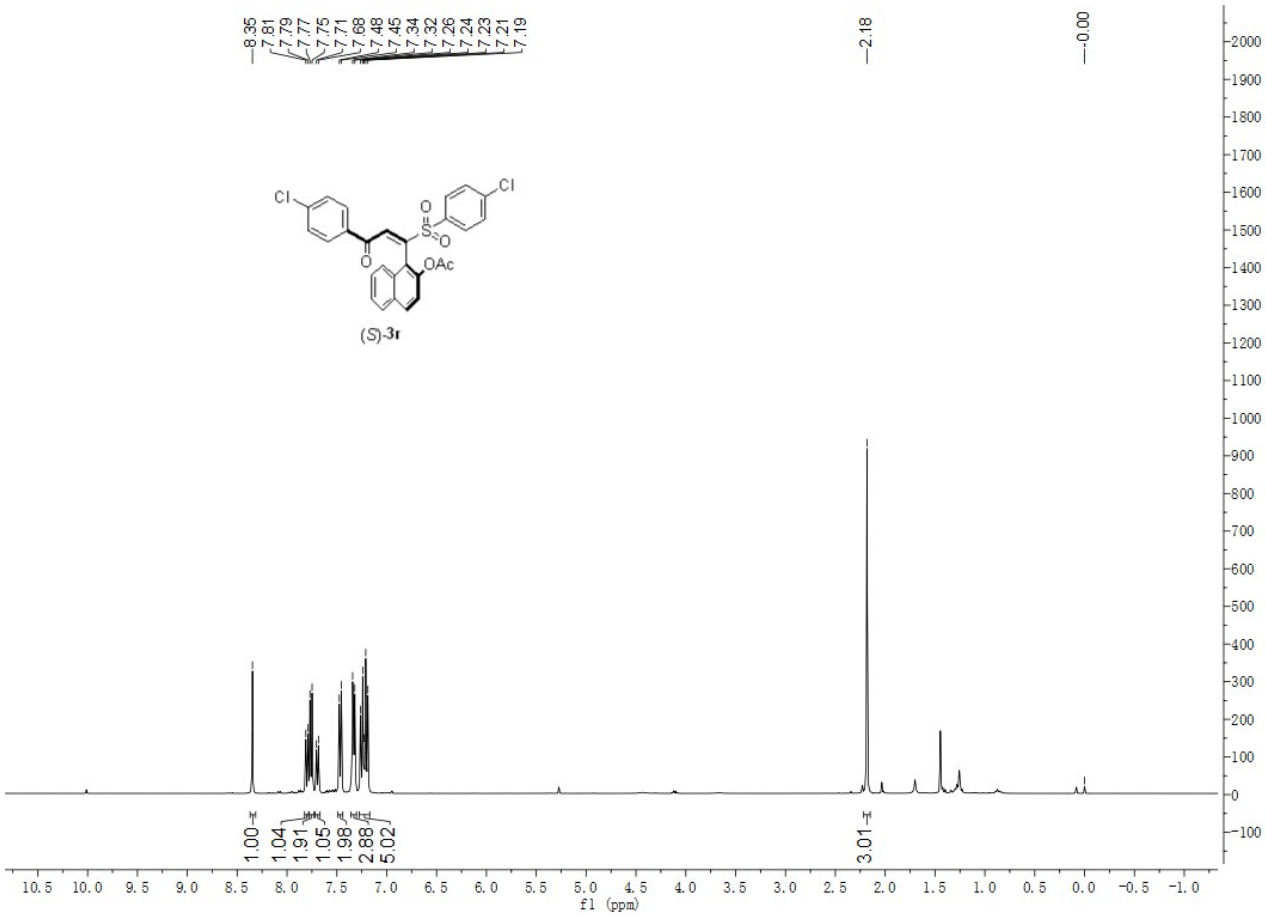
140.60
135.43
134.00
132.69
132.66
132.21
132.11
131.93
131.19
130.48
130.00
128.91
127.89
126.76
125.67
124.62
121.43
117.01
116.17
115.96
77.00
21.01
Cl
F
O
S
O
O
OAc
(S)-3q
f1 (ppm)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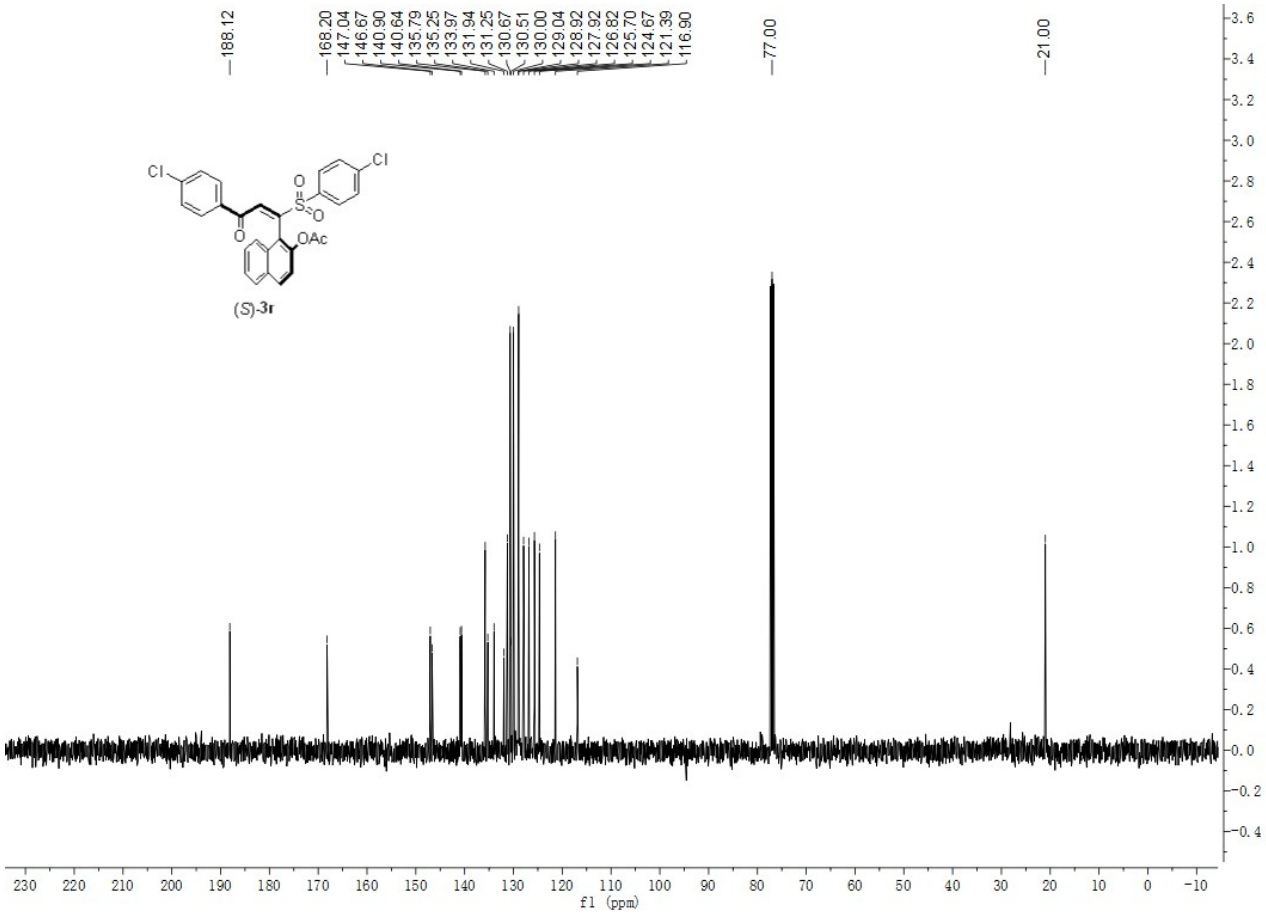
7.79
7.77
7.75
7.71
7.68
7.48
7.45
7.34
7.32
7.26
7.24
7.23
7.21
7.19
2.18
0.00
Cl
O
S
O
O
OAc
Cl
(S)-3r
1.00
1.04
1.91
1.05
1.98
2.88
5.02
3.01
f1 (ppm)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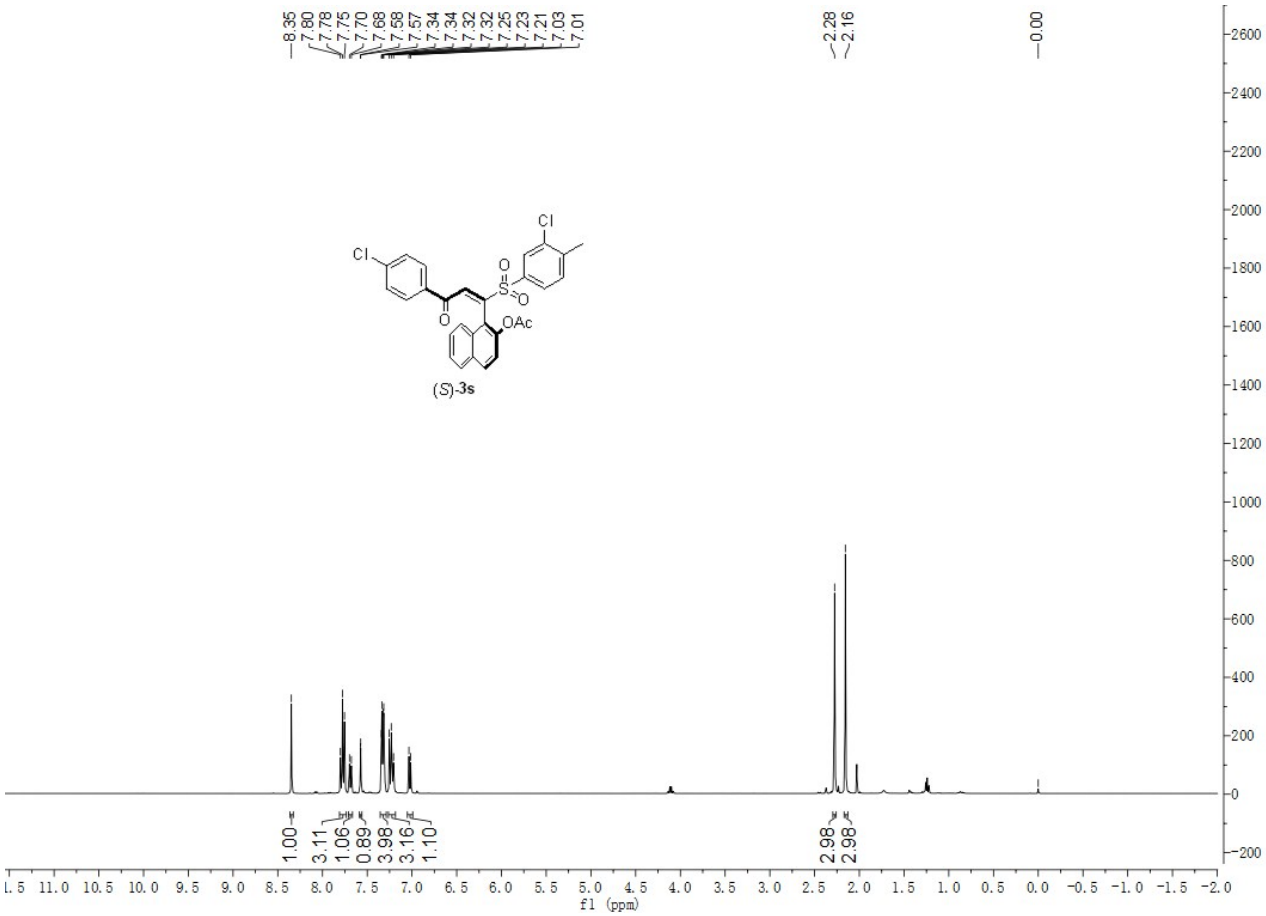
131.25
130.67
130.51
130.00
129.04
128.92
127.92
126.82
125.70
124.67
121.39
116.90
77.00
21.00
Cl
O
S
O
O
OAc
Cl
(S)-3r
f1 (ppm)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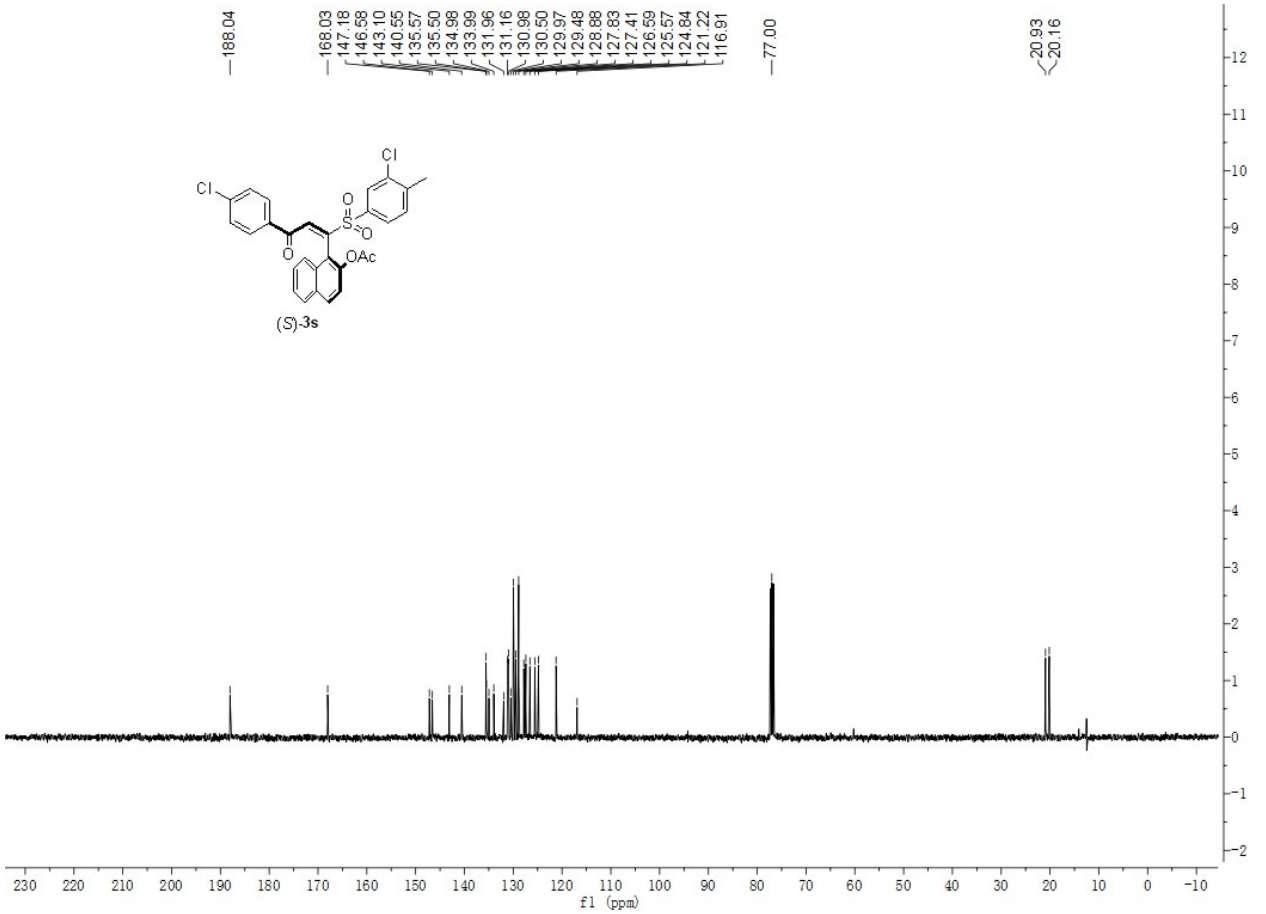
7.68
7.58
7.57
7.34
7.32
7.25
7.23
7.21
7.03
7.01
2.28
2.16
0.00
Cl
Cl
O
S
O
O
OAc
(S)-3s
1.00
3.11
1.06
0.89
3.98
3.16
1.10
2.98
2.98
f1 (ppm)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135.50
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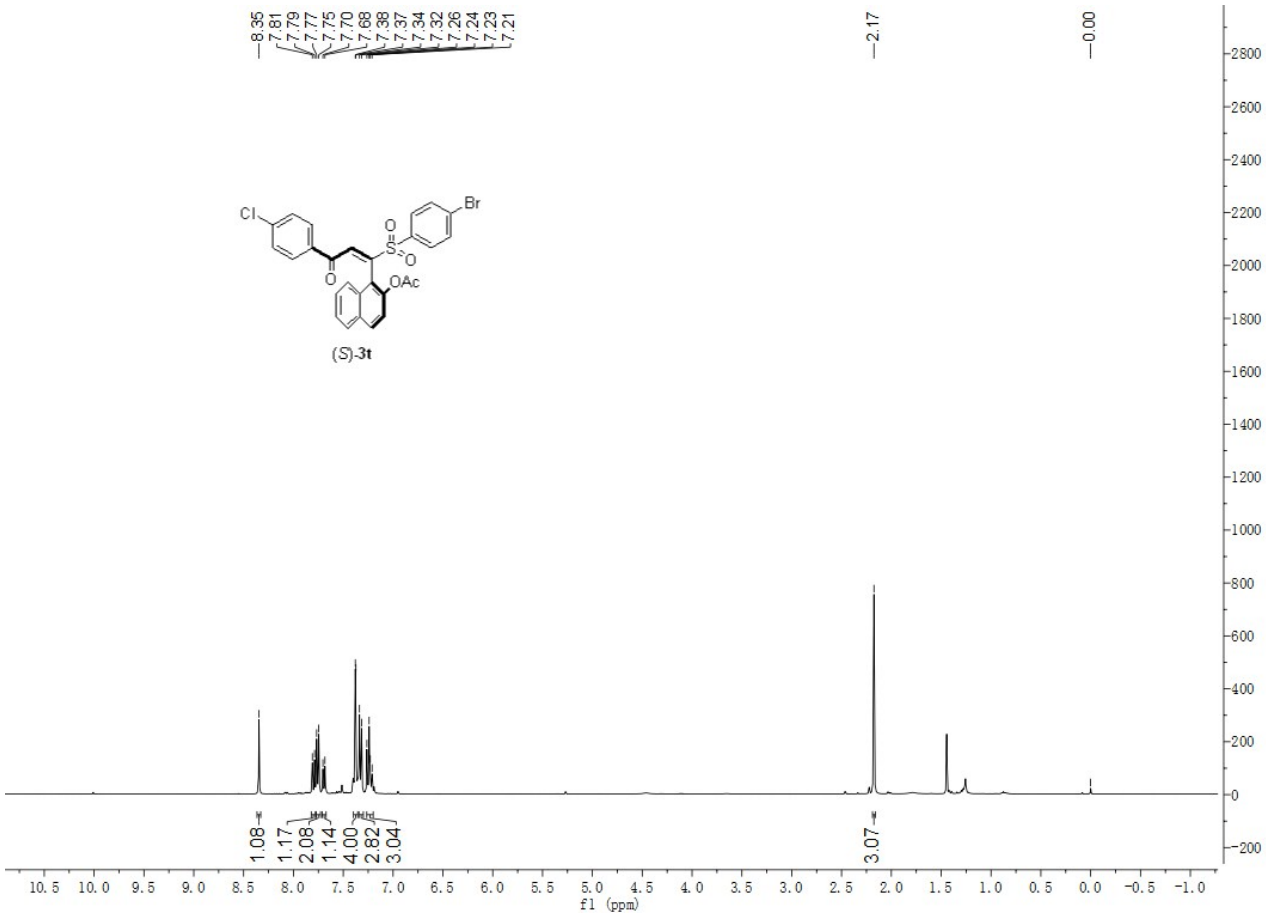
133.99
131.96
131.16
130.98
130.50
129.97
129.48
128.88
127.83
127.41
126.59
125.57
124.84
121.22
116.91
77.00
20.93
20.16
Cl
Cl
O
S
O
O
OAc
(S)-3s
f1 (ppm)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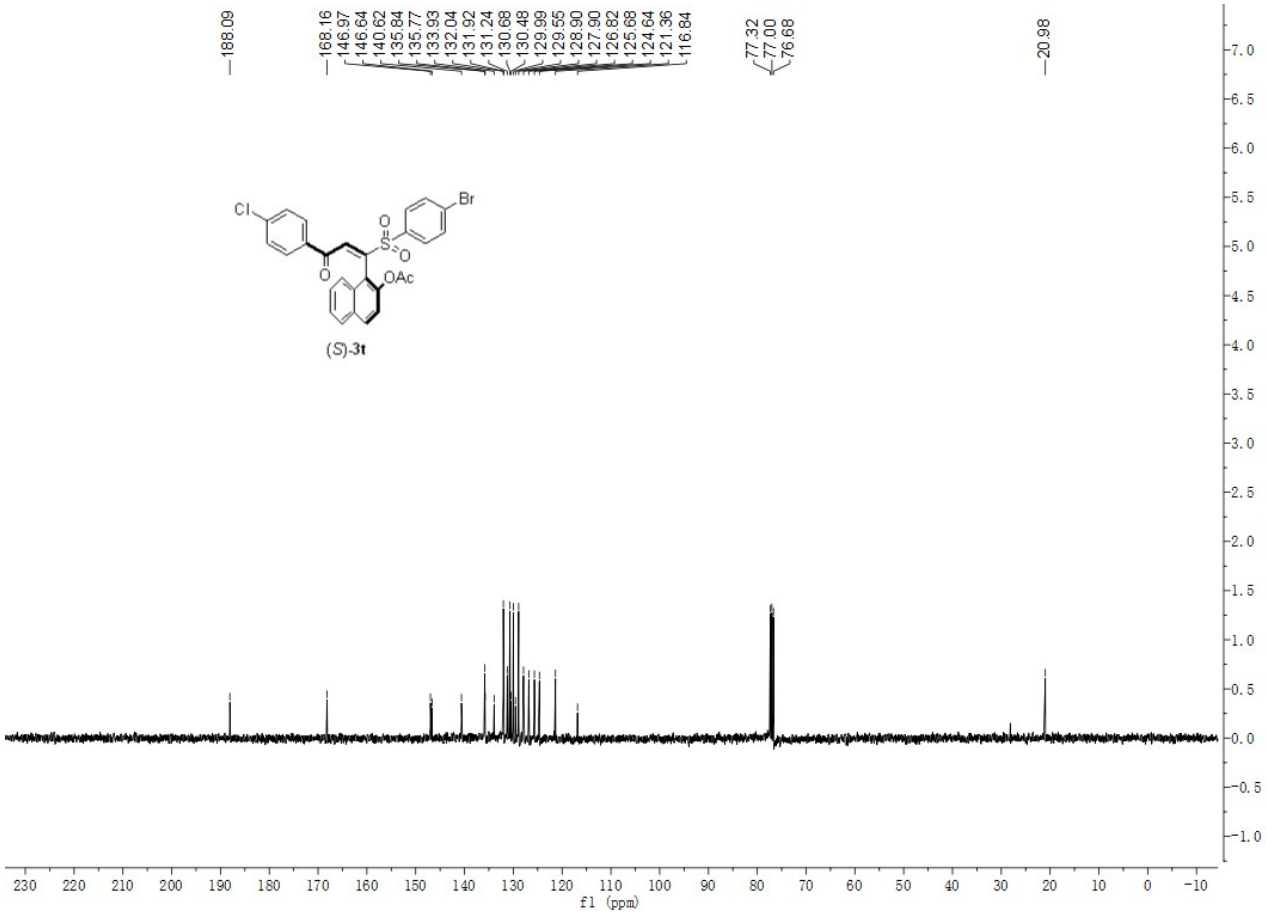
7.70
7.68
7.38
7.37
7.34
7.32
7.26
7.24
7.23
7.21
2.17
0.00
Cl
Br
O
S
O
O
OAc
(S)-3t
1.08
1.17
2.08
1.14
4.00
2.82
3.04
3.07
f1 (ppm)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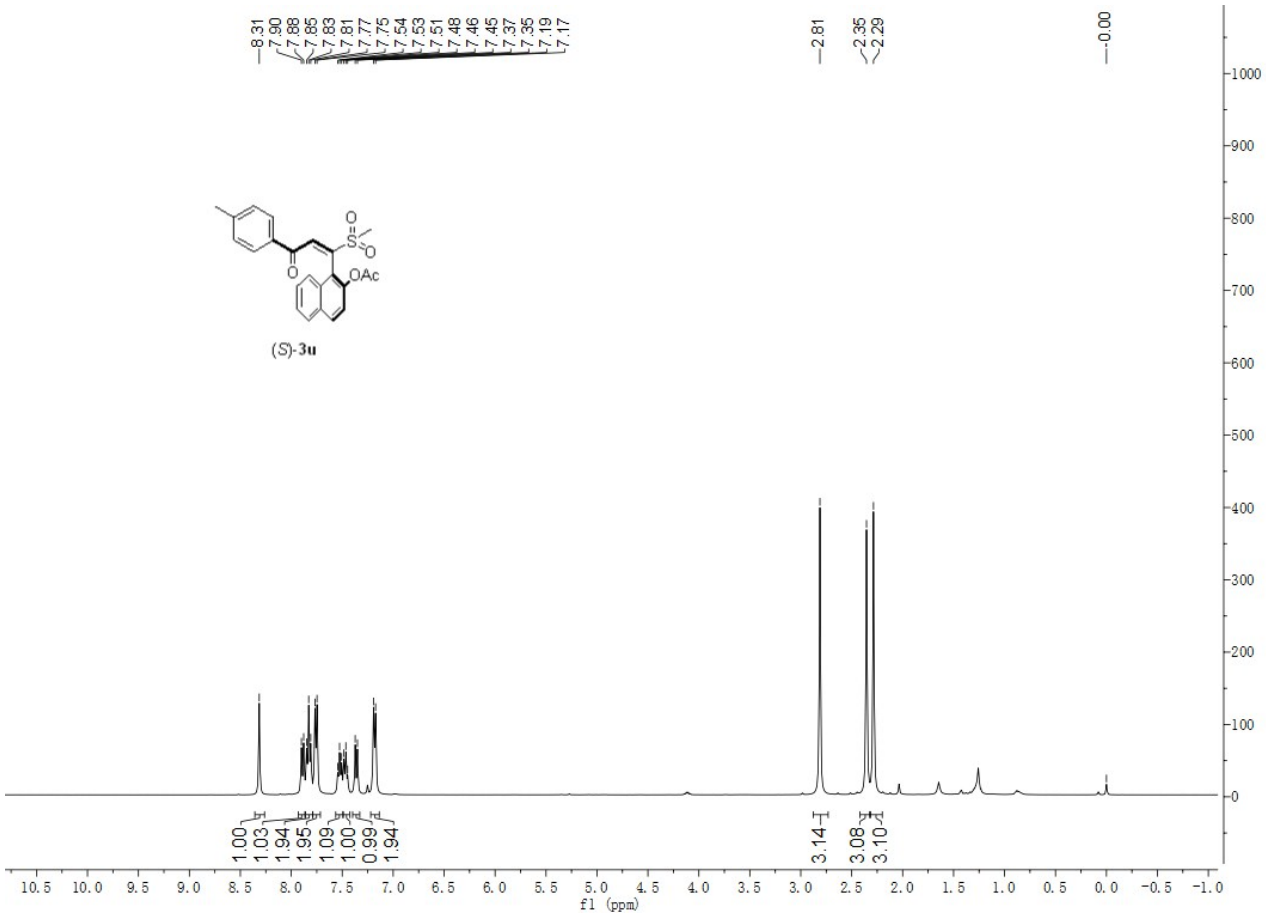
133.93
132.04
131.92
131.24
130.68
130.48
129.99
129.55
128.90
127.90
126.82
125.68
124.64
121.36
116.84
77.32
77.00
76.68
20.98
Cl
Br
O
S
O
O
OAc
(S)-3t
f1 (ppm)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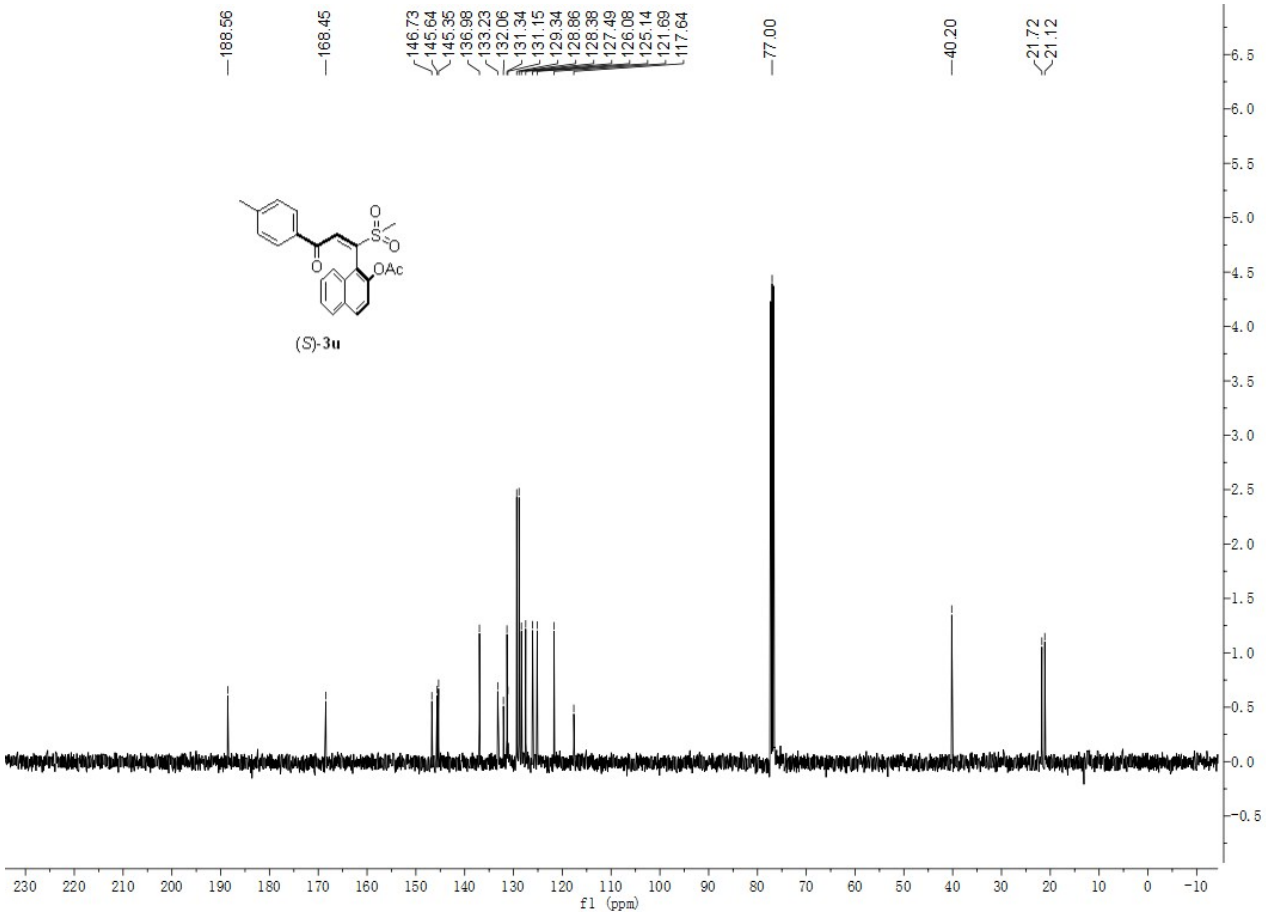
7.48
7.46
7.45
7.37
7.35
7.19
7.17
2.81
2.35
2.29
0.00
OAc
(S)-3u
1.00
1.03
1.94
1.95
1.09
1.00
0.99
1.94
3.14
3.08
3.10
f1 (ppm)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131.15
129.34
128.86
128.38
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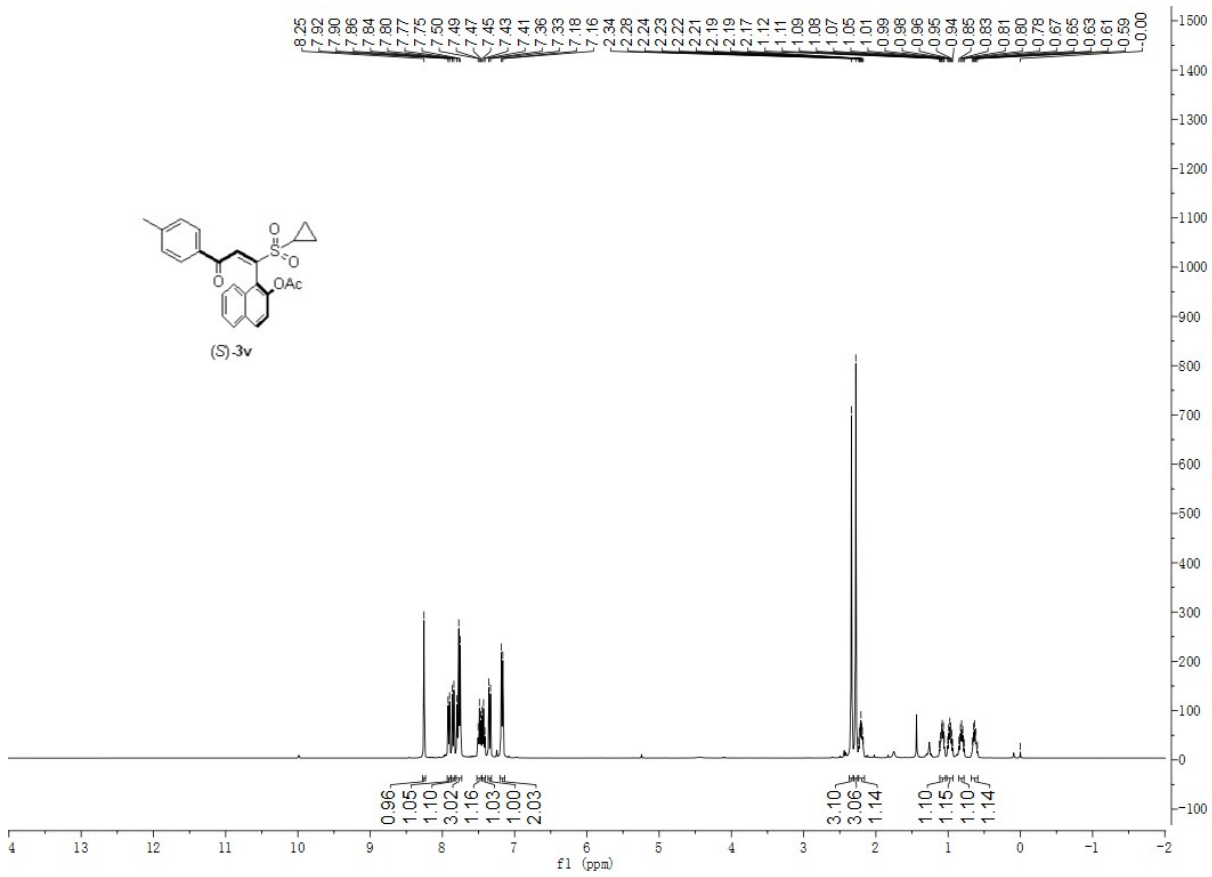
125.14
121.69
117.64
77.00
40.20
21.72
21.12
OAc
(S)-3u
f1 (ppm)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7.90
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7.80
7.77
7.75
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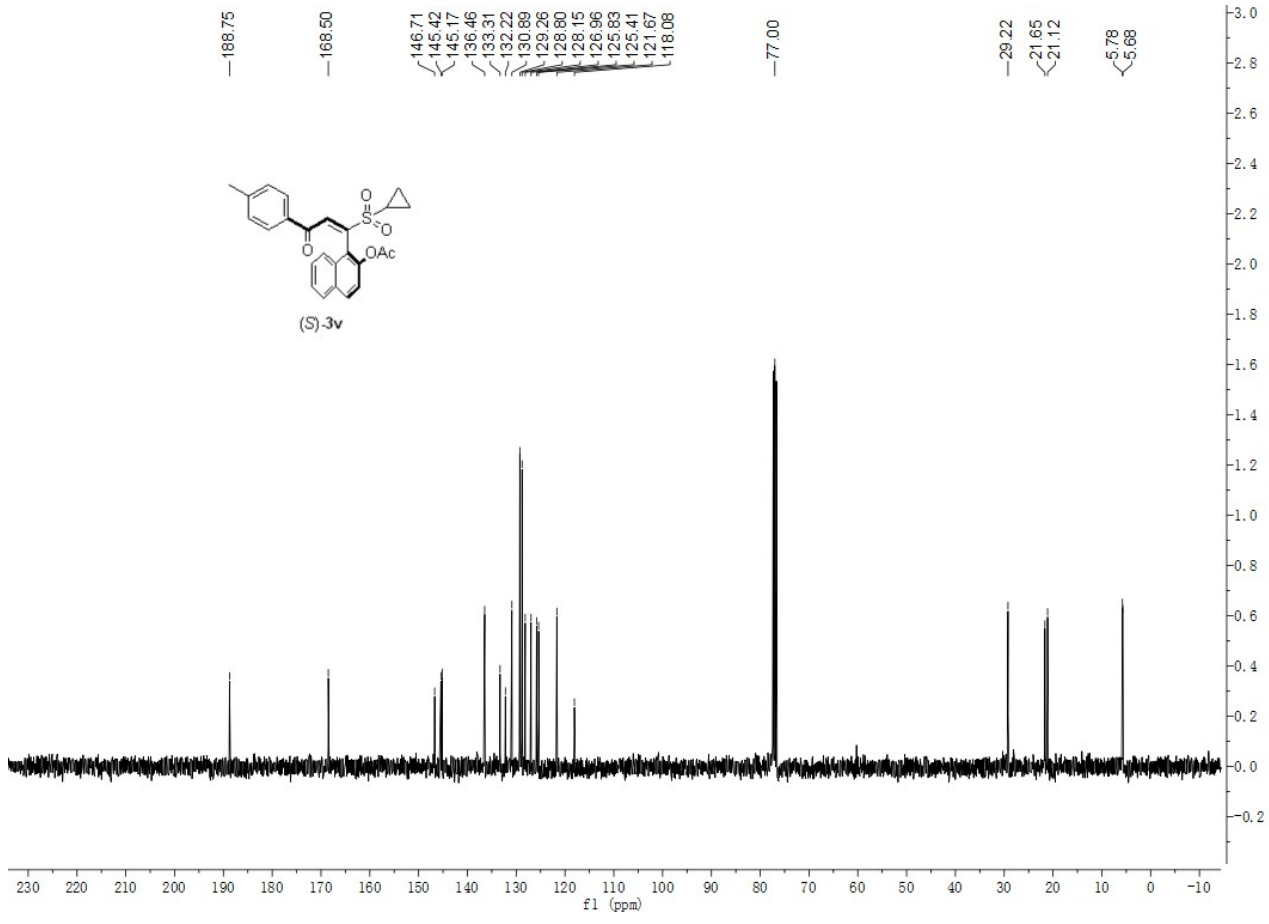
7.49
7.47
7.45
7.43
7.41
7.36
7.33
7.18
7.16
2.34
2.28
2.24
2.23
2.22
2.21
2.19
2.19
2.17
1.12
1.11
1.09
1.08
1.07
1.05
1.01
0.99
0.98
0.96
0.95
0.94
0.85
0.83
0.81
0.80
0.78
0.67
0.65
0.63
0.61
0.59
0.00
OAc
(S)-3v
0.96
1.05
1.10
3.02
1.16
1.03
1.00
2.03
3.10
3.06
1.14
1.10
1.15
1.10
1.14
f1 (ppm)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132.22
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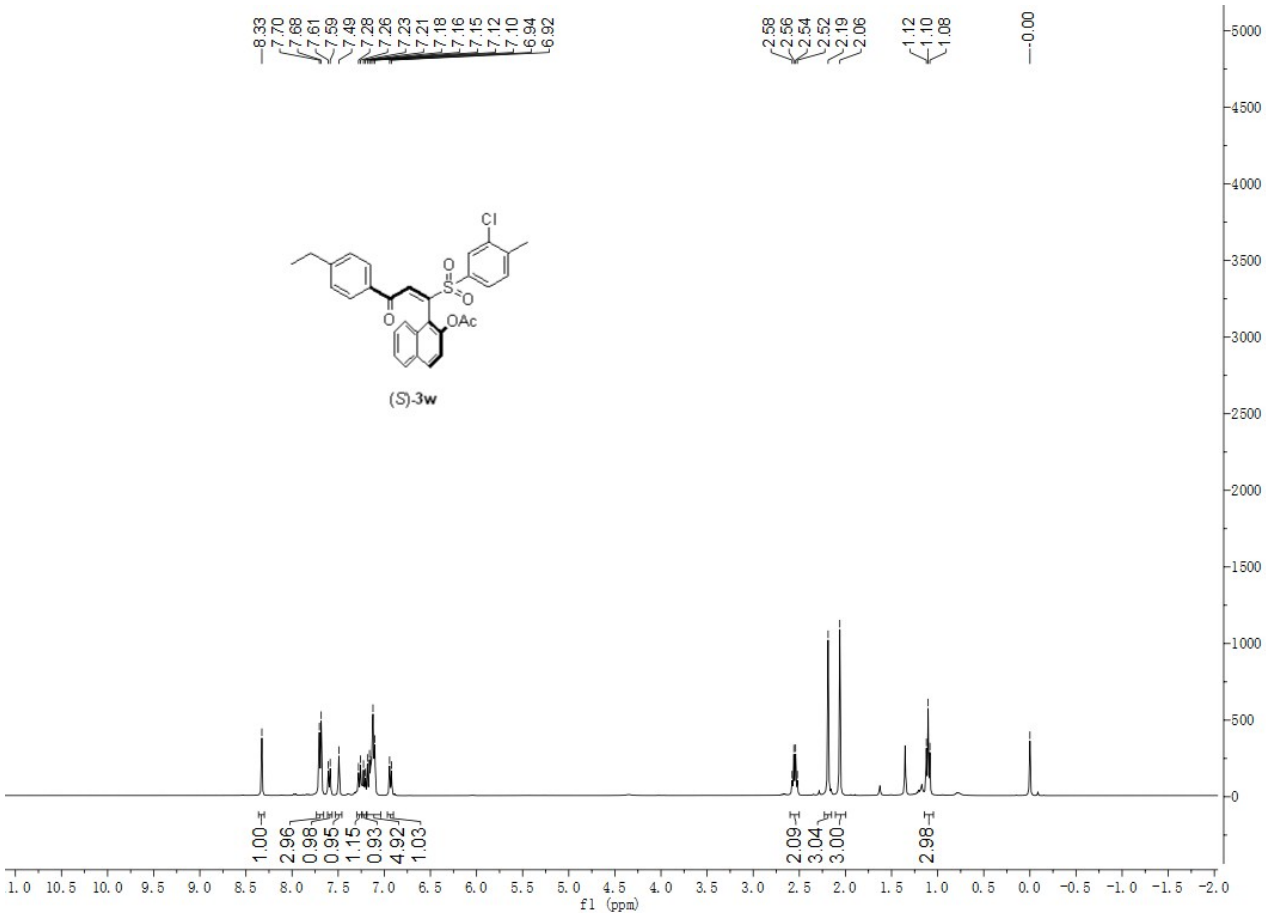
129.26
128.80
128.15
126.96
125.83
125.41
121.67
118.08
77.00
29.22
21.65
21.12
5.78
5.68
OAc
(S)-3v
f1 (ppm)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7.49
7.28
7.26
7.23
7.21
7.18
7.16
7.15
7.12
7.10
6.94
6.92
2.58
2.56
2.54
2.52
2.19
2.06
1.12
1.10
1.08
0.00
Cl
O
S
O
O
OAc
(S)-3w
1.00
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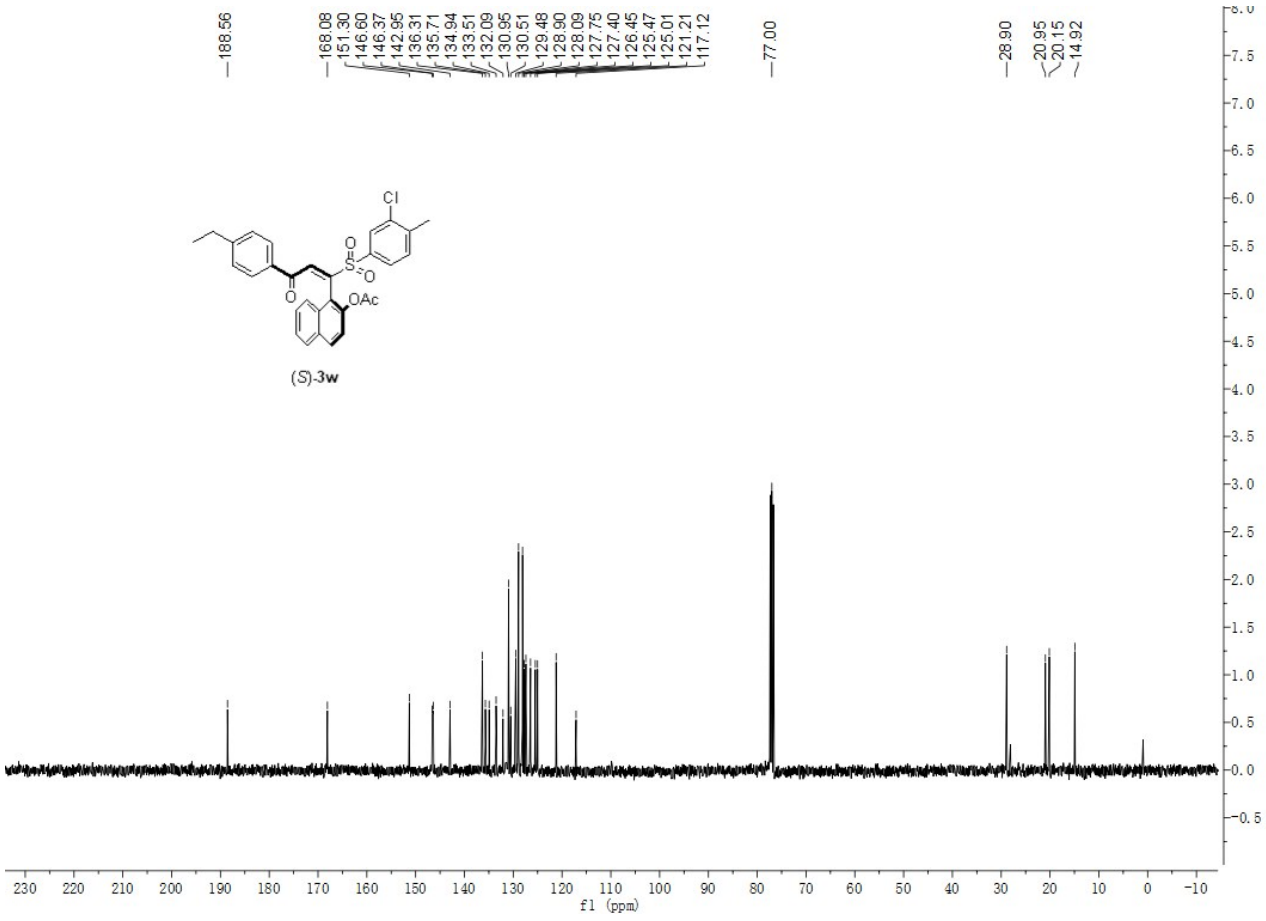
0.98
0.95
1.15
0.93
4.92
1.03
2.09
3.04
3.00
2.98
f1 (ppm)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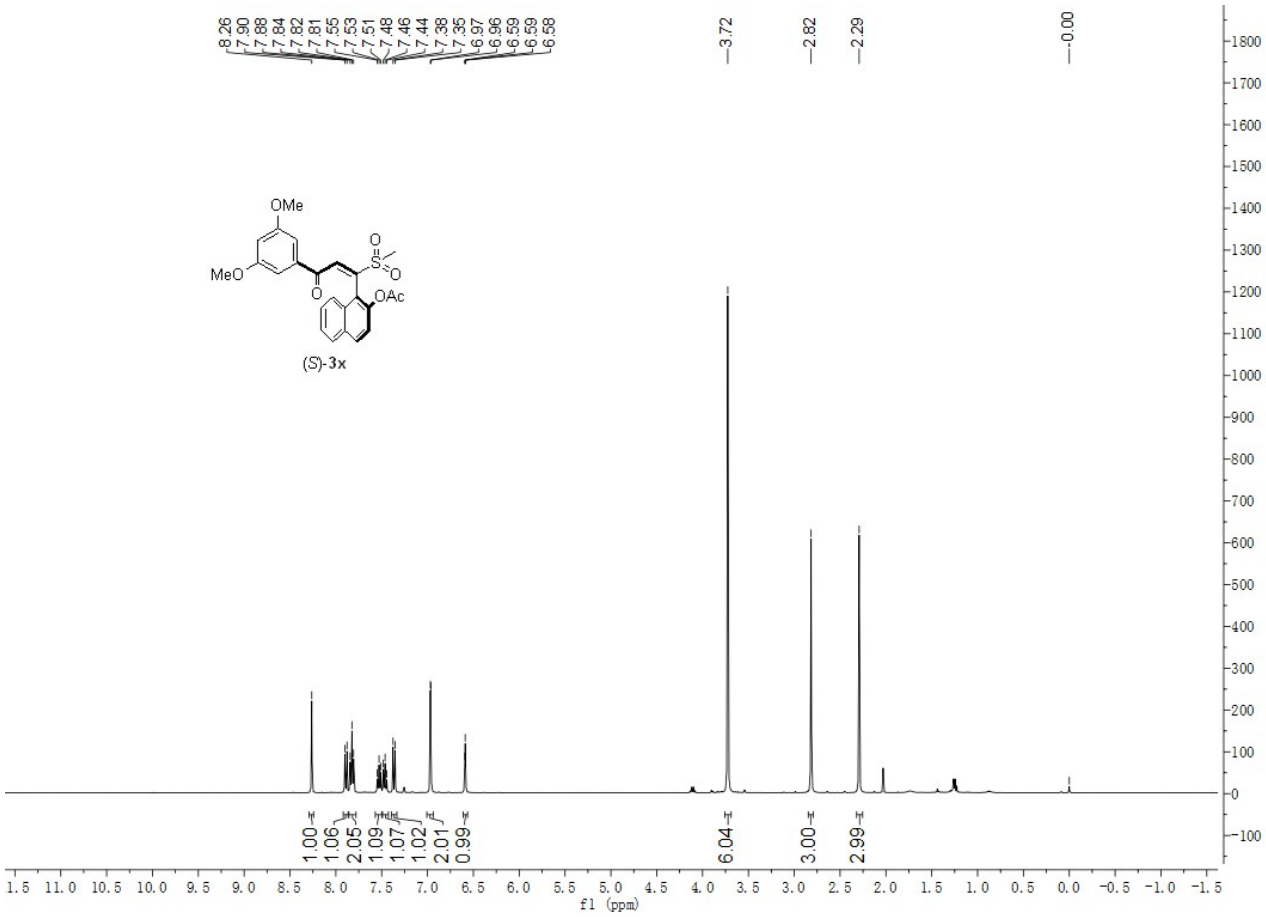
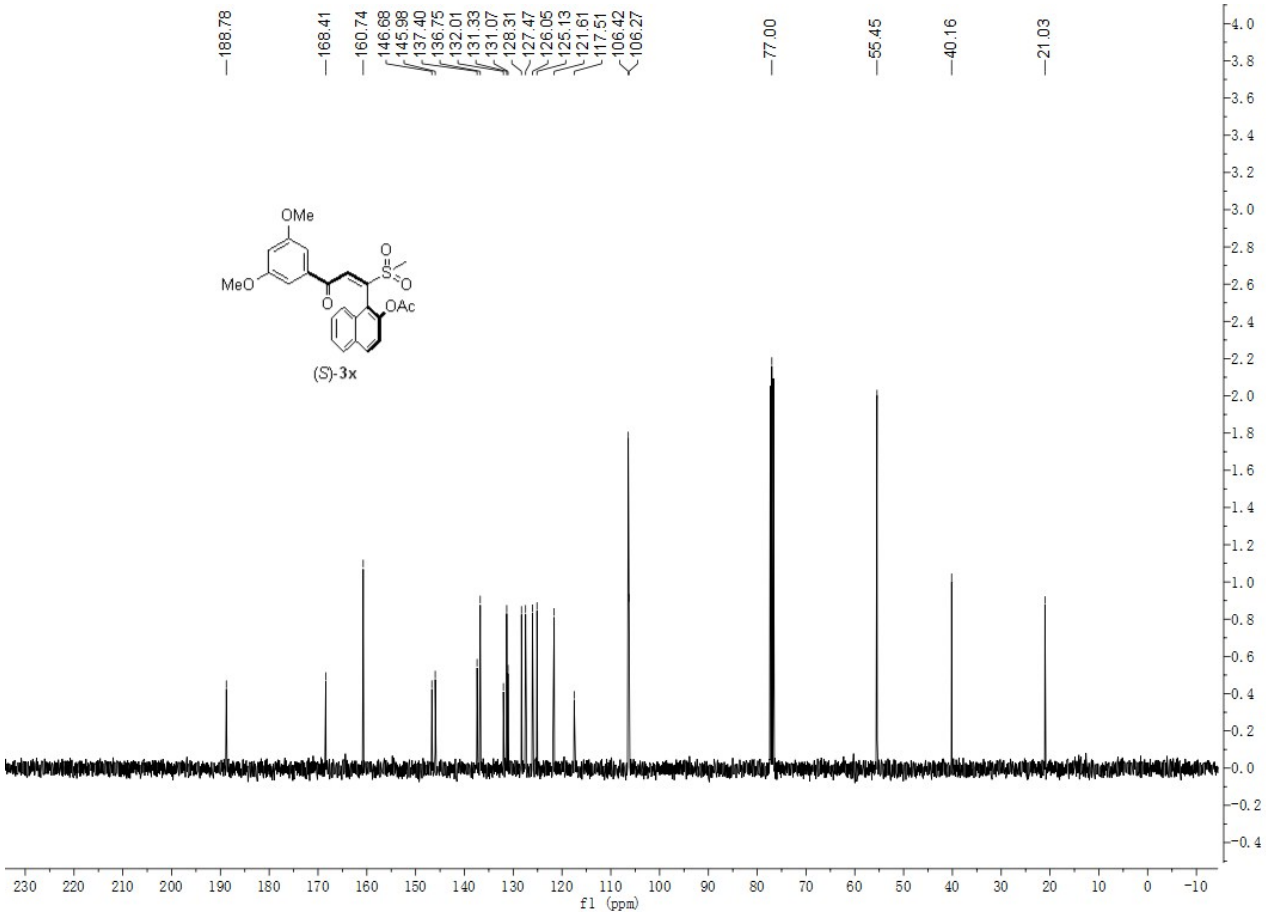
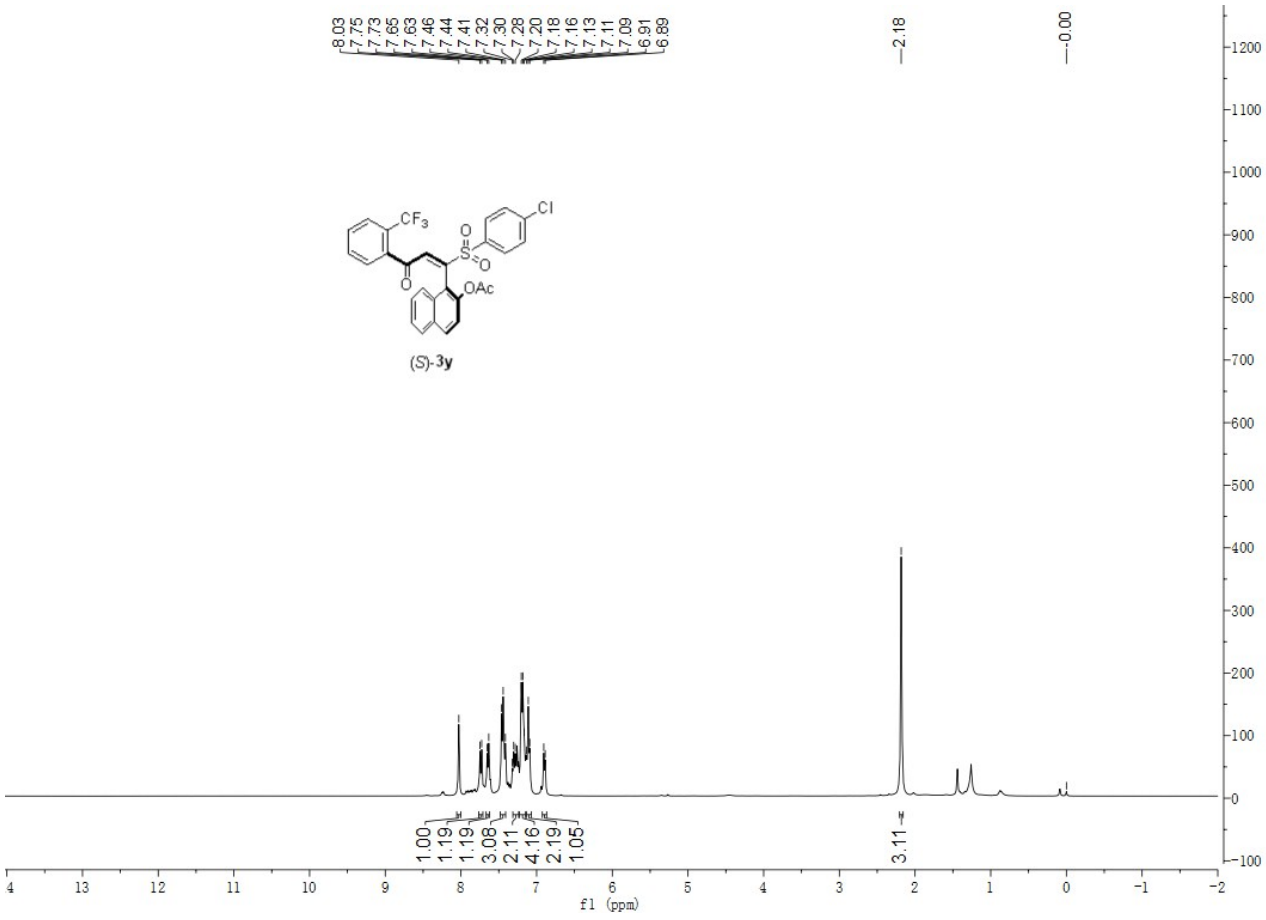
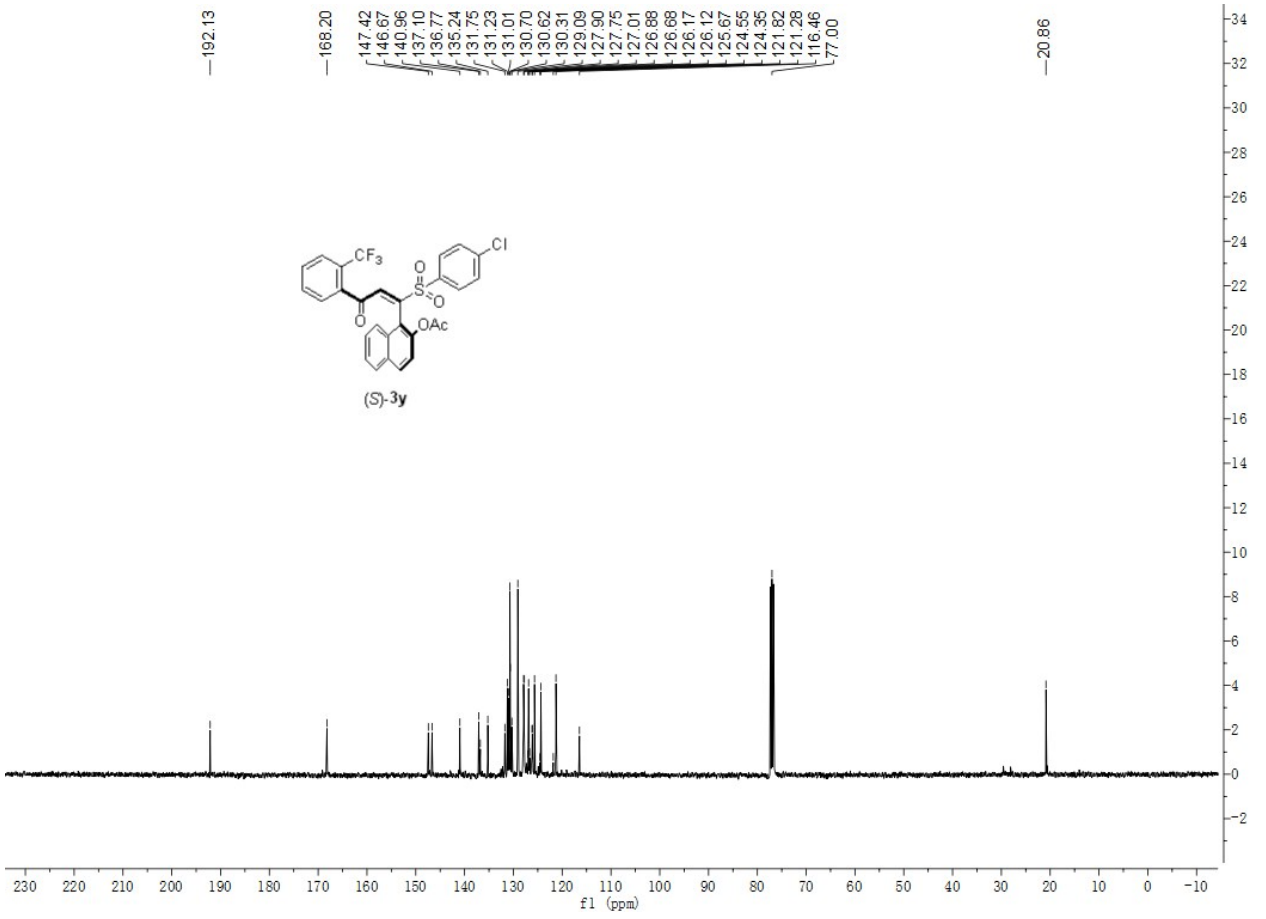
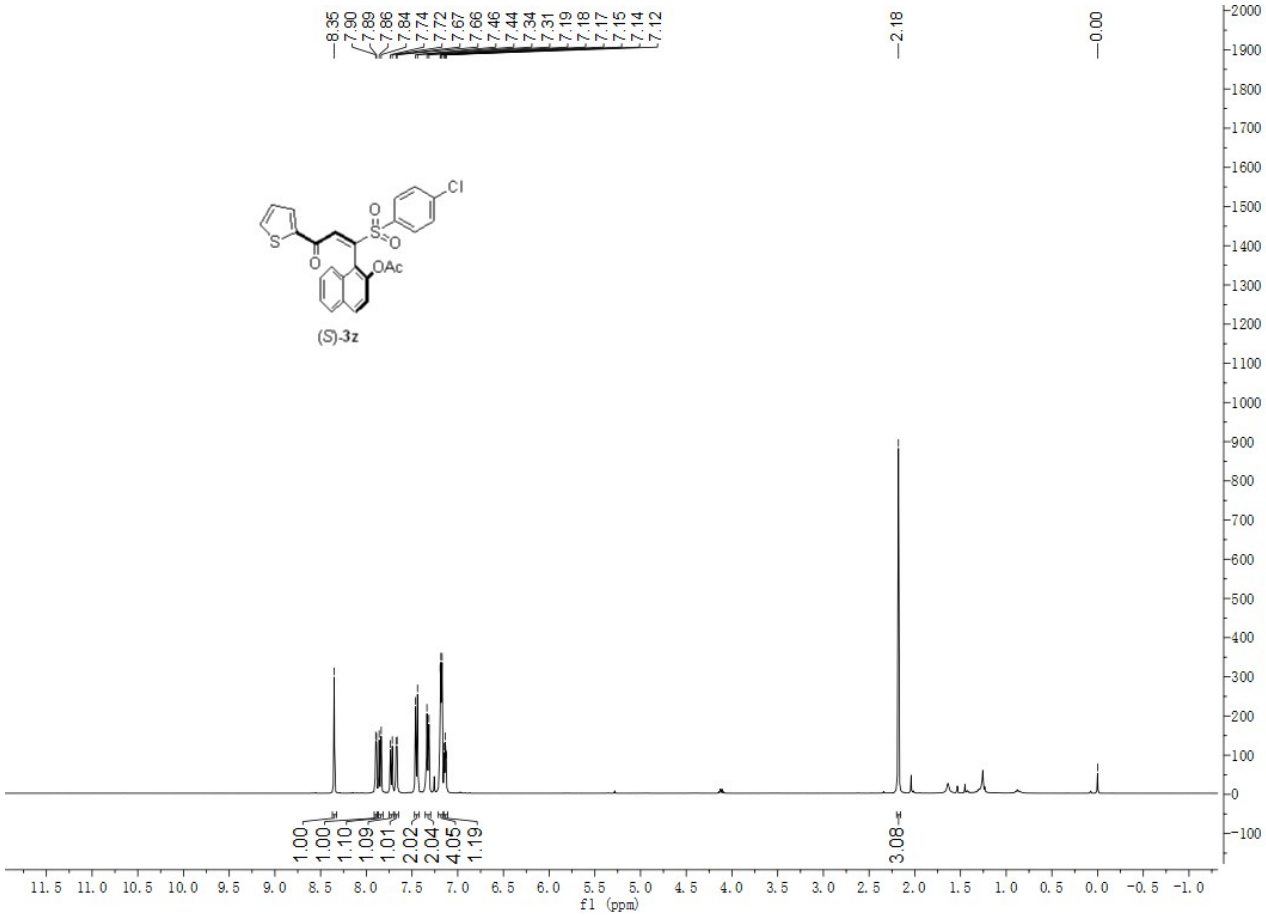
146.60
146.37
142.95
136.31
135.71
134.94
133.51
132.09
130.95
130.51
129.48
128.90
128.09
127.75
127.40
126.45
125.47
125.01
121.21
117.12
77.00
28.90
20.95
20.15
14.92
Cl
O
S
O
O
OAc
(S)-3w
f1 (ppm)

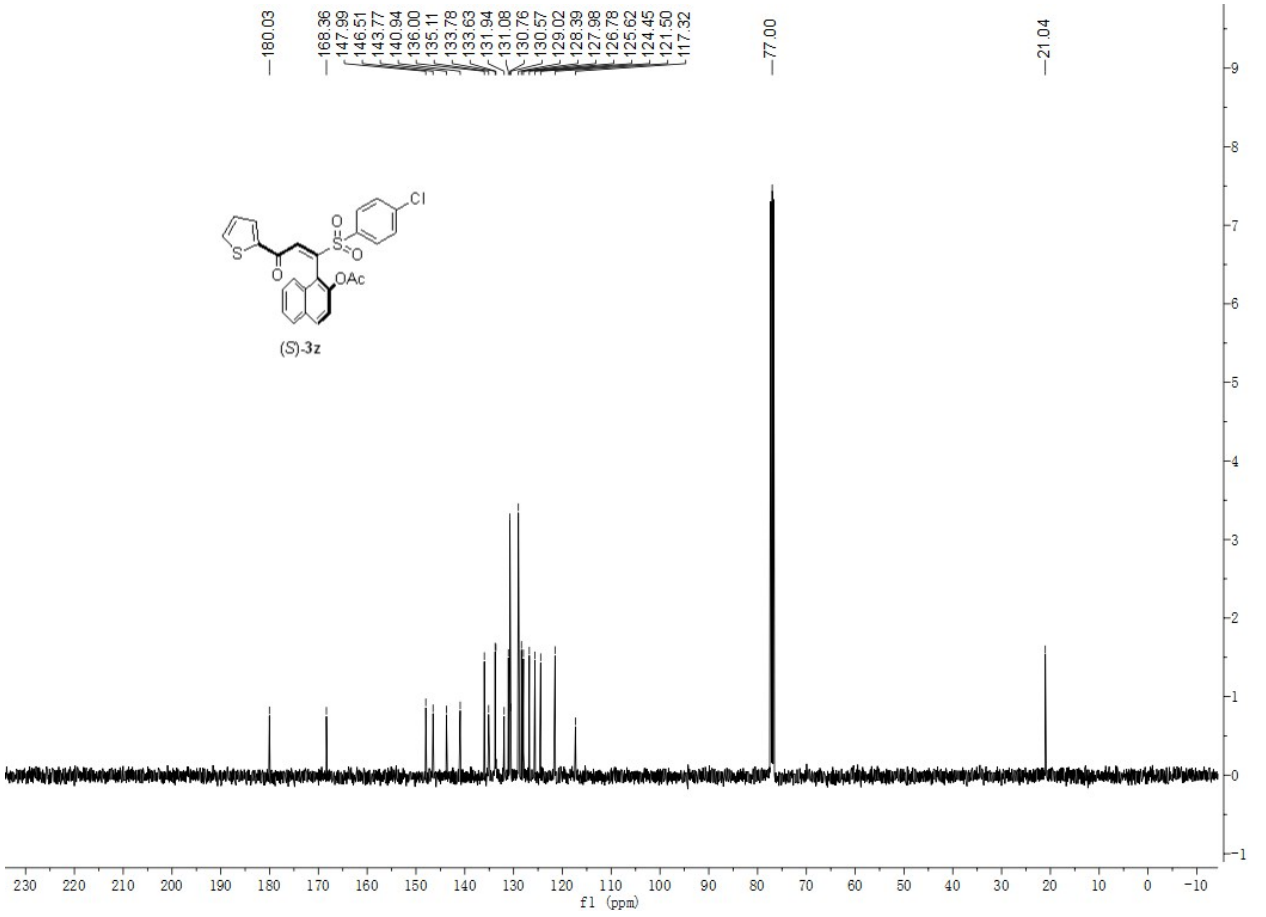

8.26
7.90
7.88
7.84
7.82
7.81
7.55
7.53
7.51
7.48
7.46
7.44
7.38
7.36
6.97
6.96
6.59
6.59
6.58
3.72
2.82
2.29
0.00
OMe
MeO
O
S
O
O
OAc
(S)-3x
1.00
1.06
2.05
1.09
1.07
1.02
2.01
0.99
6.04
3.00
2.99
f1 (ppm)


188.78
168.41
160.74
146.68
145.98
137.40
136.75
132.01
131.33
131.07
128.31
127.47
126.05
125.13
121.61
117.51
106.42
106.27
77.00
55.45
40.16
21.03
OMe
MeO
O
S
O
O
OAc
(S)-3x
f1 (ppm)


8.03
7.75
7.73
7.65
7.63
7.46
7.44
7.41
7.32
7.30
7.28
7.20
7.18
7.16
7.13
7.11
7.09
6.91
6.89
2.18
0.00
CF3
Cl
O
S
O
OAc
(S)-3y
1.00
1.19
1.19
3.08
2.11
4.16
2.19
1.05
3.11
f1 (ppm)


192.13
168.20
147.42
146.67
140.96
137.10
136.77
135.24
131.75
131.23
131.01
130.70
130.62
130.31
129.09
127.90
127.75
127.01
126.88
126.68
126.17
126.12
125.67
124.55
124.35
121.82
121.28
116.46
77.00
20.86
CF3
Cl
O
S
O
OAc
(S)-3y
f1 (ppm)


8.35
7.90
7.89
7.86
7.84
7.74
7.72
7.67
7.66
7.46
7.44
7.34
7.31
7.19
7.18
7.17
7.15
7.14
7.12
2.18
0.00
Cl
O
S
O
O
OAc
(S)-3z
1.00
1.00
1.10
1.09
1.01
2.02
2.04
4.05
1.19
3.08
f1 (ppm)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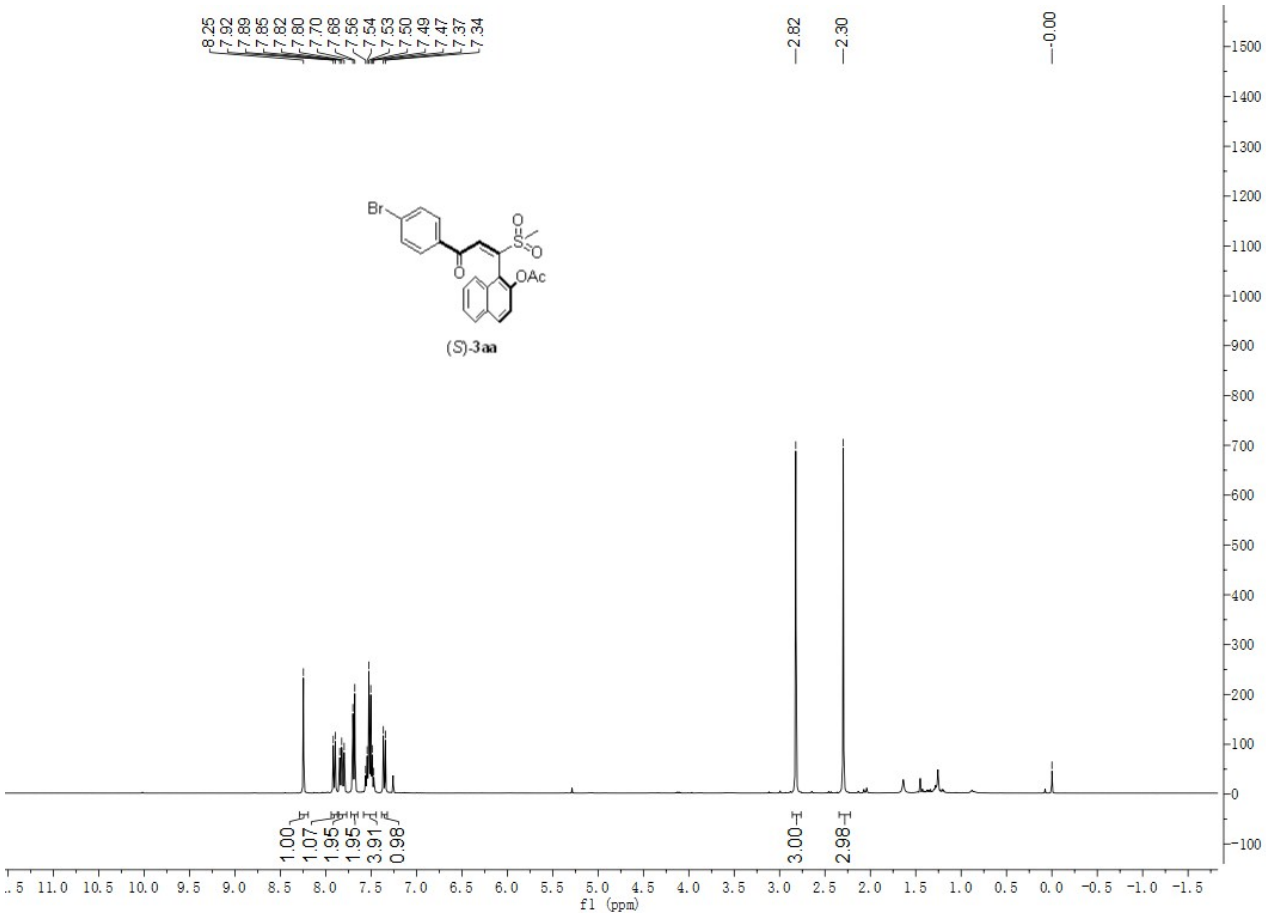
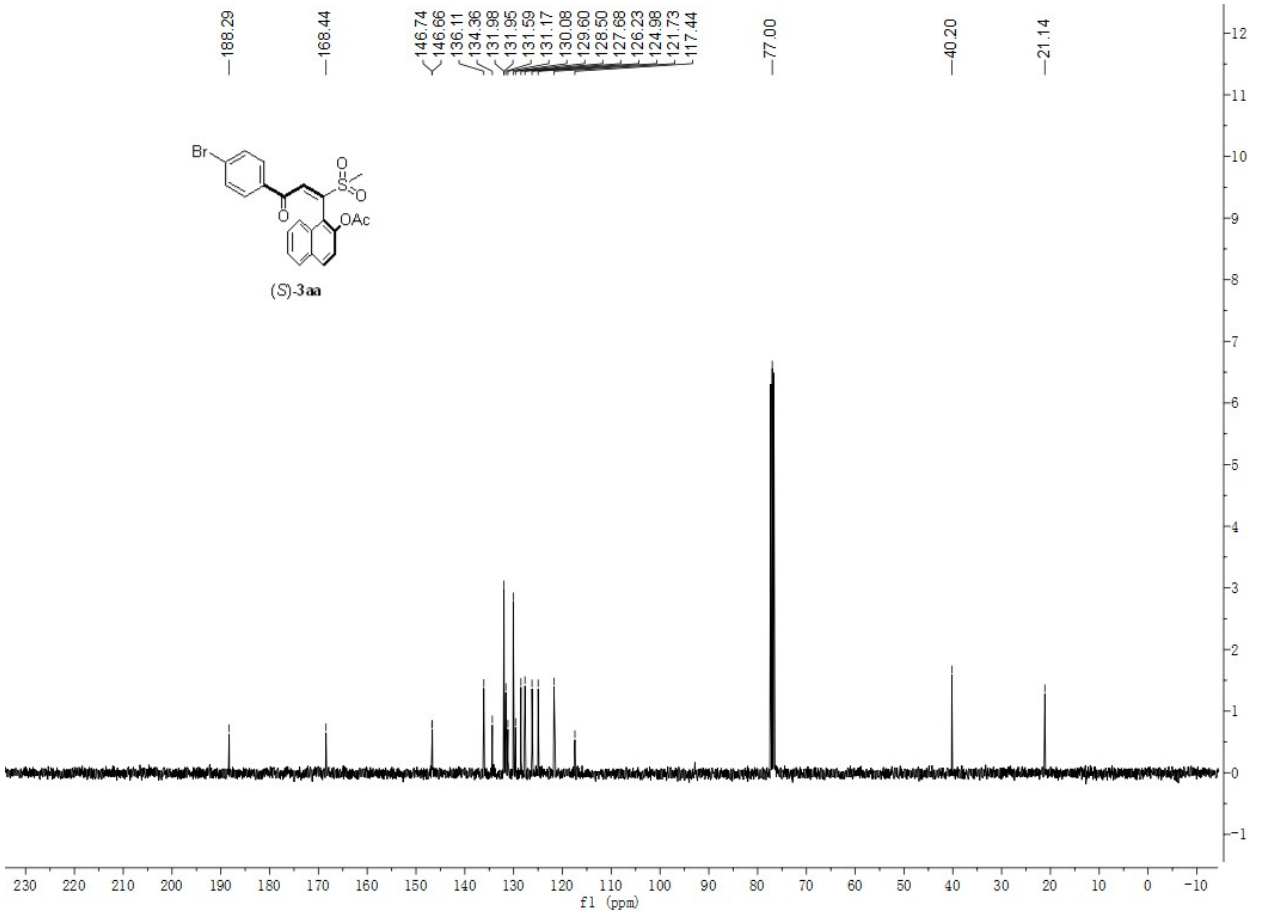
143.77
140.94
136.00
135.11
133.78
133.63
131.94
131.08
130.76
130.57
129.02
128.39
127.98
126.78
125.62
124.45
121.50
117.32
77.00
21.04
Cl
O
S
O
O
OAc
(S)-3z
f1 (ppm)


8.25
7.92
7.89
7.85
7.82
7.80
7.70
7.68
7.56
7.54
7.53
7.50
7.49
7.47
7.37
7.34
2.82
2.30
0.00
Br
O
S
O
O
OAc
(S)-3aa
1.00
1.07
1.95
1.95
3.91
0.98
3.00
2.98
f1 (ppm)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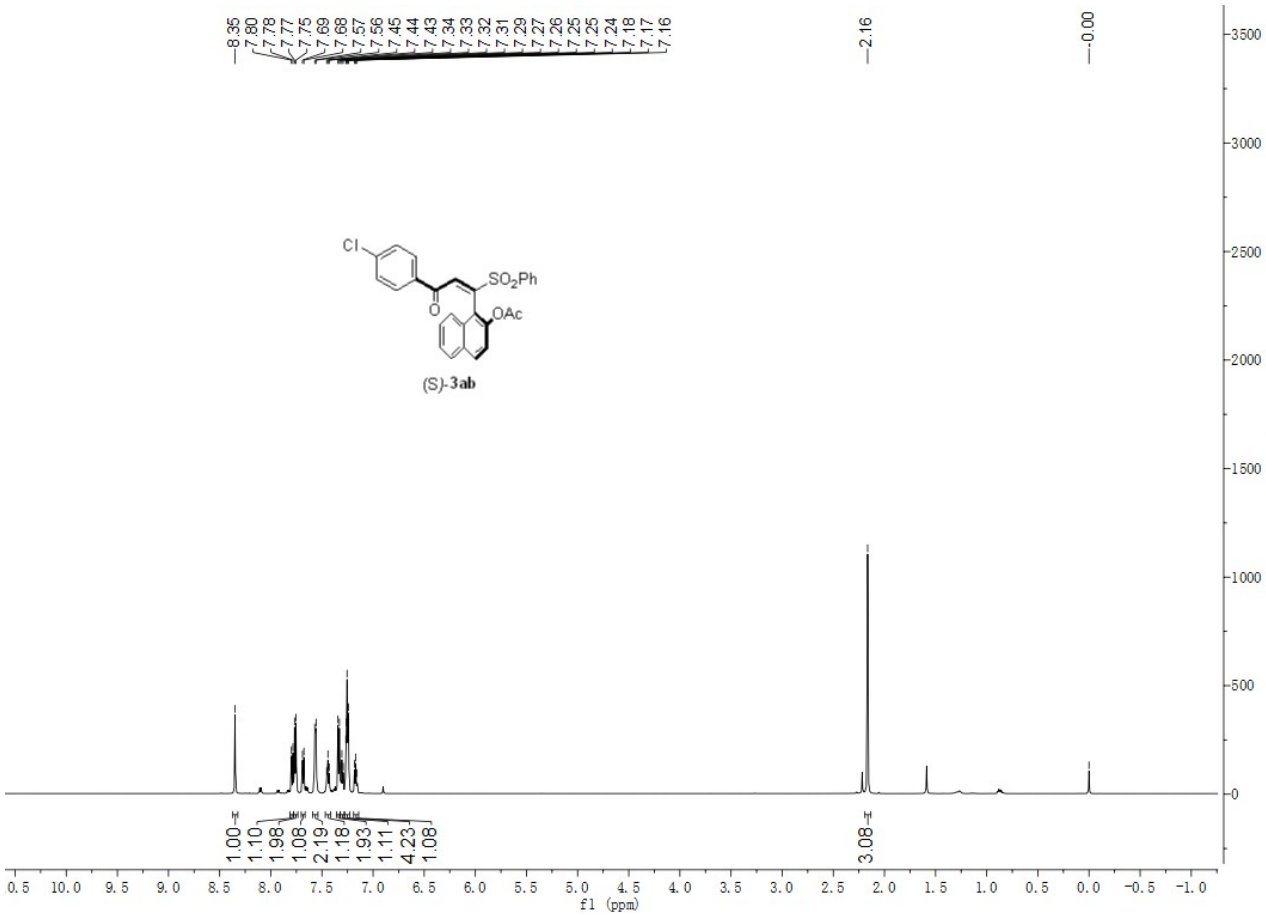
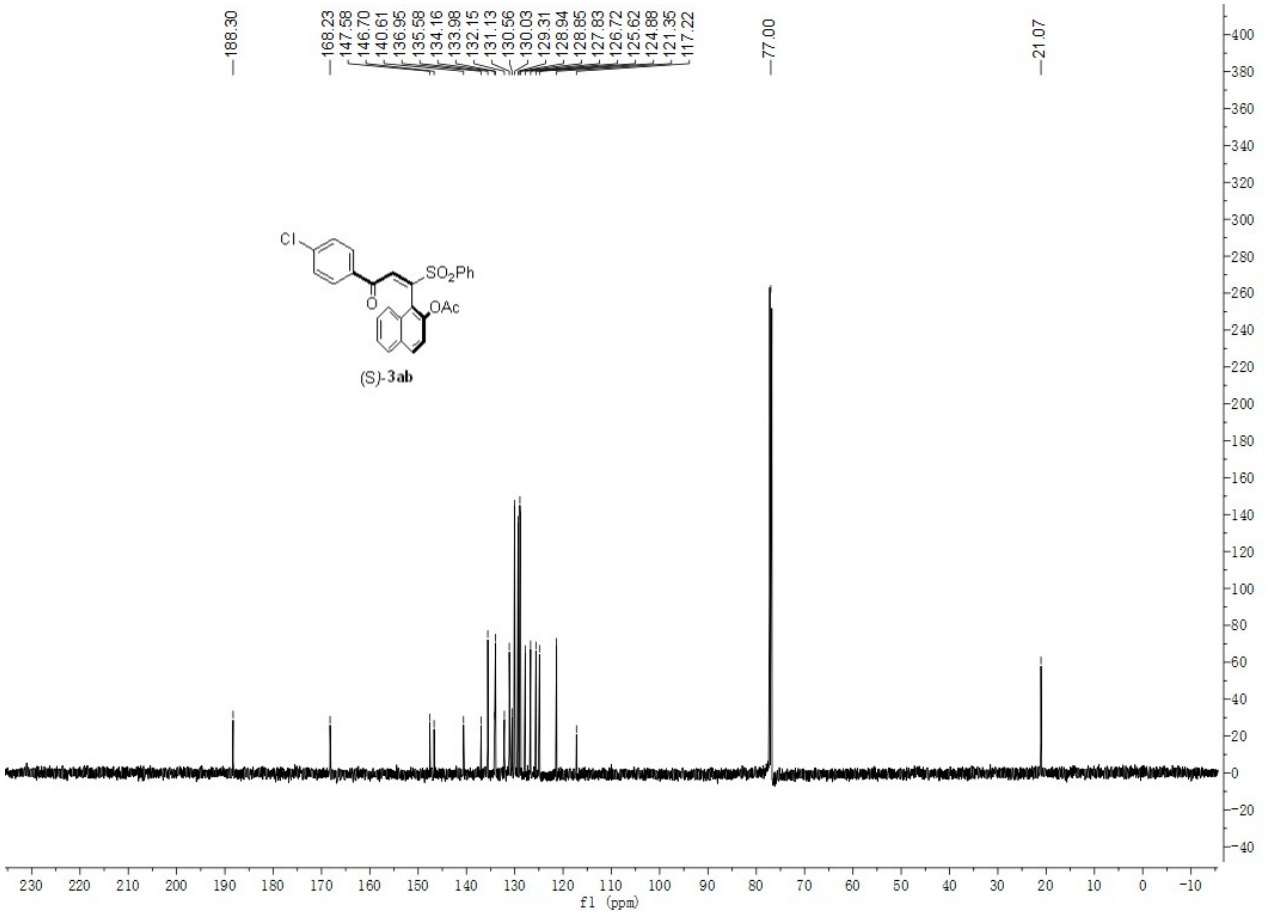
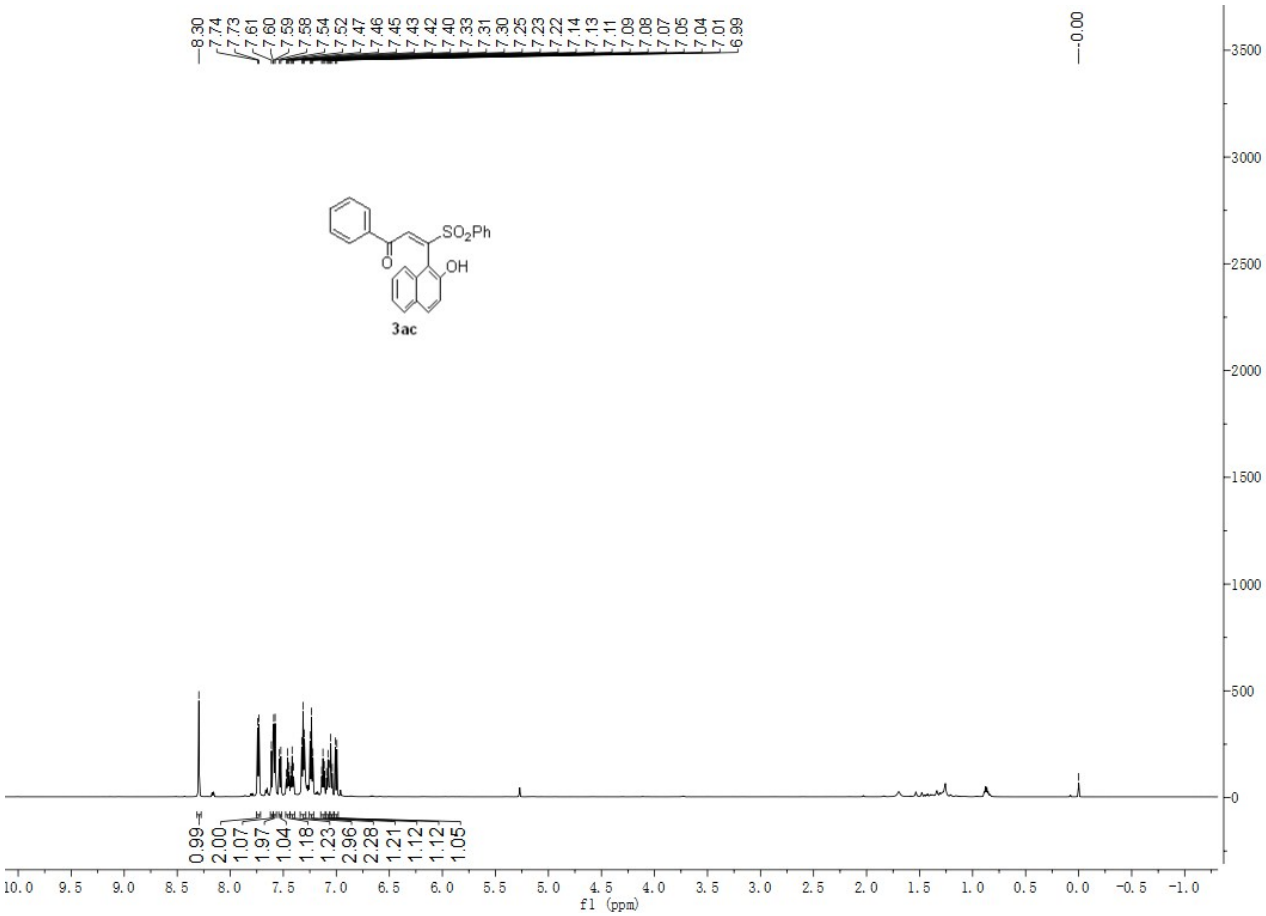
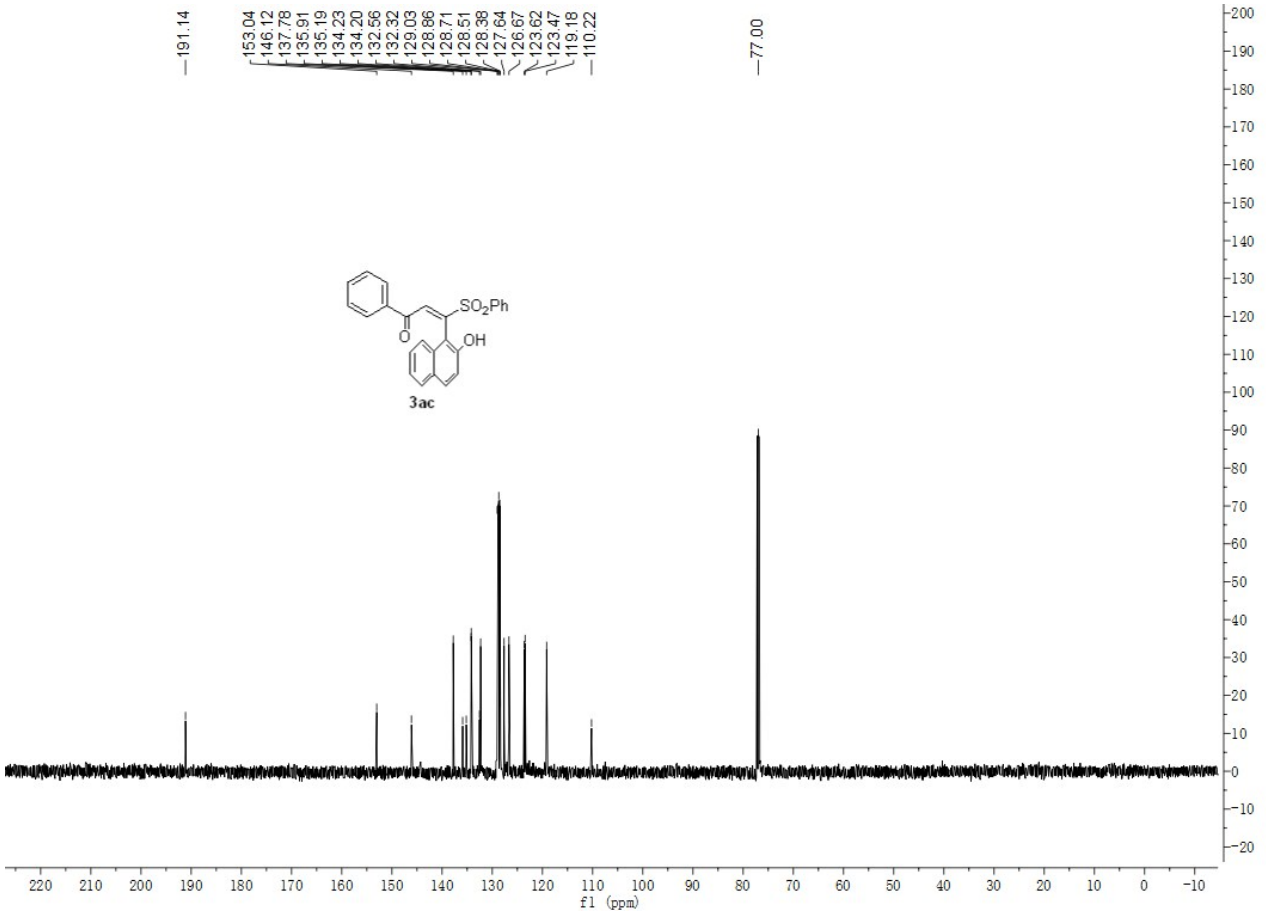
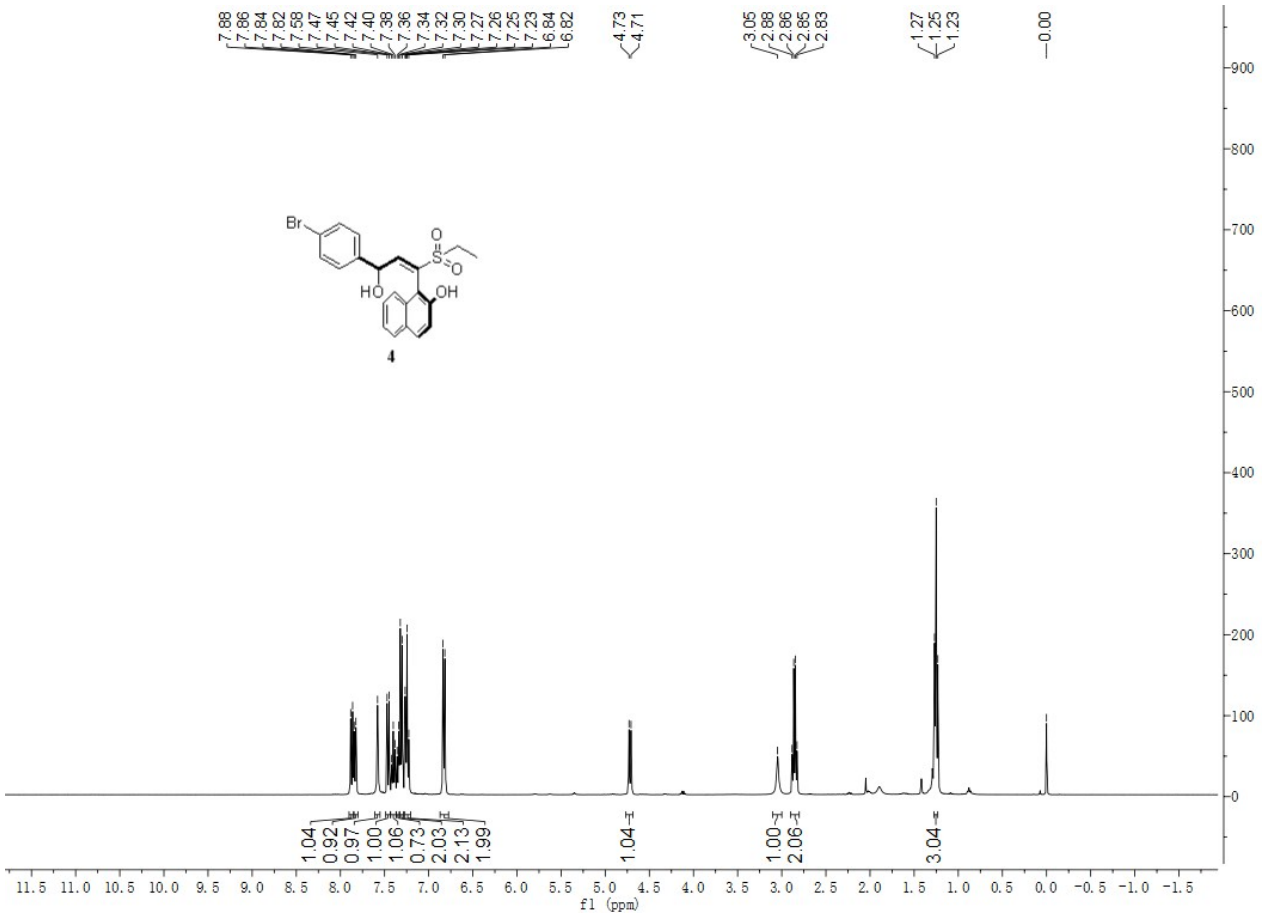
168.44
146.74
146.66
136.11
134.36
131.98
131.95
131.59
131.17
130.08
129.60
128.50
127.68
126.23
124.98
121.73
117.44
77.00
40.20
21.14
Br
O
S
O
O
OAc
(S)-3aa
f1 (ppm)

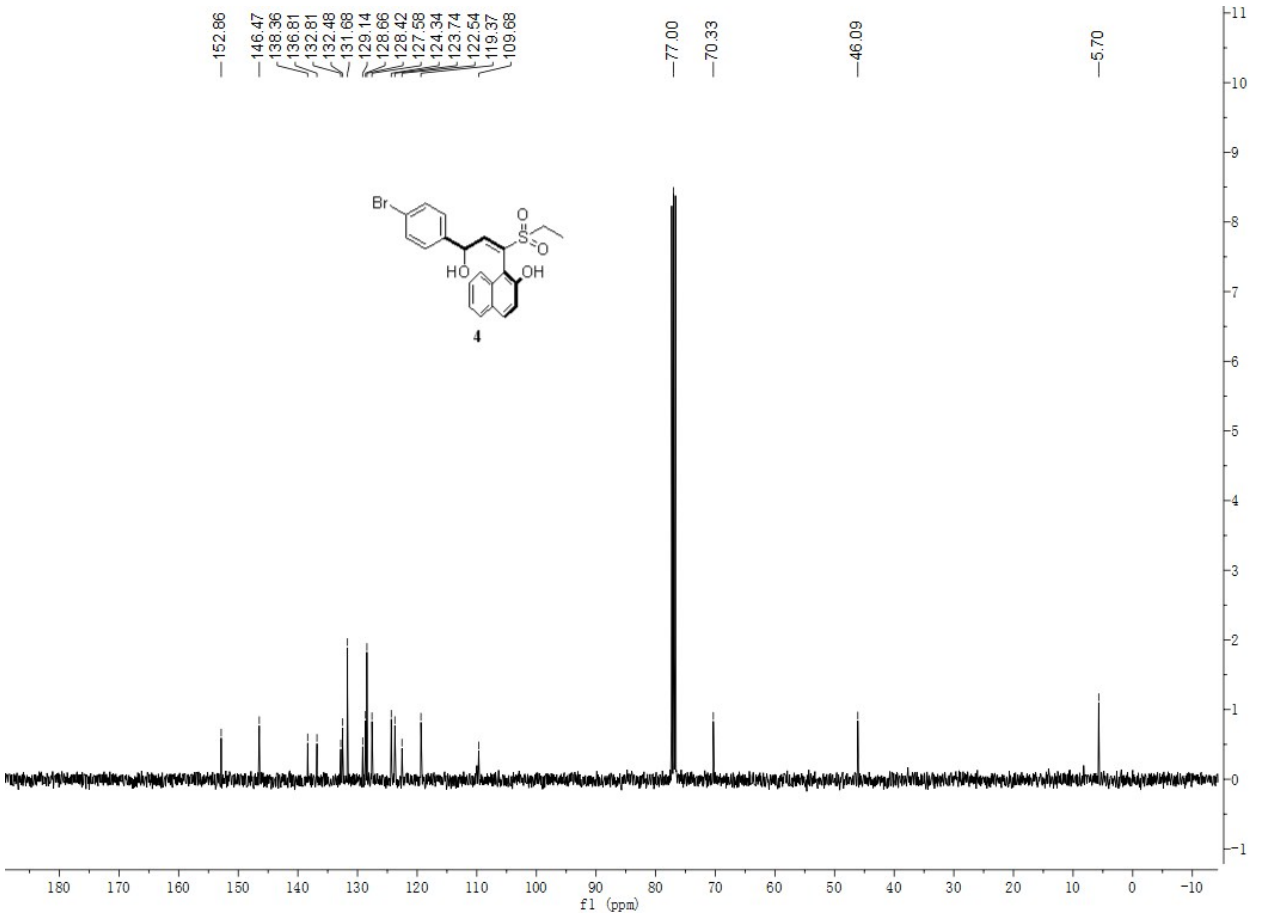

8.35
7.80
7.78
7.77
7.75
7.69
7.68
7.57
7.56
7.45
7.44
7.43
7.34
7.33
7.32
7.31
7.29
7.27
7.26
7.25
7.24
7.18
7.17
7.16
2.16
0.00
Cl
SO2Ph
O
OAc
(S)-3ab
1.00
1.10
1.98
1.08
2.19
1.18
1.93
1.11
4.23
1.08
3.08
f1 (ppm)


188.30
168.23
147.58
146.70
140.61
136.95
135.58
134.16
133.98
132.15
131.13
130.56
130.03
129.31
128.94
128.85
127.83
126.72
125.62
124.88
121.35
117.22
77.00
21.07
Cl
SO2Ph
O
OAc
(S)-3ab
f1 (ppm)


8.30
7.74
7.73
7.61
7.60
7.59
7.58
7.54
7.52
7.47
7.46
7.45
7.43
7.42
7.40
7.33
7.31
7.30
7.25
7.23
7.22
7.14
7.13
7.11
7.09
7.08
7.07
7.05
7.04
7.01
6.99
0.00
SO2Ph
OH
3ac
0.99
2.00
1.07
1.97
1.04
1.18
1.23
2.96
2.28
1.21
1.12
1.12
1.05
f1 (ppm)


191.14
153.04
146.12
137.78
135.91
135.19
134.23
134.20
132.56
132.32
129.03
128.86
128.71
128.51
128.38
127.64
126.67
123.62
123.47
119.18
110.22
77.00
SO2Ph
OH
3ac
f1 (ppm)


7.88
7.86
7.84
7.82
7.58
7.47
7.45
7.42
7.40
7.38
7.36
7.34
7.32
7.30
7.27
7.26
7.25
7.23
6.84
6.82
4.73
4.71
3.05
2.88
2.86
2.85
2.83
1.27
1.25
1.23
0.00
Br
O
S
O
HO
OH
4
1.04
0.92
0.97
1.00
1.06
0.73
2.03
2.13
1.99
1.04
1.00
2.06
3.04
f1 (ppm)


152.86
146.47
138.36
136.81
132.81
132.48
131.68
129.14
128.66
128.42
127.58
124.34
123.74
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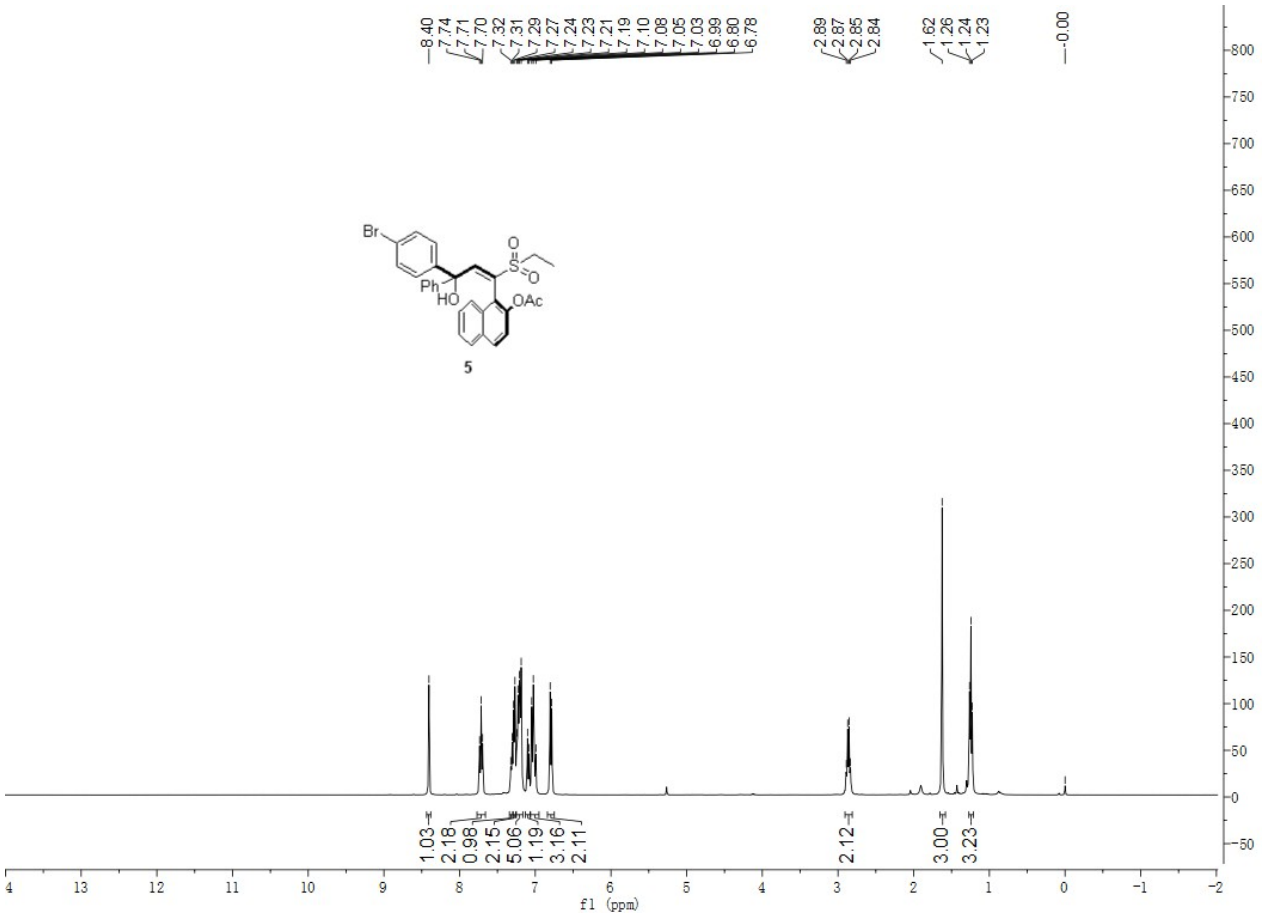
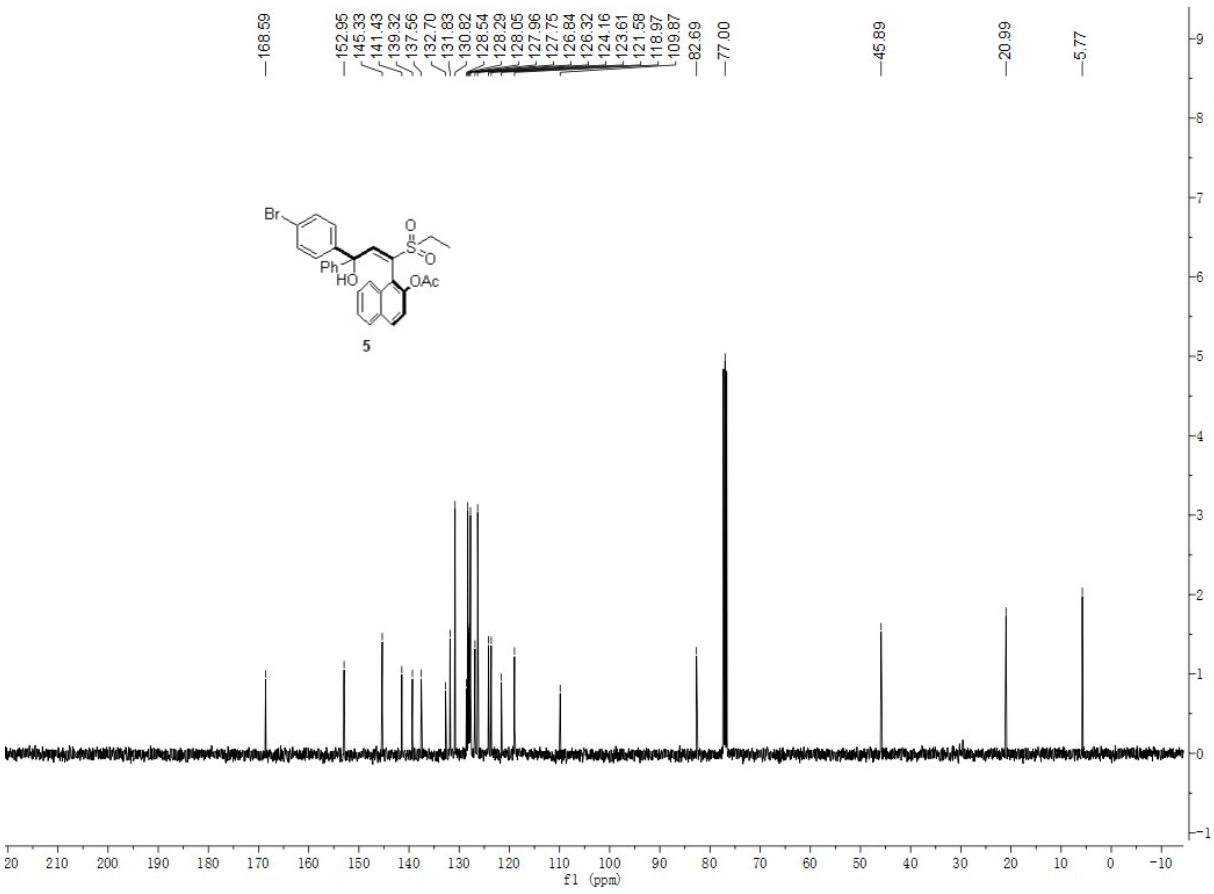
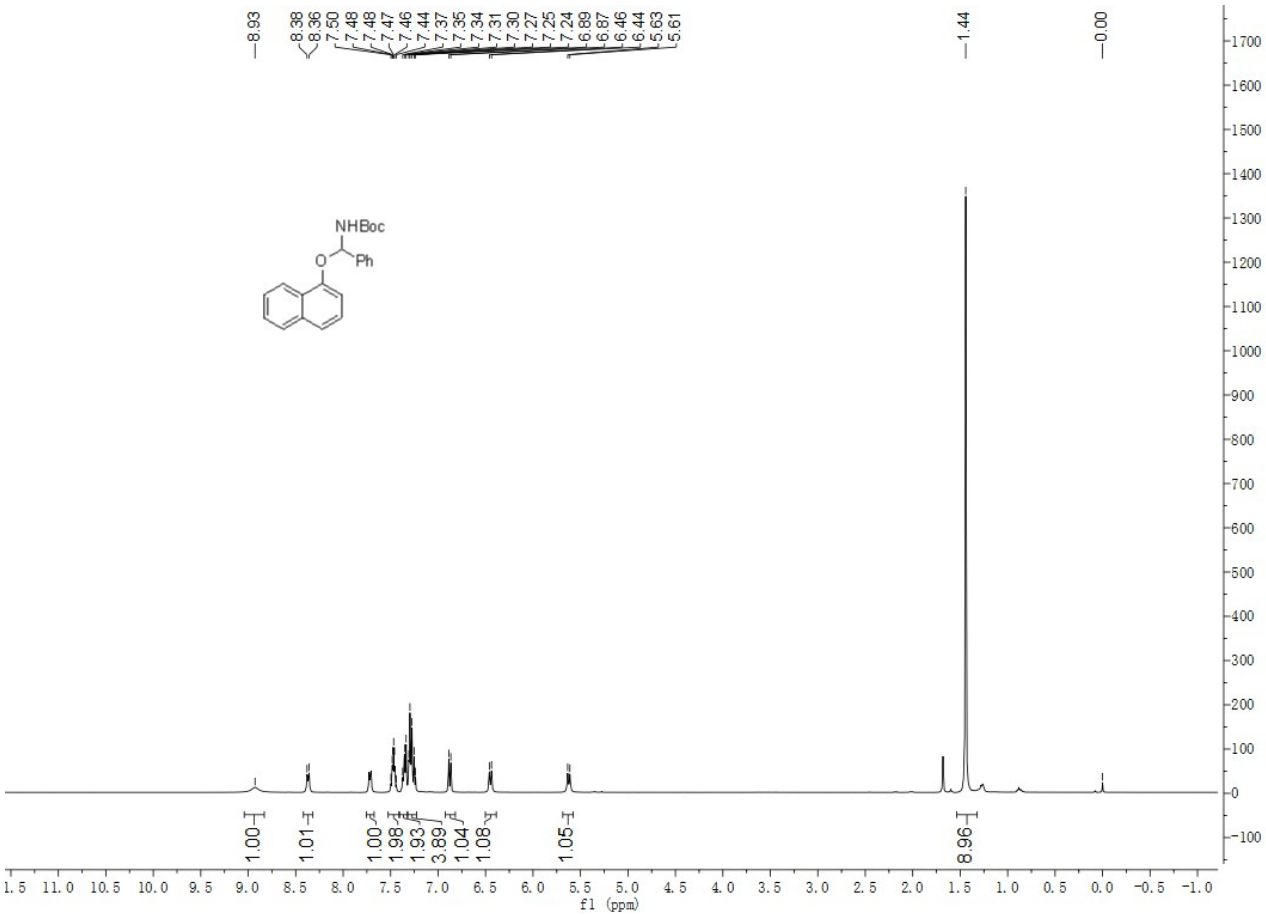
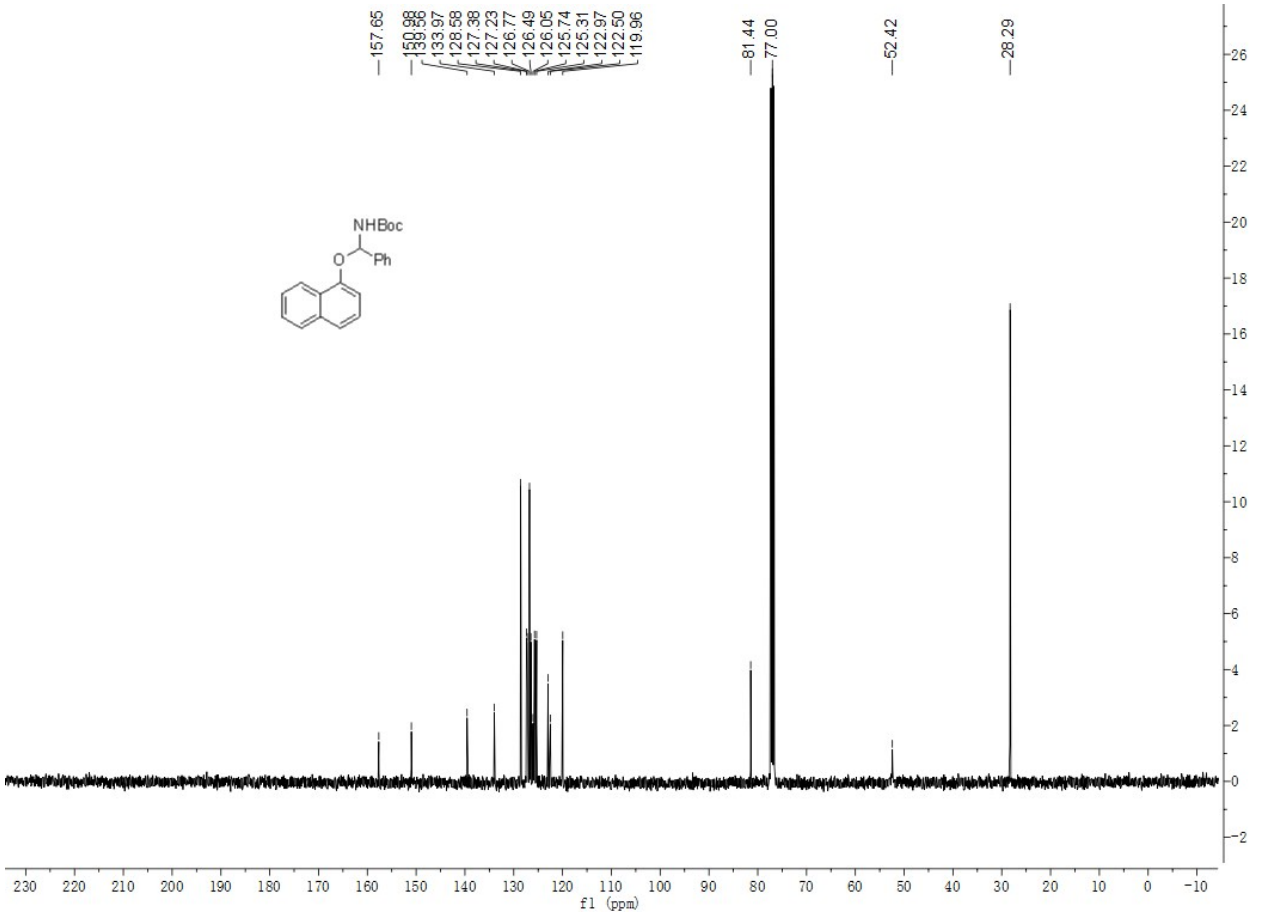
Br
O
S
O
HO
OH
4
f1 (ppm)


8.40
7.74
7.71
7.70
7.32
7.31
7.29
7.27
7.24
7.23
7.21
7.19
7.10
7.08
7.05
7.03
6.99
6.80
6.78
2.89
2.87
2.85
2.84
1.62
1.26
1.24
1.23
0.00
Br
Ph
HO
O
S
O
OAc
5
1.03
2.18
0.98
2.15
5.06
1.19
3.16
2.11
2.12
3.00
3.23
f1 (ppm)


168.59
152.95
145.33
141.43
139.32
137.56
132.70
131.83
130.82
128.54
128.29
128.05
127.96
127.75
126.84
126.32
124.16
123.61
121.58
118.97
109.87
82.69
77.00
45.89
20.99
5.77
Br
Ph
HO
O
S
O
OAc
5
f1 (ppm)


8.93
8.38
8.36
7.50
7.48
7.48
7.47
7.46
7.44
7.37
7.35
7.34
7.31
7.30
7.27
7.25
7.24
6.89
6.87
6.46
6.44
5.63
5.61
1.44
0.00
NHBoc
O
Ph
1.00
1.01
1.00
1.98
1.93
3.89
1.04
1.08
1.05
8.96
f1 (ppm)


157.65
150.98
139.96
133.97
128.58
127.38
127.23
126.77
126.49
126.05
125.74
125.31
122.97
122.50
119.96
81.44
77.00
52.42
28.29
NHBoc
O
Ph
f1 (ppm)

IX. Crystallographic details of (*S*)-3b

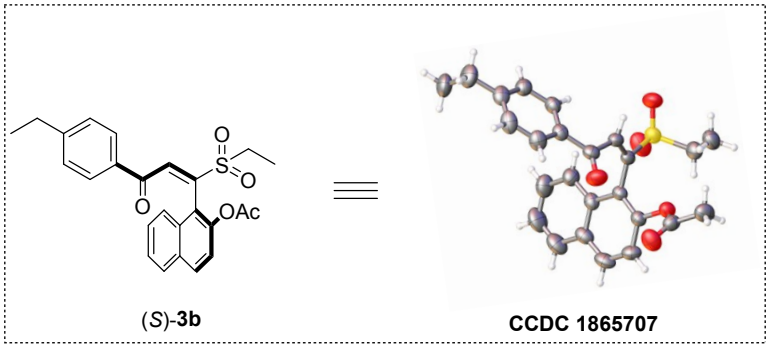


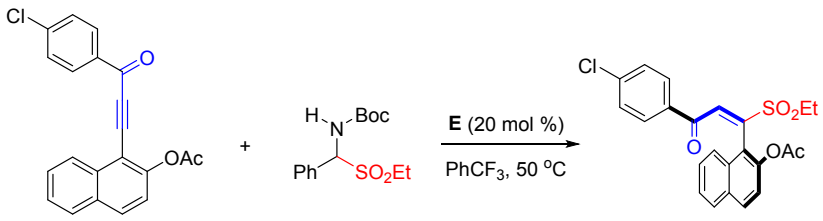
Fig.S1 X-ray crystal structure of (*S*)-3b

Bond precision: C-C = 0.0056 A Wavelength=0.71073
Cell: a=9.1789(3) b=10.5740(3) c=11.4116(4)
alpha=90 beta=91.684(3) gamma=90
Temperature: 292 K

	Calculated	Reported
Volume	1107.11(6)	1107.11(6)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C25 H24 O5 S	C25 H24 O5 S
Sum formula	C25 H24 O5 S	C25 H24 O5 S
Mr	436.50	436.50
Dx,g cm-3	1.309	1.309
Z	2	2
Mu (mm-1)	0.180	0.180
F000	460.0	460.0
F000’	460.47	
h,k,lmax	11,13,14	11,13,14
Nref	4548[2403]	4539
Tmin,Tmax	0.934,0.947	0.894,1.000
Tmin’	0.934	

Correction method= # Reported T Limits: Tmin=0.894 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 1.89/1.00 Theta(max)= 26.372
R(reflections)= 0.0464(3601) wR2(reflections)= 0.1016(4539)
S = 1.046 Npar= 283

X. Equilibration process of the reaction



1h **2a** (*S*)-**3h**

entry	time (h)	conversion of (*S*)-**3h** (%)	ee of (*S*)-**3h** (%)	imine (%)
1	1	5	97	5
2	2	12	97	14
3	3	14	97	22
4	4	22	97	25
5	5	25	97	36
6	6	28	97	40
7	8	32	97	50
8	10	40	97	55
9	12	45	97	58
10	14	45	97	68
11	16	54	97	70
12	18	65	97	77
13	20	71	97	85
14	22	85	97	85
15	24	93	97	87
16	32	93	97	80
17	40	93	97	72
18	48	93	97	60
19	59	93	97	42
20	70	93	97	20

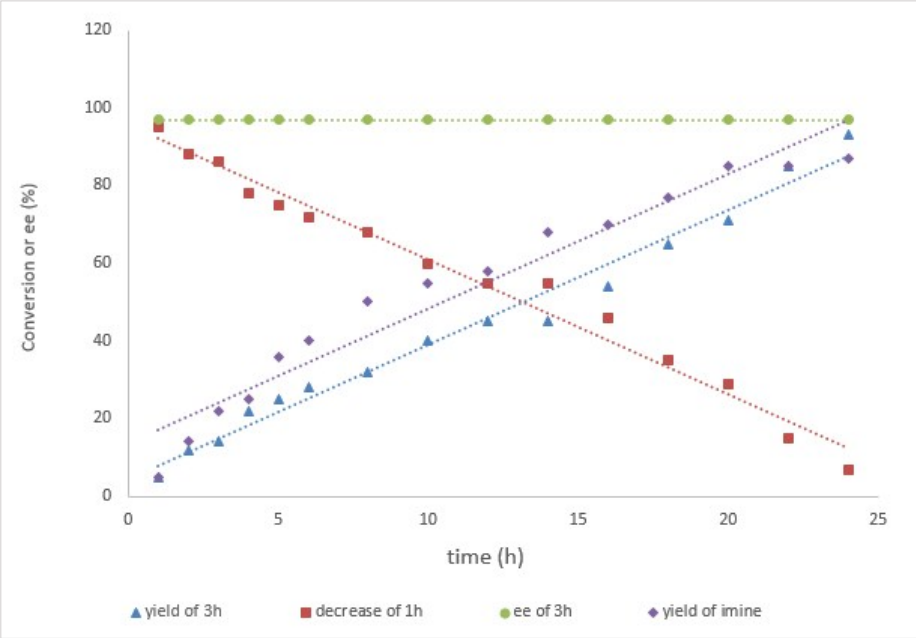


Fig.S2 Equilibration process of the reaction in 24 h