Electronic Supplementary Material (ESI) for ChemComm.


# Rh(II)/Phosphine-cocatalyzed Synthesis of Dithioketal Derivatives from Diazo Compounds through Simultaneous Construction of Two Different C-S Bonds

Changqing Rao, Shaoyu Mai and Qiuling Song*

Institute of Next Generation Matter Transformation, College of Chemical Engineering and College of Material Sciences Engineering at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China

## Table of Contents

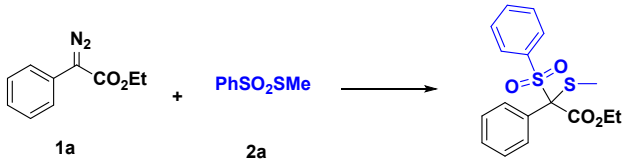
# 1. General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. DCE, $CH_3CN$ was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a sealed tube under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

$^1$H-NMR and $^{13}$C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ ($\delta$ = 7.26 for $^1$H-NMR, $\delta$ = 77.00 for $^{13}$C-NMR) as an internal reference. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument. Coupling constants (*J*) were reported in Hertz (Hz).

## 2、Optimization of experimental conditions

## Table S1. Screening of Catalyst and its dosages

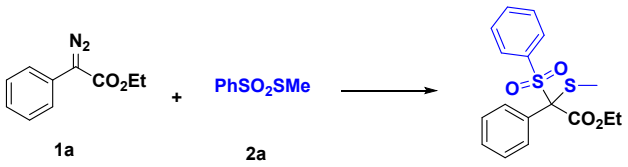



1a 2a

| entry | 1a:2a | Catalyst [xmol%] | Cocatalyst [10mol%] | T [°C]/t [h] | Yield [a] /% |
|---|---|---|---|---|---|
| 1 | 2:1 | CuOTf/5 | $Cy_3P$ | 70/12 | 0 |
| 2 | 2:1 | $CuCl_2$/5 | $Cy_3P$ | 70/12 | 16 |
| 3 | 2:1 | $CuBr_2$/5 | $Cy_3P$ | 70/12 | 20 |
| 4 | 2:1 | $Cu(OAc)_2$/5 | $Cy_3P$ | 70/12 | 45 |
| 5 | 2:1 | $CuF_2$/5 | $Cy_3P$ | 70/12 | 15 |
| 6 | 2:1 | $Cu(acac)_2$/5 | $Cy_3P$ | 70/12 | 20 |
| 7 | 2:1 | $Pd(OAc)_2$/5 | $Cy_3P$ | 70/12 | 30 |
| 8 | 2:1 | $Pd(PPh_3)Cl_2$/5 | $Cy_3P$ | 70/12 | trace |
| 9 | 2:1 | $Pd_2(dba)_3$/5 | $Cy_3P$ | 70/12 | trace |
| 10 | 2:1 | $Rh_2(OAc)_4$/5 | $Cy_3P$ | 70/12 | 75 |
| 11 | 2:1 | $Rh_2(OAc)_4$/10 | $Cy_3P$ | 70/12 | 65 |
| 12 | 2:1 | $Rh_2(OAc)_4$/2.5 | $Cy_3P$ | 70/12 | 79 |
| 13 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 70/12 | 80 |

Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL) , $N_2$. [a] Isolated yields.

## Table S2. Screening of Time and Temperatrue.

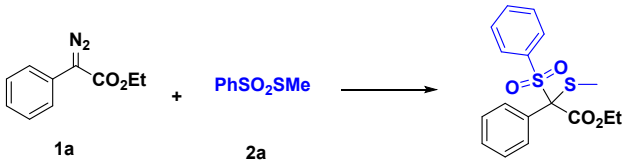



1a 2a

| entry | 1a:2a | Catalyst [x mol%] | Cocatalyst [10 mol%] | T [°C]/t [h] | Yield [a] /% |
|---|---|---|---|---|---|
| 1 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/12 | 94 |
| 2 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 40/12 | 85 |
| 3 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 60/12 | 78 |
| 4 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 90/12 | 60 |
| 5 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/24 | 93 |
| 6 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/7 | 90 |
| 7 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/3 | 89 |
| 8 | 2:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/1 | 82 |

Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL) , $N_2$. [a] Isolated yields.

## Table S3. Screening of and Cocatalyst



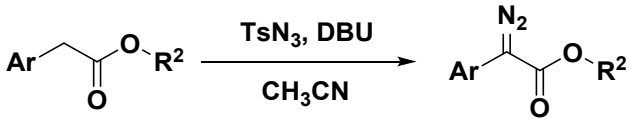

1a 2a

| entry | 1a:2a | Catalyst [x mol%] | Cocatalyst [10 mol%] | T [°C]/t [h] | Yield [a] /% |
|---|---|---|---|---|---|
| 1 | 1.5:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/3 | 89 |
| 2 | 1:1 | $Rh_2(OAc)_4$/1 | $Cy_3P$ | 25/3 | 71 |
| 3 | 1.5:1 | $Rh_2(OAc)_4$/1 | dppp | 25/3 | 94 |
| 4 | 1.5:1 | $Rh_2(OAc)_4$/1 | dppb | 25/3 | 82 |
| 5 | 1.5:1 | $Rh_2(OAc)_4$/1 | $PPh_3$ | 25/3 | 25 |
| 6 | 1.5:1 | $Rh_2(OAc)_4$/1 | - | 25/3 | N.D |
| 7 | 1.5:1 | - | dppp | 25/3 | trace |

Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL) , $N_2$. [a] Isolated yields.

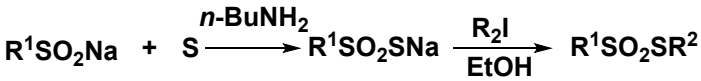
## 3. Preparation of starting materials.

### 3.1 Typical procedure for the preparation of α-diazo arylacetates[1]



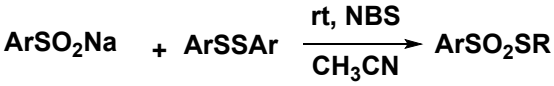

At room temperature, a solution of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (2.28 g, 15mmol, 1.5 equiv) in anhydrous $CH_3CN$ (10 mL) was added dropwise to a solution of ethylphenyl acetate (1.64 g, 10 mmol, 1.0 equiv) and *p*-toluenesulfonyl azide (TsN3) (2.37 g, 12mmol, 1.2 equiv) in anhydrous $CH_3CN$ (50 mL). Then the reaction mixture was stirred at room temperature for 15 hours. After water (40 mL) was added, the resulting mixture was extracted with diethyl ether (3 × 40 mL). The combined organic layer was washed with brine (40 mL) and dried over anhydrous MgSO4. After the removal of the solvent under reduced pressure, the residual was purified by a silica gel column chromatography with petroleum ether (PE)/ethyl acetate (EA) (30:1) as the eluent.

### 3.2 Typical procedure for the preparation of S-alkyl benzenesulfonothioate.[2]



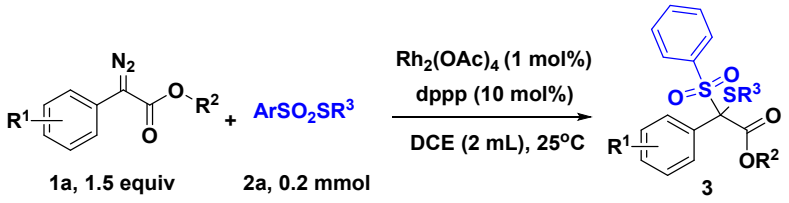
A mixture of $PhSO_2Na$ (6.56 g, 40 mmol) and S (1.28 g, 40 mmol) in n-$BuNH_2$ (40 mL) was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the residue was washed by $Et_2O$ to obtain a white solid $PhSO_2SNa$.Then $PhSO_2SNa$ was dissolved in EtOH (40 mL), then R-X (11.36 g, 80 mmol) was added to the solution. The reaction mixture was stirred at 40-45℃ for 24 h. After removal of the solvent under reduced pressure, the reaction mixture was poured on a solution of $Na_2S_2O_3$ and $CH_2Cl_2$ (30 mL). The precipitate was filtered and dried by anhydrous $Na_2SO_4$, the residue was purified through column chromatography (petroleum ether: EtOAc = 20:1) afforded the desired product S-alkyl benzenesulfonothioate as a yellow oil.

### 3.3 Typical procedure for the preparation of S-Ar benzenesulfonothioate[3]



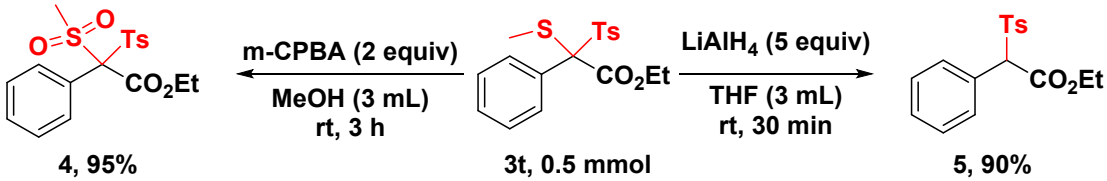

A mixture of sulfinate **1** (8 mmol), disulfide **2** (2 mmol) and NBS (4 mmol) in $CH_3CN$ (30 mL) was stirred at room temperature for respective time. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (300—400 mesh) with petroleum ether-EtOAc as eluent to provide the desired S-Ar benzenesulfonothioate.

## 4. General procedure for preparation of compound 3




To a mixture of $Rh_2(OAc)_4$ (1 mol%), dppp (0.1 equiv) and **2a** (0.2 mmol) in DCE (2 mL) under $N_2$ atmosphere, **1a** (0.3 mmol, 1.5 equiv) were added. The system was stirred at 25 ℃ for 3 h. The reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 5:1) to give the products.

## 5. General procedure for preparation of compound 4 and 5

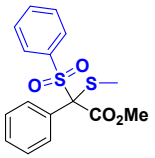


Procedure of **4**: To a mixture 3t (0.5 mmol) in MeOH (3 mL) under air, m-CPBA (2 equiv) was added slowly. The system was stirred at room temperature for 3 h. The reaction mixture was evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 2:1) to give **4**.

Procedure of **5**: To a mixture 3t (0.5 mmol) in THF (3 mL) under air, $LiAlH_4$ (5 equiv) was added slowly. The system was stirred at room temperature for 30 min. The reaction mixture was evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 5:1) to give **5**.

## 5. Characterization data for products

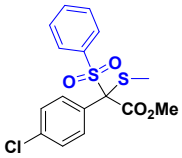
**methyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3a**



3a

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (56 mg, 84%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 1H), 7.47 – 7.43 (m, 2H), 7.34 (dd, *J* = 9.6, 4.3 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.19 (m, 1H), 3.90 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.5, 135.6, 133.7, 131.6, 131.4, 129.7, 129.4, 128.0, 127.7, 83.4, 53.5, 15.6. HRMS (DART Positive) calcd for $C_{16}H_{16}O_4S_2(M+NH_4)^+$: 354.0828; Found: 354.0826.

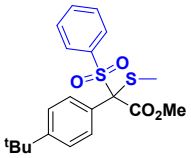
**methyl 2-(4-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3b**



3b

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (61 mg, 82%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.37 – 7.32 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 3.89 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.2, 136.0, 135.4, 134.0, 131.4, 130.9, 130.1, 128.2, 127.9, 82.6, 53.7, 15.6. HRMS (DART Positive) calcd for $C_{16}H_{15}O_4ClS_2(M+NH_4)^+$: 388.0439; Found: 388.0435.

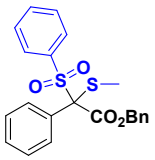
**methyl 2-(4-(tert-butyl)phenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3c**



3c

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (71 mg, 90%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 2.43 (s, 3H), 1.29 (t, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.6, 153.1, 135.8, 133.6, 131.3, 129.1, 128.3, 127.6, 125.0, 83.3, 53.5, 34.7, 31.2, 15.6. HRMS (DART Positive) calcd for $C_{20}H_{24}O_4S_2(M+NH_4)^+$: 410.1454; Found: 410.1451.

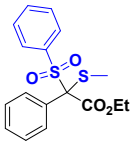
**benzyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3d**



3d

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (70 mg, 85%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 1H), 7.41 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.24 (d, 2H), 7.21 – 7.14 (m, 4H), 5.33 (dd, *J* = 49.0, 12.0 Hz, 2H), (s, 2.30, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 135.6, 134.6, 133.7, 131.6, 131.4, 129.6, 129.5, 128.9, 128.8, 128.6, 127.9, 127.7, 83.1, 68.4, 15.4. HRMS (ESI) calcd for $C_{22}H_{20}O_4S_2$ $(M+Na)^+$: 435.0695; Found: 435.0695

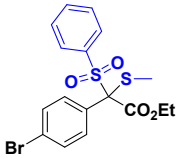
**ethyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3e**



3e

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (66 mg, 94%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 1H), 7.44 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.25 – 7.19 (m, 4H), 4.45 – 4.31 (m, 2H), 2.46 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 135.7, 133.7, 131.7, 131.4, 129.6, 129.4, 128.0, 127.7, 83.3, 63.0, 15.6, 14.1. HRMS (EI) calcd for $C_{17}H_{18}O_4S_2(M)^+$: 350.0647; Found: 350.0645.

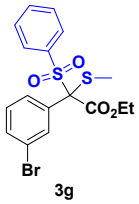
**ethyl 2-(4-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3f**



3f

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (66 mg, 77%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 17.8, 7.5 Hz, 3H), 7.40 – 7.31 (m, 4H), 7.13 (t, *J* = 5.7 Hz, 2H), 4.42 – 4.31 (m, 2H), 2.41 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 135.8, 134.2, 131.7, 131.4, 131.4, 131.0, 128.1, 124.4, 82.9, 63.5, 15.8, 14.4. HRMS (DART Positive) calcd for $C_{17}H_{17}O_4BrS_2(M+NH_4)^+$: 446.0090; Found: 446.0085.

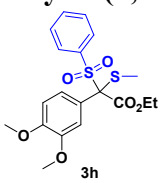
**ethyl 2-(3-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3g**



3g

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (80 mg, 93%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.56 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.34 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.27 (t, *J* = 1.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 4.39 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 – 1.30 (t, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.4, 135.2, 134.0, 133.8, 132.6, 132.5, 131.4, 129.3, 128.3, 127.8, 121.8, 82.5, 63.2, 15.5, 14.1. HRMS (DART Positive) calcd for $C_{17}H_{17}O_4BrS_2(M+NH_4)^+$: 446.0090; Found: 446.0086.

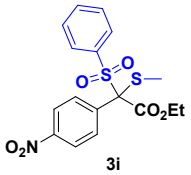
**ethyl 2-(3,4-dimethoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3h**[4]



3h

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (78 mg, 95%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 3H), 7.30 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.77 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.44 – 4.31 (m, 2H), 3.86 (s, 3H), 3.66 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 150.0, 148.0, 135.9, 133.5, 131.3, 127.6, 123.6, 122.5, 112.3, 110.1, 83.0, 62.9, 55.9, 55.8, 15.6, 14.1.

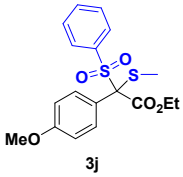
**ethyl 2-(methylthio)-2-(4-nitrophenyl)-2-(phenylsulfonyl)acetate 3i**[4]



3i

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (35 mg, 44%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 7.62 – 7.55 (m, 3H), 7.53 – 7.47 (m, 2H), 7.36 (dd, *J* = 8.4, 7.4 Hz, 2H), 4.42 – 4.35 (m, 2H), 2.38 (s, 3H), 1.32 (t, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.1, 148.1, 138.5, 135.2, 134.3, 131.4, 130.9, 128.1, 122.8, 824, 63.5, 15.5, 14.0.

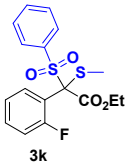
**ethyl 2-(4-methoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3j**[4]



3j

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (67 mg, 88%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.56 (m, *J* = 7.6, 1.2 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.34 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.27 (t, *J* = 1.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 4.39 (t, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 – 1.30 (t, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 158.9, 135.7, 133.6, 132.9, 131.4, 128.8, 127.6, 121.8, 115.6, 114.8, 83.3, 63.0, 55.3, 15.6, 14.1.

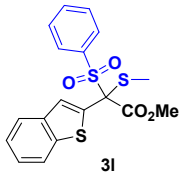
**ethyl 2-(2-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3k**



3k

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (53 mg, 72%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.32 (dd, *J* = 8.3, 7.5 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.01 (m, 2H), 6.98 (dt, *J* = 10.2, 2.2 Hz, 1H), 4.45 – 4.30 (m, 2H), 2.43 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.2,161.6 (d, *J* = 247.1 Hz), 135.2, 133.6, 131.0 129.09 (d, *J* = 8.1 Hz), 127.51 (s), 125.07 (d, *J* = 3.1 Hz), 116.60 (d, *J* = 24.3 Hz), 116.3(d, *J* = 20.9 Hz), 82.4 630 29.4, 15.2, 13.8. RMS (DART Positive) calcd for $C_{17}H_{17}O_4FS_2$ $(M+NH_4)^+$: 386.0891; Found: 386.0886.

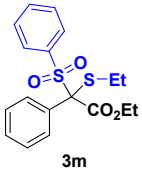
**methyl 2-(benzo[b]thiophen-2-yl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3l**



3l

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (50 mg, 64%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.51 (td, *J* = 7.5, 1.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.28 (t, *J* = 11.8, 4.0 Hz, 2H), 7.25 – 7.18 (m, 4H), 3.89 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.4, 135.5, 133.7, 131.5, 131.3, 129.6, 129.4, 128.0, 127.6, 83.3, 53.5, 15.6. HRMS (DART Positive) calcd for $C_{18}H_{16}O_4S_3$ $(M+NH_4)^+$: 410.0549; Found: 410.0547.

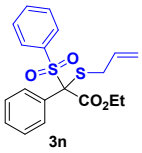
**ethyl 2-(ethylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3m**



3m

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (56 mg, 77%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.50 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.22 (d, *J* = 4.3 Hz, 4H), 4.36 (q, 2H), 3.25 – 3.13 (m, 1H), 2.81 – 2.70 (m, 1H), 1.30 (q, *J* = 14.2, 7.3 Hz, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.2, 135.7, 133.5, 131.8, 131.4, 129.5, 129.4, 127.8, 127.6, 83.6, 62.9, 26.6, 14.0, 13.3. HRMS (DART Positive) calcd for $C_{18}H_{20}O_4S_2$ $(M+NH_4)^+$: 382.1141; Found: 382.1141.

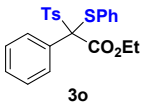
**ethyl 2-(allylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3n**



3n

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (38 mg, 50%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.50 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 2H), 7.23 (d, *J* = 4.3 Hz, 4H), 5.98 – 5.80 (m, 1H), 5.31 (dt, *J* = 17.0, 2.7, 1.3 Hz, 1H), 5.23 – 5.16 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.89 – 3.77 (m, 1H), 3.56 – 3.47 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.1, 135.7, 133.6, 131.7, 131.7, 131.4, 129.59, 129.4, 127.9, 127.6, 119.6, 83.2, 63.0, 35.6, 14.0. HRMS (DART Positive) calcd for $C_{19}H_{20}O_4S_2$ $(M+NH_4)^+$: 394.1141; Found: 394.1139.

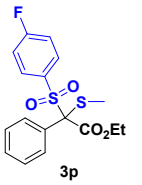
**ethyl 2-phenyl-2-(phenylthio)-2-tosylacetate 3o**



3o

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (53 mg, 62%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 3H), 7.09 (dd, *J* = 8.5, 0.5 Hz, 2H), 3.94 – 3.85 (m, 1H), 3.83 – 3.75 (m, 1H), 2.37 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.0, 144.7, 137.1, 133.1, 132.8, 131.6, 130.2, 130.1, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 127.7, 86.7, 62.6, 21.6, 13.5. HRMS (DART Positive) calcd for $C_{23}H_{22}O_4S_2$ $(M+NH_4)^+$: 444.1298; Found: 444.1291.

**ethyl 2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3p**

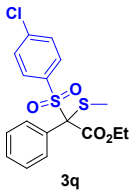


3p

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (59 mg, 80%).$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.38 – 7.32 (m, 1H), 7.28 – 7.18 (m, 4H), 6.94 (dd, *J* = 9.0, 8.4 Hz, 2H), 4.45 – 4.30 (m, 2H), 2.47 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8(t,

*J*=128.4), 134.2, 134.1, 131.6, 129.7, 129.3, 128.0, 115.0, 114.8, 83.3, 63.0, 15.5, 14.1. HRMS (DART Positive) calcd for $C_{17}H_{17}O_4FS_2$ $(M+NH_4)^+$: 386.0891; Found: 386.0887.

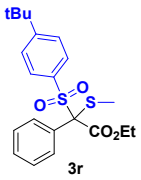
**ethyl 2-((4-chlorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3q**



3q

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (68 mg, 88%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.29 – 7.19 (m, 6H), 4.47 – 4.32 (m, 2H), 2.48 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 140.5, 134.3, 132.7, 131.5, 129.8, 129.3, 128.1, 127.9, 83.5, 63.1, 15.6, 14.1. HRMS (ESI) calcd for $C_{21}H_{26}ClO_4S_2$ $(M+Na)^+$: 407.0149; Found: 407.0141

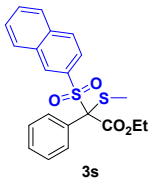
**ethyl 2-((4-(tert-butyl)phenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3r**



3r

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (78 mg, 97%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 (p, *J* = 2.1 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.19 (m, 4H), 4.46 – 4.29 (m, 2H), 2.43 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.0, 157.7, 132.7, 131.8, 131.1, 129.5, 129.4, 127.8, 124.6, 83.2, 62.9, 35.1, 31.0, 15.5, 14.1. HRMS (ESI) calcd for $C_{21}H_{26}O_4S_2$ $(M+Na)^+$: 429.1165; Found: 429.1165

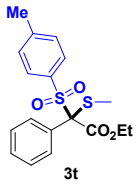
**ethyl 2-(methylthio)-2-(naphthalen-2-ylsulfonyl)-2-phenylacetate 3s**



3s

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (69 mg, 86%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.62 (td, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.54 (td, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.41 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.25 – 7.15 (m, 4H), 4.46 – 4.27 (m, 2H), 2.51 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.9, 135.2, 133.6, 132.8, 131.8, 131.3, 129.6, 129.5, 129.5, 129.2, 127.9, 127.7, 127.2, 127.1, 125.9, 83.5, 77.3, 77.0, 76.8, 63.0, 15.6, 14.1. HRMS (DART Positive) calcd for $C_{21}H_{20}O_4S_2(M+NH_4)^+$: 418.1141; Found: 418.1137.

**ethyl 2-(methylthio)-2-phenyl-2-tosylacetate 3t**

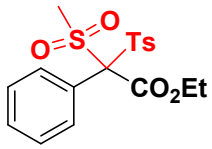


3t

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (66 mg, 88%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 3H), 7.22 (d, *J* = 4.5 Hz, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 4.42 – 4.29 (m, 2H), 2.43

(s, 3H), 2.34 (s, 3H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.8, 144.6, 132.6, 131.6, 131.2, 129.4, 129.3, 128.2, 127.8, 83.0, 62.8, 21.5, 15.4, 14.0. HRMS (ESI) calcd for $C_{18}H_{20}O_4S_2$ $(M+Na)^+$: 387.0695; Found: 387.0698.

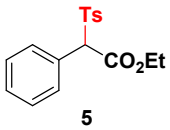
**ethyl 2-(methylsulfonyl)-2-phenyl-2-tosylacetate 4**



4

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a white solid (188 mg, 95%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.57 (m, 4H), 7.50 – 7.42 (m, 1H), 7.37 (t, $J$ = 7.8 Hz, 2H), 7.18 (d, $J$ = 8.1 Hz, 2H), 4.48 – 4.30 (m, 2H), 3.26 (s, 3H), 2.39 (s, 3H), 1.33 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.3, 146.0, 133.8, 131.8, 131.2, 130.4, 128.6, 128.2, 127.1, 96.8, 77.3, 77.0, 76.8, 64.1, 42.5, 21.7, 13.6.

**ethyl (R)-2-phenyl-2-tosylacetate 5**



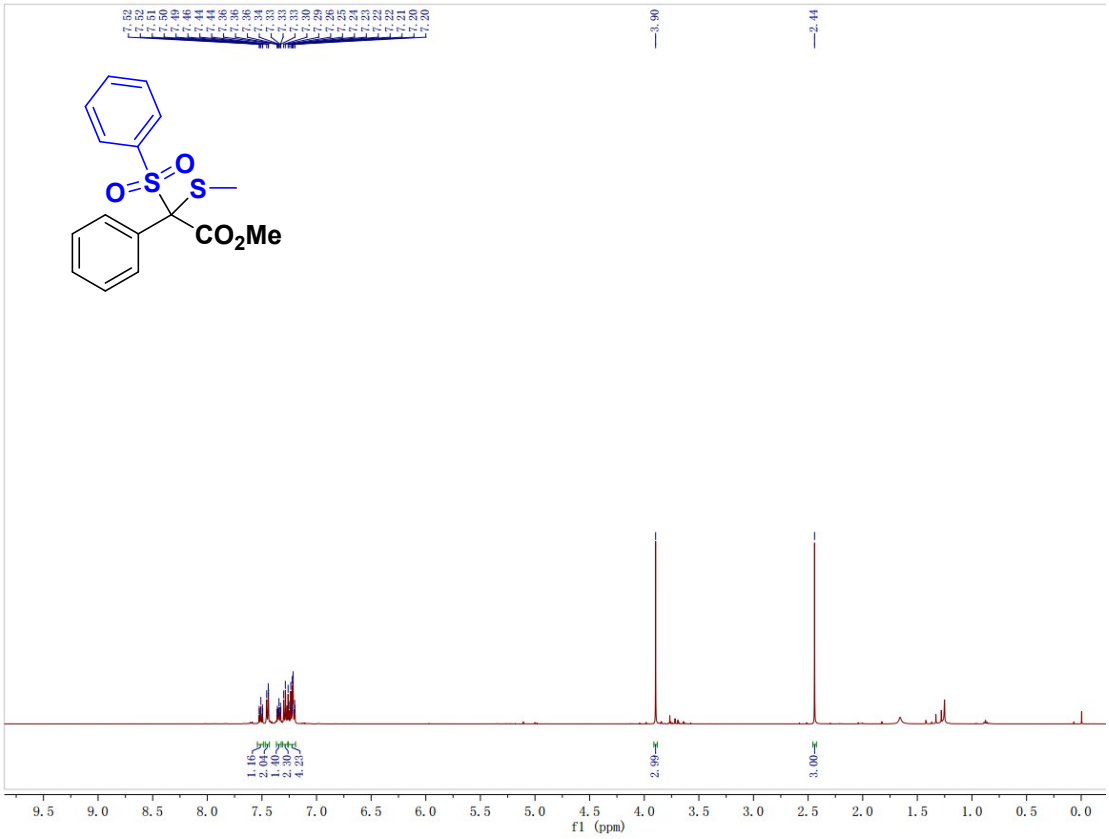
5

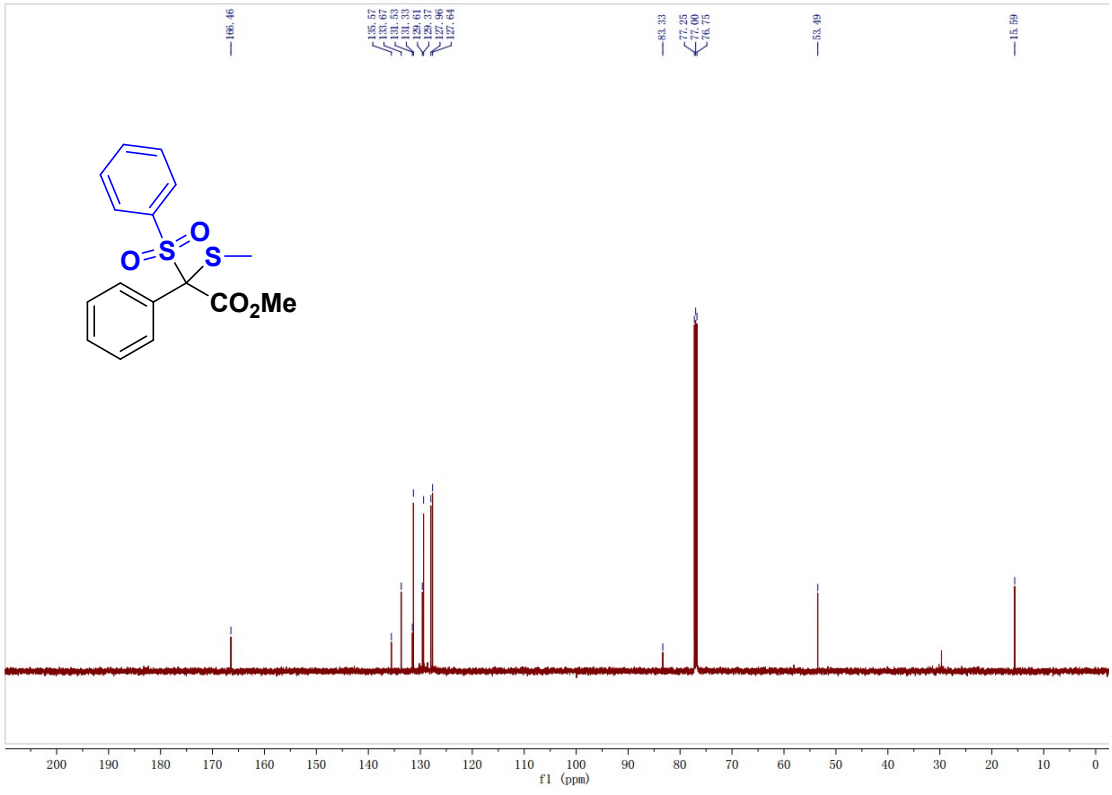
.The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a white solid (143 mg, 90%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, $J$ = 11.6, 8.4 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.33 – 7.27 (m, 2H), 7.22 (t, $J$ = 8.5 Hz, 2H), 5.07 (s, 1H), 4.32 – 4.11 (m, 2H), 2.41 (s, 3H), 1.28 – 1.18 (t, 3H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.3, 1456.0, 133.8, 131.8, 131.2, 130.4, 128.6, 128.2, 127.1, 96.8, 77.3, 77.0, 76.7, 64.1, 42.5, 21.7, 13.6.

## References

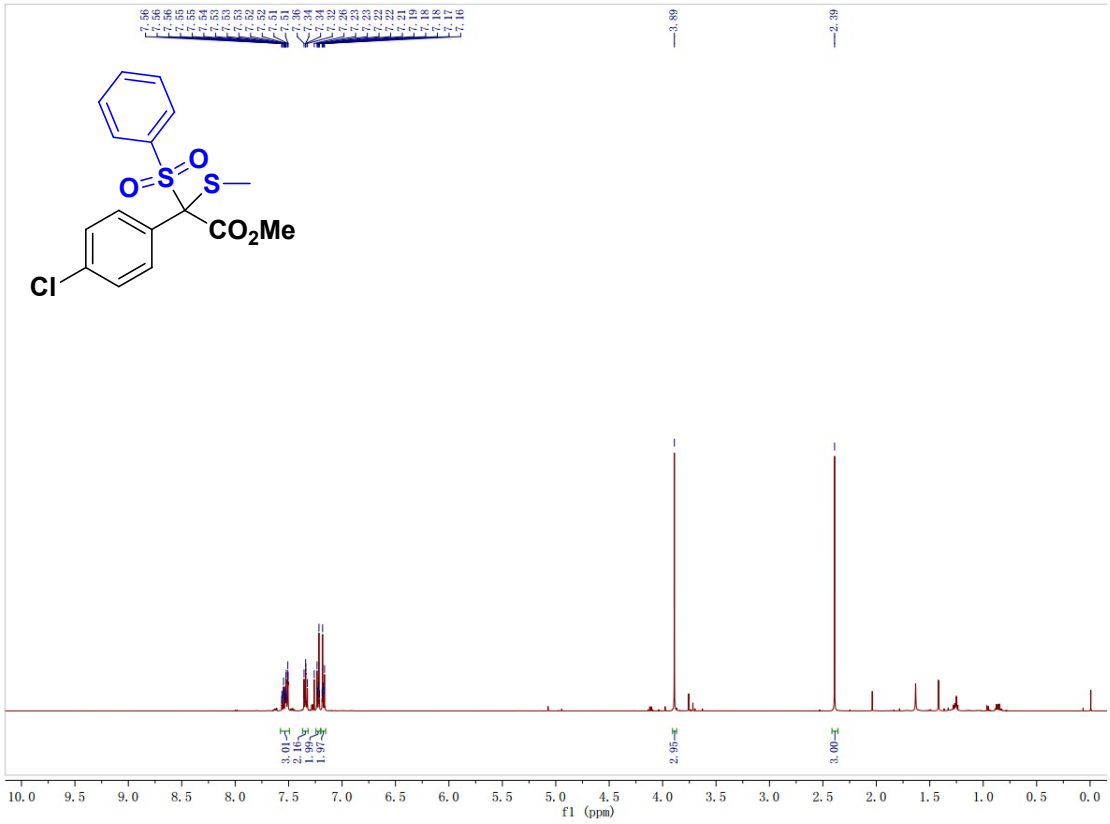

1. Bélanger, D.; Tong, X.; Soumaré, S.; Dory , Y. L.; Zhao, Y. *Chem. Eur. J.* **2009**, *15*, 4428.
2. W. Wang, X. Peng, F. Wei, C. Tung, and Z. Xu. *Angew. Chem. Int. Ed.* **2016**, *55*, 649-653.
3. G. Liang, M. Liu, W. Gao, J. Ding, J. Chen, H. Wu. *Chin. J. Chem.* **2012**, *30,* 1611-1616.
4. L. Marzorati, N. Ferreira, C. Junior, C. D. Vitta, B. Wladislaw. *Synthesis.* **1997**, *4*, 420-422.

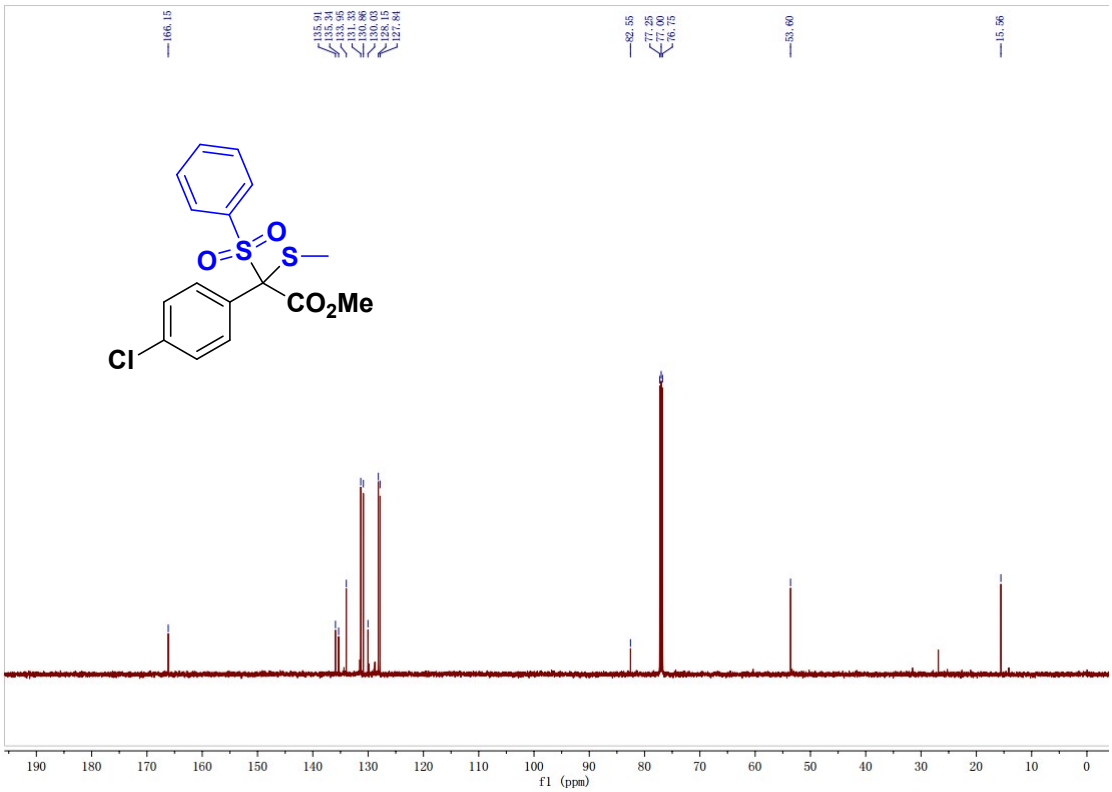
**NMR spectroscopic data**
**methyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3a**



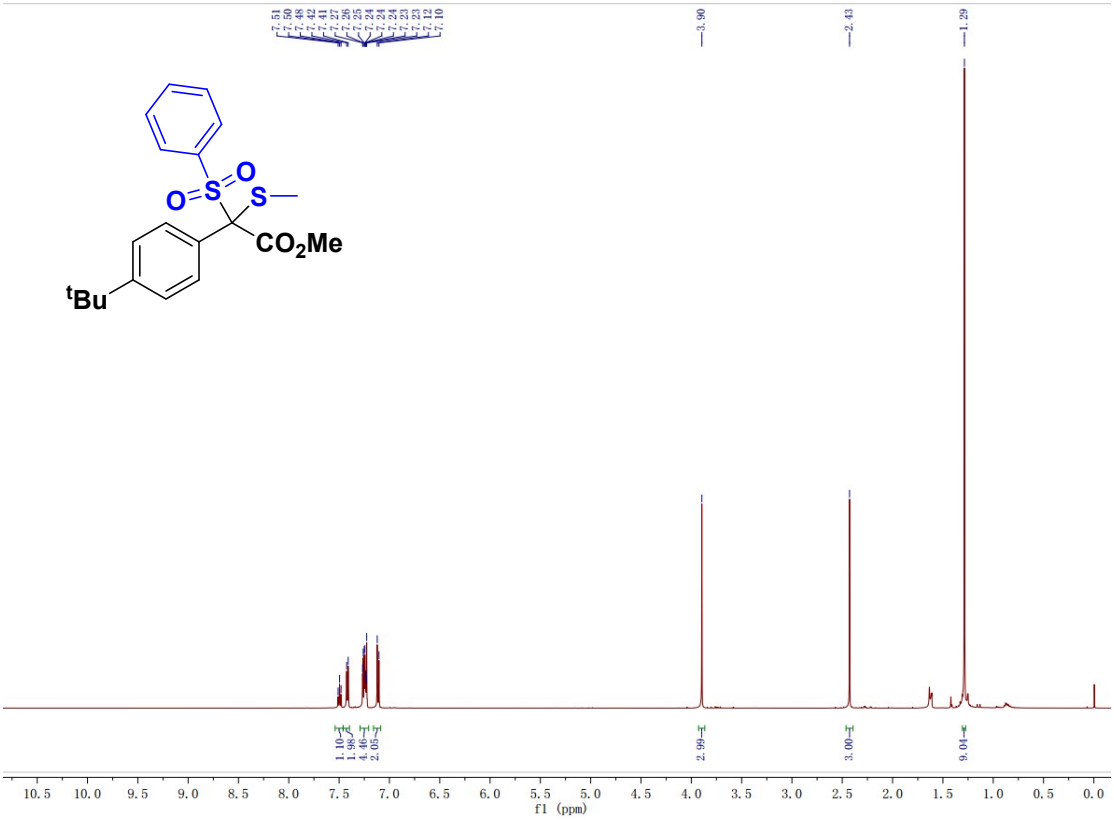



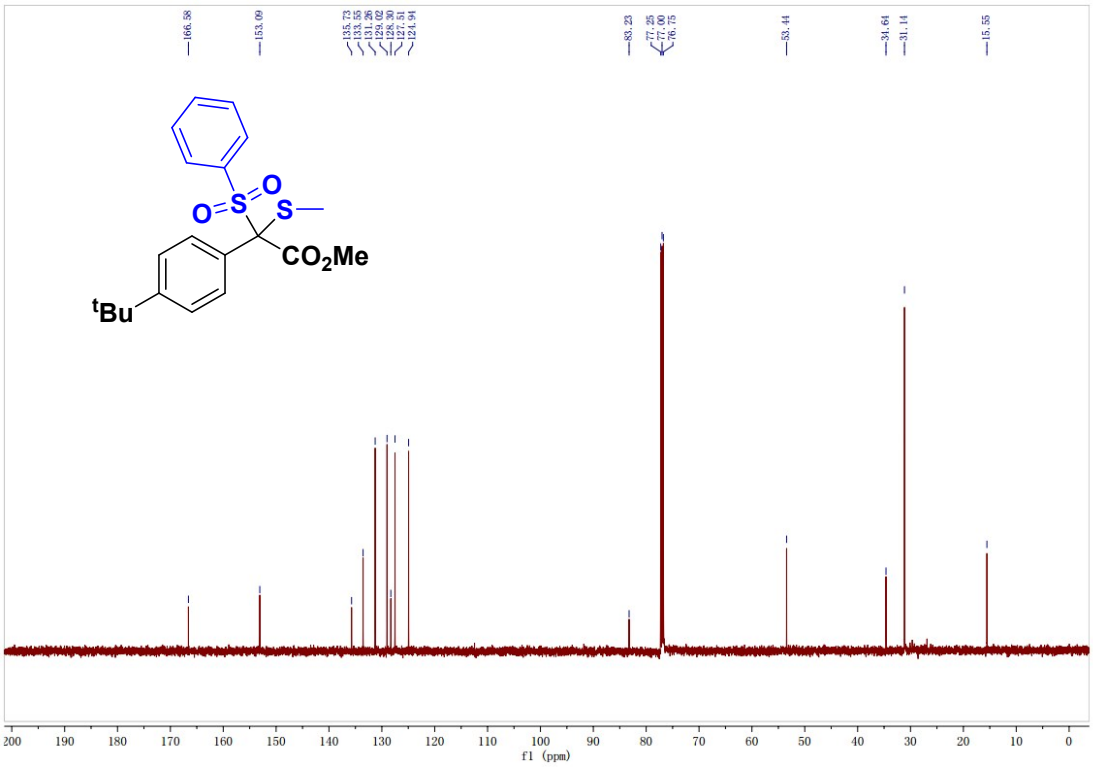
**methyl 2-(4-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3b**



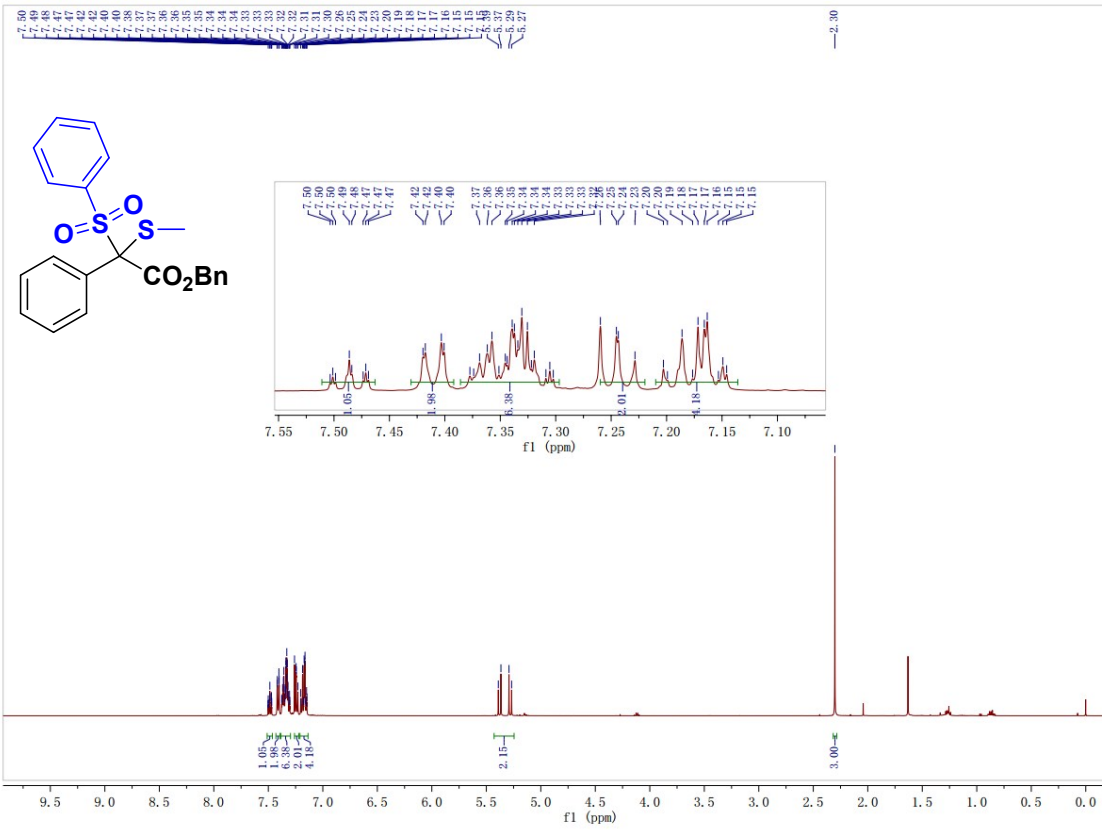



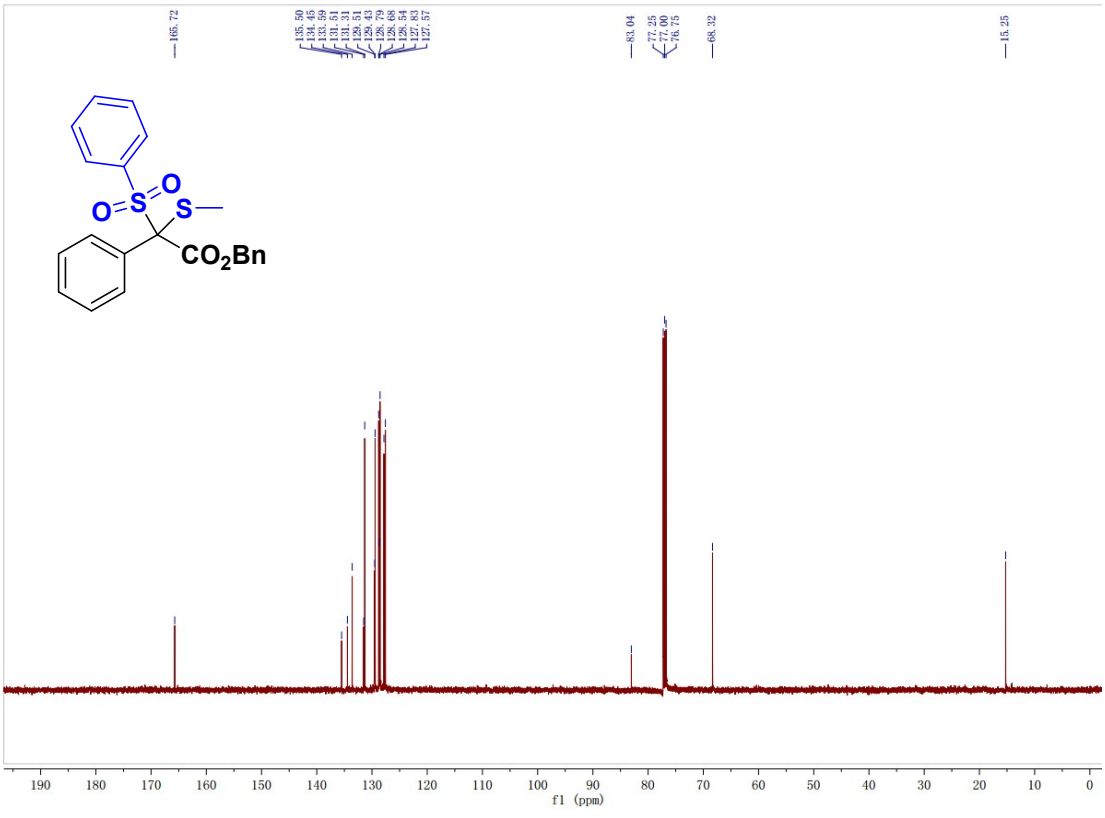
**methyl 2-(4-(tert-butyl)phenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3c**



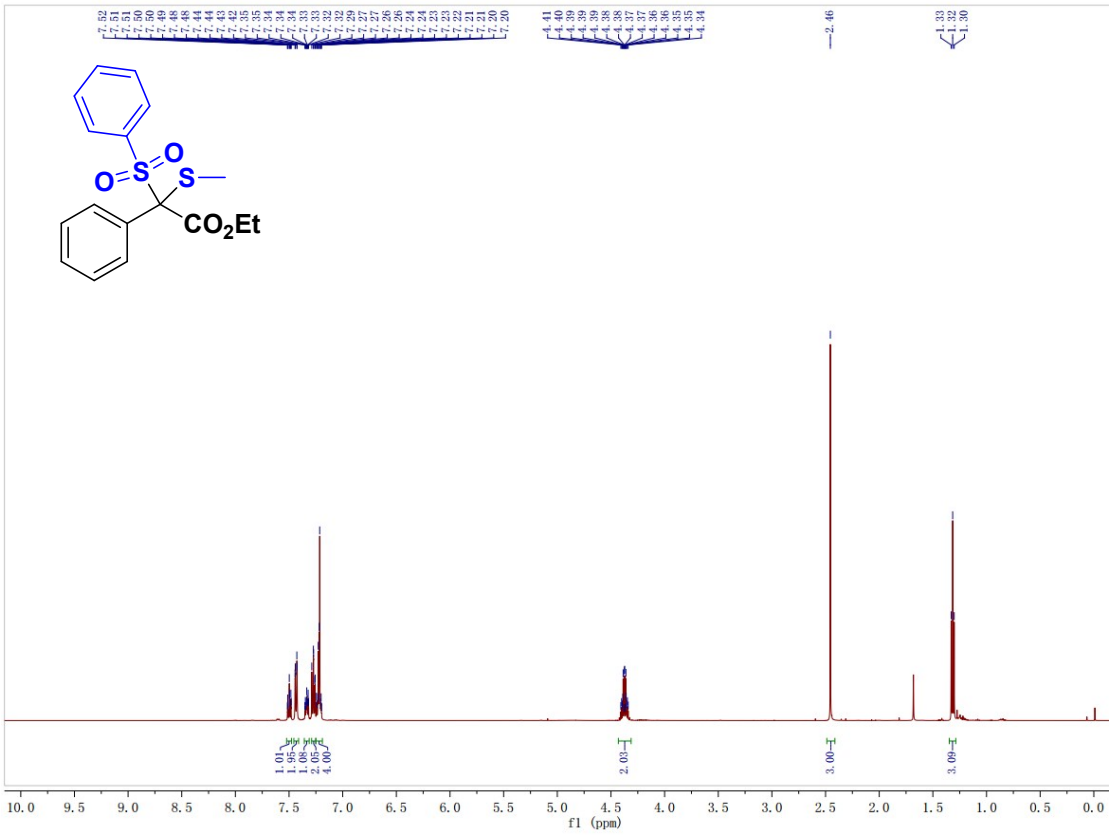



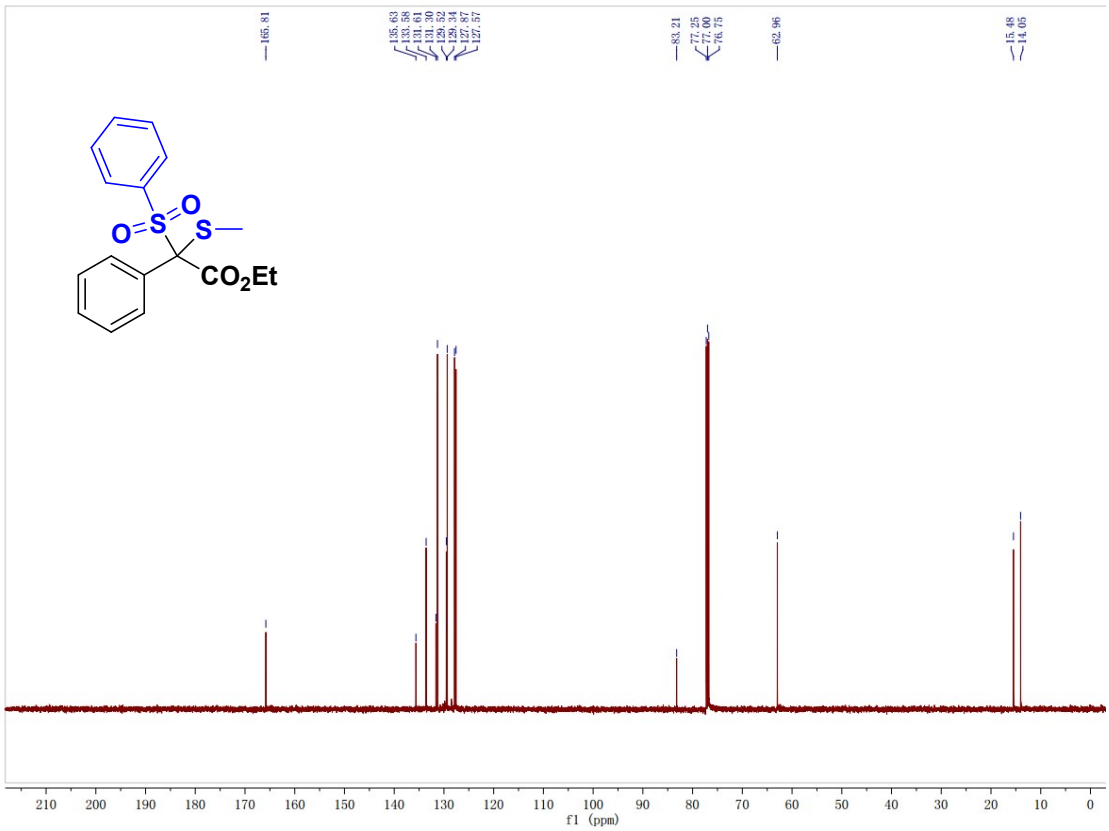
**benzyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3d**



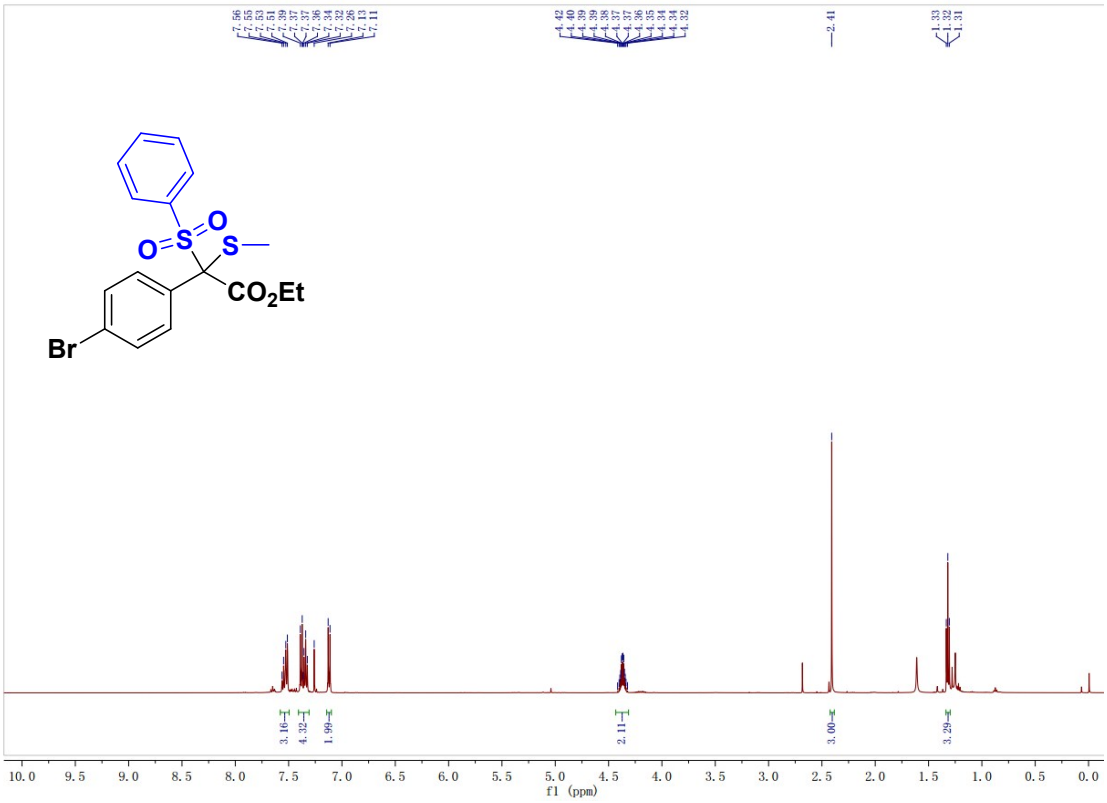



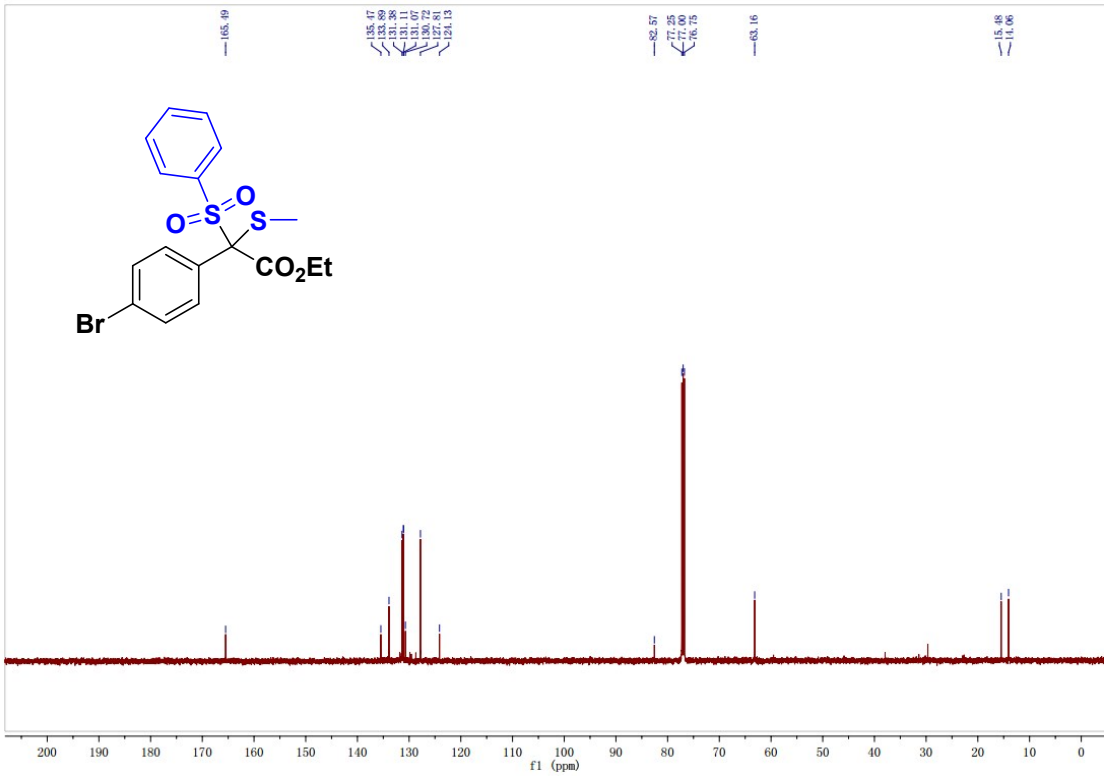
**ethyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3e**



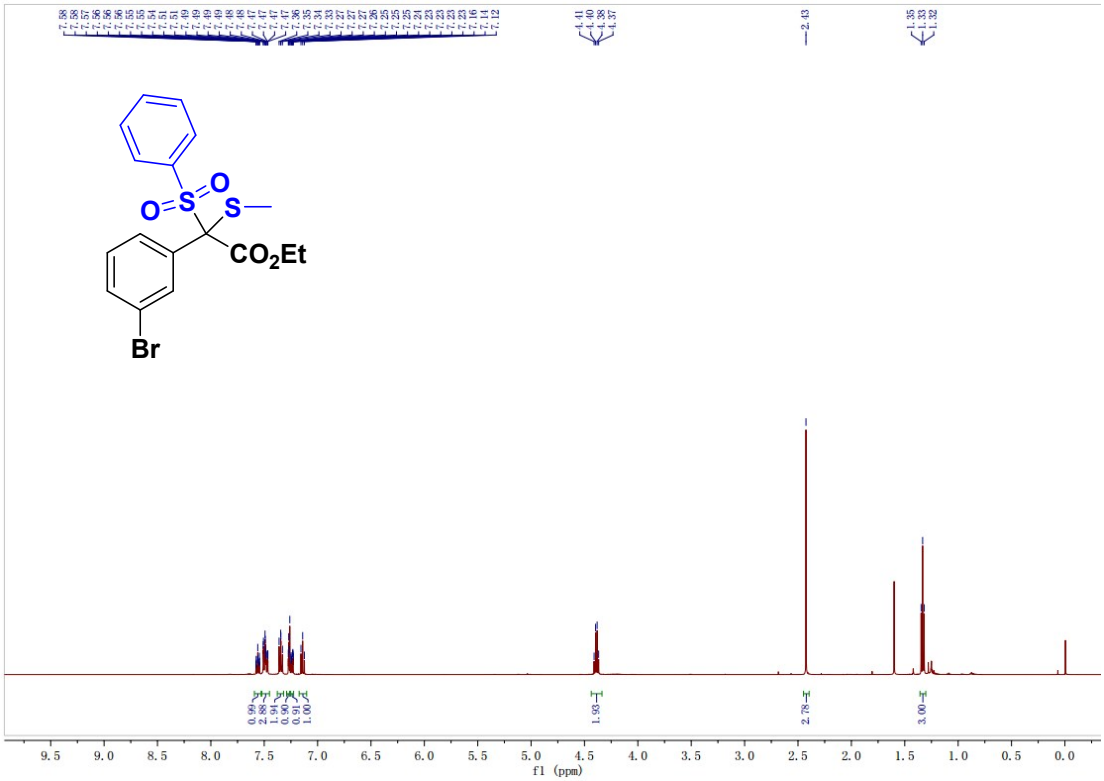



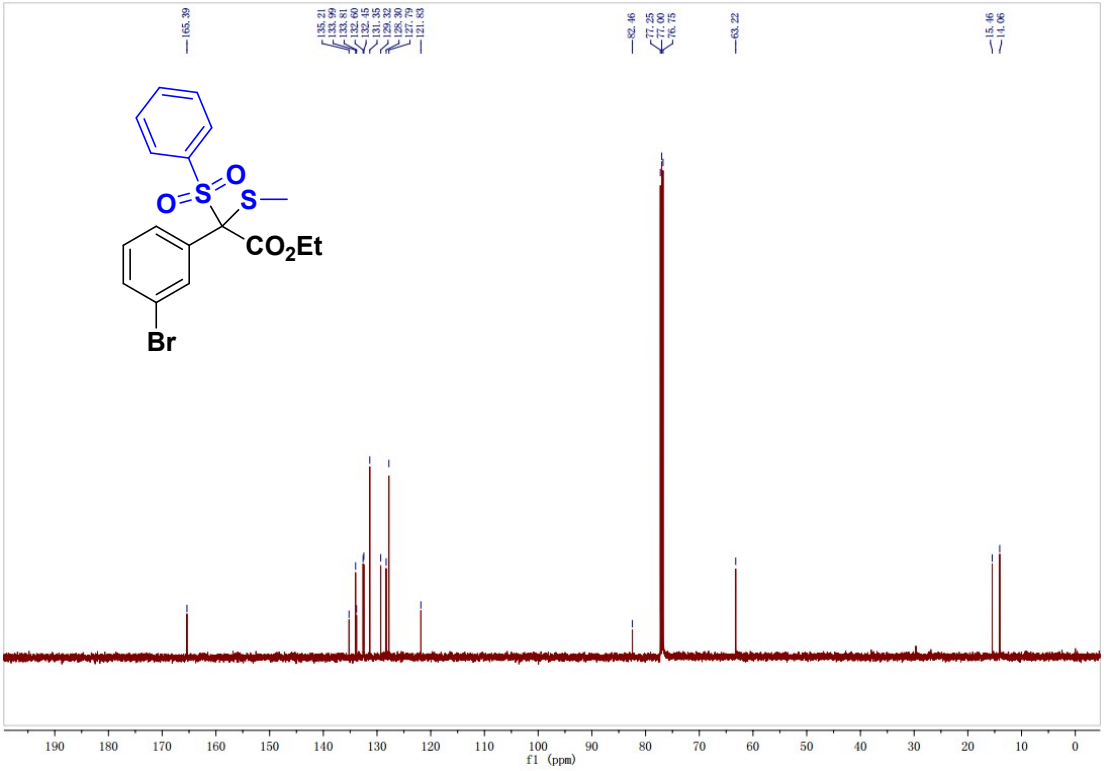
**ethyl 2-(4-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3f**



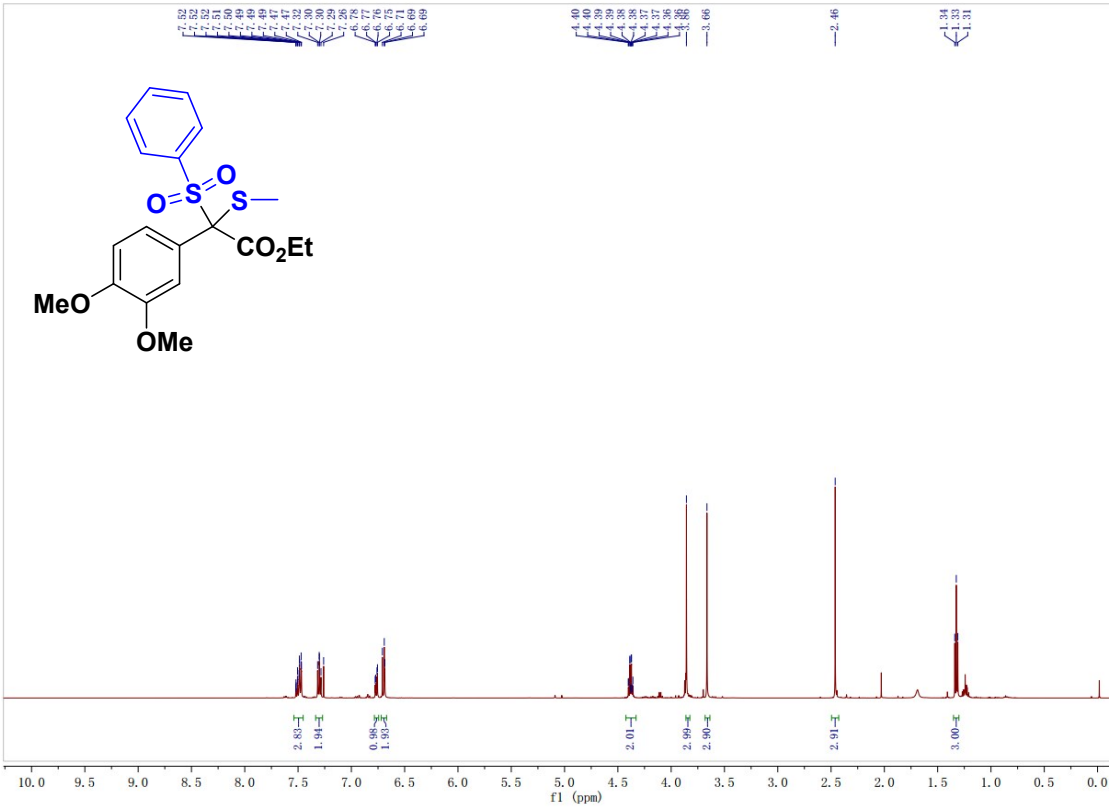



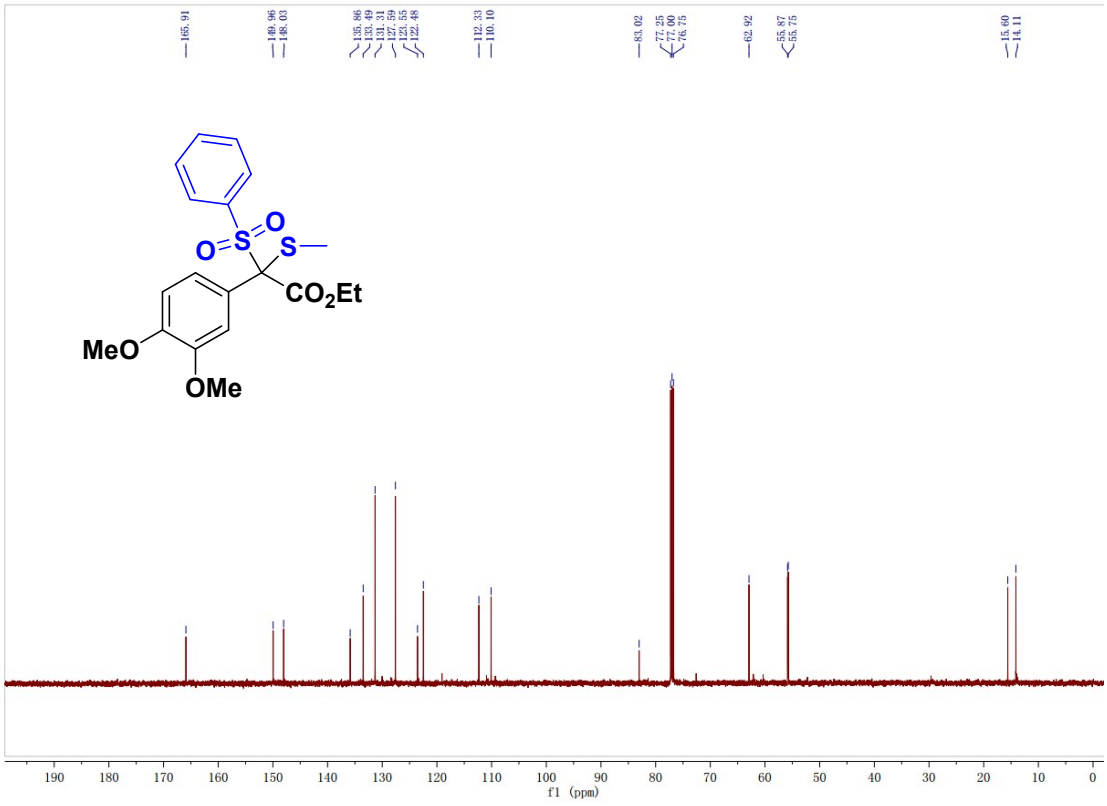
**ethyl 2-(3-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3g**



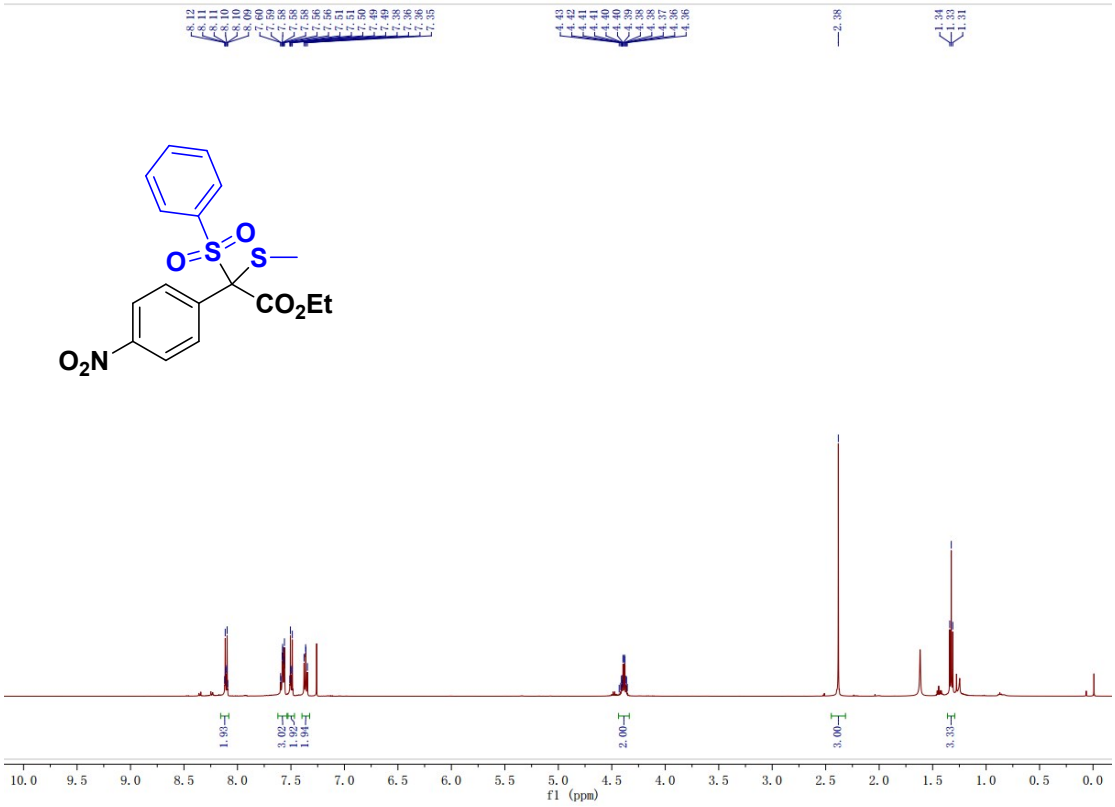



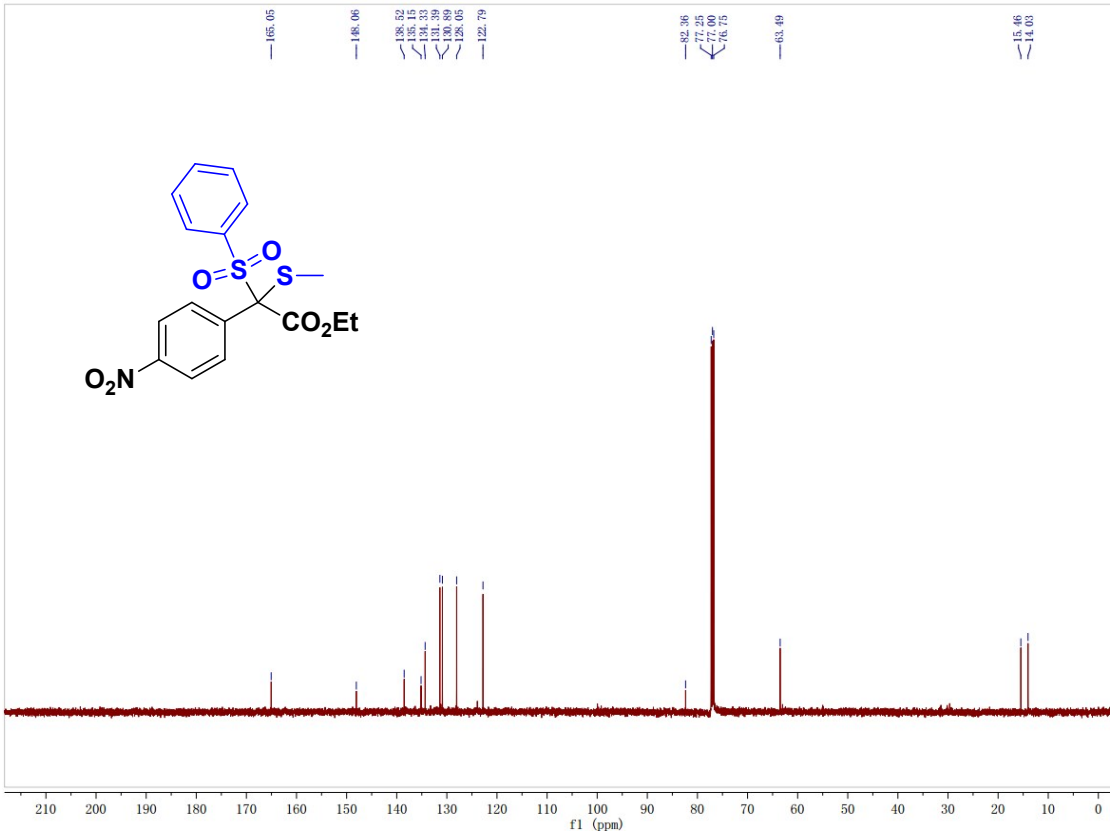
**ethyl 2-(3,4-dimethoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3h**



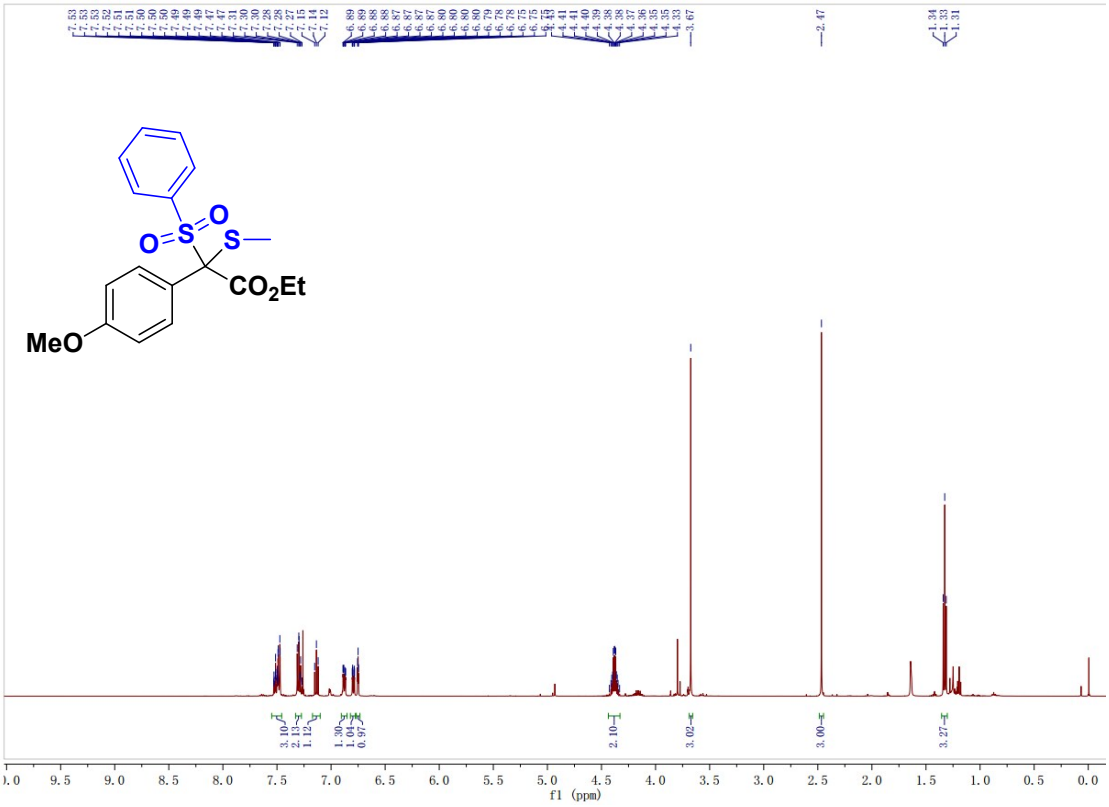



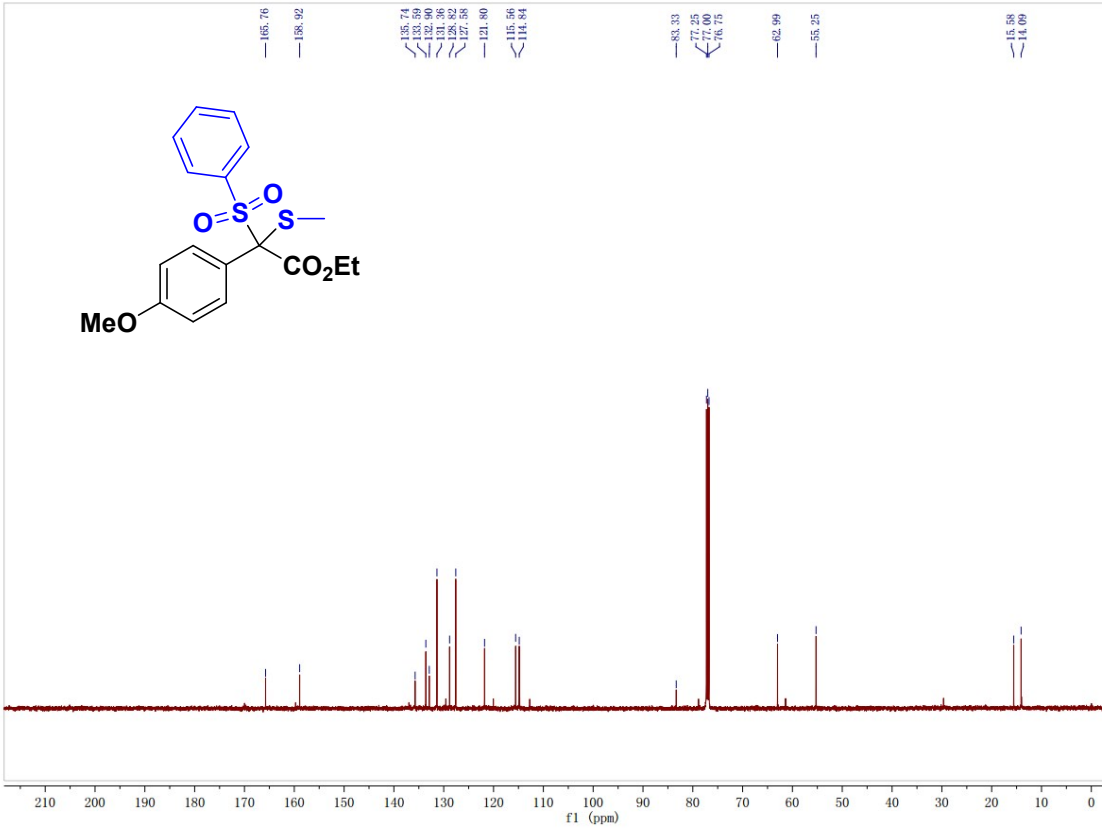
**ethyl 2-(methylthio)-2-(4-nitrophenyl)-2-(phenylsulfonyl)acetate 3i**



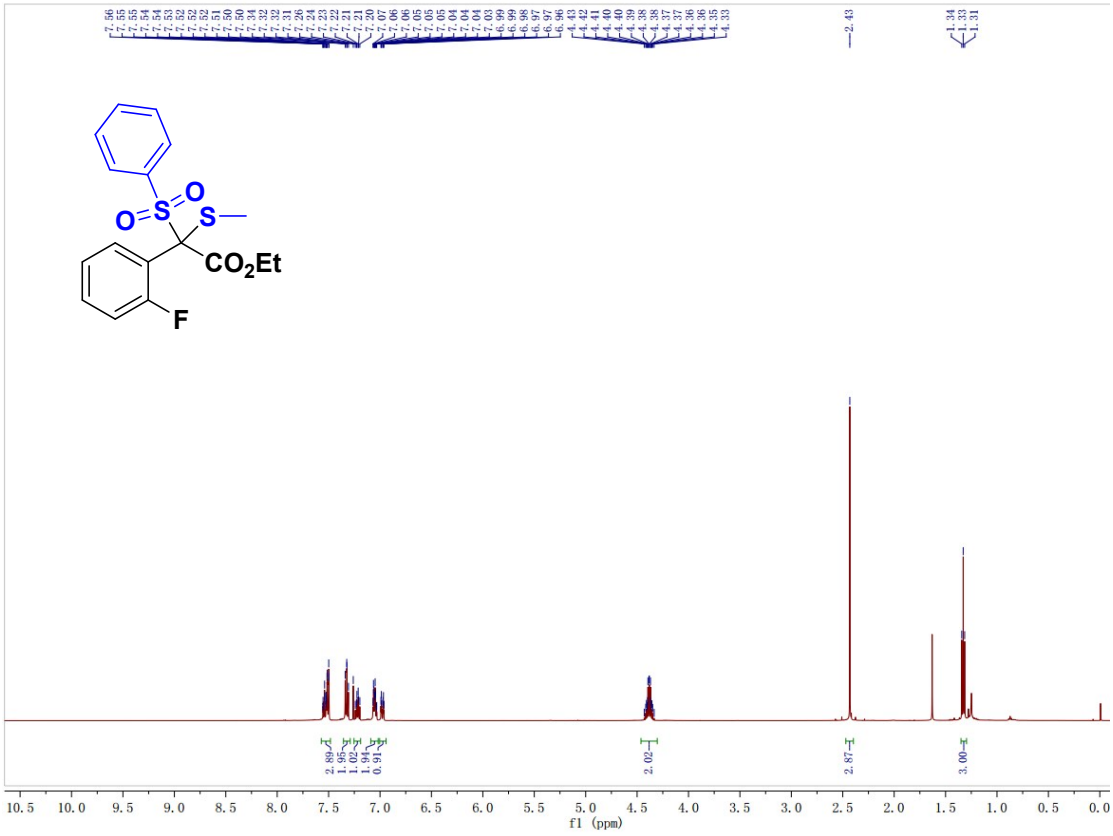



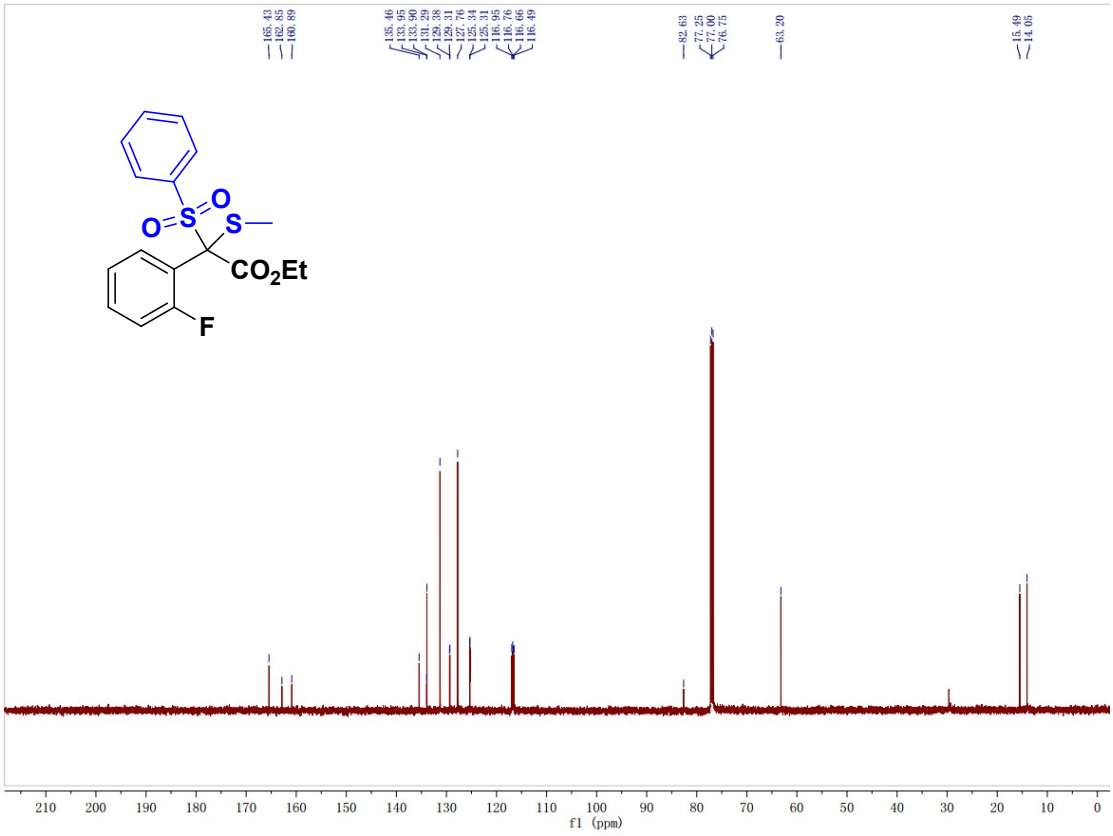
**ethyl 2-(4-methoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3j**



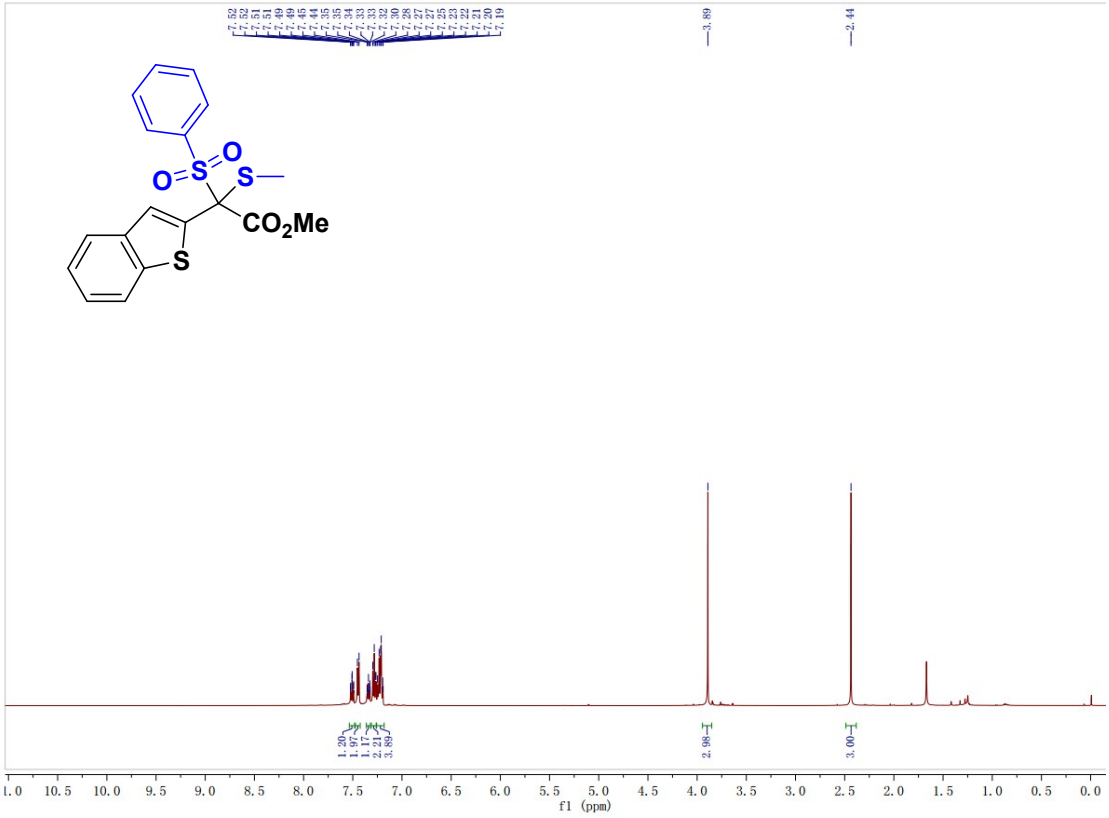



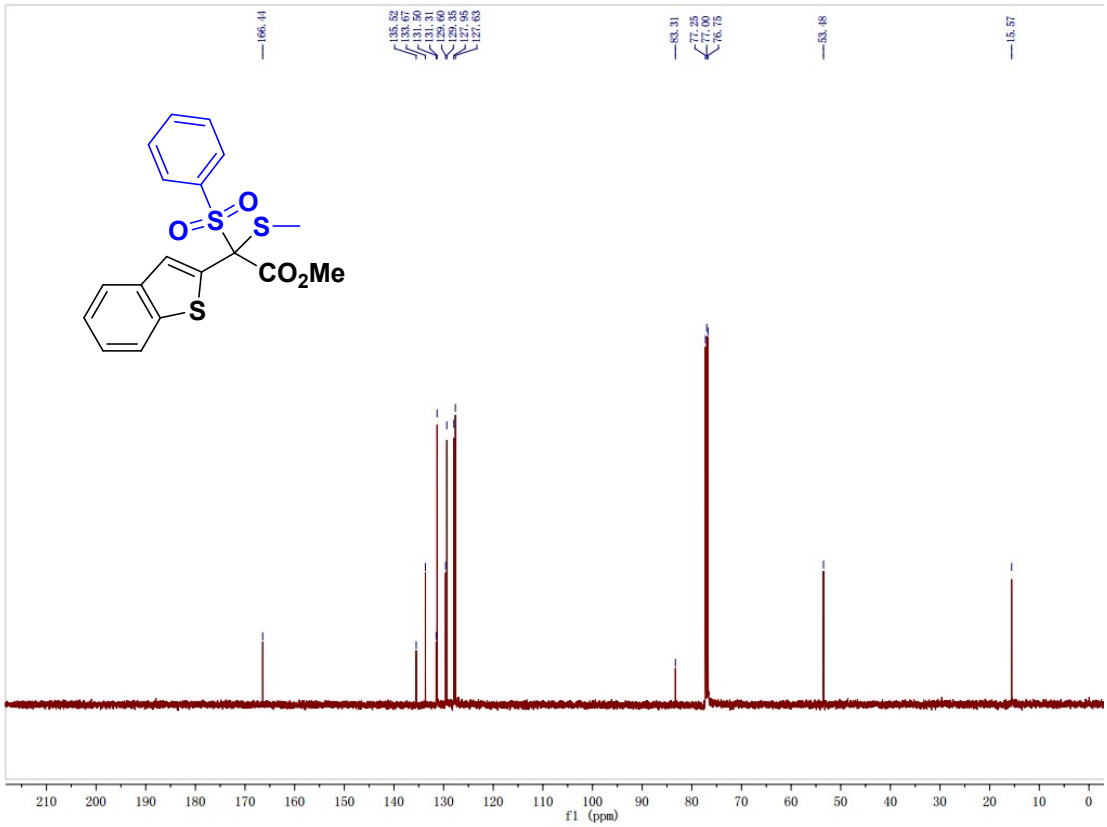
**ethyl 2-(2-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3k**



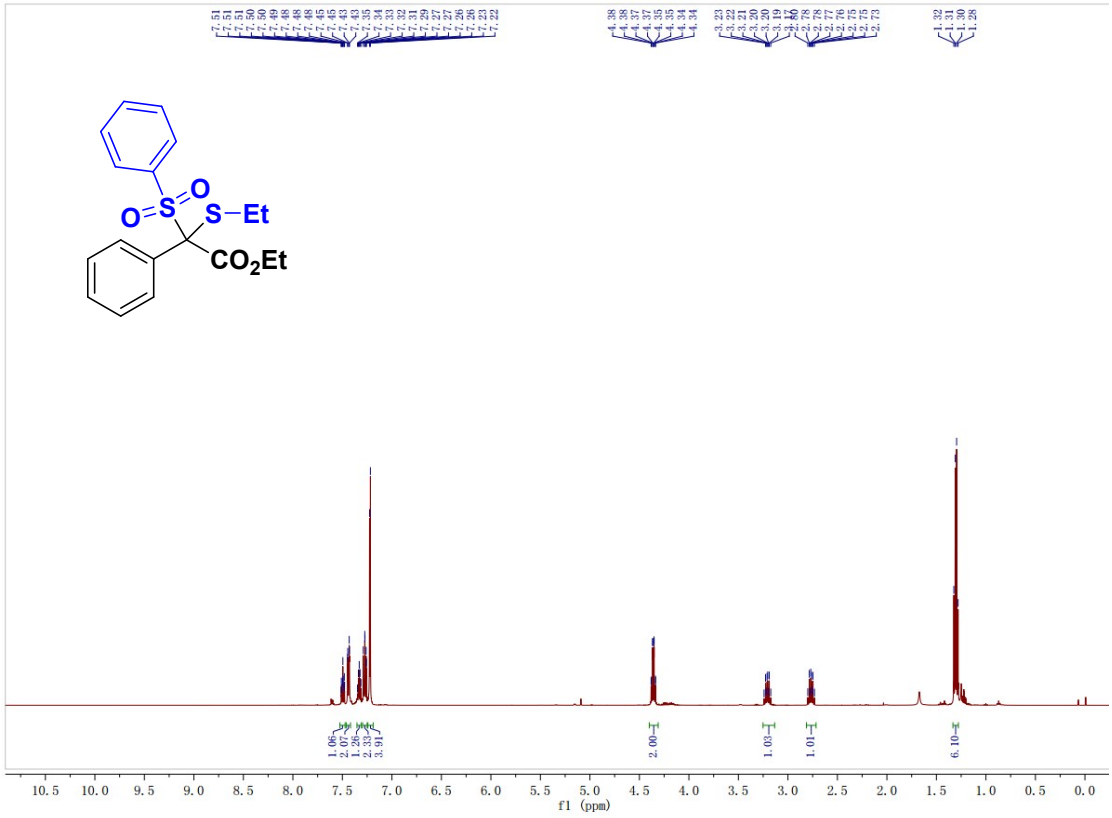



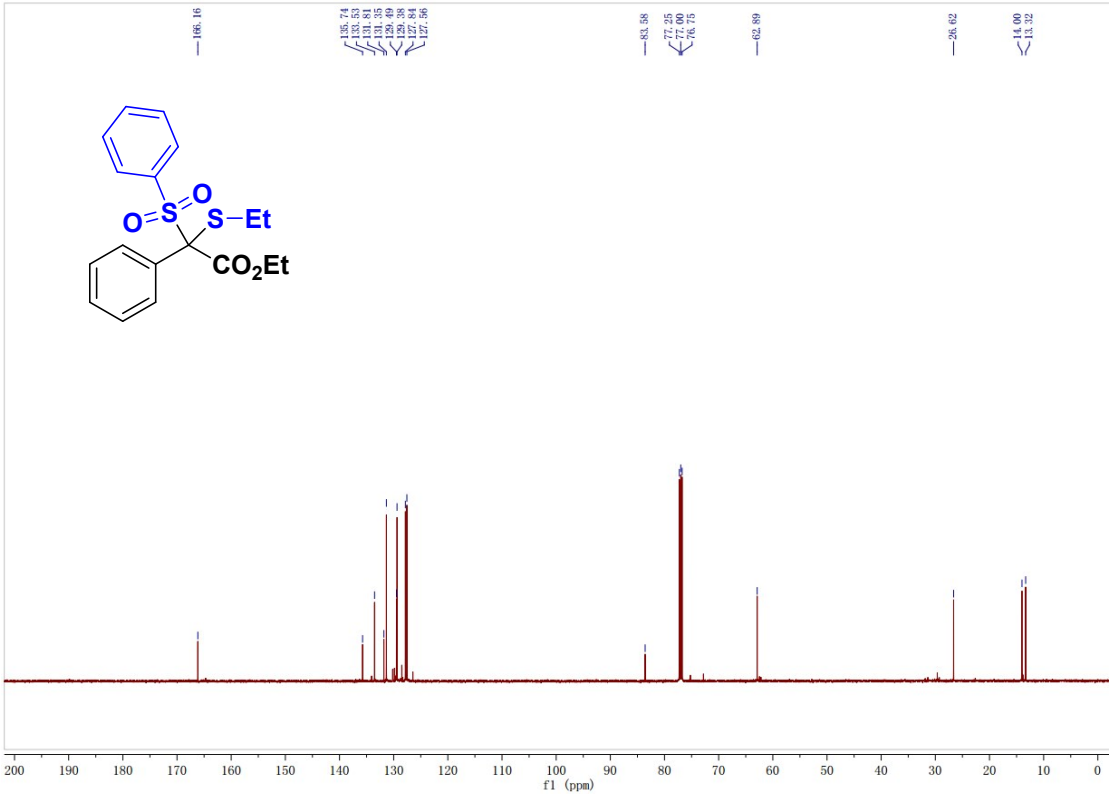
**methyl 2-(benzo[b]thiophen-2-yl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3l**



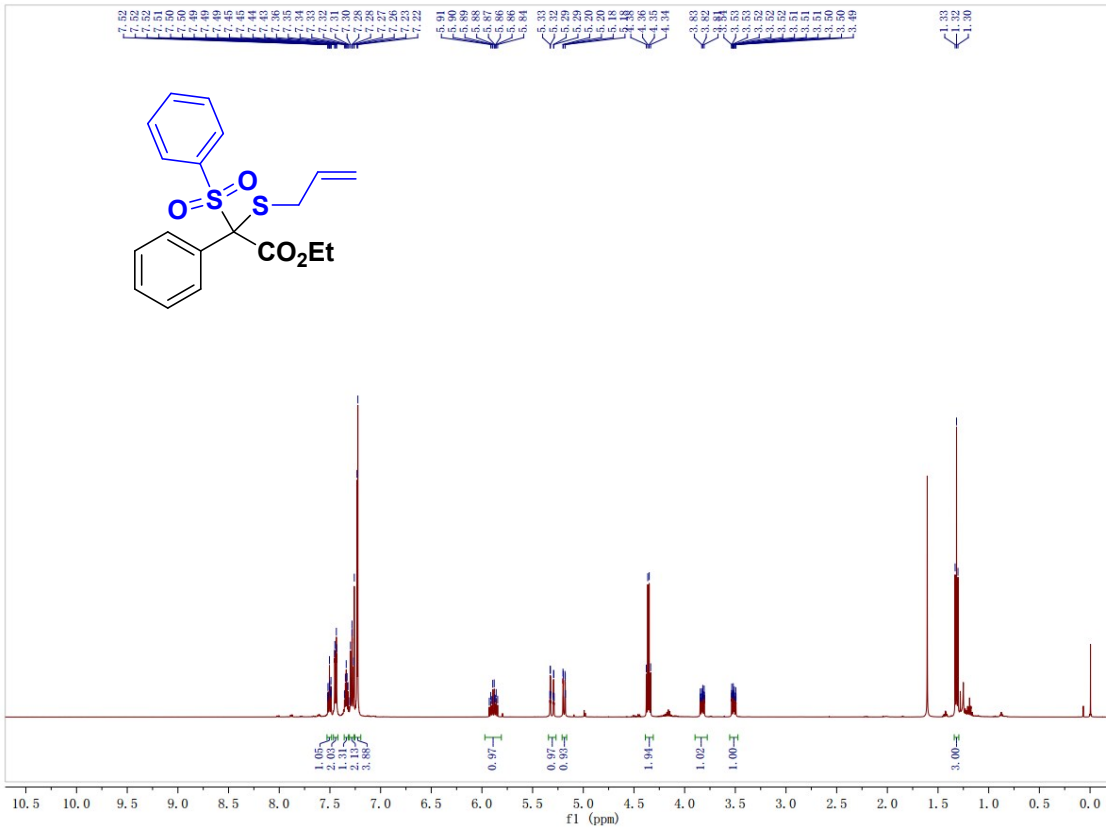



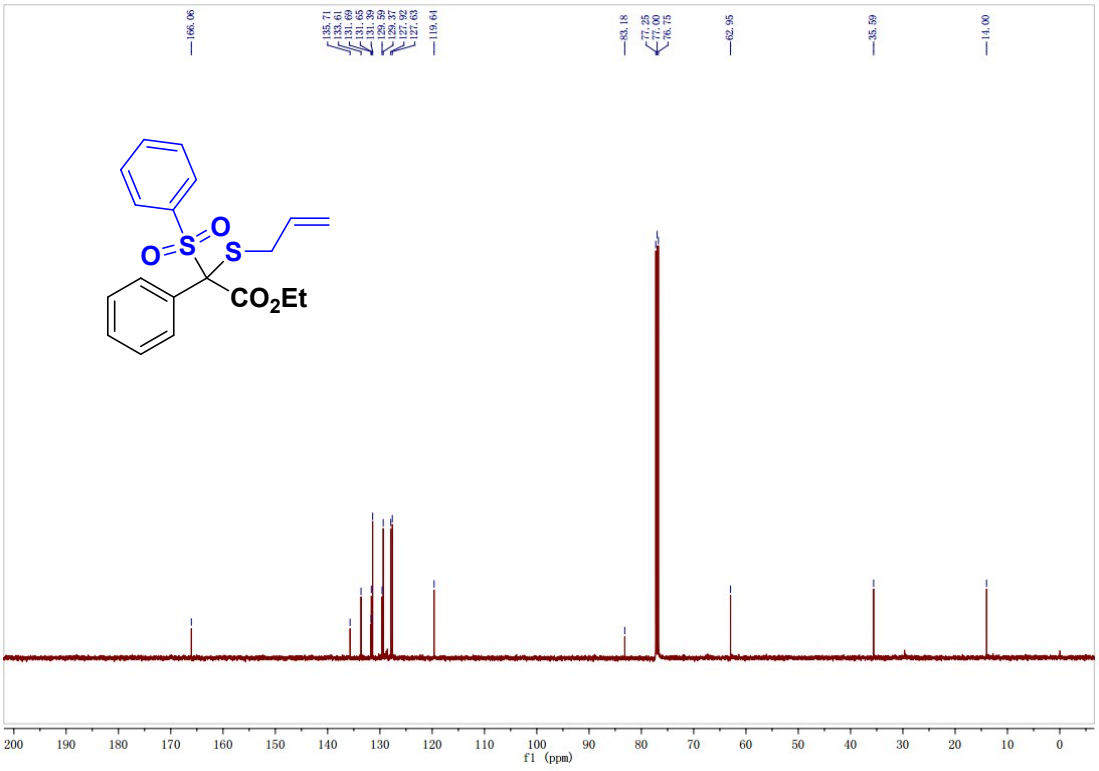
**ethyl 2-(ethylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3m**



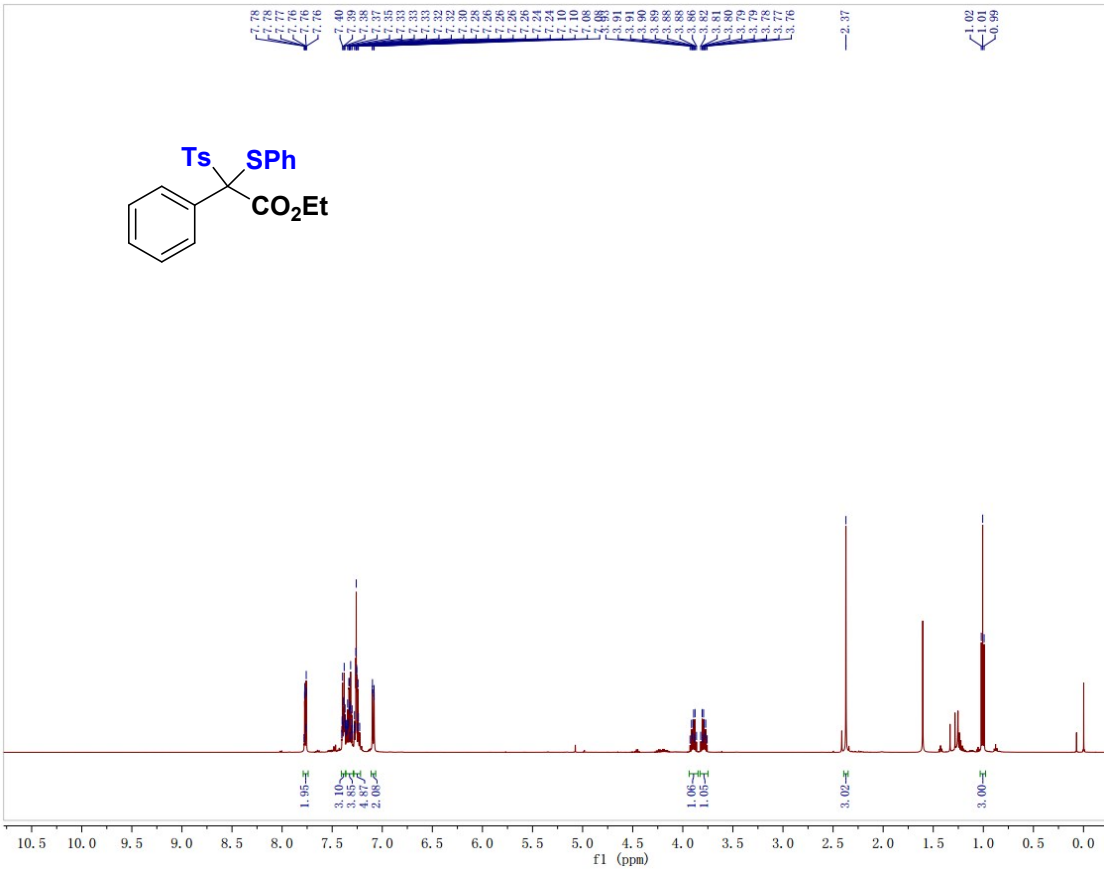



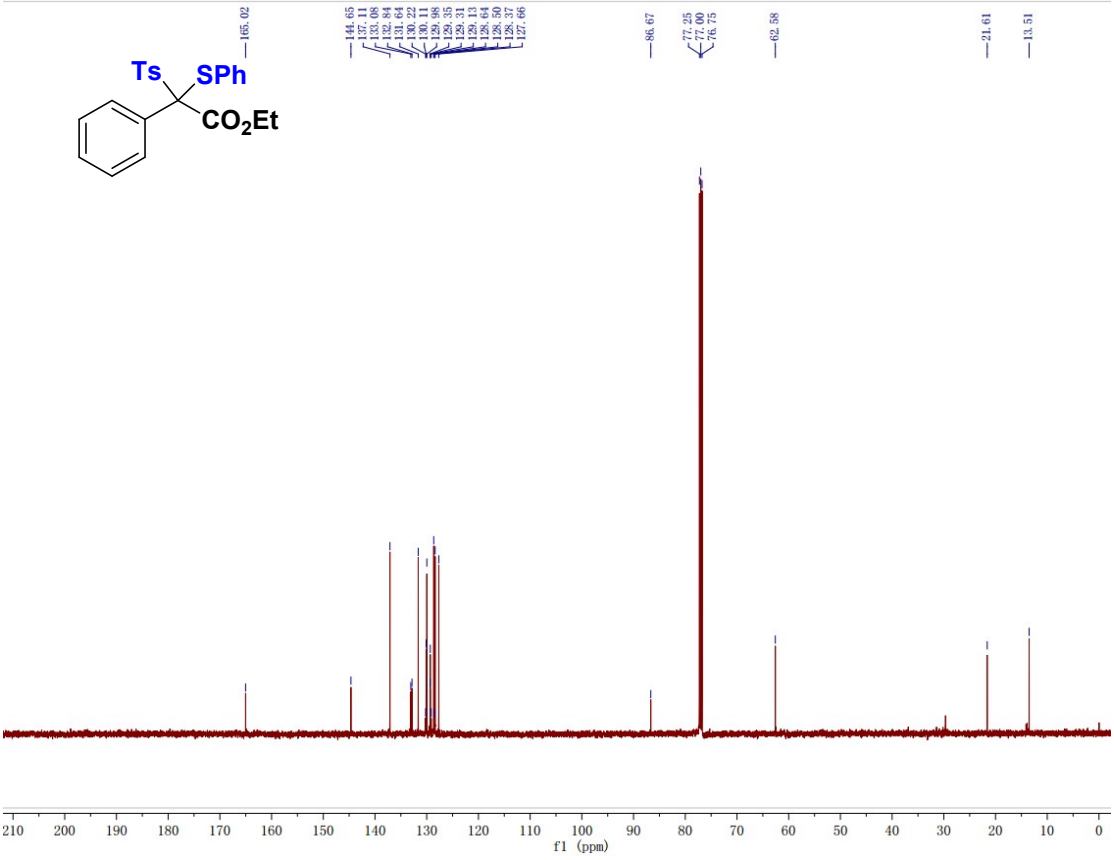
**ethyl 2-(allylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3n**



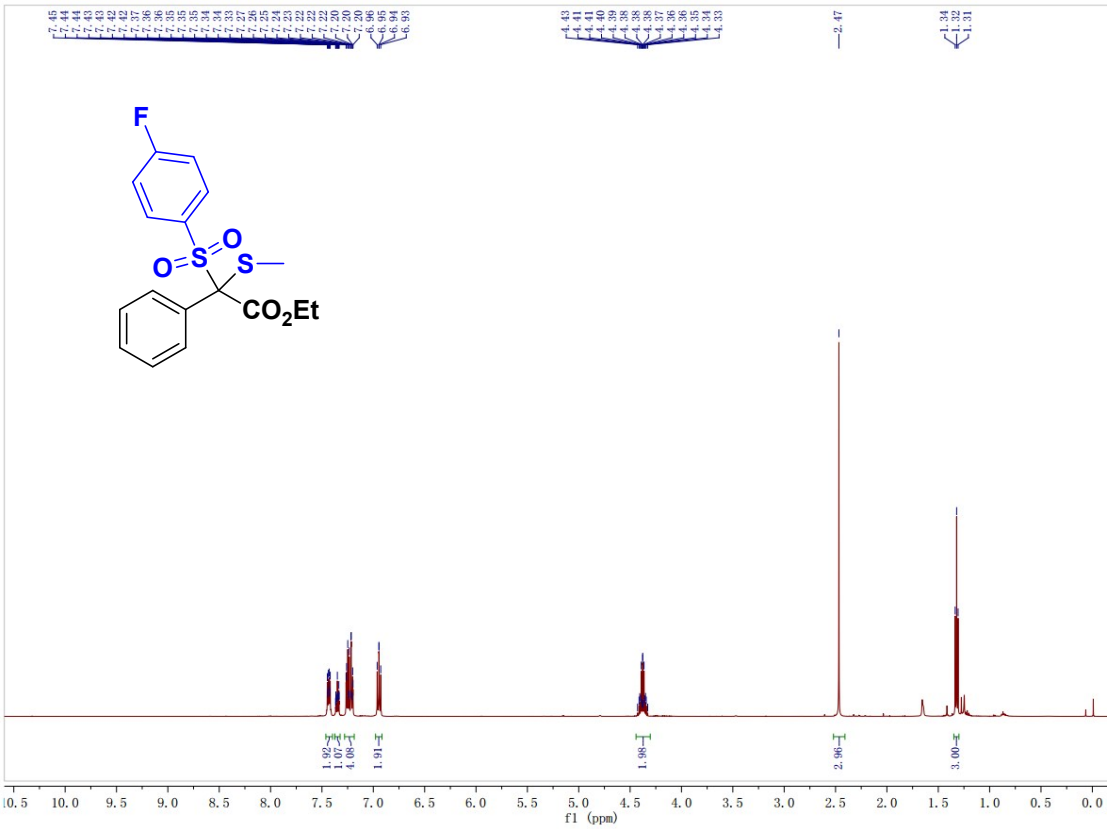



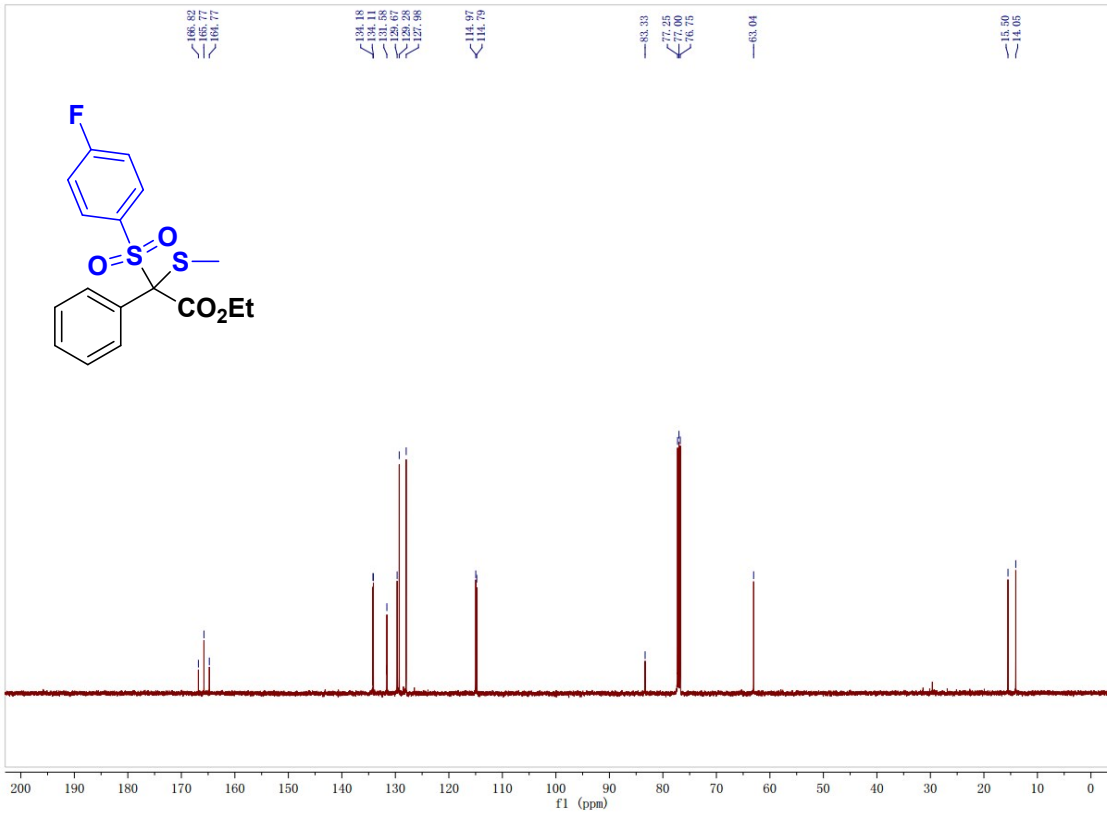
**ethyl 2-phenyl-2-(phenylthio)-2-tosylacetate 3o**



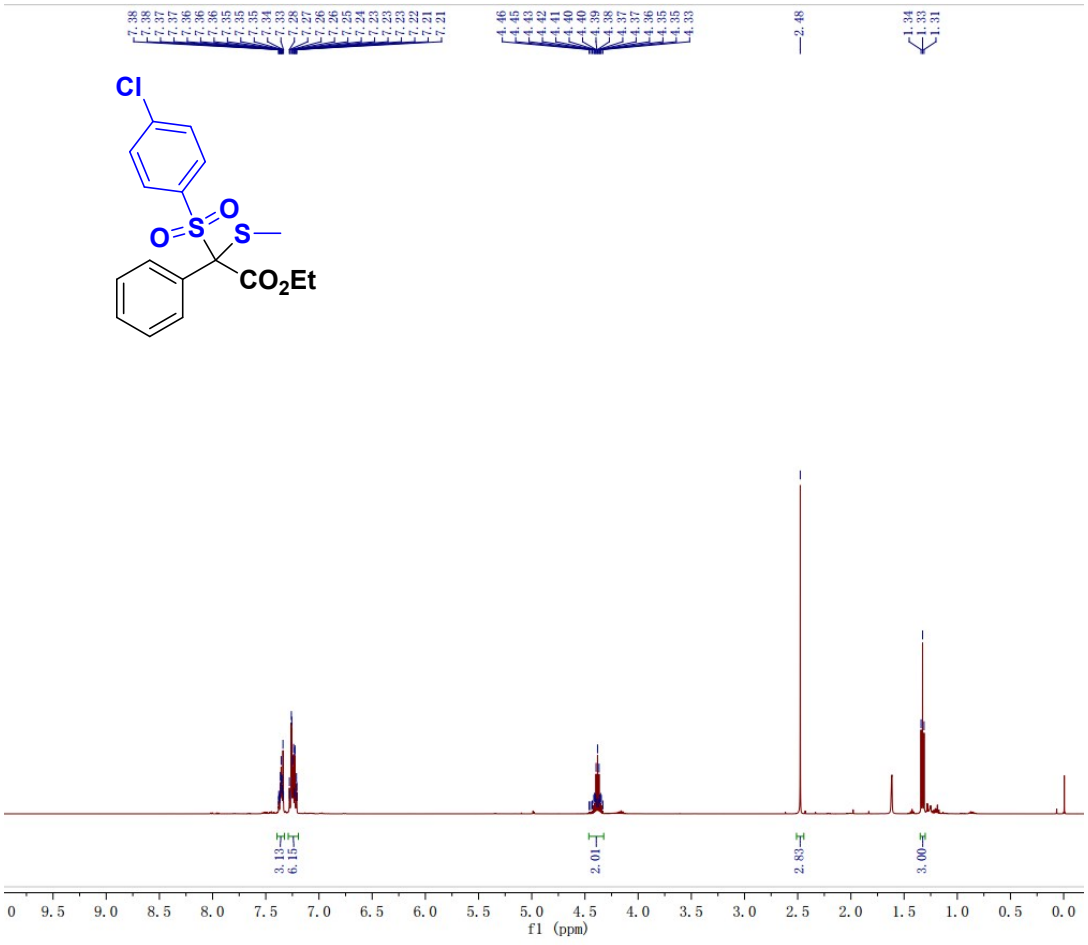



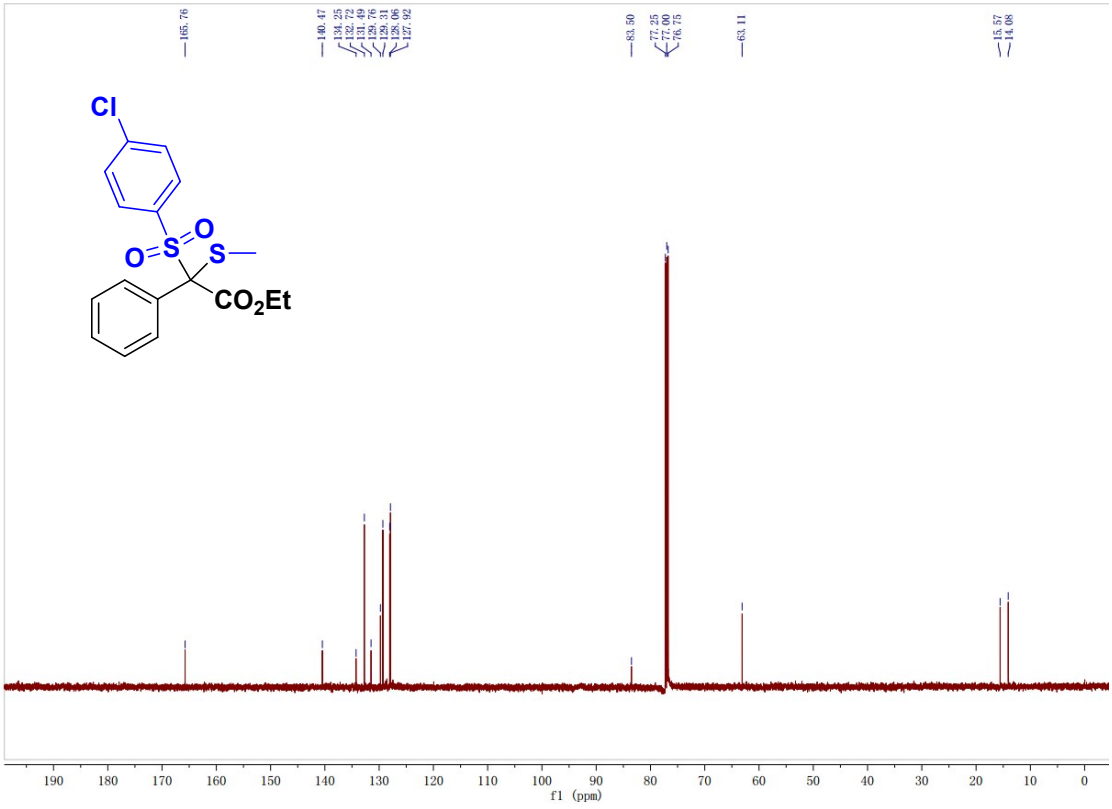
**ethyl 2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3p**



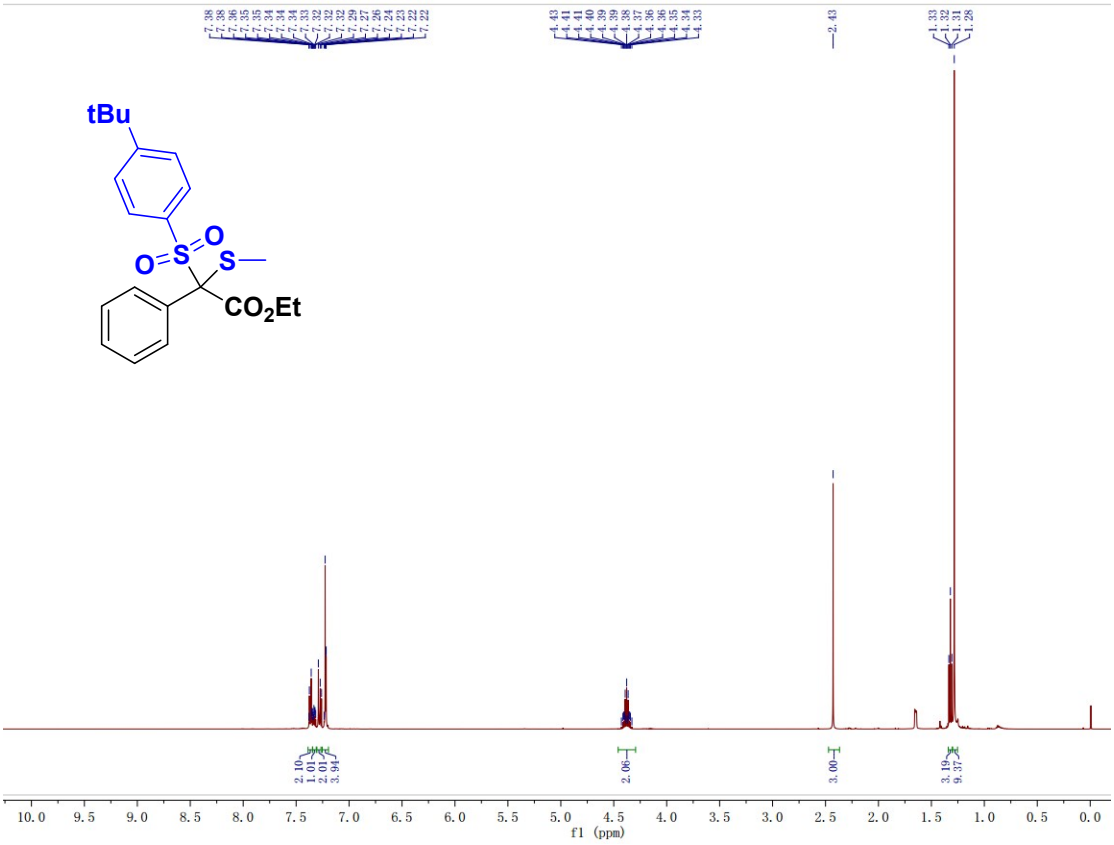



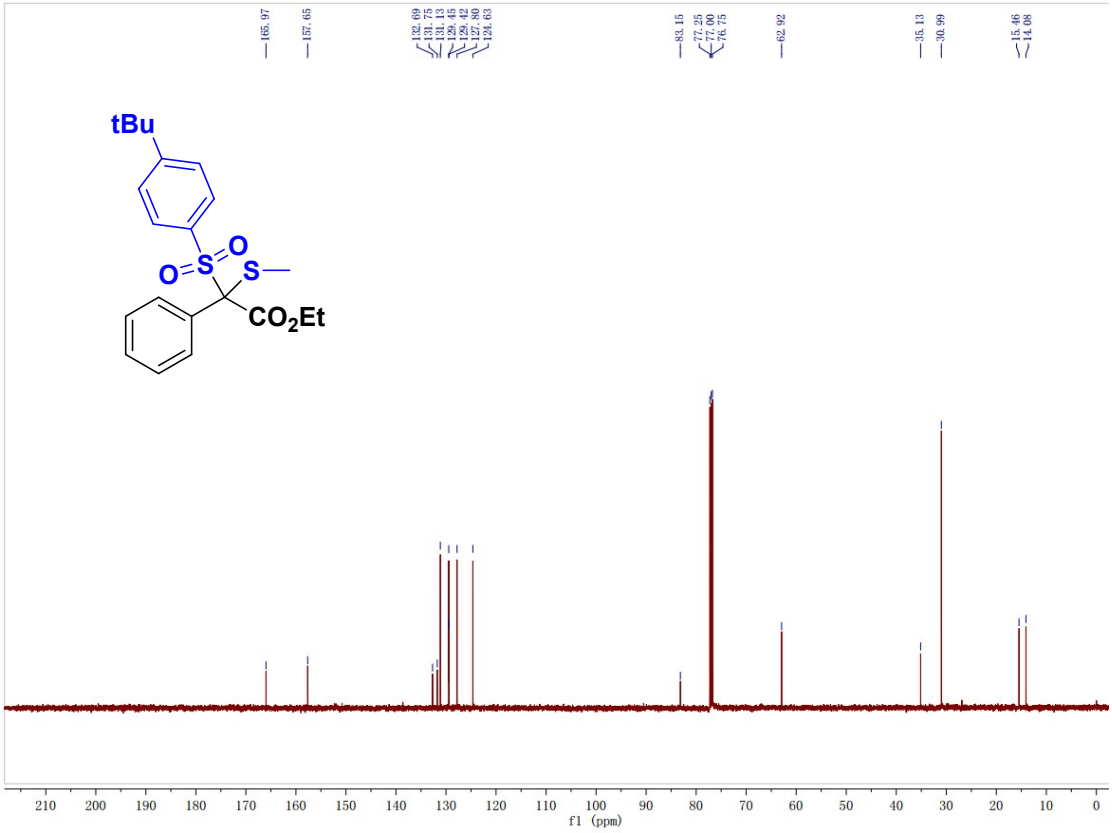
**ethyl 2-((4-chlorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3q**



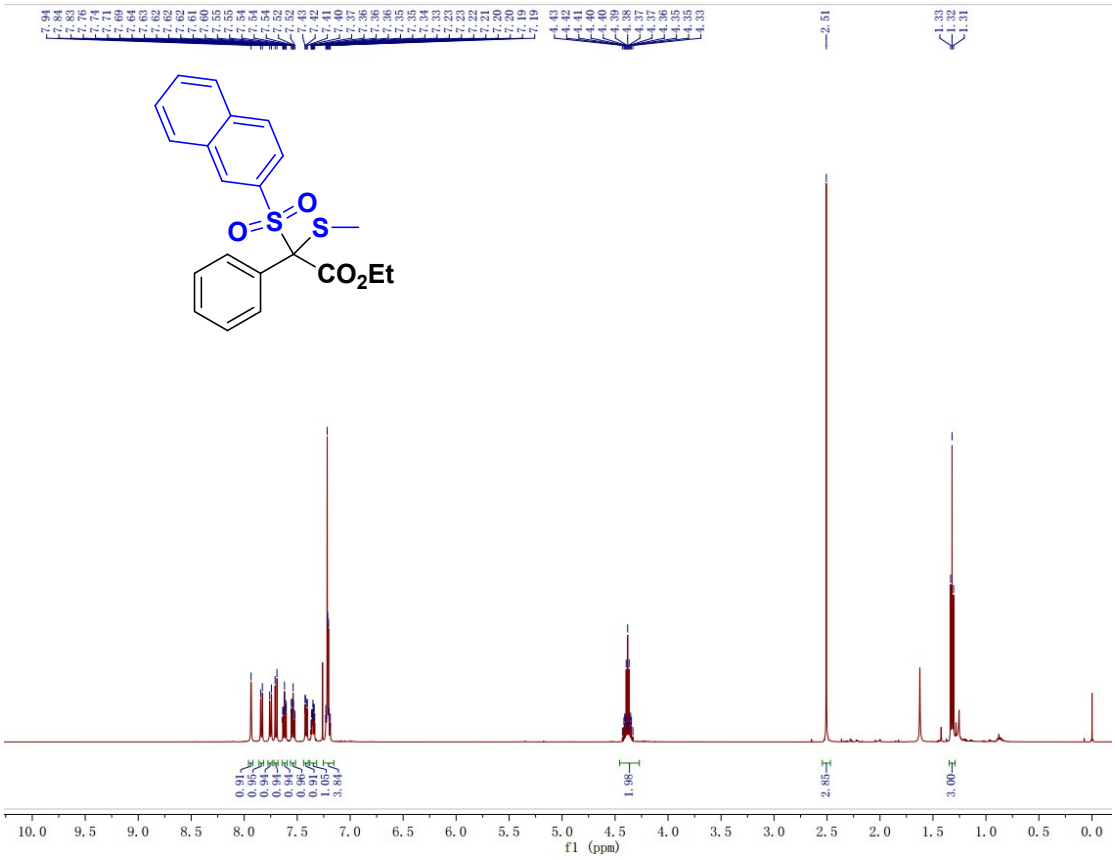



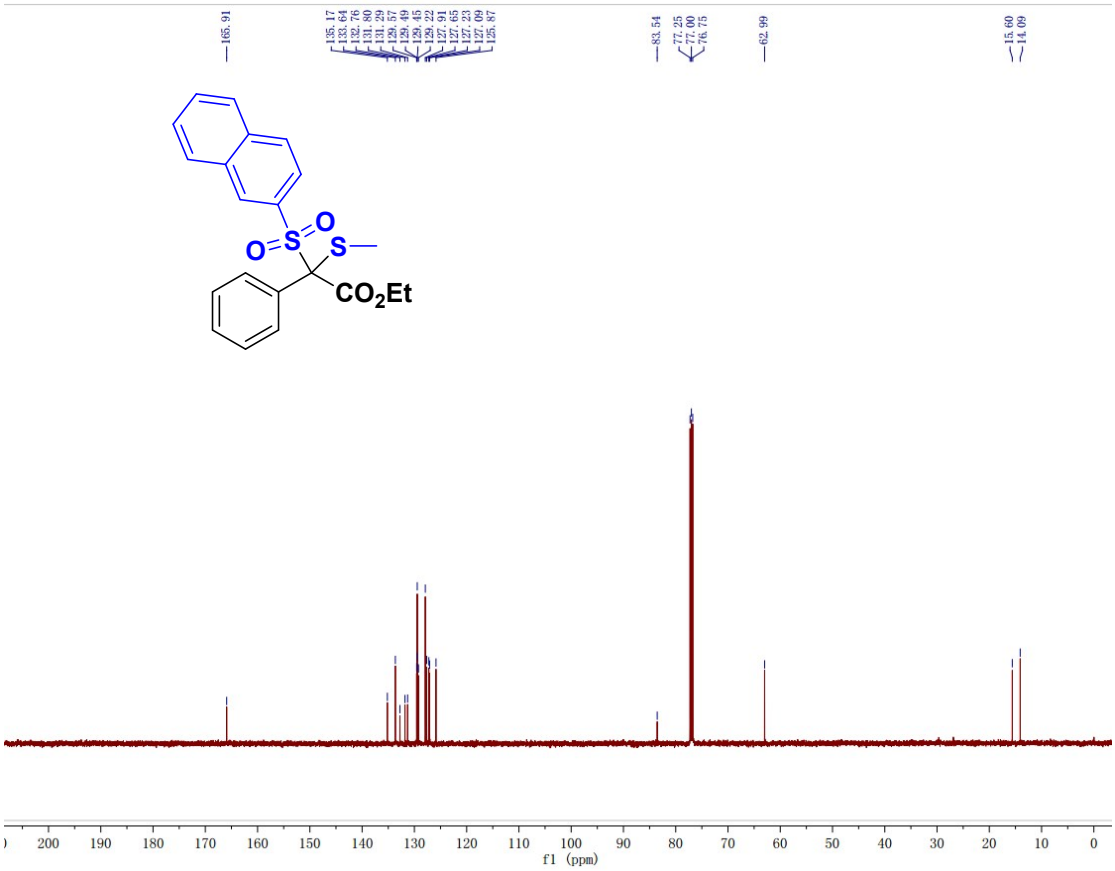
**ethyl 2-((4-(tert-butyl)phenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3r**



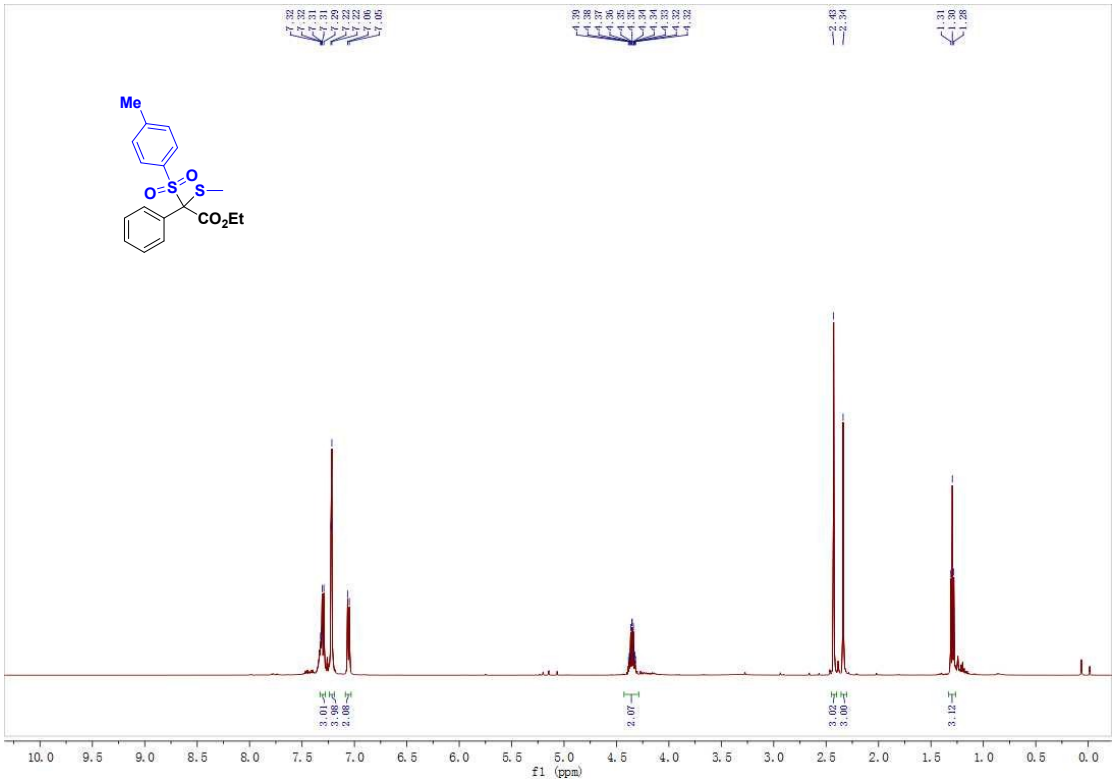



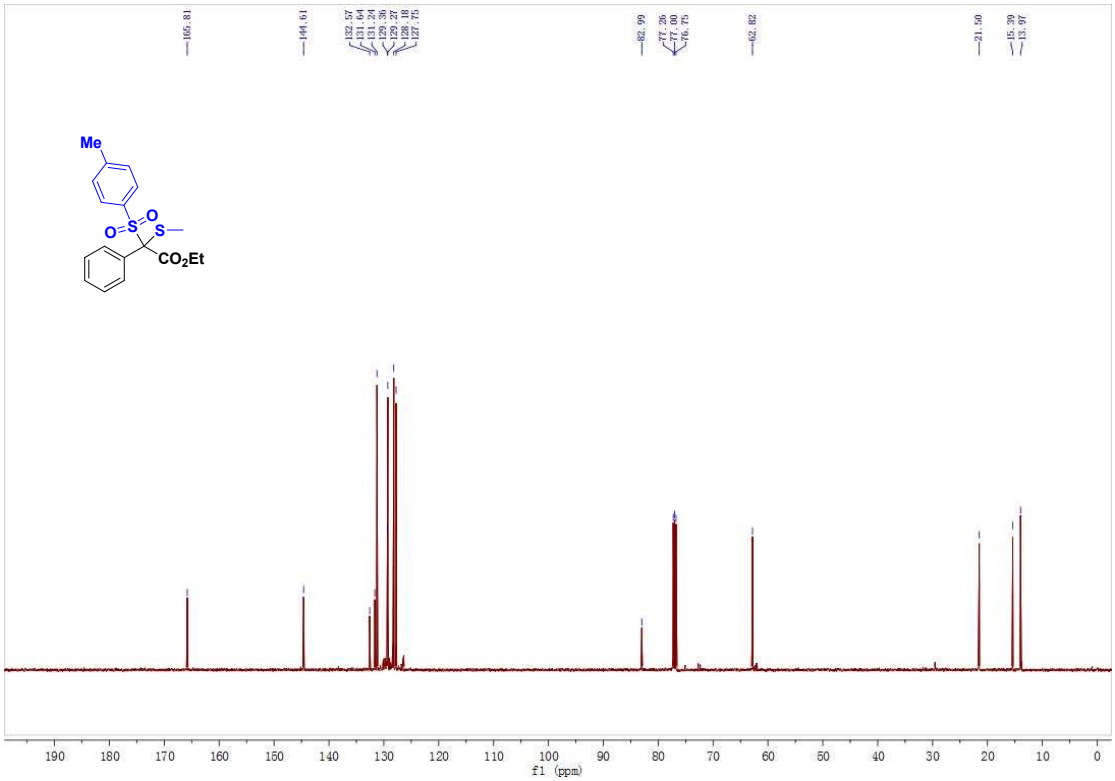
**ethyl 2-(methylthio)-2-(naphthalen-2-ylsulfonyl)-2-phenylacetate 3s**



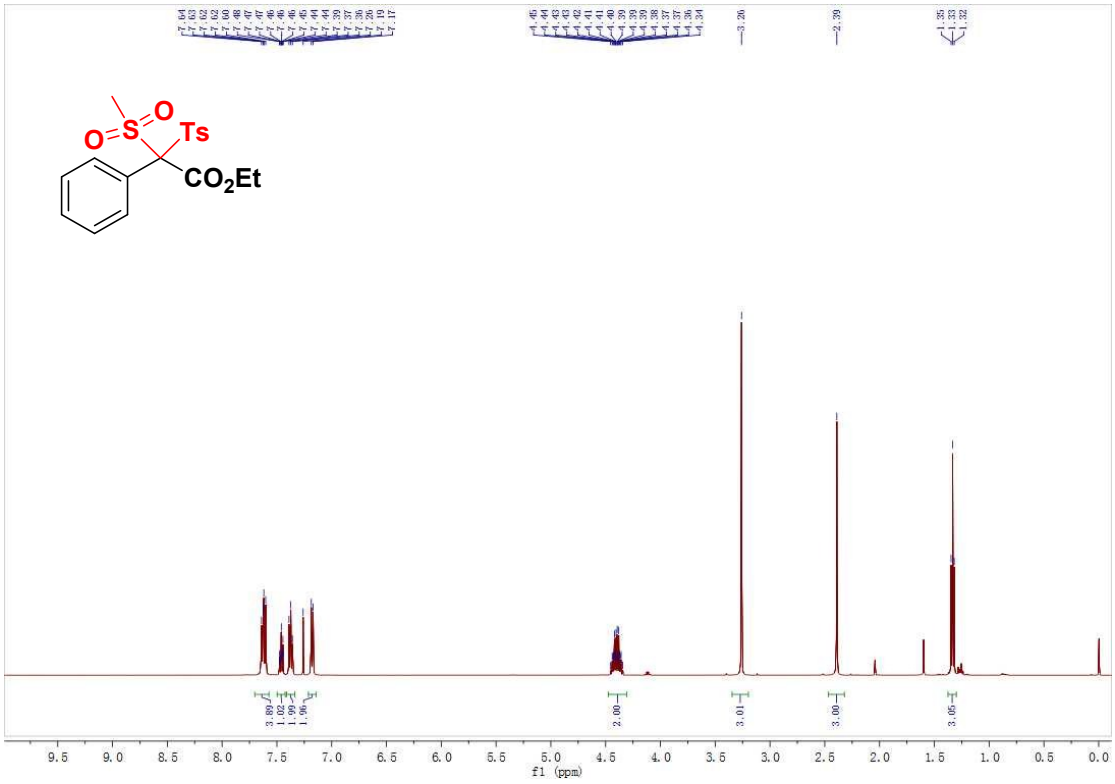



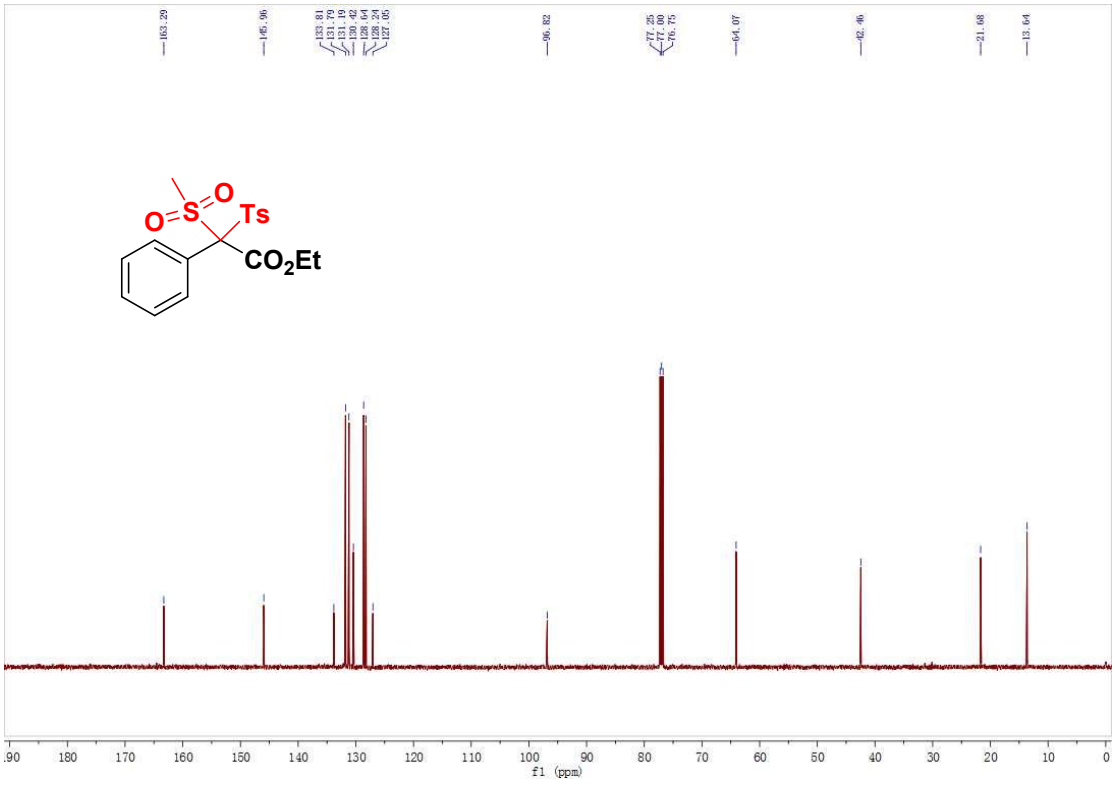
**ethyl 2-(methylthio)-2-phenyl-2-tosylacetate 3t**



**ethyl 2-(methylsulfonyl)-2-phenyl-2-tosylacetate 4**



**ethyl (R)-2-phenyl-2-tosylacetate 5**