Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-catalyzed carbene insertion into sulfur-sulfur bond of benzenesulfonothioate

General information

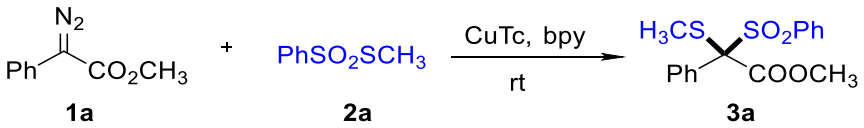
Unless otherwise noted, all the reagents were obtained commercially and used without further purification and reactions were monitored by TLC. DCM used were dried by CaH_2. All NMR spectra were recorded on Bruker-500 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments.

Synthesis of the starting materials

(1) Benzenesulfonothioates were prepared according to reported procedure[1].

(2) Diazomalonates were prepared according to reported procedure[2].

General procedure for condition3a



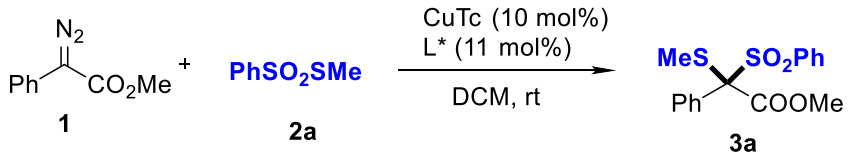
To a mixture of CuTc (10 mol %), bpy (10 mol %) and 4 Å molecular sieve (100 mg) in DCM (2 mL) under N_2 atmosphere, **1a** (0.4 mmol), **2a** (0.2 mmol) were added. The system was stirred at room temperature overnight. The reaction mixture was filtered and evaporated under reduced pressure, and purified by column chromatography to give the desired product **3a**. Yield: 80%. (pet.ether/EtOAc = 8/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, J=7.4 Hz, 1H), 7.45 (d, J=7.8 Hz, 2H), 7.34 (t, J=6.8 Hz, 1H), 7.29 (t, J=7.8 Hz, 2H), 7.23 (q, J=8.5 Hz, 4H), 3.89 (s,

3H), 2.44 (s, 3H).^{13}CNMR (126 MHz, CDCl3) δ 166.50, 135.66, 133.72, 131.60, 131.38, 129.66, 129.43, 128.01, 127.70, 83.40, 53.52, 15.62;HRMS exact mass calcd for $C_{16}H_{16}O_4S_2$ $[M+Na]^+$ requires m/z **359.0382**, found m/z **359.0366**.

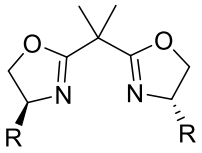
General procedure for the catalytic asymmetric reaction

To a mixture of CuTc (10 mol %), L* (11 mol %) and 4 Å molecular sieve (100 mg) in DCM (2 mL) under N_2 atmosphere, **1a** (0.4 mmol), **2a** (0.2 mmol) were added. The system was stirred at room temperature overnight. The reaction mixture was filtered and evaporated under reduced pressure, and purified by column chromatography to give the desired product **3a**.

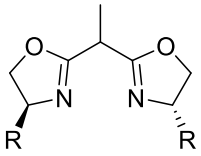
Optimization of chiral oxazoline ligands[a]



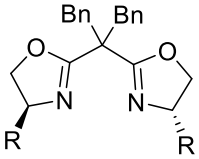
1 2a 3a



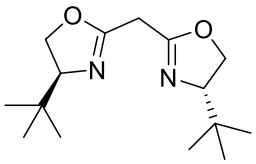
L_1:R=^{i}Pr, trace
L_2:R=^{t}Bu,Yield:61%,ee:35.5%
L_3:R=Ph,Yield:54%,ee:1.1%
L_4:R=Bn,Yield:58%,ee:42.34%



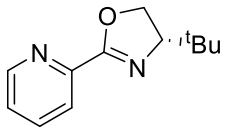
L_5:R=^{i}Pr, trace
L_6:R=Bn, trace



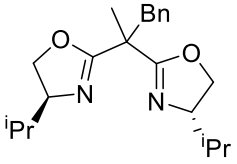
L_7:R=^{i}Pr,Yield:95%,ee:-9.1%
L_8:R=^{t}Bu,Yield:95%,ee:29.3%
L_{21}:R=Bn,Yield:65%,ee:55.3%



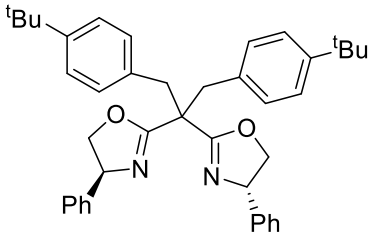
L_9:Yield:60%,ee:17.8%



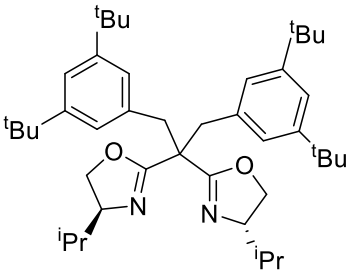
L_{10}:Yield:65%,ee:-2%



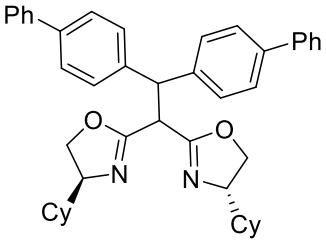
L_{11}:Yield:63%,ee:27.8%



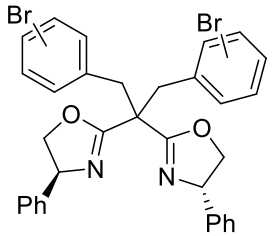
L_{12}:Yield:95%,ee:33.7%



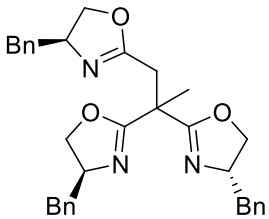
L_{13}:Yield:51%,ee:11.44%



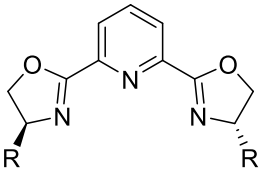
L_{14}:Yield:57%,ee:35.1%



L_{15}:p-Br:Yield:65%,ee:30%
L_{16}:o-Br:Yield:70%,ee:37.3%



L_{17}:Yield:20%,ee:28.9%

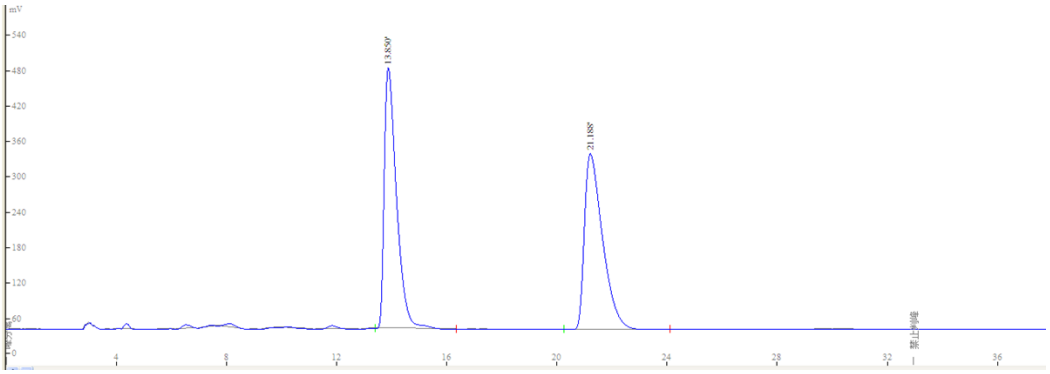


L_{18}:R=^{i}Pr,Yield:61%,ee:35.5%
L_{19}:R=Ph,Yield:43%,ee:3.6%
L_{20}:R=Bn,Yield:45%,ee:-7.6%

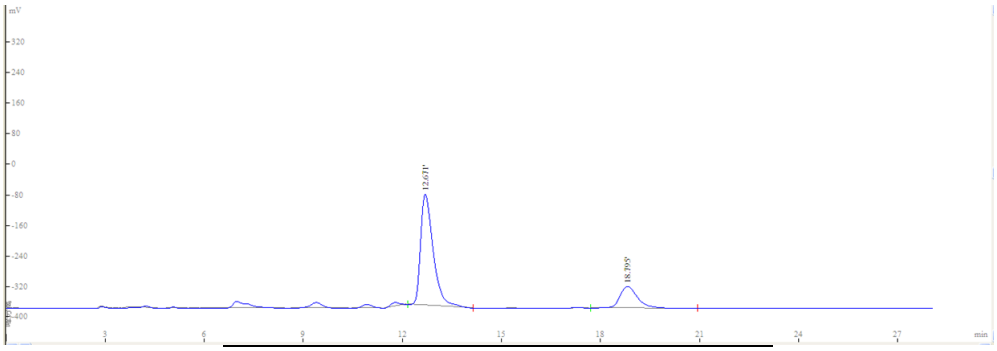
[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), CuTc (10 mol %), L* (11 mol %) and 4 Å molecular sieve (100 mg) in dry DCM (2 mL) under N_2 atmosphere for 10 h.

Copies of HPLC data

The enantiomeric excess of **3a** was determined by HPLC with a Chiralpak OD-H column, hexane: 2-propanol= 86:14, flow rate= 1 mL/min, 254 nm UV detector.



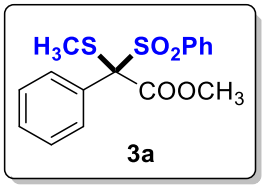
Entry	Time	Concentration	Area
1	13.850	49.95	13712394
2	21.188	50.05	13737949
Total		100	27450343



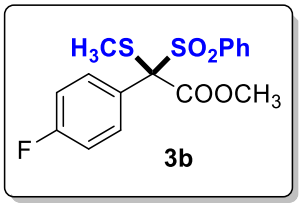
Entry	Time	Concentration	Area
1	12.671	77.66	7736526
2	18.795	22.34	2225117
Total		100	9961643

ee: 55%

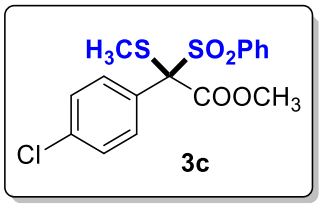
Characterization Data of Products.



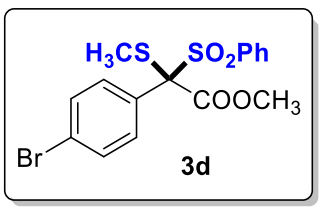
Yield:80% (pet. ether/EtOAc = 10/1).(white solid, pet.ether/EtOAc = 8/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, J=7.4 Hz, 1H), 7.45 (d, J=7.8 Hz, 2H), 7.34 (t, J=6.8 Hz, 1H), 7.29 (t, J=7.8 Hz, 2H), 7.23 (q, J=8.5 Hz, 4H), 3.89 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 166.50, 135.66, 133.72, 131.60, 131.38, 129.66, 129.43, 128.01, 127.70, 83.40, 53.52, 15.62;HRMS exact mass calcd for $C_{16}H_{16}O_4S_2$ $[M+Na]^+$ requires m/z **359.0382**, found m/z **359.0366**.



Yield:73% (pet. ether/EtOAc = 10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (t, J=7.5 Hz, 1H), 7.50 (d, J=7.7 Hz, 2H), 7.33 (t, J=7.8 Hz, 2H), 7.23 (dd, J=8.7, 5.1 Hz, 2H), 6.94 (t, J=8.5 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.36, 164.26(d, $J_{C\text{-}F}$ = 251.8 Hz), 135.51, 133.91, 131.64(d, $J_{C\text{-}F}$ = 8.6 Hz), 131.33, 127.86, 127.51(d, $J_{C\text{-}F}$ = 3.5 Hz), 115.19(d, $J_{C\text{-}F}$ = 21.9 Hz), 82.53, 53.61, 15.66.HRMS (ESI, m/z) calcd for$C_{16}H_{15}FO_4S_2$ $[M+Na]^+$ **377.0288**, found **377.0288**.

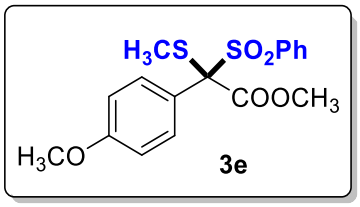


Yield:80% (pet. ether/EtOAc = 10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58–7.50 (m, 3H), 7.35 (t, J = 7.9 Hz, 2H), 7.25–7.21 (m, 2H), 7.20–7.16 (m, 2H), 3.89 (s, 3H), 2.40 (s, 3H).^{13}C NMR(126 MHz, $CDCl_3$) δ 166.21, 135.96, 135.40, 134.01, 131.39, 130.92, 130.10, 128.22, 127.90, 82.60, 53.66, 15.62.HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2[M+NH_4]^+$**388.0439**, found **388.0431**.

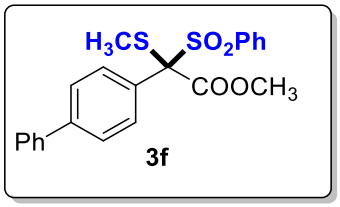


Yield:80% (pet. ether/EtOAc = 10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (ddd, J=11.3,

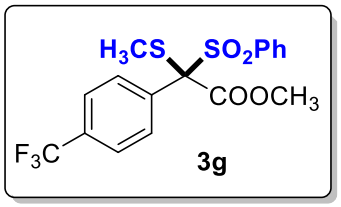
7.9, 1.1 Hz, 3H), 7.41–7.32 (m, 4H), 7.15–7.09 (m, 2H), 3.89 (s, 3H), 2.39 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.15, 135.36, 134.04, 131.40, 131.18, 131.16, 130.62, 127.92, 124.25, 82.68, 53.67, 15.60.HRMS (ESI, m/z) calcd for $C_{16}H_{15}BrO_4S_2$ $[M+Na]^+$ **436.9487**,found **436.9489**.



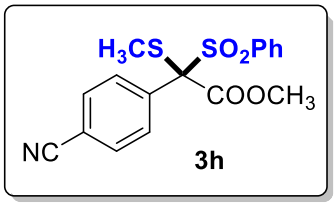
Yield:77% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.54–7.46 (m, 3H), 7.31 (t, J=7.9 Hz, 2H), 7.16–7.10 (m, 2H), 6.78–6.73 (m, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 2.42 (s, 3H).^{13}C NMR(126 MHz, $CDCl_3$) δ 166.69, 160.52, 135.82, 133.67, 131.37, 130.84, 127.71, 123.28, 113.41, 82.90, 55.39, 53.49, 15.68.HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_5S_2$ $[M+Na]^+$ **389.0488**, found **389.0489**.



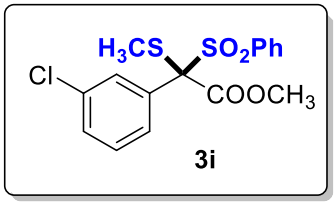
Yield:54% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.56 (d, J=7.3 Hz, 2H), 7.52 (t, J=7.6 Hz, 3H), 7.46 (dd, J=14.7, 8.0 Hz, 4H), 7.38 (t, J=7.3 Hz, 1H), 7.30 (t, J=8.1 Hz, 4H), 3.92 (s, 3H), 2.45 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 142.46, 139.79, 135.71, 133.80, 131.45, 130.37, 129.90, 128.95, 127.99, 127.76, 127.13, 126.60, 83.22, 53.59, 15.65. HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$ **435.0695**, found **435.0694**.



Yield:56% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.56 (t, J=7.5 Hz, 1H), 7.52 (d, J=7.5 Hz, 4H), 7.40 (d, J=8.2 Hz, 2H), 7.34 (t, J=7.7 Hz, 2H), 3.91 (s, 3H), 2.39 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.00, 135.24, 134.17, 131.35, 130.77, 130.15, 129.81, 128.85, 127.95, 124.90, 124.88, 124.85, 124.82, 82.74, 53.72, 15.52.HRMS (ESI, m/z) calcd for $C_{17}H_{15}F_3O_4S_2$ $[M+Na]^+$ **427.0256**, found **427.0260**. Melting point: 162-164 °C.

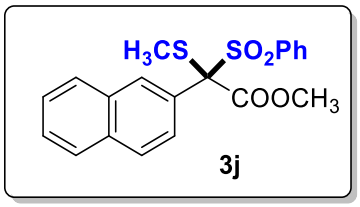


Yield: 36% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.54–7.44 (m, 5H), 7.37–7.32 (m, 2H), 7.30 (t, J = 7.9 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.71, 135.58, 134.11, 133.31, 130.52, 130.33, 129.49, 127.05, 116.87, 112.42, 81.64, 52.79, 14.48. HRMS (ESI, m/z) calcd for $C_{17}H_{15}NO_4S_2$ $[M+Na]^+$ **384.0335**, found **384.0338**.



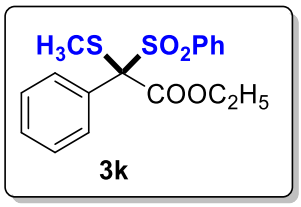
3i

Yield: 66% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.52–7.46 (m, 1H), 7.44 (dd, J = 8.4, 1.1 Hz, 2H), 7.30–7.24 (m, 3H), 7.15–7.07 (m, 3H), 3.84 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.06, 135.22, 134.09, 134.03, 133.50, 131.37, 129.79, 129.66, 129.17, 127.87, 82.68, 53.71, 15.58. HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2$ $[M+Na]^+$**392.9992**, found **392.9989**.



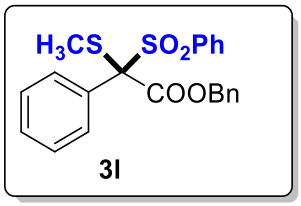
3j

Yield:65% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.81 (d, J=8.1 Hz, 1H), 7.73 (d, J=8.7 Hz, 1H), 7.65 (dd, J=15.7, 4.8 Hz, 2H), 7.55–7.50 (m, 1H), 7.46 (ddd, J=14.9, 8.0, 4.2 Hz, 4H), 7.35 (dd, J=8.7, 2.0 Hz, 1H), 7.20 (t, J=7.9 Hz, 2H), 3.92 (s, 3H), 2.47 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.61, 135.41, 133.80, 133.26, 132.23, 131.42, 129.71, 128.82, 128.55, 127.69, 127.50, 127.49, 126.65, 126.12, 83.46, 53.63, 15.69. HRMS (ESI, m/z) calcd for $C_{20}H_{18}O_4S_2$ $[M+Na]^+$ **409.0539**, found **409.0546**.

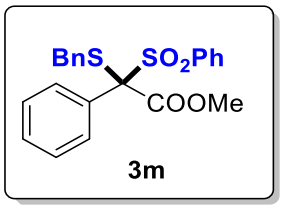


3k

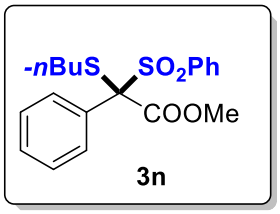
Yield:66% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.51 (t, J=7.4 Hz, 1H), 7.45 (d, J=7.3 Hz, 2H), 7.34 (ddd, J=8.7, 5.8, 2.6 Hz, 1H), 7.31–7.26 (m, 2H), 7.26–7.20 (m, 4H), 4.43–4.33 (m, 2H), 2.46 (s, 3H), 1.33 (t, J=7.1 Hz, 3H).^{13}C NMR(126 MHz, $CDCl_3$) δ 165.91, 135.78, 133.65, 131.73, 131.40, 129.59, 129.44, 127.96, 127.65, 83.32, 63.03, 15.56, 14.13. HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_4S_2$$[M+Na]^+$ **373.0539**, found **373.0532**.



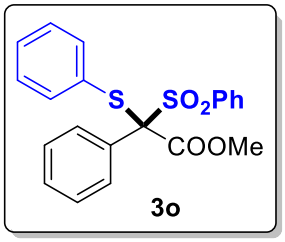
Yield:84% (pet. ether/EtOAc =10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.44 (m, 1H), 7.41 (dd, J=8.2, 1.0 Hz, 2H), 7.38–7.34 (m, 2H), 7.34–7.29 (m, 4H), 7.24 (t, J=8.0 Hz, 2H), 7.21–7.13 (m, 4H), 5.32 (dd, J=49.1, 12.0 Hz, 2H), 2.30 (s, 3H).^{13}C NMR(126 MHz, $CDCl_3$). δ 165.80, 135.59, 134.53, 133.68, 131.59, 131.39, 129.60, 129.51, 128.87, 128.76, 128.62, 127.91, 127.66, 83.11, 68.39, 15.32. HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$ **430.1141**, found **430.1140**.



Yield: 74% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.55–7.44 (m, 3H), 7.39 (d, J=7.6 Hz, 2H), 7.33 (t, J=7.4 Hz, 3H), 7.27 (dd, J=13.1, 5.5 Hz, 3H), 7.23 (dd, J=13.6, 4.8 Hz, 4H), 4.42 (d, J=11.7 Hz, 1H), 4.05 (d, J=11.8 Hz, 1H), 3.76 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.57, 135.63, 135.31, 133.75, 131.71, 131.42, 129.71, 129.57, 129.37, 128.75, 128.04, 127.81, 127.75, 83.37, 53.40, 37.14.HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$ **430.1141**, found **430.1137**.

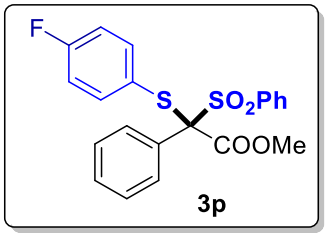


Yield:53% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.51 (t, J=7.4 Hz, 1H), 7.45 (d, J=7.6 Hz, 2H), 7.34 (ddd, J=8.6, 5.7, 2.6 Hz, 1H), 7.28 (dd, J=12.8, 4.7 Hz, 2H), 7.26–7.19 (m, 4H), 3.88 (s, 3H), 3.22–3.12 (m, 1H), 2.76–2.66 (m, 1H), 1.62 (dd, J=15.2, 7.5 Hz, 2H), 1.50–1.40 (m, 2H), 0.93 (t, J=7.3 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.88, 135.71, 133.64, 131.84, 131.41, 129.61, 129.49, 127.95, 127.66, 83.50, 53.43, 32.18, 30.51, 22.00, 13.68.HRMS (ESI, m/z) calcd for $C_{19}H_{22}O_4S_2$ $[M+Na]^+$ **401.0852**, found **401.0845**.

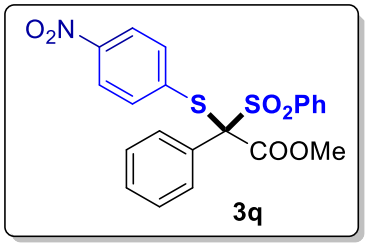


Yield:85% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.56 (d, J=7.3 Hz,

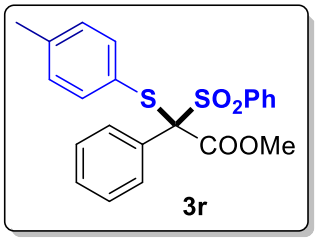
2H), 7.52 (t, J=7.6 Hz, 3H), 7.46 (dd, J=14.7, 8.0 Hz, 4H), 7.38 (t, J=7.3 Hz, 1H), 7.30 (t, J=8.1 Hz, 4H), 3.92 (s, 3H), 2.45 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.53, 142.46, 139.79, 135.71, 133.80, 131.45, 130.37, 129.90, 128.95, 127.99, 127.76, 127.13, 126.60, 83.22, 53.59, 15.65. HRMS (ESI, m/z) calcd for $C_{21}H_{18}O_4S_2$ $[M+Na]^+$ **421.0539**, found **421.0546**.



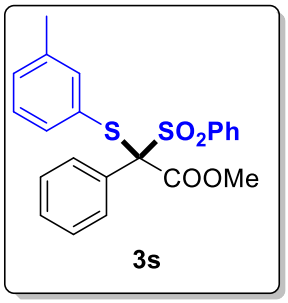
Yield:70% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.70 (dd, J=8.7, 5.4 Hz, 2H), 7.44 (dd, J=14.0, 7.4 Hz, 3H), 7.25 (dt, J=15.7, 7.5 Hz, 3H), 7.16 (dt, J=12.5, 5.1 Hz, 4H), 6.96 (t, J=8.6 Hz, 2H), 3.40 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.37, 164.27(d, J_{C-F} = 252.6 Hz),139.01(d, J_{C-F} = 8.8 Hz), 134.87, 132.73, 131.39, 130.52, 128.78, 128.57, 126.85, 126.80, 123.15(d, J_{C-F} = 3.4 Hz), 115.01(d, J_{C-F} = 21.9 Hz), 85.89, 51.87. HRMS (ESI, m/z) calcd for $C_{21}H_{17}FO_4S_2$ $[M+Na]^+$ **439.0444**, found **439.0451**.



Yield:80% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 8.16 (d, J=8.7 Hz, 2H), 7.91 (d, J=8.7 Hz, 2H), 7.54 (t, J=7.4 Hz, 1H), 7.49 (d, J=7.7 Hz, 2H), 7.38 (t, J=7.1 Hz, 1H), 7.32 (t, J=7.8 Hz, 2H), 7.29–7.20 (m, 4H), 3.54 (s, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.39, 148.37, 138.36, 136.28, 135.61, 134.07, 131.73, 131.44, 129.96, 129.56, 128.17, 127.99, 123.51, 86.87, 53.32. HRMS (ESI, m/z) calcd for $C_{21}H_{17}NO_6S_2$ $[M+Na]^+$ **466.0389**, found **466.0398**.

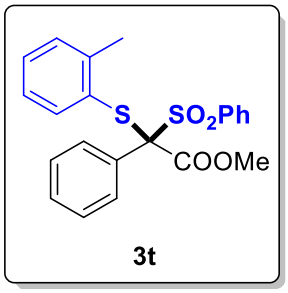


Yield:83% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.62 (d, J=7.9 Hz, 2H), 7.57–7.46 (m, 3H), 7.37–7.19 (m, 7H), 7.14 (d, J=7.9 Hz, 2H), 3.43 (s, 3H), 2.34 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.50, 141.02, 137.61, 136.06, 133.67, 132.60, 131.64, 130.02, 129.59, 129.51, 127.79, 127.78, 125.29, 86.96, 52.81, 21.41.HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$ **430.1141**, found **430.1139**.



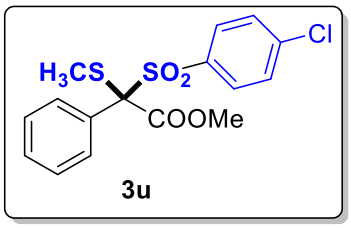
3s

Yield:75% (pet. ether/EtOAc = 10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J=7.9 Hz, 2H), 7.53 (d, J=6.6 Hz, 3H), 7.33 (dt, J=15.3, 7.1 Hz, 4H), 7.29–7.17 (m, 5H), 3.40 (s, 3H), 2.31 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.42, 138.53, 137.99, 137.47, 136.07, 134.44, 133.69, 132.55, 131.73, 131.25, 130.07, 129.51, 128.63, 128.57, 127.80, 87.01, 52.73, 21.22.HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$ **435.0695**, found **435.0701**.



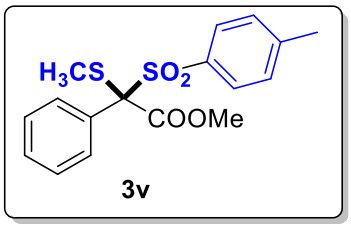
3t

Yield: 68% (pet. ether/EtOAc = 10/1).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J=17.6, 7.7 Hz, 3H), 7.47 (t, J=7.4 Hz, 1H), 7.33 (d, J=7.6 Hz, 2H), 7.27 (dd, J=14.5, 6.9 Hz, 3H), 7.19 (dd, J=14.7, 7.2 Hz, 3H), 7.12 (d, J=7.1 Hz, 1H), 7.05 (t, J=7.5 Hz, 1H), 3.12 (s, 3H), 2.31 (s, 3H). δ 165.26, 144.54, 138.17, 136.27, 133.70, 132.59, 131.93, 130.59, 130.41, 129.94, 129.46, 128.97, 127.79, 127.67, 126.47, 87.58, 52.47, 21.45. HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$ **435.0695**, found **435.0699**.



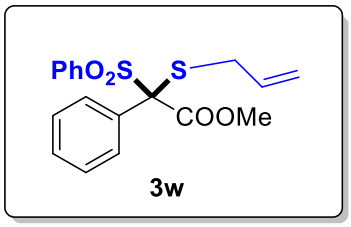
3u

Yield:64% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 3H), 7.30–7.24 (m, 4H), 7.24–7.19 (m, 2H), 3.90 (s, 3H), 2.46 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.41, 140.60, 134.16, 132.76, 131.41, 129.89, 129.35, 128.17, 128.02, 83.59, 53.62, 15.70.HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2$ $[M+NH_4]^+$ **388.0439**, found **388.0429**.



3v

Yield:74% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.39–7.28 (m, 3H), 7.29–7.20 (m, 4H), 7.08 (d, J=8.1 Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.61, 144.83, 132.69, 131.72, 131.42, 129.58, 129.45, 128.39, 127.99, 83.26, 53.50, 21.66, 15.64.HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_4S_2$ $[M+NH_4]^+$ **368.0985**, found **368.0983**.



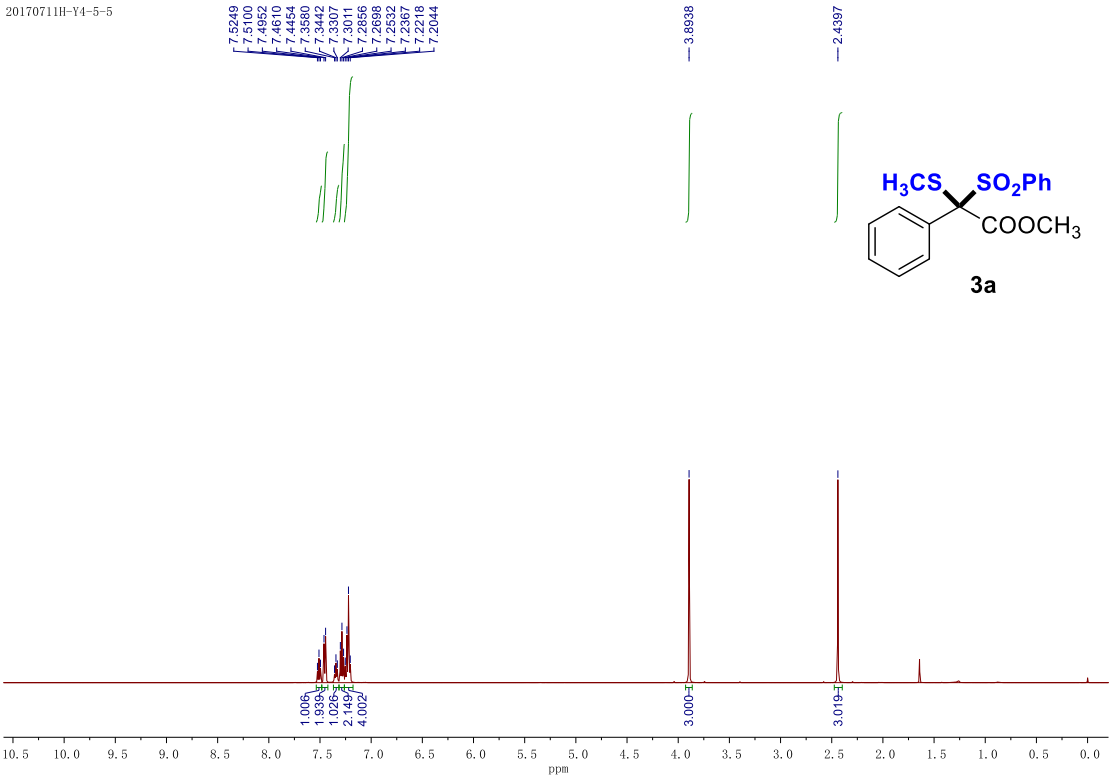
3w

Yield:74% (pet. ether/EtOAc = 10/1).^{1}H NMR(500 MHz, $CDCl_3$) δ 7.55–7.44 (m, 3H), 7.39 (d, J=7.6 Hz, 2H), 7.33 (t, J=7.4 Hz, 3H), 7.27 (dd, J=13.1, 5.5 Hz, 3H), 7.23 (dd, J=13.6, 4.8 Hz, 4H), 4.42 (d, J=11.7 Hz, 1H), 4.05 (d, J=11.8 Hz, 1H), 3.76 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 166.69, 135.60, 133.75, 131.69, 131.64, 131.43, 129.71, 129.41, 128.03, 127.72, 119.69, 83.04, 53.44, 35.61.HRMS (ESI, m/z) calcd for $C_{18}H_{18}O_4S_2$ $[M+Na]^+$ **385.0539**, found **385.0544**.

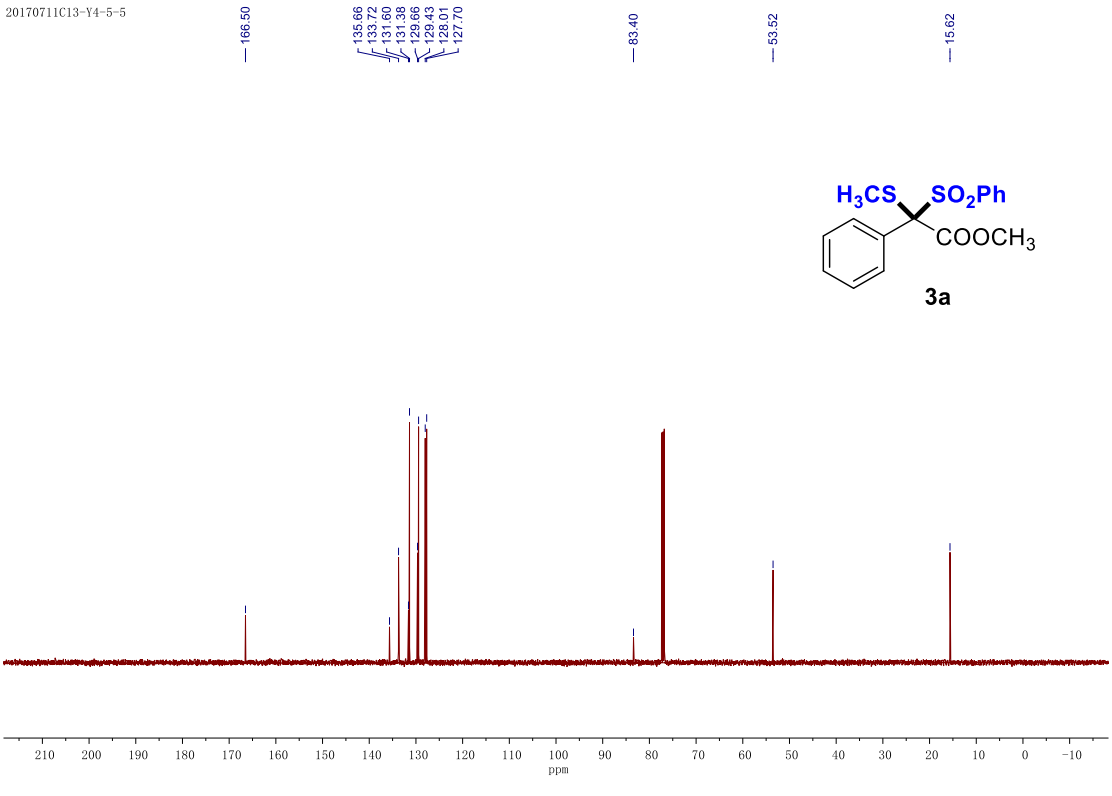
References

(1) (a) W. Wang, X. Peng, F. Wei, C. Tung, Z. Xu, *Angew. Chem. Int. Ed.*, 2016, **55**, 649; (b) H. Li, C. Shan, C. Tung and Z. Xu, *Chem. Sci*., 2017, **8**, 2610 –2615.
(2) S. Chuprakov, M. Rubin and V. Gevorgyan, *J. Am. Chem. Soc*., 2005, **127**, 3714−3715.

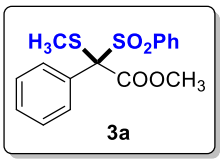
NMR spectra for the products



3a

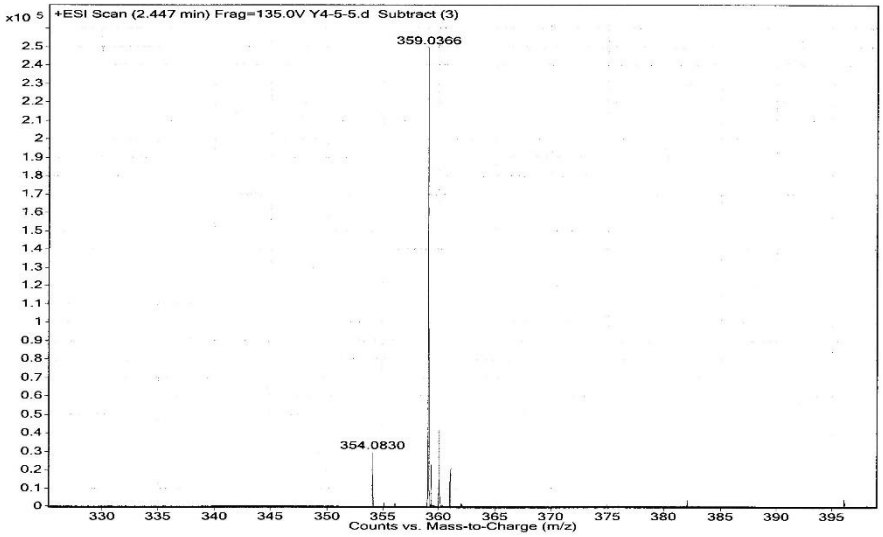


3a

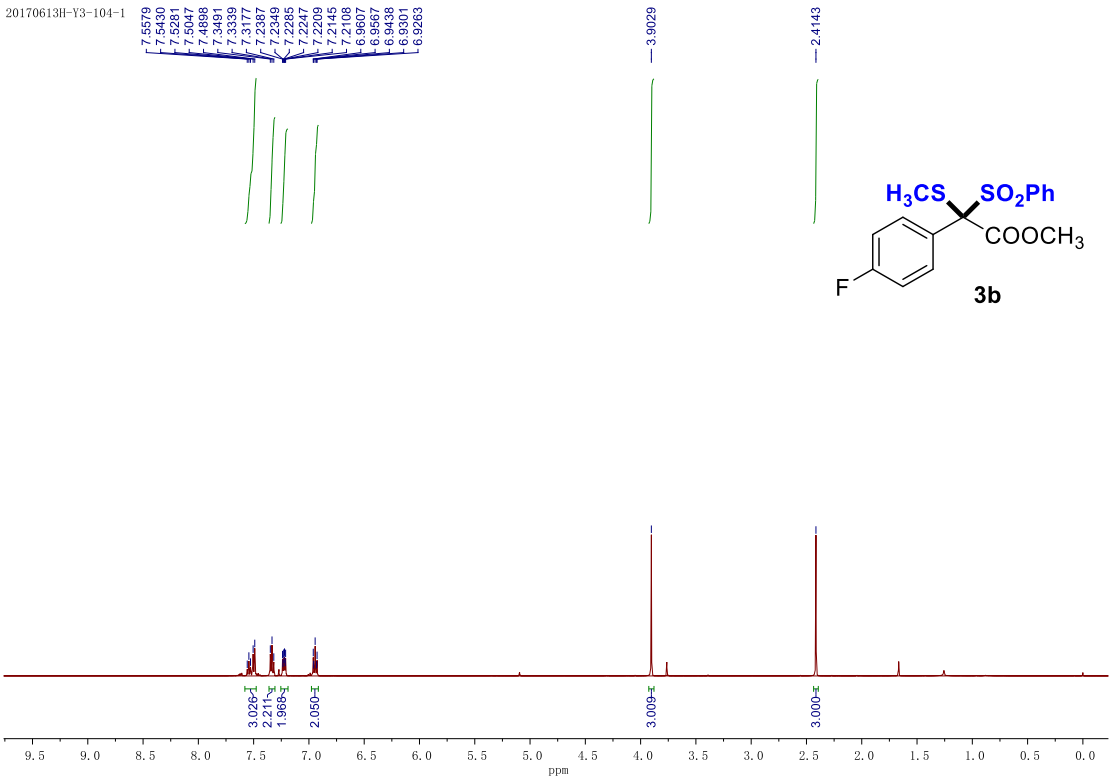


3a

Chemical Formula: $C_{16}H_{16}O_4S_2$
Exact Mass: 336.0490
Molecular Weight: 336.4200
m/z: 336.0490 (100.0%), 337.0524 (17.3%), 338.0448 (9.0%), 337.0484 (1.6%), 339.0482 (1.6%), 338.0557 (1.4%)
Elemental Analysis: C, 57.12; H, 4.79; O, 19.02; S, 19.06



HRMS (ESI, m/z) calcd for $C_{16}H_{16}O_4S_2$ $[M+Na]^+$**359.0382**, found **359.0366**.


20170613H-Y3-104-1
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7.5281
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7.2285
7.2247
7.2209
7.2145
7.2108
6.9607
6.9567
6.9438
6.9301
6.9263
3.9029
2.4143
H3CS
SO2Ph
COOCH3
F
3b
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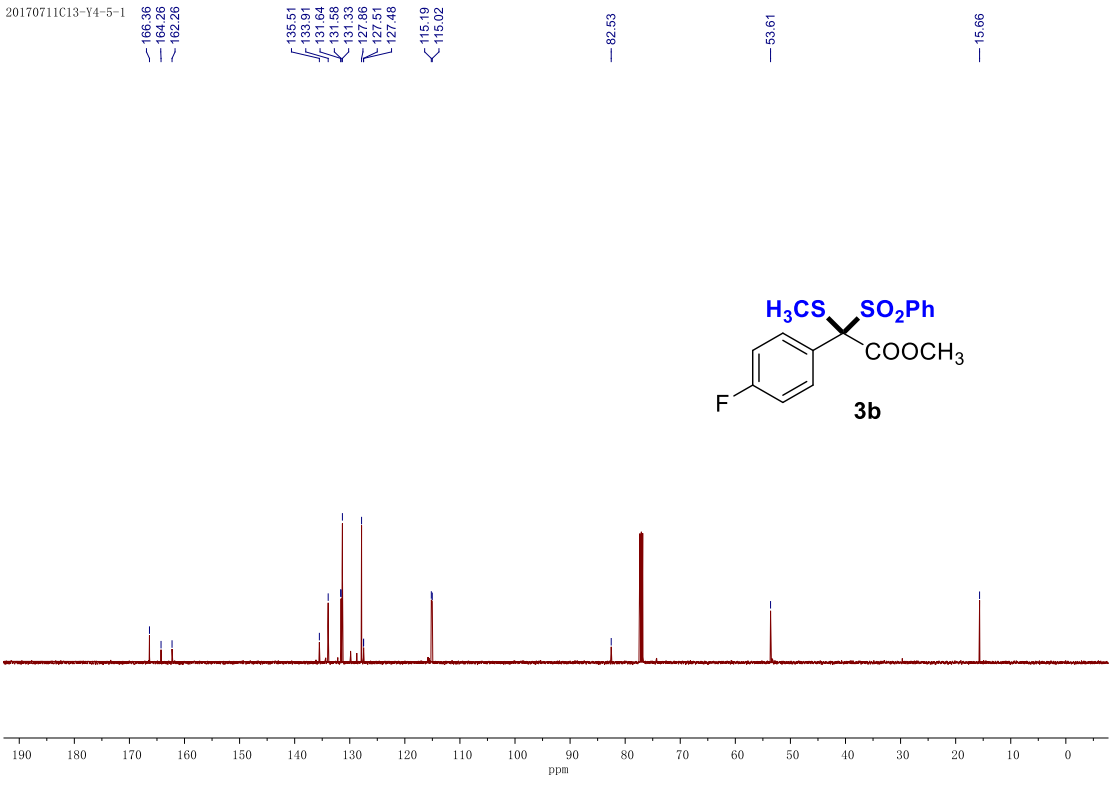
3.000
ppm


20170711C13-Y4-5-1
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162.26
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133.91
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131.58
131.33
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115.02
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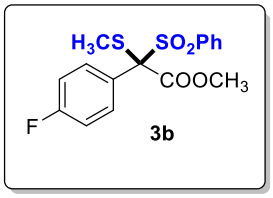
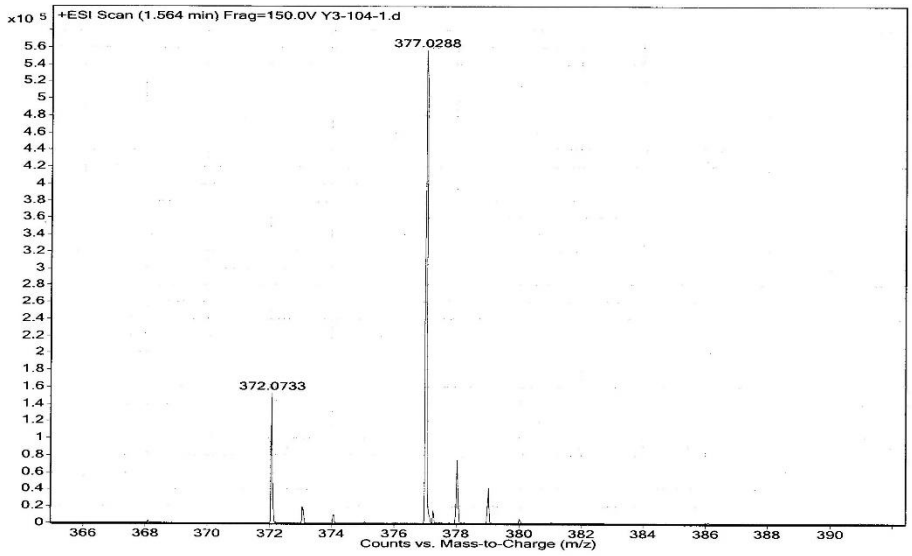
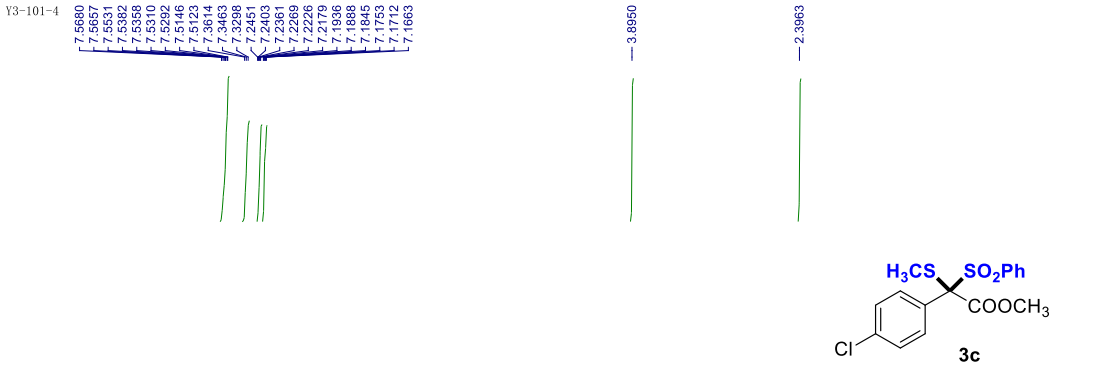
53.61
15.66
H3CS
SO2Ph
COOCH3
F
3b
ppm



Chemical Formula: $C_{16}H_{15}FO_4S_2$
Exact Mass: 354.0396
Molecular Weight: 354.4104
m/z: 354.0396 (100.0%), 355.0429 (17.3%), 356.0354 (9.0%), 355.0390 (1.6%), 357.0387 (1.6%), 356.0463 (1.4%)
Elemental Analysis: C, 54.22; H, 4.27; F, 5.36; O, 18.06; S, 18.09



HRMS (ESI, m/z) calcd for$C_{16}H_{15}FO_4S_2$ $[M+Na]^+$**377.0288**, found **377.0288**.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7.3463
7.3298
7.2451
7.2403
7.2361
7.2269
7.2226
7.2179
7.1936
7.1888
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7.1712
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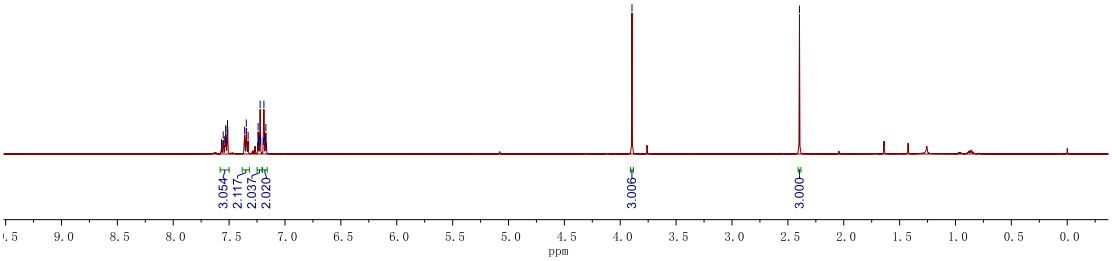
2.3963

H3CS
SO2Ph
COOCH3
Cl

3c


3.054
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2.037
2.020
3.006
3.000
ppm


Y3-101-4
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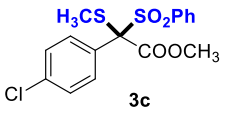
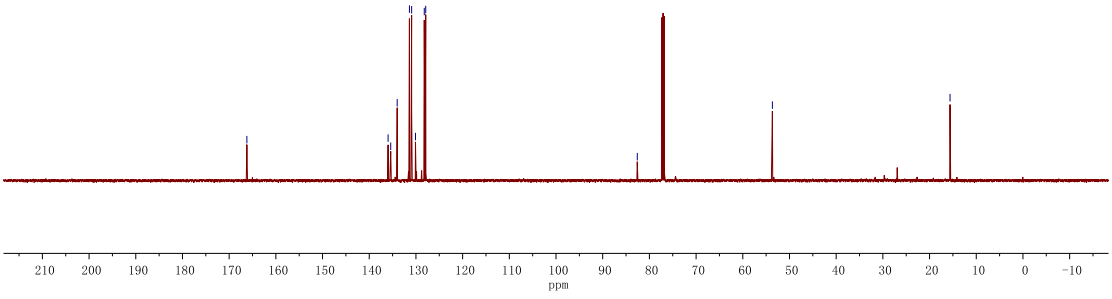
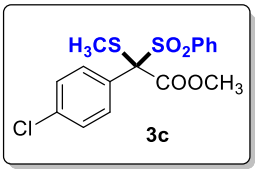
128.22
127.90
82.60
53.66
15.62

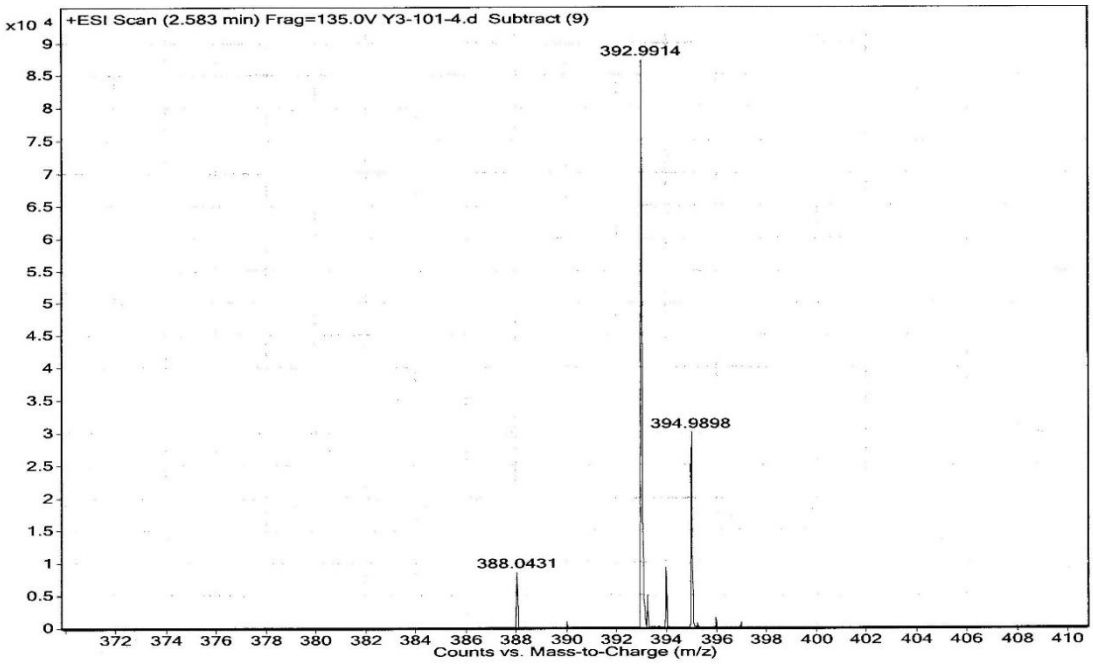

H3CS
SO2Ph
COOCH3
Cl

3c

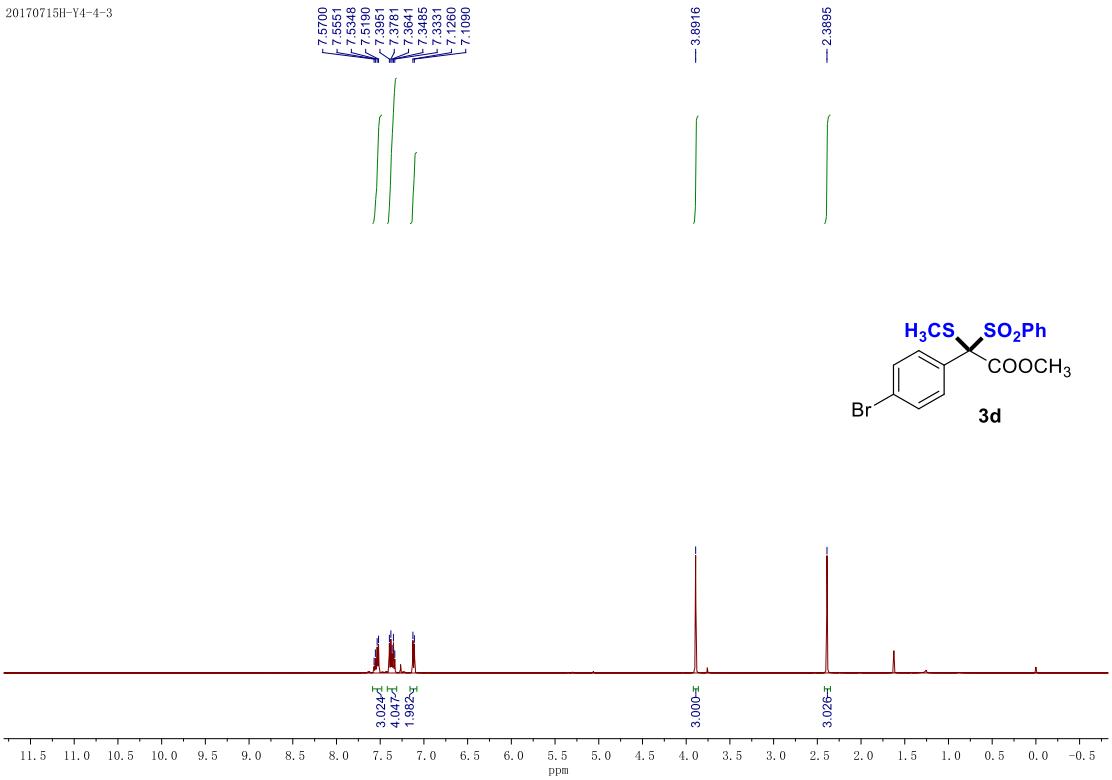

ppm



Chemical Formula: $C_{16}H_{15}ClO_4S_2$
Exact Mass: 370.0100
Molecular Weight: 370.8620



HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2$ $[M+NH_4]^+$**388.0439**, found **388.0431**.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7.3331
7.1260
7.1090
3.8916
2.3895
H3CS
SO2Ph
COOCH3
Br
3d
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4.047
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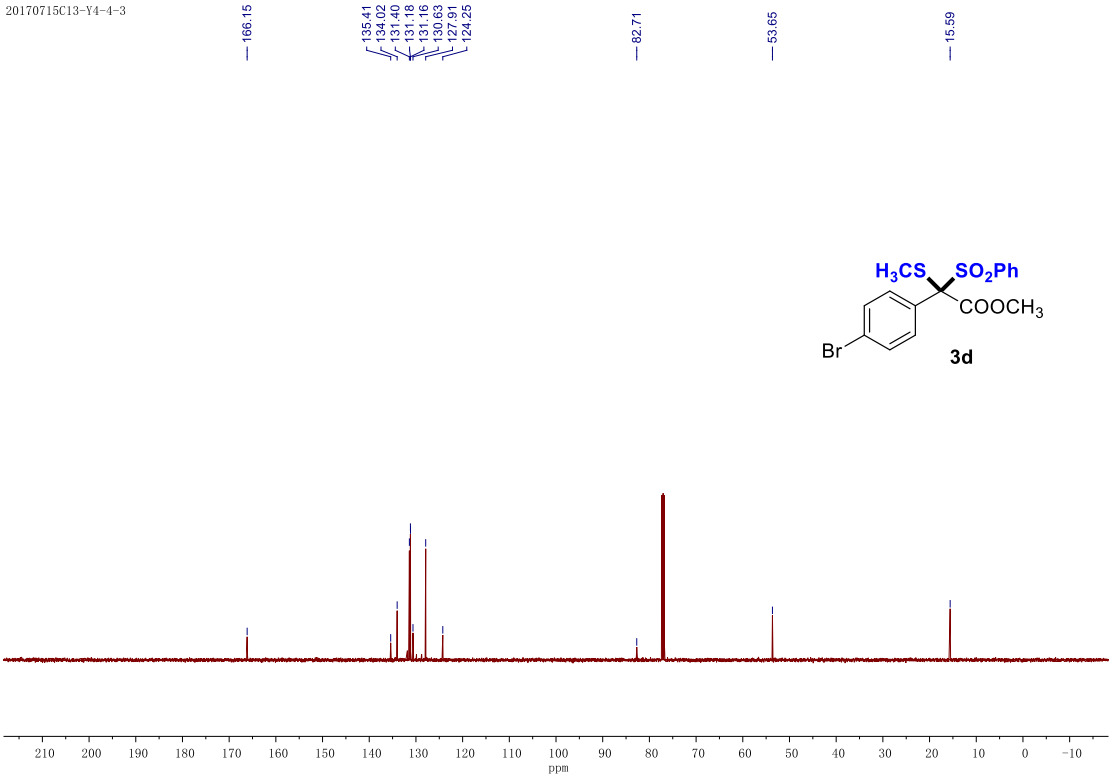
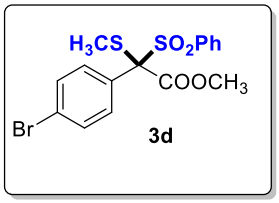
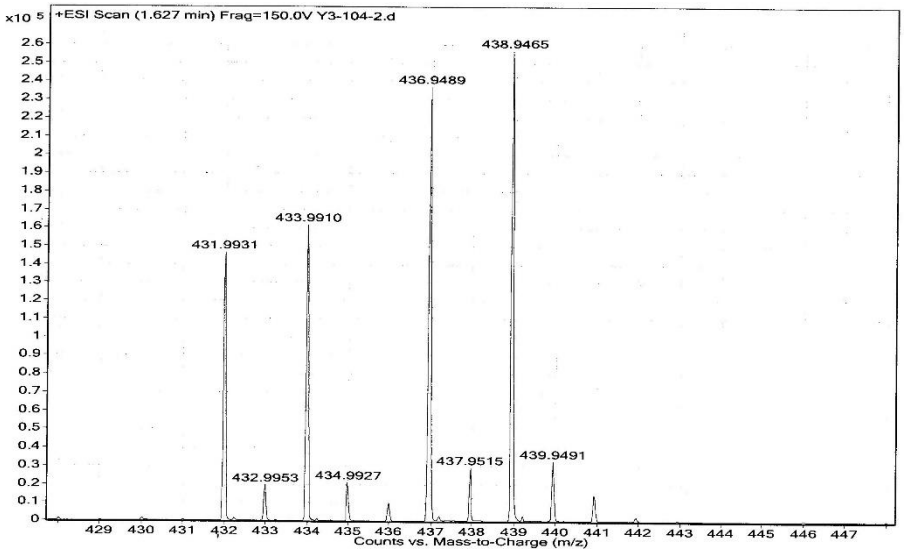
3.026
ppm

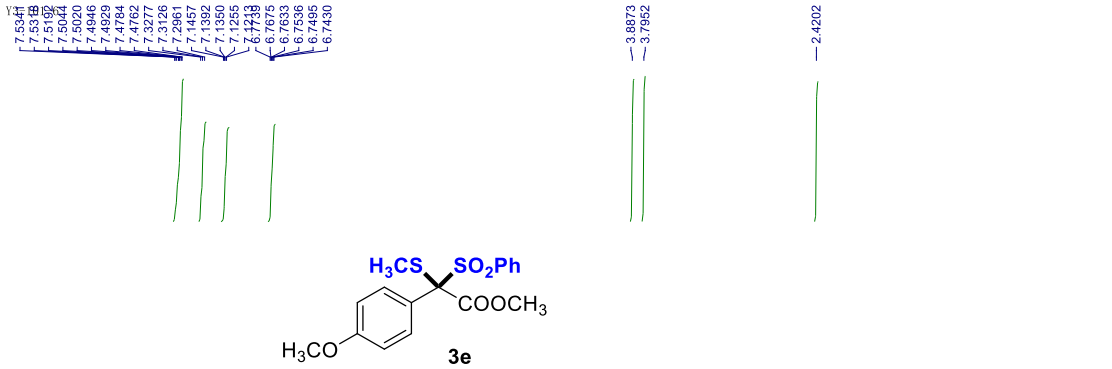

20170715C13-Y4-4-3
166.15
135.41
134.02
131.40
131.18
131.16
130.63
127.91
124.25
82.71
53.65
15.59
H3CS
SO2Ph
COOCH3
Br
3d
ppm



Chemical Formula: $C_{16}H_{15}BrO_4S_2$
Exact Mass: 413.9595
Molecular Weight: 415.3160
m/z: 413.9595 (100.0%), 415.9575 (97.3%), 416.9608 (16.8%), 414.9629 (16.2%), 415.9553 (9.0%), 417.9533 (8.8%), 414.9589 (1.6%), 416.9569 (1.6%), 418.9566 (1.5%), 416.9587 (1.5%), 417.9642 (1.2%), 414.9629 (1.1%), 415.9662 (1.1%)
Elemental Analysis: C, 46.27; H, 3.64; Br, 19.24; O, 15.41; S, 15.44

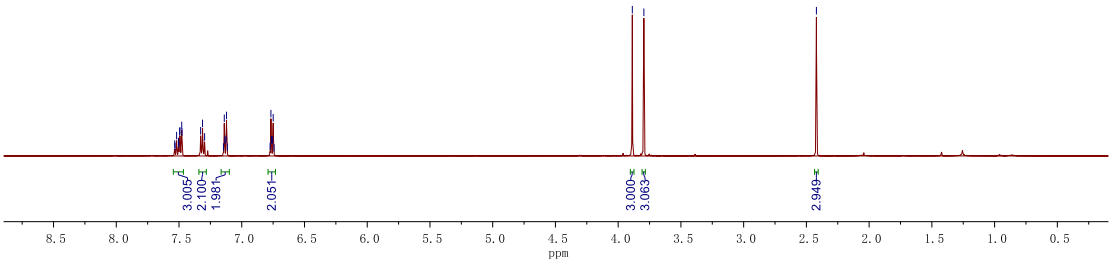


HRMS (ESI, m/z) calcd for $C_{16}H_{15}BrO_4S_2$ $[M+Na]^+$**436.9487**, found **436.9489**.

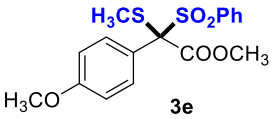

7.5341
7.5318
7.5192
7.5044
7.5020
7.4946
7.4929
7.4784
7.4762
7.3277
7.3126
7.2961
7.1457
7.1392
7.1350
7.1255
7.1213
6.7739
6.7675
6.7633
6.7536
6.7495
6.7430
3.8873
3.7952
2.4202

H3CS
SO2Ph
COOCH3
H3CO

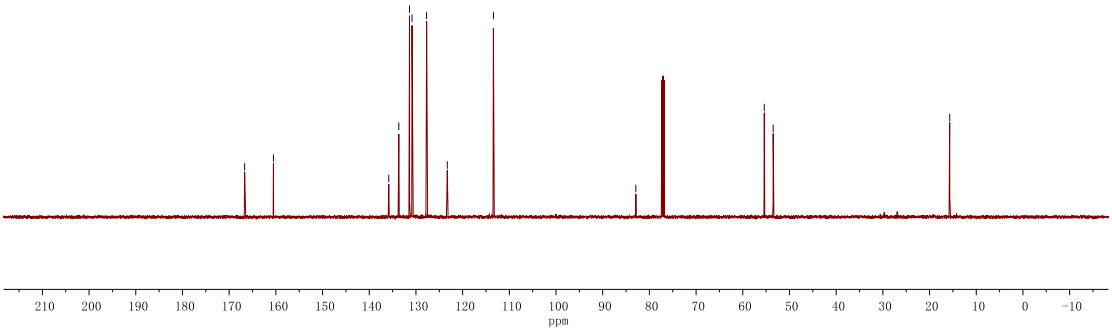
3e

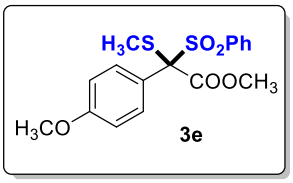

3.005
2.100
1.981
2.051
3.000
3.063
2.949
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Y3-101-6
166.69
160.52
135.82
133.67
131.37
130.84
127.71
123.28
113.41
82.90
55.39
53.49
15.68

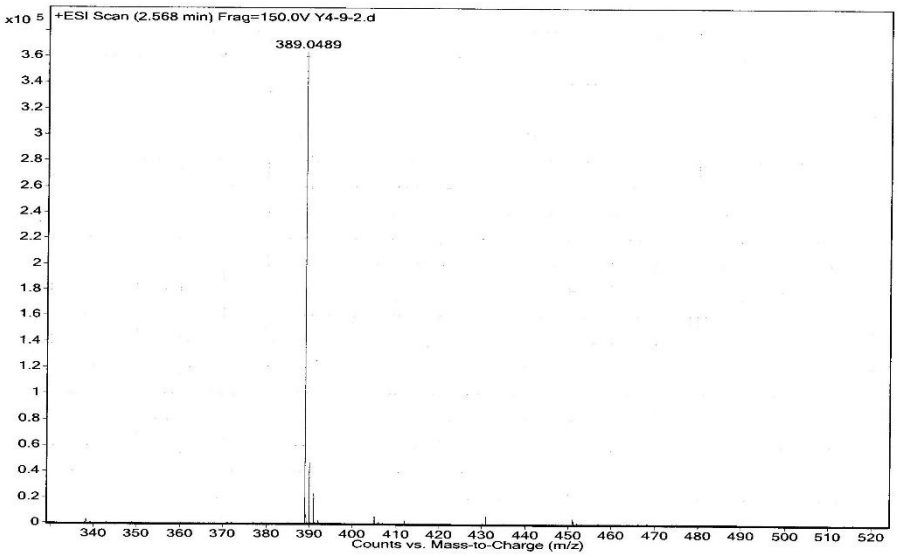

H3CS
SO2Ph
COOCH3
H3CO

3e

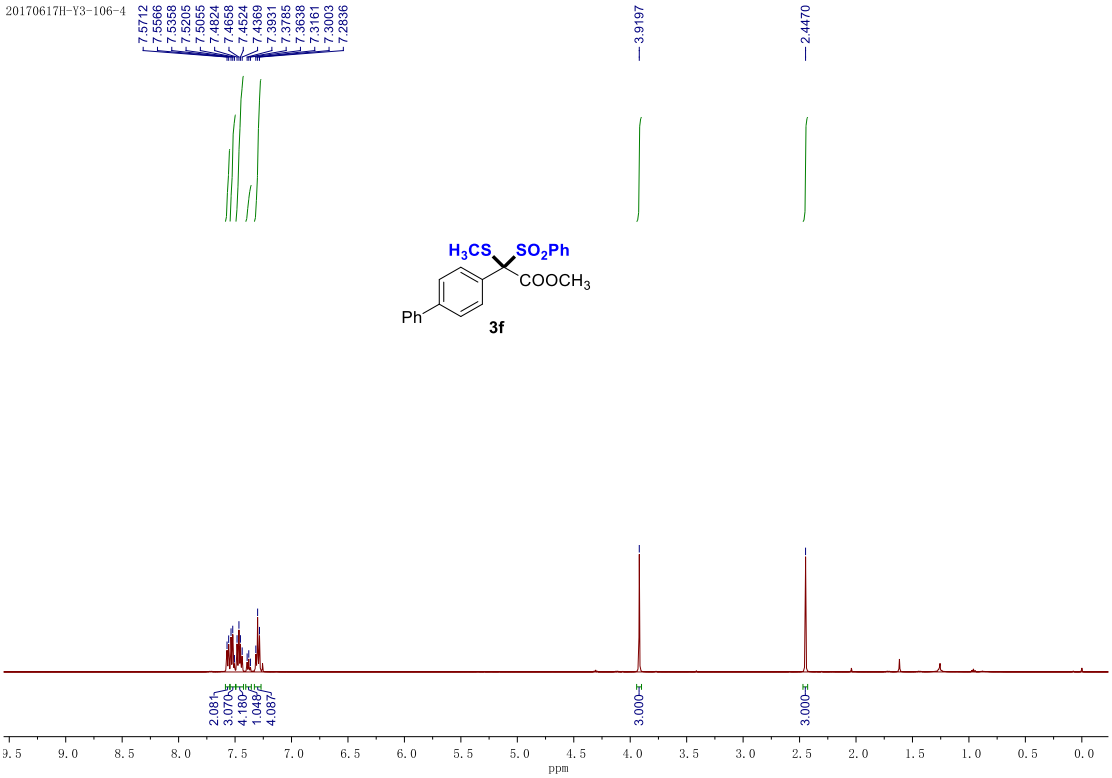

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

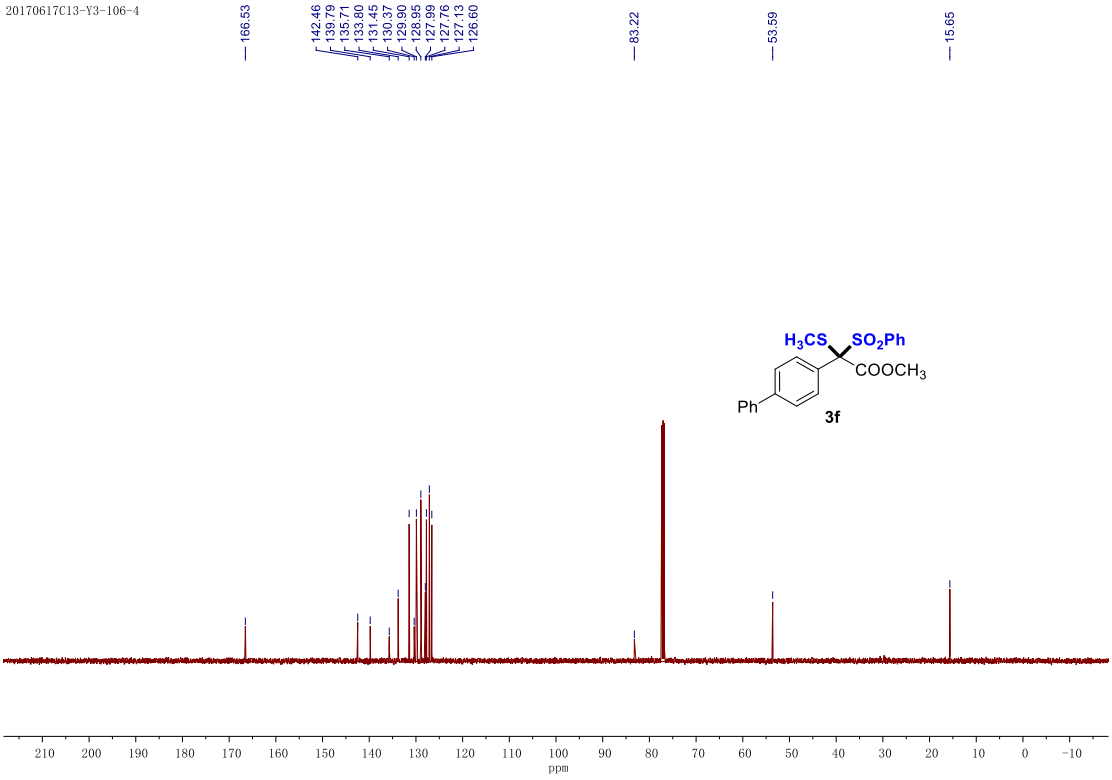


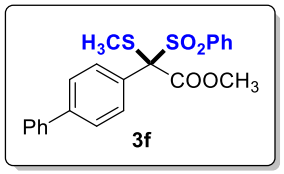
Chemical Formula: $C_{17}H_{18}O_5S_2$
Exact Mass: 366.0596
Molecular Weight: 366.4460
m/z: 366.0596 (100.0%), 367.0629 (18.4%), 368.0554 (9.0%), 369.0587 (1.7%), 367.0590 (1.6%), 368.0663 (1.6%), 368.0638 (1.0%)
Elemental Analysis: C, 55.72; H, 4.95; O, 21.83; S, 17.50



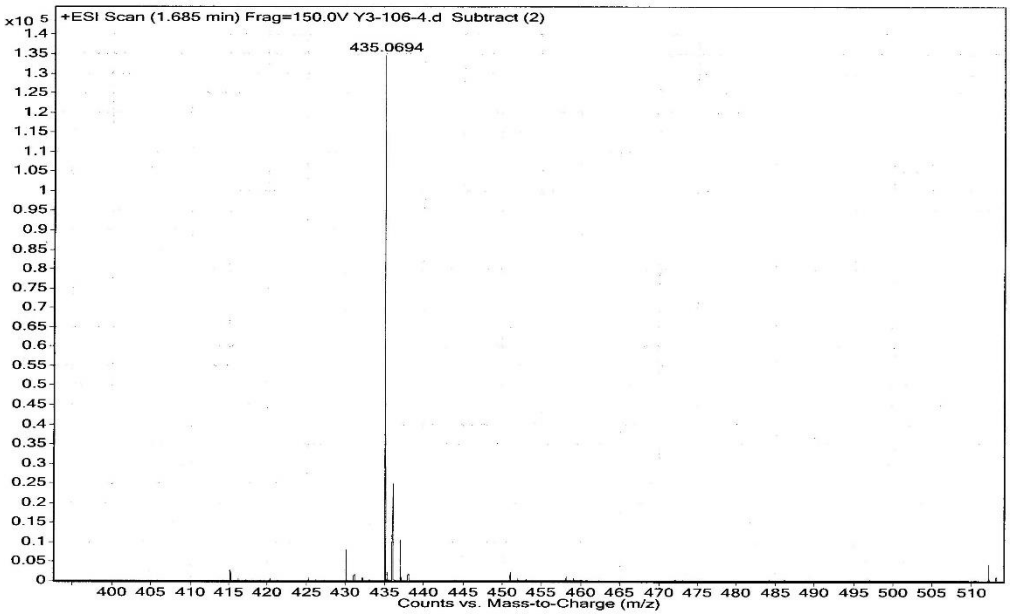
HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_5S_2$ $[M+Na]^+$**389.0488**, found **389.0489**.


20170617H-Y3-106-4
7.5712
7.5566
7.5358
7.5205
7.5055
7.4824
7.4658
7.4524
7.4369
7.3931
7.3785
7.3638
7.3161
7.3003
7.2836
3.9197
2.4470
H3CS
SO2Ph
COOCH3
Ph
3f
2.081
3.070
4.180
1.049
4.087
3.000
3.000
ppm

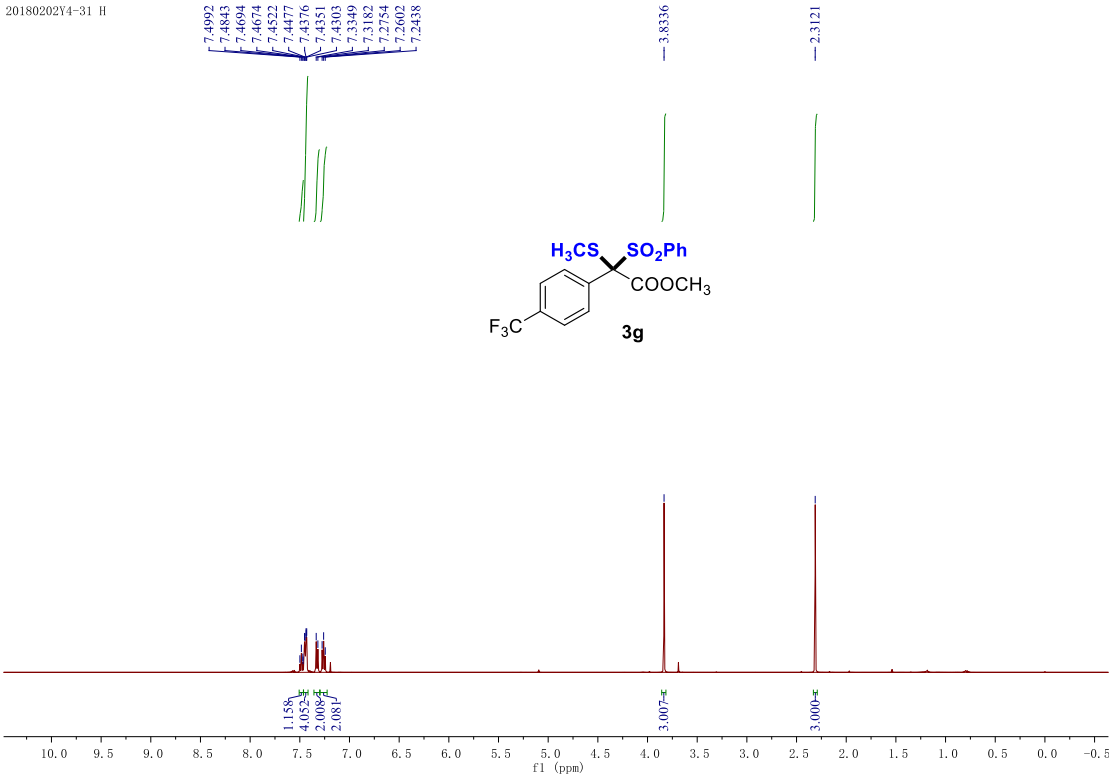

20170617C13-Y3-106-4
166.53
142.46
139.79
135.71
133.80
131.45
130.37
129.90
128.95
127.99
127.76
127.13
126.60
83.22
53.59
15.65
H3CS
SO2Ph
COOCH3
Ph
3f
ppm

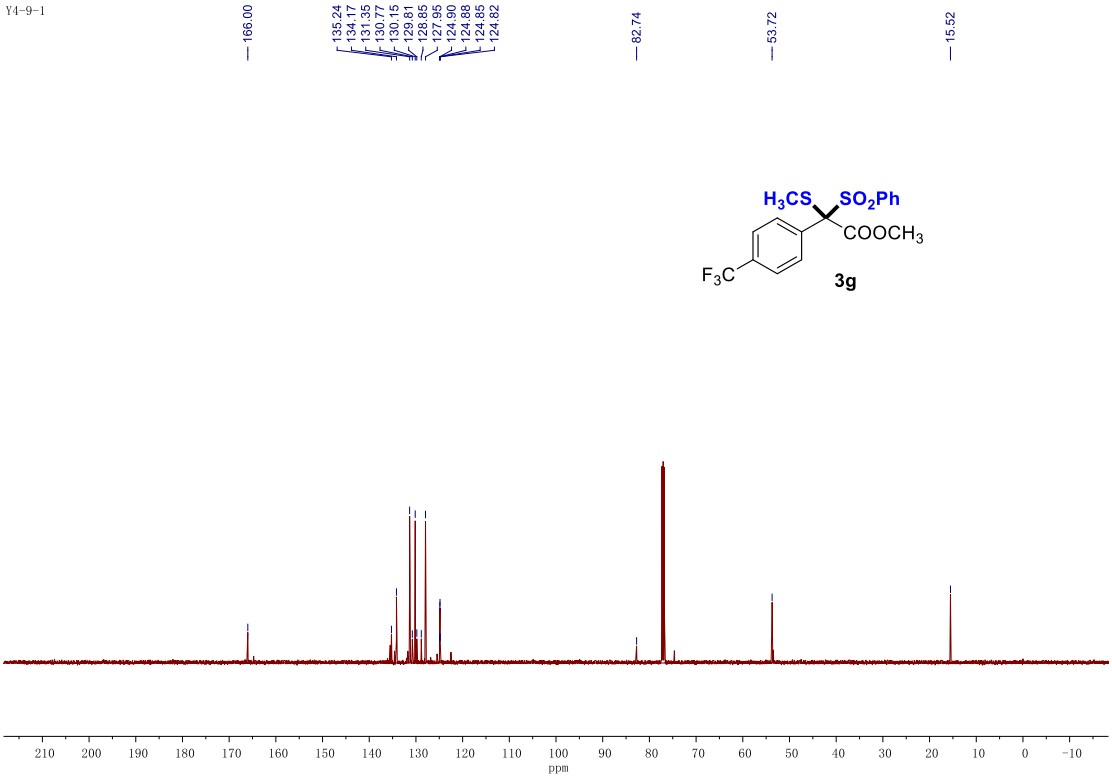


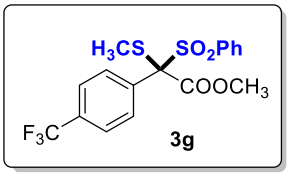
Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54



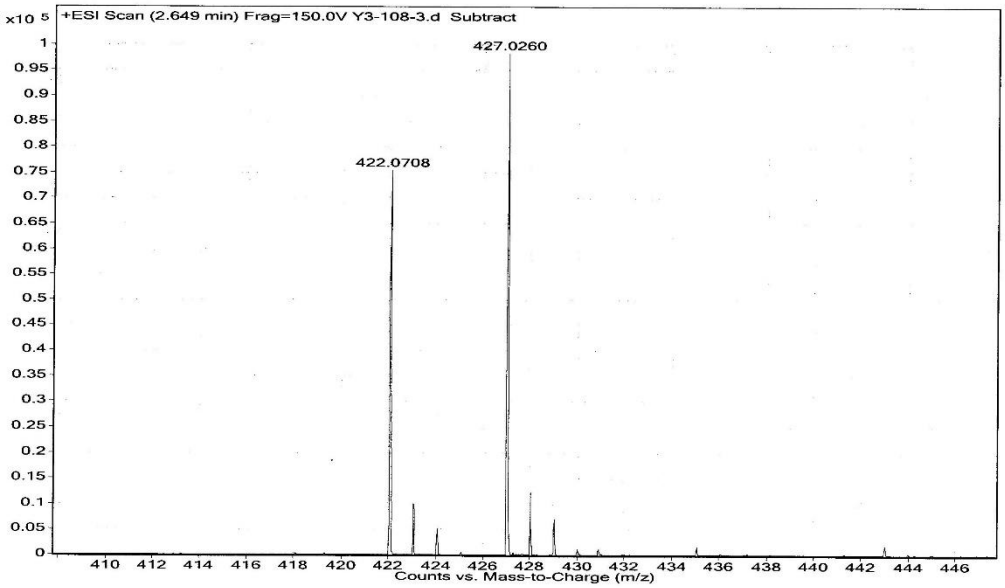
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$ **435.0695**, found **435.0694**.


20180202Y4-31 H
7.4992
7.4843
7.4694
7.4674
7.4522
7.4477
7.4376
7.4351
7.4303
7.3349
7.3182
7.2754
7.2602
7.2438
3.8336
2.3121
H3CS
SO2Ph
COOCH3
F3C
3g
1.158
4.052
2.008
2.081
3.007
3.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Y4-9-1
166.00
135.24
134.17
131.35
130.77
130.15
129.81
128.85
127.95
124.90
124.88
124.85
124.82
82.74
53.72
15.52
H3CS
SO2Ph
COOCH3
F3C
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

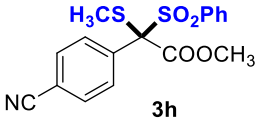


Chemical Formula: $C_{17}H_{15}F_3O_4S_2$
Exact Mass: 404.0364
Molecular Weight: 404.4182
m/z: 404.0364 (100.0%), 405.0397 (18.4%), 406.0322 (9.0%), 407.0355 (1.7%), 405.0358 (1.6%), 406.0431 (1.6%)
Elemental Analysis: C, 50.49; H, 3.74; F, 14.09; O, 15.82; S, 15.85

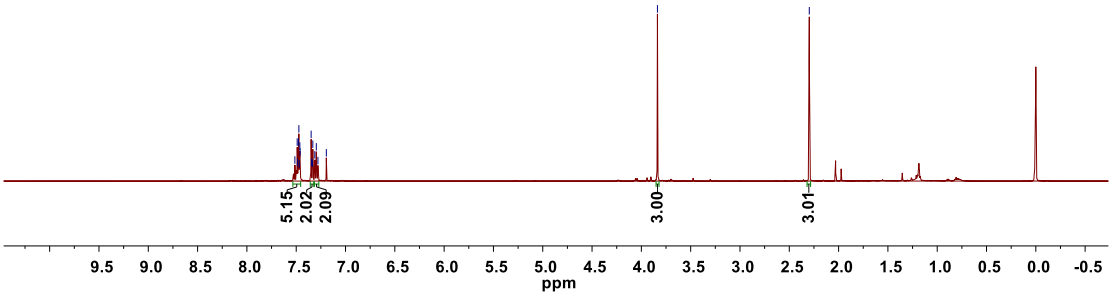


HRMS (ESI, m/z) calcd for $C_{17}H_{15}F_3O_4S_2$ $[M+Na]^+$**427.0256**, found **427.0260**.

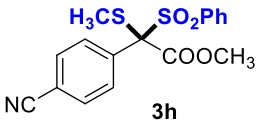
20180204-Y4-31-3 H



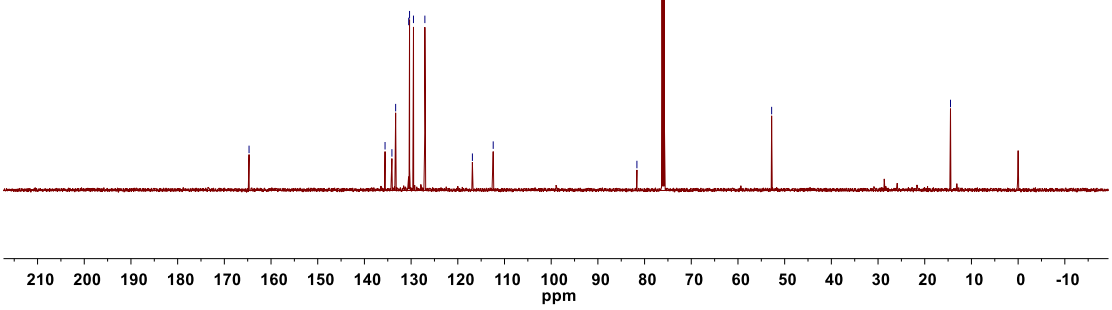
3h

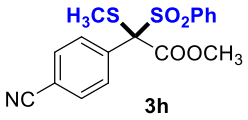


20180204-Y4-31-3 C13



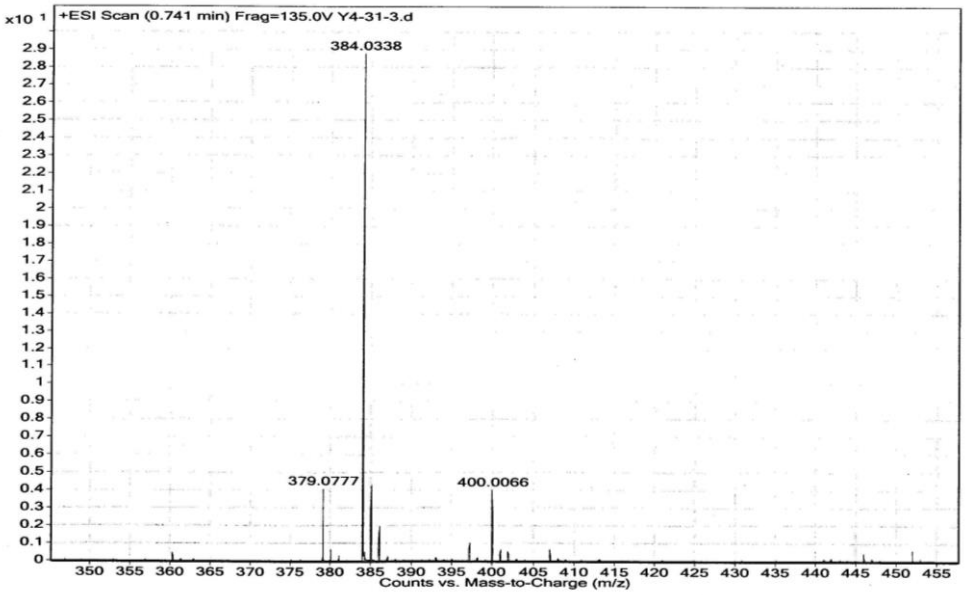
3h



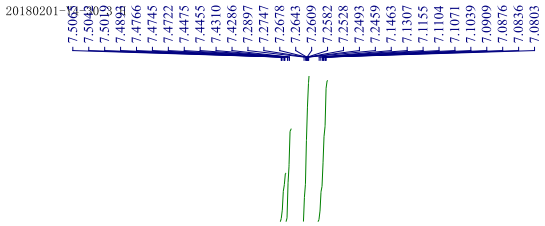


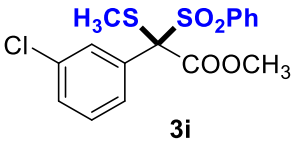
3h

Chemical Formula: $C_{17}H_{15}NO_4S_2$
Exact Mass: 361.0442
Molecular Weight: 361.4300
m/z: 361.0442 (100.0%), 362.0476 (18.4%), 363.0400 (9.0%), 364.0434 (1.7%), 362.0436 (1.6%), 363.0510 (1.6%)
Elemental Analysis: C, 56.49; H, 4.18; N, 3.88; O, 17.71; S, 17.74

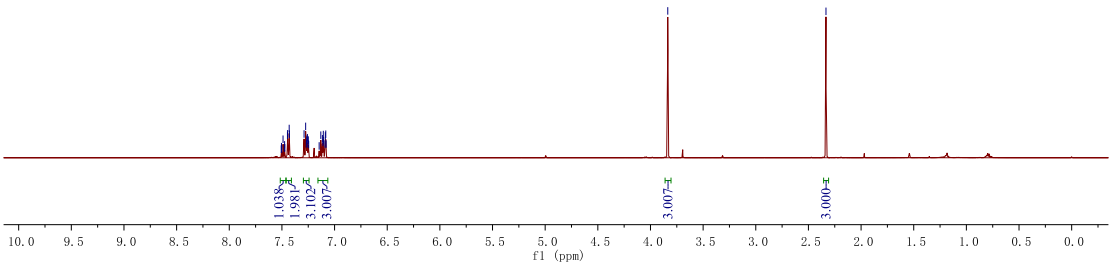


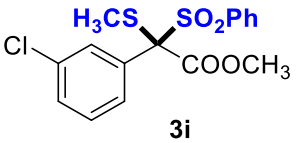
HRMS (ESI, m/z) calcd for $C_{17}H_{15}NO_4S_2$ $[M+Na]^+$ **384.0335**, found **384.0338**.



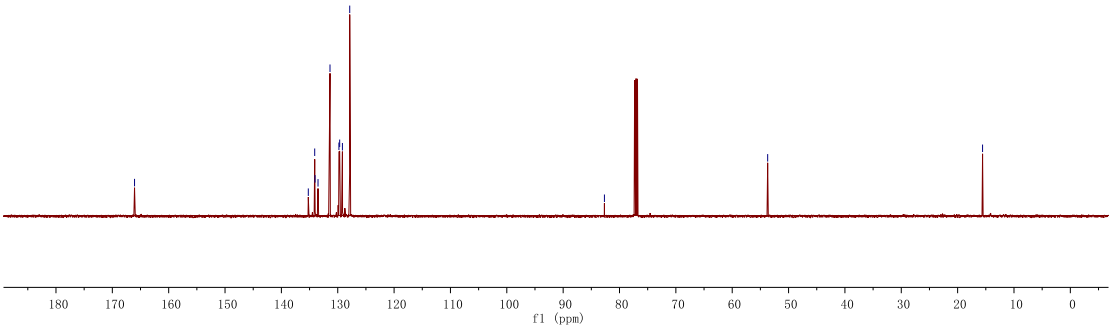

H3CS
SO2Ph
Cl
COOCH3

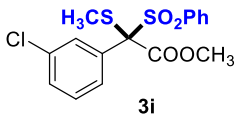
3i


1.038
1.981
3.102
3.007
3.007
3.000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3CS
SO2Ph
Cl
COOCH3

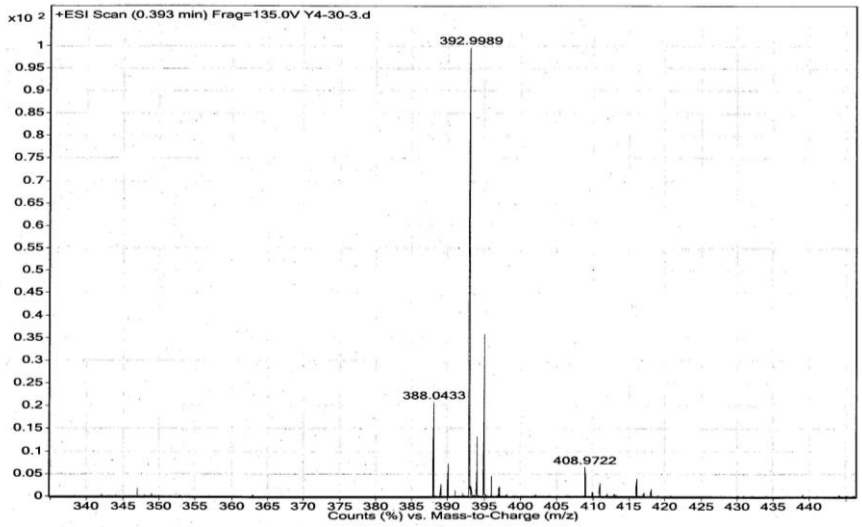
3i


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

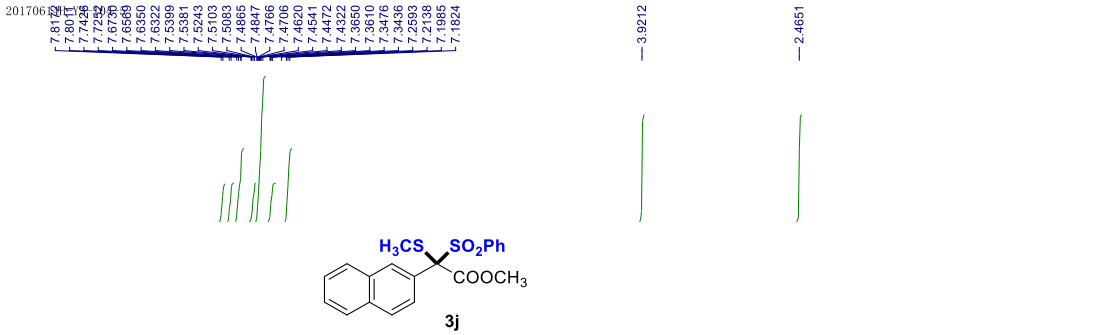


3i

Chemical Formula: $C_{16}H_{15}ClO_4S_2$
Exact Mass: 370.0100
Molecular Weight: 370.8620
m/z: 370.0100 (100.0%), 372.0071 (32.0%), 371.0134 (17.3%), 372.0058 (9.0%), 373.0104 (5.5%), 374.0029 (2.9%), 371.0094 (1.6%), 373.0092 (1.6%), 372.0167 (1.4%)
Elemental Analysis: C, 51.82; H, 4.08; Cl, 9.56; O, 17.26; S, 17.29

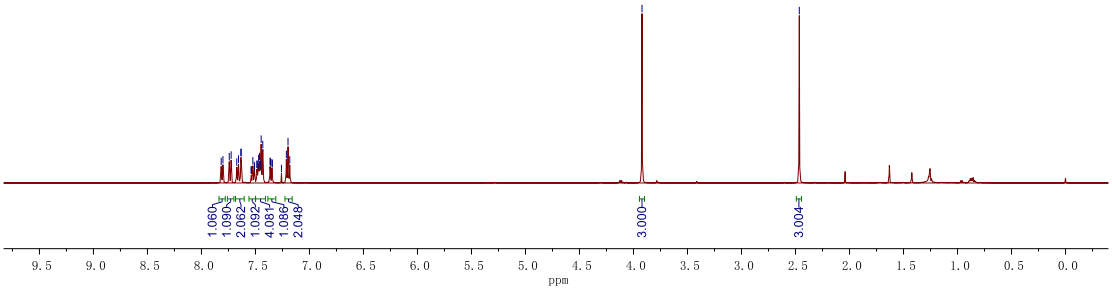


HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2$ $[M+Na]^+$**392.9992**, found **392.9989**.

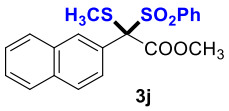

7.8172
7.8011
7.7428
7.7292
7.6736
7.6569
7.6350
7.6322
7.5399
7.5381
7.5243
7.5103
7.5083
7.4865
7.4847
7.4766
7.4706
7.4620
7.4541
7.4472
7.4322
7.3650
7.3610
7.3476
7.3436
7.2593
7.2138
7.1985
7.1824
3.9212
2.4651

H3CS
SO2Ph
COOCH3

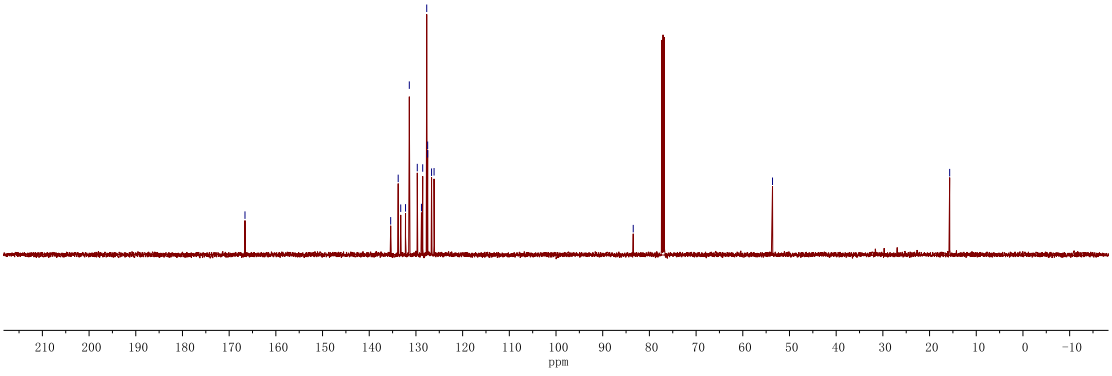
3j

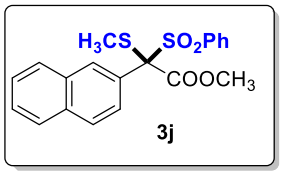

1.060
1.090
2.062
1.092
4.081
1.086
2.048
3.000
3.004
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


20170614C13-Y3-104-5
166.61
135.41
133.80
133.26
132.23
131.42
129.71
128.82
128.55
127.69
127.50
127.49
126.65
126.12
83.46
53.63
15.69


H3CS
SO2Ph
COOCH3

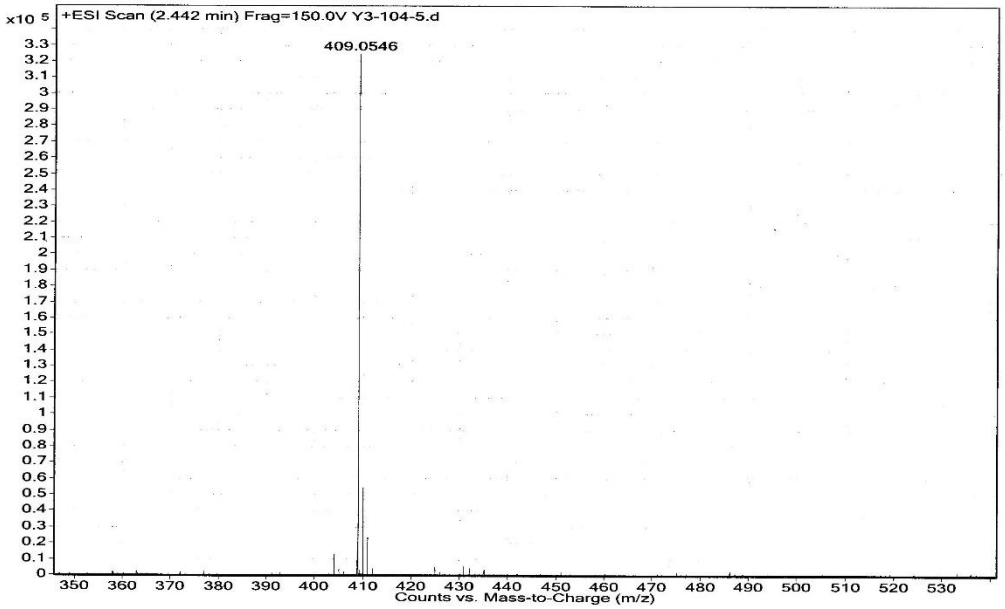
3j


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

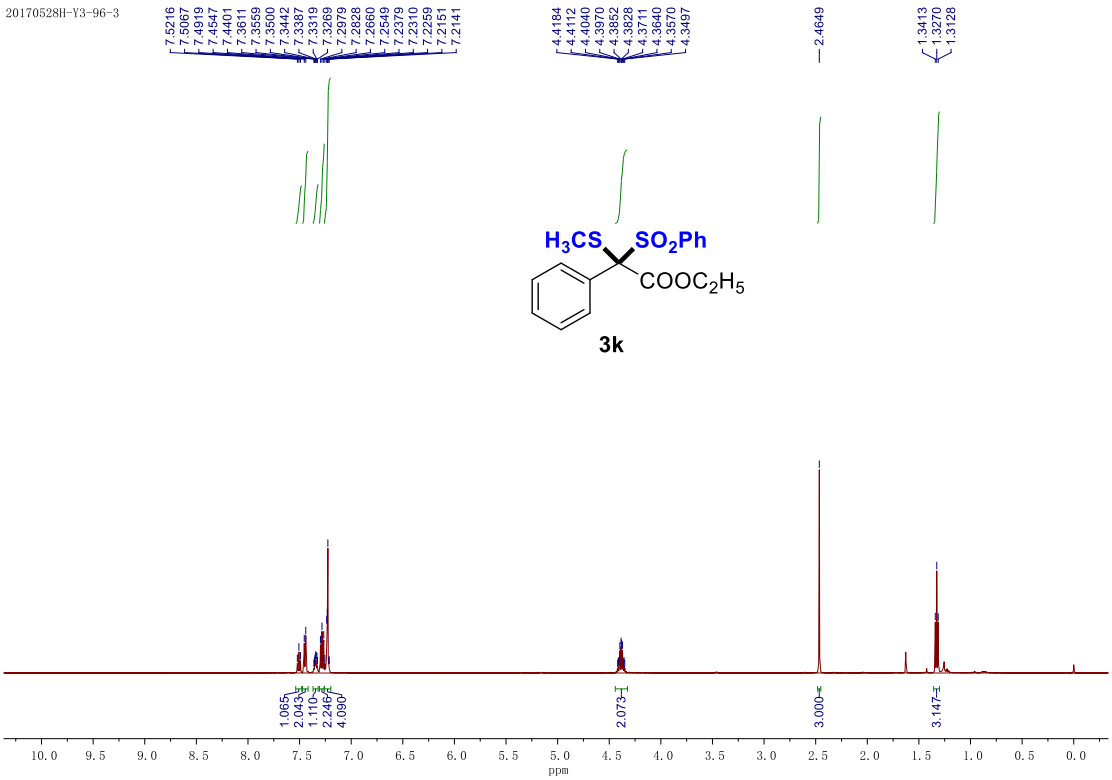


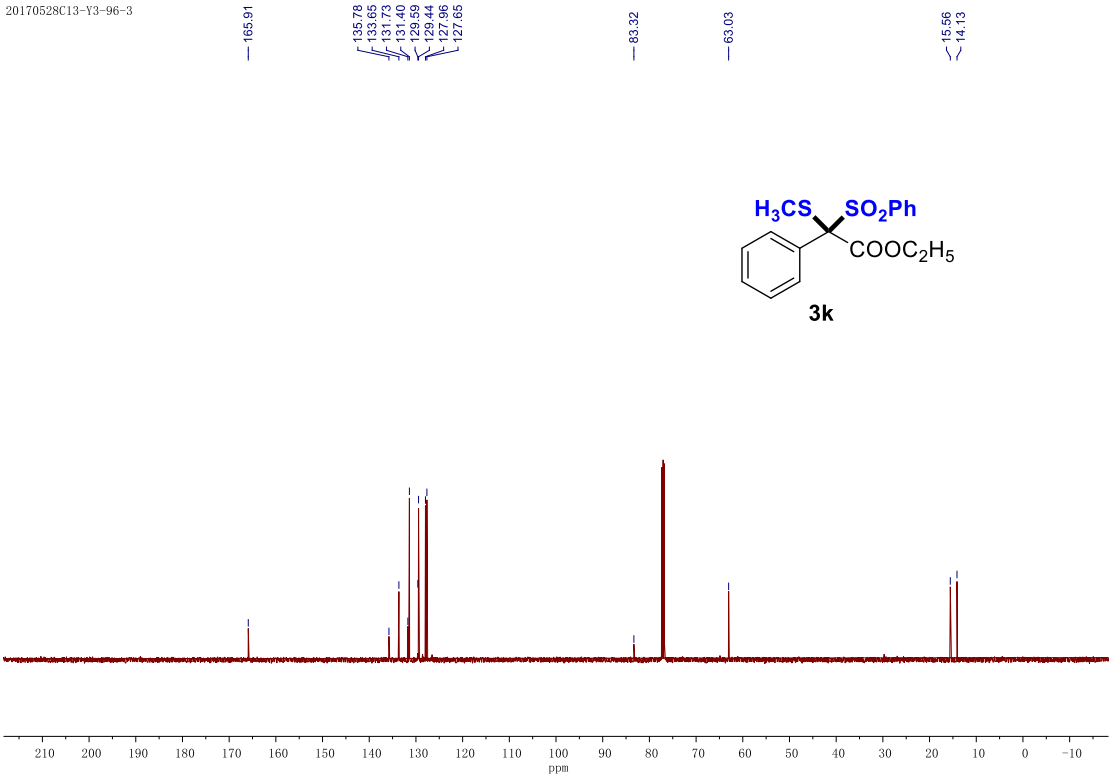
3j

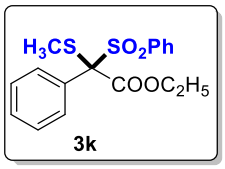
Chemical Formula: $C_{20}H_{18}O_4S_2$
Exact Mass: 386.0647
Molecular Weight: 386.4800
m/z: 386.0647 (100.0%), 387.0680 (21.6%), 388.0604 (9.0%), 388.0714 (2.2%), 389.0638 (2.0%), 387.0640 (1.6%)
Elemental Analysis: C, 62.16; H, 4.69; O, 16.56; S, 16.59



HRMS (ESI, m/z) calcd for $C_{20}H_{18}O_4S_2$ $[M+Na]^+$**409.0539**, found **409.0546**.

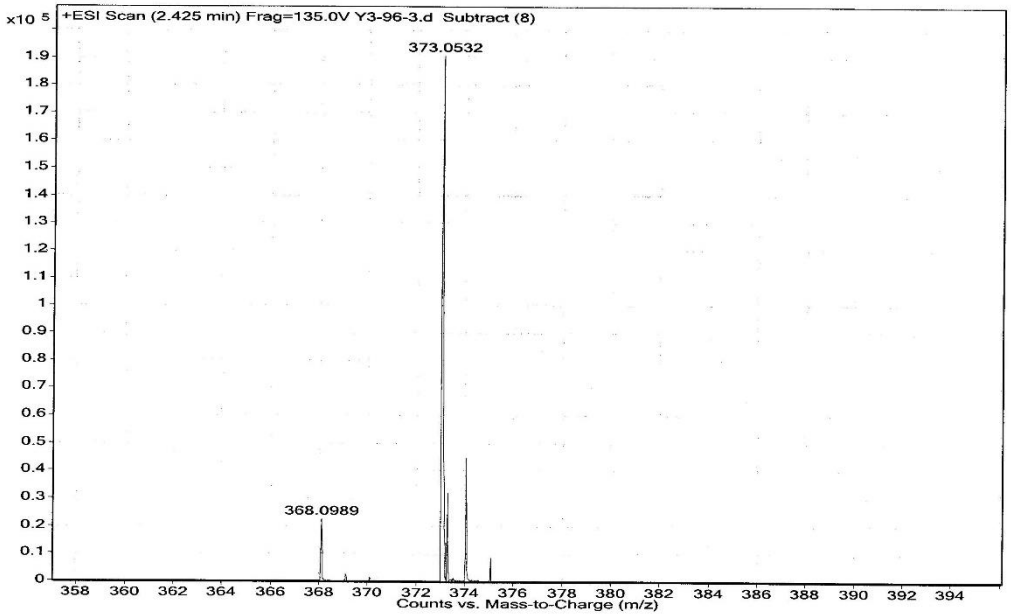

20170528H-Y3-96-3
7.5216
7.5067
7.4919
7.4547
7.4401
7.3611
7.3559
7.3500
7.3442
7.3387
7.3319
7.3269
7.2979
7.2828
7.2660
7.2549
7.2379
7.2310
7.2259
7.2151
7.2141
4.4184
4.4112
4.4040
4.3970
4.3852
4.3828
4.3711
4.3640
4.3570
4.3497
2.4649
1.3413
1.3270
1.3128
H3CS
SO2Ph
COOC2H5
3k
1.065
2.043
1.110
2.246
4.090
2.073
3.000
3.147
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


20170528C13-Y3-96-3
165.91
135.78
133.65
131.73
131.40
129.59
129.44
127.96
127.65
83.32
63.03
15.56
14.13
H3CS
SO2Ph
COOC2H5
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

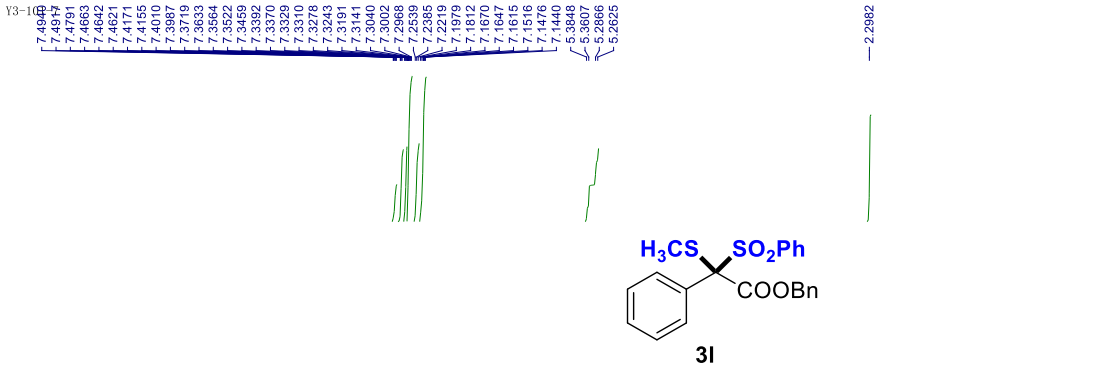


3k

Chemical Formula: $C_{17}H_{18}O_4S_2$
Exact Mass: 350.0647
Molecular Weight: 350.4470
m/z: 350.0647 (100.0%), 351.0680 (18.4%), 352.0604 (9.0%), 353.0638 (1.7%), 351.0640 (1.6%), 352.0714 (1.6%)
Elemental Analysis: C, 58.26; H, 5.18; O, 18.26; S, 18.30

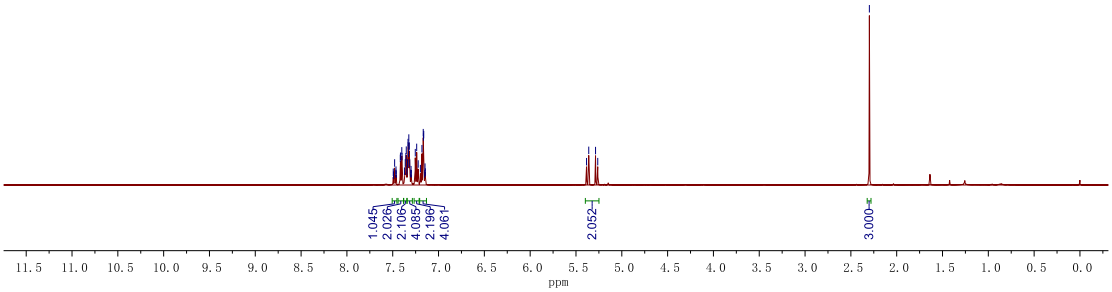


HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_4S_2$ $[M+Na]^+$**373.0539**, found **373.0532**.

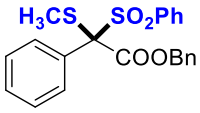

Y3-101
7.4994
7.4947
7.4791
7.4663
7.4642
7.4621
7.4171
7.4155
7.4010
7.3987
7.3719
7.3633
7.3564
7.3522
7.3459
7.3392
7.3370
7.3329
7.3310
7.3278
7.3243
7.3191
7.3141
7.3040
7.3002
7.2968
7.2539
7.2385
7.2219
7.1979
7.1812
7.1670
7.1647
7.1615
7.1516
7.1476
7.1440
5.3848
5.3607
5.2866
5.2625
2.2982

H3CS
SO2Ph
COOBn

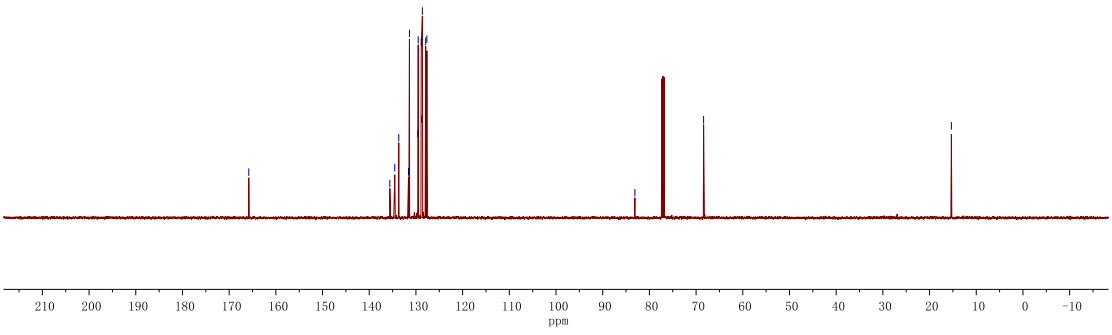
3l

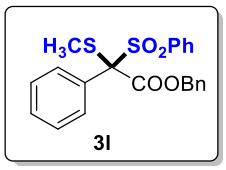

1.045
2.026
2.105
4.085
2.196
4.061
2.052
3.000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


Y3-101-7
165.80
135.59
134.53
133.68
131.59
131.39
129.60
129.51
128.87
128.76
128.62
127.91
127.66
83.11
68.39
15.32


H3CS
SO2Ph
COOBn

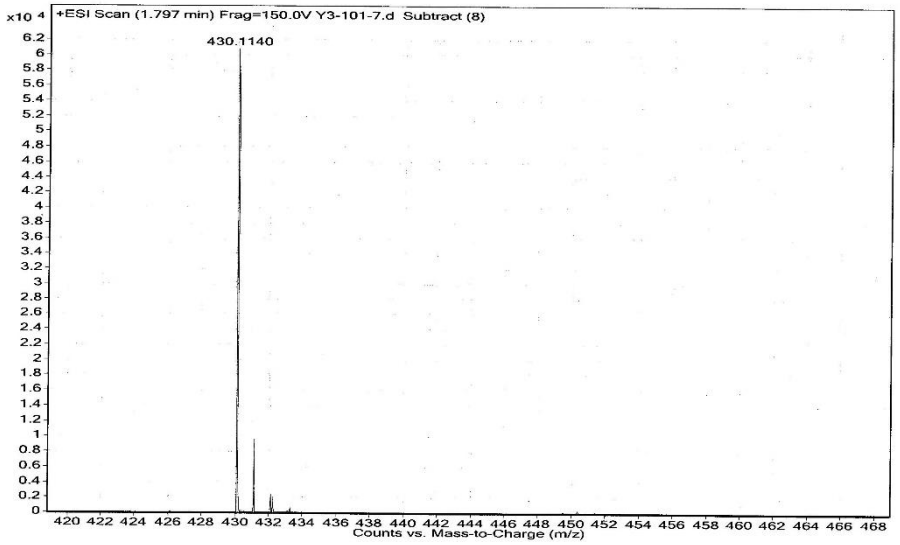
3l


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

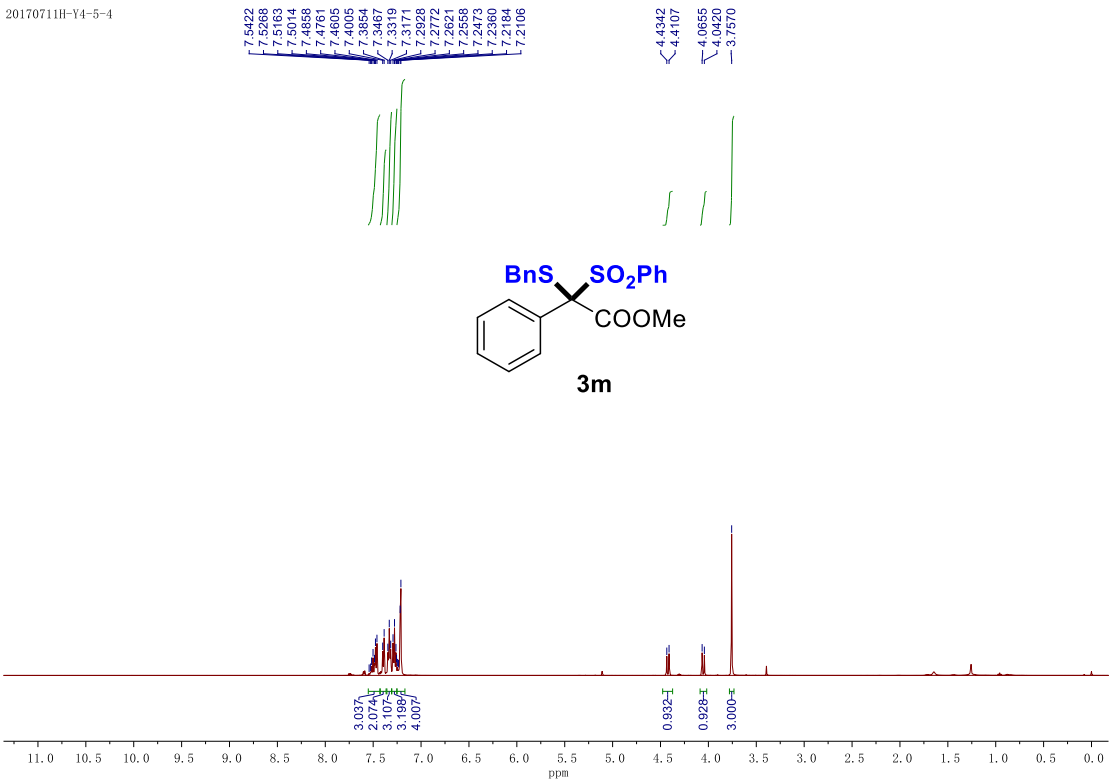


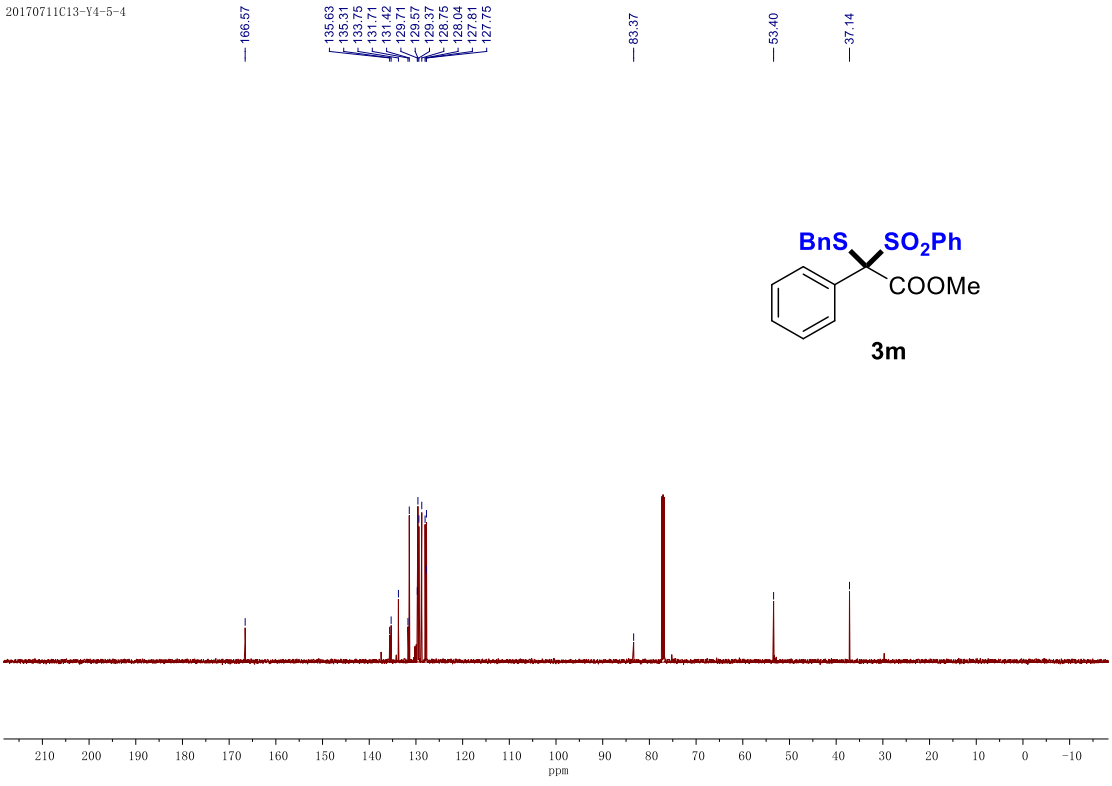
3l

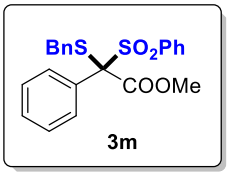
Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54



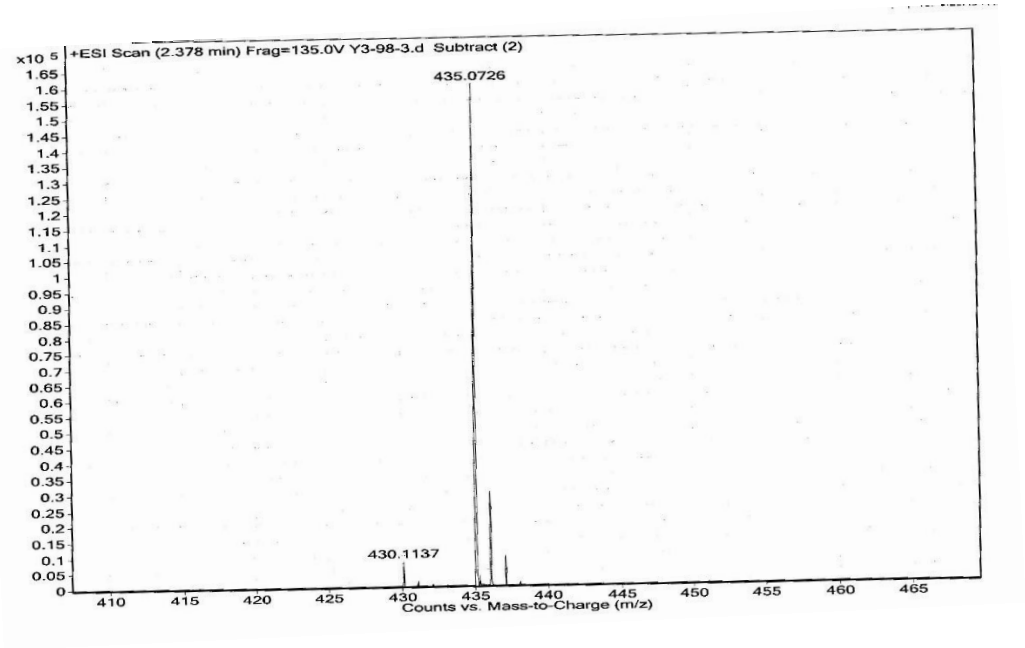
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$**430.1141**, found **430.1140**.


20170711H-Y4-5-4
7.5422
7.5268
7.5163
7.5014
7.4858
7.4761
7.4605
7.4005
7.3854
7.3467
7.3319
7.3171
7.2928
7.2772
7.2621
7.2558
7.2473
7.2360
7.2184
7.2106
4.4342
4.4107
4.0655
4.0420
3.7570
BnS
SO2Ph
COOMe
3m
3.037
2.074
3.107
3.198
4.007
0.932
0.928
3.000
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

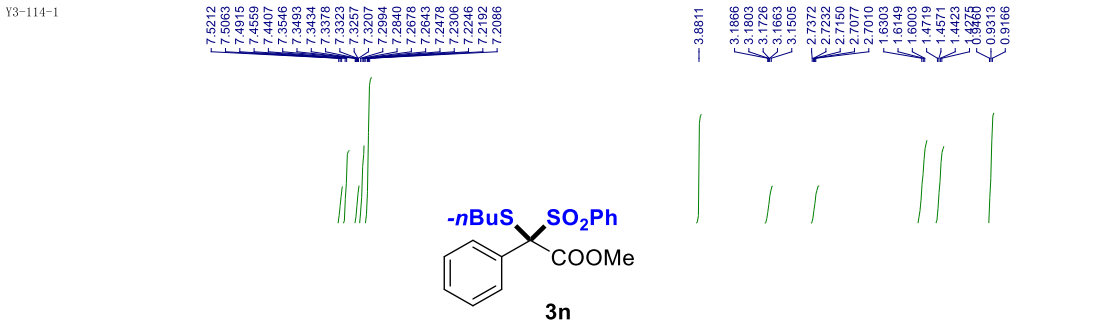

20170711C13-Y4-5-4
166.57
135.63
135.31
133.75
131.71
131.42
129.71
129.57
129.37
128.75
128.04
127.81
127.75
83.37
53.40
37.14
BnS
SO2Ph
COOMe
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

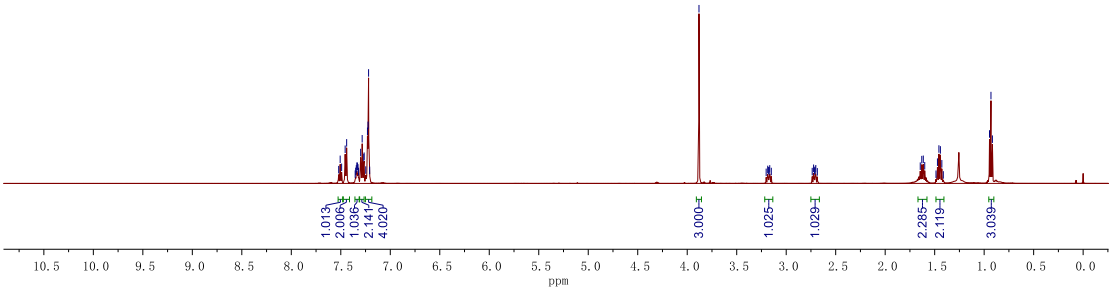


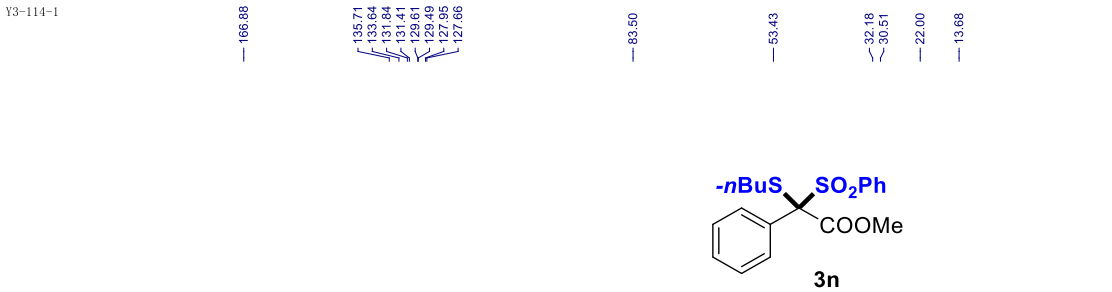
Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54

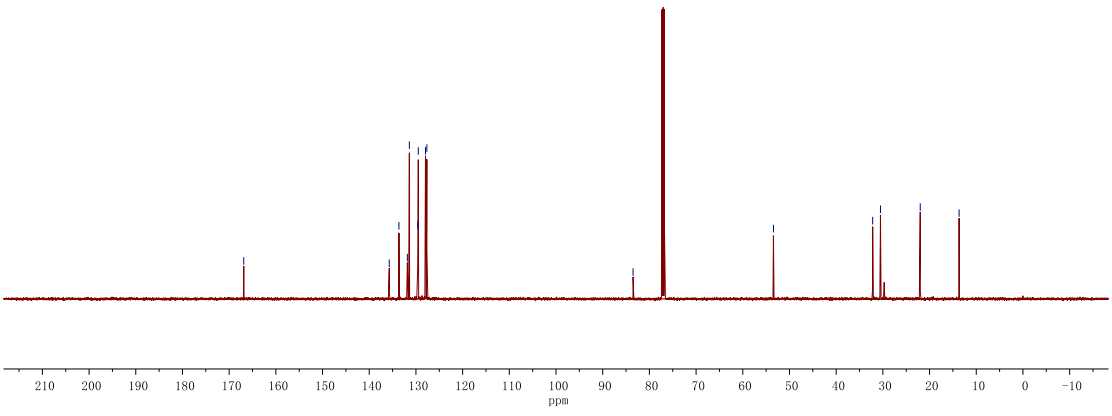


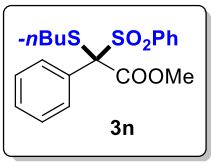
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$**430.1141**, found **430.1137**.


Y3-114-1
7.5212
7.5063
7.4915
7.4559
7.4407
7.3546
7.3493
7.3434
7.3378
7.3323
7.3257
7.3207
7.2994
7.2840
7.2678
7.2643
7.2478
7.2306
7.2246
7.2192
7.2086
3.8811
3.1866
3.1803
3.1726
3.1663
3.1505
2.7372
2.7232
2.7150
2.7077
2.7010
1.6303
1.6149
1.6003
1.4719
1.4571
1.4423
0.9313
0.9166
-nBuS
SO2Ph
COOMe
3n

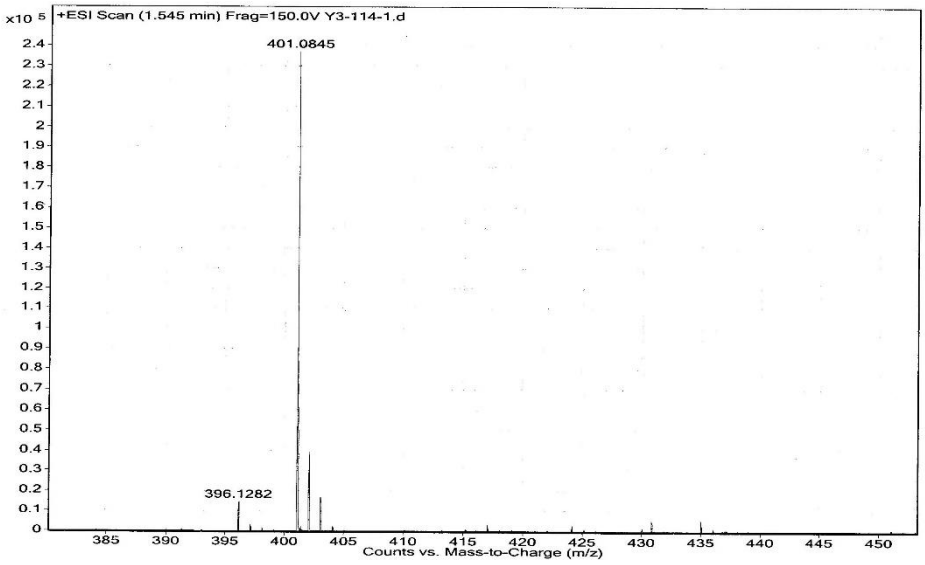

1.013
2.006
1.036
2.141
4.020
3.000
1.025
1.029
2.285
2.119
3.039
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


Y3-114-1
166.88
135.71
133.64
131.84
131.41
129.61
129.49
127.95
127.66
83.50
53.43
32.18
30.51
22.00
13.68
-nBuS
SO2Ph
COOMe
3n

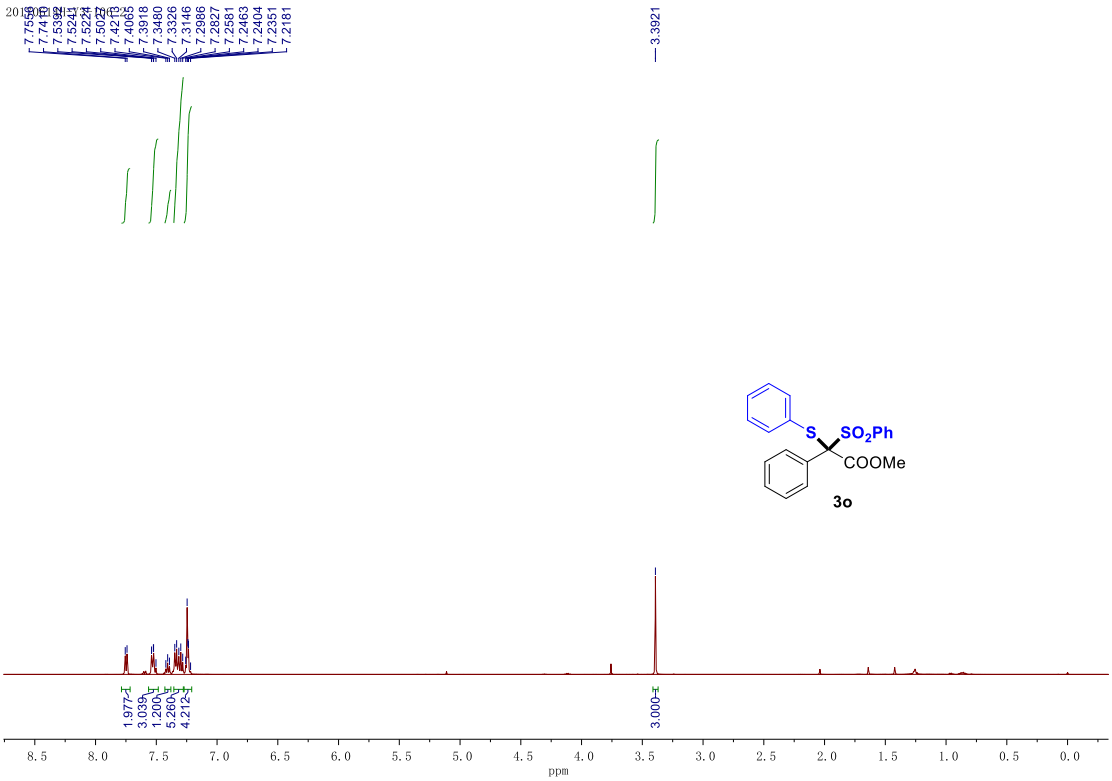

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



Chemical Formula: $C_{19}H_{22}O_4S_2$
Exact Mass: 378.0960
Molecular Weight: 378.5010
m/z: 378.0960 (100.0%), 379.0993 (20.5%), 380.0917 (9.0%), 380.1027 (2.0%), 381.0951 (1.9%), 379.0953 (1.6%)
Elemental Analysis: C, 60.29; H, 5.86; O, 16.91; S, 16.94

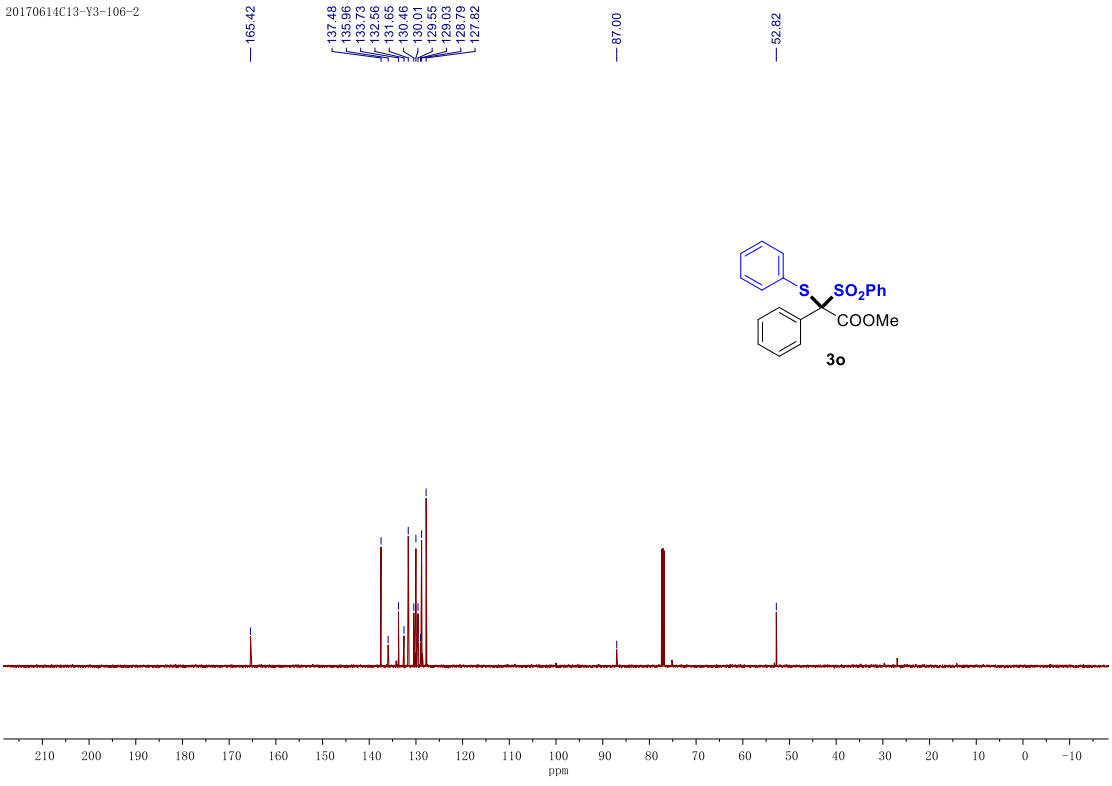


HRMS (ESI, m/z) calcd for $C_{19}H_{22}O_4S_2$ $[M+Na]^+$**401.0852**, found **401.0845**.


7.7550
7.7415
7.5392
7.5241
7.5224
7.5022
7.4213
7.4065
7.3918
7.3480
7.3326
7.3146
7.2986
7.2827
7.2581
7.2463
7.2404
7.2351
7.2181
3.3921
1.977
3.039
1.200
5.260
4.212
3.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

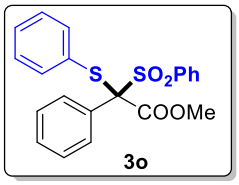
S
SO2Ph
COOMe

3o


20170614C13-Y3-106-2
165.42
137.48
135.96
133.73
132.56
131.65
130.46
130.01
129.55
129.03
128.79
127.82
87.00
52.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

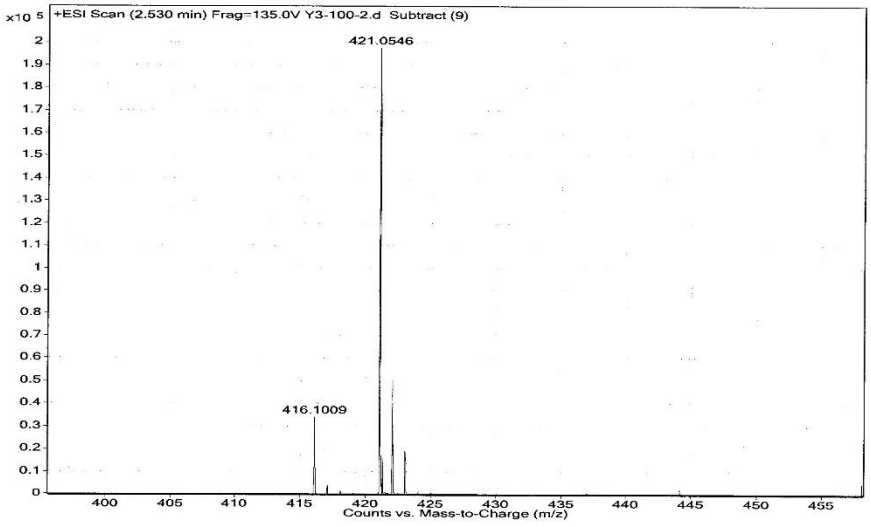
S
SO2Ph
COOMe

3o

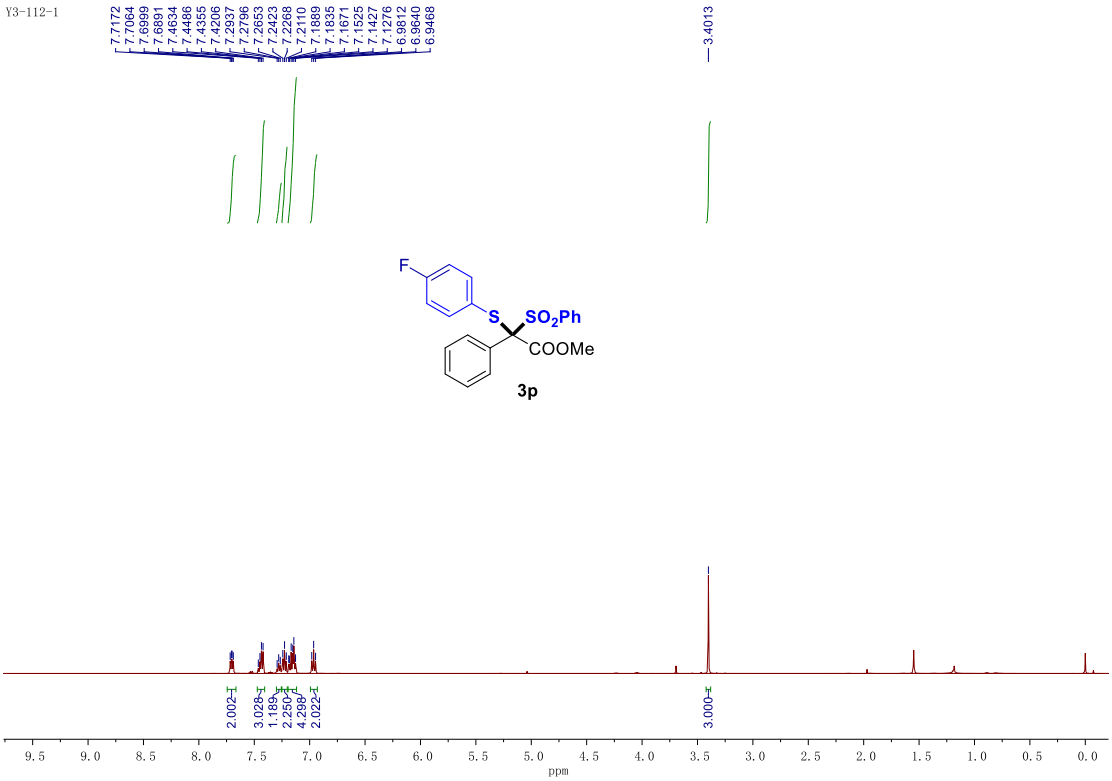


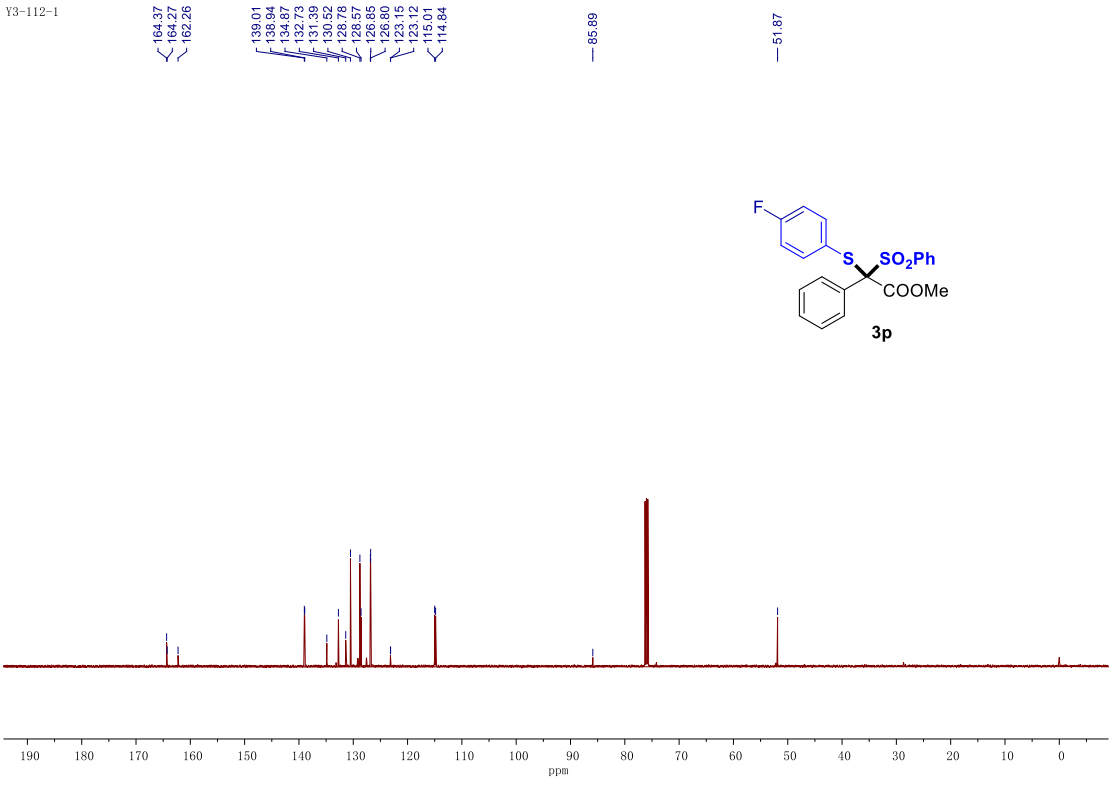
3o

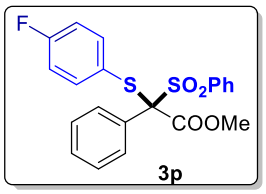
Chemical Formula: $C_{21}H_{18}O_4S_2$
Exact Mass: 398.0647
Molecular Weight: 398.4910
m/z: 398.0647 (100.0%), 399.0680 (22.7%), 400.0604 (9.0%), 400.0714 (2.5%), 401.0638 (2.1%), 399.0640 (1.6%)
Elemental Analysis: C, 63.30; H, 4.55; O, 16.06; S, 16.09



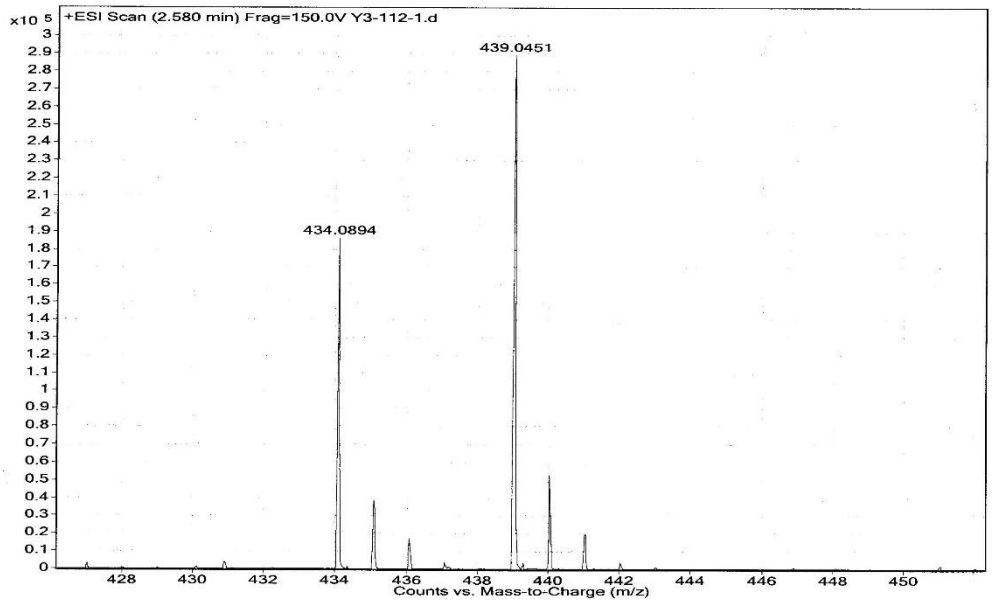
HRMS (ESI, m/z) calcd for $C_{21}H_{18}O_4S_2$ $[M+Na]^+$**421.0539**, found **421.0546**.


Y3-112-1
7.7172
7.7064
7.6999
7.6891
7.4634
7.4486
7.4355
7.4206
7.2937
7.2796
7.2653
7.2423
7.2268
7.2110
7.1889
7.1835
7.1671
7.1525
7.1427
7.1276
6.9812
6.9640
6.9468
3.4013
F
S
SO2Ph
COOMe
3p
2.002
3.028
1.189
2.250
4.298
2.022
3.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

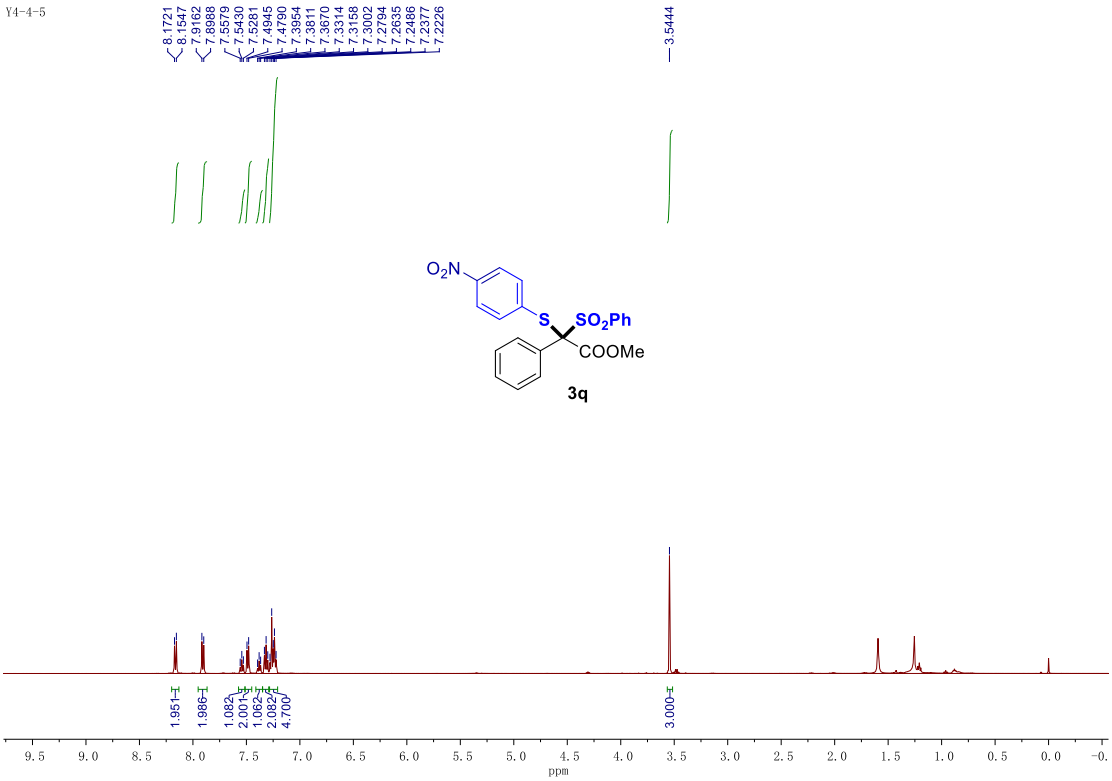

Y3-112-1
164.37
164.27
162.26
139.01
138.94
134.87
132.73
131.39
130.52
128.78
128.57
126.85
126.80
123.15
123.12
115.01
114.84
85.89
51.87
F
S
SO2Ph
COOMe
3p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

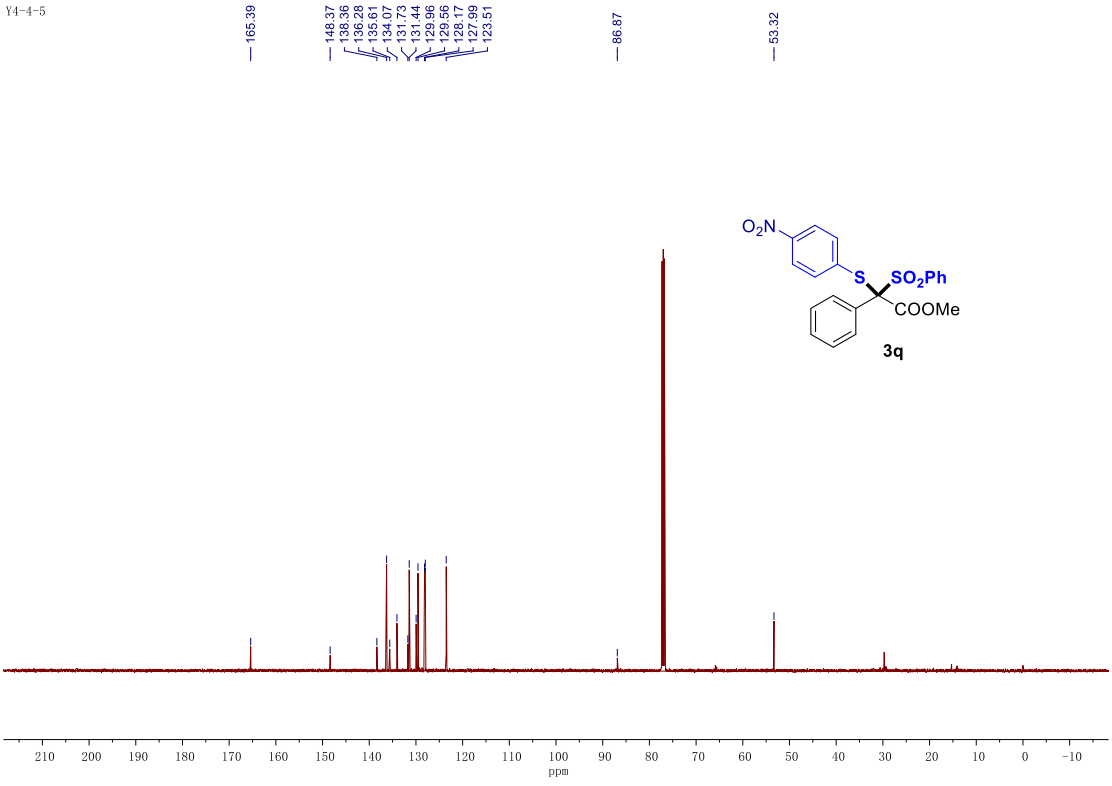


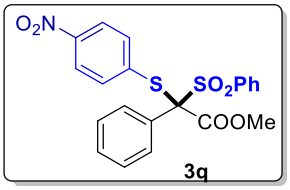
Chemical Formula: $C_{21}H_{17}FO_4S_2$
Exact Mass: 416.0552
Molecular Weight: 416.4814
m/z: 416.0552 (100.0%), 417.0586 (22.7%), 418.0510 (9.0%), 418.0619 (2.5%), 419.0544 (2.1%), 417.0546 (1.6%)
Elemental Analysis: C, 60.56; H, 4.11; F, 4.56; O, 15.37; S, 15.40



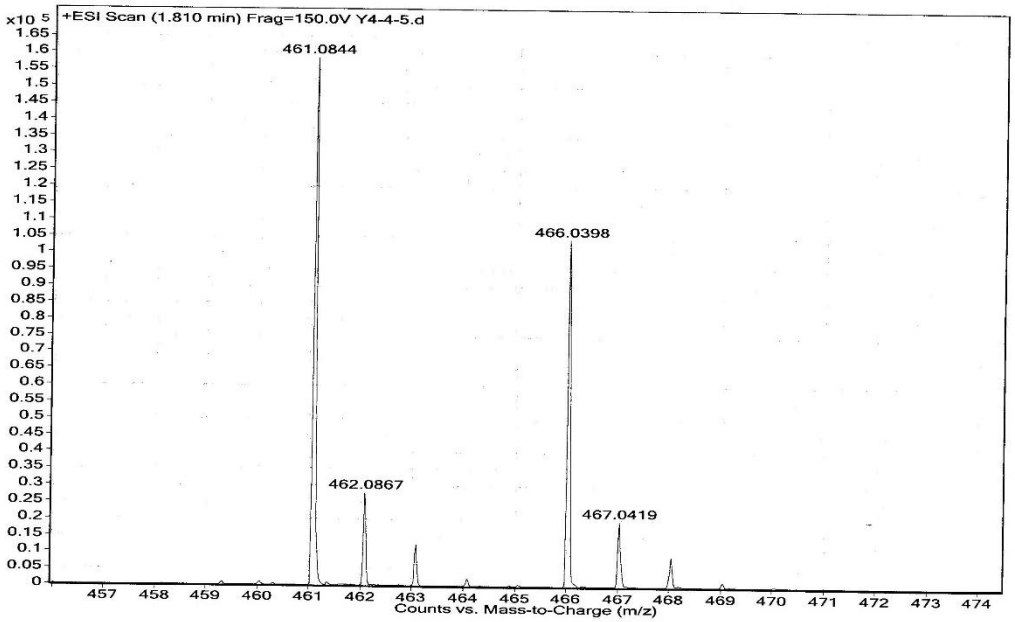
HRMS (ESI, m/z) calcd for $C_{21}H_{17}FO_4S_2$ $[M+Na]^+$**439.0444**, found **439.0451**.


Y4-4-5
8.1721
8.1547
7.9162
7.8988
7.5579
7.5430
7.5261
7.4945
7.4790
7.3954
7.3811
7.3670
7.3314
7.3158
7.3002
7.2794
7.2635
7.2486
7.2377
7.2226
3.5444
O2N
S
SO2Ph
COOMe
3q
1.951
1.986
1.082
2.001
1.062
2.082
4.700
3.000
ppm

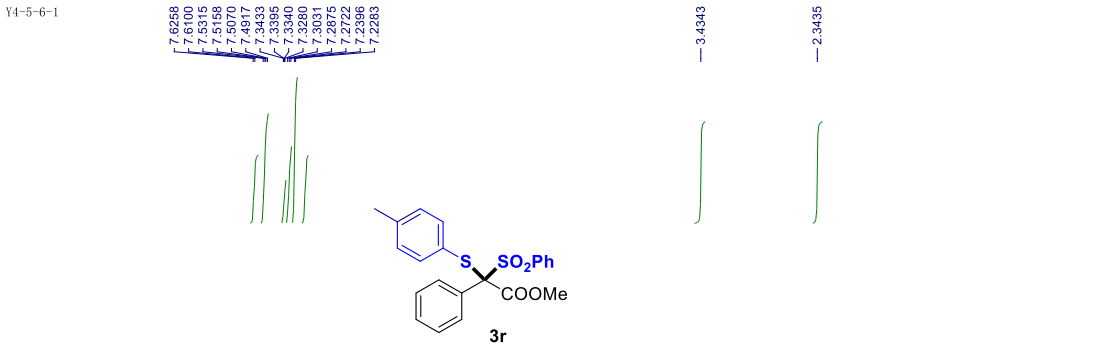

Y4-4-5
165.39
148.37
138.36
136.28
135.61
134.07
131.73
131.44
129.96
129.56
128.17
127.99
123.51
86.87
53.32
O2N
S
SO2Ph
COOMe
3q
ppm

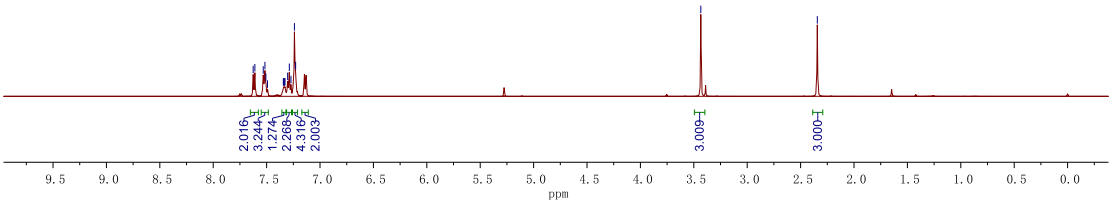


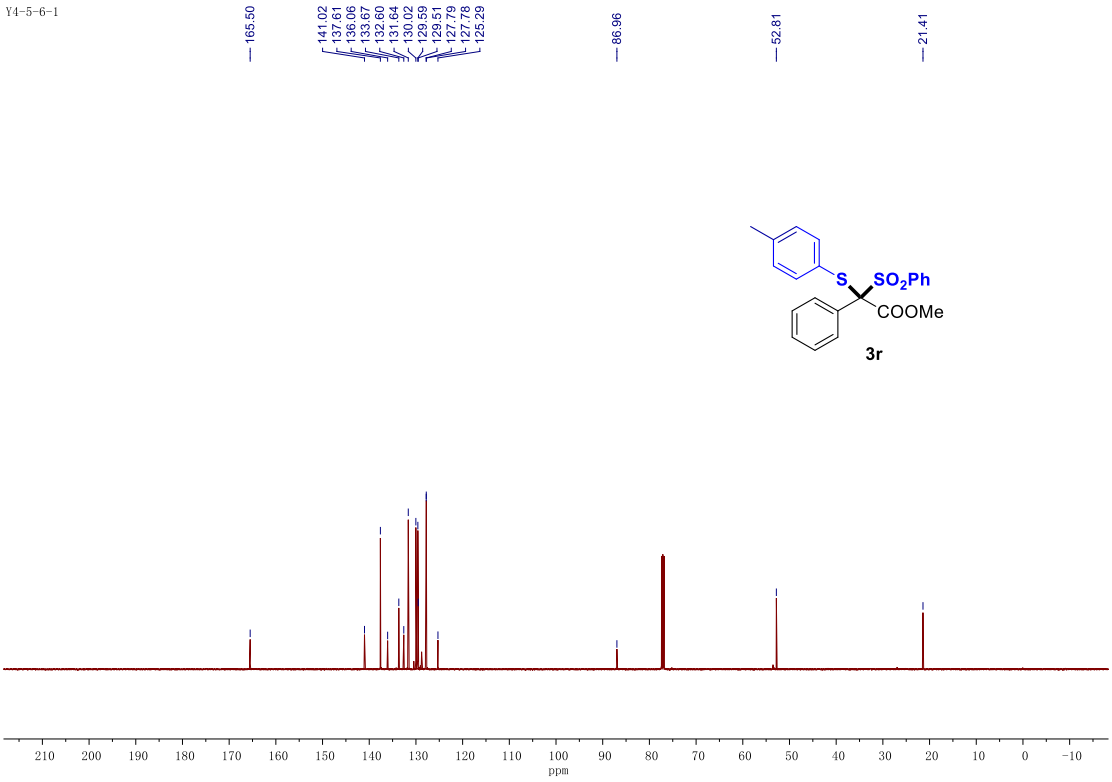
Chemical Formula: $C_{21}H_{17}NO_6S_2$
Exact Mass: 443.0497
Molecular Weight: 443.4880
m/z: 443.0497 (100.0%), 444.0531 (22.7%), 445.0455 (9.0%), 445.0564 (2.5%), 446.0489 (2.1%), 444.0491 (1.6%), 445.0540 (1.2%)
Elemental Analysis: C, 56.87; H, 3.86; N, 3.16; O, 21.65; S, 14.46

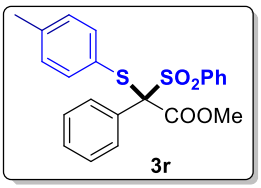


HRMS (ESI, m/z) calcd for $C_{21}H_{17}NO_6S_2$ $[M+Na]^+$**466.0389**, found **466.0398**.

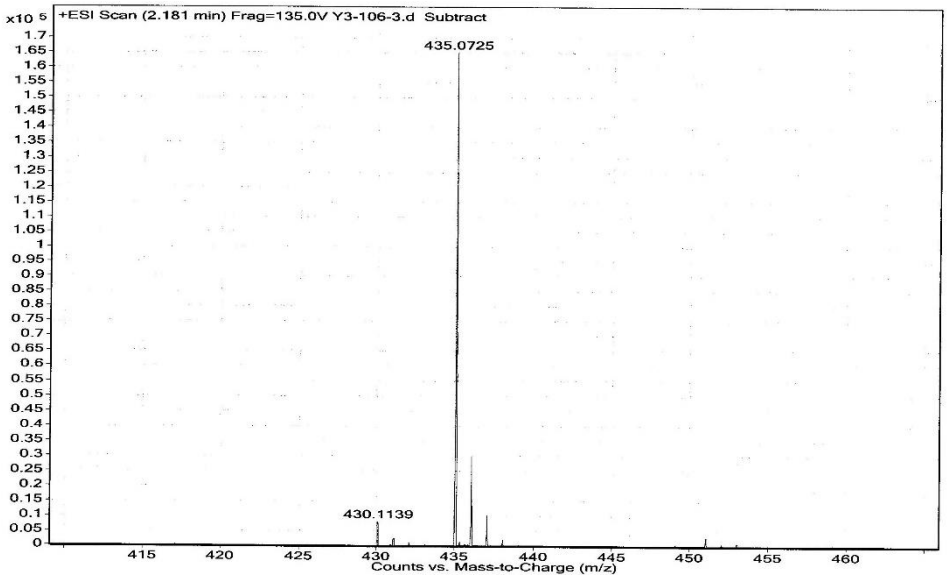

Y4-5-6-1
7.6258
7.6100
7.5315
7.5158
7.5070
7.4917
7.3433
7.3395
7.3340
7.3280
7.3031
7.2875
7.2722
7.2396
7.2283
3.4343
2.3435
S
SO2Ph
COOMe
3r


2.016
3.244
1.274
2.268
4.316
2.003
3.009
3.000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

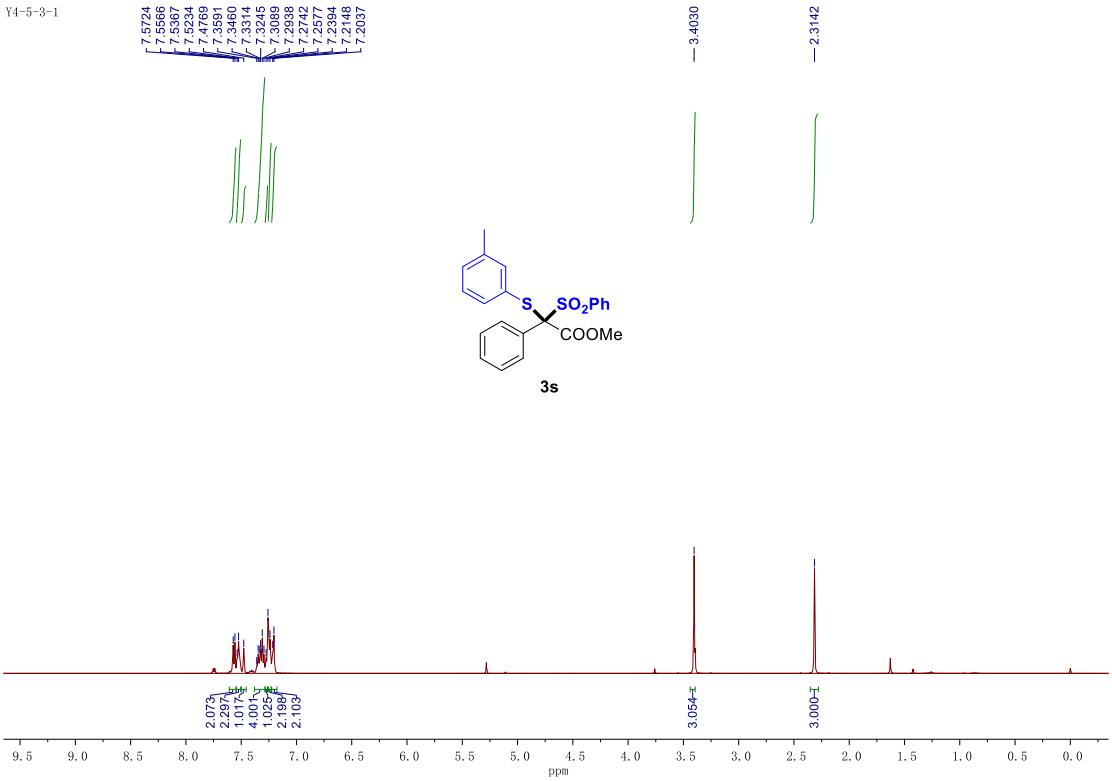

Y4-5-6-1
165.50
141.02
137.61
136.06
133.67
132.60
131.64
130.02
129.59
129.51
127.79
127.78
125.29
86.96
52.81
21.41
S
SO2Ph
COOMe
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

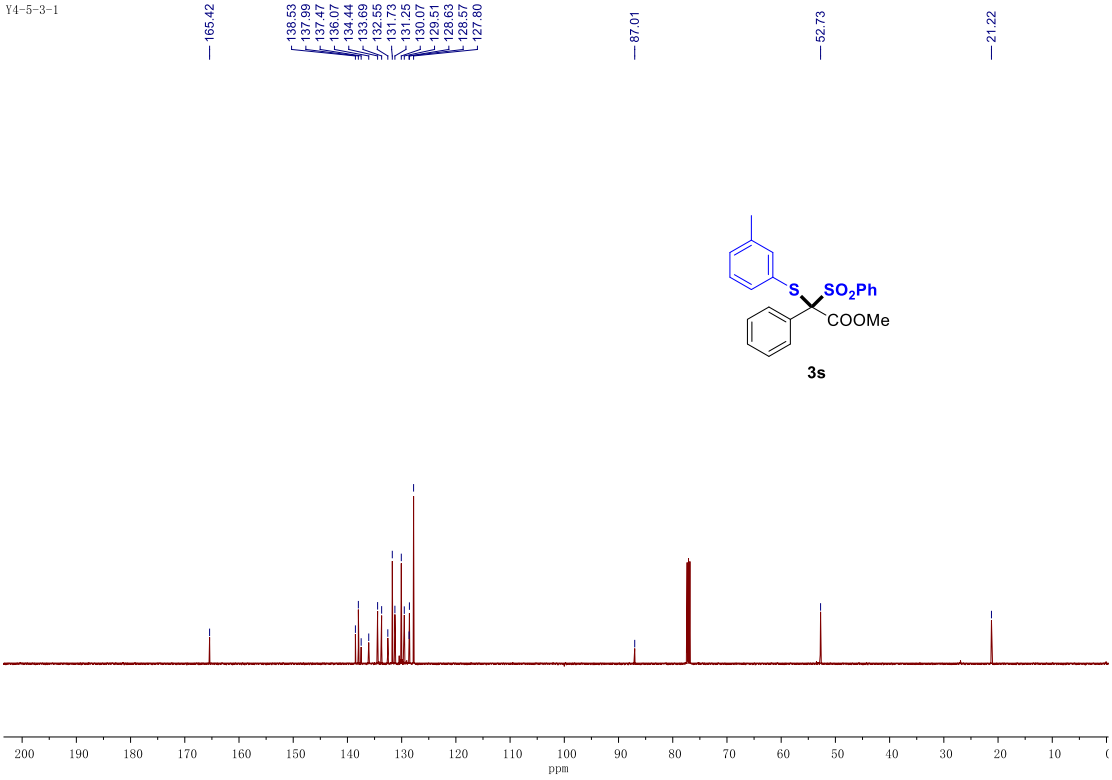


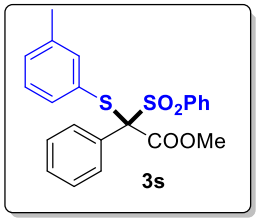
Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54



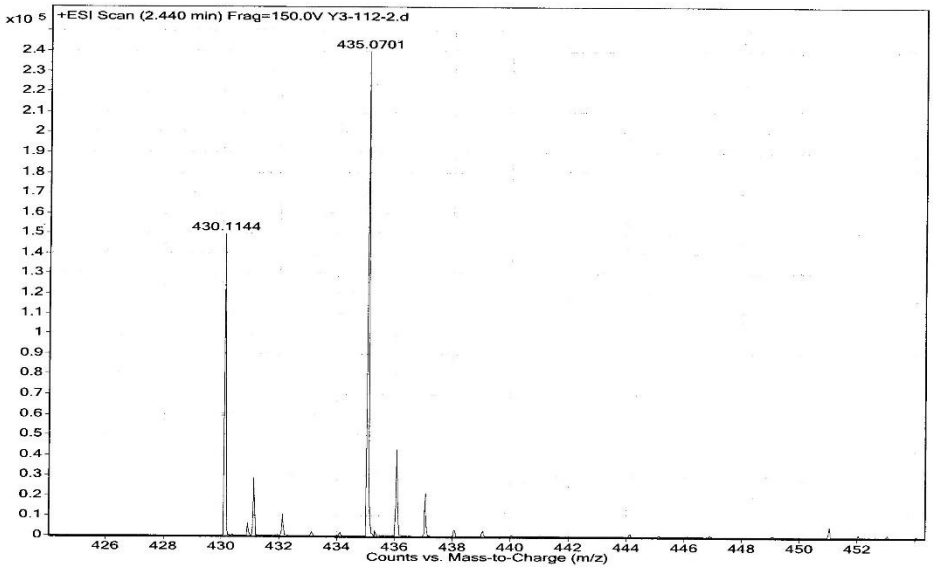
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+NH_4]^+$**430.1141**, found **430.1139**.


Y4-5-3-1
7.5724
7.5566
7.5367
7.5234
7.4769
7.3591
7.3460
7.3314
7.3245
7.3089
7.2938
7.2742
7.2577
7.2394
7.2148
7.2037
3.4030
2.3142
S
SO2Ph
COOMe
3s
2.073
2.297
1.017
4.001
1.025
2.199
2.103
3.054
3.000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

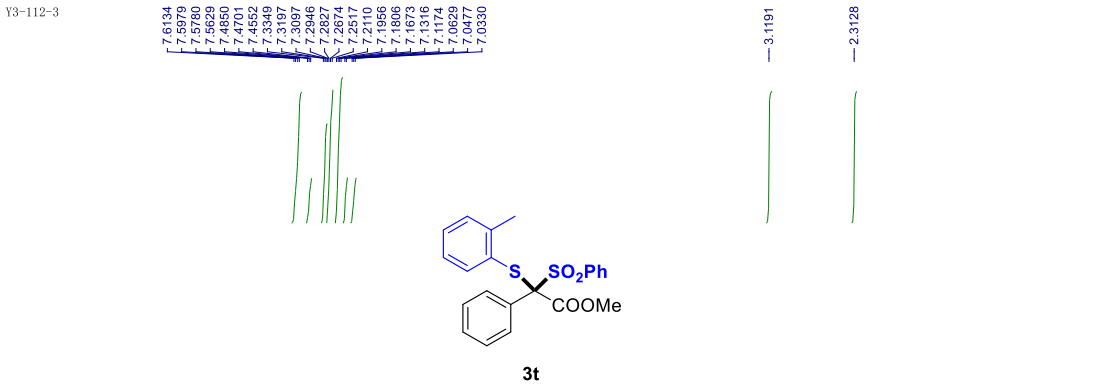

Y4-5-3-1
165.42
138.53
137.99
137.47
136.07
134.44
133.69
132.55
131.73
131.25
130.07
129.51
128.63
128.57
127.80
87.01
52.73
21.22
S
SO2Ph
COOMe
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



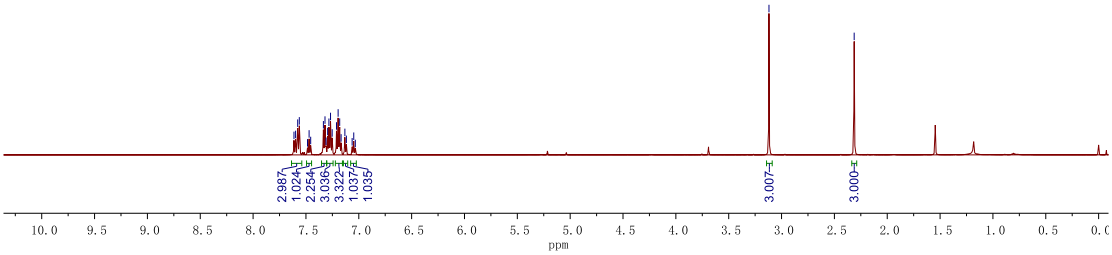
Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54



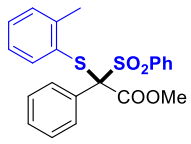
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$ **435.0695**, found **435.0701**.


Y3-112-3
7.6134
7.5979
7.5780
7.5629
7.4850
7.4701
7.4552
7.3349
7.3197
7.3097
7.2946
7.2827
7.2674
7.2517
7.2110
7.1956
7.1806
7.1673
7.1316
7.1174
7.0629
7.0477
7.0330
3.1191
2.3128
S
SO2Ph
COOMe

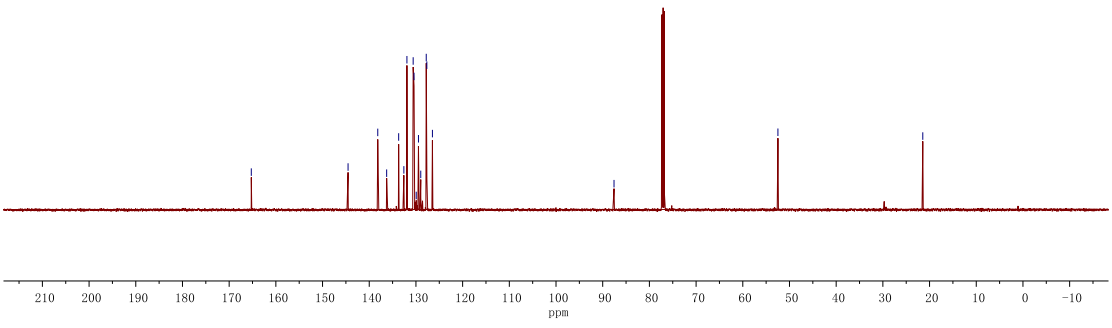
3t

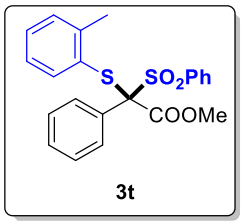

2.987
1.024
2.254
3.036
3.322
1.037
1.039
3.007
3.000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Y3-112-3
165.26
144.54
138.17
136.27
133.70
132.59
131.93
130.89
130.41
129.94
129.46
128.97
127.79
127.67
126.47
87.58
52.47
21.45


S
SO2Ph
COOMe

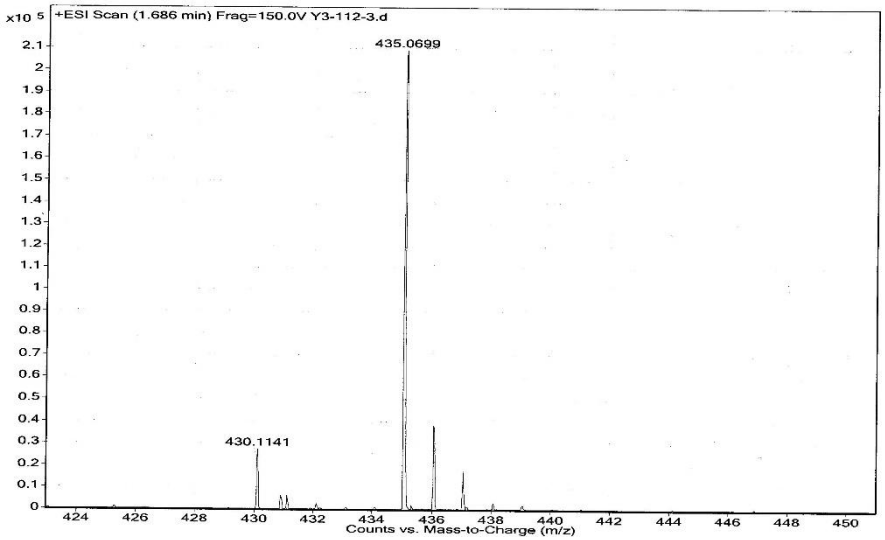
3t


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

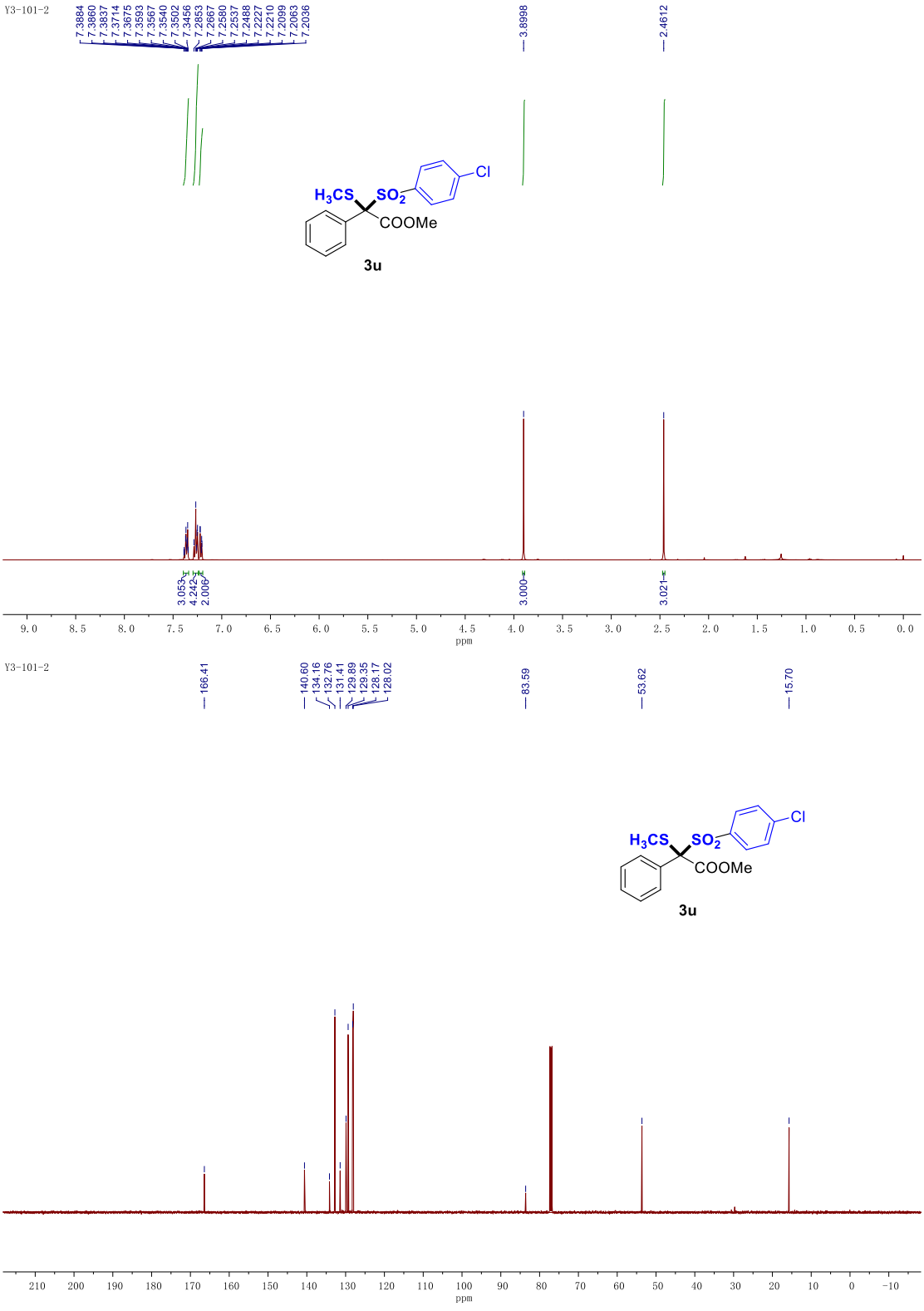


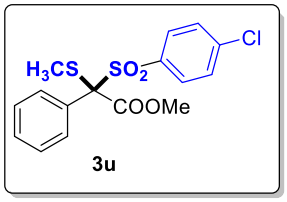
3t

Chemical Formula: $C_{22}H_{20}O_4S_2$
Exact Mass: 412.0803
Molecular Weight: 412.5180
m/z: 412.0803 (100.0%), 413.0837 (23.8%), 414.0761 (9.0%), 414.0870 (2.7%), 415.0795 (2.2%), 413.0797 (1.6%)
Elemental Analysis: C, 64.06; H, 4.89; O, 15.51; S, 15.54



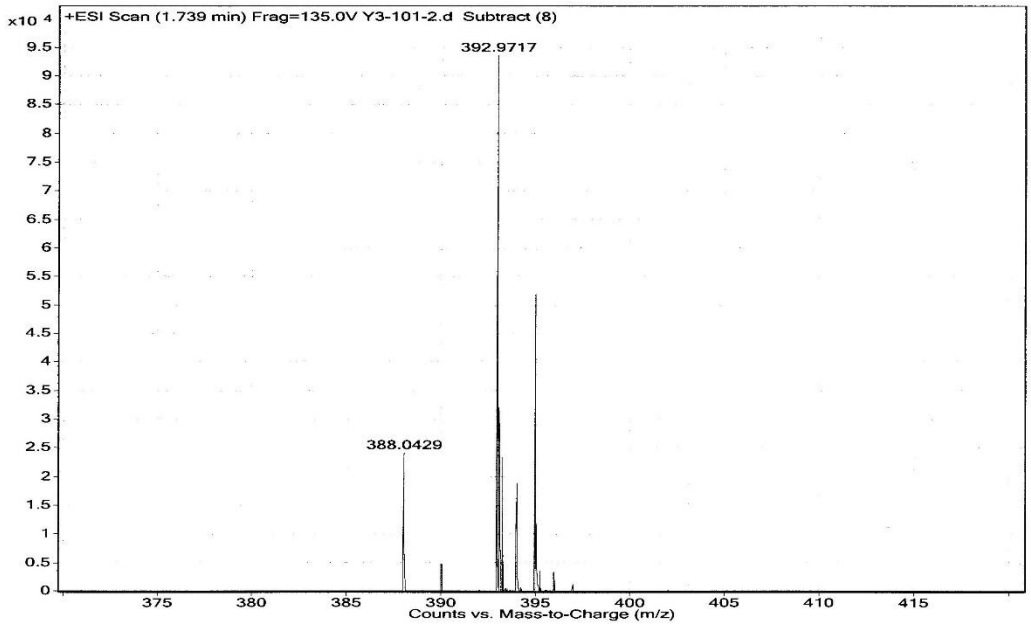
HRMS (ESI, m/z) calcd for $C_{22}H_{20}O_4S_2$ $[M+Na]^+$**435.0695**, found **435.0699**.


Y3-101-2
7.3884
7.3860
7.3837
7.3714
7.3675
7.3593
7.3567
7.3540
7.3502
7.3456
7.2853
7.2667
7.2580
7.2537
7.2488
7.2227
7.2210
7.2099
7.2063
7.2036
3.8998
2.4612
H3CS
SO2
Cl
COOMe
3u
3.053
4.242
2.006
3.000
3.021
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
Y3-101-2
166.41
140.60
134.16
132.76
131.41
129.89
129.35
128.17
128.02
83.59
53.62
15.70
H3CS
SO2
Cl
COOMe
3u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

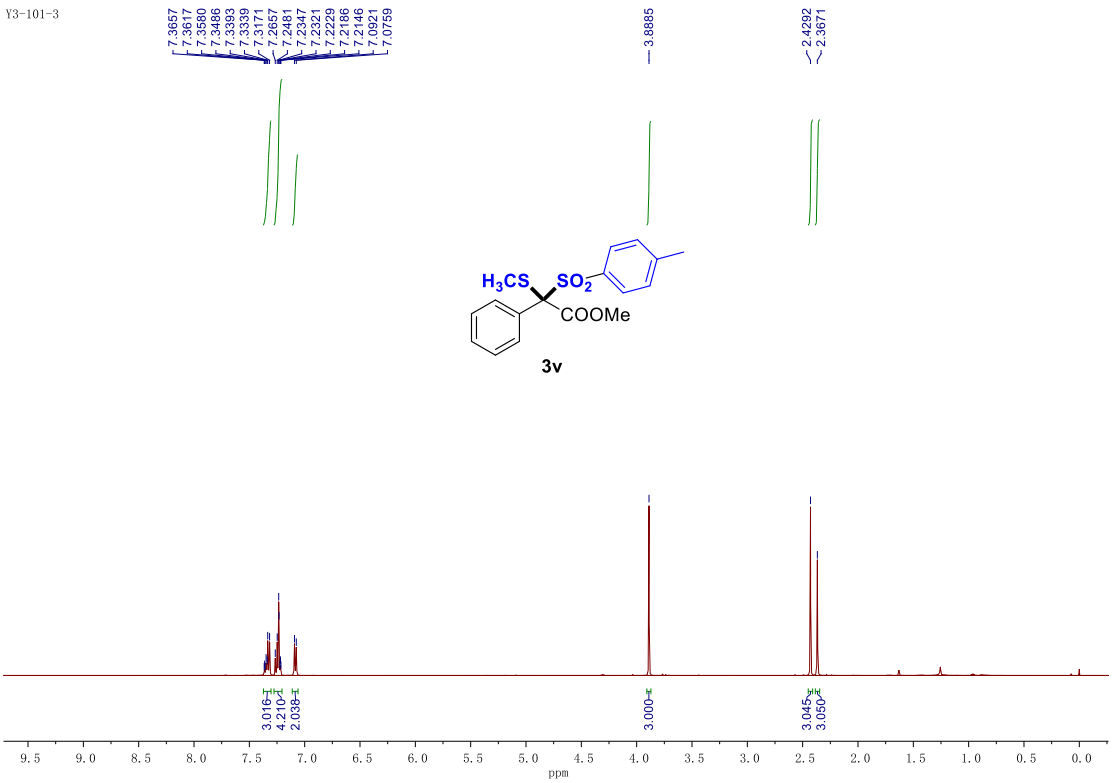


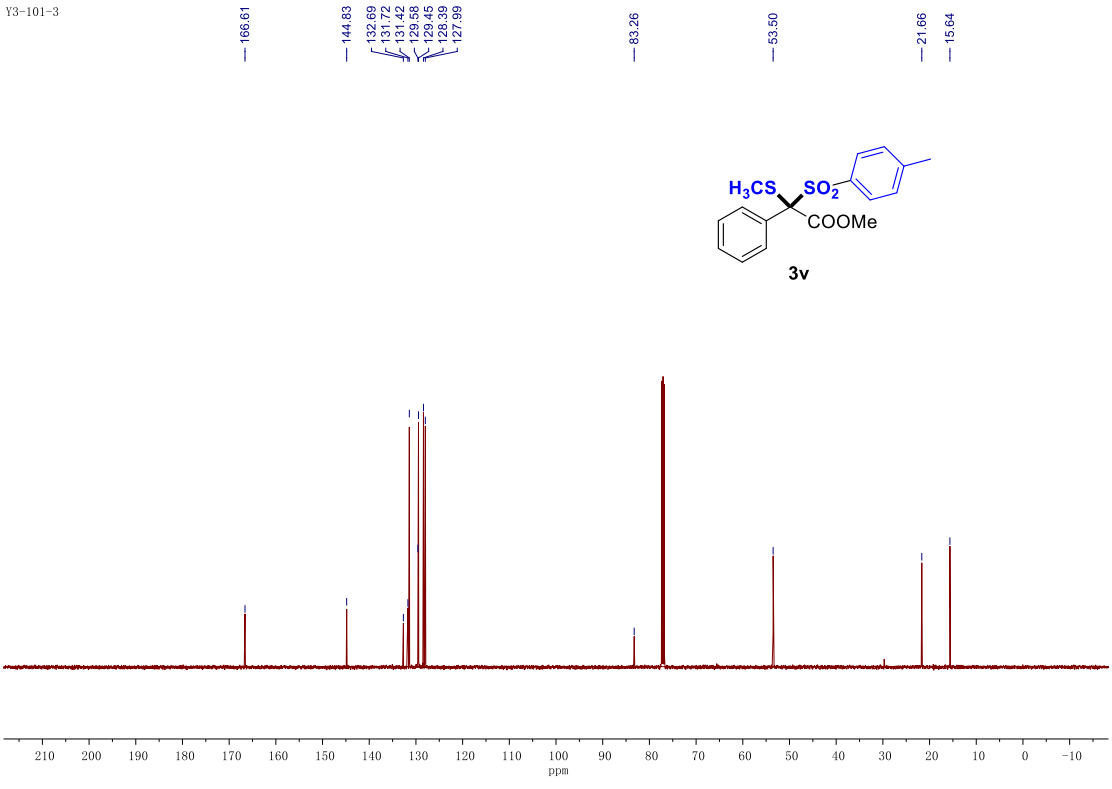
3u

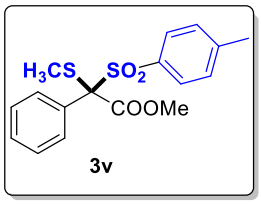
Chemical Formula: $C_{16}H_{15}ClO_4S_2$
Exact Mass: 370.0100
Molecular Weight: 370.8620
m/z: 370.0100 (100.0%), 372.0071 (32.0%), 371.0134 (17.3%), 372.0058 (9.0%), 373.0104 (5.5%), 374.0029 (2.9%), 371.0094 (1.6%), 373.0092 (1.6%), 372.0167 (1.4%)
Elemental Analysis: C, 51.82; H, 4.08; Cl, 9.56; O, 17.26; S, 17.29



HRMS (ESI, m/z) calcd for $C_{16}H_{15}ClO_4S_2$ $[M+NH_4]^+$**388.0439**, found **388.0429**.

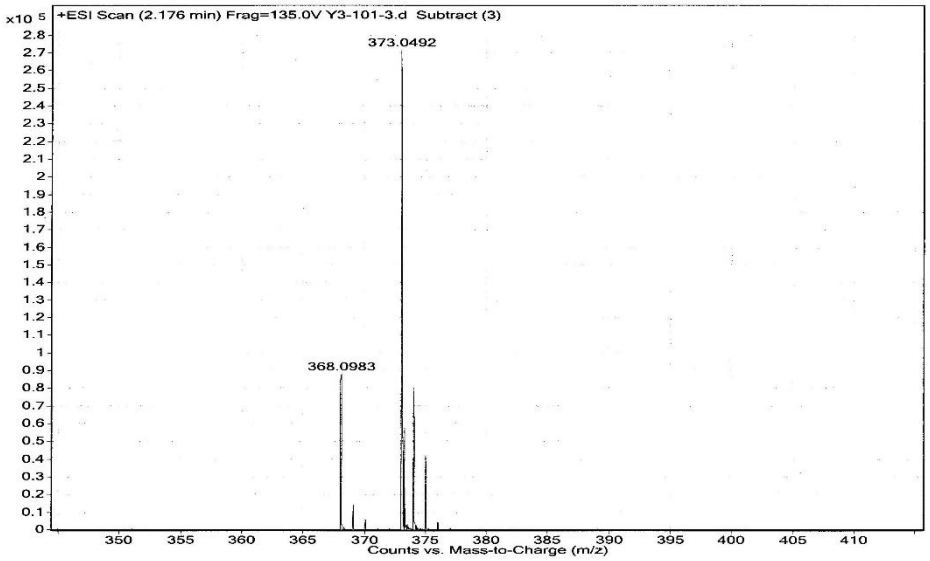

Y3-101-3
7.3657
7.3617
7.3580
7.3486
7.3393
7.3339
7.3171
7.2657
7.2481
7.2347
7.2321
7.2229
7.2186
7.2146
7.0921
7.0759
3.8885
2.4292
2.3671
H3CS
SO2
COOMe
3v
3.016
4.210
2.038
3.000
3.045
3.050
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Y3-101-3
166.61
144.83
132.69
131.72
131.42
129.58
129.45
128.39
127.99
83.26
53.50
21.66
15.64
H3CS
SO2
COOMe
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

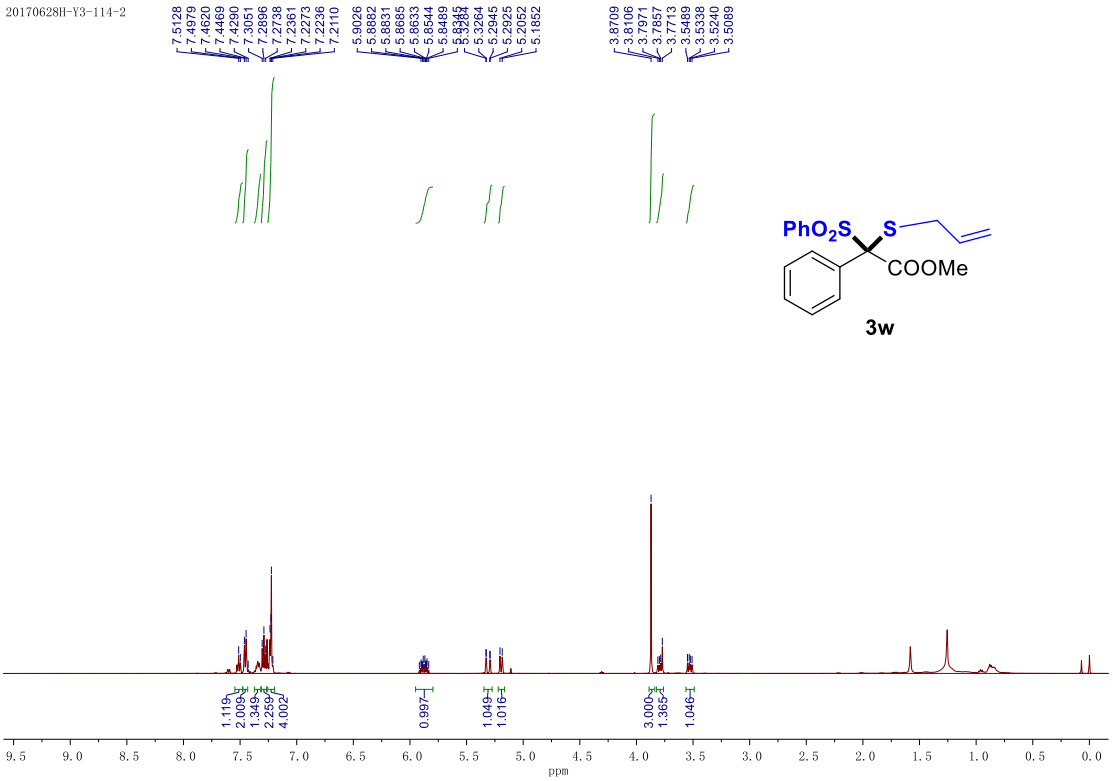


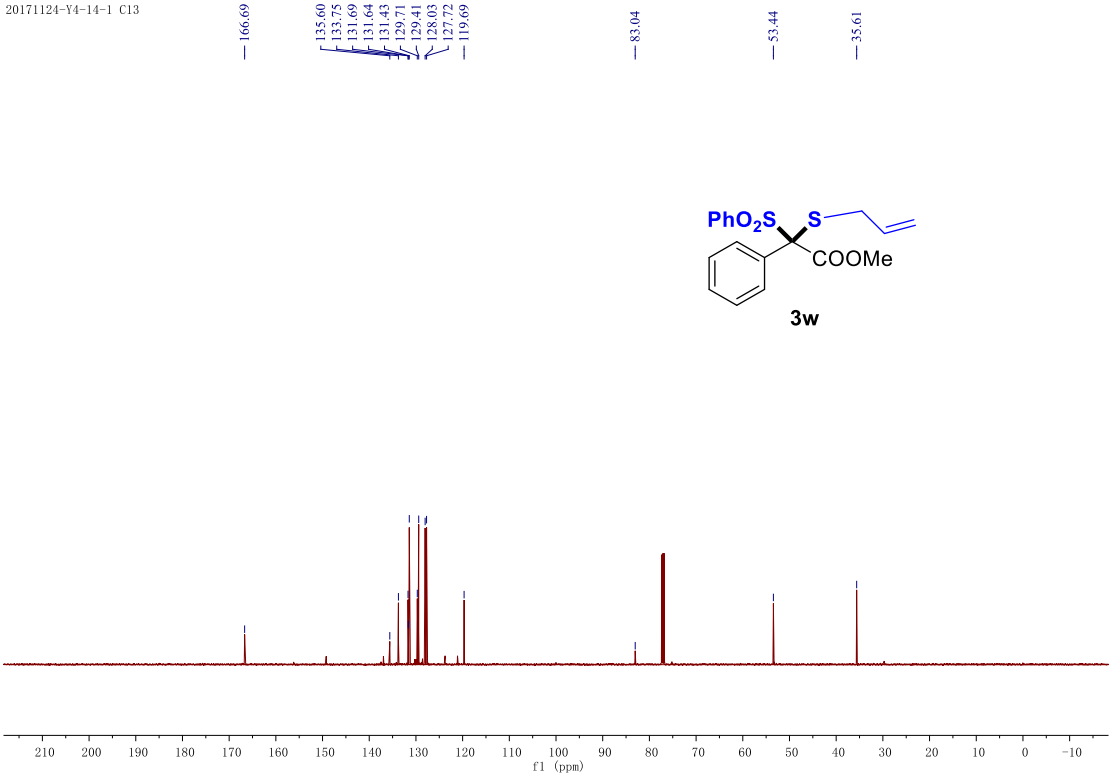
3v

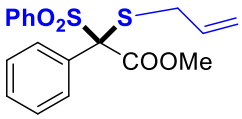
Chemical Formula: $C_{17}H_{18}O_4S_2$
Exact Mass: 350.0647
Molecular Weight: 350.4470
m/z: 350.0647 (100.0%), 351.0680 (18.4%), 352.0604 (9.0%), 353.0638 (1.7%), 351.0640 (1.6%), 352.0714 (1.6%)
Elemental Analysis: C, 58.26; H, 5.18; O, 18.26; S, 18.30



HRMS (ESI, m/z) calcd for $C_{17}H_{18}O_4S_2$ $[M+NH_4]^+$**368.0985**, found **368.0983**.

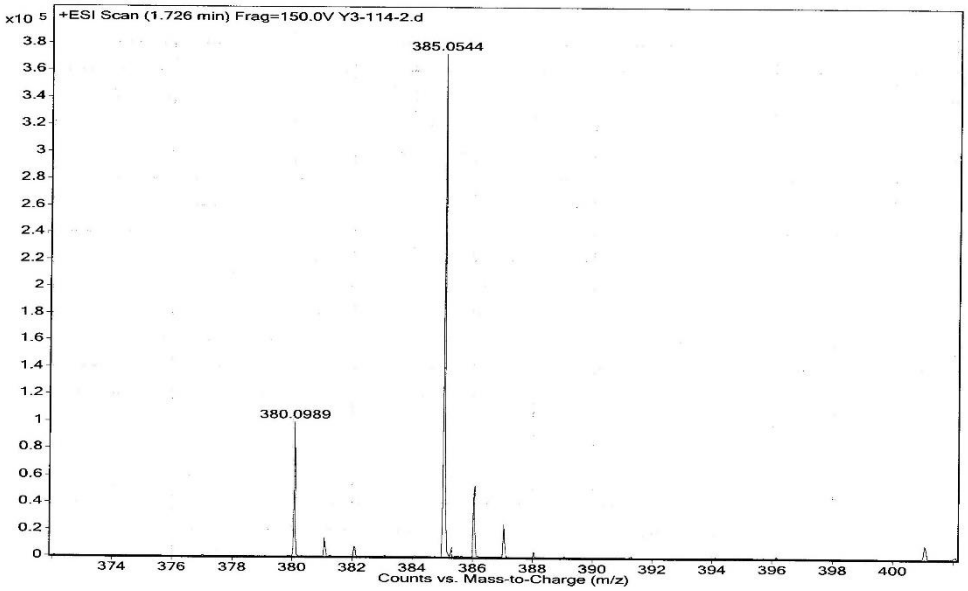

20170628H-Y3-114-2
7.5128
7.4979
7.4620
7.4469
7.4290
7.3051
7.2896
7.2738
7.2361
7.2273
7.2236
7.2110
5.9026
5.8882
5.8831
5.8685
5.8633
5.8544
5.8489
5.3264
5.2945
5.2925
5.2052
5.1852
3.8709
3.8106
3.7971
3.7857
3.7713
3.5489
3.5338
3.5240
3.5089
PhO2S
S
COOMe
3w
1.119
2.009
1.349
2.259
4.002
0.997
1.049
1.016
3.000
1.365
1.046
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


20171124-Y4-14-1 C13
166.69
135.60
133.75
131.69
131.64
131.43
129.71
129.41
128.03
127.72
119.69
83.04
53.44
35.61
PhO2S
S
COOMe
3w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3w

Chemical Formula: $C_{18}H_{18}O_4S_2$
Exact Mass: 362.06
Molecular Weight: 362.46
m/z: 362.06 (100.0%), 363.07 (19.8%), 364.06 (9.0%), 364.07 (3.0%), 365.06 (1.8%), 363.06 (1.6%)
Elemental Analysis: C, 59.65; H, 5.01; O, 17.66; S, 17.69



HRMS (ESI, m/z) calcd for $C_{18}H_{18}O_4S_2$ $[M+Na]^+$**385.0539**, found **385.0544**.