Supporting Information

Rh-Catalyzed Asymmetric Hydrogenation of Allylic Sulfones for Synthesis of Chiral *β*-Ester Sulfones

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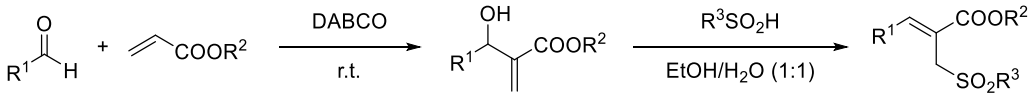
1. Experimental Section

General Information: All the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in a nitrogen-filled glovebox. THF, dioxane and toluene were distilled from sodium benzophenone ketyl. DCM and DCE was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AV (400 MHz) spectrometers and JEOL JNM-ECX600P and JNM-ECS600 (400 MHz or 600 MHz) spectrometers. ($CDC1_3$ was the solvent used for the NMR analysis, with TMS as the internal standard). Optical rotation was determined using Autopol III Automatic polarimeter (Rudolph research Analyical). HPLC analysis was conducted on Agilent 1260 series instrument. SFC analysis was conducted on Agilent 1260 series instrument. HRMS were recorded on a Waters LCT Premier XE mass spectrometer with TOF.

2. General procedure for the synthesis of substrates 1 and 3

General Procedure 1 and 3[1-5]



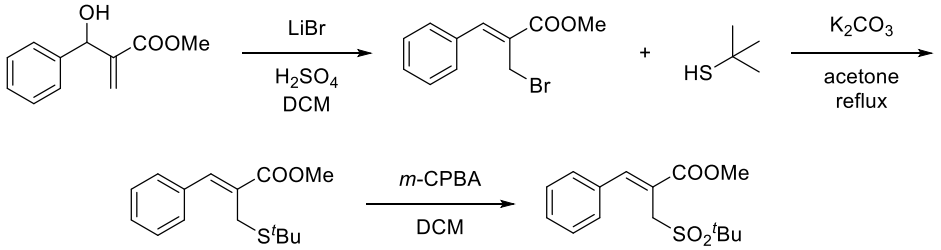
1 and **3**

Take the aldehydes (5.0 mmol), methyl acrylates (2.5 equiv.) and DABCO (1.0 equiv) in a 25 mL oven dried round bottom flask and seal with a rubber septum. Stir the resultant reaction mixture at room temperature under solvent free condition for 7-14 hours. Monitor the progress of the reaction was monitored by TLC. Admix the reaction mixture with ethyl acetate (50 mL). Wash the mixture successively with saturated solution of sodium bicarbonate (2 x 25 mL) and brine solution (2 x 25 mL). Dry the organic layer over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography to (PE:EA = 5:1) yield the Morita-Baylis-Hillman alcohols.

Dissolve phenyl- or methyl-substituted sulfinic acid (1.5 equiv) and Morita-Baylis-Hillman alcohols (1.0 equiv) in aqueous media 10.0 mL (ethanol/deionized water, V/V = 1/1). Stir the reaction mixture vigorously for 48 hours at 30 °C. After complete

conversion, precipitate the product from the solvent. Extract the aqueous media with ethyl acetate (3 x 30 mL). Dry the combined organic layers over Na_2SO_4. Concentrate the combined organic layers by rotary evaporation. Purify the crude product via column chromatography (PE:EA = 3:1) to afford the corresponding allyl sulfones **1** and **3**.

General Procedure 3e, 3f, 3i, 3j and 3k[6-9]

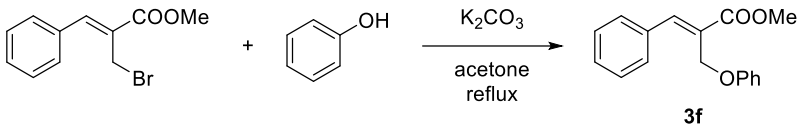


3e

Morita-Baylis-Hillman alcohols (1.0 equiv), LiBr (3.0 equiv) and H_2SO_4 (1.5 equiv) were stirred in dichloromethane for 16 hours. Na_2CO_3 (aq. sat.) was added and the mixture was extracted with DCM. The combined organic layers were dried over $MgSO_4$. Concentrate the combined organic layers by rotary evaporation. Purify the crude product via column chromatography (PE:EA = 20:1) to afford the corresponding allylic bromide.

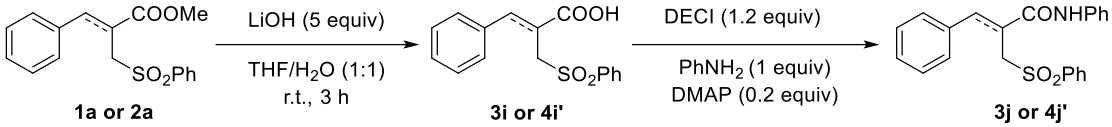
To a solution of allylic bromide (1.0 equiv), *tert*-butyl mercaptan (2.0 equiv) and K_2CO_3 (2.0 equiv) in acetone were stirred by reflux for 3 hours. Monitor the progress of the reaction was monitored by TLC. NH_4Cl (aq. sat.,) was added and the mixture was extracted with DCM. The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. Purify the crude product via column chromatography (PE:EA = 20:1) to afford the corresponding allylic sulfide.

85% *m*-CPBA (3.0 equiv.) is added to a solution of allylic sulfide (1.0 mmol) in CH_2Cl_2 (15 mL), and the reaction is left under magnetic stirring at 20 °C for 18 hours. The solution is diluted with water (10 mL) and extracted with a 10% w/v solution of $NaHCO_3$ (3 x 20 mL) and NaCl saturated solution (20 mL), dried Na_2SO_4 and and the volatiles were removed under reduced pressure. Purify the crude product via column chromatography (PE:EA = 3:1) to afford the corresponding vinylic sulfone **3e**.



3f

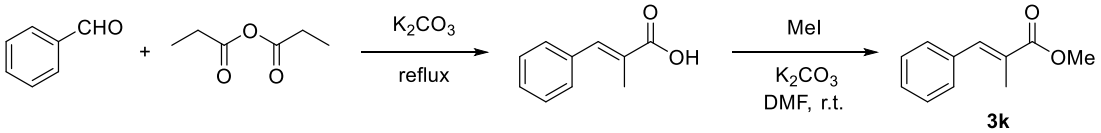
To a solution of allylic bromide (1.0 equiv), phenol (2.0 equiv) and K_2CO_3 (2.0 equiv) in acetone were stirred by reflux for 3 hours. Monitor the progress of the reaction was monitored by TLC. NH_4Cl (aq. sat.,) was added and the mixture was extracted with DCM. The combined organic layers were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. Purify the crude product via column chromatography (PE:EA = 20:1) to afford the corresponding allyl phenyl ether **3f**.



1a or 2a **3i or 4i'** **3j or 4j'**

Methyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate **1a** (3.0 mmol, 1.0 equiv) was dissolved in a mixture of 6 ml of tetrahydrofuran and 6 ml of water, and mixed with LiOH (5.0 equiv). The mixture was then stirred at 80°C. After 3 hours, the reaction mixture was acidified by adding one molar hydrochloric acid solution and extracted with EA (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and subsequently the solvent was removed in vacuum to obtain the acid as a white solid.

Treat dropwise a solution of acid (1.0 equiv) in CH_2Cl_2 with EDCI (1.2 equiv) and DMAP (0.2 equiv) at 0 ℃. Stir the resulting mixture at this temperature for 4 hours. Concentrate the reaction mixture in vacuo. Dissolve the residue in CH_2Cl_2. Separate the layers and extract the aqueous phase with CH_2Cl_2 (3 x 30 mL). Dry the combined organics over $MgSO_4$ and concentrate in vacuo. Purify the crude product via column chromatography (PE:EA = 3:1) to afford the corresponding sulfone **3j** or **4j'**.



3k

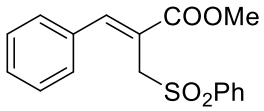
Add appropriate anhydride (30.0 mmol, 1.6 equiv) to potassium carbonate (22.4 mmol, 1.2 equiv) at 0 °C. Add appropriate aromatic aldehyde (18.6 mmol, 1.0 equiv) after stirring for 5 min to mix up. Heat the mixture to reflux for 12 h. Add water and solid

Na_2CO_3 (3.0 g) to the above reaction mixture after cooling with an ice bath. Acidify the reaction mixture to pH 6.0 using concentrated HCl to obtain 2-methyl-3-phenylacrylic acid after filter the resultant yellow precipitate.

To a dried 50 mL flask, cinnamic acid (5.0 mmol, 1.0 equiv) was added to a stirred suspension of potassium carbonate (10.0 mmol, 2.0 equiv) in 15 mL DMF at room temperature. After 10 min, CH_3I (7.5 mmol, 1.5 equiv) was added slowly at ambient temperature while stirring, the reaction was stirred at room temperature under TLC analysis. After 5 h, water (20 mL) was added, and aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were sequentially washed with 4 N hydrochloric acid and brine, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography on silica gel (PE:EA = 10:1) to afford the desired product **3k**.

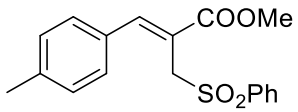
3. The characterization data for substrates 1 and 3

Methyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**1a**)



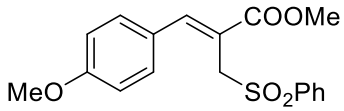
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.23 g, yield: 78% (two steps); m.p. 64-66 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.87 – 7.85 (m, 2H), 7.63 – 7.60 (m, 1H), 7.51 – 7.47 (m, 4H), 7.39 – 7.37 (m, 3H), 4.49 (s, 2H), 3.59 (s, 3H). The analytical data are consistent with the literature.[5]

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(*p*-tolyl)acrylate (**1b**)



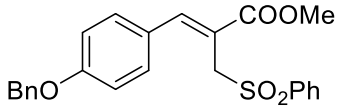
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.17g, yield: 71% (two steps); m.p. 96-98 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.88 – 7.86 (m, 2H), 7.63 – 7.60 (m, 1H), 7.52 – 7.49 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.50 (s, 2H), 3.56 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.0, 146.6, 140.3, 139.5, 133.7, 130.8, 129.5, 129.5, 129.0, 128.6, 119.8, 55.3, 52.3, 21.4. The analytical data are consistent with the literature.[10]

Methyl (*Z*)-3-(4-methoxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1c**)



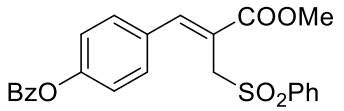
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) afforded the product as pale yellow oil; 1.20 g, yield: 0.69 g (two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 – 7.88 (m, 3H), 7.63 – 7.57 (m, 3H), 7.53 – 7.50 (m, 2H), 6.94 – 6.91 (m, 2H), 4.50 (s, 2H), 3.84 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.3, 161.2, 146.4, 139.7, 133.8, 131.7, 129.1, 128.7, 126.3, 118.2, 114.4, 55.6, 55.5, 52.3. The analytical data are consistent with the literature.[10]

Methyl (*Z*)-3-(4-(benzyloxy)phenyl)-2-((phenylsulfonyl)methyl)acrylate (**1d**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.27 g, yield: 60% (two steps); m.p. 104-105 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.89 – 7.87 (m, 2H), 7.61 – 7.56 (m, 3H), 7.51 – 7.48 (m, 2H), 7.45 – 7.43 (m, 2H), 7.42 – 7.40 (m, 2H), 7.37 – 7.34 (m, 1H), 7.01 – 6.98 (m, 2H), 5.11 (s, 2H), 4.52 (s, 2H), 3.52 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.1, 160.2, 146.2, 139.5, 136.4, 133.7, 131.6, 129.0, 128.7, 128.6, 128.2, 127.4, 126.4, 118.2, 115.2, 70.0, 55.4, 52.2. TOF-HRMS Calcd. for $C_{24}H_{23}O_5S$ [M+H$^+$]: 423.1261, found 423.1257.

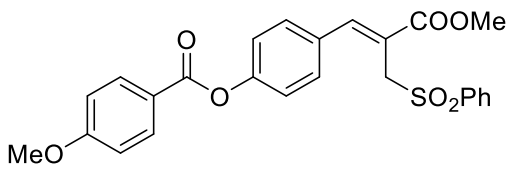
(*Z*)-4-(3-methoxy-3-oxo-2-((phenylsulfonyl)methyl)prop-1-en-1-yl)phenyl benzoate (**1e**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.18 g, yield: 54% (two steps); m.p. 136-138 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 – 8.21 (m, 2H), 7.96 (s, 1H), 7.88 – 7.87 (m, 2H), 7.68 – 7.62 (m, 2H), 7.60 – 7.58 (m, 2H), 7.55 – 7.52 (m, 4H), 7.27 – 7.24 (m, 2H), 4.51 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 164.8, 152.0, 145.4, 139.2, 133.8, 131.3, 130.6, 130.2, 129.2, 129.1, 128.7, 128.5, 122.2, 121.0, 55.1, 52.4. TOF-HRMS Calcd. for $C_{24}H_{21}O_6S$ [M+H$^+$]: 437.1053, found 437.1052.

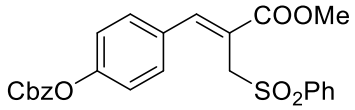
(*Z*)-4-(3-methoxy-3-oxo-2-((phenylsulfonyl)methyl)prop-1-en-1-yl)phenyl 4-

methoxybenzoate (**1f**)



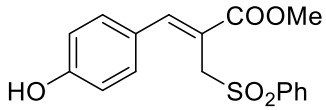
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.45 g, yield: 62% (two steps); m.p. 123-124 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 – 8.21 (m, 2H), 7.96 (s, 1H), 7.88 – 7.87 (m, 2H), 7.68 – 7.62 (m, 2H), 7.60 – 7.58 (m, 2H), 7.55 – 7.52 (m, 4H), 7.26 – 7.24 (m, 2H), 4.51 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 164.8, 152.0, 145.4, 139.2, 133.8, 131.3, 130.6, 130.2, 129.2, 129.1, 128.7, 128.5, 122.2, 121.0, 55.1, 52.4. TOF-HRMS Calcd. for $C_{25}H_{23}O_7S$ [M+H$^+$]: 467.1159, found 467.1157.

Methyl (*Z*)-3-(4-(((benzyloxy)carbonyl)oxy)phenyl)-2-((phenylsulfonyl)methyl)acrylate (**1g**)



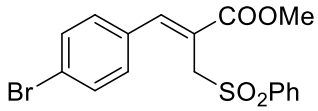
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.33 g, yield: 57% (two steps); m.p. 112-113 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.87 – 7.84 (m, 2H), 7.68 – 7.58 (m, 1H), 7.55 – 7.48 (m, 4H), 7.47 – 7.36 (m, 5H), 7.23 – 7.19 (m, 2H), 5.29 (s, 2H), 4.47 (s, 2H), 3.60 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.7, 153.2, 152.0, 145.1, 139.2, 134.5, 133.8, 131.4, 130.6, 129.1, 128.9, 128.7, 128.6, 128.5, 121.5, 121.2, 70.6, 55.0, 52.4. TOF-HRMS Calcd. for $C_{25}H_{23}O_7S$ [M+H$^+$]: 467.1159, found 467.1156.

Methyl (*Z*)-3-(4-hydroxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1h**)



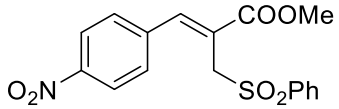
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.25 g, yield: 75% (two steps); m.p. 74-75 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.90 – 7.88 (m, 2H), 7.64 – 7.62 (m, 1H), 7.54 – 7.51 (m, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.47 (br s, 1H), 4.55 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.3, 158.0, 146.8, 139.2, 133.9, 131.9, 129.1, 128.6, 125.9, 117.4, 115.9, 55.5, 52.3. TOF-HRMS Calcd. for $C_{17}H_{17}O_5S$ [M+H$^+$]: 333.0791, found 333.0791.

Methyl (*Z*)-3-(4-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1i**)



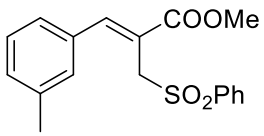
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.72 g, yield: 87% (two steps); m.p. 96-98 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.86 – 7.85 (m, 2H), 7.65 – 7.62 (m, 1H), 7.53 – 7.50 (m, 4H), 7.40 – 7.38 (m, 2H), 4.43 (s, 2H), 3.58 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.6, 145.1, 139.3, 133.9, 132.5, 132.0, 130.7, 129.1, 128.5, 124.3, 121.5, 55.1, 52.5. The analytical data are consistent with the literature.[5]

Methyl (*Z*)-3-(4-nitrophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1j**)



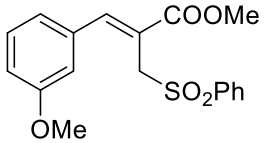
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.25 g, yield: 69% (two steps); m.p. 154-156 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 – 8.23 (m, 2H), 7.98 (s, 1H), 7.87 – 7.85 (m, 2H), 7.68 – 7.64 (m, 3H), 7.55 – 7.52 (m, 2H), 4.40 (s, 2H), 3.63 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.0, 148.1, 143.5, 140.0, 139.1, 134.1, 129.9, 129.2, 128.5, 124.2, 123.9, 54.9, 52.7. The analytical data are consistent with the literature.[11]

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(*m*-tolyl)acrylate (**1k**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.04 g, yield: 63% (two steps); m.p. 74-76 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 (s, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.49 (s, 2H), 3.60 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 146.5, 139.3, 138.4, 133.6, 133.6, 130.4, 129.8, 128.9, 128.6, 128.5, 126.1, 120.7, 55.1, 52.3, 21.3. The analytical data are consistent with the literature.[10]

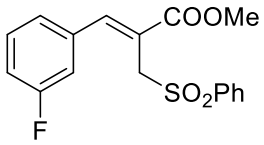
Methyl (*Z*)-3-(3-methoxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1l**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.37 g, yield: 79% (two steps); m.p. 60-70 °C. ^{1}H NMR

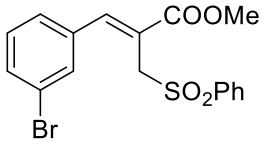
(600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.87 – 7.85 (m, 2H), 7.61 (tt, *J* = 7.0, 1.2 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 2.1 Hz, 1H), 7.04 – 7.02 (m, 1H), 6.93 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 4.50 (s, 2H), 3.85 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 159.8, 146.4, 139.4, 134.9, 133.7, 129.8, 129.0, 128.5, 121.6, 121.1, 116.1, 113.9, 55.5, 55.3, 52.4. The analytical data are consistent with the literature.[10]

Methyl (*Z*)-3-(3-fluorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1m**)



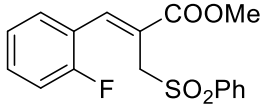
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.35 g, yield: 81% (two steps); m.p. 96-98 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.61 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.34 (td, *J* = 7.9, 5.8 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.11 (dt, *J* = 9.7, 2.1 Hz, 1H), 7.06 (td, *J* = 8.4, 2.6 Hz, 1H), 4.45 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 162.7 (d, *J* = 247.6 Hz), 144.7, 139.1, 135.7 (d, *J* = 7.7 Hz), 133.8, 130.4 (d, *J* = 8.4 Hz), 128.8 (d, *J* = 86.5 Hz), 124.7 (d, *J* = 3.1 Hz), 122.3, 116.5 (d, *J* = 21.1 Hz), 115.8 (d, *J* = 22.5 Hz), 54.9, 52.5. TOF-HRMS Calcd. for $C_{17}H_{16}FO_4S$ [M+H$^+$]: 335.0748, found 335.0740.

Methyl (*Z*)-3-(3-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1n**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.48 g, yield: 71% (two steps); m.p. 84-85 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 3H), 7.65 – 7.62 (m, 1H), 7.51 – 7.47 (m, 3H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.42 – 7.40 (m, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 4.44 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 144.4, 138.9, 135.6, 133.9, 132.5, 131.7, 130.3, 129.1, 128.5, 127.3, 122.8, 122.5, 54.8, 52.6. The analytical data are consistent with the literature.[10]

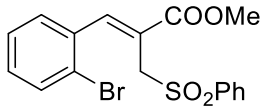
Methyl (*Z*)-3-(2-fluorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1o**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white

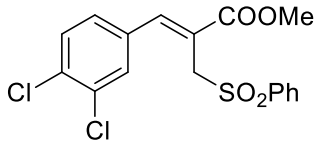
solid; 1.12 g, yield: 67% (two steps); m.p. 134-136 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.95 (m, 1H), 7.82 – 7.80 (m, 2H), 7.66 – 7.58 (m, 2H), 7.50 – 7.46 (m, 2H), 7.38 – 7.32 (m, 1H), 7.16 (td, *J* = 7.5, 1.2 Hz, 1H), 7.06 – 7.01 (m, 1H), 4.45 (s, 2H), 3.63 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 160.1 (d, *J* = 250.8 Hz), 139.0 (d, *J* = 7.5 Hz), 133.8, 131.5 (d, *J* = 8.3 Hz), 130.0, 129.0, 128.5, 124.5 (d, *J* = 3.7 Hz), 123.1, 121.7 (d, *J* = 13.2 Hz), 115.7 (d, *J* = 21.3 Hz), 55.1, 52.5. TOF-HRMS Calcd. for $C_{17}H_{16}FO_4S$ [M+H$^+$]: 335.0748, found 335.0747.

Methyl (*Z*)-3-(2-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1p**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.64 g, yield: 83% (two steps); m.p. 98-99 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.85 – 7.83 (m, 2H), 7.63 – 7.60 (m, 2H), 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.24 – 7.21 (m, 1H), 4.36 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.3, 145.2, 139.4, 134.0, 133.7, 132.9, 130.7, 130.1, 129.1, 128.4, 127.6, 124.0, 122.8, 54.9, 52.5. The analytical data are consistent with the literature.[10]

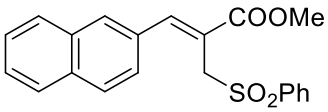
Methyl (*Z*)-3-(3,4-dichlorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1q**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.27 g, yield: 66% (two steps); m.p. 97-99 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.82 (s, 1H), 7.66 – 7.63 (m, 1H), 7.53 – 7.50 (m, 2H), 7.49 (dd, *J* = 2.1, 0.7 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 2.1, 0.7 Hz, 1H), 4.42 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.3, 143.4, 139.0, 134.0, 133.5, 133.1, 130.8, 130.8, 129.1, 128.5, 128.1, 122.8, 54.9, 52.6. TOF-HRMS Calcd. for $C_{17}H_{15}{}^{35}Cl_2O_4S$ [M+H$^+$]: 385.0063, found 385.0061; TOF-HRMS Calcd. for $C_{17}H_{15}{}^{37}Cl_2O_4S$ [M+H$^+$]: 387.0033, found 387.0027.

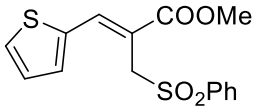
Methyl (*Z*)-3-(naphthalen-2-yl)-2-((phenylsulfonyl)methyl)acrylate (**1r**)

Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and



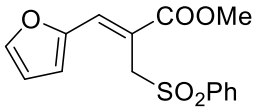
recrystallization afforded the product as white solid; 1.54 g, yield: 84% (two steps); m.p. 124-126 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.04 – 8.03 (m, 1H), 7.87 – 7.86 (m, 3H), 7.84 – 7.82 (m, 2H), 7.57 – 7.51 (m, 4H), 7.46 – 7.43 (m, 2H), 4.58 (s, 2H), 3.64 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 146.4, 139.4, 133.7, 133.5, 133.0, 131.1, 129.5, 129.0, 128.7, 128.6, 128.5, 127.6, 127.4, 126.7, 126.0, 121.0, 55.3, 52.4. The analytical data are consistent with the literature.[11]

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(thiophen-2-yl)acrylate (**1s**)



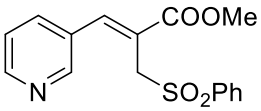
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.24 g, yield: 77% (two steps); m.p. 119-120 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.93 – 7.90 (m, 2H), 7.63 – 7.59 (m, 1H), 7.54 – 7.49 (m, 4H), 7.12 – 7.10 (m, 1H), 4.64 (s, 2H), 3.52 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 139.4, 138.3, 136.8, 134.2, 133.8, 130.9, 129.0, 128.7, 127.8, 116.2, 56.0, 52.3. The analytical data are consistent with the literature.[10]

Methyl (*Z*)-3-(furan-2-yl)-2-((phenylsulfonyl)methyl)acrylate (**1t**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.12 g, yield: 73% (two steps); m.p. 98-100 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.54 – 7.52 (m, 2H), 7.45 – 7.43 (m, 2H), 7.41 (d, *J* = 1.8 Hz, 1H), 6.69 (d, *J* = 3.5 Hz, 1H), 6.42 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.80 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.9, 150.1, 145.8, 139.4, 133.5, 130.7, 128.7, 128.6, 119.0, 115.5, 112.2, 55.4, 52.4. The analytical data are consistent with the literature.[11]

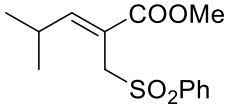
Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(pyridin-3-yl)acrylate (**1u**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) afforded the product as colorless oil; 0.95 g, yield: 60% (two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.61 – 8.60 (m, 2H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.91 (s, 1H), 7.86 – 7.84 (m, 2H), 7.65 – 7.62 (m, 1H), 7.53 – 7.50 (m,

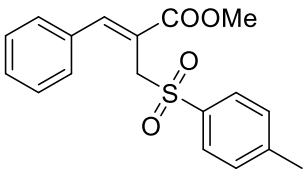
2H), 7.37 (dd, *J* = 7.9, 4.8 Hz, 1H), 4.43 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 150.0, 149.8, 142.3, 139.0, 136.3, 134.0, 129.9, 129.2, 128.5, 123.7, 123.5, 54.9, 52.6. TOF-HRMS Calcd. for $C_{16}H_{16}NO_4S$ [M+H$^+$]: 318.0795, found 318.0789.

Methyl (*Z)*-4-methyl-2-((phenylsulfonyl)methyl)pent-2-enoate (**1v**)



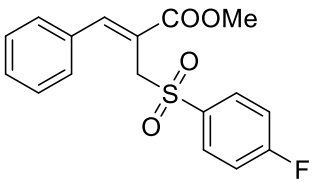
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) afforded the product as yellow oil; 0.73 g, yield: 52% (two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.64 – 7.51 (m, 1H), 7.54 – 7.51 (m, 2H), 6.89 (dt, *J* = 10.9, 1.3 Hz, 1H), 4.23 (s, 2H), 3.46 (s, 3H), 1.01 (d, *J* = 1.5 Hz, 3H), 1.00 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.2, 157.5, 138.9, 133.7, 128.9, 128.7, 118.0, 53.9, 52.0, 29.0, 21.5. The analytical data are consistent with the literature.[12]

Methyl (*Z*)-3-phenyl-2-(tosylmethyl)acrylate (**3a**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.37 g, yield: 83% (two steps); m.p. 116-118 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.72 – 7.70 (m, 2H), 7.47 – 7.45 (m, 2H), 7.38 – 7.36 (m, 3H), 7.27 – 7.26 (m, 3H), 4.47 (s, 2H), 3.61 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.0, 146.2, 144.7, 136.4, 133.7, 129.6, 129.2, 128.7, 128.6, 121.1, 55.1, 52.4, 21.6. The analytical data are consistent with the literature.[10]

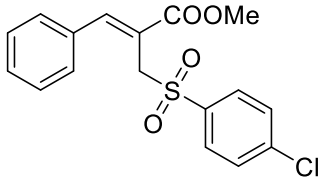
Methyl (*Z*)-2-(((4-fluorophenyl)sulfonyl)methyl)-3-phenylacrylate (**3b**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.42 g, yield: 85% (two steps); m.p. 92-93 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.84 – 7.82 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.37 (m, 3H), 7.15 – 7.12 (m, 2H), 4.51 (s, 2H), 3.66 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 165.9 (d, *J* = 256.5 Hz), 146.4, 135.2, 133.6, 131.4 (d, *J* = 9.6 Hz), 129.8, 129.1, 128.8, 120.8, 116.2 (d, *J* = 22.6

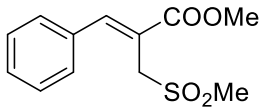
Hz), 55.1, 52.1. The analytical data are consistent with the literature.[10]

Methyl (*Z*)-2-(((4-chlorophenyl)sulfonyl)methyl)-3-phenylacrylate (**3c**)



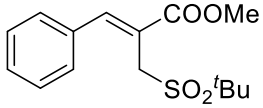
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.37 g, yield: 78% (two steps); m.p. 96-98 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.74 – 7.71 (m, 2H), 7.42 – 7.37 (m, 7H), 4.51 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.8, 146.4, 140.6, 137.5, 133.5, 130.0, 129.7, 129.3, 129.0, 128.8, 120.8, 54.9, 52.5. The analytical data are consistent with the literature.[10]

(*Z*)-2-((methylsulfonyl)methyl)-3-phenylacrylate (**3d**)



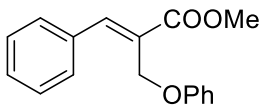
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.09 g, yield: 86% (two steps); m.p. 92-94 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.60 – 7.58 (m, 2H), 7.46 – 7.40 (m, 3H), 4.35 (s, 2H), 3.89 (s, 3H), 2.97 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.2, 147.1, 133.6, 130.1, 129.4, 129.0, 120.7, 54.2, 52.7, 42.5. The analytical data are consistent with the literature.[13]

Methyl (*Z*)-2-((*tert*-butylsulfonyl)methyl)-3-phenylacrylate (**3e**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.10 g, yield: 74% (three steps); m.p. 79-80 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.70 – 7.68 (m, 2H), 7.44 – 7.38 (m, 3H), 4.30 (s, 2H), 3.88 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 146.2, 133.9, 129.7, 129.2, 128.7, 120.1, 60.4, 52.6, 45.4, 23.3. TOF-HRMS Calcd. for $C_{15}H_{21}O_4S$ [M+H$^+$]: 297.1155, found 297.1147.

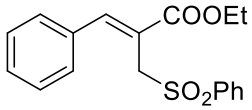
Methyl (*E*)-2-(phenoxymethyl)-3-phenylacrylate (**3f**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) afforded the product as pale yellow oil; 0.87 g, yield: 65% (three steps); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.51 – 7.48 (m,

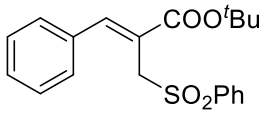
2H), 7.38 – 7.37 (m, 3H), 7.34 – 7.30 (m, 2H), 7.02 – 6.98 (m, 3H), 4.84 (s, 2H), 3.86 (s, 3H). The analytical data are consistent with the literature.[7]

Ethyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**3g**)



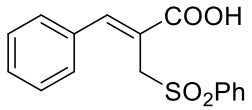
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) afforded the product as colorless oil; 1.44 g, yield: 87% (two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.86 – 7.84 (m, 2H), 7.61 – 7.58 (m, 1H), 7.49 – 7.46 (m, 4H), 7.37 – 7.35 (m, 3H), 4.49 (s, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.4, 146.0, 139.3, 133.7, 129.6, 129.1, 129.0, 128.7, 128.5, 121.2, 61.5, 55.0, 14.0. The analytical data are consistent with the literature.[14]

Tert-butyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**3h**)



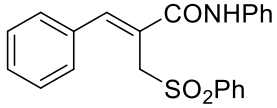
Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 1.58 g, yield: 88% (two steps); m.p. 76-78 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.82 (m, 3H), 7.61 – 7.56 (m, 1H), 7.49 – 7.45 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.32 (m, 3H), 4.47 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.4, 145.3, 139.4, 133.9, 133.6, 129.3, 129.0, 129.0, 128.7, 128.5, 122.5, 81.9, 54.9, 27.9. TOF-HRMS Calcd. for $C_{20}H_{23}O_4S$ [M+H$^+$]: 359.1312, found 359.1310.

(*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylic acid (**3i**)



By recrystallization the product as white solid; 0.91 g, yield: 90%; m.p. 180-182 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.89 – 7.88 (m, 2H), 7.65 – 7.62 (m, 1H), 7.56 – 7.54 (m, 2H), 7.53 – 7.50 (m, 2H), 7.42 – 7.40 (m, 3H), 4.50 (s, 2H). The analytical data are consistent with the literature.[15]

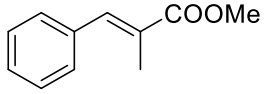
(*Z*)-*N*,3-diphenyl-2-((phenylsulfonyl)methyl)acrylamide (**3j**)



Purification by column chromatography (silica gel, PE:EA = 3:1, 5 x 22 cm) and recrystallization afforded the product as white solid; 0.74 g, yield: 65% (two steps); m.p. 148-144 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.52 (br s, 1H), 7.87 – 7.85 (m, 2H), 7.75 – 7.74 (m, 1H), 7.59 – 7.54

(m, 3H), 7.46 – 7.43 (m, 4H), 7.39 – 7.33 (m, 5H), 7.15 (tt, *J* = 7.4, 1.1 Hz, 1H), 4.51 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.7, 142.4, 138.6, 137.9, 134.1, 133.8, 129.3, 129.3, 129.0, 128.8, 128.7, 128.2, 125.9, 124.6, 120.1, 55.8. TOF-HRMS Calcd. for $C_{22}H_{20}NO_3S$ [M+H$^+$]: 378.1158, found 378.1149.

Methyl (*E*)-2-methyl-3-phenylacrylate (**3k**)



Purification by column chromatography (silica gel, PE:EA = 10:1, 5 x 22 cm) afforded the product as colorless oil; 0.87 g, yield: 99%; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.40 (d, *J* = 4.3 Hz, 4H), 7.34 – 7.31 (m, 1H), 3.82 (s, 3H), 2.13 (d, *J* = 1.5 Hz, 3H). The analytical data are consistent with the literature.[9]

4. General procedure for asymmetric hydrogenation of 1 and 3

General procedure: A stock solution was made by mixing 1.0 mol % $[Rh(COD)Cl]_2$ with 2.2 mol % (*R*,*R*)-f-spiroPhos in solvent (MeOH) at room temperature for 20 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (2.0 mL, 0.0025 mmol) was transferred by syringe into the vials charged with different substrates (0.125 mmol for each). The vials were subsequently transferred into which hydrogen gas was charged. The reaction was then stirred under H_2 (10 atm) at 90 ℃ for 48 h. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The conversion of products were determined by GC or ^{1}H NMR analysis. The crude products were concentrated and purified by flash column chromatography and the ee values were determined by HPLC, SFC analysis on a chiral stationary phase.

Gram scale experiment: A stock solution was made by mixing 1.0 mol % $[Rh(COD)Cl]_2$ with 2.2 mol % (*R*,*R*)-f-spiroPhos in solvent (MeOH) at room temperature for 20 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.064 mmol) was transferred by syringe into the vials charged with substrates **1a** (3.2 mmol). The vials were subsequently transferred into which hydrogen gas was charged. The reaction was then stirred under H_2 (10 atm) at 90 ℃ for 48 h. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of

silica gel to remove the metal complex. The solid was washed with CH_2Cl_2, and filtered to give the product **2a** as a white solid (0.99 g, 97% yield) with 96% ee determined by HPLC with a chiral column.

A stock solution was made by mixing 1.0 mol % $[Rh(COD)Cl]_2$ with 2.2 mol % (*R*,*R*)-f-spiroPhos in solvent (MeOH) at room temperature for 20 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (0.0035 mmol) was transferred by syringe into the vials charged with substrates **3e** (3.5 mmol). The vials were subsequently transferred into which hydrogen gas was charged. The reaction was then stirred under H_2 (80 atm) at 90 ℃ for 5 d. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The solid was washed with CH_2Cl_2, and filtered to give the product **4e** as a white solid (1.00 g, 96% yield) with 97% ee determined by SFC with a chiral column.

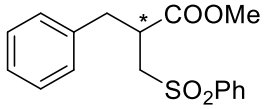
Deuteration experiment: A stock solution was made by mixing 1.0 mol % $[Rh(COD)Cl]_2$ with 2.2 mol % (*R*,*R*)-f-spiroPhos in solvent (MeOH) at room temperature for 20 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (2.0 mL, 0.0025 mmol) was transferred by syringe into the vials charged with substrates **1a** (0.125 mmol). The vials were subsequently transferred into which D_2 gas was charged. The reaction was then stirred under D_2 (10 atm) at 90 ℃ for 48 h. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The product was analyzed by ^{1}H NMR analysis. **2a-D-1**: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.66 – 7.63 (m, 1H), 7.55 – 7.52 (m, 2H), 7.26 – 7.20 (m, 3H), 7.05 – 7.04 (m, 2H), 3.65 – 3.61 (m, 1H), 3.53 (m, 3H), 3.13 – 3.10(m, 1H), 2.85 – 2.81 (m, 1H).

A stock solution was made by mixing 1.0 mol % $[Rh(COD)Cl]_2$ with 2.2 mol % (*R*,*R*)-f-spiroPhos in solvent (CD_3OD) at room temperature for 20 min in a nitrogen-filled glovebox. An aliquot of the catalyst solution (2.0 mL, 0.0025 mmol) was transferred by syringe into the vials charged with substrates **1a** (0.125 mmol). The vials were subsequently transferred into which H_2 gas was charged. The reaction was then

stirred under H_2 (10 atm) at 90 ℃ for 48 h. The hydrogen gas was released slowly and carefully. The solution was passed through a short column of silica gel to remove the metal complex. The product was analyzed by ^{1}H NMR analysis. **2a-D-2**: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.19 (m, 3H), 7.06 – 7.04 (m, 2H), 3.64 (dd, *J* = 14.2, 9.2 Hz, 1H), 3.53 (s, 3H), 3.23 – 3.09 (m, 2H), 3.03 (dd, *J* = 13.7, 6.9 Hz, 1H), 2.83 (dd, *J* = 13.7, 7.8 Hz, 1H).

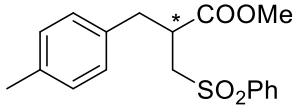
5. NMR, HPLC or SFC and HPLC, optical rotation and HRMS data of compounds 2 and 4

Methyl 2-benzyl-3-(phenylsulfonyl)propanoate (**2a**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 39.4 mg, yield: 99%; 98% ee; HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 12.0 min (major), t_R = 14.7 min (minor); m.p. 102-104 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.83 (m, 2H), 7.66 – 7.63 (m, 1H), 7.55 – 7.52 (m, 2H), 7.26 – 7.20 (m, 3H), 7.05 – 7.04 (m, 2H), 3.66 – 3.62 (m, 1H), 3.53 (m, 3H), 3.21 – 3.17 (m, 1H), 3.11 (ddd, *J* = 14.4, 3.4, 1.2 Hz, 1H), 3.03 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.82 (dd, *J* = 13.7, 7.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.8, 138.8, 136.5, 133.8, 129.2, 128.8, 128.7, 128.7, 128.1, 127.1, 56.2, 52.1, 41.7, 38.0. TOF-HRMS Calcd. for $C_{17}H_{19}O_4S$ [M+H$^+$]: 319.0999, found 319.0994.

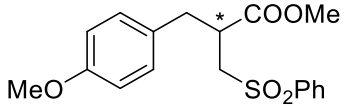
Methyl 2-(4-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2b**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as pale yellow solid; 40.7 mg, yield: 98%; 97% ee; $[\alpha]_D^{30}$ = + 10.7 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 13.9 min (major), t_R = 16.9 min (minor); m.p. 67-68 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 3.62 (dd, *J* = 14.2, 9.2 Hz, 1H), 3.54 (s, 3H), 3.19 – 3.15 (m, 1H), 3.11 (dd, *J* = 14.0, 3.4 Hz, 1H), 2.99 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.78 (dd, *J* =

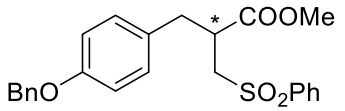
13.8, 8.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 138.9, 136.7, 133.8, 133.3, 129.4, 129.2, 128.7, 128.1, 56.2, 52.1, 41.8, 37.6, 21.0. TOF-HRMS Calcd. for $C_{18}H_{21}O_4S$ [M+H$^+$]: 333.1155, found 333.1150.

Methyl 2-(4-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2c**)



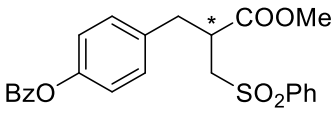
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as pale yellow oil; 43.1 mg, yield: 99%; 92% ee; $[\alpha]_D^{30}$ = + 16.2 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 19.2 min (major), t_R = 24.3 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.64 – 7.61 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.96 – 6.94 (m, 2H), 6.78 – 6.76 (m, 2H), 3.76 (s, 3H), 3.61 (dd, *J* = 14.1, 9.0 Hz, 1H), 3.52 (s, 3H), 3.18 – 3.08 (m, 2H), 2.96 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.76 (dd, *J* = 13.9, 7.7 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 158.6, 138.8, 133.7, 129.8, 129.2, 128.4, 128.1, 114.0, 56.1, 55.1, 52.1, 41.9, 37.1. TOF-HRMS Calcd. for $C_{18}H_{21}O_5S$ [M+H$^+$]: 349.1104, found 349.1101.

Methyl 2-(4-(benzyloxy)benzyl)-3-(phenylsulfonyl)propanoate (**2d**)



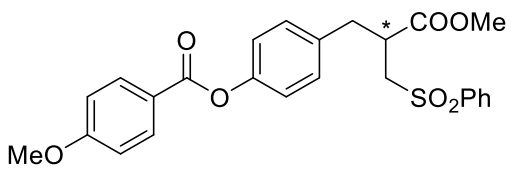
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 51.5 mg, yield: 97%; 92% ee; $[\alpha]_D^{30}$ = + 11.7 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-2 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 230 nm; t_R = 5.7 min (major), t_R = 7.4 min (minor); m.p. 98-99 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.32 (m, 1H), 6.97 – 6.96 (m, 2H), 6.87 – 6.85 (m, 2H), 5.03 (s, 2H), 3.62 (dd, *J* = 14.1, 9.0 Hz, 1H), 3.53 (s, 3H), 3.18 – 3.10 (m, 1H), 2.97 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.77 (dd, *J* = 13.9, 7.7 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 157.8, 138.9, 136.9, 133.8, 129.9, 129.2, 128.7, 128.6, 128.1, 128.0, 127.4, 115.1, 70.0, 56.2, 52.2, 41.9, 37.2. TOF-HRMS Calcd. for $C_{24}H_{25}O_5S$ [M+H$^+$]: 425.1417, found 425.1417.

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl benzoate (**2e**)



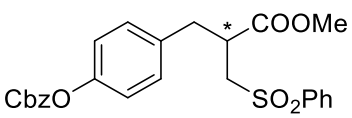
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 52.6 mg, yield: 96%; 96% ee; $[\alpha]_D^{30}$ = + 8.4 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 6.3 min (major), t_R = 6.9 min (minor); m.p. 156-158 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.18 (m, 2H), 7.88 – 7.85 (m, 2H), 7.68 – 7.62 (m, 2H), 7.58 – 7.49 (m, 4H), 7.13 – 7.11 (m, 4H), 3.65 (dd, *J* = 14.0, 8.7 Hz, 1H), 3.56 (s, 3H), 3.25 – 3.13 (m, 2H), 3.06 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.90 (dd, *J* = 13.8, 7.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 165.0, 150.0, 138.8, 134.2, 133.9, 133.6, 130.1, 129.9, 129.4, 129.3, 128.6, 128.1, 122.0, 56.2, 52.3, 41.7, 37.3. TOF-HRMS Calcd. for $C_{24}H_{23}O_6S$ [M+H$^+$]: 439.1210, found 439.1207.

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl 4-methoxybenzoate (**2f**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 56.2 mg, yield: 96%; 92% ee; $[\alpha]_D^{30}$ = + 9.6 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 70:30, 3 mL/min, 210 nm; t_R = 9.8 min (minor), t_R = 11.3 min (major); m.p. 120-121 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 – 8.13 (m, 2H), 7.87 – 7.85 (m, 2H), 7.67 – 7.64 (m, 1H), 7.57 – 7.54 (m, 2H), 7.11 – 7.09 (m, 4H), 7.00 – 6.97 (m, 2H), 3.90 (s, 3H), 3.65 (dd, *J* = 14.3, 8.9 Hz, 1H), 3.56 (s, 3H), 3.23 – 3.19 (m, 1H), 3.15 (dd, *J* = 14.3, 3.7 Hz, 1H), 3.05 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.89 (dd, *J* = 13.8, 7.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.8, 164.8, 163.9, 150.1, 138.8, 134.0, 133.9, 132.3, 129.9, 129.3, 128.2, 122.1, 121.7, 113.9, 56.2, 55.5, 52.3, 41.7, 37.3.TOF-HRMS Calcd. for $C_{25}H_{25}O_7S$ [M+H$^+$]: 469.1316, found 469.1310.

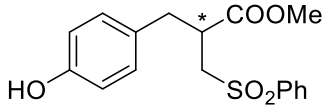
Methyl 2-(4-(((benzyloxy)carbonyl)oxy)benzyl)-3-(phenylsulfonyl)propanoate (**2g**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 56.8

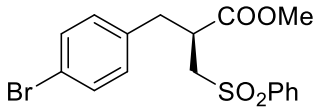
mg, yield: 97%; 93% ee; $[\alpha]_D^{30}$ = + 4.5 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 6.7 min (major), t_R = 7.3 min (minor); m.p. 90-92 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H), 7.68 – 7.60 (m, 1H), 7.55 – 7.51 (m, 2H), 7.45 – 7.36 (m, 5H), 7.11 – 7.03 (m, 4H), 5.26 (s, 2H), 3.66 – 3.60 (m, 1H), 3.53 (s, 3H), 3.21 – 3.10 (m, 2H), 3.01 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.86 (dd, *J* = 13.8, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 153.4, 150.1, 138.7, 134.6, 134.3, 133.8, 129.8, 129.2, 128.7, 128.6, 128.4, 128.0, 121.2, 70.3, 56.1, 52.2, 41.6, 37.1. TOF-HRMS Calcd. for $C_{25}H_{25}O_7S$ [M+H$^+$]: 469.1316, found 469.1314.

Methyl 2-(4-hydroxybenzyl)-3-(phenylsulfonyl)propanoate (**2h**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 39.7 mg, yield: 95%; 92% ee; $[\alpha]_D^{30}$ = + 5.9 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 8.3 min (major), t_R = 9.5 min (minor); m.p. 136-138 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 6.90 – 6.89 (m, 2H), 6.70 – 6.69 (m, 2H), 3.61 (dd, *J* = 14.0, 9.0 Hz, 1H), 3.52 (s, 3H), 3.16 – 3.09 (m, 2H), 2.95 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.75 (dd, *J* = 13.9, 7.6 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.1, 154.8, 138.8, 133.9, 130.1, 129.3, 128.4, 128.2, 115.6, 56.2, 52.2, 41.9, 37.2. TOF-HRMS Calcd. for $C_{17}H_{19}O_5S$ [M+H$^+$]: 335.0948, found 335.0942.

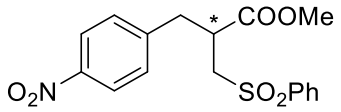
(*S*)-Methyl 2-(4-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2i**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 48.2 mg, yield: 97%; 99% ee; $[\alpha]_D^{30}$ = + 11.0 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 18.4 min (major), t_R = 22.9 min (minor); m.p. 88-90 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.68 – 7.65 (m, 1H), 7.56 – 7.53 (m, 2H), 7.39 – 7.36 (m, 2H), 6.96 – 6.93 (m, 2H), 3.61 (dd, *J* = 14.3, 8.7 Hz, 1H), 3.54 (s, 3H), 3.20 – 3.16 (m, 1H), 3.09 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.99 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.84 (dd,

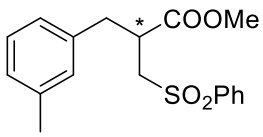
J = 13.9, 7.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.6, 138.8, 135.6, 133.9, 131.8, 130.6, 129.3, 128.1, 121.1, 56.2, 52.3, 41.5, 37.3. TOF-HRMS Calcd. for $C_{17}H_{18}{}^{79}BrO_4S$ [M+H$^+$]: 397.0104, found 397.0103; TOF-HRMS Calcd. for $C_{17}H_{18}{}^{81}BrO_4S$ [M+H$^+$]: 399.0090, found 399.0083.

Methyl 2-(4-nitrobenzyl)-3-(phenylsulfonyl)propanoate (**2j**)



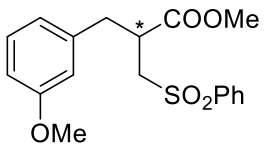
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 41.8 mg, yield: 92%; 98% ee; $[\alpha]_D^{30}$ = + 22.8 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 30:70, 1 mL/min, 210 nm; t_R = 54.2 min (major), t_R = 63.4 min (minor); m.p. 116-118 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.65 – 7.62 (m, 1H), 7.54 – 7.51 (m, 2H), 6.82 – 6.81 (m, 2H), 6.57 – 6.56 (m, 2H), 3.60 (dd, *J* = 15.0, 10.1 Hz, 1H), 3.52 (s, 3H), 3.13 – 3.08 (m, 2H), 2.91 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.69 (dd, *J* = 13.9, 7.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 145.3, 138.8, 133.8, 129.7, 129.2, 128.1, 126.1, 115.3, 56.1, 52.1, 41.9, 37.3. TOF-HRMS Calcd. for $C_{17}H_{18}NO_6S$ [M+H$^+$]: 364.0849, found 364.0842.

Methyl 2-(3-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2k**)



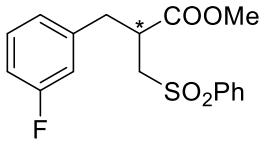
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 40.7 mg, yield: 98%; 98% ee; $[\alpha]_D^{30}$ = + 1.3 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 13.3 min (major), t_R = 16.5 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.63 (dd, *J* = 14.0, 9.2 Hz, 1H), 3.54 (s, 3H), 3.19 – 3.10 (m, 2H), 2.99 (dd, *J* = 13.6, 6.5 Hz, 1H), 2.76 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 138.8, 138.3, 136.4, 133.7, 129.6, 129.2, 128.5, 128.1, 127.8, 125.8, 56.1, 52.1, 41.8, 37.9, 21.3. TOF-HRMS Calcd. for $C_{18}H_{21}O_4S$ [M+H$^+$]: 333.1155, found 333.1147.

Methyl 2-(3-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2l**)



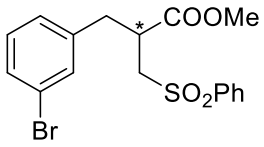
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 41.4 mg, yield: 95%; 95% ee; $[\alpha]_D^{30}$ = - 3.4 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-2 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 4.6 min (minor), t_R = 4.9 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.64 (td, *J* = 7.4, 1.3 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.17 – 7.14 (m, 1H), 6.76 – 6.75 (m, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.59 – 6.58 (m, 1H), 3.75 (s, 3H), 3.63 (dd, *J* = 14.6, 9.4 Hz, 1H), 3.55 (s, 3H), 3.20 – 3.15 (m, 1H), 3.14 – 3.11 (m, 1H), 3.01 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.80 – 2.77 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.8, 159.8, 138.0, 133.8, 129.7, 129.2, 128.1, 121.1, 114.4, 112.5, 56.1, 55.1, 52.2, 41.6, 37.9. TOF-HRMS Calcd. for $C_{18}H_{21}O_5S$ [M+H$^+$]: 349.1104, found 349.1102.

Methyl 2-(3-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2m**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 40.8 mg, yield: 97%; 99.2% ee; $[\alpha]_D^{30}$ = + 2.7 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 2.8 min (minor), t_R = 3.6 min (major); m.p. 70-72 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.19 (m, 1H), 6.91 (td, *J* = 8.5, 2.5 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 9.6 Hz, 1H), 3.62 (dd, *J* = 14.2, 8.7 Hz, 1H), 3.54 (s, 3H), 3.21 – 3.15 (m, 1H), 3.13 – 3.08 (m, 1H), 3.02 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.86 (dd, *J* = 13.8, 7.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 162.7 (d, *J* = 246.9 Hz), 139.0 (d, *J* = 7.3 Hz), 138.6, 133.9, 130.2 (d, *J* = 8.4 Hz), 129.3, 128.1, 124.6 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 21.1 Hz), 114.1 (d, *J* = 20.9 Hz), 56.1, 52.2, 41.5, 37.5. TOF-HRMS Calcd. for $C_{17}H_{18}FO_4S$ [M+H$^+$]: 337.0904, found 337.0896.

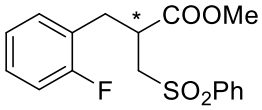
Methyl 2-(3-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2n**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 47.7 mg, yield: 96%; 99.8% ee; $[\alpha]_D^{30}$ = +3.3 (c = 1.0, CH_2Cl_2); SFC condition: Lux

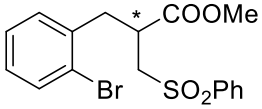
5u Amylose-2 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R =5.4 min (minor), t_R = 6.2 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.67 – 7.65 (m, 1H), 7.57 – 7.54 (m, 2H), 7.35 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.20 (t, *J* = 1.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.00 (dt, *J* = 7.7, 1.3 Hz, 1H), 3.62 (dd, *J* = 14.3, 8.8 Hz, 1H), 3.54 (s, 3H), 3.19 – 3.14 (m, 1H), 3.10 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.99 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.83 (dd, *J* = 13.8, 7.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 138.9, 138.7, 134.0, 131.9, 130.3, 130.2, 129.3, 128.1, 127.5, 122.7, 56.2, 52.3, 41.6, 37.4. TOF-HRMS Calcd. for $C_{17}H_{18}{}^{79}BrO_4S$ [M+H$^+$]: 397.0104, found 397.0103; TOF-HRMS Calcd. for $C_{17}H_{18}{}^{81}BrO_4S$ [M+H$^+$]: 399.0090, found 399.0083.

Methyl 2-(2-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2o**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 40.8 mg, yield: 97%; 96% ee; $[\alpha]_D^{30}$ = + 5.2 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 4.2 min (minor), t_R = 6.4 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 2H), 7.66 – 7.62 (m, 1H), 7.55 – 7.51 (m, 2H), 7.21 (dddd, *J* = 9.0, 7.2, 5.1, 2.3 Hz, 1H), 7.08 – 7.03 (m, 2H), 7.01 – 6.97 (m, 1H), 3.67 (ddd, *J* = 14.0, 9.4, 4.6 Hz, 1H), 3.51 (s, 3H), 3.26 – 3.19 (m, 1H), 3.13 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.97 – 2.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 161.0 (d, *J* = 246.0 Hz), 138.7, 133.8, 131.1 (d, *J* = 4.3 Hz), 129.2, 129.1 (d, *J* = 8.2 Hz), 128.1, 124.2 (d, *J* = 3.8 Hz), 123.5 (d, *J* = 15.6 Hz), 115.5 (d, *J* = 21.9 Hz). TOF-HRMS Calcd. for $C_{17}H_{18}FO_4S$ [M+H$^+$]: 337.0904, found 337.0901.

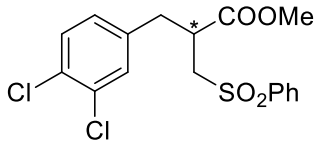
Methyl 2-(2-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2p**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 45.7 mg, yield: 92%; 97% ee; $[\alpha]_D^{30}$ = + 8.8 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-2 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 5.7 min (minor), t_R = 6.3 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.65 – 7.63 (m, 1H),

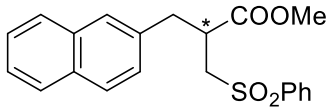
7.54 – 7.51 (m, 2H), 7.47 (d, *J* = 1.3 Hz, 1H), 7.20 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 (ddd, *J* = 15.5, 7.7, 1.7 Hz, 2H), 3.74 (dd, *J* = 14.4, 10.2 Hz, 1H), 3.51 (s, 3H), 3.31 – 3.26 (m, 1H), 3.14 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.04 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.94 (dd, *J* = 13.7, 7.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.7, 138.6, 136.1, 133.8, 133.2, 131.0, 129.2, 128.9, 128.2, 127.6, 124.5, 56.5, 52.2, 40.3, 38.4. TOF-HRMS Calcd. for $C_{17}H_{18}{}^{79}BrO_4S$ [M+H$^+$]: 397.0104, found 397.0103; TOF-HRMS Calcd. for $C_{17}H_{18}{}^{81}BrO_4S$ [M+H$^+$]: 399.0090, found 399.0083.

Methyl 2-(3,4-dichlorobenzyl)-3-(phenylsulfonyl)propanoate (**2q**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 45.5 mg, yield: 94%; 99.9% ee; $[\alpha]_D^{30}$ = + 13.6 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 5.9 min (minor), t_R = 7.9 min (major); m.p. 92-94 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 – 7.54 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.93 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.61 (dd, *J* = 14.1, 8.2 Hz, 1H), 3.55 (s, 3H), 3.20 – 3.14 (m, 1H), 3.10 (dd, *J* = 14.1, 4.3 Hz, 1H), 2.98 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.86 (dd, *J* = 13.8, 7.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 138.6, 136.9, 134.1, 132.6, 131.3, 130.8, 130.6, 129.3, 128.3, 128.1, 56.1, 52.4, 41.4, 36.8. TOF-HRMS Calcd. for $C_{17}H_{17}{}^{35}Cl_2O_4S$ [M+H$^+$]: 387.0219, found 387.0215; TOF-HRMS Calcd. for $C_{17}H_{17}{}^{37}Cl_2O_4S$ [M+H$^+$]: 389.0189, found 389.0181.

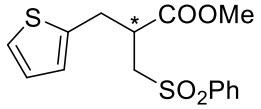
Methyl 3-(naphthalen-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2r**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 43.3 mg, yield: 94%; 94% ee; $[\alpha]_D^{30}$ = + 10.5 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 50:50, 1 mL/min, 210 nm; t_R = 20.2 min (major), t_R = 23.7 min (minor); m.p. 98-100 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 3H), 7.75 – 7.72 (m, 1H), 7.63 – 7.59 (m, 1H), 7.51 – 7.45 (m, 5H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.69 (dd, *J* = 14.3, 9.2 Hz, 1H), 3.54 (s, 3H), 3.34 – 3.27 (m, 1H),

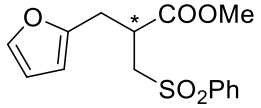
3.23 – 3.15 (m, 2H), 2.99 (dd, *J* = 13.6, 7.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 138.8, 134.0, 133.8, 133.3, 132.4, 129.2, 128.5, 128.1, 127.7, 127.6, 127.5, 126.7, 126.2, 125.8, 56.2, 52.2, 41.7, 38.1. TOF-HRMS Calcd. for $C_{21}H_{21}O_4S$ [M+H$^+$]: 369.1155, found 369.1154.

Methyl 3-(phenylsulfonyl)-2-(thiophen-2-ylmethyl)propanoate (**2s**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 38.9 mg, yield: 96%; 99.9% ee; $[\alpha]_D^{30}$ = - 3.4 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 20:80, 1 mL/min, 210 nm; t_R = 36.2 min (major), t_R = 39.8 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.87 (m, 2H), 7.67 – 7.64 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.89 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.77 (dd, *J* = 3.5, 1.1 Hz, 1H), 3.64 – 3.60 (m, 4H), 3.30 – 3.27 (m, 1H), 3.25 – 3.20 (m, 1H), 3.19 – 3.15 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.3, 138.9, 138.3, 133.9, 129.3, 128.1, 127.0, 126.7, 124.8, 55.7, 52.4, 41.8, 31.6. TOF-HRMS Calcd. for $C_{15}H_{17}O_4S_2$ [M+H$^+$]: 325.0563, found 325.0556.

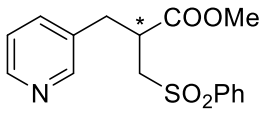
Methyl 3-(furan-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2t**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 37.4 mg, yield: 97%; 99.9% ee; $[\alpha]_D^{30}$ = - 6.2 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 4.1 min (major), t_R = 5.0 min (minor). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 2H), 7.67 – 7.64 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.24 (m, 1H), 6.24 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.03 (dd, *J* = 3.2, 0.9 Hz, 1H), 3.66 (dd, *J* = 14.4, 8.4 Hz, 1H), 3.59 (s, 3H), 3.27 – 3.23 (m, 1H), 3.18 (dd, *J* = 14.4, 4.2 Hz, 1H), 3.05 (dd, *J* = 15.1, 6.2 Hz, 1H), 2.98 – 2.94 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.4, 150.4, 142.1, 138.8, 133.9, 129.3, 128.1, 110.2, 107.8, 56.0, 52.4, 39.4, 30.2. TOF-HRMS Calcd. for $C_{15}H_{17}O_5S$ [M+H$^+$]: 309.0791, found 309.0789.

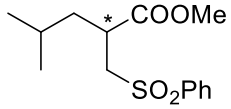
Methyl 3-(phenylsulfonyl)-2-(pyridin-3-ylmethyl)propanoate (**2u**)

Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the



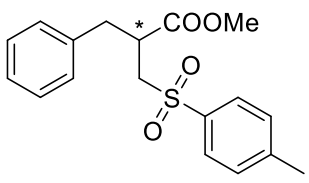
product as pale yellow solid; 37.9 mg, yield: 95%; 98% ee; $[\alpha]_D^{30}$ = + 10.6 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 20:80, 1 mL/min, 210 nm; t_R = 23.9 min (major), t_R = 26.0 min (minor); m.p. 68-70 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.35 (s, 1H), 7.88 – 7.83 (m, 2H), 7.67 – 7.63 (m, 1H), 7.57 – 7.52 (m, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.24 (dt, *J* = 8.8, 5.1 Hz, 1H), 3.61 (dd, *J* = 14.1, 8.1 Hz, 1H), 3.51 (s, 3H), 3.26 – 3.19 (m, 1H), 3.12 (dd, *J* = 14.2, 4.6 Hz, 1H), 2.99 (qd, *J* = 14.0, 7.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 149.7, 148.1, 138.7, 136.9, 134.1, 132.6, 129.4, 128.1, 123.7, 56.3, 52.4, 41.3, 34.8. TOF-HRMS Calcd. for $C_{16}H_{18}NO_4S$ [M+H$^+$]: 320.0951, found 320.0947.

Methyl 4-methyl-2-((phenylsulfonyl)methyl)pentanoate (**2v**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 5.3 mg, yield: 15%; 95% ee; $[\alpha]_D^{30}$ = - 32.9 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 3.3 min (minor), t_R = 3.8 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 – 7.89 (m, 2H), 7.67 – 7.64 (m, 1H), 7.58 – 7.55 (m, 2H), 3.64 (dd, *J* = 14.3, 10.0 Hz, 1H), 3.57 (s, 3H), 3.08 (dd, *J* = 14.3, 2.9 Hz, 1H), 2.99 – 2.95 (m, 1H), 1.55 (ddd, *J* = 13.1, 8.6, 6.2 Hz, 1H), 1.51 – 1.45 (m, 1H), 1.32 (ddd, *J* = 13.2, 7.8, 6.6 Hz, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.9, 138.9, 133.9, 129.2, 128.2, 57.8, 52.1, 41.6, 38.3, 25.7, 22.3, 21.8. TOF-HRMS Calcd. for $C_{14}H_{21}O_4S$ [M+H$^+$]: 285.1155, found 285.1152.

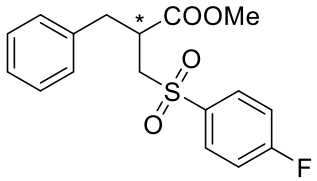
Methyl 2-benzyl-3-tosylpropanoate (**4a**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 40.7 mg, yield: 98%; 98% ee; $[\alpha]_D^{30}$ = + 4.9 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 20:80, 1 mL/min, 210 nm; t_R = 38.5 min (major), t_R = 45.6 min (minor); m.p. 85-87 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.72 – 7.71 (m, 2H), 7.33 – 7.31 (m, 2H), 7.26 –

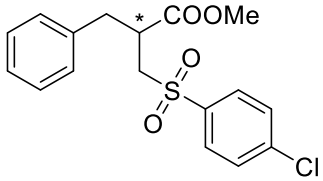
7.21 (m, 3H), 7.06 – 7.04 (m, 2H), 3.63 – 3.59 (m, 1H), 3.54 (s, 3H), 3.21 – 3.16 (m, 1H), 3.10 (dd, *J* = 14.3, 3.6 Hz, 1H), 3.02 (dd, *J* = 13.8, 7.1 Hz, 1H), 2.83 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.9, 144.8, 136.6, 136.0, 129.8, 128.9, 128.7, 128.2, 127.1, 56.4, 52.1, 41.8, 38.0, 21.6. TOF-HRMS Calcd. for $C_{18}H_{21}O_4S$ [M+H$^+$]: 333.1155, found 333.1148.

Methyl 2-benzyl-3-((4-fluorophenyl)sulfonyl)propanoate (**4b**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as pale yellow oil; 39.9 mg, yield: 95%; 97% ee; $[\alpha]_D^{30}$ = - 3.3 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 3.0 min (minor), t_R = 4.2 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.82 (m, 2H), 7.28 – 7.18 (m, 5H), 7.06 – 7.03 (m, 2H), 3.64 (dd, *J* = 14.1, 9.3 Hz, 1H), 3.56 (s, 3H), 3.20 – 3.08 (m, 2H), 3.03 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.81 (dd, *J* = 13.7, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 165.8 (d, *J* = 256.8 Hz), 136.3, 134.8 (d, *J* = 3.2 Hz), 131.0 (d, *J* = 9.7 Hz), 128.8, 128.7, 127.2, 116.5 (d, *J* = 22.6 Hz), 56.3, 52.2, 41.8, 38.0. TOF-HRMS Calcd. for $C_{17}H_{18}FO_4S$ [M+H$^+$]: 337.0904, found 337.0898.

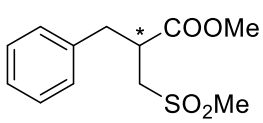
Methyl 2-benzyl-3-((4-chlorophenyl)sulfonyl)propanoate (**4c**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as pale yellow solid; 42.8 mg, yield: 97%; 96% ee; $[\alpha]_D^{30}$ = + 6.9 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Cellulose-2 (250 × 4.60 mm), ipa:hex = 20:80, 1 mL/min, 210 nm; t_R = 20.9 min (minor), t_R = 22.5 min (major); m.p. 64-66 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 – 7.74 (m, 2H), 7.50 – 7.48 (m, 2H), 7.27 – 7.22 (m, 3H), 7.05 – 7.03 (m, 2H), 3.64 (dd, *J* = 14.3, 9.3 Hz, 1H), 3.56 (s, 3H), 3.18 – 3.15 (m, 1H), 3.10 (dd, *J* = 14.3, 3.3 Hz, 1H), 3.04 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.81 (dd, *J* = 13.7, 8.1 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.8, 140.6, 137.3, 136.3, 129.6, 129.5, 128.8, 128.7, 127.2, 56.2, 52.2, 41.8, 38.0. TOF-HRMS Calcd. for $C_{17}H_{18}{}^{35}ClO_4S$ [M+H$^+$]: 353.0609, found 353.0603; TOF-HRMS

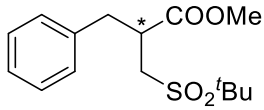
Calcd. for $C_{17}H_{18}{}^{37}ClO_4S$ [M+H$^+$]: 355.0582, found 353.0577.

Methyl 2-benzyl-3-(methylsulfonyl)propanoate (**4d**)



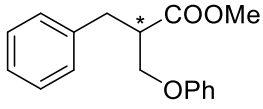
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 31.7 mg, yield: 99%; 99.6% ee; $[\alpha]_D^{30}$ = + 12.0 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 5.2 min (minor), t_R = 8.2 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 3H), 7.16 – 7.13 (m, 2H), 3.69 (d, *J* = 2.5 Hz, 3H), 3.57 – 3.51 (m, 1H), 3.36 – 3.29 (m, 1H), 3.13 – 3.00 (m, 1H), 3.02 (dt, *J* = 14.2, 3.0 Hz, 1H), 2.92 – 2.83 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 136.4, 128.9, 128.7, 127.2, 54.8, 52.3, 41.5, 41.4, 37.8. TOF-HRMS Calcd. for $C_{12}H_{17}O_4S$ [M+H$^+$]: 257.0842, found 257.0837.

Methyl (*Z*)-2-((*tert*-butylsulfonyl)methyl)-3-phenylacrylate (**4e**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow solid; 44.2 mg, yield: 98%; 97% ee; $[\alpha]_D^{30}$ = - 2.8 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 2.2 min (major), t_R = 3.0 min (minor); m.p. 79-80 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.18 – 7.16 (m, 2H), 3.66 (s, 3H), 3.47 – 3.39 (m, 2H), 3.11 (dd, *J* = 13.7, 6.7 Hz, 1H), 3.00 – 2.94 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.5, 136.9, 129.0, 128.6, 127.0, 59.3, 52.2, 45.8, 40.0, 37.9, 23.2. The analytical data are consistent with the literature.[16]

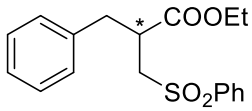
Methyl 2-benzyl-3-phenoxypropanoate (**4f**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 32.4 mg, yield: 96%; 94% ee; $[\alpha]_D^{30}$ = - 16.5 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 95:5, 3 mL/min, 210 nm; t_R = 5.2 min (minor), t_R = 5.5 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 4H), 7.25 – 7.22 (m, 1H), 7.21 – 7.19 (m, 2H), 6.97 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.90 – 6.88 (m, 2H), 4.16 (dd, *J* = 9.1, 6.6 Hz, 1H), 4.07 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.69 (s, 3H), 3.19 – 3.10 (m, 2H), 3.02

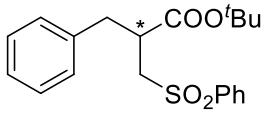
(dd, J = 13.6, 7.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 173.5, 158.5, 138.3, 129.4, 129.0, 128.5, 126.6, 121.0, 114.6, 67.2, 51.8, 47.1, 34.5. TOF-HRMS Calcd. for $C_{17}H_{19}O_3$ [M+H$^+$]: 271.1329, found 271.1323.

Ethyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4g**)



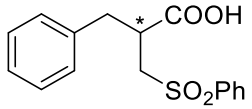
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as yellow oil; 39.9 mg, yield: 96%; 98% ee; $[\alpha]_D^{30}$ = + 3.6 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5u Amylose-1 (250 × 4.60 mm), ipa:hex = 5:95, 1 mL/min, 210 nm; t_R = 36.9 min (minor), t_R = 39.1 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 – 7.83 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.06 – 7.04 (m, 2H), 3.95 (qd, J = 7.1, 1.4 Hz, 2H), 3.64 (dd, J = 14.3, 9.1 Hz, 1H), 3.19 – 3.14 (m, 1H), 3.11 (dd, J = 14.3, 3.5 Hz, 1H), 3.00 (dd, J = 13.7, 7.2 Hz, 1H), 2.83 (dd, J = 13.7, 7.8 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.3, 138.8, 136.5, 133.7, 129.1, 128.8, 128.5, 128.0, 126.9, 61.1, 56.2, 41.7, 38.0, 13.8. TOF-HRMS Calcd. for $C_{18}H_{21}O_4S$ [M+H$^+$]: 333.1155, found 333.1148.

Tert-butyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4h**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 42.8 mg, yield: 95%; 97% ee; $[\alpha]_D^{30}$ = - 9.0 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Amylose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210 nm; t_R = 5.7 min (minor), t_R = 7.3 min (major); m.p. 88-89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.66 – 7.62 (m, 1H), 7.56 – 7.51 (m, 2H), 7.26 – 7.18 (m, 3H), 7.08 – 7.06 (m, 2H), 3.66 – 3.59 (m, 1H), 3.12 – 3.04 (m, 2H), 2.97 (dd, J = 13.7, 7.2 Hz, 1H), 2.82 (dd, J = 13.7, 7.4 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 139.1, 136.7, 133.7, 129.2, 129.0, 128.5, 128.0, 126.9, 81.7, 56.4, 42.2, 38.2, 27.7. TOF-HRMS Calcd. for $C_{20}H_{25}O_4S$ [M+H$^+$]: 361.1468, found 368.1463.

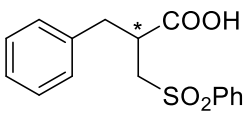
2-Benzyl-3-(phenylsulfonyl)propanoic acid (**4i**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as colorless oil; 35.8 mg, yield: 94%;

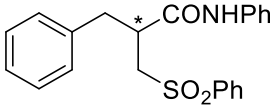
96% ee; $[\alpha]_D^{30}$ = - 3.0 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.97 (br s, 1H), 7.45 – 7.42 (m, 2H), 7.31 – 7.29 (m, 3H), 7.24 – 7.19 (m, 5H), 3.09 (dd, *J* = 13.5, 6.5 Hz, 2H), 2.79 – 2.78 (m, 1H), 2.68 (dd, *J* = 13.5, 8.1 Hz, 2H). The analytical data are consistent with the literature.[14] The product **4i** was dissolved in CH_2Cl_2, followed by addition of aniline, EDC, and DMAP at 0 °C, and stirred for 4 h. The corresponding amide was purified by chromatography. SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 254 nm; t_R = 7.0 min (major), t_R = 9.6 min (minor).

2-Benzyl-3-(phenylsulfonyl)propanoic acid (**4i'**)



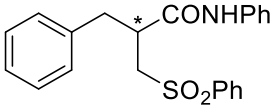
Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as colorless oil; 36.1 mg, yield: 95%; $[\alpha]_D^{30}$ = - 3.5 (c = 1.0, CH_2Cl_2).

2-Benzyl-*N*-phenyl-3-(phenylsulfonyl)propenamide (**4j**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 44.1 mg, yield: 93%; 92% ee; $[\alpha]_D^{30}$ = - 24.3 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 254 nm; t_R = 7.2 min (minor), t_R = 9.3 min (major); 124-125 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 – 7.86 (m, 2H), 7.60 – 7.58 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.22 (m, 5H), 7.19 – 7.15 (m, 4H), 7.07 (td, *J* = 7.2, 1.3 Hz, 1H), 3.86 (dd, *J* = 14.1, 8.6 Hz, 1H), 3.25 – 3.19 (m, 2H), 3.05 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.93 (dd, *J* = 13.5, 6.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.7, 139.1, 137.3, 137.1, 133.9, 129.3, 129.0, 128.9, 128.8, 127.9, 127.1, 124.6, 120.2, 57.5, 44.3, 39.1. TOF-HRMS Calcd. for $C_{22}H_{22}NO_3S$ [M+H$^+$]: 380.1315, found 380.1312.

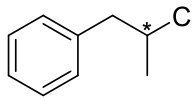
2-Benzyl-*N*-phenyl-3-(phenylsulfonyl)propenamide (**4j'**)



Purification by flash column chromatography (silica gel, PE:EA = 3:1) afforded the product as white solid; 41.0 mg, yield: 91%; 97% ee; $[\alpha]_D^{30}$ = + 28.4 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-1 (250 × 4.60 mm), CO_2:MeOH = 80:20, 3 mL/min, 210

nm; t_R = 7.1 min (major), t_R = 9.5 min (minor).

Methyl 2-methyl-3-phenylpropanoate (**4k**)



Purification by flash column chromatography (silica gel, PE:EA = 10:1) afforded the product as yellow oil; 21.2 mg, yield: 95%; 99% ee; $[\alpha]_D^{30}$ = - 16.9 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5u Cellulose-3 (250 × 4.60 mm), CO_2:MeOH = 95:5, 3 mL/min, 210 nm; t_R = 1.8 min (minor), t_R = 1.9 min (major). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.18 – 7.16 (m, 2H), 3.64 (s, 3H), 3.04 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.78 – 2.72 (m, 1H), 2.67 (dd, *J* = 13.4, 7.8 Hz, 1H), 1.16 (d, *J* = 6.9 Hz, 3H). The analytical data are consistent with the literature.[17]

6. References

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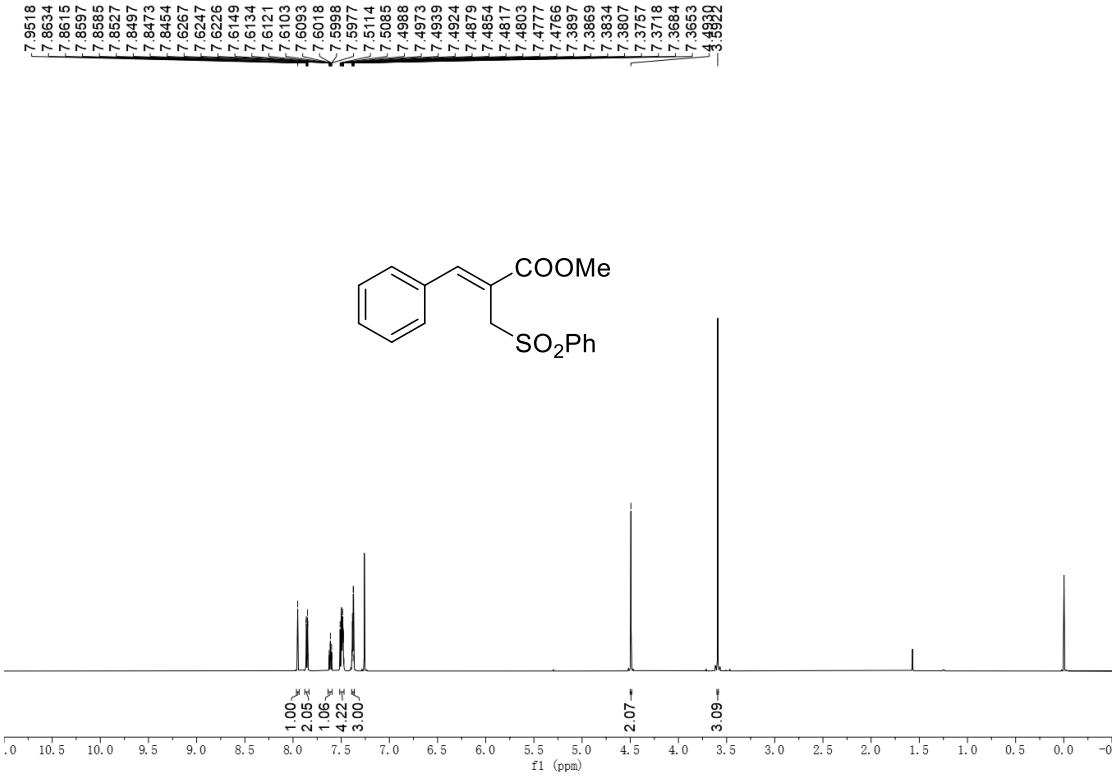
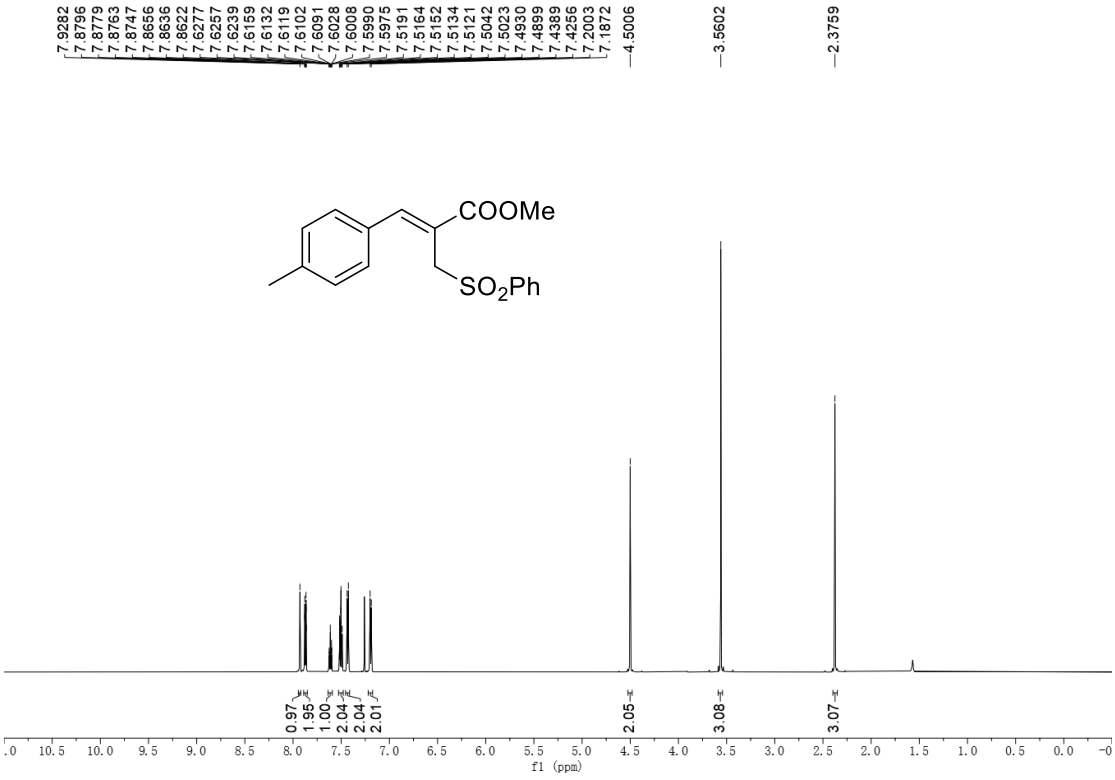
7. NMR, SFC and HPLC spectra

Methyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**1a**)

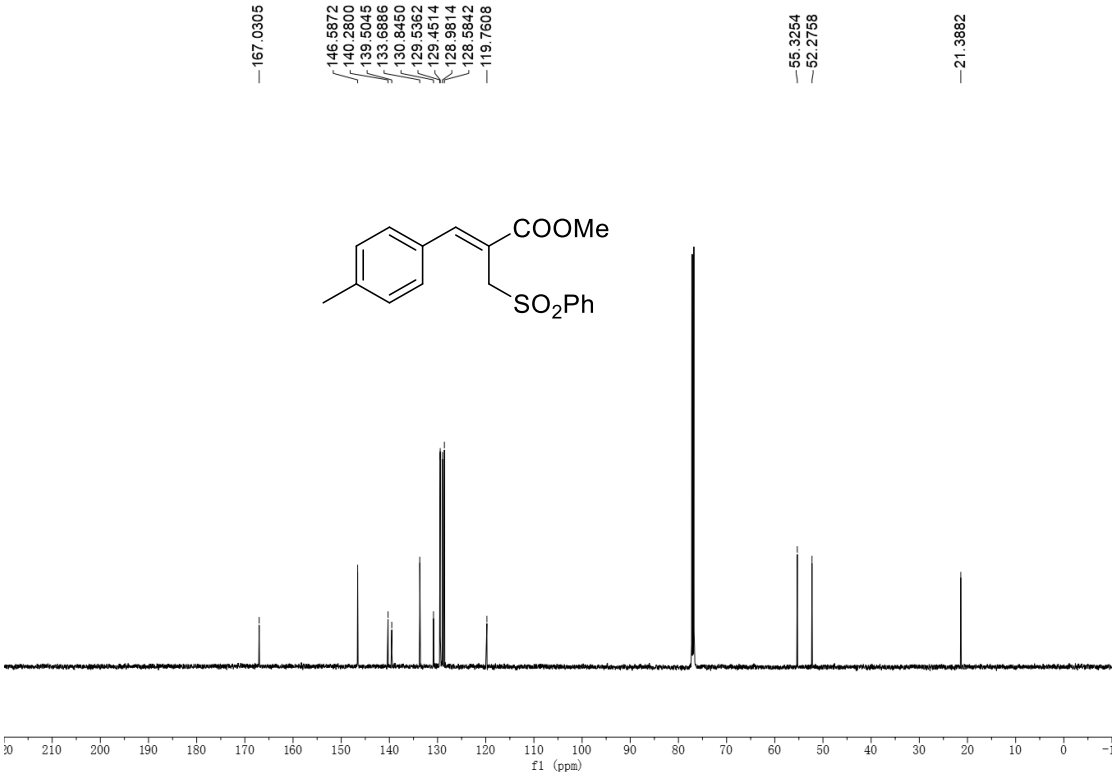


^{1}H NMR (600 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(*p*-tolyl)acrylate (**1b**)

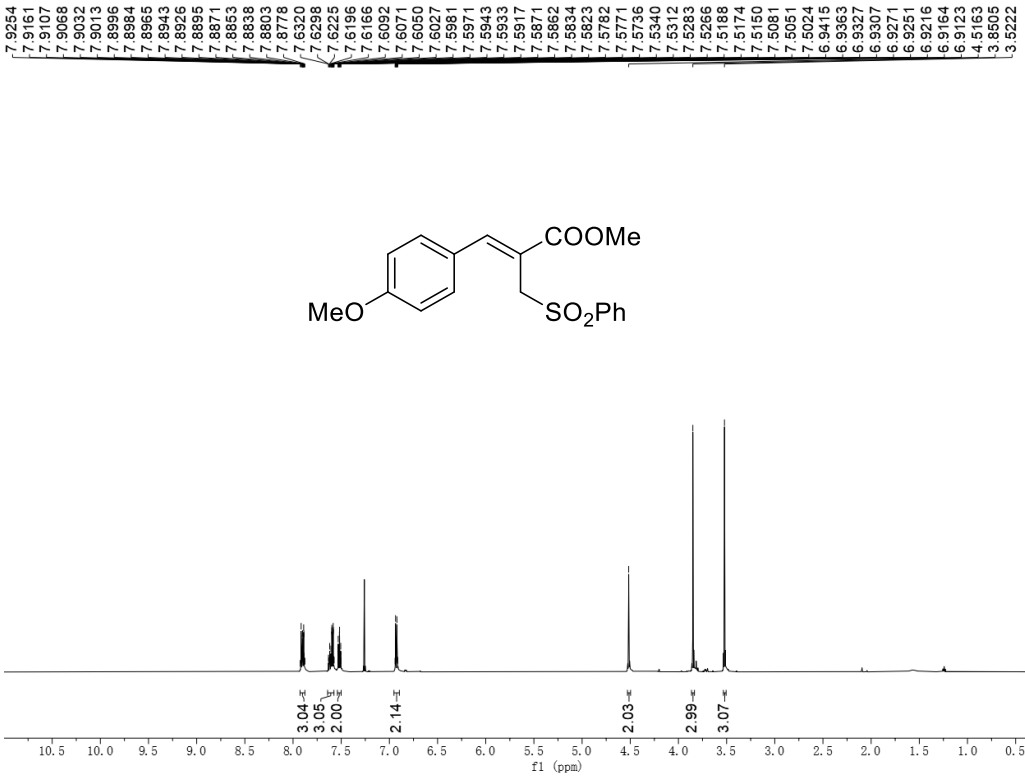


^{1}H NMR (600 MHz, Chloroform-*d*)

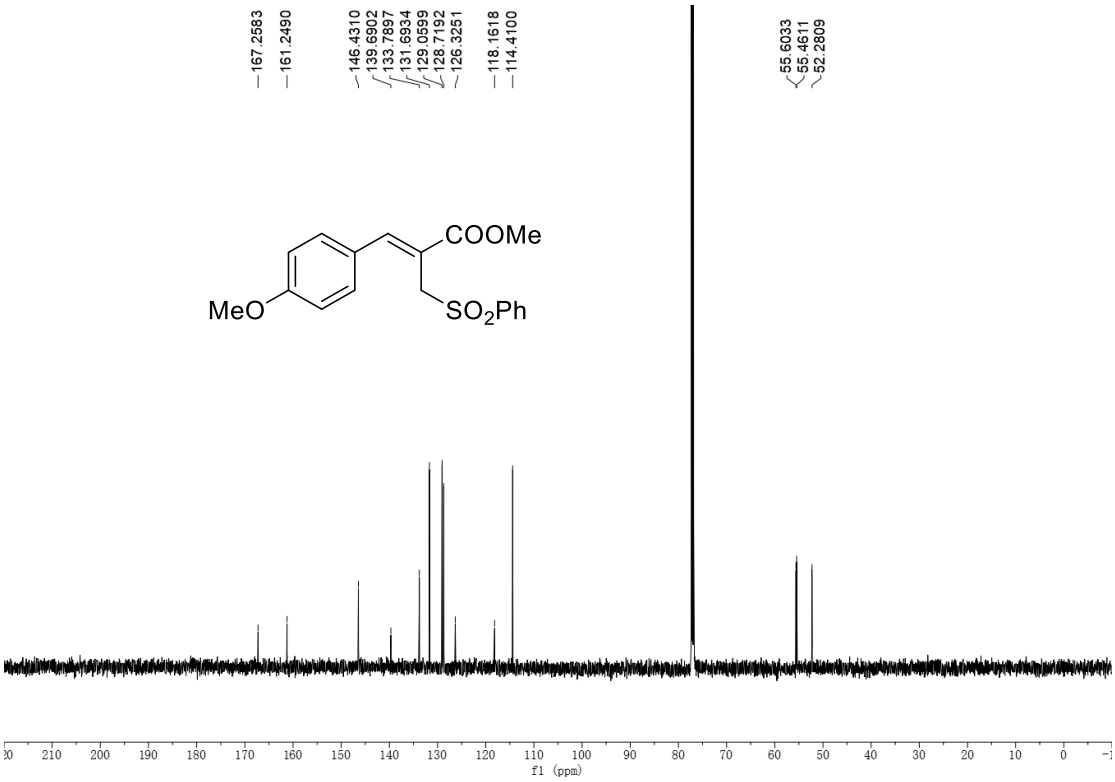


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-methoxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1c**)

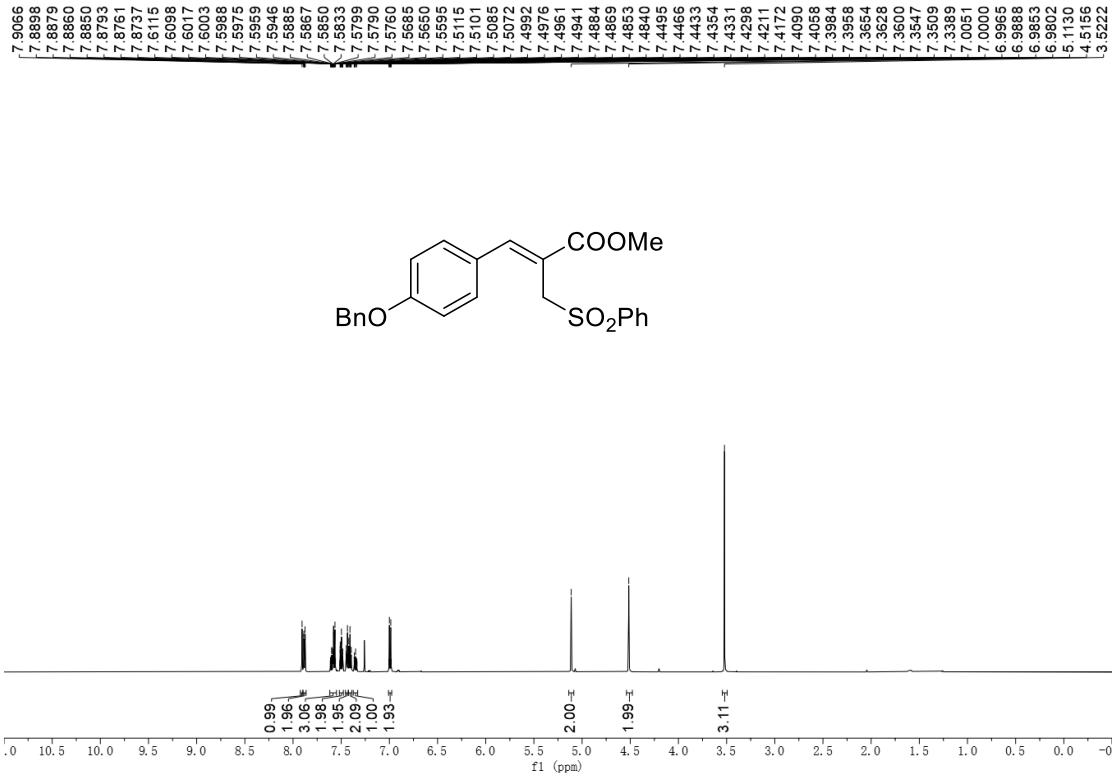


^{1}H NMR (600 MHz, Chloroform-*d*)

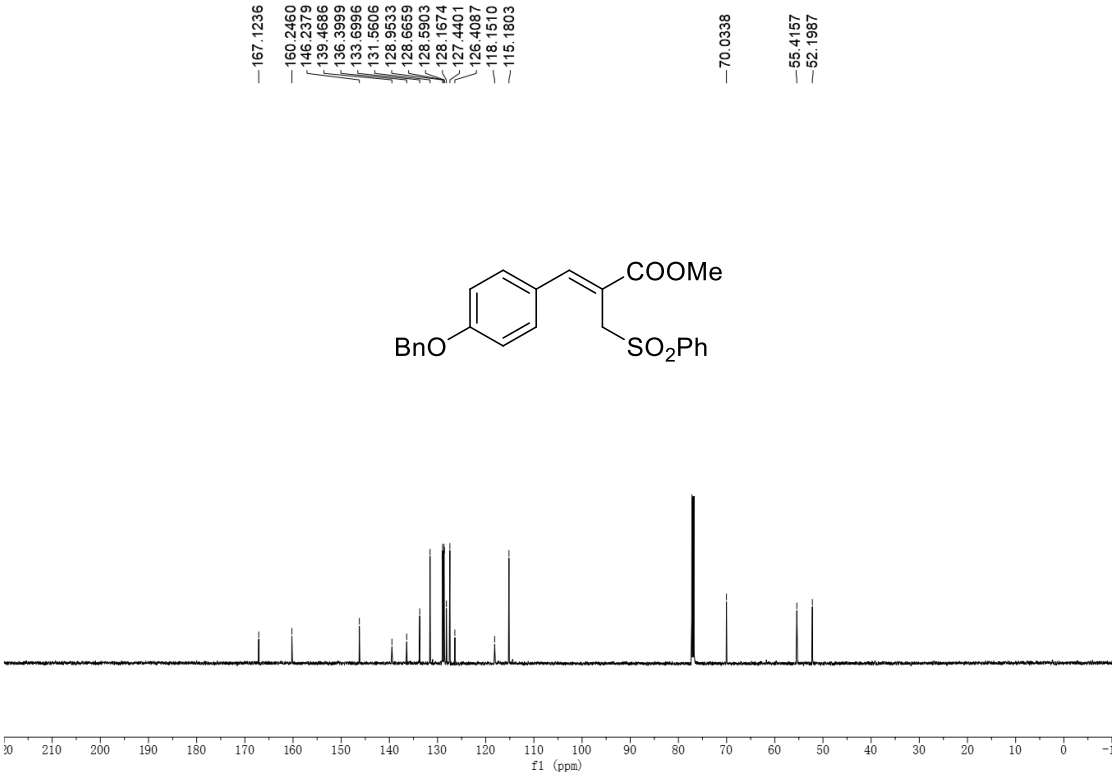


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-(benzyloxy)phenyl)-2-((phenylsulfonyl)methyl)acrylate (**1d**)

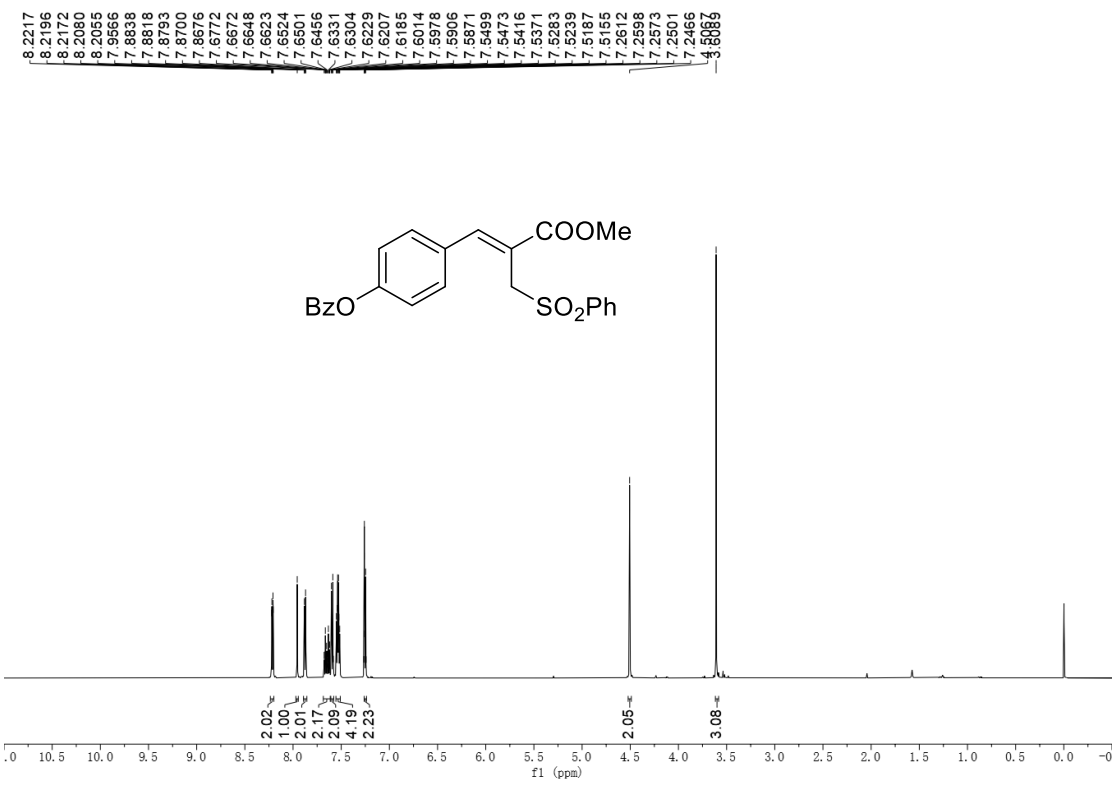


^{1}H NMR (600 MHz, Chloroform-*d*)

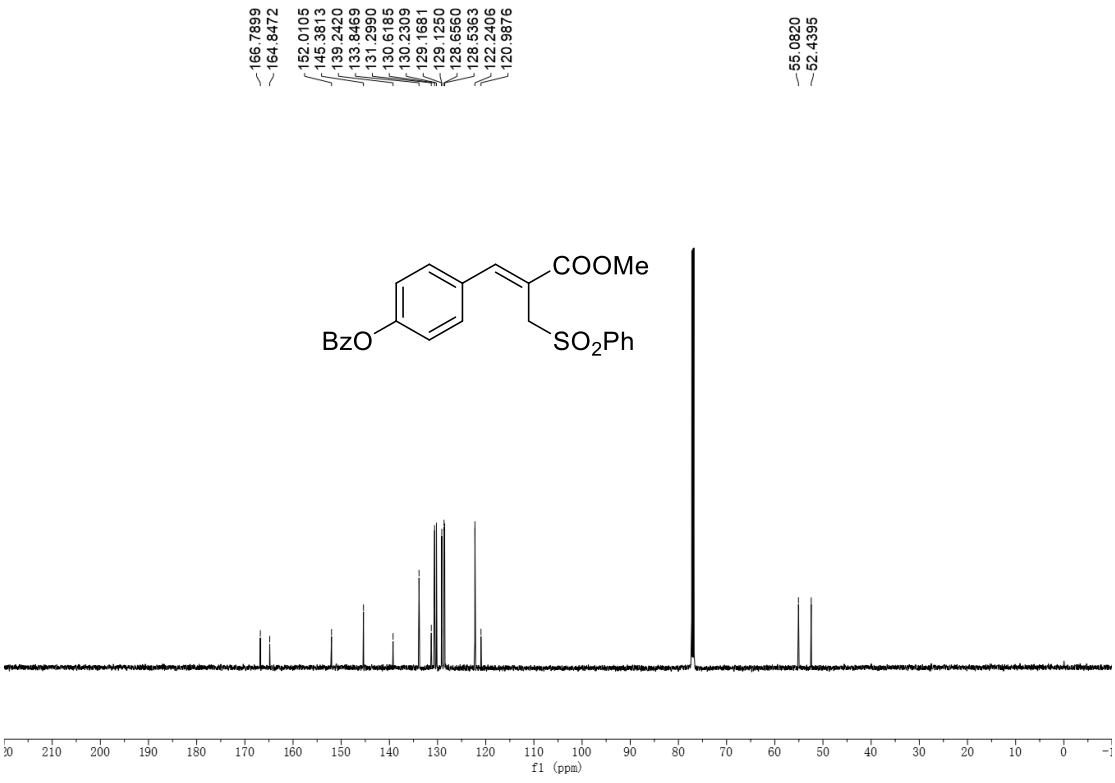


^{13}C NMR (151 MHz, Chloroform-*d*)

(*Z*)-4-(3-methoxy-3-oxo-2-((phenylsulfonyl)methyl)prop-1-en-1-yl)phenyl benzoate (**1e**)

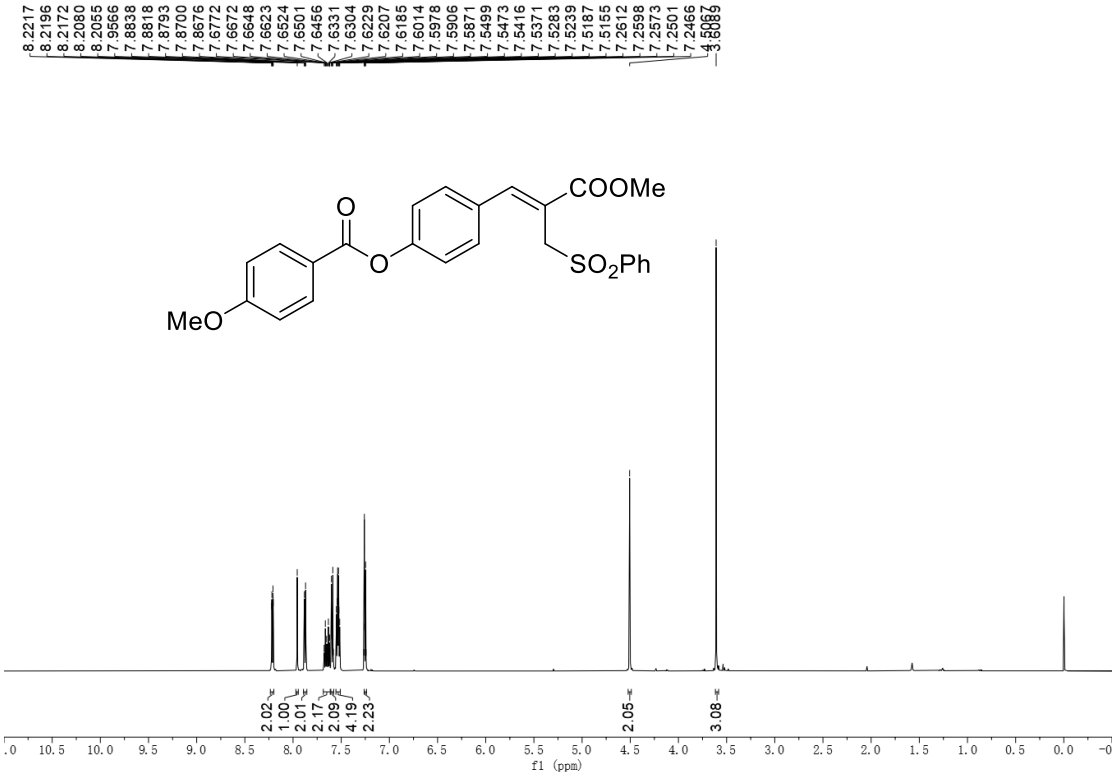


^{1}H NMR (600 MHz, Chloroform-*d*)

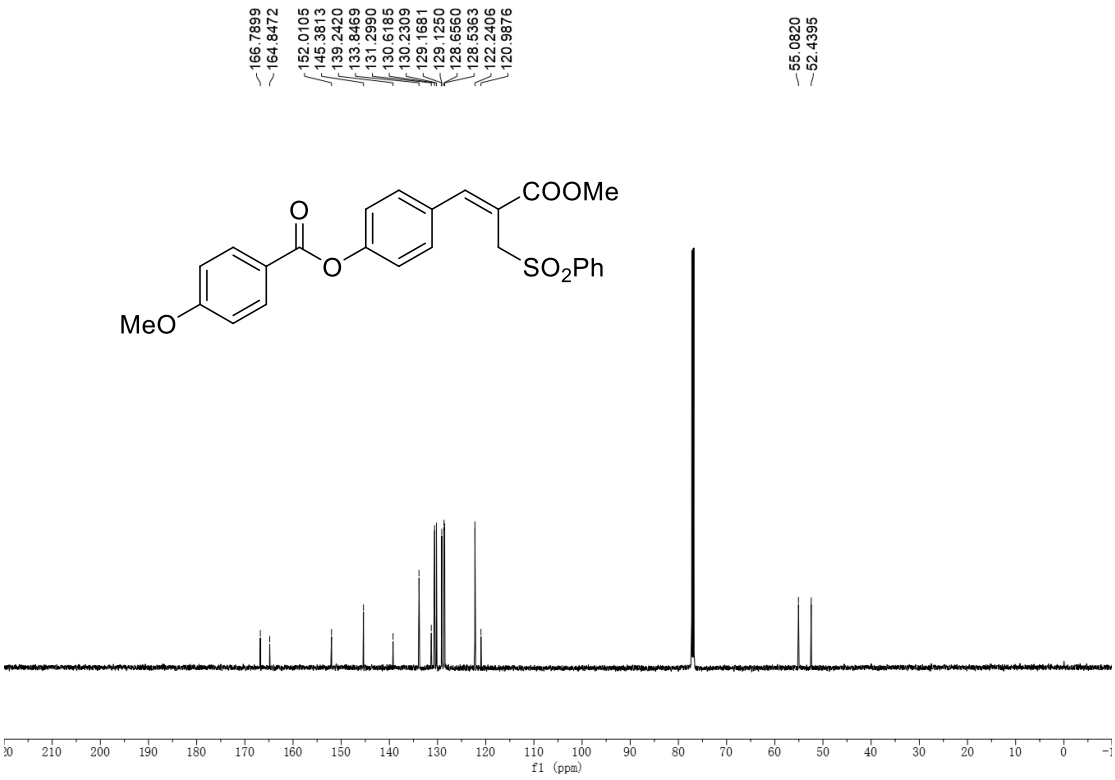


^{13}C NMR (151 MHz, Chloroform-*d*)

(*Z*)-4-(3-methoxy-3-oxo-2-((phenylsulfonyl)methyl)prop-1-en-1-yl)phenyl 4-methoxybenzoate (**1f**)

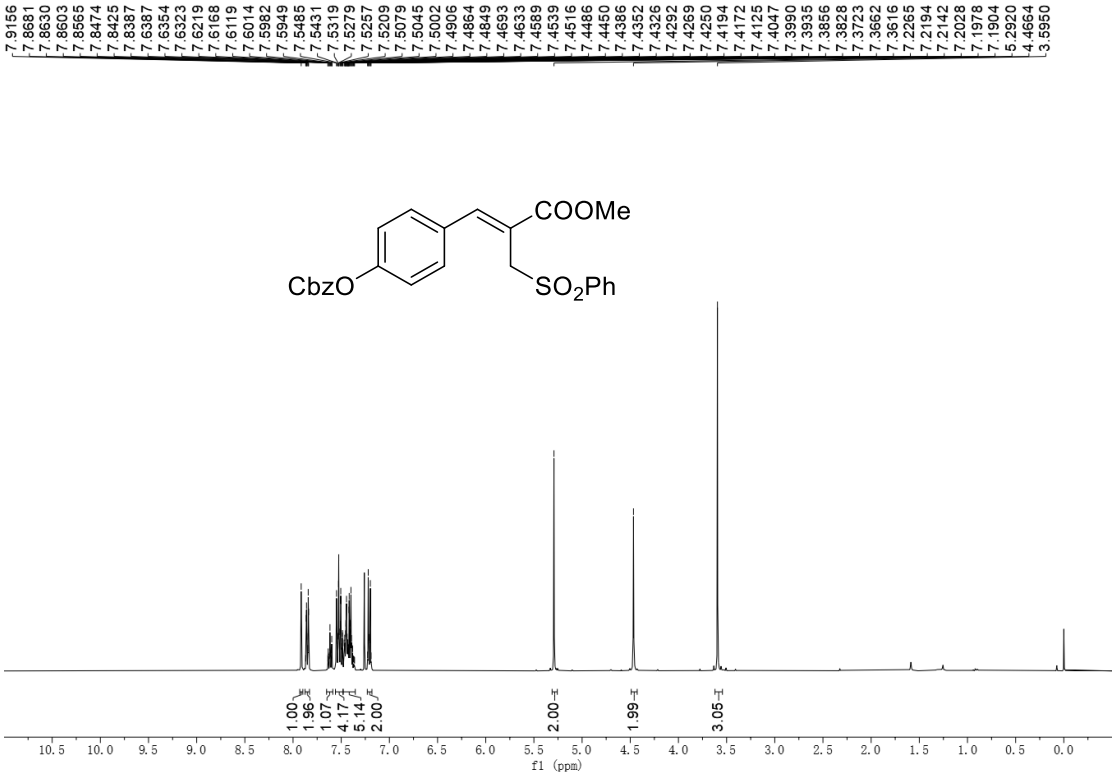


^{1}H NMR (600 MHz, Chloroform-*d*)

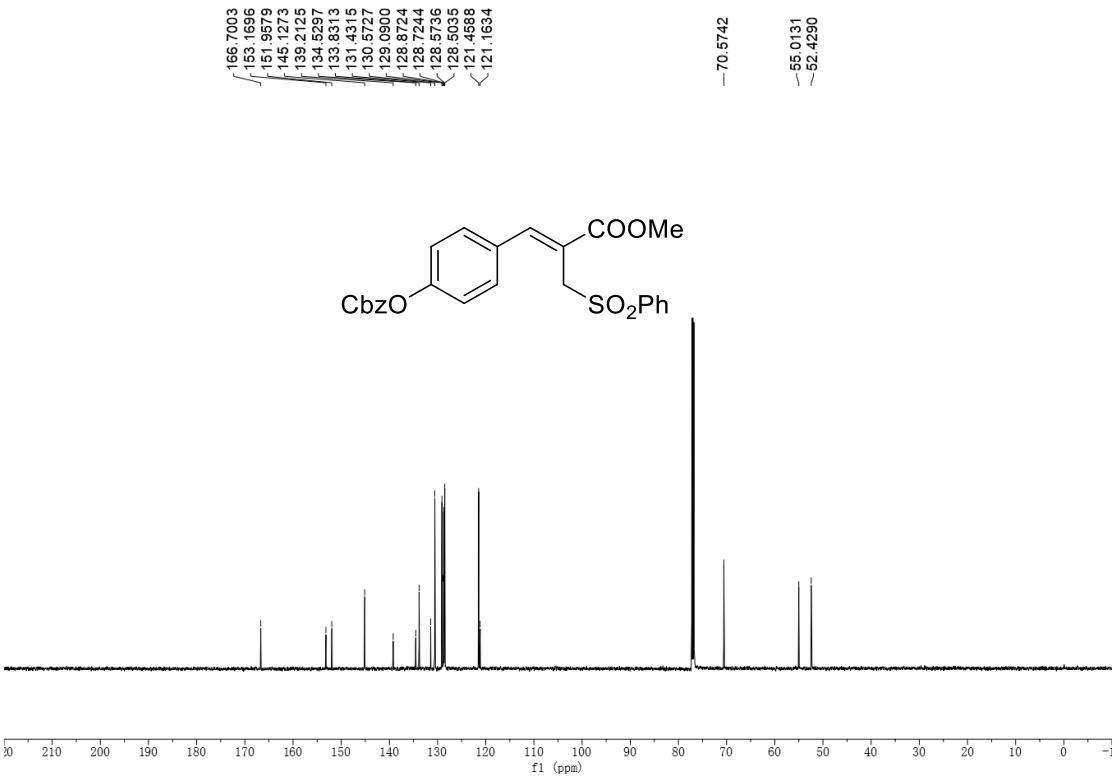


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-(((benzyloxy)carbonyl)oxy)phenyl)-2-((phenylsulfonyl)methyl)acrylate (**1g**)

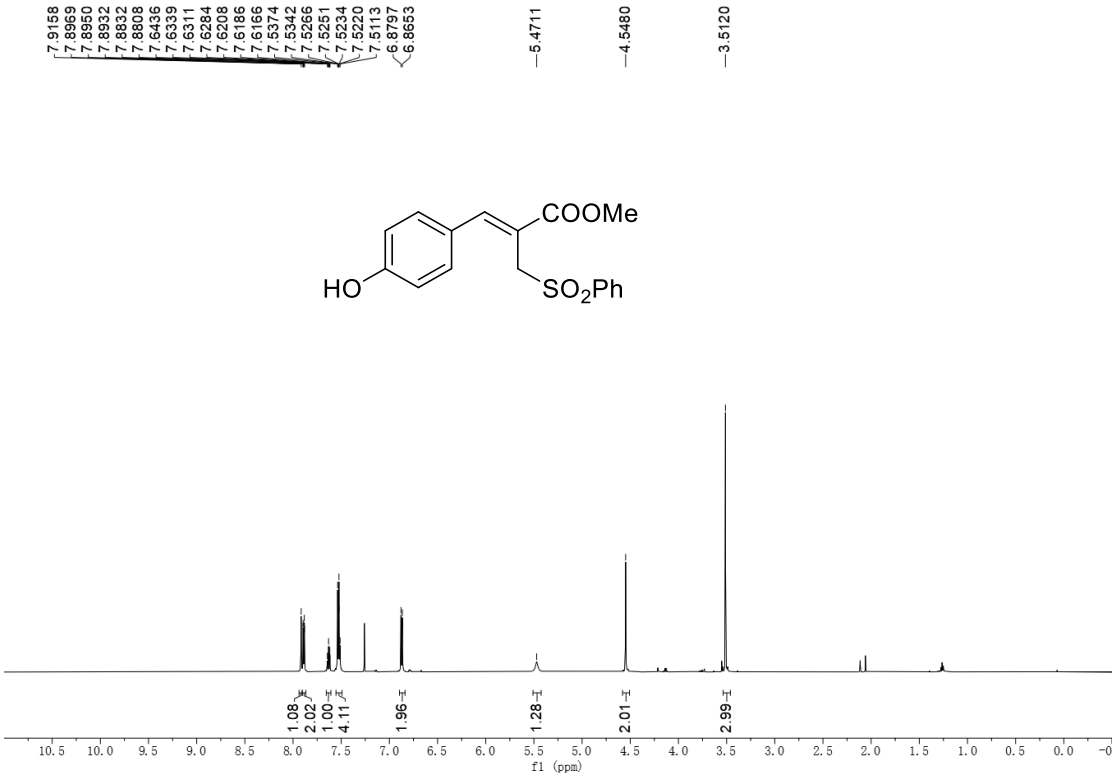


^{1}H NMR (400 MHz, Chloroform-*d*)

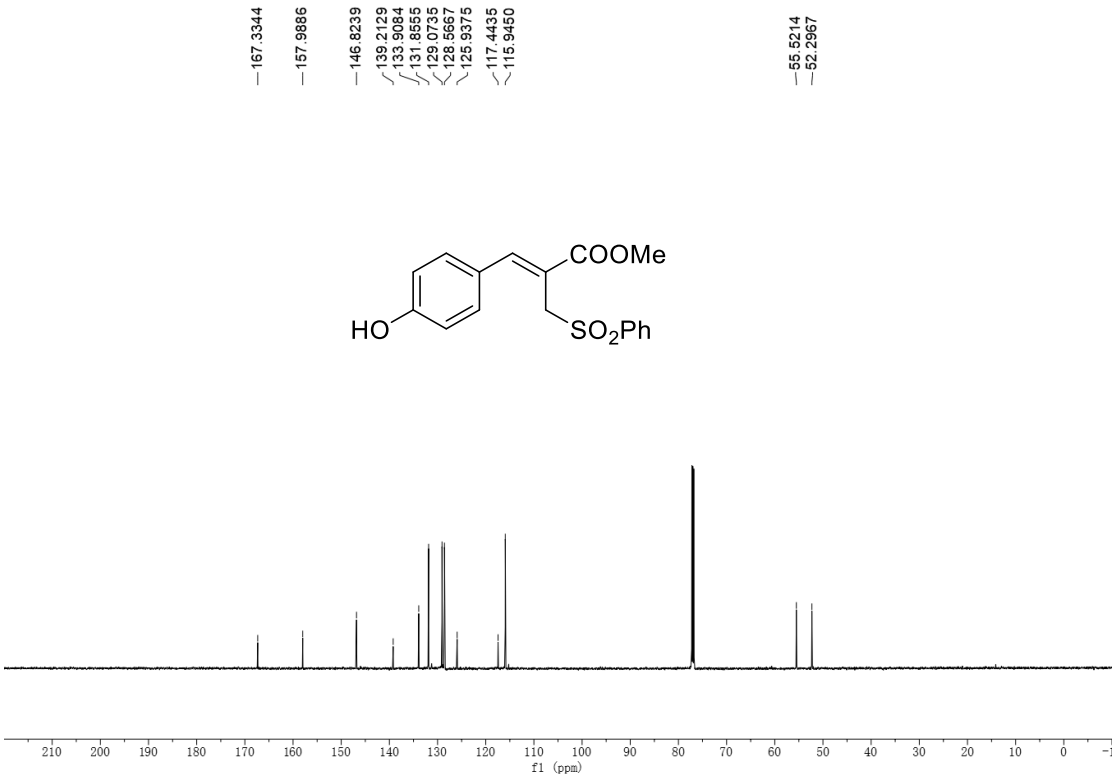


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-hydroxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1h**)

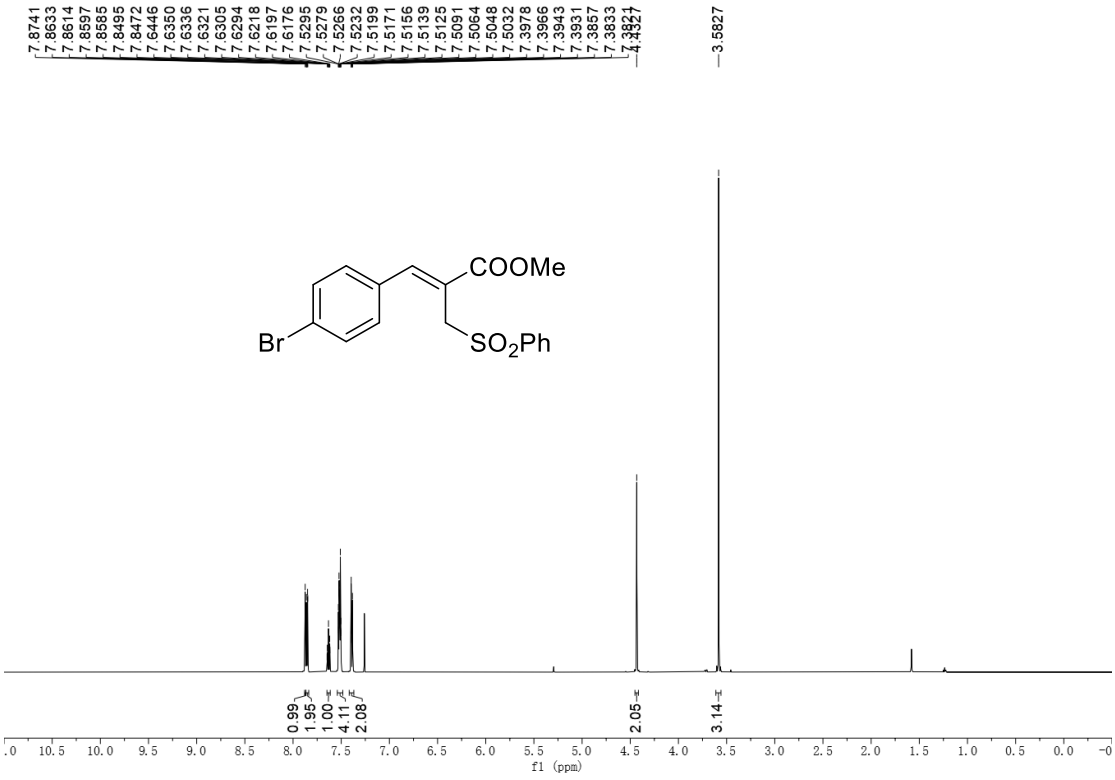


^{1}H NMR (600 MHz, Chloroform-*d*)

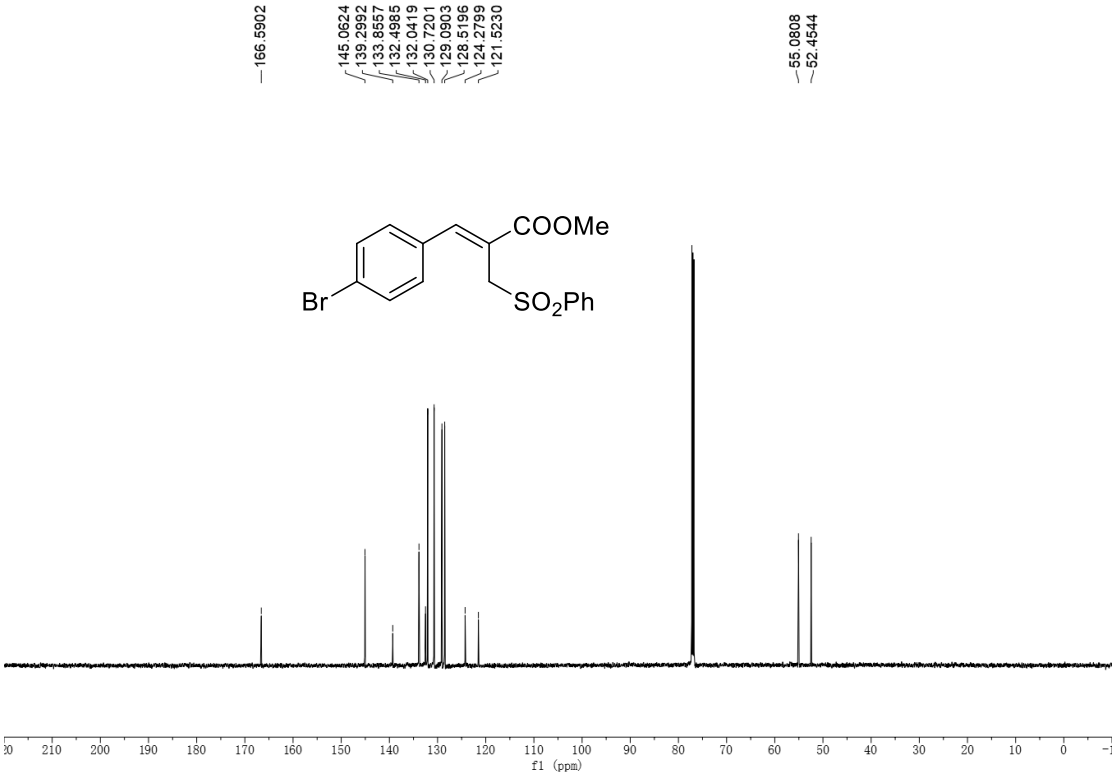


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1i**)

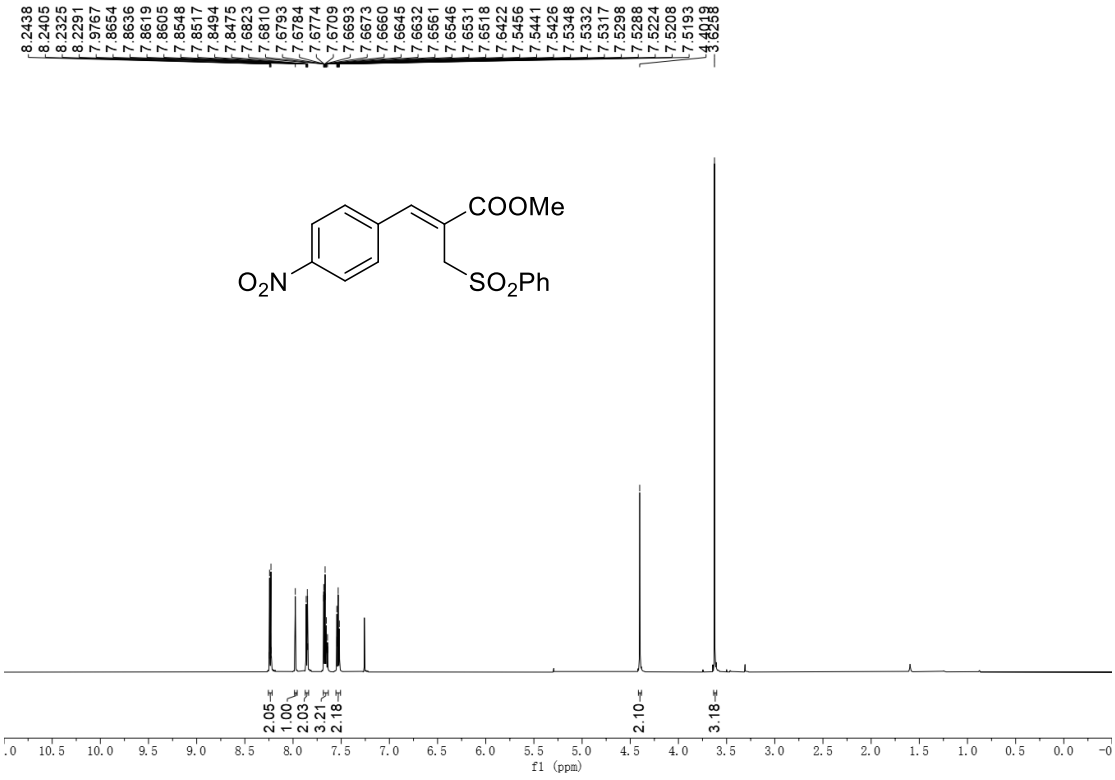


^{1}H NMR (600 MHz, Chloroform-*d*)

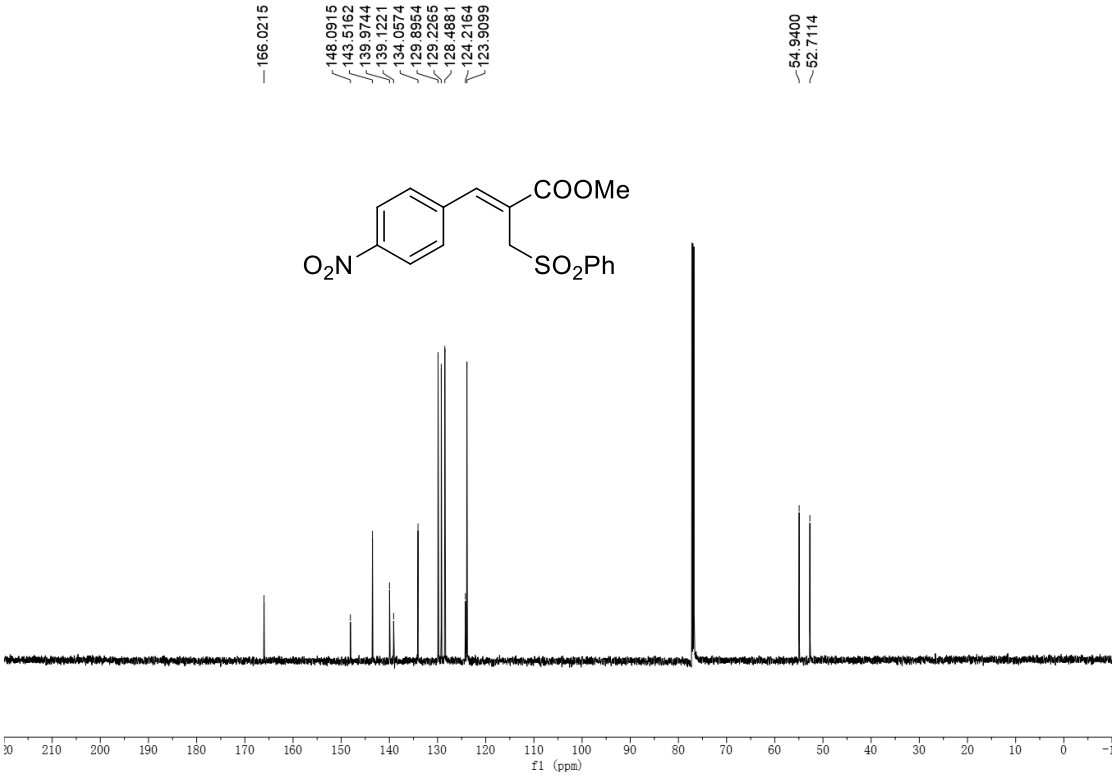


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(4-nitrophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1j**)

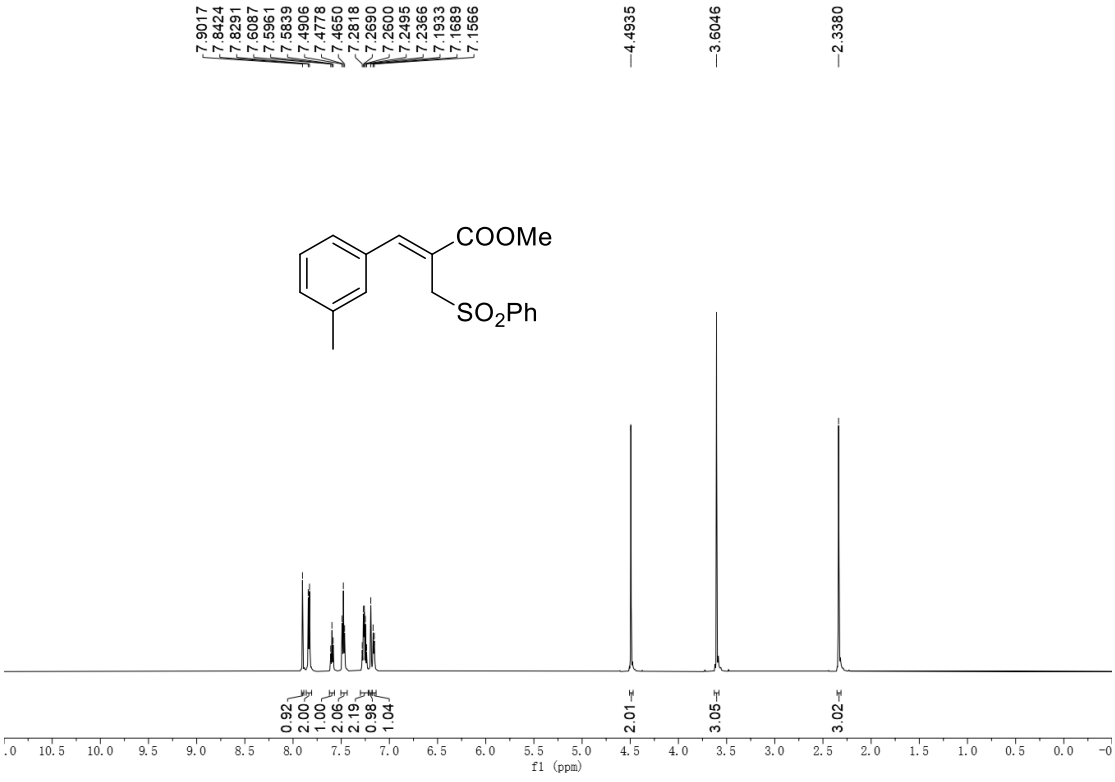


^{1}H NMR (600 MHz, Chloroform-*d*)

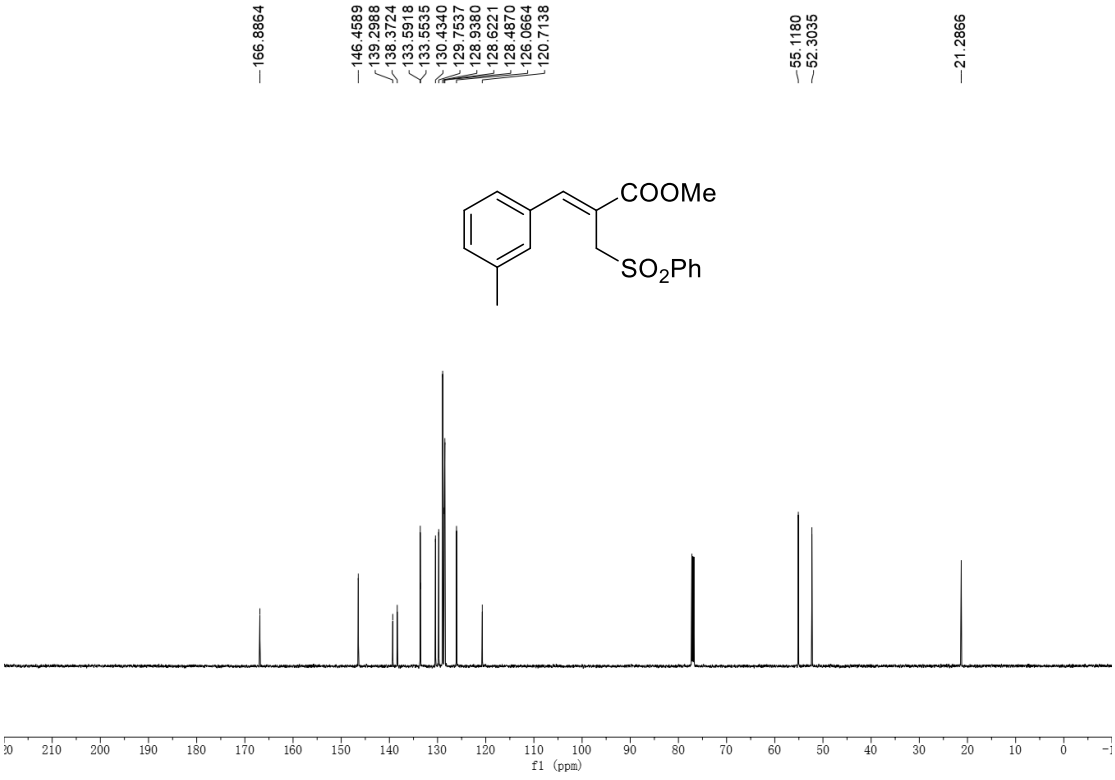


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(*m*-tolyl)acrylate (**1k**)

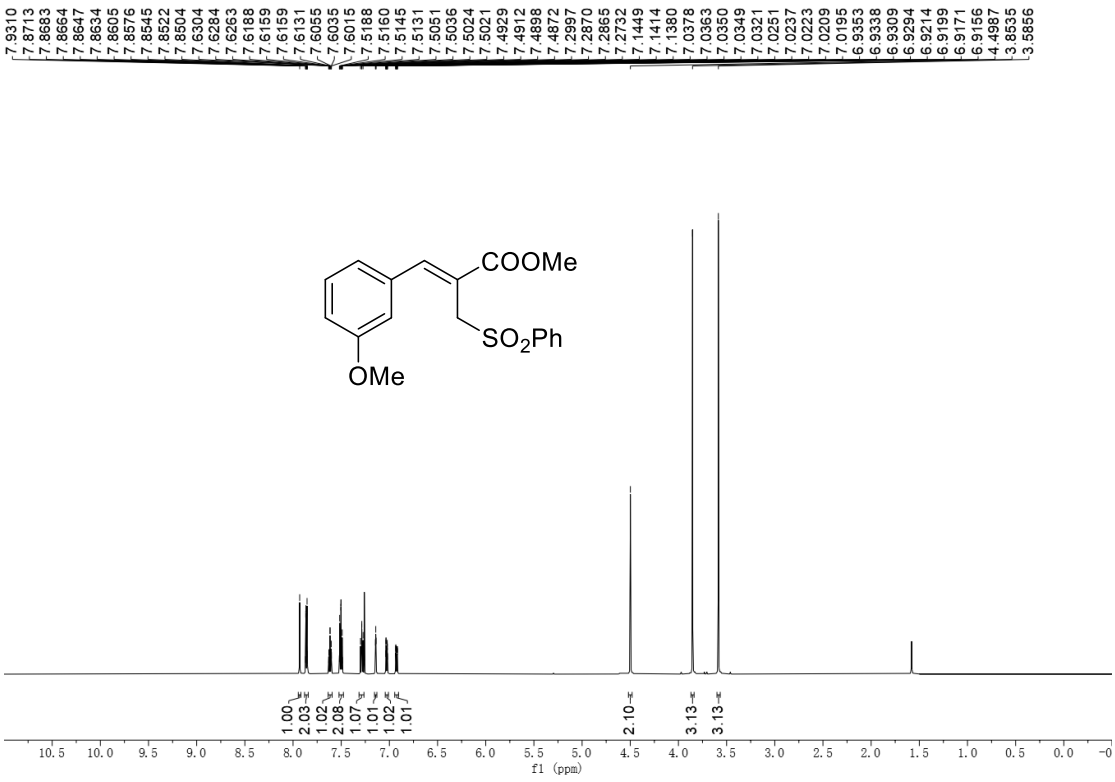


^{1}H NMR (600 MHz, Chloroform-*d*)

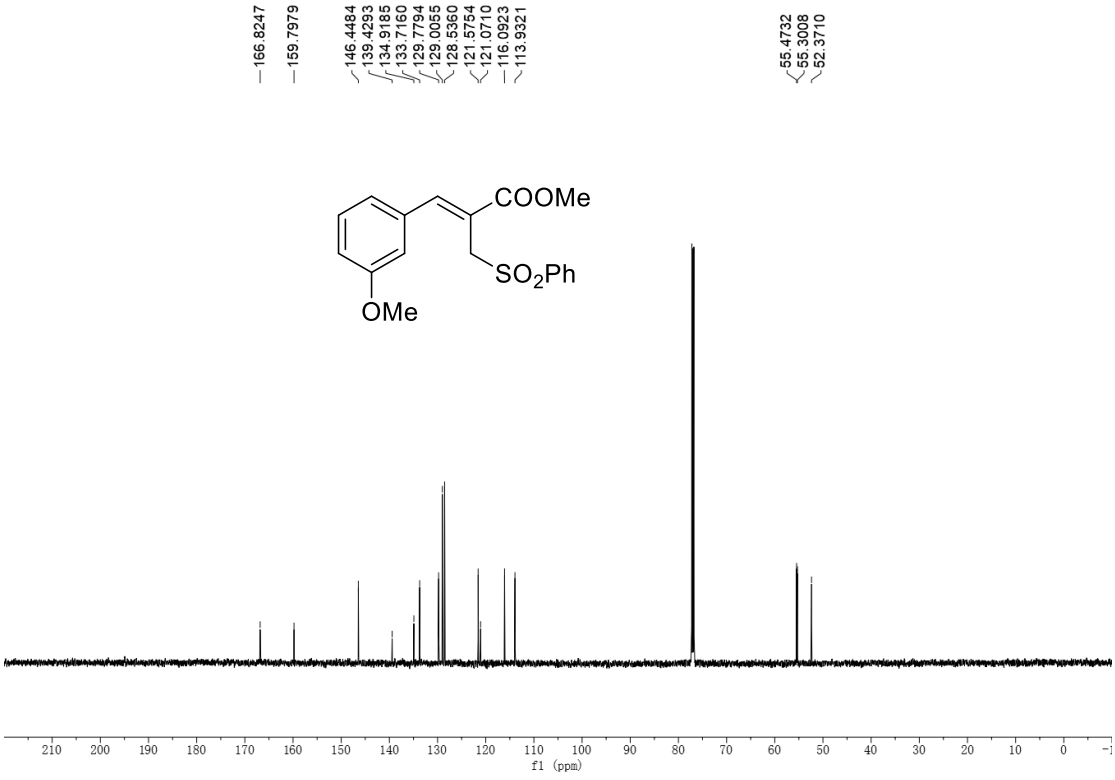


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(3-methoxyphenyl)-2-((phenylsulfonyl)methyl)acrylate (**1l**)

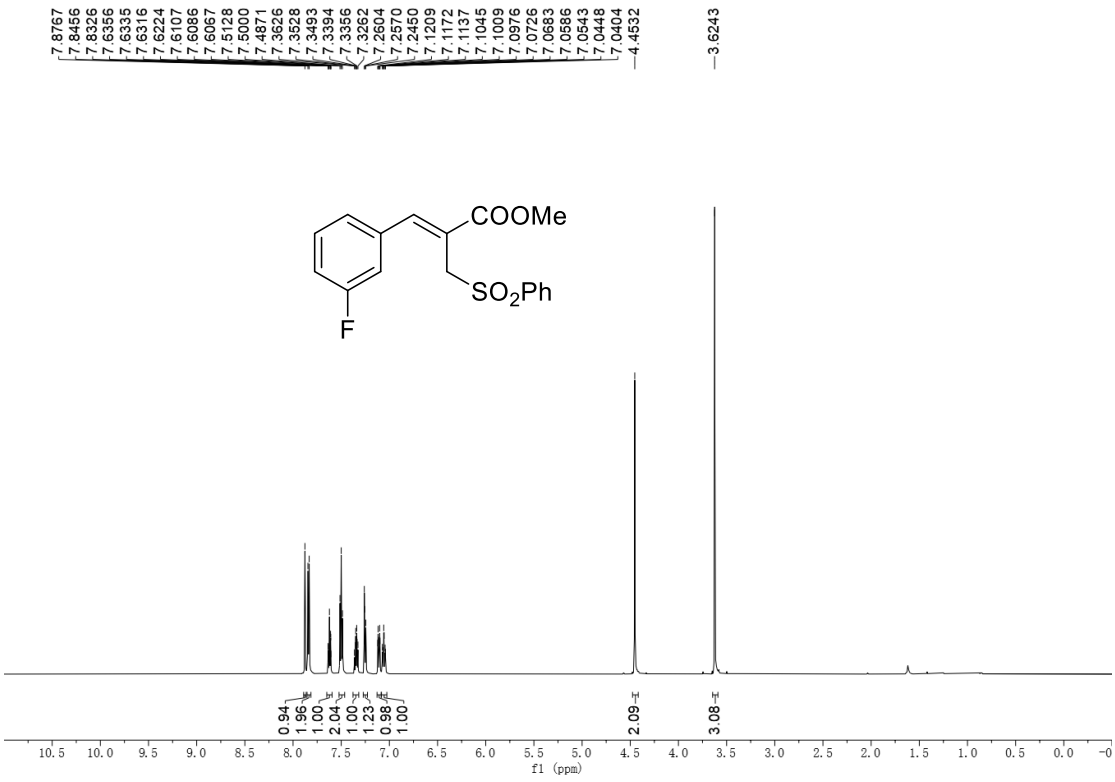


^{1}H NMR (600 MHz, Chloroform-*d*)

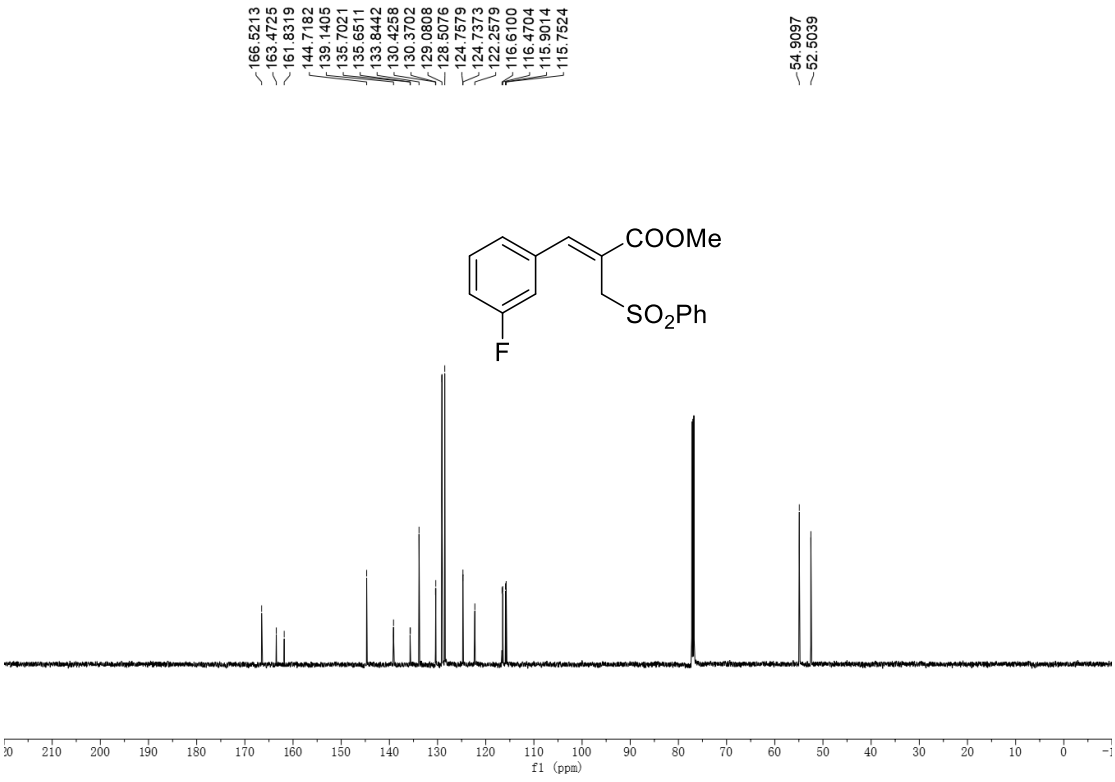


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(3-fluorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1m**)

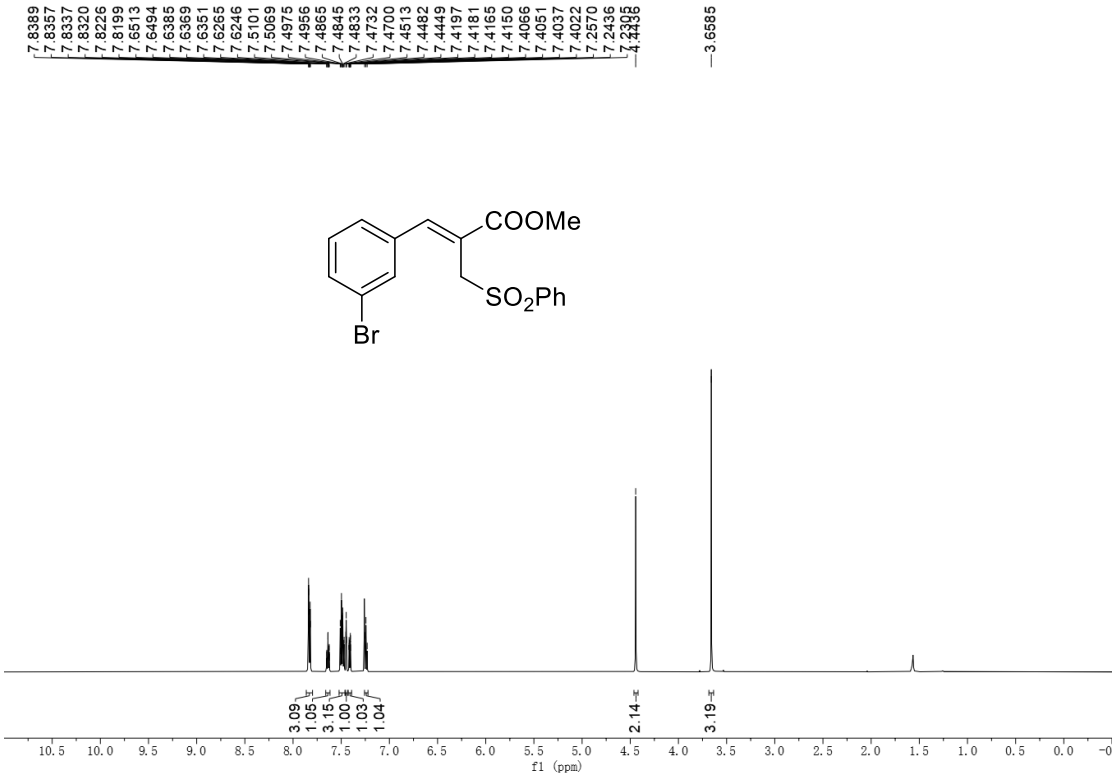


^{1}H NMR (600 MHz, Chloroform-*d*)

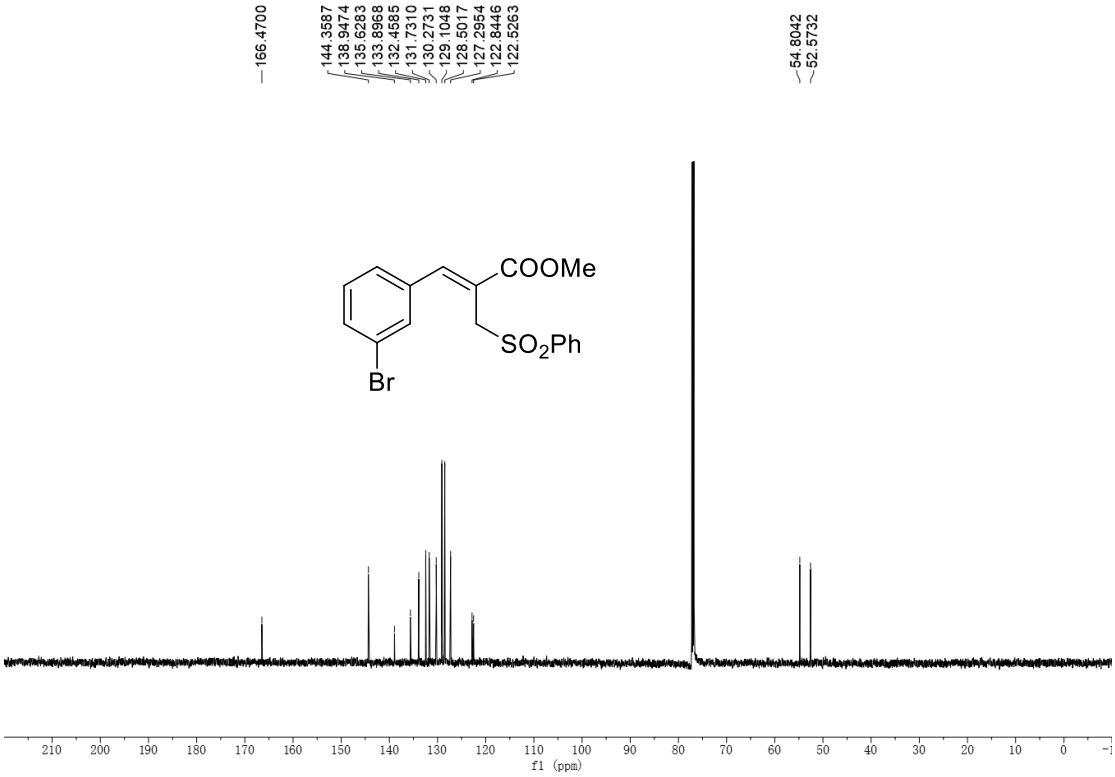


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(3-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1n**)

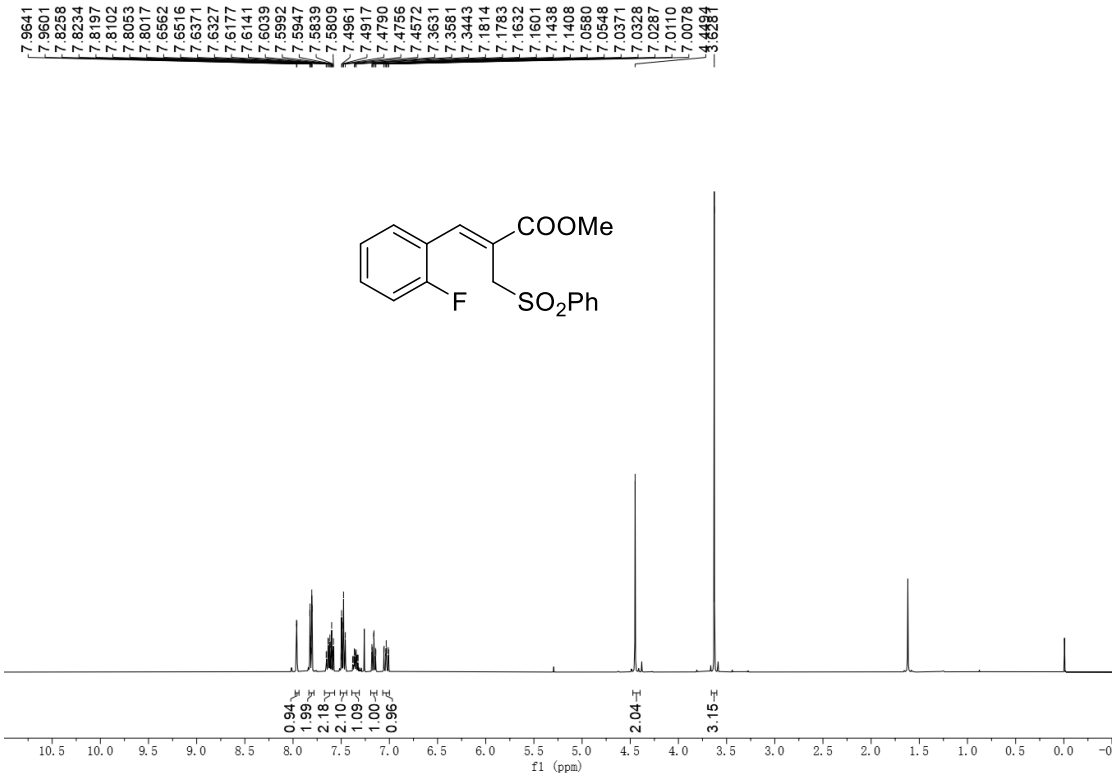


^{1}H NMR (600 MHz, Chloroform-*d*)

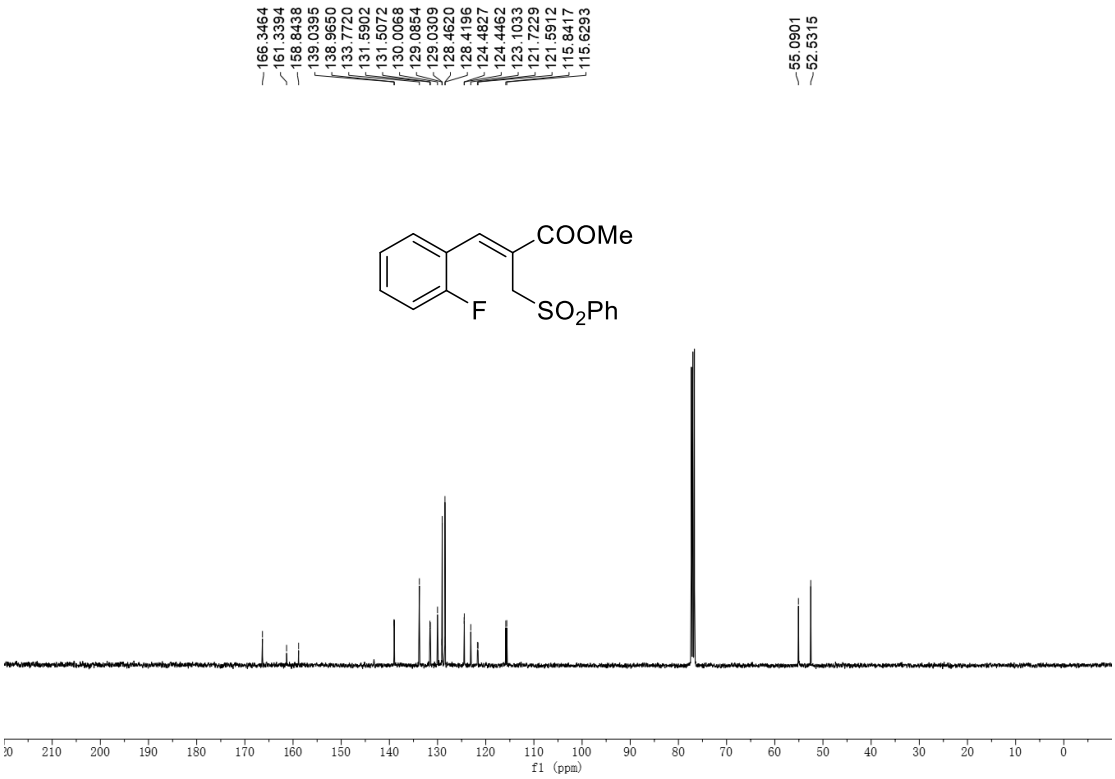


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(2-fluorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1o**)

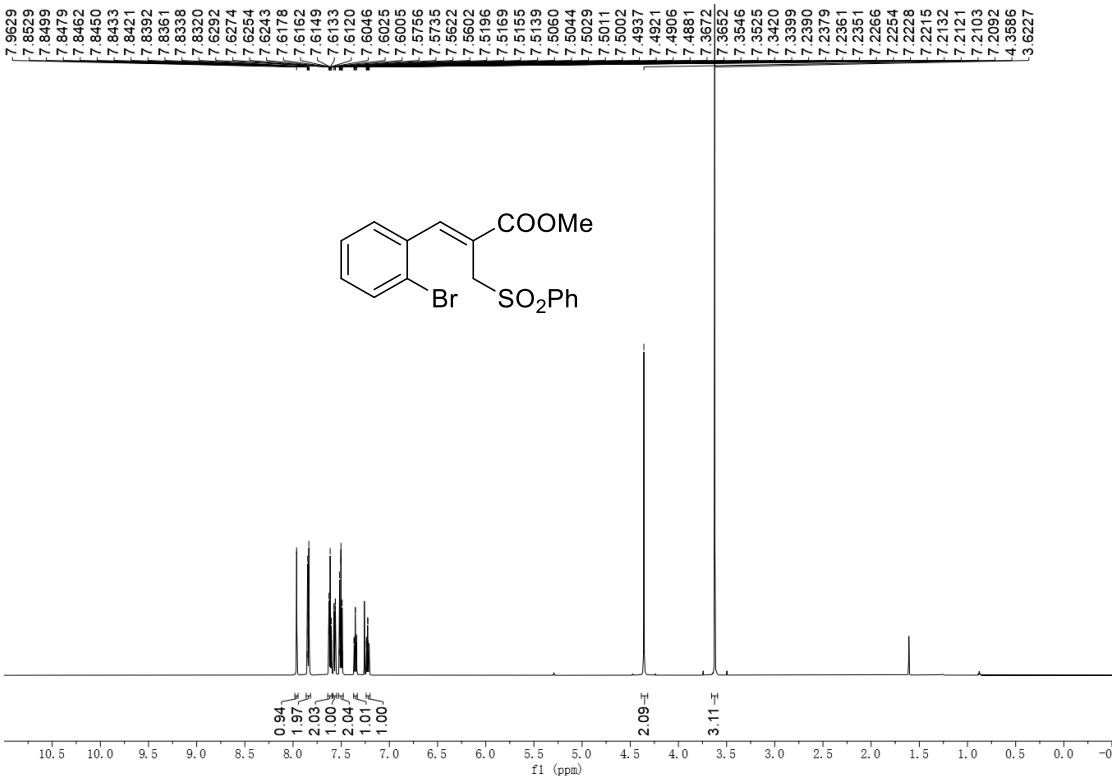


^{1}H NMR (400 MHz, Chloroform-*d*)

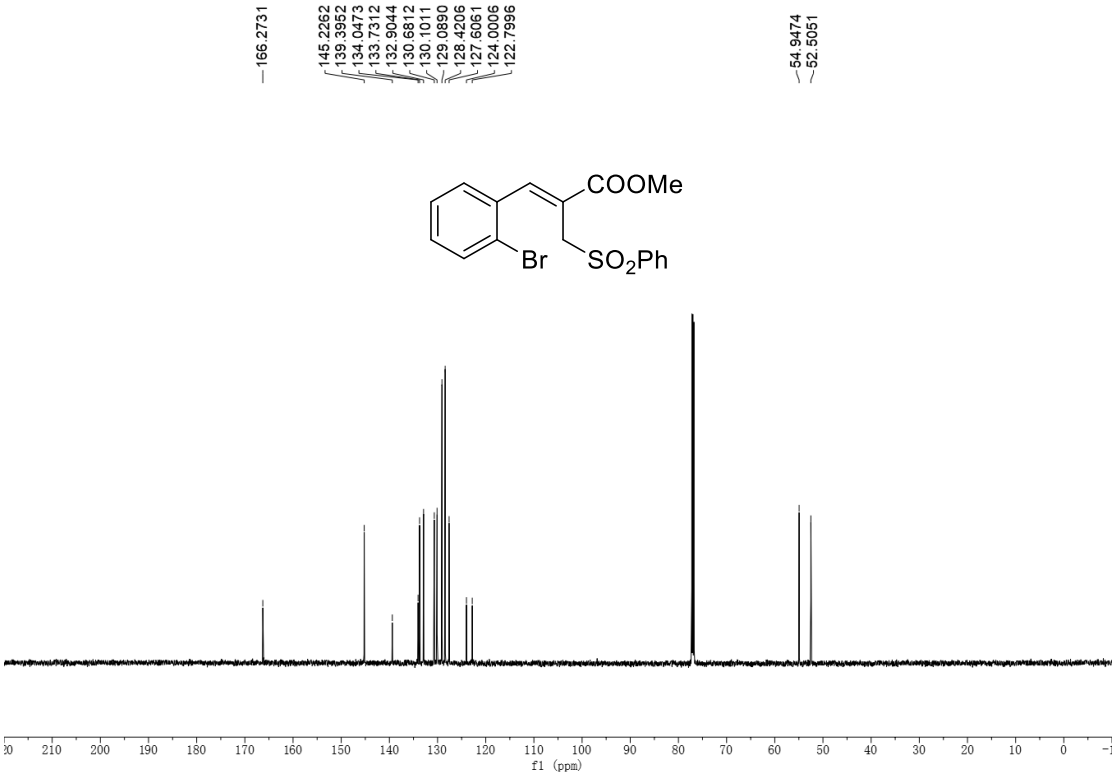


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(2-bromophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1p**)

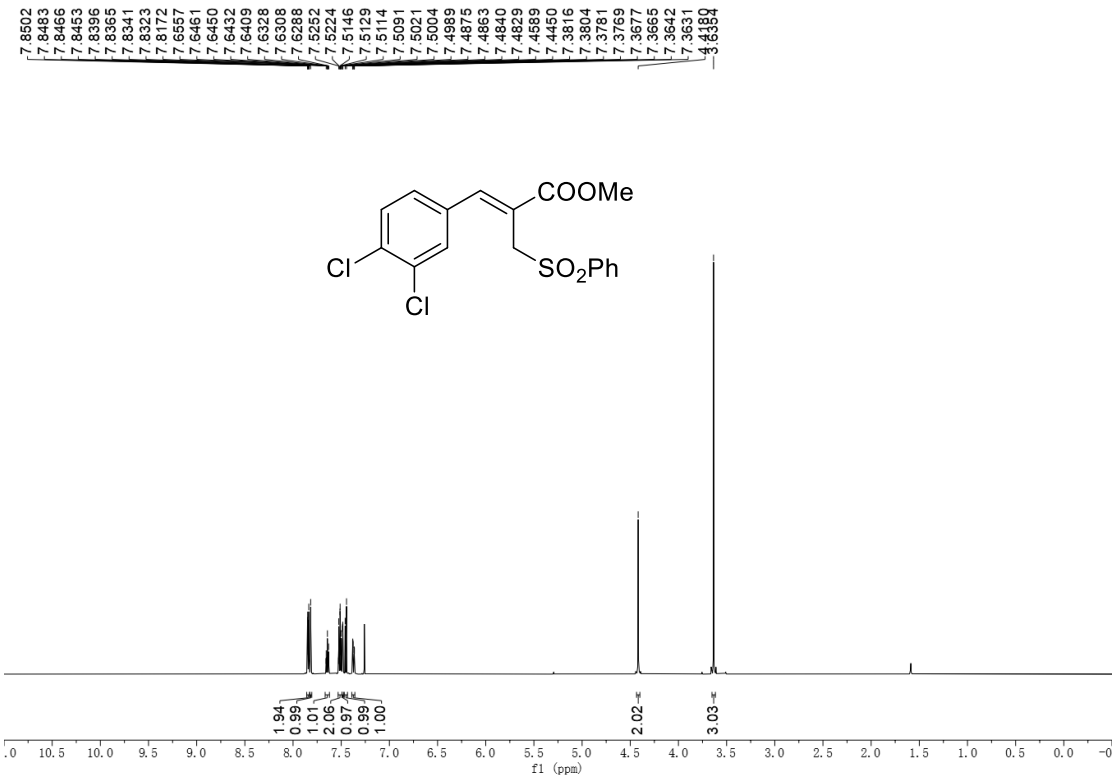


^{1}H NMR (600 MHz, Chloroform-*d*)

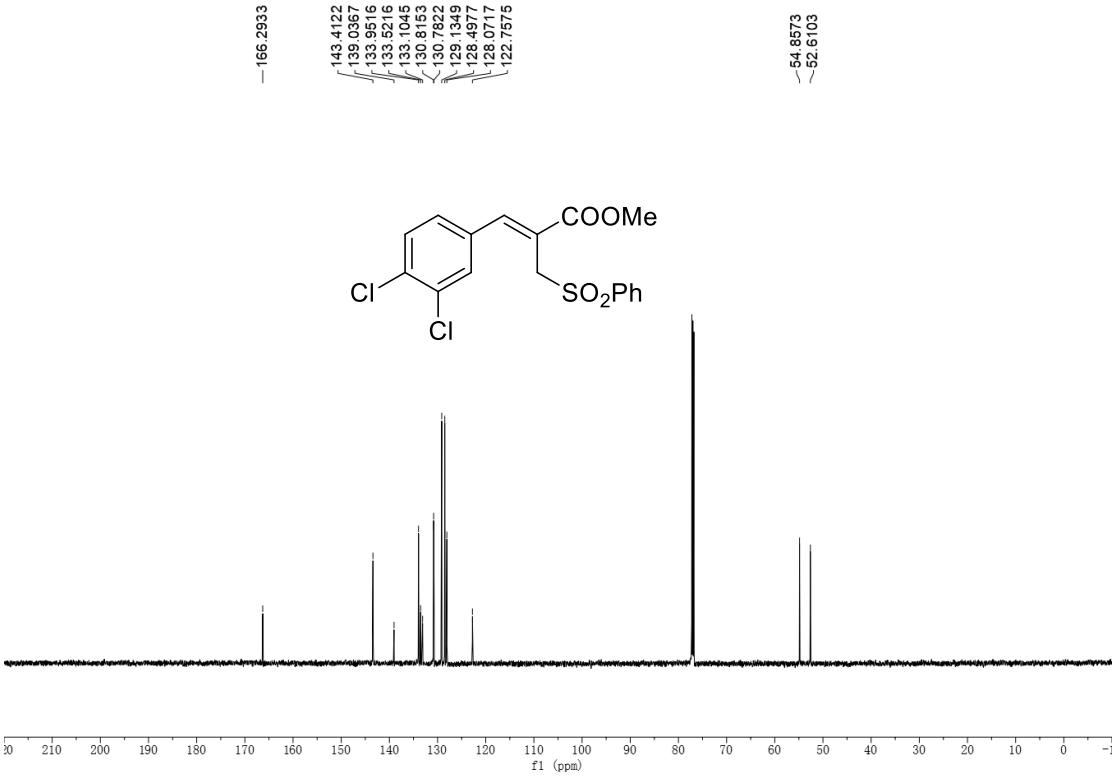


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(3,4-dichlorophenyl)-2-((phenylsulfonyl)methyl)acrylate (**1q**)

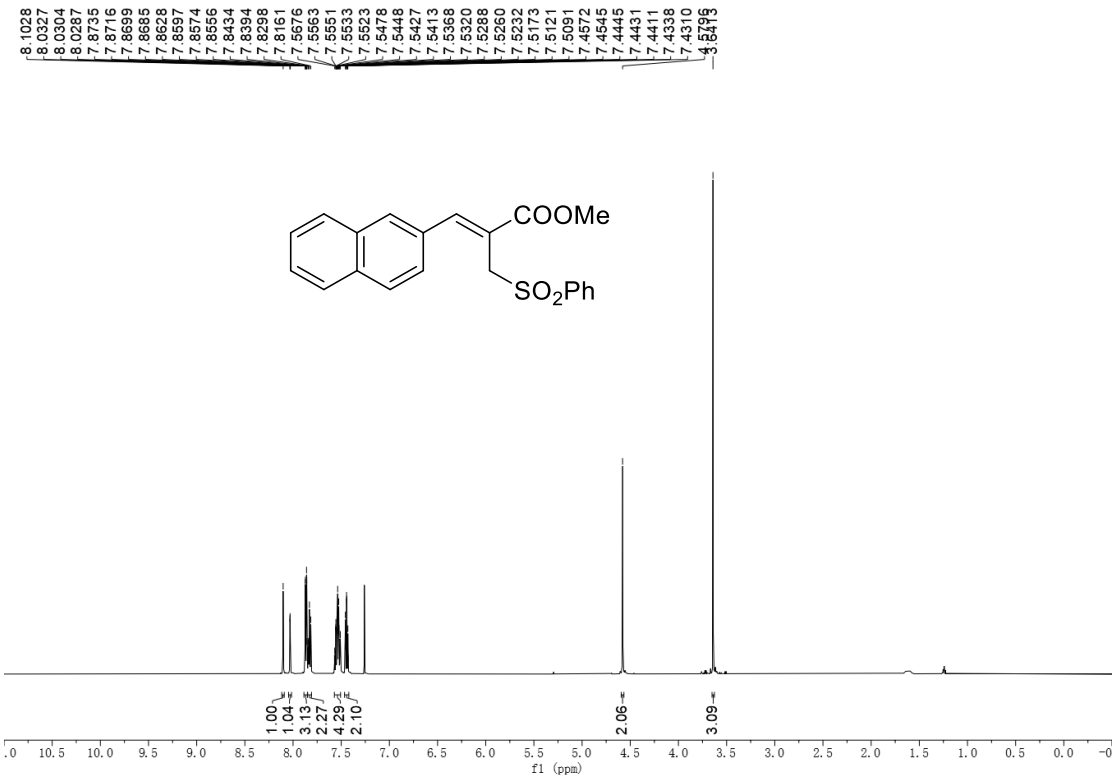


^{1}H NMR (600 MHz, Chloroform-*d*)

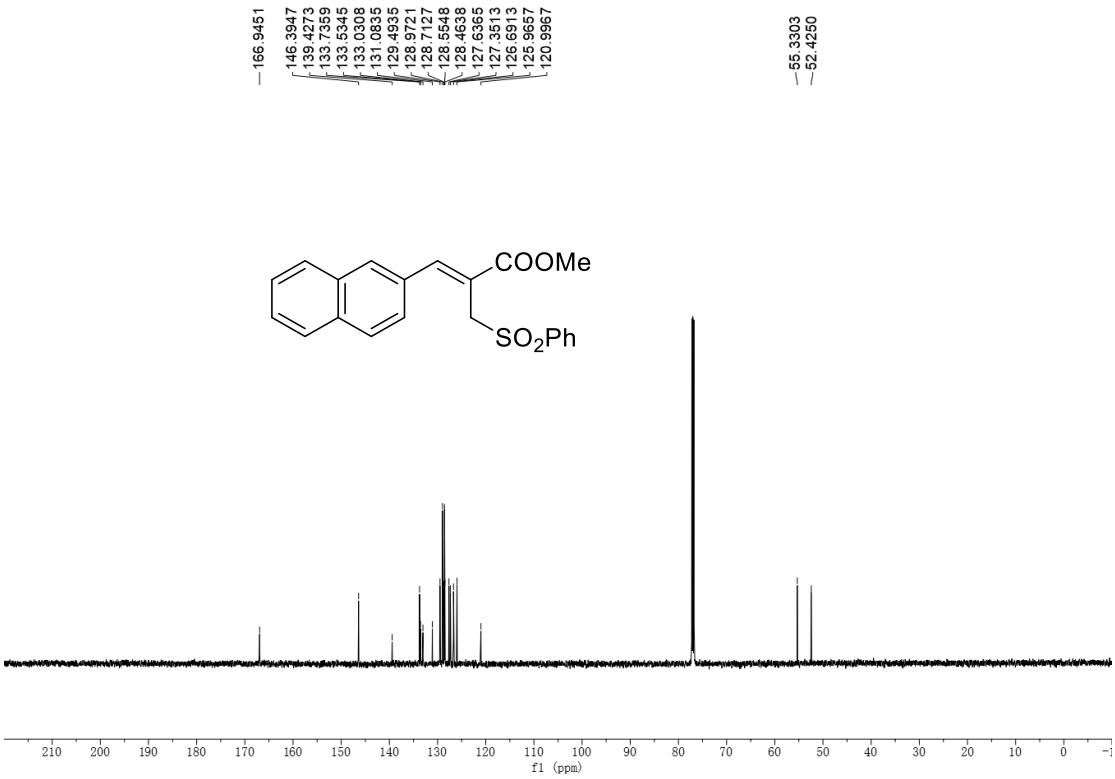


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(naphthalen-2-yl)-2-((phenylsulfonyl)methyl)acrylate (**1r**)

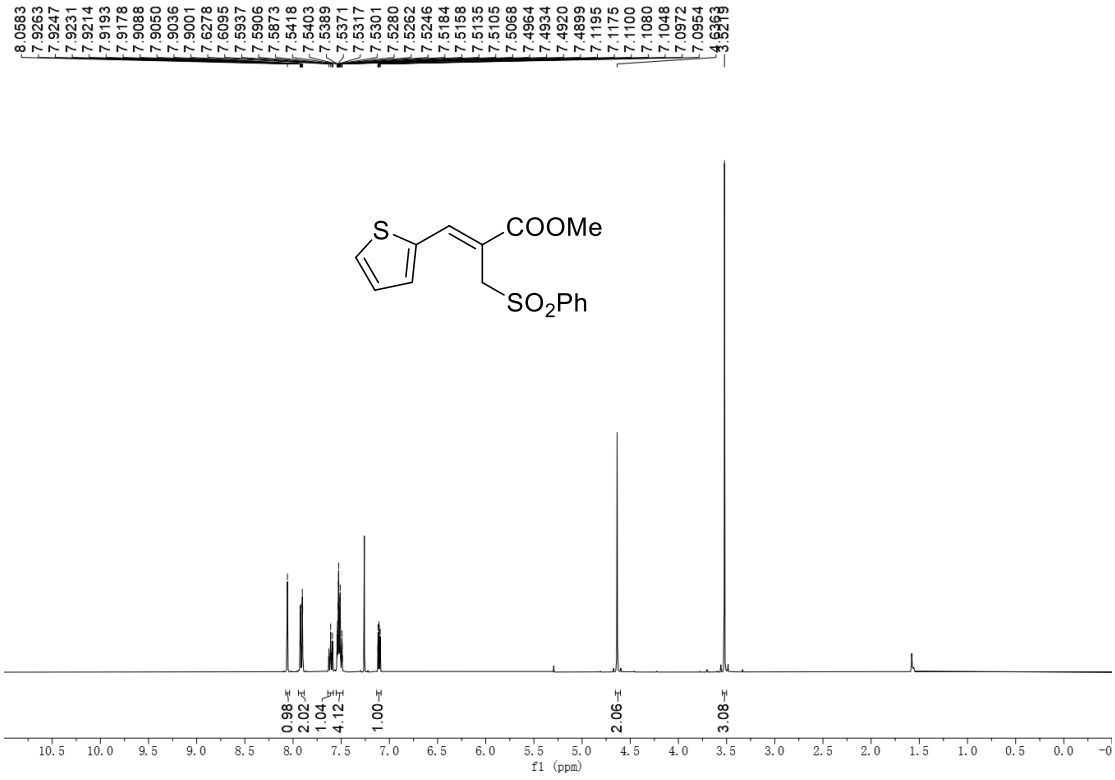


^{1}H NMR (600 MHz, Chloroform-*d*)

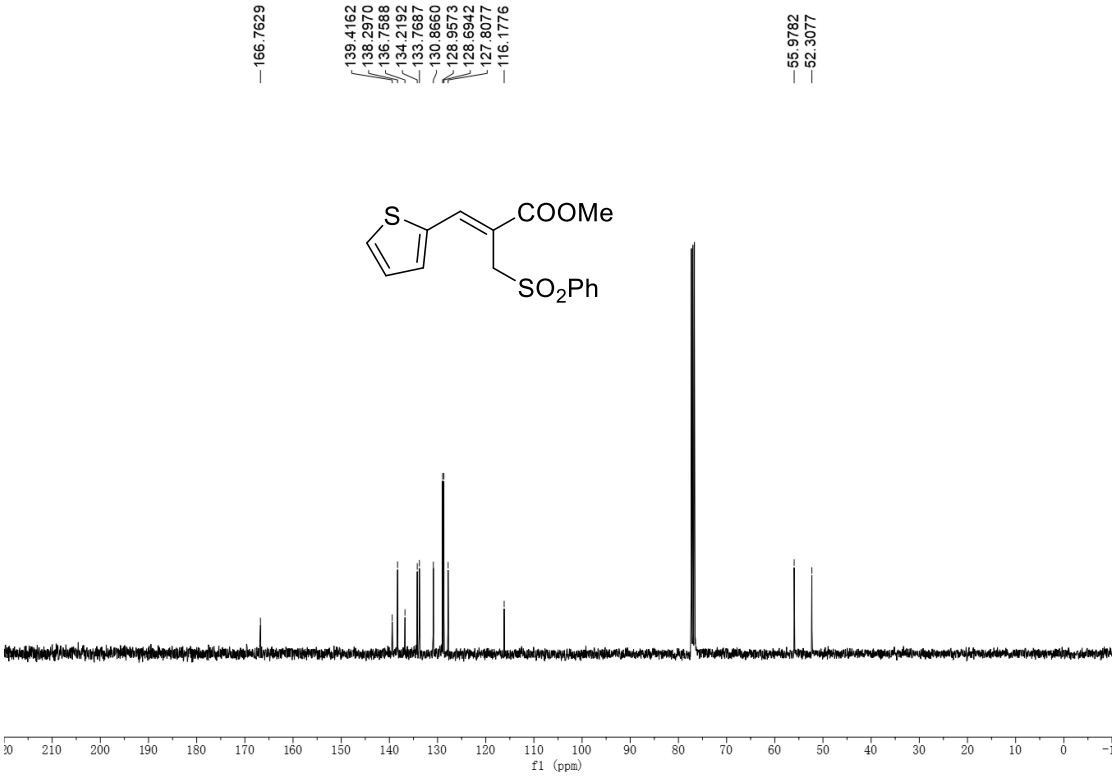


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(thiophen-2-yl)acrylate (**1s**)

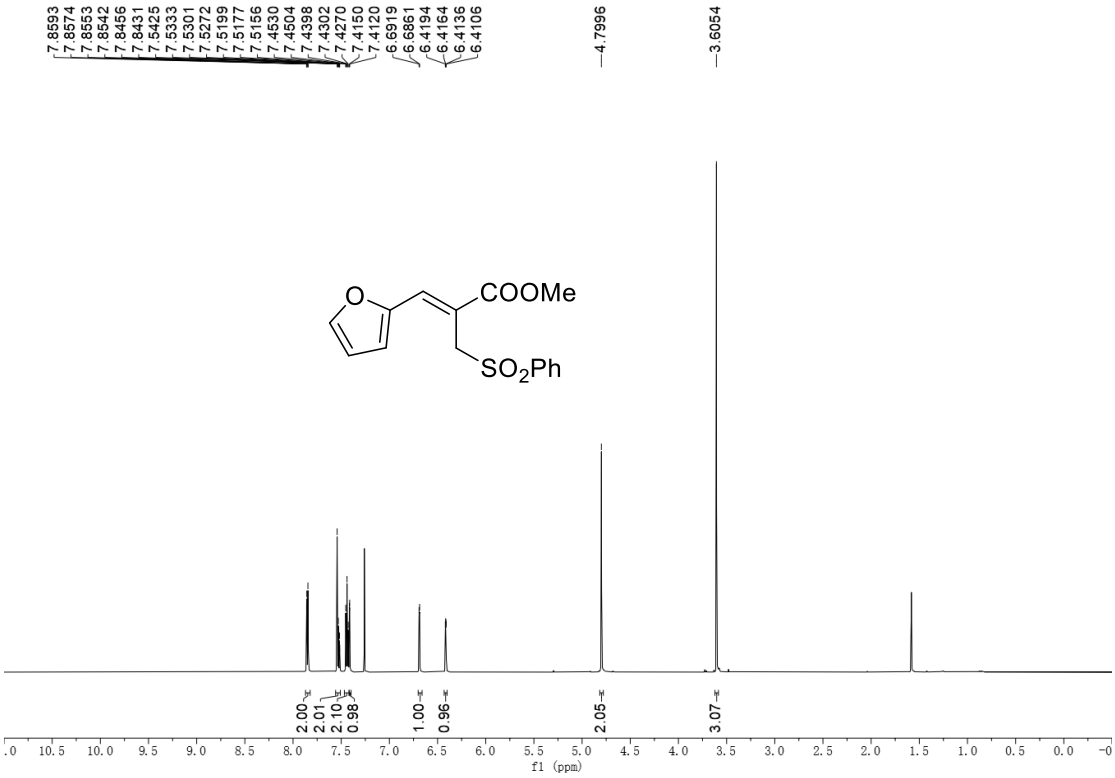


^{1}H NMR (400 MHz, Chloroform-*d*)

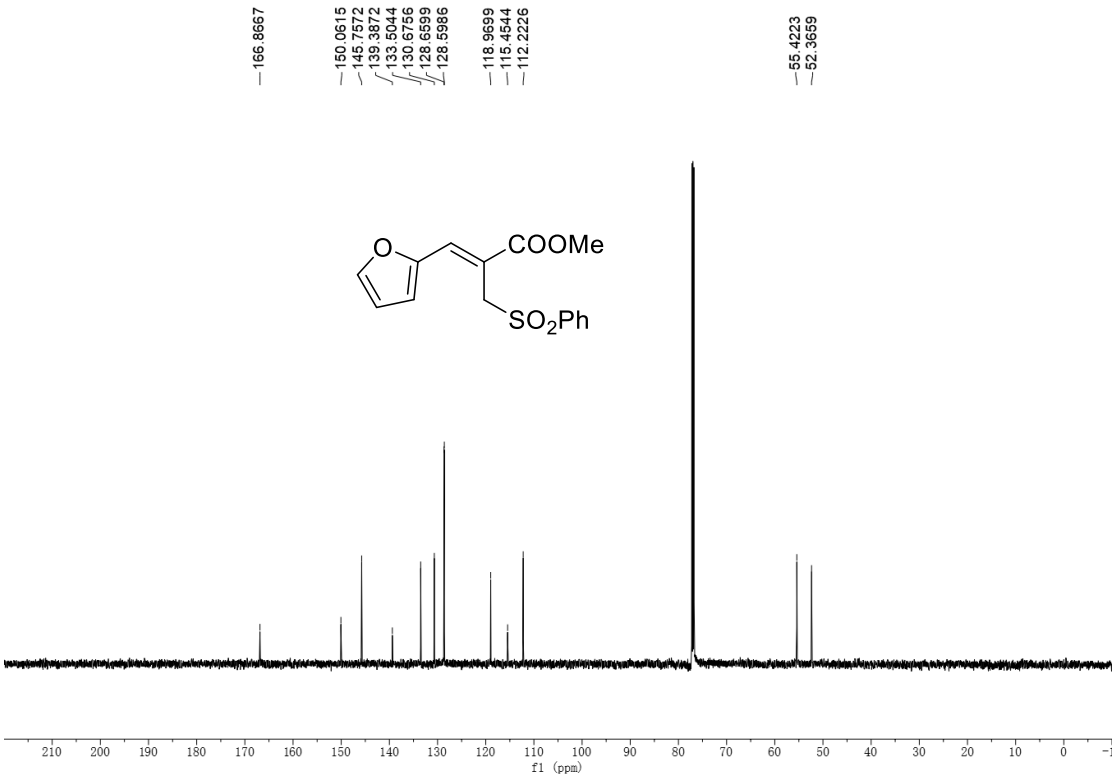


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl (*Z*)-3-(furan-2-yl)-2-((phenylsulfonyl)methyl)acrylate (**1t**)

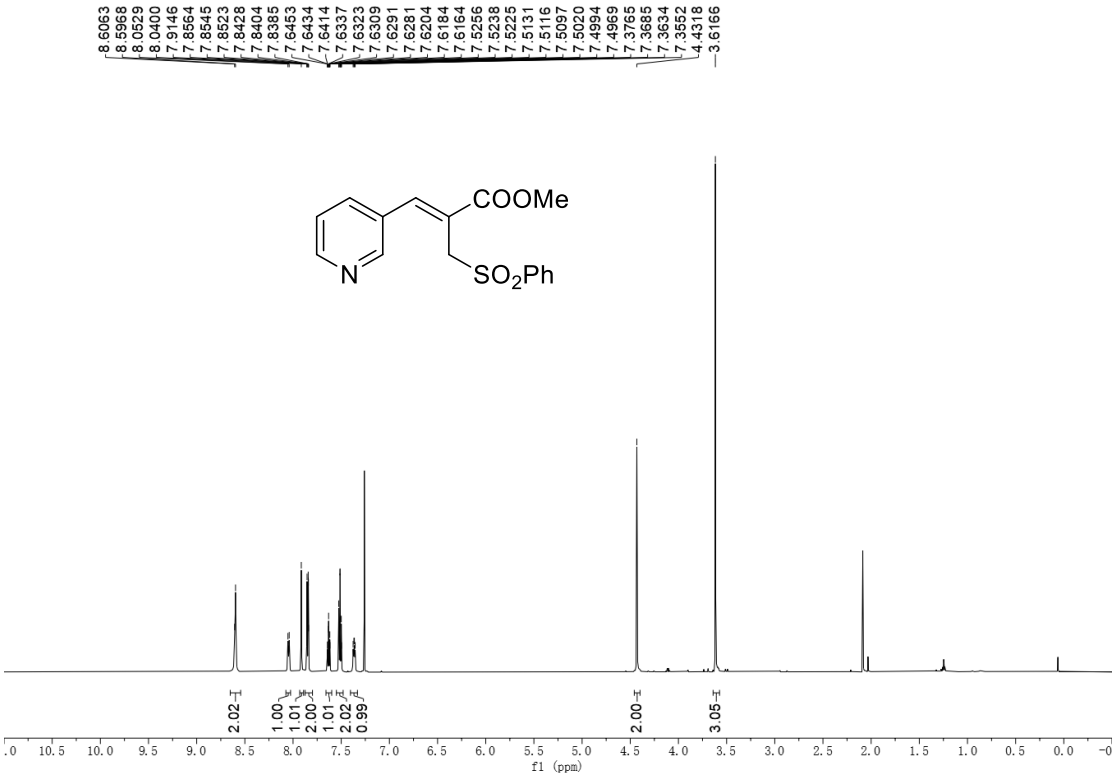


^{1}H NMR (600 MHz, Chloroform-*d*)

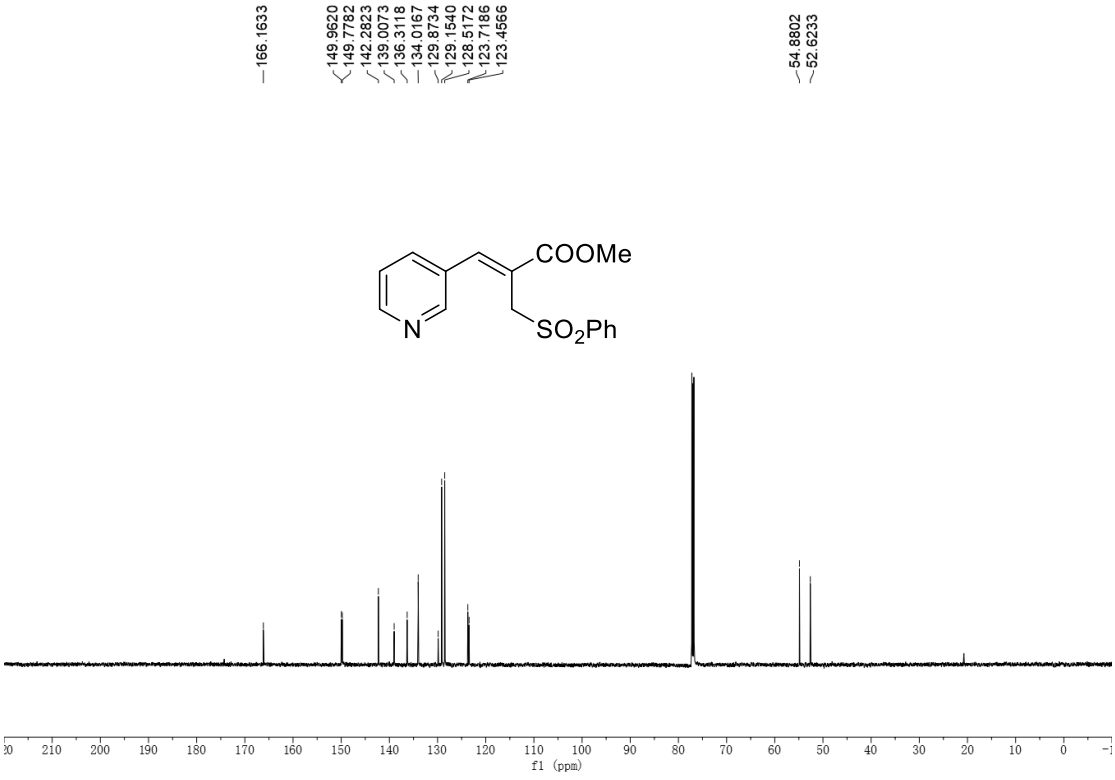


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((phenylsulfonyl)methyl)-3-(pyridin-3-yl)acrylate (**1u**)

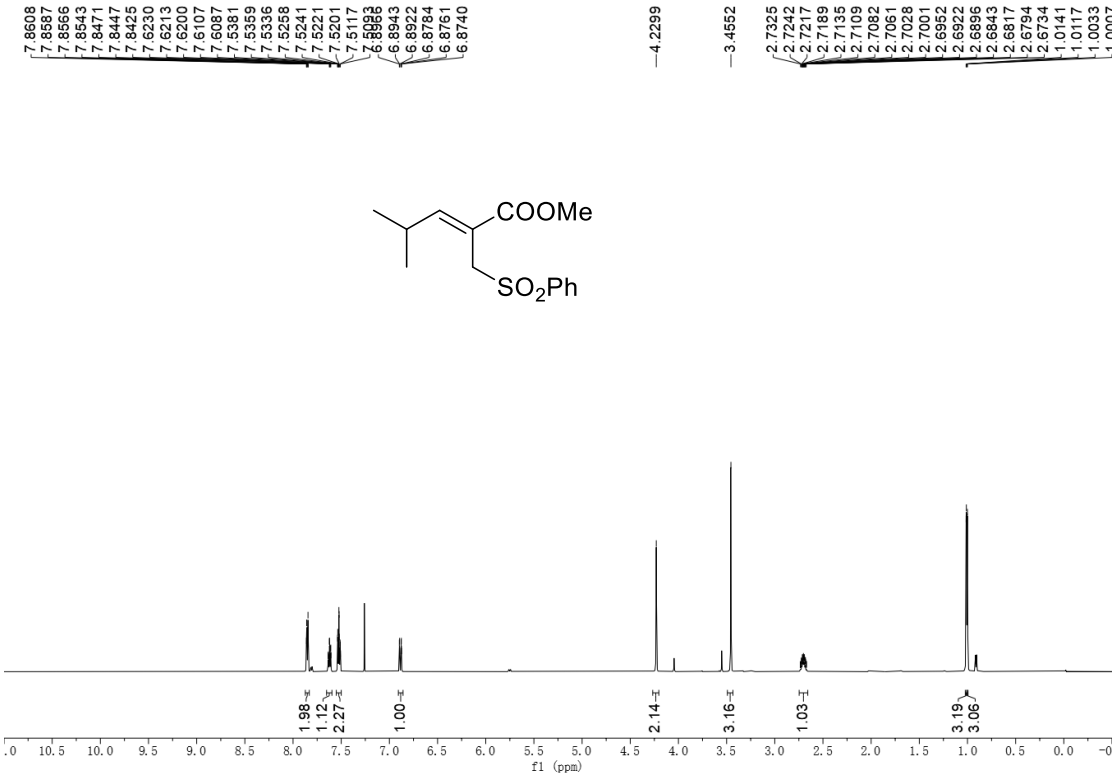


^{1}H NMR (600 MHz, Chloroform-*d*)

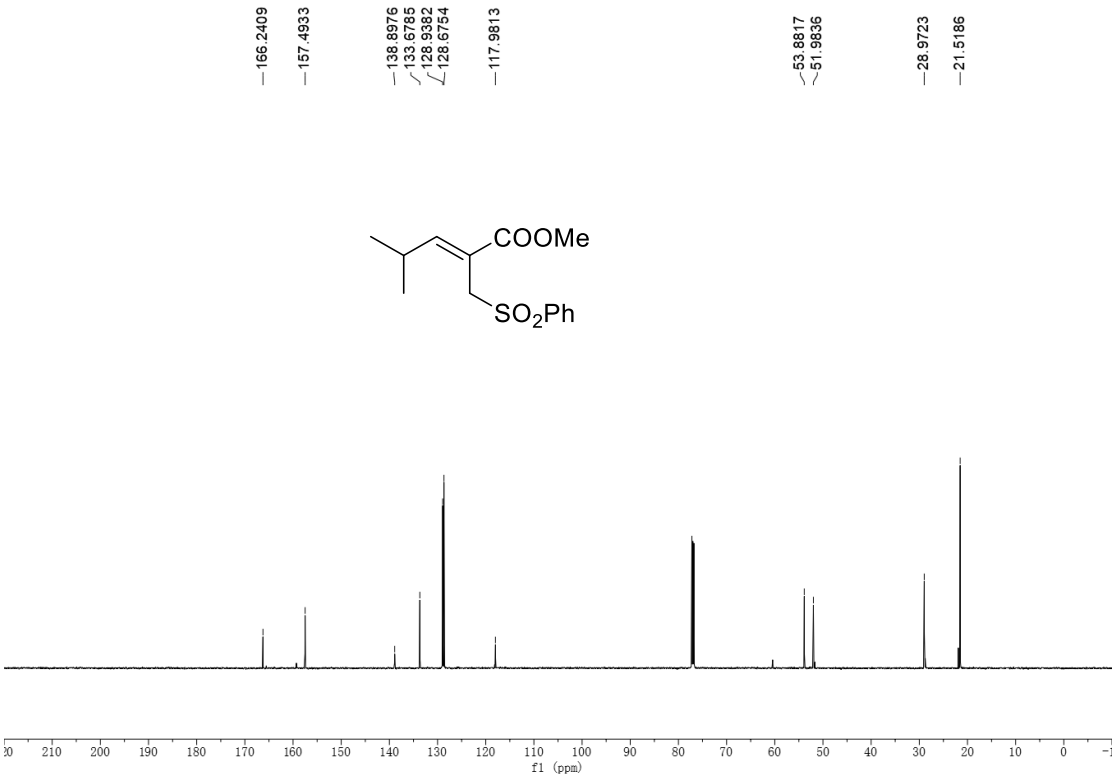


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-4-methyl-2-((phenylsulfonyl)methyl)pent-2-enoate (**1v**)

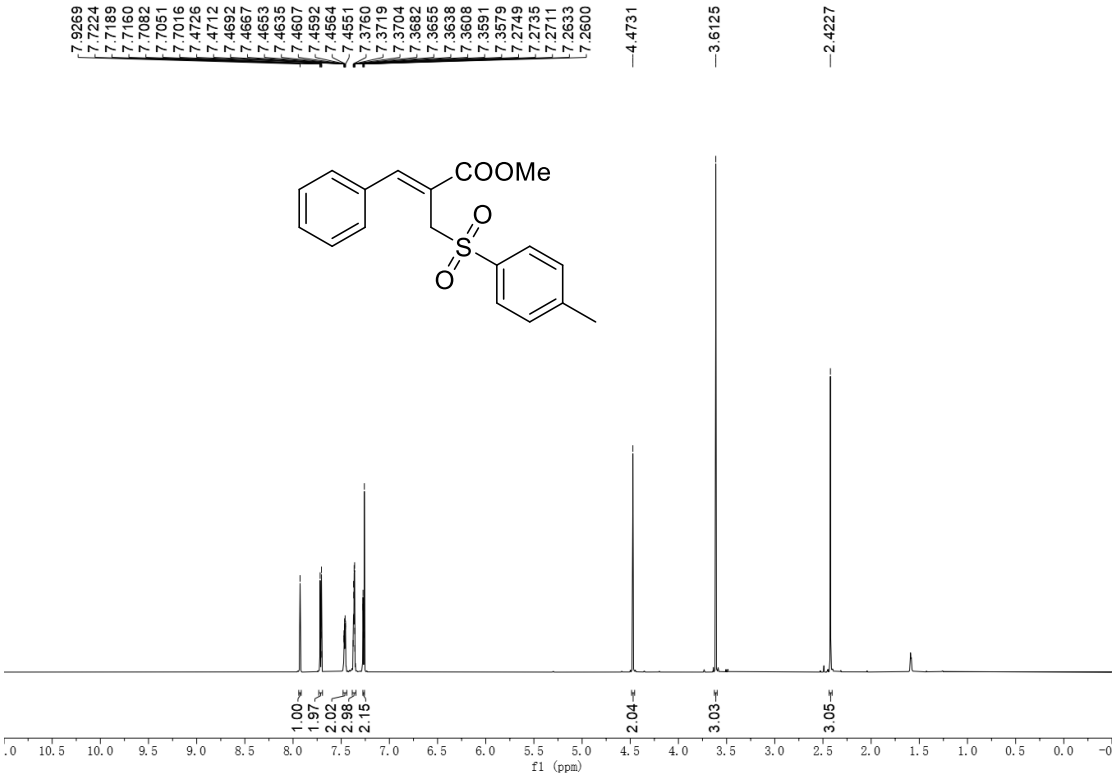


^{1}H NMR (600 MHz, Chloroform-*d*)

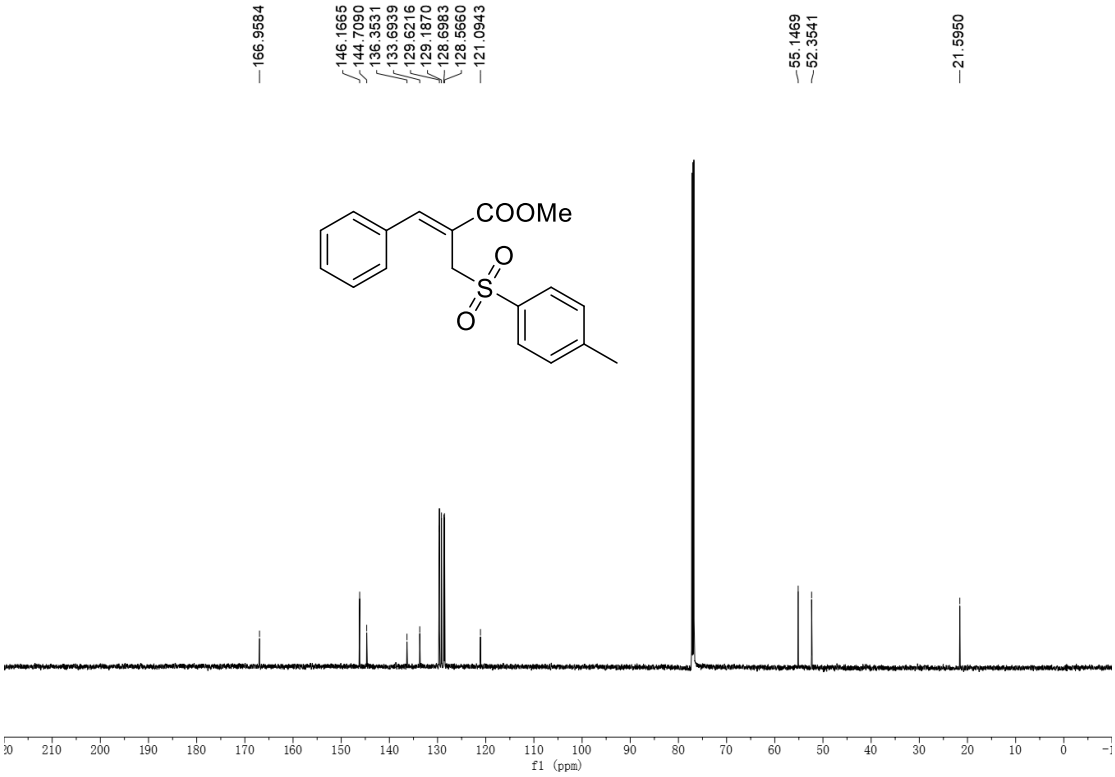


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-3-phenyl-2-(tosylmethyl)acrylate (**3a**)

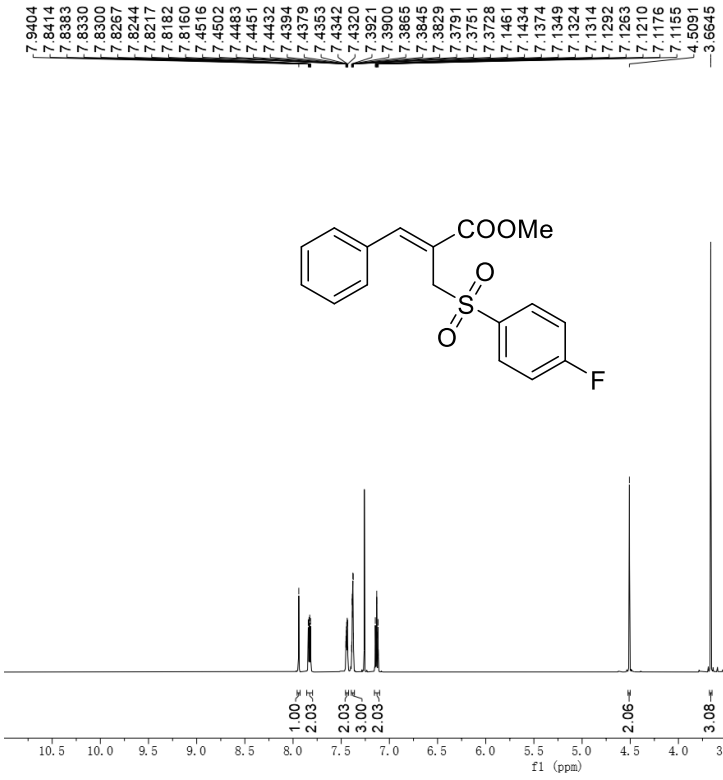


^{1}H NMR (600 MHz, Chloroform-*d*)

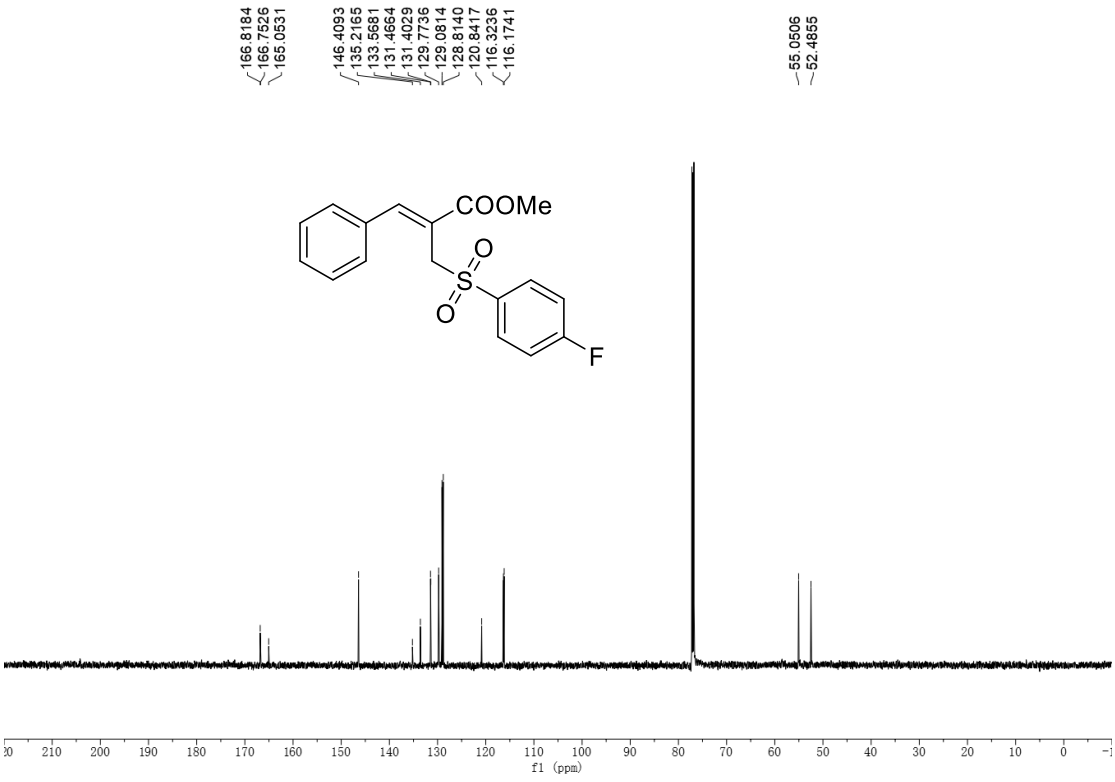


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-(((4-fluorophenyl)sulfonyl)methyl)-3-phenylacrylate (**3b**)

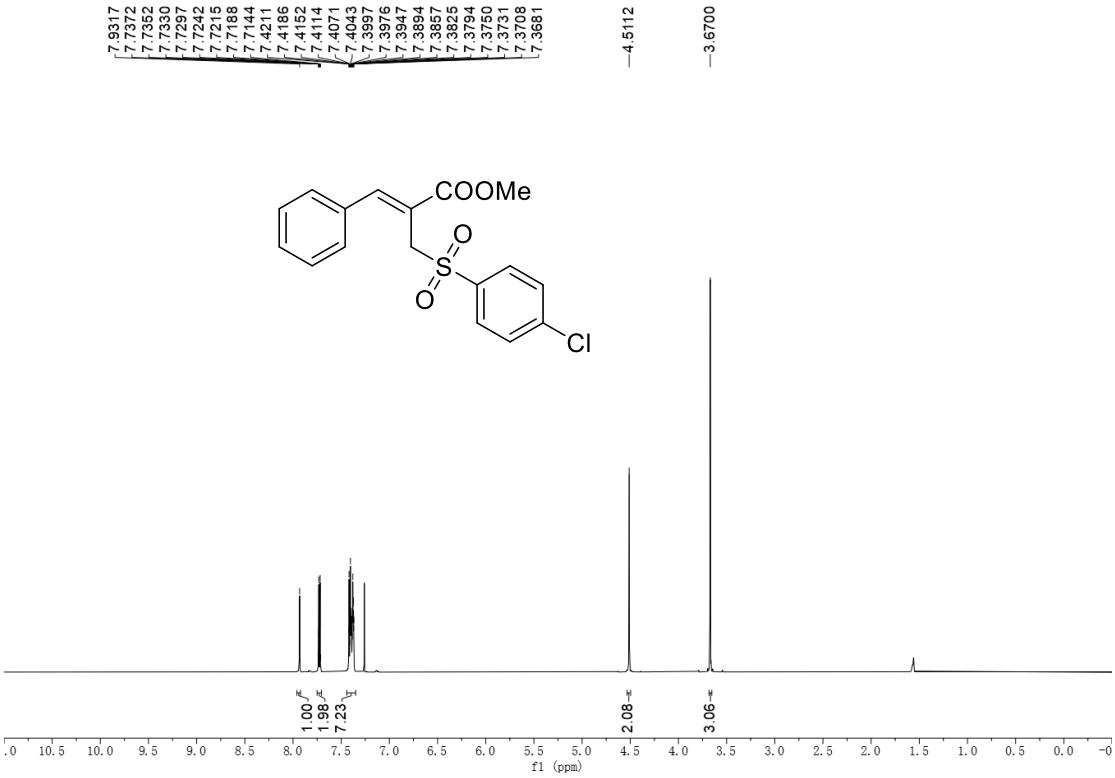


^{1}H NMR (600 MHz, Chloroform-*d*)

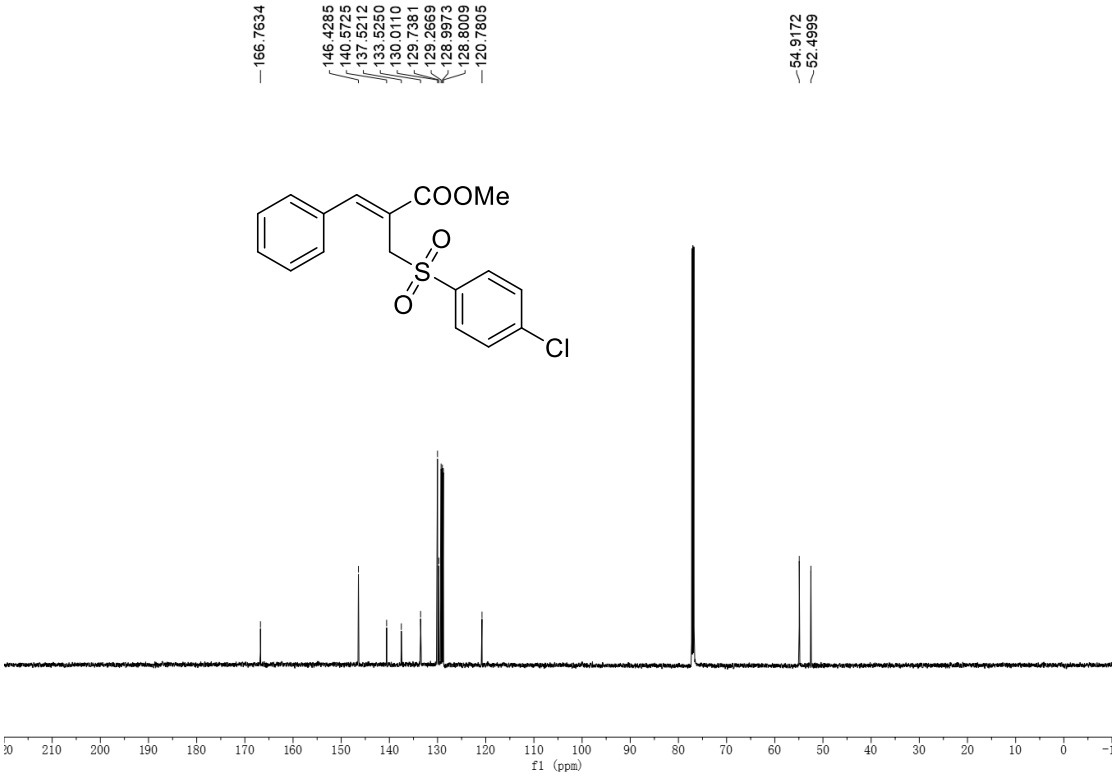


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-(((4-chlorophenyl)sulfonyl)methyl)-3-phenylacrylate (**3c**)

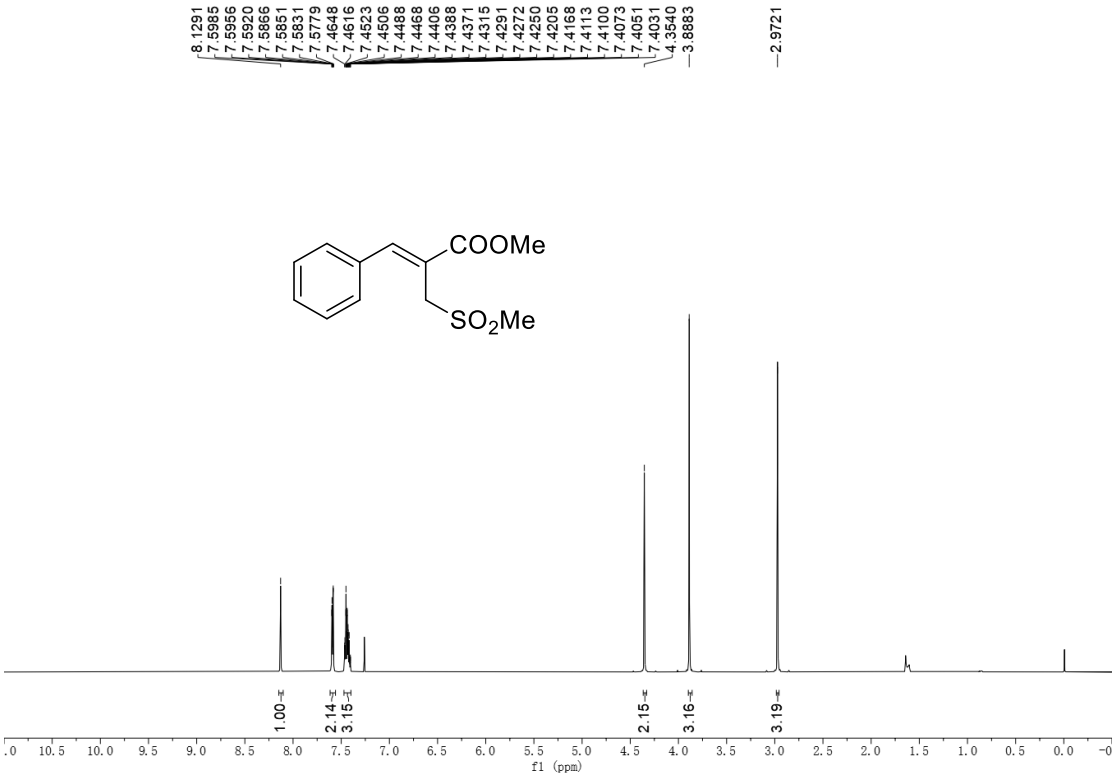


^{1}H NMR (600 MHz, Chloroform-*d*)

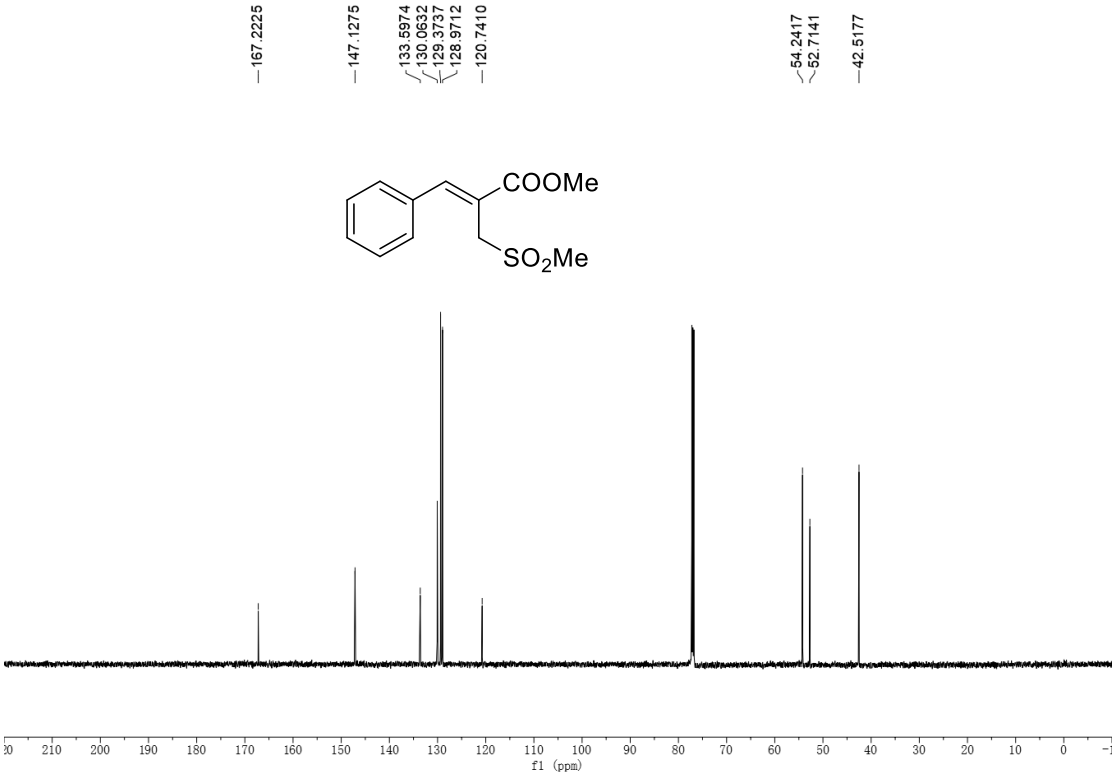


^{13}C NMR (151 MHz, Chloroform-*d*)

(*Z*)-2-((methylsulfonyl)methyl)-3-phenylacrylate (**3d**)

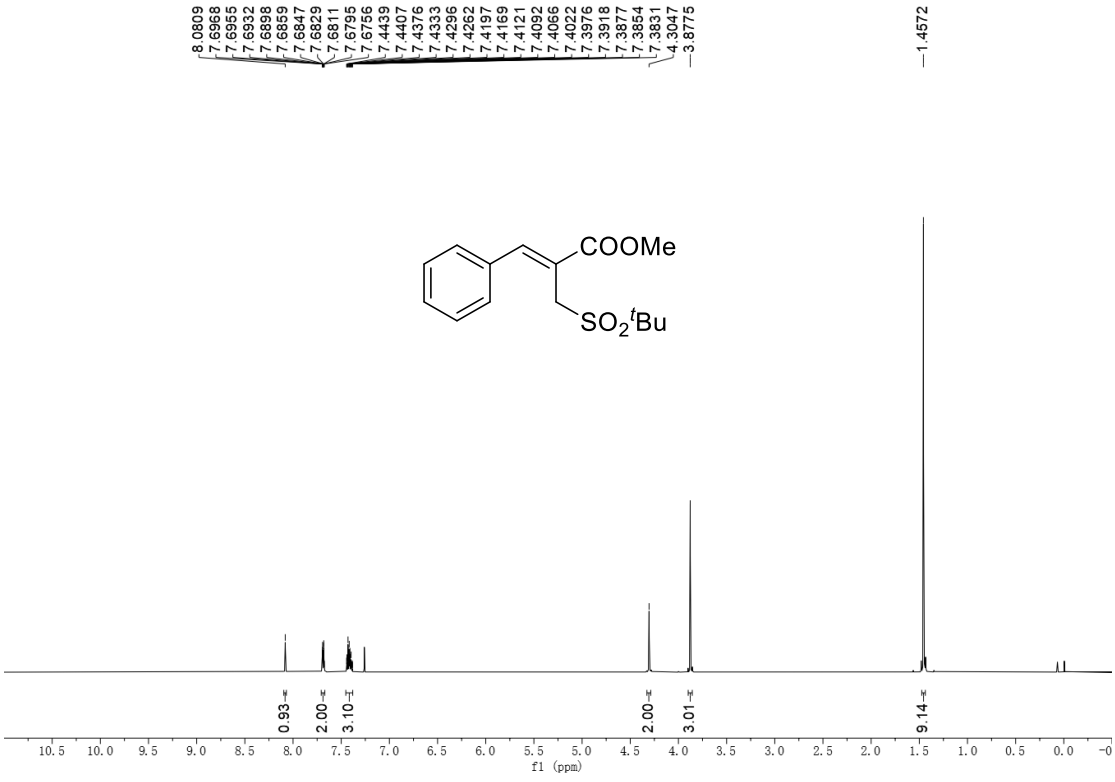


^{1}H NMR (600 MHz, Chloroform-*d*)

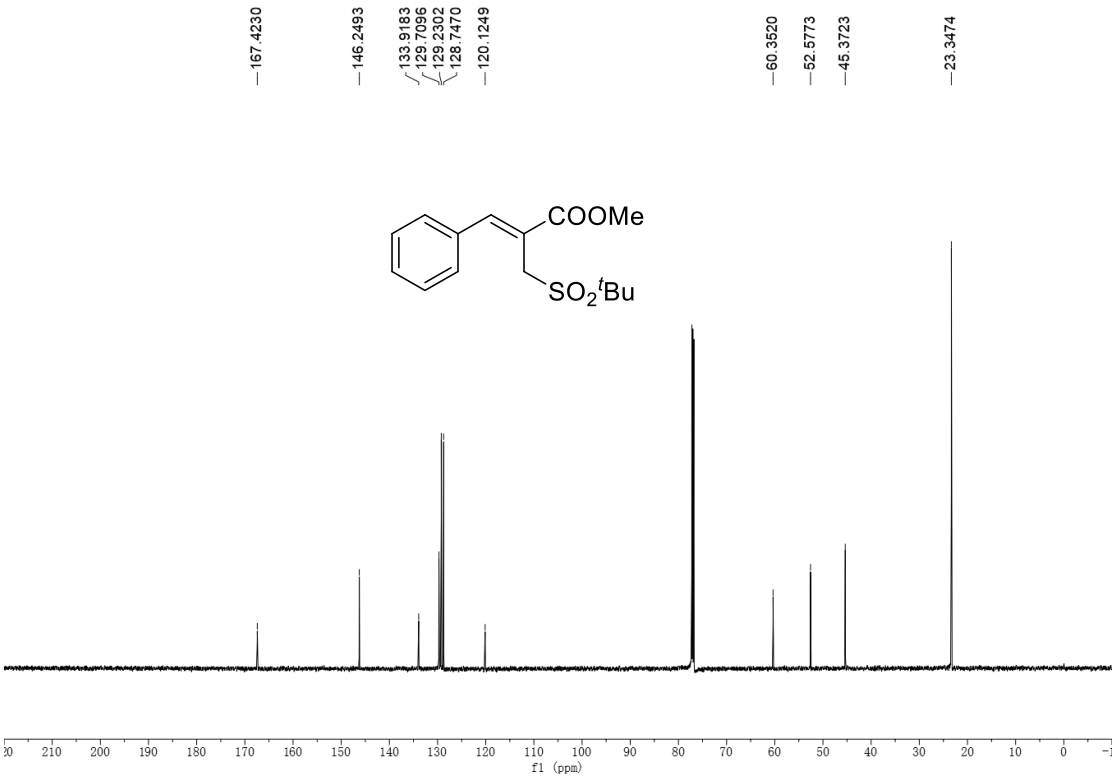


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((*tert*-butylsulfonyl)methyl)-3-phenylacrylate (**3e**)

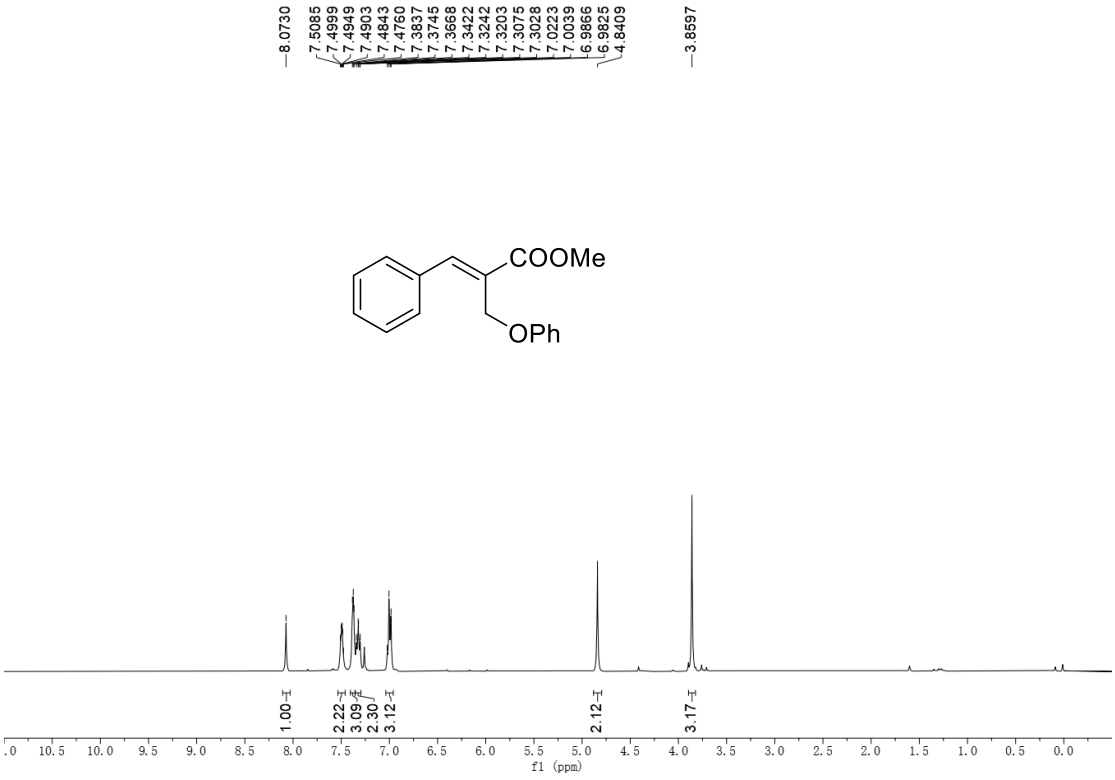


^{1}H NMR (600 MHz, Chloroform-*d*)



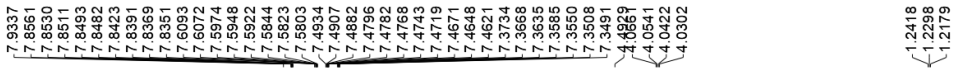
^{13}C NMR (151 MHz, Chloroform-*d*)

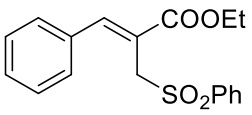
Methyl (*E*)-2-(phenoxymethyl)-3-phenylacrylate (**3f**)

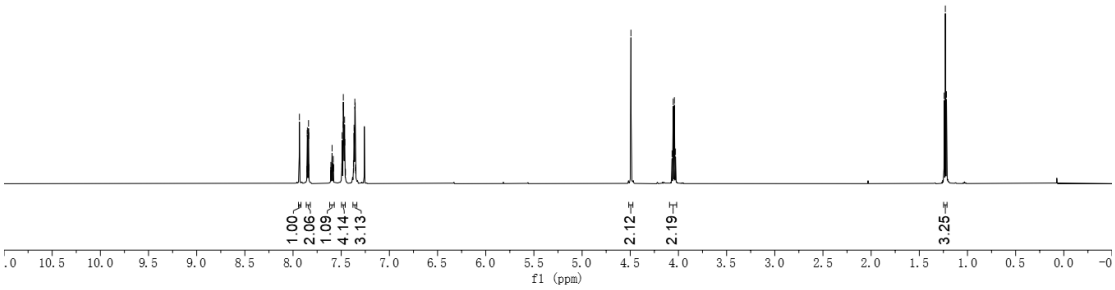


^{1}H NMR (400 MHz, Chloroform-*d*)

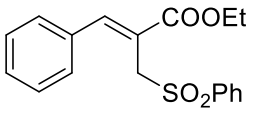
Ethyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**3g**)

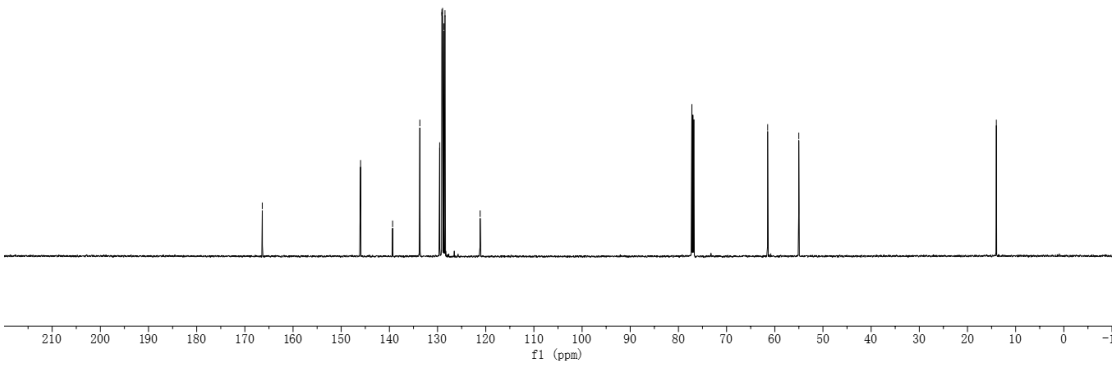






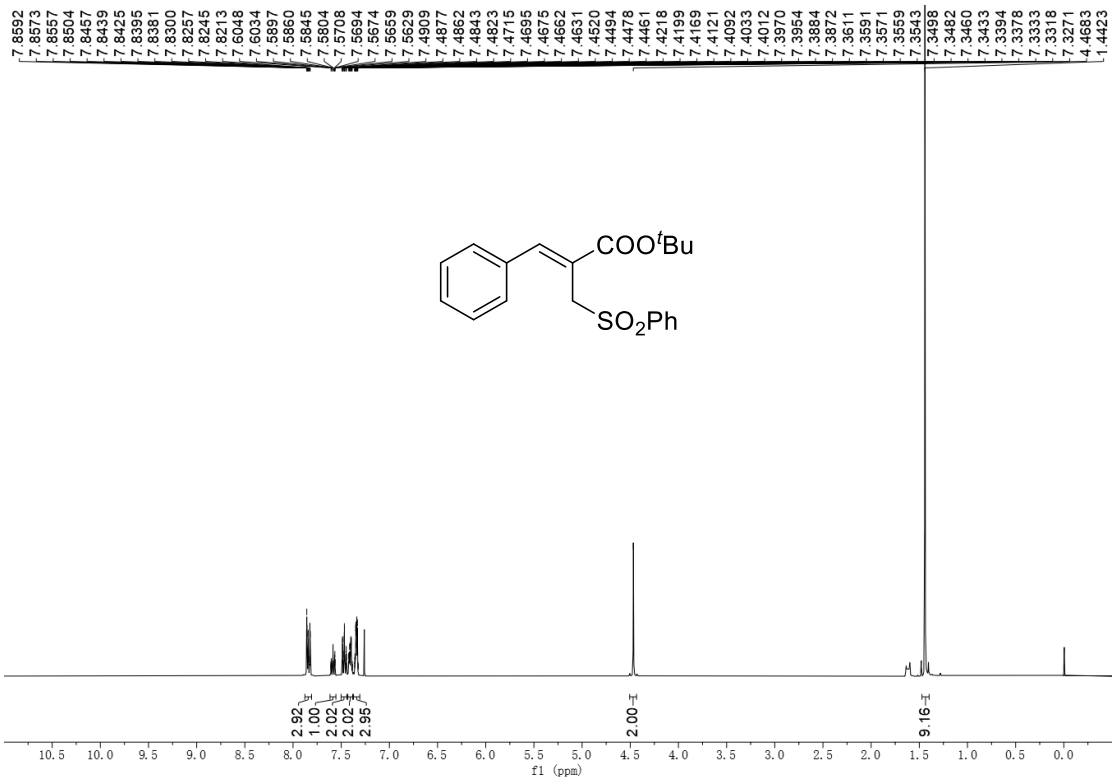
^{1}H NMR (600 MHz, Chloroform-*d*)



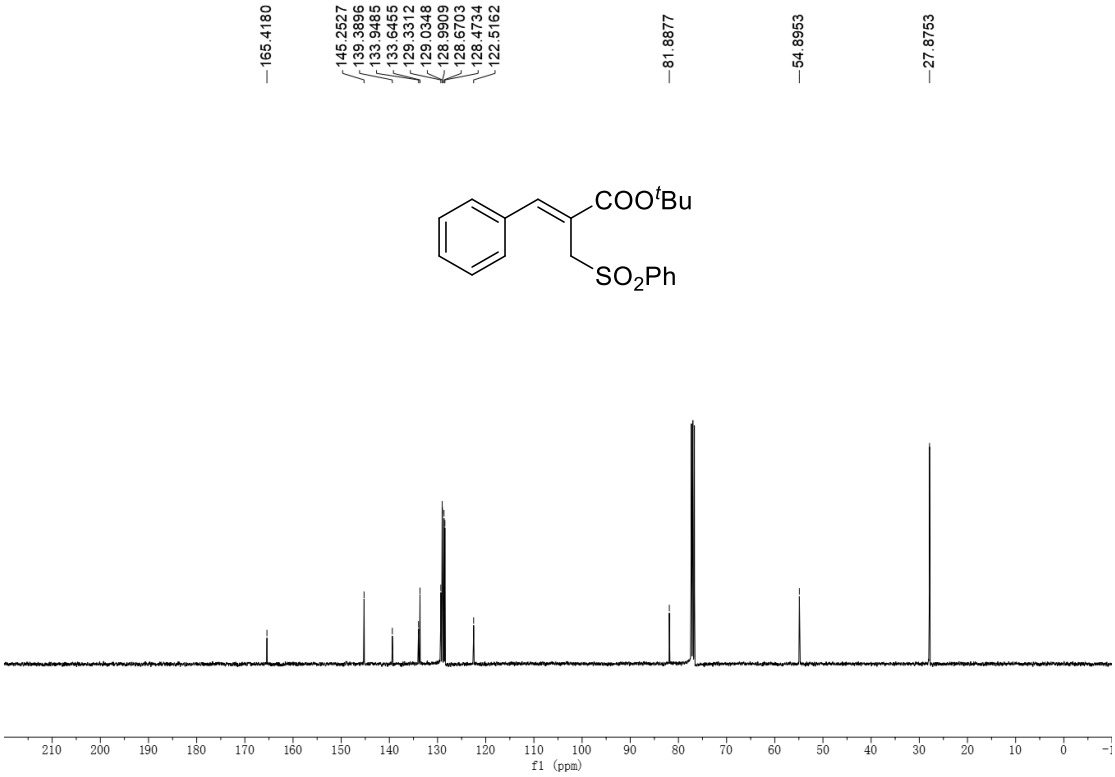


^{13}C NMR (151 MHz, Chloroform-*d*)

Tert-butyl (*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylate (**3h**)

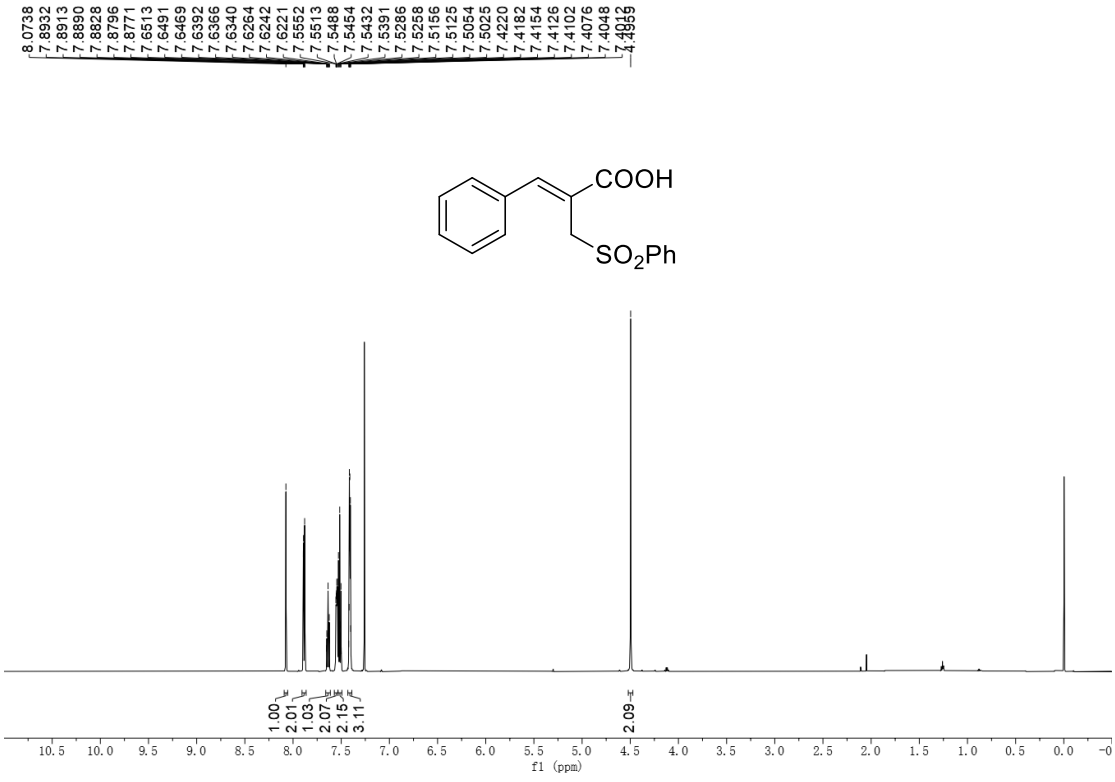


^{1}H NMR (400 MHz, Chloroform-*d*)



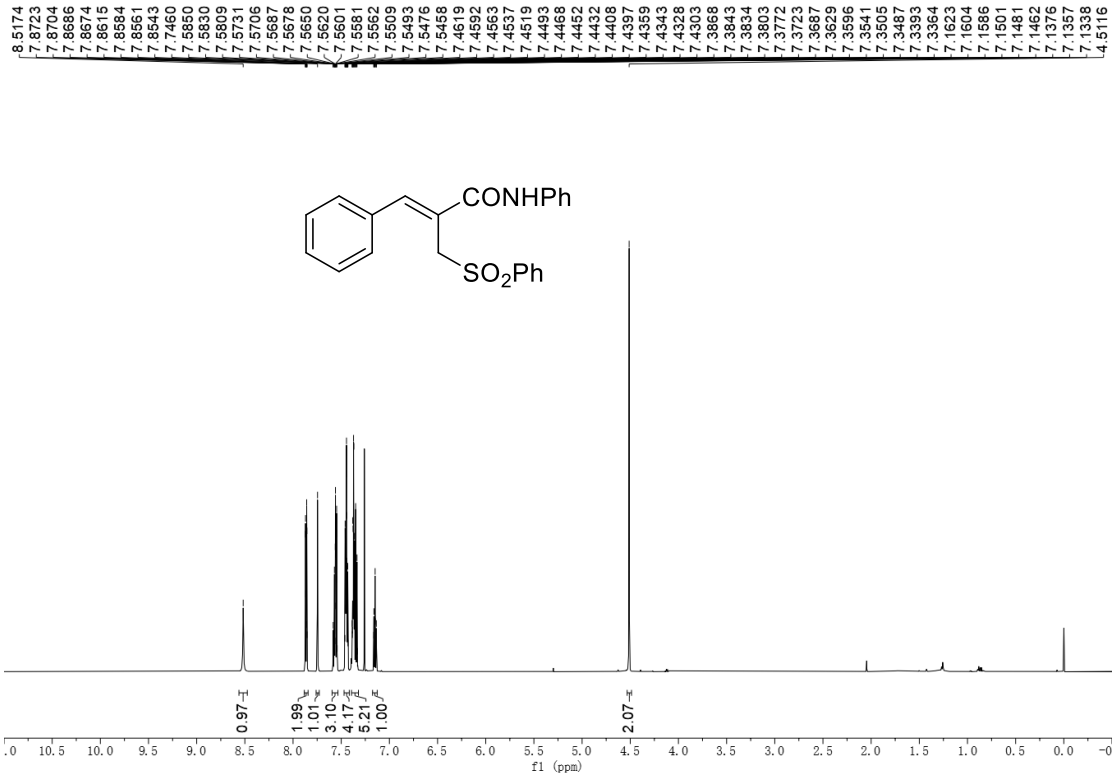
^{13}C NMR (101 MHz, Chloroform-*d*)

(*Z*)-3-phenyl-2-((phenylsulfonyl)methyl)acrylic acid (**3i**)

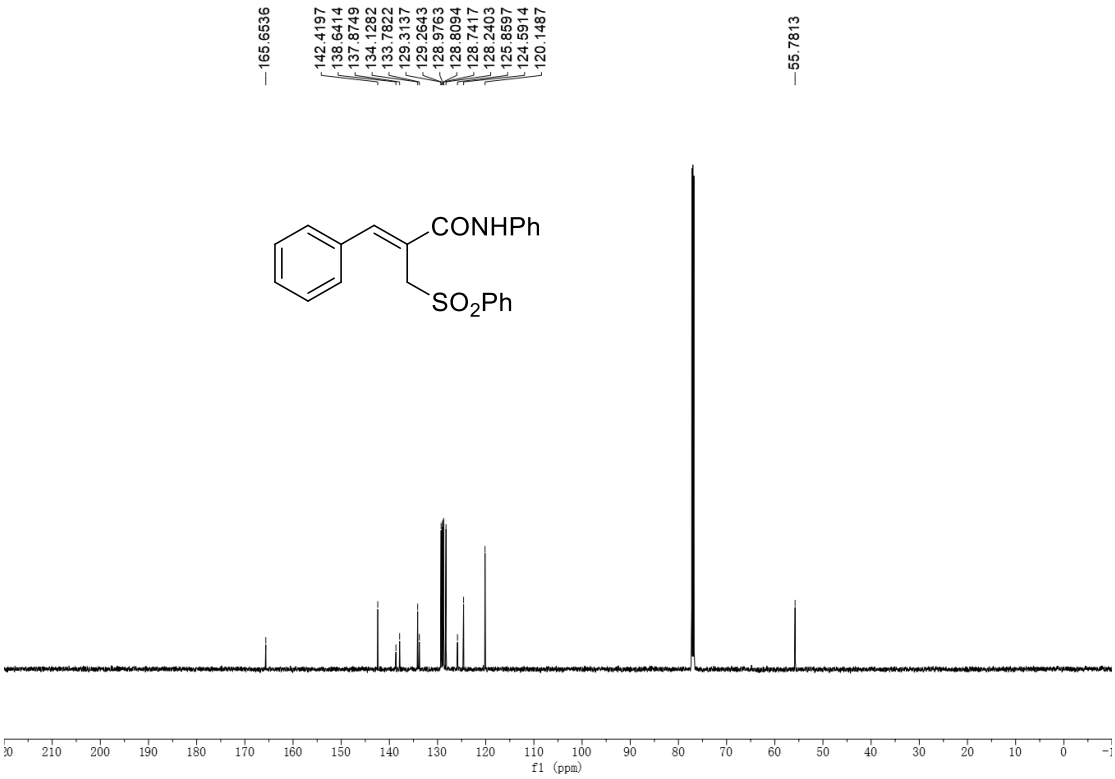


^{1}H NMR (600 MHz, Chloroform-*d*)

(*Z*)-*N*,3-diphenyl-2-((phenylsulfonyl)methyl)acrylamide (**3j**)

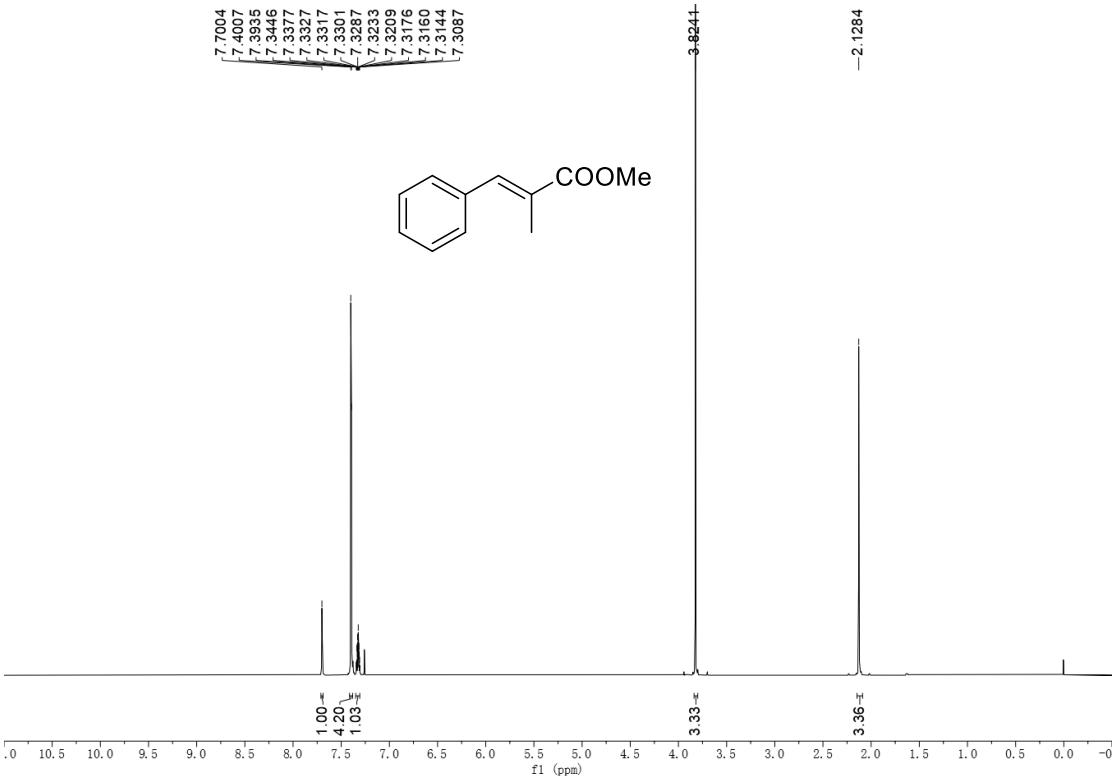


^{1}H NMR (600 MHz, Chloroform-*d*)



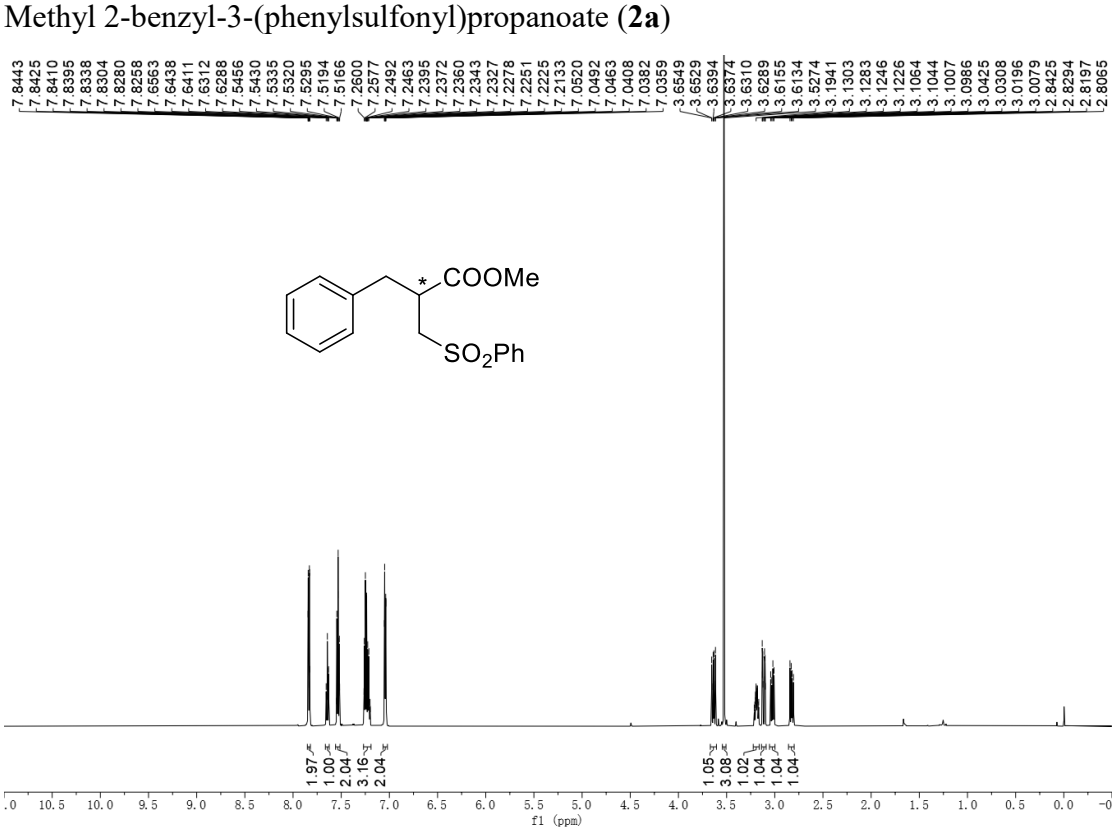
^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl (*E*)-2-methyl-3-phenylacrylate (**3k**)

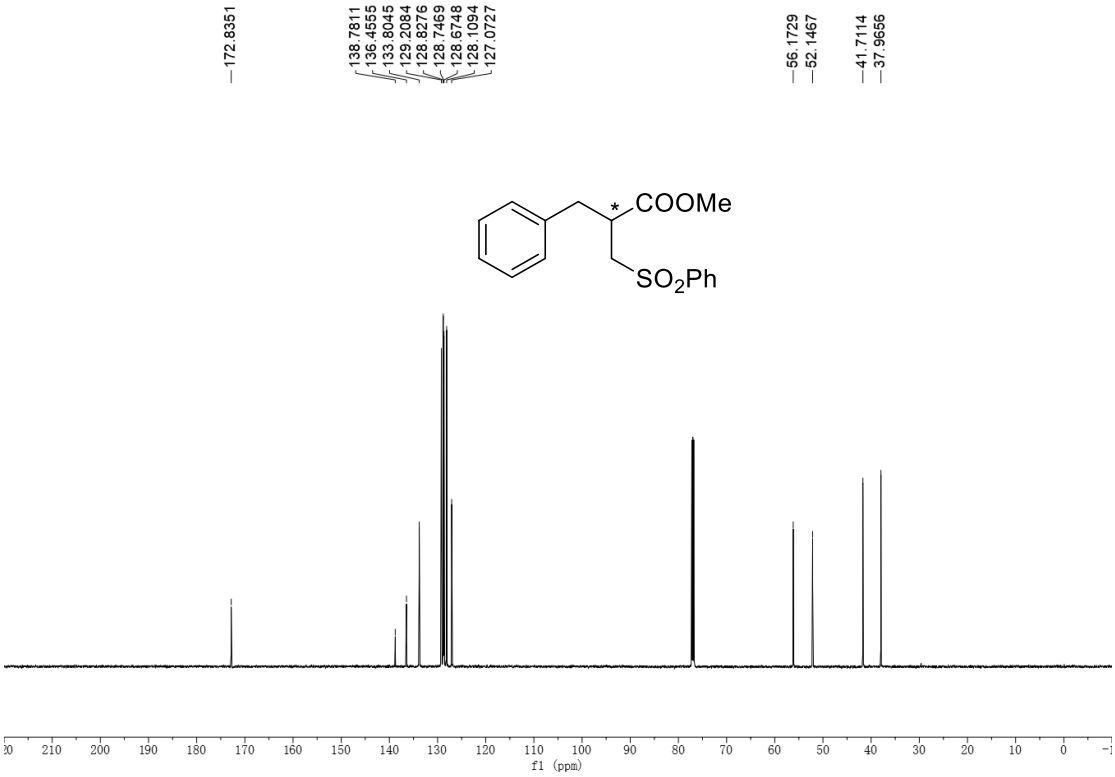


^{1}H NMR (600 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-(phenylsulfonyl)propanoate (**2a**)

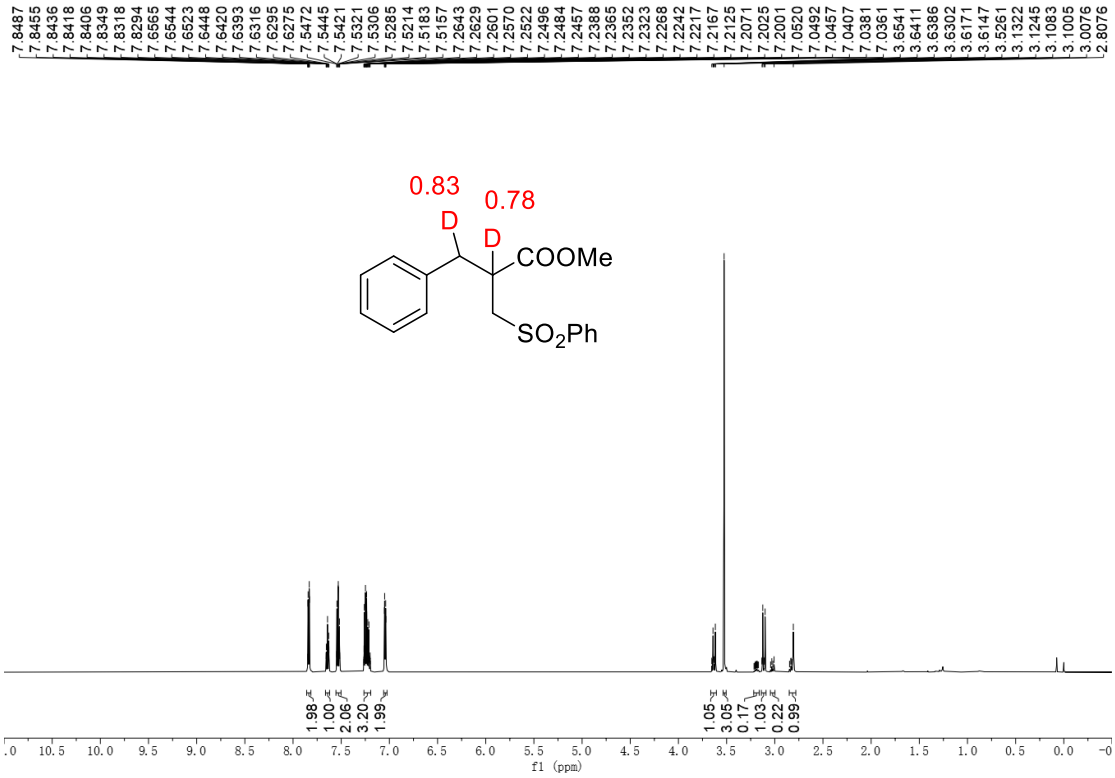


^{1}H NMR (600 MHz, Chloroform-*d*)



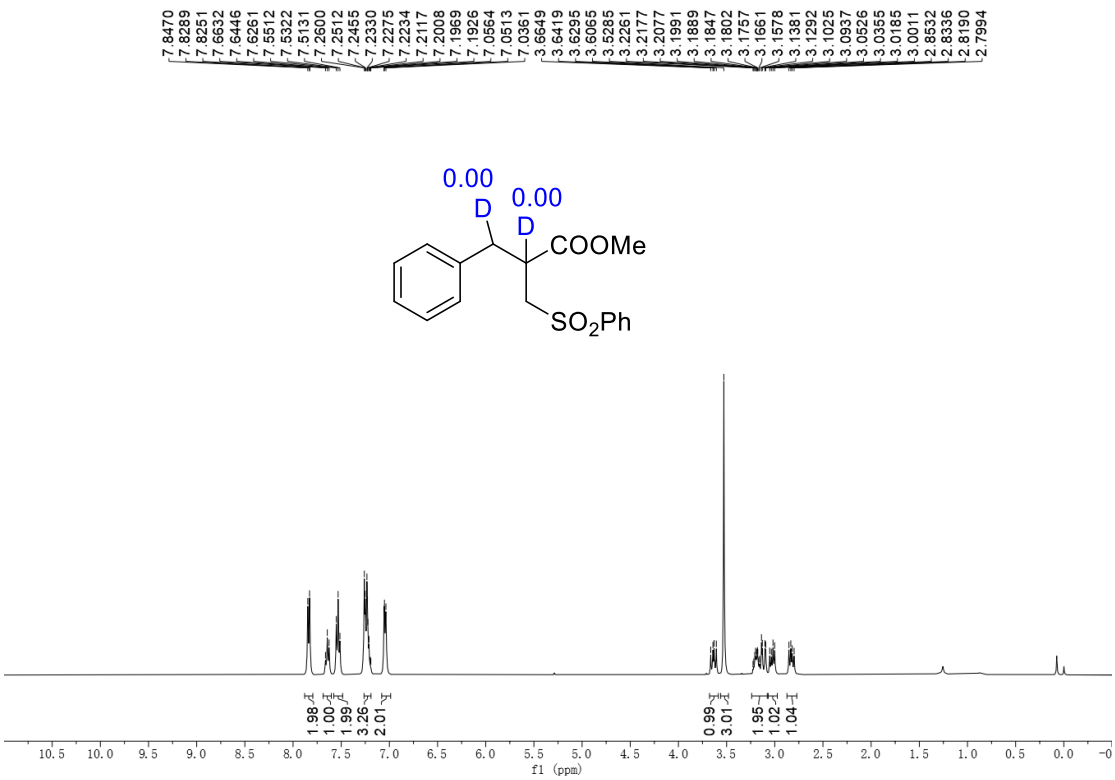
^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 3-phenyl-2-((phenylsulfonyl)methyl)propanoate-2,3-d_2 (**2a-D-1**)



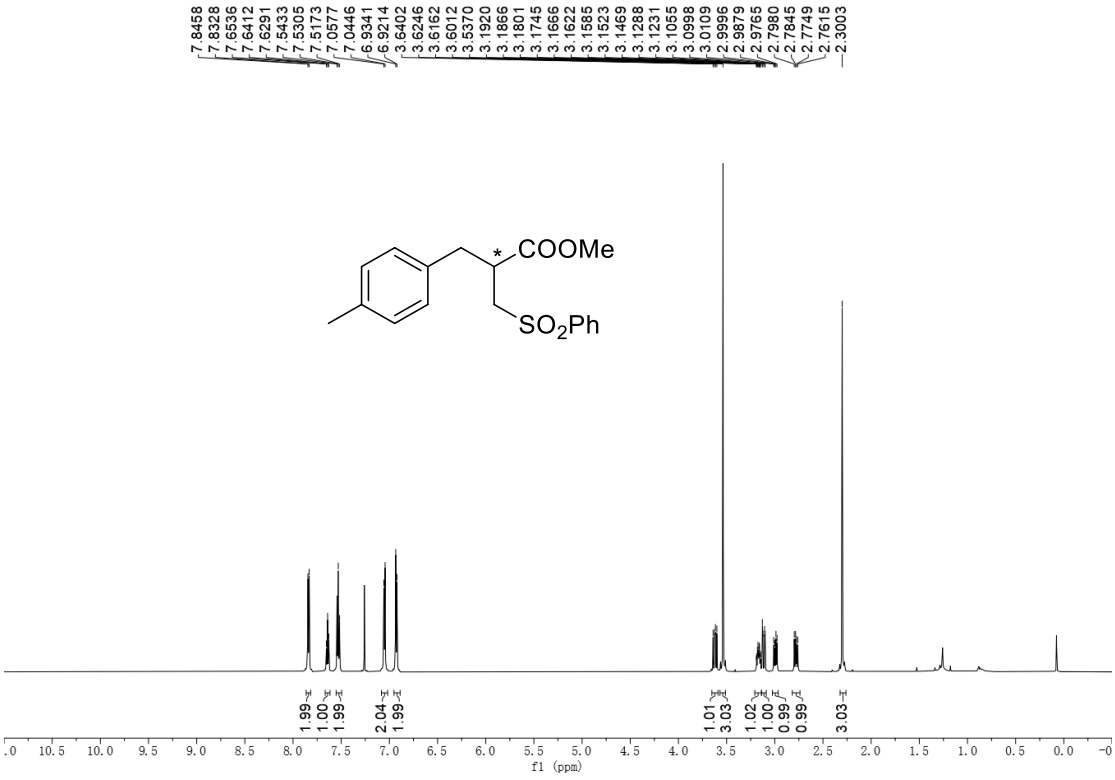
^{1}H NMR (600 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-(phenylsulfonyl)propanoate (**2a-D-2**)

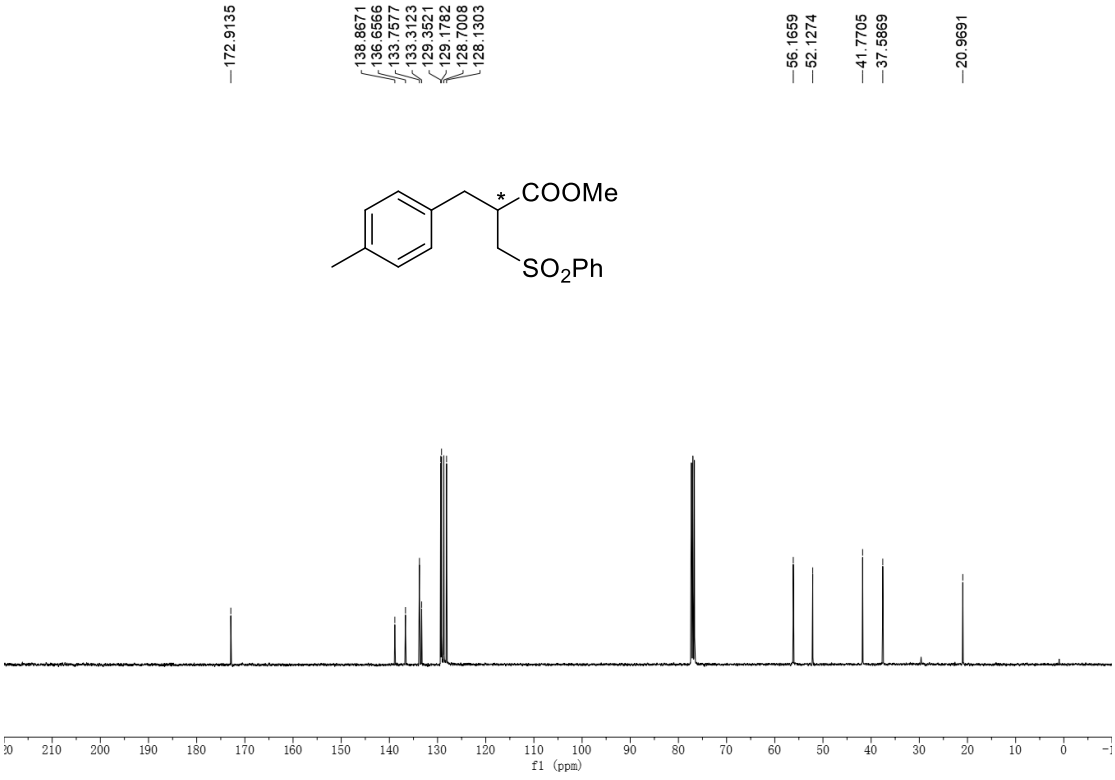


^{1}H NMR (400 MHz, Chloroform-*d*)

Methyl 2-(4-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2b**)

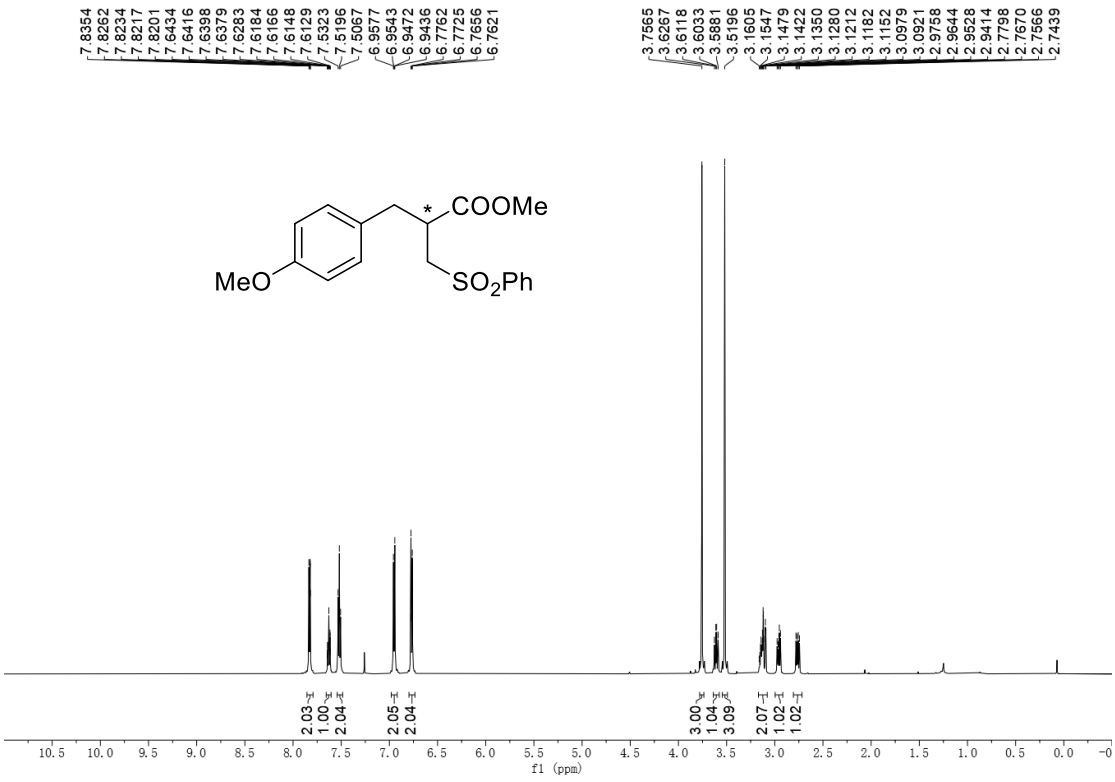


^{1}H NMR (600 MHz, Chloroform-*d*)

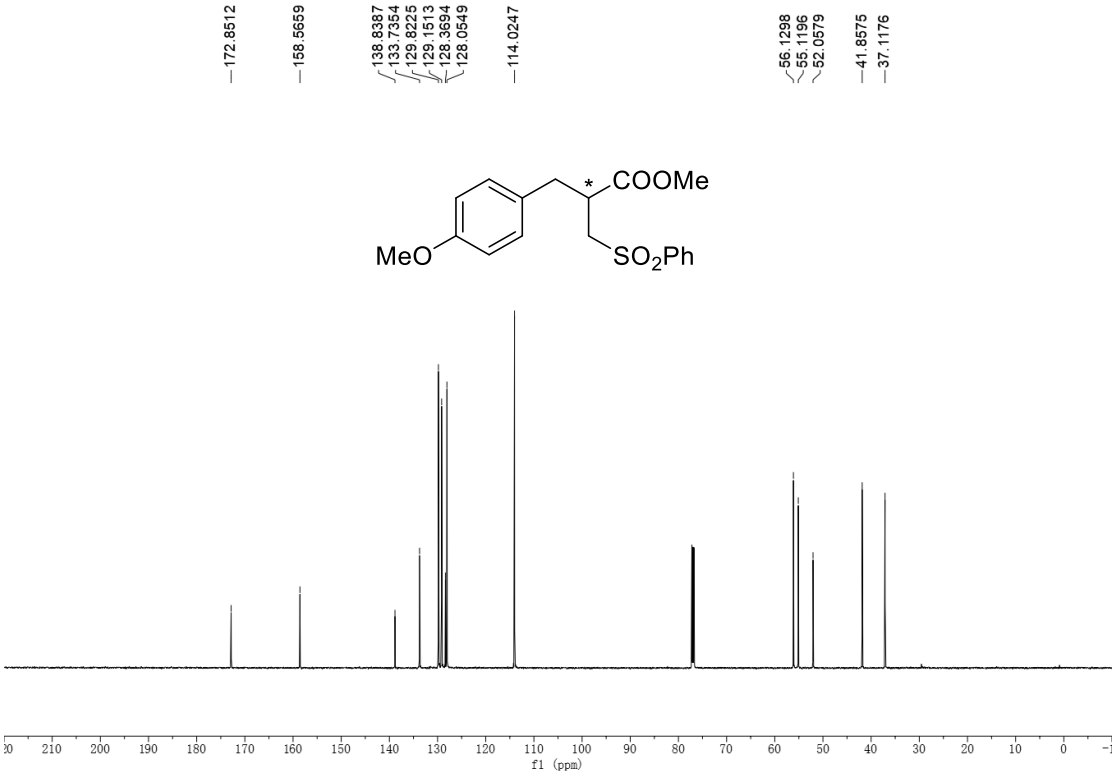


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 2-(4-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2c**)

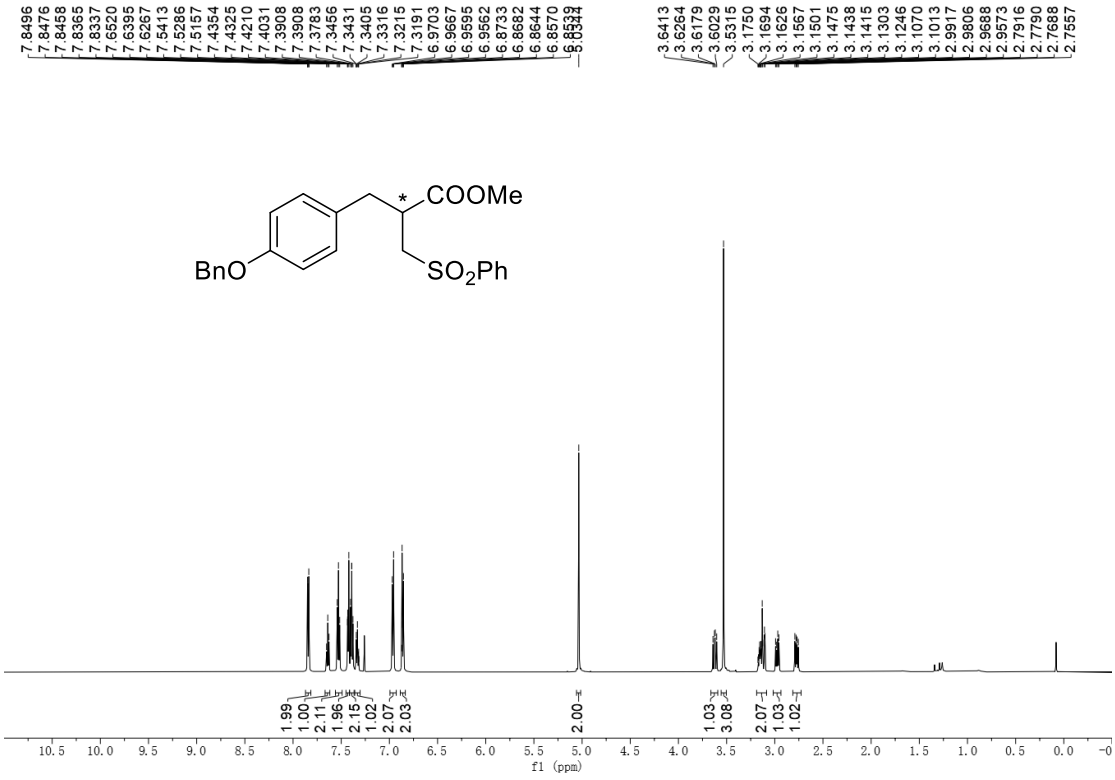


^{1}H NMR (600 MHz, Chloroform-*d*)

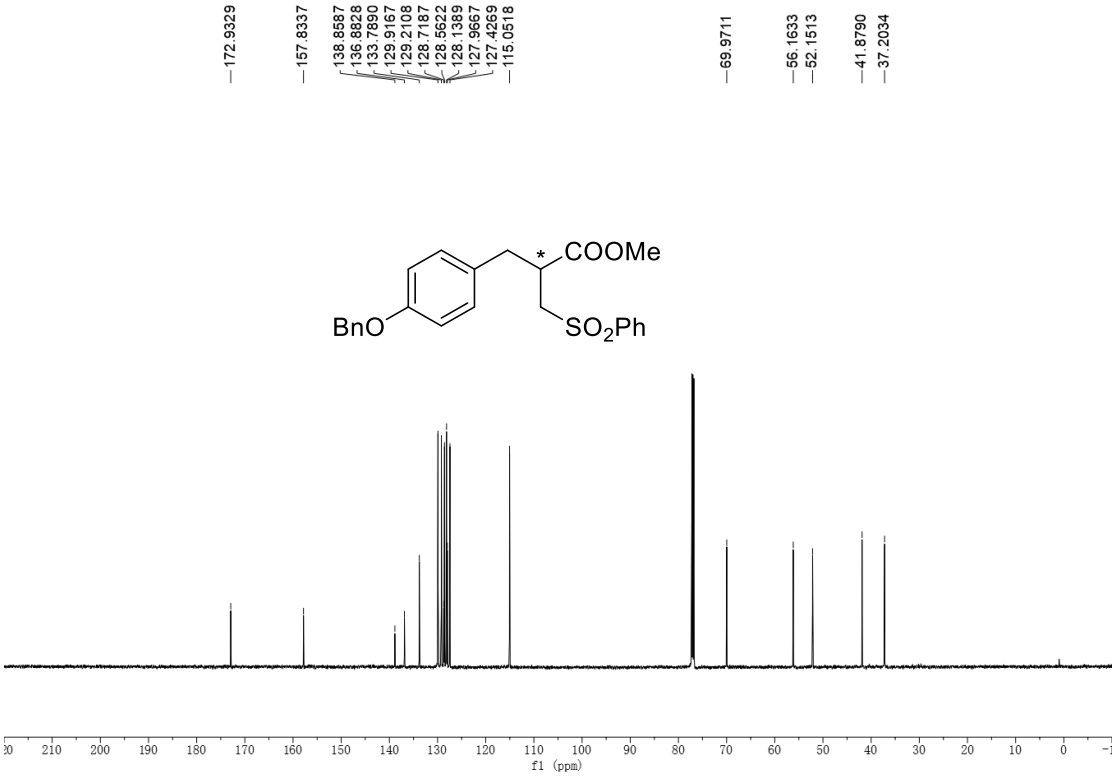


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(4-(benzyloxy)benzyl)-3-(phenylsulfonyl)propanoate (**2d**)

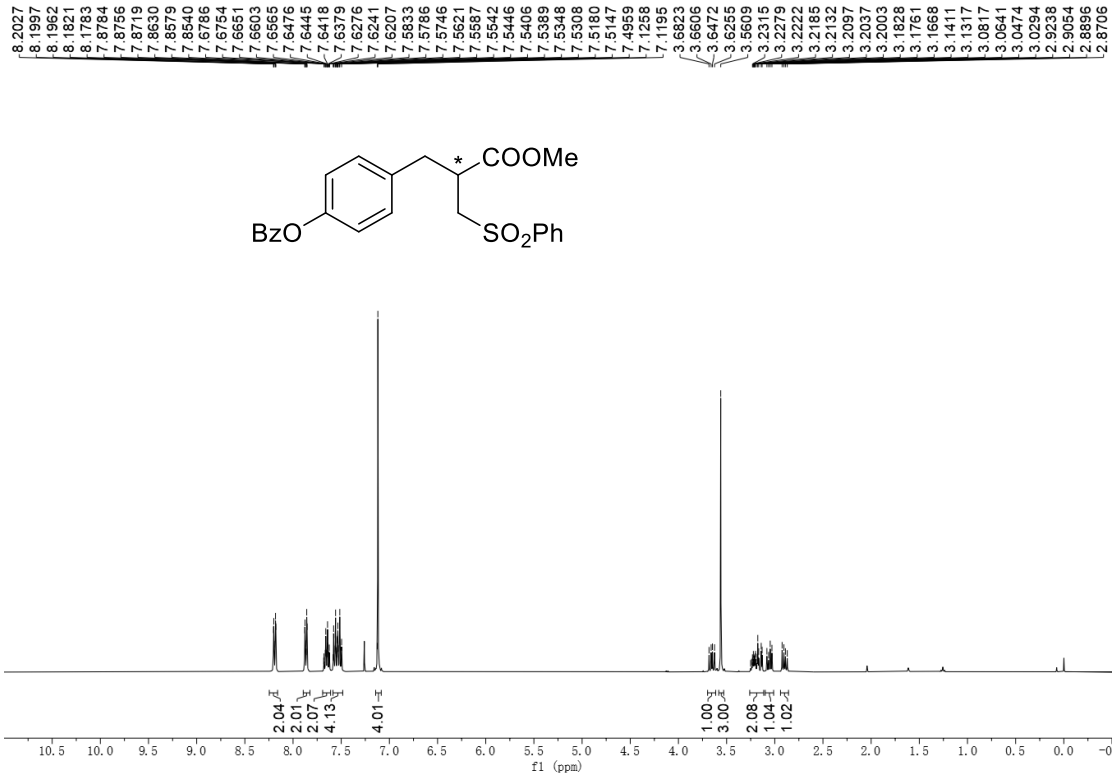


^{1}H NMR (600 MHz, Chloroform-*d*)

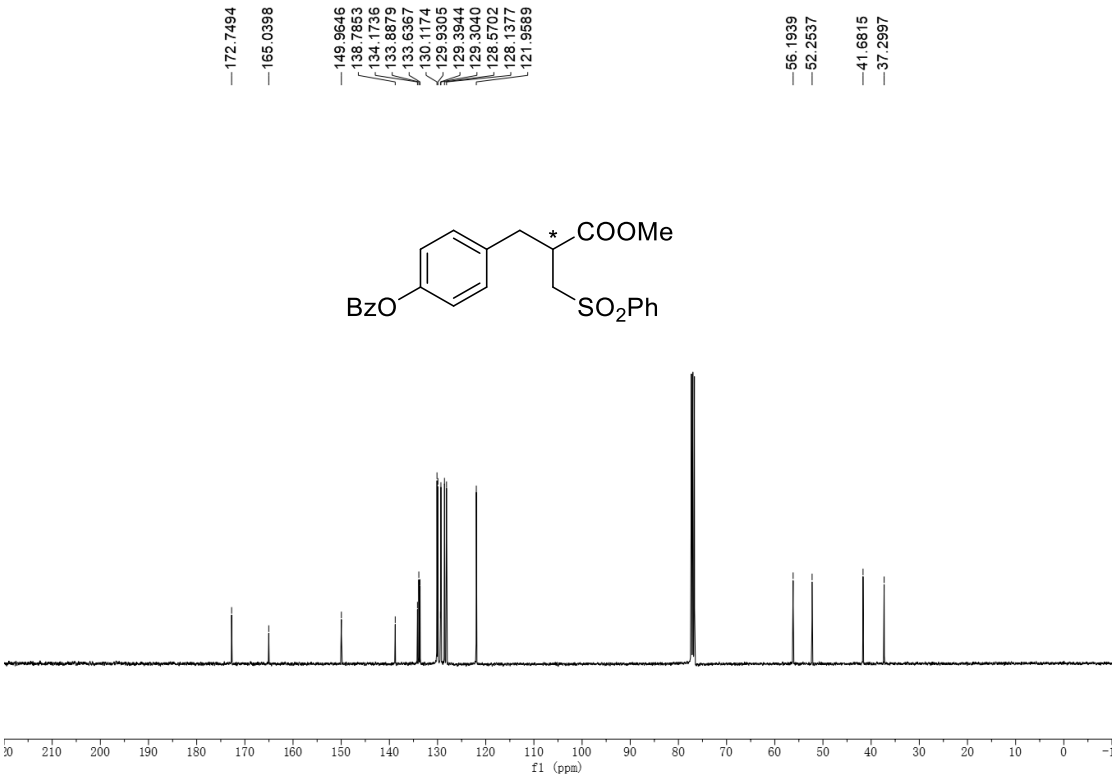


^{1}H NMR (600 MHz, Chloroform-*d*)

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl benzoate (**2e**)

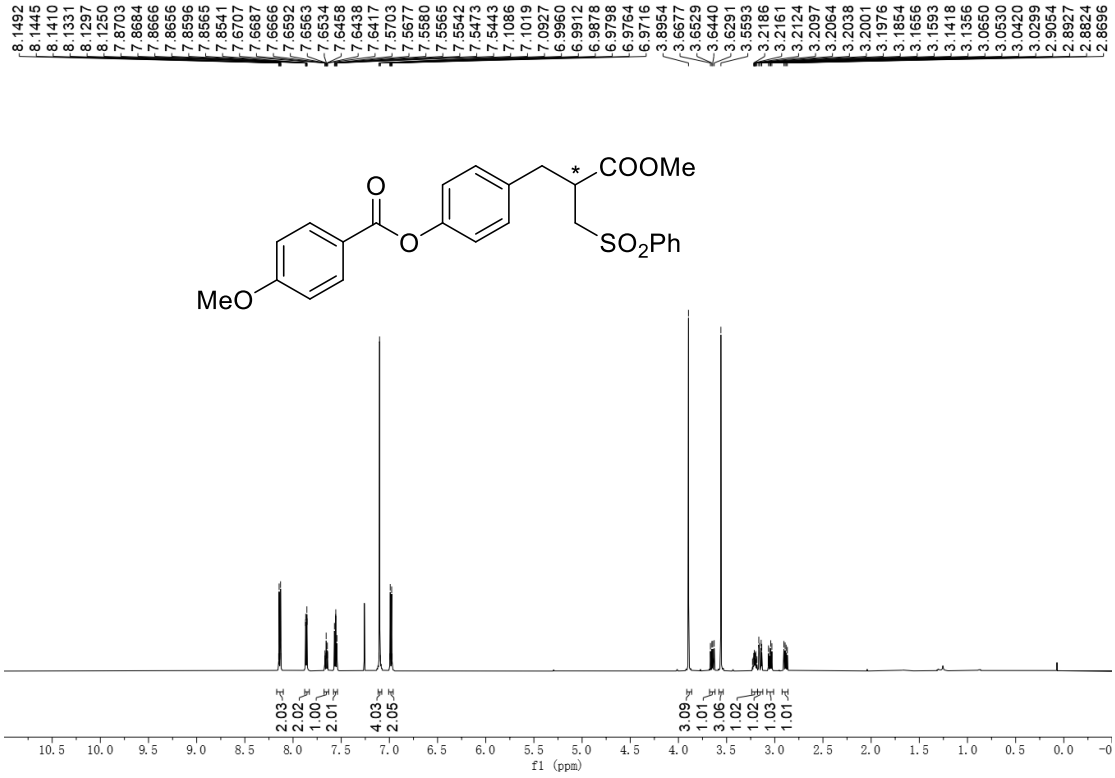


^{1}H NMR (400 MHz, Chloroform-*d*)

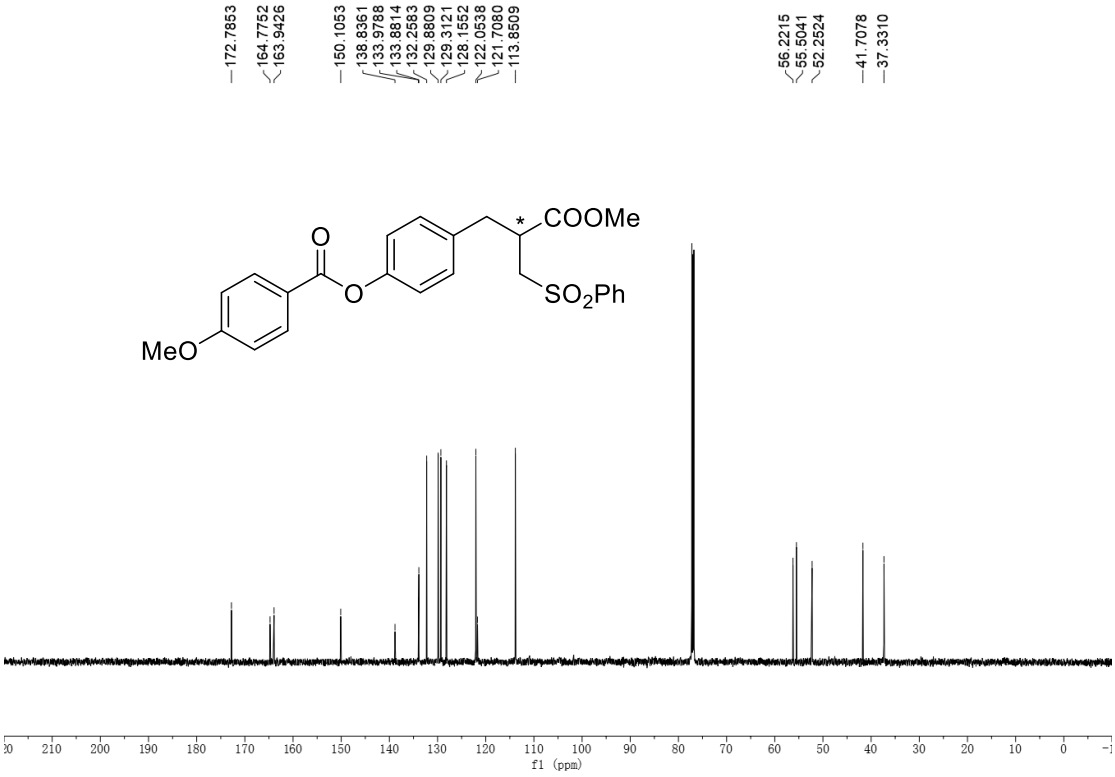


^{13}C NMR (101 MHz, Chloroform-*d*)

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl 4-methoxybenzoate (**2f**)

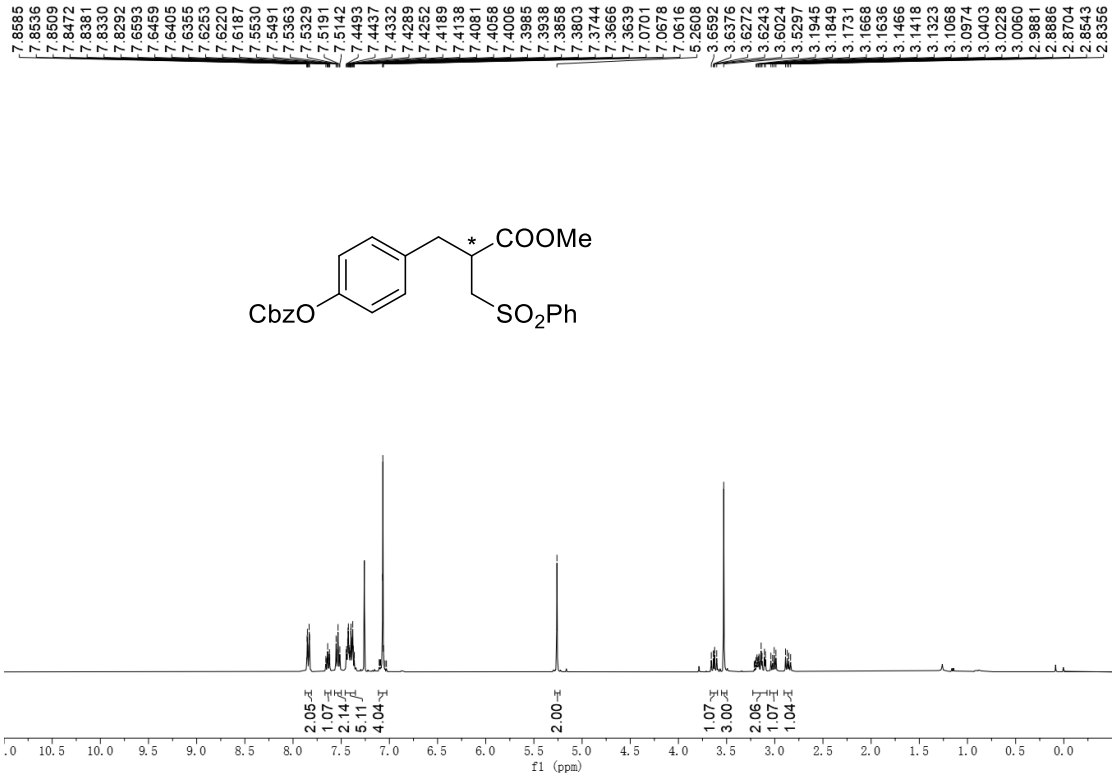


^{1}H NMR (600 MHz, Chloroform-*d*)

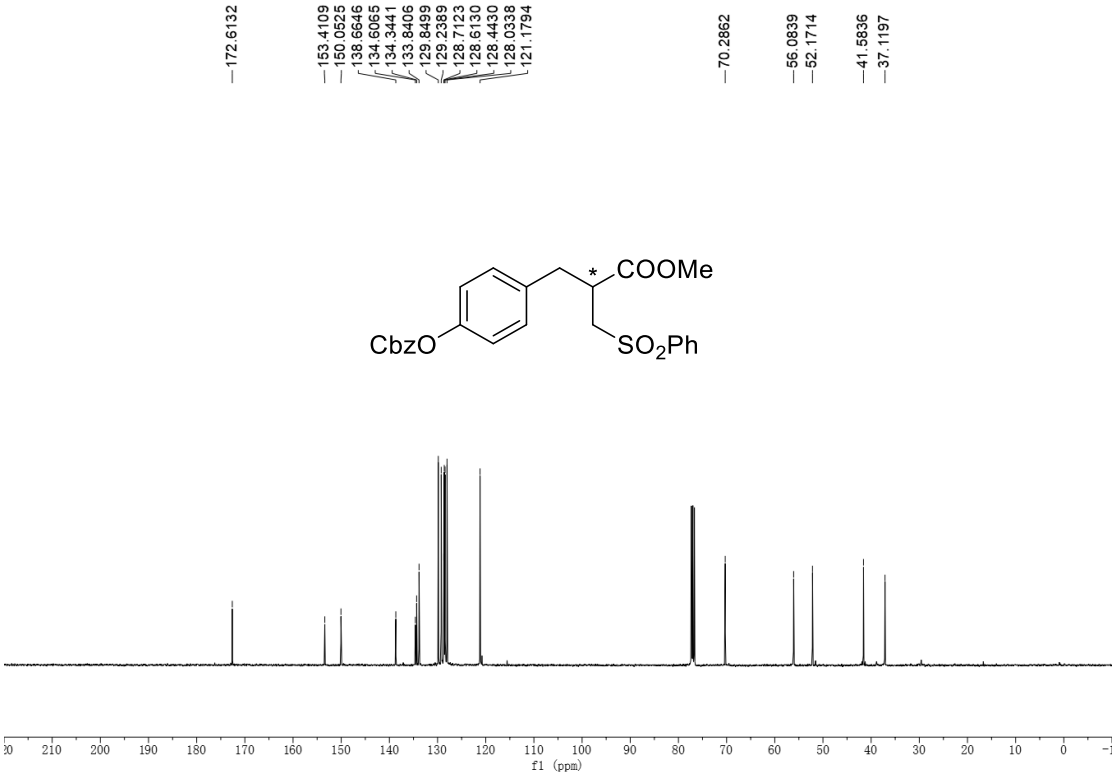


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(4-(((benzyloxy)carbonyl)oxy)benzyl)-3-(phenylsulfonyl)propanoate (**2g**)

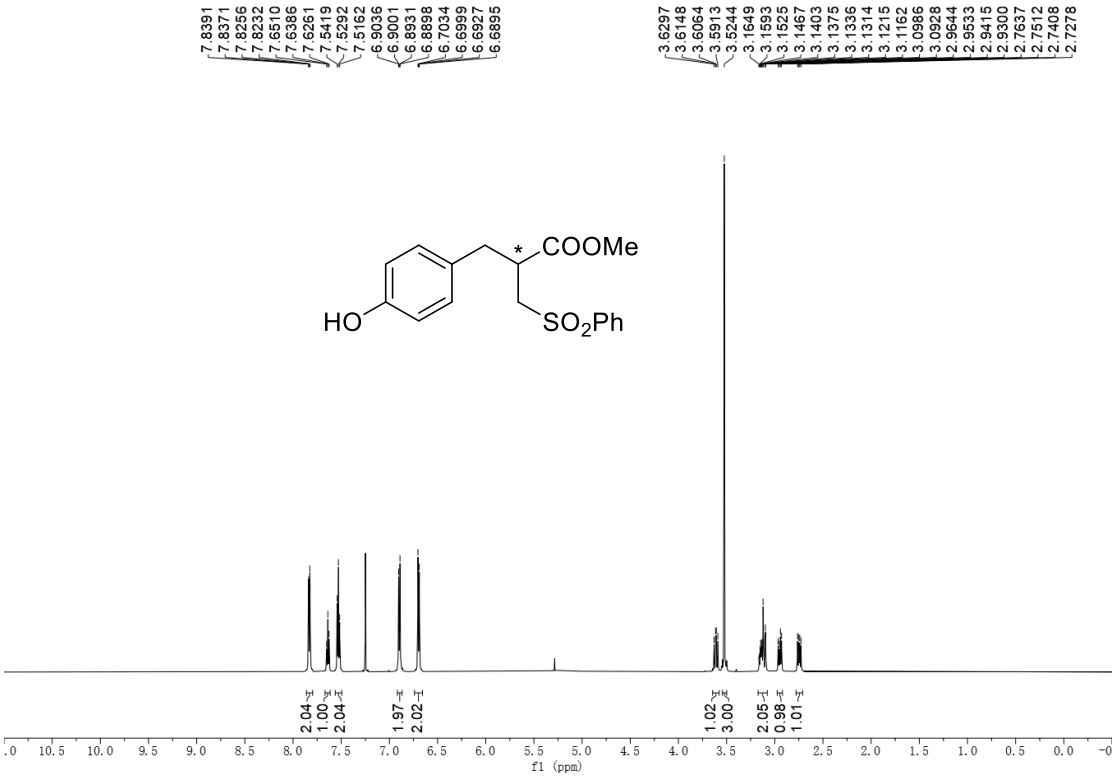


^{1}H NMR (400 MHz, Chloroform-*d*)

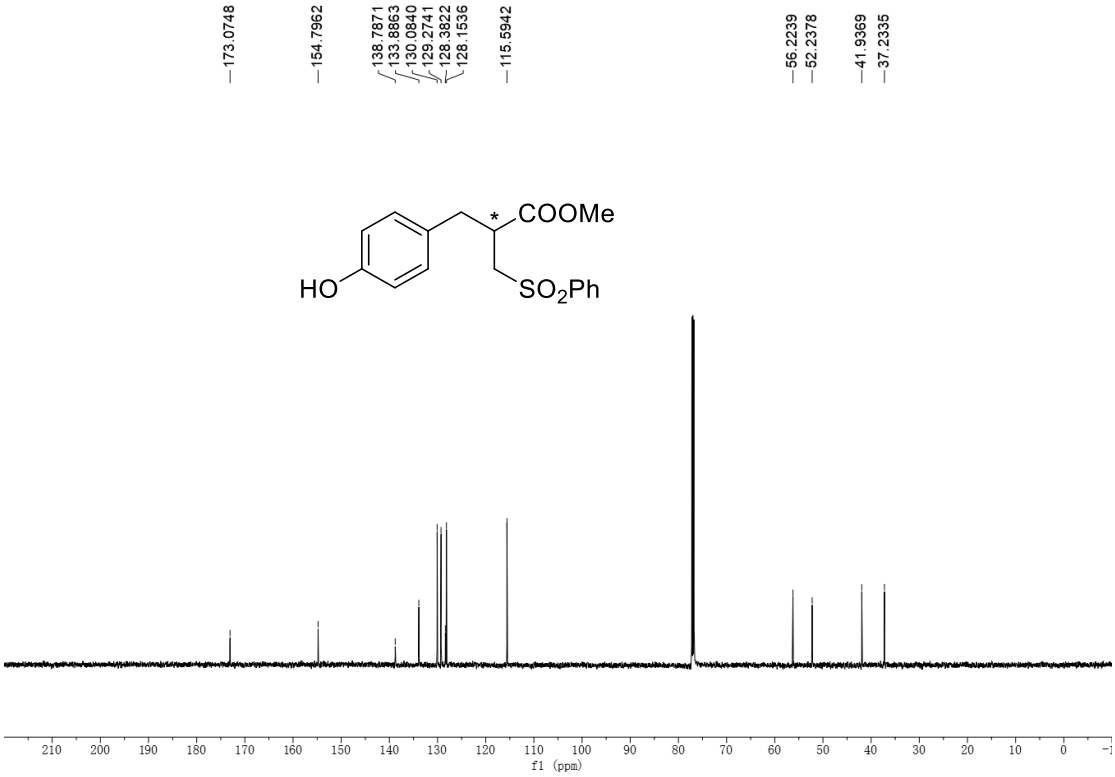


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 2-(4-hydroxybenzyl)-3-(phenylsulfonyl)propanoate (**2h**)

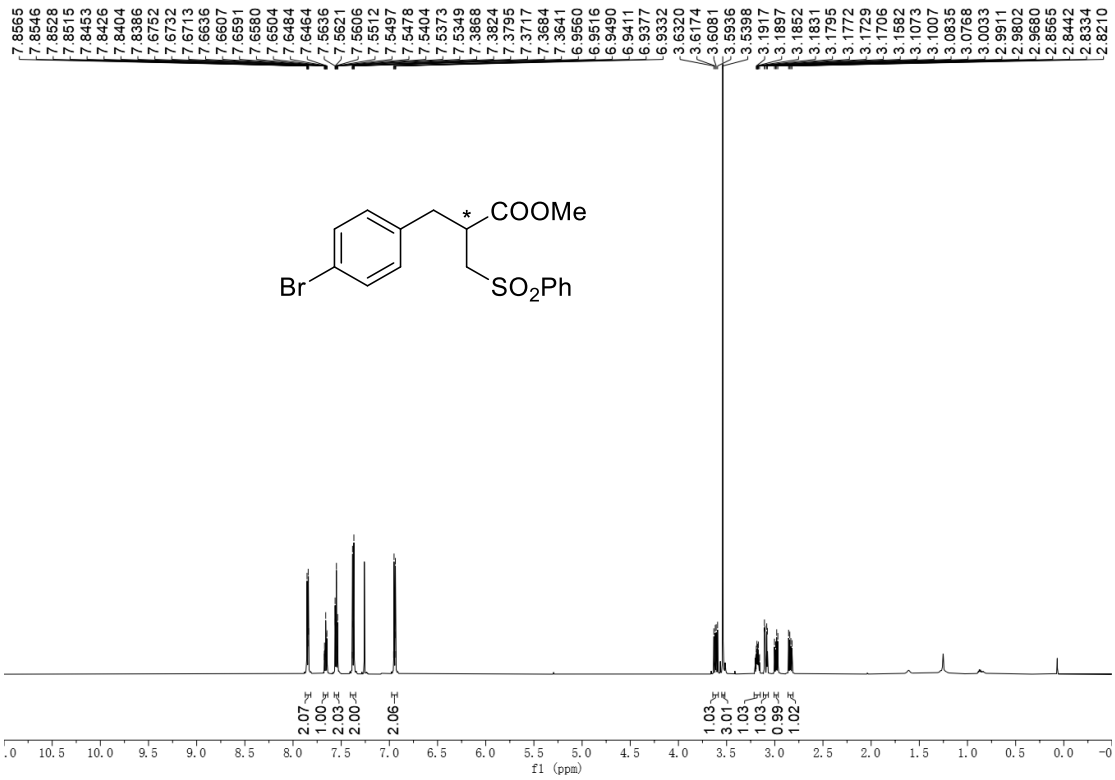


^{1}H NMR (600 MHz, Chloroform-*d*)

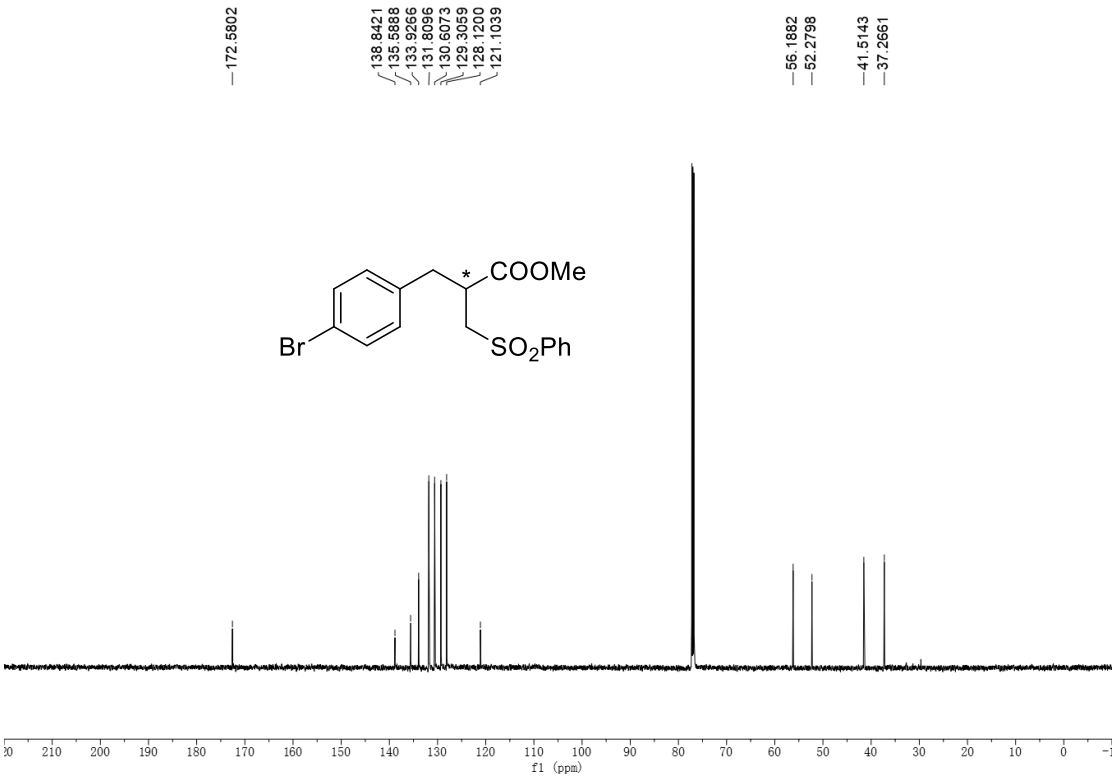


^{13}C NMR (151 MHz, Chloroform-*d*)

(*S*)-Methyl 2-(4-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2i**)

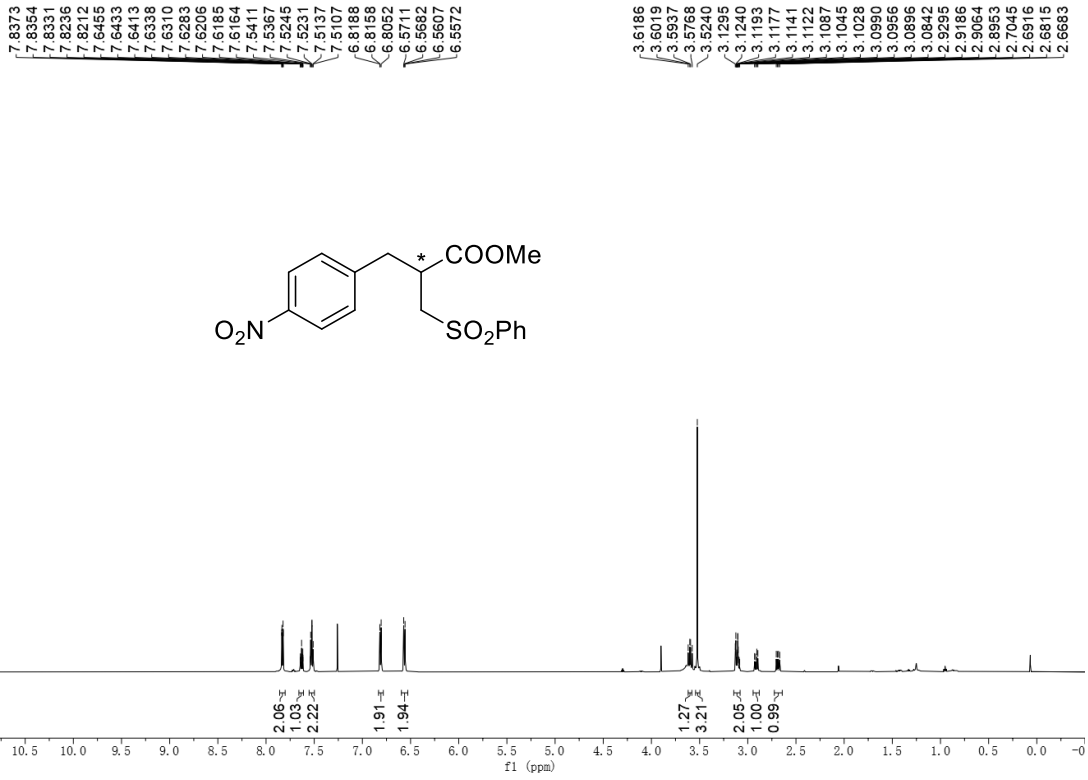


^{1}H NMR (600 MHz, Chloroform-*d*)

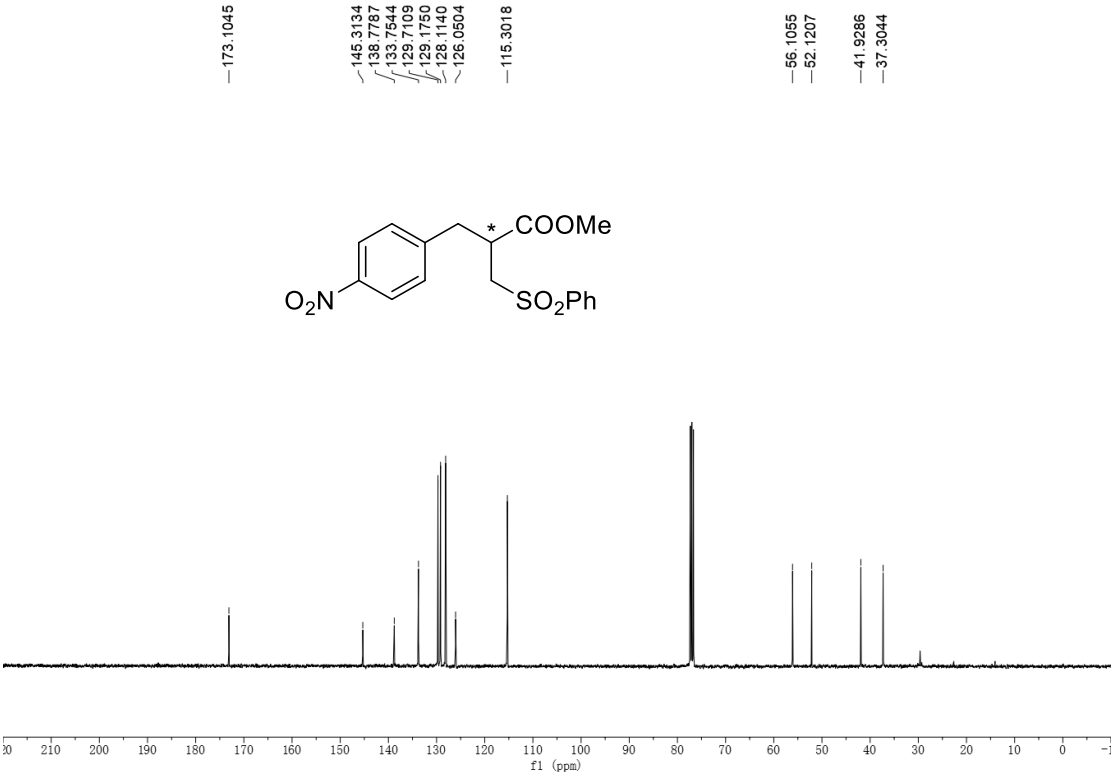


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(4-nitrobenzyl)-3-(phenylsulfonyl)propanoate (**2j**)

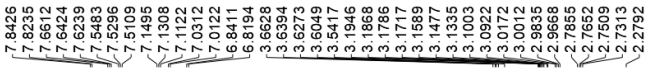


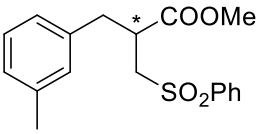
^{1}H NMR (600 MHz, Chloroform-*d*)

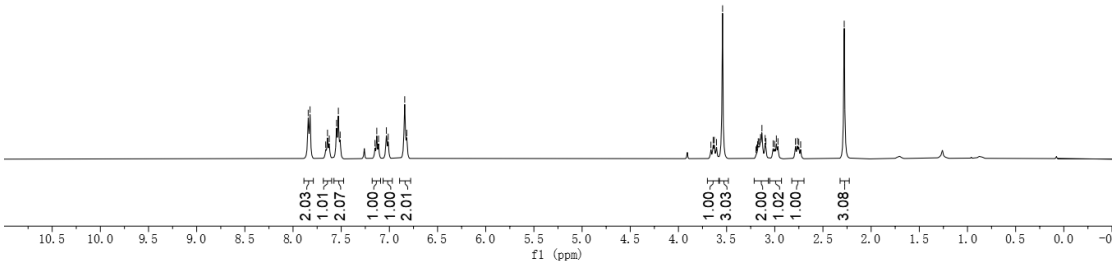


^{13}C NMR (101 MHz, Chloroform-*d*)

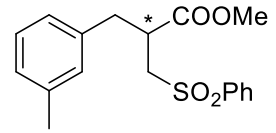
Methyl 2-(3-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2k**)

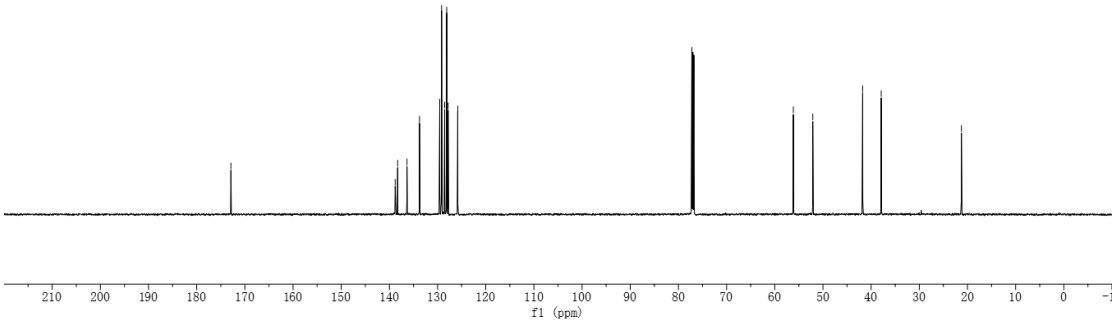






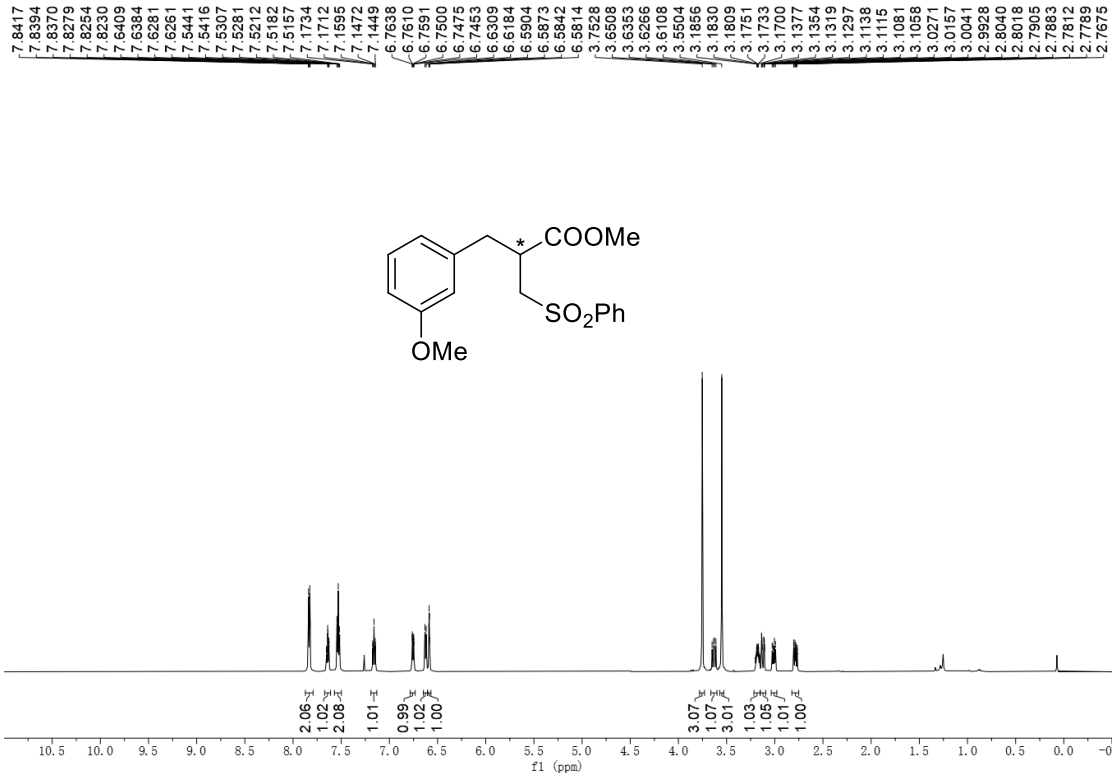
^{1}H NMR (400 MHz, Chloroform-*d*)



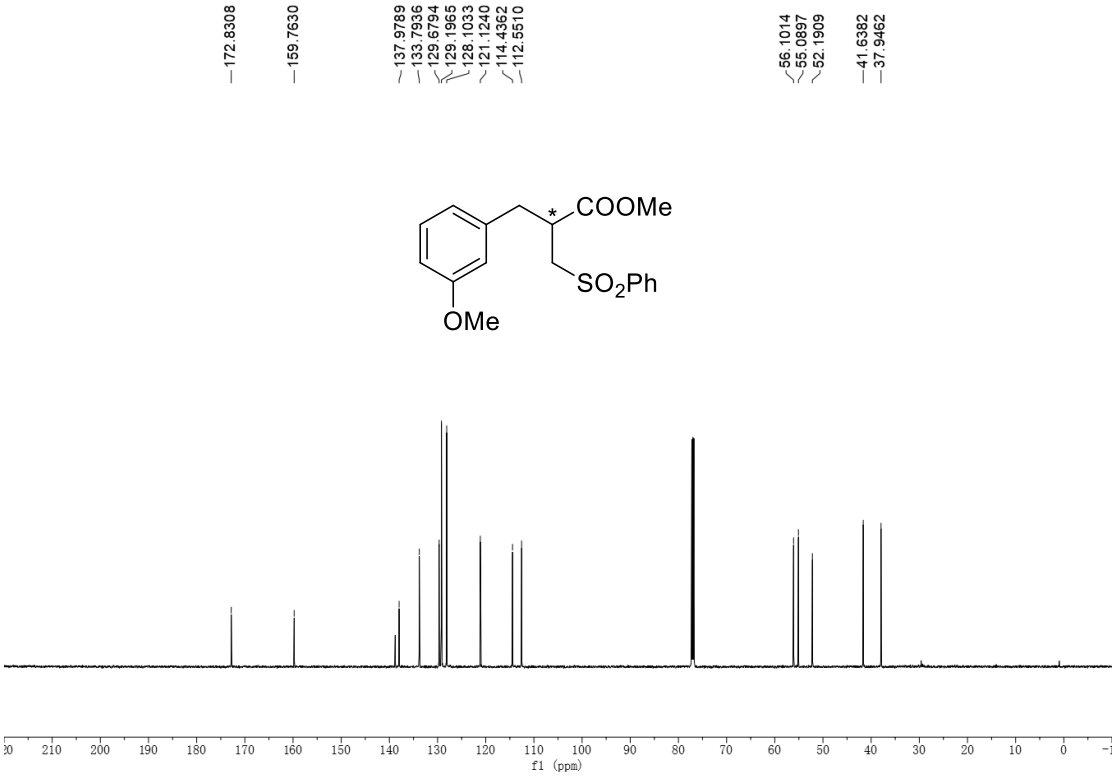


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(3-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2l**)

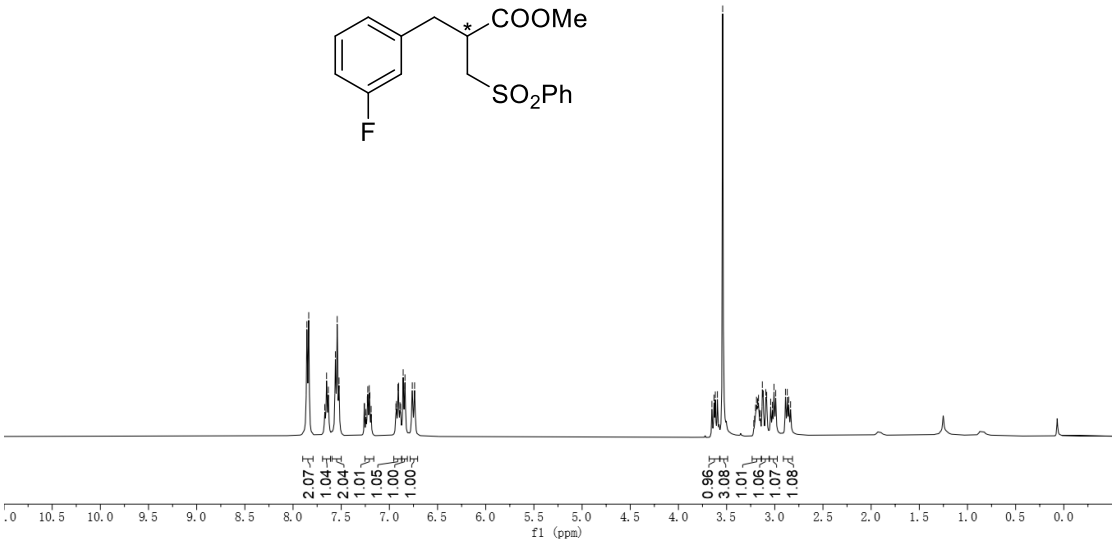


^{1}H NMR (600 MHz, Chloroform-*d*)

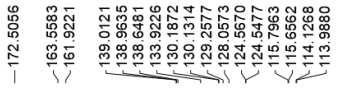


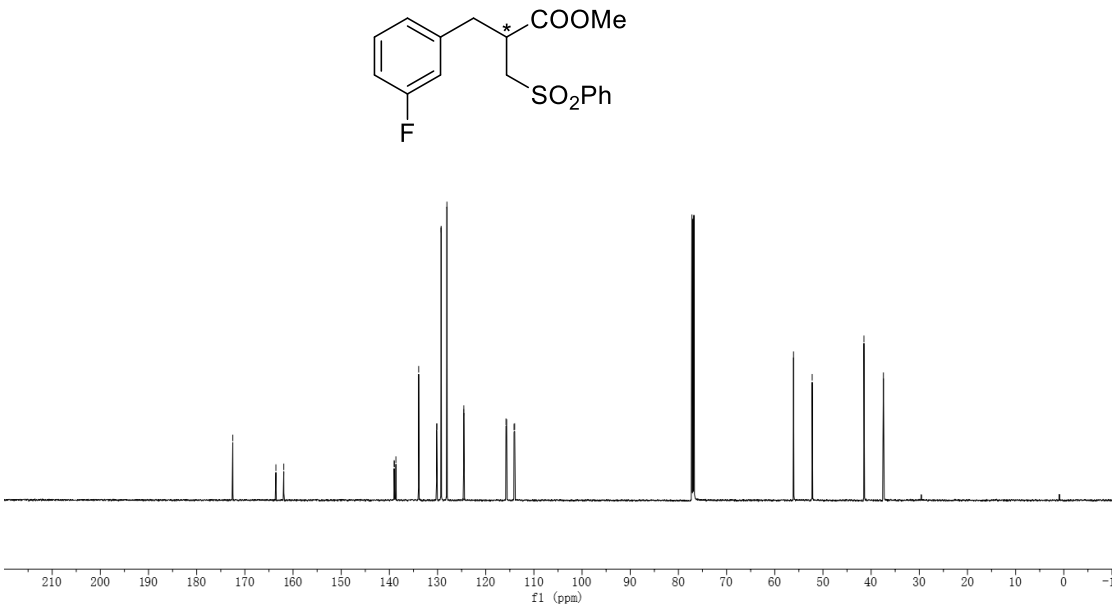
^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(3-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2m**)



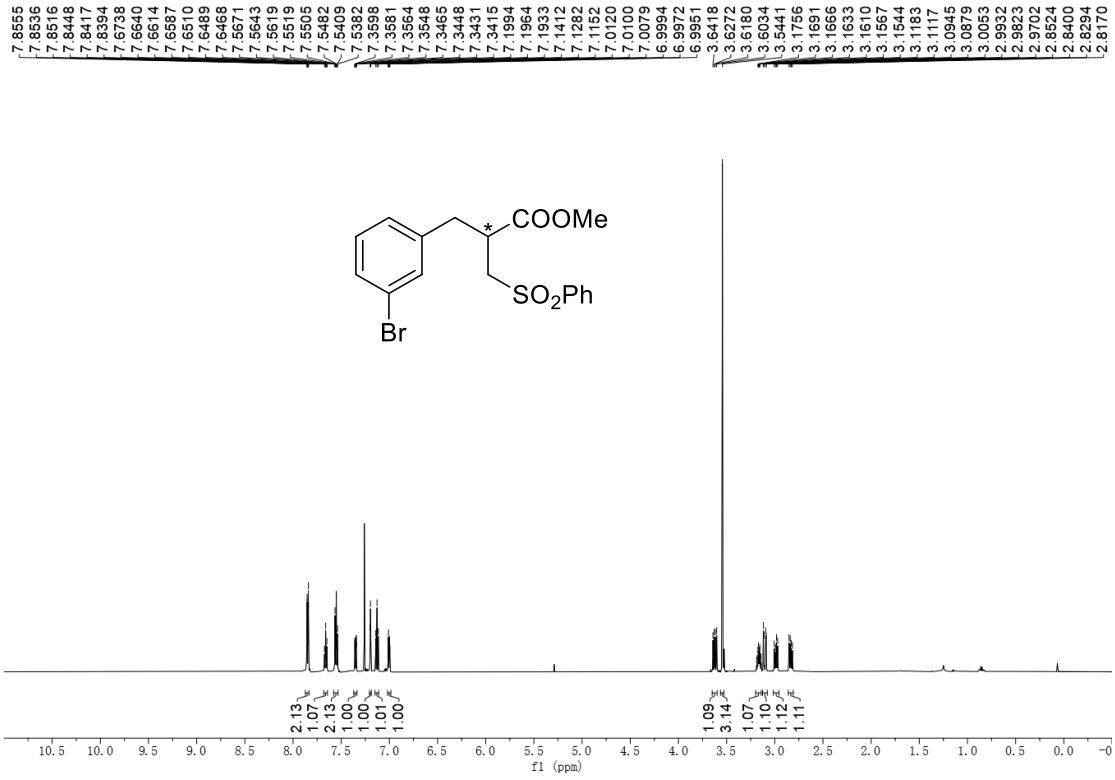
^{1}H NMR (400 MHz, Chloroform-*d*)



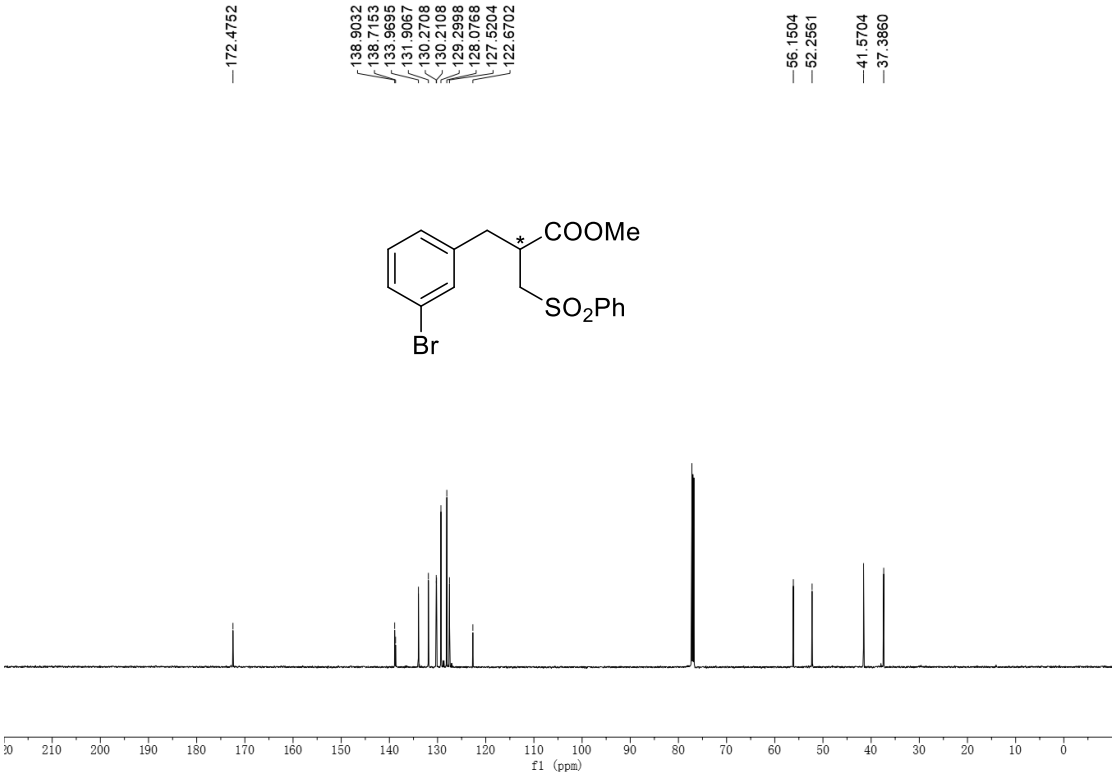


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(3-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2n**)

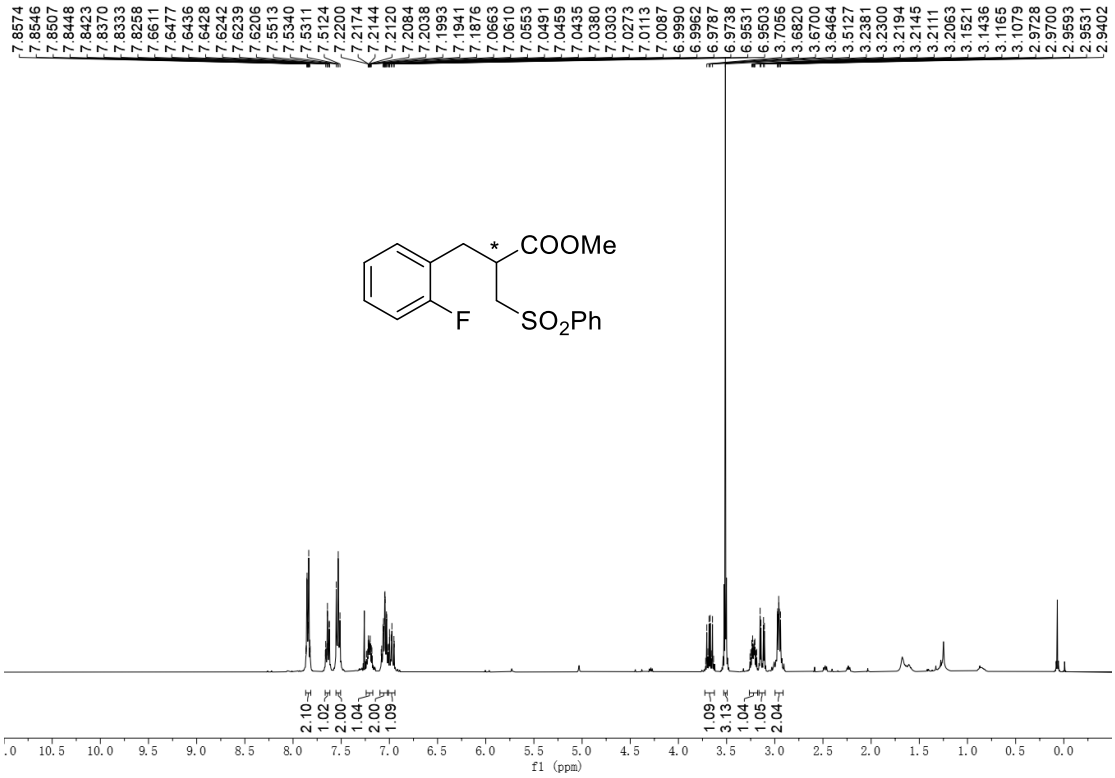


^{1}H NMR (600 MHz, Chloroform-*d*)

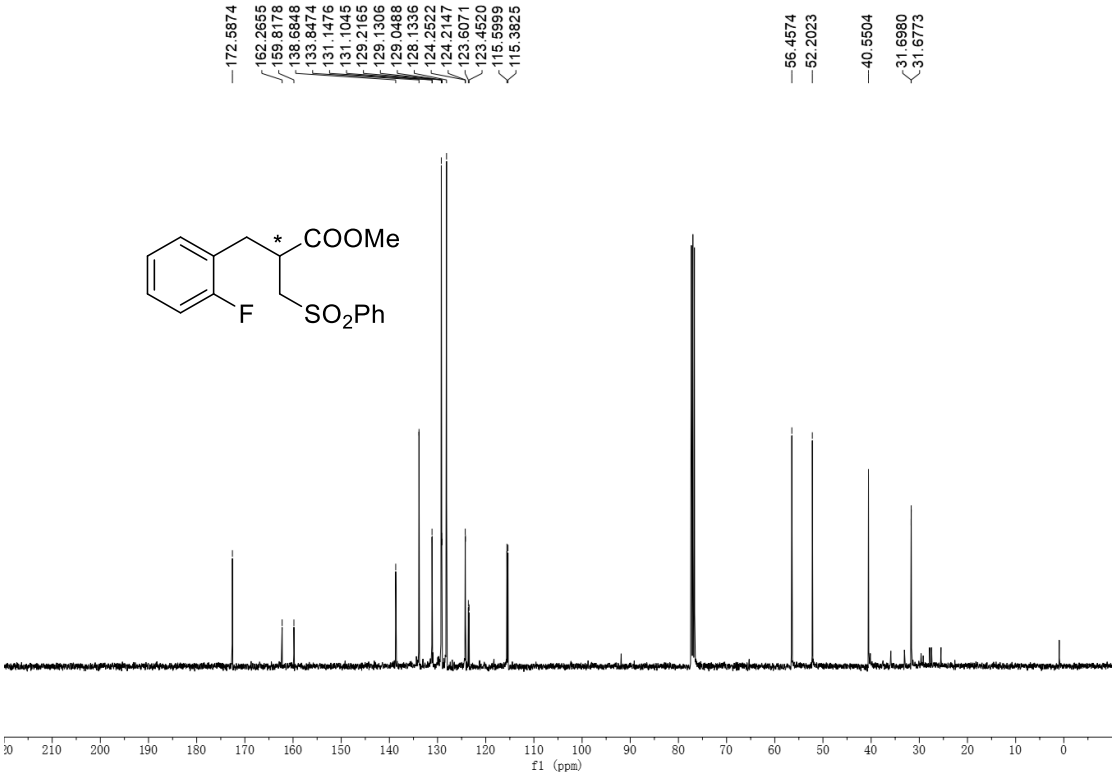


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(2-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2o**)

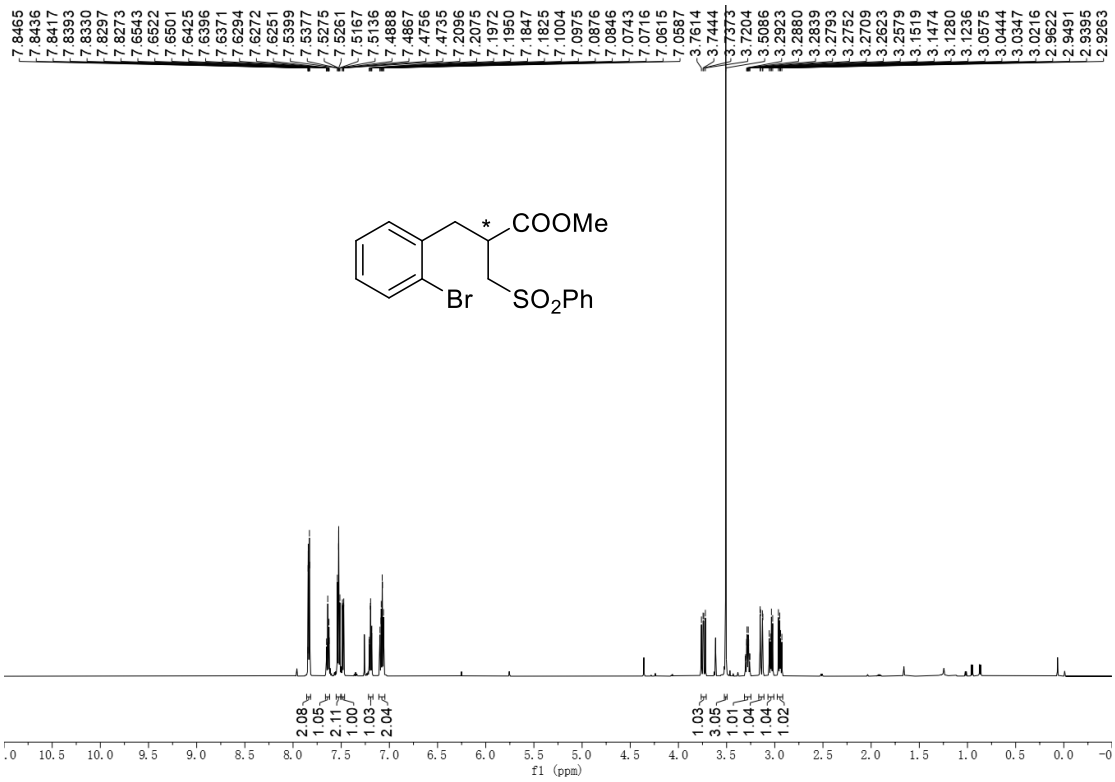


^{1}H NMR (400 MHz, Chloroform-*d*)

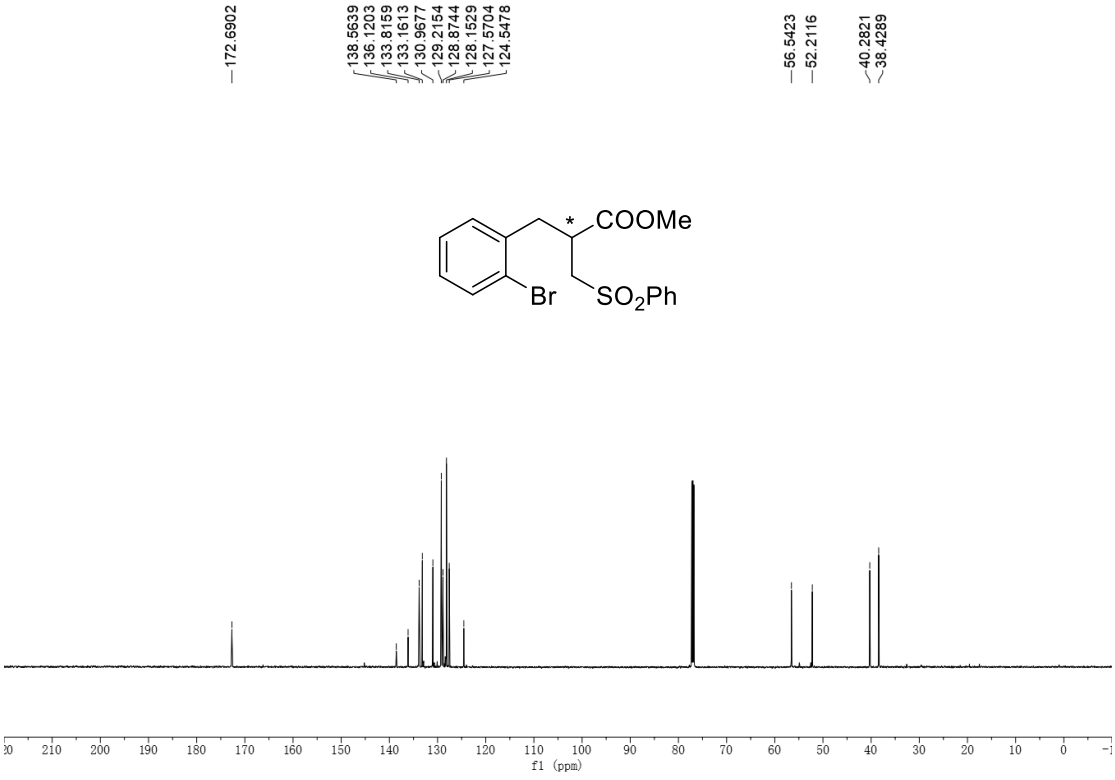


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 2-(2-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2p**)

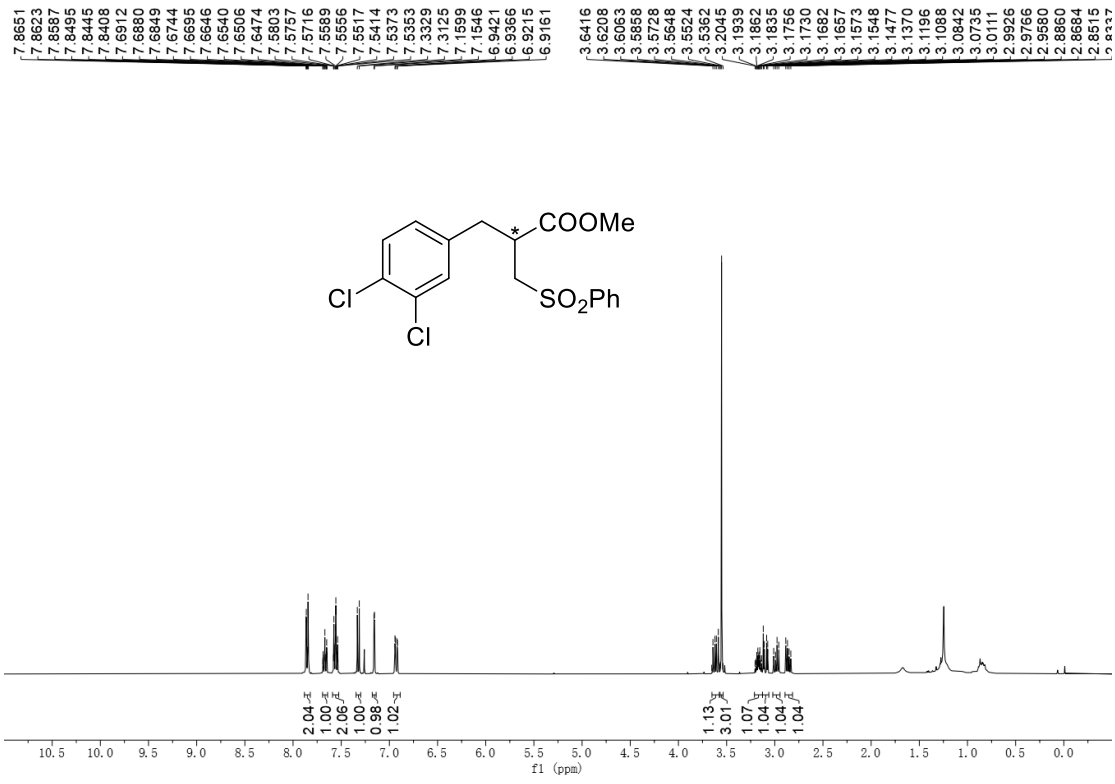


^{1}H NMR (600 MHz, Chloroform-*d*)

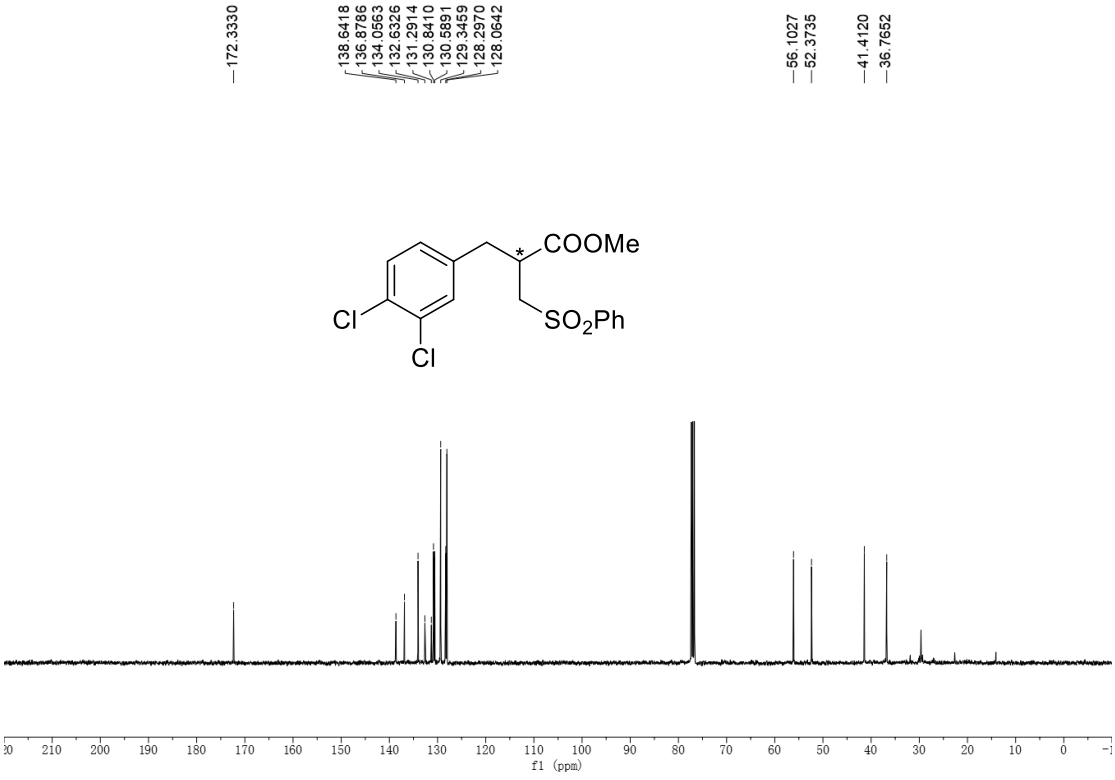


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-(3,4-dichlorobenzyl)-3-(phenylsulfonyl)propanoate (**2q**)

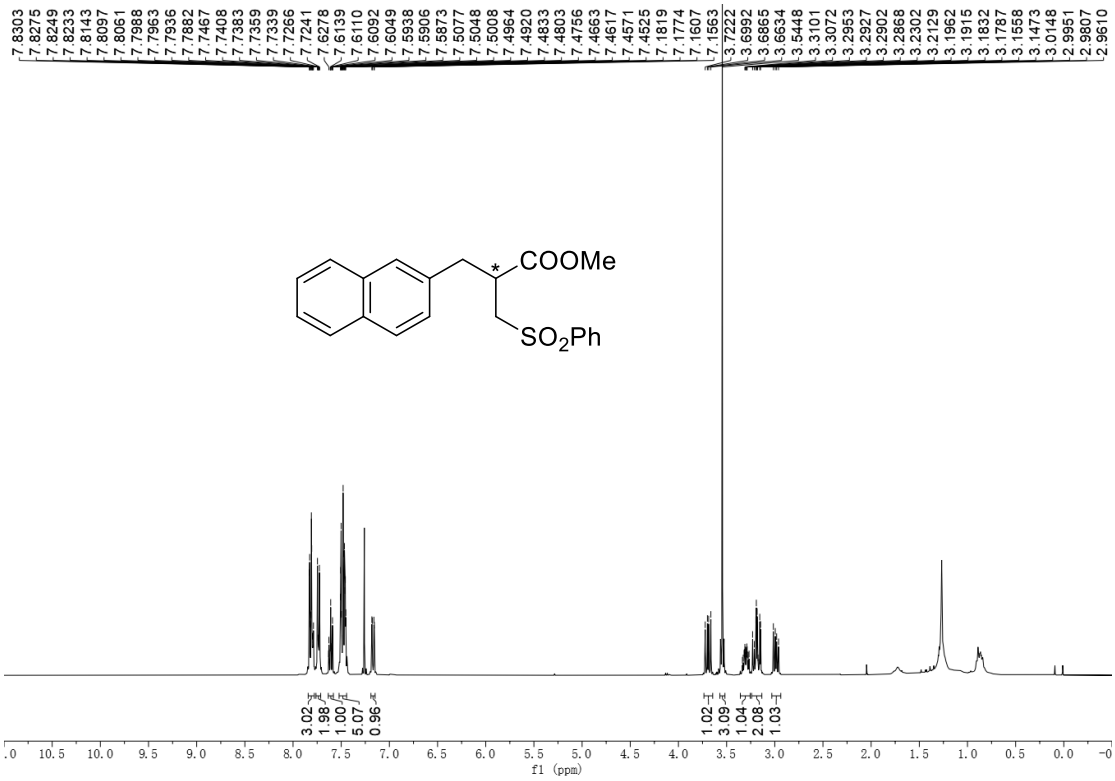


^{1}H NMR (400 MHz, Chloroform-*d*)

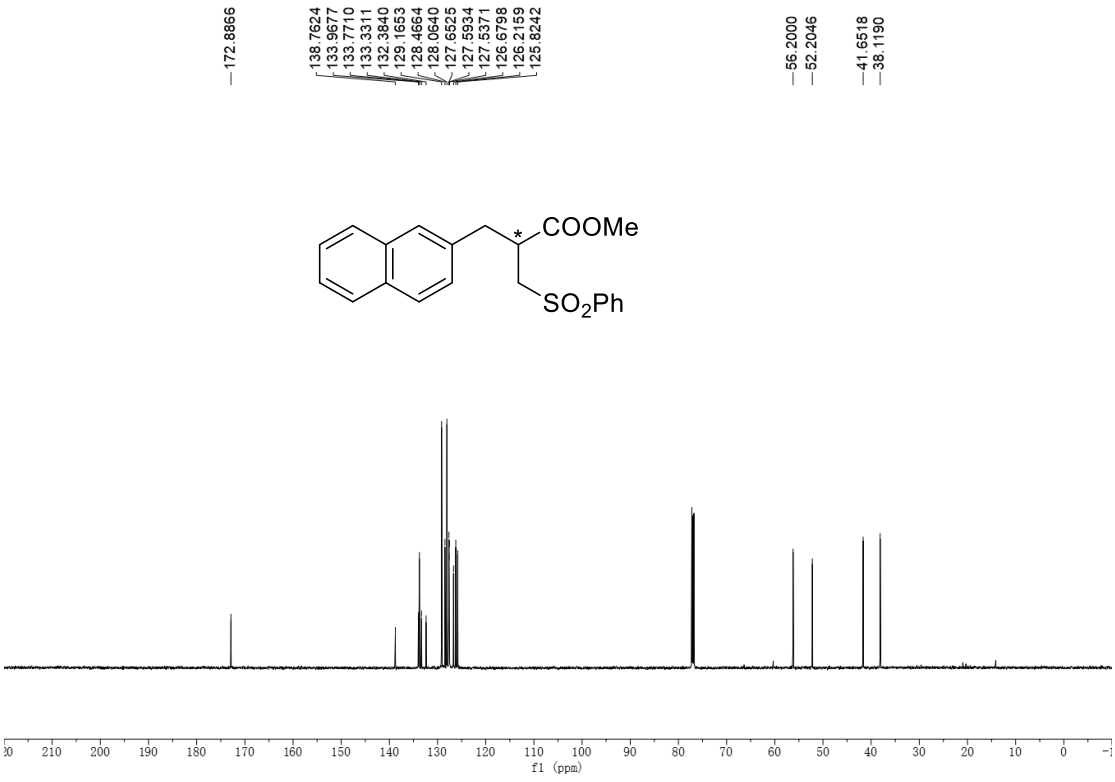


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 3-(naphthalen-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2r**)

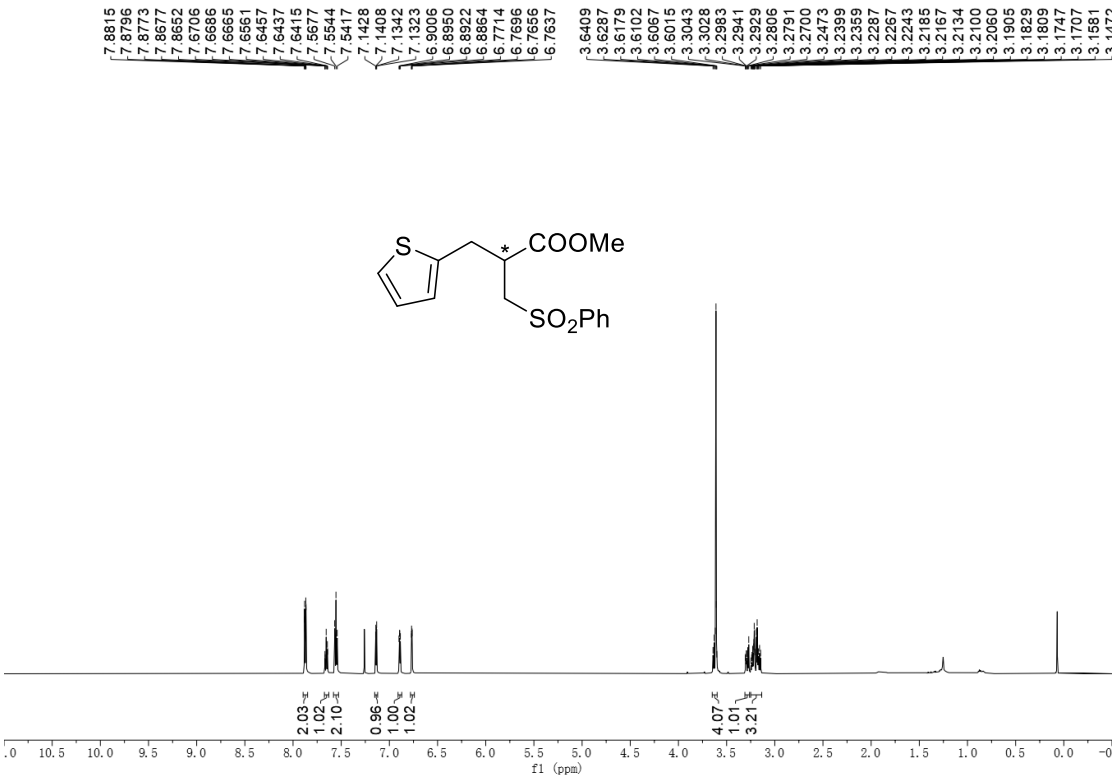


^{1}H NMR (400 MHz, Chloroform-*d*)

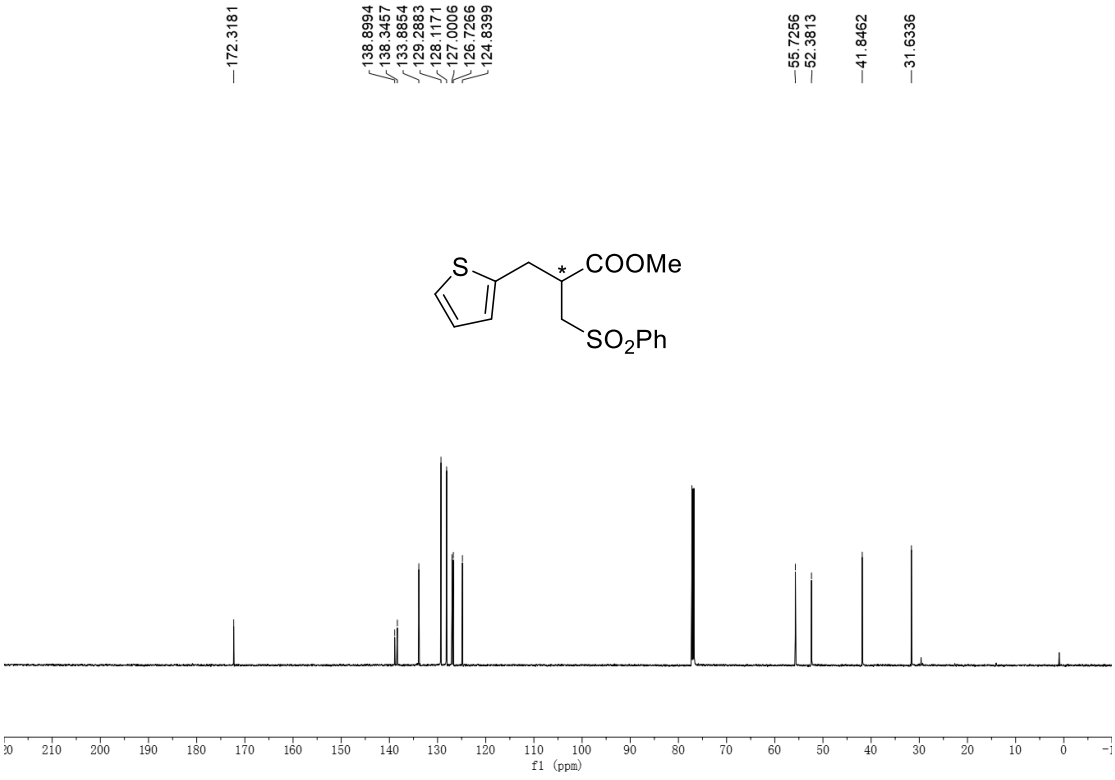


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 3-(phenylsulfonyl)-2-(thiophen-2-ylmethyl)propanoate (**2s**)

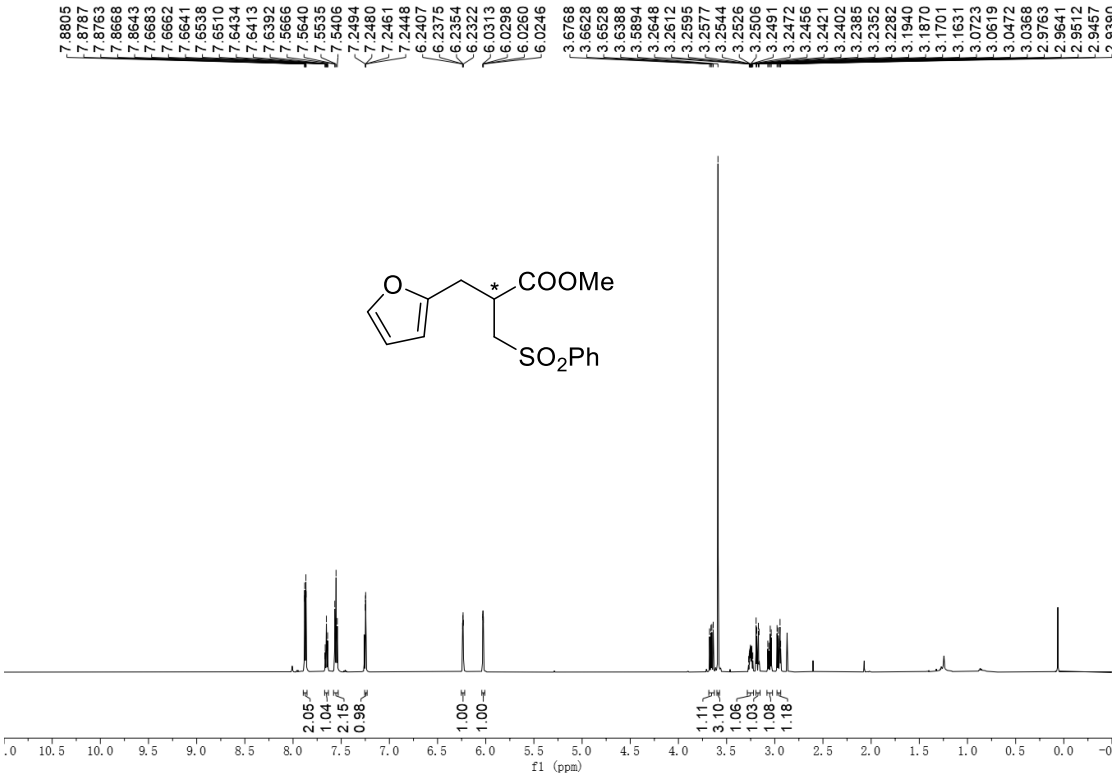


^{1}H NMR (600 MHz, Chloroform-*d*)

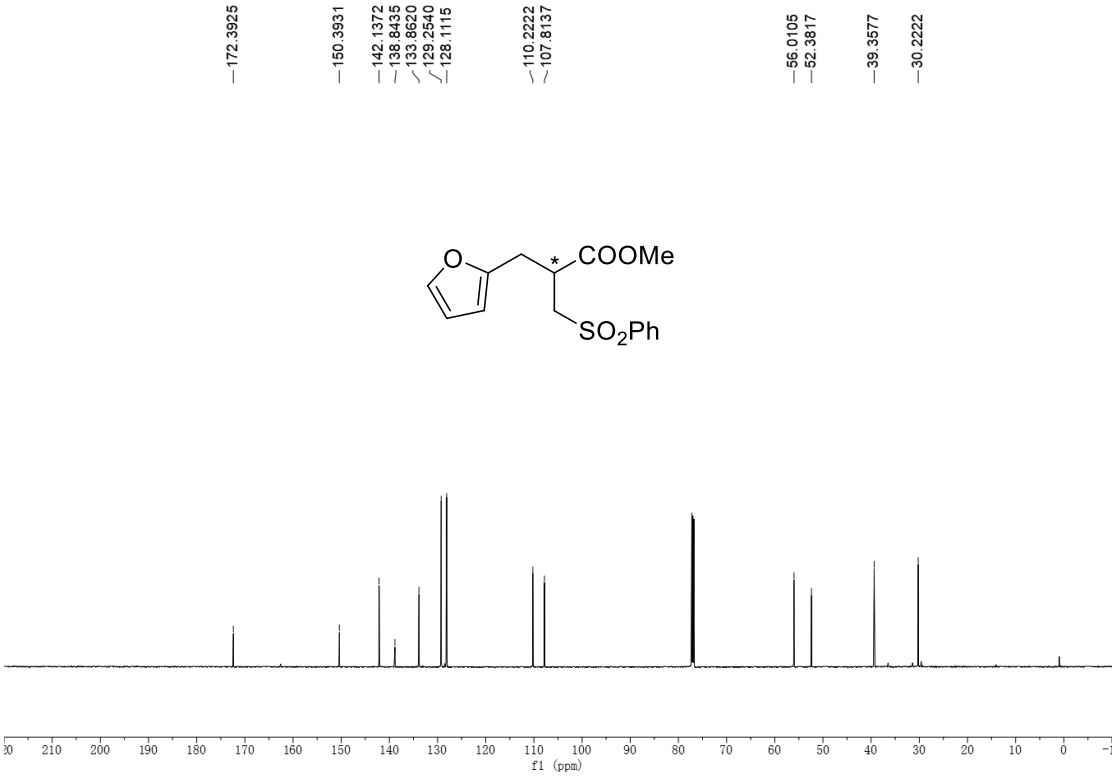


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 3-(furan-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2t**)

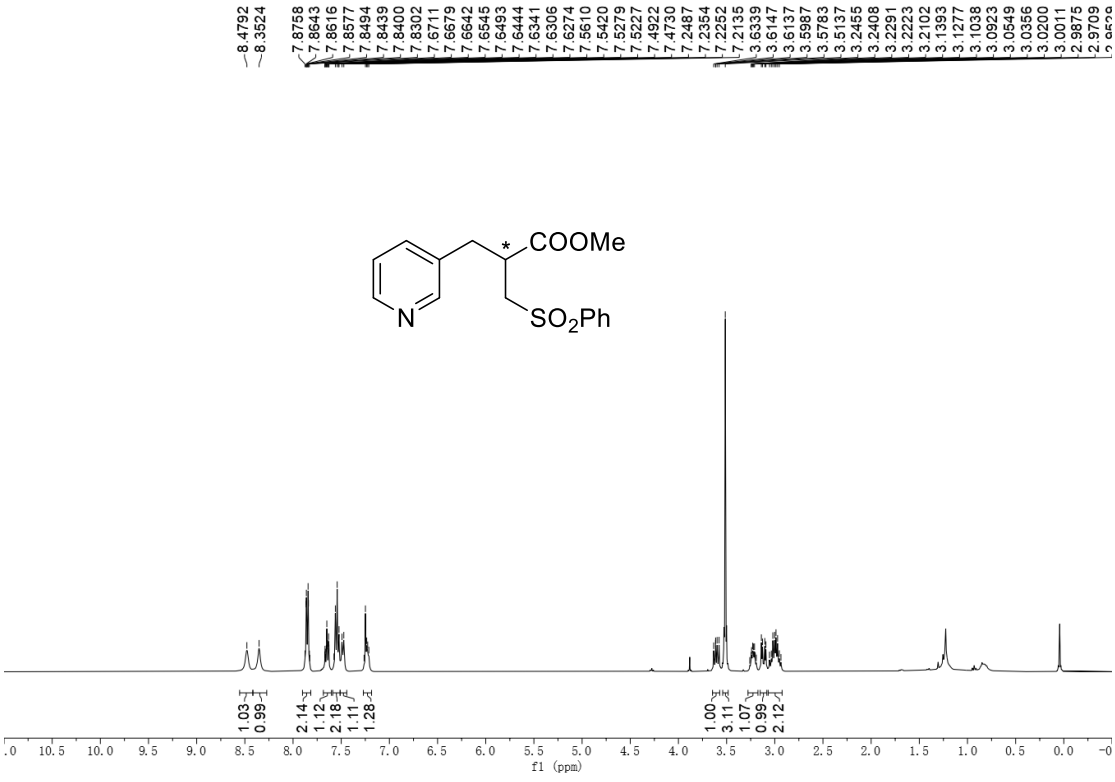


^{1}H NMR (600 MHz, Chloroform-*d*)

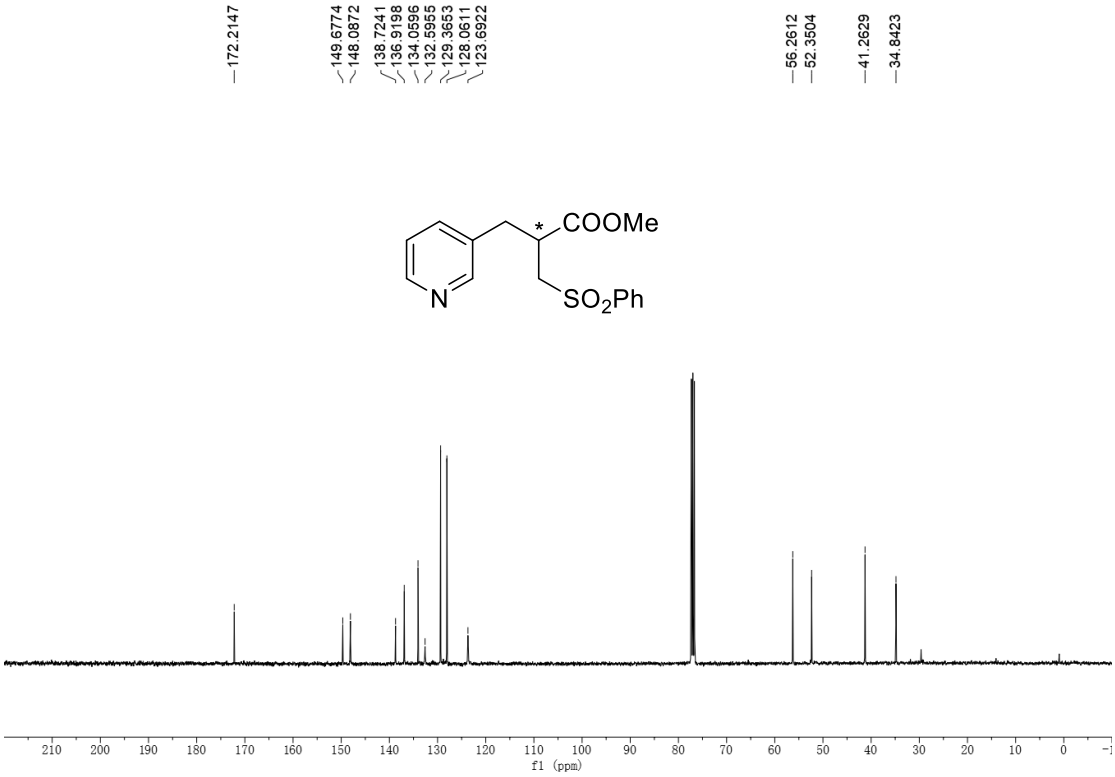


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 3-(phenylsulfonyl)-2-(pyridin-3-ylmethyl)propanoate (**2u**)

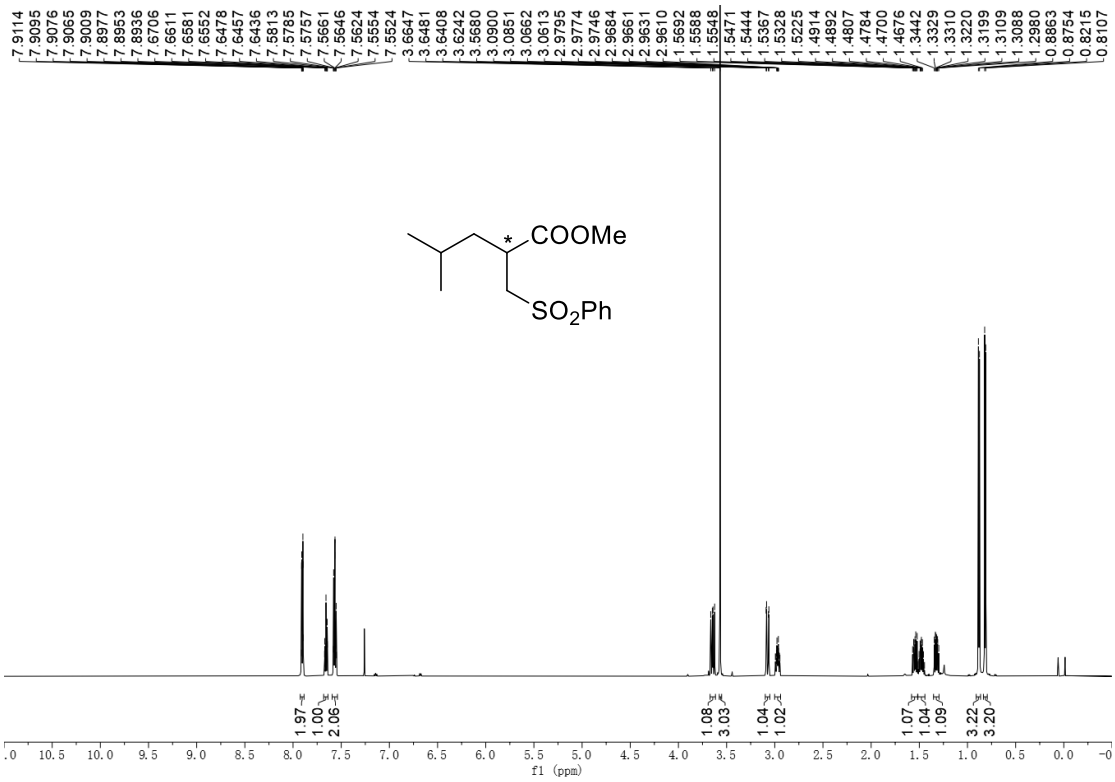


^{1}H NMR (400 MHz, Chloroform-*d*)

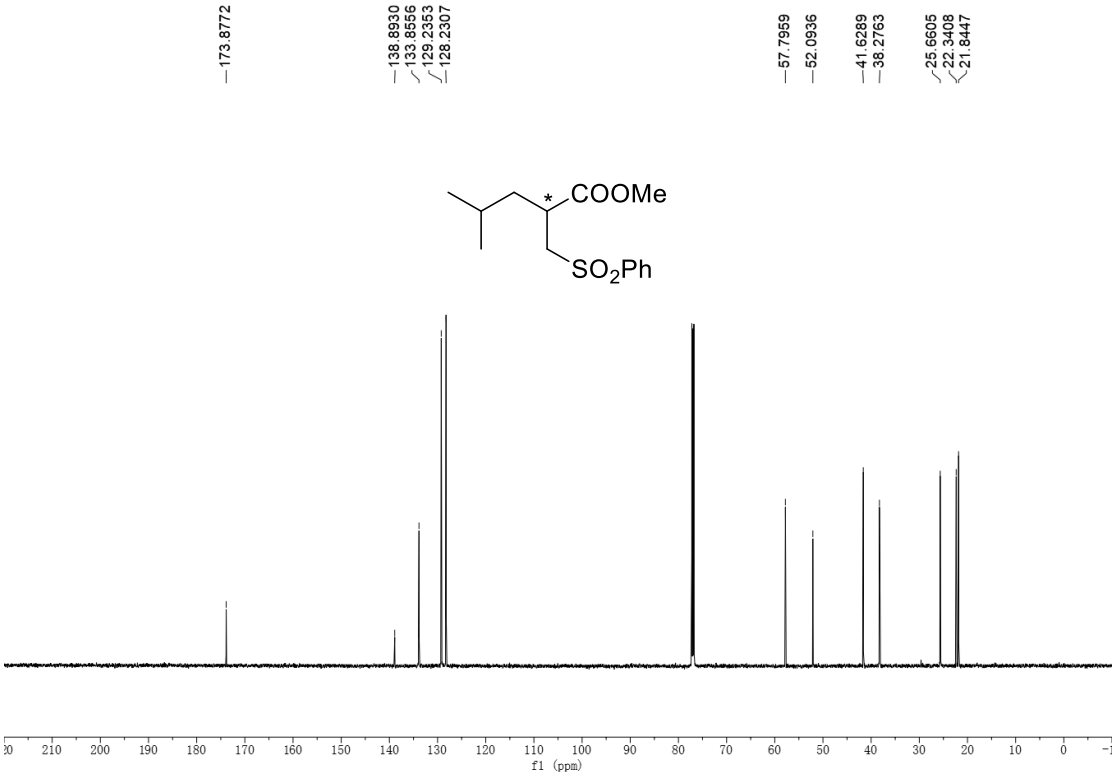


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 4-methyl-2-((phenylsulfonyl)methyl)pentanoate (**2v**)

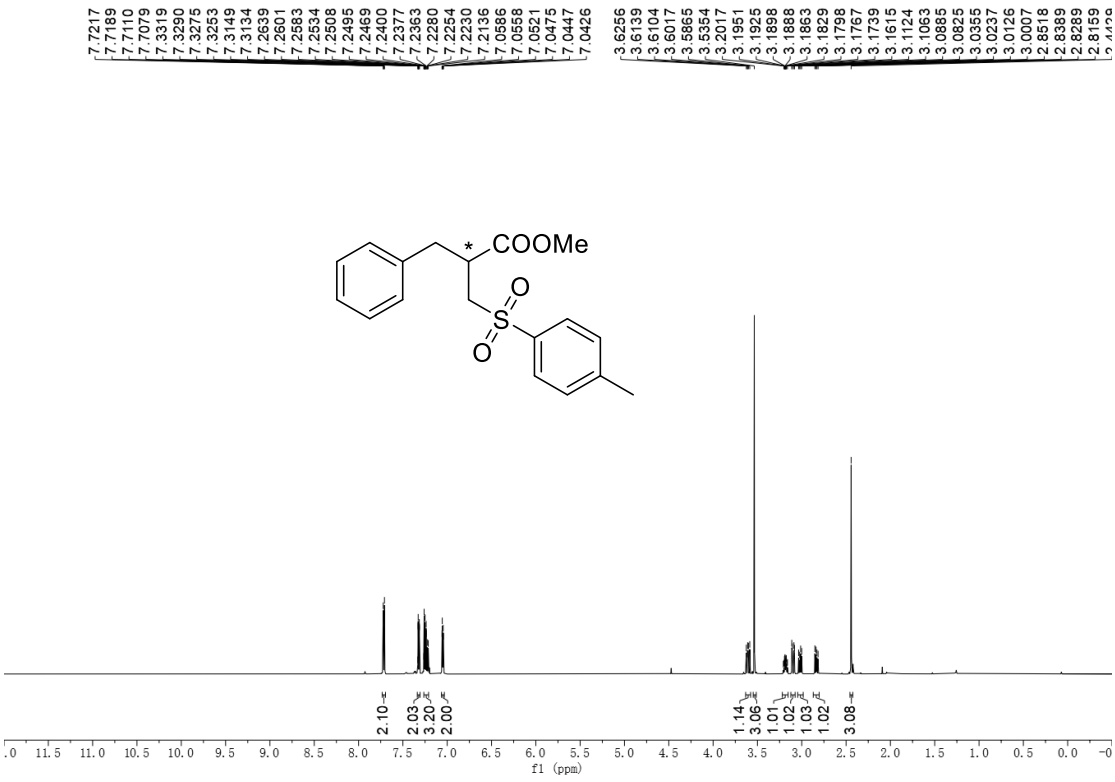


^{1}H NMR (600 MHz, Chloroform-*d*)

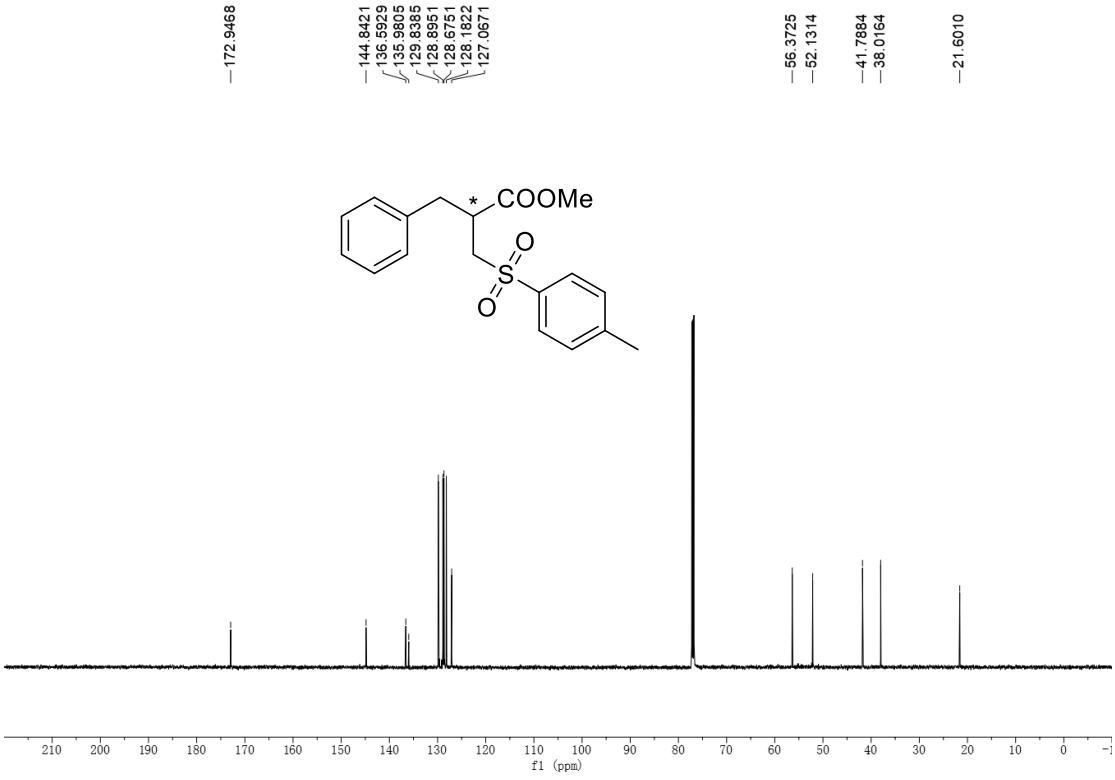


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-tosylpropanoate (**4a**)

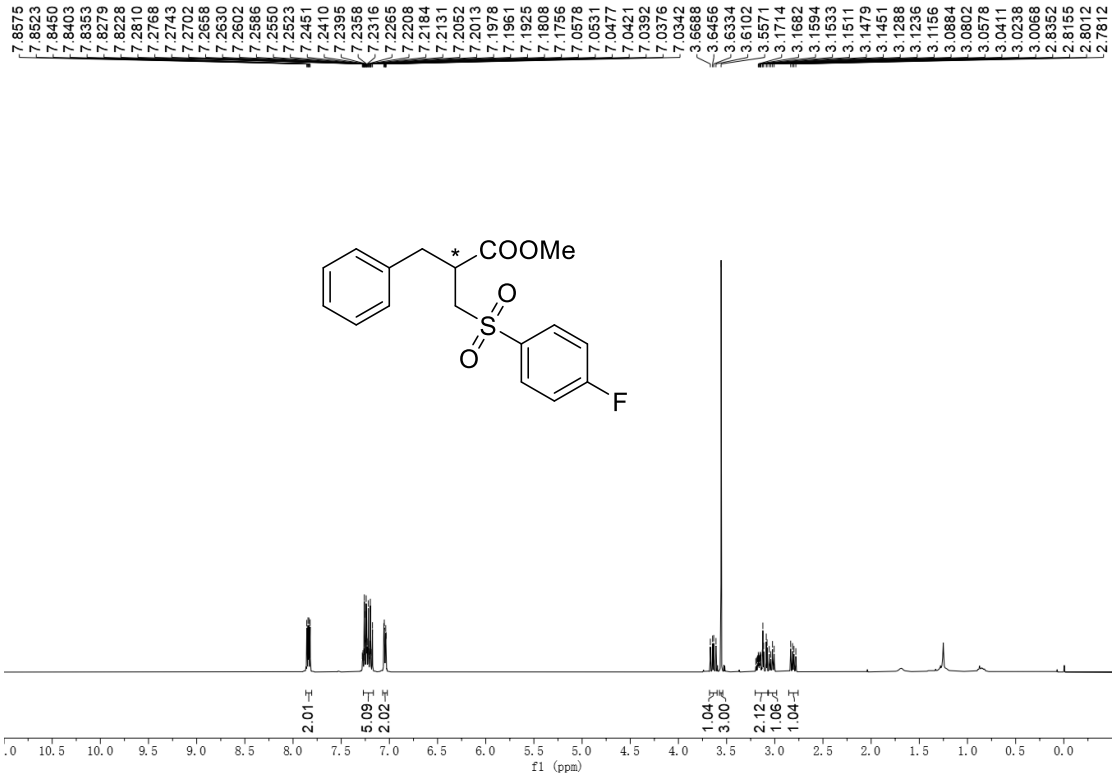


^{1}H NMR (600 MHz, Chloroform-*d*)

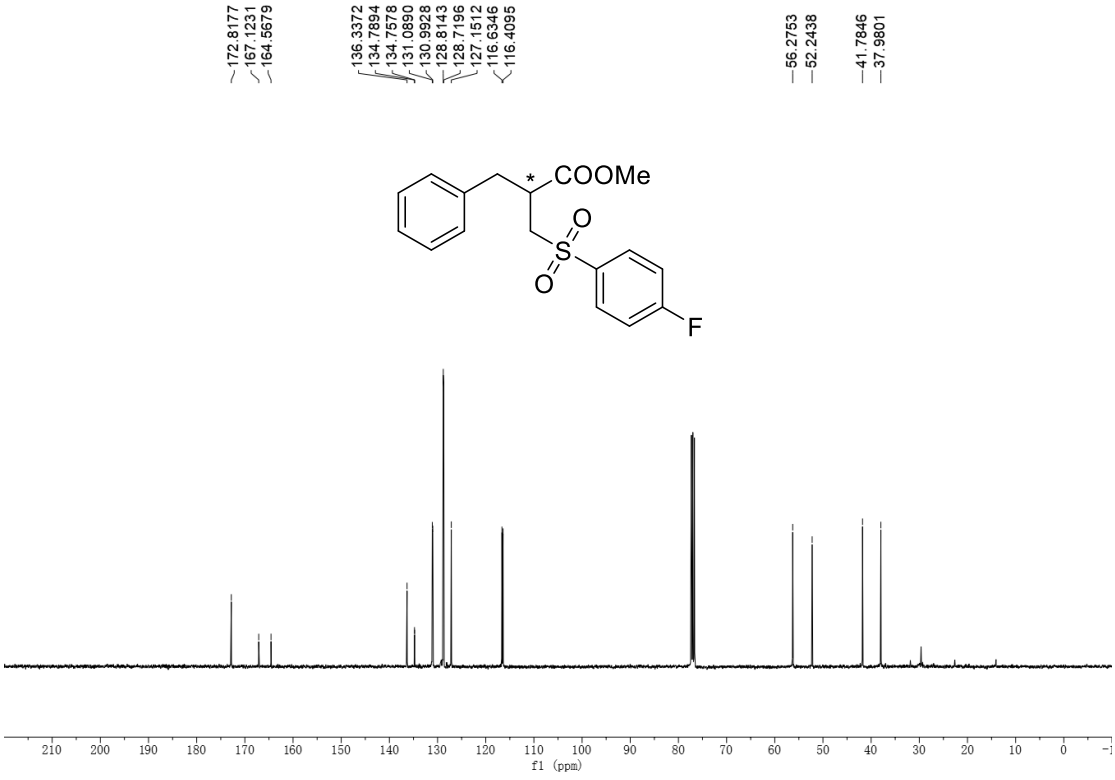


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-((4-fluorophenyl)sulfonyl)propanoate (**4b**)

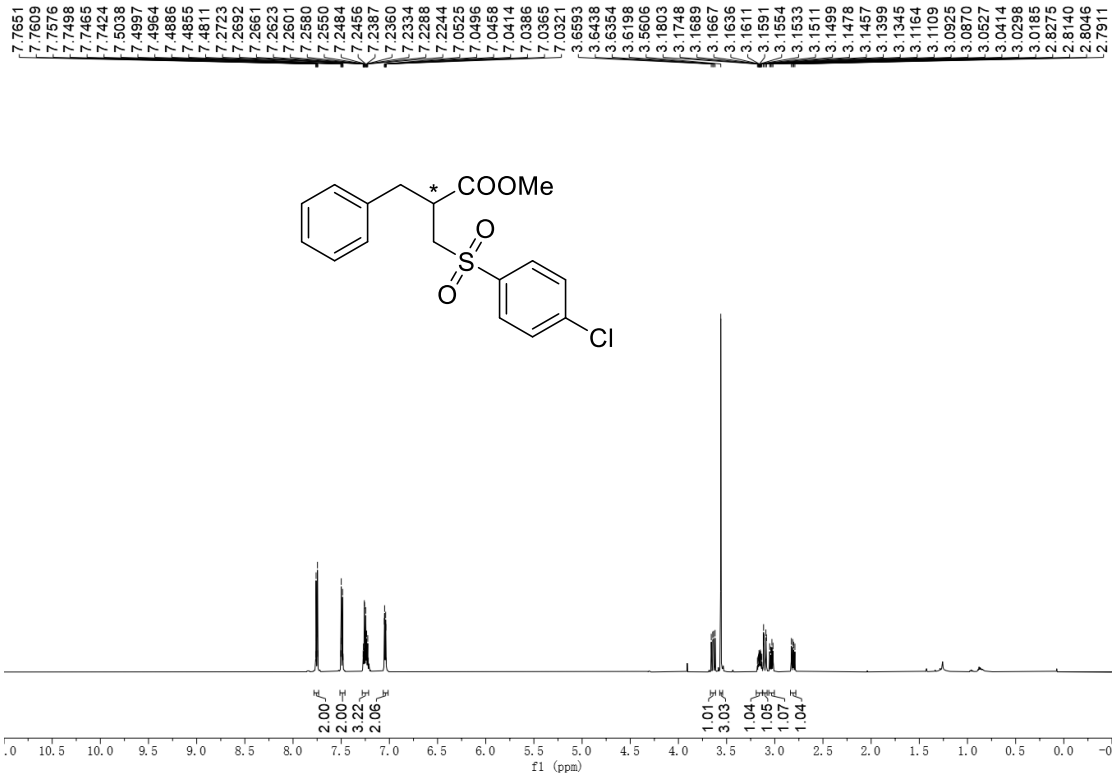


^{1}H NMR (400 MHz, Chloroform-*d*)

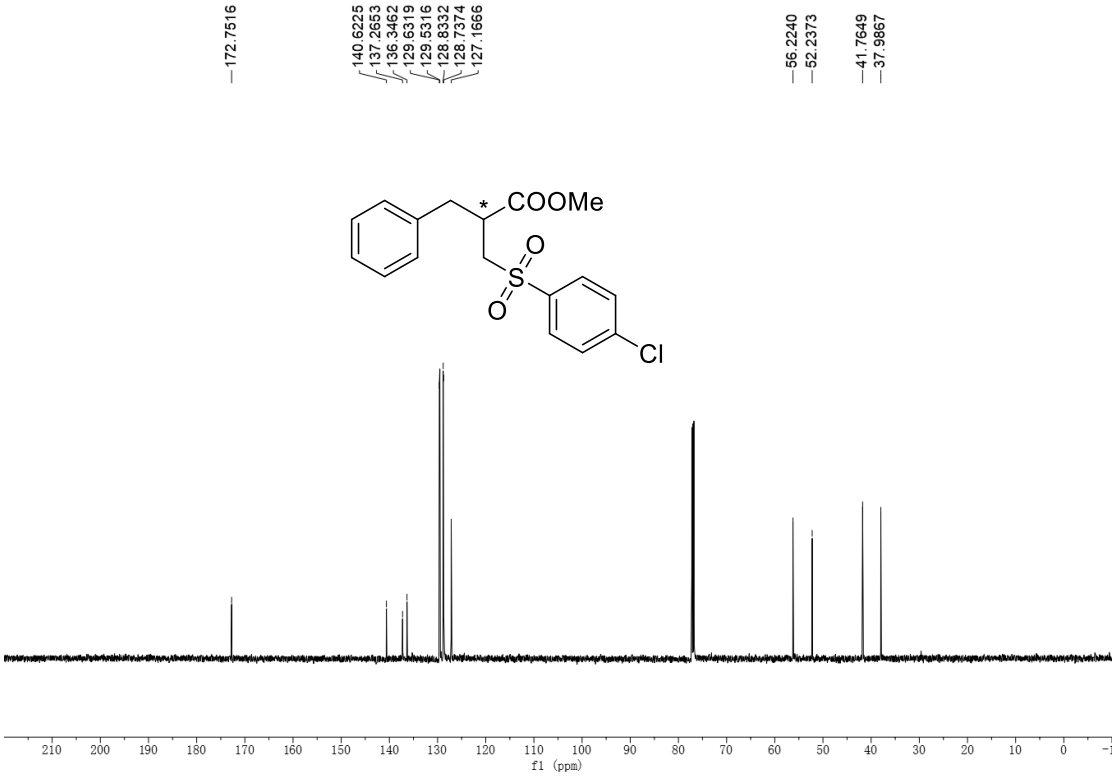


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-((4-chlorophenyl)sulfonyl)propanoate (**4c**)

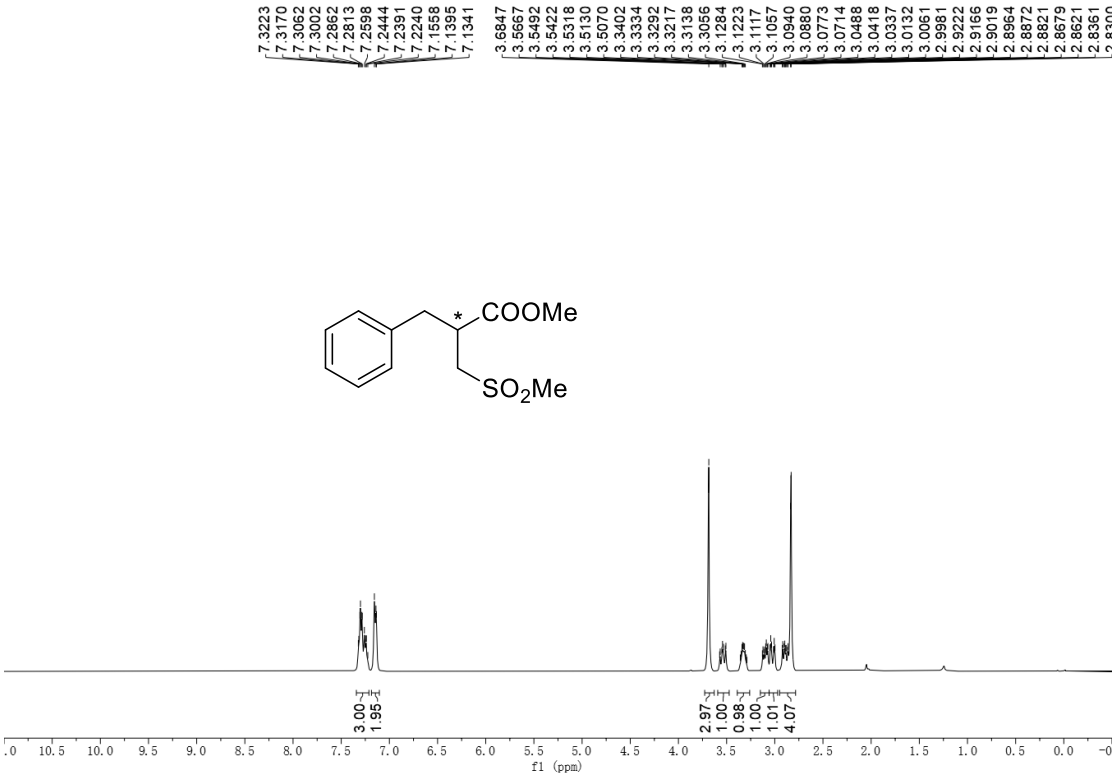


^{1}H NMR (600 MHz, Chloroform-*d*)

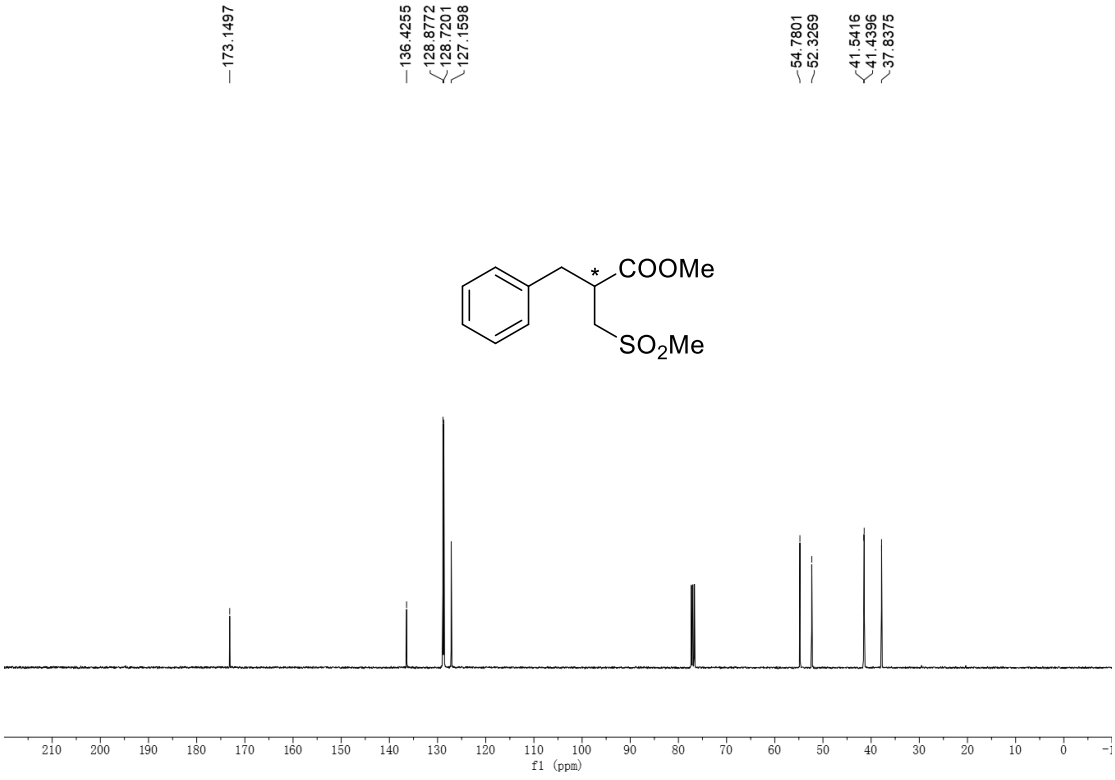


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-(methylsulfonyl)propanoate (**4d**)

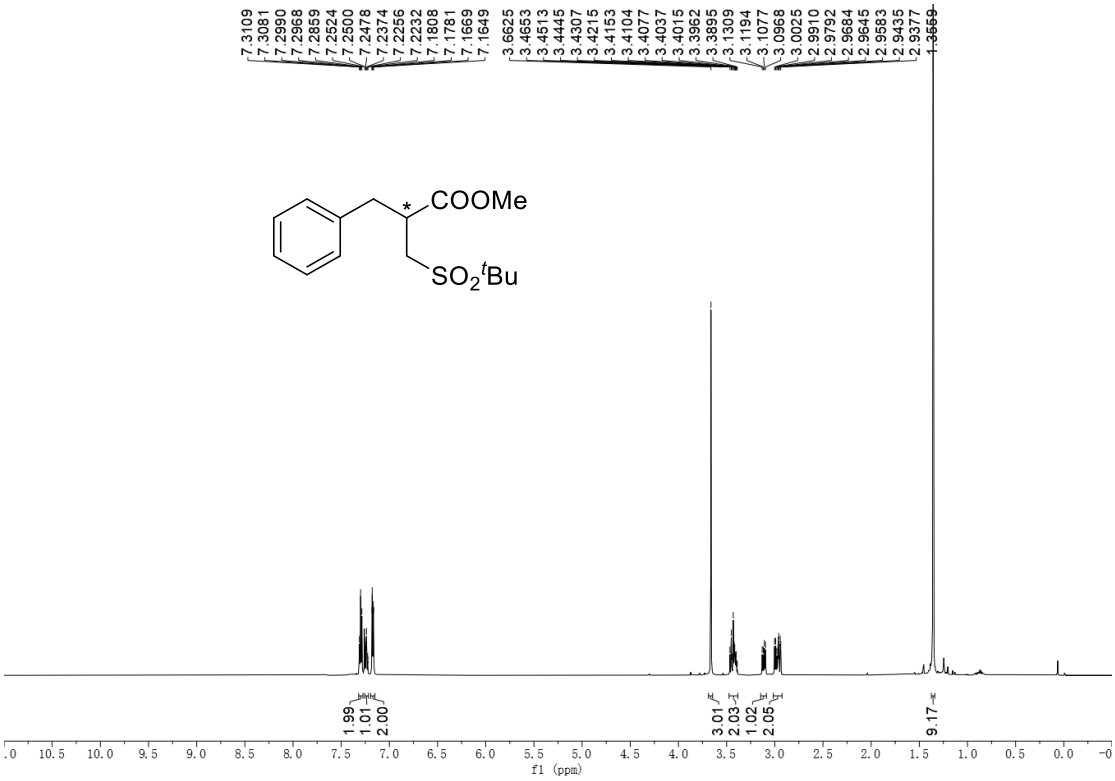


^{1}H NMR (400 MHz, Chloroform-*d*)

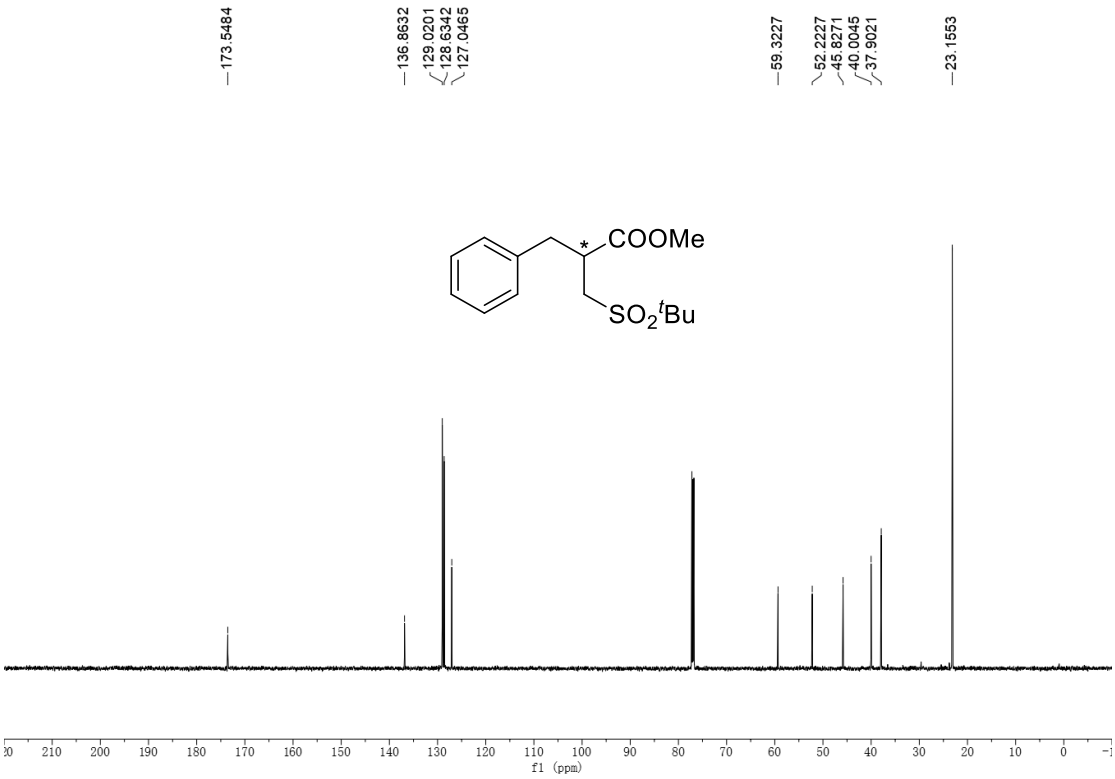


^{13}C NMR (101 MHz, Chloroform-*d*)

Methyl (*Z*)-2-((*tert*-butylsulfonyl)methyl)-3-phenylacrylate (**4e**)

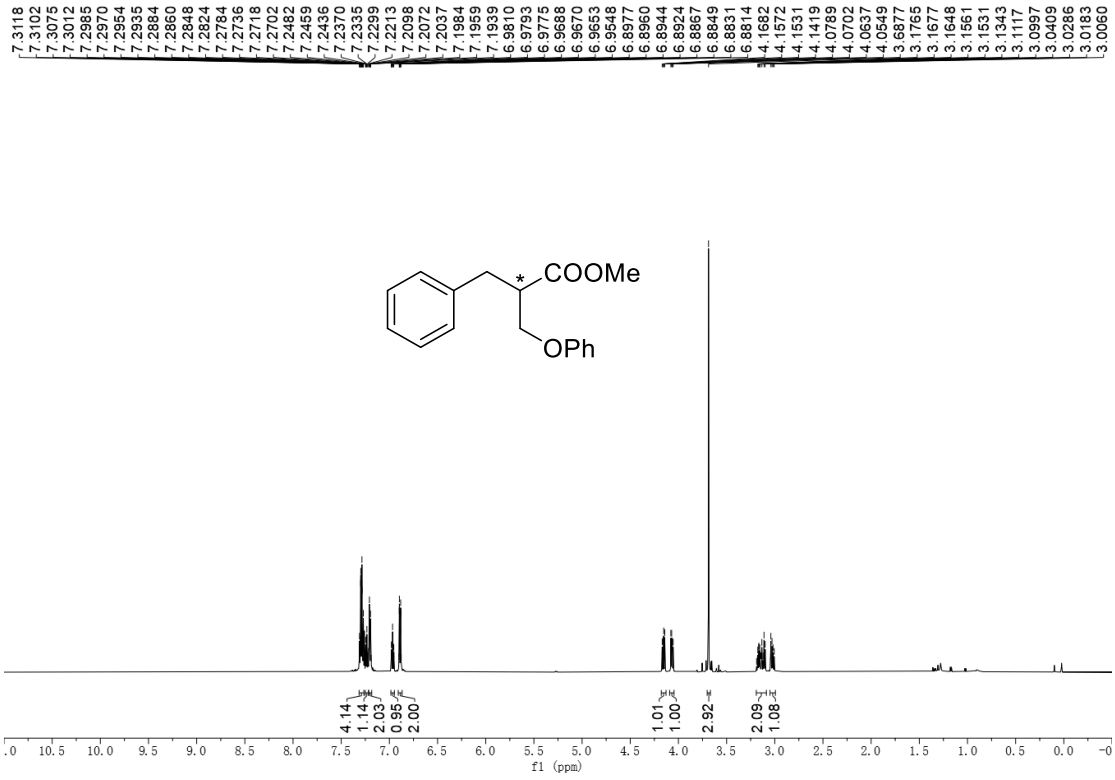


^{1}H NMR (600 MHz, Chloroform-*d*)

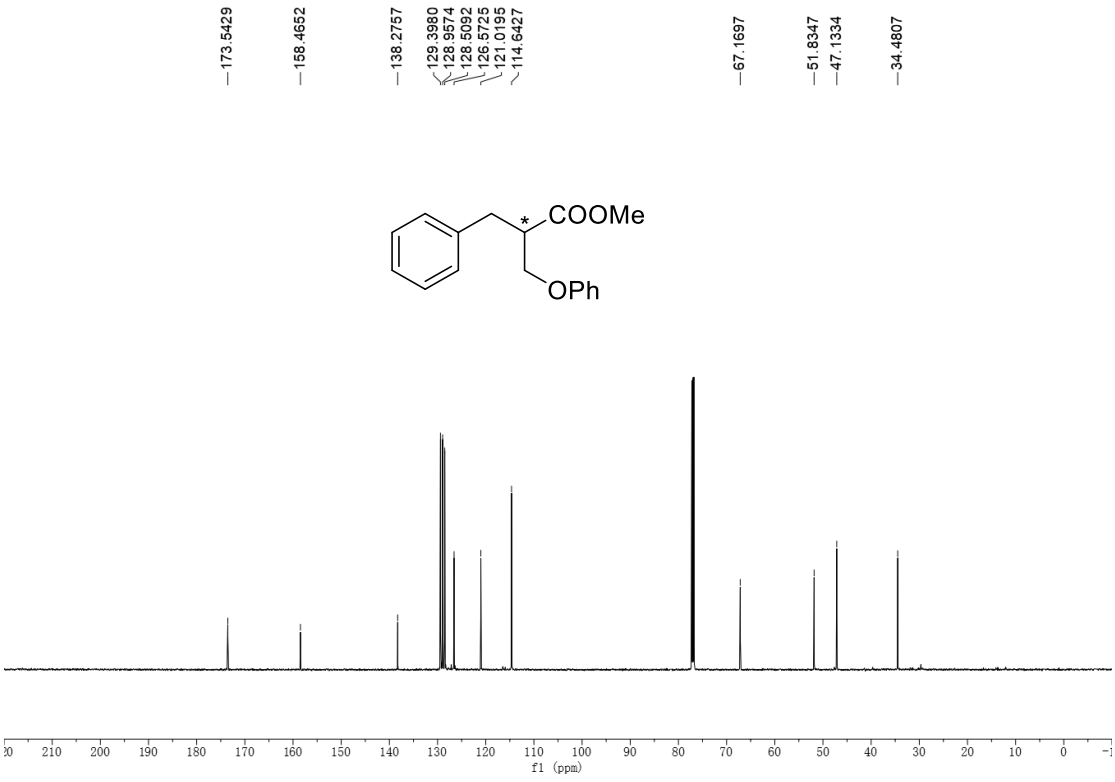


^{13}C NMR (151 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-phenoxypropanoate (**4f**)

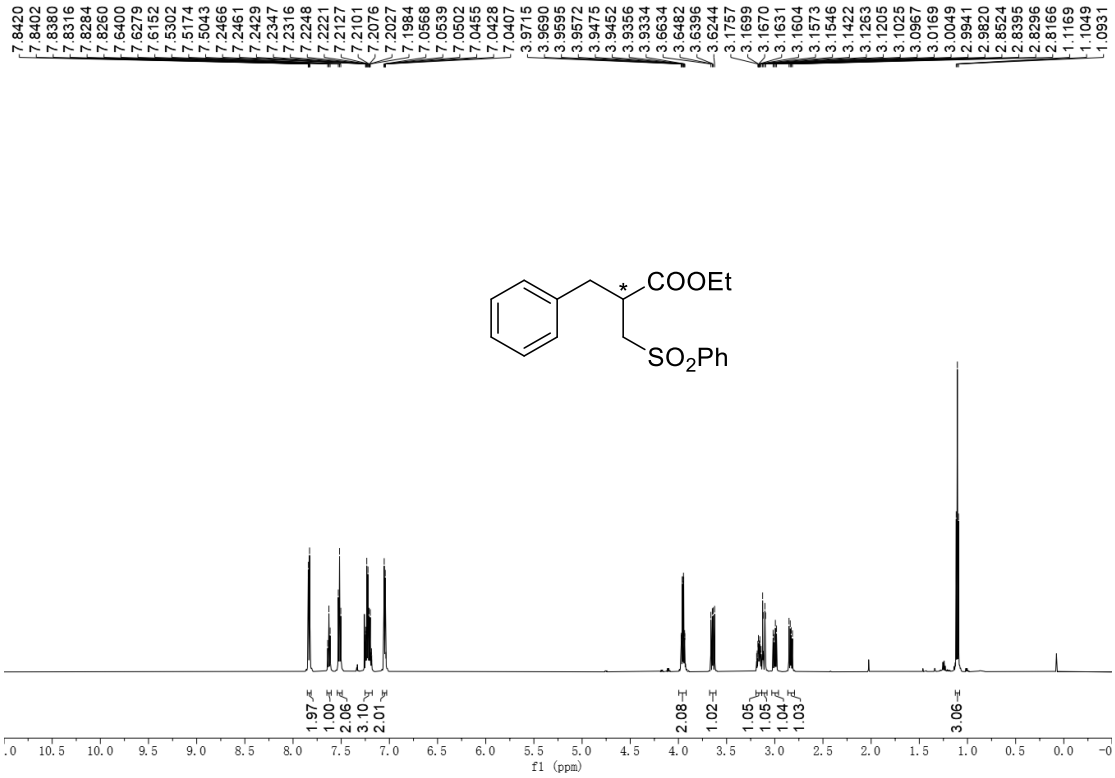


^{1}H NMR (600 MHz, Chloroform-*d*)

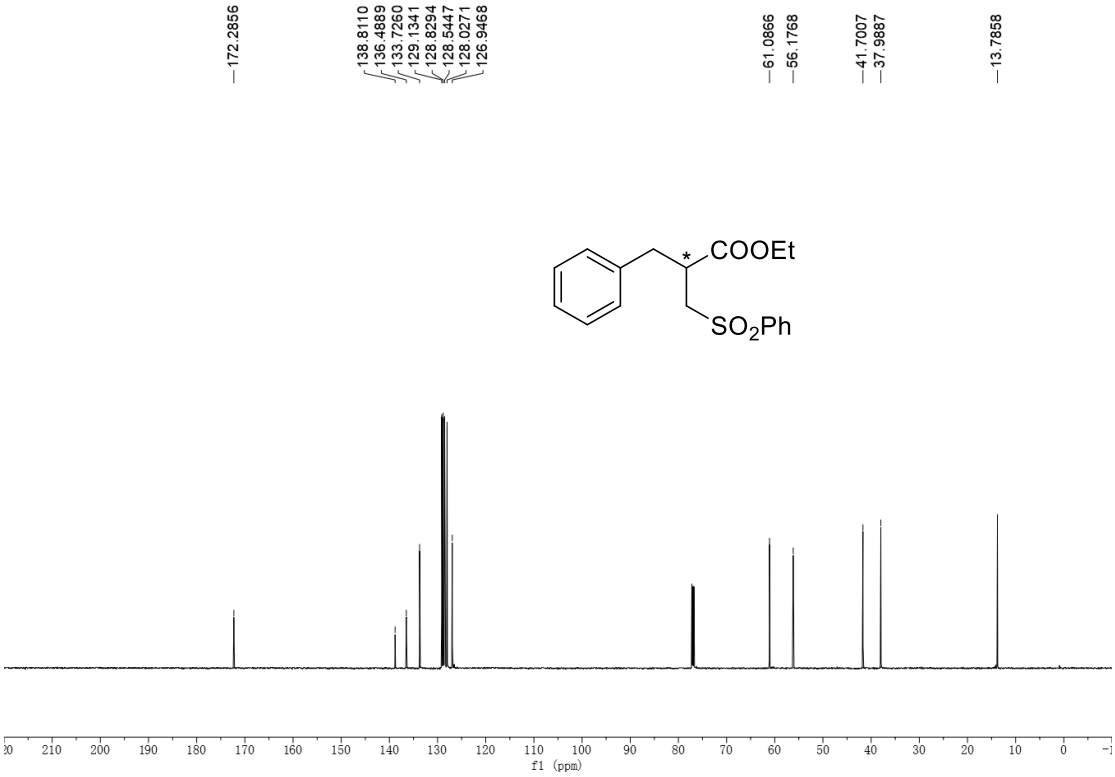


^{13}C NMR (151 MHz, Chloroform-*d*)

Ethyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4g**)

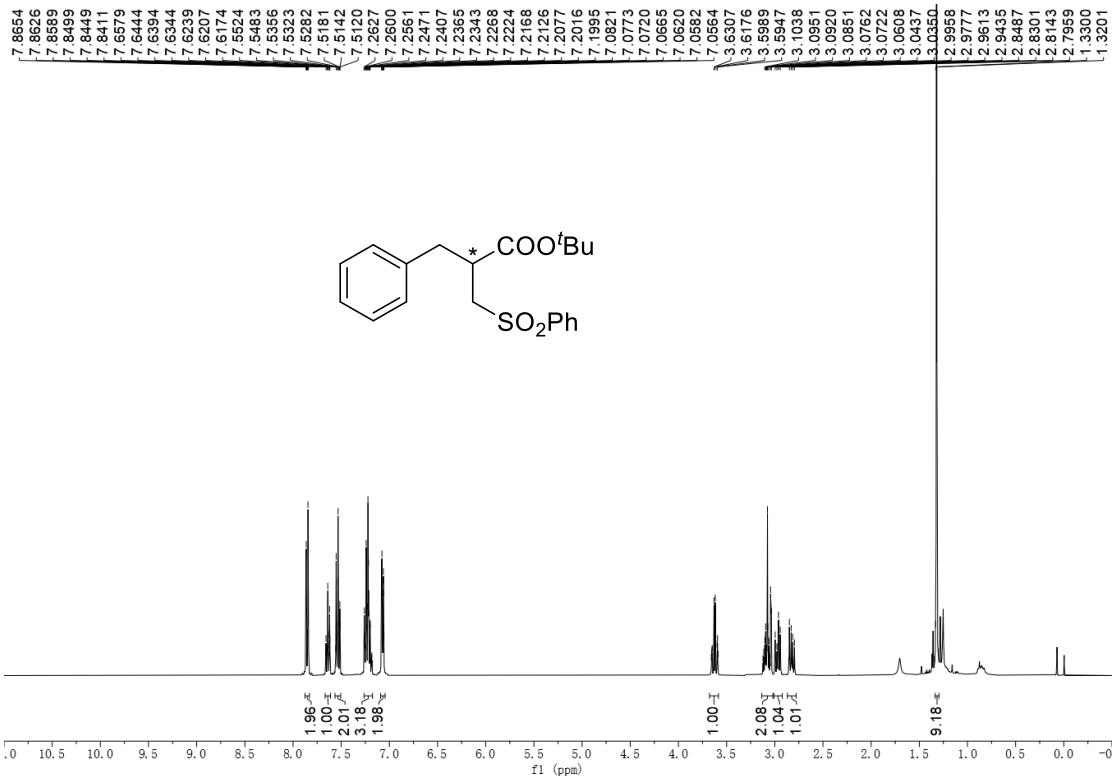


^{1}H NMR (600 MHz, Chloroform-*d*)

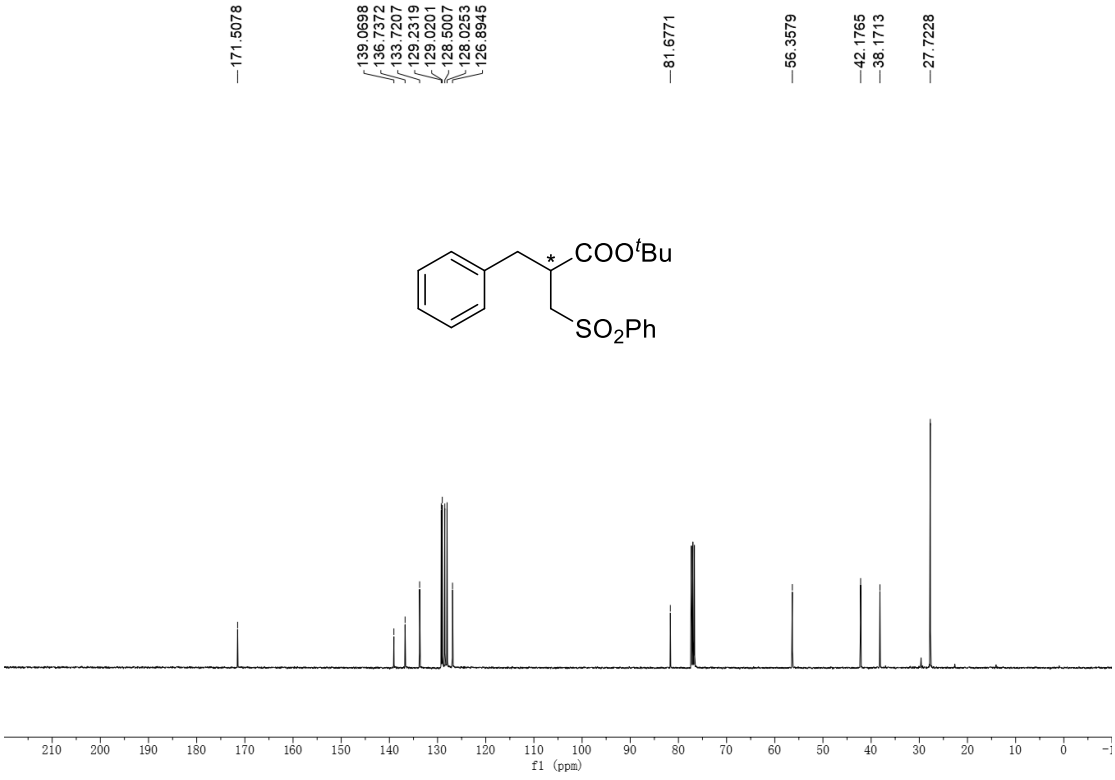


^{13}C NMR (151 MHz, Chloroform-*d*)

Tert-butyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4h**)

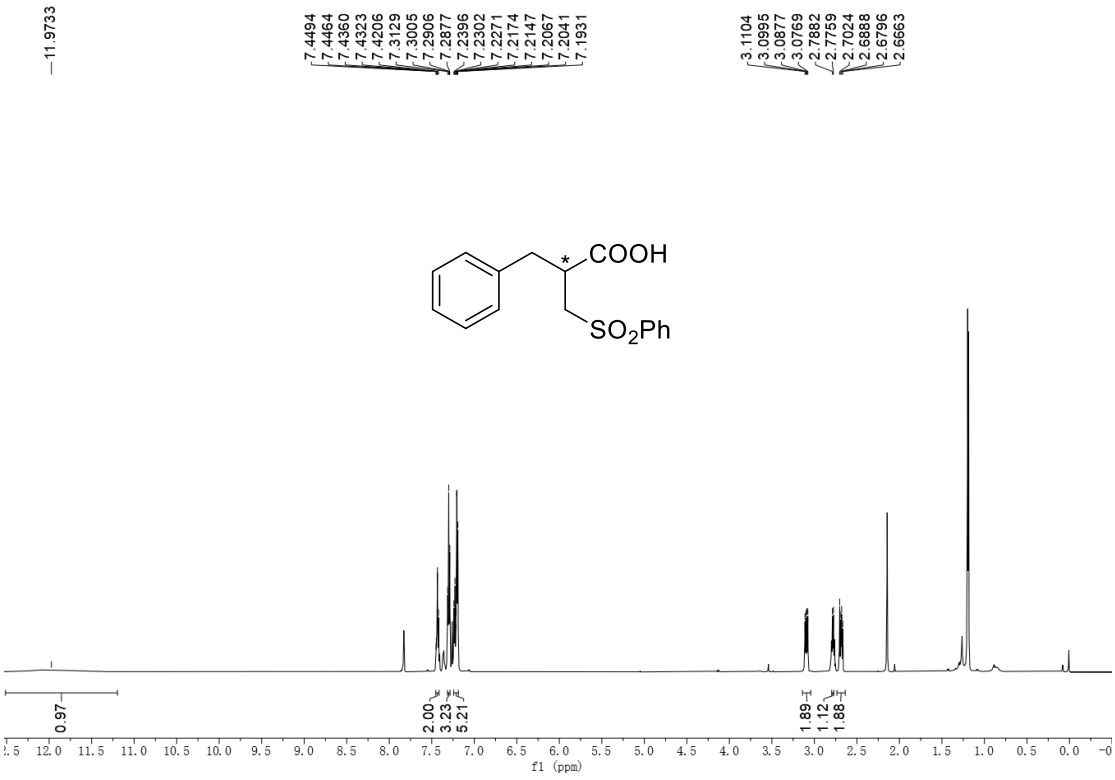


^{1}H NMR (400 MHz, Chloroform-*d*)



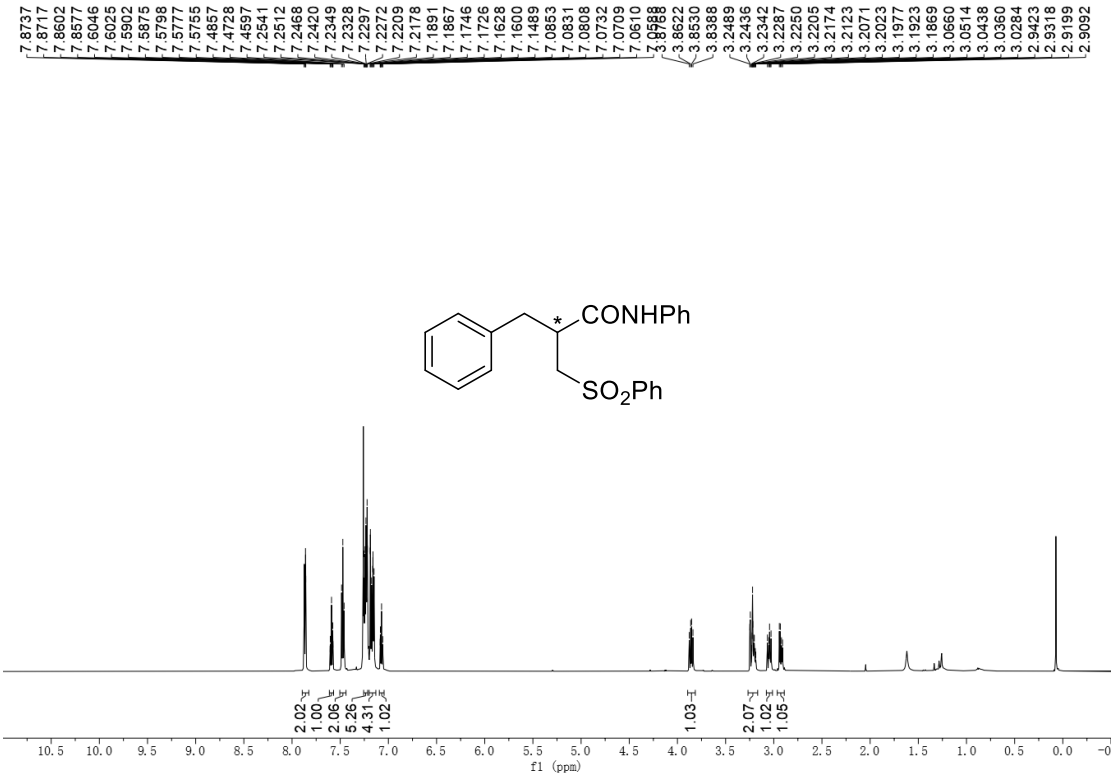
^{13}C NMR (101 MHz, Chloroform-*d*)

2-Benzyl-3-(phenylsulfonyl)propanoic acid (**4i/4i'**)

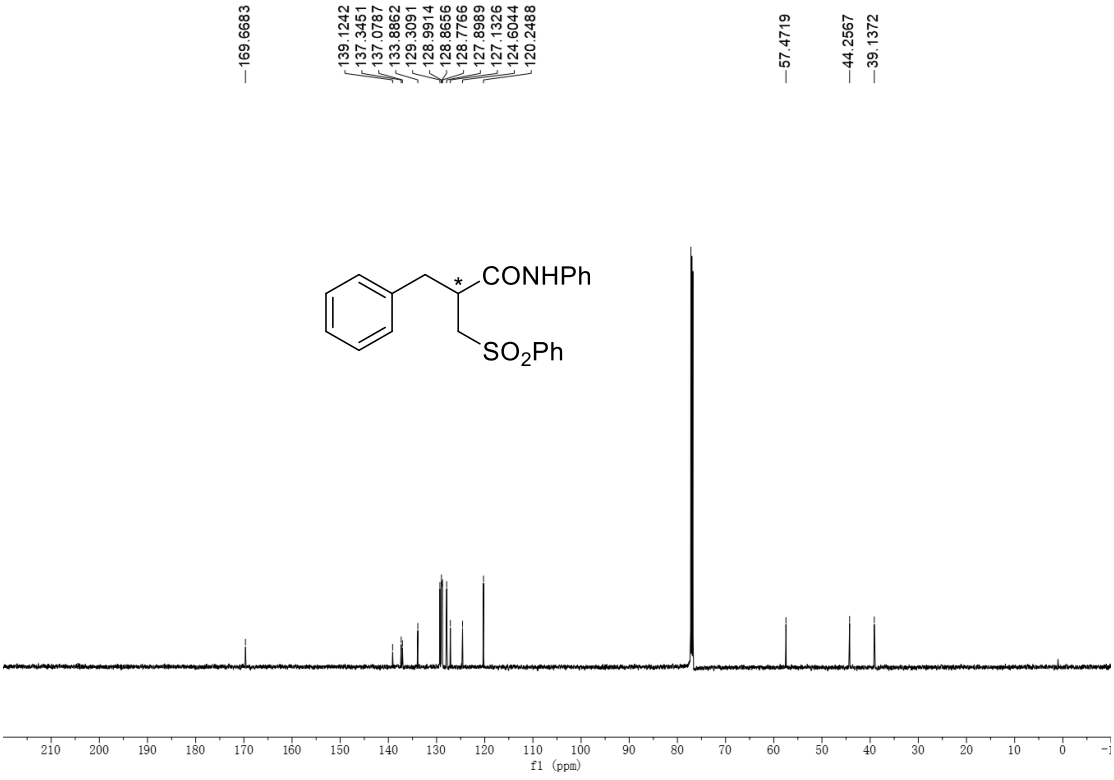


^{1}H NMR (600 MHz, Chloroform-*d*)

2-Benzyl-*N*-phenyl-3-(phenylsulfonyl)propenamide (**4j/4j'**)

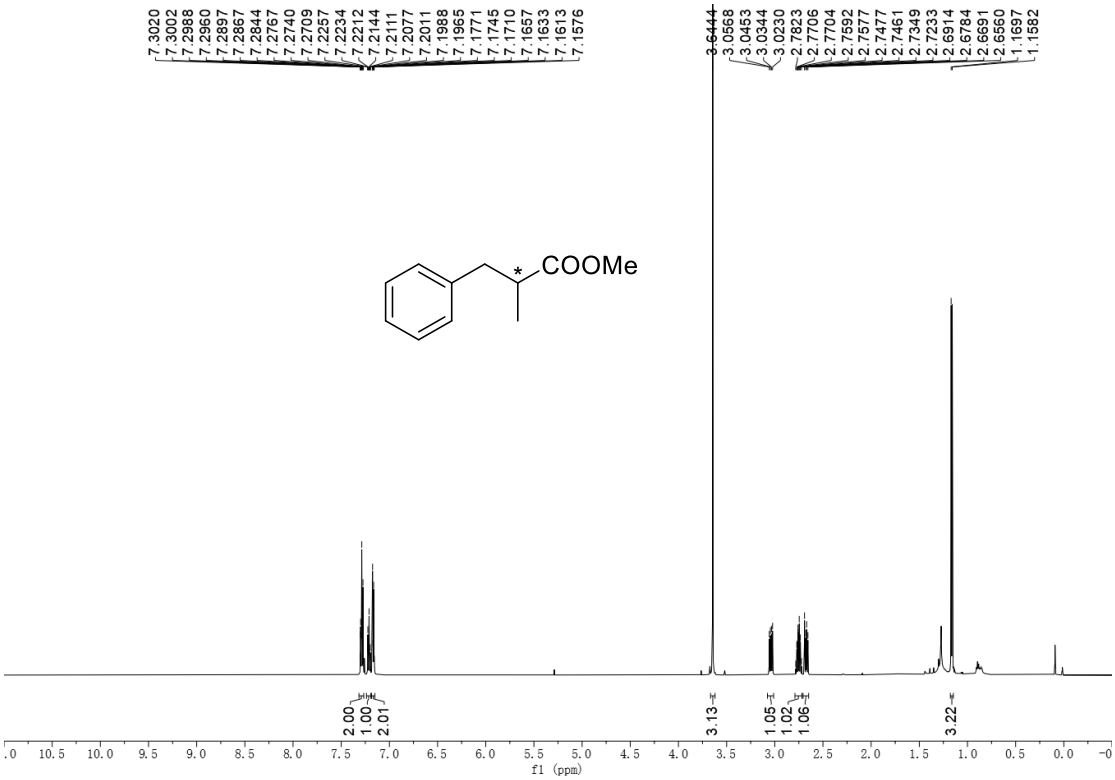


^{1}H NMR (600 MHz, Chloroform-*d*)



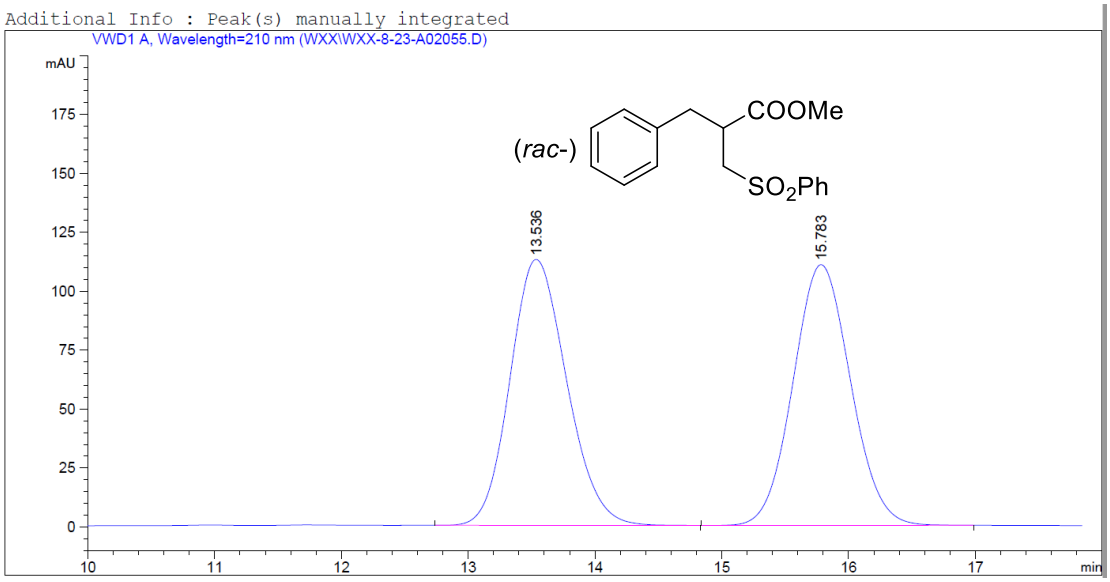
^{13}C NMR (151 MHz, Chloroform-*d*)

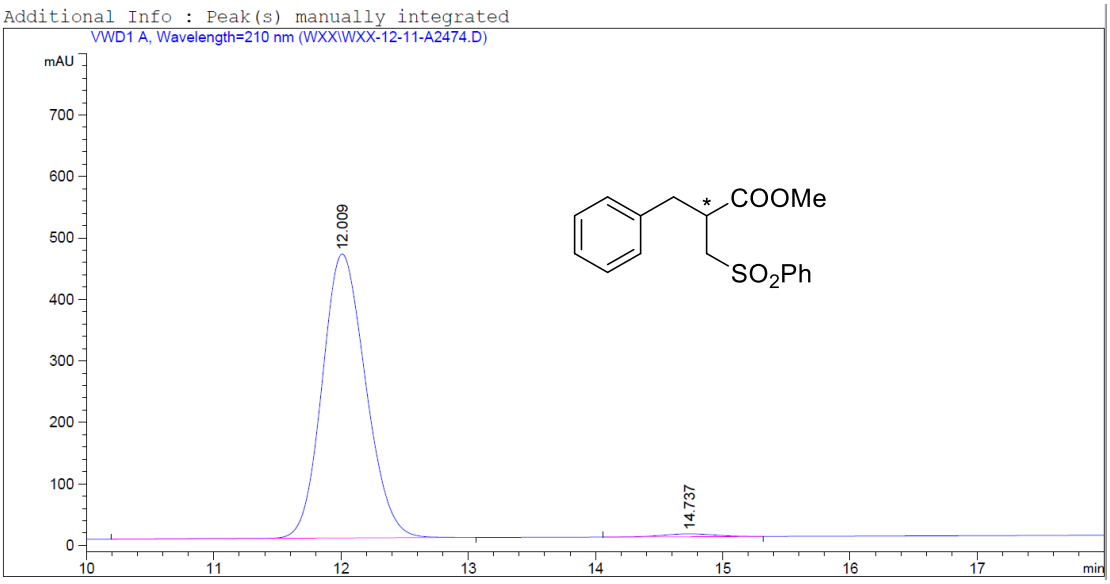
Methyl 2-methyl-3-phenylpropanoate (**4k**)



^{1}H NMR (600 MHz, Chloroform-*d*)

Methyl 2-benzyl-3-(phenylsulfonyl)propanoate (**2a**)





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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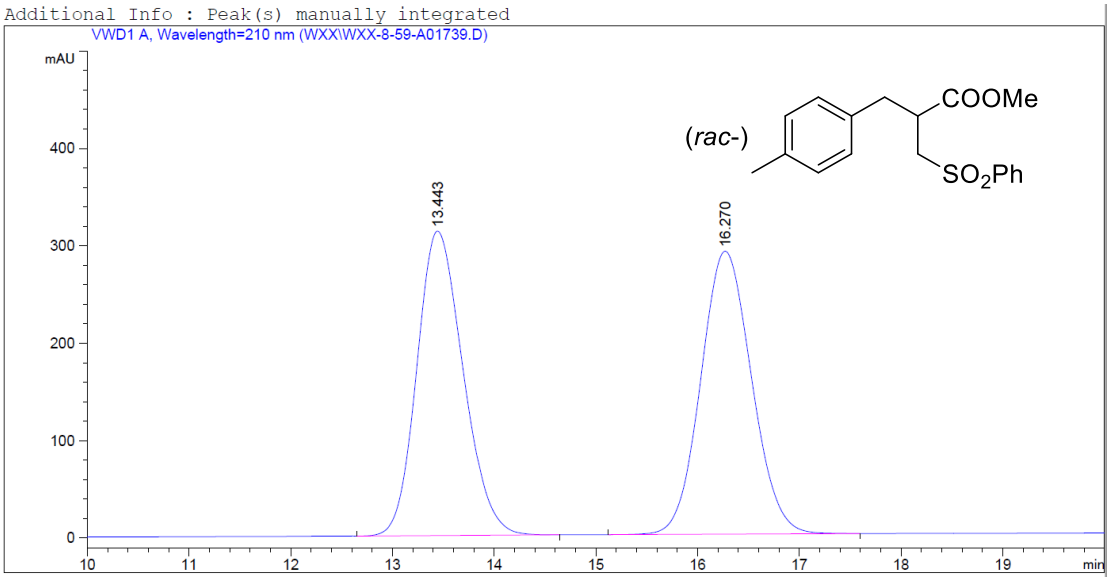
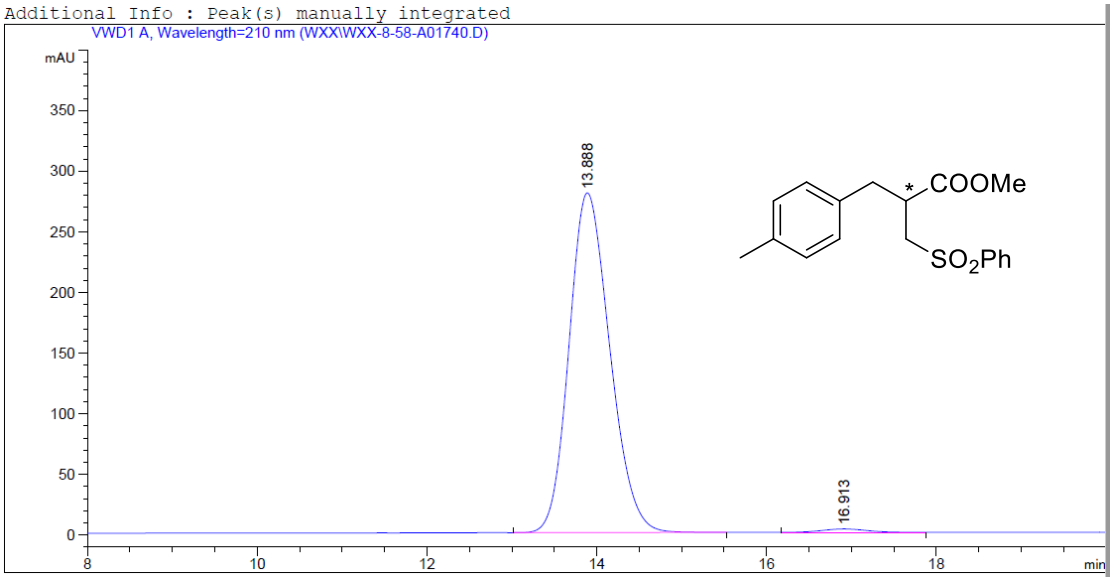
2	14.737	BB	0.4373	132.64473	4.68552	1.1960
Totals :				1.10906e4	466.64783	

Methyl 2-(4-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2b**)

Additional Info : Peak(s) manually integrated



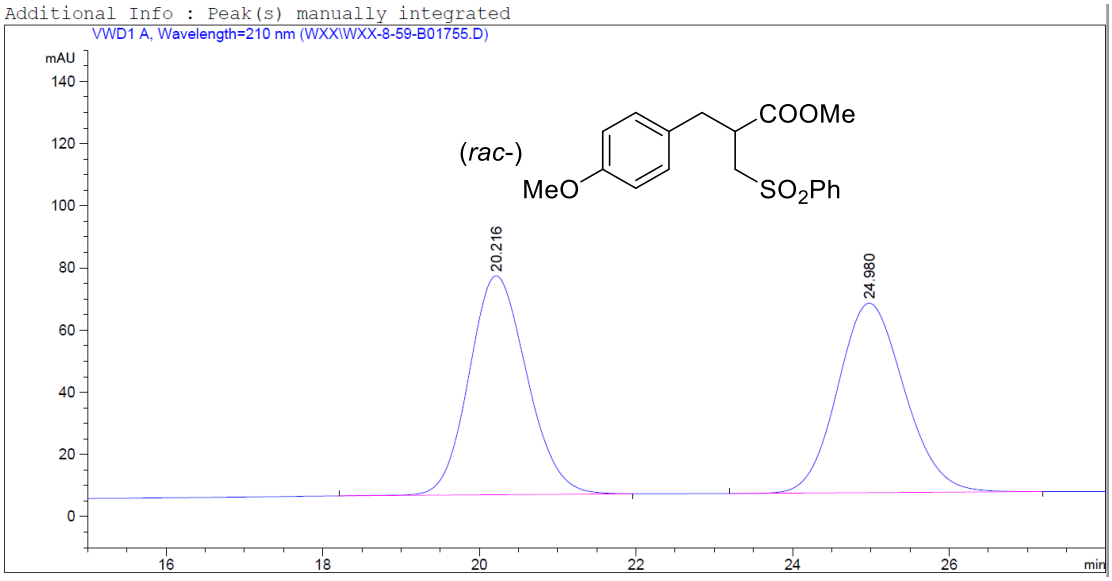
Additional Info : Peak(s) manually integrated



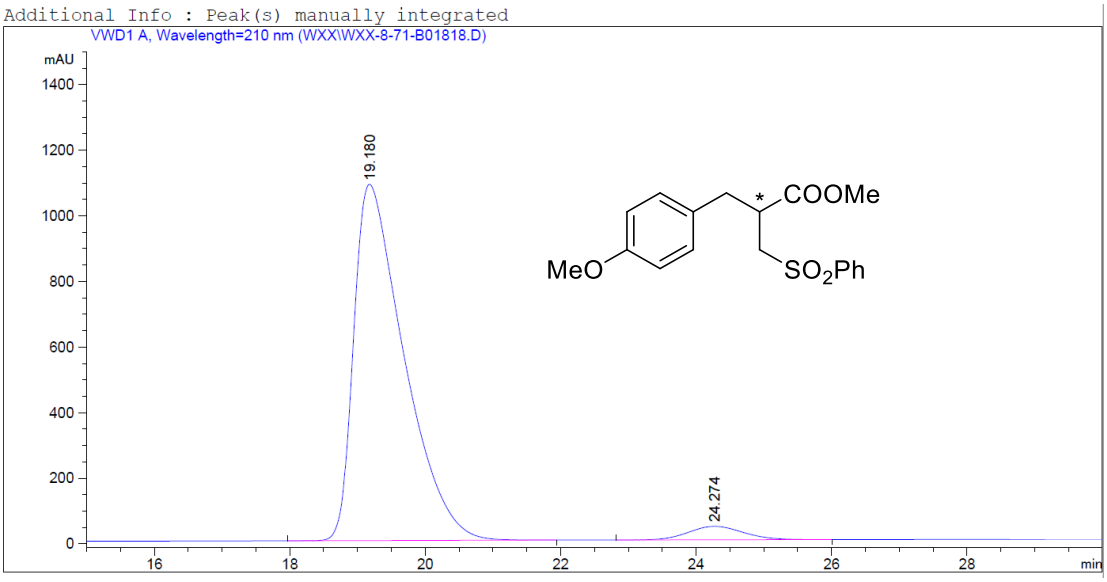
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.888	BB	0.5164	9348.04492	280.08875	98.9653
2	16.913	BB	0.5330	97.73553	2.74083	1.0347
Totals :				9445.78045	282.82958	

Methyl 2-(4-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2c**)

Additional Info : Peak(s) manually integrated



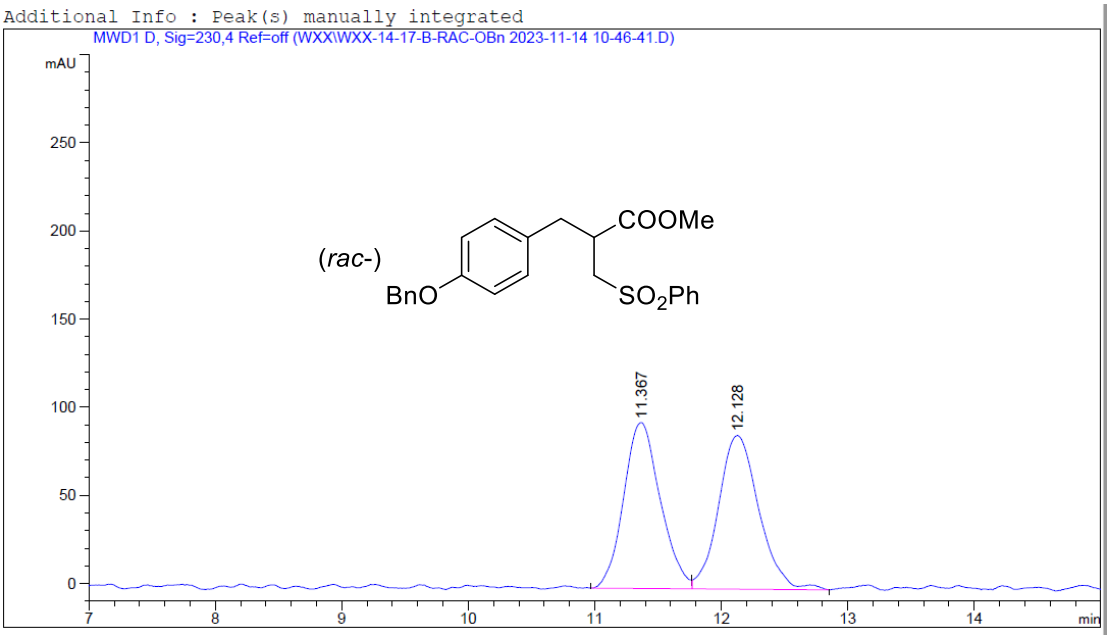
Additional Info : Peak(s) manually integrated



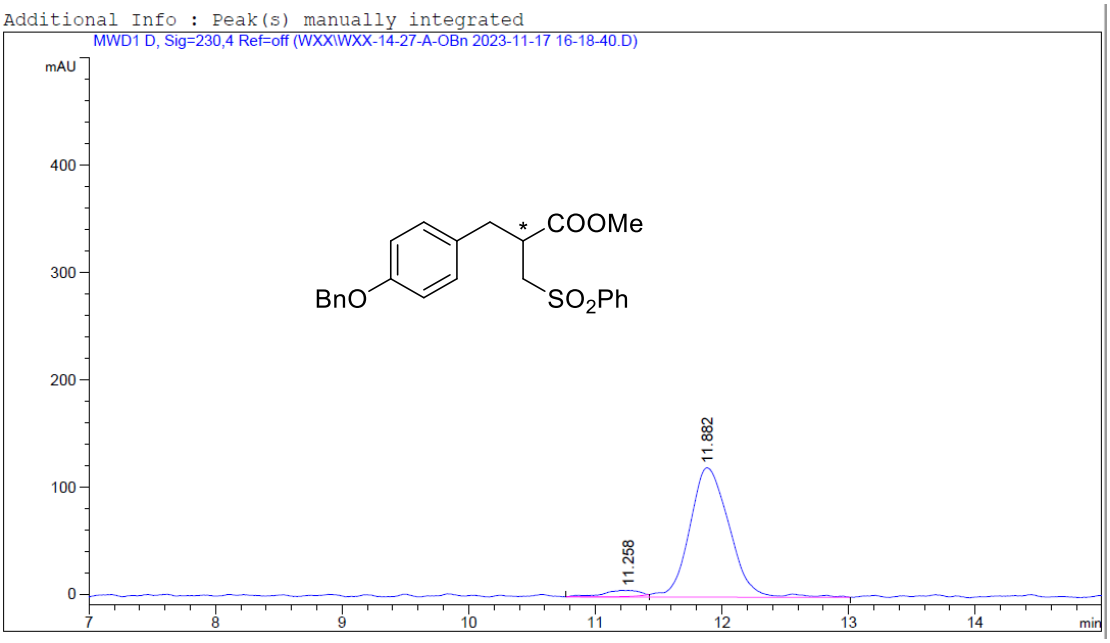
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.180	BB	0.7660	5.58199e4	1085.41919	96.0113
2	24.274	BB	0.8773	2318.95435	41.03266	3.9887
Totals :				5.81388e4	1126.45185	

Methyl 2-(4-(benzyloxy)benzyl)-3-(phenylsulfonyl)propanoate (**2d**)

Additional Info : Peak(s) manually integrated



Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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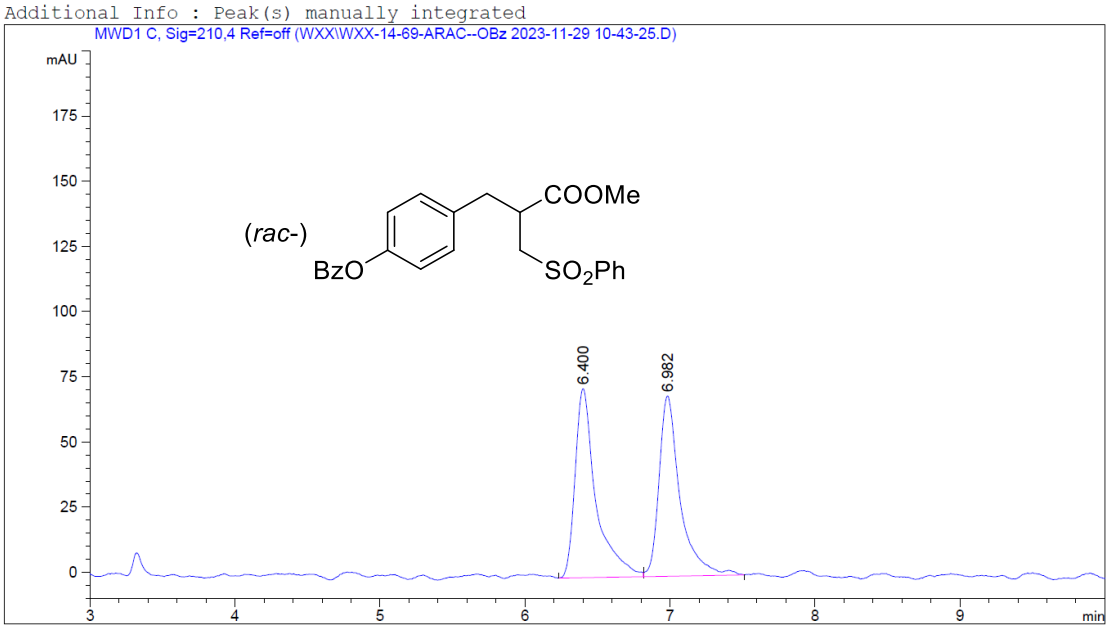
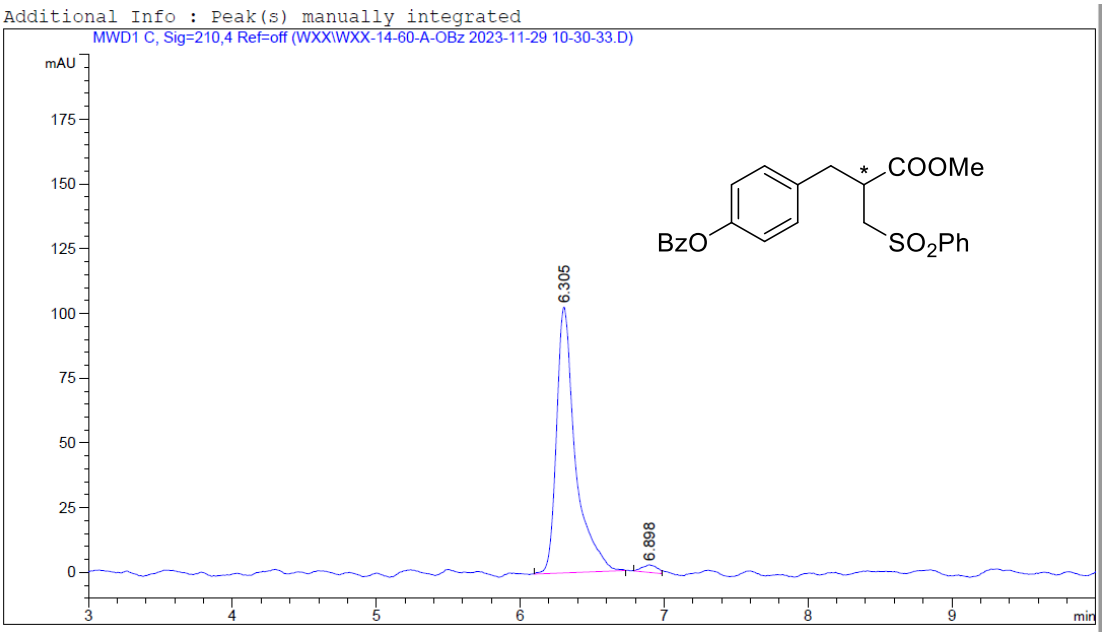
2	11.882	VV R	0.3201	2649.19067	120.64447	95.7610
Totals :				2766.46237	126.28609	

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl benzoate (**2e**)

Additional Info : Peak(s) manually integrated

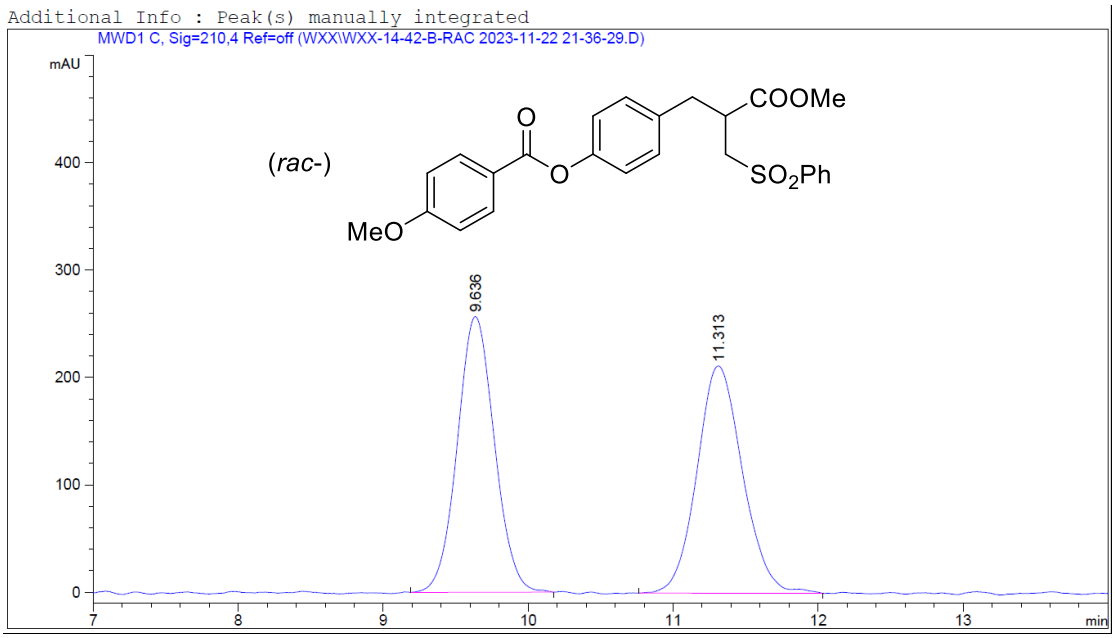


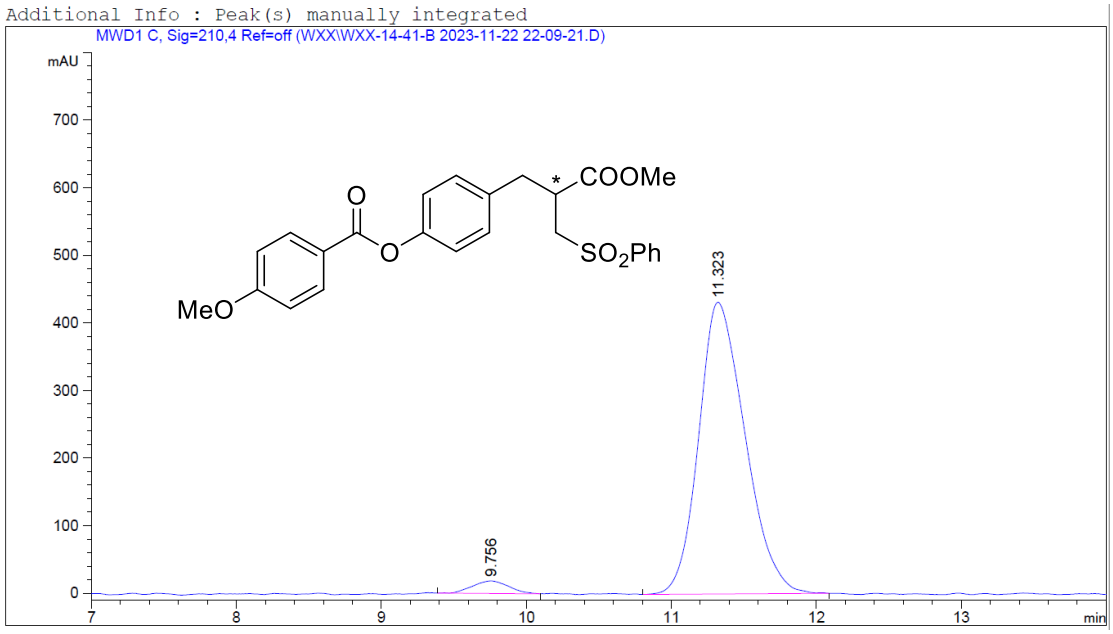
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.305	VV R	0.1320	936.75104	102.63485	97.8102
2	6.898	BV	0.0862	20.97224	2.95778	2.1898
Totals :				957.72328	105.59263	

4-(3-Methoxy-3-oxo-2-((phenylsulfonyl)methyl)propyl)phenyl 4-methoxybenzoate (**2f**)

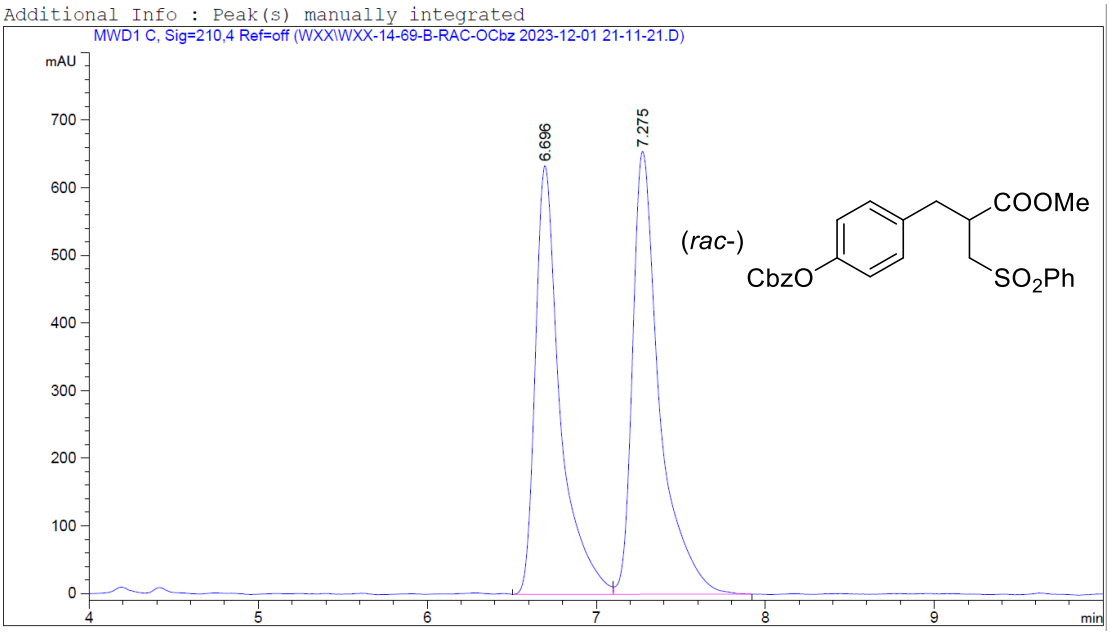




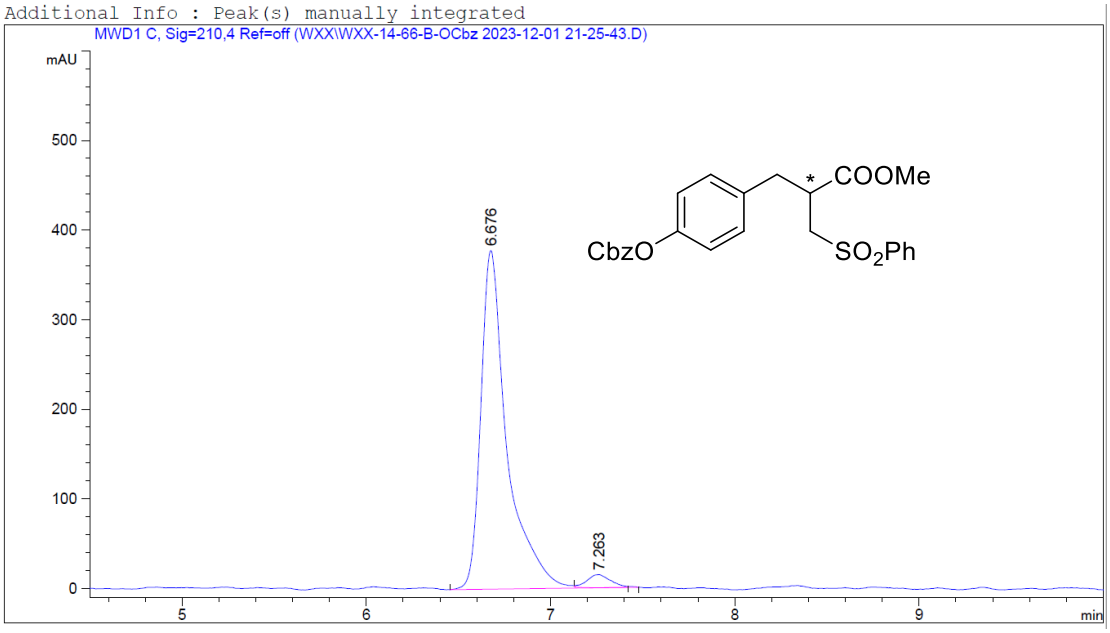
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.756	VB R	0.2065	321.12201	18.59181	3.2342
2	11.323	VV R	0.2951	9607.85059	431.74139	96.7658
Totals :				9928.97260	450.33320	

Methyl 2-(4-(((benzyloxy)carbonyl)oxy)benzyl)-3-(phenylsulfonyl)propanoate (**2g**)

Additional Info : Peak(s) manually integrated



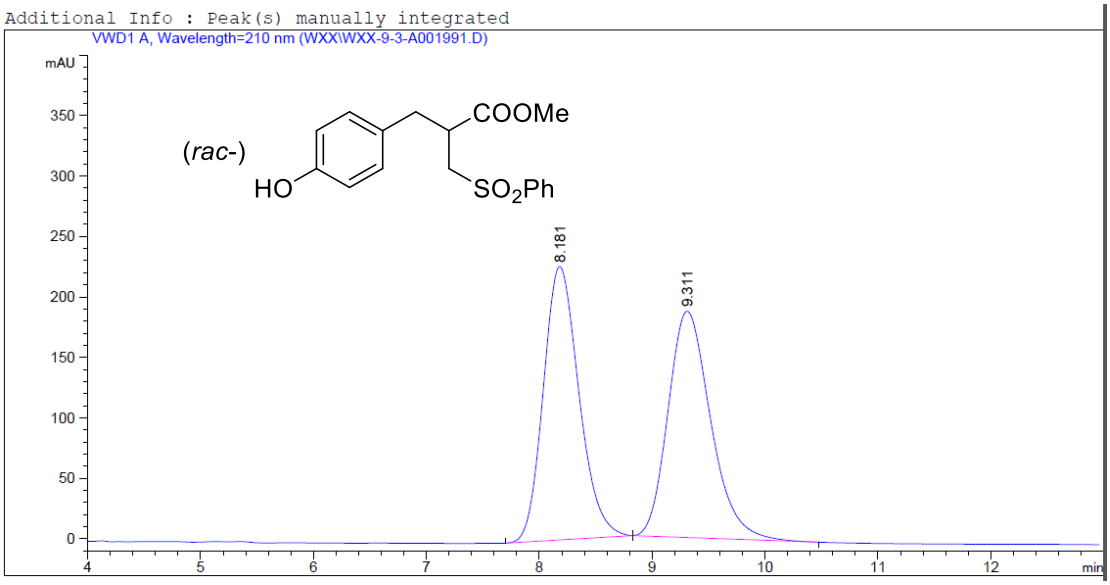
Additional Info : Peak(s) manually integrated



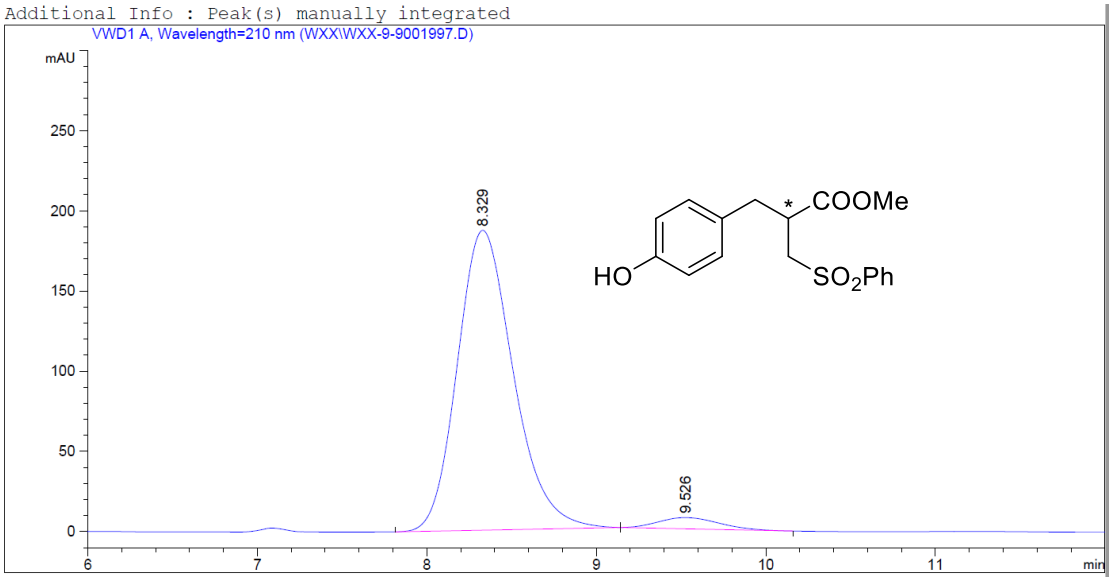
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.676	BV R	0.1436	3728.74487	377.96875	96.6770
2	7.263	VV E	0.1080	128.16551	14.58389	3.3230
Totals :				3856.91039	392.55264	

Methyl 2-(4-hydroxybenzyl)-3-(phenylsulfonyl)propanoate (**2h**)

Additional Info : Peak(s) manually integrated



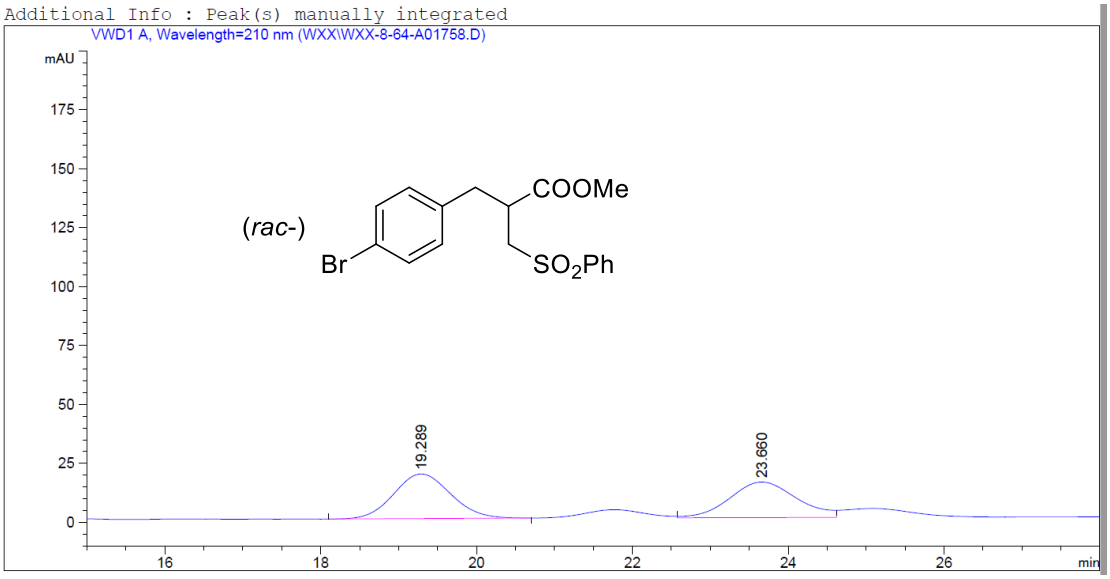
Additional Info : Peak(s) manually integrated



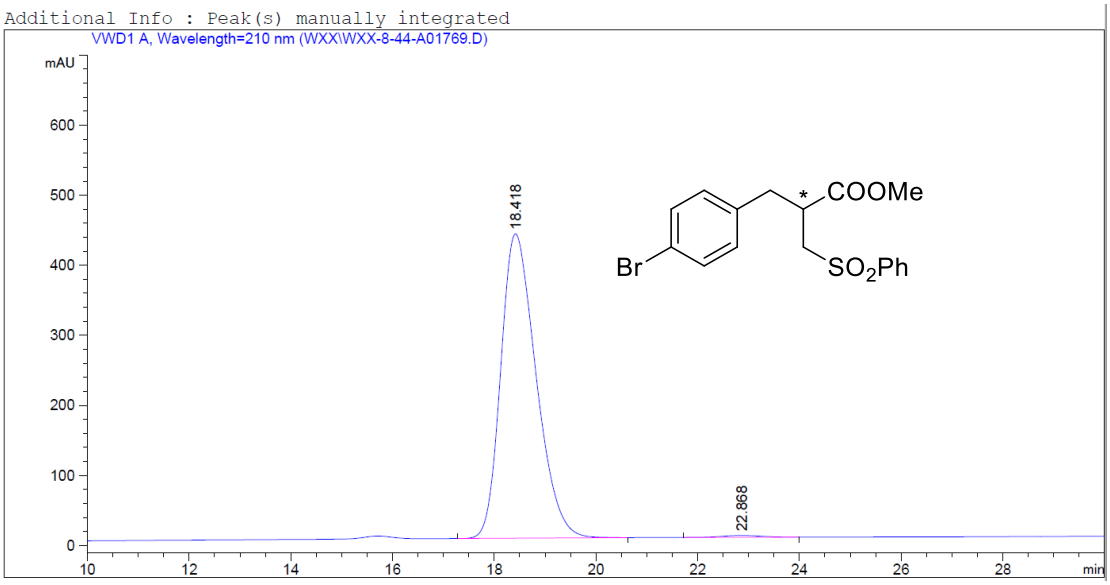
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.329	BB	0.3538	4288.23389	186.83214	96.1115
2	9.526	BB	0.3906	173.49446	7.01293	3.8885
Totals :				4461.72835	193.84507	

(*S*)-Methyl 2-(4-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2i**)

Additional Info : Peak(s) manually integrated



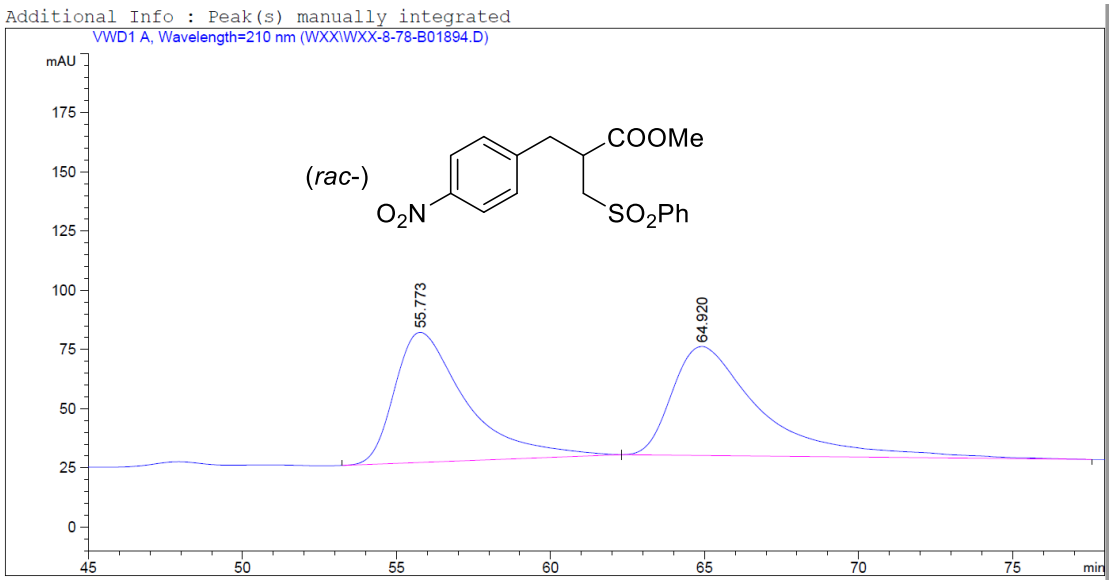
Additional Info : Peak(s) manually integrated



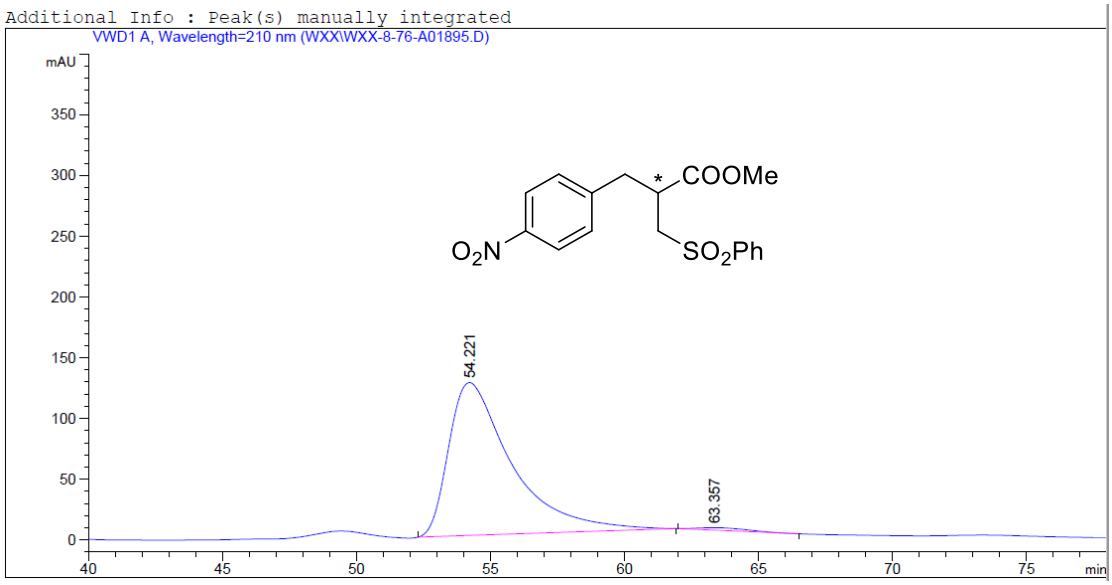
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.418	BB	0.7411	2.09289e4	434.41965	99.3567
2	22.868	BB	0.7705	135.49841	2.51530	0.6433
Totals :				2.10644e4	436.93494	

Methyl 2-(4-nitrobenzyl)-3-(phenylsulfonyl)propanoate (**2j**)

Additional Info : Peak(s) manually integrated



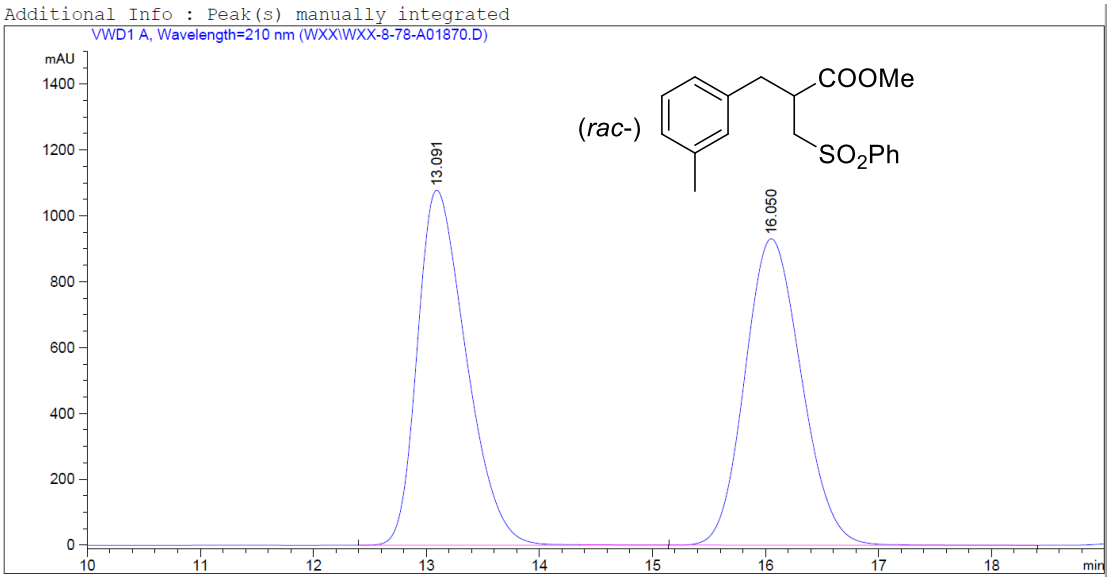
Additional Info : Peak(s) manually integrated



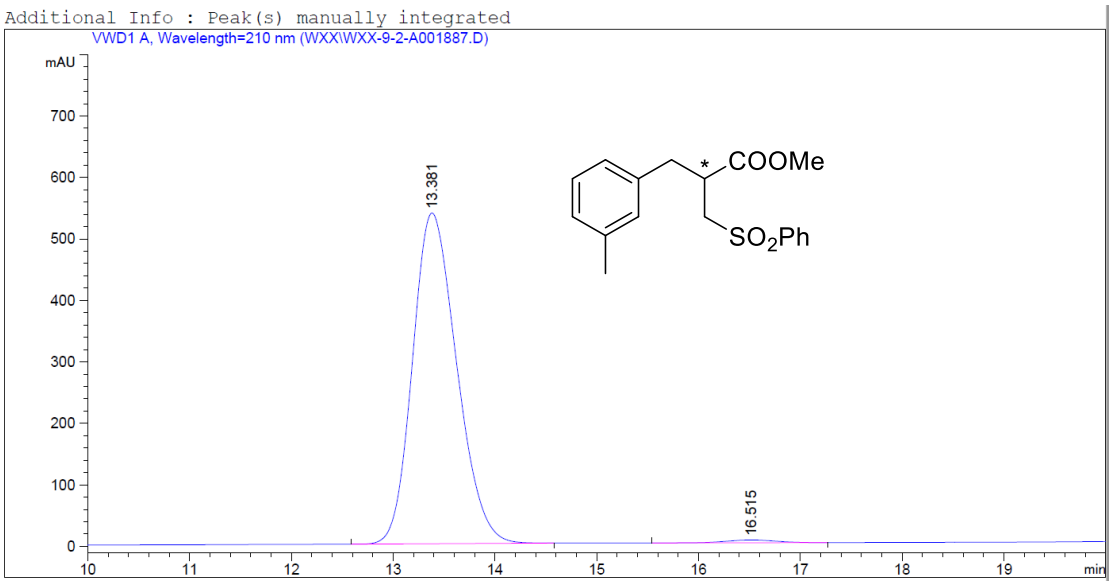
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	54.221	BB	2.2572	2.06254e4	125.83629	98.7063
2	63.357	BB	1.5965	270.32550	1.97915	1.2937
Totals :				2.08957e4	127.81543	

Methyl 2-(3-methylbenzyl)-3-(phenylsulfonyl)propanoate (**2k**)

Additional Info : Peak(s) manually integrated

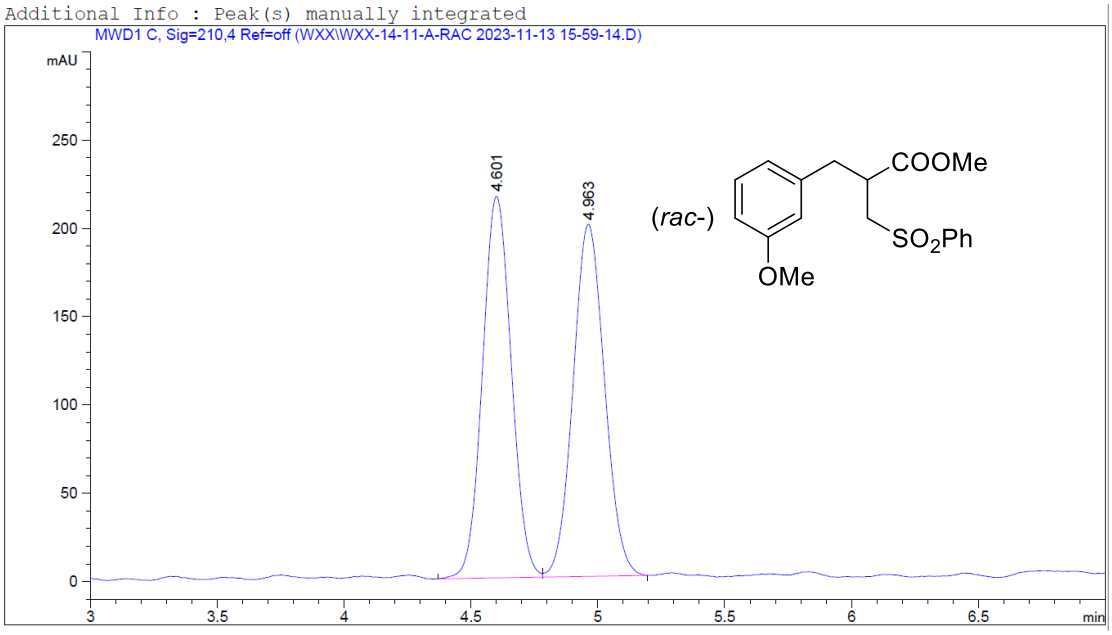


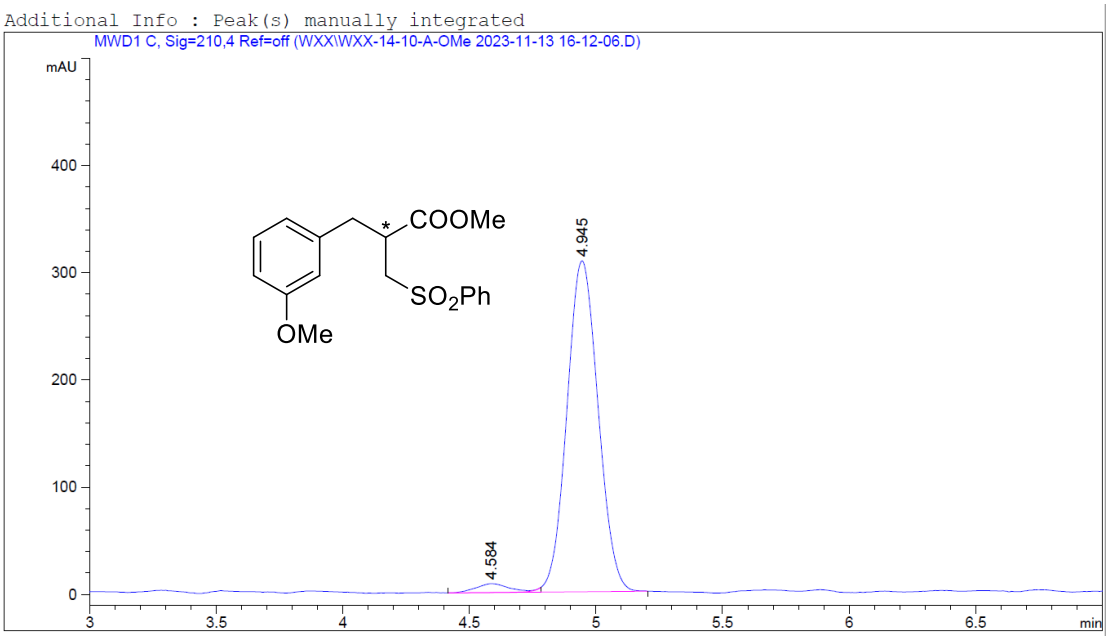
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.381	BB	0.4670	1.61850e4	537.98120	99.0584
2	16.515	BB	0.5354	153.84949	4.49357	0.9416
Totals :				1.63389e4	542.47477	

Methyl 2-(3-methoxybenzyl)-3-(phenylsulfonyl)propanoate (**2l**)

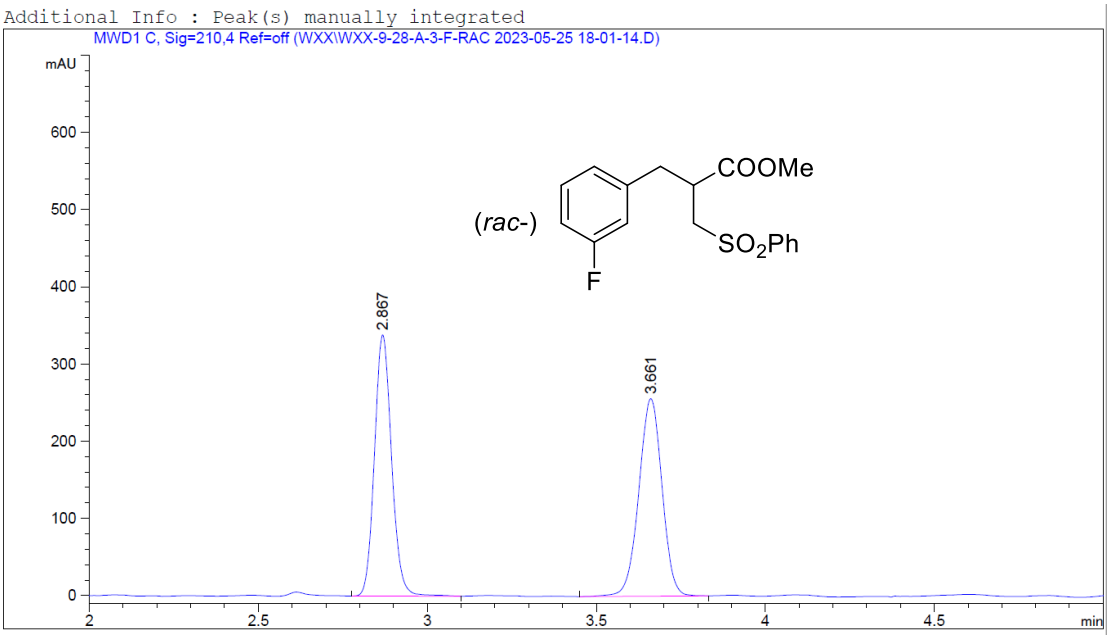




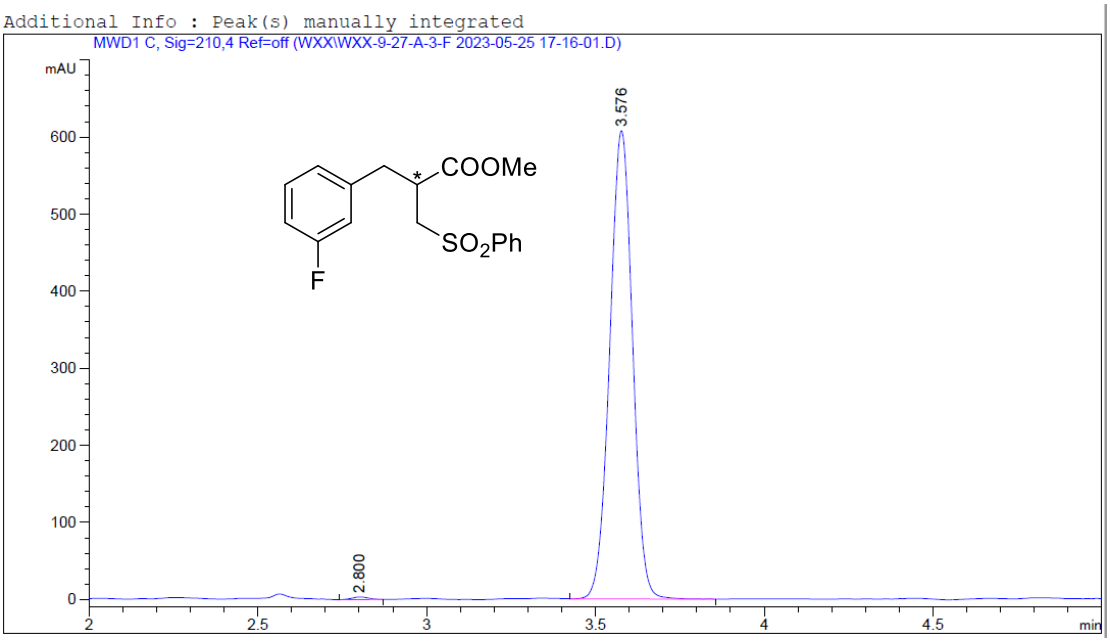
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.584	BV E	0.1082	74.86328	8.34327	2.7491
2	4.945	VB R	0.1341	2648.30957	308.63998	97.2509
Totals :				2723.17285	316.98325	

Methyl 2-(3-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2m**)

Additional Info : Peak(s) manually integrated



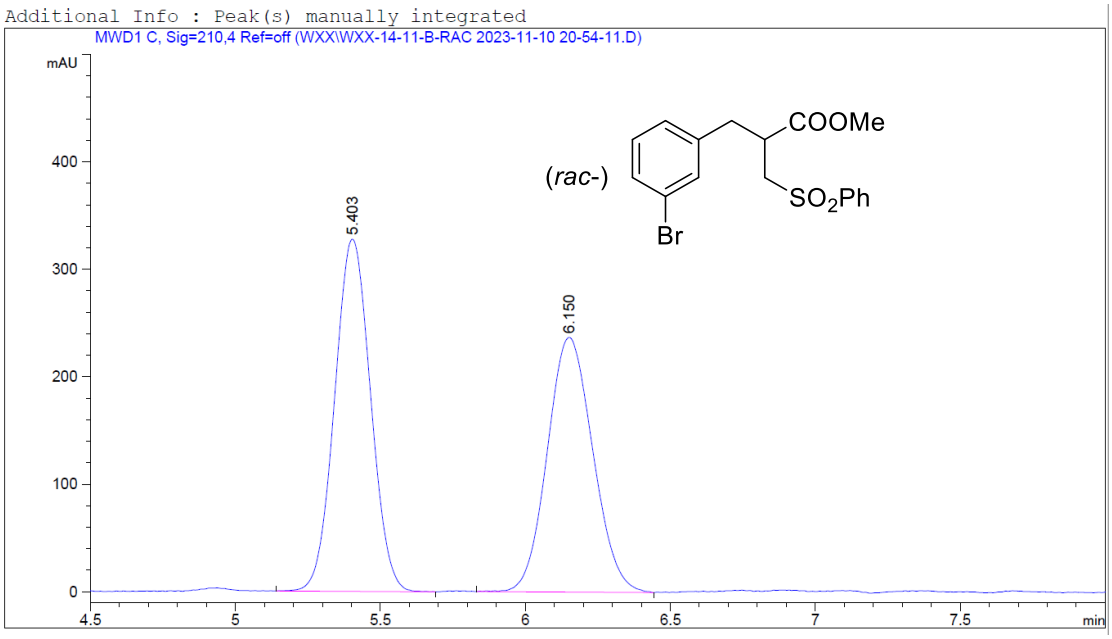
Additional Info : Peak(s) manually integrated



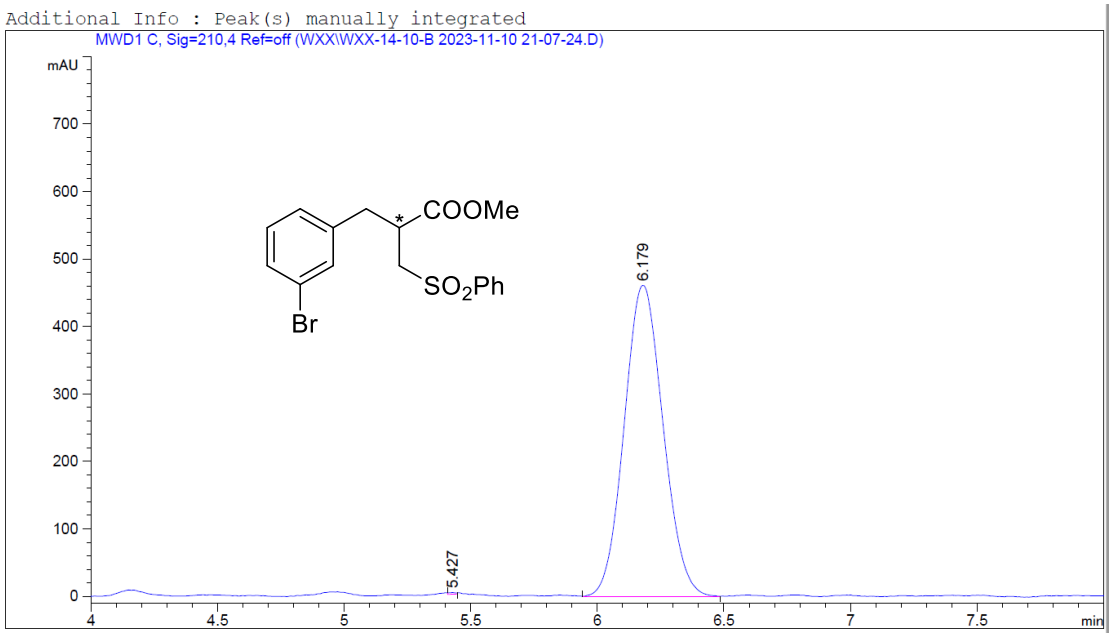
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.800	BB	0.0466	11.93172	3.42624	0.4175
2	3.576	BV R	0.0726	2845.84570	607.60809	99.5825
Totals :				2857.77742	611.03434	

Methyl 2-(3-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2n**)

Additional Info : Peak(s) manually integrated

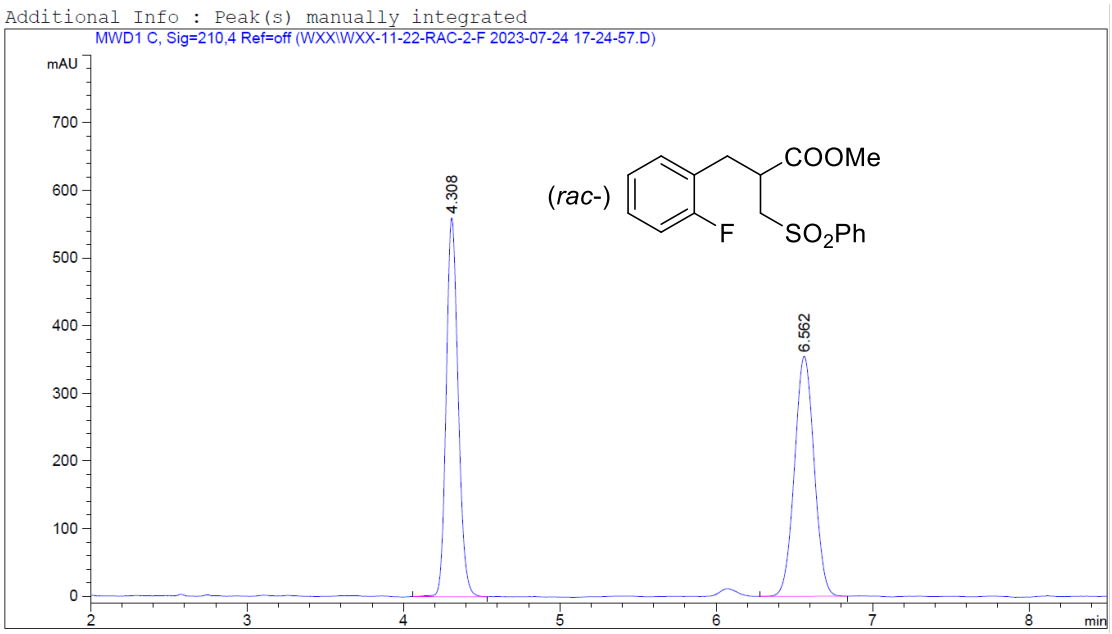


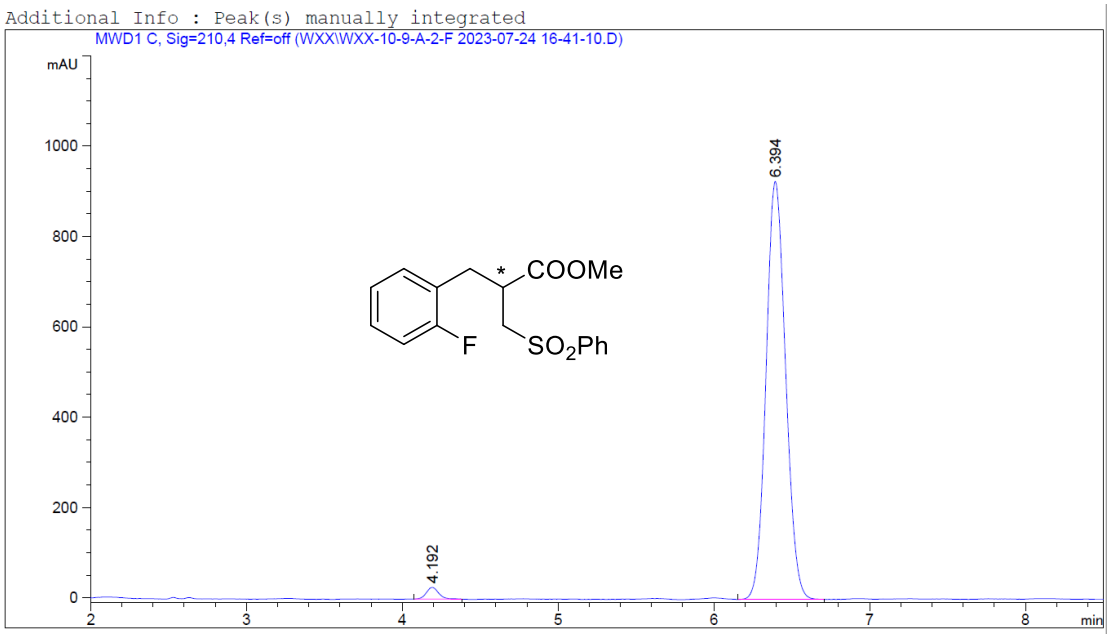
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.427	VV	0.0260	4.80424	2.44031	0.0976
2	6.179	BB	0.1476	4919.75488	460.69174	99.9024
Totals :				4924.55913	463.13205	

Methyl 2-(2-fluorobenzyl)-3-(phenylsulfonyl)propanoate (**2o**)

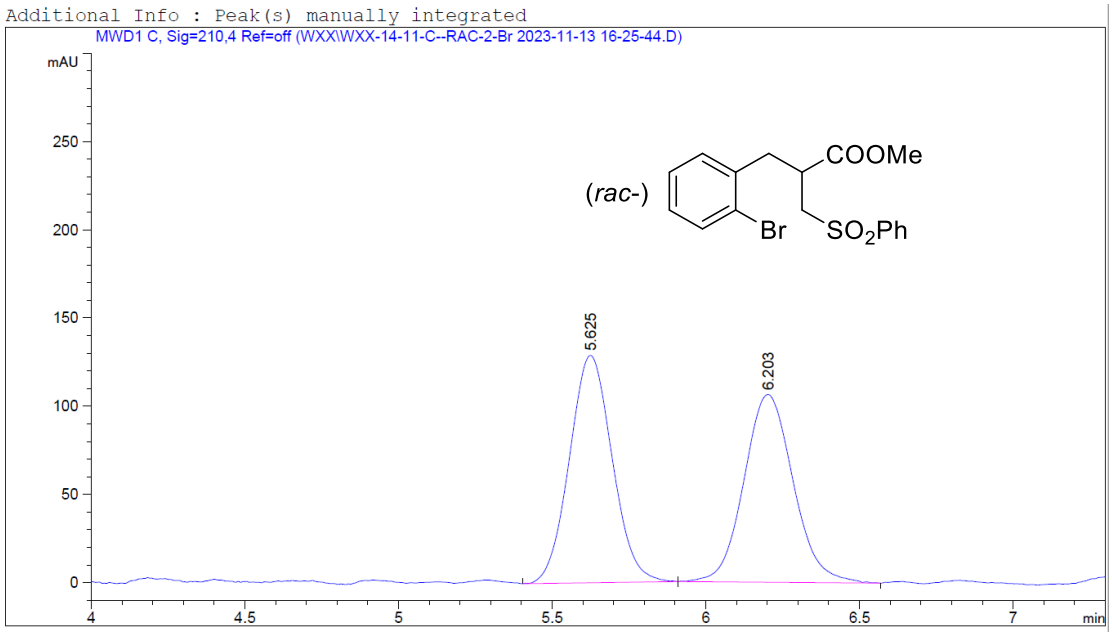




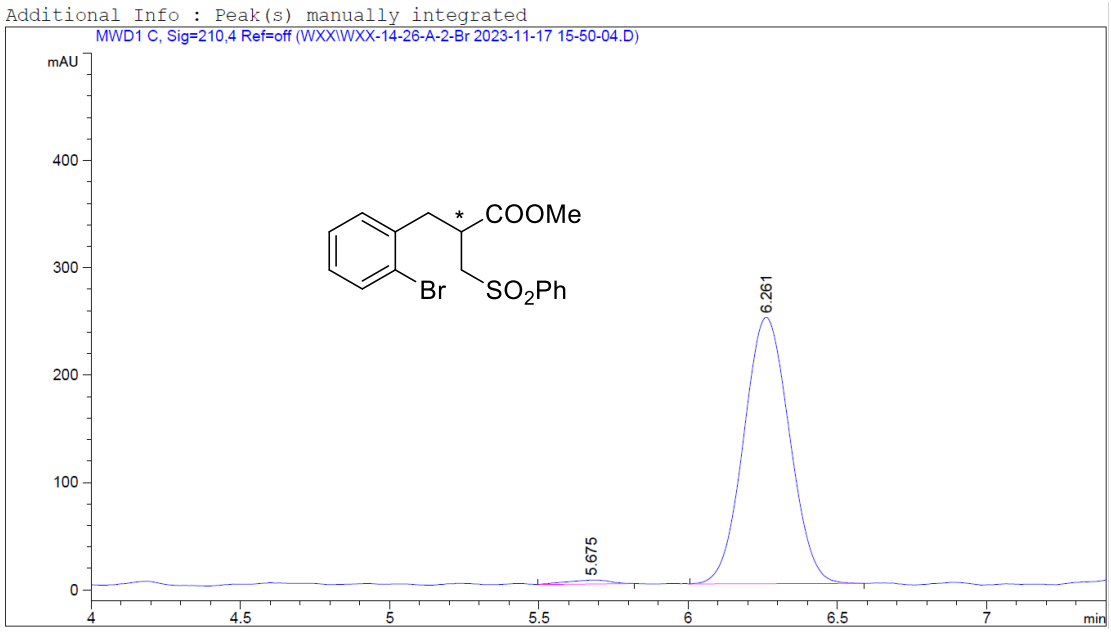
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.192	BV R	0.0837	145.16386	25.96060	1.7685
2	6.394	BB	0.1342	8063.11670	925.14130	98.2315
Totals :				8208.28056	951.10190	

Methyl 2-(2-bromobenzyl)-3-(phenylsulfonyl)propanoate (**2p**)

Additional Info : Peak(s) manually integrated



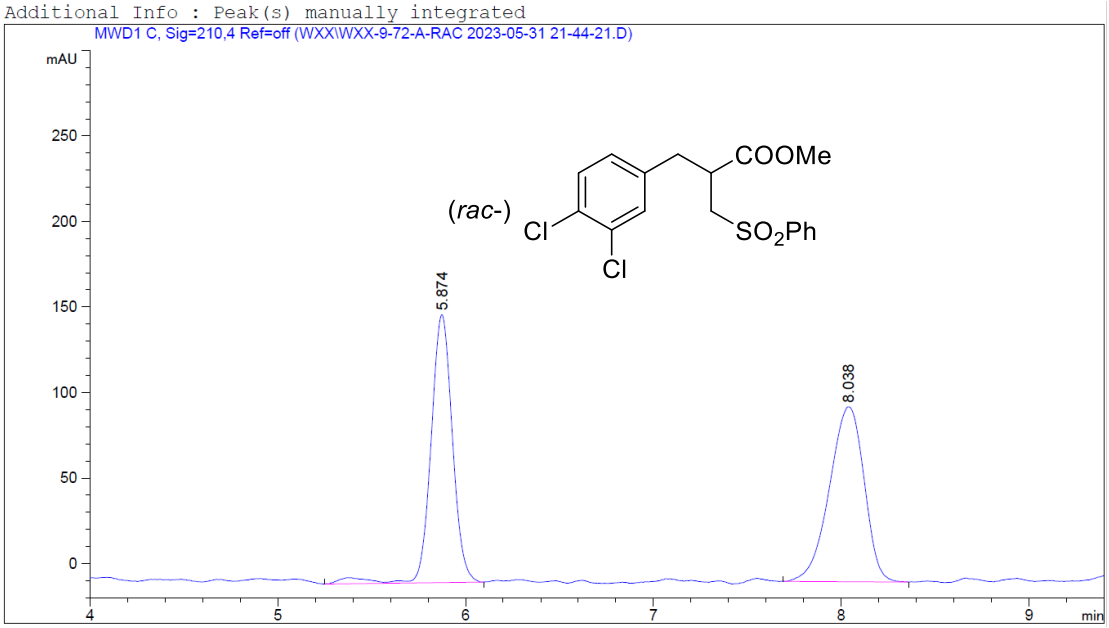
Additional Info : Peak(s) manually integrated



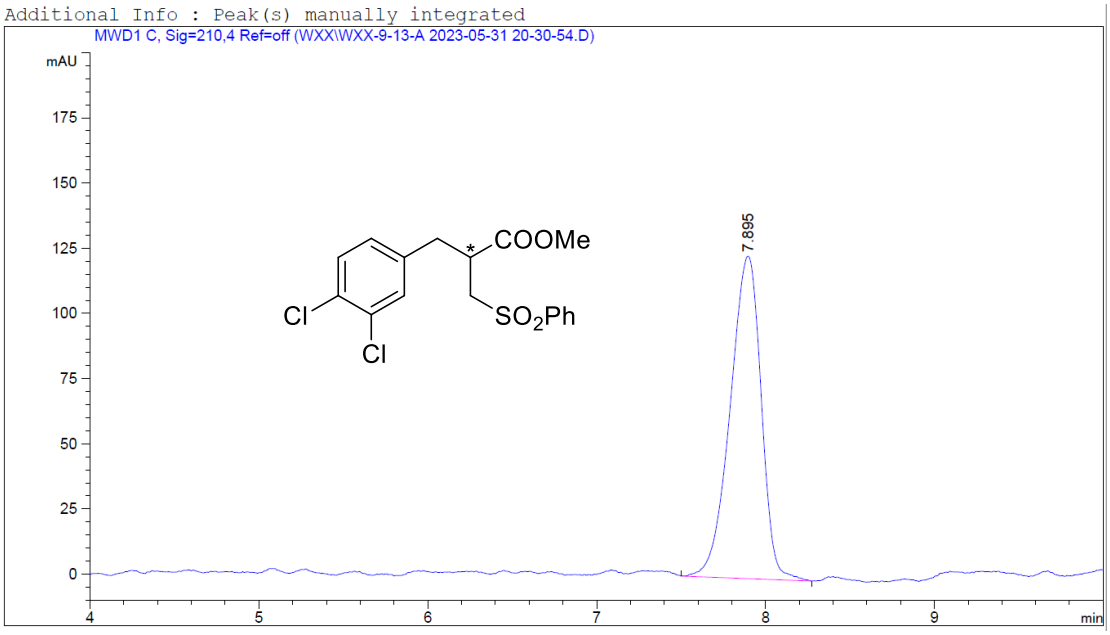
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.675	BV R	0.1218	37.43353	3.73799	1.3985
2	6.261	BB	0.1621	2639.31396	248.17355	98.6015
Totals :				2676.74749	251.91155	

Methyl 2-(3,4-dichlorobenzyl)-3-(phenylsulfonyl)propanoate (**2q**)

Additional Info : Peak(s) manually integrated

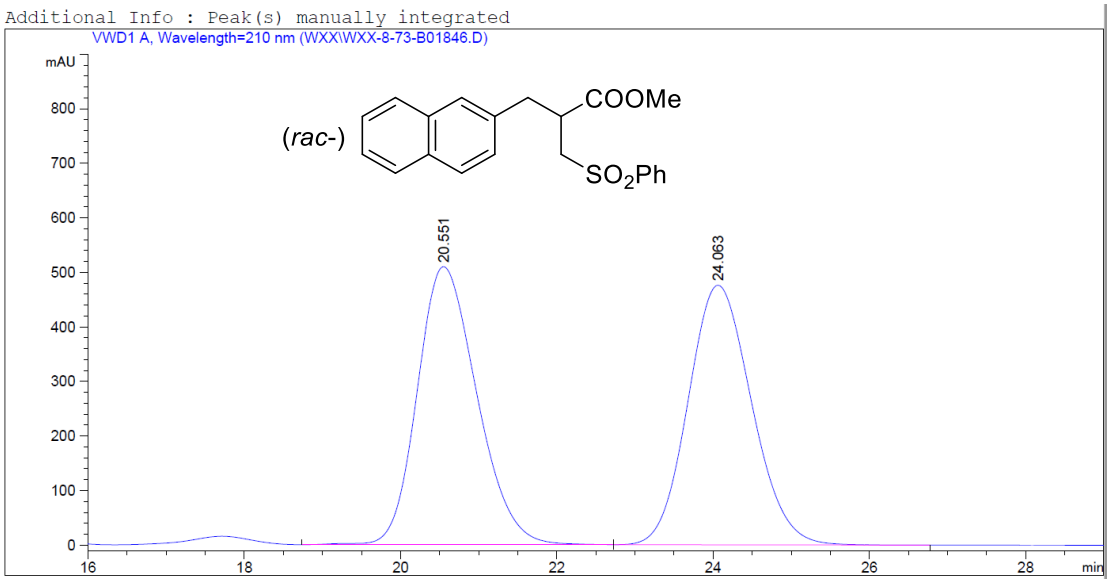


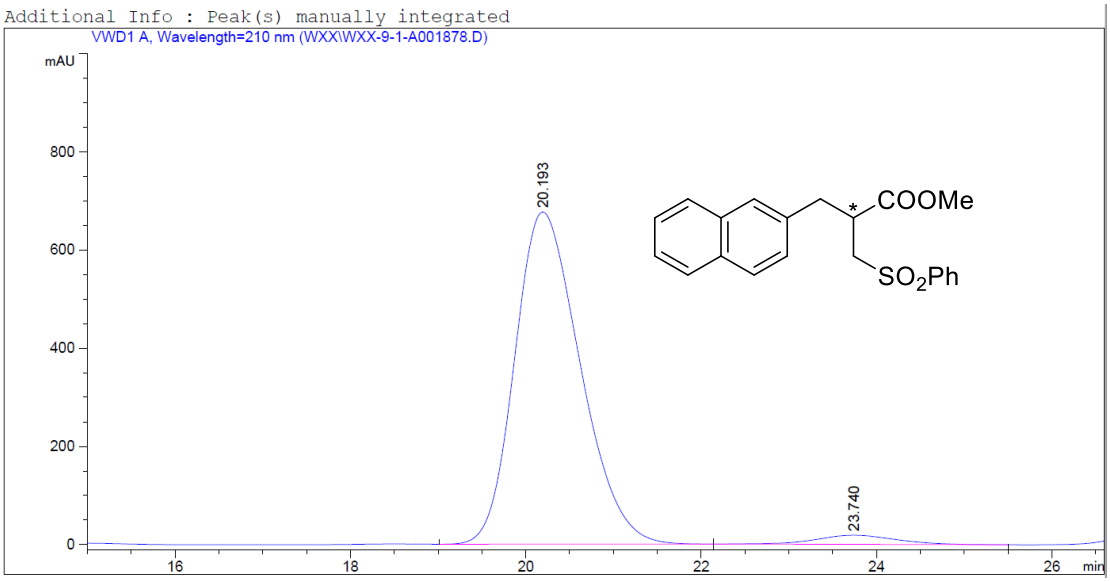
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.895	BB	0.1837	1576.19458	123.68316	100.0000
Totals :				1576.19458	123.68316	

Methyl 3-(naphthalen-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2r**)

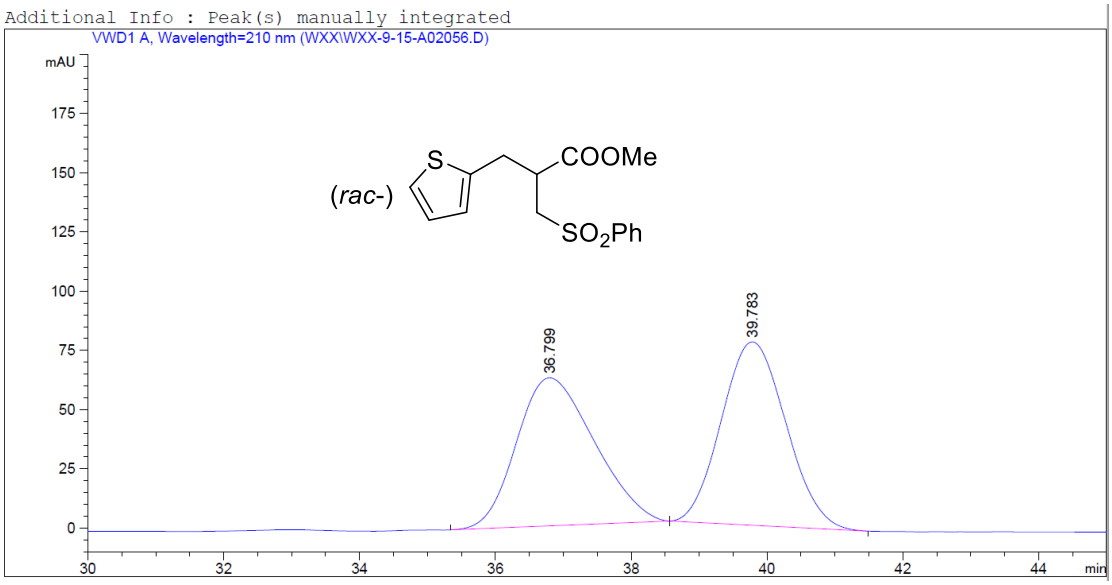




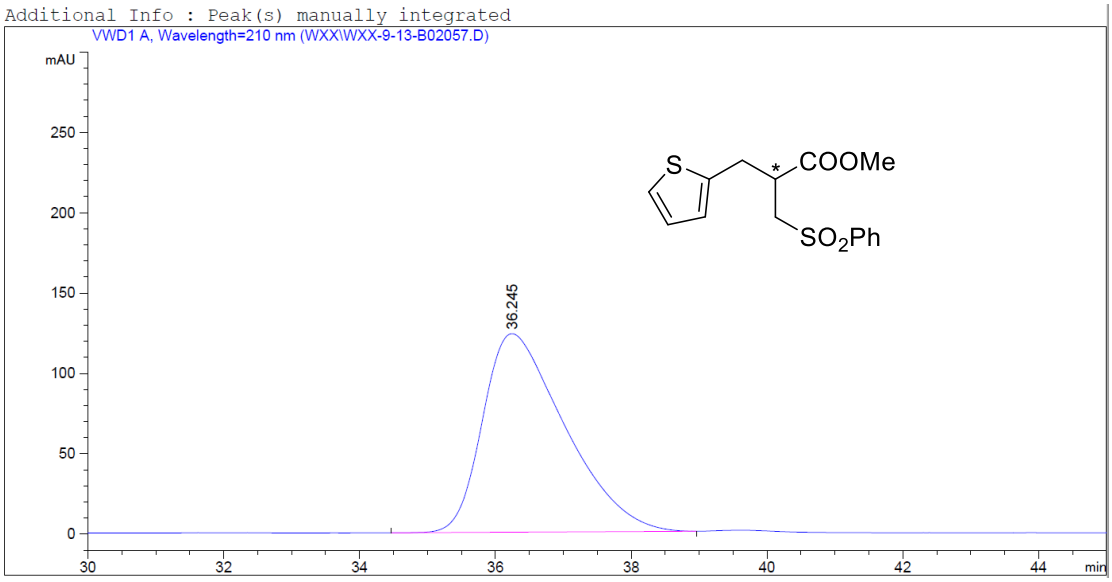
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.193	BB	0.8036	3.50285e4	675.88385	96.7580
2	23.740	BB	0.9520	1173.68811	18.55353	3.2420
Totals :				3.62022e4	694.43738	

Methyl 3-(phenylsulfonyl)-2-(thiophen-2-ylmethyl)propanoate (**2s**)

Additional Info : Peak(s) manually integrated



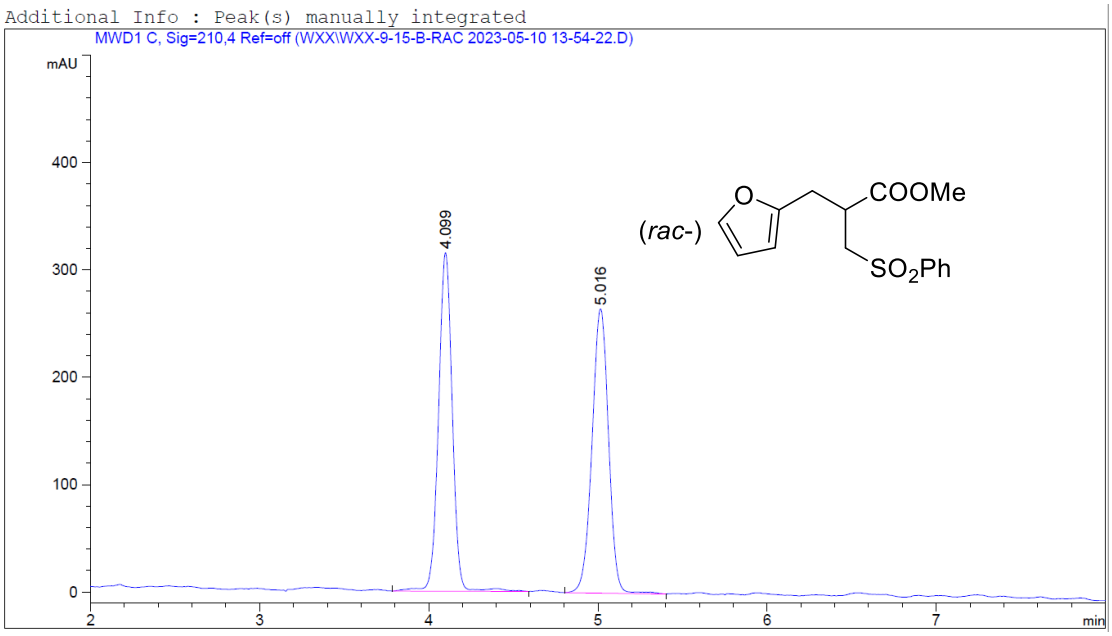
Additional Info : Peak(s) manually integrated



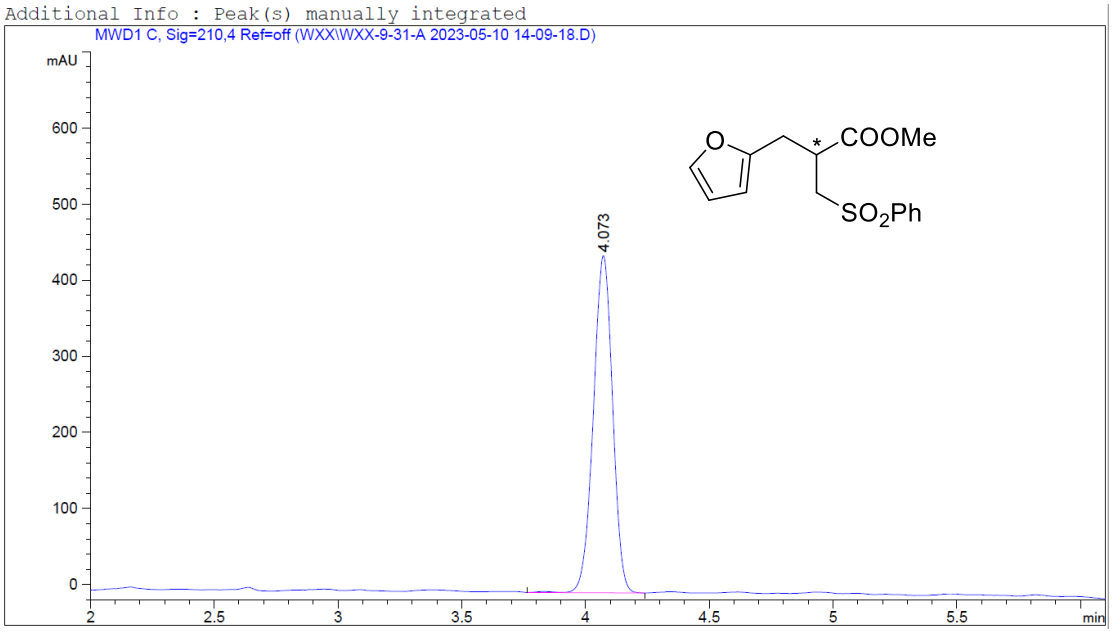
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.245	BB	1.2445	1.03675e4	123.48174	100.0000
Totals :				1.03675e4	123.48174	

Methyl 3-(furan-2-yl)-2-((phenylsulfonyl)methyl)propanoate (**2t**)

Additional Info : Peak(s) manually integrated



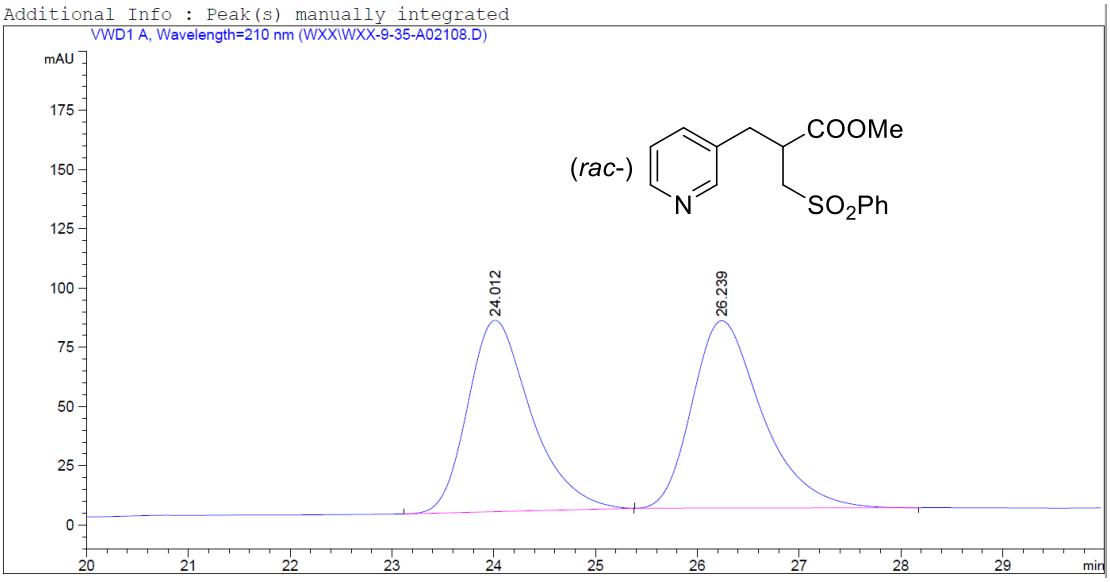
Additional Info : Peak(s) manually integrated



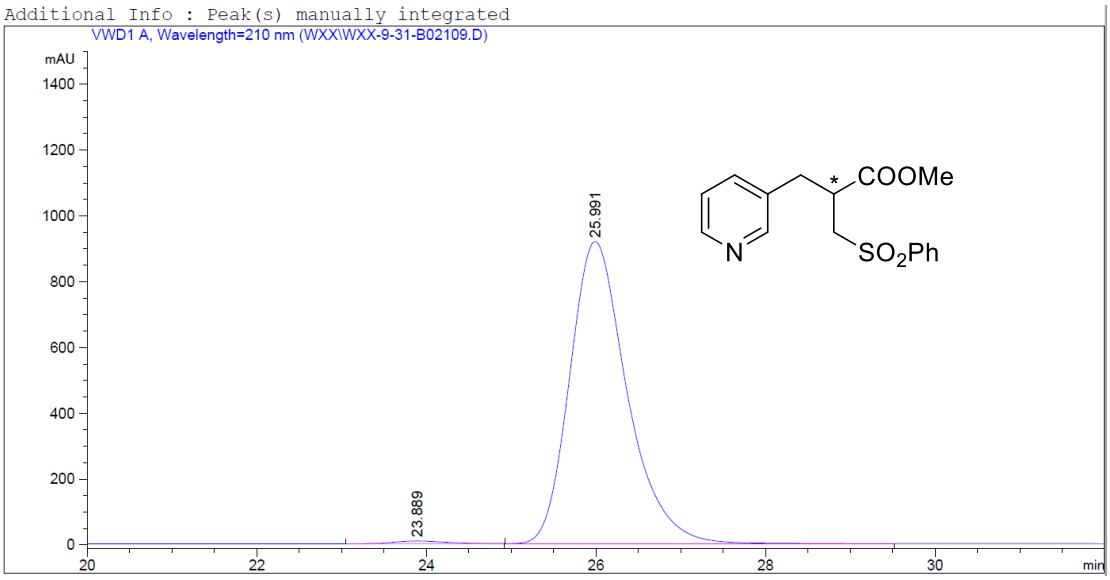
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.073	VB R	0.0833	2399.35059	442.17075	100.0000
Totals :				2399.35059	442.17075	

Methyl 3-(phenylsulfonyl)-2-(pyridin-3-ylmethyl)propanoate (**2u**)

Additional Info : Peak(s) manually integrated



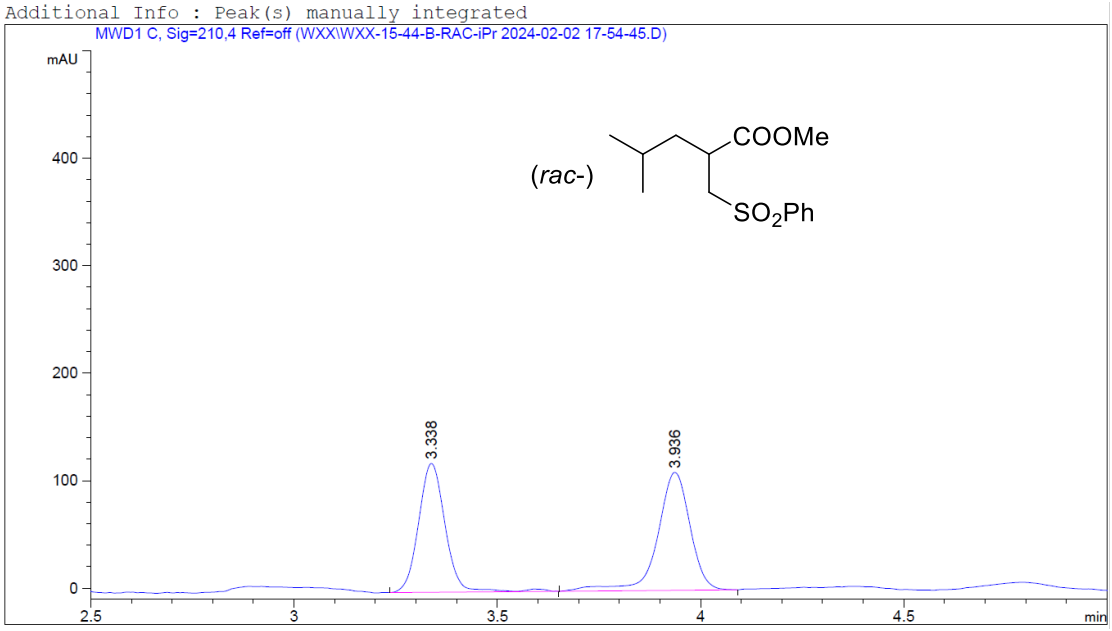
Additional Info : Peak(s) manually integrated



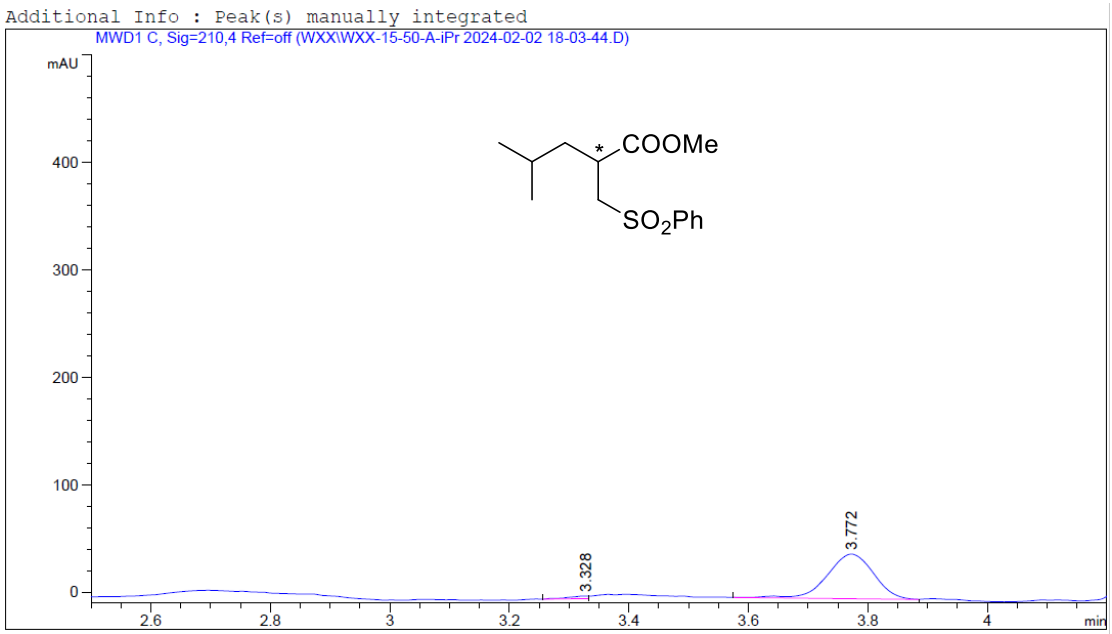
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.889	BB	0.6373	350.81351	8.27950	0.8089
2	25.991	BB	0.7139	4.30162e4	917.66730	99.1911
Totals :				4.33670e4	925.94680	

Methyl 4-methyl-2-((phenylsulfonyl)methyl)pentanoate (**2v**)

Additional Info : Peak(s) manually integrated



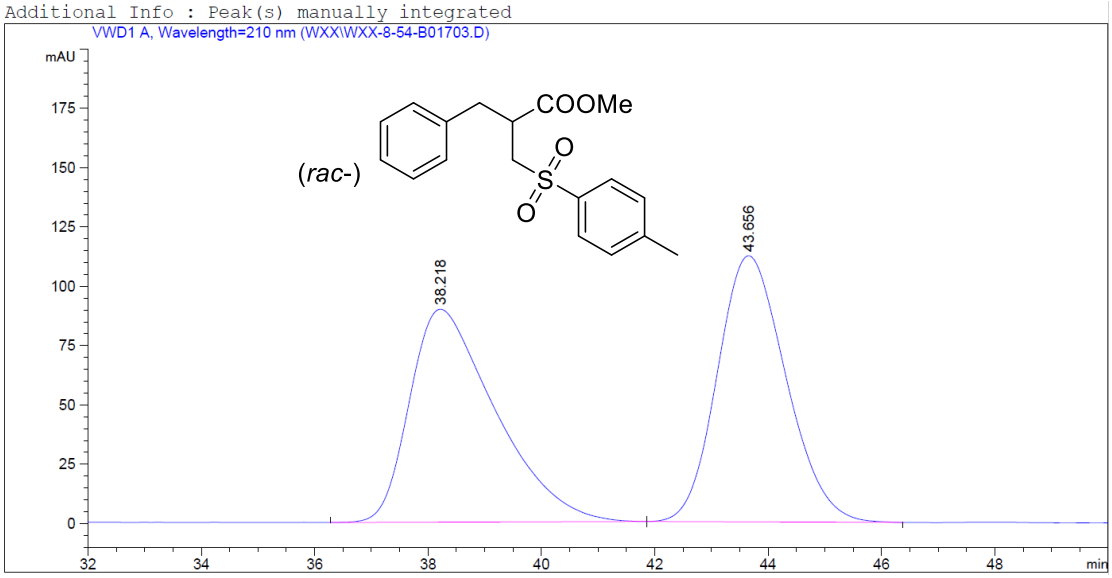
Additional Info : Peak(s) manually integrated



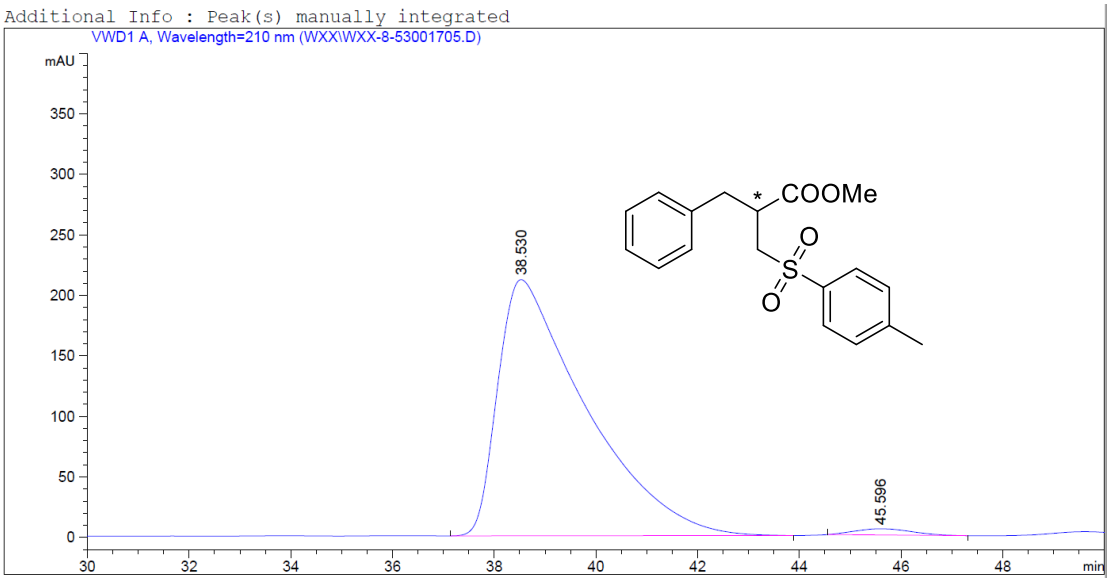
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.328	BV	0.0340	5.82434	2.34460	2.5450
2	3.772	VB R	0.0821	223.02681	41.55473	97.4550
Totals :				228.85115	43.89933	

Methyl 2-benzyl-3-tosylpropanoate (**4a**)

Additional Info : Peak(s) manually integrated



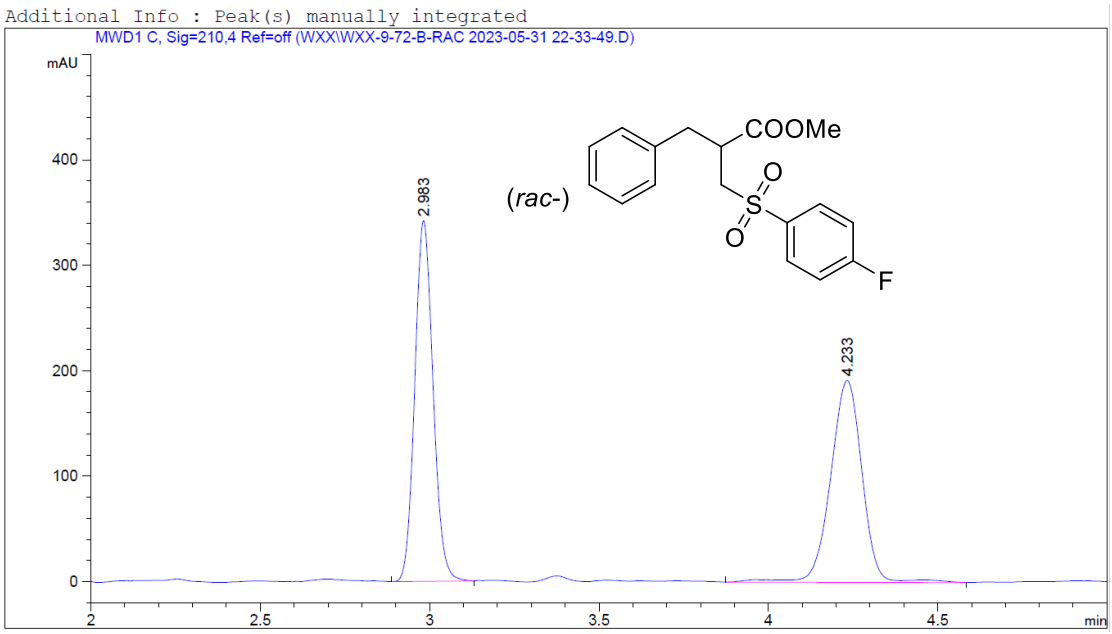
Additional Info : Peak(s) manually integrated



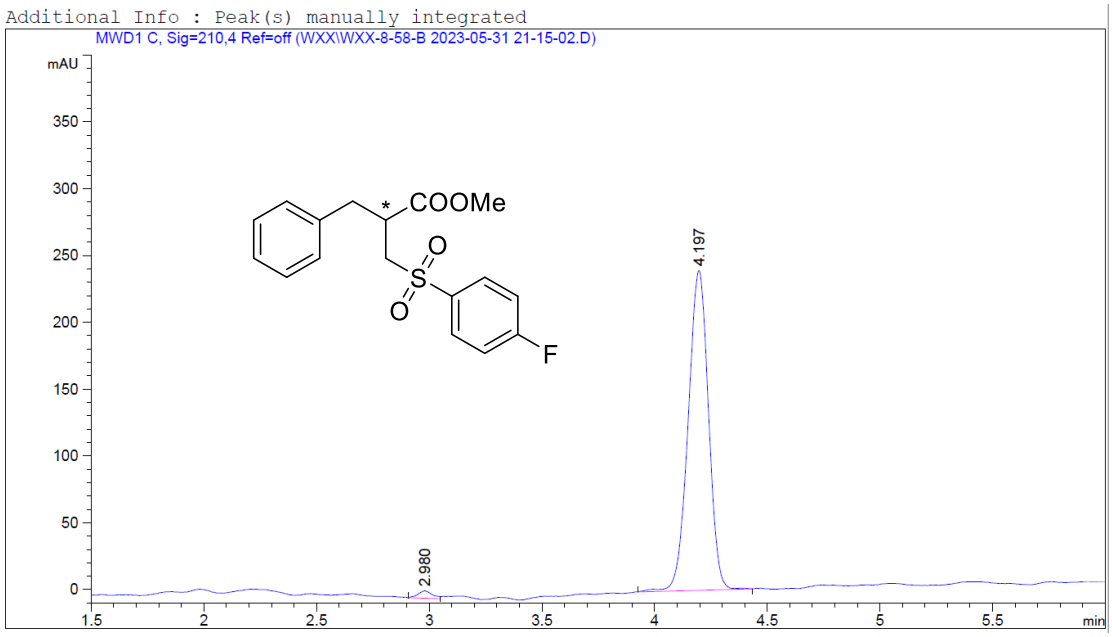
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.530	BB	1.6240	2.53826e4	211.66817	98.4703
2	45.596	BB	1.0187	394.31860	5.12436	1.5297
Totals :				2.57769e4	216.79252	

Methyl 2-benzyl-3-((4-fluorophenyl)sulfonyl)propanoate (**4b**)

Additional Info : Peak(s) manually integrated

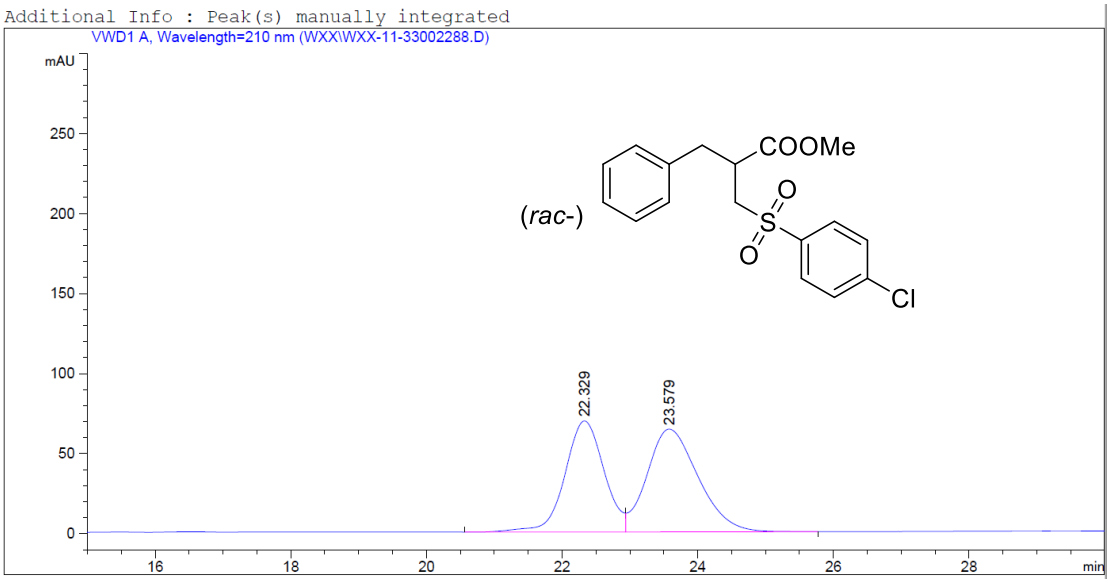


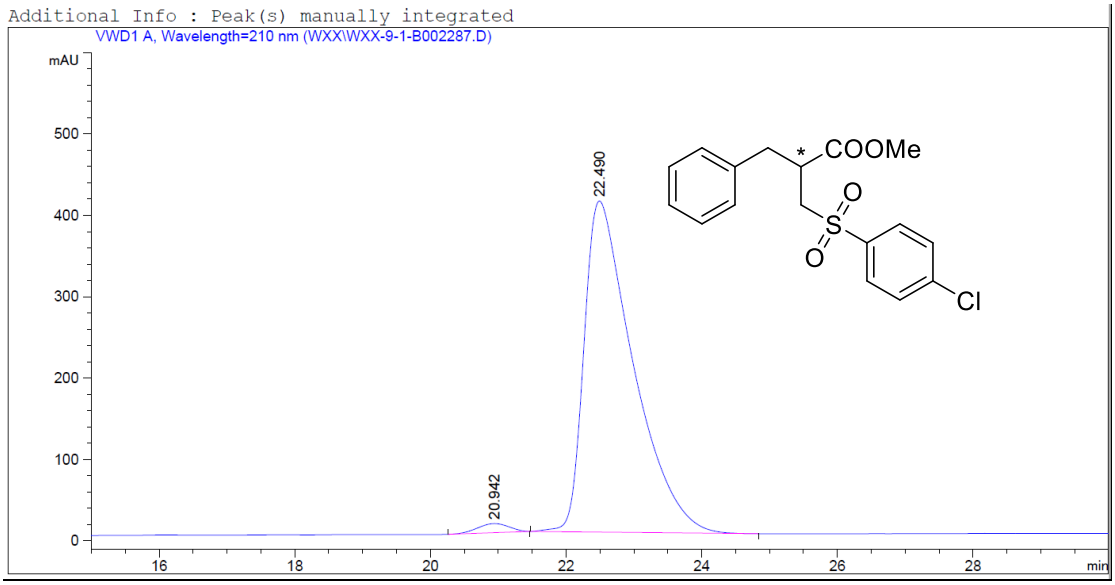
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.980	BV	0.0549	23.75104	5.49862	1.5569
2	4.197	VV R	0.0987	1501.80298	239.24866	98.4431
Totals :				1525.55401	244.74728	

Methyl 2-benzyl-3-((4-chlorophenyl)sulfonyl)propanoate (**4c**)

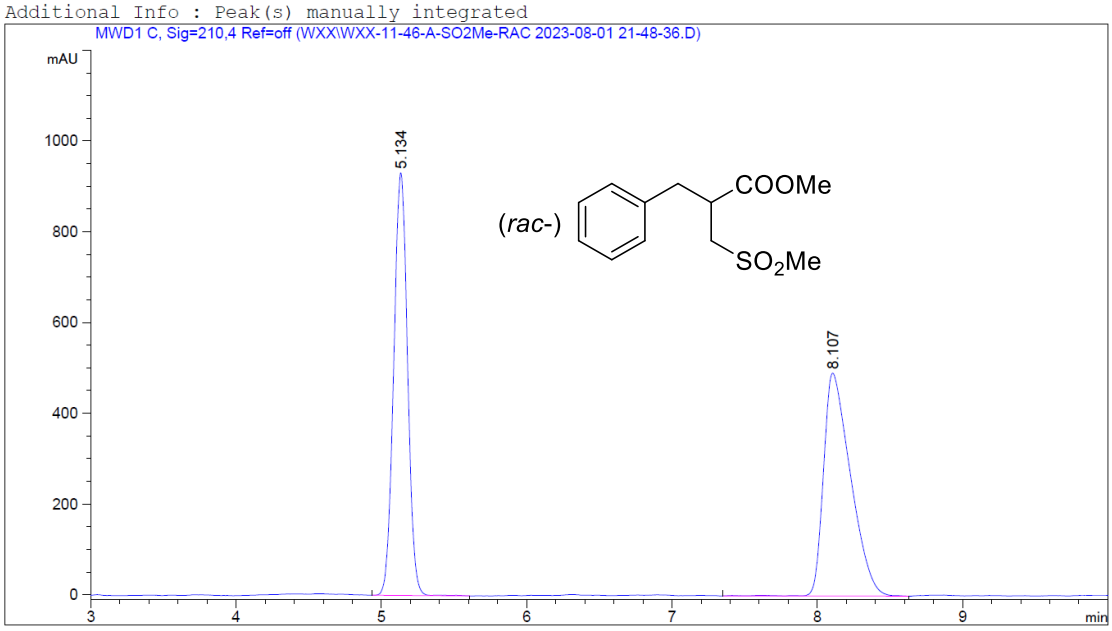




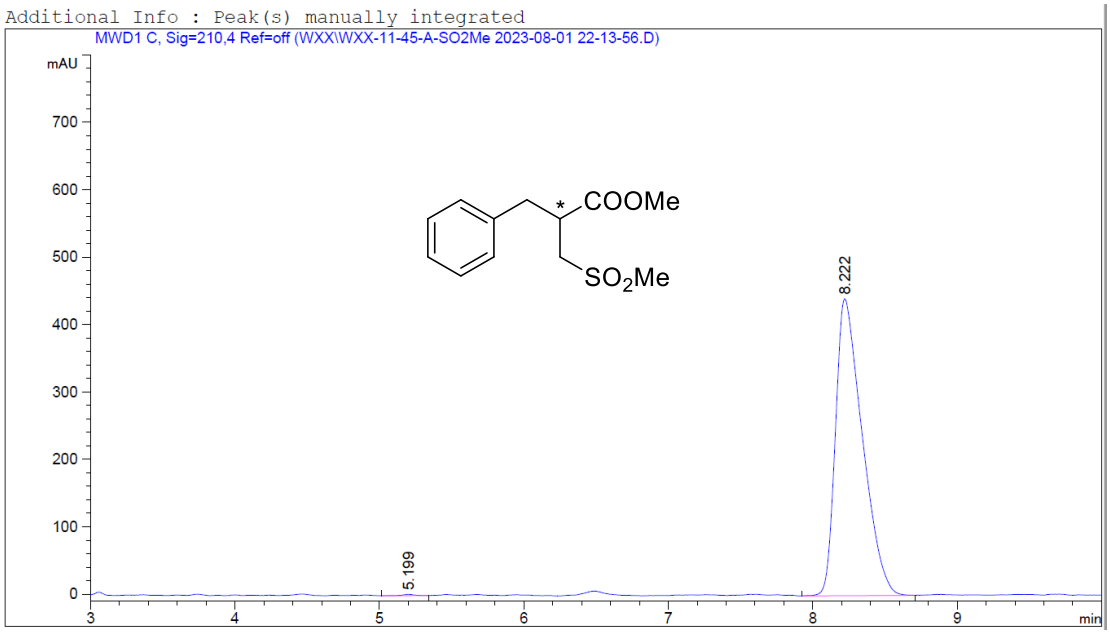
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.942	BB	0.5228	360.84949	11.17367	1.7310
2	22.490	BB	0.7354	2.04857e4	406.85208	98.2690
Totals :				2.08466e4	418.02575	

Methyl 2-benzyl-3-(methylsulfonyl)propanoate (**4d**)

Additional Info : Peak(s) manually integrated



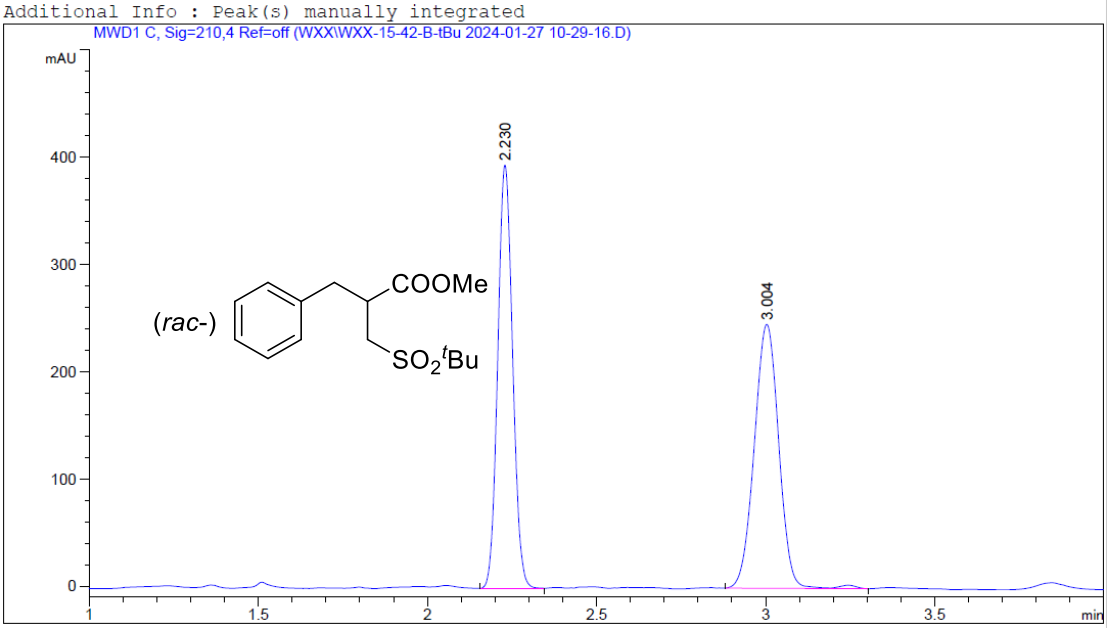
Additional Info : Peak(s) manually integrated



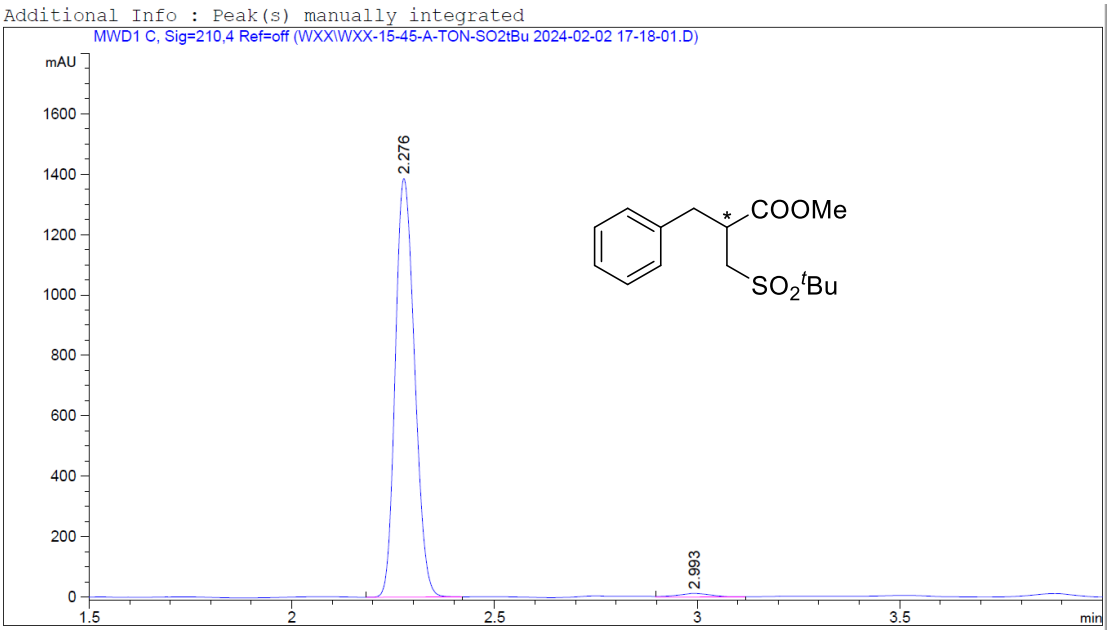
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.199	BB	0.0805	11.56411	1.96838	0.2034
2	8.222	BB	0.1923	5673.06201	440.28922	99.7966
Totals :				5684.62612	442.25760	

Methyl (Z)-2-((*tert*-butylsulfonyl)methyl)-3-phenylacrylate (**4e**)

Additional Info : Peak(s) manually integrated



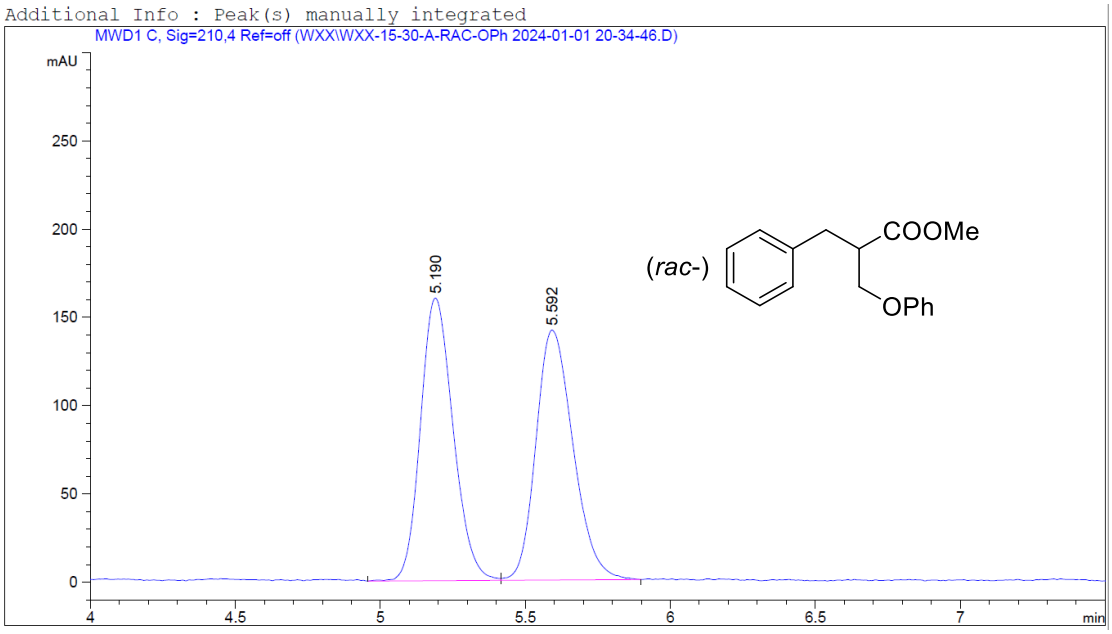
Additional Info : Peak(s) manually integrated



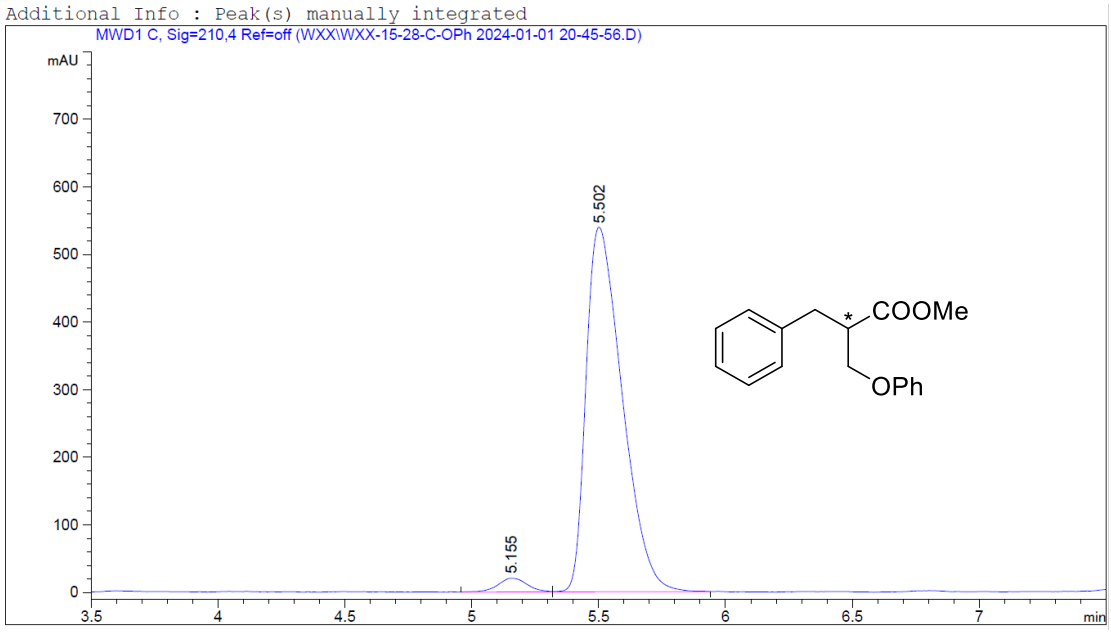
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.276	BB	0.0520	4580.00049	1386.21118	98.5050
2	2.993	VV R	0.0836	69.50828	12.26748	1.4950
Totals :				4649.50877	1398.47866	

Methyl 2-benzyl-3-phenoxypropanoate (**4f**)

Additional Info : Peak(s) manually integrated



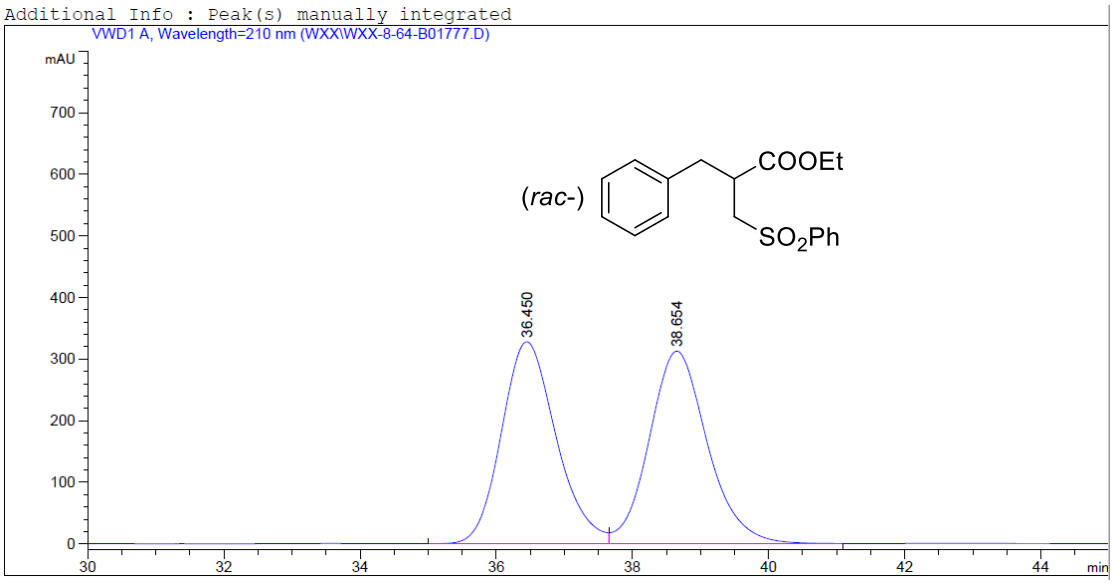
Additional Info : Peak(s) manually integrated



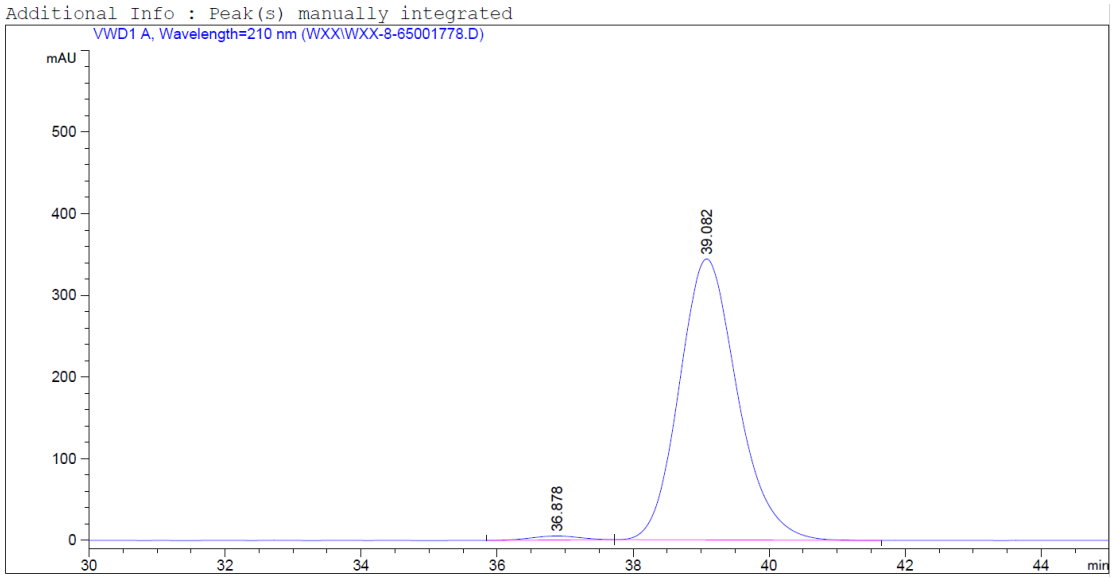
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.155	VV R	0.1034	165.47737	20.56747	3.0048
2	5.502	VV R	0.1550	5341.68945	539.59766	96.9952
Totals :				5507.16682	560.16512	

Ethyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4g**)

Additional Info : Peak(s) manually integrated



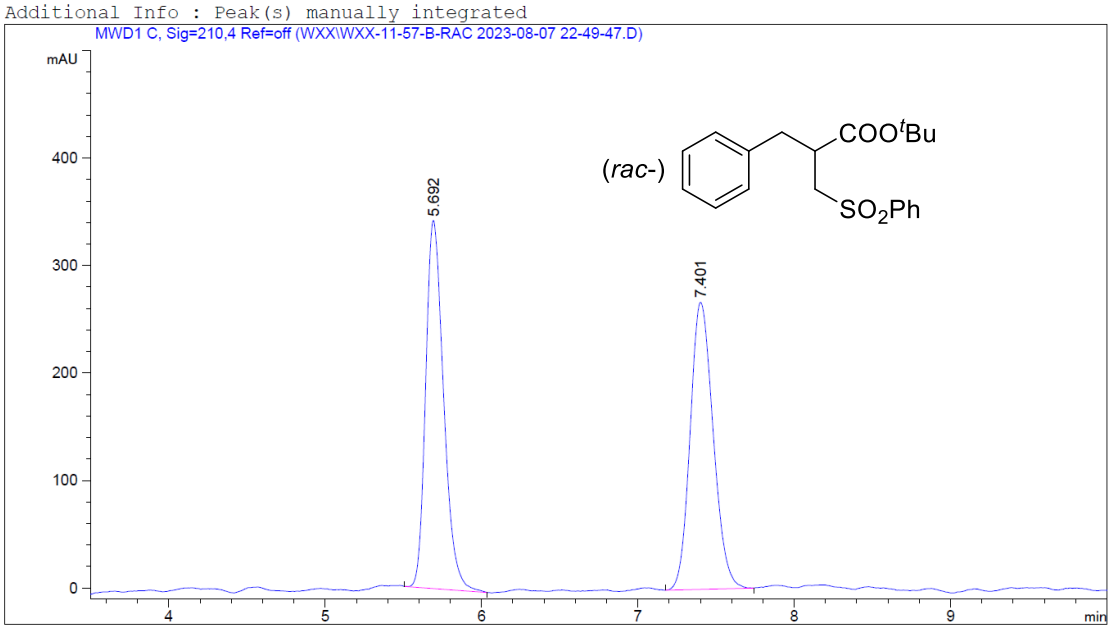
Additional Info : Peak(s) manually integrated



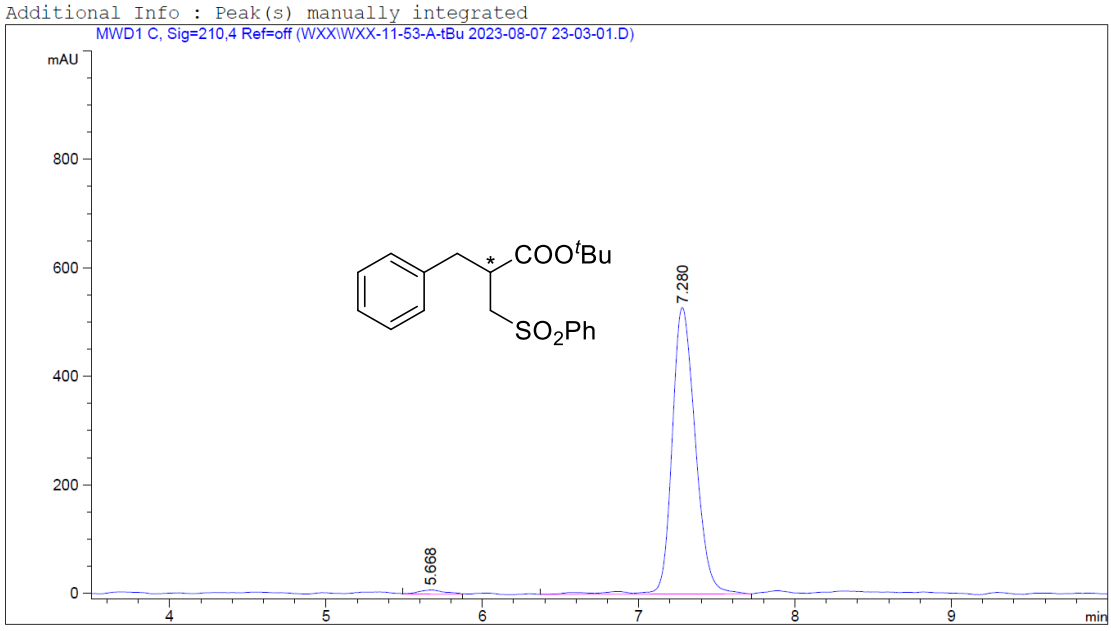
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.878	BB	0.7324	238.74438	4.93493	1.1555
2	39.082	BB	0.9134	2.04222e4	344.09827	98.8445
Totals :				2.06610e4	349.03319	

Tert-butyl 2-benzyl-3-(phenylsulfonyl)propanoate (**4h**)

Additional Info : Peak(s) manually integrated



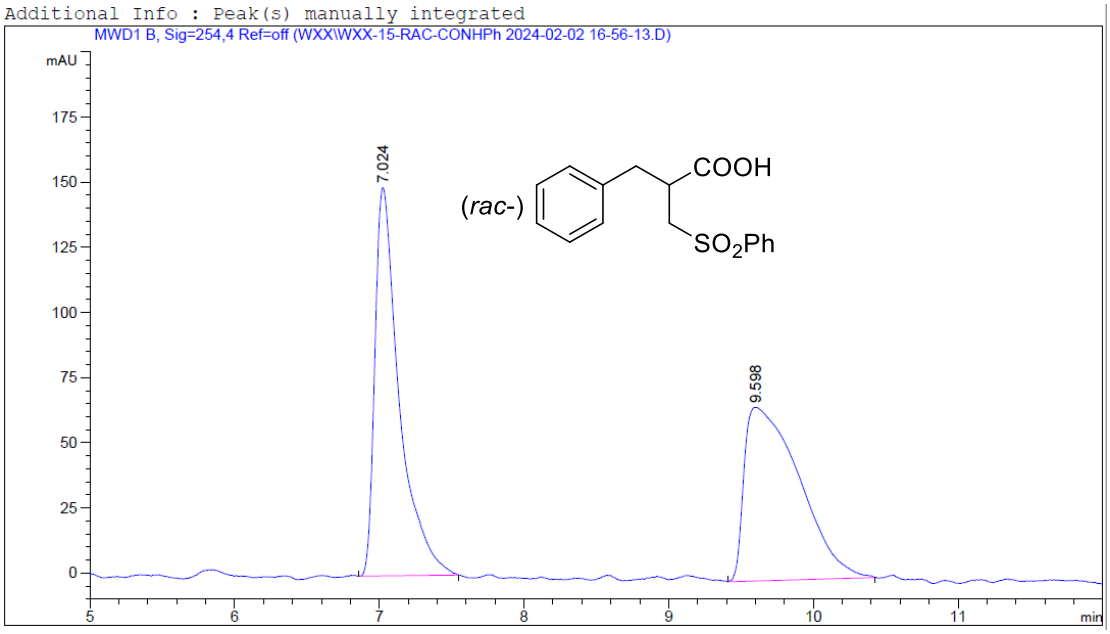
Additional Info : Peak(s) manually integrated



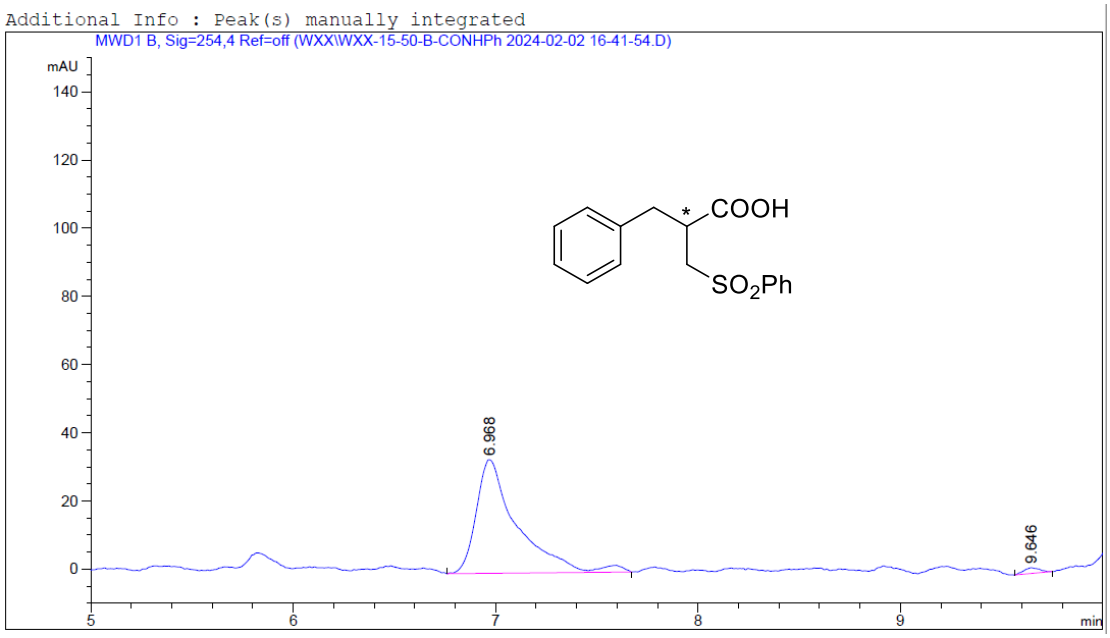
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.668	VV	0.1441	91.61042	7.73825	1.6402
2	7.280	VB R	0.1596	5493.68848	527.87885	98.3598
Totals :				5585.29890	535.61709	

2-Benzyl-3-(phenylsulfonyl)propanoic acid (**4i**)

Additional Info : Peak(s) manually integrated

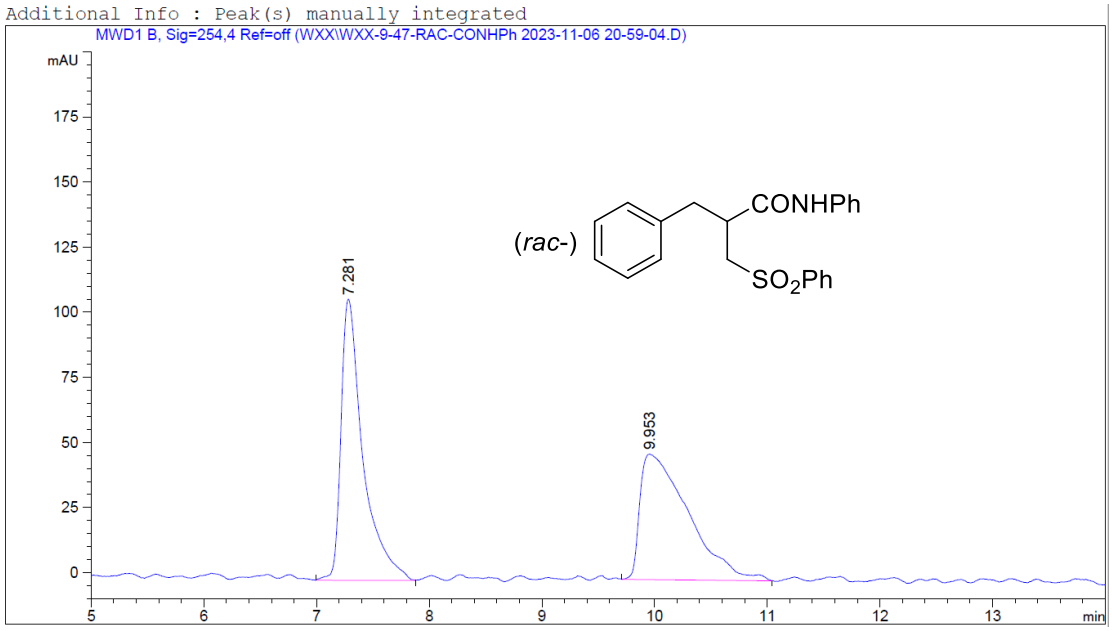


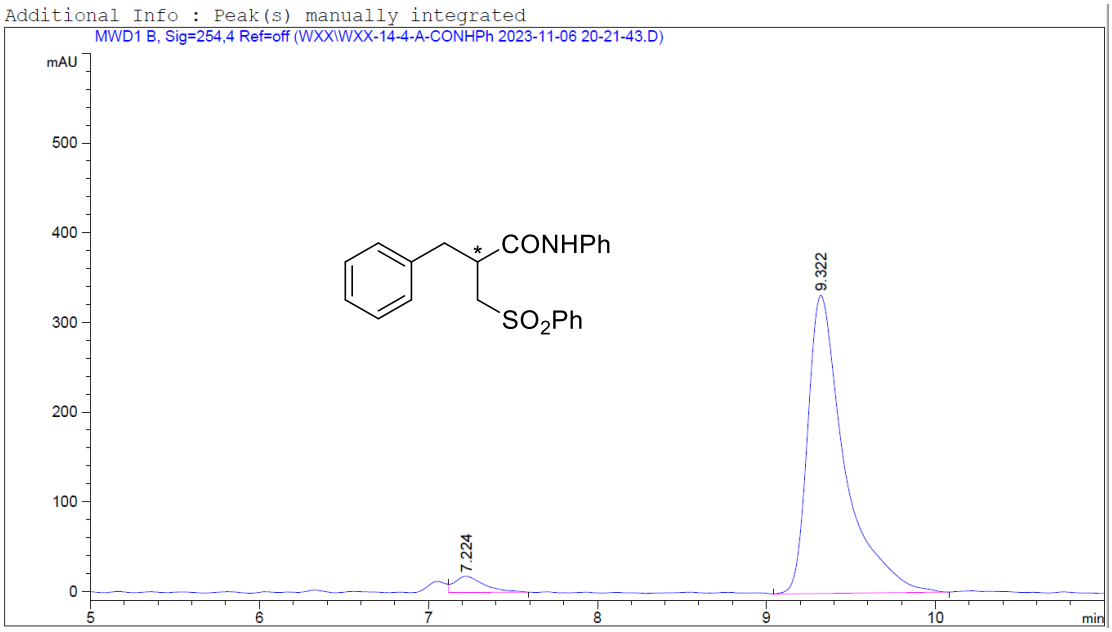
Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.968	VV R	0.1885	469.07953	33.33142	98.0955
2	9.646	BV R	0.0657	9.10690	1.73700	1.9045
Totals :				478.18643	35.06842	

2-Benzyl-*N*-phenyl-3-(phenylsulfonyl)propenamide (**4j**)

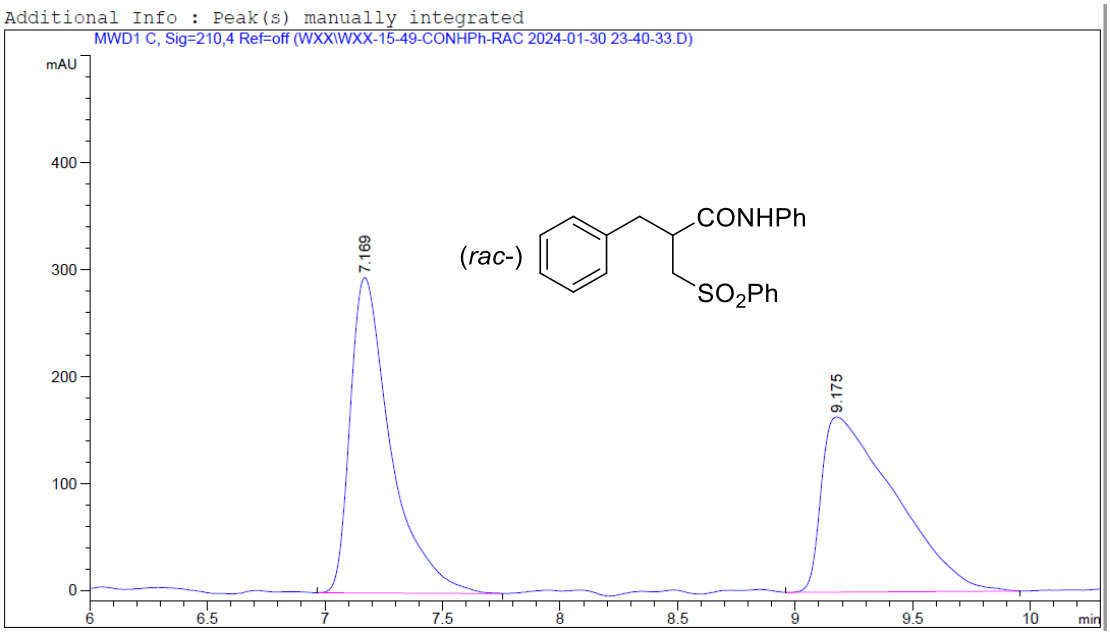




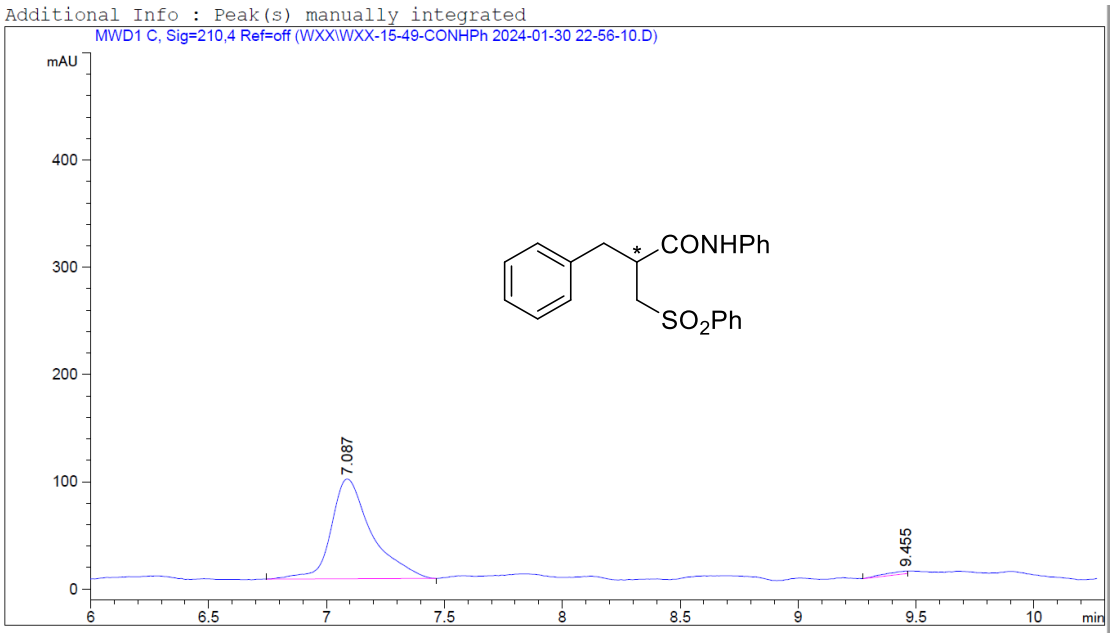
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.224	VV R	0.1574	219.90819	18.07463	4.1970
2	9.322	BV R	0.2192	5019.76514	332.28152	95.8030
Totals :				5239.67332	350.35616	

2-Benzyl-*N*-phenyl-3-(phenylsulfonyl)propenamide (**4j'**)

Additional Info : Peak(s) manually integrated



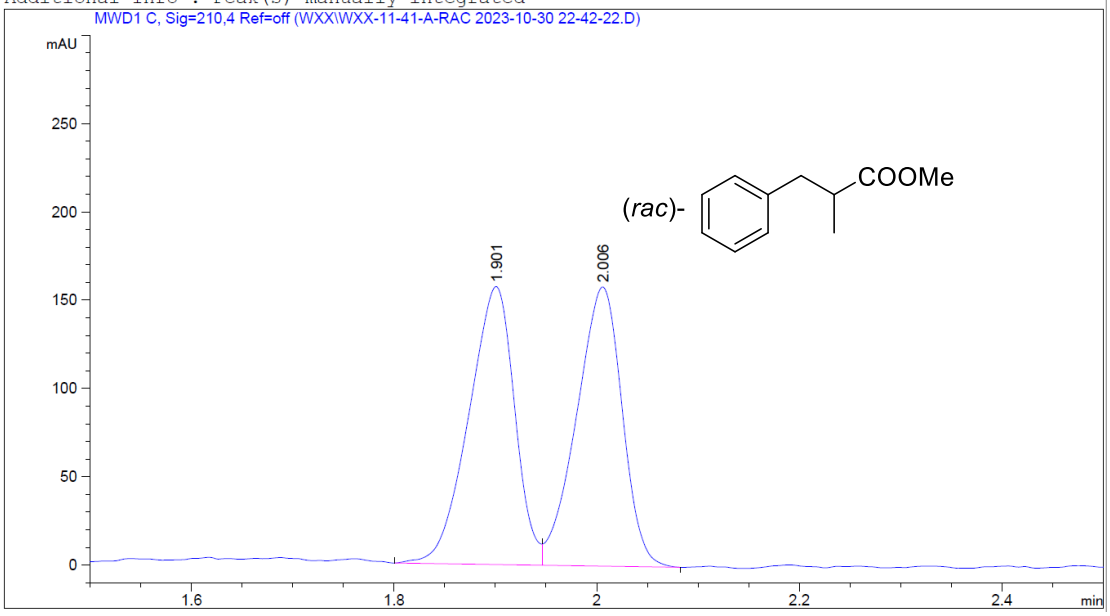
Additional Info : Peak(s) manually integrated



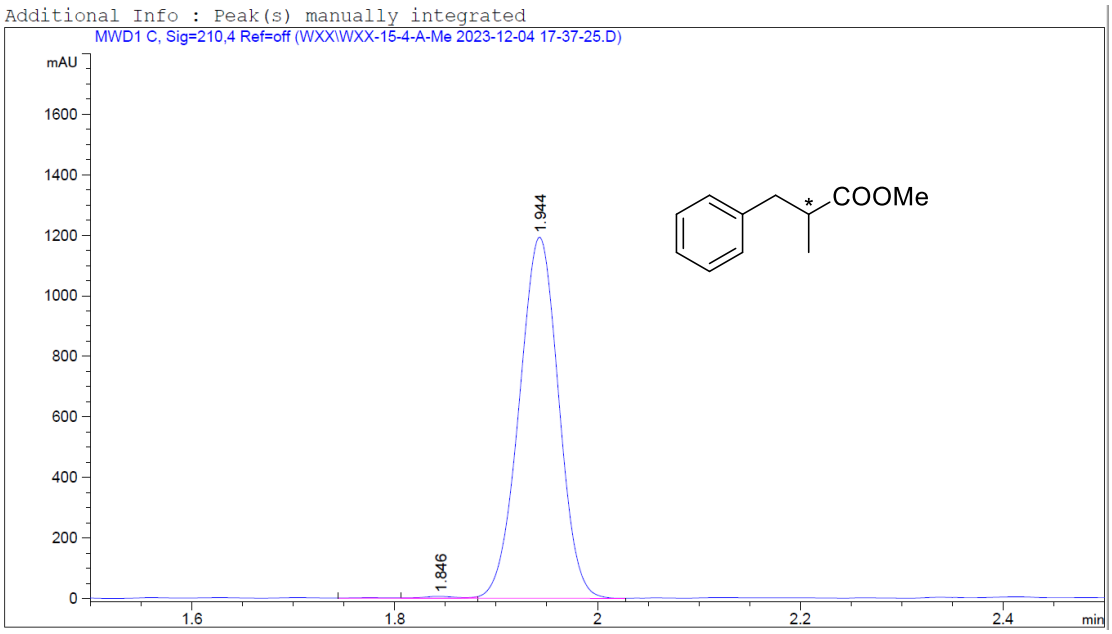
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.087	VB R	0.1707	1109.70435	92.99034	98.3235
2	9.455	BV	0.0912	18.92140	2.51770	1.6765
Totals :				1128.62574	95.50804	

Methyl 2-methyl-3-phenylpropanoate (**4k**)

Additional Info : Peak(s) manually integrated



Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.846	VV E	0.0362	13.87439	6.06008	0.4284
2	1.944	VB R	0.0420	3224.60449	1193.37988	99.5716
Totals :				3238.47889	1199.43996	

8. X-ray crystallographic analysis of compound (*S*)-2i.

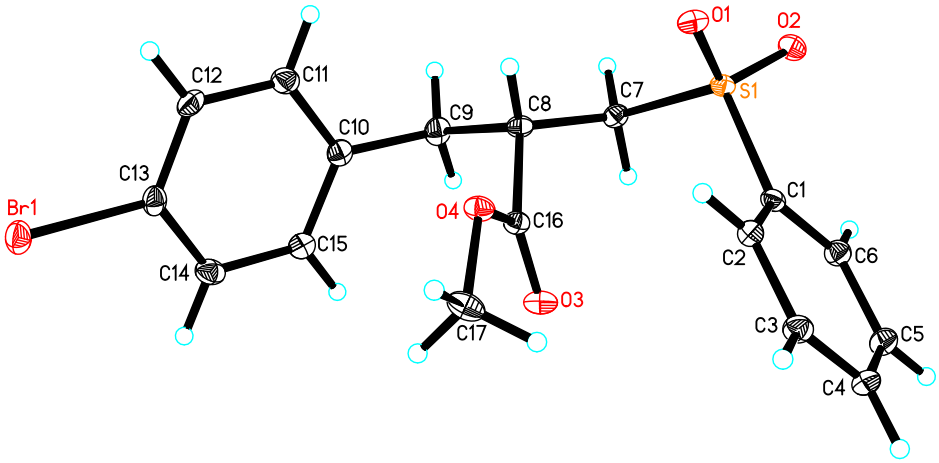


Table S1. Crystal Data and Experimental Parameters for Compound (*S*)-2i

CCDC No.	2344449	Empirical formula	$C_{17}H_{17}BrO_4S$
Formula weight	397.27	Reflections collected	5846
Temperature/K	100.00(10) K	Crystal system	Orthorhombic
Space group	P 21 21 21	*a* [Å]	5.43490(10)
b [Å]	12.9371(2)	*c* [Å]	23.6678(4)
α [deg]	90.00	*β* [deg]	90.00
γ [deg]	90.00	Volume/ [Å^3]	1664.13(5)
Z	4	ρ_{calc} (g/cm^3)	1.586
Absorption coefficient/mm^{-1}	4.693	F(000)	808
crystal size (mm^3)	0.2 × 0.05 × 0.02	Radiation	Cu-K*α* (*λ* = 1.54184)
2Θ range for data collection/°	7.546 to 150.526	Index ranges	-6 ≤ h ≤ 6 -15 ≤ k ≤ 16 -18 ≤ l ≤ 29

Independent reflections	2989 [R_{int} = 0.0369, R_{sigma} = 0.0452]	Data/restraints/parameters	2989/0/209
Goodness-of-fit on F^2	1.058	Final R indexes [I>=2σ (I)]	R_1 = 0.0295 wR_2 = 0.0756
Final R indexes [all data]	R_1 = 0.0318 wR_2 = 0.0772	Largest diff. peak/hole/e Å^{-3}	0.36/-0.47
Absolute structure parameter	-0.035(13)		