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

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1. General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. DCE, CH$_3$CN was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a sealed tube under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

$^1$H-NMR and $^{13}$C-NMR spectra were recorded in CDCl$_3$ on a Bruker Avance 500 spectrometer (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature. Chemical shifts were reported in ppm on the scale relative to CDCl$_3$ ($\delta = 7.26$ for $^1$H-NMR, $\delta = 77.00$ for $^{13}$C-NMR) as an internal reference. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument. Coupling constants ($J$) were reported in Hertz (Hz).
2、Optimization of experimental conditions

Table S1. Screening of Catalyst and its dosages

<table>
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<tr>
<th>entry</th>
<th>1a:2a</th>
<th>Catalyst [xmol%]</th>
<th>Cocatalyst [10mol%]</th>
<th>T [°C]/t [h]</th>
<th>Yield a/%</th>
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Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL), N2. a Isolated yields.

Table S2. Screening of Time and Temperature.

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<th>Catalyst [x mol%]</th>
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<th>Yield a/%</th>
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Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL), N2. a Isolated yields.
Table S3. Screening of and Cocatalyst

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Reaction conditions: 2a (0.2 mmol), in DCE (2.0 mL), N$_2$. * Isolated yields.

3. Preparation of starting materials.

3.1 Typical procedure for the preparation of α-diazo arylacetates$^1$

![Diazo group formation](image)

At room temperature, a solution of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) (2.28 g, 15mmol, 1.5 equiv) in anhydrous CH$_3$CN (10 mL) was added dropwise to a solution of ethylphenyl acetate (1.64 g, 10 mmol, 1.0 equiv) and $p$-toluenesulfonyl azide (TsN$_3$) (2.37 g, 12mmol, 1.2 equiv) in anhydrous CH$_3$CN (50 mL). Then the reaction mixture was stirred at room temperature for 15 hours. After water (40 mL) was added, the resulting mixture was extracted with diethyl ether (3 x 40 mL). The combined organic layer was washed with brine (40 mL) and dried over anhydrous MgSO$_4$. After the removal of the solvent under reduced pressure, the residual was purified by a silica gel column chromatography with petroleum ether (PE)/ethyl acetate (EA) (30:1) as the eluent.

3.2 Typical procedure for the preparation of S-alkyl benzenesulfonothioate.$^2$

![Thioether formation](image)
A mixture of PhSO$_2$Na (6.56 g, 40 mmol) and S (1.28 g, 40 mmol) in n-BuNH$_2$ (40 mL) was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the residue was washed by Et$_2$O to obtain a white solid PhSO$_2$SNa. Then PhSO$_2$SNa was dissolved in EtOH (40 mL), then R-X (11.36 g, 80 mmol) was added to the solution. The reaction mixture was stirred at 40-45°C for 24 h. After removal of the solvent under reduced pressure, the reaction mixture was poured on a solution of Na$_2$S$_2$O$_3$ and CH$_2$Cl$_2$ (30 mL). The precipitate was filtered and dried by anhydrous Na$_2$SO$_4$, the residue was purified through column chromatography (petroleum ether: EtOAc = 20:1) afforded the desired product S-alkyl benzenesulfonothioate as a yellow oil.

3.3 Typical procedure for the preparation of S-Ar benzenesulfonothioate

\[
\text{ArSO}_2\text{Na} + \text{ArSSAr} \xrightarrow{\text{rt, NBS}} \text{CH}_3\text{CN} \xrightarrow{\text{ArSO}_2\text{SR}}
\]

A mixture of sulfinate 1 (8 mmol), disulfide 2 (2 mmol) and NBS (4 mmol) in CH$_3$CN (30 mL) was stirred at room temperature for respective time. After the completion of the reaction, as monitored by TLC and GC-MS analysis, the reaction mixture was washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel (300—400 mesh) with petroleum ether-EtOAc as eluent to provide the desired S-Ar benzenesulfonothioate.

4. General procedure for preparation of compound 3

To a mixture of Rh$_2$(OAc)$_4$ (1 mol%), dppp (0.1 equiv) and 2a (0.2 mmol) in DCE (2 mL) under N$_2$ atmosphere, 1a (0.3 mmol, 1.5 equiv) were added. The system was stirred at 25 °C for 3 h. The reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 5:1) to give the products.

5. General procedure for preparation of compound 4 and 5

To a mixture of Sulfinates 3t (0.5 mmol) in MeOH (3 mL) under N$_2$ atmosphere, m-CPBA (2 equiv) were added. The system was stirred at rt for 3 h. The reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 10:1) to give the products.
Procedure of 4: To a mixture 3t (0.5 mmol) in MeOH (3 mL) under air, m-CPBA (2 equiv) was added slowly. The system was stirred at room temperature for 3 h. The reaction mixture was evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 2:1) to give 4.

Procedure of 5: To a mixture 3t (0.5 mmol) in THF (3 mL) under air, LiAlH₄ (5 equiv) was added slowly. The system was stirred at room temperature for 30 min. The reaction mixture was evaporated under reduced pressure and purified by column chromatography (petroleum ether: EtOAc = 5:1) to give 5.
5. Characterization data for products

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (56 mg, 84%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.48 (m, 1H), 7.47 – 7.43 (m, 2H), 7.34 (dd, $J$ = 9.6, 4.3 Hz, 1H), 7.29 (t, $J$ = 7.9 Hz, 2H), 7.26 – 7.19 (m, 1H), 3.90 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.5, 135.6, 133.7, 131.6, 131.4, 129.7, 129.4, 128.0, 127.7, 83.4, 53.5, 15.6. HRMS (DART Positive) calcd for C$_{16}$H$_{16}$O$_4$S$_2$(M+NH$_4^+$): 354.0828; Found: 354.0826.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (61 mg, 82%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.49 (m, 3H), 7.37 – 7.32 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 3.89 (s, 3H), 2.39 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.2, 136.0, 135.4, 134.0, 131.4, 130.9, 130.1, 128.2, 127.9, 82.6, 53.7, 15.6. HRMS (DART Positive) calcd for C$_{16}$H$_{15}$O$_4$ClS$_2$(M+NH$_4^+$): 388.0439; Found: 388.0435.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (71 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (t, $J$ = 7.4 Hz, 1H), 7.42 (d, $J$ = 7.5 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.11 (d, $J$ = 8.6 Hz, 2H), 3.90 (s, 3H), 2.43 (s, 3H), 1.29 (t, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.6, 153.1, 135.8, 133.6, 131.3, 129.1, 128.3, 127.6, 125.0, 83.3, 53.5, 34.7, 31.2, 15.6. HRMS (DART Positive) calcd for C$_{20}$H$_{24}$O$_4$S$_2$(M+NH$_4^+$): 410.1454; Found: 410.1451.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (70 mg, 85%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.51 – 7.46 (m, 1H), 7.41 (dd, $J$ = 8.4, 1.1 Hz, 2H), 7.39 – 7.29 (m, 6H), 7.24 (d, 2H), 7.21 – 7.14 (m, 4H), 5.33 (dd, $J$ = 49.0, 12.0 Hz, 2H), (s, 2.30, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8, 135.6, 134.6, 133.7, 131.3, 131.4, 129.6, 129.5, 128.9, 128.8, 128.6, 127.9, 127.7, 83.1, 68.4, 15.4. HRMS (ESI) calcd for C$_{22}$H$_{20}$O$_4$S$_2$(M+Na)$^+$: 435.0695; Found: 435.0695
ethyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3e

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (66 mg, 94%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53 – 7.47 (m, 1H), 7.44 (dd, $J$ = 8.3, 1.1 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.25 – 7.19 (m, 4H), 4.45 – 4.31 (m, 2H), 2.46 (s, 3H), 1.32 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 135.7, 133.7, 131.7, 131.4, 129.6, 129.4, 128.0, 127.7, 83.3, 63.0, 15.6, 14.1. HRMS (EI) calcd for C$_{17}$H$_{18}$O$_4$S$_2$: 350.0647; Found: 350.0645.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (66 mg, 77%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 (dd, $J$ = 17.8, 7.5 Hz, 3H), 7.40 – 7.31 (m, 4H), 7.13 (t, $J$ = 5.7 Hz, 2H), 4.42 – 4.31 (m, 2H), 2.41 (s, 3H), 1.32 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8, 135.8, 134.2, 131.7, 131.4, 131.0, 128.1, 124.4, 82.9, 63.5, 15.8, 14.4. HRMS (DART Positive) calcd for C$_{17}$H$_{17}$O$_4$BrS$_2$(M+NH$_4$)$^+$: 446.0090; Found: 446.0085.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (80 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.56 (tt, $J$ = 7.6, 1.2 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.34 (dd, $J$ = 8.4, 7.5 Hz, 2H), 7.27 (t, $J$ = 1.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.14 (t, $J$ = 7.9 Hz, 1H), 4.39 (t, $J$ = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 – 1.30 (t, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.4, 150.0, 148.0, 135.9, 133.5, 131.3, 127.6, 123.6, 132.5, 132.5, 131.4, 129.3, 128.3, 127.8, 121.8, 82.5, 63.2, 15.5, 14.1. HRMS (DART Positive) calcd for C$_{17}$H$_{17}$O$_4$BrS$_2$(M+NH$_4$)$^+$: 446.0090; Found: 446.0086.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (78 mg, 95%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 – 7.45 (m, 3H), 7.30 (dd, $J$ = 8.4, 7.4 Hz, 2H), 6.77 (dd, $J$ = 8.5, 2.3 Hz, 1H), 6.73 – 6.67 (m, 2H), 4.44 – 4.31 (m, 2H), 3.86 (s, 3H), 3.66 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.9, 150.0, 148.0, 135.9, 133.5, 131.3, 127.6, 123.6, 122.5, 112.3, 110.1, 83.0, 62.9, 55.9, 55.8, 15.6, 14.1.
ethyl 2-(methylthio)-2-(4-nitrophenyl)-2-(phenylsulfonyl)acetate 3i

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (35 mg, 44%).$^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 – 8.07 (m, 2H), 7.62 – 7.55 (m, 3H), 7.53 – 7.47 (m, 2H), 7.36 (dd, J = 8.4, 7.4 Hz, 2H), 4.42 – 4.35 (m, 2H), 2.38 (s, 3H), 1.32 (t, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.1, 148.1, 138.5, 135.2, 134.3, 131.4, 130.9, 128.1, 122.8, 824, 63.5, 15.5, 14.0.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (67 mg, 88%).$^1$H NMR (500 MHz, CDCl$_3$) δ 7.56 (m, J = 7.6, 1.2 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.34 (dd, J = 8.4, 7.5 Hz, 1H), 7.27 (t, J = 1.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.14 (t, J = 7.9 Hz, 1H), 4.39 (t, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.36 – 1.30 (t, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8, 158.9, 135.7, 133.6, 132.9, 131.4, 128.8, 127.6, 121.8, 115.6, 114.8, 83.3, 63.0, 55.3, 15.6, 14.1.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (53 mg, 72%).$^1$H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.48 (m, 3H), 7.32 (dd, J = 8.3, 7.5 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.09 – 7.01 (m, 2H), 6.98 (dt, J = 10.2, 2.2 Hz, 1H), 4.45 – 4.30 (m, 2H), 2.43 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).$^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.2, 161.6 (d, J = 247.1 Hz), 135.2, 133.6, 131.0 129.09 (d, J = 8.1 Hz), 127.51 (s), 125.07 (d, J = 3.1 Hz), 116.60 (d, J = 24.3 Hz), 116.3(d, J = 20.9 Hz), 82.4 630 29.4, 15.2, 13.8. RMS (DART Positive) calcd for C$_{17}$H$_{17}$O$_4$FS$_2$ (M+NH$_4$)$^+$: 386.0891; Found: 386.0886.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (50 mg, 64%).$^1$H NMR (500 MHz, CDCl$_3$) δ 7.51 (td, J = 7.5, 1.0 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.28 (t, J = 11.8, 4.0 Hz, 2H), 7.25 – 7.18 (m, 4H), 3.89 (s, 3H), 2.44 (s, 3H).$^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.4, 135.5, 133.7, 131.5, 131.3, 129.6, 129.4, 128.0, 127.6, 83.3, 53.5, 15.6. HRMS (DART Positive) calcd for C$_{18}$H$_{16}$O$_4$S$_3$ (M+NH$_4$)$^+$: 410.0549; Found: 410.0547.
ethyl 2-(ethylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3m

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (56 mg, 77%). $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.50 (tt, $J = 7.6, 1.2$ Hz, 1H), 7.44 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.35 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.22 (d, $J = 4.3$ Hz, 4H), 4.36 (q, 2H), 3.25 – 3.13 (m, 1H), 2.81 – 2.70 (m, 1H), 1.30 (q, $J = 14.2, 7.3$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.2, 135.7, 133.5, 131.8, 131.4, 129.5, 129.4, 127.8, 127.6, 83.6, 62.9, 26.6, 14.0, 13.3. HRMS (DART Positive) calcd for C$_{18}$H$_{20}$O$_4$S$_2$(M+NH$_4$)$^+$: 382.1141; Found: 382.1141.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (38 mg, 50%). $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.50 (tt, $J = 7.6, 1.2$ Hz, 1H), 7.44 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 2H), 7.23 (d, $J = 4.3$ Hz, 4H), 5.98 – 5.80 (m, 1H), 5.31 (dt, $J = 17.0, 2.7, 1.3$ Hz, 1H), 5.23 – 5.16 (m, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.89 – 3.77 (m, 1H), 3.56 – 3.47 (m, 1H), 1.32 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 166.1, 135.7, 133.6, 131.7, 131.7, 131.4, 129.5, 129.4, 127.9, 127.6, 119.6, 83.2, 63.0, 35.6, 14.0. HRMS (DART Positive) calcd for C$_{19}$H$_{20}$O$_4$S$_2$(M+NH$_4$)$^+$: 394.1141; Found: 394.1139.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (53 mg, 62%). $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.77 (dt, $J = 8.4, 1.8$ Hz, 2H), 7.41 – 7.36 (m, 3H), 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 3H), 7.09 (dd, $J = 8.5, 0.5$ Hz, 2H), 3.94 – 3.85 (m, 1H), 3.83 – 3.75 (m, 1H), 2.37 (s, 3H), 1.01 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.0, 144.7, 137.1, 133.1, 132.8, 131.6, 130.2, 130.1, 130.0, 129.4, 129.3, 129.1, 128.6, 128.5, 128.4, 127.7, 86.7, 62.6, 21.6, 13.5. HRMS (DART Positive) calcd for C$_{23}$H$_{22}$O$_4$S$_2$(M+NH$_4$)$^+$: 444.1298; Found: 444.1291.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatography (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (59 mg, 80%). $^{1}$H NMR (500 MHz, CDCl$_3$) δ 7.47 – 7.40 (m, 2H), 7.38 – 7.32 (m, 1H), 7.28 – 7.18 (m, 4H), 6.94 (dd, $J = 9.0, 8.4$ Hz, 2H), 4.45 – 4.30 (m, 2H), 2.47 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 165.8(t,
ethy1 2-((4-chlorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3q

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (68 mg, 88%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.32 (m, 3H), 7.29 – 7.19 (m, 6H), 4.47 – 4.32 (m, 2H), 2.48 (s, 3H), 1.33 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 165.8, 140.5, 132.7, 131.5, 129.8, 129.3, 128.1, 127.9, 83.5, 63.1, 15.6, 14.1. HRMS (ESI) calcd for C\(_{21}\)H\(_{26}\)ClO\(_4\)S\(_2\)(M+Na)\(^+\): 407.1165; Found: 407.1165

ethy1 2-((4-(tert-butyl)phenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3r

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow liquid (78 mg, 97%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.36 (p, \(J = 2.1\) Hz, 2H), 7.34 – 7.31 (m, 1H), 7.28 (d, \(J = 8.8\) Hz, 2H), 7.25 – 7.19 (m, 4H), 4.46 – 4.29 (m, 2H), 2.43 (s, 3H), 1.32 (t, \(J = 7.1\) Hz, 3H), 1.28 (s, 9H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 166.0, 157.7, 132.7, 131.8, 131.1, 129.5, 129.4, 127.8, 124.6, 83.2, 62.9, 35.1, 31.0, 15.5, 14.1. HRMS (ESI) calcd for C\(_{21}\)H\(_{26}\)O\(_4\)S\(_2\)(M+Na)\(^+\): 429.1165; Found: 429.1165

ethy1 2-(methylthio)-2-(naphthalen-2-ylsulfonyl)-2-phenylacetate 3s

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (69 mg, 86%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.94 (s, 1H), 7.84 (d, \(J = 8.2\) Hz, 1H), 7.75 (d, \(J = 8.1\) Hz, 1H), 7.70 (d, \(J = 8.7\) Hz, 1H), 7.62 (td, \(J = 8.2, 6.9, 1.2\) Hz, 1H), 7.54 (td, \(J = 8.1, 7.0, 1.1\) Hz, 1H), 7.41 (dd, \(J = 8.7, 1.7\) Hz, 1H), 7.38 – 7.31 (m, 1H), 7.25 – 7.15 (m, 4H), 4.46 – 4.27 (m, 2H), 2.51 (s, 3H), 1.32 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 165.9, 135.2, 133.6, 132.8, 131.8, 131.3, 129.6, 129.5, 129.2, 127.9, 127.7, 127.2, 127.1, 125.9, 83.5, 77.3, 77.0, 76.8, 63.0, 15.6, 14.1. HRMS (DART Positive) calcd for C\(_{21}\)H\(_{20}\)O\(_4\)S\(_2\)(M+NH\(_4\))\(^+\): 418.1141; Found: 418.1137.

ethy1 2-(methylthio)-2-phenyl-2-tosylacetate 3t

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid (66 mg, 88%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.28 (m, 3H), 7.22 (d, \(J = 4.5\) Hz, 4H), 7.06 (d, \(J = 8.1\) Hz, 2H), 4.42 – 4.29 (m, 2H), 2.43
ethyl 2-(methylsulfonyl)-2-phenyl-2-tosylacetate 4

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a white solid (188 mg, 95%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.70 – 7.57 (m, 4H), 7.50 – 7.42 (m, 1H), 7.37 (t, $J$ = 7.8 Hz, 2H), 7.18 (d, $J$ = 8.1 Hz, 2H), 4.48 – 4.30 (m, 2H), 3.26 (s, 3H), 2.39 (s, 3H), 1.33 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.3, 146.0, 133.8, 131.8, 131.2, 130.4, 128.6, 128.2, 127.1, 96.8, 77.3, 77.0, 76.8, 64.1, 42.5, 21.7, 13.6.

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

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 4:1, v/v) to give the product as a white solid (143 mg, 90%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.48 (dd, $J$ = 11.6, 8.4 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.33 – 7.27 (m, 2H), 7.22 (t, $J$ = 8.5 Hz, 2H), 5.07 (s, 1H), 4.32 – 4.11 (m, 2H), 2.41 (s, 3H), 1.28 – 1.18 (t, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.3, 145.6, 133.8, 131.8, 131.2, 130.4, 128.6, 128.2, 127.1, 96.8, 77.3, 77.0, 76.7, 64.1, 42.5, 21.7, 13.6.

References

NMR spectroscopic data
methyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3a
methyl 2-(4-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3b
methyl 2-(4-(tert-butyl)phenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3c
benzyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3d
ethyl 2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3e
ethyl 2-(4-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3f
ethyl 2-(3-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3g
ethyl 2-(3,4-dimethoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3h
ethyl 2-(methylthio)-2-(4-nitrophenyl)-2-(phenylsulfonyl)acetate 3i
ethyl 2-(4-methoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3j
ethyl 2-(2-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3k
methyl 2-(benzo[b]thiophen-2-yl)-2-(methylthio)-2-(phenylsulfonyl)acetate 3l
ethyl 2-(ethylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3m
ethyl 2-(allylthio)-2-phenyl-2-(phenylsulfonyl)acetate 3n
ethyl 2-phenyl-2-(phenylthio)-2-tosylacetate 3o
ethyl 2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3p
ethyl 2-((4-chlorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3q
ethyl 2-((4-(tert-butyl)phenyl)sulfonyl)-2-(methylthio)-2-phenylacetate 3r
ethyl 2-(methylthio)-2-(naphthalen-2-ylsulfonyl)-2-phenylacetate 3s
ethyl 2-(methylthio)-2-phenyl-2-tosylacetate 3t
ethyl 2-(methylsulfonyl)-2-phenyl-2-tosylacetate 4
ethyl (R)-2-phenyl-2-tosylacetate 5

![Diagram of ethyl (R)-2-phenyl-2-tosylacetate 5]