Supporting Information

Direct Access to \( \alpha \)-Sulfenylated Amides/Esters via Sequential Oxidative Sulfenylation and C-C Bond Cleavage of 3-Oxobutyric Amides/esters

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General Information:
All reactions were carried out in a dry solvent under argon atmosphere unless otherwise noted. NMR spectra were recorded on Bruker 400 MHz (400 MHz for \(^1\)H NMR and 100 MHz for \(^{13}\)C NMR) spectrometers. Proton chemical shifts are reported relative to a residual solvent peak (CDCl\(_3\) at 7.26 ppm, CD\(_3\)COCD\(_3\) at 2.05 ppm). Carbon chemical shifts are reported relative to a residual solvent peak (CDCl\(_3\) at 77.2 ppm, CD\(_3\)COCD\(_3\) at 29.8 ppm). The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet NEXUS 670 instrument. High-resolution mass spectra (HRMS) were measured on a Brucker Daltonics Apex II 47e Specification (for HRMS). Substrates were purchased from commercial sources and used as received. Substrates 1a-1o, 1a', 2a, 2b, 2d, 2g-2i, 4a-4c are commercially available. Substrates 2a\(^1\), 2c\(^2\), 2e\(^2\), 2f\(^3\), 2j\(^4\) are known compounds.

Optimization of Reaction Conditions.
A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol), N,N-dimethyl-3-oxobutanamide 2a (0.20 mmol), base (0.30 mmol) and solvent (1 mL) under oxygen atmosphere. The resulting mixture was stirred under indicated temperature for 12 h, then the reaction solution was cooled to ambient temperature. The reaction was quenched by saturated NaHCO\(_3\) aqueous solution, and extracted with ethyl acetate (3*25mL),
the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 2:1) to give 3a as colorless oil.

Table S1. Optimization of Reaction Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp [°C]</th>
<th>Yield [%]</th>
</tr>
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<tbody>
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<td>1</td>
<td>NaOH</td>
<td>DMSO</td>
<td>110</td>
<td>N.R.</td>
</tr>
<tr>
<td>2</td>
<td>NaOH</td>
<td>DMF</td>
<td>110</td>
<td>N.R.</td>
</tr>
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<td>3</td>
<td>NaOH</td>
<td>Dioxane</td>
<td>110</td>
<td>23%</td>
</tr>
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<td>4</td>
<td>NaOH</td>
<td>butyronitrile</td>
<td>110</td>
<td>36%</td>
</tr>
<tr>
<td>5</td>
<td>DBU</td>
<td>butyronitrile</td>
<td>110</td>
<td>N.R.</td>
</tr>
<tr>
<td>6</td>
<td>CH₃CO₂K</td>
<td>butyronitrile</td>
<td>110</td>
<td>N.R.</td>
</tr>
<tr>
<td>7</td>
<td>K₃PO₄</td>
<td>butyronitrile</td>
<td>110</td>
<td>19%</td>
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<td>8</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>80</td>
<td>41%</td>
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<td>9</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>50</td>
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</tr>
<tr>
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<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>62%</td>
</tr>
<tr>
<td>11</td>
<td>/</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>N.R.</td>
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<tr>
<td>12</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>67%</td>
</tr>
<tr>
<td>13</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>83%</td>
</tr>
<tr>
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<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>95%</td>
</tr>
<tr>
<td>15</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>82%</td>
</tr>
<tr>
<td>16</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>N.R.</td>
</tr>
<tr>
<td>17</td>
<td>NaOH</td>
<td>CH₃CN</td>
<td>r.t.</td>
<td>84%</td>
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aReaction conditions: 1a (0.20 mmol, 1.0 eq), 2a (0.20 mmol, 1.0 eq), base (0.30 mmol, 1.5 eq), solvent (1.0 mL), 12 h. Isolated yields. cThe substrate concentration was 0.20 mmol/mL. d18h. e2a was used as 1.2 eq. fNaOH was used as 1.2 eq. gArgon atomsphere for 18 h. hAir atomsphere for 18 h. r.t.=room temperature, 22 °C~25 °C.
Table S2. Optimization of Reaction Conditions$^a$

![Chemical Structure]

<table>
<thead>
<tr>
<th>entry</th>
<th>Base</th>
<th>Ester (4a)</th>
<th>Yield [%]$^b$</th>
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</thead>
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<tr>
<td>1</td>
<td>NaOH (1.5 eq)</td>
<td>1.2 eq</td>
<td>29%</td>
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<tr>
<td>2</td>
<td>NaOH (1.5 eq)</td>
<td>1.5 eq</td>
<td>32%</td>
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<tr>
<td>3</td>
<td>NaOH (1.5 eq)</td>
<td>2.0 eq</td>
<td>35%</td>
</tr>
<tr>
<td>4</td>
<td>NaOH (1.5 eq)</td>
<td>2.5 eq</td>
<td>41%</td>
</tr>
<tr>
<td>5</td>
<td>NaOH (1.5 eq)</td>
<td>3.0 eq</td>
<td>40%</td>
</tr>
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<tr>
<td>8</td>
<td>NaOH (3.0 eq)</td>
<td>2.5 eq</td>
<td>54%</td>
</tr>
<tr>
<td>9</td>
<td>NaOH (3.5 eq)</td>
<td>2.5 eq</td>
<td>65%</td>
</tr>
<tr>
<td>10</td>
<td>NaOH (4.0 eq)</td>
<td>2.5 eq</td>
<td>69%</td>
</tr>
<tr>
<td>11</td>
<td>NaOH(4.5 eq)</td>
<td>2.5 eq</td>
<td>61%</td>
</tr>
<tr>
<td>12$^c$</td>
<td>NaOH (4.0 eq)</td>
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<td>72%</td>
</tr>
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<td>13$^{c,d}$</td>
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<td>2.5 eq</td>
<td>82%</td>
</tr>
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<td>14$^{e}$</td>
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<td>2.5 eq</td>
<td>78%</td>
</tr>
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<td>15$^{c,d,f}$</td>
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<td>2.5 eq</td>
<td>N.R</td>
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<td>16$^{c,d,g}$</td>
<td>NaOH (4.0 eq)</td>
<td>2.5 eq</td>
<td>73%</td>
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</table>

$^a$Reaction conditions: 1a (0.20 mmol, 1.0 eq), 4a (x mmol, x eq), base (x mmol, x eq), solvent (1 mL), 12 h. $^b$Isolated yields. $^c$The substrate concentration was 0.20 mmol/mL. $^d$18h. $^e$24h. $^f$Argon atmosphere for 18 h. $^g$Air atmosphere for 18 h. r.t.=room temperature, 22 °C~25 °C.

**Typical Procedure for the thiophenol 1a sulfuration of the α-C-H bond of the corresponding amides 2a.** A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol), N,N-dimethyl-3-oxobutanamide 2a (0.24 mmol), NaOH (0.30 mmol) and CH$_3$CN (1 mL) under O$_2$ atmosphere. The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO$_3$ aqueous solution, and extracted with ethyl acetate (3*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 2 : 1) to give 3a as colorless oil.
Typical Procedure for the thiophenol 1a sulfuration of the \( \alpha \)-C-H bond of the corresponding esters 4a. A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol), ethyl 2-methyl-3-oxobutanoate 4a (0.50 mmol), NaOH (0.80 mmol) and CH\(_3\)CN (1 mL) under O\(_2\) atmosphere. The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO\(_3\) aqueous solution, and extracted with ethyl acetate (3*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 60 : 1) to give 4a as colorless oil.

N,N-dimethyl-2-(phenylthio)acetamide (3aa):
37.0 mg, 95%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.48 – 7.40 (m, 2H), 7.29 (t, \( J = 7.5 \) Hz, 2H), 7.22 (d, \( J = 7.1 \) Hz, 2H), 3.75 (s, 2H), 3.04 (s, 2H), 2.95 (s, 3H); ; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.6, 135.4, 130.3, 129.2, 127.0, 38.0, 37.1, 36.0; IR (KBr, \( \nu / \text{cm}^{-1} \)) 3453, 3058, 2927, 2850, 1737, 1648, 1243, 1046, 741; HRMS (ESI\(^+\)) Calcd for C\(_{10}\)H\(_{13}\)NOS (M+Na\(^+\)) 218.0610, Found 218.0610.

N,N-dimethyl-2-(p-tolylthio)acetamide (3ba):
39.4 mg, 94%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.35 (d, \( J = 8.1 \) Hz, 2H), 7.10 (d, \( J = 8.0 \) Hz, 2H), 3.69 (s, 2H), 2.31 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.7, 137.4, 131.4, 131.3, 129.9, 38.0, 37.7, 35.9, 21.2; IR (KBr, \( \nu / \text{cm}^{-1} \)) 3464, 3019, 2925, 2870, 1647, 1493, 1396, 805; HRMS (ESI\(^+\)) Calcd for C\(_{11}\)H\(_{15}\)NOS (M+Na\(^+\)) 232.0767, Found 232.0768.

2-((4-(tert-butyl)phenyl)thio)-N,N-dimethylacetamide(3ca):
46.2 mg, 92%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.39 (d, \( J = 8.5 \) Hz, 2H), 7.32 (d, \( J = 8.4 \) Hz, 2H), 3.72 (s, 2H), 2.96 (s, 3H), 2.30 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.8, 150.5, 131.8, 130.6, 126.3, 38.0, 37.5, 36.0, 34.7, 31.4; IR (KBr, \( \nu / \text{cm}^{-1} \)) 3448, 3048, 2925, 2870, 1647, 1493, 1396, 805; HRMS (ESI\(^+\)) Calcd for C\(_{14}\)H\(_{21}\)NOS (M+Na\(^+\)) 274.1236, Found 274.1235.

2-((4-methoxyphenyl)thio)-N,N-dimethylacetamide (3da):
40.0 mg, 89%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.43 (d,
$J = 8.8 \text{ Hz, 2H}$, $6.84 (d, J = 8.8 \text{ Hz, 2H})$, $3.78 (s, 3H)$, $3.63 (s, 2H)$, $2.99 (s, 3H)$, $2.93 (s, 3H)$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.9, 159.8, 134.5, 125.1, 114.8, 55.5, 38.7, 38.0, 35.9; IR (KBr, ν / cm$^{-1}$) 3462, 3001, 2937, 2837, 1646, 1494, 1246, 1029, 830; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{15}$NO$_2$S (M+Na$^+$) 248.0716, Found 248.0717.

2-((4-fluorophenyl)thio)-N,N-dimethylacetamide (3ea):
41.0 mg, 96%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (dd, $J = 8.3, 5.5 \text{ Hz, 2H}$), $6.99 (t, J = 8.6 \text{ Hz, 2H})$, $3.68 (s, 2H)$, $3.02 (s, 3H)$, $2.94 (s, 3H)$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 163.7, 161.2, 133.7, 133.6, 130.05, 130.02, 116.4, 116.2, 38.0, 36.0; IR (KBr, ν / cm$^{-1}$) 3450, 3055, 2933, 2846, 1736, 1647, 1492, 1397, 1244, 736; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{12}$FNOS (M+Na$^+$) 236.0516, Found 236.0514.

2-((4-chlorophenyl)thio)-N,N-dimethylacetamide (3fa):
43.0 mg, 94%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.32 (m, 2H), $3.73 (s, 2H)$, $3.06 (s, 3H)$, $2.96 (s, 3H)$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.3, 133.9, 133.1, 131.7, 129.3, 38.0, 37.1, 36.0; IR (KBr, ν / cm$^{-1}$) 3397, 3079, 2949, 2808, 1641, 1400, 1117, 1098, 817, 742; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{12}$ClNOS (M+Na$^+$) 252.0220, Found 252.0218.

2-((4-bromophenyl)thio)-N,N-dimethylacetamide (3ga):
49.2 mg, 90%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.6 \text{ Hz, 2H}$), $7.31 (d, J = 8.6 \text{ Hz, 2H})$, $3.72 (s, 2H)$, $3.05 (s, 3H)$, $2.95 (s, 3H)$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.2, 134.6, 132.2, 131.7, 121.0, 38.0, 36.9, 36.0; IR (KBr, ν / cm$^{-1}$) 3075, 2949, 1839, 1475, 1400, 1115, 1093, 814, 736; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{12}$BrNOS (M+Na$^+$) 295.9715, Found 295.9717.

N,N-dimethyl-2-(o-tolylthio)acetamide (3ha):
34.8 mg, 83%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.37 (m, 1H), $7.23 – 7.06 (m, 3H)$, $3.71 (s, 2H)$, $3.05 (s, 3H)$, $2.95 (s, 3H)$, $2.41 (s, 3H)$; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 138.5, 134.6, 130.3, 130.0, 127.0, 126.8, 38.0, 36.4, 36.0, 20.5; IR (KBr, ν / cm$^{-1}$) 3473, 2931, 1646, 1470, 1395, 1133, 1065, 748; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{15}$NOS (M+Na$^+$) 232.0767, Found 232.0767.
2-((2-chlorophenyl)thio)-N,N-dimethylacetamide (3ia):
40.4 mg, 88%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.37 (dd, $J = 7.9$, 1.3 Hz, 1H), 7.23 (td, $J = 7.7$, 1.4 Hz, 1H), 7.15 (td, $J = 7.7$, 1.5 Hz, 1H), 3.77 (s, 2H), 3.09 (s, 3H), 2.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.0, 134.6, 134.3, 130.5, 129.8, 127.8, 127.6, 38.0, 36.0, 35.6; IR (KBr, $\nu$/cm) 2927, 1643, 1449, 1413, 1134, 747; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{12}$ClNOS (M+Na$^+$) 252.0220, Found 252.0225.

2-((2,6-dimethylphenyl)thio)-N,N-dimethylacetamide (3ja):
36.6 mg, 82%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17–7.07 (m, 3H), 3.44 (s, 2H), 2.93 (s, 3H), 2.92 (s, 3H), 2.54 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.1, 143.6, 132.1, 129.1, 128.4, 37.9, 36.7, 35.8, 22.0; IR (KBr, $\nu$/cm) 3466, 3055, 2926, 1647, 1461, 1393, 1265, 1107, 774; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{17}$NOS (M+Na$^+$) 246.0923, Found 246.0924.

N,N-dimethyl-2-(m-tolylthio)acetamide (3ka):
36.4 mg, 87%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, $J = 9.9$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.4$ Hz, 1H), 3.75 (s, 2H), 3.04 (s, 3H), 2.96 (s, 3H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.6, 139.0, 135.1, 130.9, 129.0, 127.9, 127.3, 38.0, 37.1, 36.0, 21.5; IR (KBr, $\nu$/cm) 3054, 2928, 1646, 1576, 1557, 1460, 1396, 774, 751, 688, 612; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{15}$NOS (M+Na$^+$) 232.0767, Found 232.0769.

2-((3-bromophenyl)thio)-N,N-dimethylacetamide (3la):
49.2 mg, 90%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (t, $J = 1.7$ Hz, 1H), 7.42–7.30 (m, 2H), 7.16 (t, $J = 7.9$ Hz, 1H), 3.76 (s, 2H), 3.07 (s, 3H), 2.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.1, 137.9, 132.3, 130.5, 129.9, 128.4, 122.9, 38.0, 36.8, 36.1; IR (KBr, $\nu$/cm) 3054, 2928, 1646, 1576, 1557, 1460, 1396, 774, 751, 678; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{12}$BrNOS (M+Na$^+$) 295.9715, Found 295.9718.

2H-benzo[b][1,4]thiazin-3(4H)-one (3ma):
26.8 mg, 81%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1H), 7.32
(d, J = 7.7 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.06 – 6.97 (m, 1H), 6.85 (d, J = 7.9 Hz, 1H), 3.44 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.1, 136.5, 128.0, 127.4, 124.1, 120.2, 117.4, 30.2; IR (KBr, ν / cm$^{-1}$) 1687, 1479, 1386, 797, 741, 659, 527; HRMS (ESI$^+$) Calcd for C$_8$H$_7$NOS (M+Na$^+$) 188.0141, Found 188.0147.

N,N-dimethyl-2-(thiophen-2-ylthio)acetamide (3na):
35.8 mg, 89%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (dd, J = 5.3, 1.1 Hz, 1H), 7.20 (dd, J = 3.5, 1.2 Hz, 1H), 6.98 (dd, J = 5.3, 3.6 Hz, 1H), 3.66 (s, 2H), 2.96 (s, 3H), 2.95 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.2, 135.2, 132.6, 130.6, 127.9, 41.2, 37.9, 36.0; IR (KBr, ν / cm$^{-1}$) 3078, 2930, 1644, 1496, 1397, 1263, 1217, 1134, 847, 708; HRMS (ESI$^+$) Calcd for C$_8$H$_{11}$NOS$_2$ (M+Na$^+$) 224.0174, Found 224.0175.

N,N-dimethyl-2-(phenethylthio)acetamide (3oa):
35.2 mg, 79%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.22 (d, J = 7.2 Hz, 3H), 3.30 (s, 2H), 3.05 (s, 3H), 2.96 (s, 3H), 2.92 (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.4, 140.5, 128.8, 128.6, 126.5, 38.1, 36.0, 33.8, 33.5; IR (KBr, ν / cm$^{-1}$) 3427, 3026, 2926, 2856, 1641, 1396, 1262, 1104, 699; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{17}$NOS (M+Na$^+$) 246.0923, Found 246.0924.

N,N-dimethyl-2-(phenylselanyl)acetamide (3a’a):
45.6 mg, 94%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.56 (m, 2H), 7.31 – 7.26 (m, 3H), 3.71 (d, J = 5.4 Hz, 2H), 2.96 (s, 3H), 2.94 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.7, 133.9, 129.4, 129.3, 128.0, 38.3, 36.0, 28.4; IR (KBr, ν / cm$^{-1}$) 2929, 1640, 1479, 1392, 1266, 1091, 739, 691; HRMS (ESI$^+$) Calcd for C$_{10}$H$_{13}$NOS (M+Na$^+$) 266.0055, Found 266.0057.

N,N-diethyl-2-(phenylthio)acetamide (3ab):
42.0 mg, 94%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.42 (m, 2H), 7.33 – 7.25 (m, 2H), 7.22 (t, J = 7.3 Hz, 1H), 3.74 (s, 2H), 3.36 (dq, J = 21.7, 7.1 Hz, 4H), 1.20 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.7, 135.5, 130.6, 129.1, 127.0, 42.7, 40.6, 37.2, 14.6, 13.0; IR (KBr, ν / cm$^{-1}$) 3461, 2975, 2932, 1639, 1480, 1461, 1438, 1381, 1097, 740, 692; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{17}$NOS (M+Na$^+$) 246.0923, Found 246.0926.
2-(phenylthio)-1-(pyrrolidin-1-yl)ethanone (3ac):
42.0 mg, 94%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 – 7.43 (m, 2H), 7.29 (t, \(J = 7.3 \text{ Hz}, 2\)H), 7.21 (t, \(J = 7.3 \text{ Hz}, 1\)H), 3.68 (s, 2H), 3.46 (dt, \(J = 11.2, 6.8 \text{ Hz}, 4\)H), 1.93 (dt, \(J = 12.7, 6.6 \text{ Hz}, 2\)H), 1.84 (dt, \(J = 13.4, 6.6 \text{ Hz}, 2\)H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.0, 135.6, 130.4, 129.1, 127.0, 47.0, 46.3, 38.0, 26.3, 24.4; IR (KBr, \(\nu / \text{ cm}^{-1}\)) 3434, 2971, 2948, 2878, 1630, 1452, 1438, 911, 727, 686; HRMS (ESI\(^+\)) Calcd for C\(_{12}\)H\(_{17}\)NOS (M+Na\(^+\)) 244.0767, Found 244.0759.

1-morpholino-2-(phenylthio)ethanone (3ad):
45.0 mg, 95%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (dd, \(J = 5.2, 3.3 \text{ Hz}, 2\)H), 7.34 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 3.73 (s, 2H), 3.68 – 3.63 (m, 4H), 3.61 (d, \(J = 5.0 \text{ Hz}, 2\)H), 3.50 – 3.45 (m, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.3, 134.7, 130.6, 129.3, 127.4, 66.9, 66.7, 47.0, 42.4, 36.5; IR (KBr, \(\nu / \text{ cm}^{-1}\)) 3449, 2970, 2869, 1645, 1460, 1439, 1266, 1115, 1039, 736, 702; HRMS (ESI\(^+\)) Calcd for C\(_{12}\)H\(_{15}\)NO\(_2\)S (M+Na\(^+\)) 260.0716, Found 260.0720.

N-methoxy-N-methyl-2-(phenylthio)acetamide (3ae):
38.0 mg, 90%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46 (d, \(J = 7.3 \text{ Hz}, 2\)H), 7.29 (t, \(J = 7.5 \text{ Hz}, 2\)H), 7.21 (t, \(J = 7.3 \text{ Hz}, 1\)H), 3.83 (s, 2H), 3.71 (s, 3H), 3.21 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 135.8, 130.1, 129.1, 126.9, 61.7, 35.6, 32.6; IR (KBr, \(\nu / \text{ cm}^{-1}\)) 3433, 1648, 1498, 1375, 743, 659; HRMS (ESI\(^+\)) Calcd for C\(_{10}\)H\(_{13}\)NO\(_2\)S (M+Na\(^+\)) 234.0559, Found 234.0563.

N-methyl-N-phenyl-2-(phenylthio)acetamide (3af):
46.8 mg, 91%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (t, \(J = 7.3 \text{ Hz}, 2\)H), 7.37 – 7.31 (m, 3H), 7.29 – 7.22 (m, 2H), 7.20 (d, \(J = 7.1 \text{ Hz}, 1\)H), 7.15 (d, \(J = 7.3 \text{ Hz}, 2\)H), 3.52 (s, 2H), 3.29 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.9, 143.6, 135.8, 130.4, 130.1, 129.1, 128.3, 127.5, 126.9, 38.0, 37.4; IR (KBr, \(\nu / \text{ cm}^{-1}\)) 3432, 1651, 1481, 1384, 1118, 744, 700; HRMS (ESI\(^+\)) Calcd for C\(_{15}\)H\(_{15}\)NOS (M+Na\(^+\)) 280.0767, Found 280.0769.

N-methyl-3-oxo-N-phenyl-2-(phenylthio)butanamide (3af\'):
56.2 mg, 94%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (t, \(J = 7.3\) Hz, 3H), 7.21 (s, 6H), 7.13 (d, \(J = 7.8\) Hz, 2H), 4.38 (s, 1H), 3.31 (s, 3H), 2.30 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.3, 166.3, 142.9, 133.2, 132.4, 130.2, 129.4, 128.8, 128.4, 127.7, 61.2, 38.2, 27.5; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3320, 1742, 1652, 759, 644; HRMS (ESI\(^+\)) Calcd for C\(_{17}\)H\(_{17}\)NO\(_2\)S (M+Na\(^+\)) 322.0872, Found 322.0871.

**N-methyl-2-(phenylthio)acetamide (3ag):**
31.6 mg, 87%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 – 7.16 (m, 5H), 6.85 (s, 1H), 3.64 (s, 2H), 2.82 (d, \(J = 4.9\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.5, 135.0, 129.5, 127.9, 126.7, 37.3, 38.7; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3334, 2918, 1664, 1544, 1482, 1442, 738, 691; HRMS (ESI\(^+\)) Calcd for C\(_9\)H\(_{11}\)NOS (M+Na\(^+\)) 204.0454, Found 204.0451.

**N-phenyl-2-(phenylthio)acetamide (3ah):**
40.8 mg, 84%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.58 (s, 1H), 7.48 (d, \(J = 7.6\) Hz, 2H), 7.34 (dt, \(J = 15.7, 7.6\) Hz, 7H), 7.23 (d, \(J = 7.1\) Hz, 1H), 7.12 (t, \(J = 7.4\) Hz, 1H), 3.77 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.1, 137.4, 134.3, 129.7, 129.2, 128.6, 127.3, 125.0, 120.1, 38.7; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3318, 2918, 1664, 1544, 1482, 1442, 738, 691; HRMS (ESI\(^+\)) Calcd for C\(_{14}\)H\(_{13}\)NOS (M+Na\(^+\)) 266.0610, Found 266.0603.

**2-(phenylthio)acetamide (3ai):**
27.8 mg, 83%, colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.31 (d, \(J = 4.3\) Hz, 4H), 7.25 – 7.19 (m, 1H), 6.69 (s, 1H), 5.60 (s, 1H), 3.63 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.8, 134.7, 129.6, 128.3, 127.0, 37.1; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3356, 3177, 1657, 1383, 1238, 744, 735, 690, 655; HRMS (ESI\(^+\)) Calcd for C\(_8\)H\(_9\)NOS (M+Na\(^+\)) 190.0297, Found 190.0294.

**N,N-diethyl-2-(phenylselanyl)acetamide (3a'b):**
51.0 mg, 94%, colorless oil; \(^1\)H NMR (400 MHz, Acetone) \(\delta\) 7.63 – 7.56 (m, 2H), 7.28 (q, \(J = 5.3\) Hz, 3H), 3.86 (d, \(J = 4.1\) Hz, 2H), 3.44 – 3.30 (m, 4H), 1.18 (t, \(J = 7.1\) Hz, 3H), 1.05 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (100 MHz, Acetone) \(\delta\) 168.5, 133.4, 131.2, 129.9, 127.8, 43.3, 40.7, 14.7, 13.2; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3459, 2953,
HRMS (ESI+) Calcd for C_{12}H_{17}NOSe (M+Na^+) 294.0368, Found 294.0371.

1-(azepan-1-yl)-2-(phenylselanyl)ethanone (3a'j):
51.6 mg, 87%, colorless oil; ^1H NMR (400 MHz, Acetone) δ 7.64 – 7.54 (m, 2H), 7.32 – 7.22 (m, 3H), 3.89 (s, 2H), 3.52 (t, J = 6.1 Hz, 2H), 3.48 – 3.43 (m, 2H), 1.75 (dt, J = 12.0, 6.0 Hz, 2H), 1.63 (dd, J = 11.5, 5.8 Hz, 2H), 1.55 (dd, J = 11.4, 6.9 Hz, 4H); ^13C NMR (100 MHz, Acetone) δ 168.8, 133.1, 131.4, 129.9, 127.7, 49.1, 46.3, 28.3, 28.0, 27.2; IR (KBr, ν / cm⁻¹) 3436, 2948, 1634, 1452, 1070, 911, 730, 687; HRMS (ESI+) Calcd for C_{14}H_{19}NOSe (M+Na^+) 328.0524, Found 328.0519.

N-methyl-N-phenyl-2-(phenylselanyl)acetamide (3a'f):
52.4 mg, 86%, colorless oil; ^1H NMR (400 MHz, CDCl₃) δ 7.40 (t, J = 7.3 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.27 – 7.22 (m, 2H), 7.20 (d, J = 7.3 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 3.52 (s, 2H), 3.29 (s, 3H); ^13C NMR (100 MHz, CDCl₃) δ 168.9, 143.6, 135.8, 130.4, 130.1, 129.1, 128.3, 127.5, 126.9, 38.0, 37.4; IR (KBr, ν / cm⁻¹) 3433, 2928, 1650, 1388, 1115, 1059, 745, 691; HRMS (ESI+) Calcd for C_{15}H_{15}NOSe (M+Na^+) 328.0211, Found 328.0212.

N-methyl-2-(phenylselanyl)acetamide (3a'g):
39.8 mg, 87%, colorless oil; ^1H NMR (400 MHz, CDCl₃) δ 7.46 (dd, J = 6.3, 3.0 Hz, 2H), 7.31 – 7.26 (m, 3H), 6.45 (s, 1H), 3.55 (s, 2H), 2.79 (s, 2H), 2.78 (s, 2H); ^13C NMR (100 MHz, CDCl₃) δ 169.2, 132.1, 129.6, 129.4, 127.8, 30.4, 27.0; IR (KBr, ν / cm⁻¹) 3337, 2921, 1646, 1535, 1168, 1078, 740, 692; HRMS (ESI+) Calcd for C_{9}H_{11}NOSe (M+Na^+) 251.9898, Found 251.9895.

N-phenyl-2-(phenylselanyl)acetamide (3a'h):
44.8 mg, 77%, colorless oil; ^1H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.56 (dd, J = 6.3, 2.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 6.1 Hz, 5H), 7.11 (t, J = 7.3 Hz, 1H), 3.67 (s, 2H); ^13C NMR (100 MHz, CDCl₃) δ 167.0, 137.7, 132.9, 129.8, 129.2, 128.8, 128.2, 124.8, 120.0, 31.5; IR (KBr, ν / cm⁻¹) 3319, 2917, 1666, 1544, 1072, 740, 691; HRMS (ESI+) Calcd for C_{14}H_{13}NOSe (M+Na^+) 314.0055, Found 314.0059.
2-(phenylselanyl)acetamide (3a'i):
35.2 mg, 82%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (dd, $J$ = 4.8, 2.4 Hz, 2H), 7.29 (dd, $J$ = 4.4, 1.2 Hz, 3H), 6.26 (s, 1H), 5.68 (s, 1H), 3.59 – 3.47 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.6, 132.5, 129.7, 129.1, 128.0, 30.0; IR (KBr, $\nu$ / cm$^{-1}$) 3355, 3178, 1659, 1398, 1239, 1024, 745, 690; HRMS (ESI$^+$) Calcd for C$_8$H$_9$NOSe (M+Na$^+$) 237.9742, Found 237.9748.

Ethyl 2-(phenylthio)propanoate (5a):
34.4 mg, 82%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.41 (m, 2H), 7.31 (tt, $J$ = 4.6, 2.5 Hz, 3H), 4.11 (qd, $J$ = 7.1, 1.2 Hz, 2H), 3.79 (q, $J$ = 7.1 Hz, 1H), 1.48 (d, $J$ = 7.1 Hz, 3H), 1.17 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 136.9, 133.5, 133.2, 129.1, 128.1, 61.4, 45.5, 17.6, 14.2; IR (KBr, $\nu$ / cm$^{-1}$) 3441, 2980, 2933, 1732, 1259, 1174, 1159, 749, 692; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{14}$O$_2$S (M+Na$^+$) 233.0607, Found 233.0607.

Ethyl 2-(p-tolylthio)propanoate (5b):
35.8 mg, 80%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 7.9 Hz, 2H), 3.79 (q, $J$ = 7.1 Hz, 1H), 2.33 (s, 3H), 1.45 (d, $J$ = 7.1 Hz, 3H), 1.17 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.9, 138.6, 134.0, 129.8, 129.5, 61.3, 45.8, 21.3, 17.5, 14.2; IR (KBr, $\nu$ / cm$^{-1}$) 3436, 2980, 2933, 1732, 1259, 1174, 1159, 749, 692; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{16}$O$_2$S (M+Na$^+$) 247.0763, Found 247.0764.

Ethyl 2-((4-(tert-butyl)phenyl)thio)propanoate (5c):
43.2 mg, 81%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 8.5 Hz, 2H), 7.32 (d, $J$ = 8.5 Hz, 2H), 3.73 (q, $J$ = 7.1 Hz, 1H), 1.47 (d, $J$ = 7.1 Hz, 3H), 1.30 (s, 9H), 1.16 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.0, 151.6, 133.5, 129.7, 126.1, 61.3, 45.7, 34.8, 31.4, 17.6, 14.2; IR (KBr, $\nu$ / cm$^{-1}$) 3441, 2965, 2905, 1734, 1169, 1065, 830, 738; HRMS (ESI$^+$) Calcd for C$_{15}$H$_{22}$O$_2$S (M+Na$^+$) 289.1233, Found 289.1235.

Ethyl 2-((4-methoxyphenyl)thio)propanoate (5d):
37.0 mg, 77%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41
(d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 3.62 (q, J = 7.1 Hz, 1H), 1.42 (d, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.9, 160.4, 136.7, 123.3, 114.6, 61.2, 55.5, 46.2, 17.4, 14.3; IR (KBr, ν / cm$^{-1}$) 3436, 2979, 1731, 1592, 1494, 1248, 1173, 1029, 830; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{16}$O$_3$S (M+Na$^+$) 263.0712, Found 263.0714.

**Ethyl 2-((4-fluorophenyl)thio)propanoate (5ea):**

36.2 mg, 85%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.40 (m, 2H), 7.01 (dd, J = 11.9, 5.4 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.69 (q, J = 7.1 Hz, 1H), 1.45 (d, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.6, 164.5, 162.0, 139.1, 136.4, 136.3, 128.2, 116.3, 116.1, 61.4, 46.0, 17.4, 14.3; IR (KBr, ν / cm$^{-1}$) 3443, 2979, 1733, 1461, 1328, 1157, 1024, 773; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{13}$FO$_2$S (M+Na$^+$) 251.0512, Found 251.0515.

**Ethyl 2-((4-chlorophenyl)thio)propanoate (5fa):**

40.0 mg, 82%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.26 (m, 2H), 4.16 – 4.08 (m, 2H), 3.74 (q, J = 7.1 Hz, 1H), 1.47 (d, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.6, 138.1, 134.6, 134.5, 131.9, 129.3, 61.5, 45.5, 17.4, 14.2; IR (KBr, ν / cm$^{-1}$) 3442, 2981, 1732, 1477, 1160, 1095, 1014, 823, 746; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{13}$ClO$_2$S (M+Na$^+$) 267.0217, Found 267.0218.

**Ethyl 2-((4-bromophenyl)thio)propanoate (5ga):**

47.8 mg, 83%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.75 (q, J = 7.1 Hz, 1H), 1.47 (d, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.6, 134.7, 132.6, 122.5, 61.5, 45.4, 17.5, 14.2; IR (KBr, ν / cm$^{-1}$) 2980, 1732, 1474, 1160, 1069, 1009, 818, 730; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{13}$BrO$_2$S (M+Na$^+$) 310.9712, Found 310.9714.

**Ethyl 2-(o-tolylthio)propanoate (5ha):**

33.2 mg, 74%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, J = 7.2 Hz, 1H), 7.23 – 7.10 (m, 3H), 4.08 (q, J = 7.1 Hz, 2H), 3.76 (q, J = 7.1 Hz, 1H), 2.44 (s, 3H), 1.50 (d, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100
MHz, CDCl$_3$) δ 173.0, 140.7, 133.6, 133.1, 130.5, 128.2, 126.6, 61.3, 44.9, 20.9, 17.6, 14.2; IR (KBr, ν / cm$^{-1}$) 2980, 1733, 1470, 1255, 1173, 1158, 1063, 753; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{16}$O$_2$S (M+Na$^+$) 247.0763, Found 247.0763.

Ethyl 2-((2-chlorophenyl)thio)propanoate (5ia):
38.0 mg, 78%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 – 7.49 (m, 1H), 7.41 (dd, $J = 5.9$, 3.4 Hz, 1H), 7.25 – 7.18 (m, 2H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.93 (q, $J = 7.1$ Hz, 1H), 1.53 (d, $J = 7.2$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.5, 136.9, 133.9, 133.2, 130.1, 129.1, 127.3, 61.5, 44.2, 17.2, 14.2; IR (KBr, ν / cm$^{-1}$) 2981, 1733, 1452, 1259, 1174, 1159, 1035, 753; HRMS (ESI$^+$) Calcd for C$_{11}$H$_{13}$ClO$_2$S (M+Na$^+$) 267.0217, Found 267.0213.

Ethyl 2-((2,6-dimethylphenyl)thio)propanoate (5ja):
33.8 mg, 71%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (dt, $J = 16.4$, 5.6 Hz, 3H), 3.98 (dddd, $J = 17.9$, 10.7, 7.1, 3.6 Hz, 2H), 3.57 (q, $J = 7.0$ Hz, 1H), 2.52 (s, 6H), 1.47 (d, $J = 7.0$ Hz, 3H), 1.07 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.0, 143.8, 132.0, 129.0, 128.3, 61.2, 44.6, 22.2, 17.3, 14.0; IR (KBr, ν / cm$^{-1}$) 2982, 1732, 1590, 1491, 1224, 1157, 834; HRMS (ESI$^+$) Calcd for C$_{13}$H$_{18}$O$_2$S (M+Na$^+$) 261.0920, Found 261.0921.

Ethyl 2-((m-tolylthio)propanoate (5ka):
35.4 mg, 79%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, $J = 12.4$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.4$ Hz, 1H), 4.12 (pd, $J = 6.6$, 3.7 Hz, 2H), 3.78 (q, $J = 7.1$ Hz, 1H), 2.33 (s, 3H), 1.48 (d, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.9, 138.8, 133.8, 133.2, 130.1, 129.0, 128.9, 61.3, 45.5, 21.4, 17.6, 14.2; IR (KBr, ν / cm$^{-1}$) 2980, 2932, 1733, 1256, 1158, 778, 692; HRMS (ESI$^+$) Calcd for C$_{12}$H$_{16}$O$_2$S (M+Na$^+$) 247.0763, Found 247.0762.

Ethyl 2-((3-bromophenyl)thio)propanoate (5la):
46.0 mg, 80%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.26 (m, 2H), 4.16 – 4.08 (m, 2H), 3.74 (q, $J = 7.1$ Hz, 1H), 1.47 (d, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.5, 136.0, 135.1, 131.2, 131.0, 130.4, 122.7, 61.6, 45.3, 17.5, 14.2; IR (KBr, ν / cm$^{-1}$) 3441, 2979, 1734, 1560, 1460, 1259, 1158, 1068, 780, 680; HRMS
(ESI⁺) Calcd for C₁₁H₁₃BrO₂S (M+Na⁺) 310.9712, Found 310.9715.

**Ethyl 2-(thiophen-2-ylthio)propanoate (5ma):**
32.4 mg, 75%, colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.38 (m, 1H), 7.21 – 7.15 (m, 1H), 7.00 (dd, J = 5.3, 3.6 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.60 (q, J = 7.1 Hz, 1H), 1.45 (d, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 136.7, 131.4, 130.5, 127.8, 61.4, 47.7, 17.2, 14.3; IR (KBr, ν / cm⁻¹) 3440, 2980, 1732, 1219, 1174, 1067, 707; HRMS (ESI⁺) Calcd for C₉H₁₂O₂S (M+Na⁺) 239.0171, Found 239.0171.

**Ethyl 2-(pyridin-3-ylthio)propanoate (5na):**
34.2 mg, 81%, colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, J = 4.8 Hz, 1H), 7.48 (td, J = 8.0, 1.8 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 6.99 (dd, J = 7.3, 5.0 Hz, 1H), 4.58 (q, J = 7.3 Hz, 1H), 4.24 – 4.11 (m, 2H), 1.61 (d, J = 7.3 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 157.6, 149.6, 136.2, 122.5, 120.1, 61.5, 41.8, 17.8, 14.3; IR (KBr, ν / cm⁻¹) 3442, 1738, 1256, 1193, 1157, 734; HRMS (ESI⁺) Calcd for C₁₀H₁₃NO₂S (M+Na⁺) 234.0559, Found 234.0560.

**Ethyl 2-(benzo[d]thiazol-2-ylthio)propanoate (5oa):**
43.8 mg, 82%, colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 4.68 (q, J = 7.3 Hz, 1H), 4.22 (qd, J = 7.2, 3.7 Hz, 2H), 1.71 (d, J = 7.3 Hz, 3H), 1.26 (t, J = 7.1 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 171.8, 164.5, 153.2, 135.8, 126.3, 124.7, 122.0, 121.2, 62.0, 45.4, 18.2, 14.3; IR (KBr, ν / cm⁻¹) 3395, 2927, 1745, 1260, 1158, 1075, 1021, 732; HRMS (ESI⁺) Calcd for C₁₂H₁₃NO₂S₂ (M+Na⁺) 290.0280, Found 290.0283.

**methyl 2-(phenylthio)pent-4-enolate (5ab):**
35.0 mg, 74%, colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, J = 7.3, 2.1 Hz, 2H), 7.34 – 7.28 (m, 3H), 5.80 (ddt, J = 17.0, 10.0, 6.9 Hz, 1H), 5.12 (dd, J = 20.5, 5.0 Hz, 2H), 3.71 (dd, J = 8.6, 6.5 Hz, 1H), 3.66 (s, 3H), 2.62 (dt, J = 15.5, 7.8 Hz, 1H), 2.56 – 2.48 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 134.0, 133.3, 129.2, 128.3, 127.8, 118.3, 52.4, 50.5, 36.1; IR (KBr, ν / cm⁻¹) 3398, 2951, 1736, 1438, 1157, 743, 692; HRMS (ESI⁺) Calcd for C₁₃H₁₆O₂S (M+Na⁺) 259.0763, Found 259.0766.
diethyl 2-(phenylthio)hexanedioate (5ac):
42.8 mg, 69%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.49 – 7.42 (m, 2H), 7.29 (t, $J = 5.2$ Hz, 3H), 4.12 (q, $J = 7.1$
Hz, 4H), 3.66 – 3.60 (m, 1H), 2.32 (t, $J = 7.0$ Hz, 2H), 1.96 –
1.87 (m, 1H), 1.86 – 1.68 (m, 4H), 1.24 (t, $J = 7.1$ Hz, 4H), 1.17 (t, $J = 7.1$
Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 173.2, 172.2, 133.5, 133.2,
129.1, 128.2, 61.4, 60.6, 50.8, 33.9, 31.2, 22.8, 14.4, 14.2; IR (KBr, $\nu /
\text{cm}^{-1}$) 3351, 2925, 1677, 1527, 1458, 909, 733; HRMS (ESI$^+$)
Calcd for C$_{16}$H$_{22}$O$_4$S (M+Na$^+$) 333.1131, Found 333.1130.

N-methoxy-N-methyl-2-(phenylthio)pent-4-enamide (Y1):
45.6 mg, 91%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 –
7.41 (m, 2H), 7.36 – 7.27 (m, 3H), 5.94 – 5.66 (m, 1H), 5.09 (dd, $J =
19.0, 13.7$ Hz, 2H), 4.18 (s, 1H), 3.59 (s, 3H), 3.17 (s, 3H), 2.72 – 2.60
(m, 1H), 2.55 – 2.42 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 134.8,
134.0, 133.2, 129.0, 128.3, 117.9, 61.6, 46.4, 36.4, 32.7. IR (KBr, $\nu /
\text{cm}^{-1}$) 3332, 2937, 1663, 1439, 1383, 991, 743, 692; HRMS (ESI$^+$)
Calcd for C$_{16}$H$_{22}$O$_4$S (M+Na$^+$) 274.0872, Found 274.0867.

1-(phenylthio)butan-2-one (Y2):
33.8 mg, 94%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J =
7.3$ Hz, 1H), 7.29 (t, $J = 7.7$ Hz, 1H), 7.20 (dd, $J = 10.5, 3.8$ Hz, 1H),
3.68 (s, 1H), 2.61 (q, $J = 7.3$ Hz, 1H), 1.05 (t, $J = 7.3$ Hz, 2H); $^{13}$C NMR
(100 MHz, CDCl$_3$) $\delta$ 206.4, 135.1, 129.7, 129.3, 127.0, 43.8, 34.1, 8.0. IR
(KBr, $\nu /
\text{cm}^{-1}$) 3398, 2944, 1723, 786, 637; HRMS (ESI$^+$) Calcd for C$_{16}$H$_{22}$O$_4$S
(M+Na$^+$) 203.0501, Found 203.0501.

3-((phenylthio)methyl)pentan-3-ol (Y3):
37.2 mg, 83%, colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (d, $J =
7.3$ Hz, 2H), 7.28 (d, $J = 7.4$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H), 3.10
(s, 2H), 2.03 (d, $J = 9.5$ Hz, 1H), 1.55 – 1.49 (m, 2H), 1.30 (dd, $J = 23.2,
14.3, 7.1$ Hz, 3H), 0.89 (td, $J = 7.4, 5.4$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$)
$\delta$ 137.3, 129.9, 129.1, 126.4, 74.5, 45.19, 40.7, 31.4, 17.1, 14.7, 8.2; IR
(KBr, $\nu /
\text{cm}^{-1}$) 3439, 1762, 1070, 834, 779; HRMS (ESI$^+$) Calcd for C$_{16}$H$_{22}$O$_4$S
(M+Na$^+$) 247.1127, Found 247.1131.
2-(phenylthio)acetaldehyde (Y4):
28.0 mg, 92%, colorless oil; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.55 (t, \(J = 3.1\) Hz, 1H), 7.35 (d, \(J = 7.2\) Hz, 2H), 7.30 (t, \(J = 7.4\) Hz, 2H), 7.23 (d, \(J = 7.0\) Hz, 1H), 3.60 (d, \(J = 3.1\) Hz, 2H); \(^13C\) NMR (100 MHz, Acetone) \(\delta\) 195.2, 133.7, 130.3, 129.5, 127.5, 44.0, 29.9; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3419, 2925, 1722, 1440, 1266, 1025, 737, 691; HRMS (ESI\(^+\)) Calcd for C\(_8\)H\(_8\)OS (M+Na\(^+\)) 175.0188, Found 175.0192.

2-(phenylthio)ethanol (Y5):
29.2 mg, 95%, colorless oil; \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44–7.36 (m, 2H), 7.30 (t, \(J = 7.5\) Hz, 2H), 7.22 (t, \(J = 7.3\) Hz, 1H), 3.74 (dd, \(J = 10.8, 5.3\) Hz, 2H), 3.12 (t, \(J = 6.0\) Hz, 2H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 135.0, 130.4, 129.3, 126.9, 60.5, 37.5; IR (KBr, \(\nu / \text{cm}^{-1}\)) 3400, 2928, 1734, 1584, 1480, 1439, 1044, 738, 692; HRMS (ESI\(^+\)) Calcd for C\(_{16}\)H\(_{22}\)O\(_4\)S (M+Na\(^+\)) 177.0345, Found 177.0342.

**Scheme S1.** Gram-scale experiment.

A gram-scale experiment was carried out under standard condition: a round flask equipped with a magnetic stir bar was charged with thiol 1a (1.20 g, 1eq), N,N-dimethyl-3-oxobutanamide 2a (1.69 g, 1.2 eq), NaOH (0.56 g, 1.5 eq), CH\(_3\)CN (20 ml). The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO\(_3\) aqueous solution, and extracted with ethyl acetate (3*50mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 60 : 1) to give 3aa as colorless oil (1.87g, 87% yield).

**Scheme S2.** Mechanism study
(a) Reaction in eq 1
According to previous reports\(^5\), thiophenol 1a or benzeneselenol 1a' could be oxidized to 1,2-diphenyldisulfane 1aa or 1,2-diphenyldisolane 1a'a' by oxygen under O\(_2\) atmosphere.

**(b) Reaction in eq 2**

\[
\begin{align*}
\text{standard condition} \\
\text{X=S 1aa} & \quad \text{X=Se 1a'a'}
\end{align*}
\]

A test tube equipped with a magnetic stir bar was charged with 1,2-diphenyldisulfane 1aa (0.1 mmol) or 1,2-diphenyldisolane 1a'a' (0.1 mmol), N-methyl-3-oxo-N-phenylbutanamide 2f (0.24 mmol), NaOH (0.30 mmol) and CH\(_3\)CN (1 mL) under O\(_2\) atmosphere. The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO\(_3\) aqueous solution, and extracted with ethyl acetate (3*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 2:1) respectively, giving 3af and 3a'f as colorless oil (3af, 94%; 3a'f, 88%).

**(c) Reaction in eq 3**

\[
\begin{align*}
\text{standard condition} \\
\text{X=S 1a} & \quad \text{X=Se 1a'}
\end{align*}
\]

A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol) or benzeneselenol 1a' (0.20 mmol), N-methyl-3-oxo-N-phenylbutanamide 2f (0.24 mmol), NaOH (0.30 mmol), BHT or TEMPO (0.40 mmol) and CH\(_3\)CN (1 mL) under O\(_2\) atmosphere. The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO\(_3\) aqueous solution, and extracted with ethyl acetate (3*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 2:1) respectively, giving 3af and 3a'f as colorless oil (3af, 82%; 3a'f, 79%).

**(d) Reaction in eq 4 and eq 5**
A test tube equipped with a magnetic stir bar was charged with N-methyl-3-oxo-N-phenylbutanamide 2f (0.24 mmol), NaOH (0.30 mmol), and CH$_3$CN (1 mL) under O$_2$ atmosphere (eq 4). The resulting mixture was stirred at room temperature for 18 h. However, no acetyl degradation product 2ff was detected. A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol) or benzeneselenol 1a' (0.20 mmol), N-methyl-N-phenylacetamide 2ff (0.24 mmol), t-BuOK (0.30 mmol), and CH$_3$CN (1 mL) under O$_2$ atmosphere. The resulting mixture was stirred at room temperature for 18 h. And another test tube equipped with a magnetic stir bar was charged with N-methyl-N-phenylacetamide 2ff (0.24 mmol), KHMDS (0.30 mmol), THF (1 mL) under O$_2$ atmosphere, the resulting mixture was stirred at -78 °C for 30 min, then thiophenol 1a (0.20 mmol) or benzeneselenol 1a' (0.20 mmol) was dropwise added to the resulting mixture. The resulting mixture was stirred for 30 min, moved to room temperature and stirred overnight. However, for both the scenario no desired product 3af or 3a'f was detected.

(e) Reaction in eq. 6 and 7
According to the previous report, we prepared 3af' and 3a'f' (eq 6). A test tube equipped with a magnetic stir bar was charged with N-methyl-3-oxo-N-phenyl-2-(phenylthio)butanamide 3af' (0.20 mmol) or N-methyl-3-oxo-N-phenyl-2-(phenylselanyl)butanamide 3a'f' (0.20 mmol), NaOH (0.30 mmol), and CH₃CN (1 mL) under O₂ atmosphere (eq 7). The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO₃ aqueous solution, and extracted with ethyl acetate (3*25mL), the combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (hexane / EtOAc = 2:1) respectively, giving 3af and 3a'f as colorless oil (3af, 89%; 3a'f, 84%).

(f) Reaction in eq 8

A test tube equipped with a magnetic stir bar was charged with thiophenol 1a (0.20 mmol) or benzeneselenol 1a' (0.20 mmol), N-methyl-3-oxo-N,3-diphenylpropanamide 2f' (0.24 mmol) NaOH (0.30 mmol), and CH₃CN (1 mL) under O₂ atmosphere (eq 8). The resulting mixture was stirred at room temperature for 18 h, then quenched by saturated NaHCO₃ aqueous solution, and extracted with ethyl acetate (3*25mL), and the desired product 3af and 3a'f was isolated in the yield of 89% and 83% respectively; the aqueous phase was acidified with aqueous HCl solution until PH=1, and the white crystal was precipitation after filtration and desiccation Benzoic acid was obtained respectively (yield: 85%; 78%).
A proposed mechanism.

Scheme S3. A proposed mechanism.

Scheme S1: (1) Thiol/Benzeneselenol was oxidized into dimer under O₂ atmosphere. (2) Enolate A attacked the dimer with cleavage the S-S/Se-Se bond to afford intermediate B together with generating one molecule of R-SH/R-SeH, which could be oxidized to dimer and participated in the next reaction cycle. (3) The most electron deficient carbonyl group of intermediate B was attacked by the nucleophilic species (OH⁻) to afford intermediate C. (4) Intermediate C decomposed to afford the final product 3, with the release of one molecule of carboxylic anion simultaneously.

References
3ga
3ja
3ja
3ka
3ma
3na
3na
3ac
3ad
3ae
$3af'$
3af'
3ag
3ah
$\text{3ai}$

[Chemical结构图]

[核磁共振谱图]
3a'b
3a'b
3a'g
3a'i
5da
5da
5ea
5fa
5ha
5ha
5ia
5ka
5na
5oa

Chemical Shifts:
- H1: 7.4 ppm
- H2: 7.3 ppm
- H3: 7.2 ppm
- H4: 7.1 ppm
- H5: 7.0 ppm
- H6: 6.9 ppm
- H7: 6.8 ppm
- H8: 6.7 ppm
- H9: 6.6 ppm
- H10: 6.5 ppm
- H11: 6.4 ppm
- H12: 6.3 ppm
- H13: 6.2 ppm
- H14: 6.1 ppm
- H15: 6.0 ppm
- H16: 5.9 ppm
- H17: 5.8 ppm
- H18: 5.7 ppm
- H19: 5.6 ppm
- H20: 5.5 ppm
- H21: 5.4 ppm
- H22: 5.3 ppm
- H23: 5.2 ppm
- H24: 5.1 ppm
- H25: 5.0 ppm
- H26: 4.9 ppm
- H27: 4.8 ppm
- H28: 4.7 ppm
- H29: 4.6 ppm
- H30: 4.5 ppm
- H31: 4.4 ppm
- H32: 4.3 ppm
- H33: 4.2 ppm
- H34: 4.1 ppm
- H35: 4.0 ppm
- H36: 3.9 ppm
- H37: 3.8 ppm
- H38: 3.7 ppm
- H39: 3.6 ppm
- H40: 3.5 ppm
- H41: 3.4 ppm
- H42: 3.3 ppm
- H43: 3.2 ppm
- H44: 3.1 ppm
- H45: 3.0 ppm
- H46: 2.9 ppm
- H47: 2.8 ppm
- H48: 2.7 ppm
- H49: 2.6 ppm
- H50: 2.5 ppm
- H51: 2.4 ppm
- H52: 2.3 ppm
- H53: 2.2 ppm
- H54: 2.1 ppm
- H55: 2.0 ppm
- H56: 1.9 ppm
- H57: 1.8 ppm
- H58: 1.7 ppm
- H59: 1.6 ppm
- H60: 1.5 ppm
- H61: 1.4 ppm
- H62: 1.3 ppm
- H63: 1.2 ppm
- H64: 1.1 ppm
- H65: 1.0 ppm
- H66: 0.9 ppm
- H67: 0.8 ppm
- H68: 0.7 ppm
- H69: 0.6 ppm
- H70: 0.5 ppm
- H71: 0.4 ppm
- H72: 0.3 ppm
- H73: 0.2 ppm
- H74: 0.1 ppm
- H75: 0.0 ppm
- H76: -0.1 ppm
- H77: -0.2 ppm
Y3