Supporting information

Bifunctionalization of styrene through ring-opening-recombination strategy of phenylpropathiazole salt

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1. General information

All the obtained products were characterized by melting points (m.p), 1H-NMR and 13C-NMR. Solid products were characterized by melting points (m.p). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected; 1H-NMR and 13C \(^1\)H NMR spectra were obtained on Bruker-500 and referenced to 7.26 ppm and 77.16 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, \(\delta\)) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (Energy chemical, J&K Chemic, TCI, Fluka, Acros, SCRC), used without further purification. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

2. Typical procedure for the synthesis of the corresponding products

**Typical synthesis procedure of 3a.** Benzothiazole salt 1a (0.2 mmol, 1.0 equiv.) and styrene 2a (0.3 mmol, 1.5 equiv.) were first added into the test tube, then DTBP (0.3 mmol, 1.5 equiv.) was added, and finally 1 mL THF:H\(_2\)O = 9:1 was added. The reaction tube was put into the reactor to react at 80 °C, and the reaction was completed after 8 h. Then the target product was developed by chromatography in the
ratio of PE:EA = 3:1, and it was extracted with 30 ml of CH₂Cl₂:CH₃OH = 10:1 mixed solution, followed by rotary evaporation concentration and vacuum filtration to finally obtain the product 5a.

**General procedure synthesis of benzothiazole salt**

![Chemical structure of benzothiazole salt]

\[
\begin{align*}
R & \quad \stackrel{\text{S}}{\quad} \quad X^2+ \quad \stackrel{R-X^1}{\quad} \quad \text{(1.2 equiv.)} \quad \rightarrow \quad R \quad \text{N}^+ \quad \text{S} \quad X^2 \quad \text{X}^1- \\
X^1 &= \text{Br, I; } R = \text{alkyl, benzyl} \\
X^2 &= \text{H, Me}
\end{align*}
\]

Benzothiazoles (5 mmol), the corresponding halide (7.5 mmol, 1.5 equiv) and acetone (2 ml) were introduced in a round bottom flask, and it was stirred at 70 °C for 24 hours, until the solution was completely hardened. The reaction mixture was washed with small amount of diethyl ether and finally dried under vacuum to get 1.
3. Control experiments

$^1$H NMR spectrum of deuterated product of 6a

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D}
\]

The reaction is shown as follows:

\[
\text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D} \quad \text{D}
\]

The reaction conditions are as follows:

- NaOAc (1.5 equiv.)
- I$_2$ (0.5 equiv.)
- EtOH:D$_2$O = 9:1
$^1$H NMR spectrum of deuterated product of 7a
The O\(^{18}\) labeling experiment was analyzed by HRLP of 8a

\[
\text{NaOAc (1.5 equiv.)} + \text{I}_2 (0.5 \text{ equiv.}) \rightarrow \text{EtOH:H}_2\text{O}^{18}=4:1
\]

85\% \text{ H}_{2}^{18}\text{O}

Chemical Formula: C\(_{24}\)H\(_{25}\)NO\(^{18}\)OS

Exact Mass: 393.1648

C\(_{24}\)H\(_{25}\)NO\(^{18}\)O [M+H]\(^{+}\) calcd:394.1721 Found: 394.1724

Mass Analysis about Results of H\(_{2}\)\(^{18}\)O Experiment
$^1$H NMR spectrum of deuterated product of 10a

$$\text{Ph-S-S-Ph} + \text{Ph} \xrightleftharpoons{\text{NaOAc (1.5 equiv.)}} \xrightarrow{\text{I}_2 (0.5 \text{ equiv.})} \text{Ph-S-Ph}$$

EtOH:H$_2^{18}$O = 4:1

76%
$^{13}$C {1H} NMR spectrum of deuterated product of 10a
4. Single crystal X-ray diffraction of 3g

At -10 °C, a white and transparent 3g bulk single crystal was grown in the solution of n-hexane and chloroform. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-K α radiation (λ = 0.71073 Å). Data were collected at 296 K, using the ω- and φ - scans to a maximum θ value of 25.025 °. The data were refined by full-matrix least-squares techniques on F2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. An ORTEP representation of the structure is shown below.

Figure 1. ORTEP drawing of 3g with the numbering scheme.
<table>
<thead>
<tr>
<th>Identification code</th>
<th>3g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C25 H24 N2 O2 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>416.52</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P21/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 27.15(5) Å</td>
<td>a = 90°</td>
</tr>
<tr>
<td>b = 9.961(16) Å</td>
<td>b = 90.85(4)°</td>
</tr>
<tr>
<td>c = 8.810(15) Å</td>
<td>g = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2382(7) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
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</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.158 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>880</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.200 x 0.200 x 0.200 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.251 to 24.746°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-31&lt;=h&lt;=31, -11&lt;=k&lt;=11, -10&lt;=l&lt;=9</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>4065 [R(int) = 0.1075]</td>
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<td>Completeness to theta = 24.746°</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.052</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0789, wR2 = 0.1554</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1734, wR2 = 0.1893</td>
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<tr>
<td>Extinction coefficient</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.231 and -0.214 e.Å⁻³</td>
</tr>
</tbody>
</table>
5. Analytical data of the obtained compounds

(1)

\[ \text{1 -N-benzyl-N-}(2-\text{((2-ethoxy-2-phenylethyl)thio)phenyl})\text{formamide (3a). Red oil (36.9 mg, 95% yield); R}^f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); \]
\[ ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta 8.18 (s, 1H), 7.40 (s, 1H), 7.38 (s, 3H), 7.37 (s, 1H), 7.35 (dd, J = 3.0, 1.8 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.26-7.21 (m, 5H), 7.03 (t, J = 7.5 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.92 (s, 2H), 4.49 (dd, J = 8.4, 4.7 Hz, 1H), 3.49-3.36 (m, 2H), 3.33 (dd, J = 12.8, 8.4 Hz, 1H), 3.09 (dd, J = 12.9, 4.7 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H). \]
\[ ^{13}\text{C NMR (126 MHz, CDCl}_3\text{)} \delta 163.2, 140.9, 137.9, 137.4, 136.7, 130.0, 129.2, 129.0, 128.7, 128.4, 128.3, 128.1, 127.6, 126.6, 125.8, 80.6, 64.8, 48.5, 40.5, 15.3. \]
\[ \text{HRMS (ESI) m/z calcd for C}_{24}\text{H}_{25}\text{NO}_2\text{SNa [M+Na}^+\text{]}: 414.1498; \text{found: 414.1494.} \]

(2)

\[ \text{N-(4-chlorobenzyl)-N-}(2-\text{((2-ethoxy-2-phenylethyl)thio)phenyl})\text{formamide (3b). Yellow oil (30.1 mg, 71% yield); R}^f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); \]
\[ ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta 8.16 (s, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.38-7.33 (m, 5H), 7.28 (t, J = 10.0 Hz 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.87 (s, 2H), 4.47 (dd, J = 8.4, 4.7 Hz, 1H), 3.47-3.35 (m, 2H), 3.32 (dd, J = 12.8, 8.4 Hz, 1H), 3.09 (dd, J = 12.8, 4.7 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). \]
\[ ^{13}\text{C NMR (126 MHz,CDCl}_3\text{)} \delta 163.1, 140.9, 137.6, 137.5, 135.2, 133.5, 130.7, 130.0, 129.9, 129.1, 128.9, 128.7, 128.6, 128.3, 128.1, 126.6, 125.8, 80.7, 64.8, 47.9, 40.5, 15.2. \]
\[ \text{HRMS (ESI) m/z calcd for C}_{24}\text{H}_{24}\text{ClNO}_2\text{SNa [M+Na}^+\text{]}: 448.1109; \text{found: 448.1102.} \]
N-(4-bromobenzyl)-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide  (3c).
Yellow oil (33.9 mg, 72% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v);
1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H), 7.39 (s, 2H), 7.38-7.36 (m, 3H), 7.35 (d, J = 6.6 Hz, 2H), 7.33 (s, 1H), 7.28 (t, J = 5.0 Hz, 1H), 7.10 (d, J = 8.3 Hz, 2H), 7.06 (t, J = 8.3 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.84 (s, 2H), 4.47 (dd, J = 8.4, 4.7 Hz, 1H),
3.47-3.35 (m, 2H), 3.32 (dd, J = 12.8, 8.4 Hz, 1H), 3.09 (dd, J = 12.8, 4.7 Hz, 1H),
1.20 (t, J = 7.0 Hz, 3H).
13C NMR (126 MHz, Chloroform-d) δ 163.1, 140.9, 137.6, 137.4, 135.2, 133.5, 130.7, 129.9, 129.1, 128.7, 128.3, 128.1, 126.1, 125.8, 121.7, 80.6, 64.8, 47.9, 40.5, 15.3. HRMS (ESI) m/z calcd for C_{24}H_{24}BrNO_2SNa [M+Na]^+: 492.0603; found: 492.0599.

N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-(4-iodobenzyl)formamide  (3d).
Yellow oil (29.9 mg, 78% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v);
1H NMR (500 MHz, CDCl_3) δ 8.16 (s, 1H), 7.43-7.35 (m, 4H), 7.35 (d, J = 3.7 Hz, 2H), 7.28 (t, J = 5.0 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.07 (t, J = 8.3 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.87 (s, 2H), 4.47 (dd, J = 8.4, 4.7 Hz, 1H),
3.49-3.35 (m, 2H), 3.32 (dd, J = 12.8, 8.4 Hz, 1H), 3.09 (dd, J = 12.7, 4.7 Hz, 1H),
1.20 (t, J = 7.0 Hz, 3H).
13C NMR (126 MHz, CDCl_3) δ 163.1, 140.9, 137.6, 137.5, 135.2, 133.5, 130.7, 129.9, 129.1, 128.7, 128.3, 128.1, 126.1, 125.8, 80.6, 64.8, 47.9, 40.5, 15.2. HRMS (ESI) m/z calcd for C_{24}H_{24}INO_2SNa [M+Na]^+: 540.0465; found: 540.0472.
N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-(4-methylbenzyl)formamide (3e). Write solid (31.1 mg, 77% yield); m.p: 86.9-87.2 °C; \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 3/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 8.16 (s, 1H), 7.39 (dd, \( J = 14.6, 7.4 \) Hz, 4H), 7.35 (d, \( J = 7.1 \) Hz, 2H), 7.29-7.25 (t, \( J = 10 \) Hz, 1H), 7.11 (d, \( J = 7.6 \) Hz, 2H), 7.07 (d, \( J = 7.9 \) Hz, 3H), 6.75 (d, \( J = 7.8 \) Hz, 1H), 4.86 (s, 2H), 4.47 (dd, \( J = 8.4, 4.7 \) Hz, 1H), 3.48-3.35 (m, 2H), 3.31 (dd, \( J = 12.8, 8.4 \) Hz, 1H), 3.07 (dd, \( J = 12.8, 4.7 \) Hz, 1H), 2.32 (s, 3H), 1.21 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \): 163.1, 141.0, 138.0, 137.4, 137.2, 133.7, 130.1, 129.2, 129.1, 128.9, 128.7, 128.3, 128.1, 126.6, 125.7, 80.6, 64.8, 48.2, 40.5, 21.2, 15.2. HRMS (ESI) m/z calcd for C\(_{25}\)H\(_{27}\)NO\(_2\)SNa \([\text{M+Na}]^+\) : 428.1654; found: 428.1653.

N-(4-(tert-butyl)benzyl)-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide (3f). Yellow oil (31.4 mg, 70% yield); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 3/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 8.18 (s, 1H), 7.41-7.37 (m, 4H), 7.36-7.33 (m, 3H), 7.30 (d, \( J = 8.3 \) Hz, 2H), 7.28 (d, \( J = 9.0 \) Hz, 1H), 7.17 (d, \( J = 8.3 \) Hz, 2H), 7.06 (t, \( J = 7.6 \) Hz, 1H), 6.80 (d, \( J = 7.8 \) Hz, 1H), 4.87 (s, 2H), 4.49 (dd, \( J = 8.4, 4.7 \) Hz, 1H), 3.49 -3.37 (m, 2H), 3.33 (dd, \( J = 12.9, 8.4 \) Hz, 1H), 3.10 (dd, \( J = 12.8, 4.7 \) Hz, 1H), 1.31 (s, 9H), 1.21 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \): 163.2, 150.4, 141.0, 138.2, 137.4, 133.7, 130.1, 128.9, 128.7, 128.3, 128.1, 126.6, 125.7, 80.6, 64.8, 48.3, 40.5, 21.2, 15.3. HRMS (ESI) m/z calcd for C\(_{28}\)H\(_{33}\)NO\(_2\)SNa \([\text{M+Na}]^+\) : 470.2124; found: 470.2123.
N-(4-cyano benzyl)-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide (3g).
White solid (35 mg, 64% yield); m.p: 60.9-61.6 °C; R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.18 (s, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 7.0 Hz, 2H), 7.36 (d, J = 3.3 Hz, 3H), 7.34 (d, J = 6.5 Hz, 3H), 7.31 (d, J = 7.5 Hz, 1H), 7.12-7.05 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.90 (s, 2H), 4.46 (dd, J = 8.4, 4.6 Hz, 1H), 3.45-3.35 (m, 2H), 3.31 (dd, J = 12.8, 4.7 Hz, 1H), 3.10 (dd, J = 12.8, 4.7 Hz, 1H), 1.19 (t, J = 7.0 Hz, 3H). ^13C NMR (126 MHz, CDCl_3) δ 163.3, 142.0, 140.8, 137.5, 137.4, 132.3, 129.8, 129.6, 129.3, 128.7, 128.4, 128.3, 126.6, 126.0, 118.7, 111.5, 80.5, 64.8, 48.4, 40.4, 15.2. HRMS (ESI) m/z calcld for C_{25}H_{24}N_2O_2SNa [M+Na]^+: 439.1451; found: 439.1447.

N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-(4-methoxybenzyl)formamide (3h).
Yellow oil (32.8 mg, 78% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.14 (s, 1H), 7.39 (s, 1H), 7.40-7.34 (m, 3H), 7.35 (d, J = 1.4 Hz, 1H), 7.34 (d, J = 4.9 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 8.6 Hz, 2H), 7.04 (t, J = 7.3 Hz, 1H), 6.79 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 7.8 Hz, 1H), 4.83 (s, 2H), 4.47 (dd, J = 8.4, 4.7 Hz, 1H), 3.77 (s, 3H), 3.48-3.35 (m, 2H), 3.31 (dd, J = 12.8, 8.5 Hz, 1H), 3.08 (dd, J = 12.8, 4.7 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^13C NMR (126 MHz, CDCl_3) δ 163.1, 159.0, 140.9, 137.9, 137.5, 130.6, 130.1, 128.9, 128.9, 128.7, 128.3, 128.1, 126.6, 125.7, 113.7, 80.6, 64.8, 55.2, 47.8, 40.5, 15.2. HRMS (ESI) m/z calcld for C_{25}H_{27}NO_3SNa [M+Na]^+: 444.1603; found: 444.1600.
N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-(3-(trifluoromethyl)benzyl)formamide (3i). Yellow oil (35.3 mg, 67% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.19 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.2 Hz, 2H), 7.42-7.37 (m, 5H), 7.35 (d, J = 9.0 Hz, 2H), 7.29 (d, J = 3.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 4.92 (s, 2H), 4.48 (dd, J = 8.4, 4.7 Hz, 1H), 3.48-3.35 (m, 2H), 3.33 (dd, J = 12.8, 8.4 Hz, 1H), 3.10 (dd, J = 12.8, 4.7 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^13C NMR (126 MHz, CDCl_3) δ 163.19, 140.84, 137.65, 137.49, 137.45, 132.58, 130.69 (q, J = 32.2 Hz), 129.76, 129.23, 128.93, 128.69, 128.30, 128.11, 126.56, 125.84, 124.46 (q, J = 3.8 Hz), 123.99 (q, J = 272.4 Hz), 80.55, 64.77, 48.10, 40.39, 15.20. ^19F NMR (471 MHz, CDCl_3) δ -62.56. HRMS (ESI) m/z calcd for C_{25}H_{24}F_{3}NO_{2}SNa [M+Na]^+: 482.1372; found: 482.1370.

Methyl-4-((N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamido)methyl)benzoate (3j). Yellow oil (16.5 mg, 47% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.19 (s, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.41-7.34 (m, 5H), 7.34 (d, J = 7.3 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.8 Hz, 1H), 4.96 (s, 2H), 4.46 (dd, J = 8.4, 4.7 Hz, 1H), 3.91 (s, 3H), 3.48-3.34 (m, 3H), 3.31 (dd, J = 12.8, 8.4 Hz, 1H), 3.08 (dd, J = 12.8, 4.7 Hz, 1H), 1.19 (t, J = 7.0 Hz, 3H). ^13C NMR (126 MHz, CDCl_3) δ 166.9, 163.2, 141.8, 140.8, 137.6, 137.4, 129.8, 129.7, 129.4, 129.1, 128.7, 128.6, 128.3, 128.2, 126.6, 125.8, 80.6, 64.8, 52.1,
N-((1,1'-biphenyl)-4-ylmethyl)-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide (3k). Yellow oil (42.4 mg, 91% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.22 (s, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.7 Hz, 2H), 7.42-7.37 (m, 6H), 7.36 (s, 1H), 7.34 (d, J = 5.2 Hz, 2H), 7.32 (s, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 4.97 (s, 2H), 4.50 (dd, J = 8.4, 4.6 Hz, 1H), 3.50-3.37 (m, 2H), 3.35 (dd, J = 12.8, 8.4 Hz, 1H), 3.11 (dd, J = 12.8, 4.7 Hz, 1H), 1.22 (t, J = 7.0 Hz, 3H). ^13C NMR (126 MHz, CDCl_3) δ 163.2, 140.9, 140.7, 140.4, 138.0, 137.4, 135.8, 130.0, 129.7, 129.1, 128.8, 128.7, 128.3, 128.2, 127.4, 127.1, 127.1, 126.6, 125.8, 80.6, 64.8, 48.3, 40.6, 15.3. HRMS (ESI) m/z calcd for C_{30}H_{29}NO_2S Na [M+Na]^+: 490.1811; found: 490.1801.

N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-(naphthalen-2-ylmethyl)formamide (3l). Brown oil (32.4 mg, 74% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ^1H NMR (500 MHz, CDCl_3) δ 8.23 (s, 1H), 7.82 (d, J = 9.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.64 (s, 1H), 7.47 (d, J = 9.5 Hz, 2H), 7.40 (dd, J = 14.7, 7.5 Hz, 3H), 7.35 (d, J = 7.1 Hz, 4H), 7.25 (t, J = 7.7 Hz, 1H), 6.98 (t, J =
7.5 Hz, 1H), 6.74 (dd, J = 7.8, 1.4 Hz, 1H), 5.08 (s, 2H), 4.45 (dd, J = 8.4, 4.7 Hz, 1H),
3.47-3.35 (m, 2H), 3.33 (dd, J = 12.8, 8.4 Hz, 1H), 3.08 (dd, J = 12.8, 4.7 Hz, 1H),
1.21 (t, J = 7.0 Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 163.3, 140.9, 137.8, 137.4, 134.2, 133.2, 132.8, 130.0, 129.0, 128.7, 128.3, 128.2, 128.1, 128.1, 127.9, 127.7, 127.1, 126.6, 126.1, 126.0, 125.8, 80.6, 64.8, 48.6, 40.5, 15.2. HRMS (ESI) m/z calcd for C\(_{28}\)H\(_{27}\)NO\(_2\)SK [M+K]^+: 480.1394; found: 480.1384.

(13)

\[\text{N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-methylformamide (3m), Yellow oil (22.8 mg, 72% yield); R}_f = 0.5 \text{ (petroleum ether/ethyl acetate = 3/1, v/v);} \]
\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.12 (s, 1H), 7.40-7.34 (m, 2H), 7.36 (s, 1H), 7.36-7.28 (m, 4H), 7.22 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.7 Hz, 1H), 4.45 (dd, J = 8.4, 4.7 Hz, 1H), 3.44-3.34 (m, 2H), 3.30 (d, J = 8.4 Hz, 1H), 3.22 (s, 3H), 3.09 (dd, J = 13.0, 4.7 Hz, 1H),
1.17 (t, J = 7.0 Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 163.3, 140.9, 138.1, 137.7, 129.7, 129.7, 128.9, 128.6, 128.2, 127.9, 126.5, 125.8, 80.6, 64.7, 40.4, 32.8, 15.2. HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{21}\)NO\(_2\)SNa [M+Na]^+: 338.1185; found: 338.1182.

(14)

\[\text{N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)-N-ethylformamide (3n), Yellow oil (29.9 mg, 91% yield); R}_f = 0.5 \text{ (petroleum ether/ethyl acetate = 3/1, v/v);} \]
\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.06 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.35-7.34 (m, 3H), 7.31 (d, J = 5.7 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 4.45 (dd, J = 8.4, 4.7 Hz, 1H), 3.77 (s, 2H), 3.40 (d, J = 7.0 Hz, 1H), 3.39-3.28 (m, 2H), 3.10 (dd, J = 12.9, 4.7 Hz, 1H), 1.17 (t, J = 7.0 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 162.9, 140.9, 138.1, 137.7, 129.7, 128.9, 128.6, 128.2, 127.9, 126.5, 125.8, 80.6, 64.7, 40.3, 40.0, 15.2, 12.9. HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{23}\)NO\(_2\)SNa [M+Na]^+: 352.1342; found: 352.1338.
N-benzyl-N-(5-chloro-2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide  (3o).
Red oil (36.0 mg, 85% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ¹H NMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.43-7.36 (m, 3H), 7.35 (d, J = 5.6 Hz, 4H), 7.30 (d, J = 1.5 Hz, 1H), 7.27 (d, J = 4.1 Hz, 1H), 7.24 (t, J = 7.1 Hz, 3H), 6.80 (s, 1H), 4.87 (s, 2H), 4.45 (dd, J = 8.5, 4.5 Hz, 1H), 3.49-3.33 (m, 2H), 3.28 (dd, J = 12.8, 8.5 Hz, 1H), 3.04 (dd, J = 12.9, 4.6 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.8, 140.7, 139.0, 136.2 (d, J = 3.5 Hz), 131.2, 129.8, 129.4, 129.1, 128.7, 128.6, 128.4, 127.8, 126.5, 80.6, 64.8, 48.6, 40.8, 15.2. HRMS (ESI) m/z calcd for C₂₄H₂₄ClNO₂SNa [M+Na]^+: 448.1109; found: 448.1104.

N-benzyl-N-(5-bromo-2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide  (3p).
Red oil (32.3 mg, 69% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); ¹H NMR (500 MHz, CDCl₃) δ 8.16 (s, 1H), 7.43-7.35 (m, 4H), 7.35 (d, J = 7.1 Hz, 3H), 7.30 (s, 1H), 7.27 (s, 1H), 7.22 (t, J = 7.5 Hz, 3H), 6.93 (s, 1H), 4.90 (s, 2H), 4.45 (dd, J = 8.5, 4.6 Hz, 1H), 3.47-3.34 (m, 2H), 3.28 (dd, J = 12.9, 8.5 Hz, 1H), 3.04 (dd, J = 12.9, 4.6 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.8, 140.7, 139.1, 137.0, 136.2, 132.7, 131.9, 129.5, 129.2, 128.7, 128.6, 128.4, 127.8,
126.6, 118.6, 80.6, 64.8, 48.6, 40.6, 15.3. HRMS (ESI) m/z calcd for C_{24}H_{24}BrNO_{2}SNa [M+Na]^+: 492.0603; found: 492.0598.

(17)

N-benzyl-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)acetamide (3q). Yellow oil (36.2 mg, 89% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45-7.36 (m, 4H), 7.36 (d, $J = 6.2$ Hz, 1H), 7.30 (d, $J = 1.7$ Hz, 1H), 7.26 (d, $J = 5.4$ Hz, 4H), 7.26-7.20 (m, 2H), 6.97 (t, $J = 5.4$ Hz, 1H), 6.62 (d, $J = 7.7$ Hz, 1H), 5.65 (dd, $J = 14.3$, 11.1 Hz, 1H), 4.51 (dd, $J = 8.4$, 5.1 Hz, 1H), 3.96 (dd, $J = 14.4$, 7.5 Hz, 1H), 3.50 – 3.38 (m, 2H), 3.37 (d, $J = 12.8$ Hz, 1H), 3.14 (t, $J = 11.8$ Hz, 1H), 1.85 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.8 (d, $J = 13.3$ Hz), 141.0, 139.1 (d, $J = 3.2$ Hz), 137.9 – 137.3 (m), 130.1 (d, $J = 7.7$ Hz), 129.4 (d, $J = 3.2$ Hz), 128.8, 128.7, 128.3 (d, $J = 2.5$ Hz), 128.3, 127.3, 126.6 (d, $J = 2.3$ Hz), 126.2, 126.1, 125.1, 80.5 (d, $J = 6.6$ Hz), 64.8 (d, $J = 2.7$ Hz), 50.5, 39.3 (d, $J = 12.8$ Hz), 22.3 (d, $J = 2.7$ Hz), 15.2. HRMS (ESI) m/z calcd for C_{25}H_{27}NO_{2}SNa [M+Na]^+: 428.1655; found: 428.1652.

(18)

N-benzyl-N-(2-((2-ethoxy-2-(p-tolyl)ethyl)thio)phenyl)formamide (4a). Yellow oil (37.4 mg, 92% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) 8.19 (s, 1H), 7.36 (d, $J = 6.5$ Hz, 1H), 7.30 (d, $J = 14.1$ Hz, 1H), 7.30-7.24 (m, 5H), 7.27-7.19 (m, 4H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.9$ Hz, 1H), 4.89 (s, 2H), 4.45 (d, $J = 8.4$, 4.7 Hz, 1H), 3.48-3.35 (m, 2H), 3.33 (dd, $J = 12.8$, 4.7 Hz, 1H), 1.85 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.8 (d, $J = 13.3$ Hz), 141.0, 139.1 (d, $J = 3.2$ Hz), 137.9 – 137.3 (m), 130.1 (d, $J = 7.7$ Hz), 129.4 (d, $J = 3.2$ Hz), 128.8, 128.7, 128.3 (d, $J = 2.5$ Hz), 128.3, 127.3, 126.6 (d, $J = 2.3$ Hz), 126.2, 126.1, 125.1, 80.5 (d, $J = 6.6$ Hz), 64.8 (d, $J = 2.7$ Hz), 50.5, 39.3 (d, $J = 12.8$ Hz), 22.3 (d, $J = 2.7$ Hz), 15.2. HRMS (ESI) m/z calcd for C_{25}H_{27}NO_{2}SNa [M+Na]^+: 428.1655; found: 428.1652.
8.4 Hz, 1H), 3.08 (dd, \( J = 12.8, 4.8 \) Hz, 1H), 2.39 (s, 3H), 1.21 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 163.2, 138.0, 137.9, 137.9, 137.5, 136.7, 130.0, 129.4, 129.2, 129.0, 128.4, 128.0, 127.6, 126.6, 125.7, 80.4, 64.6, 48.5, 40.5, 21.3, 15.3. HRMS (ESI) m/z calcd for C\(_{25}\)H\(_{27}\)NO\(_2\)SNa \([M+Na]^+\) : 428.1654; found: 428.1653.

N-benzyl-N-(2-((2-ethoxy-2-(4-methoxyphenyl)ethyl)thio)phenyl)formamide (4b).
Red oil (36.9 mg, 88% yield); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 3/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.17 (s, 1H), 7.35 (d, \( J = 8.0 \) Hz, 1H), 7.30 (s, 1H), 7.27 (d, \( J = 6.1 \) Hz, 5H), 7.22 (dd, \( J = 7.0, 2.1 \) Hz, 2H), 7.04 (t, \( J = 7.5 \) Hz, 1H), 6.92 (d, \( J = 8.6 \) Hz, 2H), 6.74 (d, \( J = 7.8 \) Hz, 1H), 4.90 (s, 2H), 4.42 (dd, \( J = 8.3, 5.0 \) Hz, 1H), 3.84 (s, 3H), 3.45–3.34 (m, 2H), 3.32 (dd, \( J = 12.7, 8.3 \) Hz, 1H), 3.06 (dd, \( J = 12.7, 4.9 \) Hz, 1H), 1.19 (t, \( J = 7.0 \) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 163.2, 159.5, 137.9, 137.5, 136.7, 132.9, 130.0, 129.2, 129.0, 128.4, 128.0, 127.8, 127.6, 125.7, 114.0, 80.1, 64.5, 55.3, 48.5, 40.4, 15.2. HRMS (ESI) m/z calcd for C\(_{25}\)H\(_{27}\)NO\(_2\)SNa \([M+Na]^+\) : 444.1603; found: 444.1606.

N-benzyl-N-(2-((2-ethoxy-2-(4-fluorophenyl)ethyl)thio)phenyl)formamide (4c).
Brown oil (29.7 mg, 73% yield); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 3/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.17 (s, 1H), 7.37–7.31 (m, 2H), 7.32 (d, \( J = 5.4 \) Hz,
1H), 7.30-7.23 (m, 4H), 7.22 (dd, J = 7.4, 2.2 Hz, 2H), 7.11-7.03 (m, 3H), 6.76 (d, J = 7.8 Hz, 1H), 4.89 (s, 2H), 4.45 (dd, J = 8.1, 5.0 Hz, 1H), 3.46-3.33 (m, 2H), 3.29 (dd, J = 12.8, 8.2 Hz, 1H), 3.04 (dd, J = 12.8, 5.0 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 163.12, 162.58 (d, J = 246.4 Hz), 138.02, 137.16, 136.61, 130.02, 129.21, 128.65 (d, J = 16.0 Hz), 128.62 (d, J = 89.7 Hz), 128.41, 128.20, 127.60, 125.89, 115.57 (d, J = 21.5 Hz), 79.97, 64.76, 48.54, 40.48, 15.20. 19F NMR (471 MHz, CDCl3) δ -113.88. HRMS (ESI) m/z calcd for C24H24FNO2SNa [M+Na]+: 432.1403; found: 432.1411.

(21)

N-benzyl-N-(2-((2-(4-bromophenyl)-2-ethoxyethyl)thio)phenyl)formamide (4d).
Yellow oil (33.8 mg, 72% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 8.18 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 6.5 Hz, 1H), 7.28 (d, J = 6.8 Hz, 2H), 7.25 (d, J = 5.1 Hz, 3H), 7.22 (d, J = 7.4 Hz, 3H), 7.06 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 4.91 (s, 2H), 4.43 (dd, J = 8.1, 4.9 Hz, 1H), 3.45-3.35 (m, 2H), 3.27 (dd, J = 12.9, 8.1 Hz, 1H), 3.04 (dd, J = 12.9, 5.0 Hz, 1H), 1.19 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 163.1, 140.0, 138.1, 137.0, 136.6, 131.8, 130.0, 129.2, 129.0, 128.4, 128.3, 128.3, 127.6, 126.0, 122.1, 80.1, 64.9, 48.6, 40.3, 15.2. HRMS (ESI) m/z calcd for C24H24BrNO2SK [M+K]+: 508.0342; found: 508.0348.

(22)

N-benzyl-N-(2-((2-(4-chlorophenyl)-2-ethoxyethyl)thio)phenyl)formamide (4e).
Yellow oil (32.2 mg, 73% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 8.18 (s, 1H), 7.35 (t, J = 9.3 Hz, 3H), 7.30 (s, 2H), 7.26
(d, J = 7.2 Hz, 4H), 7.22 (d, J = 7.7 Hz, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 4.88 (s, 2H), 4.44 (dd, J = 8.1, 4.9 Hz, 1H), 3.45-3.35 (m, 2H), 3.28 (dd, J = 12.9, 8.1 Hz, 1H), 3.04 (dd, J = 12.9, 4.9 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 163.1, 139.4, 138.1, 137.1, 136.6, 134.0, 130.0, 129.2, 129.0, 128.9, 128.4, 128.3, 128.0, 127.6, 126.0, 80.0, 64.9, 48.6, 40.4, 15.2. HRMS (ESI) m/z calcd for C24H24ClNO2SNa [M+Na]+: 448.1108; found: 448.1114.

(23)

N-benzyl-N-(2-((2-(4-cyanophenyl)-2-ethoxyethyl)thio)phenyl)formamide (4f). Yellow oil (27.9 mg, 67% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 8.17 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.1 Hz, 1H), 7.30-7.22 (m, 4H), 7.25-7.18 (m, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 4.88 (s, 2H), 4.50 (dd, J = 7.8, 5.0 Hz, 1H), 3.47-3.36 (m, 2H), 3.25 (dd, J = 13.0, 7.9 Hz, 1H), 3.03 (dd, J = 13.0, 5.0 Hz, 1H), 1.20 (t, J = 7.0 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 163.0, 146.4, 138.3, 136.6, 136.5, 132.5, 130.1, 129.2, 129.0, 128.5, 128.4, 127.7, 127.3, 126.3, 118.6, 112.1, 80.1, 65.4, 48.6, 40.2, 15.2. HRMS (ESI) m/z calcd for C25H24N2O2SNa [M+Na]+: 439.1450; found: 439.1458.

(24)

N-benzyl-N-(2-((2-ethoxy-2-(4-(trifluoromethyl)phenyl)ethyl)thio)phenyl)formamide (4g). Yellow oil (18.4 mg, 40% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 8.18 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.33 (d, J =
7.9 Hz, 1H), 7.30-7.23 (m, 4H), 7.25-7.19 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 4.91 (s, 2H), 4.52 (dd, J = 8.1, 4.9 Hz, 1H), 3.42 (q, J = 7.0 Hz, 1.2 Hz, 2H), 3.28 (dd, J = 13.0, 8.1 Hz, 1H), 3.06 (dd, J = 13.0, 5.0 Hz, 1H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C\text{ NMR}\ (126\text{ MHz, CDCl}_3)\ \delta\ 163.09, 145.03, 138.14, 136.85, 136.56, 130.58\ (d,\ J = 32.8\text{ Hz}), 130.02, 129.21, 129.00, 128.39\ (d,\ J = 8.2\text{ Hz}), 127.62, 126.94, 126.10, 125.65\ (q,\ J = 3.7\text{ Hz}), 80.19, 65.16, 48.60, 40.35, 15.19. ^{19}\text{F\ NMR}\ (471\text{ MHz, Chloroform-d})\ \delta\ -62.52.\ HRMS\ (ESI)\ m/z\ \text{calcd for}\ C_{25}H_{24}F_3NO_2SNa\ [M+Na]^+:\ 482.1372;\ \text{found:}\ 482.1363.

(25)

\begin{center}
\begin{tikzpicture}[scale=0.5]
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\end{tikzpicture}
\end{center}

\textit{N-benzyl-N-(2-((2-ethoxy-2-(4-nitrophenyl)ethyl)thio)phenyl)formamide (4h).} Yellow oil (29.9 mg, 69% yield); R\text{\_f} = 0.5\ (petroleum\ ether/ethyl\ acetate = 3/1, v/v); \textit{^1H\ NMR} (500\ MHz, CDCl\textsubscript{3})\ \delta\ 8.25 (d,\ J = 8.7\ Hz, 2H), 8.18 (s, 1H), 7.54 (d,\ J = 8.5 Hz, 2H), 7.34 (d,\ J = 6.6\ Hz, 1H), 7.30 (d,\ J = 8.4\ Hz, 1H), 7.27 (d,\ J = 6.9\ Hz, 3H), 7.24-7.19 (m, 2H), 7.09 (t,\ J = 7.6\ Hz, 1H), 6.80 (d,\ J = 7.8\ Hz, 1H), 4.90 (s, 2H), 4.56 (dd,\ J = 7.8, 5.0\ Hz, 1H), 3.47-3.39 (m, 2H), 3.28 (dd,\ J = 13.0, 7.8\ Hz, 1H), 3.05 (dd,\ J = 13.0, 5.0\ Hz, 1H), 1.22 (t,\ J = 6.9\ Hz, 3H). \textit{^{13}C\ NMR}\ (126\text{ MHz, CDCl}_3)\ \delta\ 163.0, 148.4, 147.9, 138.3, 136.5, 136.5, 130.1, 129.2, 129.0, 128.5, 128.4, 127.7, 127.5, 126.3, 123.9, 80.0, 65.5, 48.7, 40.2, 15.2.\ HRMS\ (ESI)\ m/z\ \text{calcd for}\ C_{24}H_{22}N_2O_4S[K+]:\ 475.1088;\ \text{found:}\ 475.1090.

(26)

\begin{center}
\begin{tikzpicture}[scale=0.5]
% Diagram code here
\end{tikzpicture}
\end{center}

\textit{N-benzyl-N-(2-((2-butoxy-2-phenylethyl)thio)phenyl)formamide (4i).} Grey oil (34.5 mg, 71% yield); R\text{\_f} = 0.5\ (petroleum\ ether/ethyl\ acetate = 3/1, v/v); \textit{^1H\ NMR} (500\ MHz, CDCl\textsubscript{3})\ \delta\ 8.18 (s, 1H), 7.44-7.35 (m, 3H), 7.35 (d,\ J = 8.3\ Hz, 4H), 7.30-7.21 (m, 3H), 7.24 (d,\ J = 7.7\ Hz, 2H), 7.04 (t,\ J = 7.6\ Hz, 1H), 6.75 (d,\ J = 7.8 Hz,
1H, 4.91 (s, 2H), 4.46 (dd, J = 8.5, 4.6 Hz, 1H), 3.39 (dd, J = 9.1, 6.6 Hz, 1H), 3.37-3.28 (m, 2H), 3.08 (dd, J = 12.9, 4.6 Hz, 1H), 1.61-1.52 (m, 2H), 1.38 (dt, J = 14.9, 7.2 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). 13C NMR (126 MHz, CDCl3) δ 163.2, 141.0, 137.9, 137.5, 136.7, 130.0, 129.2, 129.0, 128.7, 128.4, 128.2, 128.0, 127.6, 126.6, 125.7, 80.9, 69.2, 48.5, 40.5, 31.8, 19.4, 13.9. HRMS (ESI) m/z calcd for C26H29NO2SNa [M+Na]+: 442.1811; found: 442.1820.

(27)

N-benzyl-N-(2-((2-methoxy-2-phenylethyl)thio)phenyl)formamide (4j). Grey oil (25.5 mg, 68% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 8.18 (s, 1H), 7.40 (d, J = 7.1 Hz, 2H), 7.39-7.28 (m, 4H), 7.30 (d, J = 12.7 Hz, 1H), 7.30-7.24 (m, 3H), 7.23 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 4.89 (s, 2H), 4.36 (dd, J = 8.4, 4.6 Hz, 1H), 3.31 (d, J = 4.4 Hz, 1H), 3.28 (s, 3H), 3.09 (dd, J = 12.9, 4.6 Hz, 1H). 13C NMR (126 MHz, CDCl3) δ 163.1, 140.2, 138.0, 137.3, 136.7, 130.1, 129.2, 129.0, 128.7, 128.4, 128.2, 127.6, 126.7, 125.8, 82.4, 57.1, 48.5, 40.5. HRMS (ESI) m/z calcd for C23H23NO2SNa [M+Na]+: 400.1341; found: 400.1348.

(28)

N-benzyl-N-(2-((2-methoxy-2-(p-tolyl)ethyl)thio)phenyl)acetamide (4k). Yellow oil (38.3 mg, 95% yield); Rf = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); 1H NMR (500 MHz, CDCl3) δ 7.31-7.25 (m, 4H), 7.26 (d, J = 1.1 Hz, 3H), 7.23 (d, J = 5.7 Hz, 4H), 6.98 (t, J = 6.4 Hz, 1H), 6.62 (dd, J = 7.7, 4.2 Hz, 1H), 5.66 (t, J = 14.5 Hz, 1H), 4.38 (dt, J = 8.3, 5.1 Hz, 1H), 3.96 (t, J = 14.5 Hz, 1H), 3.36 (dd, J = 7.8, 4.8 Hz, 1H), 3.28 (s, 3H), 3.12 (dd, J = 12.8, 4.8 Hz, 1H), 2.39 (s, 3H), 1.84 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 170.8 (d, J = 12.5 Hz), 139.2 (d, J = 3.4 Hz), 138.2, 137.7 (d, J = 4.1
(25) 137.2 (d, $J = 2.8$ Hz), 130.1 (d, $J = 6.9$ Hz), 129.5, 129.4, 129.3, 128.8, 128.3 (d, $J = 3.1$ Hz), 127.3, 126.7 (d, $J = 2.9$ Hz), 126.2 (d, $J = 8.2$ Hz), 125.1 (d, $J = 1.7$ Hz), 82.1 (d, $J = 6.4$ Hz), 57.0, 50.5, 39.2 (d, $J = 9.0$ Hz), 22.3 (d, $J = 2.4$ Hz), 21.2. HRMS (ESI) m/z calcd for C$_{25}$H$_{27}$NO$_2$SNa [M+Na]$^+$: 428.1654; found: 428.1661.

(29) N-benzyl-N-2-((1S,2R)-1-ethoxy-1-phenylpropan-2-yl)(thio)phenylformamide (4l). Yellow oil (24.3 mg, 60% yield); $R_f = 0.5$ (petroleum ether/ethyl acetate = 3/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.40-7.32 (m, 4H), 7.31 (d, $J = 6.8$ Hz, 1H), 7.26 (q, $J = 5.3$, 3.8 Hz, 4H), 7.21 (d, $J = 7.7$ Hz, 2H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 4.90 (s, 2H), 4.43 (d, $J = 5.1$ Hz, 1H), 3.53-3.44 (m, 2H), 3.40 (q, $J = 9.5$, 8.2 Hz, 1H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.24 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 163.1, 140.0, 139.2, 136.7, 136.2, 130.5, 130.1, 129.2, 128.8, 128.4, 128.3, 127.9, 127.5, 127.2, 126.4, 83.9, 65.2, 48.8, 48.7, 16.2, 15.2. HRMS (ESI) m/z calcd for C$_{25}$H$_{27}$NO$_2$SNa [M+Na]$^+$: 414.1498; found: 414.1505.

(30) 2-((2-(N-benzylformamido)phenyl)thio)-1-phenylethyl formate (5a). Yellow oil (21.1 mg, 54% yield); $R_f = 0.5$ (petroleum ether/ethyl acetate = 5/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15 (s, 1H), 8.12 (s, 1H), 7.45-7.39 (m, 2H), 7.39 (d, $J = 7.2$ Hz, 4H), 7.36 (d, $J = 8.9$ Hz, 1H), 7.33 (d, $J = 7.9$ Hz, 1H), 7.25 (t, $J = 7.2$ Hz, 3H), 7.22 (d, $J = 7.8$ Hz, 2H), 7.12 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 9.2$ Hz, 1H), 6.01 (dd, $J = 7.8$, 5.4 Hz, 1H), 4.85 (s, 2H), 3.40 (dd, $J = 13.9$, 8.0 Hz, 1H), 3.24 (dd, $J = 13.9$, 5.5 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 163.0, 159.9, 138.6, 137.9, 136.5, 135.5, 130.3, 129.2, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 127.7, 126.7, 73.7, 48.7, 38.1. HRMS (ESI) m/z calcd for C$_{23}$H$_{21}$NO$_3$SNa [M+Na]$^+$: 414.1134; found: 414.1132.
2-((2-(N-(4-cyanobenzyl)formamido)phenyl)thio)-1-phenylethyl formate (5b).
Yellow oil (23.7 mg, 57% yield); $R_f = 0.5$ (petroleum ether/ethyl acetate = 5/1, v/v); 
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 8.12 (s, 1H), 7.57 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.43-7.35 (m, 5H), 7.36 (d, $J = 5.4$ Hz, 2H), 7.33 (s, 1H), 7.16 (t, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 6.02 (dd, $J = 8.0$, 5.4 Hz, 1H), 4.87 (s, 2H), 3.43 (dd, $J = 13.9$, 8.0 Hz, 1H), 3.29 (dd, $J = 13.9$, 5.4 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.1, 159.9, 141.8, 138.0, 137.7, 135.5, 135.2, 132.3, 129.9, 129.8, 129.6, 129.1, 128.9, 128.6, 126.8, 126.7, 118.7, 111.6, 73.5, 48.5, 37.9. HRMS (ESI) m/z calcd for C$_{24}$H$_{20}$N$_2$O$_3$SNa [M+Na]$^+$: 439.1086; found: 439.1083.

2-((2-(N-(4-methylbenzyl)formamido)phenyl)thio)-1-phenylethyl formate (5c).
Yellow oil (24.3 mg, 60% yield); $R_f = 0.5$ (petroleum ether/ethyl acetate = 5/1, v/v); 
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13 (s, 1H), 8.12 (s, 1H), 7.43 (d, $J = 9.4$ Hz, 2H), 7.39 (d, $J = 3.2$ Hz, 3H), 7.37 (d, $J = 6.7$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 1H), 7.11 (d, $J = 11.5$ Hz, 3H), 7.08 (d, $J = 8.3$ Hz, 3H), 7.05 (d, $J = 7.0$ Hz, 1H), 6.81 (d, $J = 7.9$ Hz, 1H), 6.01 (dd, $J = 8.2$, 5.7 Hz, 1H), 4.81 (s, 2H), 3.39 (dd, $J = 13.8$, 8.1 Hz, 1H), 3.21 (dd, $J = 13.9$, 5.4 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.0, 159.9, 138.7, 137.9, 137.3, 135.4, 133.5, 130.3, 129.2, 129.1, 129.1, 129.0, 128.8, 128.8,
126.7, 126.7, 73.7, 48.4, 38.1, 21.1. HRMS (ESI) m/z calcd for C_{24}H_{23}NO_{3}SNa [M+Na]^+ : 428.1290; found: 428.1288.

(33)

2-((2-(N-benzylformamido)phenyl)thio)-1-phenylethyl acetate (5d). Yellow oil (24.7 mg, 61% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.16 (s, 1H), 7.45 (d, \(J = 8.0\) Hz, 1H), 7.39 (d, \(J = 5.9\) Hz, 2H), 7.36 (d, \(J = 8.8\) Hz, 3H), 7.33 (t, \(J = 7.8\) Hz, 2H), 7.26 (d, \(J = 7.5\) Hz, 2H), 7.22 (d, \(J = 7.8\) Hz, 2H), 7.10 (t, \(J = 7.6\) Hz, 1H), 6.79 (d, \(J = 7.8\) Hz, 1H), 5.92 (dd, \(J = 8.0, 5.4\) Hz, 1H), 4.86 (s, 2H), 3.39 (dd, \(J = 13.8, 8.1\) Hz, 1H), 3.22 (dd, \(J = 13.9, 5.4\) Hz, 1H), 2.09 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 170.1, 163.1, 138.6, 138.5, 136.5, 135.8, 130.2, 129.2, 129.2, 128.8, 128.7, 128.6, 128.5, 127.7, 126.6, 126.5, 74.0, 48.6, 38.2, 21.1. HRMS (ESI) m/z calcd for C_{24}H_{23}NO_{3}SNa [M+Na]^+ : 428.1290; found: 428.1286.

(34)

2-((2-(N-(4-(tert-butyl)benzyl)formamido)phenyl)thio)-1-phenylethyl acetate (5e). Yellow oil (22.6 mg, 49% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1H), 7.46 (d, \(J = 7.9\) Hz, 1H), 7.41-7.33 (m, 4H), 7.34 (d, \(J = 7.9\) Hz, 2H), 7.30 (d, \(J = 8.4\) Hz, 2H), 7.16 (d, \(J = 8.3\) Hz, 2H), 7.12 (t, \(J = 7.6\) Hz, 1H), 6.83 (d, \(J = 7.8\) Hz, 1H), 5.93 (dd, \(J = 8.0, 5.4\) Hz, 1H), 4.82 (s, 2H), 3.40 (dd, \(J = 13.8, 8.0\) Hz, 1H), 3.24 (dd, \(J = 13.8, 5.4\) Hz, 1H), 2.09 (s, 3H), 1.30 (s, 9H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 170.1, 163.1, 150.5, 138.7, 138.6, 135.8, 133.5, 130.3, 129.1, 128.8, 128.8, 128.7 (d, \(J = 1.8\) Hz), 126.64, 126.48, 125.32, 74.02, 48.38, 38.25, 34.51, 31.34, 21.07. HRMS (ESI) m/z calcd for C_{28}H_{31}NO_{3}SNa [M+Na]^+ : 484.1916; found: 484.1912.
2-((2-(N-methylformamido)phenyl)thio)-1-phenylethyl acetate (5f). Yellow oil (16.8 mg, 51% yield); R$_f$ = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.10 (s, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.38 (d, $J$ = 7.8 Hz, 2H), 7.36 (s, 1H), 7.34 (d, $J$ = 7.2 Hz, 3H), 7.27 (d, $J$ = 7.5 Hz, 1H), 7.17 (d, $J$ = 7.7 Hz, 1H), 5.88 (dd, $J$ = 8.0, 5.4 Hz, 1H), 3.41 (dd, $J$ = 13.9, 8.0 Hz, 1H), 3.24 (d, $J$ = 5.7 Hz, 1H), 3.20 (s, 3H), 2.06 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.1, 163.2, 140.6, 138.5, 135.3, 129.1, 129.0, 128.7, 128.6, 128.5, 127.1, 126.6, 74.0, 38.2, 32.9, 21.0. HRMS (ESI) m/z calcd for C$_{18}$H$_{19}$NO$_3$SNa [$M$+Na]$^+$ : 352.0977; found: 352.0975.

2-((2-(N-ethylformamido)phenyl)thio)-1-phenylethyl acetate (5g). Yellow oil (18.5 mg, 54% yield); R$_f$ = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.04 (s, 1H), 7.46 (d, $J$ = 7.9 Hz, 1H), 7.42-7.35 (m, 2H), 7.35 (d, $J$ = 4.4 Hz, 3H), 7.33 (d, $J$ = 3.5 Hz, 1H), 7.26 (t, $J$ = 7.6 Hz, 1H), 7.14 (d, $J$ = 7.7 Hz, 1H), 5.89 (dd, $J$ = 8.0, 5.5 Hz, 1H), 3.73 (s, 2H), 3.42 (dd, $J$ = 13.8, 8.0 Hz, 1H), 3.27 (dd, $J$ = 13.9, 5.5 Hz, 1H), 2.06 (s, 3H), 1.10 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.1, 162.9, 138.6, 138.6, 136.1, 129.9, 129.1, 128.7, 128.6, 128.3, 126.6, 126.5, 74.0, 40.1, 37.9, 21.0, 12.9. HRMS (ESI) m/z calcd for C$_{19}$H$_{21}$NO$_3$SNa [$M$+Na]$^+$ : 366.1134; found: 366.1133.
Methyl 4-((N-(2-((2-acetoxy-2-phenylethyl)thio)phenyl)formamido)methyl)benzoate (5h). Yellow oil (22.7 mg, 51% yield); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 5/1, v/v); \( \text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3 \) \( \delta \) 8.16 (s, 1H), 7.95 (d, \( J = 8.0 \) Hz, 2H), 7.45 (d, \( J = 8.0 \) Hz, 1H), 7.38 (d, \( J = 5.6 \) Hz, 2H), 7.38-7.30 (m, 4H), 7.30 (d, \( J = 8.3 \) Hz, 2H), 7.10 (t, \( J = 8.3 \) Hz, 1H), 6.77 (d, \( J = 7.8 \) Hz, 1H), 5.92 (dd, \( J = 8.0, 5.4 \) Hz, 1H), 4.89 (s, 2H), 3.92 (s, 3H), 3.40 (dd, \( J = 13.8, 8.1 \) Hz, 1H), 3.24 (dd, \( J = 13.8, 5.4 \) Hz, 1H), 2.08 (s, 3H). \( \text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3 \) \( \delta \) 170.1, 166.8, 163.1, 141.6, 138.5, 138.2, 135.8, 130.1, 129.8, 129.5, 129.3, 129.1, 128.8, 128.6, 126.6, 73.9, 52.1, 48.3, 38.1, 21.1. HRMS (ESI) m/z calcd for C\textsubscript{26}H\textsubscript{25}NO\textsubscript{5}SNa [M+Na]\(^+\) : 486.1345; found: 486.1343.

2-((2-(N-(naphthalen-2-ylmethyl)formamido)phenyl)thio)-1-phenylethyl acetate (5i). Yellow oil (25.0 mg, 55% yield); \( R_f = 0.5 \) (petroleum ether/ethyl acetate = 5/1, v/v); \( \text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3 \) \( \delta \) 8.21 (s, 1H), 7.82 (t, \( J = 4.4 \) Hz, 1H), 7.78 (d, \( J = 8.3 \) Hz, 2H), 7.63 (s, 1H), 7.50-7.43 (m, 2H), 7.43 (d, \( J = 9.6 \) Hz, 1H), 7.39 (d, \( J = 5.6 \) Hz, 3H), 7.36 (t, \( J = 5.4 \) Hz, 3H), 7.31 (t, \( J = 7.7 \) Hz, 1H), 7.04 (t, \( J = 7.6 \) Hz, 1H), 6.77 (d, \( J = 7.9 \) Hz, 1H), 5.94 (dd, \( J = 8.1, 5.4 \) Hz, 1H), 5.03 (s, 2H), 3.40 (dd, \( J = 13.8, 8.1 \) Hz, 1H), 3.23 (dd, \( J = 13.8, 5.4 \) Hz, 1H), 2.09 (s, 3H). \( \text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3 \) \( \delta \) 170.1, 163.2, 138.6, 138.4, 135.8, 134.1, 133.2, 132.8, 130.2, 129.2, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 127.7, 127.1, 126.6, 126.5, 126.1, 126.0, 74.0, 48.7, 38.2, 21.1. HRMS (ESI) m/z calcd for C\textsubscript{28}H\textsubscript{25}NO\textsubscript{3}SNa [M+Na]\(^+\) : 478.1447; found: 478.1444.
2-((2-(N-benzylformamido)phenyl)thio)-1-(4-chlorophenyl)ethyl acetate (5j).
Yellow oil (26.3 mg, 60% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); 
^1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.5 Hz, 3H), 7.34-7.28 (m, 3H), 7.26 (d, J = 7.1 Hz, 2H), 7.21 (d, J = 7.7 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 5.86 (dd, J = 7.8, 5.6 Hz, 1H), 4.86 (s, 2H), 3.34 (dd, J = 13.8, 7.8 Hz, 1H), 3.16 (dd, J = 13.8, 5.6 Hz, 1H), 2.08 (s, 3H). ^13C NMR (126 MHz, CDCl_3) δ 170.0, 163.1, 138.6, 137.0, 136.4, 135.5, 134.6, 130.2, 129.2, 129.2, 128.9, 128.8, 128.5, 128.1, 127.7, 126.7, 73.4, 48.7, 38.1, 21.0. HRMS (ESI) m/z calcd for C_{24}H_{22}ClNO_3SNa [M+Na]^+: 462.0901; found: 462.0891.

2-((2-(N-benzylformamido)phenyl)thio)-1-(4-bromophenyl)ethyl acetate (5k).
Yellow oil (29.0 mg, 60% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); 
^1H NMR (500 MHz, CDCl_3) δ 8.15 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 8.2 Hz, 3H), 7.24-7.18 (m, 3H), 7.12 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.9 Hz, 1H), 5.84 (dd, J = 7.8, 5.6 Hz, 1H), 4.86 (s, 2H), 3.34 (dd, J = 13.8, 7.8 Hz, 1H), 3.16 (dd, J = 13.8, 5.6 Hz, 1H), 2.08 (s, 3H). ^13C NMR (126 MHz, CDCl_3) δ 170.0, 163.1, 138.6, 137.0, 136.4, 135.5, 131.9, 130.2, 129.2, 129.2, 128.8, 128.5, 128.4, 127.7, 126.7, 122.8, 73.4, 48.7, 38.1, 21.0. HRMS (ESI) m/z calcd for C_{24}H_{22}BrNO_3SNa [M+Na]^+: 506.0395; found:506.0394.

2-((2-(N-benzylformamido)phenyl)thio)-1-(p-tolyl)ethyl acetate (5l). Yellow oil (22.6 mg, 54% yield); R_f = 0.5 (petroleum ether/ethyl acetate = 5/1, v/v); 
^1H NMR
(500 MHz, CDCl$_3$) $\delta$ 8.15 (s, 1H), 7.46 (d, $J$ = 8.1 Hz, 1H), 7.34 (d, $J$ = 7.6 Hz, 1H), 7.29-7.24 (m, 3H), 7.25 (s, 2H), 7.21 (t, $J$ = 8.4 Hz, 4H), 7.09 (t, $J$ = 7.6 Hz, 1H), 6.78 (d, $J$ = 7.8 Hz, 1H), 5.89 (dd, $J$ = 8.0, 5.5 Hz, 1H), 4.85 (s, 2H), 3.39 (dd, $J$ = 13.8, 8.0 Hz, 1H), 3.21 (dd, $J$ = 13.8, 5.6 Hz, 1H), 2.37 (s, 3H), 2.07 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.1, 163.1, 138.6, 138.4, 136.4, 135.9, 135.6, 130.2, 129.4, 129.2, 128.4, 127.6, 126.6, 126.4, 73.9, 48.6, 38.1, 21.2, 21.1. HRMS (ESI) m/z calcd for C$_{25}$H$_{25}$NO$_3$S [M]$^+$: 442.1447; found: 442.1440.

N-benzyl-N-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide-d (6a). Yellow oil (31.4 mg, 82% yield); $R_f$ = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (s, 0.19H), 7.41 (d, $J$ = 7.2 Hz, 1H), 7.38 (d, $J$ = 7.4 Hz, 3H), 7.35 (d, $J$ = 5.5 Hz, 2H), 7.27 (d, $J$ = 1.9 Hz, 1H), 7.26 (d, $J$ = 2.3 Hz, 2H), 7.23 (dd, $J$ = 7.4, 2.1 Hz, 2H), 7.04 (t, $J$ = 7.6 Hz, 1H), 6.75 (d, $J$ = 7.8 Hz, 1H), 4.91 (s, 2H), 4.47 (dd, $J$ = 8.4, 4.7 Hz, 1H), 3.49-3.34 (m, 2H), 3.32 (dd, $J$ = 12.8, 8.4 Hz, 1H), 3.08 (dd, $J$ = 12.8, 4.7 Hz, 1H), 1.21 (t, $J$ = 7.0 Hz, 3H). HRMS (ESI) m/z calcd for C$_{24}$H$_{24}$DNO$_3$SNa [M+Na]$^+$: 415.1560; found: 415.1557.

N-benzyl-N-((2-(methoxy-d3)-2-phenylethyl)thio)phenyl)formamide-d (7a).
Yellow oil (30.5 mg, 80% yield); R$_f$ = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (s, 0.16H), 7.40 (d, J = 7.2 Hz, 2H), 7.38-7.31 (m, 4H), 7.30 (d, J = 12.3 Hz, 1H), 7.27 (d, J = 7.4 Hz, 3H), 7.22 (d, J = 7.7 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 4.92 (s, 2H), 4.36 (dd, J = 8.4, 4.6 Hz, 1H), 3.31 (dd, J = 12.9, 8.5 Hz, 1H), 3.08 (dd, J = 12.9, 4.7 Hz, 1H), 0.90 (t, J = 6.8 Hz, 0.67H). HRMS (ESI) m/z calcd for C$_{23}$H$_{19}$D$_4$NO$_2$SNa [M+Na]$^+$: 404.1592; found: 404.1598.

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N-benzyl-N-(2-((2-ethoxy-2-phenylethyl)thio)phenyl)formamide-$^{18}$O (8a). Yellow oil (33.4 mg, 85% yield); R$_f$ = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v); HRMS (ESI) m/z calcd for C$_{24}$H$_{25}$NO$_2$SNa [M+H]$^+$:394.1721; found: 394.1724

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(2-ethoxy-2-phenylethyl)(phenyl)sulfane (10a). Yellow oil (19.6 mg, 76% yield); R$_f$ = 0.5 (petroleum ether/ethyl acetate = 3/1, v/v);$^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 (s, 2H), 7.38 (d, J = 3.6 Hz, 3H), 7.36 (d, J = 4.2 Hz, 1H), 7.31 (q, J = 7.5 Hz, 3H), 7.21 (t, J = 7.3 Hz, 1H), 4.45 (dd, J = 8.1, 5.1 Hz, 1H), 3.45 (dd, J = 9.3, 7.1 Hz, 1H), 3.42-3.36 (m, 2H), 3.16 (dd, J = 13.2, 5.1 Hz, 1H), 1.22 (t, J = 7.0 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 141.3, 136.8, 129.3, 128.9, 128.5, 128.0, 126.7, 126.0, 80.7, 64.7, 41.6, 15.3. HRMS (ESI) m/z calcd for C$_{31}$H$_{28}$N$_2$O$_2$SNa [M+H]$^+$: 259.1151; found: 259.1149.
6. NMR spectra of products

$^1$H NMR spectra of 3a (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3a (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3b (500 MHz, CDCl$_3$)
$^1$H NMR spectra of 3b (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3c (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3c (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3d (500 MHz, CDCl$_3$)
$^{13}$C $\{^1H\}$ NMR spectra of 3d (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3e (500 MHz, CDCl$_3$)
$^{13}$C $\{1H\}$ NMR spectra of 3e (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3f (500 MHz, CDCl$_3$)
$^{13}$C \{1H\} NMR spectra of 3f (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3g (500 MHz, CDCl$_3$)
$^{13}$C-{$^{1}H$} NMR spectra of 3g (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3h (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3h (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3i (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3i (126 MHz, CDCl$_3$)
$^{19}$F NMR spectra of 3i (471 MHz, CDCl$_3$)
$^1$H NMR spectra of 3j (500 MHz, CDCl$_3$)
$^{13}$C $\{^{1}H\}$ NMR spectra of 3j (126 MHz, CDCl$_3$)
$^1{H}$ NMR spectra of 3k (500 MHz, CDCl$_3$)
$^{13}$C {$^1$H} NMR spectra of 3k (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3l (500 MHz, CDCl$_3$)

$^{13}$C (1H) NMR spectra of 3l (126 MHz, CDCl$_3$)
$^{1}H$ NMR spectra of 3m (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3m (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3n (500 MHz, CDCl$_3$)

$^{13}$C {$^1$H} NMR spectra of 3n (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3o (500 MHz, CDCl$_3$)
$^{13}$C (1H) NMR spectra of 3o (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3p (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3p (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 3q (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 3q (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4a (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 4a (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4b (500 MHz, CDCl$_3$)
$^{13}$C \{1H\} NMR spectra of 4b (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4c (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 4c (126 MHz, CDCl$_3$)
$^{19}$F NMR spectra of 4c (471 MHz, CDCl$_3$)
$^1$H NMR spectra of 4d (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 4d (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4e (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 4e (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4f (500 MHz, CDCl$_3$)
$^{13}$C{1H} NMR spectra of 4f (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4g (500 MHz, CDCl$_3$)
$^{13}$C {^1H} NMR spectra of 4g (126 MHz, CDCl$_3$)
$^{19}$F NMR spectra of 4g (471 MHz, CDCl$_3$)
$^1$H NMR spectra of 4h (500 MHz, CDCl$_3$)
\(^{13}\)C\{}^{1H}\} NMR spectra of 4h (126 MHz, CDCl\textsubscript{3})
\textsuperscript{1}H NMR spectra of 4i (500 MHz, CDCl\textsubscript{3})
$^{13}$C {1H} NMR spectra of 4i (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4j (500 MHz, CDCl$_3$)
$^{13}$C $^1$H NMR spectra of 4j (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4k (500 MHz, CDCl$_3$)
$^{13}$C $\{1H\}$ NMR spectra of 4k (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 4l (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 4l (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5a (500 MHz, CDCl$_3$)
$^{13}$C {$^1$H} NMR spectra of 5a (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5b (500 MHz, CDCl$_3$)
$^{13}$C $\{1H\}$ NMR spectra of 5b (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5c (500 MHz, CDCl$_3$)
$^{13}$C {$^{1}H$} NMR spectra of 5c (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5d (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 5d (126 MHz, CDCl$_3$)
"\(^1\)H NMR spectra of 5e (500 MHz, CDCl\(_3\))"
$^{13}$C NMR spectra of 5e (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5f (500 MHz, CDCl$_3$)
$^{13}$C $\{1H\}$ NMR spectra of 5f (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5g (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 5g (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5h (500 MHz, CDCl$_3$)
$^{13}$C–$^{1}$H NMR spectra of 5h (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5i (500 MHz, CDCl$_3$)
$^{13}$C \{1H\} NMR spectra of 5i (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5j (500 MHz, CDCl$_3$)
$^{13}$C {1H} NMR spectra of 5j (126 MHz, CDCl$_3$)
$^1$H NMR spectra of 5k (500 MHz, CDCl$_3$)
$^{13}\text{C} \{1\text{H}\} \text{ NMR spectra of 5k (126 MHz, CDCl}_3\}$
$^1$H NMR spectra of 5i (500 MHz, CDCl$_3$)
$^{13}$C \{1H\} NMR spectra of 5i (126 MHz, CDCl$_3$)