Supporting Information

Synthesis of Dithioacetals via Gold-Catalyzed Hydrothiolation of Vinyl Sulfides

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1. General Information

All reactions were conducted under a nitrogen atmosphere with oven-dried glassware and standard Schlenk or vacuum line techniques. Oil baths were used as a heat source for a reaction. All solutions were handled under nitrogen and transferred via syringe. Anhydrous solvents were purchased and stored over activated 4 Å molecular sieves. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar or TCI. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plate and visualized by shortwave ultraviolet light as well as by treatment with basic solution of potassium permanganate. Flash chromatography was performed with Silica Flash P60 silica gel (230 – 400 mesh). $^1$H and $^{13}$C NMR spectra were obtained using an Agilent 400-MR DD2 Fourier-transform NMR spectrometer at 400 and 100 MHz, respectively. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The residual solvent signals were taken as the reference (CDCl$_3$, 7.26 ppm for $^1$H NMR spectra and CDCl$_3$, 77.0 ppm for $^{13}$C NMR spectra). The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). High resolution mass analysis was performed with JOEL AccuTOF 4G+ DART-HRMS and JMS-700. Systematic nomenclature for the compounds follows the numbering system as defined by IUPAC with assistance from CS Chemdraw® software.
2. Optimization of reaction conditions

An oven-dried reaction tube equipped with a magnetic stirrer bar, was charged with catalyst (x mol%) and degassed with N₂ then added the solvent (2 mL) and followed by the addition of benzenethiol 2a (1.5 equiv., 0.3 mmol) and methyl 3-(decylthio)acrylate 1a (0.2 mmol). The reaction mixture was stirred at room temperature according to optimization table. After the reaction completion, the reaction was filtered and solvent had been removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford desired product methyl 3-(decylthio)-3-(phenylthio)propanoate 3aa.

Table S1. Optimization of the reaction conditions

<table>
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<tr>
<th>Entry</th>
<th>Cat (X mol%)</th>
<th>Solvent</th>
<th>% Yield of 3aaa</th>
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<tr>
<td>1</td>
<td>AgOTf (5 mol%)</td>
<td>DCE</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>AgNTf₂ (5 mol%)</td>
<td>DCE</td>
<td>-</td>
</tr>
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<td>3</td>
<td>JohnPhosAuOTf (5 mol%)</td>
<td>DCE</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>IPrAu(MeCN)BF₄ (5 mol%)</td>
<td>DCE</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>SIPrAuCl (5 mol%)</td>
<td>DCE</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>NaAuCl₄ (5 mol%)</td>
<td>DCE</td>
<td>-</td>
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<tr>
<td>7</td>
<td>AuCl₃ (5 mol%)</td>
<td>DCE</td>
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<td>8</td>
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<td>9</td>
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<td>14</td>
<td>PPh₃AuNTf₂ (1 mol%)</td>
<td>Toluene</td>
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<tr>
<td>16</td>
<td>-</td>
<td>DCE</td>
<td>-</td>
</tr>
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</table>
3. General procedure and characterization of Dithioacetals

\[
\begin{align*}
\text{R}^1\text{R}^2\text{R}^3\text{S} & + \text{R}^4\text{SH} \xrightarrow{\text{PPh}_3\text{AuNTf}_2 (1 \text{ mol\%})} \text{DCE (0.1 M)} \rightarrow \\
\text{R}^1\text{R}^2\text{R}^3\text{S} & \text{R}^4\text{S}
\end{align*}
\]

*General procedure (A)*: An oven-dried reaction tube equipped with a magnetic stirrer bar, was charged with PPh$_3$AuNTf$_2$ (1 mol%) and degassed with N$_2$ then added DCE (0.1 M, 2 mL) and followed by the addition of thiol (1.5 equiv., 0.3 mmol) and vinyl sulfide (0.2 mmol). The reaction mixture was stirred until alkene was consumed. After the reaction completion, the reaction mixture was filtered and solvent had been removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford dithioacetal derivatives.

**Methyl 3-(decylthio)-3-(phenylthio)propanoate (3aa)**

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and benzenethiol 2a at r.t., 2 h, 93% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, J = 6.9 Hz, 2H), 7.38 – 7.30 (m, 3H), 4.50 (t, J = 7.5 Hz, 1H), 3.69 (s, 3H), 2.88 – 2.66 (m, 4H), 1.67 – 1.56 (m, 2H), 1.42 – 1.23 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.5, 133.7, 133.0, 128.9, 128.2, 51.9, 50.3, 41.4, 31.9, 31.7, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for C$_{20}$H$_{32}$NaO$_2$S$_2$ $^+$ ([M+Na]$^+$)
Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate (3ab)

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{Br} & \quad \text{S} \\
\text{C}_{10}\text{H}_{21} & \quad \text{O}
\end{align*}
\]

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 2-bromobenzenethiol 2b at r.t., 2 h, 93% yield; Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.60 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.34 – 7.25 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 4.68 (dd, J = 9.0, 5.6 Hz, 1H), 3.67 (s, 3H), 2.90 (dd, J = 16.0, 5.6 Hz, 1H), 2.86 – 2.77 (m, 2H), 2.77 – 2.67 (m, 1H), 1.61 (dd, J = 13.4, 5.8 Hz, 2H), 1.42 – 1.23 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 170.4, 135.3, 133.6, 133.4, 129.0, 127.9, 127.2, 52.0, 49.1, 41.3, 31.9, 31.7, 29.5, 29.5, 29.3, 29.2, 29.1, 28.8, 22.7, 14.1; HRMS (ESI) m/z calcd. for C\textsubscript{20}H\textsubscript{31}BrNaO\textsubscript{2}S\textsubscript{2}\(^{[\text{M+Na}]}\) 469.0841, found 469.0845.

Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate (3ac)

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{Br} & \quad \text{S} \\
\text{C}_{10}\text{H}_{21} & \quad \text{O}
\end{align*}
\]

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-bromobenzenethiol 2c at r.t., 2 h, 95% yield; Colorless oil; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.45 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.47 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.85 – 2.71 (m, 3H), 2.72 – 2.63 (m, 1H), 1.66 – 1.53 (m, 2H), 1.40 – 1.26 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 170.4, 135.2, 132.0, 131.9, 122.7, 52.0, 50.4, 41.2, 31.8, 31.6, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for C\textsubscript{20}H\textsubscript{31}BrNaO\textsubscript{2}S\textsubscript{2}\(^{[\text{M+Na}]}\) 469.0841, found 469.0834.

Methyl 3-((4-chlorophenyl)thio)-3-(decylthio)propanoate (3ad)
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-chlorobenzenethiol 2d at r.t., 2 h, 94% yield; Colorless oil; $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.82 – 2.72 (m, 3H), 2.71 – 2.63 (m, 1H), 1.59 (p, J = 7.5, 7.1 Hz, 2H), 1.40 – 1.25 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}$$C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 135.1, 134.6, 131.2, 129.1, 52.0, 50.6, 41.2, 31.8, 31.6, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for C$_{20}$H$_{31}$ClNaO$_2$S$_2^+ ([M+Na]$^+$) 425.1346, found 425.1344

**Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate (3ae)**

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 2-methoxybenzenethiol 2e at r.t., 2 h, 79% yield; Colorless oil; $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.42 (m, 1H), 7.32 – 7.25 (m, 1H), 6.94 – 6.87 (m, 2H), 4.67 (dd, J = 9.1, 5.6 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H), 2.88 – 2.80 (m, 2H), 2.76 – 2.66 (m, 2H), 1.66 – 1.57 (m, 2H), 1.41 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}$$C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 159.1, 134.9, 129.8, 121.5, 120.9, 110.9, 55.7, 51.8, 47.9, 41.5, 31.9, 31.5, 29.5, 29.5, 29.3, 29.2, 29.2, 28.9, 22.6, 14.1; HRMS (ESI) m/z calcd. for C$_{21}$H$_{34}$NaO$_3$S$_2^+ ([M+Na]$^+$) 421.1842, found 421.1842

**Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate (3af)**

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-chlorobenzenethiol 2d at r.t., 2 h, 94% yield; Colorless oil; $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.82 – 2.72 (m, 3H), 2.71 – 2.63 (m, 1H), 1.59 (p, J = 7.5, 7.1 Hz, 2H), 1.40 – 1.25 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}$$C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.3, 135.1, 134.6, 131.2, 129.1, 52.0, 50.6, 41.2, 31.8, 31.6, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for C$_{20}$H$_{31}$ClNaO$_2$S$_2^+ ([M+Na]$^+$) 425.1346, found 425.1344

**Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate (3ae)**

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 2-methoxybenzenethiol 2e at r.t., 2 h, 79% yield; Colorless oil; $^1$$H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.42 (m, 1H), 7.32 – 7.25 (m, 1H), 6.94 – 6.87 (m, 2H), 4.67 (dd, J = 9.1, 5.6 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H), 2.88 – 2.80 (m, 2H), 2.76 – 2.66 (m, 2H), 1.66 – 1.57 (m, 2H), 1.41 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}$$C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 159.1, 134.9, 129.8, 121.5, 120.9, 110.9, 55.7, 51.8, 47.9, 41.5, 31.9, 31.5, 29.5, 29.5, 29.3, 29.2, 29.2, 28.9, 22.6, 14.1; HRMS (ESI) m/z calcd. for C$_{21}$H$_{34}$NaO$_3$S$_2^+ ([M+Na]$^+$) 421.1842, found 421.1842

**Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate (3af)**
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-methoxybenzenethiol 2f at r.t., 2 h, 81% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.35 (t, J = 7.5 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.84 – 2.74 (m, 2H), 2.71 – 2.64 (m, 2H), 1.60 (ddt, J = 14.9, 9.4, 3.6 Hz, 2H), 1.44 – 1.22 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 160.2, 136.9, 122.7, 114.4, 55.3, 51.9, 51.1, 41.2, 31.9, 31.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.6, 14.1; HRMS (ESI) m/z calcd. for C$_{21}$H$_{34}$NaO$_3$S$_2^+ ([M+Na]^+) 421.1842, found 421.1842

Methyl 3-(decylthio)-3-(p-tolylthio)propanoate (3ag)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-methylbenzenethiol 2g at r.t., 2 h, 68% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 4.43 (t, J = 7.3 Hz, 1H), 3.69 (s, 3H), 2.85 – 2.76 (m, 2H), 2.74 – 2.64 (m, 2H), 2.35 (s, 3H), 1.66 – 1.58 (m, 2H), 1.38 – 1.26 (m, 14H), 0.88 (t, J = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 138.6, 134.4, 129.7, 129.0, 51.9, 50.6, 41.3, 31.9, 31.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 21.2, 14.1; HRMS (ESI) m/z calcd. for C$_{21}$H$_{34}$NaO$_2$S$_2^+ ([M+Na]^+) 405.1892, found 405.1892

Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3ah)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and 4-(trifluoromethyl)benzenethiol 2h at r.t., 2 h, 88% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (s, 4H), 4.62 (dd, J = 7.9, 6.8 Hz, 1H), 3.70 (s, 3H), 2.91 – 2.77 (m, 2H), 2.81 – 2.72 (m, 1H), 2.73 – 2.63 (m, 1H), 1.60 (dt, J = 14.8, 6.8 Hz, 2H), 1.44 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.2, 138.7, 131.9, 129.54 (q, J = 32.7
Hz), 125.71 (q, J = 3.7 Hz), 123.91 (q, J = 272.2 Hz), 52.0, 49.6, 41.3, 31.9, 31.7, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for C_{21}H_{31}FNaO_2S^2⁺ ([M+Na]⁺) 459.1610, found 459.1608

**Methyl 3-(decylthio)-3-(naphthalen-2-ythio)propanoate (3ai)**

![Diagram](attachment:image.png)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and naphthalene-2-thiol 2i at r.t., 2 h, 76% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (s, 1H), 7.86 – 7.75 (m, 3H), 7.59 – 7.53 (m, 1H), 7.49 (dt, J = 9.4, 4.8 Hz, 2H), 4.61 (dd, J = 8.2, 6.6 Hz, 1H), 3.67 (s, 3H), 3.03 – 2.59 (m, 4H), 1.61 (p, J = 8.1 Hz, 2H), 1.43 – 1.22 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 133.5, 132.7, 130.6, 130.4, 128.5, 127.7, 127.7, 126.6, 126.6, 52.0, 50.3, 41.5, 31.9, 31.8, 29.5, 29.5, 29.3, 29.2, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for C_{24}H_{34}NaO_2S^2⁺ ([M+Na]⁺) 441.1892, found 441.1893

**Methyl 3-(decylthio)-3-(thiophen-2-ythio)propanoate (3aj)**

![Diagram](attachment:image.png)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and thiophene-2-thiol 2j at 50 °C, overnight, 43% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, J = 5.3 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.08 – 7.00 (m, 1H), 4.32 (t, J = 7.1 Hz, 1H), 3.71 (s, 3H), 2.83 (td, J = 13.9, 12.2, 7.0 Hz, 2H), 2.69 (dd, J = 14.9, 7.7 Hz, 2H), 1.63 (dt, J = 13.8, 6.8 Hz, 2H), 1.46 – 1.23 (m, 14H), 0.88 (t, J = 6.0 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.4, 136.7, 131.3, 129.9, 127.6, 52.3, 52.0, 40.9, 31.9, 31.9, 29.5, 29.5, 29.3, 29.2, 29.0, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for C_{18}H_{30}NaO_2S^3⁺ ([M+Na]⁺) 397.1300, found 397.1302
**Methyl 3-(cyclohexylthio)-3-(phenylthio)propanoate (3ba)**

Prepared according to General procedure (A) using methyl 3-(cyclohexylthio)acrylate 1b and benzenethiol 2a at r.t., 4 h, 95% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 6.8\) Hz, 2H), 7.33 (d, \(J = 6.3\) Hz, 3H), 4.57 (t, \(J = 7.3\) Hz, 1H), 3.68 (s, 3H), 3.00 (td, \(J = 10.1, 4.6\) Hz, 1H), 2.83 (dd, \(J = 15.8, 6.3\) Hz, 1H), 2.70 (dd, \(J = 15.8, 8.4\) Hz, 1H), 2.11 – 1.90 (m, 2H), 1.80 – 1.69 (m, 2H), 1.67 – 1.49 (m, 1H), 1.42 – 1.32 (m, 3H), 1.30 – 1.22 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 133.6, 133.2, 129.0, 128.2, 51.9, 46.6, 45.0, 42.8, 31.1; HRMS (ESI) m/z calcd. for C\(_{16}\)H\(_{22}\)NaO\(_2\)S\(_2\)\(^{+}\) ([M+Na]\(^+\)) 333.0953, found 333.0957

**Methyl 3-(tert-butylthio)-3-(phenylthio)propanoate (3ca)**

Prepared according to General procedure (A) using methyl 3-(tert-butylthio)acrylate 1c and benzenethiol 2a at r.t., 3 h, 87% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.50 (d, \(J = 7.5\) Hz, 2H), 7.38 – 7.27 (m, 3H), 4.54 (dd, \(J = 9.1, 5.5\) Hz, 1H), 3.67 (s, 3H), 2.85 (dd, \(J = 16.2, 5.2\) Hz, 1H), 2.71 (dd, \(J = 15.4, 9.2\) Hz, 1H), 1.40 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.7, 134.3, 133.0, 129.0, 128.0, 51.8, 46.6, 45.0, 42.8, 31.1; HRMS (ESI) m/z calcd. for C\(_{14}\)H\(_{20}\)NaO\(_2\)S\(_2\)\(^{+}\) ([M+Na]\(^+\)) 307.0797, found 307.0794

**Methyl 3-(benzylthio)-3-(phenylthio)propanoate (3da)**

Prepared according to General procedure (A) using methyl 3-(benzylthio)acrylate 1d and benzenethiol 2a at 50 °C, 2 h, 70% yield, Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 (dd, \(J = 6.3, 2.8\) Hz, 3H), 7.31 (dd, \(J = 6.0, 2.9\) Hz, 11H), 7.29 – 7.23 (m, 3H), 4.34 (t, \(J = 7.4\) Hz, 1H), 4.05 – 3.84 (m, 2H), 3.62 (s, 4H), 2.78 (dd, \(J = 15.8, 7.0\) Hz, 1H), 2.69 (dd, \(J = 15.9, 7.9\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.2, 137.2, 133.7, 132.6, 129.1, 129.0, 128.6,
Methyl 3,3-bis(decylthio)propanoate (3ak)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and decane-1-thiol 2k at r.t., 2 h, 84% yield; Colorless oil; $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 4.21 (t, J = 7.6 Hz, 1H), 3.72 (s, 3H), 2.81 (d, J = 7.6 Hz, 2H), 2.72 – 2.63 (m, 2H), 2.62 – 2.54 (m, 2H), 1.58 (q, J = 9.1, 8.0 Hz, 4H), 1.41 – 1.24 (m, 28H), 0.88 (t, J = 6.7 Hz, 6H); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 51.9, 47.1, 41.7, 31.9, 30.4, 29.5, 29.5, 29.3, 29.2, 29.2, 29.0, 22.7, 14.1; HRMS (ESI) m/z calcd. for C$_{24}$H$_{48}$NaO$_2$S$_2^+$ ([M+Na]$^+$) 455.2988, found 455.2981

Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3al)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and hexane-1-thiol 2l at r.t., 6 h, 71% yield; Colorless oil; $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 4.21 (t, J = 7.6 Hz, 1H), 3.72 (s, 3H), 2.81 (d, J = 7.6 Hz, 2H), 2.68 (dt, J = 14.2, 7.4 Hz, 2H), 2.62 – 2.54 (m, 2H), 1.59 (p, J = 7.2 Hz, 4H), 1.43 – 1.26 (m, 20H), 0.92 – 0.86 (m, 6H); $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 170.6, 51.9, 47.1, 41.7, 31.9, 31.4, 30.4, 29.5, 29.5, 29.3, 29.2, 29.2, 28.9, 28.6, 22.6, 22.5, 14.1, 14.0; HRMS (ESI) m/z calcd. for C$_{20}$H$_{40}$NaO$_2$S$_2^+$ ([M+Na]$^+$) 399.2362, found 399.2400

Methyl 3-(benzylthio)-3-(decylthio)propanoate (3am)
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and phenylmethanethiol 2m at r.t., 4 h, 63% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 – 7.27 (m, 4H), 7.28 – 7.19 (m, 1H), 4.09 (t, J = 7.6 Hz, 1H), 3.93 – 3.76 (m, 2H), 3.68 (s, 3H), 2.77 (d, J = 7.6 Hz, 2H), 2.62 (dt, J = 12.5, 7.4 Hz, 1H), 2.53 (dt, J = 12.4, 7.5 Hz, 1H), 1.53 (p, J = 7.3 Hz, 2H), 1.39 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.4, 137.7, 129.0, 128.5, 127.1, 51.9, 46.6, 41.5, 35.1, 31.9, 30.3, 29.6, 29.5, 29.3, 29.2, 29.0, 22.7, 14.1; HRMS (ESI) m/z calcd. for C$_{21}$H$_{34}$NaO$_2$S$_2^+$ ([M+Na]$^+$) 405.1892, found 405.1897

Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3an)

Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and cyclohexanethiol 2n at r.t., 3 h, 42% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.27 (t, J = 7.5 Hz, 1H), 3.72 (s, 3H), 2.88 (tt, J = 10.0, 3.9 Hz, 1H), 2.81 (d, J = 7.6 Hz, 2H), 2.71 – 2.56 (m, 2H), 1.97 (ddd, J = 20.2, 9.9, 4.7 Hz, 2H), 1.75 (dt, J = 9.5, 4.5 Hz, 2H), 1.59 (p, J = 7.6, 7.1 Hz, 3H), 1.44 – 1.20 (m, 19H), 0.88 (t, J = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 51.9, 45.6, 43.4, 42.2, 33.8, 33.5, 31.9, 30.2, 29.5, 29.5, 29.3, 29.2, 28.9, 26.1, 25.8, 25.7, 22.7, 14.1; HRMS (ESI) m/z calcd. for C$_{20}$H$_{38}$NaO$_2$S$_2^+$ ([M+Na]$^+$) 397.2205, found 397.2202

Decyl(1-(phenylthio)octyl)sulfane (3ea)

Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane 1e and benzenethiol 2a at reflux, 10 h, 38% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 – 7.42 (m, 2H), 7.35 – 7.23 (m, 3H), 4.08 (t, J = 6.7 Hz, 1H), 2.76 (dt, J = 12.5, 7.3 Hz, 1H), 2.65 (dt, J = 12.5, 7.5 Hz, 1H), 1.90 – 1.69 (m, 2H), 1.63 – 1.52 (m, 4H), 1.41 – 1.24 (m, 2H), 0.92 – 0.83 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.6, 132.9, 128.8, 127.5, 55.4, 36.0,
Octane-1,1-diylbis(decylsulfane) (3ek)

Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane 1e and decane-1-thiol 2k at reflux, 20 h, 74% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

3.73 (t, J = 7.0 Hz, 1H), 2.65 (dt, J = 14.5, 7.4 Hz, 2H), 2.54 (dt, J = 12.4, 7.4 Hz, 2H), 1.77 (q, J = 7.3 Hz, 2H), 1.55 (dp, J = 15.3, 7.6, 7.2 Hz, 6H), 1.43 – 1.22 (m, 36H), 0.88 (t, J = 6.8 Hz, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$

52.0, 36.1, 31.9, 31.8, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 29.1, 27.5, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for C$_{28}$H$_{58}$NaS$_2^+$ ([M+Na]$^+$) 481.3872, found 481.3873

Benzyl(1-(decylthio)octyl)sulfane (3em)

Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane 1e and phenylmethanethiol 2m at reflux, 1 h, 36% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

7.35 – 7.20 (m, 5H), 3.91 – 3.73 (m, 2H), 3.58 (t, J = 7.0 Hz, 1H), 2.65 – 2.47 (m, 2H), 1.75 (q, J = 7.4 Hz, 2H), 1.54 (dd, J = 14.3, 6.8 Hz, 2H), 1.45 (td, J = 6.9, 3.9 Hz, 2H), 1.36 (dd, J = 8.4, 5.2 Hz, 2H), 1.31 – 1.23 (m, 20H), 0.88 (td, J = 6.8, 4.2 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$

138.3, 129.0, 128.4, 126.9, 51.2, 35.8, 34.8, 31.9, 31.8, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 29.0, 27.3, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for C$_{25}$H$_{44}$NaS$_2^+$ ([M+Na]$^+$) 431.2777, found 431.2771

Cyclohexyl(1-(decylthio)octyl)sulfane (3en)
Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane 1e and cyclohexanethiol 2n at reflux, 20 h, 35% yield; Colorless oil; $^1$H NMR ($400$ MHz, CDCl$_3$) $\delta$ 3.81 (t, $J = 6.9$ Hz, 1H), 2.88 (tt, $J = 9.9$, 3.9 Hz, 1H), 2.64 (dt, $J = 12.4$, 7.4 Hz, 1H), 2.56 (dt, $J = 12.4$, 7.4 Hz, 1H), 1.96 (ddd, $J = 21.6$, 10.0, 4.7 Hz, 2H), 1.83 – 1.73 (m, 3H), 1.63 – 1.48 (m, 5H), 1.44 – 1.22 (m, 28H), 0.88 (t, $J = 6.6$ Hz, 6H); $^{13}$C NMR ($100$ MHz, CDCl$_3$) $\delta$ 50.4, 42.9, 36.6, 34.1, 33.7, 31.9, 31.8, 29.8, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.1, 29.0, 27.4, 26.1, 25.9, 25.8, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for C$_{24}$H$_{48}$NaS$_2$$^+$ ([M+Na]$^+$) 423.3090, found 423.3092

**Decyl(1-(isopentylthio)octyl)sulfane (3eo)**

Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane 1e and 3-methylbutane-1-thiol 2o at 50 °C, 1 h, 51% yield; Colorless oil; $^1$H NMR ($400$ MHz, CDCl$_3$) $\delta$ 3.74 (t, $J = 7.0$ Hz, 1H), 2.72 – 2.59 (m, 2H), 2.56 (dq, $J = 12.4$, 7.4 Hz, 2H), 1.78 (q, $J = 7.9$, 7.2 Hz, 2H), 1.69 (dt, $J = 13.3$, 6.7 Hz, 1H), 1.60 – 1.51 (m, 3H), 1.50 – 1.44 (m, 3H), 1.42 – 1.24 (m, 22H), 0.91 (d, $J = 6.6$ Hz, 6H), 0.89 – 0.86 (m, 6H). $^{13}$C NMR ($100$ MHz, CDCl3) $\delta$ 52.0, 38.4, 36.1, 36.1, 31.9, 31.8, 30.0, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.0, 27.5, 27.5, 22.7, 22.6, 22.3, 22.2, 14.1, 14.1; HRMS (EI) m/z calcd. for C$_{23}$H$_{48}$S$_2$$^+$ ([M$^+$]) 388.3197, found 388.3200

**Decyl(3-phenyl-1-(phenylthio)propyl)sulfane (3fa)**

Prepared according to General procedure (A) using decyl(3-phenylprop-1-en-1-yl)sulfane 1f and benzenethiol 2a at 50 °C, 2 h, 79% yield; Colorless oil; $^1$H NMR ($400$ MHz, CDCl$_3$) $\delta$
7.39 (dd, J = 7.5, 1.8 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.19 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.1 Hz, 2H), 4.03 (dd, J = 7.6, 5.9 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.75 (dt, J = 12.7, 7.3 Hz, 1H), 2.65 (dt, J = 12.4, 7.6 Hz, 1H), 2.22 – 1.99 (m, 2H), 1.63 – 1.49 (m, 2H), 1.42 – 1.24 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.9, 134.2, 132.7, 128.8, 128.5, 128.3, 127.5, 126.0, 54.0, 37.3, 33.0, 31.9, 31.3, 29.5, 29.3, 29.3, 29.2, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for C$_{25}$H$_{36}$NaS$_2^+$ ([M+Na]$^+$) 423.2151, found 423.2153

**Decyl(1-(isopentylthio)-3-phenylpropyl)sulfane (3fo)**

Prepared according to General procedure (A) using decyl(3-phenylprop-1-en-1-yl)sulfane 1f and 3-methylbutane-1-thiol 2o at 50 °C, 1 h, 80% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.14 (m, 5H), 3.69 (t, J = 7.0 Hz, 1H), 2.85 (t, J = 7.6 Hz, 2H), 2.65 (dt, J = 14.5, 7.6, 2.5 Hz, 2H), 2.55 (dq, J = 12.5, 7.5 Hz, 2H), 2.09 (q, J = 7.4 Hz, 2H), 1.67 (dt, J = 13.3, 6.7 Hz, 1H), 1.54 (q, J = 8.4 Hz, 2H), 1.44 (q, J = 7.4 Hz, 2H), 1.39 – 1.24 (m, 14H), 0.91 – 0.86 (m, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.2, 128.5, 128.4, 126.0, 51.0, 38.4, 37.7, 33.5, 31.9, 30.1, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 28.1, 27.6, 22.7, 22.4, 22.3, 14.1; HRMS (EI) m/z calcd. for C$_{24}$H$_{42}$S$_2^+$ ([M$^+$]$^+$) 394.2728, found 394.2730

**Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate (3gc)**

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 4-bromobenzenthiole 2c at 50 °C, 4 h, 81% yield; Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (dd, J = 12.7, 6.8 Hz, 4H), 7.38 – 7.31 (m, 5H), 4.77 (t, J = 7.3 Hz, 1H), 3.70 (s, 3H), 2.80 (dd, J = 7.0, 4.5 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.3, 135.0, 133.5, 132.7, 132.2, 132.1, 129.1, 128.4, 122.8, 53.6, 52.1, 40.9; HRMS (ESI) m/z calcd. for C$_{16}$H$_{15}$BrNaO$_2$S$_2^+$ ([M+Na]$^+$) 404.9589, found 404.9587
Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate (3gd)

![Chemical structure of 3gd]

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 4-chlorobenzenethiol 2d at 50 °C, 3 h, 82% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (dd, J = 6.4, 2.9 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 – 7.26 (m, 5H), 4.77 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.80 (dd, J = 7.4, 4.4 Hz, 2H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 134.9, 134.6, 133.5, 132.8, 131.3, 129.2, 129.1, 128.4, 53.7, 52.1, 40.9; HRMS (ESI) m/z calcd. for C\(_{16}\)H\(_{15}\)ClNaO\(_2\)S\(_2\)\(^\dagger\) ([M+Na]\(^\dagger\)) 361.0094, found 361.0097

Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate (3gf)

![Chemical structure of 3gf]

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 4-methoxybenzenethiol 2f at 50 °C, 5 h, 47% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.47 (dd, J = 12.4, 7.8 Hz, 4H), 7.37 – 7.27 (m, 3H), 6.87 (d, J = 8.0 Hz, 2H), 4.67 (t, J = 7.4 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.77 (d, J = 7.4 Hz, 2H); \(^1\)\(^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.5, 160.3, 136.8, 133.4, 133.0, 129.0, 128.0, 122.7, 114.5, 55.3, 54.2, 52.0, 40.9; HRMS (ESI) m/z calcd. for C\(_{17}\)H\(_{18}\)NaO\(_3\)S\(_2\)\(^\dagger\) ([M+Na]\(^\dagger\)) 357.0590, found 357.0587

Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate (3gg)

![Chemical structure of 3gg]

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 4-methylbenzenethiol 2g at 50 °C, 5 h, 95% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, J = 5.5 Hz, 1H), 7.39 (d, J = 7.7 Hz, 3H), 7.32 (d, J = 5.6 Hz, 2H), 7.14 (d, J = 7.5 Hz, 3H), 4.71 (dt, J = 24.7, 7.3 Hz, 1H), 3.69 (s, 3H), 2.78 (dd, J = 10.7, 7.7 Hz, 2H), 2.35 (s, 3H);
\[^{13}\text{C} \text{NMR}\ (100 \text{ MHz}, \text{CDCl}_3) \delta 170.5, 138.5, 134.2, 134.0, 133.4, 133.3, 129.8, 129.0, 128.1, 53.7, 51.9, 41.0, 21.2; \text{HRMS (ESI) m/z calcd. for C}_{17}\text{H}_{18}\text{NaO}_2\text{S}_2^+ ([M+Na]^+) 341.0640, found 341.0639

\textbf{Methyl 3-\(\text{(phenylthio)}\)-3-\((4\text{-(trifluoromethyl)phenylthio})\)propanoate (3gh)}

![Methyl 3-(phenylthio)-3-(4-(trifluoromethyl)phenylthio)propanoate](image)

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 4-(trifluoromethyl)benzenethiol 2h at 50 °C, 5 h, 77% yield; Colorless oil; \[^1\text{H} \text{NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 7.54 (s, 4H), 7.50 – 7.46 (m, 2H), 7.34 – 7.31 (m, 3H), 4.90 (t, J = 7.4 Hz, 1H), 3.71 (s, 3H), 2.85 (t, J = 7.4 Hz, 2H); \[^{13}\text{C} \text{NMR}\ (100 \text{ MHz}, \text{CDCl}_3) \delta 170.2, 138.6, 133.8, 132.2, 131.7, 129.56 (q, J = 32.6 Hz), 129.1, 128.7, 125.77 (q, J = 3.7 Hz), 123.88 (q, J = 27.2 Hz), 52.8, 52.1, 40.8; \text{HRMS (ESI) m/z calcd. for C}_{17}\text{H}_{15}\text{F}_3\text{NaO}_2\text{S}_2^+ ([M+Na]^+) 395.0358, found 395.0358

\textbf{Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate (3gi)}

![Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate](image)

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and naphthalene-2-thiol 2i at 50 °C, 5 h, 95% yield; Colorless oil; \[^1\text{H} \text{NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 7.96 (s, 1H), 7.78 (dq, J = 14.5, 6.9, 5.4 Hz, 4H), 7.58 – 7.47 (m, 6H), 7.32 (d, J = 4.7 Hz, 1H), 4.96 (dt, J = 43.3, 7.4 Hz, 1H), 3.69 (s, 3H), 2.88 (dd, J = 18.0, 7.3 Hz, 2H); \[^{13}\text{C} \text{NMR}\ (100 \text{ MHz}, \text{CDCl}_3) \delta 170.5, 133.6, 133.4, 132.6, 132.6, 130.3, 130.2, 129.0, 128.6, 128.3, 127.7, 126.6, 126.6, 53.4, 52.0, 41.1; \text{HRMS (ESI) m/z calcd. for C}_{20}\text{H}_{18}\text{NaO}_2\text{S}_2^+ ([M+Na]^+) 377.0640, found 377.0638

\textbf{Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate (3gj)}
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and thiophene-2-thiol 2j at reflux, 8 h, 36% yield; Colorless oil; There were inseparable mixture, the yield was obtained by NMR yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.43 (m, 3H), 7.38 – 7.30 (m, 3H), 7.20 (d, J = 3.4 Hz, 1H), 7.04 (t, J = 4.6 Hz, 1H), 4.63 (t, J = 7.1 Hz, 1H), 3.71 (s, 3H), 2.82 (q, J = 8.7, 8.1 Hz, 2H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.3, 136.8, 133.4, 133.3, 131.5, 129.1, 129.0, 128.3, 127.7, 55.3, 52.1, 40.6; HRMS (ESI) m/z calcd. for C\(_{14}\)H\(_{14}\)NaO\(_2\)S\(_2\)\(^+\) ([M+Na]) 333.0048, found 333.0047

**Methyl 3-(hexylthio)-3-(phenylthio)propanoate (3gl)**

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and hexane-1-thiol 2l at 50 °C, 6 h, 39% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 4.50 (dd, J = 8.1, 6.8 Hz, 1H), 3.69 (s, 3H), 2.89 – 2.76 (m, 2H), 2.80 – 2.65 (m, 2H), 1.61 (dd, J = 10.6, 3.4 Hz, 2H), 1.42 – 1.26 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.6, 133.7, 133.0, 128.9, 128.2, 52.0, 50.3, 41.4, 31.7, 31.3, 29.1, 28.5, 22.5, 14.0; HRMS (ESI) m/z calcd. for C\(_{16}\)H\(_{24}\)NaO\(_2\)S\(_2\)\(^+\) ([M+Na]) 335.1110, found 335.1114

**Methyl 3-(isopentylthio)-3-(phenylthio)propanoate (3go)**

Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate 1g and 3-methylbutane-1-thiol 2o at 50 °C, 6 h, 52% yield; Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51 – 7.48 (m, 2H), 7.36 – 7.30 (m, 3H), 4.51 (dd, J = 8.2, 6.7 Hz, 1H), 3.69 (s, 3H), 2.88 – 2.66 (m, 4H), 1.66 (dt, J = 13.3, 6.7 Hz, 1H), 1.49 (q, J = 7.5 Hz, 2H), 0.91 (dd, J = 6.6, 3.5
4. Synthesis of vinyl sulfides

4.1. General procedure of 1a, 1b, 1c, 1d, 1g

General procedure (B) : In a dry, clean round bottom flask, add corresponding thiol (1.1 equiv.) to the solution of methyl propiolate (1 equiv.) in DCM, followed by the addition of triethylamine (0.5 equiv.). Stir the reaction contents at room temperature until the reaction completion. After the reaction completion, most of the solvent had been removed under reduced pressure; the residue was used for the purification via column chromatography. The synthesized mixture of E and Z vinyl sulfides.

Methyl 3-(decylthio)acrylate (1a)

Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and decane-1-thiol (1.1 equiv.), E:Z = 10:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, $J = 15.1$ Hz, 1H), 7.10 (d, $J = 10.1$ Hz, 0.1H), 5.85 (d, $J = 10.3$ Hz, 1H), 5.75 (d, $J = 15.1$ Hz, 0.1H), 3.74 (s, 0.3H), 3.73 (s, 3H), 2.79 (t, $J = 7.4$ Hz, 2H), 1.74 – 1.59 (m, 3H), 1.51 – 1.22 (m, 14H), 0.88 (t, $J = 6.6$ Hz, 3H); The compound was identified by spectral comparison with literature data.$^1$

Methyl 3-(cyclohexylthio)acrylate (1b)
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and cyclohexanethiol (1.1 equiv.), E:Z = 10:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 15.3$ Hz, 1H), 7.17 (d, $J = 10.2$ Hz, 0.1H), 5.80 (d, $J = 15.3$ Hz, 1.1H), 3.72 (s, 0.3H), 3.70 (s, 3H), 3.05 (ddd, $J = 14.2$, 8.7, 4.0 Hz, 1.1H), 2.07 – 1.96 (m, 2H), 1.83 – 1.72 (m, 2H), 1.67 – 1.58 (m, 1H), 1.51 – 1.20 (m, 5H); The compound was identified by spectral comparison with literature data.\textsuperscript{2}

\textbf{Methyl 3-(tert-butylthio)acrylate (1c)}

Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and 2-methylpropane-2-thiol (1.1 equiv.), E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 15.5$ Hz, 1H), 7.29 (d, $J = 11.0$ Hz, 0.3H), 5.93 (d, $J = 15.5$ Hz, 1H), 5.89 (d, $J = 10.5$ Hz, 0.3H), 3.74 (s, 1H), 3.73 (s, 3H), 1.43 (s, 9H), 1.41 (s, 3H). The compound was identified by spectral comparison with literature data.\textsuperscript{3}

\textbf{Methyl 3-(benzylthio)acrylate (1d)}

Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and phenylmethanethiol (1.1 equiv.), E:Z = 5:1; White solid; The NMR spectrum was obtained as a mixture of E/Z isomers; \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ 7.70 (d, $J = 15.2$ Hz, 1H), 7.36 – 7.27 (m, 6H), 7.06 (d, $J = 10.2$ Hz, 0.2H), 5.81 (d, $J = 15.2$ Hz, 1.2H), 4.02 (s, 2H), 3.96 (s, 0.4H), 3.72 (s, 0.6H), 3.71 (s, 3H); The compound was identified by spectral comparison with literature data.\textsuperscript{4}
Methyl 3-(phenylthio)acrylate (1g)

Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and benzenethiol (1.1 equiv.), E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 15.1$ Hz, 1H), 7.51 – 7.45 (m, 3H), 7.43 – 7.34 (m, 3.6H), 7.29 (d, $J = 10.1$ Hz, 0.3H), 5.93 (d, $J = 10.1$ Hz, 0.3H), 5.66 (d, $J = 15.1$ Hz, 1H), 3.79 (s, 1H), 3.70 (s, 3H); The compound was identified by spectral comparison with literature data.\(^5\)

4.2. General procedure and characterization of 1e and 1f

General procedure (C) : In a dry, clean reaction tube, AIBN (10 mol%) was taken and degassed with N$_2$ three times, then added the solution of alkyne in toluene followed by the addition of corresponding thiol (1.1 equiv.). The reaction contents are heated to 80 °C until the reaction completion. After the reaction completion, the reaction was diluted with DCM and washed with water followed by brine solution. The organic layer was dried over anhydrous Na$_2$SO$_4$. The solvent had been removed under reduced pressure. The crude product was purified via column chromatography.

Decyl(oct-1-en-1-yl)sulfane (1e)

Prepared according to General procedure (C) using oct-1-yne (1 equiv.) and decane-1-thiol (1.1 equiv.), 85% yield, E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.91 (d, $J = 5.6$ Hz, 0.3H), 5.89 (d, $J = 9.4$ Hz, 1H), 5.66 – 5.51 (m, 1.3H), 2.63 (q, $J = 7.3$ Hz, 2.6H), 2.09 (dq, $J = 14.4$, 6.9 Hz, 2.6H), 1.65 – 1.58 (m, 2.6H), 1.42 – 1.23 (m, 29H), 0.88 (t, $J = 6.3$ Hz, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$)
δ 130.8, 129.5, 124.9, 122.6, 33.9, 33.2, 32.7, 31.9, 31.7, 31.7, 30.3, 29.5, 29.5, 29.5, 29.3, 29.2, 29.1, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.4, 22.7, 22.6, 22.6, 14.1, 14.1; HRMS (DART) m/z calcd. for C$_{18}$H$_{37}$S$^+$ ([M+H$^+$]) 285.2610, found 285.2610

Decyl(3-phenylprop-1-en-1-yl)sulfane (1f)

Prepared according to General procedure (C) using prop-2-yn-1-ylbenzene (1 equiv.) and decane-1-thiol (1.1 equiv.), 73% yield, E:Z = 1:2.2; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.14 (m, 7.26H), 6.05 (d, J = 9.3 Hz, 1H), 6.01 (d, J = 15.1 Hz, 0.45H), 5.73 (q, J = 7.3 Hz, 1.45H), 3.48 (d, J = 7.1 Hz, 2H), 3.42 (d, J = 6.9 Hz, 0.9H), 2.70 (t, J = 7.3 Hz, 2H), 2.65 (t, J = 7.4 Hz, 0.9H), 1.64 (dq, J = 13.6, 6.8 Hz, 2.9H), 1.47 – 1.21 (m, 20.6H), 0.88 (t, J = 6.4 Hz, 4.36H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.4, 140.0, 128.5, 128.4, 128.4, 127.7, 127.7, 126.3, 126.1, 126.0, 125.4, 124.8, 39.8, 39.4, 35.4, 34.0, 32.5, 31.9, 31.9, 30.3, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 28.8, 28.6, 22.7, 22.4, 14.2, 14.1; HRMS (DART) m/z calcd. for C$_{19}$H$_{31}$S$^+$ ([M+H$^+$]) 291.2141, found 291.2147
5. References


6. NMR spectra

$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(phenylthio)propanoate (3aa)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(phenylthio)propanoate (3aa)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate (3ab)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate (3ab)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate (3ac)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate (3ac)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(decylthio)propanoate (3ad)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(decythio)propanoate (3ad)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate (3ae)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate (3ae)
$^{1}$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate (3af)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate (3af)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(p-tolylthio)propanoate (3ag)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(p-tolylthio)propanoate (3ag)
$^{1}H$ NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3ah)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3ah)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(naphthalen-2-ylthio)propanoate (3ai)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(naphthalen-2-ylthio)propanoate (3ai)
$^{1}$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(thiophen-2-ylthio)propanoate (3aj)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)-3-(thiophen-2-ylthio)propanoate (3aj)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-phenylthio)propanoate (3ba)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-(phenylthio)propanoate (3ba)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(tert-butylthio)-3-(phenylthio)propanoate (3ca)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(tert-butythio)-3-(phenylthio)propanoate (3ca)
H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(benzylthio)-3-(phenylthio)propanoate (3da)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(benzylthio)-3-(phenylthio)propanoate (3da)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3,3-bis(decylthio)propanoate (3ak)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3,3-bis(decylthio)propanoate (3ak)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3a1)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3al)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(benzylthio)-3-(decylthio)propanoate (3am)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(benzylthio)-3-(decylthio)propanoate (3am)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3an)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3an)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Decyl(1-(phenylthio)octyl)sulfane (3ea)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Decyl(1-(phenylthio)octyl)sulfane (3ea)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Octane-1,1-diylbis(decylsulfane) (3ek)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Octane-1,1-diylbis(decylsulfane) (3ek)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Benzyl(1-(decylthio)octyl)sulfane (3em)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Benzyl(1-(decylthio)octyl)sulfane (3em)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Cyclohexyl(1-(decylthio)octyl)sulfane (3en)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Cyclohexyl(1-(decylthio)octyl)sulfane (3en)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Decyl(1-(isopentylthio)octyl)sulfane (3eo)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Decyl(1-(isopentylthio)octyl)sulfane (3eo)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Decyl(3-phenyl-1-(phenylthio)propyl)sulfane (3fa)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Decyl(3-phenyl-1-(phenylthio)propyl)sulfane (3fa)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Decyl(1-(isopentylthio)-3-phenylpropyl)sulfane (3fo)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of decyl(1-(isopentylthio)-3-phenylpropyl)sulfane (3fo)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate (3gc)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate (3gc)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate (3gd)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate (3gd)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate (3gf)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate (3gf)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate (3gg)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate (3gg)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3gh)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3gh)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate (3gi)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate (3gi)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate (3gj)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate (3gj)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(hexylthio)-3-(phenylthio)propanoate (3gl)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of Methyl 3-(hexylthio)-3-(phenylthio)propanoate (3gl)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(isopentylthio)-3-(phenylthio)propanoate (3go)
$^{13}$C NMR (100 MHz, CDCl₃) spectra of Methyl 3-(isopentylthio)-3-(phenylthio)propanoate (3go)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(decylthio)acrylate (1a)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(cyclohexylthio)acrylate (1b)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(tert-butylthio)acrylate (1c)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(benzylthio)acrylate (1d)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of decyl(oct-1-en-1-yl)sulfane (1e)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of decyl(oct-1-en-1-yl)sulfane (1e)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of decyl(3-phenylprop-1-en-1-yl)sulfane (1f)
$^{13}$C NMR (100 MHz, CDCl$_3$) spectra of decyl(3-phenylprop-1-en-1-yl)sulfane (1f)
$^1$H NMR (400 MHz, CDCl$_3$) spectra of Methyl 3-(phenylthio)acrylate (1g)