Supporting Information

S-alkylation of cysteine-containing peptides using thianthenium salts as alkyl source in flow

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1. General Information

All commercially available reagents and solvents used in this study were purchased from Alfa Aesar, Sigma Aldrich or Energy Chemical and used without further purification. Thin layer chromatography (TLC) was measured on EMD preloaded plates (silica gel 60 F254) and was visualized under ultraviolet light (254 nm and 365 nm). Column chromatography was performed with silica gel (200-300 mesh).

All new compounds were characterized by $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy and mass spectrometry. NMR spectra were recorded on a Bruke Avance operating for $^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz, and $^{19}$F NMR at 376 MHz. Chemical shifts (δ) were reported in ppm referenced to Tetramethylsilane (TMS) as internal standard. NMR spectra uses the following abbreviations to describe the multiplicity: s = single, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, td = triple doublet. Coupling constants (J) were reported in hertz (Hz). Known products were characterized by comparing to the corresponding $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR from literature. NMR data was processed using the MestReNova 9.0.1 software package. High resolution mass spectra were obtained on Agilent Technologies 6520 Accurate Series Q-TOF equipped with ESI. Coil was used commercially available PFA (perfluoroalkoxyalkane) tube with an inner diameter of 0.6 mm.
2. General procedure

Methyl (tert-butoxycarbonyl)-L-phenylalanyl-L-cysteinate 1a (0.4 mmol, 1.0 eq.) was dissolved in DMSO (2.0 mL) and then added Et₃N (0.6 mmol, 1.5 eq.). A second reaction solution was to dissolve the thianthrenium salts 2a (0.48 mmol, 1.2 eq.) in DMSO (2.0 mL). The two solutions were transferred into two 5 mL BD plastic syringes and introduced into the microreactor (a high purity perfluoroalkoxyalkane, PFA capillary tubing, ID = 600 μm) through syringe pump. The two liquid streams were merged with a Y-Mixer before entering the reactor. The flow rate was set to 0.1 mL/min (0.05 mL/min per syringe), thus resulting in 14 min residence time (volume of reactor = 1.4 mL). After reaching steady state, the reaction sample was collected in a glass vial. Solution remaining in the microreactor was then discharged with DMSO (2.0 mL × 2) via syringe pump, and was also collected in the same glass vial. After the reaction completed, diluted with DCM and water, and extracted with DCM (10.0 mL) for three times, combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. Purification by flash column chromatography afforded the desired product 3a.

Supplementary Figure 1. The reaction equipment
3. Optimization of reaction conditions

Supplementary Table 1 Screening of bases

![Chemical structure of reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Bases</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMAP</td>
<td>60</td>
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<tr>
<td>2</td>
<td>Et3N</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>TBD</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>DIPEA</td>
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<tr>
<td>5</td>
<td>TMG</td>
<td>92</td>
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<tr>
<td>6</td>
<td>DBU</td>
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<tr>
<td>11</td>
<td>None</td>
<td>N.D.</td>
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*Standard condition: 1a (1.0 eq., 0.4 mmol), 2a (1.2 eq., 0.48 mmol), base (1.5 eq., 0.6 mmol), DCM (4.0 mL). Stirred at room temperature for 12 hours. Isolated yield is based on 1a.

Supplementary Table 2 Screening of solvents

![Chemical structure of reaction](image)
<table>
<thead>
<tr>
<th>Entry a</th>
<th>Solvents</th>
<th>Yield(%) b</th>
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</thead>
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<td>2</td>
<td>THF</td>
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</tr>
<tr>
<td>3</td>
<td>CH₃CN</td>
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<td>4</td>
<td>DCE</td>
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<tr>
<td>9</td>
<td>H₂O</td>
<td>73</td>
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</table>

a Standard condition: 1a (1.0 eq., 0.4 mmol), 2a (1.2 eq., 0.48 mmol), Et₃N (1.5 eq., 0.6 mmol), Solvent (4.0 mL). Stirred at room temperature for 12 hours. b Isolated yield is based on 1a.

**Supplementary Table 3** Screening of amounts of 2a

<table>
<thead>
<tr>
<th>Entry a</th>
<th>Amounts of 2a(equiv)</th>
<th>Yield (%) b</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>90</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>1.2</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>87</td>
</tr>
</tbody>
</table>

a Standard condition: 1a (1.0 eq., 0.4 mmol), 2a (x equiv), Et₃N (1.5 eq., 0.6 mmol), Solvent (4.0 mL). Stirred at room temperature for 12 hours. b Isolated yield is based on 1a.
**Supplementary Table 4** Screening of reaction time

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time (h)</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>1</td>
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<td>65</td>
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<td>81</td>
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<tr>
<td>3</td>
<td>10</td>
<td>88</td>
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<tr>
<td>4</td>
<td>12</td>
<td>95</td>
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</tbody>
</table>

<sup>a</sup> Standard condition: 1a (1.0 eq., 0.4 mmol), 2a (1.2 eq., 0.48 mmol), Et₃N (1.5 eq., 0.6 mmol), solvent (4.0 mL). Stirred at room temperature for x hours. <sup>b</sup> Isolated yield is based on 1a.

**Supplementary Table 5** Screening of flow rate

<table>
<thead>
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<th>Entry</th>
<th>Rate (mL/min)</th>
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<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>6</td>
<td>0.4</td>
<td>1.75</td>
<td>58</td>
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<sup>a</sup> Standard condition: 1a (1.0 eq., 0.4 mmol) and Et₃N (1.5 eq., 0.6 mmol) was dissolved in DMSO (2.0
mL); 2a (1.2 eq., 0.48 mmol) was dissolved in DMSO (2.0 mL). The solution was transferred into syringe and introduced into microreactor through syringe pump. Isolated yield is based on 1a.

**Supplementary Table 6** Screening of flow solvent

<table>
<thead>
<tr>
<th>Entry a</th>
<th>Solvents</th>
<th>Yield (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃OH</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>CH₃CN</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>80</td>
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<td>5</td>
<td>Acetone</td>
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<tr>
<td>6</td>
<td>DMSO</td>
<td>96</td>
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<td>7</td>
<td>DMF</td>
<td>87</td>
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<tr>
<td>8</td>
<td>DMA</td>
<td>82</td>
</tr>
<tr>
<td>9</td>
<td>DMSO/H₂O(4:1)</td>
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<tr>
<td>10</td>
<td>DMSO/H₂O(7:3)</td>
<td>82</td>
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<tr>
<td>11</td>
<td>DMSO/H₂O(3:2)</td>
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<tr>
<td>12</td>
<td>DMSO/H₂O(1:1)</td>
<td>69</td>
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<tr>
<td>13</td>
<td>H₂O</td>
<td>/</td>
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</tbody>
</table>

\[ a \] Standard condition: 1a (1.0 eq., 0.4 mmol) and Et₃N (1.5 eq., 0.6 mmol) were dissolved in Solvents (2.0 mL); 2a (1.2 eq., 0.48 mmol) was dissolved in Solvents (2.0 mL). The solution was transferred into syringe and introduced into microreactor through syringe pump (PFA tube, ID = 600 μm) for 14 min. Isolated yield is based on 1a.
**Supplementary Table 7** Screening of flow pipe diameter

<table>
<thead>
<tr>
<th>Entry a</th>
<th>diameter</th>
<th>Yield (%)b</th>
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<tbody>
<tr>
<td>1</td>
<td>500 μm</td>
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<tr>
<td>2</td>
<td>600 μm</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>800 μm</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>1000 μm</td>
<td>79</td>
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</tbody>
</table>

*a Standard condition: 1a (1.0 eq., 0.4 mmol) and Et3N (1.5 eq., 0.6 mmol) was dissolved in DMSO (2.0 mL); 2a (1.2 eq., 0.48 mmol) was dissolved in DMSO (2.0 mL). The solution was transferred into syringe and introduced into microreactor through syringe pump for 14 min. b Isolated yield is based on 1a.

**Supplementary Table 8** The comparison between batch and flow

<table>
<thead>
<tr>
<th>Product</th>
<th>Isolated yield (%)a (in batch)</th>
<th>Timea (in batch)</th>
<th>Space time yield (mol/L·h)a (in batch)</th>
<th>Isolated yield (%)b (in flow)</th>
<th>Timeb (in flow)</th>
<th>Space time yield (mol/L·h)b (in flow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>95</td>
<td>12 h</td>
<td>8.3*10^{-3}</td>
<td>96</td>
<td>14 min</td>
<td>6.1*10^{-1}</td>
</tr>
<tr>
<td>4a</td>
<td>87</td>
<td>12 h</td>
<td>8.3*10^{-3}</td>
<td>92</td>
<td>14 min</td>
<td>6.1*10^{-1}</td>
</tr>
<tr>
<td>5a</td>
<td>81</td>
<td>12 h</td>
<td>8.3*10^{-3}</td>
<td>85</td>
<td>14 min</td>
<td>6.1*10^{-1}</td>
</tr>
</tbody>
</table>

*a Reaction condition: 1a (0.2 mmol), 2a (0.24 mmol), Et3N (0.3 mmol), Solvent (2.0 mL). Stirred in the seal reaction tube (25 mL) at room temperature

*b Reaction conditions: the reaction was carried out in the microfluidic chip reactor (1.4 mL) with a flow rate of 0.05 mL/min at room temperature
4. NMR Spectra

**Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-phenethyl-L-cysteinate (3a)**
White solid (Flow:186.6 mg, 96% yield; Batch:184.7 mg, 95% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.31 – 7.25 (m, 4H), 7.24 – 7.16 (m, 6H), 6.69 (d, $J = 7.2$ Hz, 1H), 4.99 (s, 1H), 4.78 – 4.70 (m, 1H), 4.47 – 4.33 (m, 1H), 3.71 (s, 3H), 3.13 – 3.02 (m, 2H), 2.97 – 2.89 (m, 2H), 2.86 – 2.79 (m, 2H), 2.77 – 2.69 (m, 2H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 171.1, 170.7, 155.4, 140.0, 136.5, 129.3, 128.7, 128.5(3), 128.5(0), 127.0, 126.5, 80.3, 52.6, 52.0, 38.2, 36.1, 34.2, 34.0, 28.3. HRMS (ESI) m/z: calcd for $C_{26}H_{34}N_2O_5SNa$ [M+Na]$^+$: 509.2081, found: 509.2076.

**Methyl N-((tert-butoxycarbonyl)glycyl)-S-phenethyl-L-cysteinate (3b)**
Light yellow oil (Flow:112.5 mg, 71% yield; Batch:109.3mg, 69% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.23 – 7.18 (m, 2H), 7.15 – 7.03 (m, 4H), 5.36 (t, $J = 5.5$ Hz, 1H), 4.77 – 4.71 (m, 1H), 3.81 – 3.70 (m, 2H), 3.65 (s, 3H), 2.95 – 2.84 (m, 2H), 2.80 – 2.74 (m, 2H), 2.72 – 2.66 (m, 2H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 171.1, 169.6, 156.1, 140.0, 128.5, 80.2, 52.7, 51.9, 44.2, 36.1, 34.1, 34.0, 28.3. HRMS (ESI) m/z: calcd for $C_{19}H_{28}N_2O_5SNa$ [M+Na]$^+$: 419.1611, found: 419.1615.

**Methyl N-((tert-butoxycarbonyl)-L-alanyl)-S-phenethyl-L-cysteinate (3c)**
Colorless oil (Flow:137.6 mg, 84% yield; Batch:137.7mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.22 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 7.02 (s, 1H), 5.25 – 5.09 (m, 1H), 4.74 – 4.68 (m, 1H), 4.16 (s, 1H), 3.65 (s, 3H), 2.95 – 2.84 (m, 2H), 2.79 – 2.74 (m, 2H), 2.71 – 2.66 (m, 2H), 1.36 (s, 9H), 1.27 (d, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 172.8, 171.1, 155.4, 140.1, 128.5, 126.4, 80.0, 52.6, 51.9, 50.0, 36.1, 34.1, 34.0, 28.3, 18.3. HRMS (ESI) m/z: calcd for $C_{20}H_{30}N_2O_5SNa$ [M+Na]$^+$: 433.1768, found: 433.1771.

**Methyl N-((tert-butoxycarbonyl)-L-valyl)-S-phenethyl-L-cysteinate (3d)**
Colorless oil (Flow: 151.6 mg, 87% yield; Batch: 144.6 mg, 83% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.23 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 6.87 (d, $J$ = 7.3 Hz, 1H), 5.16 (d, $J$ = 8.5 Hz, 1H), 4.75 – 4.69 (m, 1H), 4.01 – 3.88 (m, 1H), 3.64 (s, 3H), 2.93 – 2.86 (m, 2H), 2.79 – 2.74 (m, 2H), 2.72 – 2.66 (m, 2H), 2.11 – 2.01 (m, 1H), 1.36 (s, 9H), 0.90 (d, $J$ = 6.8 Hz, 3H), 0.84 (d, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.7, 171.1, 155.8, 140.0, 128.5, 126.4, 79.8, 52.6, 51.8, 36.1, 34.1, 34.0, 31.0, 28.3, 19.2, 17.7. HRMS (ESI) m/z: calcd for C$_{22}$H$_{34}$N$_2$O$_5$SNa [M+Na]$^+$: 461.2081, found: 461.2082.

Methyl N-((tert-butoxycarbonyl)-L-leucyl)-S-phenethyl-L-cysteinate (3e)
Colorless oil (Flow: 166.6 mg, 92% yield; Batch: 159.4 mg, 88% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.22 – 7.17 (m, 2H), 7.14 – 7.08 (m, 3H), 7.04 (d, $J$ = 5.9 Hz, 1H), 5.05 (d, $J$ = 7.4 Hz, 1H), 4.74 – 4.66 (m, 1H), 4.11 (s, 1H), 3.64 (s, 3H), 2.95 – 2.85 (m, 2H), 2.79 – 2.74 (m, 2H), 2.71 – 2.65 (m, 2H), 1.64 – 1.53 (m, 2H), 1.43 – 1.39 (m, 1H), 1.36 (s, 9H), 0.85 (dd, $J$ = 6.2, 3.3 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 173.0, 171.2, 155.7, 140.1, 128.5(0), 128.4(7), 126.4, 79.7, 53.0, 52.5, 52.1, 41.2, 36.0, 33.9, 33.9, 28.3, 24.6, 23.0, 22.0. HRMS (ESI) m/z: calcd for C$_{23}$H$_{36}$N$_2$O$_5$SNa [M+Na]$^+$: 475.2237, found: 475.2240.

Methyl N-((tert-butoxycarbonyl)-L-isoleucyl)-S-phenethyl-L-cysteinate (3f)
Colorless oil (Flow: 161.8 mg, 89% yield; Batch: 165.4 mg, 91% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.22 – 7.18 (m, 2H), 7.14 – 7.08 (m, 3H), 6.86 (d, $J$ = 7.2 Hz, 1H), 5.14 (d, $J$ = 8.4 Hz, 1H), 4.75 – 4.69 (m, 1H), 4.02 – 3.92 (m, 1H), 3.65 (s, 3H), 2.92 – 2.87 (m, 2H), 2.79 – 2.74 (m, 2H), 2.72 – 2.65 (m, 2H), 1.85 – 1.75 (m, 1H), 1.48 – 1.41 (m, 1H), 1.36 (s, 9H), 1.11 – 1.01 (m, 1H), 0.88 – 0.80 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.9, 171.2, 154.1, 140.2, 128.5(0), 128.4(7), 126.4, 79.6, 59.1, 52.5, 51.9, 37.4, 36.0, 33.9, 28.3, 24.7, 23.0, 15.4, 11.4. HRMS (ESI) m/z: calcd for C$_{23}$H$_{36}$N$_2$O$_5$SNa [M+Na]$^+$: 475.2237, found: 475.2239.

Methyl (S)-3-((tert-butoxycarbonyl)amino)-4-(((R)-1-methoxy-1-oxo-3-(phenethyl thio) propan-2-yl)amino)-4-oxobutanoate (3g)
Colorless oil (Flow: 157.4 mg, 84% yield; Batch: 148 mg, 79% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.27 (d, $J$ = 7.2 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.12 (t, $J$ = 7.4 Hz, 3H), 5.69 (d, $J$ = 8.1 Hz, 1H), 4.71 – 4.65 (m, 1H), 4.55 – 4.45 (m, 1H), 3.65 (s, 3H), 3.59 (s, 3H), 2.92 – 2.85 (m, 3H), 2.80
– 2.75 (m, 2H), 2.72 – 2.59 (m, 3H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 172.1, 170.8, 170.7, 155.5, 140.1, 128.5, 126.4, 80.5, 52.6, 52.1(2), 52.0(7), 50.6, 36.1, 35.8, 34.0, 33.9, 28.3. HRMS (ESI) m/z: calcld for C$_{22}$H$_{32}$N$_{2}$O$_{7}$SNa [M+Na]$^+$: 491.1822, found: 491.1823.

Methyl (S)-4-((tert-butoxycarbonyl)amino)-5-(((R)-1-methoxy-1-oxo-3-(phenethyl thio) propan-2-yl)amino)-5-oxopentanoate (3h)

Colorless oil (Flow: 167.2 mg, 87% yield; Batch: 159.5mg, 83% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.23 – 7.18 (m, 2H), 7.17 – 7.07 (m, 4H), 5.39 (d, $J = 7.4$ Hz, 1H), 4.73 – 4.66 (m, 1H), 4.27 – 4.10 (m, 1H), 3.65 (s, 3H), 3.59 (s, 3H), 2.94 – 2.85 (m, 2H), 2.80 – 2.75 (m, 2H), 2.72 – 2.66 (m, 2H), 2.45 – 2.35 (m, 2H), 2.12 – 2.02 (m, 1H), 1.92 – 1.81 (m, 1H), 1.36 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 173.7, 171.7, 171.0, 155.6, 140.0, 128.4(8), 128.4(6), 126.4, 79.8, 53.5, 52.6, 52.0, 51.8, 36.0, 33.8, 30.1, 28.3, 27.9. HRMS (ESI) m/z: calcld for C$_{23}$H$_{34}$N$_{2}$O$_{7}$SNa [M+Na]$^+$: 505.1979, found: 505.1979.

Methyl N-((tert-butoxycarbonyl)-L-seryl)-S-phenethyl-L-cysteinate (3i)

Colorless oil (Flow: 115.8 mg, 68% yield; Batch: 107.3mg, 63% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.31 (s, 1H), 7.24 – 7.19 (m, 2H), 7.16 – 7.08 (m, 3H), 5.56 (d, $J = 7.1$ Hz, 1H), 4.76 – 4.66 (m, 1H), 4.17 (s, 1H), 3.94 (s, 1H), 3.67 (s, 3H), 3.63 – 3.56 (m, 1H), 3.26 (s, 1H), 2.98 – 2.84 (m, 2H), 2.80 – 2.75 (m, 2H), 2.73 – 2.66 (m, 2H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 171.3, 171.1, 155.9, 140.0, 128.5(3), 128.4(9), 126.5, 80.5, 63.0, 55.3, 52.8, 52.0, 36.0, 34.0, 33.9, 28.3. HRMS (ESI) m/z: calcld for C$_{20}$H$_{30}$N$_{2}$O$_{6}$SNa [M+Na]$^+$: 449.1717, found: 449.1716.

Methyl N-((tert-butoxycarbonyl)-L-threonyl)-S-phenethyl-L-cysteinate (3j)

Colorless oil (Flow: 141.2 mg, 80% yield; Batch: 134.1mg, 76% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.48 (m, 1H), 7.30 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 5.76 – 5.67 (m, 1H), 4.84 – 4.75 (m, 1H), 4.31 (s, 1H), 4.21 (d, $J = 7.1$ Hz, 1H), 3.82 (d, $J = 10.5$ Hz, 1H), 3.73 (s, 3H), 3.03 – 2.98 (m, 1H), 2.94 – 2.89 (m, 1H), 2.87 – 2.82 (m, 2H), 2.80 – 2.74 (m, 2H), 1.45 (s, 9H), 1.19 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 171.2, 171.1, 156.2, 140.0, 128.5, 126.5, 80.3, 67.2, 58.6, 52.7, 51.9, 36.0, 34.0, 33.8, 28.3, 18.2. HRMS (ESI) m/z: calcld for C$_{21}$H$_{32}$N$_{2}$O$_{5}$SNa [M+Na]$^+$: 463.1873, found: 463.1873.
Methyl N-((tert-butoxycarbonyl)-L-methionyl)-S-phenethyl-L-cysteinate (3k)

Colorless oil (Flow: 165.6 mg, 88% yield; Batch: 158.1 mg, 84% yield). \(^1\)H NMR (400 MHz, Chloroform-\(\text{d}\)) \(\delta\) 7.23 – 7.19 (m, 2H), 7.16 – 7.05 (m, 4H), 5.32 (d, \(J = 7.5\) Hz, 1H), 4.74 – 4.68 (m, 1H), 4.36 – 4.19 (m, 1H), 3.66 (s, 3H), 2.93 – 2.87 (m, 2H), 2.80 – 2.75 (m, 2H), 2.72 – 2.67 (m, 2H), 2.51 (t, \(J = 7.2\) Hz, 2H), 2.05 – 1.98 (m, 4H), 1.91 – 1.83 (m, 1H), 1.36 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(\text{d}\)) \(\delta\) 171.7, 171.0, 155.5, 140.0, 128.5, 126.4, 80.0, 53.3, 52.7, 51.9, 36.0, 33.9, 31.8, 30.0, 28.3, 15.2. HRMS (ESI) m/z: calcd for \(\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_5\text{S}_2\text{Na}\) [M+Na]+: 493.1801, found: 493.1801.

Methyl N-((tert-butoxycarbonyl)-L-tyrosyl)-S-phenethyl-L-cysteinate (3l)

Colorless oil (Flow: 171.4 mg, 85% yield; Batch: 159.3 mg, 79% yield). \(^1\)H NMR (400 MHz, Chloroform-\(\text{d}\)) \(\delta\) 7.82 (s, 1H), 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 7.07 – 6.95 (m, 3H), 6.74 (d, \(J = 7.2\) Hz, 2H), 5.28 (s, 1H), 4.74 (s, 1H), 4.38 (s, 1H), 3.67 (s, 3H), 3.01 – 2.88 (m, 4H), 2.84 – 2.79 (m, 2H), 2.76 – 2.68 (m, 2H), 1.40 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(\text{d}\)) \(\delta\) 172.0, 170.9, 155.7, 155.6, 140.1, 130.4, 128.5, 127.3, 126.5, 115.7, 80.5, 56.0, 52.8, 52.1, 37.6, 36.0, 34.0, 33.9, 28.3. HRMS (ESI) m/z: calcd for \(\text{C}_{26}\text{H}_{34}\text{N}_2\text{O}_6\text{S}_{\text{Na}}\) [M+Na]+: 525.2030, found: 525.2024.

Methyl N-((tert-butoxycarbonyl)-L-tryptophyl)-S-phenethyl-L-cysteinate (3m)

Light yellow oil (Flow: 189.2 mg, 90% yield; Batch: 185 mg, 88% yield). \(^1\)H NMR (400 MHz, Chloroform-\(\text{d}\)) \(\delta\) 8.34 (s, 1H), 7.53 (d, \(J = 7.8\) Hz, 1H), 7.23 – 7.17 (m, 3H), 7.16 – 7.11 (m, 1H), 7.09 – 6.98 (m, 4H), 6.92 (s, 1H), 6.63 (d, \(J = 7.5\) Hz, 1H), 5.14 (s, 1H), 4.63 – 4.54 (m, 1H), 4.41 (s, 1H), 3.54 (s, 3H), 3.27 – 3.16 (m, 1H), 3.13 – 3.06 (m, 1H), 2.76 – 2.63 (m, 4H), 2.52 – 2.44 (m, 2H), 1.34 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(\text{d}\)) \(\delta\) 171.8, 170.8, 155.6, 140.2, 136.4, 128.6, 127.5, 126.5, 123.6, 122.1, 119.6, 118.8, 111.4, 110.0, 80.3, 55.2, 52.7, 52.1, 36.0, 34.1, 34.0, 28.4. HRMS (ESI) m/z: calcd for \(\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_5\text{S}_{\text{Na}}\) [M+Na]+: 548.2190, found: 548.2186.
Methyl N-(N\(^2\)-acetyl-N\(^6\)-(tert-butoxycarbonyl)-L-lysyl)-S-phenethyl-L-cysteinate (3n)
White solid (Flow: 192.4 mg, 94% yield; Batch: 169.9 mg, 83% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 7.03 (d, \(J = 7.5\) Hz, 1H), 6.37 (d, \(J = 7.0\) Hz, 1H), 4.78 – 4.71 (m, 2H), 4.53 – 4.47 (m, 1H), 3.75 (s, 3H), 3.14 – 3.05 (m, 2H), 3.00 – 2.94 (m, 2H), 2.88 – 2.82 (m, 2H), 2.79 – 2.74 (m, 2H), 2.01 – 1.95 (m, 4H), 1.88 – 1.81 (m, 1H), 1.70 – 1.63 (m, 1H), 1.52 – 1.47 (m, 2H), 1.43 (s, 9H), 1.38 – 1.35 (m, 1H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.7, 171.0, 170.3, 156.2, 140.0, 128.5, 126.5, 79.1, 52.9, 52.7, 51.9, 39.9, 36.0, 33.9(8), 33.9(6), 31.9, 29.6, 28.5, 23.1, 22.3. HRMS (ESI) \(m/z\): calcd for C\(_{25}\)H\(_{39}\)N\(_3\)O\(_6\)SNa \([M+Na]^+\): 532.2452, found: 532.2456.

Methyl N-((S)-2-((tert-butoxycarbonyl)amino)-4-phenylbutanoyl)-S-phenethyl-L-cysteinate (3o)
Colorless oil (Flow: 172.6 mg, 86% yield; Batch: 162.6 mg, 81% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.29 – 7.24 (m, 4H), 7.22-7.15 (m, 6H), 6.86 (d, \(J = 7.2\) Hz, 1H), 5.09 (d, \(J = 8.0\) Hz, 1H), 4.80 – 4.75 (m, 1H), 4.22 – 4.08 (m, 1H), 3.73 (s, 3H), 3.01 – 2.93 (m, 2H), 2.87 – 2.82 (m, 2H), 2.79 – 2.73 (m, 2H), 2.69 (t, \(J = 7.8\) Hz, 2H), 2.20 – 2.12 (m, 1H), 1.94 – 1.88 (m, 1H), 1.44 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.8, 171.0, 155.5, 140.9, 140.0, 128.5(3), 128.5(1), 128.4(6), 126.5, 126.2, 80.2, 54.2, 52.7, 51.9, 36.1, 34.1(4), 34.0(7), 34.0, 31.7, 28.3. HRMS (ESI) \(m/z\): calcd for C\(_{27}\)H\(_{36}\)N\(_2\)O\(_5\)SNa \([M+Na]^+\): 523.2237, found: 523.2254.

Methyl N-(tert-butoxycarbonyl)-L-alanyl-L-phenylalanyl-S-phenethyl-L-cysteinate (4a)
White solid (Flow: 205.6 mg, 92% yield; Batch: 194.4 mg, 87% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.30 – 7.22 (m, 4H), 7.22 – 7.14 (m, 6H), 7.13 – 7.06 (m, 1H), 6.98 (d, \(J = 7.0\) Hz, 1H), 5.24 (s, 1H), 4.84 – 4.76 (m, 1H), 4.75 – 4.67 (m, 1H), 4.19 (s, 1H), 3.69 (s, 3H), 3.08 (d, \(J = 5.8\) Hz, 2H), 2.95 – 2.78 (m, 4H), 2.75 – 2.68 (m, 2H), 1.41 (s, 9H), 1.27 (d, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 172.7, 170.8, 170.7, 155.5, 140.1, 136.3, 129.4, 128.6, 128.5, 126.9, 126.4, 80.1, 54.1, 52.6, 52.1, 50.3, 38.2, 36.0, 34.0, 33.9, 28.4, 18.5. HRMS (ESI) \(m/z\): calcd for C\(_{29}\)H\(_{36}\)N\(_3\)O\(_6\)SNa \([M+Na]^+\): 580.2452, found: 580.2456.
Methyl N-(tert-butoxycarbonyl)-L-valyl-L-phenylalanyl-S-phenethyl-L-cysteinate (4b)
White solid (Flow: 208.2 mg, 89% yield; Batch: 187.1 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.30 – 7.13 (m, 10H), 7.10 – 7.00 (m, 1H), 6.90 (d, $J = 7.0$ Hz, 1H), 5.24 (d, $J = 7.9$ Hz, 1H), 4.88 – 4.77 (m, 1H), 4.75 – 4.66 (m, 1H), 3.98 (s, 1H), 3.69 (s, 3H), 3.06 (d, $J = 6.3$ Hz, 2H), 2.91 – 2.77 (m, 4H), 2.72 (d, $J = 6.5$ Hz, 2H), 2.15 – 2.01 (m, 1H), 1.43 (s, 9H), 0.89 (d, $J = 5.5$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 171.7, 170.7(2), 170.6, 170.5, 155.9, 140.1, 136.3, 129.4, 128.6, 128.5, 126.4, 79.9, 60.0, 54.1, 52.6, 52.0, 38.4, 36.0, 34.0, 33.9, 30.8, 28.4, 19.3, 17.7. HRMS (ESI) m/z: calcld for C$_{31}$H$_{43}$N$_3$O$_6$SNa [M+Na]$^+$: 608.2765, found: 608.2772.

Methyl N-(tert-butoxycarbonyl)-L-phenylalanyl-L-phenylalanyl-S-phenethyl-L-cysteinate (4c)
White solid (Flow: 210.2 mg, 83% yield; Batch: 212.7 mg, 84% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.28 – 7.12 (m, 14H), 7.11 – 7.07 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 5.23 (d, $J = 6.6$ Hz, 1H), 4.81 (q, $J = 6.9$ Hz, 1H), 4.69 (q, $J = 5.9$ Hz, 1H), 4.43 (s, 1H), 3.68 (s, 3H), 2.92 – 2.84 (m, 2H), 2.83 – 2.78 (m, 2H), 2.74 – 2.68 (m, 2H), 1.35 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 171.4, 170.8, 170.5, 155.5, 140.1, 136.7, 136.2, 129.5, 129.4, 128.6, 128.5, 126.4, 80.1, 55.7, 54.1, 52.6, 52.2, 38.4, 38.3, 36.1, 34.0, 33.9, 28.3. HRMS (ESI) m/z: calcld for C$_{32}$H$_{43}$N$_3$O$_6$SNa [M+Na]$^+$: 656.2765, found: 656.2768.

Methyl N-(tert-butoxycarbonyl)-L-valyl-L-alanyl-S-phenethyl-L-cysteinate (4d)
White solid (Flow: 189.0 mg, 93% yield; Batch: 176.8 mg, 87% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.31 – 7.25 (m, 3H), 7.23 – 7.16 (m, 3H), 6.93 (d, $J = 6.8$ Hz, 1H), 5.34 (d, $J = 8.8$ Hz, 1H), 4.81 – 4.74 (m, 1H), 4.68 – 4.59 (m, 1H), 4.06 – 3.96 (m, 1H), 3.74 (s, 3H), 2.95 (d, $J = 5.7$ Hz, 2H), 2.87 – 2.81 (m, 2H), 2.79 – 2.73 (m, 2H), 2.15 – 2.06 (m, 1H), 1.44 (s, 9H), 1.39 (d, $J = 7.0$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz, 1H), 0.90 (d, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 172.1, 171.6, 171.0, 156.0, 140.1, 128.5, 126.4, 79.8, 59.8, 52.6, 52.0, 48.8, 36.0, 34.0, 33.9, 31.1, 28.3, 19.4, 18.5, 17.8. HRMS (ESI) m/z: calcld for C$_{25}$H$_{39}$N$_3$O$_6$SNa [M+Na]$^+$: 532.2452, found: 532.2455.
Methyl N-(tert-butoxycarbonyl)glycyl-L-prolyl-S-phenethyl-L-cysteinate (4e)
Colorless oil (Flow: 155.6 mg, 79% yield; Batch: 149.7 mg, 76% yield, d.r = 1:4.3). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.52 (d, $J$ = 7.7 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 5.62 – 5.49 (m, 1H), 4.78 – 4.70 (m, 1H), 4.64 – 4.56 (m, 1H), 4.01 – 3.91 (m, 1H), 3.85 – 3.78 (m, 1H), 3.73 (s, 3H), 3.49 – 3.30 (m, 2H), 3.03 – 2.89 (m, 2H), 2.88 – 2.81 (m, 2H), 2.79 – 2.72 (m, 2H), 2.34 – 2.25 (m, 1H), 2.13 – 2.03 (m, 1H), 1.99 – 1.86 (m, 2H), 1.46 – 1.40 (m, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 171.1, 170.9, 168.6, 155.8, 140.1, 128.5, 126.4, 79.6, 59.9, 52.6, 52.2, 46.2, 43.0, 34.0, 33.9, 28.3, 27.7, 24.7. HRMS (ESI) m/z: calcd for C$_{24}$H$_{35}$N$_3$O$_6$SNa [M+Na]$^+$: 516.2139, found: 516.2144.

Methyl N-(tert-butoxycarbonyl)-L-valyl-L-prolyl-S-phenethyl-L-cysteinate (4f)
Colorless oil (Flow: 177.6 mg, 83% yield; Batch: 171.2 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.44 (d, $J$ = 7.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 5.33 (d, $J$ = 9.3 Hz, 1H), 4.76 – 4.70 (m, 1H), 4.64 – 4.58 (m, 1H), 4.32 – 4.25 (m, 1H), 3.73 (s, 3H), 3.69 (d, $J$ = 4.2 Hz, 1H), 3.59 – 3.52 (m, 1H), 2.98 – 2.90 (m, 2H), 2.87 – 2.82 (m, 2H), 2.80 – 2.74 (m, 2H), 2.29 (d, $J$ = 9.5 Hz, 1H), 2.05 – 1.90 (m, 4H), 1.43 (s, 9H), 1.00 (d, $J$ = 6.7 Hz, 3H), 0.92 (d, $J$ = 6.7 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 172.4, 171.1, 171.0, 155.8, 140.1, 128.5, 128.4, 126.4, 79.5, 59.9, 56.7, 52.5, 52.1, 47.5, 36.0, 34.1, 33.9, 31.4, 28.3, 27.5, 25.0, 19.6, 17.4. HRMS (ESI) m/z: calcd for C$_{27}$H$_{41}$N$_3$O$_6$SNa [M+Na]$^+$: 558.2608, found: 558.2611.

Methyl N-(tert-butoxycarbonyl)-L-phenylalanyl-L-valyl-S-phenethyl-L-cysteinate (4g)
White solid (Flow: 201.3 mg, 86% yield, Batch: 191.9 mg, 82% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.31 (d, $J$ = 7.6 Hz, 1H), 7.27 – 7.22 (m, 4H), 7.20 – 7.14 (m, 6H), 6.97 (d, $J$ = 7.4 Hz, 1H), 5.39 (d, $J$ = 7.3 Hz, 1H), 4.81 – 4.75 (m, 1H), 4.53 – 4.42 (m, 2H), 3.72 (s, 3H), 3.13-3.07 (m, 1H), 3.04 – 2.98 (m, 1H), 2.94 (d, $J$ = 5.6 Hz, 2H), 2.86 – 2.80 (m, 2H), 2.78 – 2.73 (m, 2H), 2.16 – 2.06 (m, 1H), 1.37 (s, 9H), 0.92 (dd, $J$ = 12.8, 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 171.6, 171.1, 170.9, 155.6, 140.1, 136.8, 129.4, 128.6, 128.5, 126.8, 126.4, 80.0, 58.4, 55.8, 52.6, 52.0, 38.1, 36.1, 34.0, 33.9, 31.2, 28.3, 19.0, 18.1. HRMS (ESI) m/z: calcd for C$_{31}$H$_{43}$N$_3$O$_6$SNa [M+Na]$^+$: 608.2765, found: 608.2771.
Methyl N-(tert-butoxycarbonyl)-L-valyl-L-methionyl-S-phenethyl-L-cysteinate (4h)

White solid (Flow: 193.6 mg, 85% yield; Batch: 184.5 mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.48 (d, $J = 7.7$ Hz, 1H), 7.33 – 7.25 (m, 3H), 7.22 – 7.16 (m, 3H), 5.46 (d, $J = 8.5$ Hz, 1H), 4.79 (q, $J = 5.9$ Hz, 2H), 4.05 (d, $J = 7.2$ Hz, 1H), 3.73 (s, 3H), 2.95 (d, $J = 5.7$ Hz, 2H), 2.87 – 2.81 (m, 2H), 2.80 – 2.73 (m, 2H), 2.58 (t, $J = 7.2$ Hz, 2H), 2.13 – 1.99 (m, 6H), 1.49 (s, 9H), 0.95 – 0.89 (dd, $J = 10.9$, 6.8 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.9, 171.0, 170.9, 155.9, 140.0, 128.5, 126.4, 79.7, 59.9, 52.6, 52.0, 36.0, 33.9, 31.7, 31.0, 29.8, 28.4, 19.3, 18.0, 15.1. HRMS (ESI) m/z: calcd for C$_{27}$H$_{43}$N$_3$O$_6$S$_2$Na $[M{+Na}]^+$: 592.2485, found: 592.2490.

Methyl N-(tert-butoxycarbonyl)-L-tryptophyl-L-methionyl-S-phenethyl-L-cysteinate (4i)

White solid (Flow: 241.4 mg, 92% yield; Batch: 228.3 mg, 87% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.59 (s, 1H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.03 (s, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.98 – 6.89 (m, 1H), 5.29 (d, $J = 7.0$ Hz, 1H), 4.71 – 4.59 (m, 2H), 3.70 (s, 3H), 3.34 – 3.16 (m, 2H), 2.94 – 2.79 (m, 4H), 2.76 – 2.70 (m, 2H), 2.37 (t, $J = 6.5$ Hz, 2H), 1.99 – 1.84 (m, 5H), 1.41 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 172.0, 170.9, 170.8, 155.7, 140.1, 136.2, 128.5, 126.5, 123.5, 122.2, 119.7, 118.8, 111.4, 80.3, 55.4, 52.7, 52.4, 52.0, 36.0, 33.9, 33.8, 30.8, 29.6, 28.4, 28.1, 14.9. HRMS (ESI) m/z: calcd for C$_{33}$H$_{43}$N$_3$O$_6$S$_2$Na $[M{+Na}]^+$: 679.2594, found: 679.2597.

Methyl N-(tert-butoxycarbonyl)-L-tyrosyl-L-methionyl-S-phenethyl-L-cysteinate (4j)

White solid (Flow: 230.4 mg, 91% yield; Batch: 222.8 mg, 88% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.73 (s, 1H), 7.45 (d, $J = 7.0$ Hz, 1H), 7.29 – 7.13 (m, 6H), 6.98 (d, $J = 8.1$ Hz, 2H), 6.75 (d, $J = 8.1$ Hz, 2H), 5.39 – 5.26 (m, 1H), 4.79 – 4.67 (m, 2H), 4.43 – 4.28 (m, 1H), 3.71 (s, 3H), 2.96 (s, 4H), 2.86 – 2.80 (m, 2H), 2.79 – 2.73 (m, 2H), 2.51 (t, $J = 6.8$ Hz, 2H), 2.01 (d, $J = 13.3$ Hz, 5H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 172.0, 171.1, 170.9, 155.8, 155.6, 140.0,
Methyl N-(tert-butoxycarbonyl)-L-phenylalanyl-L-methionyl-S-phenethyl-L-cysteinate (4k)

White solid (Flow: 229.6 mg, 93% yield; Batch: 219.7 mg, 89% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.39 (d, $J = 7.8$ Hz, 1H), 7.29 – 7.24 (m, 4H), 7.22 – 7.20 (m, 1H), 7.20 – 7.14 (m, 6H), 5.29 (d, $J = 6.7$ Hz, 1H), 4.79 – 4.71 (m, 2H), 4.51 – 4.39 (m, 1H), 3.72 (s, 3H), 3.11 – 3.01 (m, 2H), 2.95 (d, $J = 5.3$ Hz, 2H), 2.87 – 2.82 (m, 2H), 2.79 – 2.73 (m, 2H), 2.51 (t, $J = 7.3$ Hz, 2H), 2.05 (s, 3H), 2.03 – 1.94 (m, 2H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.5, 170.9, 170.8, 155.5, 140.0, 136.6, 129.4, 128.6, 128.5, 126.9, 126.4, 80.1, 55.7, 52.6, 52.2, 52.0, 38.2, 36.1, 33.9, 31.5, 29.7, 28.3, 15.1. HRMS (ESI) m/z: calcd for C$_{31}$H$_{43}$N$_3$O$_7$S$_2$Na [M+Na]$^+$: 656.2435, found: 656.2437.

Methyl N-(tert-butoxycarbonyl)-L-valyl-L-tryptophyl-S-phenethyl-L-cysteinate (4l)

White solid (Flow: 234.6 mg, 94% yield; Batch: 234.6 mg, 94% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.49 (s, 1H), 7.65 (d, $J = 7.5$ Hz, 1H), 7.31 – 7.24 (m, 3H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.16 – 7.06 (m, 4H), 7.02 (s, 1H), 6.93 – 6.83 (m, 2H), 5.18 (d, $J = 7.3$ Hz, 1H), 4.88 – 4.76 (m, 1H), 4.65 – 4.58 (m, 1H), 4.06 – 3.94 (m, 1H), 3.62 (s, 3H), 3.35 – 3.26 (m, 1H), 3.18 – 3.09 (m, 1H), 2.81 – 2.75 (m, 4H), 2.65 – 2.57 (m, 2H), 2.18 – 2.07 (m, 1H), 1.40 (s, 9H), 0.90 (d, $J = 6.7$ Hz, 3H), 0.80 (d, $J = 6.6$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.6, 171.2, 170.7, 156.0, 140.1, 136.3, 128.5(4), 128.5(1), 127.5, 126.5, 123.8, 122.1, 119.6, 118.7, 111.4, 109.9, 80.0, 60.1, 53.8, 52.5, 52.2, 36.0, 34.0, 33.9, 30.8, 28.3, 28.1, 19.3, 17.5. HRMS (ESI) m/z: calcd for C$_{33}$H$_{44}$N$_4$O$_6$SNa [M+Na]$^+$: 647.2874, found: 647.2878.

Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(4-fluorophenethyl)-L-cysteinate (5a)

130.4, 128.5, 127.4, 126.5, 115.7, 80.5, 56.0, 52.7, 52.3, 52.1, 37.4, 36.0, 33.9, 33.8, 31.3, 29.7, 28.3, 15.1. HRMS (ESI) m/z: calcd for C$_{31}$H$_{43}$N$_3$O$_7$S$_2$Na [M+Na]$^+$: 656.2435, found: 656.2437.
White solid (Flow: 171.0 mg, 85% yield; Batch: 162.9mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 7.15 – 7.09 (m, 2H), 6.99 – 6.93 (m, 2H), 6.87 (d, $J$ = 7.2 Hz, 1H), 5.16 (d, $J$ = 8.0 Hz, 1H), 4.78 – 4.70 (m, 1H), 4.51 – 4.34 (m, 1H), 3.70 (s, 3H), 3.14 – 3.00 (m, 2H), 2.97 – 2.86 (m, 2H), 2.82 – 2.76 (m, 2H), 2.74 – 2.65 (m, 2H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.3, 170.8, 161.6 (d, $J$ = 242.7 Hz, 1C), 155.4, 136.5, 135.7 (d, $J$ = 3.0 Hz, 1C), 130.0, 129.9, 129.3, 128.6, 127.7, 126.9, 80.2, 55.7, 52.6, 52.0, 38.3, 35.2, 34.1, 34.0, 28.3. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ 116.60. HRMS (ESI) m/z: calcd for C$_{26}$H$_{33}$FN$_2$O$_5$SNa [M+Na]$^+$: 527.1986, found: 527.1991.

Methyl S-(4-bromophenethyl)-N-((tert-butoxycarbonyl)-L-phenylalanyl)-L-cysteinate (5b)
White solid (Flow: 209.8 mg, 93% yield; Batch: 196.3mg, 87% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.40 (d, $J$ = 8.3 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.18 (m, 3H), 7.05 (d, $J$ = 8.3 Hz, 2H), 6.81 (d, $J$ = 7.5 Hz, 1H), 5.09 (d, $J$ = 7.9 Hz, 1H), 4.78 – 4.70 (m, 1H), 4.48 – 4.35 (m, 1H), 3.70 (s, 3H), 3.13 – 3.02 (m, 2H), 2.97 – 2.87 (m, 2H), 2.81 – 2.74 (m, 2H), 2.74 – 2.65 (m, 2H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.3, 170.7, 155.4, 139.0, 136.5, 131.6, 130.3, 129.3, 128.7, 127.0, 120.3, 80.2, 55.7, 52.7, 52.0, 38.3, 35.4, 34.2, 33.7, 28.3. HRMS (ESI) m/z: calcd for C$_{26}$H$_{33}$BrN$_2$O$_5$SNa [M+Na]$^+$: 587.1186, found: 587.1178.

Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(4-iodophenethyl)-L-cysteinate (5c)
White solid (Flow: 209.4 mg, 86% yield; Batch: 202.1mg, 83% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.60 (d, $J$ = 8.1 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.18 (m, 3H), 6.92 (d, $J$ = 8.1 Hz, 2H), 6.77 (d, $J$ = 7.0 Hz, 1H), 5.10 – 5.00 (m, 1H), 4.78 – 4.69 (m, 1H), 4.47 – 4.35 (m, 1H), 3.70 (s, 3H), 3.13 – 3.01 (m, 2H), 2.97 – 2.86 (m, 2H), 2.79 – 2.74 (m, 2H), 2.73 – 2.65 (m, 2H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.2, 170.7, 155.3, 139.6, 137.5, 136.5, 136.0, 129.3, 128.7, 127.0, 91.7, 80.2, 55.7, 52.7, 52.0, 38.3, 35.4, 34.2, 33.7, 28.3. HRMS (ESI) m/z: calcd for C$_{26}$H$_{33}$IN$_2$O$_5$SNa [M+Na]$^+$: 635.1047, found: 635.1051.
Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(4-cyanophenethyl)-L-cysteinate (5d)
White solid (Flow: 121.9 mg, 60% yield; Batch: 136.1 mg, 67% yield). 1H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.58 (d, \(J = 7.7\) Hz, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 6.69 (s, 1H), 5.00 (s, 1H), 4.78 – 4.69 (m, 1H), 4.47 – 4.28 (m, 1H), 3.71 (s, 3H), 3.13 – 3.01 (m, 2H), 2.99 – 2.86 (m, 4H), 2.82 – 2.70 (m, 2H), 1.40 (s, 9H). 13C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.3, 170.7, 155.4, 145.5, 136.4, 132.3, 129.4, 129.3, 128.7, 127.0, 118.9, 110.3, 80.2, 55.7, 52.7, 52.0, 38.3, 35.9, 34.2, 33.2, 28.2. HRMS (ESI) m/z: calcd for C\(_{26}\)H\(_{33}\)FN\(_2\)O\(_5\)SNa \([\text{M+Na}]^+\): 527.1986, found: 527.1991. HRMS (ESI) m/z: calcd for C\(_{27}\)H\(_{33}\)N\(_3\)O\(_5\)SNa \([\text{M+Na}]^+\): 534.2033, found: 534.2045.

Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(2-(thiophen-2-yl)ethyl)-L-cysteinate (5e)
White solid (Flow: 148.2 mg, 75% yield; Batch: 144.2 mg, 73% yield). 1H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.30 – 7.25 (m, 2H), 7.23 – 7.18 (m, 3H), 7.14 – 7.10 (m, 1H), 6.93 – 6.89 (m, 1H), 6.85 – 6.69 (m, 2H), 5.10 (d, \(J = 7.8\) Hz, 1H), 4.78 – 4.71 (m, 1H), 4.49 – 4.36 (m, 1H), 3.71 (s, 3H), 3.13 – 3.00 (m, 4H), 2.98 – 2.89 (m, 2H), 2.78 – 2.72 (m, 2H), 1.40 (s, 9H). 13C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.2, 170.7, 155.3, 142.5, 136.5, 129.4, 128.7, 126.9, 126.9, 125.1, 123.8, 80.2, 55.7, 52.7, 52.1, 38.3, 34.2(1), 34.1(6), 30.3, 28.3. HRMS (ESI) m/z: calcd for C\(_{24}\)H\(_{32}\)N\(_2\)O\(_5\)S\(_2\)Na \([\text{M+Na}]^+\): 515.1645, found: 515.1653.

Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-ethyl-L-cysteinate (5f)
White solid (Flow: 146.0 mg, 89% yield; Batch: 142.7 mg, 87% yield). 1H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.23 – 7.18 (m, 2H), 7.17 – 7.12 (m, 3H), 6.82 (d, \(J = 7.3\) Hz, 1H), 5.14 (d, \(J = 8.0\) Hz, 1H), 4.67 (q, \(J = 5.4\) Hz, 1H), 4.46 – 4.29 (m, 1H), 3.65 (s, 3H), 3.07 – 2.94 (m, 2H), 2.90 – 2.80 (m, 2H), 2.41 (q, \(J = 7.4\) Hz, 2H), 1.32 (s, 9H), 1.12 (t, \(J = 7.4\) Hz, 3H). 13C NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.3, 170.9, 155.3, 136.6, 129.4, 128.6, 126.9, 80.0, 55.6, 52.6, 52.0, 38.3, 33.5, 28.3, 26.4, 14.6. HRMS (ESI) m/z: calcd for C\(_{20}\)H\(_{30}\)N\(_2\)O\(_2\)SNa \([\text{M+Na}]^+\): 433.1768, found: 433.1770.
Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-octadecyl-L-cysteinate (5g)
White solid (Flow: 227.0 mg, 90% yield; Batch: 216.7 mg, 87% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 6.89 (d, $J = 7.5$ Hz, 1H), 5.21 (d, $J = 8.0$ Hz, 1H), 4.74 (d, $J = 7.1$ Hz, 1H), 4.52 – 4.36 (m, 1H), 3.71 (s, 3H), 3.15 – 3.01 (m, 2H), 2.96 – 2.85 (m, 2H), 2.45 (t, $J = 7.4$ Hz, 2H), 1.54 – 1.48 (m, 2H), 1.40 (s, 9H), 1.33 – 1.21 (m, 30H), 0.88 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.2, 170.9, 155.3, 136.6, 129.4, 128.5, 126.8, 80.0, 55.6, 52.5, 52.0, 38.4, 34.0, 32.6, 31.9, 29.6(9), 29.6, 29.5(2), 29.4(9), 29.3, 29.2, 28.8, 28.2, 22.7, 14.1. HRMS (ESI) m/z: calcd for C$_{36}$H$_{62}$N$_2$O$_5$SNa [M+Na]$^+$: 657.4272, found: 657.4279.

Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(3-iodopropyl)-L-cysteinate (5h)
White solid (Flow: 186.6 mg, 85% yield; Batch: 173.4 mg, 79% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 6.90 (d, $J = 6.8$ Hz, 1H), 5.18 (d, $J = 8.0$ Hz, 1H), 4.78 – 4.72 (m, 1H), 4.54 – 4.34 (m, 1H), 3.74 (s, 3H), 3.23 (t, $J = 6.7$ Hz, 2H), 3.14 – 3.01 (m, 2H), 2.99 – 2.87 (m, 2H), 2.57 (t, $J = 6.9$ Hz, 2H), 2.03 – 1.96 (m, 2H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.3, 170.7, 155.3, 136.5, 129.4, 128.6, 126.9, 80.2, 55.6, 52.7, 52.1, 38.3, 34.0, 33.0, 32.6, 28.3, 4.8. HRMS (ESI) m/z: calcd for C$_{21}$H$_{31}$IN$_2$O$_5$SNa [M+Na]$^+$: 573.0891, found: 573.0897.

Methyl S-(5-bromopentyl)-N-((tert-butoxycarbonyl)-L-phenylalanyl)-L-cysteinate (5i)
Light yellow solid (Flow: 187.2 mg, 88% yield; Batch: 180.8 mg, 85% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.31 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 6.86 (d, $J = 7.4$ Hz, 1H), 5.15 (d, $J = 7.9$ Hz, 1H), 4.77 – 4.69 (m, 1H), 4.50 – 4.34 (m, 1H), 3.73 (s, 3H), 3.39 (t, $J = 6.7$ Hz, 2H), 3.14 – 3.01 (m, 2H), 2.97 – 2.86 (m, 2H), 2.48 (t, $J = 6.8$ Hz, 2H), 1.88 – 1.81 (m, 2H), 1.60 – 1.47 (m, 4H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 171.2, 170.8, 155.3, 136.5, 129.3, 128.6, 126.9, 80.1, 55.6, 52.6, 52.0, 38.3, 34.0, 33.5, 32.3, 32.2, 28.5, 28.3, 27.2. HRMS (ESI) m/z: calcd for C$_{23}$H$_{35}$BrN$_2$O$_5$SNa [M+Na]$^+$: 553.1342, found: 553.1363.
Methyl N-((tert-butoxycarbonyl)-L-phenylalanyl)-S-(3-methoxypropyl)-L-cysteinate (5j)

Colorless oil (Flow: 155.6 mg, 86% yield; Batch: 152mg, 84% yield). \(^1^H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 7.00 (d, \(J = 6.9\) Hz, 1H), 5.32 (d, \(J = 8.2\) Hz, 1H), 4.81 – 4.73 (m, 1H), 4.46 (s, 1H), 3.72 (s, 3H), 3.44 – 3.38 (m, 2H), 3.31 (s, 3H), 3.18 – 3.11 (m, 1H), 3.04 – 2.97 (m, 1H), 2.96 – 2.85 (m, 2H), 2.59 – 2.51 (m, 2H), 1.82 – 1.73 (m, 2H), 1.39 (s, 9H). \(^1^C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.3, 170.8, 155.4, 136.7, 129.3, 128.5, 126.8, 80.0, 70.8, 58.5, 55.5, 52.5, 52.2, 38.2, 33.9, 29.5, 29.3, 28.2. HRMS (ESI) m/z: calcd for C\(_{22}\)H\(_{34}\)N\(_2\)O\(_6\)SNa [M+Na]\(^+\): 477.2030, found: 477.2033.

Methyl S-(3-(benzyloxy)propyl)-N-((tert-butoxycarbonyl)-L-phenylalanyl)-L-cysteinate (5k)

Light yellow solid (Flow: 182.2 mg, 86% yield; Batch: 175.8mg, 83% yield). \(^1^H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.34 – 7.24 (m, 7H), 7.22 – 7.18 (m, 3H), 6.91 (d, \(J = 6.7\) Hz, 1H), 5.21 (d, \(J = 7.4\) Hz, 1H), 4.77 – 4.71 (m, 1H), 4.48 (s, 2H), 4.43 (s, 1H), 3.69 (s, 3H), 3.51 (t, \(J = 6.1\) Hz, 2H), 3.15 – 2.99 (m, 2H), 2.96 – 2.87 (m, 2H), 2.57 (t, \(J = 7.3\) Hz, 2H), 1.86 – 1.78 (m, 2H), 1.39 (s, 9H). \(^1^C\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.3, 170.8, 155.4, 138.3, 136.6, 129.4, 128.6, 128.4, 127.7, 127.6, 126.9, 80.1, 73.0, 68.5, 55.6, 52.6, 52.1, 38.3, 34.0, 29.7, 29.4, 28.3. HRMS (ESI) m/z: calcd for C\(_{28}\)H\(_{38}\)N\(_2\)O\(_6\)SNa [M+Na]\(^+\): 553.2343, found: 553.2346.

Ethyl (6S,9R)-6-benzyl-9-(methoxycarbonyl)-2,2-dimethyl-4,7-dioxo-3-oxa-11-thia-5,8-diazahexadecan-17-oate (5l)

White solid (Flow: 94.7 mg, 45% yield; Batch: 111.5mg, 53% yield). \(^1^H\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 6.75 (d, \(J = 7.4\) Hz, 1H), 5.18 – 5.02 (m, 1H), 4.77 – 4.70 (m, 1H), 4.47 – 4.35 (m, 1H), 4.16 – 4.08 (q, \(J = 7.1\) Hz, 2H), 3.73 (s, 3H), 3.15 – 3.02 (m, 2H), 2.97 – 2.86 (m, 2H), 2.47 (t, \(J = 7.2\) Hz, 2H), 2.29 (t, \(J = 7.4\) Hz, 2H), 1.66 – 1.58 (m, 2H),
1.57 – 1.51 (m, 2H), 1.41 (s, 9H), 1.39 – 1.32 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). \(^1^C\)NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 173.6, 171.1, 170.8, 155.3, 136.5, 129.3, 128.6, 126.9, 80.2, 60.3, 55.6, 52.6, 52.0, 38.2, 34.1(1), 34.0(8), 32.4, 29.0, 28.3, 28.1, 24.4, 14.2. HRMS (ESI) m/z: calcd for C\(_{26}\)H\(_{40}\)N\(_2\)O\(_7\)SNa [M+Na]\(^+\): 547.2448, found: 547.2458.

**Methyl N-(tert-butoxycarbonyl)-L-phenylalanyl)-S-cyclopentyl-L-cysteinate (5m)**

White solid (Flow: 117.2 mg, 65% yield; Batch: 110mg, 61% yield). \(^1^H\)NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.32 – 7.27 (m, 2H), 7.26 – 7.20 (m, 3H), 6.71 (d, J = 7.3 Hz, 1H), 5.12 – 4.98 (m, 1H), 4.78 – 4.71 (m, 1H), 4.47 – 4.36 (m, 1H), 3.73 (s, 3H), 3.14 – 3.01 (m, 3H), 2.98 – 2.90 (m, 2H), 1.98 – 1.90 (m, 2H), 1.76 – 1.66 (m, 2H), 1.59 – 1.51 (m, 2H), 1.47 – 1.38 (m, 11H). \(^1^C\)NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.1, 170.9, 155.3, 136.5, 129.4, 128.6, 126.9, 80.2, 55.6, 52.6, 52.0, 44.1, 38.4, 33.7(4), 33.7(1), 33.6(7), 28.3, 24.7. HRMS (ESI) m/z: calcd for C\(_{23}\)H\(_{34}\)N\(_2\)O\(_5\)SNa [M+Na]\(^+\): 473.2081, found: 473.2089.

**Methyl S-(2-((3R,5R,7R)-adamantan-1-yl)ethyl)-N-(tert-butoxycarbonyl)-L-phenyl alanyl) -L-cysteinate (5n)**

Colorless oil (Flow: 204.5 mg, 94% yield; Batch: 193.6mg, 89% yield). \(^1^H\)NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 6.76 (d, J = 7.4 Hz, 1H), 5.13 – 5.01 (m, 1H), 4.77 – 4.70 (m, 1H), 4.48 – 4.35 (m, 1H), 3.73 (s, 3H), 3.14 – 3.03 (m, 2H), 2.97 – 2.86 (m, 2H), 2.45 – 2.38 (m, 2H), 1.94 (s, 2H), 1.72 – 1.66 (m, 3H), 1.64 – 1.58 (m, 3H), 1.45 (s, 6H), 1.41 (s, 9H), 1.32 – 1.24 (m, 3H). \(^1^C\)NMR (100 MHz, Chloroform-\(d\)) \(\delta\) 171.2, 170.9, 155.3, 136.5, 129.4, 128.6, 126.9, 80.2, 55.6, 52.6, 51.9, 44.2, 42.2, 38.3, 37.0, 34.1, 32.7, 28.6, 28.3, 26.6. HRMS (ESI) m/z: calcd for C\(_{30}\)H\(_{44}\)N\(_2\)O\(_5\)SNa [M+Na]\(^+\): 567.2864, found: 567.2873.
5. Copies of NMR Spectra

$^1$H NMR Spectrum of Compound 3a (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3a (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3b (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3b (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3c (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3c (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3d (400 MHz, CDCl$_3$)
13C NMR Spectrum of Compound 3f (100 MHz, CDCl3)

1H NMR Spectrum of Compound 3g (400 MHz, CDCl3)
$^{13}$C NMR Spectrum of Compound 3g (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3h (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3h (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3i (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3i (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3j (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3k (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3l (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3l (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3m (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 3m (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 3n (400 MHz, CDCl$_3$)
13C NMR Spectrum of Compound 3n (100 MHz, CDCl3)

1H NMR Spectrum of Compound 3o (400 MHz, CDCl3)
$^{13}$C NMR Spectrum of Compound 3o (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 4a (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 4a (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 4b (400 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 4c (400 MHz, CDCl₃)
$^1$H NMR Spectrum of Compound 4d (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 4c (100 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound $4e$ (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound $4f$ (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of Compound 4f (100 MHz, CDCl₃)

$^1$H NMR Spectrum of Compound 4g (400 MHz, CDCl₃)
$^{13}$C NMR Spectrum of Compound 4g (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of Compound 4h (400 MHz, CDCl$_3$)
13C NMR Spectrum of Compound 4h (100 MHz, CDCl₃)

1H NMR Spectrum of Compound 4i (400 MHz, CDCl₃)
$^{13}$C NMR Spectrum of Compound 5a (100 MHz, CDCl$_3$)

$^{19}$F NMR Spectrum of Compound 5a (376 MHz, CDCl$_3$)
1H NMR Spectrum of Compound 5b (400 MHz, CDCl₃)

13C NMR Spectrum of Compound 5b (100 MHz, CDCl₃)
$^1$H NMR Spectrum of Compound 5d (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5d (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 5e (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5e (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 5f (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5f (100 MHz, CDCl$_3$)
$^{1}H$ NMR Spectrum of Compound 5g (400 MHz, CDCl$_3$)

$^{13}C$ NMR Spectrum of Compound 5g (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 5h (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5h (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 5i (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5i (100 MHz, CDCl$_3$)
1H NMR Spectrum of Compound 5j (400 MHz, CDCl₃)

13C NMR Spectrum of Compound 5j (100 MHz, CDCl₃)
$^{1}H$ NMR Spectrum of Compound 5k (400 MHz, CDCl$_3$)

$^{13}C$ NMR Spectrum of Compound 5k (100 MHz, CDCl$_3$)
1H NMR Spectrum of Compound 51 (400 MHz, CDCl₃)

13C NMR Spectrum of Compound 51 (100 MHz, CDCl₃)
$^1$H NMR Spectrum of Compound 5m (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5m (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of Compound 5n (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of Compound 5n (100 MHz, CDCl$_3$)