SUPPORTING INFORMATION

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General Information

Instrumentation and Chemicals
NMR spectra were recorded on Bruker 400 M and 500 M nuclear resonance spectrometers unless otherwise specified, respectively. CDCl$_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shift values for $^1$H and $^{13}$C are referenced to residual solvent peaks (CHCl$_3$ in CDCl$_3$: 7.26 ppm for $^1$H, 77.00 ppm for $^{13}$C). Chemical shifts are reported in δ ppm. All coupling constants (J values) were reported in Hertz (Hz). Data for $^1$H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) in the State-authorized Analytical Center in Peking University.

Experimental Section
All reactions were carried out under air atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. To be specific, Pd(OAc)$_2$ was purchased from Acros Organics, and Ce(SO$_4$)$_2$ was purchased from Sigma-Aldrich. DMF was acquired from solvent-processing system. All the solvents and other reagents were used directly from the purchased without any further purification unless otherwise specified.
General Procedure for the Preparation of Dipeptides (1aa-1l, 1o, 1r, 1u)

To a stirring solution of 1 (100 mmol) in MeOH (0.33 M) was added SOCl\textsubscript{2} (5.0 equiv) dropwise under ice bath. Then the mixture was refluxed for 5 h. MeOH and excessive SOCl\textsubscript{2} were removed under vacuum and 2 was obtained quantitatively as a white solid. 5 was also obtained under similar conditions (for L-aspartic acid and L-glutamic acid to prepare 1h and 1i, respectively, 7.5 equiv SOCl\textsubscript{2} was applied).

To a solution of 2 in DCM (0.5 M) was added NE\textsubscript{t}\textsubscript{3} (2.5 equiv) and then Tf\textsubscript{2}O (1.0 equiv) slowly at –78 \textdegree C. 1 h later, the reaction mixture was quenched with excessive water. After separation, the organic layer was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under reduced pressure to afford crude 3 (light yellow oil).

Crude 3 was mixed with 1 M aqueous NaOH (0.25 M) and was stirred overnight. The mixture was then washed with Et\textsubscript{2}O, acidified with concentrated HCl and extracted with EtOAc. After concentration, crude product 4 was obtained as a light yellow solid, which could be used directly without further purification\textsuperscript{1}.

4 (5.0 mmol), 5 (1.0 equiv) and iPr\textsubscript{2}NH (2.5 equiv) were stirred in DCM (0.2 M) under 0 \textdegree C for 15 min. Without changing temperature, HOBt (1.2 equiv) was added, and 30 min later, EDCI (1.5 equiv) was added. The mixture was stirred under 0 \textdegree C for 3 h and under room temperature (r.t., the same below) for another 5 h. Then to the mixture was added water. After separation, organic layer was washed with brine and dried over Na\textsubscript{2}SO\textsubscript{4}. Solvent was removed under reduced pressure and further purification was conducted by column chromatography (for 1aa, PE:DCM:EA = 4:1:1 as eluent, 78\% yield).

For 1ab, 1ac, 1ad, 1b and 1l, corresponding stereoisomers of starting substances were employed.

For 1o, 8 was prepared according to ref. 2 and was used\textsuperscript{2} instead of 5.

For 1r and 1u, 4 was replaced by N-Ac-phenylalanine and N-Boc-phenylalanine, respectively.
**Procedure for the Preparation of Dipeptide 1m-1n**

![Chemical Reaction Diagram]

11 was synthesized under the similar condition in which 6 was synthesized from 4 and 5, but only 1.5 equiv of NEt₃ was used. Further purification was conducted by column chromatography (PE:DCM:EA = 2:1:1 as eluent).

To a solution of 11 (10 mmol) and NEt₃ (2.0 equiv) in DCM (0.2 M) was added slowly Ac₂O (2.0 equiv). After stirred at r.t. for 8 h, the mixture was washed with water, brine, and organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. Further purification was conducted by column chromatography (PE:DCM:EA = 4:2:1 as eluent) to afford 12.

Then 12 was added slowly to a solution of TFA in DCM (v:v = 1:1) and stirred until all starting material were consumed (monitored by TLC). The mixture was diluted with excessive DCM and water, and then saturated aqueous NaHCO₃ was added slowly until the pH of mixture reached about 9. Extraction was performed with DCM, and combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to afford 13 as crude product.

Crude 13 was triflated under the similar condition in which 3 was prepared from 2, but only 1.5 equiv of NEt₃ was used. Further purification was conducted by column chromatography (PE:DCM:EA = 4:4:1 as eluent).
Procedure for the Preparation of Dipeptide 1p

17 (10 mmol) could be obtained from 15 according to ref. 3 and ref. 4. The process to prepare 1p from 17 is the same with that from 2 to 6. Further purification was conducted by column chromatography (PE:DCM:EA = 4:1:1 as eluent) to afford 1p.

Procedure for the Preparation of Dipeptide 1q

22 (20 mmol) could be obtained from 20 according to ref. 5 and ref. 6. The process to prepare 1q from 22 is the same with that from 12 to 13 and from 2 to 6. Further purification was conducted by column chromatography (PE:DCM:EA = 3:1:1 as eluent) to afford 1q.
Procedure for the Preparation of Dipeptides 1s-1t

1u was deprotected to obtain 26 under the same condition in which 13 was synthesized from 12.

A round-bottom flask equipped with a magnetic stirring bar was charged with amine (5 mmol) and THF (0.5 M). After the solution had been cooled to 0 °C, a solution of the TsCl (0.95 equiv) in THF was added over a period of 5 min subsequently. NEt₃ (1.15 equiv) was added at the same temperature. Then the reaction mixture was allowed to warm to r.t. and was stirred for 24 h. After that, the reaction mixture was extracted with water and washed with brine. The organic solvent was removed under vacuum and the crude product was purified by column chromatography (PE:EA = 4:1 as eluent) to afford 1s in 86% yield.

To a solution of 26 (5 mmol) in DCM (0.5 M) was added NEt₃ (1.1 equiv) and TFA₂O (1.0 equiv) at –78 °C. 1 h later, the reaction mixture was quenched with excessive water. After separation, the organic layer was washed with water, brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. Further purification was conducted by column chromatography (PE:EA = 4:1 as eluent) to afford 1t in 73% yield.

General Procedure for the Cyclization of Dipeptides

Dipeptide (0.1 mmol), Pd(OAc)₂ (2.2 mg, 0.1 equiv) and Ce(SO₄)₂ (199.0 mg, 6.0 equiv) were placed in a vial under air. DCM (0.8 mL), DMF (47 μL, 6.0 equiv) and MsOH (0.2 mL of 0.1 M solution in DCM) were added sequentially. The mixture was stirred at room temperature for 5 min and then was stirred for 2 d at 120 °C. After the reaction mixture was cooled to room temperature, salts were removed by filtration through silica gel with EA, and solution was removed under vacuum. The residue was further purified by column chromatography (for 1aa, PE:DCM:Et₂O = 4:1:1 as eluent) to afford cyclized product.
Characterization Data of Dipeptides

(S)-methyl-3-methyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butanoate (1aa).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.36 (m, 3H), 7.22 (d, $J = 6.7$ Hz, 2H), 6.19 (br s, 1H), 6.04 (br d, $J = 8.4$ Hz, 1H), 4.47 (dd, $J = 8.5$ Hz, 4.5 Hz, 1H), 4.27-4.34 (m, 1H), 3.72 (s, 3H), 3.24 (dd, $J = 13.7$ Hz, 5.6 Hz, 1H), 3.10 (dd, $J = 13.7$ Hz, 8.8 Hz, 1H), 1.97-2.06 (m, 1H), 0.72 (dd, $J = 6.9$ Hz, 5.1 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.8, 169.3, 134.9, 129.4, 128.9, 127.6, 119.4 (q, $J = 319.0$ Hz), 59.5, 57.5, 52.3, 40.3, 31.1, 18.5, 17.52.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{16}$H$_{22}$F$_3$N$_2$O$_5$S$,^+$ 411.1196; found, 411.1198.

(R)-methyl-3-methyl-2-((S)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butanoate (1ab).
White solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-7.34 (m, 3H), 7.23 (d, $J = 6.8$ Hz, 2H), 6.82 (br s, 1H), 6.28 (br d, $J = 8.5$ Hz, 1H), 4.48 (dd, $J = 8.6$ Hz, 4.7 Hz, 1H), 4.32 (dd, $J = 8.2$ Hz, 6.4 Hz, 1H), 3.72 (s, 3H), 3.20 (dd, $J = 13.7$ Hz, 6.0 Hz, 1H), 3.14 (dd, $J = 13.8$ Hz, 8.6 Hz, 1H), 1.98-2.04 (m, 1H), 0.72 (dd, $J = 6.9$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.8, 169.3, 134.9, 129.4, 128.9, 127.6, 119.4 (q, $J = 319.0$ Hz), 59.5, 57.5, 52.4, 40.3, 31.1, 18.5, 17.5.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{16}$H$_{22}$F$_3$N$_2$O$_5$S$,^+$ 411.1196; found, 411.1204.

(S)-methyl-3-methyl-2-((S)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butanoate (1ac).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.35 (m, 3H), 7.20 (d, $J = 6.2$ Hz, 2H), 6.19 (br s, 1H), 5.99 (br d, 1H), 4.44 (dd, $J = 8.5$ Hz, 4.9 Hz, 1H), 4.26 (t, $J = 6.1$ Hz, 1H), 3.71 (s, 3H), 3.19 (dd, $J = 13.6$ Hz, 5.6 Hz, 1H), 3.06 (dd, $J = 13.7$ Hz, 8.1 Hz, 1H), 2.05-2.17 (m, 1H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.82 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.7, 169.6, 134.8, 129.4, 128.8, 127.5, 119.4 (q, $J = 319.0$ Hz), 59.5, 57.8, 52.3, 40.2, 31.4, 18.5, 17.6.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{16}$H$_{22}$F$_3$N$_2$O$_5$S$,^+$ 411.1196; found, 411.1200.
(R)-methyl-3-methyl-2-((R)-3-phenyl-2-(trifluormethylsulfonamido)propanamido)butanoate (1ad).

White solid.

\textbf{H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.28-7.35 (m, 3H), 7.20 (d, \(J = 6.4\) Hz, 2H), 5.92 (br, 2H), 4.44 (dd, \(J = 8.5\) Hz, 4.9 Hz, 1H), 4.26 (d, \(J = 13.7\) Hz, 7.7 Hz, 1H), 3.71 (s, 3H), 3.20 (dd, \(J = 13.6\) Hz, 5.4 Hz, 1H), 3.06 (dd, \(J = 13.6\) Hz, 8.2 Hz, 1H), 2.06-2.15 (m, 1H), 0.86 (d, \(J = 6.9\) Hz, 3H), 0.82 (d, \(J = 6.9\) Hz, 3H).

\textbf{C NMR} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 171.7, 169.6, 134.8, 129.4, 128.8, 127.5, 119.4 (q, \(J = 319.0\) Hz), 59.5, 57.6, 52.3, 40.2, 31.4, 18.5, 17.6.

HRMS-ESI (m/z): \([\text{M+H}]^+\) calcd for C\textsubscript{16}H\textsubscript{22}F\textsubscript{3}N\textsubscript{2}O\textsubscript{5}S\textsuperscript{+}, 411.1196; found, 411.1196.

(S)-methyl-2-(3-phenyl-2-(trifluormethylsulfonamido)propanamido)acetate (1b).

White solid.

\textbf{H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.29-7.36 (m, 3H), 7.20 (d, \(J = 6.6\) Hz, 2H), 6.35 (br d, \(J = 13.9\) Hz, 7.6 Hz, 1H), 4.06 (dd, \(J = 18.4\) Hz, 5.3 Hz, 1H), 3.93 (dd, \(J = 18.4\) Hz, 5.0 Hz, 1H), 3.76 (s, 3H), 3.20 (dd, \(J = 13.8\) Hz, 5.9 Hz, 1H), 3.06 (dd, \(J = 13.7\) Hz, 5.9 Hz, 1H).

\textbf{C NMR} (125 MHz, CDCl\textsubscript{3}) \(\delta\) 169.5, 169.2, 134.6, 129.4, 129.0, 127.7, 119.4 (q, \(J = 319.0\) Hz), 59.0, 52.6, 41.4, 40.3.

HRMS-ESI (m/z): \([\text{M+H}]^+\) calcd for C\textsubscript{13}H\textsubscript{16}F\textsubscript{3}N\textsubscript{2}O\textsubscript{5}S\textsuperscript{+}, 369.0726; found, 369.0733.

(S)-methyl-2-((R)-3-phenyl-2-(trifluormethylsulfonamido)propanamido)propanoate (1c).

White solid.

\textbf{H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.28-7.35 (m, 3H), 7.21 (d, \(J = 8.0\) Hz, 2H), 6.50 (br, 1H), 6.10 (br, 1H), 4.52 (dd, \(J = 14.6\) Hz, 7.3 Hz, 1H), 4.22-4.32 (m, 1H), 3.73 (s, 3H), 3.22 (dd, \(J = 13.5\) Hz, 5.8 Hz, 1H), 3.06 (dd, \(J = 13.4\) Hz, 8.8 Hz, 1H), 1.20 (d, \(J = 7.1\) Hz, 3H).

\textbf{C NMR} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 172.9, 168.7, 134.9, 129.4, 128.9, 127.6, 119.4 (q, \(J = 319.0\) Hz), 59.2, 52.7, 48.1, 40.6, 17.9.

HRMS-ESI (m/z): \([\text{M+H}]^+\) calcd for C\textsubscript{14}H\textsubscript{18}F\textsubscript{3}N\textsubscript{2}O\textsubscript{5}S\textsuperscript{+}, 383.0883; found, 383.0891.
(S)-methyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butanoate (1d).
White solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-7.34 (m, 3H), 7.22 (d, $J = 6.8$ Hz, 2H), 6.74 (br s, 1H), 6.28 (d, $J = 7.6$ Hz, 1H), 4.52 (dt, $J = 6.1$ Hz, 5.8 Hz, 1H), 4.29 (dd, $J = 8.2$ Hz, 6.4 Hz, 1H), 3.72 (s, 3H), 3.20 (dd, $J = 13.6$ Hz, 6.0 Hz, 1H), 3.12 (dd, $J = 13.6$ Hz, 8.7 Hz, 1H), 1.56-1.72 (m, 2H), 0.65 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.4, 169.2, 135.0, 129.4, 128.8, 127.5, 119.4 (q, $J = 319.0$ Hz), 59.4, 53.4, 52.57, 40.4, 25.2, 9.0.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{15}$H$_{20}$F$_3$N$_2$O$_5$S$^+$, 397.1040; found, 397.1040.

(57x481)-methyl-4-methyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)pentanoate (1e).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.35 (m, 3H), 7.21 (d, $J = 6.9$ Hz, 2H), 6.33 (br, 1H), 5.90 (br, 1H), 4.52 (dd, $J = 13.8$ Hz, 8.3 Hz, 1H), 4.52 (dd, $J = 14.4$ Hz, 8.5 Hz, 1H), 3.71 (s, 3H), 3.23 (dd, $J = 13.5$ Hz, 5.5 Hz, 1H), 3.08 (dd, $J = 13.5$ Hz, 8.8 Hz, 1H), 1.43-1.52 (m, 1H), 1.18-1.35 (m, 2H), 0.84 (t, $J = 6.0$ Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.8, 169.1, 134.9, 129.4, 128.9, 127.5, 119.4 (q, $J = 319.0$ Hz), 59.4, 52.5, 50.9, 41.2, 40.3, 24.4, 22.6, 21.7.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{17}$H$_{24}$F$_3$N$_2$O$_5$S$^+$, 425.1352; found, 425.1361.

(57x269)-methyl-3-phenyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)propanoate (1f).
Light yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.35 (m, 3H), 7.22-7.25(m, 3H), 7.12 (d, $J = 6.1$ Hz, 2H), 6.84-6.89 (m, 2H), 6.24 (br, 1H), 6.13 (br, 1H), 4.85 (dd, $J = 13.8$ Hz, 5.8 Hz, 1H), 4.22 (t, $J = 7.0$ Hz, 1H), 3.69 (s, 3H), 3.12 (dd, $J = 13.8$ Hz, 5.8 Hz, 1H), 2.99-3.06 (m, 2H), 2.92 (dd, $J = 13.9$ Hz, 5.8 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.2, 168.8, 135.1, 134.6, 129.5, 129.1, 129.0, 128.7, 127.7, 127.3, 119.4 (q, $J = 319.0$ Hz), 59.2, 53.3, 52.5, 40.1, 37.7.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{20}$H$_{22}$F$_3$N$_2$O$_5$S$^+$, 459.1196; found, 459.1197.
(2S,3S)-methyl-3-methyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)pentanoate (1g).
Light yellow solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.34 (m, 3H), 7.22 (d, $J = 7.1$ Hz, 2H), 6.69 (br s, 1H), 6.20 (br s, 1H), 4.51 (dd, $J = 8.4$ Hz, 4.7 Hz, 1H), 4.29 (dd, $J = 8.5$ Hz, 6.0 Hz, 1H), 3.71 (s, 3H), 3.21 (dd, $J = 13.7$ Hz, 5.8 Hz, 1H), 3.10 (dd, $J = 13.6$ Hz, 8.9 Hz, 1H), 1.64-1.71 (m, 1H), 1.19-1.27 (m, 1H), 0.88-0.96 (m, 1H), 0.84 (t, $J = 7.1$ Hz, 3H), 0.66 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.7, 169.1, 134.9, 129.4, 128.9, 127.5, 119.4 (q, $J = 319.0$ Hz), 59.5, 56.7, 52.3, 40.4, 37.8, 24.9, 15.0, 11.4.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{17}$H$_{24}$F$_3$N$_2$O$_5$S$^+$, 425.1352; found, 425.1356.

(S)-dimethyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)succinate (1h).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23-7.32 (m, 3H), 7.18 (d, $J = 6.8$ Hz, 2H), 6.72 (br d, $J = 8.5$ Hz, 1H), 6.41 (br d, $J = 7.1$ Hz, 1H), 4.80 (quint, $J = 4.2$ Hz, 1H), 4.32 (dd, $J = 12.7$ Hz, 6.4 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.20 (dd, $J = 13.5$ Hz, 5.8 Hz, 1H), 3.06 (dd, $J = 13.6$ Hz, 8.8 Hz, 1H), 2.96 (dd, $J = 17.6$ Hz, 3.9 Hz, 1H), 2.45 (dd, $J = 22.2$ Hz, 4.3 Hz, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.5, 169.2, 168.9, 134.9, 129.4, 128.8, 127.4, 119.5 (q, $J = 319.0$ Hz), 59.2, 52.9, 52.2, 48.1, 40.6, 35.4.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{16}$H$_{20}$F$_3$N$_2$O$_7$S$^+$, 441.0938; found, 441.0940.

(S)-dimethyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)pentanedioate (1i).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.35 (m, 3H), 7.20 (d, $J = 6.9$ Hz, 2H), 6.43 (br d, $J = 7.1$ Hz, 1H), 5.94 (br d, $J = 7.2$ Hz, 1H), 4.50 (dd, $J = 12.4$ Hz, 7.4 Hz, 1H), 4.26 (dd, $J = 13.9$ Hz, 8.0 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.23 (dd, $J = 13.6$ Hz, 5.4 Hz, 1H), 3.06 (dd, $J = 13.7$ Hz, 8.6 Hz, 1H), 1.95-2.22 (m, 3H), 1.82-1.92 (m, 1H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.2, 171.5, 169.2, 134.8, 129.4, 128.9, 127.6, 119.4 (q, $J = 319.0$ Hz), 59.3, 52.7, 51.9, 40.3, 29.5, 26.6.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{17}$H$_{22}$F$_3$N$_2$O$_7$S$^+$, 455.1094; found, 455.1092.
(S)-methyl-3,3-dimethyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butanoate (1j).
White solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26-7.36 (m, 3H), 7.24 (d, \(J = 6.8\) Hz, 2H), 6.40 (br s, 1H), 5.97 (br s, 1H), 4.18 (dd, \(J = 8.6\) Hz, 5.3 Hz, 1H), 3.72 (s, 3H), 3.22 (dd, \(J = 13.6\) Hz, 9.0 Hz, 1H), 1.46 (s, 3H), 1.42 (s, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.3, 168.2, 134.9, 129.5, 128.9, 127.6, 119.5 (q, \(J = 319.0\) Hz), 59.5, 57.2, 52.8, 40.5, 23.9.
HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{13}\)H\(_{20}\)F\(_3\)N\(_2\)O\(_5\)S\(^+\), 397.1040; found, 397.1035.

(R)-methyl-2-methyl-2-(3-phenyl-2-(trifluoromethylsulfonamido)propanamido)propanoate (1k).
White solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.26-7.36 (m, 3H), 7.24 (d, \(J = 6.8\) Hz, 2H), 6.40 (br s, 1H), 5.97 (br s, 1H), 4.18 (dd, \(J = 8.6\) Hz, 5.3 Hz, 1H), 3.72 (s, 3H), 3.22 (dd, \(J = 13.6\) Hz, 5.1 Hz, 1H), 3.02 (dd, \(J = 13.6\) Hz, 9.0 Hz, 1H), 1.46 (s, 3H), 1.42 (s, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 174.3, 168.2, 134.9, 129.5, 128.9, 127.6, 119.5 (q, \(J = 319.0\) Hz), 59.5, 57.2, 52.8, 40.5, 23.9.
HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{13}\)H\(_{20}\)F\(_3\)N\(_2\)O\(_5\)S\(^+\), 397.1040; found, 397.1035.

(S)-N-(tert-butyl)-3-phenyl-2-(trifluoromethylsulfonamido)propanamide (1l).
Light yellow solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30-7.37 (m, 3H), 7.21 (d, \(J = 6.6\) Hz, 2H), 6.30 (br s, 1H), 4.82 (br s, 1H), 4.02 (dd, \(J = 9.9\) Hz, 4.9 Hz, 1H), 3.24 (dd, \(J = 13.5\) Hz, 5.1 Hz, 1H), 2.96 (dd, \(J = 13.4\) Hz, 9.9 Hz, 1H), 1.17 (s, 9H).
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 167.8, 135.3, 129.5, 129.0, 127.6, 119.5 (q, \(J = 319.0\) Hz), 60.0, 52.1, 41.0, 28.2.
HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{14}\)H\(_{20}\)F\(_3\)N\(_2\)O\(_3\)S\(^+\), 353.1141; found, 353.1144.
(S)-3-methyl-2-((R)-3-phenyl-2-(trifluoromethylsulfonamido)propanamido)butyl acetate (1m).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.35 (m, 3H), 7.22 (d, $J = 7.0$ Hz, 2H), 6.26 (br, 1H), 5.58 (br, 1H), 4.19 (dd, $J = 8.2$ Hz, 5.4 Hz, 1H), 4.10 (dd, $J = 11.6$ Hz, 7.0 Hz, 1H), 4.00 (dd, $J = 11.6$ Hz, 3.6 Hz, 1H), 3.90-3.97 (m, 1H), 3.23 (dd, $J = 13.5$ Hz, 5.4 Hz, 1H), 3.08 (dd, $J = 13.6$ Hz, 8.8 Hz, 1H), 2.01 (s, 3H), 0.74 (dd, $J = 18.9$ Hz, 6.8 Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.5, 169.3, 136.0, 129.4, 129.0, 127.6, 119.4 (q, $J = 319.0$ Hz), 63.8, 59.7, 54.2, 40.1, 29.3, 20.6, 18.8, 18.2.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{17}$H$_{24}$F$_3$N$_2$O$_5$S$^+$, 425.1352; found, 425.1359.

(2S)-methyl-2-(3-(4-fluorophenyl)-2-(trifluoromethylsulfonamido)propanamido)-3-methylbutanoate (1p).
White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.35 (m, 3H), 7.22 (d, $J = 6.9$ Hz, 2H), 6.69 (br, 1H), 5.46 (br d, $J = 8.2$ Hz, 1H), 4.10-4.20 (m, 2H), 3.98 (d, $J = 4.7$ Hz, 2H), 3.22 (dd, $J = 13.4$ Hz, 5.5 Hz, 1H), 3.08 (dd, $J = 13.3$ Hz, 9.2 Hz, 1H), 2.01 (s, 3H), 0.84 (dd, $J = 6.22$ Hz, 2.3 Hz, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.2, 168.8, 135.0, 129.4, 128.9, 127.6, 119.5 (q, $J = 319.0$ Hz), 65.6, 59.6, 47.2, 40.3, 40.1, 24.3, 22.8, 22.0, 20.6.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{18}$H$_{26}$F$_3$N$_2$O$_5$S$^+$, 439.1509; found, 439.1506.

(2S)-methyl-2-(3-methyl-2-(trifluoromethylsulfonamido)propanamido)-3-methylbutanoate (1o).

White solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27-7.35 (m, 3H), 7.22 (d, $J = 6.7$ Hz, 2H), 6.41 (br s, 1H), 5.78 (br d, $J = 9.5$ Hz, 1H), 4.16-4.22 (m, 1H), 3.71-3.77 (m, 1H), 3.44 (dd, $J = 9.8$ Hz, 3.8 Hz, 1H), 3.27 (s, 3H), 3.19-3.26 (m, 2H), 3.10 (dd, $J = 13.7$ Hz, 8.6 Hz, 1H), 1.65-1.74 (m, 1H), 0.80 (d, $J = 6.8$ Hz, 3H), 0.67 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 169.0, 135.0, 129.4, 128.9, 127.5, 119.5 (q, $J = 319.0$ Hz), 71.8, 59.9, 58.9, 54.9, 40.2, 29.0, 19.2, 18.9.

HRMS-ESI (m/z): [M+H]$^+$ calcd for C$_{18}$H$_{26}$F$_3$N$_2$O$_4$S$^+$, 397.1403; found, 397.1415.
**1H NMR** (500 MHz, CDCl3) δ 7.16-7.22 (m, 2H), 7.11 (br s, 1H), 7.98-7.03 (m, 2H), 6.33 (d, J = 8.4 Hz, 0.56 × 1H), 6.19 (d, J = 8.4 Hz, 0.44 × 1H), 4.48 (dd, J = 8.4 Hz, 4.6 Hz, 0.56 × 1H), 4.45 (dd, J = 8.6 Hz, 4.0 Hz, 0.44 × 1H), 4.26 (t, J = 7.2 Hz, 0.56 × 1H), 4.22 (t, J = 6.8 Hz, 0.44 × 1H), 3.73 (s, 0.56 × 3H), 3.72 (s, 0.44 × 3H), 3.04-3.17 (m, 2H), 2.09-2.16 (m, 0.44 × 1H), 2.01-2.07 (m, 0.56 × 1H), 0.88 (dd, J = 20.0 Hz, 6.8 Hz, 0.44 × 6H), 0.75 (dd, J = 6.9 Hz, 4.3 Hz, 0.56 × 6H).

**13C NMR** (125 MHz, CDCl3) δ 171.6, 171.5, 169.5, 169.4, 162.3 (d, J = 245.0 Hz), 131.0 (d, J = 7.5 Hz), 130.6 (d, J = 3.8 Hz), 130.5 (d, J = 3.8 Hz), 119.4 (q, J = 319.0 Hz), 115.9 (d, J = 12.5 Hz), 115.7 (d, J = 12.5 Hz), 59.6, 59.5, 57.7, 57.6, 52.4, 52.4, 39.2, 39.2, 31.5, 31.1, 18.6, 18.5, 17.6, 17.5.

HRMS-ESI (m/z): [M+H]+ calcd for C16H21F4N2O5S+, 429.1102; found, 429.1102.

(S)-methyl-2-((S)-3-(4-methoxyphenyl)-2-(trifluoromethylsulfonamido)propanamido)-3-methylbutanoate (1q).

Light yellow solid.

**1H NMR** (400 MHz, CDCl3) δ 7.11 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.07 (br s, 1H), 5.94 (br d, J = 8.0 Hz, 1H), 4.42 (dd, J = 8.4 Hz, 4.8 Hz, 1H), 4.22 (dd, J = 14.2 Hz, 8.3 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.15 (dd, J = 13.9 Hz, 5.6 Hz, 1H), 3.00 (dd, J = 13.8 Hz, 8.1 Hz, 1H), 2.07-2.15 (m, 1H), 0.85 (dd, J = 6.9 Hz, 6H).

**13C NMR** (125 MHz, CDCl3) δ 171.5, 169.3, 159.1, 130.5, 126.6, 119.5 (q, J = 319.0 Hz), 114.3, 59.5, 57.6, 52.4, 39.2, 31.5, 18.6, 18.5, 17.6.

HRMS-ESI (m/z): [M+H]+ calcd for C17H24F3N2O6S+, 441.1302; found, 441.1305.

(S)-methyl-2-((R)-2-acetamido-3-phenylpropanamido)-3-methylbutanoate (1r).

White solid.

**1H NMR** (500 MHz, CDCl3) δ 7.20-7.30 (m, 5H), 6.62 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 7.8 Hz, 1H), 4.82 (dd, J = 14.6 Hz, 8.0 Hz, 1H), 4.40 (dd, J = 8.5 Hz, 5.0 Hz, 1H), 3.69 (s, 3H), 3.10 (dd, J = 13.8 Hz, 6.6 Hz, 1H), 3.06 (dd, J = 13.8 Hz, 8.1 Hz, 1H), 1.98-2.02 (m, 1H), 1.97 (s, 3H), 0.76 (dd, J = 6.8 Hz, 4.9 Hz, 6H).

**13C NMR** (125 MHz, CDCl3) δ 171.8, 171.1, 170.0, 136.6, 129.2, 128.6, 126.9, 57.4, 54.5, 52.0, 38.6, 30.9, 23.0, 18.7, 17.7.

HRMS-ESI (m/z): [M+H]+ calcd for C17H23N2O5+, 321.1809; found, 321.1806.

(S)-methyl-3-methyl-2-((R)-2-(4-methylphenylsulfonamido)-3-phenylpropanamido)butanoate (1s).

White solid.
**1H NMR** (400 MHz, CDCl₃) δ 7.49 (d, J = 8.3 Hz, 2H), 7.15-7.20 (m, 5H), 6.92 (d, J = 6.6 Hz, 2H), 6.80 (d, J = 9.0 Hz, 1H), 4.84 (d, J = 6.2 Hz, 1H), 4.44 (dd, J = 8.9 Hz, 4.8 Hz, 1H), 3.88 (q, J = 6.2 Hz, 1H), 3.73 (s, 3H), 2.99 (dd, J = 14.0 Hz, 5.9 Hz, 1H), 2.91 (dd, J = 14.2 Hz, 7.8 Hz, 1H), 2.42 (s, 3H), 2.08-2.16 (m, 1H), 0.88 (dd, J = 11.0 Hz, 6.8 Hz, 6H).

**13C NMR** (100 MHz, CDCl₃) δ 171.8, 170.0, 143.8, 135.3, 135.0, 129.7, 129.0, 129.0, 127.2, 127.1, 57.9, 57.3, 52.1, 38.3, 31.2, 21.5, 18.8, 17.5.


**(S)-methyl-3-methyl-2-((R)-3-phenyl-2-(2,2,2-trifluoroacetamido)propanamido)butanoate (1t).**

White solid.

**1H NMR** (400 MHz, CDCl₃) δ 7.24-7.36 (m, 5H), 5.89 (br s, 1H), 4.72 (dd, J = 14.1 Hz, 9.0 Hz, 1H), 4.42 (dd, J = 8.5 Hz, 4.6 Hz, 1H), 3.71 (s, 3H), 3.23 (dd, J = 13.8 Hz, 5.6 Hz, 1H), 3.02 (dd, J = 13.9 Hz, 9.1 Hz, 1H), 1.95-2.03 (m, 1H), 0.71 (dd, J = 14.9 Hz, 6.8 Hz, 6H).

**13C NMR** (100 MHz, CDCl₃) δ 171.6, 169.2, 156.7 (q, J = 38.0 Hz), 135.3, 129.2, 128.9, 127.5, 115.6 (q, J = 286.0 Hz), 57.5, 54.8, 52.3, 38.7, 31.0, 18.6, 17.6.

HRMS-ESI (m/z): [M+H]+ calcd for C₁₇H₂₂F₃N₂O₄⁺, 375.1526; found, 375.1529.

**(S)-methyl-2-((R)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-methylbutanoate (1u).**

White solid.

**1H NMR** (400 MHz, CDCl₃) δ 7.25-7.32 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 6.35 (br d, J = 7.4 Hz, 1H), 4.97 (br s, 1H), 4.48 (dd, J = 8.8 Hz, 4.5 Hz, 1H), 4.39 (d, J = 6.6 Hz, 1H), 3.71 (s, 3H), 3.08 (d, J = 7.0 Hz, 2H), 2.01-2.09 (m, 1H), 1.42 (s, 9H), 0.79 (dd, J = 14.8 Hz, 6.9 Hz, 6H).

**13C NMR** (125 MHz, CDCl₃) δ 171.9, 171.1, 155.3, 136.6, 129.2, 128.7, 126.9, 80.2, 57.1, 55.8, 52.0, 38.2, 31.0, 28.2, 18.7, 17.6.

HRMS-ESI (m/z): [M+H]+ calcd for C₂₀H₃₁N₂O₅⁺, 379.2228; found, 379.2238.

### Characterization Data of Cyclization Products

**(S)-methyl-3-methyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butanoate (2aa).**
White solid.

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 7.56 (d, \(J = 7.9\) Hz, 1H), 7.26-7.30 (m, 2H), 7.20 (t, \(J = 6.8\) Hz, 1H), 6.89 (br d, \(J = 8.3\) Hz, 1H), 5.03 (dd, \(J = 9.5\) Hz, 3.0 Hz, 1H), 4.52 (dd, \(J = 8.8\) Hz, 4.6 Hz, 1H), 3.66 (s, 3H), 3.51-3.63 (m, 2H), 2.19-2.27 (m, 1H), 0.94 (dd, \(J = 19.0\) Hz, 6.9 Hz, 6H).

**13C NMR** (100 MHz, CDCl₃) \(\delta\) 171.4, 168.6, 138.2, 130.6, 128.5, 126.8, 125.7, 120.1 (q, \(J = 324.0\) Hz), 116.1, 64.9, 57.4, 52.2, 32.6, 31.3, 18.8, 17.5.


(R)-methyl-3-methyl-2-((S)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butanoate (2ab).

White solid.

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 7.56 (d, \(J = 7.6\) Hz, 1H), 7.25-7.30 (m, 2H), 7.20 (t, \(J = 7.4\) Hz, 1H), 6.89 (br d, \(J = 8.4\) Hz, 1H), 5.03 (dd, \(J = 9.5\) Hz, 2.5 Hz, 1H), 4.52 (dd, \(J = 8.8\) Hz, 4.6 Hz, 1H), 3.66 (s, 3H), 3.51-3.61 (m, 2H), 2.17-2.27 (m, 1H), 0.94 (dd, \(J = 18.8\) Hz, 6.9 Hz, 6H).

**13C NMR** (100 MHz, CDCl₃) \(\delta\) 171.4, 168.6, 138.2, 130.6, 128.5, 126.8, 125.7, 120.1 (q, \(J = 324.0\) Hz), 116.1, 64.9, 57.4, 52.2, 32.6, 31.3, 18.8, 17.4.

HRMS-ESI (m/z): [M+H]+ calcd for C₁₆H₂₀F₃N₂O₅S⁺, 409.1040; found, 409.1051.

(S)-methyl-3-methyl-2-((S)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butanoate (2ac).

White solid.

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 7.53 (d, \(J = 8.0\) Hz, 1H), 7.25-7.29 (m, 2H), 7.18 (t, \(J = 7.6\) Hz, 1H), 6.84 (br d, \(J = 8.4\) Hz, 1H), 5.01 (t, \(J = 5.9\) Hz, 1H), 4.50 (dd, \(J = 8.7\) Hz, 4.7 Hz, 1H), 3.76 (s, 3H), 3.56 (d, \(J = 5.9\) Hz, 2H), 2.11-2.19 (m, 1H), 0.80 (dd, \(J = 6.8\) Hz, 4.3 Hz, 6H).

**13C NMR** (100 MHz, CDCl₃) \(\delta\) 171.5, 168.4, 138.3, 130.8, 128.4, 126.7, 125.6, 120.1 (q, \(J = 324.0\) Hz), 115.9, 64.9, 57.4, 52.3, 32.5, 31.1, 18.7, 17.3.


(R)-methyl-3-methyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butanoate (2ad).

White solid.

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 7.53 (d, \(J = 8.0\) Hz, 1H), 7.25-7.29 (m, 2H), 7.19 (t, \(J = 7.5\) Hz, 1H), 6.83 (br d, \(J = 7.9\) Hz, 1H), 5.01 (t, \(J = 5.8\) Hz, 1H), 4.50 (dd, \(J = 8.6\) Hz, 4.6 Hz, 1H), 3.76 (s, 3H), 3.56 (d, \(J = 5.8\) Hz, 2H),
2.11-2.19 (m, 1H), 0.80 (dd, \( J = 6.7 \text{ Hz}, 4.1 \text{ Hz}, 6\text{H} \)).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 171.5, 168.4, 138.3, 130.8, 128.4, 126.7, 125.3, 120.1 (q, \( J = 324.0 \text{ Hz} \)), 116.0, 64.9, 57.4, 52.3, 32.5, 31.1, 18.7, 17.3.

HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{16}\)H\(_{20}\)F\(_3\)N\(_2\)O\(_5\)S\(^+\), 409.1040; found, 409.1043.

\((S)-\text{methyl-2-}((R)-1-((\text{trifluoromethyl})\text{sulfonyl})\text{indoline-2-carboxamido})\text{propanoate} \) (2c).

Light yellow solid.

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.55 (d, \( J = 7.8 \text{ Hz}, 1\text{H} \)), 7.27-7.30 (m, 2H), 7.20 (t, \( J = 6.6 \text{ Hz}, 1\text{H} \)), 6.95 (br d, \( J = 6.4 \text{ Hz}, 1\text{H} \)), 5.00 (dd, \( J = 9.5 \text{ Hz}, 2.8 \text{ Hz}, 1\text{H} \)), 4.53 (quint, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 3.69 (s, 3H), 3.50-3.63 (m, 2H), 1.45 (d, \( J = 7.2 \text{ Hz}, 3\text{H} \)).

\(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 172.5, 168.8, 138.2, 130.6, 128.4, 126.8, 125.7, 120.1 (q, \( J = 325.0 \text{ Hz} \)), 116.2, 64.8, 52.6, 48.5, 32.7, 18.1.

HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{14}\)H\(_{16}\)F\(_3\)N\(_2\)O\(_5\)S\(^+\), 381.0726; found, 381.0733.

\((S)-\text{methyl-2-}((R)-1-((\text{trifluoromethyl})\text{sulfonyl})\text{indoline-2-carboxamido})\text{butanoate} \) (2d).

Light yellow solid.

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.56 (d, \( J = 7.9 \text{ Hz}, 1\text{H} \)), 7.27-7.30 (m, 2H), 7.20 (t, \( J = 7.0 \text{ Hz}, 1\text{H} \)), 6.92 (br d, \( J = 7.9 \text{ Hz}, 1\text{H} \)), 5.02 (dd, \( J = 9.7 \text{ Hz}, 2.7 \text{ Hz}, 1\text{H} \)), 4.53 (dd, \( J = 12.6 \text{ Hz}, 7.0 \text{ Hz}, 1\text{H} \)), 3.68 (s, 3H), 3.50-3.64 (m, 2H), 1.91-2.01 (m, 1H), 1.77 (sept, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 0.93 (t, \( J = 7.4 \text{ Hz}, 3\text{H} \)).

\(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 171.9, 168.5, 138.2, 130.6, 128.5, 126.8, 125.7, 120.6 (q, \( J = 324.0 \text{ Hz} \)), 116.2, 64.8, 53.6, 52.4, 32.7, 25.3, 9.2.

HRMS-ESI (m/z): [M+H]\(^+\) calcd for C\(_{15}\)H\(_{18}\)F\(_3\)N\(_2\)O\(_5\)S\(^+\), 395.0883; found, 395.0887.

\((S)-\text{methyl-4-methyl-2-}((R)-1-((\text{trifluoromethyl})\text{sulfonyl})\text{indoline-2-carboxamido})\text{pentanoate} \) (2e).

White solid.

\(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.55 (d, \( J = 8.3 \text{ Hz}, 1\text{H} \)), 7.26-7.30 (m, 2H), 7.20 (t, \( J = 7.1 \text{ Hz}, 1\text{H} \)), 6.74 (br d, \( J = 8.3 \text{ Hz}, 1\text{H} \)), 5.00 (dd, \( J = 9.4 \text{ Hz}, 2.9 \text{ Hz}, 1\text{H} \)), 4.60 (dt, \( J = 8.6 \text{ Hz}, 4.7 \text{ Hz}, 1\text{H} \)), 3.65 (s, 3H), 3.51-3.61 (m, 2H), 1.58-1.71 (m, 3H), 0.95 (d, \( J = 5.8 \text{ Hz}, 6\text{H} \)).

\(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 172.4, 168.6, 138.2, 130.6, 128.4, 126.8, 125.7, 120.6 (q, \( J = 324.0 \text{ Hz} \)), 116.2,
64.8, 52.3, 51.1, 41.2, 32.6, 24.8, 22.8, 21.8.
HRMS-ESI (m/z): [M+H]+ calcd for C_{17}H_{22}F_{3}N_{2}O_{5}S^+, 423.1196; found, 423.1198.

(S)-methyl-3-phenyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)propanoate (2f).
Light yellow solid.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 (d, \( J = 9.0\) Hz, 1H), 7.21-7.33 (m, 5H), 7.17 (t, \( J = 7.1\) Hz, 1H), 7.12 (d, \( J = 6.4\) Hz, 2H), 6.79 (br d, \( J = 7.5\) Hz, 1H), 4.96 (dd, \( J = 9.9\) Hz, 1.5 Hz, 1H), 4.80 (dt, \( J = 8.0\) Hz, 5.7 Hz, 1H), 3.62 (s, 3H), 3.40-3.59 (m, 2H), 3.16 (dd, \( J = 13.8\) Hz, 5.4 Hz, 1H), 3.11 (dd, \( J = 13.9\) Hz, 5.9 Hz, 1H).

\( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.9, 168.5, 138.1, 135.1, 130.6, 129.2, 128.8, 128.4, 127.3, 126.8, 125.6, 120.1 (q, \( J = 324.0\) Hz), 116.2, 64.9, 53.3, 52.4, 37.6, 32.9.
HRMS-ESI (m/z): [M+H]+ calcd for C\(_{20}\)H\(_{20}\)F\(_3\)N\(_2\)O\(_5\)S\(^{+}\), 457.1040; found, 457.1041.

(2S,3R)-methyl-3-methyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)pentanoate (2g).
White solid.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.56 (d, \( J = 8.3\) Hz, 1H), 7.26-7.30 (m, 2H), 7.20 (t, \( J = 6.9\) Hz, 1H), 6.92 (br d, \( J = 8.2\) Hz, 1H), 5.02 (dd, \( J = 9.4\) Hz, 3.2 Hz, 1H), 4.54 (dd, \( J = 8.6\) Hz, 4.6 Hz, 1H), 3.65 (s, 3H), 3.44-3.63 (m, 2H), 1.91-2.01 (m, 1H), 1.39-1.44 (m, 1H), 1.15-1.24 (m, 1H), 0.93 (d, \( J = 5.2\) Hz, 3H), 0.93 (t, \( J = 5.8\) Hz, 3H).

\( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.4, 168.5, 138.2, 130.7, 128.5, 126.8, 125.7, 120.1 (q, \( J = 325.0\) Hz), 116.1, 64.9, 56.8, 52.2, 37.8, 32.6, 25.0, 15.4, 11.5.
HRMS-ESI (m/z): [M+H]+ calcd for C\(_{17}\)H\(_{22}\)F\(_3\)N\(_2\)O\(_5\)S\(^{+}\), 423.1196; found, 423.1192.

(2S)-dimethyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)succinate (2h).
Yellow solid.

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.56 (d, \( J = 7.8\) Hz, 1H), 7.42 (br d, \( J = 7.8\) Hz, 1H), 7.26-7.30 (m, 2H), 7.20 (t, \( J = 7.4\) Hz, 1H), 5.00 (dd, \( J = 10.2\) Hz, 2.2 Hz, 1H), 4.78 (dt, \( J = 8.2\) Hz, 4.5 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.48-3.62 (m, 2H), 3.04 (dd, \( J = 17.1\) Hz, 4.2 Hz, 1H), 2.88 (dd, \( J = 17.1\) Hz, 4.7 Hz, 1H).

\( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.0, 170.3, 168.8, 138.3, 130.4, 128.5, 126.7, 125.6, 120.1 (q, \( J = 325.0\) Hz), 116.0, 64.8, 52.9, 52.2, 48.8, 35.7, 32.8.
HRMS-ESI (m/z): [M+H]+ calcd for C\(_{16}\)H\(_{18}\)F\(_3\)N\(_2\)O\(_5\)S\(^{+}\), 439.0781; found, 439.0788.
**(S)-dimethyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)pentanedioate (2i).**

Yellow solid.

**¹H NMR** (400 MHz, CDCl₃) δ 7.58 (d, J = 7.8 Hz, 1H), 7.29-7.31 (m, 3H), 7.20 (t, J = 7.5 Hz, 1H), 5.00 (dd, J = 10.0 Hz, 2.1 Hz, 1H), 4.56 (dt, J = 7.8 Hz, 4.8 Hz, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 3.47-3.65 (m, 2H), 2.35-2.49 (m, 2H), 2.21-2.30 (m, 1H), 2.04 (sextet, J = 7.0 Hz, 1H).

**¹³C NMR** (125 MHz, CDCl₃) δ 173.4, 171.3, 169.1, 138.3, 130.5, 128.4, 126.8, 125.6, 120.1 (q, J = 325.0 Hz), 116.2, 64.7, 52.6, 52.0, 32.9, 29.7, 26.4.


**(S)-methyl-3,3-dimethyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butanoate (2j).**

White solid.

**¹H NMR** (400 MHz, CDCl₃) δ 7.56 (d, J = 8.0 Hz, 1H), 7.29-7.30 (m, 2H), 7.20 (t, J = 6.7 Hz, 1H), 6.96 (br d, J = 9.2 Hz, 1H), 5.01 (dd, J = 9.2 Hz, 3.1 Hz, 1H), 4.40 (d, J = 9.4 Hz, 1H), 3.62 (s, 3H), 3.52-3.60 (m, 2H), 1.00 (s, 9H).

**¹³C NMR** (100 MHz, CDCl₃) δ 170.9, 168.3, 138.1, 130.7, 128.5, 126.9, 125.7, 120.1 (q, J = 325.0 Hz), 116.1, 64.9, 60.5, 51.8, 35.1, 32.5, 26.4.


**(R)-methyl-2-methyl-2-(1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)propanoate (2k).**

White solid.

**¹H NMR** (400 MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 1H), 7.25-7.28 (m, 2H), 7.19 (t, J = 8.2 Hz, 1H), 7.00 (br s, 1H), 4.92 (dd, J = 8.2 Hz, 3.9 Hz, 1H), 3.71 (s, 3H), 3.53-3.55 (m, 2H), 1.55 (s, 6H).

**¹³C NMR** (100 MHz, CDCl₃) δ 174.5, 167.9, 138.3, 130.7, 128.4, 126.6, 125.6, 120.1 (q, J = 325.0 Hz), 64.9, 57.1, 52.8, 32.4, 24.4, 24.3.

(S)-N-(tert-butyl)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamide (2l).

White solid.

**1H NMR** (400 MHz, CDCl3) δ 7.50 (d, J = 8.1 Hz, 1H), 7.24-7.28 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 6.15 (br s, 1H), 4.84 (dd, J = 8.6 Hz, 3.0 Hz, 1H), 3.47-3.59 (m, 2H), 1.33 (s, 9H).

**13C NMR** (125 MHz, CDCl3) δ 167.6, 138.3, 131.0, 128.2, 126.7, 125.7, 120.1 (q, J = 325.0 Hz), 116.0, 65.2, 51.8, 32.4, 28.5.

HRMS-ESI (m/z): [M+H]+ calcd for C14H18F3N2O3S+, 395.0985; found, 351.0992.

(S)-3-methyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)butyl acetate (2m).

Light yellow solid.

**1H NMR** (400 MHz, CDCl3) δ 7.54 (d, J = 8.7 Hz, 1H), 7.26-7.29 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.48 (br d, J = 8.5 Hz, 1H), 4.99 (t, J = 6.1 Hz, 1H), 4.12 (dd, J = 12.4 Hz, 7.7 Hz, 1H), 3.96-4.00 (m, 2H), 3.57 (d, J = 6.0 Hz, 2H), 1.88 (sextet, J = 7.0 Hz, 1H), 1.76 (s, 3H), 0.98 (dd, J = 6.8 Hz, 2.9 Hz, 6H).

**13C NMR** (100 MHz, CDCl3) δ 170.8, 168.6, 138.1, 130.9, 128.4, 126.8, 125.7, 120.1 (q, J = 325.0 Hz), 116.2, 64.9, 63.5, 54.0, 32.6, 29.6, 20.3, 19.2, 18.3.


(S)-4-methyl-2-((R)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)pentyl acetate (2n).

Light yellow solid.

**1H NMR** (400 MHz, CDCl3) δ 7.53 (d, J = 8.0 Hz, 1H), 7.26-7.29 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 6.36 (br d, J = 8.2 Hz, 1H), 4.95 (t, J = 6.0 Hz, 1H), 4.21-4.26 (m, 1H), 3.98 (d, J = 4.8 Hz, 2H), 3.56 (d, J = 6.0 Hz, 2H), 1.82 (s, 3H), 1.61-1.69 (m, 1H), 1.42-1.49 (m, 1H), 1.29-1.36 (m, 1H), 0.94 (t, J = 7.2 Hz, 6H).

**13C NMR** (100 MHz, CDCl3) δ 170.8, 168.4, 138.1, 130.9, 128.3, 126.8, 125.7, 120.1 (q, J = 324.0 Hz), 116.2, 65.4, 64.9, 47.3, 40.4, 32.6, 24.7, 22.9, 22.1, 20.3.

**(R)-N-((S)-1-methoxy-3-methylbutan-2-yl)-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamide (2o).**

White solid.

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 7.52 (d, J = 8.0 Hz, 1H), 7.25-7.28 (m, 2H), 7.19 (t, J = 6.6 Hz, 1H), 6.55 (br d, J = 8.6 Hz, 1H), 4.98 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 3.76-3.81 (m, 1H), 3.51-3.61 (m, 2H), 3.42 (dd, J = 9.8 Hz, 4.0 Hz, 1H), 3.16 (dd, J = 9.8 Hz, 4.2 Hz, 1H), 3.13 (s, 3H), 1.91 (sextet, J = 6.8 Hz, 1H), 0.94 (d, J = 6.7 Hz, 6H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 168.4, 138.3, 131.0, 128.3, 126.7, 125.7, 120.1 (q, J = 324.0 Hz), 116.1, 72.2, 65.1, 58.6, 54.8, 32.9, 29.3, 19.4, 18.6. \]


\[(2S)-methyl-2-(6-fluoro-1-((trifluoromethyl)sulfonyl)indoline-2-carboxamido)-3-methylbutanoate (2p).\]

Light yellow solid.

\[ \text{H NMR (500 MHz, CDCl}_3 \text{) } \delta 7.30 (dd, J = 9.0 Hz, 2.2 Hz, 0.56 × 1H), 7.26 (dd, J = 9.0 Hz, 2.2 Hz, 0.44 × 1H), 7.21 (t, J = 5.4 Hz, 1H), 6.87-6.92 (m, 1H), 6.84 (br d, J = 8.6 Hz, 0.56 × 1H), 6.76 (br d, J = 7.8 Hz, 0.44 × 1H), 5.04 (dd, J = 9.1 Hz, 3.3 Hz, 0.56 × 1H), 5.02 (dd, J = 8.5 Hz, 3.8 Hz, 0.44 × 1H), 4.49-4.53 (m, 1H), 3.76 (s, 0.44 × 3H), 3.68 (s, 0.56 × 3H), 3.48-3.57 (m, 2H), 2.20-2.26 (0.56 × 1H), 2.14-2.20 (0.44 × 1H), 0.94 (dd, J = 21.3 Hz, 6.9 Hz, 0.56 × 6H), 0.84 (t, J = 6.0 Hz, 0.44 × 6H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 171.6, 171.4, 168.3, 168.1, 162.6 (d, J = 245.0 Hz), 139.6 (d, J = 12.5 Hz), 139.4 (d, J = 12.5 Hz), 126.4 (d, J = 10.0 Hz), 126.3 (d, J = 10.0 Hz), 126.1 (d, J = 2.5 Hz), 126.0 (d, J = 2.5 Hz), 120.1 (q, J = 325.0 Hz), 113.8 (d, J = 22.5 Hz), 113.5 (d, J = 22.5 Hz), 104.5 (d, J = 27.5 Hz), 104.3 (d, J = 27.5 Hz), 65.7, 57.5, 52.3, 52.3, 32.0, 31.8, 31.3, 31.1, 18.8, 18.8, 17.5, 17.4. \]

HRMS-ESI (m/z): [M+H]^+ calcd for C16H19F4N2O5S^+, 427.0945; found, 427.0953.

\[(S)-methyl-2-(6-methoxy-1-((trifluoromethyl)sulfonyl)-1H-indole-2-carboxamido)-3-methylbutanoate (2q).\]

Light yellow solid.

\[ \text{H NMR (400 MHz, CDCl}_3 \text{) } \delta 7.49 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.08 (s, 1H), 7.01 (dd, J = 8.6 Hz, 2.2 Hz, 1H), 6.58 (br d, J = 9.0 Hz, 1H), 4.74 (dd, J = 8.8 Hz, 4.6 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 2.26-2.34 (m, 1H), 1.04 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H). \]

\[ \text{C NMR (125 MHz, CDCl}_3 \text{) } \delta 172.0, 160.0, 159.6, 139.0, 133.9, 123.1, 121.8, 119.7 (q, J = 324.0 Hz), 116.1, 114.9, 99.6, 57.6, 55.8, 52.3, 31.5, 18.8, 17.8. \]

HRMS-ESI (m/z): [M+H]^+ calcd for C17H20F3N2O6S^+, 437.0989; found, 437.0995.
Reference

NMR Spectra