

Supporting Information

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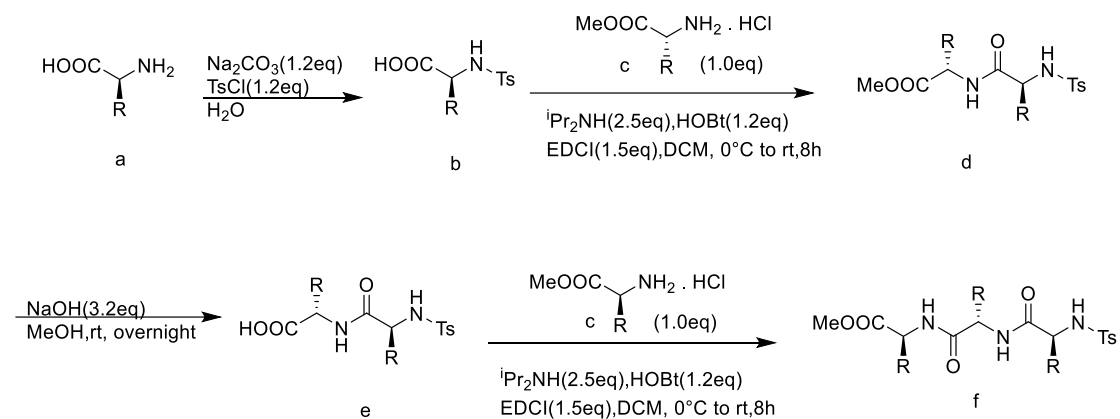
Instrumentation and Chemicals

NMR spectra were recorded on Bruker 400 and 600 M spectrometers, operating at 400 and 600 MHz for ^1H NMR and 100 and 150 MHz for ^{13}C NMR spectrophotometer using CDCl_3 and TMS as the internal standard. Chemical shift values for ^1H and ^{13}C are referenced to residual solvent peaks (CHCl_3 in CDCl_3 : 7.26 ppm for ^1H NMR, 77.00 ppm for ^{13}C NMR; Chemical shifts are reported in δ ppm. All coupling constants (J values) were reported in Hertz (Hz). Data for ^1H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, 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 electron-spray ionization (ESI) technique.

Experimental Section

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard note procedures unless otherwise noted. HOBt was purchased from Shanghai Bide Pharmatech Ltd., EDCI was purchased from Alfa Aesar Chemical Co., Ltd., DCC was purchased from Shanghai Adamas Reagent Co., Ltd, Anhydrous DCE was purchased from Energy Chemical Reagent Co., Ltd.

General Procedure for the Preparation of Dipeptides and Tripeptides



Synthesis of *N*-Ts-*L*-Amino acid (b)

Sodium carbonate (Na_2CO_3 , 1.590 g, 15 mmol) was added to a solution of amino acids a (L-Isoleucine, L-Norvaline, D-Norleucine, 12.5 mmol) in water (15 mL) with continuous stirring until all the solutes had dissolved. The solution was cooled to -5°C and the *p*-Toluoyl chloride (15 mmol) was added in four portions over a period of 1 h. The slurry was further stirred at room temperature for about 4 h. The progress of the reaction was monitored using TLC (MeOH/DCM, 1:9). Upon completion, the mixture was acidified using 1M hydrochloric acid to pH 2. The crystals were filtered via suction and dried over to give the crude product.

Synthesis of *L*-Amino acid methyl ester hydrochloride(c)

To a stirring solution of L-Amino acid (30mmol, 1.0 equiv.) in MeOH (30 mL) was added SOCl_2 (60mmol, 2.0 eq.) dropwise under ice bath. Then the reaction mixture was stirred for 2h under refluxing condition and then allowed to cool to room temperature. The solvent was removed in vacuo and **c** was obtained quantitatively as a white solid.

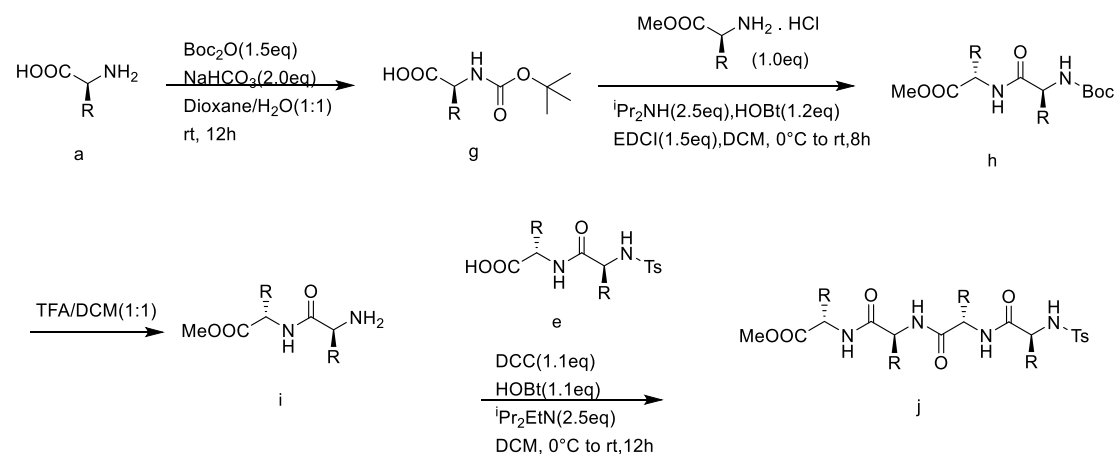
Synthesis of Dipeptides(d) and Tripeptides(f)

b (5.0 mmol), **c** (1.0 equiv) and $i\text{Pr}_2\text{NH}$ (2.5 equiv) were stirred in DCM (0.2 M) under 0°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°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 1M HCl (20 mL), sat. NaHCO_3 (3 x 20 mL) and brine (20 mL). The organic layers were then dried over MgSO_4 . Solvent was removed under reduced pressure and further purification was conducted by column chromatography (for **d** or **f**, PE:DCM:EA = 5:1:1 as eluent, 78% yield) to give Dipeptides(**d**) or Tripeptides(**f**) as a white solid.

Synthesis of hydrolysis of methyl ester(**e**)

To a solution of **d** (1 equiv.) in MeOH, 2M NaOH solution (3.2 equiv.) was added. The solution was stirred overnight at room temperature and evaporated in vacuo. The resulting residue was dissolved in water and acidified with 2 M HCl. The solution was extracted with AcOEt three times. The combined organic layer was dried over MgSO_4 and evaporated in vacuo to give a product.

General Procedure for the Preparation of Tetrapeptide(1aa-1ad)



Synthesis of *N*-Boc-*L*- Amino acid(**g**)

In a 500-mL round-bottom flask under N_2 atmosphere, 1 M NaOH solution (63

mL) in distilled water and 3.93 g L- Amino acid (30 mmol) were added in sequence. The system was then immersed into the ice bath for cooling for 15 min. After the solution become clear, 7.86 g Boc₂O dissolved in THF (84 mL, 36 mmol) were added and stirred for 10 min; the pH was adjusted to around 10.5. The reaction temperature was then slowly increased to room temperature, and the solution was stirred overnight. After 24 h, the solvent was removed by vacuum distillation, and the rest was extracted twice using 200 mL ethyl ether. The resultant aqueous phase was cooled in the ice bath, acidified by adding an appropriate amount of 1 M HCl solution to increase the pH to 2. Then, the aqueous phase was further extracted three times with ethyl acetate (150 mL), washed twice with saturated NaCl solution (150 mL). Subsequently, the organic layer was dried by anhydrous sodium sulfate and filtered. After complete distillation of the organic solvent, white powder were obtained (yield 75%).

Synthesis of (i)

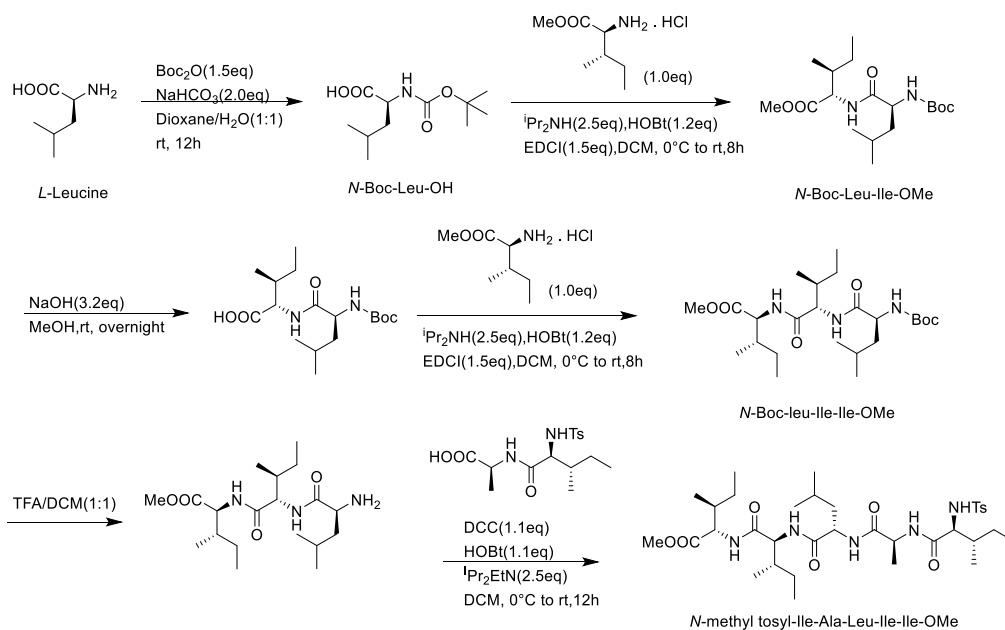
h was synthesis according to the procedure of synthesis of **d**. And TFA (1 mL/mmol) was added dropwise to a solution of the **h** in CH₂Cl₂ (1 mL/mmol) at 0 °C. The reaction mixture was allowed to stir for 30 min at room temperature. The mixture was concentrated in vacuo, and the residue was basified with saturated aqueous NH₄OH. The mixture was extracted with CH₂Cl₂ twice. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo to afford the crude sample.

Synthesis of Tetrapeptide(j)

To a solution of dipeptide **e** (1 mmol) in CH₂Cl₂ (10 mL/mmol) at 0°C were added DCC (1.1mmol, 1.1 equiv), HOBt (1.1mmol, 1.1 equiv) and N,N-diisopropylethylamine (2.5 equiv). After being stirred for 10 min, the mixture was treated with **i** (1.0 mmol). The reaction mixture was warmed to room temperature and allowed to stir for 12 h. The mixture was concentrated in vacuo and treated with ethyl acetate. After filtration, the filtrate was washed with 1 M HCl, saturated aqueous

NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate/dichloromethane (1/2/2, v/v/v) as the eluent to afford **j** as white solid (30 - 45% yield).

Synthesis of Pentapeptide



(1) In a 500-mL round-bottom flask under N₂ atmosphere, 1 M NaOH solution (63 mL) in distilled water and 3.93 g L-Leucine (30 mmol) were added in sequence. The system was then immersed into the ice bath for cooling for 15 min. After the solution become clear, 7.86 g Boc₂O dissolved in THF (84 mL, 36 mmol) were added and stirred for 10 min; the pH was adjusted to around 10.5. The reaction temperature was then slowly increased to room temperature, and the solution was stirred overnight. After 24 h, the solvent was removed by vacuum distillation, and the rest was extracted twice using 200 mL ethyl ether. The resultant aqueous phase was cooled in the ice bath, acidified by adding an appropriate amount of 1 M HCl solution to increase the pH to 2. Then, the aqueous phase was further extracted three times with ethyl acetate (150 mL), washed twice with saturated NaCl solution (150 mL). Subsequently, the organic layer was dried by anhydrous sodium sulfate and filtered. After complete distillation of the organic solvent, white powder were obtained (yield 75%)

(2) *N*-Boc-Leu-OH (20.0 mmol), methyl *L*-isoleucinate hydrochloride (1.0 equiv) and *i*Pr₂NH (2.5 equiv) were stirred in DCM (0.2 M) under 0 °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 °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 1M HCl (20 mL), sat. NaHCO₃ (3 x 20 mL) and brine (20 mL). The organic layers were then dried over MgSO₄. Solvent was removed under reduced pressure and further purification was conducted by column chromatography (for d or f, PE:DCM:EA = 10:1:1 as eluent, 78% yield) to give Dipeptides as a white solid.

(3) To a solution of *N*-Boc-leu-Ile-OMe (1 equiv.) in MeOH, 2M NaOH solution (3.2 equiv.) was added. The solution was stirred overnight at room temperature and evaporated in vacuo. The resulting residue was dissolved in water and acidified with 2 M HCl. The solution was extracted with AcOEt three times. The combined organic layer was dried over MgSO₄ and evaporated in vacuo to give a product.

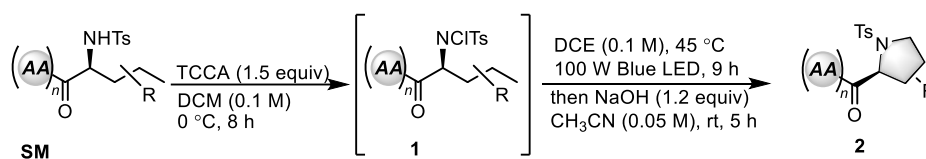
(4) *N*-Boc-Leu-Ile-OH and methyl *L*-isoleucinate hydrochloride added together according to procedure (3) to afford *N*-Boc-Leu-Ile-Ile-OMe as a white solid.

(5) TFA (1 mL/mmol) was added dropwise to a solution of the h in CH₂Cl₂ (1 mL/mmol) at 0 °C. The reaction mixture was allowed to stir for 30 min at room temperature. The mixture was concentrated in vacuo, and the residue was basified with saturated aqueous NH₄OH. The mixture was extracted with CH₂Cl₂ twice. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo to afford the crude sample.

(6) To a solution of *N*-Ts-Ile-Ala-OH (1 mmol) in CH₂Cl₂ (10 mL/mmol) at 0 °C were added DCC (1.1mmol, 1.1 equiv), HOBt (1.1mmol, 1.1 equiv) and *N,N*-diisopropylethylamine (2.5 equiv). After being stirred for 10 min, the mixture was treated with crude sample (1.0 mmol). The reaction mixture was warmed to room temperature and allowed to stir for 12 h. The mixture was concentrated in vacuo and

treated with ethyl acetate. After filtration, the filtrate was washed with 1 M HCl, saturated aqueous NaHCO₃ and brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate/dichloromethane (1/2/2, v/v/v) as the eluent to afford **j** as white solid (40% yield).

General procedure for C(sp³)-H Amidation



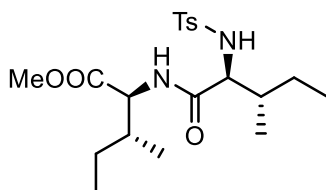
To an ice-cooled solution of peptides (**SM**, 5.0 mmol, 1.0 equiv.) in CH₂Cl₂ (50 mL) was added trichloroisocyanuric acid (TCCA) (1.1-1.5 equiv.). After the reaction was complete (as judged by TLC analysis, about 3-6 h), the mixture was poured into a separatory funnel containing 50 mL of H₂O. The layer was separated and the aqueous layer was extracted with CH₂Cl₂ (20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel (PE:EA:DCM =5:1:1) to afford the desired product **1**.

A 8 mL-round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with compound **1a** (0.1 mmol, 1.0 equiv). The flask was evacuated and back filled with nitrogen for 3 times. DCE (1.0 mL, 0.1 M) was added with syringe under nitrogen. The mixture was then irradiated by 100 W blue LED strips. After the starting material was disappeared (as judged by TLC analysis), the solvent was removed under vacuum, NaOH (s, 0.12mmol, 1.2 equiv) and CH₃CN (2mL, 0.05M) was added into the solution and stirred for another 5h. The mixture was added 5 mL Saturated brine. The layers were separated and the aqueous layer was extracted with EA (3 × 5mL). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure after filtration. The crude product was purified by flash chromatography on silica gel (PE: EtOAc: CH₂Cl₂=4:1:1) to afford the desired product

2a (yield 85%).

Characterization Data

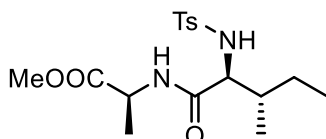
methyl tosyl-*L*-isoleucyl-*L*-alloisoleucinate(SM-a)



SM-a

White solid. mp 153.9-154.8 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 6.14 (d, $J = 8.4$ Hz, 1H), 5.35 (d, $J = 8.4$ Hz, 1H), 4.37 (dd, $J = 8.1, 4.5$ Hz, 1H), 3.71 (s, 3H), 3.56 (dd, $J = 8.7, 5.4$ Hz, 1H), 1.72 – 1.77 (m, 1H), 1.63 (s, 3H), 1.56 – 1.62 (m, 1H), 1.40 – 1.47 (m, 1H), 1.25 – 1.33 (m, 1H), 1.06 – 1.14 (m, 1H), 0.97 – 1.05 (m, 1H), 0.88 (d, $J = 6.9$ Hz, 3H), 0.84 – 0.87 (m, 6H), 0.66 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.74, 170.03, 143.45, 136.86, 129.60, 127.35, 61.21, 56.55, 52.17, 38.59, 37.76, 25.16, 24.31, 21.50, 15.39, 15.09, 11.58, 11.39. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_5\text{S}$, 413.2105; found, 413.2093. **IR** (KBr, cm^{-1}): ν 3364, 3271, 2965, 2875, 1729, 1650, 1333, 1164, 817, 668.

methyl tosyl-*L*-isoleucyl-*L*-alaninate(SM-b)

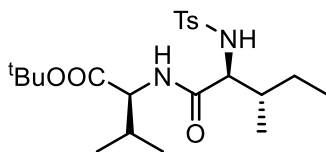


SM-b

White solid. mp 114.0-114.8 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.13 (d, $J = 6.6$ Hz, 1H), 5.23 (d, $J = 8.7$ Hz, 1H), 4.33 (p, $J = 7.2$ Hz, 1H), 3.73 (s, 3H), 2.54-2.58 (m, 1H), 2.40 (s, 3H), 1.69 – 1.80 (m, 1H), 1.47 – 1.54 (m, 1H), 1.13 (d, $J = 7.2$ Hz, 3H), 1.08 – 1.12 (m, 1H), 0.82 – 0.89 (m, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.72, 167.88, 143.51, 137.11, 129.63, 127.45, 61.34, 52.57, 48.05, 38.37, 24.46, 21.49, 18.08, 15.35, 11.30. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_5\text{SNa}$, 393.1455; found, 393.1461. **IR** (KBr, cm^{-1}): ν 3348, 3260,

2968, 1734, 1645, 1336, 1160, 819, 673.

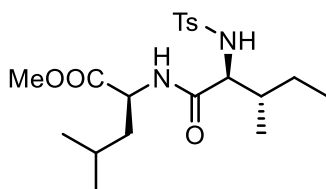
tert-butyl tosyl-L-isoleucyl-L-valinate(SM-c)



SM-c

White solid. mp 168.8-169.7 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 6.08 (d, $J = 8.4$ Hz, 1H), 5.40 (d, $J = 8.4$ Hz, 1H), 4.20 (dd, $J = 8.4, 4.8$ Hz, 1H), 3.55 (dd, $J = 8.4, 5.4$ Hz, 1H), 2.38 (s, 3H), 1.89 (d, $J = 4.8$ Hz, 1H), 1.72 – 1.80 (m, 1H), 1.42 – 1.48 (m, 10H), 1.07 – 1.15 (m, 1H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.85 (t, $J = 7.5$ Hz, 3H), 0.75 (d, $J = 6.9$ Hz, 3H), 0.67 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.33, 169.96, 143.45, 136.79, 129.62, 127.32, 82.33, 61.22, 57.74, 38.69, 31.23, 27.95, 24.31, 21.45, 18.47, 17.61, 15.45, 11.38. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{36}\text{N}_2\text{O}_5\text{SNa}$, 463.2237; found, 463.2244. **IR** (KBr, cm^{-1}): ν 3317, 3266, 2967, 1714, 1650, 1544, 1382, 1168, 665.

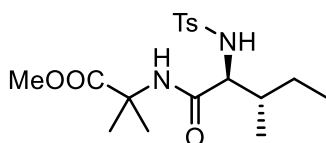
methyl tosyl-L-isoleucyl-L-leucinate(SM-d)



SM-d

White solid. mp 154.1-155.3 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 5.94 (d, $J = 8.1$ Hz, 1H), 5.28 (d, $J = 8.4$ Hz, 1H), 4.39 (td, $J = 8.4, 5.4$ Hz, 1H), 3.69 (s, 3H), 3.54 (dd, $J = 8.4, 5.1$ Hz, 1H), 2.39 (s, 3H), 1.75 (dd, $J = 15.9, 9.6$ Hz, 1H), 1.38 – 1.53 (m, 2H), 1.25 – 1.38 (m, 2H), 1.02 – 1.14 (m, 1H), 0.83 – 0.93 (m, 9H), 0.79 – 0.83 (m, 4H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.73, 169.98, 143.46, 136.91, 129.60, 127.32, 61.15, 52.29, 50.81, 41.40, 38.60, 24.65, 24.30, 22.64, 21.85, 21.54, 15.35, 11.40. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_5\text{S}$, 413.2105; found, 413.2116. **IR** (KBr, cm^{-1}): ν 3365, 3270, 2964, 1728, 1649, 1436, 1165, 817, 668.

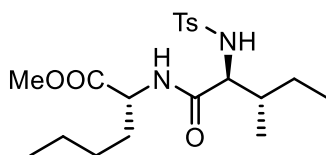
methyl 2-methyl-2-((2S,3S)-3-methyl-2-((4-methylphenyl)sulfonamido) pentanamido) propanoate(SM-e)



SM-e

White solid. mp 118.6-120.0 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 6.39 (d, *J* = 5.1 Hz, 1H), 5.30 (t, *J* = 8.6 Hz, 1H), 3.70 (s, 3H), 3.52 (dd, *J* = 8.1, 5.4 Hz, 1H), 2.39 (s, 3H), 1.76 – 1.80 (m, 1H), 1.46 – 1.48 (m, 1H), 1.35 (s, 3H), 1.33 (s, 3H), 1.05 – 1.11 (m, 1H), 0.84 – 0.89 (m, 6H). ¹³C NMR (150MHz, CDCl₃) δ 174.59, 169.30, 143.65, 136.73, 129.68, 127.38, 61.40, 56.57, 52.64, 38.33, 24.42, 24.27, 24.02, 21.47, 15.31, 11.46. HRMS-ESI(*m/z*): [M+Na]⁺ calcd. for C₁₈H₂₈N₂O₅SNa, 407.1611; found, 407.1607. IR (KBr, cm⁻¹): ν 3347, 3166, 2966, 1740, 1666, 1548, 1456, 1291, 1156, 812, 673.

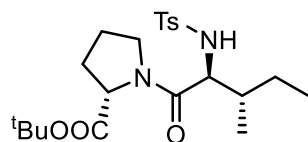
methyl (R)-2-((2S,3S)-3-methyl-2-((4-methylphenyl)sulfonamido) pentanamido) hexanoate(SM-f)



SM-f

White solid. mp 163.8-164.6 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 7.5 Hz, 1H), 5.23 (d, *J* = 8.1 Hz, 1H), 4.33 (dd, *J* = 12.6, 7.2 Hz, 1H), 3.74 (s, 3H), 3.59 (d, *J* = 2.7 Hz, 1H), 2.40 (s, 3H), 1.79 – 1.86 (m, 1H), 1.56 – 1.63 (m, 1H), 1.43 – 1.50 (m, 1H), 1.26 – 1.29 (m, 3H), 1.14 – 1.23 (m, 2H), 1.02 – 1.11 (m, 1H), 0.82 – 0.88 (m, 6H), 0.79 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 172.45, 169.89, 143.63, 136.42, 129.59, 127.38, 61.55, 52.30, 52.11, 37.99, 31.89, 27.02, 24.17, 22.14, 21.48, 15.41, 13.74, 11.36. HRMS-ESI(*m/z*): [M+Na]⁺ calcd. for C₂₀H₃₂N₂O₅SNa, 435.1924; found, 435.1922. IR (KBr, cm⁻¹): ν 3442, 2958, 1736, 1643, 1531, 1015, 666.

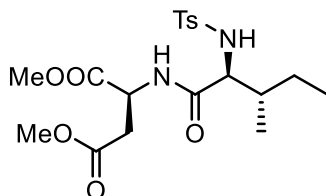
tert-butyl tosyl-L-isoleucyl-L-prolinate(SM-g)



SM-g

White solid. mp 174.4-176.0 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.69 (d, $J = 7.5$ Hz, 2H), 7.26 – 7.21 (m, 2H), 5.48 (d, $J = 9.6$ Hz, 1H), 3.80 (d, $J = 6.0$ Hz, 1H), 3.64 – 3.71 (m, 1H), 3.40 (d, $J = 6.3$ Hz, 1H), 3.12 (dd, $J = 15.3, 7.5$ Hz, 1H), 2.41 (s, 3H), 1.85 – 1.94 (m, 1H), 1.75 – 1.85 (m, 2H), 1.67 (d, $J = 7.8$ Hz, 3H), 1.40 (s, 9H), 1.16 (d, $J = 6.3$ Hz, 1H), 1.01 (t, $J = 10.5$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.56, 169.55, 143.31, 136.86, 129.23, 127.40, 81.47, 59.45, 58.59, 46.69, 38.09, 28.60, 27.83, 24.46, 24.03, 21.42, 15.09, 10.90. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{35}\text{N}_2\text{O}_5\text{S}$, 439.2261; found, 439.2255. **IR** (KBr, cm^{-1}): ν 3253, 2970, 2879, 1735, 1634, 1367, 1161, 816, 667.

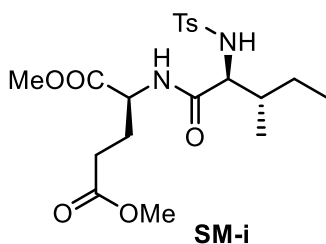
dimethyl tosyl-L-isoleucyl-L-aspartate(SM-h)



SM-h

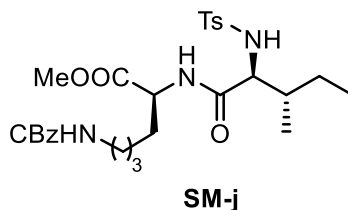
White solid. mp 168.3-169.4 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 6.86 (d, $J = 8.1$ Hz, 1H), 5.68 (dd, $J = 9.0, 4.2$ Hz, 1H), 4.68 (dt, $J = 8.4, 4.5$ Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.58 (dd, $J = 8.7, 6.3$ Hz, 1H), 2.87 (dd, $J = 17.3, 4.2$ Hz, 1H), 2.41 (s, 3H), 2.36 (dd, $J = 17.4, 4.8$ Hz, 1H), 1.71 – 1.719 (m, 1H), 1.48 – 1.56 (m, 1H), 1.09 – 1.16 (m, 1H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.84 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.35, 170.52, 170.25, 143.41, 136.92, 129.37, 127.33, 61.16, 52.70, 52.01, 48.12, 38.23, 35.52, 24.29, 21.34, 15.14, 11.13. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_7\text{SNa}$, 451.1509; found, 451.1508. **IR** (KBr, cm^{-1}): ν 3238, 2969, 1737, 1637, 1162, 1094, 816, 665.

dimethyl tosyl-L-isoleucyl-L-glutamate(SM-i)



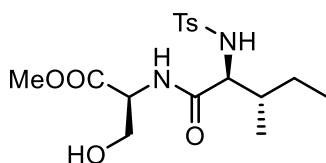
White solid. mp 95.6-96.3 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.74 (d, $J = 7.5$ Hz, 1H), 4.35 (td, $J = 7.8, 5.4$ Hz, 1H), 3.72 (d, $J = 6.6$ Hz, 3H), 3.70 (s, 3H), 3.59 (dd, $J = 8.7, 5.8$ Hz, 1H), 2.40 (s, 3H), 2.26 (dt, $J = 16.9, 7.5$ Hz, 1H), 2.16 (ddd, $J = 17.0, 7.5, 6.7$ Hz, 1H), 2.00 (dtd, $J = 14.7, 7.4, 5.4$ Hz, 2H), 1.85 (td, $J = 14.4, 7.8$ Hz, 1H), 1.70 – 1.78 (m, 1H), 1.44 – 1.48 (m, 1H), 1.04 – 1.14 (m, 1H), 0.87 (d, $J = 6.8$ Hz, 3H), 0.83 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 173.29, 171.58, 170.44, 143.52, 136.80, 129.53, 127.27, 61.12, 52.46, 51.88, 51.78, 38.34, 29.76, 26.66, 24.30, 21.40, 15.18, 11.24. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_7\text{SNa}$, 465.1666; found, 465.1664. **IR** (KBr, cm^{-1}): ν 3358, 2956, 1739, 1663, 1331, 1165, 1094, 817, 665.

methyl N⁶-((benzyloxy)carbonyl)-N²-(tosyl-L-isoleucyl)-L-lysinate(SM-j)



Yellow gum $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (dd, $J = 13.6, 8.1$ Hz, 4H), 7.33 – 7.27 (m, 4H), 6.55 (d, $J = 7.8$ Hz, 1H), 5.46 (d, $J = 9.0$ Hz, 1H), 5.05 (t, $J = 6.0$ Hz, 1H), 4.37 (td, $J = 7.9, 4.8$ Hz, 1H), 3.71 (s, 3H), 3.60 (d, $J = 2.6$ Hz, 1H), 2.91 (dd, $J = 9.5, 6.4$ Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H), 1.71 – 1.80 (m, 2H), 1.56 (dt, $J = 15.0, 7.7$ Hz, 1H), 1.41 – 1.52 (m, 3H), 1.24 – 1.31 (m, 2H), 1.01 – 1.08 (m, 1H), 0.82 (d, $J = 6.9$ Hz, 3H), 0.80 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.16, 170.73, 143.58, 143.35, 136.89, 136.82, 129.71, 28.81, 127.44, 127.01, 61.18, 52.43, 51.89, 42.34, 37.88, 31.17, 28.54, 24.32, 21.68, 21.53, 21.49, 15.29, 11.17. **IR** (KBr, cm^{-1}): ν 3310, 2984, 1736, 1556, 1377, 1146, 817, 665.

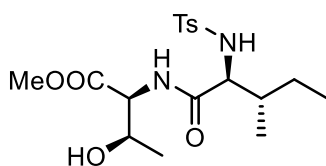
methyl tosyl-L-isoleucyl-L-serinate(SM-k)



SM-k

White solid. mp 173.0-173.8 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 7.2$ Hz, 1H), 5.53 (d, $J = 9.0$ Hz, 1H), 4.48 – 4.55 (m, 1H), 3.85 – 3.92 (m, 1H), 3.80 (s, 3H), 3.66 – 3.73 (m, 1H), 3.58 (dd, $J = 8.9, 6.6$ Hz, 1H), 2.67 (t, $J = 6.0$ Hz, 1H), 2.44 (s, 3H), 1.77 (dd, $J = 8.1, 5.1$ Hz, 1H), 1.49 – 1.57 (m, 1H), 1.05 – 1.16 (m, 1H), 0.87 (d, $J = 6.9$ Hz, 3H), 0.83 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.05, 170.52, 143.86, 136.56, 129.59, 127.49, 62.59, 61.31, 54.74, 52.78, 37.84, 24.37, 21.50, 15.25, 11.03. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_6\text{SNa}$, 409.1404; found, 409.1398. **IR** (KBr, cm^{-1}): ν 3256, 2964, 1749, 1650, 1322, 1161, 815, 672.

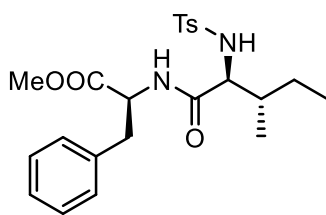
methyl tosyl-L-isoleucyl-L-threoninate(SM-l)



SM-l

White solid. mp 172.9-173.3 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 5.4$ Hz, 2H), 6.52 (d, $J = 8.7$ Hz, 1H), 5.49 (d, $J = 8.7$ Hz, 1H), 4.43 (d, $J = 8.7$ Hz, 1H), 4.27 (s, 1H), 3.75 (s, 3H), 3.59 – 3.67 (m, 1H), 2.39 (s, 3H), 2.31 (s, 1H), 1.74 – 1.82 (m, 1H), 1.39 – 1.51 (m, 1H), 1.02 – 1.19 (m, 2H), 0.96 (d, $J = 6.3$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.83 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.99, 170.91, 143.62, 136.76, 129.64, 127.39, 67.78, 61.18, 57.21, 52.62, 38.46, 24.19, 21.47, 19.62, 15.34, 11.33. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_6\text{SNa}$, 423.1560; found, 423.1553. **IR** (KBr, cm^{-1}): ν 3415, 3234, 2958, 1744, 1659, 1540, 1158, 817, 666.

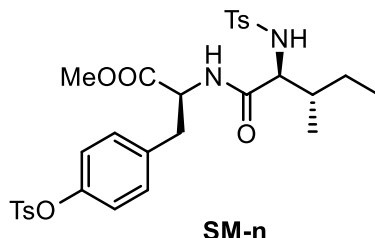
methyl tosyl-L-isoleucyl-L-phenylalaninate(SM-m)



SM-m

White solid. mp 134.8-135.7 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 3H), 7.25 (dd, $J = 4.0, 3.0$ Hz, 2H), 6.93 (dd, $J = 7.3, 2.0$ Hz, 2H), 6.17 (d, $J = 7.8$ Hz, 1H), 5.31 (d, $J = 8.4$ Hz, 1H), 4.69 (dt, $J = 7.8, 6.0$ Hz, 1H), 3.67 (s, 3H), 3.54 (dd, $J = 8.4, 5.1$ Hz, 1H), 2.95 (dd, $J = 13.8, 5.7$ Hz, 1H), 2.84 (dd, $J = 13.8, 5.7$ Hz, 1H), 2.36 (s, 3H), 1.70 – 1.75 (m, 1H), 1.63 (s, 1H), 1.25 – 1.35 (m, 1H), 0.94 – 1.04 (m, 1H), 0.79 (dd, $J = 14.2, 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.28, 169.78, 143.72, 136.72, 135.46, 129.62, 129.08, 128.62, 127.42, 127.23, 61.16, 53.20, 52.31, 38.36, 37.86, 24.17, 21.50, 15.28, 11.39. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_5\text{S}$, 447.1948; found, 447.1942. **IR** (KBr, cm^{-1}): ν 3440, 3390, 1746, 1647, 1162, 666.

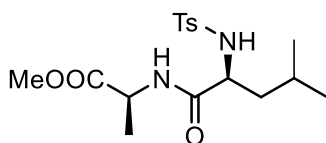
methyl tosyl-L-isoleucyl-L-tyrosinate(SM-n)



SM-n

Colorless gum. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 6.85 – 6.90 (m, 4H), 6.29 (d, $J = 7.5$ Hz, 1H), 5.24 (d, $J = 8.4$ Hz, 1H), 4.69 (dd, $J = 13.5, 6.0$ Hz, 1H), 3.65 (s, 3H), 3.52 (dd, $J = 8.4, 5.1$ Hz, 1H), 2.92 (dd, $J = 14.1, 6.0$ Hz, 1H), 2.86 (dd, $J = 14.1, 6.0$ Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 1.65 – 1.78 (m, 1H), 1.26 – 1.32 (m, 1H), 0.92 – 1.05 (m, 1H), 0.77 (t, $J = 6.6$ Hz, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.04, 170.00, 148.75, 145.43, 143.85, 136.64, 134.73, 132.43, 130.35, 129.80, 129.66, 128.49, 127.46, 122.52, 61.16, 53.17, 52.41, 38.17, 37.29, 24.23, 21.72, 21.50, 15.33, 11.36. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{30}\text{H}_{37}\text{N}_2\text{O}_8\text{S}_2$, 617.1986; found, 617.1979. **IR** (KBr, cm^{-1}): ν 3354, 3246, 1735, 1668, 1375, 1166, 866, 676.

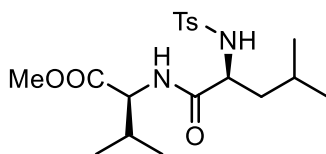
methyl tosyl-L-leucyl-L-alaninate(SM-o)



SM-o

White solid. mp 186.4-189.1 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 6.9 Hz, 1H), 5.34 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.34 (p, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 3.69 – 3.72 (m, 1H), 2.40 (s, 3H), 1.75 (s, 1H), 1.68 – 1.73 (m, 1H), 1.44 – 1.50 (m, 2H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.8 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 172.90, 170.87, 143.66, 136.73, 129.62, 127.39, 55.22, 52.54, 48.03, 42.50, 24.19, 22.87, 21.48, 21.34, 18.04. **HRMS-ESI(m/z)**: [M+H]⁺ calcd. for C₁₇H₂₇N₂O₅S, 371.1635; found, 371.1629. **IR** (KBr, cm⁻¹): ν 3342, 3261, 2957, 1737, 1651, 1536, 1311, 1161, 819, 674.

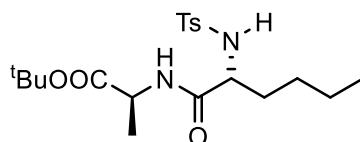
methyl tosyl-L-leucyl-L-valinate(SM-p)



SM-p

White solid. mp 109.9-110.0 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 1H), 5.86 (s, 1H), 4.30 – 4.40 (m, 1H), 3.75 – 3.85 (m, 1H), 3.71 (s, 3H), 2.36 (s, 3H), 1.93 – 2.00 (m, 1H), 1.63 – 1.72 (m, 1H), 1.40 – 1.52 (m, 2H), 0.82 (s, 3H), 0.76 – 0.80 (m, 3H), 0.69 – 0.75 (m, 6H). **¹³C NMR** (150 MHz, CDCl₃) δ 171.89, 171.53, 143.43, 136.88, 129.55, 127.22, 57.19, 55.19, 52.08, 42.46, 31.10, 24.11, 22.86, 21.37, 21.23, 18.54, 17.69. **HRMS-ESI(m/z)**: [M+H]⁺ calcd. for C₁₉H₃₁N₂O₅S, 399.1948.; found, 399.1954. **IR** (KBr, cm⁻¹): ν 3349, 2962, 1729, 1646, 1535, 1341, 1174, 812, 663.

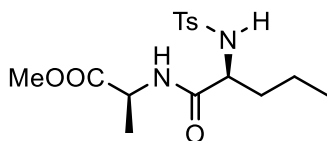
tert-butyl ((R)-2-((4-methylphenyl)sulfonamido)hexanoyl)-L-alaninate(SM-q)



SM-q

White solid. mp 148.5-149.2 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H), 6.56 (d, $J = 7.2$ Hz, 1H), 5.25 (d, $J = 7.5$ Hz, 1H), 4.18 (p, $J = 7.2$ Hz, 1H), 3.69 (dt, $J = 7.5, 5.1$ Hz, 1H), 2.41 (s, 3H), 1.67 – 1.72 (m, 1H), 1.51 – 1.61 (m, 1H), 1.47 (s, 9H), 1.28 (d, $J = 7.2$ Hz, 3H), 1.18 – 1.22 (m, 3H), 1.10 – 1.15 (m, 1H), 0.80 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.71, 170.07, 143.66, 136.64, 129.65, 127.34, 82.22, 56.83, 48.68, 32.99, 27.93, 27.04, 22.10, 21.49, 18.32, 13.73. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_5\text{SNa}$, 435.1924; found, 435.1915. **IR** (KBr, cm^{-1}): ν 3384, 3270, 1724, 1656, 1346, 1164, 820, 674.

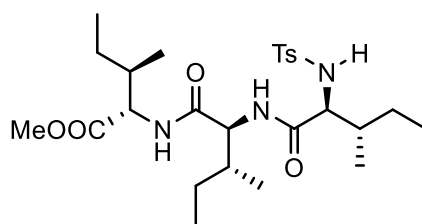
methyl ((S)-2-((4-methylphenyl)sulfonamido)pentanoyl)-L-alaninate(SM-r)



SM-r

White solid. mp 121.3-123.0 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 6.30 (d, $J = 8.1$ Hz, 1H), 5.21 (d, $J = 8.1$ Hz, 1H), 4.36 (dd, $J = 8.7, 4.8$ Hz, 1H), 3.74 (s, 3H), 3.64 – 3.70 (m, 1H), 2.41 (s, 3H), 1.64 – 1.67 (m, 1H), 1.47 – 1.56 (m, 1H), 1.33 – 1.37 (m, 1H), 1.24 – 1.27 (m, 1H), 1.16 (d, $J = 6.6$ Hz, 3H), 0.85(t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.87, 170.42, 143.68, 136.74, 129.65, 127.34, 56.48, 52.55, 48.07, 35.58, 21.47, 18.29, 18.07, 13.48. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_5\text{SNa}$, 379.1298; found, 379.1289. **IR** (KBr, cm^{-1}): ν 3257, 2959, 1737, 1648, 1163, 1017, 676.

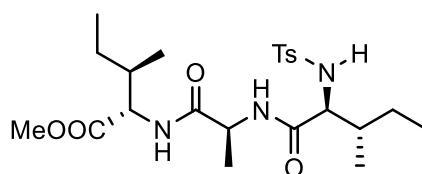
methyl tosyl-L-isoleucyl-L-alloisoleucyl-L-alloisoleucinate(SM-s)



SM-s

White solid. mp 206.5-208 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 6.51 (d, $J = 8.4$ Hz, 1H), 6.46 (d, $J = 8.4$ Hz, 1H), 5.29 (d, $J = 7.5$ Hz, 1H), 4.54 (dd, $J = 8.4, 5.4$ Hz, 1H), 4.21 (dd, $J = 8.4, 6.3$ Hz, 1H), 3.73 (s, 3H), 3.54 (dd, $J = 7.5, 5.1$ Hz, 1H), 2.41 (s, 3H), 1.85 – 1.91 (m, 1H), 1.78 – 1.83 (m, 1H), 1.71 – 1.77 (m, 1H), 1.36 – 1.45 (m, 2H), 1.26 – 1.34 (m, 1H), 1.12 – 1.19 (m, 1H), 1.01 – 1.08 (m, 1H), 0.93 – 1.00 (m, 1H), 0.88 (dd, $J = 9.6, 5.1$ Hz, 5H), 0.84 – 0.87 (m, 4H), 0.82 (t, $J = 7.5$ Hz, 3H), 0.78 – 0.79 (m, 3H), 0.77 – 0.78 (m, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.98, 170.40, 170.13, 143.78, 134.85, 129.71, 127.50, 61.46, 58.02, 56.60, 52.07, 38.23, 37.57, 37.08, 25.13, 24.74, 24.20, 21.56, 15.45, 15.43, 15.27, 11.43. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{26}\text{H}_{43}\text{N}_3\text{O}_6\text{SNa}$, 548.2765; found, 548.2752. **IR** (KBr, cm^{-1}): ν 3450, 2964, 1740, 1638, 1542, 1306, 1160, 817, 671.

methyl tosyl-*L*-isoleucyl-*L*-alanyl-*L*-alloisoleucinate(SM-t)

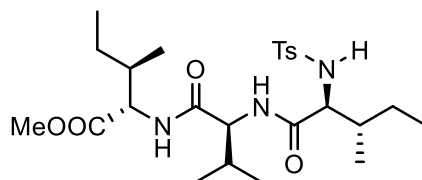


SM-t

White solid. mp 226.2-227.6 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 1H), 6.69 (d, $J = 7.8$ Hz, 1H), 5.68 (d, $J = 8.4$ Hz, 1H), 4.54 (dd, $J = 8.4, 5.1$ Hz, 1H), 4.42 – 4.50 (m, 1H), 3.75 (s, 3H), 3.56 (dd, $J = 8.4, 6.0$ Hz, 1H), 2.40 (s, 3H), 1.83 – 1.91 (m, 1H), 1.70 – 1.77 (m, 1H), 1.47 – 1.54 (m, 1H), 1.36 – 1.44 (m, 1H), 1.12 – 1.17 (m, 1H), 1.09 (d, $J = 6.9$ Hz, 3H), 1.03 – 1.08 (m, 1H), 0.87 – 0.89 (m, 3H), 0.86 – 0.87 (m, 3H), 0.84 (t, $J = 7.5$ Hz, 3H), 0.79 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.08, 171.56, 170.15, 143.63, 0.79 (d, $J = 6.9$ Hz, 3H).

136.51, 129.61, 127.45, 61.47, 56.69, 52.15, 48.70, 38.12, 37.74, 25.10, 24.39, 21.49, 18.39, 15.40, 15.35, 11.48, 11.27. **HRMS-ESI**(m/z): [M+Na]⁺ calcd. for C₂₃H₃₇N₃O₆SNa, 506.2295; found, 506.2285. **IR** (KBr, cm⁻¹): ν 3453, 2972, 1742, 1634, 1532, 1164, 813, 672.

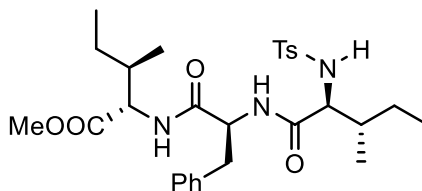
methyl tosyl-L-soleucyl-L-valyl-L-alloisoleucinate(SM-u)



SM-u

White solid. mp 240+ °C. **¹H NMR** (600 MHz, DMSO) δ 8.12 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.15 (t, *J* = 7.2 Hz, 1H), 4.01 – 4.08 (m, 1H), 3.66 (dd, *J* = 8.7, 7.4 Hz, 1H), 3.59 (s, 3H), 2.34 (s, 3H), 1.70 – 1.82 (m, 2H), 1.49 – 1.59 (m, 1H), 1.33 – 1.43 (m, 2H), 1.10 – 1.25 (m, 1H), 0.92 – 1.04 (m, 1H), 0.82 (d, *J* = 5.1 Hz, 3H), 0.80 – 0.81 (m, 3H), 0.75 (d, *J* = 6.9 Hz, 3H), 0.71 (d, *J* = 7.5 Hz, 3H), 0.68 – 0.70 (m, 3H), 0.65 (d, *J* = 6.6 Hz, 3H). **¹³C NMR** (150 MHz, DMSO) δ 172.20, 171.47, 170.49, 142.61, 138.89, 129.65, 127.08, 60.45, 57.63, 56.76, 51.93, 38.06, 36.36, 31.01, 25.12, 24.42, 21.39, 19.25, 18.54, 15.79, 15.59, 11.43, 11.31. **HRMS-ESI**(m/z): [M+Na]⁺ calcd. for C₂₅H₄₁N₃O₆SNa, 534.2608; found, 534.2601. **IR** (KBr, cm⁻¹): ν 3449, 2966, 1741, 1638, 1328, 1165, 819, 671.

methyl tosyl-L-soleucyl-L-phenylalanyl-L-alloisoleucinate(SM-v)

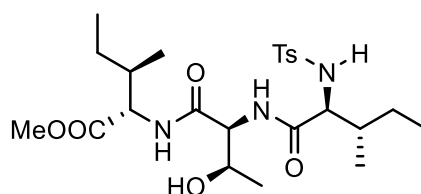


SM-v

White solid. mp 227.2-228.3 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.30 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 5.07 (d, *J* = 6.6 Hz,

1H), 4.65 (dd, $J = 15.0, 7.2$ Hz, 1H), 4.44 (dd, $J = 8.4, 5.7$ Hz, 1H), 3.70 (s, 3H), 3.47 (dd, $J = 6.6, 4.8$ Hz, 1H), 3.01 (dd, $J = 14.0, 6.9$ Hz, 1H), 2.82 (dd, $J = 14.0, 6.9$ Hz, 1H), 2.38 (s, 3H), 1.78 – 1.85 (m, 1H), 1.72 – 1.78 (m, 1H), 1.30– 1.39 (m, 1H), 1.01 – 1.13 (m, 2H), 0.85 (t, $J = 7.5$ Hz, 3H), 0.82 (d, $J = 6.9$ Hz, 3H), 0.78 – 0.80 (m, 1H), 0.69 (t, $J = 7.2$ Hz, 3H), 0.60 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.59, 170.22, 170.12, 144.19, 136.43, 135.49, 129.81, 129.14, 128.77, 127.63, 127.09, 61.71, 56.89, 54.39, 51.96, 38.08, 37.44, 25.18, 23.81, 21.54, 15.36, 15.30, 11.39. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{29}\text{H}_{41}\text{N}_3\text{O}_6\text{SNa}$, 582.2608; found, 582.2595. **IR** (KBr, cm^{-1}): ν 3460, 2968, 1741, 1639, 1333, 1166, 671.

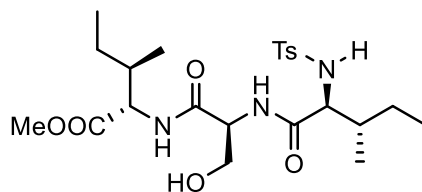
methyl tosyl-*L*-isoleucyl-*L*-allothreonyl-*L*-alloisoleucinate(SM-w)



SM-w

White solid. mp 185.7-187.6 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.75 (d, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.25 (s, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 5.83 (d, $J = 7.8$ Hz, 1H), 4.48 (dd, $J = 7.8, 5.4$ Hz, 1H), 4.36 (d, $J = 7.5$ Hz, 1H), 4.14 – 4.22 (m, 1H), 3.74 (s, 3H), 3.57 – 3.62 (m, 1H), 3.54 (s, 1H), 2.41 (s, 3H), 1.86 – 1.97 (m, 1H), 1.79 – 1.81 (m, 1H), 1.38 – 1.52 (m, 2H), 1.17 – 1.21 (m, 1H), 1.02 – 1.13 (m, 1H), 0.98 (d, $J = 6.3$ Hz, 3H), 0.89 – 0.92 (m, 6H), 0.79 – 0.83 (m, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.94, 171.39, 170.44, 143.81, 136.36, 129.70, 127.42, 66.58, 61.45, 56.96, 56.93, 52.16, 38.11, 37.23, 25.15, 24.31, 21.54, 17.87, 15.55, 15.38, 11.50, 11.27. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{40}\text{N}_3\text{O}_7\text{S}$, 514.2581; found, 514.2580. **IR** (KBr, cm^{-1}): ν 3328, 2970, 1741, 1641, 1383, 1164, 671.

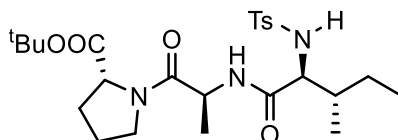
methyl tosyl-*L*-isoleucyl-*L*-seryl-*L*-alloisoleucinate(SM-x)



SM-x

White solid. mp 166.7-168.2 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.75 (d, $J = 8.1$ Hz, 2H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.27 (d, $J = 8.1$ Hz, 2H), 6.28 (d, $J = 8.4$ Hz, 1H), 4.55 – 4.60 (m, 1H), 4.52 (dd, $J = 8.1, 5.1$ Hz, 1H), 3.75 (s, 3H), 3.69 – 3.71 (m, 1H), 3.65 – 3.69 (m, 1H), 3.41 (s, 1H), 2.42 (s, 3H), 1.84 – 1.98 (m, 1H), 1.68 – 1.80 (m, 1H), 1.47 – 1.59 (m, 1H), 1.38 – 1.42 (m, 1H), 1.13 – 1.23 (m, 1H), 1.06 – 1.11 (m, 1H), 0.90 (d, $J = 6.9$ Hz, 3H), 0.86 – 0.90 (m, 3H), 0.78 – 0.82 (m, 6H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.17, 171.51, 170.47, 143.71, 136.55, 129.58, 127.38, 62.64, 61.41, 57.08, 54.09, 52.22, 37.91, 37.24, 25.09, 24.37, 21.46, 15.46, 15.30, 11.47, 11.14. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{37}\text{N}_3\text{O}_7\text{SNa}$, 522.2244; found, 522.2245. **IR** (KBr, cm^{-1}): ν 3270, 2966, 1728, 1641, 1333, 1168, 815, 666.

tert-butyl tosyl-L-isoleucyl-L-alanyl-L-prolinate (SM-y)

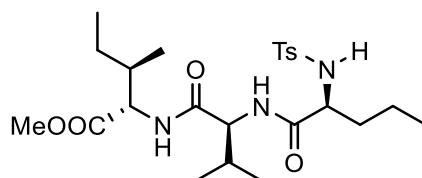


SM-y

White solid. mp 221.5-222.7 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 6.58 (d, $J = 7.2$ Hz, 1H), 5.45 (d, $J = 9.0$ Hz, 1H), 4.45 (p, $J = 6.9$ Hz, 1H), 4.38 (dd, $J = 8.1, 4.5$ Hz, 1H), 3.56 (dt, $J = 9.9, 6.7$ Hz, 1H), 3.50 (dt, $J = 9.9, 6.7$ Hz, 1H), 3.47 (dd, $J = 9.0, 5.7$ Hz, 1H), 2.37 (s, 3H), 2.17 – 2.23 (m, 1H), 2.00 – 2.05 (m, 1H), 1.89 – 1.99 (m, 2H), 1.66 – 1.71 (m, 1H), 1.46 – 1.52 (m, 1H), 1.45 (s, 9H), 1.06 – 1.17 (m, 1H), 1.01 (d, $J = 6.9$ Hz, 3H), 0.86 (d, $J = 6.9$ Hz, 3H), 0.84 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.66, 170.12, 169.18, 143.37, 136.83, 129.58, 127.44, 81.55, 61.32, 59.56, 46.82, 46.80, 38.64, 28.91, 27.93, 24.79, 24.32, 21.43, 17.75, 15.44, 11.25. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for

C₂₅H₃₉N₃O₆SNa, 532.2452; found, 532.2447. IR (KBr, cm⁻¹): ν 3547, 2971, 1737, 1632, 1456, 1327, 1168, 814, 681.

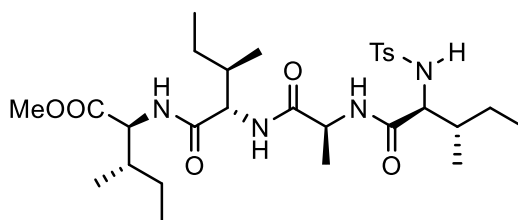
Methyl ((S)-2-((4-methylphenyl)sulfonamido) pentanoyl) -L-valyl-L-alloisoleucinate(SM-z)



SM-z

White solid. mp 205.8-207.6 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 1H), 5.75 (d, *J* = 7.5 Hz, 1H), 4.56 (dd, *J* = 8.4, 5.4 Hz, 1H), 4.28 (dd, *J* = 9.0, 6.6 Hz, 1H), 3.72 – 3.76 (m, 4H), 2.40 (s, 3H), 1.98 – 2.01 (m, 1H), 1.81 – 1.93 (m, 1H), 1.62 – 1.67 (m, 1H), 1.49 – 1.58 (m, 1H), 1.36 – 1.42 (m, 1H), 1.27 – 1.35 (m, 1H), 1.12 – 1.22 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.82 (d, *J* = 6.9 Hz, 3H), 0.76 – 0.79 (m, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 172.06, 171.10, 170.66, 143.67, 136.50, 129.70, 127.33, 58.57, 56.67, 56.60, 52.09, 37.58, 35.83, 30.78, 25.07, 21.49, 18.95, 18.43, 17.81, 15.40, 13.46, 11.41. HRMS-ESI(*m/z*): [M+Na]⁺ calcd. for C₂₄H₃₉N₃O₆SNa, 520.2452; found, 520.2449. IR (KBr, cm⁻¹): ν 3455, 2963, 1743, 1643, 1387, 1162, 700.

methyl tosyl-L-isoleucyl-L-alanyl-L-alloisoleucyl-L-isoleucinate(SM-aa)

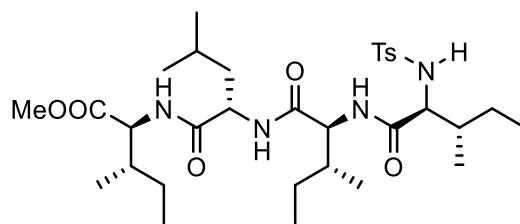


SM-aa

White gum. ¹H NMR (600 MHz, DMSO) δ 8.31 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.36 (t, *J* = 8.4 Hz, 1H), 4.17 (m, 2H), 3.61 (s, 3H), 3.59 (m, 1H), 2.35 (s, 3H), 1.76 – 1.85 (m, 1H), 1.71 – 1.75 (m, 1H), 1.55 – 1.58 (m, 1H), 1.35 – 1.48 (m, 3H), 1.15 – 1.30 (m, 2H), 1.09 – 1.12 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.81

– 0.85 (m, 9H), 0.80 (t, $J = 7.5$ Hz, 3H), 0.69 – 0.73 (m, 6H). ^{13}C NMR (150 MHz, DMSO) δ 172.17, 172.00, 171.88, 169.96, 142.81, 138.66, 129.62, 127.03, 61.23, 57.03, 56.50, 51.92, 48.17, 37.30, 37.20, 36.44, 33.81, 25.41, 24.72, 21.38, 19.68, 15.83, 15.52, 15.39, 11.59, 11.21, 11.02. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{29}\text{H}_{48}\text{N}_4\text{O}_7\text{SNa}$, 619.3136; found, 619.3126. IR (KBr, cm^{-1}): ν 3293, 3072, 2930, 2851, 1729, 1645, 1313, 1162, 815, 670.

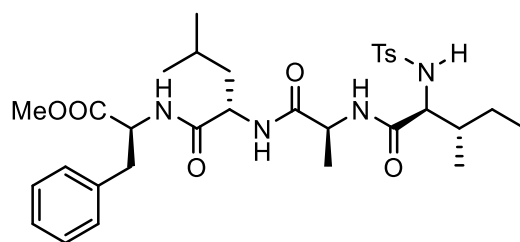
methyl tosyl-*L*-isoleucyl-*L*-alloisoleucyl-*L*-leucyl-*L*-isoleucinate(SM-ab)



SM-ab

White gum. ^1H NMR (600 MHz, DMSO) δ 7.97 (d, $J = 8.4$ Hz, 1H), 7.90 – 7.96 (m, 2H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 9.3$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 4.34 – 4.38 (m, 1H), 4.16 – 4.19 (m, 1H), 3.95 (t, $J = 8.4$ Hz, 1H), 3.66 (dd, $J = 9.3, 7.0$ Hz, 1H), 3.58 (s, 3H), 2.35 (s, 3H), 1.71 – 1.80 (m, 1H), 1.49 – 1.61 (m, 2H), 1.43 – 1.50 (m, 1H), 1.13 – 1.43 (m, 4H), 1.08 – 1.27 (m, 2H), 0.93 – 1.06 (m, 1H), 0.85 (d, $J = 6.6$ Hz, 3H), 0.80 – 0.83 (m, 7H), 0.79 (d, $J = 6.6$ Hz, 3H), 0.74 (d, $J = 6.9$ Hz, 3H), 0.69 – 0.72 (m, 6H), 0.66 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, DMSO) δ 172.49, 172.18, 170.90, 170.32, 142.54, 138.94, 129.61, 127.04, 60.33, 57.05, 56.65, 52.04, 51.13, 41.27, 39.58, 38.19, 36.90, 36.70, 25.08, 24.72, 24.41, 23.53, 21.94, 21.42, 15.76, 15.53, 15.38, 11.50, 11.41, 11.36. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{54}\text{N}_4\text{O}_7\text{SNa}$, 661.3605; found, 661.3600. IR (KBr, cm^{-1}): ν 3279, 2960, 1744, 1635, 1326, 1162, 816, 665.

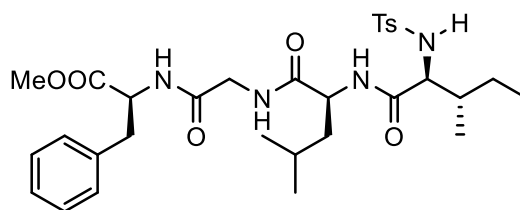
methyl tosyl-*L*-isoleucyl-*L*-alanyl-*L*-leucyl-*L*-phenylalaninate(SM-ac)



SM-ac

White gum. $^1\text{H NMR}$ (600 MHz, DMSO) δ 8.24 (d, $J = 7.5$ Hz, 1H), 7.98 (d, $J = 7.5$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 9.3$ Hz, 1H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.26 (t, $J = 12.0$ Hz, 2H), 7.21 – 7.22 (m, 1H), 7.17 – 7.21 (m, 2H), 4.41 – 4.50 (m, 1H), 4.22 – 4.28 (m, 1H), 3.91 (p, $J = 7.2$ Hz, 1H), 3.55 (s, 3H), 3.52 (dd, $J = 9.3, 7.8$ Hz, 1H), 3.00 (dd, $J = 13.8, 6.0$ Hz, 1H), 2.92 (dd, $J = 13.8, 8.7$ Hz, 1H), 2.36 (s, 3H), 1.49 – 1.54 (m, 2H), 1.43 – 1.45 (m, 1H), 1.30 – 1.37 (m, 2H), 1.01 – 1.08 (m, 1H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.84 (d, $J = 6.6$ Hz, 3H), 0.79 (d, $J = 6.6$ Hz, 3H), 0.74 (t, $J = 7.5$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, DMSO) δ 172.35, 172.20, 171.85, 170.05, 142.70, 138.73, 137.49, 129.55, 129.48, 128.67, 127.19, 126.98, 60.52, 53.82, 52.24, 51.11, 48.12, 41.43, 37.54, 36.97, 24.66, 24.40, 23.40, 22.13, 21.41, 17.99, 15.38, 11.08. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{46}\text{N}_4\text{O}_7\text{SNa}$, 653.2979; found, 653.2976. **IR** (KBr, cm^{-1}): ν 3279, 2960, 1744, 1635, 1162, 816, 665.

methyl tosyl-*L*-isoleucyl-*L*-leucylglycyl-*L*-phenylalaninate(SM-ad)

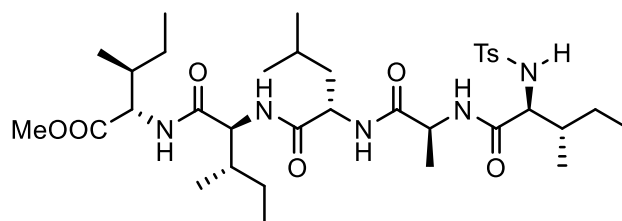


SM-ad

White solid. mp 163.5-164.1 °C. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 3H), 7.23 – 7.25 (m, 1H), 7.15 – 7.23 (m, 2H), 7.12 (d, $J = 6.9$ Hz, 2H), 6.87 (d, $J = 7.8$ Hz, 2H), 5.38 (d, $J = 6.3$ Hz, 1H), 4.85 (dd, $J = 14.1, 6.3$ Hz, 1H), 4.36 – 4.39 (m, 1H), 3.99 (dd, $J = 16.8, 5.7$ Hz, 1H), 3.87 (dd, $J = 16.8, 5.7$ Hz, 1H), 3.68 (s, 3H), 3.53 (t, $J = 6.0$ Hz, 1H), 3.14 (dd, $J = 13.8, 6.0$ Hz, 1H), 3.07 (dd, J

= 13.8, 6.0 Hz, 1H), 2.43 (s, 3H), 1.78 – 1.82 (m, 1H), 1.71 – 1.73 (m, 1H), 1.44 – 1.52 (m, 2H), 1.37 – 1.43 (m, 1H), 0.99 – 1.07 (m, 1H), 0.92 (d, $J = 6.3$ Hz, 3H), 0.87 (d, $J = 6.3$ Hz, 3H), 0.78 (t, $J = 7.5$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.32, 171.96, 170.65, 168.54, 143.04, 137.28, 135.94, 129.48, 129.24, 128.44, 127.20, 126.87, 99.95, 61.16, 53.64, 52.40, 51.36, 42.87, 41.86, 38.38, 38.04, 24.63, 22.77, 22.32, 21.55, 15.31, 11.27. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{31}\text{H}_{44}\text{N}_4\text{O}_7\text{SNa}$, 639.2823; found, 639.2809. **IR** (KBr, cm^{-1}): ν 3299, 2959, 1743, 1637, 1329, 1163, 817, 669.

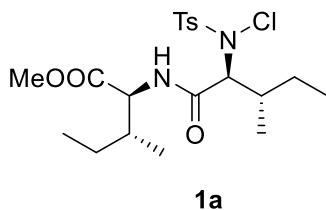
methyl tosyl-*L*-isoleucyl-*L*-alanyl-*L*-leucyl-*L*-isoleucyl-*L*-isoleucinate(SM-ae)



SM-ae

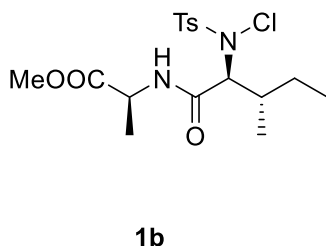
White gum. ^1H NMR (600 MHz, DMSO) δ 8.13 (d, $J = 7.5$ Hz, 1H), 8.01 (d, $J = 7.2$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 7.8$ Hz, 3H), 7.30 (d, $J = 7.8$ Hz, 2H), 4.23 – 4.27(m, 2H), 4.16 (t, $J = 6.9$ Hz, 1H), 3.88 – 4.00 (m, 1H), 3.59 (s, 3H), 3.52 (t, $J = 6.6$ Hz, 1H), 2.36 (s, 3H), 1.72 – 1.83 (m, 1H), 1.65 – 1.70 (m, 1H), 1.51 – 1.58 (m, 2H), 1.31 – 1.43 (m, 4H), 1.13 – 1.21 (m, 1H), 1.00 – 1.08 (m, 3H), 0.93 (d, $J = 6.9$ Hz, 3H), 0.76 – 0.85 (m, 18H), 0.72 – 0.76 (m, 6H). ^{13}C NMR (150 MHz, DMSO) δ 172.12, 172.06, 171.87, 171.63, 170.03, 142.70, 138.73, 129.54, 127.21, 60.54, 56.80, 56.67, 51.96, 51.46, 48.16, 41.10, 37.57, 37.37, 36.47, 25.19, 24.68, 24.51, 23.45, 22.10, 21.41, 18.10, 15.81, 15.53, 15.42, 11.50, 11.38, 11.08. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{35}\text{H}_{59}\text{N}_5\text{O}_8\text{SNa}$, 732.3977; found, 732.3963. **IR** (KBr, cm^{-1}): ν 3325, 2930, 1745, 1385, 1161, 814, 665.

methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alloisoleucinate(1a)



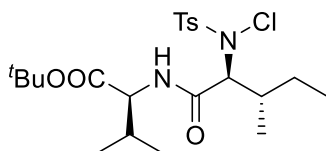
Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 6.56 (d, $J = 8.0$ Hz, 1H), 4.49 (dd, $J = 8.0, 4.5$ Hz, 1H), 4.35 (d, $J = 9.6$ Hz, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 2.09–2.16 (m, 1H), 1.89–1.95 (m, 1H), 1.51–1.57 (m, 1H), 1.39–1.48 (m, 1H), 1.21–1.27 (m, 1H), 1.14–1.19 (m, 1H), 0.96 (d, $J = 9.0$ Hz, 3H), 0.94 (d, $J = 9.0$ Hz, 3H), 0.93 (t, $J = 7.4$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.70, 167.02, 145.21, 132.75, 129.57, 128.90, 66.91, 56.37, 51.95, 37.74, 33.75, 25.13, 24.89, 21.59, 15.26, 15.03, 11.53, 10.21. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{31}\text{ClN}_2\text{NaO}_5\text{S}$, 469.1534; found, 469.1539. **IR** (KBr, cm^{-1}): ν 3302, 3256, 2931, 1736, 1650, 1357, 850, 668.

methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alaninate(1b)



Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.52 (d, $J = 6.6$ Hz, 1H), 4.42 (quint, $J = 7.2$ Hz, 1H), 4.28 (d, $J = 9.9$ Hz, 1H), 3.74 (s, 3H), 2.45 (s, 3H), 2.13 (dd, $J = 15.0, 6.6$ Hz, 1H), 1.63–1.55 (m, 1H), 1.39 (d, $J = 7.2$ Hz, 3H), 1.24–1.18 (m, 1H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.84, 166.66, 145.26, 132.65, 129.58, 129.03, 66.91, 52.39, 48.02, 33.64, 24.83, 21.62, 17.95, 14.93, 10.09. **HRMS-ESI** (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{25}\text{ClN}_2\text{NaO}_5\text{S}$, 427.1065; found, 427.1067. **IR** (KBr, cm^{-1}): ν 3316, 2966, 1743, 1535, 1162, 899, 666.

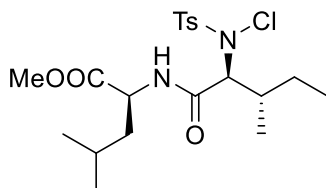
***tert*-butyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-valinate(1c)**



1c

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.52 (d, $J = 8.1$ Hz, 1H), 4.38–4.32 (m, 2H), 2.45 (s, 3H), 2.16–2.21 (m, 1H), 2.11–2.15 (m, 1H), 1.51–1.54 (m, 1H), 1.47 (s, 9H), 1.20–1.11 (m, 1H), 0.98 (d, $J = 6.9$ Hz, 3H), 0.96 (d, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 7.2$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.48, 167.08, 145.22, 132.93, 129.67, 128.95, 82.03, 66.98, 57.71, 33.75, 31.37, 28.02, 25.00, 21.68, 18.65, 17.75, 15.21, 10.35. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{35}\text{ClN}_2\text{NaO}_5\text{S}$, 497.1847; found, 497.1845. **IR** (KBr, cm^{-1}): ν 3315, 2969, 1714, 1545, 1450, 1376, 1165, 880, 668.

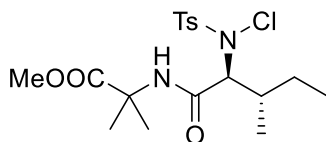
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-leucinate(1d)



1d

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 6.37 (d, $J = 7.5$ Hz, 1H), 4.51 (dt, $J = 7.5, 6.0$ Hz, 1H), 4.32 (d, $J = 9.6$ Hz, 1H), 3.72 (s, 3H), 2.45 (s, 3H), 2.10–2.17 (m, 1H), 1.69–1.75 (m, 1H), 1.60–1.65 (m, 1H), 1.52–1.60 (m, 2H), 1.14–1.20 (m, 1H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.85, 167.05, 145.26, 132.83, 129.63, 128.95, 66.72, 52.17, 50.82, 41.30, 33.65, 24.89, 24.59, 22.69, 21.89, 21.64, 15.04, 10.22. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{31}\text{ClN}_2\text{NaO}_5\text{S}$, 469.1534; found, 469.1539. **IR** (KBr, cm^{-1}): ν 3375, 2962, 1744, 1668, 1533, 1164, 846, 666.

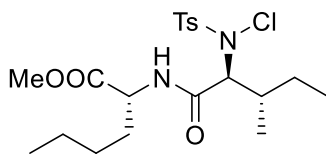
Methyl 2-2-((*N*-chloro-4-methylphenyl)sulfonamido)-3-methylpentanamido)-2-methylpropanoate(1e)



1e

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 6.58 (br s, 1H), 4.25 (d, $J = 9.6$ Hz, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 2.07–2.16 (m, 1H), 1.53–1.57 (m, 1H), 1.51 (s, 3H), 1.48 (s, 3H), 1.14–1.21 (m, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 174.51, 166.23, 145.25, 132.79, 129.66, 128.93, 66.84, 56.59, 52.48, 33.56, 24.81, 24.48, 23.93, 21.60, 14.82, 10.19. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{27}\text{ClN}_2\text{NaO}_5\text{S}$, 441.1221; found, 441.1215. **IR** (KBr, cm^{-1}): ν 3438, 2967, 2878, 1741, 1361, 1166, 882, 668.

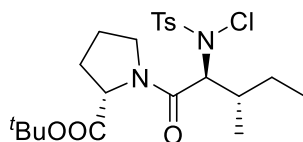
methyl(*R*)-2-((2*S*,3*S*)-2-((*N*-chloro-4-methylphenyl)sulfonamido)-3-methylpentanamido)hexanoate(1f)



1f

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.43 (d, $J = 7.2$ Hz, 1H), 4.41 (dt, $J = 7.2, 6.6$ Hz, 1H), 4.30 (d, $J = 9.5$ Hz, 1H), 3.77 (s, 3H), 2.45 (s, 3H), 2.04–2.11 (m, 1H), 1.69–1.75 (m, 1H), 1.56–1.64 (m, 2H), 1.24–1.30 (m, 2H), 1.13–1.24 (m, 3H), 0.96 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.87 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.34, 166.93, 145.20, 132.49, 129.55, 129.12, 67.43, 52.33, 52.16, 34.16, 31.71, 27.14, 25.09, 22.20, 21.68, 14.93, 13.79, 10.28. **HRMS-ESI**(m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{20}\text{H}_{31}\text{ClN}_2\text{KO}_5\text{S}$, 485.1274; found, 485.1272. **IR** (KBr, cm^{-1}): ν 3316, 2961, 2932, 1744, 1664, 1531, 1168, 849, 666.

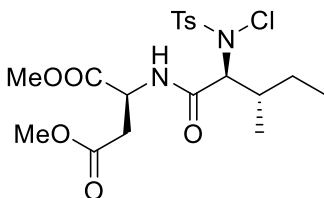
***tert*-butyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-prolinate(1g)**



1g

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 4.59 (d, $J = 10.5$ Hz, 1H), 4.16 (dd, $J = 8.4, 3.9$ Hz, 1H), 4.02 (dt, $J = 9.6, 7.2$ Hz, 1H), 3.66 (ddd, $J = 9.6, 7.8, 4.2$ Hz, 1H), 2.45 (s, 3H), 2.20–2.25 (m, 1H), 2.13–2.17 (m, 1H), 2.06–2.10 (m, 1H), 2.01–2.06 (m, 1H), 1.92–1.97 (m, 1H), 1.62–1.69 (m, 1H), 1.43 (s, 9H), 1.19–1.26 (m, 1H), 1.04 (d, $J = 6.9$ Hz, 3H), 0.94 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.97, 166.86, 145.10, 132.97, 129.46, 128.71, 81.35, 61.80, 59.70, 47.02, 34.73, 29.02, 27.95, 24.90, 24.67, 21.69, 14.17, 10.01. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{22}\text{H}_{33}\text{ClN}_2\text{NaO}_5\text{S}$, 495.1691; found, 495.1686. **IR** (KBr, cm^{-1}): ν 3440, 2971, 2933, 1736, 1636, 1367, 1161, 818, 665.

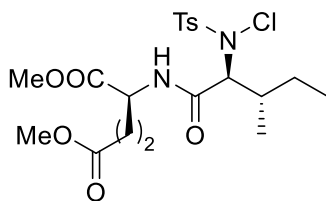
dimethyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-aspartate(1h)



1h

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 1H), 4.79 (dt, $J = 8.1, 3.9$ Hz, 1H), 4.29 (d, $J = 9.9$ Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.02 (dd, $J = 17.4, 3.9$ Hz, 1H), 2.88 (dd, $J = 17.4, 3.9$ Hz, 1H), 2.45 (s, 3H), 2.11 – 2.19 (m, 1H), 1.51 – 1.61 (m, 1H), 1.14 – 1.23 (m, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.14, 170.59, 166.88, 145.23, 132.46, 129.50, 128.95, 66.33, 52.63, 51.95, 48.12, 35.50, 33.31, 24.56, 21.54, 14.66, 9.92. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{27}\text{ClN}_2\text{NaO}_7\text{S}$, 485.1120; found, 485.1124. **IR** (KBr, cm^{-1}): ν 3263, 2963, 2928, 1738, 1650, 1359, 1164, 858, 616.

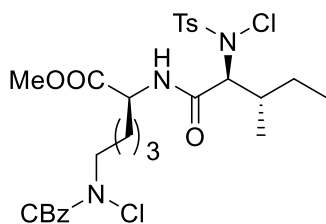
dimethyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-glutamate(1i)



1i

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 6.77 (d, $J = 7.2$ Hz, 1H), 4.49 (dt, $J = 7.2, 5.1$ Hz, 1H), 4.32 (d, $J = 9.9$ Hz, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 2.52–2.39 (m, 5H), 2.17–2.24 (m, 1H), 2.10–2.15 (m, 1H), 1.98–2.05 (m, 1H), 1.54–1.60 (m, 1H), 1.15–1.22 (m, 1H), 0.96 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.05, 171.52, 167.18, 145.16, 132.46, 129.45, 128.80, 66.32, 52.22, 51.58, 51.46, 33.46, 29.59, 26.72, 24.62, 21.43, 14.69, 9.92. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{29}\text{ClN}_2\text{NaO}_7\text{S}$, 499.1276; found, 499.1288. **IR** (KBr, cm^{-1}): ν 3315, 2962, 1740, 1667, 1346, 1167, 891, 667.

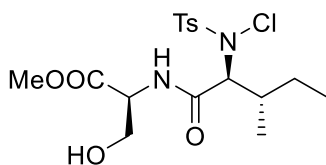
methyl N^6 -((benzyloxy)carbonyl)- N^2 -(N -chloro- N -tosyl- L -isoleucyl)- L -lysinate(1j**)**



1j

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 4H), 7.33 (d, $J = 7.7$ Hz, 3H), 6.56 (d, $J = 7.5$ Hz, 1H), 5.18 (s, 2H), 4.47 (dt, $J = 7.5, 5.1$ Hz, 1H), 4.31 (d, $J = 9.6$ Hz, 1H), 3.72 (s, 3H), 3.62 (dd, $J = 9.8, 6.4$ Hz, 2H), 2.44 (s, 3H), 2.09–2.17 (m, 1H), 1.82–1.92 (m, 1H), 1.69–1.76 (m, 2H), 1.63–1.67 (m, 1H), 1.50–1.57 (m, 1H), 1.39–1.47 (m, 1H), 1.31–1.38 (m, 1H), 1.17–1.21 (m, 1H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.09, 166.93, 155.74, 145.24, 135.57, 132.62, 129.57, 128.96, 128.49, 128.24, 127.90, 68.87, 66.63, 53.77, 52.30, 51.89, 33.51, 31.59, 26.65, 24.76, 21.61, 21.50, 14.98, 10.10. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{28}\text{H}_{37}\text{Cl}_2\text{N}_3\text{NaO}_7\text{S}$, 652.1621; found, 652.1630. **IR** (KBr, cm^{-1}): ν 3310, 1738, 1535, 1398, 1167, 815, 667.

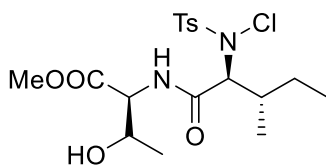
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-serinate(1k)



1K

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 7.2$ Hz, 1H), 4.65 (dt, $J = 7.2, 5.1$ Hz, 1H), 4.38 (d, $J = 10.3$ Hz, 1H), 4.07 (d, $J = 10.0$ Hz, 1H), 3.97 (d, $J = 10.8$ Hz, 1H), 3.81 (s, 3H), 3.21 (br s, 1H), 2.46 (s, 3H), 2.18–2.27 (m, 1H), 1.51–1.58 (m, 1H), 1.17–1.22 (m, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.92 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.36, 166.63, 145.73, 131.94, 129.73, 129.07, 65.65, 62.41, 54.95, 52.67, 32.39, 24.19, 21.64, 14.78, 9.77. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{25}\text{ClN}_2\text{NaO}_6\text{S}$, 443.1014; found, 443.1029. **IR** (KBr, cm^{-1}): ν 3305, 2964, 1744, 1653, 1161, 815, 670.

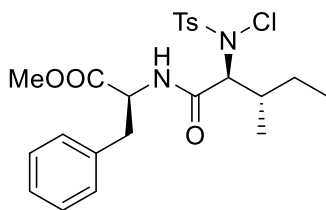
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-allothreoninate(1l)



1l

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 1H), 4.58 (dd, $J = 8.4, 2.1$ Hz, 1H), 4.47 (d, $J = 10.2$ Hz, 1H), 4.31–4.39 (m, 1H), 3.77 (s, 3H), 3.05 (br s, 1H), 2.45 (s, 3H), 2.15–2.25 (m, 1H), 1.49–1.59 (m, 1H), 1.33 (d, $J = 6.3$ Hz, 3H), 1.14–1.21 (m, 1H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.89, 167.63, 145.38, 132.40, 129.62, 128.87, 68.40, 65.80, 57.38, 52.43, 32.87, 24.40, 21.55, 20.08, 14.77, 9.89. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{18}\text{H}_{28}\text{ClN}_2\text{O}_6\text{S}$, 435.1351; found, 435.1356. **IR** (KBr, cm^{-1}): ν 3337, 3239, 2964, 2877, 1734, 1659, 1539, 1158, 860, 668.

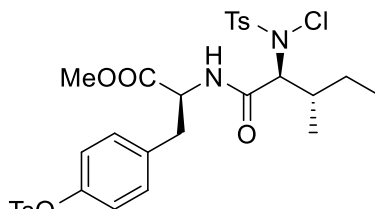
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-phenylalaninate(1m)



1m

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 2H), 6.44 (d, $J = 7.5$ Hz, 1H), 4.75 (dt, $J = 7.5, 5.7$ Hz, 1H), 4.27 (d, $J = 9.6$ Hz, 1H), 3.67 (s, 3H), 3.15 (dd, $J = 13.8, 5.7$ Hz, 1H), 3.06 (dd, $J = 13.8, 5.7$ Hz, 1H), 2.45 (s, 3H), 2.02–2.12 (m, 1H), 1.58–1.48 (m, 1H), 1.12–1.18 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.35, 167.07, 145.25, 135.52, 132.55, 129.58, 129.30, 129.04, 128.58, 127.14, 66.85, 53.07, 52.14, 37.87, 33.88, 24.95, 21.64, 14.92, 10.16. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{30}\text{ClN}_2\text{O}_5\text{S}$, 503.1378; found, 503.1381. **IR** (KBr, cm^{-1}): ν 3476, 3415, 1776, 1399, 1162, 667.

methyl(*S*)-2-((2*S*,3*S*)-2-((*N*-chloro-4-methylphenyl)sulfonamido)-3-methylpentanamido)-3-(4-(tosyloxy)phenyl)propanoate(1n)

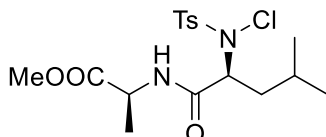


1n

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78 (d, $J = 7.8$ Hz, 2H), 7.66 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.90 (d, $J = 8.1$ Hz, 2H), 6.48 (d, $J = 7.2$ Hz, 1H), 4.76 (dt, $J = 7.2, 5.7$ Hz, 1H), 4.27 (d, $J = 9.3$ Hz, 1H), 3.66 (s, 3H), 3.11 (dd, $J = 13.5, 5.7$ Hz, 1H), 3.05 (dd, $J = 13.5, 5.7$ Hz, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 2.05–2.13 (m, 1H), 1.45–1.55 (m, 1H), 1.08–1.20 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.14, 167.10, 148.68, 145.42, 145.26, 134.81, 132.49, 132.24, 130.53, 129.68, 129.66, 128.99, 128.44, 122.48, 66.66, 52.99, 52.25, 37.29, 33.74, 24.91, 21.65, 14.99,

10.19. **HRMS-ESI(m/z):** $[M+Na]^+$ calcd. for $C_{30}H_{35}ClN_2NaO_8S_2$, 673.1416; found, 673.1406. **IR** (KBr, cm^{-1}): ν 3321, 3206, 1714, 1628, 1374, 1158, 674.

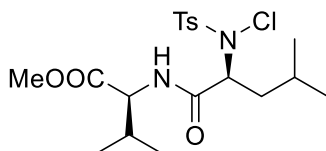
methyl *N*-chloro-*N*-tosyl-*L*-leucyl-*L*-alaninate(1o)



1o

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 6.6$ Hz, 1H), 4.80 (dd, $J = 7.8, 6.3$ Hz, 1H), 4.50 (p, $J = 7.2$ Hz, 1H), 3.76 (s, 3H), 2.47 (s, 3H), 1.84 (ddd, $J = 14.1, 8.1, 6.3$ Hz, 1H), 1.64–1.71 (m, 1H), 1.56 (ddd, $J = 14.1, 7.8, 5.7$ Hz, 1H), 1.40 (d, $J = 7.2$ Hz, 3H), 0.94 (d, $J = 5.4$ Hz, 3H), 0.93 (d, $J = 5.4$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.76, 167.59, 145.55, 132.41, 129.75, 128.99, 62.03, 52.40, 48.25, 37.2, 24.52, 22.65, 21.62, 21.58, 18.00. **HRMS-ESI(m/z):** $[M+Na]^+$ calcd. for $C_{17}H_{25}ClN_2NaO_5S$, 427.1065; found, 427.1059. **IR** (KBr, cm^{-1}): ν 3325, 3316, 1745, 1569, 1360, 1124, 845, 664.

methyl *N*-chloro-*N*-tosyl-*L*-leucyl-*L*-valinate(1p)

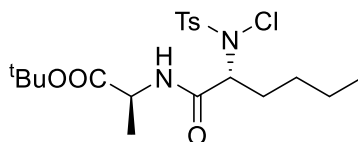


1p

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 4.87 (dd, $J = 7.5, 6.3$ Hz, 1H), 4.51 (dd, $J = 8.4, 4.8$ Hz, 1H), 3.76 (s, 3H), 2.48 (s, 3H), 2.17–2.22 (m, 1H), 1.89 (ddd, $J = 14.3, 8.1, 6.3$ Hz, 1H), 1.63–1.90 (m, 1H), 1.57 (ddd, $J = 14.3, 7.5, 6.2$ Hz, 1H), 0.96 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.90 (d, $J = 6.9$ Hz, 3H). **^{13}C NMR** (150- MHz, $CDCl_3$) δ 171.81, 168.09, 145.61, 132.59, 129.85, 128.99, 62.24, 57.35, 52.15, 37.24, 31.19, 24.58, 22.76, 21.69, 21.59, 18.92, 17.48. **HRMS-ESI(m/z):**

[M+Na]⁺ calcd. for C₁₉H₂₉ClN₂NaO₅S, 455.1378; found, 455.1368. **IR** (KBr, cm⁻¹): ν 3320, 2961, 1734, 1684, 1356, 1167, 815, 665.

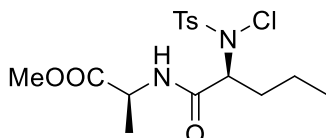
tert-butyl((R)-2-((N-chloro-4-methylphenyl)sulfonamido)hexanoyl)-L-alaninate(1q)



1q

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 6.9 Hz, 1H), 4.62 (t, *J* = 6.9 Hz, 1H), 4.38 (p, *J* = 7.2 Hz, 1H), 2.47 (s, 3H), 1.97–2.02 (m, 1H), 1.49–1.53 (m, 1H), 1.47 (s, 9H), 1.35 (d, *J* = 7.2 Hz, 3H), 1.27–1.33 (m, 2H), 1.17–1.25 (m, 2H), 0.83 (t, *J* = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 171.25, 167.54, 145.48, 132.40, 129.71, 128.85, 81.90, 64.52, 48.83, 28.53, 27.80, 22.07, 21.56, 18.18, 13.65. **HRMS-ESI**(*m/z*): [M+Na]⁺ calcd. for C₂₀H₃₁ClN₂NaO₅S, 469.1534; found, 469.1526. **IR** (KBr, cm⁻¹): ν 3343, 3256, 1736, 1653, 1372, 1162, 818, 681.

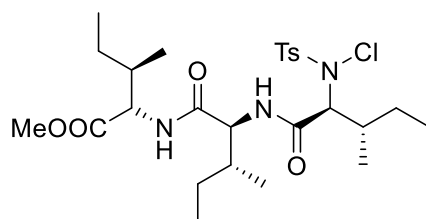
methyl((S)-2-((N-chloro-4-methylphenyl)sulfonamido)pentanoyl)-L-alaninate(1r)



1r

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 6.6 Hz, 1H), 4.68 (t, *J* = 6.9 Hz, 1H), 4.52 (p, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 2.48 (s, 3H), 1.94–2.00 (m, 1H), 1.46–1.56 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H), 1.31–1.40 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 172.79, 167.58, 145.62, 132.44, 129.82, 128.99, 63.84, 52.46, 48.28, 30.56, 21.67, 19.58, 18.08, 13.55. **HRMS-ESI**(*m/z*): [M+Na]⁺ calcd. for C₁₆H₂₃ClN₂NaO₅S, 413.0908; found, 413.0905. **IR** (KBr, cm⁻¹): ν 3258, 2959, 2874, 1734, 1655, 1379, 1162, 882, 666.

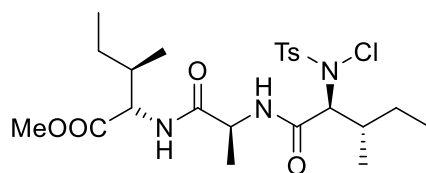
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alloisoleucyl-*L*-alloisoleucinate(1s)



1s

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 6.60 (d, $J = 8.1$ Hz, 1H), 6.28 (d, $J = 8.4$ Hz, 1H), 4.58 (dd, $J = 8.4, 4.8$ Hz, 1H), 4.32 (dd, $J = 8.1, 4.8$ Hz, 1H), 4.31 (d, $J = 9.3$ Hz, 1H), 3.74 (s, 3H), 2.46 (s, 3H), 2.11–2.19 (m, 1H), 1.87–1.97 (m, 2H), 1.54–1.60 (m, 1H), 1.47–1.53 (m, 1H), 1.40–1.45 (m, 1H), 1.23–1.30 (m, 1H), 1.16–1.23 (m, 1H), 1.09–1.15 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.91 (t, $J = 7.8$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.95, 170.48, 167.51, 145.32, 132.87, 129.72, 128.94, 66.68, 57.81, 56.50, 52.06, 37.66, 37.12, 33.84, 25.09, 24.99, 24.86, 21.69, 15.42, 15.28, 15.14, 11.49, 11.31, 10.42. **HRMS-ESI**(m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{26}\text{H}_{42}\text{ClN}_3\text{KO}_6\text{S}$, 598.2114; found, 598.2106. **IR** (KBr, cm^{-1}): ν 3287, 2966, 2932, 1741, 1639, 1382, 1162, 816, 670.

methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alanyl-*L*-alloisoleucinate(1t)

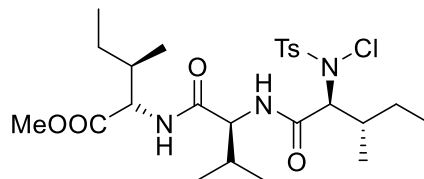


1t

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.8$ Hz, 2H), 7.35 (d, $J = 7.8$ Hz, 2H), 6.82 (d, $J = 8.1$ Hz, 1H), 6.76 (d, $J = 6.9$ Hz, 1H), 4.49–4.58 (m, 2H), 4.27 (d, $J = 9.6$ Hz, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 2.15–2.22 (m, 1H), 1.83–1.95 (m, 1H), 1.51–1.61 (m, 1H), 1.41–1.47 (m, 1H), 1.38 (d, $J = 6.6$ Hz, 3H), 1.15–1.19 (m, 2H), 0.87–

0.95 (m, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.99, 171.62, 167.24, 145.31, 132.58, 129.63, 128.96, 66.38, 56.62, 52.01, 48.79, 37.59, 33.48, 25.02, 24.72, 21.62, 17.61, 15.33, 14.91, 11.42, 10.12. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{36}\text{ClN}_3\text{NaO}_6\text{S}$, 540.1906; found, 540.1899. **IR** (KBr, cm^{-1}): ν 3277, 3208, 2966, 1741, 1636, 1536, 1384, 1162, 812, 671.

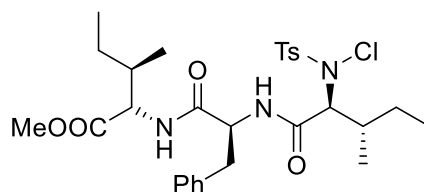
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-valyl-*L*-alloisoleucinate(1u)



1u

White foam. ^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 4.58 (dd, $J = 8.4, 5.1$ Hz, 1H), 4.31–4.38 (m, 2H), 3.73 (s, 3H), 2.46 (s, 3H), 2.11–2.21 (m, 2H), 1.86–1.93 (m, 1H), 1.49–1.53 (m, 1H), 1.39–1.45 (m, 1H), 1.18–1.26 (m, 1H), 1.11–1.17 (m, 1H), 1.01 (dd, $J = 6.6, 3.6$ Hz, 6H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.89 (dt, $J = 9.9, 6.6$ Hz, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.99, 170.69, 167.65, 145.24, 132.86, 129.66, 128.88, 66.41, 58.60, 56.48, 52.00, 37.48, 33.78, 30.87, 25.00, 24.90, 21.63, 19.04, 18.13, 15.37, 15.03, 11.40, 10.37. **HRMS-ESI**(m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{25}\text{H}_{40}\text{ClN}_3\text{KO}_6\text{S}$, 584.1958; found, 584.1958. **IR** (KBr, cm^{-1}): ν 3294, 2965, 1742, 1646, 1379, 1165, 845, 667.

methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-phenylalanyl-*L*-alloisoleucinate(1v)

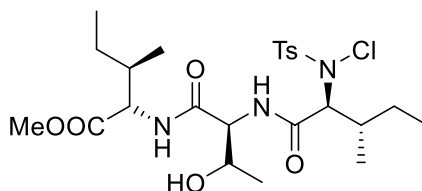


1v

White foam. ^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 7.9$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.29 (s, 4H), 7.22 (d, $J = 3.3$ Hz, 1H), 6.77 (d, $J = 7.2$ Hz, 1H), 6.35 (d, $J =$

7.8 Hz, 1H), 4.69 (dt, $J = 7.2, 5.7$ Hz, 1H), 4.45 (dd, $J = 7.8, 5.7$ Hz, 1H), 4.28 (d, $J = 9.0$ Hz, 1H), 3.67 (s, 3H), 3.15 (dd, $J = 13.6, 5.7$ Hz, 1H), 3.02 (dd, $J = 13.6, 5.7$ Hz, 1H), 2.43 (s, 3H), 2.04–2.17 (m, 1H), 1.73–1.86 (m, 1H), 1.51–1.56 (m, 1H), 1.29–1.40 (m, 1H), 1.11–1.17 (m, 1H), 1.04–1.08 (m, 1H), 0.83–0.91 (m, 9H), 0.80 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.34, 170.04, 167.42, 145.31, 136.31, 132.40, 129.63, 129.37, 128.97, 128.56, 126.89, 66.61, 56.66, 54.53, 51.83, 37.69, 37.42, 33.90, 24.99, 24.93, 21.57, 15.18, 14.84, 11.31, 10.26. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{29}\text{H}_{41}\text{ClN}_3\text{O}_6\text{S}$, 594.2399; found, 594.2389. **IR** (KBr, cm^{-1}): ν 3306, 2966, 2934, 1741, 1651, 1355, 1168, 846, 677.

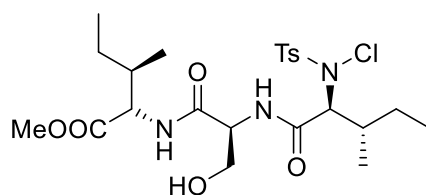
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-allothreonyl-*L*-alloisoleucinate(1w)



1w

White foam. ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 1H), 4.52 (dd, $J = 8.4, 5.1$ Hz, 1H), 4.47 (dd, $J = 7.2, 3.0$ Hz, 1H), 4.36 (d, $J = 9.6$ Hz, 1H), 4.31–4.34 (m, 1H), 3.74 (s, 3H), 3.70 (s, 1H), 2.46 (s, 3H), 2.12–2.20 (m, 1H), 1.88–1.93 (m, 1H), 1.52–1.56 (m, 1H), 1.41–1.45 (m, 1H), 1.24 (d, $J = 6.6$ Hz, 3H), 1.15–1.22 (m, 2H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.88, 170.34, 168.32, 145.45, 132.48, 129.72, 129.06, 66.79, 66.43, 56.98, 56.80, 52.12, 37.31, 33.74, 25.09, 24.85, 21.70, 17.85, 15.56, 15.06, 11.49, 10.21. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{24}\text{H}_{38}\text{ClN}_3\text{NaO}_7\text{S}$, 570.2011; found, 570.2013. **IR** (KBr, cm^{-1}): ν 3301, 2965, 2933, 1739, 1648, 1381, 1163, 846, 668.

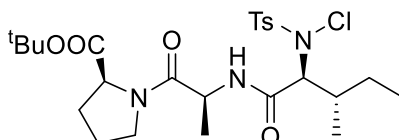
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-seryl-*L*-alloisoleucinate(1x)



1x

White foam. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 11.1$ Hz, 1H), 7.10 (d, $J = 11.1$ Hz, 1H), 4.52–4.56 (m, 2H), 4.34 (d, $J = 9.9$ Hz, 1H), 4.01 (dd, $J = 11.1, 5.7$ Hz, 1H), 3.68–3.81 (m, 4H), 3.54 (dd, $J = 11.1, 5.7$ Hz, 1H), 2.46 (s, 3H), 2.15–2.20 (m, 1H), 1.87–1.95 (m, 1H), 1.54–1.60 (m, 1H), 1.39–1.49 (m, 1H), 1.17–1.26 (m, 2H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.04, 170.21, 167.87, 145.55, 132.21, 129.73, 129.11, 66.32, 62.38, 56.91, 54.14, 52.20, 37.33, 33.34, 25.10, 24.64, 21.69, 15.51, 14.94, 11.49, 10.05. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{36}\text{ClN}_3\text{NaO}_7\text{S}$, 556.1855; found, 556.1849. **IR** (KBr, cm^{-1}): ν 3673, 3305, 3212, 2967, 2879, 1740, 1652, 1362, 1167, 846, 672.

***tert*-butyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alanyl-*L*-prolinate(**1y**)**

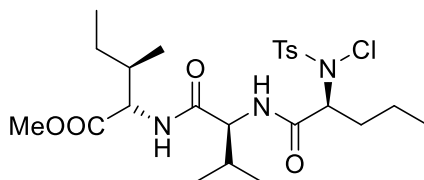


1y

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 6.90 (d, $J = 6.9$ Hz, 1H), 4.54–4.63 (m, 1H), 4.41 (dd, $J = 8.4, 4.2$ Hz, 1H), 4.24 (d, $J = 9.9$ Hz, 1H), 3.60–3.66 (m, 1H), 3.54–3.58 (m, 1H), 2.44 (s, 3H), 2.17–2.25 (m, 1H), 2.08–2.14 (m, 1H), 2.02–2.06 (m, 1H), 1.93–2.01 (m, 2H), 1.56–1.60 (m, 1H), 1.46 (s, 9H), 1.35 (d, $J = 6.9$ Hz, 3H), 1.17–1.23 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.71, 170.39, 166.56, 144.94, 132.87, 129.53, 129.08, 81.44, 66.92, 59.55, 46.77, 46.68, 33.68, 28.93, 27.91, 24.85, 24.75, 21.63, 17.47, 14.95, 10.07. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for

C₂₅H₃₈ClN₃NaO₆S, 566.2062; found, 566.2054. IR (KBr, cm⁻¹): ν 3189, 3117, 1778, 1632, 1331, 1161, 670.

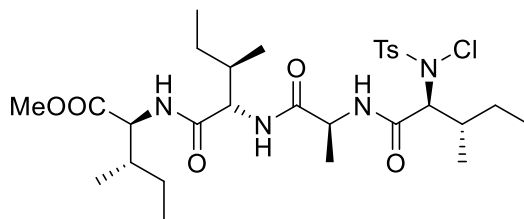
methyl((S)-2-((N-chloro-4-methylphenyl)sulfonamido)pentanoyl)-L-valyl-L-alloisoleucinate(1z)



1z

White foam. ¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 4.72 (dd, *J* = 7.5, 6.3 Hz, 1H), 4.59 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.29 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.74 (s, 3H), 2.48 (s, 3H), 2.19–2.24 (m, 1H), 2.01–2.06 (m, 1H), 1.89–1.94 (m, 1H), 1.54–1.61 (m, 1H), 1.40–1.47 (m, 1H), 1.31–1.37 (m, 2H), 1.17–1.24 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 171.96, 170.56, 168.47, 145.69, 132.35, 129.88, 128.98, 64.11, 58.72, 56.53, 52.05, 37.61, 30.75, 30.68, 25.08, 21.67, 19.55, 19.17, 17.72, 15.40, 13.52, 11.48. HRMS-ESI(*m/z*): [M+Na]⁺ calcd. for C₂₄H₃₈ClN₃NaO₆S, 554.2062; found, 554.2058. IR (KBr, cm⁻¹): ν 3290, 3201, 1742, 1643, 1384, 1161, 814, 664.

methyl N-chloro-N-tosyl-L-isoleucyl-L-alanyl-L-alloisoleucyl-L-isoleucinate(1aa)

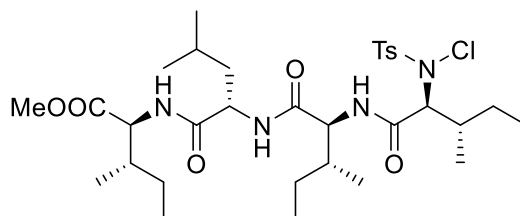


1aa

White foam. ¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.60 (dd, *J* = 7.8, 5.4 Hz, 1H), 4.51–4.54 (m, 1H), 4.42–4.45 (m, 1H), 4.33 (d, *J* = 9.6

Hz, 1H), 3.73 (s, 3H), 2.45 (s, 3H), 2.10–2.18 (m, 1H), 1.90–1.94 (m, 1H), 1.79–1.84 (m, 1H), 1.57–1.82 (m, 1H), 1.48–1.54 (m, 1H), 1.37–1.41 (m, 1H), 1.35 (d, $J = 6.6$ Hz, 3H), 1.14–1.20 (m, 2H), 1.08–1.11 (m, 1H), 0.82–0.89 (m, 18H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.15, 171.95, 170.98, 167.47, 145.34, 132.65, 129.68, 129.08, 66.29, 57.87, 56.50, 52.12, 48.86, 37.62, 37.18, 33.72, 25.07, 24.87, 21.70, 17.84, 15.41, 15.27, 14.92, 11.46, 11.24, 10.30. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{29}\text{H}_{48}\text{ClN}_4\text{O}_7\text{S}$, 631.2927; found, 631.2921. **IR** (KBr, cm^{-1}): ν 3285, 3029, 2966, 2781, 1778, 1639, 1398, 1161, 812, 668.

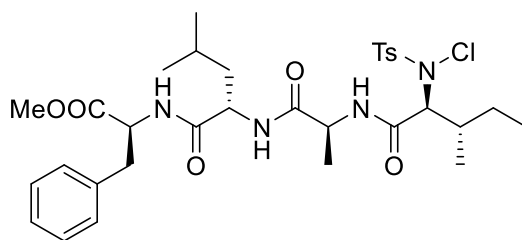
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alloisoleucyl-*L*-leucyl-*L*-isoleucinate(1ab)



1ab

White foam. ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.5$ Hz, 2H), 6.83 (d, $J = 7.8$ Hz, 1H), 4.65 (dd, $J = 14.4, 8.4$ Hz, 1H), 4.57 (dd, $J = 8.7, 5.4$ Hz, 1H), 4.32–4.42 (m, 2H), 3.73 (s, 3H), 2.46 (s, 3H), 2.06–2.17 (m, 1H), 1.93–1.96 (m, 1H), 1.62–1.72 (m, 2H), 1.51–1.60 (m, 3H), 1.39–1.43 (m, 1H), 1.07–1.22 (m, 3H), 0.83–0.96 (m, 24H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.17, 171.71, 170.86, 168.15, 145.38, 132.61, 129.72, 129.04, 57.90, 56.52, 52.03, 51.64, 40.86, 37.63, 36.87, 34.33, 25.10, 25.03, 24.83, 24.70, 22.86, 22.09, 21.70, 15.49, 15.34, 15.00, 11.44, 11.33, 10.50. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{53}\text{ClN}_4\text{NaO}_7\text{S}$, 695.3216; found, 695.3217. **IR** (KBr, cm^{-1}): ν 3383, 2662, 1729, 1447, 1159, 842.

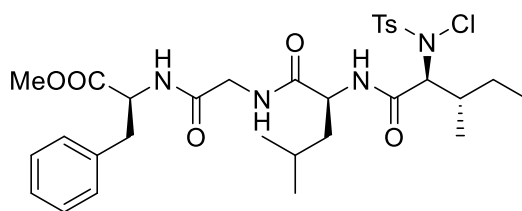
methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alanyl-*L*-leucyl-*L*-phenylalaninate(1ac)



1ac

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 2H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 6.66 (d, $J = 6.9$ Hz, 1H), 4.82 (dt, $J = 7.5$, 6.3 Hz, 1H), 4.36–4.48 (m, 2H), 4.23 (d, $J = 9.3$ Hz, 1H), 3.70 (s, 3H), 3.15 (dd, $J = 13.8$, 6.3 Hz, 1H), 3.07 (dd, $J = 13.8$, 6.3 Hz, 1H), 2.47 (s, 3H), 2.09–2.18 (m, 1H), 1.59–1.87 (m, 2H), 1.48–1.58 (m, 2H), 1.37 (d, $J = 6.9$ Hz, 3H), 1.14–1.21 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.86–0.91 (m, 9H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.71, 171.61, 171.43, 167.56, 145.67, 135.89, 132.08, 129.78, 129.24, 129.17, 128.53, 127.05, 66.73, 53.31, 52.29, 51.87, 49.16, 40.67, 37.80, 33.90, 24.94, 24.65, 22.84, 21.88, 21.73, 17.47, 15.00, 10.29. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{45}\text{ClN}_4\text{NaO}_7\text{S}$, 687.2590; found, 687.2581. **IR** (KBr, cm^{-1}): ν 3277, 2960, 1743, 1636, 1161, 814, 670.

methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-leucylglycyl-*L*-phenylalaninate(1ad)

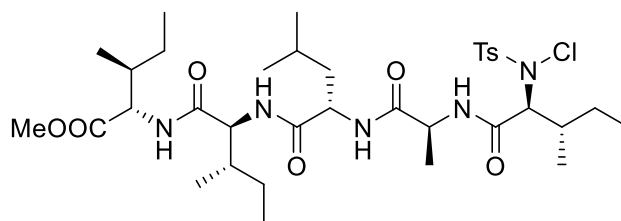


1ad

White foam. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.27 (t, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J = 7.8$ Hz, 2H), 6.75 (d, $J = 6.9$ Hz, 1H), 4.77–4.81 (m, 1H), 4.31 (d, $J = 9.6$ Hz, 1H), 4.27–4.34 (m, 1H), 4.03 (dd, $J = 16.8$, 5.8 Hz, 1H), 3.86 (dd, $J = 16.8$, 5.8 Hz, 1H), 3.65 (s, 3H), 3.14 (dd, $J = 13.8$, 6.9 Hz, 1H), 3.09 (dd, $J = 13.8$, 6.9 Hz, 1H), 2.46 (s,

3H), 2.10–2.17 (m, 1H), 1.69–1.73 (m, 1H), 1.63–1.67 (m, 2H), 1.49–1.55 (m, 1H), 1.11–1.18 (m, 1H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.87 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.98, 171.81, 168.59, 167.99, 145.60, 136.05, 132.22, 129.76, 129.18, 129.07, 128.47, 126.96, 66.22, 53.66, 52.46, 52.21, 43.01, 40.03, 37.71, 33.64, 24.76, 24.60, 22.99, 21.70, 15.00, 10.17. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{31}\text{H}_{44}\text{ClN}_4\text{O}_7\text{S}$, 651.2614; found, 651.2615. **IR** (KBr, cm^{-1}): ν 3293, 2961, 1742, 1651, 1327, 1161, 815, 667.

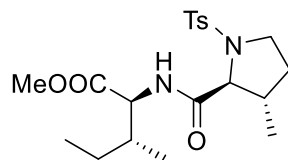
Methyl *N*-chloro-*N*-tosyl-*L*-isoleucyl-*L*-alanyl-*L*-leucyl-*L*-isoleucyl-*L*-isoleucinate (1ae)



1ae

White foam. ^1H NMR (400 MHz, CDCl_3) ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.1$ Hz, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 1H), 4.83 (dd, $J = 14.3, 8.4$ Hz, 1H), 4.71 (dd, $J = 8.6, 5.4$ Hz, 1H), 4.32 – 4.42 (m, 2H), 4.36 (dd, $J = 16.9, 5.8$ Hz, 1H), 3.71 (s, 3H), 2.41 (s, 3H), 2.06–2.17 (m, 1H), 1.87–1.91 (m, 1H), 1.76–1.79 (m, 1H), 1.43–1.45 (m, 3H), 1.19–1.23 (m, 3H), 0.96 (d, $J = 6.7$ Hz, 3H), 0.83–0.94 (m, 24H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.18, 172.08, 171.95, 171.47, 167.25, 145.51, 132.12, 129.69, 129.02, 65.92, 57.54, 56.61, 52.12, 51.94, 48.69, 37.66, 37.46, 33.78, 25.03, 24.82, 24.76, 24.66, 23.01, 22.03, 21.61, 18.91, 15.39, 15.00, 14.77, 11.44, 11.28, 10.18. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{35}\text{H}_{58}\text{ClN}_5\text{NaO}_8\text{S}$, 766.3587; found, 766.3584. **IR** (KBr, cm^{-1}): ν 3284, 2962, 2931, 1725, 1384, 1160, 893, 669.

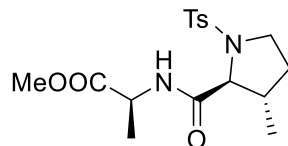
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alloisoleucinate(2a)



2a

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 1H), 4.55 (dd, $J = 8.2, 5.1$ Hz, 1H), 3.77 (s, 3H), 3.66 (d, $J = 3.3$ Hz, 1H), 3.46–3.55 (m, 1H), 3.32–3.42 (m, 1H), 2.53–2.59 (m, 1H), 2.45 (s, 3H), 1.88–1.94 (m, 2H), 1.40–1.51 (m, 1H), 1.24–1.32 (m, 1H), 1.20–1.23 (m, 1H), 0.93 (t, $J = 6.9$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.62, 170.87, 144.27, 133.13, 129.80, 127.86, 68.83, 56.63, 52.06, 48.19, 38.05, 37.74, 31.78, 25.06, 21.54, 18.08, 15.47, 11.51. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{NaO}_5\text{S}$, 433.1768; found, 433.1772. **IR** (KBr, cm^{-1}): ν 3553, 3477, 2965, 1742, 1162, 1305, 858.

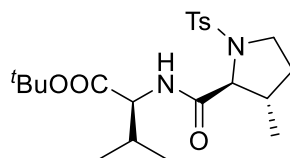
methyl ((2S,3S)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-L-alaninate(2b)



2b

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 4.55 (quint, $J = 7.2$ Hz, 1H), 3.78 (s, 3H), 3.64 (d, $J = 3.6$ Hz, 1H), 3.50 (ddd, $J = 12.0, 7.2, 5.4$ Hz, 1H), 3.37 (ddd, $J = 12.6, 10.0, 5.4$ Hz, 1H), 2.50–2.56 (m, 1H), 2.45 (s, 3H), 1.86–1.92 (m, 1H), 1.45 (d, $J = 7.2$ Hz, 3H), 1.21–1.27 (m, 1H), 0.62 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.82, 170.84, 144.33, 133.25, 129.86, 127.94, 68.78, 52.47, 48.32, 38.22, 31.85, 21.59, 18.27, 18.21. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{NaO}_5\text{S}$, 391.1298; found, 391.1299. **IR** (KBr, cm^{-1}): ν 3555, 3412, 2961, 1744, 1638, 1346, 868.

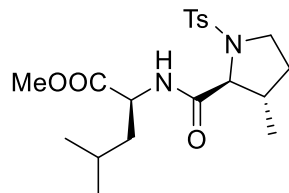
tert-butyl ((2S,3S)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-L-valinate(2c)



2c

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 4.39 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.67 (d, *J* = 3.4 Hz, 1H), 3.51 (ddd, *J* = 11.8, 7.2, 4.9 Hz, 1H), 3.36 (ddd, *J* = 11.2, 7.8, 4.9 Hz, 1H), 2.51–2.57 (m, 1H), 2.45 (s, 3H), 2.15–2.20 (m, 1H), 1.88–1.94 (m, 1H), 1.51 (s, 9H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.60 (d, *J* = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 170.87, 170.05, 144.22, 133.42, 129.81, 127.96, 82.04, 69.07, 57.90, 48.18, 38.31, 31.86, 31.58, 28.04, 21.56, 18.98, 18.20, 17.78. **HRMS-ESI(*m/z*):** [M+Na]⁺ calcd. for C₂₂H₃₄N₂NaO₅S, 461.2081; found, 461.2081. **IR** (KBr, cm⁻¹): ν 3554, 3477, 1732, 1683, 1350, 846.

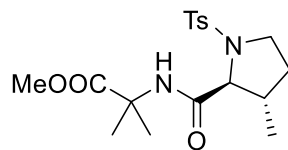
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-leucinate(2d)



2d

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 4.59 (td, *J* = 8.4, 5.4 Hz, 1H), 3.76 (s, 3H), 3.66 (d, *J* = 3.6 Hz, 1H), 3.49 (ddd, *J* = 10.5, 7.2, 5.1 Hz, 1H), 3.37 (ddd, *J* = 10.2, 7.8, 5.1 Hz, 1H), 2.51–2.57 (m, 1H), 2.45 (s, 3H), 1.86–1.91 (m, 1H), 1.67–1.72 (m, 1H), 1.62–1.66 (m, 2H), 1.22–1.26 (m, 1H), 0.95 (s, 3H), 0.94 (s, 3H), 0.60 (d, *J* = 7.0 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 172.70, 170.95, 144.33, 133.26, 129.86, 127.93, 68.84, 52.29, 51.04, 48.30, 41.28, 38.12, 31.85, 24.98, 22.82, 21.98, 21.59, 18.19. **HRMS-ESI(*m/z*):** [M+Na]⁺ calcd. for C₂₀H₃₀N₂NaO₅S, 433.1768; found, 433.1770. **IR** (KBr, cm⁻¹): ν 3553, 3417, 2924, 1741, 1638, 1261, 618.

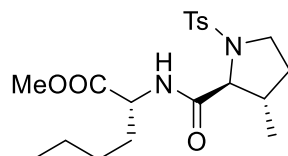
Methyl 2-methyl-2-((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carboxamido)propanoate (2e)



2e

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.23 (s, 1H), 3.74 (s, 3H), 3.56 (d, $J = 3.7$ Hz, 1H), 3.52–3.55 (m, 1H), 3.37 (ddd, $J = 10.2, 7.8, 5.1$ Hz, 1H), 2.49–2.54 (m, 1H), 2.45 (s, 3H), 1.88–1.94 (m, 1H), 1.60 (s, 3H), 1.54 (s, 3H), 1.19–1.24 (m, 1H), 0.60 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 174.62, 170.48, 144.33, 132.99, 129.83, 127.85, 68.96, 56.29, 52.49, 48.33, 38.31, 31.69, 25.20, 24.24, 21.54, 18.16. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{NaO}_5\text{S}$, 405.1455; found, 405.1461. **IR** (KBr, cm^{-1}): ν 3523, 3303, 2958, 1738, 1628, 749, 671.

methyl (R)-2-((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carboxamido)hexanoate (2f)

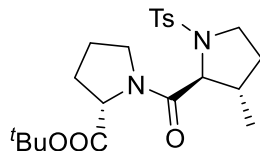


2f

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 4.61 (dt, $J = 8.4, 5.1$ Hz, 1H), 3.74 (s, 3H), 3.62 (d, $J = 3.7$ Hz, 1H), 3.59 (ddd, $J = 10.8, 7.2, 5.1$ Hz, 1H), 3.36 (ddd, $J = 12.6, 7.8, 5.1$ Hz, 1H), 2.45–2.49 (m, 1H), 2.45 (s, 3H), 1.87–1.96 (m, 2H), 1.70–1.76 (m, 1H), 1.38–1.44 (m, 2H), 1.31–1.39 (m, 2H), 1.18–1.24 (m, 1H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.61 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.84, 170.98, 144.37, 132.77, 129.84, 127.87, 68.98, 52.21, 52.01, 48.37, 38.86, 31.81, 31.59, 27.24, 22.13, 21.56, 18.31,

13.77. **HRMS-ESI(*m/z*):** $[M+Na]^+$ calcd. for $C_{20}H_{30}N_2NaO_5S$, 433.1768; found, 433.1772. **IR** (KBr, cm^{-1}): ν 3525, 3474, 2958, 2927, 1743, 1676, 1349, 857.

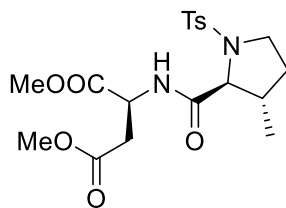
***tert*-butyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-prolinate (2g)**



2g

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 4.44 (dd, $J = 8.4, 4.2$ Hz, 1H), 4.22 (d, $J = 4.8$ Hz, 1H), 3.84 (dd, $J = 16.3, 7.2$ Hz, 1H), 3.58–3.63 (m, 1H), 3.47–3.52 (m, 1H), 3.33–3.36 (m, 1H), 2.45–2.51 (m, 1H), 2.41 (s, 3H), 2.13–2.21 (m, 2H), 1.98–2.07 (m, 2H), 1.92–1.98 (m, 1H), 1.48–1.52 (m, 1H), 1.44 (s, 9H), 1.06 (d, $J = 6.8$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.23, 169.89, 143.27, 136.24, 129.45, 127.56, 81.16, 65.67, 59.71, 47.28, 46.90, 39.23, 32.66, 28.87, 27.98, 24.88, 21.51, 18.23. **HRMS-ESI(*m/z*):** $[M+Na]^+$ calcd. for $C_{22}H_{32}N_2NaO_5S$, 459.1924; found, 459.1931. **IR** (KBr, cm^{-1}): ν 3682, 2970, 1735, 1660, 1344, 1158, 815.

dimethyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-aspartate(2h)

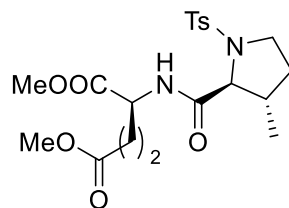


2h

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 4.82 (dt, $J = 12.3, 5.1$ Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.63 (d, $J = 3.6$ Hz, 1H), 3.45–3.51 (m, 1H), 3.32–3.39 (m, 1H), 2.97 (dq, $J = 15.9, 5.1$ Hz, 2H), 2.44–2.49 (m, 1H), 2.45 (s, 3H), 1.89 (td, $J = 13.6, 7.2$ Hz, 1H), 1.14–1.25 (m, 1H), 0.66 (d, $J = 6.9$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.14, 170.92, 170.60, 144.24, 133.27, 129.81, 127.89, 68.81, 52.82, 52.02, 49.01, 48.17, 38.59, 36.08,

31.82, 21.55, 18.11. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{19}H_{26}N_2NaO_7S$, 449.1353; found, 449.1358. **IR** (KBr, cm^{-1}): ν 3354, 2957, 1741, 1674, 1347, 1162, 855.

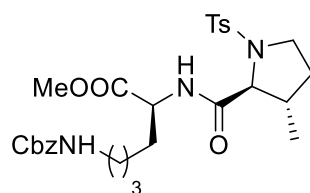
dimethyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-glutamate(2i)



2i

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 4.59 (dt, $J = 13.0, 7.5$ Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.62 (d, $J = 3.6$ Hz, 1H), 3.49–3.55 (m, 1H), 3.33–3.40 (m, 1H), 2.48–2.54 (m, 1H), 2.42–2.47 (m, 1H), 2.44 (s, 3H), 2.35–2.40 (m, 1H), 2.27 (td, $J = 13.8, 7.2$ Hz, 1H), 2.08 (td, $J = 14.4, 7.8$ Hz, 1H), 1.91 (td, $J = 13.5, 7.2$ Hz, 1H), 1.21–1.26 (m, 1H), 0.64 (d, $J = 6.9$ Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.03, 171.55, 171.30, 144.30, 133.20, 129.83, 127.91, 68.86, 52.50, 51.79, 51.76, 48.31, 38.48, 31.92, 29.94, 27.17, 21.55, 18.16. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{20}H_{28}N_2NaO_7S$, 463.1509; found, 463.1513. **IR** (KBr, cm^{-1}): ν 3553, 3414, 2924, 1739, 1637, 803.

methyl N^6 -((benzyloxy)carbonyl)- N^2 -((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-lysinate(2j)

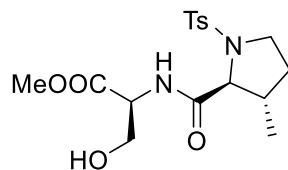


2j

Colorless oil. **1H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, $J = 7.9$ Hz, 2H), 7.31–7.39 (m, 7H), 7.27–7.31 (m, 1H), 5.08 (s, 2H), 4.89–4.96 (m, 1H), 4.56 (dt, $J = 12.8, 7.5$ Hz, 1H), 3.77 (s, 3H), 3.64 (d, $J = 3.3$ Hz, 1H), 3.45–3.51 (m, 1H), 3.30–3.34 (m, 1H), 3.13–3.23 (m, 2H), 2.49–2.55 (m, 1H), 2.44 (s, 3H), 1.85–1.93 (m, 2H), 1.72–1.78 (m, 1H), 1.50–1.59 (m, 2H), 1.33–1.41 (m, 2H), 1.17–1.23 (m, 1H), 0.58 (d, $J = 6.9$ Hz,

3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.14, 171.06, 156.43, 144.32, 136.66, 133.15, 129.84, 128.45, 128.01, 127.96, 127.89, 68.84, 66.50, 52.42, 52.11, 48.22, 40.68, 38.09, 31.92, 31.91, 29.14, 22.37, 21.57, 18.09. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{28}\text{H}_{37}\text{N}_3\text{NaO}_7\text{S}$, 582.2244; found, 582.2250. **IR** (KBr, cm^{-1}): ν 3750, 2955, 1740, 1535, 857.

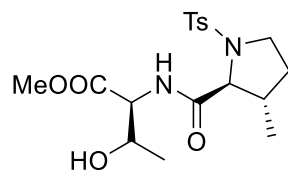
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-serinate(2k)



2k

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.54 (d, $J = 6.9$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 4.60 (dt, $J = 7.5, 3.9$ Hz, 1H), 4.00 (d, $J = 3.9$ Hz, 2H), 3.82 (s, 3H), 3.63 (d, $J = 4.5$ Hz, 1H), 3.53 (ddd, $J = 10.5, 6.6, 4.2$ Hz, 1H), 3.37 (ddd, $J = 10.2, 7.2, 4.2$ Hz, 1H), 3.07 (br s, 1H), 2.51 (quint, $J = 6.0$, 1H), 2.45 (s, 3H), 1.94–1.99 (m, 1H), 1.22–1.28 (m, 1H), 0.70 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.95, 170.30, 144.40, 133.18, 129.90, 127.89, 69.00, 63.07, 55.42, 52.78, 48.36, 38.77, 32.08, 21.59, 18.07. **HRMS-ESI**(m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{25}\text{N}_2\text{O}_6\text{S}$, 385.1428; found, 385.1432. **IR** (KBr, cm^{-1}): ν 3687, 3413, 2962, 1745, 1679, 1161, 856.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-allothreoninate(2l)

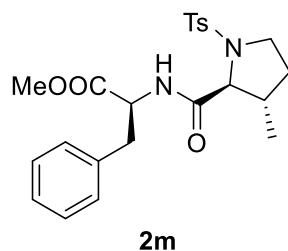


2l

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.79 (d, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 2H), 4.57 (d, $J = 8.7$ Hz, 1H), 4.35–4.41 (m, 1H), 3.81 (s, 3H), 3.69 (d, $J = 3.6$ Hz, 1H), 3.51–3.56 (m, 1H), 3.33–3.39 (m, 1H), 2.72 (br s, 1H), 2.49–2.56 (m, 1H), 2.45 (s, 3H), 1.97 (dt, $J = 13.6, 6.8$ Hz, 1H), 1.23–1.28 (m, 1H),

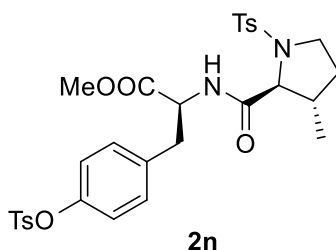
1.24 (d, $J = 6.3$ Hz, 3H), 0.66 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.95, 170.87, 144.35, 133.11, 129.87, 127.90, 69.00, 68.03, 57.69, 52.64, 48.28, 38.68, 31.98, 21.59, 19.87, 18.11. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_2\text{NaO}_6\text{S}$, 421.1404; found, 421.1409. IR (KBr, cm^{-1}): ν 3704, 3555, 3412, 2931, 1744, 1680, 1160, 860.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-phenylalaninate(2m)



Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.26–7.28 (m, 2H), 7.21–7.23 (m, 2H), 7.14 (d, $J = 6.9$ Hz, 2H), 4.86 (ddd, $J = 13.3, 7.5, 6.0$ Hz, 1H), 3.77 (s, 3H), 3.59 (d, $J = 3.6$ Hz, 1H), 3.30–3.34 (m, 1H), 3.26 (dd, $J = 13.8, 5.9$ Hz, 2H), 3.06 (dd, $J = 13.8, 7.5$ Hz, 1H), 2.44 (s, 3H), 2.29–2.35 (m, 1H), 1.57–1.63 (m, 1H), 1.10–1.15 (m, 1H), 0.54 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 171.42, 170.71, 144.25, 136.08, 133.19, 129.81, 129.26, 128.44, 127.87, 126.98, 68.78, 53.17, 52.39, 48.10, 38.21, 37.91, 31.50, 21.55, 18.18. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}$, 467.1611; found, 467.1616. IR (KBr, cm^{-1}): ν 3728, 2928, 1744, 1674, 1348, 1161, 853.

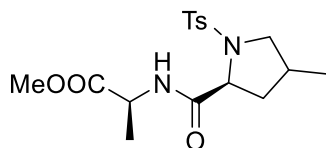
methyl (S)-2-((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carboxamido)-3-(4-(tosyloxy)phenyl)propanoate(2n)



Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 1H),

7.08 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 4.81 (ddd, $J = 9.3, 7.5f, 5.8$ Hz, 1H), 3.75 (s, 3H), 3.57 (d, $J = 3.6$ Hz, 1H), 3.29–3.34 (m, 1H), 3.25–3.29 (m, 1H), 3.22 (dd, $J = 14.1, 5.4$ Hz, 1H), 3.02 (dd, $J = 14.1, 7.5k$ Hz, 1H), 2.44 (s, $2 \times 3H$), 2.29–2.36 (m, 1H), 1.60–1.65 (m, 1H), 1.12–1.16 (m, 1H), 0.54 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.15, 170.78, 148.61, 145.32, 144.37, 135.32, 133.09, 132.34, 130.45, 129.85, 129.78, 128.45, 127.87, 122.40, 68.78, 53.03, 52.44, 48.17, 38.11, 37.33, 31.63, 21.66, 21.65, 18.14. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{30}H_{34}N_2NaO_8S_2$, 637.1649; found, 637.1657. **IR** (KBr, cm^{-1}): ν 3688, 3440, 3069, 1739, 1628, 1473, 867.

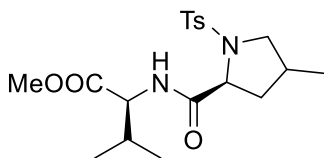
methyl ((2*S*)-4-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alaninate(2o)



2o

Colorless oil. 1H NMR (600 MHz, $CDCl_3$) isomer δ 7.76 (d, $J = 7.8$ Hz, 2H), 7.47 (d, $J = 6.3$ Hz, 1H), 7.36 (d, $J = 7.8$ Hz, 2H), 4.55 (quint, $J = 7.2$ Hz, 1H), 4.11 (d, $J = 9.0$ Hz, 1H), 3.78 (s, 3H), 3.63 (dt, $J = 7.2, 6.3$ Hz, 1H), 2.64 (t, $J = 9.8$ Hz, 1H), 2.46 (s, 3H), 2.28 (dd, $J = 12.3, 5.4$ Hz, 1H), 2.18–2.24 (m, 1H), 1.45 (d, $J = 7.2$ Hz, 3H), 1.10–1.15 (m, 1H), 0.89 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.72, 170.93, 144.35, 132.67, 129.90, 127.99, 62.54, 56.27, 52.47, 48.45, 37.54, 32.36, 21.58, 18.27, 16.31. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{17}H_{24}N_2NaO_5S$, 391.1298; found, 391.1303. **IR** (KBr, cm^{-1}): ν 3679, 3300, 2930, 1740, 1677, 1534, 855.

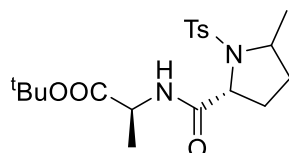
methyl ((2*S*)-4-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-valinate(2p)



2p

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 4.50 (dd, $J = 8.4, 5.1$ Hz, 1H), 4.13 (d, $J = 8.7$ Hz, 1H), 3.77 (s, 3H), 3.64 (dd, $J = 8.7, 7.2$ Hz, 1H), 2.65 (dd, $J = 9.9, 7.2$ Hz, 1H), 2.46 (s, 3H), 2.30 (dd, $J = 12.4, 5.6$ Hz, 1H), 2.19–2.26 (m, 2H), 1.08–1.13 (m, 1H), 0.96 (d, $J = 7.2$ Hz, 3H), 0.95 (d, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.62, 171.13, 144.33, 132.69, 129.91, 127.99, 62.68, 57.55, 56.24, 52.14, 37.46, 32.52, 31.25, 21.58, 19.08, 17.84, 16.40. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{NaO}_5\text{S}$, 419.1611; found, 419.1610. **IR** (KBr, cm^{-1}): ν 3684, 3524, 2963, 1734, 1628, 1526, 870.

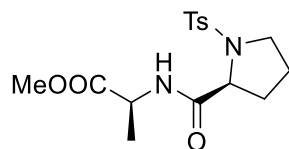
***tert*-butyl ((2*R*)-5-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alaninate(2q)**



2q

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) isomer δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 6.77 (d, $J = 7.6$ Hz, 1H), 4.43 (quint, $J = 7.2$ Hz, 1H), 4.24–4.29 (m, 1H), 4.23 (dd, $J = 8.7, 7.5$ Hz, 1H), 2.42 (s, 3H), 2.20–2.25 (m, 1H), 2.13–2.19 (m, 1H), 2.07–2.10 (m, 1H), 1.55 (dd, $J = 11.4, 5.3$ Hz, 1H), 1.47 (s, 9H), 1.37 (d, $J = 7.2$ Hz, 3H), 1.18 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.78, 171.15, 143.61, 137.49, 129.62, 127.61, 81.85, 62.59, 57.60, 48.69, 31.90, 29.29, 27.98, 21.50, 19.89, 18.12. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{NaO}_5\text{S}$, 433.1768; found, 433.1771. **IR** (KBr, cm^{-1}): ν 3770, 3415, 2925, 1663, 1372, 811.

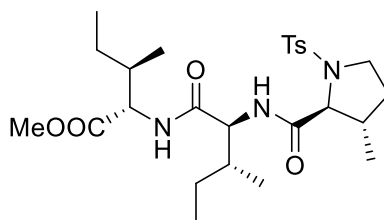
methyl tosyl-*L*-prolyl-*L*-alaninate(2r)



2r

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 5.7$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 4.54 (quint, $J = 7.2$ Hz 1H), 4.11 (dd, $J = 8.4, 2.1$ Hz, 1H), 3.78 (s, 3H), 3.50–3.57 (m, 1H), 3.18–3.22 (m, 1H), 2.45 (s, 3H), 2.16–2.23 (m, 1H), 1.71–1.79 (m, 1H), 1.62–1.67 (m, 1H), 1.52–1.57 (m, 1H), 1.45 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.74, 170.85, 144.34, 133.07, 129.95, 127.91, 62.22, 52.48, 49.82, 48.42, 29.70, 24.45, 21.57, 18.25. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{NaO}_5\text{S}$, 377.1142; found, 377.1145. **IR** (KBr, cm^{-1}): ν 3682, 2970, 1735, 1660, 1595, 1344, 815.

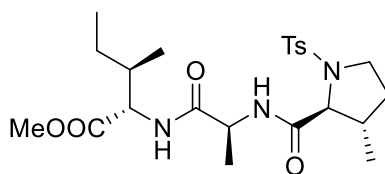
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alloisoleucyl-*L*-alloisoleucinate(2s)



2s

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 9.3$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 4.54 (dd, $J = 8.4, 6.0$ Hz, 1H), 4.44 (dd, $J = 9.3, 4.5$ Hz, 1H), 3.73 (s, 3H), 3.56–3.6 (m, 1H), 3.59 (d, $J = 4.2$, 1H), 3.39 (ddd, $J = 10.2, 8.4, 7.5$ Hz, 1H), 2.47–2.49 (m, 1H), 2.47 (s, 3H), 2.20–2.26 (m, 1H), 1.87–1.94 (m, 2H), 1.42–1.52 (m, 2H), 1.22–1.28 (m, 2H), 1.10–1.16 (m, 1H), 0.95 (t, $J = 6.6$ Hz, 3H), 0.94 (d, $J = 6.3$ Hz, 3H), 0.92 (d, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H), 0.68 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.04, 171.04, 170.67, 144.69, 132.05, 129.97, 128.05, 69.14, 58.19, 56.83, 51.85, 48.55, 39.03, 37.26, 36.01, 31.93, 25.29, 24.46, 21.61, 18.34, 16.01, 15.52, 11.68, 11.34. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{26}\text{H}_{41}\text{N}_3\text{NaO}_6\text{S}$, 546.2608; found, 546.2598. **IR** (KBr, cm^{-1}): ν 3681, 2966, 1742, 1540, 1349, 1160, 817.

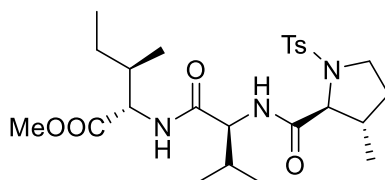
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alanyl-*L*-alloisoleucinate(2t)



2t

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.79 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 4.51–4.58 (m, 2H), 3.74 (s, 3H), 3.56–3.61 (m, 1H), 3.55 (d, J = 4.8 Hz, 1H), 3.40 (dt, J = 10.5, 7.2 Hz, 1H), 2.47 (s, 3H), 2.41–2.46 (m, 1H), 1.87–1.95 (m, 2H), 1.43–1.50 (m, 1H), 1.44 (d, J = 7.2 Hz, 3H), 1.18–1.24 (m, 2H), 0.91 (d, J = 7.2 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 172.02, 171.70, 170.87, 144.66, 132.11, 129.97, 128.02, 68.96, 56.77, 51.84, 49.21, 48.65, 39.06, 37.43, 32.00, 25.23, 21.59, 18.35, 17.85, 15.45, 11.42. **HRMS-ESI**(m/z): [M+Na]⁺ calcd. for C₂₃H₃₅N₃NaO₆S, 504.2139; found, 504.2147. **IR** (KBr, cm⁻¹): ν 3660, 3523, 1741, 1656, 1380, 1162, 816.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-valyl-*L*-alloisoleucinate (2u)

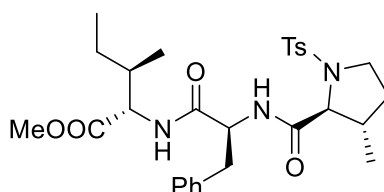


2u

Colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 7.80 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 4.56 (dd, J = 7.8, 6.3 Hz, 1H), 4.41 (dd, J = 9.0, 4.5 Hz, 1H), 3.73 (s, 3H), 3.60 (d, J = 3.9 Hz, 1H), 3.59 (m, 1H), 3.37–3.41 (m, 1H), 2.49–2.56 (m, 2H), 2.47 (s, 3H), 1.88–1.97 (m, 2H), 1.44–1.50 (m, 1H), 1.20–1.30 (m, 2H), 0.97 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H), 0.67 (d, J = 6.8 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 172.03, 171.09, 170.66, 144.68, 132.09, 129.97, 128.05, 69.17, 58.47, 56.79,

51.85, 48.54, 39.00, 37.30, 31.93, 29.52, 25.26, 21.61, 19.55, 18.33, 17.12, 15.52, 11.34. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{25}H_{39}N_3NaO_6S$, 532.2452; found, 532.2445. **IR** (KBr, cm^{-1}): ν 3684, 3524, 2966, 1742, 1656, 1349, 1160, 816.

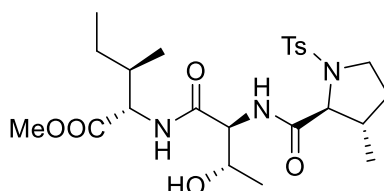
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-phenylalanyl-*L*-alloisoleucinate(2v)



2v

Colorless oil. **¹H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.27–7.32 (m, 2H), 7.20–7.25 (m, 3H), 7.08 (d, $J = 8.1$ Hz, 1H), 6.95 (d, $J = 9.0$ Hz, 1H), 4.84 (td, $J = 9.0, 5.1$ Hz, 1H), 4.50 (dd, $J = 8.1, 6.0$ Hz, 1H), 3.73 (s, 3H), 3.45 (d, $J = 4.2$ Hz, 1H), 3.32–3.41 (m, 2H), 3.21–3.29 (m, 1H), 3.07 (dd, $J = 11.7, 7.8$ Hz, 1H), 2.44 (s, 3H), 2.00–2.10 (m, 1H), 1.82–1.92 (m, 1H), 1.37–1.51 (m, 2H), 1.11–1.23 (m, 1H), 1.01–1.10 (m, 1H), 0.88 (d, $J = 10.2$ Hz, 3H), 0.87 (t, $J = 10.8$ Hz, 3H), 0.55 (d, $J = 6.9$ Hz, 3H). **¹³C NMR** (150 MHz, $CDCl_3$) δ 171.74, 170.83, 170.52, 144.60, 136.75, 131.98, 129.90, 129.09, 128.58, 127.87, 126.91, 68.91, 56.98, 53.49, 51.81, 48.29, 38.88, 37.27, 37.20, 31.46, 25.22, 21.55, 18.20, 15.35, 11.31. **HRMS-ESI**(m/z): $[M+Na]^+$ calcd. for $C_{29}H_{39}N_3NaO_6S$, 580.2452; found, 580.2446. **IR** (KBr, cm^{-1}): ν 3523, 3308, 1659, 1379, 1192.

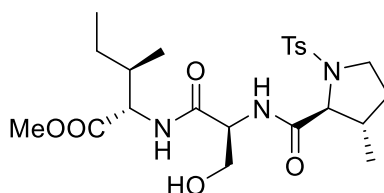
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-allothreonyl-*L*-alloisoleucinate (2w)



2w

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 9.0$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 1H), 4.57–4.60 (m, 1H), 4.48–4.55 (m, 2H), 3.74 (s, 3H), 3.58–3.61 (m, 1H), 3.59 (d, $J = 4.8$ Hz, 1H), 3.38 (dt, $J = 10.5, 7.2$ Hz, 1H), 3.08 (br s, 1H), 2.46 (s, 3H), 2.39–2.40 (m, 1H), 1.94 (td, $J = 13.2, 6.6$ Hz, 2H), 1.45–1.52 (m, 1H), 1.30–1.26 (m, 1H), 1.21–1.25 (m, 1H), 1.16 (d, $J = 6.5$ Hz, 3H), 0.93 (d, $J = 6.9$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H), 0.76 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.05, 171.83, 170.68, 144.59, 132.30, 129.94, 127.99, 69.21, 66.29, 57.12, 51.94, 48.44, 39.64, 37.08, 32.15, 29.23, 25.26, 21.59, 18.69, 18.28, 15.48, 11.37. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{24}\text{H}_{37}\text{N}_3\text{NaO}_7\text{S}$, 534.2244; found, 534.2238. **IR** (KBr, cm^{-1}): ν 3524, 3440, 2968, 2933, 1742, 1669, 859.

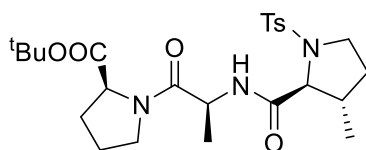
methyl **((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-seryl-*L*-alloisoleucinate(2x)**



2x

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 1H), 4.62 (dt, $J = 7.8, 3.9$ Hz, 1H), 4.52 (dd, $J = 8.1, 5.7$ Hz, 1H), 4.18–4.20 (m, 1H), 3.74 (s, 3H), 3.67–3.72 (m, 1H), 3.55–3.60 (m, 1H), 3.56 (d, $J = 4.8$ Hz, 1H), 3.39 (dt, $J = 10.5, 6.9$ Hz, 1H), 3.08 (t, $J = 5.7$ Hz, 1H), 2.46 (s, 3H), 2.41 (quint, $J = 6.3$ Hz, 1H), 1.89–1.96 (m, 2H), 1.45–1.51 (m, 1H), 1.18–1.23 (m, 2H), 0.94 (d, $J = 6.9$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H), 0.76 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.90, 171.66, 170.49, 144.59, 132.37, 129.95, 127.99, 69.11, 62.65, 57.15, 54.09, 51.98, 48.54, 39.46, 37.13, 32.17, 25.26, 21.58, 18.29, 15.50, 11.40. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{35}\text{N}_3\text{NaO}_7\text{S}$, 520.2088; found, 520.2083. **IR** (KBr, cm^{-1}): ν 3520, 3440, 2955, 1737, 1628, 1575, 1160, 813.

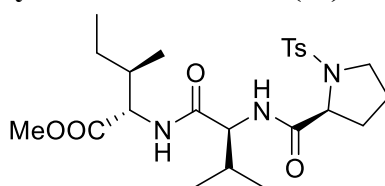
tert-butyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alanyl-*L*-prolinate(2y)



2y

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.77 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 6.9$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 4.70 (quint, $J = 6.9$ Hz, 1H), 4.49 (dd, $J = 8.7, 4.2$ Hz, 1H), 3.65–3.71 (m, 1H), 3.61 (d, $J = 4.2$ Hz, 1H), 3.57–3.60 (m, 1H), 3.49 (ddd, $J = 10.5, 7.2, 5.4$ Hz, 1H), 3.35 (dt, $J = 10.5, 7.2$ Hz, 1H), 2.40–2.47 (m, 1H), 2.43 (s, 3H), 2.17–2.24 (m, 1H), 1.99–2.06 (m, 2H), 1.94–1.99 (m, 1H), 1.91 (dt, $J = 13.8, 6.3$ Hz, 1H), 1.46 (s, 9H), 1.40 (d, $J = 6.8$ Hz, 3H), 1.21–1.24 (m, 1H), 0.68 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.00, 170.60, 170.34, 144.07, 133.60, 129.77, 128.02, 81.31, 68.91, 59.54, 48.22, 46.94, 46.77, 38.93, 32.02, 29.02, 28.00, 24.76, 21.56, 18.31, 18.05. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{25}\text{H}_{37}\text{N}_3\text{NaO}_6\text{S}$, 530.2295; found, 530.2284. **IR** (KBr, cm^{-1}): ν 3524, 3304, 1727, 1629, 1369, 1157, 802.

methyl tosyl-*L*-prolyl-*L*-valyl-*L*-alloisoleucinate(2z)

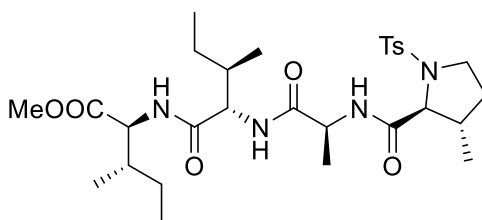


2z

Colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.25 (s, 1H), 7.01 (d, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 8.4, 5.8$ Hz, 1H), 4.39 (dd, $J = 9.2, 4.8$ Hz, 1H), 4.07 (dd, $J = 8.0, 3.2$ Hz, 1H), 3.73 (s, 3H), 3.64 (ddd, $J = 9.8, 6.0, 3.4$ Hz, 1H), 3.17–3.24 (m, 1H), 2.42–2.53 (m, 1H), 2.46 (s, 3H), 2.13–2.20 (m, 1H), 1.88–1.98 (m, 1H), 1.72–1.80 (m, 2H), 1.63–1.70 (m, 1H), 1.42–1.52 (m, 1H),

1.18–1.28 (m, 1H), 0.98 (d, $J = 10.8$ Hz, 3H), 0.96 (d, $J = 10.8$ Hz, 3H), 0.92 (d, $J = 10.0$ Hz, 3H), 0.89 (t, $J = 11.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.06, 171.33, 170.56, 144.66, 132.00, 130.04, 128.07, 62.47, 58.67, 56.71, 51.85, 50.23, 37.38, 30.51, 29.55, 25.21, 24.48, 21.57, 19.52, 17.16, 15.51, 11.36. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{24}\text{H}_{37}\text{N}_3\text{NaO}_6\text{S}$, 518.2295; found, 518.2301. IR (KBr, cm^{-1}): ν 3664, 3524, 2963, 1740, 1657, 1348, 1159, 802.

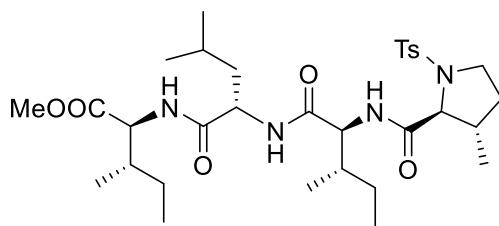
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alanyl-*L*-alloisoleucyl-*L*-isoleucinate(2aa)



2aa

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, $J = 7.8$ Hz, 2H), 7.38 (d, $J = 7.8$ Hz, 2H), 7.25 (d, $J = 7.8$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.68 (d, $J = 8.1$ Hz, 1H), 4.49–4.59 (m, 2H), 4.45 (t, $J = 6.9$ Hz, 1H), 3.70 (s, 3H), 3.58 (ddd, $J = 11.1, 9.9, 6.6$ Hz, 1H), 3.50 (d, $J = 4.8$ Hz, 1H), 3.38 (ddd, $J = 11.7, 8.1, 6.6$ Hz, 1H), 2.47 (s, 3H), 2.42 (quint, $J = 6.3$ Hz, 1H), 2.11 (dt, $J = 13.0, 6.6$ Hz, 1H), 1.88–1.93 (m, 2H), 1.51 (d, $J = 7.2$ Hz, 3H), 1.40–1.48 (m, 2H), 1.15–1.24 (m, 3H), 0.94 (d, $J = 7.2$ Hz, 3H), 0.93 (d, $J = 7.5$ Hz, 3H), 0.90 (d, $J = 7.8$ Hz, 3H), 0.89 (d, $J = 7.2$ Hz, 3H), 0.73 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.51, 172.23, 171.19, 171.12, 144.77, 131.88, 130.03, 127.90, 68.98, 57.29, 56.57, 51.95, 49.52, 48.55, 39.15, 37.39, 35.90, 32.16, 26.34, 25.29, 21.63, 18.22, 17.85, 15.48, 14.47, 11.56, 11k.52. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{29}\text{H}_{46}\text{N}_4\text{NaO}_7\text{S}$, 617.2979; found, 617.2977. IR (KBr, cm^{-1}): ν 3693, 3525, 3127, 1740, 1628, 1275, 1161, 817.

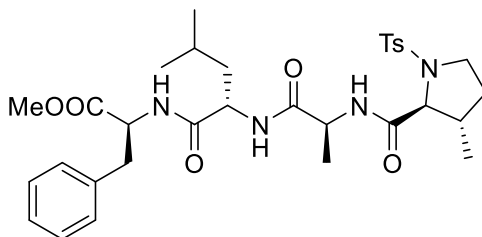
methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alloisoleucyl-*L*-leucyl-*L*-isoleucinate(2ab)



2ab

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 1H), 7.00 (d, $J = 8.1$ Hz, 1H), 6.99 (d, $J = 8.7$ Hz, 1H), 4.52 (dd, $J = 8.4, 5.4$ Hz, 1H), 4.45–4.49 (m, 2H), 3.73 (s, 3H), 3.62 (dt, $J = 11.6, 6.4$ Hz, 1H), 3.45 (d, $J = 5.1$ Hz, 1H), 3.37 (dt, $J = 10.4, 6.4$ Hz, 1H), 2.48 (s, 3H), 2.38 (dt, $J = 12.3, 6.3$ Hz, 1H), 2.28–2.34 (m, 1H), 1.89–1.98 (m, 2H), 1.64–1.75 (m, 3H), 1.42–1.51 (m, 2H), 1.20–1.27 (m, 2H), 1.10–1.17 (m, 1H), 0.98 (d, $J = 5.4$ Hz, 3H), 0.97 (d, $J = 5.1$ Hz, 3H), 0.93 (d, $J = 7.5$ Hz, 3H), 0.92 (t, $J = 5.7$ Hz, $2 \times 3\text{H}$), 0.88 (d, $J = 6.0$ Hz, 3H), 0.76 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.98, 171.90, 171.30, 171.15, 145.04, 131.29, 130.08, 127.99, 69.47, 58.30, 56.69, 51.96, 51.88, 48.53, 39.57, 38.96, 37.40, 35.59, 32.26, 25.12, 24.64, 24.32, 23.14, 21.66, 21.07, 18.36, 16.17, 15.47, 11.84, 11.63. **HRMS-ESI**(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{52}\text{N}_4\text{NaO}_7\text{S}$, 659.3449; found, 659.3441. **IR** (KBr, cm^{-1}): ν 3713, 3414, 2925, 1741, 1628, 1275, 1161, 618.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alanyl-*L*-leucyl-*L*-phenylalaninate(2ac)

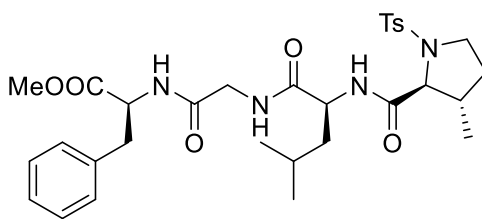


2ac

Colorless oil. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.16–7.24 (m, 3H), 7.11 (d, $J = 7.8$ Hz, 1H), 6.94 (d, $J = 7.8$ Hz, 1H), 6.93 (d, $J = 7.2$ Hz, 1H), 4.81 (dd, $J = 13.8, 6.9$ Hz, 1H), 4.50 (quint, $J = 7.2$ Hz, 1H), 4.36–4.40 (m, 1H), 3.70 (s, 3H), 3.59 (dt, $J = 10.8, 6.6$ Hz, 1H), 3.46 (d,

$J = 5.7$ Hz, 1H), 3.36 (dt, $J = 10.6, 6.9$ Hz, 1H), 3.19 (dd, $J = 13.8, 6.0$ Hz, 1H), 3.09 (dd, $J = 13.8, 6.9$ Hz, 1H), 2.47 (s, 3H), 2.38 (dt, $J = 12.8, 6.3$ Hz, 1H), 1.91 (dt, $J = 12.8, 6.4$ Hz, 1H), 1.63–1.70 (m, 2H), 1.58 (dd, $J = 9.9, 8.7$ Hz, 1H), 1.48 (d, $J = 7.3$ Hz, 3H), 1.18 (ddd, $J = 11.1, 7.2, 6.9$ Hz, 1H), 0.89 (d, $J = 6.0$ Hz, 3H), 0.87 (d, $J = 6.0$ Hz, 3H), 0.79 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.00, 171.77, 171.45, 171.25, 144.97, 136.51, 131.52, 130.11, 129.31, 128.42, 128.04, 126.78, 69.37, 53.53, 52.17, 52.15, 49.59, 48.62, 39.47, 37.88, 32.36, 24.82, 22.93, 21.86, 21.53, 18.35, 17.72. HRMS-ESI(m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{32}\text{H}_{44}\text{N}_4\text{NaO}_7\text{S}$, 651.2823; found, 651.2816. IR (KBr, cm^{-1}): ν 3714, 2960, 2929, 1735, 1638, 1380, 1161, 623.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-leucylglycyl-*L*-phenylalaninate(2ad)

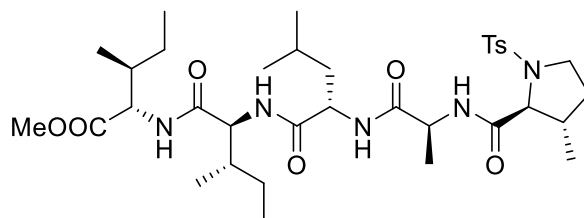


2ad

Colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 7.8$ Hz, 2H), 7.46 (t, $J = 4.5$ Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.2$ Hz, 2H), 7.22 (t, $J = 6.9$ Hz, 1H), 7.15 (d, $J = 7.2$ Hz, 2H), 6.98 (d, $J = 8.1$ Hz, 1H), 6.82 (d, $J = 7.5$ Hz, 1H), 4.84 (dd, $J = 12.8, 6.0$ Hz, 1H), 4.52–4.55 (m, 1H), 3.96 (dd, $J = 16.4, 6.0$ Hz, 1H), 3.88 (dd, $J = 16.4, 6.0$ Hz, 1H), 3.69 (s, 3H), 3.59 (dt, $J = 10.2, 6.3$ Hz, 1H), 3.47 (d, $J = 5.1$ Hz, 1H), 3.36 (dt, $J = 9.6, 6.9$ Hz, 1H), 3.16 (dd, $J = 13.8, 5.7$ Hz, 1H), 3.10 (dd, $J = 13.8, 6.1$ Hz, 1H), 2.47 (s, 3H), 2.38 (dt, $J = 11.9, 6.0$ Hz, 1H), 1.87–1.95 (m, 2H), 1.53–1.65 (m, 2H), 1.17–1.23 (m, 1H), 0.97 (d, $J = 6.3$ Hz, 3H), 0.93 (d, $J = 6.3$ Hz, 3H), 0.75 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.62, 171.62, 171.36, 168.80, 144.98, 136.14, 131.45, 130.08, 129.33, 128.50, 127.99, 126.90, 69.31, 53.39, 52.22, 52.06, 48.60, 43.51, 40.03, 39.53, 37.83, 32.26, 25.27, 23.15, 21.64, 21.24, 18.24. HRMS-

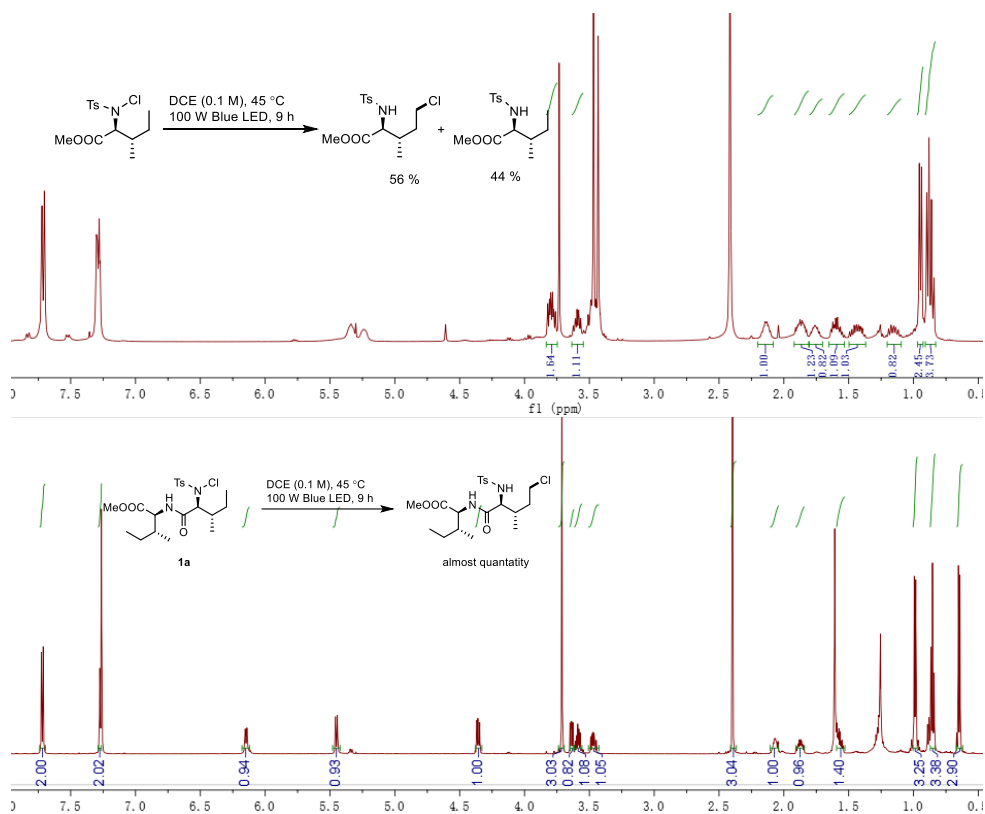
ESI(*m/z*): [M+Na]⁺ calcd. for C₃₁H₄₂N₄NaO₇S, 637.2666; found, 637.2656. IR (KBr, cm⁻¹): ν 3693, 3420, 2959, 2925, 1740, 1566, 1157, 667.

methyl ((2*S*,3*S*)-3-methyl-1-tosylpyrrolidine-2-carbonyl)-*L*-alanyl-*L*-leucyl-*L*-isoleucyl-*L*-isoleucinate(2ae)



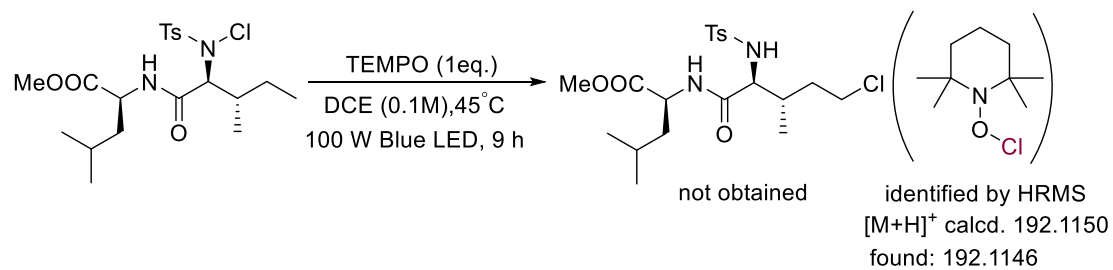
2ae

Colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 4.54 (dd, *J* = 8.1, 5.4 Hz, 1H), 4.49 (dd, *J* = 14.4, 7.2 Hz, 1H), 4.35–4.45 (m, 2H), 3.72 (s, 3H), 3.53 (d, *J* = 5.7 Hz, 1H), 3.47–3.52 (m, 1H), 3.37 (dt, *J* = 10.5, 6.9 Hz, 1H), 2.46 (s, 3H), 2.41 (dt, *J* = 12.9, 6.6 Hz, 1H), 1.94–2.02 (m, 2H), 1.89–1.94 (m, 1H), 1.60–1.66 (m, 2H), 1.53–1.58 (m, 1H), 1.47–1.52 (m, 1H), 1.40–1.47 (m, 1H), 1.45 (d, *J* = 7.2 Hz, 3H), 1.18–1.25 (m, 2H), 1.11–1.16 (m, 1H), 0.87–0.91 (m, 5×3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 172.28, 172.09, 171.77, 171.66, 171.17, 144.58, 132.94, 129.97, 127.86, 69.33, 57.95, 56.64, 52.68, 51.97, 49.21, 48.33, 40.88, 39.28, 37.54, 36.73, 32.44, 25.12, 24.84, 24.79, 22.92, 21.70, 21.59, 17.95, 17.19, 15.44, 15.40, 11.48, 11.23. HRMS-ESI(*m/z*): [M+Na]⁺ calcd. for C₃₅H₅₇N₅NaO₈S, 730.3820; found, 730.3812. IR (KBr, cm⁻¹): ν 3695, 3432, 3281, 2963, 2929, 1741, 1640, 1351, 1161, 816.



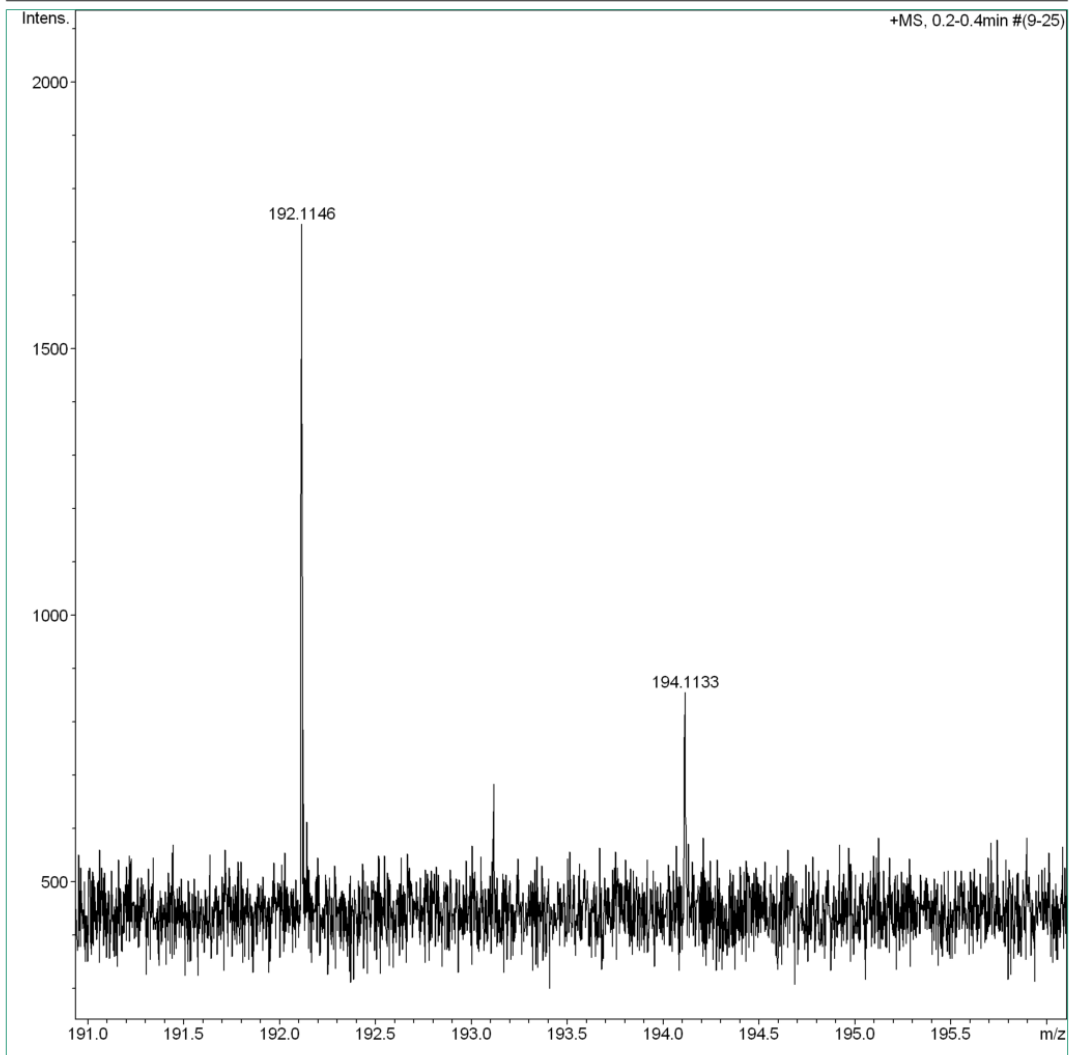
Comparison results of amino acid and dipeptide (crude ^1H NMR)

TEMPO Trapped Experiment



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	200.0 Vpp	Set Divert Valve	Waste



NMR Spectra

