Supporting Information To Accompany:

A Simple Nanoscale Method for Determining the Relative Stereochemistry of Statine Units.

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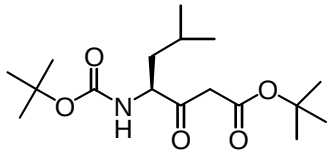
General Experimental Procedures. Optical rotations were measured at the sodium line (589 nm). IR bands were measured as a thin film on a NaCl disc. NMR spectra were acquired at 500 or 125 Mz using the residual solvent signals as an internal reference ($CDCl_3$ δ_H 7.24 ppm, δ_C 77.0 ppm). High-resolution mass spectral data were obtained using the ESI or APCI mode.

General Procedure for Production BOC-β-keto-γ-amino t-butyl esters. One gram of the protected amino acid (1 eq.) was dissolved in 20 mL of dry THF. To this solution was added 1.1 eq. of 1,1′-carbonyldiimidazole (recrystallized from THF) with stirring under dry nitrogen at room temperature. Butyl lithium (2.2M hexane solution, 3.3 equivalents) under nitrogen was diluted with 20 mL of THF and cooled to 0°C with an ice bath. To this was added dropwise diisopropylamine (3.6 equivalents). After stirring for ten minutes at 0°C, the solution was diluted with 70 mL of THF and cooled to -78°C. To the LDA solution was added either *t*-butyl acetate or allyl acetate (3.5 equivalents). After ten minutes, the BOC-amino acid/imidazole solution was cooled to -78°C and canulated into the enolate solution under nitrogen. The reaction was allowed to stir for 30 minutes at -78°C then quenched with 50 mL of 10% citric acid and allowed to warm to room temperature. The aqueous solution was extracted with 200 mL EtOAc (4x 50 mL) and washed with 100 mL saturated $NaHCO_3$ (2x50 mL), 50 mL brine, and dried over $MgSO_4$. The solvent was evaporated and crude material purified on silica mixtures of hexane/EtOAc).

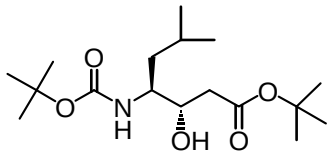
General procedure for Redution to Statine Amino Units. To a flame dried flask was added 0.5 g (1 eq.) of BOC-β-keto-γ-amino *t*-butyl ester dissolved in 20 mL dry THF and cooled to -78°C under nitrogen. To this solution was added 1.3 eq of $LiBH_4$ (recrystalized from Et_2O) which was stirred at -78°C until the reaction reached completion by as determined by TLC. The reaction was quenched by the addition of 1 N HCl and allowed to warm to room temperature over 15 min. This aqueous soltuion was extracted with 60 mL Et_2O (3x20 mL) and then dried over $MgSO_4$. Purification over silica eluting with Hexane/EtOAc provided a mixture of diastereomers. HPLC purification on silica provided pure diastereomers as needed.

Physical Data:



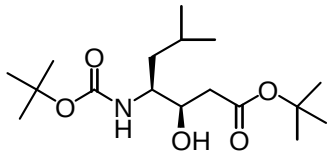
4a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-6-methyl-3-oxoheptanoate (4a):** amorphous powder: $[\alpha]^{26}_{D}$ = -4.4 (c 10, $CHCl_3$); IR (film) ν_{max} : 3349, 1722, 1705, 1689 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 4.90 (d, *J* =9.8 Hz, 1H), δ 4.31 (m, 1H), δ 3.49 (d, *J* =15.7 Hz, 1H), δ 3.40 (d, *J* =15.6 Hz, 1H), δ 1.68 (m, 3H), δ 1.47 (s, 9H), δ 1.42 (s, 9H), δ 0.94 (d, *J* =6.0 Hz, 3H), δ 0.91 (d, *J* =6.0 Hz, 3H); ^{13}C NMR 203.4, 166.2, 155.5, 82.0, 79.9, 58.1, 40.3, 39.8, 28.2, 27.8, 24.7, 23.2, 21.5; HRESI-MS *m/z* 352.2093 $[M + Na]^+$ [Calc. for $C_{17}H_{31}NO_5Na^+$, 352.2100, error 0.4 ppm].



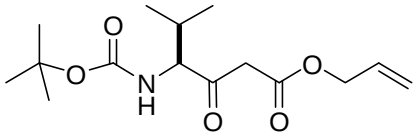
6a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-6-methylheptanoate (6a):** amorphous powder; $[\alpha]^{29}_{D}$ = -35 (c 1, $CHCl_3$); IR (film) ν_{max} : 3441, 3362, 1710, 1155 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 4.70 (d, *J* =9.8 Hz, 1H), δ 3.96 (m, 1H), δ 3.60 (m, 1H), δ 3.39 (d, *J* =4.6 Hz, 1H), δ 2.47 (dd, *J* =16.8, 10.2 Hz, 1H), δ 2.34 (dd, *J* =16.8, 2.4 Hz, 1H), δ 1.85 (m, 1H), δ 1.46 (s, 9H), δ 1.43 (s, 9H), δ 1.30 (m, 2H), δ 0.92 (d, *J* =5.9 Hz, 6H); ^{13}C NMR 172.3, 165.0, 81.4, 79.4, 71.3, 52.6, 39.0, 38.6, 28.3, 28.0, 24.7, 23.7, 21.5; HRESI-MS *m/z* 354.2246 $[M + Na]^+$ [Calc. for $C_{17}H_{33}NO_5Na^+$, 354.2257, 1.2 ppm error].



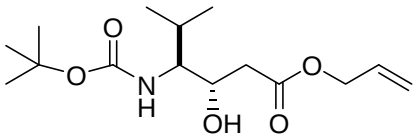
6b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-6-methylheptanoate (6b):** amorphous powder; $[\alpha]^{27}_{D}$ = -16.3 (c 1.5, $CHCl_3$); IR (film) ν_{max} : 3365, 1712 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 4.60 (d, *J* =9.8 Hz, 1H), δ 3.96 (m, 1H), δ 3.62 (m, 1H), δ 3.43 (d, *J* =8.9 Hz, 1H), δ 2.47 (dd, *J* =16.4, 2.2 Hz, 1H), δ 2.34 (dd, *J* =16.4, 8.9 Hz, 1H), δ 1.66 (m, 1H), δ 1.45 (s, 9H), δ 1.43 (s, 9H), δ 1.29 (m, 2H), δ 0.92 (d, *J* =6.7 Hz, 3H), δ 0.89 (d, *J* =6.5 Hz, 3H); ^{13}C NMR 172.3, 156.0, 81.3, 79.4, 71.3, 52.6, 39.0, 38.6, 28.4, 28.1, 24.7, 23.7, 21.6; HRESI-MS *m/z* 354.2120 $[M+Na]^+$ [Calc. for $C_{17}H_{33}NO_5Na^+$, 354.2099, 4.3 ppm error].



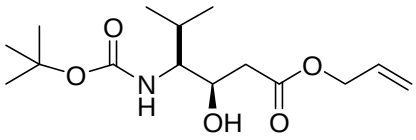
4b

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-5-methyl-3-oxohexanoate (4b): amorphous powder: $[\alpha]^{27}_{D}$ = +8.5 (c 5.4, $CHCl_3$); UV (*i*-PrOH) λ max (log ε) 248 (8.10) nm; IR (film) ν_{max} : 3369, 1749, 1246, 1168 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.90 (ddt, *J* =17.2, 10.4, 5.6 Hz, 1H), δ 5.33 (dd, *J* =17.2, 1.5 Hz, 1H), δ 5.28 (dd, *J* =10.4, 1.5 Hz, 1H) δ 5.06 (d, *J* =8.3 Hz, 1H), δ 4.63 (d, *J* =5.6 Hz, 2H), δ 4.32 (dd, *J* =8.7, 4.1 Hz, 1H), δ 3.57 (s, 2H), δ 2.24 (m, 1H), δ 1.48 (s, 9H), δ 1.01 (d, *J* =6.8 Hz, 3H), δ 0.82 (d, *J* =6.8 Hz, 3H); ^{13}C NMR 202.0, 166.2, 155.7, 131.5, 80.0, 66.0, 64.3, 47.0, 29.5, 28.2, 19.8, 16.7; HRESI-MS *m/z* 322.1636 $[M+Na]^+$ [Calc. for $C_{15}H_{25}NO_5Na^+$, 322.1631, -3.8 ppm error].



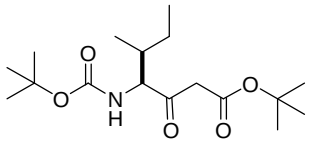
7a

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-5-methyl-3(*S*)-hydroxyhexanoate (7a): amorphous powder: $[\alpha]^{27}_{D}$ = -1.7 (c 1.0, $CHCl_3$); UV (*i*-PrOH) λ max (log ε) 248 (8.10) nm; IR (film) ν_{max} 3375, 1715, 1506, 1261, 1172 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.90 (ddt, *J* =17.2, 10.4 Hz, 1H), δ 5.33 (dq, *J* =17.2, 1.5 Hz, 1H), δ 5.26 (dd, *J* =10.4, 1.5 Hz, 1H), δ 4.83 (d, *J* =9.8 Hz, 1H), δ 4.60 (dt, *J* =5.8, 1.5 Hz, 2H), δ 4.20 (br. d, *J* =9.4 Hz, 1H), δ 3.20 (d, *J* =2.6 Hz, 1H), δ 3.15 (dt, *J* =10.5, 1.7 Hz, 1H), δ 2.60 (dd, *J* =16.9, 9.8 Hz, 1H), δ 2.51 (dd, *J* =16.9, 3.2 Hz, 1H), δ 1.86 (dm,1H), δ 1.43 (m, 9H), δ 0.99 (d, *J* =6.7 Hz, 3H), δ 0.96 (d, *J* =6.8 Hz, 3H); ^{13}C NMR: 173.3, 156.4, 131.7, 118.7, 79.2, 67.0, 65.5, 59.6, 39.0, 30.3, 29.7, 28.4, 19.8, 19.5; HRESI-TOF *m/z* 324.1767 $[M + Na]^+$ [Calc. for $C_{15}H_{27}NO_5Na^+$, 324.1787, -4.5 ppm error].



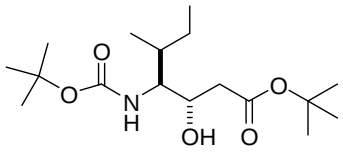
7b

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-5-methyl-3(*R*)-hydroxyhexanoate (7b): $[\alpha]^{24}_{D}$ = +7.9 (c 1.0, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 203 nm (7.56), 205 nm (5.54); IR (Film) ν_{max} : 3456, 3369, 1696 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.98 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.33 (ddt, *J* =17.2, 2.7, 1.5 Hz, 1H), δ 5.24 (dd, *J* =10.4, 1.1 Hz, 1H), δ 4.57 (dt, *J* =5.8, 1.3 Hz, 2H), δ 4.50 (d, *J* =9.6 Hz, 1H), δ 3.89 (td, *J* =8.4, 2.9 Hz, 1H), δ 3.49 (m, 1H), δ 2.58 (dd, *J* =16.5, 2.9 Hz, 1H), δ 2.46 (dd, *J* =16.5, 8.8 Hz, 1H), δ 2.09 (m, 1H), δ 1.43 (m, 9H), δ 0.94 (d, *J* =6.9 Hz, 3H), δ 0.88 (d, *J* =6.8 Hz, 3H); ^{13}C NMR 172.9, 156.4, 131.8, 118.6, 79.6, 69.2, 65.5, 58.8, 38.3, 28.3, 27.5, 20.1, 16.3; HRESI-TOF *m/z* 302.1955 $[M + H]^+$ [Calc. for $C_{15}H_{28}NO_5^+$, 302.1962, 2.4 ppm error].



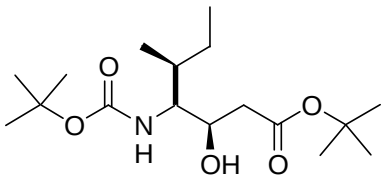
4c

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-methyl-3-oxoheptanoate (4c):** amorphous powder; $[\alpha]^{27}_{D}$ = -16.3 (c 1.5, $CHCl_3$); IR (film) ν_{max} : 3345, 1713, 1161 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.10 (d, *J* =8.6 Hz, 1H), δ 4.27 (m, 1H), δ 3.37 (m, 2H), δ 1.90 (m, 1H), δ 1.40 (s, 9H), δ 1.37 (s, 9H), δ 1.24 (m, 2H), δ 0.92 (d, *J* =6.7 Hz, 3H), δ 0.83 (t, *J* =7.3 Hz, 3H); ^{13}C NMR 202.7, 165.9, 155.7, 82.2, 79.9, 64.4, 48.5, 36.4, 28.3, 27.9, 24.1, 16.0, 11.7; HRESI-MS *m/z* 352.2107 $[M + Na]^+$ [Calc. for $C_{17}H_{31}NO_5Na^+$, 352.2100, error +1.9 ppm].



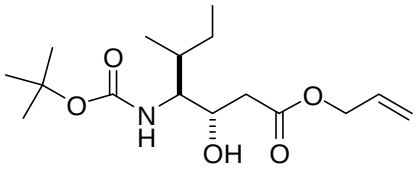
8a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-6-methylheptanoate (8a):** amorphous powder; $[\alpha]_D$ –17.5 (0.002, MeOH); IR (Film) ν_{max} : 3446, 3389, 1716, 1155 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 4.83 (d, *J* =10.0 Hz, 1H), δ 4.21 (d, *J* =10.0 Hz, 1H), δ 3.37 (s, 1H), δ 3.19 (t, *J* =9.4 Hz, 1H) δ 2.48 (dd, *J* =10.1, 16.8 Hz, 1H), δ 2.40 (dd, *J* =16.8, 2.8 Hz, 1H), δ 1.87 (m, 1H), δ 1.46 (s, 9H), δ 1.43 (s, 9H), δ 1.25 (m, 2H), δ 0.91 (s, 9H), δ 0.83 (t, *J* =7.3 Hz, 3H); ^1H NMR (DMSO at room temperature) δ 6.06 (d, *J* =9.9 Hz, 1H), δ 4.56 (d, *J* =7.3 Hz, 1H), δ 4.02 (ddd, *J* =8.4, 7.1, 1.9 Hz, 1H), δ 3.12 (td, *J* =9.8, 1.7 Hz, 1H), δ 2.21 (m, 2H), δ 1.52 (m, 3H), δ 1.38 (s, 9H), δ 1.37 (s, 9H), δ 0.86 (d, *J* =6.7 Hz, 3H), δ 0.83 (t, *J* =7.3 Hz, 3H); ^{13}C NMR 173.3, 156.4, 81.5, 79.0, 66.9, 58.0, 39.9, 36.6, 28.3, 28.1, 25.6, 15.7, 11.2; HRESI-MS *m/z* 354.2264 $[M + Na]^+$ [Calc. for $C_{17}H_{33}NO_5Na^+$, 354.2264, +2.0 ppm error].



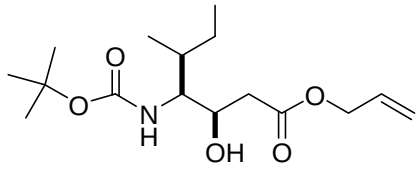
8b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]- 3(*R*)-hydroxy-6-methylheptanoate (8b):** amorphous powder; $[\alpha]^{26}_{D}$ = -4.4 (c 10, $CHCl_3$); IR (Film) ν_{max} 3451, 3366, 1705, 1156 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 4.42 (d, *J* =9.9 Hz, 1H), 3.93 (m, 1H), δ 3.53 (m, 1H), δ 3.38 (d, *J* =4.4 Hz, 1H), δ 2.54 (dd, *J* =16.4, 2.8 Hz, 1H), δ 2.42 (dd, *J* =16.4, 8.8 Hz, 1H), δ 1.79 (m, 1H), δ 1.57 (m, 2H), δ 1.45 (s, 9H), δ 1.42 (s, 9H), δ 0.89 (m, 6H); ^1H NMR (DMSO at room temperature) δ 4.73 (d, *J* =7.1 Hz, 1H), δ 3.82 (m, 1H), δ 2.26 (dd, *J* =8.4, 4.5 Hz, 1H); δ 2.32 (dd, *J* =15.1, 2.8 Hz, 1H), δ 2.06 (dd, *J* =15.1, 9.6 Hz, 1H), δ 1.60 (m, 1H), δ 1.46 (m, 2H), δ 1.39 (s, 9H), δ 1.36 (s, 9H), δ 0.82 (t, *J* =7.1 Hz, 3H), δ 0.78 (d, *J* =6.8 Hz, 3H); ^{13}C NMR 11.7, 16.3, 23.2, 28.0, 28.3, 34.5, 39.3, 58.8, 68.9, 79.3, 81.2, 156.3, 173.6; HRESI-MS *m/z* 354.2247 $[M + Na]^+$ [Calc. for $C_{17}H_{33}NO_5Na^+$, 354.2256, –2.7 ppm error].



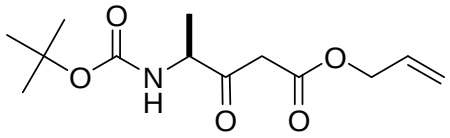
9a

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]- 3(*S*)-hydroxy-6-methylheptanoate (9a): amorphous powder; $[\alpha]_D$ –40.3 (0.2, MeOH); IR (Film) ν_{max} 3444, 3388, 1717, 1505, 1176 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.94 (m, 1H), δ 5.35 (d, *J* =17.3 Hz, 1H), δ 5.28 (d, *J*=10.4 Hz, 1H), δ 4.85 (d, *J*=9.9 Hz, 1H), δ 4.64 (d, , *J*=5.6 Hz, 2H), δ 4.30 (d, , *J*=9.6 Hz, 1H), δ 3.24 (m, 2H), δ 2.62 (dd, *J*= 16.9, 9.9 Hz, 1H), δ 2.50 (dd, *J*=16.9, 2.5, 1H), δ 1.60 (m, 1H), δ 1.22 (m, 2H), δ 0.98 (d, *J*= 6.6 Hz, 3H), δ 0.91 (t, *J*= 7.3 Hz, 3H). ^{13}C NMR 174.2, 160.2, 131.5,. 118.6, 66.8, 65.3, 57.9, 38.8, 36.3, 28.2, 25.4, 15.6, 11.0; HRESI-MS *m/z* 338.1945 $[M + Na]^+$ [Calc. for $C_{16}H_{29}NO_5Na^+$, 338.1943, –2.3 ppm error].



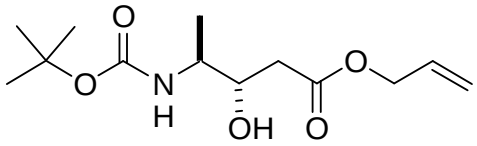
9b

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]- 3(*R*)-hydroxy-6-methylheptanoate (9b): amorphous powder; $[\alpha]_D$ +9.2 (0.2, MeOH); IR (Film) ν_{max} 3436, 3362, 1711, 1519, 1168 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.92 (m, 1H), δ 5.33 (d, *J* =17.2 Hz, 1H), δ 5.23 (d, J=10.4 Hz, 1H), δ 4.62 (d, *J*=5.7 Hz, 2H), δ 4.40 (d, , *J*=9.8 Hz, 2H), δ 4.02 (d, *J*=7.0 Hz, 1H), δ 3.57 (m, 1H), δ 2.61 (dd, *J*= 16.4, 10.8 Hz, 1H), δ 2.48 (dd, *J*=16.4, 2.4, 1H), δ 1.87 (m, 1H), δ 1.78 (m, 2H), δ 0.98 (d, *J*= 6.7 Hz, 3H), δ 0.91 (t, *J*= 7.3 Hz, 3H); HRESI-MS *m/z* 338.1956 $[M + Na]^+$ [Calc. for $C_{16}H_{29}NO_5Na^+$, 338.1943, –5.7 ppm error].



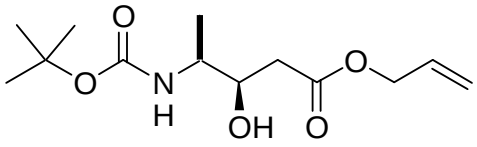
4d

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3-oxopentanoate (4d): amorphous powder $[\alpha]^{27}_{D}$ = +3.73 (c 10, $CHCl_3$), UV (ethyl acetate) λ_{max} (log ε) 257 nm (7.42); IR (Film) ν_{max} : 3375, 1713, 1690, 1648, 1512 cm^{-1}, ^1H NMR ($CDCl_3$ at room temperature) δ 5.90 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.34 (ddd, *J* =17.7, 3.3, 1.5 Hz, 1H), δ 5.25 (ddd, *J* =17.7, 2.3, 1.2 Hz, 1H), δ 5.10 (d, *J* =7.1 Hz, 1H), δ 4.60 (dt, *J* =5.8, 1.4 Hz, 2H), δ 4.37 (p, *J* =7.4, 7.2 Hz, 1H), δ 3.60 (d, *J* =16.1 Hz, 1H), δ 3.56 (d, *J* =16.1 Hz, 1H),δ 1.43 (s,9H), δ 1.35 (d, *J* =7.2 Hz, 3H); ^{13}C NMR 202.3, 166.6, 155.2, 131.4, 118.9, 80.1, 66.0, 55.4, 45.7, 28.3, 16.9; HRESI-MS *m/z* 294.1340 $[M+Na]^+$ [Calc. for $C_{13}H_{21}NO_5Na^+$, 294.1320, -1.9 ppm error].



10a

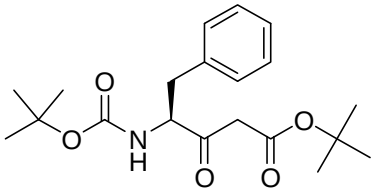
Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxypentanoate (10a): amorphous powder, $[\alpha]^{26}_{D}$ = -17.4 (c 1, $CHCl_3$), UV (*i*-PrOH) λ_{max} (log ε) 238 nm (6.04); IR (Film) ν_{max} : 3375, 1713, 1690, 1648, 1512 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.90 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.32 (dq, *J* =17.2, 1.5 Hz, 2H), δ 5.31 (br. d, *J* =10.4 Hz, 1H), δ 4.80 (br s, 1H), δ 4.62 (d, *J* =5.9 Hz, 2H), δ 3.99 (br. s, 1H), δ 3.66 (m, 1H), δ 3.32 (br s, 1H), δ 2.54 (m, 2H), δ 1.43 (s, 9 H), δ 1.21 (d, *J* =6.7 Hz, 3H); ^1H NMR (acetone-d_6 at room temperature) δ 6.24 (ddt, *J* =17.2, 10.9, 5.5 Hz, 1H), δ 5.90 (br d, *J* =6.9 Hz, 1H), δ 5.60 (dq, *J* =17.4, 1.4 Hz, 1H), δ 5.48 (dq, *J* =17.3, 1.6 Hz, 1H), δ 4.87 (dt, *J* =5.4, 1.5 Hz, 2H), δ 4.45 (d, 5.5 Hz, 1H), δ 4.44 (m ,1H), δ 4.00 (m, 1H), δ 2.84 (dd, *J* =15.6, 4.4 Hz, 1H), δ 2.77 (dd, *J* =15.6, 8.9 Hz, 1H), δ 1.74 (s, 9H), δ 1.46 (d, 6.9 Hz, 3H), ^1H NMR (DMSO at room temperature) δ 6.48 (d, *J* =8.4 Hz, 1H), δ 5.91 (ddt, *J* =17.2, *J* =10.4, *J* =5.8 Hz, 1H), δ 5.30 (br. d, *J* =17.3 Hz, 1H), δ 5.19 (br. d, *J* =10.5 Hz, 1H), δ 4.89 (d, *J* =5.9 Hz, 1H), δ 4.54 (d, *J* =4.3 Hz, 2H), δ 3.85 (m, 1H), δ 3.54 (br.m, 1H), δ 2.46 (dd, *J* =15.6, 2.9 Hz, 1H), δ 2.21 (dd, *J* =15.1, 9.7 Hz, 1H), δ 1.40 (s, 9H), δ 0.98 (d, *J* =6.8 Hz, 3H); 172.6, 155.8, 131.7, 118.5, 79.3, 70.5 65.4, 49.7, 38.7, 28.3, 18.2; HRESI-MS *m/z* 296.1482 $[M+Na]^+$ [Calc. for $C_{13}H_{23}NO_5Na^+$, 296.1474, -4.9 ppm error].



10b

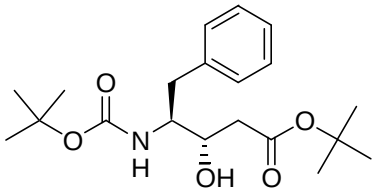
Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxypentanoate (10b): amorphous powder, $[\alpha]^{31}_{D}$ = +1.6 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 206 nm (6.99), 278 nm (5.85); IR (Film) ν_{max} : 3376, 1716, 1699, 1684, 1259, 1160 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.93 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.33 (dq, *J* =17.2, 1.5 Hz, 1H), 5.26 (dq, *J* =10.4, 1.5 Hz, 1H), δ 4.74 (d, *J* =6.4 Hz, 1H), δ 4.62 (dt, *J* =5.8, 1.3 Hz, 2H), δ 4.04 (sext, *J* =4.8,1H), δ 3.70 (m, 1H), δ 3.48 (d, *J* =4.3 Hz, 1H), δ 3.35 (br. s,1H), δ 2.50 (m, 2H), δ 1.44 (s, 9 H), δ1.13 (d, *J* =6.8 Hz, 3H); ^1H NMR (DMSO at room temperature) δ 6.62 (d, *J* =9.1 Hz, 1H), δ 5.90 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.30 (dm, *J* =17.3 Hz, 1H), δ 5.29 (dm, *J* =10.5 Hz, 1H), δ 4.93 (d, *J* =6.0 Hz, 1H), δ

4.54 (d, *J* =5.2 Hz, 1H), δ 3.73 (m, 1H), δ 3.31 (m, 1H), δ 2.46 (dd, *J* =15.2, 3.5 Hz, 1H), δ 2.24 (dd, *J* =15.2, 9.9 Hz, 1H), δ 1.37 (s, 9H), δ 0.99 (d, *J* =6.6 Hz, 1H); ^{13}C NMR 172.4, 155. 8, 131.8, 118.7, 79.3, 70.9, 65.5, 49.6, 38.0, 28.4, 15.2; HRESI-MS *m/z* 296.1482 $[M+Na]^+$ [Calc. for $C_{13}H_{23}NO_5Na^+$, 296.1474, -4.8 ppm].



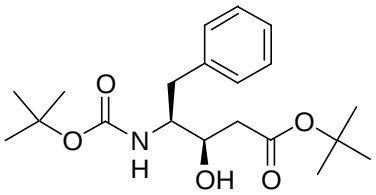
4e

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-phenyl-3-oxopentanoate (4e):** amorphous powder; $[\alpha]^{27}_D$ = +3.73 (c 10, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 210 nm (8.85), 244 nm (8.05); IR (Film) ν_{max} 3357, 1705, 1689, 1499, 1252, 1167 cm^{-1}; ^{1}H NMR δ 7.27 (m, 5H), δ 5.06 (d, *J* =7.6 Hz, 2H), δ 4.58 (q, *J* =7.3 Hz,1H), δ 3.43 (d, *J* =15.9 Hz, 1H), δ 3.36 (d, *J* =15.9 Hz, 1H), δ 3.16 (dd, 14.1, 6.0 Hz, 1H), δ2.98 (dd, 14.1, 7.2 Hz, 1H), δ 1.46 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR: 202.3, 166.1, 136.2, 19.2, 128.6, 126.9, 82.2, 80.1, 60.4, 48.1, 37.0, 28.2, 27.9; HRESI-MS *m/z* 386.1941 $[M+Na]^+$ [Calc. for $C_{20}H_{29}NO_5Na^+$, 386.1944, -0.7 ppm error].



11a

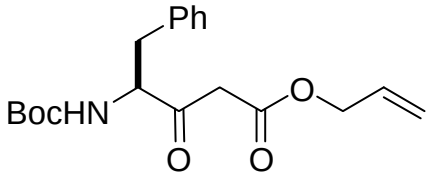
***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy 4-phenylpentanoate (11a):** amorphous powder; $[\alpha]_D$ –36.6 (c 1, MeOH), $[\alpha]^{27}_D$ = -1.3 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 209 (3.95) nm; IR (Film) ν_{max} : 3365, 1698 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 7.24 (m, 5H), δ 4.98 (d, *J* =9.4 Hz, 1H), δ3.92 (d, *J* =10.5 Hz, 1H), δ 3.68 (m, 1H), δ 2.90 (d, *J* =7.6 Hz, 2H), δ 2.51 (dd, *J* =16.9, 10.4 Hz, 1H), δ 2.27 (dd, *J* =16.9, 2.4 Hz, 1H), δ1.42 (s, 9H), δ 1.40 (s, 9H); ^{1}H NMR (DMSO at room temperature) δ 7.22 (m, 5H), δ 6.45 (d, *J* =9.2 Hz, 1H), δ 4.92 (d, *J* =6.2 Hz, 1H), δ 3.85 (m, 1H), δ 3.65 (m, 1H), δ 2.80 (dd, *J* =13.6, 5.1 Hz, 1H), δ 2.56 (dd, *J* =13.5, 9.5 Hz, 1H), δ 2.34 (dd, *J* =15.1, 4.2 Hz, 1H), δ 2.17 (dd, *J* =15.2, 8.8 Hz, 1H), δ 1.37 (s, 9H), δ 1.30 (s, 9H); ^{13}C NMR 172.8, 155.7, 138.2, 129.4, 128.3, 126.2, 81.3, 79.2, 66.9, 55.3, 39.6, 38.6, 28.3, 28.0; HRESI-MS *m/z* 388.2095 $[M+Na]^+$ [Calc. for $C_{20}H_{31}NO_5Na^+$, 388.2089, –1.3 ppm error].



11b

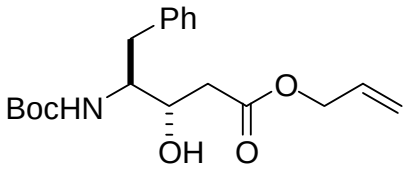
***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-4-phenylpentanoate (11b):** amorphous powder; $[\alpha]_D$ –14.5 (c 1, MeOH), $[\alpha]^{28}_D$ = 1.9 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 209 (4.17) nm; IR (Film) ν_{max} : 3367, 1728, 1690, 1158 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 7.24 (m, 5H), δ 4.57 (d, *J* =8.2 Hz, 1H), δ3.99 (m, 1H), δ3.82 (m, 1H), δ3.66 (br. s, 1H), δ 2.96 (dd, *J* =13.8, 3.5 Hz, 1H), δ2.83 (dd, *J* =13.7, *J* =8.4 Hz, 1H), δ 2.52 (dd, *J* =16.6, 2.4 Hz, 1H), δ 2.40 (dd, *J* =16.5, 8.9 Hz, 1H), δ 1.46 (s, 9H), δ1.33 (s, 9H); ^{1}H NMR

(DMSO at room temperature) δ 7.20 (m, 5H), δ 4.56 (br d, *J* =8.8 Hz, 1H), δ 3.93 (m, 1H) δ 3.82 (m, 1H), 3.67 (m, 1H), δ 3.00 (dd, *J* =14.1, 4.1 Hz,1H), δ 2.88 (dd, *J* =13.4, 9.0 Hz, 1H), δ2.52 (dd, *J* =17.2, 3.0 Hz, 1H), 2.41 (dd, *J* =16.5, 8.8 Hz, 1H), δ 1.40 (s, 9H), δ 1.33 (s, 9H); ^{13}CNMR 172.4, 155.6, 137.8, 129.5, 128.3, 126.3, 81.4, 79.4, 70.1, 55.1, 39.2, 35.7, 28.2, 28.0; HRESI-MS *m/z* 388.2094 $[M+Na]^+$ [Calc. for $C_{20}H_{31}NO_5Na^+$, 388.2089, 0.2 ppm error].



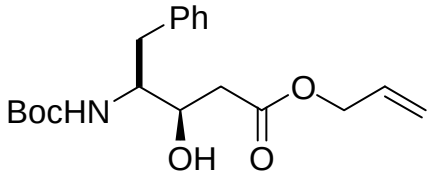
4f

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-phenyl-3-oxopentanoate (4g): amorphous powder; $[\alpha]^{25}_D$ = -6.65 (c 1, $CHCl_3$); UV (ethyl acetate) λ_{max} (log ε) 254 nm (7.98), 257 nm (7.94), 288 nm (6.78); IR (Film) ν_{max}: 3345, 1745, 1713, 1690, 1517 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 7.32 (m, 5H), δ 5.93 (ddt, *J* =17.2, 10.4, 5.8 1H), δ 5.33 (d, *J* =17.2 Hz, 1H), δ 5.25 (dm, *J* =10.4 Hz, 1H), δ 5.01 (d, *J* =6.7 Hz, 1H), δ 4.61 (d, *J* =5.4 Hz, 2H), δ 4.52 (m, 1H), δ 3.63 (d, *J* =16.8 Hz, 1H), δ 3.54 (d, *J* =16.2 Hz, 1H), 3.51 (d, *J* =16.2 Hz, 1H), δ 3.15 (dd, *J* =14.0, 6.0 Hz, 1H), δ 2.98 (dd, *J* =14.0, 7.4 Hz, 1H), δ 1.39 (s, 9H); ^{13}C NMR 201.7, 166.3, 154.8, 136.0, 131.4, 129.7, 128.5, 126.9, 118.7, 80.0, 65.9, 60.4, 46.6, 36.6, 28.1; HRESI-MS *m/z* 370.1637 $[M+Na]^+$ [Calc. for $C_{19}H_{25}NO_5Na$, 370.1631, -3.5 ppm error].



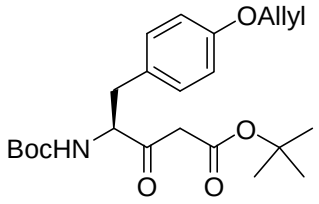
12a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy 4-phenylpentanoate (12a):** amorphous powder; $[\alpha]^{22}_D$ = -16.5 (c 1, $CHCl_3$);UV (*i*-PrOH) λ_{max} (log ε) 206 nm (7.07), 210 nm (7.04); IR (Film) ν_{max} 3492, 3358, 1715, 1686, 1519, 1366, 1260, 1166 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 7.26 (m, 5H), δ 5.88 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.28 (dq, *J* =17.2, 1.4 Hz, 1H), δ 5.24 (d, *J* =10.4 Hz, 1H), δ 4.94 (d, *J* =9.5 Hz, 1H), δ 4.57 (d, *J* =5.8 Hz, 2H), δ 3.99 (d, *J* =10.0 Hz, 1H), δ 3.73 (q, *J* =8.3 Hz, 1H), δ 3.42 (br.s, 1H), δ 2.91 (d, *J* =7.8 Hz, 2H), δ 2.63 (dd, *J* =17.1, 10.3 Hz, 1H), δ 2.41 (dd, *J* =17.0, 2.6 Hz, 1H), δ 1.40 (s, 9H); ^{13}C NMR 173.2, 155.8, 138.1, 131.6, 129.4, 128.5, 126.4, 118.7, 79.4, 67.0, 65.5, 55.4, 38.6, 28.3; HRESI-MS *m/z* 350.1958 $[M+H]^+$ [Calc. for $C_{19}H_{28}NO_5$, 350.1958, 1.3 ppm error].



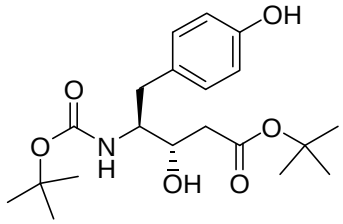
12b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy 4-phenylpentanoate (12b):** amorphous powder; $[\alpha]^{20}_{D}$ = +2.1 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 203 nm (7.22), 211 nm (6.98), 240 nm (5.87); IR (Film) ν_{max} 3353, 1734, 1680, 1523, 1270, 1170 cm^{-1}; ^1H NMR δ 7.20 (m, 5H), δ 5.97 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* =17.3, 1.5 Hz, 1H), 5.31 (dq, *J* =10.4, 1.5 Hz, 1H), δ 4.67 (dt *J* =5.8, 1.4 Hz, 2H), δ 4.62 (br d, *J* =8.8 Hz, 1H), δ 4.07 (m, 1H) δ 3.92 (m, 1H), δ 3.04 (dd, *J* =14.1, 4.6 Hz, 1H), δ 2.95 (dd, *J* =14.1, 8.9 Hz, 1H), δ2.78 (dd, *J* =16.4, 3.0 Hz, 1H), 2.64 (dd, *J* =16.5, 8.8 Hz, 1H), δ 1.40 (s, 9H); ^{13}C NMR 172.5, 155.8, 137.6, 131.7, 129.4, 128.4, 126.4, 118.6, 79.6, 65.5, 64.3, 55.3, 38.3, 35.8, 28.2; HRESI-MS *m/z* 350.1948 $[M+H]^+$ [Calc. for $C_{19}H_{28}NO_5$, 350.1958, 4.2 ppm error].



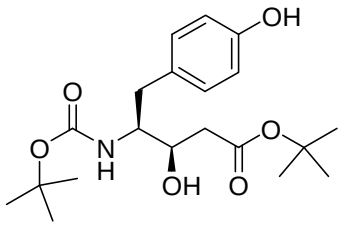
4g

***tert*-butyl 5-(4-(allyloxy)phenyl)-4-(*tert*-butoxycarbonylamino)-3-oxopentanoate (4g):** $[\alpha]^{24}_{D}$ = +10 (c 1, $CHCl_3$);UV (*i*-PrOH) λ_{max} (log ε) 205 nm (6.88), 228 nm (6.83), 278 nm (5.66); IR (Film) ν_{max} 3364, 1714, 1511, 1246, 1164 cm^{-1}; ^1H NMR δ 7.09 (d, *J* =8.2 Hz, 2H), 6.93 (d, *J* =8.2 Hz, 2H), 6.05 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.42 (d, *J* =17.2 Hz, 1H), δ 5.35 (d, *J* =10.2 Hz, 1H), δ 5.04 (d, *J* =5.9 Hz, 1H), δ 4.53 (br. d, *J* =4.1 Hz, 2H), 4.13 (q, *J* =8.3 Hz, 1H), 3.74 (br. s, 1H), δ 3.42 (d, *J* =15.9 Hz, 1H), 3.38 (d, *J* =15.5 Hz, 1H), δ 3.09 (dd, *J* =14.1, 6.4 Hz, 1H), δ 2.94 (dd, *J* =13.5, 6.7 Hz, 1H), δ 1.47 (s, 9H), δ 1.41 (s, 9H); ^{13}C NMR: 202.0, 165.8, 157.1, 154.9, 132.9, 114.4, 81.4, 79.3, 77.4, 68.2, 41.1, 35.4, 27.8, 27.5; HRESI-MS *m/z* 420.2365 $[M+H]^+$ [Calc. for $C_{23}H_{34}NO_6$, 420.2381, 3.8 ppm error].



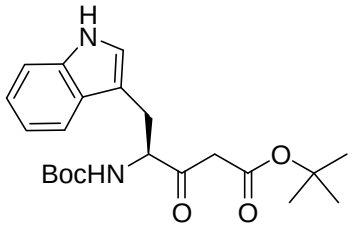
13a

***tert*-butyl 5-(4-(allyloxy)phenyl)-4(*S*)-(*tert*-butoxycarbonylamino)-3(*S*)-hydroxypentanoate (13a):** $[\alpha]^{28}_{D}$ = -22.5 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 227 nm (6.53), 279 nm (5.72); IR (Film) ν_{max} : 3363, 1715, 1697, 1684, 1157 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.11 (d, *J* =8.3 Hz, 2H), δ 6.81 (d, *J* =8.5 Hz, 2H), δ 4.99 (d, *J* =9.8 Hz, 1H), δ 3.94 (br d, *J* =10.2,1H), δ 3.73 (m, 1H), δ 2.83 (d, *J* =7.5 Hz, 2H), δ 2.51 (dd, *J* =17.0, 10.4 Hz, 1H), δ 2.28 (dd, *J* =17.0, 2.6 Hz, 1H), δ 1.44 (s, 9H), δ 1.42 (s, 9H); ^{13}C NMR 173.2, 155.9, 154.3 130.5, 130.2 115.3, 81.6, 79.5, 66.8, 55.6, 39.4, 37.8, 28.4, 28.1; HRESI-MS *m/z* 382.2229 $[M + H]^+$ [Calc. for $C_{20}H_{32}NO_6^+$, 382.2230, -1.3 ppm error].



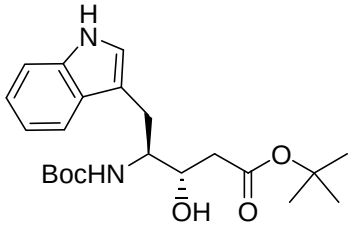
13b

***tert*-butyl 5-(4-(allyloxy)phenyl)-4(*S*)-(*tert*-butoxycarbonylamino)-3(*R*)-hydroxypentanoate (13b):** $[\alpha]^{28}_{D}$ = +2.4 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 226 nm (6.25), 278 nm (5.39); IR (Film) ν_{max} : 3398, 1681, 1649, 1155 cm^{-1}; ^1H NMR δ 7.08 (d, *J* =8.4 Hz, 2H), δ 6.84 (d, *J* =8.5 Hz, 2H), δ 4.56 (d, *J* =8.5 Hz, 1H), δ 3.93 (m, 1H), δ 3.78 (m, 1H), δ 3.64,(m, 1H), δ 2.88 (dd, *J* =14.2, 4.6 Hz, 1H), δ 2.82 (dd, *J* =14.2, 7.8 Hz, 1H), δ 2.51 (dd, *J* =16.4, 2.9 Hz, 1H), δ 2.41 (dd, *J* =16.6, 8.8 Hz, 1H), δ 1.47 (s, 9H), δ 1.36 (s, 9H); ^{13}C NMR 172.5, 155.8, 154.5, 130.5, 129.3, 115.3, 81.6, 79.7, 70.0, 55.3, 39.1, 34.9, 28.3, 28.1; HRESI-MS *m/z* 382.2210 $[M + H]^+$ [Calc. for $C_{20}H_{32}NO_6^+$, 382.2230, 3.8 ppm error].



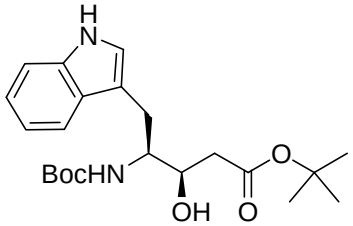
4h

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-indole-3-oxopentanoate (4h):** amorphous powder; $[\alpha]^{25}_{D}$ = +3.46 (c 10, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 224 nm (7.75), 282 nm (7.01); IR (Film) ν_{max} : 3402, 1705, 1690, 1164, 743 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 8.83 (br. s, 1H), δ 7.69 (d, *J* =7.8 Hz, 1H), δ 7.40 (d, *J* =7.9 Hz, 1H); δ 7.19 (t, *J* =7.2 Hz, 1H); 7.16 (t, *J* =7.4 Hz, 1H), δ 6.95 (br. s, 1H), δ 5.40 (d, *J* =7.6 Hz, 1H), δ 4.70 (q, *J* =6.5 Hz, 1H), δ 3.42 (d, *J* =5.8 Hz, 2H), δ 3.30 (dd, *J* =16.5, 7.6 Hz, 1H), δ 3.25 (dd, *J* =14.9, 6.5 Hz, 1H), δ 1.46 (s, 9H), δ 1.44 (s, 9H); ^{13}C NMR 203.0, 166.2, 155.3, 136.1, 127.3, 123.0, 122.0, 119.4, 118.5, 111.3, 109.6, 82.0, 79.9, 59.9, 48.0, 28.2, 27.8, 26.8; HRESI-MS *m/z* 425.2038 $[M + Na]^+$ [Calc. for $C_{22}H_{30}N_2O_5Na^+$, 425.2053, 2.7 ppm error].



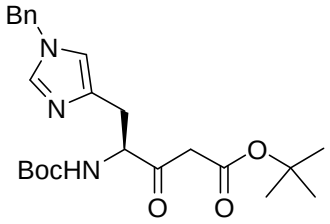
14a

***t*-Butyl 4(*S*)-[(tert-butoxycarbonyl)-amino]-3(*S*)-hydroxy 4-indolepentanoate (14a):** amorphous powder; $[\alpha]^{28}_{D}$ = -5.8 (c 2, $CHCl_3$); UV (EtOAc) λ_{max} (log ε) 285 nm (7.75), IR (Film) ν_{max} : 3415, 1713, 1690, 1681, 1251, 1162, 742 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 8.23 (br. s, 1H), δ 7.75 (d, *J* =7.8 Hz, 1H), δ 7.34 (d, *J* =8.0 Hz, 1H); δ 7.18 (t, *J* =7.2 Hz, 1H), 7.12 (t, *J* =7.0 Hz, 1H), 7.05 (s, 1H), δ 5.10 (d, *J* =9.6 Hz, 1H), δ 4.03 (br. d, *J* =10.3 Hz, 1H), δ 3.83 (q, *J* =7.9 Hz, 1H), δ 3.63 (br s, 1H), δ 3.07 (d, *J* =7.7 Hz, 2H), δ 2.53 (dd, *J* =16.9, 10.5 Hz, 1H), δ 2.25 (dd, *J* =16.9, 2.6 Hz, 1H), δ 1.45 (s, 9H), δ 1.41 (s, 9H); ^{13}C NMR 173.0, 156.0, 136.2, 127.6, 122.8, 121.8, 119.3, 119.0, 112.1, 111.0, 81.4, 79.2, 67.0, 57.5, 39.6, 28.4, 28.2, 27.9; HRESI-MS *m/z* 427.2232 $[M + Na]^+$ [Calc. for $C_{22}H_{32}N_2O_5Na^+$, 427.2214, 5.2 ppm error].



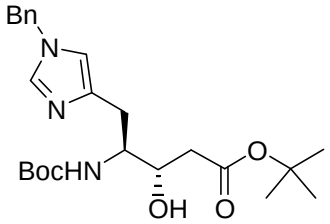
14b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy 4-indolepentanoate (14b):** amorphous powder; $[\alpha]^{28}_{D}$ = +3.1 (c 2, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 224 nm (7.39), 285 nm (6.58); IR (Film) ν_{max} : 3361, 1706, 1690, 1157 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 8.23 (br. s, 1H), δ 7.65 (d, *J* =7.8 Hz, 1H), δ 7.36 (d, *J* =7.9 Hz, 1H), δ 7.16 (dt, *J* =7.0, 1.2 Hz, 1H), 7.13 (dt, *J* =7.3, 1.2 Hz, 1H) δ 7.08 (br. s, 1H), δ 4.66 (d, *J* =5.8 Hz, 1H), δ 3.94 (m, 2H), δ 3.77 (br. s, 1H), δ 3.08 (br. s, 1H), δ 2.53 (dd, *J* =16.9, 1.0 Hz, 1H), δ 2.46 (dd, *J* =16.6, 8.0 Hz, 1H), δ 1.45 (s, 9H), δ 1.36 (s, 9H); ^{13}CNMR 172.5, 155.9, 136.1, 127.9, 122.9, 121.8, 119.3, 118.8, 111.2, 111.1, 81.4, 79.4, 69.9, 54.5, 39.1, 28.3, 28.0, 25.4; HRESI-MS *m/z* 427.2206 $[M + Na]^+$ [Calculated for $C_{22}H_{32}N_2O_5Na^+$, 427.2210, -0.8 ppm error].



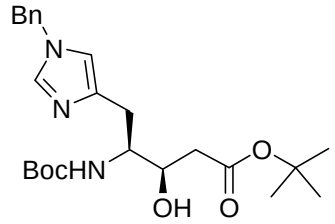
4i

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-(*N*-benzyl-imidazole)-3-oxopentanoate (4i):** amorphous powder; $[\alpha]^{25}_{D}$ = +0.45 (c 10, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 210 nm (8.48); IR (Film) ν_{max} : 3332, 1740, 1721, 1707, 1164 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.33-7.20 (m, 6H), δ 6.64 (br.s, 1H), δ 6.13 (d, *J* =7.2 Hz, 1H), δ 4.97 (br. s, 2H), δ 4.44 (q, *J* =5.4 Hz, 1H), δ 3.39 (br. s, 2H), δ 3.02 (dd, *J* =15.0, 5.7 Hz, 1H), δ 2.93 (dd, *J* =14.9, 5.0 Hz, 1H), δ 1.38 (s, 9H), δ 1.36 (s, 9H); ^{13}C NMR 203.1, 166.3, 155.5, 137.4, 136.8, 135.7, 128.8, 128.1, 127.1, 81.6, 79.6, 63.9, 59.7, 35.4, 28.8, 28.0; HRESI-MS *m/z* 444.2506 $[M + H]^+$ [Calc. for $C_{24}H_{33}N_3O_5^+$, 444.2499, -2.9 ppm error].



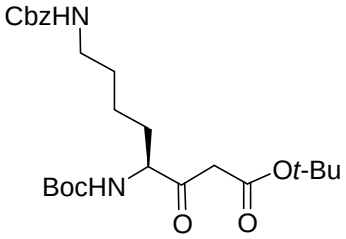
15a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-(*N*-benzyl-imidazole)-3(*S*)-hydroxypentanoate (15a):** $[\alpha]^{27}_{D}$ = +11.9 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 205 nm (7.70), 209 nm (7.57); IR (Film) ν_{max} : 3335, 1717, 1699, 1260, 1161cm^{-1}; ^1H NMR ($CHCl_3$ at room temperature) δ 7.68 (s, 1H), δ 7.40-7.22 (m, 5H), δ 6.73 (br.s, 1H), δ 5.33 (d, *J* =7.0 Hz, 1H), δ 5.19 (d, *J* =9.3 Hz, 1H), δ 5.14 (br. s, 2H), δ 4.19 (dd, *J* =7.4, 5.6 Hz,1H), δ 3.74 (m, 1H), δ 3.10 (dd, *J* =14.5, 8.2 Hz, 1H), δ 2.91 (dd, *J* =14.6, 4.7 Hz, 1H), δ 2.58 (dd, *J* =15.9, 8.2 Hz, 1H), δ 2.38 (dd, *J* =15.8, 5.0 Hz, 1H), δ 1.45 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR 171.6, 155.9, 135.8, 129.0 128.4, 127.3, 80.8, 78.9, 69.3, 53.2, 50.9, 40.3, 31.6, 29.7, 28.3, 28.1; HRESI-MS *m/z* 446.2649 $[M + H]^+$ [Calc. for $C_{24}H_{36}N_3O_5^+$, 446.2656, 0.1 ppm error].



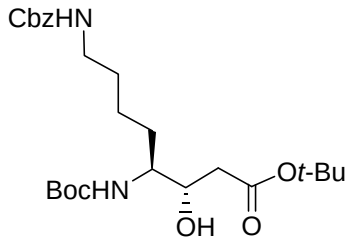
15b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-4-(*N*-benzyl-imidazole)-3(*R*)-hydroxypentanoate (15b):** amorphous powder: $[\alpha]^{26}_{D}$ = +45.6 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 205 nm (8.09), 286 nm (6.87); IR (film) ν_{max} : 3300, 1683, 1161 cm^{-1}; ^1H NMR ($CHCl_3$ at room temperature) δ 7.48 (s, 1H), δ 7.33-7.14 (m, 5H), δ 6.73 (br.s, 1H), δ 5.34 (d, *J* =5.9 Hz, 1H), δ 5.06 (br. s, 2H), δ 3.48 (m, 2H), δ 2.97 (dd, *J* =15.0, 2.4 Hz, 1H), δ 2.84 (dd, *J* =14.5, 1.6 Hz, 1H), δ 2.51 (m, 2H), δ 1.45 (s, 9H), δ 1.40 (s, 9H); ^1H NMR (CD_3OD at room temperature) δ 7.68 (s, 1H), δ 7.33 (m, 5H), δ 6.73 (br.s, 1H), δ 5.05 (br. s, 2H), δ 3.79 (m, 1H), δ 3.58 (m, 1H), δ 3.84 (dd, *J* =14.9, 3.5 Hz, 1H), δ 2.97 (dd, *J* =14.9, 2.4 Hz, 1H), δ 2.84 (dd, *J* =14.9 Hz, 1H), δ 1.46 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR: 172.1, 155.7, 138.4, 136.6, 135.9, 129.0 128.3, 127.3, 117.6, 80.8, 79.1, 69.9, 53.3, 50.9, 40.2, 29.7, 28.3, 28.1; HRESI-MS *m/z* 446.2653 $[M + H]^+$ [Calc. for $C_{24}H_{36}N_3O_5^+$, 446.2656, -0.8 ppm error].



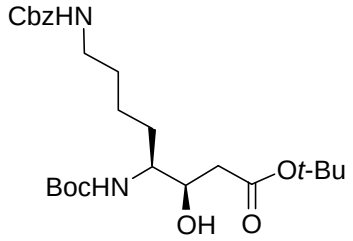
4j

***t*-Butyl 4(*S*),8-di[(*tert*-butoxycarbonyl)-amino]-3-oxooctanoate (4j):** amorphous powder; $[\alpha]^{27}_{D}$ = +1.5 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 210 nm (6.48), 235 nm (7.22); IR (Film) ν_{max}: 3339, 1707, 1249, 1163 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.32 (m, 5H), δ 5.37 (d, *J* =7.6 Hz, 1H), δ 5.18 (m, 1H), δ 5.01 (br. s, 2H), δ 4.23 (m, 1H), δ 3.42 (d, *J* =15.9 Hz, 1H), δ 3.34 (d, *J* =15.7 Hz, 1H), δ 3.09 (m, 2H), δ 1.76 (m, 6H), δ 1.40 (br. s, 9H) 1.36 (br s, 9H); ^{13}C NMR: 202.7, 166.1, 156.5, 136.5, 128.4, 128.0, 82.2, 78.0, 66.5, 59.3, 40.3, 30.4, 29.3, 28.2, 27.8, 22.1; HRESI-MS *m/z* 479.2748 $[M + H]^+$ [Calc. for $C_{25}H_{39}N_2O_7^+$, 479.2758, 0.9 ppm error].



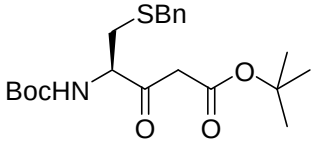
16a

***t*-Butyl 4(*S*),8-di[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxyoctanoate (16a):** amorphous powder, $[\alpha]^{29}_{D}$ = -27.9 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 209 nm (6.64), 214 nm (6.61), 233 nm (6.58); IR (film) ν_{max} : 3338, 1705, 1694, 1250, 1155 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.33 (m, 5H), δ 5.09 (s, 2H), δ 4.83 (m, 2H), δ 3.98 (m, 1H), δ 3.48 (m, 2H), δ 3.18 (m, 2H), δ 2.48 (d, *J* =16.7, 9.8 Hz, 1H), δ 2.36 (d, *J* =16.7, 3.2 Hz, 1H), δ 1.59 (m, 6H), δ 1.45 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR 172.8, 156.5, 156.1, 136.6, 128.4, 128.1, 127.9, 81.4, 79.2, 70.9, 69.0, 66.5, 53.6, 40.6, 39.6, 32.2, 29.5, 28.3, 28.0, 22.9**;** HR-APCI-MS *m/z* 481.2912 $[M + H]^+$ [Calc. for $C_{25}H_{41}N_2O_7^+$, 481.2915, -0.6 ppm error].



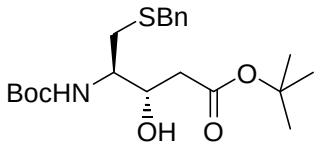
16b

***t*-Butyl 4(*S*),8-di[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxyoctanoate (16b):** amorphous powder; $[\alpha]^{27}_{D}$ = -6.3 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 206 nm (7.12), 233 nm (7.05); IR (Film) ν_{max}: 3337, 1695, 1256, 1153 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.34 (m, 5H), δ 5.09 (s, 2H), δ 4.85 (m, 1H), δ 4.73 (d, *J* =8.8 Hz, 1H), δ 3.95 (m, 1H), δ 3.57 (m, 1H), δ 3.46 (d, *J* =3.1 Hz, 1H), δ 3.20 (q, *J* =6.3 Hz, 1H), δ 2.42 (m, 2H), δ 1.60 (m, 6H), δ 1.45 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR 172.3, 156.5, 156.1, 136.6, 128.5, 128.1, 128.0, 81.5, 79.5, 70.9, 66.6, 54.0, 40.7, 39.0, 29.6, 29.1, 28.4, 28.1, 22.8; HR-APCI-MS *m/z* 481.2908 $[M + H]^+$ [Calc. for $C_{25}H_{41}N_2O_7^+$, 481.2915, 0.1 ppm error].



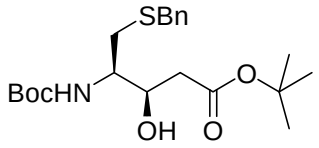
4k

***t*-Butyl 4(*R*)-[(*tert*-butoxycarbonyl)-amino]-3-oxo-5-(benzylthia)-pentanoate (4k):** amorphous powder; $[\alpha]^{25}_{D}$ = +0.35 (c 3.4, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 207 nm (7.71); IR (film) ν_{max}: 2975, 1740, 1712, 1706, 1695, 1158 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.31 (m, 5H), δ 5.31 (d, *J* =6.3 Hz, 1H), δ 4.48 (m, 1H), δ 3.73 (br. s, 2H), δ 3.48 (d, *J* =15.8 Hz, 1H), δ 3.38 (d, *J* =15.9 Hz, 1H), δ 2.88 (dd, *J* =13.7, 4.3 Hz, 1H), 2.74 (dd, *J* =13.2, 6.4 Hz, 1H), δ 1.45 (s, 18H); ^{13}C NMR 201.4, 166.0, 155.2, 137.6, 129.0, 128.6, 127.3, 82.3, 80.3, 58.6, 47.7, 36.7, 32.2, 28.3, 27.9; HRESI-MS *m/z* 432.1816 $[M+Na]^+$ [Calc. for $C_{21}H_{31}NO_5SNa^+$, 432.1821, -0.3 ppm error].



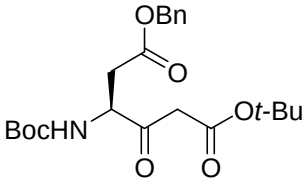
17a

***t*-Butyl 4(*R*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-5-(benzylthia)-pentanoate (17a):** amorphous powder; $[\alpha]^{26}_{D}$ = +4.5 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 205 nm (6.95), 238 nm (6.34); IR (film) ν_{max}: 3440, 1706, 1156 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.23 (m, 5H), δ 4.89 (d, *J* =8.4 Hz, 1H), δ 4.21 (d, *J* =9.9 Hz, 1H), δ 3.69 (br. s, 2H), δ 3.55 (s, 1H), δ 3.42 (br. s, 1H), δ 2.52 (m, 2H), δ 2.47 (dd, *J* =16.6, 10.2 Hz, 1H), δ 2.26 (dd, *J* =16.6, 1.0 Hz, 1H), δ 1.24 (br. s, 18H); ^{13}C NMR 172.7, 155.7, 138.2, 129.1, 128.4, 126.9, 81.6, 79.5, 67.0, 53.1, 39.5, 36.1, 33.2, 28.3, 28.0; HR-ESI-TOF *m/z* 412.2152 $[M + H]^+$ [Calc. for $C_{21}H_{34}NO_5S^+$, 412.2152, 4.1 ppm error].



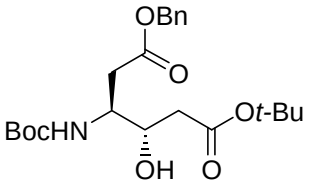
17b

***t*-Butyl 4(*R*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-5-(benzylthia)-pentanoate (17b):** amorphous powder; $[\alpha]^{26}_{D}$ = -3.7 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 222 nm (6.96), 283 nm (6.09); IR (Film) ν_{max}: 3372, 1704, 1689, 1156 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.89 (m, 5H), δ 4.86 (d, *J* =7.6 Hz, 1H), δ 3.96 (m, 1H), δ 3.75 (s, 2H), δ 3.74 (s, 1H), δ 3.52 (br. s, 1H), δ 2.69 (m, 2H), δ 2.47 (dd, *J* =16.6, 3.0 Hz, 1H), δ 2.35 (dd, *J* =16.6, 9.0 Hz, 1H), δ 1.45 (s, 9H), δ 1.42 (s, 9H); ^{13}C NMR 172.3, 155.6, 138.1, 128.9, 125.5, 127.1, 81.6, 79.7, 69.8, 53.2, 39.0, 36.6, 32.1, 28.3, 28.0; HR-APCI-TOF *m/z* 412.2157 $[M + H]^+$ [Calc. for $C_{21}H_{34}NO_5S^+$, 412.2152, -1.2 ppm error].



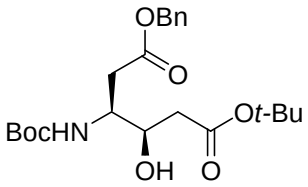
4l

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3-oxo-6-benzyl-hexandioate (4l)**: $[\alpha]^{27}_{D}$ = -4.3 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 207 nm (6.79), 212 nm (6.67), 258 nm (5.92); IR (Film) ν_{max} : 3365, 1716, 1162 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.36 (m, 5H), δ 5.48 (d, *J* =8.8 Hz, 1H), δ 5.13 (br. s, 2H); δ 4.58 (m, 1H), δ 3.52 (s, 2H), δ 3.02 (dd, *J* =15.9, 4.1 Hz, 1H), δ 2.81 (dd, *J* =15.9, 3.6 Hz, 1H), δ 1.49 (s, 9H), δ 1.44 (s, 9H); ^{13}C NMR 201.7, 171.3, 166.1, 155.3, 135.3, 128.6, 128.4, 128.2, 82.2, 80.5, 66.9, 56.0, 47.1, 35.3, 28.3, 27.9; HRESI-MS *m/z* 444.2013 $[M+Na]^+$ [Calc. for $C_{22}H_{31}NO_7Na^+$, 444.1999, -4.8 ppm].



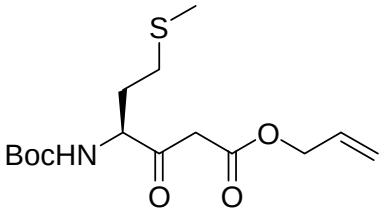
18a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-6-benzyl-hexandioate (18a)**: amorphous powder; $[\alpha]^{25}_{D}$ = +27.18 (c 0.13, $CHCl_3$); UV (ethyl acetate) λ_{max} (log ε) 255 nm (5.09); IR (film) ν_{max} : 3388, 1704, 1687, 1260 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.35 (m, 5H), δ 5.1 (m, 2H), δ 4.09 (m, 1H), δ 3.97 (m, 1H), δ 3.66 (br.s, 1H), δ 2.74 (dd, *J* =15.7, 7.4 Hz, 1H), δ 2.65 (dd, *J* =15.8, 6.0 Hz, 1H), δ 2.48 (dd, *J* =16.7, 10.0 Hz, 1H), δ 2.40 (dd, *J* =16.7, 3.0 Hz, 1H), δ 1.45 (s, 9H), δ 1.42 (s, 9H); HRESI-TOF *m/z* 424.2330 $[M+H]^+$ [Calc. for $C_{22}H_{34}NO_7$, 424.2336, 1.5 ppm error].



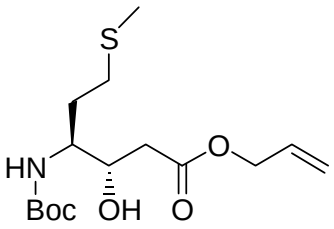
18b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-6-benzyl-hexandioate (18b)**: $[\alpha]^{25}_{D}$ = + 9.27 (c 2.2, $CHCl_3$); UV (ethyl acetate) λ_{max} (log ε) 255 nm (4.7); IR (Film) ν_{max} : 3370, 1703, 1696, 1685, 1260, 1649 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.35 (m, 5H), δ 5.31 (d, *J* =10.3 Hz, 1H), δ 5.13 (s, 2H), δ 4.01 (m, 1H), δ 3.90 (m, 1H), δ 3.60 (br.s, 1H), δ 2.74 (dd, *J* =15.7, 7.0 Hz, 1H), δ 2.64 (dd, *J* =16.1, 4.3 Hz, 1H), δ 2.52 (dd, *J* =16.4, 3.0 Hz, 1H), δ 2.47 (dd, *J* =17.9, 6.8 Hz, 1H), δ 1.45 (s, 9H), δ 1.41 (s, 9H); ^{13}C NMR 172.3, 172.0, 155.3, 135.6, 128.6, 128.3, 128.2, 81.6, 79.7, 69.6, 66.5, 51.1, 39.0, 34.5, 28.3, 28.0; HRESI-TOF *m/z* 424.2323 $[M+H]^+$ [Calc. for $C_{22}H_{34}NO_7^+$, 424.2336, -3.1 ppm error].



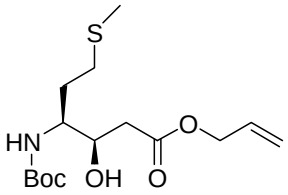
4m

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3-oxo-6-methylthiahexanoate (4m): amorphous powder; $[\alpha]^{25}_{D}$ = -18.1 (c 10, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 207 nm (8.03); IR (Film) ν_{max} : 3360, 1712, 1648, 1250, 1167 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.89 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.29 (dd *J* =17.2, 1.4 Hz, 2H), δ 5.17 (dd, *J* =10.4, 1.3 Hz, 1H), δ 5.08 (d, *J* =5.7 Hz, 1H), δ 4.60 (m, 2H), δ 4.39 (m, 1H), δ 3.46 (s, 2H), δ 2.50 (t, *J* =7.4 Hz, 2H), δ 2.20 (m, 1H), δ 1.72 (m, 1H), δ 2.01 (s, 3H), δ 1.40 (br. s, 9H); ^{13}C NMR 200.0, 131.4, 118.8, 65.9, 65.9, 60.3, 52.7, 49.9, 32.0, 29.8, 28.2; HRESI-MS *m/z* 354.1347 $[M+Na]^+$ [Calc. for $C_{15}H_{25}NO_5SNa^+$, 354.1351, -0.3 ppm error].



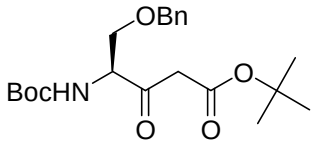
19a

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-6-methylthiahexanoate (19a): amorphous powder; $[\alpha]^{26}_{D}$ = +13.7 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 206 nm (6.97); IR (Film) ν_{max} : 3355, 1712, 1690, 1501, 1162 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.98 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.33 (dd, *J* =17.2, 1.4 Hz, 2H), δ 5.25 (dd, *J* =10.4, 1.1 Hz, 1H), δ 4.82 (d, *J* =9.5 Hz, 1H), 4.62 (d, *J* =5.4 Hz, 1H), δ 4.09 (m, 1H), δ 3.66 (m, 1H), δ 3.34 (br s, 1H), δ 2.54 (m, 4H), δ 1.60 (s, 3H), δ 1.88 (m, 2H), δ 1.45 (br. s, 9H); ^{13}C NMR 173.0, 156.0, 131.7, 118.8, 79.5, 69.1, 65.5, 53.1, 38.6, 32.3, 30.7, 28.3, 15.5; HRESI-MS *m/z* 356.1506 $[M+Na]^+$ [Calc. for $C_{15}H_{27}NO_5SNa^+$, 356.1508, –1.0 ppm error].



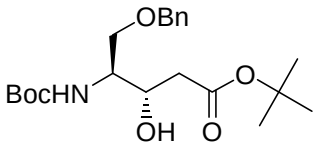
19b

Allyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-6-methylthiahexanoate (19b): amorphous powder; $[\alpha]^{28}_{D}$ = +7.1 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) nm; IR (Film) ν_{max} : 3355, 1731, 1681, 1648, 1170 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.91 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.33 (dd *J* =17.2, 1.4 Hz, 2H), δ 5.25 (dd, *J* =10.4, 1.1 Hz, 1H), δ 4.76 (d, *J* =8.5 Hz, 1H), δ 4.62 (d, *J* =5.9 Hz, 2H), δ 4.04 (m, 1H), δ 3.68 (m, 1H), δ 3.34 (m, 1H), δ 2.52 (m, 4H), δ 2.10 (s, 3H), δ 1.85 (m, 1H), 1.65 (m, 1H), δ 1.44 (br. s, 9H); ^{13}C NMR 172.4, 156.0 (not detected), 131.7, 118.7, 79.8, 70.7, 65.6, 53.8, 38.2, 30.8, 29.5, 28.3, 15.6; HRESI-MS *m/z* 356.1505 $[M+Na]^+$ [Calc. for $C_{15}H_{27}NO_5SNa^+$, 356.1509, -0.1 ppm error].



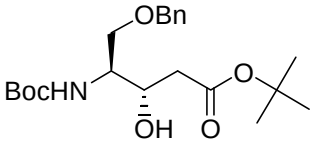
4n

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3-oxo-5-benzyloxapentanoate (4n):** amorphous powder; $[\alpha]^{27}_{D}$ = +19.8 (c 5, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 211 nm (6.54), 249 nm (5.61); IR (film) ν_{max}: 3434, 3355, 1745, 1713, 1164 cm^{-1}; ^1H NMR δ 7.31 (m, 5H), δ 5.47 (d, *J* =7.2 Hz, 1H), δ 4.50 (m, 3H), δ 3.90 (dd, *J* =9.7, 3.6 Hz, 1H), δ 3.65 (dd, *J* =9.7, 4.3 Hz, 1H), δ 3.52 (d, *J* =15.9 Hz, 1H), δ 3.43 (d, *J* =15.9 Hz, 1H), δ 1.45 (s, 9H), δ 1.43 (s, 9H); ^{13}C NMR 201.1, 166.0, 155.3, 137.3, 128.5, 127.9, 127.7, 82.1, 80.1 73.4, 69.3, 59.7, 47.9, 28.3, 27.9; HRESI-MS *m/z* 394.22245 $[M+H]^+$ [Calc. for $C_{21}H_{32}NO_6^+$, 394.2230, -0.1 ppm error].



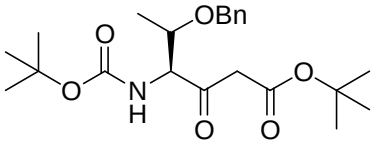
20a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-5-benzlyoxapentanoate (20a):** amorphous powder; $[\alpha]^{29}_{D}$ = +2.6 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 259 nm (6.15); IR (Film) ν_{max}: 3443, 3382, 1711, 1689, 1156 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.23 (m, 5H), δ 5.08 (d, *J* =9.1 Hz, 1H), δ 4.52 (br. s, 2H), δ 4.26 (br. d, *J* =9.1 Hz, 1H), δ 3.55 (m, 1H), δ 3.63 (d, *J* =4.9 Hz, 2H), δ 3.39 (br. s, 1H); δ 2.49 (dd, *J* =16.3, 8.9 Hz, 1H), δ 2.47 (dd, *J* =16.4, 4.0 Hz, 1H), δ 1.45 (s, 9H); δ 1.34 (s, 9H); ^{13}C NMR 172.0, 155.8, 137.6, 128.4, 127.8, 127.7, 81.2, 79.5, 73.4, 71.1, 68.0, 52.7, 39.5, 28.3, 28.1; HRESI-MS *m/z* 396.2394 $[M+H]^+$ [Calc. for $C_{21}H_{34}NO_6^+$, 396.2387, -3.3 ppm error].



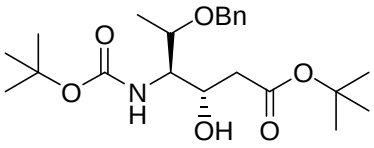
20b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-5-benzlyoxapentanoate (20b):** amorphous powder; $[\alpha]^{29}_{D}$ = +12.3 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 259 nm (6.04); IR (film) ν_{max}: 3440, 3366, 1705, 1689 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.34 (m, 5H), δ 5.12 (d, *J* =8.5 Hz, 1H), δ 4.52 (br. s, 2H), δ 4.06 (br. s, 1H), δ 3.81 (dd, *J* =9.4, 3.1 Hz, 1H), δ 3.71 (br. m, 1H), δ 3.58 (dd, *J* =9.4, 3.1 Hz, 1H); δ 3.50 (br. s, 1H), δ 2.53 (dd, *J* =16.3, 3.7 Hz, 1H), δ 2.43 (dd, *J* =16.4, 8.5 Hz, 1H), δ 1.45 (s, 9H); δ 1.43 (s, 9H); ^{13}C NMR 172.1, 155.8, 137.7, 128.4, 127.8, 127.6, 81.2, 79.6, 73.4, 71.1, 67.9, 53.4, 39.5, 28.4, 28.1; HRESI-MS *m/z* 396.2381 $[M+H]^+$[Calc. for $C_{21}H_{34}NO_6$, 396.2387, -0.1 ppm error].



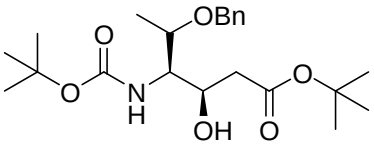
4o

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3-oxo-5(*S*)-benzlyoxahexanoate (4o):** amorphous powder; $[\alpha]^{26}_{D}$ = +11.9 (c 10, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 205 nm (7.09); IR (Film) ν_{max} : 3441, 1713, 1163 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.32 (m, 5H), δ 5.37 (d, *J* =8.5 Hz, 1H); δ 4.49 (d, *J* =11.2 Hz, 1H), δ 4.40 (d, *J* =11.2 Hz, 1H), δ 4.35 (dd, *J* =8.7, 2.4 Hz, 1H), δ 4.14 (dq, *J* =6.26, 2.6, 1), δ 3.44 (d, *J* =16.9 Hz, 1H), δ 3.37 (d, *J* =16.1 Hz, 1H); δ 1.44 (s, 9H), δ 1.25 (s, 9H), δ 1.20 (d, *J* =6.3 Hz, 3H); ^{13}C NMR 202.0, 166.0, 155.7, 137.6, 128.4, 127.8, 127.7, 81.9, 80.0, 74.0, 71.0, 63.4, 48.5, 28.2, 27.9, 15.9; HRESI-MS *m/z* 430.2199 $[M + Na]^+$ [Calc. for $C_{22}H_{33}NO_6Na$, 430.2206, 0.3 ppm error].



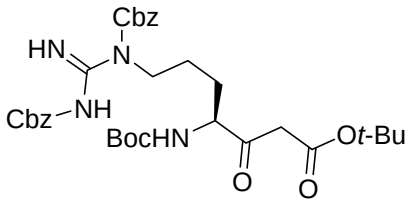
21a

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*S*)-hydroxy-5(*S*)-benzlyoxahexanoate (21a):** amorphous powder; $[\alpha]^{28}_{D}$ = -7.5 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 209 nm (7.21); IR (Film) ν_{max}: 3452, 1713, 1501, 1157 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.34 (m, 5H), δ 5.06 (d, *J* =9.81 Hz, 1H), δ 4.65 (d, *J* =11.3 Hz, 1H), δ 4.39 (d, *J* =11.3 Hz, 1H), δ 4.21 (br t, *J* =6.3 Hz, 1H), δ 3.88 (m, 1H), δ 3.63 (m, 1H), δ 3.52 (br s. 1H), δ 2.42 (dd, *J* =16.3, 8.4 Hz, 1H), δ 2.33 (dd, *J* =16.3, 5.3 Hz, 1H), δ 1.45 (s, 9H), δ 1.43 (s, 9H), δ 1.26 (d, *J* =6.3 Hz, 3H); ^{13}C NMR 171.4, 156.5, 137.5, 128.6, 128.0, 127.9, 80.9, 79.3, 77.5, 70.4, 70.2, 56.6, 39.8, 28.3, 28.1, 15.9; HRESI-MS *m/z* 410.2544 $[M+H]^+$ [Calc. for $C_{22}H_{36}NO_6$, $[M+H]^+$, 410.2543, -1.9 ppm error].



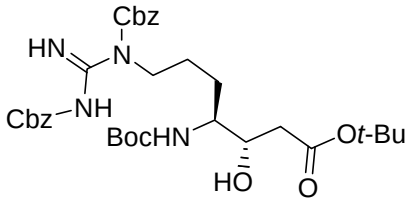
21b

***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3(*R*)-hydroxy-5(*S*)-benzlyoxahexanoate (21b):** $[\alpha]^{29}_{D}$ = +18.9 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 205 nm (7.03); IR (film) ν_{max} 3444, 1715, 1154 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.34 (m, 5H), δ 4.93 (d, *J* =9.9 Hz, 1H), δ 4.62 (d, *J* =11.3 Hz, 1H), δ 4.43 (d, *J* =11.3 Hz, 1H), δ 4.15 (m, 1H), δ 3.98 (m, 1H), δ 3.48 (m, 1H), δ 3.47 (br. s, 1H), δ 2.56 (dd, *J* =16.6, 3.2 Hz, 1H), δ 2.38 (dd, *J* =16.6, 8.7 Hz, 1H), δ 1.46 (s, 9H), δ 1.43 (s, 9H); δ 1.20 (d, *J* =6.3 Hz, 3H); ^{13}C NMR 172.7, 156.2, 138.2, 128.4, 127.9, 127.8, 81.3, 79.4, 72.1, 71.1, 68.5, 58.1, 39.2, 28.3, 28.1, 16.3; HRESI-MS *m/z* 410.2552 $[M+H]^+$ [Calc. for $C_{22}H_{36}NO_6$, $[M+H]^+$, 410.2543, -3.4 ppm error].



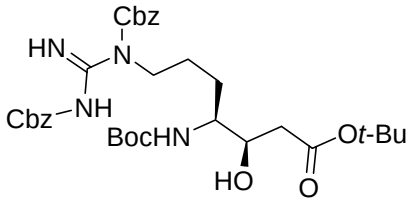
4p

***t*-butyl 7-(1,3-bis(benzyloxycarbonyl)guanidino)-4(*S*)-(*tert*-butoxycarbonylamino)-3-oxoheptanoate (4p)**: amorphous powder; $[\alpha]^{26}_{D}$ = +0.36 (c 9.7, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 210 nm (6.48), 235 nm (7.22); IR (Film) ν_{max} : 3389, 1706, 1613, 1257 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 9.41 (br. s, 1H), δ 9.27 (br. s, 1H), δ 7.36 (m, 10H), δ 5.57 (d, *J* =7.9 Hz, 1H), δ 5.24 (br. s, 2H), δ 5.15 (br. s, 2H), δ 4.30 (m, 1H), δ 3.95 (m, 2H), δ 3.37 (br. s, 2H), δ 1.84 (m, 2H), δ 1.63 (m, 2H), δ 1.40 (s, 9H), δ 1.42 (s, 9H); ^{13}C NMR 202.8, 166.3, 163.6, 160.5, 155.7, 136.6, 134.5, 128.7, 128.3, 127.9, 81.9, 79.8, 68.9, 67.0, 64.1, 59.2, 47.4, 44.1, 28.2, 27.8, 26.9, 24.6; HR-APCI-TOF *m/z* 641.3184 $[M+H]^+$ [Calc. for $C_{33}H_{45}N_4O_9^+$, 641.3187, -0.4 ppm error].



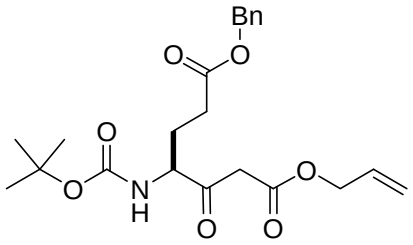
22a

***t*-butyl 7-(1,3-bis(benzyloxycarbonyl)guanidino)-4(*S*)-(*tert*-butoxycarbonylamino)-3(S)-hydroxy-heptanoate (22a)**: amorphous powder; $[\alpha]^{26}_{D}$ = -8.2 (c 1, $CHCl_3$)*;* UV (*i*-PrOH) λ_{max} (log ε) 209 nm (6.64), 214 nm (6.61), 233 nm (6.58); IR (Film) ν_{max} : 3386, 1711, 1610, 1255 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 9.44 (br. s, 1H), δ 9.27 (br. s, 1H), δ 7.36 (m, 10H), δ 5.23 (s, 2H), δ 5.16 (d, *J* =12.6 Hz, 1H), δ 5.11 (d, *J* =12.6 Hz, 1H), δ 4.93 (d, 9.6 Hz, 1H), δ 3.95 (m, 3H), 3.47 (d, *J* =3.6 Hz, 1H), δ 3.46 (m, 1H), δ 2.40 (dd, *J* =16.7, 9.5 Hz, 1H), δ 2.27 (dd, *J* =16.4, 3.3 Hz, 1H), δ 1.61 (m, 4H), δ 1.45 (s, 9H), δ 1.40 (s, 9H); ^{13}C NMR 172.7, 163.8, 160.6, 156.1, 155.9, 136.8, 134.7, 128.8, 128.4, 128.3, 127.8, 127.7, 81.3, 79.1, 69.1, 68.8, 66.9, 53.6, 44.5, 39.6, 29.3, 28.3, 28.0, 25.5; HRESI-MS *m/z* 375.2610 $[M+H-2Cbz]^+$ [Calc. for $C_{17}H_{34}N_4O_5$, 375.2602, -2.2 ppm error].



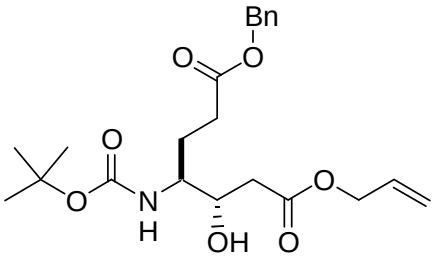
22b

7-(1,3-bis(benzyloxycarbonyl)guanidino)-4(*S*)-(*tert*-butoxycarbonylamino)-3(*R*)-hydroxy-heptanoate (22b): amorphous powder; $[\alpha]^{26}_{D}$ = +1 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 206 nm (7.12), 233 nm (7.05); IR (Film) ν_{max} : 3386, 1724, 1711, 1610, 1257 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 9.44 (br. s, 1H), δ 9.27 (br. s, 1H), δ 7.36 (m, 10H), δ 5.23 (s, 2H), 5.14 (s, 2H), δ 5.01 (d, *J* =9.1 Hz, 1H), δ 3.98 (m, 3H), δ 3.49 (m, 2H), δ 2.37 (dd, *J* =16.5, 3.5 Hz, 1H), δ 2.27 (dd, *J* =16.4, 8.9 Hz, 1H), 1.61 (m, 4H), 1.45 (s, 9H), 1.40 (s, 9H); ^{13}C NMR 172.2, 163.7, 160.6, 156.1, 155.8, 136.8, 134.6, 128.7, 128.3, 128.2, 127.8, 127.7, 81.2, 79.2, 70.7, 68.8, 66.9, 54.3, 44.5, 39.1, 28.3, 28.0, 26.0, 25.3**;** HRESI-MS *m/z* 375.2602 $[M+H-2Cbz]^+$ [Calc. for $C_{17}H_{34}N_4O_5$, 375.2602, -3.0 ppm error].



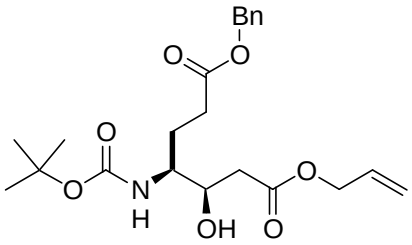
4q

7-benzyl 1-*t*-butyl 4-(*tert*-butoxycarbonylamino)-3-oxoheptanedioate (4q): amorphous powder; $[\alpha]^{27}_{D}$ = +0.3 (c 10, $CHCl_3$); IR (Film) ν_{max} : 3368, 1729, 1713, 1690, 1501, 1167 cm^{-1}; ^1H NMR δ 7.38 (m, 5H), δ 5.91 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.32 (dd *J* =17.2, 1.4 Hz, 2H), δ 5.25 (dd, *J* =10.4, 1.4 Hz, 1H), δ 5.11 (s, 2H), δ 4.64 (br. m, 3H), δ 4.40 (m, 1H), δ 3.60 (m, 2H), δ 2.20 (br. m, 4H), δ 1.41 (br. s, 9H); ^{13}C NMR 201.5, 172.6, 171.9, 155.3, 135.7, 131.4, 128.5, 128.2, 128.2, 118.9, 80.3, 80.0, 66.5, 58.9, 45.9, 30.3, 29.6, 28.2; HRESI-MS *m/z* 442.1819 $[M + Na]^+$ [Calc. for $C_{22}H_{29}NO_7Na^+$, 442.1836, 4.0 ppm error].



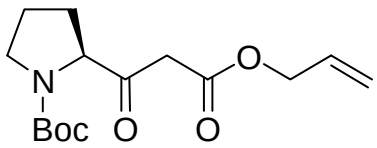
23a

7-benzyl 1-*t*-butyl 4-(*tert*-butoxycarbonylamino)-3(*S*)-hydroxyheptanedioate (23a): amorphous powder; $[\alpha]^{25}_D$ –9.5 (0.01, MeOH), $[\alpha]^{26}_D$ = -10.8 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 210 (3.65) 207 nm (3.69); IR (Film) ν_{max} : 3391, 1734, 1715 cm^{-1}; ^1H NMR δ 7.34 (m, 5H), δ 5.91 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.32 (dd *J* =17.2, 1.4 Hz, 2H), δ 5.25 (dd, *J* =10.4, 1.4 Hz, 1H), δ 5.11 (s, 2H), δ 4.83 (d, *J* =9.9 Hz, 1H), δ 4.62 (dm, 2H), 4.06 (d, *J* =9.5 Hz, 1H), δ 3.58 (q, *J* =7.8 Hz, 1H), δ 2.57 (m, 2H), δ 2.46 (t, *J* =7.4 Hz, 2H), δ 1.93 (m, 2H), δ 1.41 (br. s, 9H); ^{13}C NMR 173.3, 172.8, 156.0, 135.9, 131.7, 128.6, 128.3, 118.7, 79.5, 69.1, 66.4, 65.5, 53.3, 38.5, 30.8, 29.7, 28.3; HRESI-MS *m/z* 422.2179 $[M + H]^+$ [Calc. for $C_{22}H_{32}NO_7^+$, 422.2180, –1.4 ppm error].



23b

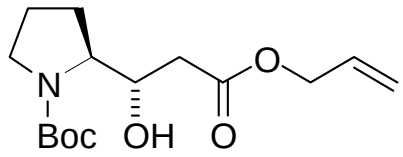
7-benzyl 1-*t*-butyl 4-(*t*-butoxycarbonylamino)-3(*R*)-heptanedioate (23b): $[\alpha]^{25}_D$ –5.6 (c 1, MeOH), $[\alpha]^{26}_D$ = -2 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 255 nm (5.04), 260 nm (4.90); IR (Film) ν_{max} : 3375, 1717, 1689, 1509, 1170 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 7.34 (m, 5H), δ 5.90 (ddt, *J* =17.2, 10.4, 5.8 Hz, 1H), δ 5.32 (dd *J* =17.2, 1.4 Hz, 2H), δ 5.25 (dd, *J* =10.4, 1.0 Hz, 1H), δ 5.11 (s, 2H), δ 4.82 (d, 9.5 Hz, 1H), δ 4.60 (d, 2H), 4.02 (m, 1H), δ 3.60 (m, 1H), δ 2.49 (m, 4H), δ 1.96 (m, 1H), δ 1.71 (m, 1H), δ 1.41 (br. s, 9H); ^{13}C NMR 172.3, 171.4, 154.9, 134.8, 130.7, 127.5, 117.6, 78.6, 75.5, 69.7, 65.5, 64.5, 52.9, 37.1, 29.8, 27.3, 23.7; HRESI-MS *m/z* 444.2007 $[M + Na]^+$ [Calc. for $C_{22}H_{31}NO_7Na^+$, 444.1998, error 2.0 ppm].



4r

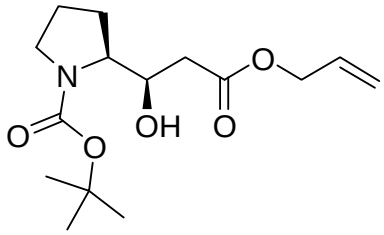
***t*-butyl 2(*S*)-(3-(allyloxy)-3-oxopropanoyl)pyrrolidine-1-carboxylate (4r):** amorphous powder; $[\alpha]^{22}_D$ –39.9 (c 10.3, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 246 nm (5.95); IR (Film) ν_{max} : 1750, 1694, 1394, 1164 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature) δ 5.91 (ddt *J* =16.2, 11.0, 5.8 Hz, 1H), δ 5.34 (d, *J* =17.2 Hz, 1H), δ 5.24 (d,

J =10.2 Hz, 1H), δ 4.63 (m, 2H), δ 4.30 (m, 1H), 3.49 (m, 2H), δ 2.04 (m, 6H), δ 1.44 (s, 9H); ^{13}C NMR 202.5, 166.5, 153.7 131.4, 118.7, 80.7, 65.9, 65.4, 46.6, 45.0, 28.1, 24.3, 23.6; HRESI-MS *m/z* 320.1472 $[M+Na]^+$ [Calc. for $C_{15}H_{23}NO_5Na^+$, 320.1474, –1.1 ppm error].



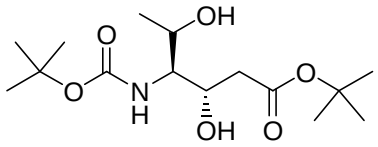
24a

***t*-butyl 2(*S*)-(3-(allyloxy)-1(*S*)-hydroxy-3-oxopropyl)pyrrolidine-1-carboxylate (24a):** amorphous powder; $[\alpha]^{25}_D$ –40.3 (0.01, MeOH), $[\alpha]^{26}_D$ = -25.4 (c 1, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 277 (2.35) 207 (3.55) nm; IR (Film) ν_{max} : 3427, 1739, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 5.91 (ddd *J* =16.2, 11.0, 5.8 Hz, 1H), δ 5.33 (d, *J* =17.2 Hz, 1H), δ 5.24 (d, *J* =10.2 Hz, 1H), δ 4.63 (m, 2H), δ 4.39 (d, 5.1 Hz, 1H), δ 4.36 (d, 5.1 Hz, 1H), δ 4.28 (d, *J* =5.4 Hz, 1H), δ 4.25 (d, *J* =5.7 Hz, 1H), δ 3.48 (m, 3H), δ 2.10 (m, 2H), δ 1.87 (dt, *J* =12.6, 12.3, 6.2 Hz, 1H), δ 1.43 (s, 9H); ^{13}C NMR 172.1, 156.3, 132.0, 118.3, 80.1, 70.3, 65.3, 62.2, 47.8, 45.0, 37.8 28.4, 27.6, 24.0; HRESI-TOF *m/z* 300.1802 $[M+H]^+$ [Calc. for $C_{15}H_{26}NO_5$, 300.1812, 1.3 ppm error].



24b

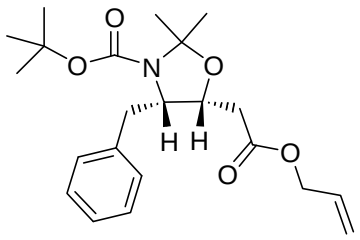
***t*-butyl 2(*S*)-(3-(allyloxy)-1(*R*)-hydroxy-3-oxopropyl)pyrrolidine-1-carboxylate (24b):** $[\alpha]^{24}_D$ –54.8 (0.01, MeOH); UV (MeOH) λ_{max} (log ε) 278 (2.41) 217 (314) 207 (3.10) nm; IR (Film) ν_{max} : 3439, 1724, 1690, 1394, 1166 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 5.93 (dd, *J* =10.9, 5.7 Hz, 1H), δ 5.34 (d, *J* =17.2 Hz, 1H), δ 5.24 (d, *J* =10.4, 1.0 Hz, 1H), δ 5.00 (s, 1 H), δ 4.63 (d, 5.5 Hz, 2H), δ 4.10 (br. m, 1H), δ 3.93 (m, 1H), δ 3.52 (m, 1H), δ 3.30 (m, 1H), δ 2.56 (dd, 15.2, 2.9 Hz, 1H),δ 2.46 (dd, 15.1, 8.6 Hz, 1H), δ 1.88 (br. m, 4H), δ 1.47 (s, 9H); ^{13}C NMR 171.5, 157.5, 132.0, 118.2, 80.39, 72.5, 65.3, 61.9, 47.3, 40.1, 28.3, 24.1; HRESI-TOF *m/z* 322.1613 $[M+Na]^+$ [Calc. for $C_{15}H_{25}NO_5Na^+$, 322.1631,–1.7 ppm error].



21c

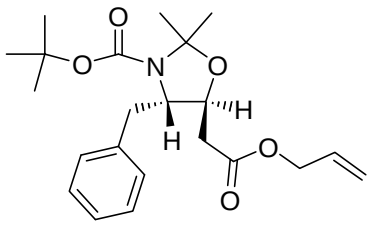
***t*-Butyl 4(*S*)-[(*tert*-butoxycarbonyl)-amino]-3*S*,5*S*-dihydroxypentanoate (21c):** amorphous powder; $[\alpha]^{26}_D$ = +5.3 (c 1, $CHCl_3$); IR (Film) ν_{max} : 3441, 1705, 1690, 1259, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$ at room temperature) δ 5.42 (d, *J* =10.0 Hz, 1H), δ 4.31 (d, 10.0 Hz, 1 H), δ 4.01 (s, 1H), δ 3.43 (d, 10.0 Hz, 1H), δ 2.53 (dd, 17.0, 9.8 Hz, 1H),δ 2.43 (dd, 17.1, 3.3 Hz, 1H), δ 1.47 (s, 9H), δ 1.46 (s, 9H), δ 1.18 (d, 6.3 Hz, 3H); ^{13}C NMR 173.1,

151.9, 81.9, 79.5, 72.1, 70.7, 56.4, 38.9, 28.3, 28.1, 19.9; HRESI-MS *m/z* 342.1892 $[M + Na]^+$ [Calc. for $C_{15}H_{29}NO_6Na^+$, 342.18871, -1.5 ppm error].



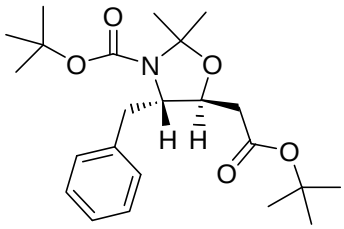
12c

Compound 12c: $[\alpha]^{27}_D$ = -21.5 (c 1, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 211 nm (7.26); IR (Film) ν_{max} : 1720, 1700, 1257 cm^{-1}; ^1H NMR (mixture of conformers) $J_{H3,H4}$ = 4.5 Hz; δ 7.23 (m, 5H), δ 5.79 (m, 1H), δ 5.25 (ddd, *J* = 17.2, 2.9, 1.5 Hz, 1H), δ 5.21 (dm, *J* = 10.3 Hz, 1H), δ 4.39 (m, 2H), δ 4.34 (m, 1H), δ 4.28 (dd, *J* = 13.2, 5.8 Hz, 0.6 H), δ 4.49 (dt, *J* = 11.8, 6.1 Hz, 1H), δ 3.01 (d, *J*=3.3 Hz), δ 2.90 (dd, *J*=13.8, 4.7 Hz, 0.7 Hz), δ 2.78 (dd, 14.1, 9.0 Hz, 1H), δ 2.68 (m, 1H), δ 2.48 (m, 1H), δ 1.67 (s,3H) δ 1.57 (s, 9H), δ 1.47 (s, 3H), δ 1.25 (s, 9H); ^{13}C NMR 169.9, 151.5, 138.3, 131.9, 129.3, 128.5, 128.3, 126.2, 118.4, 79.8, 72.9, 75.0, 65.3, 60.1, 59.8, 36.5, 35.8, 34.7, 34.5, 29.7, 28.8, 27.9, 27.3, 23.6, 22.7; HRESI-MS *m/z* 412.2103 $[M + Na]^+$ [Calc. for $C_{22}H_{31}NO_5Na^+$, 412.2100, -2.1 ppm error].



12d

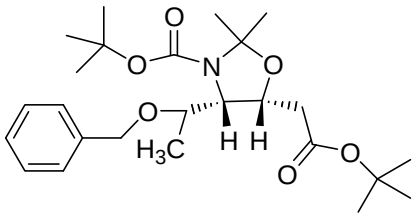
Compound 12d: $[\alpha]^{27}_D$ = -2.8 (c 7.6, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 208 nm (6.90); IR (Film) ν_{max} : 1740, 1701, 1257, 1172 cm^{-1}; ^1H NMR (mixture of conformers) $J_{H3,H4}$ = 2.9 Hz; ^{13}C NMR 169.9, 137.6, 131.9, 129.7, 129.3, 128.7, 128.5, 126.7, 118.2, 80.3, 75.8, 75.0, 68.1, 65.2, 63.3, 40.6, 40.1, 37.8, 29.7, 28.7, 28.5, 27.7, 27.2; HRESI-MS *m/z* 412.2082 $[M + Na]^+$ [Calc. for $C_{22}H_{31}NO_5Na^+$, 412.2100, 3.09 ppm error].



11c

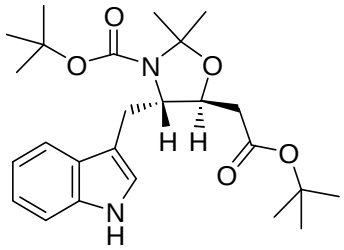
Compound 11c: $[\alpha]^{26}_D$ = +6.9 (c 5, $CHCl_3$); UV (*i*-PrOH) λ_{max} (log ε) 212 nm (6.34); IR (Film) ν_{max} : 1733, 1704, 1256, 1170 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature): (mixture of conformers) $J_{H3,H4}$ = 2.9 Hz; δ 7.26 (m, 5H), δ 4.34 (m, 1H), δ 3.87 (m, 1H), 3.18 (m, 1H), δ 2.83 (m, 1H), δ 2.38 (dd, *J*= 14.8, 7.8 Hz, 1H), δ 2.19 (m, 1H), δ 1.52 (s, 9H), δ 1.35 (s, 9H); ^{13}C NMR 169.5, 155.7, 137.6, 137.5, 129.8, 129.4, 128.7, 128.4, 126.6,

126.5, 80.8, 76.1, 75.1, 63.2, 41.8, 41.3, 39.8, 37.6, 29.7, 28.5, 27.9, 27.2; HRESI-MS *m/z* 428.241 $[M + Na]^+$ [Calc. for $C_{23}H_{35}NO_5Na^+$, 428.2413, -0.4 ppm error].



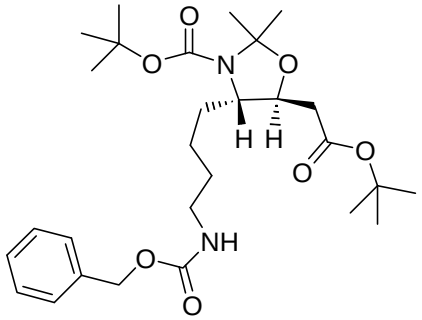
21d

Compound 21d: $[\alpha]^{27}_D$ = -40.6 (c 0.5, $CHCl_3$); UV (ethyl acetate) λ_{max} (log ε) 257 nm (5.49); IR (Film) ν_{max} : 1732, 1695 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature): (mixture of conformers) $J_{H3,H4}$ = 4.7 Hz; δ 7.31 (m, 5H), δ 4.61 (d, *J*= 12.1 Hz, 1H), δ 4.53 (br s, 1H), δ 4.49 (m, 1H), 2.66 (m, 1H), 2.62 (m, 1H), 1.56 (s, 3H), 1.48 (s, 3H), 1.46 (s, 9H) ^{13}C NMR 169.9, 129.3, 127.3, 80.7, 63.4, 42.1, 39.8, 29.7, 28.4, 28.2, 14.0; HRESI-MS *m/z* 450.2856 $[M+H]^+$ [Calc. for $C_{22}H_{34}NO_7$, 450.2856, -1.2 ppm error].



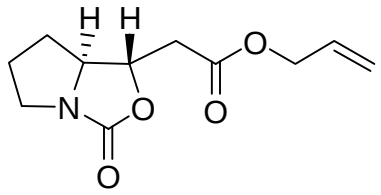
22c

Compound 22c: $[\alpha]^{27}_D$ = -20.2 (c 1, $CHCl_3$); IR (Film) ν_{max} : 3348, 1723, 1689, 1258, 1158 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature): (mixture of conformers) $J_{H3,H4}$ = 2.7 Hz; δ 8.09 (s, 1H), δ 7.79 (m, 0.5H), δ 7.68 (m, 0.5H), δ 7.34 (m, 1H), δ 7.18 (m, 1H), δ 7.10 (t, *J* = 7.3 Hz, 1H), δ 7.05 (s, 1H), δ 4.39 (br. s, 1H), δ 4.04 (dt, *J* = 9.8, 2.8 Hz, 1H), δ 3.36 (t, *J*= 14.4 Hz, 1H), δ 2.99 (m, 0.5H), δ 2.90 (m, 0.5H), δ 2.38 (dd, *J*= 14.6, 7.7 Hz, 1H), δ 2.16 (m, 1H), δ 1.56 (s, 9H), δ 1.28 (s, 9H), ^{13}C NMR: 169.7, 152.0, 136.2, 127.8, 122.8, 122.0, 119.4, 118.8, 111.9, 111.2, 110.9, 80.7, 80.1, 75.9, 62.4, 61.6, 41.8, 41.6, 29.7, 28.9, 28.5, 27.9; HRESI-MS *m/z* 467.2524 $[M + H]^+$ [Calc. for $C_{24}H_{36}N_2O_5Na^+$, 467.2522, -1.6 ppm error].



16c

Compound 16c: $[\alpha]^{27}_{D}$ = +0.45 (c 3.3, $CHCl_3$); UV (MeOH) λ_{max} (log ε) 255 nm (6.04); IR (Film) ν_{max} : 3349, 1722, 1704, 1689, 1259 cm^{-1}; ^1H NMR ($CDCl_3$ at room temperature): (mixture of conformers) $J_{H3,H4}$= 3.5 Hz; δ ^{13}C NMR 169.9, 156.4, 128.5, 128.3, 81.1, 75.9, 66.5, 62.1, 44.6, 40.1, 32.1, 29.7, 28.4, 28.4, 22.9; HR APCI-TOF *m/z* 521.3225 $[M + H]^+$ [Calc. for $C_{28}H_{44}N_2O_7^+$, 521.3228, -0.7 ppm error].



24c

Compound 24c. ^1H NMR ($CDCl_3$) δ 5.95 (dt, *J*=9.1, 4.0 Hz, 1H), δ 5.88 (m, 1H), δ 5.32 (ddt, *J*=17.1, 1.4, 1.3 Hz, 1H), δ 5.26 (br. dd 10.4, 0.8 Hz, 1H), δ 4.60 (d, *J*=6.1 Hz, 2H), δ 4.19 (dt, 7.0, 4.0 Hz, 1H), δ 3.72 (dt, *J*=10.8, 7.3 Hz, 1H), δ 3.51 (m, 1H); δ 2.78 (dd, *J*=16.6, 9.3 Hz, 1H), δ 2.71 (dd, *J*=16.6, 4.3 Hz, 1H), δ 2.03 (m, 4H), ^{13}C NMR ($CDCl_3$) 168.3, 148.3, 131.3, 119.3, 72.9, 60.1, 61.2, 50.8, 36.2, 25.9, 23.3. HR APCI-TOF *m/z* 226.1075 $[M + H]^+$ [Calc. for $C_{11}H_{16}NO_4^+$, 226.1076, -0.4 ppm error].