Supporting Information for:

Asymmetric Syntheses of All Stereoisomers of 3-Hydroxyproline; A Constituent of Several Bioactive Compounds

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Experimental procedure and spectral data for ent-10 to ent-13

\((2R,3R)-3-[2-(4-Methoxybenzyloxy)ethyl]oxiran-2-yl]methanol (ent-10)\)
Experimental procedure is same as 10 except for use of D-(–)-DET instead of L-(+)-DET.
\([\alpha]_D^{25} +25.4 \ (c \ 1.0, \ \text{CHCl}_3)\).
Spectral data of ent-10 are identical to those of 10.

\((2R,3R)-2-[(\text{tert-Butyldimethylsiloxy})methyl]3-[2-(4-Methoxybenzyloxy)ethyl]oxirane (ent-11)\)
Experimental procedure and spectral data of ent-11 are identical to those of 11.
\([\alpha]_D^{25} +21.1 \ (c \ 1.1, \ \text{CHCl}_3)\).

\(2-\{(2R,3R)-3-[(\text{tert-Butyldimethylsiloxy})methyl]oxiran-2-yl\}ethanol\)
Experimental procedure and spectral data of (2R,3R) compound are identical to those of (2S,3S) compound.
\([\alpha]_D^{25} +20.2 \ (c \ 1.1, \ \text{CHCl}_3)\).

\((2R,3R)-2-[(\text{tert-Butyldimethylsiloxy})methyl]-3-[2-(tosyloxy)ethyl]oxirane (ent-12)\)
Experimental procedure and spectral data of ent-12 are identical to those of 12.
\([\alpha]_D^{25} +18.1 \ (c \ 1.1, \ \text{CHCl}_3)\).

\((2R,3R)-2-(2-Azidoethyl)-3-[(\text{tert-butyldimethylsiloxy})methyl]oxirane (ent-13)\)
Experimental procedure and spectral data of ent-13 are identical to those of 13.
\([\alpha]_D^{25} +17.3 \ (c \ 1.0, \ \text{CHCl}_3)\).

Experimental procedure and spectral data for [(2S,3R)-14] to [(2R,3R)-16] (leading to 3)

\(\text{tert-Butyl} \ (2S,3R)-2-[(\text{tert-Butyldimethylsiloxy})methyl]-3-hydroxypyrrolidine-1-carboxylate \ [(2S,3R)-14]\)
Experimental procedure and spectral data of [(2S,3R)-14] are identical to those of [(2R,3S)-14].
\([\alpha]_D^{25} +37.9 \ (c \ 1.3, \ \text{CHCl}_3)\).

\(\text{tert-Butyl} \ (2S,3R)-3-[(\text{tert-Butyldimethylsiloxy})methyl]pyrrolidine-1-carboxylate\)
Experimental procedure and spectral data of (2S,3R) compound are identical to those of (2R,3S) compound.
[α]D^25 +20.9 (c 1.3, CHCl₃).

tert-Butyl (2S,3R)-3-(tert-Butyldimethylsiloxy)-2-(hydroxymethyl)pyrrolidine-1-carboxylate [(2S,3R)-15]
Experimental procedure and spectral data of [(2S,3R)-15] are identical to those of [(2R,3S)-15].
[α]D^25 +8.7 (c 1.2, CHCl₃).

(2R,3R)-1-(tert-Butoxycarbonyl)-3-(tert-butyldimethylsiloxy)pyrrolidine-2-carboxylic Acid [(2R,3R)-16]
Experimental procedure and spectral data of [(2R,3R)-16] are identical to those of [(2S,3S)-16].
[α]D^25 +18.3 (c 1.0, CHCl₃).

Experimental procedure for [(2R,3R)-14] to [(2S,3R)-16] (Leading to 2)
tert-Butyl (2R,3R)-2-[tert-Butyldimethylsiloxy]methyl]-3-hydroxypyrrolidine-1-carboxylate [(2R,3R)-14]
[α]D^25 –46.9 (c 1.0, CHCl₃).
IR (neat): 3379, 2928, 2808 1701, 1502, 1119, 830 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 4.31 (s, 1 H), 3.84 (dd, J = 6.2, 2.4 Hz 1 H), 3.46 (m, 4 H), 2.08 (s, 2 H), 1.82 (s, 1 H), 1.44 (s, 9 H), 0.88 (s, 9 H), 0.08 (s, 6 H).
¹³C NMR (75 MHz, CDCl₃): δ = 154.7, 79.2, 73.7, 66.1, 62.6, 44.5, 31.1, 27.8, 24.9, 17.9, –5.5.

tert-Butyl (2R,3R)-3-(tert-Butyldimethylsiloxy)-2-[(tert-butyldimethylsiloxy)methyl]pyrrolidine-1-carboxylate
Experimental procedure for (2R,3R) compound is same as that for (2R,3S) compound.
[α]D^25 –43.9 (c 0.8, CHCl₃).
¹H NMR (300 MHz, CDCl₃): δ = 4.45 (d, J = 2.2, 1 H), 3.94–3.37 (m, 5 H), 2.07–2.02 (m, 1 H), 1.96–1.81 (m, 1 H), 1.48 (s, 9 H), 0.96 (s, 18 H), 0.08 (s, 12 H).
MS (ESI): m/z = 468 [M + Na]^+.

tert-Butyl (2R,3R)-3-(tert-Butyldimethylsiloxy)-2-(hydroxymethyl)pyrrolidine-1-carboxylate [(2R,3R)-15]
Experimental procedure for [(2R,3R)-15] is same as that for [(2R,3S)-15].
[α]D^25 –32.7 (c 1.1, CHCl₃).
IR (neat): 3453, 2932, 2834, 1702, 1668, 1298, 1099 cm⁻¹.
¹H NMR (300 MHz, CDCl₃): δ = 4.22 (s, 1 H), 4.03 (m, 1 H), 3.69–3.52 (m, 3 H), 3.29 (m, 1 H), 2.03–1.94 (m, 1 H), 1.78–1.72 (m, 1H), 1.47 (s, 9 H), 0.89 (s, 9 H), 0.08 (s, 6 H).
MS (ESI): m/z = 332 [M + H]^+.

(2S,3R)-1-(tert-Butoxycarbonyl)-3-(tert-butyldimethylsiloxy)pyrrolidine-2-carboxylic Acid [(2S,3R)-16]
Experimental procedure for [(2S,3R)-16] is same as that for [(2S,3S)-16].
$[\alpha]_D^{25} -82.7 (c 0.6, \text{CHCl}_3)$.
IR (neat): 3162, 1749, 1675, 1459, 1208 cm$^{-1}$.
$^1$H NMR (300 MHz, CD$_3$OD): $\delta = 4.39-4.51$ (m, 1 H), 3.75–3.46 (m, 3 H), 2.27–1.98 (m, 1 H), 1.82–1.77 (m, 1 H), 1.41 (s, 9 H), 0.88 (s, 9 H), 0.09 (s, 6 H).

**Experimental procedure and spectral data for [(2S,3S)-14] to [(2R,3S)-16] (Leading to 4)**

**tert-Butyl(2S,3S)-2-[(tert-Butyldimethylsiloxy)methyl]-3-hydroxypyrrolidine-1-carboxylate [(2S,3S)-14]**
Experimental procedure and spectral data of [(2S,3S)-14] are identical to those of [(2R,3R)-14].
$[\alpha]_D^{25} +47.2 (c 1.2, \text{CHCl}_3)$.

**tert-Butyl (2S,3S)-3-[(tert-Butyldimethylsiloxy)-2-[(tert-butyldimethylsiloxy)methyl]pyrrolidine-1-carboxylate**
Experimental procedure and spectral data of (2S,3S) compound are identical to those of (2R,3R) compound.
$[\alpha]_D^{25} +44.1 (c 1.3, \text{CHCl}_3)$.

**tert-Butyl (2S,3S)-3-[(tert-Butyldimethylsiloxy)-2-(hydroxymethyl)pyrrolidine-1-carboxylate [(2S,3S)-15]**
Experimental procedure and spectral data of [(2S,3S)-15] are identical to those of [(2R,3R)-15].
$[\alpha]_D^{25} +33.9 (c 1.0, \text{CHCl}_3)$.

**(2R,3S)-1-(tert-Butoxycarbonyl)-3-(tert-butyldimethylsiloxy)pyrrolidine-2-carboxylic Acid [(2R,3S)-16]**
Experimental procedure and spectral data of [(2R,3S)-16] are identical to those of [(2S,3R)-16].
$[\alpha]_D^{25} +81.6 (c 0.5, \text{CHCl}_3)$.