

SUPPORTING INFORMATION: REPRESENTATIVE PROCEDURES

4-(*tert*-Butoxycarbonylamino)-1-trimethylsilyl-6-methyl-1-heptyn-3-one (6a). To a stirred solution of 1.0 mL (7.1 mmol) of trimethylsilylacetylene in 5 mL of anh. THF at –78 °C, 4.2 mL (6.7 mmol) of a solution of BuLi in hexanes were added dropwise. The solution was stirred 30 minutes and then allowed to warm to 0 °C. Then, a solution of 800 mg (2.92 mmol) of amide **11** in 3 mL of anh. THF was dropwise added and the mixture was stirred at 0 °C. The progress of the reaction was monitored by TLC. After 40 min, the reaction mixture was slowly added via cannula into *p*H 7 phosphate buffer (50 mL) and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude which was purified by a short flash chromatography (CH_2Cl_2) to yield 672 mg (74%) of ketone **6a** as an oil: R_f 0.54 (CH_2Cl_2); $[\alpha]^{20}_D$ +25.5 (*c* 1.4, $CHCl_3$). ^1H NMR ($CDCl_3$, 200 MHz) δ 0.23 (s, 9H), 0.94 (d, 3H, *J* = 6.2 Hz), 0.95 (d, 3H, *J* = 2.1 Hz), 1.40 (m, 2H), 1.42 (s, 9H), 1.73 (m, 1H), 4.36 (m, 1H), 5.02 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 1.1, 21.5, 23.0, 24.7, 28.1, 40.5, 59.6, 79.9, 100.1, 101.6, 155.3, 187.4; IR (film) 3360, 2149, 1718, 1684.
Further elution with CH_2Cl_2/MeOH (95:5) led to recover 120 mg (15%) of starting amide **11**.

Reduction of ketone 6a with BH_3:SMe_2 catalysed by (*S*)-7. A solution of **6a** (300 mg, 0.96 mmol) in THF (3 mL) was slowly added in ~25 min to a solution of (*S*)-**7** (0.19 mmol) and BH_3:SMe_2 (100 μL, 1 mmol) in THF (1 mL) at 0 °C under Ar. Upon completion of the addition, TLC revealed the disappearance of the starting ketone. Reaction was cautiously quenched by slow addition of MeOH (1 mL) at 0 °C. The solution was stirred for 15 min at r.t. and 40 mL of CH_2Cl_2 were added. The solution was washed several times with 5% aq. citric acid and the organic layer was dried over $MgSO_4$, filtered, and the volatiles were removed *in vacuo*. The residue was purified by flash chromatography (99:1 CH_2Cl_2/MeOH) to yield 229 mg (76%) of alcohol *anti*-**10a**. Pale yellowish oil; R_f 0.54 (9:1 CH_2Cl_2/AcOEt); $[\alpha]^{20}_D$ –57.0 (*c* 1.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 9H), 0.92 (d, 3H, *J* = 2.7 Hz), 0.95 (d, 3H, *J* = 3.0 Hz), 1.45 (s, 9H), 1.46 (m, 2H), 1.70 (m, 1H), 3.21 (broad s, 1H, O*H*), 3.76 (m, 1H), 4.30 (d, 1H, *J* = 5.4 Hz), 4.65 (d, 1H, *J* = 8.4 Hz, N*H*); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 0.2, 22.0, 23.2, 24.7, 28.3, 40.0, 53.6, 66.8, 79.9, 91.0, 103.5, 156.7; IR (film) 3400, 2174, 1696.
An analytical sample of the crude was treated with an excess of (*S*)-Mosher acid chloride (derived from (*R*)-acid) to give the Mosher ester. The analysis by ^{19}F NMR revealed a 94% d.e.

Hydroboration of alcohol *anti*-10a. To a solution of 0.19 mL (1.88 mmol) of cyclohexene in 2 mL of anh. THF, 95 μL (0.95 mmol) of BH_3:SMe_2 were added at 0 °C under Ar. When the stirred solution was allowed to warm to r.t. a white suspension of dicyclohexylborane was observed. After 1 h, the mixture was cooled again to 0 °C and a solution of 60 mg (0.19 mmol) of *anti*-**10a** in 2 mL of anh. THF were added dropwise. After 1,5 h of stirring at r.t., TLC (98:2 CH_2Cl_2/MeOH) revealed

the disappearance of the starting alcohol. The reaction flask was then quenched by addition of a solution of 320 mg (3.8 mmol) of $NaHCO_3$ in 2 mL of water and 0.7 mL of 30% H_2O_2 under vigorous stirring for 3 h at r.t.. Afterwards, 0.43 mL (7.58 mmol) of AcOH were cautiously added at 0 °C and the mixture was stirred at r.t. overnight. It was then extracted with CH_2Cl_2, dried ($MgSO_4$) and the volatiles (solvent and most of cyclohexanol) were eliminated *in vacuo*. The residue was purified by flash chromatography (95:5 CH_2Cl_2/MeOH) to yield 39 mg (75%) of acid *anti*-**8**: m.p. 132–134 °C; R_f 0.07 (95:5 CH_2Cl_2/MeOH); $[\alpha]^{20}_D$ –25.3 (*c* 0.2, MeOH); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (d, 3H, *J* = 6.6 Hz), 0.94 (d, 3H, *J* = 6.6 Hz), 1.32 (m, 2H), 1.45 (s, 9H), 1.66 (m, 1H), 2.59 (m, 2H), 3.70 (m, 1H), 4.01 (broad s, 1H), 4.72 (d, 1H, *J* = 8.1 Hz, N*H*), 5.90 (broad s, 1H, O*H*); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.5, 23.5, 24.7, 28.3, 37.2, 38.8, 53.0, 71.4, 80.1, 156.6, 175.8; IR (KBr) 3340, 1716, 1686.

(4*S*,5*R*)-*N*-*tert*-Butoxycarbonyl-2,2-dimethyl-4-isobutyl-5-(1-trimethylsilylethynyl) oxazolidine (*erythro*-14a). A solution of 174 mg (0.56 mmol) of *anti*-**10a**, 0.72 mL (5.86 mmol) of 2,2-dimethoxypropane, and 37 mg (0.15 mmol) of pyridinium *p*-toluenesulfonate (PPTS) in 9 mL of anh. toluene was heated at 90–100 °C until TLC (CH_2Cl_2/hexane 1:1) analysis of the reaction showed no starting amino alcohol (4 h). Then, the solution was allowed to cool to r.t. The solvent was eliminated *in vacuo*, the crude was dissolved in 20 mL of CH_2Cl_2 and the resulting solution was washed with aqueous saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude was purified by flash chromatography (99:1 hexane/AcOEt) to yield 171 mg (87%) of *erythro*-**14a**: m.p. 72-75 °C; R_f 0.30 (1:1 CH_2Cl_2/hexane); $[\alpha]^{20}_D$ +4.50 (*c* 1.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.17 (s, 9H), 0.94 (d, 3H, *J* = 5.0 Hz), 0.96 (d, 3H, *J* = 6.3 Hz), 1.48 (s, 9H), 1.60 (s, 3H), 1.76 (s, 3H), 1.81 (m, 3H), 3.98 (broad s, 1H), 4.71 (d, 1H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 0.6, 21.5, 23.7, 25.7, 26.4, 28.1, 28.5, 40.2, 62.7, 69.2, 80.1, 93.1, 95.6, 105.0, 156.7; IR (KBr) 2174, 1696.

(4*S*,5*R*)-*N*-*tert*-Butoxycarbonyl-2,2-dimethyl-4-isobutyloxazolidine-5-carboxylic acid (*threo*-9). To 100 mg (0.28 mmol) of *threo*-**14a** in a mixture of 4.5 mL of CCl_4, 4.5 mL of CH_3CN and 7 mL of H_2O, 390 mg (1.82 mmol) of $NaIO_4$ and 12 mg (0.06 mmol) of $RuCl_3 H_2O$ were added at r.t. The mixture was vigorously stirred for 3 h and the reaction was quenched by pouring the reaction mixture into 15 mL of 40% aq. $NaHSO_3$. After 45 min, the mixture was extracted with CH_2Cl_2 (5 x 20 mL) and AcOEt (3 x 20 mL). The organic layers were dried over $MgSO_4$, filtered and the volatiles were eliminated *in vacuo*. The residue was purified by flash chromatography (95:5 CH_2Cl_2/MeOH) to yield 76 mg (90%) of acid *threo*-**9** as a viscous oil; R_f 0.13 (9:1 CH_2Cl_2/AcOEt); $[\alpha]^{20}_D$ –5.9 (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (d, 3H, *J* = 3.9 Hz), 0.99 (d, 3H, *J* = 5.7 Hz), 1.26 (m, 2H), 1.46 (s, 9H), 1.58 (s, 3H), 1.66 (s, 3H), 1.70 (m, 3H), 4.31 (broad s, 1H), 4.40 (s, 1H), 8.20 (broad s, 1H, COO*H*); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.1, 23.7, 25.7, 27.8, 28.4, 29.6, 43.8, 59.1, 77.8, 96.4, 80.5, 156.5, 175.5; IR (KBr) 3350, 1701, 1653. MS (CI, NH_3) *m/z* (rel. int. %): 302 (M+1, 42%), 319 (M+18, 100%).