A STEREODIVERGENT APPROACH TO AMINO ACIDS, AMINO ALCOHOLS, OR OXAZOLIDINONES OF HIGH ENANTIOMERIC PURITY

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Supporting Information

General.

All reactions were performed under an inert atmosphere of argon in glassware that had been oven or flame dried. Solvents were distilled from potassium/benzophenone ketyl (Et₂O, THF, benzene, toluene) or from calcium hydride (CH₂Cl₂, triethylamine) prior to use. Reagents were purchased from Aldrich and used without purification. Cerium trichloride was purchased as the hydrated form and dried at 200 °C under 0.1 torr over 12 h. Flash chromatography was performed using Merck silica gel (230-400 Mesh ASTM) with solvents distilled prior to use. ¹H NMR spectra were recorded on a Bruker AC-300 (300 MHz) spectrometer. The following abbreviations were used: s, singlet, d, doublet, q, quarter, qi, quinter, sx, sextet, hept, septet. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm, DMSO-*d*₆: 2.49 ppm, acetone-*d*₆: 2.04 ppm, CD₃OD: 3.30 ppm). Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrometer with a thin layer of the product over a NaCl disk. High-resolution spectrometry was performed on a ZAB-1F micromass spectrometer. Diastereomeric and enantiomeric ratios were determined by gas chromatography (HP 5890 serie II) coupled with a mass spectrometer (HP 5971) or by chiral HPLC (HP 1100, Chiralcel-OD and Chiralcel-OB columns).

General Procedure for the formation of vinylic iodides

Biscyclopentadienylzirconium dichloride (1.5 eq.) was dissolved in tetrahydrofuran (0.09 M), and cooled to 0 °C while shielding the reaction from daylight. Lithium triethylborohydride (1.5 eq., 1 M in THF) was added dropwise. The mixture was warmed to room temperature and stirred for 1.5 h. The protected propargylic alcohol (1.0 eq.) was added via canula as a tetrahydrofuran solution (0.14 M). The orange solution was stirred for 2 h and then solid iodine (1.7 eq.) was added in small portions. The mixture was stirred for 10 h at room temperature while shielding the reaction from daylight. The mixture was quenched with a solution of saturated aqueous sodium bicarbonate and stirred until the color disappeared. Diethyl ether was added, the two phases were separated and the aqueous phase was extracted twice with diethyl ether. The organic phases were combined, washed with a solution of saturated aqueous sodium thiosulfate, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel, eluting with ethyl acetate / hexanes (0 : 100 to 5 : 95) furnished a clear oil.

3-*t*-Butyldiphenylsilyloxy-1-iodo-1-propene **12a**

The reaction was performed with 8.00 g (27.17 mmol) of TBDPS-protected propargylic alcohol to give vinylic iodide **12a** (9.08 g, 79%) as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 7.69-7.60 (m, 4H), δ 7.49-7.34 (m, 6H), δ 6.59 (dt, 1H, J = 14.3, 4.4 Hz), δ 6.36 (dt, 1H, J = 14.3, 1.7 Hz), δ 4.11 (dd, 2H, J = 4.4, 1.7 Hz), δ 1.05 (s, 9H).

3-*t*-Butyldimethylsilyloxy-1-iodo-1-propene **12b**

The reaction was performed with 3.01 g (17.67 mmol) of TBS-protected propargylic alcohol to give vinylic iodide **12b** (3.65 g, 69%) as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 6.60 (dt, 1H, J = 14.3, 4.6 Hz) δ 6.28 (dt, 1H, J = 14.3, 1.8 Hz) δ 4.11 (dd, 2H, J = 4.6, 1.8 Hz) δ 0.90 (s, 9H) δ 0.07 (s, 6H); **LRMS** (m/z , relative intensity): 298 (M^+ , 1), 241 (90), 185 (100), 167 (20); **HRMS** calcd for $\text{C}_9\text{H}_{19}\text{OSi}$: 298.0250, found : 298.0255.

General procedure for the addition of vinyl lithium to (-)-menthone

The appropriate alkyne or vinyl bromide (1.2 eq) was dissolved in dry cold ($-78\text{ }^\circ\text{C}$) THF (0.7 M) and *n*-BuLi (1.2 eq, 2.5 M in hexanes) or *t*-BuLi (2.4 eq, 1.4 M in pentane) respectively was slowly added. Dry cerium trichloride (1.0 eq) was added and after stirring for 60 min, (-)-menthone (1.0 eq) was added over 5 min. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h after which time, saturated sodium chloride was poured into the cold solution. The aqueous phase was separated, and extracted with diethyl ether, and the combined organic phases were washed with brine, dried over magnesium sulfate, filtered, concentrated *in vacuo*, and purified by flash chromatography on silica gel to give exclusively the axial alcohol.

Alcohol **13a**

The reaction was performed with 8.30 g (19.7 mmol) of vinylic iodide **12a** and 2.53 g (16.4 mmol) of (-)-menthone to give alcohol **13a** (5.41 g, 73%) as a colorless oil. **¹H NMR**(CDCl₃, 300 MHz) : δ 7.70-7.67 (m, 4H), δ 7.45-7.34 (m, 6H), δ 5.82-5.69 (m, 2H), δ 4.25 (d, 2H, *J* = 2.8 Hz), δ 2.01-1.93 (m, 1H), δ 1.83-1.68 (m, 2H), δ 1.57-1.38 (m, 3H), δ 1.27-1.05 (m, 3H), δ 1.06 (s, 9H), δ 0.89-0.84 (m, 9H); **IR** (neat, cm⁻¹) : 3600, 3573, 3489; **LRMS** (m/z, relative intensity) : 393 (M⁺-C₄H₉, 10), 199 (90), 177 (100), 135 (45), 121 (50); **HRMS** calcd for C₂₅H₃₃O₂Si : 393.2250, found : 393.2645. $[\alpha]_D^{20} = -7.0$ (c 1.92, CHCl₃).

Alcohol **13b**

The reaction was performed with 7.36 g (24.7 mmol) of vinylic iodide **12b** and 3.23 g (21.0 mmol) of (-)-menthone to give alcohol **13b** (4.98 g, 73%) as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 5.77 (dt, 1H, *J* = 15.5, 4.3 Hz), δ 5.66 (d, 1H, *J* = 15.6 Hz), δ 4.21 (d, 2H, *J* = 4.3 Hz), δ 1.96 (hept d, 1H, *J* = 6.9, 1.8 Hz), δ 1.81-1.68 (m, 2H), δ 1.55-1.38 (m, 4H), δ 1.22-1.06 (m, 2H), δ 0.91 (s, 9H), δ 0.86 (d, 6H, *J* = 4.4 Hz), δ 0.84 (d, 3H, *J* = 4.5 Hz), δ 0.07 (s, 6H); **IR** (neat, cm⁻¹) : 3607, 3491; **LRMS** (m/z, relative intensity) : 326 (M⁺, 1), 265 (50), 175 (30), 133 (30), 105 (30), 75 (100); **HRMS** calcd for C₁₉H₃₈O₂Si : 326.2641, found : 326.2635. $[\alpha]_D^{20} = -20.2$ (c 1.74, CHCl₃).

General procedure for the formation of carbonates

The appropriate alcohol was dissolved in dry cold (-78 °C) THF (to a concentration of ca. 0.1 M) and *n*-BuLi (2 eq, 2.5 M in hexanes) was added dropwise, the yellow solution was stirred at -78 °C for 30 min and then at 0 °C for another 30 min. Then dimethyl carbonate (2 eq.) was added and the reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 1.5 h, after which time saturated ammonium chloride was poured into the cold solution. The aqueous phase was separated and extracted with diethyl ether and the combined organic phases were washed with brine, dried over magnesium sulfate, filtered, and concentrated *in vacuo* to give the carbonate, which was used crude in the next reaction.

Carbonate from 13a

This carbonate is unstable and was used directly without purification. **¹H NMR** (CDCl₃, 300 MHz): δ 7.72-7.66 (m, 4H), δ 7.49-7.35 (m, 6H), δ 6.00 (d, 1H, J = 16.0 Hz), δ 5.54 (dt, 1H, J = 16.0, 5.0 Hz), δ 4.33-4.18 (m, 2H), δ 3.71 (s, 3H), δ 2.73 (dm, 1H, J = 14.3 Hz), δ 2.25-2.11 (m, 1H), δ 1.88-1.73 (m, 1H), δ 1.65-1.47 (m, 3H), δ 1.39-1.10 (m, 3H), δ 1.05 (s, 9H), δ 0.96-0.83 (m, 9H).

Carbonate from 13b

This carbonate is unstable and was used directly without purification. **¹H NMR** (CDCl₃, 300 MHz): δ 5.91 (d, 1H, J = 15.9 Hz), δ 5.53 (dt, 1H, J = 15.9, 5.0 Hz), δ 4.21 (d, 2H, J = 5.0 Hz), δ 3.70 (s, 3H), δ 2.72 (dt, 1H, J = 14.3, 2.8 Hz), δ 2.20-2.08 (m, 1H), δ 1.81-1.76 (m, 1H), δ 1.61-1.49 (m, 3H), δ 1.32-1.07 (m, 3H), δ 0.90 (s, 9H), δ 0.91-0.80 (m, 9H), δ 0.07 (s, 6H).

Carbonate from 16

This carbonate is unstable and was used directly without purification. **¹H NMR** (CDCl₃, 300 MHz): δ 5.65 (d, 1H, J = 16.5 Hz), δ 5.34 (dd, 1H, J = 16.5, 6.6 Hz), δ 3.70 (s, 3H), δ 2.68 (dt, 1H, J = 14.3, 2.8 Hz), δ 2.26-2.08 (hept d, 1H, J = 6.6, 0.6 Hz), δ 2.07-1.91 (m, 1H), δ 1.82-1.41 (m, 8H), δ 1.37-1.00 (m, 8H), δ 1.00-0.82 (m, 1H), δ 0.88 (d, 3H, J = 7.2 Hz), δ 0.87 (d, 3H, J = 6.6 Hz), δ 0.84 (d, 3H, J = 6.6 Hz).

General procedure for the addition of cuprate reagents to carbonates

The cuprate reagents were prepared by adding 1.5 eq. of the organolithium (or cyclohexylmagnesium bromide) to a suspension of copper cyanide (1.5 eq) in dry THF (0.1 M) at -78 °C. The suspension was stirred for 30 min at -78 °C, after which time the crude carbonate (1 eq) dissolved in THF was added. The reaction mixture was warmed to room temperature for 4 h, after which time a solution of saturated ammonium chloride and ammonium hydroxide (9:1) was poured into the reaction mixture. The aqueous phase was separated and extracted with diethyl ether, the combined organic phases were washed with brine, dried over magnesium sulfate, filtered, concentrated *in vacuo*, and purified by flash chromatography on silica gel (100% hexanes) to give exclusively the *anti* S_N2' diastereomer.

Adduct 7a

The reaction was performed according to the general procedure for the addition of cuprate reagents to carbonates starting with 1.06 g (3.25 mmol) of allylic alcohol **13b** and *t*-BuLi (3.5 mL, 4.88 mmol, 1.4 M in pentane) to give the cuprate adduct **7a** (1.09 g, 91 %) as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 5.00 (d, 1H, *J* = 10.3 Hz), δ 3.71 (dd, 1H, *J* = 9.8, 4.6 Hz), δ 3.43 (dd, 1H, *J* = 9.7, 7.2 Hz), δ 2.42 (dd, 1H, *J* = 12.1, 3.0 Hz), δ 2.26, (ddd, 1H, *J* = 11.6, 7.2, 4.5 Hz), δ 1.93 (octet, 1H, *J* = 6.8 Hz), δ 1.78-1.72 (m, 2H), δ 1.62-1.50 (m, 2H), δ 1.25-1.04 (m, 3H), δ 0.93-0.86 (m, 9H), δ 0.89 (s, 9H), δ 0.87 (s, 9H), δ 0.00 (s, 6H); **IR** (neat, cm⁻¹) : 2907, 2862; **LRMS** (*m/z*, relative intensity) : 309 ((M⁺-C₄H₉) ,40) 177 (30), 111 (40), 74 (100); **HRMS** calcd for C₁₉H₃₇OSi (M⁺-C₄H₉): 309.2614, found : 309.2622. [α]_D²⁰ = -43.0 (c 1.65, CHCl₃).

Adduct 7b

The reaction was performed according to the general procedure for the addition of cuprate reagents to carbonates starting with 1.57 g (3.08 mmol) of allylic alcohol **13a**. A 0.34 M solution of 1-naphthyllithium in THF was used (13.6 mL, 4.6 mmol), which was prepared by treating 1 eq. of 1-naphthyl bromide with 1 eq. of *n*-butyllithium (2.5 M in hexanes) at -78 °C and stirring for 1 h before using the solution. This gave the cuprate adduct **7b** (1.50 g, 90 %) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) : δ 7.81 (d, 2H, *J* = 8.3 Hz), δ 7.68 (dd, 1H, *J* = 7.2, 2.2 Hz), δ 7.59-7.50 (m, 4H), δ 7.44-7.28 (m, 10H), δ 5.61 (d, 1H, *J* = 8.3 Hz), δ 4.57 (q, 1H, *J* = 7.7 Hz), δ 3.96-3.84 (m, 2H), δ 2.35 (dd, 1H, *J* = 13.2, 3.6 Hz), δ 2.02 (octet, 1H, *J* = 6.6 Hz), δ 1.79-1.50 (m, 4H), δ 1.36-1.25 (m, 2H), δ 1.14-1.00 (m, 1H), δ 0.99-0.88 (m, 15H), δ 0.66 (d, 3H, *J* = 6.6 Hz); IR (neat, cm⁻¹) : 3049 ; LRMS (m/z, relative intensity) : 503 ((M⁺-C₄H₉) ,100) 309 (30), 291 (35), 199 (70), 141 (60), 135 (40); HRMS calcd for C₃₅H₃₉OSi (M⁺-C₄H₉): 503.2770, found : 503.2762. [α]_D²⁰ = -43.0 (c 1.65, CHCl₃).

Adduct **7c**

The reaction was performed according to the general procedure for the addition of cuprate reagents to carbonates starting with 1.10 g (2.43 mmol) of allylic alcohol **13a**. A 0.34 M solution of 2-naphthyllithium in THF was used (10.7 mL, 3.6 mmol), which was prepared by treating 1 eq. of 2-naphthyl bromide with 1 eq. of *n*-butyllithium (2.5 M in hexanes) at -78 °C and stirring for 1 h before using the solution. This gave the cuprate adduct **7c** (1.13 g, 85 %) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) : δ 7.81-7.73 (m, 3H), δ 7.64 (s, 1H), δ 7.56-7.50 (m, 4H), δ 7.49-7.25 (m, 9H), δ 5.46 (d, 1H, *J* = 8.8 Hz), δ 3.98-3.83 (m, 3H), δ 2.45-2.34 (m, 1H), δ 1.97 (octet, 1H, *J* = 6.6 Hz), δ 1.85-1.57 (m, 5H), δ 1.36-1.24 (m, 1H), δ 1.20-1.03 (m, 1H), δ 0.96 (s, 9H), δ 0.91 (d, 3H, *J* = 6.6 Hz), δ 0.89 (d, 3H, *J* = 6.6 Hz), δ 0.76 (d, 3H, *J* = 6.1 Hz); IR (neat, cm⁻¹) : 3052, ; LRMS (m/z, relative intensity) : 503 (M⁺-C₄H₉, 100), 309 (25), 291 (30), 199 (37), 141 (32); HRMS calcd for C₃₅H₃₉OSi (M⁺-C₄H₉): 503.2770, found : 503.2762. [α]_D²⁰ = +21.5 (c 1.71, CHCl₃).

Adduct 7d

The reaction was performed according to the general procedure for the addition of cuprate reagents to carbonates starting with 501 mg (1.54 mmol) of allylic alcohol **13b**. A 0.5 M solution of cyclohexylmagnesium bromide in THF was used (4.62 mL, 2.31 mmol), which was prepared by treating 1 eq. of cyclohexylbromide with 1.5 eq. of magnesium turnings in refluxing THF and stirring 24 h before using the solution. This gave the cuprate adduct **7d** (494 mg, 82 %) as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 4.92 (d, 1H, J = 9.9Hz), δ 3.54-3.42 (m, 2H), δ 2.42-2.28 (m, 2H), δ 1.90 (octet, 1H, J = 6.6Hz), δ 1.80-1.40 (m, 10H), δ 1.33-0.92 (m, 8H), δ 0.90-0.79 (m, 9H), δ 0.88 (s, 9H), 0.01 (s, 6H); **IR** (neat, cm⁻¹) : 1645; **LRMS** (m/z, relative intensity) : 352 (M⁺, 1), 335 ((M⁺-C₄H₉), 151 (25), 137 (25), 109 (48), 95 (38); **HRMS** calcd for C₂₁H₄₁OSi (M-C₄H₉⁺): 335.2770, found : 335.2777. [α]_D²⁰ = -39.2 (c 1.27, CHCl₃).

Adduct 7e

The reaction was performed according to the general procedure for the addition of cuprate reagents to carbonates starting with 650 mg (2.46 mmol) of allylic alcohol **16**. A 0.33 M solution of *t*-butoxymethyl lithium in methyl-*t*-butylether was used (29.8 mL, 9.84 mmol), which was prepared by treating 1 eq. of potassium *t*-butoxide in methyl-*t*-butylether with 1 eq. of *s*-butyllithium (1.3 M in cyclohexane) at -78 °C, stirring for 2h at -78 °C, for 0.5 h at -50 °C, and cooling back to -78 °C before using the solution. This gave the cuprate adduct **7e** (655 mg, 80 %) as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 4.92 (d, 1H, J = 9.9 Hz), δ 3.29 (t, 1H, J = 8.3 Hz), δ 3.20-3.15 (m, 1H), δ 2.47-2.33 (m, 1H), δ 2.33-2.22 (m, 1H), δ 1.93 (hept, 1H, J = 6.6 Hz), δ 1.87-1.46 (m, 11H), δ 1.39-0.86 (m, 7H), δ 1.16 (s, 9H), δ 0.91-0.85 (m, 9H); **IR** (neat, cm⁻¹) : 2924, 2859, 1425; **¹³C NMR** (CDCl₃, 75.5 MHz) : δ 140.7 (s), 122.1 (s), 72.1 (s), 63.3 (t), 51.8 (d), 43.0 (d), 38.8 (d), 35.3 (t), 32.0 (d), 31.8 (t), 31.5 (t), 28.3 (t), 27.6 (q), 26.7 (t), 26.6 (d), 26.5 (t), 22.2 (q), 20.4 (q), 19.9

(q); **LRMS** (m/z (relative intensity)) : 334 (M^+ , 1), 278 (10), 151 (75), 109 (100), 81 (95) ; **HRMS** calcd for $C_{23}H_{42}O$: 334.3235, found : 334.3231. $[\alpha]_D^{20} = +8.4$ (c 1.10, $CHCl_3$).

General procedure for the formation of carbamates **8a-d, f, g**

The TBDPS-protected alcohol (1.0 eq.) was dissolved in tetrahydrofuran (0.13 M) and a solution of tetrabutylammonium fluoride (1.5 eq.) was added slowly. The mixture was stirred at room temperature for 15 h. Then saturated ammonium chloride and diethyl ether were added and the two phases were separated. The aqueous phase was extracted twice with diethyl ether and the organic fractions were combined, washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with ethyl acetate / hexanes (6 : 94 to 15 : 85) furnished the corresponding alcohol.

The alcohol (or in the case of TBDMS-protected alcohols, the silyl ether) (1.0 eq.) was dissolved in acetone (0.3 M) and cooled 0 °C. Jones' reagent (3.0 eq, 2.67 M, prepared as follows : mix 26.7g of CrO_3 with 23 mL of conc. H_2SO_4 . Slowly dilute with distilled water to a total volume of 100 mL) was added slowly and the mixture was stirred at 0 °C for 2 h. 2-Propanol was added until the solution turned green and the solvents were then evaporated. Dichloromethane and water were added and the two phases were separated. The aqueous phase was extracted twice with dichloromethane. The organic fractions were combined, washed with water and brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography eluting with ethyl acetate / dichloromethane (0 : 100 to 10 : 90) afforded colorless oils.

The carboxylic acid (1.0 eq.) was dissolved in toluene (0.1 M), then triethylamine (1.3 eq.) and diphenylphosphoryl azide (1.2 eq.) were added. The mixture was refluxed for 1 h, after which time it was cooled to room temperature and the solvent evaporated. A solution of sodium methanoate (4.5 eq.) in methanol (0.5 M) was added and the mixture was heated to reflux again for 1 h (this step is necessary to convert the small amount of carbamoyl azide formed back to the methyl carbamate). After cooling to room temperature and evaporating the methanol, water and diethyl ether were poured in and the two phases were separated. The aqueous phase was extracted twice with diethyl ether. The combined organic fractions were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography was done as indicated in each case.

Carbamate 8a

The direct deprotection/oxidation was performed using the general procedure described above for the Jones' oxidation starting with 1.08 g (2.95 mmol) of TBS-ether **7a** to give 785 mg (100%) of carboxylic acid as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 5.25 (d, 1H, $J = 10.3$ Hz), δ 3.16 (d, 1H, $J = 10.3$ Hz), δ 2.42 (dd, 1H, $J = 17.3, 8.3$ Hz), δ 1.95 (octet, 1H, $J = 6.8$ Hz), δ 1.82-1.73 (m, 2H), δ 1.67-1.57 (m, 2H), 1.28-1.05 (m, 3H), δ 1.00 (s, 9H), δ 0.92-0.84 (m, 9H); **IR** (neat, cm^{-1}): 3690-2140 (br), 2927, 2866, 1700; **LRMS** (m/z , relative intensity): 266 (M^+ , 8), 210 (80), 167 (100), 149 (100), 81 (50); **HRMS** calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2$: 266.2246, found: 266.2251. $[\alpha]_{\text{D}}^{20} = -79.9$ (c 1.32, CHCl_3).

The Curtius rearrangement was carried out starting from 148 mg (0.56 mmol) of carboxylic acid, following the general procedure described above. Flash chromatography eluting with ethyl acetate / hexanes (8 : 92) gave 124 mg (76 %) of carbamate **8a** as a white solid. m.p. : 108-109 °C; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 5.01 (d, 1H, $J = 9.4$ Hz), δ 4.49 (d, 1H, $J = 9.2$ Hz), δ 4.23 (br, 1H), δ 3.65 (s, 3H), δ 2.48 (q, 1H, $J = 9.1$ Hz), δ 1.88 (octet, 1H, $J = 6.8$ Hz), δ 1.80-1.73 (m, 2H), δ 1.66-1.57 (m, 3H), δ 1.23-0.95 (m, 2H), δ 0.93-0.83 (m, 9H), δ 0.90 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 156.6 (s), 144.7 (s), 119.0 (d), 56.4 (d), 52.0 (q), 51.1 (d), 37.0 (t), 34.9 (d), 33.2 (d), 32.7 (d), 27.7 (t), 26.8 (d), 26.1 (q), 22.0 (q), 21.2 (q), 19.7 (q); **IR** (neat, cm^{-1}): 3325, 1696; **LRMS** (m/z , relative intensity): 238 ($\text{M}^+ - \text{C}_4\text{H}_9$, 100), 163 (35), 128 (20); **HRMS** calcd for $\text{C}_{14}\text{H}_{22}\text{NO}_2$ ($\text{M}^+ - \text{C}_4\text{H}_9$): 238.1807, found: 238.1801. $[\alpha]_{\text{D}}^{20} = +19.3$ (c 1.08, CHCl_3).

Carbamate 8b

The deprotection was performed starting with 514 mg (0.92 mmol) of **7b** 290 mg (98 %) to give an alcohol as a white solid. m.p. : 72-74 °C; $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 8.17 (d, 1H, $J = 8.3$ Hz), δ 7.88-7.85 (m, 1H), δ 7.76-7.73 (m, 1H), δ 7.56-7.40 (m, 4H), δ 5.44 (d, 1H, $J = 8.8$ Hz), δ 4.72-4.64

(m, 1H), δ 4.00-3.92 (m, 1H), δ 3.83-3.75 (m, 1H), δ 2.53 (dd, 1H, $J = 13.0, 4.1$ Hz), δ 1.99 (octet, 1H, $J = 6.6$ Hz), δ 1.86-1.64 (m, 4H), δ 1.50 (dd, 1H, $J = 7.7, 5.5$ Hz), δ 1.43-1.21 (m, 1H), δ 1.16-1.07 (m, 1H), δ 0.91 (d, 3H, $J = 6.6$ Hz), δ 0.88 (d, 3H, $J = 6.6$ Hz), δ 0.77 (d, 3H, $J = 6.6$ Hz); **IR** (neat, cm^{-1}): 3568, 3047, 2923; **LRMS** (m/z , relative intensity) : 322 (M^+ , 10), 291 (100), 167 (30), 141 (75); **HRMS** calcd for $\text{C}_{23}\text{H}_{30}\text{O}$: 322.2297, found : 322.2299. $[\alpha]_D^{20} = -42.9$ (c 1.02, CHCl_3).

The oxidation was performed with 277 mg (0.86 mmol) of alcohol to give 154 mg (53 %) of the carboxylic acid as a white solid. m.p. : 104-107 $^{\circ}\text{C}$; **^1H NMR** (CDCl_3 , 300 MHz) : δ 8.12 (d, 1H, $J = 8.2$ Hz), δ 7.88-7.85 (m, 1H), δ 7.77 (d, 1H, $J = 8.3$ Hz) δ 7.57-7.42 (m, 4H), δ 5.74 (d, 1H, $J = 8.8$ Hz), δ 5.29 (d, 1H, $J = 8.8$ Hz), δ 2.40-2.37 (m, 1H), δ 1.99 (octet, 1H, $J = 6.6$ Hz), δ 1.79-1.66 (m, 5H), δ 1.36-1.26 (m, 1H), δ 1.13-1.07 (m, 1H), δ 0.92-0.88 (m, 6H), δ 0.71 (d, 3H, $J = 6.1$ Hz); **IR** (neat, cm^{-1}): 3400-2210, 3052, 2935, 2866, 1700; **LRMS** (m/z , relative intensity) : 336 (M^+ , 25), 172 (65), 155 (95), 141 (90), 127 (100); **HRMS** calcd for $\text{C}_{23}\text{H}_{28}\text{O}_2$: 336.2089, found : 336.2084. $[\alpha]_D^{20} = -51.9$ (c 1.27, CHCl_3).

The Curtius rearrangement was carried out starting from 153 mg (0.46 mmol) of carboxylic acid following the general procedure described above, except that in this case the toluene was not evaporated prior to adding the methanol. Flash chromatography eluting with dichloromethane / hexanes (20 : 80) gave 138 mg (83 %) of carbamate **8b** as a colorless oil. **^1H NMR** (CDCl_3 , 300 MHz) : δ 8.10 (d, 1H, $J = 7.7$ Hz), δ 7.88-7.85 (m, 1H), δ 7.77 (d, 1H, $J = 8.3$ Hz) δ 7.55-7.41 (m, 4H), δ 6.22 (br, 1H), δ 5.39 (d, 1H, $J = 8.2$ Hz), δ 5.01 (s, 1H), δ 3.67 (s, 3H), δ 2.63-2.49 (m, 1H), δ 1.94 (octet, 1H, $J = 6.6$ Hz), δ 1.90-1.81 (m, 4H), δ 1.68-1.63 (m, 1H), δ 1.35-1.25 (m, 1H), δ 1.20-1.11 (m, 1H), δ 0.91-0.84 (m, 9H); **^{13}C NMR** (CDCl_3 , 75.5 MHz) : δ 155.9 (s), 145.3 (s), 138.7 (s), 134.0 (s), 130.8 (s), 128.8 (s), 128.0 (d), 126.0 (d), 125.6 (d), 125.3 (d), 123.8 (d), 123.5 (d), 122.2 (d), 52.2 (q), 50.9 (d), 49.7 (d), 36.4 (t), 32.9 (d), 32.1 (t), 27.1 (t), 26.6 (d), 22.1 (q), 20.9 (q), 19.6 (q); **IR** (neat, cm^{-1}): 3445, 3330, 1705; **LRMS** (m/z , relative intensity) : 365 (M^+ , 25), 290 (25), 247 (40), 227 (45), 214 (100); **HRMS** calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_2$: 365.2355, found : 365.2346. $[\alpha]_D^{20} = -22.9$ (c 1.79, CHCl_3).

Carbamate **8c**

The deprotection was performed as per the general procedure with 729 mg (1.30 mmol) of TBDPS ether **7c** to give 400 mg (95 %) of alcohol as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 7.85-7.78 (m, 3H), δ 7.69 (s, 1H), δ 7.51-7.38 (m, 3H), δ 5.38 (d, 1H, *J* = 9.3 Hz), δ 4.00 (dd, 1H, *J* = 16.5, 7.2 Hz), δ 3.95-3.83 (m, 1H), δ 3.82-3.69 (m, 1H), δ 2.46 (dd, 1H, *J* = 12.7, 3.9 Hz), δ 1.98 (octet, 1H, *J* = 6.6 Hz), δ 1.90-1.61 (m, 4H), δ 1.49-1.22 (m, 2H), δ 1.20-1.06 (m, 1H), δ 0.92 (d, 3H, *J* = 6.6 Hz), δ 0.88 (d, 3H, *J* = 6.6 Hz), δ 0.83 (d, 3H, *J* = 6.6 Hz); **IR** (neat, cm⁻¹): 3625-3117, 3568; **LRMS** (m/z, relative intensity) : 322 (M⁺, 5), 291 (32), 261 (24), 181 (24), 167 (37), 141 (100); **HRMS** calcd for C₂₃H₃₀O: 322.2297, found : 322.2290. [α]_D²⁰ = +79.9 (c 1.42, CHCl₃).

The oxidation was performed as per the general procedure with 423 mg (1.31 mmol) of alcohol to give 266 mg (60 %) of carboxylic acid as a white solid. m.p. : 101-104 °C; **¹H NMR** (CDCl₃, 300 MHz) : δ 7.88-7.78 (m, 4H), δ 7.53-7.41 (m, 3H), δ 5.69 (d, 1H, *J* = 9.4 Hz), δ 4.77 (d, 1H, *J* = 9.4 Hz), δ 2.51-2.38 (m, 1H), δ 1.99 (octet, 1H, *J* = 6.6 Hz), δ 1.87-1.49 (m, 5H), δ 1.43-1.27 (m, 1H), δ 1.19-1.05 (m, 1H), δ 0.91 (d, 3H, *J* = 6.6 Hz), δ 0.88 (d, 3H, *J* = 6.6 Hz), δ 0.80 (d, 3H, *J* = 6.1 Hz); **IR** (neat, cm⁻¹) : 3383-2400, 3060, 1705; **LRMS** (m/z, relative intensity) : 336 (M⁺, 45), 291 (75), 247 (100), 211 (37), 191 (52), 167 (45), 141 (100); **HRMS** calcd for C₂₃H₂₈O₂: 336.2089, found : 336.2084. [α]_D²⁰ = +30.5 (c 1.04, CHCl₃).

The Curtius rearrangement was carried out as per the general procedure starting from 237 mg (0.70 mmol) of carboxylic acid. Flash chromatography eluting with dichloromethane / hexane (20 : 80) gave 200 mg (78 %) of carbamate **8c** as a white solid. In this case, the toluene was not evaporated prior to adding the methanol. m.p. : 112-114 °C; **¹H NMR** (CDCl₃, 300 MHz) : δ 7.87-7.79 (m, 3H), δ 7.76 (s, 1H), δ 7.52-7.38 (m, 3H), δ 5.72 (br, 1H), δ 5.28 (d, 1H, *J* = 8.8 Hz), δ 5.04 (br, 1H), δ 3.68 (s, 3H), δ 2.55 (m, 1H), δ 2.05-1.72 (m, 5H), δ 1.71-1.60 (m, 1H), δ 1.46-1.26 (m, 1H), δ 1.24-1.09 (m, 1H), δ 1.00-0.85 (m, 9H); **¹³C NMR** (CDCl₃, 75.5 MHz) : δ 156.2 (s), 144.8 (s), 140.5 (s), 133.4 (s), 132.6 (s), 128.4 (d), 127.9 (d), 127.6 (d), 126.0 (d), 125.7 (d), 124.9 (d), 124.6 (d), 121.9 (d), 52.5 (d), 52.2 (q), 51.1 (d), 36.0 (t), 32.6 (d), 31.6 (t), 26.7 (t), 26.5 (d), 22.0 (q), 20.6 (q), 19.7 (q); **IR** (neat, cm⁻¹): 3321, 3049, 1703; **LRMS** (m/z, relative intensity) : 365 (M⁺, 15), 290 (50), 247 (62), 227 (100), 214 (100), 191 (45), 141 (82); **HRMS** calcd for C₂₄H₃₁NO₂: 365.2355, found : 365.2346. [α]_D²⁰ = +36.5 (c 1.00, CHCl₃).

Carbamate **8d**

The deprotection/oxidation was performed using the general procedure described above for the Jones' oxidation (except that in this case, the reaction was stirred at room temperature for 1 h prior to adding 2-propanol) starting with 488 mg (1.24 mmol) of TBS-ether **7d** to give 361 mg (99%) of carboxylic acid as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 5.06 (d, 1H, *J* = 9.4 Hz), δ 3.08 (t, 1H, *J* = 9.4 Hz), δ 2.45-2.30 (m, 1H), δ 1.92 (hept, 1H, *J* = 6.6 Hz), δ 1.86-1.56 (m, 12H), δ 1.39-0.70 (m, 6H), 0.91 (d, 3H, *J* = 6.1 Hz), δ 0.88 (d, 3H, *J* = 6.6 Hz), δ 0.84 (d, 3H, *J* = 6.6 Hz); **IR** (neat, cm⁻¹) : 3404-2937, 2927, 2856, 1703; **LRMS** (*m/z* (relative intensity)) : 292 (M⁺, 20) 203 (60), 167 (100), 149 (75); **HRMS** calcd for C₁₉H₃₂O₂: 292.2402, found : 292.2408. [α]_D²⁰ = -88.3 (c 1.29, CHCl₃).

The Curtius rearrangement was carried out as per the general procedure starting from 317 mg (1.08 mmol) of carboxylic acid. Flash chromatography eluting with ethyl acetate / hexanes (4 : 96) gave 250 mg (72 %) of carbamate **8d** as a white solid. m.p. : 129.4 °C **¹H NMR** (CDCl₃, 300 MHz) : δ 4.93 (d, 1H, *J* = 8.8 Hz), δ 4.44 (br, 1H), δ 4.22 (br, 1H), δ 3.64 (s, 3H), δ 2.48-2.38 (m, 1H), δ 1.88 (octet, 1H, *J* = 6.6 Hz), δ 1.84-1.53 (m, 11H), δ 1.49-0.98 (m, 7H), δ 0.98-0.79 (m, 9H); **¹³C NMR** (CDCl₃, 75.5 MHz) : δ 156.4 (s), 144.2 (s), 120.9 (d), 53.2 (d), 51.8 (q), 51.0 (d), 43.3 (d), 36.5 (t), 32.8 (d), 32.2 (t), 29.2 (t), 27.2 (t), 26.6 (d), 26.5 (t), 26.2 (t), 22.0 (q), 20.9 (q), 19.7 (q); **IR** (neat, cm⁻¹) : 3329, 1694; **LRMS** (*m/z*, relative intensity) : 238 (MH⁺, 20), 238 (100), 170 (58), 163 (25); **HRMS** calcd for C₁₄H₂₂NO₂ (MH⁺): 322.2746, found : 322.2752. [α]_D²⁰ = +2.8 (c 1.55, CHCl₃).

Carbamate **8f**

The Curtius rearrangement was carried out as per the general procedure starting from 178 mg (0.668 mmol) of carboxylic acid. *t*-Butanol was used instead of methanol. Flash chromatography eluting with diethyl ether / hexanes (10 : 90) gave 103 mg (46 %) of carbamate **8f** as a white solid along with 30 mg (17%) of recovered isocyanate. **¹H NMR** (300 MHz, CDCl₃) : δ 5.02 (d, 1H, *J* = 9.1 Hz), 4.38-4.35 (m, 1H), 4.17 (t, 1H, *J* = 9.2 Hz), 2.48 (d, 1H, *J* = 9.2 Hz), 1.88 (hept, 1H, *J* = 6.9 Hz), 1.78-1.54 (m, 4H), 1.41 (s, 9H), 1.25-1.04 (m, 2H), 0.90 (d, 3H, *J* = 6.5 Hz), 0.88 (s, 9H), 0.86-0.84 (m, 6H). **¹³C NMR** (75.5 MHz, CDCl₃) : δ 155.8 (s), 145.0 (s), 119.9 (d), 79.1 (s), 55.9 (d), 51.6 (d), 37.4 (t), 35.3 (s), 33.6 (d), 33.1 (t), 28.9 (q), 28.1 (t), 27.3 (d), 26.7 (q), 22.6 (q), 21.7

(q), 20.3 (q). **IR** (neat, cm^{-1}): 3265, 1702, 1490. **LRMS** (m/z , relative intensity): 280 ($\text{M}^+ - \text{C}_4\text{H}_9$, 15), 224 (100). **HRMS** calcd for $\text{C}_{17}\text{H}_{30}\text{NO}_2$: 280.2276, found : 280.2270.

Carbamate **8g**

The Curtius rearrangement was carried out as per the general procedure starting from 90 mg (0.388 mmol) of carboxylic acid. 9-Fluorenylmethanol was used instead of methanol and in this case the toluene was not evaporated prior to adding the alcohol. Flash chromatography eluting with diethyl ether / hexanes (10 : 90) gave 111 mg (72 %) of carbamate **8g** as a white solid. **^1H NMR** (300 MHz, CDCl_3) : δ 7.78 (d, 2H, $J = 7.5$ Hz), 7.62 (t, 2H, $J = 7.0$ Hz), 7.41 (t, 2H, $J = 7.3$ Hz), 7.33 (t, 2H, $J = 7.4$ Hz), 5.12 (d, 1H, $J = 9.3$ Hz), 4.68 (d, 1H, $J = 9.6$ Hz), 4.42 (d, 2H, $J = 7.0$ Hz), 4.34 (t, 1H, $J = 9.6$ Hz), 4.25 (t, 1H, $J = 6.8$ Hz), 2.50 (d, 1H, $J = 10.2$ Hz), 1.92 (hept, 1H, $J = 6.7$ Hz), 1.80-1.64 (m, 5H), 1.34-1.24 (m, 1H), 1.17-1.12 (m, 1H), 0.96-0.89 (m, 18H). **^{13}C NMR** (75.5 MHz, CDCl_3) : δ 155.9 (s), 145.1 (s), 144.2 (s), 141.4 (s), 127.7 (d), 127.0 (d), 125.1 (d), 120.0 (d), 119.3 (d), 66.5 (t), 56.4 (d), 51.3 (d), 47.4 (d), 36.7 (t), 35.0 (s), 33.1 (d), 32.3 (t), 27.6 (t), 26.9 (d), 26.3 (q), 22.2 (q), 21.1 (q), 20.0 (q). **IR** (neat, cm^{-1}): 3445, 3338, 1716, 1504. **LRMS** (m/z , relative intensity): 402 ($\text{M}^+ - \text{C}_4\text{H}_9$, 30), 178 (95), 165 (60), 86 (85), 84 (100). **HRMS** calcd for $\text{C}_{27}\text{H}_{32}\text{NO}_2$: 402.2433, found : 402.2424. $[\alpha]_{\text{D}}^{20} = -1.6$ (c 0.92, CHCl_3).

Carbamate (*S*)-**8d** (made from **7e**)

t-Butylether **7e** (1.54 g, 4.60 mmol) was dissolved in diethyl ether (23 mL, 0.2 M) and acetic anhydride (2.35 g, 23.0 mmol) and iron trichloride (111 mg, 0.69 mmol) were added. The mixture was stirred at room temperature for 15 h before a saturated solution of sodium hydrogenophosphate was poured in. The phases were separated and the aqueous phase was extracted twice with ether. The combined organic fractions were washed with brine, filtered, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give 1.47 g (100%) of the acetate product,

which was used in the next step without purification. $^1\text{H NMR}$ (CDCl_3 , 300MHz) : δ 4.91 (d, 1H, $J = 9.9\text{Hz}$), δ 4.07 (dd, 1H, $J = 10.5, 6.3\text{Hz}$), δ 3.98 (dd, 1H, $J = 10.5, 7.2\text{ Hz}$), δ 2.60-2.45 (m, 1H), δ 2.28 (dd, 1H, $J = 16.0, 7.2\text{ Hz}$), δ 2.01 (s, 3H), δ 2.00-1.85 (m, 1H), δ 1.83-1.50 (m, 9H), δ 1.45-0.82 (m, 9H), δ 0.91-0.84 (m, 9H).

The crude acetate was dissolved in methanol (77 mL, 0.06 M), and potassium carbonate (1.27 g, 9.20 mmol) was added in one portion. The mixture was stirred at room temperature for 16 h and the solvent was evaporated. Diethyl ether and a saturated aqueous sodium bicarbonate solution were added, the phases were separated and the aqueous phase was extracted twice with ether. The combined organic fractions were washed with brine, filtered, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude product was purified using a mixture of ethyl acetate: hexane (8 : 92) to give (1.23 mg, 96 %) of alcohol as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 4.86 (d, 1H, $J = 10.5\text{Hz}$), δ 3.68 (dd, 1H, $J = 10.2, 5.3\text{ Hz}$), δ 3.38 (t, 1H, $J = 9.3\text{ Hz}$), δ 2.50-2.35 (m, 2H), δ 1.96 (hept, 1H, $J = 6.6\text{ Hz}$), δ 1.87-1.52 (m, 10H), δ 1.39-0.81 (m, 8H), δ 0.96-0.85 (m, 9H); **IR** (neat, cm^{-1}) : 3665-3085, 2924, 2855, 1450; **LRMS** (m/z (relative intensity)) : 278 (M^+ , 15), 247 (30), 135 (75), 109 (85), 95 (85), 81 (95) ; **HRMS** calcd for $\text{C}_{19}\text{H}_{34}\text{O}$: 278.2610, found : 278.2607. $[\alpha]_{\text{D}}^{20} = -35.1$ (c 1.09, CHCl_3).

The oxidation was performed as per the general procedure (except the crude product was purified using dichloromethane as eluant) with 1.23 g (4.42 mmol) of alcohol and gave 1.15 g (89 %) of carboxylic acid as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300MHz) : δ 5.09 (d, 1H, $J = 9.9\text{ Hz}$), δ 3.07 (t, 1H, $J = 9.4\text{ Hz}$), δ 2.38-2.25 (m, 1H), δ 1.95 (hept, 1H, $J = 6.6\text{ Hz}$), δ 1.86-1.55 (m, 11H), δ 1.38-0.95 (m, 6H), δ 0.92-0.72 (m, 10H); **IR** (neat, cm^{-1}) : 3350-2385, 2925, 2853, 1695, 1449; **LRMS** (m/z (relative intensity)) : 292 (M^+ , 10), 203 (30), 167 (100), 81 (50) ; **HRMS** calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2$: 292.2402, found : 292.2408. $[\alpha]_{\text{D}}^{20} = +45.7$ (c 1.80, CHCl_3).

The Curtius rearrangement was performed as per the general procedure with 734 mg (2.51 mmol) of carboxylic acid and gave 554 mg (69 %) of carbamate (*S*)-**8d** as a white solid. m.p. : 65-66 °C; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 4.93 (d, 1H, $J = 9.4\text{ Hz}$), δ 4.58-7-4.42 (m, 1H), δ 4.30-4.12 (m, 1H), δ 3.64 (s, 3H), δ 2.46-2.32 (m, 1H), δ 1.92 (hept, 1H, $J = 6.6\text{ Hz}$), δ 1.86-1.55 (m, 11H), δ 1.44-1.08 (m, 5H), δ 1.07-0.69 (m, 2H), δ 0.90 (d, 3H, $J = 6.6\text{ Hz}$), δ 0.88 (d, 3H, $J = 6.6\text{ Hz}$), δ 0.85 (d, 3H, $J = 6.6\text{ Hz}$); **IR** (neat, cm^{-1}) : 3449, 3325, 1700, 1532; **LRMS** (m/z (relative intensity)) : 321 (M^+ , 1), 238 (100), 163 (45); **HRMS** calcd for $\text{C}_{20}\text{H}_{35}\text{NO}_2$: 321.2668, found : 321.2673. $[\alpha]_{\text{D}}^{20} = -42.1$ (c 1.54, CHCl_3).

Amino acids **9b,c** and **9g** see after oxazolidinones **18**

Carbamate 10b

Cuprate adduct **7b** (617 mg, 1.10 mmol) was dissolved in dichloromethane (19 mL, 0.06 M) and in 6 mL of methanol (0.18 M). Three drops of sudan III were added and the mixture was cooled to -78 °C. Ozone was bubbled in the reaction mixture and, after the disappearance of the pink color, nitrogen was bubbled through. The mixture was slowly allowed to warm to 0 °C and placed in an ice bath. Sodium borohydride (213 mg, 5.1 eq.) was slowly added. The mixture was stirred at 0 °C for 2.5 h and at room temperature for 15 h. A 1N HCl solution was added slowly, and the methanol was evaporated under reduced pressure before adding water. The aqueous phase was extracted with diethyl ether. The combined organic fractions were washed with water and brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was dissolved in 10 mL of acetone at 0 °C and 1.5 mL of Jones' reagent (3.6 eq, 2.67 M, prepared as described in the general procedure for the formation of carbamates **8a-d, f, g**) was added. The mixture was stirred at 0 °C for 15 min and 2-propanol was added until the solution turned green. After evaporating the solvents *in vacuo*, water was added and the aqueous phase was extracted three times with dichloromethane. The combined organic fractions were washed with water and brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with diethyl ether / hexanes (30 : 70) gave a colorless oil (314 mg, 0.69 mmol, 63 %). ¹H NMR (CDCl₃, 300 MHz) : δ 7.86-7.71 (m, 3H), δ 7.62 (d, 4H, *J* = 7.7 Hz), δ 7.50-7.29 (m, 10H), δ 4.69 (dd, 1H, *J* = 9.3, 5.3 Hz), δ 4.41 (t, 1H, *J* = 9.4 Hz), δ 3.95 (dd, 1H, *J* = 9.9, 5.0 Hz) δ 1.01 (s, 9H); IR (neat, cm⁻¹) : 3370-2430, 2857, 1709; LRMS (*m/z*, relative intensity) : 397 (M⁺-C₄H₉, 30), 199 (100), 153 (23); HRMS calcd for C₂₅H₂₁O₃Si (M⁺-C₄H₉): 397.1260, found : 397.1255. [α]_D²⁰ = -21.1 (c 1.77, CHCl₃).

The general procedure for the Curtius rearrangement was followed starting with 289 mg (0.64 mmol) of carboxylic acid, except that in this case, the toluene was not evaporated prior to adding sodium methanoate. Flash chromatography eluting with dichloromethane gave 198 mg (71 %) of the carbamate **10b** as a white solid. m.p. : 40-44 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 7.91-7.09 (m, 17H), δ 5.69-5.58 (m, 2H), δ 4.12-4.04 (m, 1H), δ 3.96-3.84 (m, 1H), δ 3.70 (s, 3H), δ 0.99 (s, 9H); IR (neat, cm⁻¹) : 3445, 3334, 1713; LRMS (*m/z*, relative intensity) : 426 (M⁺-C₄H₉, 100), 351

(300), 273 (40), 214 (67); **HRMS** calcd for $C_{26}H_{24}NO_3Si$ ($M^+ - C_4H_9$): 426.1525, found : 426.1512. $[\alpha]_D^{20} = -4.1$ (c 1.08, $CHCl_3$).

Propargyl alcohols 15

Diastereomer A (major)

Diastereomer B (minor)

Carbon tetrabromide (23.5 g, 71.0 mmol) was dissolved in dichloromethane (190 mL, 0.37 M) and cooled to 0 °C. Triphenylphosphine (35.38 g, 134.9 mmol) was added and the mixture was stirred for 15 min. Triethylamine (3.58 g, 35.5 mmol) was added and the mixture was cooled to -78 °C. The cyclohexylcarboxaldehyde (4.95 mL, 35.5 mmol) dissolved in dichloromethane (50 mL, 0.75 M) was added and the mixture was stirred at -78 °C for 2 h and at room temperature during 5 h. Then saturated sodium carbonate was added and the two phases were separated. The aqueous phase was extracted twice with dichloromethane and the organic fractions were combined, washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The crude residue was triturated three times with hexane to give 7.84 g (84 %) of the dibromide and was used as such for the addition on menthone. **¹H NMR** ($CDCl_3$, 300 MHz) : δ 6.23 (d, 1H, $J = 9.4$ Hz), δ 2.33-2.20 (m, 1H), δ 1.71-1.60 (m, 5H), δ 1.41-1.01 (m, 5H); **IR** (neat, cm^{-1}) : 3004, 2927, 2851, 1447; **LRMS** (m/z (relative intensity)) : 268 (M^+ , 40), 212 (30), 82 (100), 67 (60); **HRMS** calcd for $C_8H_{12}Br_2$: 265.9306, found : 265.9311.

The dibromide (7.84 g, 29.26 mmol) was dissolved in tetrahydrofuran (80 mL, 0.36 M) and cooled to -78 °C. A solution of *n*-butyllithium (24.6 mL, 61.4 mmol, 2.5 M in hexanes) was added and the mixture was stirred for 1.5 h at -78 °C, 30 min. at 0 °C, and cooled again to -78 °C. Then (-)-menthone (4.51 g, 29.26 mmol) dissolved in tetrahydrofuran (10 mL) was then added. The mixture was stirred 1 h at -78 °C, 1 h from -78 °C to 0 °C, 1 h at 0 °C, and 15 h at room temperature. Then a solution of hydrochloric acid (1 N) and diethyl ether were added and the two phases were separated. The aqueous phase was extracted twice with diethyl ether and the organic fractions were combined, washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with dichloromethane / hexanes (30 : 70 to 70 : 30) furnished both pure diastereomers A (5.56 g) and B in a (7.4 : 1) ratio, both as colorless oil for a total of 83 % yield. Diastereomer A : **¹H NMR** ($CDCl_3$, 300 MHz) : δ 2.48-2.30

(m, 2H), δ 1.97-1.86 (m, 1H), δ 1.82-1.58 (m, 6H), δ 1.54-1.19 (m, 10H), δ 0.99-0.80 (m, 1H), δ 0.95 (d, 3H, $J = 7.2$ Hz), δ 0.92 (d, 3H, $J = 6.6$ Hz), δ 0.86 (d, 3H, $J = 6.0$ Hz); **IR** (neat, cm^{-1}) : 3617, 3650-3333, 1450; **LRMS** (m/z (relative intensity)) : 262 (M^+ , 5), 247 (5), 177 (100); **HRMS** calcd for $\text{C}_{18}\text{H}_{30}\text{O}$: 262.2297, found : 262.2293. $[\alpha]_{\text{D}}^{20} = +10.1$ (c 1.14, CHCl_3).

Diastereomer B : **^1H NMR** (CDCl_3 , 300 MHz) : δ 2.47-2.30 (m, 1H), δ 2.21-2.08 (m, 1H) δ 1.97-1.86 (m, 1H), δ 1.85-1.58 (m, 7H), δ 1.56-1.06 (m, 8H), δ 1.03-0.75 (m, 2H), δ 0.97 (d, 6H, $J = 6.6$ Hz), δ 0.90 (d, 3H, $J = 6.1$ Hz); **IR** (neat, cm^{-1}) : 3611, 3683-3133, 1707, 1451; **LRMS** (m/z (relative intensity)) : 262 (M^+ , 5), 247 (5), 205 (10), 177 (100); **HRMS** calcd for $\text{C}_{18}\text{H}_{30}\text{O}$: 262.2297, found : 262.2293. $[\alpha]_{\text{D}}^{20} = -17.0$ (c 1.15, CHCl_3).

Alcohol 16

Propargyl alcohol **15** (4.95 g, 18.86 mmol) was dissolved in tetrahydrofuran (95 mL, 0.2 M) and cooled to 0 °C. A solution of Red-Al (28.29 mmol, 3.2 M in toluene) was added slowly, and the solution was warmed at reflux for 15 h. The mixture was then cooled to 0 °C, and a solution of 10 % aqueous H_2SO_4 and diethyl ether were added and the two phases were separated. The aqueous phase was extracted twice with diethyl ether and the organic fractions were combined, washed with a saturated solution of sodium bicarbonate, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with dichloromethane / hexanes (30 : 70 to 40 : 60) furnished the corresponding alcohol **16** (4.53 g, 91 %) as a colorless oil. **^1H NMR** (CDCl_3 , 300 MHz) : δ 5.57 (dd, 1H, $J = 16.0, 6.6$ Hz), δ 5.38 (d, 1H, $J = 16.0$ Hz), δ 2.02-1.87 (m, 2H), δ 1.81-1.59 (m, 5H), δ 1.58-1.40 (m, 5H), δ 1.39-1.00 (m, 7H), δ 0.98-0.80 (m, 4H), δ 0.86 (d, 3H, $J = 7.1$ Hz), δ 0.83 (d, 3H, $J = 6.6$ Hz); **IR** (neat, cm^{-1}) : 3606, 3680-3340, 1450; **LRMS** (m/z (relative intensity)) : 264 (M^+ , 10), 179 (100), 97 (50); **HRMS** calcd for $\text{C}_{18}\text{H}_{32}\text{O}$: 264.2453, found : 264.2447. $[\alpha]_{\text{D}}^{20} = -29.6$ (c 1.09, CHCl_3).

General procedure for cleaving the auxiliary with ozone

The carbamate (1.0 eq.) was dissolved in dichloromethane (0.1 M) and the mixture was cooled to -78 °C. Sudan III was added to the reaction mixture and ozone was bubbled in the reaction mixture until the reaction was completed (when the pink color disappeared). Nitrogen was then bubbled to

remove excess ozone. The mixture was then warmed to 0 °C and placed in an ice bath after which methanol was added (same amount as dichloromethane). Sodium borohydride (5.0 eq.) was then slowly added and the mixture was stirred at room temperature for 15 h. A solution of 1N HCl was added slowly and after stirring for 5 min, the methanol was evaporated and water was poured in. The aqueous phase was extracted three times with diethyl ether. The organic fractions were combined, washed with water and brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography was performed as indicated.

N-protected amino alcohol (*R*)-17a

The ozonolysis was performed as described in the general procedure starting with 226 mg (0.76 mmol) of carbamate **8a**. Flash chromatography eluting with ethyl acetate / hexanes (10 : 90 to 50 : 50) gave 108 mg (81 %) of alcohol (*R*)-**17a** as a white solid. m.p. : 76-77 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 4.82 (br, 1H), δ 3.88-3.83 (m, 1H), δ 3.69 (s, 3H), δ 3.59-3.45 (m, 2H), δ 2.32 (br, 1H), δ 0.94 (s, 9H); IR (neat, cm⁻¹) : 3700-3100, 1700; LRMS (m/z, relative intensity) : 144 ((M⁺-OMe), 100), 118 (50), 100(20), 86 (85); HRMS calcd for C₇H₁₄NO₂ (M⁺-OMe): 144.1024, found : 144.1029. [α]_D²⁰ = +8.0 (c 1.49, CHCl₃).

N-protected amino alcohol (*R*)-17b

The ozonolysis was performed as described in the general procedure starting with 49 mg (0.13 mmol) of carbamate **8b** (in this case, dichloromethane was used for the extraction rather than diethyl ether). Flash chromatography eluting with ethyl acetate / hexanes (40 : 60) gave 25 mg (76 %) of alcohol (*R*)-**17b** as a white solid. m.p. : 147-148 °C; ¹H NMR (CD₃OD, 300 MHz) : δ 8.18 (d, 1H, 8.3 Hz), δ 7.88 (d, 1H, *J* = 8.3 Hz), δ 7.79 (d, 1H, *J* = 7.7 Hz), δ 7.58-7.42 (m, 4H), δ 5.62-5.52 (m, 1H), δ 4.89 (s, 3H), δ 3.92-3.87 (m, 1H), δ 3.74-3.68 (m, 1H), δ 3.64 (s, 2H); IR (neat, cm⁻¹) : (3600-3300), 3324, 3050, 2936, 1695; LRMS (m/z, relative intensity) : 245 (M⁺, 5), 214 (100),

182 (10), 171 (15), 154 (35), 128 (25); **HRMS** calcd for $C_{14}H_{15}NO_3$: 245.1052, found : 245.1054. $[\alpha]_D^{20} = +5.6$ (c 1.10, acetone).

N-Protected amino alcohol (S)-17b

The general procedure for the deprotection of silylated alcohol was followed starting with 250 mg (0.52 mmol) of carbamate **10b**. Flash chromatography eluting with dichloromethane / ethyl acetate (50 : 50) gave 119 mg (93 %) of alcohol as a white solid. m.p. : 150-151 °C; **¹H NMR** (CD_3OD , 300 MHz) : δ 8.18 (d, 1H, 8.2 Hz), δ 7.87 (d, 1H, $J = 8.3$ Hz), δ 7.78 (d, 1H, $J = 7.7$ Hz) δ 7.59-7.40 (m, 4H), δ 5.62-5.52 (m, 1H), δ 3.95-3.80 (m, 1H), δ 3.78-3.51 (m, 1H), δ 3.64 (s, 3H); **IR** (neat, cm^{-1}) : (3700-3150), 3400, 3150, 3075, 1679; **LRMS** (m/z, relative intensity) : 246 (MH^+ , 2), 245 (M^+ , 1), 215 (100), 214 ($M^+ - OMe$, 50), 171 (12), 155 (25), 127 (20); **HRMS** calcd for $C_{14}H_{15}NO_3$: 245.1052, found : 245.1057. $[\alpha]_D^{20} = -6.2$ (c 1.03, acetone).

N-protected amino alcohol (R)-17c

The ozonolysis was performed as described in the general procedure starting with 57 mg (0.16 mmol) of carbamate **8c**. In this case, chloroform was used for the extraction rather than diethyl ether. Flash chromatography eluting with ethyl acetate / dichloromethane (30 : 70 to 40 : 60) gave 22 mg (58 %) of alcohol (**R**)-**17c** as a white solid. m.p. : 92-93 °C; **¹H NMR** ($CDCl_3$, 300 MHz) : δ 7.89-7.70 (m, 4H), δ 7.55-7.35 (m, 3H), δ 5.56 (br, 1H) δ 5.00 (br, 1H), δ 3.96 (br, 2H), δ 3.69 (s, 3H), δ 2.05 (br, 1H); **IR** (neat, cm^{-1}) : (3570-3110), 3052, 2946, 1696, 1532; **LRMS** (m/z (relative intensity)) : 245 (M^+ , 5), 214 (100), 171 (30), 154 (20), 128 (20); **HRMS** calcd for $C_{14}H_{15}NO_3$: 245.1052, found : 245.1059. $[\alpha]_D^{20} = -69.5$ (c 1.02, $CHCl_3$).

N-protected amino alcohol (*R*)-**17d** (90% ee)

The ozonolysis was performed as described in the general procedure starting with 194 mg (0.60 mmol) of carbamate **8d**, which was made from **7d** (90% de). In this case, the dichloromethane was evaporated prior to adding methanol. Flash chromatography eluting with ethyl acetate / hexanes (40 : 60 to 50 : 50) gave 80 mg (65 %) of alcohol (*R*)-**17d** as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) : δ 4.90-4.75 (m, 1H), δ 3.79-3.59 (m, 2H), δ 3.67 (s, 3H), δ 3.55-3.40 (m, 1H), δ 2.06-1.87 (m, 1H), δ 1.82-1.59 (m, 4H), δ 1.58-1.39 (m, 1H), δ 1.32-0.86 (m, 5H) ; IR (neat, cm⁻¹) : 3650-3133(br), 1700; LRMS (m/z, relative intensity) : 170 ((M⁺-OMe), 100), 118 (25), 95(45), 88 (82); HRMS calcd for C₉H₁₆NO₂ (M⁺-OMe): 170.1181, found : 170.1185. [α]_D²⁰ = +7.5 (c 1.41, CHCl₃).

N-protected amino alcohol (*S*)-**17d**

The ozonolysis was performed as described in the general procedure (in this case, the dichloromethane was evaporated prior to adding methanol) starting with 204 mg (0.63 mmol) of carbamate **8d**, which was made from **7e** (>99% de). Flash chromatography eluting with ethyl acetate / hexanes (60 : 40 to 70 : 30) gave 103 mg (81 %) of alcohol (*S*)-**17d** as a gummy white solid. ¹H NMR (CDCl₃, 300 MHz) : δ 4.90-4.72 (m, 1H), δ 3.79-3.58 (m, 2H), δ 3.67 (s, 3H), δ 3.55-3.39 (m, 1H), δ 2.25-2.02 (m, 1H), δ 1.82-1.59 (m, 5H), δ 1.58-1.41 (m, 1H), δ 1.34-0.88 (m, 5H) ; IR (neat, cm⁻¹) : 3690-3117, 1713; LRMS (m/z (relative intensity)) : 170 ((M-OMe)⁺, 90), 118 (20), 95(40), 88 (100); HRMS calcd for C₉H₁₆NO₂ (M⁺-OMe): 170.1181, found : 170.1180. [α]_D²⁰ = -8.2 (c 1.06, CHCl₃).

General procedure for the cyclization to oxazolidinones

The Carbamate-alcohol (1.0eq.) was dissolved in toluene (0.2 M) and a catalytic quantity of potassium carbonate was added. The mixture was refluxed for 3 h. Toluene was evaporated and

water was added. The aqueous phase was extracted three times with dichloromethane. The organic fractions were combined, washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The crude white solids were usually very pure and did not need further purification in most case.

(4*R*)-4-*t*-Butyloxazolidin-2-one (*R*)-18a

The cyclization was performed as per the general procedure with 36 mg (0.20 mmol) of alcohol (*R*)-**17a** and gave 21 mg (73 %) of oxazolidinone (*R*)-**18a** as a white solid. m.p. : 115-116 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 5.23 (m, 1H) δ 4.38 (t, 1H, *J* = 9.0 Hz), δ 4.20 (dd, 1H, *J* = 9.0, 5.5 Hz), δ 3.58 (dd, 1H, *J* = 8.8, 5.6 Hz), δ 0.91 (s, 9H); IR (neat, cm⁻¹) : 3237, 3133, 1749; LRMS (m/z, relative intensity) : 161 ((MNH₄)⁺, 10), 144 ((MH)⁺, 100); HRMS calcd for C₇H₁₄NO₂ (MH⁺): 144.1024, found : 144.1033. [α]_D²⁰ = -8.0 (c 1.74, CHCl₃).

(4*R*)-4-Naphth-1-yl-oxazolidin-2-one (*R*)-18b

The cyclization was performed as per the general procedure with 24 mg (0.09 mmol) of alcohol (*R*)-**17b** and gave 16 mg (82 %) of oxazolidinone (*R*)-**18b** as a white solid. m.p. : 112-113 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 7.95-7.91 (m, 1H), δ 7.87 (d, 1H, *J* = 8.2 Hz), δ 7.81-7.77 (m, 1H), δ 7.66 (d, 1H, *J* = 7.2 Hz), δ 7.61-7.50 (m, 3H), δ 5.76 (t, 1H, *J* = 7.7 Hz), δ 5.68 (br, 1H), δ 5.02 (t, 1H, *J* = 8.8 Hz), δ 4.24 (dd, 1H, *J* = 8.8, 6.6 Hz); IR (neat, cm⁻¹) : 3289, 3075, 1751; LRMS (m/z, relative intensity) : 213 (M⁺, 100), 154 (85), 128 (50); HRMS calcd for C₁₃H₁₁NO₂: 213.0790, found : 213.0787. [α]_D²⁰ = -44.8 (c 1.05, CHCl₃).

(4*S*)-4-Naphth-1-yl-oxazolidin-2-one (*S*)-18b

The general procedure for the cyclization to oxazolidinone was carried out starting from 21 mg (0.09 mmol) of (*S*)-**17b**. Recrystallisation from chloroform and hexanes gave 15 mg (82 %) of oxazolidinone (*S*)-**18b** as a white solid. m.p. : 111-112 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 7.98-7.91 (m, 1H), δ 7.87 (d, 1H, *J* = 8.3 Hz), δ 7.82-7.77 (m, 1H), δ 7.65 (d, 1H, *J* = 7.2 Hz), δ 7.62-7.50 (m, 3H), δ 5.76 (t, 1H, *J* = 7.7 Hz), δ 5.46 (m, 1H), δ 5.02 (t, 1H, *J* = 8.3 Hz), δ 4.24 (dd, 1H, *J* = 8.3, 6.6 Hz); IR (neat, cm⁻¹) : 3730-2765, 3298, 3064, 3015, 1753, 1407, 1240, 1028; LRMS (m/z, relative intensity) : 213 (M⁺, 95), 154 (100), 141 (25), 128 (50); HRMS calcd for C₁₃H₁₁NO₂: 213.0790, found : 213.0785. [α]_D²⁰ = +177.1 (c 0.91, CHCl₃).

(4*R*)-4-Naphth-2-yl-oxazolidin-2-one (*R*)-18c

The cyclization was performed as per the general procedure with 13 mg (0.05 mmol) of alcohol (*R*)-**17c** and gave 9 mg (80 %) of oxazolidinone (*R*)-**18c** as a white solid. m.p. : 142-143 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 7.91 (d, 1H, *J* = 8.3 Hz), δ 7.85 (dd, 2H, *J* = 9.3, 6.1 Hz), δ 7.78 (s, 1H), δ 7.58-7.49 (m, 2H), δ 7.46 (dd, 1H, *J* = 8.3, 1.9 Hz), δ 5.55 (br, 1H), δ 5.12 (dd, 1H, *J* = 8.3, 7.1 Hz), δ 4.81 (t, 1H, *J* = 8.8 Hz), δ 4.27 (dd, 1H, *J* = 8.8, 7.1 Hz); IR (neat, cm⁻¹) : 3410-2970, 3228, 3132, 3030, 2953, 2918, 1771, 1235, 1025; LRMS (m/z (relative intensity)) : 213 (M⁺, 100), 155 (70), 128 (40); HRMS calcd for C₁₃H₁₁NO₂: 213.0790, found : 213.0793. [α]_D²⁰ = -14.3 (c 0.91, CHCl₃).

(4*R*)-4-cyclohexyloxazolidin-2-one (*R*)-18d

The cyclization was performed as per the general procedure with 38 mg (0.19 mmol) of alcohol (*R*)-**17d** (90% ee) and gave 31 mg (96 %) of oxazolidinone (*R*)-**18d** (90% ee) as a white solid.

The same oxazolidinone (*R*)-**18d** (>99% ee) was prepared from (2*R*)-3-hydroxy-2-cyclohexylpropanoic acid **20** as follows: Carboxylic acid **20** (104 mg, 0.60 mmol) was dissolved in toluene (6 mL, 0.1 M), triethylamine (0.10 mL, 0.72 mmol) and diphenylphosphoryl azide (0.16 mL, 0.74 mmol) were added. The mixture was refluxed during 3.5 h and toluene was evaporated under reduced pressure. A saturated solution of sodium bicarbonate and diethyl ether was added. The two phases were separated and the aqueous phase was extracted twice with diethyl ether. The combined organic fractions were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with ethyl acetate / hexane (60 : 40) gave (79 mg, 78 %) of oxazolidinone (*R*)-**18d** as a white solid. m.p. : 122-123 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 6.52 (br, 1H) δ 4.43 (t, 1H, *J* = 8.8 Hz), δ 4.12 (dd, 1H, *J* = 8.8, 6.6 Hz), δ 3.58 (dd, 1H, *J* = 14.8, 7.1 Hz), δ 1.66-1.52 (m, 5H), δ 1.49-0.79 (m, 6H); IR (neat, cm⁻¹) 3240, 3135, 1751; LRMS (m/z, relative intensity) : 169 (M⁺, 10), 87 (100), 85 (94); HRMS calcd for C₉H₁₅NO₂: 169.1103, found : 169.1108. [α]_D²⁰ = +2.1 (c 1.12, CHCl₃).

(4*S*)-4-(cyclohexyl)-oxazolidin-2-one (*S*)-18d

The cyclization was performed as per the general procedure with 28 mg (0.14 mmol) of alcohol (*S*)-**17d** (>99% ee, made from **7e**) and gave 21 mg (92 %) oxazolidinone (*S*)-**18d** as a white solid. m.p. : 124-125 °C; ¹H NMR (CDCl₃, 300 MHz) : δ 5.34 (br, 1H) δ 4.44 (t, 1H, *J* = 8.8 Hz), δ 4.13 (dd, 1H, *J* = 8.8, 6.1 Hz), δ 3.59 (dd, 1H, *J* = 14.8, 7.1 Hz), δ 1.86-1.54 (m, 5H), δ 1.52-1.34 (m, 1H), δ 1.34-1.06 (m, 3H) δ 1.05-0.70 (m, 2H); IR (neat, cm⁻¹) : 3263, 1749, 1722, 1404, 1241; LRMS

(*m/z* (relative intensity)) : 169 (M^+ , 10), 87 (85), 86 (100), 85 (85); **HRMS** calcd for $C_9H_{15}NO_2$: 169.1103, found : 169.1105. P.f. 123.9 °C. $[\alpha]_D^{20} = -1.1$ (c 1.92, $CHCl_3$).

General procedure for the oxidation of *N*-protected amino alcohols to *N*-protected amino acids

The *N*-protected amino alcohol (1.0 eq.) was dissolved in dichloromethane (0.05 M) and cooled to 0 °C. Jones' reagent (2.0 eq, 2.67 M, prepared as described in the general procedure for the formation of carbamates **8a-d**, **f**, **g**) was added dropwise. The mixture was stirred at 0 °C during 30 minutes and at room temperature for 30 minutes, 2-propanol was then added until the solution turned green. After evaporating the solvents *in vacuo*, brine was added and the aqueous phase was extracted three times with a mixture (1:1) of dichloromethane and ethyl acetate. The combined organic fractions were washed with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography was performed as indicated.

N-protected amino acid (*R*)-**9b**

The reaction was performed as per the general procedure with 27 mg (0.11 mmol) of *N*-protected amino alcohol (*R*)-**17b**. Flash chromatography eluting with a mixture of dichloromethane and methanol (95 : 5 to 90 : 10) gave 18 mg (64 %) of *N*-protected amino acid (*R*)-**9b** as a colorless oil. 1H NMR ($CDCl_3$, 300 MHz) : δ 9.60-8.75 (m, 1H), δ 8.14 (d, 1H, $J = 7.7$ Hz), δ 7.94-7.73 (m, 2H), δ 7.61-7.36 (m, 4H), δ 6.15 (d, 1H, $J = 7.7$ Hz), δ 5.71 (d, 1H, $J = 7.7$ Hz), δ 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) : δ 175.5 (s), 156.3 (s), 134.1 (s), 131.9 (s), 130.8 (s), 129.7 (d), 129.0 (d), 127.1 (d), 126.2 (d), 125.7 (d), 125.3 (d), 123.1 (d), 55.0 (d), 52.6 (q); **IR** (neat, cm^{-1}) : 3530-2400, 3409, 3316, 3056, 3020, 2959, 1718, 1510; **LRMS** (*m/z* (relative intensity)) : 259 (M^+ , 5), 214 (40), 154 (100), 127 (40), 83 (85); **HRMS** calcd for $C_{14}H_{13}NO_4$: 259.0844, found : 259.0851. $[\alpha]_D^{20} = -130.0$ (c 1.42, acetone).

N-protected amino acid (*S*)-**9b**

The reaction was performed as per the general procedure with 23 mg (0.09 mmol) of *N*-protected amino alcohol (*S*)-**17b**. Flash chromatography eluting with a mixture of dichloromethane and methanol (95 : 5) gave 18 mg (72 %) of *N*-protected amino acid (*S*)-**9b** as a colorless oil. **¹H NMR** (CDCl₃, 300 MHz) : δ 8.14 (d, 1H, *J* = 8.2 Hz), δ 7.96-7.78 (m, 2H), δ 7.62-7.36 (m, 4H), δ 6.15 (d, 1H, *J* = 7.7 Hz), δ 5.66 (d, 1H, *J* = 7.7 Hz), δ 3.69 (s, 3H); **¹³C NMR** (CDCl₃, 75.5 MHz) : δ 175.3 (s), 156.3 (s), 134.1 (s), 131.9 (s), 130.8 (s), 129.7 (d), 129.0 (d), 127.1 (d), 126.2 (d), 125.7 (d), 125.3 (d), 123.1 (d), 55.0 (d), 52.6 (q); **IR** (neat, cm⁻¹) : 3690-2490, 3414, 3334, 3056, 2959, 1713, 1510; **LRMS** (*m/z* (relative intensity)) : 259 (*M*⁺, 5), 214 (35), 154 (100), 127 (50); **HRMS** calcd for C₁₄H₁₃NO₄ : 259.0844, found : 259.0851. [α]_D²⁰ = +135.9 (c 1.13, acetone).

N-protected amino acid (*R*)-**9c**

The reaction was performed with 25 mg (0.10 mmol) of *N*-protected amino alcohol (*R*)-**17c**. Flash chromatography eluting with a mixture of dichloromethane and methanol (95 : 5 to 90 : 10) gave 22 mg (81 %) of *N*-protected amino acid (*R*)-**9c** as a gummy white solid. **¹H NMR** (CD₃OD, 300 MHz) : δ 7.92-7.79 (m, 4H), δ 7.54-7.41 (m, 3H), δ 5.40 (s, 1H), δ 3.67 (s, 3H); **¹³C NMR** (CD₃OD, 75.5 MHz) : δ 176.3 (s), 161.3 (s), 138.3 (s), 137.2 (s), 132.0 (d), 131.5 (d), 131.2 (d), 130.2 (d), 129.9 (d), 128.7 (d), 55.3 (d), 51.5 (q); **IR** (neat, cm⁻¹) : 3660-2700, 3404, 3315, 3059, 2958, 1719, 1514; **LRMS** (*m/z* (relative intensity)) : 259 (*M*⁺, 10), 214 (70), 154 (100), 127 (60); **HRMS** calcd for C₁₄H₁₃NO₄ : 259.0844, found : 259.0853. [α]_D²⁰ = -145.4 (c 1.00, acetone).

N-protected amino acid (*S*)-**9d**

The reaction was performed with 21 mg (0.11 mmol) of *N*-protected amino alcohol (*S*)-**17d**. Flash chromatography eluting with a mixture of dichloromethane and methanol (95 : 5 to 90 : 10) gave 19 mg (84 %) of *N*-protected amino acid (*S*)-**9d** as a gummy white solid. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 5.15 (d, 1H, $J = 9.4$ Hz), δ 4.36-4.22 (m, 1H), δ 3.70 (s, 3H), δ 1.94-1.57 (m, 6H), δ 1.38-0.98 (m, 5H); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz) : δ 176.8 (s), 156.9 (s), 58.6 (d), 52.4 (q), 40.6 (d), 29.4 (t), 27.8 (t), 25.9 (t); **IR** (neat, cm^{-1}) : 3640-2300, 3330, 2932, 2857, 1713, 1532, 1259, 1073; **LRMS** (m/z (relative intensity)) : 233 ($(\text{M}+\text{NH}_4^+)^+$, 15), 216 (MH^+ , 100), 170 (45); **HRMS** calcd for $\text{C}_{10}\text{H}_{18}\text{NO}_4$ (MH^+): 216.1236, found : 216.1240. $[\alpha]_{\text{D}}^{20} = +12.8$ (c 1.47, MeOH).

N-protected amino acid (*R*)-**9g**

32.1 mg (69.8 μmol) of the carbamate **8g** was dissolved in 0.7 mL of dichloromethane and the solution was cooled to -78°C . An ozone stream (6.5 PSI, 1.5 LPM of oxygen; 75V) was bubbled through the solution until a fade blue color remained and no starting material was left (ca. 4 min, as monitored by TLC analysis). Nitrogen was bubbled for 5 min to purge the solution of ozone and methyl sulfide (51 μL , 0.70 mmol) was added. The reaction was allowed to warm slowly to room temperature and was stirred for 4 h, after which time the solvent was removed *in vacuo* to afford a solid residue which was used as such in the next step. $^1\text{H NMR}$ (CDCl_3 , 300 MHz) : δ 9.86 (s, 1H), 7.77 (d, 2H, $J = 7.7$ Hz), 7.61 (d, 2H, $J = 7.7$ Hz), 7.41 (t, 2H, $J = 7.4$ Hz), 7.32 (t, 2H, $J = 7.4$ Hz), 5.46 (d, 1H, $J = 8.8$ Hz), 4.43-4.39 (m, 2H), 4.30-4.21 (m, 2H), 1.07 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz) : δ 200.6 (d), 156.5 (s), 143.7 (s), 141.3 (s), 127.7 (d), 127.1 (d), 125.1 (d), 120.0 (d), 67.8 (d), 67.0 (t), 47.2 (d), 35.8 (s), 26.7 (q); **IR** (neat, cm^{-1}) : 3337, 3068, 2964, 1713, 1514; **LRMS** (m/z (relative intensity)) : 355 (MNH_4^+ , 5), 338 (MH^+ , 100), 308 ($[\text{M}-\text{CHO}]^+$, 20), 178 (80); **HRMS** calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_3$ (MH^+): 338.1756, found : 338.1764.

A 0.33 mL solution of *t*-butanol containing the crude aldehyde (69.8 μ mol) and 170 μ L of 2-methyl-2-butene was prepared. To this solution was added an aqueous solution (0.3 mL of water) containing sodium chlorite (12.6 mg, 140 μ mol) and sodium dihydrogenophosphate (19.3 mg, 140 μ mol). This mixture was vigorously stirred overnight at room temperature. The solvents were removed under reduced pressure and brine (1 mL) was added. The aqueous mixture was extracted with dichloromethane (3 x 1 mL) and the combined organic layers were dried over anhydrous magnesium sulfate, concentrated under reduced pressure and purified by flash chromatography (MeOH/CH₂Cl₂; 5:95). In this way, 21 mg (84%, 2 steps) of a white solid was isolated. **¹H NMR** (CD₃OD, 300 MHz) : δ 7.78 (d, 2H, *J* = 7.7 Hz), 7.66 (dd, 2H, *J* = 7.7 and 4.7 Hz), 7.37 (t, 2H, *J* = 7.4 Hz), 7.29 (t, 2H, *J* = 7.7 Hz), 4.37-4.33 (m, 2H), 4.22 (t, 1H, *J* = 7.1 Hz), 4.02 (s, 1H), 1.01 (s, 9H); **¹³C NMR** (CD₃OD, 75.5 MHz) : δ 174.6 (s), 158.7 (s), 145.3 (s), 128.8 (d), 128.1 (d), 126.3 (d), 120.9 (d), 68.0 (t), 64.2 (d), 34.9 (d), 30.8 (s), 27.1 (q); **IR** (neat, cm⁻¹) : 3600-2700 (br,s), 3065, 1705, 1587; **LRMS** (*m/z* (relative intensity)) : 354 (MH⁺, 3), 178 (100); **HRMS** calcd for C₂₁H₂₃NO₄ (MH⁺): 354.1705, found : 354.1714. [α]_D²⁰ = +9.5 (c 1.01, CHCl₃).

(2*R*)-3-Hydroxy-2-cyclohexylpropanoic acid **20**

Adduct **7e** (503 mg, 1.44 mmol) was dissolved in dichloromethane (15 mL, 0.1 M), a few drops of Sudan III was added and the mixture was cooled to -78 °C. Ozone was bubbled in the reaction mixture and, after the disappearance of the pink color nitrogen was bubbled through. Jones' reagent (2.8 mL, 5.0 eq, 2.67 M, prepared as described in the general procedure for the formation of carbamates **8a-d, f, g**) was then added and the mixture was stirred at -78 °C during 30 minutes and warmed to room temperature. After 1.5 h at room temperature, 2-propanol was added until the solution turned green. After evaporating the solvents *in vacuo*, water was added and the aqueous phase was extracted three times with dichloromethane. The combined organic fractions were washed with water and brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography on silica gel eluting with ethyl acetate / hexane (20 : 80 to 40 : 60) gave (299 mg, 87 %) of carboxylic acid as a white solid. m.p. : 43.6 °C; **¹H NMR** (CDCl₃, 300 MHz) : δ 3.65-3.56 (m, 2H), δ 2.45-2.33 (m, 1H), δ 1.85-1.59 (m, 6H), δ 1.37-0.91 (m, 5H), δ

1.23 (s, 9H); **IR** (neat, cm^{-1}) : 3500-2275, 2973, 2929, 2855, 1709; **LRMS** (m/z (relative intensity)) : 213 ($(\text{M}-\text{CH}_3)^+$, 20), 171 ($(\text{M}-\text{C}_4\text{H}_9)^+$, 30), 142 (70), 109 (90), 83 (100); **HRMS** calcd for $\text{C}_{12}\text{H}_{21}\text{O}_3$ ($\text{M}-\text{CH}_3$)⁺: 213.1491, found : 213.1496. $[\alpha]_{\text{D}}^{20} = -7.9$ (c 1.39, CHCl_3).

The *t*-butyl ether (53 mg, 0.23 mmol) was dissolved in dichloromethane (1 mL, 0.3 M) and B-bromocathecolborane (50,3 mg, 0.25 mmol) dissolved in dichloromethane (1.25 mL, 0.2 M) was then added. The mixture was stirred at room temperature for 1 h. Water and dichloromethane was poured in and the two phases were separated. The aqueous phase was extracted twice with dichloromethane. The combined organic fractions were washed twice with a solution of sodium hydroxide (3.0 M) and once with brine, dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Flash chromatography eluting with a mixture of ethyl acetate and hexane (40 : 60 to 100 : 0) gave 30 mg (76 %) of alcohol **20** as a white solid. m.p. : 74-75 °C; **¹H NMR** (CDCl_3 , 300 MHz) : δ 3.93-3.72 (m, 2H), δ 2.47 (dt, 1H, $J = 7.4, 3.9$ Hz), δ 1.82-1.59 (m, 6H), δ 1.34-0.90 (m, 5H); **IR** (neat, cm^{-1}) : 3700-2250, 3379, 2928, 2854, 1709; **LRMS** (m/z (relative intensity)) : 173 (MH^+ , 5), 155 ($(\text{M}-\text{OH})^+$, 5), 142 ($(\text{M}-\text{CH}_3\text{OH})^+$, 35), 90 (100), 81 (70); **HRMS** calcd for $\text{C}_9\text{H}_{17}\text{O}_3$ (MH^+): 173.1178, found : 173.1181. $[\alpha]_{\text{D}}^{20} = +1.3$ (c 1.05, CHCl_3).

Annexe 1. NMR spectra

 ^1H -NMR of alcohol **13a**

^1H -NMR of adduct **7a**

^1H -NMR of adduct **7b**

^1H -NMR of adduct **7c**

^1H -NMR of adduct **7d**

^1H -NMR of adduct **7e**

^1H -NMR of alcohol from **7b**

^1H -NMR of alcohol from **7c**

^1H -NMR of alcohol from **7e**

¹H-NMR of carboxylic acid from **7a**

^1H -NMR of carboxylic acid from **7b**

^1H -NMR of carboxylic acid from **7c**

^1H -NMR of carboxylic acid from **7d**

^1H -NMR of carboxylic acid from **7e**

^1H -NMR of methyl carbamate **8a**

^1H -NMR of methyl carbamate **8b**

^1H -NMR of methyl carbamate **8c**

^1H -NMR of methyl carbamate **8d**

^1H -NMR of methyl carbamate **8e**

^1H -NMR of carbamate-Alcohol **17a**

¹H-NMR of carbamate-alcohol **17b**

MCT020184-PUR

¹H-NMR of carbamate-alcohol **17c**

MCT-4-34-PUR3

^1H -NMR of carbamate-alcohol **17d**

MCT-2-122-PUR

^1H -NMR of carbamate-alcohol **7e**

MCT-5-58-PUR

^1H -NMR of carboxylic acid leading to carbamate **10b** from **7b**

MCT-3-44-PUR

¹H-NMR of carbamate **10b**

MCT-3-178-PURCARACT

^1H -NMR of carboxylic acid from the ozonolysis of **7e**

MCT-4-188-PUR

^1H -NMR of α -amino acid (*R*)-**9b** (made from **7b** via **8b**, see Scheme 5)

MCT-5-76-PUR2

^1H -NMR of α -amino acid (*S*)-**9b** (made from **7b** via **10b**, see Scheme 5)

MCT-5-74-PUR3

^1H -NMR of α -amino acid (*R*)-**9c** (made from **7c** via **8c**, see Scheme 5)

MCT-5-78-PUR

^1H -NMR of α -amino acid (*S*)-**9d** (made from **7e** via **8e**, see Scheme 5)

MCT-5-70-PUR2

^1H -NMR of α -amino aldehyde corresponding to amino acid (*R*)-9g

^1H -NMR of α -amino acid (*R*)-**9g** (taken in CD_3OD)

^1H -NMR of alcohol **15**

^1H -NMR of alcohol **16**

^1H -NMR of alcohol (*S*)-17b

MCT-3-50-CRISTALLIN

^1H -NMR of oxazolidinone (*R*)-**18a**

MCT-2-30-PUR

¹H-NMR of oxazolidinone (*R*)-18d

MCT-2-84-BRUT

^1H -NMR of oxazolidinone (*R*)-**18b**

MCT-4-44-BRUT

^1H -NMR of oxazolidinone (*S*)-**18b**

MCT-4-18-PUR

^1H -NMR of oxazolidinone (*R*)-**18c**

MCT-2-182-PUR

^1H -NMR of oxazolidinone (*R*)-**18e**

MCT-5-60-PUR

^1H -NMR of carboxylic acid-alcohol **20**

MCT-5-18-PUR

Annexe 2. Fluorine NMR of Mosher esters

 ^{19}F -NMR of a mixture of Mosher esters of alcohols (*R*)-**17a** and (*S*)-**17a**

^{19}F -NMR of pure Mosher ester of alcohol (*R*)-**17a** (>99% e.e)

^{19}F -NMR of the mixture of Mosher esters of alcohols (*R*)-**17d** and (*S*)-**17d** (90% e.e)

^{19}F -NMR of the Mosher ester of alcohol (*R*)-**17d** (90% e.e)

^{19}F -NMR of the mixture of Mosher esters of alcohols (*R*)-**17d** and (*S*)-**17d** (>99% e.e)

^{19}F -NMR of the Mosher ester of alcohol (*R*)-**17d** (>99% e.e)

Annexe 3. G.C.'s and HPLC's traces

H.P.L.C. of pure oxazolidinone (R)-18b

=====
 Injection Date : 04-01-19 11:39:25
 Sample Name : 2-182
 Acq. Operator : mct

Vial : 62

Inj Volume : 25 µl

Method : C:\HPCHEM\1\METHODS\MCT.M
 Last changed : 04-01-16 17:39:56 by mct

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: DAD1 A, Sig=254,100 Ref=360,100
 Results obtained with standard integrator!

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.095	BV	0.2086	151.04858	10.61396	0.9325
2	5.463	VV	0.1889	46.56580	3.85478	0.2875
3	5.899	VV	0.2327	74.12024	4.50674	0.4576
4	6.413	VB	0.2982	63.27800	3.38597	0.3906
5	18.783	BB	0.5833	1.58633e4	418.16522	97.9318

Totals : 1.61983e4 440.52668

H.P.L.C. of a mixture of oxazolidinone (R)-18b (major) and (S)-18b (minor)

```

=====
Injection Date   : 04 01 19 14:13:32
Sample Name      : 4-18 - 2 182
Acq. Operator    : not
Vial             : 60
Inj Volume       : 25 µl

Method           : C:\HPCHEM\1\METHODS\MCT.V
Last changed     : 04 01 18 17:39:58 by not
DAD1 A, Sig=254,100 Ref=350,100 (MCT\MCT15014.D)
=====

```

Area Percent Report

```

=====
Sorted By      : Signal
Multiplier     : 1.3300
Dilution       : 1.3300

```

Signal 1: DAD1 A, Sig=254,100 Ref=350,100
Results obtained with standard Integrator!

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.160	UV	0.2089	197.59506	14.18847	0.4640
2	5.924	UV	0.1651	72.24718	6.75028	0.1719
3	5.959	UV	0.2682	77.43018	3.97134	0.1818
4	6.480	UV	0.2785	261.87947	10.34577	0.4739
5	8.260	EE	0.2267	79.78390	5.35321	0.1871
6	8.231	EE	0.2358	43.67086	2.68715	0.1024
7	18.901	EV	0.7248	3.97513e4	875.94043	93.5126
8	20.848	VE	0.6143	2175.30054	59.03955	5.1283

Totals : 4.26002e4 972.22620

H.P.L.C. of oxazolidinone (R)-18c.

=====
 Injection Date : 04-01-19 15:43:12
 Sample Name : 4-44
 Acq. Operator : mct

Vial : 63

Inj Volume : 25 µl

Method : C:\HPCHEM\1\METHODS\MCT.M
 Last changed : 04-01-16 17:39:56 by mct

=====
 Area Percent Report
 =====

Sorted By : Signal
 Multiplier : 1.0000
 Dilution : 1.0000

Signal 1: DAD1 A, Sig=254,100 Ref=360,100
 Results obtained with standard integrator!

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.192	BV	0.1840	102.67081	8.60191	0.2339
2	5.532	VV	0.2012	46.50090	3.55784	0.1059
3	6.000	VV	0.2410	55.63212	3.27712	0.1267
4	8.617	BV	0.2312	64.76379	4.26488	0.1475
5	9.018	VB	0.2814	110.71468	5.86052	0.2522
6	19.781	BV	0.7441	3.91483e4	837.78363	89.1890
7	20.958	VB	0.5750	4365.06885	111.27261	9.9446

Totals : 4.38936e4 974.61851

G.C-MS of pure cuprate adduct 7e

G.C-MS of cuprate adduct **7e** enriched with the other diastereomer.

MS is that of the minor diastereomer to be compared with the MS of **7e** above.

Annexe 4. X-Rays

Carbamate **8g** (ent-**8g** shown in ORTEP)