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## Supporting Information for:

# Addition of Enantioenriched γ-Oxygenated Allylic Stannanes to *N*-Acyl Iminium Intermediates. A New Synthesis of *Syn*-Amino Alcohol Derivatives

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Representative experimental procedures for **8aa**, **8ab**, **9aa**, **10**, **11**, **12**, physical data for **9b-d**, **16**, **17.**

## Representative Experimental Procedures

**Homoallylic Carbamate 8aa.** To a solution of carbamate **7a** (0.10 g, 0.31 mmol) in $CH_2Cl_2$ (2.6 mL) at -78° C was added, dropwise, $BF_3$•$OEt_2$ (0.088 g, 0.62 mmol) and (R)-γ-siloxy-allylic stannane **2a** (0.16 g, 0.39 mmol) in $CH_2Cl_2$ (0.5 mL) sequentially. After stirring for 2 h at -78 °C the mixture was warmed to 0 °C for 15 min and then quenched with sat. aq. $NaHCO_3$ (2 mL). The mixture was allowed to warm to rt while stirring. The clear layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined extracts were dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel with 10% EtOAc-hexanes as eluant affording 0.13 g (91%) of homoallylic carbamate **8aa** as a clear colorless oil: $[\alpha]_D$= +25.8 (c 1.5, $CHCl_3$); IR (film) υ 2956, 1698 $cm^{-1}$; $^1$H NMR (300 MHz, Some signals are broad due to rotamers) δ 7.30-7.13 (m, 2H), 6.91-6.78 (m, 2H), 5.65 (m, 1H), 5.39 (m, 1H), 4.52 (m, 2H), 4.13 (m, 2H), 3.82 (s, 3H), 1.67 (dd, *J* = 6.3, 1.2 Hz, 2H), 0.49-1.41 (m, 8H).

**Oxazolidinone 9a** (A. From Silyl Ether **8aa**) To a solution of silyl ether **8aa** (0.050 g, 0.11 mmol) in THF (1 mL) was added TBAF (0.23 mL of a 1.0M solution in THF, 0.23 mmol). The resulting solution was allowed to stir at rt for 8 h and was then quenched with $H_2O$ and diluted with $Et_2O$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined extracts were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel with 20% EtOAc-hexanes as eluant affording 0.029 g (89%) of oxazolidinone **9a** as a clear colorless oil. $[\alpha]_D$ = 54.9 (c = 1.1, $CHCl_3$); $^1$H NMR (300 MHz) δ 7.30-7.25 (m, 2H), 6.97-6.82 (m, 2H), 5.8 (dqd *J* =15.3, 6.6, 0.9 Hz, 1H), 5.38 (ddq *J* =15.3, 7.8, 1.5 Hz, 1H), 4.68 and 4.24 (ABq *J* = 15.3 Hz, 2H), 4.45 (dd *J* = 7.2, 6.0 Hz, 1H), 3.83 (s, 3H), 3.23 (ddd, *J* = 7.5, 5.7, 3.0 Hz, 1H), 1.69 (dd, *J* = 6.0, 1.2 Hz, 3H), 1.63-1.26 (m, 3H), 0.89 (d, *J* =6 Hz, 3H), 0.73 (d, *J* = 6 Hz, 3H); $^{13}$C NMR δ 17.7, 21.5, 23.9, 23.9, 40.5, 41.2, 55.2, 58.4, 80.2, 110.2, 120.7, 124.1, 128.3, 129.0, 130.1, 131.1, 157.3, 157.8.

**Oxazolidinone 9b** $[\alpha]_D$ = +46.7 (c = 0.75, $CHCl_3$); NMR (300 MHz) δ 7.30–7.25 (m, 2H), 6.97-6.82 (m, 2H), 5.86-5.74 (dqd *J* = 15, 6.6, 0.60 Hz, 1H), 5.38 (dqd, *J* = 15.3, 7.8, 1.8 Hz, 1H), 4.68

and 4.24 (ABq *J* = 15.0 Hz, 2H) 4.46 (dd *J* = 6.9, 6.6 Hz, 1H), 3.83 (s, 3H), 3.20 (ddd, *J* = 9.0, 6.0, 3.0 Hz, 1H) 1.71 - 1.42 (m, 5H), 1.30-1.14 (m, 5H), 0.90 - 0.85 (m, 3H).

**Oxazolidinone 9c** $[\alpha]_D$ = +142.6 (c = 0.87, $CHCl_3$); $^1$H NMR (300 MHz) δ 7.31-7.25 (m, 2H), 6.97-6.87 (m, 2H), 5.81-5.60 (dqd *J* = 15, 6.6, 0.60 Hz, 1H), 5.34 (ddq *J* = 15, 7.5, 1.5 Hz, 1H), 4.74 and 4.18 (ABq *J* = 15.3 Hz, 2H), 4.58 (dd *J* = 7.2, 4.5 Hz, 1H), 3.83 (s, 1H), 3.13 (dd, *J* = 4.5, 4.2 Hz, 1H), 1.80-0.90 (m, 14H).

**Oxazolidinone 9d** $[\alpha]_D$ = +36.7 (c = 2.2, $CHCl_3$); $^1$H NMR (300 MHz) δ 7.42–7.41 (m, 1H), 7.30-7.24 (m, 1H), 7.19-7.16 (m, 1H), 6.93-6.84 (m, 2H), 6.35 (dd, *J* = 3.3, 2.1 Hz, 1H), 6.24 (dd *J* = 6.6, 3.3 Hz, 1H), 5.78 (dqd *J* = 15, 6.6, 0.90 Hz, 1H), 5.47 (ddq *J* = 15, 7.5, 1.8 Hz, 1H), 4.85 (dd, *J* = 7.2, 0.60 Hz, 1H), 4.69 and 4.00 (ABq *J* = 15, 2H), 4.30 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 1.70 (dd *J* = 6.6, 0.90 Hz, 3H).

**Oxazolidinone 9a** (B. From MOM Ether **8ab**.) The procedure described for homoallylic carbamate **8aa** was followed with carbamate **7a** (0.1 g) and (R)-γ–alkoxy allylic stannane **2b** (0.16 g) affording 0.11 g (90%) of homoallylic carbamate **8ab**: $[\alpha]_D$ = 14.4 (c = 2.4, $CHCl_3$); IR (film) υ 2960, 1701 $cm^{-1}$; $^1$H NMR (300 MHz) δ 7.34-7.15 (m, 2H), 6.92-6.80 (m, 2H), 5.64 (m, 1H), 5.27 (m, 1H), 4.76 -4.10 (m, 8H), 3.84 (s, 3H), 3.36 (s, 3H), 1.71-0.56 (m, 12H).

The foregoing sample of homoallylic carbamate **8ab** (0.044 g) in a solution of THF-6M HCl (9:1) (3.0 mL) was stirred at 65°C for 2 h. After cooling to 0 °C, the reaction mixture was neutralized carefully with anhydrous $NaHCO_3$, followed by dilution with $CH_2Cl_2$. The layers were separated and the organic layer was dried over $Na_2SO_4$, filtered and concentrated. The resulting alcohol was carried directly forward without purification or characterization. The alcohol was dissolved in a mixture of THF-MeOH-7.5M KOH (4:2:1) (2.1 mL) and stirred at rt for 2 h. The reaction mixture was then cooled to 0 °C and carefully neutralized with 2M HCl and extracted twice with $CH_2Cl_2$. The combined extracts were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (20% EtOAc-hexanes) afforded 0.028 g (82%) of oxazolidinone (**9a**) as a colorless oil.

**Ethoxy Carbamate 10** To a suspension of powdered activated 4 A molecular sieves (0.5 g) in $CH_2Cl_2$ (10 mL) was added 2-methoxybenzylamine (0.60 g, 4.38 mmol) followed by the DPS ether derivative of (*R*)-lactic aldehyde (1.34 g). After being stirred for 2 h at rt the molecular sieves were removed by filtration and the filtrate was concentrated to provide the intermediate *N*-2-methoxybenzyl aldimine as a colorless oil. To a solution of the crude aldimine in dry ethanol (0.86 mL) was slowly added diethyl pyrocarbonate (0.71 g, 4.38 mmol), (*caution* : $CO_2$ evolution, exothermic reaction). After 2 h at rt the excess ethanol was removed under aspirator pressure. Purification by column chromatography on silica gel with 10% EtOAc-hexanes as eluant afforded 2.09 g of an inseparable 3:1 diastereomeric mixture of carbamates **10** as a clear colorless oil. IR (film) υ 3073, 2942, 1745, 1728, 1605, 1600 $cm^{-1}$; $^1H$ NMR (300 MHz; some signals are broad due to hindred rotation) δ 7.72-7.64 (m, 4H), 7.43-7.43 (m, 6H), 7.17-7.05 (m, 2H), 6.84-6.76 (m, 2H), 4.67-3.70 (m, 11H), 1.19-1.00 (m, 18H); Anal. Calcd for $C_{32}H_{43}NO_5Si$, C 69.91; H, 7.88; N, 2.55. Found C, 69.89; H, 7.88; N, 2.49.

**Homoallylic Carbamate 11** To a solution of carbamate **10** (0.165 g, 0.30 mmol) in $CH_2Cl_2$ (3 mL) at -78°C was added, dropwise, $BF_3$•$OEt_2$ ( 0.084 g, 0.60 mmol) and (R)-γ-OMOM allylic stannane **2b** (0.16 g, 0.39 mmol) in $CH_2Cl_2$ (0.5 mL) sequentially. After stirring for 2 h at - 78 °C the mixture was warmed to 0 °C for 15 min and then quenched with sat. aq. $NaHCO_3$ (2 mL). The mixture was allowed to warm to rt while stirring. The clear layers were separated and the aqueous layer was extracted with $CH_2Cl_2$. The combined extracts were dried over $Na_2SO_4$, and filtered. The solvent was removed in vacuo. Purification by column chromatography on silica gel with 10% EtOAc-hexanes as eluant afforded 0.105g (77%) of homoallylic carbamate **11** as a clear colorless oil. $[\alpha]_D^{20}$= 73.5, (c = 1.64, $CHCl_3$). $^1H$ NMR (300 MHz; some signals are broad due to hindred roatation) δ 7.70-7.62 (m, 3H), 7.54-7.17 (m, 8H), 6.94-6.81 (m, 2H), 5.61-5.53 (m, 1H), 5.17-5.09 (m, 1H), 4.59-4.06 (m, 8H), 3.77 (s, 3H), 3.26 (s, 3H), 1.59 (m, 4H), 1.25-0.88 (m, 12H). Anal. Calcd for $C_{36}H_{49}NO_6Si$: C, 69.75; H, 7.97; N, 2.26. Found C, 69.74; H, 7.91; N, 2.30.

**Oxazolidinone 12** To a solution of homoallylic carbamate **11** (0.085 g, 0.14 mmol) in THF (0.5 mL) was added TBAF (0.41 mL of a 1.0 M solution in wet THF, 0.41 mmol). The resulting solution was allowed to stir at room temperature for 8 h and was then quenched with $H_2O$ and diluted with $Et_2O$. The layers were separated and the aqueous layer was extracted with $Et_2O$. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure yielding a clear colorless oil. The resulting alcohol was carried directly forward without purification or characterization. The alcohol was dissolved in a mixture of THF, MeOH, and 7.5 M KOH (4:2:1, 0.35 mL) and stirred at rt for 2 h. The reaction mixture was then cooled to 0 °C and carefully neutralized with 2 M HCl and extracted twice with $CH_2Cl_2$. The combined extracts were washed with brine, dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel with 20% EtOAc-hexanes as eluant afforded oxazolidinone **12** as a clear colorless oil. $[\alpha]_D^{20}$ = -65.9 (c = 1.45, $CHCl_3$), IR (film): 1737 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 6.95-6.87 (m, 2H), 5.73 (dq, *J* = 15.0, 6.6 Hz, 1H), 5.46 (ddq, *J* = 15.0, 8.4, 1.5 Hz, 1H), 4.54 (ABq, *J* = 15.3 Hz, 2H), 4.57 (ABq, *J* = 6.9 Hz, 2H), 4.56 (dq, *J* = 7.2, 6.9 Hz), 4.31 (dd, *J* = 4.4, 8.4), 3.84 (s, 3H), 3.56 (dd, *J* = 6.9, 4.2 Hz, 1H), 3.30 (s, 3H), 1.72 (dd, *J* = 6.6, 0.9 Hz, 3H), 1.49 (d, *J* = 6.9 Hz, 3H). $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 158.4, 157.5, 132.7, 130.0, 129.0, 126.7, 124.5, 120.6, 110.3, 93.5, 74.6, 74.4, 60.2, 55.7, 55.2, 41.8, 18.0, 15.3. Anal Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4.18. Found C, 64.45; H, 7.43; N, 4.24.

**Oxazolidinone 16** $[\alpha]_D$ = -84.9 (c =1.44, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.01-6.92 (m, 2H), 5.80 (dq, *J* = 5.0, 6.3 Hz, 1H), 5.32 (dd, *J* = 15.0, 1.2 Hz, 1H), 4.79 and 4.28 (ABq, *J* =14.7 Hz, 2H), 4.69 and 4.48 (ABq, *J* = 6.6 Hz, 2H), 4.50 (dq *J* = 6.3, 3.6 Hz, 1H), 4.28 (dd, *J* = 4.8, 1.2 Hz, 1H), 3.89 (s, 3H), 3.31 (s, 3H), 3.22 (dd *J* = 4.8, 3.6 Hz, 1H), 1.77 (dd, *J* = 6.3, 1.8 Hz, 3H), 1.26 (d, *J* = 6.3, 3H). $^{13}C$ NMR (300 MHz, $CDCl_3$) δ 157.8, 157.6, 133.7, 130.7, 129.3, 124.7, 123.9, 120.7, 110.3, 93.4, 75.5, 71.4, 63.1, 55.5, 55.2, 41.7, 21.5, 18.0. Anal. Calcd for $C_{18}H_{25}NO_5$: C, 64.46; H, 7.51; N, 4..18. Found: C, 64.45; H, 7.68; N, 4.12.

**Oxazolidinone 17** $[\alpha]_D$ = -54.6 (c = 0.54, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 2H), 6.95-6.87 (m, 2H), 5.74 (dq, *J* = 15.3, 6.6 Hz, 2H), 5.41 (dd, *J* = 15.3, 1.5 Hz, 1H), 4.82 and 4.37

(ABq, *J* = 14.7 Hz, 2H) 4.68 and 4.49 (ABq, *J* = 6.9 Hz, 2H), 4.59 (dq, *J* = 6.9, 7.5 Hz, 1H), 4.33 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.83 (s, 3H), 3.57 (dd, *J* = 7.5, 2.7 Hz, 1H), 3.35 (s, 3H), 1.74 (dd, *J* = 6.6, 1.2 Hz, 3H), 1.49 (d, *J* = 6.6 Hz, 2H). $^{13}$C NMR (300 MHz) δ 158.5, 157.6, 132.4, 130.1, 129.0, 126.5, 124.6, 120.5, 110.4, 93.4, 75.1, 73.7, 60.9, 55.8, 55.3, 41.6, 18.0, 15.4.