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Supporting Information for *Angew. Chem. Int. Ed.* Z17653

## **Asymmetric Allylsilane Additions to Enantiopure *N*-Acyldiazones with Dual Activation by Fluoride and In(OTf)<sub>3</sub>**

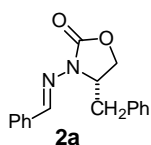
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### **Supporting Information**

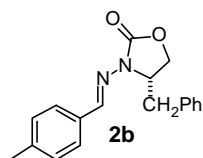
**Materials and Methods.** Reactions employed oven-dried glassware under nitrogen unless otherwise noted. Tetrahydrofuran (THF) and toluene were distilled from sodium with benzophenone as indicator and CH<sub>2</sub>Cl<sub>2</sub> from CaH<sub>2</sub> under argon. Nitrogen was dried with anhydrous CaSO<sub>4</sub>. All other materials were used as received from Aldrich. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230-400 mesh silica gel as slurry in hexane. Gradient flash chromatography was conducted by adsorption of the crude mixture on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Melting points were determined on a Meltemp apparatus and are uncorrected. Proton and carbon NMR data were obtained with a Bruker ARX 500 spectrometer. Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer. Optical rotations were determined using a Rudolph Research Autopol IV polarimeter. Low resolution mass spectra were obtained with a Finnegan 4610 quadrupole spectrometer or a Hewlett Packard 5988 GCMS. High resolution mass spectra were obtained from Washington University Resource for Biomedical and Bio-organic Mass Spectrometry. Combustion analyses were performed by Atlantic Microlab (Norcross, GA). Diastereomer ratios were determined with a Varian Star HPLC workstation using gradient elution (2-propanol/hexane) with a MICROSORB-MV™ C8 column.

**Preparation of Hydrazones (General Procedure A):** To a solution of (*S*)-3-amino-4-phenylmethyl-2-oxazolidinone (**1**, 0.1–0.3 mmol) in toluene (10 mL) was added MgSO<sub>4</sub> (200 mg), a catalytic amount of *p*-TsOH (ca. 5 mol%) and aldehyde (ca. 1.5 equiv). After heating at reflux for 10 min, concentration and flash chromatography (5:1 hexane/ethyl acetate) gave pure hydrazones **2**.



**(S)-3-(Benzylidene)amino-4-phenylmethyl-2-oxazolidinone (2a).** From **1** (60 mg, 0.31 mmol) and benzaldehyde (0.05 mL, 0.49 mmol) by General Procedure A was obtained **2a**<sup>1</sup> (70 mg, 81%) as a colorless solid.

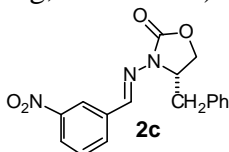
**(S)-3-(*p*-Methylbenzylidene)amino-4-phenylmethyl-2-oxazolidinone (2b).** From **1** (43 mg, 0.22 mmol) and *p*-tolualdehyde (0.04 mL, 0.34 mmol) by General Procedure A was



obtained **2b** (62 mg, 94%) as a colorless solid. m.p. 111-112°C;  $[\alpha]_D^{20} = -2.2$  (c=1.1 in CHCl<sub>3</sub>); IR(film): 3027, 2918, 1760, 1615, 1497, 1474, 1455, 1403, 1212, 1089, 815, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$ =8.87 (s, 1H), 7.63-7.03 (m, 9H), 4.50-4.43 (m, 1H), 4.28 (dd, *J*=8.0, 8.0 Hz, 1H), 4.12 (dd, *J*=8.8, 5.6 Hz, 1H), 3.30 (dd, *J*=13.9, 3.6

Hz, 1H), 2.90 (dd, *J*=13.9, 8.6 Hz, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$ =153.9, 151.2, 140.8, 135.5, 131.8, 129.5, 129.4, 128.9, 127.5, 127.3, 65.8, 58.4, 37.8, 21.5; MS (CI) *m/z* (%): 295 (100) [M+H]<sup>+</sup>; Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.31; H, 6.25; N, 9.25.

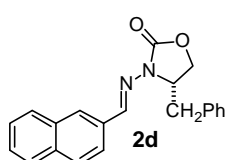
**(S)-3-(*m*-Nitrobenzylidene)amino-4-phenylmethyl-2-oxazolidinone (2c).** From **1** (50 mg, 0.26 mmol) and *m*-nitrobenzaldehyde (0.06 mL, 0.40 mmol) by General Procedure A



was obtained **2c** (75 mg, 91%) as a colorless solid. m.p. 148-150°C;  $[\alpha]_D^{20} = -28.3$  (c=0.6 in CHCl<sub>3</sub>); IR(film): 3057, 2921, 1754, 1534, 1399, 1352, 1266, 1099, 738 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C)  $\delta$ =9.07 (s, 1H), 8.51 (s, 1H), 8.21 (dddd, *J*=8.2, 1.0, 1.0, 1.0 Hz, 1H), 7.98 (dd, *J*=7.7, 0.9 Hz, 1H), 7.57 (dd, *J*=7.7, 7.7 Hz, 1H), 7.34-7.16

(m, 5H), 4.58-4.53 (m, 1H), 4.36 (dd, *J*=8.1, 8.1 Hz, 1H), 4.17 (dd, *J*=8.2, 5.6 Hz, 1H), 3.32 (dd, *J*=13.9, 4.1 Hz, 1H), 2.95 (dd, *J*=13.9, 8.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$ =153.5, 148.8, 136.5, 135.1, 133.0, 129.7, 129.4, 129.0, 127.4, 124.6, 121.7, 66.0, 58.6, 38.2; MS (EI) *m/z* (%): 325 (29) [M<sup>+</sup>]; Anal. Calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>: C, 62.76; H, 4.65; N, 12.92. Found: C, 62.64; H, 4.77; N, 12.72.

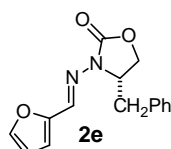
**(S)-3-(2'-Naphthylidene)amino-4-phenylmethyl-2-oxazolidinone (2d).** From **1** (43 mg, 0.22 mmol) and 2-naphthaldehyde (52 mg, 0.33 mmol) by General Procedure A was



obtained **2d** (67 mg, 92%) as a colorless solid. m.p. 147-148°C;  $[\alpha]_D^{20} = -3.8$  (c=1.2 in CHCl<sub>3</sub>); IR(film): 3027, 2918, 2850, 1752, 1651, 1456, 1397, 1265, 1222, 1093, 738 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$ =9.06 (s, 1H), 8.01-7.17 (m, 12H), 4.53-4.45 (m, 1H), 4.35 (dd, *J*=8.7, 8.7 Hz, 1H), 4.19 (dd, *J*=8.8, 5.5 Hz, 1H), 3.38 (dd, *J*=13.9, 3.8 Hz,

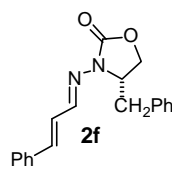
1H), 2.92 (dd, *J*=13.9, 8.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$ =153.9, 150.5, 135.4, 134.5, 133.2, 132.1, 129.6, 129.4, 129.0, 127.5, 128.6, 127.9, 127.3, 127.2, 126.7, 122.8, 65.8, 58.2, 37.7; MS (CI) *m/z* (%): 330 (25) [M<sup>+</sup>]; Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 76.34; H, 5.49; N, 8.48. Found: C, 76.63; H, 5.50; N, 8.47.

**(S)-3-(2'-Furanylidene)amino-4-phenylmethyl 2-oxazolidinone (2e).** From **1** (48 mg, 0.25 mmol) and 2-furaldehyde (0.06 mL, 0.41 mmol) by General Procedure A was

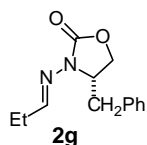


obtained **2e** (62 mg, 92%) as a pale yellow oil which decomposed quickly in air or light.  $[\alpha]_D^{20} = -6.5$  ( $c=0.6$  in  $\text{CHCl}_3$ ); IR(film): 3028, 2917, 2849, 1751, 1715, 1456, 1399, 1266, 1224, 1095, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=8.96$  (s, 1H), 7.55 (d,  $J=1.7$  Hz, 1H), 7.34-7.19 (m, 5H), 6.78 (dd,  $J=3.4$ , 0.9 Hz, 1H), 6.56 (dd,  $J=3.4$ , 1.7 Hz, 1H), 4.49-4.45 (m, 1H), 4.29 (dd,  $J=8.2$ , 8.2 Hz, 1H), 4.12 (dd,  $J=8.9$ , 5.9 Hz, 1H), 3.35 (dd,  $J=13.9$ , 3.7 Hz, 1H), 2.92 (dd,  $J=13.9$ , 8.9 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=153.8$ , 149.7, 144.8, 141.3, 135.2, 129.4, 128.9, 127.3, 114.3, 111.9, 65.7, 58.8, 37.9; MS (CI)  $m/z$  (%): 295 (100)  $[\text{M}+\text{H}]^+$ ; HRMS (FAB)  $m/z$ : 271.1066 (calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ : 271.1083); Anal. Calcd. for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ : C, 66.65; H, 5.22; N, 10.36. Found: C, 65.61; H, 5.09; N, 10.07.

**(S)-3-(trans-Cinnamylidene)amino-4-phenylmethyl-2-oxazolidinone (2f)**. From **1** (48 mg, 0.25 mmol) and *trans*-cinnamaldehyde (0.05 mL, 0.40 mmol) by General Procedure A



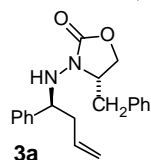
was obtained **2f** (74 mg, 97%) as a colorless solid. m.p. 88-90°C;  $[\alpha]_D^{20} = -7.1$  ( $c=0.8$  in  $\text{CHCl}_3$ ); IR(film): 3055, 2919, 2850, 1751, 1713, 1627, 1451, 1400, 1266, 1214, 1091, 739  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=8.55$  (dd,  $J=7.9$ , 7.9 Hz, 1H), 7.50 (dd,  $J=1.5$ , 1.5 Hz, 2H), 7.47-6.96 (m, 10H), 4.47-4.42 (m, 1H), 4.27 (dd,  $J=8.8$ , 8.8 Hz, 1H), 4.14 (dd,  $J=8.8$ , 5.1 Hz, 1H), 3.26 (dd,  $J=13.9$ , 3.3 Hz, 1H), 2.92 (dd,  $J=13.9$ , 8.8 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=153.9$ , 151.2, 140.8, 135.6, 131.8, 129.5, 129.4, 128.9, 127.5, 127.3, 65.8, 58.4, 37.8; MS (CI)  $m/z$  (%): 306 (25)  $[\text{M}^+]$ ; Anal. Calcd. for  $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$ : C, 74.49; H, 5.92; N, 9.14. Found: C, 74.67; H, 6.29; N, 8.64.



**(S)-3-(Propylidene)amino-4-phenylmethyl-2-oxazolidinone (2g)**. From **1** (27 mg, 0.14 mmol) and propionaldehyde (0.02 mL, 0.27 mmol) by General Procedure A was obtained **2g**<sup>1</sup> (30 mg, 92%) as a colorless oil.

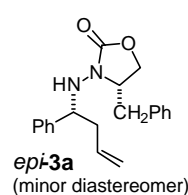
**Allylsilane Addition (General Procedure B)**: A mixture of hydrazone (0.2 mmol) and indium triflate (0.26 mmol) in  $\text{CH}_2\text{Cl}_2$  (2.2 mL) was stirred at room temperature. Meanwhile, a mixture of tetrabutylammonium triphenyldifluorosilicate<sup>2</sup> (TBAT, 0.6 mmol) and tetraallylsilane (0.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.8 mL) was stirred separately at room temperature. After 4h, the allylsilane was added to the hydrazone and the reaction mixture was stirred at room temperature for 2 d, then water (2 mL) was added and the organic phase was dried over  $\text{MgSO}_4$ . Concentration and flash chromatography (6:1  $\rightarrow$  4:1 hexane/ethyl acetate) gave pure hydrazines **3**. Diastereomer ratios were determined by HPLC in comparison with authentic mixtures (dr ca. 5:1) obtained in less selective addition reactions (one example is given below for the minor diastereomer of **3a**; other minor diastereomers were not separated in quantities sufficient for full characterization).

**(4S,1'S)-3-((1'-Phenyl-3'-buten-1'-yl)amino)-4-phenylmethyl-2-oxazolidinone (3a)**. From **2a** (56 mg, 0.20 mmol) by General Procedure B was obtained **3a** (50 mg, 78%) as a colorless oil;  $[\alpha]_D^{20} = -1.0$  ( $c=0.8$  in  $\text{CHCl}_3$ ); IR(film): 3290, 3028, 2927, 1754, 1699, 1653, 1558, 1497, 1456, 1399, 1093, 918, 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR



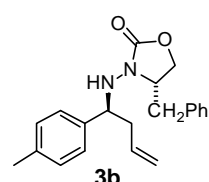
(500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 7.39-7.13 (m, 8H), 6.91 (dd,  $J$  = 7.2, 0 Hz, 2H), 5.74 (dddd,  $J$  = 10.2, 10.2, 7.8, 6.1 Hz, 1H), 5.13 (dd,  $J$  = 17.1, 1.4 Hz, 1H), 5.05 (dd,  $J$  = 10.3, 1.0 Hz, 1H), 4.43 (s, 1H), 4.23 (ddd,  $J$  = 7.9, 1.3, 1.3 Hz, 1H), 3.77-3.70 (m, 2H), 3.16 (dd,  $J$  = 13.4, 3.4 Hz, 1H), 3.06-3.04 (m, 1H), 2.45-2.40 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 157.7, 142.1, 135.99, 135.98, 134.2, 129.1, 128.8, 128.5, 127.98, 127.93, 126.9, 118.4, 65.8, 62.9, 58.2, 40.3, 36.8; MS (EI)  $m/z$  (%): 323 (40) [M+H]<sup>+</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.40; H, 6.89; N, 8.59.

**(4*S*,1'*R*)-3-((1'-Phenyl-3'-buten-1'-yl)amino)-4-phenylmethyl-2-oxazolidinone (1'-*epi*-3a).** To a mixture of **2a** (302 mg, 1.08 mmol), allyltrimethylsilane (0.51 mL, 3.23 mmol)



and 4 Å molecular sieves (200 mg) in THF (6 mL), was added TBAF (0.10 mL, 1M in THF, 0.10 mmol). The reaction mixture was stirred for 20 h, then filtered through a short silica gel column. Concentration and flash chromatography (6:1 hexane/ethyl acetate) gave a mixture of **3a** and its minor epimer 1'-*epi*-**3a** (107 mg, 33%). Fractions enriched in the minor diastereomer were pooled and further flash chromatography afforded pure 1'-*epi*-**3a** (10 mg, 3%) as a colorless solid; m.p. 63-64°C;  $[\alpha]_D^{20}$  = +6.0 (c=0.8 in CHCl<sub>3</sub>); IR(film): 3277, 3030, 2916, 1759, 1699, 1653, 1559, 1507, 1457, 1091, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 7.40-7.22 (m, 8H), 7.02 (dd,  $J$  = 7.4, 0 Hz, 2H), 5.79 (dddd,  $J$  = 10.3, 10.3, 6.5, 6.5 Hz, 1H), 5.14 (dd,  $J$  = 17.0, 1.4 Hz, 1H), 5.07 (dd,  $J$  = 10.2, 0 Hz, 1H), 4.38 (d,  $J$  = 1.5 Hz, 1H), 4.30 (ddd,  $J$  = 6.9, 1.5, 1.5 Hz, 1H), 4.02 (dd,  $J$  = 7.8, 7.6 Hz, 1H), 3.87-3.80 (m, 2H), 2.95 (dd,  $J$  = 13.8, 3.5 Hz, 1H), 2.55 (dd,  $J$  = 7.9, 7.7 Hz, 2H), 2.00 (dd,  $J$  = 10.3, 9.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 159.0, 140.9, 136.1, 134.6, 134.2, 129.1, 128.9, 128.5, 128.4, 127.98, 126.98, 118.1, 66.5, 62.9, 59.4, 39.4, 37.4; MS (EI)  $m/z$  (%): 281 (100) [M-allyl]<sup>+</sup>; Anal. Calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.50; H, 6.88; N, 8.69. Found: C, 74.70; H, 7.08; N, 8.43.

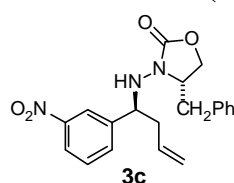
**(4*S*,1'*S*)-3-((1'-(*p*-Methylphenyl)-3'-buten-1'-yl)amino)-4-phenyl-methyl-2-oxazolidinone (3b).** From **2b** (59 mg, 0.20 mmol) by General Procedure B was obtained



**3b** (63 mg, 94%) as colorless oil;  $[\alpha]_D^{20}$  = -2.7 (c=1.0 in CHCl<sub>3</sub>); IR(film): 3286, 3026, 2918, 1757, 1638, 1604, 1497, 1454, 1237, 1092, 918, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 7.33-7.17 (m, 7H), 7.00 (dd,  $J$  = 7.0, 7.0 Hz, 2H), 5.82 (dddd,  $J$  = 17.3, 10.3, 7.7, 6.1 Hz, 1H), 5.20 (dd,  $J$  = 17.1, 1.4 Hz, 1H), 5.12 (dd,  $J$  = 10.2, 1.8 Hz, 1H), 4.47

(s, 1H), 4.26 (dd,  $J$  = 7.0, 7.0 Hz, 1H), 3.83-3.81 (m, 2H), 3.22 (dd,  $J$  = 13.3, 3.3 Hz, 1H), 3.19-3.16 (m, 1H), 2.52-2.45 (m, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 157.8, 139.0, 137.6, 136.2, 134.4, 129.3, 128.9, 127.9, 127.0, 118.4, 65.8, 62.6, 58.3, 40.4, 36.7, 21.3; MS (CI)  $m/z$  (%): 337 (4) [M+H]<sup>+</sup>; Anal. Calcd. for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.97; H, 7.19; N, 8.33. Found: C, 74.63; H, 7.27; N, 7.87.

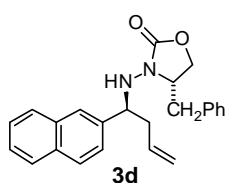
**(4*S*,1'*S*)-3-((1'-(*m*-Nitrophenyl)-3'-buten-1'-yl)amino)-4-phenylmethyl-2-oxazolidinone (3c).** From **2c** (80 mg, 0.25 mmol) by General Procedure B was obtained **3c**



(64 mg, 71%) as a colorless solid. m.p. 47-48°C;  $[\alpha]_D^{20}$  = -2.6 (c=0.35 in CHCl<sub>3</sub>); IR(film): 3291, 3064, 2917, 1756, 1642, 1531, 1351, 1267, 1096, 1002, 738 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 27°C):  $\delta$  = 8.39 (s,

1H), 8.16 (ddd,  $J=2.2, 2.2, 1.2$  Hz, 1H), 7.68-7.05 (m, 7H), 5.78 (dddd,  $J=10.1, 10.1, 7.9, 6.2$  Hz, 1H), 5.12-5.04 (m, 2H), 4.52 (s, 1H), 4.46 (dd,  $J=7.5, 7.5$  Hz, 1H), 3.91 (dd,  $J=9.0, 4.0$  Hz, 1H), 3.76-3.70 (m, 1H), 3.19-3.11 (m, 2H), 2.57 (dd,  $J=13.0, 9.6$  Hz, 1H), 2.38-2.28 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=157.9, 144.6, 135.6, 134.3, 133.1, 129.5, 129.2, 129.0, 127.2, 122.9, 122.4, 119.4, 65.8, 62.4, 58.9, 40.6, 36.9$ ; MS (EI)  $m/z$  (%): 368 (42)  $[\text{M}+\text{H}]^+$ ; Anal. Calcd. for  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4$ : C, 65.38; H, 5.76; N, 11.44. Found: C, 65.31; H, 5.79; N, 11.33.

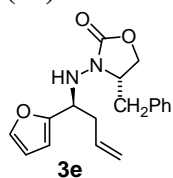
**(4S,1'S)-3-((1'-(2''-Naphthyl)-3'-buten-1'-yl)amino)-4-phenylmethyl-2-oxazolidinone (3d).** From **2d** (68 mg, 0.20 mmol) by General Procedure B was obtained **3d** (61 mg, 82%)



as a colorless oil;  $[\alpha]_{\text{D}}^{20} = -3.2$  ( $c=0.65$  in  $\text{CHCl}_3$ ); IR(film): 3286, 3059, 3027, 2917, 1755, 1638, 1497, 1403, 1220, 1093, 748  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=7.97-6.94$  (m, 12H), 5.82 (dddd,  $J=10.2, 10.2, 8.6, 6.0$  Hz, 1H), 5.21 (dddd,  $J=17.0, 1.5, 1.4, 1.5$  Hz, 1H), 5.13 (dd,  $J=10.2, 1.8$  Hz, 1H), 4.57 (dd,  $J=1.4, 1.4$  Hz, 1H), 4.47 (ddd,  $J=7.9, 7.9, 1.3$  Hz, 1H), 3.78 (dd,  $J=8.9, 4.3$  Hz, 1H), 3.69 (dd,  $J=8.8,$

7.9 Hz, 1H), 3.25 (dd,  $J=13.4, 3.3$  Hz, 1H), 3.07 (dddd,  $J=13.7, 7.7, 3.9, 3.9$  Hz, 1H), 2.58-2.48 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=157.8, 139.5, 135.9, 135.8, 134.1, 133.3, 133.2, 129.1, 128.8, 128.4, 127.9, 127.8, 127.4, 126.9, 126.4, 126.1, 125.3, 118.6, 65.7, 63.0, 58.3, 40.4, 36.8$ ; MS (EI)  $m/z$  (%): 372 (4)  $[\text{M}+\text{H}]^+$ ; Anal. Calcd. for  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2$ : C, 77.39; H, 6.49; N, 7.52. Found: C, 77.07; H, 6.81; N, 7.18.

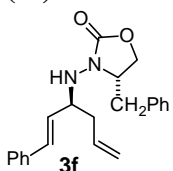
**(4S,1'S)-3-((1'-(2''-Furyl)-3'-buten-1'-yl)amino)-4-phenylmethyl-2-oxazolidinone (3e).** From **2e** (60 mg, 0.20 mmol) by General Procedure B was obtained **3e** (36 mg, 58%)



as a colorless oil;  $[\alpha]_{\text{D}}^{20} = -1.3$  ( $c=1.0$  in  $\text{CHCl}_3$ ); IR(film): 3286, 3064, 3028, 2917, 1756, 1643, 1558, 1497, 1406, 1239, 1094, 742  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=7.44-7.04$  (m, 6H), 6.35 (dd,  $J=3.2, 2.2$  Hz, 1H), 6.27 (dd,  $J=3.1, 1.5$  Hz, 1H), 5.77 (dddd,  $J=10.2, 10.2, 7.8, 6.1$  Hz, 1H), 5.20 (dddd,  $J=17.1, 1.4, 1.4, 1.4$  Hz, 1H), 5.13 (dd,  $J=9.8, 0.6$  Hz, 1H),

4.41-4.38 (m, 2H), 3.97-3.89 (m, 2H), 3.22 (dddd,  $J=15.7, 3.8, 3.8, 3.8$  Hz, 2H), 2.62-2.55 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=157.7, 154.1, 142.3, 135.9, 133.7, 129.3, 128.9, 126.9, 118.5, 110.6, 108.5, 66.1, 58.3, 56.0, 36.9$ ; MS (CI)  $m/z$  (%): 313 (0.8)  $[\text{M}+\text{H}]^+$ ; Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3$ : C, 69.21; H, 6.45; N, 8.97. Found: C, 69.39; H, 6.54; N, 8.75.

**(4S,1'S)-3-((1'-Phenylhexa-1',5'-dien-3'-yl)amino)-4-phenylmethyl-2-oxazolidinone (3f).** From **2f** (66 mg, 0.22 mmol) by General Procedure B was obtained **3f** (45 mg, 60%)

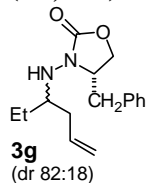


as a colorless oil;  $[\alpha]_{\text{D}}^{20} = -3.7$  ( $c=1.1$  in  $\text{CHCl}_3$ ); IR(film): 3288, 3060, 3029, 2917, 1755, 1639, 1495, 1403, 1266, 1093, 970, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=7.42-7.25$  (m, 8H), 7.12 (dd,  $J=7.9$  Hz, 2H), 6.56 (dd,  $J=15.8$  Hz, 1H), 6.09 (ddd,  $J=15.9, 8.7, 1.2$  Hz, 1H), 5.86 (dddd,  $J=17.3, 10.4, 7.0, 7.0$  Hz, 1H), 5.21 (ddd,  $J=2.9, 2.9, 1.4$  Hz, 1H), 5.15 (dd,  $J=10.3, 0$  Hz, 1H), 4.28 (s, 1H), 4.05 (dd,  $J=7.7, 7.7$  Hz, 1H), 3.96-3.89 (m, 3H), 3.29 (dd,  $J=13.5, 3.6$  Hz, 1H), 2.65 (dd,  $J=13.8, 9.5$  Hz, 1H), 2.36 (dd,  $J=6.8, 5.8$  Hz, 2H);  $^{13}\text{C}$

NMR (125 MHz,  $\text{CDCl}_3$ , 27°C):  $\delta=157.9, 136.8, 135.9, 133.9, 133.3, 130.3, 129.3, 128.9,$

128.8, 127.8, 127.1, 126.6, 118.3, 66.0, 61.7, 59.5, 38.5, 37.3; MS (CI)  $m/z$  (%): 349 (3)  $[M+H]^+$ ; Anal. Calcd. for  $C_{22}H_{24}N_2O_2$ : C, 75.83; H, 6.94; N, 8.04. Found: C, 75.61; H, 6.95; N, 7.97.

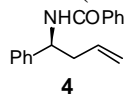
**(4*S*,3'*R*)-3-((5'-Hexen-3'-yl)amino)-4-phenyl-methyl-2-oxazolidinone (3g)**. From **2g**



(50 mg, 0.20 mmol) by General Procedure B was obtained **3g** (28 mg, 51%, dr 82:18) as a colorless oil; IR(film): 3290, 3028, 2965, 2918, 1759, 1637, 1497, 1455, 1399, 1217, 1090, 702  $cm^{-1}$ . Major diastereomer:  $^1H$  NMR (500 MHz,  $CDCl_3$ , 27°C):  $\delta$ =7.32-7.13 (m, 5H), 5.88 (dddd,  $J$ =10.2, 10.2, 7.8, 6.2 Hz, 1H), 5.18 (ddd,  $J$ =17.1, 3.4, 1.6 Hz, 1H), 5.13 (dd,  $J$ =6.5, 1.2 Hz, 1H), 4.13 (dd,  $J$ =8.9, 4.5 Hz, 1H), 4.00-3.98 (m, 1H), 3.95-3.86 (m, 2H), 3.30 (ddd,  $J$ =13.1, 3.4, 3.4 Hz, 2H), 2.30-2.21 (m, 3H), 1.51-1.48 (m, 2H), 0.98-0.90 (m, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , 27°C):  $\delta$ =158.4, 136.1, 135.0, 129.1, 128.9, 127.1, 117.6, 65.9, 65.7, 59.7, 59.3, 37.2, 36.3, 24.9, 9.3; MS (EI)  $m/z$  (%): 274 (0.9)  $[M^+]$ ; Anal. Calcd. for  $C_{16}H_{22}N_2O_2$ : C, 70.04; H, 8.08; N, 10.21. Found: C, 69.66; H, 8.11; N, 10.16.

### Stereochemical correlations

**(*S*)-*N*-(1-Phenyl-3-butenyl)benzamide (4)**. To a solution of **3a** (70 mg, 0.217 mmol) in THF (2.5 mL) at  $-78^\circ C$  was added *n*-BuLi (0.18 mL, 2.5 M in THF, 0.45 mmol). After 1

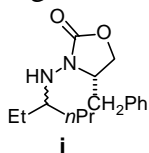


h, benzoic anhydride (102 mg, 0.434 mmol) was added in one portion. The reaction mixture was allowed to warm to r.t. overnight, then partitioned between water and  $CH_2Cl_2$ . The organic phase was washed with brine and dried over  $MgSO_4$ . Flash chromatography gave a colorless oil (75 mg, 81%). To a solution of this oil (75 mg) in THF/HMPA (20:1, 2.3 mL) at  $-78^\circ C$  was added  $SmI_2$  (10 mL, 0.1 M in THF, 1.0 mmol). After 10 min, the reaction mixture was partitioned between water and  $CH_2Cl_2$ . The organic phase was washed with brine and dried over  $MgSO_4$ . Flash chromatography gave **4** (41 mg, 93%; 75% from **3a**) as a colorless solid; m.p. 98-99°C;  $[\alpha]_D^{20} = -2.0$  ( $c=3.4$  in  $CHCl_3$ );  $^1H$  and  $^{13}C$  NMR identical to an authentic sample prepared as described below. Oxazolidinone **5** was recovered (30 mg, 96%; 78% from **3a**).

For correlation, an authentic sample of **4** was prepared by benzylation of the known homoallylic amine.<sup>3</sup> Thus, to a solution of the homoallylic amine (0.38 mmol) in  $CH_2Cl_2$  (2 mL) at 0 °C was added pyridine (0.38 mmol) and benzoyl chloride (0.45 mmol). After 1 h, water (2 mL) was added, and the organic phase was washed with 2 N HCl, 10% NaOH and brine, then dried over  $MgSO_4$ . Concentration and flash chromatography gave **4** as a colorless solid. m.p. 99-101°C;  $[\alpha]_D^{20} = -2.2$  ( $c=3.4$  in  $CHCl_3$ ); IR(film): 3334, 3064, 3030, 2916, 1634, 1592, 1491, 1304, 1073, 921, 758  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ , 27°C):  $\delta$ =7.80-7.35 (m, 10H), 6.42 (d,  $J$ =6.8 Hz, 1H), 5.76 (dddd,  $J$ =17.1, 10.1, 6.7, 6.7 Hz, 1H), 5.30 (ddd,  $J$ =7.1, 7.1, 7.1 Hz, 1H), 5.17 (ddd,  $J$ =17.1, 3.2, 1.5 Hz, 1H), 5.12 (dddd,  $J$ =3.9, 2.0, 1.1, 1.1 Hz, 1H), 2.69 (dd,  $J$ =6.6, 6.6 Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , 27°C):  $\delta$ =166.8, 141.8, 134.7, 134.2, 131.5, 128.7, 128.6, 127.4, 127.0, 126.5, 118.4, 52.9, 40.6;

MS (EI)  $m/z$  (%): 251 (42)  $[M+H]^+$ ; Anal. Calcd. for  $C_{17}H_{17}NO$ : C, 81.24; H, 6.82; N, 5.57. Found: C, 80.73; H, 6.86; N, 5.58.

**(4*S*,3'*R*)-3-(3'-Hexanamino)-4-phenylmethyl-2-oxazolidinone (6)**. A mixture of **3g** (9 mg, 0.033 mmol) and 20% Pd(OH)<sub>2</sub> on carbon (10 mg) in methanol (0.5 mL) was stirred overnight under H<sub>2</sub> (1 atm). Filtration and concentration gave **i** (10 mg, 100%) as a colorless oil; <sup>1</sup>H NMR and TLC data and HPLC retention times for both major and minor diastereomers were identical to an authentic sample produced by *n*-propyl radical addition<sup>4</sup> to **2g** (previously shown to furnish predominantly products of si-face attack<sup>1</sup>).



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