

## Allylic C—H Amination for the Preparation of *syn*-1,3 Amino Alcohol Motifs

Grant T. Rice and M. Christina White\*

*Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801*

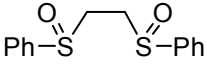
**General Information:** All commercially obtained reagents for the allylic amination reaction were used as received; Pd(OAc)<sub>2</sub> (Johnson-Matthey Chemicals) and Pd[1,2-bis(phenylsulfanyl)ethane](OAc)<sub>2</sub> "Catalyst 1" (Strem Chemicals and Sigma-Aldrich) were stored in a glove box under an argon atmosphere at -20°C and weighed out in the air prior to use. Catalyst 1 was also prepared according to the below procedure<sup>1</sup> and used interchangeably with commercial catalyst. *p*-Nitrobenzenesulfonyl isocyanate was prepared according to the published procedure.<sup>2</sup> Tetrahydrofuran was purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). 1,2-dichloroethane was obtained from Sigma-Aldrich and used as received. All allylic amination reactions were run under oxygen or ambient air with no precautions taken to exclude moisture. All other reactions were run over a stream of N<sub>2</sub> gas unless otherwise stated. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV and potassium permanganate stain. Flash chromatography was performed as described by Still using ZEOprep 60 ECO 43-60 micron silica gel (American International Chemical, Inc.).<sup>3</sup> <sup>1</sup>H NMR spectra were recorded on a Varian Unity-400 (400 MHz), Varian Inova-500 (500 MHz), or Varian Unity-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext. = sextet, sept. = septet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. Proton-decoupled <sup>13</sup>C NMR spectra were recorded on a Varian Unity-400 (100 MHz) and Varian Unity-500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl<sub>3</sub> at 77.16 ppm). Diastereoselectivity of the allylic amination reaction was determined by <sup>1</sup>H NMR analysis of the crude reaction mixture unless otherwise noted. IR spectra were recorded as thin films on NaCl plates on a Perkin-Elmer Spectrum BX and are reported in frequency of absorption (cm<sup>-1</sup>). HPLC analysis was performed on an Agilent Technologies 1100 HPLC system with a model 1100 Quaternary Pump, Diode Array Detector, Thermostat, and Autosampler using a Chiral Technologies Inc. Chiralpak AD-RH column (0.46 cm x 15 cm). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Optical rotations were obtained using a JASCO DIP-360 digital polarimeter and a 3.5 x 50 mm cell and are reported as follows: [α]<sub>λ</sub><sup>T<sub>OC</sub></sup> (c = g/100 mL, solvent).

### **General Procedure A for the synthesis of bis-homoallylic *N*-nosyl and *N*-tosyl carbamates :**

A flame dried 250mL Ar filled round bottom flask was charged sequentially with a stir bar, the bis-homoallylic alcohol starting material (1 equiv.) and tetrahydrofuran (1M). The flask was taken to 0°C followed by the dropwise addition of *p*-Toluenesulfonyl isocyanate (TsNCO, 1.2 equiv.) or the rapid addition of solid *p*-Nitrobenzenesulfonyl isocyanate (NsNCO, 1.2 equiv.). The solution was stirred for 30 minutes and then quenched by diluting with saturated ammonium chloride. The organic layer was washed once with brine then dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. Purification by flash chromatography (15% EtOAc/hexanes, 1% AcOH) provided the pure bis-homoallylic *N*-nosyl and *N*-tosyl carbamates.

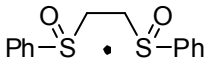
**Procedure for the synthesis of *p*-Nitrobenzenesulfonyl isocyanate (NsNCO):** A flame dried 100mL three-neck flask was equipped with a cold-finger, glass stopper and a stopcock joint (the stopcock valve is kept closed). 4-nitrobenzenesulfonamide (1.82g, 9 mmol), butyl isocyanate (400μL, 3.6 mmol) and 1,2-dichlorobenzene (14mL) were added and taken to reflux. Upon the solution turning clear, the phosgene generation cartridge (20 mmol) was connected to the stopcock and the stopcock valve was opened. The phosgene cartridge was heated to 100°C in a separate oil bath while keeping the three-neck flask at reflux. After complete evolution of the phosgene (1 hour) the cartridge was removed and quenched with absolute ethanol. The reaction flask was allowed to cool to room temperature and nitrogen gas was blown over the reaction flask for two hours. The 1,2-dichlorobenzene was then distilled away (1.0 torr, 80°C) and the remaining dark brown oil was transferred to a Kugelrohr distillation flask and distilled (1.0 torr, 170°C)

yielding a light yellow solid. The yellow solid was stored under Argon atmosphere at  $-20^{\circ}\text{C}$ . The  $\text{N}_2\text{NCO}$  did not demonstrate decomposition throughout its storage at  $-20^{\circ}\text{C}$  for 2-3 weeks and is used according to general procedure A without any further purification.

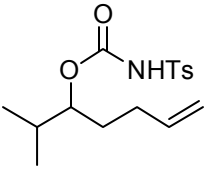
**1,2-bis(phenylsulfinyl)ethane:** A 50 mL flask was charged with a stir bar, 1,2-bis(phenylthio)ethane (2.0 g, 8.12 mmol, 1 equiv.), and acetic acid (12.2 mL).  A solution of  $\text{H}_2\text{O}_2$  (50 wt%, 16.24 mmol, 0.94 mL, 2 equiv.) in acetic acid (6.7 mL) was added dropwise at room temperature. After approximately 15 min. the solution became homogeneous and turned a pale yellow. An additional 8 mL of acetic acid was then added and the solution was allowed to stir for 24 h at room temperature. The acetic acid was removed with mild heating ( $45^{\circ}\text{C}$ ) under high vacuum. The pale yellow solid was emulsified in cold ethanol and cold filtered to yield a mixture of the meso and racemic 1,2-bis(phenylsulfinyl)ethane (2.088g, 92% yield). For spectral data see reference 1.

**Recrystallization of 1,2-bis(phenylsulfinyl)ethane:** To a solution of refluxing acetone ( $\sim 100$  ml) was added the crude ligand mixture ( $\sim 2$ g). Acetone was then added slowly to the mixture with reflux until the powder dissolved completely. The mixture was allowed to cool to room temperature. (NOTE: In the event of over-oxidation, the mono- or di-sulfone will recrystallize first as large plates in approximately 6-8 hours. In this case the mixture was filtered, rinsing with minimal cold acetone). The sulfone free mixture was left at room temperature for an hour, then cooled to  $4^{\circ}\text{C}$  over night. IMPORTANT: The meso crystallizes first as small white prisms. Extended time is needed to allow the racemic (long white needles) to crystallize. The meso crystals were collected *via* filtration with a Buchner funnel and rinsed with cold acetone to give  $\sim 75\%$  yield. Additional crops may be obtained by evaporating the mother liquor and redissolving the white solid in minimal refluxing acetone.

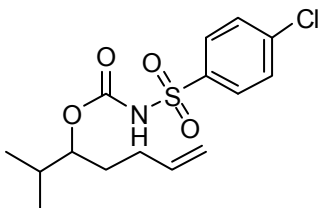
**Recrystallization of  $\text{Pd}(\text{OAc})_2$ :**  $\text{Pd}(\text{OAc})_2$  was dissolved in minimal refluxing benzene. A black precipitate was removed by hot Acrodisc® filtration. The resulting solution was cooled to room temperature without further manipulation. Amber crystals began to form after  $\sim 2$  hours. After 24 hours the solution was filtered to give the recrystallized  $\text{Pd}(\text{OAc})_2$ . For spectral data see reference 1.

**Catalyst 1:** A flame dried 250 mL flask fitted with a condenser under argon atmosphere was charged with *meso*-1,2-bis(phenylsulfinyl)ethane (2.53 g, 9.1 mmol),   $\text{Pd}(\text{OAc})_2$  (2.04 g, 9.1 mmol), and  $\text{CH}_2\text{Cl}_2$  (101 mL). The mixture was stirred at  $40^{\circ}\text{C}$  for 24h. The solution becomes dark red and homogenous during the reaction time. The solution was concentrated *in vacuo* and dried with a stream of  $\text{N}_2$  for 6 h to give a dark red solid used without further purification. **NOTE: The catalyst must be stored at or below  $4^{\circ}\text{C}$ .** The catalyst slowly decomposes at ambient temperature; however, it may be stored for prolonged periods (months) at reduced temperatures.  $^1\text{H}$  NMR and IR spectra of this catalyst look like 1,2-bis(phenylsulfinyl)ethane and  $\text{Pd}(\text{OAc})_2$ . Trace amounts of phenyl vinyl sulfoxide can be observed by  $^1\text{H}$  NMR.

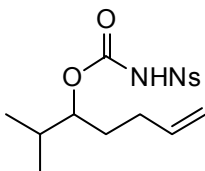
**(±)-2-methylhept-6-en-3-yl tosylcarbamate:** Product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.5$  Hz, 2H), 7.85 (bs, 1H), 7.33 (d,  $J = 8.0$  Hz, 2H), 5.63 (ddt,  $J = 17.0, 10.3, 6.5$  Hz, 1H), 4.87 (m, 2H), 4.63 (ap. q,  $J = 5.5$  Hz, 1H), 2.43 (s, 3H), 1.79 (m, 3H), 1.51 (m, 2H), 0.81 (d,  $J = 7.0$  Hz, 3H), 0.78 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 145.0, 137.6, 135.9, 129.7, 128.4, 115.1, 82.1, 31.5, 30.1, 29.6, 21.8, 18.2, 17.4; IR (film,  $\text{cm}^{-1}$ ): 3233 (br), 3077, 2965, 2937, 2877, 1745, 1716; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{23}\text{NO}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 348.1245, found 348.1259.



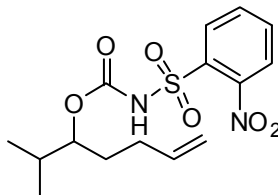
**(±)-2-methylhept-6-en-3-yl 4-chlorophenylsulfonycarbamate:** Product obtained as a light yellow solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 9.0 Hz, 2H), 7.87 (bs, 1H), 7.52 (d,  $J$  = 8.5 Hz, 2H), 5.66 (ddt,  $J$  = 17.0, 10.5, 6.5 Hz, 1H), 4.89 (m, 2H), 4.65 (dt,  $J$  = 8.0, 5.0 Hz, 1H), 1.85 (m, 2H), 1.79 (m, 1H), 1.54 (m, 2H), 0.82 (d,  $J$  = 6.5 Hz, 3H), 0.81 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 140.7, 137.4, 137.2, 129.9, 129.4, 115.3, 82.5, 31.5, 30.1, 29.6, 18.2, 17.4; IR (film,  $\text{cm}^{-1}$ ): 3234 (br), 3091, 2966, 2877, 1745; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{20}\text{NO}_4\text{SClNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 368.0699, found 368.0708.



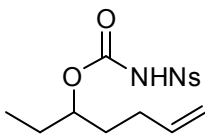
**(±)-2-methylhept-6-en-3-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (m, 2H), 8.25 (m, 2H), 7.64 (bs, 1H), 5.65 (ddt,  $J$  = 17.0, 10.5, 6.5 Hz, 1H), 4.89 (m, 2H), 4.65 (dt,  $J$  = 8.0, 4.9 Hz, 1H), 1.88 (m, 2H), 1.80 (m, 1H), 1.56 (m, 2H), 0.83 (d,  $J$  = 7.0 Hz, 3H), 0.81 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.1, 144.2, 137.2, 129.9, 124.3, 115.5, 83.0, 31.5, 30.0, 29.7, 18.3, 17.4; IR (film,  $\text{cm}^{-1}$ ): 3239 (br), 3108, 2971, 2879, 1742, 1532; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_6\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 379.0940, found 379.0952.



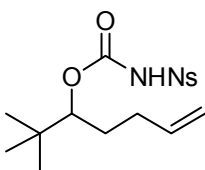
**(±)-2-methylhept-6-en-3-yl 2-nitrophenylsulfonycarbamate:** Product obtained as a light yellow solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (dd,  $J$  = 7.5, 1.8 Hz, 1H), 7.82 (m, 4H), 5.66 (m, 1H), 4.86 (m, 2H), 4.65 (dt,  $J$  = 8.0, 5.0 Hz, 1H), 1.92 (m, 2H), 1.82 (oct.,  $J$  = 6.8 Hz, 1H), 1.59 (m, 2H), 0.84 (d,  $J$  = 7.0 Hz, 3H), 0.83 (d,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 148.2, 137.4, 135.0, 133.5, 132.6, 131.7, 125.2, 115.4, 82.7, 31.6, 30.1, 29.7, 18.3, 17.4; IR (film,  $\text{cm}^{-1}$ ): 3251 (br), 3101, 2968, 2879, 1726, 1547; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_6\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 379.0940, found 379.0935.



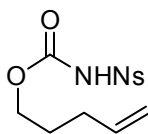
**(±)-hept-6-en-3-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (m, 2H), 8.25 (m, 2H), 8.09 (bs, 1H), 5.67 (dddd,  $J$  = 15.5, 9.0, 7.6, 6.5 Hz, 1H), 4.90 (m, 2H), 4.73 (p,  $J$  = 6.5 Hz, 1H), 1.92 (q,  $J$  = 7.3 Hz, 2H), 1.61-1.45 (m, 4H), 0.78 (t,  $J$  = 7.5 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.2, 144.2, 137.2, 129.9, 124.3, 115.4, 79.9, 32.4, 29.3, 26.8, 9.3; IR (film,  $\text{cm}^{-1}$ ): 3248 (br), 3109, 2974, 2934, 2878, 1749, 1535; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 365.0783, found 365.0788.



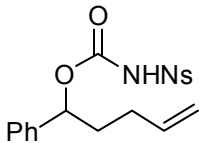
**(±)-2,2-dimethylhept-6-en-3-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (m, 2H), 8.24 (m, 2H), 7.72 (bs, 1H), 5.59 (ddt,  $J$  = 17.0, 10.5, 6.5 Hz, 1H), 4.86 (d,  $J$  = 9.0 Hz, 1H), 4.82 (dd,  $J$  = 17.3, 1.3 Hz, 1H), 4.60 (dd,  $J$  = 11.0, 1.5 Hz, 1H), 1.80 (m, 1H), 1.71 (m, 1H), 1.59 (m, 1H), 1.42 (m, 1H) 0.84 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.5, 144.3, 137.2, 129.8, 124.3, 115.4, 85.7, 34.9, 30.3, 28.7, 25.8; IR (film,  $\text{cm}^{-1}$ ): 3247 (br), 3108, 3078, 2967, 2874, 1748, 1536; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_6\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 393.1096, found 393.1101.



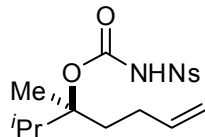
**pent-4-enyl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J$  = 8.5 Hz, 2H), 8.26 (d,  $J$  = 9.0 Hz, 2H), 8.06 (bs, 1H), 5.72 (ddt,  $J$  = 17.0, 10.5, 6.5 Hz, 1H), 4.98 (m, 2H), 4.12 (t,  $J$  = 6.5 Hz, 2H), 2.04 (q,  $J$  = 7.0 Hz, 2H), 1.69 (p,  $J$  = 7.0 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.3, 143.9, 136.8, 130.0, 124.4, 115.9, 67.1, 29.7, 27.6; IR (film,  $\text{cm}^{-1}$ ): 3252 (br), 3108, 3079, 2976, 2921, 1753; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_6\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 337.0470, found 337.0484.



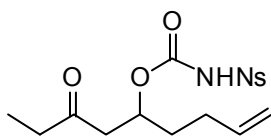
**(±)-1-phenylpent-4-enyl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.33 (m, 2H), 8.19 (m, 2H), 7.84 (bs, 1H), 7.30 (m, 3H), 7.19 (m, 2H), 5.71 (ddt, *J* = 17.0, 10.8, 6.5 Hz, 1H), 5.61 (t, *J* = 6.8 Hz, 1H), 4.94 (m, 2H), 2.05-1.81 (m, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.9, 149.6, 144.0, 138.5, 136.8, 129.9, 128.8, 128.8, 126.7, 124.3, 115.9, 79.9, 34.9, 29.5; IR (film, cm<sup>-1</sup>): 3254 (bs), 3110, 3076, 3041, 2938, 2870, 1750; HRMS (ESI) *m/z* calc'd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup>: 413.0783, found 413.0781.



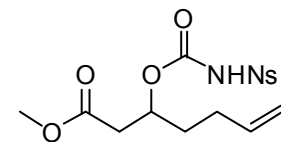
**(±)-2,3-dimethylhept-6-en-3-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 9.2 Hz, 2H), 8.22 (d, *J* = 9.2 Hz, 2H), 7.74 (bs, 1H), 5.66 (m, 1H), 4.91 (m, 2H), 2.27 (sept., *J* = 6.8 Hz, 1H), 1.87 (m, 3H), 1.77 (m, 1H), 1.31 (s, 3H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.8, 148.6, 144.4, 137.8, 129.8, 124.3, 115.0, 92.9, 34.4, 34.1, 27.5, 19.8, 17.2, 17.1; IR (film, cm<sup>-1</sup>): 3250 (br), 3108, 3074, 2963, 2941, 2883, 1722, 1641, 1609, 1533; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 371.1277, found 371.1291.



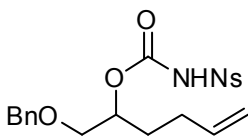
**(±)-7-oxonon-1-en-5-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.40 (m, 2H), 8.24 (m, 2H), 7.90 (bs, 1H), 5.69 (m, 1H), 5.14 (p, *J* = 6.3 Hz, 1H), 4.94 (m, 2H), 2.64 (m, 2H), 2.36 (m, 2H), 1.98 (app. q, *J* = 7.0 Hz, 2H), 1.67 (app. q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 208.1, 150.8, 150.0, 144.1, 136.8, 129.8, 124.3, 115.7, 73.9, 46.0, 36.5, 33.0, 29.2, 7.5; IR (film, cm<sup>-1</sup>): 3232 (br), 3109, 2978, 2940, 1750, 1716, 1532; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>SNa [M+Na]<sup>+</sup>: 407.0889, found 407.0908.



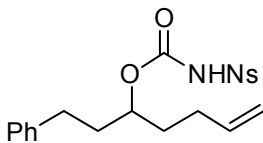
**(±)-methyl 3-(4-nitrophenylsulfonycarbamoyloxy)hept-6-enoate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.39 (m, 2H), 8.24 (m, 2H), 5.68 (m, 1H), 5.12 (ap. p, *J* = 6.4 Hz, 1H), 4.94 (m, 2H), 3.58 (s, 3H), 2.54 (d, *J* = 6.5 Hz, 2H), 1.99 (ap. q, *J* = 7.3 Hz, 2H), 1.69 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.4, 150.9, 149.9, 144.1, 136.6, 129.9, 124.3, 115.9, 74.0, 52.1, 38.6, 32.9, 29.1; IR (film, cm<sup>-1</sup>): 3229 (br.), 3109, 2954, 2874, 1755, 1538; HRMS (ESI) *m/z* calc'd for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>SNa [M+Na]<sup>+</sup>: 409.0682, found 409.0685.



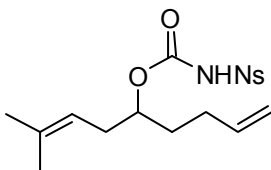
**(±)-1-(benzyloxy)hex-5-en-2-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (m, 2H), 8.20 (m, 2H), 7.66 (bs, 1H), 7.31 (m, 3H), 7.24 (m, 2H), 5.69 (m, 1H), 4.94 (m, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 3.48 (m, 2H), 1.99 (ap. q, *J* = 7.2 Hz, 2H), 1.69 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.8, 144.0, 137.6, 136.9, 130.0, 128.6, 128.1, 127.7, 124.3, 115.8, 115.1, 76.5, 73.3, 70.5, 29.6, 29.4; IR (film, cm<sup>-1</sup>): 3244 (br), 3109, 3075, 3033, 2924, 2869, 1753; HRMS (ESI) *m/z* calc'd for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>O<sub>7</sub>S [M+H]<sup>+</sup>: 435.1226, found 435.1219.



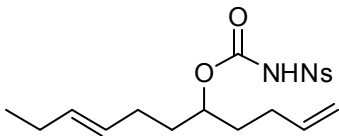
**(±)-1-phenylhept-6-en-3-yl 4-nitrophenylsulfonycarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (m, 2H), 8.26 (m, 2H), 7.88 (bs, 1H), 7.25 (m, 2H), 7.18 (m, 1H), 7.07 (m, 2H), 5.68 (ddt, *J* = 17.5, 9.5, 6.5 Hz, 1H), 4.92 (m, 2H), 4.85 (p, *J* = 6.0 Hz, 1H), 2.53 (m, 2H), 1.96 (ap. q, *J* = 7.0 Hz, 2H), 1.85 (m, 2H), 1.65 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.9, 150.0, 144.2, 140.8, 137.0, 129.9, 128.6, 128.2, 126.3, 124.3, 115.6, 78.3, 35.5, 33.0, 31.4, 29.3; IR (film, cm<sup>-1</sup>): 3256 (br), 3107, 3082, 3028, 2922, 2867, 1750; HRMS (ESI) *m/z* calc'd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup>: 441.1096, found 441.1105.



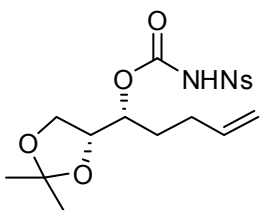
**(±)-8-methylnona-1,7-dien-5-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 7.79 (bs, 1H), 5.68 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 4.92 (m, 3H), 4.75 (ap. p, *J* = 6.0 Hz, 1H), 2.21 (ap. t, *J* = 6.3 Hz, 2H), 1.96 (q, *J* = 7.0 Hz, 2H), 1.61 (s, 3H), 1.59 (m, 2H), 1.53 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.9, 149.9, 144.1, 137.2, 135.6, 129.9, 124.3, 117.8, 115.5, 78.5, 32.6, 32.4, 29.5, 25.9, 18.0; IR (film, cm<sup>-1</sup>): 3246 (br), 3115, 3072, 2977, 2920, 2864, 1749, 1641, 1608, 1535; HRMS (ESI) *m/z* calc'd for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup>: 405.1096, found 405.1111.



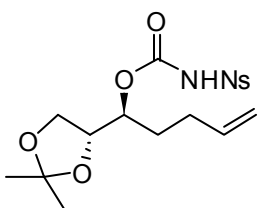
**(±)-(E)-undeca-1,8-dien-5-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 2H), 7.51 (bs, 1H), 5.68 (ddt, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.36 (m, 1H), 5.25 (m, 1H), 4.92 (m, 2H), 4.79 (p, *J* = 6.0, 1H), 1.94 (m, 4H), 1.87 (q, *J* = 7.5 Hz, 2H), 1.58 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.8, 150.2, 144.2, 137.1, 133.3, 129.9, 127.2, 124.3, 115.4, 78.3, 33.7, 32.9, 29.2, 28.1, 25.6, 13.8; IR (film, cm<sup>-1</sup>): 3234 (br.), 3108, 3079, 2961, 2931, 2873, 2851, 1729; LRMS (ESI) *m/z* calc'd for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 397.14, found 397.10.



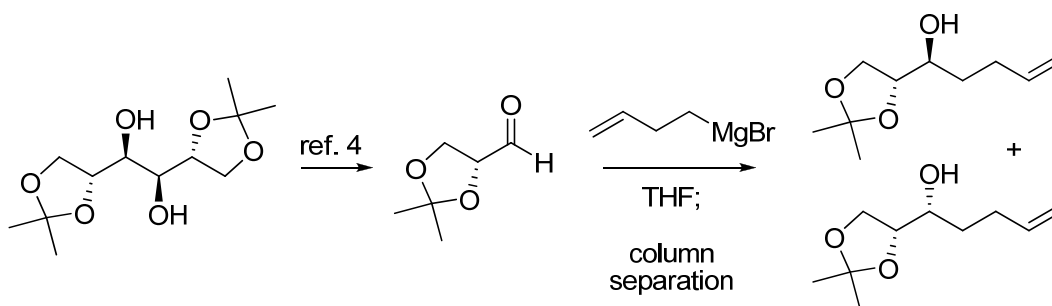
**(+)-(R)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-enyl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 9.5 Hz, 2H), 8.20 (bs, 1H), 5.66 (m, 1H), 4.93 (s, 1H), 4.90 (dd, *J* = 7.0, 1.5 Hz, 1H), 4.81 (ap. q, *J* = 6.0 Hz, 1H), 4.05 (q, *J* = 6.0 Hz, 1H), 3.97 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.65 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.97 (m, 2H), 1.60 (m, 2H), 1.30 (s, 3H), 1.27 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.9, 150.2, 144.1, 136.7, 130.0, 124.3, 115.9, 110.1, 77.3, 76.2, 65.6, 29.8, 29.2, 26.2, 25.2; IR (film, cm<sup>-1</sup>): 3232 (br), 3110, 3081, 2985, 2935, 2892, 1748, 1532; HRMS (ESI) *m/z* calc'd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>8</sub>S [M+H]<sup>+</sup>: 415.1175, found 415.1182. [α]<sub>D</sub><sup>27</sup> = +9.2° (c = 1.0, CHCl<sub>3</sub>).



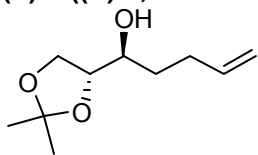
**(-)-(S)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-enyl 4-nitrophenyl sulfonylcarbamate:** Product obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 8.16 (bs, 1H), 5.67 (m, 1H), 4.92 (m, 3H), 4.12 (td, *J* = 6.0, 4.0 Hz, 1H), 3.97 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.73 (dd, *J* = 8.5, 6.0 Hz, 1H), 1.99 (m, 2H), 1.61 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.0, 150.0, 144.0, 136.7, 130.0, 124.3, 116.0, 110.0, 76.8, 76.3, 65.1, 29.4, 29.2, 26.1, 24.8; IR (film, cm<sup>-1</sup>): 3228 (br), 3110, 3082, 2988, 2936, 2895, 1753, 1533; HRMS (ESI) *m/z* calc'd for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>8</sub>S [M+H]<sup>+</sup>: 415.1175, found 415.1160; [α]<sub>D</sub><sup>27</sup> = -10.2° (c = 1.0, CHCl<sub>3</sub>).



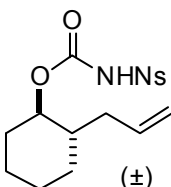
#### Synthesis of Alcohol Precursors for D-Mannitol Derived Substrates:



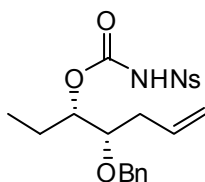
**(S)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-en-1-ol:**  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta$  5.83 (ddt,  $J = 17.2, 10.2, 6.8$  Hz, 1H), 5.06 (ddd,  $J = 17.2, 3.2, 1.6$  Hz, 1H), 4.99 (dd,  $J = 10.0, 1.6$  Hz, 1H), 4.03 (ddd,  $J = 6.8, 6.8, 4.0$  Hz, 1H), 3.98 (dd,  $J = 7.6, 6.4$  Hz, 1H), 3.91 (dd,  $J = 7.6, 7.4$  Hz, 1H), 3.80 (ddd,  $J = 9.2, 7.2, 3.6$  Hz, 1H), 2.34-2.25 (m, 1H), 2.20-2.11 (m, 1H), 1.98 (d,  $J = 3.2$  Hz, 1H), 1.59-1.53 (m, 1H), 1.50-1.43 (m, 1H), 1.43 (s, 3H), 1.37 (s, 3H). Spectral data is in agreement with reference 5.



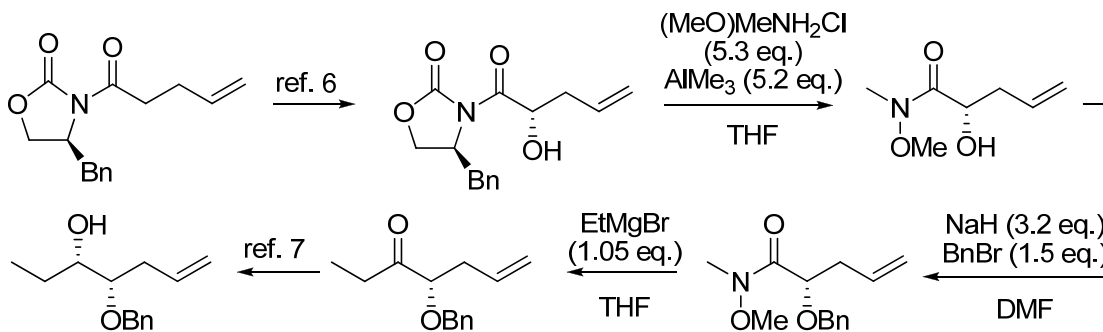
**(±)-(1R,2S)-2-allylcyclohexyl 4-nitrophenylsulfonylcarbamate:** Product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (m, 2H), 8.25 (m, 2H), 7.80 (bs, 1H), 5.60 (dddd,  $J = 17.5, 10.3, 7.5, 6.9$  Hz, 1H), 4.90 (dd,  $J = 10.0, 1.0$  Hz, 1H), 4.86 (dd,  $J = 17.3, 1.8$  Hz, 1H), 4.42 (m, 1H), 2.06 (m, 1H), 1.92 (m, 1H), 1.79 (m, 2H), 1.70 (m, 1H), 1.60 (m, 1H), 1.47 (m, 1H), 1.30-1.10 (m, 3H), 0.98 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.0, 144.2, 135.7, 129.9, 124.3, 116.6, 81.0, 41.6, 36.6, 31.6, 30.0, 24.8, 24.3; IR (film,  $\text{cm}^{-1}$ ): 3253 (br), 3109, 3077, 2939, 2862, 1747, 1535; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 391.0940, found 391.0948.



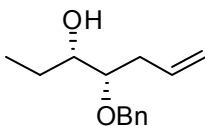
**(+)-(3S,4S)-4-(benzyloxy)hept-6-en-3-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (bs, 1H), 8.12 (s, 4H), 7.34 (m, 5H), 5.71 (ddt,  $J = 17.0, 10.3, 7.0$  Hz, 1H), 5.00 (m, 2H), 4.78 (m, 1H), 4.64 (d,  $J = 11.0$  Hz, 1H), 4.42 (d,  $J = 11.0$  Hz, 1H), 3.48 (td,  $J = 6.5, 3.5$  Hz, 1H), 2.33 (m, 1H), 2.20 (m, 1H), 1.62 (m, 2H), 0.76 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 150.3, 143.9, 137.8, 133.5, 130.1, 128.6, 128.2, 124.1, 118.3, 80.0, 78.5, 72.8, 34.8, 23.5, 9.7; IR (film,  $\text{cm}^{-1}$ ): 3249 (br), 3105, 3077, 3035, 2975, 2944, 2875, 1792; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_7\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 471.1202, found 471.1212;  $[\alpha]_{\text{D}}^{29} = +9.8^\circ$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).



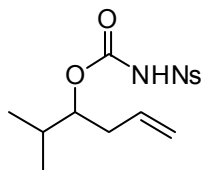
#### Synthesis of Alcohol Precursor for Homoallylic BnO- Substrate:



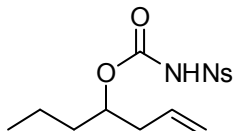
**(+)-(3S,4S)-4-(benzyloxy)hept-6-en-3-ol:**  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (m, 4H), 7.29 (m, 1H), 5.87 (ddt,  $J = 17.0, 10.0, 7.0$  Hz, 1H), 5.16-5.08 (m, 2H), 4.71 (d,  $J = 11.0$  Hz, 1H), 4.49 (d,  $J = 11.5$  Hz, 1H), 3.47 (ap. sext.,  $J = 4.7$  Hz, 1H), 3.35 (dt,  $J = 5.7, 5.5$  Hz, 1H), 2.49 (m, 1H), 2.36 (m, 1H), 2.26 (d,  $J = 5.5$  Hz, 1H), 1.56 (m, 1H), 1.47 (m, 1H), 0.96 (t,  $J = 7.5$  Hz, 3H). Spectral data is in agreement with reference 8.  $[\alpha]_{\text{D}}^{25} = +36.8^\circ$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ ) [lit. 8 for enantiomer (3R,4R)-4-(benzyloxy)hept-6-en-3-ol  $[\alpha]_{\text{D}}^{24} = -32.4^\circ$  ( $c = 5.88$ ,  $\text{CH}_2\text{Cl}_2$ ).



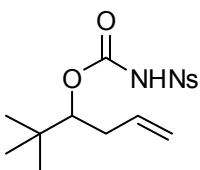
**(±)-2-methylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow solid.  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J = 9.0$  Hz, 2H), 8.24 (d,  $J = 9.0$  Hz, 2H), 7.67 (bs, 1H), 5.56 (m, 1H), 4.92 (m, 2H), 4.66 (ddd,  $J = 8.0, 5.8, 4.5$  Hz, 1H), 2.29 (m, 1H), 2.18 (m, 1H), 1.82 (oct.,  $J = 6.5$  Hz, 1H), 0.86 (d,  $J = 7.0$  Hz, 3H), 0.82 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.0, 144.2, 133.1, 129.9, 124.3, 118.2, 82.3, 35.8, 31.1, 18.5, 17.5; IR (film,  $\text{cm}^{-1}$ ): 3248 (br), 3111, 2966, 2879, 1747, 1533; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 365.0783, found 365.0782.



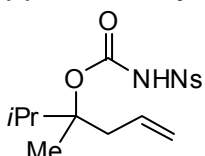
**(±)-hept-1-en-4-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow solid.  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J = 9.0$  Hz, 2H), 8.24 (d,  $J = 9.0$  Hz, 2H), 7.80 (bs, 1H), 5.59 (ddt,  $J = 16.5, 10.5, 7.0$  Hz, 1H), 4.97 (m, 2H), 4.81 (pent.,  $J = 6.0$  Hz, 1H), 2.30 (m, 1H), 2.22 (m, 1H), 1.48 (m, 2H), 1.20 (m, 2H), 0.84 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 150.0, 144.1, 132.6, 129.9, 124.3, 118.6, 77.9, 38.4, 35.5, 18.4, 13.9; IR (film,  $\text{cm}^{-1}$ ): 3234 (br), 3111, 3080, 2962, 2937, 2875, 1747, 1533; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 365.0783, found 365.0775.



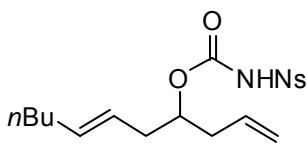
**(±)-2,2-dimethylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow solid.  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (d,  $J = 8.5$  Hz, 2H), 8.22 (d,  $J = 9.0$  Hz, 2H), 7.79 (bs, 1H), 5.49 (m, 1H), 4.77 (m, 2H), 4.64 (dd,  $J = 11.0, 2.3$  Hz, 1H), 2.32 (m, 1H), 2.04 (m, 1H), 0.87 (s, 9H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 150.3, 144.3, 134.1, 129.8, 124.3, 117.8, 84.6, 34.7, 34.4, 25.8; IR (film,  $\text{cm}^{-1}$ ): 3246 (br), 3114, 2968, 2875, 1751, 1535; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 379.0940, found 379.0941.



**(±)-2,3-dimethylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow solid.  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J = 8.5$  Hz, 2H), 8.22 (d,  $J = 9.0$  Hz, 2H), 8.01 (bs, 1H), 5.51 (m, 1H), 4.88 (m, 2H), 2.60 (dd,  $J = 14.5, 7.3$  Hz, 1H), 2.48 (dd,  $J = 14.5, 7.5$  Hz, 1H), 2.25 (sept.,  $J = 6.8$  Hz, 1H), 1.29 (s, 3H), 0.84 (d,  $J = 7.0$  Hz, 3H), 0.81 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 148.7, 144.3, 132.2, 129.8, 124.2, 118.8, 92.2, 39.9, 34.0, 19.2, 17.3, 16.9; IR (film,  $\text{cm}^{-1}$ ): 3248 (br), 3109, 3079, 2978, 1745, 1535; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 379.0934, found 379.0951.



**(±)-(E)-undeca-1,6-dien-4-yl 4-nitrophenylsulfonylcarbamate:** Product obtained as a light yellow oil.  $^1\text{H NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (d,  $J = 9.0$  Hz, 2H), 8.24 (d,  $J = 9.0$  Hz, 2H), 7.81 (bs, 1H), 5.60 (m, 1H), 5.41 (dt,  $J = 15.0, 6.9$  Hz, 1H), 5.18 (dt,  $J = 15.5, 7.0$  Hz, 1H), 4.99 (m, 2H), 4.79 (pent.,  $J = 6.5$  Hz, 1H), 2.31 (m, 1H), 2.22 (m, 3H), 1.90 (m, 2H), 1.26 (m, 4H), 0.86 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.9, 149.8, 144.2, 135.3, 132.6, 129.9, 124.3, 123.4, 118.6, 77.4, 37.7, 36.6, 32.3, 31.5, 22.3, 14.0; IR (film,  $\text{cm}^{-1}$ ): 3249 (br), 3109, 2958, 2927, 2872, 1749, 1535; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_6\text{SNa}$   $[\text{M}+\text{Na}]^+$ : 419.1253, found 419.1263.



### Optimization of Allylic Amination Reaction

**Table 1.** Allylic C-H Amination Reaction Optimization

Entry	R		Time	Isolated Yield <sup>b</sup>	dr <sup>c</sup>
1	<i>p</i> -Tol	<b>(2a)</b>	72 h	15%	5.1:1
2	<i>p</i> -ClPh	<b>(2b)</b>	24 h	38%	3.7:1
3	<i>p</i> -NO <sub>2</sub> Ph (Ns)	<b>(2c)</b>	24 h	67%	4.4:1
4	<i>o</i> -NO <sub>2</sub> Ph	<b>(2d)</b>	24 h	63%	2.6:1

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Entry	R'		Isolated Yield <sup>b</sup>	dr <sup>c</sup>	Isolated Syn <sup>e</sup>
5 <sup>d</sup>	<i>i</i> Propyl	<b>(2c)</b>	80%	6.0:1	65%
6 <sup>d</sup>	Ethyl	<b>(2e)</b>	87%	4.3:1	67%
7 <sup>d</sup>	<i>t</i> Butyl	<b>(2f)</b>	84%	6.3:1	68%

<sup>a</sup>BisSO Ligand = 1,2-bis(phenylsulfinyl)ethane. <sup>b</sup>Average of two runs. <sup>c</sup>Determined by GC analysis (R' = *p*-Tol) or <sup>1</sup>H NMR (R' = *p*-ClPh, *p*-NO<sub>2</sub>Ph, *o*-NO<sub>2</sub>Ph) of crude reaction mixture. <sup>d</sup>Reaction run using 10 mol% *p*-nitrobenzoic acid and oxygenated DCE. <sup>e</sup>Isolated yield of major *syn*- product, >20:1 *syn:anti*.

**Entry 1:** A 1 dram vial (topped with a Teflon-lined cap) was charged with (±)-2-methylhept-6-en-3-yl tosylcarbamate **2a** (325.3 mg, 1.00 mmol). The following solids were all first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (368.4 mg, 2.0 mmol), 1,2-bis(phenylsulfinyl)ethane (13.9 mg, 0.05 mmol), **1** (50.3 mg, 0.10 mmol), Teflon stir bar. THF (1.51 mL) was added, the vial was capped and placed in a 45°C oil bath and stirred for 72 hours. The reaction mixture was transferred to a separatory funnel and diluted with CH<sub>2</sub>Cl<sub>2</sub> (25 mL). Saturated NH<sub>4</sub>Cl (15 mL) and brine (15 mL) were added and the aqueous and organic layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 25 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by GC to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*-(±)-6-isopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one. Run 1: (49.8 mg, 0.15 mmol, 15% yield [5.3:1 dr]); Run 2: (45.3 mg, 0.14 mmol, 14% yield [4.9:1 dr]). **Average: 15% yield, 5.1:1 dr (syn: anti).**

**Entry 2:** A 1 dram vial (topped with a Teflon-lined cap) was charged with (±)-2-methylhept-6-en-3-yl 4-chlorophenylsulfonylcarbamate **2b** (103.7 mg, 0.30 mmol). The following solids were all

first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (110.5 mg, 0.6 mmol), 1,2-bis(phenylsulfinyl)ethane (4.2 mg, 0.02 mmol), **1** (15.1 mg, 0.03 mmol), Teflon stir bar. THF (453  $\mu$ L) was added, the vial was capped and placed in a 45°C oil bath and stirred for 24 hours. The reaction mixture was transferred to a separatory funnel using a minimal amount of methylene chloride and diluted with Et<sub>2</sub>O (30 mL). The organic layer was washed with saturated aqueous NaHSO<sub>3</sub> (25 mL), water (15 mL), 5% aqueous K<sub>2</sub>CO<sub>3</sub> (25 mL), and water (15 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by GC to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*-( $\pm$ )-3-(4-chlorophenylsulfonyl)-6-isopropyl-4-vinyl-1,3-oxazinan-2-one. Run 1: (37.1 mg, 0.108 mmol, 36% yield [3.4:1 dr]); Run 2: (40.2 mg, 0.117 mmol, 39% yield [4.0:1 dr]). **Average: 38% yield, 3.7:1 dr (*syn*: *anti*)**.

**Entry 3:** A 1 dram vial (topped with a Teflon-lined cap) was charged with ( $\pm$ )-2-methylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate **2c** (106.9 mg, 0.30 mmol). The following solids were all first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (110.5 mg, 0.6 mmol), 1,2-bis(phenylsulfinyl)ethane (4.2 mg, 0.02 mmol), **1** (15.1 mg, 0.03 mmol), Teflon stir bar. THF (453  $\mu$ L) was added, the vial was capped and placed in a 45°C oil bath and stirred for 24 hours. The reaction mixture was transferred to a separatory funnel using a minimal amount of methylene chloride and diluted with Et<sub>2</sub>O (30 mL). The organic layer was washed with saturated aqueous NaHSO<sub>3</sub> (25 mL), water (15 mL), 5% aqueous K<sub>2</sub>CO<sub>3</sub> (25 mL), and water (15 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by GC to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*-( $\pm$ )-6-isopropyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one. Run 1: (72.3 mg, 0.204 mmol, 68% yield [4.4:1 dr]); Run 2: (70.2 mg, 0.198 mmol, 66% yield [4.4:1 dr]). **Average: 67% yield, 4.4:1 dr (*syn*: *anti*)**.

**Entry 4:** A 1 dram vial (topped with a Teflon-lined cap) was charged with ( $\pm$ )-2-methylhept-6-en-3-yl 2-nitrophenylsulfonylcarbamate **2d** (106.9 mg, 0.30 mmol). The following solids were all first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (110.5 mg, 0.6 mmol), 1,2-bis(phenylsulfinyl)ethane (4.2 mg, 0.02 mmol), **1** (15.1 mg, 0.03 mmol), Teflon stir bar. THF (453  $\mu$ L) was added, the vial was capped and placed in a 45°C oil bath and stirred for 24 hours. The reaction mixture was transferred to a separatory funnel using a minimal amount of methylene chloride and diluted with Et<sub>2</sub>O (30 mL). The organic layer was washed with saturated aqueous NaHSO<sub>3</sub> (25 mL), water (15 mL), 5% aqueous K<sub>2</sub>CO<sub>3</sub> (25 mL), and water (15 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by GC to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*-( $\pm$ )-6-isopropyl-3-(2-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one. Run 1 (67.0 mg, 0.189 mmol, 63% [2.5:1 dr]); run 2 (65.9 mg, 0.186 mmol, 62% [2.6:1 dr]). **Average Yield: 63%, 2.6:1 dr (*syn*:*anti*)**.

**Entry 5:** A 1 dram vial (topped with a Teflon-lined cap) was charged with ( $\pm$ )-2-methylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate **2c** (106.9 mg, 0.30 mmol). The following solids were all first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (110.5 mg, 0.6 mmol), 1,2-bis(phenylsulfinyl)ethane (4.2 mg, 0.02 mmol), *p*-nitrobenzoic acid (5.1 mg, 0.03 mmol), **1** (15.1 mg, 0.03 mmol), Teflon stir bar. DCE (453  $\mu$ L, O<sub>2</sub> was bubbled through the solvent for 30 minutes prior to addition) was then added to the vial followed by blowing a stream of O<sub>2</sub> over the vial for 5 seconds before sealing and placed in a 45°C oil bath and stirred for 24 hours. The reaction mixture was transferred to a separatory funnel using a minimal amount of methylene chloride and diluted with Et<sub>2</sub>O (30 mL). The organic layer was washed with saturated aqueous NaHSO<sub>3</sub> (25 mL), water (15 mL), 5% aqueous K<sub>2</sub>CO<sub>3</sub> (25 mL), and water (15 mL). The

organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by  $^1\text{H}$ NMR to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*- ( $\pm$ )-6-isopropyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one. Run 1: (87.2 mg, 0.25 mmol, 82% yield [5.8:1 dr]); Run 2: (82.9 mg, 0.23 mmol, 78% yield [6.2:1 dr]). **Average: 80% yield, 6.0:1 dr (*syn*: *anti*).**

**Entry 6:** Following the procedure outlined in Entry 4 ( $\pm$ )-hept-6-en-3-yl 4-nitrophenylsulfonylcarbamate **2e** (102.7 mg, 0.30 mmol) was used. Run 1: (84.8 mg, 0.25 mmol, 83% yield [4.3:1 dr]); Run 2: (91.9 mg, 0.27 mmol, 90% yield [4.3:1 dr]). **Average: 87% yield, 4.3:1 dr (*syn*: *anti*).**

**Entry 7:** Following the procedure outlined in Entry 4 ( $\pm$ )-2,2-dimethylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate **2f** (111.1 mg, 0.30 mmol) was used. Run 1: (96.2 mg, 0.26 mmol, 87% yield [6.3:1 dr]); Run 2: (89.5 mg, 0.24 mmol, 81% yield [6.2:1 dr]). **Average: 84% yield, 6.3:1 dr (*syn*: *anti*).**

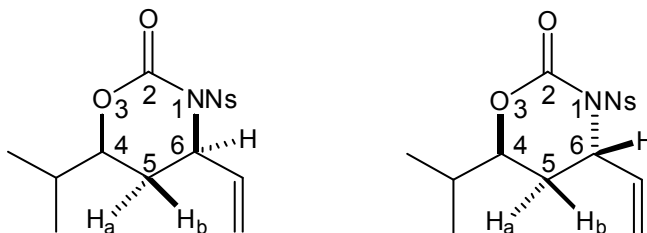
**Use of DIPEA to promote reactivity:** A 1 dram vial (topped with a Teflon-lined cap) was charged with ( $\pm$ )-2-methylhept-6-en-3-yl tosylcarbamate **2a** (325.3 mg, 1.00 mmol). The following solids were all first weighed to wax paper then sequentially added to the vial: phenyl benzoquinone (368.4 mg, 2.0 mmol), 1,2-bis(phenylsulfinyl)ethane (13.9 mg, 0.05 mmol), **1** (50.3 mg, 0.10 mmol), Teflon stir bar. To a separate vial was added DIPEA (10.5  $\mu\text{L}$ , 0.06 mmol) and transferred to the solids vial using THF (1.51 mL divided into three equal portions). The vial was capped and placed in a 45°C oil bath and stirred for 24 hours. The reaction mixture was transferred to a separatory funnel and diluted with  $\text{CH}_2\text{Cl}_2$  (25 mL). Saturated  $\text{NH}_4\text{Cl}$  (15 mL) and brine (15 mL) were added and the aqueous and organic layers were separated. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 25 mL). The combined organic layers were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. A portion of the crude reaction mixture was analyzed by GC to obtain the crude diastereoselectivity. After analysis, this sample was added back to the total crude reaction mixture. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided a mixture of *syn*- and *anti*- ( $\pm$ )-6-isopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one. Run 1: (124.2 mg, 0.384 mmol, 38% yield [1.8:1 dr]); Run 2: (116.1 mg, 0.384 mmol, 36% yield [1.8:1 dr]). **Average: 37% yield, 1.8:1 dr (*syn*: *anti*).**

### Scope of Allylic Amination Reaction

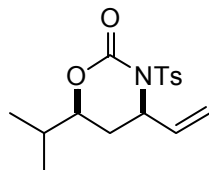
**General Procedure B for Allylic Amination Reaction:** In a one dram vial was added the corresponding carbamate starting material (1 equiv.), phenyl benzoquinone (2 equiv.), *p*-nitrobenzoic acid (0.10 equiv.), 1,2-bis(phenylsulfinyl)ethane (0.05 equiv.),  $\text{Pd}(\text{OAc})_2/$  1,2-bis(phenylsulfinyl)ethane catalyst **1** (0.10 equiv., Aldrich Chemical Company) and a Teflon stir bar. In a separate flask,  $\text{O}_2$  gas was simultaneously bubbled through 1,2-dichloroethane for thirty minutes. The oxygenated 1,2-dichloroethane (0.66 M) was then added to the previous one dram vial,  $\text{O}_2$  gas was blown over the vial for 5 seconds, and the vial was sealed with a Teflon lined cap. The reaction vial was then vortexed until the solution appeared homogeneous and stirred in a 45° C oil bath for 24 hours. The solution was allowed to cool to room temperature and then transferred using a minimum amount of dichloromethane to a 250 mL separatory funnel. The solution was diluted with 15 mL of diethyl ether and rinsed 1x 15 mL aqueous sodium bisulfite (sat.), 1x 15 mL water, 1x 15 mL 5% aqueous  $\text{K}_2\text{CO}_3/\text{H}_2\text{O}$  and 1x 15 mL water. The organic layer was collected and dried over  $\text{MgSO}_4$ , filtered and concentrated *in vacuo*. The crude reaction mixture was purified using flash column chromatography. **In general, the major *syn*-diastereomer can be isolated by flash chromatography (25-35% gradient EtOAc/hexanes) directly from the crude reaction mixture.**

The stereochemistry of the *syn*- and *anti*-diastereomers was determined through their vicinal coupling constants ( $^3J_{\text{H}_5\text{H}_6}$ ). In general, *syn*-oxazinanones show a coupling constant

between C<sub>5</sub>H<sub>a</sub> and C<sub>5</sub>H<sub>b</sub> with C<sub>6</sub>H within 7.5-8.0 Hz and 9.5-10.5 Hz respectively, and the *anti*-oxazinanones show a coupling constant within 2.5-3.5 Hz and 4.5-5.5 Hz respectively. Reference 9 provides a more detailed description of this data. A representative example of both *syn*- and *anti*- products are shown below. The relative stereochemistry was also confirmed through the crystal structure of (±)-(4*S*,4*aS*,8*aR*)-3-(4-nitrophenylsulfonyl)-4-vinyloctahydro-2H-benzo[e][1,3]oxazin-2-one and (4*R*,6*S*)-6-((*R*)-1,2-dihydroxyethyl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one.

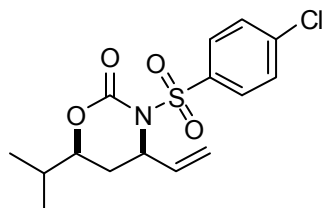


**(±)-(4*R*,6*S*)-6-isopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one:** Racemic 2-methylhept-6-en-3-yl tosylcarbamate (325.4 mg, 1.0 mmol) was reacted according to Table 1, entry 1. Purification by flash chromatography (500:500:10-25 gradient Hexanes:Methylene Chloride:Acetone) provided the mixture of *anti*- and *syn*-oxazinanone products as a white solid. Run 1: (49.8 mg, 0.15 mmol, 15% yield [5.3:1 dr]); Run 2: (45.3 mg, 0.14 mmol, 14% yield [4.9:1 dr]). **Average: 15% yield, 5.1:1 dr (*syn*:*anti*).** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.54 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1H), 5.46



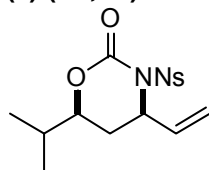
(d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.88 (ap. q, *J* = 8.7 Hz, 1H), 3.98 (ddd, *J* = 11.5, 6.0, 2.0 Hz, 1H), 2.41 (s, 3H), 2.28 (ddd, *J* = 14.0, 8.3, 1.8 Hz, 1H), 1.85 (m, 1H), 1.66 (ddd, 14.0, 11.3, 10.3 Hz, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 144.8, 137.1, 136.1, 129.7, 129.2, 118.7, 80.9, 59.0, 33.1, 31.3, 21.7, 17.7, 17.7; IR (film, cm<sup>-1</sup>): 3073, 2964, 2932, 2875, 1739, 1958; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>22</sub>NO<sub>4</sub>S [M+H]<sup>+</sup>: 324.1270, found 324.1274.

**(±)-(4*R*,6*S*)-3-(4-chlorophenylsulfonyl)-6-isopropyl-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-2-methylhept-6-en-3-yl 4-chlorophenylsulfonylcarbamate (103.7 mg, 0.30 mmol) was reacted according to Table 1, entry 2. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products as a white solid. Run 1 (37.1 mg, 0.11 mmol, 36% [3.4:1 dr]); run 2 (40.2 mg, 0.12 mmol, 39% [4.0:1 dr]). **Average Yield: 38%, 3.7:1 dr (*syn*:*anti*).** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 5.51



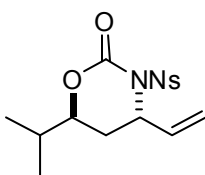
(ddd, *J* = 17.5, 9.0, 8.0 Hz, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 4.89 (ap. q., *J* = 9.0 Hz, 1H), 4.03 (ddd, *J* = 11.5, 6.0, 1.5 Hz, 1H), 2.30 (ddd, *J* = 14.0, 8.0, 1.5 Hz, 1H), 1.88 (oct., *J* = 6.5 Hz, 1H), 1.67 (dt, *J* = 14.0, 10.8 Hz, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 140.5, 137.5, 136.7, 131.3, 128.9, 119.2, 81.2, 59.3, 33.2, 31.4, 17.8, 17.7; IR (film, cm<sup>-1</sup>): 3093, 2968, 2933, 2879, 1730; HRMS (ESI) *m/z* calc'd for C<sub>15</sub>H<sub>19</sub>NO<sub>4</sub>SCl [M+H]<sup>+</sup>: 344.0723, found 344.0706.

**(±)-(4*R*,6*S*)-6-isopropyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-2-methylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate (106.9 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (87.2 mg, 0.25 mmol, 82% [5.8:1 dr]); run 2 (82.9 mg, 0.23 mmol, 78% [6.2:1 dr]). **Average Yield: 80%, 6.0:1 dr (*syn*:*anti*).** Purification by flash chromatography (25-35% gradient EtOAc/hexanes, previous purification not necessary) of a third run provided 0.20 mmol of the ***syn*-oxazinanone (65%)**. The major diastereomer was obtained



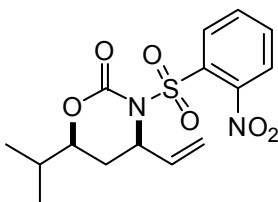
as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 5.50 (ddd,  $J = 17.0, 9.5, 8.0$  Hz, 1H), 5.42 (d,  $J = 17.0$  Hz, 1H), 5.30 (d,  $J = 9.8$  Hz, 1H), 4.91 (dt,  $J = 10.0, 8.0$  Hz, 1H), 4.07 (ddd,  $J = 11.5, 6.0, 2.0$  Hz, 1H), 2.33 (ddd,  $J = 14.0, 8.0, 2.0$  Hz, 1H), 1.90 (m, 1H), 1.70 (ddd,  $J = 14.3, 11.5, 10.3$  Hz, 1H), 1.00 (d,  $J = 6.5$  Hz, 3H), 0.96 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 150.4, 144.5, 136.3, 131.2, 123.7, 119.9, 81.5, 59.7, 33.1, 31.4, 17.7, 17.7; IR (film,  $\text{cm}^{-1}$ ): 3110, 2970, 2940, 2881, 1737, 1531; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 355.0964, found 355.0981.

**(±)-(4S,6S)-6-isopropyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Product



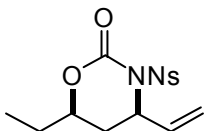
obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (m, 2H), 8.23 (m, 2H), 5.90 (ddd,  $J = 17.0, 10.5, 5.0$  Hz, 1H), 5.46 (dd,  $J = 10.5, 1.5$  Hz, 1H), 5.37 (dd,  $J = 16.8, 1.8$  Hz, 1H), 5.23 (m, 1H), 4.17 (ddd,  $J = 11.5, 6.3, 3.5$  Hz, 1H), 2.05 (ddd,  $J = 14.0, 3.5, 2.5$  Hz, 1H), 2.00 (ddd,  $J = 14.0, 11.5, 5.0$  Hz, 1H), 1.86 (m, 1H), 0.97 (d,  $J = 6.5$  Hz, 3H), 0.93 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 148.5, 144.1, 135.2, 131.0, 123.8, 119.3, 80.9, 56.5, 32.2, 30.1, 17.8, 17.6; IR (film,  $\text{cm}^{-1}$ ): 3109, 2970, 2931, 2880, 1721; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 355.0964, found 355.0968.

**(±)-6-isopropyl-3-(2-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-2-



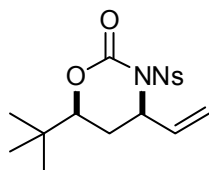
methylhept-6-en-3-yl 2-nitrophenylsulfonylcarbamate (106.9 mg, 0.30 mmol) was reacted according to Table 1, entry 4. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided an inseparable mixture of *anti*- and *syn*-oxazinanone products as a white solid. Run 1 (67.0 mg, 0.189 mmol, 63% [2.5:1 dr]); run 2 (65.9 mg, 0.186 mmol, 62% [2.6:1 dr]). **Average Yield: 63%, 2.6:1 dr (*syn:anti*).** Major *syn*-diastereomer:  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (m, 1H), 7.76 (m, 3H), 5.94 (ddd,  $J = 17.0, 10.0, 7.5$  Hz, 1H), 5.45 (d,  $J = 17.0$  Hz, 1H), 5.31 (d,  $J = 10.5$  Hz, 1H), 4.77 (dt,  $J = 10.5, 7.5$  Hz, 1H), 4.18 (ddd,  $J = 11.0, 6.0, 2.0$  Hz, 1H), 2.38 (ddd,  $J = 14.0, 7.0, 2.0$  Hz, 1H), 1.85 (m, 2H), 0.97 (d,  $J = 6.5$  Hz, 3H), 0.94 (d,  $J = 7.0$  Hz, 3H); Minor *anti*-diastereomer:  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (m, 1H), 7.75 (m, 3H), 5.93 (m, 1H), 5.56 (dd,  $J = 17.5, 2.0$  Hz, 1H), 5.45 (m, 1H), 5.04 (m, 1H), 4.20 (m, 1H), 2.20 (ddd,  $J = 14.0, 12.5, 5.0$  Hz, 1H), 2.02 (dt,  $J = 14.3, 2.5$  Hz, 1H), 1.87 (m, 1H), 0.96 (d,  $J = 7.0$  Hz, 3H), 0.92 (d,  $J = 7.0$  Hz, 1H); Carbon signals, IR wavenumbers and mass spectrometry signals for both *syn*- and *anti*- listed together:  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 148.8, 148.2, 137.0, 136.1, 136.0, 135.8, 135.0, 134.8, 132.7, 132.1, 131.9, 124.7, 124.5, 118.6, 118.6, 81.4, 80.9, 59.1, 57.0, 32.9, 32.1, 31.5, 28.4, 17.8, 17.7, 17.6; IR (film,  $\text{cm}^{-1}$ ): 3103, 2970, 2933, 2879, 1724, 1545; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 355.0964, found 355.0962.

**(±)-(4R,6R)-6-ethyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-hept-



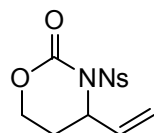
6-en-3-yl 4-nitrophenylsulfonylcarbamate (102.7 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (84.8 mg, 0.25 mmol, 83% [4.3:1 dr]); run 2 (91.9 mg, 0.27 mmol, 90% [4.3:1 dr]). **Average Yield: 87%, 4.3:1 dr (*syn:anti*).** Further purification by flash chromatography (25-35% gradient EtOAc/hexanes) provided 0.20 mmol of the ***syn*-oxazinanone (67%)**. Major diastereomer obtained as a light yellow solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 5.52 (ddd,  $J = 17.5, 9.0, 7.6$  Hz, 1H), 5.41 (d,  $J = 16.5$  Hz, 1H), 5.30 (d,  $J = 9.5$  Hz, 1H), 4.95 (app. q,  $J = 8.3$  Hz, 1H), 4.26 (dddd,  $J = 11.0, 7.0, 5.5, 2.0$  Hz, 1H), 2.37 (ddd,  $J = 14.5, 8.0, 2.3$  Hz, 1H), 1.80-1.60 (m, 3H), 1.00 (t,  $J = 7.3$ , 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 150.3, 144.5, 136.3, 131.2, 123.8, 119.9, 78.3, 59.5, 35.4, 27.2, 9.2; IR (film,  $\text{cm}^{-1}$ ): 3109, 2974, 2942, 2884, 1736, 1531; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 341.0807, found 341.0801.

**(±)-(4*R*,6*S*)-6-tert-butyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-2,2-dimethylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate (111.1 mg, 0.30 mmol) was reacted according to procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (96.2 mg, 0.26 mmol, 87% [6.3:1 dr]); run 2 (89.5 mg, 0.24 mmol, 81% [6.2:1 dr]). **Average Yield: 84%, 6.3:1 dr (*syn:anti*).** Further purification by flash chromatography (25-35% gradient EtOAc/hexanes)

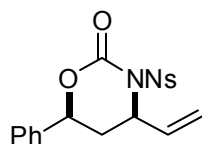


provided 0.20 mmol of the ***syn*-oxazinanone (68%)**. Major diastereomer obtained as a white solid. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.33 (m, 4H), 5.45 (m, 2H), 5.30 (m, 1H), 4.88 (dt, *J* = 10.2, 7.8 Hz, 1H), 3.96 (dd, *J* = 11.8, 1.8 Hz, 1H), 2.32 (ddd, *J* = 14.0, 7.8, 1.8 Hz, 1H), 1.67 (ddd, *J* = 14.0, 11.5, 10.5 Hz, 1H), 0.97 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.7, 150.6, 144.6, 136.3, 131.2, 123.8, 120.1, 84.0, 59.9, 33.5, 31.5, 25.4; IR (film, cm<sup>-1</sup>): 3112, 2970, 2874, 1732, 1531; HRMS (ESI) *m/z* calc'd for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 369.1120, found 369.1114.

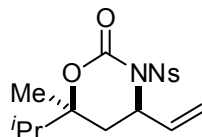
**(±)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Pent-4-enyl 4-nitrophenylsulfonylcarbamate (94.3 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided 3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one as a light yellow oil. Run 1 (63.7 mg, 0.20 mmol, 68%); run 2 (67.5 mg, 0.22 mmol, 72%). **Average Yield: 70%.** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.35 (m, 2H), 8.23 (m, 2H), 5.89 (ddd, *J* = 17.0, 10.5, 5.5 Hz, 1H), 5.48 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.39 (dd, *J* = 17.5, 1.5 Hz, 1H), 5.26 (m, 1H), 4.37 (m, 2H), 2.33 (m, 1H), 2.04 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.8, 148.3, 144.0, 134.6, 131.0, 123.9, 119.6, 65.0, 57.0, 27.4; IR (film, cm<sup>-1</sup>): 3110, 2987, 2921, 1729; HRMS (ESI) *m/z* calc'd for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 313.0494, found 313.0487.



**(±)-(4*R*,6*S*)-3-(4-nitrophenylsulfonyl)-6-phenyl-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-1-phenylpent-4-enyl 4-nitrophenylsulfonylcarbamate (117.1 mg, 0.30 mmol) was reacted according to procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (96.7 mg, 0.25 mmol, 83% [6.5:1 dr]); run 2 (95.5 mg, 0.25 mmol, 82% [7.0:1 dr]). **Average Yield: 83%, 6.8:1 dr (*syn:anti*).** Further purification by flash chromatography (25-35% gradient EtOAc/hexanes) provided 0.19 mmol of the ***syn*-oxazinanone (64%)**. Major product obtained as a white solid. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.35 (s, 4H), 7.40-7.30 (m, 5H), 5.54 (ddd, *J* = 17.0, 9.3, 8.0 Hz, 1H), 5.46 (dd, *J* = 17.0, 1.0 Hz, 1H), 5.36 (dd, *J* = 11.3, 2.3 Hz, 1H), 5.32 (d, *J* = 9.5 Hz, 1H), 5.10 (dt, *J* = 9.5, 8.0 Hz, 1H), 2.60 (ddd, *J* = 14.5, 8.0, 2.0 Hz, 1H), 2.11 (ddd, *J* = 14.5, 11.0, 10.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.7, 150.0, 144.4, 136.3, 136.0, 131.3, 129.3, 129.0, 126.1, 123.8, 120.3, 78.0, 59.6, 38.0; IR (film, cm<sup>-1</sup>): 3110, 3072, 3039, 2982, 2932, 2869, 2257, 1737; HRMS (ESI) *m/z* calc'd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 389.0807, found 389.0822.

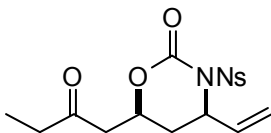


**(±)-(4*R*,6*S*)-6-isopropyl-6-methyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-2,3-dimethylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate (111.1 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-3.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (90.6 mg, 0.25 mmol, 82% [2.6:1 dr]); run 2 (90.1 mg, 0.24 mmol, 82% [2.4:1 dr]). **Average Yield: 82%, 2.5:1 dr (*syn:anti*).** Further purification by flash chromatography (10-15% gradient EtOAc/hexanes) provided 0.15 mmol of the ***syn*-oxazinanone (51%)**. The major diastereomer was obtained as a white solid. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 8.31 (m, 4H), 5.62 (ddd, *J* = 16.8, 9.8, 7.7 Hz, 1H), 5.43 (d, *J* = 16.8 Hz, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 4.91 (ap. q, *J* = 7.6 Hz, 1H), 2.15 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.89 (m, 1H), 1.84 (m, 1H), 1.42 (s, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz,



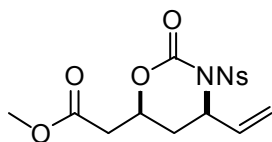
3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 149.3, 144.7, 136.3, 131.0, 123.8, 119.6, 85.1, 57.6, 37.5, 36.7, 19.5, 17.0, 16.6; IR (film,  $\text{cm}^{-1}$ ): 3108, 2971, 2940, 2881, 1727, 1532; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 369.1120, found 369.1125.

**(±)-(4R,6S)-3-(4-nitrophenylsulfonyl)-6-(2-oxobutyl)-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-7-oxonon-1-en-5-yl 4-nitrophenylsulfonyl-carbamate (114.7 mg, 0.30 mmol) was reacted according to procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 3.5-5.0% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (85.6 mg, 0.23 mmol, 75% [3.5:1 dr]); run 2 (87.9 mg, 0.23 mmol, 77% [3.2:1 dr]). **Average Yield: 76%, 3.4:1 dr (*syn:anti*)**. Further



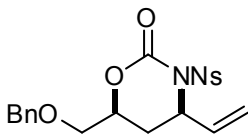
purification by flash chromatography (35-50% gradient EtOAc/hexanes) provided 0.16 mmol of the ***syn*-oxazinanone (53%)**. Major product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (m, 4H), 5.52 (ddd,  $J = 17.5, 9.8, 7.6$  Hz, 1H), 5.43 (d,  $J = 16.5$  Hz, 1H), 5.32 (d,  $J = 10.0$  Hz, 1H), 5.00 (app. q,  $J = 8.0$  Hz, 1H), 4.79 (m, 1H), 2.96 (dd,  $J = 17.5, 5.5$  Hz, 1H), 2.64 (dd,  $J = 17.5, 7.5$  Hz, 1H), 2.55-2.40 (m, 3H), 1.72 (dt,  $J = 14.0, 10.5$  Hz, 1H), 1.06 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  206.8, 150.7, 149.7, 144.3, 136.0, 131.2, 123.8, 120.2, 73.0, 59.4, 45.7, 37.0, 35.7, 7.6; IR (film,  $\text{cm}^{-1}$ ): 3109, 2980, 2941, 1732, 1532; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_7\text{S}$   $[\text{M}+\text{H}]^+$ : 383.0913, found 383.0900.

**(±)-methyl-2-((4R,6S)-3-(4-nitrophenylsulfonyl)-2-oxo-4-vinyl-1,3-oxazinan-6-yl)acetate:**



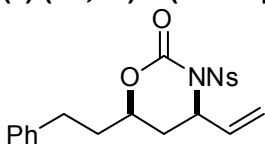
Racemic (±)-methyl 3-(4-nitrophenylsulfonylcarbamoyloxy)hept-6-enoate (Run 1: 115.9 mg, 0.30 mmol; Run 2: 77.3 mg, 0.20 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-3.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (81.9 mg, 0.21 mmol, 71% [4.1:1 dr]); run 2 (56.9 mg, 0.15 mmol, 74% [4.4:1 dr]). **Average Yield: 73%, 4.3:1 dr (*syn:anti*)**. Further purification by flash chromatography (500 mL 1:1 Hexanes:Methylene Chloride followed by 1:1 hexanes:methylene chloride, slow gradient 1.0-4.5% acetone) of run 1 provided 0.15 mmol of the ***syn*-oxazinanone (50%)**. The major diastereomer was obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (m, 2H), 8.30 (m, 2H), 5.53 (ddd,  $J = 17.0, 9.5, 8.0$  Hz, 1H), 5.44 (d,  $J = 16.5$  Hz, 1H), 5.33 (d,  $J = 10.0$  Hz, 1H), 5.01 (ap. q,  $J = 8.5$  Hz, 1H), 4.76 (m, 1H), 3.73 (s, 3H), 2.83 (dd,  $J = 16.8, 6.5$  Hz, 1H), 2.60 (dd,  $J = 16.8, 7.3$  Hz, 1H), 2.54 (ddd,  $J = 14.0, 8.0, 2.3$  Hz, 1H), 1.81 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 150.8, 149.5, 144.3, 136.0, 131.2, 123.8, 120.2, 73.1, 59.2, 52.4, 38.6, 35.5; IR (film,  $\text{cm}^{-1}$ ): 3118, 3101, 2958, 2920, 2853, 1747, 1719, 1536; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_8\text{S}$   $[\text{M}+\text{H}]^+$ : 385.0706, found 385.0708.

**(±)-(4R,6S)-6-(benzyloxymethyl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**



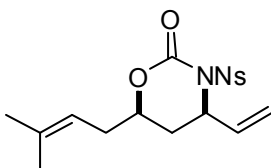
Racemic (±)-1-(benzyloxy)hex-5-en-2-yl 4-nitrophenylsulfonylcarbamate (130.4 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (97.3 mg, 0.23 mmol, 75% [4.5:1 dr]); run 2 (109.0 mg, 0.25 mmol, 84% [4.3:1 dr]). **Average Yield: 80%, 4.4:1 dr (*syn:anti*)**. Purification by flash chromatography (25-35% gradient EtOAc/hexanes, previous purification not necessary) of a third run provided 0.19 mmol of the ***syn*-oxazinanone (63%)**. The major diastereomer was obtained as a light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 7.33 (m, 5H), 5.54 (ddd,  $J = 17.2, 9.4, 8.0$  Hz, 1H), 5.41 (d,  $J = 16.8$  Hz, 1H), 5.30 (d,  $J = 10.0$  Hz, 1H), 4.98 (app. q,  $J = 8.4$  Hz, 1H), 4.55 (s, 2H), 4.49 (m, 1H), 3.63 (dd,  $J = 10.6, 4.6$  Hz, 1H), 3.62 (dd,  $J = 10.8, 4.8$  Hz, 1H), 2.43 (ddd,  $J = 14.4, 8.0, 2.4$  Hz, 1H), 1.95 (ddd,  $J = 14.4, 10.6, 9.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 149.7, 144.3, 137.3, 136.1, 131.2, 128.7, 128.2, 127.9, 123.8, 120.0, 75.7, 73.8, 69.8, 59.3, 32.5; IR (film,  $\text{cm}^{-1}$ ): 3109, 2925, 2872, 1737, 1531; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_7\text{S}$   $[\text{M}+\text{H}]^+$ : 433.1069, found 433.1057.

**(±)-(4R,6R)-3-(4-nitrophenylsulfonyl)-6-phenethyl-4-vinyl-1,3-oxazinan-2-one:** Racemic (±)-1-phenylhept-6-en-3-yl 4-nitrophenylsulfonylcarbamate (125.6 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*- oxazinanone products. Run 1 (106.2 mg, 0.26 mmol, 85% [5.3:1 dr]); run 2 (101.2 mg, 0.24 mmol, 81% [5.3:1 dr]). **Average Yield: 83%, 5.3:1 dr (*syn:anti*)**. Further purification by flash chromatography (25-35% gradient EtOAc/hexanes) provided 0.20 mmol of the ***syn*-oxazinanone (65%)**. The major diastereomer was obtained as a light yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.31 (m, 4H), 7.30 (m, 2H), 7.22 (m, 1H), 7.17 (m, 2H), 5.53 (ddd, *J* = 17.0, 10.0, 8.3 Hz, 1H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.93 (ap. q, *J* = 8.7 Hz, 1H), 4.30 (m, 1H), 2.83 (m, 1H), 2.72 (m, 1H), 2.36 (ddd, *J* = 14.5, 7.8, 2.3 Hz, 1H), 2.03 (m, 1H), 1.89 (m, 1H), 1.77 (ddd, *J* = 14.5, 11.0, 10.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 150.1, 144.4, 140.3, 136.2, 131.1, 128.7, 128.5, 126.5, 123.7, 119.9, 76.2, 59.3, 35.7, 35.7, 30.9; IR (film, cm<sup>-1</sup>): 3108, 3028, 2930, 2869, 1732, 1607, 1532; HRMS (ESI) *m/z* calc'd for C<sub>20</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 417.1120, found 417.1131.

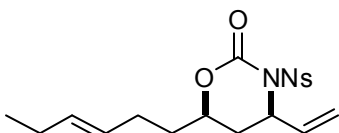


**(±)-(4R,6R)-6-(3-methylbut-2-enyl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**

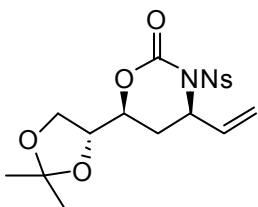
Racemic (±)-8-methylnona-1,7-dien-5-yl 4-nitrophenylsulfonylcarbamate was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*- oxazinanone products. Run 1 (74.2 mg, 0.20 mmol, 65% [4.3:1 dr]); run 2 (78.7 mg, 0.21 mmol, 69% [4.6:1 dr]). **Average Yield: 67%, 4.5:1 dr (*syn:anti*)**. Further purification by flash chromatography (15-25% gradient EtOAc/hexanes) provided 0.16 mmol of the ***syn*-oxazinanone (52%)**. Major diastereomer obtained as a white solid. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.31 (m, 4H), 5.52 (ddd, *J* = 17.5, 9.8, 8.0 Hz, 1H), 5.41 (d, *J* = 16.5 Hz, 1H), 5.30 (d, *J* = 9.5 Hz, 1H), 5.08 (ap. t, *J* = 7.3 Hz, 1H), 4.93 (ap. q, *J* = 8.8 Hz, 1H), 4.29 (m, 1H), 2.44 (m, 1H), 2.36 (ddd, *J* = 14.5, 8.0, 2.0 Hz, 1H), 2.29 (m, 1H), 1.71 (s, 3H), 1.69 (m, 1H), 1.61 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 150.2, 144.5, 136.7, 136.3, 131.2, 123.7, 119.9, 116.7, 76.9, 59.6, 35.1, 32.6, 25.9, 18.1; IR (film, cm<sup>-1</sup>): 3107, 2976, 2916, 2867, 1739, 1532; HRMS (ESI) *m/z* calc'd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 381.1120, found 381.1128.



**(±)-(4R,6R)-6-((E)-hex-3-enyl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** racemic (E)-undeca-1,8-dien-5-yl 4-nitrophenylsulfonylcarbamate (39.7 mg, 0.10 mmol) was reacted according to general procedure B for 48 hours. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*- oxazinanone products. Run 1 (26.4 mg, 0.067 mmol, 67% [4.2:1 dr]); run 2 (26.3 mg, 0.067 mmol, 67% [4.2:1 dr]). **Average Yield: 67%, 4.2:1 dr (*syn:anti*)**. The reaction was run a third time using 0.30 mmol of starting carbamate and purified directly by flash column chromatography (15-25% gradient EtOAc/hexanes) to yield 0.15 mmol of the ***syn*-oxazinanone (50%)**. Major diastereomer obtained as a yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.32 (m, 4H), 5.51 (m, 2H), 5.41 (d, *J* = 17.0 Hz, 1H), 5.35 (m, 1H), 5.30 (d, *J* = 9.5 Hz, 1H), 4.94 (ap. q, *J* = 8.7 Hz, 1H), 4.32 (m, 1H), 2.37 (ddd, *J* = 14.5, 8.0, 2.0 Hz, 1H), 2.13 (m, 2H), 2.00 (p, *J* = 7.0 Hz, 2H), 1.78 (m, 1H), 1.72 (m, 1H), 1.62 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 150.7, 150.2, 144.5, 136.2, 134.1, 131.2, 126.8, 123.8, 120.0, 76.5, 59.5, 35.8, 33.9, 27.7, 25.7, 13.9; IR (film, cm<sup>-1</sup>): 3111, 2961, 2930, 2873, 2852, 1736, 1532; LRMS (ESI) *m/z* calc'd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 395.12, found 395.20.



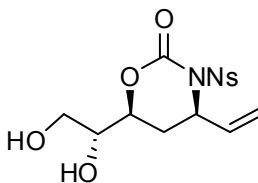
**(+)-(4R,6S)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**



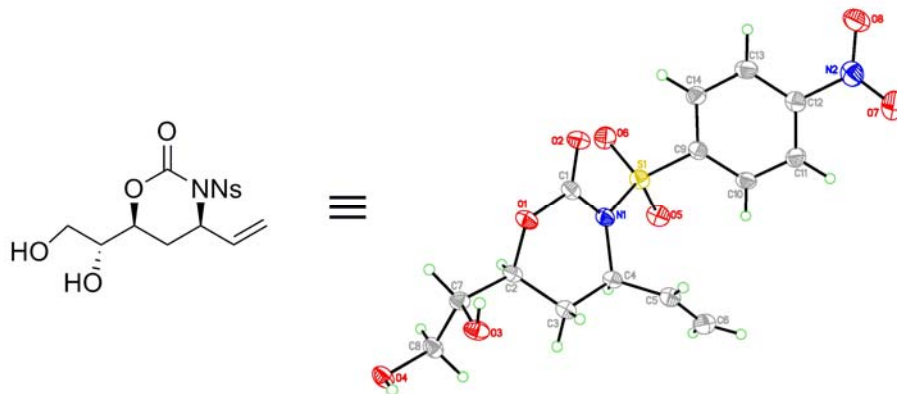
(-)-(S)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-enyl 4-nitrophenylsulfonylcarbamate (41.4 mg, 0.10 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (36.7 mg, 0.09 mmol, 89% [3.8:1 dr]); run 2 (34.6 mg, 0.08 mmol, 84% [3.4:1 dr]). **Average Yield: 87%, 3.6:1 dr (*syn:anti*)**. Purification by flash chromatography (25-35% gradient EtOAc/hexanes, previous purification

not necessary) of a third run (0.30 mmol scale) provided 0.18 mmol of the ***syn*-oxazinanone (61%)**. The major diastereomer was obtained as a light yellow solid. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.35 (m, 2H), 8.29 (m, 2H), 5.57 (ddd, *J* = 17.5, 9.8, 7.8 Hz, 1H), 5.43 (d, *J* = 17.0 Hz, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 5.00 (ap. q, *J* = 8.5 Hz, 1H), 4.18 (ddd, *J* = 10.5, 7.8, 2.8 Hz, 1H), 4.12 (dd, *J* = 9.0, 6.0 Hz, 1H), 4.05 (m, 1H), 3.98 (dd, 8.8, 4.3 Hz, 1H), 2.59 (ddd, *J* = 14.5, 8.0, 2.5 Hz, 1H), 1.85 (dt, *J* = 14.5, 9.5 Hz, 1H), 1.42 (s, 3H), 1.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.8, 149.2, 144.2, 136.0, 131.2, 123.8, 120.1, 110.5, 77.2, 75.4, 66.8, 59.3, 32.5, 26.9, 25.0; IR (film, cm<sup>-1</sup>): 3107, 2988, 2934, 2897, 1739, 1608, 1532; HRMS (ESI) *m/z* calc'd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>8</sub>S [M+H]<sup>+</sup>: 413.1019, found 413.1023; [α]<sub>D</sub><sup>27</sup> = +9.6° (c = 1.0, CHCl<sub>3</sub>).

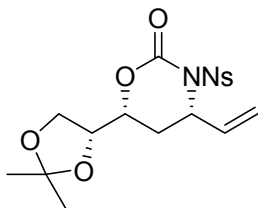
**(4R,6S)-6-((R)-1,2-dihydroxyethyl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**



(+)-(4R,6S)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one was dissolved in 5% HCl/EtOH and stirred at room temperature until completion as seen by TLC. The crude reaction mixture was concentrated *in vacuo* and crystallized using a minimum amount of methylene chloride in hexanes.



**(+)-(4S,6R)-6-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**

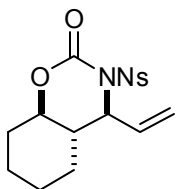


(+)-(R)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-enyl 4-nitrophenylsulfonylcarbamate (Run 1: 41.4 mg, 0.10 mmol; Run 2: 124.3 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-3.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (30.9 mg, 0.08 mmol, 75% [4.7:1 dr]); run 2 (86.6 mg, 0.21 mmol, 70% [4.6:1 dr]). **Average Yield: 73%, 4.7:1 dr (*syn:anti*)**. Purification by flash chromatography (25-35% gradient

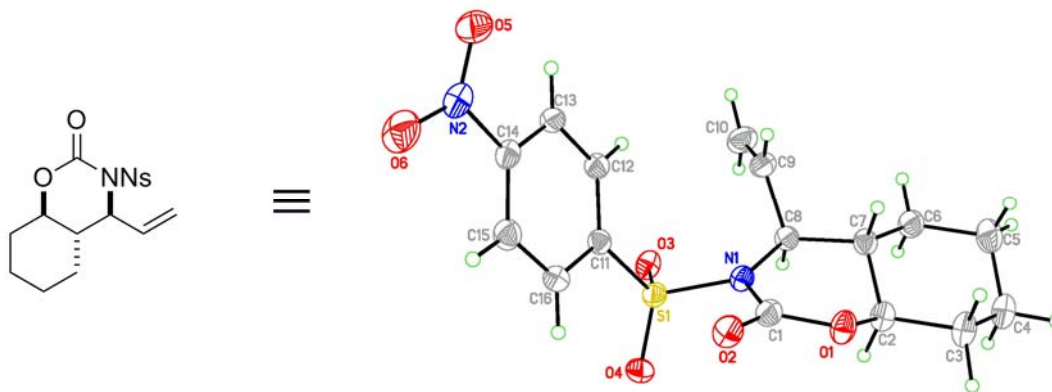
EtOAc/hexanes, previous purification not necessary) of a third run (0.30 mmol scale) provided 0.17 mmol of the ***syn*-oxazinanone (55%)**. The major diastereomer was obtained as a light

yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (m, 4H), 5.54 (dt,  $J = 17.0, 8.6$  Hz, 1H), 5.45 (d,  $J = 17.0$  Hz, 1H), 5.33 (d,  $J = 9.5$  Hz, 1H), 4.97 (ap. q,  $J = 8.7$  Hz, 1H), 4.37 (m, 1H), 4.24 (m, 1H), 4.06 (dd,  $J = 8.5, 7.0$  Hz, 1H), 3.95 (dd,  $J = 9.0, 6.3$  Hz, 1H), 2.36 (ddd,  $J = 14.5, 8.0, 2.0$  Hz, 1H), 1.93 (ap. dt,  $J = 14.0, 10.8$  Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.8, 149.7, 144.3, 136.0, 131.3, 123.8, 120.4, 110.6, 75.4, 74.8, 64.7, 59.4, 31.7, 26.2, 25.2; IR (film,  $\text{cm}^{-1}$ ): 3108, 2986, 2934, 1739, 1533; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_8\text{S}$   $[\text{M}+\text{H}]^+$ : 413.1019, found 413.1015.  $[\alpha]_{\text{D}}^{28} = +3.1^\circ$  ( $c = 0.5, \text{CHCl}_3$ ).

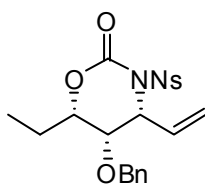
**(±)-(4S,4aS,8aR)-3-(4-nitrophenylsulfonyl)-4-vinyloctahydro-2H-benzo[e][1,3]oxazin-2-one:**



Racemic (±)-(1R,2S)-2-allylcyclohexyl 4-nitrophenylsulfonylcarbamate (110.5 mg, 0.30 mmol) was reacted according to procedure B. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the *syn*-oxazinanone product. Run 1 (66 mg, 0.18 mmol, 60% [ $>20:1$  dr]); run 2 (60.5 mg, 0.17 mmol, 55% [ $>20:1$  dr]). **Average Yield: 58%,  $>20:1$  dr (*syn:anti*).** Relative configuration was determined through crystallographic analysis (Recrystallization performed with EtOAc/Hexanes). Product obtained as a white solid.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 5.41 (m, 3H), 4.38 (m, 1H), 4.05 (td,  $J = 10.9, 4.7$  Hz, 1H), 2.20 (m, 1H), 1.96 (m, 1H), 1.88 (m, 1H), 1.78 (m, 1H), 1.47 (m, 1H), 1.30 (m, 2H), 1.20 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6, 150.1, 144.6, 135.3, 131.3, 123.7, 121.3, 78.4, 66.0, 44.2, 30.5, 28.1, 24.4, 23.6; IR (film,  $\text{cm}^{-1}$ ): 3118, 2942, 2869, 1732, 1531; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_6\text{S}$   $[\text{M}+\text{H}]^+$ : 367.0964, found 367.0966.



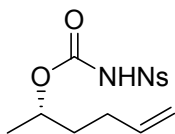
**(-)-(4R,5S,6S)-5-(benzyloxy)-6-ethyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:**



(+)-(3S,4S)-4-(benzyloxy)hept-6-en-3-yl 4-nitrophenylsulfonylcarbamate (89.7 mg, 0.20 mmol) was reacted according to general procedure B for 72 hours. Purification by flash chromatography (1:1 hexanes:methylene chloride, gradient 1.0-3.5% acetone) provided the mixture of *anti*- and *syn*-oxazinanone products. Run 1 (61.6 mg, 0.14 mmol, 69% [ $2.2:1$  dr]); run 2 (60.7 mg, 0.14 mmol, 68% [ $2.3:1$  dr]). **Average Yield: 69%, 2.3:1 dr (*syn:anti*).** The major diastereomer was obtained as a light yellow oil.  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (m, 4H), 7.32 (m, 3H), 7.25 (m, 2H), 5.73 (ddd,  $J = 17.5, 9.0, 8.1$  Hz, 1H), 5.53 (d,  $J = 17.0$ , 1H), 5.43 (d,  $J = 10.0$  Hz, 1H), 4.99 (dd,  $J = 9.0, 6.0$  Hz, 1H), 4.65 (d,  $J = 11.0$  Hz, 1H), 4.49 (d,  $J = 11.0$  Hz, 1H), 4.21 (ddd,  $J = 8.0, 6.0, 2.0$  Hz, 1H), 4.00 (dd,  $J = 6.0, 1.5$  Hz, 1H), 1.86 (m, 1H), 1.63 (m, 1H), 0.93 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 149.6, 144.5, 136.6, 132.9, 131.1, 128.7, 128.5, 128.2, 123.8, 121.7, 81.5, 75.0, 74.9, 64.4, 23.2, 9.8; IR (film,  $\text{cm}^{-1}$ ): 3110, 3072, 3034, 2974, 2934, 2880, 1729, 1607, 1533; HRMS (ESI)  $m/z$  calc'd for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_7\text{S}$   $[\text{M}+\text{H}]^+$ : 447.1226, found 447.1243;  $[\alpha]_{\text{D}}^{27} = -10.8^\circ$  ( $c = 1.0, \text{CHCl}_3$ ).

## Synthesis of (+)-allosedridine

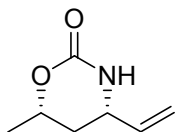
**(+)-(S)-hex-5-en-2-yl 4-nitrophenylsulfonylcarbamate:** In a flame dried 250mL flask was added (S)-(+)-5-Hexen-2-ol (99.2 mg, 0.99 mmol, >99% ee) and tetrahydrofuran (10 mL). The flask was cooled to 0°C followed by the addition of *p*-nosylsulfonyl isocyanate (251.0 mg, 1.1 mmol). The solution was stirred for 60 minutes and then quenched with saturated aqueous ammonium chloride (15 mL), extracted once with brine (15 mL) and dried over MgSO<sub>4</sub>. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (15% EtOAc/hexanes, 1% AcOH) yielding 302.3 mg (93%) of a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.40 (m, 2H), 8.25 (m, 2H), 7.68 (bs, 1H), 5.70 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1H), 4.94 (m, 2H), 4.82 (ap. sext., *J* = 6.0 Hz, 1H), 1.99 (ap q, *J* = 7.3 Hz, 2H), 1.66 (m, 1H), 1.56 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.7, 149.5, 143.9, 136.8, 129.7, 124.0, 115.3, 75.1, 34.6, 29.2, 19.6; IR (film, cm<sup>-1</sup>): 3237 (br), 3115, 2982, 2937, 2873, 1748; HRMS (ESI) *m/z* calc'd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup>: 351.0627, found 351.0642; [α]<sub>D</sub><sup>27</sup> = +5.7° (c = 1.0, CHCl<sub>3</sub>).



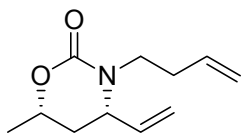
**(+)-(4S,6S)-6-methyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one:** (+)-(S)-hex-5-en-2-yl 4-nitrophenylsulfonylcarbamate (98.5 mg, 0.30 mmol) was reacted according to general procedure B. Purification by flash column chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) provided the mixture of *anti*- and *syn*- oxazinanone products. Run 1 (76.4 mg, 0.23 mmol, 78% [4.1:1 dr]); run 2 (77.3 mg, 0.24 mmol, 79% [4.5:1 dr]). **Average Yield: 79%, 4.3:1 dr (syn:anti).** Further purification by flash chromatography (10-25% gradient EtOAc/hexanes) provided 0.18 mmol of the **syn-oxazinanone (61%)**. The major diastereomer was obtained as a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.30 (m, 4H), 5.53 (ddd, *J* = 17.0, 9.5, 8.0 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.95 (ap q, *J* = 8.7 Hz, 1H), 4.48 (m, 1H), 2.38 (ddd, *J* = 14.0, 8.0, 2.0 Hz, 1H), 1.73 (dt, *J* = 14.5, 10.5, 1H), 1.38 (d, *J* = 6.0 Hz, 3H), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 150.1, 144.4, 136.2, 131.1, 123.7, 119.9, 73.6, 59.4, 37.3, 20.0; IR (film, cm<sup>-1</sup>): 3110, 2985, 2936, 2875, 1732, 1533; HRMS (ESI) *m/z* calc'd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 327.0651, found 327.0651; [α]<sub>D</sub><sup>27</sup> = +4.0° (c = 1.0, CHCl<sub>3</sub>).

Racemic standard (±)-(4S,6S)-6-methyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one was synthesized according to this procedure. Chiral HPLC (Chiral Technologies Inc. Chiralpak AD-RH column (0.46 cm x 15 cm)) was used to determine the enantio-purity of (+)-22 which was determined to be >99% ee. This indicates that the allylic C—H amination proceeds with no erosion of ee.

**(-)-(4S,6S)-6-methyl-4-vinyl-1,3-oxazinan-2-one:** To a 10 mL flame dried flask was added (+)-(4S,6S)-6-methyl-3-(4-nitrophenylsulfonyl)-4-vinyl-1,3-oxazinan-2-one (372.5 mg, 1.14 mmol), K<sub>2</sub>CO<sub>3</sub> (472.6 mg, 3.42 mmol) and a Teflon stir bar. The reaction flask was purged with argon followed by the addition of DMF (2.85 mL). The mixture was cooled to 0°C then PhSH was added (140 μL, 1.37 mmol) dropwise slowly. The reaction mixture was stirred for 30 minutes then filtered over a silica plug followed by 150 mL of 10% MeOH/methylene chloride. The crude mixture was concentrated *in vacuo* under high heat (50-60°C) to remove the remaining DMF. Purification by flash column chromatography (3% MeOH/methylene chloride) yielded 146.4 mg (91%) of a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 5.95 (bs, 1H), 5.71 (ddd, *J* = 17.0, 10.0, 7.0 Hz, 1H), 5.28 (d, *J* = 17.0 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 4.40 (ap. dtd, *J* = 18.0, 6.3, 2.0 Hz, 1H), 3.98 (ddd, *J* = 11.5, 7.0, 4.5 Hz, 1H), 2.00 (m, 1H), 1.51 (dt, *J* = 13.5, 11.5 Hz, 1H), 1.37 (d, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.4, 137.3, 117.5, 73.3, 53.9, 35.5, 21.1; IR (film, cm<sup>-1</sup>): 3248 (br), 3115, 2980, 2931, 1704; HRMS (ESI) *m/z* calc'd for C<sub>7</sub>H<sub>12</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 142.0868, found 142.0864; [α]<sub>D</sub><sup>27</sup> = -0.4 (c = 1.0, CHCl<sub>3</sub>).

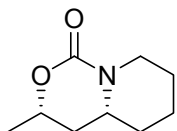


**(-)-(4S,6S)-3-(but-3-enyl)-6-methyl-4-vinyl-1,3-oxazinan-2-one:** To a 10 mL flask was added (4S,6S)-6-methyl-4-vinyl-1,3-oxazinan-2-one (102.6 mg, 0.73 mmol). Toluene (1mL) was then added to the flask and removed *in vacuo* three times. A Teflon stir bar was then added followed by purging the flask with an argon balloon. THF (1.5 mL) was added to the flask then cooled to -78°C. *n*-BuLi (0.45mL, 1.6M in hexanes) was then added dropwise. The



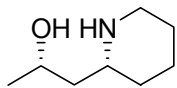
reaction was stirred for 30 minutes followed by the quick addition of but-3-enyl trifluoromethanesulfonate (178.1 mg, 0.87 mmol). The reaction was stirred at -78°C for an additional 30 minutes then warmed to 0°C for 30 minutes. The reaction was quenched with water, extracted with Et<sub>2</sub>O (3 x 25 mL) and the combined organic extracts were dried over MgSO<sub>4</sub>. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (1.5% MeOH/methylene chloride) yielding 126.3 mg (89%) of a light yellow oil. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 5.74 (m, 1H), 5.59 (dt, *J* = 17.0, 9.5 Hz, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.06 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.02 (d, *J* = 10.0 Hz, 1H), 4.26 (ap. dtd, *J* = 17.5, 6.0, 2.0 Hz, 1H), 3.93 (ap. dq, *J* = 9.0, 5.5 Hz, 1H), 3.76 (ddd, *J* = 14.0, 8.0, 6.5 Hz, 1H), 3.09 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 2.37 (m, 1H), 2.23 (m, 1H), 2.02 (ddd, *J* = 14.0, 5.8, 2.0 Hz, 1H), 1.66 (dt, 14.0, 11.0 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.2, 138.1, 135.4, 118.6, 117.0, 71.5, 59.0, 44.7, 37.1, 32.0, 20.9; IR (film, cm<sup>-1</sup>): 3078, 2978, 2934, 1699, 1641; HRMS (ESI) *m/z* calc'd for C<sub>11</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 196.1338, found 196.1341; [α]<sub>D</sub><sup>28</sup> = -17.0° (c = 1.0, CHCl<sub>3</sub>).

**(-)-(3S,4aR)-3-methylhexahydropyrido[1,2-c][1,3]oxazin-1(3H)-one:** To a 50 mL sealed tube was added (-)-(4S,6S)-3-(but-3-enyl)-6-methyl-4-vinyl-1,3-oxazinan-2-one (126.5 mg, 0.65 mmol), Grubb's (II) catalyst (44.0 mg, 0.05 mmol), toluene (13.0 mL) and a Teflon stir bar. The reaction was heated to 65°C for 3 hours. The solution was then allowed to cool to room temperature then passed through a silica plug using 5% EtOAc:methylene chloride to remove the catalyst then 10% EtOAc:Methylene Chloride to remove the product. The crude mixture was



concentrated *in vacuo* and taken on to the next step without further purification. To a flame dried flask was added Pd-C (10% w/v, 99.0 mg), MeOH (6.5 mL) and a Teflon stir bar. H<sub>2</sub> gas was bubbled through the solution for 30 minutes followed by the addition of crude (3S,4aS)-3-methyl-4,4a,7,8-tetrahydropyrido[1,2-c][1,3]oxazin-1(3H)-one. The mixture was stirred until complete conversion was shown by TLC. The mixture was filtered through a celite plug then concentrated *in vacuo*. Purification by flash column chromatography (0.5% MeOH:methylene chloride) yielding 87.7 mg (80%) of a white solid. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 4.46 (m, 1H), 4.27 (dq, *J* = 12.5, 6.5, 2.0 Hz, 1H), 3.27 (tdd, *J* = 11.5, 5.5, 2.5 Hz, 1H), 2.65 (td, *J* = 13.0, 3.0 Hz, 1H), 2.05 (ddd, *J* = 13.5, 5.8, 1.8 Hz, 1H), 1.81 (m, 2H), 1.69 (m, 1H), 1.56 (dt, *J* = 13.5, 11.5 Hz, 1H), 1.45 (m, 1H), 1.37 (m, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), 1.07 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.8, 71.4, 53.9, 44.6, 37.5, 33.5, 25.0, 23.6, 20.8; IR (film, cm<sup>-1</sup>): 2976, 2935, 2857, 1693, 1431; HRMS (ESI) *m/z* calc'd for C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 170.1181, found 170.1181; [α]<sub>D</sub><sup>27</sup> = -16.8 (c = 1.0, CHCl<sub>3</sub>).

**(+)-allosedridine:** (-)-(3S,4aR)-3-methylhexahydropyrido[1,2-c][1,3]oxazin-1(3H)-one (16.9 mg, 0.10 mmol) was added to a 10 mL sealed tube followed by KOH:EtOH solution (2.7 mL, 1.7M) and a Teflon stir bar. The reaction was stirred in a 45°C oil bath for 2 hours. The solution was then transferred to a 100 mL flask and diluted with 20mL of methylene chloride. The reaction mixture was dried over MgSO<sub>4</sub> and

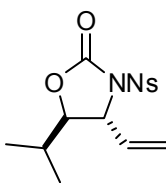


concentrated under stream of N<sub>2</sub>. The product was purified by sublimation yielding 10.5 mg (73%) of a white solid. [α]<sub>D</sub><sup>26</sup> = +17.7 (c = 1.0, MeOH) [lit.10 [α]<sub>D</sub><sup>29</sup> = +16.2 (c = 4.01, MeOH)]. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 6.1 (bs, 1H), 3.99 (dtd, *J* = 16.5, 6.0, 2.0 Hz, 1H), 3.03 (ddd, *J* = 13.5, 7.0, 2.0 Hz, 1H), 2.70 (tt, *J* = 11.0, 2.3 Hz, 1H), 2.58 (m, 1H), 1.83-1.79 (m, 1H), 1.64-1.57 (m, 2H), 1.55-1.45 (m, 2H), 1.30-1.22 (m, 2H), 1.12 (d, *J* = 6.0 Hz, 3H), 1.11-1.03 (m, 1H). Spectral properties match reported values.<sup>10</sup>

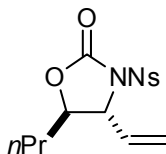
## Expansion of Scope for 1,2-Amination System

**General Procedure C for Allylic Amination Reaction:** In a one dram vial was added the corresponding carbamate starting material (1.00 equiv.), phenyl benzoquinone (1.05 equiv.), 1,2-bis(phenylsulfinyl)ethane (0.05 equiv.), Pd(OAc)<sub>2</sub>/ 1,2-bis(phenylsulfinyl)ethane catalyst **1** (0.10 equiv.) and a Teflon stir bar. THF (0.66 M) was then added to the vial and sealed with a Teflon lined cap. The reaction vial was then vortexed until the solution appeared homogeneous then added to a 45° C oil bath and stirred for 24 hours. The solution was allowed to cool to room temperature and then transferred using dichloromethane to a 250 mL separatory funnel. 15 mL of saturated aqueous ammonium chloride was added to the separatory funnel. The aqueous layer was rinsed 3x 15 mL dichloromethane. The organic layer was collected and dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude reaction mixture was purified using flash column chromatography (1:1 hexanes:methylene chloride, gradient 1.0-2.5% acetone) providing the mixture of *anti*- and *syn*- oxazolidinone products.

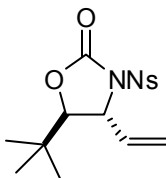
**(±)-(4R,5R)-5-isopropyl-3-(4-nitrophenylsulfonyl)-4-vinyloxazolidin-2-one:** Racemic (±)-2-methylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate (102.7 mg, 0.30 mmol), was reacted according to general procedure C. The product was obtained as a white solid. Run 1 (76.2 mg, 0.224 mmol, 75% [5.0:1 dr]); run 2 (81.2 mg, 0.239 mmol, 80% [4.9:1 dr]). **Average Yield: 78%, 5.0:1 dr (*anti:syn*).** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.38 (m, 2H), 8.23 (m, 2H), 5.74 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.50 (d, *J* = 16.5 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 4.68 (dd, *J* = 9.0, 3.8 Hz, 1H), 3.99 (dd, *J* = 6.0, 3.8 Hz, 1H), 1.97 (oct., *J* = 7.0 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.2, 151.0, 143.6, 133.9, 130.1, 124.3, 121.5, 85.2, 62.2, 32.1, 17.2, 16.7; IR (film, cm<sup>-1</sup>): 3109, 2968, 2937, 2879, 1782, 1533; HRMS (ESI) *m/z* calc'd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 341.0807, found 341.0797.



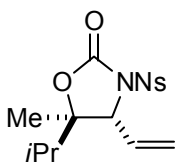
**(±)-(4R,5R)-3-(4-nitrophenylsulfonyl)-5-propyl-4-vinyloxazolidin-2-one:** Racemic (±)-hept-1-en-4-yl 4-nitrophenylsulfonylcarbamate (102.7 mg, 0.30 mmol) was reacted according to general procedure C. Flash column chromatography providing an inseparable mixture of *anti*- and *syn*- oxazolidinone products as a white solid. Run 1 (78.6 mg, 0.231 mmol, 77% [1.7:1 dr]); run 2 (82.7 mg, 0.243 mmol, 81% [1.7:1 dr]). **Average Yield: 79%, 1.7:1 dr (*anti:syn*).** Major *anti*-diastereomer: <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 9.0 Hz, 2H), 8.26 (d, *J* = 8.5 Hz, 2H), 5.75 (ddd, *J* = 17.0, 10.0, 8.8 Hz, 1H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.43 (d, *J* = 10.0 Hz, 1H), 4.53 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.21 (dt, *J* = 7.5, 4.5 Hz, 1H), 1.72-1.39 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 3H); Minor *syn*-diastereomer: <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.36 (m, 2H), 8.26 (m, 2H), 5.58 (m, 1H), 5.50 (m, 2H), 4.89 (dd, *J* = 8.5, 7.0 Hz, 1H), 4.67 (m, 1H), 1.72-1.39 (m, 6H), 0.93 (t, *J* = 7.0 Hz, 3H); Carbon signals, IR wavenumbers and mass spectrometry signals for both *anti*- and *syn*- listed together: <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.2, 151.1, 143.6, 143.5, 133.2, 130.4, 130.2, 129.3, 124.4, 124.2, 123.6, 121.7, 80.7, 79.7, 64.9, 64.0, 35.8, 31.6, 18.7, 17.8, 13.7, 13.6; IR (film, cm<sup>-1</sup>): 3109, 2964, 2937, 2875, 1782, 1533; HRMS (ESI) *m/z* calc'd for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 341.0807, found 341.0806.



**(±)-(4R,5R)-5-tert-butyl-3-(4-nitrophenylsulfonyl)-4-vinyloxazolidin-2-one:** Racemic (±)-2,2-dimethylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate (106.9 mg, 0.30 mmol) was reacted according to general procedure C for 72 h. The product was obtained as a white solid. Run 1 (20.3 mg, 0.057 mmol, 19% [>20:1 dr]); run 2 (22.5 mg, 0.063 mmol, 21% [>20:1 dr]). **Average Yield: 20%, >20:1 dr (*anti:syn*).** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 9.0 Hz, 2H), 8.25 (d, *J* = 9.0 Hz, 2H), 5.75 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 4.75 (dd, *J* = 8.5, 3.3 Hz, 1H), 3.90 (d, *J* = 4.0 Hz, 1H), 0.96 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.3, 151.0, 143.7, 134.4, 130.1, 124.3, 121.2, 87.9, 60.3, 35.1, 24.2; IR (film, cm<sup>-1</sup>): 3109, 2962, 2927, 2873, 2854, 1782, 1535; HRMS (ESI) *m/z* calc'd for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 355.0964, found 355.0954.

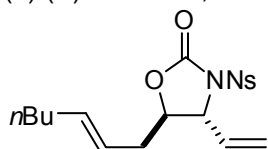


**(±)-(4R,5R)-5-isopropyl-5-methyl-3-(4-nitrophenylsulfonyl)-4-vinyloxazolidin-2-one:** Racemic (±)-2,3-dimethylhex-5-en-3-yl 4-nitrophenylsulfonylcarbamate (106.9 mg, 0.30mmol) was reacted according to general procedure C for 72 h. No products were observed by <sup>1</sup>H NMR.



**(±)-(4R,5R)-5-((E)-hept-2-enyl)-3-(4-nitrophenylsulfonyl)-4-vinyloxazolidin-2-one:** Racemic (±)-(E)-undeca-1,6-dien-4-yl 4-nitrophenylsulfonylcarbamate (119.0 mg, 0.30 mmol) was reacted

according to general procedure C. The product was obtained as a white solid. Run 1 (78.1 mg, 0.198 mmol, 66% [5.4:1 dr]); run 2 (82.8 mg, 0.210 mmol, 70% [5.3:1 dr]). **Average Yield: 68%, 5.4:1 dr (anti:syn).** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 9.0 Hz, 2H), 8.23 (d, *J* = 9.0 Hz, 2H), 5.74 (ddd, *J* = 17.0, 10.0, 8.5 Hz, 1H), 5.66 (dt, *J* = 15.0, 7.0 Hz, 1H), 5.46 (d, *J* = 17.5 Hz, 1H), 5.42 (d, *J* = 10.0 Hz, 1H), 5.30 (dt, *J* = 15.0, 7.0 Hz, 1H), 4.62 (dd, *J* = 8.3, 3.5 Hz, 1H), 4.24 (td, *J* = 6.0, 4.0 Hz, 1H), 2.43 (ap. t, *J* = 6.5 Hz, 2H), 2.01 (m, 2H), 1.31 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.1, 151.0, 143.6, 137.8, 133.2, 130.1, 124.3, 121.6, 120.5, 80.1, 63.5, 36.7, 32.4, 31.3, 22.3, 14.0; IR (film, cm<sup>-1</sup>): 3109, 2958, 2929, 2872, 2858, 1784, 1533; HRMS (ESI) *m/z* calc'd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup>: 395.1277, found 395.1278.



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