Supporting information for

Synthesis of *anti*-1,3-Amino Alcohol Motifs via Pd(II)/SOX catalysis with the Capacity for Stereodivergence

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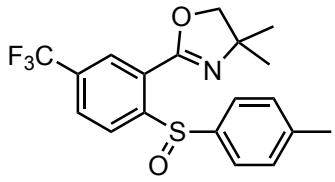
General Information

The following commercially obtained reagents were used as received: $Pd(OAc)_2$ (Johnson Mattey Chemicals) was stored in a glove box, and weighted out in the air at room temperature prior to use. 1,4 benzoquinone (bright yellow solid. If not, sublimation is required to achieve optimal yield), phenylbenzoquinone and 2,5 dimethylbenzoquinone was purchased from Sigma-Aldrich and used as received. Diphenyl phosphinic acid was purchased from Sigma-Aldrich and used as received. All amination reactions were run under ambient air with no precautions taken to exclude moisture. All other reactions were run in flame- or oven-dried glassware under an atmosphere of N_2 or Ar gas with dry solvents unless otherwise stated. All products were filtered through a glass wool plug prior to obtaining a final weight. Anhydrous solvents were purified by passage through a bed of activated alumina immediately prior to use (Glass Countour, Laguna Beach, California). Chloroform-*d* was stored over 3Å molecular sieves in a secondary container with drierite. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized with UV and Cerium-ammonium-molybdate and potassium permanganate stains. Flash chromatography was performed using American International ZEOprep 60 ECO silica gel (230-400 mesh).

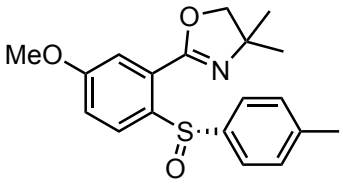
^{1}H-NMR spectra were recorded on a Varian Inova-500 (500 MHz), Varian Unity-500 (500 MHz) or Carver-Bruker 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sxt = sextet, hept = septet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Varian Unity-500 (125 MHz) or Carver-Bruker 500 (125MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm). Chiral gas chromatographic (GC) analysis was performed on an Agilent 6890N Series instrument equipped with FID detectors using a J&W Cyclosil-B column. Chiral high pressure liquid chromatography (HPLC) analysis was performed on an Agilent 1100 Series instrument equipped with a UV detector, using a CHIRALPAK AD-RH or OJ-H column. Optical rotations were measured using a 1 mL cell with a 50 mm path length on a Jasco P-1020 polarimeter. Optical rotations were obtained with a sodium lamp and are reported as follows: $[\alpha]_\lambda T^oC$ (*c* = g/100 mL solvent). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Electrospray ionization (ESI) spectra were performed on a Waters Q-Tof μLtima spectrometer, and electron ionization (EI) and field desorption (FD) spectra were performed on a Micromass 70-VSE spectrometer.

Synthesis of (±)-SOX Ligands

Ligand intermediate, (±)-MeO-SOX, (±)-SOX, (±)-CF_3-SOX were synthesized according to the reported general procedure.[1]



(±)-CF_3-SOX. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.54 (d, J = 8.3 Hz, 1H), 8.14 (d, J = 1.9 Hz, 1H), 7.96 (dd, J = 8.4, 1.9 Hz, 1H), 7.58 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.06 (d, J = 8.1 Hz, 1H), 4.03 (d, J = 8.1 Hz, 1H), 2.33 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 158.3, 151.2, 143.0, 141.6, 132.6 (q, J = 33.3 Hz), 129.7, 128.3 (q, J = 3.7 Hz), 127.1, 126.9 (q, J = 3.7 Hz), 126.4, 125.9, 123.5 (q, J = 272.7 Hz).79.2, 69.1, 28.7, 28.2, 21.5. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -62.85. HRMS (ESI) m/z calculated for $C_{19}H_{19}NO_2SF_3$ [M+H]+: 382.1089, found 382.1091.

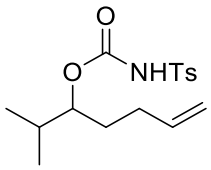


(-)-(*S*)-MeO-SOX. ^{1}H NMR and ^{13}C NMR match reported (±)-MeO-SOX[1]**. Optical rotation**: $[\alpha]^{23}_D$ = -254.4 (c = 0.50, $CHCl_3$).

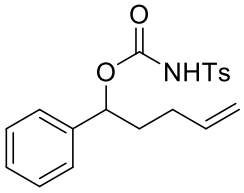
Synthesis of bis-Homoallylic *N*-Tosyl Carbamate Substrates

General Procedure for the synthesis of bis-homoallylic alcohols:
A flame dried 100 mL round bottom flask under argon was charged with a stir bar, aldehyde (10 mmol), and THF (20 mL). The flask was cooled to 0 °C and 3-butenylmagnesium bromide (1.0 M, 12 mL, 12 mmol, 1.2 equiv.) was added dropwise. The reaction was stirred for 30 min and warmed up to room temperature then quenched with sat. aq. NH_4Cl. The mixture was transferred into a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (30 mL x 2). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica plug (acetone/hexanes or ethyl acetate hexanes) provide pure bis-homoallylic alcohols.

General Procedure for the synthesis of bis-homoallylic *N*-tosyl carbamates:
A flame dried 100 mL round bottom flask under argon was charged with a stir bar, homoallylic alcohol (10 mmol), and THF (10 mL). The flask was cooled to 0 °C and *p*-toluenesulfonyl isocyanate (1.84 mL, 12 mmol) was added dropwise. The reaction was stirred for 30 min and then quenched with sat. aq. NH_4Cl. The mixture was diluted with ethyl acetate (50 mL) and washed once with brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash silica plug (acetone/hexanes or ethyl acetate hexanes) provided pure bis-homoallylic *N*-tosyl carbamates.

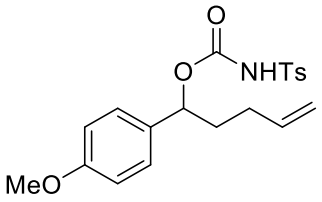


2-methylhept-6-en-3-yl tosylcarbamate (S1) was synthesized from 2-methylhept-6-en-3-ol (1.28g, 10 mmol) following the general procedure in 79% yield (2.57 g, 7.91 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.68 (br. s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.64 (ddt, *J* = 16.9, 10.4, 6.6 Hz, 1H), 4.91 – 4.84 (m, 2H), 4.63 (dt, *J* = 7.1, 5.4 Hz, 1H), 2.43 (s, 3H), 1.88 – 1.73 (m, 3H), 1.56 – 1.46 (m, 2H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.7, 145.1, 137.6, 136.0, 129.7, 128.4, 115.1, 82.2, 31.6, 30.2, 29.6, 21.8, 18.3, 17.5. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{23}NO_4S$ $[M-H]^+$: 324.1270, found 324.1270. Spectra match literature report.[2]

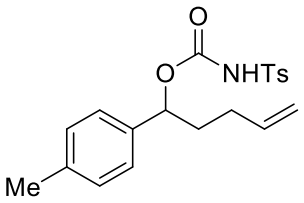


1-phenylpent-4-en-1-yl tosylcarbamate (**S2**) was synthesized from 1-phenylpent-4-en-1-ol (1.62g, 10 mmol) following the general procedure in 71% yield (3.54 g, 7.06 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, J = 8.4 Hz, 2H), 7.69 (br s, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.31-7.26 (m, 3H), 7.19-7.13 (m, 2H), 5.70 (ddt, J = 16.7, 10.5, 6.3 Hz, 1H), 5.63-5.59 (m, 1H), 5.00-4.86 (m, 2H), 2.44 (s, 3H), 2.04-1.87 (m, 3H), 1.86-1.76 (m, 1H). **^{13}C NMR**

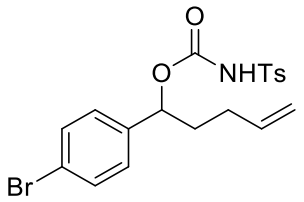
(126 MHz, Chloroform-*d*) δ 149.9, 145.1, 139.1, 137.0, 135.8, 129.7, 128.6, 128.5, 128.4, 126.5, 115.6, 79.1, 35.3, 29.5, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{21}NO_4S$ $[M+Na]^+$: 382.1089, found 382.1102.



1-(4-methoxyphenyl)pent-4-en-1-yl tosylcarbamate (**S3**) was synthesized from 1-(4-methoxyphenyl)pent-4-en-1-ol (1.92g, 10 mmol) following the general procedure in 78% yield (3.04 g, 7.80 mmol) as a yellow oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.60 (br s, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.70 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.56 (t, *J* = 6.9 Hz, 1H), 4.96 – 4.89 (m, 2H), 3.78 (s, 3H), 2.44 (s, 3H), 1.99-1.93 (m, 1H), 1.92-1.86 (m, 2H), 1.82 – 1.74 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.7, 149.9, 145.1, 137.1, 135.8, 131.1, 129.7, 128.4, 128.1, 115.6, 114.0, 78.9, 55.4, 35.1, 29.6, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{23}NO_5S$ $[M-H]^+$: 388.1219, found 388.1213.

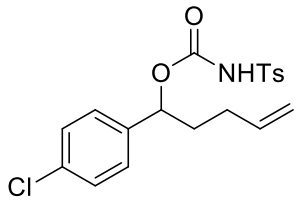


(±)-1-(p-tolyl)pent-4-en-1-yl tosylcarbamate (**S4**). was synthesized from 1-(p-tolyl)pent-4-en-1-ol (1.76g, 10 mmol) following the general procedure in 71% yield (2.63 g, 7.05 mmol) as a white solid. Product obtained as a yellow oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8,4 Hz, 2H), 7.86 (br s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.71 (ddt, *J* = 16.6, 10.4, 6.2 Hz, 1H), 5.58 (t, *J* = 6.6 Hz, 1H), 5.01-4.82 (m, 2H), 2.44 (s, 3H), 2.32 (s, 3H), 2.06-1.88 (m, 3H), 1.83-1.73 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.0, 145.0, 138.2, 137.1, 136.1, 135.8, 129.7, 129.3, 128.4, 126.5, 115.5, 79.0, 35.2, 29.5, 21.8, 21.3. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{23}NO_4S$ $[M+Na]^+$: 396.1245, found 396.1237.

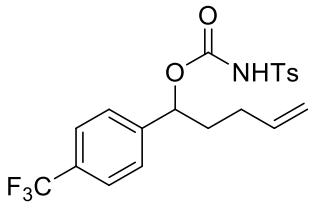


1-(4-bromophenyl)pent-4-en-1-yl tosylcarbamate (**S5**). was synthesized from 1-(4-bromophenyl)pent-4-en-1-ol (2.41 g, 10 mmol) following the general procedure in 89% yield (3.90 g, 8.92 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.44 (br s, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.69

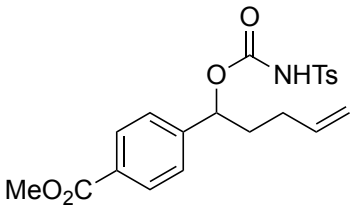
(ddt, *J* = 16.5, 10.4, 6.3 Hz, 1H), 5.57 – 5.51 (m, 1H), 4.97-4.88 (m, 2H), 2.45 (s, 3H), 1.96-1.87 (m, 3H), 1.81-1.73 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.7, 145.3, 138.2, 136.8, 135.7, 131.9, 129.8, 128.4, 128.2, 122.5, 115.9, 78.3, 35.1, 29.4, 21.9 **HRMS (ESI)** *m/z* calculated for $C_{19}H_{20}BrNO_4S$ $[M+Na]^+$: 460.0194, found 460.0194.



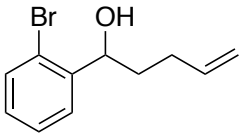
1-(4-chlorophenyl)pent-4-en-1-yl tosylcarbamate (**S6**). was synthesized from 1-(4-chlorophenyl)pent-4-en-1-ol (1.97g, 10 mmol) following the general procedure in 52% yield (2.05 g, 5.21 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.32 (br s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 5.68 (ddt, *J* = 16.5, 10.3, 6.2 Hz, 1H), 5.59 – 5.53 (m, 1H), 5.00 – 4.85 (m, 2H), 2.44 (s, 3H), 1.97 – 1.81 (m, 3H), 1.82 – 1.69 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.1, 145.2, 137.7, 136.8, 135.6, 134.1, 129.7, 128.7, 128.3, 127.8, 115.7, 78.1, 35.1, 29.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{20}ClNO_4S$ $[M+Na]^+$: 416.0699, 416.0704.



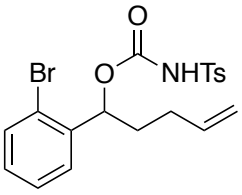
1-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl tosylcarbamate (**S7**). was synthesized from 1-(4-(trifluoromethyl)phenyl)pent-4-en-1-ol (2.30 g, 10 mmol) following the general procedure in 66% yield (2.82 g, 6.60 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.28 (br s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.67 - 5.62 (m, 2H), 4.98 – 4.88 (m, 2H), 2.44 (s, 3H), 2.00-1.85 (m, 3H), 1.86-1.71 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.0, 145.3, 143.3, 143.3, 136.7, 134.4 (q, *J* = 32.5Hz), 129.8, 128.4, 126.6, 125.6 (q, J = 3.7 Hz), 124.0 (q, *J* = 272.2 Hz), 115.9, 78.0, 35.3, 27.3, 21.7. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -62.65. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{20}NO_4F_3S$ $[M-H]^+$: 426.0987, found 426.0986.



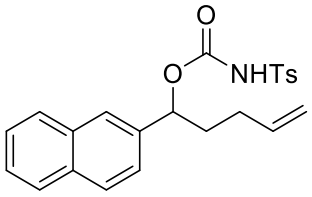
Methyl-4-(1-((tosylcarbamoyl)oxy)pent-4-en-1-yl)benzoate (S8) was synthesized from Methyl-4-(1-hydroxypent-4-en-1-yl)benzoate (1.1 g, 5.00 mmol) following the general procedure in 55% yield (1.15g, 2.75 mmol) as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 8.35, 2H), 7.89 (d, *J* = 8.35, 2H), 7.45 (br s, 1H), 7.33 (d, *J* = 8.0, 2H), 7.20 (d, *J* = 8.2, 2H), 5.76-5.66 (m, 1H), 5.66-5.61 (m, 1H), 4.99 – 4.88 (m, 2H), 3.91 (s, 3H), 2.45 (s, 3H), 1.98 – 1.88 (m, 3H), 1.85 – 1.75 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.7, 149.7, 145.4, 144.2, 136.7, 135.7, 130.2, 130.0, 129.8, 128.5, 126.3, 115.9, 78.4, 52.4, 35.3, 29.4, 21.8. **HRMS** (ESI) m/z calculated for $C_{21}H_{24}NO_6S$ $[M+H]^+$: 418.1316, found 418.1324.



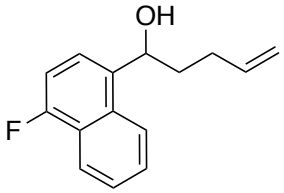
1-(2-bromophenyl)pent-4-en-1-ol (S9a) was synthesized from commercially available 2-bromo-benzaldehyde (2.00 g, 10.80 mmol) following a modified general procedure (3.0 equiv. 3-butenylmagnesium bromide and quenched at 0 °C) in 53% yield (1.39g, 5.76 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 5.89 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.13 – 5.04 (m, 2H), 5.01 (ddt, *J* = 10.2, 2.2, 1.3 Hz, 1H), 2.34 – 2.17 (m, 2H), 1.99 (d, *J* = 3.7 Hz, 1H), 1.93 – 1.84 (m, 1H), 1.81 – 1.73 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.7, 138.2, 132.8, 128.9, 127.8, 127.4, 122.1, 115.2, 72.6, 36.8, 30.2. **HRMS** (ESI) m/z calculated for $C_{11}H_{13}OBr$ $[M+H]^+$: 240.0149, found 240.0140.



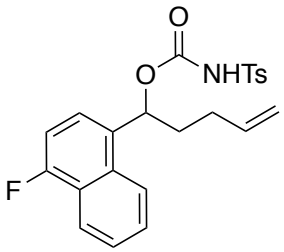
1-(2-bromophenyl)pent-4-en-1-yl tosylcarbamate (S9) was synthesized from 1-(2-bromophenyl)pent-4-en-1-ol (1.39 g, 5.76 mmol) following the general procedure in 80% yield (2.01 g, 4.59 mmol) as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.0, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.26-7.21 (m, *J* = 7.5, 1.4 Hz, 1H), 7.17 – 7.10 (m, 2H), 5.98 (dd, *J* = 8.5, 4.5, 1H), 5.72 (ddt, *J* = 17.2, 10.8, 6.5, 1H), 4.97 – 4.89 (m, 2H), 2.45 (s, , 3H), 2.01 – 1.94 (m, 2H), 1.91 – 1.76 (m, 2H). (NH proton not shown) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.4, 145.3, 139.1, 136.9, 135.8, 133.0, 129.8, 129.6, 128.5, 127.9, 127.0, 121.9, 115.6, 77.7, 34.6, 29.5, 21.8. HRMS (ESI) m/z calculated for $C_{19}H_{20}NO_4SBr$ $[M+Na]^+$: 460.0194, found 460.0204.



1-(naphthalen-2-yl)pent-4-en-1-yl tosylcarbamate (**S10**) was synthesized from 1-(naphthalen-2-yl)pent-4-en-1-ol (2.12g, 10 mmol) following the general procedure in 77% yield (3.17g, 7.73 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.77 (m, 1H), 7.77 – 7.72 (m, 2H), 7.64 – 7.62 (m, 1H), 7.51 – 7.45 (m, 2H), 7.29 – 7.26 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.83 – 5.78 (m, 1H), 5.78 – 5.70 (m, 1H), 4.98 – 4.91 (m, 2H), 2.39 (s, 3H), 2.10 – 2.00 (m, 1H), 1.99 – 1.94 (m, 2H), 1.94 – 1.86 (m, 1H). (NH proton not observed) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.2, 145.1, 137.0, 136.5, 135.8, 133.3, 133.1, 129.7, 128.6, 128.4, 128.2, 127.8, 126.4, 126.4, 125.9, 123.9, 115.6, 79.2, 35.2, 29.5, 21.7. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{23}NO_4S$ $[M+Na]^+$: 432.1245, found 432.1229.

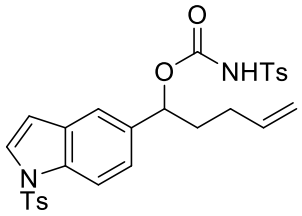


1-(4-fluoronaphthalen-1-yl)pent-4-en-1-ol (S11a) was synthesized from 4-fluoro-1-naphthaldehyde (2.1 g, 12.0 mmol) following a modified general procedure (3.0 equiv. 3-butenylmagnesium bromide and quenched at 0 °C) in 74% yield (2.08 g, 9.03mmol) as a colorless oil. **S11a** was characterized to simplify the interpretation of spectra of **S11**. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.17 – 8.12 (m, 1H), 8.12 – 8.08 (m, 1H), 7.59 – 7.52 (m, 3H), 7.12 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.89 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.42 (dd, *J* = 7.6, 5.2 Hz, 1H), 5.13 – 4.98 (m, 2H), 2.31 – 2.20 (m, 2H), 2.07 (br s, 1H), 2.04 – 1.96 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.4 (d, *J* = 251.5 Hz), 138.2, 136.2 (d, *J* = 4.4 Hz), 131.8 (d, *J* = 4.3 Hz), 127.0, 126.0 (d, *J* = 2.1 Hz), 124.1 (d, *J* = 16.2 Hz), 123.3 (d, *J* = 2.8 Hz), 123.0 (d, *J* = 8.6 Hz), 121.4 (d, *J* = 6.0 Hz), 115.4, 108.9 (d, *J* = 19.8 Hz), 70.6, 37.5, 30.5.. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}OF[M+Na]^+$: 253.1005, found 253.1015.

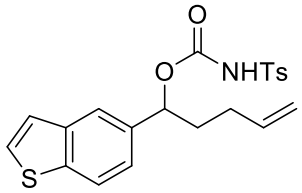


1-(4-fluoronaphthalen-1-yl)pent-4-en-1-yl tosylcarbamate (S11) was synthesized from 1-(4-fluoronaphthalen-1-yl)pent-4-en-1-ol (2.0 g, 8.68 mmol) following the general procedure in 78%

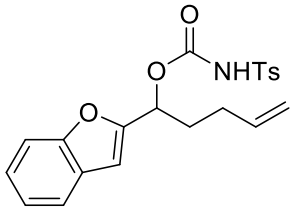
yield (2.92g, 6.83mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 1H), 7.99-7.93 (m, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.51 (m, 2H), 7.40 (br s, 1H), 7.33-7.27 (m, 3H), 7.07 (dd, *J* = 10.0, 8.0 Hz, 1H), 6.35 (dd, *J* = 8.0, 4.5 Hz, 1H), 5.75 (ddt, *J* = 16.3, 10.0, 6.0 Hz, 1H), 5.02 – 4.93 (m, 2H), 2.45 (s, 3H), 2.14 - 1.98 (m, 4H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.9 (d, *J* = 253.1 Hz) 149.8, 145.3, 136.9, 135.7, 131.6 (d, *J* = 4.6 Hz), 131.1 (d, *J* = 4.4 Hz), 129.8, 128.4, 127.6, 126.3, 124.1 (d, *J* = 9.0 Hz), 124.0 (d, *J* = 16.0 Hz),, 123.0 (d, *J* = 2.6 Hz), 121.5 (d, *J* = 6.0 Hz), 115.9, 108.9 (d, *J* = 20.2 Hz), 76.0, 35.1, 29.8, 21.8. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -122.2 (dd, *J* = 10.6, 5.4 Hz). **HRMS** (ESI) m/z calculated for $C_{23}H_{22}NO_4SF$[M+Na]+: 450.1151, found 450.116



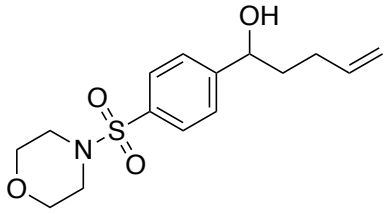
1-(1-tosyl-1H-indol-5-yl)pent-4-en-1-yl tosylcarbamate (**S12**). was synthesized from 1-(1-tosyl-1H-indol-5-yl)pent-4-en-1-ol (3.55 g, 10 mmol) following the general procedure in 51% yield (2.66 g, 5.09 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 1.6 Hz 1H), 7.26 (d,, *J* = 7.7Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.7, 1.7 Hz, 1H), 6.57 (d, *J* = 3.7, 1H), 5.72 – 5.66 (m, 1H), 5.66 – 5.61 (m, 1H), 4.94 – 4.86 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 1.99 – 1.92 (m, 1H), 1.88 (app q, *J* = 6.9 Hz, 2H), 1.83 – 1.70 (m, 1H). (NH proton is underneath 7.86 doublet) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.0, 145.3, 145.1, 137.0, 135.6, 135.2, 134.5, 134.3, 130.8, 130.1, 129.7, 128.4, 127.0, 126.9, 123.0, 119.6, 115.6, 113.6, 109.0, 79.1, 35.4, 29.5, 21.8, 21.7. **HRMS (ESI)** *m/z* calculated for $C_{28}H_{28}N_2O_3S_2$ $[M+Na]^+$: 575.1287, found 575.1312.



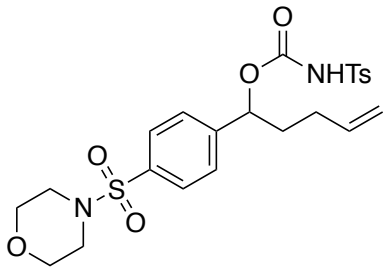
1-(benzo[b]thiophen-5-yl)pent-4-en-1-yl tosylcarbamate (**S13**). was synthesized from 1-(benzo[b]thiophen-5-yl)pent-4-en-1-ol (654.9 mg, 3 mmol) following the general procedure in 67% yield (834.7 mg, 2.01 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 5.4 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.14 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.79 – 5.66 (m, 2H), 4.99 – 4.91 (m, 2H), 2.41 (s, 3H), 2.08 – 1.99 (m, 1H), 1.98 – 1.92 (m, 2H), 1.91 – 1.82 (m, 1H). (NH proton is a very broad peak around 8.0-7.5 ppm) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.9, 145.0, 139.7, 139.6, 136.9, 135.7, 135.3, 129.6, 128.3, 127.2, 123.8, 122.7, 122.6, 121.7, 115.5, 79.2, 35.3, 29.5, 21.7 **HRMS (ESI)** *m/z* calculated for $C_{21}H_{21}NO_4S_2$ $[M-H]^+$: 414.0834, found 413.0831.



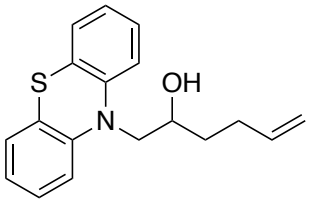
1-(benzofuran-5-yl)pent-4-en-1-yl tosylcarbamate (**S14**). was synthesized from 1-(benzofuran-2-yl)pent-4-en-1-ol (2.71 g, 13.4 mmol) following the general procedure in 62% yield (3.31 g, 8.30 mmol) as a yellow solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz. 1H),), 7.52 (d, *J* = 8.2 Hz. 1H), 7.40 (br s, 1H), 7.30 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1H), 7.25 – 7.20 (m, 3H), 6.63 (s, 1H), 5.83 (t, *J* = 7.1 Hz, 1H), 5.73 (ddt, *J* = 17.8, 9.4, 6.5 Hz, 1H), 4.99-4.92 (m, 2H), 2.37 (s, 3H), 2.14 – 2.06 (m, 2H), 2.05 – 1.95 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 154.9, 153.2, 149.8, 145.2, 136.6, 135.4, 129.7, 128.5, 127.6, 125.0, 123.1, 121.5, 116.0, 111.5, 106.1, 71.8, 31.4, 29.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{21}NO_5S$ $[M-H]^+$: 398.1062, found 398.1059.



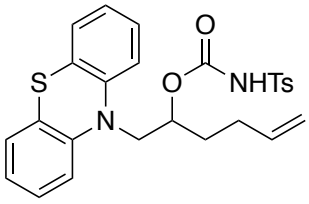
1-(4-(morpholinosulfonyl)phenyl)pent-4-en-1-ol (S15a) was synthesized from 4-(morpholinosulfonyl)benzaldehyde (1.54 g, 6.03 mmol) following a modified general procedure (3.0 equiv. 3-butenylmagnesium bromide and quenched at 0 °C) in 48% yield (0.829g, 2.66 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 5.84 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.86 – 4.77 (m, 1H), 3.74 (t, *J* = 4.8 Hz, 4H), 3.00 (t, *J* = 4.6 Hz, 4H), 2.23 – 2.11 (m, 2H), 2.05 (br d, *J* = 3.6 Hz, 1H), 1.94 – 1.76 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.3, 137.8, 134.2, 128.2, 126.6, 115.7, 73.3, 66.26, 46.1, 38.4, 30.0. **HRMS** (ESI) m/z calculated for $C_{15}H_{22}NO_4S$ $[M+H]^+$: 312.1270, found 312.1270.



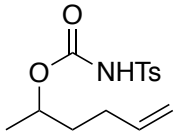
1-(4-(morpholinosulfonyl)phenyl)pent-4-en-1-yl tosylcarbamate (S15) was synthesized from 1-(4-(morpholinosulfonyl)phenyl)pent-4-en-1-ol (830 mg, 2.66 mmol) following the general procedure. The crude residue was purified via flash column chromatography (10% => 30% acetone in hexanes) to afford pure product as a white solid in 66% yield (888mg, 1.74 mmol). **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1, 5.8 Hz, 2H), 7.53 (br s, 1H), 7.35 (d, *J* = 8.3, 2H), 5.71 – 5.62 (m, 2H), 4.99 – 4.88 (m, 2H), 3.75 (t, *J* = 4.7 Hz, 4H), 3.01 (t, *J* = 4.5 Hz, 4H), 2.45 (s, 3H), 1.97 – 1.86 (m, 3H), 1.84 – 1.73 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 149.7, 145.4, 144.8, 136.5, 135.7, 135.3, 129.84, 128.4, 128.3, 127.0, 116.1, 77.7, 66.2, 46.0, 35.4, 29.3, 21.8. **HRMS** (ESI) m/z calculated for $C_{19}H_{20}NO_4SBr$ $[M+Na]^+$: 460.0194, found 460.0204.



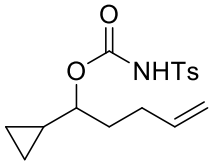
1-(10H-phenothiazin-10-yl)hex-5-en-2-ol (S16a) was synthesized from 2-(10H-phenothiazin-10-yl)acetaldehyde (386 mg, 1.59 mmol) following a modified general procedure (3.0 equiv. 3-butenylmagnesium bromide and quenched at 0 °C) in 35% yield (167 mg, 0.56 mmol) as a light yellow oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.24 – 7.13 (m, 4H), 7.02 – 6.89 (m, 4H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6, 1H), 5.09 – 4.94 (m, 2H), 4.08 – 3.97 (m, 2H), 3.86 – 3.76 (m, 1H), 2.34 – 2.24 (m, 1H), 2.23 – 2.17 (m, 1H), 1.75 – 1.60 (m, 2H). 2.00-1.20 (br s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 145.5, 138.4, 127.9, 127.5, 126.9, 123.3, 116.3, 115.1, 66.9, 54.0, 33.6, 30.0. **HRMS** (ESI) m/z calculated for $C_{18}H_{20}NOS$ $[M+H]^+$: 298.1266, found 298.1261.



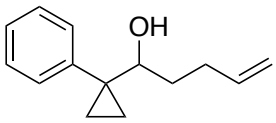
1-(10H-phenothiazin-10-yl)hex-5-en-2-yl tosylcarbamate (S16) was synthesized from 1-(10H-phenothiazin-10-yl)hex-5-en-2-ol (167 mg, 0.56 mmol) following the general procedure in 38% (105 mg, 0.21 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3, 2H), 7.33 – 7.29 (m, 3H) (NH proton underneath), 7.14 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 2H), 7.09 (dd, *J* = 7.7, 1.5 Hz, 2H), 6.92 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 2H), 6.87 (dd, *J* = 8.2, 1.2 Hz, 2H), 5.62 (ddt, *J* = 17.4, 9.7, 6.5 Hz, 1H), 5.13 (dtd, *J* = 7.9, 6.5, 3.9 Hz, 1H), 4.89-4.81 (m, 2H), 4.01 (dd, *J* = 13.7, 6.2 Hz, 1H), 3.87 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.46 (s, 3H), 1.99 – 1.92 (m, 2H), 1.83 (dddd, *J* = 14.0, 8.7, 6.7, 4.0 Hz, 1H), 1.66 (dtd, *J* = 14.4, 8.1, 6.6 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.1, 145.2, 145.1, 137.8, 135.7, 129.7, 128.4, 127.8, 127.5, 126.4, 123.1, 116.0, 115.4, 73.8, 49.7, 30.8, 29.1, 21.9. **HRMS** (ESI) m/z calculated for $C_{26}H_{27}N_2O_4S_2$ $[M+H]^+$: 495.1418, found 495.1412.



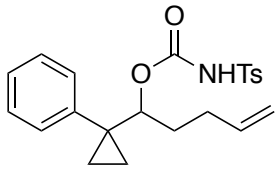
Hex-5-en-2-yl tosylcarbamate (S17) was synthesized from hex-5-en-2-ol (1.4 g, 14.0 mmol) following the general procedure in 67% yield (2.80 g, 9.40 mmol) as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.39 (br s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.70 (dddd, *J* = 18.4, 10.5, 7.2, 6.0 Hz, 1H), 4.97- 4.90 (m, 2H), 4.85 – 4.75 (m, 1H), 2.45 (s, 3H), 1.96 (tdd, *J* = 7.9, 6.5, 1.4 Hz, 2H), 1.69 – 1.60 (m, 1H), 1.53 (dtd, *J* = 13.7, 7.8, 5.5 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.1, 145.1, 137.4, 135.8, 129.7, 128.5, 115.3, 74.5, 34.9, 29.4, 21.8, 19.9. **HRMS (ESI)** *m/z* calculated for $C_{14}H_{19}NO_4S$ $[M+Na]^+$: 320.0932, found 320.0929.



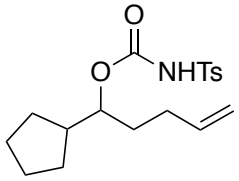
1-cyclopropylpent-4-en-1-yl tosylcarbamate (**S18**) was synthesized from 1-cyclopropylpent-4-en-1-ol (1.00 g, 7.92 mmol) following the general procedure in 76% yield (1.958 g, 6.05 mmol) as a colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.68 (ddt, *J* = 18.0, 9.1, 6.5 Hz, 1H), 4.96 – 4.86 (m, 2H), 4.12 (ddd, *J* = 8.8, 7.0, 5.6 Hz, 1H), 2.44 (s, 3H), 2.01 – 1.87 (m, 2H), 1.76 – 1.64 (m, 2H), 0.94 - 0.84 (m, 1H), 0.56 – 0.49 (m, 1H), 0.42 – 0.29 (m, 2H), 0.22-0.16 (m, 1H). (NH proton not observed) **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.7, 144.9, 137.5, 135.91, 129.6, 128.4, 115.1, 82.3, 33.7, 29.4, 21.7, 15.0, 3.3, 3.2. **HRMS** (ESI) *m/z* calculated for $C_{16}H_{21}NO_4S$ $[M+Na]^+$: 346.1100, found 346.1089



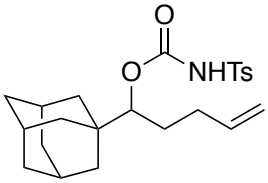
1-(1-phenylcyclopropyl)pent-4-en-1-ol (S19a) was synthesized from 1-phenylcyclopropane-1-carbaldehyde (598 mg, 4.09 mmol) following a modified general procedure (3.0 equiv. 3-butenylmagnesium bromide and quenched at 0 °C) in 55% (462 mg, 2.28 mmol) yield as a colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.22 (m, 1H), 5.78 (ddt, *J* = 17.0, 10.2, 6.7, 1H), 5.05 – 4.90 (m, 2H), 3.11 (ddd, *J* = 9.2, 5.2, 3.4 Hz, 1H), 2.25 – 2.04 (m, 2H), 1.69 – 1.54 (m, 1H), 1.47 (d, J = 5.4 Hz, 1H), 1.39 – 1.26 (m, 1H), 0.91 – 0.83 (m, 2H), 0.83 – 0.70 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 141.4, 138.6, 131.2, 128.2, 126.9, 114.9, 78.4, 34.4, 31.6, 30.6, 11.4, 10.3. **HRMS** (ESI) m/z calculated for $C_{14}H_{18}O$ $[M+Na]^+$: 225.1264, found 225.1255.



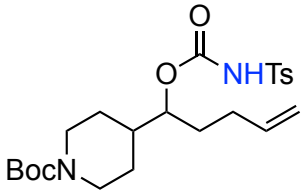
1-(1-phenylcyclopropyl)pent-4-en-1-yl tosylcarbamate (S19) was synthesized from 1-(1-phenylcyclopropyl)pent-4-en-1-ol (462 mg, 2.28 mmol) following the general procedure in 55% yield as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.3 2H), 7.32 (s, 1H), 7.31 – 7.27 (m, 7H), 5.54 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 4.85 – 4.75 (m, 2H), 4.34 (ddd, *J* = 9.6, 4.0, 1.5 Hz, 1H), 2.42 (s, 3H), 1.80 (m, 1H), 1.75-1.65 (m, 1H), 1.61 – 1.53 (m, 1H), 1.39-1.30 (m, 1H), 1.00 – 0.94 (m, 1H), 0.94 – 0.88 (m, 1H), 0.78-0.72 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.5, 145.1, 140.4, 137.3, 135.7, 131.4, 129.7, 128.5, 128.1, 127.3, 115.3, 83.9, 32.1, 29.9, 29.4, 21.80, 12.0, 11.2. **HRMS** (ESI) m/z calculated for $C_{22}H_{25}NO_4S$ $[M+Na]^+$: 422.1386, found 422.1390.



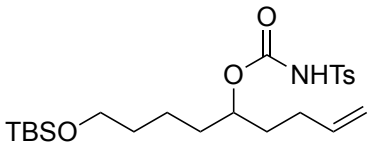
1-cyclopentylpent-4-en-1-yl tosylcarbamate (S20) was synthesized from 1-cyclopentylpent-4-en 1-ol (300 mg, 1.94 mmol) following the general procedure in 80% yield (548 mg, 1.55 mmol) as a light yellow oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.93 – 7.86 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H) (NH proton underneath), 5.65 (ddt, *J* = 17.0, 10.4, 6.6 Hz, 1H), 4.92 – 4.85 (m, 2H), 4.75 – 4.67 (m, 1H), 2.44 (s, 3H), 1.94 (m, 1H), 1.89 – 1.80 (m, 2H), 1.65 – 1.37 (m, 8H), 1.20 – 1.04 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.5, 145.1, 137.6, 135.9, 129.7, 128.5, 115.1, 81.2, 43.9, 32.6, 29.5, 28.9, 28.4, 25.5, 25.3, 21.8. **HRMS** (ESI) *m/z* calculated for $C_{18}H_{25}NO_4S$ $[M+Na]^+$: 374.1418, found 374.1402



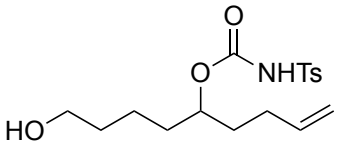
1-((3R,5R,7R)-adamantan-1-yl)pent-4-en-1-yl tosylcarbamate (S21) was synthesized from 1-((3r,5r,7r)-adamantan-1-yl)pent-4-en-1-ol (426 mg, 1.93 mmol) following the general procedure in 42% yield (343 mg, 0.82 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.90(d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.59 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 4.89 – 4.78 (m, 2H), 4.44 (dd, *J* = 11.0, 2.0 Hz, 1H), 2.43 (br s, 3H), 1.95 – 1.90 (m, 3H), 1.70 – 1.63 (m, 5H), 1.59 – 1.51 (m, 4H), 1.44 – 1.38 (m, 7H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.7, 145.1, 137.7, 136.0, 129.7, 128.4, 115.1, 85.2, 37.9, 37.0, 36.6, 30.2, 28.2, 27.3, 21.8. **HRMS** (ESI) m/z calculated for $C_{23}H_{31}NO_4S$[M+Na]+: 440.1896, found 440.1876.



tert-Butyl 4-(1-((tosylcarbamoyl)oxy)pent-4-en-1-yl)piperidine-1-carboxylate (S22) was synthesized from tert-butyl 4-(1-hydroxypent-4-en-1-yl)piperidine-1-carboxylate (2.69 g, 10 mmol) following the general procedure in 79% yield (3.69 g, 7.9 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.62 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 4.95 – 4.82 (m, 2H), 4.65 (dt, *J* = 8.0, 5.5 Hz, 1H), 4.07 (m, 2H), 2.58-2.54 (m, 2H), 2.44 (s, 3H), 1.83 (td, *J* = 8.2, 4.0 Hz, 2H), 1.62 – 1.50 (m, 2H), 1.44 (s, 9H), 1.48-1.38 (m, 2H), 1.15-1.05 (m, 2H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.8, 150.5, 145.1, 137.3, 136.2, 129.7, 128.4, 115.4, 80.3, 79.7, 43.8, 40.0, 30.3, 29.4, 28.6, 27.9, 21.7. **HRMS** (ESI) *m/z* calculated for $C_{23}H_{35}N_2O_6S$ $[M+H]^+$: 467.2216, found 467.2213.

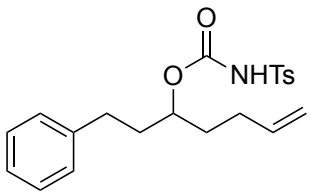


9-((tert-butyldimethylsilyl)oxy)non-1-en-5-yl tosylcarbamate (**S23**). was synthesized from 9-((tert-butyldimethylsilyl)oxy)non-1-en-5-ol (2.73g, 10 mmol) following the general procedure in 83% yield (3.91 g, 8.32 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.61 (br. s, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.73 – 5.61 (m, 1H), 4.94 – 4.87 (m, 2H), 4.76 (p, *J* = 6.3 Hz, 1H), 3.53 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 3H), 1.95 – 1.84 (m, 2H), 1.61 – 1.53 (m, 2H), 1.54 – 1.45 (m, 2H), 1.46 – 1.38 (m, 2H), 1.24 – 1.16 (m, 2H), 0.88 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.4, 145.1, 137.5, 135.8, 129.7, 128.4, 115.2, 77.8, 62.9, 33.7, 33.0, 32.6, 29.3, 26.1, 21.8, 21.4, 18.5, -5.2, -5.2. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{39}NO_5SSi$ $[M+H]^+$: 470.2396, found 470.2387.

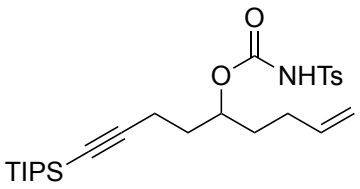


9-hydroxynon-1-en-5-yl tosylcarbamate (**S24**). To a 100 mL over-dride roud-bottom flask was added **S23** (1.41g, 3.0 mmol), THF (25 mL) and tetrabutylammonium fluoride solution TBAF (1M in THF, 9 mL, 9 mmol, 3 equiv). The reaction was stirred at room temperature overnight. The reaction mixture was concentrated and purified via flash column chromatography (0% => 30% ethyl acetate in hexanes) to afford the desired **S24** in 91% yield (968 mg, 2.72 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.72 – 5.60 (m, 1H), 4.93 – 4.89 (m, 1H), 4.89 – 4.84 (m, 1H), 4.81 – 4.72 (m, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.92 – 1.82 (m, 2H), 1.63 – 1.39 (m, 6H), 1.31 – 1.18 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.8, 145.0, 137.4, 135.9, 129.6, 128.4, 115.2, 77.5, 62.5, 33.6, 33.0,

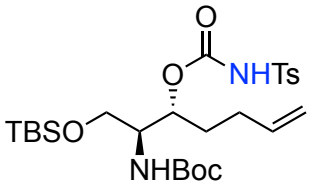
32.3, 29.4, 21.8, 21.2. **HRMS (ESI)** *m/z* calculated for $C_{17}H_{25}NO_5S$ $[M+H]^+$: 356.1532, found 356.1544.



1-phenylhept-6-en-3-yl tosylcarbamate (**S25**) was synthesized from 1-phenylhept-6-en-3-ol (1.90g, 10 mmol) following the general procedure in 82% yield (3.17 g, 8.17 mmol) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.69 (br s, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.27 (dd, *J* = 8.3 Hz, 6.8 Hz, 2H), 7.23-7.16 (m, 1H), 7.08 (d, *J* = 7.0, 2H), 5.77-5.64 (m, 1H), 4.96-4.90 (m, 2H), 4.85 (tt, *J* = 7.2, 5.2 Hz, 1H), 2.53-2.47 (m, 2H), 2.44 (s, 3H), 1.99-1.92 (m, 2H), 1.89-1.77 (m, 2H), 1.73-1.56 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.4, 145.2, 141.2, 137.3, 135.9, 129.7, 128.6, 128.5, 128.3, 126.1, 115.3, 77.4, 35.7, 33.2, 31.4, 29.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{25}NO_4S$ $[M+H]^+$: 388.1583, found 388.1582.

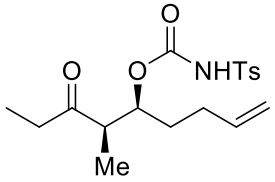


9-(triisopropylsilyl)non-1-en-8-yn-5-yl tosylcarbamate (**S26**). was synthesized from 9-(triisopropylsilyl)non-1-en-8-yn-5-ol (2.95 g, 10 mmol) following the general procedure in 62% yield (3.05 g, 6.20 mmol) as a white solid.**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.42 (br s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.67 (ddt, *J* = 18.1, 9.6, 6.5 Hz, 1H), 4.95 – 4.88 (m, 2H), 4.85 (p, *J* = 6.2 Hz, 1H), 2.44 (s, 3H), 2.17-2.07 (m, 2H), 1.96 – 1.87 (m, 2H), 1.79 – 1.71 (m, 2H), 1.67 – 1.56 (m, 2H), 1.08 – 0.96 (m, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.1, 145.2, 137.2, 135.7, 129.7, 128.4, 115.4, 107.2, 81.2, 76.9, 33.2, 32.9, 29.3, 21.8, 18.7, 16.0, 11.3. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{41}NO_4SSi$ $[M+H]^+$: 492.2604, found 492.2624.

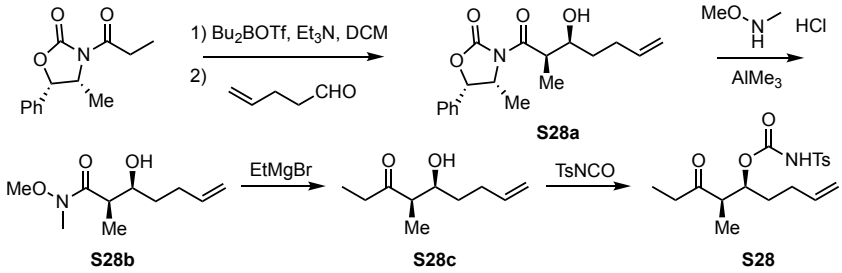


(+)-tert-butyl ((2S, 3R)-1-((tert-butyldimethylsilyl)oxy)-3-((tosylcarbamoyl)oxy)hept-6-en-2-yl)carbamate (S27) was synthesized following the procedure developed for chiral diamino alcohols (**Page S56**) as a white solid. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.77 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.62 (ddt, *J* = 17.8, 9.2, 6.5 Hz, 1H), 4.88 (br s, 1H), 4.87 – 4.80 (m, 2H), 4.78 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 1H), 3.58 – 3.48 (m, 2H), 2.43 (s, 3H), 1.94 – 1.77 (m, 2H), 1.72 (dddd, *J* = 13.9, 9.9, 5.9, 3.5 Hz, 1H), 1.58-1.52 (m, 1H), 1.43 (s, 9H), 0.84

(s, 9H), -0.02 (s, 3H), -0.05 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.6, 149.9, 145.1, 137.5, 135.9, 129.7, 128.5, 115.1, 79.9, 76.1, 61.7, 53.3, 30.2, 29.1, 28.5, 25.9, 21.8, 18.3, -5.5, -5.6. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{45}N_2O_7SSi$ $[M+H]^+$: 557.2717, found 557.2715. **Optical rotation**: $[\alpha]^{23}_D = 6.5$ (c = 1.05, $CHCl_3$).



Scheme S1: Synthesis of chiral *N*-tosyl carbamate S28



(4R,5S)-3-((2R,3S)-3-hydroxy-2-methylhept-6-enoyl)-4-methyl-5-phenyloxazolidin-2-one (S28a) was synthesized following Scheuer's procedure[3] using pent-4-enal in 77% yield (4.88g, 15.4 mmol).

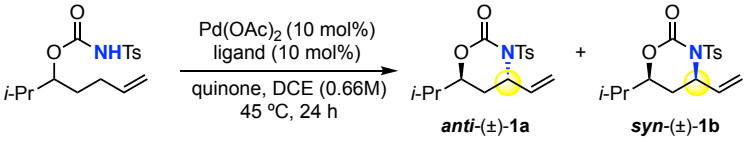
(2R,3S)-3-hydroxy-*N*-methoxy-*N*,2-dimethylhept-6-enamide (S28b). To an 100 mL oven-dried round bottom flask equipped with a stir bar was added N,O-Dimethylhydroxylamine hydrochloride (2.34g, 24 mmol) and THF. The reaction was cooled to 0 °C and $AlMe_3$ (2.0M in toluene, 12 mL, 24 mmol) was added dropwise. The reaction was allow to warm up to room temperature for 1 hour and cooled back to 0 °C. **S28a** in 5 mL THF was added dropwise, then the reaction was warmed to room temperature and stirred for 2 hours. After completion, the reaction was cooled to 0 °C and 20 mL 1M HCl was added dropwise followed by 20 mL Et_2O. The mixture was stirred for 1 hour at room temperature and transferred into a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (30 mL x 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via silica plug (30% ethyl acetate in hexanes) to afford the desired **S28b** in quantitative yield.

(4R,5S)-5-hydroxy-4-methylnon-8-en-3-one (S28c). To an 100 mL oven-dried round bottom flask was added **S28b** (8 mmol) and 20 mL THF. The reaction was cooled to 0 °C and ethylmagnesium bromide (1.0 M in THF, 16 mL, 16 mmol) was added dropwise. The reaction was allowed to warm up to room temperature and stirred for 30 min. The reaction was cooled back to 0 °C and quenched with sat. aq. NH_4Cl. The mixture transferred into a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (30 mL x 2). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the desired **S28c** in 80% yield (1.08g, 6.36 mmol) as a colorless oil.

(−)-(5S, 6R)-6-methyl-7-oxonon-1-en-5-yl tosylcarbamate (**S28**) was synthesized from (4R,5S)-5-hydroxy-4-methylnon-8-en-3-one (**S28c**) (341 mg, 2.00 mmol) following the general procedure in 99% yield (813 mg, 2.21 mmol) as a colorless gel.**^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.51 (s, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.62 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 (ddd, *J* = 8.9, 5.7, 4.2 Hz, 1H), 4.93 – 4.84 (m, 2H), 2.73 (qd, *J* = 7.0, 5.6 Hz, 1H), 2.44 (s, 3H), 2.48 – 2.32 (m, 2H), 1.92 – 1.77 (m, 2H), 1.62 – 1.47 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 211.6, 150.1, 145.2, 137.0, 135.7, 129.8, 128.4, 115.6, 77.6, 49.2, 35.5, 31.1, 29.7, 21.8, 11.9, 7.7. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{25}NO_5S$ $[M-H]^+$: 366.1375, found 366.1375. **Optical rotation**: $[\alpha]^{23}_D$ = -13.8 (c = 1.05, $CHCl_3$).

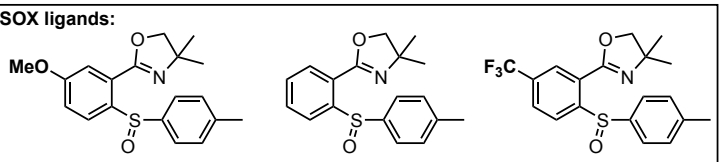
Reaction Optimization

Table S1. Reaction development.



Entry	Ligand	Quinone	Yield % (anti:syn)[a]	Yield % (isolated)[b]
1[c]	Bis-SO	Ph-BQ (2.0 eq.)	40 (1:4.7)	29 (syn)
2	(±)-MeO-SOX	Ph-BQ (2.0 eq.)	<5%	-
3	(±)-MeO-SOX	2,5 DMBQ (2.0 eq.)	88 (7.3:1)	72 (anti)
4	(±)-MeO-SOX[e,j]	2,5 DMBQ (1.2 eq.)	91 (7.8:1; 8.0:1[d])	78 (anti)
5	(±)-MeO-SOX	2,5 DMBQ + BQ[f]	12 (1:7.1[d])	8 (syn)
6	(±)-SOX	2,5 DMBQ (2.0 eq.)	86 (3.6:1)	61 (anti)
7	(±)-CF_3-SOX	2,5 DMBQ (2.0 eq.)	69 (1:4.3)	51 (syn)
8	(±)-CF_3-SOX	BQ (2.0 eq.)	76 (1:6.8)	60 (syn)
9	(±)-CF_3-SOX	BQ (1.6 eq.)	87 (1:6.7; 1:7.0[d])	71 (syn)
10	(±)-CF_3-SOX	BQ (1.2 eq.)	72 (1:6.7)	57 (syn)
11[g]	(±)-MeO-SOX	2,5 DMBQ (1.2 eq.)	88 (6.4:1)[h,j]	72 (anti)
12[g]	(±)-CF_3-SOX	BQ (1.6 eq.)	92 (1:4.0)[i,j]	69 (syn)
13[c]	Bis-SO	2,5 DMBQ (1.2 eq.)	60 (1:5.5)	46 (syn)
14[c]	Bis-SO	BQ (1.6 eq.)	53 (1:4.6)	38 (syn)

SOX ligands:



(±)-**MeO-SOX** (±)-**SOX** (±)-**CF_3-SOX**

[a] Yield and dr determined by crude ^{1}H NMR. [b] Isolated yield of pure diastereomer with >20:1 dr. [c] Commercial $Pd(OAc)_2$ bis-sulfoxide catalyst used with additional 5% bis-sulfoxide ligand. [d] Determined by HPLC. [e] Using enantiomeric pure MeO-SOX ligand, no substantial kinetic resolution observed. [f] 1.2 equiv 2.5 DMBQ and 0.1 equiv BQ was used. [g] 10% $Ph_2P(O)OH$ was added; 6h. [h] No acid: 58% (2.0:1); isolated: 35% (*anti*). [i] No acid: 80% (1:6.8); isolated: 67% (*syn*). [j] See Supporting Information.

Entry 1.

Reaction proceeded according to reported procedure[2] using $Pd(OAc)_2$/bis-sulfoxide catalyst (10 mg, 0.02 mmol, 0.1 equiv), 2-methylhept-6-en-3-yl tosylcarbamate (**S1**) (65.1 mg, 0.2 mmol, 1.0 equiv), phenyl benzoquinone (PhBQ) (73.7mg, 0.4 mmol, 2.0 equiv) and dichloroethane (0.3 mL, 0.67 M). After 24 hours, the reaction concentrated under reduced pressure, the remaining mixture was diluted with 2 mL $CDCl_3$ and crude ^{1}H NMR was taken with internal standard (Nitrobenzene, 12.3 mg, 0.1 mmol, 0.5 equiv). 40% crude NMR yield (4.7:1 *syn*:*anti*). The mixture was concentrated under reduced pressure and subjected to flash column chromatography (0% => 20% ethyl acetate in hexanes) to provide **1b** as a white solid.

Run 1: Crude: 39% yield, 4.7:1 dr (*syn:anti*). Isolated **1b** (>20:1 dr): 19.1mg, 0.059 mmol, 29.5% yield;
Run 2: Crude: 40% yield, 4.6:1 dr (*syn:anti*). Isolated **1b** (>20:1 dr): 18.8 mg, 0.058 mmol 29.1% yield;
Average: Crude 40% yield, 4.7:1 dr (*syn:anti*). Isolated **1b: 29% yield (>20:1 dr).**

Entry 2.

To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (6.9 mg, 0.02 mmol, 0.1 equiv), phenyl benzoquinone benzoquinone (PhBQ) (73.7 mg, 0.4 mmol, 2.0 equiv), 2-methylhept-6-en-3-yl tosylcarbamate (**S1**) (65.1 mg, 0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 24 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL $CDCl_3$ and analyzed by crude ^1H NMR with internal standard (nitrobenzene, 12.3 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and dissolved in 30 mL diethyl ether and washed sequentially with 1M aq. NaOH (10 mL) and sat. aq. $NaHSO_3$ (10 mL) (repeat this sequence for 3 times). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (0% => 20% ethyl acetate in hexanes). Trace amount of product was observed by crude ^1H NMR. No product was isolated by flash column chromatography.

Entry 3.

To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 dimethylbenzoquinone (2,5 DMBQ) (54.5 mg, 0.4 mmol, 2.0 equiv), 2-methylhept-6-en-3-yl tosylcarbamate (**S1**) (65.1 mg, 0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 24 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL $CDCl_3$ and analyzed by crude ^1H NMR with internal standard (nitrobenzene, 12.3 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and dissolved in 30 mL diethyl ether and washed sequentially with 1M aq. NaOH (10 mL) and sat. aq. $NaHSO_3$ (10 mL) (repeat this sequence for 3 times). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (0% => 20% ethyl acetate in hexanes) to provide **1a** as a white solid.

Run 1: Crude: 87% yield, 7.1:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 46.3 mg, 0.143 mmol, 71.6 % yield;
Run 2: Crude: 89% yield, 7.4:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 46.8 mg, 0.145 mmol 72.4 % yield;
Average: Crude 88% yield, 7.3:1 dr (*anti:syn*). Isolated **1a: 72% yield (>20:1 dr).**

Entry 4.

Following the same procedure of Entry 3 using 1.2 equiv of 2,5 dimethylbenzoquinone (2,5 DMBQ) (32.7 mg, 0.24 mmol, 1.2 equiv).
Run 1: Crude: 89% yield, 7.9:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 49.9 mg, 0.154 mmol, 77.1 % yield;
Run 2: Crude: 92% yield, 7.7:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 51.3 mg, 0.159 mmol 79.3 % yield;
Average: Crude 91% yield, 7.8:1 dr (*anti:syn*). Isolated **1a: 78% yield (>20:1 dr).**

HPLC dr was determined by following procedure:
Aliquots (10 μL) were taken at the 24h from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Zorbax C-N, 3% isopropanol/hexanes, 1 mL/min, 35 °C, 214 nm). The yields were determined by integration of the **1a** (24.4) and **1b** (20.2 min) relative to the 4-nitroacetophenone internal standard peak (8.3 min) and corrected by a standard curve. 8.0:1 dr (*anti:syn*).

Entry 5.

Following the same procedure of Entry 3 adding 1,4 benzoquinone (BQ) (0.1 equiv).
Run 1: Crude: 11% yield, 1:7.1 dr (*anti:syn*) by HPLC. Isolated **1b** (>20:1 dr): 4.4 mg, 0.014 mmol, 7.0% yield;
Run 2: Crude: 12% yield, 1:7.0 dr (*anti:syn*) by HPLC. Isolated **1b** (>20:1 dr): 5.0 mg, 0.016 mmol, 8.0% yield;
Average: Crude 12% yield, 1:7.1 dr (*anti:syn*). Isolated **1a: 8% yield (>20:1 dr).**

Entry 6.

Following the same procedure of Entry 3 using (±)-SOX ligand (6.3 mg, 0.02 mmol, 0.1 equiv).
Run 1: Crude: 87% yield, 3.4:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 40.0 mg, 0.124 mmol, 61.8 % yield;
Run 2: Crude: 84% yield, 3.7:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 38.4 mg, 0.119 mmol 59.4 % yield;
Average: Crude 86% yield, 3.6:1 dr (*anti:syn*). Isolated **1a: 61% yield (>20:1 dr).**

Entry 7.

Following the same procedure of Entry 3 using (±)-CF_3-SOX ligand (7.6 mg, 0.02 mmol, 0.1 equiv).
Run 1: Crude: 69% yield, 1:4.3 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 33.0 mg, 0.102 mmol, 51.0 % yield;
Run 2: Crude: 69% yield, 1:4.2 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 33.3 mg, 0.103 mmol 51.5 % yield;
Average: Crude 69% yield, 1:4.3 dr (*anti:syn*). Isolated **1b: 51% yield (>20:1 dr).**

Entry 8.

Following the same procedure of Entry 3 using (±)-CF_3-SOX ligand (7.6 mg, 0.02 mmol, 0.1 equiv) and 1,4 benzoquinone (BQ) (43.2 mg, 0.4 mmol, 2.0 equiv).
Run 1: Crude: 77% yield, 1:6.8 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 39.8 mg, 0.123 mmol, 61.6 % yield;
Run 2: Crude: 75% yield, 1:6.8 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 38.2 mg, 0.118 mmol 59.1 % yield;
Average: Crude 76% yield, 1:6.8 dr (*anti:syn*). Isolated **1b: 60% yield (>20:1 dr).**

Entry 9.

Following the same procedure of Entry 3 using (±)-CF_3-SOX ligand (7.6 mg, 0.02 mmol, 0.1 equiv) and 1,4 benzoquinone (BQ) (34.6 mg, 0.32 mmol, 1.6 equiv).
Run 1: Crude: 85% yield, 1:6.8 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 45.2 mg, 0.140 mmol, 69.9 % yield;
Run 2: Crude: 89% yield, 1:6.6 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 46.3 mg, 0.143 mmol 71.6 % yield;
Average: Crude 87% yield, 1:6.7 dr (*anti:syn*). Isolated **1b: 71% yield (>20:1 dr).**

HPLC dr was determined following procedure of entry 4: 1:7.0 (anti:syn).

Entry 10.

Following the same procedure of Entry 3 using (±)-CF_3-SOX ligand (7.6 mg, 0.02 mmol, 0.1 equiv) and 1,4 benzoquinone (BQ) (34.6 mg, 0.24 mmol, 1.2 equiv).
Run 1: Crude: 73% yield, 1:6.6 dr (*anti:syn*) Isolated **1b** (>20:1 dr): 37.4 mg, 0.116 mmol, 57.8 % yield;
Run 2: Crude: 71% yield, 1:6.7 dr (*anti:syn*) Isolated **1b** (>20:1 dr): 36.7 mg, 0.113 mmol 56.7 % yield;
Average: Crude 72% yield, 1:6.7 dr (*anti:syn*). 1:7.0 dr by HPLC. Isolated **1b: 57% yield (>20:1 dr).**

Entry 11.

Following the same procedure of Entry 4 with addition of Diphenyl phosphinic acid ($Ph_2P(O)OH$, 4.4 mg, 0.02 mmol, 0.1 equiv) for 6 hours.
Run 1: Crude: 89% yield, 6.5:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 47.4 mg, 0.147 mmol, 73.3 % yield;
Run 2: Crude: 87% yield, 6.3:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 45.4 mg, 0.140 mmol 70.2 % yield;
Average: Crude 88% yield, 6.4:1 dr (*anti:syn*). Isolated **1a: 72% yield (>20:1 dr).**

Controlled reaction with no $Ph_2P(O)OH$ (6 hours):

Run 1: Crude: 58% yield, 2.0:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 22.1 mg, 0.068 mmol, 34.2 % yield;
Run 2: Crude: 57% yield, 2.0:1 dr (*anti:syn*). Isolated **1a** (>20:1 dr): 23.0mg, 0.071 mmol 35.6 % yield;
Average: Crude 58% yield, 2.0:1 dr (*anti:syn*). Isolated **1a: 35% yield (>20:1 dr).**

Entry 12.

Following the same procedure of Entry 8 with addition of Diphenyl phosphinic acid ($Ph_2P(O)OH$, 4.4 mg, 0.02 mmol, 0.1 equiv) for 6 hours.
Run 1: Crude: 92% yield, 1:4.0 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 45.6 mg, 0.141 mmol, 70.5 % yield;

Run 2: Crude: 93% yield, 1:3.9 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 44.0 mg, 0.136 mmol 68.0 % yield;
Average: Crude 92% yield, 1:4.0 dr (*anti:syn*). Isolated **1b: 69% yield (>20:1 dr).**

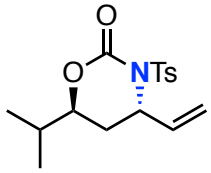
Controlled reaction with no $Ph_2P(O)OH$ (6 hours):

Run 1: Crude: 81% yield, 1:6.7 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 43.4 mg, 0.134 mmol, 67.1 % yield;
Run 2: Crude: 79% yield, 1:6.8 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 42.8 mg, 0.132 mmol 66.2 % yield;
Average: Crude 80% yield, 1:6.8 dr (*anti:syn*). Isolated **1b: 67% yield (>20:1 dr).**

Entry 13.

Following the same procedure of Entry 3 using $Pd(OAc)_2$/bis-sulfoxide catalyst (10 mg, 0.02 mmol, 0.1 equiv).
Run 1: Crude: 61% yield, 1:5.4 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 29.3 mg, 0.091 mmol, 45.3 % yield;
Run 2: Crude: 59% yield, 1:5.6 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 29.7 mg, 0.092 mmol 45.9 % yield;
Average: Crude 60% yield, 1:5.5 dr (*anti:syn*). Isolated **1b: 46% yield (>20:1 dr).**

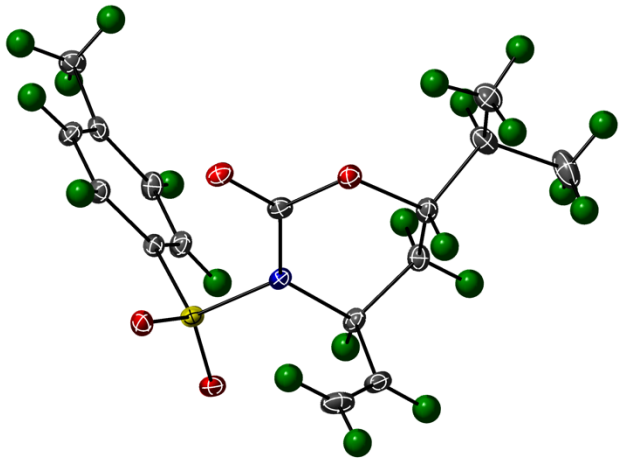
Entry 14.
Following the same procedure of Entry 3 using $Pd(OAc)_2$/bis-sulfoxide catalyst (10 mg, 0.02 mmol, 0.1 equiv) and 1,4 benzoquinone (BQ) (34.6 mg, 0.32 mmol, 1.6 equiv).
Run 1: Crude: 55% yield, 1:4.3 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 24.7 mg, 0.076 mmol, 38.2 % yield;
Run 2: Crude: 51% yield, 1:4.9 dr (*anti:syn*). Isolated **1b** (>20:1 dr): 24.0 mg, 0.074 mmol 37.1 % yield;
Average: Crude 53% yield, 1:4.6 dr (*anti:syn*). Isolated **1b: 38% yield (>20:1 dr).**



(±)-(4S,6S)-6-isopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**1a**).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 5.0 Hz, 1H), 5.40 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.34 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.21 (dt, *J* = 3.9, 2.5 Hz, 1H), 4.11 (ddd, *J* = 11.8, 6.2, 3.2 Hz, 1H), 2.41 (s, 3H), 2.12-1.86 (m, 2H), 1.81 (dq, *J* = 13.4, 6.7 Hz, 1H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.6, 144.9, 135.6, 129.4, 129.2, 118.6, 80.3, 56.0, 32.1, 29.9, 21.7, 17.7, 17.5. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{21}NO_4S$ $[M+H]^+$: 324.1270, found 324.1273. Spectra match literature reports.[2,4]

Single Crystal structure X-ray analysis of (±)-1a:

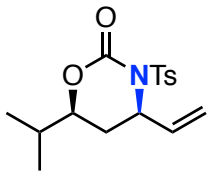


Details of the crystal data and a summary of the intensity data for **(±)-1a** are listed in Table S2. CCDC: 1899082

Table S2. Crystal data and structure refinement for **(±)-1a**.

Identification code	dd25esa_sq	
Empirical formula	C16 H21 N O4 S	
Formula weight	323.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.9677(3) Å	a= 106.578(2)°.
	b = 11.8753(6) Å	b= 100.198(2)°.
	c = 15.0703(7) Å	g = 104.470(2)°.
Volume	955.00(8) $Å^3$	
Z	2	
Density (calculated)	1.125 Mg/m^3	
Absorption coefficient	0.184 mm^{-1}	

F(000)	344
Crystal size	0.247 x 0.152 x 0.072 mm^3
Theta range for data collection	2.760 to 27.191°.
Index ranges	-7<=h<=7, -15<=k<=15, -19<=l<=19
Reflections collected	30439
Independent reflections	4237 [R(int) = 0.0437]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Integration
Max. and min. transmission	1.0000 and 0.9417
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4237 / 0 / 202
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0963
R indices (all data)	R1 = 0.0469, wR2 = 0.1008
Extinction coefficient	n/a
Largest diff. peak and hole	0.235 and -0.457 e.$Å^{-3}$

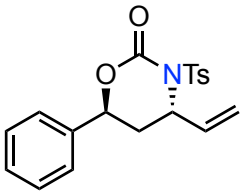


(±)-(4R, 6S)-6-isopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**1b**).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.55 (ddd, *J* = 16.9, 10.0, 8.1 Hz, 1H), 5.37 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.89 (dt, *J* = 9.9, 8.1 Hz, 1H), 4.00 (ddd, *J* = 11.4, 6.0, 2.0 Hz, 1H), 2.42 (s, 3H), 2.29 (ddd, *J* = 14.2, 8.0, 2.1 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.67 (ddd, *J* = 14.1, 11.3, 9.9 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.6, 144.8, 137.1, 136.2, 129.7, 129.2, 118.6, 81.0, 59.0, 33.2, 31.4, 21.7, 11.7 **HRMS (ESI)** *m/z* calculated for $C_{16}H_{21}NO_4S$ $[M+H]^+$: 324.1270, found 324.1280. Spectra match literature reports.[2,4]

Reaction Scope (*Anti*)

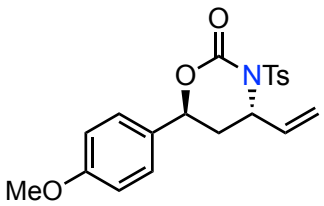
General procedure for *anti*-1,3 oxazinanone:
To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 dimethylbenzoquinone (2,5 DMBQ) (32.7 mg, 0.24 mmol, 1.2 equiv), *N*-tosyl carbamate (0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 24 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL $CDCl_3$ and analyzed by crude ^1H NMR with internal standard (nitrobenzene, 12.3 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and dissolved in 30 mL diethyl ether and washed sequentially with 1M aq. NaOH (10 mL) and sat. aq. $NaHSO_3$ (10 mL) (repeat this wash sequence for 3 times). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (ethyl acetate in hexanes) to provide *anti*-1,3-oxazinanone product.



(±)-(4S,6S)-6-phenyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**2**). Racemic carbamate **S2** (71.8 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude*: 89%, 9.1:1 dr; *isolated*: 59.7 mg, 0.167 mmol, 83.5%, >20:1 dr);
Run 2 (*crude:* 92%, 8.9:1 dr; *isolated:* 56.0 mg, 0.157 mmol, 78.3%, >20:1 dr);
Run 3 (*crude:* 91%, 8.8:1 dr; *isolated*: 57.5 mg, 0.161 mmol, 80.4%, >20:1 dr).
Average: *crude*: **91% yield, 8.9:1 dr** (*anti:syn*). *isolated*: **81%, >20:1 dr** (*anti:syn*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.42-7.27 (m, 7H), 6.02 (ddd, J = 17.1, 10.5, 4.8 Hz, 1H), 5.51 (dd, J = 10.6, 1.5 Hz, 1H), 5.46 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.39 (t, *J* = 7.6 Hz, 1H), 5.31 – 5.26 (m, 1H), 2.44 (s, 3H), 2.30-2.21 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 145.3, 137.7, 135.5, 135.5, 129.6, 129.4, 129.0, 128.9, 125.9, 119.1, 77.0, 56.4, 35.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{19}NO_4S$ $[M+H]^+$: 358.1113, found 358.1101. Spectra match literature report.[4]

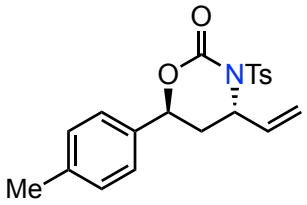


(±)-(4S,6S)-6-(4-methoxyphenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**3**). Racemic carbamate **S3** (83.4 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash

chromatography (10 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a colorless oil.

Run 1 (*crude:* 80%, 5.9:1 dr; *isolated:* 55.3 mg, 0.143 mmol, 71.4%, >20:1 dr);
Run 2 (*crude:* 80%, 5.5:1 dr; *isolated:* 54.0 mg, 0.139 mmol, 69.7%, >20:1 dr);
Run 3 (*crude:* 80%, 5.6:1 dr; *isolated:* 53.6 mg, 0.138 mmol, 69.2%, >20:1 dr).
Average: *crude*: **80% yield, 5.7:1 dr** (*anti:syn*). *isolated*: **70%, >20:1 dr** (*anti:syn*).

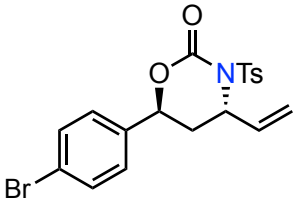
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.00 (ddd, *J* = 17.1, 10.5, 4.8 Hz, 1H), 5.49 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.45 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.33 (dd, *J* = 11.7, 3.4 Hz, 1H), 5.30 – 5.25 (m, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.32 – 2.17 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.1, 148.5, 145.2, 135.6, 129.7, 129.6, 129.4, 127.5, 119.0, 114.2, 76.9, 56.4, 55.4, 35.0, 21.8 (one signal missing due to overlapping). **HRMS (ESI)** *m/z* calculated for $C_{20}H_{21}NO_5S$ $[M+H]^+$: 388.1219, found 388.1211. Spectra match literature report.[4]



(±)-(4S,6S)-6-(p-tolyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**4**). Racemic carbamate **S4** (74.7 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 93%, 9.1:1 dr; *isolated:* 51.0 mg, 0.137 mmol, 68.6%, >20:1 dr);
Run 2 (*crude:* 90%, 9.0:1 dr; *isolated:* 50.5 mg, 0.136 mmol, 68.0%, >20:1 dr);
Run 3 (*crude:* 92%, 8.7:1 dr; *isolated:* 53.2 mg, 0.143 mmol, 71.6%, >20:1 dr).
Average: *crude*: **92% yield, 8.9:1 dr** (*anti:syn*). *isolated*: **69%, >20:1 dr** (*anti:syn*).

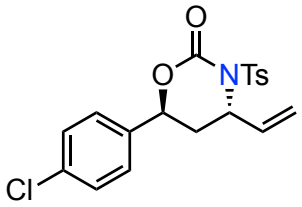
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.6, 2H), 7.19 – 7.14 (m, 4H), 6.01 (ddd, *J* = 17.1, 10.5, 4.9 Hz, 1H), 5.51 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.46 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.35 (dd, *J* = 10.8, 4.3 Hz, 1H), 5.28 (tdt, *J* = 4.8, 3.2, 1.6 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 2.29 – 2.19 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 145.2, 139.0, 135.7, 135.6, 134.8, 129.6, 129.5, 129.4, 125.9, 119.1, 77.0, 56.4, 35.3, 21.9, 21.3. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{21}NO_4S$ $[M+Na]^+$: 394.1089, found 394.1079. Spectra match literature report.[4]



(±)-(4S,6S)-6-(4-bromophenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**5**). Racemic carbamate **S5** (87.7 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 82%, 9.5:1 dr; *isolated:* 62.5 mg, 0.143 mmol, 71.6%, >20:1 dr);
Run 2 (*crude:* 79%, 9.6:1 dr; *isolated:* 65.4 mg, 0.150 mmol, 74.9%, >20:1 dr);
Run 3 (*crude:* 81%, 10.3:1 dr; *isolated:* 59.9 mg, 0.137 mmol, 68.6%, >20:1 dr).
Average: *crude*: **81% yield, 9.8:1 dr** (*anti:syn*). *isolated*: **72%, >20:1 dr** (*anti:syn*).

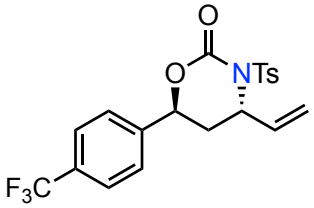
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.01 (ddd, *J* = 17.0, 10.5, 4.8 Hz, 1H), 5.52 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.46 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.35 (dd, *J* = 11.0, 4.1 Hz, 1H), 5.29 (m, 1H), 2.45 (s, 3H), 2.27-2.14 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.2, 145.4, 136.8, 135.4, 135.4, 132.1, 129.7, 129.4, 127.6, 120.0, 119.3, 76.3, 56.3, 35.3, 21.9. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{18}BrNO_4S$ $[M+H]^+$: 436.0218, found 436.0210. Spectra match literature report.[4]



(±)-(4S,6S)-6-(4-chlorophenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**6**). Racemic carbamate **S6** (78.8 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 81%, 10.2:1 dr; *isolated:* 53.9 mg, 0.138 mmol, 68.7%, >20:1 dr);
Run 2 (*crude:* 81%, 9.8:1 dr; *isolated:* 54.5 mg, 0.139 mmol, 69.5%, >20:1 dr);
Run 3 (*crude:* 78%, 9.7:1 dr; *isolated:* 53.3 mg, 0.136 mmol, 68.0%, >20:1 dr).
Average: *crude*: **80% yield, 9.9:1 dr** (*anti:syn*). *isolated*: **69%, >20:1 dr** (*anti:syn*).

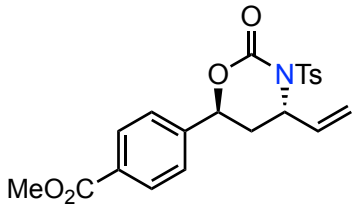
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.01 (ddd, *J* = 17.1, 10.6, 4.7 Hz, 1H), 5.52 (d, *J* = 10.6 Hz, 1H), 5.46 (d, *J* = 17.2 Hz, 1H), 5.36 (dd, *J* = 10.8, 4.3 Hz, 1H), 5.31 – 5.26 (m, 1H), 2.44 (s, 3H), 2.27 – 2.15 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.3, 145.4, 136.2, 135.3, 134.9, 129.6, 129.4, 129.1, 127.3, 119.3, 76.2, 56.3, 35.2, 21.9. (one peak missing due to overlap). **HRMS (ESI)** *m/z* calculated for $C_{19}H_{18}ClNO_4S$ $[M+Na]^+$: 414.0543, found 414.0530.



(±)-(4S,6S)-3-tosyl-6-(4-(trifluoromethyl)phenyl)-4-vinyl-1,3-oxazinan-2-one (**7**). Racemic carbamate **S7** (85.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 57%, >20:1 dr; *isolated:* 46.7 mg, 0.110 mmol, 54.8%, >20:1 dr);
Run 2 (*crude:* 56%, >20:1 dr; *isolated:* 43.7 mg, 0.103 mmol, 51.4%, >20:1 dr);
Run 3 (*crude:* 60%, >20:1 dr; *isolated:* 46.4 mg, 0.109 mmol, 54.5%, >20:1 dr).
Average: *crude*: **58% yield, >20:1 dr** (*anti:syn*). *isolated*: **54%, >20:1 dr** (*anti:syn*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.03 (ddd, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.54 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.51 – 5.39 (m, 2H), 5.34 – 5.28 (m, 1H), 2.45 (s, 3H), 2.33 – 2.14 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.1, 145.5, 141.8, 135.4, 135.3, 131.2 (q, *J* = 32.7 Hz), 129.7, 129.5, 126.1, 125.9 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.4 Hz), 119.5, 76.1, 56.2, 35.4, 21.9. **^{19}F NMR** (470 MHz, Chloroform-*d*) δ -63.1. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{18}F_3NO_4S$ $[M+H]^+$: 426.0987, found 426.0995. Spectra match literature report.[4]

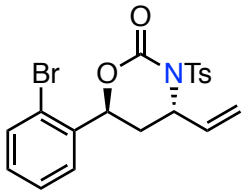


(±)-Methyl 4-((4S,6S)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)benzoate (8)

Racemic carbamate **S8** (83.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude*: 60%, >20:1 dr; *isolated*: 46.4 mg, 0.112 mmol, 55.8%, >20:1 dr),
Run 2 (*crude*: 57%, >20:1 dr; *isolated*: 45.8 mg, 0.110 mmol, 55.1%, >20:1 dr),
Run 3 (*crude*: 62%, >20:1 dr; *isolated*: 48.4 mg, 0.116 mmol, 58.2%, >20:1 dr),
Average: *crude*: **60% yield, >20:1 dr** (*anti:syn*). *isolated*: **56%, >20:1 dr** (*anti:syn*).

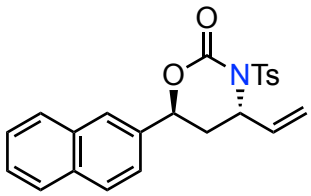
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.02 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 5.53 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.49 – 5.41 (m, 2H), 5.33-5.27 (m, 1H), 3.91 (s, 3H), 2.44 (s, 3H), 2.33 – 2.12 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.6, 148.2, 145.4, 142.6, 135.4, 135.3, 130.7, 130.2, 129.6, 129.4, 125.7, 119.3, 76.3, 56.3, 52.4, 35.3, 21.9. **HRMS (ESI)** m/z calculated for $C_{21}H_{22}NO_6S$ $[M+H]^+$: 416.1168, found 416.1172.



(±)-(4*S*,6*S*)-6-(2-bromophenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (9). Racemic carbamate **S9** (87.6 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 50% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude*: 79%, 20:1 dr; *isolated*: 64.8 mg, 0.149 mmol, 74.3%, >20:1 dr);
Run 2 (*crude*: 80%, 20:1 dr; *isolated*: 65.3 mg, 0.150 mmol, 74.8%, >20:1 dr);
Run 3 (*crude*: 80%, 20:1 dr; *isolated*: 66.9 mg, 0.153 mmol, 76.7%, >20:1 dr).
Average: *crude*: **80% yield, 20:1 dr** (*anti:syn*). *isolated*: **75%, >20:1 dr** (*anti:syn*).

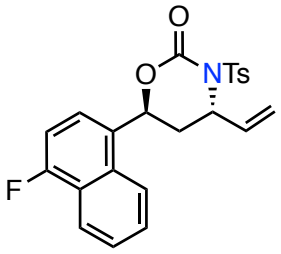
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 1H), 7.52 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.34 (m, 3H), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H), 6.07 (ddd, *J* = 16.9, 10.5, 4.7 Hz, 1H), 5.74 (dd, *J* = 12.0, 2.7 Hz, 1H), 5.56 – 5.46 (m, 2H), 5.31 – 5.26 (m, 1H), 2.51 (dt, *J* = 14.4, 2.5 Hz, 1H), 2.45 (s, 3H), 1.98 (ddd, *J* = 14.2, 12.0, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 148.5, 145.7, 137.2, 135.5, 135.04, 133.0, 130.2, 129.7, 129.4, 128.3, 127.4, 120.7, 119.2, 76.3, 56.5, 33.9, 21.9. **HRMS (ESI)** m/z calculated for $C_{19}H_{19}NO_4SBr$ $[M+H]^+$: 436.0218, found 436.0232.



(±)-(4S,6S)-6-(naphthalen-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**10**). Racemic carbamate **S10** (81.9 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 72%, 12:1 dr; *isolated:* 54.1 mg, 0.133 mmol, 66.4%, >20:1 dr);
Run 2 (*crude:* 71%, 13:1 dr; *isolated:* 53.8 mg, 0.132 mmol, 66.0%, >20:1 dr);
Run 3 (*crude:* 69%, 13:1 dr; *isolated:* 52.9 mg, 0.130 mmol, 65.0%, >20:1 dr).
Average: *crude*: **71% yield, 13:1 dr** (*anti:syn*). *isolated*: **66%, >20:1 dr** (*anti:syn*).

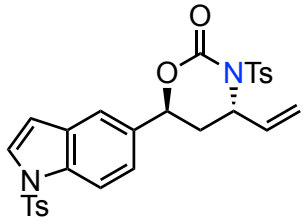
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.87–7.73 (m, 4H), 7.55–7.44 (m, 2H), 7.38 – 7.30 (m, 3H), 6.07 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 5.59 – 5.53 (m, 2H), 5.51 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.35–5.30 (m, 1H), 2.45 (s, 3H), 2.37–2.28 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 145.3, 135.6, 135.1, 133.5, 133.2, 129.7, 129.4, 128.9, 128.2, 127.9, 126.8, 125.2, 123.2, 119.2, 77.1, 56.4, 35.4, 21.9. (two peaks missing due to overlapping). **HRMS (ESI)** *m/z* calculated for $C_{23}H_{21}NO_4S$ $[M+H]^+$: 408.1270, found 408.1280.



(±)-(4*R*,6*S*)-6-(4-fluoronaphthalen-1-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (11)
Racemic carbamate **S11** (85.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (0 => 25% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude:* 65%, 7.7:1 dr; *isolated*: 46.2 mg, 0.109 mmol, 54.3%, >20:1 dr);
Run 2 (*crude:* 67%, 7.2:1 dr; *isolated:* 47.2 mg, 0.111 mmol, 55.5%, >20:1 dr);
Run 3 (*crude:* 63%, 7.6:1 dr; *isolated:* 45.4 mg, 0.107 mmol, 53.3%, >20:1 dr).
Average: *crude*: **65% yield, 7.5:1 dr** (*anti:syn*). *isolated*: **54%, >20:1 dr** (*anti:syn*).

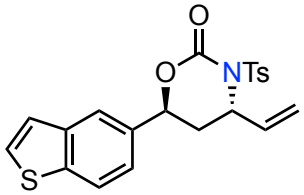
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.71 (dt, *J* = 7.0, 2.0 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.53 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.13 (dd, *J* = 10.0, 8.1 Hz, 1H), 6.23 – 6.10 (m, 2H), 5.70 – 5.53 (m, 2H), 5.37-5.33 (m, 1H), 2.49 – 2.43 (m, 1H), 2.46 (s, 3H), 2.31 (ddd, *J* = 14.4, 12.0, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 159.2 (d, *J* = 254.1 Hz), 148.6, 145.4, 135.7, 135.2, 131.1 (d, *J* = 4.5 Hz), 129.7, 129.5, 120.00 (d, *J* = 4.4 Hz), 127.9, 126.4 (d, *J* = 1.9 Hz), 124.0 (d, *J* = 16.3 Hz), 123.88 (d, *J* = 9.1 Hz), 121.90 (d, *J* = 3.3 Hz), 121.9 (d, *J* = 6.3 Hz), 119.4, 109.1 (d, *J* = 20.3 Hz), 73.5, 56.5, 34.7, 21.9. **HRMS (ESI)** m/z calculated for $C_{23}H_{21}NO_4FS$ [M+H]+: 426.1175, found 426.1181.



(±)-(4S,6S)-3-tosyl-6-(1-tosyl-1H-indol-5-yl)-4-vinyl-1,3-oxazinan-2-one (**12**). Racemic carbamate **S12** (110.3 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 25% acetone/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 73%, 10:1 dr; *isolated:*71.5 mg, 0.130 mmol, 64.9%, >20:1 dr);
Run 2 (*crude:* 75%, 10:1 dr; *isolated:*72.3 mg, 0.131 mmol, 65.7%, >20:1 dr);
Run 3 (*crude:* 74%, 10:1 dr; *isolated:*72.9 mg, 0.132 mmol, 66.2%, >20:1 dr).
Average: *crude*: **74% yield, 10:1 dr** (*anti:syn*). *isolated*: **66%, >20:1 dr** (*anti:syn*).

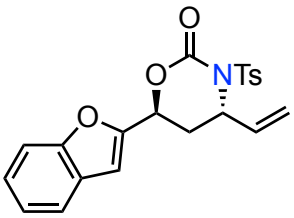
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (app. d, *J* = 8.4 Hz, 3H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.23-7.13 (m, 3H), 6.59 (d, *J* = 3.8, 1H), 6.01 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 5.50 (dd, J = 10.6, 1.5 Hz, 1H), 5.48-5.39 (m, 2H), 5.31 – 5.25 (m, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 2.29-2.21 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 145.3, 145.3, 135.5, 135.5, 135.1, 134.9, 132.8, 131.0, 130.1, 129.6, 129.4, 127.4, 126.9, 122.5, 119.2, 119.1, 113.9, 109.0, 77.2, 56.4, 35.4, 21.8, 21.7. **HRMS (ESI)** *m/z* calculated for $C_{28}H_{26}N_2O_6S_2$ $[M+H]^+$: 551.1311, found 551.1317.



(±)-(4S,6S)-6-(benzo[b]thiophen-5-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**13**). Racemic carbamate **S13** (83.1 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 67%, 9.6:1 dr; *isolated:* 45.2 mg, 0.109 mmol, 54.6%, >20:1 dr);
Run 2 (*crude:* 68%, 9.2:1 dr; *isolated:* 48.0 mg, 0.116 mmol, 58.0%, >20:1 dr);
Run 3 (*crude:* 67%, 9.7:1 dr; *isolated:* 49.1 mg, 0.119 mmol, 59.4%, >20:1 dr).
Average: *crude*: **67% yield, 9.5:1 dr** (*anti:syn*). *isolated*: **58%, >20:1 dr** (*anti:syn*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 5.4 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.30 (dd, *J* = 5.5, 0.8 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.05 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 5.57 – 5.44 (m, 3H), 5.34 – 5.29 (m, 1H), 2.45 (s, 3H), 2.34 – 2.26 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.5, 145.3, 140.2, 139.8, 135.5, 135.5, 134.0, 129.6, 129.4, 127.8, 123.9, 123.0, 121.9, 121.1, 119.2, 77.4, 56.4, 35.6, 21.9. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{19}NO_4S_2$ $[M+H]^+$: 414.0834, found 414.0829.

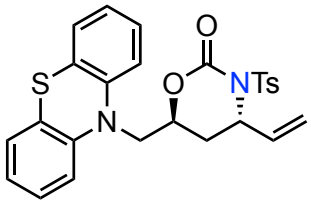


(±)-(4S,6S)-6-(benzofuran-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (14). Racemic carbamate **S14** (79.9 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10-25% gradient ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude:* 71%, 3.9:1 dr; *isolated:* 43.5 mg, 0.109 mmol, 54.7%, >20:1 dr);
Run 1 (*crude:* 68%, 4.3:1 dr; *isolated:* 43.0 mg, 0.108 mmol, 54.1%, >20:1 dr);
Run 1 (*crude:* 73%, 4.1:1 dr; *isolated:* 44.8 mg, 0.112 mmol, 56.4%, >20:1 dr).

Average: *crude*: **71% yield, 4.1:1 dr** (*anti:syn*). *isolated*: **55%, >20:1 dr** (*anti:syn*).

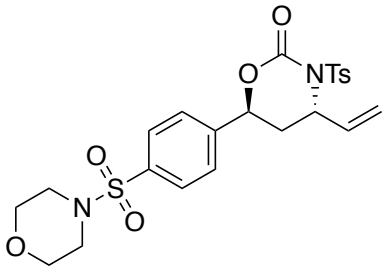
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 6.76 (s, 1H), 6.00 (ddd, *J* = 17.1, 10.6, 4.6 Hz, 1H), 5.57 – 5.50 (m, 2H), 5.47 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.40 – 5.35 (m, 1H), 2.62 (ddd, *J* = 14.3, 12.3, 5.2 Hz, 1H), 2.44 (s, 3H), 2.40 – 2.34 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.1, 151.9, 147.7, 145.4, 135.3, 135.0, 129.6, 129.4, 127.4, 125.4, 123.3, 121.7, 119.4, 111.6, 106.0, 71.0, 56.0, 31.4, 21.9.**HRMS (ESI)** *m/z* calculated for $C_{21}H_{19}NO_5S$ $[M+H]^+$: 398.1062, found 398.1060.



(±)-(4R,6R)-6-((10H-phenothiazin-10-yl)methyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (15). Racemic carbamate **S15** (98.0 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 20% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (crude: 65%, 12:1 dr, isolated: 55.3 mg, 0.112 mmol, 56.1%, >20:1 dr);
Run 2 (crude: 62%, 12:1 dr, isolated: 56.7 mg, 0.115 mmol, 57.6%, >20:1 dr);
Run 3 (crude: 63%, 12:1 dr, isolated: 55.7 mg, 0.113 mmol, 56.5%, >20:1 dr).
Average: *crude*: **63% yield, 12:1 dr** (*anti:syn*). *isolated*: **57%, >20:1 dr** (*anti:syn*).

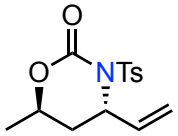
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90-7.86 (m, 2H), 7.33–7.29 (m, 2H), 7.20-7.14 (m, 4H), 7.00-6.92 (m, 2H), 6.92-6.87 (m, 2H), 5.73 (ddt, *J* = 16.9, 11.0, 4.2 Hz, 1H), 5.25-5.20 (m, 3H), 4.76-4.70 (m, 1H), 4.36-4.32 (m, 1H), 3.99-3.95 (m, 1H), 2.43 (s, 3H), 2.40-2.36 (m, 1H), 1.95 – 1.84 (m, 1H). ^{3}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 145.2, 144.8, 135.5, 135.2, 129.5, 129.4, 128.0, 127.7, 126.5, 123.6, 118.6, 116.1, 72.6, 56.2, 50.8, 31.2, 21.8. **HRMS (ESI)** m/z calculated for $C_{26}H_{25}N_2O_4S_2$ $[M+H]^+$: 493.1256, found 493.1239.



(±)-(4*S*,6*S*)-6-(4-(morpholinosulfonyl)phenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (16)
Racemic carbamate **S16** (101.7 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (20 => 65% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid.

Run 1 (*crude*: 60%, 15:1 dr; *isolated*: 54.3 mg, 0.107 mmol, 53.6%, >20:1 dr);
Run 2 (*crude*: 63%, 15:1 dr; *isolated:* 56.7 mg, 0.112 mmol, 56.0%, >20:1 dr);
Run 3 (*crude*: 58%, 14:1 dr; *isolated*: 54.9 mg, 0.108 mmol, 54.2%, >20:1 dr).
Average: *crude*: **60% yield, 15:1 dr** (*anti:syn*). *isolated*: **55%, >20:1 dr** (*anti:syn*).

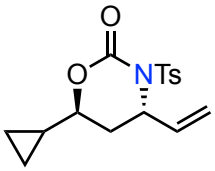
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.03 (ddd, *J* = 17.1, 10.6, 4.7 Hz, 1H), 5.54 (app dd, *J* = 10.5, 1.5 Hz, 1H), 5.50 – 5.43 (m, 2H), 5.33 (td, *J* = 4.9, 2.3 Hz, 1H), 3.75 – 3.69 (m, 4H), 3.00 – 2.95 (m, 4H), 2.45 (s, 3H), 2.31 (ddd, *J* = 14.3, 2.8, 2.8 Hz, 1H), 2.21 (ddd, *J* = 14.3, 12.1, 5.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.9, 145.5, 143.1, 135.8, 135.3, 135.2, 129.7, 129.5, 128.5, 126.5, 119.5, 75.9, 66.2, 56.2, 46.1, 35.2, 21.9. **HRMS (ESI)** m/z calculated for $C_{23}H_{27}N_2O_7S_2$ [M+H]+: 507.1260, found 570.1269.



(±)-(4S,6R)-6-methyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (17)
Racemic carbamate **S17** (59.4 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude*: 78%, 5.3:1 dr; *isolated*: 38.5 mg, 0.130 mmol, 65.2%, >20:1 dr);
Run 2 (*crude*: 78%, 5.2:1 dr; *isolated*: 39.9 mg, 0.135 mmol, 67.5%, >20:1 dr);
Run 3 (*crude*: 80%, 5.2:1 dr; *isolated*: 37.9 mg, 0.128 mmol, 64.2%, >20:1 dr).
Average: *crude*: **79% yield, 5.2:1 dr** (*anti:syn*). *isolated*: **66%, >20:1 dr** (*anti:syn*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 5.89 (ddd, *J* = 16.9, 10.5, 4.9 Hz, 1H), 5.44 – 5.33 (m, 2H), 5.20-5.16 (m, 1H), 4.53 (app dq, *J* = 12.5, 6.3, 1H), 2.42 (s, 3H), 2.05 – 1.88 (m, 2H), 1.33 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 145.1, 135.8, 135.7, 129.5, 129.3, 118.6, 72.3, 56.3, 34.5, 21.8, 20.9. **HRMS (ESI)** m/z calculated for $C_{14}H_{18}NO_4S$ $[M+H]^+$: 296.0951, found 296.0957.

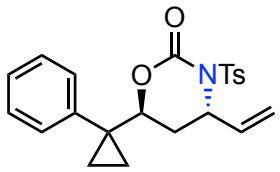


(±)-(4S,6S)-6-cyclopropyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**18**).
Racemic carbamate **S18** (64.7 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a yellow oil.

Run 1 (*crude:* 93%, 6.2:1 dr; *isolated:* 48.0 mg, 0.149 mmol, 74.6%, >20:1 dr);
Run 2 (*crude:* 91%, 6.4:1 dr; *isolated:* 50.2 mg, 0.156 mmol, 78.1%, >20:1 dr);

Run 3 (*crude:* 94%, 6.0:1 dr; *isolated*: 52.4 mg, 0.163 mmol, 81.5%, >20:1 dr).
Average: *crude*: **93% yield, 6.2:1 dr** (*anti:syn*). *isolated*: **78%, >20:1 dr** (*anti:syn*).

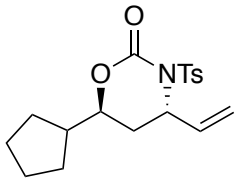
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.84 (ddd, *J* = 17.0, 10.5, 4.9 Hz, 1H), 5.37 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.32 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.22-5.17 (m, 1H), 3.64 (ddd, *J* = 10.9, 8.5, 3.8 Hz, 1H), 2.42 (s, 3H), 2.17-2.04 (m, 2H), 0.98 (qt, *J* = 8.2, 4.8, 1H), 0.62 (tdd, *J* = 8.2, 5.8, 4.7 Hz, 1H), 0.56 (tdd, *J* = 8.7, 5.7, 4.6 Hz, 1H), 0.46-0.40 (m, 1H), 0.24-0.15 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 145.1, 135.7, 135.6, 129.5, 129.3, 118.7, 80.6, 56.1, 33.1, 21.8, 14.9, 3.7, 2.1. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{21}NO_4S$ $[M-H]^+$: 322.1113, found 322.1108. Spectra match literature report.[4]



(±)-(4R,6R)-6-(1-phenylcyclopropyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (19)
Racemic carbamate **S19** (79.9 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 20% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude*: 84%, >20:1 dr; *isolated*: 58.1 mg, 0.141 mmol, 73%, >20:1 dr);
Run 2 (*crude*: 80%, >20:1 dr; *isolated*: 56.9 mg, 0.139 mmol, 72%, >20:1 dr);
Run 3 (*crude*: 83%, >20:1 dr; *isolated*: 60.2 mg, 0.148 mmol, 76%, >20:1 dr).
Average: *crude*: **82% yield, >20:1 dr** (*anti:syn*). *isolated*: **75%, >20:1 dr** (*anti:syn*).

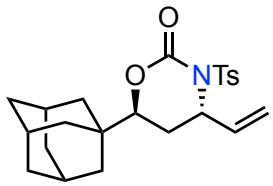
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.29 – 7.20 (m, 5H), 5.83 (dddd, *J* = 17.0, 10.5, 5.0, 1.2 Hz, 1H), 5.36 (dt, *J* = 10.6, 1.4 Hz, 1H), 5.28 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.11-5.06 (m, 1H), 3.89 (ddd, *J* = 12.2, 2.9, 1.3 Hz, 1H), 2.41 (s, 3H), 2.00 (dt, *J* = 14.3, 2.7 Hz, 1H), 1.79 (dddd, *J* = 14.2, 12.2, 5.3, 1.3 Hz, 1H), 1.01 – 0.95 (m, 1H), 0.94 – 0.86 (m, 2H), 0.83 – 0.76 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.5, 145.0, 139.3, 135.6, 135.5, 131.2, 129.5, 129.2, 128.4, 127.5, 118.6, 81.8, 55.8, 31.2, 28.6, 21.8, 11.6, 9.9. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{23}NO_4S$ $[M+H]^+$: 398.1429, found 398.1426.



(±)-(4S,6S)-6-cyclopentyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (20)
Racemic carbamate **S20** (70.3 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 15% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.
Run 1 (*crude*: 82%, 8.1:1 dr; *isolated*: 48.0 mg, 0.137 mmol, 68.7%, >20:1 dr);
Run 2 (*crude*: 79%, 8.3:1 dr; *isolated*: 48.2 mg, 0.138 mmol, 69.0%, >20:1 dr);
Run 3 (*crude*: 80%, 7.9:1 dr; *isolated*: 45.3 mg, 0.130 mmol, 64.8%, >20:1 dr).

Average: *crude*: **80% yield, 8.1:1 dr** (*anti:syn*). *isolated*: **68%, >20:1 dr** (*anti:syn*).

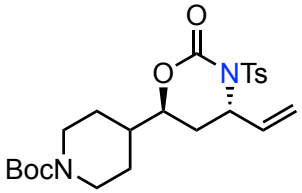
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 5.0 Hz, 1H), 5.44 – 5.31 (m, 2H), 5.22 – 5.15 (m, 1H), 4.17 (ddd, *J* = 11.0, 7.6, 2.9 Hz, 1H), 2.42 (s, 3H), 2.05 – 1.92 (m, 3H), 1.86 – 1.76 (m, 1H), 1.71– 1.45 (m, 5H), 1.39 – 1.30 (m, 1H), 1.23 – 1.12 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.7, 145.0, 135.8, 135.7, 129.5, 129.2, 118.6, 79.5, 56.2, 44.3, 32.2, 28.6, 28.4, 25.5, 25.4, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{23}NO_4S$ $[M+H]^+$: 350.1426, found 350.1436.



(±)-(4*R*,6*R*)-6-((3*R*,5*R*,7*R*)-adamantan-1-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (21). Racemic carbamate **S21** (83.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 20% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude*: 74%, 5.4:1 dr; *isolated*: 45.0 mg, 0.108 mmol, 54.1%, >20:1 dr);
Run 2 (*crude*: 77%, 5.2:1 dr; *isolated*: 42.0 mg, 0.101 mmol, 50.5%, >20:1 dr);
Run 3 (*crude*: 76%, 5.2:1 dr; *isolated*: 43.4 mg, 0.104 mmol, 52.2%, >20:1 dr).
Average: *crude*: **76% yield, 5.3:1 dr** (*anti:syn*). *isolated*: **52%, >20:1 dr** (*anti:syn*).

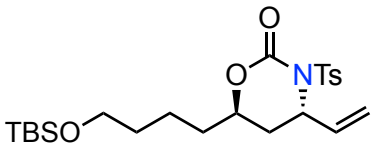
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.91 – 5.82 (m, 1H), 5.43 – 5.30 (m, 2H), 5.24 – 5.17 (m, 1H), 3.88 (dd, *J* = 11.7, 3.5 Hz, 1H), 2.42 (s, 3H), 2.04 – 1.91 (m, 5H), 1.74 – 1.66 (m, 3H), 1.64 – 1.56 (m, 6H), 1.50 – 1.42 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 149.0, 145.0, 135.7, 129.5, 129.3, 118.7, 83.3, 55.9, 37.5, 37.0, 35.6, 28.1, 26.7, 21.8. (one peak missing due to overlapping) **HRMS (ESI)** m/z calculated for $C_{23}H_{30}NO_4S$ $[M+H]+$: 416.1896, found 416.1888.



(±)-tert-butyl 4-((4S,6S)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)piperidine-1-carboxylate (22). Racemic carbamate **S22** (93.3 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 35% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude*: 74%, 6.0:1 dr, *isolated*: 50.5 mg, 0.109 mmol, 54.3%, >20:1 dr);
Run 2 (*crude*: 74%, 5.7:1 dr, *isolated*: 52.1 mg, 0.112 mmol, 56.1%, >20:1 dr);
Run 3 (*crude*: 76%, 5.8:1 dr, *isolated*: 51.8 mg, 0.111 mmol, 55.7%, >20:1 dr).
Average: *crude*: **75% yield, 5.8:1 dr** (*anti:syn*). *isolated*: **55%, >20:1 dr** (*anti:syn*).

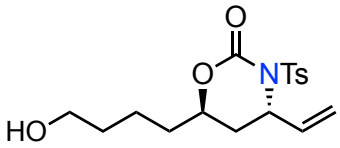
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.86 (ddd, *J* = 17.1, 10.5, 4.9 Hz, 1H), 5.43 – 5.31 (m, 2H), 5.22 (td, *J* = 4.8, 2.4 Hz, 1H), 4.19 – 4.00 (m, 3H), 2.63-2.59 (m, 2H), 2.42(s, 3H), 2.01 (dt, *J* = 14.0, 2.9 Hz, 1H), 1.93 (ddd, *J* = 14.0, 11.9, 5.1 Hz, 1H), 1.84 (d, *J* = 12.8 Hz, 1H), 1.65 (dtd, *J* = 13.5, 7.5, 3.3 Hz, 1H), 1.53 (dt, *J* = 12.8, 3.1 Hz, 1H), 1.43 (s, 9H), 1.22-1.16 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.7, 148.4, 145.2, 135.5, 135.4, 129.5, 129.3, 118.9, 79.7, 78.9, 55.9, 43.3, 40.5, 30.2, 28.5, 27.1, 21.8. **HRMS (ESI)** m/z calculated for $C_{23}H_{33}N_2O_6S$ $[M+H]^+$: 465.2059, found 465.2049.



(±)-(4S,6R)-6-(4-((tert-butyldimethylsilyl)oxy)butyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**23**). Racemic carbamate **S23** (93.9 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude:* 89%, 7.9:1 dr; *isolated:* 69.9 mg, 0.144 mmol, 74.7%, >20:1 dr);
Run 2 (*crude:* 84%, 8.3:1 dr; *isolated:* 66.6 mg, 0.142 mmol, 71.2%, >20:1 dr);
Run 3 (*crude:* 86%, 8.0:1 dr; *isolated:* 69.1 mg, 0.145 mmol, 73.9%, >20:1 dr).
Average: *crude*: **86% yield, 8.1:1 dr** (*anti:syn*). *isolated*: **73%, >20:1 dr** (*anti:syn*).

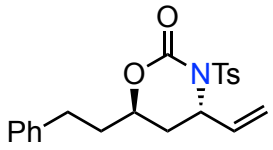
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 4.9 Hz, 1H), 5.40 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.36 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.21 – 5.16 (m, 1H), 4.36 (dddd, *J* = 12.2, 7.8, 5.0, 2.9 Hz, 1H), 3.56 (t, *J* = 6.1 Hz, 2H), 2.41 (s, 3H), 2.01 (dt, *J* = 14.2, 2.7 Hz, 1H), 1.91 (ddd, *J* = 14.1, 11.8, 5.2 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.59 – 1.51 (m, 1H), 1.51 – 1.42 (m, 3H), 1.42 – 1.31 (m, 1H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.6, 145.1, 135.7, 135.6, 129.5, 129.3, 118.7, 75.8, 62.8, 56.2, 34.8, 32.8, 32.4, 26.1, 21.8, 21.1, 18.4, -5.2. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{38}NO_5SSi$ $[M+H]^+$: 468.2240, found 468.2234.



(±)-(4S,6R)-6-(4-hydroxybutyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**24**). Racemic carbamate **S24** (71.1 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (20 => 60% ethyl acetate/hexanes) afforded the *anti*- diastereomer as a white solid (Solvent was very difficult to remove. Ethyl acetate is integrated out when reporting yield.).

Run 1 (*crude:* 85%, 8.5:1 dr; *isolated:* 49.9 mg, 0.141 mmol, 70.6%, >20:1 dr);
Run 2 (*crude:* 89%, 8.3:1 dr; *isolated:* 53.5 mg, 0.151 mmol, 75.7%, >20:1 dr);
Run 3 (*crude:* 88%, 8.9:1 dr; *isolated*: 49.8 mg, 0.141 mmol, 70.4%, >20:1 dr).
Average: *crude*: **87% yield, 8.6:1 dr** (*anti:syn*). *isolated*: **72%, >20:1 dr** (*anti:syn*).

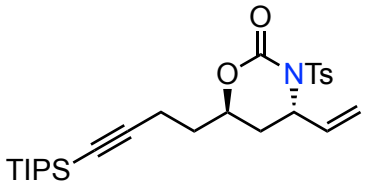
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 4.9 Hz, 1H), 5.41 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.36 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.23 – 5.15 (m, 1H), 4.38 (dddd, *J* = 11.9, 7.8, 4.6, 3.0 Hz, 1H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.04 – 1.99 (m, 1H), 1.94 (ddd, *J* = 14.2, 11.7, 5.2 Hz, 1H), 1.74 – 1.64 (m, 1H), 1.64 – 1.47 (m, 4H), 1.46 – 1.36 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.6, 145.1, 135.7, 135.7, 129.6, 129.3, 118.8, 75.8, 62.6, 56.2, 34.8, 32.9, 32.3, 21.8, 21.1. **HRMS (ESI)** *m/z* calculated for $C_{17}H_{24}NO_5S$ $[M+H]^+$: 354.1375, found 354.1384.



(±)-(4S,6R)-6-phenethyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**25**).
Racemic carbamate **S25** (77.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude:* 84%, 7.5:1 dr; *isolated*: 54.8 mg, 0.142 mmol, 71.1%, >20:1 dr);
Run 2 (*crude:* 87%, 7.2:1 dr; *isolated:* 54.7 mg, 0.142 mmol, 70.9%, >20:1 dr);
Run 3 (*crude:* 88%, 7.2:1 dr; *isolated:* 53.1 mg, 0.138 mmol, 68.9%, >20:1 dr).
Average: *crude*: **86% yield, 7.3:1 dr** (*anti:syn*) (8.6:1 dr by HPLC). *isolated*: **70%, >20:1 dr** (*anti:syn*).

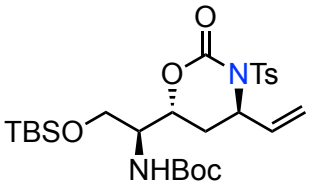
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30-7.25 (m, 2H), 7.23-7.17 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 5.87 (ddd, *J* = 17.1, 10.5, 5.0 Hz, 1H), 5.41-5.34 (m, 2H), 5.23 - 5.18 (m, 1H), 4.43 -4.38 (m, 1H), 2.81 (ddd, *J* = 13.9, 9.8, 5.5 Hz 1H), 2.68 (ddd, *J* = 13.8, 9.5, 6.7 Hz, 1H), 2.44 (s, 3H), 2.06-1.92 (m, 3H), 1.89 – 1.78 (m, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.5, 145.1, 140.6, 135.6, 135.6, 129.5, 129.3, 128.6, 128.4, 126.3, 118.7, 75.0, 56.2, 36.8, 32.9, 31.0, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{24}NO_4S$ $[M+H]^+$: 386.1426, found 386.1414.



(±)-(4S,6R)-3-tosyl-6-(4-(triisopropylsilyl)but-3-yn-1-yl)-4-vinyl-1,3-oxazinan-2-one (**26**).
Racemic carbamate **S26** (98.4 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude:* 89%, 8.0:1 dr; *isolated :*76.2 mg, 0.156 mmol, 78%, >20:1 dr);
Run 2 (*crude:* 93%, 8.0:1 dr; *isolated:* 71.0 mg, 0.145 mmol, 73%, >20:1 dr);
Run 3 (*crude:* 90%, 7.8:1 dr; *isolated:* 72.3 mg, 0.148 mmol, 74%, >20:1 dr).
Average: *crude*: **91% yield, 7.9:1 dr** (*anti:syn*). *isolated*: **75%, >20:1 dr** (*anti:syn*).

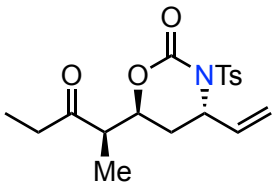
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.87 (ddd, *J* = 17.1, 10.5, 4.8 Hz, 1H), 5.42 – 5.33 (m, 2H), 5.24 – 5.18 (m, 1H), 4.68 – 4.57 (m, 1H), 2.49 – 2.43 (m, 1H), 2.43 (s, 3H), 2.36 (dt, *J* = 17.2, 6.1 Hz, 1H), 2.08 (dt, *J* = 14.1, 2.7 Hz, 1H), 1.96 (ddd, *J* = 14.1, 12.0, 5.1 Hz, 1H), 1.88 (ddt, *J* = 14.3, 8.3, 6.0 Hz, 1H), 1.71 (dddd, *J* = 13.5, 8.7, 6.1, 4.4 Hz, 1H), 1.07 – 0.94 (m, 21H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 148.4, 145.2, 135.5, 135.4, 129.6, 129.3, 118.9, 106.6, 81.9, 74.4, 56.2, 34.2, 32.8, 21.8, 18.8, 15.7, 11.3. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{39}NO_4SSiNa$ $[M+Na]^+$: 513.2339, found 513.2336.



(–)-*tert*-butyl ((*S*)-2-((*tert*-butyldimethylsilyl)oxy)-1-((4*R*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)ethyl)carbamate (27).
Racemic carbamate **S27** (111.4 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a white solid.

Run 1 (*crude:* 92%, 7.2:1 dr; *isolated :*90.9 mg, 0.164 mmol, 81.9%, >20:1 dr);
Run 2 (*crude:* 91%, 7.4:1 dr; *isolated:* 85.7 mg, 0.154 mmol, 77.2%, >20:1 dr);
Run 3 (*crude:* 90%, 7.2:1 dr; *isolated:* 89.1 mg, 0.161 mmol, 80.3%, >20:1 dr).
Average: *crude*: **91% yield, 7.3:1 dr** (*anti:syn*). *isolated*: **80%, >20:1 dr** (*anti:syn*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.89 (ddd, *J* = 17.1, 10.6, 4.3 Hz, 1H), 5.47 – 5.35 (m, 2H), 5.25-5.21 (m, 1H), 4.94 (d, *J* = 9.1 Hz, 1H), 4.38 (app q, *J* = 8.1 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.64-3.62 (m, 1H), 3.58 (dd, *J* = 10.3, 3.3 Hz, 1H), 2.43 (s, 3H), 2.15 – 2.04 (m, 2H), 1.44 (s, 9H), 0.85 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.6, 148.0, 145.2, 135.6, 135.6, 129.4, 129.3, 118.6, 80.3, 73.9, 61.0, 56.4, 54.1, 30.0, 28.5, 25.9, 21.8, 18.3, -5.4, -5.4. **HRMS (ESI)** *m/z* $C_{26}H_{43}N2O_7SSi$ $[M+H]^+$: 555.2560, found 555.2582. **Optical rotation**: $[\alpha]^{23}_D$ = -7.1 (c = 1.05, $CHCl_3$).



(+)-(4S,6S)-6-((R)-3-oxopentan-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (28).
Racemic carbamate **S28** (73.1 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 25% acetone/hexanes) afforded the *anti*- diastereomer as a white solid.

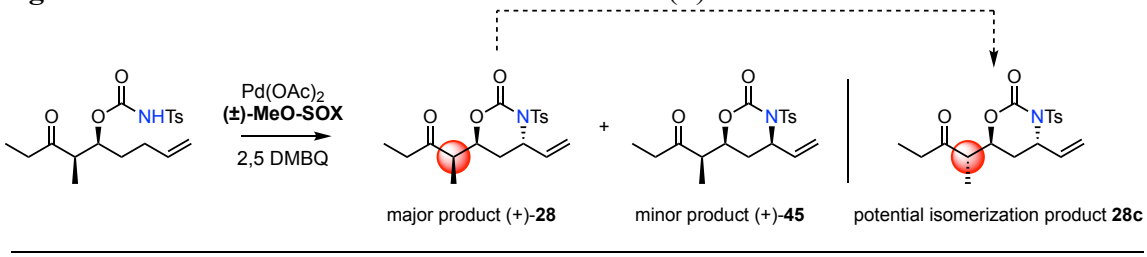
Run 1 (*crude:*74%, 13:1 dr; *isolated:* 49.0 mg, 0.134 mmol, 67.0%, >20:1 dr);
Run 2 (*crude:*76%, 12:1 dr; *isolated:* 48.5 mg, 0.133 mmol, 66.4%, >20:1 dr);

Run 3 (*crude:*77%, 13:1 dr; *isolated:* 53.1 mg, 0.145 mmol, 72.7%, >20:1 dr).
Average: *crude*: **76% yield, 13:1 dr** (*anti:syn*). *isolated*: **69%, >20:1 dr** (*anti:syn*).

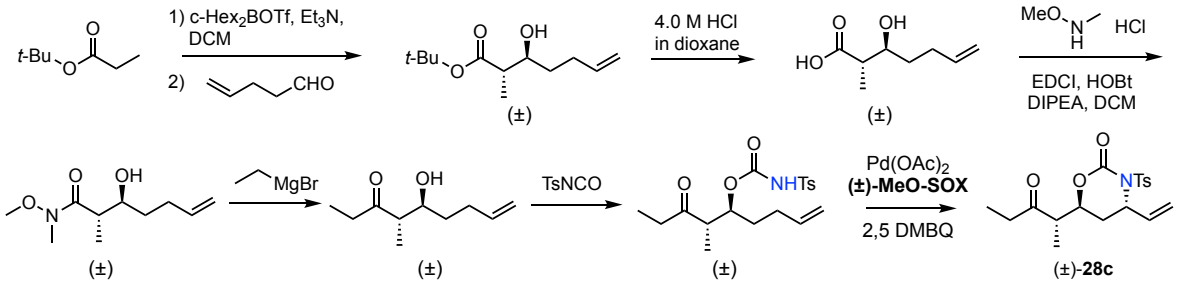
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 4.9 Hz, 1H), 5.42 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.34 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.18 (app tt, *J* = 5.0, 2.1 Hz, 1H), 4.53 (ddd, *J* = 12.0, 7.6, 2.8 Hz, 1H), 2.76 (app p, *J* = 7.2 Hz, 1H), 2.55 (dq, *J* = 18.1, 7.2 Hz, 1H), 2.46 – 2.35 (m, 1H), 2.42 (s, 3H), 2.08 (dt, *J* = 14.0, 2.6 Hz, 1H), 1.90 (ddd, *J* = 14.0, 12.0, 5.2 Hz, 1H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.9, 148.3, 145.2, 135.4, 135.2, 129.5, 129.3, 118.9, 76.7, 56.0, 49.8, 36.0, 30.5, 21.8, 13.3, 7.6. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{23}NO_5S$ $[M+Na]^+$: 366.1375, found 366.1375. Optical rotation: $[\alpha]^{23}_D$ = +6.8 (c = 1.02, $CHCl_3$).

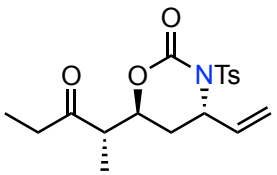
*Complete stereoretention of acidic methyl containing stereocenter (α to ketone) was proven by ^{1}H NMR analysis. If the stereocenter (α to ketone) in **28** was isomerized under our reaction condition, we would see formation of **28c** (inverse stereochemistry at the methyl containing stereocenter α to ketone) in our reaction. We didn't observed any 28c by crude ^{1}H NMR or isolated .*

Figure S1: Stereoretention of acidic stereocenter in (+)-28.



Synthesis of (±)-**28c** as standard for ^{1}H NMR analysis:

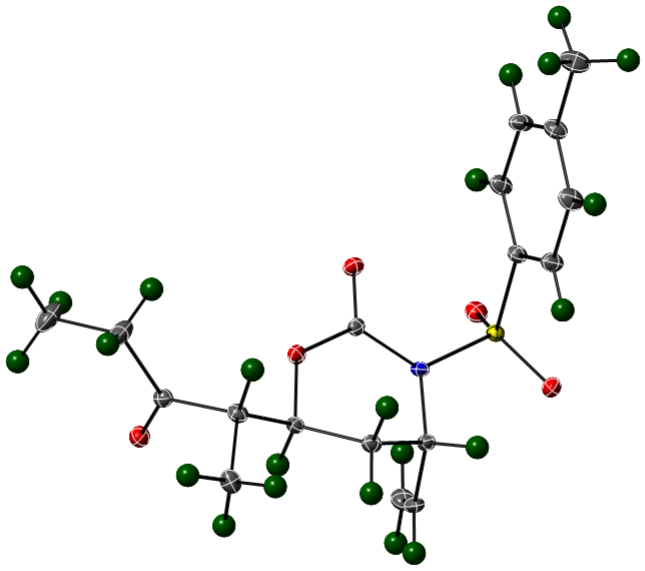




(±)-(4S,6S)-6-((S)-3-oxopentan-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (28c) was synthesized following reported procedure of *anti*-Aldol reaction[5] using using pent-4-enal, tert-butyl ester hydrolysis[6], ketone synthesis through Weinreb amide[7] (also see synthesis of S28), *N*-tosyl carbamate synthesis following the general procedure (Page S4) and general procedure of *anti*-oxazinanone (Page S25) to afford **28c** as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.88 (ddd, *J* = 17.1, 10.5, 5.1, 1H), 5.41 (dd, *J* = 10.5, 1.5 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.26 – 5.19 (m, 1H), 4.63 (ddd, *J* = 12.2, 7.7, 2.7 Hz, 1H), 2.82 (app p, *J* = 7.3, 1H), 2.54 – 2.46 (m, 2H), 2.42 (s, 3H), 2.13 (dt, *J* = 14.0, 2.7 Hz, 1H), 1.92 (td, *J* = 12.2, 5.21H), 1.05-0.99 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.7, 147.9, 145.2, 135.4, 135.1, 129.6, 129.3, 119.1, 77.0, 55.9, 49.4, 36.4, 30.2, 21.8, 12.3, 7.4. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{23}NO_5S$ $[M+Na]^+$: 366.1375, found 366.1373.

Single Crystal structure X-ray analysis of (±)-28c:



Details of the crystal data and a summary of the intensity data for **(±)-28c** are listed in Table S3. CCDC: 1899081

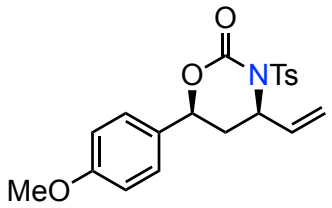
Table S3. Crystal data and structure refinement for (±)**-28c**

Identification code	dm07tsa
Empirical formula	C20.15 H27.88 Cl1.42 N O5 S
Formula weight	446.67
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.9675(3) Å	a= 80.064(2)°.
	b = 11.0636(5) Å	b= 89.981(2)°.
	c = 16.9266(8) Å	g = 75.078(2)°.
Volume	1062.50(9) $Å^3$	
Z	2	
Density (calculated)	1.396 Mg/m^3	
Absorption coefficient	0.363 mm^{-1}	
F(000)	472	
Crystal size	0.257 x 0.180 x 0.075 mm^3	
Theta range for data collection	1.936 to 27.184°.	
Index ranges	-7<=h<=7, -14<=k<=14, -21<=l<=21	
Reflections collected	32605	
Independent reflections	4701 [R(int) = 0.0430]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Integration	
Max. and min. transmission	0.9966 and 0.8700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4701 / 124 / 305	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0644, wR2 = 0.1853	
R indices (all data)	R1 = 0.0715, wR2 = 0.1951	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.463 and -1.022 $e.Å^{-3}$	

Reaction Scope (*Syn*)

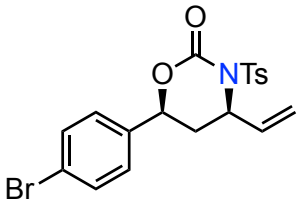
General procedure for *syn*-1,3 oxazinanone:
To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO-SOX ligand (6.9 mg, 0.02 mmol, 0.1 equiv), 1,4 benzoquinone (BQ) (34.6 mg, 0.32mmol, 1.6 equiv), *N*-tosyl carbamate (0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 24 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL $CDCl_3$ and analyzed by crude ^{1}H NMR with internal standard (nitrobenzene, 12.3 mg, 0.1 mmol, 0.5 equiv). The mixture was then concentrated under reduced pressure and dissolved in 30 mL diethyl ether and washed sequentially with 1M aq. NaOH (10 mL) and sat. aq. $NaHSO_3$ (10 mL) (repeat this wash sequence for 3 times). The organic layer was dried over $MgSO_4$, concentrated under reduced pressure and subjected to flash column chromatography (ethyl acetate in hexanes) to provide *syn*-1,3 oxazinanone product.



(±)-(4R,6S)-6-(4-methoxyphenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**29**). Racemic carbamate **S3** (77.9 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *anti*-diastereomer as a yellow oil.

Run 1 (*crude:* 67%, 6.0:1 dr; *isolated:* 42.2 mg, 0.109 mmol, 54.5%, >20:1 dr);
Run 2 (*crude:* 68%, 6.3:1 dr; *isolated:* 42.7 mg, 0.110 mmol, 55.1%, >20:1 dr);
Run 3 (*crude:* 66%, 6.2:1 dr; *isolated:* 41.2 mg, 0.106 mmol, 53.2%, >20:1 dr).
Average: *crude*: **67% yield, 6.2:1 dr** (*syn:anti*). *isolated*: **54%, >20:1 dr** (*syn:anti*).

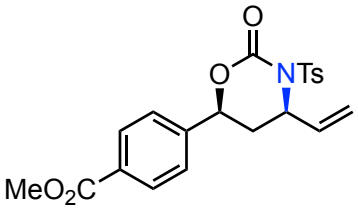
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.59 (ddd, *J* = 16.9, 10.1, 8.1 Hz, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.29 – 5.20 (m, 2H), 5.05 (dt, *J* = 9.7, 8.0 Hz, 1H), 3.80 (s, 3H), 2.52 (ddd, *J* = 14.4, 8.0, 2.3 Hz, 1H), 2.44 (s, 3H), 2.07 (ddd, *J* = 14.3, 11.3, 9.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 150.3, 145.1, 136.8, 136.0, 129.8, 129.3, 128.9, 127.7, 119.0, 114.3, 77.5, 59.1, 55.5, 38.2, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{20}H_{21}NO_5S$ $[M+H]^+$: 388.1219, found 388.1217. Spectra match literature report.[4]



(±)-(4R,6S)-6-(4-bromophenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**30**). Racemic carbamate **S5** (87.7 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 82%, 6.7:1 dr; *isolated:* 54.0 mg, 0.124 mmol, 61.9%, >20:1 dr);
Run 2 (*crude:* 83%, 6.8:1 dr; *isolated:* 54.5 mg, 0.125 mmol, 62.5%, >20:1 dr);
Run 3 (*crude:* 86%, 6.1:1 dr; *isolated:* 56.6 mg, 0.130 mmol, 64.9%, >20:1 dr).
Average: *crude*: **84% yield, 6.5:1 dr** (*syn:anti*). *isolated*: **63%, >20:1 dr** (*syn:anti*).

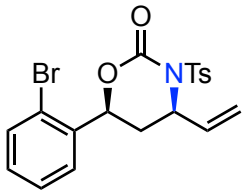
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.57 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.27-5.23 (m, 2H), 5.07 (dt, *J* = 9.6, 8.0 Hz, 1H), 2.55 (ddd, *J* = 14.5, 7.9, 2.5 Hz, 1H), 2.44 (s, 3H), 2.02 (ddd, *J* = 14.5, 11.1, 9.6 Hz, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 145.2, 136.5, 136.0, 135.8, 132.1, 129.9, 129.3, 127.7, 123.1, 119.3, 58.9, 38.2, 29.9, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{19}H_{18}BrNO_4S$ $[M+H]^+$: 436.0218, found 436.0208. Spectra match literature report.[4]



(±)-Methyl 4-((4R,6S)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)benzoate (31)
Racemic carbamate **S8** (83.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 25% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude*: 70%, 5.9:1 dr; *isolated*: 44.1 mg, 0.106 mmol, 53.1%, >20:1 dr);
Run 2 (*crude*: 71%, 5.6:1 dr; i*solated*: 43.9 mg, 0.106 mmol, 52.8%, >20:1 dr);
Run 3 (*crude*: 67%, 6.1:1 dr; *isolated*: 42.5 mg, 0.102 mmol, 51.1%, >20:1 dr).
Average: *crude*: **69% yield, 5.9:1 dr** (*syn:anti*). *isolated*: **52%, >20:1 dr** (*syn:anti*).

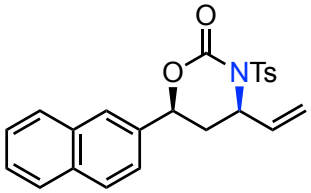
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.56 (dddd, *J* = 16.8, 9.8, 8.0, 1.1 Hz, 1H), 5.43 – 5.33 (m, 2H), 5.25 (d, *J* = 10.1 Hz, 1H), 5.13 – 5.07 (m, 1H), 3.92 (s, 3H), 2.60 (dddd, *J* = 14.4, 7.8, 2.6, 1.1 Hz, 1H), 2.45 (s, 3H), 2.06 (ddd, *J* = 14.5, 9.9, 9.2, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 149.8, 145.2, 141.8, 136.5, 135.8, 130.8, 130.2, 129.9, 129.4, 125.9, 119.3, 77.0, 58.9, 52.4, 38.2, 21.8. **HRMS (ESI)** m/z calculated for $C_{21}H_{23}NO_6S$ $[M+H]^+$: 416.1168, found 416.1172.



(±)-(4*S*,6*S*)-6-(2-bromophenyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (32)
Racemic carbamate **S9** (87.6 mg, 0.2 mmol) was reacted according to the general procedure for 48 hours. Purification by flash chromatography (5 => 20% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude*: 71%, 9.0:1 dr; *isolated*: 52.5 mg, 0.120 mmol, 60.2%, >20:1 dr);
Run 2 (*crude*: 69%, 9.2:1 dr; *isolated*: 50.7 mg, 0.116 mmol, 58.1%, >20:1 dr);
Run 3 (*crude*: 72%, 8.9:1 dr; *isolated*: 55.0 mg, 0.126 mmol, 63.0%, >20:1 dr).
Average: *crude*: **71% yield, 9.0:1 dr** (*syn:anti*). *isolated*: **60%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.20 (td, *J* = 7.7, 1.7 Hz, 1H), 5.63 – 5.55 (m, 2H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 5.10 (dt, *J* = 9.7, 7.9 Hz, 1H), 2.72 (ddd, *J* = 14.5, 7.8, 2.3 Hz, 1H), 2.44 (s, 3H), 1.84 (ddd, *J* = 14.4, 10.9, 9.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.1, 145.2, 136.5, 136.4, 135.9, 133.0, 130.2, 129.9, 129.3, 128.2, 127.4, 121.1, 119.3, 76.7, 59.1, 37.6, 21.8. HRMS (ESI) m/z calculated for $C_{19}H_{20}NO_4SBr$ [M+H]+: 436.0218, found 436.0232.

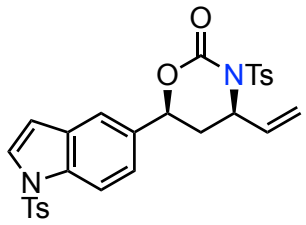


(±)-(4R,6S)-6-(naphthalen-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**33**). Racemic carbamate **S10** (81.9 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 74%, 6.2:1 dr; *isolated:* 46.7 mg, 0.114 mmol, 57.2%, >20:1 dr);
Run 2 (*crude:* 72%, 5.9:1 dr; *isolated:* 45.8 mg, 0.112 mmol, 56.1%, >20:1 dr);
Run 3 (*crude:* 71%, 6.5:1 dr; *isolated:* 45.2 mg, 0.111 mmol, 55.3%, >20:1 dr).
Average: *crude*: **72% yield, 6.2:1 dr** (*syn:anti*). *isolated*: **56%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.79 (m, 4H), 7.51 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.61 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.46 (dd, *J* = 11.0, 2.4 Hz, 1H), 5.42 (d, *J* = 17.0 Hz, 1H), 5.25 (d, *J* = 10.1 Hz, 1H), 5.12 (dt, *J* = 9.6, 8.0 Hz, 1H), 2.65 (ddd, *J* = 14.4, 7.9, 2.5 Hz, 1H), 2.44 (s, 3H), 2.21 – 2.12 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 145.1, 136.7, 135.9, 134.2, 133.5, 133.1, 129.8, 129.3,

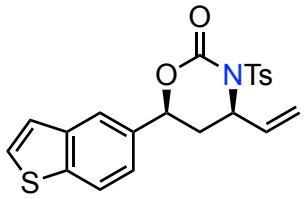
128.9, 128.3, 127.9, 126.8, 126.8, 125.4, 123.3, 119.2, 77.7, 59.1, 38.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{22}NO_4S$ $[M+H]^+$: 408.1270, found 408.1272. Spectra match literature report.[4]



(±)-(4R,6S)-3-tosyl-6-(1-tosyl-1H-indol-5-yl)-4-vinyl-1,3-oxazinan-2-one (34). Racemic carbamate **S11** (110.3 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (5 => 25% acetone/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 65%, 4.4:1 dr; *isolated:*55.6 mg, 0.101 mmol, 50.5%, >20:1 dr);
Run 2 (*crude:* 67%, 4.3:1 dr; *isolated:*57.5 mg, 0.104 mmol, 52.2%, >20:1 dr);
Run 3 (*crude:* 64%, 4.6:1 dr; *isolated:*56.5 mg, 0.103 mmol, 51.3%, >20:1 dr).
Average: *crude*: **65% yield, 4.4:1 dr** (*syn:anti*). *isolated*: **51%, >20:1 dr** (*syn:anti*).

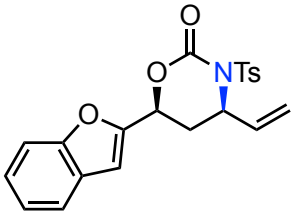
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.24 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.63 (d, *J* = 3.7 Hz, 1H), 5.57 (ddd, *J* = 16.9, 10.0, 8.1 Hz, 1H), 5.40 (d, *J* = 17.0 Hz, 1H), 5.33 (dd, *J* = 11.3, 2.2 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 5.06 (app dt, *J* = 9.8, 8.0 Hz, 1H), 2.54 (ddd, *J* = 14.4, 7.9, 2.2 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 2.08 (ddd, *J* = 14.4, 11.3, 9.9 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.2, 145.3, 145.1, 136.6, 135.9, 135.0, 135.0, 131.9, 130.1, 130.0, 129.8, 129.3, 127.4, 126.9, 122.7, 119.3, 119.2, 113.9, 109.1, 77.7, 59.1, 38.4, 21.8, 21.7. **HRMS (ESI)** *m/z* calculated for $C_{28}H_{26}N_2O_6S_2$ $[M+H]^+$: 551.1311, found 551.1299.



(±)-(4R,6S)-6-(benzo[b]thiophen-5-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**35**). Racemic carbamate **S12** (83.1 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 89%, 4.3:1 dr; *isolated:* 51.4 mg, 0.124 mmol, 62.2%, >20:1 dr);
Run 2 (*crude:* 86%, 4.0:1 dr; *isolated:* 54.1 mg, 0.131 mmol, 65.4%, >20:1 dr);
Run 3 (*crude:* 88%, 4.1:1 dr; *isolated:* 51.1 mg, 0.124 mmol, 61.8%, >20:1 dr).
Average: *crude*: **88% yield, 4.1:1 dr** (*syn:anti*). *isolated*: **63%, >20:1 dr** (*syn:anti*).

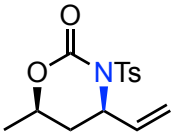
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4, 0.8 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H), 7.49 (d, *J* = 5.5 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.28 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.60 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.44 – 5.39 (m, 2H), 5.25 (dd, *J* = 10.1, 0.8 Hz, 1H), 5.10 (dt, *J* = 9.9, 8.0 Hz, 1H), 2.61 (ddd, *J* = 14.5, 7.9, 2.4 Hz, 1H), 2.44 (s, 3H), 2.14 (ddd, *J* = 14.4, 11.1, 9.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.2, 145.1, 140.3, 139.8, 136.7, 136.0, 133.1, 129.8, 129.3, 127.8, 124.0, 123.1, 122.0, 121.3, 119.1, 77.8, 59.1, 38.6, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{20}NO_4S_2$ $[M+H]^+$: 414.0834, found 414.0842.



(±)-(4*R*,6*S*)-6-(benzofuran-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (36).
Racemic carbamate **S13** (110.3 mg, 0.2 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv). Purification by flash chromatography (5 => 25% acetone/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 85%, 2.5:1 dr; *isolated:*40.1 mg, 0.101 mmol, 50.4%, >20:1 dr);
Run 2 (*crude:* 89%, 2.3:1 dr; *isolated:*43.1 mg, 0.108 mmol, 54.2%, >20:1 dr);
Run 3 (*crude:* 87%, 2.5:1 dr; *isolated:*41.2 mg, 0.104 mmol, 51.8%, >20:1 dr).
Average: *crude*: **87% yield, 2.4:1 dr** (*syn:anti*). *isolated*: **52%, >20:1 dr** (*syn:anti*).

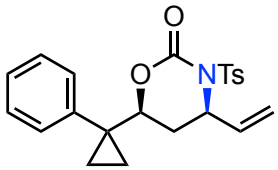
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.25 – 7.22 (m, 1H), 6.77 (s, 1H), 5.60 (ddd, *J* = 17.0, 10.1, 7.8 Hz, 1H), 5.49 (dd, *J* = 9.3, 3.3 Hz 1H), 5.39 (app d, *J* = 16.9 Hz, 1H), 5.21 (app d, *J* = 10.1 Hz, 1H), 5.14 (app q, *J* = 7.9 Hz, 1H), 2.71 (ddd, *J* = 14.5, 7.8, 3.3 Hz, 1H), 2.52 – 2.45 (m, 1H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.1, 151.6, 149.2, 145.3, 136.2, 135.7, 129.8, 129.4, 127.6, 125.3, 123.4, 121.7, 119.2, 111.6, 105.9, 71.8, 58.3, 33.8, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{20}NO_5S$ $[M+H]^+$: 398.1062, found 398.1051.



(±)-(4S,6S)-6-methyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (37)
Racemic carbamate **S17** (59.5 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude*: 86%, 8.1:1 dr; *isolated*: 42.0 mg, 0.142 mmol, 71.1%, >20:1 dr);
Run 2 (*crude*: 91%, 8.1:1 dr; *isolated*: 47.0 mg, 0.159 mmol, 79.6%, >20:1 dr);
Run 3 (*crude*: 92%, 7.8:1 dr; *isolated*: 48.2 mg, 0.163 mmol, 81.6%, >20:1 dr).
Average: *crude*: **90% yield, 8.0:1 dr** (*syn:anti*). *isolated*: **77%, >20:1 dr** (*syn:anti*).

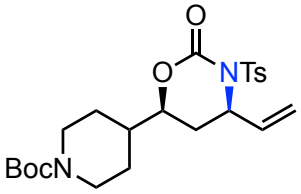
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.59 (ddd, *J* = 17.3, 10.1, 7.9 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 4.94 (app q., *J* = 8.5 Hz, 1H), 4.40 (dqd, *J* = 10.3, 6.3, 2.3 Hz, 1H), 2.42 (s, 3H), 2.34 (ddd, *J* = 14.2, 8.1, 2.4 Hz, 1H), 1.71 (ddd, *J* = 14.3, 10.7, 9.6 Hz, 1H), 1.35 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.3, 145.0, 137.0, 136.1, 129.7, 129.2, 118.7, 73.1, 58.8, 37.6, 21.8, 20.2. **HRMS (ESI)** *m/z* calculated for $C_{14}H_{18}NO_4S$ $[M+H]^+$: 296.0951, found 296.0957.



(±)-(4R,6S)-6-(1-phenylcyclopropyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (38).
Racemic carbamate **S19** (79.9 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 15% ethyl acetate/hexanes) afforded the *syn* diastereomer as a white solid.

Run 1 (*crude*: 90%, 7.8:1 dr; *isolated*: 57.0 mg, 0.143 mmol, 71.7%, >20:1 dr);
Run 2 (*crude*: 90%, 7.6:1 dr; *isolated*: 56.8 mg, 0.143 mmol, 71.4%, >20:1 dr);
Run 3 (*crude*: 86%, 8.1:1 dr; *isolated*: 53.7 mg, 0.135 mmol, 67.5%, >20:1 dr).
Average: *crude*: **89% yield, 7.9:1 dr** (*syn:anti*). *isolated*: **70%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.26 (m, 5H), 5.42 – 5.29 (m, 2H), 5.17 (dd, *J* = 9.3, 1.5 Hz, 1H), 4.82 (dt, *J* = 10.4, 7.8 Hz, 1H), 3.84 (dd, *J* = 11.6, 1.9 Hz, 1H), 2.42 (s, 3H), 2.31 (ddd, *J* = 14.4, 8.0, 1.9 Hz, 1H), 1.50 (ddd, *J* = 14.3, 11.5, 10.4 Hz, 1H), 1.09 – 1.00 (m, 1H), 0.99 – 0.90 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.3, 144.9, 139.3, 136.8, 136.1, 131.3, 129.8, 129.2, 128.4, 127.6, 118.9, 82.1, 59.1, 34.5, 28.0, 21.8, 11.6, 10.2. **HRMS (ESI)** *m/z* calculated for $C_{22}H_{24}NO_4S$ $[M+H]^+$: 398.1429, found 398.1426.

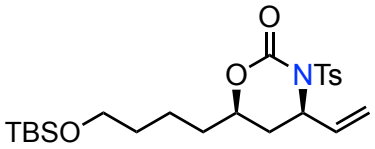


(±)-tert-butyl 4-((4R,6S)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)piperidine-1-carboxylate (39). Racemic carbamate **S22** (92.9 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 35% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude*: 71%, 5.5:1 dr, *isolated*: 53.2 mg, 0.109 mmol, 57.2%, >20:1 dr);
Run 2 (*crude*: 71%, 5.0:1 dr, *isolated*: 52.4 mg, 0.112 mmol, 56.4%, >20:1 dr);
Run 3 (*crude*: 73%, 5.3:1 dr, *isolated*: 54.2 mg, 0.111 mmol, 58.3%, >20:1 dr).
Average: *crude*: **72% yield, 5.3:1 dr** (*syn:anti*). *isolated*: **53%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.55 (ddd, *J* = 16.8, 10.0, 8.1 Hz, 1H), 5.37 (app d, *J* = 16.9, 1H), 5.24 (app d, *J* = 10.0, 1H), 4.90 (dt, *J* = 9.4,

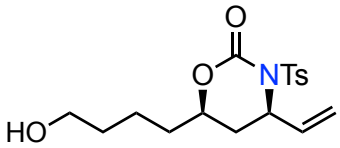
8.0 Hz, 1H), 4.24 – 4.09 (m, 2H), 4.06-4.02 (m, 1H), 2.68 – 2.58 (m, 2H), 2.43 (s, 3H), 2.32 (dd, *J* = 13.8, 7.7 Hz, 1H), 1.85 (d, *J* = 13.1 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.59-1.52 (m, 1H), 1.45 (s, 9H), 1.32 – 1.17 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.8, 150.4, 145.0, 136.9, 136.1, 129.8, 129.3, 118.9, 79.8, 79.5, 58.8, 43.7, 39.7, 33.4, 28.6, 27.2, 21.8. **HRMS (ESI)** m/z calculated for $C_{23}H_{33}N_2O_6S$ $[M+H]^+$: 465.2059, found 465.2049.



(±)-(4R,6R)-6-(4-((tert-butyldimethylsilyl)oxy)butyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**40**). Racemic carbamate S23 (93.9 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 25% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude:* 72%, 7.3:1 dr; *isolated:* 54.1 mg, 0.115 mmol, 55.7%, >20:1 dr);
Run 2 (*crude:* 74%, 7.4:1 dr; *isolated:* 53.4 mg, 0.113 mmol, 56.9%, >20:1 dr);
Run 3 (*crude:* 73%, 7.4:1 dr; *isolated:* 50.9 mg, 0.108 mmol, 54.2%, >20:1 dr).
Average: *crude*: **73% yield, 7.4:1 dr** (*syn:anti*). *isolated*: **56%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.56 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.37 (app d, *J* = 16.9 Hz, 1H), 5.23 (app d, *J* = 10.0 Hz, 1H), 4.92 (dt, *J* = 9.7, 8.1 Hz, 1H), 4.24 (dddd, *J* = 10.9, 7.5, 5.1, 2.2 Hz, 1H), 3.59 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.32 (ddd, *J* = 14.3, 8.0, 2.3 Hz, 1H), 1.76 – 1.63 (m, 3H), 1.63 – 1.54 (m, 1H), 1.50 (ddt, *J* = 12.8, 9.5, 5.2 Hz, 2H), 1.44 – 1.35 (m, 1H), 0.88 (s, 9H), 0.03 (s, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 144.9, 137.0, 136.0, 129.7, 129.2, 118.8, 76.6, 62.8, 58.9, 35.9, 33.9, 32.4, 26.1, 21.8, 21.3, 18.5, -5.2. **HRMS (ESI)** *m/z* calculated for $C_{23}H_{38}NO_5SSi$ $[M+H]^+$: 468.2240, found 468.2231.

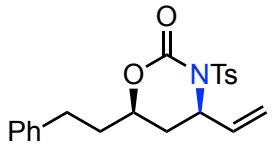


(±)-(4R,6R)-6-(4-hydroxybutyl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (41)

Racemic carbamate **S24** (71.1 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (30 => 60% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude:* 84%, 6.6:1 dr; *isolated:* 42.7 mg, 0.120 mmol, 60.1%, >20:1 dr);
Run 2 (*crude:* 81%, 6.9:1 dr; *isolated:* 45.6 mg, 0.128 mmol, 64.2%, >20:1 dr);
Run 3 (*crude*: 83%, 6.2:1 dr; *isolated:* 48.6 mg, 0.137 mmol, 68.4%, >20:1 dr).
Average: *crude*: **83% yield, 6.6:1 dr** (*syn:anti*). *isolated*: **64%, >20:1 dr** (*syn:anti*).

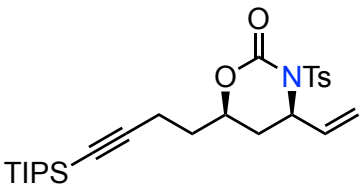
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.57 (ddd, *J* = 16.8, 10.1, 8.0 Hz, 1H), 5.36 (app d, *J* = 17.0 Hz, 1H), 5.23 (app d, *J* = 10.1 Hz, 1H), 4.96 – 4.89 (m, 1H), 4.25 (dddd, *J* = 10.7, 7.3, 4.8, 2.5 Hz, 1H), 3.64 (t, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 2.33 (ddd, *J* = 14.2, 8.1, 2.3 Hz, 1H), 1.77 – 1.65 (m, 2H), 1.63 – 1.50 (m, 4H), 1.50 – 1.39 (m, 1H), 1.36 – 1.28 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 145.0, 137.0, 136.0, 129.7, 129.3, 118.7, 76.5, 62.6, 58.8, 36.0, 34.0, 32.3, 21.8, 21.2. **HRMS (ESI)** *m/z* calculated for $C_{17}H_{24}NO_5S$ $[M+H]^+$: 354.1375, found 354.1381.



(±)-(4R,6R)-6-phenethyl-3-tosyl-4-vinyl-1,3-oxazinan-2-one (**42**).
Racemic carbamate **S25** (77.5 mg, 0.2 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *syn*-diastereomer as a white solid.

Run 1 (*crude:* 84%, 6.1:1 dr; *isolated*: 53.4 mg, 0.139 mmol, 69.3%, >20:1 dr);
Run 2 (*crude:* 83%, 6.2:1 dr; *isolated:* 51.4 mg, 0.133 mmol, 66.7%, >20:1 dr);
Run 3 (*crude:* 81%, 6.7:1 dr; *isolated:* 51.2 mg, 0.133 mmol, 66.4%, >20:1 dr).
Average: *crude*: **83% yield, 6.3:1 dr** (*syn:anti*). *isolated*: **67%, >20:1 dr** (*syn:anti*).

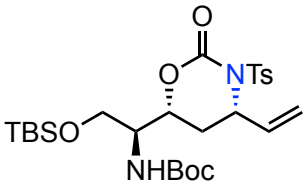
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 5.64 – 5.53 (m, 1H), 5.36 (app d, *J* = 17.0, 1H), 5.24 (app d, *J* = 10.0, 1H), 4.96 – 4.87 (m, 1H), 4.23 (tdd, *J* = 8.0, 4.4, 2.4 Hz, 1H), 2.81 (ddd, *J* = 14.6, 9.6, 5.4 Hz, 1H), 2.70 (ddd, *J* = 13.9, 9.3, 7.1 Hz, 1H), 2.44 (s, 3H), 2.32 (ddd, *J* = 14.3, 7.9, 2.4 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.85 (dddd, *J* = 14.2, 9.6, 7.1, 4.6 Hz, 1H), 1.74 (ddd, *J* = 14.3, 10.7, 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.4, 145.0, 140.6, 136.9, 136.0, 129.7, 129.3, 128.8, 128.5, 126.4, 118.8, 75.7, 58.8, 36.0, 36.0, 31.0, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{21}H_{24}NO_4S$ $[M+H]^+$: 386.1426, found 386.1420.



(±)-(4R,6R)-3-tosyl-6-(4-(triisopropylsilyl)but-3-yn-1-yl)-4-vinyl-1,3-oxazinan-2-one (**43**).
Racemic carbamate **S26** (98.4 mg, 0.20 mmol) was reacted according to the general procedure with addition of $Ph_2P(O)OH$ (4.4 mg, 0.02 mmol, 0.1 equiv).. Purification by flash chromatography (10 => 20% ethyl acetate/hexanes) afforded the *syn*- diastereomer as a white solid (with 3% starting material).

Run 1 (*crude:* 82%, 6.0:1 dr; *isolated:* 64.8 mg, 0.132 mmol, 66.1%, >20:1 dr);
Run 2 (*crude:* 87%, 5.2:1 dr; *isolated:* 61.9 mg, 0.126 mmol, 63.2%, >20:1 dr);
Run 3 (*crude:* 83%, 5.4:1 dr; *isolated:* 62.1 mg, 0.127 mmol, 63.4%, >20:1 dr).
Average: *crude*: **84% yield, 5.5:1 dr** (*syn:anti*). *isolated*: **64%, >20:1 dr** (*syn:anti*).

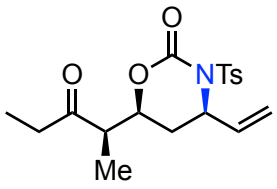
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.59 (ddd, *J* = 16.9, 10.1, 8.0 Hz, 1H), 5.38 (app d, *J* = 17.1 Hz, 1H), 5.25 (app d, *J* = 10.1 Hz, 1H), 4.92 (dt, *J* = 9.6, 7.9 Hz, 1H), 4.42 (dddd, *J* = 10.3, 7.5, 5.0, 2.3 Hz, 1H), 2.46 – 2.38 (m, 3H), 2.42 (s, 3H), 1.92 (ddt, *J* = 14.2, 7.7, 6.5 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.09 – 0.96 (m, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.1, 145.0, 136.9, 135.9, 129.7, 129.3, 118.9, 106.7, 82.1, 75.3, 58.9, 35.7, 33.2, 21.8, 18.8, 15.8, 11.3. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{40}NO_4SSi$ $[M+H]^+$: 490.2447, found 490.2437.



(–)-*tert*-butyl ((*S*)-2-((*tert*-butyldimethylsilyl)oxy)-1-((4*S*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)ethyl)carbamate (44). Racemic carbamate **S27** (111.4 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (10 => 30% ethyl acetate/hexanes) afforded the *syn*- diastereomer as a white solid.

Run 1 (*crude:* 92%, 4.4:1 dr; *isolated:* 79.8 mg, 0.144 mmol, 71.9%, >20:1 dr);
Run 2 (*crude:* 95%, 4.1:1 dr; *isolated:* 85.7 mg, 0.154 mmol, 77.2%, >20:1 dr);
Run 3 (*crude:* 91%, 4.1:1 dr; *isolated:* 78.0 mg, 0.141 mmol, 70.3%, >20:1 dr).
Average: *crude*: **93% yield, 4.2:1 dr** (*syn:anti*). *isolated*: **73%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.62 (ddd, *J* = 17.4, 10.1, 7.7 Hz, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 4.94-4.90 (m, 2H), 4.24 – 4.18 (m, 1H), 3.92 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.62 (dd, *J* = 10.3, 3.5 Hz, 1H), 2.42 (s, 3H), 2.42-2.37 (m, 1H), 1.92 (q, *J* = 11.0 Hz, 1H), 1.44 (s, 9H), 0.87 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 149.6, 144.9, 136.6, 135.8, 129.6, 129.1, 118.6, 80.1, 74.7, 60.8, 58.9, 53.3, 33.0, 28.3, 25.9, 21.6, 18.2, -5.5, -5.6. **HRMS (ESI)** *m/z* $C_{26}H_{43}N2O_7SSi$ $[M+H]^+$: 555.2560, found 555.2582. Optical rotation: $[\alpha]^{23}_D$ = -32.6 (c = 1.00, $CHCl_3$).



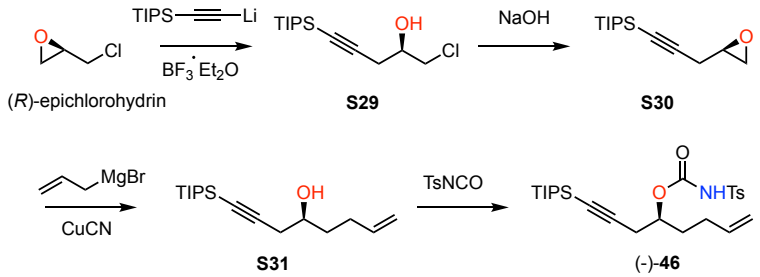
(+)-(4R,6S)-6-((R)-3-oxopentan-2-yl)-3-tosyl-4-vinyl-1,3-oxazinan-2-one (28b). Racemic carbamate **S28** (110.3 mg, 0.20 mmol) was reacted according to the general procedure. Purification by flash chromatography (5 => 25% acetone/hexanes) afforded the *syn*- diastereomer as a colorless oil.

Run 1 (*crude:*88%, 4.9:1 dr; *isolated:* 48.3 mg, 0.132 mmol, 66.1%, >20:1 dr);
Run 2 (*crude:*85%, 4.2:1 dr; *isolated:* 44.8 mg, 0.123 mmol, 61.3%, >20:1 dr);
Run 3 (*crude:*87%, 4.4:1 dr; *isolated:* 45.7 mg, 0.125 mmol, 62.5%, >20:1 dr).
Average: *crude*: **87% yield, 4.5:1 dr** (*syn:anti*). *isolated*: **63%, >20:1 dr** (*syn:anti*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.54 (ddd, *J* = 17.1, 10.1, 8.0 Hz, 1H), 5.37 (app d, *J* = 17.0 Hz, 1H), 5.24 (app d, *J* = 10.1 Hz, 1H), 4.90 (dt, *J* = 10.0, 8.0 Hz, 1H), 4.39 (ddd, *J* = 10.3, 7.7, 2.1 Hz, 1H), 2.82 (app p, *J* = 7.2 Hz, 1H), 2.58 (dq, *J* = 18.4, 7.2 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.42 (s, 3H), 2.33 (ddd, *J* = 14.1, 7.9, 2.1 Hz, 1H), 1.64 (ddd, *J* = 14.1, 10.9, 9.8 Hz, 1H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.8, 150.1, 145.1, 136.8, 135.9, 129.7, 129.3, 119.0, 77.2, 59.0, 49.0, 36.2, 33.9, 21.8, 13.6, 7.6. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{23}NO_5SNa$ $[M+Na]^+$: 388.1195, found 388.1186. Optical rotation: $[\alpha]^{23}_D$ = +16.8 (c = 0.98, $CHCl_3$).

Streamlining the Synthesis of Chiral Amino Alcohol Motifs to Vitamin D3 Derivatives.

Scheme S2. Synthesis of chiral *N*-tosyl carbamate (-)-46



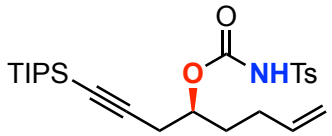
S29. A cooled (-78 °C) solution of (triisopropylsilyl)acetylene (11.6 mL, 51.9 mmol) in THF (60 mL) was treated with *n*-BuLi (1.6 M in hexanes, 36.4 mL, 58.3 mmol) and the suspension was stirred for 30 min at -78 °C. After addition of boron trifluoride diethyl etherate (7.24 mL, 58.3 mmol), the mixture was stirred for 30 min and treated with a solution of (*R*)-epichlorohydrin (3.00g, 32.4 mmol) in THF (50 mL) slowly. The reaction was stirred at -78 °C for 3 hours and quenched by addition of sat. aq. NH_4Cl. The mixture was transferred into a separatory funnel with diethyl ether (100 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (100 mL X 3). The combined organic the layers were washed by sat. aq. $NaHCO_3$, brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the desired product in 88% yield (7.86 g, 28.6 mmol) as a colorless oil.

S30. A cooled (0 °C) solution of **S29** (7.86g, 28.6 mmol) in dichloromethane (200 mL) was treated with powdered NaOH (4.00 g, 100 mmol) and was stirred for 1 hour while warming to room temperature. The reaction was quenched by addition of ice cooled H_2O (100 mL). The mixture was transferred into a separatory funnel and the layers were separated. The aqueous layer was extracted with dichloromethane (100 mL X 3). The combined organic the layers were washed with H_2O (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the desired product in 79% yield (5.40 g, 22.6 mmol) as a colorless oil.

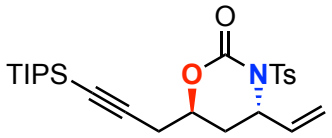
S31. To an oven-dried flask equipped with a stir bar was added copper(I) cyanide (90 mg, 1.0 mmol, 0.05 equiv.), THF (60 mL) and **S30** (5.40 g , 22.6 mmol, 1.0 equiv.). The reaction flask was cooled to -78 °C and 3-butenylmagnesium bromide (0.5 M, 60 mL, 30 mmol, 1.0 equiv.) was added dropwise. The reaction was stirred at -78 °C for 1 hours and allowed to warm up to room temperature. The reaction was quenched by addition of sat. aq. NH_4Cl. The mixture was transferred into a separatory funnel with diethyl ether (100 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (100 mL X 3). The combined organic layers were washed by brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the desired homoallylic alcohol product in 78% yield (4.96 g, 17.7 mmol) as a colorless oil.

(−)-(*S*)-1-(triisopropylsilyl)oct-7-en-1-yn-4-yl tosylcarbamate (46) was synthesized following general procedure for making *N*-tosyl carbamate **(Page S4)** using homoallylic alcohol **S31** (4.96g, 17.7 mmol) in 81% yield (6.87 g, 14.4 mmol) as a colorless gel.

44% overall yield over 4 steps.



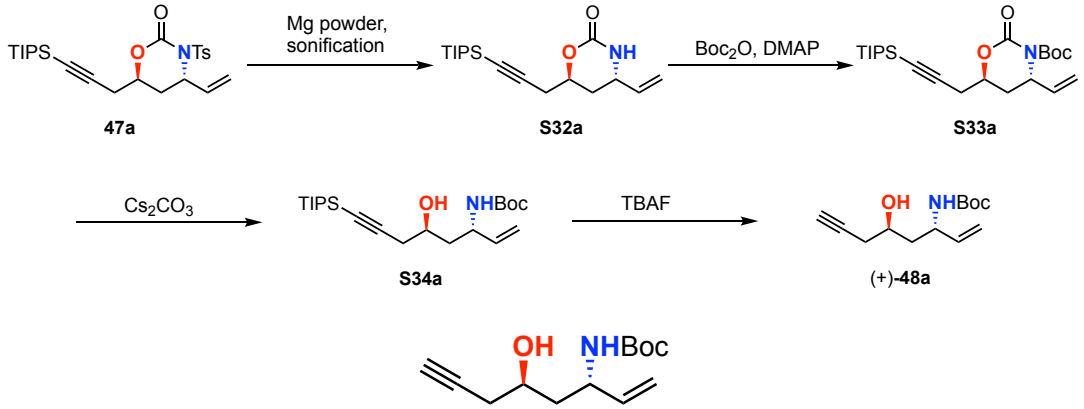
(−)-(*S*)-1-(triisopropylsilyl)oct-7-en-1-yn-4-yl tosylcarbamate (46). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.57 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.69 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 4.98 – 4.88 (m, 2H), 4.81 (ddd, *J* = 9.9, 7.3, 5.0 Hz, 1H), 2.56 – 2.44 (m, 2H), 2.44 (s, 3H), 2.01-1.97 (m, 2H), 1.89 – 1.79 (m, 1H), 1.76-1.72 (m, 1H), 1.08 – 0.93 (m, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.0, 145.2, 137.1, 135.6, 129.7, 128.5, 115.5, 102.5, 83.9, 75.2, 32.0, 29.1, 25.2, 21.8, 18.7, 11.3. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{40}NO_4SSi$ $[M+H]^+$: 478.2447, found 478.2445. Optical rotation: $[\alpha]^{23}_D$ = -24.3 (c = 0.80, $CHCl_3$).



(−)- (4*S*,6*R*)-3-tosyl-6-(3-(triisopropylsilyl)prop-2-yn-1-yl)-4-vinyl-1,3-oxazinan-2-one (47a). *N*-tosyl carbamate **46** reacted following general procedure (**Page S25**) of Pd(II)/ (±)-MeO SOX catalyzed allylic C-H amination for *syn*-1,3 oxazinanone on a 3 mmol scale.
Run 1 (*crude*: 77%, 19:1 dr; *isolated: 974.7 mg* , 2.05 mmol, 68.3%, >20:1 dr);
Run 2 (*crude*: 79%, 18:1 dr; *isolated*: 1.024 g, 2.15 mmol, 71.8% >20:1 dr),
Average yield: 70%, >20:1 dr (***anti:syn***).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.89 (ddd, *J* = 16.9, 10.6, 4.6 Hz, 1H), 5.43 (dd, *J* = 10.6, 1.6 Hz, 1H), 5.39 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.27-5.23 (m, 1H), 4.55 – 4.45 (m, 1H), 2.71 (dd, *J* = 16.9, 4.3 Hz, 1H), 2.55 (dd, *J* = 16.9, 8.3 Hz, 1H), 2.43 (s, 3H), 2.32-2.28 (m, 1H), 2.06 (ddd, *J* = 14.1, 12.0, 5.2 Hz, 1H), 1.04-0.96 (m, 21H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 145.2, 135.6, 135.5, 129.5, 129.4, 118.8, 101.3, 85.1, 73.7, 56.2, 31.9, 26.4, 21.8, 18.7, 11.2. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}NO_4SiS$ $[M+H]^+$: 476.2291, found 476.2298. Optical rotation: $[\alpha]^{23}_D$ = -13.6 (c = 0.81, $CHCl_3$).

Scheme S3. *N*-tosyl carbamate cleavage and deprotection.



(+)- *tert*-butyl ((3*S*,5*R*)-5-hydroxyoct-1-en-7-yn-3-yl)carbamate (48a).
To a 1 dram vial (equipped with Teflon cap) under argon was added **47a** (475.7mg, 1.0 mmol), MeOH (0.5 mL), THF (0.2 mL) and Mg powder[8] (120 mg, 5.0 mmol, 5.0 equiv.). The reaction was sonicated for 1 hour under room temperature. The mixture was transferred into a separatory funnel with ethyl acetate (5 mL) and the layers were separated. The aqueous layer was extracted with ethyl acetate (10 mL X 3). The combined organic layers were washed by brine, dried over anhydrous $MgSO_4$ filtered and concentrated under reduced pressure into a 20 mL vial. The crude product **S32a** was carried through the next step without purification.

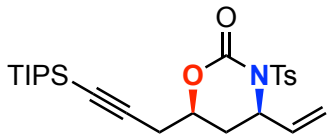
To the 20 mL vial with the crude product **S32a** was added a stir bar, CH_2Cl_2 (5 mL), Boc_2O (436.4 mg, 2.0 mmol, 2.0 equiv.) and DMAP (24.4 mg, 0.2 mmol, 0.2 equiv.). The reaction was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure and purified by a silica plug (15% ethyl acetate/hexanes) to afford the product **S33a** as a colorless oil.

To a 20 mL vial was added a stir bar, the **S33a**, Cs_2CO_3 [9] (163mg, 0.5 mmol. 0.5 equiv.) and MeOH (10 mL, 0.1M). The reaction was stirred under room temperature overnight. The mixture was transferred into a separatory funnel with diethyl ether (5 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (10 mL X 3). The combined organic layers were washed by brine, dried over anhydrous $MgSO_4$ filtered and concentrated under reduced pressure into a 20 mL vial. The crude product **S34a** was carried through the next step without purification.

To the 20 mL vial charged **S34a** was added a stir bar, THF (2 mL, 0.5M) and TBAF (1.0 M in THF, 2.0 mL, 2.0 equiv.). The reaction was stirred under room temperature for 2 hours. Upon completion, the reaction mixture was transferred into a separatory funnel with diethyl ether (5 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (10 mL X 3). The combined organic layers were washed by brine, dried over anhydrous $MgSO_4$ filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the **48a** as a colorless oil.
Over 4 steps: Run 1: 73.9% yield (176.8 mg, 0.739 mmol); Run 2: 68.7% yield (164.4 mg, 0.687 mmol)). **Average: 71% yield.**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.76 (ddd, *J* = 17.3, 10.5, 5.0 Hz, 1H), 5.13 (ddd, *J* = 17.3, 1.8, 0.9 Hz, 1H), 5.06 (app dt, *J* = 10.5, 1.3 Hz, 1H), 4.71 (d, *J* = 9.1 Hz, 1H), 4.37-4.33 (m, 1H), 3.85 – 3.79 (m, 1H), 3.76 (d, *J* = 7.5 Hz, 1H), 2.39 (ddd, *J* = 16.6, 6.0, 2.7 Hz, 1H), 2.30 (ddd, *J* = 16.6, 6.6, 2.7 Hz, 1H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.67 (ddd, *J* = 13.9, 10.5, 3.5 Hz, 1H), 1.58 (ddd,

J = 13.7, 10.4, 2.6 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.9, 138.2, 114.9, 81.2, 80.3, 70.6, 66.5, 49.3, 42.2, 28.5, 27.0. **HRMS (ESI)** *m/z* calculated for $C_{13}H_{21}NO_3Na$ $[M+Na]^+$: 262.1419, found 262.1428. Optical rotation: $[\alpha]^{23}_D$ = +10.24 (c = 0.99, $CHCl_3$). ^{1}H NMR and ^{13}C NMR match literature report.[10]

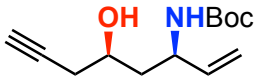


(–)- (4*R*,6*R*)-3-tosyl-6-(3-(triisopropylsilyl)prop-2-yn-1-yl)-4-vinyl-1,3-oxazinan-2-one (47b). *N*-tosyl carbamate (–)-**46** reacted following a modified general procedure of Pd(II)/ (±)-CF_3 SOX catalyzed allylic C-H amination for *syn*-1,3 oxazinanone using 2,5 dimethylbenzoquinone (2,5 DMBQ) (1.2 equiv) in 3 mmol scale.

Run 1 (*crude*: 83%, 4.0:1 dr; *isolated:* 900.5 mg, 1.89 mmol, 63.1 %, >20:1 dr);
Run 2 (*crude*: 78%, 4.2:1 dr; *isolated*: 859.1 mg, 1.81 mmol, 59.5 % >20:1 dr),
Average yield: 61%, >20:1 dr (***syn:anti***).

Slightly lower yield was achieved following the general procedure (Pd(II) / (±)-CF_3 SOX / BQ condition) with addition of 10% $Ph_2P(O)OH$ (0.2 mmol scale):
(*crude*: 69%, 5.2:1 dr; *isolated:* 52.4 mg, 0.110 mmol, 55.1 %, >20:1 dr);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.62 (ddd, J = 17.5, 10.2, 7.6 Hz, 1H), 5.37 (app d, J = 17.0 Hz, 1H), 5.26 (app d, J = 10.1 Hz, 1H), 4.99 (app q, J = 8.1 Hz, 1H), 4.38 (dddd, J = 10.1, 8.6, 4.6, 2.8 Hz, 1H), 2.75 (dd, J = 16.9, 4.6 Hz, 1H), 2.62 – 2.51 (m, 2H), 2.42 (s, 3H), 1.93 (ddd, J = 14.2, 10.2, 8.9 Hz, 1H), 1.07-0.97 (m, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.7, 145.1, 136.7, 135.8, 129.7, 129.3, 118.8, 101.2, 85.2, 74.5, 58.4, 34.5, 25.7, 21.8, 18.7, 11.3. **HRMS (ESI)** *m/z* calculated for $C_{25}H_{38}NO_4SiS$ $[M+H]^+$: 476.2291, found 476.2293. Optical rotation: $[\alpha]^{23}_D$ = -5.6 (c = 0.068, $CHCl_3$).

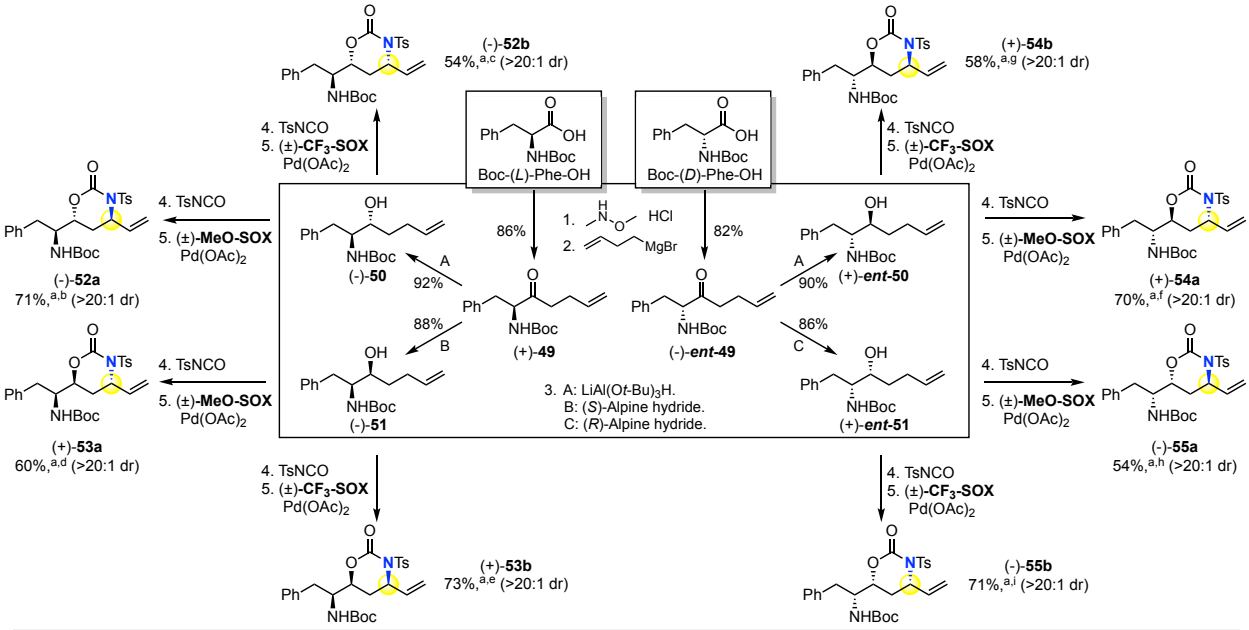


(–)-*tert*-butyl ((3*R*,5*R*)-5-hydroxyoct-1-en-7-yn-3-yl)carbamate (48b) was synthesized following the same procedure of **48a** using **47b** as a colorless oil.
Over 4 steps: Run 1 66.2% yield (158.4 mg, 0.662 mmol); Run 2 69.6% yield (166.6 mg, 0.696 mmol)). **Average: 68% yield.**

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.77 (ddd, J = 16.8, 10.3, 6.1 Hz, 1H), 5.20 (app dt, J = 17.2, 1.3 Hz, 1H), 5.12 (app dt, J = 10.4, 1.3 Hz, 1H), 4.75-4.71 (m, 1H), 4.26-4.22 (m, 1H), 3.87 (dddd, J = 8.4, 5.8, 5.8, 4.1 Hz, 1H), 2.60-2.47 (m, 1H), 2.47 – 2.35 (m, 2H), 2.05 (t, J = 2.6 Hz, 1H), 1.81-1.77 (m, 1H), 1.76 – 1.69 (m, 1H), 1.43 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.7, 138.6, 115.3, 80.6, 79.8, 71.2, 67.9, 51.1, 41.4, 28.5, 27.7. **HRMS (ESI)** *m/z* calculated for $C_{13}H_{21}NO_3Na$ $[M+Na]^+$: 262.1419, found 262.1423. Optical rotation: $[\alpha]^{23}_D$ = -18.8 (c = 1.01, $CHCl_3$). ^{1}H NMR and ^{13}C NMR match literature report.[10]

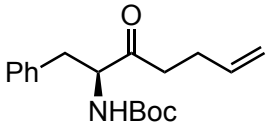
Stereodivergent Synthesis of Chiral Diamino Alcohol Motif in 8 Diastereomers

Figure S2. Stereodivergent synthesis of chiral diamino alcohol motif in 8 diastereomers



[a]Isolated yield of major diastereomer (>20:1 dr) over two steps. Crude yield and dr determined by ^{1}H NMR: [b]89%, 9.1: dr. [c]68%, 6.5:1 dr. [d]85%, 3.3:1 dr. [e]86%, 13:1 dr. [f]84%, 9.3:1. [g]72%, 7.4:1 dr. [h]79% 3.5:1 dr. [i]82%, 14:1 dr.

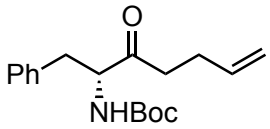
1. Synthesis of amino ketones (49 and *ent*-49):



(+)-*tert*-butyl (*S*)-(3-oxo-1-phenylhept-6-en-2-yl)carbamate (49).

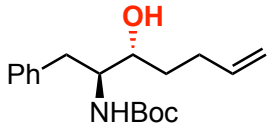
49 was synthesized via weinreb amide substitution with the Grignard reagent 3-butenylmagnesium bromide following a literature procedure for a similar compound[11] using Boc-(*L*)-phenylalanine (2.65g, 10 mmol) in 86% yield (2.62g, 8.63 mmol) over two steps as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.23 (app t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.0 Hz, 2H), 5.73 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.11 (d, *J* = 7.8 Hz, 1H), 5.02 – 4.93 (m, 2H), 4.53 (app q, *J* = 7.0 Hz, 1H), 3.05 (dd, *J* = 13.9, 6.8 Hz, 1H), 2.95 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.51 (ddd, *J* = 17.6, 8.5, 6.4 Hz, 1H), 2.43 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.35 – 2.20 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.6, 155.3, 136.9, 136.3, 129.4, 128.8, 127.1, 115.6, 80.0, 60.2, 40.1, 38.0, 28.4, 27.4. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{26}NO_3$ $[M+H]^+$: 304.1913, found 304.1901. Optical rotation: $[\alpha]^{23}_D$ = +54.1 (c = 0.99, $CHCl_3$).



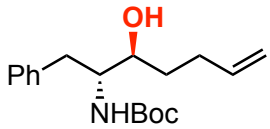
(–)-*tert*-butyl (*R*)-(3-oxo-1-phenylhept-6-en-2-yl)carbamate (*ent*-49).
***ent*-49** was synthesized following the same procedure of **49** using Boc-(*D*)-phenylalanine in 82% yield (2.49g, 8.21 mmol). ^{1}H NMR ,^{13}C NMR match **49** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{18}H_{26}NO_3$ $[M+H]^+$: 304.1913, found 304.1905. Optical rotation: $[\alpha]^{23}_D$ = -53.8 (c = 0.90, $CHCl_3$).

2. Synthesis of amino alcohols (50, *ent*-50, 51, *ent*-51):



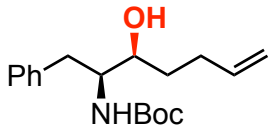
(–)-*tert*-butyl ((2*S*,3*R*)-3-hydroxy-1-phenylhept-6-en-2-yl)carbamate (50).
Following literature procedure for diastereoselective reduction of α-amino ketone to *anti* 1,2 amino alcohol.[12] To a solution of LiAl(O*t*-Bu)$_3$H (1.017g, 4.0 mmol, 2.0 equiv.) in EtOH (12 mL) at -78 °C was added dropwise an ice cooled solution of **49** (606.8 mg, 2.0 mmol, 1.0 equiv.) in EtOH (16 mL). After 2 hours, the reaction was quenched with 10% citric acid solution. The mixture was transferred into a separatory funnel with ethyl acetate (50 mL) and the layers were separated. The aqueous layer was extracted with ethyl acetate (25 mL X 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via a silica plug (ethyl acetate in hexanes) to afford the desired product **33** in 92% yield (562.5 mg, 1.84 mmol) as a white solid (>20:1 *anti* : *syn*). Relative stereochemistry was confirmed by formation of cyclic carbamate (see following section).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 5.85 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.07 (app d, *J* = 17.1, 1H), 4.99 (app d, *J* = 10.2 Hz, 1H), 4.66 – 4.55 (m, 1H), 3.87 – 3.79 (m, 1H), 3.77 – 3.67 (m, 1H), 2.89 (dd, *J* = 14.2, 4.8 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.31 (dq, *J* = 14.4, 7.0 Hz, 1H), 2.21 – 2.10 (m, 1H), 1.66 – 1.51 (m, 2H), 1.35 (s, 9H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.4, 138.4, 138.3, 129.4, 128.6, 126.5, 115.3, 79.8, 73.8, 56.9, 35.7, 32.7, 30.5, 28.4. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$: 306.2069, found 306.2056. **Optical rotation**: $[\alpha]^{23}_D$ = -28.5 (c = 0.99, $CHCl_3$).



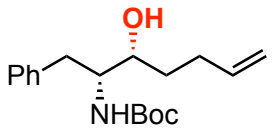
(+)-*tert*-butyl ((2*R*,3*S*)-3-hydroxy-1-phenylhept-6-en-2-yl)carbamate (*ent*-50).
Following the same procedure of **50** using ***ent*-49**. The desired product ***ent*-50** was afforded in 90% yield (550.9 mg, 1.80 mmol) as a white solid (>20:1 *anti* : *syn*). Relative stereochemistry was confirmed by formation of cyclic carbamate (see following section).

^{1}H NMR ,^{13}C NMR match **50** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$: 306.2069, found 306.2056. **Optical rotation**: $[\alpha]^{23}_D$ = +28.6 (c = 0.93, $CHCl_3$).



(–)-*tert*-butyl ((2*S*,3*S*)-3-hydroxy-1-phenylhept-6-en-2-yl)carbamate (51).
Following literature procedure for diastereoselective reduction of α-amino ketone to *syn*- 1,2 amino alcohol.[12] (*S*)-Alpine-Hydride solution was freshly prepared according to H. C. Brown's procedure:[13] To a flamed dried 100 mL round bottom flask with stir bar was added commercial (*S*)-Alpine-Borane solution (0.5 M in THF from Sigma Aldrich, 8.0 mL, 4.0 mmol). The flask was cooled to -78 °C and *t*-BuLi solution (1.7 M in pentane, 4.7 mL, 8.0 mmol) was added dropwise. The reaction was stirred at -78 °C for 5 min and allowed to warm up to room temperature until the reaction turned a homogenous and colorless solution from a bright yellow heterogeneous mixture. Freshly prepared (*S*)-Alpine-Hydride solution (cooled to -78 °C) was added dropwise to a solution of **32** (606.8 mg, 2.0 mmol, 1.0 equiv.) at -78 °C, and the reaction was stirred at 78 °C for 1 hour. The reaction was quenched with 10% citric acid solution. The mixture was transferred into a separatory funnel with diethyl ether (30 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (25 mL X 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude mixture was purified via flash column chromatography (ethyl acetate in hexanes) to afford the desired product **51** in 88% yield (545.4 mg, 1.79 mmol) as a white solid (>20:1 *syn* : *anti*). Relative stereochemistry was confirmed by formation of cyclic carbamate (see following section).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 5.77 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (app d, *J* = 17.1, 1H), 4.93 (app d, *J* = 10.2 Hz, 1H), 4.89-4.85 (m, 1H), 3.76-3.72 (m, 1H), 3.59 (ddd, *J* = 7.9, 5.1, 2.3 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.19 (s, 1H), 2.12 (app p, *J* = 7.0 Hz, 2H), 1.68 – 1.47 (m, 2H), 1.40 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.3, 138.6, 138.3, 129.4, 128.6, 126.5, 115.2, 79.5, 71.4, 55.7, 38.7, 33.7, 30.2, 28.5. **HRMS (ESI)** *m/z* calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$: 306.2069, found 306.2068. **Optical rotation**: $[\alpha]^{23}_D$ = -22.6 (c = 1.04, $CHCl_3$).

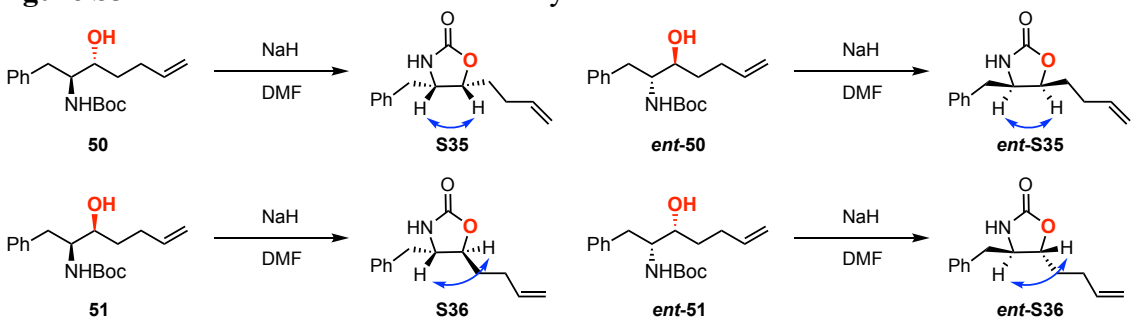


(+)-*tert*-butyl ((*R*,3*R*)-3-hydroxy-1-phenylhept-6-en-2-yl)carbamate (*ent*-51).
***ent*-31** was prepared following the same procedure as **51** using ***ent*-49** and (*R*)-Alpine-Hydride solution (prepared using the same procedure[13] as (*S*)-Alpine-Hydride using commercial (*R*)-Alpine-Borane solution (0.5 M in THF from Sigma Aldrich)) in 86% yield (524.7 mg, 1.72 mmol) as a white solid (>20:1 *syn* : *anti*). Relative stereochemistry was confirmed by formation of cyclic carbamate (see following section).

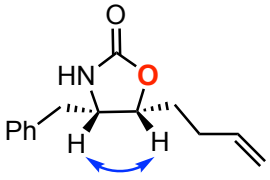
^{1}H NMR ,^{13}C NMR match **51** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{18}H_{28}NO_3$ $[M+H]^+$: 306.2069, found 306.2056. **Optical rotation**: $[\alpha]^{23}_D$ = +22.8 (c = 0.89, $CHCl_3$).

3. Confirm relative stereochemistry of amino alcohols (50/*ent*-50/51/*ent*-51).

Figure S3. Confirm relative stereochemistry of amino alcohols.

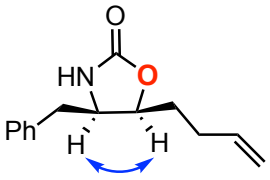


To confirm the relative stereochemistry of Boc protected amino alcohol (**50**/***ent*-50**/**51**/***ent*-51**). They were transformed into corresponding cyclic carbamates following literature procedure:[14] To a stirred 0 °C suspension of NaH (26.7 mg of 90% NaH, 1.0 mmol, 2.0 equiv.) in DMF (2.0 mL) was added a 0 °C solution of Boc protected amino alcohol (**50**/***ent*-50**/**51**/***ent*-51**) (152.7 mg, 0.5 mmol,1.0 equiv.) in DMF (1 mL). After 2 hours, the reaction was quenched with 0.5 M HCl solution. The mixture was transferred into a separatory funnel with diethyl ether (10 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (10 mL X 3). The combined organic layers were washed by brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction were analyzed by ^{1}H NMR. The relative stereochemistry is confirmed according to literature report, based on coupling constant of oxazolidinone.[14,15]



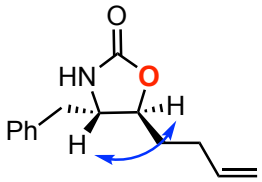
(J =7.4 Hz)

S35. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 7.18 – 7.14 (m, 2H), 5.92 – 5.77 (m, 1H), 5.14 – 5.02 (m, 2H), 4.91 (s, 1H), **4.69** (ddd, J = 10.2, **7.4**, 3.8 Hz, 1H), **3.96** (ddd, J = 11.1, **7.4**, 3.6 Hz, 1H), 2.87 (dd, J = 13.4, 3.6 Hz, 1H), 2.67 (dd, J = 13.4, 11.1 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.21 (ddtt, J = 14.3, 8.4, 7.0, 1.3 Hz, 1H), 1.98 (dddd, J = 14.0, 10.2, 8.7, 5.2 Hz, 1H), 1.74 (dddd, J = 14.0, 9.1, 7.0, 3.8 Hz, 1H). See spectrum for assignment.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.6, 136.9, 136.7, 129.2, 129.1, 127.3, 116.2, 79.2, 56.9, 36.5, 30.1, 28.9. **HRMS (ESI)** *m/z* calculated for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found 232.1335.



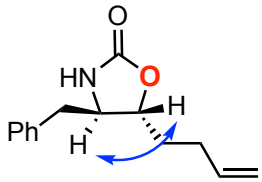
(J =7.4 Hz)

***ent*-S35.** Spectra match **S35**.



(J = 5.1-5.4 Hz)

S36. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.24 (m, 1H), 7.19 – 7.14 (m, 2H), 5.72 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.67 (br s, 1H), 5.05 – 4.94 (m, 2H), **4.30** (dt, J = 8.3, **5.1** Hz, 1H), **3.67** (tdd, J = 6.8, **5.4**, 1.0 Hz, 1H), 2.84 (d, J = 6.9 Hz, 2H), 2.22 – 2.05 (m, 2H), 1.77 (dtd, J = 14.1, 8.5, 5.7 Hz, 1H), 1.57 (dddd, J = 13.8, 9.0, 6.9, 4.6 Hz, 1H). See spectrum for assignment. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.8, 136.9, 136.1, 129.2, 129.1, 127.4, 115.9, 81.3, 59.2, 41.7, 33.9, 28.9. **HRMS (ESI)** *m/z* calculated for $C_{14}H_{18}NO_2$ $[M+H]^+$: 232.1338, found 232.1335.

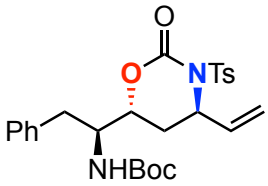


(J = 5.1-5.4 Hz)

***ent*-S36**. Spectra match **S36**.

4. Synthesis of chiral diamino alcohol motifs

General procedure for synthesizing *N*-tosyl carbamate from Boc protected amino alcohol (**50**/*ent*-**50**/**51**/*ent*-**51**): A flame dried 100 mL round bottom flask under argon was charged with a stir bar, Boc protected amino alcohol (**50**/*ent*-**50**/**51**/*ent*-**51**) (1.0 mmol), and THF (3 mL). The flask was cooled to 0 °C and *p*-toluenesulfonyl isocyanate (0.15 mL, 1.0 mmol) was added dropwise. The reaction was stirred for 30 min and then quenched with sat. aq. NH_4Cl. The mixture was diluted with ethyl acetate (10 mL) and washed once with brine (10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by a flash silica plug (30% ethyl acetate / hexanes) provided pure bis-homoallylic N-tosyl carbamates.

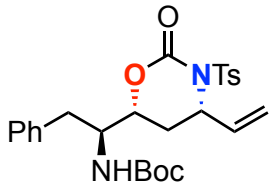


(–)-*tert*-butyl ((*S*)-1-((4*R*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (52a). *N*-tosyl carbamate was synthesized from **(–)-50** in quantitative

yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/MeO-SOX catalyzed allylic C—H amination for *anti*-1,3 oxazinanone to afford (–)-**52a.**

Run 1 (*crude:*86%, 9.3:1 dr; *isolated:* 70.4 mg, 0.141 mmol, 70.3%, >20:1 dr);
Run 2 (*crude:*88%, 9.0:1 dr; *isolated:* 71.3 mg, 0.142 mmol, 71.2%, >20:1 dr);
Run 3 (*crude:*90%, 8.9:1 dr; *isolated:* 72.8 mg, 0.145 mmol, 72.7%, >20:1 dr).
Average yield: *crude*: **89%, 9.1:1** (*anti:syn*)**,** *isolated*: **71%, >20:1 dr** (*anti:syn*).

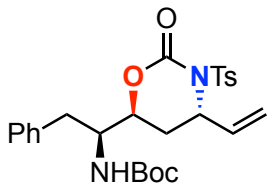
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 5.84 (ddd, *J* = 17.1, 10.5, 4.8 Hz, 1H), 5.40 (dd, *J* = 10.6, 1.5 Hz, 1H), 5.36 (app d, *J* = 17.5 Hz, 1H), 5.22 (br s, 1H), 4.55 (br d, *J* = 9.4 Hz, 1H), 4.36-4.32 (m, 1H), 3.94-3.90 (m, 1H), 2.98 (dd, *J* = 14.1, 4.6 Hz, 1H), 2.79 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.44 (s, 3H), 2.15 – 1.95 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.3, 148.2, 145.3, 136.6, 135.5, 135.3, 129.5, 129.5, 129.4, 128.8, 126.9, 119.0, 80.1, 77.1 56.2, 53.7, 35.6, 30.1, 28.3, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2047. **Optical rotation**: $[\alpha]^{23}_D$ = –43.1 (c = 0.71, $CHCl_3$).



(–)-*tert*-butyl ((*S*)-1-((4*S*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (52b). *N*-tosyl carbamate was synthesized from **(–)-50** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/CF_3-SOX catalyzed allylic C—H amination for *syn*-1,3 oxazinanone to afford (–)-**52b**.

Run 1 (*crude:*70%, 6.3:1 dr; *isolated:* 56.8 mg, 0.113 mmol, 56.7%, >20:1 dr);
Run 2 (*crude:*66%, 6.6:1 dr; *isolated:* 52.4 mg, 0.105 mmol, 52.3%, >20:1 dr);
Run 3 (*crude:*68%, 6.6:1 dr; *isolated:* 53.6 mg, 0.107 mmol, 53.5%, >20:1 dr).
Average yield: *crude*: **68%, 6.5:1** (*syn:anti*)**,** *isolated*: **54%, >20:1 dr** (*syn:anti*).

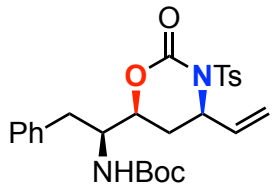
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 7.20 – 7.15 (m, 2H), 5.67 – 5.54 (m, 1H), 5.38 (app d, *J* = 17.0 Hz, 1H), 5.28 (app d, *J* = 10.1 Hz, 1H), 4.93 (app q, *J* = 8.3, 1H), 4.61 – 4.53 (m, 1H), 4.25-4.21 (m, 1H), 4.02-3.98 (m, 1H), 3.01 (dd, *J* = 14.2, 4.4 Hz, 1H), 2.82 (dd, *J* = 14.3, 8.8 Hz, 1H), 2.46 (s, 3H), 2.38 (dd, *J* = 14.1, 7.8 Hz, 1H), 1.84 (ddd, *J* = 14.3, 10.9, 9.6 Hz, 1H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 150.1, 145.3, 136.7, 135.9, 129.9, 129.6, 129.4, 129.4, 128.9, 127.0, 119.2, 80.3, 77.7, 59.0, 53.1, 35.6, 33.3, 28.5, 21.9. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2064. **Optical rotation**: $[\alpha]^{23}_D$ = –60.3 (c = 0.76, $CHCl_3$).



(+)-*tert*-butyl ((*S*)-1-((4*S*,6*S*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (53a). *N*-tosyl carbamate was synthesized from **(–)-51** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/MeO-SOX catalyzed allylic C—H amination for *anti*-1,3 oxazinanone to afford (+)-**53a**.

Run 1 (*crude:*85%, 3.0:1 dr; *isolated:* 58.4 mg, 0.117 mmol, 58.3%, >20:1 dr);
Run 2 (*crude:*85%, 3.5:1 dr; *isolated:* 60.7 mg, 0.121 mmol, 60.6%, >20:1 dr);
Run 3 (*crude:*86%, 3.4:1 dr; *isolated:* 62.0 mg, 0.124 mmol, 61.9%, >20:1 dr).
Average yield: *crude*: **85%, 3.3:1** (*anti:syn*)**,** *isolated*: **60%, >20:1 dr** (*anti:syn*).

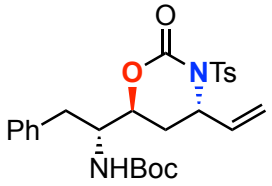
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.14 (m, 2H), 5.77 (ddd, *J* = 16.9, 10.5, 5.0 Hz, 1H), 5.30 (app d, *J* = 10.5 Hz, 1H), 5.23 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.21 – 5.16 (m, 1H), 4.64 (br d, *J* = 9.9 Hz, 1H), 4.34 (br d, *J* = 11.3 Hz, 1H), 3.90 (app q, *J* = 7.2 Hz, 1H), 2.88 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.16 – 2.03 (m, 1H), 1.89 (dt, *J* = 14.4, 2.6 Hz, 1H), 1.37 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.8, 148.6, 145.3, 137.0, 135.5, 135.4, 129.7, 129.6, 129.3, 128.7, 126.9, 118.7, 80.1, 75.6, 55.8, 53.7, 38.3, 30.0, 28.4, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2061. **Optical rotation**: $[\alpha]^{23}_D$ = +10.0 (c = 1.00, $CHCl_3$).



(+)-*tert*-butyl ((*S*)-1-((4*R*,6*S*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (53b). *N*-tosyl carbamate was synthesized from **(–)-51** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/CF_3-SOX catalyzed allylic C—H amination for *syn*-1,3 oxazinanone to afford (+)-**53b**.

Run 1 (*crude:*89%, 12:1 dr; *isolated:* 73.6 mg, 0.147 mmol, 73.5%, >20:1 dr);
Run 2 (*crude:*85%, 13:1 dr; *isolated:* 75.2 mg, 0.150 mmol, 75.1%, >20:1 dr);
Run 3 (*crude:*85%, 13:1 dr; *isolated:* 70.3 mg, 0.140 mmol, 70.2%, >20:1 dr).
Average yield: *crude*: **86%, 13:1** (*syn:anti*)**,** *isolated*: **73%, >20:1 dr** (*syn:anti*).

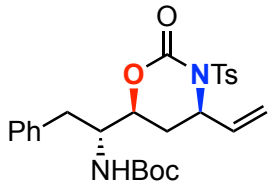
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.22 (m, 6H), 7.20 – 7.17 (m, 2H), 5.54 (ddd, *J* = 17.6, 10.1, 8.0 Hz, 1H), 5.34 (app d, *J* = 17.0 Hz, 1H), 5.23 (app d, *J* = 10.1 Hz, 1H), 4.83 (dt, *J* = 10.2, 8.0 Hz, 1H), 4.70 (d, *J* = 10.0 Hz, 1H), 4.19 – 4.12 (m, 1H), 3.98 (q, *J* = 9.0 Hz, 1H), 2.95-2.84 (m, 2H), 2.45 (s, 3H), 2.21 (ddd, *J* = 14.5, 7.9, 2.1 Hz, 1H), 1.85 (app dt, *J* = 14.4, 10.8 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.7, 150.3, 145.1, 136.9, 136.7, 135.9, 129.7, 129.4, 129.3, 128.9, 127.0, 119.1, 80.1, 75.7, 58.8, 53.3, 38.4, 33.2, 28.4, 21.8. **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2052. **Optical rotation**: $[\alpha]^{23}_D$ = +18.2 (c = 0.86, $CHCl_3$).



(+)-*tert*-butyl ((*R*)-1-((4*S*,6*S*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (54a). *N*-tosyl carbamate was synthesized from **(+)-*ent*-50** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/MeO-SOX catalyzed allylic C—H amination for *anti*-1,3 oxazinanone to afford (+)-**54a**.

Run 1 (*crude:*86%, 9.1:1 dr; *isolated:* 72.0 mg, 0.144 mmol, 71.9%, >20:1 dr);
Run 2 (*crude:*83%, 9.6:1 dr; *isolated:* 71.4 mg, 0.143 mmol, 71.3%, >20:1 dr);
Run 3 (*crude:*83%, 9.3:1 dr; *isolated:* 68.0 mg, 0.136 mmol, 67.9%, >20:1 dr).
Average yield: *crude*: **84%, 9.3:1** (*anti:syn*)**,** *isolated*: **70%, >20:1 dr** (*anti:syn*).

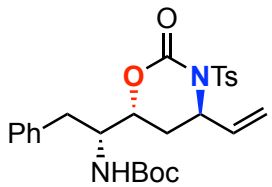
^{1}H NMR ,^{13}C NMR match **52a** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2051. **Optical rotation**: $[\alpha]^{23}_D$ = +42.6 (c = 0.99, $CHCl_3$).



(+)-*tert*-butyl ((*R*)-1-((4*R*,6*S*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (54b). *N*-tosyl carbamate was synthesized from **(+)-*ent*-50** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/CF_3-SOX catalyzed allylic C—H amination for *syn*-1,3 oxazinanone to afford (+)-**54b**.

Run 1 (*crude:*73%, 7.3:1 dr; *isolated:* 57.8 mg, 0.115 mmol, 57.7%, >20:1 dr);
Run 2 (*crude:*70%, 7.6:1 dr; *isolated:* 56.2 mg, 0.112 mmol, 56.1%, >20:1 dr);
Run 3 (*crude:*74%, 7.2:1 dr; *isolated:* 59.9 mg, 0.120 mmol, 59.8%, >20:1 dr).
Average yield: *crude*: **72%, 7.4:1** (*syn:anti*)**,** *isolated*: **58%, >20:1 dr** (*syn:anti*).

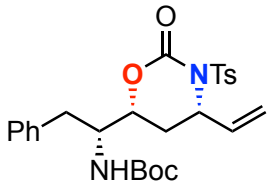
^{1}H NMR ,^{13}C NMR match **52b** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2054. **Optical rotation**: $[\alpha]^{23}_D$ = +59.9 (c = 1.01, $CHCl_3$).



(–)-*tert*-butyl ((*R*)-1-((4*R*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (55a). *N*-tosyl carbamate was synthesized from (+)-***ent*-51** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/MeO-SOX catalyzed allylic C—H amination for *anti*-1,3 oxazinanone to afford (–)-**55a**.

Run 1 (*crude:*80%, 3.4:1 dr; *isolated:* 52.0 mg, 0.104 mmol, 51.9%, >20:1 dr);
Run 2 (*crude:*79%, 3.6:1 dr; *isolated:* 54.6 mg, 0.109 mmol, 54.5%, >20:1 dr);
Run 3 (*crude:*79%, 3.6:1 dr; *isolated:* 54.9 mg, 0.110 mmol, 54.8%, >20:1 dr).
Average yield: *crude*: **79%, 3.5:1** (*anti:syn*)**,** *isolated*: **54%, >20:1 dr** (*anti:syn*).

^{1}H NMR ,^{13}C NMR match **53a** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2060. **Optical rotation**: $[\alpha]^{23}_D = -10.2$ (c = 0.75, $CHCl_3$).



(–)-*tert*-butyl ((*R*)-1-((4*S*,6*R*)-2-oxo-3-tosyl-4-vinyl-1,3-oxazinan-6-yl)-2-phenylethyl)carbamate (55b). *N*-tosyl carbamate was synthesized from (+)-***ent*-51** in quantitative yield. *N*-tosyl carbamate was reacted under general procedure of Pd(II)/CF_3-SOX catalyzed allylic C—H amination for *syn*-1,3 oxazinanone to afford (–)-**55b**.

Run 1 (*crude:*83%, 14:1 dr; *isolated:* 73.2 mg, 0.146 mmol, 73.1%, >20:1 dr);
Run 2 (*crude:*84%, 14:1 dr; *isolated:* 69.7 mg, 0.139 mmol, 69.6%, >20:1 dr);
Run 3 (*crude:*80%, 13:1 dr; *isolated:* 70.8 mg, 0.141 mmol, 70.7%, >20:1 dr).
Average yield: *crude*: **82%, 14:1** (*syn:anti*)**,** *isolated*: **71%, >20:1 dr** (*syn:anti*).

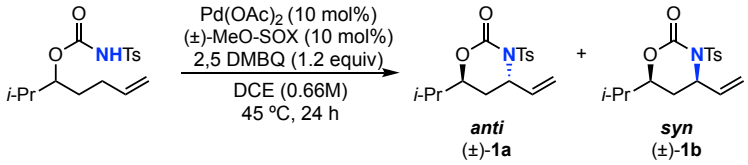
^{1}H NMR ,^{13}C NMR match **53b** (see spectra). **HRMS (ESI)** *m/z* calculated for $C_{26}H_{33}N_2O_6S$ $[M+H]^+$: 501.2059, found 501.2050. **Optical rotation**: $[\alpha]^{23}_D = -18.6$ (c = 1.01, $CHCl_3$).

Mechanistic Studies

1. Reaction profiles

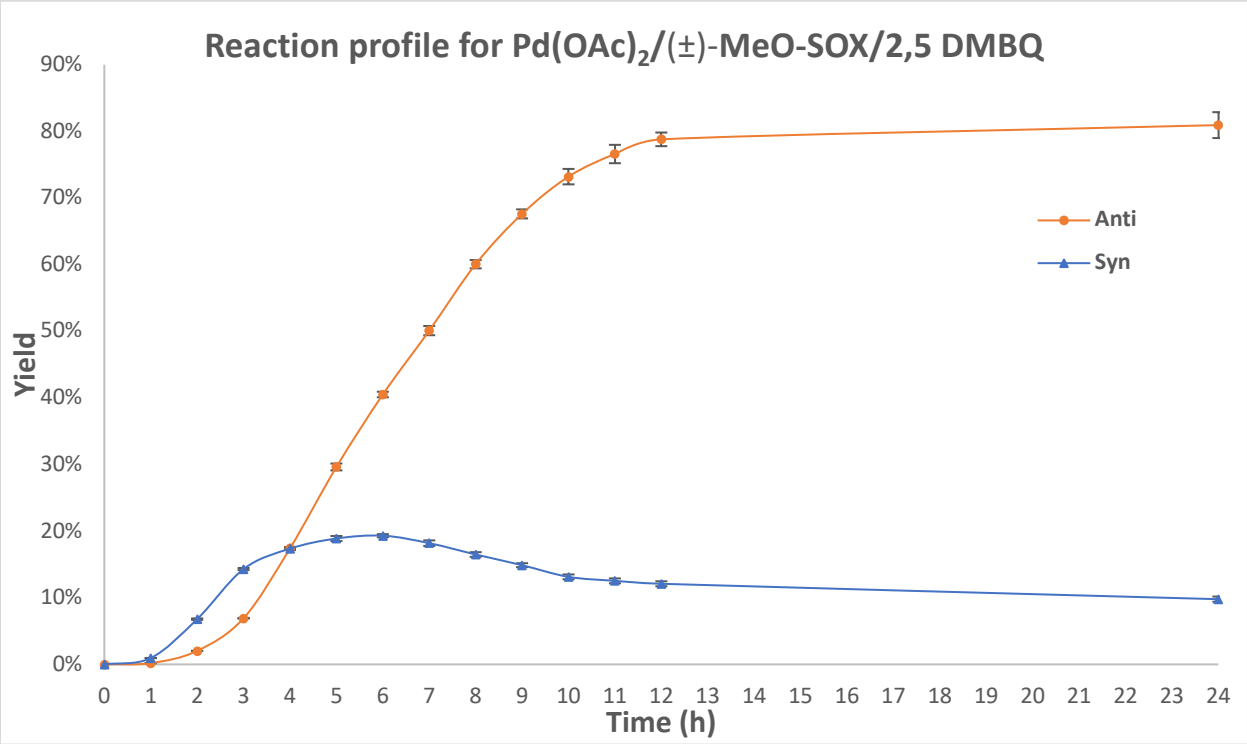
Reaction profile of $Pd(OAc)_2$/(±)-MeO SOX/2,5 DMBQ:

Scheme S4. $Pd(OAc)_2$/(±)-MeO SOX/2,5 DMBQ



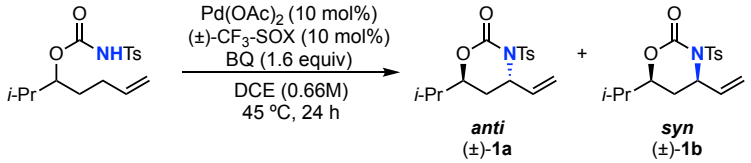
To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-MeO SOX (6.9 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (2,5-dimethylbenzoquinone) (32.6 mg, 0.24 mmol, 1.2 equiv), 2-methylhept-6-en-3-yl tosylcarbamate **(S1)** (0.2 mmol, 1.0 equiv), and 4-nitroacetophenone (13.2 mg, 0.08 mmol, 0.4 equiv) as internal standard. Dichloroethane (0.3 mmol, 0.67 M) was added and the vial was capped and heated to 45 °C. Aliquots (10 µL) were taken at the corresponding times from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Zorbax C-N, 3% isopropanol/hexanes, 1 mL/min, 35 °C, 214 nm). The yields were determined by integration of the ***anti*-(±)-1a** (24.4.2 min) and ***syn*-(±)-1b** (20.2 min) relative to the 4-nitroacetophenone internal standard peak (8.3 min) and corrected by a standard curve. Errors were calculated via propagation of the standard error of the mean for each set of rates.

Figure S4. Reaction profile for $Pd(OAc)_2$/(±)-MeO-SOX/2,5 DMBQ condition.



Reaction profile of $Pd(OAc)_2$/(±)-CF_3 SOX/BQ:

Scheme S5. $Pd(OAc)_2$/(±)-CF_3-SOX/BQ



To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-CF_3 SOX (7.6 mg, 0.02 mmol, 0.1 equiv), BQ (1,4-dibenzoquinone) (34./6 mg, 0.24 mmol, 1.6 equiv), 2-methylhept-6-en-3-yl tosylcarbamate **(S1)** (0.2 mmol, 1.0 equiv), and 4-nitroacetophenone (13.2 mg, 0.08 mmol, 0.4 equiv) as internal standard. Dichloroethane (0.3 mmol, 0.67 M) was added and the vial was capped and heated to 45 °C. Aliquots (10 µL) were taken at the corresponding times from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Zorbax C-N, 3% isopropanol/hexanes, 1 mL/min, 35 °C, 214 nm). The yields were determined by integration of the **1a** (24.4) and **1b** (20.2 min) relative to the 4-nitroacetophenone internal standard peak (8.3 min) and corrected by a standard curve. Errors were calculated via propagation of the standard error of the mean for each set of rates.

Figure S5. Reaction profile for $Pd(OAc)_2$ /(±)-CF_3-SOX/BQ condition.

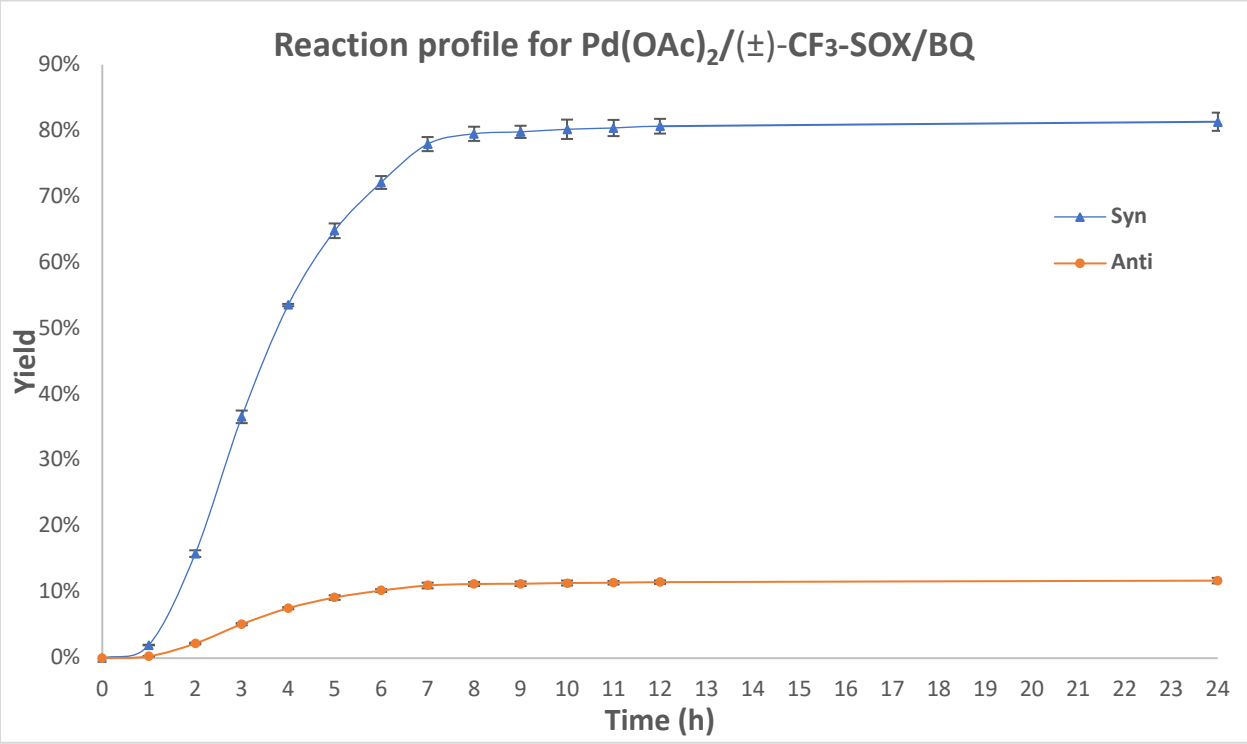
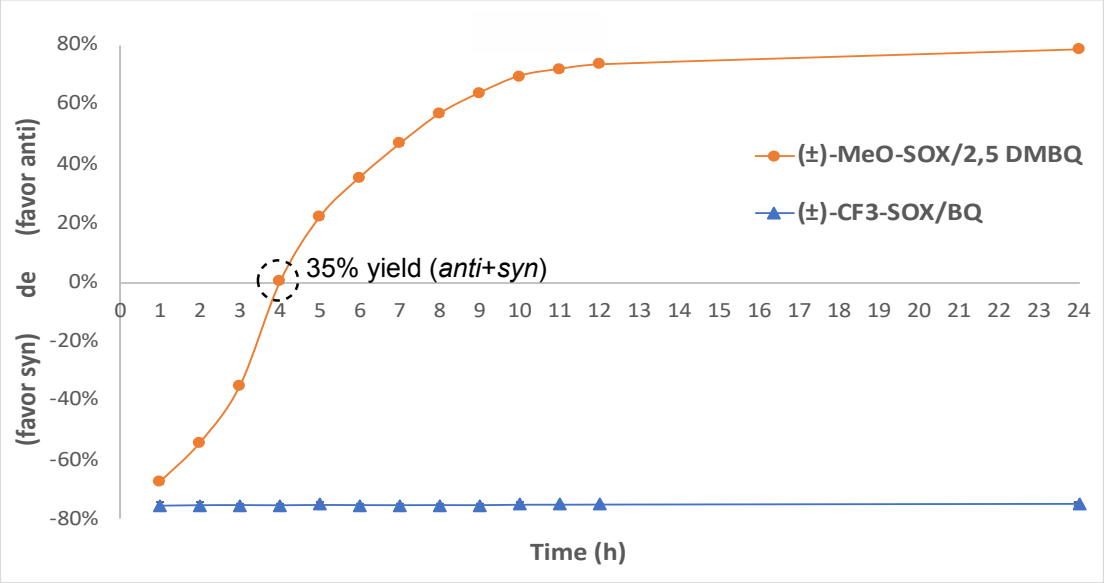
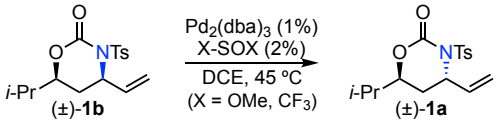


Figure S6. Diastereomeric excess over time ($Pd(OAc)_2$/(±)-MeO SOX/2,5 DMBQ and $Pd(OAc)_2$/(±)-CF_3 SOX/BQ)



2. Pd(0) isomerization

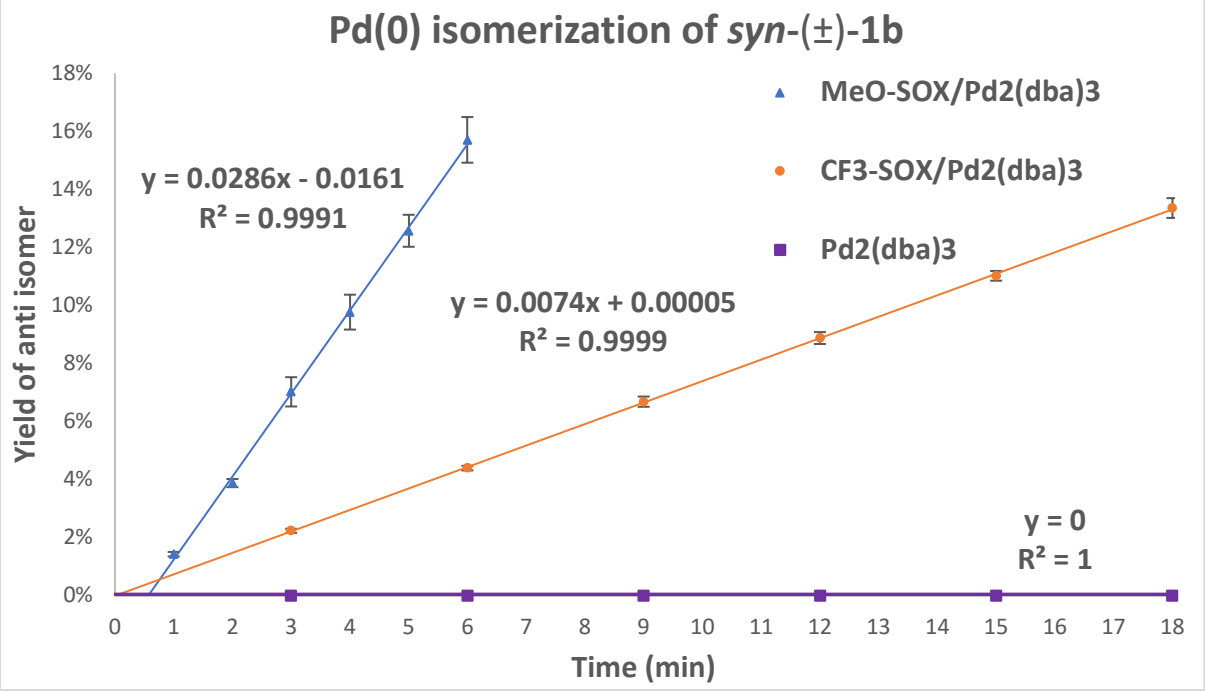
Scheme S6. Pd(0) isomerization



To a ½ dram vial was added a stir bar, **1b** (32.3 mg, 0.1 mmol, 1.0 equiv.), nitrobenzene (12.3 mg, 1.0 equiv.) as internal standard. The vial was capped and placed on a heating aluminum block at 45 °C. SOX ligand + $Pd_2(dba)_3$ from a stock solution (1 mL, 0.01 mmol SOX ligand, 0.005 mmol $Pd_2(dba)_3$ in 5 mL dichloroethane) was added through the cap. Aliquots (10 µL) were taken at the corresponding times from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Zorbax C-N, 3% isopropanol/hexanes, 1 mL/min, 35 °C, 214 nm). The yield was determined by integration of the **1a** (24.4 min) relative to the nitrobenzene internal standard peak (4.8 min) and corrected by a standard curve. Errors were calculated via propagation of the standard error of the mean for each set of rates.

Experiment 1 (blue **triangle**): (±)-MeO SOX was used;
Experiment 2 (orange **circle**): (±)-CF_3 SOX was used;
Experiment 3 (purple **square**): No ligand is used (control experiment)

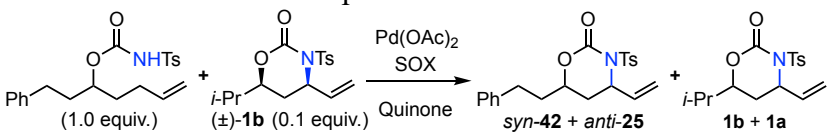
Figure S7. Pd(0) isomerization of *syn*-(±)-1b



$\mathbf{k}_{(\pm)\text{-MeO-SOX}}$ / $\mathbf{k}_{(\pm)\text{-CF3-SOX}}$ = 3.9.

3. Cross-over experiments

Scheme S7. Cross-over experiments.



To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), SOX ligand (0.02 mmol, 0.1 equiv), quinone, **S25** (0.2 mmol, 1.0 equiv), and **1b** (6.5 mg, 0.02 mmol, 0.1 equiv). Dichloroethane (0.3 mmol, 0.67 M) was added and the vial was capped and heated to 45 °C. Aliquots (10 µL) were taken at the 24 hour from the reaction vial, and filtered through a silica plug with diethyl ether (0.6 mL) for HPLC analysis (Zorbax C-N, 2% isopropanol/hexanes, 1 mL/min, 35 °C, 214 nm). The diastereomeric ratio was determined by ratio between integration of the **25** (30.1 min) and **42** (25.3 min); the ratio between **1a** (23.8 min) and **1b** (19.7 min).

Experiment 1: (±)-MeO SOX and 2, 5 DMBQ were used.
dr (42:25) = 1:8.7 (*syn : anti*); dr (1b:1a) = 1:8.3 (*syn : anti*)

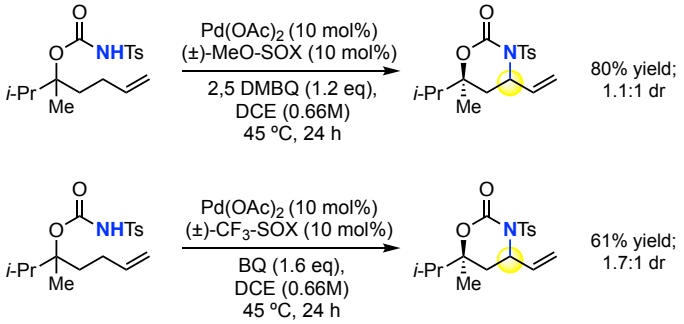
Experiment 2: (±)-MeO SOX and BQ were used.
dr (42:25) = 6.5:1 (*syn : anti*) (low conversion); dr (1b:1a) >20:1 (*syn : anti*)

Experiment 3: (±)-CF_3 SOX and BQ were used.

dr (42:25) = 7.2:1 (*syn : anti*); dr (1b:1a) > 20:1 (*syn : anti*)
Experiment 4: (±)-CF_3 SOX and 2,5 DMBQ were used .
dr (42:25) = 3.1:1 (*syn : anti*); dr (1b:1a) = 3.5:1 (*syn : anti*)

Exploratory studies on tertiary alcohol carbamate substrate

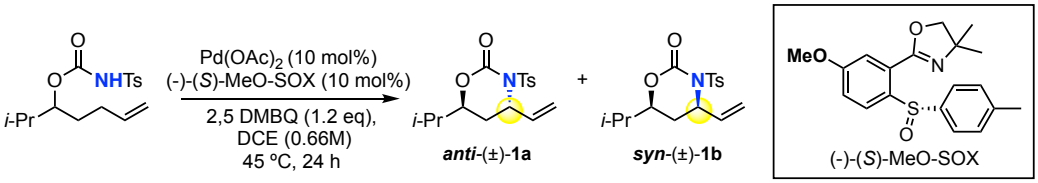
Scheme S8. Tertiary alcohol carbamate substrate



Following general procedure. To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (±)-SOX ligand (0.02 mmol, 0.1 equiv), quinone oxidant (2,5 DMBQ: 32.7 mg, 0.24 mmol, 1.2 equiv. or BQ, 34.6 mg, 0.32 mmol, 1.6 equiv.), tertiary carbamate substrate (67.9 mg, 0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 24 hours. The vial was allowed to cool to room temperature and diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure, diluted with 2 mL $CDCl_3$ and analyzed by crude ^{1}H NMR with internal standard (trifluorotuluene, 14.6 mg, 0.1 mmol, 0.5 equiv). (See spectra). The *anti*- and *syn*- cannot be separated by flash column chromatography.

Exploratory studies on kinetic resolution using chiral SOX ligand

Scheme S9. Kinetic resolution using chiral SOX ligand



Following general procedure. To a ½ dram vial was added a stir bar, $Pd(OAc)_2$ (4.4 mg, 0.02 mmol, 0.1 equiv), (-)-(*S*)-MeO-SOX ligand (6.6 mg, 0.02 mmol, 0.1 equiv), 2,5 DMBQ (32.7 mg, 0.24 mmol, 1.2 equiv), 2-methylhept-6-en-3-yl tosylcarbamate (**S1**) (65.1 mg, 0.2 mmol, 1.0 equiv), and dichloroethane (0.3 mL, 0.67 M). The vial was capped and heated to 45 °C for 5 hours (nearly 50% conversion according to reaction profile; see figure S4). The reaction was diluted with 1 mL acetone. The reaction mixture was filtered through a pipette silica plug into a 20 mL vial with acetone. The mixture was concentrated under reduced pressure and subjected to flash column chromatography (0% => 20% ethyl acetate in hexanes) to provide **1b**, **1a** and recovered starting material **S1**.
The enantiomeric excess of **1a** was determined by HPLC analysis (OJ-H, 10% isopropanol/hexanes, 1 mL/min, 30 °C, 225 nm). t_R(major)=14.16 min, t_R(minor)=17.48 min. **6% ee**. The enantiomeric excess of recovered **S1** was determined by HPLC analysis (OJ-H, 5%

isopropanol/hexanes, 1 mL/min, 30 °C, 225 nm). t_R(major)=7.57 min, t_R(minor)=10.48 min. **5% ee**.

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