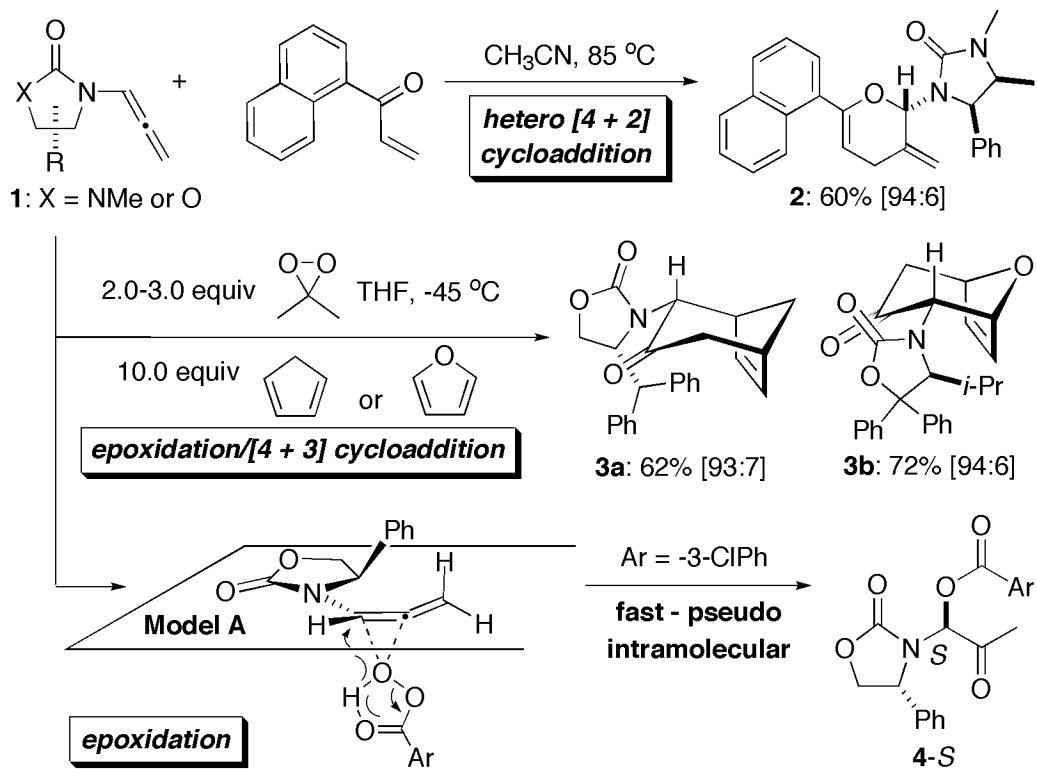


Supplemental Scheme 1: Stereoselective methodologies with allenamides.



Supplemental Experimental 1: Characterizations of other new allenamides:

Allenamide 7b. $R_f = 0.66$ (25% EtOAc in hexane); mp 140-142 °C; $[\alpha]_D^{20} - 346.7$ [c 1.18, EtOH]; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.79 (d, 3H, $J = 7.0$ Hz), 1.01 (d, 3H, $J = 7.0$ Hz), 1.93 (dhept, 1H, $J = 7.0$ Hz, 2.4 Hz), 4.55 (d, 1H, $J = 2.4$ Hz), 5.47 (d, 2H, $J = 6.6$ Hz), 6.88 (t, 1H, $J = 6.6$ Hz), 7.28 (m, 10H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 16.1, 22.3, 29.6, 66.0, 88.4, 89.2, 97.7, 125.7, 126.2, 127.8, 128.2, 128.4, 128.7, 138.6, 143.5, 154.3, 202.2; IR (neat) cm^{-1} 3062m, 2973s, 2928m, 1960w, 1749s, 1749s, 1465s, 1399s, 1273m, 1225s, 1027s; mass spectrum (EI): m/e [%relative intensity] 319 (5) M^+ , 274 (72), 260 (15), 232 (76), 207 (78), 165 (54), 129 (34), 109 (100); m/e calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ 319.1572, found 319.1572.

Allenamide 7c. $R_f = 0.63$ (50% EtOAc in hexane); mp 91-93 °C; $[\alpha]_D^{20} + 518.4$ [c 0.96, CH_2Cl_2]; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.40 (brd, 2H, $J = 3.3$ Hz), 5.29 (d, 1H, $J = 6.9$ Hz), 5.30 (m, 1H), 5.61 (dt, 1H, $J = 6.6, 10.2$ Hz), 5.71 (dt, 1H, $J = 6.6, 10.2$ Hz), 6.91 (t, 1H, $J = 6.6$ Hz), 7.29 (m, 3H), 7.51 (d, 1H, $J = 7.5$ Hz); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 38.2, 63.2, 78.6, 88.6, 96.5, 125.5, 126.2, 127.7, 129.6, 138.4, 140.2, 154.5, 201.4; IR (neat) cm^{-1} : 3072w, 3038m, 2976w, 1967w, 1747s, 1466s, 1395s, 1285s, 1114s, 880s, 752s; mass spectrum (EI): m/e [%relative intensity] 213 (23) M^+ , 168 (20), 141 (10), 116 (100); m/e calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$ 213.0790, found 213.0789.

Allenamide 7d. $R_f = 0.75$ (50% EtOAc in CH_2Cl_2); oily material; $[\alpha]_D^{20} + 33.6$ [c 0.89, EtOH]; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 0.89 (s, 3H), 0.99 (s, 3H), 1.33 (s, 3H), 1.54 (m, 1H), 1.76 (dd, 2H, $J = 6.1, 7.5$ Hz), 2.00 (m, 1H), 2.34 (d, 1H, $J = 4.20$ Hz), 5.27 (ddd, 2H, $J = 6.6, 10.2, 15.1$ Hz), 6.66 (t, 1H, $J = 6.6$ Hz); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 12.6, 17.7, 18.4, 23.8, 32.2, 49.2, 54.3, 72.4, 84.7, 91.8, 176.8, 202.8; IR (neat) cm^{-1} 2994m, 2956m, 1702s, 1451m, 1390m, 1375w; mass spectrum (EI): m/e [%relative intensity] 191 (81) M^+ , 162(24), 148 (60), 109 (100), 95 (24); m/e calcd for $\text{C}_{12}\text{H}_{17}\text{NO}$ 191.1310, found 191.1308.

Supplemental Figure 1:

Plots showing the relative energy minimizations for the rotation of the allene moiety around the N1-C3 bond every two degrees for allenamides 7a-7d.

