SUPPORTING INFORMATION

for
the
communication
entitled

Regio- and Stereoselective Isomerizations of Allenamides: Synthesis of 2-Amido-Dienes and Their Tandem Isomerization–Electrocyclic Ring-Closure.

authored by

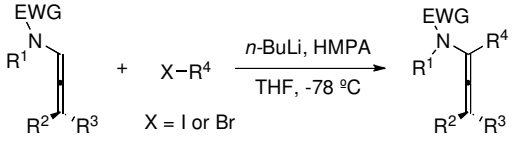
Ryuji Hayashi, Richard P. Hsung*, John B. Feltenberger, and Andrew G. Lohse

Division of Pharmaceutical Sciences and Department of Chemistry,
7111 Rennebohm Hall, 777 Highland Avenue
University of Wisconsin at Madison, Madison, WI 53705-2222

GENERAL EXPERIMENTAL INFORMATION

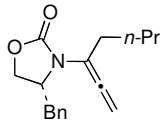
All reactions were performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased from Aldrich, Acros, Alfa Aesar, or TCI) unless otherwise noted. Chromatographic separations were performed using Silicycle 43-60 Å SiO_2. ^1H and ^{13}C NMR spectra were obtained on Varian VI-400 and VI-500 spectrometers using $CDCl_3$ with TMS or residual solvent as standard unless otherwise noted. Melting points were determined using a Laboratory Devices MEL-TEMP and are uncorrected/calibrated. Infrared spectra were obtained on Bruker EQUINOX 55 FTIR. TLC analysis was performed using Aldrich 254 nm polyester-backed plates (60 Å, 250 μm) and visualized using UV and $KMnO_4$ stains. Low-resolution mass spectra were obtained using an Agilent 1100 series LS/MSD and are APCI. High-resolution mass spectral analysis performed at University of Wisconsin School of Pharmacy and Department of Chemistry Mass Spectrometry Laboratories. All spectral data obtained for new compounds are reported here.

GENERAL PROCEDURE FOR PREPARATIONS OF ALLENAMIDES VIA ⟨-ALKYLATIONS.[i]



To a cooled (-78 ºC) solution of a given allenamide (1.0 equiv) and HMPA (1.5 equiv) in anhyd THF (0.1 *M*) was added dropwise *n*-BuLi (1.5 equiv, 2.5 *M* in Hexanes). After stirring for 45 min for complete deprotonation, a corresponding halide (1.5 equiv) was added dropwise. The resulting solution was stirred at -78 ºC for 1 h and gradually warmed up to rt over ~2 h. The solution was washed with sat aq NaCl twice, dried over Na_2SO_4, and concentrated under reduced pressure. Separation and purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired α-substituted allenamides.

CHARACTERIZATIONS OF ALLENAMIDES.



5a

Allenamide **5a** (58.0 mg, 0.20 mmol) was prepared in 39% yield according to the general procedure.

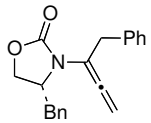
5a: R_f = 0.42 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -3.48° [c 0.027 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, 3H, *J* = 5.6 Hz), 1.22–1.49 (m, 4H), 2.53 (ddd, 2H, *J* = 2.8, 5.2, 8.4 Hz), 2.65 (dd, 1H, *J* = 7.6, 10.8 Hz), 3.24 (dd, 1H, *J* = 3.2, 11.2 Hz), 4.05-4.14 (m, 2H), 4.14 (t, 1H, *J* = 6.4 Hz), 5.24 (dt, 1H, *J* = 2.4, 8.0 Hz), 5.35 (dt, 1H, *J* = 1.6, 8.0 Hz), 7.16 (d, 1H, *J* = 6.8 Hz), 7.26 (d, 2H, *J* = 6.0 Hz), 7.32 (t, 2H, *J* = 5.6 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.4, 29.4, 29.6, 38.7, 58.0, 66.9, 84.5, 109.6, 127.4, 129.1, 129.3, 135.9, 155.8, 204.3;

IR (neat) cm^{-1} 3035w, 2963w, 1751s, 1479m, 1392w;

mass spectrum (APCI): m/e (% relative intensity) 272.2 (100) $(M+H)^+$.



5b

Allenamide **5b** (200.0 mg, 0.66 mmol) was prepared in 66% yield according to the general procedure.

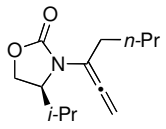
5b: R_f = 0.33 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -4.33° [c 0.009 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (dd, 1H, *J* = 9.6, 13.6 Hz), 2.99 (dd, 1H, *J* = 3.2, 13.6 Hz), 3.73 (dt, 1H, *J* = 2.0, 15.2 Hz), 3.90-4.13 (m, 3H), 5.22 (ddd, 1H, *J* = 2.0, 3.2, 6.4 Hz), 5.34 (ddd, 1H, *J* = 2.0, 3.2, 6.4 Hz), 7.22-7.32 (m, 10H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 37.0, 38.3, 58.1, 67.1, 84.0, 108.7, 127.0, 127.3, 128.6, 129.0, 129.2, 129.5, 135.9, 138.2, 156.0, 204.9;

IR (neat) cm^{-1} 3035w, 2963w, 1754s, 1478m, 1396w, 1356w;

mass spectrum (APCI): m/e (% relative intensity) 306.2 (100) $(M+H)^+$.



7a

Allenamide **7a** (68.0 mg, 0.28 mmol) was prepared in 27% yield according to the general procedure.

7a: R_f = 0.30 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +52.4° [c 0.012 Benzene]; colorless oil;

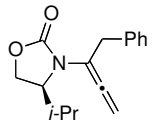
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87-0.94 (m, 9H), 1.25-1.48 (m, 4H), 2.08-2.17 (m, 1H), 2.37-2.51 (m, 2H), 3.86 (ddd, 1H, *J* = 4.0, 6.0, 9.5 Hz), 4.10 (dd, 1H, *J* = 6.0, 9.0 Hz), 4.26 (t, 1H, *J* = 9.0 Hz), 5.12 (dt, 1H, *J* = 3.5, 10.0 Hz), 5.24 (dt, 1H, *J* = 3.5, 10.0 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 14.7, 18.0, 22.5, 28.3, 29.3, 29.6, 60.7, 63.1, 83.9, 108.9, 159.4,

204.8;

IR (neat) cm^{-1} 2961w, 2874w, 1750s, 1701m, 1480w, 1466w;

mass spectrum (APCI): m/e (% relative intensity) 224.1 (100) $(M+H)^+$.



7b

Allenamide **7b** (71.0 mg, 0.28 mmol) was prepared in 28% yield according to the general procedure.

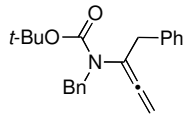
7b: R_f = 0.28 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +73.0 ^{o} [c 0.010 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56 (d, 3H, *J* = 6.5 Hz), 0.77 (d, 3H, *J* = 7.0 Hz), 1.91 -1.99 (m, 1H), 3.67-3.73 (m, 2H), 3.96 (dt, 1H, *J* = 3.0, 6.5 Hz), 4.00 (dd, 1H, *J* = 5.5, 9.0 Hz), 4.14 (t, 1H, *J* = 9.5 Hz), 5.11 (dt, 1H, *J* = 2.0, 10.5 Hz), 5.25 (dt, 1H, *J* = 2.0, 10.5 Hz), 7.22 (dd, 1H, *J* = 4.0, 8.5 Hz), 7.27 (d, 4H, *J* = 4.5 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 18.0, 28.6, 37.0, 60.9, 63.0, 83.7, 108.5, 127.0, 128.6, 129.6, 138.2, 156.5, 205.2;

IR (neat) cm^{-1} 3035w, 2963w, 1751s, 1479m, 1392w;

mass spectrum (APCI): m/e (% relative intensity) 258.2 (100) $(M+H)^+$.



11

Allenamide **11** (114.0 mg, 0.34 mmol) was prepared in 65% yield according to the general procedure.

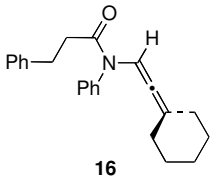
11: R_f = 0.38 [9% EtOAc/hexanes]; pale yellow oil;

^{1}H NMR (500 MHz, $CDCl_3$, 55 ^{o}C) δ 1.44 (s, 9H), 3.48 (s, 2H), 4.42 (s, 2H), 4.79 (s, 2H), 7.06 (d, 2H, *J* = 7.0 Hz), 7.13-7.23 (m, 8H);

^{13}C NMR (125 MHz, $CDCl_3$, 55 ^{o}C) δ 28.6, 39.0, 52.9, 80.6, 81.3, 112.5, 126.5, 127.1, 128.3, 128.4, 129.6, 138.3, 138.7, 154.6, 207.5 *(one sp^2 carbon missing due to overlap or line-broadening)*;

IR (thin film) cm^{-1} 2957m, 1698s, 1453m, 1367m, 1150s;

mass spectrum (APCI): m/e (% relative intensity) 236 (100) $(M+H\text{-}Boc)^+$.



16

Allenamide **16** (99.0 mg, 0.30 mmol) was prepared in 33% yield according to the general procedure.

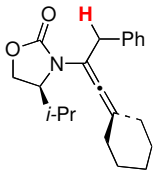
16: R_f = 0.19 [1:9 EtOAc/hexanes]; yellow solid; mp 83-88 ^{o}C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (m, 2H), 1.22 (m, 1H), 1.37 (m, 1H), 1.48 (dddd, 2H, *J* = 3.6, 4.4, 5.2, 12.4 Hz), 1.86 (m, 4H), 2.38 (t, 2H, *J* = 8.0 Hz), 2.93 (t, 2H, *J* = 8.0 Hz), 7.01 (d, 2H, *J* = 6.8 Hz), 7.06 (d, 2H, *J* = 7.6 Hz), 7.13-7.25 (m, 3H), 7.29-7.38 (m, 3H), 7.45 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 27.4, 31.7, 32.5, 37.0, 99.4, 114.8, 126.3, 128.3, 128.6, 128.7, 128.8, 129.5, 140.7, 141.4, 170.3, 191.0;

IR (thin film) cm^{-1} 2928w, 2361s, 1966w, 1658s, 1596w, 1494w, 1432w, 1375m;

mass spectrum (APCI): m/e (% relative intensity) 332.2 (100) $(M+H)^{+}$.



27a

Allenamide **27a** (120.2 mg, 0.37 mmol) was prepared in 37% yield according to the general procedure.

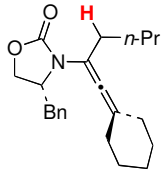
27a: R_f = 0.32 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -80.4^{o} [c 0.005 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (d, 3H, *J* = 8.5 Hz), 0.77 (d, 1H, *J* = 9.0 Hz), 0.83-0.90 (m, 1H), 1.32-1.56 (m, 6H), 1.96-2.12 (m, 4H), 3.69-3.77 (m, 2H), 3.83 (bd, 1H, *J* = 19.0 Hz), 4.02 (dd, 1H, 7.5, 11.0 Hz), 4.16 (t, 1H, *J* = 11.5 Hz), 7.17-7.28 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 18.2, 26.1, 27.5, 27.6, 27.7, 27.7, 32.2, 32.3, 37.7, 61.1, 62.7, 105.8, 112.2, 126.6, 128.4, 129.7, 139.2, 156.7, 193.1;

IR (neat) cm^{-1} 2928m, 1961w, 1750s, 1479m, 1445m, 1392m;

mass spectrum (APCI): m/e (% relative intensity) 326.3 (100) (M+H).



27b

Allenamide **27b** (68.0 mg, 0.20 mmol) was prepared in 40% yield according to the general procedure.

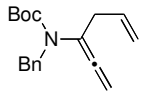
27b: R_f = 0.50 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +23.6° [c 0.015 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85-0.91 (m, 2H), 0.94 (t, 3H, *J* = 7.2 Hz), 1.26-1.71 (m, 10H), 2.16-2.29 (m, 3H), 2.46-2.67 (m, 2H), 3.25 (dd, 1H, *J* = 3.2, 13.2 Hz), 3.99-4.22 (m, 3H), 7.14 (d, 2H, *J* = 6.8 Hz), 7.23-7.34 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.3, 26.2, 27.7, 27.9, 29.6, 30.2, 32.7, 32.9, 38.2, 58.2, 66.6, 106.4, 112.5, 127.3, 129.1, 129.3, 129.3, 136.1, 156.0, 191.4;

IR (neat) cm^{-1} 2929m, 1960w, 1754s, 1476m, 1395m;

mass spectrum (APCI): m/e (% relative intensity) 340.2 (100) (M+H).



29

Allenamide **29** (214.0 mg, 0.75 mmol) was prepared in 49% yield according to the general procedure. ^{13}C NMR spectra for the *N*-Boc examples were taken at 50-55 °C due to broadening and complication of signals caused by rotameric isomers.

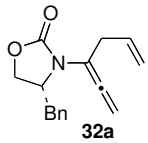
29: R_f = 0.43 [9% EtOAc/hexanes]; clear oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (s, 9H), 2.92 (brs, 2H), 4.54 (s, 1H), 4.93-4.95 (m, 2H), 4.96-5.01 (m, 2H), 5.59 (ddt, 1H, *J* = 17.2, 10, 7.2 Hz), 7.23-7.30 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 28.6, 36.8, 52.9, 80.5, 80.7, 111.4, 116.7, 127.2, 128.2, 128.3, 134.5, 138.8, 154.5, 207.0;

IR (film) cm^{-1} 2978m, 1695s, 1443m, 1382m, 1161s;

mass spectrum (APCI): m/e (% relative intensity) 186 (100) $(M+H-Boc)^+$.



32a

Allenamide **32a** (42.9 mg, 0.37 mmol) was prepared in 37% yield according to the general procedure.

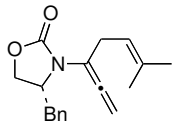
32a: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +3.85° [c 0.007 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.67 (dd, 1H, *J* = 9.5, 14.0 Hz), 3.22 (dd, 1H, *J* = 3.5, 13.0 Hz), 3.29-3.36 (m, 2H), 4.06 (dd, 1H, *J* = 5.5, 8.5 Hz), 4.11 (ddd, 1H, *J* = 3.0, 7.5, 11.5 Hz), 4.20 (t, 1H, *J* = 8.0 Hz), 5.10 (ddd, 1H, *J* = 1.0, 3.0, 10.0 Hz), 5.20 (dd, 1H, *J* =1.5, 15. Hz), 5.25 (dt, 1H, *J* = 3.0, 10.5 Hz), 5.84 (dq, 1H, *J* = 7.0, 17.0 Hz), 7.15 (d, 2H, *J* = 7.0 Hz), 7.20-7.34 (m, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 34.7, 38.7, 58.1, 67.0, 84.8, 108.1, 117.8, 127.5, 129.2, 129.3, 134.2, 136.0, 204.5;

IR (neat) cm^{-1} 3029w, 2930w, 2363, 1754s, 1604w, 1497m, 1479m, 1454m;

mass spectrum (APCI): m/e (% relative intensity) 256.1 (100) $(M+H)^+$.



32b

Allenamide **32b** (150.0 mg, 0.53 mmol) was prepared in 53% yield according to the general procedure.

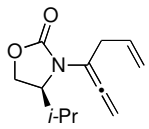
32b: R_f = 0.31 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -1.67° [c 0.015 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67 (s, 3H), 1.73 (s, 3H), 2.65 (dd, 1H, *J* = 11.5, 17.0 Hz), 3.17-3.26 (m, 3H), 4.03-4.4.16 (m, 2H), 4.19 (t, 1H, *J* = 9.5 Hz), 5.18-5.23 (m, 2H), 5.33 (dt, 1H, *J* = 4.0, 13.0 Hz), 7.14 (d, 2H, *J* = 8.0 Hz), 7.21-7.34 (m, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 18.3, 25.9, 29.3, 38.6, 58.1, 66.9, 84.3, 108.7, 119.7, 127.4, 129.1, 129.3, 135.0, 136.0, 155.9, 204.6;

IR (neat) cm^{-1} 2969w, 2358w, 1752s, 1701m, 1604w, 1497m, 1478m, 1453m, 1397m;

mass spectrum (APCI): m/e (% relative intensity) 284.1 (100) $(M+H)^+$.



35

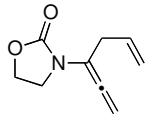
Allenamide **35** (80.0 mg, 0.39 mmol) was prepared in 39% yield according to the general procedure.

35: R_f = 0.32 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +21.1° [c 0.008 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.5 Hz), 2.10-2.15 (m, 1H), 3.22-3.26 (m, 1H), 3.86 (ddd, 1H, *J* = 4.0, 6.0, 9.5 Hz), 4.11 (dd, 1H, 5.5, 9.0 Hz), 4.26 (t, 1H, *J* = 9.0 Hz), 5.09 (ddd, 1H, *J* = 1.0, 2.5, 7.0 Hz), 5.12-5.18 (m, 2H), 5.81 (dq, 1H, *J* = 7.0, 17.0 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 18.0, 28.3, 34.8, 60.8, 63.1, 84.2, 107.4, 117.7, 134.2, 156.4, 204.9;

IR (neat) cm^{-1} 2965m, 2361w, 1744s, 1486m, 1391m, 1324;
mass spectrum (APCI): m/e (% relative intensity) 208.1 (100) (M+H).

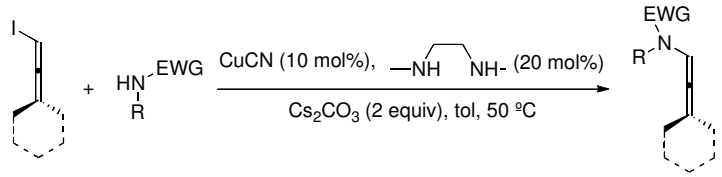


36

Allenamide **36** (79.1 mg, 0.63 mmol) was prepared in 63% yield according to the general procedure.

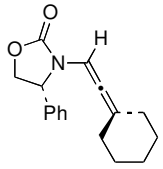
36: R_f = 0.45 [40% EtOAc/hexanes]; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34-3.37(m, 2H), 3.66 (dd, 2H, *J* = 6.8, 8.0 Hz), 4.35 (dd, 2H, 7.2, 8.0 Hz), 5.07 (ddd, 1H, *J* = 1.2, 2.8, 10.0 Hz), 5.15 (ddd, 1H, *J* = 1.6, 3.2, 16.8 Hz), 5.26 (t, 2H, 3.2 Hz), 5.83 (dq, 1H, *J* = 5.6, 13.6 Hz 1H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 33.9, 46.5, 61.9, 85.3, 109.8, 117.2, 134.4, 155.6, 203.2;
IR (neat) cm^{-1} 2981w, 2919w, 2362w, 1743s, 1641w, 1481m, 1451m, 1401m;
mass spectrum (APCI): m/e (% relative intensity) 166.1 (100) (M+H).

GENERAL PROCEDURES FOR ALLENAMIDE SYNTHESIS VIA CU(I)-CATALYZED CROSS-COUPLING.[ii]



A solution of amide (1.2 equiv), CuCN (10 mol%), Cs_2CO_3 (2.0 equiv), *N*, *N*'-dimethylethylene diamine (20 mol%) and allenyl iodide (1 equiv) in toluene (0.1 *M*) was heated to 50 °C for 18 h before being cooled to rt. After filtration through Celite™, the filtrate was concentrated under reduced pressure. Separation and purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired allenamide.

CHARACTERIZATIONS OF ALLENAMIDES.

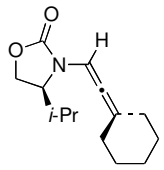


13a

Allenamide **13a** (145.0 mg, 0.54 mmol) was prepared in 26% yield according to the general

procedure.

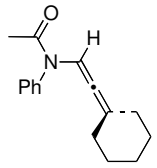
13a: R_f = 0.50 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -134.0° [c 0.002Benzene]; white solid; mp 79-83 ºC;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90-0.96 (m, 1H), 1.23-1.59 (m, 7H), 1.99-2.08 (m, 2H), 4.09 (dd, 1H, *J* = 6.0, 8.5 Hz), 4.67 (t, 1H, *J* = 9.0 Hz), 4.85 (dd, 1H, *J* = 6.0, 9.0 Hz), 6.59 (t, 1H, *J* = 1.5 Hz), 7.22 (d, 2H, *J* = 9.0 Hz), 7.32 (t, 1H, *J* = 5.0 Hz), 7.37 (t, 2H, *J* = 7.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 26.6, 27.2, 32.2, 32.9, 59.6, 70.6, 92.8, 115.6, 126.4, 128.6, 129.2, 139.1, 156.2, 189.6;
IR (neat) cm^{-1} 3033w, 2930w, 2854w, 1968w, 1747s, 1454m, 1395s, 1355m;
mass spectrum (APCI): m/e (% relative intensity) 270.2 (100) (M+H).



13c

Allenamide **13c** (926.0 mg, 3.9 mmol) was prepared in 52% yield according to the general procedure.

13c: R_f = 0.39 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +13.0° [c 0.003 Benzene]; white solid; mp 97-100 ºC;
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 6H, *J* = 7.2 Hz), 1.51-1.61 (m, 4H), 1.69-1.77 (m, 2H), 2.13-2.21 (m, 2H), 2.34 (ddd, 1H, *J* =3.2, 6.8, 10.4 Hz), 3.82 (dt, 1H, *J* = 8.0, 8.8 Hz), 4.16 (dd, 1H, 4.4, 9.2 Hz), 4.26 (t, 1H, *J* = 8.8 Hz), 6.59 (t, 1H, *J* = 1.6 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 18.1, 26.2, 26.7, 27.7, 33.1, 33.2, 59.3, 63.1, 93.0, 115.4, 188.5;
IR (neat) cm^{-1} 2929m, 1968w, 1731s, 1460m, 1398m;
mass spectrum (APCI): m/e (% relative intensity) 236.2 (100) (M+H).



14

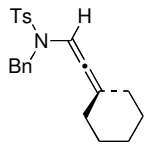
Allenamide **14** (251.0 mg, 1.00 mmol) was prepared in 34% yield according to the general procedure.

14: R_f = 0.28 [1:4 EtOAc/hexanes]; white solid; mp 122-125 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (m, 2H), 1.24 (m, 1H), 1.39 (m, 1H), 1.49 (m, 2H), 1.88 (m, 7H), 7.16 (m, 2H), 7.32-7.45 (m, 4H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 25.9, 27.4, 32.5, 99.2, 114.8, 128.3, 128.7, 129.5, 141.3, 168.6,

190.8;

IR (thin film) cm^{-1} 2926w, 2360w, 1968w, 1661s, 1596w, 1491w, 1432w, 1375m;

mass spectrum (APCI): m/e (% relative intensity) 242.2 (100) $(M+H)^+$.



15

Allenamide **15** (431.0 mg, 1.17 mmol) was prepared in 46% yield according to the general procedure.

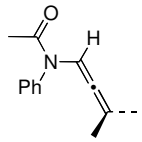
15: R_f = 0.59 [1:4 EtOAc/hexanes]; yellow solid; mp 82-85 ^oC;

^1H NMR (400 MHz, $CDCl_3$) δ 1.26-1.46 (m, 6H), 1.70 (m, 2H), 1.79 (m, 2H), 2.42 (s, 3H), 4.25 (s, 2H), 6.58 (p, 1H, J = 1.6 Hz), 7.15-7.29 (m, 5H), 7.31 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 25.9, 27.1, 32.6, 50.3, 96.9, 115.8, 127.3, 127.5, 127.6, 128.4, 129.8, 135.7, 136.7, 143.7, 190.3;

IR (thin film) cm^{-1} 2929w, 2361m, 1959w, 1598w, 1495w, 1444m, 1351s;

mass spectrum (APCI): m/e (% relative intensity) 368.2 (100) $(M+H)^+$.



18

Allenamide **18** (185.0 mg, 0.92 mmol) was prepared in 31% yield according to the general procedure.

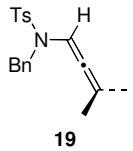
18: R_f = 0.28 [1:4 EtOAc/hexanes]; yellow solid; mp 85-87 ^oC;

^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 6H), 1.89 (s, 3H), 7.14 (d, 2H, J = 7.6 Hz), 7.29-7.44 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 23.3, 99.2, 107.6, 128.3, 128.4, 129.4, 141.2, 168.7, 194.2;

IR (thin film) cm^{-1} 3047w, 2982w, 2361w, 1970w, 1665s, 1597w, 1491m, 1412m, 1372s;

mass spectrum (APCI): m/e (% relative intensity) 202.1 (100) $(M+H)^+$.



19

Allenamide **19** (602.0 mg, 1.84 mmol) was prepared in 30% yield using the general procedure.

19: R_f = 0.55 [1:4 EtOAc/hexanes]; pale orange solid; mp 80-82 ^{o}C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (d, 6H, *J* = 2.4 Hz), 2.42 (s, 3H), 4.25 (s, 2H), 6.57 (sept, 1H, *J* = 2.4 Hz), 7.18-7.30 (m, 5H), 7.32 (d, 2H, *J* = 8.0 Hz), 7.73 (d, 2H, *J* = 8.0 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 21.8, 50.4, 97.2, 109.2, 127.3, 127.5, 127.7, 128.4, 129.8, 135.6, 136.8, 143.8, 193.8;
IR (thin film) cm^{-1} 2985w, 2361m, 1962w, 1598w, 1495w, 1454w, 1410w, 1347s;
mass spectrum (APCI): m/e (% relative intensity) 328.2 (100) $(M+H)^+$.

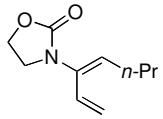
GENERAL PROCEDURE FOR THE THERMAL ISOMERIZATION OF ALLENAMIDES.

A solution of a respective allenamide in anhyd CH_3CN (0.1 *M*) in a sealed tube was heated to appropriate temperature (115 ºC or 135 ºC). Upon completion of the reaction (16 h), the solution was cooled to RT and solvent was removed *in vacuo* afforded a crude product. Separation and purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired 1- or 2-amido-diene.

GENERAL PROCEDURE FOR THE ACID-CATALYZED ISOMERIZATION OF ALLENAMIDES.

To a solution of a respective allenamide (1.0 equiv) in anhyd CH_2Cl_2 (0.1 *M*) in a small vial was added a appropriate acid (PTSA or CSA, 10 mol%) in a small screw-cap scintillation vial equipped with a magnetic stir bar. The solution was stirred for 10 min and filtered through a short pad of silica gel. Elution with EtOAc/Hexanes (1:1) followed by concentration *in vacuo* afforded a crude product. Separation and purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired 1- or 2-amido-diene.

CHARACTERIZATIONS OF 1- AND 2-AMIDO DIENES.



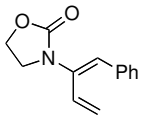
2

Thermal condition: 2-Amido-diene **2** (29.0 mg, 0.16 mmol) was isolated in 78% yield from allenamide **1** (37.0 mg, 0.20 mmol) according to the general procedure.

Acid-catalyzed condition: 2-Amido-diene **2** (14.0 mg, 0.077 mmol) was isolated in 74% yield from allenamide **1** (19.0 mg, 0.105 mmol) according to the general procedure.

2: R_f = 0.50 [40% EtOAc/hexanes]; colorless oil;

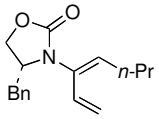
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, 3H, *J* = 7.5 Hz), 1.49 (ddd, 1H, *J* = 3.0, 7.5, 14.5 Hz), 2.24 (q, 2H, *J* = 7.5 Hz), 3.76 (t, 3H, *J* = 8.0 Hz), 4.41 (t, 2H, *J* = 8.0 Hz), 5.25 (dd, 2H, *J* = 7.0, 17.0 Hz), 5.69 (t, 1H, *J* = 7.5 Hz), 6.52 (dd, 1H, *J* = 11.0, 17.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.7, 29.5, 47.6, 62.2, 115.6, 127.9, 132.7, 134.0, 157.4;
IR (neat) cm^{-1} 2959w, 1745s, 1645w, 1598w, 1481w, 1406m;
mass spectrum (APCI): m/e (% relative intensity) 182.1 (100) $(M+H)^+$.



4

Thermal condition: 2-Amido-diene **4** (39.0 mg, 0.18 mmol) was isolated in 71% yield from allenamide **3** (55.0 mg, 0.25 mmol) according to the general procedure.

4: R_f = 0.48 [40% EtOAc/hexanes]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (t, 2H, *J* = 8.0 Hz), 4.47 (t, 2H, *J* = 7.5 Hz), 5.36 (d, 1H, *J* = 11 Hz), 5.38 (d, 1H, *J* = 17.5Hz), 6.66 (dd, 1H, *J* = 11.0, 12.5 Hz), 6.70 (s, 1H), 7.20-7.38 (m, 5H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 47.4, 62.3, 118.0, 128.1, 128.6, 128.6, 128.8, 129.0, 129.7, 130.0, 134.8, 135.1, 157.2;
IR (neat) cm^{-1} 2921w, 1747s, 1594w, 1482w, 1404s;
mass spectrum (APCI): m/e (% relative intensity) 216.1 (100) $(M+H)^+$.



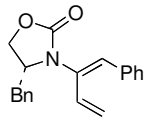
8a

Thermal condition: 2-Amido-diene **8a** (46.0 mg, 0.16 mmol) was isolated in 77% yield from allenamide **5a** (60.0 mg, 0.22 mmol) according to the general procedure.

Acid-catalyzed condition: 2-Amido-diene **8a** (20.0 mg, 0.074 mmol) was isolated in 87% yield from allenamide **5a** (23.0 mg, 0.085 mmol) according to the general procedure.

8a: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -23.3° [c 0.022 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, 3H, *J* = 7.5 Hz), 1.44 (dt, 2H, *J* = 2.5, 7.0 Hz), 2.29 (dd, 2H, *J* = 7.5, 15.0 Hz), 2.60 (dd, 1H, *J* = 10.0, 13.5 Hz), 3.07 (dd, 1H, *J* = 3.5, 13.5 Hz), 4.10 (dd, 1H, *J* = 5.5, 8.0 Hz), 4.18-4.25 (m, 1H), 4.27 (t, 1H, *J* = 8.5 Hz), 5.29 (dd, 2H, *J* = 9.5, 20.5 Hz), 5.74 (t, 1H, *J* = 8.0 Hz), 6.58 (dd, 1H, *J* = 11.0, 17.5 Hz), 7.12 (d, 2H, *J* = 7.5 Hz), 7.26 (dd, 1H, *J* = 3.0, 10 Hz), 7.31 (t, 2H, *J* = 6.5 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 20.6, 27.5, 37.4, 56.1, 65.4, 113.7, 125.2, 126.3, 127.0, 127.0, 127.1, 127.1, 130.1, 132.9, 133.8, 155.0;
IR (neat) cm^{-1} 2961w, 2361w, 1753s, 1600w, 1454w, 1402m;
mass spectrum (APCI): m/e (% relative intensity) 272.1 (100) $(M+H)^+$.

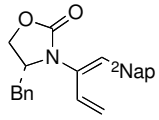


8b

Thermal condition: 2-Amido-diene **8b** (88.0 mg, 0.29 mmol) was isolated in 74% yield from allenamide **5b** (120.0 mg, 0.39 mmol) according to the general procedure.

Acid-catalyzed condition: 2-Amido-diene **8b** (38.0 mg, 0.12 mmol) was isolated in 83% yield from allenamide **5b** (45.0 mg, 0.15 mmol) according to the general procedure.

8b: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +80.9° [c 0.021 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (dd, 1H, *J* = 8.0, 14.0 Hz), 3.13 (dd, 1H, *J* = 3.5, 13.0 Hz), 4.19 (dd, 1H, *J* = 6.5, 11.5 Hz), 4.31-4.39 (m, 2H), 4.39 (d, 1H, *J* = 10.5 Hz), 5.45 (d, 1H, *J* = 17.0 Hz), 6.71 (d, 1H, *J* = 6.5, 17.5 Hz), 6.75 (s, 1H), 7.12 (d, 2H, *J* = 7.5 Hz), 7.25 (d, 2H, *J* = 6.5 Hz), 7.30 (t, 3H, *J* = 7.0 Hz), 7.35 (t, 4H, *J* = 6.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 37.2, 55.9, 65.3, 115.9, 125.3, 126.1, 126.7, 126.8, 127.0, 127.1, 127.3, 127.7, 130.1, 130.1, 130.8, 132.9, 133.6, 154.8;
IR (neat) cm^{-1} 3057w, 2363w, 1752s, 1602w, 1478w, 1446w, 1405, 1401m;
mass spectrum (APCI): m/e (% relative intensity) 306.1 (100) $(M+H)^+$.

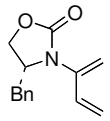


8c

Thermal condition: 2-Amido-diene **8c** (22.0 mg, 0.062 mmol) was isolated in 73% yield from allenamide **5c** (30.0 mg, 0.084 mmol) according to the general procedure.

8c: R_f = 0.15 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +87.6° [c 0.005 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (dd, 1H, *J* = 9.5, 13.5 Hz), 3.18 (dd, 1H, *J* = 4.0, 13.5 Hz), 4.19 (dd, 1H, *J* = 5.5, 8.0 Hz), 4.32-4.43 (m, 2H), 5.46 (d, 1H, *J* = 11.0 Hz), 5.53 (d, 1H, *J* = 17.0 Hz), 6.79 (dd, 1H, *J* = 10.5, 17.0 Hz), 6.90 (s, 1H), 7.16 (d, 2H, *J* = 7.0 Hz), 7.23-7.26 (m, 1H), 7.25 (t, 2H, *J* = 7.5 Hz), 7.45 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.50 (ddd, 2H, *J* =2.5, 3.5, 5.5 Hz), 7.83 (dt, 4H, *J* = 3.5, 4.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 39.5, 58.1, 67.5, 118.4, 126.7, 126.8, 127.4, 127.5, 128.0, 128.2, 128.4,

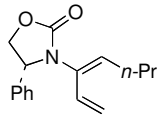
129.2, 129.3, 129.3, 129.6, 132.3, 133.1, 133.3, 133.4, 135.8, 156.9;
IR (neat) cm^{-1} 3057w, 2925w, 1751s, 1601w, 1498w, 1478w, 1475w, 1454w, 1400m,;
mass spectrum (APCI): m/e (% relative intensity) 356.1 (100) $(M+H)^+$.



8d

Thermal condition: 2-Amido-diene **8d** (17.0 mg, 0.075 mmol) was isolated in 69% yield from allenamide **5d** (25.0 mg, 0.11 mmol) according to the general procedure. Alumina column was used for isolation.

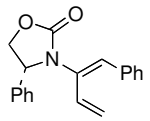
8d: R_f = 0.19 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -2.89° [c 0.003 Benzene]; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61-2.70 (m, 1H), 3.14 (dd, 1H, *J* = 3.2, 13.6 Hz), 4.11-4.30 (m, 3H), 5.27 (s, 1H), 5.32 (d, 1H, *J* = 10.8 Hz), 5.40 (s, 1H), 5.46 (d, 1H, *J* = 17.2 Hz), 6.41 (dd, 1H, *J* =10.8, 17.2 Hz), 7.14 (d, 2H, *J* = 7.2 Hz), 7.20-7.34 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 38.7, 58.0, 66.3, 67.1, 113.6, 117.1, 127.4, 129.2, 129.2, 129.6, 133.1, 135.6, 140.4, 156.4;
IR (neat) cm^{-1} 2921m, 2853m, 2360w, 1758s, 1702w, 1595w, 1478w, 1455w, 1404m, 1376w;
mass spectrum (APCI): m/e (% relative intensity) 230.2 (100) $(M+H)^+$.



9a

Acid-catalyzed condition: 2-Amido-diene **9a** (45.1 mg, 0.16 mmol) was isolated in 82% yield from allenamide **6a** (55.0 mg, 0.19 mmol) according to the general procedure.

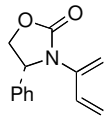
9a: R_f = 0.22 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -86.4° [c 0.037 Benzene]; yellow solid; mp 35-37 ºC;
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (t, 3H, *J* = 7.6 Hz), 1.12-1.27 (m, 2H), 2.05 (dd, 2H, *J* = 7.2, 12.4 Hz), 4.34 (dd, 1H, *J* = 7.2, 8.8 Hz), 4.74 (dt, 1H, *J* = 2.0, 8.8 Hz), 5.02 (dd, 1H, *J* = 7.2, 8.8 Hz), 5.24 (t, 1H, *J* = 11.2 Hz), 5.35 (t, 1H, *J* = 8.8 Hz), 6.40 (dd, 1H, *J* = 10.8, 17.2 Hz), 7.26-7.41 (m, 5H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 22.4, 29.3, 61.6, 67.0, 115.5, 127.8, 128.0, 129.2, 129.2, 131.9, 135.3, 138.3, 157.2;
IR (neat) cm^{-1} 2959w, 1756s, 1479w, 1458w, 1396w;
mass spectrum (APCI): m/e (% relative intensity) 258.2 (100) $(M+H)^+$.



9b

Acid-catalyzed condition: 2-Amido-diene **9b** (404.0 mg, 1.39 mmol) was isolated in 76% yield from allenamide **6b** (530.0 mg, 1.82 mmol) according to the general procedure.

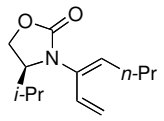
9b: R_f = 0.33 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +25.3° [c 0.103 Benzene]; yellow oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (dd, 1H, *J* = 6.5, 8.5 Hz), 4.79 (t, 1H, *J* = 8.5 Hz), 5.15 (dd, 1H, *J* = 6.5, 8.5 Hz), 5.36 (dt, 1H, *J* = 1.0, 11.0 Hz), 5.49 (bd, 1H, *J* = 17.0 Hz), 6.39 (s, 1H), 6.50 (dd, 1H, *J* = 10.5, 17.5 Hz), 7.10 (d, 2H, *J* = 7.5 Hz), 7.19-7.40 (m, 8H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 61.5, 70.0, 117.8, 127.8, 128.0, 128.9, 129.0, 129.2, 129.4, 129.4, 129.6, 132.4, 132.9, 135.1, 138.1, 157.0;
IR (neat) cm^{-1} 3032w, 1750s, 1599w, 1495w, 1457w, 1395m;
mass spectrum (APCI): m/e (% relative intensity) 292.2 (100) $(M+H)^+$.



9c

Thermal condition: 2-Amido-diene **9c** (104.0 mg, 0.48 mmol) was isolated in 69% yield from allenamide **6c** (150.0 mg, 0.69 mmol) according to the general procedure. Alumina column was used for isolation.

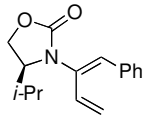
9c: R_f = 0.15 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -40.9° [c 0.021 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 (dd, 1H, *J* = 7.0, 9.0 Hz), 4.72 (t, 1H, *J* = 8.5 Hz), 4.82 (s, 1H), 5.06 (s, 1H), 5.13 (dd, 1H, *J* = 6.5, 8.5 Hz), 5.22 (d, 1H, *J* = 11.0 Hz), 5.43 (d, 1H, *J* = 17.0 Hz), 6.29 (dd, 1H, *J* =11.0, 17.5 Hz), 7.27-7.40 (m, 5H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 61.5, 70.2, 111.7, 116.7, 127.1, 129.3, 129.4, 132.9, 138.1, 140.5, 156.4;
IR (neat) cm^{-1} 2953w, 2361w, 1748s, 1637w, 1590w, 1458m, 1392m;
mass spectrum (APCI): m/e (% relative intensity) 216.1 (100) $(M+H)^+$.



10a

Thermal condition: 2-Amido-diene **10a** (19.0 mg, 0.082 mmol) was isolated in 62% yield from allenamide **7a** (30.0 mg, 0.14 mmol) according to the general procedure.

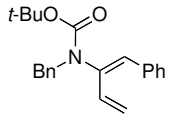
10a: R_f = 0.22 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -15.0° [c 0.007 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 7.5 Hz), 0.92 (d, 3H, *J* = 7.0 Hz), 0.95 (d, 3H, *J* = 7.5 Hz), 1.49 (sep, 1H, *J* = 7.0 Hz), 1.90 (dt, 1H, *J* = 3.5, 7.5 Hz), 2.27 (q, 2H, *J* = 7.5 Hz), 3.94 (ddd, 1H, *J* = 4.0, 6.0, 9.0 Hz), 4.16 (dd, 1H, *J* = 5.5, 8.5 Hz), 4.35 (t, 1H, *J* = 9.0 Hz), 5.23 (dd, 2H, *J* = 9.5, 17.5 Hz), 5.70 (t, 1H, *J* = 8.0 Hz), 6.52 (dd, 1H, *J* = 9.5, 17.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.9, 18.3, 22.7, 29.0, 29.6, 60.8, 63.5, 115.8, 128.1, 132.3, 134.6, 157.7;
IR (neat) cm^{-1} 2960w, 2361w, 1750s, 1646w, 1599w, 1464w, 1406m;
mass spectrum (APCI): m/e (% relative intensity) 224.1 (100) $(M+H)^+$.



10b

Thermal condition: 2-Amido-diene **10b** (27.0 mg, 0.11 mmol) was isolated in 82% yield from allenamide **7b** (33.0 mg, 0.13 mmol) according to the general procedure.

10b: R_f = 0.21 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -110.0° [c 0.005 Benzene]; white solid; mp 128-131 ºC;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (d, 3H, *J* = 7.0 Hz), 0.99 (t, 3H, *J* = 7.0 Hz), 1.98 (dt, 1H, *J* = 3.5, 7.5 Hz), 4.09 (ddd, 1H, *J* = 4.0, 5.5, 9.5 Hz), 4.21 (dd, 1H, *J* = 5.5, 9.0 Hz), 4.39 (t, 1H, *J* = 9.0 Hz), 5.37 (d, 1H, *J* = 11 Hz), 5.44 (bd, 1H, *J* =17.0 Hz) 6.64 (dd, 1H, *J* = 10.5, 17.5 Hz), 6.72 (s, 1H), 7.27-7.37 (m, 5H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 18.3, 29.3, 60.7, 63.7, 118.1, 128.1, 128.5, 129.2, 129.8, 131.6, 131.7, 133.3, 135.3, 157.5;
IR (neat) cm^{-1} 2964w, 2929w, 1750s, 1632w, 1591w, 1485w, 1402m;
mass spectrum (APCI): m/e (% relative intensity) 258.2 (100) $(M+H)^+$.



12

Thermal condition: 2-Amido-diene **12** (15.0 mg, 0.045 mmol) was isolated in 45% yield from allenamide **11** (33.0 mg, 0.10 mmol) according to the general procedure.

Acid-catalyzed condition: 2-Amido-diene **12** (20.0 mg, 0.060 mmol) was isolated in 61% yield from allenamide **11** (33.0 mg, 0.10 mmol) according to the general procedure.

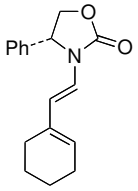
12: R_f = 0.38 [10% EtOAc/hexanes];

^{1}H NMR (500 MHz, $CDCl_3$, 55 °C) δ 1.45 (s, 9H), 4.60 (s, 2H), 5.16 (d, 1H, *J* = 10.0 Hz), 5.26 (d, 1H, *J* = 17.0 Hz), 6.59 (dd, 1H, *J* = 17.0, 10.5 Hz), 7.13 (d, 2H, *J* = 7.5 Hz), 7.20-7.35 (m, 8H);

^{13}C NMR (125 MHz, $CDCl_3$, 55 °C) δ 28.5, 52.4, 80.1, 116.1, 127.5, 127.6, 128.4, 128.5, 129,2, 129.4, 130.4, 131.9, 136.0, 138.9, 139.1, 143.8, 155.5;

IR (thin film) cm^{-1} 2972m, 1736s, 1366s, 1227m, 1147s;

mass spectrum (APCI): m/e (% relative intensity) 236 (100) $(M+H\text{-}Boc)^+$.



20a

Acid-catalyzed condition: 1-Amido-diene **20a** (19.5 mg, 0.072 mmol) was isolated in 95% yield from the allenamide **13a** (20.0 mg, 0.074 mmol) according to the general procedure.

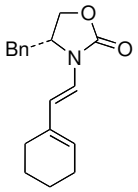
20a: R_f = 0.29 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -166.6° [c 0.015 Benzene]; white solid; mp 117-122 ºC;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54 (p, 2H, *J* =6.5 Hz), 1.62 (p, 2H, *J* = 6.0 Hz), 2.00 (dd, *J* = 3.5, 5.5 Hz), 2.05 (d, 2H, *J* = 5.0 Hz), 4.13 (dd, 1H, *J* = 5.0, 9.0 Hz), 4.71 (t, 1H, *J* = 9.0 Hz), 5.03 (dd, 1H, *J* = 5.0, 9.0 Hz), 5.32 (d, 1H, *J* = 15.0 Hz), 5.38 (t, 1H, *J* = 4.0 Hz), 6.73 (d, 1H, *J* = 15.0 Hz), 7.27 (d, 2H, *J* = 1.5, 5.0 Hz), 7.33-7.41 (m, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 22.6, 24.5, 25.9, 58.8, 70.9, 117.4, 119.9, 126.0, 127.6, 128.9, 129.7, 133.7, 138.7, 156.1;

IR (neat) cm^{-1} 3034w, 2930w, 1757s, 1651w, 1478w, 1457w, 1402m;

mass spectrum (APCI): m/e (% relative intensity) 270.2 (100) $(M+H)^+$.



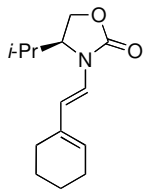
20b

Acid-catalyzed condition: 1-Amido-diene **20b** (40.0 mg, 0.14 mmol) was isolated in 96% yield from allenamide **13b** (42.0 mg, 0.15 mmol) according to the general procedure.

20b: R_f = 0.40 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +27.5° [c 0.002 Benzene]; white solid; mp 170-176 ºC;

δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (ddd, 2H, *J* =2.0, 6.0, 8.0 Hz), 1.69 (ddd, 2H, *J* = 5.6, 9.2, 10.8 Hz), 2.12-2.17 (m, 4H), 2.79 (dd, 1H, *J* = 8.8, 13.6 Hz), 3.25 (dd, 1H, *J* = 2.8, 13.6 Hz), 4.17-4.34 (m, 3H), 4.71 (t, 1H, *J* = 7.2 Hz), 5.72 (t, 1H, *J* = 3.6 Hz), 5.77 (bd, 1H, *J* = 14.8 Hz), 6.72 (d, 1H, *J* = 15.2

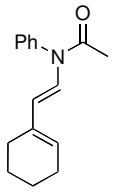
Hz), 7.19 (dd, 2H, *J* = 1.6, 3.6 Hz), 7.30 (dt, 1H, *J* = 1.2, 6.4 Hz), 7.36 (dt, 2H, *J* = 1.2, 6.4 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 22.7, 24.8, 26.1, 36.5, 55.1, 66.7, 116.3, 119.8, 127.6, 127.7, 129.2, 129.5, 133.9, 135.6, 155.4;
IR (neat) cm^{-1} 2924w, 2360w, 1753s, 1650w, 1624w, 1411m;
mass spectrum (APCI): m/e (% relative intensity) 284.2 (100) $(M+H)^+$.



20c

Acid-catalyzed condition: 1-Amido-diene **20c** (35.0 mg, 0.15 mmol) was isolated in 100% yield from allenamide **13c** (35.0 mg, 0.15 mmol) according to the general procedure.

20c: R_f = 0.48 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -19.0° [c 0.001 Benzene]; white solid; mp 98-100 ºC;
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (d, 3H, *J* = 6.8 Hz), 0.95 (d, 3H, *J* = 7.2 Hz), 1.62 (ddd, 2H, *J* =2.0, 6.0, 8.0 Hz), 1.69 (ddd, 2H, *J* = 5.6, 9.2, 10.8 Hz), 2.12-2.17 (m, 4H), 2.79 (dd, 1H, *J* = 8.8, 13.6 Hz), 3.25 (dd, 1H, *J* = 2.8, 13.6 Hz), 4.17-4.34 (m, 3H), 4.71 (t, 1H, *J* = 7.2 Hz), 5.72 (t, 1H, *J* = 3.6 Hz), 5.77 (bd, 1H, *J* = 14.8 Hz), 6.66 (bd, 1H, *J* = 14.8 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 18.1, 22.6, 22.7, 24.7, 26.1, 26.4, 58.6, 63.1, 116.1, 119.9, 127.3, 133.9, 155.9;
IR (neat) cm^{-1} 2918w, 2360w, 1734s, 1650w, 1626w, 1416s;
mass spectrum (APCI): m/e (% relative intensity) 236.2 (100) $(M+H)^+$.



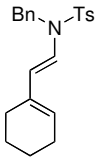
21

Thermal condition: 1-Amido-diene **21** (31.9 mg, 0.132 mmol) was isolated in 99% yield from allenamide **14** (32 mg, 0.133 mmol) according to the general procedure but heated in toluene at 175 °C for 24 h.

Acid-catalyzed condition: 1-Amido-diene **21** (23.5 mg, 0.097 mmol) was isolated in 90% yield from allenamide **14** (26.0 mg, 0.108 mmol) according to the general procedure with the addition of 26.0 mg 4 Å MS.

21: R_f = 0.35 [1:4 EtOAc/hexanes]; yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (ddd, 2H, *J* = 5.6, 5.6, 6.0 Hz), 1.67 (ddd, 2H, *J* = 5.6, 6.0, 6.0 Hz), 1.86 (s, 3H), 2.03 (m, 2H), 2.19 (m, 2H), 5.02 (d, 1H, *J* = 14.8 Hz), 5.40 (m, 1H), 7.17 (m, 2H), 7.40-7.53 (m, 3H), 7.62 (d, 1H, *J* = 14.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 22.7, 23.6, 24.9, 26.0, 118.4, 125.7, 127.7, 128.9, 129.2, 130.2, 134.3, 140.0, 168.8;
IR (thin film) cm^{-1} 2937w, 2362m, 1672s, 1621m, 1597m, 1544w, 1495m, 1442m, 1373s;
mass spectrum (APCI): m/e (% relative intensity) 242.2 (100) $(M+H)^+$.

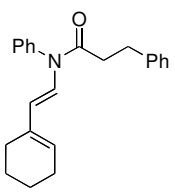


22

Thermal condition: 1-Amido-diene **22** (35.6 mg, 0.097 mmol) was isolated in 96% yield from allenamide **15** (37.0 mg, 0.101 mmol) according to the general procedure but heated in toluene at 175 °C for 24 h.

Acid-catalyzed condition: 1-Amido-diene **22** (29.3 mg, 0.080 mmol) was isolated in 97% yield from allenamide **15** (30.0 mg, 0.082 mmol) according to the general procedure with the addition of 30.0 mg 4 Å MS.

22: R_f = 0.59 [1:4 EtOAc/hexanes]; pale orange solid; mp 112-115 °C;
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (ddd, 2H, *J* = 3.2, 5.6, 6.0 Hz), 1.62 (ddd, 2H, *J* = 3.2, 5.6, 6.0 Hz), 1.98-2.10 (m, 4H), 2.42 (s, 3H), 4.52 (s, 2H), 5.38 (d, 1H, *J* = 14.4 Hz), 5.41 (m, 1H), 6.81 (d, 1H, *J* = 14.4 Hz), 7.20-7.32 (m, 7H), 7.67 (d, 2H, *J* = 8.4 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.6, 22.7, 24.8, 49.6, 117.0, 123.4, 127.1, 127.3, 127.6, 128.8, 130.1, 133.7, 136.0, 136.3, 144.0;
IR (thin film) cm^{-1} 2926w, 2361m, 1644w, 1621w, 1598w, 1495w, 1455w, 1355s;
mass spectrum (APCI): m/e (% relative intensity) 368.2 (100) $(M+H)^+$.



23

Thermal condition: 1-Amido-diene **23** (35.2 mg, 0.106 mmol) was isolated in 98% yield from allenamide **16** (36.0 mg, 0.109 mmol) according to the general procedure but heated in toluene at 175 °C for 24 h.

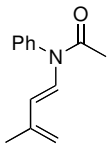
23: R_f = 0.27 [1:9 EtOAc/hexanes]; yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55 (ddd, 2H, *J* = 2.8, 6.0, 8.4 Hz), 1.65 (ddd, 2H, *J* = 2.8, 6.0, 8.4 Hz), 2.02 (m, 2H), 2.19 (m, 2H), 2.34 (t, 2H, *J* = 7.6 Hz), 2.92 (t, 2H, *J* = 7.6 Hz), 4.98 (d, 1H, *J* = 14.8 Hz), 5.38 (t, 1H, *J* = 4.0 Hz), 7.03 (m, 4H), 7.18-7.26 (m, 3H), 7.36-7.46 (m, 3H), 7.64 (d, 1H, *J* = 14.8 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 22.8, 24.9, 26.1, 31.7, 37.1, 118.5, 125.8, 126.3, 127.8, 128.6, 128.6, 128.9, 130.2, 134.3, 139.3, 141.2, 170.5;

IR (thin film) cm^{-1} 2928w, 2361w, 1667s, 1619m, 1595m, 1542w, 1493m, 1452w, 1377m;

mass spectrum (APCI): m/e (% relative intensity) 332.2 (100) $(M+H)^+$.



25

Thermal condition: 1-Amido-diene **25** was formed in 46% NMR yield from allenamide **18** (24.0 mg, 0.119 mmol) based on phenanthrene as an internal standard according to the general procedure but heated in toluene at 175 °C for 24 h.

Acid-catalyzed condition: 1-Amido-diene **25** (26.2 mg, 0.130 mmol) was isolated in 97% yield from allenamide **18** (27.0 mg, 0.134 mmol) according to the general procedure with the addition of 27 mg 4 Å MS.

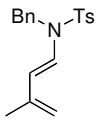
25: R_f = 0.35 [1:4 EtOAc/hexanes]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 3H), 1.90 (s, 3H), 4.64 (s, 1H), 4.76 (s, 1H), 5.13 (d, 1H, *J* = 14.8 Hz), 7.19 (m, 2H), 7.42-7.54 (m, 3H), 7.71 (d, 1H, *J* = 14.8 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 23.6, 114.7, 117.2, 128.8, 129.0, 129.1, 130.3, 139.8, 140.9, 169.1;

IR (thin film) cm^{-1} 2976w, 2363m, 1782w, 1676s, 1638m, 1597m, 1544w, 1495m, 1455w, 1371s;

mass spectrum (APCI): m/e (% relative intensity) 202.2 (100) $(M+H)^+$.



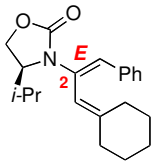
26

Thermal condition: 1-Amido-diene **26** was formed in 77% NMR yield from allenamide **19** (29.0 mg, 0.089 mmol) based on phenanthrene as an internal standard according to the general procedure but heated for 48 h.

Acid-catalyzed condition: 1-Amido-diene **26** (36.6 mg, 0.112 mmol) was isolated in 99% yield from allenamide **19** (37.0 mg, 0.113 mmol) according to the general procedure described with the

addition of 37.0 mg 4 Å MS.

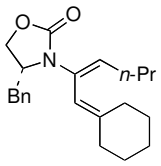
26: R_f = 0.59 [1:4 EtOAc/hexanes]; yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.42 (s, 3H), 4.55 (s, 2H), 4.65 (s, 1H), 4.73 (s, 1H), 5.48 (d, 1H, *J* = 14.4 Hz), 6.94 (d, 1H, *J* = 14.4 Hz), 7.20-7.33 (m, 7H), 7.67 (d, 2H, *J* = 8.4 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.8, 49.6, 114.3, 115.5, 126.9, 127.1, 127.1, 127.7, 128.8, 130.1, 135.7, 136.2, 140.3, 144.2;
IR (thin film) cm^{-1} 2975w, 2361m, 1636m, 1598w, 1495w, 1454w, 1355m;
mass spectrum (APCI): m/e (% relative intensity) 328.1 (100) $(M+H)^+$.



28a

Thermal condition: 2-Amido-diene **28a** (43.0 mg, 0.13 mmol) was isolated in 71% yield from allenamide **27a** (60.0 mg, 0.18 mmol) according to the general procedure.

28a; R_f = 0.20 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -44.3° [c 0.003 Benzene]; white solid; mp 102-104 ºC;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, 3H, *J* = 7.0 Hz), 0.94 (d, 3H, *J* = 6.5 Hz), 1.24-1.38 (m, 2H), 1.38-1.45 (m, 1H), 1.48-1.64 (m, 3H), 1.80 (p, 1H, *J* =6.5 Hz), 1.93 (sep, 1H, *J* = 3.0 Hz), 2.04-2.26 (m, 3H), 3.97 (p, 1H, *J* = 3.5 Hz), 4.13 (dd, 1H, *J* = 5.0, 9.5 Hz), 4.26 (t, 1H, *J* = 9.0 Hz), 5.65 (s, 1H), 6.69 (s, 1H), 7.17 (t, 1H, *J* = 7.5 Hz), 7.26 (t, 1H, *J* = 7.0 Hz), 7.38 (d, 2H, *J* = 7.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 18.0, 26.5, 26.9, 28.4, 29.5, 30.3, 37.1, 59.9, 62.6, 115.3, 126.7, 127.1, 128.3, 129.4, 130.8, 136.6, 148.7, 156.6;
IR (neat) cm^{-1} 2929w, 1744s, 1626w, 1485w, 1446m, 1400m, 1371m;
mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



28b

2-Amido-diene **28b** (41.0 mg, 0.12 mmol) was synthesized from allenamide **27b** (43.0 mg, 0.13 mmol) according to the general procedure.

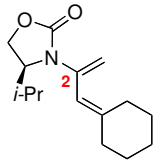
28b: R_f = 0.50 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +131.1° [c 0.009 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84-0.92 (m, 2H), 0.94 (t, 3H, *J* = 7.0 Hz), 1.49 (dt, 2H, *J* = 7.5, 15.0 Hz), 1.53-1.71 (m, 4H), 2.01-2.25 (m, 3H), 2.24 (ddd, 3H, *J* = 4.5, 9.5, 15.5), 2.60 (ddd, 1H, *J* = 3.0, 6.5,

9.5 Hz), 3.05 (dd, 1H, *J* = 3.0, 13.5 Hz), 4.00 (dd, 1H, *J* =11.0, 20.5 Hz), 4.14 (ddd, 2H, *J* = 7.0, 8.0, 13.0 Hz), 5.50 (s, 1H), 5.77, (t, 1H, *J* = 7.5 Hz), 7.12 (d, 2H, *J* = 7.0 Hz), 7.26 (d, 1H, *J* = 6.5 Hz), 7.31 (t, 2H, *J* =7.0 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 26.7, 27.6, 28.8, 30.6, 30.7, 37.1, 39.3, 57.4, 66.4, 115.1, 127.3, 128.9, 129.2, 129.4, 129.4, 136.1, 148.0, 156.5;

IR (neat) cm^{-1} 2928m, 2360w, 1753s, 1647w, 1479w, 1449m, 1399m;

mass spectrum (APCI): m/e (% relative intensity) 340.2 (100) (M+H).



28c

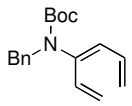
28c: R_f = 0.46 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -120.5^o [c 0.013 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 6H, *J* = 6.8 Hz), 1.46-1.67 (m, 6H), 1.99 (dtt, 1H, *J* = 4.0, 7.2, 10.8 Hz), 2.17 (dd, 2H, *J* = 5.2, 6.0), 2.33 (ddd, 1H, *J* = 3.2, 8.8, 12.0 Hz), 2.44 (ddd, 1H, *J* = 4.4, 6.8, 13.6 Hz), 3.96 (dt, 1H, *J* =4.0, 8.0 Hz), 4.10 (dd, 1H, *J* = 4.4, 8.8 Hz), 4.24 (t, 1H, *J* =8.8 Hz), 4.92 (d, 1H, *J* = 1.2Hz), 5.37 (s, 1H), 5.57 (d, 1H, *J* = 0.8 Hz);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 17.9, 26.7, 28.1, 28.8, 29.3, 29.9, 37.5, 60.3, 62.5, 109.3, 117.8, 137.3, 148.1, 156.2;

IR (neat) cm^{-1} 2928m, 2362w, 1750s, 1619w, 1447w, 1402m;

mass spectrum (APCI): m/e (% relative intensity) 250.2 (100) (M+H).



30

Acid-catalyzed condition: 3-Amido-triene **30** (31.0 mg, 0.11 mmol) was isolated in 86% yield from allenamide **29** (36.0 mg, 0.13 mmol) according to the general procedure.

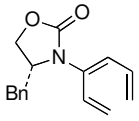
30: R_f = 0.12 [20% EtOAc/hexanes]; clear oil;

^{1}H NMR (500 MHz, $CDCl_3$, 55 ^{o}C) δ 1.41 (s, 9H), 4.53 (s, 2H), 5.12-5.17 (m, 4H), 5.76 (d, 1H *J* = 11.5 Hz), 6.58-6.68 (m, 2H), 7.22-7.28 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$, 55 ^{o}C) δ 28.5, 52.8, 80.2, 115.6, 119.9, 127.4, 128.4, 128.8, 129.1, 131.2, 131.4, 135.7, 139.0, 155.3;

IR (thin film) cm^{-1} 2979m, 1694s, 1384m, 1167s;

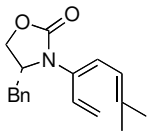
mass spectrum (APCI): m/e (% relative intensity) 186 (100) $(M+H\text{-}Boc)^+$.



33a

Acid-catalyzed condition: 3-Amido-triene **33a** (44.0 mg, 0.17 mmol) was isolated in 89% yield from allenamide **32a** (50.0 mg, 0.19 mmol) according to the general procedure.

33a: R_f = 0.20 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +1.33 ^{o} [c 0.015 Benzene]; colorless oil;
δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.62 (ddd, 1H, *J* =4.5, 9.0, 15.0 Hz), 3.08 (dd, 1H, *J* = 3.5, 13.5 Hz), 4.15 (dt, 1H, *J* = 4.0, 10.0 Hz), 4.24-4.30 (m, 2H), 5.39 (ddd, 4H, *J* = 10.0, 18.5, 20.0 Hz), 6.29 (d, 1H, *J* = 11.0 Hz); 6.66-6.80 (m, 2H), 7.12 (d, 2H, *J* = 7.5 Hz), 7.23-7.32 (m, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 39.3, 58.3, 67.4, 117.7, 121.7, 128.4, 129.2, 129.2, 131.0, 131.6, 132.7, 135.7, 156.7;
IR (neat) cm^{-1} 3092w, 2365w, 1759s, 1480m, 1456m, 1412m, 1397w;
mass spectrum (APCI): m/e (% relative intensity) 256.2 (100) $(M+H)^+$.



33b

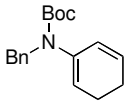
Thermal condition: 3-Amido-triene **33b** (54.0 mg, 0.19 mmol) was isolated in 77% yield from allenamide **32b** (70.0 mg, 0.25 mmol) according to the general procedure.

33b: R_f = 0.18 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +8.0^o [c 0.002 Benzene]; colorless oil;
δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 1.89 (s, 3H), 2.61 (dd, 1H, *J* =2.0, 10.4, 13.6 Hz), 3.09 (dd, 1H, *J* = 3.6, 13.6 Hz), 4.09-4.15 (m, 1H), 4.21-4.30 (m, 2H), 5.27 (d, 1H, *J* = 3.6 Hz), 5.30 (d, 1H, *J* = 5.2 Hz), 6.26 (dp, 1H, *J* =1.2, 11.6 Hz), 6.45 (d, 1H, *J* = 12.0 Hz); 6.73 (dd, 1H, *J* = 10.8, 17.6 Hz), 7.10 (d, 2H, *J* = 8.4 Hz), 7.22-7.32 (m, 3H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 18.9, 26.9, 39.4, 58.2, 67.4, 115.7, 119.4, 127.3, 128.4, 128.5, 129.1, 129.2, 129.4, 135.9, 141.3, 157.1;
IR (neat) cm^{-1} 3032w, 2913w, 1754s, 1639w, 1574w, 1500w, 1456w, 1403m;
mass spectrum (APCI): m/e (% relative intensity) 284.1 (100) $(M+H)^+$.

GENERAL PROCEDURE FOR THE ELECTROCYCLIC RING-CLOSURE.

A solution of a respective allenamide or triene in anhyd CH_3CN (0.1 *M*) in a sealed tube was heated to 135 ºC. Upon completion of the reaction (16 h), the solution was cooled to RT and solvent was removed *in vacuo* afforded a crude product. Separation and purification of the resulting crude residue via silica gel flash column chromatography (gradient eluent: EtOAc in hexane) afforded the desired 2-amido-1,3-cyclohexadienes.

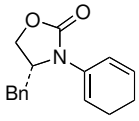
CHARACTERIZATIONS OF CYCLIC 2-AMIDO DIENES.



31

Cyclic 2-amido-diene **31** (11.0 mg, 0.04 mmol) was isolated in 35% yield from 3-amido-triene **30** (31.0 mg, 0.11 mmol) according to the general procedure.

31: R_f = 0.33 [17% EtOAc/hexanes]; pale yellow oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.09-2.17 (m, 4H), 4.59 (s, 2H), 5.43 (brs, 1H), 5.76-5.82 (m, 2H), 7.23-7.31 (m, 5H);
^{13}C NMR (125 MHz, $CDCl_3$, 55 ^{o}C) δ 21.9, 22.2, 28.5, 53.1, 80.3, 118.7, 126.8, 127.0, 127.1, 127.8, 128.5, 138.2, 139.3, 154.9;
IR (thin film) cm^{-1} 3031m, 1698s, 1387m, 1165s;
mass spectrum (APCI): m/e (% relative intensity) 186 (100) $(M+H-Boc)^+$.



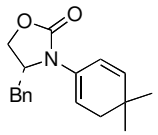
34a

Cyclic 2-amido-diene **34a** (14.0 mg, 0.053 mmol) was isolated in 43% yield from allenamide **32a** (32.0 mg, 0.14 mmol) according to the general procedure.

Cyclic 2-amido-diene **34a** (120.0 mg, 0.46 mmol) was isolated in 84% yield from the 3-amido-triene **33a** (143.0 mg, 0.55 mmol) according to the general procedure.

34a: R_f = 0.22 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +25.0 ^{o} [c 0.004 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.17-2.40 (m, 4H), 2.71 (dd, 1H, *J* = 9.0, 13.5 Hz), 3.16 (dd, 1H, *J* = 4.0, 14.0 Hz), 4.11 (dd, 1H, *J* = 5.5, 8.5 Hz), 4.24 (t, 1H, *J* =8.5 Hz)), 4.28-4.37 (m, 1H), 5.71 (dt, 1H, *J* = 1.5, 5.0 Hz), 6.02 (dt, 1H, *J* = 5.0, 9.5 Hz); 6.17 (dq, 1H, *J* = 1.5,

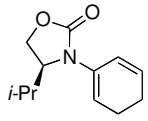
9.5 Hz), 7.14 (d, 2H, *J* = 6.5 Hz), 7.27 (d, 1H, *J* = 1.5, 7.5), 7.31 (t, 2H, *J* = 7.0);
^{13}C NMR (125 MHz, $CDCl_3$) δ 22.0, 22.0, 38.3, 57.2, 66.6, 116.1, 122.9, 127.4, 129.2, 129.2, 129.4, 129.5, 131.8, 135.8, 155.9;
IR (neat) cm^{-1} 2926w, 2361w, 1748s, 1600w, 1498w, 1479w, 1405m;
mass spectrum (APCI): m/e (% relative intensity) 254.1 (100) $(M+H)^+$.



34b ***Not seen.***

Instead of the desired cyclic 2-amido-diene **34b**, another with an unknown identity at this point was isolated (21.0 mg) from 3-amido-triene **33b**.

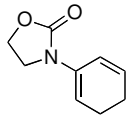
Collected Characterizations for the unknown: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -15.8 ^{o} [c 0.004 Benzene]; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (d, 3H, *J* = 7.0 Hz), 1.83 (s, 3H), 2.61 (dd, 1H, *J* = 8.0, 16.5 Hz), 2.78 (ddd, 1H, *J* = 3.0, 9.5, 13.0 Hz), 3.26 (ddd, 2H, *J* = 3.0, 10.0, 17.0 Hz), 4.11 (dd, 1H, *J* =3.5, 8.5 Hz), 4.15-4.25 (m,2H), 5.55 (d, 1H, *J* = 5.5 Hz), 5.67-5.69 (m, 1H), 7.16-7.38 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 23.5, 28.3, 37.3, 37.8, 58.4, 66.1, 111.4, 17.5, 127,5, 129.2, 129.4, 129.7, 132.0, 136.0, 137.2, 154.8; IR (neat) cm^{-1} 2919w, 2361w, 1751s, 1655w, 1596w, 1478w, 1452w; mass spectrum (APCI): m/e (% relative intensity) 256.1 (10) $(M+H-CO)^+$.



37

Cyclic 2-amido-diene **37** (39.0 mg, 0.19 mmol) was isolated in 54% yield from allenamide **35** (72.0 mg, 0.37 mmol) according to the general procedure.

37: R_f = 0.20 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -27.1 ^{o} [c 0.009 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 6H, *J* = 7.0 Hz), 2.11 (sep, 1H, *J* =3.5 Hz), 2.16-2.38 (m, 4H), 4.06 (ddd, 1H, *J* = 3.5, 8.5, 12.5 Hz), 4.11 (dd, 1H, *J* = 5.5, 9.0 Hz), 4.29 (t, 1H, *J* = 9.0 Hz), 5.67 (ddd, 1H, *J* = 1.0, 1.5, 4.5 Hz), 5.98 (dt, 1H, *J* = 4.0, 9.0 Hz), 6.05 (dt, 1H, *J* = 2.0, 10.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.8, 17.9, 21.9, 21.9, 60.3, 63.0, 116.9, 123.0, 129.2, 131.8, 156.4;
IR (neat) cm^{-1} 2964w, 2361w, 1746s, 1482w, 1408m, 1392m;
mass spectrum (APCI): m/e (% relative intensity) 206.1 (30) $(M-H_2+H)^+$.



38

Cyclic 2-amido-diene **38** (23.0 mg, 0.14 mmol) was isolated in 57% yield from allenamide **36** (40.0 mg, 0.24 mmol) according to the general procedure.

38: R_f = 0.39 [40% EtOAc/hexanes]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.11-2.28 (m, 4H), 3.79 (t, 2H, *J* = 9.0 Hz), 4.39 (t, 2H, *J* = 8.5 Hz), 5.27 (t, 1H, *J* = 4.0 Hz), 5.99 (dt, 1H, *J* = 4.5, 9.0 Hz), 6.58 (dt, 1H, *J* = 2.0, 12.0 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8, 23.2, 45.5, 61.6, 106.5, 122.6, 123.7, 136.7, 154.8;

IR (neat) cm^{-1} 2922w, 1737s, 1649w, 1599w, 1479w, 1405m;

mass spectrum (APCI): m/e (% relative intensity) 166.2 (100) $(M-H_2+H)^+$.

---

[i] Xiong, H.; Hsung, R. P.; Wei, L. –L.; Berry, C. R.; Mulder, J. A.; Stockwell, B. *Org. Lett.* **2000,** *2,* 2869.

[ii] Shen, L.; Hsung, R. P.; Zhang, Y.; Antoline, J. E.; Zhang, X. *Org. Lett.* **2005,** *7,* 3081.