SUPPORTING INFORMATION

for
the
communication
entitled

Torquoselective Ring-Closures of Chiral Amido-Trienes Derived from Allenamides. A Tandem Allene Isomerization-Pericyclic Ring-Closure-Intramolecular Diels-Alder Cycloaddition.

authored by

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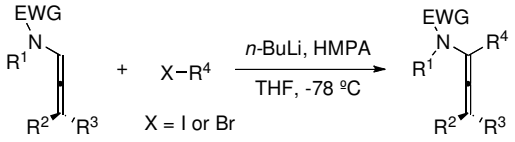
GENERAL EXPERIMENTAL INFORMATION

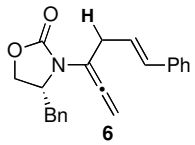
All reactions were performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased from Aldrich, Acros, Alfa Aesar, or TCI) unless otherwise noted. Chromatographic separations were performed using Silicycle 43-60 Å SiO_2. ^1H and ^{13}C 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 α-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 allelic 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.

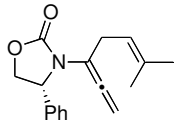
CHARACTERIZATIONS OF ALLENAMIDES.



6

Allenamide **6** (302 mg, 0.91 mmol) was prepared in 38% yield according to the general procedure.

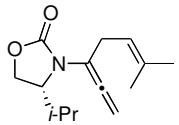
6: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -0.83° [c 0.060 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.67 (dd, 1H, *J* = 9.5, 13.5 Hz), 3.27 (dd, 1H, *J* = 3.5, 13.5 Hz), 3.41-3.54 (m, 2H), 4.05 (dd, 1H, *J* = 5.5, 8.5 Hz), 4.12 (ddd, 1H, *J* = 3.0, 7.5, 11.5 Hz), 4.20 (t, 1H, *J* = 8.0 Hz), 5.26 (dt, 1H, *J* = 3.0, 10.5 Hz), 5.39 (dt, 1H, *J* = 3.0, 10.5 Hz), 6.22 (dt, 1H, *J* = 7.0, 14.0 Hz), 6.55 (bd, 1H, *J* = 15.5 Hz), 7.12 (d, 2H, *J* = 7.0 Hz), 7.20-7.32 (m, 6H), 7.38 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.0, 38.7, 58.2, 67.0, 85.0, 125.8, 126.5, 127.5, 127.6, 129.2, 129.2, 129.4, 132.9, 135.9, 137.6, 155.9, 204.5;
IR (neat) cm^{-1} 3031w, 2927w, 2363w. 1752s, 1703m, 1498m, 1480m, 1455m, 1400m, 1358;
mass spectrum (APCI): m/e (% relative intensity) 332.1 (100) $(M+H)^+$.



10a

Allenamide **10a** (170.0 mg, 0.63 mmol) was prepared in 42% yield according to the general procedure.

10a: R_f = 0.35 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -86.6 ° [c 0.007 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 3H), 1.67 (s, 3H), 3.07 (dd, 1H, *J* = 7.0, 16.5 Hz), 3.17 (ddd, 1H, *J* = 3.5, 11.0, 19.5 Hz), 4.12 (t, 1H, *J* = 8.0 Hz), 4.62 (t, 1H, *J* = 9.0 Hz), 4.90-4.94 (m, 2H), 5.00 (ddd, 1H, *J* = 3.0, 10.0, 13.0 Hz), 5.04 (dt, 1H, *J* = 1.5, 8.5 Hz), 7.28-7.39 (m, 5H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 25.9, 29.3, 61.6, 70.1, 84.4, 108.5, 119.6, 127.4, 129.0, 129.1, 135.1, 138.6, 156.4, 205.0;
mass spectrum (APCI): m/e (% relative intensity) 293.4 (100) $(M+Na)^+$.



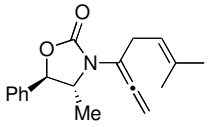
10c

Allenamide **10c** (210.0 mg, 0.89 mmol) was prepared in 60% yield according to the general procedure.

10c: R_f = 0.43 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -23.4° [c 0.007 Benzene]; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (dd, 6H, *J* = 4.4, 6.8 Hz), 1.64 (s, 3H), 1.71 (d, 3H, *J* = 1.2 Hz), 2.10 (ddd, 1H, *J* = 4.5, 6.8, 13.6 Hz), 3.17 (t, 2H, *J* = 3.6 Hz), 3.84 (ddd, 1H, *J* = 3.6, 5.6, 9.2 Hz), 4.10 (dd, 1H, *J* = 5.6, 8.4 Hz), 4.25 (t, 1H, *J* = 8.8 Hz), 5.10 (dt, 1H, *J* = 3.2, 10.0 Hz), 5.16-5.25 (m, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.6, 17.9, 18.2, 19.1, 25.9, 28.2, 29.3, 63.1, 83.8, 108.2, 134.9, 156.4,

205.0;

mass spectrum (APCI): m/e (% relative intensity) 259.9 (100) $(M+Na)^+$.



10d

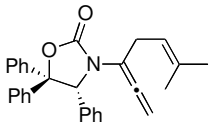
Allenamide **10d** (90.0 mg, 0.32 mmol) was prepared in 40% yield according to the general procedure.

10d: R_f = 0.50 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +30.5° [c 0.002 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, 3H, *J* = 6.0 Hz), 1.66 (s, 3H), 1.71 (s, 3H), 3.17 (dd, 1H, *J* = 7.0, 16.0 Hz), 3.17 (ddd, 1H, *J* = 3.5, 12.5, 16.0 Hz), 4.20 (ddd, 1H, *J* = 6.0, 7.5, 12.5 Hz), 5.12-5.18 (m, 2H), 5.24 (dt, 1H, *J* = 3.0, 10.5 Hz), 5.60 (d, 1H, *J* = 8.0 Hz), 7.27-7.40 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1, 18.3, 26.0, 29.6, 57.1, 79.0, 83.8, 108.2, 119.8, 126.5, 128.7, 128.8, 135.1, 135.4, 155.5, 204.9;

mass spectrum (APCI): m/e (% relative intensity) 284.1(40) $(M+H)^+$.



10e

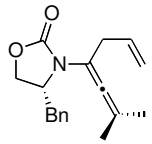
Allenamide **10e** (160.0 mg, 0.46 mmol) was prepared in 46% yield according to the general procedure.

10e: R_f = 0.47 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +165.5° [c 0.019 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 3H), 1.58 (s, 3H), 3.09 (t, 2H, *J* = 4.0 Hz), 4.89-4.99 (m, 2H), 5.59 (s, 1H), 6.69- 7.10 (m, 10H), 7.31-7.39 (m, 1H), 7.41 (t, 1H, *J* = 8.0 Hz0), 7.65 (dd, 2H, *J* = 1.6, 7.2 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 18.1, 25.8, 29.5, 70.8, 84.2, 87.9, 108.5, 119.8, 126.4, 126.9, 127.5, 127.7, 128.1, 128.4, 128.7, 128.9, 128.9, 134.9, 136.1, 139.3, 143.4, 154.8, 205.1;

mass spectrum (APCI): m/e (% relative intensity) 420.2 (100) $(M-H)^+$.



15

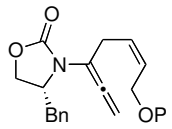
Allenamide **15** (161 mg, 0.57 mmol) was isolated in 55% yield according to the general procedure.

15: R_f = 0.36 [1:4 EtOAc/hexanes]; $[\alpha]_D^{23}$ = +57.6° [c 0.046 C_6H_6] yellow oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.83 (s, 3H), 1.88 (s, 3H), 2.63 (dd, 2H, *J* = 9.5, 13.5 Hz), 3.23 (dd, 1H, *J* = 2.5, 13.5 Hz), 3.28 (ddt, 1H, *J* = 1.5, 7.0, 16.0 Hz), 3.31 (ddt, 1H, *J* = 1.5, 7.0, 16.0 Hz), 4.01-4.08 (m, 2H), 4.11-4.18 (m, 1H), 5.07 (ddt, 1H, *J* = 1.0, 1.5, 10.5 Hz), 5.16 (ddt, 1H, *J* = 1.5, 1.5, 17.0 Hz), 5.82 (ddt, 1H, *J* = 7.0, 10.5, 17.0 Hz), 7.12 (d, 2H, *J* = 7.0 Hz), 7.24-7.28 (m, 1H), 7.30-7.34 (m, 2H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 21.9, 35.4, 38.3, 58.3, 66.7, 105.2, 105.7, 117.0, 127.4, 129.2, 129.4, 135.0, 136.1, 156.0, 195.5;

mass spectrum (APCI): m/e (% relative intensity) 284.2 (100) $(M+H)^+$.



20-*Z*: P = TBDPS

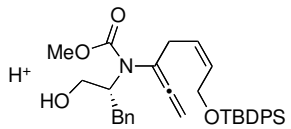
Allenamide **20**-*Z* (311.3 mg, 0.60 mmol) was prepared in 44% yield according to the general procedure.

20-*Z***:** R_f = 0.38 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -1.0° [c 0.004 Benzene]; colorless oil;

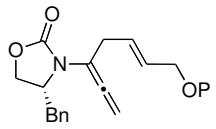
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 9H), 2.58 (ddt, 1H, *J* = 2.8, 6.4, 13.2 Hz), 3.09-3.16 (m, 3H), 3.99-4.17 (m, 3H), 4.29 (ddd, 2H, *J* = 0.4, 1.6, 7.5 Hz), 5.17 (dt, 1H, *J* = 3.2, 10.4 Hz), 5.26 (dt, 1H, *J* = 3.2, 10.4 Hz), 5.46-5.53 (m, 1H), 5.72-5.78 (m, 1H), 7.09 (dd, 2H, *J* = 3.6, 8.0 Hz), 7.22-7.43 (m, 9H), 7.67-7.70 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 19.4, 22.9, 27.0, 28.6, 31.8, 38.6, 58.0, 60.6, 66.9, 85.0, 108.2, 125.7, 127.4, 127.9, 129.1, 129.3, 129.8, 132.2, 134.0, 135.8, 135.8, 204.2;

mass spectrum (APCI):



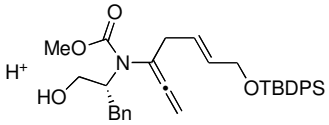
m/e (% relative intensity) 558.3 (10) $(M+H)^+$.



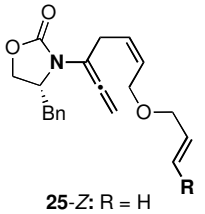
20-*E*: P = TBDPS

Allenamide **20**-*E* (336.6 mg, 0.64 mmol) was prepared in 50% yield according to the general procedure.

20-*E*: R_f = 0.33 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -11.5° [c 0.020 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (s, 9H), 2.64 (dd, 1H, *J* = 9.0, 13.5 Hz), 3.22 (dd, 1H, *J* = 4.0, 14.0 Hz), 3.30-3.33 (m, 2H), 4.04 (dd, 1H, *J* = 6.0, 8.5 Hz), 4.05-4.21 (m, 4H), 5.24 (dt, 1H, *J* = 3.0, 10.0 Hz), 5.33 (dt, 1H, *J* = 3.0, 10.0 Hz), 5.70-5.79 (m, 2H), 7.11 (d, 2H, *J* = 7.0 Hz), 7.25 (t, 1H, *J* = 6.5 Hz), 7.30 (t, 2H, *J* = 7.5 Hz), 7.34-7.42 (m, 6H), 7.67 (ddd, 4H, *J* = 1.0, 2.5, 7.5 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 19.5, 22.9, 27.1, 31.8, 33.2, 35.0, 38.8, 58.2, 64.3, 67.0, 84.8, 108.4, 125.8, 127.5, 127.9, 129.2, 129.4, 129.9, 132.2, 134.0, 134.1, 135.8, 136.0, 155.9, 204.5;
mass spectrum (APCI):



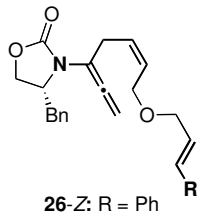
m/e (% relative intensity) 558.2 (15) $(M+H)^+$.



25-*Z*: R = H

Allenamide **25**-*Z* (140.1 mg, 0.43 mmol) was prepared in 22% yield according to the general procedure.

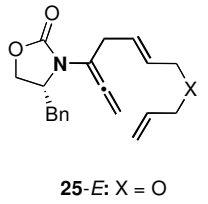
25-*Z*: R_f = 0.28 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -10.0° [c 0.004 Benzene]; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (dd, 1H, *J* = 9.2, 13.2 Hz), 3.22 (dd, 1H, *J* = 3.2, 13.2 Hz), 3.34-3.37 (m, 2H), 3.97-4.15 (m, 5H), 4.20 (t, 1H, *J* = 8.0 Hz), 5.19 (ddd, 1H, *J* = 1.2, 4.0, 10.4 Hz), 5.24-5.31 (m, 2H), 5.36 (dt, 1H, *J* = 3.2, 10.0 Hz), 5.59-5.76 (m, 2H), 5.88-5.98 (m, 1H), 7.15 (dd, 2H, *J* = 1.6, 8.4 Hz), 7.24-7.34 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 38.7, 58.2, 66.1, 67.1, 71.6, 85.2, 108.3, 117.4, 127.5, 128.2, 129.2, 129.3, 129.3, 135.1, 135.9, 204.3, ;
mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



26-*Z*: R = Ph

Allenamide **26**-*Z* (181.0 mg, 0.45 mmol) was prepared in 45% yield according to the general procedure.

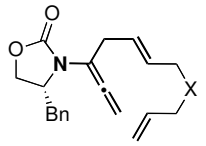
26-*Z*: R_f = 0.34 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -6.4° [c 0.007 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (dd, 1H, *J* = 9.5, 13.5 Hz), 3.21 (dd, 1H, *J* = 4.0, 14.0 Hz), 3.33-3.42 (m, 2H), 5.26 (dt, 1H, *J* = 3.0, 10.5 Hz), 5.37 (dt, 1H, *J* = 3.0, 10.5 Hz), 5.63-5.68 (m, 1H), 5.73-5.78 (m, 1H), 6.31 (dt, 1H, *J* = 6.0, 16.0 Hz), 6.60 (d, 1H, *J* = 16.0 Hz), 7.12-7.39 (m, 10H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 38.7, 58.2, 66.1, 67.1, 71.2, 85.2, 108.3, 126.4, 126.8, 127.5, 127.9, 128.4, 128.8, 129.2, 129.3, 129.3, 132.8, 135.9, 137.0, 156.0, 204.3;
mass spectrum (APCI): m/e (% relative intensity) 402.3 (100) $(M+H)^+$.



25-*E*: X = O

Allenamide **25**-*E* (254.8 mg, 0.78 mmol) was prepared in 59% yield according to the general procedure.

25-*E*: R_f = 0.28 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -30.0° [c 0.012 Benzene]; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (dd, 1H, *J* = 8.8, 13.2 Hz), 3.23 (dd, 1H, *J* = 3.2, 13.6 Hz), 3.30-3.33 (m, 2H), 3.96-3.98 (m, 3H), 4.04-4.14 (m, 2H), 4.20 (t, 1H, *J* = 7.6 Hz), 5.16-5.19 (m, 1H), 5.23-5.30 (m, 2H), 5.37 (dt, 1H, *J* = 3.2, 10.4 Hz), 5.72-5.74 (m, 2H), 5.86-5.96 (m, 1H), 7.15 (dd, 2H, *J* = 2.0, 8.4 Hz), 7.24-7.34 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 33.2, 38.6, 58.0, 66.9, 70.6, 71.1, 84.9, 108.1, 117.2, 127.4, 129.1, 129.3, 129.7, 135.0, 135.9, 155.8, 204.4;
mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



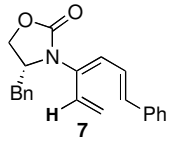
29-*E*: X = NTs

Allenamide **29**-*E* (200.1 mg, 0.42 mmol) was prepared in 42% yield according to the general procedure.

29-*E*: R_f = 0.45 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +1.5° [c 0.002 Benzene]; colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.66 (dd, 1H, *J* = 9.0, 13.5 Hz), 3.21 (dd, 1H, *J* = 3.5, 13.5 Hz), 3.23-3.26 (m, 2H), 3.78 (t, 4H, *J* = 5.0 Hz), 4.04-4.14 (m, 2H), 4.20 (t, 1H, *J* = 8.0 Hz), 5.09-5.16 (m, 2H), 5.25 (dt, 1H, *J* = 3.5, 10.0 Hz), 5.36 (dt, 1H, *J* = 3.5, 10.0 Hz), 5.55-5.64 (m, 2H), 7.13 (d, 2H, *J* = 7.0 Hz), 7.25-7.33 (m, 5H), 7.71 (d, 2H, *J* = 8.5 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 33.1, 38.6, 48.7, 49.5, 58.1, 67.0, 85.2, 108.2, 119.2, 127.5, 127.5, 127.6, 129.2, 129.3, 130.0, 130.7, 133.0, 135.9, 137.7, 143.5, 155.8, 204.3;
mass spectrum (APCI): m/e (% relative intensity) 501.2 (20) $(M+Na)^+$.

GENERAL PROCEDURE FOR THE ACID-CATALYZED ISOMERIZATION OF ALLENAMIDES.[ii]

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.



7

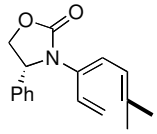
Triene **7** (32.4 mg, 0.098 mmol) was prepared in 72% yield according to the general procedure.

7: R_f = 0.20 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +1.33 ° [c 0.015 Benzene]; white wax;
^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.65 (ddd, 1H, *J* =3.0, 6.5, 15.0 Hz), 3.09 (dd, 1H, *J* = 3.5, 13.5 Hz), 4.15 (dt, 1H, *J* = 7.5, 13.0 Hz), 4.26-4.32 (m, 2H), 5.42 (ddd, 4H, *J* = 4.0, 11.0, 21.5 Hz), 6.45 (d, 1H, *J* = 11.5 Hz); 6.73 (bd, 1H, *J* = 15.5 Hz), 6.81 (dd, 1H, *J* = 10.5, 17.0 Hz), 7.13 (d, 2H, *J* = 7.0 Hz), 7.14-7.37 (m, 6H), 7.45 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 39.4, 58.4, 67.4, 117.4, 122.9, 127.1, 127.3, 127.5, 128.5, 128.6, 129.0, 129.2, 129.2, 129.3, 131.5, 132.2,

135.8, 136.5, 137.1, 156.8;

IR (neat) cm^{-1} 3057w, 2307w, 1753s, 1402m;

mass spectrum (APCI): m/e (% relative intensity) 332.1 (100) $(M+H)^+$.



11a

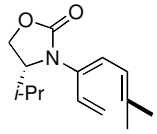
Triene **11a** (85.0 mg, 0.32 mmol) was prepared in 89% yield according to the general procedure.

11a: R_f = 0.22 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -14.7° [c 0.018 Benzene]; white wax;

^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.75 (s, 3H), 4.35 (dd, 1H, *J* = 6.5, 8.5 Hz), 4.75 (t, 1H, *J* = 8.5 Hz), 5.04 (dd, 1H, *J* = 6.5, 9.0 Hz), 5.26 (dd, 2H, *J* = 11.0, 17.0 Hz), 6.03 (s, 2H), 6.53 (dd, 1H, *J* = 11.0, 17.0 Hz), 7.31-7.39 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 18.6, 26.8, 61.8, 70.0, 115.3, 119.3, 127.7, 128.2, 128.6, 129.2, 129.3, 129.4, 138.7, 141.0, 157.2;

mass spectrum (APCI): m/e (% relative intensity) 270.1 (30) $(M+H)^+$.



11c

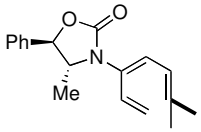
Triene **11c** (154.0 mg, 0.66 mmol) was prepared in 91% yield according to the general procedure.

11c: R_f = 0.16 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +28.9° [c 0.022 Benzene]; colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 6.8 Hz), 0.93 (d, 3H, *J* = 6.8 Hz), 1.80 (s, 3H), 1.88 (s, 3H), 1.88-1.95 (m, 1H), 4.01 (dt, 1H, *J* = 3.6, 8.8 Hz), 4.17 (dd, 1H, *J* = 5.6, 8.8 Hz), 4.36 (t, 1H, *J* = 9.2 Hz), 5.26 (dd, 2H, *J* = 4.0, 11.2 Hz), 6.23 (dd, 1H, *J* = 1.2, 11.6 Hz), 6.42 (d, 1H, *J* =11.6 Hz), 6.63 (dd, 1H, *J* = 10.8, 17.2 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9, 18.2, 18.8, 26.9, 29.1, 61.0, 63.5, 115.8, 119.5, 128.0, 128.2, 129.8, 140.9, 157.7;

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



11d

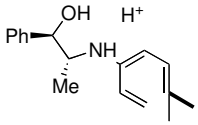
Triene **11d** (25.3 mg, 0.089 mmol) was prepared in 74% yield according to the general procedure.

11d: R_f = 0.40 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +18.0° [c 0.004 Benzene]; white wax;

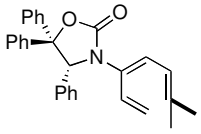
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, 3H, *J* = 6.5 Hz), 1.80 (s, 3H), 1.87 (s, 3H), 4.35 (dt, 1H, *J* = 7.0, 13.5 Hz), 5.26 (d, 1H, *J* = 10.0 Hz), 5.35 (d, 1H, *J* = 17.5 Hz), 5.74 (d, 1H, *J* = 8.0 Hz), 6.22 (dt, 1H, *J* = 1.5, 12.0 Hz), 6.36 (d, 1H, *J* =11.5 Hz), 6.72 (dd, 1H, *J* = 10.5, 17.0 Hz) 7.26-7.43 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 15.5, 18.9, 27.0, 57.3, 78.9, 115.5, 119.5, 126.3, 128.4, 128.7, 128.8, 129.5, 135.5, 141.3, 156.8;

mass spectrum (APCI):



m/e (% relative intensity) 258.1 (40) $(M+H)^+$.



11e

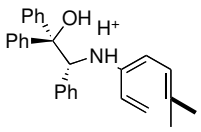
Triene **11e** (160.0 mg, 0.38 mmol) was prepared in 86% yield according to the general procedure.

11e: R_f = 0.48 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +49.4° [c 0.055 Benzene]; white wax;

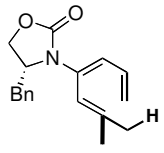
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 3H), 1.71 (s, 3H), 4.61 (d, 1H, *J* = 17.0 Hz), 4.94 (d, 1H, *J* = 11.0 Hz), 5.57 (s, 1H), 5.98 (t, 1H, *J* = 13.0 Hz), 6.45 (dd, 1H, *J* = 11.0, 17.5 Hz), 6.98-7.06 (m, 3H), 7.10-7.15 (m, 5H), 7.21 (dd, 2H, *J* = 1.5, 8.5 Hz), 7.34 (t, 1H, *J* = 5.5 Hz), 7.42 (t, 2H, *J* = 7.5 Hz), 7.80 (d, 2H, *J* = 8.5 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 26.8, 72.2, 88.1, 115.4, 119.3, 125.5, 126.5, 127.4, 128.0, 128.3, 128.5, 128.6, 128.7, 129.1, 129.2, 129.5, 136.9, 139.7, 141.1, 144.4, 156.0;

mass spectrum (APCI):



m/e (% relative intensity) 395.3 (40) $(M+H)^+$.



16

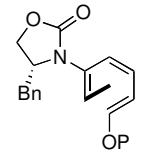
Triene **16** (52 mg, 0.18 mmol) was isolated in 84% yield according to the general procedure.

16: R_f = 0.23 [1:4 EtOAc/hexanes]; $[\alpha]_D^{23}$ = +9.18° [c 0.0476 C_6H_6]; clear oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (d, 3H, *J* = 1.2 Hz), 1.93 (d, 3H, *J* = 1.6 Hz), 2.63 (ddd, 1H, *J* = 2.0, 8.0, 13.6 Hz), 2.99 (dd, 1H, *J* = 3.2, 13.6 Hz), 4.02-4.08 (m, 1H), 4.14-4.22 (m, 2H), 5.14 (dd, 1H, *J* = 2.0, 10.0 Hz), 5.31 (dd, 1H, *J* = 1.2, 16.8 Hz), 5.70 (brs, 1H), 6.32 (ddd, 1H, *J* = 10.0, 11.2, 16.8 Hz), 6.48 (d, 1H, *J* = 11.2 Hz), 7.09 (m, 2H), 7.24-7.35 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 26.0, 39.3, 57.7, 66.1, 117.9, 118.5, 124.7, 127.4, 129.2, 129.3, 132.2, 133.6, 135.9, 142.3, 155.7;

mass spectrum (APCI): m/e (% relative intensity) 284.2 (100) $(M+H)^+$.



21: P = TBDPS

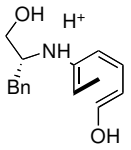
Triene **21** (40.9 mg, 0.078 mmol) was prepared in 74% yield according to the general procedure.

21: R_f = 0.20 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -8.0^o [c 0.004 Benzene]; colorless oil;

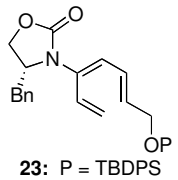
^{1}H NMR (500 MHz, C_6D_6) δ 0.76 (s, 9H), 1.28 (dd, 3H, *J* = 1.0, 7.5 Hz), 1.79 (dd, 1H, *J* = 10.5, 13.5 Hz), 2.83 (dd, 1H, *J* = 3.5, 13.5 Hz), 3.15-3.23 (m, 2H), 3.35 (ddd, 1H, *J* = 4.5, 8.5, 13.0 Hz), 5.02 (d, 1H, *J* = 11.5 Hz), 5.50 (t, 1H, *J* = 11.5 Hz), 5.68 (dd, 1H, *J* = 7.5, 14.5 Hz), 5.89 (t, 1H, *J* = 12.0 Hz), 6.42 (d, 1H, *J* = 12.0 Hz), 6.48 (d, 2H, *J* = 7.0 Hz), 6.73-6.87 (m, 11H), 7.37-7.40 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.1, 19.4, 26.6, 27.1, 39.2, 57.6, 66.5, 110.9, 117.3, 124.3, 127.2, 128.0, 128.1, 128.2, 129.0, 129.2, 129.2, 129.4, 130.0, 130.4, 130.5, 132.1, 132.2, 135.6, 135.6, 135.7, 136.2, 149.1, 156.2;

mass spectrum (APCI):



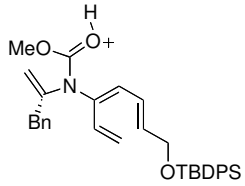
m/e (% relative intensity) 258.2 (20) $(M+H)^+$.



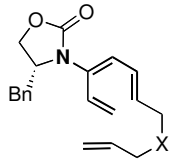
23: P = TBDPS

Triene **23** (250.5 mg, 0.48 mmol) was prepared in 84% yield according to the general procedure.

23: R_f = 0.23 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +8.7° [c 0.030 Benzene]; colorless oil;
^{1}H NMR (500 MHz, C_6D_6) δ 1.09 (s, 9H), 2.61 (dd, 1H, *J* = 3.0, 10.5 Hz), 3.09 (dd, 1H, *J* = 3.5, 14.0 Hz), 4.13 (ddd, 1H, *J* = 4.5, 9.0, 16.0 Hz), 4.21-4.29 (m, 2H), 4.33 (d, 2H, *J* = 1.5 Hz), 5.40 (d, 1H, *J* = 4.5 Hz), 5.36 (s, 1H), 5.95 (dt, 1H, *J* = 4.5, 15.0 Hz), 6.31 (d, 1H, *J* = 11.5 Hz), 6.68 (dd, 1H, *J* = 10.5, 17.0 Hz), 6.81 (tt, 1H, *J* = 2.0, 13.5 Hz), 7.11 (d, 2H, *J* = 7.0 Hz), 7.24 (t, 1H, *J* = 7.0 Hz), 7.31 (d, 2H, *J* = 7.0 Hz), 7.35-7.45 (m, 6H), 7.69 (dt, 4H, *J* = 2.0, 8.0 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 19.6, 23.0, 27.1, 31.9, 39.4, 58.4, 64.2, 67.4, 116.9, 123.4, 127.4, 128.1, 128.4, 129.2, 129.3, 130.1, 131.1, 131.5, 133.6, 133.7, 135.8, 135.8, 137.2, 156.9;
mass spectrum (APCI):



m/e (% relative intensity) 538.8 (10) $(M+H)^+$.

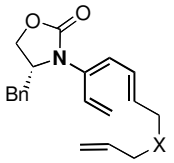


30a: X = O

Triene **30a** (135.8 mg, 0.42 mmol) was prepared in 75% yield according to the general procedure.

30a: R_f = 0.43 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +7.4° [c 0.015 Benzene]; white wax;
^{1}H NMR (400 MHz, C_6D_6) δ 2.62 (dd, 1H, *J* = 10.4, 14.0 Hz), 3.01 (dd, 1H, *J* = 3.6, 16.5 Hz), 4.02 (dt, 1H, *J* = 1.6, 6.0 Hz), 4.10-4.16 (m, 3H), 4.22-4.31 (m, 2H), 5.22 (dq, 1H, *J* = 1.2, 10.4 Hz), 5.28-5.29 (m, 1H), 5.38 (d, 1H, *J* = 9.6 Hz), 5.88-6.00 (m, 2H), 6.30 (d, 1H, *J* = 11.6 Hz), 6.66-6.74 (m, 2H), 7.11 (d, 2H, *J* = 6.8 Hz), 7.22-7.32 (m, 3H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.9, 31.8, 39.3, 58.3, 67.3, 70.2, 71.6, 117.3, 117.5, 126.0, 127.4, 128.3, 129.1, 129.2, 130.6, 132.2, 134.4, 134.8, 135.7, 156.7;

mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



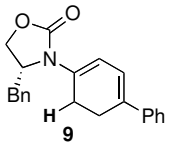
30b: X = NTs

Triene **30b** (90.6 mg, 0.19 mmol) was prepared in 62% yield according to the general procedure.

30b: R_f = 0.27 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +17.9° [c 0.011 Benzene]; white wax;
^{1}H NMR (400 MHz, C_6D_6) δ 2.43 (s, 3H), 2.62 (dd, 1H, *J* = 9.5, 13.5 Hz), 3.04 (dd, 1H, *J* = 3.5, 13.5 Hz), 3.82 (dd, 2H, *J* = 6.5 Hz), 3.92 (d, 2H, *J* = 6.0 Hz), 4.12 (dd, 1H, *J* = 5.0, 8.0 Hz), 4.22-4.30 (m, 2H), 5.22 (dt, 2H, *J* = 1.5, 7.5 Hz), 5.38 (dd, 2H, *J* = 7.0, 11.0 Hz), 5.59-5.70 (m, 2H), 6.17 (d, 1H, *J* = 11.0 Hz), 6.49 (dd, 1H, *J* = 11.5, 15.5 Hz), 6.57 (dd, 1H, *J* = 11.0, 17.5 Hz), 7.00 (d, 2H, *J* = 7.0 Hz), 7.24-7.32 (m, 5H), 7.70 (d, 2H, *J* = 8.5 Hz),;
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.8, 22.9, 31.9, 39.3, 48.7, 50.0, 58.2, 67.3, 117.9, 119.5, 127.5, 127.7, 128.2, 129.2, 129.3, 129.8, 130.1, 132.1, 132.6, 132.9, 132.1, 132.6, 135.6, 137.6, 143.7, 156.7;
mass spectrum (APCI): m/e (% relative intensity) 479.2 (20) $(M+H)^+$.

GENERAL PROCEDURE FOR THE ELECTROCYCLIC RING-CLOSURE.

A solution of a respective allenamide or triene in a proper solvent (CH_3CN, toluene, or xylene, 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 amido-1,3-cyclohexadienes.



9

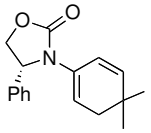
Cyclic diene **9** (43.7 mg, 0.13 mmol) was prepared in 95% yield according to the general procedure.

9: R_f = 0.15 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +21.0 ° [c 0.001 Benzene]; white solid; mp: 130 - 133 ºC;
^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70-2.83 (m, 4H), 3.03 (dd, 1H, *J* = 6.5, 19.0 Hz), 3.23 (dd, 1H, *J* = 3.5, 14.0 Hz), 4.13 (dd, 1H, *J* = 4.0, 9.0 Hz), 4.25 (t, 1H, *J* =9.0 Hz), 4.40 (sep, 1H, *J* = 4.0 Hz), 5.95 (d, 1H, *J* = 6.0 Hz), 6.41 (d, 1H, *J* = 6.5 Hz); 7.17 (d, 2H, *J* = 7.0 Hz),

7.22-7.29 (m, 2H), 7.34 (t, 3H, *J* = 7.5), 7.46 (d, 2H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.8, 26.3, 37.9, 57.1, 66.3, 112.0, 120.2, 125.1, 127.2, 127.6, 128.8, 129.3, 129.5, 133.4, 134.2, 135.7, 140.6, 155.0;

IR (neat) cm^{-1} 3029w, 2939w, 2828w, 2362w, 1747s, 1638w, 1600w, 1495w, 1446w, 1399s;

mass spectrum (APCI): m/e (% relative intensity) 330.1 (100) $(M+H)^+$.



13a

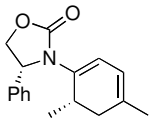
Cyclic diene **13a** (6.5 mg, 0.024 mmol) was prepared in 14% yield according to the general procedure.

13a: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -9.4 ^{o} [c 0.076 Benzene]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (s, 3H), 0.86 (s, 3H), 2.05 (ddd, 2H, *J* = 5.0, 11.5, 17.5 Hz), 4.12 (dd, 1H, *J* = 7.0, 8.5 Hz), 4.67 (t, 1H, *J* = 9.0 Hz), 5.11 (dd, 1H, *J* =7.0, 9.0 Hz), 5.26 (dt, 1H, *J* =1.5, 4.5 Hz), 5.56 (d, 1H, *J* = 10.0 Hz), 6.10 (dd, 1H, *J* = 1.5, 9.5 Hz), 7.27-7.41 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 27.0, 28.1, 30.8, 37.0, 60.9, 70.1, 110.0, 114.4, 120.3, 126.8, 129.0, 129.4, 138.5, 140.1, 155.4;

mass spectrum (APCI): m/e (% relative intensity) 270.2 (40) $(M+H)^+$.



14a

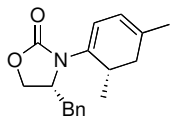
Cyclic diene **14a** (30.3 mg, 0.11 mmol) was prepared in 63% yield according to the general procedure.

14a: R_f = 0.28 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -115.3 ^{o} [c 0.016 Benzene]; white solid; mp: 118 – 121 ºC;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (d, 3H, *J* = 6.5 Hz), 1.72 (s, 3H), 1.83 (dd, 1H, *J* = 2.5, 17.0 Hz), 2.49 (dd, 1H, *J* = 8.5, 17.0 Hz), 3.301 (ddd, 1H, *J* = 2.5, 6.5, 13.0 Hz), 4.11 (dd, 1H, *J* =3.5, 8.5 Hz), 4.64 (t, 1H, *J* =8.5 Hz), 4.94 (dd, 1H, *J* =3.5, 8.5 Hz), 5.12 (d, 1H, *J* = 6.0 Hz), 5.41-5.44 (m, 1H), 7.27-7.41 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 17.8, 23.5, 27.9, 36.9, 62.3, 70.1, 111.7, 117.4, 126.1, 126.8, 126.8, 128.9, 129.4, 129.6, 131.5, 137.7, 140.1, 155.4;

mass spectrum (APCI): m/e (% relative intensity) 270.2 (20) $(M+H)^+$.



14b

Cyclic diene **14b** (21.2 mg, 0.075 mmol) was prepared in 52% yield according to the general procedure.

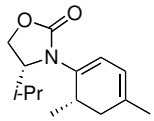
14b: R_f = 0.25 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -15.8 ^{o} [c 0.004 Benzene]; colorless oil;

^{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) 284.1 (100) $(M+H)^+$.



14c

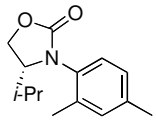
Cyclic diene **14c** (29.7 mg, 0.13 mmol) was prepared in 62% yield according to the general procedure.

14c: R_f = 0.35 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -105.6 ^{o} [c 0.015 Benzene]; colorless oil;

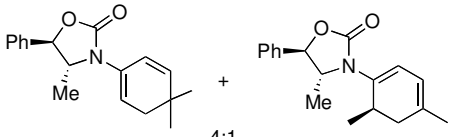
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, 6H, *J* = 5.5 Hz), 1.11 (d, 3H, *J* = 7.0 Hz), 1.80 (s, 3H), 1.91 (dd, 1H, *J* = 3.0, 17.0 Hz), 2.29-2.36 (m, 1H), 2.56 (dd, 1H, *J* = 7.5, 17.0 Hz), 3.05 (ddd, 2H, *J* = 3.5, 7.0, 14.5 Hz), 3.99 (dd, 1H, *J* =4.0, 7.5 Hz), 4.15 (dd, 1H, *J* =4.0, 9.0 Hz), 4.25 (t, 1H, *J* = 9.0 Hz), 5.45 (d, 1H, *J* = 5.5 Hz), 5.61-5.63 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 18.1, 18.3, 23.5, 27.6, 28.7, 37.5, 61.6, 62.5, 112.7, 117.6, 132.1, 136.9, 155.5;

mass spectrum (APCI):



m/e (% relative intensity) 234.2 (60) $(M+H)^+$.

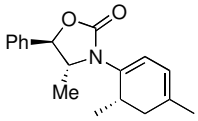


13d 4:1 **14d (minor)**

4:1 inseparable mixtures of cyclic diene **13d** (8.4 mg, 0.030 mmol) and minor diastereomer of **14d** were isolated in 21% yield with according to the general procedure.

13d: R_f = 0.45 [25% EtOAc/hexanes];

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, 3H, *J* = 6.5 Hz), 0.98 (s, 3H), 1.04 (s, 3H), 2.20 (dd, 1H, *J* = 5.0, 17.5 Hz), 2.33 (d, 1H, *J* = 4.5, 17.5 Hz), 4.37 (dt, 1H, *J* = 7.0, 13.5 Hz), 5.66 (ddd, 3H, *J* = 7.0, 10.0, 16.0 Hz), 6.01 (dd, 1H, *J* =2.0, 10.0 Hz), 7.26-7.42 (m, 5H);
mass spectrum (APCI): m/e (% relative intensity) 285.1 (40) $(M+H)^+$.



14d

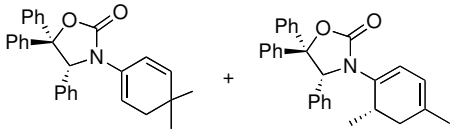
Cyclic diene **14d** (11.4 mg, 0.040 mmol) was prepared in 38% yield according to the general procedure.

14d: R_f = 0.51 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +11.0º [c 0.002 Benzene]; white wax;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 7.0 Hz), 1.10 (d, 3H, *J* = 7.0 Hz), 1.80 (s, 3H), 1.90 (dd, 1H, *J* = 3.0, 17.5 Hz), 2.56 (dd, 1H, *J* = 8.0, 17.0 Hz), 3.29 (ddd, 1H, *J* = 3.0, 7.0, 15.0 Hz), 4.30 (dt, 1H, *J* =6.5, 13.0 Hz), 5.42 (d, 1H, *J* =6.0 Hz), 5.61-5.64 (m, 2H), 7.26-7.42 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7, 18.1, 23.5, 28.4, 37.1, 57.8, 111.3, 117.5, 126.2, 128.7, 128.8, 131.8, 134.9, 137.4, 154.4;

mass spectrum (APCI): m/e (% relative intensity) 284.1 (50) $(M+H)^+$.



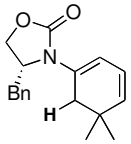
13e 1:3 (6:1 *dr*) **14e**

3:1 inseparable mixtures of cyclic diene **14e** (37.9 mg, 0.090 mmol, 6:1 *dr*) and **13e** were isolated in 45% yield with according to the general procedure.

13 e, 14d: R_f = 0.51 [25% EtOAc/hexanes];

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (d, 3H, *J* = 7.0 Hz, major), 0.79 (s, 3H, minor), 0.84 (s, 3H, minor), 0.87 (d, 1H, *J* = 7.0 Hz, major), 1.70 (s, 3H, major), 1.76-1.82 (m, 1H, major and minor), 2.02 (dd, 1H,

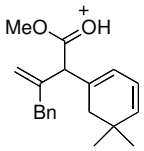
J = 1.5, 4.5 Hz, major), 2.23-2.40 (m, 1H), 2.51 (dd, 1H, *J* = 8.5, 17.0 Hz, major), 2.97 (ddd, 1H, *J* = 2.0, 7.0, 15.5 Hz, minor), 3.43 (ddd, 1H, *J* = 1.5, 8.5, 15.5 Hz, major), 5.10 (d, 1H, *J* = 5.5 Hz, major), 5.33 (dt, 1H, *J* = 1.5, 4.5 Hz, minor), 5.40 (ddd, 1H, *J* = 1.5, 3.0, 4.5 Hz, major), 5.47-5.49 (m, 1H, major and minor), 5.55 (dd, 1H, *J* = 6.5, 18.5 Hz, major and minor), 5.74 (d, 1H, *J* = 14.5 Hz, major), 6.07 (dd, 1H, *J* =2.0, 10.0 Hz, minor), 6.98-7.13 (m, 10H, major and minor), 7.34-7.37 (m, 1H, major and minor), 7.42 (t, 2H, *J* = 8.0 Hz, major and minor), 7.67 (t, 2H, *J* = 7.5 Hz, major and minor),;
mass spectrum (APCI): m/e (% relative intensity) 420.1 (20) $(M-H)^+$.



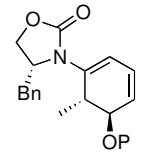
19

Amidodiene **19** (15 mg, 0.05 mmol) was isolated in 34% yield according to the general procedure.

19: R_f = 0.30 [1:4 EtOAc/hexanes]; $[\alpha]_D^{23}$ = +7.54° [c 0.010 C_6H_6] yellow oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.11 (s, 3H), 2.45 (dd, 1H, *J* = 1.5, 17.5 Hz), 2.72 (dd, 1H, *J* = 10.0, 13.5 Hz), 2.74 (dd, 1H, *J* = 1.5, 17.5 Hz), 3.23 (dd, 1H, *J* = 3.0, 13.5 Hz), 4.10 (dd, 1H, *J* = 5.0, 9.0 Hz), 4.22 (t, 1H, *J* = 8.5 Hz), 4.36 (dddd, 1H, *J* = 3.5, 4.5, 8.0, 9.5 Hz), 5.45 (d, 1H, *J* = 9.5 Hz), 5.77 (dd, 1H, *J* = 1.5, 6.0 Hz), 5.87 (dd, 1H, *J* = 6.0, 9.5 Hz), 7.16 (d, 2H, *J* = 7.0 Hz), 7.25-7.30 (m, 1H), 7.31-7.36 (m, 2H);
^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 28.1, 32.8, 38.1, 39.0, 57.1, 66.3, 111.0, 121.0, 127.6, 129.3, 129.4, 133.3, 135.2, 135.7, 155.2;
mass spectrum (APCI):



m/e (% relative intensity) 298.1 (100) $(M+H)^+$.



22: P = TBDPS

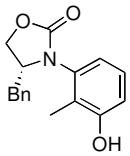
Cyclic diene **22** (19.2mg, 0.037 mmol) was prepared in 77% yield according to the general procedure.

22: R_f = 0.29 [25% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -8.0 ^{o} [c 0.004 Benzene]; colorless oil;

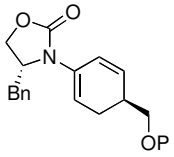
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, 3H, *J* = 7.2 Hz), 1.03 (s, 9H), 2.85 (dd, 1H, *J* = 9.6, 14.0 Hz), 3.35 (dd, 1H, *J* = 3.2, 14.0 Hz), 3.65 (q, 1H, *J* = 7.2 Hz), 3.94 (dd, 1H, *J* =2.0, 5.6 Hz), 4.10-4.22 (m, 2H), 4.34 (ddd, 1H, *J* =2.8, 6.4, 10.8 Hz), 5.39 (dd, 1H, *J* = 5.2, 9.2 Hz), 5.57 (d, 1H, *J* =6.0 Hz), 6.07 (dd, 1H, *J* =6.0, 9.2 Hz), 7.13 (d, 2H, *J* = 5.6 Hz), 7.21-7.45 (m, 9H), 7.63-7.70 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 19.5, 27.3, 37.2, 57.6, 65.7, 70.9, 106.0, 121.5, 124.9, 127.5, 127.7, 128.0, 129.3, 129.5, 129.8, 130.0, 134.3, 134.9, 135.9, 136.1, 136.2, 140.9, 154.0;

mass spectrum (APCI):



m/e (% relative intensity) 268.2 (10) $(M+H)^+$.



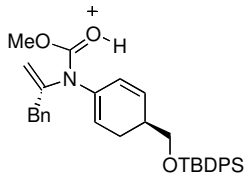
24: P = TBDPS

Cyclic diene **24** (51.0 mg, 0.098 mmol) was prepared in 93% yield and 3:1 *dr* according to the general procedure.

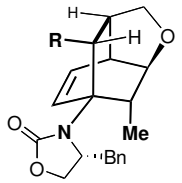
24: R_f = 0.29 [25% EtOAc/hexanes]; colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (s, 9H, major and minor), 2.44 (ddd, 2H, *J* = 4.0, 8.5, 13.0 Hz, major and minor), 2.57-2.70 (m, 2H, major and minor), 3.03 (dd, 1H, *J* = 3.0, 13.5 Hz, major), 3.11(dd, 1H, *J* = 4.0, 14.0 Hz, minor), 3.62 (ddd, 2H, *J* = 6.5, 10.0, 13.5 Hz, major), 3.67 (dd, 2H, *J* = 10.0, 17.0 Hz, minor), 4.07 (ddd, 1H, *J* =1.0, 6.0, 9.0 Hz, major and minor), 4.19-4.36 (m, 2H, major and minor), 5.57 (dt, 1H, *J* = 1.0, 3.5 Hz, major), 5.68 (bs, 1H, minor), 5.90 (dd, 1H, *J* =5.0, 10.0 Hz, major and minor), 6.20 (dt, 1H, *J* =1.5, 10.0 Hz, major and minor), 7.11 (d, 2H, *J* = 7.0 Hz), 7.24-7.43 (m, 8H), 7.63-7.71 (m, 5H);

mass spectrum (APCI):



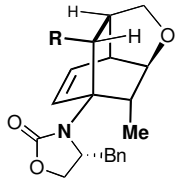
m/e (% relative intensity) 539.6 (10) $(M+H)^+$.



28a: R = H

Tetrahydrofuran **28a** (24.4 mg, 0.075 mmol) was prepared in 55% yield according to the general procedure.

28a: R_f = 0.35 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -11.2 ^{o} [c 0.014 Benzene]; white solid; mp: 97 - 99 ºC;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, 3H, *J* = 7.5 Hz), 1.62 (dd, 1H, *J* = 10.5, 12.5 Hz), 2.27 (dt, 1H, *J* = 3.5, 8.5 Hz), 2.67 (d, 1H, *J* = 12.0 Hz), 2.71 (dd, 1H, *J* =11.0, 13.5 Hz), 2.89 (q, 1H, *J* =7.5 Hz), 2.98 (dd, 1H, *J* =5.5, 11.0 Hz), 3.12 (dd, 1H, *J* =2.5, 13.5 Hz), 3.66 (d, 1H, *J* =5.5 Hz), 3.82 (d, 1H, *J* =8.0 Hz), 3.89 (dd, 1H, *J* =4.5, 8.0 Hz), 4.06-4.12 (m, 2H), 4.18 (ddd, 1H, *J* =2.5, 6.5, 10.0 Hz), 6.27 (dd, 1H, *J* = 6.5, 9.0 Hz), 6.61 (d, 1H, *J* =8.5 Hz), 7.18 (d, 1H, *J* =7.0 Hz), 7.28 (t, 1H, *J* = 7.5 Hz), 7.35 (t, 2H, *J* =7.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 36.4, 39.6, 40.4, 42.0, 44.4, 58.1, 60.6, 65.6, 74.6, 81.6, 127.4, 127.5, 129.3, 129.4, 129.5, 132.6, 136.2, 156.2;
mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



28b: R = Ph

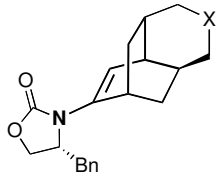
Tetrahydrofuran **28b** (12.2 mg, 0.030 mmol) was prepared in 45% yield according to the general procedure.

28b: R_f = 0.35 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = -19.3 ^{o} [c 0.006 Benzene]; white wax;
^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, 3H, *J* = 9.0 Hz), 1,55-1.58 (m, 1H), 2.66 (dd, 1H, *J* = 4.5, 7.0

Hz), 2.85 (dd, 1H, *J* = 9.5, 18.5 Hz), 3.18 (dd, 1H, *J* = 5.5, 14.5 Hz), 3.75 (d, 1H, *J* =6.5 Hz), 3.77-3.82 (m, 1H), 3.88-3.94 (m, 2H), 3.98 (d, 1H, *J* =9.5 Hz), 4.05 (dt, 1H, *J* =1.5, 11.0 Hz), 4.18 (d, 1H, *J* =3.0 Hz), 6.20 (d, 1H, *J* =10.5 Hz), 6.53 (dd, 1H, *J* = 8.5, 11.0 Hz), 6.88 (dd, 1H, *J* =2.0, 8.5 Hz), 7.16-7.26 (m, 8H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 22.9, 37.4, 42.2, 45.5, 46.9, 52.1, 58.1, 66.2, 66.6, 74.7, 80.9, 126.0, 127.2, 127.3, 128.3, 128.8, 129.0, 129.1, 129.7, 136.8, 143.6, 156.4;

mass spectrum (APCI): m/e (% relative intensity) 402.3 (100) $(M+H)^+$.



31a: X = O

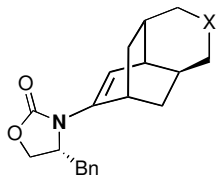
Pyran **31a** (64.7 mg, 0.20 mmol) was prepared in 68% yield according to the general procedure.

31a: R_f = 0.27 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +17.8 ^{o} [c 0.006 Benzene]; colorless oil;

^{1}H NMR (500 MHz, C_6D_6) δ 1.25 (d, 1H, *J* = 10.5 Hz), 1.34 (d, 1H, *J* = 11.5 Hz), 1.56 (dt, 1H, *J* = 3.0, 11.5 Hz), 1.62-1.69 (m, 2H), 1.88 (t, 1H, *J* = 12.5 Hz), 2.02 (t, 1H, *J* =6.5 Hz), 2.13 (dt, 1H, *J* =3.0, 13.0 Hz), 2.79 (dt, 1H, *J* = 4.0, 14.0 Hz), 3.21 (d, 2H, *J* = 10.5 Hz), 3.41-3.52 (m, 3H), 3.66 (d, 3H, *J* = 11.0, 15.5 Hz), 5.71 (d, 1H, *J* = 5.0 Hz), 6.78 (dd, 2H, *J* = 11.5, 16.5 Hz), 7.02-7.11 (m, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 31.0, 31.2, 31.3, 32.0, 36.0, 38.1, 56.8, 66.6, 71.3, 71.4, 117.3, 127.5, 129.2, 129.4, 135.8, 142.3, 155.4;

mass spectrum (APCI): m/e (% relative intensity) 326.2 (100) $(M+H)^+$.



31b: X = NTs

31b (17.8 mg, 0.037 mmol) was prepared in 78% yield according to the general procedure.

31b: R_f = 0.25 [40% EtOAc/hexanes]; $[\alpha]_D^{23}$ = +1.5 ^{o} [c 0.002 Benzene]; white solid; mp: 210 - 213 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60-1.69 (m, 3H), 1.77-1.82 (m, 2H), 2.11 (dq, 1H, *J* = 3.0, 7.0 Hz), 2.32 (dd, 2H, *J* = 2.5, 11.5 Hz), 2.44 (s, 3H), 2.69 (dd, 1H, *J* = 9.5, 14.0 Hz), 3.15 (dd, 1H, *J* = 3.5, 14.0 Hz), 3.24 (d, 1H, *J* =2.5 Hz), 3.70 (dt, 2H, *J* = 2.5, 11.5 Hz), 4.08 (dd, 1H, *J* = 5.0, 9.0 Hz), 4.22 (t, 1H, *J* = 8.0 Hz), 4.33 (ddd, 1H, *J* = 4.5, 8.0, 16.5 Hz), 5.98 (dd, 1H, *J* = 2.0, 7.0 Hz), 7.13 (d, 2H, *J* = 7.0 Hz), 7.27 (t, 2H, *J* = 7.5 Hz), 7.32 (t, 3H, *J* = 7.0 Hz), 7.65 (d, 2H, *J* = 8.0 Hz),;

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 30.7, 30.8, 31.0, 31.7, 36.2, 38.4, 50.3, 50.4, 56.7, 66.5, 117.1,

127.6, 127.8, 129.3, 129.4, 129.9, 134.4, 135.7, 142.4, 143.7, 155.3;

mass spectrum (APCI): m/e (% relative intensity) 479.2 (100) $(M+H)^+$.

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[ii] Hayashi, R.; Hsung, R. P.; Feltenberger, J. B.; Lohse, A. G. *Org. Lett.* **2009,** *11,* 2125.