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Torquoselective 6π-Electron Electrocyclic Ring-Closure of 1-Azatrienes Containing Acyclic Chirality at the *C*-terminus.

authored by

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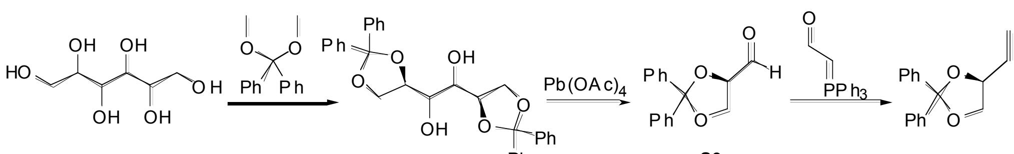
EXPERIMENTAL SECTION

All reactions performed in flame-dried glassware under nitrogen atmosphere. Solvents were distilled prior to use. Reagents were used as purchased (Aldrich, Acros), except where noted. Chromatographic separations were performed using Bodman 60 Å SiO_2. ^1H and ^{13}C NMR spectra were obtained on Varian VI-300, VX-300, VI-400 and VI-500 spectrometers using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Melting points were determined using a Laboratory Devices MEL-TEMP and are uncorrected/calibrated. Infrared spectra were obtained using NaCl plates on a Midac M2000 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 analyses performed at University of Minnesota Department of Chemistry Mass Spectrometry Laboratory and University of Wisconsin School of Pharmacy Mass Spectrometry Laboratory. X-Ray analysis performed at University of Minnesota Department of Chemistry X-Ray facility. All spectral data obtained for new compounds are reported here.

PREPARATION OF CHIRAL ALDEHYDES

Aldehyde 8.



A mixture of D-manitol (**S1**) (2.0 g, 10.1 mmol), 1,3-dimethoxybenzophenone (5.01 g, 21.9 mmol) and $SnCl_2$ (0.025 g, 0.13 mmol) in freshly distilled DME (50 mL) was heated at reflux until all solid dissolved (~ 14 h). Solvent was evaporated; the reminder was suspended in hexane (50 mL), and then filtered. The resulting solid was suspended in acetone (35 mL) and stirred for 1h and then filtered. The filtrate was evaporated giving diol **S2** (1.18 g, 56% BRSM), as a white solid.

S2: R_f = 0.17 [EtOAc];

^1H NMR (500 MHz, $CDCl_3$): δ 3.93 (d, 2 H, J = 6.5 Hz), 4.06 (dd, 4 H, J = 7.5, 6.5 Hz), 4.28 (q, 2 H, J = 6.5 Hz), 7.31 (d, 8 H, J = 7.0 Hz), 7.33 – 7.36 (m, 6 H), 7.42 – 7.49 (m, 6 H), 7.54 (d, 4 H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 67.2, 71.4, 77.6, 110.2, 126.2, 126.4, 128.5, 142.3.

A solution of 1,2-bis(2,2-diphenyl-1,3-dioxolan-4-yl)ethane-1,2-diol (**S2**) (1.18 g, 2.3 mmol) in benzene (25 mL) was cooled down to 10 °C and $Pb(OAc)_4$ (2.05 g, 4.6 mmol) was then added. The resulting suspension was stirred for 40 min at room temperature. After TLC analysis showed consumption of starting material,

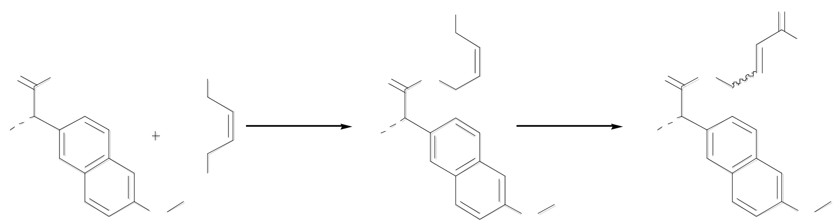
$Pb(OAc)_4$ was filtered and the filtrate was washed with sat. $NaHCO_3$ solution 3 times, brine, then dried over Na_2SO_4. Crude 2,2-diphenyl-1,3-dioxolane-4-carbaldehyde (**S3**) was immediately used in the next step without isolation.

To a solution of formylmethyl triphenylphosphonium chloride (0.31 g, 0.91 mmol) in toluene (10 mL) was added Et_3N (0.15 mL, 0.11 mmol) and the resulting mixture was stirred for 30 min. A solution of aldehyde **S3** (estimated 0.23 g, 0.91 mmol) in benzene (15 mL) was added then and the reaction mixture was stirred at room temperature for 6 h. After TLC analysis showed consumption of starting material, solvent was evaporated and the reminder was suspended in Et_2O (10 mL), then filtered. The filtrate was concentrated under the reduced pressure and aldehyde **8** (0.22 g, 88 %) was isolated after purification via silica gel flash column chromatography (gradient eluent: 5%-20% Et_2O in hexanes).

8: R_f = 0.27 [EtOAc : hexanes = 1 : 3];

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (dd, 1 H, J = 8.0, 7.0 Hz), 4.26 (dd, 1 H, J = 8.0, 7.0 Hz), 4.89 (ddd, 1 H, J = 13.5, 7.0, 1.0 Hz), 6.35 (ddd, 1 H, J = 15.5, 7.5, 1.5 Hz), 6.78 (dd, 1 H, J = 15.5, 6.0 Hz), 7.31 – 7.38 (m, 6 H), 7.55 (t, 4 H, J = 7.5 Hz), 9.56 (d, 1 H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 14.31, 69.3, 75.6, 126.1, 126.2, 128.3, 128.40, 128.46, 128.5, 132.9, 141.7, 141.8, 152.4, 193.0; IR (Film, cm^{-1}): 3052s, 2988s, 1703s, 1595s; *m*/*e* calcd for $C_{18}H_{17}O_3$ (M^+ + H) 281.1178, found 281.1169.

Aldehyde 11.



To a solution of (*S*)-2-(6-methoxynaphthalen-2-yl)-propionyl chloride (**S4**) (7.4g, 29.7 mmol) in CH_2Cl_2 (50 mL) were added Et_3N (10.39 mL) and DMAP (0.15 g, 1.23 mmol). Reaction mixture was cooled down to 0 °C and 2-buten-1,4-diol (**S5**) (4.9 mL, 59.4 mmol) was added by dropwise. Reaction mixture was gradually warmed up to room temperature and stirred overnight. After 2-(6-methoxynaphthalen-2-yl)-propionyl chloride was consumed, the reaction mixture was filtered, the filtrate was concentrated under reduced pressure, and (*S*)-4-hydroxybut-2-enyl 2-(6-methoxynaphthalen-2-yl)propanoate (**S6**) (7.9 g, 83 %) was isolated after purification via silica gel flash column chromatography (gradient eluent: 0%-40% EtOAc in hexanes).

R_f = 0.24 [EtOAc : hexanes = 1 : 1]; $[\alpha]_D^{20}$ = 67.0 ° [c = 1, $CHCl_3$];

S6: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (d, 3 H, J = 7.0 Hz), 3.84 (q, 1 H, J = 7.0 Hz), 3.90 (s, 3 H), 4.17 (dd, 2 H, J = 6.0, 5.5 Hz), 4.66 (ddd, 2 H, J = 13.0, 12.5, 7.5 Hz), 5.51 – 5.57 (m, 1 H), 5.76 – 5.81 (m, 1 H), 7.10 (d, 1 H, J = 2.0 Hz), 7.14 (dd, 1 H, J = 8.5, 2.0 Hz), 7.38 (dd, 1 H, J = 8.5, 2.0 Hz), 7.65 (s, 1 H), 7.69 (d, 2 H, J = 8.5

Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 18.7, 45.6, 55.5, 58.6, 60.6, 105.8, 119.2, 125.6, 126.1, 126.3, 127.4, 129.1, 129.4, 133.6, 133.9, 135.6, 157.8, 174.9.

A solution of alcohol **S6** (0.95 g, 3.2 mmol) in acetone (10 mL) was vigorously stirred with MnO_2 (6.28 g, 64 mmol) for 14 h at room temperature. After TLC analysis showed consumption of starting material, MnO_2 was filtered and solvent was evaporated giving aldehyde **11** (0.69 g, 73 %) as a mixture of *cis* and *trans* isomers.

11: R_f = 0.32/0.38 [EtOAc : hexanes = 1 : 1]; $[\alpha]_D^{20}$ = 21.2 ° [c = 1, $CHCl_3$]; IR (Film, cm^{-1}): 3102s, 2978s, 1731s, 1600s; *m/e* calcd for $C_{18}H_{18}O_4Na$ (M^+ + Na) 321.1103, found 321.1107.

***cis* isomer:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (d, 3 H, *J* = 7.0 Hz), 3.89 (s, 3 H), 3.92 (q, 1 H *J* = 7.0 Hz), 5.03 – 5.16 (m, 2 H), 6.00 – 6.05 (m, 1 H), 6.40 (ddd, 1 H, *J* = 12.0, 11.5, 6.0 Hz), 7.11 (s, 1 H), 7.14 (dd, 1 H, *J* = 8.5, 2.0 Hz), 7.39 (td, 1 H, *J* = 8.5, 1.0 Hz), 7.63 - 7.72 (m, 3 H), 9.43 (d, 1 H, *J* = 6.5 Hz).

***trans* isomer:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.61 (d, 3 H, *J* = 7.0 Hz), 3.89 (s, 3 H), 3.92 (q, 1 H *J* = 7.0 Hz), 4.77 – 4.86 (m, 2 H), 6.14 (dd, 1 H, *J* = 16.0, 8.0 Hz), 6.70 (dt, 1 H, *J* = 16.0, 4.0 Hz), 7.11 (s, 1 H), 7.14 (dd, 1 H, *J* = 8.5, 2.0 Hz), 7.39 (td, 1 H, *J* = 8.5, 1.0 Hz), 7.63 - 7.72 (m, 3 H), 9.48 (d, 1 H, *J* = 8.0 Hz);

PREPARATION OF VINYLOGOUS AMIDES

Amide 32

To a round bottom flask were added tetronic acid (3 g, 29.97 mmol) and diphenylmethane amine (5.66 mL, 32.97 mmol). Freshly distilled toluene (100 mL) and absolute ethanol (3 mL) were then added and the reaction mixture was heated at 85 °C under a water–cooled condenser for 14 h. Removal of the solvent under vacuum produced dark-orange oil. The desired tetronamide **32** was isolated after purification via silica gel flash column chromatography (gradient eluent: 40%-100% EtOAc in hexanes) in 76% yield (6.04 g) as a yellow solid.

32: R_f = 0.16 [EtOAc], mp = 187 – 189 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.51 (s, 1 H), 4.70 (s, 2 H), 5.46 (d, 1 H, *J* = 6.0 Hz), 6.61 (d, 1 H, *J* = 4.8 Hz), 7.25 – 7.28 (m, 3 H), 7.29 (d, 1 H, *J* = 1.6 Hz), 7.31 (t, 1 H, *J* = 1.6 Hz), 7.33 – 7.35 (m, 4 H), 7.37 (t, 1 H, *J* = 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 63.6, 68.0, 83.0, 127.3, 128.1, 129.0, 140.2, 167.7, 176.8; IR (Film, cm^{-1}): 3347brs, 2971s, 1690m; *m/e* calcd for $C_{17}H_{15}NO_2Na$ (M^+ + Na) 288.0995, found 288.0986.

Amide 36

To a round bottom flask were added 1,3-cyclohexanedione (1 g, 8.9 mmol) and diphenylmethane amine (1.68 mL, 9.8 mmol). Freshly distilled toluene (40 mL) and absolute ethanol (1.5 mL) were then added and the reaction mixture was heated at 85 °C under a water–cooled condenser for 14 h. Removal of the solvent under vacuum produced orange solid. It was further purified by recrystallization from EtOAc to give vinylogous amide **36** (1.85 g, 75 %) as a yellow solid.

36: R_f = 0.20 [EtOAc], mp = 176 – 178 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98 (quintet, 1 H, *J* = 6.4 Hz), 2.27 (t, 2 H, *J* = 6.4 Hz), 2.41 (t, 2 H, *J* = 6.4 Hz), 4.93 (s, 1 H), 5.02 (s, 1 H), 5.54 (d, 2 H, *J* = 5.6 Hz), 7.19 – 7.23 (m, 4 H), 7.25 – 7.29 (m, 2 H), 7.31 – 7.35 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): 22.1, 36.6, 61.8, 99.7, 127.5, 128.1, 128.9, 129.1, 140.8, 162.7, 197.6; IR (Film, cm^{-1}): 3244 brs, 3031m, 2946s, 1574s, 1534s; *m*/*e* calcd for $C_{19}H_{20}NO$ (M^+ + H) 278.1539, found 278.1538.

PREPARATION OF 1,2-DIHYDROPYRIDINES

General procedure A.

To a flame-dried flask were added enal (2.0 mmol, pre-filtered through silica gel) and anhydrous EtOAc (6 mL). The solution was cooled to –10 °C, and piperidine (0.20 ml, 2.0 mmol) and then acetic anhydride (0.19 mL, 2.0 mmol) were added dropwise via syringe. Reaction mixture was sealed under nitrogen and heated at 85 °C for 1 h. The resulting iminium salt solution was transferred via a cannula to a suspension of a vinylogous amide (1.0 mmol) in anhydrous toluene (8 mL) in a flame-dried sealed tube. The reaction mixture was sealed under nitrogen and heated at 110 - 170 °C in a sand bath for 24 - 72 h. Reaction progress was monitored using TLC analysis. After vinylogous amide was consumed, the reaction mixture was concentrated under reduced pressure, and formal cycloadduct was isolated after purification via silica gel flash column chromatography (gradient eluent: 0%-63% EtOAc in hexanes).

General procedure B.

To a flame-dried flask were added Na_2SO_4 (5 g), enal (2.0 mmol, pre-filtered through silica gel) and anhydrous EtOAc (5 mL). The solution was cooled to –10 °C, and a solution of piperidine trifluoroacetate (0.40 g, 2.0 mmol) in EtOAc (1 mL) was added dropwise via syringe. Reaction mixture was sealed under nitrogen and heated at 85 °C for 1 h. The resulting iminium salt solution was transferred via a cannula to a suspension of a vinylogous amide (1.0 mmol) in anhydrous toluene (8 mL) in a flame-dried sealed tube. The reaction mixture was sealed under nitrogen and heated at 110 - 170 °C in a sand bath for 24 - 72 h. Reaction progress was monitored using TLC analysis. After vinylogous amide was consumed, the reaction mixture was concentrated under reduced pressure, and formal cycloadduct was isolated after purification via silica gel flash column chromatography (gradient eluent: 0%-63% EtOAc in hexanes).

Cycloadduct 13: Procedure **A**, 160 °C, 48 h, 66 %;

13a major: R_f = 0.27 [EtOAc : hexanes = 2 : 1]; $[\alpha]_D^{20}$ = 348.0 ° [c = 1.5, $CHCl_3$];
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 3 H), 1.43 (s, 3 H), 3.68 (dd, 1 H, J = 9.0, 6.5 Hz), 4.05 (dd, 1 H, J = 9.0, 6.5 Hz), 4.11 (dd, 1 H, J = 8.0, 5.5 Hz), 4.39 – 4.43 (m, 1 H), 4.43 (d, 1 H, J = 15.5 Hz), 4.63 (d, 1 H, J = 16.0 Hz), 4.80 (d, 1 H, J = 16.0 Hz), 4.84 (d, 1 H, J = 15.5 Hz), 4.92 (dd, 1 H, J = 9.0, 5.5 Hz), 6.40 (d, 1 H, J = 9.0 Hz), 7.23 (d, 2 H, J = 7.5 Hz), 7.33 – 7.39 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 25.6, 26.9, 54.6, 62.1, 65.5, 65.8, 77.9, 95.0, 109.8, 110.2, 121.5, 127.1, 128.5, 129.4, 135.2, 164.9, 171.2; IR (Film, cm^{-1}): 3053s, 2986s, 2936m, 1736s, 1623s, 1265s; mass spectrum (APCI): m/z (% rel intensity) 328 (100) M^+ + H, 288 (15), 270 (80), 240 (21), 101 (25), 87 (30); *m/e* calcd for $C_{19}H_{21}NO_4Na$ (M^+ + Na) 350.1368, found 350.1350.
13b minor: R_f = 0.24 [EtOAc : hexanes = 2 : 1]; $[\alpha]_D^{20}$ = -252.8 ° [c = 2, $CHCl_3$];
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 3 H), 1.50 (s, 3 H), 3.96 (dd, 1 H, J = 11.5, 10.0 Hz), 4.05 – 4.09 (m, 1 H), 4.26 – 4.31 (m, 1H), 4.38 (d, 1 H, J = 16.5 Hz), 4.58 (d, 1 H, J = 16.0 Hz), 4.63 (d, 1 H, J = 15.5 Hz), 4.79 (d, 1 H, J = 15.5 Hz), 4.82 (d, 1 H, J = 16.5 Hz), 5.05 (dd, 1 H, J = 9.5, 4.5 Hz), 6.34 (d, 1 H, J = 9.5 Hz), 7.22 (d, 2 H, J = 7.5 Hz), 7.25 – 7.40 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 24.8, 26.5, 54.6, 60.0, 65.1, 65.4, 79.7, 94.6, 109.7, 112.0, 120.2, 126.8, 128.5, 129.5, 134.9, 166.2, 171.1; IR (Film, cm^{-1}): 3053s, 2986s, 2936m, 1736s, 1623s, 1265s; mass spectrum (APCI): m/z (% rel intensity) 328 (100) M^+ + H, 288 (15), 270 (80), 240 (21), 101 (25), 87 (30); *m/e* calcd for $C_{19}H_{21}NO_4Na$ (M^+ + Na) 350.1368, found 350.1350.

Cycloadduct 14: Procedure **A**, 150 °C, 24 h, 63 %, inseparable;
R_f = 0.35 [EtOAc : hexanes = 3 : 2]; IR (Film, cm^{-1}): 3055s, 2987s, 1743s, 1713m, 1423s; mass spectrum (APCI): m/z (% rel intensity) 452 (100) M^+ + H, 270 (20), 226 (35), 167 (40); *m/e* calcd for $C_{29}H_{25}NO_4Na$ (M^+ + Na) 474.1681, found 474.1690.
14a major: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (dd, 1 H, J = 9.0, 6.0 Hz), 4.02 (dd, 1 H, J = 9.0, 7.0 Hz), 4.19 (dd, 1 H, J = 8.0, 5.5 Hz), 4.42 (d, 1 H, J = 16.0 Hz), 4.48 – 4.53 (m, 1 H), 4.57 (d, 1 H, J = 16.0 Hz), 4.67 – 4.69 (m, 1 H), 4.77 (d, 1 H, J = 16.0 Hz), 4.94 (dd, 1 H, J = 9.5, 5.5 Hz), 6.41 (d, 1 H, J = 9.5 Hz), 7.03 – 7.07 (m, 2 H), 7.25 – 7.39 (m, 9 H), 7.45 – 7.53 (m, 3 H), 7.58 – 7.61 (m, 1 H).
14b minor: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (dd, 1 H, J = 9.0, 6.0 Hz), 4.02 (dd, 1 H, J = 9.0, 7.0 Hz), 4.08 – 4.11 (m, 1 H), 4.31 (dd, 1 H, J = 8.0, 5.5 Hz), 4.48 – 4.53 (m, 1 H), 4.63 (d, 1 H, J = 16.0 Hz), 4.66 (d, 1 H, J = 16.0 Hz), 4.78 (d, 1 H, J = 16.0 Hz), 5.03 (dd, 1 H, J = 9.5, 5.5 Hz), 6.36 (d, 1 H, J = 9.5 Hz), 7.03 – 7.07 (m, 2 H), 7.25 – 7.39 (m, 9 H), 7.45 – 7.53 (m, 3 H), 7.58 – 7.61 (m, 1H).

Cycloadduct 15: Procedure **A**, 160 °C, 72 h, 32 %;
15a major: R_f = 0.51 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = -196.0 ° [c = 1, $CDCl_3$];
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 9 H), 1.48 (s, 3 H), 1.52 (s, 3 H), 3.88 (dd, 1 H, J = 9.0, 6.0 Hz), 4.00 (d, 1 H, J = 9.5 Hz), 4.18 – 4.23 (m, 1 H), 4.27 – 4.40 (m, 2 H), 4.48 (d, 1 H, J = 15.5 Hz), 4.50 – 4.63 (m, 1 H),

4.79 (d, 1 H, J = 15.5 Hz), 5.18 (dd, 1 H, J = 9.5, 5.0 Hz), 6.47 (d, 1 H, J = 9.5 Hz), 7.17 (d, 2 H, J = 7.0 Hz), 7.27 – 7.37 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 28.6, 29.8, 29.9, 48.1, 54.2, 59.5, 61.7, 63.9, 65.6, 81.0, 94.1, 111.6, 120.6, 126.7, 127.0, 128.5, 136.6, 164.0, 165.6, 176.7; IR (Film, cm^{-1}): 3004s, 2898s, 2782m, 1747s, 1735s, 1639s, 1480s, 1225s; mass spectrum (APCI): m/z (% rel intensity) 427 (18) M^+ + H, 371 (30), 327 (100), 267 (70), 226 (50), 178 (45); *m/e* calcd for $C_{24}H_{30}N_2O_5Na$ (M^+ + Na) 449.2052, found 449.2095.

15b minor: R_f = 0.51 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = 152.2 ° [c = 0.1, $CDCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26 (s, 9 H), 1.47 (s, 3 H), 1.48 (s, 3 H), 3.84 (d, 1 H, J = 9.5 Hz), 4.00 (dd, 1 H, J = 9.5, 7.0 Hz), 4.27 (d, 1 H, J = 7.0 Hz), 4.34 – 4.46 (m, 2 H), 44.56 (d, 1 H, J = 15.5 Hz), 4.66 – 4.69 (m, 1 H), 4.74 (d, 1 H, J = 15.5 Hz), 5.16 (dd, 1 H, J = 9.5, 5.0 Hz), 6.44 (d, 1 H, J = 9.5 Hz), 7.22 – 7.25 (m, 2 H), 7.30 – 7.34 (m, 1H), 7.38 (t, 2 H, J = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 26.4, 28.4, 29.9, 53.1, 59.3, 60.5, 62.0, 64.7, 65.7, 81.0, 95.6, 112.4, 120.9, 127.0, 128.5, 129.4, 135.0, 154.1, 167.2, 171.4; IR (Film, cm^{-1}): 3004s, 2898s, 2782m, 1747s, 1735s, 1639s, 1480s, 1225s; mass spectrum (APCI): m/z (% rel intensity) 427 (18) M^+ + H, 371 (30), 327 (100), 267 (70), 226 (50), 178 (45); *m/e* calcd for $C_{24}H_{30}N_2O_5Na$ (M^+ + Na) 449.2052, found 449.2065.

Cycloadduct 16: Procedure **A**, 150 °C, 72 h, 64 %;

16a major: R_f = 0.22 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = -213.70 ° [c = 2, $CHCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.95 (s, 3 H), 2.00 (s, 3 H), 2.07 (s, 3 H), 4.18 (dd, 1 H, J = 13.0, 5.0 Hz), 4.26 (dd, 1 H, J = 13.0, 2.5 Hz), 4.32 – 4.34 (m, 1H), 4.34 (d, 1 H, J = 15.5 Hz), 4.53 (d, 1 H, J = 15.5 Hz), 4.62 (s, 2 H), 5.11 (dd, 1 H, J = 10.0, 5.0 Hz), 5.22 – 5.26 (m, 1 H), 5.30 (dd, 1 H, J = 9.5, 1.5 Hz), 6.46 (d, 1 H, J = 10.0 Hz), 7.27 (d, 2 H, J = 7.0 Hz), 7.35 – 7.43 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.8, 20.9, 21.0, 52.4, 59.1, 62.1, 65.3, 67.3, 69.9, 94.6, 110.0, 121.5, 127.5, 128.8, 129.5, 133.8, 165.8, 169.8, 170.6, 170.7, 170.8; IR (Film, cm^{-1}): 3057s, 2987s, 2931s, 1753s, 1632s, 1601s, 1266s; mass spectrum (APCI): m/z (% rel intensity) 444 (20) M^+ + H, 418 (15), 402 (25), 298 (45), 282 (100), 226 (60); *m/e* calcd for $C_{23}H_{25}NO_8Na$ (M^+ + Na) 466.1478, found 466.1492.

16b minor: R_f = 0.16 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = 158.0 ° [c = 0.5, $CHCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (s, 6 H), 2.12 (s, 3 H), 4.21 (dd, 1 H, J = 12.5, 6.5 Hz), 4.37 (dd, 1 H, J = 12.5, 3.0 Hz), 4.39 – 4.42 (m, 1 H), 4.43 (d, 1 H, J = 16.5 Hz), 4.52 (d, 1 H, J = 16.5 Hz), 4.60 (d, 1 H, J = 16.0 Hz), 4.79 (d, 1 H, J = 16.0 Hz), 5.14 (dd, 1 H, J = 9.5, 5.0 Hz), 5.26 (t, 1 H, J = 5.0 Hz), 5.33 – 5.36 (m, 1 H), 6.47 (d, 1 H, J = 9.5 Hz), 7.21 (d, 2 H, J = 7.0 Hz), 7.34 – 7.41 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.9, 21.0, 21.1, 54.0, 60.5, 62.3, 65.6, 70.1, 72.9, 96.0, 110.6, 121.4, 126.8, 128.8, 129.5, 134.7, 165.4, 169.9, 170.2, 170.8, 170.9; IR (Film, cm^{-1}): 3057s, 2987s, 2931s, 1753s, 1632s, 1601s, 1266s; mass spectrum (APCI): m/z (% rel intensity) 444 (75) M^+ + H, 402 (90), 360 (30), 324 (25), 282 (40), 226 (100); *m/e* calcd for $C_{23}H_{25}NO_8Na$ (M^+ + Na) 466.1478, found 466.1506.

Cycloadduct 17: Procedure **A**, 150 °C, 72 h, 73 %;

17a major: R_f = 0.44 [EtOAc : hexanes = 2 : 1]; $[\alpha]_D^{20}$ = -194.4 ° [c = 1, $CDCl_3$];

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59 (d, 3 H, J = 7.2 Hz), 3.69 (d, 1 H, J = 16.5 Hz), 3.85 – 3.90 (m, 2 H), 3.92 (s, 3 H), 4.02 (d, 1 H, J = 16.5 Hz), 4.25 – 4.41 (m, 3 H), 4.58 – 4.70 (m, 1 H), 4.97 (dd, 1 H, J = 9.6, 5.0 Hz), 6.36 (d, 1 H, J = 9.6 Hz), 6.82 (dd, 2 H, J = 6.6, 2.1 Hz), 7.10 – 7.26 (m, 5 H), 7.40 (dd, 1 H, J = 8.0, 1.5 Hz), 7.66 – 7.73 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 18.4, 45.8, 53.2, 55.5, 58.9, 65.2, 65.5, 94.8, 105.7, 111.6, 119.6, 120.6, 126.2, 126.4, 126.6, 127.6, 128.4, 129.0, 129.3, 129.4, 129.5, 134.0, 134.6, 135.5, 157.8, 164.7, 174.6; IR (Film, cm^{-1}): 3071s, 2988s, 1730s, 1720s, 1629s; mass spectrum (APCI): m/z (% rel intensity) 470 (100) M^+ + H, 275 (10), 258 (30), 240 (45), 185 (48); *m/e* calcd for $C_{29}H_{27}NO_5Na$ (M^+ + Na) 492.1787, found 492.1761.

17b minor: R_f = 0.41 [EtOAc : hexanes = 2 : 1]; $[\alpha]_D^{20}$ = 138.78° [c = 1.15, $CDCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (d, 3 H, J = 7.5 Hz), 3.83 – 3.93 (m, 3 H), 3.92 (s, 3 H), 3.97 (d, 1 H, J = 16.0 Hz), 4.17 (d, 1 H, J = 15.5 Hz), 4.24 – 4.27 (m, 2 H), 4.32 (d, 1 H, J = 15.5 Hz), 4.99 (dd, 1 H, J = 9.5, 5.0 Hz), 6.37 (d, 1 H, J = 9.5 Hz), 6.80 (d, 2 H, J = 7.5 Hz), 7.11 – 7.27 (m, 5 H), 7.36 (dd, 1 H, J = 8.0, 1.5 Hz), 7.66 – 7.73 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 18.4, 45.6, 53.1, 55.5, 59.0, 65.2, 65.3, 94.7, 105.7, 112.0, 119.6, 120.5, 126.1, 126.4, 126.7, 127.6, 128.5, 129.1, 129.3, 129.4, 129.5, 134.0, 134.4, 135.4, 158.0, 164.9, 174.7; IR (Film, cm^{-1}): 3054s, 2988s, 1737s, 1716s, 1635m; mass spectrum (APCI): m/z (% rel intensity) 470 (100) M^+ + H, 275 (10), 258 (30), 240 (45), 185 (48); *m/e* calcd for $C_{29}H_{27}NO_5Na$ (M^+ + Na) 492.1787, found 492.1723.

Cycloadduct 23: Procedure **A**, 110 °C, 24 h, 58 %;

23a major: R_f = 0.40 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = 76.6 ° [c = 2, $CHCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (s, 3 H), 1.30 (s, 3 H), 3.29 (s, 3 H), 3.33 – 3.36 (m, 1 H), 3.42 (s, 3 H), 3.55 (dd, 1 H, J = 8.0, 6.5 Hz), 3.85 (dd, 1 H, J = 4.5, 4.0 Hz), 4.18 – 4.29 (m, 1 H), 4.36 (d, 1 H, J = 15.5 Hz), 4.43 (d, 1 H, J = 15.5 Hz), 5.20 (dd, 1 H, J = 7.0, 5.5 Hz), 5.99 (d, 1 H, J = 7.0 Hz), 7.22 – 7.38 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): 25.2, 26.4, 28.3, 34.6, 35.2, 56.5, 65.4, 76.2, 94.5, 108.8, 110.4, 127.7, 128.4, 129.2, 134.3, 151.2, 153.0, 162.5, 167.3; IR (Film, cm^{-1}): 3050s, 2908m, 1700s, 1695s, 1658s, 1635s; mass spectrum (APCI): m/z (% rel intensity) 384 (5) M^+ + H, 382 (40), 326 (100), 308 (10), 282 (30); *m/e* calcd for $C_{21}H_{25}N_3O_4Na$ (M^+ + Na) 406.1743, found 406.1746.

23b minor (inseparable from major)**:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (s, 3 H), 1.38 (s, 3 H), 3.31 (s, 3 H), 3.33 – 3.36 (m, 1 H), 3.44 (s, 3 H), 3.53 (dd, 1 H, J = 5.5, 5.0 Hz), 3.77 (dd, 1 H, J = 8.0, 6.5 Hz), 4.20 – 4.26 (m, 1 H), 4.30 (d, 1 H, J = 15.5 Hz), 4.33 (d, 1 H, J = 15.5 Hz), 5.27 (dd, 1 H, J = 7.0, 5.5 Hz), 6.02 (d, 1 H, J = 7.0 Hz), 7.22 – 7.38 (m, 5 H).

Cycloadduct 24: Procedure **A**, 130 °C, 48 h, 49 %;

24a major: R_f = 0.17 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = 6.25 ° [c = 0.8, $CDCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (s, 3 H), 2.14 (s, 6 H), 3.35 (s, 3 H), 3.37 – 3.39 (m, 1 H), 3.50 (s, 3 H), 4.03 (d, 1 H, J = 14.5 Hz), 4.15 (d, 1 H, J = 14.5 Hz), 4.37 (dd, 1 H, J = 8.0, 6.5 Hz), 4.42 – 4.48 (m, 1 H), 5.27 (dd, 1 H, J = 9.5, 6.0 Hz), 5.49 (t, 1 H, J = 6.0 Hz), 6.79 (d, 1 H, J = 9.5 Hz), 7.25 – 7.30 (m, 2 H), 7.35 – 7.40 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.8, 20.9, 21.0, 28.7, 29.7, 32.5, 61.7, 71.5, 71.6, 109.3, 115.7, 125.6, 128.7, 129.0, 129.4, 139.8, 149.4, 151.7, 161.4, 164.1, 169.9, 170.1, 170.6; IR (Film, cm^{-1}): 3050s, 2980 - 2966s, 1755s, 1701s, 1696s, 1632s, 1601s, 1266s; mass spectrum (APCI): m/z (% rel intensity) 500 (5) M^+ + H, 440 (100), 381 (20), 322 (45), 108 (40); *m/e* calcd for $C_{25}H_{29}N_3O_8Na$ (M^+ + Na) 522.1852, found 522.1830.

24b minor: was not characterized due to insufficient amount of material.

Cycloadduct 25: Procedure **A**, 130 °C, 24 h, 65 %, inseparable;

R_f = 0.35 [EtOAc : hexanes = 2 : 1]; IR (Film, cm^{-1}): 3054s, 2898s, 1740s, 1699s, 1635s, 1667s; mass spectrum (APCI): m/z (% rel intensity) 526 (8) M^+ + H, 296 (100), 206 (15), 185 (35); *m/e* calcd for $C_{31}H_{31}N_3O_5Na$ (M^+ + Na) 548.2161, found 548.2152.

25a major: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.51 (d, 3 H, J = 7.0 Hz), 3.08 (s, 3 H), 3.30 (s, 3 H), 3.59 (d, 1 H, J = 7.0 Hz), 3.66 – 3.70 (m, 2 H), 3.78 – 3.84 (m, 2 H), 3.89 (s, 3 H), 3.93 (d, 1 H, J = 16.0 Hz), 5.01 (dd, 1 H, J = 7.0, 5.0 Hz), 5.72 (d, 1 H, J = 7.0 Hz), 7.03 (dd, 2 H, J = 7.5, 4.0 Hz), 7.08 – 7.15 (m, 5 H), 7.41 (dd, 1 H, J = 8.5, 1.5 Hz), 7.59 – 7.70 (m, 3 H).

25b minor: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.54 (d, 3 H, J = 7.0 Hz), 3.32 (s, 3 H), 3.34 (s, 3 H), 3.62 (d, 1 H, J = 7.0 Hz), 3.66 – 3.70 (m, 2 H), 3.78 – 3.84 (m, 2 H), 3.89 (s, 3 H), 4.12 (d, 1 H, J = 16.0 Hz), 5.06 (dd, 1 H, J = 7.0, 5.0 Hz), 5.74 (d, 1 H, J = 7.0 Hz), 6.98 (dd, 2 H, J = 7.5, 4.0 Hz), 7.22 – 7.29 (m, 5 H), 7.34 (dd, 1 H, J = 8.5, 1.5 Hz), 7.59 – 7.70 (m, 3 H).

Cycloadduct 26: Procedure **B**, 170 °C, 48 h, 61 %, inseparable;

R_f = 0.42 [EtOAc : hexanes = 2 : 1]; IR (Film, cm^{-1}): 3056s, 2987s, 1795s, 1745s, 1692s, 1426s; mass spectrum (APCI): m/z (% rel intensity) 470 (65) M^+ + H, 428 (50), 410 (10), 386 (25), 252 (100); *m/e* calcd for $C_{25}H_{27}NO_8Na$ (M^+ + Na) 492.1634, found 492.1652.

26a major: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 3 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 2.12 (s, 3 H), 4.18 (dd, 1 H, J = 9.6, 5.6 Hz), 4.26 (dd, 1 H, J = 5.0, 2.5 Hz), 4.31 – 4.37 (m, 2 H), 4.40 (d, 1 H, J = 16.5 Hz), 4.76 (d, 1 H, J = 16.5 Hz), 5.25 (dd, 1 H, J = 10.2, 2.4 Hz), 5.29 – 5.33 (m, 1 H), 5.70 (s, 1H), 6.82 (d, 1 H, J = 10.2 Hz), 7.24 (dd, 2 H, J = 7.6, 1.5 Hz), 7.28 – 7.42 (m, 3 H)

26b minor: ^{1}H NMR (500 MHz, $CDCl_3$): 1.89 (s, 3 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 2.11 (s, 3 H), 4.09 – 4.15 (m, 1 H), 4.24 – 4.38 (m, 3 H), 4.48 (d, 1 H, *J* = 16.5 Hz), 4.85 (d, 1 H, *J* = 16.5 Hz), 5.22 (dd, 1 H, *J* = 10.2, 2.6 Hz), 5.33 – 5.36 (m, 1 H), 5.77 (s, 1 H), 6.80 (d, 1 H, *J* = 10.2 Hz), 7.17 (dd, 2 H, *J* = 7.6, 1.5 Hz), 7.28 – 7.42 (m, 3 H).

Cycloadduct 27: Procedure **B**, 180 °C, 24 h, 84 %, inseparable;
R_f = 0.45 [EtOAc : hexanes = 3 : 2]; IR (Film, cm^{-1}): 3055s, 2980s, 1733s, 1690s, 1607s, 1524s; mass spectrum (APCI): m/z (% rel intensity) 496 (55) M^+ + H, 469 (80), 204 (100), 267 (15), 240 (40); *m/e* calcd for $C_{31}H_{29}NO_5Na$ (M^+ + Na) 518.1943, found 518.1910.
27a major: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (d, 3 H, *J* = 7.5 Hz), 1.98 (s, 3 H), 3.80 – 3.90 (m, 2 H), 3.90 (s, 3 H), 3.93 – 3.96 (m, 2 H), 4.12 – 4.22 (m, 2 H), 5.14 (dd, 1 H, *J* = 9.5, 5.5 Hz), 5.43(s, 1H), 6.70 (d, 1 H, *J* = 9.5 Hz), 6.72 – 6.76 (m, 2 H), 7.09 – 7.21 (m, 5 H), 7.35 – 7.42 (m, 1 H), 7.66 – 7.74 (m, 3 H).
27b minor: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (d, 3 H, *J* = 7.5 Hz), 2.02 (s, 3 H), 3.80 – 3.90 (m, 2 H), 3.92 (s, 3 H), 3.93 – 3.96 (m, 2 H), 4.12 – 4.22 (m, 2 H), 5.13 (dd, 1 H, *J* = 9.5, 5.5 Hz), 5.27 (s, 1 H), 6.68 (d, 1 H, *J* = 9.5 Hz), 6.72 – 6.76 (m, 2 H), 7.09 – 7.21 (m, 5 H), 7.35 – 7.42 (m, 1 H), 7.66 – 7.74 (m, 3 H).

Cycloadduct 28: Procedure **A**, 150 °C, 24 h, 76 %;
28a major: R_f = 0.51 [EtOAc : hexanes = 4 : 1]; $[\alpha]_D^{20}$ = -176.1 ° [c = 0.2, $CDCl_3$];
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.79 -1.84 (m, 2 H), 1.95 (s, 3 H), 2.04 (s, 6 H), 2.23 (q, 2 H, *J* = 6.5 Hz), 2.34 (q, 2 H, *J* = 6.5 Hz), 4.13 – 4.18 (m, 2 H), 4.24 (dd, 1H, *J* = 13.0, 2.5 Hz), 4.38 (d, 1 H, *J* = 17.0 Hz), 4.82 (d, 1 H, *J* = 17.0 Hz), 5.09 (dd, 1 H, *J* = 10.0, 5.5 Hz), 5.17 – 5.21 (m, 1 H), 5.27 (dd, 1 H, *J* = 9.0, 2.5 Hz), 6.88 (d, 1 H, *J* = 10.0 Hz), 7.18 (d, 2 H, *J* = 7.5 Hz), 7.24 – 7.29 (m, 1 H), 7.35 (t, 2 H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 20.8, 20.9, 21.1, 24.6, 25.6, 26.5, 42.6, 47.6, 59.9, 62.1, 67.8, 70.6, 107.1, 124.9, 126.3, 128.1, 129.3, 136.1, 161.3, 168.8, 169.8, 170.6, 191.8; IR (Film, cm^{-1}): 3057s, 2930s, 1737s, 1730s, 1616s, 1539s; mass spectrum (APCI): m/z (% rel intensity) 456 (100) M^+ + H, 414 (20), 396 (15), 294 (35), 239 (70), 148 (30); *m/e* calcd for $C_{25}H_{29}NO_7Na$ (M^+ + Na) 478.1842, found 478.1817.
28b minor: R_f = 0.48 [EtOAc : hexanes = 4 : 1]; $[\alpha]_D^{20}$ = 212.0 ° [c = 0.2, $CDCl_3$];
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.87 -1.94 (m, 2 H), 2.06 (s, 6 H), 2.13 (s, 3 H), 2.31 (t, 2 H, *J* = 6.5 Hz), 2.46 (q, 2 H, *J* = 6.5 Hz), 4.41 (d, 1H, *J* = 17.5 Hz), 4.42 – 4.45 (m, 1 H), 4.46 (dd, 1 H, *J* = 13.5, 6.5 Hz), 4.51 (dd, 1 H, *J* = 13.5, 6.5 Hz), 4.59 (d, 1 H, *J* = 5.5 Hz), 4.76 (d, 1 H, *J* = 17.5 Hz), 5.09 (dd, 1 H, *J* = 10.5, 5.5 Hz), 5.42 (t, 1 H, *J* = 6.5 Hz), 6.38 (d, 1 H, *J* = 10.0 Hz), 7.22 (d, 2 H, *J* = 7.0 Hz), 7.27 – 7.32 (m, 1 H), 7.38 (t, 2 H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 20.7, 20.9, 21.3, 26.7, 35.6, 43.8, 52.0, 58.7, 62.6, 107.7, 110.3, 113.7, 122.9, 126.3, 127.9, 129.3, 136.0, 147.7, 160.6, 168.8, 168.9, 170.8, 192.0; IR (Film, cm^{-1}): 3057s, 2930s,

1737s, 1730s, 1616s, 1539s; mass spectrum (APCI): m/z (% rel intensity) 456 (80) M^+ + H, 414 (40), 396 (80), 294 (100), 239 (60), 148 (20); *m*/*e* calcd for $C_{25}H_{29}NO_7Na$ (M^+ + Na) 478.1842, found 478.1799.

Cycloadduct 29: Procedure **A**, 150 °C, 24 h, 75 %, inseparable;
R_f = 0.36 [EtOAc : hexanes = 3 : 1]; IR (Film, cm^{-1}): 3056s, 2988s, 1735s, 1635m, 1608s; mass spectrum (APCI): m/z (% rel intensity) 482 (100) M^+ + H, 270 (15), 252 (25), 185 (5), 148 (10); *m*/*e* calcd for $C_{31}H_{31}NO_4Na$ (M^+ + Na) 504.2151, found 504.2168.
29a major : ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60 (d, 3 H, *J* = 7.5 Hz), 1.67 – 1.71 (m, 1 H), 1.78 (quintet, 1 H, *J* = 6.5 Hz), 2.03 (t, 1 H, *J* = 6.5 Hz), 2.21 – 2.32 (m, 3 H), 3.73 – 3.78 (m, 2 H), 3.85 – 3.91 (m, 2 H), 3.93 (s, 3 H), 4.04 – 4.09 (m, 1 H), 4.30 (dd, 1 H, *J* = 10.5, 9.0 Hz), 5.02 (dd, 1 H, *J* = 10.0, 5.5 Hz), 6.61 (d, 2 H, *J* = 7.5 Hz), 6.81 (d, 1 H, *J* = 10.0 Hz), 7.10 – 7.21 (m, 5 H), 7.44 (dd, 1 H, *J* = 8.5, 1.5 Hz), 7.67 – 7.77 (m, 3 H).
29b minor : ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.61 (d, 3 H, *J* = 7.5 Hz), 1.67 – 1.82 (m, 2 H), 2.00 (t, 1 H, *J* = 6.5 Hz), 2.12 – 2.29 (m, 3 H), 3.72 (d, 2 H, *J* = 17.5 Hz), 3.85 – 3.89 (m, 2 H), 3.93 (s, 3 H), 4.02 – 4.08 (m, 1 H), 4.22 (d, 1 H, *J* = 17.5 Hz), 5.03 (dd, 1 H, *J* = 10.0, 5.5 Hz), 6.59 (dd, 2 H, *J* = 7.5, 2.0 Hz), 6.83 (d, 1 H, *J* = 10.0 Hz), 7.12 – 7.20 (m, 5H), 7.41 (dd, 1 H, *J* = 8.5, 1.5 Hz), 7.70 – 7.77 (m, 3 H).

Cycloadduct 33: Procedure **A**, 160 °C, 72 h, 36 %;
33a major: R_f = 0.16 [EtOAc : hexanes = 1 : 1]; $[\alpha]_D^{20}$ = -243.5 ° [c = 0.375, $CHCl_3$];
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (s, 3 H), 1.96 (s, 3 H), 2.03 (s, 3 H), 3.97 (dd, 1 H, *J* = 12.0, 4.6 Hz), 4.05 (d, 1 H, *J* = 16.5 Hz), 4.10 (dd, 1 H, *J* = 12.0, 3.0 Hz), 4.25 (d, 1 H, *J* = 16.5 Hz), 4.43 (dd, 1 H, *J* = 6.0, 1.2 Hz), 4.91 (dd, 1 H, *J* = 9.2, 1.6 Hz), 5.08 (ddd, 1 H, *J* = 9.2, 4.6, 2.4 Hz), 5.19 (dd, 1 H, *J* = 9.6, 6.0 Hz), 5.86 (s, 1 H), 6.57 (d, 1 H, *J* = 9.6 Hz), 7.20 – 7.23 (m, 4 H), 7.28 – 7.44 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): 20.8, 20.9, 21.0, 58.4, 61.9, 66.7, 67.1, 69.0, 72.5, 98.3, 109.5, 122.6, 128.2, 128.9, 129.19, 129.24, 129.5, 130.1, 137.4, 138.5, 165.7, 169.7, 170.5, 170.90, 170.92; IR (Film, cm^{-1}) 3062s, 2939m, 1746s, 1623m, 1593s; *m*/*e* calcd for $C_{29}H_{29}NO_8Na$ (M^+ + Na) 542.1785, found 542.1802.
33b minor: was not characterized due to insufficient amount of material.

Cycloadduct 35: Procedure **A**, 130 °C, 24 h, 82 %;
35a major: R_f = 0.11 [EtOAc : hexanes = 4 : 1]; $[\alpha]_D^{20}$ = - 159.3 ° [c = 0.55, $CHCl_3$];
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 3 H), 2.07 (s, 3 H), 2.10 (s, 3 H), 2.97 (s, 3 H), 4.18 (ddd, 1 H, *J* = 12.8, 2.4, 1.6 Hz), 4.27 (dd, 1 H, *J* = 12.8, 1.6 Hz), 4.37 (d, 1 H, *J* = 4.8 Hz), 4.52 (d, 1 H, *J* = 16.0 Hz), 4.67 (d, 1 H, *J* = 16.0 Hz), 5.08 (dd, 1 H, *J* = 10.0, 4.8 Hz), 5.24 – 5.29 (m, 2H), 6.40 (d, 1 H, *J* = 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 20.9, 21.1, 21.2, 36.7, 62.3, 63.1, 65.1, 67.6, 69.9, 93.9, 109.7, 121.6, 166.1, 170.0, 170.7, 170.8,

170.9; IR (Film, cm^{-1}): 3009w, 2941s, 2859m, 1746s, 1633s; *m/e* calcd for $C_{17}H_{21}NO_8Na$ (M^+ + Na) 390.1159, found 390.1161.

35b minor (inseparable from major): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 3 H), 2.04 (s, 3 H), 2.11 (s, 3 H), 3.02 (s, 3 H), 4.20 (dd, 1 H, J = 12.4, 6.0 Hz), 4.34 (d, 1 H, J = 2.8 Hz), 4.43 (td, 1 H, J = 4.8, 0.8 Hz), 4.71 (s, 2 H), 5.07 (dd, 1 H, J = 10.0, 4.8 Hz), 5.20 (t, 1 H, J = 0.8 Hz), 5.29 (ddd, 1 H, J = 6.0, 4.8, 2.4 Hz), 6.38 (d, 1 H, J = 10.0 Hz).

Cycloadduct 39: Procedure **A**, 150 °C, 24 h, 54 %;

39a major: R_f = 0.20 [EtOAc : hexanes = 4 : 1]; $[\alpha]_D^{20}$ = - 413.3.0 ° [c = 1, $CHCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.80 – 1.84 (m, 1 H), 1.86 (s, 3 H), 1.91 (s, 3 H), 1.98 (s, 3 H), 2.27 (ddd, 2 H, J = 16.5, 6.5, 2.0 Hz), 2.36 (ddd, 1 H, J = 16.5, 7.5, 5.5 Hz), 2.67 (ddd, 2 H, J = 16.5, 6.5, 5.0 Hz), 3.80 (dd, 1 H, J = 12.5, 4.5 Hz), 3.93 (dd, 1 H, J = 12.5, 2.5 Hz), 4.31 (dd, 1 H, J = 6.0, 2.0 Hz), 4.46 (dd, 1 H, J = 9.5, 2.0 Hz), 4.93 (ddd, 1 H, J = 9.5, 4.5, 2.0 Hz), 5.23 (dd, 1 H, J = 9.5, 6.0 Hz), 6.44 (s, 1 H), 7.02 (d, 1 H, J = 9.5 Hz), 7.12 (d, 2 H, J = 7.5 Hz), 7.29 (d, 2 H, J = 7.5 Hz), 7.35 (t, 2 H, J = 7.5 Hz), 7.37 - 7.90 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.9, 21.1, 21.3, 21.5, 27.5, 35.8, 54.7, 61.8, 67.0, 67.4, 73.1, 106.7, 113.1, 125.9, 127.0, 127.8, 128.8, 128.9, 129.3, 132.1, 138.4, 140.0, 161.7, 169.6, 170.5, 170.9, 192.6; IR (Film, cm^{-1}): 3061w, 3030w, 2950m, 1745s, 1621s; *m/e* calcd for $C_{31}H_{34}NO_7H$ (M^+ + H) 532.2330, found 532.2329.

39b minor: was not characterized due to insufficient amount of material.

Diol 18.

Cycloadduct **13a** (0.062g, 0.19 mmol) was dissolved in CH_2Cl_2 (5 mL) and pyridine (0.1 mL) and the solution was cooled down to - 40 °C. Solution of OsO_4 (0.067g, 0.26 mmol) in CH_2Cl_2 (1 mL) was added than by dropwise. Reaction mixture was allowed to worm up to room temperature over 2 h period and then stirred for additional 4 h at this temperature. Reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with sodium bisulfate solution three times, brine. CH_2Cl_2 solution was dried over Na_2SO_4, solvent was evaporated and crude product was purified on the column (gradient eluent: 50%-100 % EtOAc in hexanes) to give the diol **18** (0.024 g, 46 %) as a white solid.

18: R_f = 0.24 [CH_2Cl_2 : CH_3OH = 10 : 1]; $[\alpha]_D^{20}$ = - 69.8 ° [c = 2, $CDCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (s, 3 H), 1.41 (s, 3 H), 3.21 (s, 1 H), 3.57 (dd, 1 H, J = 9.0, 2.5 Hz), 3.61 – 3.66 (m, 1 H), 3.76 (dd, 1 H, J = 4.0, 2.5 Hz), 4.03 – 4.18 (m, 3 H), 4.45 (d, 1 H, J = 16.0 Hz), 4.49 (d, 1 H, J = 16.0 Hz), 4.60 (d, 1 H, J = 4.0 Hz), 4.70 (dd, 1 H, J = 16.0, 1.5 Hz), 4.72 (d, 1 H, J = 16.0 Hz), 7.29 – 7.36 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$): 25.8, 26.7, 54.7, 61.9, 65.5, 65.8, 66.0, 66.7, 75.7, 90.1, 110.2, 127.4, 128.3, 129.1, 135.7, 163.2, 174.2; IR (Film, cm^{-1}): 3517brs, 3102m, 2988s, 1736s, 1618s, 1265s; mass spectrum

(APCI): m/z (% rel intensity) 362 (60) M^+ + H, 344 (100), 304 (50), 286 (50), 242 (60), 232 (15); *m*/*e* calcd for $C_{19}H_{23}NO_6Na$ (M^+ + Na) 384.1423, found 384.1414.

Hydrogynated 19.

Cycloadduct **16a** (0.031 g, 0.07 mmol) was dissolved in 10 mL of MeOH, and 10% Pd/C (0.01 g, 1 mol%) was added. The flask was fitted with a hydrogen balloon and allowed to stir at room temperature overnight. Filtration of catalyst and removal of solvent gave the desired product **19** (0.029 g, 93%) as a white solid.

19: R_f = 0.22 [EtOAc : hexanes = 3 : 2]; $[\alpha]_D^{20}$ = 68.8 ° [c = 1, $CDCl_3$];

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.52 (septet, 1 H, *J* = 6.5 Hz), 1.94 (s, 3 H), 1.97 (s, 3 H), 2.06 (s, 3 H), 2.14 (dd, 1 H, *J* = 12.5, 5.0 Hz), 2.24 – 2.32 (m, 1 H), 2.37 (dd, 1 H, *J* = 16.0, 6.0 Hz),3.39 (s, 1 H), 4.15 (dd, 1 H, *J* = 12.5, 5.0 Hz), 4.29 (d, 1 H, *J* = 16.5 Hz), 4.30 (d, 1 H, *J* = 2.0 Hz), 4.45 (d, 1 H, *J* = 16.5 Hz), 4.60 – 4.66 (m, 2 H), 5.19 – 5.31 (m, 1 H), 5.46 (dd, 1 H, *J* = 8.0, 3.0 Hz), 7.17 (d, 2 H, *J* = 7.5 Hz), 7.33 (t, 1 H, *J* = 7.5 Hz), 7.37 (t, 2 H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 15.8, 20.8, 20.9 (2H), 21.4, 52.6, 54.2, 62.0, 65.8, 69.0, 69.4, 92.0, 127.2, 128.5, 129.4, 135.5, 163.5, 169.9, 170.1, 170.7, 173.8; IR (Film, cm^{-1}): 3050s, 2983s, 1745s, 1641s, 1600s; mass spectrum (APCI): m/z (% rel intensity) 446 (100) M^+ + H, 428 (10), 404 (15), 344 (10), 284 (10); *m*/*e* calcd for $C_{23}H_{27}NO_8Na$ (M^+ + Na) 468.1634, found 468.1632.