Enyne Metathesis for the Formation of Macrocyclic Chiral 1,3-Dienes

Eric C. Hansen, Daesung Lee*

Department of Chemistry, University of Wisconsin, Madison, WI 53706

Supporting Information**Materials and Methods**

Compounds were purchased from Aldrich. THF was distilled from sodium/benzophenone and methylene chloride was distilled from CaH_2 . Flash chromatography was performed using silica gel 60 Å (32-63 mesh) from Sorbent Technologies. Reactions were monitored by thin layer chromatography (TLC) using 0.25 mm E. Merk precoated silica gel 60 (particle size 0.040 – 0.063 mm). ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AC-250 or a Bruker AC-300 spectrometer. Chemical shifts are reported in δ values relative to the internal standard tetramethyl silane (TMS).

Experimental

Representative procedure for the synthesis of compounds **6a–6i**.

Synthesis of **6a**:

(2R,3R,5R,6R)-Dimethoxy-5,6-dimethyl-[1,4]dioxane-2,3-dicarboxylic ester (5 g, 17.1 mmol) was dissolved in 30 mL THF. 1.0 M NaOH was added (37 mL) and the reaction stirred 12 h. The reaction was adjusted to pH = 4 with 6 M HCl and the solvent removed *in vacuo* yielding 6.42 g (excess mass is present due to NaCl salt) of a white solid. The diacid (375 mg, 1.42 mmol) was then dissolved in CH₂Cl₂ under N₂ atmosphere. Propargyl alcohol (183 mg, 3.27 mmol) was added along with EDC (600 mg, 3.12 mmol) and a catalytic amount of DMAP. The reaction stirred at room temperature for approx. 8 hours. After this time, the solvent was removed and the residue purified by silica gel chromatography yielding a colorless oil (250 mg, 52%). The diester (250 mg, 0.735 mmol) was dissolved in THF (5 mL) and cooled to 0°C. 0.2 M KOH (4.4 mL, 0.88 mmol) was added and the reaction was allowed to warm to room temperature over 4 hours. The solvent was removed *in vacuo* and the residue was filtered through a short plug of silica gel using EtOAc to remove unreacted diester (92 mg, 37%) along with propargyl alcohol and EtOAc/HOAc (10:1) to liberate the monoacid (136 mg, 61%). To the monoacid (136 mg, 0.45 mmol) in CH₂Cl₂ was added allyl alcohol (32 mg, 0.55 mmol), EDC (105 mg, 0.55 mmol), and a catalytic amount of DMAP. The reaction stirred at room temperature for 4 hours. The solvent was removed *in vacuo* and the

residue was purified by silica gel chromatography (Hex:EtOAc 5:1) yielding **6a** as a colorless oil (115 mg, 75%).

6a: ^1H NMR (300 MHz, CDCl_3) δ 5.94 (ddt, $J=16.4, 10.6, 6.0$ Hz, 1H), 5.31 (m, 2H), 4.74 (d, $J=2.5$ Hz, 2H), 4.66 (dd, $J=5.9, 1.3$ Hz, 2H), 4.56 (s, 2H), 3.33 (s, 6H), 2.50 (t, $J=2.6$ Hz, 1H), 1.36 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.67, 167.43, 131.60, 119.14, 99.41, 99.39, 77.01, 75.76, 68.76, 68.72, 66.34, 53.08, 48.66, 48.63, 17.49, 17.45; Mass calcd for $\text{C}_{16}\text{H}_{22}\text{O}_8$ (MNa^+): 365.1212 Found: 365.1221.

6b: ^1H NMR (300 MHz, CDCl_3) δ 5.95 (ddt, $J=17.2, 10.5, 5.8$ Hz, 1H), 5.37 (dq, $J=17.2, 1.5$ Hz, 1H), 5.26 (dq, $J=10.5, 1.5$ Hz, 1H), 4.70 (m, 4H), 4.55 (s, 2H), 3.33 (s, 6H), 1.85 (t, $J=2.4$, 3H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.75, 167.65, 131.66, 119.04, 99.42, 84.00, 72.65, 68.86, 68.82, 66.33, 54.04, 48.70, 48.64, 17.53, 17.51, 3.88; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1389.

6c: ^1H NMR (300 MHz, CDCl_3) δ 5.77 (ddt, $J=17, 10.2, 6.7$ Hz, 1H), 5.14 (m, 2H), 4.75 (d, $J=2.7$ Hz, 2H), 4.54, 4.53 (ab quart, $J=10.1$ Hz, 2H), 4.22 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.51 (t, $J=2.7$ Hz, 1H), 2.42 (bq, $J=6.9$ Hz, 2H), 1.36 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.90, 167.44, 133.65, 117.65, 99.38, 99.31, 77.04, 75.76, 68.72, 68.65, 64.76, 53.05, 48.65, 48.58, 32.91, 17.50, 17.45; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1375.

6d: ^1H NMR (300 MHz, CDCl_3) δ 5.81 (dq, $J=17.0, 10.1, 6.9$ Hz, 1H), 5.12 (dq, $J=17, 1.5$ Hz, 1H), 5.08 (dq, $J=10.1, 1.5$ Hz, 1H), 4.71 (q, $J=2.3$ Hz, 2H), 4.52 (s, 2H), 4.19 (m, 2H), 3.326 (s, 3H), 3.320 (s, 3H), 2.41 (qq, $J=6.9, 1.5$ Hz, 2H), 1.84 (t, $J=2.3$ Hz, 3H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.98, 167.68, 133.74, 117.64, 9.44, 99.42, 83.99, 72.74, 68.85, 64.77, 54.01, 48.68, 48.59, 32.95, 17.55, 3.87; Mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$ (MNa^+): 393.1525 Found: 393.1520.

6e: ^1H NMR (300 MHz, CDCl_3) δ 6.71 (bs, 1H), δ 5.79 (ddt, $J=16.9, 10.3, 6.6$ Hz, 1H), 5.09 (m, 2H), 4.57 (d, $J=10.0$ Hz, 1H), 4.30 (dt, $J=10.7, 7.0$ Hz, 1H), 4.23 (d, $J=10.0$ Hz, 1H), 4.19 (dt $J=10.7, 7.0$ Hz, 1H), 4.10 (dd, $J=5.8, 2.6$ Hz, 1H), 4.02 (dd, $J=5.2, 2.6$ Hz, 1H), 3.30 (s, 3H), 3.28 (s, 3H), 2.46 (q, $J=6.9$ Hz, 2H), 2.27 (t, $J=2.6$ Hz, 1 H), 1.37 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.85, 167.50, 133.98, 117.30, 99.79, 98.98, 79.15, 72.08, 70.27, 69.11, 64.68, 48.68, 48.53, 32.86, 28.76, 17.70, 17.49; Mass calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_7$ (MNa^+): 378.1529 Found: 378.1522.

6f: ^1H NMR (300 MHz, CDCl_3) δ 5.93 (ddt, $J=17.3, 10.5, 5.6$ Hz, 1H), 5.35 (dq, $J=17.3, 1.2$ Hz, 1H), 5.27 (dq, $J=10.5, 1.2$ Hz, 1H), 4.67 (dq, $J=5.6, 1.2$ Hz, 2H), 4.54, 4.53 (ab quart, $J=10.2$ Hz, 2H), 4.26 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.54 (td, $J=7.2, 2.9$ Hz, 2H), 1.99 (t, $J=2.7$ Hz, 1H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.90, 167.83,

131.63, 119.08, 99.42, 99.38, 79.66, 70.35, 68.80, 66.32, 63.20, 48.65, 48.64, 18.87, 17.51; Mass calcd for $C_{17}H_{24}O_8$ (MNa^+): 379.1369 Found: 379.1362.

6g: 1H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddt, $J=16.9, 10.1, 6.6$ Hz, 1H), 5.10 (m, 2H), δ 4.51 (s, 2H), 4.24 (m, 4H), 3.32 (s, 6H), 2.56 (td, $J=7.2, 2.9$ Hz, 2H), 2.44 (qt, $J=6.9, 1$ Hz, 2H), 2.00 (t, $J=2.4$ Hz, 1H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.03, 167.89, 133.60, 117.69, 99.34, 99.31, 79.56, 70.33, 68.73, 68.70, 64.72, 63.17, 48.55, 48.54, 32.92, 18.86, 17.48, 17.46; Mass calcd for $C_{18}H_{26}O_8$ (MNa^+): 393.1525 Found: 393.1513.

6h: 1H NMR (300 MHz, $CDCl_3$) δ 5.79 (ddt, $J=17.2, 10.2, 6.9$ Hz, 1H), 5.09 (m, 2H), 4.50 (s, 2H), 4.24 (m, 4H), 3.32 (s, 3H), 3.31 (s, 3H), 2.41 (qt, $J=6.8, 1.3$ Hz, 2H), 2.28 (td, $J=6.8, 2.6$ Hz, 2H), 1.96 (t, 2.6 Hz, 1H), 1.86 (t, $J=6.8$ Hz, 2H), 1.35 (bs, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.18, 168.14, 133.64, 117.74, 99.37, 83.07, 69.35, 68.77, 64.75, 64.24, 48.61, 48.60, 32.98, 27.58, 17.54, 15.31; Mass calcd for $C_{19}H_{28}O_8$ (MNa^+): 407.1682 Found: 407.1696.

6i: 1H NMR (300 MHz, $CDCl_3$) δ 5.80 (ddt, $J=16.9, 10.3, 6.6$ Hz, 1H), 5.08-4.95 (m, 2H), 4.50 (s, 2H), 4.27 (m, 2H), 4.17 (m, 2H), 3.33 (s, 6H), 2.28 (td, $J=6.8, 2.5$ Hz, 2H), 2.12 (bq, $J=7.3$ Hz, 2H), 1.96 (t, $J=2.5$ Hz, 1H), 1.88 (quint, $J=6.7$ Hz, 2H), 1.76 (quint, $J=7.0$ Hz, 2H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.24, 168.17, 137.48,

115.63, 99.38, 83.06, 69.37, 68.82, 68.80, 65.18, 64.23, 48.59, 48.58, 30.07, 27.77, 27.62, 17.54, 15.31; Mass calcd for $C_{20}H_{30}O_8$ (MNa^+): 421.1838 Found: 421.1833.

General Procedure for enyne metathesis

Enyne (30 mg) was dissolved in CH_2Cl_2 (100ml) in a 250 ml round bottom flask and nitrogen bubbled through the solution for 10 min. The flask was fitted with a reflux condenser and Grubbs catalyst was added in 1 ml of CH_2Cl_2 . The reaction was refluxed approx. 3h under N_2 . The solvent was then removed *in vacuo* and the crude material chromatographed.

7a: 1H NMR (300 MHz, $CDCl_3$) δ 6.32 (dd, $J=17.5, 11.0$ Hz, 1H), 5.88 (t, $J=5.4$ Hz, 1H), 5.32 (d, $J=17.5$ Hz, 1H), 5.18 (dd, $J=14.4, 6.6$ Hz, 1H), 5.16 (d, $J=11.0$ Hz, 2H), 4.59 (d, $J=11.0$ Hz, 1H), 4.57, 4.56 (ab quart, $J=9.5$ Hz, 2H), 4.45 (dd, $J=14.5, 4.4$ Hz, 1H), 3.25 (s, 6H), 1.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.21, 167.35, 138.24, 137.82, 128.78, 114.53, 100.25, 100.20, 69.866, 69.68, 61.38, 60.83, 48.65, 48.60, 17.66; Mass calcd for $C_{16}H_{22}O_8$ (MNa^+): 365.1212 Found: 365.1204.

7b: 1H NMR (300 MHz, $CDCl_3$) δ 5.98 (dd, $J=6.7, 4.2$ Hz, 1H), 5.15 (s, 1H), 5.14 (dd, $J=14.2, 6.7$ Hz, 1H), 5.07 (s, 1H), 5.05 (d, $J=12.3$ Hz, 1H), 4.64 (d, $J=12.3$ Hz, 1H), 4.58, 4.56 (ab q, $J=9.3$ Hz, 2H), 4.49 (dd, $J=14.2, 4.2$ Hz, 1H), 3.24 (s, 6H), 1.92 (s, 3H), 1.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.44, 137.15, 142.33, 140.83, 128.77, 127.86, 127.19, 125.32, 114.32, 100.34, 100.25, 69.81, 69.52, 65.61, 62.91, 61.53, 48.62, 48.59, 21.30, 17.65; Mass calcd for $C_{17}H_{24}O_8$ (MNa^+): 379.1369 Found: 379.1376.

7c: ^1H NMR (300 MHz, CDCl_3) δ 6.33 (dd, $J=17.2, 10.8$ Hz, 1H), 5.76 (dd, $J=11, 5.9$ Hz, 1H), 5.47 (d, $J=17.2$ Hz, 1H), 5.23 (d, $J=12.3$ Hz, 1H), 5.11 (d, $J=10.8$ Hz, 1H), 4.99 (bd, $J=11.0$ Hz, 1H), 4.57 (d, $J=9.7$ Hz, 1H), 4.43 (d, $J=9.7$ Hz, 1H), 4.41 (d, $J=12.3$ Hz, 1H), 3.76 (bt, $J=10.8$ Hz, 1H), 3.28 (s, 3H), 3.24 (s, 3H), 2.66 (m, 1H), 2.26 (m, 1H), 1.37 (s, 3H), 1.3 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.43, 137.64, 136.66, 133.81, 113.64, 99.76, 99.53, 69.81, 69.67, 63.06, 58.50, 48.63, 48.51, 28.74, 17.61, 17.58; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1354.

7d: ^1H NMR (300 MHz, CDCl_3) δ 5.84 (dd, $J=10.4, 6.7$ Hz, 1H), 5.30 (s, 1H), 5.29 (bd, $J=10.4$ Hz, 1H), 5.04 (s, 1H), 4.95 (bs, 1H), 4.56, 4.44 (abq, $J=9.8$ Hz, 2H), 4.49 (bd, $J=9.7$ Hz, 1H), 3.80 (t, $J=10.4$ Hz, 1H), 3.28 (s, 3H), 3.24 (s, 3H), 2.66 (bq, $J=9.7$ Hz, 1H), 2.31 (bs, 1H), 1.93 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.48, 167.46, 142.01, 138.41, 130.02, 113.75, 99.77, 99.64, 69.89, 69.72, 60.61, 48.65, 48.54, 34.43, 22.55, 17.60, 17.58, 14.28; Mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$ (MNa^+): 393.1525 Found: 393.1543.

8c: ^1H NMR (300 MHz, CDCl_3) δ 5.91 (d, $J=15.8$ Hz, 1H), 5.55 (ddd, $J=15.8, 8.7, 6.2$ Hz, 1H), 5.22 (d, $J=12.2$ Hz, 1H), 5.12 (s, 2H), δ 4.72 (dt, $J=10.8, 4.3$ Hz, 1H), 4.57 (d, $J=10.1$ Hz, 1H), 4.47 (d, $J=12.2$ Hz, 1H), 4.46 (d, $J=10.1$ Hz, 1H), 4.01 (ddd, $J=10.8, 5.5,$

2.4 Hz, 1H), 3.313 (s, 3H), 3.31 (s, 3H), 2.41 (m, 2H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.73, 167.34, 141.72, 131.17, 129.84, 116.82, 99.31, 99.15, 69.47, 69.26, 66.73, 63.45, 48.67, 48.63, 32.11, 17.56, 17.52; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1369.

8d: ^1H NMR (300 MHz, CDCl_3) δ 5.48 (ddd, $J=10.8, 3.5, 1.0$ Hz, 1H), 5.02 (ddd, $J=12.7, 10.4, 4.5$ Hz, 1H), 5.02 (s, 1H), 4.99 (d, $J=12.0$ Hz, 1H), 4.85 (d, $J=1.4$ Hz, 1H), 4.59 (d, $J=9.6$ Hz, 1H), 4.41 (d, $J=9.6$ Hz, 1H), 4.31 (dt, $J=12.0, 1.4$ Hz, 1H), 3.80 (dd, $J=10.4, 6.1$ Hz, 1H), 3.29 (s, 3H), 3.26 (s, 3H), 2.69 (dddd, $J=14.4, 12.7, 10.8, 6.1$ Hz, 1H), 2.34 (bd, $J=14.4$ Hz, 1H), 1.94 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.99, 167.78, 144.66, 141.79, 128.72, 116.89, 99.35, 70.94, 70.68, 65.45, 63.36, 48.60, 48.54, 28.49, 21.88, 17.61, 17.59; Mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$ (MNa^+): 393.1525 Found: 393.1518.

8e: ^1H NMR (300 MHz, CDCl_3) δ 5.91 (d, $J=15.9$ Hz, 1H), 5.92 (s, 1H), 5.82 (ddd, $J=15.9, 8.5, 5.2$ Hz, 1H), 5.04 (s, 1H), 5.00 (s, 1H), 4.44 (m, 1H), 4.41 (d, $J=9.3$ Hz, 1H), 4.34 (d, $J=9.3$ Hz, 1H), 4.23 (dd, $J=13.9, 6.3$ Hz, 1H), 4.01 (m, 1H), 3.99 (dd, $J=13.9, 5.4$ Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H), 2.39 (m, 2H), 1.32 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.43, 165.92, 143.99, 130.64, 129.65, 116.02, 99.54, 99.44, 72.19, 70.80, 63.75, 48.17, 48.11, 42.08, 31.29, 17.31, 17.27; Mass calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_7$ (MNa^+): 378.1529 Found: 378.1516.

trans-8f: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.36 (d, $J=15.9$ Hz, 1H), 5.82 (ddd, $J=15.9$, 8.6, 6.0, 1H), 5.02 (d, $J=11.4$ Hz, 2H), 4.82 (dd, $J=10.8$, 6.7 Hz, 1H), 4.65 (dd, $J=10.8$, 6.7 Hz, 1H), 4.59 (d, $J=9.8$ Hz, 1H), 4.41 (d, $J=9.8$ Hz, 1H), 4.19 (t, $J=4.4$ Hz, 2H), 3.31 (s, 3H), 3.28 (s, 3H), 2.67 (m, 1H), 2.49 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 167.38, 167.06, 144.76, 138.55, 125.15, 116.74, 99.84, 99.21, 70.81, 69.91, 67.82, 65.79, 48.77, 48.59, 33.39, 17.65, 17.56; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1356.

cis-8f: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.14 (d, $J=11.7$ Hz, 1H), 5.80 (ddd, $J=11.7$, 9.5, 6.2, 1H), 5.18 (dd, $J=11.4$, 9.9 Hz, 1H), 5.13 (s, 1H), 4.97 (s, 1H), 4.51, 4.41 (ab quar, $J=10.2$ Hz, 2H), 4.30 (dt, $J=11.5$, 5.0 Hz, 1H), 4.28 (dd, $J=11.4$, 3.1 Hz, 1H), 4.05 (dt, $J=11.4$, 4.2 Hz, 1H), 3.28 (s, 3H), 3.27 (s, 3H), 2.63-2.42 (m, 2H), 1.37 (s, 3H), 1.36 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 168.32, 167.45, 140.81, 138.28, 124.72, 116.83, 99.56, 99.24, 69.85, 69.46, 63.73, 60.00, 48.68, 48.65, 34.88, 17.63, 17.58; Mass calcd for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (MNa^+): 379.1369 Found: 379.1356.

8g: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 5.89 (d, $J=11.1$ Hz, 1H), 5.49 (dt, $J=11.1$, 7.0 Hz, 1H), 5.13 (s, 1H), 4.87 (s, 1H), 4.54 (d, $J=10.4$ Hz, 1H), 4.49 (m, 1H), 4.39 (dt, $J=11.1$, 3.1 Hz, 1H), 4.38 (d, $J=10.4$ Hz, 1H), 4.17 (dt, $J=11.1$, 3.1 Hz, 1H), 4.08 (m, 1H), 3.32 (s, 6H), 2.71 (m, 1H), 2.51 (m, 3H), 1.36 (s, 3H), 1.33 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 168.46, 167.78, 141.74, 131.98, 129.57, 116.75, 99.38, 98.95, 68.72, 68.52, 65.72, 65.19, 48.71, 35.65, 27.93, 17.56, 17.50; Mass calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$ (MNa^+): 393.1525 Found: 393.1534.

8h: *E/Z* mixture (2:1) ^1H NMR (300 MHz, CDCl_3) trans: δ 6.12 (d, $J=15.8$ Hz, 1H), 5.73 (ddd, $J=15.8, 8.1, 6.2$ Hz, 1H), 4.96 (s, 1H), 4.95 (s, 1H), 4.59, 4.48 (ab quart, $J=10.2$ Hz, 2H), 4.35-4.00 (m, 4H), 3.35 (s, 3H), 3.34 (s, 3H), 2.50-2.14 (m, 4H), 1.84 (m, 2H), 1.38 (s, 3H), 1.36 (s, 3H). cis: δ 5.96 (d, $J=11.3$ Hz, 1H), 5.42 (ddd, $J=11.3, 9.3, 5.5$ Hz, 1H), 5.03 (s, 1H), 4.87 (s, 1H), 4.52, 4.44 (ab quart, $J=11.2$ Hz, 2H), 4.35-4.00 (m, 4H), 3.32 (s, 3H), 3.30 (s, 3H), 2.50-2.14 (m, 4H), 1.84 (m, 2H), 1.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) trans: δ 168.15, 167.39, 145.70, 133.94, 126.71, 115.99, 99.47, 99.34, 69.30, 68.78, 65.31, 65.25, 48.68, 31.64, 29.08, 28.89, 17.58, 17.52. cis: δ 167.92, 167.68, 144.00, 133.21, 128.46, 115.94, 99.58, 99.27, 70.09, 69.00, 65.58, 64.20, 48.78, 48.61, 31.81, 28.29, 26.27, 17.61, 17.55; Mass calcd for $\text{C}_{19}\text{H}_{28}\text{O}_8$ (MNa^+): 407.1682 Found: 407.1690.

8i: *E/Z* mixture ^1H NMR (300 MHz, CDCl_3) trans: δ 6.08 (d, $J=15.7$ Hz, 1H), 5.75 (dt, $J=15.7, 7.2$ Hz, 1H), 4.92 (s, 2H), 4.55, 4.50 (ab quart, $J=10.3$, 2H), 4.40-4.18 (m, 4H), 3.34 (s, 3H), 3.33 (s, 3H), 2.17-2.09 (m, 4H), 1.98-1.90 (m, 4H), 1.36 (s, H). cis: δ 5.96 (d, $J=12.0$ Hz, 1H), 5.31 (dt, $J=12.0, 7.6$ Hz, 1H), 4.96 (s, 1H), 4.88 (s, 1H), 4.53, 4.49 (ab quart, $J=10.3$ Hz, 2H), 4.40-4.18 (m, 4H), 3.33 (s, 3H), 3.32 (s, 3H), 2.17-2.09 (m, 4H), 1.98-1.90 (m, 4H), 1.35 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 168.23, 168.20, 168.10, 167.90, 146.00, 145.65, 132.91, 131.71, 130.75, 129.90, 116.06, 115.12, 99.37, 99.32, 99.31, 99.25, 69.07, 68.95, 68.85, 68.64, 66.76, 65.62, 65.47, 65.15, 48.70, 32.76, 31.15, 31.00, 29.33, 29.02, 28.82, 27.27, 27.10, 25.57, 17.55; Mass calcd for $\text{C}_{20}\text{H}_{30}\text{O}_8$ (MNa^+): 421.1838 Found: 421.1839.

12: ^1H NMR (300 MHz, CDCl_3) δ 7.40 (dd, $J=8.0, 1.7$ Hz, 1H), 7.27 (td, $J=8.0, 1.7$ Hz, 1H), 6.88 (m, 2H), 5.74 (qt, $J=10.3, 6.6$ Hz, 1H), 5.09 (m, 2H), 5.01 (s, 2H), 4.55 (m, 3H), 4.21 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.38 (q, $J=6.6$ Hz, 2H), 1.37 (d, $J=6.1$ Hz, 6H), 1.37 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.85, 167.51, 159.23, 134.06, 133.56, 130.22, 120.73, 117.54, 115.05, 113.23, 111.42, 99.31, 99.30, 85.84, 84.08, 71.96, 68.78, 68.71, 64.68, 54.27, 48.56, 48.49, 32.82, 22.22, 17.45, 17.41; Mass calcd for $\text{C}_{26}\text{H}_{34}\text{O}_9$ (MNa^+): 513.2101 Found: 513.2114

7a:

7a:

7a: nOe

2.64

-100.00

7b:

7b:

7b: nOe

-100.00

2.00

3.03

7c:

7c: nOe

2.17

-100.00

0.76

7d:

7d:

7d: nOe

-100.00

3.40

8c:

8c:

8d:

8d:

8e:

8f: cis

8f: trans

8f: trans

8g:

8h:

8h:

8i:

8i: