Supporting Information

Mn(III)-BASED OXIDATIVE RADICAL RING-EXPANSION REACTION USING SQUARATE DERIVATIVES: SELECTIVE SYNTHESIS OF BIS(BUTANOLIDE)S AND THE ACETATE MONOMERS

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Table of Contents:

- 1. Spectral Data, and ¹H and ¹³C NMR Spectra of the Starting Materials **1a-l**: P.2–P.18.
- 2. ¹H and ¹³C NMR Spectra of the Bis(butenolide)s **2a-h**: P.19-P.34.
- 3. COSY Spectrum of *meso-2d*: P.25.
- 4. ¹H and ¹³C NMR Spectra of the Butenolide Monomers 3a, 3a', 3b, 3b', 3c', 3e, 3e', 3f, 3f', 3g and 3g': P.35-P. 44.
- 5. ¹H and ¹³C NMR Spectra of the Products **4i**, **5**, **6**, **4j**, **7**, **4k**, and **4l**: P.45-P.52.
- 6. HMQC Spectrum of 4j: P.49.
- 7. ¹H and ¹³C NMR Spectra of the Products **8i**, **8k**, **8l**, **9k**, **10k**, and **11k**: P.53-P.61.
- 8. HMQC Spectrum of 8k: P.55.
- 9. X-ray Crystal Structures of meso-2a, rac-2a, meso-2f, meso-2h, and 8i: P.62-68.

Spectral Data, and ¹H and ¹³C NMR spectra of the Starting Materials 1a-l.



4-Hydroxy-2,3-diisopropoxy-4-phenylcyclobut-2-en-1-one (1a)^{9a}: yellowish oil; IR (CHCl₃) v3400 (OH), 1775 (C=O), 1625 (>C=C<); ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.26 (5H, m, arom H), 4.94 (1H, sept, J = 6.1 Hz, >CH-O), 4.84 (1H, sept, J = 6.1 Hz, >CH-O), 3.83 (1H, s, OH), 1.39 (3H, d, J = 6.1 Hz, CH₃), 1.28 (3H, d, J = 6.1 Hz, CH₃), 1.26 (3H, d, J = 6.1 Hz, CH₃), 1.25 (3H, d, J = 6.1Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 184.1 (C-1), 166.0 (C-3), 137.7 (C-2), 133.2 (arom C), 128.5 (2C), 128.0, 125.9 (2C) (arom CH), 87.2 (C-4), 77.5, 73.7 (>CH-O), 22.7 (2C), 22.5, 22.3 (CH₃).







4-Hydroxy-2,3-dimethoxy-4-phenylcyclobut-2-en-1-one (1b): colorless microcryatals (from MnOH/jexane); mp 95-98 °C (lit,²² mp 96-98 °C); ¹H NMR (300 MHz, CDCl₃) δ 7.53-7.50 (2H, m, arom H), 7.40-7.31 (3H, m, arom H), 4.05 (3H, s, CH₃O), 4.00 (3H, s, CH₃O), 3.48 (1H, s, OH); ¹³C NMR (75 MHz, CDCl₃) δ 184.1 (C-1), 166.1 (C-3), 137.1 (C-2), 135.3 (arom C), 128.6 (2C), 128.4, 125.9 (2C) (arom CH), 87. 6 (C-4), 60.3, 58.7 (CH₃O).





2,3-Diethoxy-4-hydroxy-4-phenylcyclobut-2-en-1-one (1c)^{11a}: yellowish oil; ¹H NMR (300 MHz, CDCl₃) δ 7.54-7.32 (5H, m, arom H), 4.42 (2H, q, *J* = 6.0 Hz, CH₂O), 4.35 (2H, q, *J* = 6.0 Hz, CH₂O), 3.55 (1H, s, OH), 1.36 (3H, t, *J* = 6.0 Hz, CH₃), 1.33 (3H, t, *J* = 6.0 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 184.7 (C-1), 166.1 (C-3), 137.6 (C-2), 134.5 (arom C), 128.8 (2C), 128.4, 126.1 (2C) (arom CH), 87.6 (C-4), 66.9, 67.2 (<u>C</u>H₂-O), 15.6, 15.1 (CH₃).





i-PrO 0 *i*-PrO 0H 1e

4-Hydroxy-2,3-diisopropoxy-4-methylcyclobut-2-en-1-one (1e)^{9a}: $R_f = 0.35$ (7:3 Et₂O/hexane v/v); yield 72%; colorless solid; mp 35-36 °C; IR (CHCl₃) v 3370 (OH), 1766 (C=O), 1620 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 4.88 (2H, sept, J = 6.1 Hz, >CH-O ×2), 3.31 (1H, s, OH), 1.51 (3H, s, CH₃), 1.41 (3H, d, J = 6.1 Hz, CH₃), 1.40 (3H, d, J = 6.1 Hz, CH₃), 1.28 (3H, d, J = 6.1 Hz, CH₃), 1.26 (3H, d, J = 6.1 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 187.6 (C-1), 168.5 (C-2), 130.7 (C-3), 83.1 (C-4), 76.8, 73.2 (>CH-O), 22.7 (2C), 22.5, 22.4, 19.2 (CH₃).





4-Allyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1f): $R_f = 0.29$ (7:3 Et₂O/hexane v/v); yellow solid; mp 37-38 °C; IR (CHCl₃) *v* 3373 (OH), 1767 (C=O), 1620 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 5.86-5.72 (1H, m, -CH=), 5.17 (1H, d, *J* = 17.1 Hz, =C<u>H</u>_{trans}H_{cis}), 5.13 (1H, d, *J* = 10.7 Hz, =CH_{trans}<u>H</u>_{cis}), 4.88 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.86 (1H, sept, *J* = 6.1 Hz, >CH-O), 3.03 (1H, s, OH), 2.60 (2H, d, *J* = 6.4 Hz, -CH₂-), 1.40 (3H, d, *J* = 6.1 Hz, CH₃), 1.38 (3H, d, *J* = 6.1 Hz, CH₃), 1.28 (3H, d, *J* = 6.1 Hz, CH₃), 1.25 (3H, d, *J* = 6.1 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 186.5 (C-1), 167.3 (C-3), 132.4 (-CH=), 131.9 (C-2), 119.5 (=CH₂), 85.3 (C-4), 77.1, 73.5 (>CH-O), 37.8 (-CH₂-), 22.74, 22.72, 22.6, 22.4 (CH₃).







4-Butyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (1g)^{9a}: $R_f = 0.15$ (CHCl₃); yield 83%; yellow oil; IR (CHCl₃) v 3370 (OH), 1765 (C=O), 1616 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 4.89 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 3.62 (1H, s, OH), 1.88-1.75 (2H, m, -CH₂-), 1.41 (6H, d, J = 6.1 Hz, CH₃ ×2), 1.27 (3H, d, J = 6.1 Hz, CH₃), 1.26 (3H, d, J = 6.1 Hz, CH₃), 1.39-1.28 (4H, m, -CH₂- ×2), 0.89 (3H, t, J = 6.9 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 187.8 (C-1), 168.1 (C-3), 131.8 (C-2), 86.4 (C-4), 76.99, 73.4 (>CH-O), 32.4, 27.2, 22.9 (-CH₂-), 22.7 (2C), 22.6, 22.4, 13.95 (CH₃).





2-Hydroxy-2-phenylbenzocyclobuten-1(*2H*)-one (1h)¹⁸: R_f = 0.09 (CHCl₃); colorless microcrystals (from CHCl₃/hexane); mp 102-103 °C; IR (KBr) *v* 3400-3200 (OH), 1760 (>C=O); ¹H NMR (300 MHz, CDCl₃) δ 7.79-7.73 (1H, m, arom H), 7.70-7.54 (3H, m, arom H), 7.43-7.30 (5H, m, arom H), 3.63 (1H, s, OH); ¹³C NMR (75 MHz, CDCl₃) δ 191.9 (>C=O), 159.8, 148.3, 138.7 (arom C), 136.7, 131.8, 128.8, 128.6, 126.3, 123.7, 122.7 (arom CH), 96.8 (C-OH).







4-Hydroxy-2,3-diisopropoxy-4-vinylcyclobut-2-en-1-one (1i)²⁵: $R_f = 0.47$ (7:3 Et₂O/hexane v/v); yield 60%; yellow oil; IR (CHCl₃) v 3375 (OH), 1768 (C=O), 1619 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 5.97 (1H, dd, J = 17.3, 10.7 Hz, -CH=), 5.53 (1H, dd, J = 17.3, 0.9 Hz, =C<u>H</u>_{trans}H_{cis}), 5.34 (1H, dd, J = 10.7, 0.9 Hz, =CH_{trans}<u>H</u>_{cis}), 4.95-4.80 (2H, m, >CH-O), 3.90 (1H, s, OH), 1.40 (3H, d, J = 6.1 Hz, CH₃), 1.38 (3H, d, J = 6.1 Hz, CH₃), 1.30 (3H, d, J = 6.1 Hz, CH₃), 1.28 (3H, d, J = 6.1 Hz, CCl₃) δ 185.2 (C-1), 166.9 (C-3), 135.0 (-CH=), 132.5 (C-2), 118.2 (=CH₂), 86.7 (C-4), 77.5, 73.7 (>CH-O), 22.7, 22.69, 22.55, 22.5 (CH₃).





(*E*)-4-Hydroxy-2,3-diisopropoxy-4-styrylcyclobut-2-en-1-one (1j): $R_f = 0.55$ (7:3 Et₂O/hexane v/v); yellow solid; mp 83-85 °C; IR (CHCl₃) v 3362 (OH), 1767 (C=O), 1618 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.33 (2H, m, arom H), 7.29-7.21 (3H, m, arom H), 6.83 (1H, d, *J* = 16.2 Hz, -CH=), 6.29 (1H, d, *J* = 16.2 Hz, -CH=), 4.89 (2H, sept, *J* = 6.1 Hz, >CH-O ×2), 4.05 (1H, s, OH), 1.40 (3H, d, *J* = 6.1 Hz, CH₃), 1.37 (3H, d, *J* = 6.1 Hz, CH₃), 1.30 (3H, d, *J* = 6.1 Hz, CH₃), 1.29 (3H, d, *J* = 6.1 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 185.4 (C-1), 167.4 (C-3), 136.5 (C-2), 132.8 (-CH=), 132.5 (arom C), 128.7 (2C) (arom CH), 128.1 (arom CH), 126.9 (2C) (arom CH), 126.1 (-CH=), 86.6 (C-4), 77.7, 73.8 (>CH-O), 22.7 (2C), 22.6, 22.4 (CH₃).





i-PrO 1 O 3 4 Pr *i*-PrO OH 1k

4-Hydroxy-2,3-diisopropoxy-4-(phenylethynyl)cyclobut-2-en-1-one (1k)^{9a}: $R_f = 0.49$ (7:3 Et₂O/hexane v/v); yellow microcrystals (from Et₂O-hexane); mp 104-105 °C (lit,^{5b} mp 73-7 °C from CH₂Cl₂-hexane); IR (CHCl₃) v 3306 (OH), 2226 (C=C), 1774 (C=O), 1626 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 7.44-7.41 (2H, m, arom H), 7.30-7.22 (3H, m, arom H), 5.07 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 4.43 (1H, s, OH), 1.46 (3H, d, J = 6.1 Hz, CH₃), 1.44 (3H, d, J = 6.1 Hz, CH₃), 1.28 (6H, d, J = 6.1 Hz, CH₃ ×2); ¹³C NMR (75 MHz, CDCl₃) δ 181.6 (C-1), 165.2 (C-3), 133.9 (C-2), 132.1 (2C), 128.9, 128.4 (2C) (arom CH), 122.2 (arom C), 88.5 (C-4), 83.9 (C=C), 78.9 (C=C), 78.2, 74.2 (>CH-O), 22.74, 22.72, 22.68, 22.55 (CH₃).





4-(Hex-1-yn-1-yl)-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (**11**)^{9a}: $R_f = 0.20$ (CHCl₃); yield 98%; colorless oil; IR (CHCl₃) *v* 3342 (OH), 2233 (C=C), 1774 (C=O), 1614 (>C=C<); ¹H NMR (300 MHz, CDCl₃) δ 5.02 (1H, sept, J = 6.1 Hz, >CH-O), 4.85 (1H, sept, J = 6.1 Hz, >CH-O), 3.82 (1H, s, OH), 2.25 (2H, t, J = 7.0 Hz, -CH₂-), 1.55-1.33 (4H, m, -CH₂- ×2), 1.44 (3H, d, J = 6.1 Hz, CH₃), 1.43 (3H, d, J = 6.1 Hz, CH₃), 1.30 (3H, d, J = 6.1 Hz, CH₃), 1.28 (3H, d, J = 6.1 Hz, CH₃), 0.90 (3H, t, J = 7.0 Hz, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 182.1 (C-1), 165.5 (C-3), 133.7 (C-2), 89.9 (C-4), 78.7 (C=C), 77.9 (>CH-O), 75.0 (C=C), 74.0 (>CH-O), 30.4 (-CH₂-), 22.73 (2C), 22.71, 22.6 (CH₃), 22.0, 18.7 (-CH₂-), 13.6 (CH₃).







meso-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2H,2'H)-dione (meso-2a):



rac-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2a):



meso-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2H,2'H)-dione (meso-2b):



rac-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2H,2'H)-dione (rac-2b):



meso-3,3',4,4'-Tetraethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2c):



meso-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2d):







rac-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2d):



meso-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2e):



rac-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2H,2'H)-dione (rac-2e):



meso-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2f):



rac-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2f):



meso-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2H,2'H)-dione (meso-2g):



rac-2,2'-dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2H,2'H)-dione (*rac*-2g):



meso-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*meso*-2h):



rac-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*rac*-2h)¹⁹:



3,4-Diisopropoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3a):



5-Hydroxy-3,4-diisopropoxy-5-phenylfuran-2(5*H*)-one (3a'):

A Mixture of 3,4-Dimethoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3b) and 5-Hydroxy-3,4-dimethoxy-5-phenylfuran-2(5*H*)-one (3b')^{11a,11c,22}:



3,4-Diethoxy-5-hydroxy-5-phenylfuran-2(5*H***)-one (3c')**^{11a,11c}:





3,4-Diisopropoxy-2-methyl-5-oxo-2,5-dihydrofuran-2-yl acetate (3e):

5-Hydroxy-3,4-diisopropoxy-5-methylfuran-2(5H)-one (3e'):

2-Allyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3f):

5-Allyl-5-hydroxy-3,4-diisopropoxyfuran-2(5*H*)-one (3f'):

2-Butyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3g):

5-Butyl-5-hydroxy-3,4-diisopropoxyfuran-2(5H)-one (3g'):

-75 5.64 5.55 5.55 5.55 5.51 5.55 5.51 5.55 5.51 5.55 5.51 5.55 5.51 5.55 5.51 5.51 5.51 5.51 5.51 5.51 5.51 5.55 5.51 5.55 5 2772 2772 2772 2772 2772 140 136 136 136 136 106 -70 *i*-PrO_5__(1_____ OEt -65 -60 **1**/3 *i*-PrO⁴ 4i -55 5 -50 -45 -40 -35 -30 -25 -20 -15 -10 -5 <u>ki</u> -0 111 ٣ Τť 35.79-J ٣ H 4.60 - 11.0 --5 2.56 3.98 2.00 9.0 8.5 7.5 5.5 5.0 4.5 f1 (ppm) 3.0 2.0 1.5 0.5 0.0 9.5 8.0 7.0 6.5 6.0 4.0 3.5 2.5 1.0

2-(Ethoxymethyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4i):

2,3-Diisopropoxycyclohexa-2,5-diene-1,4-dione (5)³⁰:

6.46 6.45 6.45 3.16 3.11 3.11 2.75 2.75 2.75 134 132 132 130 0.00 -90 -85 O 此 O*i*-Pr -80 *i*-PrO、 -75 ⁽⁴⁾O*i*−Pr -70 i-PrO ₩ 0 $\hat{\mathbf{O}}$ 6 -65 / 1 1 1 -60 -55 -50 -45 -40 -35 -30 -25 -20 -15 -10 -5 A. -0 T ٣ T -----T 27.97-I --5 2.49 2.07 00 2.29 1.04 5.0 4.5 f1 (ppm) 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -193.69 184.87 _150.37 _146.07 _145.85 ~144.14 -132.42 8 -36 76.74 76.74 76.74 76.21 76.12 -48.02 22.96 -34 -32 の此 -30 *Oi*-Pr Ο, *i*-PrO (2) **(**(3) -28 ⁽⁴⁾O*i*-Pr -26 1(5) i-PrO² 3 ¥ Ò 6 -24 0 -22 -20 -18 -16 -14 -12 -10 -8 -6 -4 -2 hadalaharalan hadranan hanan dina laharan di kuran hadan pendari "Pengebilan kahadahan kelaperan dalampaha perk Addition -0 --2 100 f1 (ppm) 0 190 180 170 160 150 140 130 120 110 90 80 70 60 50 40 30 20 10

5-((3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-yl)methyl)-2,3-diisopropoxycyclohexa-2,5-diene-1,4-dione (6):

0.00 -70 8.20 8.19 8.17 7.44 7.43 7.43 <1.40 -65 0 i-PrO -60 -55 Ph i-PrO 0 4j li -50 ſ -45 -40 -35 -30 -25 -20 -15 -10 -5 -0 2:00 T 74 12.22-87 88 --5 5.5 5.0 4.5 f1 (ppm) 0.0 .0 1.5 9.5 9.0 8.5 8.0 7.5 6.5 6.0 4.0 3.5 3.0 2.5 2.0 0.5 7.0 1.0 ~186.96 ∠137.18 ∠133.27 ∠133.03 √131.65 √128.70 ~128.70 77.16 76.74 76.74 75.02 74.91 -23.09 --0.00 -55 -50 0 *i*-PrO -45 (³ *i*-PrO Ρh -40 4j -35 -30 -25 -20 -15 -10 -5 wanelighamena waa hay haladaaa kumaadaan iyo aana daan ka may ka madaan waxaa maana kumaa ka aa ka aa ka aa ka m International States and the second states and the delikitetie --5 180 140 100 f1 (ppm) 10 0)0 190 170 160 150 130 120 110 90 80 70 60 50 40 30 20

2-Benzylidene-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4j):

(*E*)-3-Isopropoxy-4-styrylcyclobut-3-ene-1,2-dione (7)³¹:

(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)(phenyl)methyl acetate (4k):

5.48 5.48 5.44 5.42 5.42 5.38 5.38 2.286 2.231 1.159 1.159 1.151 1.151 1.151 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.140 1.125 1.155 -90 -85 С i-PrO 5 QAc -80 -75 i-PrO Bu зĨ -70 O 41 -65 ſ 5 -60 -55 -50 -45 -40 -35 -30 -25 -20 -15 -10 -5 -0 --٣ ٣ 4 2.40 ---5 2.00 1.82 2.74 54 0.0 8.0 7.5 6.0 5.5 5.0 f1 (ppm) 3.5 2.0 1.0 0.5 9.5 9.0 8.5 7.0 6.5 4.5 4.0 3.0 2.5 1.5 0.00 <149.60 -40 ~185.65 -168.01 -161.23 -115.86 77.60 -77.17 -76.75 -76.75 -74.85 -31.64 -28.40 -23.05 -23.05 -22.49 -13.82 -35 i-PrO_5 OAc -30 Ъu *i*-PrO Tد O 41 -25 -20 -15 -10 -5 human huma huma huma human human

1-(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)pentyl acetate (4l):

90

80

70

60

50

40

30

20

0

10

100 f1 (ppm)

00 190

180

170

160

150

140

130

120

110

2-(3,3-diphenylallyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8i):

4,5-Diisopropoxy-2-(1,3,3-triphenylallylidene)cyclopent-4-ene-1,3-dione (8k):

2-(1,1-Diphenylhept-1-en-3-ylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8l):

(*E*)-2-(1,3-Diphenylallylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (9k):

An equilibrium mixture of 2-(3-hydroxy-1,3-diphenylpropylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione and 7a-hydroxy-6,7-diisopropoxy-2,4-diphenyl-3,7adihydrocyclopenta[b]pyran-5(2H)-one (10k):

D₂O Exchange Experiment of 10k:

7-Isopropoxy-2,4-diphenyl-2,3-dihydrocyclopenta[b]pyran-5,6-dione (11k):

X-ray Crystal Structure of meso-2a:

X-ray Crystal Structure of *rac*-2a:

X-ray Crystal Structure of meso-2f:

X-ray Crystal Structure of meso-2h:

X-ray Crystal Structure of 8i:

