Ruthenium-Catalyzed Tandem Olefin Metathesis-Oxidations

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General Information

All chemicals were purchased from established commercial suppliers. Tetrahydrofuran (THF), diethyl ether (Et₂O), and dichloromethane (CH₂Cl₂) were dried on alumina columns using a solvent dispensing system.* Hexane used in chromatography was distilled prior to use. Acetonitrile (MeCN) was dried over CaH₂ and freshly distilled before its use. All reactions were conducted in oven (135 °C) or flame-dried glassware under an inert atmosphere of dry nitrogen. Evaporation refers to removal of solvent under reduced pressure on a rotary evaporator. Analytical TLC was performed on glass plates (5 × 1.5 cm) pre-coated (0.25 mm) with silica gel (EM Science, Kieselgel 60 F₂₅₄). Compounds were visualized by exposure to UV light or by staining with a 1% Ce(SO₄)₂·4H₂O 2.5% (NH₄)Mo₇O₂₄·4H₂O in 10% H₂SO₄ followed by heating on a hot plate. Flash column chromatography was performed with silica gel (60, 230–400 mesh). Vinylcyclohexane (**22**), styrene (**27**), methylacrylate (**23**), methyl methacrylate (**29**) and octan-1-ol (**52**) were used following distillation.

Infrared (IR) spectra were recorded on a Nicolet Avatar 360 spectrophotometer or a Mattson Galaxy Series FTIR 5000. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). ¹H-NMR spectra were recorded on a Varian Unity 300 (300 MHz), Varian Gemini 400 (400 MHz) or Varian Inova 500 (500 MHz). Chemical shifts are reported with the solvent as the internal standard (CHCl₃ δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ¹³C-NMR spectra were recorded on a Varian Gemini 400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the solvent as an internal reference (CDCl₃ δ 77.2 ppm). A Hewlett Packard HP 6890 Series II Gas Chromatograph was used for all reactions monitored by GC utilizing a Zebron ZB-1 100 % methyl polysiloxane column. High-resolution mass spectral analyses (HRMS) were performed on a Micromass LCT electrospray mass spectrometer with a TOF analyzer or by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign.

(A) General procedure for tandem ring-closing metathesis/α-ketohydroxylation

To a stirring solution of the diene (1 equiv) in EtOAc (1.2 mL) was added Grubbs' II catalyst **2** (0.05 equiv) and the resulting reaction mixture was stirred at room temperature for 90 min., or the reaction was judged to be complete by TLC or GC/MS analysis. The suspension was diluted with MeCN (1.2 mL) and H₂O (0.2 mL) and cooled to 0 °C. To the solution was added NaHCO₃ (2.5 equiv) and Oxone[®] (5.0 equiv). After stirring, until the oxidation was judged complete (≤ 1 h), the resulting mixture was diluted with EtOAc (2.0 mL) and filtered. The filtrate was washed with a saturated solution of Na₂SO₃ (3 mL) and dried over Na₂SO₄. Filtration and concentration *in vacuo* gave an amber oil. Purification by flash chromatography afforded the acyloin.

(B) General procedure for tandem cross-metathesis/α-ketohydroxylation

To a stirring solution of the starting olefin (1 equiv) in CH₂Cl₂ (0.15-0.25 M) was added cross-metathesis partner (2 equiv) and Grubbs' catalyst **2** (0.05 equiv) and the resulting reaction mixture was stirred at reflux until analysis by TLC or GC indicated that the starting olefin was consumed. The suspension was allowed to cool to room temperature and concentrated *in vacuo* to remove solvent and excess cross-metathesis partner. Residue was dissolved in MeCN (3 mL), EtOAc (3 mL) and H₂O (0.5 mL) and cooled to 0 °C. To the solution was added NaHCO₃ (2.5

* Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518.

equiv) and Oxone[®] (5.0 equiv). After stirring at 0 °C until the oxidation was complete the mixture was diluted with EtOAc (2.0 mL) and filtered. The filtrate was washed with a saturated solution of Na₂SO₃ (3 mL) and dried over Na₂SO₄. Filtration and concentration *in vacuo* gave an amber oil. Purification by flash chromatography afforded the acyloin.

(C) General procedure for tandem ring-closing metathesis/dihydroxylation

To a stirring solution of the diene (1 equiv) in EtOAc (3 mL) was added Grubbs' catalyst **2** (0.05 equiv) and the resulting reaction mixture was stirred at room temperature for 90 min. or the reaction was judged to be complete by TLC or GC/MS analysis. In another flask, a suspension of NaIO₄ (1.5 equiv) in H₂O (0.3 mL) was treated with CeCl₃·7H₂O (0.1 equiv) and heated gently until suspension was bright yellow, at this point the suspension was diluted with MeCN (3 mL) and cooled to 0 °C. To the yellow suspension was then added metathesis solution and stirred at 0 °C until oxidation was complete (10-20 min.). The reaction was quenched with the addition of solid Na₂SO₃ and Na₂SO₄ and after stirring for 10 min., the solution was filtered through Celite (1 cm plug). The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography to give the diol.

(D) General procedure for tandem cross-metathesis/dihydroxylation

To a stirring solution of starting olefin (1 equiv) in CH₂Cl₂ (0.15-0.25 M) was added the cross-metathesis partner (2 equiv) and Grubbs' catalyst **2** (0.05 equiv) and the resulting reaction mixture was stirred at reflux until analysis by TLC or GC/MS indicated that the starting olefin was consumed. The suspension was cooled to room temperature and concentrated *in vacuo* to remove solvent and excess cross-metathesis partner. In another flask, a suspension of NaIO₄ (1.5 equiv) in H₂O (0.3 mL) was treated with CeCl₃·7H₂O (0.1 equiv) and heated gently until the reaction was bright yellow, at this point the suspension was diluted with MeCN (3 mL) and cooled to 0 °C. To this yellow suspension was then added the metathesis solution (in 3 mL of EtOAc) and stirred at 0 °C until the oxidation was complete (10-20 min.). The reaction was quenched with the addition of solid Na₂SO₃ and Na₂SO₄ and after stirring for 10 min., the solution was filtered through Celite (1 cm plug). The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography to give the diol.

5-Hydroxy-1-(toluene-4-sulfonyl)-azepan-4-one (**7**).

General procedure **A** was followed. *N,N*-Di-but-3-enyl-4-methyl-benzenesulfonamide (**6**) (20 mg, 0.072 mmol), Grubbs' catalyst **2** (3.0 mg, 0.0036 mmol), NaHCO₃ (15.0 mg, 0.18 mmol) and Oxone[®] (220 mg, 0.36 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compound **7** as a white solid (12.3 mg, 61%). **mp** 113-114 °C; **IR** (thin film, NaCl) 3471, 2924, 1711, 1333, 1158, 1092, 908, 883, 868, 713, 697 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 7.66 (2H, d, *J* = 8.4 Hz), 7.32 (2H, d, *J* = 8.4 Hz), 4.31 (1H, dt, *J* = 11.2, 3.6 Hz), 3.86-3.81 (2H, m), 3.77 (1H, d, *J* = 4.4 Hz), 3.06-2.95 (2H, m), 2.89 (1H, ddd, *J* = 18.0, 10.8, 3.6 Hz), 2.71 (1H, ddd, *J* = 18.0, 5.2, 2.4 Hz), 2.43 (3H, s), 2.16-2.10 (1H, m), 1.87-1.77 (1H, m). **¹³C-NMR** (100 MHz, CDCl₃) δ 209.6, 143.7, 129.8,

126.9, 94.3, 76.1, 47.5, 43.6, 41.3, 34.3, 21.6; **HRMS** (EI) Calc'd for $[M]^+$ $C_{13}H_{17}NO_4S$ 283.0878, found 283.0889.

4-Hydroxy-5-oxo-cycloheptane-1,1-dicarboxylic acid diethyl ester (**9**).

General procedure **A** was followed. 2,2-Di-*tert*-butyl-3,6-dimethyl-malononic acid diethyl ester (**8**) (30 mg, 0.11 mmol), Grubbs' catalyst **2** (4.8 mg, 0.056 mmol), NaHCO₃ (24 mg, 0.28 mmol) and Oxone[®] (344 mg, 0.56 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 4:1) provided compound **9** as a colorless oil (18 mg, 60%). **IR** (thin film, NaCl) 3473, 2981, 1729, 1452, 1297, 1240, 1182, 1095, 1065, 1041 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.27 (1H, dd, J = 8.8, 4.0 Hz), 4.24-4.12 (4H, m), 3.76 (1H, bs), 2.77 (1H, ddd, J = 16.8, 8.4, 2.4 Hz), 2.51 (1H, ddd, J = 17.2, 11.2, 2.8 Hz), 2.37-2.30 (2H, m), 2.20 (1H, dddd, J = 15.2, 8.4, 2.8, 0.8 Hz), 2.09-2.01 (2H, m), 1.94-1.84 (1H, m), 1.27-1.21 (6H, m). **¹³C-NMR** (100 MHz, CDCl₃) δ 211.3, 171.2, 170.1, 76.4, 61.7, 61.6, 57.0, 35.4, 30.7, 28.9, 28.2, 14.1; **HRMS** (EI) Calc'd for $[M]^+$ $C_{13}H_{20}O_6$ 272.1260, found 272.1259.

4-Hydroxy-3-oxo-cyclohexane-1,1-dicarboxylic acid diethyl ester (**11a**) and 3-Hydroxy-4-oxo-cyclohexane-1,1-dicarboxylic acid diethyl ester (**11b**).

General procedure **A** was followed. 2-Allyl-2-*tert*-butyl-3-enyl-malononic acid diethyl ester (**10**) (40 mg, 0.16 mmol), Grubbs' catalyst **2** (6.7 mg, 0.0079 mmol), NaHCO₃ (33 mg, 0.39 mmol) and Oxone[®] (484 mg, 0.79 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided two regioisomers, compounds **11a** (12.5 mg, 31%) and **11b** (8 mg, 20%) as colorless oils. Data for **11a**: **IR** (thin film, NaCl) 3487, 2982, 1731, 1448, 1368, 1299, 1252, 1086, 1024, 870 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.25-4.16 (4H, m), 4.09 (1H, ddd, J = 12.0, 6.8, 1.2 Hz), 3.58 (1H, bs), 3.18 (1H, dd, J = 14.8, 3.2 Hz), 2.60 (1H, dd, J = 14.8, 1.6 Hz), 2.49 (1H, ddd, J = 14.4, 6.4, 3.2 Hz), 2.44-2.37 (1H, ddd, J = 14.4, 6.8, 3.2 Hz), 2.23 (1H, dt, J = 14.4, 3.6 Hz), 1.64-1.53 (1H, m), 1.26 (3H, t, J = 6.8 Hz), 1.24 (3H, t, J = 6.8 Hz); **¹³C-NMR** (100 MHz, CDCl₃) δ 206.4, 169.5, 74.2, 62.2, 57.7, 43.3, 31.0, 28.8, 14.1; **HRMS** (ESI) Calc'd for $[M+H]^+$ $C_{12}H_{19}O_6$ 259.1182, found 259.1176.

Data for **11b**: **IR** (thin film, NaCl) 3481, 2982, 1731, 1446, 1368, 1297, 1241, 1212, 1181, 1099, 1065, 1024, 859 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.33-4.22 (2H, m), 4.21-4.16 (3H, m), 3.55 (1H, d, J = 3.2 Hz), 3.03 (1H, ddd, J = 13.2, 6.4, 3.2 Hz), 2.73-2.52 (3H, m), 2.08 (1H, dd, J = 13.6, 8.4 Hz), 1.94 (1H, dd, J = 13.2, 12.4 Hz), 1.31 (3H, t, J = 3.2 Hz), 1.25 (3H, t, J = 6.8 Hz); **¹³C-NMR** (100 MHz, CDCl₃) δ 209.2, 169.7, 71.6, 62.1, 40.1, 35.7, 31.9, 14.2, 14.1; **HRMS** (ESI) Calc'd for $[M+H]^+$ $C_{12}H_{19}O_6$ 259.1182, found 259.1176.

3-Hydroxy-4-oxo-cyclopentane-1,1-dicarboxylic acid diethyl ester (13).

General procedure **A** was followed. 2,2-Diallyl-malonic acid diethyl ester (**12**) (20 mg, 0.083 mmol), Grubbs' catalyst **2** (3.5 mg, 0.0042 mmol), NaHCO₃ (17.5 mg, 0.21 mmol) and Oxone[®] (256 mg, 0.42 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compound **13** as a colorless oil (9.3 mg, 46%). **IR** (thin film, NaCl) 3480, 2984, 1755, 1731, 1393, 1299, 1268, 1249, 1179, 1156, 1097, 859 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.30-4.21 (5H, m), 3.05-2.99 (2H, m), 2.85 (1H, d, *J* = 20.0 Hz), 2.85 (1H, bs), 2.16 (1H, dd, *J* = 13.6, 11.6 Hz), 1.27 (3H, t, *J* = 7.2 Hz), 1.27 (3H, t, *J* = 7.2 Hz). **¹³C-NMR** (100 MHz, CDCl₃) δ 212.7, 170.6, 169.9, 73.8, 62.5, 62.4, 52.3, 41.5, 37.2, 14.1; **HRMS** (EI) Calc'd for [M]⁺ C₁₁H₁₆O₆ 244.0947, found 244.0944.

3-Hydroxy-3-methyl-4-oxo-cyclopentane-1,1-dicarboxylic acid diethyl ester (15).

General procedure **A** was followed. 2-Allyl-2-(2-methyl-allyl)-malonic acid diethyl ester (**14**) (20 mg, 0.079 mmol), Grubbs' catalyst **2** (6.7 mg, 0.0079 mmol), NaHCO₃ (16.5 mg, 0.20 mmol) and Oxone[®] (242 mg, 0.39 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 3:1) provided compound **15** as a pale yellow oil (10.4 mg, 51%). **IR** (thin film, NaCl) 3481, 2983, 1748, 1732, 1392, 1369, 1298, 1252, 1187, 1130, 1096, 1063, 864 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.23 (4H, q, *J* = 7.2 Hz), 3.11 (1H, dd, *J* = 19.6, 1.6 Hz), 2.92 (1H, dd, *J* = 19.2, 2.0 Hz), 2.74 (1H, dd, *J* = 14.8, 1.6 Hz), 2.68 (1H, bs), 2.50 (1H, d, *J* = 14.8 Hz), 1.29 (3H, s), 1.27 (3H, t, *J* = 7.2 Hz), 1.26 (3H, t, *J* = 7.2 Hz); **¹³C-NMR** (100 MHz, CDCl₃) δ 213.4, 171.1, 170.5, 75.9, 62.5, 62.3, 53.5, 43.9, 42.5, 23.1, 14.1, 14.1; **HRMS** (ESI) Calc'd for [M+H]⁺ C₁₂H₁₉O₆ 259.1182, found 259.1176.

3-Hydroxy-4-oxo-cyclopentane-1,1,3-tricarboxylic acid diethyl ester methyl ester (17).

General procedure **A** was followed. 2-Allyl-2-ethoxycarbonyl-4-methylene-pentanedioic acid 1-ethyl ester 5-methyl ester (**16**) (30 mg, 0.10 mmol), Grubbs' catalyst **2** (8.5 mg, 0.10 mmol), NaHCO₃ (21.1 mg, 0.25 mmol) and Oxone[®] (309 mg, 0.50 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:1) provided compound **17** as a colorless oil (16 mg, 53%). **IR** (thin film, NaCl) 3468, 2986, 1767, 1736, 1443, 1369, 1266, 1187, 1008, 860 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 4.27-4.19 (4H, m), 3.77 (4H, s), 3.21 (1H, dd, *J* = 18.8, 2.0 Hz), 3.14 (1H, d, *J* = 14.8 Hz), 2.94 (1H, d, *J* = 19.2 Hz), 2.77 (1H, dd, *J* = 14.8, 2.0 Hz), 1.26 (3H, t, *J* = 7.2 Hz), 1.25 (3H, t, *J* = 7.2 Hz); **¹³C-NMR** (100 MHz, CDCl₃) δ 207.4, 170.5, 169.9, 169.6, 79.6, 62.5, 62.4, 54.1, 53.4, 43.0, 41.1, 14.1, 14.0; **HRMS** (ESI) Calc'd for [M+H]⁺ C₁₃H₁₉O₈ 303.1080, found 303.1181.

3-Hydroxy-4-oxo-3-phenyl-cyclopentane-1,1-dicarboxylic acid diethyl ester (**19**).

General procedure **A** was followed. Allyl-2-(2-phenyl-allyl)-malonic acid diethyl ester (**18**) (45 mg, 0.14 mmol), Grubbs' catalyst **2** (12.1 mg, 0.014 mmol), NaHCO₃ (30 mg, 0.36 mmol) and Oxone[®] (437 mg, 0.72 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compound **19** as a pale yellow oil (19.1 mg, 42%). **IR** (thin film, NaCl) 3461, 2988, 1748, 1732, 1448, 1368, 1298, 1253, 1187, 1062, 871, 764, 701 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 7.37-7.28 (5H, m), 4.30-4.24 (2H, m), 4.13-4.05 (2H, m), 3.27 (1H, dd, *J* = 19.2, 2.0 Hz), 3.21 (1H, bs), 3.07 (1H, d, *J* = 19.2 Hz), 3.02 (1H, dd, *J* = 14.8, 1.6 Hz), 2.94 (1H, d, *J* = 14.8 Hz), 1.27 (3H, t, *J* = 7.2 Hz), 1.19 (3H, t, *J* = 7.2 Hz); **¹³C-NMR** (100 MHz, CDCl₃) δ 212.2, 170.9, 170.0, 139.7, 128.4, 128.1, 125.7, 80.1, 62.5, 62.3, 53.7, 45.6, 43.9, 14.1, 14.0; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₇H₂₀O₆Na 343.1158, found 343.1148.

2-Hydroxy-3-oxocyclohexyl benzoate (*anti*-**21a**) and 3-Hydroxy-2-oxocyclohexyl benzoate (**21b**).¹

General procedure **A** was followed. Benzoic acid 1-vinyl-hex-5-enyl ester (**20**) (20 mg, 0.087 mmol), Grubbs' catalyst **2** (3.7 mg, 0.0043 mmol), NaHCO₃ (18 mg, 0.22 mmol) and Oxone[®] (267 mg, 0.43 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compounds **21a** and **21b** as a 2:1 mixture of regioisomers (12 mg, 60%). Data for **21a**: **IR** (CH₂Cl₂ cast) 3401, 2923, 3002, 1719, 1450, 1274 cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃) δ 8.07 (2H, m), 7.55 (1H, m), 7.43 (2H, m), 4.99 (1H, ddd, *J* = 11.6, 10.0, 4.8 Hz), (1H, m), 4.34 (1H, dd, *J* = 10.0, 2.4 Hz), 3.69 (1H, d, *J* = 4.0 Hz), 2.63 (1H, dqn, *J* = 14.0, 2.4 Hz), 2.43-2.37 (2H, m), 2.09 (1H, m), 1.88 (1H, ddt, *J* = 13.2, 11.2, 4.0 Hz), 1.63 (2H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 207.0, 165.8, 133.2, 130.0, 129.8, 128.4, 78.9 (2C), 38.8, 29.5, 21.0; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₃H₁₄O₄Na 257.0790, found 257.0777.

3-Cyclohexyl-2-hydroxy-3-oxo-propionic acid methyl ester (**24**).²

General procedure **B** was followed. Vinylcyclohexane (**22**) (52 mg, 0.47 mmol), methylacrylate (**23**) (86 μL, 0.94 mmol), Grubbs' catalyst **2** (20 mg, 0.024 mmol), NaHCO₃ (99 mg, 1.18 mmol) and Oxone[®] (1.45 g, 2.36 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compound **24** as a 1:1

mixture of regioisomers (62 mg, 66%). **IR** (CH_2Cl_2 cast) 3351, 2944, 2859, 1705, 1260 cm^{-1} ; **^1H -NMR** (CDCl_3 , 400 MHz) δ 4.88 (1H, m), 3.80 (3H, s), 2.80 (1H, m), 1.96-1.62 (4H, m), 1.50-1.19 (4H, m), 1.50-1.19 (6H, m); **^{13}C -NMR** (CDCl_3 , 100 MHz) δ 207.0, 168.8, 76.4, 53.3, 46.8, 29.5, 28.0, 25.9; **HRMS** (EI) Calc'd for $[\text{M}^+]$ $\text{C}_{10}\text{H}_{16}\text{O}_4$ 200.1049, found 200.1049.

Isomerization Control Experiments

To a stirring solution of 3-cyclohexyl-2-hydroxy-3-oxo-propionic acid methyl ester (**24**) (11 mg, 0.055 mmol) in a 6:6:1 mixture of MeCN:EtOAc: H_2O (1.3 mL) was added Grubbs' catalyst **2** (2.5 mg, 0.003 mmol), NaHCO_3 (12 mg, 0.14 mmol) and Oxone[®] (169 mg, 0.28 mmol) at 0 °C. The resulting reaction mixture was stirred at 0 °C for 1 h, at which time the mixture was diluted with EtOAc (2.0 mL) and filtered. The filtrate was washed with a saturated solution of Na_2SO_3 and dried over Na_2SO_4 . Filtration and concentration *in vacuo* gave an amber oil. *^1H -NMR analysis of the reaction mixture indicated a nearly 1:1 ratio of 3-cyclohexyl-2-hydroxy-3-oxo-propionic acid methyl ester (**24**) to its regioisomer 3-cyclohexyl-3-hydroxy-2-oxo-propionic acid methyl ester.*

To a stirring solution of 3-cyclohexyl-3-hydroxy-2-oxo-propionic acid methyl ester (16 mg, 0.08 mmol) in a 6:6:1 mixture of MeCN:EtOAc: H_2O (1.3 mL) was added Grubbs' catalyst **2** (3.5 mg, 0.004 mmol), NaHCO_3 (17 mg, 0.20 mmol) and Oxone[®] (246 mg, 0.40 mmol) at 0 °C. The resulting reaction mixture was stirred at 0 °C for 1 h, at which time the mixture was diluted with EtOAc (2.0 mL) and filtered. The filtrate was washed with a saturated solution of Na_2SO_3 and dried over Na_2SO_4 . Filtration and concentration *in vacuo* gave an amber oil. *^1H -NMR analysis of the reaction mixture indicated that no isomerization had occurred. These observations suggest the results obtained are a non-thermodynamic ratio of the two diketohydroxides.*

7-Acetoxy-2-hydroxy-3-oxo-heptanoic acid methyl ester (**26**).

General procedure **B** was followed. 1-Hexen-6-yl acetate (**25**) (43 mg, 0.30 mmol), methylacrylate (**23**) (55 μL , 0.60 mmol), Grubbs' catalyst **2** (13 mg, 0.015 mmol), NaHCO_3 (63 mg, 0.76 mmol) and Oxone[®] (928 mg, 1.51 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 2:1) provided compound **26** as a 1.5:1 mixture of regioisomers (39 mg, 56%). **IR** (CH_2Cl_2 cast) 3428, 2959, 1713, 1255 cm^{-1} ; **^1H -NMR** (CDCl_3 , 400 MHz) δ 4.95 (2H, m), 4.04 (2H, t, $J = 6.8$ Hz), 3.84 (3H, s), 2.62 (2H, t, $J = 6.8$ Hz), 2.02 (3H, s), 1.74-1.58 (4H, m); **^{13}C -NMR** (CDCl_3 , 100 MHz) δ 202.7, 171.1, 169.4, 92.6, 64.0, 54.1, 35.4, 28.0, 21.2, 20.1; **HRMS** (EI) calc'd for $[\text{M}^+]$ $\text{C}_{10}\text{H}_{16}\text{O}_6$ 232.0947, found 232.0955.

2-Hydroxy-3-oxo-3-phenyl-propionic acid methyl ester (**28**).²

General procedure **B** was followed. Styrene (**27**) (58 mg, 0.58 mmol), methylacrylate (**23**) (100 μ L, 1.11 mmol), Grubbs' catalyst **2** (24 mg, 0.028 mmol), NaHCO_3 (117 mg, 1.39 mmol) and Oxone[®] (1.71 g, 2.79 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 2:1) provided compound **28** as a 2:1 mixture of regioisomers (60 mg, 56%). **IR** (CH_2Cl_2 cast) 3412, 3060, 3026, 2926, 1746, 1687, 1291, 1238, 1128 cm^{-1} ; **¹H-NMR** (CDCl_3 , 400 MHz) δ 8.07 (2H, m), 7.64 (1H, m), 7.50 (2H, m), 5.60 (1H, m), 4.27 (1H, bs), 3.71 (3H, s); **¹³C-NMR** (CDCl_3 , 100 MHz) δ 193.5, 169.1, 134.8, 129.5, 128.9, 74.6, 53.4; **HRMS** (EI) calc'd for $[\text{M}^+]$ $\text{C}_{10}\text{H}_{10}\text{O}_4$ 194.0579, found 194.0580.

3-Cyclohexyl-2-hydroxy-2-methyl-3-oxo-propionic acid methyl ester (**30**).^{2,3}

General procedure **B** was followed. Vinylcyclohexane (**22**) (63 mg, 0.57 mmol), methyl methacrylate (**29**) (122 μ L, 1.14 mmol), Grubbs' catalyst **2** (24 mg, 0.029 mmol), NaHCO_3 (120 mg, 1.43 mmol) and Oxone[®] (1.76 g, 2.86 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 2:1) provided compound **30** as a colorless oil (60 mg, 49%). **IR** (CH_2Cl_2 cast) 3476, 2946, 2897, 2859, 1743, 1719, 1264, 1148 cm^{-1} ; **¹H-NMR** (CDCl_3 , 400 MHz) δ 4.22 (1H, s), 3.76 (1H, s), 2.83 (1H, tt, $J = 11.2, 3.2$ Hz), 1.79-1.59 (5H, m), 1.56 (3H, s), 1.42-1.31 (2H, m), 1.29-1.17 (3H, m); **¹³C-NMR** (CDCl_3 , 100 MHz) δ 209.9, 171.8, 81.0, 53.4, 45.3, 29.8, 29.7, 25.8, 22.1; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+$ $\text{C}_{11}\text{H}_{18}\text{O}_4\text{Na}$ 237.1103, found 237.1109.

7-Acetoxy-2-hydroxy-2-methyl-3-oxo-heptanoic acid methyl ester (**31**).

General procedure **B** was followed. 1-Hexen-6-yl acetate (**25**) (59 mg, 0.42 mmol), methyl methacrylate (**29**) (89 μ L, 0.83 mmol), Grubbs' catalyst **2** (18 mg, 0.021 mmol), NaHCO_3 (87 mg, 1.04 mmol) and Oxone[®] (1.28 g, 2.08 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 2:1) provided compound **31** as a colorless oil (78 mg, 76%). **IR** (CH_2Cl_2 cast) 3466, 2956, 1745, 1738, 1369, 1243 cm^{-1} ; **¹H-NMR** (CDCl_3 , 400 MHz) δ 4.20 (1H, bs), 4.00 (2H, t, $J = 6$ Hz), 3.74 (3H, s), 2.60 (2H, m), 1.98 (3H, s), 1.67-1.50 (7H, m); **¹³C-NMR** (CDCl_3 , 100 MHz) δ 206.5, 171.9, 171.1, 81.0, 64.1, 53.6, 36.0, 28.1, 22.3, 20.3; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+$ $\text{C}_{11}\text{H}_{18}\text{O}_6\text{Na}$ 269.1001, found 269.0988.

3-Chloro-2-hydroxy-1-phenylpropan-1-one (33).⁴

General procedure **B** was followed. Styrene (**27**) (63 mg, 0.61 mmol), *cis*-1,4-dichloro-2-butene (**32**) (127 μ L, 1.21 mmol), Grubbs' catalyst **2** (51 mg, 0.061 mmol), NaHCO₃ (127 mg, 1.51 mmol) and Oxone[®] (1.86 g, 3.03 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 2:1) provided compound **33** as a colorless oil (53 mg, 47%). **IR** (CH₂Cl₂ cast) 3434, 3060, 3029, 1712, 1697, 1289, 1165 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 7.89 (2H, m), 7.64 (1H, m), 7.51 (2H, m), 5.34 (1H, bs), 4.10 (1H, m), 3.93 (1H, dd, *J* = 11.6, 3.5 Hz), 3.75 (1H, dd, *J* = 11.6, 4.0 Hz); **¹³C-NMR** (CDCl₃, 100 MHz) δ 197.8, 134.5, 130.2, 129.2, 128.6, 72.8, 47.6; **HRMS** (EI) Calc'd for [M⁺] C₉H₉ClO₂ 184.0291, found 184.0283.

(3S, 4R)-1-(Toluene-4-sulfonyl)-pyrrol-3,4-diol (35).⁵

General procedure **C** was followed. *N,N*-Diallyl-4-methylbenzenesulfonamide (**34**) (80 mg, 0.32 mmol), Grubbs' catalyst **2** (14 mg, 0.016 mmol), NaIO₄ (102 mg, 0.48 mmol) and CeCl₃·7H₂O (12 mg, 0.032 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **35** as an amber oil (38 mg, 63%). **IR** (CH₂Cl₂ cast) 3489, 3409, 2928, 2909 cm⁻¹; **¹H-NMR** (CDCl₃, 300MHz) δ 7.68 (2H, m), 7.31 (2H, m), 4.12 (2H, m), 3.48 (2H, dd, *J* = 10.6, 5.7 Hz), 3.18 (2H, dd, *J* = 10.6, 3.8 Hz), 2.89 (2H, bs), 2.42 (3H, s); **¹³C-NMR** (CDCl₃, 100 MHz) δ 130.1, 129.8, 127.8, 127.6, 70.9, 52.4, 21.9; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₁H₁₅NO₄NaS 280.0619, found 280.0616.

(3S, 4R)-1-(Toluene-4-sulfonyl)-piperidine-3,4-diol (37).⁵

General procedure **C** was followed. *N*-Allyl-*N*-but-3-enyl-4-methylbenzenesulfonamide (**36**) (50 mg, 0.19 mmol), Grubbs' catalyst **2** (8 mg, 0.009 mmol), NaIO₄ (61 mg, 0.285 mmol) and CeCl₃·7H₂O (7 mg, 0.02 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **37** as an amber oil (35 mg, 69%). **IR** (CH₂Cl₂ cast) 3371, 3060, 3028, 1336, 1162 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 7.63 (2H, m), 7.31 (2H, m), 3.86 (1H, bs), 3.75 (1H, bs), 3.15 (1H, m), 3.01 (3H, m), 2.41 (3H, s), 2.20 (1H, m), 2.09 (1H, m), 1.84 (2H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 143.9, 133.1, 129.9, 127.7, 68.0, 67.7, 48.1, 42.2, 29.7, 21.9; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₂H₁₇NO₄NaS 294.0776, found 294.0786.

(3S, 4R)-3,4-Dihydroxycyclohexane-1,1-dicarboxylic acid diethyl ester (38).⁵

General procedure C was followed. *N,N*-Dibut-3-enyl-4-methyl-benzenesulfonamide (**6**) (54 mg, 0.19 mmol), Grubbs' catalyst **2** (8 mg, 0.0097 mmol), NaIO₄ (61 mg, 0.29 mmol) and CeCl₃·7H₂O (7 mg, 0.019 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **38** as an amber oil (38 mg, 65%). **IR** (CH₂Cl₂ cast) 3433, 3015, 2920, 1643, 1160 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 7.66 (2H, m), 7.30 (2H, m), 3.96 (2H, d, *J* = 7.6 Hz), 3.43 (2H, ddd, *J* = 12.8, 8.0, 4.0 Hz), 3.18 (2H, ddd, *J* = 11.2, 7.6, 3.6 Hz), 2.42 (3H, s), 2.17 (2H, bs), 2.06 (2H, m), 1.80 (2H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 143.4, 135.7, 129.8, 127.0, 72.5, 42.4, 31.3, 21.8; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₃H₁₉NO₄Na 308.0932, found 308.0923.

(4S, 5R)-4,5-Dihydroxycycloheptane-1,1-dicarboxylic acid diethyl ester (39).

General procedure C was followed. 2-Allyl-2-but-3-enyl-malonic acid diethyl ester (**8**) 60 mg, 0.19 mmol), Grubbs' catalyst **2** (10 mg, 0.011 mmol), NaIO₄ (72 mg, 0.34 mmol) and CeCl₃·7H₂O (8 mg, 0.022 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **39** as an amber oil (41 mg, 67%). **IR** (CH₂Cl₂ cast) 3409, 2961, 1727 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 4.14 (4H, m), 3.76 (2H, m), 2.34 (2H, m), 2.26 (2H, bs), 1.85 (2H, m), 1.62 (2H, t, *J* = 13.2 Hz), 1.22 (6H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 172.6, 73.1, 61.6, 61.5, 56.7, 34.1, 26.9, 25.9, 14.3; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₃H₂₂O₆Na 297.1314, found 297.1311.

(1S, 2S, 3S)-2,3-Dihydroxycyclohexylacetate (41).^{5,6}

General procedure C was followed. Acetic acid 1-vinyl-hex-5-enyl ester (**40**) (65 mg, 0.39 mmol), Grubbs' catalyst **2** (16 mg, 0.019 mmol), NaIO₄ (124 mg, 0.58 mmol) and CeCl₃·7H₂O (15 mg, 0.04 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **41** as a 22:1 mixture of diastereomers (40 mg, 60%). **IR** (CH₂Cl₂ cast) 3408, 2949, 2871, 1721, 1376, 1262 cm⁻¹; **¹H-NMR** (CDCl₃, 300 MHz) δ 4.98 (1H, m), 4.08 (1H, m), 3.57 (1H, dd, *J* = 8.9, 2.3 Hz), 3.02 (1H, bs), 2.57 (1H, bs), 2.09 (3H, s), 2.01-1.84 (2H, m), 1.77-1.66 (1H, m), 1.57-1.26 (3H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 171.8, 74.5, 74.3, 70.1, 30.1, 29.4, 21.6, 18.4; **HRMS** (ESI) calc'd for [M+Na]⁺ C₈H₁₄O₄Na 197.0790, for 197.0787.

(1*S*, 2*S*, 3*S*)-2,3-Dihydroxycycloxybenzoate (42**).⁷**

General procedure **C** was followed. Benzoic acid 1-vinyl-hex-5-enyl ester (**20**) (59 mg, 0.26 mmol), Grubbs' catalyst **2** (11 mg, 0.013 mmol), NaIO₄ (81 mg, 0.38 mmol) and CeCl₃·7H₂O (10 mg, 0.026 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **42** as an amber oil (48 mg, 81%). **IR** (CH₂Cl₂ cast) 3390, 3026, 2924, 1712, 1602, 1276 cm⁻¹; **¹H-NMR** (CDCl₃) δ 8.01 (2H, m), 7.53 (1H, m), 7.40 (2H, m), 5.24 (1H, m), 4.09 (2H, m), 3.72 (1H, dd, *J* = 8.2, 2.8 Hz), 3.52 (1H, bs), 3.08 (1H, bs), 2.02 (1H, m), 1.87 (1H, m), 1.73 (1H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 170.0, 133.2, 130.2, 129.7, 128.4, 75.0, 74.1, 70.1, 30.0, 29.1, 18.5; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₃H₁₆O₄Na 259.0946, found 259.0938.

(3*R*, 4*S*, 6*R*)-6-Cyclohexyl-tetrahydro-pyran-3,4-diol (44**).**

General procedure **C** was followed. (1-Allyloxy-but-3-enyl)-cyclohexane (**43**) (57 mg, 0.29 mmol), Grubbs' catalyst **2** (13 mg, 0.015 mmol), NaIO₄ (93 mg, 0.44 mmol) and CeCl₃·7H₂O (11 mg, 0.029 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **44** as an 3:2 mixture of diastereomers (40 mg, 69%). **IR** (CH₂Cl₂ cast) 3408, 3316, 2915, 2857, 1244 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 4.03 (1H, dd, *J* = 12.5, 2.2 Hz), 3.73 (2H, m), 3.46 (1H, dd, *J* = 12.5, 0.9 Hz), 3.00 (1H, ddd, *J* = 11.7, 6.8, 2.2 Hz), 2.17 (2H, m), 1.94-1.159 (7H, m), 1.44 (1H, m), 2.21 (3H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 81.1, 70.7, 69.5, 68.6, 42.8, 32.9, 29.3, 28.8, 26.8, 26.4, 26.3; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₁H₂₀O₃Na 223.1310, found 223.1321.

(3*R*, 4*S*, 6*R*)-6-(4-Methoxy-phenyl)-1-(toluene-4-sulfonyl)-piperidine-3,4-diol (46**).**

General procedure **C** was followed. *N*-Allyl-*N*-[1-(4-methoxy-phenyl)-but-3-enyl]-4-methylbenzenesulfonamide (**45**) (51 mg, 0.14 mmol), Grubbs' catalyst **2** (6 mg, 0.007 mmol), NaIO₄ (44 mg, 0.206 mmol) and CeCl₃·7H₂O (5 mg, 0.014 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:4) provided diol **46** as an 7:1 mixture of diastereomers (40 mg, 77%). **IR** (CH₂Cl₂ cast) 3424, 3032, 2928, 2899, 1610, 1513, 1325, 1251, 1157 cm⁻¹; **¹H-NMR** (CDCl₃, 500 MHz) δ 7.83 (2H, m), 7.33 (2H, m), 7.19 (2H, m), 6.85 (2H, m), 5.35 (1H, m), 3.97 (1H, dt, *J* = 15.2, 2.1 Hz), 3.81 (3H, s), 3.74 (1H, bs), 3.66 (1H, m), 3.11 (1H, dd, *J* = 15.6, 1.6 Hz), 2.52 (1H, d, *J* = 5.2 Hz), 2.46 (3H, s), 2.37

(1H, m), 2.15 (1H, d, $J = 8.2$ Hz), 2.04 (1H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 158.8, 143.5, 129.6, 129.1, 127.7, 127.6, 114.3, 67.3, 66.0, 55.5, 55.1, 45.9, 30.7, 21.9; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+ \text{C}_{19}\text{H}_{23}\text{NO}_5\text{SNa}$ 400.1195, found 400.1185.

(2S, 3R)-3-Cyclohexyl-2,3-dihydroxypropanoic acid methyl ester (47).⁸

General procedure **D** was followed. Vinylcyclohexane (**22**) (68 mg, 0.62 mmol), methylacrylate (**23**) (111 μL , 1.23 mmol), Grubbs' catalyst **2** (26 mg, 0.031 mmol), NaIO_4 (198 mg, 0.93 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (23 mg, 0.062 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 2:1) provided diol **47** as an amber oil (90 mg, 77%). **IR** (CH_2Cl_2 cast) 3414, 2948, 2897, 2855, 1741, 1441, 1278, 1225, 1118 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ 4.29 (1H, m), 3.81 (3H, s), 3.54 (1H, m), 3.00 (1H, m), 2.01 (1H, m), 1.81 (1.59 (6H, m), 1.28-0.96 (4H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 174.7, 71.1, 53.0, 40.6, 29.6, 29.4, 26.6, 26.2; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+ \text{C}_{10}\text{H}_{18}\text{O}_4\text{Na}$ 225.1103, found 225.1092.

(2S, 3R)-7-Acetoxy-2,3-dihydroxyheptanoic acid methyl ester (48).

General procedure **D** was followed. 1-Hexen-6-yl acetate (**25**) (61 mg, 0.43 mmol), methylacrylate (**23**) (78 μL , 0.86 mmol), Grubbs' catalyst **2** (18 mg, 0.022 mmol), NaIO_4 (138 mg, 0.64 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (16 mg, 0.043 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 1:1) provided diol **48** as an amber oil (56 mg, 56%). **IR** (CH_2Cl_2 cast) 3536, 2953, 2915, 1738, 1248 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 4.08 (3H, m), 3.84 (4H, m), 3.04 (1H, dd, $J = 5.3, 2.0$ Hz), 2.05 (3H, s), 1.94 (1H, s), 1.74-1.40 (6H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 173.9, 171.2, 73.4, 72.4, 64.5, 53.0, 33.5, 28.7, 22.5, 21.3; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+ \text{C}_{10}\text{H}_{18}\text{O}_6\text{Na}$ 257.1001, found 257.0990.

(2S, 3R)-3-Cyclohexyl-2,3-dihydroxy-2-methylpropanoic acid methyl ester (49).

General procedure **D** was followed. Vinylcyclohexane (**22**) (65 mg, 0.59 mmol), methyl methacrylate (**29**) (127 μL , 1.18 mmol), Grubbs' catalyst **2** (25 mg, 0.029 mmol), NaIO_4 (189 mg, 0.88 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (22 mg, 0.059 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO_2 , hexanes:EtOAc, 1:1) provided diol **49** as an amber oil (63 mg, 50%). **IR** (CH_2Cl_2 cast) 3399, 2921, 1735 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ 3.79 (3H, s), 3.58 (1H, bs), 3.44 (1H, s), 2.11 (1H, b), 1.86 (1H, m), 1.73 (2H, m), 1.65-1.51 (4H, m), 1.36 (3H, s), 1.33-1.05 (4H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 177.3, 78.7, 77.9, 53.4, 38.9, 31.9, 27.0, 26.5, 22.9; **HRMS** (ESI) Calc'd for $[\text{M}+\text{Na}]^+ \text{C}_{11}\text{H}_{20}\text{O}_4\text{Na}$ 239.1259,

found 239.1264.

(2S, 3R)-7-Acetoxy-2,3-dihydroxy-2-methylheptanoic acid methyl ester (50).

General procedure **D** was followed. 1-Hexen-6-yl acetate (**25**) (67 mg, 0.47 mmol), methyl methacrylate (**29**) (101 μ L, 0.94 mmol), Grubbs' catalyst **2** (20 mg, 0.024 mmol), NaIO₄ (151 mg, 0.71 mmol) and CeCl₃·7H₂O (18 mg, 0.047 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:1) provided diol **50** as an amber oil (89 mg, 76%). **IR** (CH₂Cl₂ cast) 3432, 2955, 2329, 1735, 1256 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 4.05 (3H, m), 3.50 (3H, s), 3.40 (2H, m), 2.03 (4H, m), 1.92 (1H, m), 1.32 (3H, s), 1.72-1.60 (2H, m), 1.46-1.32 (2H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 176.6, 171.3, 77.7, 75.5, 64.6, 53.2, 30.0, 28.7, 22.6, 22.0, 21.3; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₁H₂₀O₆Na 271.1158, found 271.1146.

(2S, 3R)-2,3-Dihydroxy-3-phenyl-propionic acid methyl ester (51).⁸

General procedure **D** was followed. Styrene (**27**) (51 mg, 0.49 mmol), methylacrylate (**23**) (88 μ L, 0.98 mmol), Grubbs' catalyst **2** (21 mg, 0.025 mmol), NaIO₄ (157 mg, 0.74 mmol) and CeCl₃·7H₂O (18 mg, 0.049 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:1) provided diol **51** as an amber oil (52 mg, 56%). **IR** (CH₂Cl₂ cast) 3395, 3032, 2954, 2872, 1739, 1439, 1276, 1120 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 7.43-7.32 (5H, m), 5.04 (1H, dd, *J* = 7.3, 2.9 Hz), 4.39 (1H, dd, *J* = 6.1, 2.9 Hz), 3.83 (3H, s), 3.06 (1H, d, *J* = 6.1 Hz), 2.66 (1H, d, *J* = 7.3 Hz); **¹³C-NMR** (CDCl₃, 100 MHz) δ 173.1, 139.9, 128.5, 128.1, 126.3, 75.0, 74.6, 53.1; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₀H₁₂O₄Na 219.0633, found 219.0641.

(2S, 3R)-2, 3, 11-Trihydroxyundecanoic acid methyl ester (53).

General procedure **D** was followed. 9-Decen-1-ol (**52**) (51 mg, 0.33 mmol), methylacrylate (**23**) (59 μ L, 0.65 mmol), Grubbs' catalyst **2** (14 mg, 0.016 mmol), NaIO₄ (105 mg, 0.49 mmol) and CeCl₃·7H₂O (12 mg, 0.033 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:2) provided diol **53** as an amber oil (44 mg, 54%). **IR** (CH₂Cl₂ cast) 3411, 2951, 2859, 1739 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 4.08 (1H, m), 3.86 (1H, m), 3.81 (3H, s), 3.61 (2H, t, *J* = 6.8 Hz), 3.03 (1H, d, *J* = 5.6 Hz), 1.90 (1H, m), 1.62-1.50 (5H, m), 1.47-1.41 (1H, m), 1.38-1.24 (8H, m); **¹³C-NMR** (CDCl₃, 100 MHz) δ 174.0, 73.2, 72.6, 63.3, 53.1, 34.0, 33.0, 29.7, 29.6, 26.0; **HRMS** (ESI) Calc'd for [M+Na]⁺ C₁₂H₂₄O₅Na 271.1521, found 271.1508.

(1*S*, 2*S*)-Chloro-1-phenyl-propane-1,2-diol (54).⁴

General procedure **D** was followed. Styrene (**27**) (70 mg, 0.67 mmol), *cis*-1,4-dichloro-2-butene (**32**) (141 μ L, 1.34 mmol), Grubbs' catalyst **2** (28 mg, 0.037 mmol), NaIO₄ (431 mg, 2.016 mmol) and CeCl₃·7H₂O (50 mg, 0.13 mmol) were used in this transformation. Purification of the product by flash chromatography (SiO₂, hexanes:EtOAc, 1:1) provided diol **54** as an amber oil (53 mg, 42%). **IR** (CH₂Cl₂ cast) 3383, 2833, 1633, 1433, 1058 cm⁻¹; **¹H-NMR** (CDCl₃, 400 MHz) δ 7.35 (5H, m), 4.70 (1H, d, *J* = 6.8 Hz), 3.89 (2H, m), 3.61 (1H, m), 3.53 (1H, dd, *J* = 11.6, 3.8 Hz), 3.35 (1H, dd, *J* = 11.6, 6.8 Hz), 3.18 (1H, bs), 2.98 (1H, bs); **¹³C-NMR** (CDCl₃, 100 MHz) δ 139.8, 125.8, 128.6, 126.7, 75.6, 71.3, 46.3; **HRMS** (EI) Calc'd for [M⁺] C₉H₁₁ClO₂ 186.0448, found 186.0455.

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