Supporting Information

An Efficient Oxidative Lactonization of 1,4-Diols Catalyzed by Cp*Ru(PN) Complexes

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CONTENTS

Compound numbers **1b and **2b** in section 3 were incorrect in the version published July 2, 2007. The correct numbers are **1a** and **2a**, respectively. The corrected version was published July 5, 2007.**

1) General methods. All manipulation of oxygen and moisture-sensitive materials were conducted under purified argon atmosphere (BASF–Catalyst R3-11) by the use of standard Schlenk techniques. All reactions were performed in commercially available anhydrous solvents unless otherwise noted. Column chromatography was performed using Kanto Chemical Co. Silica Gel 60 N (spherical, neutral, 63–210 μm). ^{1}H (300 MHz) and ^{13}C{^{1}H} (75 MHz) spectra were recorded on a JEOL JNM–LA300 spectrometer using $CDCl_3$ and chemical shifts were referenced to tetramethylsilane (0.0 ppm) unless otherwise noted. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology or on a Perkin-Elmer 2400II CHN analyzer.

Chemicals. Unless otherwise noted, all reagents and solvents were purchased and used as delivered. Dehydrated acetone was purchased from Kanto Chemical Co. and degassed by argon bubbling prior to use. Cp*RuCl(cod)[S1] and Ru complexes **2a**[S2] were prepared as reported. $Ph_2P(CH_2)_2NH(CH_3)$ and $Ph_2P(CH_2)_2N(CH_3)_2$ were prepared by the literature methods.[S2] Commercially available diols (**3a**, **3b**, **3f**, **3j**, **3n**, **3v**, **3w**), phthalide **4a**, and phthaldialdehyde **7a** were used as delivered. The diols **3g** and **3h** were prepared by the hydrogenation of **3j** and **3k**, respectively as reported.[S3]

2) Preparation of diols and triols (3).

***cis*-Cyclopropane-1,2-dimethanol (3c).** To a solution of 3-oxabicyclo[3.1.0]hexane-2,4-dione (Aldrich 391174, 1.0 g, 8.92 mmol) in THF (30 mL) was added $LiAlH_4$ (1.0 M in THF, 13.4 mL, 13.4 mmol) at 0 °C and the resulting mixture was refluxed for 13 h. The reaction mixture was cooled to 0 °C, diluted with diethyl ether (45 mL), quenched by successive addition of H_2O (0.50 mL), 3 M NaOH aq. (0.50 mL), and H_2O (1.5 mL). The resulting white solids were removed by filtration through a pad of Celite, and the filtrate was concentrated to give a crude oil, which was purified by bulb-to-bulb distillation to give the title compound as colorless liquid (755 mg, 83% yield); ^{1}H NMR δ 0.20 (dt, J = 5.1, 5.0 Hz, 1H), 0.80 (dt, J = 5.1, 10 Hz, 1H), 1.24–1.38 (m, 2H), 2.70–3.20 (br, 2H), 3.18–3.30 (m, 2H), 4.05–4.12 (m, 2H); ^{13}C{^{1}H} NMR δ 8.6, 17.6, 63.1.[S4]

***cis*-Cyclobutane-1,2-dimethanol (3d).** To a solution of *cis*-cyclobutane-1,2-dicarboxylic acid (Fluka 28682, 2.0 g, 13.9 mmol) in THF (28 mL) was slowly added $LiAlH_4$ (1.0 M in THF, 28 mL, 28 mmol) at 0 °C over 30 min. An exothermic reaction with rapid evolution of gas occurred during which initially formed precipitates dissolved again to give a colorless solution, which was refluxed for 24 h. The reaction mixture was cooled to 0 °C, diluted with diethyl ether (50 mL), quenched by successive addition of H_2O (1.1 mL), 3 M NaOH aq. (1.1 mL), and H_2O (3.2 mL). The resulting white solids were removed by filtration through a pad of Celite, and the filtrate was concentrated to give a crude oil, which was purified by bulb-to-bulb distillation to give the title compound as colorless liquid (1.41 g, 88% yield).; ^{1}H NMR δ 1.53–1.59 (m, 2H), 1.97–2.06 (m, 2H), 2.73 (br, 2H), 3.34 (br, 2H), 3.59 (dd, J = 4.4, 11.2 Hz, 2H), 3.81–3.88 (m, 2H).[S5]

***cis*-Cyclopentane-1,2-dimethanol (3e).** The reported method[S6a] was modified as follows: To a solution of 1-cyclopentene-1,2-dicarboxylic anhydride (Fluka 29822, 965.4 mg, 6.99 mmol) in ethanol (10 mL) was added conc. H_2SO_4 (3.0 mL) and the mixture was heated under reflux for 6 h. Then, approximately half of the solvent was evaporated and the residue was diluted with H_2O and neutralized by adding K_2CO_3. The resulting mixture was extracted with diethyl ether, washed with brine, dried over Na_2SO_4, filtered through a pad of Celite. The filtrate was concentrated to leave an oil, which was purified by bulb-to-bulb distillation to give diethyl cyclopent-1-ene-1,2-dicarboxylate as colorless liquid (1.18 g, 92% yield, ^{1}H NMR δ 1.30 (t, J = 7.1 Hz, 6H),

2.00 (quint, J = 7.8 Hz, 2H), 2.74 (t, J = 7.8 Hz, 4H), 4.23 (q, J = 7.1 Hz, 4H)). Thus obtained diester (523.2 mg, 2.47 mmol) was dissolved in 99.5% ethanol (5.0 mL) and the resulting solution was transferred to 5% Pd/C (27 mg) placed in a stainless autoclave. The mixture was degassed by freeze-pump-thaw cycles (x3) and then hydrogen (0.7 MPa) was introduced in the autoclave. After stirring the reaction mixture vigorously at 30 °C for 18 h, hydrogen was released carefully and the resulting mixture was filtered through a pad of Celite and activated charcoal. The filtrate was concentrated *in vacuo* to give crude *cis*-diethyl cyclopentane-1,2-dicarboxylate (527.0 mg, ^{1}H NMR δ 1.24 (t, J = 7.3 Hz, 6H), 1.53–1.68 (m, 1H), 1.81–2.03 (m, 5H), 2.96–3.05 (m, 2H), 4.08 (q, J = 7.3 Hz, 4H); ^{13}C{^{1}H} NMR δ 14.1, 23.8, 28.7, 46.9, 60.4, 174.0.), which was used without further purification for the next step. To a solution of *cis*-diethyl cyclopentane-1,2-dicarboxylate (501.9 mg, 2.34 mmol) in anhydrous THF (50 mL) was added $LiAlH_4$ (267.0 mg, 7.05 mmol) portionwise at 0 °C. The resulting mixture was heated under reflux for 12 h. Then the mixture was diluted with diethyl ether and carefully quenched by adding Na_2SO_4•$10H_2O$ and $MgSO_4$ at 0 °C. The resultant white precipitates were stirred until they are well-separated from the supernatant liquid, and then filtered through a pad of Celite and washed with ethyl acetate. The combined filtrate was concentrated *in vacuo* to give the crude product, which was purified by bulb-to-bulb distillation to afford the title compound as colorless liquid (275.5 mg, 90% yield, ^{1}H NMR δ 1.19–1.28 (m, 2H), 1.41–1.77 (m, 4H), 2.26–2.34 (m, 2H), 3.11 (br, 2H), 3.61–3.73 (m, 4H); ^{13}C{^{1}H} NMR δ 21.9, 28.4, 43.3, 63.4.[S6b]

***cis*-4-Cyclohexene-1,2-dimethanol (3i).** To a solution of *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (TCI C0493, 5.07 g, 33.3 mmol) in THF (50 mL) was slowly added $LiAlH_4$ (1.0 M in THF, 50 mL, 50 mmol) at 0 °C and the resulting mixture was refluxed for 15 h. The reaction mixture was cooled to 0 °C, diluted with diethyl ether (100 mL), quenched by successive addition of H_2O (1.9 mL), 3 M NaOH aq. (1.9 mL), and H_2O (5.7 mL). The resulting white solids were removed by filtration through a pad of Celite, and the filtrate was concentrated to give a crude oil, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (4.05 g, 86% yield); ^{1}H NMR δ 2.00–2.20 (m, 6H), 2.54 (brs, 2H), 3.59 (dd, J = 3.4, 11.0 Hz, 2H), 3.73 (dd, J = 3.4, 11.0 Hz, 2H), 5.62 (s, 2H).[S7]

***cis-endo*-2,3-Bis(hydroxymethyl)bicyclo[2.2.2]oct-5-ene (3k).** This diol was prepared by $LiAlH_4$ reduction of *endo*-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (Aldrich 10914-2) in 61% yield, according to the literature method.[S3] ^{1}H NMR δ 1.20–1.30 (m, 2H), 1.54–1.66 (m, 2H), 2.22–2.25 (m, 2H), 2.44–2.51 (br, 2H), 3.20–3.50 (br, 2H), 3.50–3.75 (m, 4H), 6.12–6.15 (m, 2H).

***trans*-2,3-Dibenzyl-1,4-diol (3l).** According to the method of Belletire (the procedure B in reference S8a), the dianion of 3-phenylpropionic acid (TCI H0183, 16.5 mmol) was treated with iodine (2.10 g, 8.27 mmol) to give an orange solid (3.03 g). ^{1}H NMR analysis showed that this crude material was a mixture of *cis*- and *trans*-2,3-dibenzylsuccinic acid, 3-phenylpropionic acid, and cinnamic acid (the latter two compounds were likely formed by the disproportionation of a radical anion intermediate). Recrystallization of this solid from toluene afforded an inseparable *cis*/*trans* mixture of 2,3-dibenzylsuccinic acid as a colorless solid (0.97 g, 39% yield, ^{1}H NMR (CD_3OD) δ 2.90–3.00 (m, 3H), 3.06–3.07 (m, 3H), 7.15–7.32 (m, 10H)). Thus obtained diacid (0.81 g) was dissolved in THF (30 mL) and to this was cautiously added $LiAlH_4$ (0.31 g, 8.17 mmol) portionwise at 0 °C. The mixture was heated under reflux for 14 h and cooled. The resulting mixture was diluted with diethyl ether and quenched by addition of Na_2SO_4•$10H_2O$ at 0 °C. The gradually formed white cake was removed by filtration through a pad of Celite and the filtrate was concentrated to

give a colorless paste (0.69 g). Purification of this paste by silica gel chromatography eluting *n*-hexane/ethyl acetate (1/1) gave *trans*-2,3-dibenzyl-1,4-diol (0.36 g, 48% yield; ^{1}H NMR δ 1.87–2.01 (m, 2H), 2.73 (dd, J = 14.0, 6.0 Hz, 2H), 2.84 (dd, J = 14.0, 8.0 Hz, 2H), 3.02 (br, 2H), 3.51 (dd, J = 11.0, 4.6 Hz, 2H), 3.81 (dd, J = 11.0, 1.9 Hz, 2H), 7.10–7.31 (m, 10H); R_f 0.50) and *cis*-2,3-dibenyl-1,4-diol (0.20 g, 27% yield; ^{1}H NMR δ 1.96–2.10 (m, 2H), 2.57-2.78 (m, 4H), 3.45 (dd, J = 11.0, 3.0 Hz, 2H), 3.55 (dd, J = 11.0, 7.0 Hz, 2H), 4.12 (br, 2H), 7.07–7.40 (m, 10H); R_f 0.35).[S8b]

***trans*-2,3-Bis(piperonyl)-1,4-butanediol (3m).** To a solution of $[RhCl(cod)]_2$ (Aldrich 227951, 273.0 mg, 0.55 mmol) and 3,4-(methylenedioxy)phenylboronic acid (Aldrich 499994, 3.36 g, 20.3 mmol) in aqueous 1,4-dioxane (6/1 v/v, 60 mL) was added triethylamine (2.05 g, 20.2 mmol) and dimethyl itaconate (2.92 g, 18.4 mmol) at room temperature. The orange solution was stirred at 30 °C for 27 h, during which white precipitates were gradually formed. The resulting mixture was quenched with 1 M citric acid aq. and extracted with diethyl ether. The oragnic layer was washed with brine, dried over $MgSO_4$, filtered through a silica plug, and evaporated. The crude oil was purified by bulb-to-bulb distillation to give the dimethyl 2-piperonylsuccinate (4.59 g, 89% yield, ^{1}H NMR δ 2.41 (dd, J = 16.7, 6.0 Hz, 1H), 2.66 (dd, J = 16.7, 8.5 Hz, 1H), 2.68 (dd, J = 13.5, 8.5 Hz, 1H), 2.96 (dd, J = 13.5, 6.0 Hz, 1H), 3.04–3.12 (m, 1H), 3.65 (s, 3H), 3.68 (s, 3H), 5.92 (s, 2H), 6.59 (dd, J = 7.8, 1.7 Hz, 1H), 6.64 (d, J = 1.7 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H). Thus obtained diester (2.16 g, 7.72 mmol) was subsequently hydrolyzed by refluxing in ethanol (65 mL) solution containing KOH (1.51 g, 26.9 mmol) for 5 h. Then the volume of the resultant mixture was reduced to 1/3 under reduced pressure, to which was added water and washed with diethyl ether. The aqueous layer was acidified with 6 M HCl aq. and extracted with diethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* to give the crude 2-piperonylsuccinic acid (1.86 g, 95% yield), which was used in the next step without further purification. To a solution of 2-piperonylsuccinic acid (887.4 mg, 3.52 mmol) in THF (10 mL) was added LDA (0.31 M in THF, 40 mL, 12.3 mmol) at -78 °C. The resulting mixture was allowed to react at 0 °C for 1 h. Then the mixture was cooled to -78 °C again and to this was added a solution of piperonyl bromide[S9a] (1.14 g, 4.63 mmol) in THF (10 mL) at this temperature. The mixture was allowed to react at room temperature for 4 days and then quenched by adding sat.NH_4Cl aq. The resultant mixture was basicified with 1 M NaOH aq. and the aqueous layer was washed with diethyl ether. The aqueous layer was acidified with 6 M HCl aq. and extracted with diethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* to give the crude 2,3-bis(piperonyl)succinic acid as an slightly orange solid (887.4 mg, 65% yield, ^{1}H NMR (CD_3COCD_3) δ 2.87–3.03 (m, 6H), 5.93 (s, 4H), 6.63–6.77 (m, 6H)), which was reduced with $LiAlH_4$ and purified as in the preparation of **3l**, to give the title compound as a white solid (0.59 g, 72% yield). ^{1}H NMR δ 1.82–1.84 (m, 2H), 2.74 (dd, J = 13.8, 8.6 Hz, 2H), 2.84 (brs, 2H), 3.49 (dd, J = 11.2, 3.9 Hz, 2H), 3.46–3.74 (m, 2H), 3.76 (d, J = 11.2 Hz, 2H), 5.90 (s, 4H), 6.51–6.63 (m, 4H), 6.70 (d, J = 7.8 Hz, 2H).[S9b]

α-Methyl-α-deutrio-1,2-benzenedimethanol (3n-*d*$_1$, 96% atom D). To a solution of **4a** (1.30 g, 9.67 mmol) in THF (50 mL) was added MeLi (1.14 M in diethyl ether, 9.3 mL, 10.6 mmol) at -78 °C. The reaction mixture was stirred for 30 min to give a clear yellow solution,[S10a] to which was added methanol (0.5 mL, 12.3 mmol) at the same temperature. To the resulting colorless solution was added a suspension of $NaBD_4$ (Aldrich 20559-1, 1.21 g, 28.9 mmol) in ethanol (30 mL) at -78 °C and the mixture was allowed to react at 30 °C for 3 h. The reaction mixture were evaporated, diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and filtered through a pad of Celite.

The resulting viscous oil was purified by bulb-to-bulb distillation to give the title compound as colorless liquid (1.28 g, 86% yield) which crystallize upon standing; ^{1}H NMR δ 1.52 (s, 3H), 3.40 (s, 2H), 4.56 (d, J = 12.0 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 5.16–5.18 (m, 0.04H), 7.23–7.45 (m, 4H); ^{13}C{^{1}H} NMR d 22.6, 63.6, 66.5, 125.8, 127.8, 128.5, 129.8, 137.9, 143.2; Anal. Calcd for $C_9H_{11}DO_2$: C, 70.56; H, 7.24; D, 1.31. Found: C, 70.39; H, 7.21; D, 1.26.; R_f 0.50 (diethyl ether).[S10b]

α,α-Dimethyl-1,2-benzenedimethanol (3o). To a solution of **4a** (2.77 g, 20.7 mmol) in THF (65 mL) was added MeMgBr (3.0 M in diethyl ether, 15 mL, 45 mmol) at 0 °C. The reaction mixture was allowed to react at 30 °C for 12.5 h and the resulting white suspension was quenched with sat. NH_4Cl aq. The organic layer was washed with brine, dried over Na_2SO_4, and filtered through a pad of Celite. The filtrate was concentrated to give a crude oil, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (3.04 g, 88% yield), which crystallize upon standing; ^{1}H NMR δ 1.68 (s, 6H), 4.83 (s, 2H), 7.20–7.38 (m, 4H) (OH signal was not observed); R_f 0.55 (diethyl ether).[S10a]

1,4-Nonanediol (3p). To a solution of γ-butyrolactone (TCI B0767, 1.5 mL, 19.5 mmol) in CH_2Cl_2 (40 mL) was added (i-Bu)$_2$AlH (0.95 M in hexane, 21.0 mL, 20 mmol) at -78 °C and the resulting solution was stirred at the same temperature for 1 h. The reaction mixture was quenched by addition of Na_2SO_4•10H_2O at -78 °C and allowed to react at 30 °C for 29 h. The resultant white cake was removed by filtration through a pad of Celite and the filtrate was evaporated to give a colorless oil, which was redissolved in diethyl ether (40 mL) and to this was added n-pentyl magnesium bromide (2.0 M in diethyl ether, 15 mL, 30 mmol) at -78 °C. The reaction mixture was allowed to react at 30 °C for 11 h, quenched with sat. NH_4Cl aq., washed with brine, dried over Na_2SO_4, and evaporated to give a crude product, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (1.37 g, 44 % yield); ^{1}H NMR δ 0.84–0.89 (m, 3H), 1.27–1.28 (m, 6H), 1.43–1.44 (m, 3H), 1.66–1.67 (m, 3H), 2.00–2.25 (m, 2H), 3.46–3.69 (m, 3H); R_f 0.15 (diethyl ether).

1,4-Undecanediol (3q). To a solution of γ-butyrolactone (TCI B0767, 1.5 mL, 19.5 mmol) in CH_2Cl_2 (40 mL) was added (i-Bu)$_2$AlH (0.95 M in hexane, 21.0 mL, 20 mmol) at -78 °C and the resulting solution was stirred at the same temperature for 0.5 h. The reaction mixture was quenched by addition of Na_2SO_4•10H_2O at -78 °C and allowed to react at 30 °C for 11 h. The resultant white cake was removed by filtration through a pad of Celite and the filtrate was evaporated to give a colorless oil, which was redissolved in diethyl ether (40 mL) and to this was added n-heptyl magnesium bromide (1.0 M in diethyl ether, 40 mL, 40 mmol) at -78 °C. The reaction mixture was allowed to react at 30 °C for 1.5 h, quenched with sat. NH_4Cl aq., washed with brine, dried over Na_2SO_4, and evaporated to leave an oil, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (2.50 g, 68 % yield); ^{1}H NMR δ 0.85 (t, J = 6.6 Hz, 3H), 1.22–1.68 (m, 16H), 2.53 (brs, 2H), 3.59–3.69 (m, 3H); R_f 0.20 (diethyl ether).[S11]

***cis*-Decane-1,4,5-triol (3r).** This triol was obtained from ethyl (*E*)-dec-4-enoate (TCI D1931) in two steps according to the reported method.[S12] The crude product was purified by silica gel column chromatography eluting with n-hexane/ethyl acetate (from 3/2 to 0/1) to give the title compound as white solids; ^{1}H NMR δ 0.89 (t, J = 6.6 Hz, 3H), 1.25–1.58 (m, 9H), 1.66–1.76 (m, 3H), 2.68 (brs, 1H), 3.01 (brs, 1H), 3.41–3.46 (m, 3H), 3.61–3.74 (m, 2H).[S12]

***cis*-Heptadecane-1,4,5-triol (3s).** (*E*)-heptadec-4-ene-1-ol was prepared from tridecanal (Aldrich 269239) by vinylation, Johnson-Claisen rearrangement, and $LiAlH_4$ reduction by the literature method.[S13a,b] Then, this compound was subjected to the OsO_4-catalyzed dihydroxylation[S12] to give the title compound as waxy colorless solids.

^{1}H NMR δ 0.88 (t, J = 6.7 Hz, 3H), 1.23–1.85 (m, 26H), 2.20–2.31 (m, 2H), 3.04 (brs, 1H), 3.43–3.45 (m, 2H), 3.66–3.73 (m,2H); ^{13}C{^{1}H} NMR(CD_3OD) δ 14.8, 24.0, 27.4, 30.5, 30.7, 30.8, 30.8, 31.1, 31.1, 31.1, 31.1, 31.2, 33.4, 34.2, 63.4, 75.5, 75.7; Anal. Calcd for $C_{17}H_{36}O_3$: C, 70.78; H, 12.58. Found: C, 70.91; H, 12.44.

Hexane-1,3,6-triol (3t). γ-Carboxymethylbutanolide was prepared from *trans*-2-butene-1,4-dicarboxylic acid (TCI H0477) by the reported method.[S14a] This compound (0.89 g, 6.2 mmol) was dissolved in THF (55 mL) and to this was added $LiAlH_4$ (0.70 g, 18.6 mmol) portionwise at 0 °C. The mixture was heated under reflux for 12 h and cooled. The resulting mixture was diluted with diethyl ether and quenched by addition of Na_2SO_4•$10H_2O$ and $MgSO_4$ at 0 °C. The resultant white precipitates were stirred until they are well-separated from the supernatant liquid, and then filtered through a pad of Celite and washed with ethyl acetate. The filtrate was concentrated *in vacuo* to give the crude product, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (0.43 g, 52% yield, ^{1}H NMR (CD_3OD) δ 1.43–1.72 (m, 6H), 3.56 (t, J = 6.3 Hz, 2H), 3.66–3.75 (m, 3H).[S14b]

Heptane-1,4,7-triol (3u). According to the reference S15a, diethyl 4-oxoheptanedioate was prepared from furylacrylic acid (Aldrich F2080-7) in 61% yield. (^{1}H NMR δ 1.25 (t, J = 7.1 Hz, 6H), 2.60 (t, J = 6.6 Hz, 4H), 2.78 (t, J = 6.6 Hz, 4H), 4.12 (q, J = 7.1 Hz, 4H)). To a solution of diethyl 4-oxoheptanedioate (4.18 g, 18.2 mmol) in THF (200 mL) was added $LiAlH_4$ (3.44 g, 90.8 mmol) portionwise at 0 °C. The mixture was heated under reflux for 20 h and cooled. The resulting mixture was diluted with diethyl ether and quenched by addition of Na_2SO_4•$10H_2O$ and $MgSO_4$ at 0 °C. The resultant white precipitates were stirred until they are well-separated from the supernatant liquid, and then filtered through a pad of Celite and washed with methanol. The filtrate was concentrated *in vacuo* to give the crude product, which was purified by bulb-to-bulb distillation to give the title compound as a colorless oil (2.06 g, 77% yield, ^{1}H NMR (CD_3OD) δ 1.41–1.68 (m, 8H), 3.56 (t, J = 6.3 Hz, 4H), 3.55–3.57 (m, 1H).[S15b]

(2'-Hydroxymethyl-biphenyl-2-yl)diphenylmethanol (3x). To a solution of **4v** (1.58 g, 7.51 mmol) in THF (57 mL) was slowly added phenyl magnesium bromide (1.03 M in THF, 18.0 mL, 18.5 mmol) at 0 °C and the resulting mixture was refluxed for 6 h. The reaction mixture was cooled, diluted with diethyl ether, quenched with sat. NH_4Cl aq.. The separated organic layer was washed with brine, dried over $MgSO_4$, and filtered through a pad of Celite, and concentrated. The resultant solid was purified by recrystallization from toluene/hexane to give the title compound as a white solid (2.72 g, 98% yield); ^{1}H NMR δ 3.00–3.25 (m, 2H), 4.34 (d, J = 11.5 Hz, 1H), 4.53 (d, J = 11.5 Hz, 1H), 6.24 (dd, J = 7.5, 1.0 Hz, 1H), 6.78 (dd, J = 7.8, 1.2 Hz, 1H), 6.89 (dd, J = 7.5, 1.5 Hz, 1H), 7.02–7.08 (m, 5H), 7.18–7.34 (m, 9H), 7.45 (dd, J = 7.8, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR δ 63.5, 83.7, 126.5, 126.8, 127.0, 127.2, 127.3, 127.5, 127.7, 127.8, 127.9, 128.3, 129.0, 129.3, 130.5, 131.9, 138.4, 138.8, 141.4, 144.7, 146.6, 147.1; Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22; H, 6.05. Found: C, 85.26; H, 6.01.; R_f 0.20 (diethyl ether).

3) General procedure for the oxidative lactonization of diols or triols (3) catalyzed by Cp*Ru(PN) complexes and KO*t*-Bu. A degassed solution of **3** in acetone (0.05–1.0 M) was transferred to a mixture either of Cp*RuCl(cod), **1a**, and KO*t*-Bu (ternary), or of **2a** and KO*t*-Bu (binary) (1 mol% unless otherwise noted) placed in a 20-mL Schlenk tube. Then the mixture was stirred at 30 °C till the consumption of **3** was confirmed by TLC analysis and filtered through a plug of silica gel. The filtrate was concentrated under reduced pressure, and the residue was analyzed by ^{1}H NMR

spectroscopy. Yields of **4** were determined by integrating well-resolved characteristic resonances of **3** and **4**.

4a (0.5 M, ternary, yields after 1 h are indicated in the text) ^{1}H NMR δ 5.34 (s, 2H), 7.50–7.60 (m, 3H), 7.90–7.91 (m, 1H).

4b (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 2.22–2.33 (m, 2H), 2.50 (t, J = 7.6 Hz, 2H)), 4.35 (t, J = 7.6 Hz, 2H).

4c (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 0.88 (dd, J = 4.7, 3.4 Hz, 1H), 1.26–1.32 (m, 1H), 2.04–2.10 (m, 1H), 2.22–2.30 (m, 1H), 4.23 (d, J = 9.3 Hz, 1H), 4.36 (dd, J = 9.3, 4.9 Hz, 1H).[S16]

4d (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 2.05–2.20 (m, 2H), 2.39–2.45 (m, 1H), 2.50–2.63 (m, 1H), 3.07–3.25 (m, 2H), 4.24 (d, J = 9.3 Hz, 1H), 4.36 (dd, J = 9.3, 6.4 Hz, 1H).[S17]

4e (0.5 M, binary, 1 h, >99%) ^{1}H NMR δ 1.53–1.77 (m, 3H), 1.83–1.98 (m, 2H), 2.06–2.08 (m, 1H), 2.90–3.05 (m, 2H), 3.99 (dd, J = 9.3, 2.9 Hz, 1H), 4.47 (dd, J = 9.3, 7.8 Hz, 1H).[S18]

4f (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.20–1.26 (m, 3H), 1.60–1.67 (m, 3H), 1.79–1.86 (br, 1H), 2.09–2.19 (m, 1H), 2.43–2.53 (m, 1H), 2.65 (br, 1H), 3.96 (d, J = 8.8 Hz, 1H), 4.21 (dd, J = 8.8, 5.0 Hz, 1H).[S19]

4g (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.45–1.56 (m, 6H), 2.35 (brs, 1H), 2.62–2.65 (m, 1H), 2.81–2.89 (m, 1H), 2.93–2.99 (m, 1H), 4.22 (dd, J = 10.0, 2.9 Hz, 1H), 4.28 (dd, J = 10.0, 7.8 Hz, 1H).[S20]

4h (0.5 M, binary, 1 h, >99%) ^{1}H NMR δ 1.40–1.75 (m, 9H), 2.04–2.14 (m, 1H), 2.64–2.71 (m, 2H), 4.19–4.23 (m, 1H), 4.43–4.49 (m, 1H).[S21]

4i (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.85–2.00 (m, 1H), 2.20–2.85 (m, 5H), 4.03 (dd, J = 8.8, 2.0 Hz, 1H), 4.32 (dd, J = 8.8, 5.1 Hz, 1H), 5.74 (br, 1H), 5.75 (br, 1H).[S22]

4j (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.47 (d, J = 8.5 Hz, 1H), 1.65 (d, J = 8.5 Hz, 1H), 3.09–3.14 (m, 2H), 3.23–3.28 (m, 1H), 3.34 (br, 1H), 3.80 (dd, J = 9.8, 3.3 Hz, 1H), 4.29 (dd, J = 9.8, 8.5 Hz, 1H), 6.29-6.30 (m, 2H).[S23]

4k (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.25–1.62 (m, 4H), 2.66–2.82 (m, 3H), 3.09 (br, 1H), 3.84 (dd, J = 9.0, 3.4 Hz, 1H), 4.34 (dd, J = 9.0, 8.5 Hz, 1H), 6.25–6.35 (m, 2H).[S21]

4l (0.5 M, 3 mol%, binary, 1 h, 99%) ^{1}H NMR δ 2.41–2.48 (m, 2H), 2.51–2.59 (m, 2H), 2.88 (dd, J = 14.0, 7.0 Hz, 1H), 3.02 (dd, J = 14.0, 5.3 Hz, 1H), 3.78 (dd, J = 9.0, 7.6 Hz, 1H), 4.00 (dd, J = 9.0, 6.8 Hz, 1H), 6.91–6.93 (m, 2H), 7.08–7.25 (m, 8H).[S24]

4m (0.5 M, 3 mol%, binary, 8 h, >99%) ^{1}H NMR δ 2.44–2.63 (m, 4H), 2.84 (dd, J = 14.0, 6.9 Hz, 1H), 2.98 (dd, J = 14.0, 4.7 Hz, 1H), 4.00–4.04 (m, 1H), 4.10–4.15 (m, 1H), 5.93 (s, 4H), 6.47 (s, 2H), 6.59–6.62 (m, 2H), 6.68–6.77 (m, 2H).[S9b, S25]

4n (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.64 (d, J = 6.6 Hz, 3H), 5.57 (q, J = 6.6 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H).[S10b]

4n-d_1, 96% atom D (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.64 (s, 3H), 5.57 (q, J = 6.6 Hz, 0.04H), 7.45 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H).

4o (0.5 M, ternary, 1 h, >99%) ^{1}H NMR δ 1.67 (s, 6H), 7.41 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H). This spectrum was identical to those of commercially available **4o**.

4p (0.5 M, binary, 1 h, 96%) ^{1}H NMR δ 0.89 (t, J = 7.0 Hz, 3H), 1.33–1.86 (m, 9H), 2.33–2.34 (m, 1H), 2.52 (d, J = 7.0 Hz, 1H), 2.53 (d, J = 6.6 Hz, 1H), 4.49–4.52 (m, 1H). This spectrum was identical to those of commercially available **4p**.

4q (0.5 M, binary, 1 h, 95%) ^{1}H NMR δ 0.88 (t, J = 6.6 Hz, 3H), 1.20–1.92 (m, 13H), 2.27–2.38 (m, 1H), 2.51 (d, J = 7.0 Hz, 1H), 2.54 (d, J = 6.6 Hz, 1H), 4.44–4.53 (m, 1H). This spectrum was identical to those of commercially available **4q**.

4r (0.5 M, 3 mol%, binary, 1 h, >99%) ^{1}H NMR δ 0.90 (t, J = 6.6 Hz, 3H), 1.26–1.61 (m, 8H), 2.01–2.31 (m, 3H), 2.47–2.66 (m, 2H), 3.57–3.59 (m, 1H), 4.43 (dt, J = 7.3, 4.4 Hz, 1H).[S26]

4s (0.05 M, binary, 1 h, >99%) ^{1}H NMR δ 0.88 (t, J = 6.7 Hz, 3H), 1.26–1.61 (m, 22H), 2.06–2.31 (m, 3H), 2.47–2.68 (m, 2H), 3.57–3.59 (m, 1H), 4.43 (dt, J = 7.3, 4.4 Hz, 1H).[S27]

4t (0.5 M, 3 mol%, binary, 31 h, >99%) ^{1}H NMR δ 1.64 (brs, 1H), 1.90–2.00 (m, 3H), 2.34–2.45 (m, 1H), 2.56 (dd, J = 9.4, 6.7 Hz, 2H), 3.84 (t, J = 6.0 Hz, 2H), 4.64–4.76 (m, 1H).[S28]

4u (0.1 M, 3 mol%, binary, 48 h, 97%) ^{1}H NMR δ 1.56–1.88 (m, 6H), 2.23–2.34 (m, 1H), 2.50 (dd, J = 9.5, 6.8 Hz, 2H), 3.59 (t, J = 6.0 Hz, 2H), 4.46–4.50 (m, 1H).[S29]

4v (0.25 M, ternary, 1 h, >99%) ^{1}H NMR δ 5.80 (s, 2H), 7.34–7.38 (m, 1H), 7.53 (dd, J = 8.3, 7.1 Hz, 1H), 7.63 (dd, J = 8.3, 7.1 Hz, 1H), 7.82 (dd, J = 8.3, 0.8 Hz, 1H), 8.08 (dd, J = 8.3, 1.0 Hz, 1H), 8.36 (dd, J = 7.1, 1.0 Hz, 1H). This spectrum was identical to those of commercially available **4v**.

4w (0.5 M, ternary, 2 h, 93%) ^{1}H NMR δ 5.00 (d, J = 16 Hz, 2H), 7.25–7.70 (m, 7H), 7.94–7.96 (m, 1H). This spectrum was identical to those of commercially available **4w**.

4x (0.5 M, binary, >99%, 3 h) ^{1}H NMR δ 6.47 (d, J = 8.8 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.64 (dd, J = 7.8, 1.0 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.97 (t, J = 7.8 Hz, 1H), 7.08–7.22 (m, 4H), 7.24–7.36 (m, 4H), 7.47–7.62 (m, 4H), 8.15 (d, J = 8.5 Hz, 1H).[S30]

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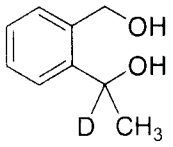
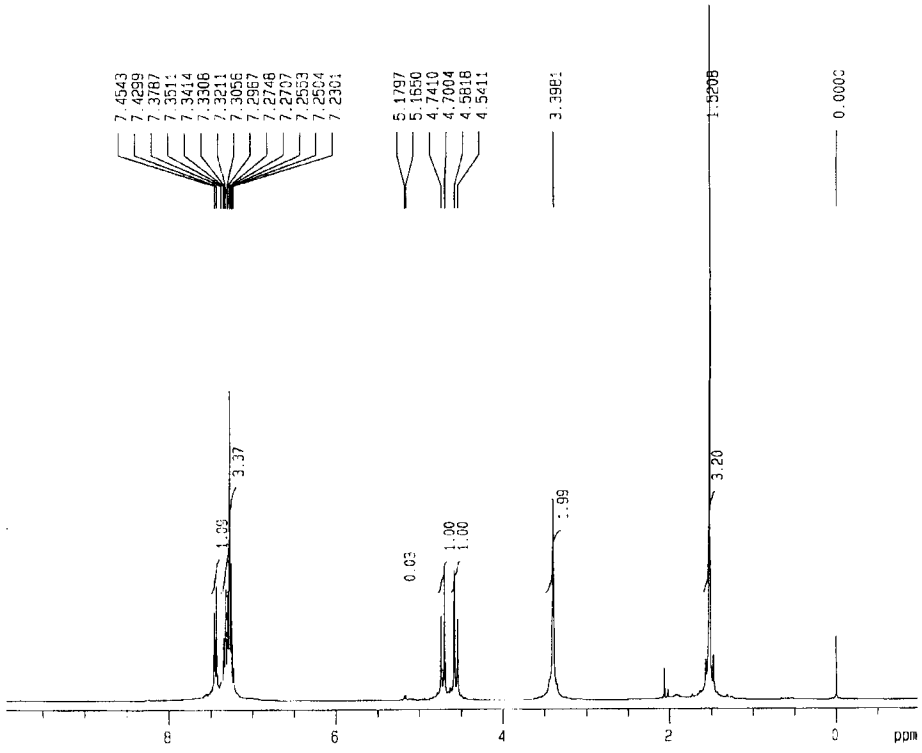
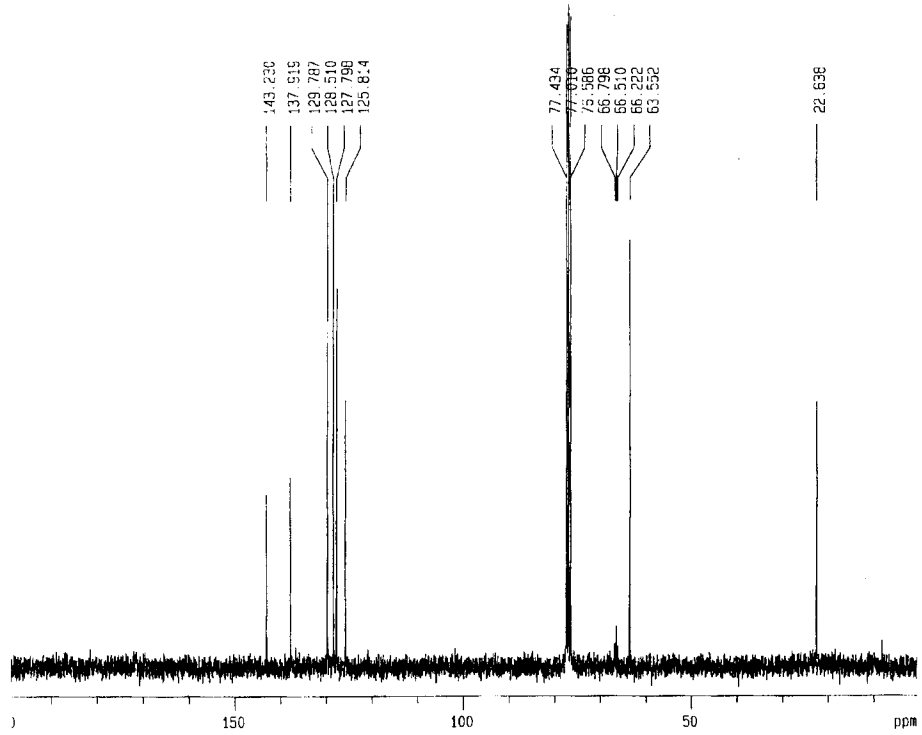
5) NMR spectra

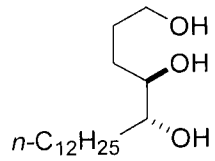
α-Methyl-α-deutrio-1,2-benzenedimethanol (**3n-d_1, 96% atom D**)

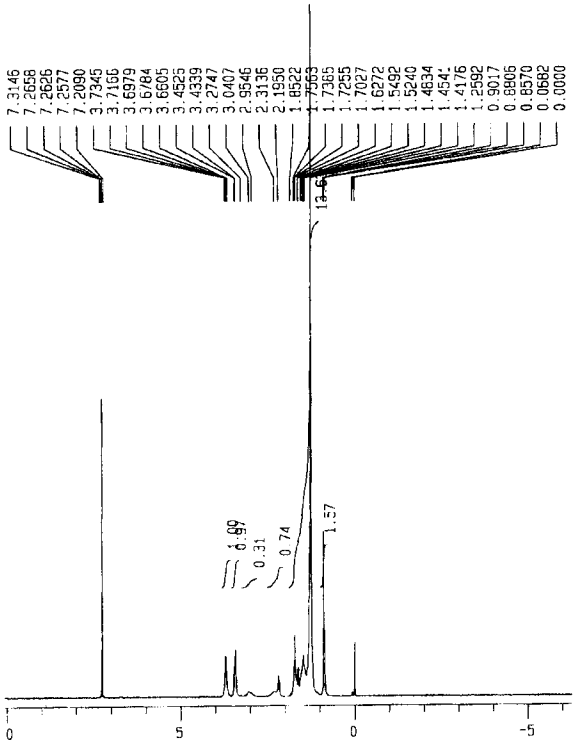


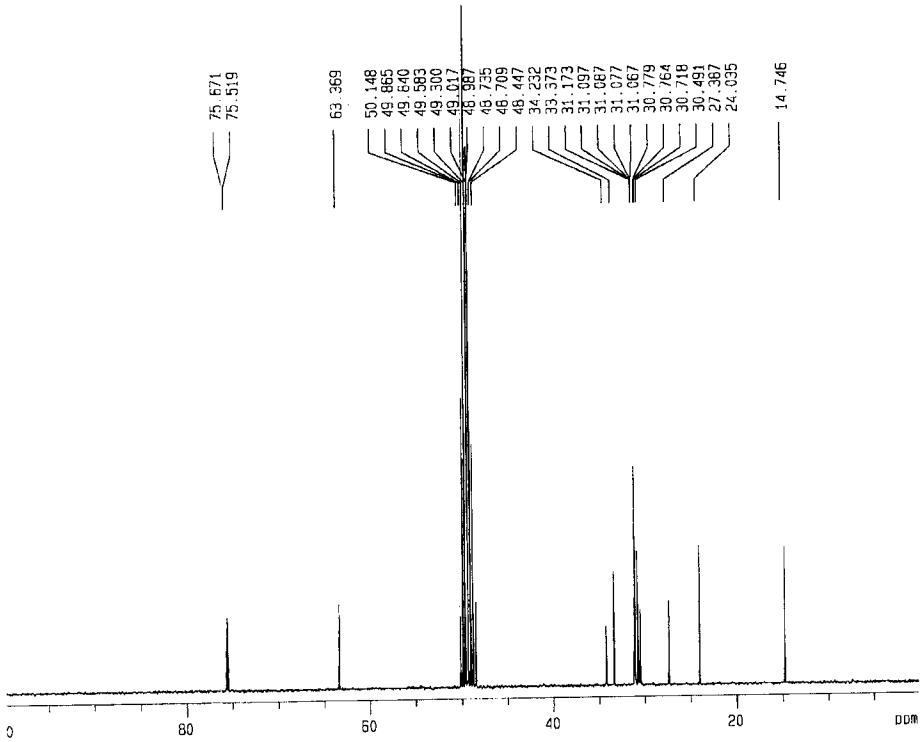




cis-Heptadecane-1,4,5-triol (**3s**)







(2'-Hydroxymethyl-biphenyl-2-yl)diphenylmethanol (**3x**)