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Base- and Co(II)-Catalyzed Ring-Opening Reactions of Perhydrooxireno[2,3-*d*][1,2]dioxines: An Efficient Route to 4-Hydroxy-2,3-epoxy-ketones

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A series of 3,4,6-substituted 3,6-dihydro-1,2-dioxines were epoxidized with *m*-chloroperbenzoic acid to furnish perhydrooxireno[2,3-*d*][1,2]dioxines (epoxy-1,2-dioxines) in yields ranging from 51% to 93% with de's from 26% to 100%. Unsymmetrical epoxy-1,2-dioxines were ring-opened using triethylamine to yield 4-hydroxy-2,3-epoxy-ketones quantitatively, and *meso*-epoxy-1,2-dioxines were ring-opened using Co(II) salen complexes to afford 4-hydroxy-2,3-epoxy-ketones in 77−98% yield. The first reported examples of the catalytic asymmetric ring-opening of *meso*-epoxy-1,2-dioxines using a range of chiral Co(II) salen and *β*-ketoiminato complexes to afford highly enantio-enriched 4-hydroxy-2,3-epoxy-ketones are also presented.

Introduction

3,6-Dihydro-1,2-dioxines **1** (endoperoxides) are an important class of organic peroxides because of their versatility in organic synthesis.[1] 1,2-Dioxines may be homolytically or heterolytically ring-opened as a result of their weak O−O bond to yield bis-epoxides or reactive *cis*-*γ*-hydroxy enones, which may then undergo further reaction.[2] The transition-metal-catalyzed (homolytic) ring-opening of 3,6-dihydro-1,2-dioxines of type **1** may be effected by complexes of Fe(II), Ru(II), and Co(II).[3−5] The base-induced ring-opening proceeds readily with neutral amine bases in high yield.[6] Furthermore, we have reported that *meso*-1,2-dioxines may be ring-opened using chiral Co(II) salen or *β*-ketoiminato complexes to furnish *cis*-*γ*-hydroxyenones with high enantiomeric excesses.[7] To increase the scope of this asymmetric ring-opening reaction we decided to examine 1,2-dioxines where the double bond had been either modified or removed. This led us to consider epoxidation of the parent *meso*-3,6-dihydro-1,2-dioxines **1**, as the products from the reaction would again be *meso*. Although many tricyclic perhydrooxireno-[2,3-*d*][1,2]dioxines (epoxy-1,2-dioxines) have been previously synthesized, few examples of bicyclic epoxy-1,2-dioxines **2** exist, and none of the products from the reaction with transition metals have been characterized.[8] Moreover, a unique opportunity exists for an examination of the selectivity of the transition-metal-catalyzed ring-opening reaction of epoxy-1,2-dioxines **2**. Application of the asymmetric version of the ring-opening could then be applied with the aim of generating useful chiral synthons. Nonsymmetrical epoxy-1,2-dioxines could similarly yield substituted 4-hydroxy-2,3-epoxy-ketones if ring-opened with an appropriate base. The current report describes the preparation of epoxy-1,2-dioxines **2**, their ring-opening reactions, and the characterization of the product 4-hydroxy-2,3-epoxy-ketones.

Results and Discussion

Preparation of Epoxy-1,2-dioxines. 1,2-Dioxines **1a−g** used in this study were prepared by the Rose

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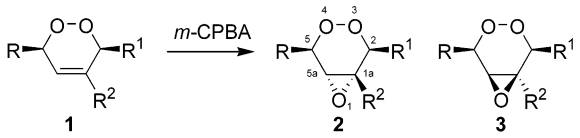
TABLE 1. Oxidation of 3,6-Dihydro-1,2-dioxines Using *m*-CPBA

entry[a]	1,2-dioxine	time (d)	**2**:**3**	yield[b]
1	**1a**	14[c]	100:0	83
2	**1b**	7	84:16	93
3	**1c**	10	84:16	74
4	**1d**	1	63:37	85
5[d]	**1e**	1	77:23	84
6	**1f**	3	69:31	51
7	**1g**	2	93:7	92

[a] Reactions were typically performed on a 1 mmol scale with 1.2 equiv of *m*-CPBA in CH_2Cl_2 (5 mL). [b] Combined isolated yield. [c] 94% complete by ^{1}H NMR. [d] 1.8 equiv of *m*-CPBA was used.

SCHEME 1



1a R = Ph, R^1 = Ph, R^2 = H
1b R = Ph, R^1 = Me, R^2 = H
1c R = Ph, R^1 = H, R^2 = H
1d R = *n*-Pr, R^1 = *n*-Pr, R^2 = H
1e R = C_6H_{11}, R^1 = C_6H_{11}, R^2 = H
1f R = *i*-Pr, R^1 = *i*-Pr, R^2 = H
1g R = Ph, R^1 = H, R^2 = Me

Bengal sensitized addition of singlet oxygen to the corresponding 1,3-butadiene as previously reported.[2a,9] The epoxidation of the 1,2-dioxines was carried out in a procedure analogous to that reported by Herz.[3b] Thus, when **1** was allowed to react with *m*-CPBA, the sole isolable products were epoxy-1,2-dioxines **2** and **3** with moderate to good diastereoselectivity in excellent yield, Table 1, Scheme 1. Diastereoselectivity was greatest for the 3,6-diphenyl dioxine **1a** where none of the all-*cis* isomer was detectable by ^{1}H NMR or TLC, although the reaction proceeded only sluggishly, entry 1. Substitution at the 4-position in the parent 1,2-dioxine **1g** was found to increase the observed diastereoselectivity; compare entries 3 and 7.

The identity of the major *trans*-isomer **2** was determined by ^{1}H NMR. Typically, the protons attached to C1a and C2 showed no or very little coupling as a result of an approximate 90° dihedral angle and therefore appeared as broadened singlets as in **2a** or doublets where not symmetrical, **2b**,**c**. The minor isomer **3** with all groups *cis* typically showed a larger coupling between the C1a and C2 protons, causing the signals to appear as non-first-order multiplets. Both isomers were considerably more stable than their 3,6-dihydro counterparts **1** and could be stored neat at room temperature for several months without decomposition.

We next examined the ring-opening of epoxy-1,2-dioxines **2** and **3** using either a mild amine base or transition metal catalyst, the results of which are summarized in Scheme 2 and Table 2. Exploiting either method resulted in the corresponding 4-hydroxy 2,3-epoxy-ketones **4** or **5** being formed in excellent yields. The proposed mechanisms for the ring-openings of these

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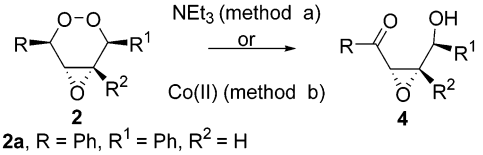
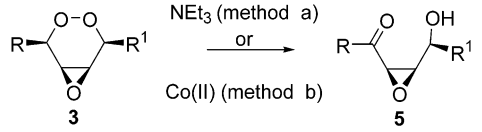
SCHEME 2



2a, R = Ph, R^1 = Ph, R^2 = H
2b, R = Ph, R^1 = Me, R^2 = H
2c, R = Ph, R^1 = H, R^2 = H
2d, R = *n*-Pr, R^1 = *n*-Pr, R^2 = H
2e, R = C_6H_{11}, R^1 = C_6H_{11}, R^2 = H
2f, R = *i*-Pr, R^1 = *i*-Pr, R^2 = H
2g, R = Ph, R^1 = H, R^2 = Me



3b, R = Ph, R^1 = Me
3e, R = C_6H_{11}, R^1 = C_6H_{11}

TABLE 2. Ring-Opening of 2 or 3 Using NEt_3 (Method a) or Co(II) Salen (Method b) Affording 2,3-Epoxy-ketones 4 and 5

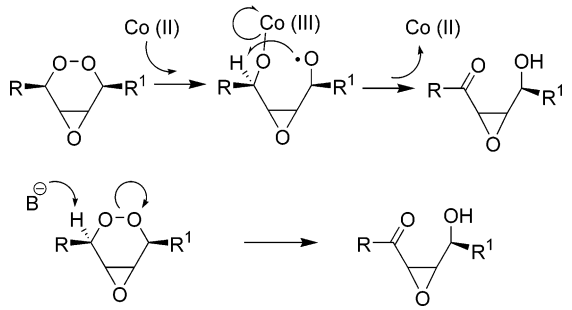
entry[a]	dioxine	method	product	yield[b]
1	**2a**	a	**4a**	100
2	**2a**	b	**4a**	98
3	**2b**	a	**4b**	100
4	**2c**	a	**4c**	86
5	**2d**	b	**4d**	96
6	**2e**	b	**4e**	95
7	**2f**	b	**4f**	89
8	**2g**	a	**4g**	84
9	**3b**	a	**5b**	83
10	**3e**	b	**5e**	77

[a] Reactions were typically performed on a 40 mg scale with 1 equiv of triethylamine or 2.5% w/w of *N*,*N*′-bis(salicylidene)ethylenediaminocobalt(II). [b] Isolated yield by silica gel chromatography.

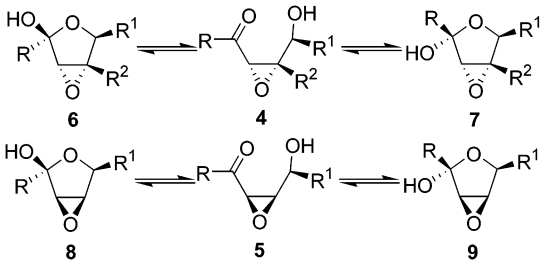
epoxy-1,2-dioxines (**2** or **3**) are analogous to the ring-opening reactions of 3,6-dihydro-1,2-dioxines. Thus, in the case of Co(II) catalysis, single electron transfer from the cobalt to oxygen affords an oxygen-centered radical that then undergoes a 1,5-hydrogen atom abstraction, regenerating the Co(II) catalyst, Scheme 3.[7,10] The outcome of the Co(II)-catalyzed ring-opening does not rely on the acidity of the proton(s) α to the O−O linkage but does, however, depend on the steric size of the attached R-groupings. This reaction was only applied to the use of symmetrical epoxy-1,2-dioxines to avoid formation of regioisomers. Base catalysis involves the removal of the most acidic proton α to the O−O linkage and then rearrangement through cleavage of the O−O linkage to afford the 4-hydroxy-2,3-epoxy-ketones.[6] The presence of an α-phenyl grouping significantly increases the acidity of the α-proton, causing the ring-opening to proceed regioselectively.

(10) The synthesis of catalysts **10a**−**e** and **11a**−**d** will be reported elsewhere. (a) For general syntheses of *β*-ketoiminato catalysts, see: Nagata, T.; Imagawa, K.; Yamada, T. *Inorg. Chim. Acta* **1994**, *220*, 283. Sugi, K. D.; Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1994**, 1259. (b) For the syntheses of cobalt salen catalysts, see: Fukuda, T.; Katsuki, T. *Tetrahedron* **1997**, *53*, 7201. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. *Tetrahedron: Asymmetry* **1991**, *2*, 481.

SCHEME 3



SCHEME 4



The characterization of the product hydroxy ketones by NMR was complicated as the products existed in both their acyclic and *cis* and *trans* cyclic furanol forms, Scheme 4. 2D ^{1}H and ^{13}C NMR was used to assign the resonances in the 1D ^{1}H spectra from which isomeric ratios could be determined. The furanol forms showed resonances at ca. δ 100 ppm in their ^{13}C NMR spectra, consistent with a hemiketal carbon, whereas phenyl-substituted hydroxy ketones showed resonances at ca. δ 200 ppm for the aryl ketone. Long range ^{1}H−^{13}C correlation spectroscopy (HMBC) was used to link resonances in the 1D ^{1}H with the identifying ^{13}C signals. It was not possible to assign all aromatic peaks in the ^{13}C spectra to a specific anomer for all furanols. A lack of through-space interactions in the 2D ^{1}H NMR of the furanols **6**/**7** and **8**/**9** made assignment of the anomeric carbon difficult, and thus although all signals could be assigned to an anomer, the relative configuration of the anomers could not be determined.

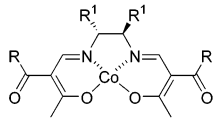
The Nujol mull IR spectra of the 4-hydroxy-2,3-epoxy-ketones were used to determine whether the epoxy-ketone existed in its cyclic or acyclic form in the solid state. Typically, phenyl-substituted epoxy-ketones existed in their acyclic form when in the solid state, as they showed an aryl−carbonyl stretching adsorption at 1670−1680 cm^{-1}. The alkyl-substituted epoxy-ketones existed solely in their cyclic forms both in the solid state and in solution, as could be seen by an absence of the carbonyl absorption. Specific population ratios for each of the epoxy-ketones are given in Table 3. X-ray crystallography was used to confirm the identity of the epoxy-ketone **4b**, validating the assignment of structure in the solid state for the series of epoxy-ketones **4** and the *trans* relationship between the epoxidic oxygen and R-groups in the parent epoxy-1,2-dioxine **2b**.

Asymmetric Ring-Opening of *meso*-1,2-Dioxines. We have recently shown that *meso*-3,6-dihydro-1,2-dioxines **1** may be ring-opened with high enantioselectivity using chiral Schiff base complexes of Co(II).[7] We anticipated that this methodology could also be applied to the

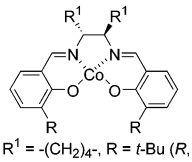
TABLE 3. Isomeric Ratios of 4-Hydroxy-2,3-epoxy-ketones Measured When Neat and Dissolved in $CDCl_3$

entry	ketone	neat[a]	ratio[b] **4:(6:7)**
1	**4a**	**4a**	57:(37:6)
2	**4b**	**4b**	41:(51:8)
3[c]	**4b**		27:(68:5)
4	**4c**	oil[d]	39:(55:6)
5	**4d**	**6d/7d**	0:(79:21)
6	**4e**	**6e/7e**	0:(78:22)
7	**4f**	**6f/7f**	0:(70:30)
8	**4g**	**6g/7g**	34:(57:9)
9	**5b**	**5b**	26:(61:13)[e]
10	**5e**	**8e/9e**	0:(77:23)[e]

[a] Refers to which isomeric form the 4-hydroxy-2,3-epoxy-ketone exists in when neat. Determined by IR. [b] Ratio determined by ^{1}H NMR by dissolving sample in $CDCl_3$ and allowing it to equilibrate for 1 h before integrating peak height. Anomers **6** and **7** could not be unambiguously assigned. [c] Measured in the presence of 0.5 equiv of DABCO. [d] Could not be determined. [e] Ratio of **5** : **8**: **9**.



10a R^1 = Ph, R = ethyl (*S*, *S* isomer)
10b R^1 = Ph, R = (-) bornoxy (*R*, *R* isomer)
10c R^1 = Ph, R = (-) bornoxy (*S*, *S* isomer)
10d R^1 = Ph, R = (-) menthoxy (*R*, *R* isomer)
10e R^1 = Ph, R = (+) menthoxy (*S*, *S* isomer)



11a R^1 = -$(CH_2)_4$-, R = *t*-Bu (*R*, *R* isomer)
11b R^1 = Ph, R = *t*-Bu (*R*, *R* isomer)
11c R^1 = Ph, R = H (*R*, *R* isomer)
11d R^1 = -$(CH_2)_4$-, R = H (*R*, *R* isomer)

FIGURE 1. Catalysts for the asymmetric ring-opening of *meso*-epoxy-1,2-dioxines.

TABLE 4. Asymmetric Ring-Opening of *meso*-1,2-Dioxines 2a or 2f

entry[a]	dioxine	catalyst	mol %	temp	ratio[b] (ee)
1	**2a**	**10a**	5	20	70:30 (40)
2		**10b**	5	20	12:88 (76)
3		**10c**	5	20	79:21 (58)
4		**10d**	5	20	16:84 (68)
5		**10e**	2.5	20	85:15 (70)
6		**10e**	5	20	84:16 (68)
7		**10e**	7.5	20	92:8 (84)
8		**10e**	5	0	89:11 (78)
9		**10e**	5	−15	89:11 (78)
10		**10e**	7.5	0	92:8 (84)
11[c]		**10e**	5	20	86:14 (72)
12		**11a**	5	20	17:83 (66)
13		**11b**	5	20	16:84 (68)
14		**11c**	5	20	20:80 (60)
15		**11d**	5	20	35:65 (30)
16	**2f**	**10a**	5	20	67:33 (34)
17		**10e**	5	20	82:18 (64)

[a] Reactions were performed in THF (1 mL) on a 20 mg scale by dissolving catalyst in solvent and allowing it to equilibrate for 1 h before addition of 1,2-dioxine. [b] Ratio determined by chiral shift NMR using europium tris[3-(heptafluoropropylhydroxymethylene)]-(+)-camphorate in $CDCl_3$. [c] Reaction performed in CH_2Cl_2.

ring-opening of the *meso*-1,2-dioxines generated in this study. Thus, 1,2-dioxines **2a** and **2f** were treated with a range of chiral Co(II) complexes **10a**−**e** and **11a**−**d** (Figure 1)to afford the hydroxy-ketones **4a** and **4f** as the sole products, the results of which are summarized in Table 4.[10]

The trends observed were similar to those observed for the 3,6-dihydro-1,2-dioxines **1**; however, ee's were slightly improved in the two systems tested here. Best results

obtained for the diaryl 1,2-dioxine **2a** were from **10e** at a catalyst concentration of 7.5%. Menthyl ester catalysts **10d** and **10e** with *R,R* and *S,S* backbone stereochemistry, respectively, gave equal and opposite enantiomeric ratios as expected. The dialkyl 1,2-dioxine **2f** gave ee's slightly lower than the diaryl 1,2-dioxine **2a**, entries 1, 5, and 16−17, a result analogous to that found when starting with **1**. Higher ee's were also seen from the bis-iminato complexes as compared to the salen type complexes. Over the range studied, no great changes in ratio due to temperature were observed, however, a slight increase in ee was seen with increasing catalyst concentrations. This also agrees with the results obtained for the ring-opening of **1a**. The absolute stereochemistry of the cis-γ-hydroxyenone obtained from the reaction of **1** has been previously determined unambiguously by several methods.[2c,7,11] Although the expected selectivity for the epoxy-1,2-dioxines is the same, the assignment of the absolute stereochemistry of the product epoxy-ketone **4** obtained from **2** is not yet confirmed and will be made in an upcoming natural product synthesis.

In summary, epoxy-1,2-dioxines **2** can be readily prepared from 3,6-dihydro-1,2-dioxines **1** in high yield and good to excellent de. Exposure of these epoxy-1,2-dioxines to either triethylamine or Co(II) complexes allowed for the preparation of 4-hydroxy-2,3-epoxy-ketones **4**/**5** in excellent yields. The use of chiral Co(II) complexes allowed for the asymmetric ring-opening of *meso*-epoxy-1,2-dioxines in a highly enantioselective manner, again affording these useful synthons **4**/**5**.

Experimental Section

General Procedure for the Epoxidation of 3,6-Dihydro-1,2-dioxines. To a stirred solution of 1,2-dioxine (1 mmol) in CH_2Cl_2 (5 mL) was added 70% *m*-chloroperbenzoic acid (295 mg, 1.2 mmol), and the reaction was left to stir at ambient temperature until complete by TLC. The solvent was removed under reduced pressure, and the products were purified by flash chromatography.

(±)-(1a*R*,2*S*,5*R*,5a*S*)-2,5-Diphenylperhydrooxireno[2,3-*d*][1,2]dioxine 2a. Colorless solid; mp 97−99 °C; R_f 0.25 (90:10 hexane/ethyl acetate); IR (Nujol) 1492, 740, 695 cm^{-1}; ^1H NMR (300 MHz) δ 3.73 (s, 2H), 5.43 (s, 2H), 7.38−7.49 (m, 10H); ^{13}C NMR (75 MHz) δ 52.8, 80.1, 127.8, 128.8, 128.9, 136.0; MS (EI) *m/z* (%) 254 (M^+, 10), 222 (95), 193 (70),131 (50), 77 (100). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.54. Found: C, 75.8; H, 5.58.

(±)-(1a*R*,2*S*,5*R*,5a*S*)-2-Methyl-5-phenylperhydrooxireno-[2,3-*d*][1,2]dioxine 2b. Colorless solid; mp 72−72 °C; R_f 0.20 (1:1 hexane/CH_2Cl_2); IR (Nujol) 1492, 1042, 749, 696 cm^{-1}; ^1H NMR (300 MHz) δ 1.48 (d, J = 6.6 Hz, 3H), 3.33 (d, J = 4.2 Hz, 1H), 3.55 (d, J = 4.2 Hz, 1H), 4.54 (q, J = 6.6 Hz, 1H), 5.30 (s, 1H), 7.38−7.44 (m, 5H); ^{13}C NMR (150 MHz) δ 15.9, 52.6, 52.9, 74.2, 80.1, 127.9, 128.7, 128.9, 136.0; MS (EI) *m/z* (%) 192 (M^+, 60), 160 (90), 131 (100), 105 (90). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.76; H, 6.50.

(±)-(1a*S*,2*R*,5a*S*)-2-Phenylperhydrooxireno[2,3-*d*][1,2]-dioxine 2c. Colorless oil; R_f 0.37 (1:1 hexane/CH_2Cl_2); IR (neat) 3033, 2913, 1494, 1455, 1036 cm^{-1}; ^1H NMR (300 MHz) δ 3.51 (br d, J = 4.5 Hz, 1H), 3.59 (dd, J = 4.5, 0.6 Hz, 1H), 4.42 (d, J = 13.5 Hz, 1H), 4.58 (dd, J = 13.5, 1.2 Hz, 1H), 5.38 (s, 1H), 7.39−7.42 (m, 5H); ^{13}C NMR (50 MHz) δ 48.6, 53.4, 69.2, 81.3, 127.9, 128.8, 129.2, 135.5; MS (EI) *m/z* (%) 178 (M^+, 20), 131 (30), 105 (100); HRMS of **2c** $C_{10}H_{10}O_3$ calcd 178.0629, found 178.0628.

(±)-(1a*R*,2*S*,5*R*,5a*S*)-2,5-Dipropylperhydrooxireno[2,3-*d*][1,2]dioxine 2d. Colorless oil; R_f 0.31 (1:1 hexane/CH_2Cl_2); IR (neat) 2961, 2874, 1465, 1380, 1068, 1005, 802 cm^{-1}; ^1H NMR (300 MHz) δ 0.96 (t, J = 6.9 Hz, 6H), 1.44−1.57 (m, 6H), 1.60−1.82 (m, 2H), 3.19 (d, J = 0.6 Hz, 2H), 4.24 (dd, J = 7.8, 4.2 Hz, 2H); ^{13}C NMR (75 MHz) δ 13.8, 18.4, 32.3, 52.3, 77.8; MS (EI) *m/z* (%) 186 (M^+, 20), 154 (50), 125 (70), 57 (60), 43 (100); HRMS of **2d** $C_{10}H_{18}O_3$ calcd 186.1255, found 186.1250.

(±)-(1a*R*,2*S*,5*R*,5a*S*)-2,5-Dicyclohexylperhydrooxireno-[2,3-*d*][1,2]dioxine 2e. Colorless solid; mp 61.5−63 °C; R_f 0.21 (1:1 hexane/CH_2Cl_2); IR (Nujol) 1450, 1100, 1013, 845 cm^{-1}; ^1H NMR (300 MHz) δ 1.13−1.29 (m, 10H), 1.64−1.91 (m, 12H), 3.32 (s, 2H), 3.96 (d, J = 6.9 Hz, 2H); ^{13}C NMR (75 MHz) δ 25.7, 25.8, 26.1, 28.3, 29.0, 39.1, 51.3, 81.7; MS (EI) *m/z* (%) 266 (M^+, 20), 249 (15), 234 (10), 83 (100). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.83. Found: C, 72.37; H, 9.86.

(±)-(1a*R*,2*S*,5*R*,5a*S*)-2,5-Diisopropylperhydrooxireno-[2,3-*d*][1,2]dioxine 2f. Colorless oil; R_f 0.15 (1:1 hexane/CH_2Cl_2); IR (neat) 2964, 1469, 1389, 1370, 991 cm^{-1}; ^1H NMR (300 MHz) δ 1.03 (d, J = 6.9 Hz, 6H), 1.03 (d, J = 6.9 Hz, 6H), 2.02 (oct, J = 6.9 Hz, 2H), 3.30 (d, J = 0.9 Hz, 2H), 3.91 (d, J = 6.9 Hz, 2H); ^{13}C NMR (75 MHz) δ 18.4, 18.6, 29.4, 51.2, 82.4; MS (EI) *m/z* (%) 186 (M^+, 5), 101 (30), 71 (70), 43 (100); HRMS of **2f** $C_{10}H_{18}O_3$ calcd 186.1255, found 186.1247.

(±)-(1a*S*,5*R*,5a*R*)-1a-Methyl-5-phenylperhydrooxireno-[2,3-*d*][1,2]dioxine 2g. Colorless solid; mp 61.5−63 °C; R_f 0.43 (CH_2Cl_2); IR (Nujol) cm^{-1}; ^1H NMR (300 MHz) δ 1.48 (s, 3H), 3.39 (s, 1H), 4.21 (d, J = 13.2 Hz, 1H), 4.43 (d, J = 13.2 Hz, 1H), 5.37 (s, 1H), 7.35−7.42 (m, 5H); ^{13}C NMR (75 MHz) δ 18.0, 54.5, 60.6, 72.4, 81.4, 127.9, 128.8, 129.2, 135.5; MS (EI) *m/z* (%) 192 (M^+, 20), 160 (95), 105 (90), 43 (100). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.75; H, 6.51.

(±)-(1a*S*,2*S*,5*R*,5a*R*)-2-Methyl-5-phenylperhydrooxireno-[2,3-*d*][1,2]dioxine 3b. Colorless oil; R_f 0.28 (1:1 hexane/CH_2Cl_2); IR (neat) 2996, 2932, 1496, 1454, 1371, 1024, 700 cm^{-1}; ^1H NMR (300 MHz) δ 1.75 (d, J = 6.6 Hz, 3H), 3.79 (dd, J = 4.4, 4.4 Hz, 1H), 3.84 (dd, J = 4.4, 1.6 Hz, 1H), 4.77 (dq, J = 6.6, 3.6 Hz, 1H), 5.55 (d, J = 1.6 Hz, 1H), 7.51−7.67 (m, 3H), 7.77−7.82 (m, 2H); ^{13}C NMR (50 MHz) δ 14.9, 52.1, 53.7, 73.4, 79.1, 128.2, 128.7, 128.9, 135.5; MS (EI) *m/z* (%) 192 (M^+, 100), 160 (50), 131 (70), 105 (65); HRMS of **3b** $C_{11}H_{12}O_3$ calcd 192.0786, found 192.0778.

(±)-(1a*R*,2*R*,5a*R*)-2-Phenylperhydrooxireno[2,3-*d*][1,2]-dioxine 3c. Colorless oil; R_f 0.40 (1:1 hexane/CH_2Cl_2); IR (neat) 2917, 1494, 1454, 1423, 1030 cm^{-1}; ^1H NMR (300 MHz) δ 3.53 (ddd, J = 4.5, 0.9, 0.6 Hz, 1H), 3.66 (ddd, J = 4.5, 4.5, 1.2 Hz, 1H), 4.38 (dd, J = 13.5, 4.5 Hz, 1H), 4.60 (ddd, J = 13.5, 1.2, 0.6 Hz, 1H), 5.37 (d, J = 0.9 Hz, 1H), 7.39−7.42 (m, 5H); ^{13}C NMR (150 MHz) δ 50.5, 51.0, 70.1, 79.8, 128.6, 128.6, 129.3, 134.8; MS (EI) *m/z* (%) 178 (M^+, 60), 131 (90), 105 (100); HRMS of **3c** $C_{10}H_{10}O_3$ calcd 178.0629, found 178.0634.

(±)-(1a*R*,2*R*,5*S*,5a*S*)-2,5-Dipropylperhydrooxireno[2,3-*d*][1,2]dioxine 3d. Colorless oil; R_f 0.48 (1:1 hexane/CH_2Cl_2); IR (neat) 2961, 2874, 1465, 1379, 1253, 913, 668 cm^{-1}; ^1H NMR (300 MHz) δ 0.96 (t, J = 7.2 Hz, 6H), 1.43−1.78 (m, 8H), 3.37−3.38 (m, 2H), 4.21−4.26 (m, 2H); ^{13}C NMR (75 MHz) δ 13.9, 18.5, 31.3, 52.3, 77.2; MS (EI) *m/z* (%) 186 (M^+, 5), 154 (30), 125 (30), 71 (50), 43 (100); HRMS of **3d** $C_{10}H_{18}O_3$ calcd 186.1255, found 186.1249.

(±)-(1a*R*,2*R*,5*S*,5a*S*)-2,5-Dicyclohexylperhydrooxireno-[2,3-*d*][1,2]dioxine 3e. Colorless oil; R_f 0.54 (1:1 hexane/CH_2Cl_2); IR (neat) 2925, 2852, 1449, 1254, 983, 911 cm^{-1}; ^1H NMR (300 MHz) δ 0.96−1.36 (m, 10H), 1.67−2.00 (m, 12H), 3.42−3.43 (m, 2H), 3.89 (br d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz) δ 25.4, 25.7, 26.3, 28.4, 29.5, 37.4, 51.1, 81.8; MS (EI) *m/z* (%) 266 (M^+, trace), 249 (10), 234 (10), 216 (20), 83 (100); HRMS of **3e** $C_{16}H_{26}O_3$ calcd 266.1881, found 266.1871.

(±)-(1a*R*,2*R*,5*S*,5a*S*)-2,5-Diisopropylperhydrooxireno-[2,3-*d*][1,2]dioxine 3f. Colorless oil; R_f 0.42 (1:1 hexane/CH_2-

(11) The backbone (diamine portion) stereochemistry is responsible for the sign of the induction. *R,R* backbone stereochemistry in the catalyst gives *S* absolute stereochemistry in the product obtained from **1a**; *S,S* backbone stereochemistry yields *R* absolute stereochemistry.

Cl_2); IR (neat) 2961, 2874, 1465, 1379, 1253, 913 cm^{-1} ; ^1H NMR (300 MHz) δ 1.02 (d, J = 6.6 Hz, 6H), 1.06 (d, J = 6.6 Hz, 6H), 2.11 (dsept, J = 9.0, 6.6 Hz, 2H), 3.43−3.46 (m, 2H), 3.78−3.82 (m, 2H); ^{13}C NMR (75 MHz) δ 18.3, 19.3, 28.3, 51.3, 82.8; MS (EI) *m*/*z* (%) 186 (M^+, trace), 139 (30), 71 (60), 43 (100); HRMS of **3f** $C_{10}H_{18}O_3$ calcd 186.1255, found 186.1256.

(±)-(1a*R*,5*R*,5a*S*)-1a-Methyl-5-phenylperhydrooxireno-[2,3-*d*][1,2]dioxine 3g. Colorless oil; R_f 0.53 (CH_2Cl_2); IR (neat) 2915, 1495, 1454, 1267, 1004, 734, 698 cm^{-1}; ^1H NMR (200 MHz) δ 1.51 (s, 3H), 3.39 (s, 1H), 4.20 (d, J = 13.6 Hz, 1H), 4.50 (dd, J = 13.6, 0.4 Hz, 1H), 5.35 (m, 1H), 7.36−7.41 (m, 3H), 7.50−7.54 (m, 2H); ^{13}C NMR (75 MHz) δ 20.0, 57.3, 57.6, 73.6, 79.5, 128.3, 128.5, 129.1, 135.0; MS (EI) *m*/*z* (%) 192 (M^+, 20), 145 (70), 131 (80), 105 (100); HRMS of **3g** $C_{11}H_{12}O_3$ calcd 192.0786, found 192.0790.

General Procedure for the Ring-Opening of Perhydrooxireno[2,3-*d*][1,2]dioxines using Co(II) Salen. To a stirred solution of *N*,*N*′-bis(salicylidene)ethylenediaminocobalt-(II) (10 mg, 0.03 mol) in CH_2Cl_2 (5 mL) at ambient temperature was added 1,2-dioxine (1 mmol), and the reaction left to stir until complete by TLC (3−16 h). All volatiles were then removed in vacuo, and the product purified by flash chromatography.

(±)-{(2*S*,3*S*)-3-[(1*S*)-1-Hydroxy-1-phenylmethyl]oxiran-2-yl}(phenyl)methanone 4a. Colorless solid; mp 148−150 °C; R_f 0.50 (60:40 hexane/ethyl acetate); IR (Nujol) 3408, 1673, 1595, 1252, 1103, 977 cm^{-1}; ^1H NMR (600 MHz) δ 2.34 (br d, J = 3.0 Hz, 1H), 3.59 (dd, J = 6.6, 4.5 Hz, 1H), 4.26 (d, J = 4.5 Hz, 1H), 4.57 (dd, J = 6.6, 3.0 Hz, 1H), 7.30−7.68 (m, 8H), 8.01−8.09 (m, 2H); ^{13}C NMR (150 MHz) δ 57.6, 61.5, 71.2, 126.0−140.0 (8 ^{13}C signals), 193.9; MS (EI) *m*/*z* (%) 335 ($MH^+ - H_2O$, 8), 316 (15), 290 (20),105 (100). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.54. Found: C, 75.31; H, 5.41.

(±)-(1a*S*,4*S*,4a*R*)-2,4-Diphenyltetrahydrooxireno[2,3-*c*]furan-2-ol 6a/7a. Major anomer: ^1H NMR (600 MHz) δ 3.05 (br s, 1H), 3.98 (s, 2H), 5.42 (s, 1H), 7.29−7.69 (m, 10H); ^{13}C NMR (150 MHz) δ 59.9, 62.0, 81.8, 103.0, 126.0−140.0 (8 ^{13}C signals). Minor anomer: ^1H NMR (600 MHz) δ 3.83 (br s, 1H), 4.06 (d, J = 2.4 Hz, 1H), 4.17 (d, J = 2.4 Hz, 1H), 5.48 (s, 1H), 7.29−7.69 (m, 10H).

(±)-{(2*S*,3*S*)-3-[(1*S*)-1-Hydroxyethyl]oxiran-2-yl}(phenyl)methanone 4b. Colorless solid; mp 90−92 °C; R_f 0.50 (60:40 hexane/ethyl acetate); IR (Nujol) 3448, 2924, 2854, 1677, 1597, 1450, 1274, 1234, 1065, 982, 964, 705 cm^{-1}; ^1H NMR (600 MHz) δ 1.31 (d, J = 6.6 Hz, 3H), 3.29 (dd, J = 6.6, 4.8 Hz, 1H), 3.57 (dq, J = 6.6, 6.6 Hz, 1H), 4.16 (d, J = 4.8 Hz, 1H), 7.49−7.53 (m, 2H), 7.59−7.61 (m, 1H), 8.04−8.06 (m, 2H); ^{13}C NMR (150 MHz) δ 20.5, 57.4, 61.6, 64.7, 128.5, 128.6, 133.8, 135.5, 193.9; MS (EI) *m*/*z* (%) 192 (M^+, 4), 149 (10), 123 (20), 105 (90), 86 (100). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.85; H, 6.40.

(±)-(1a*S*,4*S*,4a*R*)-2-Methyl-4-phenyltetrahydrooxireno-[2,3-*c*]furan-2-ol 6b/7b. Major anomer: ^1H NMR (600 MHz) δ 1.38 (d, J = 7.2 Hz, 3H), 3.64 (d, J = 3.0 Hz, 1H), 3.72 (d, J = 3.0 Hz, 1H), 4.45 (q, J = 7.2 Hz, 1H), 7.27−7.34 (m, 3H), 7.53−7.55 (m, 2H); ^{13}C NMR (150 MHz) δ 19.0, 59.1, 61.1, 75.0, 101.9, 126.4, 127.8, 128.1, 140.8. Minor anomer: ^1H NMR (600 MHz) δ 1.25 (d, J = 6.6 Hz, 3H), 3.63 (d, J = 3.0 Hz, 1H), 3.93 (d, J = 3.0 Hz, 1H), 4.58 (q, J = 6.6 Hz, 1H), 7.27−7.34 (m, 3H), 7.53−7.55 (m, 2H).

(±)-[(2*S*,3*S*)-3-(Hydroxymethyl)oxiran-2-yl](phenyl)-methanone 4c.[12] Colorless oil that decomposed over a period of several days; R_f 0.43 (60:40 hexane/ethyl acetate); IR (neat) 3430, 1688, 1597, 1450, 1229, 1042, 701 cm^{-1}; ^1H NMR (600 MHz) δ 3.61 (dt, J = 5.4, 4.2 Hz, 1H), 3.67 (br dd, J = 12.6, 5.4 Hz, 1H), 3.71 (br dd, J = 12.6, 5.4 Hz, 1H), 4.23 (d, J = 4.2 Hz, 1H), 7.34−7.62 (m, 3H), 8.00−8.02 (m, 2H); ^{13}C NMR (150 MHz) δ 56.8, 58.0, 59.9, 125.7−128.9 (4 Aryl ^{13}C), 193.5; MS (EI) *m*/*z* (%) 178 (M^+, 10), 161 (30), 147 (20), 105 (100).

(12) Boeckman, R. K., Jr.; Thomas, E. W. *J. Am. Chem. Soc.* **1979**, *101*, 987. Boeckman, R. K., Jr.; Thomas, E. W. *Tetrahedron Lett.* **1976**, *17*, 4045.

(±)-(1a*S*,4a*R*)-2-Phenyltetrahydrooxireno[2,3-*c*]furan-2-ol 6c/7c. Major anomer: ^1H NMR (600 MHz) δ 3.76 (d, J = 3.0 Hz, 1H), 3.84 (dd, J = 3.0, 0.6 Hz, 1H), 4.02 (dd, J = 10.8, 0.6 Hz, 1H), 4.20 (d, J = 10.8 Hz, 1H), 7.34−7.62 (m, 5H); ^{13}C NMR (150 MHz) δ 54.8, 60.0, 66.7, 102.0, 125.7−128.9 (4 Aryl ^{13}C).

(±)-(1a*S*,4*S*,4a*R*)-2,4-Dipropyltetrahydrooxireno[2,3-*c*]-furan-2-ol 6d/7d. Major anomer: colorless oil; R_f 0.50 (70:30 hexane/ethyl acetate); IR (neat) 3422, 2961, 1456, 1423, 1380, 1237, 1146, 1009; ^1H NMR (300 MHz) δ 0.93−0.99 (m, 6H), 1.35−1.85 (m, 8H), 2.28 (s, 1H), 3.61 (d, J = 3.0 Hz, 1H), 3.62 (d, J = 3.0 Hz, 1H), 4.09 (dd, J = 8.4, 5.7 Hz, 1H); ^{13}C NMR (75 MHz) δ 13.9, 14.2, 17.3, 19.0, 35.4, 38.8, 57.8, 58.4, 78.5, 103.3; MS (LSIMS) *m*/*z* (%) 187 (MH^+, 25), 169 (100); HRMS of **6d/7d** + H $C_{10}H_{19}O_3$ calcd 187.1334; found, 187.1332. Minor anomer: ^1H NMR (300 MHz) δ 0.93−0.99 (m, 6H), 1.35−1.85 (m, 8H), 3.22 (s, 1H), 3.62 (d, J = 3.0 Hz, 1H), 3.66 (d, J = 3.0 Hz, 1H), 4.20−4.24 (m, 1H); ^{13}C NMR (75 MHz) δ 13.8, 14.4, 16.4, 18.6, 35.1, 39.7, 60.7, 61.4, 77.9, 103.3.

(±)-(1a*S*,4*S*,4a*R*)-2,4-Dicyclohexyltetrahydrooxireno-[2,3-*c*]furan-2-ol 6e/7e. Major anomer: colorless solid; mp 81−83 °C; R_f 0.38 (80:20 hexane/ethyl acetate); IR (Nujol) 3400, 1304, 1241, 1021, 866 cm^{-1}; ^1H NMR (600 MHz) δ 0.95−1.95 (m, 22H), 2.16 (s, 1H), 3.62 (d, J = 3.0 Hz, 1H), 3.68 (d, J = 3.0 Hz, 1H), 3.73 (d, J = 9.6 Hz, 1H); ^{13}C NMR (150 MHz) δ 25.5, 25.6, 25.9, 26.0, 26.2, 26.2, 26.3, 28.2, 29.3, 29.6, 40.6, 43.9, 56.2, 58.0, 83.4, 104.6; MS (EI) *m*/*z* (%) 266 (M^+, 10), 248 (30), 230 (40), 83 (90), 55 (100). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.83. Found: C, 71.85; H, 9.83. Minor anomer:^1H NMR (600 MHz) δ 0.95−1.95 (m, 22H), 3.14 (s, 1H), 3.72 (d, J = 3.0 Hz, 1H), 3.75 (d, J = 3.0 Hz, 1H), 3.89 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, partial) δ 26.1, 26.3, 27.2, 28.8, 29.1, 40.3, 44.3, 60.9, 82.9, 104.5

(±)-(1a*S*,4*S*,4a*R*)-2,4-Diisopropyltetrahydrooxireno-[2,3-*c*]furan-2-ol 6f/7f. Major anomer: colorless solid; mp 66−68 °C; R_f 0.52 (60:40 hexane/ethyl acetate); IR (Nujol) 3363, 1414, 1211, 1060, 1010, 868 cm^{-1}; ^1H NMR (600 MHz) δ 1.0 (d, J = 6.6 Hz, 6H), 1.05 (d, J = 6.6 Hz, 6H), 1.81 (d sept, J = 9.0, 6.6 Hz, 1H), 2.04 (sept, J = 6.6 Hz, 1H), 2.11 (s, 1H), 3.63 (d, J = 3.0 Hz, 1H), 3.67 (d, J = 3.0 Hz, 1H), 3.68 (d, J = 9.0 Hz, 1H); ^{13}C NMR (150 MHz) δ 18.0, 19.4, 31.9, 33.8, 56.5, 58.2, 84.7, 105.0; MS (EI) *m*/*z* (%) 187 (M^+ + H, 10), 169 (100), 97 (40), 71 (70). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74. Found: C, 64.24; H, 9.96. Minor anomer: ^1H NMR (600 MHz) δ 0.96 (d, J = 6.6 Hz, 6H), 1.04 (d, J = 6.6 Hz, 6H), 1.63 (d sept, J = 9.3, 6.6 Hz, 1H), 1.93 (sept, J = 6.6 Hz, 1H), 3.12 (s, 1H), 3.72 (d, J = 3.0 Hz, 1H), 3.76 (d, J = 3.0 Hz, 1H), 3.84 (d, J = 9.3 Hz, 1H); ^{13}C NMR (150 MHz) δ 15.6, 18.7, 30.8, 34.3, 61.5, 60.9, 84.0, 105.1.

(±)-[(2*S*,3*S*)-3-(Hydroxymethyl)-3-methyloxiran-2-yl](phenyl)methanone 4g. ^1H NMR (300 MHz) δ 1.63 (s, 3H), 1.70−1.80 (br s, 1H), 3.63 (br s, 2H), 4.02 (s, 1H), 7.35−7.63 (m, 3H), 7.98−8.01 (m, 2H); ^{13}C NMR (150 MHz, partial) δ 19.3, 63.4, 63.8, 193.1

(±)-(1a*S*,4a*S*)-4a-Methyl-2-phenyltetrahydrooxireno-[2,3-*c*]furan-2-ol 6g/7g. Major anomer: colorless solid; mp 78−81 °C; R_f 0.45 (60:40 hexane/ethyl acetate); IR (Nujol) 3352, 1262, 1105, 1022, 1002, 763 cm^{-1}; ^1H NMR (300 MHz) δ 1.61 (s, 3H), 2.82 (br s, 1H), 3.58 (s, 1H), 3.99 (d, J = 9.9 Hz, 1H), 4.08 (d, J = 9.9 Hz, 1H), 7.35−7.63 (m, 5H); ^{13}C NMR (150 MHz, partial) δ 13.6, 69.4, 65.5, 102.8; MS (EI) *m*/*z* (%) 174 ($M^+ - H_2O$, 5), 161 (60), 123 (20), 105 (100). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 69.00; H, 6.41. Minor anomer: ^1H NMR (300 MHz) δ 1.53 (s, 3H), 3.51 (br s, 1H), 3.65 (s, 1H), 3.87 (d, J = 10.5 Hz, 1H), 4.25 (d, J = 10.5 Hz, 1H), 7.35−7.63 (m, 5H).

(±)-{(2*R*,3*R*)-3-[(1*S*)-1-Hydroxyethyl]oxiran-2-yl}(phenyl)methanone 5b. Colorless solid; mp 69−71 °C; R_f 0.50 (60:40 hexane/ethyl acetate); IR (Nujol) 3400, 1690, 1597, 1226, 1093, 1038, 984, 707 cm^{-1}; ^1H NMR (600 MHz) δ 1.13 (d, J = 6.6 Hz, 3H), 2.31 (br d, J = 3.0 Hz, 1H), 3.38 (dd, J = 7.2, 4.8 Hz, 1H), 3.56 (ddq, J = 6.6, 6.6, 3.0 Hz, 1H), 4.28 (d,

J = 4.8 Hz, 1H), 7.33−7.65 (m, 3H), 7.99−8.01 (m, 2H); ^{13}C NMR (150 MHz) δ 19.0,57.5, 67.4, 65.4, 125.7−139.1 (4 aryl ^{13}C), 193.1; MS (EI) *m*/*z* (%) 193 (MH^+, 15), 175 (40), 154 (100), 137 (80); HRMS of **7b** $C_{11}H_{13}O_3$ (MH^+) calcd 193.0864, found 193.0864.

(±)-(1a*R*,4*S*,4a*S*)-2-Methyl-4-phenyltetrahydrooxireno-[2,3-*c*]furan-2-ol 8b/9b. Major anomer: ^{1}H NMR (600 MHz) δ 1.42 (d, J = 6.0 Hz, 3H), 3.21 (br s, 1H), 3.67 (dd, J = 3.0, 0.6 Hz, 1H), 3.70 (d, J = 3.0 Hz, 1H), 4.32 (dq, J = 6.0, 0.6 Hz, 1H), 7.33−7.60 (m, 5H); ^{13}C NMR (150 MHz) δ 15.2, 57.7, 60.7, 72.9, 102.2, 125.7−139.1 (4 aryl ^{13}C). Minor anomer: ^{1}H NMR (600 MHz) δ 1.43 (d, J = 6.6 Hz, 3H), 3.71 (dd, J = 3.0, 0.6 Hz, 1H), 3.80 (d, J = 3.0 Hz, 1H), 4.24 (dq, J = 6.6, 0.6 Hz, 1H), 7.33−7.60 (m, 5H); ^{13}C NMR (150 MHz) δ 16.3, 60.1, 61.6, 74.0 104.0, 125.7−139.1 (4 aryl ^{13}C).

(±)-(1a*R*,4*S*,4a*S*)-2,4-Dicyclohexyltetrahydrooxireno-[2,3-*c*]furan-2-ol 8e/9e. Major anomer: colorless solid; mp 94−95 °C; R_f 0.19 (CH_2Cl_2); IR (Nujol) 3400, 1304, 1241, 1021, 866 cm^{-1}; ^{1}H NMR (600 MHz) δ 0.97−1.32 (m, 10H), 1.58−1.96 (m, 12H), 2.20 (s, 1H), 3.58 (d, J = 3.0 Hz, 1H), 3.63 (dd, J = 3.0, 0.6 Hz, 1H), 3.70 (br d, J = 8.4 Hz, 1H); ^{13}C NMR (150 MHz,) δ 25.7, 25.8, 26.0, 26.0, 26.3, 26.4, 26.4, 27.9, 29.2, 30.1, 38.7, 43.6, 54.3, 57.1, 80.8, 104.2; MS (EI) *m*/*z* (%) 266 (M^+, 4), 248 (15), 230 (30), 83 (100); HRMS of **8e/9e** $C_{16}H_{26}O_3$ calcd 266.1887, found 266.1881. Minor anomer: ^{1}H NMR (600 MHz) δ 0.97−1.32 (m, 10H), 1.58−1.96 (m, 12H), 2.93 (s, 1H), 3.54 (dd, J = 7.8, 1.2 Hz, 1H), 3.65 (d, J = 3.0 Hz, 1H), 3.73 (dd, J = 3.0, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, partial) δ 25.7, 26.0, 26.2, 26.3, 26.3, 26.8, 39.9, 44.2, 58.5, 59.2, 82.6, 104.7.

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Supporting Information Available: Ortep representation of **4b** and ^{1}H NMR of 1,2-dioxines **2c**,**d**,**f** and **3b**−**g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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