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Ruthenium Porphyrin-Catalyzed Aerobic Oxidation of Terminal Aryl Alkenes to Aldehydes by a Tandem Epoxidation–Isomerization Pathway**

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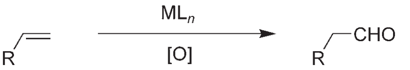
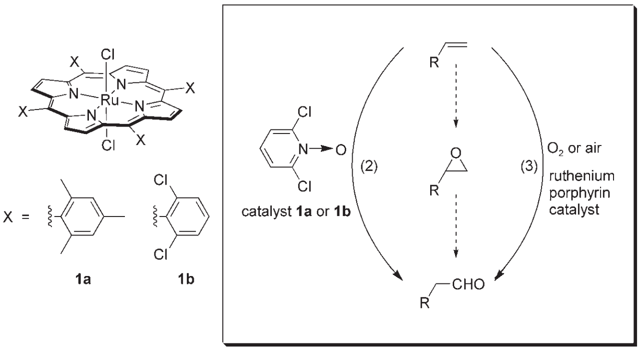
Metal-catalyzed selective oxidation of organic substrates under mild conditions, with dioxygen or air as the sole terminal oxidant, is an economic and green methodology for the synthesis of epoxides, alcohols, ketones, and aldehydes.[1] For catalytic oxidation of 1-alkenes to aldehydes without C=C bond cleavage (Reaction (1), Scheme 1), a widely known industrial process is the Wacker oxidation of ethylene to acetaldehyde catalyzed by $PdCl_2$, with $CuCl_2$ and dioxygen as oxidants.[2] Extension of the Wacker process, or its recent modifications, to higher 1-alkenes using dioxygen as the sole terminal oxidant,[3] usually affords methyl ketones instead of aldehydes. A reversal of such selectivity (methyl ketone vs. aldehyde) has been noted in the Wacker oxidation of 1-alkenes functionalized with vicinal heteroatoms, or 1,5-dienes,[4,5a–f] and in recently reported $PdCl_2$-catalyzed Reaction (1) (Scheme 1, R = aryl) using heteropolyacid $H_4[PMo_{11}VO_{40}]$ as a terminal oxidant.[5g] The Wacker oxidation of unfunctionalized 1-alkenes in tertiary alcohols[5a,d] gives a mixture of aldehydes and methyl ketones or otherwise affords aldehyde in approximately 10% yield.[5a]



(1)

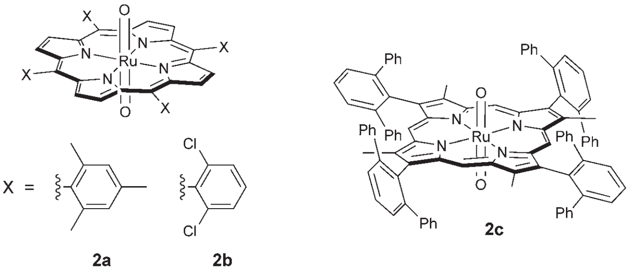
Scheme 1. General scheme for the metal-catalyzed oxidation of 1-alkenes to aldehydes; ML$_n$ = metal catalyst, [O] = oxidant.

Several years ago, we reported a version of Reaction (1) (Scheme 1, R = aryl), catalyzed by ruthenium porphyrin and employing 2,6-dichloropyridine *N*-oxide (2,6-Cl_2pyNO) as terminal oxidant. The ruthenium-porphyrin-catalyzed aldehyde formation reaction proceeded by a tandem epoxidation–isomerization (E–I) pathway, affording aldehydes in up to 99% yield with the catalyst $[Ru^{IV}(tmp)Cl_2]$ (**1a**, tmp = 5,10,15,20-tetramesitylporphyrinato dianion) or $[Ru^{IV}(2,6\text{-}Cl_2tpp)Cl_2]$ (**1b**, 2,6-Cl_2tpp = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato dianion) (Reaction (2), Scheme 2).[6] A great challenge subsequently faced is to develop a similar tandem E–I reaction with air or dioxygen, instead of 2,6-Cl_2pyNO, as terminal oxidant (Reaction (3), Scheme 2).[7]



Scheme 2. Ruthenium porphyrin-catalyzed oxidation of 1-alkenes to aldehydes (E–I reaction).

Herein we report the first examples of an aerobic E–I reaction (Reaction (3), Scheme 2), which gave aldehydes in up to 94% yield using catalyst **1a** or $[Ru^{VI}(tmp)O_2]$ (**2a**, Scheme 3), and with up to 1144 product turnovers (after



Scheme 3. Dioxoruthenium(VI) porphyrin catalysts **2a**–**c**.

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recycling the catalyst five times) by employing a new ruthenium porphyrin catalyst [$\mathrm{Ru^{VI}(tmttp)O_2}$] (**2c**, Scheme 3, tmttp = 1,3,5,7-tetramethyl-2,4,6,8-tetraterphenylporphyrinato dianion), thus providing a unique example of an efficient metal-catalyzed analogue of Reaction (1) (Scheme 1) at ambient temperature and pressure with dioxygen as the sole terminal oxidant.

In previous work,[6] the oxidation of *p*-methoxystyrene (**3a**) by 2,6-$\mathrm{Cl_2}$pyNO in $\mathrm{CDCl_3}$, catalyzed by **1b** (2 mol%) at 25 °C for 0.5 h, afforded 2-(4-methoxyphenyl)-acetaldehyde (**4a**, Scheme 4) in 99% yield. However, a similar aerobic reaction in $\mathrm{CDCl_3}$ using catalyst **1b** or **1a** (2 mol%) in the absence of 2,6-$\mathrm{Cl_2}$ pyNO for 7 days gave only a trace amount of **4a**, as revealed by ^{1}H NMR spectroscopy. Neither raising the temperature to 60 °C nor irradiating the mixture with light increased the yield of **4a**.

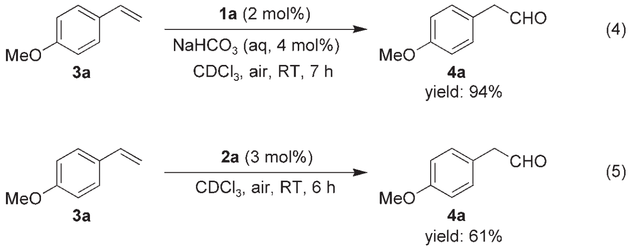
Strikingly, upon addition of a solution of $\mathrm{NaHCO_3}$ (4 mol%) in water (0.3 mL), the aerobic oxidation of **3a** (0.1 mmol) in $\mathrm{CDCl_3}$ (1 mL) with **1a** as catalyst gave **4a** in 94% yield after 7 h (Reaction (4), Scheme 4). The aqueous $\mathrm{NaHCO_3}$ solution seemingly served as a "switch" in the **1a**-catalyzed aerobic oxidation, the presence of which allowed aldehyde formation to proceed. By using 4 mol% of other additives, such as 2,6-dichloropyridine, triethylphosphite, trifluoroacetic acid, or aqueous hydrochloric acid, instead of aqueous $\mathrm{NaHCO_3}$, no **4a** was detected in the reaction mixture after at least 9 h.

Examination of the solvent effect revealed chloroform as the solvent of choice. Changing the solvent to dichloromethane and 1,2-dichloroethane lowered the yield of **4a** to 68% and 10%, respectively. No reaction was found when the solvent was changed to benzene, toluene, acetone, diethyl ether, or methanol. The effect of porphyrin ligands in the catalysis has also been examined. Changing the catalyst from **1a** to **1b** led to the formation of **4a** in less than 3% yield after a 12 h reaction, in sharp contrast with the virtually identical activity of **1a** and **1b** in catalyzing the 2,6-$\mathrm{Cl_2}$pyNO oxidation of **3a** to **4a**.[6]

Complex **2a** was found to catalyze the aerobic oxidation of **3a** to give **4a** in 61% yield after 6 h without the need for added aqueous $\mathrm{NaHCO_3}$ (Reaction (5), Scheme 4).[8] At the end of the catalytic process, the reaction mixture was found to contain [$\mathrm{Ru^{II}(tmp)(CO)}$], as encountered in other alkene oxidations catalyzed by **2a**[8a,d] and **1b**.[6] Because **2a** is less stable than **1a**, we used the latter as catalyst in subsequent aerobic oxidation reactions.

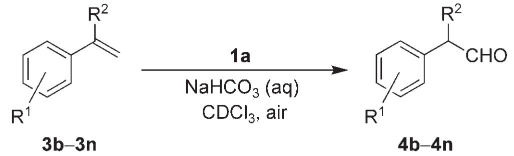
By employing 2 mol% catalyst **1a** and 4 mol% $\mathrm{NaHCO_3}$, the oxidation of alkoxy-substituted styrenes **3b**–**3f** with air afforded **4b**–**4f**, respectively, in 87–93% yields within 4–7 h (Table 1, entries 1–5).

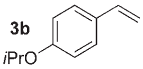
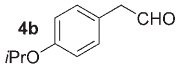
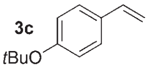
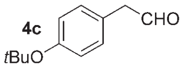
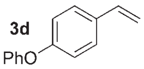
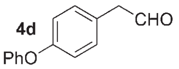
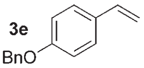
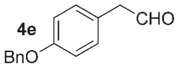
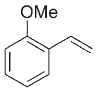
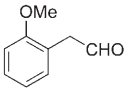
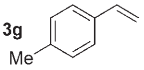
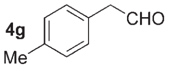
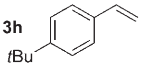
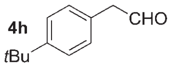
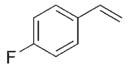
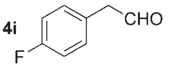
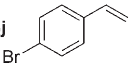
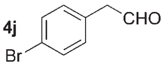
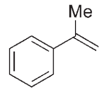
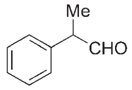
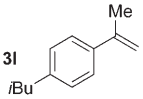
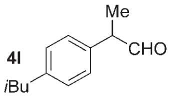
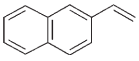
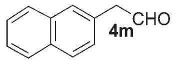
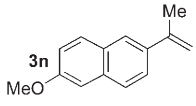
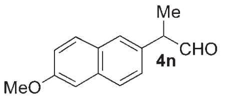
Styrenes **3g**–**3l**, bearing alkyl or halo substituents, can also be converted into their respective aldehydes **4g**–**4l** by aerobic oxidation catalyzed by **1a**. However, a higher reaction temperature and higher loadings of catalyst **1a** and additive $\mathrm{NaHCO_3}$ were needed to obtain the aldehyde products in good yields. Under the conditions of 3 mol% **1a**, 8 mol% $\mathrm{NaHCO_3}$, 0.3 mL $\mathrm{H_2O}$, and 50 °C, the oxidation of **3g**–**3l** gave aldehydes **4g**–**4l**, respectively, in 69–84% yields within 5–7 h (Table 1, entries 6–11).



Scheme 4. Aerobic oxidation of **3a** to **4a** catalyzed by **1a** and **2a**.

Table 1: Aerobic oxidation of 1-alkenes catalyzed by **1a**.[a]

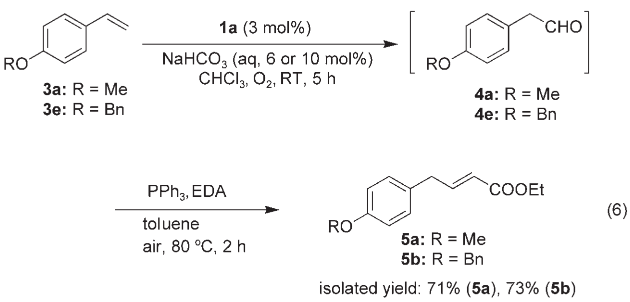


Entry	Substrate	Product	Time [h]	Yield [%][b]
1	**3b** 	**4b** 	4.5	92
2	**3c** 	**4c** 	7	87
3	**3d** 	**4d** 	5	87
4	**3e** 	**4e** 	4	89
5	**3f** 	**4f** 	7	93
6[c]	**3g** 	**4g** 	5	84
7[c]	**3h** 	**4h** 	5	81
8[c]	**3i** 	**4i** 	7	71
9[c]	**3j** 	**4j** 	7	69
10[c]	**3k** 	**4k** 	7	81
11[c]	**3l** 	**4l** 	7	71 (64[d])
12[c]	**3m** 	**4m** 	5	73
13[c]	**3n** 	**4n** 	7	74 (68[d])

[a] Reaction conditions: substrate (0.1 mmol), **1a** (2 mol%), $\mathrm{CDCl_3}$ (1 mL), $\mathrm{NaHCO_3}$ (4 mol%), $\mathrm{H_2O}$ (0.3 mL), open to air, room temperature. [b] Determined by ^{1}H NMR spectroscopy. [c] **1a** (3 mol%), $\mathrm{NaHCO_3}$ (8 mol%), 50 °C. [d] Yield of isolated product.

1-Vinylnaphthalene (**3m**) and its derivative **3n** exhibited a reactivity comparable to that of **3g**–**3l** toward the **1a**-catalyzed aerobic oxidation, with the aldehydes **4m** and **4n** being formed in 73 % and 74 % yields under similar conditions (Table 1, entries 12 and 13).

The efficient aerobic oxidation of **3a** to **4a** catalyzed by **1a** in the presence of $NaHCO_3$ (aq), along with previous reports on the metalloporphyrin-catalyzed olefination of aldehydes with ethyl diazoacetate (EDA) and triphenylphosphine (PPh_3),[9] prompted us to develop a "one-pot" olefination process that features in situ generation of an aldehyde from alkene oxidation with dioxygen, instead of 2,6-Cl_2pyNO employed in our earlier work.[6] Interestingly, when a mixture of **3a** (0.8 mmol), **1a** (3 mol %), and $NaHCO_3$ (aq, 10 mol %) in $CHCl_3$ was stirred under dioxygen (1 atm) at room temperature for 5 h, followed by removal of the solvent and subsequent treatment of the residue with PPh_3 (1.2 equiv), toluene (10 mL), and EDA (1.2 equiv) at 80 °C for 2 h, the olefination product **5a** was isolated in 71 % yield (Reaction (6), Scheme 5). A similar one-pot olefination of **3e** afforded **5b** in 73 % yield.



Scheme 5. "One-pot" olefination reaction involving the aerobic oxidation of **3** to **4** catalyzed by **1a**.

To obtain an insight into the mechanism of the **1a**-catalyzed aerobic oxidation of alkenes with additive $NaHCO_3$ (aq), we examined the course of the reaction for **3f** over time by ^{1}H NMR spectroscopy. The time course plot resembles that previously reported for the 2,6-Cl_2pyNO oxidation of 1-alkene catalyzed by **1b** through the E–I pathway (see the Supporting Information, Figure S1).[6] These studies revealed that the **1a**-catalyzed oxidation of **3f** exhibited an induction period of about 4 min, followed by the formation of **2a** and initiation of the alkene oxidation. [Ru^{II}(tmp)(CO)], generated in the reaction, exhibits no catalytic activity toward the aldehyde formation.

In view of the stoichiometric alkene epoxidation[8a,10] and catalytic aerobic alkene epoxidation[8a–d,11] by dioxoruthenium(VI) porphyrins, including those using **2a**, pioneered by Groves and Quinn,[8a] we propose that aldehyde formation from the aerobic oxidation of **3**, catalyzed by **1a**, proceeds by a tandem E–I mechanism, in which **2a**, generated in situ from the oxidation of **1a** by air, is mainly responsible for the epoxidation step. Indeed, for the **1a**-catalyzed oxidation of **3a** in the presence of aqueous $NaHCO_3$, the yield of **4a** did not depend on the dioxygen pressure when dioxygen was used as terminal oxidant, and by replacing H_2O^{16} of aqueous $NaHCO_3$ with H_2O^{18}, the oxidation with air resulted in approximately 72 % incorporation of O^{18} in **4a** (see the Supporting Information). These results recall the dioxygen pressure-independent epoxide yields reported by Groves and Quinn,[8a] and the 81 % O^{18}-incorporation from H_2O^{18} into the epoxide product reported by Hirobe and co-workers[12] for the **2a**-catalyzed aerobic epoxidation of alkenes. The active intermediate for the epoxide isomerization step is unclear. Examples of isomerization of epoxides to aldehydes in the presence of metal catalysts, including an iron porphyrin catalyst, have been reported in the literature.[13]

A comparison among the behavior of **1a**, **2a**, and [Ru^{II}(tmp)(CO)] toward the catalytic isomerization of epoxides to aldehydes is given in the Supporting Information (Table S1). Treatment of styrene oxide (0.1 mmol) with 2 mol % **1a** in $CDCl_3$ (1 mL) at 50 °C for 6 h afforded phenylacetaldehyde in over 98 % yield. Under similar conditions, **2a** is also an active catalyst for this isomerization process, affording phenylacetaldehyde in 62 % yield after 3 h, accompanied by conversion of **2a** into [Ru^{II}(tmp)(CO)]. No phenylacetaldehyde was formed by employing [Ru^{II}(tmp)(CO)] as catalyst. The activity of **2a** in catalyzing both aerobic epoxidation of alkenes[8a] and epoxide isomerization to aldehyde can rationalize the formation of **4a** from **2a**-catalyzed aerobic oxidation of **3a** (Reaction (5), Scheme 4).

As the aqueous solution of $NaHCO_3$ functioned as a "switch" in the **1a**-catalyzed aldehyde formation, we monitored (by ^{1}H NMR and IR spectroscopy) a solution of **1a** (approx. 2 mg) in $CDCl_3$ (1 mL) open to air with and without addition of $NaHCO_3$ (aq). These experiments revealed the formation of **2a** in almost quantitative yield upon stirring the solution of **1a** with $NaHCO_3$ (aq, 10 equiv, 0.3 mL) at room temperature for 6.5 h; however, in the absence of $NaHCO_3$ (aq), no **2a** was formed. Evidently, the role of $NaHCO_3$ (aq) in the **1a**-catalyzed aldehyde formation is to facilitate the oxidation of **1a** to **2a** by air during catalysis.

As complex **1b** contains a less electron-rich porphyrin ligand, its oxidation by air to **2b** (Scheme 3) should be less effective. Indeed, only ≈ 10 % yield of **2b** was detected, by ^{1}H NMR spectroscopy, in a $CDCl_3$ solution of **1b** mixed with $NaHCO_3$ (aq, 10 equiv) after the mixture was exposed to air and stirred at room temperature for 12 h. Not surprisingly, **2b** exhibited a substantially lower activity than **2a** in catalyzing aerobic oxidation of **3a** to **4a**; only a 22 % yield of **4a** was obtained under the conditions of catalyst (2 mol %), $CDCl_3$ (1 mL), room temperature, 12 h. These factors could account for the dramatic difference between the catalytic activity of **1a** and **1b** toward the aerobic oxidation of **3a**.

Given the inactivity of [Ru^{II}(tmp)(CO)] and the instability of **2a** for aerobic oxidation of alkenes as described by Groves and Quinn,[8a] and for the aerobic E–I reactions as described above, the formation of [Ru^{II}(tmp)(CO)] is a step accounting for the deactivation of catalysts **1a** and **2a** in aerobic oxidations of alkenes. For Reaction (3) (Scheme 2) catalyzed by **1a** or **2a**, the product turnovers are less than 50 under the employed reaction conditions. We envisaged that the modified bis-pocket porphyrin ligand tmttp, first reported by Chang and co-workers,[14] could be better than tmp in the design of sterically encumbered robust ruthenium catalysts.

Therefore we prepared [Ru$^{\mathrm{II}}$(tmttp)(CO)(H$_2$O)] (see the Supporting Information) and determined its structure by X-ray crystallography[15] (Figure 1). Oxidation of [Ru$^{\mathrm{II}}$(tmttp)(CO)(H$_2$O)] with *m*-chloroperbenzoic acid (*m*-CPBA) gave **2c** (Scheme 3), which was characterized by ^{1}H NMR, UV/Vis, and IR spectroscopy and mass spectrometry.[16]

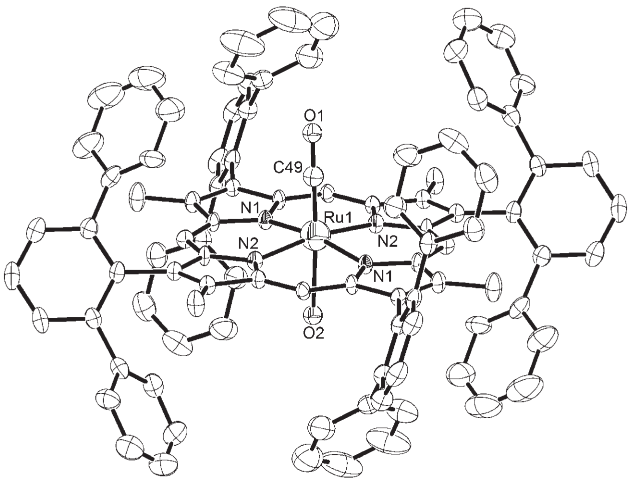


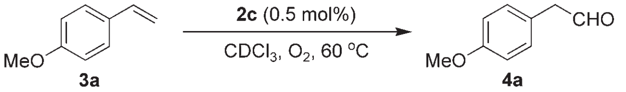
Figure 1. ORTEP drawing for [Ru$^{\mathrm{II}}$(tmttp)(CO)(H$_2$O)]. Hydrogen atoms are omitted for clarity; ellipsoids are set at 30% probability.

By using **2c** (0.2 mol%) as catalyst with dioxygen (1 atm) as terminal oxidant, product turnovers of 396, 377, 368, 243, and 320 were obtained for the oxidation of **3a**, **3g**, **3h**, **3j**, and **3k** to **4a**, **4g**, **4h**, **4j**, and **4k**, respectively, in CDCl$_3$ at 60 °C for 7 or 12 h (see the Supporting Information). No other products of alkene oxidation were detected in the reaction mixtures by ^{1}H NMR spectroscopy. These product turnovers are significantly higher than those (< 50) obtained for the **2a**- or **1a**-catalyzed oxidations. For the oxidation of **3a** to **4a** by dioxygen catalyzed by 0.5 mol% **2c** at 60 °C, [Ru$^{\mathrm{II}}$(tmttp)(CO)] was formed in nearly quantitative yield (approx. 96%) at the end of the reaction, which contrasts with the approximately 70% yield of [Ru$^{\mathrm{II}}$(tmp)(CO)] formed from the same reaction catalyzed by 2 mol% **2a** at room temperature.

Catalysts **2c** and **2a** can be recycled by oxidation of their deactivated forms [Ru$^{\mathrm{II}}$(tmttp)(CO)] and [Ru$^{\mathrm{II}}$(tmp)(CO)], respectively, with *m*-CPBA (see the Supporting Information). In the case of the oxidation of **3a** with dioxygen, catalyzed by 2 mol% **2a** at room temperature, which gave **4a** in 67% yield after 12 h, the first recycle decreased the yield of **4a** to 49% (reaction time: 20 h). In contrast, for the same reaction catalyzed by 0.5 mol% **2c** at 60 °C, the catalyst can be recycled five times without a significant decrease in the yield of **4a**, as shown in Table 2. The total number of product turnovers after five recycles reaches 1144.

In summary, we have developed a ruthenium porphyrin-catalyzed oxidation of 1-alkenes to aldehydes, without C=C bond cleavage, using ambient air as the sole terminal oxidant, together with a new, recyclable ruthenium catalyst for such catalytic aerobic oxidation reactions, which exhibits > 1000 product turnovers after recycling the catalyst five times. The presence of an aqueous NaHCO$_3$ solution plays a pivotal role in aldehyde formation from the aerobic oxidation catalyzed by dichlororuthenium(IV) complex **1a**.[17] To our knowledge, the present work provides the first example of selective aldehyde formation from 1-alkenes by a metal-catalyzed tandem epoxidation–isomerization reaction with air as the terminal oxidant,[18] a catalytic process complementing the conventional Wacker oxidations that usually afford methyl ketones.

Table 2: Catalyst recycling for oxidation of **3a** to **4a** with dioxygen catalyzed by **2c**.[a]



Entry	Recycle	Time [h]	Yield [%][b]	Total TON[c]
1		5	99	198
2	1st	5	97	392
3	2nd	5	96	584
4	3rd	6	96	776
5	4th	6	94	964
6	5th	8	90	1144

[a] Reaction conditions: **3a** (0.1 mmol), **2c** (0.5 mol%), CDCl$_3$ (1 mL) for initial reaction (entry 1); *m*-CPBA (2.5 mol%) in CDCl$_3$ (0.1 mL) and **3a** (0.1 mmol) were sequentially added to start each recycle. [b] Determined by ^{1}H NMR spectroscopy. [c] Total number of product turnovers.

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[16] Spectroscopic data for **2c**: ^1H NMR (400 MHz, $CDCl_3$): δ_H = 9.61 (s, 4H), 7.85–7.80 (m, 12H), 7.09–7.06 (m, 16H), 6.43–6.40 (m, 24H), 2.96 ppm (s, 12H); UV/Vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) 418 (5.13), 517 (4.11), 550 nm (4.23); IR: $\tilde{\nu} = 820\ cm^{-1}$ [$\nu(RuO_2)$]; ESI MS: m/z 1411 (M^+).

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[18] Currently we cannot exclude the possibility that small amounts of the arylacetaldehydes **4** resulted from a direct oxidation of the corresponding aryl alkenes rather than from isomerization of epoxides. For examples of arylacetaldehyde formation from direct oxidation of styrenes by oxoiron porphyrins or by iodosylbenzene or hypochlorite in the presence of iron and manganese porphyrin catalysts, see: a) J. T. Groves, R. S. Myers, *J. Am. Chem. Soc.* **1983**, *105*, 5791 – 5796; b) J. P. Collman, T. Kodadek, J. I. Brauman, *J. Am. Chem. Soc.* **1986**, *108*, 2588 – 2594; c) Z. Gross, S. Nimri, *J. Am. Chem. Soc.* **1995**, *117*, 8021 – 8022; d) Z. Gross, S. Nimri, C. M. Barzilay, L. Simkhovich, *J. Biol. Inorg. Chem.* **1997**, *2*, 492 – 506.