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Cobalt-Catalyzed Oxygenation/Dearomatization of Furans

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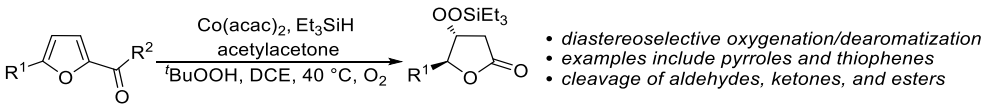
Supporting Information



ABSTRACT: The dearomatization of aromatic compounds using cobalt(II) acetylacetonate with triplet oxygen and triethylsilane converts furans, benzofurans, pyrroles, and thiophenes to a variety of products, including lactones, silyl peroxides, and ketones.

INTRODUCTION

The cobalt-catalyzed oxygenation of alkenes[1] is a synthetically useful reaction for the production of a number of oxidized products, including alcohols,[2,3] peroxides,[2–6] epoxides,[6] and ketones.[7] The conditions are mild, requiring a bis-(1,3-diketonato)cobalt(II) catalyst, such as $Co(acac)_2$, $Co(thd)_2$,[7,8] or $Co(modp)_2$ (Figure 1),[8–10] in the presence of a silane and triplet oxygen, usually at room temperature. The reaction is chemoselective for highly substituted electron-rich carbon–carbon double bonds over less substituted ones.[10] Because the reaction generates a carbon-centered radical intermediate, functionalization typically occurs at the more substituted carbon atom. Alkenes with aromatic groups are also generally oxidized readily.[8,10,11] In this Article, we report that the cobalt catalyst is reactive enough that it can functionalize the π-system of some aromatic compounds, including furans, pyrroles, and thiophenes, resulting in dearomatization. These reactions lead to the formation of products such as lactones, silyl peroxides, and ketones.

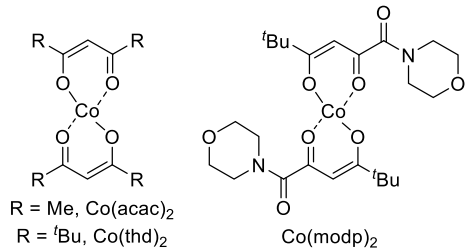
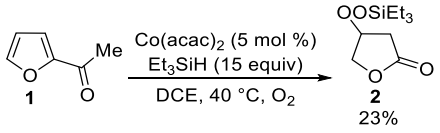


Figure 1. Structure of Co(II) catalysts

RESULTS AND DISCUSSION

During our investigation into the synthesis of endoperoxides using $Co(acac)_2$, Et_3SiH, and oxygen gas,[9–11] we observed that furan-substituted alkenes gave products that suggested that the aromatic ring had reacted. Although phenyl groups are generally unreactive under these conditions,[8,10,11] furyl groups, considering that they are not as strongly stabilized by aromaticity,[12,13] could be reactive, as they are in other oxidation transformations.[14,15] Control experiments supported this hypothesis: when 2-acetylfuran (**1**) was treated with the standard oxidation conditions, lactone **2** was formed as the sole identifiable product (Scheme 1). The formation of this product was not anticipated, considering that it involved not only dearomatization, but also loss of a substituent (the acetyl group).

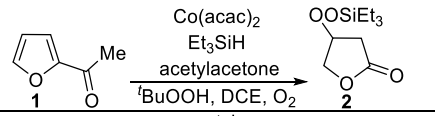
Scheme 1. Co-Catalyzed Oxygenation of 2-Acetylfuran



The yield of the dearomatized product **2** could be improved by adjusting the reaction conditions (Table 1). Because lactone **2** (Scheme 1) decomposed in the presence of $Co(acac)_2$ over time, the catalyst loading was decreased. Furthermore, *t*-BuOOH was added to decrease the induction period of the reaction,[11,16] which limited the exposure of the product to the reaction conditions. The addition of acetylacetone also allowed for decreased catalyst loading in addition to reduced reaction times (Table 1, entry 5), likely because it served as a supporting ligand to limit catalyst decomposition. Excessive amounts of acetylacetone did not have a positive impact on the yield, however (Table 1, entry 4). The addition of more equivalents of Et_3SiH also increased the yield, suggesting that an unproductive pathway consumed the silane, although addition of more than 15 equivalents did not increase the yield significantly (Table 1, entry 10 and 11). Increasing the reaction temperature to 40 °C allowed the catalyst loading to be decreased to 2 mol %, and reactions were complete in four hours with a 62% yield, as determined by ^1H NMR spectroscopy (Table 1, entry 12). Other cobalt(II) catalysts were screened (Table 1, entry 7 and 8) using the optimized conditions, but they proved to be less effective than $Co(acac)_2$.

An important clue as to how the acetyl group was removed was provided by experiments with a 2-furoic acid ester. When 2-methylfuroate (**3**) was subjected to the reaction conditions (Scheme 2), the lactone **2** was formed as the major isolable product, indicating that a carbomethoxy group can also be removed upon oxidation. In addition, however, two products were isolated that retained the carbomethoxy group. These products were the two diastereomers of a bis(silylperoxy) ester (**4** and **5**).

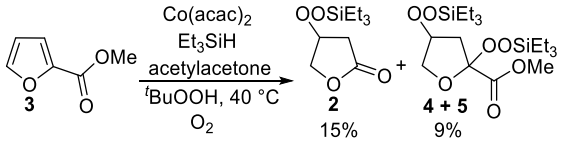
Table 1. Optimization of Co-Catalyzed Oxgenation of Furans



Entry	CoL_2 (mol %)	Et_3SiH (equiv)	acetyl acetone (equiv)	temp	time	yield **2**[a] (NMR)
1	acac (40)	10	-	rt	24 h	38%
2	acac (40)	10	1	rt	2 h	45%
3	acac (40)	10	2	rt	2 h	49%
4	acac (40)	10	5	rt	2 h	39%
5	acac (10)	10	2	rt	2 h	48%
6	acac (5)	10	1	40 °C	1.5 h	49%
7	modp (5)	15	1	40 °C	1.5 h	24%
8	thd (5)	15	1	40 °C	1.5 h	28%
9	acac (5)	15	1	40 °C	1.5 h	58%
10	acac (5)	20	1	40 °C	1 h	59%
11	acac (5)	25	1	40 °C	1 h	53%
12	acac (2)	15	1	40 °C	4 h	62%

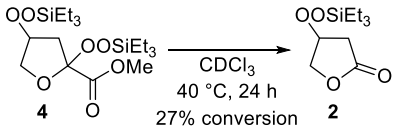
[a] Yield by ^{1}H NMR spectroscopy with mesitylene as internal standard.

Scheme 2. Co-Catalyzed Oxygenation of 2-Methyl Furoate



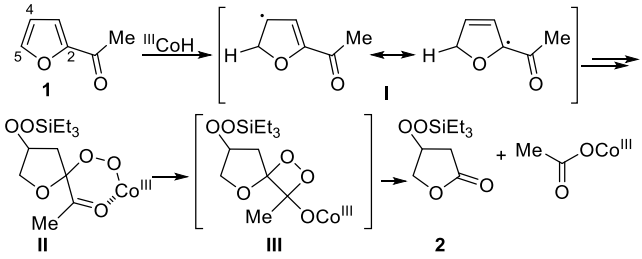
The isolation of both lactone products and bis(silylperoxy) esters suggested that the bis(peroxide), or a structurally similar intermediate, could be a precursor to the lactone products. Upon standing in a deuterated solvent, a purified sample of bis(silylperoxy) ester **4** decomposed into the lactone (Scheme 3). This observation suggests that an intermediate resembling the bis(peroxide) is the first-formed product in these reactions.

Scheme 3. Bis(peroxide) Decomposition



A mechanism can be proposed that is consistent with these observations (Scheme 4). First, addition of a cobalt-hydride[11] to the C_4–C_5 double bond of furan **1** would form a stabilized, captodative radical (**I**).[17] Capture of this radical by O_2 at C_4, followed by silyl peroxide formation, precedes a second peroxidation via a captodative radical at C_2, which would form Co(III)–alkylperoxo complex **II**. This Co(III)–alkylperoxo complex resembles the intermediate in the conversion of bis(peroxides) **4** and **5** to lactone **2** (Scheme 3). Conversion of Co(III)–alkylperoxo complex **II** to lactone **2** likely first involves cyclization of **II** to dioxetane **III**, followed by a [2 + 2] cycloreversion of dioxetane **III**, resulting in cleavage of the carbonyl group and formation of lactone **2**. Related cleavage reactions have been observed for other α-acylperoxides.[18–20] The Co(III)–alkylperoxo complex **II** is a more plausible intermediate than the corresponding silyl peroxide because although bis(peroxides) **4** and **5** are converted to lactone **2**, it occurs more slowly (Scheme 3).

Scheme 4. Proposed Mechanism for the Co-Catalyzed Oxygenation of Furans



The cobalt-catalyzed oxygenation was general for several substituted furans (Table 2). When the furan was substituted at the 2-position with a carbonyl group, lactones were observed as the principal product. More sterically hindered furans **8a**–**8c**, which were synthesized from furan **6** as outlined in Scheme 5, exhibited decreased yields and typically required longer reaction times (Table 2, entries 4-7), likely because of steric hindrance during the initial addition of the cobalt-hydride species.[11] Whereas furan-derived ketones and esters both gave the product where the side-chain had been removed, the corresponding carboxylic acid was unreactive (entry 3). The peroxidation of disubstituted furans was diastereoselective, forming the resulting lactones as single diastereomers (entries 4-7). The relative configuration of the disubstituted lactones was found to be *trans*, which was determined by converting silyl peroxide **9** to the known alcohol (**9a**, Scheme 6) and comparing the ^{1}H and ^{13}C NMR chemical shifts to reported values.[21] Isolating only one diastereomer[22] of product was not expected because the cobalt-catalyzed oxygenation of alkenes is typically not diastereoselective.[23–25] Selectivity has only been observed in systems where the diastereotopic faces of the alkenes are sterically quite distinct.[26–29]

Scheme 5. Disubstituted Furan Synthesis

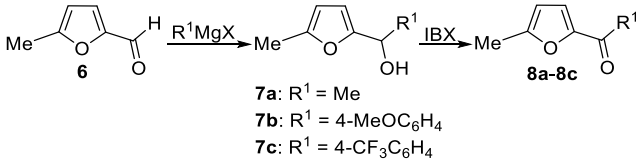
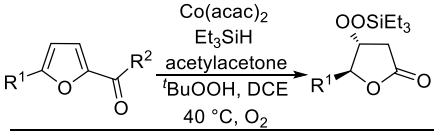
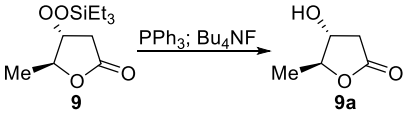


Table 2. Substituted Furan Screen



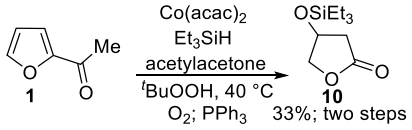
Entry	R^1	R^2	$Co(acac)_2$ mol %	time	Yield
1	H	Me	5	2 h	23%
2	H	OMe	5	2.5 h	15%
3	H	OH	40	24 h	-
4	Me	Me	5	4 h	19%
5	Me	H	20	4 h	8%
6	Me	4-$MeOC_6H_4$	5	2 h	7%
7	Me	4-$CF_3C_6H_4$	5	2 h	4%

Scheme 6. Formation of Alcohol 9a

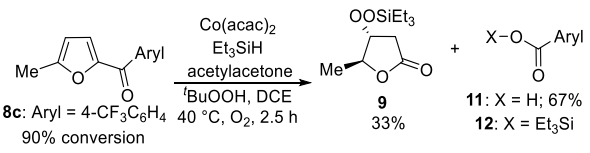


Considering that the yields determined by NMR spectroscopy (Table 1) for 2-acetylfuran (**1**) are about 40% higher than the isolated yield of this compound (Table 2, entry 1), the product must be unstable. In general, α-peroxy carbonyl compounds can be difficult to synthesize and isolate in high yield.[30–32] The products were found to be sensitive to chromatography, which was determined by converting the silyl peroxide to the more stable silyl ether (**10**, Scheme 7) using triphenylphosphine,[33] which resulted in an increased yield compared to the silyl peroxide (Table 2, entry 1). The products were also found to decompose during the course of the reaction. In the dearomatization reaction, the peroxide moiety is sensitive to the reaction conditions used, particularly to the presence of the metal catalyst.[11] Evidence for this sensitivity was found when furan **8c** was subjected to peroxidation conditions, resulting in formation of lactone **9** in addition to carboxylic acid **11** (Scheme 8). Silyl ester **12** could have been an intermediate, but it likely hydrolyzed to the carboxylic acid **11**.[34] Based on the yields of carboxylic acid **11** (Scheme 8), most of the starting material was converted to lactone **9** through the mechanism shown in Scheme 4, but during the course of the reaction, lactone **9** decomposed.

Scheme 7. Silyl Ether Formation



Scheme 8. Formation of Carboxylic Acid 11[a]

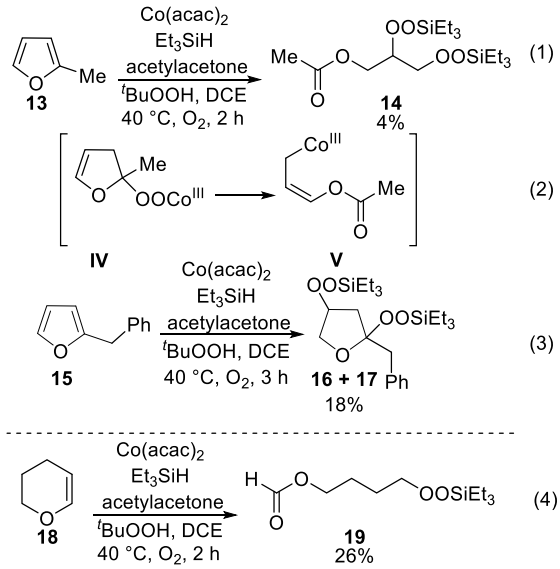


[a] Yields by ^{1}H NMR spectroscopy with mesitylene as internal standard.

The presence of a carbonyl group was not essential to observe peroxidation of furans, although different types of products were formed. Peroxidation of 2-methylfuran (**13**) formed only one product,[35] bis(silylperoxide) **14** (Scheme 9, eq 1), although the yield was low due to instability of bis(silylperoxide) **14** to chromatography. This product can be rationalized as involving initial peroxidation of **13** to form **IV**, followed by fragmentation to generate cobalt-alkyl species **V** (Scheme 9, eq 2). This complex would lead to the primary silyl peroxide, and then a second peroxidation would form bis(silylperoxide) **14** (Scheme 9, eq 2). 2-Benzylfuran (**15**, Scheme 9, eq 3) was also subjected to peroxidation conditions and instead of isolating a ring-opened product as seen with 2-methylfuran (**13**, Scheme 9, eq 1), diastereomeric bis(silylperoxides) **16** and **17** were isolated (Scheme 9, eq 3). In this case, the electron-withdrawing effect of the phenyl group seems to discourage the ring-opening mechanism depicted in Scheme 9, eq 2.

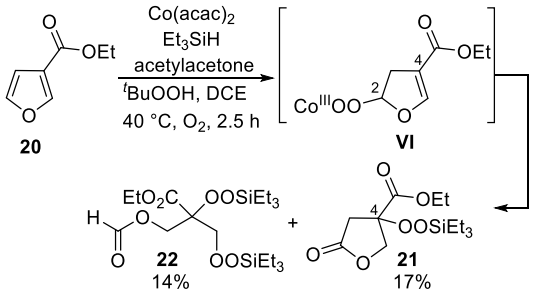
An experiment with dihydropyran **18** provided additional evidence supporting this ring-opening mechanistic hypothesis (Scheme 9, eq 2). Treatment of pyran **18** to the reaction conditions also produced a ring-opened product (**19**, Scheme 9, eq 4), likely through a similar pathway. The product, a primary peroxide, is difficult to synthesize by traditional cobalt-catalyzed peroxidation of alkenes, which forms secondary and tertiary peroxides.[4]

Scheme 9. Co-Catalyzed Oxygenation of 2-Methylfuran



The position of the carbonyl group on the furan influences reactivity. When the carbonyl group was placed at the 3-position, as seen in ethyl 3-furoate (**20**), lactone **21** and bis(silylperoxide) **22** were isolated (Scheme 10). A possible explanation for the formation of lactone **21** first involves formation of cobalt-alkyl species **VI** (Scheme 10). Decomposition of the peroxide at C_2 of cobalt-alkyl species **VI** would generate the lactone (Scheme 10), a process observed for furans substituted at this position with a hydroperoxyl group.[36–38] Finally, another peroxide formation at C_4 would occur to give lactone **21** (Scheme 10). Bis(silylperoxide) **22** (Scheme 10) could be formed through a ring-opening mechanism analogous to the one shown in Scheme 9.

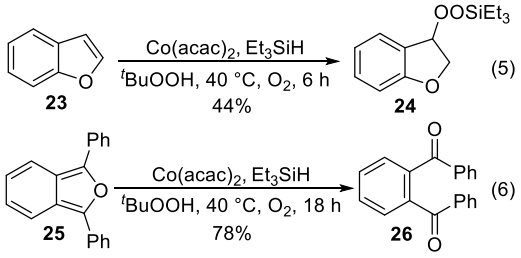
Scheme 10. Co-Catalyzed Oxygenation of Ethyl 3-Furoate



Other furan-containing aromatic compounds undergo dearomatization during cobalt-catalyzed oxygenation. Both 2,3-benzofuran (**23**) and 1,3-diphenyl isobenzofuran (**25**) produced oxidized products upon exposure to the reaction conditions optimized for 2-acetylfuran (Scheme 11). 2,3-Benzofuran (**23**) produced the corresponding silyl peroxide (**24**, Scheme 11,

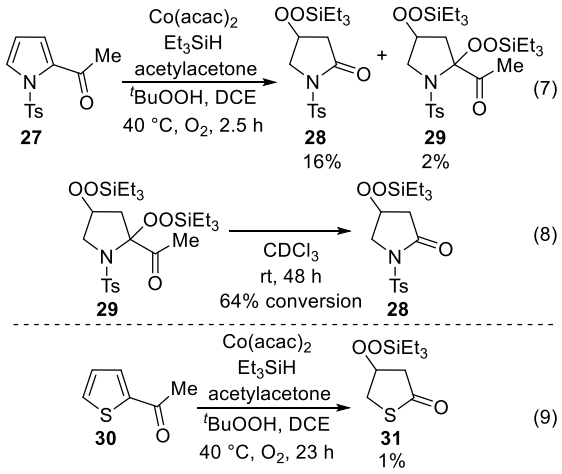
eq 5), which likely involves a stabilized benzylic radical intermediate.[10] The reaction of 1,3-diphenylisobenzofuran (**25**) produced dione **26** (Scheme 11, eq 6), a transformation that may follow a similar mechanism to the one proposed for reactions of **25** with peroxyl radicals.[39]

Scheme 11. Co-Catalyzed Oxygenation of Benzofurans



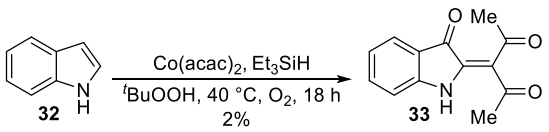
This cobalt-catalyzed dearomatization is not limited to furans. Pyrroles and thiophenes showed similar reactivity. Cobalt-catalyzed oxygenation of protected pyrrole **27** generated lactam **28** and only one isolable diastereomer of bis(silylperoxide) **29** (Scheme 12, eq 7), which is structurally analogous to bis(silylperoxide) **4** and **5** generated from 2-methylfuroate (Scheme 2). Just as in the case of the furan, this bis(silylperoxide) was shown to be a competent intermediate for the formation of the lactam (Scheme 12, eq 8). Similarly, 2-acetylthiophene (**30**) generated thiolactone **31**, although this reaction only proceeded to 1% conversion after 23 h (Scheme 12, eq 9). The yields and rates of reaction of the five-membered ring heteroaromatic compounds correlate with the degree of aromaticity that these three heteroarenes exhibit. Furans, the least aromatic of the three, converted most rapidly, while thiophenes showed the lowest conversions because of their greater aromaticity.[13]

Scheme 12. Co-Catalyzed Oxygenation of Pyrroles and Thiophenes



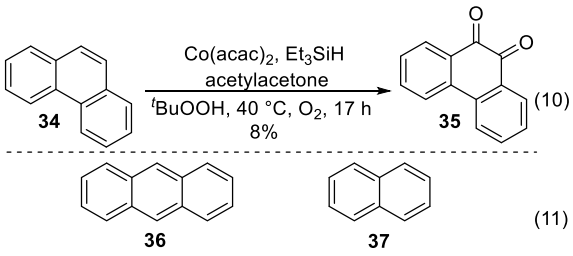
Indole (**32**) also reacted when subjected to cobalt-catalyzed oxygenation, although the reaction was slow. A trace amount of conjugated indolinone **33** (Scheme 13) was isolated, but indole **32** went mostly unreacted after 18 h. Indolinone **33** could be formed by incorporation of acetylacetonate into a 3*H*-indol-3-one.[40]

Scheme 13. Co-Catalyzed Oxygenation of Indoles



The cobalt-catalyzed oxygenation is not restricted to heteroaromatic compounds. Phenanthrene (**34**) was oxidized under these reaction conditions to form dione **35** (Scheme 14, eq 10). Anthracene (**36**) and naphthalene (**37**) were unreactive to cobalt-catalyzed oxygenation (Scheme 14, eq 11).[2,41]

Scheme 14. Co-Catalyzed Oxygenation of Arenes



CONCLUSION

In summary, we have demonstrated that cobalt-catalyzed oxygenation of aromatic compounds can occur. Under optimal conditions, furans, pyrroles, and thiophenes were dearomatized, yielding the corresponding lactones, lactams, and thiolactones. A mechanism has been suggested involving the formation of a bis(peroxy) intermediate, followed by cleavage of the carbonyl group. More structurally complex aromatic compounds, such as benzofuran and indole derivatives, were also oxidized. Cobalt-catalyzed oxygenation of indole allows for the incorporation of acetylacetonate, generating a highly conjugated indole derivative. Even arenes could be oxidized, indicating this reaction is not restricted to heteroarenes.

EXPERIMENTAL SECTION

General Information. All ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature using Brunker AVIII-400 (400 and 100 MHz, respectively), AV-500 (500 and 125 MHz, respectively) and AVIII-600 with TCI cryoprobe (600 and 150 MHz, respectively) spectrometers. The data were reported as follows: chemical shifts are reported in ppm from internal tetramethylsilane or from residual solvent peaks (^{1}H NMR: $CDCl_3$ δ 7.26; C_6D_6 δ 7.16; DMSO δ 2.50; and ^{13}C NMR: $CDCl_3$ δ 77.23; C_6D_6 δ 128.4; DMSO δ 39.5) on the δ scale, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (Hz), and integration. Multiplicity of carbon peaks was determined using HSQC or DEPT experiments. Infrared (IR) spectra were recorded using a Thermo Nicolet AVATAR Fourier Transform IR spectrometer using attenuated total reflectance (ATR). High-resolution mass spectra (HRMS) were recorded using an Agilent 6224 Accurate-Mass time-of-flight spectrometer with atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI) ionization sources. Melting points were reported uncorrected. Analytical thin layer chromatography was performed on Silicycle silica gel 60 Å F254 plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Silicycle silica gel (SiO_2) 60 (230-400 mesh). THF and Et_2O were dried and degassed using a solvent purification system before use. All reactions were run under a nitro-

gen atmosphere in glassware that had been flame-dried under vacuum unless otherwise stated. All reactions that were ran under an oxygen atmosphere used glassware that was not flame dried. The synthesis and characterization of compounds were reported previously. Unless otherwise noted, all reagents were commercially available. Compounds **3**,[42] **15**,[43] and **27**,[44] were prepared by known methods. $Co(acac)_2$,[45] Co(thd)2,[6] and $Co(modp)_2$,[8] were synthesized by known methods.

Optimization of Co-Catalyzed Oxygenation of Furans. Optimization reactions were performed as follows: A flask containing DCE (1,2-dichloroethane, 5 mL) was sparged with oxygen for 15 min. To a separate flask was added CoL_2 followed by 2-acetylfuran (0.050 g, 0.227 mmol). The oxygenated DCE (1.1 mL) was added to the reaction flask and the reaction flask was sparged with oxygen for 5 min. A solution of *tert*-butyl hydroperoxide in CH_2Cl_2 (1.0 M, 0.011 mL, 0.011 mmol) was added, followed by acetylacetone. Triethylsilane was added and the mixture stirred at the corresponding temperature under a balloon of oxygen for the time described in **Table 1**. The reaction mixture was filtered through a 3-cm plug of silica, eluted with CH_2Cl_2 (50 mL), and concentrated *in vacuo*. $CDCl_3$ (0.70 mL) was added and the crude reaction mixture was transferred to an NMR tube followed by mesitylene (0.020 mL, 0.144 mmol, internal standard). The yield of lactone **2** was determined based on ^{1}H NMR spectroscopic analysis of the area of the internal standard (δ 6.77) and the area of the methine group (δ 4.80) of lactone **2**.

Synthesis of Disubstituted Furan Substrates

Alcohol 7a. To a solution of furan **6** (0.271 mL, 2.73 mmol) in THF (4.1 mL) was added a solution of methylmagnesium chloride in Et_2O (3.0 M, 1.0 mL, 3.0 mmol). The resulting reaction mixture was stirred for 30 min. Saturated aqueous NH_4Cl (4 mL) was added and the mixture was extracted with diethyl ether (3 × 4 mL). The combined organic layers were dried over Na_2SO_4, and concentrated *in vacuo*. Alcohol **7a** was isolated as a yellow oil (0.316 g, 92%) and used without further purification. The spectroscopic data are consistent with the data reported:[46] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.07 (d, J = 3.0, 1H), 5.87 (d, J = 2.9, 1H), 4.78 (q, J = 6.5, 1H), 2.54 (s, 1H), 2.26 (s, 3H), 1.48 (d, J = 6.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 151.6, 106.0, 105.9, 63.6, 21.3, 13.6; IR (ATR) 3345, 2979, 1563, 1220, 1073, 1015, 782 cm^{-1}.

Alcohol 7b. To a solution of magnesium turnings (0.078 g, 3.21 mmol) in THF (2.4 mL) was added 4-bromoanisole (0.201 mL, 1.60 mmol). The resulting solution was stirred for 1 h, then furan **6** (0.160 mL, 1.60 mmol) was added. The resulting solution was stirred for 1 h. Saturated aqueous NH_4Cl (3 mL) was added and the mixture was extracted with Et_2O (3 × 3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Alcohol **7b** was isolated as a yellow oil (0.302 g, 86%) and used without further purification: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5, 2H), 6.91 (d, J = 8.5, 2H), 5.95 (d, J = 3.0, 1H), 5.89 (d, J = 2.9, 1H), 5.73 (d, J = 4.2, 1H), 3.82 (s, 3H), 2.32 (d, J = 4.3, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (C), 154.6 (C), 152.5 (C), 133.5 (C), 128.2 (CH), 114.0 (CH), 108.5 (CH), 106.3 (CH), 70.0 (CH), 55.5 (CH_3), 13.8 (CH_3); IR (ATR) 3409, 1611, 1511, 1172, 1030, 778 cm^{-1}; HRMS (APCI) m/z calcd for $C_{13}H_{13}O_2$ (M + H – H_2O)$^+$ 201.0910, found 201.0909.

Alcohol 7c. To a solution of magnesium turnings (0.076 g, 3.11 mmol) in THF (2.3 mL) was added 4-bromobenzotrifluoride (0.220 mL, 1.56 mmol). The resulting solution was stirred for 1 h, then **6** (0.155 mL, 1.56 mmol) was added. The resulting solution was stirred for 1 h. Saturated aqueous NH_4Cl (3 mL) was added and the mixture was extracted with Et_2O (3 × 3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 90:10) afforded alcohol **7c** (0.317 g, 80%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, J = 8.3, 2H), 7.57 (d, J = 8.1, 2H), 5.97 (d, J = 3.1, 1H), 5.91 (d, J = 3.1, 1H), 5.82 (d, J = 3.9, 1H), 2.61 (d, J = 3.8, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5 (C), 153.0 (C), 144.9 (C), 130.2 (q, J = 31.5, C), 127.1 (CH), 125.5 (q, J = 3.0, CH), 124.3 (q, J = 270.3, C), 109.1 (CH), 106.5 (CH), 69.6 (CH), 13.7 (CH_3); IR (ATR) 3332, 1620, 1322, 1162, 1120, 1066, 1016, 779 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{10}F_3O$ (M + H – H_2O)$^+$ 239.0678, found 239.0681. Anal. Calcd for $C_{13}H_{11}F_3O_2$: C, 60.94; H, 4.33. Found: C, 61.03; H, 4.41.

Ketone 8a. To a solution of alcohol **7a** (0.316 g, 2.50 mmol) in EtOAc (4.5 mL) was added 2-iodoxybenzoic acid (2.10 g, 7.51 mmol). The resulting suspension was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a glass frit. The filter cake was washed with EtOAc (3 × 5 mL) and the filtrate was concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 90:10) afforded ketone **8a** (0.227 g, 73%) as a yellow oil. The spectroscopic data are consistent with the data reported:[47] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 3.4, 1H), 6.16 (d, J = 3.4, 1H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.3, 158.1, 151.8, 119.6, 109.1, 25.9, 14.3; IR (ATR) 1669, 1515, 1372, 1209, 1027, 667 cm^{-1}; HRMS (APCI) m/z calcd for $C_7H_9O_2$ (M + H)$^+$ 125.0597, found 125.0596.

Ketone 8b. To a solution of alcohol **7b** (0.301 g, 1.38 mmol) in EtOAc (2.5 mL) was added 2-iodoxybenzoic acid (1.15 g, 4.14 mmol). The resulting suspension was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a glass frit. The filter cake was washed with EtOAc (3 × 5 mL) and the filtrate was concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 90:10) afforded ketone **8b** (0.115 g, 39%) as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9, 2H), 7.10 (d, J = 3.4, 1H), 6.96 (d, J = 8.9, 2H), 6.20 (d, J = 3.5, 1H), 3.87 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.1 (C), 163.2 (C), 158.2 (C), 151.4 (C), 131.6 (CH), 130.4 (C), 122.0 (CH), 113.8 (CH), 109.0 (CH), 55.6 (CH_3), 14.3 (CH_3); IR (ATR) 1631, 1597, 1502, 1254, 1161, 1025, 883, 762 cm^{-1}; HRMS (APCI) m/z calcd for $C_{13}H_{13}O_3$ (M + H)$^+$ 217.0859, found 217.0857.

Ketone 8c. To a solution of alcohol **7c** (0.245 g, 0.960 mmol) in EtOAc (1.7 mL) was added 2-iodoxybenzoic acid (0.621 g, 2.87 mmol). The resulting suspension was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and filtered through a glass frit. The filter cake was washed with EtOAc (3 × 5 mL) and the filtrate was concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 95:5) afforded ketone **8c** (0.124 g, 51%) as a white solid: mp 110−114 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.8, 2H), 7.75 (d, J = 7.8, 2H), 7.15 (d, J = 2.8, 1H), 6.26 (d, J = 2.6, 1H), 2.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.0 (C), 159.7 (C), 150.8 (C), 140.9 (C), 133.8 (q, J = 31.5, C), 129.6 (CH), 125.6 (q, J = 3.0, CH) 123.9 (q, J = 271.7, C), 123.7 (CH), 109.7 (CH), 14.4 (CH_3); IR (ATR) 1637, 1514, 1329, 1163, 1067, 767 cm^{-1}; HRMS (APCI) m/z calcd for $C_{13}H_{10}F_3O_2$ (M + H)$^+$ 255.0627, found 255.0631. Anal. Calcd for $C_{13}H_9F_3O_2$: C, 61.42; H, 3.57. Found: C, 61.15; H, 3.53.

Representative Procedure for the Co-Catalyzed Oxygenation of Aromatic Compounds (Lactone 2). A flask containing DCE (1,2-dichloroethane, 10 mL) was sparged with oxygen for 15 min. To a separate flask was added $Co(acac)_2$ (0.013 g, 0.050 mmol) followed by furan **1** (0.110 g, 1.00 mmol). The oxygenated DCE (4.5 mL) was added to the reaction flask and the reaction vessel was sparged with oxygen for 5 min. A solution of *tert*-butyl hydroperoxide in CH_2Cl_2 (1.0 M, 0.050 mL, 0.050 mmol) was added followed by acetylacetone (0.103 mL, 1.00 mmol). Triethylsilane (2.39 mL, 15.0 mmol) was added and the reaction mixture was stirred at 40 °C under a balloon of oxygen for 2 h. The reaction mixture was filtered through a 3-cm plug of silica, eluted with CH_2Cl_2 (50 mL), and concentrated *in vacuo*. Purification by flash chromatography (pentane:Et_2O = 80:20) afforded lactone **2** (0.050 g, 23%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (t, J

= 5.5, 1H), 4.57 (d, *J* = 10.9, 1H), 4.34 (dd, *J* = 10.9, 4.7, 1H), 2.71 (dd, *J* = 18.5, 6.5, 1H), 2.62 (d, *J* = 18.5, 1H), 0.96 (t, *J* = 8.0, 9H), 0.67 (q, *J* = 8.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3 (C), 79.9 (CH), 71.7 (CH_2), 33.1 (CH_2), 6.7 (CH_3), 3.8 (CH_2); IR (ATR) 2957, 2878, 1785, 1165, 1005, 793, 741 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{10}H_{21}O_4Si$ $(M + H)^+$ 233.1204, found 233.1203.

Lactone 2 and bis(silylperoxy) esters 4 and 5. Lactone **2** and bis(silylperoxy) esters **4** and **5** were prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using methyl 2-furoate (**3**, 0.085 mL, 0.793 mmol), $Co(acac)_2$ (0.010 g, 0.040 mmol), *tert*-butyl hydroperoxide (0.040 mL, 0.040 mmol), acetylacetone (0.081 mL, 0.793 mmol), and triethylsilane (1.89 mL, 11.9 mmol) in DCE (3.6 mL). The reaction time was 2.5 h. Purification by flash chromatography (hexane:EtOAc = 90:10) afforded lactone **2** as a colorless oil (0.028 g, 15%) and diastereomeric silyl peroxides **4** and **5** separately as colorless oils (0.015 g, 4%; 0.017 g, 5%, respectively). The spectroscopic data are consistent with the data reported above for lactone **2**. **Bis(silylperoxy) ester 4**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.70 (m, 1H), 4.36 (d, *J* = 10.4, 1H), 4.05 (dd, *J* = 10.4, 4.3, 1H), 3.80 (s, 3H), 2.42 (dd, *J* = 15.8, 2.6, 1H), 2.36 (dd, *J* = 15.7, 6.4, 1H), 0.95 (m, 18H), 0.66 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6 (C), 110.6 (C), 83.5 (CH), 72.2 (CH_2), 52.8 (CH_3), 38.9 (CH_2), 6.84 (CH_3), 6.76 (CH_3), 3.87 (CH_2), 3.82 (CH_2); IR (ATR) 2954, 1772, 1751, 1127, 1005, 800, 730 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{38}NaO_7Si_2$ $(M + Na)^+$ 445.2048, found 445.2050. **Bis(silylperoxy) ester 5**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.71 (m, 1H), 4.32 (dd, *J* = 10.2, 6.0, 1H), 4.15 (dd, *J* = 10.2, 3.6, 1H), 3.82 (s, 3H), 2.38 (d, *J* = 4.8, 2H), 0.99 (t, *J* = 8.4, 18H), 0.70 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) 168.1 (C), 109.9 (CH), 82.7 (CH), 72.6 (CH_2), 52.8 (CH_3), 39.1 (CH_2), 6.85 (CH_3), 6.74 (CH_3), 3.8 (CH_2); IR (ATR) 2954, 1767, 1240, 1106, 807, 740 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{38}NaO_7Si_2$ $(M + Na)^+$ 445.2048, found 445.2047.

Lactone 9 prepared from furan 8a. Lactone **9** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using ketone **8a** (0.100 g, 0.806 mmol), $Co(acac)_2$ (0.010 g, 0.040 mmol), *tert*-butyl hydroperoxide (0.040 mL, 0.040 mmol), acetylacetone (0.083 mL, 0.806 mmol), and triethylsilane (1.93 mL, 12.1 mmol) in DCE (3.7 mL). The reaction time was 4 h. Purification by flash chromatography (hexane:EtOAc = 90:10) afforded lactone **9** as a colorless oil (0.038 g, 19%): ^{1}H NMR (600 MHz, C_6D_6) δ 4.55 (q, *J* = 6.9, 1H), 3.85 (d, *J* = 6.9, 1H), 2.31 (dd, *J* = 18.4, 2.2, 1H), 2.09 (dd, *J* = 18.4, 6.9, 1H), 0.94 (t, *J* = 8.0, 9H), 0.75 (d, *J* = 6.9, 3H), 0.60 (q, *J* = 7.9, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7 (C), 84.8 (CH), 78.4 (CH), 31.9 (CH_2), 18.5 (CH_3), 6.5 (CH_3), 3.6 (CH_2); IR (ATR) 1789, 1617, 1453, 1329, 1166, 743 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{11}H_{22}NaO_4Si$ $(M + Na)^+$ 269.1180, found 269.1184.

Lactone 9 prepared from furan 8b. Lactone **9** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using ketone **8b** (0.100 g, 0.463 mmol), $Co(acac)_2$ (0.006 g, 0.023 mmol), *tert*-butyl hydroperoxide (0.023 mL, 0.023 mmol), acetylacetone (0.047 mL, 0.463 mmol), and triethylsilane (1.11 mL, 6.94 mmol) in DCE (2.1 mL). The reaction time was 3 h. Purification by repeated flash chromatography (twice, pentane:Et_2O = 90:10) afforded lactone **9** as a colorless oil (0.008 g, 7%). The spectroscopic data matched the reported values above for lactone **9**.

Lactone 9 prepared from furan 8c. Lactone **9** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using ketone **8c** (0.100 g, 0.393 mmol), $Co(acac)_2$ (0.005 g, 0.020 mmol), *tert*-butyl hydroperoxide (0.020 mL, 0.050 mmol), acetylacetone (0.040 mL, 0.393 mmol), and triethylsilane (0.942 mL, 15.0 mmol) in DCE (1.8 mL). The reaction time was 2.25 h. Purification by repeated flash chromatography (twice, pentane:Et_2O = 90:10) afforded lactone **9** as a colorless oil (0.004 g, 4%). The spectroscopic data match the reported values above for lactone **9**.

Lactone 9 prepared from furan 6. Lactone **9** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using furan **6** (0.100 mL, 1.00 mmol), $Co(acac)_2$ (0.051 g, 0.200 mmol), *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol), acetylacetone (0.103 mL, 1.00 mmol), and triethylsilane (2.39 mL, 15.0 mmol) in DCE (4.5 mL). The reaction time was 4 h. Purification by flash chromatography (pentane:Et_2O = 95:5 → pentane:Et_2O = 90:10) afforded lactone **9** as a colorless oil (0.020 g, 8%). The spectroscopic data match the reported values above for lactone **9**.

Alcohol 9a. To a solution of lactone **9** (0.038 g, 0.154 mmol) in EtOAc (0.70 mL) was added triphenylphosphine (0.061 g, 0.231 mmol). The reaction mixture was stirred at room temperature for 5 h, then it was concentrated *in vacuo*. Purification by flash column chromatography (hexane:EtOAc = 90:10) afforded the silyl ether product as a colorless oil (0.020 g, 57%): ^{1}H NMR (600 MHz, C_6D_6) δ 4.02 (m, 1H), 3.48 (q, *J* = 5.4, 1H), 2.24 (dd, *J* = 17.2, 6.6, 1H), 2.10 (dd, *J* = 17.2, 5.3, 1H), 0.89 (d, *J* = 6.6, 3H), 0.82 (t, *J* = 8.0, 9H), 0.37 (q, *J* = 8.0, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 173.5 (C), 83.3 (CH), 74.0 (CH), 38.5 (CH_2), 18.5 (CH_3), 7.1 (CH_2), 5.2 (CH_3); IR ATR 2956, 2877, 1786, 1168, 1077, 1010, 747 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{22}NaO_3Si$ $(M + Na)^+$ 253.1230, found 253.1231.

To a solution of the above silyl ether (0.020 g, 0.089 mmol) in Et_2O (0.89 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 M, 0.13 mL, 0.13 mmol). The resulting reaction mixture was stirred for 1.5 h. H_2O (1 mL) was added and the mixture was extracted with Et_2O (3 × 1 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under a stream of nitrogen. Purification by flash chromatography (hexane:EtOAc = 50:50) afforded alcohol **9a** as a colorless oil (0.001 g, 10%). The spectroscopic data are consistent with the data reported:[21] ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.50 (m, 1H), 4.27 (m, 1H), 2.87 (dd, *J* = 17.9, 6.5, 1H), 2.53 (dd, *J* = 17.9, 3.8, 1H), 2.00 (d, *J* = 4.2, 1H), 1.39 (d, *J* = 6.6, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.7, 83.9, 73.3, 37.6, 18.8.

Silyl ether 10. A flask containing DCE (1,2-dichloroethane, 10 mL) was sparged with oxygen for 15 min. To a separate flask was added $Co(acac)_2$ (0.013 g, 0.05 mmol) followed by 2-acetylfuran (0.110 g, 1.00 mmol). The oxygenated DCE (4.5 mL) was added to the reaction flask and the reaction vessel was sparged with oxygen for 5 min. A solution of *tert*-butyl hydroperoxide (0.050 mL, 0.050 mmol) in CH_2Cl_2 was added followed by acetylacetone (0.103 mL, 1.00 mmol). Triethylsilane (2.39 mL, 15.0 mmol) was added and the reaction mixture was stirred at 40 °C under a balloon of oxygen for 2 h. Triphenylphosphine (0.262 g, 1.00 mmol) was added directly to the reaction mixture, which was stirred at room temperature for 3 h. The reaction mixture was filtered through a 3-cm plug of silica, eluted with CH_2Cl_2 (50 mL), and concentrated *in vacuo*. Purification by flash chromatography (pentane:Et_2O = 80:20) afforded silyl ether **10** (0.072 g, 33%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.58 (m, 1H), 4.35 (dd, *J* = 9.7, 4.7, 1H), 4.14 (dd, *J* = 9.7, 1.8, 1H), 2.67 (dd, *J* = 17.5, 6.2, 1H), 2.41 (dd, *J* = 17.5, 2.4, 1H), 0.92 (t, *J* = 8.1, 9H), 0.59 (q, *J* = 8.0, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9 (C), 76.3 (CH), 67.9 (CH_2), 38.3 (CH_2), 6.7 (CH_3), 4.7 (CH_2); IR (ATR) 2955, 2877, 1780, 1162, 1092, 999, 727 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{10}H_{21}O_3Si$ $(M + H)^+$ 217.1254, found 217.1256. Anal. Calcd for $C_{10}H_{20}O_3Si$: C, 55.52; H, 9.32. Found: C, 55.78; H, 9.21.

Lactone 9 and Carboxylic acid 11 from furan 8c. Lactone **9** was prepared using the using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using ketone **8c** (0.055 g, 0.220 mmol), $Co(acac)_2$ (0.003 g, 0.011 mmol), *tert*-butyl hydroperoxide (0.011 mL, 0.011 mmol), acetylacetone (0.022 mL,

0.220 mmol), and triethylsilane (0.530 mL, 3.30 mmol) in DCE (1.0 mL). The reaction time was 2.5 h. $CDCl_3$ (0.70 mL) was added and the crude reaction mixture was transferred to an NMR tube followed by mesitylene (0.031 mL, 0.220 mmol, internal standard). The yield of lactone **9** and carboxylic acid **11** was determined based on ^{1}H NMR spectroscopic analysis of the area of the internal standard (δ 6.77) and the area of the methine group of lactone **9** (δ 4.81) and carboxylic acid **11** (δ 8.16). Purification by flash chromatography (hexane:EtOAc = 75:25 → hexane:EtOAc = 50:50) afforded an analytical sample of carboxylic acid **11** (0.004 g, 10%) as a white solid. The spectroscopic data are consistent with the data reported:[48] ^{1}H NMR (600 MHz, DMSO) δ 8.14 (d, J = 8.0, 2H), 7.88 (d, J = 8.1, 2H); ^{13}C NMR (150 MHz, DMSO) δ 166.2, 134.9, 132.3 (q, J = 31.6), 130.1, 125.6, 124.7 (q, J = 272.2); IR (ATR) 3312, 1762 cm^{-1}.

Silyl peroxide 14. Silyl peroxide **14** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using 2-methylfuran (**13**, 0.080 mL, 0.914 mmol), $Co(acac)_2$ (0.012 g, 0.046 mmol), *tert*-butyl hydroperoxide (0.046 mL, 0.046 mmol), acetylacetone (0.093 mL, 0.914 mmol), and triethylsilane (2.19 mL, 13.7 mmol) in DCE (4.2 mL). The reaction time was 2 h. Purification by flash chromatography (hexane:EtOAc = 95:5) afforded silyl peroxide **14** as a colorless oil (0.015 g, 4%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.44 (m, 1H), 4.34 (dd, J = 12.1, 3.8, 1H), 4.27 (dd, J = 12.1, 5.7, 1H), 4.20 (dd, J = 12.1, 5.6, 1H), 4.08 (dd, J = 12.1, 4.9, 1H), 2.08 (s, 3H), 0.98 (m, 18H), 0.70 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0 (C), 80.8 (CH), 74.4 (CH_2), 62.2 (CH_2), 21.0 (CH_3), 6.85 (CH_3), 6.84 (CH_3), 3.81 (CH_2), 3.79 (CH_2); IR (ATR) 2958, 2878, 1747, 1236, 849, 740 cm^{-1}; HRMS (APCI) m/z calcd for $C_{17}H_{39}O_6Si_2$ $(M + H)^+$ 395.2279, found 395.2277.

Bis(silylperoxide) 16 and 17. Bis(silylperoxides) **16** and **17** were prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using 2-benzylfuran (**15**, 0.055 g, 0.348 mmol), $Co(acac)_2$ (0.005 g, 0.017 mmol), *tert*-butyl hydroperoxide (0.017 mL, 0.017 mmol), acetylacetone (0.036 mL, 0.348 mmol), and triethylsilane (0.833 mL, 5.22 mmol) in DCE (1.6 mL). The reaction time was 2.5 h. Purification by flash chromatography (hexane → hexane:EtOAc = 98:2) afforded bis(silylperoxides) **16** and **17** as an inseparable 59:41 mixture of diastereomers: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.21 (m, 8.5H), 4.75 (m, 0.6H), 4.43 (m, 1H), 4.17 (d, J = 9.8, 0.7H), 4.13 (dd, J = 9.8, 4.4, 0.7H), 4.09 (dd, J = 9.6, 6.4, 1H), 4.00 (dd, J = 9.7, 4.9, 1H), 3.25 (d, J = 10.6, 0.7H), 3.23 (d, J = 10.5, 1H), 3.15 (d, J = 13.9, 1H), 2.27 (dd, J = 15.0, 7.2, 0.7H), 2.08 (dd, J = 15.0, 8.1, 1H), 1.96 (m, 1.7H), 1.05–0.93 (m, 36.9H), 0.80–0.62 (m, 24.6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.9 (C), 136.6 (C), 130.74 (CH), 130.71 (CH), 128.2 (CH), 128.1 (CH), 126.69 (CH), 126.66 (CH), 114.6 (C), 114.0 (C), 85.3 (CH), 83.7 (CH), 72.7 (CH_2), 71.9 (CH_2), 42.2 (CH_2), 40.9 (CH_2), 37.5 (CH_2), 37.2 (CH_2), 6.93 (CH_3), 6.91 (CH_3), 6.90 (CH_3), 6.84 (CH_3), 4.04 (CH_2), 3.99 (CH_2), 3.89 (CH_2), 3.80 (CH_2); IR (ATR) 2954, 2877, 1456, 1239, 1006, 803, 740, 701 cm^{-1}; HRMS (APCI) m/z calcd for $C_{23}H_{46}NO_5Si_2$ $(M + NH_4)^+$ 472.2909, found 472.2904.

Silyl peroxide 19. Silyl peroxide **19** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using pyran **18** (0.054 mL, 0.594 mmol), $Co(acac)_2$ (0.008 g, 0.030 mmol), *tert*-butyl hydroperoxide (0.030 mL, 0.030 mmol), acetylacetone (0.061 mL, 0.594 mmol), and triethylsilane (1.42 mL, 8.92 mmol) in DCE (2.7 mL). The reaction time was 2 h. Purification by flash chromatography (hexane:EtOAc = 95:5) afforded silyl peroxide **19** as a colorless oil (0.038 g, 26%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 4.18 (t, J = 6.3, 2H), 4.00 (t, J = 6.1, 2H), 1.73 (m, 4H), 0.99 (t, J = 8.0, 9H), 0.69 (q, J = 7.9, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.3 (CH), 76.3 (CH_2), 63.9 (CH_2), 25.5 (CH_2), 24.6 (CH_2), 6.9 (CH_3), 3.9 (CH_2); IR (ATR) 2955, 2877, 1726, 1168, 1006, 863, 730 cm^{-1}; HRMS (APCI) m/z calcd for $C_{11}H_{24}KO_4Si$ $(M + K)^+$ 287.1075, found 287.1067.

Lactone 21 and Silyl peroxide 22. Lactone **21** and silyl peroxide **22** were prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using ethyl 3-furoate (**20**, 0.096 mL, 0.714 mmol), $Co(acac)_2$ (0.009 g, 0.036 mmol), *tert*-butyl hydroperoxide (0.036 mL, 0.036 mmol), acetylacetone (0.073 mL, 0.714 mmol), and triethylsilane (1.71 mL, 10.7 mmol) in DCE (3.2 mL). The reaction time was 2.5 h. Purification by flash chromatography (hexane:EtOAc = 95:5) afforded lactone **21** as a colorless oil (0.037 g, 17%) and silyl peroxide **22** as a colorless oil (0.044 g, 14%). **Lactone 21**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (d, J = 10.9, 1H), 4.53 (d, J = 10.9, 1H), 4.27 (q, J = 7.2, 2H), 3.04 (d, J = 18.5, 1H), 2.90 (d, J = 18.6, 1H), 1.31 (t, J = 7.2, 3H), 0.96 (t, J = 8.0, 9H), 0.68 (q, J = 7.9, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.4 (C), 168.4 (C), 87.9 (C), 71.7 (CH_2), 62.5 (CH_2), 36.3 (CH_2), 14.2 (CH_3), 6.7 (CH_3), 3.7 (CH_2); IR (ATR) 2957, 1794, 1743, 1310, 1030, 803, 742 cm^{-1}; HRMS (APCI) m/z calcd for $C_{13}H_{25}O_6Si$ $(M + H)^+$ 305.1415, found 305.1417. **Silyl peroxide 22**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 4.81 (d, J = 12.0, 1H), 4.62 (d, J = 12.1, 1H), 4.32 (d, J = 12.0, 1H), 4.22 (m, 2H), 4.17 (d, J = 12.0, 1H), 1.29 (t, J = 7.2, 3H), 0.95 (t, J = 8.1, 18H), 0.66 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6 (C), 160.7 (CH), 85.6 (C), 74.0 (CH_2), 61.6 (CH_2), 60.6 (CH_2), 14.2 (CH_3), 6.77 (CH_3), 6.73 (CH_3), 3.79 (CH_2), 3.73 (CH_2); IR (ATR) 2956, 2878, 1735, 1172, 1019, 847, 733 cm^{-1}; HRMS (APCI) m/z calcd for $C_{19}H_{44}NO_8Si_2$ $(M + NH_4)^+$ 470.2600, found 470.2600.

Silyl peroxide 24. Silyl peroxide **24** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using benzofuran **23** (0.090 mL, 0.847 mmol), $Co(acac)_2$ (0.011 g, 0.042 mmol), *tert*-butyl hydroperoxide (0.042 mL, 0.042 mmol), and triethylsilane (0.676 mL, 4.23 mmol) in DCE (3.8 mL). The reaction time was 6 h. Purification by flash chromatography (pentane → pentane:Et_2O = 95:5) afforded silyl peroxide **24** (0.099 g, 44%) as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2, 1H), 7.30 (t, J = 7.8, 1H), 6.93 (t, J = 7.2, 1H), 6.89 (d, J = 7.8, 1H), 5.61 (dd, J = 6.0, 1.8, 1H), 4.78 (dd, J = 11.4, 2.0, 1H), 4.47 (dd, J = 11.1, 6.0, 1H), 0.99, (t, J = 7.8, 9H), 0.70 (q, J = 7.8, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8 (C), 131.6 (CH), 127.3 (CH), 123.5 (C), 120.7 (CH), 110.7 (CH), 84.9 (CH), 75.4 (CH_2), 6.9 (CH_3), 3.9 (CH_2); IR (ATR) 2954, 2877, 1612, 1600, 1479, 1246, 1015, 963, 832 cm^{-1}; HRMS (APCI) m/z calcd for $C_{14}H_{21}O_2Si$ $(M + H - H_2O)^+$ 249.1305, found 249.1306.

Dione 26. Dione **26** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using isobenzofuran **25** (0.050 g, 0.185 mmol), $Co(acac)_2$ (0.002 g, 0.009 mmol), *tert*-butyl hydroperoxide (0.009 mL, 0.009 mmol), and triethylsilane (0.440 mL, 2.78 mmol) in DCE (1.7 mL). The reaction time was 18 h. Following the workup as described above, dione **26** isolated as a white, off-yellow solid (0.041 g, 78%). Characterization was performed without further purification. The spectroscopic data are consistent with the data reported:[49] mp 130–133 °C, which is lower than reported literature value (138–139 °C)[49] due to residual impurities; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 1.2, 2H), 7.70 (d, J = 1.1, 2H), 7.63 (d, J = 1.1, 4H), 7.53 (m, 2H), 7.39 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8 (C), 140.2 (C), 137.4 (C), 133.2 (CH), 130.6 (CH), 130.0 (CH), 129.9 (CH), 128.5 (CH); IR (ATR) 1659, 1596, 1278, 937, 704 cm^{-1}; HRMS (ESI) m/z calcd for $C_{20}H_{14}NaO_2$ $(M + Na)^+$ 309.0886, found 309.0898.

Lactam 28 and Bis(silylperoxy) ketone 29. Lactam **28** and bis(silyl peroxy) ketone **29** were prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using pyrrole **27** (0.100 g, 0.380 mmol), $Co(acac)_2$ (0.020 g, 0.076 mmol), *tert*-butyl hydroperoxide (0.019 mL, 0.019 mmol), acetylacetone (0.039 mL, 0.380 mmol), and triethylsilane (0.909 mL, 5.70 mmol) in DCE (1.7 mL). The reaction time was 2.5 h.

Purification by flash chromatography (pentane:Et_2O = 95:5 → pentane:Et_2O = 90:10) afforded lactam **28** as a colorless oil (0.024 g, 16%) and silyl peroxide **29** as a colorless oil (0.004 g, 2%). **Lactam 28**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4, 2H), 7.33 (d, J = 8.4, 2H), 4.64 (t, J = 5.4, 1H), 4.24 (d, J = 12.0, 1H), 4.00 (dd, J = 12.0, 5.4, 1H), 2.72 (dd, J = 18.4, 6.7, 1H), 2.53 (d, J = 18.3, 1H), 2.44 (s, 3H), 0.92 (t, J = 7.8, 9H), 0.61 (q, J = 7.8, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9 (C), 145.4 (C), 135.4 (C), 129.8 (CH), 128.3 (CH), 76.0 (CH), 51.6 (CH_2), 37.3 (CH_2), 21.9 (CH_3), 6.8 (CH_3), 3.8 (CH_2); IR (ATR) 2956, 2877, 1742, 1362, 1169, 1089, 663 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{27}NNaO_5SSi$ $(M + Na)^+$ 408.1271, found 408.1268. Anal. Calcd for $C_{17}H_{27}NO_5SSi$: C, 52.99; H, 7.06. Found: C, 52.69; H, 7.06. **Bis(silylperoxy) ketone 29**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4, 2H), 7.29 (d, J = 8.3, 2H), 4.87 (m, 1H), 3.78 (dd, J = 9.6, 6.6, 1H), 3.48 (dd, J = 9.6, 3.6, 1H), 2.60 (dd, J = 14.4, 7.6, 1H), 2.42 (s, 3H), 2.40 (s, 3H), 2.28 (dd, J = 14.2, 5.7, 1H), 0.99 (t, J = 7.8, 9H), 0.94 (t, J = 7.8, 9H), 0.73 (q, J = 7.8, 6H), 0.69 (q, J = 7.8, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.6 (C), 143.7 (C), 136.0 (C), 129.5 (CH), 128.4 (CH), 103.3 (C), 82.2 (CH), 53.4 (CH_2), 41.0 (CH_2), 27.4 (CH_3), 21.8 (CH_3), 6.84 (CH_3), 6.83 (CH_3), 4.0 (CH_2), 3.8 (CH_2); IR (ATR) 2956, 2877, 1737, 1349, 1011, 784, 676 cm^{-1}; HRMS (APCI) m/z calcd for $C_{25}H_{49}N_2O_7SSi_2$ $(M + NH_4)^+$ 577.2794, found 577.2799.

Thiolactone 31. Thiolactone **31** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using thiophene **30** (0.085 mL, 0.793 mmol), $Co(acac)_2$ (0.041 g, 0.159 mmol), *tert*-butyl hydroperoxide (0.039 mL, 0.039 mmol), acetylacetone (0.081 mL, 0.793 mmol), and triethylsilane (1.89 mL, 11.9 mmol) in DCE (3.6 mL). The reaction time was 23 h. Purification by flash chromatography (hexane:EtOAc = 90:10) afforded thiolactone **31** as a colorless oil (0.001 g, 1%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.85 (m, 1H), 3.78 (dd, J = 12.2, 2.2, 1H), 3.59 (dd, J = 12.3, 4.6, 1H), 2.77 (dd, J = 17.4, 5.4, 1H), 2.72 (dd, J = 17.4, 3.0, 1H), 1.00 (t, J = 7.8, 9H), 0.71 (q, J = 7.8, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.3 (C), 81.2 (CH), 45.3 (CH_2), 36.3 (CH_2), 6.9 (CH_3), 3.9 (CH_2); IR (ATR) 2955, 1711, 1008, 792, 742 cm^{-1}; HRMS (APCI) m/z calcd for $C_{10}H_{19}O_2SSi$ $(M + H - H_2O)^+$ 231.0870, found 231.0870.

Dione 33. Dione **33** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using indole **32** (0.100 g, 0.854 mmol), $Co(acac)_2$ (0.044 g, 0.171 mmol), *tert*-butyl hydroperoxide (0.043 mL, 0.043 mmol), and triethylsilane (0.273 mL, 1.71 mmol) in DCE (3.9 mL). The reaction time was 18 h. Workup was performed as describe above except the silica plug was eluted with 100 mL of hexane:EtOAc (80:20). Purification by flash chromatography (hexane:EtOAc = 85:15 → hexane:EtOAc = 80:20 → hexane:EtOAc = 70:30) afforded dione **33** as a red solid (0.003 g, 2%): mp 205−208 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.19 (br, 1H), 7.65 (d, J = 9.0, 1H), 7.52 (t, J = 9.6, 1H), 7.03 (t, J = 9.0, 1H), 6.95 (d, J = 9.6, 1H), 2.58 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.7 (C), 197.9 (C), 188.8 (C), 153.1 (C), 140.4 (C), 137.9 (CH), 125.9 (CH), 122.8 (CH), 119.6 (C), 117.0 (C), 112.4 (CH), 32.5 (CH_3), 29.2 (CH_3); IR (ATR) 3300, 1714, 1682, 1639, 1614, 1573, 1464, 1176 cm^{-1}; HRMS (APCI) m/z calcd for $C_{13}H_{10}NO_2$ $(M + H - H_2O)^+$ 212.0706, found 212.0706.

Dione 35. Dione **35** was prepared using the representative procedure for the Co-catalyzed oxygenation of aromatic compounds using arene **34** (0.100 g, 0.561 mmol), $Co(acac)_2$ (0.029 g, 0.112 mmol), *tert*-butyl hydroperoxide (0.028 mL, 0.028 mmol), acetylacetone (0.057 mL, 0.561 mmol), and triethylsilane (1.34 mL, 8.42 mmol) in DCE (2.6 mL). The reaction time was 17 h. Purification by flash chromatography (hexane:EtOAc:Et_3N = 85:14:1) afforded dione **35** as an orange solid (0.009 g, 8%). The spectroscopic data are consistent with the data reported:[50] mp 192–194 °C, which is lower than reported literature value (207–208 °C)[50] due to impurities which could not be removed by chromatography; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0, 2H), 8.03 (d, J = 8.0, 2H), 7.73 (t, J = 7.5, 2H), 7.48 (t, J = 8.0, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6 (C), 136.2 (CH), 136.1 (C), 131.3 (C), 130.7 (CH), 129.8 (CH), 124.2 (CH); IR (ATR) 1679, 1596, 1452, 1286, 924, 766 cm^{-1}; HRMS (APCI) m/z calcd for $C_{14}H_9O_2$ $(M + H)^+$ 209.0597, found 209.0597.

ASSOCIATED CONTENT

Supporting Information

Spectral data and stereochemical proof of alcohol **9a.** The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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