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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Efficient and Selective Cu/Nitroxyl-Catalyzed Methods for Aerobic Oxidative Lactonization of Diols

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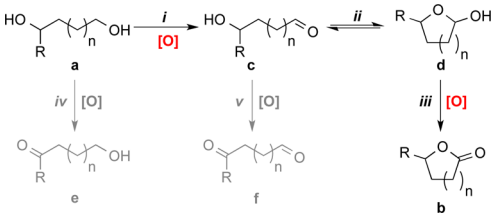
Supporting Information

ABSTRACT: Cu/nitroxyl catalysts have been identified that promote highly efficient and selective aerobic oxidative lactonization of diols under mild reaction conditions using ambient air as the oxidant. The chemo- and regioselectivity of the reaction may be tuned by changing the identity of the nitroxyl cocatalyst. A Cu/ABNO catalyst system (ABNO = 9-azabicyclo[3.3.1]-nonan-*N*-oxyl) shows excellent reactivity with symmetrical diols and hindered unsymmetrical diols, whereas a Cu/TEMPO catalyst system (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyl-*N*-oxyl) displays excellent chemo- and regioselectivity for the oxidation of less hindered unsymmetrical diols. These catalyst systems are compatible with all classes of alcohols (benzylic, allylic, aliphatic), mediate efficient lactonization of 1,4-, 1,5-, and some 1,6-diols, and tolerate diverse functional groups, including alkenes, heterocycles, and other heteroatom-containing groups.

Lactones are important structural motifs in natural products and pharmaceuticals, building blocks for the production of fine chemicals, and monomers for the preparation of polyesters.[1] The oxidative lactonization of diols, involving sequential oxidation of a 1° alcohol and an intermediate hemiacetal (lactol), is an appealing route to these molecules (Scheme 1; steps *i*–*iii*). Numerous stoichiometric oxidants and

Scheme 1. Oxidative Lactonization of Diols



catalytic methods have been explored to achieve this goal.[2,3] Aerobic oxidation methods offer a compelling alternative,[4] but existing catalysts face limitations associated with forcing reaction conditions, restricted functional group tolerance, and/or poor chemo/regioselectivity. Oxidation of the second alcohol, which in many cases is a more reactive 2° alcohol (Scheme 1, step *iv* or *v*), presents a key challenge for this transformation. We anticipated that recently reported Cu/nitroxyl catalyst systems for aerobic alcohol oxidation[5,6] could provide a unique solution to this challenge. These catalyst systems exhibit broad scope and functional group compatibility, and they operate efficiently at room temperature with ambient air as the source of oxidant. The identity of the nitroxyl can be varied to alter the activity and selectivity of the catalyst. A Cu/TEMPO catalyst, consisting of $[Cu(CH_3CN)_4]OTf$, 2,2′-bipyridine (bpy), *N*-methyl imidazole (NMI), and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), is very sterically sensitive and promotes highly selective oxidation of diverse primary alcohols to aldehydes.[6b] Meanwhile, a Cu/ABNO catalyst system, which employs the less sterically hindered nitroxyl 9-azabicyclo[3.3.1]nonane *N*-oxyl (ABNO),[6c] shows excellent reactivity with both 1° and 2° alcohols. Here we show that these catalyst systems exhibit high activity and selectivity in the aerobic oxidative lactonization of diols.

Our initial catalyst development efforts focused on oxidative lactonization of the symmetrical diol, diethylene glycol (**1a**). The lactone product **1b** is an important precursor to degradable polyesters that have diverse biomedical applications.[7] We tested the previously reported Cu/TEMPO catalyst system[6b] with **1a** in acetonitrile at room temperature under ambient air. The reaction reached moderate conversion (78%) of **1a** after 4 h, affording a mixture of lactone **1b** and hemiacetal **1d** in 34 and 44% yields, respectively. Elevated temperatures and higher loading of TEMPO did not improve the outcome (see Supporting Information, Scheme S1). A number of other nitroxyl cocatalysts were then tested under similar reaction conditions. Examples include the more oxidizing TEMPO derivatives 4-MeO-TEMPO and 4-oxo-TEMPO and the sterically less hindered ABNO, keto-ABNO, AZADO, and Me-AZADO nitroxyls (Figure 1). The latter bi- and tricyclic nitroxyls were quite effective, in each case affording near-quantitative yield of lactone **1b** within 1 h at room temperature. ABNO exhibited a slightly higher conversion rate. Because of its commercial availability and lower cost than the AZADO derivatives, we proceeded with this nitroxyl. A quantitative yield of **1b** was obtained within 1 h, even when the ABNO loading was decreased to 1 mol % (see Table S1). Catalysts with electron-rich bipyridyl ligands, such 4,4′-dimethoxybipyridine, show faster initial rates, but they deactivate prior to complete conversion to the lactone (see Supporting Information for additional catalyst optimization data).

Reaction profiles for the oxidative lactonization of **1a** catalyzed by Cu/TEMPO and Cu/ABNO were monitored by ^{1}H NMR spectroscopy (Figure 2). The hemiacetal intermediate **1d** is evident with both catalyst systems. The Cu/TEMPO

Received: January 30, 2015
Published: March 9, 2015

DOI: 10.1021/jacs.5b01036
J. Am. Chem. Soc. 2015, 137, 3767–3770

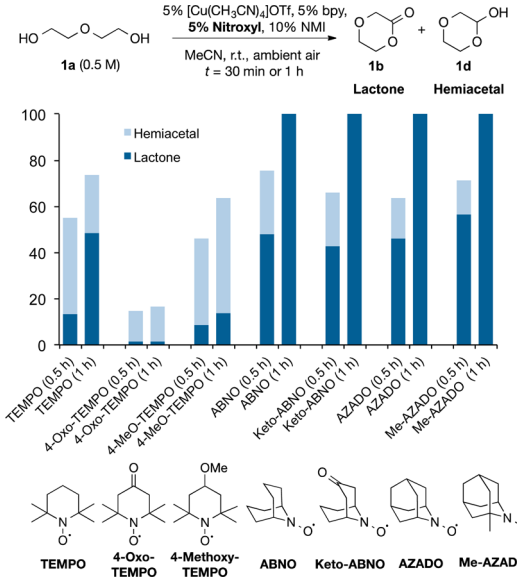


Figure 1. Results of Cu/nitroxyl-catalyzed aerobic oxidative lactonization of diethylene glycol with different nitroxyls after 0.5 and 1 h (0.5 mmol scale).

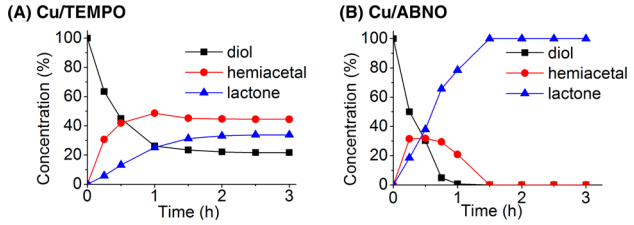
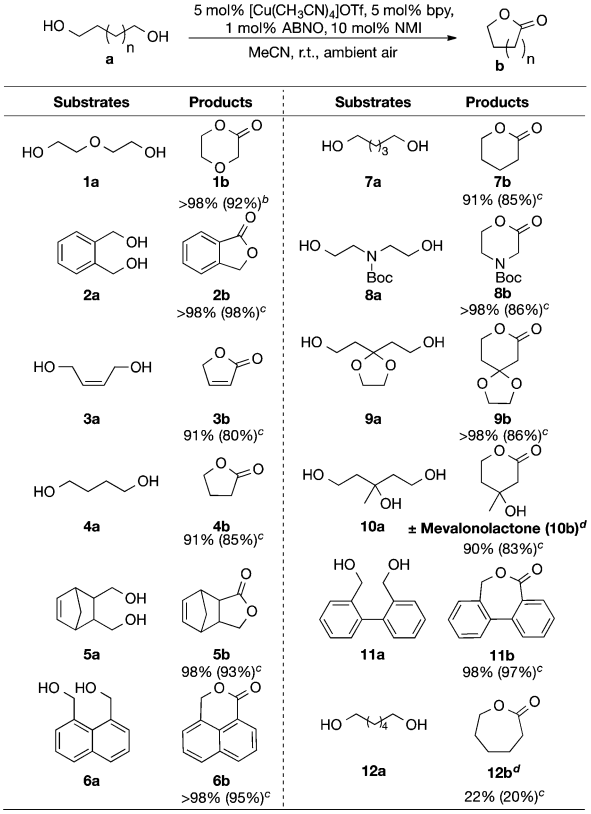


Figure 2. Reaction profiles of the oxidative lactonization of diethylene glycol **1a**, catalyzed by (A) Cu/TEMPO and (B) Cu/ABNO (1 mmol scale). Reaction conditions: **1a** (1.0 mmol), $[Cu(CH_3CN)_4]OTf$ (0.05 mmol, 5%), bpy (0.05 mmol, 5%), TEMPO or ABNO (0.05 mmol, 5%), NMI (0.1 mmol, 10%), CD_3CN (5.0 mL).

catalyst exhibits good initial reactivity but appears to deactivate after 1.5 h, with negligible further conversion beyond this time (Figure 2A). Build-up and decay of the hemiacetal is also evident with the Cu/ABNO catalyst system, but complete conversion to the lactone is achieved within 1.5 h (Figure 2B).[8] The relative catalyst activity trends in this reaction may be rationalized by steric effects. The Cu/TEMPO catalyst is very sterically sensitive, for example, showing high selectivity in the oxidation of 1° over 2° alcohols.[6] On the other hand, the Cu/ABNO catalyst mediates efficient oxidation of both 1° over 2° alcohols.[6c,9] These considerations account for the higher reactivity of Cu/ABNO in the oxidation of the hemiacetal, which is more sterically hindered than the initial 1° alcohol.

The scope of (bpy)Cu^{I}/ABNO-catalyzed lactonization was probed initially with a series of symmetrical diols (Table 1). The reactions led to efficient formation of a number of five- and six-membered lactones, including the bioactive molecule mevalonolactone (**10b**), at room temperature under ambient air. Most reactions achieved complete substrate conversion within 2 h and afforded isolated products in >90% yield. Efficient reactivity was observed with benzylic, allylic, and aliphatic substrates. The seven-membered-ring lactone **11b** was generated in 97% yield,[10] while the less conformationally constrained 1,6-hexanediol afforded caprolactone in only 22% yield with 5 mol % of ABNO. The major product in this case is

Table 1. Scope of Cu/ABNO-Catalyzed Aerobic Oxidative Lactonization of Symmetrical Diols[a]



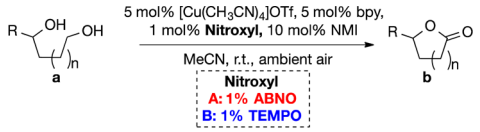
[a]Reaction conditions: diols (1.0 mmol), $[Cu(CH_3CN)_4]OTf$ (0.05 mmol, 5%), bpy (0.05 mmol, 5%), ABNO (0.01 mmol, 1%), NMI (0.10 mmol, 10%), CH_3CN (5.0 mL), yield based on ^1H NMR analysis (int. std. = biphenyl), reactions run in an open round-bottom flask (50 mL). [b]Diol (5.0 g, 47 mmol). [c]Isolated yield. [d]ABNO (0.05 mmol, 5%).

the α,ω-dialdehyde (adipaldehyde, 74% yield). The reaction conditions scale effectively; oxidative lactonization of diethylene glycol (**1a**) afforded a 92% isolated yield of lactone **1b** when performed on a 5 g scale.

Oxidative lactonization of unsymmetrical diols presents a more stringent challenge. The catalyst must not only promote oxidation of the hemiacetal intermediate but also discriminate between two different alcohols, for example, between 1° and 2° alcohols (cf. Scheme 1) or between sterically or electronically differentiated 1° alcohols. The first classes of substrates examined were aliphatic and benzylic diols that featured one 1° alcohol together with a 2° or 3° alcohol (Table 2). The Cu/ABNO catalyst system showed good activity and selectivity in the lactonization of these substrates; however, dicarbonyl compounds (cf. **f**, Scheme 1) were obtained as byproducts in some cases, reflecting the high activity of the Cu/ABNO catalyst for oxidation of both 1° and 2° alcohols.[6c] For example, the oxidation of 1,5-hexanediol **16a** affords 5-hexanolide **16b** in 88% yield, together with an 8% yield of 5-oxohexanal **16f**.[11] Substrates **13a**, **14a**, and **16a** exhibited improved results when ABNO was replaced with the more sterically hindered TEMPO cocatalyst. For example, use of 5 mol % of TEMPO in the lactonization of **16a** led to a 97% yield of the lactone **16b**. A variation of the Cu/TEMPO catalyst conditions even enabled selective conversion of heptane-1,6-diol **18a** to the seven-membered-ring product 6-methyl-ε-caprolactone **18b** in 92%

DOI: 10.1021/jacs.5b01036
J. Am. Chem. Soc. 2015, 137, 3767–3770

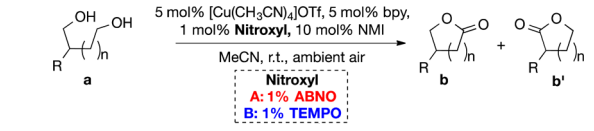
Table 2. Scope of Cu/Nitroxyl-Catalyzed Aerobic Oxidative Lactonization of Unsymmetric Diols with Primary and Secondary Hydroxyl Groups[a]



Substrates	Products	Substrates	Products
13a	13b A: 85% B: 97% (94%)[b]	16a	16b A: 88% B[c]: 97% (95%)[b]
14a	14b A: 91% B: 92% (83%)[b]	17a	17b A: 97% (89%)[b] B: 60%
15a	15b A: >98% (91%)[b] B: 66%	18a	18b A[c]: 23% B[d]: 92% (86%)[b]

[a]Reaction conditions: diols (1.0 mmol), $[Cu(CH_3CN)_4]OTf$ (0.05 mmol, 5%), bpy (0.05 mmol, 5%), nitroxyl (0.01 mmol, 1%), NMI (0.10 mmol, 10%), CH_3CN (5.0 mL), yield based on ^1H NMR analysis (int. std. = biphenyl), reactions run in an open round-bottom flask (50 mL). [b]Isolated yield. [c]With 5 mol % of nitroxyl (0.05 mmol). [d]With 10 mol % of TEMPO (0.10 mmol), 3 Å M.S. (300 mg), O_2 balloon, rt.

Table 3. Scope of Cu/Nitroxyl-Catalyzed Aerobic Oxidative Lactonization of Unsymmetrical Diols with Two Different Primary Hydroxyl Groups[a]



Substrates	Products	Substrates	Products
19a	19b (A: 63%, B: 90% (81%)[b]) 19b' (37%, 10%)	24a	24b (A: 33%, B[d]: 82%(71%)[b]) 24b' (67%, 18%)
20a	20b (A: 79%, B[c]: 92% (80%)[b]) 20b' (21%, –)	25a	25b (A: 45%, B[d]: 92%(85%)[b]) 25b' (55%, 8%)
21a	21b (A: 63%, B: 92% (92%)[b]) 21b' (A: 27%, B: 3.2%)	26a	26b (A: 43%, B[d]: 88%(79%)[b]) 26b' (57%, 12%)
22a	22b (A: 58%, B[d]: 80%(80%)[b]) 22b' (18%, 2%)	27a	27b (A: 58%, B[d]: 83%(81%)[b]) 27b' (32%, 7%)
23a	23b (A[d]: 33%, B[e]: –) 23b' (67% (60%)[b], –)	28a	28b (A[c]: 80%(80%)[b], B[c]: –) 28b' (3%, –)

[a]Reaction conditions: diols (1.0 mmol), $[Cu(CH_3CN)_4]OTf$(0.05 mmol, 5%), bpy (0.05 mmol, 5%), nitroxyl (0.01 mmol, 1%), NMI (0.10 mmol, 10%), CH_3CN (5.0 mL), yield based on ^1H NMR analysis (int. std. = biphenyl), reactions run in an open round-bottom flask (50 mL). [b]Isolated yield. [c]TEMPO or ABNO (0.05 mmol, 5%). [d]TEMPO (0.03 mmol, 3%). [e]TEMPO (0.1 mmol, 10%).

yield.[12] These observations are consistent with the known ability of Cu/TEMPO to discriminate more effectively between 1° and 2° alcohols, relative to Cu/ABNO.[6b,13]

The most difficult class of unsymmetrical diols features two different primary alcohols. The steric and/or electronic differences between the two alcohols in these substrates can be quite subtle, and successful examples of these transformations are rare.[14] Previously reported aerobic lactonization methods exhibit low selectivity in these cases,[4] but considerable success was achieved with Cu/nitroxyl catalysts. The Cu/TEMPO catalyst generally performed better than Cu/ABNO (Table 3, blue vs red). The enhanced steric discrimination of Cu/TEMPO relative to Cu/ABNO presumably accounts for the selectivities observed here; however, electronic effects also contribute (see below).

A ≥9:1 regioselectivity was observed with the 2-methyl- or 2,2-dimethyl-substituted diols **19a** and **20a**. Use of the Cu/ABNO catalyst with these substrates led to reduced selectivity (<2:1 and 4:1, respectively). In the naphthalene-derived diol **21a**, a phenyl substituent provided adequate steric differentiation of the alcohols to enable formation of lactone **21b** in high yield. Successful discrimination between the benzylic and aliphatic alcohols was achieved in substrate **22a**, consistent with the significantly higher rates for benzylic versus aliphatic alcohols observed previously with the Cu/TEMPO catalyst.[6b] The 2-NHBoc-substituted pentanediol **23a** was unreactive with the Cu/TEMPO catalyst, but use of the Cu/ABNO catalyst afforded lactones **23b**/**b**′ in excellent yield with 2:1 regioselectivity, favoring alcohol oxidation proximal to the NHBoc group. Preferential oxidation of the more hindered alcohol could arise from chelation of the NHBoc group or from an electronic effect, as elaborated below. The Cu/ABNO catalyst showed similar reactivity with 2-aminobutanediol derivatives **24a**–**26a**. It afforded the five-membered lactones in good yield, again favoring oxidation of the more hindered alcohol. Diols **24a**–**26a** underwent more selective lactonization with the Cu/TEMPO catalyst, favoring oxidation of the less hindered alcohol in a range from 4.5 to 11.5:1. Finally, the pyridine-derived diols **27a** and **28a** underwent regioselective lactonization with the Cu/TEMPO and Cu/ABNO catalysts, respectively. The hydroxymethyl groups in the *ortho* and *para* positions of diols **27a** and **28a** should be more acidic than those in the *meta* position, and we have previously reported Hammett studies of different benzyl alcohols, which show that more acidic alcohols are oxidized more rapidly.[8a] The observed selectivity is readily rationalized on the basis of the expected alcohol acidity. These results show that electronic effects can be as important as steric effects in controlling the reaction selectivity.

In summary, the results described herein show that Cu/nitroxyl catalyst systems exhibit excellent activity and selectivity for the oxidative lactonization of diols. The selectivity patterns observed with unsymmetrical diols match that expected from

DOI: 10.1021/jacs.5b01036
J. Am. Chem. Soc. 2015, 137, 3767–3770

previous studies of alcohol oxidation, whereby the Cu/TEMPO catalyst shows excellent steric discrimination, even between two different primary alcohols. The Cu/ABNO catalyst shows higher overall reactivity and is particularly effective in the lactonization of symmetrical diols, as well as electronically differentiated primary alcohols (cf. **28a**). The collective features of these reactions, including the predictable nature of the selectivity/activity trends, the broad functional group tolerance of the catalysts, and the ability to perform the reactions at room temperature with ambient air as the oxidant, suggest that these reactions could find widespread application for the synthesis of lactones.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full reaction development data, experimental procedures, and product characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the DOE for financial support of this work (DE-FG02-05ER15690) and Sigma-Aldrich for generous donation of samples of ABNO.

■ REFERENCES

(1) (a) Jefford, C. W.; Jaggi, D.; Sledeski, A. W.; Boukouvalas, J. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1989; Vol. 3, part B, pp 157−171. (b) Procter, G. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming. I., Ley, S. V., Eds.; Pergamon: Oxford, 1991; pp 305−327. (c) Libiszowski, J.; Kowalski, A.; Szymanski, R.; Duda, A.; Raquez, J.-M.; Degée, P.; Dubois, P. *Macromolecules* **2004**, *37*, 52−59. (d) Williams, C. K. *Chem. Soc. Rev.* **2007**, *36*, 1573−1580.

(2) For leading references on methods that employ stoichiometric oxidants, see the following. Cr oxides: (a) Tojo, G.; Fernández, M. *Oxidation of Alcohols to Aldehydes and Ketones*; Springer: New York, 2010. (b) Kim, K. S.; Szarek, W. A. *Carbohydr. Res.* **1982**, *104*, 328−333. MnO_2: (c) Bagley, M. C.; Lin, Z.; Phillips, D. J.; Graham, A. E. *Tetrahedron Lett.* **2009**, *50*, 6823−6825. $NaBrO_3$: (d) Kageyama, T.; Kawahara, S.; Kitamura, K.; Ueno, Y.; Okawara, M. *Chem. Lett.* **1983**, 1097−1100. (e) Morimoto, T.; Hirano, M.; Iwasaki, K.; Ishikawa, T. *Chem. Lett.* **1994**, 53−54.

(3) For leading references on catalytic lactonization methods, see the following. TEMPO/bleach and TEMPO/$PhI(OAc)_2$: (a) Hansen, T. M.; Florence, G. J.; Lugo-Mas, P.; Chen, J.; Abrams, J. N.; Forsyth, C. J. *Tetrahedron Lett.* **2003**, *44*, 57−59. (b) Brückner, C. In *Stable Radicals: Fundamental and Applied Aspects of Odd-Electron Compounds*; Hicks, R. G., Ed.; John Wiley & Sons: New York, 2010; pp 433−460. (c) Ebine, M.; Suga, Y.; Fuwa, H.; Sasaki, M. *Org. Biomol. Chem.* **2010**, *8*, 39−42. TPAP/NMO: (d) Bloch, R.; Brillet, C. *Synlett* **1991**, 892−830. Heteropolyacids/H_2O_2: (e) Ishii, Y.; Yoshida, T.; Yamawaki, K.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 5549−5552.

(4) For important precedents for aerobic oxidative lactonization of diols, see: (a) Aït-Mohand, S.; Muzart, J. *J. Mol. Catal. A* **1998**, *129*, 135−139. (b) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750−6755. (c) Shimizu, H.; Onitsuka, S.; Egami, H.; Katsuki, T. *J. Am. Chem. Soc.* **2005**, *127*, 5396−5413. (d) Mitsudome, T.; Noujima, A.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Green Chem.* **2009**, *11*, 793−797. (e) Endo, Y.; Bäckvall, J.-E. *Chem.—Eur. J.* **2011**, *17*, 12596−12601. (f) Díaz-Rodríguez, A.; Lavandera, I.; Kanbak-Aksu, S.; Sheldon, R. A.; Gotor, V.; Gotor-Fernández, V. *Adv. Synth. Catal.* **2012**, *354*, 3405−3408. (g) Chung, K.; Banik, S. M.; De Crisci, A. G.; Pearson, D. M.; Blake, T. R.; Olsson, J. V.; Ingram, A. J.; Zare, R. N.; Waymouth, R. M. *J. Am. Chem. Soc.* **2013**, *135*, 7593−7602. (h) Blake, T. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **2014**, *136*, 9252−9255.

(5) For reviews, see: (a) Ryland, B. L.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2014**, *53*, 8824−8838. (b) Cao, Q.; Dornan, L. M.; Rogan, L.; Hughes, N. L.; Muldoon, M. J. *Chem. Commun.* **2014**, *50*, 4524−4543.

(6) (a) Kumpulainen, E. T. T.; Koskinen, A. M. P. *Chem.—Eur. J.* **2009**, *15*, 10901−10911. (b) Hoover, J. M.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 16901−16910. (c) Steves, J. E.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 15742−15745. (d) Sasano, Y.; Nagasawa, S.; Yamazaki, M.; Shibuya, M.; Park, J.; Iwabuchi, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 3236−3240.

(7) Numerous catalyst oxidative and dehydrogenative routes have been explored for the preparation of this lactone. See refs 1c, 4b, 4h, and the following: (a) Guest, H. R.; Kiff, B. W. U.S. Patent 2,900,395, 1959. (b) Forschner, T. C. U.S. Patent 5,310,945, 1994. (c) Kaneda, K.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K. *Molecules* **2010**, *15*, 8988−9007. (d) Musa, S.; Shaposhnikov, I.; Cohen, S.; Gelman, D. *Angew. Chem., Int. Ed.* **2011**, *50*, 3533−3537.

(8) Mechanistic studies have shown that the rate of these reactions depends on the partial pressure of O_2 and can be affected by mass transfer into solution. The slightly longer reaction time in Figure 2 relative to that in Figure 1 reflects the larger reaction scale, which can affect gas−liquid mixing. For details, see: (a) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 2357−2367. (b) Hoover, J. M.; Ryland, B. L.; Stahl, S. S. *ACS Catal.* **2013**, *3*, 2599−2605. (c) Rogan, L.; Hughes, N. L.; Cao, Q.; Dornan, L. M.; Muldoon, M. J. *Catal. Sci. Technol.* **2014**, *4*, 1720−1725.

(9) For mechanistic studies that provide insights into the origin of the different steric effects in the Cu/TEMPO and Cu/ABNO catalyst systems, see ref 13.

(10) Fétizon, M.; Golfier, M.; Louis, J. M. *J. Chem. Soc. D* **1969**, 1118−1119.

(11) Full product distributions for the substrates in Table 2 are provided in Supporting Information Table S3.

(12) For leading references describing diol lactonization to afford seven- and eight-membered lactones, see refs 3c, 4e, and the following: (a) Jung, H. M.; Choi, J. H.; Lee, S. O.; Kim, Y. H.; Park, J. H.; Park, J. *Organometallics* **2002**, *21*, 5674−5677. (b) Nicklaus, C. M.; Phua, P. H.; Buntara, T.; Noel, S.; Heeres, H. J.; de Vries, J. G. *Adv. Synth. Catal.* **2013**, *355*, 2839−2844.

(13) Ryland, B. L.; McCann, S. D.; Brunold, T. C.; Stahl, S. S. *J. Am. Chem. Soc.* **2014**, *136*, 12166−12173.

(14) The most successful precedents employ hydrogen-transfer catalysis (e.g., with acetone as the H_2 acceptor). The functional group compatibility of these methods has not been demonstrated or explored. For leading references, see: (a) Murahashi, S.; Ito, K.; Naota, T.; Maeda, Y. *Tetrahedron Lett.* **1981**, *22*, 5327−5330. (b) Ishii, Y.; Suzuki, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *J. Org. Chem.* **1986**, *51*, 2822−2824. (c) Lin, Y.; Zhu, X.; Zhou, Y. *J. Organomet. Chem.* **1992**, *429*, 269−274. (d) Suzuki, T.; Morita, K.; Tsuchida, M.; Hiroi, K. *Org. Lett.* **2002**, *4*, 2361−2363. (e) Ito, M.; Shiibashi, A.; Ikariya, T. *Chem. Commun.* **2011**, *47*, 2134−2136.

DOI: 10.1021/jacs.5b01036
J. Am. Chem. Soc. 2015, 137, 3767−3770