Aerobic Oxidation

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Room-Temperature Copper-Catalyzed Oxidation of Electron-Deficient Arenes and Heteroarenes Using Air**

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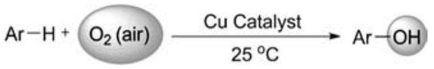
Although transition-metal-catalyzed direct functionalization of C—H bonds has emerged as a powerful method to construct new C—C and C—heteroatom bonds,[1] oxidative functionalization of C—H bonds under mild conditions (at room temperature and using air as the oxidant) still remains a very challenging field.[2] In particular, the synthesis of phenols by direct oxidation of arenes with O_2 as the oxidant is still regarded as one of the main challenges for catalysis, and is rarely reported.[3] A groundbreaking method reported by Fujiwara and co-workers used $Pd(OAc)_2$ as the catalyst to convert benzene into phenol with molecular oxygen; however, this method gave low yields (2–3 %) and used extremely forcing reaction conditions (15 atm O_2, 15 atm CO, 180 °C).[4] Recently, Yu and Zhang reported a novel Pd-catalyzed direct *ortho* hydroxylation of potassium benzoates in the presence of O_2 (1 atm) as the oxidant.[5] However, several drawbacks still remain including the high catalyst loading (10 mol % of $Pd(OAc)_2$) and high temperature (115 °C). Thus, it is still necessary to develop a powerful synthetic method for the oxidative hydroxylation of C—H bonds under mild reaction conditions.

Recent advances in the broad array of copper-catalyzed aerobic oxidative C—H functionalizations highlight the potential to achieve the oxidative hydroxylation of arenes utilizing copper catalysts.[1e,2a] Additionally, copper is the metal element of choice for many biological oxidation metabolisms.[6] Examples include copper-containing oxidases, which combine the oxidation of substrates and the reduction of O_2 to H_2O or H_2O_2, and oxygenases, which mediate oxygen-atom transfer onto the substrates.[7] These enzymes are widely distributed in plant and animal tissues; one example is tyrosinase, which performs copper-catalyzed hydroxylation of aromatic compounds with O_2 under mild conditions.[8] From a synthetic point of view, copper-catalyzed oxidative hydroxylation of C—H bonds is an elegant approach but also a challenging method to develop. Towards this target, Yu and co-workers, reported that stoichiometric amounts of $Cu(OAc)_2$ mediated *ortho*-selective hydroxylation of 2-phenylpyridines employing O_2 (1 atm) as the oxidant and proceeding through an acetoxylation/hydroxylation sequence at 130 °C.[9] Moreover, a serial of copper-catalyzed aerobic oxidative C—N,[10] C—C,[11] and C—S[12] couplings of electron-deficient arenes and heteroarenes have been achieved. Inspired by these reports and by the efficiency of copper-containing oxidizing enzymes in nature, we have developed a copper-catalyzed "oxygenase-type" oxidation of arenes and heteroarenes at room temperature in the presence of air (1 atm) as the oxidant, thus accomplishing the oxygen-atom transfer from O_2 in the air onto the substrates (Scheme 1). To the best of our knowledge, most copper-catalyzed aerobic C—H oxidation reactions are oxidase-type reactions,[2a] and there are very few examples of oxygenase-type reactions.[13]



Scheme 1. Copper-catalyzed "oxygenase-type" oxidation of arenes and heteroarenes.

For the optimization study, we focused our attention on the oxidation of benzothiazole **1a** by sequential oxidative hydroxylation and keto–enol tautomerization (Table 1). The use of 5 mol % of $CuCl_2$ and 1.2 equivalents of NaO*t*Bu in DMF under air (balloon) at 25 °C gave the best result for the aerobic oxidation of heteroarenes (Table 1, entry 1). More satisfactory yields (80 %) were obtained by increasing the copper catalyst loading to 15 mol % and the amount of base to 1.5 equivalents. Other reaction parameters also had an impact on the efficiency of this reaction (Table 1) . Among the bases we tested, the use of NaO*t*Bu provided the best yield of **2a** (Table 1, entries 1–3). Better results were achieved when the reaction was performed in polar solvents rather than nonpolar solvents, such as DCE and toluene (Table 1, entries 4–7). Changing the copper salts also influenced the result (Table 1, entries 8–11). Notably, the use of CuCl gave similar results to $CuCl_2$ but within a shorter reaction time (20 min), thus demonstrating that both Cu^I and Cu^{II} catalyst precursors were able to facilitate this transformation (Table 1, entry 10). Consequently, it is possible that the conversion between Cu^{II} and Cu^I species might occur during this reaction process. The ligand effects were also examined and it was found that the reaction was slightly inhibited by all the tested N- and O-

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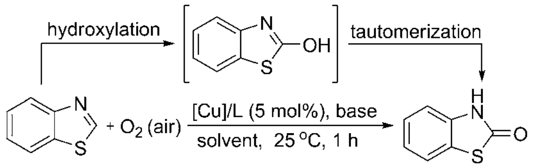
Table 1: Impact of reaction parameters on the efficiency of copper-catalyzed aerobic oxidation of **1a**.[a]



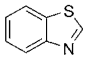
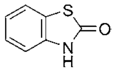
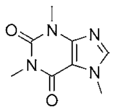
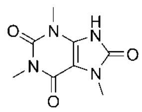
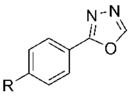
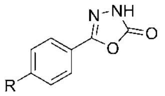
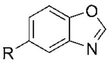
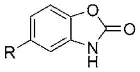
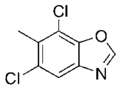
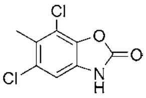
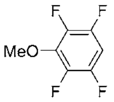
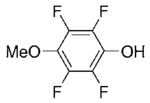
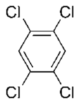
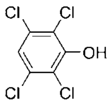
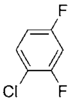
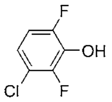
1a **2a**

Entry	Base	Solvent	[Cu]	Ligand	Yield [%][b]
1[c]	NaO*t*Bu	DMF	$CuCl_2$	–	70 (80)
2	LiO*t*Bu	DMF	$CuCl_2$	–	46
3	KO*t*Bu	DMF	$CuCl_2$	–	54
4	NaO*t*Bu	DMSO	$CuCl_2$	–	30
5	NaO*t*Bu	NMP	$CuCl_2$	–	42
6	NaO*t*Bu	DCE	$CuCl_2$	–	N.R.
7	NaO*t*Bu	toluene	$CuCl_2$	–	N.R.
8	NaO*t*Bu	DMF	$CuBr_2$	–	59
9	NaO*t*Bu	DMF	$Cu(OAc)_2$	–	7
10[d]	NaO*t*Bu	DMF	CuCl	–	63
11	NaO*t*Bu	DMF	CuI	–	45
12	NaO*t*Bu	DMF	$CuCl_2$	1,10-phen	55
13	NaO*t*Bu	DMF	$CuCl_2$	TMEDA	58
14	NaO*t*Bu	DMF	$CuCl_2$	bipy	67
15	NaO*t*Bu	DMF	$CuCl_2$	L1	57
16	NaO*t*Bu	DMF	–	–	N.R.
17	–	DMF	$CuCl_2$	–	N.R.
18[e]	NaO*t*Bu	DMF	$CuCl_2$	–	N.R.

[a] Reaction conditions: **1a** (0.5 mmol), NaO*t*Bu (0.6 mmol), 5 mol% of copper catalyst precursor in 2 mL of solvent under air (balloon). [b] Yield of the isolated product. [c] The yield in parenthesis was obtained by the use of 15 mol% of $CuCl_2$ and NaO*t*Bu (0.75 mmol). [d] The reaction time was 20 min. [e] In the absence of air. bipy = 2,2′-bipyridine, DCE = 1,2-dichloroethane, DMF = *N*,*N*′-dimethylformamide, DMSO = dimethyl sulfoxide, L1 = cyclohexane-1,3-dione, NMP = *N*-methylpyrrolidone, N.R. = no reaction, phen = phenanthroline, TMEDA = tetramethylethylenediamine.

Table 2: Copper-catalyzed oxidation of arenes and heteroarenes.[a]

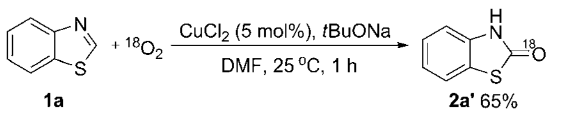
$$\underset{\mathbf{1}}{\text{Ar−H}} + O_2\,(\text{air}) \xrightarrow[\text{DMF, 25 °C}]{CuCl_2\text{ (5 mol\%), }t\text{BuONa}} \underset{\mathbf{2}}{\text{Ar−OH}}$$

Entry	Ar−H	Ar−OH	*t* [h]	Yield [%][b]
1		 **2a**	1	70(80)
2[c]		 **2b**	9	36
				
3[h]	R = H	**2c**	4	84
4[h,i]	R = Me	**2d**	3	84
5[h,i]	R = OMe	**2e**	3	79
6[h]	R = Cl	**2f**	6	37(63)
7[h]	R = Br	**2g**	6	76
				
8[d,e]	R = H	**2h**	5	73
9[d,e]	R = Me	**2i**	5	67
10[d,e]	R = *t*Bu	**2j**	5	73
11[d,e,f]	R = Cl	**2k**	5	51
12[e]		 **2l**	5	57
13[g]		 **2m**	9	68
14[e,g]		 **2n**	12	89
15[g]		 **2o**	12	58

[a] Reaction conditions: 1 (0.5 mmol), NaO*t*Bu (0.6 mmol), 5 mol% of $CuCl_2$ in 2 mL of DMF under air (balloon). The data in the parenthesis were obtained by the use of 15 mol% of $CuCl_2$ and NaO*t*Bu (0.75 mmol). [b] Yield of the isolated product. [c] KO*t*Bu (0.6 mmol) was used instead of NaO*t*Bu. [d] NaO*t*Bu (1.25 mmol) was used. [e] The reaction temperature was 60 °C. [f] 5 mol% of TMEDA was added. [g] NaO*t*Bu (0.85 mmol). [h] LiO*t*Bu (0.6 mmol) was used instead of NaO*t*Bu. [i] NaOAc (1 mmol) was added.

donor ligands (Table 1, entries 12–15). Finally, control reactions demonstrated that the oxidation product **2a** was not formed in the absence of either copper catalyst, base, or air (Table 1, entries 16–18).

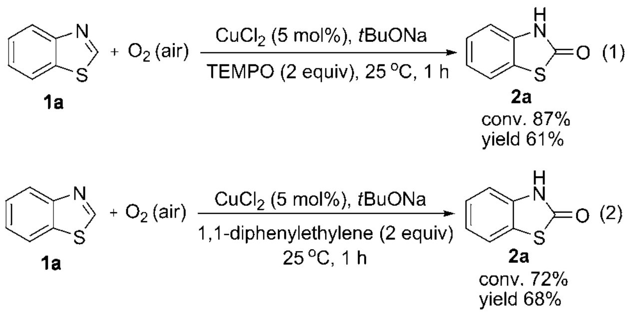
We next explored the substrate scope of the copper-catalyzed aerobic oxidation reactions (Table 2). 2-Aryl-1,3,4-oxadiazoles could be successfully converted into the desired products in high yield (Table 2, entries 3–7) and Cl, Br, and OMe groups on the aryl ring were tolerated. Benzoxazoles were also suitable substrates, although higher reaction temperatures (60 °C) and larger amounts of base (2.5 equiv) were required to give good yields (Table 2, entries 8–12); Cl and *t*Bu substituents on the benzoxazoles were well tolerated. The reaction of the useful alkaloid heterocycle compound caffeine, produced the oxydate **2b** in 36% yield (Table 2, entry 2). As the activated heterocyclic C−H bonds showed a propensity for the C−H activation/oxidation, the activated arenes were subjected to the optimized reaction conditions as well. To our delight, the transformations employing electron-deficient arenes as substrates afforded the corresponding hydroxylated products, albeit in varying yields (Table 2, entries 13–15). The yield for the reaction of 1,2,4,5-tetrachlorobenzene **1n** was 89% (Table 2, entry 14). The reaction yields were shown to improve when the catalyst loading and the amount of base were increased simultaneously (Table 2, entries 1 and 6).



Scheme 2. ^{18}O isotope labeling experiments.

To gain additional insights into the mechanism, we conducted ^{18}O isotope labeling experiments (Scheme 2). The reaction proceeded smoothly under an $^{18}O_2$ atmosphere to provide the oxidation product **2a′** in 65% yield (Scheme 2). The EI-MS spectrum showed a *m*/*z* signal at 153.3, which was attributed to the $[M+2]^+$ ion of **2a**. This result indicates that O_2 took part in this reaction and that the oxygen atom was transferred onto the substrate **1a**.

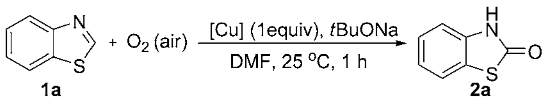
When investigating the reaction mechanisms of copper-catalyzed oxidative C—H functionalizations single electron transfer (SET) is an obvious consideration.[2a] Therefore, radical-trapping experiments were carried out (Scheme 3). The addition of TEMPO and 1,1-diphenylethylene slowed down the reaction slightly but did not stop it, thus suggesting that radical intermediates were not active species involved in the catalytic cycle.



Scheme 3. Radical trapping experiments. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy.

Next we performed a series of stoichiometric reactions to acquire further understanding of the reaction mechanism (Table 3). No reaction was observed when a 1:1:1 ratio of CuCl$_2$, NaO*t*Bu, and **1a** was used (Table 3, entry 1). Notably, when the amount of base was increased to 2 equivalents, the yield of the reaction was very similar to that of the catalytic reaction (Table 3, entry 2). When the amount of base was further increased to 3 equivalents the reaction was complete in 5 minutes at 25 °C and a quantitative yield was obtained (Table 3, entry 3). These results suggest that when CuCl$_2$ is used 1 equivalent of NaO*t*Bu is probably required to generate an active copper species, which facilitates this aerobic oxidation reaction. Based on this consideration, we propose that CuCl$_2$ initially reacts with NaO*t*Bu to produce CuCl and a *tert*-butoxyl radical by a SET process and that the Cu^I species is catalytically active for this reaction.[14] As we know, CuCl can react with NaO*t*Bu to produce CuO*t*Bu. Thus, CuCl and CuO*t*Bu were used in the stoichiometric reactions to verify our hypothesis as well. The reaction between 1 equivalent of CuCl and NaO*t*Bu afforded the desired product in 45% yield in 1 hour, while the reaction involving 2 equivalents of base was much faster and was complete in 10 minutes with a 74% yield of product upon isolation (Table 3, entries 4 and 5). No reaction occurred when 1 equivalent of CuO*t*Bu was used in the absence of base (Table 3, entry 6). However, the reaction was highly efficient when CuO*t*Bu and 1 equivalent of base were combined (Table 3, entry 7). Overall, the results of these stoichiometric reactions indicate that CuO*t*Bu could be the best catalyst precursor or catalytic active species and that NaO*t*Bu is necessary for the deprotonation of the substrate. CuO*t*Bu was employed as the catalyst instead of CuCl$_2$ under the optimized conditions and the desired product **2a** was isolated in 86% yield.

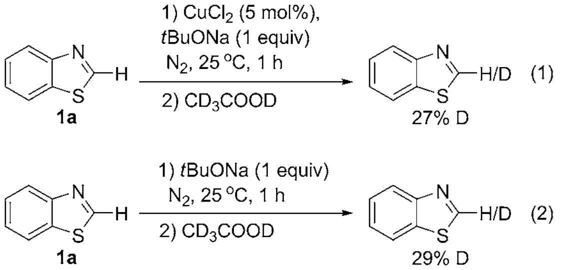
Table 3: Stoichiometric experiments.[a]



Entry	[Cu]	NaO*t*Bu (equiv)	*t* [min]	Yield [%][b]
1	CuCl$_2$	1	60	0
2	CuCl$_2$	2	60	78
3	CuCl$_2$	3	5	100
4	CuCl	1	60	45
5	CuCl	2	10	74
6	CuO*t*Bu	none	60	0
7	CuO*t*Bu	1	5	84

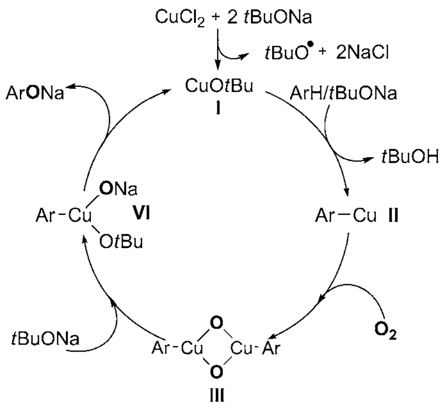
[a] Reaction conditions: **1a** (0.25 mmol), 1–3 equiv NaO*t*Bu, 1 equiv of [Cu] in 2 mL of DMF under air (balloon). [b] Yield of the isolated product.

To further verify these hypotheses, deuteration experiments were implemented (Scheme 4). In the presence of 1 equivalent of NaO*t*Bu, 29% of **1a** was deuterated by [D$_4$]acetic acid after 1 h in a N_2 atmosphere [Scheme 4, Eq. (2)]. The addition of a catalytic amount of CuCl$_2$ didn't affect this reaction significantly [Scheme 4, Eq. (1)]. These observations indicate that the reversible deprotonation of **1a** by NaO*t*Bu can happen without of the assistance of copper catalyst.



Scheme 4. Deuteration experiments.

The proposed reaction pathway is depicted in Scheme 5. The catalyst precursor CuCl$_2$ could be reduced to CuCl by NaO*t*Bu, which could subsequently react with NaO*t*Bu to form the active copper species CuO*t*Bu (**I**).[15] Substrate ArH could be deprotonated by NaO*t*Bu to afford ArNa and



Scheme 5. Proposed mechanism.

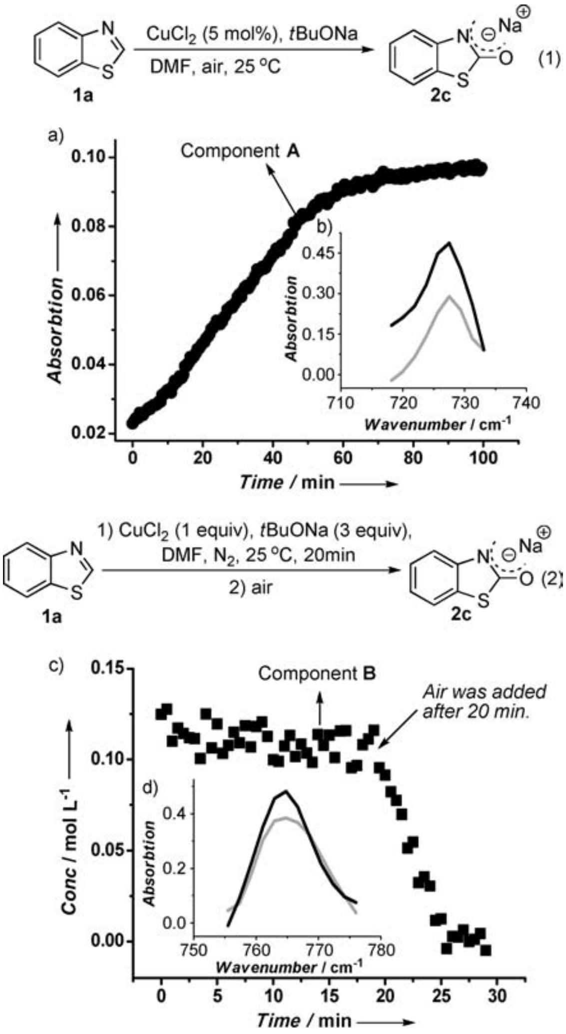


Figure 1. a) Kinetic profile of the reaction (1). b) IR spectra of the component **A** (black curve) and authentic sample of **2c** (gray curve). c) Kinetic profile of the reaction (2). d) IR spectra of component **B** (black curve) and authentic sample of **1a** (gray curve).

*t*BuOH. Next, CuO*t*Bu (**I**) could undergo transmetallation with ArNa to give $ArCu^{I}$ complex **II** and regenerate NaO*t*Bu.[16] Complex **II** could be oxidized by oxygen and the O−O bond cleaved to generate bis(μ-oxo)dicopper(III) complex (**III**).[6c,17] Tolman and co-workers have reported that a bis(μ-oxo)dicopper core is capable of hydroxylating an arene by intramolecular direct oxidative C−H bond functionlization.[18] Nucleophilic attack of NaO*t*Bu at the Cu^{III} complex **III** could break the $[Cu_2(\mu\text{-}O)_2]^{2+}$ core, thus affording intermediate **IV**, which could undergo reductive elimination to produce ArONa. The isolated product ArOH could be thereafter formed from ArONa by the subsequent aqueous work-up.

To probe the feasibility of this pathway and detect the formation of ArONa, we attempted to use in situ IR to monitor the reaction of **1a** under standard reaction conditions. The kinetic profile of reaction (1), Figure 1, clearly revealed a new IR band at 727 cm^{-1} (component **A**), which increased in intensity as the reacion proceeded (Figure 1 A); this IR band was assigned to ArONa (**2c**) by comparison with an authentic sample of **2c** (Figure 1 B).

The stoichiometric reaction of **1a** was monitored by in situ IR as well (Reaction (2), Figure 1). The decreasing IR band 764 cm^{-1} (component **B**) was assigned to the substrate **1a** (Figure 1 D). Under the N_2 atmosphere, the conversion was very low when **1a** was treated with 1 equivalent of $CuCl_2$ and 3 equivalents of NaO*t*Bu for 20 minutes. Interestingly, **1a** was consumed within 5 minutes after the reaction vessel was purged with air (Figure 1 C). This result revealed that the oxidation of $ArCu^{I}$ species was a facile transformation driving the overall reaction.

In conclusion, we have reported a copper-catalyzed "oxygenase-type" oxidation of arenes and heteroarenes at room temperature under air (balloon). This reaction involves oxygen-atom transfer from O_2 in the air onto the substrate. A reaction mechanism that includes a C−H activation process and sequentially facile oxidation of $ArCu^{I}$ species, has been corroborated through a series of deuteration and kinetics experiments. Moreover, CuO*t*Bu is believed to be the active copper species and could be generated in situ from $CuCl_2$ and NaO*t*Bu by a SET process. Nevertheless, the following catalytic cycle follows a typical organometallic mechanism. Therefore, this copper-catalyzed aerobic oxidation reaction is believed to incorporates a novel combination of SET initiation and organometallic catalytic cycle. Further improvement of the catalytic efficiency of this transformation and expansion of the substrate scopes are ongoing.

Experimental Section

General procedure: In a glove box, a 25 mL schlenk tube equipped with a stir bar was charged with $CuCl_2$ (0.025 mmol) and NaO*t*Bu (0.6 mmol). The tube was fitted with a rubber seal and removed from the glove box. A balloon filled with dry air was connected to the Schlenk tube through the side arm. The mixture was purged with air for 1 min before substrate **1** (0.5 mmol) and DMF (2 mL) were added. The reaction mixture was stirred at 25 °C for 1 h. Then the reaction was quenched with water (6 mL) and the resulting mixture was extracted by ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was then purified by flash chromatography on silica gel with a mixed eluent of petroleum ether and ethyl acetate. After concentrating the fractions containing the product, the residue was dried under vacuum.

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Keywords: aerobic oxidation · C—H activation · copper · hydroxylation

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[1] a) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910–1925; b) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677–685; c) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890–931; d) J. A. Ashenhurst, *Chem. Soc. Rev.* **2010**, *39*, 540–548; e) O. Daugulis, *Top. Curr. Chem.* **2010**, *292*, 57–84; f) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242–3272.

[2] a) A. E. Wendlandt, A. M. Suess, S. S. Stahl, *Angew. Chem.* **2011**, *123*, 11256–11283; *Angew. Chem. Int. Ed.* **2011**, *50*, 11062–11087; b) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439–2463; c) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514.

[3] a) Y. Izawa, D. Pun, S. S. Stahl, *Science* **2011**, *333*, 209–213; b) D. A. Alonso, C. Najera, I. M. Pastor, M. Yus, *Chem. Eur. J.* **2010**, *16*, 5274–5284; c) B. Luecke, K. V. Narayana, A. Martin, K. Jaehnisch, *Adv. Synth. Catal.* **2004**, *346*, 1407–1424; d) B. Cornils, W. A. Herrmann, *J. Catal.* **2003**, *216*, 23–31.

[4] a) T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1991**, 193; b) T. Jintoku, K. Nishimura, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1990**, 1687–1688.

[5] Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 14654–14655.

[6] a) L. Que, Jr., W. B. Tolman, *Nature* **2008**, *455*, 333–340; b) E. Kim, E. E. Chufan, K. Kamaraj, K. D. Karlin, *Chem. Rev.* **2004**, *104*, 1077–1133; c) E. A. Lewis, W. B. Tolman, *Chem. Rev.* **2004**, *104*, 1047–1076; d) L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013–1045.

[7] a) R. A. Himes, K. D. Karlin, *Curr. Opin. Chem. Biol.* **2009**, *13*, 119–131; b) E. E. Chufán, S. C. Puiu, K. D. Karlin, *Acc. Chem. Res.* **2007**, *40*, 563–572; c) A. C. Rosenzweig, M. H. Sazinsky, *Curr. Opin. Struct. Biol.* **2006**, *16*, 729–735.

[8] C. J. Cooksey, P. J. Garratt, E. J. Land, S. Pavel, C. A. Ramsden, P. A. Riley, N. P. M. Smit, *J. Biol. Chem.* **1997**, *272*, 26226–26235.

[9] X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790–6791.

[10] a) M. Miyasaka, K. Hirano, T. Satoh, R. Kowalczyk, C. Bolm, M. Miura, *Org. Lett.* **2011**, *13*, 359–361; b) S. Guo, B. Qian, Y. Xie, C. Xia, H. Huang, *Org. Lett.* **2011**, *13*, 522–525; c) A. Armstrong, J. C. Collins, *Angew. Chem.* **2010**, *122*, 2332–2335; *Angew. Chem. Int. Ed.* **2010**, *49*, 2282–2285; d) H. Zhao, M. Wang, W. Su, M. Hong, *Adv. Synth. Catal.* **2010**, *352*, 1301–1306; e) D. Monguchi, T. Fujiwara, H. Furukawa, A. Mori, *Org. Lett.* **2009**, *11*, 1607–1610; f) Q. Wang, S. L. Schreiber, *Org. Lett.* **2009**, *11*, 5178–5180.

[11] a) L. Chu, F.-L. Qing, *J. Am. Chem. Soc.* **2012**, *134*, 1298–1304; b) Y. Wei, H. Zhao, J. Kan, W. Su, M. Hong, *J. Am. Chem. Soc.* **2010**, *132*, 2522–2523; c) M. Kitahara, K. Hirano, H. Tsurugi, T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 1772–1775; d) Y. Li, J. Jin, W. Qian, W. Bao, *Org. Biomol. Chem.* **2010**, *8*, 326–330; e) H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2009**, *131*, 17052–17053.

[12] S.-i. Fukuzawa, E. Shimizu, Y. Atsuumi, M. Haga, K. Ogata, *Tetrahedron Lett.* **2009**, *50*, 2374–2376.

[13] a) F.-T. Du, J.-X. Ji, *Chem. Sci.* **2012**, *3*, 460–465; b) H. Wang, Y. Wang, D. Liang, L. Liu, J. Zhang, Q. Zhu, *Angew. Chem.* **2011**, *123*, 5796–5799; *Angew. Chem. Int. Ed.* **2011**, *50*, 5678–5681; c) C. Zhang, Z. Xu, L. Zhang, N. Jiao, *Angew. Chem.* **2011**, *123*, 11284–11288; *Angew. Chem. Int. Ed.* **2011**, *50*, 11088–11092; d) C. Zhang, N. Jiao, *J. Am. Chem. Soc.* **2010**, *132*, 28–29; e) J. B. Hewgley, S. S. Stahl, M. C. Kozlowski, *J. Am. Chem. Soc.* **2008**, *130*, 12232–12233.

[14] a) A. Studer, D. P. Curran, *Angew. Chem.* **2011**, *123*, 5122–5127; *Angew. Chem. Int. Ed.* **2011**, *50*, 5018–5022; b) Y.-X. Jia, E. P. Kundig, *Angew. Chem.* **2009**, *121*, 1664–1667; *Angew. Chem. Int. Ed.* **2009**, *48*, 1636–1639; c) A. Perry, R. J. K. Taylor, *Chem. Commun.* **2009**, 3249–3251.

[15] N. Matsuda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 2860–2863.

[16] H.-Q. Do, O. Daugulis, *J. Am. Chem. Soc.* **2008**, *130*, 1128–1129.

[17] L. Que, Jr., W. B. Tolman, *Angew. Chem.* **2002**, *114*, 1160–1185; *Angew. Chem. Int. Ed.* **2002**, *41*, 1114–1137.

[18] P. L. Holland, K. R. Rodgers, W. B. Tolman, *Angew. Chem.* **1999**, *111*, 1210–1213; *Angew. Chem. Int. Ed.* **1999**, *38*, 1139–1142.