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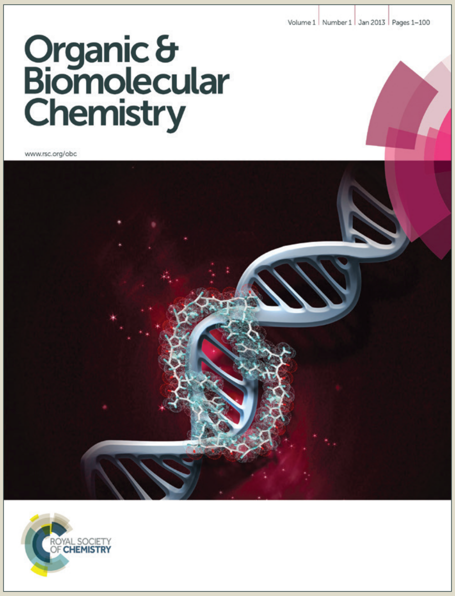

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Allylic and benzylic sp^3 C-H oxidation in water

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A copper-catalyzed method for the oxidation of allylic and benzylic sp^3 C-H by aqueous *tert*-butyl hydroperoxide (T-Hydro) in water using a recyclable fluorous ligand has been developed. The reaction procedure is tolerant to additional functional groups and the fluorous ligand could be reused with little loss of catalytic activity.

Introduction

Allylic and benzylic oxidations via the direct sp^3 C-H bond activation of alkenes and alkylarenes to the corresponding α,β-unsaturated enones and carbonyl compounds are important transformations with a wide variety of industrial applications[1] including the synthesis of drug precursors and building blocks in many organic syntheses.[2] Although several organocatalysts have been developed for these oxidations,[3] the efficiency of metal-catalyzed allylic and benzylic oxidations remains remarkable.[4] To-date several protocols for sp^3 C-H oxidation catalysed by metal complexes in combination with *tert*-butyl hydroperoxide (TBHP) have been reported.[4a-f,5] However amongst the different metals, fewer oxidations have been done using Cu as catalyst, even though copper proteins found in nature are catalysts, especially for oxidation reactions.[6]

Previously, we have reported a recyclable, fluorous catalyst that efficiently promoted carbon-carbon bond formation reactions in water.[7] Since development of aqueous-phase reaction is an active field in organic synthesis due to demands for realization of green chemical processes[8] and many classic reactions that are commonly used in organic synthesis are currently being re-examined in order to develop cleaner chemical processes and to reduce or eliminate existing drawbacks and inefficiencies, we herein report a protocol for room temperature, copper-catalyzed allylic and benzylic oxidation by T-Hydro in water using a recyclable fluorous ligand **L1** (Fig. 1). To the best of our knowledge, there are no earlier publications on metal-catalyzed allylic oxidation in water.

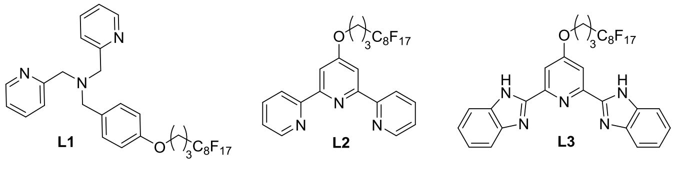


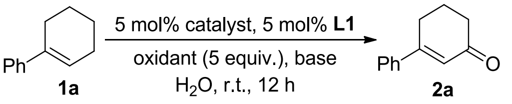
Fig. 1 Structure of fluorous ligand **L1**.

Results and discussion

In the initial assessment of the allylic oxidation reaction, 1-phenyl-1-cyclohexene **1a** was chosen as the model substrate. We investigated the optimization reaction conditions by varying the solvent, catalyst, base and oxidants (Table 1a). When the allylic oxidation was conducted using **1a**, 5 mol% CuI, 5 mol% **L1** as ligand, TBHP (6M in decane), K_2CO_3 and water as solvent at room temperature, the desired 3-phenylcyclohex-2-enone **2a** was obtained after 12 h in 29% yield (Table 1a, entry 1). When water was replaced with acetonitrile, compound **2a** was obtained in similar yield (Table 1a, entry 2). To optimize the reaction, we varied the metal catalyst and found that the reaction in aqueous medium was most efficient with CuI (Table 1a, entries 3-10). Next we varied the base and established that the reaction was most efficient in the absence of base (Table 1a, entries 11-14). Subsequently, we screened different oxidants on the reaction which indicated that TBHP was a more effective oxidant than H_2O_2, DTBP or *m*-CPBA. In addition, both T-Hydro and TBHP provided compound **2a** in similar yields (Table 1a, entries 15-21). Hence we decided to use T-Hydro as the oxidant since the absence of decane would increase the environmental friendliness of the reaction. We also examined the effect of varying the ratio of CuI and **L1** but this provided compound **2a** in lower yield (Table 1b, entries 2-4). The minimum time for the reaction to reach completion was also determined to be 2h (Table 1b, entry 5). The amount of oxidant employed was also examined. Lowering the amount of oxidant to 4 equivalents increased the yield of **2a** to 62% but further decreasing the amount of oxidant was detrimental to the reaction yield (Table 1b, entries 5-8).

It was previously reported that surfactant molecules, could aid in reaction rates.[8a,9] Thus the effect of additives was investigated and the reaction was most effective when 5 mol% of sodium dodecyl sulfate (SDS) was added. The addition of 5 mol% SDS not only halved the reaction time but also provided compound **2a** in a higher yield (Table 1b, entries 9-12). Besides **L1**, we also tested two other fluorous ligands, **L2** and **L3** (Fig. 1). but found **L1** to be the most effective ligand for facilitating the allylic oxidation reaction (Table 1b, entries 13-14). Finally, a control experiment in the absence of **L1**, only trace amount of **2a** was obtained (Table 1b, entry 15).

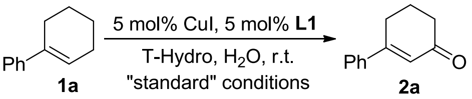
Table 1a Optimization of the allylic oxidation reaction of 1-phenyl-1-cyclohexene **1a**[a]



Entry	Catalyst	Oxidant	Base	Yield[b] (%)
1	CuI	TBHP	K_2CO_3	29
2[c]	CuI	TBHP	K_2CO_3	30
3	CuBr	TBHP	K_2CO_3	24
4	$CuBr_2$	TBHP	K_2CO_3	27
5	$Cu(OTf)_2$	TBHP	K_2CO_3	23
6	$FeCl_2$	TBHP	K_2CO_3	5
7	$FeCl_3$	TBHP	K_2CO_3	21
8	$CoCl_2$	TBHP	K_2CO_3	0
9	$Ni(OAc)_2$	TBHP	K_2CO_3	0
10	MnO_2	TBHP	K_2CO_3	16
11	CuI	TBHP	Ag_2CO_3	6
12	CuI	TBHP	KOAc	43
13	CuI	TBHP	KOH	Trace
14	CuI	TBHP	-	53
15	CuI	H_2O_2	-	Trace
16	$FeCl_3$	H_2O_2	-	Trace
17	CuI	DTBP	-	Trace
18	CuI	Urea, H_2O_2	-	Trace
19	CuI	$NaBO_3.H_2O$	-	17
20	CuI	*m*-CPBA	-	20
21	CuI	T-Hydro	-	51

[a] Reaction condition: **1a** (0.5 mmol), catalyst (5 mol%), **L1** (5 mol%), oxidant, base (0.5 equiv.), H_2O (1.0 mL), r.t., 12 h. [b] Isolated yields. [c] Using CH_3CN as solvent instead.

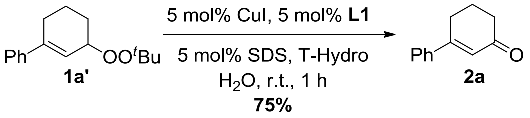
Table 1b Optimization of the allylic oxidation reaction of 1-phenyl-1-cyclohexene **1a**[a]



Entry	T-Hydro (Equiv.)	Change from standard condition	Time (h)	Yield[b] (%)
1	5	None	12	51
2	5	10 mol% **L1**	12	35
3	5	10 mol% CuI and 10 mol% **L1**	12	33
4	5	1 mol% CuI and 1 mol% **L1**	12	30
5	5	None	2	52
6	4	None	2	62
7	3	None	2	41
8	2	None	2	38
9	4	5 mol% $PhNHNH_2$ added	2	23
10	4	5 mol% TBAB added	1	60
11	4	5 mol% SDS added	1	71
12	4	1 mol% SDS added	1	61
13[c]	4	5 mol% **L2** instead of **L1**, 5 mol% SDS added	12	35
14[d]	4	5 mol% **L3** instead of **L1**, 5 mol% SDS added	12	23
15	4	Absence of **L1**, 5 mol% SDS	1	Trace

[a] Reaction condition: **1a** (0.5 mmol), CuI (5 mol%), **L1** (5 mol%), T-Hydro, H_2O (1.0 mL), r.t. [b] Isolated yields. [c] 25% starting material recovered. [d] 50% starting material recovered.

Having established the optimal reaction condition, different alkenes were tested to explore the generality of this oxidation transformation. As shown in Table 2, the reaction condition was compatible with both electron-withdrawing and –donating substituents as well as reactive functional group (entries 3-5). The oxidation reaction was also regioselective at the least hindered allylic carbon which is consistent with previously published results.[4e] It is worth noting that the allylic oxidation of substrate **1c** did not occur at the methyl substituent (entry 3). Attempts to extend the substrate scope to linear allylic alkenes (1-hexene, 1-octene, 1-decene, 3-pentenenitrile) were unsuccessful under the optimized conditions.

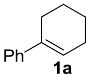
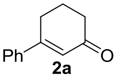
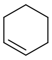
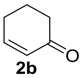
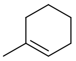
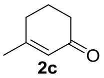


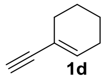
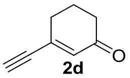
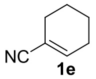
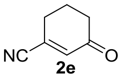
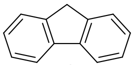
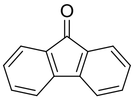
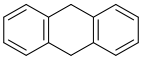
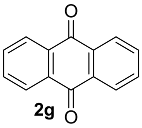
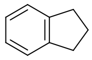
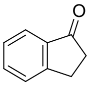
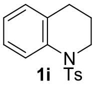
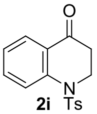
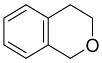
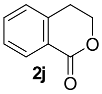
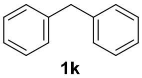
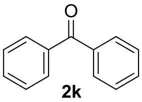
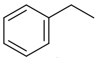
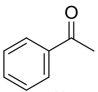
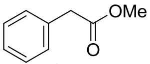
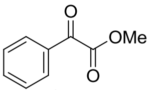
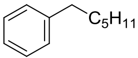
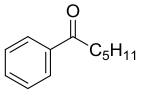
Scheme 1 Reaction of 1a' under optimized reaction condition

Tert-butyl peroxy ether of the allylic substrates was observed as the by-product in the allylic oxidation reaction (Table 2, entries 1-5). 3-*t*-Butylperoxy-1-phenylcyclohexene **1a'** was isolated from the allylic oxidation of **1a** in 10% yield (Table 2, entry 1). When the isolated **1a'** was subjected to the allylic oxidation condition, **2a** was obtained in 75% yield (Scheme 1). Purification and isolation of *tert*-butyl peroxy ether of **1b-1e** was unsuccessful but ^1H NMR of the by-product fraction shows the *t*-Bu signal in the 1.2 ppm region.

Table 2 Copper-catalyzed allylic and benzylic oxidation[a]

$$\text{Substrate} \xrightarrow[\substack{\text{5 mol\% SDS, T-Hydro} \\ H_2O\text{, r.t.}}]{\text{5 mol\% CuI, 5 mol\% } \mathbf{L1}} \text{Product}$$

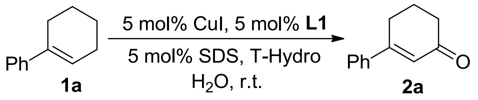
Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	1	71 (10[c])
2	 **1b**	 **2b**	2	58 (10[c])
3	 **1c**	 **2c**	1	62 (5[c])

4	 **1d**	 **2d**	1	58 (8^c)
5	 **1e**	 **2e**	1	74 (8^c)
6	 **1f**	 **2f**	6 (2^d)	88 (90^d)
7	 **1g**	 **2g**	6 (2^d)	81 (84^d)
8	 **1h**	 **2h**	1	70
9	 **1i**	 **2i**	3^d	51^d
10	 **1j**	 **2j**	1	68
11	 **1k**	 **2k**	6 (2^d)	85 (86^d)
12	 **1l**	 **2l**	1	68
13	 **1m**	 **2m**	1	73
14	 **1n**	 **2n**	1	51

[a] Reaction condition: Substrate (0.5 mmol), CuI (5 mol%), **L1** (5 mol%), T-Hydro (4.0 equiv.), SDS (5 mol%), H_2O (1.0 mL), r.t. [b] Isolated yields. [c] Yields of *tert*-butyl peroxy ether by-products. [d] Oil bath temperature of 50 °C.

Encouraged by the promising results, we extended the optimized condition to benzylic oxidation (Table 2, entries 6-13). We found that diphenylmethane type substrates gave the corresponding products in good yields (Table 2, entries 6, 7 and 11) although the reaction required a longer time to complete. This could be attributed to these substrates being solids at room temperature and have poor solubilities in water. When the temperature was increased to 50 °C, the reaction time was considerably shortened and the products were obtained in comparable yields. Substrates bearing a heteroatom were also compatible with the reaction condition and provided the benzylic oxidation products in moderate yields (Table 2, entries 9-10). Alkylarenes bearing an electron-withdrawing group on the alkyl moiety are difficult substrates for direct oxidation due to the inert benzylic C-H bond.[10] Gratifyingly, we were able to apply our condition to the oxidation of substrate **1m** to obtain compound **2m** in 73% yield (Table 2, entry 13). The methyl ester functionality of substrate **1m** was tolerated under the mild condition with no hydrolyzed product observed. Long chain aryl alkanes **1n** was also successfully oxidized to the corresponding ketone albeit lower (51%) yield (Table 2, entry 14).

Table 3 Recycling of **L1**[a]

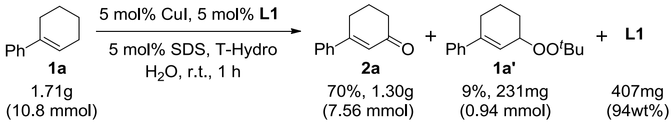


Cycle	Time (h)	Yield[b] (%)	Recovered **L1**[c] (wt%)
1	1	71	95
2	1	69	93
3	1.5	66	93
4	1.5	64	90
5	2	60	81

[a] Reaction condition: **1a** (2.5 mmol), CuI (5 mol%), **L1** (5 mol%), T-Hydro (4.0 equiv.), SDS (5 mol%), H_2O (5.0 mL), r.t. [b] Isolated yields. [c] Recovered *via* F-SPE.

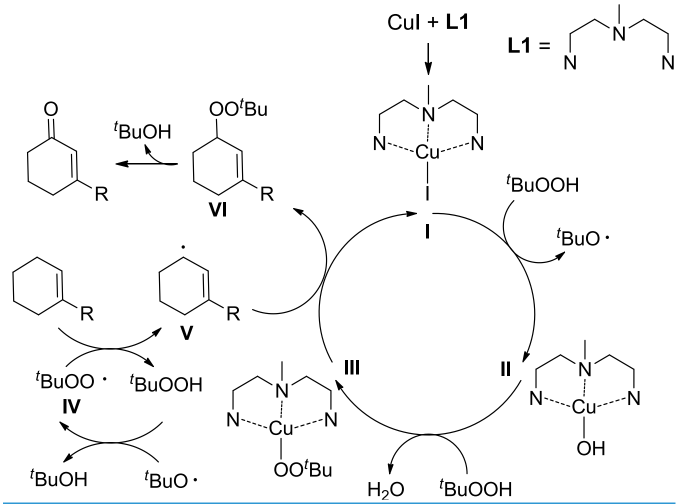
Next we investigated the possibility of recycling and reusing **L1**. 1-Phenyl-1-cyclohexene **1a** was used for the model study under the optimized reaction condition. The recycling experiments were carried out over 5 cycles and the time taken for the reaction to complete was 1-2 h to provide **2a** in 81-95% yields (Table 3). The recovered **L1** showed a slow decline in catalytic activity after several recoveries. In addition, the recovery of **L1** via F-SPE was good except in the 5th cycle. The fluorous silica gel used in F-SPE could be reused[10] which minimized waste thus making the recovery of **L1** a greener procedure.

Finally to apply this reaction in gram-scale reaction, 10.8 mmol (1.71 g) of **1a** was used for the allylic oxidation reaction under the optimized reaction condition. The reaction proceeded smoothly, gave the corresponding product **2a** in similar (70%) yield with 9% of **1a'** and the recovery of **L1** was also high (94%).



Scheme 2 Gram-scale synthesis of **2a**

A proposed catalytic cycle of the **L1**/CuI catalyzed allylic oxidation is depicted in Scheme 3. The copper complex **I** was formed *in-situ* from **L1** and CuI. The formation of *tert*-butyl peroxy radical **IV** abstracts a hydrogen atom from the alkene to give the radical **V** which forms the *tert*-butylperoxy intermediate **VI**. This is supported by the reaction of **1a'** in Scheme 1.



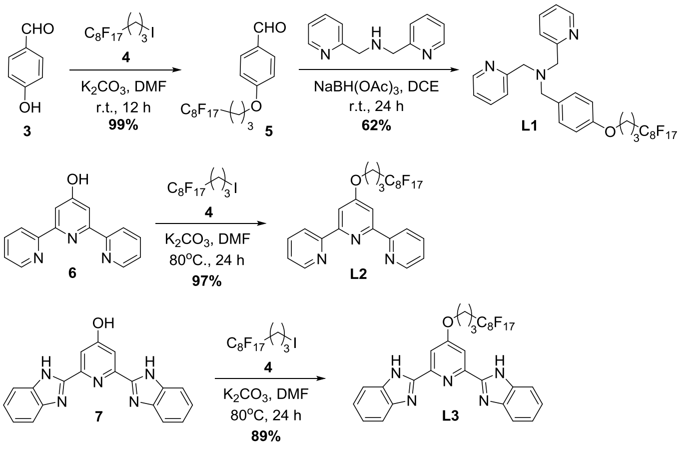
Scheme 3 Proposed catalytic cycle of **L1**/CuI catalyzed allylic oxidation

Experimental

General

All chemicals purchased were used without further purification. Compound **6**[11] and **7**[12] were synthesized according to previously reported procedure. Moisture-sensitive reactions were carried out under nitrogen with commercially obtained anhydrous solvents. Analytical thin-layer chromatography (TLC) was carried out on precoated F254 silica plates and visualized with UV light. Column chromatography was performed with silica (Merck, 230 – 400 mesh). F-SPE was performed with Fluoro*Flash*® silica gel (40 micron). ^{1}H and ^{13}C NMR spectra were recorded at 298K. Chemical shifts are expressed in terms of δ (ppm) relative to the internal standard tetramethylsilane (TMS). Mass spectra were performed under EI and ESI mode.

Synthesis of fluorous ligands L1-L3



Scheme 4 Synthesis of fluorous ligands **L1** to **L3**

Synthesis of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadeca fluoroundecyloxy)benzaldehyde (5). To a solution of 4-hydroxybenzaldehyde **3** (0.61 g, 5.0 mmol) in DMF (10 mL) was added K_2CO_3 (1.38 g, 10 mmol) and $C_8F_{17}(CH_2)_3I$ **4** (1.96 g, 3.33 mmol). The reaction mixture was stirred at room temperature for 12 h, quenched with H_2O (5 mL) and consecutively washed with EtOAc (20 mL x 3). The combined organic layer was washed with brine (10 mL x 3), dried over anhydrous $MgSO_4$, filtered and concentrated. The desired product **5** (2.90 g, 99%) was obtained as a white solid after purification by F-SPE.

Synthesis of *N*-(4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadeca fluoroundecyloxy)benzyl)-1-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (L1). To a solution of compound **5** (0.58 g, 1.0 mmol) in dichloroethane (15 mL) was added di-(2-picolyl)amine (0.22 mL, 1.2 mmol). The reaction mixture was stirred at room temperature for 1 h. Thereafter NaBH(OAc)$_3$ (305 mg, 1.44 mmol) was added and the reaction mixture was further stirred for 24 h. After which, the reaction mixture was quenched with H_2O (5 mL) and the organic layer was separated. The aqueous layer was further extracted with dichloromethane (15 mL) and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The desired product **L1** (377 mg, 62%) was obtained as a yellow oil after purification by F-SPE.

Synthesis of 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-hepta decafluoroundecyloxy)-2,6-di(2-pyridyl)pyridine (L2). To a solution of [2,2':6',2"-terpyridin]-4'-ol **6** (125 mg, 0.5 mmol) in DMF (5.7 mL) was added K_2CO_3 (104 mg, 0.75 mmol). The reaction mixture was stirred at 80 °C for 30 min. Thereafter $C_8F_{17}(CH_2)_3I$ **4** (441 mg, 0.75 mmol) was added and the reaction mixture was further stirred for 24 h, quenched with H_2O (2 mL) and filtered. The desired product **L2** (345 mg, 97%) was obtained as a white solid after washing with hexane (5 mL x 2) to remove residual $C_8F_{17}(CH_2)_3I$.

Synthesis 2,2'-(4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyloxy)pyridine-2,6-diyl)bis(1*H*-benzo[*d*]imidazole) (L3). To a solution of 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridin-4-ol **7** (164 mg, 0.5 mmol) in DMF (5.7 mL) was added K_2CO_3 (104 mg, 0.75 mmol). The reaction mixture was stirred at 80 °C for 30 min. After which, $C_8F_{17}(CH_2)_3I$ **4** (441 mg, 0.75 mmol) was added and the reaction mixture was further stirred for 24 h, then quenched with H_2O (2 mL) and filtered. The desired product **L3** (352 mg, 89%) was obtained as an off-white solid after washing with hexane (5 mL x 2) to remove residual $C_8F_{17}(CH_2)_3I$.

General procedure for the copper-catalyzed allylic and benzylic oxidation. A mixture of the substrate (0.5 mmol), **L1** (5 mol%), CuI (5 mol%), SDS (5 mol%) and water (1.0 mL) was stirred at room temperature. T-Hydro (4 equiv.) was added dropwise to the stirred solution. The reaction was monitored by TLC. When the reaction has completed, the reaction mixture was diluted with EtOAc (20 mL) and the organic layer was separated. The aqueous layer was further extracted with EtOAc (20 mL). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The crude product was then purified by column chromatography.

General procedure for the recycling experiment using F-SPE. Recycling experiments were carried out on a 2.50 mmol scale using the general procedure described above. The crude product was first diluted with THF–H_2O = 7: 3 (1 mL) and loaded into a F-SPE fluorous silica column (column diameter: 2.20 cm; amount of fluorous silica required: 10% of crude product by weight). The crude product was then eluted using THF–H_2O = 7: 3 (30 mL) as eluent and **L1** was subsequently eluted with THF (20 mL). The fluorous silica was regenerated and reused (5 times) after washing with acetone (10 mL). To determine the amount of product formed after each recycling experiment, the solution of crude product was concentrated, diluted with EtOAc (20 mL) and washed with water (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, concentrated and then purified accordingly.

Conclusion

An environmentally benign procedure for the room temperature, copper-catalyzed allylic and benzylic oxidation by aqueous TBHP in water using a recyclable fluorous ligand has been developed. Pre-generation of the organometallic reagent was not required. This increases the green aspect of the reaction. Fluorous ligand **L1** was recycled and reused with little loss of catalytic activity. The oxidation procedure would also be applied to gram-scale reaction.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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1 (a) L. Kesavan, R. Tiruvalam, M. H. Ab Rahim, M. I. Bin Saiman, D. I. Enache, R. L. Jenkins, N. Dimitratos, J. A. Lopez-Sanchez, S. H. Taylor, D. W. Knight, C. J. Kiely and G. J. Hutchings, *Science*, 2011, **331**, 195; (b) A. Aguadero, H. Falcon, J. M. Campos-Martin, S. M. Al-Zahrani, J. L. G. Fierro and J. A. Alonso, *Angew. Chem. Int. Ed*., 2011, **50**, 6557; (c) X. Wu and A. E. V. Gorden, *Eur. J. Org. Chem.*, 2009, 503; (d) S. E. Dapurkar, Z. Shervani, T. Yokoyama, Y. Ikushima and H. Kawanami, *Catal, Lett.*, 2009, **130**, 42.

2 (a) P. C. B. Page and T. McCarthy, *Comprehensive Organic Synthesis*, Pergamon, Oxford, UK, 1991, Vol 7, pp 83-149.

3 (a) T. Dohi, N. Takenaga, A. Goto, H. Fujioka and Y. Kita, *J. Org. Chem.*, 2008, **73**, 7365; (b) M. Ochiai, T. Ito, H. Takahashi, A. Nakanishi, M. Toyonari, T. Sueda, S. Goto and M. Shiro, *J. Am. Chem. Soc.*, 1996, **118**, 7716; (c) Y. Zhao and Y.-Y. Yeung, *Org. Lett.*, 2010, **12**, 2128.

4 (a) M. A. Fousteric, A. I. Koutsourea, S. S. Nikolaropoulos, A. Riahi and J. Muzart, *J. Mol. Catal.*, 2006, **250**, 70; (b) J. Q. Yu and E. J. Corey, *Org. Lett.*, 2002, **4**, 2727; (c) A. J. Catino, R. E. Forslund and M. P. Doyle, *J. Am. Chem. Soc.*, 2004, **126**, 13622; (d) H. Peng, A. Lin, Y. Zhang, H. Jiang, J. Zhou, Y. Cheng, C. Zhu and H. Hu, *ACS Catal.*, 2012, **2**, 163; (e) Y. Li, T. B. Lee, T. Wang, A. V. Gamble and A. E. V. Gorden, *J. Org. Chem.*, 2012, **77**, 4628. (f) M. Jurado-Gonzalez, A. C. Sullivan and J. R. H. Wilson, *Tetrahedron Lett.*, 2003, **44**, 4283; (g) T. K. M. Shing, Y.-Y. Yeung and P. L. Su, *Org. Lett.*, 2002, **4**, 3149; (h) J. A. R. Salvador and J. H. Clark, *Chem. Commun.*, 2001, **6**, 33; (i) J. A. S. Coelho, A. F. Trindade, R. Wanke, B. G. M. Rocha, L. F. Veiros, P. M. P. Gois, A. J. L. Pombeiro and C. A. M. Afonso, *Eur. J. Org. Chem.*, 2013, 1471; (j) J-B. Xia, K. W. Cormier and C. Chen, *Chem. Sci.*, 2012, **3**, 2240; (k) C. Zou, Z. Zhang, X. Xu, Q. Gong, J. Li and C-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 87; (l) X-L. Yang, M-H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 10638; (m) C. S. Yi, K-H. Kwon and D. W. Lee, *Org. Lett.*, 2009, **11**, 1567; (n) T. Nagano and S. Kobayashi, *Chem. Lett.*, 2008, **37**, 1042.

5 (a) J. Muzart, *Chem. Rev.*, 1992, **92**, 113; (b) B. Retchera, J.-S. Costa, J. Tang, R. Hage, P. Gameza and J. Reedijk, *J. Mol. Catal. A: Chem.*, 2008, **286**, 1. (c) K. Kamata, J. Kasai, K. Yamaguchi and N. Mizuno, *Org. Lett.*, 2004, **6**, 3577; (d) E. Burri, M. Öhm, C. Daguenet and K. Severin, *Chem.-Eur. J.*, 2005, **11**, 5055.

6 (a) I. Blain, P. Slama, M. Giorgi, T. Tron and M. Réglier, *Rev. Mol. Biotechnol.*, 2002, **90**, 95; (b) J. P. Klinman, *Chem. Rev.*, 1996, **96**, 2541; (c) Y. Matoba, T. Kumagai, A. Yamamoto, H. Yoshitsu and M. Sugiyama, *J. Biol. Chem.*, 2006, **281**, 8981; (d) J. W. Whittaker, *Arch. Biochem. Biophys.*, 2005, **433**, 227; (e) A. Rompel, H. Fischer, D. Meiwes, K. Büldt-Karentzopoulos, R. Dillinger, F. Tuczek, H. Witzel and B. Krebs, *J. Biol. Inorg. Chem.*, 1999, **4**, 56.

7 W. Susanto, C.-Y. Chu, W. J. Ang, T.-C. Chou, L.-C. Lo and Y. Lam, *Green Chem.*, 2012, **14**, 77

8 (a) U. M. Lindstron, *Chem. Rev.*, 2002, **102**, 2751; (b) J. E. Klijn and J. B. F. N. Engberts, *Nature*, 2005, **435**, 746; (c) C.-J. Li and L. Chen, *Chem. Soc. Rev*., 2006, **35**, 68.

9 (a) B. H. Lipshutz, A. R. Abela, Z. V. Boskovic, T. Nishikata, C. Duplais and A. Krasovskiy, *Top. Catal.*, 2010, **53**, 985; (b) K. Holmberg, *Eur. J. Org. Chem.*, 2007, 731; (c) M. N. Khan, *Micellar Catalysis: Surfactant Science Series*, Vol 133, pp.1-482, Boca Raton, New York, London: CRC Press, Taylor and Francis Group LLC, 2006; (d) T. Dwars, E. Paetzold and G. Oehme, *Angew. Chem. Int. Ed.*, 2005, **44**, 7174; (e) E. H. Cordes and R. B. Dunlap, *Acc. Chem. Res.*, 1969, **2**, 329.

10 K. Moriyama, M. Takemura and H. Togo, *Org. Lett.*, 2012, **14**, 2414.

11 H. A. Saadeh, E. A. A. Shairah, N. Charef and M. S. Mubarak, *J. Appl. Polym. Sci.*, 2012, **124**, 2717.

12 P. Froidevaux, J. M. Harrowfield and A. N. Sobolev, *Inorg. Chem.*, 2000, **39**, 4678.