SHORT COMMUNICATION

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Ruthenium-Catalyzed Transfer Hydrogenation of Amino- and Amido-Substituted Acetophenones

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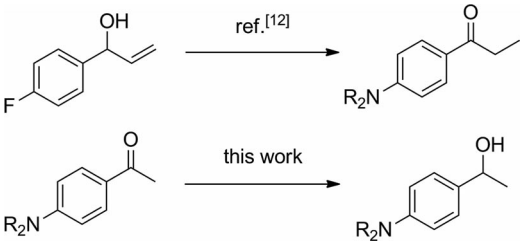
The ruthenium-catalyzed transfer hydrogenation of electron-rich amino-substituted acetophenones is reported. Variation of the reductant, ligands, base, and solvent allowed reaction optimization. A key discovery was the use of 1,4-butanediol as an irreversible reducing agent, which significantly improved the conversion. A range of amino- and amido-substituted aryl ketones were explored, and they all gave the corresponding alcohols in good yield, which demonstrates the wider applicability of this process.

Introduction

Transfer hydrogenation is a long-established process that dates back to the metal-catalyzed reactions originally discovered by Meerwein,[1] Ponndorf,[2] and Verley.[3] Although organocatalytic transfer hydrogenation, for example, by using diimide[4] or Hantzsch esters[5] as reductants, has become a field of considerable interest, metal-catalyzed processes are still very significant. Some areas of current research activity include the development of transition-metal catalysts for the asymmetric reduction of prochiral ketones,[6] imines,[7] and heterocycles.[8] Of the many transition metals that have been used to mediate transfer hydrogenation,[9] ruthenium complexes have demonstrated high catalytic activity (Scheme 1).



Scheme 1. Related work.

The use of ruthenium complexes to catalyze the transfer hydrogenation of acetophenones is well established.[10] However, challenges still exist in this field, such as the extension of the basic process to allow the reduction of electron-rich aromatic ketones.[11] For example, during a recent study it was noted that the transfer hydrogenation of amino-substituted acetophenones was particularly difficult.[12] In fact, a survey of the existing literature revealed only a single report of the ruthenium-catalyzed transfer hydrogenation of amido-substituted acetophenones;[13] moreover, there were only two examples of the reduction present in that study. Similarly, there exist only a limited number of examples of the direct hydrogenation of this type of substrate class by using ruthenium catalysts.[14]

Results and Discussion

The lack of a precedent in the literature for the reduction of amido- and amino-substituted aryl ketones initiated an investigation into the transfer hydrogenation of these substrates. Commercially available electron-rich amino-substituted acetophenone **1** was chosen for reaction development. It was reasoned that if reduction of electron-rich amino-substituted aryl ketones could be achieved, then reduction of the less electron-rich amido-substituted acetophenones should also be possible under similar conditions.

Previously, a trace amount of transfer hydrogenation had been observed under the reaction conditions reported by Williams and co-workers[12] for which a "borrowing hydrogen"[15] approach was applied to the synthesis of these alcohols, and therefore, a similar, but simplified, system was chosen as the starting point. Using the same model substrate (**1**), catalyst {$[Ru(PPh_3)_3(CO)(H)_2]$}, and solvent (DMSO), a screen of typical reducing agents was undertaken (Scheme 2). The use of formic acid as the stoichiometric reductant was a promising starting point, as alcohol **2** was produced with 45% conversion, although a large excess amount of the reductant was required (Scheme 2). The use of 2-propanol also resulted in reduction, but with a significantly reduced conversion (25%). A more recent approach to the reduction of ketones by transfer hydrogenation involved the use of 1,4-butanediol,[16,17] which upon

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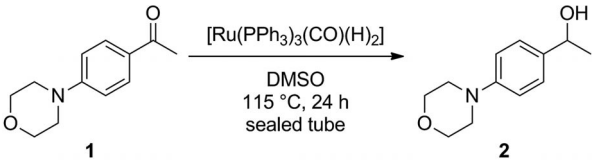
oxidation cyclized to the lactol, and this was then further oxidized to give γ-butyrolactone and 2 equiv. of hydrogen.[18] In a similar manner, the use of 1,4-butanediol proved to be advantageous in this study, as a much improved conversion (63%) was obtained.



Hydrogen source	Conversion [%]
formic acid (5 equiv.)	45
2-propanol (13 equiv.)	25
1,4-butanediol (1.5 equiv.)	63

Scheme 2. Initial study.

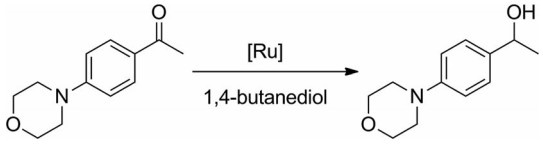
These initial results indicated that the use of reversible hydrogen transfer agents such as 2-propanol led to poor conversion. Resonance stabilization of the ketone through conjugation with the ring nitrogen atom, which is presumably the underlying reason why catalytic reduction of these ketones is so difficult, should also mean that for a reversible process the position of the equilibrium lies firmly to the side of the ketone. However, the use of an irreversible hydrogen donor had allowed the reaction to be driven to a higher conversion, and so this avenue of investigation was pursued further.

1,4-Butanediol was used as the reaction solvent as well as the hydrogen source by Williams and co-workers to reduce ketones in similar ruthenium-catalyzed systems.[19] Furthermore, the fact that it is readily available from renewable sources by the fermentation of sugars[20] makes it a very attractive hydrogen source. It can also be easily removed by an aqueous wash, or through chromatography.

A comparison of efficacy of selected ruthenium precatalysts under the chosen conditions highlighted the choice of $[Ru(PPh_3)_3(CO)(H)_2]$ (Table 1, Entry 1) in preference to either $[RuCl_2(PPh_3)_3]$[21] (Table 1, Entry 2) or $[Ru(p\text{-cymene})Cl_2]_2$[22] (Table 1, Entry 3), both of which were previously used for transfer hydrogenation. This higher activity can be attributed to the active hydride species that is already preformed.[21c] This was more apparent upon adding a range of bases to the reaction (Table 1, Entries 4–8), which resulted in lower conversions (40–65%). Unexpectedly, the addition of a variety of diphosphine ligands to the reaction mixture did not improve the conversion (Table 1, Entries 9–15), a result that was rather surprising given the previous improvements in transfer hydrogenation that were observed upon combining $[Ru(PPh_3)_3(CO)(H)_2]$ with either DPEphos[16] or xantphos.[23]

A further improvement in conversion was achieved upon using DMSO as the cosolvent (Table 1, Entry 16), in a process similar to the initially trialed conditions (Scheme 2). A range of other solvents were also screened (Table 1, Entries 17–23). The use of heptane (Table 1, Entry 18) resulted in an improved conversion relative to that obtained with toluene (71 vs. 58%). The use of oxygen-containing solvents

Table 1. Optimization of conditions.[a]



Entry	Catalyst	Solvent[b]	Additive[c]	Conv. [%][d]
1	$[Ru(PPh_3)_3(CO)(H)_2]$	–	–	73
2	$[RuCl_2(PPh_3)_3]$	–	–	39
3	$[[Ru(p\text{-cymene})Cl_2]_2]$	–	–	16
4	$[Ru(PPh_3)_3(CO)(H)_2]$	–	NaOH	60
5	$[Ru(PPh_3)_3(CO)(H)_2]$	–	Na_2CO_3	65
6	$[Ru(PPh_3)_3(CO)(H)_2]$	–	KOH	57
7	$[Ru(PPh_3)_3(CO)(H)_2]$	–	K_2CO_3	56
8	$[Ru(PPh_3)_3(CO)(H)_2]$	–	KO*t*Bu	40
9	$[Ru(PPh_3)_3(CO)(H)_2]$	–	dppm	26
10	$[Ru(PPh_3)_3(CO)(H)_2]$	–	dppe	9
11	$[Ru(PPh_3)_3(CO)(H)_2]$	–	dppp	41
12	$[Ru(PPh_3)_3(CO)(H)_2]$	–	dppb	32
13	$[Ru(PPh_3)_3(CO)(H)_2]$	–	dpppent	15
14	$[Ru(PPh_3)_3(CO)(H)_2]$	–	xantphos	32
15	$[Ru(PPh_3)_3(CO)(H)_2]$	–	DPEphos	46
16	$[Ru(PPh_3)_3(CO)(H)_2]$	DMSO	–	81
17	$[Ru(PPh_3)_3(CO)(H)_2]$	toluene	–	58
18	$[Ru(PPh_3)_3(CO)(H)_2]$	heptane	–	71
19	$[Ru(PPh_3)_3(CO)(H)_2]$	1,4-dioxane	–	79
20	$[Ru(PPh_3)_3(CO)(H)_2]$	*tert*-amyl alcohol	–	74
21	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	–	85
22	$[Ru(PPh_3)_3(CO)(H)_2]$	Bu_2O	–	75
23	$[Ru(PPh_3)_3(CO)(H)_2]$	H_2O	–	0
24	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	–	85[e]
25	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	–	74[f]
26	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	–	60[e,g]
27	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	dppp	16[e]
28	$[Ru(PPh_3)_3(CO)(H)_2]$	DME	Na_2CO_3	66[e]

[a] Conditions: Ketone (1 mmol), 1,4-butanediol (5 equiv.), catalyst (5 mol-% in Ru), 115 °C, 24 h. [b] 1 mL, DME = 1,2-dimethoxyethane. [c] 5 mol-% in the case of phosphines, 10 mol-% for bases. dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dpppent = 1,5-bis(diphenylphosphino)pentane, xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, DPEphos = bis[2-(diphenylphosphino)phenyl] ether. [d] Determined by analysis of **2** by ^1H NMR spectroscopy. [e] 2 equiv. of diol. [f] 1 equiv. of diol. [g] 3 mol-% catalyst loading.

(Table 1, Entries 19–22) generally did not result in an improvement in the conversion, except in the case of DME (85%). This could be due to the solvent acting as a ligand in the reaction. The use of water (Table 1, Entry 23) led to no conversion, and only starting material was recovered, which suggests that the catalyst was not stable under these conditions. It was concluded that DME was the optimal solvent for the reaction owing to a combination of the slightly improved conversion and its ease of removal at the end of the reaction, particularly if compared to DMSO.

With DME as the solvent, the amount of 1,4-butanediol could be reduced to 2 equiv. (Table 1, Entry 24) without affecting the conversion. However, the use of less than 2 equiv. (Table 1, entry 25) had a detrimental effect on the reaction conversion. This result contrasts somewhat with

the stoichiometry of the reaction, as each molecule of 1,4-butanediol should be capable of reducing two molecules of ketone, and so only half an equivalent should be required.

Final tuning reactions showed that lower conversions were obtained if a lower catalyst loading was used (Table 1, Entry 26) and that the same conversion was obtained after both 24 and 48 h, which was indicative of catalyst deactivation during the reaction. Re-introduction of base or phosphine (Table 1, Entries 27 and 28) also hindered the reaction, as seen previously.

Having established a set of conditions that gave the product in good conversion, a range of amino ketones were screened to evaluate the reaction scope (Table 2). Initial studies on a range of tertiary amines showed a large variation of reaction efficiency with ring size in the case of the cyclic compounds. The amine containing a seven-membered ring (Table 2, Entry 4) returned the lowest yield (47%), whereas the corresponding six-membered ring material (Table 2, Entry 3) gave the highest yield (74%). The five-membered ring compound (Table 2, Entry 2) reacted similarly to that containing a dimethylamino group (Table 2, Entry 1). The introduction of further heteroatoms into the ring (Table 2, Entries 5–7) had little effect on the yield of the reaction, all of which were higher than 75%; this indicated the tolerance of the process to remote functionalization and its potential application to pharmaceutically active compounds.

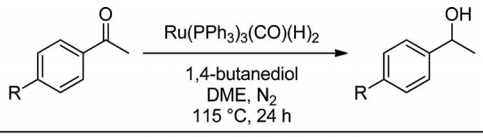
To further test the reaction scope, the use of amido and sulfonamido substrates were investigated. Reduction of a Boc-protected aromatic amine (Table 2, Entry 8) was previously reported,[13] and although the yield obtained here was higher (59 vs. 43% reported[13]), the direct comparison of these yields is somewhat unfair, as in this case the reaction was run for eight times longer at a much higher temperature. Interestingly, the other example reported in that paper,[13] the *N*-acetamide (Table 2, Entry 9), also gave a poor yield of product (31 vs. 28% reported[13]). In contrast, the *N*-benzamide (Table 2, Entry 10) gave the corresponding product in a significantly higher yield (74%). This was surprising as one may expect that the reactivity of the ketones in the acetamide and benzamide should be very similar.

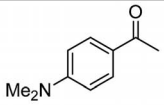
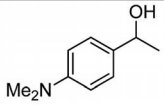
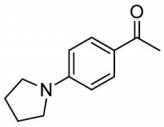
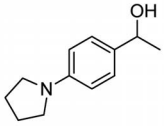
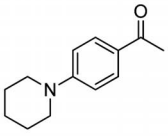
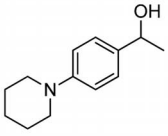
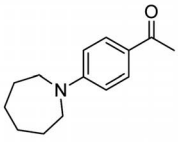
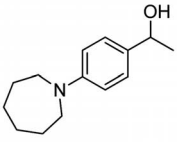
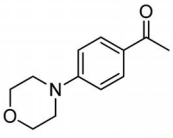
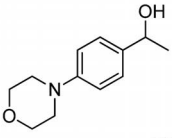
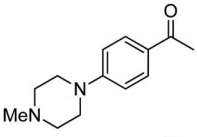
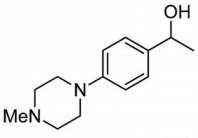
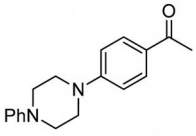
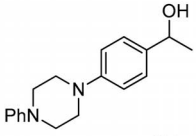
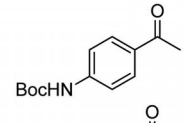
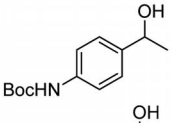
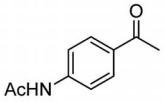
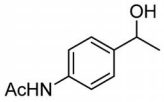
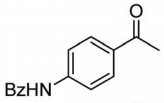
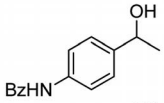
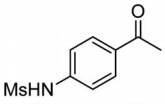
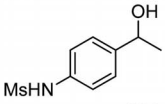
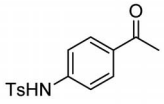
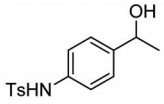
However, an analogous trend was observed with the sulfonamides; the methyl sulfonamide (Table 2, Entry 11) only gave a poor yield of the product (35%) in a similar manner to the acetamide, whereas the tosyl sulfonamide (Table 2, Entry 12) performed more than twice as well (76%). At this point, it is unclear why this is the case, as analyses of the crude reaction mixtures by NMR spectroscopy revealed that the only other compound present was the starting material, which precludes yield reduction by side reactions.

Cyclic imides such as succinimide and phthalimide were not tolerated; the ring-opened amido esters were obtained instead of any reduced products (Scheme 3).

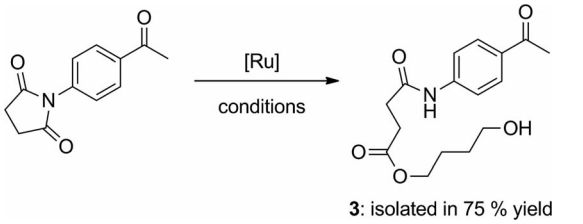
To conclude this study, three other compounds were examined as substrates (Scheme 4). Moving the morpholino substituent to the *ortho* position as in **4**, which may be expected to increase the steric bulk around the carbonyl

Table 2. Reaction scope.[a]



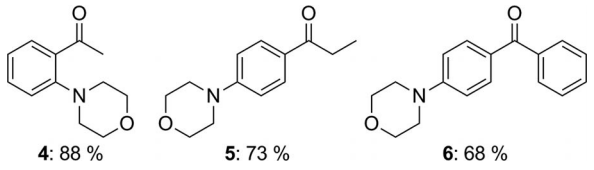
Entry	Starting material[b]	Product	Yield [%][c]
1			60
2			59[d]
3			74
4			47[d]
5			79
6			80
7			79
8			59
9			28[d]
10			74
11			35[d]
12			76

[a] Conditions: Ketone (3 mmol), 1,4-butanediol (2 equiv.), $[Ru(PPh_3)_3(CO)(H)_2]$ (5 mol-%), DME (3 mL), 115 °C, 24 h. [b] Boc = *tert*-butoxycarbonyl, Ac = acetyl, Bz = benzoyl, Ms = methanesulfonyl, Ts = *para*-toluenesulfonyl. [c] Yield of isolated product. [d] Conversion was determined by ^{1}H NMR spectroscopy.



Scheme 3. Ring opening of imides.

group, actually had very little effect on the reaction yield (88%). Finally, both ethyl- and phenyl-substituted ketones **5** and **6** were found to be good substrates for the reaction (73 and 68%, respectively), which indicates application of the process beyond acetophenones.



Scheme 4. Substrate scope.

Conclusions

This study represents the first systematic examination of ruthenium-catalyzed transfer hydrogenation of amino- and amido-substituted aromatic ketones. It was found that 1,4-butanediol was the best hydrogen source under the reaction conditions. Furthermore, the yields were generally good for a challenging reduction reaction, and a range of amines, amides, and substituted ketones were tolerated. It is therefore concluded that this method provides a robust catalytic alternative to traditional reducing agents. Future areas for study include the potential development of an asymmetric version of this reaction.

Experimental Section

Standard Procedure for the Formation of Amino Ketones: 4-Fluoroacetophenone (3.6 mL, 30 mmol) was dissolved in DMSO (40 mL) under N_2, and the amine (66 mmol, 2.2 equiv.) was added before the mixture was heated to 115 °C for 16 h. The mixture was then cooled to room temperature before it was poured into H_2O (100 mL) and mixed with brine (100 mL). The mixture was extracted with Et_2O (3 × 100 mL), and the combined organic layers were then dried ($MgSO_4$), filtered, and concentrated under vacuum. The crude material was then purified by column chromatography (petroleum ether/EtOAc) to afford the corresponding ketone in good yield.

Standard Procedure for the Reduction of Aminoacetophenones: 1,4-Butanediol (0.53 mL, 6 mmol) and 1,2-dimethoxyethane (3 mL) were added to an oven-dried, nitrogen-purged Young's tube containing $[Ru(PPh_3)_3(CO)(H)_2]$ (138 mg, 0.15 mmol) and the amino ketone (3 mmol). The reaction tube was then purged with nitrogen for 10 min before diluting with CH_2Cl_2 (50 mL). The mixture was then extracted with aqueous NaOH (1 M, 20 mL). The organic layer was then concentrated, and the crude product was purified by flash column chromatography to afford the corresponding alcohol in good yield.

Standard Procedure for the Reduction of Amidoacetophenones: 1,4-Butanediol (0.53 mL, 6 mmol) and 1,2-dimethoxyethane (3 mL) were added to an oven-dried, nitrogen-purged Young's tube containing $[Ru(PPh_3)_3(CO)(H)_2]$ (138 mg, 0.15 mmol) and the amido ketone (3 mmol). The reaction tuve was then purged with nitrogen for 10 min before it was heated to 115 °C for 24 h. On completion, the reaction mixture was cooled to room temperature before concentrating under vacuum. The crude product was purified by flash column chromatography before recrystallizing from CH_2Cl_2/hexane to afford the corresponding alcohol in good yield.

Supporting Information (see footnote on the first page of this article): Complete experimental details, characterization data, and copies of the ^1H and ^{13}C NMR spectra.

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[1] H. Meerwein, R. Schmidt, *Justus Liebigs Ann. Chem.* **1925**, *444*, 221–238.
[2] W. Ponndorf, *Angew. Chem.* **1926**, *39*, 138–143.
[3] A. Verley, *Bull. Soc. Chim. Fr.* **1925**, *37*, 537.
[4] a) J. J. Looker, *J. Org. Chem.* **1967**, *32*, 472–473; b) B. J. Marsh, D. C. Carbery, *J. Org. Chem.* **2009**, *74*, 3186–3188.
[5] a) N. J. A. Martin, B. List, *J. Am. Chem. Soc.* **2006**, *128*, 13368–13369; b) N. J. A. Martin, L. Ozores, B. List, *J. Am. Chem. Soc.* **2007**, *129*, 8976–8977; c) S. G. Ouellet, A. M. Walji, D. W. C. Macmillan, *Acc. Chem. Res.* **2007**, *40*, 1327–1339.
[6] a) A. Kišić, M. Stephan, B. Mohar, *Org. Lett.* **2013**, *15*, 1614–1617; b) S. K. Murphy, V. M. Dong, *J. Am. Chem. Soc.* **2013**, *135*, 5553–5556; c) W. Du, P. Wu, Q. Wang, Z. Yu, *Organometallics* **2013**, *32*, 3083–3090.
[7] a) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916–4917; b) E. Vedejs, P. Trapencieris, E. Suna, *J. Org. Chem.* **1999**, *64*, 6724–6729; c) S. Kang, J. Han, E. S. Lee, E. B. Choi, H.-K. Lee, *Org. Lett.* **2010**, *12*, 4184–4187; d) A. A. Mikhailine, M. I. Maishan, R. H. Morris, *Org. Lett.* **2012**, *14*, 4638–4641.
[8] a) C. Wang, C. Li, X. Wu, A. Pettman, J. Xiao, *Angew. Chem.* **2009**, *121*, 6646–6650; *Angew. Chem. Int. Ed.* **2009**, *48*, 6524–6528; b) J. Tan, W. Tang, Y. Sun, Z. Jiang, F. Chen, L. Xu, Q. Fan, J. Xiao, *Tetrahedron* **2011**, *67*, 6206–6213; c) J. Wu, C. Wang, W. Tang, A. Pettman, J. Xiao, *Chem. Eur. J.* **2012**, *18*, 9525–9529; d) J. Wu, W. Tang, A. Pettman, J. Xiao, *Adv. Synth. Catal.* **2013**, *355*, 35–40.
[9] a) T. Hashimoto, S. Urban, R. Hoshino, Y. Ohki, K. Tatsumi, F. Glorius, *Organometallics* **2012**, *31*, 4474–4479; b) M. A. Ariger, E. M. Carreira, *Org. Lett.* **2012**, *14*, 4522–4524; c) V. Gierz, A. Urbanaite, A. Seyboldt, D. Kunz, *Organometallics* **2012**, *31*, 7532–7538; d) E. Vega, E. Lastra, M. P. Gamasa, *Inorg. Chem.* **2013**, *52*, 6193–6198; e) C. Battilocchio, J. M. Hawkins, S. V. Ley, *Org. Lett.* **2013**, *15*, 2278–2281.
[10] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; b) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226–236; c) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300–1308.
[11] a) T. C. Johnson, W. G. Totty, M. Wills, *Org. Lett.* **2012**, *14*, 5230–5233; b) F. K. Cheung, C. Lin, F. Minissi, A. L. Crivillé, M. A. Graham, D. J. Fox, M. Wills, *Org. Lett.* **2007**, *9*, 4659–4662; c) A. B. Zaitsev, H. Adolfsson, *Org. Lett.* **2006**, *8*, 5129–5132; d) R. Guo, C. Elpelt, X. Chen, D. Song, R. H. Morris,

Chem. Commun. **2005**, 3050–3052; e) J. Hannedouche, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2004**, *126*, 986–987; f) S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563.

[12] A. J. A. Watson, B. N. Atkinson, A. C. Maxwell, J. M. J. Williams, *Adv. Synth. Catal.* **2013**, *355*, 734–740.

[13] J. Wettergren, A. Bøgevig, M. Portier, H. Adolfsson, *Adv. Synth. Catal.* **2006**, *348*, 1277–1282.

[14] a) D. Chaplin, P. Harrison, J. P. Henschke, I. C. Lennon, G. Meek, P. Moran, C. J. Pilkington, J. A. Ramsden, S. Watking, A. Zanotti-Gerosa, *Org. Process Res. Dev.* **2003**, *7*, 89–94; b) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1998**, *120*, 13529–13530.

[15] a) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575; b) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753–762; c) A. J. A. Watson, J. M. J. Williams, *Science* **2010**, *329*, 635–636.

[16] H. C. Maytum, B. Tavassoli, J. M. J. Williams, *Org. Lett.* **2007**, *9*, 4387–4389.

[17] J. R. Zbieg, E. Yamaguchi, E. L. McInturff, M. J. Krische, *Science* **2012**, *336*, 324–327.

[18] S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda, H. Taki, *J. Org. Chem.* **1987**, *19*, 4319–4327.

[19] H. C. Maytum, J. Francos, D. J. Whatrup, J. M. J. Williams, *Chem. Asian J.* **2010**, *5*, 538–542.

[20] H. Yim, R. Haselbeck, W. Niu, C. Pujol-Baxley, A. Burgard, J. Boldt, J. Khandurina, J. D. Trawick, R. E. Oosterhout, R. Stephen, J. Estadilla, S. Teisan, H. B. Schreyer, S. Andrae, T. H. Yang, S. Y. Lee, M. J. Burk, S. Van Dien, *Nat. Chem. Biol.* **2011**, *7*, 445–452.

[21] a) Y. R. S. Laxmi, J. E. Bäckvall, *Chem. Commun.* **2000**, 611–612; b) A. Aranyos, G. Csjernyik, K. J. Szabó, J. E. Bäckvall, *Chem. Commun.* **1999**, 351–352; c) R. L. Chowdhury, J. E. Bäckvall, *J. Chem. Soc., Chem. Commun.* **1991**, 1063–1064.

[22] a) T. Koike, K. Murta, T. Ikariya, *Org. Lett.* **2000**, *2*, 3833–3836; b) I. M. Pastor, P. Västilä, H. Adolfsson, *Chem. Commun.* **2002**, 2046–2047; c) M. J. Palmer, J. A. Kenny, T. Walsgrove, A. M. Kawamoto, M. Wills, *J. Chem. Soc. Perkin Trans. 1* **2002**, 416–427; d) P. Västilä, J. Wettergren, H. Adolfsson, *Chem. Commun.* **2005**, 4039–4041; e) M. T. Reetz, X. Li, *J. Am. Chem. Soc.* **2006**, *128*, 1044–1045; f) T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval, R. Noyori, *J. Am. Chem. Soc.* **2006**, *128*, 8724–8725; g) B. Zhang, M.-H. Xu, G.-Q. Lin, *Org. Lett.* **2009**, *11*, 4712–4715.

[23] a) N. J. Wise, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 3639–3641; b) J. M. Nichols, L. M. Bishop, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2010**, *132*, 12554–12555; c) A. Wu, B. O. Patrick, O. Chung, B. R. James, *Dalton Trans.* **2012**, *41*, 11093–11106; d) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *Org. Biomol. Chem.* **2012**, *10*, 240–243.

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