Organic & Biomolecular Chemistry

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Org. Biomol. Chem.*, 2018, **16**, 8175

Received 3rd August 2018,
Accepted 8th October 2018

DOI: 10.1039/c8ob01886c

rsc.li/obc

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.

Manganese catalyzed *N*-alkylation of anilines with alcohols: ligand enabled selectivity†

Vinod G. Landge, Akash Mondal, Vinit Kumar, Avanashiappn Nandakumar and Ekambaram Balaraman *

Ligand enabled Earth-abundant manganese catalyzed *N*-alkylation of amines with alcohols *via* a hydrogen auto-transfer strategy is reported. The choice of the ligand plays a significant role in the alcohol reactivity (aliphatic or aromatic) toward *N*-alkylation reactions.

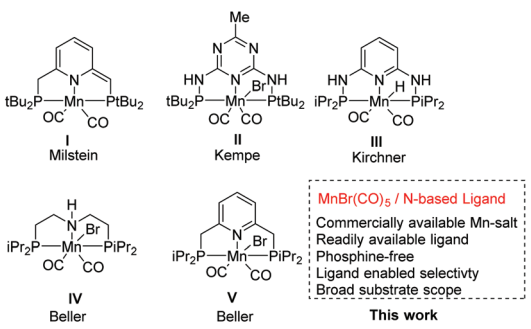
Introduction

Amines constitute an important class of compounds and find manifold applications in the synthesis of pharmaceuticals, agrochemicals, polymers, dyes, and fine chemicals.[1–3] In this regard, the development of sustainable methods for the formation of the C–N bond is in high demand. Traditionally, the C–N bond formation has been carried out using the reaction of amines with alkyl halides. However, this process has serious limitations such as over-alkylation, and the formation of non-selective byproducts. An alternative method for the synthesis of amines is the reduction of amides by utilizing stoichiometric amounts of reactive reagents which produce copious waste. Also, the Buchwald–Hartwig reaction,[4] the Ullmann reaction[5] and hydroamination[6] impose a serious challenge to *N*-alkylation, as these reactions use hazardous, prefunctionalized chemicals which leads to low atom- and step-economy.

Of late, the hydrogen auto-transfer (HA) or borrowing hydrogen (BH) strategy is one of the chemical reactions in the chemist's tool-box for the preparation of amines.[7] Mechanistically, HA includes three principal steps: (1) dehydrogenation of an alcohol to a reactive carbonyl compound, (2) condensation of the amine with the carbonyl derivative to yield an imine, (3) *in situ* hydrogenation of the imine using the hydrogen generated in the initial dehydrogenation step selectively leading to the *N*-alkylated amine. This domino reaction seldom requires an oxidant in the initial step, and an external hydrogen source for the final hydrogenation step. Thus, it can circumvent the generation of metal salt waste to yield the desired *N*-alkylated product with the formation of water. In the last few decades, this concept had taken an elegant leap from both synthesis and application points of view.[8–12]

Manganese is the third Earth-abundant metal in the Earth's crust, cheap, and biorelevant.[13] In recent times, the use of manganese as a benign alternative to precious metal catalysts in homogeneous catalysis is interesting and has received much attention. The research group of Milstein used a Mn–PNP pincer complex for the coupling of alcohols and amines to form aldimines.[14] Noteworthy progress has been made using electron-rich phosphine based Mn-complexes by various groups.[15] The pioneering work by Beller and co-workers demonstrated that a well-defined Mn-complex stabilized with an electron-rich tridentate phosphine ligand is an efficient catalyst for the *N*-alkylation of amines using alcohol as an alkylating reagent (Scheme 1).[15b,c]

Notably, the known Mn-catalytic systems consist of electron-rich phosphine ligands. Despite the widespread applications and tremendous success of phosphine ligands in homogeneous catalysis,[16,17] the identification of an alternative ligand system to electron-rich phosphines is in high demand in academia and industry. Here, we report a manganese catalytic system in combination with a simple and efficient nitro-



Scheme 1 Selected phosphine based Mn-complexes for (de)hydrogenation reactions.

Organic Chemistry Division, Dr. Homi Bhabha Road, CSIR-National Chemical Laboratory (CSIR-NCL), Pune – 411008, India. E-mail: eb.raman@ncl.res.in

†Electronic supplementary information (ESI) available: Details of experimental procedures, characterization of compounds and copy of NMR data. See DOI: 10.1039/c8ob01886c

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.

gen based ligand for selective *N*-alkylation of amines with alcohols.

Results and discussion

Initially, we began our investigation of the manganese catalyzed *N*-alkylation reaction using *m*-toluidine **1a**, and benzyl alcohol **2a** as the benchmark substrates. To our delight, the *N*-alkylated product **4a** was obtained in 65% yield, by employing commercially available $MnBr(CO)_5$ (5 mol%) as the Mn-source, dppb (5 mol%) as the ligand, and KO*t*Bu (1.1 equiv.) as the base, in toluene (Table 1, entry 1). Next, we examined the effect of a nitrogen based ligand such as 1,10-phenanthroline under the same reaction conditions. However, the required product (**4a**) was obtained in poor yield (Table 1, entry 2). Indeed, the commercially available tridentate ligand **L1** was found to be beneficial for this transformation and gave 92% isolated yield of **4a** (Table 1, entry 3). By changing tridentate to NON-ligand **L2**, a moderate yield of **4a** was observed (Table 1, entry 4). Gratifyingly, sulfur containing tridentate SNS-ligands **L3** and **L4** were also effective in this C–N bond forming reaction and gave **4a** in 74% and 80% yields, respectively (Table 1, entries 5 and 6). Notably, the salen based ligand **L5** also reacted well and gave **4a** in 91% yield.

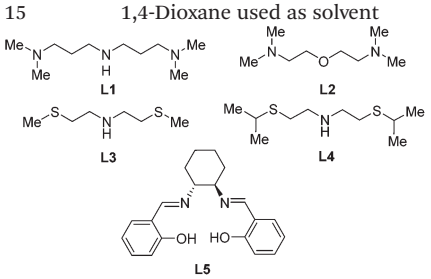
Under the optimal conditions, other manganese salts ($MnCl_2$, $Mn(OAc)_2$, $MnBr_2$, and $Mn_2(CO)_8$) failed to give **4a**. By lowering the oil-bath temperature from 140 to 100 °C, 60% yield of **4a** was obtained (Table 1, entry 9). The control experiments revealed that the catalyst, ligand, and base are important for this transformation (Table 1, entries 10–12). The efficiency of the reaction was significantly affected in the absence of the base, and KO*t*Bu showed significant improvement in the yield of **4a** (Table 1, entries 12–14). The reaction was carried out with a catalytic amount of KO*t*Bu under optimal conditions; however, the *N*-alkylated product **4a** was observed in lower yield (30%). The effect of other bases was examined under our Mn-catalyzed conditions (see the ESI†). Further screening of the solvent did not influence the *N*-alkylation of amine (Table 1, entry 15).

After establishing the optimized reaction conditions (Table 1), we set out to prove its versatility in the *N*-alkylation of various substituted alcohols and amines. The developed synthetic methodology is general and has a broad substrate scope (Tables 2 and 3). Regardless of the positions of the electron-donating and the electron-withdrawing substituents on anilines, the reaction proceeded smoothly under manganese catalysis. Aniline derivatives possessing the *para* substituents, such as methoxy, and chloro substituents were converted into the corresponding products in moderate to good yields (**3b** in

Table 1 Optimization of the reaction conditions[a,b]

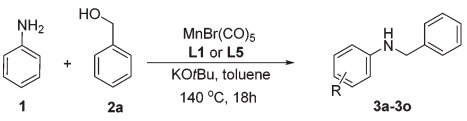
1a 2a 4a

Entry	Reaction conditions[a]	Yield of **4a** [b] (%)
1	dppb used as ligand	65
2	1,10-Phenanthroline used as ligand	18
3	L1 used as ligand	92 (58)[c]
4	L2 used as ligand	70
5	L3 used as ligand	74
6	L4 used as ligand	80
7	L5 used as ligand	91
8	$MnCl_2$ used as [Mn] source	Trace
9	At 100 °C	60
10	Without [Mn] cat.	n.d.
11	Without L1	20
12	Without KO*t*Bu	Trace
13	KOH instead of KO*t*Bu	40
14	LiO*t*Bu instead of KO*t*Bu	51
15	1,4-Dioxane used as solvent	75

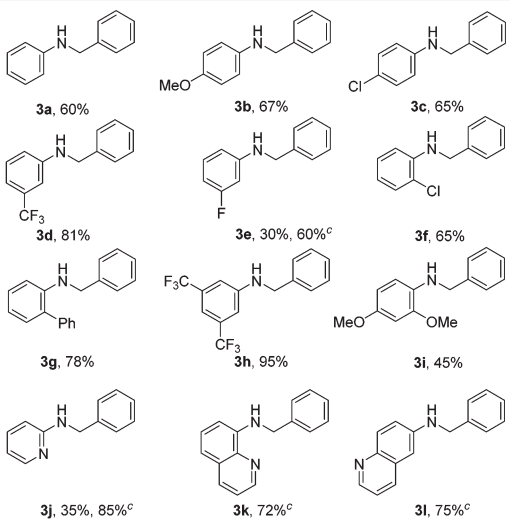


[a] Reaction conditions: Aniline **1a** (0.5 mmol), alcohol **2a** (0.55 mmol), $MnBr(CO)_5$ (5 mol%), ligand (5 mol%), KO*t*Bu (0.55 mmol), 1 mL toluene, 140 °C (oil-bath temperature), 18 h. [b] Isolated yields. **L1** = N^1-(3-(Dimethylamino)propyl)-N^3,N^3-dimethylpropane-1,3-diamine; **L2** = 2,2′-Oxybis(*N*,*N*-dimethylethanamine); **L3** = Bis(2-(methylthio)ethyl) amine; **L4** = Bis(2 (isopropylthio)ethyl)amine. [c] Under open air atm.

Table 2 Scope of amines[a,b]



1 2a 3a-3o

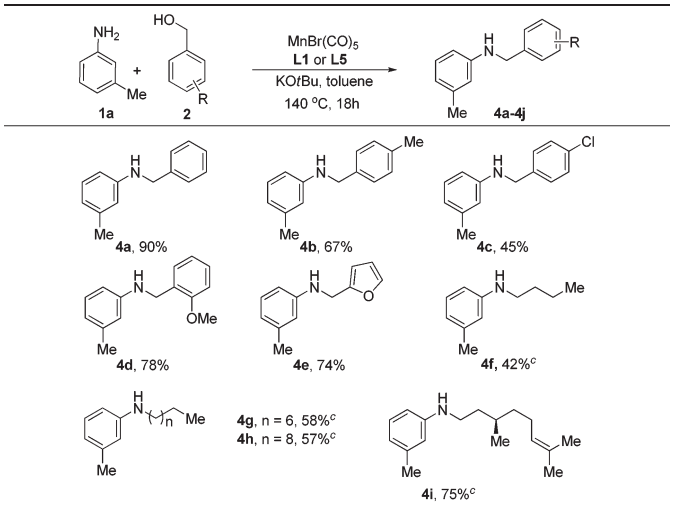


[a] Reaction conditions: Aniline **1** (0.5 mmol), alcohol **2a** (0.55 mmol), $MnBr(CO)_5$ (5 mol%), ligand (5 mol%), KO*t*Bu (0.55 mmol), 1 mL toluene, 140 °C (oil-bath temperature), 18 h. [b] Isolated yield. [c] Ligand **L5** was used.

This journal is © The Royal Society of Chemistry 2018

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.

Table 3 Scope of alcohols[a,b]



[a] Reaction conditions: Aniline **1a** (0.5 mmol), alcohol **2** (0.55 mmol), $MnBr(CO)_5$ (5 mol%), ligand (5 mol%), KO*t*Bu (0.55 mmol), 1 mL toluene, 140 °C (oil-bath temperature), 18 h. [b] Isolated yield. [c] Ligand **L5** was used.

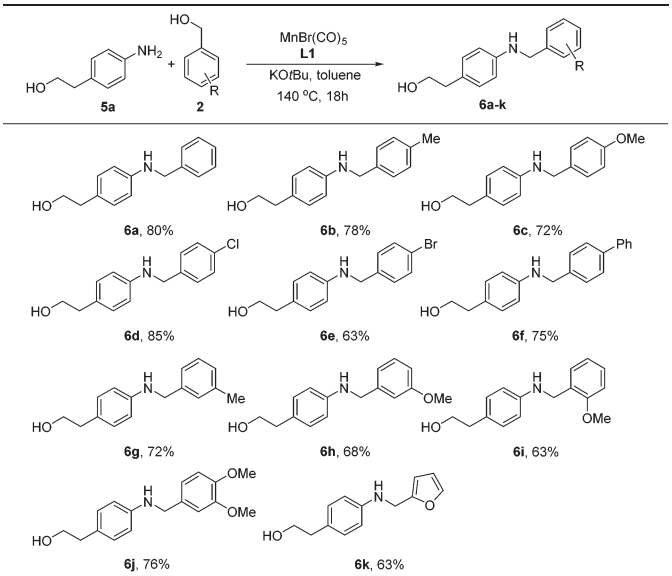
67%, and **3c** in 65% yields). The substituents on anilines such as trifluoromethyl, fluoro, chloro and phenyl substituents were tolerated and provided the corresponding C–N bonded products (**3d**, and **3d–3g**) in moderate yields. The disubstituted trifluoromethyl (**1h**), and dimethoxy (**1i**) anilines underwent the *N*-alkylation reaction and afforded the expected products **3h** and **3l** in 95% and 45% isolated yields, respectively. The heterocyclic anilines such as 2-aminopyridine, 8-aminoquinoline, and 6-aminoquinoline were well tolerated under Mn-catalysis in the presence of the **L5** ligand to give the expected products **3j** in 85%, **3k** in 72%, and **3l** in 75% yields. However, the ligand **L1** under optimized reaction conditions gave a poor yield of **3j** (35% yield). This is because the amine **1j** provides a stronger coordination site than **L1** to the Mn center. Unfortunately, aliphatic amines such as 1-pentyl amine and octylamine were ineffective and did not yield the desired *N*-alkylated products under optimal conditions.

Next, the scope of alcohol substrates in Mn-catalyzed C–N bond forming reactions was tested, and the results are summarized in Table 3. Benzyl alcohols containing various substituents such as 4-Me and 4-Cl had undergone *N*-alkylation under the optimized conditions to offer the desired products (**4b–c**) in moderate to good yields. The *ortho*-substituted methoxybenzyl alcohol reaction proceeded smoothly and gave the product **4d** in 78% isolated yield. Gratifyingly, the heterocyclic furfuryl alcohol was well tolerated and afforded the *N*-alkylated product **4e** in 74% yield. Notably, aliphatic alcohols were also susceptible to the *N*-alkylation process under optimized conditions in the presence of ligand **L5**. Thus, various aliphatic alcohols such as *n*-butanol, octanol, and decanol underwent *N*-alkylation smoothly to give the corresponding products **4f** (42%), **4g** (58%), and **4h** (57%) in moderate yields. Notably, under similar reaction conditions, ligand **L1** and the Mn source gave a poor yield of the products. This experiment result highlights the ligand enabled selectivity in the alcohol reactivity towards *N*-alkylation reactions. Remarkably, (*R*)-(+)-β-citronellol underwent *N*-alkylation selectively to give **4i** in 75% yield with the retention of the double bond and the chirality under our Mn-catalysis (Mn/**L5**).

The choice of the ligand plays a critical role in the alcohol reactivity (aliphatic *vs*. aromatic) towards the present C–N bond formation by the Mn-catalyst. To demonstrate this phenomenon, 4-amino phenyl ethyl alcohol (**5a**) was selected as a model substrate (Table 4). Thus, the reaction of **5a** with benzyl alcohols (**2**) in the presence of the **L1** ligand under standard reaction conditions led to the *N*-alkylated products in moderate to good yields (63%–85% yield). Interestingly, the alcoholic motif in **5a** remains intact. Various *para*-substituted benzyl alcohols such as 4-Me, 4-Cl, 4-Br, and 4-Ph substituted alcohols underwent the *N*-alkylation reaction under optimized conditions to give the corresponding products in 63–85% yields. The *ortho*- and *meta*-substituted benzyl alcohols are also suitable substrates for this *N*-alkylation process and offered the expected products in moderate to good yields (Table 4, products **6g–6i**). Notably, 3,4-dimethoxy benzyl alcohol and furfuryl alcohol underwent the *N*-alkylation reaction and afforded **6j** in 76% and **6k** in 63% isolated yields, respectively.

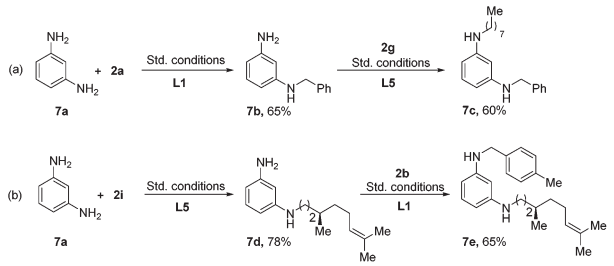
To highlight the synthetic utility of this procedure and the switching of *N*-alkylation under different ligand systems a sequential *N*-alkylation of diamine such as *m*-phenylenediamine **7a** was carried out using **L1** and **L5** ligands under optimal conditions (Scheme 2). The reaction proceeded

Table 4 Scope of amines[a,b]



[a] Reaction conditions: **5a** (0.5 mmol), alcohol **2** (0.55 mmol), $MnBr(CO)_5$ (5 mol%), ligand **L1** (5 mol%), KO*t*Bu (0.55 mmol), 1 mL toluene, 140 °C (oil-bath temperature), 24 h. [b] Yield of the isolated product.

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.



Scheme 2 Sequential *N*-alkylation of diamine.

efficiently with benzyl alcohol and afforded the selective mono-*N*-alkylated product **7b** in 65% isolated yield using ligand **L1**. Then applying the **L5** ligand yielded the unsymmetrical *N*-alkylated product **7c** in 60% yield using octanol as the alkylating reagent. Similarly, (*R*)-(+)-β-citronellol (**2i**) underwent selective sequential *N*-alkylation and gave **7e** in good yield.

Interestingly, the salen-based Mn-complex is very efficient in the present *N*-alkylation of amines with alcohols. Indeed, the isolation of the salen–Mn complex was unsuccessful. Notably, performing the *N*-alkylation reaction in the presence of Bu_4NBr (a salt known to stabilize nano-particles)[18] did not enhance the either the rate of the reaction or the yield of the product **4a**. Indeed, a low yield of **4a** (65%) was observed. Moreover, the addition of 200 equiv. of mercury to the catalytic reaction mixture slightly reduced the reaction yield (84%), though it could not quench the reaction completely. All these experimental findings showed that the present Mn-catalyst is homogeneous in nature and less likely to transform into another active catalytic species (manganese nanoparticles). Performing the reaction in the presence of radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; 2 equiv.) did not affect the yield of the product. This result indicates that the radical reaction pathway could be ruled out. Indeed, in the absence of an amine coupling partner the formation of an aldehyde product and H_2 gas was observed by GC. This result showed that the *N*-alkylation proceeds *via* a dehydrogenative coupling strategy. The inductively coupled plasma atomic emission spectroscopy analysis confirmed the absence of other metallic impurities. Notably, time-dependent experiments for the *N*-alkylation of **1a** using **2a** showed that the present Mn/**L1** or Mn/**L5** catalytic system is stable during the catalysis.[19]

Conclusions

In summary, we have reported ligand system enabled manganese catalyzed *N*-alkylation of anilines with alcohols under phosphine ligand-free conditions. The sequential *N*-alkylation of diamines with benzyl and aliphatic alcohol by employing different ligand systems has been shown. This unified strategy has a broad substrate scope and functional group tolerance. We observed that the presence of the –NH group in the tridentate ligand is crucial to obtain the *N*-alkylated product in a higher yield. Interestingly, the salen ligand also showed a similar reactivity to the tridentate ligand. At this moment, it is challenging to mention in which fashion the ligand coordinates to the Mn-center and how the alcohol gets activated (the alcohol reactivity). Indeed, the isolation of the Mn complex with the salen ligand and detailed mechanistic investigation are in progress in our laboratory.

Experimental section

General information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were of reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone followed by distillation under an argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230–400 mesh). ^1H NMR (400 or 500 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded using an NMR spectrometer. Deuterated chloroform was used as the solvent, and the chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for 1H (chloroform-d) and δ 77.2 for $^{13}C\{^1H\}$ (chloroform-d)]. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instrument with an ionization voltage of 70 eV. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and an electron impact (EI) ionization technique (magnetic sector–electric sector double focusing mass analyzer). HPLC analysis was performed on an Agilent Technologies 1260 Infinity with a UV detector.

General procedure for the manganese-catalyzed *N*-alkylation of anilines

Into an oven-dried 10 mL screw-capped vial, $MnBr(CO)_5$ (0.025 mmol, 5 mol%), ligand **L1** or **L5** (0.025 mmol, 5 mol%), alcohol **2** (0.55 mmol, 1.1 equivalents), amine **1** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalents), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept under stirring at 140 °C (oil-bath temperature) for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 × 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230–400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

 This journal is © The Royal Society of Chemistry 2018

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is supported by the SERB (EMR/2015/000030) and CSIR-INPROTICS P&A (HCP0011-A). VGL thanks the CSIR and AM thanks the UGC for the fellowships.

Notes and references

1 G. Guillena, D. J. Ramon and M. Yus, *Chem. Rev.*, 2010, **110**, 1611.
2 (*a*) *Pharmaceuticals: Classes, Therapeutic Agents, Areas of Application*, ed. J. L. McGuire, Wiley-VCH, 2000, vol. 1–4; (*b*) Z. J. Rappoport and F. Liebman, *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*, Wiley, New York, 2009, p. 609.
3 S. A. Lawrence, *Amine: Synthesis Properties and Applications*, Cambridge University, Cambridge, 2004.
4 (*a*) J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177; (*b*) A. S. Kumar and R. Nagarajan, *Org. Lett.*, 2011, **13**, 1398; (*c*) R. R. Suresh and K. C. K. Swamy, *Tetrahedron Lett.*, 2009, **50**, 6004; (*d*) B. Lü, P. Li, C. Fu, L. Xue, Z. Lin and S. Ma, *Adv. Synth. Catal.*, 2011, **353**, 100.
5 E. Sperotto, G. P. M. van Klink, G. van Koten and J. G. de Vries, *Dalton Trans.*, 2010, **39**, 10338.
6 L. Huang, M. Arndt, K. Gooßen, H. Heydt and L. J. Gooßen, *Chem. Rev.*, 2015, **115**, 2596.
7 (*a*) M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, **349**, 1555; (*b*) T. D. Nixon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.*, 2009, 753; (*c*) K.-I. Shimizu, *Catal. Sci. Technol.*, 2015 **5**, 1412; (*d*) A. Nandakumar, S. P. Midya, V. G. Landge and E. Balaraman, *Angew. Chem., Int. Ed.*, 2015, **54**, 11022.
8 (*a*) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell and M. Beller, *Chem. – Asian J.*, 2007, **2**, 403; (*b*) M. H. S. A. Hamid and J. M. J. Williams, *Chem. Commun.*, 2007, 725; (*c*) M. H. S. A. Hamid and J. M. J. Williams, *Tetrahedron Lett.*, 2007, **48**, 8263; (*d*) C. Gunanathan and D. Milstein, *Angew. Chem., Int. Ed.*, 2008, **47**, 8661; (*e*) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. H. Maxwell, C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 1766; (*f*) S. Imm, S. B-hn, L. Neubert, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 8126; (*g*) M. Zhang, S. Imm, S. Bähn, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 11197; (*h*) F. E. Fernandez, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 6868; (*i*) J. J. A. Celaje, X. Zhang, F. Zhang, L. Kam and J. R. Herron, *ACS Catal.*, 2017, **7**, 1136; (*j*) L. Tang, H. Sun, Y. Li, Z. Zha and Z. Wang, *Green Chem.*, 2012, **14**, 3423.
9 (*a*) D. Morton and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1987, 248–249; (*b*) T. Zweifel, J.-V. Naubron and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2009, **48**, 559.
10 (*a*) D. Balcells, A. Nova, E. Clot, D. Gnanamgari, R. H. Crabtree and O. Eisenstein, *Organometallics*, 2008, **27**, 2529; (*b*) B. Blank, M. Madalska and R. Kempe, *Adv. Synth. Catal.*, 2008, **350**, 749; (*c*) A. Prades, R. Corberan, M. Poyatos and E. Peris, *Chem. – Eur. J.*, 2008, **14**, 11474; (*d*) D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**, 321; (*e*) B. Blank, S. Michlik and R. Kempe, *Adv. Synth. Catal.*, 2009, **351**, 2903; (*f*) R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.*, 2010, **132**, 15108; (*g*) S. Michlik and R. Kempe, *Chem. – Eur. J.*, 2010, **16**, 13193; (*h*) O. Saidi, A. J. R. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Chem. Commun.*, 2010, **46**, 1541; (*i*) R. Kawahara, K. Fujita and R. Yamaguchi, *Adv. Synth. Catal.*, 2011, **353**, 1161; (*j*) I. Cumpstey, S. Agrawal, E. K. Borbas and B. Martin-Matute, *Chem. Commun.*, 2011, **47**, 7827; (*k*) S. Michlik, T. Hille and R. Kempe, *Adv. Synth. Catal.*, 2012, **354**, 847; (*l*) S. Agrawal, M. Lenormand and B. Martin-Matute, *Org. Lett.*, 2012, **14**, 1456; (*m*) J.-Q. Li and P. G. Andersson, *Chem. Commun.*, 2013, **49**, 6131.
11 (*a*) T. Yan, B. L. Feringa and K. Barta, *Nat. Commun.*, 2014, **5**, 5602; (*b*) T. Yan, B. L. Feringa and K. Barta, *ACS Catal.*, 2016, **6**, 381; (*c*) A. J. Rawlings, L. J. Diorazio and M. Wills, *Org. Lett.*, 2015, **17**, 1086; (*d*) H.-J. Pan, T. W. Ng and Y. Zhao, *Chem. Commun.*, 2015, **51**, 11907; (*e*) B. Emayavaramban, M. Roy and B. Sundararaju, *Chem. – Eur. J.*, 2016, **22**, 3952; (*f*) M. Bala, P. K. Verma, U. Sharma, N. Kumar and B. Singh, *Green Chem.*, 2013, **15**, 1687.
12 (*a*) S. Rösler, M. Ertl, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2015, **54**, 15046; (*b*) G. Zhang, Z. Yin and S. Zheng, *Org. Lett.*, 2016, **18**, 300; (*c*) Z. Yin, H. Zeng, J. Wu, S. Zheng and G. Zhang, *ACS Catal.*, 2016, **6**, 6546; (*d*) M. Mastalir, G. Tomsu, E. Pittenauer, G. Allmaier and K. Kirchner, *Org. Lett.*, 2016, **18**, 3462; (*e*) A. Quintard and J. Rodriguez, *ChemSusChem*, 2016, **9**, 28.
13 D. A. Valyaev, G. Lavigne and N. Lugan, *Coord. Chem. Rev.*, 2016, **308**, 191.
14 A. Mukherjee, A. Nerush, G. Leitus, L. J. Shimon, Y. Ben David, N. A. E. Jalapa and D. Milstein, *J. Am. Chem. Soc.*, 2016, **138**, 4298.
15 For Mn-catalyzed transfer hydrogenation, see: (*a*) M. Peña-López, P. Piehl, S. Elangovan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2016, **55**, 14967; (*b*) S. Elangovan, J. Neumann, S. Jean-Baptiste, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641; (*c*) J. Neumann, S. Elangovan, A. Spannenberg, K. Junge and M. Beller, *Chem. – Eur. J.*, 2017, **23**, 5410; (*d*) A. B. Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J. B. Jean-Baptiste Sortais, *J. Catal.*, 2017, **347**, 57; (*e*) D. H. Nguyen, X. Trivelli, F. Capet, J.-F. Paul, F. Dumeignil and R. M. Gauvin, *ACS Catal.*, 2017, **7**, 2022.
16 For Mn-catalyzed dehydrogenation, see: (*a*) M. Andérez-Fernández, L. K. Vogt, S. Fischer, W. Zhou, H. Jiao,

Published on 08 October 2018. Downloaded by Iowa State University on 1/21/2019 1:10:24 AM.

M. Garbe, S. Elangovan, K. Junge, H. Junge, R. Ludwig and M. Beller, *Angew. Chem., Int. Ed.*, 2017, **56**, 559; (*b*) M. Mastalir, M. Glatz, E. Pittenauer, G. Allmaier and K. Kirchner, *J. Am. Chem. Soc.*, 2016, **138**, 15543; (*c*) N. Deibl and R. Kempe, *Angew. Chem., Int. Ed.*, 2017, **56**, 1663; (*d*) F. Kallmeier, B. Dudziec, T. Irrgang and R. Kempe, *Angew. Chem., Int. Ed.*, 2017, **56**, 7261; (*e*) S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitus, L. Avram and D. Milstein, *Angew. Chem., Int. Ed.*, 2017, **56**, 4229.

17 For Mn-catalyzed hydrogenation, see: (*a*) F. Kallmeier, T. Irrgang, T. Dietel and R. Kempe, *Angew. Chem., Int. Ed.*, 2016, **55**, 11806; (*b*) S. Elangovan, M. Garbe, H. Jiao, A. Spannenberg, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2016, **55**, 15364; (*c*) N. A. Espinosa-Jalapa, A. Nerush, L. J. W. Shimon, G. Leitus, L. Avram, Y. Ben-David and D. Milstein, *Chem. – Eur. J.*, 2017, **23**, 5934; (*d*) R. van Putten, E. A. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort and E. A. Pidko, *Angew. Chem., Int. Ed.*, 2017, **56**, 7531; (*e*) F. Bertini, M. Glatz, N. Gorgas, B. Stöger, M. Peruzzini, L. F. Veiros, K. Kirchner and L. Gonsalvi, *Chem. Sci.*, 2017, **8**, 5024; (*f*) A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi and J. R. Khusnutdinova, *ACS Catal.*, 2017, **7**, 3864; (*g*) V. Papa, J. R. Cabrero-Antonino, E. Alberico, A. Spanneberg, K. Junge, H. Junge and M. Beller, *Chem. Sci.*, 2017, **8**, 3576.

18 V. Artero and M. Fontecave, *Chem. Soc. Rev.*, 2013, **42**, 2338.

19 See ESI.†

 This journal is © The Royal Society of Chemistry 2018