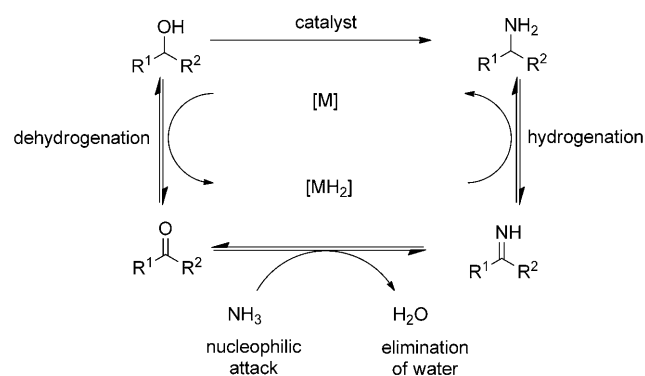


Improved Ruthenium-Catalyzed Amination of Alcohols with Ammonia: Synthesis of Diamines and Amino Esters**

Sebastian Imm, Sebastian Bähn, Min Zhang, Lorenz Neubert, Helfried Neumann, Florian Klasovsky, Jan Pfeffer, Thomas Haas, and Matthias Beller*

Amines are essential intermediates in the chemical industry, for example, for large-scale production of numerous polymers and dyes. In addition, they represent interesting building blocks for the synthesis of pharmaceuticals and agrochemicals.^[1] In nature a plethora of biologically important compounds such as alkaloids, amino acids, and nucleotides contain amino groups. Among the different types of amines, primary amines in particular are useful intermediates for further derivatization reactions.^[2] For the preparation of aliphatic amines the reductive amination of the corresponding carbonyl compounds has been the method of choice both on the laboratory and the industrial scale.

Instead of using aldehydes or ketones it is also possible to employ alcohols and amines as starting materials. Here, an initial catalytic dehydrogenation of the alcohol takes place to give the corresponding carbonyl compound and hydrogen. Subsequent formation of the imine and final hydrogenation leads to the desired amination product (Scheme 1).



Scheme 1. Catalytic amination of alcohols.

This overall atom-efficient transformation makes use of the so-called “borrowing-hydrogen” methodology,^[3] also known as “hydrogen auto-transfer” reaction.^[4] Advantageously, the hydrogen required for the final hydrogenation step is generated completely by dehydrogenation of the alcohol. Hence, there is no need for additional hydrogen gas. Furthermore, the sensitive carbonyl compound is produced in situ in low concentration, thereby minimizing unwanted side reactions.

Notably, heterogeneously catalyzed aminations of simple alcohols, for example methanol and ethanol, are performed on a multi-thousand-ton-scale.^[5] Because of the limited activity of the heterogeneous catalysts, relatively harsh conditions (>200 °C) are required for alcohol aminations. Thus, for structurally more diverse alcohols the chemoselectivity of the respective reactions is in general low and the substrate scope has been limited so far. On the other hand, there is increasing interest to produce and use chemical products based on functionalized alcohols from renewable resources.^[6] Here, especially biomass-derived carbohydrate building blocks and fatty acid derivatives constitute interesting and abundantly available feedstocks for the production of more sustainable polymers.^[7] However, to the best of our knowledge aminations of such challenging substrates with ammonia have not been described yet.

In order to achieve improved activity and selectivity, the use of defined organometallic catalysts is an attractive option. In this respect, the first homogeneously catalyzed aminations of alcohols using amines were independently reported by Grigg et al.^[8] and Watanabe et al.^[9] More recent examples for the further development of this methodology have come from the groups of Williams,^[10] Fujita,^[11] Kempe,^[12] Milstein,^[13] and Vogt^[14] and from us.^[15] Noteworthy, ammonium salts^[11b,c,16] and aqueous ammonia^[11a] were successfully applied in the synthesis of secondary and tertiary amines from alcohols.

The selective amination of primary alcohols with ammonia to give primary amines was first described by Milstein and co-workers.^[13] In the presence of a molecular defined ruthenium PNP-pincer complex different primary alcohols were converted into primary amines in good to excellent yields. More recently, the selective amination of secondary alcohols with ammonia to give primary amines has been reported independently by Vogt et al.^[14] and by us.^[15a]

Based on our continuing interest in “borrowing-hydrogen” methodology using alcohols^[17] and amines,^[18] in a joint cooperation with industry we became involved in a program to extend the substrate scope of alcohol aminations. As a starting point of our investigations we tested the amination of isosorbide with ammonia (Scheme 2). The resulting diamine

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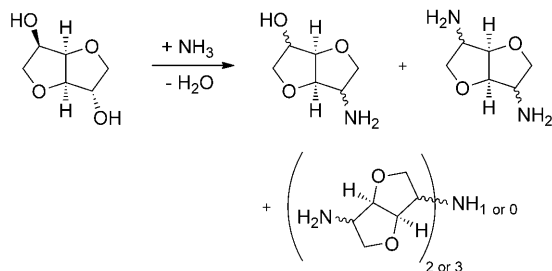
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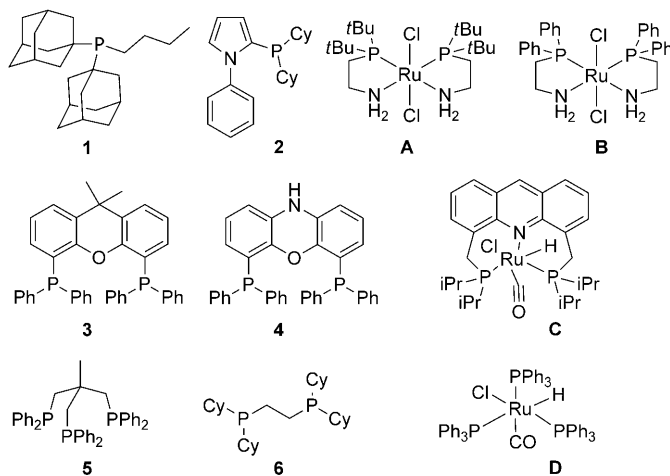
is an attractive monomer for novel polymers synthesized from renewable starting materials. Isosorbide is easily formed by dehydration of sorbitol, which is prepared on an industrial scale by the catalytic hydrogenation of D-glucose.



Scheme 2. Possible products of the amination of isosorbide.

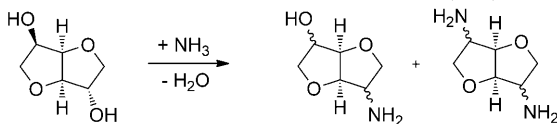
Despite the recent progress in catalytic aminations, the chemoselective synthesis of primary diamines using ammonia is a highly challenging goal. Owing to their nucleophilicity, primary amines are in general more reactive than ammonia, and the sequential formation of secondary and tertiary amines results. In the case of isosorbide, apart from different mono- and diaminated primary amines even oligomerization reactions are likely (Scheme 2).

Previously, we have demonstrated that the combination of $[\text{Ru}_3(\text{CO})_{12}]$ and various phosphine ligands generate active catalysts for the amination of alcohols.^[19] Therefore, we tested this catalyst precursor with different ligands^[20] in the benchmark reaction. A selection of ligands is shown in Scheme 3. In most cases unwanted isomerization of isosorbide took place, and no aminated products were obtained. This proves the challenging nature of this substrate for direct amination. Only two catalyst systems: $[\text{Ru}_3(\text{CO})_{12}]$ in the presence of *n*-butyldi-1-adamantylphosphine **1** or Xantphos^[21] (4,5-bis-(diphenylphosphino)-9,9-dimethylxanthene, **3**) were slightly active in the initial screening. Here, the monoaminated product was observed in up to 5% yield (Table 1, entries 1 and 3).



Scheme 3. Amination of isosorbide: selected examples of tested phosphine ligands and ruthenium complexes.

Table 1: Amination of isosorbide: variation of the catalyst system.^[a]



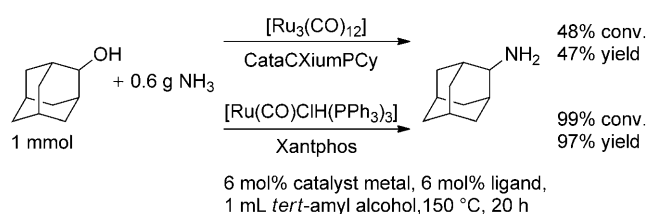
Entry	Catalyst	Ligand	Conv. [%] ^[b]	Yield of amino alcohol [%] ^[b]	Yield of diamine [%] ^[b]
1	$[\text{Ru}_3(\text{CO})_{12}]$	1	34	5	—
2	$[\text{Ru}_3(\text{CO})_{12}]$	2	42	—	—
3	$[\text{Ru}_3(\text{CO})_{12}]$	3	28	5	—
4	$[\text{Ru}_3(\text{CO})_{12}]$	5	—	—	—
5	$[\{\text{IrCp}^*\text{Cl}_2\}_2], \text{K}_2\text{CO}_3$	—	67	—	—
6	$[\text{Ru}(\text{acac})_3]$	5	50	35	—
7	A , KO^tBu	—	85	40	traces
8	B , KO^tBu	—	—	—	—
9	C	—	100	50	40
10	D	—	24	—	—
11	D	1	27	—	—
12	D	3	90	50	20
13	D	6	90	45	traces
14 ^[c]	C	—	100	32	65
15 ^[c]	D	3	100	—	96

[a] Reaction conditions: 1 mmol isosorbide, 0.6 g ammonia, 0.06 mmol catalyst (mmol of the metal), 0.06 mmol ligand, 150 °C, 20 h. [b] Conversion and yield were determined by GC analysis with hexadecane as the internal standard. Conversion and yield are based on isosorbide. [c] 170 °C. acac = acetylacetonate, $\text{Cp}^* = \text{C}_5\text{Me}_5$.

The differences between conversions and yields are explained by the isomerization of the starting material to isoidide and isomannide. Consequently, further ruthenium-based catalysts were tested. However, $[\text{Ru}(\text{acac})_3]/1,1,1$ -tris(diphenylphosphinomethyl)ethane **5**^[22] and dichlorobis[2-di-*tert*-butylphosphino)ethylamine]ruthenium **A**,^[23] gave also only traces of the diaminated product (Table 1, entries 6 and 7). Nevertheless, Milstein's catalyst **C** (Table 1, entry 9) and the in situ formed $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$ system (Table 1, entry 12) gave the diaminated products in more than 5% yield. When both catalysts were applied at higher temperature, $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$ turned out to be the most active catalyst and the diaminated products were obtained in a remarkable yield of 96% (Table 1, entry 15)! Noteworthy, excellent chemoselectivity is obtained and secondary amines or higher oligomers are not observed.

To get more information on the improved activity of the novel $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$ catalyst system, it was compared with $[\text{Ru}_3(\text{CO})_{12}]/\text{CataCXiumPCy}$, which we had found to be the best catalyst for the amination of secondary alcohols with ammonia in our previous work.^[15a] Thus, both catalysts were applied in the amination of 2-adamantanol as a sterically bulky substrate (Scheme 4).^[24] Again, $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$ catalyzed the amination reaction with full conversion and 97% yield of the primary 2-adamantylamine, while only 47% yield was achieved with the $[\text{Ru}_3(\text{CO})_{12}]/\text{CataCXiumPCy}$ system.

Next, we demonstrated the general applicability of the $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$ system for the amination of



Scheme 4. Amination of 2-adamantol: comparison of catalysts $[\text{Ru}_3(\text{CO})_{12}]/\text{CataCXiumPCy}$ and $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]/\text{Xantphos}$.

diols and other alcohols. In general, catalytic experiments were performed in the presence of 3 mol % $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ and Xantphos with 1 mmol of diol in *tert*-amyl alcohol as the solvent at 140–150 °C. The results are summarized in Table 2. We were pleased to find that various diols reacted smoothly with ammonia to give the desired products in good to excellent yields. The reactivity of primary diols is higher than the reactivity of secondary ones; see, for example, 1,4-cyclohexanediol and 4,4'-isopropylidenedicyclohexanol (Table 2, entries 6 and 7). Differences between conversions and yields are explained by the formation of monoaminated products. In return the selectivity towards the formation of primary diamines is higher in the amination of secondary diols. In addition to the synthesis of primary diamines, the amination of different primary alcohols such as 1-octanol (Table 2, entries 8–10) and 2-phenylethanol (Table 2, entry 11) to the corresponding primary amines proceeded in good to excellent yields. In the case of 1-octanol a higher amount of solvent resulted in a higher selectivity for the primary amine at 130 °C but also in incomplete conversion (Table 2, entries 8 and 9). However at 140 °C full conversion and about 80 % yield of the desired octylamine was obtained (Table 2, entry 10). The difference between conversion and yield is caused by the formation of dioctylamine.

Finally, our novel catalyst system was tested in the amination of hydroxy-substituted esters. This class of compounds is easily obtained from naturally occurring unsaturated fatty acid derivatives. Obviously, the ester function should be highly sensitive towards amines and ammonia. To our surprise both secondary as well as primary hydroxy-substituted esters can be converted at 130 °C to give the corresponding primary amines in good to excellent yields. To the best of our knowledge such aminations have not been reported before. The resulting products represent interesting monomers for polyamides prepared from renewable substrates.

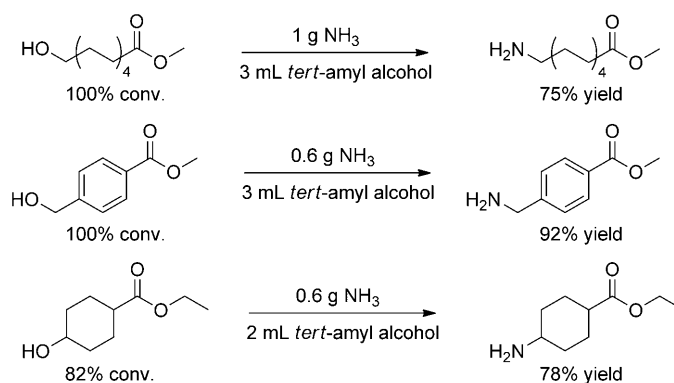
The amination of methyl 10-hydroxydecanoate and methyl 4-(hydroxymethyl)benzoate afforded the desired products in 75 and 92 % yield, respectively (Scheme 5). In the case of ethyl 4-hydroxycyclohexanecarboxylate as a secondary hydroxy ester the desired amine was formed in 78 % yield.

In summary, we have presented the first homogeneous selective catalytic diaminations of primary and secondary diols with ammonia to give the corresponding diamines in good yields and high selectivity. This atom-efficient transformation was successfully applied for the selective

Table 2: Amination of different alcohols using ammonia.^[a]

$\text{R}^1\text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow[\text{Xantphos}]{[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]} \text{R}^1\text{CH}_2\text{NH}_2 + \text{H}_2\text{O}$					
Entry	Alcohol	$V_{\text{sol.}}$ [mL]	T [°C]	Conv. [%] ^[b]	Yield [%] ^[b]
1 ^[c,d]		1	170	100	96
2		1	140	100	97
3		3	150	100	48
4		5	150	100	76
5		5	150	100	70
6		1	140	95	71
7		1	150	99	96
8		1	130	99	52
9		3	130	80	63
10		3	140	99	79
11		3	140	99	93
12		3	140	100	87
13		3	140	100	96

[a] Reaction conditions: 1 mmol alcohol, 1 g ammonia, 0.03 mmol $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$, 0.03 mmol Xantphos, solvent = *tert*-amyl alcohol, 20 h. [b] Conversion and yield were determined by GC analysis with hexadecane as the internal standard. Conversion and yield were based on the alcohol. [c] 0.6 g NH_3 . [d] 0.06 mmol $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$, 0.06 mmol Xantphos.



reaction conditions: 1 mmol hydroxy ester, 0.03 mmol **D**, 0.03 mmol **3**, 130 °C, 20 h

Scheme 5. Amination of hydroxy esters. Yield determined by GC analysis.

diamination of isosorbide, which is easily obtained from glucose. The resulting diamines are of industrial interest as novel monomers for polyamides. Our methodology relies on the presence of commercially available $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ /Xantphos catalysts in an ammonia atmosphere without the need for additional hydrogen sources. In addition, other primary as well as secondary alcohols and diols including hydroxy-substituted esters can be efficiently converted to the corresponding primary amines or diamines in good to excellent yields. We are convinced that this amination procedure is of general interest for the conversion of bio-based chemicals.

Experimental Section

General procedure for preparation of 2-adamantylamine: In a steel pressure tube under an argon atmosphere $[\text{Ru}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ (28.5 mg, 0.03 mmol), Xantphos (17.3 mg, 0.03 mmol), and 2-adamantanol (152 mg, 1 mmol) were dissolved in *tert*-amyl alcohol (1 mL). Next, the pressure tube was closed and cooled in dry ice so that ammonia (0.6 g) could be condensed into it. After the reaction mixture had been stirred at 150 °C in an oil bath under reflux conditions for 20 h, the solvent was removed under vacuum and the residue was dissolved in methanol; this solution was applied to an Isolute SCX-2 column (2 g/15 mL, Biotage). The amine was retained by the SPE column and the alcohol passed through. Afterwards the column was washed with methanol and the product was stepwise eluted with an ammonia solution in methanol (7 N). Methanol was removed under vacuum to give 2-adamantylamine as a pale yellow solid (124 mg, 82 %).

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- [1] a) H. A. Wittcoff, B. G. Reuben, J. S. Plotkin, in *Industrial Organic Chemicals*, 2nd ed., Wiley-Interscience, New York, **2004**; b) J. F. Hartwig in *Handbook of Organo-palladium Chemistry for Organic Synthesis Vol. 1* (Ed.: E.-I. Negishi), Wiley-Interscience, New York, **2002**, p. 1051.
- [2] Selected recent examples: a) P. W. Roesky, *Angew. Chem.* **2009**, *121*, 4988–4991; *Angew. Chem. Int. Ed.* **2009**, *48*, 4892–4894; b) K. Krüger, A. Tillack, M. Beller, *ChemSusChem* **2009**, *2*, 715–719; c) T. E. Müller, K. C. Hultsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892; d) O. Y. Lee, K. L. Law, C. Y. Ho, D. Yang, *J. Org. Chem.* **2008**, *73*, 8829–8837; e) I. Aillaud, J. Collin, J. Hannedouche, E. Schulz, *Dalton Trans.* **2007**, 5105–5118.
- [3] For reviews about borrowing-hydrogen methodology, see: a) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; b) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753–762; c) G. W. Lamb, J. M. J. Williams, *Chim. Oggi* **2008**, *26*, 17–19; d) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575.
- [4] a) G. Guillena, D. J. Ramón, M. Yus, *Chem. Rev.* **2010**, *110*, 1611–1641; b) G. Guillena, D. J. Ramon, M. Yus, *Angew. Chem.* **2007**, *119*, 2410–2416; *Angew. Chem. Int. Ed.* **2007**, *46*, 2358–2364.
- [5] K. Weissmehl, H.-J. Arpe, *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, Weinheim, **2003**, p. 51.
- [6] Selected recent examples: a) A. N. Parvulescu, D. Mores, E. Stavitski, C. M. Teodorescu, P. C. A. Bruijninx, R. J. M. Klein Gebbink, B. M. Weckhuysen, *J. Am. Chem. Soc.* **2010**, *132*, 10429–10439; b) A. Behr, J. Pérez Gomes, *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 31–50; c) A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyer, *Angew. Chem.* **2009**, *121*, 3652–3669; *Angew. Chem. Int. Ed.* **2009**, *48*, 3598–3614; d) A. M. Ruppert, A. N. Parvulescu, M. Arias, P. J. C. Hausoul, P. C. A. Bruijninx, R. J. M. Klein Gebbink, B. M. Weckhuysen, *J. Catal.* **2009**, *268*, 251–259; e) A. Behr, J. Leschinski, C. Awungacha, S. Simic, T. Knoth, *ChemSusChem* **2009**, *2*, 71–76; f) A. Grotevendt, R. Jackstell, D. Michalik, M. Gomez, M. Beller, *ChemSusChem* **2009**, *2*, 63–70; g) A. Behr, J. Elting, K. Irawadi, J. Leschinski, F. Lindner, *Chem. Today* **2008**, *26*, 32–36; h) A. Behr, J. Elting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* **2008**, *10*, 13–30; i) Z. C.-H. C. Zhou, J. N. Beltrami, Y.-X. Fan, G. Q. M. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527–549.
- [7] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
- [8] R. Grigg, T. R. B. Mitchell, S. Suthivaiyakit, N. Tongpenyai, *J. Chem. Soc. Chem. Commun.* **1981**, 611–612.
- [9] Y. Watanabe, Y. Tsuji, Y. Ohsugi, *Tetrahedron Lett.* **1981**, *22*, 2667–2670.
- [10] a) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden, J. M. J. Williams, *Chem. Commun.* **2010**, *46*, 1541–1543; b) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden, J. M. J. Williams, *Angew. Chem.* **2009**, *121*, 7511–7514; *Angew. Chem. Int. Ed.* **2009**, *48*, 7375–7378; c) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* **2009**, *131*, 1766–1774; d) G. W. Lamb, A. J. A. Watson, K. E. Jolley, A. C. Maxwell, J. M. J. Williams, *Tetrahedron Lett.* **2009**, *50*, 3374–3377.
- [11] a) R. Kawahara, K.-i. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2010**, *132*, 15108–15111; b) R. Yamaguchi, Z. Mingwen, S. Kawagoe, C. Asai, K.-i. Fujita, *Synthesis* **2009**, 1220–1223; c) R. Yamaguchi, S. Kawagoe, C. Asai, K.-i. Fujita, *Org. Lett.* **2008**, *10*, 181–184; d) K.-i. Fujita, Y. Enoki, R. Yamaguchi, *Tetrahedron* **2008**, *64*, 1943–1954.
- [12] a) B. Blank, S. Michlik, R. Kempe, *Chem. Eur. J.* **2009**, *15*, 3790–3799; b) B. Blank, S. Michlik, R. Kempe, *Adv. Synth. Catal.* **2009**, *351*, 2903–2911; c) B. Blank, M. Madalska, R. Kempe, *Adv. Synth. Catal.* **2008**, *350*, 749–758.
- [13] C. Gunanathan, D. Milstein, *Angew. Chem.* **2008**, *120*, 8789–8792; *Angew. Chem. Int. Ed.* **2008**, *47*, 8661–8664.
- [14] a) D. Pinggen, C. Müller, D. Vogt, *Angew. Chem.* **2010**, *122*, 8307–8310; *Angew. Chem. Int. Ed.* **2010**, *49*, 8130–8133.
- [15] a) S. Imm, S. Bähn, L. Neubert, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 8303–8306; *Angew. Chem. Int. Ed.* **2010**, *49*, 8126–8129; b) S. Bähn, A. Tillack, S. Imm, K. Mevius, D. Michalik, D. Hollmann, L. Neubert, M. Beller, *ChemSusChem* **2009**, *2*, 551–557; c) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, *2*, 403–410; d) S. Bähn, D. Hollmann, A. Tillack, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2099–2103.
- [16] M. H. S. A. Hamid, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 8263–8265.
- [17] S. Bähn, S. Imm, K. Mevius, L. Neubert, A. Tillack, J. M. J. Williams, M. Beller, *Chem. Eur. J.* **2010**, *16*, 3590–3593.
- [18] a) S. Imm, S. Bähn, A. Tillack, K. Mevius, L. Neubert, M. Beller, *Chem. Eur. J.* **2010**, *16*, 2705–2709; b) D. Hollmann, S. Bähn, A. Tillack, R. Parton, R. Altink, M. Beller, *Tetrahedron Lett.* **2008**, *49*, 5742–5745; c) D. Hollmann, S. Bähn, A. Tillack, M. Beller, *Angew. Chem.* **2007**, *119*, 8440–8444; *Angew. Chem. Int. Ed.* **2007**, *46*, 8291–8294.
- [19] a) A. Tillack, D. Hollmann, K. Mevius, D. Michalik, S. Bähn, M. Beller, *Eur. J. Org. Chem.* **2008**, 4745–4750; b) A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8881–8885.

- [20] For a complete list of tested ligands, see the Supporting Information.
- [21] S. J. Pridmore, P. A. Slatford, A. Daniel, M. K. Whittlesey, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 5115–5120.
- [22] H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1998**, 1367–1368; H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1997**, 667–668.
- [23] K. Abdur-Rashid, R. Guo, A. J. Lough, R. H. Morris, D. Song, *Adv. Synth. Catal.* **2005**, *347*, 571–579.
- [24] 2-Adamantanol turned out to be a very challenging substrate in our previous investigations and a reaction temperature of 170°C was required to achieve good yield.
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