

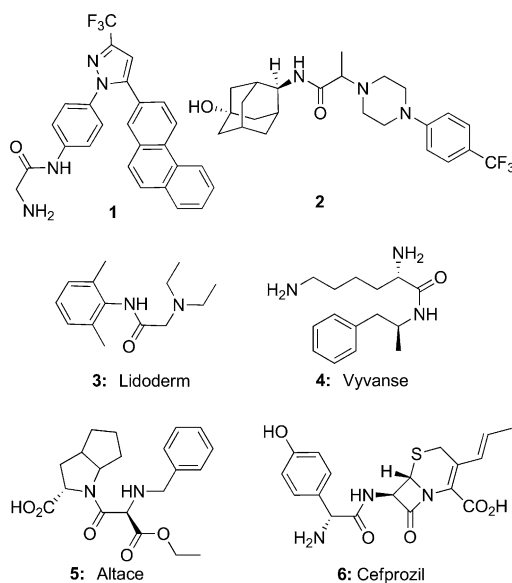
Synthesis of α -Amino Acid Amides: Ruthenium-Catalyzed Amination of α -Hydroxy Amides**

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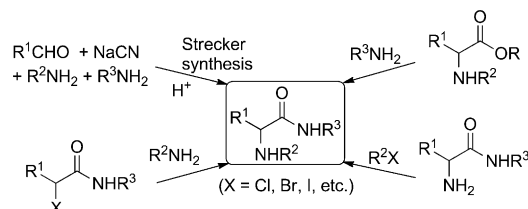
Dedicated to Professor Christian Bruneau on the occasion of his 60th birthday

α -Amino acid amides represent an interesting subclass of amino acid derivatives. In general, such compounds are biologically active and possess therapeutically useful properties. Selected examples of such compounds are: **1**, which is used for the treatment of metabolic syndrome,^[1] potent inhibitors for 11- β -hydroxysteroid dehydrogenase 1 (**2**),^[2] and top-selling drugs such as Lidoderm (**3**), Vyvanse (**4**), Altace (**5**), and Cefprozil (**6**; Scheme 1). Additionally, α -amino acid amides serve as synthetically useful intermediates for organic synthesis^[3] as well as organocatalysts^[4] and bidentate ligands^[5] for stereoselective transformations.

Owing to the importance of α -amino acid amides, numerous protocols have been developed for their preparation (Scheme 2).^[6] For example, simple α -amino acid amides



Scheme 1. Selected examples of biologically and therapeutically active α -amino amides.



Scheme 2. Selected syntheses of α -amino acid amides.

have been prepared by the classical Strecker reaction and subsequent hydrolysis of the α -amino nitriles. Most often, nucleophilic substitution reactions of naturally occurring α -amino acids with amines are applied for the synthesis of dipeptides, etc. For more sophisticated products, for example, N-aryl-substituted amides, modern catalytic reactions such as cross-coupling protocols are also known. Despite all these achievements, the development of novel atom-efficient procedures for the preparation of N-substituted amino acid amides still remains an interesting goal.

Among the various methods for C–N bond formation, in recent years the catalytic amination of alcohols has become a useful tool for the synthesis of substituted amines. Notably, water is the only sideproduct in this reaction, and less environmentally benign alkylating agents such as alkyl halides can be avoided.

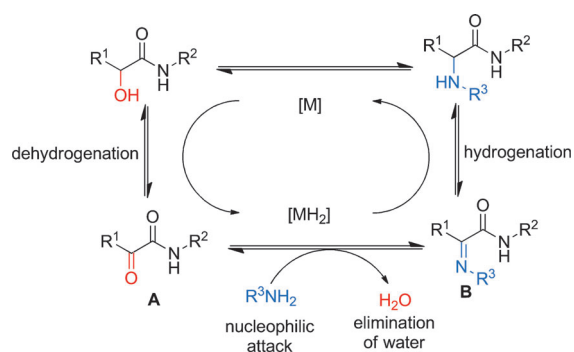
Starting with the pioneering work of Grigg et al.^[7] and Watanabe et al.^[8] in the early 80s, a series of ruthenium- and iridium-catalyzed aminations of simple primary and secondary alcohols have been described.^[9] More recent examples for such transformations came from the groups of Williams,^[10] Fujita,^[11] Kempe,^[12] and our group.^[13] However, to the best of our knowledge, the direct amination of α -hydroxy acid derivatives to yield α -amino acid derivatives has not been reported yet. Such a transformation differs significantly in reactivity from known alcohol aminations. Notably, the amide group may reduce the catalytic activity by blocking necessary coordination sites on the metal centre.^[14]

Based on our previous work on the amination of alcohols^[15] and amines,^[16] we became interested in the catalytic reaction of α -hydroxy amides with aryl and alkyl amines as well as ammonia. In agreement with known “borrowing-hydrogen”^[17] or “hydrogen autotransfer” processes^[18] this transformation should proceed by the following domino sequence (Scheme 3): 1) In situ dehydrogenation of the α -hydroxy amide leads to the corresponding α -carbonyl amide **A**. 2) **A** undergoes condensation with the amine to generate an α -imino amide **B**. 3) Final hydrogenation of **B**

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Scheme 3. Proposed mechanism for the ruthenium-catalyzed amination of α -hydroxy amides.

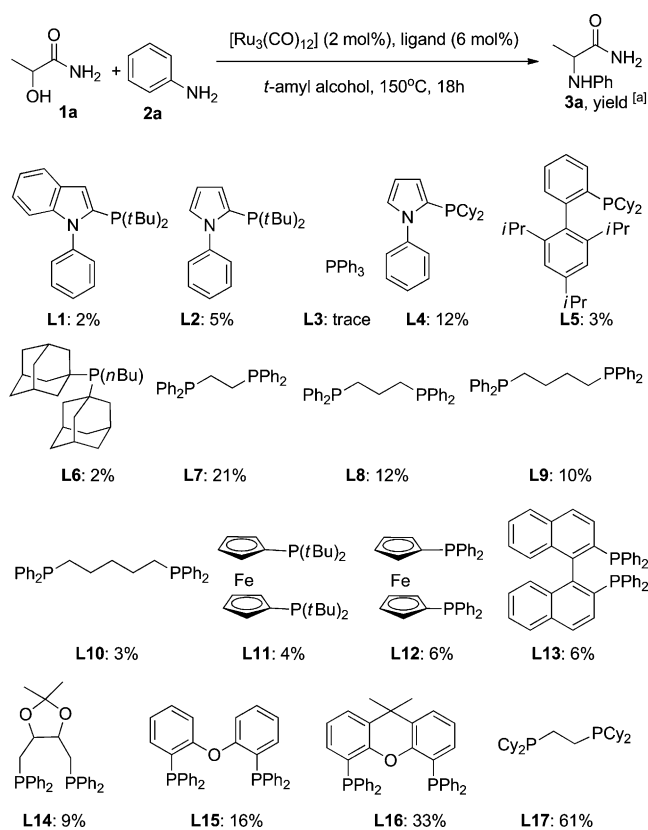
releases the product and regenerates the catalyst. Advantageously, the hydrogen required for the final hydrogenation step is completely generated by the dehydrogenation of the alcohol in the first step. Hence, there is no need for additional hydrogen.

Previous studies from our group showed that $[\text{Ru}_3(\text{CO})_{12}]$ in combination with bulky phosphine ligands led to high conversion and selectivity for the amination of nonfunctionalized aliphatic and benzylic alcohols.^[19] We therefore tested this catalyst precursor together with 17 different ligands in the model reaction of lactic acid amide with aniline to give 2-(phenylamino)propanamide **3a**. Typically, 2-hydroxypropanamide **1a** was reacted with 1.1 equiv of aniline **2a** in the presence of 2 mol % of $[\text{Ru}_3(\text{CO})_{12}]$ and 6 mol % of ligand in *tert*-amyl alcohol as solvent.

As shown in Scheme 4 the tested monodentate ligands (**L1**–**L6**) were not effective for the reaction (< 12% yield of **3a**). However, the bidentate ligands Xantphos **L16** and 1,2-bis(dicyclohexylphosphino)ethane (DCPE; **L17**) gave improved yields of **3a** (33 and 61%, respectively). Notably, in all reactions small amounts of the corresponding imine were formed, which is in agreement with the proposed mechanism (Scheme 3; intermediate **B**).

With the most promising ligand in hand, the influence of temperature, solvent, and catalyst precursor on the model reaction was further evaluated. Applying *tert*-amyl alcohol as the solvent and heating to 160 °C the product yield of **3a** increased to 90% (Table 1, entry 2). Changing the solvent to *n*-heptane, toluene, 1,4-dioxane, and DMSO resulted in lower yields of **3a** (Table 1, entries 3–6). In addition, several other catalyst precursors such as $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$,^[20] $[\{\text{Ru}(p\text{-cymene})\text{Cl}_2\}_2]$,^[10c,d] and $[\{\text{Cp}^*\text{IrCl}_2\}_2]$ ^[11] were also tested in combination with **L17** for the model reaction but gave low to moderate yields (Table 1, entries 7–9). As expected the reaction under ligand-free conditions only resulted in a trace amount of product (Table 1, entry 11).

Next, we examined the scope and limitations of this ruthenium-catalyzed amination under the optimized reaction conditions. As shown in Table 2, different α -hydroxy amides and arylamines were effectively converted into the desired amino acid amides. Both electron-withdrawing and electron-donating substituents as well as *ortho* substitution on the aryl ring of the anilines were tolerated (Table 2, entries 1–10).



Scheme 4. Screening of ligands for the model reaction. [a] Yield determined by GC using hexadecane as an internal standard. Cy = cyclohexyl.

Table 1: Variation of reaction conditions for the synthesis of **3a**.^[a]

Entry	Catalyst	Solvent	Yield [%] ^[b]
1	$[\text{Ru}_3(\text{CO})_{12}]$	<i>t</i> -amyl alcohol	88 ^[c]
2	$[\text{Ru}_3(\text{CO})_{12}]$	<i>t</i> -amyl alcohol	90
3	$[\text{Ru}_3(\text{CO})_{12}]$	<i>n</i> -heptane	9
4	$[\text{Ru}_3(\text{CO})_{12}]$	toluene	34
5	$[\text{Ru}_3(\text{CO})_{12}]$	1,4-dioxane	41
6	$[\text{Ru}_3(\text{CO})_{12}]$	DMSO	8
7	$[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ ^[d]	<i>t</i> -amyl alcohol	26
8	$[\{\text{Ru}(p\text{-cymene})\text{Cl}_2\}_2]$ ^[e]	<i>t</i> -amyl alcohol	2
9	$[\{\text{Cp}^*\text{IrCl}_2\}_2]$ ^[e]	<i>t</i> -amyl alcohol	42
10	$[\text{Ru}_3(\text{CO})_{12}]$	<i>t</i> -amyl alcohol	66 ^[f]
11	$[\text{Ru}_3(\text{CO})_{12}]$	<i>t</i> -amyl alcohol	< 1 ^[g]

[a] Unless otherwise specified, all reactions were carried out with **1a** (1 mmol), **2a** (1.1 mmol), $[\text{Ru}_3(\text{CO})_{12}]$ (0.02 mmol), and **L17** (0.06 mol) in *t*-amyl alcohol (1 mL) at 160 °C for 24 h. [b] Yield of **3a** determined by GC using hexadecane as an internal standard. [c] Reaction time: 20 h. [d] Catalyst (0.06 mmol), **L17** (0.06 mmol). [e] Catalyst (0.03 mmol), **L17** (0.06 mmol). [f] Catalyst (0.01 mmol), **L17** (0.03 mol). [g] Catalyst (0.02 mmol), ligand free. $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, DMSO = dimethylsulfoxide.

More specifically, anilines containing electron-donating methoxy or methyl substituents in the *para* position resulted in higher product yields (Table 2, entries 2, 5, 7 and 8)

Table 2: Amination of α -hydroxy amides **1** using different anilines.^[a]

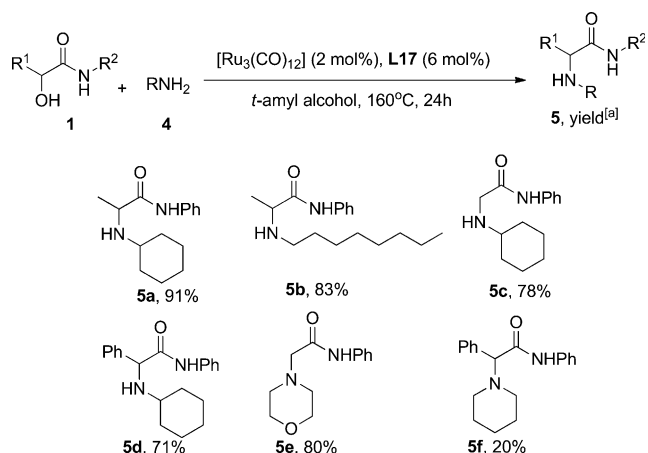
Entry	1	2	Product 3	Yield [%] ^[b]
1				78
2				83
3				72
4				42
5				91
6				56
7				89
8				78
9				79
10				61

[a] All reactions were carried out with **1** (1 mmol), **2** (1 mmol) $[\text{Ru}_3(\text{CO})_{12}]$ (0.02 mmol) and **L17** (0.06 mol) in *t*-amyl alcohol (1 mL) at 160°C for 24 h. [b] Yield of the isolated product.

compared with the electron-poor 4-chloroaniline **2 f** (Table 2, entry 6). Sterically hindered *ortho*-methoxy-substituted aniline **2 d** (Table 2, entry 4) as well as α -phenyl-substituted

amide **1 d** (Table 2, entry 10) provided moderate yields of the α -amination products.

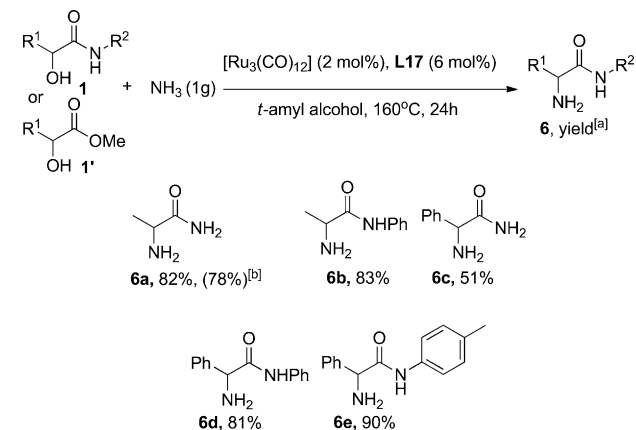
Furthermore, our protocol was tested by applying different alkylamines as the coupling partner. As shown in Scheme 5, primary amines such as *n*-octylamine and cyclo-



Scheme 5. Amination of α -hydroxy amides **1** using alkylamines. [a] Yield of the isolated product.

hexylamine exhibited high reactivity and provided the corresponding products in good to excellent yields upon isolation (**5 a–5 d**). Under the same reaction conditions, the secondary amine morpholine also showed good reactivity and gave product **5 e** in 80% yield, while the reaction between piperidine and 2-hydroxy-*N*,2-diphenylacetamide resulted in **5 f** in only 20% yield. This latter result indicates that steric factors are a major influence on the employed catalyst system.

Finally, we focused on the synthesis of α -amino acid amides using ammonia, which is the most challenging coupling partner.^[11a, 19a, 20] To our delight, in all cases examined the catalytic amination proceeded smoothly and furnished the products in good yields (Scheme 6). The less-reactive α -phenyl substituted amides were well tolerated and gave products **6 c**, **6 d**, and **6 e** in moderate to excellent yields upon



Scheme 6. Direct amination of α -hydroxy amides **1** with ammonia. [a] Yield of the isolated product. [b] Products arising from α -hydroxy esters.

isolation. Gratifyingly, α -hydroxy esters such as methyl 2-hydroxypropanoate can also be effectively employed for the amination protocol and provided product **6a** in 78% yield.

In summary, we have developed the first catalytic aminations of α -hydroxy acid derivatives. Using a variety of amines including anilines, primary and secondary aliphatic amines, and ammonia, a wide range of amino acid amides is easily available from α -hydroxy amides or esters. This atom-efficient amination protocol proceeds efficiently in the presence of a commercially available $[\text{Ru}_3(\text{CO})_{12}]/\text{DCPE}$ catalyst system without special equipment.

Experimental Section

Typical procedure for the preparation of 2-(phenylamino)propanamide (**3a**): In a glass pressure tube (50 mL) under argon $[\text{Ru}_3(\text{CO})_{12}]$ (12.8 mg, 0.02 mmol), 1,2-bis(dicyclohexylphosphino)ethane (25.3 mg, 0.06 mmol), 2-hydroxypropanamide (**1a**; 89 mg, 1 mmol), and aniline (**2a**; 102 mg, 1.1 mmol) were dissolved in *tert*-amyl alcohol (1 mL). Next, the pressure tube was closed and the resulting mixture was stirred at reflux at 160°C in an oil bath for 24 h. After cooling down to room temperature, the solvent was removed under vacuum. The residue was directly purified by flash chromatography on silica gel eluting with heptane/ethanol (15:1) to give 2-(phenylamino)propanamide (**3a**) as a white solid (128 mg, 78%). For the amination of α -hydroxy amides using alkylamines and ammonia, see in the Supporting Information for a detailed procedure.

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- [1] L. M. Porchia, M. Guerra, Y. C. Wang, Y. L. Zhang, A. V. Espinosa, M. Shinohara, S. K. Kulp, L. S. Kirschner, M. Saji, C. S. Chen, M. D. Ringel, *Mol. Pharmacol.* **2007**, *72*, 1124–1131.
- [2] J. J. Rohde, M. A. Plushchev, B. K. Sorensen, D. Wodka, Q. Shuai, J. H. Wang, S. Fung, K. M. Monzon, W. J. Chiou, L. P. Pan, X. Q. Deng, L. E. Chovan, A. Ramaiya, M. Mullally, R. F. Henry, D. F. Stolarik, H. M. Imade, K. C. Marsh, D. W. A. Beno, T. A. Fey, B. A. Droz, M. E. Brune, H. S. Camp, H. L. Sham, E. U. Frevert, P. B. Jacobson, J. T. Link, *J. Med. Chem.* **2007**, *50*, 149–164.
- [3] a) E. J. Yoo, M. Wasa, J. Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 17378–17380; b) W. L. Scott, Z. Zhou, J. G. Martynow, M. J. O'Donnell, *Org. Lett.* **2009**, *11*, 3558–3561; c) S. M. Dumbris, D. J. Diaz, L. M. White, *J. Org. Chem.* **2009**, *74*, 8862–8865; d) D. Zhang, X. C. Xing, G. D. Cuny, *J. Org. Chem.* **2006**, *71*, 1750–1753; e) T. Ooi, M. Takeuchi, D. Kato, Y. Uematsu, E. Tayama, D. Sakai, K. Maruoka, *J. Am. Chem. Soc.* **2005**, *127*, 5073–5083; f) L. Calvo, A. González-Ortega, R. Navarro, M. Pérez, M. C. Sanudo, *Synthesis* **2005**, 3152–3158; g) J. Blid, P. Brandt, P. Somfai, *J. Org. Chem.* **2004**, *69*, 3043–3049.
- [4] Y. M. Xu, A. Cordova, *Chem. Commun.* **2006**, 460–462.
- [5] a) M. I. Burguete, M. Collado, J. Escorihuela, F. Galindo, E. García-Verdugo, S. V. Luis, M. J. Vicent, *Tetrahedron Lett.* **2003**, *44*, 6891–6894; b) S. Sengupta, S. Mondal, D. Das, *Tetrahedron Lett.* **1999**, *40*, 4107–4110.
- [6] a) S. Hirner, P. Somfai, *J. Org. Chem.* **2009**, *74*, 7798–7803; b) W. L. Noorduin, T. Izumi, A. Millemaggi, M. Leeman, H. Meekers, W. J. P. Van Enkevort, R. M. Kellogg, B. Kaptein, E. Vlieg, D. G. Blackmond, *J. Am. Chem. Soc.* **2008**, *130*, 1158–1159; c) R. Löser, M. Frizler, K. Schilling, M. Gutschow, *Angew. Chem.* **2008**, *120*, 4403–4406; *Angew. Chem. Int. Ed.* **2008**, *47*, 4331–4334; d) R. Ntaganda, T. Milovic, J. Tiburcioz, A. N. Thadani, *Chem. Commun.* **2008**, 4052–4054; e) M. K. S. Vink, R. Wijtmans, C. Reisinger, R. J. F. Van den Berg, C. A. Schortinghuis, H. Schwab, H. E. Schoemaker, F. P. J. T. Rutjes, *Biotechnol. J.* **2006**, *1*, 569–573; f) G. Zvilichovsky, I. Gbara-Haj-Yahia, *J. Org. Chem.* **2004**, *69*, 4966–4973; g) B. Alcaide, P. Almendros, C. Aragoncillo, *Chem. Eur. J.* **2002**, *8*, 3646–3652; h) M. X. Wang, S. J. Lin, *J. Org. Chem.* **2002**, *67*, 6542–6545; i) Y. S. Lin, H. Alper, *Angew. Chem.* **2001**, *113*, 801–803; *Angew. Chem. Int. Ed.* **2001**, *40*, 779–781; *Angew. Chem.* **2001**, *113*, 801–803; j) M. Takamura, Y. Hamashima, H. Usuda, M. Kanai, M. Shibasaki, *Angew. Chem.* **2000**, *112*, 1716–1718; *Angew. Chem. Int. Ed.* **2000**, *39*, 1650–1652; *Angew. Chem.* **2000**, *112*, 1716–1718; k) J. R. Porter, W. G. Wirschn, K. W. Kuntz, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 2657–2658.
- [7] R. Grigg, T. R. B. Mitchell, S. Sutthivaiyakit, N. Tongpenyai, *J. Chem. Soc. Chem. Commun.* **1981**, 611–612.
- [8] Y. Watanabe, Y. Tsuji, Y. Ohsugi, *Tetrahedron Lett.* **1981**, *22*, 2667–2670.
- [9] a) K.-i. Fujita, Z. Li, N. Ozeki, R. Yamaguchi, *Tetrahedron Lett.* **2003**, *44*, 2687–2690; b) R. A. T. M. Abbenhuis, J. Boersma, G. v. Koten, *J. Org. Chem.* **1998**, *63*, 4282–4290; c) Y. Watanabe, Y. Morisaki, T. Kondo, T. Mitsodu, *J. Org. Chem.* **1996**, *61*, 4214–4218; d) N. Tanaka, M. Hatanaka, Y. Watanabe, *Chem. Lett.* **1992**, 575–578; e) S. C. Shim, C. H. Doh, *Bull. Korean Chem. Soc.* **1990**, *11*, 45–49.
- [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; *Angew. Chem.* **2009**, *121*, 7511–7514; 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, *Adv. Synth. Catal.* **2011**, *353*, 1161–1168; b) R. Kawahara, K.-i. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2010**, *132*, 15108–15111; c) R. Yamaguchi, Z. Mingwen, S. Kawagoe, C. Asai, K.-i. Fujita, *Synthesis* **2009**, 1220–1223; d) R. Yamaguchi, S. Kawagoe, C. Asai, K.-i. Fujita, *Org. Lett.* **2008**, *10*, 181–184; e) 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] D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, *2*, 403–410.
- [14] a) W. Yang, H. Fu, Q. J. Song, M. Zhang, Y. Q. Ding, *Organometallics* **2011**, *30*, 77–83; b) M. B. Jones, B. S. Newell, W. A. Hoffert, K. I. Hardcastle, M. P. Shores, C. E. MacBeth, *Dalton Trans.* **2010**, 39, 401–410; c) Z. Zhang, D. C. Leitch, M. Lu, B. O. Patrick, L. L. Schafer, *Chem. Eur. J.* **2007**, *13*, 2012–2022; d) J. M. Hoerter, K. M. Otte, S. H. Gellman, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 5177–5183; e) R. K. Thomson, J. A. Bexrud, L. L. Schafer, *Organometallics* **2006**, *25*, 4069–4071.
- [15] S. Bähn, S. Imm, K. Mevius, L. Neubert, A. Tillack, J. M. J. Williams, M. Beller, *Chem. Eur. J.* **2010**, *16*, 3590–3593.
- [16] a) S. Imm, S. Bähn, A. Tillack, K. Mevius, L. Neubert, M. Beller, *Chem. Eur. J.* **2010**, *16*, 2705–2709; b) S. Bähn, D. Hollmann, A. Tillack, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2099–2103; c) D. Hollmann, S. Bähn, A. Tillack, R. Parton, R. Altink, M. Beller, *Tetrahedron Lett.* **2008**, *49*, 5742–5745; d) D. Hollmann, S. Bähn,

- A. Tillack, M. Beller, *Angew. Chem.* **2007**, *119*, 8440–8444; *Angew. Chem. Int. Ed.* **2007**, *46*, 8291–8294; *Angew. Chem.* **2007**, *119*, 8440–8444.
- [17] For reviews about the “borrowing-hydrogen” methodology, see: a) R. H. Crabtree, *Organometallics* **2011**, *30*, 17–19; b) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; c) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753–762; d) G. W. Lamb, J. M. J. Williams, *Chim. Oggi* **2008**, *26*, 17–19; e) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575.
- [18] 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; *Angew. Chem.* **2007**, *119*, 2410–2416.
- [19] a) S. Imm, S. Bähn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas, M. Beller, *Angew. Chem.* **2011**, *123*, 7741–7745; *Angew. Chem. Int. Ed.* **2011**, *50*, 7599–7603; b) S. Imm, S. Bähn, L. Neubert, H. Neumann, M. Beller, *Angew. Chem.* **2010**, *122*, 8303–8306; *Angew. Chem. Int. Ed.* **2010**, *49*, 8126–8129; c) S. Bähn, A. Tillack, S. Imm, K. Mevius, D. Michalik, D. Hollmann, L. Neubert, M. Beller, *ChemSusChem* **2009**, *2*, 551–557; d) A. Tillack, D. Hollmann, K. Mevius, D. Michalik, S. Bähn, M. Beller, *Eur. J. Org. Chem.* **2008**, 4745–4750; e) A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8881–8885.
- [20] a) J. L. Klinkenberg, J. F. Hartwig, *Angew. Chem.* **2011**, *123*, 88–98; *Angew. Chem. Int. Ed.* **2011**, *50*, 86–95; b) D. Pinggen, C. Muller, D. Vogt, *Angew. Chem.* **2010**, *122*, 8307–8310; *Angew. Chem. Int. Ed.* **2010**, *49*, 8130–8133.