ChemPubSoc Europe

DOI: 10.1002/cctc.201500821

CHEMCATCHEM Communications

Ruthenium-Catalyzed Asymmetric Transfer Hydrogenation of Propargylic Ketones

Andrey Shatskiy, Tove Kivijärvi, Helena Lundberg, Fredrik Tinnis, and Hans Adolfsson*[a]

The asymmetric transfer hydrogenation of α,β-propargyl ketones catalyzed by an in situ formed ruthenium–hydroxyamide complex was explored. The acetylenic alcohols were isolated in good to excellent yields with excellent *ee* values (typically >90%) after short reaction times at room temperature.

Enantiomerically pure propargylic alcohols are valuable and versatile synthetic building blocks that are widely used in organic synthesis.[1] These compounds can be transformed into, for example, asymmetric allenes[2] and enantiomerically pure aliphatic and allylic alcohols.[3,4] Natural products such as prostaglandins,[5] macrolides,[6] pheromones,[7] and musclides[8] have been produced by utilizing homochiral propargylic alcohols as key elements in their synthesis, and these particular building blocks are frequently employed in the formation of cyclic and polycyclic compounds with several stereogenic centers.[9]

Enantiomerically enriched propargylic alcohols can be formed by different synthetic methods.[1,10] Asymmetric addition of acetylenes to carbonyls is a common strategy,[3b,11] and asymmetric addition of carbon nucleophiles to alkynals[12] and alkynones[13] has also been reported. Kinetic resolution[14] and dynamic kinetic resolution[15] of racemic propargylic alcohols constitute two other approaches. Asymmetric propargylic alcohols are also available by reduction of the corresponding ketones. This family of methods spans from stoichiometric reductions, for example, by using chiral boron reagents[16] and aluminum hydride reagents,[7b,17] to catalytic protocols with enzymes[18] or chiral phosphoric acids.[19] In addition, propargylic alcohols are available through ruthenium-catalyzed asymmetric hydrogenation and asymmetric transfer hydrogenation (ATH). However, to date, only a handful of catalytic protocols are known for these transformations.[20,21] Further development of milder and more cost-efficient methods in this field is therefore of great value for the chemical community.

We previously reported the use of transition-metal catalysts in combination with amino acid derived hydroxyamide ligands for the asymmetric transfer hydrogenation of aryl alkyl ketones by using alcohols as terminal reductants.[22] We also demonstrated that some of our amino acid based catalytic systems could mediate the enantioselective reduction of ketones, including an aliphatic ketone, in a water system with formate as the hydrogen donor.[23] Herein, we show that propargylic ketones can successfully be added to the substrate scope of this class of ATH catalysts. Excellent yields and enantioselectivities of propargylic alcohols were obtained at room temperature with the use of low catalyst loadings of the $[Ru(p\text{-cym})Cl_2]_2$ (*p*-cym = *p*-cymene) complex in combination with ligand (*S*,*S*)-**L1** (Figure 1).

The initial screening was performed by using 4-phenyl-3-butyn-2-one (**1a**) as a model substrate and by employing conditions previously developed for the asymmetric transfer hydrogenation of ketones.[22f] Using the ruthenium catalyst (2 mol%), it was found that the reaction mixture needed to be diluted from 0.2 to 0.01 M in a mixture of THF/*i*PrOH (1:1) to reach a reasonable yield of the propargylic alcohol (Table 1, entry 1). Further evaluation of solvent mixtures and concentrations revealed that high yield and enantioselectivity of the model substrate alcohol was obtained after only 5 min at room temperature by using a mixture of *i*PrOH/toluene (1:1) at a concentration of 0.1 M (Table 1, entry 6). Performing the reaction in isopropanol without a co-solvent resulted in a reaction that was slower than that performed in a 1:1 mixture with toluene at the same reactant concentration (Table 1, entries 3 and 6). No product was formed if the reaction was conducted without the catalyst and ligand present with all other conditions identical. Instead, substrate decomposition was seen to some

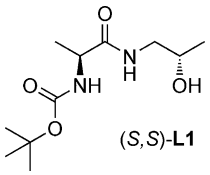
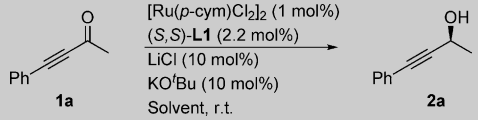


Figure 1. Hydroxyamide ligand (*S*,*S*)-**L1** derived from L-alanine.

Table 1. Influence of solvent and ketone concentration.[a]



Entry	Solvent	Concentration [M]	Time [min]	Conversion[b] [%]	*ee*[c] [%]
1	*i*PrOH/THF (1:1)	0.01	30	full	97
2	*i*PrOH/THF (1:1)	0.05	120	51	95
3	*i*PrOH	0.05	60	71	n.d.
4	*i*PrOH/hexane (1:1)	0.05	60	17	n.d.
5	*i*PrOH/toluene (1:1)	0.05	15	full	98
6	*i*PrOH/toluene (1:1)	0.1	5	full	98
7	*i*PrOH/PhCl (1:1)	0.1	30	full	97
8	*i*PrOH/*t*BuOH (1:1)	0.1	60	–	n.d.

[a] For the experimental procedure, see the Supporting Information. [b] Conversion was determined by ^{1}H NMR spectroscopy. [c] The enantioselectivity was determined by HPLC on a chiral stationary phase (Chiralcel OB column). n.d. = not determined.

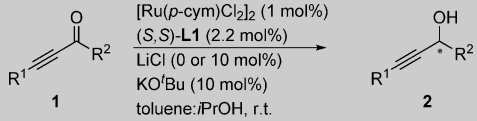
[a] *A. Shatskiy, T. Kivijärvi, Dr. H. Lundberg, Dr. F. Tinnis, Prof. H. Adolfsson*
Department of Organic Chemistry, Arrhenius Laboratory
Stockholm University
106 91 Stockholm (Sweden)
E-mail: hans.adolfsson@su.se

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500821.

extent. The screening in Table 1 was performed by using dry toluene, *i*PrOH, and THF (< 30 ppm water content). Lithium chloride was used as an additive in the screening, as earlier work with this catalyst showed that it has a beneficial effect on the enantiomeric excess (*ee*) and conversion as a result of the ion's participation in hydride delivery.[22d,e]

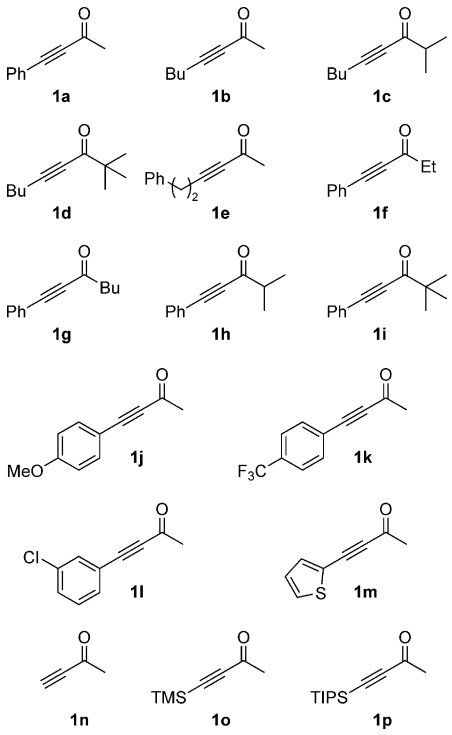
The substrate scope of the reaction was evaluated, and the optimal reaction time for each substrate was determined (Table 2). Interestingly, and in contrast to previous work on the asymmetric transfer hydrogenation of aryl ketones by using the herein reported catalyst, it was found that LiCl did not enhance the yield or the *ee* for the majority of the propargylic ketones. The reason behind this unexpected finding is not clear but might be due to catalyst interactions that are more favorable for propargylic substrates than for aryl ketones. It is also possible that the resulting decrease in polarity of the reaction mixture as a result of the use of toluene as a co-solvent instead of previously employed THF leads to a more contracted transition state, which makes the lithium ion redundant.[22e] The results for the substrate evaluation with and without LiCl present are found in Table 2. Propargylic ketones **1b**–**d** containing only aliphatic substituents were all reduced with high *ee* values (Table 2, entries 1–3), which indicates that the triple bond alone is sufficient for directing the substrate to the asymmetric catalyst. The reaction worked well with substituents with varying degrees of steric hindrance in the α position to the carbonyl group, with the exception of aliphatic *tert*-butyl-substituted ketone **1d** (Table 2, entry 3). Interestingly, the alcohol of the analogous phenyl-substituted alkynone **1i** was obtained in considerably higher yield after a short reaction time (Table 2, entry 10). Both electron-rich and electron-poor aryl-substituted alkynones **1j**–**l** were reduced with high *ee* values and in high yields, even though the electron-poor substrates required more dilute conditions to reach acceptable yields (Table 2, entry 11 vs. entries 12 and 13).[24] The same behavior was observed for heteroaromatic substrate **1m** (Table 2, entry 14).

Table 2. Substrate evaluation.[a]

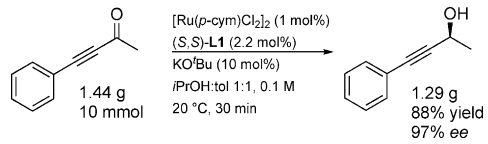


Entry	1	Conc. [M]	Time [min]	Yield[b] [%]/*ee*[d] [%] 10 mol% LiCl	No LiCl	Abs. config.
1	**1b**	0.1	20	80/98[h]	91/97[h]	*S*[e]
2	**1c**	0.1	20	81/>99[h]	78/>99[h]	*S*[e]
3	**1d**	0.1	180	11/n.d.	–	n.d.
4	**1e**	0.1	20	81/>99[h]	53/95[h]	*S*[i]
5	**1a**	0.1	10	83/96	91/97	*S*[f]
6	**1a**	0.1	35	67/97	–	*R*[f,g]
7	**1f**	0.1	10	94/98	98/98	*S*[f]
8	**1g**	0.1	15	92/98	89/>99	*S*[f]
9	**1h**	0.1	10	92/>99	98/>99	*S*[f]
10	**1i**	0.1	30	73/>99	78/>99	*S*[f]
11	**1j**	0.1	10	97/97	92/97	*S*[f]
12	**1k**	0.01	30	89/98[h]	–	n.d.
13	**1l**	0.01	25	91/98	99[c]/97	*S*[f]
14	**1m**	0.01	30	98/98	82/97	*S*[i]
15	**1n**	various conditions		0	0	–
16	**1o**	various conditions		0	0	–
17	**1p**	0.1	35	–	94/>99[h]	*S*[e]

[a] For the experimental details, see the Supporting Information. n.d. = not determined. [b] Yield of isolated product. [c] Yield was determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC on a chiral stationary phase (Chiralcel OB or IS column). [e] Determined by optical rotation and comparison to literature data.[14a,16c,25] [f] Determined by circular dichroism.[26] [g] (*R*,*R*)-Configured ligand **L1** (*ent*-**L1**) was used for the transformation. [h] Determined by GC on a chiral stationary phase (CP Chirasil DEX CB column) as the corresponding acetate. [i] Determined by analysis of the corresponding (*S*)-methoxyphenylacetic ester by NMR spectroscopy with and without barium trifluoromethanesulfonate [$Ba(OTf)_2$] at −20 °C.[27]



All propargylic alcohols were found to exhibit the (*S*) configuration when (*S*,*S*)-**L1** was used, which is in line with the chiral induction previously seen in the ruthenium-catalyzed ATH of aryl methyl ketones with the use of this ligand.[22] Terminal alkynes were reported by Noyori to inhibit the catalytic reduction of alkynones using the Ru–TsDPEN catalyst TsDPEN = *N*-4-toluenesulfonyl-1,2-diphenylethylenediamine, presumably by catalyst poisoning.[20a] Therefore, it was not surprising to find that reduction of unsubstituted alkynone substrate **1n** failed (Table 2, entry 15). The same result was also found for TMS-protected alkynone **1o**, likely because of cleavage of the TMS group under the reaction conditions (Table 2, entry 16). Gratifyingly, the reduction of triisopropylsilyl (TIPS)-protected alkynone **1p** resulted in isolation of the alcohol product in 94% yield with >99% *ee* (Table 2, entry 17). Furthermore, the reaction was demonstrated to be scalable, and model sub-



Scheme 1. Scaled-up ATH reaction.

strate **1a** was reduced on a 10 mmol scale to yield 88% of the desired alcohol with 97% *ee* (Scheme 1).

Homochiral propargylic alcohols can easily be subjected to further functionalization and synthetic manipulations.[9f,28] The ATH protocol presented herein can furnish a range of propargylic alcohols with high enantiomeric excess values, and notably, products of opposite stereochemistry are easily obtained by the use of ligand (*R*,*R*)-**L1** (Table 2, entry 6). The latter ligand is readily prepared from the corresponding *tert*-butoxycarbonyl (Boc)-protected D-alanine and (*R*)-2-aminopropanol.

To conclude, we developed a catalytic protocol for the asymmetric reduction of propargylic ketones under transfer-hydrogenation conditions by using isopropanol as the terminal reductant. The reaction is catalyzed by a half-sandwich ruthenium complex, in situ generated from $[Ru(p\text{-cym})Cl_2]_2$ and an amino acid based hydroxyamide ligand (Figure 1). A number of asymmetric secondary acetylenic alcohols were obtained in good to excellent yields and enantioselectivities. Alkynones substituted with aromatic, heteroaromatic, aliphatic, and silyl protecting groups were all tolerated under the reaction conditions to afford propargylic alcohols, which are synthetically relevant for a large number of potential applications.

Experimental Section

General procedure for the asymmetric transfer hydrogenation of propargylic ketones

$[Ru(p\text{-cym})Cl_2]_2$ (1 mol%) was added to a reaction vial equipped with a stirring bar. The vial was fitted with a septum, and the atmosphere was exchanged to N_2. Pseudo-dipeptide ligand (2.2 mol%, 0.682 % w/w solution in *i*PrOH), ketone (0.5 mmol), and, when needed, LiCl (10 mol%, 0.532 % w/w solution in *i*PrOH) were added to degassed specified solvents. The mixture was then stirred for 10 min, after which time potassium *tert*-butoxide (10 mol%, 1.4% w/w solution in *i*PrOH) was added. The mixture was stirred at room temperature for the specified amount of time. The crude product was purified by flash chromatography (ethyl acetate/pentane).

Acknowledgements

We gratefully acknowledge the K & A Wallenberg Foundation and the Swedish Research Council for financial support. We would like to thank Drs. E. Buitrago, H. G. Andersson, and P. Ryberg for fruitful discussions at an early stage of this project, Dr. Johannes Björneråas for assistance with circular dichroism measurements, and Kristina Romare for guidance with the NMR spectroscopy experiments.

Keywords: alkynones · asymmetric catalysis · hydrogenation · propargylic alcohols · ruthenium

[1] J. S. Yadav, S. Chandrasekhar, *Drug Discovery and Development: Drug Development, Vol. 2* (Ed.: M. S. Chorghade), John Wiley & Sons, Hoboken, **2007**, chapt. 21, pp. 141 – 160.

[2] H. Ohno, Y. Nagaoka, K. Tomioka *Enantioselective Synthesis of Allenes* (Eds.: N. Krause, A. S. K. Hashmi) Wiley-VCH, Weinheim, **2008**, chapt. 4, pp. 141 – 181.

[3] A. Lumbroso, M. L. Cooke, B. Breit, *Angew. Chem. Int. Ed.* **2013**, *52*, 1890 – 1932; *Angew. Chem.* **2013**, *125*, 1942 – 1986.

[4] a) E. B. Bauer, *Synthesis* **2012**, *44*, 1131 – 1151; b) B. M. Trost, A. H. Weiss, *Adv. Synth. Catal.* **2009**, *351*, 963 – 983.

[5] J. Fried, J. C. Sih, *Tetrahedron Lett.* **1973**, *14*, 3899 – 3902.

[6] See, for example, a) W. R. Roush, R. J. Sciotti, *J. Am. Chem. Soc.* **1994**, *116*, 6457 – 6458; b) D. R. Williams, W. S. Kissel, *J. Am. Chem. Soc.* **1998**, *120*, 11198 – 11199; c) L. Ferrié, S. Reymond, P. Capdevielle, J. Cossy, *Org. Lett.* **2007**, *9*, 2461 – 2464; d) J. Jägel, A. Schmauder, M. Binanzer, M. E. Maier, *Tetrahedron* **2007**, *63*, 13006 – 13017; e) L. Ferrié, L. Boulard, F. Pradaux, S. Bouzbouz, S. Reymond, P. Capdevielle, J. Cossy, *J. Org. Chem.* **2008**, *73*, 1864 – 1880; f) J. Gagnepain, E. Moulin, A. Fürstner, *Chem. Eur. J.* **2011**, *17*, 6964 – 6972.

[7] a) K. Mori, H. Akao, *Tetrahedron Lett.* **1978**, *19*, 4127 – 4130; b) R. Noyori, I. Tomino, M. Yamada, M. Nishizawa, *J. Am. Chem. Soc.* **1984**, *106*, 6717 – 6725.

[8] J. Ortiz, X. Ariza, J. Garcia, *Tetrahedron: Asymmetry* **2003**, *14*, 1127 – 1131.

[9] a) G. Stork, E. Nakamura, *J. Am. Chem. Soc.* **1983**, *105*, 5510 – 5512; b) G. Zhu, X. Lu, *J. Org. Chem.* **1995**, *60*, 1087 – 1089; c) H. Y. Kim, K. Stein, P. L. Toogood, *Chem. Commun.* **1996**, 1683 – 1684; d) M. T. Crimmins, K. A. Emmitte, *J. Am. Chem. Soc.* **2001**, *123*, 1533 – 1534; e) T. J. Greshock, D. M. Johns, Y. Noguchi, R. M. Williams, *Org. Lett.* **2008**, *10*, 613 – 616; f) A. Nakayama, N. Kogure, M. Kitajima, H. Takayama, *Angew. Chem. Int. Ed.* **2011**, *50*, 8025 – 8028; *Angew. Chem.* **2011**, *123*, 8175 – 8178.

[10] For a comprehensive overview, see for example, P. Forgione, L. D. Fader, *Sci. Synth.* **2008**, *36*, 531 – 571.

[11] E. M. Carreira, D. E. Frantz, *Science of Synthesis Stereoselective Synthesis 2: Stereoselective Reactions of Carbonyl and Imino Groups, 1st ed.* (Ed.: G. A. Molander), Thieme, **2011**, chapt. 2.10., pp. 497 – 514.

[12] D.-H. Ko, K. H. Kim, D.-C. Ha, *Org. Lett.* **2002**, *4*, 3759 – 3762.

[13] a) M. Nakamura, A. Hirai, M. Sogi, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 5846 – 5847; b) M. Yus, D. J. Ramon, O. Prieto, *Tetrahedron: Asymmetry* **2002**, *13*, 2291 – 2293.

[14] For enzyme catalysis see, *for example*, a) K. Burgess, L. D. Jennings, *J. Am. Chem. Soc.* **1991**, *113*, 6129 – 6139; b) M. Schober, M. Toesch, T. Knaus, G. A. Strohmeier, B. van Loo, M. Fuchs, F. Hollfelder, P. Macheroux, K. Faber, *Angew. Chem. Int. Ed.* **2013**, *52*, 3277 – 3279; *Angew. Chem.* **2013**, *125*, 3359 – 3361. For synthetic catalysts, see, for example, c) B. Tao, J. C. Ruble, D. A. Hoic, G. C. Fu, *J. Am. Chem. Soc.* **1999**, *121*, 5091 – 5092; d) D. Belmessieri, C. Joannesse, P. A. Woods, C. MacGregor, C. Jones, C. D. Campbell, C. P. Johnston, N. Duguet, C. Concellon, R. A. Bragg, A. D. Smith, *Org. Biomol. Chem.* **2011**, *9*, 559 – 570; e) X. Li, H. Jiang, E. W. Uffman, L. Guo, Y. Zhang, X. Yang, V. B. Birman, *J. Org. Chem.* **2012**, *77*, 1722 – 1737.

[15] a) M.-J. Kim, Y. I. Chung, Y. K. Choi, H. K. Lee, D. Kim, J. Park, *J. Am. Chem. Soc.* **2003**, *125*, 11494 – 11495; b) J. H. Choi, Y. K. Choi, Y. H. Kim, E. S. Park, E. J. Kim, M.-J. Kim, J. Park, *J. Org. Chem.* **2004**, *69*, 1972 – 1977.

[16] See, for example, a) M. M. Midland, D. C. McDowell, R. L. Hatch, A. Tramontano, *J. Am. Chem. Soc.* **1980**, *102*, 867 – 869; b) C. J. Helal, P. A. Magriotis, E. J. Corey, *J. Am. Chem. Soc.* **1996**, *118*, 10938 – 10939; c) S. Eagon, C. DeLieto, W. J. McDonald, D. Haddenham, J. Saavedra, J. Kim, B. Singaram, *J. Org. Chem.* **2010**, *75*, 7717 – 7725; d) N. Arai, T. Ohkuma, *Modern Reduction Methods* (Eds.: P. G. Andersson, I. J. Munslow) Wiley-VCH, Weinheim, **2008**, chapt. 7, pp. 159 – 181.

[17] See, for example, a) J. P. Vigneron, V. Bloy, *Tetrahedron Lett.* **1979**, *20*, 2683 – 2686; b) N. Cohen, R. J. Lopresti, C. Neukom, G. Saucy, *J. Org. Chem.* **1980**, *45*, 582 – 588; c) J. P. Vigneron, V. Bloy, *Tetrahedron Lett.* **1980**, *21*, 1735 – 1738.

[18] See, for example, a) T. Schubert, W. Hummel, M. Muller, *Angew. Chem. Int. Ed.* **2002**, *41*, 634 – 637; *Angew. Chem.* **2002**, *114*, 656 – 659; b) M.

Muller, M. Wolberg, T. Schubert, W. Hummel, *Technology Transfer in Biotechnology: From Lab to Industry to Production, Vol. 92* (Ed.: U. Kragl), Berlin, **2005**, pp. 261 – 287.

[19] Z. Zhang, P. Jain, J. C. Antilla, *Angew. Chem. Int. Ed.* **2011**, *50*, 10961 – 10964; *Angew. Chem.* **2011**, *123*, 11153 – 11156.

[20] Asymmetric transfer hydrogenation: a) K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1997**, *119*, 8738 – 8739; Asymmetric hydrogenation: b) R. Noyori, T. Okuma, K. Tsutsumi, N. Utsumi, K. Murata, US pat. US 20070225528, **2007**.; Jap. pat., JP 2010285443, **2010**; c) N. Arai, H. Satoh, N. Utsumi, K. Murata, K. Tsutsumi, T. Ohkuma, *Org. Lett.* **2013**, *15*, 3030 – 3033.

[21] Asymmetric transfer hydrogenation: a) D. J. Morris, A. M. Hayes, M. Wills, *J. Org. Chem.* **2006**, *71*, 7035 – 7044; b) Z. Fang, M. Wills, *J. Org. Chem.* **2013**, *78*, 8594 – 8605.

[22] a) I. M. Pastor, P. Västilä, H. Adolfsson, *Chem. Commun.* **2002**, 2046 – 2047; b) A. Bøgevig, I. M. Pastor, H. Adolfsson, *Chem. Eur. J.* **2004**, *10*, 294 – 302; c) J. Wettergren, A. Bøgevig, M. Portier, H. Adolfsson, *Adv. Synth. Catal.* **2006**, *348*, 1277 – 1282; d) P. Västilä, A. B. Zaitsev, J. Wettergren, T. Privalov, H. Adolfsson, *Chem. Eur. J.* **2006**, *12*, 6190; e) J. Wettergren, E. Buitrago, P. Ryberg, H. Adolfsson, *Chem. Eur. J.* **2009**, *15*, 5709; f) E. Buitrago, H. Lundberg, H. Andersson, P. Ryberg, H. Adolfsson, *ChemCatChem* **2012**, *4*, 2082.

[23] a) K. Ahlford, J. Lind, L. Mäler, H. Adolfsson, *Green Chem.* **2008**, *10*, 832 – 835; b) K. Ahlford, H. Adolfsson, *Catal. Commun.* **2011**, *12*, 1118 – 1121.

[24] Since the ATH reactions are performed under equilibrium conditions, lower concentration normally leads to higher yields. R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97 – 102.

[25] For alcohol R^1 = Bu, R^2 = Me: a) V. B. Birman, L. Guo, *Org. Lett.* **2006**, *8*, 4859 – 4861; b) K. Ishihara, A. Mori, I. Arai, H. Yamamoto, *Tetrahedron Lett.* **1986**, *27*, 983 – 986; c) G. Giacomelli, L. Lardicci, F. Palla, A. M. Caporusso, *J. Org. Chem.* **1984**, *49*, 1725 – 1728; See also Refs. [7b] and [20a]. For alcohol R^1 = Bu, R^2 = *i*Pr: d) G. Giacomelli, L. Lardicci, F. Palla, *J. Org. Chem.* **1984**, *49*, 310 – 313; See also Ref. [20a]. For alcohol R^1 = Bu, R^2 = *t*Bu: e) M. Falorni, L. Lardicci, C. Rosini, G. Giacomelli, *J. Org. Chem.* **1986**, *51*, 2030 – 2033; For alcohol R^1 = TIPS, R^2 = Me: f) J. A. Marshall, P. Eidam, H. S. Eidam, *J. Org. Chem.* **2006**, *71*, 4840 – 4844; g) J. A. Marshall, P. Eidam, H. S. Eidam, *Org. Synth.* **2007**, *84*, 120 – 128; h) R. V. Edwankar, C. R. Edwankar, J. Deschamps, J. M. Cook, *Org. Lett.* **2011**, *13*, 5216 – 5219.

[26] J. Naito, Y. Yamamoto, M. Akagi, S. Sekiguchi, M. Watanabe, N. Harada, *Monatsh. Chem.* **2005**, *136*, 411 – 445.

[27] For a description of the Ba(II)-assisted NMR method for absolute configuration, see: a) R. García, J. M. Seco, S. A. Vázquez, E. Quiñoá, R. Riguera, *J. Org. Chem.* **2002**, *67*, 4579 – 4589; b) J. M. Seco, E. Quiñoá, R. Riguera, *Chem. Rev.* **2004**, *104*, 17 – 118.

[28] a) H. Lebel, E. N. Jacobsen, *J. Org. Chem.* **1998**, *63*, 9624 – 9625; b) K. Fujii, K. Maki, M. Kanai, M. Shibasaki, *Org. Lett.* **2003**, *5*, 733 – 736; c) K. Maki, R. Motoki, K. Fujii, M. Kanai, T. Kobayashi, S. Tamura, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 17111 – 17117; d) G. Kumaraswamy, M. Padmaja, *J. Org. Chem.* **2008**, *73*, 5198 – 5201; e) V. Druais, M. J. Hall, C. Corsi, S. V. Wendeborn, C. Meyer, J. Cossy, *Org. Lett.* **2009**, *11*, 935 – 938; f) V. Druais, C. Meyer, J. Cossy, *Org. Lett.* **2012**, *14*, 516 – 519; g) B. M. Trost, M. J. Bartlett, *Org. Lett.* **2012**, *14*, 1322 – 1325; h) N. Kesava Reddy, S. Chandrasekhar, *J. Org. Chem.* **2013**, *78*, 3355 – 3360.

Received: July 24, 2015
Published online on September 18, 2015