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The Magnesium(II)-Catalyzed Asymmetric Ketone–Ene Reaction under Solvent-Free Conditions: Stereocontrolled Access to Enantioenriched Trifluoromethyl-Substituted Compounds

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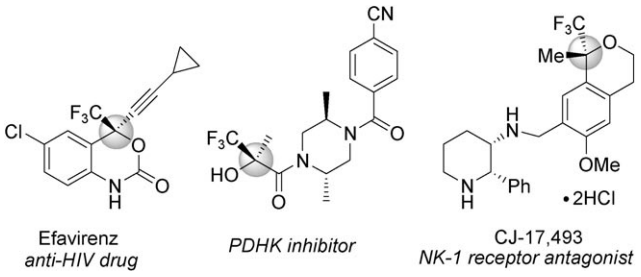
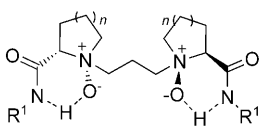
The alkaline earth metals, such as magnesium complexes, are promising Lewis acid catalysts with inherently milder Lewis acidity than the traditional transition metals. Increasingly, interest has been focused on their application to various transformations due to their abundance and low toxicity.[1,2] The combination of chiral ligands with magnesium(II) has been used to generate a stereochemical arrangement that leads to good enantioselectivity in asymmetric reactions. Since the first report by Corey and co-workers,[3] several chiral magnesium complexes, especially magnesium–bisoxazoline complexes,[4] have successfully been applied as catalysts in a variety of asymmetric carbon–carbon bond forming reactions.[5] However, their reactivities and selectivities are, in most cases, lower than those of other chiral metal-catalyzed reactions. To make magnesium complexes more feasible catalysts in these applications, it is, therefore, very important to improve their efficiency and selectivity by searching for hetero-atom-containing chiral ligands with properly hindered and flexible stereoenvironments that form chiral magnesium complexes.

In recent years, trifluoromethylated compounds have received considerable attention due to their unique chemical, physical, and biological properties.[6] Chiral quaternary alcohols containing a CF_3 group with a well-defined configuration are a recurring motif in drug molecules, such as Efavirenz (anti-HIV) and CJ-17,493 (NK-1 receptor antagonist).[7] As one of the most efficient routes to such structures, the asymmetric ketone–ene reaction of trifluoropyruvate could provide an efficient synthesis, which has rarely been addressed.[8] Herein, we examine highly efficient chiral magnesium complexes as catalysts for the asymmetric ketone–ene reaction of trifluoropyruvate by employing C_2-symmetric *N,N′*-dioxides as the ligand for the first time.[9] The corresponding trifluoromethylated α-hydroxy esters containing a carbon–carbon double bond, which could easily be transformed into other functional groups, were obtained in excellent enantioselectivities (up to >99% *ee*) for a broad range of substrates, under low catalyst loading.



At the outset of this study, we investigated the reaction of 2-phenylpropene (**1a**) and ethyl trifluoropyruvate (**2**) in the presence of chiral catalysts, prepared from alkaline earth metal salts and a chiral (*S*)-pipecolic acid derived *N,N′*-dioxide **L2** (Table 1, entries 1–3). To our delight, the $Mg(ClO_4)_2$–**L2** complex catalyzed the reaction, displaying promising reactivity and enantioselectivity (73% yield, 67% *ee*; Table 1, entry 1). The enantioselectivity was further improved to 75% *ee* by using $Mg(OTf)_2$ instead of $Mg(ClO_4)_2$ (Table 1, entry 4). Encouraged by these results, various *N,N′*-dioxides were then synthesized and investigated. As shown in



L1: n = 1, R^1 = phenyl
L2: n = 2, R^1 = phenyl
L3: n = 2, R^1 = 2-bromophenyl
L4: n = 2, R^1 = 2-methylphenyl
L5: n = 2, R^1 = 2-dimethylphenyl
L6: n = 2, R^1 = 2,6-diisopropylphenyl

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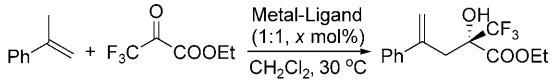
Table 1. Optimization of the reaction conditions.[a]



1a 2 3a

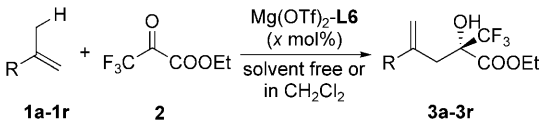
Entry	Metal	Ligand	x	t [h]	Yield [%][b]	*ee* [%][c]
1	$Mg(ClO_4)_2$	**L2**	10	24	73	67
2	$Ca(ClO_4)_2$	**L2**	10	24	10	2
3	$Ba(ClO_4)_2$	**L2**	10	24	58	8
4	$Mg(OTf)_2$	**L2**	10	24	65	75
5	$Mg(OTf)_2$	**L1**	10	24	50	11[d]
6	$Mg(OTf)_2$	**L3**	10	24	52	86
7	$Mg(OTf)_2$	**L4**	10	24	57	88
8	$Mg(OTf)_2$	**L5**	10	12	70	95
9	$Mg(OTf)_2$	**L6**	10	6	99	>99
10	$Mg(OTf)_2$	**L6**	2.5	12	95	>99
11	$Mg(OTf)_2$	**L6**	1	32	93	99
12	$Mg(OTf)_2$	**L6**	0.5	60	80	96
13[e]	$Mg(OTf)_2$	**L6**	2.5	12	91	98

[a] Unless otherwise noted, the reactions were carried out with ethyl trifluoropyruvate **2** (0.1 mmol) and 2-phenylpropene **1a** (1.1 equiv) in CH_2Cl_2 (1.0 mL) at 30 °C for 6–60 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The opposite configuration of **3a** was obtained. [e] Under solvent-free conditions with ethyl trifluoropyruvate **2** (0.3 mmol) and 2-phenylpropene **1a** (1.2 equiv).

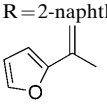
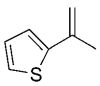
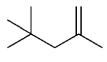
Table 1, the (*S*)-pipecolic acid derived *N,N′*-dioxide **L2** gave better results than the L-proline derived **L1** (Table 1, entries 4 vs. 5). An interesting trend was that ligands with a bulkier electron-donating group at the *ortho* position of aniline gave higher reactivity and enantioselectivity (Table 1, entry 6 vs. entries 7–9). The best result was obtained with ligand **L6** for which product **3a** was obtained in 99% yield with >99% *ee*. Reducing the catalyst loading seemed to have little influence on the selectivity of the reaction. The catalyst loading could be reduced to 0.5 mol% with only a slight reduction in enantioselectivity, although the reaction rate was decreased (Table 1, entries 10–12). Other conditions such as the temperature, solvent, and additive were also examined, but no superior results were obtained (see the Supporting Information). We were delighted that the yield and *ee* were maintained when the reaction was carried out under solvent-free conditions (91% yield, 98% *ee*; Table 1, entry 13), which provides an ideal, environmentally safe process in a practical synthesis.[10,11] It should be noted that this process was extremely simple to perform [the pre-prepared $Mg(OTf)_2$–**L6** complex (molar ratio: 1:1) was added to a mixture of the two substrates and stirred at 30 °C without any protective procedures] and atmospheric oxygen and humidity did not affect the results at all.

With these optimal conditions established, the scope of the reaction with respect to various alkenes was examined (Table 2). To our delight, this catalyst system exhibited a remarkably broad substrate scope and the corresponding trifluoromethylated α-hydroxy esters were obtained in excellent enantioselectivities (95–>99% *ee*). The aromatic alkenes underwent the ketone–ene reaction smoothly, in excellent enantioselectivities, regardless of the electronic nature and position of the substituents on the aromatic ring

Table 2. Substrate scope for the catalytic asymmetric ketone–ene reaction.[a]



1a-1r 2 3a-3r

Entry	1		x [mol%]	t [h]	Yield [%][b,d]	*ee* [%][c,d]
1	**1a**	R=Ph	2.5	12	95 (91)	>99 (98)
2	**1b**	R=2-MeC_6H_4	2.5	24	92 (90)	99 (97)
3	**1c**	R=4-MeC_6H_4	1.0	24	96 (95)	97 (97)
4	**1d**	R=2-$MeOC_6H_4$	2.5	24	95	98
5	**1e**	R=3-$MeOC_6H_4$	2.5	24	90 (90)	97 (97)
6[e]	**1f**	R=4-$MeOC_6H_4$	1.0	12	92 (92)	99 (98)
7	**1g**	R=3-ClC_6H_4	1.0	24	80 (82)	>99 (99)
8	**1h**	R=4-ClC_6H_4	1.0	24	90 (92)	>99 (99)
9	**1i**	R=3,4-$Cl_2C_6H_3$	2.5	48	92	>99
10	**1j**	R=2-FC_6H_4	2.5	72	75	>99
11	**1k**	R=4-FC_6H_4	1.0	12	82 (85)	99 (98)
12	**1l**	R=4-BrC_6H_4	2.5	8	90	>99
13	**1m**	R=2-naphthyl	2.5	12	95	99
14	**1n**		1.0	12	84	95
15	**1o**		1.0	6	97 (92)	97 (95)
16	**1p**		2.5	48	92 (91)	99 (91)
17	**1q**		1.0	32	95 (91)	>99 (98)
18	**1r**		2.5	24	83	>99

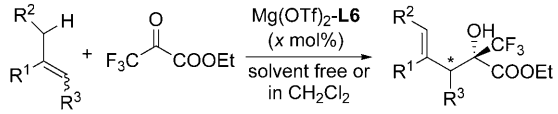
[a] Unless otherwise noted, the reaction was carried out with $Mg(OTf)_2$–**L6** (1.0–2.5 mol%), ethyl trifluoropyruvate **2** (0.1 mmol), and alkene **1** (1.1 equiv) in CH_2Cl_2 (1.0 mL) at 30 °C for 6–72 h. [b] Isolated yield. [c] Determined by chiral HPLC or GC analysis. [d] The data in parentheses were obtained under the solvent-free conditions with 2.5 mol% catalyst, ethyl trifluoropyruvate **2** (0.3 mmol), and alkene **1** (1.2 equiv). [e] The data in parentheses were obtained with alkene **1** (0.3 mmol, solid) and ethyl trifluoropyruvate **2** (1.3 equiv) under the solvent-free conditions.

of the alkenes, although electron-withdrawing substituents at the *ortho* position were less reactive and required longer reaction times (97–>99% *ee*; Table 2, entries 1–12). It is worth noting that the condensed-ring and heteroaromatic alkenes performed well, giving the corresponding products in high yields (84–97%) with up to 99% *ee* (Table 2, entries 13–15). Aliphatic alkenes also reacted with trifluoropyruvate **2** to afford the corresponding products in extremely high enantioselectivities (up to >99% ee; Table 2, entries 16–18).

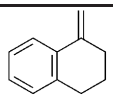
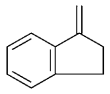
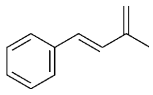
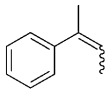
In order to expand upon the synthetic utility of the reaction, we subjected various other alkenes to our optimized reaction conditions. Pleasingly, excellent enantioselectivities were observed for both benzocyclic alkenes **1s** and **t** and α,β-unsaturated alkene **1u**, some of the products of which were syntheisized for the first time in this asymmetric

ketone–ene reaction (Table 3, entries 1–3). A cyclic alkene was also tolerated by this procedure and afforded the expected product in >99% *ee* (Table 3, entry 4). In addition,

Table 3. Substrate scope for the catalytic asymmetric ketone–ene reaction.[a]



1s-1w 2 3s-3w

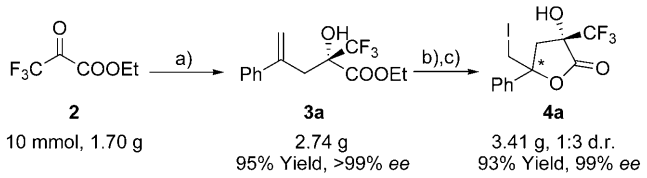
Entry	1		x [mol%]	t [h]	Yield [%][b,d]	ee [%][c,d]
1	**1s**		1.0	6	97 (95)	98 (95)
2	**1t**		1.0	8	95 (91)	96 (95)
3	**1u**		0.5	12	88 (95)	99 (97)
4	**1v**		2.5	5	93 (90)	>99 (98)
5	**1w**		10	72	60	96; >99:1 d.r.

[a] Unless otherwise noted, the reaction was carried out with $Mg(OTf)_2$–**L6** (0.5–2.5 mol%), ethyl trifluoropyruvate **2** (0.1 mmol), and alkene **1** (1.1 equiv) in CH_2Cl_2 (1.0 mL) at 30°C for 6–72 h. [b] Isolated yield. [c] Determined by chiral HPLC or GC analysis. [d] The data in parentheses were obtained under the solvent-free conditions with catalyst (2.5 mol%), ethyl trifluoropyruvate **2** (0.3 mmol), and alkene **1** (1.2 equiv).

α-substituted alkene **1w** was found to be a suitable substrate for the reaction and afforded the desired product **3w** with excellent diastereo- and enantioselectivity (>99:1 d.r., 96% *ee*; Table 3, entry 5).

To further evaluate the synthetic potential of this catalyst system, the scope of this methodology under the solvent-free conditions, which meet the requirements of green chemistry, was also investigated. We were pleased to observe that both aromatic and aliphatic alkenes, as well as heteroaromatic alkenes, were tolerated in terms of both yields and enantioselectivities, providing up to 95% yield and 99% *ee* (data in parentheses in Tables 2 and 3).

The mild reaction conditions, low catalyst loading, and inexpensive catalyst for this ketone–ene reaction offer a practical way to scale-up production. In the presence of the $Mg(OTf)_2$–**L6** complex (2 mol%), ethyl trifluoropyruvate **2** (10.0 mmol) reacted with 2-phenylpropene (**1a**; 1.1 equiv) to provide the desired addition product **3a** in 95% yield (2.76 g) with >99% *ee*. In addition, product **3a** can be easily transformed into the corresponding functionalized γ-butyrolactone (**4a**) in excellent yield without affecting the stereoinduction (3.41 g, 93% yield, 99% *ee*; Scheme 1).

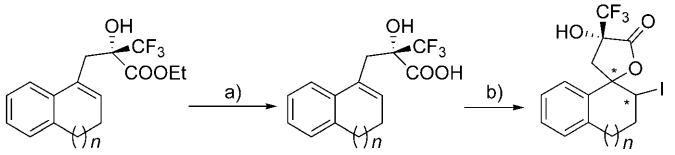


2 3a 4a

10 mmol, 1.70 g 2.74 g, 95% Yield, >99% *ee* 3.41 g, 1:3 d.r., 93% Yield, 99% *ee*

Scheme 1. The asymmetric ketone–ene reaction of trifluoropyruvate **2** on a gram scale and synthesis of the trifluoromethyl-substituted γ-butyrolactone **4a**. Conditions: a) $Mg(OTf)_2$–**L6** (2 mol%), **1a** (11 mmol, 1.36 g), 30°C, 12 h; b) KOH (20% aq.), CH_3OH, 40°C, 3 h; c) I_2, $NaHCO_3$, CH_3CN, 25°C, 16 h.

The products of ketone–ene reactions containing carbon–carbon double bonds as well as an ester group facilitate further synthetic transformations. Optically active spirocyclic compounds are key intermediates and building blocks in the synthesis of natural products and pharmaceuticals.[12] We developed an efficient method for the construction of such spirocyclic frameworks containing a trifluoromethylated quaternary stereocenter. Compounds **3s** and **t** were readily transformed into the corresponding trifluoromethyl-substituted spirocyclic compounds **4s** and **t**, respectively, by hydrolysis (Scheme 2).



3s, *n* = 1, 99% *ee*

3t, *n* = 0, 99% *ee*

4s, *n* = 1, d.r. = 1:3, 83% Yield, 98% *ee*

4t, *n* = 0, d.r. = 1:1, 80% Yield, 98% *ee*

Scheme 2. The synthesis of the trifluoromethyl-substituted chiral spirocyclic compounds **4s** and **t**. Conditions: a) KOH (20% aq.), CH_3OH, 40°C, 3 h; b) I_2, $NaHCO_3$, CH_3CN, 25°C, 24 h.

In conclusion, we have described a highly enantioselective ketone–ene reaction of trifluoropyruvate catalyzed by a new $Mg(OTf)_2$ complex of an *N,N′*-dioxide ligand. The reaction can also be conducted under solvent-free conditions, which meet the requirements of green chemistry. This method enables efficient access to enantioenriched trifluoromethyl-substituted compounds, which are important building blocks for the synthesis of natural products and pharmaceuticals. Moreover, the extremely high enantioselectivity, broad substrate scope, facile procedure, and mild reaction conditions show the potential of the catalytic system. Further studies into the applications of chiral magnesium complexes to other reactions are underway.

Experimental Section

General experimental procedure for the ketone–ene reaction of trifluoropyruvate: The $Mg(OTf)_2$–**L6** complex was prepared by mixing *N,N′*-dioxide **L6** and $Mg(OTf)_2$ (molar ratio = 1:1) in CH_2Cl_2 at 30°C for 30 min. A dry reaction tube was then charged with the $Mg(OTf)_2$–**L6** complex

(2.4 mg, 2.5 mol%) and ethyl trifluoropyruvate **2** (0.1 mmol) and 2-phenylpropene **1a** (1.1 equiv) were added at 30°C. After stirring for 8 h, the reaction mixture was purified directly by column chromatography on silica gel (ether/petroleum ether, 1:50) to afford **3a** in 95% yield as a colorless liquid. The enantiomeric excess of **3a** was determined to be >99% by using chiral HPLC analysis.

Acknowledgements

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Keywords: asymmetric synthesis · ene reaction · green chemistry · magnesium · trifluoromethylated compounds

[1] For selected reviews, see: a) *Lewis Acids in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**, pp. 59–85; b) *The Chemistry of Organomagnesium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, New York, **2008**, Part 1; c) F. Bickelhaupt, *Chem. Soc. Rev.* **1999**, *28*, 17–23; d) K. W. Henderson, W. J. Kerr, *Chem. Eur. J.* **2001**, *7*, 3430–3437; e) J. J. Eisch, *Organometallics* **2002**, *21*, 5439–5463; f) P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis, V. A. Vu, *Angew. Chem.* **2003**, *115*, 4438–4456; *Angew. Chem. Int. Ed.* **2003**, *42*, 4302–4320; g) R. W. Hoffmann, *Chem. Soc. Rev.* **2003**, *32*, 225–230; h) T. Satoh, *Chem. Soc. Rev.* **2007**, *36*, 1561–1572.

[2] For notable examples of magnesium(I) compounds, see: a) S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754–1757; b) M. Westerhausen, *Angew. Chem.* **2008**, *120*, 2215–2217; *Angew. Chem. Int. Ed.* **2008**, *47*, 2185–2187; c) S. P. Green, C. Jones, A. Stasch, *Angew. Chem.* **2008**, *120*, 9219–9223; *Angew. Chem. Int. Ed.* **2008**, *47*, 9079–9083; d) S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem.* **2009**, *121*, 3017–3021; *Angew. Chem. Int. Ed.* **2009**, *48*, 2973–2977.

[3] E. J. Corey, K. Ishihara, *Tetrahedron Lett.* **1992**, *33*, 6807–6810.

[4] For selected examples of asymmetric reactions using magnesium–bisoxazoline catalysts, see: a) G. Desimoni, G. Faita, P. P. Righetti, *Tetrahedron Lett.* **1996**, *37*, 3027–3030; b) M. P. Sibi, N. A. Porter, *Acc. Chem. Res.* **1999**, *32*, 163–171; c) D. Yang, S. Gu, Y. Yan, N. Zhu, K. Cheung, *J. Am. Chem. Soc.* **2001**, *123*, 8612–8613; d) M. P. Sibi, Y. Asano, *J. Am. Chem. Soc.* **2001**, *123*, 9708–9709; e) L. Quaranta, O. Corminboeuf, P. Renaud, *Org. Lett.* **2002**, *4*, 39–42; f) M. C. Willis, G. A. Cutting, V. J.-D. Piccio, M. J. Durbin, M. P. John, *Angew. Chem.* **2005**, *117*, 1567–1569; *Angew. Chem. Int. Ed.* **2005**, *44*, 1543–1545; g) A. T. Parsons, J. S. Johnson, *J. Am. Chem. Soc.* **2009**, *131*, 3122–3123; h) P. Goodrich, C. Hardacre, C. Paun, V. I. Pârvulescu, I. Podolean, *Adv. Synth. Catal.* **2008**, *350*, 2473–2476.

[5] a) O. Jacques, S. J. Richards, R. F. W. Jackson, *Chem. Commun.* **2001**, 2712–2713; b) B. M. Choudary, K. V. S. Ranganath, U. Pal, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 13167–13171; c) B. M. Trost, S. Hisaindee, *Org. Lett.* **2006**, *8*, 6003–6005; d) B. M. Trost, S. Malhotra, B. A. Fried, *J. Am. Chem. Soc.* **2009**, *131*, 1674–1675; e) H. Du, X. Zhang, Z. Wang, H. Bao, T. You, K. Ding, *Eur. J. Org. Chem.* **2008**, 2248–2254; f) T. Yoshino, H. Morimoto, G. Lu, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 17082–17083; g) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill, P. A. Procopiou, *J. Am. Chem. Soc.* **2009**, *131*, 9670–9685; h) J. Lv, X. Li, L. Zhong, S. Luo, J. Cheng, *Org. Lett.* **2010**, *12*, 1096–1099.

[6] a) *Organofluorine Compounds: Chemistry Applications* (Ed.: T. Hiyama), Springer, New York, **2000**; b) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**; c) R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell, Oxford, **2004**; d) P. Shah, A. D. Westwell, *J. Enzyme Inhib. Med. Chem.* **2007**, *22*, 527–540; e) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; f) K. L. Kirk, *Org. Process Res. Dev.* **2008**, *12*, 305–321; g) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320–330.

[7] a) E. J. J. Grabowski, *Chirality* **2005**, *17*, S249–S259; b) M. E. Pierce, R. L. Parsons, Jr., L. A. Radesca, Y. S. Lo, S. Silverman, J. R. Moore, Q. Islam, A. Choudhury, J. M. D. Fortunak, D. Nguyen, C. Luo, S. J. Morgan, W. P. Davis, P. N. Confalone, C. Y. Chen, R. D. Tillyer, L. Frey, L. Tan, F. Xu, D. Zhao, A. S. Thompson, E. G. Corley, E. J. J. Grabowski, R. Reamer, P. J. Reider, *J. Org. Chem.* **1998**, *63*, 8536–8543; c) S. Caron, N. M. Do, J. E. Sieser, P. Arpin, E. Vazquez, *Org. Process Res. Dev.* **2007**, *11*, 1015–1024; d) T. D. Aicher, R. C. Anderson, J. Gao, S. S. Shetty, G. M. Coppola, J. L. Stanton, D. C. Knorr, D. M. Sperbeck, L. J. Brand, C. C. Vinluan, E. L. Kaplan, C. J. Dragland, H. C. Tomaselli, A. Islam, R. J. Lozito, X. Liu, W. M. Maniara, W. S. Fillers, D. DelGrande, R. E. Walter, W. R. Mann, *J. Med. Chem.* **2000**, *43*, 236–249, and references therein.

[8] a) D. A. Evans, S. W. Tregay, C. S. Burgey, N. A. Paras, T. Vojkovsky, *J. Am. Chem. Soc.* **2000**, *122*, 7936–7943; b) S. Doherty, J. G. Knight, C. H. Smyth, R. W. Harrington, W. Clegg, *J. Org. Chem.* **2006**, *71*, 9751–9764; c) K. Aikawa, S. Kainuma, M. Hatano, K. Mikami, *Tetrahedron Lett.* **2004**, *45*, 183–185; d) K. Mikami, K. Aikawa, S. Kainuma, Y. Kawakami, T. Saito, N. Sayo, H. Kumobayashi, *Tetrahedron: Asymmetry* **2004**, *15*, 3885–3889; e) M. Rueping, T. Theissmann, A. Kuenkel, R. M. Koenigs, *Angew. Chem.* **2008**, *120*, 6903–6906; *Angew. Chem. Int. Ed.* **2008**, *47*, 6798–6801; f) J. Zhao, T. W. Tjan, B. Tan, T. Loh, *Org. Lett.* **2009**, *11*, 5714–5716.

[9] For selected examples of *N,N'*-dioxide–metal complexes, see: a) Z. P. Yu, X. H. Liu, Z. H. Dong, M. S. Xie, X. M. Feng, *Angew. Chem.* **2008**, *120*, 1328–1331; *Angew. Chem. Int. Ed.* **2008**, *47*, 1308–1311; b) X. Li, X. H. Liu, Y. Z. Fu, L. J. Wang, L. Zhou, X. M. Feng, *Chem. Eur. J.* **2008**, *14*, 4796–4798; c) K. Zheng, J. Shi, X. H. Liu, X. M. Feng, *J. Am. Chem. Soc.* **2008**, *130*, 15770–15771; d) X. Zhou, D. J. Shang, Q. Zhang, L. L. Lin, X. H. Liu, X. M. Feng, *Org. Lett.* **2009**, *11*, 1401–1404; e) Y. L. Liu, D. J. Shang, X. Zhou, X. H. Liu, X. M. Feng, *Chem. Eur. J.* **2009**, *15*, 2055–2058; f) M. S. Xie, X. H. Chen, Y. Zhu, B. Gao, L. L. Lin, X. H. Liu, X. M. Feng, *Angew. Chem.* **2010**, *122*, 3887–3890; *Angew. Chem. Int. Ed.* **2010**, *49*, 3799–3802, and references therein.

[10] M. Tokunaga, J. F. Larrow, F. Kakiuchi, E. N. Jacobsen, *Science* **1997**, *277*, 936–938.

[11] For selected examples of solvent-free asymmetric catalysis, see: a) K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025–1074; b) T. Perrard, J. C. Plaquevent, J. R. Desmurs, D. Hébrault, *Org. Lett.* **2000**, *2*, 2959–2962; c) N. K. Anand, E. M. Carreira, *J. Am. Chem. Soc.* **2001**, *123*, 9687–9688; d) S. J. Dolman, E. S. Sattely, A. H. Hoveyda, R. R. Schrock, *J. Am. Chem. Soc.* **2002**, *124*, 6991–6997; e) J. Long, J. Hu, X. Shen, B. Ji, K. Ding, *J. Am. Chem. Soc.* **2002**, *124*, 10–11; f) B. Rodríguez, A. Bruckmann, T. Rantanen, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 2213–2233; g) D. Almasi, D. A. Alonso, C. Nájera, *Adv. Synth. Catal.* **2008**, *350*, 2467–2472; h) C. Chang, S. Li, R. J. Reddy, K. Chen, *Adv. Synth. Catal.* **2009**, *351*, 1273–1278; i) B. Bradshaw, G. Etxebarría-Jardi, J. Bonjoch, S. F. Viózquez, G. Guillena, C. Nájera, *Adv. Synth. Catal.* **2009**, *351*, 2482–2490; j) R. Villano, M. R. Acocella, A. Massa, L. Palombi, A. Scettri, *Tetrahedron* **2009**, *65*, 5571–5576.

[12] a) E. J. Corey, A. Guzman-Perez, *Angew. Chem.* **1998**, *110*, 402–415; *Angew. Chem. Int. Ed.* **1998**, *37*, 388–401; b) R. Pradhan, M. Patra, A. K. Behera, B. K. Mishra, R. K. Behera, *Tetrahedron* **2006**, *62*, 779–828; c) S. Kotha, A. C. Deb, K. Lahiri, E. Manivannan, *Synthesis* **2009**, 165–193, and references therein.

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