Asymmetric Catalysis

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Redox Tuning of a Direct Asymmetric Aldol Reaction**

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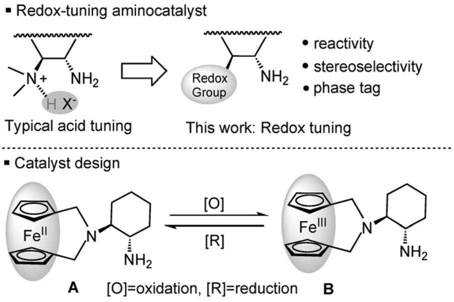
Abstract: *Presented herein is a redox tuning strategy for asymmetric aminocatalysis with a designed chiral ferrocenophane. Under redox control, the ferrocenophane catalyst efficiently catalyzes the asymmetric aldol reaction at room temperature with excellent yield and good stereoselectivity. Moreover, the redox-active ferrocene moiety also served as phase-tag to facilitate catalyst recovery and reuse. The catalyst can be reused for five cycles without much loss of activity. Ferrocenium of the oxidized ferrocenophane was proposed to serve as Lewis acidic site, thus accounting for the stereo control.*

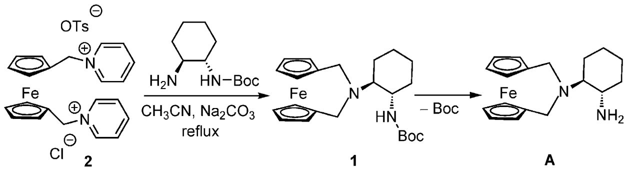
Additives are ubiquitous and essential in tuning activity and selectivity in asymmetric catalysis. This use of additives is particularly true with organocatalysis wherein acid/base additives are frequently utilized to attain optimal performance (Scheme 1). In fact, exquisite control and fine tuning of reactivity and selectivity of a catalytic process by external stimulus is a long sought-after aim in asymmetric catalysis and synthesis.[1] Departure from the typical acid/base additive effect, redox tuning, which is realized by incorporating a redox reversible moiety within the catalysts, has recently appeared as a promising external tuning strategy.[2–5] In extreme cases, switchable catalytic performance can be realized by varying the oxidation state of the catalytic metal centers.[6] However, most of these advances focused on reactivity tuning for catalysis employing metal-ligand complexes, and examples of redox tuning for selectivity are rare. In addition, thus far there is no example of a redox-active organocatalyst, despite the prevalence of organocatalysis since its renaissance in 2000.[7] Herein, we report a rare example of a redox-active primary amine catalyst and the redox tuning leads to not only enhanced stereoselectivity but also facile phase separation, thus allowing catalyst recovery and reuse.[8]



Scheme 1. Redox-active primary aminocatalyst.

Recently, bioinspired chiral primary amines for a number of enamine/iminium-based transformations have been developed.[9] In these cases, the use of acidic additives are essential for achieving optimal activity and stereoselectivity. Encouraged by the redox tuning in transition-metal catalysis, we envisioned that primary amine organocatalysts linked with a redox switchable moiety may have unique redox-controlled properties in either enamine- or iminium-based transformations. In this study, we selected ferrocene as the redox moiety because it is easy to modify,[10] has good redox properties, and has the potential to be Lewis acidic in its oxidized form.[2] Indeed, diastereo-and enantioselective ON/OFF switches as well as phase-tag properties were observed with this new organocatalyst. Herein, we report our results.

The ferrocenophane **A** could be accessed by removal of the Boc group from **1** (Scheme 2). The crucial intermediate **1** was efficiently synthesized from the nucleophilic substitution of 1,1′-ferrocene-bis(methylenepyridinium) (**2**) with *N*-Boc-(*S*,*S*)-1,2-diaminocyclohexane in 85 % yield as a yellow solid.[11] Correspondingly, **A** was obtained in 93 % yield as a yellow solid.



Scheme 2. Synthesis of the ferrocenophane **A**. Boc = *tert*-butoxycarbonyl.

The ferrocenophane **A** was subjected to cyclic voltammetry (CV), and a reversible CV peak resulted (see Figure S1 in the Supporting Information). A redox process was present at $E_{1/2} = +488$ mV, and was assigned to the Fe^{II}/Fe^{III} redox process of the ferrocene moiety in **A**. The half-wave potential

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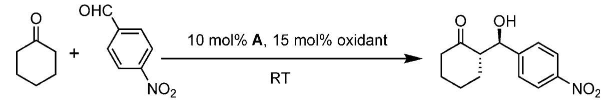
of the Fc/Fc$^+$ (Fc = ferrocene) groups in **A** was slightly negative compared to that of the corresponding ferrocene (see Figure S2). Additionally, redox peaks of tertiary amines were not observed in the CV curve. Therefore, it would be possible to selectively oxidize the ferrocene moiety. After oxidizing **A** with ferrocenium tetrafluoroborate, the EPR spectrum of the corresponding **A**$^+$[BF$_4$] revealed a feature at $g_\parallel = 4.38$ (see Figure S3), a result consistent with the presence of ferrocenium species.[12] The broadening of the $g_\perp$ feature may result from the interference of the bulky group of **A**$^+$[BF$_4$].

To examine the catalytic activity of **A**, the direct aldol reaction of cyclohexanone and *p*-nitrobenzaldehyde was conducted in the presence of 10 mol % **A** and 15 mol % oxidant at room temperature (Table 1). Initially, different oxidants were tested. Rather poor results were obtained in the absence of an oxidant (Table 1, entry 1). When I$_2$, CAN (CAN = ceric ammonium nitrate), and DDQ (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) were selected as oxidants, the desired products were obtained with excellent yields and *ee* values, but with poor diastereoselectivities (entries 2–4). [FeCp$_2$]$^+$BF$_4$ (ferrocenium tetrafluoroborate) provided satisfactory results in terms of diastereoselectivity (90:10 d.r.), enantioselectivity (93 % *ee*), and yield (94 %; entry 5).

Table 1: Screening of the oxidants.

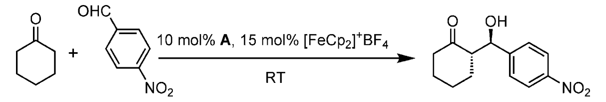


Entry[a]	Oxidants	Yield [%][b]	*anti*/*syn*[c]	*ee* [%][d]
1[e]	–	38	42:58	24
2	I$_2$	92	63:37	90
3	CAN	94	80:20	92
4	DDQ	93	80:20	90
5	[FeCp$_2$]$^+$BF$_4$	94	90:10	93

[a] Reaction conditions: cyclohexanone (0.6 mmol), *p*-nitrobenzaldehyde (0.2 mmol), **A** (10 mol %), and oxidant (15 mol %) at room temperature for 48 h. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by HPLC analysis. [e] Reaction time: 72 h. Cp = cyclopentadienyl.

Various solvents were then screened (Table 2). The results showed that the reaction tolerated a number of solvents including highly polar organic solvents, water, and other nonpolar organic solvents (entries 1–11). Finally, dichloromethane was chosen as the optimal reaction medium.

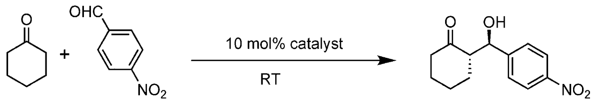
Table 2: Screening of solvents.[a]



Entry	Solvents	Yield [%][b]	*anti*/*syn*[c]	*ee* [%][d]
1	toluene	90	91:9	93
2	THF	91	92:8	92
3	CH$_2$Cl$_2$	94	95:5	94
4	CHCl$_3$	93	95:5	93
5	DCE	90	92:8	92
6	CH$_3$CN	92	94:6	90
7	1,4-dioxane	91	91:9	90
8	DMF	88	89:11	94
9	DMSO	86	89:11	90
10[e]	MeOH	82	94:6	95
11[f]	H$_2$O	65	95:5	95

[a] The reaction was performed with cyclohexanone (0.6 mmol), *p*-nitrobenzaldehyde (0.2 mmol), **A** (10 mol %), and [FeCp$_2$]$^+$BF$_4$ (15 mol %) in 0.2 mL solvent at room temperature. [b] Yield of isolated product. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. [e] 8 % by-product. [f] 9 % by-product. DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

Table 3: Control experiments.



Entry	Catalyst	Yield [%]	*anti*/*syn*	*ee* [%]
1[a]	**A**/[FeCp$_2$]$^+$BF$_4$	94	95:5	94
2[b]	**B**	92	96:4	92
3	**A**/TFA	78	60:40	91
4	**A**/TfOH	48	54:46	24
5[c]	**C**	trace	–	–
6	**C**/DDQ	n.r.	–	–
7	**C**/[FeCp$_2$]$^+$BF$_4$	88	86:14	92
8a[d]	**A**	5	42:58	24
8b[d]	**A**/[FeCp$_2$]$^+$BF$_4$	38	92:8	94
8c[d]	**A**/[FeCp$_2$]$^+$BF$_4$/Na$_2$S$_2$O$_4$	52	67:33	92

[a] Reaction conditions: *p*-nitrobenzaldehyde (0.2 mmol), cyclohexanone (0.6 mmol), **A** (0.02 mmol), [FeCp$_2$]$^+$BF$_4$ (0.03 mmol), and 0.2 mL CH$_2$Cl$_2$ at room temperature for 48 h. [b] 10%mol **B**. [c] **C** = (*S*,*S*)-*N*^{1},*N*^{1}-dipropylcyclohexane diamine. [d] *p*-Nitrobenzaldehyde (0.2 mmol), cyclohexanone (0.6 mmol), **A** (0.02 mmol), and 0.2 mL CH$_2$Cl$_2$ at room temperature for 5 h (entry 8a). Then [FeCp$_2$]$^+$BF$_4$ (0.03 mmol) was added and the reaction run for an additional 12 h (entry 8b). Then Na$_2$S$_2$O$_4$ (0.035 mmol) was added and the reaction run for an additional 36 h (entry 8c). TFA = trifluoroacetic acid, Tf = trifluoromethanesulfonyl.

Control experiments were performed to confirm the catalytic mechanism (Table 3). Excellent results were obtained for the ferrocenophane-**B**-catalyzed reaction (entry 2). In contrast, poor stereoselectivities were obtained with **A**/TFA and **A**/TfOH (entries 3 and 4), thus indicating that a protonated amino moiety did not work well as a stereocontrolling hydrogen-bonding unit in this case, and that the ferrocenium species, likely serving as Lewis acid, played an important role in the stereocontrol. Using (*S*,*S*)-*N*^{1},*N*^{1}-dipropylcyclohexanediamine (**C**) as the catalyst resulted in only trace amounts of the desired product, and when DDQ was added, no product was obtained (entries 5 and 6), thus suggesting redox control did not work in this case (entry 6 versus Table 1, entry 4). In contrast, the combined use of **C**/[FeCp$_2$]$^+$BF$_4$ led to slightly inferior results in terms of both activity and stereoselectivity (Table 3, entry 7 versus entry 1). It is known that Lewis acids may also effect stereocontrol in enamine catalysis.[7k] Considering the inertness of DDQ, it was believed that [FeCp$_2$]$^+$BF$_4$ mainly served as a Lewis acid to facilitate the reaction, and further confirmed the role of ferrocenium in the oxidized form **A** (entry 7).

Additionally, to further demonstrate the stereoselective ON/OFF switch controlled by the redox process of ferrocene, the aldol reaction was repeated using **A**. After 5 hours, about 5% yield, 42:58 d.r., and 24% *ee* was obtained (Table 3, entry 8a). At this point, 15 mol% $[FeCp_2]^+BF_4$ as an oxidant was added and excellent diastereo- and enantioselectivity resulted (entry 8b). After another 12 hours, sodium hydrosulfite was added as a reductant, and the reactivity and diastereoselectivity decreased remarkably, perhaps because the ferrocenium was reduced to (neutral) ferrocene (entry 8c). These results suggested that the ferrocene moiety in **A** could serve as a redox switch to control the reactivity and diastereoselectivity through its redox process. For comparison, N^1,N^1-disubstituted cyclohexanediamines, which have no redox properties, mostly depended on the protonated amino moiety as a hydrogen-bonding stereocontrolling unit in this reaction.[9b–d,13b] The reaction was proposed to proceed via an anticlinal transition state as depicted in Figure 1. The ferrocenium as a directing Lewis-acidic site interacts with the aldehyde, and the enamine attacks the aldehyde from the *Si* face, thus leading to the formation of the major stereoisomer.

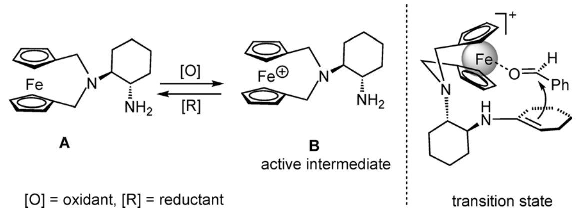
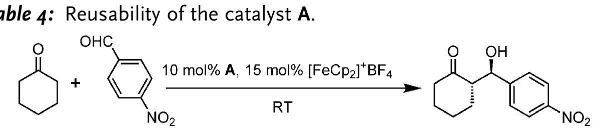


Figure 1. Proposed transition-state model.

The ferrocenophane **B** as an organic ion salt could be recovered by precipitation, and was used directly in the next run. Similar reactivity and stereoselectivity were obtained. The results are summarized in Table 4. It was not until the fifth cycle that the yield and stereoselectivity were found to be decreased.

Under the identified optimal reaction conditions, the scope of substrates was examined and the results are presented in Tables 5 and 6. In general, the reactions worked extremely well and generated aldol adducts in excellent yields with both high *anti* diastereoselectivity and enantioselectivity (Table 5). The absolute configuration of the products was determined to be (1*R*,2*S*), which was consistent with transition state in which the enamine attacks the aldehyde from the *Si* face (Figure 1). Simple cyclic ketones provided the desired products with excellent results (Table 5, entries 1–4). The electron-deficient aryl aldehydes as aldol acceptors afforded moderate yields with excellent stereoselectivities (entries 5–7) and acetone afforded the desired adduct with 81% *ee* (entry 10).

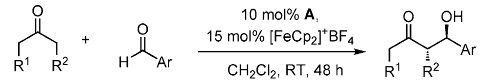
Table 4: Reusability of the catalyst **A**.



Cycle	Yield [%]	*anti/syn*	*ee* [%]
1[a]	94	95:5	94
2	92	94:6	93
3	93	95:5	94
4	89	92:8	90
5	78	90:10	88

[a] The reaction was performed with *p*-nitrobenzaldehyde (0.6 mmol), cyclohexanone (1.8 mmol), **A** (10 mol%), $[FeCp_2]^+BF_4$ (15 mol%), and 0.6 mL CH_2Cl_2 at room temperature for 48 h. The recovered $I^+[BF_4]$ and $[FeCp_2]^+BF_4$ were not isolated, but were used directly in the next run.

Table 5: Asymmetric aldol reaction of ketones with aryl aldehydes.[a]

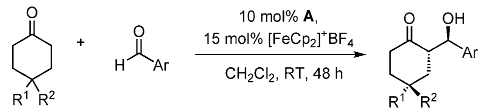


Entry	R^1	R^2	Aryl	Yield [%][b]	*anti/syn*[c]	*ee* [%][d]
1	$(CH_2)_3$		$4\text{-}NO_2C_6H_4$	94	95:5	94
2	$(CH_2)_2$		$4\text{-}NO_2C_6H_4$	89	84:16	91
3	$(CH_2)_3$		$3\text{-}NO_2C_6H_4$	94	91:9	91
4	$(CH_2)_3$		$2\text{-}NO_2C_6H_4$	93	96:4	93
5	$(CH_2)_3$		$4\text{-}CF_3C_6H_4$	42	90:10	94
6	$(CH_2)_3$		$4\text{-}PhC_6H_4$	48	96:4	91
7	$(CH_2)_3$		$4\text{-}CNC_6H_4$	45	86:14	93
8[e]	CH_2OCH_2		$4\text{-}NO_2C_6H_4$	86	91:9	91
9[e]	CH_2SCH_2		$4\text{-}NO_2C_6H_4$	84	91:9	94
10[e]	H	H	$4\text{-}NO_2C_6H_4$	72	–	81

[a] The reaction was performed with arylaldehydes (0.2 mmol), ketones (0.6 mmol), **A** (0.02 mmol), ferrocenium tetrafluoroborate (0.03 mmol), and 0.2 mL CH_2Cl_2 at room temperature for 48 h. [b] Yield of isolated product. [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. Ref. [13]. [e] 72 h.

With regard to the 4-substituted cyclohexanones as donors, a mixture was produced and the (1*R*,2*S*,4*S*) isomer was formed predominantly with high enantioselectivity (Table 6, entries 1–3). In addition, more complicated ketone substrates also gave satisfactory results (entries 4 and 5). The absolute configurations of all products were determined by

Table 6: Asymmetric aldol reaction of 4-substituted cyclohexanones with *p*-nitrobenzaldehyde.[a]



Entry	R^1	R^2	Aryl	Yield [%][b]	d.r.[c]
1	H	CH_3	$4\text{-}NO_2C_6H_4$	77	85:15
2	H	CH_3CH_2	$4\text{-}NO_2C_6H_4$	73	82:18
3[e]	H	Ph	$4\text{-}NO_2C_6H_4$	65	72:28
4[f]	$(CH_2)_2$		$4\text{-}NO_2C_6H_4$	78	89:11
5	$O(CH_2)_2O$		$4\text{-}NO_2C_6H_4$	96	40:60

[a] The reaction was performed with arylaldehydes (0.2 mmol), ketones (0.6 mmol), **A** (0.02 mmol), ferrocenium tetrafluoroborate (0.03 mmol), and 0.2 mL CH_2Cl_2 at room temperature for 48 h. [b] Yield of isolated product. [c] For entries 1–3: d.r. = the ratio of the major isomer shown with all the other isomers based on the isolated products; for entries 4 and 5: d.r. = *anti/syn*, determined by ^1H NMR analysis of crude reaction mixture. [d] Determined by HPLC analysis. Ref. [13]. [e] 72 h. [f] 60 h.

comparing the retention time from HPLC data on the products with those in the literature data.[13]

In summary, we have developed a novel redox-tunable organocatalyst for the asymmetric aldol reaction, in which the stereoselectivity is controlled by the redox activity of ferrocene. This strategy highlights the first use of a chiral primary amine ferrocenium salt in an approach which differs from the well-known organocatalysis and transition metal-based catalysis. Additional notable features are the recyclability of the catalysts and a convenient experimental protocol.

Keywords: aldol reaction · asymmetric catalysis · iron · organocatalysis · redox chemistry

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[1] F. A. Leibfarth, K. M. Mattson, B. P. Fors, H. A. Collins, C. J. Hawker, *Angew. Chem. Int. Ed.* **2013**, *52*, 199–210; *Angew. Chem.* **2013**, *125*, 210–222.

[2] a) A. M. Allgeier, C. A. Mirkin, *Angew. Chem. Int. Ed.* **1998**, *37*, 894–908; *Angew. Chem.* **1998**, *110*, 936–952; b) V. K. K. Praneeth, M. R. Ringenberg, T. R. Ward, *Angew. Chem. Int. Ed.* **2012**, *51*, 10228–10234; *Angew. Chem.* **2012**, *124*, 10374–10380; c) O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440–1459.

[3] I. M. Lorkovic, R. R. Duff, M. S. Wrighton, *J. Am. Chem. Soc.* **1995**, *117*, 3617–3618.

[4] For selected examples, see: a) A. J. D. Magenau, N. C. Strandwitz, A. Gennaro, K. Matyjaszewski, *Science* **2011**, *332*, 81–84; b) P. Neumann, H. Dib, A. M. Caminade, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2015**, *54*, 311–314; *Angew. Chem.* **2015**, *127*, 316–319; c) X. Wang, A. Thevenon, J. L. Brosmer, I. Yu, S. I. Khan, P. Mehrkhodavandi, P. L. Diaconescu, *J. Am. Chem. Soc.* **2014**, *136*, 11264–11267; d) A. B. Biernesser, B. Li, J. A. Byers, *J. Am. Chem. Soc.* **2013**, *135*, 16553–16560; e) K. Arumugam, C. D. Varnado, Jr., S. Sproules, V. M. Lynch, C. W. Bielawski, *Chem. Eur. J.* **2013**, *19*, 10866–10875; f) E. M. Broderick, N. Guo, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, P. Mehrkhodavandi, P. L. Diaconescu, *J. Am. Chem. Soc.* **2011**, *133*, 9278–9281; g) A. G. Tennyson, V. M. Lynch, C. W. Bielawski, *J. Am. Chem. Soc.* **2010**, *132*, 9420–9429; h) M. R. Ringenberg, S. L. Kokatam, Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2008**, *130*, 788–789; i) C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, *J. Am. Chem. Soc.* **2006**, *128*, 7410–7411; j) M. Fujiwara, S. Terashima, Y. Endo, K. Shiokawa, H. Ohue, *Chem. Commun.* **2006**, 4635–4637.

[5] L. H. Peeck, S. Leuthäusser, H. Plenio, *Organometallics* **2010**, *29*, 4339–4345.

[6] a) S. Mortezaei, N. R. Catarineu, J. W. Canary, *J. Am. Chem. Soc.* **2012**, *134*, 8054–8057; for examples of switchable asymmetric catalysts via other methods, see: b) J. Wang, B. L. Feringa, *Science* **2011**, *331*, 1429–1432; c) V. Blanco, D. A. Leigh, V. Marcos, J. A. Morales-Serna, A. L. Nussbaumer, *J. Am. Chem. Soc.* **2014**, *136*, 4905–4908.

[7] a) C. F. Barbas III, *Angew. Chem. Int. Ed.* **2008**, *47*, 42–47; *Angew. Chem.* **2008**, *120*, 44–50; b) P. Melchiorre, M. Marigo, A. Carlone, G. Bartoli, *Angew. Chem. Int. Ed.* **2008**, *47*, 6138–6171; *Angew. Chem.* **2008**, *120*, 6232–6265; for enamine-based organocatalysis of asymmetric direct aldol reactions: c) B. List, R. A. Lerner, C. F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2395–2396; d) K. Sakthivel, W. Notz, T. Bui, C. F. Barbas III, *J. Am. Chem. Soc.* **2001**, *123*, 5260–5267; e) P. L. Dalko, L. Moisan, *Angew. Chem. Int. Ed.* **2004**, *43*, 5138–5175; *Angew. Chem.* **2004**, *116*, 5248–5286; f) A. B. Northrup, D. W. C. MacMillan, *Science* **2004**, *305*, 1752–1755; g) S. Mitsumori, H. Zhang, P. H. Cheong, K. N. Houk, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc.* **2006**, *128*, 1040–1041; h) H. Torii, M. Nakadai, K. Ishihara, S. Saito, H. Yamamoto, *Angew. Chem. Int. Ed.* **2004**, *43*, 1983–1986; *Angew. Chem.* **2004**, *116*, 2017–2020; i) Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima, M. Shoji, *Angew. Chem. Int. Ed.* **2006**, *45*, 958–961; *Angew. Chem.* **2006**, *118*, 972–975; j) T. Kano, J. Takai, O. Tokuda, K. Maruoka, *Angew. Chem. Int. Ed.* **2005**, *44*, 3055–3057; *Angew. Chem.* **2005**, *117*, 3115–3117; k) Y. Deng, S. Kumar, H. Wang, *Chem. Commun.* **2014**, *50*, 4272–4284.

[8] M. Süßner, H. Plenio, *Angew. Chem. Int. Ed.* **2005**, *44*, 6885–6888; *Angew. Chem.* **2005**, *117*, 7045–7048.

[9] For an account, see: a) L. Zhang, S. Luo, *Synlett* **2012**, 1575–1589. For recent examples, see: b) S. Luo, H. Xu, J. Li, L. Zhang, J.-P. Cheng, *J. Am. Chem. Soc.* **2007**, *129*, 3074–3075; c) S. Luo, H. Xu, L. Chen, J.-P. Cheng, *Org. Lett.* **2008**, *10*, 1775–1778; d) S. Luo, H. Xu, L. Zhang, J. Li, J.-P. Cheng, *Org. Lett.* **2008**, *10*, 653–656; e) S. Luo, Y. Qiao, L. Zhang, J. Li, X. Li, J.-P. Cheng, *J. Org. Chem.* **2009**, *74*, 9521–9523; f) S. Luo, P. Zhou, J. Li, J.-P. Cheng, *Chem. Eur. J.* **2010**, *16*, 4457–4461; g) P. Zhou, L. Zhang, S. Luo, J.-P. Cheng, *J. Org. Chem.* **2012**, *77*, 2526–2530; h) C. Xu, L. Zhang, P. Zhou, S. Luo, J.-P. Cheng, *Synthesis* **2013**, 1939–1945; i) C. Xu, L. Zhang, S. Luo, *Angew. Chem. Int. Ed.* **2014**, *53*, 4149–4153; *Angew. Chem.* **2014**, *126*, 4233–4237; j) Y. Zhu, L. Zhang, S. Luo, *J. Am. Chem. Soc.* **2014**, *136*, 14642–14645.

[10] a) *Chiral Ferrocenes in Asymmetric Catalysis: Synthesis and Application* (Eds.: L.-X. Dai, X.-L. Hou), Wiley-VCH, Weinheim, **2010**, pp. 337–368; b) R. Gómez Arrayás, J. Adrio, J. C. Carretero, *Angew. Chem. Int. Ed.* **2006**, *45*, 7674–7715; *Angew. Chem.* **2006**, *118*, 7836–7878; c) R. Peters, D. F. Fischer, S. Jautze, *Top. Organomet. Chem.* **2011**, *33*, 139–175; d) D. Petruzziello, M. Stenta, A. Mazzanti, P. G. Cozzi, *Chem. Eur. J.* **2013**, *19*, 7696–7700; e) M. Drusan, R. Šebesta, *Tetrahedron* **2014**, *70*, 759–786.

[11] H. Plenio, C. Aberle, *Chem. Commun.* **1998**, 2697–2698.

[12] a) A. Horsfield, A. Wassermann, *J. Chem. Soc. Dalton Trans.* **1972**, 187–188; b) T. Sixt, J. Fiedler, W. Kaim, *Inorg. Chem. Commun.* **2000**, *3*, 80–82.

[13] a) N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc.* **2006**, *128*, 734–735; b) F. Peng, Z. Shao, X. Pu, H. Zhang, *Adv. Synth. Catal.* **2008**, *350*, 2199–2204; c) S. Luo, H. Xu, J. Li, L. Zhang, X. Mi, X. Zheng, J. P. Cheng, *Tetrahedron* **2007**, *63*, 11307–11314.

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