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Communication

Tetramine Ligands

Large-Scale Synthesis of Symmetric Tetramine Ligands by Using a Modular Double Reductive Amination Approach

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Abstract: Tetramine ligands play an important role in a broad range of transition metal catalyzed transformations. We here present a flexible and modular approach to this class of ligands using a double reductive amination strategy. Thus, the target molecules were prepared in a highly efficient manner in only three steps, from commercially available starting materials. Excellent overall yields, of up to 96 % were reached. Notably, chiral C_2-symmetric ligands are available using this procedure. All reactions are easily scalable and the tetramine ligands were obtained in excellent purity, while only a single chromatographic purification is required at the end of the three step sequence.

Introduction

Transition metal catalysis is a key enabling technology of modern organic synthesis. The vast majority of these processes use specifically designed ligands to control reactivity and selectivity of the catalytically active metal center.[1,2] Factors to influence these two central elements of catalysis include a.) steric shielding, b.) modulation of electronic properties, and c.) fixation of geometry (e.g. bite-angle and configuration) around the metal center. The optimization of all these parameters usually requires evaluation of a large number and broad spectrum of ligands. In order to keep this process as effective as possible a flexible and efficient ligand synthesis is desirable.[2]

Over the past years, ligand stabilized iron oxidation catalysis has attracted significant and steadily increasing attention.[3] Based on mechanistic considerations and a structural analysis of non-heme iron proteins, a number of artificial ligand systems for biomimetic oxidation catalysis have been developed, many of which are designed as methane monoxygenase (MMO) mimetics.[4–9] Structurally, most of these ligands, feature a tetramine system with two terminal pyridines connected to a central diamine unit via a C_2-bridge (Figure 1). A prototypical example is Toftlund's so-called BPMEN ligand (**L1** in Figure 1; BPMEN=*N*,*N*′-dimethyl-*N*,*N*′-bispyridine-2-ylmethyl-ethane-1,2-diamine).[4]

Many impressive applications of such ligand stabilized iron oxidations e.g. in olefin epoxidations[3,6] and biomimetic C–H-oxidations[8,9] with hydrogen peroxide as terminal oxidant have been reported.[7] The details, however, on how to control iron's delicate redox chemistry through tailor-made ligands appear far from being understood. A straight-forward and flexible synthesis of stabilizing ligands is a key to the success of this objective. The most relevant sites of ligand modification are summarized in Figure 1 (right). These include variations at the backbone (marked in red in Figure 1), in the middle wing (R′, coloured in blue in Figure 1), and at the periphery close to the aromatic nitrogen donors (R″, marked in green in Figure 1).

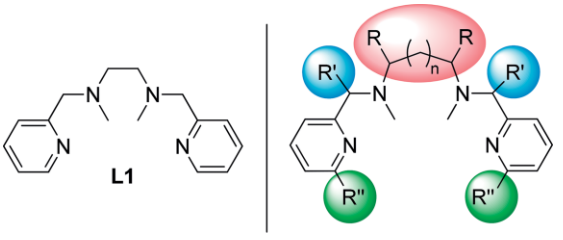

Figure 1. Toftlund's "BPMEN"-ligand **L1** and potential sites of modification.

As part of our ongoing interest in oxidation catalysis[10] and related synthetic applications,[11] we herein describe a simple, scalable and modular approach to tetramine ligands.[12]

Results and Discussion

With the aim to develop a modular synthesis of tetradentate nitrogen donor ligands,[12] we first investigated a set of different tactics for their assembly. Scheme 1 summarizes different approaches in a simplified retrosynthetic analysis. Both *N*-alkylations and reductive aminations (as well as combinations thereof) were selected as the most promising tools for the envisaged C–N-bond formations.

Strategies were evaluated for their efficiency and flexibility to access compounds of the general structure shown in Figure 1 and Scheme 1. After some experimentation we found a double reductive amination route to be most effective (Scheme 1).

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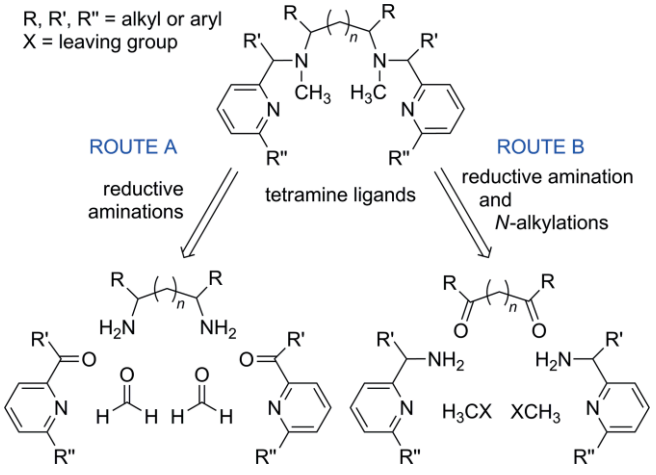


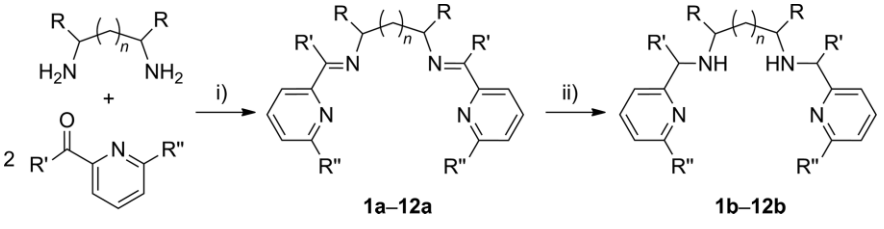
Scheme 1. Retrosynthetic considerations for the modular assembly of tetramine ligands.

Thus, a central diamine was first reductively coupled with a 2-carbonyl pyridine (Table 1). The required backbone diamines were either purchased from commercial suppliers or in the case of *rac-trans*-1,2-diaminocyclo-pentane,[13] *rac-trans*-1,2-diamino-1,2-diphen-yl-ethane[14] and *rac-trans*-9,10-dihydro-9,10-ethano-anthracene-11,12-diamine[15] synthesized according to literature procedures. In order to obtain high yields and a high purity of tetramines **1b**–**12b** it was found to be most efficient to isolate the intermediary diimines **1a**–**12a** prior to reduction (Table 1). Best results were achieved when the crystalline *E*,*E*-diimines (**1a**–**12a**) were precipitated from cold methanol (see the SI for details). It is worth of note that precipitation of *E*,*E*-diimines already occurred during the course of the reaction. Consequently, the reaction equilibrium shifted favorably leading to improved isolated yields. In addition, in situ precipitation presumably prohibited products from undergoing subsequent reactions. Both these aspects are a clear advantage of route A over route B (Scheme 1). The outcome for diimine preparations according to route A are summarized in Table 1.[16]

In most instances good to excellent yields of crystalline materials (**1a**–**11a**) with an average yield of 82 % were obtained (Table 1, entries 1–11). Results were found to be fairly independent of the backbone substitution and whether a pyridine aldehyde or ketone (Table 1, entries 7, 8 and 11, 12) was used as the substrate. Notably, *E*-selectivity was high, even when a diaryl ketone was used for condensation (cf. for instance Table 1, entry 8). Imine configuration was unambiguously determined both by X-ray crystallography (where appropriate) as well as by ^{1}H-NMR spectroscopic investigations (see Figure 2 and the SI for details). Due to a vicinal $n_N \rightarrow \sigma^*$ interaction the imine proton resonances of *E*-isomers show a clear downfield shift as compared to the *Z*-configured products. We were thus able to determine the configuration of all diimines synthesized except for diimine **12a** which proved not to be isolable (see the Supporting Information for details). In this case the crude material was directly used for the next step.

Subsequent reduction of diimines **1a**–**12a** (Table 1) with sodium borohydride in methanol proceeded smoothly and resulted in the formation of analytically pure products **1b**–**12b** in excellent yields. No further purification was required (Table 1, see the Supporting Information for details). Thus, the tetramine core structures were prepared in high efficiency without the necessity of any chromatographic purification step. It is worth noting that the reverse approach of using a reductive amination of central 1,2-dicarbonyls (either dialdehydes or oxalic acid de-

Table 1. Yields for diimine formation and their subsequent reduction.[a]



Entry	Diamine *n*, R	Pyridine R′, R″	Yield Diimine	Yield Tetramine
1	0, H	H, H	**1a** (98 %)	**1b** (99 %)
2	0, $-CH_2CH_2CH_2-$	H, H	**2a** (86 %)	**2b** (99 %)
3	0, $-CH_2(CH_2)_2CH_2-$	H, H	**3a** (62 %)	**3b** (99 %)
4	0, $-CH_2(CH_2)_2CH_2-$	H, CH_3	**4a** (43 %)	**4b** (84 %)
5	0, dihydro-ethano-anthracenediamine	H, H	**5a** (94 %)	**5b** (98 %)
6	0, dihydro-ethano-anthracenediamine	H, CH_3	**6a** (92 %)	**6b** (99 %)
7	0, H	CH_3, H	**7a** (25 %)[b]	**7b** (99 %)
8	0, H	Ph, H	**8a** (80 %)	**8b** (94 %)
9	0, Ph	H, H	**9a** (87 %)	**9b** (97 %)
10	1, H	H, H	**10a** (100 %)[c]	**10b** (96 %)
11	1, H	CH_3, H	**11a** (99 %)[c]	**11b** (89 %)
12	1, H	Ph, H	**12a** (–)[d]	**12b** (67 %)[e]

[a] Reagents and conditions: i) MeOH, HCOOH (cat.) then recrystallization; ii) $NaBH_4$ in MeOH. [b] Isolation of diimine by freeze drying. [c] This diimine did not crystallize; for details see the Supporting Information. [d] Diimine was not isolated but reduced in situ. [e] Isolated yield over two steps.

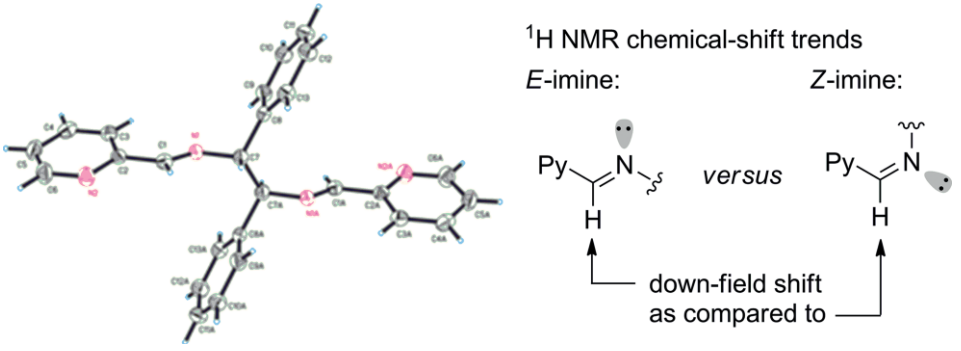
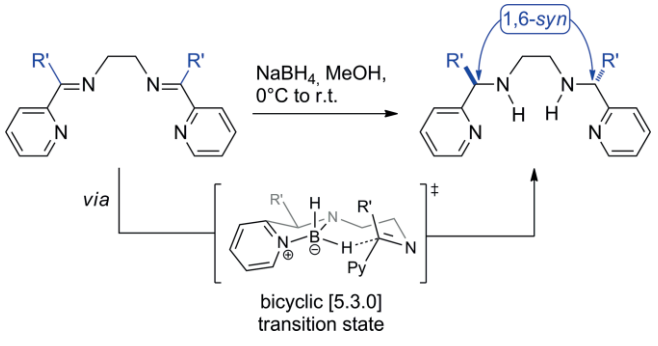


Figure 2. Representative X-ray structure of an *E,E*-diimine (**9a**) and chemical shift trends in ^{1}H-NMR analyses of *E*- vs. *Z*-imines.

rivatives) with 2-aminomethyl pyridines[16] was ineffective (Scheme 1, 1st step of Route B).

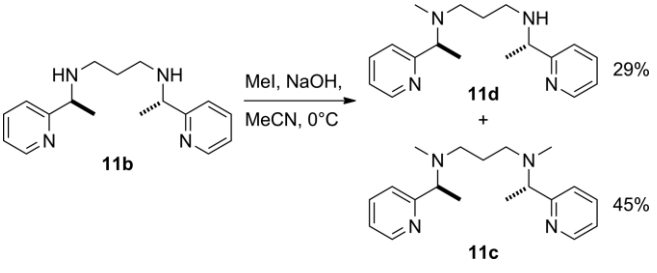
Interestingly, sodium borohydride reduction of prochiral diimines **7a** and **8a** (Table 1, entries 7 and 8) proceeded not only in high yields but also with excellent diastereoselectivities (Scheme 2). In both cases the (racemic) C_2-symmetric isomer was isolated as the only detectable isomer in 99 and 94 % yield, respectively. Control experiments revealed that the stereoselectivity was low and irreproducible when the reductive amination was carried out without isolation of crystalline *E,E*-diimine intermediates (**7a** and **8a**). The overall diastereoselectivity for the diimine reductions is most likely a result of the second reduction event occurring as an intramolecular process (Scheme 2). This reaction is believed to proceed via a seven membered transition state with the boron hydride still attached to the initially reduced imine nitrogen. In fact, the basic nitrogen of its neighboring pyridine is also likely to coordinate to the Lewis-acidic boron center and thus result in an even more highly ordered [5.3.0]-bicyclic transition state with a more highly reactive borate reducing agent (Scheme 2). The R′ substituent of the reduced imine system is assumed to adopt a *pseudo*-equatorial position. Likewise, the pyridine substituent of the prochiral imine would be positioned in a *pseudo*-equatorial orientation of the seven-membered ring of the [5.3.0]-bicycle, leading to an *intra*molecular hydride attack to the second imine with formation of the 1,6-*syn* product. This model, schematically depicted in Scheme 2, gives a conceivable explanation for the high *d,l*-selectivity (rather than formation of the *meso*-isomer or mixtures thereof) obtained in the reduction of prochiral diimines (**7a** and **8a**). In addition to spectroscopic means the stereochemical outcome of these reactions was unambiguously



Scheme 2. Diastereoselective reduction of prochiral *E,E*-diimes.

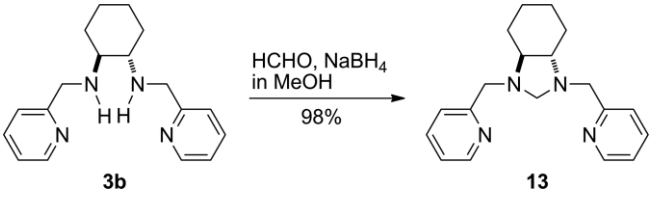
confirmed through X-ray analyses of different derivatives (vide infra). Notably, for diimine substrates (**11a** and **12a**) with an extended backbone (connecting C_3- instead of C_2-chain) the same selectivity was observed although in this case an eight-membered or [6.3.0]-bicyclic transition state has to be passed through leading to ligands with *meso*-geometry (not shown in Scheme 2).

Next, the methylation of the central secondary diamines was investigated. We first tested methyl iodide as alkylating reagent. A representative experiment is depicted in Scheme 3. Careful control of reaction conditions allowed to isolate 45 % of the desired ligand (**L11**) together with significant amounts of the mono-methylated product **11d**. It is probably not too surprising that competing N-quaternisations (not shown in Scheme 3) or some mono-methylation could not effectively be suppressed, resulting in diminished yields of the desired ligand.



Scheme 3. Exemplary alkylation of tetramine **11b** using methyl iodide.

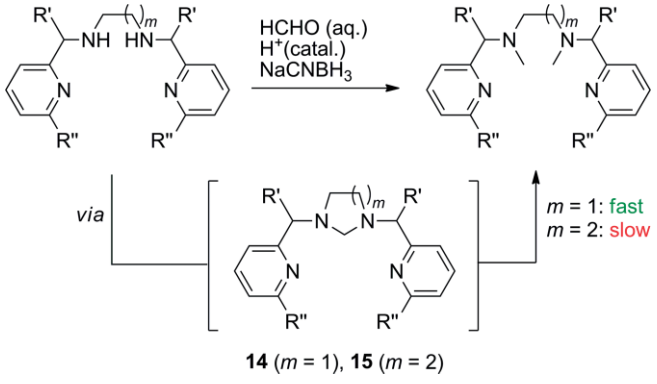
In order to avoid exhaustive or peripheral methylation we screened reductive amination conditions in parallel to the alkylation procedures. These reactions were found to proceed fairly sluggishly and products isolated after short reaction times or when using sodium borohydride (Scheme 4) were saturated cyclic aminals (imidazolidines **14** and hexahydropyrimidines **15**, respectively) rather than the desired reduction products. A se-



Scheme 4. Unwanted aminal formation during attempted reductive amination of diamine **3b**.

lected example yielding aminal **13** in high yield is shown in Scheme 4.

When using formaldehyde in the presence of an excess of sodium cyanoborohydride and catalytic amounts of formic acid aminal formation was reversible and gradually lead to the formation of the desired *N*,*N*′-dimethylated ligands (Scheme 5). This process was significantly slower for substrates **10b**, **11b**, and **12b** with an extended backbone but eventually these hexahydropyrimidines **15** were also fully converted into the final ligands (Scheme 5). Complete conversion required stirring for at least 12 hours at room temperature in these cases (see the SI for details).



Scheme 5. Reductive amination of 1,2- and 1,3-diamines via intermediary cyclic aminals.

Formation of the aminal intermediate was also confirmed through isolation of intermediary aminals (cf. Scheme 4) and also served to establish the relative stereochemistry using X-ray analysis. An example is provided with the ORTEP plot of hexahydropyrimidine **15** represented in Figure 3.

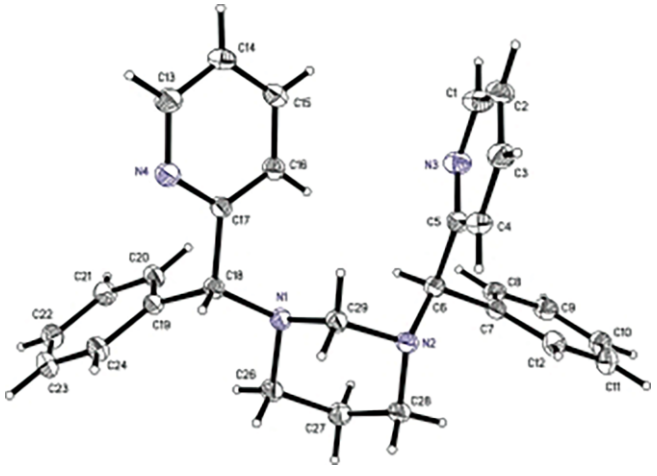
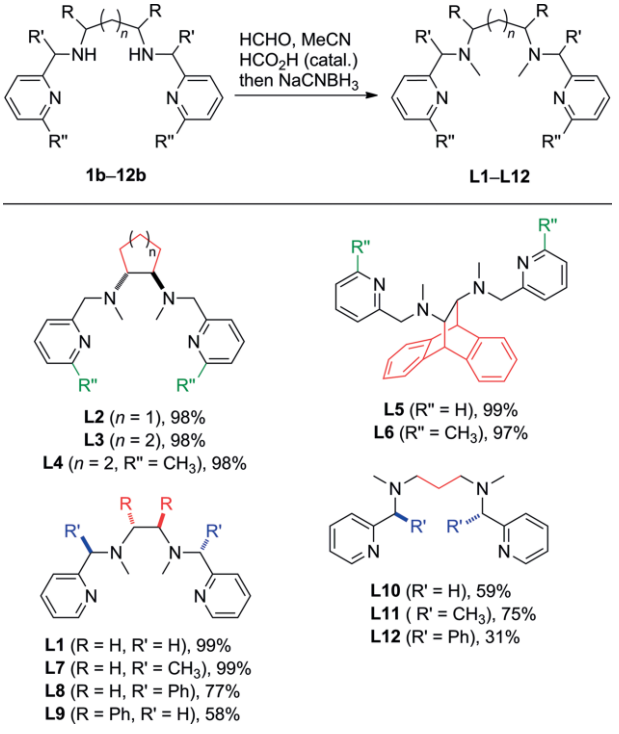


Figure 3. X-ray structure and relative stereochemistry of the hexahydropyrimidine side product **15** derived from **12b** (n = 1, R = H, R′ = Ph, R″ = H).

Under optimized conditions using formaldehyde and an excess of sodium cyanoborohydride in the presence of catalytic amounts of formic acid all starting material (**1b**–**12b**) with a central secondary diamine were smoothly converted into the desired ligands **L1**–**L12** (Scheme 6). Thus, all target compounds were easily produced in gram quantities.



Scheme 6. Reductive amination of the central diamine and final product structures.

Conclusions

In summary, we have developed a straightforward and highly efficient modular approach for the synthesis of tetramine ligands using a double reductive amination sequence. Thus, a central diamine containing two terminal primary amino groups was condensed with two equivalents of a 2-carbonyl-substituted pyridine derivative to yield a crystalline diimine intermediate. Precipitation of this intermediate was crucial in order to obtain high yields for the subsequent borohydride reduction. In the case of prochiral diimines a high diastereoselectivity in favor for the C_2-symmetric isomer was observed. A model to explain the stereoselectivity has been provided. Finally, the resulting products were then selectively methylated at the central diamine unit, again using a reductive amination. All three steps of this sequence are easily scalable and allow to prepare multi gram quantities of the target compounds. Notably, only a single chromatographic purification was required at the end of the three synthetic transformations and intermediates were usually purified through re-crystallization.

CCDC 1579819 (for **9a**) and 1579820 (for **15**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Ligand synthesis · N ligands · Amines · Tetramines · Reductive amination · Homogeneous catalysis

[1] a) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, 6th edition, **2014**; b) M. N. Zafar, A. H. Atif, M. F. Nazar, S. H. Sumrra Gul-E-Saba, R. Paracha, *Russ. J. Coord. Chem.* **2016**, *42*, 1–18 and references cited therein.

[2] a) F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev.* **2000**, *100*, 2159–2231; b) M. Hechavarrìa Fonseca, B. König, *Adv. Synth. Catal.* **2003**, *345*, 1173–1185.

[3] For reviews see: a) M. Costas, K. Chen, L. Que Jr., *Coord. Chem. Rev.* **2000**, *200–202*, 517–544; b) J. E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, **2004**; c) M. Costas, M. P. Mehn, M. P. Jensen, L. Que Jr., *Chem. Rev.* **2004**, *104*, 939–986; d) E. Y. Tshuva, S. J. Lippard, *Chem. Rev.* **2004**, *104*, 987–1012; e) G. Dyker, *Handbook of C-H Transformations*, Vol. 1–2, Wiley-VCH, Weinheim, **2005**; f) A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Springer-Verlag, Boston, **2005**; g) A. R. Dick, M. S. Sanford, *Tetrahedron* **2006**, *62*, 2439–2463; h) L. Que Jr., *Acc. Chem. Res.* **2007**, *40*, 493–500; i) W. Nam, *Acc. Chem. Res.* **2007**, *40*, 522–531; j) S. Shaik, H. Hirao, *Acc. Chem. Res.* **2007**, *40*, 532–542; k) A. Correa, O. García-Mancheno, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108–1117; l) L. Que Jr., W. B. Tolman, *Nature* **2008**, *455*, 333–340; m) M. Christmann, *Angew. Chem. Int. Ed.* **2008**, *47*, 2740–2742; *Angew. Chem.* **2008**, *120*, 2780–2783; n) A. C. Mayer, C. Bolm, S. Laschat, V. Rabe, A. Baro, O. García-Mancheno (**2008**), *Iron-Catalyzed Oxidation Reactions*, in Iron Catalysis in Organic Chemistry: Reactions and Applications (Ed.: B. Plietker), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany; o) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293–1314; p) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885–1898; q) K. Schröder, K. Junge, B. Bitterlich, M. Beller, *Top. Organomet. Chem.* **2011**, *33*, 83–109.

[4] H. Toftlund, E. Pedersen, S. Yde-Andersen, *Acta Chem. Scand. A* **1984**, *38*, 693–697.

[5] T. Okuno, S. Ito, Y. Nishida, *J. Chem. Soc., Dalton Trans.* **1997**, 3547–3551. See also: R. E. Norman, S. Yan, L. Que Jr., G. Backes, J. Ling, J. Sanders-Loehr, J. H. Zhang, C. J. O'Connor, *J. Am. Chem. Soc.* **1990**, *112*, 1554–1562.

[6] M. C. White, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2001**, *123*, 7194–7195.

[7] For other key publications in the area of ligand-stabilized iron catalyzed epoxidations, see: a) W. Nam, R. Ho, J. S. Valentine, *J. Am. Chem. Soc.* **1991**, *113*, 7052–7054; b) M. B. Francis, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **1999**, *38*, 937–941; *Angew. Chem.* **1999**, *111*, 987–991; c) S. J. Lippard, *J. Am. Chem. Soc.* **2001**, *123*, 1794–1795; d) F. G. Gelalcha, B. Bitterlich, B. Anilkumar, M. K. Tse, M. Beller, *Angew. Chem. Int. Ed.* **2007**, *46*, 7293–7296; *Angew. Chem.* **2007**, *119*, 7431–7435; e) R. Mas-Ballesté, L. Que Jr., *J. Am. Chem. Soc.* **2007**, *129*, 15964–15972; f) C. Marchi-Delapierre, A. Jorge-Robin, A. Thibon, S. Ménage, *Chem. Commun.* **2007**, 1166–1168; g) S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; *Angew. Chem.* **2008**, *120*, 3363–3367; h) H.-L. Yeung, K.-C. Sham, C.-S. Tsang, T.-C. Lau, H.-L. Kwong, *Chem. Commun.* **2008**, 3801–3803; i) M. Ostermeier, C. Limberg, C. Herwig, B. Ziemer, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1823–1830; j) E. Weber, D. Sirim, T. Schreiber, B. Thomas, J. Pleiss, M. J. Hunger, *J. Mol. Catal. B: Enzym.* **2010**, *64*, 29–37; k) Y. Nishikawa, H. J. Yamamoto, *J. Am. Chem. Soc.* **2011**, *133*, 8432–8435; l) M. Wu, C.-X. Miao, S. Wang, X. Hu, C. Xia, F. E. Kühn, W. Sun, *Adv. Synth. Catal.* **2011**, *353*, 3014–3022; m) K. Hasan, N. Brown, C. M. Kozak, *Green Chem.* **2011**, *13*, 1230–1237; n) P. Liu, Y. Liu, E. L.-M. Wong, S. Xiang, C.-M. Che, *Chem. Sci.* **2011**, *2*, 2187–2195; o) D. Clemente-Tejeda, A. López-Moreno, F. A. Bermejo, *Tetrahedron* **2013**, *69*, 2977–2986; p) V. A. Yazerski, P. Spannring, D. Gatineau, C. H. M. Woerde, S. M. Wieclawska, M. Lutz, H. Kleijn, R. J. M. Klein Gebbink, *Org. Biomol. Chem.* **2014**, *12*, 2062–2070; q) T. Chishiro, Y. Kon, T. Nakashima, M. Goto, K. Sato, *Adv. Synth. Catal.* **2014**, *356*, 623–627.

[8] a) N. A. Vermeulen, M. S. Chen, M. C. White, *Tetrahedron* **2009**, *65*, 3078–3084; b) P. D. Oldenburg, Y. Feng, I. Pryjomska-Ray, D. Ness, L. Que Jr., *J. Am. Chem. Soc.* **2010**, *132*, 17713–17723; c) B. Beunier, S. P. de Visser, S. Shaik, *Chem. Rev.* **2004**, *104*, 3947–3980.

[9] For selected references, see: a) C. Kim, K. Chen, J. Kim, L. Que Jr., *J. Am. Chem. Soc.* **1997**, *119*, 5964–5965; b) K. Neimann, R. Neumann, A. Rabion, R. M. Buchanan, R. H. Fish, *Inorg. Chem.* **1999**, *38*, 3575–3580; c) G. Roelfes, M. Lubben, R. Hage, L. Que Jr., B. L. Feringa, *Chem. Eur. J.* **2000**, *6*, 2152–2159; d) Y. Mekmouche, S. Ménage, C. Toia-Duboc, M. Fontecave, J.-B. Galey, C. Lebrun, J. Pécaut, *Angew. Chem. Int. Ed.* **2001**, *40*, 949–952; *Angew. Chem.* **2001**, *113*, 975–978; e) G. B. Shul'pin, G. V. Nizova, Y. N. Kozlov, L. Gonzalez Cuervo, G. Süss-Fink, *Adv. Synth. Catal.* **2004**, *346*, 317–332; f) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783–787; g) M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 861–864; h) L. Gómez, I. Garcia-Bosch, A. Company, J. Benet-Buchholz, A. Polo, X. Sala, X. Ribas, M. Costas, *Angew. Chem. Int. Ed.* **2009**, *48*, 5720–5723; *Angew. Chem.* **2009**, *121*, 5830–5833; i) M. S. Chen, M. C. White, *Science* **2010**, *327*, 566–571; j) G. Xue, R. De Hont, E. Münck, L. Que Jr., *Nat. Chem.* **2010**, *2*, 400–405; k) Y. He, J. D. Gorden, C. R. Goldsmith, *Inorg. Chem.* **2011**, *50*, 12651–12660; l) M. C. White, *Science* **2012**, *335*, 807–809; m) Y. Hitomi, K. Arakawa, T. Funabiki, M. Kodera, *Angew. Chem. Int. Ed.* **2012**, *51*, 3448–3452; *Angew. Chem.* **2012**, *124*, 3504–3508; n) L. Gómez, M. Canta, D. Font, I. Prat, X. Ribas, M. Costas, *J. Org. Chem.* **2013**, *78*, 1421–1433; o) P. E. Gormisky, M. C. White, *J. Am. Chem. Soc.* **2013**, *135*, 14052–14055.

[10] a) A.-K. C. Schmidt, C. B. W. Stark, *Org. Lett.* **2011**, *13*, 4164–4167; b) A.-K. C. Schmidt, C. B. W. Stark, *Org. Lett.* **2011**, *13*, 5788–5791; c) A. J. K. Roth, M. Tretbar, C. B. W. Stark, *Chem. Commun.* **2015**, *51*, 14175–14178; d) J. Adrian, S. Roth, C. B. W. Stark, *ChemCatChem* **2016**, *8*, 1679–1684.

[11] a) H. Göksel, C. B. W. Stark, *Org. Lett.* **2006**, *8*, 3433–3436; b) J. Schmidt, C. B. W. Stark, *Org. Lett.* **2012**, *14*, 4042–4045; c) D. S. Giera, C. B. W. Stark, *RSC Adv.* **2013**, *3*, 21280–21284; d) J. Schmidt, C. B. W. Stark, *J. Org. Chem.* **2014**, *79*, 1920–1928; e) J. Schmidt, Z. Khalil, R. J. Capon, C. B. W. Stark, *Beilstein J. Org. Chem.* **2014**, *10*, 1228–1232; f) J. Adrian, C. B. W. Stark, *Org. Lett.* **2014**, *16*, 5886–5889; g) J. Schmidt, J. Adrian, C. B. W. Stark, *Org. Biomol. Chem.* **2015**, *13*, 8173–8176.

[12] For other highly efficient modular approaches to tetradentate nitrogen donor ligands, see: a) E. Hao, Z. Wang, L. Jiao, S. Wang, *Dalton Trans.* **2010**, *39*, 2660–2666; b) C. H. Müller, R. Fröhlich, C. G. Daniliuc, U. Hennecke, *Org. Lett.* **2012**, *14*, 5944–5947.

[13] S. G. Gouin, J. F. Gestin, K. Joly, A. Lousouarn, A. Reliquet, J. C. Meslin, D. Deniaud, *Tetrahedron* **2002**, *58*, 1131–1136.

[14] a) S. Pikul, E. J. Corey, *Org. Synth., Coll. Vol.* **1998**, *9*, 387–390; b) X.-N. Son, Z.-J. Yao, *Tetrahedron* **2010**, *66*, 2589–2593.

[15] M. E. Fox, A. Gerlach, I. C. Lennon, G. Meek, C. Praquin, *Synthesis* **2005**, 3196–3198.

[16] a) R. Frauenlob, M. M. McCormack, C. M. Walsh, E. Bergin, *Org. Biomol. Chem.* **2011**, *9*, 6934–6937; b) S. Banerjee, J. Gangopadhyay, C. Z. Lu, J. T. Chen, A. Ghosh, *Eur. J. Inorg. Chem.* **2004**, 2533–2541; c) T. K. Karmakar, B. K. Ghosh, A. Usman, H. K. Fun, E. Rivière, T. Mallah, G. Aromí, S. K. Chandra, *Inorg. Chem.* **2005**, *44*, 2391–2399.

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