Induced Chirality

International Edition: DOI: 10.1002/anie.201501271
German Edition: DOI: 10.1002/ange.201501271

Stereochemical Communication within a Chiral Ion Pair Catalyst**

Christian Merten, Corina H. Pollok, Saihu Liao, and Benjamin List**

Abstract: *Ionic interactions are increasingly appreciated as a key, asymmetry-inducing factor in enantioselective catalytic transformations, including those involving Brønsted acid or base catalysis, phase-transfer catalysis, and related processes. However, a detailed understanding of these interactions is often lacking. Herein, we show how an enantiopure anion enforces a chiral conformation onto a catalytically relevant achiral cation. Specifically, we use vibrational circular dichroism (VCD) spectroscopy to monitor the transmission of stereochemical information from a chiral phosphate anion to a flexible manganese(III)–salen cation. We show that VCD can be used to study solvent effects and that the obtained chiroptical data directly and quantitatively correlate with the experimentally observed enantioselectivity in an asymmetric olefin epoxidation reaction.*

In recent years, ion-pairing catalysis, which has long been limited to the narrower context of cation-based phase-transfer catalysis (PTC),[1] has gained increasing interest. In particular, the emergence of asymmetric counteranion-directed catalysis (ACDC), the related anion-binding catalysis, and anion-based phase-transfer catalysis has led to a significant expansion of this area.[2] Upon ion pairing, two general modes of action can be differentiated: The presence of the chiral ion either renders the environment around the reactant ion chiral, thus blocking a certain sphere from attacks of other reactants, or the chiral ion induces a preferential chiral conformation to the achiral ion. The latter effect is known as the Pfeiffer effect,[3] and has been observed in various ionic systems.[4]

As the development of new catalysts generally benefits from a deeper understanding of the reaction mechanism, modern NMR spectroscopic techniques such as pulsed gradient spin echo (PGSE) and NOE experiments as well as electronic circular dichroism (ECD) spectroscopy have been used to probe the stereochemical communication within ion pairs.[4,5] However, while NMR spectroscopy in itself is not sensitive to chirality but, for instance, to the formation of diastereomers, electronic transitions observed in ECD usually feature quite broad absorbance bands. This may complicate the interpretation of the spectra, as, for instance, bands of cations and anions featuring similar chromophors can overlap, solvent absorbance might cover important transitions, and the prediction of ECD band intensities and signs can be challenging.[6] Clearly, additional methods and techniques are required to investigate chiral ion pairing systems.

Vibrational circular dichroism (VCD) spectroscopy is the chiroptical version of infrared spectroscopy and as such measures the very small difference in the absorbance of left-handed and right-handed circularly polarized infrared light during a vibrational transition.[7] It is mostly used to assign absolute configurations of natural products,[8] pharmaceuticals,[9] and other chiral molecules including products of catalytic asymmetric reactions.[10] However, VCD spectroscopy is not only sensitive to the chirality of a molecule but also to conformational changes,[11] self-aggregation,[12] and intermolecular interactions with solvents.[13] This unique sensitivity also led to the discovery of chirality-transfer phenomena. For instance, chiral oxiranes in water were found to induce a VCD signal for the H_2O bending modes,[14] and more recently, ammonia was shown to become optically active upon interacting with methyl lactate under matrix-isolation conditions.[15] Furthermore, chiral induction in an ion pair has been reported by Bas et al.[16] This encouraged us to apply VCD spectroscopy to study chirality-induction phenomena in ion-pair-based asymmetric catalysis with the focus on establishing structure–spectra relationships which can be used to predict catalytic selectivity.

Pioneering work by Kochi et al. introduced cationic manganese(III)–salen complexes as catalysts for the efficient epoxidation of olefins.[17] Complex cations such as **1** are C_2 symmetric and can adopt two chiral and mirror-imaged conformations (Scheme 1 A).[18] Jacobsen[19] and Katsuki[20] independently utilized this inherent chirality and locked the salen backbone conformation by introducing a rigid enantiopure backbone. These modifications led to impressive enantioselectivities, and especially Jacobsen's catalyst **2** gained significant popularity.[21] The use of neutral donor ligands such as sparteine and chiral N-oxides with achiral salen catalysts such as **1**-OAc also led to reasonably good enantioselectivities.[22] It has been hypothesized that the presence of these chiral donor ligands leads to a shift of the conformational equilibrium towards one of the enantiomeric conformations.

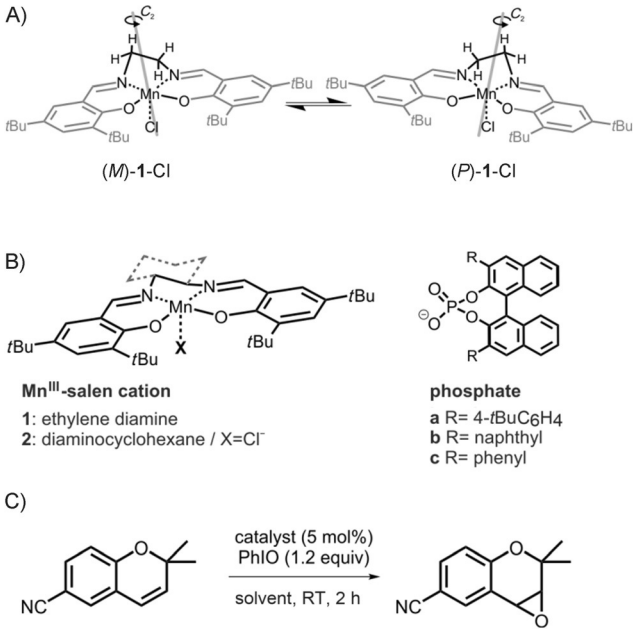
Based on the recently introduced ACDC concept,[23] we developed a new type of ion-pair catalysts consisting of an achiral Mn^{III}–salen cation **1** and an enantiopure phosphate anion (**a**–**c**, Scheme 1 B). These catalysts gave high efficiency

[*] Dr. C. Merten, C. H. Pollok
Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum
Universitätsstrasse 150, 44801 Bochum (Germany)
E-mail: christian.merten@ruhr-uni-bochum.de
Dr. S. Liao, Prof. Dr. B. List
Max-Planck Institut für Kohlenforschung
Kaiser Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
E-mail: list@kofo.mpg.de

[**] C.M. thanks the Fonds der chemischen Industrie for financial support through a Liebig fellowship. Furthermore, we gratefully acknowledge generous support from the Max Planck Society, the European Research Council (Advanced Grant "High Performance Lewis Acid Organocatalysis, HIPOCAT"), and the Deutsche Forschungsgemeinschaft (Cluster of Excellence "Ruhr Explores Solvation", RESOLV, EXC 1069).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201501271.

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. Structures of Mn^{III}–salen complexes. A) Equilibrium between the C_2-symmetric chiral conformations exemplified by **1**-Cl. b) Structures and labeling scheme of the investigated complexes. Cation **1** is combined with one of the chiral phosphate anions yielding ion pairs **1a**–**1c** or with the chloride anion **1**-Cl. The chirality descriptors *R* and *S* of the ion pairs refer to the chirality of the phosphate ion. Chirality is stabilized in cation **2** by a cyclohexane modification of the salen backbone, which is indicated with dashed lines. The acids corresponding to the phosphates **a**–**c** are referred to as **a**H–**c**H. C) Investigated model reaction.

and enantioselectivity in epoxidation and sulfoxidation reactions. In a model epoxidation reaction (Scheme 1 C),[24] we found that the performance of the catalyst strongly depends on subtle structural differences of the anion. Ion pair **1a** gave the highest enantioselectivity (95:5 e.r.), while replacing the 4-*tert*-butylphenyl with naphthyl groups (**1b**) causes a dramatic decrease in enantioselectivity, and substitution with a simple phenyl group leads to an almost complete breakdown of the enantioselectivity (75:25 e.r. for **1b**, 52:48 e.r. for **1c**). We hypothesized that the anions show a similar effect as the neutral donor ligands.[22] Since the ion-pair catalyst (*R*)-**1a** and Jacobsen's epoxidation catalyst (*R*,*R*)-**2** gave very similar enantioselectivity with different substrates, we concluded that the cation must feature a structurally similar active site in both catalysts (i.e. an *M* configuration of the Mn–salen plane).[25]

At this point, we became curious whether the hypothesis of an anion-mediated induction of chirality into the cation could somehow be verified experimentally. Although the paramagnetism of metal centers does not necessarily render a ^{1}H NMR spectrum uninterpretable,[26] the spectra obtained for the salts **1a**–**1c** in [D_6]benzene showed only few broad signals which were not suited to differentiate between possible diastereomers. Therefore, our catalyst system appeared to be highly suitable for a VCD study of chiral anion-induced chirality transfer for a particular reason: It can be reasonably assumed that there is no direct interaction between the chiral anion and the substrate. The substrate approaches the active site, a Mn^V=O functionality generated in situ, from the opposite side of the Mn–salen plane.[25] Hence, the chirality induction between the ions can be studied independent of the substrate.

Figure 1 shows the experimental IR and VCD spectra of both enantiomers of **1a** together with the spectra of the corresponding phosphoric acid **a**H as obtained in [D_1]chloroform. For comparison, the spectra of (*R*)-**2** are shown as well. On first glance, it is apparent that the

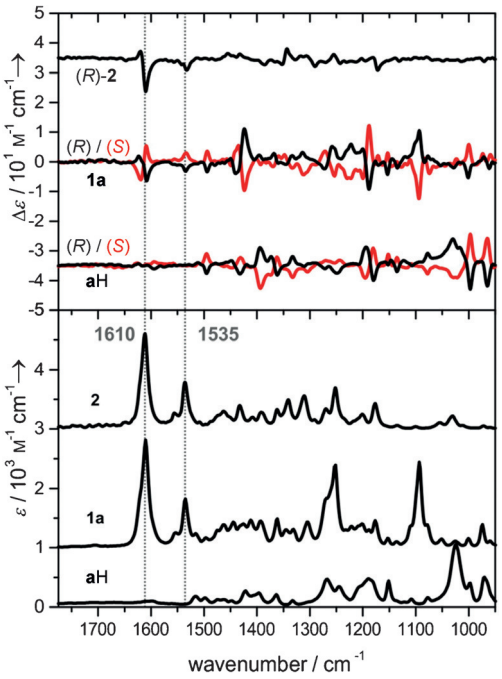


Figure 1. Experimental VCD (top) and IR (bottom) spectra of the ion-pair catalyst **1a** (c = 0.05 M), the corresponding free phosphoric acid **a**H (c = 0.08 M), and (*R*)-**2** (c = 0.15 M). The spectra were measured in [D_1]chloroform in a BaF_2 cell with an optical path length of 100 μm.

intensities of the IR bands of the free acid **a**H are relatively weak and that there are almost no observable bands in the range of 1520 to 1700 cm^{-1}. As the Mn^{III}–salen cations are structurally very similar, it is therefore also not surprising that the visual comparison of the IR spectra of the catalysts **1a** and **2** reveals only few obvious differences due to the presence of the chiral anion. Very important in context of our study are the identical band positions of the C=N and aromatic C=C stretching vibrations of the Mn^{III}–salen at 1610 cm^{-1} and 1535 cm^{-1} (indicated with dashed lines). The most noteworthy difference between the IR spectra of **1a** and **2** is the IR band at 1094 cm^{-1} in the spectrum of **1a** which corresponds to the P–O stretching vibration of the phosphate. This vibration is observed at 1024 cm^{-1} for the free acid **a**H.

Unlike the IR spectrum, the VCD spectrum of **1a** is dominated by bands of the chiral anion. Many of the rich VCD spectral features of **1a** in the region below 1500 cm^{-1} can be directly correlated with VCD bands of **a**H (see Figure S1 in the Supporting Information for details). The most relevant VCD bands in the spectrum of **1a** are those

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

appearing in the region above 1500 cm^{-1}. Here, the two IR bands of the C=N and C=C stretching motions give rise to strong VCD signals. Both the VCD couplet at 1610 cm^{-1} and the negative band at 1535 cm^{-1} observed for ion pair (*R*)-**1a** can also be found in the VCD spectrum of Jacobsen's catalyst (*R*)-**2**. These identical VCD patterns suggest that within ion-pair catalyst (*R*)-**1a**, the equilibrium between the two enantiomeric conformations of the Mn^{III}–salen cation is shifted towards the *M* conformation (Scheme 1 A).

The above empirical conclusion is supported by a semi-empirical analysis of the experimental spectra with the exciton coupling method (see the Supporting Information for details).[27] Furthermore, we also calculated the IR and VCD spectra of the (*M*)-**1** cation as well as (*R*)-**2** using density functional theory (DFT) methods.[28] The calculated spectra of **2** agree nicely with the experimentally observed spectra. The calculations also confirmed that **1** in the *M* conformation features the same VCD spectral pattern as **2** (see Figures S2 and S4). Hence, even without relying on the availability of a similar configurationally stable chiral catalyst, it is possible to determine the preferred chiral conformation of the cation.

The spectra of the catalyst were first measured in [D_1]chloroform, since the only strong solvent interference is observed below 950 cm^{-1}. However, as we have found the enantioselectivity of catalyst **1a** to be highly solvent dependent (see the Supporting Information), we also measured VCD spectra in different solvents (Figure 2, bottom traces). For example, [D_6]benzene and [H_8]THF, which afforded higher enantioselectivities also gave VCD spectra similar to that recorded in [D_1]chloroform, however, with slightly increased intensities of the bands arising from the cation. Significantly, in methanol, which gives essentially racemic product, the VCD signals for the C=N and C=C stretching modes disappear. While DMSO is not a suitable solvent for the epoxidation reaction as it is readily oxidized to the corresponding sulfone, we also measured the VCD spectrum in this ion-pair-separating solvent. As anticipated, the characteristic signals also essentially disappeared. In the corresponding IR spectra (see Figure S8), some bands change with the polarity of the solvent as well. However, these changes cannot consistently be correlated with the observed enantiomeric excess values.

A more quantitative relation between the VCD spectra and the catalytic activity of **1a** can be derived by plotting the integrated intensity of a VCD band of the cation versus the enantiomeric excess achieved in a certain solvent. In the present case, the VCD band of the C=C stretching vibration in the range from 1565–1520 cm^{-1} has been chosen for this correlation (see box in Figure 2) as it is monosignate and, due to the nature of the underlying vibration, not affected in frequency by solvent polarity (see Figure S8). The resulting correlation plot (Figure 3) reveals an almost linear relationship between *ee* and intensity, thus supporting the above conclusion that the asymmetric catalytic activity of the complex is closely linked to the induction of a preferential chiral conformation.

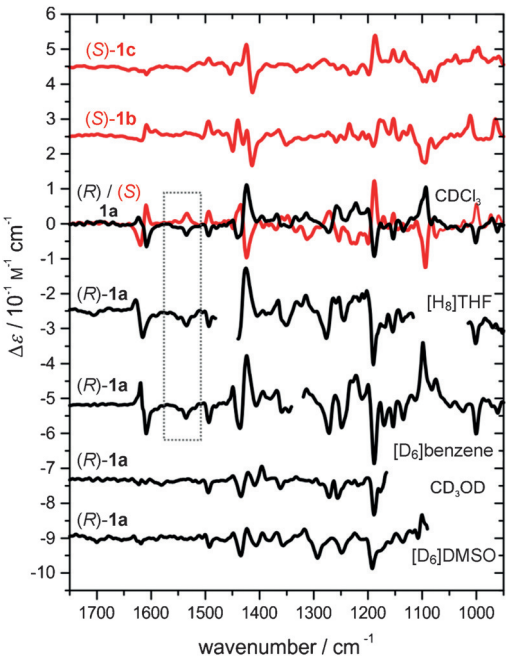


Figure 2. Comparison of experimental VCD spectra of **1a** with those of the ion pairs **1b** and **1c** in three different solvents. The top two traces show the VCD spectra of **1b** and **1c** in [D_1]chloroform. The bottom four traces show the VCD spectra of (*R*)-**1a** in THF, [D_6]benzene, [D_4]MeOH, and [D_6]DMSO. The box indicates the area used for the quantification of the chiral induction.

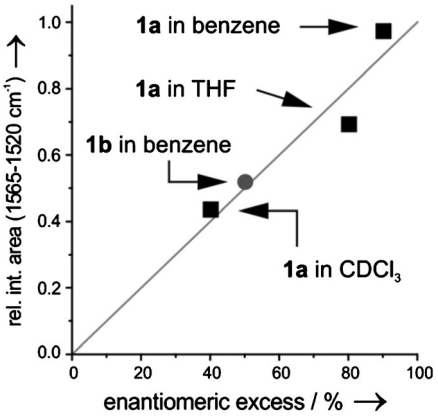


Figure 3. Plot of the integrated VCD intensity of the C=C stretching vibrations of catalyst **1a** and **1b** in various solvents versus the corresponding enantiomeric excess achieved in the catalysis experiments ($R^2 = 0.964$).

We also investigated the related ion-pair catalysts **1b** and **1c**, which display significantly decreased enantioselectivity without forfeiting much reactivity. Comparing their spectra (Figure 2, top traces) with that of catalyst **1a** clearly shows that the characteristic VCD bands decrease significantly in intensity. At the same time, the IR spectra of the ion pairs **1b** and **1c** in this range, however, are almost identical with that of **1a** (Figure S8), which suggests that the degree of ion pairing is similar for all three ion pairs. These observations correlate again lower VCD signal intensity with lower enantioselectivity and suggest that all three catalysts **1a–c** form contact ion

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

pairs in chloroform solution, but that anions **b** and **c** maybe less efficient in shifting the cation equilibrium towards one of the two enantiomeric conformations. The VCD band intensity of the C=C stretching vibration of **1b** in [D_6]benzene also nicely adds to the correlation plot in Figure 3.

Our experiments are consistent with the hypothesis of an induction of a specific chiral conformation to the cation. Therefore, we can now examine calculated structures of the ion pairs more closely. Figure 4 shows a side view of the ion

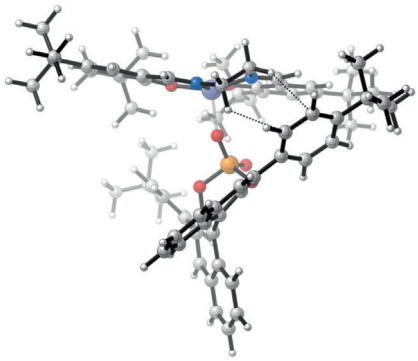


Figure 4. Optimized structure of the (*M*)-**1**/(*R*)-**a** ion pair in a side view onto the ethylene bridge. Another view as well as the structure of the (*P*)-**1**/(*R*)-**a** ion pair are shown in Figures S10 and S11.

pair (*R*)-**1a**. It is evident that steric repulsion between the ethylene bridge and the phenyl ring of the 4-*tert*-butylphenyl group (or in general, the R group of the anion in Scheme 1 B) is minimized when the bridge adopts the *M* conformation. Additional steric repulsion of the 4-*tert*-butyl groups of the anion with the 3,3′-*tert*-butyl groups of the salen ligand forces one arm of the salen ligand to bend out of the plane of the complex. This, in turn, further stabilizes the *M* conformation and allows an efficient extension of the axial chirality of the anion to the cation. The decrease in chirality transfer observed for the other two anions is related to the latter repulsion. The naphthyl and phenyl groups of the anions in **1b** and **1c** are planar and less sterically demanding, and as such do not experience steric repulsion with the alkyl groups above the ring plane.

In conclusion, using VCD spectroscopy we could show for the first time how a chiral anion forces its accompanying catalytically relevant cation into an enantiomeric conformation. Furthermore, we could prove the origin of the enantiocontrol of our catalyst system and correlate the degree of stereochemical transmission with the experimentally observed enantioselectivities.

We believe that the described approach can also aid in understanding the underlying induction mechanisms and experimentally achieved enantiomeric excesses obtained with other chiral catalysts. These can, for instance, be based on a chiral conformational locking or shifting mechanism[29] or on Lewis acid–base interactions. There are two main prerequisites for applying our approach to other systems: 1) the key intermediate, that is, the molecular complex, in which the chirality transfer occurs, must exist without addition of a second reactant (otherwise the reaction takes place and the sample begins to change over the course of measurement time), and 2) the component of the system that becomes chiral should ideally feature a functional group and an associated vibrational mode that can easily be separated from modes of the chiral auxiliary/catalyst. It should be stressed that it is not necessary to have a similar configurationally stable chiral catalyst such as **2** in order to be able to interpret the results. We are currently applying VCD spectroscopy to study other chiral catalyst systems and develop a more general protocol for studying stereochemical communication.

Experimental Section

The constituents of the chiral ion pairs, that is, the BINOL-derived phosphates **a**H–**c**H and the ethylenediamine-bridged Mn^{III}–salen complex **1**-Cl, were prepared according to previously reported procedures.[24] The diaminocyclohexane-based Mn^{III}–salen catalyst (*R*,*R*)-**2** was purchased from Sigma–Aldrich.

The IR and VCD spectra were recorded in the fingerprint region (1800–950 cm^{-1}) on a Bruker Vertex 70v FTIR spectrometer equipped with a Bruker PMA 50 module for VCD measurements (spectral resolution: 4 cm^{-1}, PEM frequency: 1500 cm^{-1}). The samples were held in a demountable BaF_2 cell with a path length of 100 μm, and about 30000 scans have been averaged for the VCD spectra. The baselines of the VCD spectra were corrected by subtraction of the spectra obtained for **1**-Cl or for the racemic mixture. Some regions in the VCD spectra of **1a** in [D_6]DMSO, [D_4]MeOH, [D_6]benzene, and [H_8]THF were cut out due to strong artefacts arising from solvent absorption.

Details on the computational approach for the geometry optimizations and spectra calculations can be found in the Supporting Information.

Keywords: asymmetric catalysis · asymmetric counterion-directed catalysis (ACDC) · chirality transfer · ionic interactions · vibrational circular dichroism

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 8841–8845
Angew. Chem. **2015**, *127*, 8967–8971

[1] S. Shirakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 4312–4348; *Angew. Chem.* **2013**, *125*, 4408–4445.
[2] a) R. R. Knowles, E. N. Jacobsen, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20678–20685; b) K. Brak, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2013**, *52*, 534–561; *Angew. Chem.* **2013**, *125*, 558–588; c) M. Mahlau, B. List, *Angew. Chem. Int. Ed.* **2013**, *52*, 518–533; *Angew. Chem.* **2013**, *125*, 540–556; d) R. J. Phipps, G. L. Hamilton, F. D. Toste, *Nat. Chem.* **2012**, *4*, 603–614.
[3] P. Pfeiffer, K. Quehl, *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2667–2671.
[4] a) J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* **2003**, *32*, 373–382; b) J. Lacour, D. Moraleda, *Chem. Commun.* **2009**, 7073–7089.
[5] a) I. Fernández, P. S. Pregosin, *Magn. Reson. Chem.* **2006**, *44*, 76–82; b) D. Nama, D. Schott, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Organometallics* **2006**, *25*, 4596–4604; c) A. Moreno, P. S. Pregosin, G. Laurenczy, A. D. Phillips, P. J. Dyson, *Organometallics* **2009**, *28*, 6432–6441; d) C. Zuccaccia, G. Bellachioma, G. Cardaci, A. Macchioni, *J. Am. Chem. Soc.* **2001**, *123*, 11020–11028; e) A. Macchioni, *Eur. J. Inorg. Chem.* **2003**, 195–205; f) A. Macchioni, *Chem. Rev.* **2005**, *105*, 2039–2074; g) D. Zuccaccia, L. Belpassi, A. Macchioni, F. Tarantelli, *Eur. J.*

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Inorg. Chem. **2013**, 4121 – 4135; h) E. Martínez-Viviente, P. S. Pregosin, L. Vial, C. Herse, J. Lacour, *Chem. Eur. J.* **2004**, *10*, 2912 – 2918; i) T. J. Wenzel, *Discrimination of Chiral Compounds Using NMR Spectroscopy*, 1st ed., Wiley, New York, **2007**; j) J. Crassous, *Chem. Soc. Rev.* **2009**, *38*, 830 – 845.
[6] J. Autschbach, *Chirality* **2009**, *21*, E116 – E152.
[7] L. A. Nafie, *Vibrational Optical Actvity*, Wiley, Chichester, **2011**.
[8] a) L. G. Felippe, J. M. Batista, Jr., D. C. Baldoqui, I. R. Nascimento, M. J. Kato, Y. He, L. A. Nafie, M. Furlan, *Org. Biomol. Chem.* **2012**, *10*, 4208 – 4214; b) C. Areche, A. San-Martín, J. Rovirosa, M. A. Muñoz, A. Hernández-Barragán, M. A. Bucio, P. Joseph-Nathan, *J. Nat. Prod.* **2010**, *73*, 79 – 82.
[9] S. Qiu, E. De Gussem, K. A. Tehrani, S. Sergeyev, P. Bultinck, W. Herrebout, *J. Med. Chem.* **2013**, *56*, 8903 – 8914.
[10] a) S. R. Domingos, S. J. Roeters, S. Amirjalayer, Z. Yu, S. Hecht, S. Woutersen, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17263 – 17267; b) J. L. Arbour, H. S. Rzepa, J. Contreras-García, L. A. Adrio, E. M. Barreiro, K. K. Hii, *Chem. Eur. J.* **2012**, *18*, 11317 – 11324.
[11] H. Sato, Y. Mori, A. Yamagishi, *Dalton Trans.* **2013**, *42*, 6873 – 6878.
[12] C. Merten, M. Amkreutz, A. Hartwig, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11635 – 11641.
[13] a) C. Merten, R. McDonald, Y. Xu, *Inorg. Chem.* **2014**, *53*, 3177 – 3182; b) V. P. Nicu, E. J. Baerends, P. L. Polavarapu, *J. Phys. Chem. A* **2012**, *116*, 8366 – 8373.
[14] a) M. Losada, Y. Xu, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3127 – 3135; b) M. Losada, P. Nguyen, Y. Xu, *J. Phys. Chem. A* **2008**, *112*, 5621 – 5627.
[15] C. Merten, Y. Xu, *Angew. Chem. Int. Ed.* **2013**, *52*, 2073 – 2076; *Angew. Chem.* **2013**, *125*, 2127 – 2130.
[16] D. Bas, T. Bürgi, J. Lacour, J. Vachon, J. Weber, *Chirality* **2005**, *17 Suppl*, S143 – 148.
[17] K. Srinivasan, P. Michaud, J. K. Kochi, *J. Am. Chem. Soc.* **1986**, *108*, 2309 – 2320.
[18] a) Y. N. Ito, T. Katsuki, *Tetrahedron Lett.* **1998**, *39*, 4325 – 4328; b) T. Hashihayata, Y. Ito, T. Katsuki, *Synlett* **1996**, 1079 – 1081; c) K. Miura, T. Katsuki, *Synlett* **1999**, 783 – 785.
[19] W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, *J. Am. Chem. Soc.* **1990**, *112*, 2801 – 2803.
[20] R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, *Tetrahedron Lett.* **1990**, *31*, 7345 – 7348.
[21] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691 – 1693.
[22] T. Hashihayata, Y. Ito, T. Katsuki, *Tetrahedron* **1997**, *53*, 9541 – 9552.
[23] S. Mayer, B. List, *Angew. Chem. Int. Ed.* **2006**, *45*, 4193 – 4195; *Angew. Chem.* **2006**, *118*, 4299 – 4301.
[24] S. Liao, B. List, *Angew. Chem. Int. Ed.* **2010**, *49*, 628 – 631; *Angew. Chem.* **2010**, *122*, 638 – 641.
[25] D. D. Ford, L. P. C. Nielsen, S. J. Zuend, C. B. Musgrave, E. N. Jacobsen, *J. Am. Chem. Soc.* **2013**, *135*, 15595 – 15608.
[26] J. Lacour, J. J. Jodry, D. Monchaud, *Chem. Commun.* **2001**, 2302 – 2303.
[27] T. Taniguchi, K. Monde, *J. Am. Chem. Soc.* **2012**, *134*, 3695 – 3698.
[28] P. J. Stephens, *J. Phys. Chem.* **1985**, *89*, 748 – 752.
[29] a) P. Dydio, C. Rubay, T. Gadzikwa, M. Lutz, J. N. H. Reek, *J. Am. Chem. Soc.* **2011**, *133*, 17176 – 17179; b) R. Dorta, L. Shimon, D. Milstein, *J. Organomet. Chem.* **2004**, *689*, 751 – 758; c) D. A. Slack, I. Greveling, M. C. Baird, *Inorg. Chem.* **1979**, *18*, 3125 – 3132.

Received: February 9, 2015
Revised: March 30, 2015
Published online: June 23, 2015

 © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim