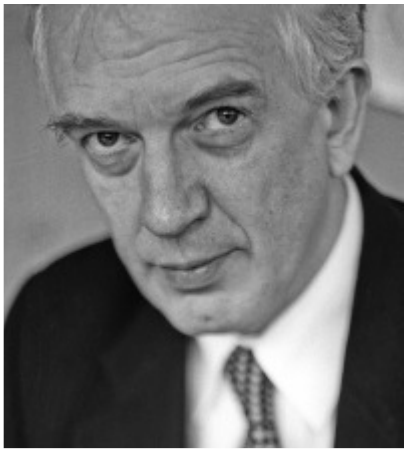
Professor Dr. Jürgen Martens
A tribute



This special issue of Arkivoc is dedicated to Professor Dr. Jürgen Martens on the occasion of his 67th birthday, to acknowledge his contribution to synthetic organic chemistry

DOI:http://dx.doi.org/10.3998/ark.5550190.p001.467

Jürgen Martens was born in Tostedt (a city in the state of Lower Saxony) in 1948, and after completing a traineeship at the company Deutsche Shell AG in Hamburg as chemistry laboratory technician he then decided to pursue an academic education studying engineering at the "Staatliche Hochschule Darmstadt" (today University of Applied Sciences Darmstadt). After obtaining the degree of an engineer he then studied chemistry at the Technical University of Berlin, graduating with a degree as "Diplom-Chemiker" in 1973. From 1973 to 1975 he carried out his doctoral thesis in the field of synthetic organic photochemistry under supervision of Professor Klaus Praefcke at the same university, receiving his doctoral degree in 1975. In 1976 he joined the group of Nobel laureate Professor Robert B. Woodward at Harvard University, Camdridge / Massachusetts as a postdoctoral research fellow funded by the Max Kade Foundation, New York. Working in the field of natural product synthesis he co-authored three publications[1-3] on the total synthesis of erythromycin in *The Journal of the American Chemical Society*, which in total have been cited more than 500 times to date.

After returning to Germany in 1977 he started a very successful, decade-long industrial career at Degussa AG. Initially being a lab manager at the research center in Hanau-Wolfgang, he rapidly was promoted to the rank of a production manager for the penicillamine plant and GMP-officer before in 1983 he became member of corporate planning and in 1984 assistant of the executive board member for pharmaceuticals. It is noteworthy that being an outstanding successful industrial chemist in various positions, he remained his dedication for scientific aspects of organic chemistry through all this time. This is underlined by impressive >30 publications in prestigious international journals resulting from his one decade work at Degussa

AG, which he published in addition to the co-invention of numerous patents and patent applications. A major part of these contributions addressed novel synthetic routes towards enantiomerically pure α-amino acids.[2]

Thus, it might be considered not as a surprise that he returned to academia by accepting an offer for a C3-professorship (associate professorship) at the University of Oldenburg in 1986. Being one of the first members in the newly established Department of Chemistry at the University of Oldenburg he strongly contributed in laying the groundwork for the prosperous development of the department. In addition, also in his academic research he remained very successful being highly visible also on the international scene as it is demonstrated, as a representative example, by the offer for a professorship from the University of Linz (which he declined). Due to his outstanding contributions he was rapidly promoted to the rank of a C4-professor (full professor) at the University of Oldenburg in 1989 and he held this position ever since.

His research achievements have been published in more than 200 publications, and he is co-inventor of more than 30 patents and patent applications. From a very early stage on, he recognized the importance of national and international research collaborations for entering new fields of sciences, encouraging his group members to actively take over responsibility for such collaborations at a scientific but also administrative level. He supervised more than 40 doctoral students and, additionally, more than 30 diploma or master students. Benefiting from both, the freedom as well as his support to develop new ideas by their own, his group members were ideally prepared from a research as well as management perspective for their later career. With respect to the latter one, he pioneered in integrating management tools in academic chemical research and education such as the "legendary" quarterly research reports which members of this research group had to deliver.

Through his more than 25 years at the University of Oldenburg, he also has been a dedicated teacher of organic chemistry for chemistry students in the bachelor and master programs (before diploma program) with a high passion also for integrating industrial aspects in teaching. Furthermore, he served as a Dean of the department of chemistry from 1998 to 2000, and since 1992 he has also been management board member of the "Studentenwerk" (student union) Oldenburg.

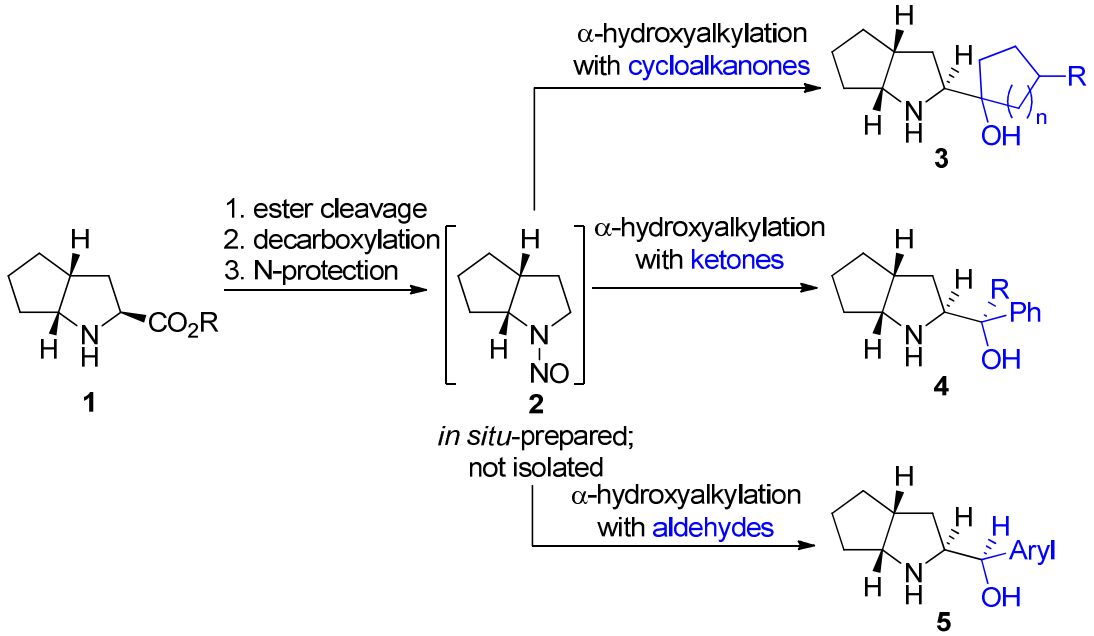
Research achievements

During his decade-long industrial and academic career, Jürgen Martens has contributed outstanding achievements in various fields of organic chemistry, in particular amino acid chemistry, heterocyclic chemistry and multi-component condensation reactions. In this connection, from a very early stage on Jürgen Martens has also been a pioneer in green chemistry at a time at which this term did not exist addressing - among other important topics - the high-level recycling of enantiomerically pure industrial waste materials. The following gives

a brief summary of selected examples of his research achievements made during his academic career at the University of Oldenburg is given:

(1) High-level recycling of industrial waste materials

By combining his expertise in both, academic and industrial fields, a major interest of Jürgen Martens, has been on the high-level recycling of undesired enantiomers resulting from large-scale resolution of drug intermediates as an attractive method for obtaining novel useful chiral molecules which can be used as reagents, ligands or directly as catalysts in asymmetric synthesis. A particular focus in his lab was on the use of the hydrochloride salt of benzyl (1*R*,3*R*,5*R*)-2-azabicyclo[3.3.0]octane-3-carboxylate (**1**) since this optically pure compound represents the unwanted enantiomer obtained in the resolution for the production of Ramipril carried out by the pharmaceutical company Sanofi-Aventis on large scale. Among many other achievements a large number of enantiomerically pure β-amino alcohol ligands derived from the waste material **1** were prepared which turned out to be suitable chiral ligands in, e.g., the asymmetric borane reduction of prochiral ketones[3f,g,i] as well as the asymmetric catalytic addition of diethyl zinc to aldehydes.[3c,d] A representative example of an efficient preparation of a library of such ligands by means of a modular synthetic strategy leading to a broad variety of β-amino alcohols with a 2-azabicyclo[3.3.0]octane core structure is shown in Scheme 1.[3g]

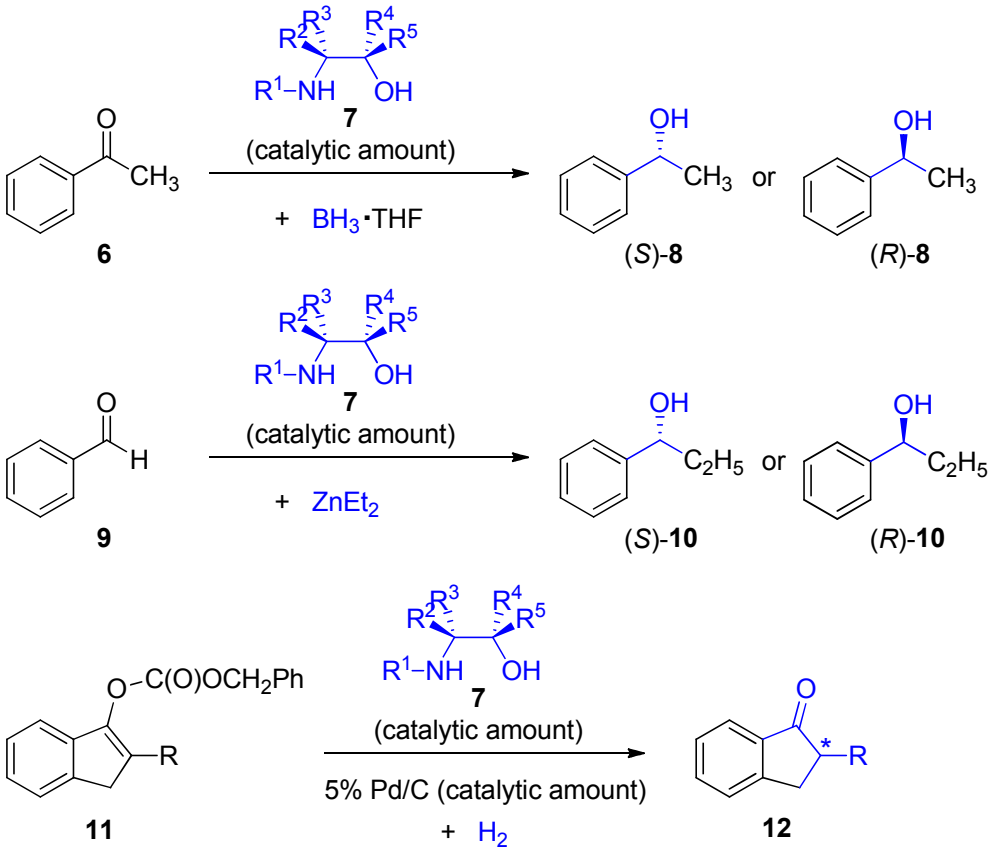


Scheme 1. Representative example of a β-amino alcohol library based on the waste material **1.**

(2) Asymmetric catalysis with amino alcohol ligands

In addition to β-amino alcohols prepared from waste material **1**, in the group of Jürgen Martens a broad and highly diverse library of 1,2-, 1,3- and 1,4-amino alcohols derived from numerous other enantiomerically pure α-amino acids was constructed. Often, additional stereogenic centers

have been formed through diastereoselective reactions. The resulting amino alcohol structures show exciting structures with promising, unique properties as ligands in metal complexes suitable as catalysts for asymmetric synthesis.[4] Probably, one of largest library of amino alcohol ligands in academia with a high structural diversity has been constructed through many years laying the basis for numerous collaborations with many research groups in the field of asymmetric catalysis. The exploration of such ligands has been successfully carried out for a broad variety of asymmetric catalytic syntheses.[4] Representative examples of such enantioselective transformations, which are also shown in Scheme 2, are borane reduction of ketones[3f,g,i,4a,b] and alkylation of aldehydes[3c,d,4c,d,j,k,m] as well as palladium-catalyzed protonation of enolates[4g,i] (e.g., **11**[4i]), which has been studied in collaboration with Professor Jacques Muzart (Université de Reims Champagne-Ardenne, France).

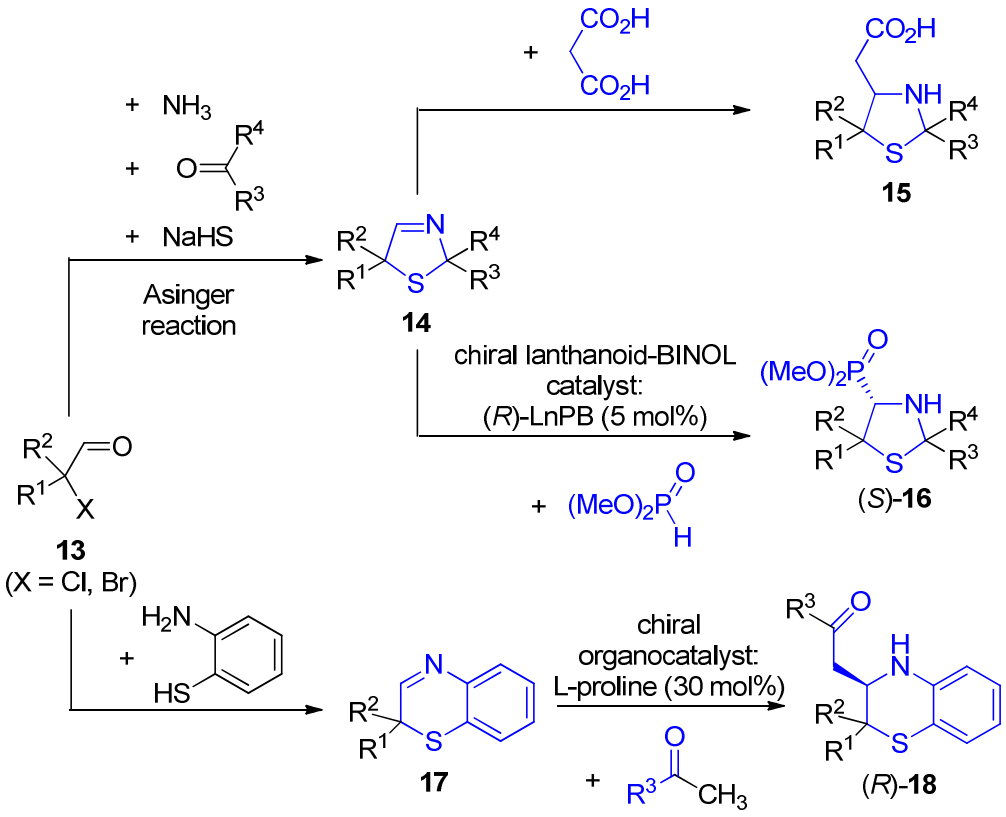


Scheme 2. Representative examples of enantioselective reactions with chiral catalysts based on β-amino alcohol ligands.

(3) Chemistry of heterocyclic imines

Due to the reactivity of the C=N double bond, heterocyclic imines represent valuable starting materials for addition reactions with formation of a broad variety of functionalized amines such as, e.g., α- and β-amino acids as well as α-amino phosphonates and their derivatives. Focusing

on both the synthesis[5] of heterocyclic imines as well as addition reactions[6] to the C=N double bond of such heterocycles, Jürgen Martens and his group contributed broadly to this field. For example, the first synthesis of an enantiomerically pure 3-thiazoline was carried out.[5d] Representative examples for addition reactions to the C=N bond of heterocyclic imines are the synthesis of novel 4-thiazolidine acetic acids **15**,[6a] the first asymmetric catalytic hydrophosphonylation of cyclic imines,[6d,f,g] which was done in collaboration with the group of Professor Masakatsu Shibasaki (University of Tokyo, Japan) and Professor Hiroaki Sasai (University of Tokyo, Japan; now: Osaka University, Japan) leading to heterocyclic α-amino phosphonates, e.g., of type (*S*)-**16**,[6d,f] and the first asymmetric organocatalytic synthesis of 3-keto-substituted chalkogenazines, e.g., (*R*)-**18** (Scheme 3).[6h]

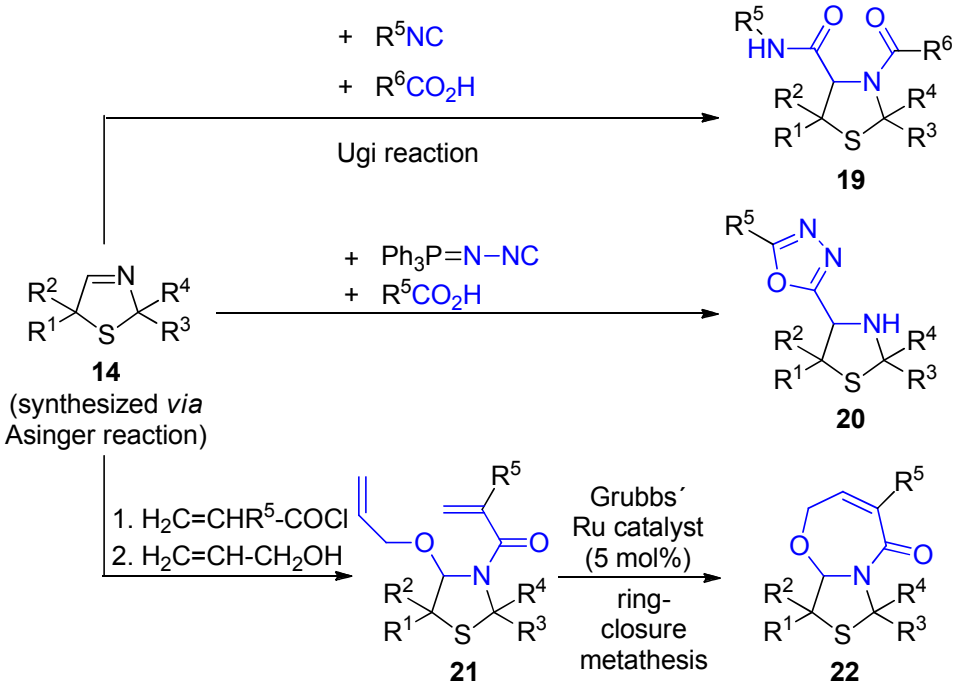


Scheme 3. Representative examples of addition reactions to heterocyclic imines.

(4) Multi-component condensation reactions and ring-closure metathesis

A further research field with tremendous contributions from Jürgen Martens and his group is the preparation of amino acid derivatives through multi-component condensation reactions.[7] For example, starting from (hetero-)cyclic imines, the Ugi reaction was successfully applied as an elegant and straightforward one-pot process to synthesize a broad range of totally protected α-amino acids bearing thiazolidine, oxazolidine and other saturated or unsaturated heterocyclic frameworks,[7a-f,m] e.g., of type **19** (Scheme 4).[7a,c] In recent work, a related multi-component

reaction was used for the synthesis of 1,3,4-oxadiazole derivatives **20** (Scheme 4).[7l] Metathesis, as a modern and highly efficient catalytic method for C=C bond formation, has also been successfully applied to construct a range of novel heterocyclic compounds,[7g-j] e.g., the first representatives of the novel compound class of α,β-unsaturated oxa-, aza- and selenolactams (e.g., **22**,[7g] Scheme 4). Also recently a library of novel valerolactams was constructed by means of an initial acid chloride addition to imines, followed by a Hosomi-Sakurai reaction and subsequent ring-closure metathesis.[7h]



Scheme 4. Representative examples of multi-component condensation and metathesis reactions.

(5) Chromatographic separation of enantiomers

Further research work, in particular conducted within a decade-long collaboration with Prof. Bushan (University of Roorkee, India), has been related to the development of novel chiral selectors for chromatographic separation of enantiomers with a particular focus on thin-layer chromatography as a still widely unexplored research field with broad application potential.[8] His recent activities also focused on the chromatographic separation of enantiomers of non-racemic enantiomeric mixtures on non-chiral stationary phases.[8g]

Prof. Dr. Harald Gröger
Chair of Organic Chemistry
Faculty of Chemistry, Bielefeld University
P.O. Box 100131, 33501 Bielefeld, Germany
E-mail: harald.groeger@uni-bielefeld.de

Selected Papers

1. (a) Woodward, R. B.; Logusch, E.; Nambiar, K. P.; Sakan, K.; Ward, D. E.; Au-Yeung, B.-W.; Balaram, P.; Browne, L. J.; Card, P. J.; Chen, C. H.; Chenevert, R. B.; Fliri, A.; Frobel, K.; Gais, H.-J.; Garratt, D. G.; Hayakawa, K.; Heggie, W.; Hesson, D. P.; Hoppe, D.; Hoppe, I.; Hyatt, J. A.; Ikeda, D.; Jacobi, P. A.; Kim, K. S.; Kobuke, Y.; Kojima, K.; Krowicki, K.; Lee, V. J.; Leutert, T.; Malchenko, S.; Martens, J. *et al*. *J. Am. Chem. Soc.* **1981**, *103*, 3210-3213. (b) Woodward, R. B.; Logusch, E.; Nambiar, K. P.; Sakan, K.; Ward, D. E.; Au-Yeung, B.-W.; Balaram, P.; Browne, L. J.; Card, P. J.; Chen, C. H.; Chenevert, R. B.; Fliri, A.; Frobel, K.; Gais, H.-J.; Garratt, D. G.; Hayakawa, K.; Heggie, W.; Hesson, D. P.; Hoppe, D.; Hoppe, I.; Hyatt, J. A.; Ikeda, D.; Jacobi, P. A.; Kim, K. S.; Kobuke, Y.; Kojima, K.; Krowicki, K.; Lee, V. J.; Leutert, T.; Malchenko, S.; Martens, J. *et al. J. Am. Chem. Soc.* **1981**, *103*, 3213-3215. (c) Woodward, R. B.; Logusch, E.; Nambiar, K. P.; Sakan, K.; Ward, D. E.; Au-Yeung, B.-W.; Balaram, P.; Browne, L. J.; Card, P. J.; Chen, C. H.; Chenevert, R. B.; Fliri, A.; Frobel, K.; Gais, H.-J.; Garratt, D. G.; Hayakawa, K.; Heggie, W.; Hesson, D. P.; Hoppe, D.; Hoppe, I.; Hyatt, J. A.; Ikeda, D.; Jacobi, P. A.; Kim, K. S.; Kobuke, Y.; Kojima, K.; Krowicki, K.; Lee, V. J.; Leutert, T.; Malchenko, S.; Martens, J. et al. *J. Am. Chem. Soc.* **1981**, *103*, 3215-3217.
2. Selected examples: (a) Kleemann, A.; Lehmann, B.; Martens, J. *Angew. Chem.* **1979**, *91*, 858-859; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 797. (b) Kleemann, A.; Leuchtenberger, W.; Martens, J.; Weigel, H. *Angew. Chem.* **1980**, *92*, 640; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 627. (c) Martens, J.; Offermanns, H.; Scherberich, P. *Angew. Chem.* **1981**, *93*, 680-683; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 668; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 584-608. (d) Martens, J.; Weigel, H. *Liebigs Ann. Chem.* **1983**, 2052-2054. (e) Martens, J.; Drauz, K. *Liebigs Ann. Chem.* **1983**, 2073-2078. (f) Drauz, K.; Koban, H. G.; Martens, J.; Schwarze, W. *Liebigs Ann. Chem.* **1985**, 448-452. (g) Drauz, K.; Kleemann, A.; Martens, J.; Scherberich, P.; Effenberger, F. *J. Org. Chem.* **1986**, *51*, 3494-3498. (h) Review: Drauz, K.; Kleemann, A.; Martens, J. *Angew. Chem.* **1982**, *94*, 590-613.
3. Selected examples: (a) Martens, J.; Lübben, S. *Liebigs Ann. Chem.* **1990**, 949-952. (b) Martens, J.; Lübben, S. *Arch. Pharm.* **1991**, *324*, 59-60. (c) Wallbaum, S.; Martens, J. *Tetrahedron: Asymmetry* **1993**, *4*, 637-640. (d) Stingl, K.; Martens, J. *Liebigs Ann. Chem.* **1994**, 491-496. (e) Wilken, J.; Wallbaum, S.; Saak, W.; Haase, D.; Pohl, S.; Patkar, L. N.; Dixit, A. N.; Chittari, P.; Rajappa, S.; Martens, J. *Liebigs Ann. Chem.* **1996**, 927-934. (f) Wilken, J.; Martens, J. *Synth. Commun.* **1996**, *26*, 4477-4485. (g) Wilken, J.; Martens, J. *Liebigs Ann. Chem.* **1997**, 563-571. (h) Wilken, J.; Kossenjans, M.; Saak, W.; Haase, D.; Pohl, S.; Martens, J. *Liebigs Ann. Chem.* **1997**, 573-579. (i) Wilken, J.; Thorey, C.; Gröger, H.; Haase, D.; Saak, W.; Pohl, S.; Muzart, J.; Martens, J. *Liebigs Ann. Chem.* **1997**, 2133-2146.
4. Selected examples: (a) Behnen, W.; Dauelsberg, C.; Wallbaum, S.; Martens, J. *Synth. Commun.* **1992**, *22*, 2143-2153. (b) Martens, J.; Dauelsberg, C.; Behnen, W.; Wallbaum, S.

Tetrahedron: Asymmetry **1992**, *3*, 347-350. (c) Behnen, W.; Mehler, T.; Martens, J. *Tetrahedron: Asymmetry* **1993**, *4*, 1413-1416. (d) Mehler, T.; Martens, J. *Tetrahedron: Asymmetry* **1993**, *4*, 1983-1986. (e) Aboulhoda, S. J.; Hénin, F.; Muzart, J.; Thorey, C.; Behnen, W.; Martens, J.; Mehler, T. *Tetrahedron: Asymmetry* **1994**, *5*, 1321-1326. (f) Thorey, C.; Wilken, J.; Hénin, F.; Martens, J.; Mehler, T.; Muzart, J. *Tetrahedron Lett.* **1995**, *36*, 5527-5530. (g) Aboulhoda, S. J.; Létinois, S.; Wilken, J.; Reiners, I.; Hénin, F.; Martens, J.; Muzart, J. *Tetrahedron: Asymmetry* **1995**, *6*, 1865-1868. (h) Reiners, I.; Martens, J.; Schwarz, S.; Henkel, H. *Tetrahedron: Asymmetry* **1996**, *7*, 1763-1770. (i) Aboulhoda, S. J.; Reiners, I.; Wilken, J.; Hénin, F.; Martens, J.; Muzart, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1847-1850. (j) Kossenjans, M.; Pennemann, H.; Martens, J.; Juanes, O.; Rodríguez-Ubis, J. C.; Brunet, E. *Tetrahedron: Asymmetry* **1998**, *9*, 4123-4125. (k) Wilken, J.; Winter, M.; Stahl, I.; Martens, J. *Tetrahedron: Asymmetry* **2000**, *11*, 1067-1071. (l) Pasquier, C.; Naili, S.; Mortreux, A.; Agbossou, F.; Pélinski, L.; Brocard, J.; Eilers, J.; Reiners, I.; Peper, V.; Martens, J. *Organometallics* **2000**, *19*, 5723-5732. (m) Burguete, M. I.; Collado, M.; García-Verdugo, E.; Vicent, M. J.; Luis, S. V.; Pennemann, H.; Graf von Keyserlingk, N.; Martens, J. *Tetrahedron* **2003**, *59*, 1797-1804.

5. Selected examples: (a) Martens, J.; Janknecht, H.-H. *Sulfur Letters* **1990**, *11*, 263-270. (b) Martens, J.; Janknecht, H.-H. *Phosphorus, Sulfur, and Silicon* **1991**, *61*, 173-176. (c) Weber, M.; Jakob, J.; Martens, J. *Liebigs Ann. Chem.* **1992**, 1-6. (d) Schlemminger, I.; Janknecht, H.-H.; Maison, W.; Saak, W.; Martens, J. *Tetrahedron Lett.* **2000**, *41*, 7289-7292.
6. Selected examples: (a) Martens, J.; Kintscher, J.; Arnold, W. *Synthesis* **1991**, 497-498. (b) Martens, J.; Kintscher, J.; Lindner, K.; Pohl, S.; Saak, W.; Haase, D. *Liebigs Ann. Chem.* **1991**, 305-310. (c) Martens, J.; Lindner, K.; Kintscher, J. *Sulfur Lett.* **1992**, *14*, 1-15. (d) Gröger, H.; Saida, Y.; Arai, S.; Martens, J.; Sasai, H.; Shibasaki, M. *Tetrahedron Lett.* **1996**, *37*, 9291-9292. (e) Gröger, H.; Martens, J.; Goerlich, J. R.; Schmutzler, R. *Phosphorus, Sulfur, and Silicon* **1997**, *128*, 153-163. (f) Gröger, H.; Saida, Y.; Sasai, H.; Yamaguchi, K.; Martens, J.; Shibasaki, M. *J. Am. Chem. Soc.* **1998**, *120*, 3089-3103. (g) Schlemminger, I.; Saida, Y.; Gröger, H.; Maison, W.; Durot, N.; Sasai, H.; Shibasaki, M.; Martens, J. *J. Org. Chem.* **2000**, *65*, 4818-4825. (h) Schulz, K.; Ratjen, L.; Martens, J. *Tetrahedron* **2011**, *67*, 546-553.
7. Selected examples: (a) Kintscher, J.; Martens, J. *Synthesis* **1992**, 837-838. (b) Gröger, H.; Hatam, M.; Martens, J. *Tetrahedron* **1995**, *51*, 7173-7180. (c) Gröger, H.; Hatam, M.; Kintscher, J. Martens, J. *Synth. Commun.* **1996**, *26*, 3383-3394. (d) Maison, W.; Lützen, A.; Kosten, M.; Schlemminger, I.; Westerhoff, O.; Martens, J. *J. Chem. Soc. Perkin I* **1999**, 3515-3526. (e) Maison. W.; Lützen, A.; Kosten, M.; Schlemminger, I.; Westerhoff, O.; Saak, W.; Martens, J. *J. Chem. Soc. Perkin I* **2000**, 1867-1871. (f) Maison, W.; Schlemminger, I.; Westerhoff, O.; Martens, J. *Bioorg. Med. Chem.* **2000**, *8*, 1343-1360. (g) Watzke, M.; Schulz, K.; Johannes, K.; Ullrich, P.; Martens, J. *Eur. J. Org. Chem.* **2008**, 3859-386. (h) Schulz, K.; Watzke, M.; Johannes, K.; Ullrich, P.; Martens, J. *Synthesis* **2009**, 665-673. (i) Schwäblein, A.; Martens, J. *Eur. J. Org. Chem.* **2011**, 4335-4344. (j) Stalling, T.; Saak, W.; Martens, J.

Eur. J. Org. Chem. **2013**, 8022-8032. (k) Stalling, T.; Pauly, J.; Schmidtmann, M.; Martens, J. *Eur. J. Org. Chem.* **2014**, 833-843. (l) Brockmeyer, F.; van Gerven, D.; Saak, W.; Martens, J. *Synthesis* **2014**, *46*, 1603-1612. (m) Brockmeyer, F.; Schoemaker, R.; Schmidtmann, M.; Martens, J. *Org. Biomol. Chem.* **2014**, 5168-5181.

8. Selected examples: (a) Günther, K.; Martens, J.; Schickedanz, M. *Angew. Chem.* **1986**, *98*, 284-285; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 278-279. (b) Martens, J.; Bhushan, B. *Chem.-Ztg.* **1988**, *112*, 367-372. (c) Martens, J.; Bhushan, R. *Int. J. Peptid Protein Res.* **1989**, *34*, 433. (d) Martens, J.; Lübben, S. *Tetrahedron* **1990**, *46*, 1231-1234. (e) Lübben, S.; Martens, J.; Haase, D.; Pohl, S.; Saak, W. *Tetrahedron Lett.* **1990**, *31*, 7127-7128. (f) Bhushan, R.; Martens, J.; Wallbaum, S.; Joshi, S.; Parshad, V. *Biomedical Chromatography* **1997**, *11*, 286-288. (g) Review: Martens, J.; Bhushan, R. *Helv. Chimica Acta* **2014**, *97*, 161-187.

