

Appendix 1

AUTOPRESENTATION OF SCIENTIFIC RESULTS

Chiral aziridine junctions as highly efficient catalysts in selected reactions of asymmetric synthesis

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1. Personal data

1.1. Full name

Michał Rachwalski

1.2. Diplomas and degrees held

I have realized my master thesis entitled *Attempts at the synthesis of compounds with potential fluorescent properties* at the Department of Organic Chemistry of the Higher Pedagogical School (actually Jan Długosz University) in Czestochowa under the supervision of dr. Barbara Bachowska.

PhD thesis entitled *Enzyme catalyzed deracemisations and desymmetrisations as methods of the synthesis of chiral heteroorganic compounds* I have done at the Institute of Heteroorganic Chemistry of the Centre of Molecular and Macromolecular Studies Polish Academy of Sciences in Lodz under the supervision of professor Piotr Kiełbasiński. This thesis released new capabilities of the application of enzymes in the synthesis of chiral non-racemic heteroorganic compounds bearing a stereogenic center located both on the sulfur and phosphorus atom or on the carbon atom bound with heteroorganic substituent. So far, for example, enzyme-catalyzed dynamic kinetic resolution of racemic aryl- β -hydroxyalkyl sulfones led to the corresponding acetyl derivatives in high chemical yields and with very high enantiomeric excess. The efficient enzymatic desymmetrisations of prochiral bis(hydroxymethylphenyl) sulfoxide, bis(cyanomethyl) sulfoxide and bis(cyanomethyl)phenylphosphine oxide were also performed. It is worth mention that enzymatic methods of desymmetrisation of such prochiral heteroorganic bis-nitriles were applied at first time. This PhD thesis has been awarded by the Research Council of the Centre of Molecular and Macromolecular Studies Polish Academy of Sciences in Lodz.

1.3. Information about the hitherto employment

01.XI.2003 – 30.IX.2008	technical employee and then assistant in the Institute of Heteroorganic Chemistry of the Centre of Molecular and Macromolecular Studies PAS in Lodz
2.X.2008 – currently	assistant professor in the Department of Organic and Applied Chemistry of University of Lodz

1.4. Numerical summary of scientific achievements

Original papers:

- overall 23 papers (22 experimental papers in full version, all in the foreign journals and 1 review article in *Chemical Society Reviews*), as the first author – 14 papers, as the corresponding author – 12 papers).

Total IF of all the papers: **88,867** (3,86 per one paper)

Sum of points of MSHE: **745** (32,39 per one paper)

*Total IF of the papers being the scientific achievement for habilitation: **12,69** (2,12 per one paper)*

*Sum of points of MSHE of the papers being the scientific achievement for habilitation: **180** (30,0 per one paper)*

Total IF of the papers before the obtainment of PhD degree: **15,632** (3,13 per one paper)

Sum of points of MSHE of the papers before the obtainment of PhD degree: **165** (33 per one paper)

Total IF of the papers after the obtainment of PhD degree: **73.235** (4,07 per one paper)

Sum of points of MSHE of the papers after the obtainment of PhD degree: **580** (32,22 per one paper)

Total amount of citations: **186** (from Web of Science), **195** (from Scopus) on 27.I.2014

Hirsch index: **9** (from Web of Science), **10** (from Scopus) on 27.I.2014

Impact factor (IF) of the scientific papers is given according to the year of publication.

2. Discussion of the most important scientific achievements

2.1. List of publications representing scientific achievements

H1. M. Rachwalski *, S. Jarzyński, S. Leśniak

Highly efficient aziridine ring-containing chiral ligands as catalysts in asymmetric synthesis

Tetrahedron: Asymmetry **2013**, 24, 421 – 425 and *Synfacts* **2013**, 9, 0751 (without **IF**)

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, description and interpretation of the results and preparation of the manuscript and sending it to the journal. My estimated percentage participation: 50%. It is worth mention that this paper is published also in *Synfacts*.

H2. M. Rachwalski *, S. Jarzyński, M. Jasiński, S. Leśniak

Mandelic acid derived α -aziridinyl alcohols as highly efficient ligands for asymmetric additions of zinc organyls to aldehydes

Tetrahedron: Asymmetry **2013**, 24, 689 – 693.

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: partial synthesis, separation and purification of the new catalysts obtained, performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, description and interpretation of the results and partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 60%.

H3. M. Rachwalski *, S. Jarzyński, S. Leśniak

Highly efficient conjugate addition of diethylzinc to enones catalyzed by chiral ligands derived from (*S*)-mandelic acid

Tetrahedron: Asymmetry **2013**, *24*, 1117 – 1119.

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: partial synthesis, separation and purification of the new catalysts obtained, performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, description and interpretation of the results and preparation of the manuscript and sending it to the journal. My estimated percentage participation: 60%.

H4. S. Leśniak, M. Rachwalski *, S. Jarzyński, E. Obijalska

Lactic acid derived aziridinyl alcohols as highly effective catalysts for asymmetric additions of organozinc species to aldehydes

Tetrahedron: Asymmetry **2013**, *24*, 1336 – 1340.

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: partial synthesis, separation and purification of the new catalysts obtained, performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, description and interpretation of the results and preparation of the manuscript and sending it to the journal. My estimated percentage participation: 70%.

H5. M. Rachwalski *

Limonene oxide derived aziridinyl alcohols as highly efficient catalysts for asymmetric additions of organozinc species to aldehydes

Tetrahedron: Asymmetry **2013**, <http://dx.doi.org/10.1016/j.tetasy.2013.11.011>

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: synthesis, separation and purification of the new catalysts obtained, performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, description and interpretation of the results and preparation of the manuscript and sending it to the journal. My estimated percentage participation: 100%.

H6. S. Leśniak, A. M. Pieczonka, S. Jarzyński, K. Justyna, **M. Rachwalski** *

Synthesis and evaluation of catalytic properties of semicarbazides derived from *N*-triphenylmethyl-aziridine-2-carbohydrazides

Tetrahedron: Asymmetry **2013**, *24*, 1341 – 1344.

IF = 2,115 (30 pkt. MSHE)

My contribution consisted in: performing of the test asymmetric reactions for all the catalysts obtained, separation and purification of the aforementioned products, HPLC analysis, partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 20%.

2.2. Introduction for research topics

Asymmetric organic synthesis is still intensively developed field of organic chemistry. Fact, which stereoisomer of the optically pure substance is obtained as a result of the stereocontrolled synthesis, is particularly important when such products will be applied especially in pharmaceutical or food industry. The obtainment of the concrete stereoisomer of the desired compound is precisely determined by the choice of the appropriate chiral catalyst. Therefore, further research on the effective catalysts for stereocontrolled synthesis remains still very essential question in synthetic organic chemistry.

My scientific interest initially covered the use of chiral, optically pure amine alcohols as effective catalysts for stereocontrolled synthesis. However, the chemical literature concerning the use of a such type of chiral catalysts for asymmetric synthesis is extremely extensive, so a spectrum of the novel chiral amines which are potentially useful for the construction of the structures of catalysts becomes more and more limited. An element of the originality of my research is the use of chiral or chiral aziridine ring as amino function for the synthesis of chiral amine alcohols as potential catalysts for asymmetric synthesis. The special feature of aziridines is the formation of stable complexes with zinc halides which was found earlier in our scientific center based on the fact that aziridine ketones form with zinc bromide or chloride extremely stable complexes consisting of two molecules of aziridine and one molecule of zinc halide.¹ The most important feature of such complexes is their ability to undergo of the fully stereoselective reduction using sodium borohydride to form the corresponding aziridine alcohols.^{2,3} From two possible diastereoisomers only one was formed. The same stereochemical result was obtained from a reduction of the free aziridine ketone using zinc borohydride. It was found that a reduction in the absence of zinc salt is a reaction with very low stereoselectivity.

One of the conventional reaction of testing of catalysts for asymmetric synthesis is a reaction of addition of diethylzinc to aldehydes. Based on the knowledge concerning complexing properties of aziridines I decided earlier to investigate an effectiveness of the ligands in which the amino function constitutes an aziridine ring. For example, amine alcohols ligands containing chiral amines and additionally, chiral sulfinyl center, exhibited moderate catalytic activity in the reaction of addition of diethylzinc to benzaldehyde

¹ R. Faure, H. Loiseleur, R. Bartnik, S. Leśniak, A. Laurent, *Cryst. Struct. Commun.* **1981**, *10*, 515 - 519.

² R. Bartnik, S. Leśniak, A. Laurent, *Tetrahedron Lett.* **1981**, 4811 – 4812.

³ R. Bartnik, S. Leśniak, A. Laurent, *J. Chem. Res.* **1982**, *287*, 2701 – 2709.

(enantiomeric excess about 50%).⁴ Modification of these compounds *via* introduction of chiral aziridines as amino functions resulted in the improvement of their effectiveness in this reaction to average 95% ee.⁵ Similarly, very high enantiomeric excess were achieved using these catalysts in the addition of diethylzinc to enones⁶ and the addition of phenylethynylzinc to aldehydes.⁷ The above observations empower me to the hypothesis that amine alcohols with aziridine ring as amino function will be very efficient catalysts/ligands for stereocontrolled reactions with the participation of zinc ions.

My research strategy comprised the synthesis of derivatives in which a ring of chiral or chiral aziridine is attached to the corresponding chiral or chiral core bearing a hydroxyl group. The simplest achiral starting materials proved to be aromatic carboxylic acids bearing additionally a hydroxyl group (**H1**). The transformation of the carboxyl group to an aziridine ring was achieved first *via* corresponding acid chloride and then with the reaction with aziridine, the corresponding amides containing an aziridine ring were obtained. Finally, a reduction of the carbonyl group of amide using triethoxysilane⁸ led to aziridine alcohols in which a chiral aziridine ring is incorporated to an achiral alcohol (**H1**).

Whereas, chiral building units bearing hydroxyl group were derivatives of optically active hydroxyacids like (*S*)-(+)-mandelic acid (**H2**, **H3**) and (*S*)-(+)-lactic acid (**H4**). The introduction of both chiral and chiral aziridine was realized *via* transformation of the carboxyl group into acid chloride, then a reaction with the corresponding aziridine and reduction of the appropriate amide using triethoxysilane to the desired aziridine alcohol. Similar research aspect comprises the synthesis of aziridine alcohols built on the monoterpene system (limonene) (**H5**). The simplest way of the synthesis of such systems is a reaction of nucleophilic cleavage of an oxirane ring of easy available optically active oxiranes of terpenes using aziridine ring as a nucleophilic reagent.

The last group of the chiral catalysts being a contents of this scientific achievement are derivatives of *N*-triphenylmethylaziridine-2-carbohydrazides (**H6**).

All the chiral catalysts obtained in optically pure form were tested in the reactions of asymmetric addition of diethylzinc and phenylethynylzinc to aromatic and aliphatic aldehydes

⁴ M. Rachwalski, M. Kwiatkowska, J. Drabowicz, M. Kłos, W. M. Wieczorek, M. Szyrej, L. Sieroń, P. Kielbasiński, *Tetrahedron: Asymmetry* **2008**, *19*, 2096 – 2101.

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.

⁶ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 1890 – 1892.

⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.

⁸ S. Das, D. Addis, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770 – 1771.

leading to the corresponding chiral alcohols in very good chemical yields and high values of enantiomeric excess. As known from the previous reports,⁹ a simple diphenyl-(1-phenylethyl)aziridine-2-yl-methanol used as a ligand in the reactions of addition of diethylzinc to aldehydes allowed to obtain the adducts with excellent enantiomeric excess, which indicates that a configuration of an aziridine ring is a factor which determines a stereochemical outcome of the addition reaction. The results being a subject of this scientific achievement are in full agreement with this observation. Moreover, the proposed set of catalysts, next to their importance as effective ligands, allowed to define the influence of the another stereogenic centers (excepting aziridine moiety) on the stereochemical outcome of the addition reactions.

The aim of research taken comprises:

- 1) The design and realization of the syntheses of all the chiral junctions bearing an aziridine ring:
 - a) elaboration and optimization of the conditions of the synthesis aforementioned potential chiral catalysts;
 - b) isolation in a pure form, full spectroscopic characterization and determination of an optical purity of the chiral aziridine junctions;
- 2) Realization of the testing asymmetric reactions for all the newly obtained chiral catalysts:
 - a) performing of the asymmetric reactions of addition of diethylzinc and phenylethynylzinc to aromatic and aliphatic aldehydes and addition of diethylzinc to enones;
 - b) isolation of all the products of the addition in a pure state, basic spectroscopic characterization (¹H NMR), determination of an optical purity and ascription of the absolute configuration of such adducts;
 - c) explanation of the influence of the structural elements of the chiral catalysts (especially stereogenic centers) on the stereochemical outcome of the addition reactions.

⁹ M.-C. Wang, Y.-H. Wang, G.-W. Li, P.-P. Sun, J.-X. Tian, H.-J. Lu, *Tetrahedron: Asymmetry* **2011**, 22, 761 – 768.

2.3. Discussion of the results described in publications representing scientific achievements

Publication H1

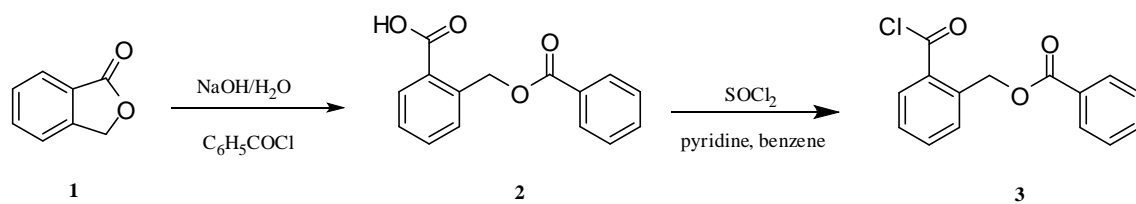
Highly efficient aziridine ring-containing chiral ligands as catalysts in asymmetric synthesis *Tetrahedron: Asymmetry* **2013**, *24*, 421 – 425 and *Synfacts* **2013**, *9*, 0751.

This work describes a highly efficient synthesis of chiral aziridine alcohols built on the simple achiral skeletons of such compounds as salicylic acid and 2-hydroxymethylbenzoic acid and containing an aziridine moiety as amino function, and also the use of the aforementioned compounds as the efficient catalysts for the reactions of asymmetric addition of diethylzinc and phenylethynylzinc to aromatic and aliphatic aldehydes. First, phthalide **1** was converted to 2-benzoyloxymethylbenzoic acid **2** under the action of NaOH and benzoyl chloride. The yield of this reaction was low (26%) but similar to that described earlier in the literature.¹⁰ Subsequently, this acid was converted to 2-benzoyloxymethylbenzoyl chloride **3** in 90% yield using thionyl chloride in the presence of pyridine (Scheme 1). In the next step of the synthesis, 2-benzoyloxymethylbenzoyl chloride **3** and earlier synthesized according to the literature,¹¹ *O*-acetylsalicyloyl chloride **4**, were subjected to the reactions with enantiomerically pure aziridines **5a-c** (obtained according to the procedure described previously¹²) to obtain the corresponding amides **6a-b** and **7a-c** in 89 – 96% yields (Scheme 2). Amides were reduced to the corresponding aziridine alcohols **8a-b** and **9a-c** using triethoxysilane in the presence of zinc acetate. The reactions of reduction of amides proceed in 90 – 96% yields (Scheme 3). In order to obtain the compounds **8a-b** after reduction, deprotection of the benzoyl group was necessary under harsh conditions (NaBH₄, THF/MeOH). Deprotection of the acetyl group (compounds **9a-c**) was spontaneous during the work-up of the mixture after reduction.

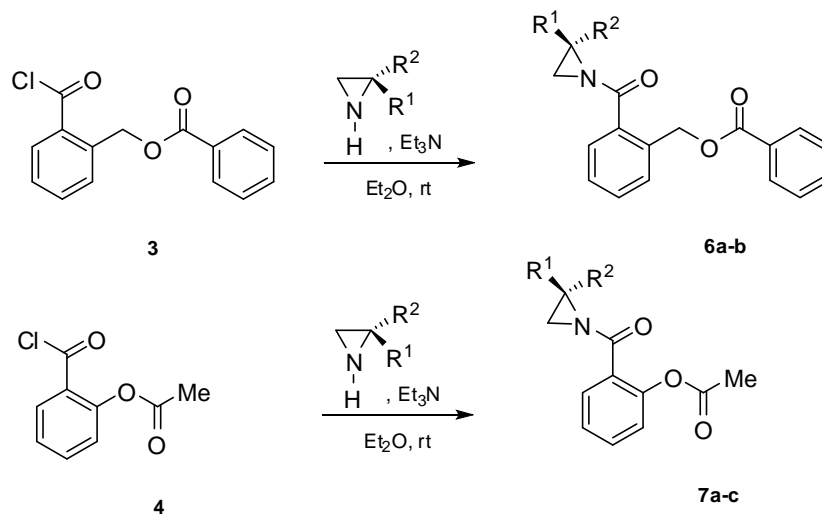
¹⁰ Y.-K. Cheng, P. Duncanson, D. Vaughan Griffiths, *Tetrahedron* **2008**, *64*, 2329 – 2338.

¹¹ K. R. A. Abdellatif, M. A. Chowdhury, Y. Dong, D. Das, G. Yu, C. A. Velázquez, M. R. Suresh, E. E. Knaus, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3014 – 3018.

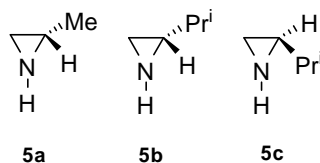
¹² J. Xu, *Tetrahedron: Asymmetry* **2002**, *13*, 1129 – 1134.



Scheme 1. Synthesis of 2-benzoyloxymethylbenzoyl chloride **3**

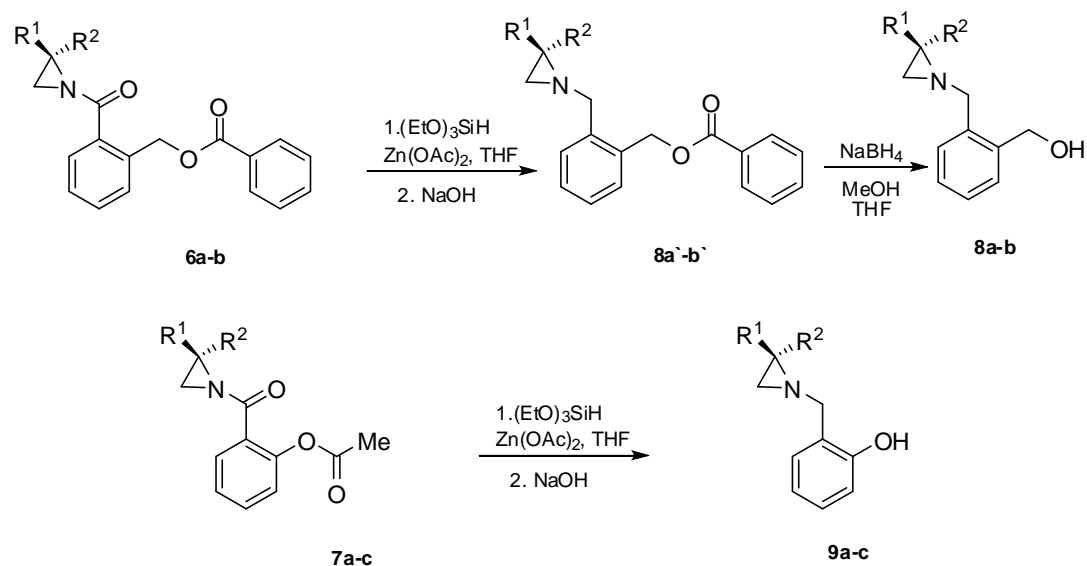


Aziridines



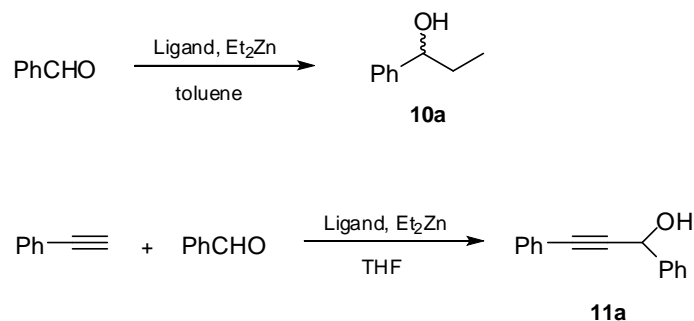
5a) (-)-(*S*)-2-methylaziridine
 5b) (-)-(*S*)-2-isopropylaziridine
 5c) (+)-(*R*)-2-isopropylaziridine

Scheme 2. Synthesis of amides **6a-b** and **7a-c**



Scheme 3. Reduction of amides to the final aziridine alcohols **8a-b** and **9a-c**

In order to investigate the catalytic activity of the compounds **8a-b** and **9a-c** in the reactions of asymmetric addition of diethylzinc and phenylethynylzinc to aldehydes, the additions of the aforementioned organozinc compounds to benzaldehyde were chosen as a model reactions (Scheme 4). The results of these transformations are collected in Table 1.



Scheme 4. Asymmetric addition of diethylzinc and phenylethynylzinc to benzaldehyde

As shown in Table 1, chiral products **10a** and **11a** were formed in good chemical yields and high enantiomeric excess. The best results were achieved using catalyst **8b** built on the scaffold of 2-hydroxymethylbenzoic acid and bearing (*S*)-2-isopropylaziridine moiety as amino function. Moreover, the use of two enantiomeric catalysts **9b** and **9c** led to the formation of opposite enantiomers of the products **10a** and **11a**. On the basis of these results it can be concluded that a stereogenic center located in aziridine moiety has a decisive influence on the stereochemistry of both addition reactions and, therefore, on the absolute configuration of the addition products.

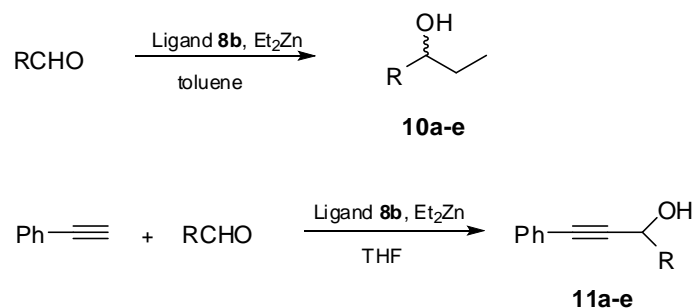
Table 1

Investigation of catalytic activity of ligands **8a-b** and **9a-c**

Entry	Ligand	Product 10a				Product 11a			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf.	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	8a	90	-42.7	95	(<i>S</i>)	86	-4.8	93	(<i>S</i>)
2	8b	93	-44.1	96	(<i>S</i>)	95	-4.9	95	(<i>S</i>)
3	9a	76	-36.0	80	(<i>S</i>)	82	-3.9	76	(<i>S</i>)
4	9b	85	-40.2	92	(<i>S</i>)	88	-4.8	93	(<i>S</i>)
5	9c	82	+38.8	86	(<i>R</i>)	80	+4.3	84	(<i>R</i>)

^aIn chloroform (c 1).^bDetermined by a chiral HPLC.^cTaken from the literature.¹³

Ligand **8b** exhibiting the highest catalytic activity in the addition reactions of diethylzinc and phenylethynylzinc to benzaldehyde, was used as a catalyst in the analogous additions using a broad spectrum of aldehydes (Scheme 5). The results are summarized in Table 2.



Scheme 5. Asymmetric addition of diethylzinc and phenylethynylzinc to aldehydes in the presence of catalyst **8b**

¹³ J.-C. Zhong, S.-C. Hou, Q.-H. Bian, M.-M. Yin, R.-S. Na, B. Zheng, Z.-Y. Li, S.-Z. Liu, M. Wang, *Chem. Eur. J.* **2009**, *15*, 3069 – 3071.

Table 2

Addition of diethylzinc and phenylethynylzinc to aldehydes in the presence of catalyst **8b**

Entry	R	Products 10a-e				Products 11a-e			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	Ph	93	-44.1	92	(S)	95	-4.9	95	(S)
2	2-MeOC ₆ H ₄	91	-47.6	91	(S)	92	-7.5	90	(R)
3	<i>n</i> -Pr	82	+6.0	85	(S)	89	-3.0	86	(S)
4	4-BrC ₆ H ₄	89	-7.9	90	(S)	82	+3.7	86	(R)
5	2-MeC ₆ H ₄	80	-39.8	89	(S)	91	-11.0	88	(R)

^aIn chloroform (c 1).^bDetermined by a chiral HPLC.^cTaken from the literature.^{5,7,14,15}

The results collected in Tables 1 and 2 clearly showed that selected ligand **8b** is an efficient catalyst for both addition reactions leading to the desired chiral products in good chemical yields and high enantiomeric excess. It is worth mention that each of the enantiomeric addition products can be obtained by the choice of the appropriate enantiomer of aziridine for the synthesis of enantiomerically pure catalyst, starting from the same achiral precursor.

Publication H2

Mandelic acid derived α -aziridinyl alcohols as highly efficient ligands for asymmetric additions of zinc organyls to aldehydes

Tetrahedron: Asymmetry **2013**, *24*, 689 – 693.

This work describes a high efficient synthesis of the chiral aziridine alcohols constructed on the chiral scaffold of (*S*)-(+)-mandelic acid bearing an aziridine moiety as amino function and the application of such junctions as effective catalysts for the reactions of

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.

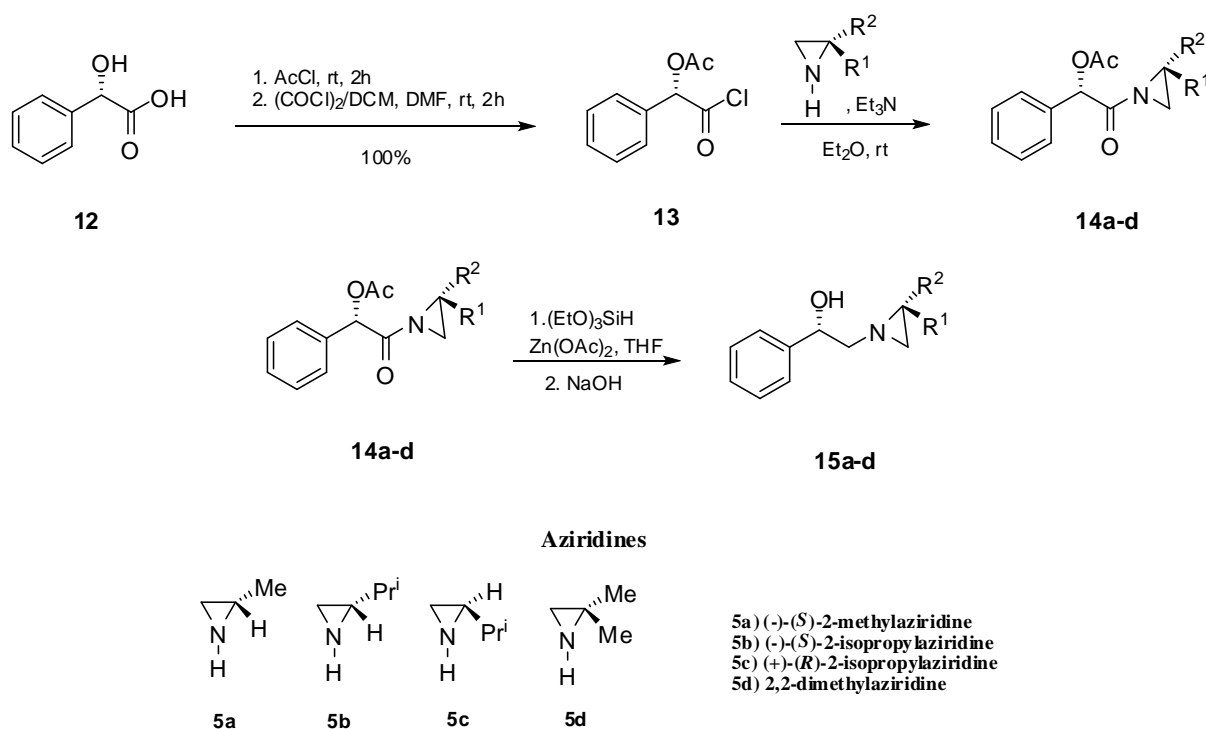
⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.

¹⁴ C.-H. Zhang, S.-J. Yan, S.-Q. Pan, R. Huang, J. Lin, *Bull. Korean. Chem. Soc.* **2010**, *31*, 869 – 873.

¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.

asymmetric addition of diethylzinc and phenylethynylzinc to aromatic and aliphatic aldehydes.

A three-step synthesis of such type of compounds comprises a protection of the free hydroxyl group of (*S*)-(+)-mandelic acid **12** using acetyl chloride and transformation into an acid chloride using oxalyl chloride to form (*S*)-*O*-acetylmandeloyl chloride **13** in quantitative yield. This chloride was then treated with the series of aziridines **5a-d** in the presence of triethylamine at room temperature to afford a series of amides type **14** in excellent yields over 97%. Finally, amides **14a-d** were reduced to the corresponding aziridine alcohols **15a-d** using triethoxysilane in the presence of zinc acetate in boiling tetrahydrofuran (Scheme 6). The chemical yields of the reductions were in the range of 81 – 85%.



Scheme 6. Three-step synthesis of aziridine alcohols **15a-d**

It is also worth mention that ^1H NMR spectra of derivatives **15a-c** bearing non-symmetrical substituted aziridine moieties, contained only one set of signals, whereas, in the proton spectrum of derivative **15d** (bearing achiral 2,2-dimethylaziridine) two sets of signals assigned to the corresponding invertomers of compound **15d** were detected.

The catalytic activity of aziridine alcohols **15d** was checked in the addition reactions of diethylzinc and phenylethynylzinc to benzaldehyde as a model substrate (Scheme 4). The results are collected in Table 3.

Table 3

Addition of diethyl- and phenylethynylzinc to aldehydes in the presence of catalysts **15a-d**

Entry	Ligand	Product 10a				Product 11a			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf.	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	15a	92	-41.4	92	(<i>S</i>)	93	-4.8	93	(<i>S</i>)
2	15b	97	-42.7	95	(<i>S</i>)	95	-4.8	94	(<i>S</i>)
3	15c	96	+41.8	93	(<i>R</i>)	93	+4.6	90	(<i>R</i>)
4	15d	62	-18.9	42	(<i>S</i>)	59	-2.1	40	(<i>S</i>)

^aIn chloroform (c 1).

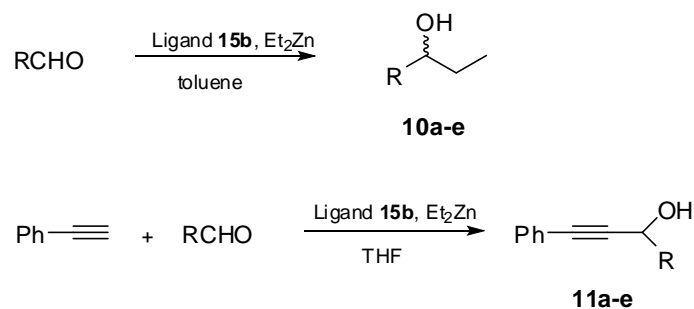
^bDetermined by a chiral HPLC.

^cTaken from the literature.¹³

As shown in Table 3, all the tested aziridine alcohols **15a-d** built on the chiral scaffold of (*S*)-(+)-mandelic acid show the catalytic activity in the aforementioned reactions of asymmetric addition to afford the desired chiral alcohols **10a** and **11a** in high chemical yields and with excellent enantiomeric excess (>92%). In the case of derivative **15d** bearing an achiral 2,2-dimethylaziridine moiety, significant decrease of those values was observed (62% and 59% of chemical yield and 42% and 40% of ee, respectively). It suggests that the presence of a stereogenic center in aziridine moiety has a decisive influence on the stereochemistry of the catalytic reaction. This is also confirmed by the experiments in which two diastereoisomeric ligands **15b-c** were used, affording both enantiomers of adducts.

¹³ J.-C. Zhong, S.-C. Hou, Q.-H. Bian, M.-M. Yin, R.-S. Na, B. Zheng, Z.-Y. Li, S.-Z. Liu, M. Wang, *Chem. Eur. J.* **2009**, *15*, 3069 – 3071.

Catalyst **15b** showing the highest effectiveness in both testing reactions was used then in the analogous testing reactions using a series of aldehydes (Scheme 7, Table 4).



Scheme 7. Asymmetric addition of diethyl- and phenylethynylzinc to aldehydes in the presence of catalyst **15b**

Table 4

Addition of diethyl- and phenylethynylzinc to aldehydes in the presence of catalyst **15b**

Entry	R	Products 10a-e				Products 11a-e			
		Y [%]	$[\alpha]_{\text{D}}^{\text{a}}$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_{\text{D}}^{\text{a}}$	ee [%] ^b	Abs. conf. ^c
1	Ph	97	-42.8	95	(S)	95	-4.8	94	(S)
2	2-MeOC ₆ H ₄	90	-46.0	88	(S)	89	-7.5	90	(R)
3	<i>n</i> -Pr	93	+6.6	94	(S)	92	-3.1	89	(S)
4	4-BrC ₆ H ₄	86	-7.8	89	(S)	85	+3.7	90	(R)
5	2-MeC ₆ H ₄	88	-40.2	90	(S)	88	-10.6	85	(R)

^aIn chloroform (c 1).

^bDetermined by a chiral HPLC.

^cTaken from the literature.^{5,7,14,15}

Data in Table 4 clearly indicate that selected ligand **15b** is a highly effective catalysts for the asymmetric reactions of addition of diethylzinc and phenylethynylzinc to aldehydes leading to the appropriate chiral alcohols in high chemical yields and with excellent enantiomeric excess.

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.

⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.

¹⁴ C.-H. Zhang, S.-J. Yan, S.-Q. Pan, R. Huang, J. Lin, *Bull. Korean. Chem. Soc.* **2010**, *31*, 869 – 873.

¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.

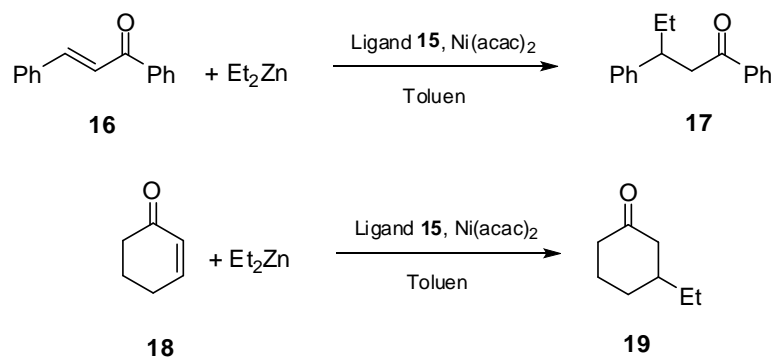
Publication H3

Highly efficient conjugate addition of diethylzinc to enones catalyzed by chiral ligands derived from (*S*)-mandelic acid

Tetrahedron: Asymmetry **2013**, *24*, 1117 – 1119.

This work describes an application of previously synthesized aziridine alcohols **15a-d** (**H2**) as chiral catalysts for the asymmetric Michael addition of diethylzinc to α,β -unsaturated carbonyl compounds (enones).

Therefore, the addition reactions of diethylzinc to chalcone **16** and cyclohexen-2-enone **18** in the presence of catalysts **15a-d** and a metal catalyst like nickel acetylacetonate Ni(acac)₂ were performed (Scheme 8). In order to prove the significance of the use of metal catalyst,^{16,17,18} an experiment without Ni(acac)₂ was also conducted. All the results are summarized in Table 5.



Scheme 8. Asymmetric Michael addition of Et₂Zn to enones in the presence of ligands **15a-d**

As shown in Table 5, the most effective catalyst was aziridine alcohol **15b** bearing (*S*)-2-isopropylaziridine subunit. The formation of enantiomerically enriched products **17** and **19** in the presence of catalyst **15d** (with achiral 2,2-dimethylaziridine subunit) suggests that a stereogenic center located in aziridine moiety has a decisive influence on the stereochemical outcome of the addition. The use of two diastereomeric ligands **15b** and **15c** led to the formation of the chiral products **17** and **19** with opposite absolute configurations. Moreover, in the case of the addition reaction performed without metal catalyst, the products **17** and **19** were formed in significant lower chemical yields and with low enantiomeric excess, which suggests, that the presence of metallic catalyst in reaction medium is necessary.

¹⁶ L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865 – 2878.

¹⁷ A. H. M. de Vries, R. Imbos, B. L. Feringa, *Tetrahedron: Asymmetry* **1997**, *9*, 1467 – 1473.

¹⁸ J. Kang, J. H. Lee, D. S. Lim, *Tetrahedron: Asymmetry* **2003**, *14*, 305 – 315.

Table 5

Asymmetric Michael addition of diethylzinc to enones catalyzed by ligands **15a-d**

Entry	Ligand	Product 17				Product 19			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	15a	90	-2.3	89	(<i>R</i>)	88	-9.5	89	(<i>S</i>)
2	15b	93	-2.3	91	(<i>R</i>)	92	-9.6	90	(<i>S</i>)
3	15b^d	50	-1.2	53	(<i>R</i>)	48	-4.9	46	(<i>S</i>)
4	15c	91	+2.3	90	(<i>S</i>)	90	+9.4	88	(<i>R</i>)
5	15d	42	-1.2	46	(<i>R</i>)	39	-4.7	44	(<i>S</i>)

^aIn chloroform (c 1).^bDetermined by a chiral HPLC.^cTaken from the literature.¹⁹^dWithout Ni(acac)₂

Publication H4

Lactic acid derived aziridinyl alcohols as highly effective catalysts for asymmetric additions of organozinc species to aldehydes

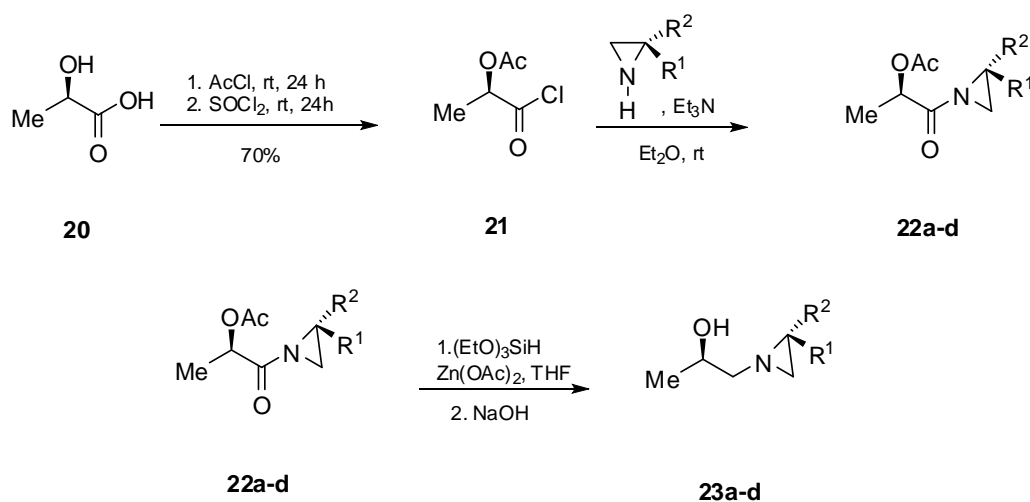
Tetrahedron: Asymmetry **2013**, *24*, 1336 – 1340.

This work describes an efficient synthesis of aziridine alcohols constructed on the chiral skeleton of commercially available (*S*)-(+)-lactic acid and its use as chiral catalysts for asymmetric reaction of addition of diethylzinc and phenylethynylzinc to aldehydes.

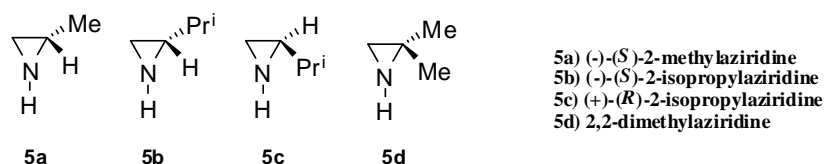
In the first step of the synthesis, (*S*)-(+)-lactic acid **20** was treated with acetyl chloride and thionyl chloride in order to obtain (*S*)-2-acetoxypropionyl chloride **21**. The synthesis ran in 70% yield.²⁰ Chloride was then treated with a series of aziridines **5a-d** in the presence of triethylamine at room temperature to afford the corresponding amides **22a-d** in high chemical yields in the range of 96 – 97%. Amides were subsequently subjected to reduction under conditions described previously (**H1**, **H2**) to afford the desired aziridine alcohols **23a-d** in 77 – 80% yields (Scheme 9).

¹⁹ A. Hajra, N. Yoshikai, E. Nakamura, *Org. Lett.* **2006**, *8*, 4153 – 4155.

²⁰ D. Buisson, R. Azerad, *Tetrahedron: Asymmetry* **1999**, *10*, 2997 – 3002.



Aziridines



Scheme 9. Synthesis of the chiral catalysts **23a-d**

Compounds **23a-d** were tested in the model additions of diethylzinc and phenylethynylzinc to benzaldehyde (Scheme 4). The results collected in Table 6 show that all the aziridine alcohols **23a-d** exhibit a catalytic activity in the model reactions of addition of organozinc compounds to benzaldehyde to afford the desired chiral alcohols **10a** and **11a** in high chemical yields (>85%) and with high enantiomeric excess (>85%). Similarly, as in the case of the catalysts built on the chiral scaffold of (*S*)-(+)-mandelic acid (**H2**), the application of the compound **23d** bearing achiral 2,2-dimethylaziridine subunit led to the formation of the products in lower chemical yield and with average enantiomeric excess. Furthermore, the use of two diastereomeric catalysts **23b** and **23c** furnished the products with comparable optical rotation values, but with opposite signs (therefore, with opposite absolute configurations). The aforementioned results suggest that a stereochemistry of the addition process is mainly dependent on the presence of a stereogenic center located in aziridine moiety.

Table 6

Testing of aziridine alcohols **23a-d** in asymmetric addition of diethylzinc and phenylethynylzinc to benzaldehyde

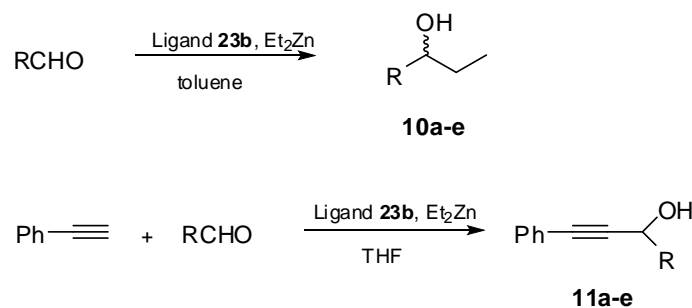
Entry	Ligand	Product 10a				Product 11a			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf.	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	23a	83	-36.0	80	(<i>S</i>)	86	-4.3	85	(<i>S</i>)
2	23b	90	-42.2	94	(<i>S</i>)	91	-4.7	92	(<i>S</i>)
3	23c	87	+39.6	88	(<i>R</i>)	88	+4.4	87	(<i>R</i>)
4	23d	49	-18.0	40	(<i>S</i>)	46	-2.1	42	(<i>S</i>)

^aIn chloroform (c 1).

^bDetermined by a chiral HPLC.

^cTaken from the literature.¹⁵

Catalyst **23b** exhibiting the highest effectiveness in both model reactions was checked in the analogous reactions using another aldehydes (Scheme 10).



Scheme 10. Additions of zinc organyls to aldehydes in the presence of catalyst **23b**

¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.

The results presented in Table 7 confirm the choice of the compound **23b** as the most effective catalyst for the addition reactions described earlier. The catalytic activity showed by all the aziridine alcohols **23a-d** constructed on the chiral platform of (*S*)-(+)-lactic acid is similar to that described previously for derivatives of (*S*)-(+)-mandelic acid (**H2**).

Table 7

Additions of zinc organyls to aldehydes in the presence of catalyst **23b**

Entry	R	Products 10a-e				Products 11a-e			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	Ph	90	-42.2	94	(<i>S</i>)	91	-4.7	92	(<i>S</i>)
2	2-MeOC ₆ H ₄	86	-44.4	85	(<i>S</i>)	85	-7.2	90	(<i>R</i>)
3	<i>n</i> -Pr	90	+6.2	89	(<i>S</i>)	88	-2.9	85	(<i>S</i>)
4	4-BrC ₆ H ₄	82	-7.4	85	(<i>S</i>)	81	+3.5	86	(<i>R</i>)
5	2-MeC ₆ H ₄	84	-38.4	86	(<i>S</i>)	83	-10.1	81	(<i>R</i>)

^aIn chloroform (c 1).

^bDetermined by a chiral HPLC.

^cTaken from the literature.^{5,7,15}

Publication H5

Limonene oxide derived aziridinyl alcohols as highly efficient catalysts for asymmetric additions of organozinc species to aldehydes

Tetrahedron: Asymmetry **2013**, <http://dx.doi.org/10.1016/j.tetasy.2013.11.011>

This work describes an efficient, one-step synthesis of aziridine alcohols built on the skeleton of the terpene compound. As known from the literature,^{21,22} *cis* diastereomer of (*R*)-(+)-limonene oxide can be isolated from commercially available (1:1) mixture of diastereomeric limonene oxides **24**. The selective opening of epoxide ring using

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.

⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.

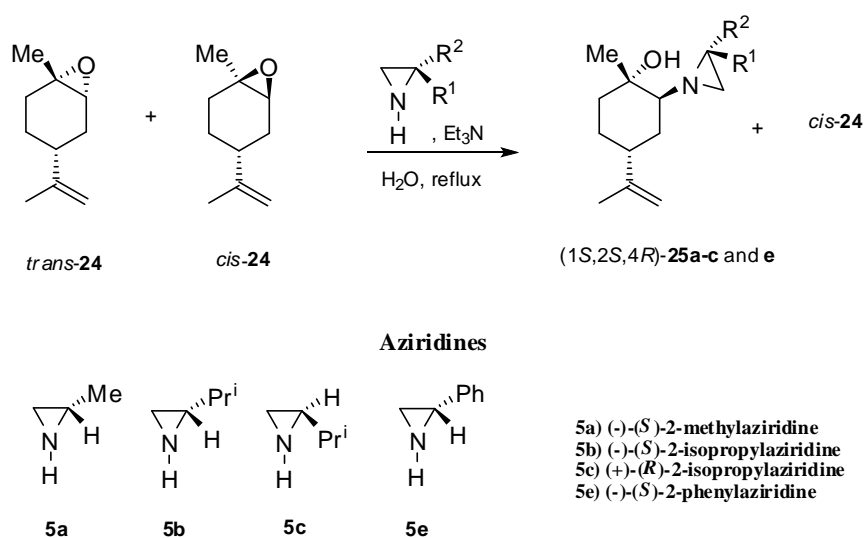
¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.

²¹ C. C. Watts, P. Thoniyot, L. C. Hirayama, T. Romano, B. Singaram, *Tetrahedron: Asymmetry* **2005**, *16*, 1829 – 1835.

²² D. Steiner, L. Ivison, C. T. Goralski, R. B. Appell, J. R. Gojkovic, B. Singaram, *Tetrahedron: Asymmetry* **2002**, *13*, 2359 – 2363.

enantiomerically pure aziridines in the presence of triethylamine allowed to obtain β -aziridine alcohols **25a-c** and **25e** exclusively from the *trans* epoxide (Scheme 11).

Using this reaction, the synthesis of four stereoisomers of β -amino alcohols **25a-c** and **25e** with absolute configuration (1*S*,2*S*,4*R*) from (+)-limonene oxide, was conducted, which is in agreement with a literature report.²³ The chiral catalysts were obtained in 82 – 85% yields.



Scheme 11. Synthesis of aziridine alcohols from (+)-limonene oxide **24**

Like in the previous papers (**H1**, **H2** i **H4**), the novel compounds **25a-c** and **25e** were tested in the model reactions of addition of diethylzinc and phenylethynylzinc to benzaldehyde (Scheme 4). The results of the reactions (collected in Table 8) showed that all the aziridine alcohols **25** are very efficient catalysts for the aforementioned testing reactions leading to the corresponding chiral alcohols **10a** and **11a** in very high chemical yield values and with big enantiomeric excess. The results also suggest that the influence of a stereogenic center located in the aziridine moiety on the stereochemical outcome of addition is not crucial in this case. The results of the addition reactions catalyzed by diastereomeric ligands **25b** and **25c**, where chiral products exhibited comparable optical rotations and identical absolute configurations, are the confirmation of this observation.

²³ D. Steiner, S. G. Sethofer, C. T. Goralski, B. Singaram, *Tetrahedron: Asymmetry* **2002**, *13*, 1477 – 1483.

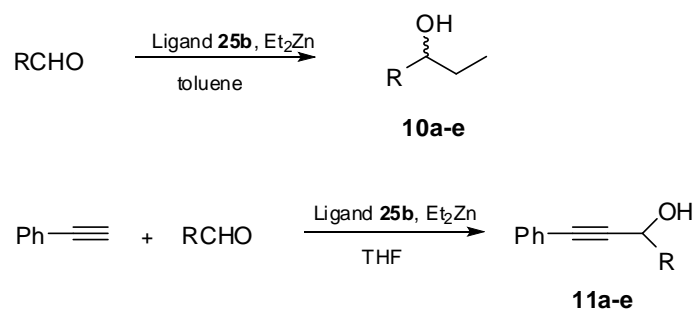
Table 8

Addition of diethyl- and phenylethynylzinc to benzaldehyde catalyzed by ligands **25**

Entry	Ligand	Product 10a				Product 11a			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf.	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	25a	92	+40.5	90	(<i>R</i>)	89	-4.5	88	(<i>S</i>)
2	25b	97	+43.1	96	(<i>R</i>)	96	-4.9	95	(<i>S</i>)
3	25c	91	+40.0	89	(<i>R</i>)	88	-4.4	86	(<i>S</i>)
4	25e	96	+42.3	94	(<i>R</i>)	92	-4.8	91	(<i>S</i>)

^aIn chloroform (c 1).^bDetermined by a chiral HPLC.^cTaken from the literature.¹³

The scope of the catalytic activity of aziridine alcohol **25b** was extended to the addition reactions of organozinc compounds to another aldehydes (Scheme 12).

Scheme 12. Addition of organozinc compounds to aldehydes catalyzed by ligand **25b**

As can be seen in Table 9, all the aforementioned addition reactions proceed very efficiently leading to the chiral alcohols **10a-e** and **11a-e** in very high chemical yields and with excellent enantiomeric excess.

¹³ J.-C. Zhong, S.-C. Hou, Q.-H. Bian, M.-M. Yin, R.-S. Na, B. Zheng, Z.-Y. Li, S.-Z. Liu, M. Wang, *Chem. Eur. J.* **2009**, *15*, 3069 – 3071.

Table 9

Addition of organozinc compounds to aldehydes in the presence of catalyst **25b**

Entry	R	Products 10a-e				Products 11a-e			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	Ph	97	+43.1	96	(<i>R</i>)	96	-4.9	95	(<i>S</i>)
2	2-MeOC ₆ H ₄	95	+48.1	92	(<i>R</i>)	91	+7.5	90	(<i>S</i>)
3	<i>n</i> -Pr	92	-6.5	93	(<i>R</i>)	92	-3.2	92	(<i>S</i>)
4	4-BrC ₆ H ₄	94	+8.3	95	(<i>R</i>)	93	-3.9	94	(<i>S</i>)
5	2-MeC ₆ H ₄	92	+41.5	93	(<i>R</i>)	90	+11.3	91	(<i>S</i>)

^aIn chloroform (c 1).^bDetermined by a chiral HPLC.^cTaken from the literature.^{5,7,14,15}

The analysis of the absolute configurations of the adducts suggest that an attack of organozinc reagents catalyzed by ligand **25b** always takes place from the same side, which is in agreement with the proposed transition state models for the reactions of addition of diethylzinc and alkynylzinc catalyzed by derivatives of (+)-limonene oxide.^{21,23} The use of chiral amine alcohols with absolute configuration of (1*S*,2*S*,4*R*) (from (+)-limonene oxide) led to the formation of the adducts with (*R*)-configuration for diethylzinc and the adducts with (*S*)-configuration for phenylethynylzinc.

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.¹⁴ C.-H. Zhang, S.-J. Yan, S.-Q. Pan, R. Huang, J. Lin, *Bull. Korean. Chem. Soc.* **2010**, *31*, 869 – 873.¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.²¹ C. C. Watts, P. Thoniyot, L. C. Hirayama, T. Romano, B. Singaram, *Tetrahedron: Asymmetry* **2005**, *16*, 1829 – 1835.²³ D. Steiner, S. G. Sethofer, C. T. Goralski, B. Singaram, *Tetrahedron: Asymmetry* **2002**, *13*, 1477 – 1483.

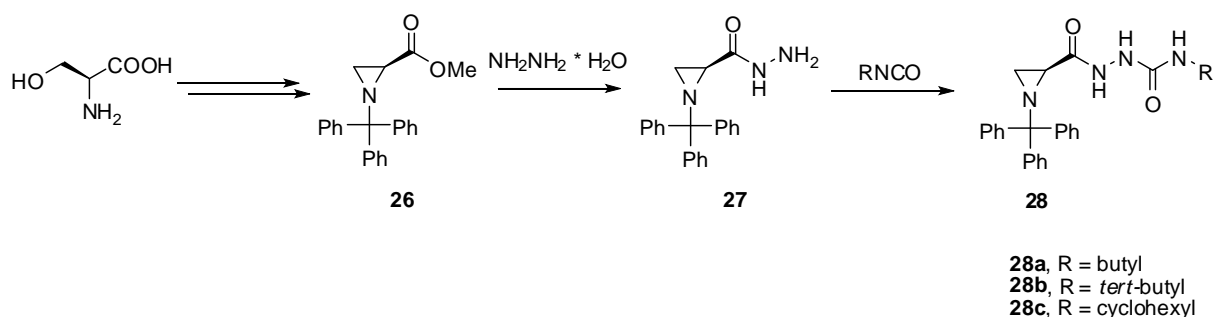
Publication H6

Synthesis and evaluation of catalytic properties of semicarbazides derived from *N*-triphenylmethyl-aziridine-2-carbohydrazides

Tetrahedron: Asymmetry **2013**, *24*, 1341 – 1344.

This work describes an efficient synthesis of semicarbazides from *N*-triphenylmethylaziridine-2-carbohydrazide and its application as catalysts in the asymmetric addition of organozinc compounds to aldehydes.

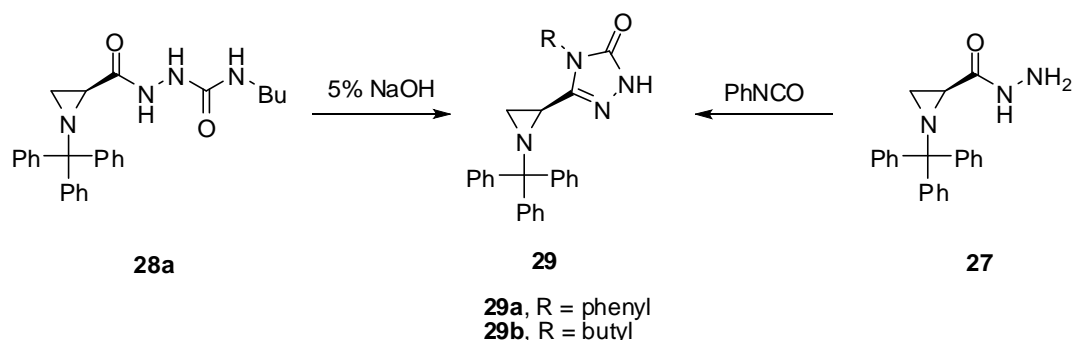
The general method of the synthesis of esters of type **26** is a cyclization of commercially available derivatives of L-serine.²⁴ Such obtained methyl (*S*)-*N*-triphenylmethylaziridinate **26** was converted into a hydrazide of (*S*)-*N*-triphenylmethylaziridine **27** using hydrazine hydrate in 90% yield. The reactions of hydrazide **27** with alkyl isocyanates in dichloromethane at room temperature afforded semicarbazides **28** in very high chemical yields (97 – 98%) (Scheme 13).



Scheme 13. Synthesis of semicarbazides **28**

It is worth mention that in the case of the reaction of compound **27** with phenyl isocyanate under analogous conditions applied in the synthesis of derivatives **28**, 1,2,4-triazole-3-one **29a** was formed as a sole product. Therefore, it was decided to synthesize 1,2,4-triazole-3-one from semicarbazide **28** under basic conditions. So far, heating of compound **28a** in 5% aqueous solution of NaOH led to the expected cyclic product **29b** in 20% yield (Scheme 14).

²⁴ H. Liu, V. R. Pattabiraman, J. C. Vederas, *Org. Lett.* **2007**, *9*, 4211 – 4214.



Scheme 14. Synthesis of 1,2,4-triazole-3-ones **29**

The catalytic activity of the new semicarbazides **28a-c** was checked in the model reactions of addition of diethylzinc and phenylethynylzinc to benzaldehyde (Scheme 4). The cyclic derivatives **29a-b** proved to be practically insoluble in the most available organic solvents, whereby its use in asymmetric synthesis proved to be impossible.

Table 10

Addition of organozinc compounds to benzaldehyde catalyzed by semicarbazides **28**

Entry	Ligand	Product 10a				Product 11a			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	28a	92	-33.8	75	(S)	84	-3.8	73	(S)
2	28b	96	-41.0	91	(S)	92	-4.6	90	(S)
3	28c	97	-41.9	93	(S)	95	-5.0	97	(S)

^aIn chloroform (c 1).

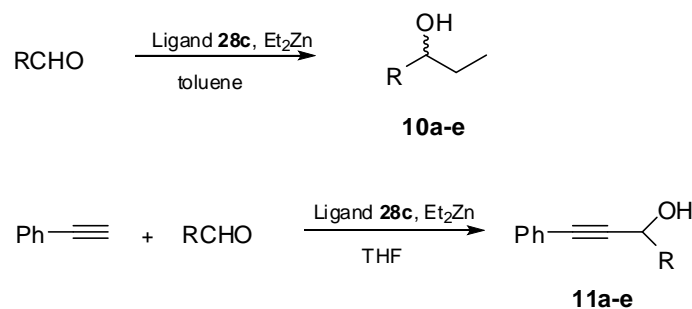
^bDetermined by a chiral HPLC.

^cTaken from the literature.²⁵

As shown in Table 10, all semicarbazides **28** proved to be efficient catalysts in the model addition reactions. The use of catalyst **28a** bearing *n*-butyl group led to the formation of chiral alcohols **10a** and **11a** in somewhat lower values of chemical yield and enantiomeric excess. This may suggest that a size of the substituent has an influence on the stereochemistry of the addition processes.

Another aldehydes were used as starting materials in the analogous addition reactions in order to extend the scope of catalytic activity of semicarbazide **28c** (Scheme 15).

²⁵ M. Rachwałski, S. Jarzyński, S. Leśniak, *Tetrahedron: Asymmetry* **2013**, *24*, 421 – 425.



Scheme 15. Additions of organozinc compounds to aldehydes in the presence of **28c**

Table 11

Additions of organozinc compounds to aldehydes catalyzed by ligand **28c**

Entry	R	Products 10a-e				Products 11a-e			
		Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c	Y [%]	$[\alpha]_D^a$	ee [%] ^b	Abs. conf. ^c
1	Ph	97	-41.9	93	(S)	95	-4.9	97	(S)
2	2-MeOC ₆ H ₄	91	-49.1	94	(S)	93	-7.8	93	(R)
3	<i>n</i> -Pr	85	+6.1	87	(S)	85	-2.9	84	(S)
4	4-BrC ₆ H ₄	93	-8.1	92	(S)	93	+3.7	91	(R)
5	2-MeC ₆ H ₄	89	-41.1	92	(S)	90	-11.3	91	(R)

^aIn chloroform (c 1).

^bDetermined by a chiral HPLC.

^cTaken from the literature.^{5,7,14,15}

As presented in Table 11, chiral alcohols **10a-e** and **11a-e** were formed in very high chemical yields and big enantiomeric excess. Somewhat lower values were obtained in the case when butyraldehyde was used as a starting material.

⁵ S. Leśniak, M. Rachwalski, E. Sznajder, P. Kielbasiński, *Tetrahedron: Asymmetry* **2009**, *20*, 2311 – 2314.

⁷ M. Rachwalski, S. Leśniak, P. Kielbasiński, *Tetrahedron: Asymmetry* **2010**, *21*, 2687 – 2689.

¹⁴ C.-H. Zhang, S.-J. Yan, S.-Q. Pan, R. Huang, J. Lin, *Bull. Korean. Chem. Soc.* **2010**, *31*, 869 – 873.

¹⁵ Y.-J. Chen, R.-X. Lin, C. Chen, *Tetrahedron: Asymmetry* **2004**, *15*, 3561 – 3571.

Conclusions and future perspectives:

The hypothesis put at the beginning of the studies assuming that amine alcohols bearing an aziridine ring as amino function will be efficient catalysts for stereocontrolled reactions with the participation of zinc ions, was fully confirmed. All the new obtained aziridine junctions built on both achiral and chiral platforms, exhibited very high catalytic activity in the testing asymmetric reactions, leading to the formation of the chiral products in high chemical yields and big enantiomeric excess. The results being the content of the publications indicated as the scientific achievements allow to plan with great optimism of the methods of the synthesis of further chiral aziridine junctions being potential efficient catalysts for asymmetric synthesis. The elaboration and realization of a methodology of the synthesis of chiral aziridine alcohols constructed on the scaffolds of bicyclic compounds and a broadening of the spectrum of the testing asymmetric reactions, constitute aims for the nearest future.

3. Other publications and achievements

3.1. Additional publications

Original papers before the obtainment of PhD degree:

- 1) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk, M. A. H. Moelands, B. Zwanenburg, F. P. J. T. Rutjes

Lipase-promoted dynamic kinetic resolution of racemic β -hydroxyalkyl sulfones

Tetrahedron: Asymmetry **2005**, *16*, 2157 – 2160, IF = 2,429 (30 points of MSHE)

My contribution consisted in: synthesis of the starting racemic sulfones, performing of chemoenzymatic DKR processes, isolation of the products, registration and interpretation of NMR spectra and determination of enantiomeric excess values. My estimated percentage participation: 50%.

- 2) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk, M. Szyrej, M. W. Wieczorek, R. Wijtmans, F. P. J. T. Rutjes

Enzyme-promoted desymmetrisation of prochiral bis(cyanomethyl) sulfoxide

Adv. Synth. Catal. **2007**, *349*, 1387 – 1392, IF = 4,977 (45 points of MSHE)

My contribution consisted in: synthesis of a prochiral bis-cyanomethyl sulfoxide, performing of enzymatic desymmetrisations, isolation of the products, registration and interpretation of NMR spectra, determination

of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

- 3) P. Kielbasiński, **M. Rachwalski**, M. Kwiatkowska, M. Mikołajczyk, W. M. Wieczorek, M. Szyrej, L. Sieroń, F. P. J. T. Rutjes

Enzyme-promoted desymmetrisation of prochiral bis(cyanomethyl)phenylphosphine oxide

Tetrahedron: Asymmetry **2007**, *18*, 2108 – 2112, IF = 2,634 (30 points of MSHE)

My contribution consisted in: synthesis of the starting prochiral phosphine oxide, performing of enzymatic desymmetrisations, isolation of the products, registration and interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

- 4) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk, F. P. J. T. Rutjes

Nitrilase-catalysed hydrolysis of cyanomethyl *p*-tolyl sulfoxide: stereochemistry and mechanism

Tetrahedron: Asymmetry **2008**, *19*, 562 – 567, IF = 2,796 (30 points of MSHE)

My contribution consisted in: synthesis of the starting racemic sulfoxide, performing of enzymatic desymmetrisations, isolation of the products, registration and interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

- 5) **M. Rachwalski**, M. Kwiatkowska, J. Drabowicz, M. Kłós, W. M. Wieczorek, M. Szyrej, L. Sieroń, P. Kielbasiński

Enzyme-promoted desymmetrization of bis(2-hydroxymethylphenyl)sulfoxide as a route to tridentate chiral catalysts

Tetrahedron: Asymmetry **2008**, *19*, 2096 – 2101, IF = 2,796 (30 points of MSHE).

My contribution consisted in: synthesis of the starting prochiral sulfoxide, performing of enzymatic desymmetrisations, isolation of the products, registration and interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 50%.

Original papers after the obtainment of PhD degree (papers are not a part of achievements included in paragraph 2.1):

- 1) **M. Rachwalski**, S. Leśniak, E. Sznajder, P. Kielbasiński

Highly enantioselective Henry reaction catalyzed by chiral tridentate heteroorganic ligands

Tetrahedron: Asymmetry **2009**, *20*, 1547 – 1549, IF = 2,625 (30 points of MSHE)

My contribution consisted in: performing of Henry reactions with various aldehydes, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

- 2) A. Chrostowska, A. Dargelos, A. Graciaa, S. Khayar, S. Leśniak, R. B. Nazarski, T.-X. Mai Nguyen, M. Maciejczyk, **M. Rachwalski**

Flash vacuum thermolysis generation and UV-photoelectron spectroscopy study of the *N*-substituted iminoacetonitriles

Tetrahedron **2009**, *65*, 9322 – 9327, IF = 3,219 (30 points of MSHE)

My contribution consisted in: synthesis of the starting compound. My estimated percentage participation: 10%.

- 3) S. Leśniak, **M. Rachwalski**, E. Sznajder, P. Kielbasiński

New highly efficient aziridine-functionalized tridentate sulfinyl catalysts for enantioselective diethylzinc addition to carbonyl compounds

Tetrahedron: Asymmetry **2009**, *20*, 2311 – 2314, IF = 2,625 (30 points of MSHE)

My contribution consisted in: performing of the addition reactions of diethylzinc to various aldehydes, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

- 4) **M. Rachwalski**, S. Leśniak, P. Kielbasiński

Highly enantioselective conjugate addition of diethylzinc to enones using aziridine-functionalized tridentate sulfinyl ligands

Tetrahedron: Asymmetry **2010**, *21*, 1890 – 1892, IF = 2,484 (30 points of MSHE)

My contribution consisted in: synthesis of the ligands, performing of the additions of diethylzinc to enones, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 70%.

- 5) **M. Rachwalski***, S. Leśniak, P. Kielbasiński

Highly enantioselective addition of phenylethynylzinc to aldehydes using aziridine-functionalized tridentate sulfinyl ligands

Tetrahedron: Asymmetry **2010**, *21*, 2687 – 2689, IF = 2,484 (30 points of MSHE)

My contribution consisted in: synthesis of the ligands, performing of addition reactions of phenylethynylzinc to various aldehydes, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 70%.

- 6) **M. Rachwalski***, S. Leśniak, P. Kielbasiński

Highly enantioselective Aza-Henry reaction promoted by amine-functionalized tridentate sulfinyl ligands

Tetrahedron: Asymmetry **2011**, 22, 1087 – 1089, IF = 2,652 (30 points of MSHE)

My contribution consisted in: synthesis of the ligands, performing of the Aza-Henry reactions, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 70%.

- 7) S. Kaczmarczyk, M. Kwiatkowska, L. Madalińska, A. Barbachowska, **M. Rachwalski**, J. Błaszczuk, L. Sieroń, P. Kiełbasiński

Enzymatic synthesis of enantiopure precursors of chiral bidentate and tridentate phosphorus catalysts

Adv. Synth. Catal. **2011**, 353, 2446 – 2454, IF = 6,048 (45 points of MSHE)

My contribution consisted in: preliminary attempts at the synthesis of organophosphorus junctions. My estimated percentage participation: 15%.

- 8) **M. Rachwalski***, S. Leśniak, P. Kiełbasiński

Highly enantioselective asymmetric direct aldol reaction catalyzed by amine-functionalized tridentate sulfinyl ligands

Tetrahedron: Asymmetry **2011**, 22, 1325 – 1327, IF = 2,652 (30 points of MSHE)

My contribution consisted in: synthesis of the ligands, performing of the reactions of aldol condensation, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 70%.

- 9) **M. Rachwalski***, T. Leenders, S. Kaczmarczyk, P. Kiełbasiński, S. Leśniak, F. P. J. T. Rutjes

Efficient catalysts for asymmetric Mannich reactions

Org. Biomol. Chem. **2013**, 11, 4207 – 4213, IF = 3,568 (35 points of MSHE)

My contribution consisted in: partial performing of Mannich reactions, isolation of the products, interpretation of NMR spectra, determination of enantiomeric excess and partial preparation of the manuscript and sending it to the journal. My estimated percentage participation: 50%.

- 10) P. Kiełbasiński, **M. Rachwalski**, S. Kaczmarczyk, S. Leśniak

Polydentate chiral heteroorganic ligands/catalysts – impact of particular functional groups on their activity in selected reactions of asymmetric synthesis

Tetrahedron: Asymmetry **2013**, 24, 1417 – 1420, IF = 2,115 (30 points of MSHE)

My contribution consisted in: partial synthesis of the ligands, performing of Henry reactions, isolation of the products, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

11) **M. Rachwalski***, S. Kaczmarczyk, S. Leśniak, P. Kielbasiński

Highly efficient asymmetric Simmons-Smith cyclopropanation promoted by chiral heteroorganic aziridinyl ligands

ChemCatChem **2014**, *6*, DOI: 10.1002/cctc.201300883, IF = 5,181 (30 points of MSHE)

My contribution consisted in: partial synthesis of the ligands, performing of Simmons-Smith reactions, isolation of the products, determination of enantiomeric excess and partial preparation of the manuscript. My estimated percentage participation: 60%.

Review article after the obtainment of PhD degree (paper is not a part of achievements included in paragraph 2.1):

1) **M. Rachwalski***, N. Vermue, F. P. J. T. Rutjes

Recent advances in enzymatic and chemical deracemisation of racemic compounds

Chem. Soc. Rev. **2013**, *42*, 9268 – 9282, IF = 24,892 (50 points of MSHE)

My contribution consisted in: partial collecting of the materials and partial preparation of the manuscript. My estimated percentage participation: 40%.

3.2. Conference reports

Oral presentations before the obtainment of PhD degree:

1) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk

Katalizowane enzymami deracemizacje i desymetryzacje jako metody syntezy chiralnych połączeń heteroorganicznych

Postępy w syntezie związków nieracemicznych, III Seminarium Sekcji Chemii Organicznej PTChem, Karpacz, 12 – 14th October 2006, Abstract K – 17.

2) **M. Rachwalski**, P. Kielbasiński

Enzyme-promoted desymmetrisation in the synthesis of chiral non-racemic organophosphorus compounds

5th European Workshop on Phosphorus Chemistry, Regensburg (Germany), 10 – 11th March 2008, Abstract 6-2

Poster presentations before the obtainment of PhD degree:

1) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk

Lipase-catalysed kinetic resolution of hydroxyalkyl sulfones

- 7th International Conference on Heteroatom Chemistry (ICHAC-7)*, Shanghai (China),
20 – 25th September 2004
- 2) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk, R. Wijnmans, F. P. J. T. Rutjes
Enzyme-promoted hydrolysis of prochiral bis(cyanomethyl) sulfoxide
22nd International Symposium on the Organic Chemistry of Sulfur, Saitama (Japan),
20 – 25th September 2006, Abstract P – 60
- 3) **M. Rachwalski**, P. Kielbasiński, W. M. Wieczorek, M. Szyrej, L. Sieroń
Crystal and molecular structure of 2-acetoxymethylphenyl-2'-hydroxymethylphenyl
sulfoxide
XIIth International Seminar on Physics and Chemistry of Solids, Ustroń Śląski, 10 –
13th Juni 2007, Abstract P2_18
- 4) P. Kielbasiński, **M. Rachwalski**, M. Mikołajczyk
Enzymatic desymmetrisation of bis(2-hydroxymethylphenyl) sulfoxide and phosphine
oxides
8th International Symposium on Biocatalysis and Biotransformations (Biotrans 2007),
Oviedo (Spain), 8 – 13th July 2007, Abstract P 162
- 5) **M. Rachwalski**, P. Kielbasiński, M. Mikołajczyk
Enzyme-promoted kinetic resolution of racemic cyanomethyl *p*-tolyl sulfoxide
5th International Congress of Young Chemists, Jurata, 10 – 14th October 2007,
Abstract P 26
- 6) P. Kielbasiński, **M. Rachwalski**, M. Kwiatkowska, M. Mikołajczyk
Katalizowana enzymami desymetryzacja jako źródło potencjalnych trójzębnych
ligandów w katalizie organicznej
VIII Ogólnopolskie Sympozjum Chemii Organicznej (OSCO-VIII), Łódź, 10 – 12th
April 2008, Abstract P – 105
- 7) P. Kielbasiński, **M. Rachwalski**, M. Kwiatkowska
New achievements in enzyme-promoted syntheses of chiral, non-racemic
heteroorganic compounds
Vth International Congress on Biocatalysis (BIOCAT 2008), Hamburg (Germany), 31st
August – 4th September 2008, Abstract L 59a

Oral presentations after the obtainment of PhD degree:

1) **M. Rachwalski**

Biotransformations as synthetic methods

Seminar lecture in the group of Professor P. Schreiner, Justus-Liebig University of Giessen (Germany), 12th December 2008.

2) **M. Rachwalski**

Chiral tridentate ligands as catalysts in asymmetric synthesis

IIIrd International Mini-Symposium – Advances in Organocatalysis and Related Problems, Lodz, 25th May 2010, Abstract L – 6.

3) **M. Rachwalski**

Chiralne ligandy trójzębne jako katalizatory w syntezie asymetrycznej

Postępy w syntezie związków nieracemicznych – V Seminarium Sekcji Chemii Organicznej PTChem, Kudowa – Zdrój, 13 – 16th October 2010, Abstract K – 18.

4) **M. Rachwalski**

Enzymy w chemii

Akademia Ciekawej Chemii 2010/2011, University of Lodz, 16th February 2011

5) **M. Rachwalski**

Chiral ligands as catalysts in asymmetric synthesis

Seminar lecture in the group of Professor P. Schreiner, Justus-Liebig University of Giessen (Germany), 16th Juni 2011

6) **M. Rachwalski**, S. Leśniak

Nowe chiralne ligandy jako katalizatory w syntezie asymetrycznej

54 Zjazd PTChem, Lublin, 18 – 22nd September 2011, Abstract S04 – K9.

7) S. Jarzyński, **M. Rachwalski**, S. Leśniak

Optycznie czyste azirydynyloalkohole jako katalizatory w syntezie asymetrycznej

30 Wiosenny zjazd Sekcji Studenckiej PTChem, Augustow, 11 – 14th April 2013, Abstract O17

8) S. Jarzyński, **M. Rachwalski**, S. Leśniak

Asymetryczna addycja dietylocynku i fenyloetynylocynku do aldehydów katalizowana chiralnymi ligandami

I Łódzkie Sympozjum Doktorantów Chemii, Lodz, 18 – 19th April 2013, Abstract (Presentation no. 10)

9) S. Jarzyński, **M. Rachwalski**, S. Leśniak

Nowe chiralne azirydnoalkohole jako efektywne katalizatory w asymetrycznej addycji związków cynkoorganicznych do aldehydów

16 Ogólnopolska Sesja Wykładowa Koła Naukowego Studentów Wydziału Chemii Politechniki Łódzkiej, Konopnica, 10 – 12th May, Abstract page 17

10) **M. Rachwalski**, P. Kiełbasiński, S. Leśniak, F. P. J. T. Rutjes

Asymetryczna reakcja Mannicha katalizowana chiralnymi ligandami i ultradźwiękami
56 Zjazd Naukowy PTChem i Stowarzyszenia Inżynierów i Techników Przemysłu Chemicznego, Siedlce, 16 – 20th September, Abstract S01K14

Komunikaty posterowe po uzyskaniu stopnia naukowego doktora:

1) **M. Rachwalski**, S. Leśniak, P. Kiełbasiński

Trójzębne ligandy jako enancjoselektywne katalizatory w syntezie asymetrycznej
52 Zjazd PTChem, Lodz, 12 – 16th September 2009, Abstract A 048

2) **M. Rachwalski**, S. Leśniak, P. Kiełbasiński

Asymetryczna addycja dietylocynku do związków karbonylowych katalizowana trójzębnymi chiralnymi ligandami
XII Ogólnopolskie Sympozjum Sekcji Chemii Heteroorganicznej PTChem – Postępy w chemii związków heteroorganicznych, Lodz, 27th November 2009, Abstract P – 40

3) **M. Rachwalski**, S. Leśniak, P. Kiełbasiński

Asymetryczna addycja fenyloetylocynku do aldehydów, katalizowana trójzębnymi chiralnymi ligandami
XIII Ogólnopolskie Sympozjum Chemii Heteroorganicznej PTChem – Postępy w chemii związków heteroorganicznych, Lodz, 19th November 2010, Abstract P – 21

4) **M. Rachwalski**, S. Leśniak, M. Jasiński, G. Młostoń

Nowe chiralne ligandy funkcjonalizowane azirydynami jako potencjalne katalizatory w syntezie asymetrycznej
IX Ogólnopolskie Sympozjum Chemii Organicznej, Warsaw, 6 – 9th April 2011, Abstract P – 42

5) **M. Rachwalski**, S. Leśniak, P. Kiełbasiński

Tridentne heteroorganiczne ligandy jako wydajne katalizatory w syntezie asymetrycznej

- XIV Ogólnopolskie Sympozjum Sekcji Chemii Heteroorganicznej PTChem – Postępy w chemii związków heteroorganicznych*, Lodz, 18th November 2011, Abstract P – 13
- 6) **M. Rachwalski**, T. Leenders, P. Kielbasiński, F. P. J. T. Rutjes
New catalysts for asymmetric Mannich reaction
NOW CW Study group meeting – Organic Chemistry & Synthesis, Lunteren (The Netherlands), 22 – 24th October 2012, Abstract 134
- 7) S. Jarzyński, S. Leśniak, **M. Rachwalski**
Synteza i badanie aktywności katalitycznej nowych chiralnych ligandów azirydynowych
III Sesja Magistrantów i Doktorantów Łódzkiego Środowiska Chemików, Lodz, 12th Juni 2012, Abstract 113
- 8) S. Kaczmarczyk, **M. Rachwalski**, S. Leśniak, P. Kielbasiński
25th International Symposium on the Organic Chemistry of Sulfur, Czestochowa, 24 – 29th Juni 2012, Abstract PC – 20
- 9) S. Jarzyński, S. Leśniak, **M. Rachwalski**
Synthesis and studies on the catalytic activity of New chiral aziridinyl ligands
XV Ogólnopolskie Sympozjum Sekcji Chemii Heteroorganicznej PTChem – Postępy w chemii związków heteroorganicznych, Lodz, 16th November 2012, Abstract P – 72
- 10) **M. Rachwalski**, S. Kaczmarczyk, T. Leenders, P. Kielbasiński, S. Leśniak, F. P. J. T. Rutjes
New tridentate sulfinyl ligands for asymmetric Mannich reactions
XV Ogólnopolskie Sympozjum Sekcji Chemii Heteroorganicznej PTChem – Postępy w chemii związków heteroorganicznych, Lodz, 16th November 2012, Abstract P – 81
- 11) S. Jarzyński, S. Leśniak, **M. Rachwalski**
Synthesis and studies on the catalytic activity of new aziridinyl ligands
15th JCF-Frühjahrssymposium, Berlin, 6 – 9th March 2013, Abstract 176
- 12) A. M. Pieczonka, **M. Rachwalski**, S. Jarzyński, K. Justyna, S. Leśniak
Synteza i badanie właściwości katalitycznych nowych semikarbazydów pochodnych hydrazynu kwasu *N*-trifenylometylo-azirydino-2-karboksyłowego

56 Zjazd Naukowy PTChem i Stowarzyszenia Inżynierów i Techników Przemysłu Chemicznego, Siedlce, 16 – 20th September 2013, Abstract S01P68

13) S. Jarzyński, **M. Rachwalski**, S. Leśniak

Nowe chiralne azirydyoalkohole jako efektywne katalizatory w syntezie asymetrycznej

56 Zjazd Naukowy PTChem i Stowarzyszenia Inżynierów i Techników Przemysłu Chemicznego, Siedlce, 16 – 20th September 2013, Abstract S01P117

14) **M. Rachwalski**

Limonene oxide derived aziridiny alcohol as highly efficient catalysts for asymmetric additions of organozinc species to aldehydes

XVI International Symposium – Advances in the chemistry of heteroorganic compounds, Lodz, 15th November 2013, Abstract P – 100

15) S. Jarzyński, S. Leśniak, **M. Rachwalski**

Mandelic acid derived α -aziridiny alcohol as effective ligands for asymmetric synthesis

XVI International Symposium – Advances in the chemistry of heteroorganic compounds, Lodz, 15th November 2013, Abstract P – 079

16) A. M. Pieczonka, **M. Rachwalski**, S. Leśniak

New aziridinesemicarbazides as highly efficient ligands in asymmetric synthesis

XVI International Symposium – Advances in the chemistry of heteroorganic compounds, Lodz, 15th November 2013, Abstract P – 096

3.3. Awards

- Award of the Research Council of the Centre of Molecular and Macromolecular Studies Polish Academy of Sciences in Lodz for PhD thesis *Enzyme catalyzed deracemisations and desymmetrisations as methods of the synthesis of chiral heteroorganic compounds*
- Scientific Award of The Foundation of The University of Lodz for The Young Scientist

3.4. Internships completed

a) long-term internships:

- **The Netherlands**, Radboud University Nijmegen (Professor F. Rutjes group), postdoctoral fellowship 1.I.2012 – 31.XI.2012 (1 year)

b) short-term internships:

- **The Netherlands**, Radboud University Nijmegen (Professor F. Rutjes group), scientific visit, November 2005 (one week)
- **The Netherlands**, Radboud University Nijmegen (Professor F. Rutjes group), scientific visit, October 2007 (two weeks)
- **The Netherlands**, Radboud University Nijmegen (Professor F. Rutjes group), scientific visit, February 2008 (1 month)
- **Germany**, Justus-Liebig University of Giessen (Professor P. R. Schreiner group), scientific visit, December 2008 (one week)
- **Germany**, Justus-Liebig University of Giessen (Professor P. R. Schreiner group), scientific visit, July 2010 (one week)
- **Germany**, Justus-Liebig University of Giessen (Professor P. R. Schreiner group), scientific visit, June 2011 (one week)

3.5. Participation in scientific projects

- Grant MSHE No. 3 T09A 166 27 – „Biokatalityczne syntezy nowych preparatywnie użytecznych, chiralnych związków heteroorganicznych” (2004-2007) – performer (140 000 PLN)
- Research task - „Nowe podejścia do katalizowanych enzymami syntez chiralnych nieracemicznych związków heteroorganicznych” (2006-2009) under a grant MSHE No. PBZ-KBN-126/T09/03 – performer (250 000 PLN)
- Grant NSC (SONATA) no. 2012/05/D/ST5/00505 – „Synteza nowych, optycznie czynnych azirydynoalkoholi i ich zastosowanie w syntezie asymetrycznej” (2013 – 2015) – head of the project (273 000 PLN).

3.6. Other activity concerning scientific, educational and organizational work

- Teaching classes conducted:
 - Organic chemistry – laboratory, 2nd year of Environmental protection
 - Organic chemistry – laboratory, 3rd year of Chemistry
 - Organic chemistry 2 – laboratory, 4th year of Chemistry (extramural)
 - Organic chemistry 2 – seminar, 3rd year of Chemistry
 - Organic chemistry – laboratory, 2nd year of Chemistry
 - Organic chemistry – laboratory, 1st year of Biotechnology
 - Organic chemistry – laboratory, 1st year of Biology
 - Organic chemistry – seminar, 2nd year of Chemistry
 - Spectroscopy – laboratory, 1st year of Chemistry, second-degree studies
 - English in the chemistry – seminar, 1st year of Chemistry, second-degree studies
 - Biomaterials – Chemistry of natural compounds – laboratory, 3rd year of Chemistry
 - Biochemistry – seminar, 3rd year of Chemistry

- The number of hours of classes:
 - in academic year 2008/2009 – 295 hours
 - in academic year 2009/2010 – 230 hours
 - in academic year 2010/2011 – 230 hours
 - in academic year 2011/2012 – 230 hours

- The number of finished master theses under my scientific care: 5
- The number of finished diploma theses under my supervision: 4
- Assistant Supervisor in the doctoral procedure: 1
- Reviews:
 - for *Current Organic Chemistry*;
 - of diploma theses on The Faculty of Chemistry of University of Lodz

3.7. Membership in scientific organizations:

- member of Polish Chemical Society