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Conformational rigidity: a necessary prerequisite of chiral modifiers used in heterogeneous enantioselective catalysis?

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Abstract

In the hydrogenation of ketopantolactone, the (*R*,*R*) and (*R*,*S*) diastereomers of a new chiral modifier, pantoyl-naphthylethylamine, afforded 74 and 40% *ee*, respectively, to (*R*)-pantolactone. On the basis of NOE studies and theoretical calculations, the different properties of the diastereomers and in particular the effect of acid on the modifier structure are deduced from differences in conformational rigidity and steric constraint. In case of the (*R*,*R*)-diastereomer, a loose, extended structure in apolar solvent changes to a compact conformation via an additional intramolecular hydrogen bond, resulting in a more defined "chiral pocket" available for the reactant on the Pt surface.

Keywords: Acid effect; Asymmetric heterogeneous catalysis; Pt/Al_2O_3; Ketopantolactone; Hydrogenation; Ab initio calculation; NOE; Modifier conformation

1. Introduction

Cinchona alkaloids are the most versatile chiral modifiers in heterogeneous enantioselective catalysis [1–5]. It was determined early, based on the efficiency of some cinchonidine derivatives in pyruvate ester hydrogenation, that there are three important features of cinchona alkaloids [6]:

(i) An extended aromatic ring that anchors (adsorbs) the modifier to the metal surface;
(ii) A basic quinuclidine N atom for interaction with the ketone reactant; and
(iii) Stereogenic centers that induce enantiodifferentiation during hydrogen uptake.

With this knowledge, cinchona analogues [7–9], epicinchona alkaloids [10–13] and other alkaloids [14,15], various other chiral amines [16–18], amino alcohols [19–28], amino acids [29], amino acid derivatives [30,31], and a diol [32] have been synthesized and tested in the enantioselective heterogeneous hydrogenation of activated ketones, mostly ethyl pyruvate. As it is clear from the reviews covering the topic [2,3,22], none of the synthetic substances prepared so far can surpass the outstanding performance of cinchona alkaloids or their simple derivatives.

Here we discuss another fundamental characteristic of an effective chiral modifier: the conformational rigidity. This is a known concept in homogeneous catalysis that may be illustrated by examples where rotation of a functionalized side chain is hindered [33], rigid aromatic backbones or ring structures restrict conformational flexibility of the ligands [34], or the accessibility of the reacting group is greatly reduced by a bulky group or an aromatic system [35]. In contrast, the effect of conformational constraints in heterogeneous asymmetric catalysis has received less attention so far. An early example is the hydrogenation of C=C and C=O bonds over Pd modified by dihydro-vinpocetine [15,36]. The modifier was synthesized by hydrogenation of apovincaminic acid ethyl ester (vinpocetine), and the different efficiencies of the *cis* and *trans* epimers could be rationalized

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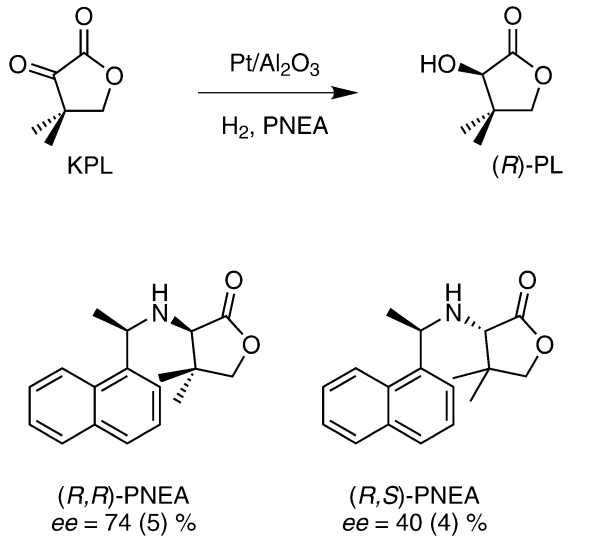

Scheme 1. Enantioselective hydrogenation of ketopantolactone to pantolactone over Pt/Al_2O_3 modified by the diastereomers of PNEA. The enantiomeric excesses (*ee*) were measured at full conversion in HOAc or toluene (in brackets) [43].

by their different conformations [37]. A comparison of cinchona and the conformationally rigid *iso*-cinchona alkaloids in which the rotation around the C(9)–C(8) bond is hindered provided interesting information concerning the probable conformation of cinchonidine during interaction with ethyl pyruvate [10–13]. Related areas are the diastereoselective hydrogenation of bulky reactants over metal catalysts [38–41] and the role of the structural rigidity of chiral molecules in adsorption on single-crystal metal surfaces [42].

We have found very recently [43] that in the hydrogenation of ketopantolactone (KPL) on Pt/Al_2O_3, numerous derivatives of (*R*)-1-(1-naphthyl)ethylamine (NEA) performed well as chiral modifiers only in acidic medium (Scheme 1). The considerably higher *ee* achieved in acidic medium (up to 79%) was attributed to the much stronger H-bond (N^+–H–O bond) formed between the protonated N atom and the keto O atom of KPL [44]. The best modifier was prepared by reductive alkylation of NEA with KPL. The efficiencies of the two diastereomers of pantoyl-naphthylethylamine, (1′*R*,2*R*)- and (1′*R*,2*S*)-PNEA, were equally poor in toluene, but in AcOH the difference in the enantioselectivities exceeded 30% (Scheme 1). A similar difference in *ee* was observed when Pt/alumina was modified by the two diastereomers synthesized by alkylation of NEA with ethyl pyruvate [43]. The aim of the present work is to show that the remarkably different behaviors of these diastereomers can be explained by differences in their conformational rigidities.

2. Experimental

Ketopantolactone (KPL) (Hoffmann–La Roche), (*R*)-1-(1-naphthyl)ethylamine (Acros), trifluoroacetic acid (TFA) (Fluka), and acetic acid (HOAc) (Fluka) were used as received. Toluene (Baker) was dried and stored over an activated molecular sieve. Synthesis of the two diastereomers of pantoyl-naphthylethylamine (PNEA) is described elsewhere [43].

A 5 wt% Pt/Al_2O_3 catalyst (Engelhard 4759) was used for the hydrogenation experiments after pre-reduction at 673 K for 1 h in flowing hydrogen [45]. The Pt dispersion was 0.33 after heat treatment, as calculated from the average particle size determined by STEM. The reactions were carried out in a stainless-steel autoclave equipped with a glass liner and PTFE cover. Solvent (5 ml) containing 6.8 μmol modifier and 236 mg KPL were added to 5 mg catalyst. When TFA was also used, the pre-reduced catalyst was stirred in 10 ml solvent under H_2 at 30 bar for 10 min. Then TFA and the modifier were added, and the mixture was further stirred for 5 min under N_2 at 1 bar. Finally KPL was added and the reaction started at room temperature and 8 bar. The products were analyzed at full conversion with gas chromatography with a Chirasil-DEX CB capillary column (ChromPack). When TFA was added, the product mixture was evaporated to dryness and diluted with ethyl acetate before injection into the column.

NMR spectra were recorded on a Bruker Avance 500 spectrometer with TMS as an internal reference. Spectra were measured at 300 K. Signal assignment was sometimes assisted through correlation spectroscopy (COSY).

3. Results and discussion

3.1. Effect of acid

The considerable difference in enantioselectivities observed in the hydrogenation of KPL to (*R*)-pantolactone in toluene and acetic acid (Scheme 1) may be attributed to protonation of the chiral modifiers (*R*,*R*)- and (*R*,*S*)-PNEA or to a solvent effect. To clarify this point, we repeated the reaction in toluene in the presence of increasing amounts of TFA (Fig. 1). When 20 eq. of TFA ($pK_a = 0.2$) related to (*R*,*R*)-PNEA was applied, the *ee* was 74%, the same as in acetic acid ($pK_a = 4.7$). Clearly, this selectivity enhancement is due to protonation of the N atom; the considerable excess of TFA relative to the stoichiometric amount of modifier is necessary to compensate for adsorption on the basic sites of the alumina support.

In the following we investigated the structural changes occurring by protonation of the more effective modifier, (*R*,*R*)-PNEA. For the other diastereomer, (*R*,*S*)-PNEA, the interpretation, especially of the theoretical calculations, would be less reliable, because the *ee* of (*R*)-PL increased from 4 to only 40% when we changed from toluene to HOAc [43].

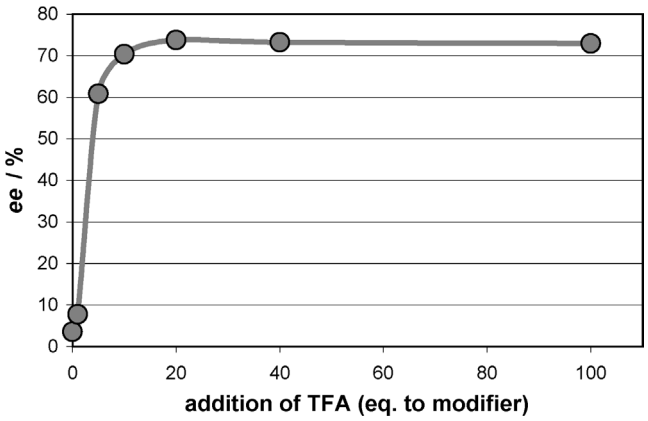

Fig. 1. Enantioselective hydrogenation of ketopantolactone to (*R*)-pantolactone over Pt/Al_2O_3 modified by (*R*,*R*)-PNEA. The solvent was toluene with increasing amount of TFA.

3.2. NOE measurements

NOE was measured by differential NOE spectroscopy, radiating at the resonance frequency of the protons H(2′) and those of both methyl groups attached to C(3) (Fig. 2). At room temperature (*R*,*R*)-PNEA revealed distinct NOE's in d-toluene, which are indicated as gray arrows in Fig. 2A. Most importantly, the methyl protons H(2′) exhibit strong NOE toward both H(2″) and H(8″) of the naphthalene ring, shown as black arrows. This means that free rotation of the naphthalene ring around the C(1″)–C(1′) bond is easy and likely to occur. According to the concept of the transition state, we cannot expect a specific reactant–modifier interaction when either the modifier or the reactant possesses too many floppy degrees of freedom. The weak enantio-discriminating properties of (*R*,*R*)-PNEA in toluene may be explained that way.

After the addition of 10 eq. of TFA, the methyl protons H(2′) exhibit strong NOE only toward H(2″) of the naphthalene ring, revealing that rotation around the C(1″)–C(1′) bond ceased (Fig. 2B). A second NOE can now be observed upon proton H(2), which was absent in the unprotonated modifier. The predominant conformer of (*R*,*R*)-PNEA in the toluene-TFA mixture must have the C(2′)-methyl group close to both protons, H(2″) and H(2). This position can only be rationalized when a H-bridge is formed between the protonated N atom and the carbonyl O atom of the adjacent ester group. This H-bridge results in a relatively rigid conformation. The 3D model of the protonated compound suggests a fixed structure leading to a pocket-like cavity with the N atom in the center, where the reactant can be located. It is expected that enantioselection is greatly facilitated by a defined structure and conformation of the modifier.

In the NOE experiment we could also clarify the absolute configuration on C(2) and identify the two diastereomers of PNEA. In the case of (*R*,*R*)-PNEA, radiating at the frequency of the H(2′) methyl protons enhanced the signal of H(2), and radiating with the frequency of methyl "down" (the methyl group pointing in the same direction as H(2), see Fig. 2) enhanced the signal of H(1′). Hence, the configuration at C(2) can only be (*R*), and the absolute configuration of this diastereomer is (1′*R*,2*R*). For the other diastereomer, (1′*R*,2*S*)-PNEA, it is constitutionally impossible to adopt any conformation in space that would exhibit all of the NOEs shown in Fig. 2 at the same time. It is expected that the conformational rigidity of this diastereomer is considerably reduced compared with (*R*,*R*)-PNEA. This can explain why (*R*,*S*)-PNEA (the "wrong" diastereomer) is a less effective modifier in its protonated form.

3.3. Theoretical calculations

The minimum energy conformations of the protonated and unprotonated modifier (*R*,*R*)-PNEA have been calculated with the use of a hybrid density functional method (b3lyp) and a 6-31G(d,p) basis set. All calculations were performed with the Gaussian98 suite of programs [46]. To

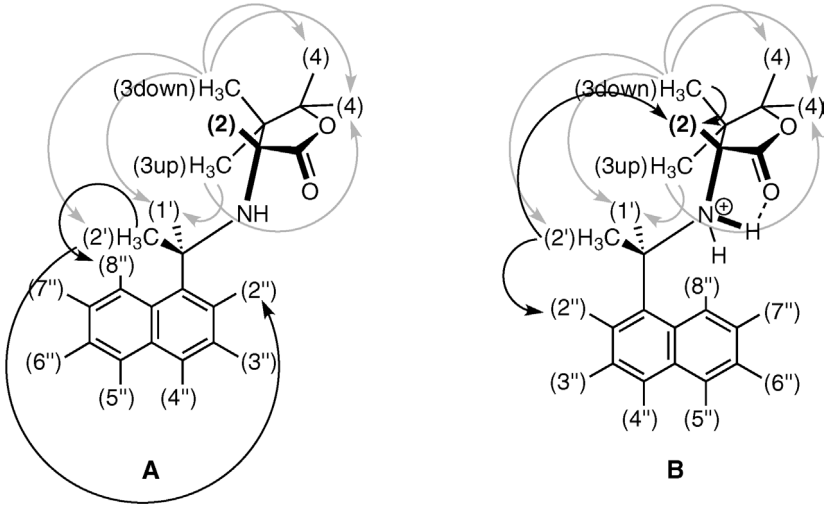

Fig. 2. NOE-enhancement of the signals in d-toluene (A) and after the addition of 10 eq. TFA (B). Note that structure B is less flexible in the side chain and rotation of the naphthyl ring is not possible after protonation.

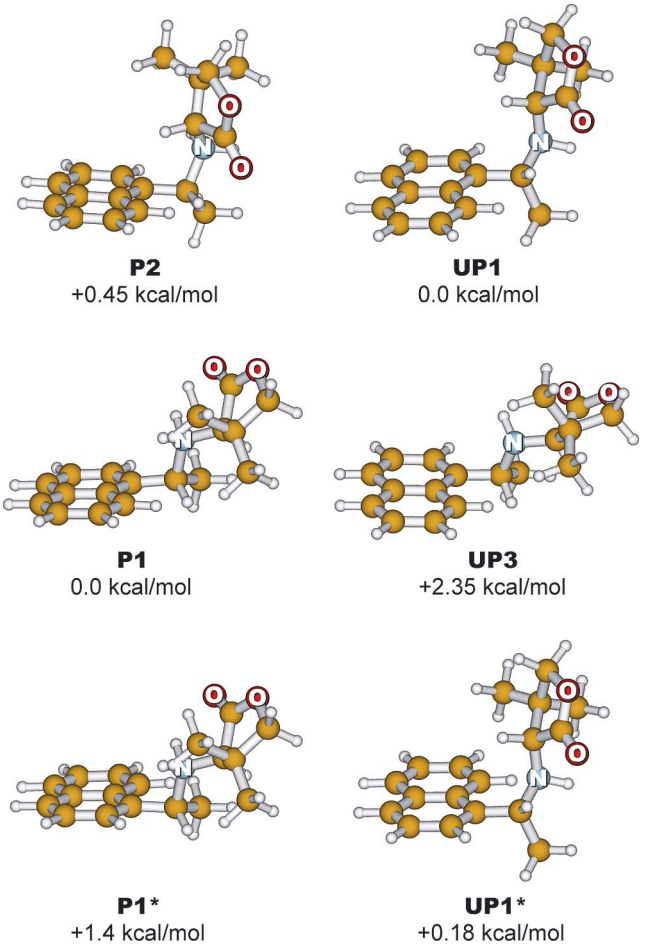

Fig. 3. Minimum energy conformations of protonated (P1, P2; left) and unprotonated (UP1, UP3; right) (*R*,*R*)-PNEA. In P1* the naphthalene ring was flipped with respect to P1, which increases the energy by 1.4 kcal/mol. Similar flipping of UP1 resulting in UP1* increases the energy by only 0.18 kcal/mol.

explore the conformational space, a two-dimensional potential energy scan was performed at the AM1 level of theory. The two degrees of freedom were the rotations around the two C–N single bonds. The low energy conformations of this scan then served as the starting geometry for the higher level calculations, where all degrees of freedom were completely relaxed. The counter-ion (in the case of the protonated modifier) and solvent were not considered in the calculations.

The two lowest-energy conformers of the protonated (P1 and P2) and the lowest- and third-lowest-energy conformers of the unprotonated (UP1 and UP3) modifier are shown in Fig. 3. The calculated relative energies are also indicated. The structure of the second-lowest-energy conformation of the unprotonated modifier UP2 (not shown) is similar to that of UP1, with only a slightly different dihedral angle around one of the C–N bonds, and UP2 is less stable than UP1 by 1.44 kcal/mol.

The conformational change of the molecule caused by protonation of the N atom is evident from Fig. 3. Note that P2 and UP1, and P1 and UP3, have similar conformations. Upon protonation the predominant conformation changes from an extended structure (UP1) to a more compact one (P1). A second important change concerns the position of the C(2′) methyl group. In the unprotonated case we have found several conformers, the two most stable of which are UP1 (Fig. 3) and UP2 (not shown), where the C(2') methyl group points perpendicular to the plane of the naphthyl ring. Flipping the naphthalene ring around the C(1′)–C(1″) bond by 180° increases the energy by only 0.18 kcal/mol, giving conformation UP1*. As a consequence there is no clear direction in which a "chiral pocket" would preferentially form to locate the reactant KPL. Furthermore, after protonation of the N atom the modifier gains considerable rigidity in the side "chain" because a stronger H bond between N^+–H and O=C of the ester group is formed.

The depicted structure P1 corresponds well to the NOEs shown in Fig. 2, and we may therefore consider it a good approximation of the "real" structure in solution. The C(2′) methyl group points almost "in plane" with the naphthalene ring, thus facilitating considerably the adsorption of the latter compared with the nonplanar position of the C(2′) methyl group of unprotonated (*R*,*R*)-PNEA. Hence, we can assume that the structure of (*R*,*R*)-PNEA on the Pt surface will probably be similar. Interestingly, the OH group of CD that is in a position analogous to that of the C(2′) group of (*R*,*R*)-PNEA points in a very similar direction, almost planar with the quinoline ring in the most stable conformation, "Open(3)," of CD [47]. The difference is that an OH group adsorbs more strongly to the Pt surface than a methyl group.

A crucial point is that flipping the naphthalene ring around the C(1′)–C(1″) bond by 180° increases the energy by 1.4 kcal/mol for P1, giving conformation P1*. There is therefore a considerable predominance of one position of the naphthalene ring for the protonated modifier, in contrast to the unprotonated modifier. Protonation may thus lead to one dominant structure of the modifier, making possible a well-defined "chiral pocket" and thus a reactant-modifier interaction leading to a high enantiomeric excess.

3.4. Mechanistic considerations

Adsorption of cinchonidine and other amine- or amino alcohol-type modifiers to Pt has been studied with direct and indirect methods and modeled thoroughly [48–53]. It is now generally accepted that the modifier is anchored to the surface via the extended aromatic ring. A parallel or slightly tilted position relative to the surface is favorable for enantioselection because it hinders the approach of the prochiral reactant to the interacting function from one side. Deviation from this adsorption mode can invert enantioselectivity [54,55]. When the naphthalene ring of another synthetic modifier, (*R*)-2-(1-pyrrolidinyl)-1-(1-naphthyl)ethanol, was replaced with a phenyl or pyridine ring, the *ee* dropped to almost zero. In contrast, when an anthracene ring was introduced instead of the naphthalene moiety, the *ee* increased by about 20% in the hydrogenation of ethyl pyruvate over

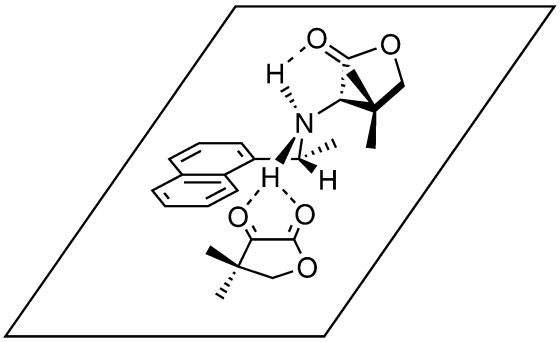

Fig. 4. Probable interaction of KPL with the protonated (*R*,*R*)-PNEA, the latter being in its optimized structure (P1) on the Pt surface. Due to repulsive interactions of the side chain and the naphthalene ring, the pro-(*R*)-orientation of KPL is greatly favored. (The positive charge on the N atom is omitted for clarity.)

Pt/Al_2O_3 [20,22]. This observation underlines the importance of selective blocking of the surface from one side to promote hydrogenation on the other side.

Considering the minimum energy conformation of protonated (*R*,*R*)-PNEA (P1 in Fig. 3), we can speculate that the space in which to approach the protonated N atom and the "chiral pocket" on the metal surface is strongly restricted for the reactant KPL. On one side the space is blocked by the aromatic ring of the modifier and the N atom is only accessible from the front, because the highly constrained side chain effectively blocks the back side (Fig. 4). When we assume a bifurcated H bond between the protonated N atom of the modifier toward the two carbonyl O atoms of KPL, the pro-(*R*)-orientation of KPL on the metal surface should be preferred for steric reasons. Note that this is the case only when the N atom is protonated; otherwise the side chain is too flexible and provides no defined shielding effect, and the naphthalene ring can flip with respect to the substituent that allows both pro-(*R*) and pro-(*S*) orientation of the reactant, thus leading to very low *ee* (ca. 5%). Moreover, for steric reasons the amine–ester interaction leading to the relatively rigid conformation of (*R*,*R*)-PNEA is not possible in the case of the (*R*,*S*)-diastereomer.

Detailed NOE spectra are available in supplementary material.

4. Conclusions

It is shown with the example of a new chiral modifier, pantoyl-naphthylethylamine (PNEA), that conformational rigidity may play a decisive role in achieving high enantioselectivity in the hydrogenation of KPL. The experimental observation that after protonation (*R*,*R*)-PNEA affords remarkably higher *ee* than the (*R*,*S*) isomer in the enantioselective hydrogenation of KPL is interpreted by an extra stabilization of the charged $NR_2H_2^+$ fragment via interaction with the neighboring ester group. This special interaction brings along both steric constraint and rigidity for the side chain and results in more than 30% improvement in *ee*. We assume that this interpretation can be applied to other diastereomeric modifier pairs, for example NEA alkylated by ethyl pyruvate [43]. To come back to the question raised in the title: is conformational rigidity a necessary prerequisite of chiral modifiers? Clearly, the convincing cases discussed in the Introduction and the present results are strong indications that conformational rigidity is an important part of enantioselection on the metal surface. However, more experimental evidence will be needed to generalize this statement.

Acknowledgments

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Supplementary material

The online version of this article contains additional supplementary material. Please visit DOI: 10.1016/j.jcat.2005.03.005.

References

[1] M. von Arx, T. Mallat, A. Baiker, Top. Catal. 19 (2002) 75.
[2] P.B. Wells, A.G. Wilkinson, Top. Catal. 5 (1998) 39.
[3] A. Baiker, J. Mol. Catal. A: Chem. 115 (1997) 473.
[4] A. Tungler, G. Fogassy, J. Mol. Catal. A: Chem. 173 (2001) 231.
[5] D.Y. Murzin, P. Mäki-Arvela, T. Salmi, Kinet. Catal. 44 (2003) 323.
[6] H.U. Blaser, H.P. Jalett, D.M. Monti, A. Baiker, J.T. Wehrli, Stud. Surf. Sci. Catal. 67 (1991) 147.
[7] C. Exner, A. Pfaltz, M. Studer, H.-U. Blaser, Adv. Synth. Catal. 345 (2003) 1253.
[8] H.U. Blaser, H.P. Jalett, W. Lottenbach, M. Studer, J. Am. Chem. Soc. 122 (2000) 12675.
[9] A. Lindholm, P. Mäki-Arvela, E. Toukoniitty, T.A. Pakkanen, J.T. Hirvi, T. Salmi, D.Y. Murzin, R. Sjöholm, R. Leino, J. Chem. Soc.-Perkin Trans. 1 (2002) 2605.
[10] M. Bartók, K. Felföldi, B. Török, T. Bartók, Chem. Commun. 23 (1998) 2605.
[11] M. Bartók, K. Felföldi, G. Szöllösi, T. Bartók, Catal. Lett. 61 (1999) 1.
[12] M. Bartók, M. Sutyinszki, K. Felföldi, G. Szöllösi, Chem. Commun. (2002) 1130.
[13] M. Bartók, M. Sutyinszki, K. Felföldi, J. Catal. 220 (2003) 207.
[14] P.B. Wells, K.E. Simons, J.A. Slipszenko, S.P. Griffiths, D.F. Ewing, J. Mol. Catal. A: Chem. 146 (1999) 159.
[15] T. Tarnai, A. Tungler, T. Máthé, J. Petró, R.A. Sheldon, G. Tóth, J. Mol. Catal. A. 102 (1995) 41.
[16] T. Heinz, G.Z. Wang, A. Pfaltz, B. Minder, M. Schürch, T. Mallat, A. Baiker, J. Chem. Soc. Chem. Commun. (1995) 1421.
[17] B. Minder, M. Schürch, T. Mallat, A. Baiker, T. Heinz, A. Pfaltz, J. Catal. 160 (1996) 261.
[18] B. Minder, M. Schürch, T. Mallat, A. Baiker, Catal. Lett. 31 (1995) 143.
[19] B. Minder, T. Mallat, A. Baiker, G. Wang, T. Heinz, A. Pfaltz, J. Catal. 154 (1995) 371.

[20] M. Schürch, T. Heinz, R. Aeschimann, T. Mallat, A. Pfaltz, A. Baiker, J. Catal. 173 (1998) 187.
[21] K.E. Simons, G. Wang, T. Heinz, T. Giger, T. Mallat, A. Pfaltz, A. Baiker, Tetrahedron: Asymmetry 6 (1995) 505.
[22] A. Pfaltz, T. Heinz, Top. Catal. 4 (1997) 229.
[23] A. Solladié-Cavallo, C. Marsol, F. Garin, Tetrahedron Lett. 43 (2002) 4733.
[24] A. Solladié-Cavallo, C. Marsol, C. Suteu, F. Garin, Enantiomer 6 (2001) 245.
[25] E. Sipos, A. Tungler, I. Bitter, in: D.G. Morrell (Ed.), Catalysis of Organic Reactions, Dekker, New York, 2003, p. 653.
[26] E. Sipos, A. Tungler, I. Bitter, React. Kinet. Catal. Lett. 79 (2003) 101.
[27] E. Sipos, A. Tungler, I. Bitter, M. Kubinyi, J. Mol. Catal. A: Chem. 186 (2002) 187.
[28] C. Thorey, S. Bouquillon, A. Helimi, F. Henin, J. Muzart, Eur. J. Org. Chem. 13 (2002) 2151.
[29] K.E. Simons, P.A. Meheux, S.P. Griffiths, I.M. Sutherland, P. Johnston, P.B. Wells, A.F. Carley, M.K. Rajumon, M.W. Roberts, A. Ibbotson, Recl. Trav. Chim. Pays-Bas 113 (1994) 465.
[30] É. Sípos, A. Tungler, I. Bitter, J. Mol. Catal. A: Chem. 198 (2003) 167.
[31] G. Szöllösi, C. Somlai, P.T. Szabó, M. Bartók, J. Mol. Catal. A: Chem. 170 (2001) 165.
[32] A. Marinas, T. Mallat, A. Baiker, J. Catal. 221 (2004) 666.
[33] V.I. Sokolov, L.L. Troitskaya, B. Gautheron, G. Tainturier, J. Organomet. Chem. 235 (1982) 369.
[34] X. Zhang, Enantiomer 4 (1999) 541.
[35] U. Maitra, P. Mathivanan, Tetrahedron: Asymmetry 5 (1994) 1171.
[36] A. Tungler, K. Fodor, T. Máthé, R.A. Sheldon, Stud. Surf. Sci. Catal. 108 (1997) 157.
[37] A. Tungler, T. Máthé, T. Tarnai, K. Fodor, G. Tóth, J. Kajtár, I. Kolossváry, B. Herényi, R.A. Sheldon, Tetrahedron: Asymmetry 6 (1995) 2395.
[38] M. Besson, C. Pinel, Top. Catal. 25 (2003) 43.
[39] P. Kukula, R. Prins, Top. Catal. 25 (2003) 29.
[40] A. Tungler, K. Fodor, Catal. Today 37 (1997) 191.
[41] L.A.M.M. Barbosa, P. Sautet, J. Catal. 217 (2003) 23.
[42] E. Mateo Marti, S.M. Barlow, S. Haq, R. Raval, Surf. Sci. 501 (2002) 191.
[43] E. Orglmeister, T. Mallat, A. Baiker, Adv. Synth. Catal. 347 (2005) 78.
[44] O. Schwalm, J. Weber, J. Margitfalvi, A. Baiker, J. Mol. Struct. 297 (1993) 285.
[45] Y. Orito, S. Imai, S. Niwa, J. Chem. Soc. Japan (1979) 1118.
[46] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A7, Gaussian, Pittsburgh, PA, 1998.
[47] T. Bürgi, A. Baiker, J. Am. Chem. Soc. 120 (1998) 12920.
[48] Z. Ma, I. Lee, J. Kubota, F. Zaera, J. Mol. Catal. A: Chem. 216 (2004) 199.
[49] S.R. Calvo, R.J. LeBlanc, C.T. Williams, P.B. Balbuena, Surf. Sci. 563 (2004) 57.
[50] D. Ferri, T. Bürgi, J. Am. Chem. Soc. 123 (2001) 12074.
[51] A. Vargas, T. Bürgi, A. Baiker, J. Catal. 226 (2004) 69.
[52] R.J. LeBlanc, C.T. Williams, J. Mol. Catal. A: Chem. 220 (2004) 207.
[53] J.M. Bonello, F.J. Williams, R.M. Lambert, J. Am. Chem. Soc. 125 (2003) 2723.
[54] S. Diezi, T. Mallat, A. Szabó, A. Baiker, J. Catal. 228 (2004) 162.
[55] S. Diezi, A. Szabó, T. Mallat, A. Baiker, Tetrahedron: Asymmetry 14 (2003) 2573.