

## Synthesis and catalytic application of novel binaphthyl-derived phosphorous ligands

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**Dedicated to Prof. Dr. Lutz F. Tietze on the occasion of his 65<sup>th</sup> birthday**

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### Abstract

We describe our recent achievements in the synthesis of chiral phosphorous ligands and their application in catalytic asymmetric hydrogenation reactions. Special attention is given to the development of novel binaphthophosphine ligands. Starting from enantiomerically pure 1,1'-binaphthol or 2,2'-dimethyl-1,1'-binaphthyl and the building blocks A or B, new chelating P-ligands have been synthesized in one step in good to excellent yields (68–95%). The resulting chiral bidentate phosphines, phosphites and phosphonites were tested in various asymmetric hydrogenation benchmark reactions. Interestingly, small structural changes within the ligands exhibit a significant influence on the enantioselectivity of the hydrogenation reactions.

**Keywords:** Asymmetric hydrogenation, homogeneous catalysis, chiral phosphines

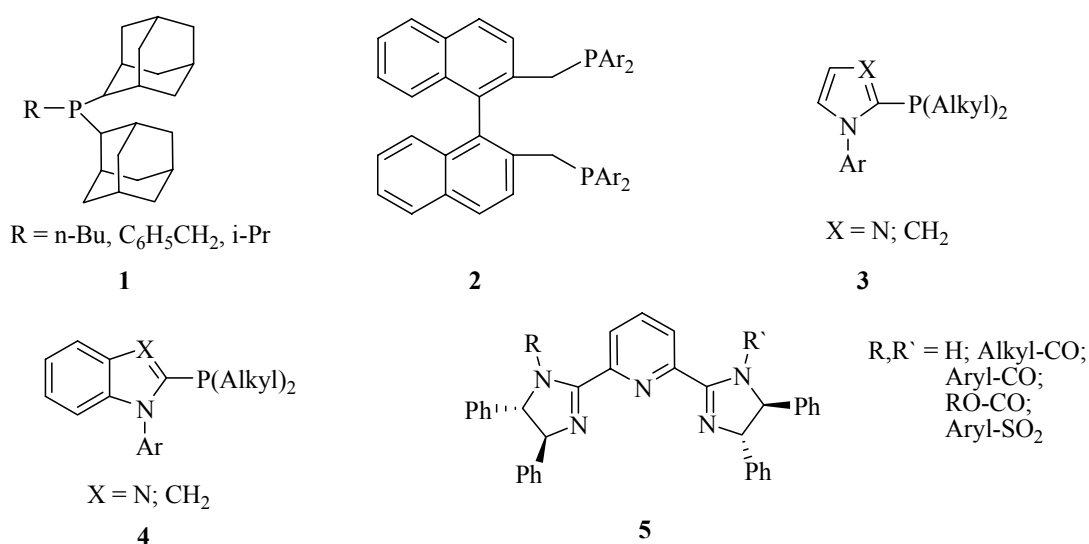
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### Introduction

Catalysis, which is the science of accelerating chemical transformations, enables the chemical and pharmaceutical industry to offer a wide range of products for our health, environment, and nutrition. This makes catalysts indispensable for the needs of today's society and important tools for increasing sustainability. Catalysts are mainly used for environmental protection, the production of bulk and fine chemicals, oil processing in refineries, and polymer synthesis.

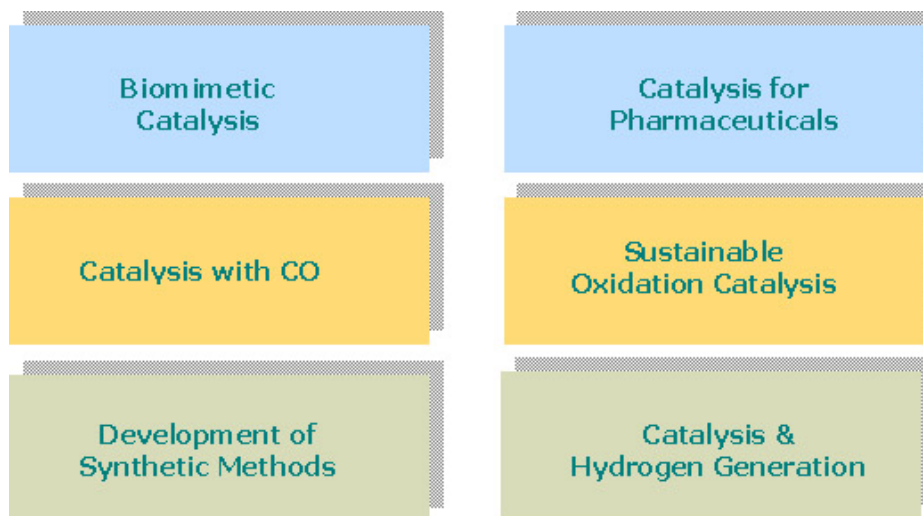
For some years our main area of scientific interest has been applied homogeneous catalysis with organometallic complexes. A key issue for controlling the activity, productivity, and selectivity of a given transition metal complex is the synthesis of molecularly defined catalytic centers. In other words, the electronic and steric properties of each active center can be controlled by using organic ligands, which coordinate to the metal center. Thus, "ligand-tailoring" constitutes an extremely powerful tool to control all kinds of selectivity for a desired catalytic reaction and to influence catalyst stability and activity. Due to the advancements in organometallic chemistry and organic ligand synthesis, nowadays a plethora of ligands [P-, N-,

and recently C-based ligands) is theoretically available ( $>>100.000$ ). A selection of ligands recently developed in our laboratory is shown in Scheme 1. Apart from new aryl and alkyl phosphines **1-4**,<sup>1</sup> tridentate nitrogen ligands<sup>2</sup> **5** and carbenes have been synthesized in recent years. In particular the importance of carbenes<sup>3</sup> is underlined by the fact that in 2005 the Nobel Prize in chemistry was awarded to Y. Chauvin, R. H. Grubbs and R. R. Schrock for the development of metathesis.



**Scheme 1.** A selection of ligands developed in our laboratory.

For more than a decade the development of synthetic methods and the application of catalysis for the preparation of biologically active compounds have attracted our interest (Figure 1). In this respect palladium-catalysis<sup>4</sup> and amination reactions<sup>5</sup> have been particularly investigated over the years.



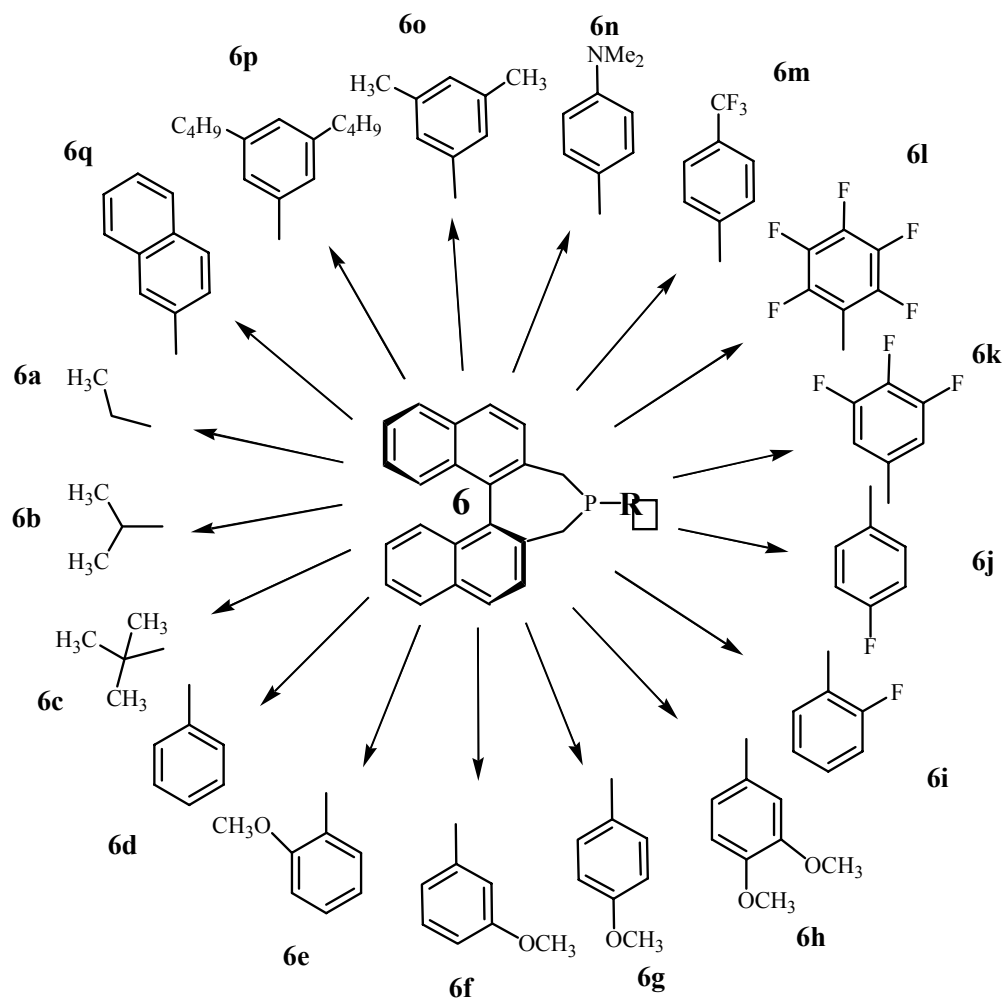
**Figure 1.** Our research areas of interest.

Since 1998 catalysis with carbon monoxide<sup>6</sup> and oxidation catalysis<sup>7</sup> using molecular oxygen or hydrogen peroxide became prominent areas. Most recently, we initiated a program on the use of homogeneous catalysis for hydrogen generation and biomimetic catalysis, which is based on Fe-catalysis. An important goal of all our work is the facilitation of innovative processes by transfer of basic research to an industrially useful level.

## Results and Discussion

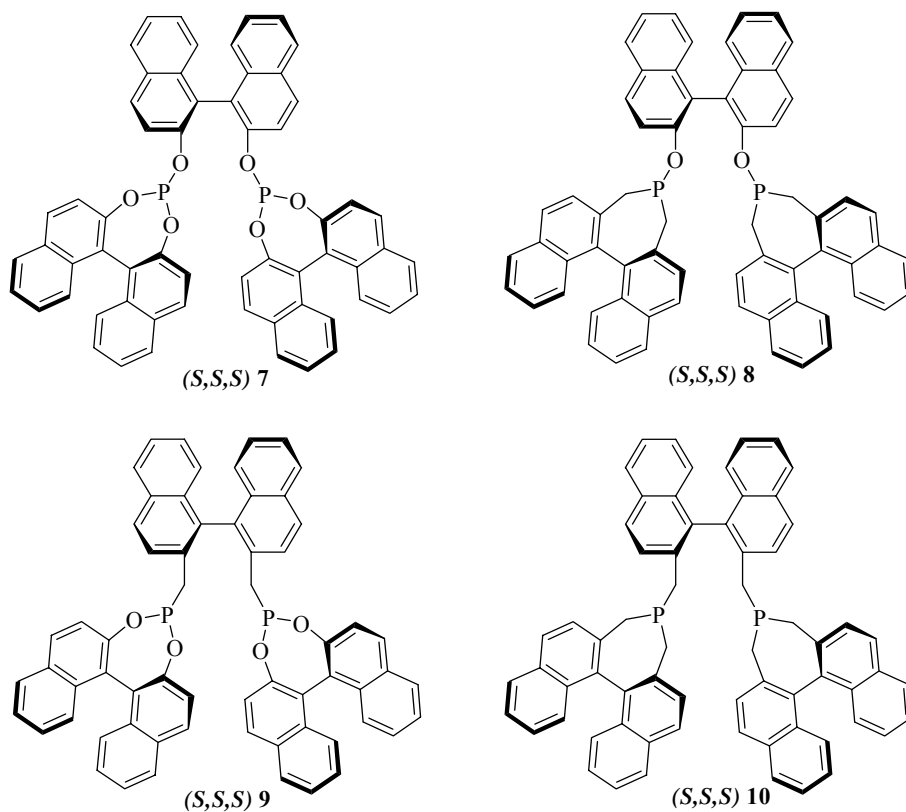
### Synthesis of novel binaphthophosphines

Clearly, transition metal-catalyzed asymmetric reactions offer efficient and elegant possibilities for the synthesis of enantiomerically pure compounds.<sup>8</sup> Among the different transition metal-catalyzed asymmetric reactions, hydrogenations of olefins, imines and ketones have been used extensively in the last two decades and are likely to provide the most important access to chiral pharmaceutical intermediates.<sup>9</sup> In general, optically active phosphine ligands have been viewed as essential in order to achieve high enantioselectivity in asymmetric hydrogenation reactions.<sup>8</sup> Inspired by the seminal work of Reetz *et al.*,<sup>10</sup> Feringa and de Vries *et al.*,<sup>11</sup> as well as Pringle and Claver *et al.*,<sup>12</sup> we became interested in the synthesis and catalytic application of chiral monodentate phosphines with a 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphine motif **6** (Scheme 2).<sup>13</sup> The first example of this class of ligands has been prepared by Gladiali *et al.*<sup>14</sup> in the mid 90's. Parallel to the work of Zhang<sup>15</sup> we established the use of **6** as enantioselective ligands for asymmetric hydrogenation of  $\alpha$ -amino acid precursors, itaconic esters,<sup>16</sup> enamides,<sup>17</sup> and  $\beta$ -ketoesters.<sup>18</sup> Since our start we have prepared a variety of monodentate ligands, which are prepared in either 1 or 2 steps from optically pure 2,2'-dimethylbinaphthyl (*ee* >99%). This building block is accessible on a 20g scale from 2,2'-binaphthol via esterification with trifluoromethanesulfonic acid anhydride in the presence of pyridine (99% yield) and subsequent nickel-catalyzed Kumada coupling with methylmagnesium bromide in diethyl ether (95% yield).



**Scheme 2.** Ligand library of 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphepines **6**.

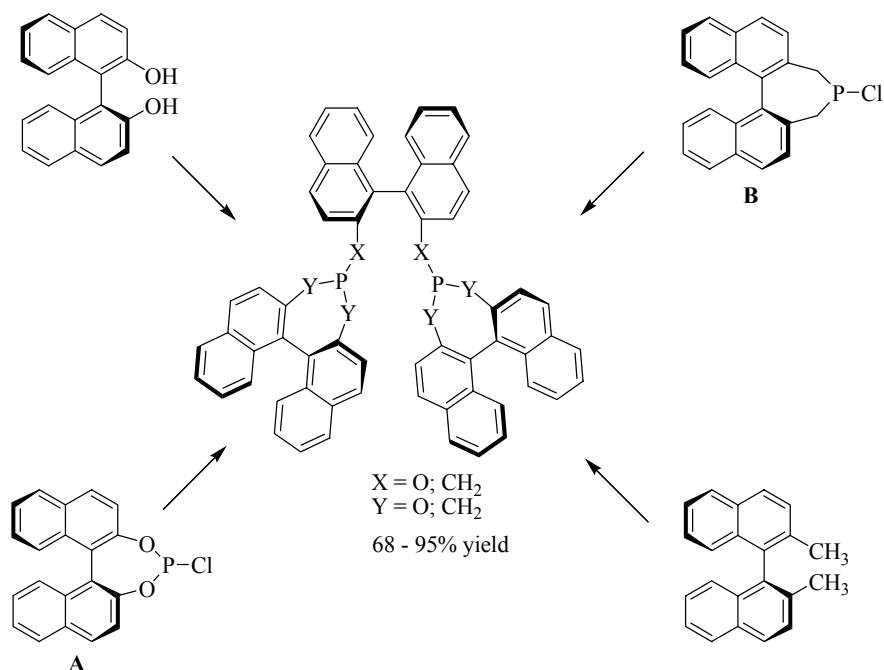
Typically, our aryl-substituted monodentate ligands gave enantioselectivities of 90–95% in standard benchmark asymmetric hydrogenations. Recently, in order to improve the enantioselectivity further, we considered the synthesis of bidentate 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphepines.<sup>19</sup> As building blocks for the novel bidentate ligands we used **A**, **B** and 1,1'-binaphthol (Figure 3; ligands **7** and **8**) as well as 2,2'-dimethyl-1,1'-binaphthyl (Figure 3; ligands **9** and **10**).



**Figure 2.** Novel chelating P-ligands.

All ligands with the exception of **9** have been synthesized in the *S,S,S*- and *S,R,S*- forms by using the *S*- and *R*- configuration of 1,1'-binaphthol and 2,2'-dimethyl-1,1'-binaphthyl bridge to identify the matched and the mismatched combinations (Figure 2).

Ligands (*S,S,S*)-**7** and (*S,R,S*)-**7** were easily prepared according to literature protocols.<sup>20–22</sup> The diphosphonites **8** were obtained in good yield by reaction of the building block *S*-**B** with *S*- or *R*-binaphthol in the presence of 1.1 equiv. of triethylamine. The crude product was purified by recrystallization as the rhodium complex [Rh(cod)**8**]BF<sub>4</sub>. For the synthesis of the corresponding phosphonites **9** and phosphines **10** the two methyl groups of 2,2'-dimethyl-1,1'-binaphthyl were lithiated selectively to form dark violet crystals.<sup>21</sup> Subsequently, chlorides **A** or **B** are quenched with the dilithium salt to produce the corresponding chelating ligands in high yield.



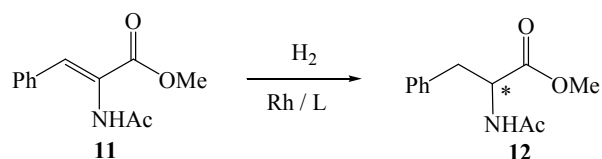
**Figure 3.** Synthesis of chelating P-ligands.

In summary, we have synthesized a small pool of chelating ligands by replacing oxygen against carbon, step by step, allowing us a systematic investigation of the structural influence on the catalytic behaviour. Prior to our work ligands **8–9** had not been prepared, while **7** and **10** had not been used for asymmetric hydrogenation reactions. The diphosphite (*S,S,S*)-**7** was first disclosed by Pringle and co-workers,<sup>22</sup> who used a Ni(0) complex of **7** for the hydrocyanation of norbornene with acetone cyanohydrin, giving the corresponding product in up to 38% *ee*. Another application of (*S,S,S*)-**7**-Cu(OTf)<sub>2</sub> was reported by Chan *et al.*<sup>20</sup> for the conjugate addition of diethylzinc to enones, where enantioselectivities up to 90% were achieved. In addition, Bakos<sup>23</sup> and Chan<sup>24</sup> tested the diphosphites **7** in the asymmetric hydroformylation of styrene and vinyl acetate, respectively. Buchwald *et al.* used a cobalt complex in combination with **7** as catalyst for intramolecular asymmetric Pauson-Khand reactions to obtain cyclopentenones in up to 75% enantiomeric excess.<sup>25</sup> The conjugate addition of arylboronic acids to dehydroalanine derivatives has been successfully carried out (up to 72% *ee*) in the presence of (*R,R,R*)-**7**.<sup>26</sup> The synthesis of diphosphine **10** as a diastereomeric mixture is also known in the literature.<sup>27</sup> Further bidentate ligands bearing the phosphepine unit **A** connected by phenyl or ferrocenyl bridges are known from the elegant work of Zhang *et al.* as binaphane and f-binaphane.<sup>19</sup>

Our initial catalytic studies focused on the asymmetric hydrogenation of  $\alpha$ -aminoacid derivatives and itaconic acid dimethyl ester. Typically, catalytic experiments were carried out with 1 mol% of the catalyst [Rh(cod)L]BF<sub>4</sub> which was prepared *in situ* from 0.01 mmol [Rh(cod)<sub>2</sub>]BF<sub>4</sub> and 1.1 equiv. of ligands **7–10**. Table 1 summarizes the results for the asymmetric hydrogenation of methyl  $\alpha$ -acetamidocinnamate **11** in toluene and ethyl acetate. In general, the

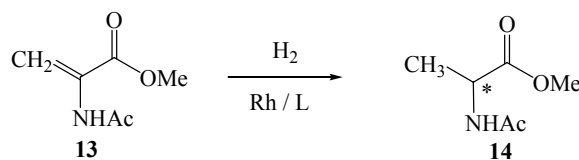
*S,S,S*-configured ligands produce higher enantioselectivity than the *S,R,S*-configured ones. This trend dramatically finds its expression for the phosphonites **8** (Table 1, entries 5 and 6) where (*S,S,S*)-**8** gave 95% *ee* and (*S,R,S*)-**8** led to the racemic mixture. Obviously the *S,S,S*-form of the ligand constitutes the matched- and the *S,R,S*-form the mis-matched case. However, both combinations of phosphine **10** (*S,S,S* and *S,R,S*) hydrogenated methyl  $\alpha$ -acetamidocinnamate **11** with moderate enantioselectivity (between 38% and 47%, Table 1, entries 11–14). Regarding the catalyst activity, the (*S,S,S*)-ligands **8** and **10** gave full conversion for this substrate within less than 1 h. On the other hand, especially ligand **7** and **9** hydrogenate so slowly that the reaction was stopped after 24 hours. The best enantioselectivity (96% *ee*) was achieved in ethyl acetate by applying (*S,S,S*)-**8** (Table 1, entry 7) which bears P-O bonds in the two seven-membered rings, and P-C bonds in the bridge.

**Table 1.** Asymmetric hydrogenation of methyl  $\alpha$ -acetamidocinnamate **11**



Entry	Ligand	Configuration	Solvent	<i>t</i> /2 [min]	Conversion [%]	<i>ee</i> [%] ( <i>R</i> )
1	<b>7</b>	<i>S,S,S</i>	EtOAc	---	39	27
2	<b>7</b>	<i>S,R,S</i>	EtOAc	---	67	18
3	<b>7</b>	<i>S,S,S</i>	Toluene	---	18	55
4	<b>7</b>	<i>S,R,S</i>	Toluene	---	39	14
5	<b>8</b>	<i>S,S,S</i>	EtOAc	5	> 99	95
6	<b>8</b>	<i>S,R,S</i>	EtOAc	---	16	Rac.
7	<b>8</b>	<i>S,S,S</i>	Toluene	540	> 99	96
8	<b>8</b>	<i>S,R,S</i>	Toluene	---	10	Rac.
9	<b>9</b>	<i>S,S,S</i>	EtOAc	---	79	45
10	<b>9</b>	<i>S,S,S</i>	Toluene	---	24	26
11	<b>10</b>	<i>S,S,S</i>	EtOAc	3	> 99	38
12	<b>10</b>	<i>S,R,S</i>	EtOAc	107	> 99	43
13	<b>10</b>	<i>S,S,S</i>	Toluene	48	> 99	47
14	<b>10</b>	<i>S,R,S</i>	Toluene	--	>99	40

Reaction conditions: 1.0 mmol substrate; 0.01 mmol [Rh(cod)<sub>2</sub>]BF<sub>4</sub>; cat. Rh:ligand = 1:1; 15 mL solvent; 25°C, 1 bar H<sub>2</sub>.

**Table 2.** Asymmetric hydrogenation of methyl  $\alpha$ -acetamidoacrylate **13**

Entry	Ligand	Configuration	Solvent	<i>t</i> /2 [min]	Conversion [%]	<i>ee</i> [%] ( <i>R</i> )
1	<b>7</b>	<i>S,S,S</i>	EtOAc	---	51	6
2	<b>7</b>	<i>S,R,S</i>	EtOAc	---	96	17
3	<b>7</b>	<i>S,S,S</i>	Toluene/SDS	---	38	42
4	<b>7</b>	<i>S,R,S</i>	Toluene	---	41	26
5	<b>8</b>	<i>S,S,S</i>	EtOAc	2	> 99	<b>98</b>
6	<b>8</b>	<i>S,R,S</i>	EtOAc	---	96	Rac.
7	<b>8</b>	<i>S,S,S</i>	Toluene	22	> 99	<b>97</b>
8	<b>8</b>	<i>S,R,S</i>	Toluene	---	40	Rac.
9	<b>9</b>	<i>S,S,S</i>	EtOAc	---	> 99	30
10	<b>9</b>	<i>S,S,S</i>	Toluene	---	> 99	3
11	<b>10</b>	<i>S,S,S</i>	THF	32	> 99	38
12	<b>10</b>	<i>S,R,S</i>	THF	60	> 99	61
13	<b>10</b>	<i>S,S,S</i>	EtOAc	4	> 99	12
14	<b>10</b>	<i>S,R,S</i>	EtOAc	---	> 99	37
15	<b>10</b>	<i>S,S,S</i>	Toluene	38	> 99	23
16	<b>10</b>	<i>S,R,S</i>	Toluene/SDS	102	>99	69

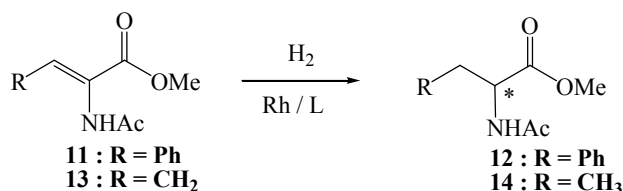
Reaction conditions: 1.0 mmol substrate; 0.01 mmol [Rh(cod)<sub>2</sub>]BF<sub>4</sub>; cat. Rh:ligand = 1:1; 15 mL solvent; 25°C, 1 bar H<sub>2</sub>.

Next, we investigated our ligand pool in the asymmetric hydrogenation of methyl  $\alpha$ -acetamidoacrylate **13**. Based on previous solvent optimization studies the reaction was carried out in toluene, toluene+SDS (sodium dodecylsulfonate), THF, and ethyl acetate. Selected results for compounds **7–10** are given in Table 2. In agreement with the hydrogenation of methyl  $\alpha$ -acetamidocinnamate **11** ligand (*S,S,S*)-**8** led to the best result. Enantioselectivities between 97% and 98% respectively (Table 2, entries 5 and 7) are obtained, while the isomeric (*S,R,S*)-**8** gave only the racemic product! These results clearly show the importance of the right combination of



the different chiral elements within the ligand. With respect to activity, in most cases complete conversion was observed in reasonable times.

**Table 3.** Asymmetric hydrogenation of  $\alpha$ -amino acid derivatives with ligand (*S,S,S*)-**8**



Entry	Substrate	Solvent	<i>t</i> /2 [min]	Conversion [%]	ee [%] ( <i>R</i> )
1	<b>11</b>	EtOAc	5	> 99	95
2 <sup>#</sup>	<b>11</b>	EtOAc	6	> 99	94
3	<b>11</b>	THF	7	> 99	90
4	<b>11</b>	Toluene	540	> 99	96
5 <sup>#</sup>	<b>11</b>	Toluene	7	> 99	<b>98</b>
6	<b>11</b>	Toluene/SDS	480	> 99	92
7 <sup>#</sup>	<b>11</b>	Toluene/SDS	28	> 99	94
8	<b>13</b>	EtOAc	2	> 99	<b>98</b>
9 <sup>#</sup>	<b>13</b>	EtOAc	3	> 99	96
10	<b>13</b>	THF	3	> 99	97
11	<b>13</b>	Toluene	22	> 99	97
12 <sup>#</sup>	<b>13</b>	Toluene	2	> 99	<b>98</b>
13	<b>13</b>	Toluene/SDS	32	> 99	94
14 <sup>#</sup>	<b>13</b>	Toluene/SDS	5	> 99	97

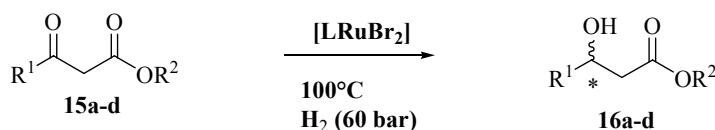
Reaction conditions: 1.0 mmol substrate; 0.01 mmol [Rh(cod)<sub>2</sub>]BF<sub>4</sub>; cat. Rh:ligand = 1:1; 15 mL solvent; 25°C, 1 bar H<sub>2</sub>. <sup>#</sup> isolated [Rh(cod)**8**]BF<sub>4</sub>.

It is noteworthy that, with the exception of ligands **8**, the general predefinition of the matched and the mismatched combination of the *R*- and *S*-configured building blocks is not clear for the hydrogenation of methyl  $\alpha$ -acetamidoacrylate **13**. In the asymmetric hydrogenation of dimethyl itaconate only moderate enantioselectivities were achieved with all ligands. For example (*S,S,S*)-**7** and (*S,S,S*)-**8** gave 32% and 39% *ee*, respectively.

After exploring the catalytic potential of the ligands in the hydrogenation of amino-acid precursors we were interested in the behaviour of (*S,S,S*)-**8** under different reaction conditions. Table 3 shows a comparison of the *in situ* catalyst and the isolated complex [Rh(cod)(*S,S,S*)-**8**]BF<sub>4</sub>. Both  $\alpha$ -amino acid derivatives were hydrogenated in up to 98% *ee* within short time. Using the isolated complex the catalyst activity is improved. Especially for the *in situ* catalytic system the hydrogenations run slowly in the non-polar solvent toluene (Table 3, entries 4 and 6). Contrary to our previous experience for asymmetric hydrogenation with monodentate ligands<sup>16</sup> the addition of SDS to toluene has no significant influence.

Finally, the bidentate phosphine **10** was also tested in the ruthenium-catalyzed asymmetric hydrogenation of various  $\beta$ -ketoesters. Other ligands were not included in this study because of the hydrolysis of the P-O bonds under the reaction conditions. All catalytic experiments were performed with 1 mol% catalyst formed *in situ* from [Ru(cod)methylallyl]<sub>2</sub>/HBr and 1 equiv. of ligand **10** in ethanol or methanol. The results obtained for the hydrogenation of different 1,3-diketoesters are summarized in Table 4. In general, the  $\beta$ -hydroxyesters were obtained in good yield, although with low to mediocre enantioselectivity. The best result (78% *ee*) is observed for the phenyl-substituted ketoester (Table 4, entry 8) using the phosphine **10** in the *S,R,S*-configuration.

**Table 4.** Asymmetric hydrogenation of  $\beta$ -ketoesters with ligand **10**



Entry	Config. of <b>10</b>	Substrate	R <sup>1</sup>	R <sup>2</sup>	<i>t</i> [h]	Yield [%]	<i>ee</i> [%]
1	<i>S,S,S</i>	<b>15a</b>	CH <sub>3</sub>	CH <sub>3</sub>	16	93	27 ( <i>S</i> )
2	<i>S,S,S</i>	<b>15b</b>	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub>	16	94	34 ( <i>S</i> )
3	<i>S,S,S</i>	<b>15c</b>	Cl-CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	16	66	11 ( <i>R</i> )
4	<i>S,S,S</i>	<b>15d</b>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub>	16	99	16 ( <i>R</i> )
5	<i>S,R,S</i>	<b>15a</b>	CH <sub>3</sub>	CH <sub>3</sub>	24	92	52 ( <i>R</i> )
6	<i>S,R,S</i>	<b>15b</b>	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub>	24	92	43 ( <i>R</i> )
7	<i>S,R,S</i>	<b>15c</b>	Cl-CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	24	87	14 ( <i>R</i> )
8	<i>S,R,S</i>	<b>15d</b>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub>	24	99	78 ( <i>S</i> )

Reaction conditions: methanol or ethanol (2 mL);  $3.8 \times 10^{-1}$  mmol  $\beta$ -ketoester **15a-d**;  $3.8 \times 10^{-3}$  mmol Ru(cod)methylallyl<sub>2</sub>/methanolic HBr;  $3.8 \times 10^{-3}$  mmol **10**; 60 bar; 100°C.

## Conclusions

In conclusion, we have synthesized a library of novel bidentate chiral ligands containing 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphepine and binaphthol building blocks. These ligands can be synthesized easily from 2,2'-binaphthol and 2,2'-dimethylbinaphthol. One of the prepared ligands ((*S,S,S*)-**8**) can be used efficiently for the rhodium-catalyzed hydrogenation of  $\alpha$ -amino acid precursors, and enantioselectivities up to 98% *ee* were achieved.

## Experimental Section

**General Procedures.**  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ - NMR spectra were recorded on a Bruker Spectrometer ARX 400 ( $^1\text{H}$ , 400.13 MHz;  $^{13}\text{C}$ , 100.6 MHz;  $^{31}\text{P}$ , 162.0 MHz). The calibration of  $^1\text{H}$ - and  $^{13}\text{C}$ - spectra was carried out on solvent signals ( $\delta(\text{CDCl}_3) = 7.27$  and  $77.0$ ;  $\delta(\text{C}_6\text{D}_6) = 7.15$  and  $128.0$ ;  $\delta(\text{CD}_3\text{COCD}_3) = 2.05$  and  $29.8$ ). The  $^{31}\text{P}$ - NMR chemical shifts are referenced to 85%  $\text{H}_3\text{PO}_4$ . The  $^1\text{H}$ - and  $^{13}\text{C}$ - NMR signals were assigned by DEPT spectra. Mass spectra were recorded on an AMD 402 spectrometer. Elemental analyses were performed using a Leco CHNS-932. Optical rotations were measured on a Gyromat-HP polarimeter. IR spectra were recorded on KBr pellets or Nujol mulls on a Nicolet Magna 550. All experiments were carried out under an argon atmosphere. The building blocks **A** and **B** have been synthesized according to the literature.<sup>16, 20,21,28</sup> Enantiomerically pure 2,2'-dimethylbinaphthyl is obtained in 92% overall yield from optically pure 2,2'-binaphthol via esterification with trifluoromethanesulfonic acid anhydride in pyridine and subsequent Ni-catalyzed Kumada coupling with  $\text{MeMgBr}$ .<sup>29</sup> Metallation<sup>30</sup> of enantiomerically pure 2,2'-dimethylbinaphthyl with *n*-BuLi/TMEDA affords the crystalline dilithio species in 70-80% yield.

### General procedure for ligand synthesis

#### General procedure for the synthesis of **7** and **8**

To 1 equiv. of 2,2'-binaphthol and 2 equiv. of  $\text{NEt}_3$  in toluene were added 2 equiv. of building block **A** or **B** at  $0^\circ\text{C}$ . After stirring the mixture for 2 h at room temperature and filtration of the precipitate the solvent is evaporated. The crude product is crystallized from ethanol/hexane (**1**) or THF/hexane (**2**).

#### General procedure for the synthesis of **9** and **10**

A suspension of 1 equiv. of the dilithium salt of 2,2'-dimethyl-1,1'-binaphthyl in toluene is added through a tube to 2 equiv. of building block **A** or **B** dissolved in toluene, over a period of 30–45 min. The color of the reaction mixture turned from dark violet to yellow. After stirring for 10 h, LiCl was filtered off under inert conditions and washed with toluene. The solvent was evaporated and the crude product purified by flash column chromatography in dry toluene.

**Selected data for (S,S,S)-7 containing 0.6 mol EtOH.** Yield: 82%.  $^1\text{H}$ - NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.15 (t, 1.8H,  $J$  = 7.0 Hz,  $\text{CH}_3$ ); 2.45 (s, 0.6H, OH); 3.63 (dd, 1.2H,  $\text{CH}_2$ ); 6.45 (d, 2H,  $J$  = 8.8 Hz); 7.15 – 7.22 (m, 14H); 7.25 – 7.33 (m, 8H); 7.45 (d, 2H,  $J$  = 8.8 Hz); 7.65 (d, 2H,  $J$  = 8.1 Hz); 7.73 (dd, 2H,  $J$  = 8.8 Hz,  $J$  = 7.9 Hz); 7.81 (d, 2H,  $J$  = 8.1 Hz); 7.88 (d, 2H,  $J$  = 8.9 Hz).  $^{13}\text{C}$ - NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 121.1; 121.7; 121.8; 122.4; 124.3; 124.6; 124.9; 125.1; 125.8; 126.1; 126.2; 126.8; 126.9; 128.0; 128.2; 128.3; 129.5; 130.0; 130.2; 130.8; 131.0; 131.4; 132.2; 132.6; 134.2; 146.9; 147.5; 148.5.  $^{31}\text{P}$ - NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.2. IR (KBr): 3423w; 3055m; 1619m; 1589m; 1505m; 1463m; 1431m; 1359m; 1325m; 1217s; 1189m; 1154m; 1069m; 978m; 943s; 865m; 825s; 785s; 770m; 751s; 696m; 682m; 644w; 629w; 599w; 569w; 556m; 526m. MS (FAB):  $m/z$  (%) = 916 ( $[\text{M}^+ + 2]$ , 45); 664 (5); 601 (13); 583 (82); 315 (95). Mp 188°C. Optical Rotation:  $[\alpha]^{23} = +337$  (c = 0.5; toluene).

**Selected data for (S,R,S)-7 containing 0.8 mol EtOH.** Yield 95%.  $^1\text{H}$ - NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.25 (t, 2.4H,  $J$  = 7.0 Hz,  $\text{CH}_3$ ); 2.65 (s, 0.8H, OH); 3.75 (dd, 2.4H,  $\text{CH}_2$ ); 5.8 (d, 2H,  $J$  = 8.7 Hz); 7.2 – 7.3 (m, 14H); 7.35 – 7.43 (m, 8H); 7.6 (d, 2H,  $J$  = 8.7 Hz); 7.75 (d, 2H,  $J$  = 7.1 Hz); 7.87 (d, 4H,  $J$  = 8.7 Hz); 8.05 (d, 2H,  $J$  = 8.3 Hz); 8.1 (d, 2H,  $J$  = 8.9 Hz).  $^{13}\text{C}$ - NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 121.1; 121.4; 121.7; 122.4; 123.0; 124.0; 124.3; 124.6; 125.0; 125.2; 125.8; 126.1; 126.3; 126.8; 126.9; 128.0; 128.1; 128.2; 129.1; 130.1; 130.3; 131.0; 131.1; 131.4; 132.1; 132.7; 134.0; 147.0; 147.3; 148.2.  $^{31}\text{P}$ -NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.8. IR (KBr): 3448m; 3055m; 1620m; 1589m; 1507m; 1463m; 1431m; 1359m; 1326m; 1215s; 1189m; 1154m; 1070m; 979m; 950s; 865m; 825s; 787s; 770m; 748s; 694m; 645w; 630w; 598w; 569w; 556w; 526m. Mp 189°C. Optical Rotation:  $[\alpha]^{23} = +194$  (c = 0.5; toluene).

**Selected data for (S,S,S)-8.** Yield: 60%.  $^1\text{H}$ - NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.9 – 2.09 (m, 4H,  $\text{CH}_2$ ); 2.2 – 2.3 (dd, 3H,  $\text{CH}_2$ ); 2.35 (d, 1H,  $\text{CH}_2$ ).  $^{31}\text{P}$ - NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.0. IR (KBr): 3423m; 3053m; 1619m; 1592m; 1507s; 1459m; 1431m; 1343m; 1256m; 1225s; 1144m; 1127m; 1071w; 1027w; 982m; 933m; 865m; 816s; 748s; 694w; 673w; 621w; 566w; 540w; 520w. MS (FAB):  $m/z$  (%) = 907 ( $[\text{M}^+]$ , 20); 859 (5); 779 (8); 720 (10); 597 (15); 495 (8); 432 (10); 367 (12); 310 (25); 282 (40); 265 (100); 198 (18). Mp 150°C. Optical rotation:  $[\alpha]^{23} = -58$  (c = 0.5; toluene).

**Selected data for (S,R,S)-8.** Yield: 81%.  $^1\text{H}$ - NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.16 – 2.25 (m, 2H,  $\text{CH}_2$ ); 2.39 – 2.51 (dd, 4H,  $\text{CH}_2$ ,  $J$  = 13.95 Hz); 2.89 – 3.07 (m, 2H,  $\text{CH}_2$ ).  $^{31}\text{P}$ - NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 156.5. IR (KBr): 3423s; 3053m; 2958m; 1619m; 1592m; 1507s; 1459m; 1426m; 1355m; 1223s; 1145m; 1071w; 1027w; 984m; 933w; 865m; 814s; 747s; 663w; 622w; 567w; 520w. MS (FAB):  $m/z$  (%) = 907 ( $[\text{M}^+]$ , 20); 859 (5); 779 (8); 720 (10); 597 (15); 495 (8); 432 (13); 367 (12); 310 (25); 282 (40); 265 (100); 198 (18). Mp 162°C. Optical rotation:  $[\alpha]^{23} = -106$  (c = 0.5; toluene).

**Selected data for (S,S,S)-9.** Yield: 79%.  $^1\text{H}$ - NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.27 (d, 2H,  $J$  = 13.5 Hz,  $\text{CH}_2$ ); 2.59 (t, 2H,  $J$  = 14.3 Hz,  $\text{CH}_2$ ); 6.39 (d, 2H,  $J$  = 8.8 Hz); 6.39 – 6.42 (d, 2H); 6.67 (d, 2H,  $J$  = 8.5 Hz); 6.74 (d, 2H,  $J$  = 8.5 Hz); 6.86 (d, 2H,  $J$  = 8.5 Hz); 7.03 – 7.14 (m, 8H); 7.21 (d, 2H,  $J$  = 8.7 Hz); 7.25 (d, 2H,  $J$  = 8.7 Hz); 7.31 (m, 2H); 7.34 (d, 2H,  $J$  = 8.0 Hz); 7.55 (d, 2H,  $J$  = 8.5 Hz); 7.71 (d, 2H,  $J$  = 7.9 Hz); 7.80 (dd, 2H,  $J$  = 8.1 Hz,  $J$  = 8.7 Hz).  $^{13}\text{C}$ - NMR (100.6 MHz,

CDCl<sub>3</sub>):  $\delta$  = 40.1 (d, CH<sub>2</sub>,  $J$  = 40.0 Hz); 121.5; 121.6; 123.2; 123.9; 124.2; 124.7; 124.8; 124.9; 125.3; 125.4; 126.1; 126.2; 126.4; 126.6; 126.8; 127.7; 128.0; 128.2; 129.0; 129.9; 130.2; 130.8; 131.3; 131.6; 132.2; 132.5; 132.8; 135.0; 147.0; 149.0. <sup>31</sup>P-NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  = 205.8. IR (KBr): 3517w; 3054m; 2923m; 2857w; 1619s; 1590s; 1507s; 1463s; 1431m; 1359m; 1326m; 1270m; 1257m; 1229s; 1155m; 1143m; 1071s; 1028w; 981m; 950s; 865m; 821s; 748s; 730m; 695m; 643w; 629w; 566w; 555m; 527w. MS (EI):  $m/z$  (%) = 596 ([M<sup>+</sup> - 314], 65); 268 (14); 181 (28); 131 (79); 69 (30). Mp 195°C. Optical Rotation:  $[\alpha]^{23}$  = 694 (c = 0.5; toluene).

**Selected data for (S,S,S)-10.** Yield: 68%. Calc. for C<sub>66</sub>H<sub>48</sub>P<sub>2</sub>: C, 87.66; H, 5.31; P, 6.86%. Found: C, 87.53; H, 5.11; P, 6.43%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.0 – 2.6 (m, 12H, CH<sub>2</sub>); 6.0 – 8.0 (m, 36H). <sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.7 (d, CH<sub>2</sub>); 31.1 (d, CH<sub>2</sub>); 35.0 (d, CH<sub>2</sub>). <sup>31</sup>P-NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.4. IR (KBr): 3432w; 3049m; 3007m; 2908m; 1710w; 1618m; 1592m; 1507s; 1421m; 1358m; 1327w; 1248m; 1222m; 1160m; 1144m; 1026m; 960m; 934m; 865m; 837s; 813s; 747s; 673m; 621m; 566w; 520w. MS (FAB):  $m/z$  (%) = 902 ([M<sup>+</sup> - 1], <5); 591 (10); 501 (3); 335 (7); 265 (65); 199 (100). Mp 233°C. Optical Rotation:  $[\alpha]^{23}$  = 10 (c = 0.5; toluene).

**Selected data for (S,R,S)-10.** Yield: 70%. Calc. for C<sub>66</sub>H<sub>48</sub>P<sub>2</sub>: C, 87.66; H, 5.31; P, 6.86%. Found: C, 87.18; H, 5.42; P, 6.34%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.0 – 2.7 (m, 12H, CH<sub>2</sub>); 6.4 – 7.9 (m, 36H). <sup>31</sup>P-NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.4. IR (KBr): 3432s; 3052m; 2958m; 1618m; 1594m; 1508s; 1406m; 1359m; 1329w; 1249m; 1228m; 1160m; 1027m; 961w; 931w; 866m; 816s; 748s; 680w; 622w; 567w; 544w; 520w. MS (FAB):  $m/z$  (%) = 903 ([M<sup>+</sup>], 15); 874 (3); 827 (1); 695 (2); 655 (3); 619 (10); 592 (100); 529 (5); 413 (7). Mp 228°C. Optical Rotation:  $[\alpha]^{23}$  = 100 (c = 0.33; toluene).

**Preparation of the Rh(II) complex of (S,S,S)-8.** A solution of ligand (S,S,S)-2 (1.2 mmol) in THF (7 mL) was added dropwise to a stirred solution of Rh(cod)acac (1.2 mmol) in the same solvent (5 mL). After 1 h at 20°C, ethereal HBF<sub>4</sub> (1.2 mmol) is added and the solution stirred for an additional hour. The solvent was removed and the residue crystallized in acetone/methanol to give red-brown solid. Calc. for C<sub>72</sub>H<sub>56</sub>O<sub>2</sub>P<sub>2</sub>RhBF<sub>4</sub>: C, 71.71; H, 4.65%. Found: C, 71.67; H, 4.89%. <sup>31</sup>P-NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.5 (d,  $J$  = 173.4 Hz). MS (FAB):  $m/z$  (%) = 1117 ([M<sup>+</sup> - 1 - BF<sub>4</sub>], 60); 1009 ([M<sup>+</sup> - 1 - BF<sub>4</sub> - cod], 70); 834 (100); 709 (100).

### Catalytic experiments

**Asymmetric hydrogenation of  $\alpha$ -aminoacids 11 and 13.** Hydrogenation was performed under normal pressure at 25°C. A mixture of 0.01 mmol [Rh(cod)<sub>2</sub>]BF<sub>4</sub>, 0.01 mmol ligand 7–10 and 0.1 mmol methyl  $\alpha$ -acetamidocinnamate 5 or methyl  $\alpha$ -acetamidoacrylate 7 was stirred for 15 min in 15 mL solvent. The hydrogenation flask was flushed several times with hydrogen. The reaction was followed by a volumetric measurement at 25°C  $\pm$  0.5°C. The enantiomeric excess of 12 (Lipodex E, 150°C isotherm) and 14 (Chirasil Val, 120°C isotherm) were determined by GC.

**Asymmetric hydrogenation of  $\beta$ -ketoesters 15a-d.** Catalytic hydrogenation experiments were carried out in a parallel autoclave (8x3 mL). In a typical experiment, the autoclave was charged

with a mixture of  $3.8 \times 10^{-3}$  mmol of catalyst [LRuBr<sub>2</sub>] prepared *in situ* and  $3.8 \times 10^{-1}$  mmol  $\beta$ -ketoester **15a–d** in 2 mL methanol or ethanol under an argon stream. The autoclave's contents were stirred at 60 bar hydrogen pressure and 100°C for 16-24 h. The autoclave was cooled to room temperature and the hydrogen was released. The reaction mixture was filtered over silica gel and the enantiomeric excess determined by GC (Lipodex E) or HPLC (Chiracel OD-H). Most of the hydrogenation products have been previously described. Methyl 3-hydroxybutyrate (**16a**): GC (25 m Lipodex E) 95°C isothermal:  $t_r(\text{min}) = 4.9$  (S), 5.7 (R); methyl 3-hydroxyvalerate (**16b**): GC (25 m Lipodex E) 85°C isothermal:  $t_r(\text{min}) = 10.9$  (S), 11.6 (R); ethyl 3-hydroxy-4-chlorobutyrate (**16c**): GC (25 m Lipodex E) 95°C isothermal:  $t_r(\text{min}) = 20.4$  (R), 20.6 (S); Ethyl 3-hydroxy-3-phenylpropionate (**16d**): HPLC (Chiracel OD-H, hexane/ethanol = 95:5, 0.5 mL/min),  $t_r(\text{min}) = 10.1$  (S), 11.5 (R).

## Acknowledgements

This work has been financed by the State of Mecklenburg-Pomerania and the Bundesministerium für Bildung und Forschung (BMBF). We thank Mrs. C. Voss, Mrs. C. Mewes, Mrs. M. Heyken, Mrs. S. Buchholz and Dr. C. Fischer (all Leibniz-Institut für Katalyse e.V. an der Universität Rostock) for their excellent technical and analytical support.

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