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Amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands and their applications in catalytic asymmetric hydrogenations in ionic liquid systems

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ABSTRACT

Herein we report the synthesis of amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands and the catalytic efficiency and reusability of their corresponding Rh-catalysts in the asymmetric hydrogenation of methyl (*Z*)-2-acetamidocinnamate in different reaction media, including classical organic solvents, ionic liquid (IL) [bmim]BF_4 (1-*n*-butyl-3-methyl-imidazolium tetrafluoroborate) and [bmim]BF_4/cosolvent systems. The effects of the ionic tag structures, IL, cosolvents, Rh precursors, and halide impurities on catalytic activity and enantioselectivity were studied in detail. In the hydrogenation reaction, the amino acid- and imidazolium modified ligands gave higher ee values than the classical pyrrolidinodiphosphine, (2*S*,4*S*)-*N*-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino) methyl] pyrrolidine (BPPM), both in pure methanol and in the [bmim]BF_4/MeOH system. The catalyst recycling experiments demonstrated that introducing the amino acid and imidazolium moieties into the pyrrolidinodiphosphine backbone resulted in much better immobilization and reusability of the Rh-catalysts in [bmim]BF_4, and after several cycles there was no significant loss in activity, enantioselectivity, or Rh.

1. Introduction

Asymmetric hydrogenation was the first catalytic asymmetric reaction that reached industrial scale application. It is currently one of the most investigated areas in chemistry research and has become the ideal method for preparing chiral compounds and drugs, including amino acids, alcohols, and amines.[1] A critical issue in asymmetric hydrogenations is the successful design of chiral ligands that complex with noble metals such as Ru, Rh, and Ir to give highly active and stereoselective chiral catalysts.[2] Nevertheless, to effectively recycle the expensive chiral catalysts from hydrogenation products has remained a great challenge and a continuing research focus in recent decades.[3] Heterogeneous catalysis has emerged as a solution to this problem, in which the chiral catalysts can be immobilized on a polymer or inorganic matrix for easy separation.[4] Alternatively, liquid-liquid biphasic catalytic systems may be used, including aqueous-organic systems,[5] fluorous-organic systems,[6] supercritical fluids,[7] ionic liquids (ILs),[8] and so on. The biphasic catalytic system using catalyst-supporting ILs has become of great interest in recent years and is expected to show great potential as a readily applicable system.[9] Although some successful use of ILs has been reported for the asymmetric hydrogenation of α-enamide esters,[10] β-ketoesters,[11] and aromatic ketones,[12] significant limitations still remain. One limitation is that the chiral catalyst tends to be lost into the product phase,[10c,d] and is prone to oxidation after many cycles, thus resulting in reduced catalytic activity and enantioselectivity.[10b] Another is that the activity and enantioselectivity of asymmetric hydrogenation in ILs are often unsatisfactory and inferior to those of the homogeneous reaction in organic solvents.[13] Therefore, a key concern in asymmetric hydrogenations using ILs is the effective dissolution and immobilization of the chiral catalyst in the ILs to avoid catalyst loss while maintaining high catalytic activity and high stereoselectivity.

Ionic liquid supported (ILS) asymmetric catalysis offers a solution to this problem.[14] In ILS asymmetric catalysis, the ionic liquid molecules (imidazolium, pyridinium, guanidinium, etc.) are embedded into the skeleton of the phosphine ligands to enhance the stability and affinity of the chiral catalyst in, and to, the IL phase.[15] In addition, it is known that the introduction of a cosolvent into the ILs catalytic system can improve the activity and stereoselectivity.[16] However, to date, there are still very few numbers of reported ILS chiral catalysts for the asymmetric hydrogenations. Systematic research is necessary to explore the applicability of this concept in other chiral ligands.[14] The synergy between the ILs/cosolvents and the chiral catalyst that affects the activity and enantioselectivity has a very complex mechanism.[16,17] It is theoretically informative to interpret this mechanism and determine the patterns in asymmetric hydrogenations using ILs.

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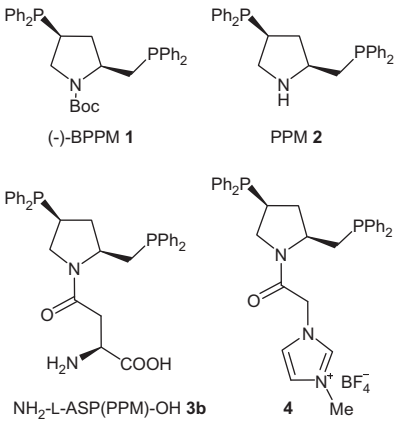
Herein, based on the 'ILS asymmetric catalysis' concept, we have synthesized amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands (Scheme 1) and tested their Rh complexes in the enantioselective hydrogenation of methyl (*Z*)-2-acetamidocinnamate (MAC). The hydrogenation reactions were carried out in classical organic solvents, [bmim]BF_4 and [bmim]BF_4/cosolvent systems. We aim to reveal the specific effects of chiral catalyst structures, IL, and cosolvents on the catalytic activity, enantioselectivity, and catalyst reusability.



Scheme 1. Studied ligands.

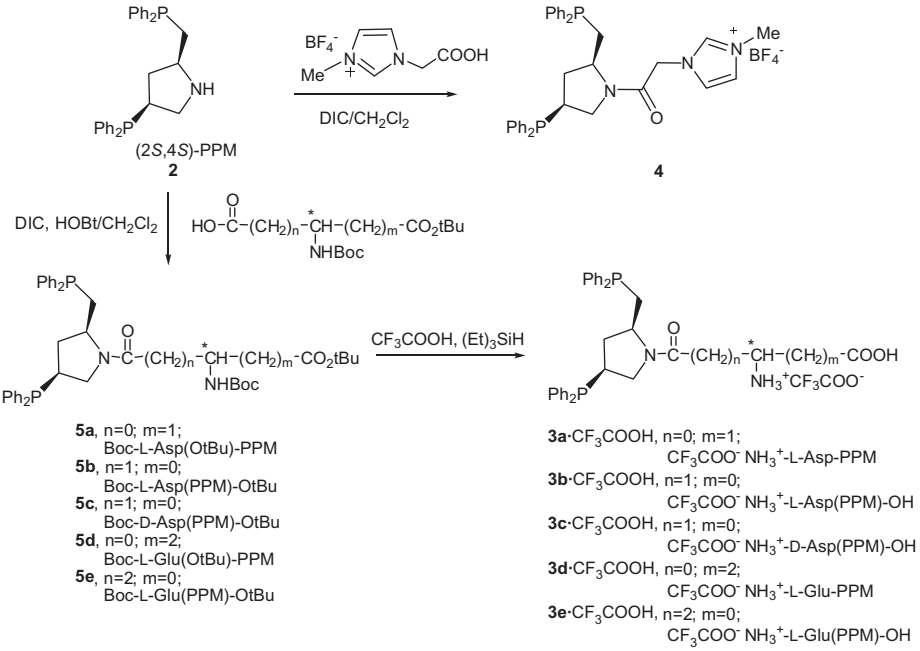
2. Results and discussion

Chiral pyrrolidinodiphosphine ligands, such as BPPM and PhCAPP, are versatile and efficient in Rh-catalyzed asymmetric hydrogenation of α-enamide esters,[18] dehydro peptides,[19] α-keto-esters,[20] dehydro α-aminophosphinic acids,[21] and in asymmetric hydroformylations.[22] Moreover, the structure of the pyrrolidinodiphosphine ligand can be readily modifiable and various substituents can be introduced onto the N atom in the pyrrolidine backbone. The synthesis of amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands is shown in Scheme 2.

The amino acid-modified ligands **3a**–**e** can be easily synthesized in two steps from **2** (PPM). Firstly, the Boc and O*t*Bu-protected aspartic acid or glutamic acid was attached to the amino group of the PPM by DIC-promoted amidation to obtain diphosphines **5a**–**e**. Next, both the Boc and O*t*Bu protecting groups were removed in the presence of trifluoroacetic acid and triethylsilane to give the trifluoroacetic acid salts of **3a–e**. Similarly, 1-carboxymethyl-3-methylimidazolium tetrafluoroborate was attached to the backbone of PPM by the same DIC-promoted amidation to give ligand **4**.

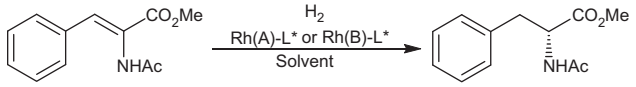
Table 1 systematically evaluates the catalytic performance of amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands in the Rh-catalyzed homogeneous asymmetric hydrogenation of MAC. The effect of different rhodium precursors, reaction solvents, ligand structures, reaction temperature, and hydrogen pressure on the stereoselective hydrogenations was determined.

Except for ligand **5a**, all other ligands gave higher ee values when using the cationic rhodium precursor [A: $[Rh(COD)_2]BF_4$] than when using the non-ionic precursor [B: $[Rh(COD)Cl]_2$]. The observed effects of classical organic solvents on enantioselectivities were in agreement with literature.[16c,23] For example, for ligands **5b** and **3b** (Table 1, entries 5, 7–9, 21, 23–25), the ee values improved significantly with rising solvent polarity. Alcohols were found to be the most suitable solvent, with methanol being the best solvent, followed by ethanol and isopropanol. This is because the alcohols can coordinate to the metal center and participate in the catalytic cycle, thus promoting the catalytic reaction.[16a,b,23] The effect of different ionic tags on the enantioselectivities showed obvious patterns. The best enantioselectivity was achieved by the imidazolium-tagged ligand **4**, which gave an ee value of 95% in MeOH. For amino acid-tagged ligands, the position of the stereogenic center in the amino acids had a significant impact on the enantioselectivity. The ee values are obtained notably lower when the stereogenic center in the amino acid was closer to the pyrrolidine ring (**5a**, **5d**, **3a**·CF_3COOH, and **3d**·CF_3COOH) and higher when the stereogenic center in the amino acid was more re-



Scheme 2. Synthesis of amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands.

Table 1
Performance of amino acid- and imidazolium-tagged PPM ligands in the Rh-catalyzed homogeneous asymmetric hydrogenation of MAC[a]



Entry	Ligand	Solvent	Rh	ee (*R*) (%)
1	BPPM	MeOH	A	92
2		MeOH	B	89
3	**5a**	MeOH	A	86
4		MeOH	B	87
5	**5b**	MeOH	A	94
6		MeOH	B	92
7		EtOH	A	88
8		EtOAc	A	78
9		CH_2Cl_2	A	68
10	**5c**	MeOH	A	93
11		MeOH	B	92
12	**5d**	MeOH	A	89
13		MeOH	B	88
14	**5e**	MeOH	A	92
15		MeOH	B	91
16	**3a**·CF_3COOH	MeOH	A	92
17		MeOH	A	84
18		MeOH	A	53
19		MeOH	A	93
20		MeOH	B	89
21	**3b**·CF_3COOH	MeOH	A	94
22		MeOH	B	91
23		EtOH	A	90
24		*i*-PrOH	A	76
25		EtOAc	A	77
26	**3b**	MeOH	A	82
27	**3b**·$N(Et)_3$	MeOH	A	23
28	**3b**·[bmim]OH	MeOH	A	29
29	**3c**·CF_3COOH	MeOH	A	93
30		MeOH	B	91
31	**3d**·CF_3COOH	MeOH	A	92
32		MeOH	B	88
33	**3e**·CF_3COOH	MeOH	A	94
34		MeOH	B	92
35	**4**	MeOH	A	95
36		MeOH	B	92
37		*i*-PrOH	A	82

[a] Reaction conditions: A: $Rh(COD)_2]BF_4$, B: $[Rh(COD)Cl]_2$, $p(H_2)$ = 1.5 atm, T = 25 °C, t = 2.5 h, ligands/Rh = 1.1, substrate/Rh = 100, 2.0 mL solvent; entry 17: $p(H_2)$ = 10 atm; entry 18: $p(H_2)$ = 50 atm; entry 19: T = 50 °C. Substrate conversion rates are all 100% except entries 26–28. Entry 26: dissolve **3b**·CF_3COOH in MeOH and add an equimolar amount of 10% $NaHCO_3$; and the white precipitates are then filtered and dried to give **3b**, conversion 70%; entry 27: **3b**·$CF_3COOH/N(Et)_3$ = 1/2, conversion 17%; entry 28: **3b**·CF_3COOH/[bmim]OH = 1/2, conversion 8%.

mote from the pyrrolidine ring (**5b**, **5c**, **5e**, **3b**·CF_3COOH, **3c**·CF_3COOH, and **3e**·CF_3COOH). This indicates that the stereogenic center in the amino acid has a negative interaction with the metal center of the stereogenic catalyst, and this negative interaction weakens as the chiral center moves away from the metal center. In addition, the stereochemistry of the amino acid tags had a relatively small influence on the enantioselectivity. The ligands **5c** and **3c**·CF_3COOH that were modified by D-aspartic acid and the ligands **5b** and **3b**·CF_3COOH that were modified by L-aspartic acid showed only a 1% difference in ee value.

Since the amino acid-tagged ligands are zwitterionic, we also investigated the influence of alkaline additives on the ligand performance. First, **3b**·CF_3COOH was neutralized with an equimolar amount of $NaHCO_3$ to give **3b**. It was found that both the activity and the enantioselectivity of Rh(A)-L**3b** decreased significantly, giving a conversion rate of 70% and an ee value of 82% (Table 1, entry 26). This resulted from the coordination of free amino groups to Rh.[18a,24] When two equivalent molar amounts of triethylamine or the strongly basic IL [bmim]OH were added, the catalytic activity and enantioselectivity decreased drastically (Table 1, entries 27 and 28). The reduced activity and enantioselectivity are likely to be due to the complexation between Rh and the carboxylate anion, which is formed in the presence of excess base.[25] The enantioselectivity decreased at a higher H_2 pressure (Table 1, entries 17 and 18) and slightly increased with rising reaction temperature (Table 1, entry 19), which is in agreement with the results reported by Ojima[18b] and indicates the same catalytic mechanism. Except for **5a** and **5d**, all other ligands gave comparable or higher enantioselectivity than BPPM (Table 1, entries 1 and 2).

In the following experiments, we investigated the impact of ligand structure and solvents on the catalytic activity using BPPM as the reference (Fig. 1). In methanol, Rh(A)-L**4** showed the highest catalytic activity with a TOF of 24,054 h^{-1}, whereas the activity of Rh(B)-L**4** declined drastically to a TOF of only 459 h^{-1}. This is in contrast with the activity of BPPM ($TOF_{Rh(B)\text{-}BPPM} > TOF_{Rh(A)\text{-}BPPM}$) and for now cannot be well rationalized. For the amino acid-modified ligands, the position of the stereogenic center in the amino acid has similar effects on both catalytic activity and enantioselectivity. The amino acid stereogenic centers in Rh-L**3b**·CF_3COOH and Rh-L**3e**·CF_3COOH are distant from the Rh, and thus have relatively high catalytic activity and similar catalytic behavior to BPPM ($TOF_{Rh(B)\text{-}L} > TOF_{Rh(A)\text{-}L}$). In contrast, the amino acid stereogenic centers in Rh-L**3a**·CF_3COOH and Rh-L**3d**·CF_3COOH are closer to the Rh, and their activity is relatively low. The D-aspartic acid modified Rh(A)-L**3c**·CF_3COOH showed higher activity than L-aspartic acid modified Rh(A)-L**3b**·CF_3COOH, but its catalytic behavior ($TOF_{Rh(B)\text{-}L\mathbf{3c}\cdot CF3COOH} < TOF_{Rh(A)\text{-}L\mathbf{3c}\cdot CF3COOH}$) was opposite to that of BPPM. With other conditions being equal, using isopropanol as the solvent gave much less catalytic activity than using methanol.

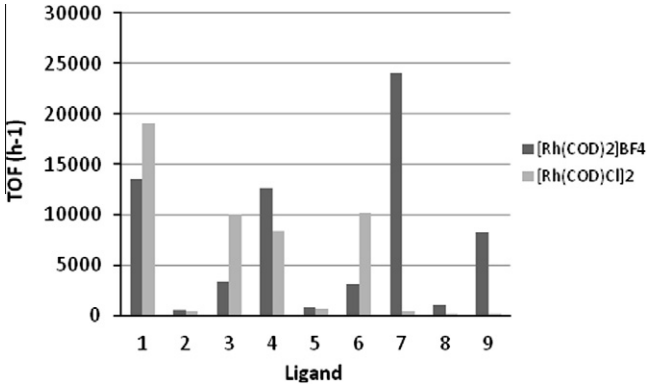


Figure 1. Effect of ligand structure and reaction solvents on the catalytic activity. Reaction conditions: $p(H_2)$ = 1.5 atm, T = 25 °C, t = 2 min, ligands/Rh = 1.1, substrate/Rh = 1000, 2.0 mL solvent. 1: BPPM/MeOH; 2: **3a**·CF_3COOH/ MeOH; 3: **3b**·CF_3COOH/MeOH; 4: **3c**·CF_3COOH/MeOH; 5: **3d**·CF_3COOH/MeOH; 6: **3e**·CF_3COOH/MeOH; 7: **4**/MeOH; 8: **3b**·CF_3COOH/*i*-PrOH; 9: **4**/*i*-PrOH.

Although the chiral pyrrolidinodiphosphine ligands bearing the amino acid and imidazolium moieties showed high efficiency in the Rh-catalyzed enantioselective hydrogenation of MAC in MeOH, we were more interested in their performance in the ILs. Therefore, we chose the most commonly used imidazole-based IL [bmim]BF_4 (1-*n*-butyl-3-methylimidazolium tetrafluoroborate) as the chiral catalyst carrier. We selected Rh-L**3b**·CF_3COOH and Rh-L**4** as the model catalysts, both of which showed high activity and enantioselectivity for the hydrogenation in methanol, and investigated their catalytic performance in [bmim]BF_4 and [bmim]BF_4/cosolvent systems (Table 2).

Table 2
Rh-catalyzed asymmetric hydrogenation of MAC using amino acid- and imidazolium-tagged chiral pyrrolidinodiphosphine ligands in [bmim]BF_4 and [bmim]BF_4/cosolvent systems[a]

Entry	Ligand	Reaction medium	Rh	Conversion (%)	ee (*R*) (%)
1	**3b**·CF_3COOH	[bmim]BF_4	A	60	19
2		[bmim]BF_4	B	36	45
3		[bmim]BF_4[b]	A	100	21
4		[bmim]BF_4[b]	B	46	33
5		[bmim]BF_4[c]	A	100	47
6		[bmim]BF_4[c]	B	66	55
7		[bmim]BF_4/*i*-PrOH[c]	A	100	66
8		[bmim]BF_4/*i*-PrOH[c]	B	100	68
9		[bmim]BF_4/MeOH	A	100	91
10		[bmim]BF_4/MeOH	B	100	92
11	**4**	[bmim]BF_4	A	100	19
12		[bmim]BF_4	B	59	50
13		[bmim]BF_4[b]	A	100	16
14		[bmim]BF_4[b]	B	91	32
15		[bmim]BF_4[c]	A	100	46
16		[bmim]BF_4[c]	B	84	56
17		[bmim]BF_4/*i*-PrOH[c]	A	100	71
18		[bmim]BF_4/*i*-PrOH[c]	B	100	72
19		[bmim]BF_4/MeOH	A	100	91
20		[bmim]BF_4/MeOH	B	100	92
21		[bmim]BF_4/MeOH[b]	A	100	91
22		[bmim]BF_4/MeOH[b]	B	100	89
23	BPPM	[bmim]BF_4/MeOH	A	100	88
24		[bmim]BF_4/MeOH	B	100	89

[a] Reaction conditions: $p(H_2)$ = 1.5 atm, T = 25 °C, t = 2.5 h, ligands/Rh = 1.1, substrate/Rh = 100, 1 g IL, 1 mL *i*-PrOH or 5 mL MeOH, the IL contained <150 ppm chloride unless otherwise noted.
[b] Use a high-purity ionic liquid that contained <10 ppm chloride.
[c] The chiral catalysts were formed in situ in the presence of both methanol and IL, then MeOH was removed at 50 °C under reduced pressure.

As expected, compared with using MeOH as the solvent, using [bmim]BF_4 greatly reduced the catalytic activity and enantioselectivity of Rh-L**3b**·CF_3COOH and Rh-L**4**, which is in agreement with the literature.[10d,e,13,16b] In particular, compared with Rh(A)-L**3b**·CF_3COOH, the Rh(B)-L**3b**·CF_3COOH had a higher activity in methanol but lower activity in [bmim]BF_4 (Table 2, entries 1 and 2).

These observations can be rationalized as follows. Firstly, the ILs have high viscosity and low H_2 solubility;[26] therefore the low H_2 concentration in [bmim]BF_4, due to inadequate mass transfer, is a major cause of decreased catalytic activity.[10c,d,16c,17d] Secondly, the chiral pyrrolidinodiphosphine ligands are a typical class of 1,4-diphosphine ligands with no C_2 axis, and they form rather fluxional seven-membered ring chelate structures with Rh (I). Ojima et al. argued that such a fluxional structure favors an 'induced-fit' in the coordination between the chiral rhodium catalyst and the substrate to form a preferred conformation.[18b] However, in highly viscous [bmim]BF_4, the chiral catalyst and the substrate have to consume more energy to realize 'induced-fit' through bond rotation and bond angle adjustment, which can be thermodynamically disfavored and leads to significantly lower ee values. Thirdly, during their studies on the hydrogenation of styrene in [bmim][CF_3SO_3], Dyson et al. found it very difficult to dissociate the chloride anion from the Ru-complex, which completely inhibited the activity of the catalyst precursor. They attributed this observation to the low solvation enthalpy of chloride in the imidazolium-based ILs.[27] Similarly for us, the chloride dissociation from the Rh complex is a vital step to form a catalytically active species when using $[Rh(COD)Cl]_2$ as the Rh precursor,[18b] and it can be argued that the retarded chloride dissociation resulted in the remarkable loss of catalytic activity in [bmim]BF_4. Fourthly, the minor amount of chloride impurities in ILs may also poison the catalyst by coordinating to Rh and consequently decrease the activity.[10a,11b,13b,28] Finally, normal solvents assist in the catalytic cycle of transition metal catalyzed reactions and thus effectively promote the catalytic reaction.[16,23] However, when ILs were employed as the sole reaction medium, the lack of solvent involvement severely impedes the catalytic activity and enantioselectivity.

To address these issues, we employed four sets of experiments in order to investigate how the catalytic activity and enantioselectivity of the asymmetric hydrogenation of MAC was influenced by chloride impurities, cosolvents, and so on. As can be seen in Table 2, a notable increase in catalytic activity could be observed when high purity [bmim]BF_4 (<10 ppm chloride) was used in the place of normal [bmim]BF_4 (<150 ppm chloride), but the ee value did not improve and even decreased (Table 2, entries 3, 4, 13, and 14), for which no explanation could be put forward. We found that if the chiral catalyst was prepared in situ in the homogeneous [bmim]BF_4/MeOH system and the hydrogenation was carried out after removal of methanol under reduced pressure, both the catalytic activity and enantioselectivity improved greatly compared with using [bmim]BF_4 alone (Table 2, entries 5, 6, 15, and 16). This result indicates that although most of the methanol was removed, the residual methanol in the IL still assisted in the catalytic cycle and enhanced the catalytic performance. Furthermore, when using $[Rh(COD)Cl]_2$ as the Rh precursor, the methanol molecules may more effectively solvate the chloride dissociated from the Rh, thus enhancing the catalytic cycle.[27] Moreover, after the in situ catalyst generation and removal of methanol under reduced pressure, we introduced the immiscible isopropanol to carry out the hydrogenation reaction in the [bmim]BF_4/*i*-PrOH biphasic system, and achieved complete substrate conversion in the same reaction time with an improved ee value. This could be attributed to; (1) higher H_2 solubility in [bmim]BF_4/*i*-PrOH that accelerated the hydrogenation; (2) participation of *i*-PrOH in the catalytic cycle; and (3) decreased viscosity of the [bmim]BF_4 phase due to partial dissolution of *i*-PrOH, which improved the enantioselectivity. In the subsequent experiments, we replaced *i*-PrOH with MeOH and carried out the hydrogenation in the homogeneous [bmim]BF_4/MeOH system. As expected, when using $[Rh(COD)_2]BF_4$ as the precursor in the [bmim]BF_4/MeOH system, the ee value obtained was slightly lower than using methanol (Table 2, entries 9 and 19). However, when using $[Rh(COD)Cl]_2$ as the precursor, the obtained ee value was closely parallel to the results in MeOH (Table 2, entry 20) and was even higher than using methanol (Table 2, entry 10). Moreover, in both cases, better enantioselectivity was achieved than using BPPM (entries 23 and 24). We believe that this observed 'homogeneous-like catalytic performance' should be accounted for, not only by the higher H_2 solubility and MeOH involvement in the catalytic cycle,[16b] but also by the drastically decreased viscosity of the [bmim]BF_4/MeOH system.

The effects of chloride impurities on the enantioselectivity is insignificant in [Bmim]BF_4/MeOH, since using high purity [bmim]BF_4 did not increase (entry 21) or even decrease the ee value (entry 22). In contrast, the chloride impurities had a greater impact on the catalytic activity. In the case of ligand **3b**·CF_3COOH (Fig. 2), the TOF declined sharply when [bmim]BF_4 was introduced to MeOH. However, the TOF recovered when high purity [bmim]BF_4 was used. In particular, when using $[Rh(COD)Cl]_2$ with high purity [bmim]BF_4, the TOF was approximately 75% of that of using MeOH.

Finally, we evaluated the recycling and reuse of the Rh chiral catalyst for the asymmetric hydrogenation of MAC with ligands **3b**·CF_3COOH, **4**, and the reference ligand BPPM (Table 3). The recycling experiments were carried out in [bmim]BF_4/MeOH in which the best catalytic activity and stereoselectivity were observed com-

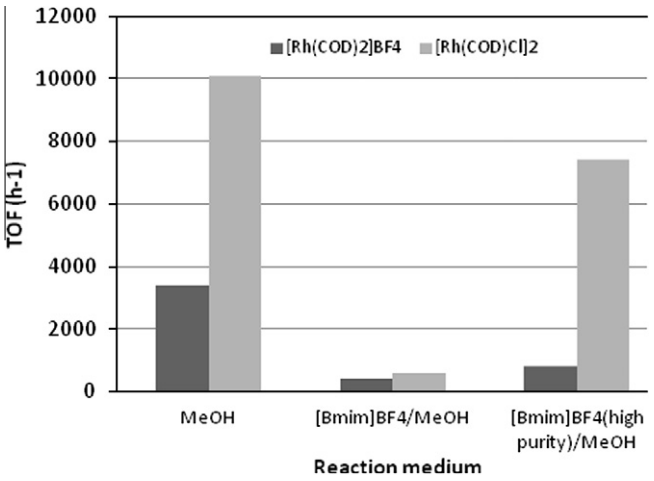


Figure 2. Effects of IL and chloride impurities on the catalytic activity of ligand **3b**·CF_3COOH. The reaction conditions are the same as those in Figure 1, using 1 g of IL and 5 mL of MeOH.

Table 3
Recycling and reuse of the chiral catalyst in the asymmetric hydrogenation of MAC in [bmim]BF_4/MeOH system[a]

Entry	Ligand	Rh	Cycle	Conversion (%)	ee (*R*) (%)	Rh leaching[b] (%)
1	**3b**·CF_3COOH	A	1	100	91	0.3
2		A	2	100	91	—
3		A	3	100	82	—
4		A	4	78	78	—
5		B	1	100	92	1.4
6		B	2	100	91	—
7		B	3	100	89	—
8		B	4	95	87	—
9	**4**	A	1	100	91	0.1
10		A	3	100	90	—
11		A	5	100	82	—
12		A	7	100	84	—
13		A	8	98	84	—
14		B	1	100	92	0.2
15		B	2	100	90	—
16		B	3	100	90	—
17		B	4	100	89	—
18		B	5	91	86	—
19		B	6	85	87	—
20	BPPM	A	1	100	88	3.1
21		A	2	100	85	—
22		A	3	94	80	—
23		B	1	100	89	3.2
24		B	2	100	86	—
25		B	3	100	85	—
26		B	4	67	76	—

[a] Reaction conditions: $p(H_2)$ = 1.5 atm, T = 25 °C, t = 2.5 h, ligands/Rh = 1.1, substrate/Rh = 100, 1 g IL, 5 mL MeOH. The [bmim]BF_4 contained <150 ppm chloride.
[b] Percentage of leached Rh in the total Rh, determined by ICP-AES analysis.

pared with using [bmim]BF_4 alone or using [bmim]BF_4/*i*-PrOH. The hydrogenation was allowed to proceed in the homogeneous [bmim]BF_4/MeOH. Upon completion of reaction, the volatile methanol was removed under reduced pressure and the non-volatile hydrogenated product was extracted using *i*-PrOH. Subsequently, new substrates were replenished into the IL for the next catalysis cycle.

It can be seen in Table 3 that Rh-L**3b**·CF_3COOH maintained high catalytic activity in the first three cycles and the conversion declined slightly in the fourth cycle. It should be noted that when using [Rh$(COD)_2$]BF_4 as the precursor, the enantioselectivity remained the same in the first two cycles but the ee value then decreased rapidly afterward, whereas the ee value showed a steady slight decrease in all four cycles when using [Rh(COD)Cl]$_2$. When BPPM was used, the conversion rate significantly decreased after three cycles and the ee value declined sharply in all four cycles. ICP-AES analysis showed that the loss of Rh into the *i*-PrOH extraction phase was more than 3% in the first cycle when using BPPM. In contrast, when using **3b**·CF_3COOH, the Rh loss after the first cycle was 0.3% and 1.4% for the [Rh$(COD)_2$]BF_4 precursor and [Rh(COD)Cl]$_2$ precursor, respectively. BPPM is hydrophobic and has inadequate affinity with the polar [bmim]BF_4, and thus leading to a partial loss of the chiral rhodium catalyst into the *i*-PrOH phase. On the contrary, the polar **3b**·CF_3COOH exists in the form of an ammonium salt and has a high affinity to [bmim]BF_4. In particular, the doubly charged Rh(A)-L**3b**·CF_3COOH has an even higher affinity to an IL than the singly charged Rh(B)-L**3b**·CF_3COOH and is thus much less susceptible to catalyst loss. The Rh-L**4** was found to have high catalytic activity and enantioselectivity over an even longer term, i.e., high catalytic activity and enantioselectivity was maintained after 8 and 6 cycles for the [Rh$(COD)_2$]BF_4 precursor and the [Rh(COD)Cl]$_2$ precursor, respectively. The variation of enantioselectivity showed a similar trend to that of **3b**·CF_3COOH. The imidazolium-tagged ligand **4** had a higher affinity to [bmim]BF_4 due to its structural resemblance, and only 0.1–0.2% Rh was lost in extraction.

According to the catalyst recycling results, we believe that the rapid loss of catalytic activity and enantioselectivity in [bmim]BF_4/MeOH with Rh-BPPM was because of both Rh loss and catalyst deactivation due to ligand oxidation. When the amino acid cation and imidazolium cation were introduced to the PPM molecule, the affinity of the chiral catalyst to IL improved greatly, which effectively reduced Rh loss. The improved affinity enabled the IL to more effectively protect the chiral catalyst and avoid aerobic oxidation,[15a,d] thus enhancing the recyclability of the chiral catalysts.

3. Conclusion

In conclusion, we have synthesized chiral pyrrolidinodiphosphine ligands bearing amino acid and imidazolium tags and applied them to the Rh catalyzed asymmetric hydrogenations of α-enamide esters in classical organic solvents, [bmim]BF_4 and [bmim]BF_4/cosolvent systems. Methanol was found to be the best solvent in the homogeneous catalysis. The imidazolium-tagged chiral pyrrolidinodiphosphine ligands showed the best activity and enantioselectivity in methanol, giving a TOF of 24,054 h^{-1} and an ee value of 95%, which well exceeded the performance of the classical pyrrolidinodiphosphine BPPM. For ligands bearing amino acid tags, the position of the stereogenic center in the amino acid had a critical impact on the catalytic efficiency. The catalytic activity and enantioselectivity declined as the stereogenic center in the amino acid approached the pyrrolidine ring, which may be due to the negative interaction between the stereogenic center in the amino acid and Rh. When using the IL systems, the H_2 solubility, type of Rh precursor, viscosity of the IL, chloride impurities, and cosolvent were major factors that affected the catalytic activity and enantioselectivity, among which the cosolvent is the most influential factor. In the case of the homogeneous [bmim]BF_4/MeOH system, the introduction of MeOH not only promoted the catalytic cycle and increased H_2 solubility, but also effectively decreased the IL viscosity; the enantioselectivity obtained closely paralleled and even exceeded that of using methanol alone. The catalyst recycling experiments using [bmim]BF_4/MeOH showed that introducing amino acid and imidazolium tags to the PPM molecule can effectively enhance the affinity of the chiral catalyst to the IL, which reduced the Rh loss and improved the catalyst stability, and after several cycles no significant loss of activity and enantioselectivity was observed.

4. Experimental

4.1. General details

PPM **2** was synthesized according to literature methods.[18b] BPPM **1** was purchased from Merck. All other reagents and ionic liquids (ILs) were obtained commercially and were used as received, except as noted. The ILs contained <0.2 wt % water and <150 ppm halide, and no precipitate formed upon addition of aqueous $AgNO_3$. The high-purity [bmim]BF_4 contained <10 ppm halide. The ionic liquid [bmim]OH was prepared using standard literature methods.[29] All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents and reagents used were rigorously deoxygenated prior to use. The hydrogenation reactions were performed in a home-made 60 ml stainless steel autoclave. The conversions and enantioselectivity were determined by GC on a CP-Chirasil-L-Val (25 m × 0.25 mm) chiral column. NMR spectra were recorded on a Bruker 500 MB instrument. High resolution mass spectra (HRMS) were obtained by electrospray technique using a Q-Tof Ultima Global mass spectrometry. ICP-AES data were measured on an IRIS IstrepidIIXSP apparatus.

4.2. General procedure for the homogeneous Rh-catalyzed asymmetric hydrogenation of MAC in organic solvents

The cationic or neutral Rh-catalysts were prepared in situ. Typically, 1.1 mg of cationic rhodium precursor [$Rh(COD)_2$]BF_4 (0.0027 mmol) and chiral ligand (0.0030 mmol) was dissolved in 1.0 mL of degassed solvent under an argon atmosphere. The solution was stirred for 15 min at room temperature. To the solution of catalyst, a solution of MAC (0.27 mmol) in 1.0 mL of solvent was added. Next, the reaction mixture was transferred to a 60 mL autoclave. The hydrogenation was carried out under 1.5 atm pressure of hydrogen at 25 °C for 2.5 h. The conversions and ee values were determined by GC on a CP-Chirasil-L-Val (25 m × 0.25 mm) chiral column.

4.3. General procedure for the Rh-catalyzed monophasic asymmetric hydrogenation of MAC in a [bmim]BF_4

Typically, 1.1 mg of [$Rh(COD)_2$]BF_4 (0.0027 mmol) and chiral ligand (0.0030 mmol) was dissolved in 1 g of [bmim]BF_4 under an argon atmosphere, and the solution was stirred for 20 min at room temperature. MAC (0.27 mmol) was added, and the solution was stirred for 1 h. Next, the solution was transferred to a 60 mL autoclave. The hydrogenation was carried out under 1.5 atm pressure of hydrogen at 25 °C for 2.5 h. After releasing the hydrogen, *i*-PrOH (1 mL × 2) was added to extract the organic product. The top solvent layer was separated for GC analysis.

4.4. General procedure for Rh-catalyzed biphasic asymmetric hydrogenation of MAC in a [bmim]BF_4/*i*-PrOH system

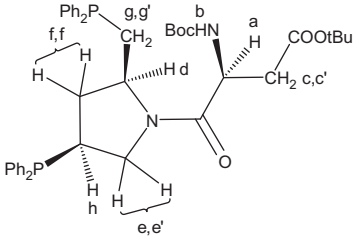
Typically, 1.1 mg of [$Rh(COD)_2$]BF_4 (0.0027 mmol), chiral ligand (0.0030 mmol), and 1 g of [bmim]BF_4 was dissolved in 2.0 mL of degassed MeOH under an argon atmosphere, and the solution was stirred for 20 min at room temperature. Next, the catalyst solution was transferred to a 60 mL autoclave. The MeOH was removed under reduced pressure. The solution of MAC (0.27 mmol) in 1.0 mL of *i*-PrOH was added via a syringe. The hydrogenation was carried out under 1.5 atm. pressure of hydrogen at 25 °C for 2.5 h. After releasing the hydrogen, the *i*-PrOH phase was removed for GC analysis.

4.5. General procedure for the Rh-catalyzed monophasic asymmetric hydrogenation of MAC in a [bmim]BF_4/MeOH System and for catalyst recycling

Typically, 1.1 mg of [$Rh(COD)_2$]BF_4 (0.0027 mmol), chiral ligand (0.0030 mmol), and 1 g of [bmim]BF_4 was dissolved in 3.0 mL of degassed MeOH under an argon atmosphere, and the solution was stirred for 20 min at room temperature. Next, the catalyst solution was transferred to a 60 mL autoclave. The solution of MAC (0.27 mmol) in 2.0 mL of MeOH was added via a syringe. The hydrogenation was carried out under 1.5 atm pressure of hydrogen at 25 °C for 2.5 h. After releasing the hydrogen, the reaction mixture was transferred to a Schlenk tube under an argon atmosphere. Next, the MeOH was removed under reduced pressure and *i*-PrOH was added to extract the product (2 mL × 2). The top solvent layer was removed by a syringe for GC analysis, and the new substrate and MeOH was added to the IL for the next catalyst recycling.

4.6. Preparation and characterization of 5a

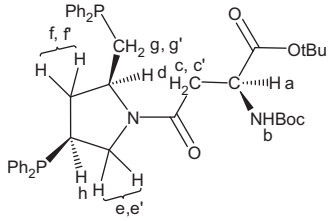
At first, **5a** was synthesized by a DIC-promoted condensation of PPM with both Boc and tBu protected aspartic acid. Typically, a mixture of PPM (2.06 g, 0.0045 mol), Boc-L-Asp(OtBu)-OH (1.32 g, 0.0045 mol), DIC (0.58 g, 0.0045 mol), and HOBt (0.62 g, 0.0045 mol) in 70 mL of degassed CH_2Cl_2 and 0.4 mL of DMF was stirred at room temperature for 4 h under an argon atmosphere. The completion of the reaction was monitored by TLC analysis. The solvent was then partially removed under reduced pressure, and the resulting white precipitate was filtered off. The filtrate was concentrated and the residue was purified by column chromatography (degassed SiO_2, petroleum ether/EtOAc = 5/1) under argon to afford pure product **5a** as a white solid; yield: 2.5 g (75.5%). mp: 66–68 °C; $[\alpha]_D^{20} = -27.0$ (*c* 0.5, CH_2Cl_2); ^{1}H NMR (500.0 MHz, $CDCl_3$): δ = 7.61–7.30 (m, 20H, Ph-H), 5.32 (d, J = 9.0 Hz, 1H, H_b), 4.63 (td, J = 9.0, 7.0 Hz, 1H, H_a), 4.13 (overlapped m, 1H, H_d), 4.08 (overlapped m, 1H, $H_{e'}$), 3.46 (dt, $J_{ee'} = J^e_{PCCH} = 10.8$ Hz, J_{eh} = 8.0 Hz, 1H, H_e), 3.18 (td, $J_{gg'}$ = 13.0 Hz, $J_{gd} = J^g_{PCH} = 3.0$ Hz, 1H, H_g), 2.82 (m, 1H, H_h), 2.62 (dd, J = 15.5, 7.0 Hz, 1H, H_c), 2.39 (dd, J = 15.5, 7.0 Hz, 1H, $H_{c'}$), 2.23 (m, 1H, H_f), 1.87 (overlapped m, 1H, $H_{g'}$), 1.84 (overlapped m, 1H, H_f), 1.41 (s, 9H, Boc-*Me* or OtBu-*Me*), 1.35 (s, 9H, OtBu-*Me* or Boc-*Me*); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 169.2, 168.9, 154.9, 139.1, 136.6, 136.4, 136.2, 133.3, 133.0, 132.8, 132.5, 129.1, 128.7, 128.6, 128.5, 128.5, 128.3, 81.1, 79.7, 56.4, 50.9, 49.2, 38.7, 36.3, 36.0, 33.1, 28.3, 27.9; ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −7.5, −8.4, −21.8, −22.9 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): m/z = 725.3248, calcd for $C_{42}H_{51}N_2O_5P_2$ $[M+1]^+$: 725.3273.



4.7. Preparation and characterization of 5b

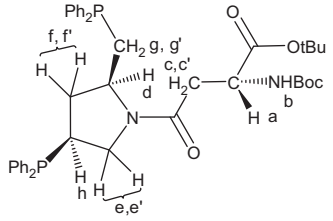
Compound **5b** was synthesized by a DIC-promoted condensation of PPM with Boc-L-Asp-OtBu as described for ligand **5a**. Column chromatography (degassed SiO_2, petroleum ether/EtOAc = 3/1) under argon afforded the pure product **5b** as a white solid; yield:

94.0%. mp: 189–191 °C; $[\alpha]_D^{20} = -10.3$ (*c* 0.5, CH_2Cl_2); ^1H NMR (500.0 MHz, $CDCl_3$): δ = 7.28–7.59 (m, 20H, Ph-H), 5.70 (d, *J* = 9.5 Hz, 1H, H_b), 4.32 (td, *J* = 9.5, 4.5 Hz, 1H, H_a), 4.19 (m, 1H, H_d), 3.52 (dd, $J_{e'e}$ = 10.7 Hz, $J_{e'h}$ = 7.2 Hz, 1H, $H_{e'}$), 3.29 (dt, $J_{ee'} = J^e_{PCCH} = 10.7$ Hz, J_{eh} = 8.2 Hz, 1H, H_e), 3.08 (td, $J_{gg'}$ = 13.0 Hz, $J_{gd} = J^g_{PCH} = 3.0$ Hz, 1H, H_g), 2.86 (dd, *J* = 16.5, 4.5 Hz, 1H, H_c), 2.79 (m, 1H, H_h), 2.26 (dd, *J* = 16.5, 4.5 Hz, 1H, $H_{c'}$), 2.24 (overlapped m, 1H, H_f), 2.19 (dd, $J_{g'g}$ = 13.0 Hz, $J_{g'd}$ = 10.0 Hz, 1H, $H_{g'}$), 1.92 (m, 1H, $H_{f'}$), 1.44 (s, 18H, Boc-*Me* and OtBu-*Me*); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 170.8, 168.4, 155.7, 138.9, 137.2, 136.5, 136.1, 133.1, 132.9, 132.8, 129.2, 128.7, 128.5, 128.4, 81.5, 79.4, 56.4, 51.3, 50.6, 37.2, 36.2, 35.8, 33.2, 28.3, 27.9; ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −6.1, −9.1, −22.2, −22.7 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 725.3253, calcd for $C_{42}H_{51}N_2O_5P_2$ $[M+H]^+$: 725.3273.



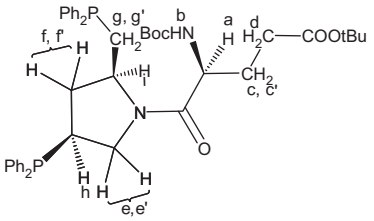
4.8. Preparation and characterization of 5c

Compound **5c** was synthesized by a DIC-promoted condensation of PPM with Boc-D-Asp-OtBu as described for ligand **5a**. Column chromatography (degassed SiO_2, petroleum ether/EtOAc = 3/1) under argon afforded the pure product **5c** as a white solid; yield: 94.3%. mp: 190–192 °C; $[\alpha]_D^{20} = -37.2$ (*c* 0.1, CH_2Cl_2); ^1H NMR (500.0 MHz, $CDCl_3$): δ = 7.27–7.57 (m, 20H, Ph-H), 5.85 (d, *J* = 9.5 Hz, 1H, H_b), 4.37 (ddd, *J* = 9.5, 4.0, 3.0 Hz, 1H, H_a), 4.11 (m, 1H, H_d), 3.49 (t, $J_{e'e} = J_{e'h}$ = 9.5 Hz, 1H, $H_{e'}$), 3.32 (q, $J_{ee'} = J^e_{PCCH} = 9.5$ Hz, 1H, H_e), 3.28 (td, $J_{gg'}$ = 12.5 Hz, $J_{gd} = J^g_{PCH} = 2.5$ Hz, 1H, H_g), 2.83 (dd, *J* = 16.5, 4.0 Hz, 1H, H_c), 2.78 (m, 1H, H_h), 2.56 (dd, J = 16.5, 3.0 Hz, 1H, $H_{c'}$), 2.22 (m, 1H, H_f), 1.89 (t, $J_{g'g} = J_{g'd}$ = 12.5 Hz, 1H, $H_{g'}$), 1.74 (m, 1H, $H_{f'}$), 1.43 (s, 9H, Boc-*Me* or OtBu-*Me*), 1.40 (s, 9H, OtBu-*Me* or Boc-*Me*); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 170.6, 168.6, 155.8, 139.0, 137.0, 136.3, 136.0, 132.7–133.1 (overlapped m, Ph-C), 128.3–129.4 (overlapped m, Ph-C), 81.6, 79.4, 56.5, 50.8, 50.6, 37.7, 36.6, 35.8, 33.7, 28.3, 27.9; ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −6.4, −8.6, −22.2, −22.4 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 725.3257, calcd for $C_{42}H_{51}N_2O_5P_2$ $[M+H]^+$: 725.3273.



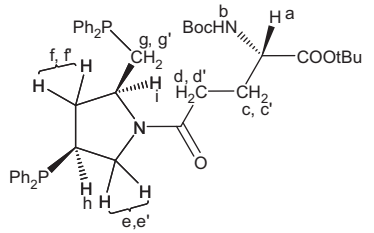
4.9. Preparation and characterization of 5d

Compound **5d** was synthesized by a DIC-promoted condensation of PPM with Boc-L-Glu(OtBu)-OH as described for ligand **5a**. Column chromatography (degassed SiO_2, petroleum ether/EtOAc = 3/1) under argon afforded the pure product **5d** as a white solid; yield: 92.7%. mp: 137–139 °C; $[\alpha]_D^{20} = -14.2$ (c 0.5, CH_2Cl_2); ^1H NMR (500.0 MHz, $CDCl_3$): δ = 7.27–7.60 (m, 20H, Ph-H), 5.37 (d, *J* = 8.5 Hz, 1H, H_b), 4.36 (dt, *J* = 8.5, 4.5 Hz, 1H, H_a), 4.16 (m, 1H, H_i), 3.96 (dd, $J_{e'e}$ = 10.6 Hz, $J_{e'h}$ = 7.6 Hz, 1H, $H_{e'}$), 3.45 (dt, $J_{ee'} = J^e_{PCCH} = 10.6$ Hz, J_{eh} = 8.3 Hz, 1H, H_e), 3.15 (td, $J_{gg'}$ = 13.0 Hz, $J_{gi} = J^g_{PCH} = 3.6$ Hz, 1H, H_g), 2.82 (m, 1H, H_h), 2.17–2.31 (overlapped m, 3H, H_d and H_f), 1.91–1.96 (overlapped m, 2H, $H_{g'}$ and H_c), 1.83 (m, 1H, $H_{f'}$), 1.65 (m, 1H, $H_{c'}$), 1.42 (s, 9H, OtBu-*Me* or Boc-*Me*), 1.40 (s, 9H, OtBu-*Me* or Boc-*Me*); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 172.0, 170.0, 155.5, 139.0, 136.7, 136.4, 136.0, 133.4, 133.3, 133.1, 132.9, 132.7, 132.5, 129.2, 128.7, 128.5, 128.4, 128.4, 80.4, 79.4, 56.5, 51.5, 51.2, 36.4, 36.1, 33.4, 30.9, 28.3, 28.1; ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −6.8, −8.0, −22.1, −22.5 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 739.3409, calcd for $C_{43}H_{53}N_2O_5P_2$ $[M+H]^+$: 739.3430.



4.10. Preparation and characterization of 5e

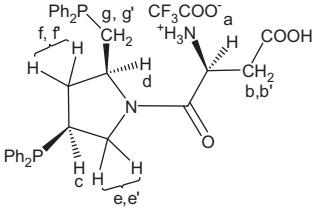
Compound **5e** was synthesized by a DIC-promoted condensation of PPM with Boc-L-Glu-OtBu as described for ligand **5a**. Column chromatography (degassed SiO_2, petroleum ether/EtOAc = 3/1) under argon afforded the pure product **5e** as a white solid; yield: 92.0%. mp: 175–176 °C; $[\alpha]_D^{20} = -8.7$ (*c* 0.5, CH_2Cl_2); ^1H NMR (500.0 MHz, $CDCl_3$): δ = 7.27–7.60 (m, 20H, Ph-H), 5.24 (d, *J* = 8.0 Hz, 1H, H_b), 4.17(m, 1H, H_i), 4.06 (dt, *J* = 8.0, 4.5 Hz,1H, H_a), 3.52 (dd, $J_{e'e}$ = 10.5 Hz, $J_{e'h}$ = 7.0 Hz, 1H, $H_{e'}$), 3.30 (dt, $J_{ee'} = J^e_{PCCH} = 10.5$ Hz, J_{eh} = 8.4 Hz, 1H, H_e), 3.14 (td, $J_{gg'}$ = 13.5 Hz, $J_{gi} = J^g_{PCH} = 3.0$ Hz, 1H, H_g), 2.82 (m, 1H, H_h), 2.29 (m, 1H, H_f), 2.23 (m, 1H, H_d), 2.11 (overlapped m, 1H, $H_{g'}$), 2.06 (overlapped m, 1H, H_c), 2.02 (overlapped m, 1H, $H_{d'}$), 1.96 (overlapped m, 1H, $H_{f'}$), 1.79 (m, 1H, $H_{c'}$), 1.42 (s, 9H, Boc-*Me* or OtBu-*Me*), 1.39 (s, 9H, OtBu-*Me* or Boc-*Me*); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 171.5, 170.1, 155.5, 138.9, 137.0, 136.6, 136.1, 133.3–132.7 (overlapped m, Ph-C), 129.3–128.3 (overlapped m, Ph-C), 81.8, 79.5, 56.3, 53.8, 51.1, 36.2, 35.7, 33.3, 31.5, 28.3, 27.9, 27.6; ^{31}P NMR (202.4 MHz, $CDCl_3$): δ = −6.6, −8.9, −22.7, −22.8 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 739.3402, calcd for $C_{43}H_{53}N_2O_5P_2$ $[M+H]^+$: 739.3430.



4.11. Preparation and characterization of 3a·CF_3COOH

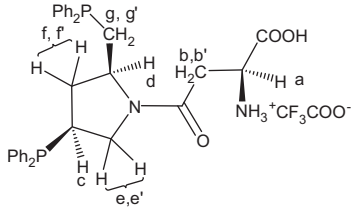
Typically, a Schlenk flask was charged with **5a** (2.3 g, 0.0032 mol), Et_3SiH (0.92 g, 0.0079 mol), and 10 mL of trifluoroacetic acid under an argon atmosphere, and the solution was stirred for 5 h at room temperature. Then, trifluoroacetic acid was evaporated

under reduced pressure to give a trifluoroacetic acid salt of **3a**. The salt was submitted to column chromatography (degassed SiO_2, EtOAc/MeOH/H_2O = 15:3:2) under argon to give the pure product **3a·CF$_3$COOH** as a white solid; yield: 2.1 g (98.0%). mp: 203–205 °C; $[\alpha]_D^{20} = -37.5$ (*c* 0.24, EtOH); ^{1}H NMR (500.0 MHz, CD_3OD): δ = 7.35–7.58 (m, 20H, Ph-H), 4.43 (dd, *J* = 8.6, 4.2 Hz, 1H, H_a), 4.26 (m, 1H, H_d), 3.80 (dd, $J_{e'e}$ = 10.5 Hz, $J_{e'c}$ = 7.5 Hz, 1H, $H_{e'}$), 3.47 (dt, $J_{ee'} = J^e_{PCCH} = 10.5$ Hz, J_{ec} = 8.0 Hz, 1H, H_e), 2.96 (overlapped m, *2*H, H_c and H_g), 2.80 (dd, *J* = 17.6, 4.2 Hz, 1H, $H_{b'}$), 2.63 (dd, *J* = 17.6, 8.6 Hz, 1H, H_b), 2.29 (dd, $J_{g'g}$ = 13.5 Hz, $J_{g'd}$ = 9.7 Hz, 1H, $H_{g'}$), 2.12 (m, 1H, $H_{f'}$), 1.74 (m, 1H, H_f); ^{13}C NMR (125.7 MHz, CD_3CN, 50 μL of HBF_4): δ = 172.1, 168.8, 135.9, 135.7, 134.7, 134.6, 134.3, 133.6, 131.2 (overlapped m), 54.9, 50.5, 49.4, 35.1, 33.8, 31.7, 27.5; ^{31}P NMR (202.4 MHz, CD_3OD, 50 μL of CF_3COOD): δ = −5.7, −8.2, −21.5, −22.5 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 569.2141, calcd for $C_{33}H_{35}N_2O_3P_2$ $[M+H]^+$: 569.2123.



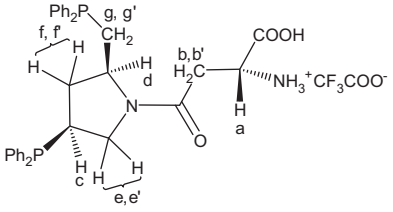
4.12. Preparation and characterization of 3b·CF$_3$COOH

The trifluoroacetic acid salt of **3b** was synthesized as described for ligand **3a·CF$_3$COOH**. Column chromatography (degassed SiO_2, EtOAc/MeOH/H_2O = 15:3:2) under argon afforded the pure trifluoroacetic acid salt of **3b** as a white solid; yield: 98.7%. mp: 128–131 °C; $[\alpha]_D^{20} = -7.8$ (*c* 0.25, MeOH); ^{1}H NMR (500.0 MHz, CD_3OD): δ = 7.32–7.50 (m, 20H, Ph-H), 4.23 (m, 1H, H_d), 4.07 (dd, *J* = 7.5, 3.5 Hz, 1H, H_a), 3.67 (t, $J_{e'e} = J_{e'c}$ = 10.0 Hz, 1H, $H_{e'}$), 3.36 (q, $J_{ee'} = J_{ec} J^e_{PCCH} = 10.0$ Hz, 1H, H_e), 3.01 (overlapped m, *2*H, H_c and H_g), 2.91 (dd, *J* = 17.6, 7.5 Hz, 1H, H_b), 2.68 (dd, *J* = 17.6, 3.5 Hz, 1H, $H_{b'}$), 2.41 (dd, $J_{g'g}$ = 13.5 Hz, $J_{g'd}$ = 9.4 Hz, 1H, $H_{g'}$), 2.18 (m, 1H, $H_{f'}$), 1.87 (m, 1H, H_f); ^{13}C NMR (125.7 MHz, CD_3OD, 50 μL of CF_3COOD): δ = 171.0, 168.9, 140.1, 139.0, 138.2, 137.7, 134.5, 134.1, 133.8, 130.4, 129.9, 129.7, 129.6, 58.2, 52.3, 50.9, 36.8, 36.5, 35.1, 34.2; ^{31}P NMR (202.4 MHz, CD_3OD, 50 μL of CF_3COOD): δ = −6.1, −7.6, −21.0, −21.8 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 569.2144, calcd for $C_{33}H_{35}N_2O_3P_2$ $[M+H]^+$: 569.2123.



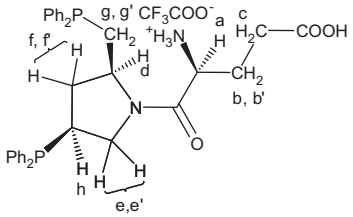
4.13. Preparation and characterization of 3c·CF$_3$COOH

The trifluoroacetic acid salt of **3c** was synthesized as described for ligand **3a·CF$_3$COOH**. Column chromatography (degassed SiO_2, EtOAc/MeOH/H_2O = 15:3:2) under argon afforded the pure trifluoroacetic acid salt of **3c** as a white solid; yield: 95.0%. mp: 88–91 °C; $[\alpha]_D^{20} = -15.0$ (*c* 0.1, MeOH); ^{1}H NMR (500.0 MHz, CD_3OD): δ = 7.27–7.55 (m, 20H, Ph-H), 4.16 (m, 1H, H_d), 3.86 (dd, *J* = 7.5, 3.5 Hz, 1H, H_a), 3.71 (t, $J_{e'e} = J_{e'c}$ = 10.0 Hz, 1H, $H_{e'}$), 3.36 (q, $J_{ee'} = J_{ec} J^e_{PCCH} = 10.0$ Hz, 1H, H_e), 3.15 (td, $J_{gg'}$ = 13.0 Hz, $J_{gd} = J^g_{PCH} = 3.0$ Hz, 1H, H_g), 3.02 (m, 1H, H_c), 2.97 (dd, *J* = 17.5, 3.5 Hz, 1H, H_b), 2.68 (dd, *J* = 17.5, 7.5 Hz, 1H,$H_{b'}$), 2.14 (m, 2H, $H_{g'}$ and $H_{f'}$), 1.74 (m, 1H, H_f); ^{31}P NMR (202.4 MHz, CD_3OD): δ = −6.5, −7.5, −20.8, −21.8 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 569.2139, calcd for $C_{33}H_{35}N_2O_3P_2$ $[M+H]^+$: 569.2123.



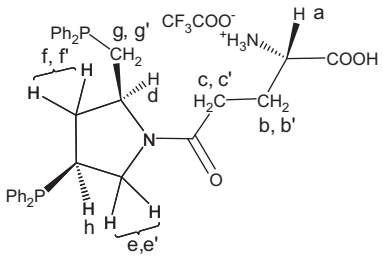
4.14. Preparation and characterization of 3d·CF$_3$COOH

The trifluoroacetic acid salt of **3d** was synthesized as described for ligand **3a·CF$_3$COOH**. Column chromatography (degassed SiO_2, EtOAc/MeOH/H_2O = 15:3:2) under argon afforded the pure trifluoroacetic acid salt of **3d** as a white solid; yield: 82.7%. mp: 97–99 °C; $[\alpha]_D^{20} = -12.0$ (*c* 0.25, MeOH); ^{1}H NMR (500.0 MHz, CD_3OD): δ = 7.27–7.55 (m, 20H, Ph-H), 4.21 (m, 1H, H_d), 4.10 (dd, *J* = 7.9, 3.5 Hz, 1H, H_a), 3.78 (dd, $J_{e'e}$ = 10.5 Hz, $J_{e'h}$ = 7.0 Hz, 1H, $H_{e'}$), 3.44 (dt, $J_{ee'} = J^e_{PCCH} = 10.5$ Hz, J_{eh} = 8.0 Hz, 1H, H_e), 3.02 (td, $J_{gg'}$ = 13.0 Hz, $J_{gd} = J^g_{PCH} = 3.3$ Hz, 1H, H_g), 2.93 (m, 1H, H_h), 2.34 (m, 2H, H_c), 2.22 (dd, $J_{g'g}$ = 13.0 Hz, $J_{g'd}$ = 10.3 Hz, 1H, $H_{g'}$), 2.07 (m, 1H, $H_{f'}$), 1.94 (m, 1H, H_b), 1.86 (m, 1H, $H_{b'}$), 1.70 (m, 1H, H_f); ^{13}C NMR (125.7 MHz, CD_3CN, 50 μL of HBF_4): δ = 175.2, 169.8, 135.8, 134.7, 134.3, 133.8, 131.1, 130.8, 55.2, 53.2, 50.3, 36.0, 32.9, 29.8, 27.4, 25.8; ^{31}P NMR (202.4 MHz, CD_3OD, 50 μL of CF_3COOD): δ = −5.3, −8.7, −22.2, −22.5 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 583.2266, calcd for $C_{34}H_{37}N_2O_3P_2$ $[M+H]^+$: 583.2279.



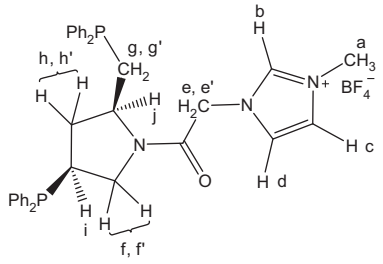
4.15. Preparation and characterization of 3e·CF$_3$COOH

The trifluoroacetic acid salt of **3e** was synthesized as described for ligand **3a·CF$_3$COOH**. Column chromatography (degassed SiO_2, EtOAc/MeOH/H_2O = 15:3:2) under argon afforded the pure trifluoroacetic acid salt of **3e** as a white solid; yield: 75.2%. mp: 70–72 °C; $[\alpha]_D^{20} = -7.8$ (*c* 0.25, MeOH); ^{1}H NMR (500.0 MHz, CD_3OD): δ = 7.28–7.56 (m, 20H, Ph-H), 4.22 (m, 1H, H_d), 3.69 (t, $J_{e'e} = J_{e'h}$ = 10.0 Hz, 1H, $H_{e'}$), 3.55 (t, $J_{ab} = J_{ab'}$ = 5.6 Hz, 1H, H_a), 3.34 (q, $J_{ee'} = J_{eh} = J^e_{PCCH} = 10$ Hz, 1H, H_e), 3.00 (m, 1H, H_h), 2.93 (td, $J_{gg'}$ = 13.5 Hz, $J_{gd} = J^g_{PCH} = 3.0$ Hz, 1H, H_g), 2.46 (td, $J_{cc'}$ = 17.0 Hz, $J_{cb} = J_{cb'}$ = 7.0 Hz, 1H, H_c), 2.38 (dd, $J_{g'g}$ = 13.5 Hz, $J_{g'd}$ = 9.5 Hz, 1H, $H_{g'}$), 2.23 (td, $J_{c'c}$ = 17.0 Hz, $J_{c'b} = J_{c'b'}$ = 7.0 Hz, 1H, $H_{c'}$), 2.14 (m, 1H, H_f), 2.00 (m, 2H, H_b, $H_{b'}$), 1.85 (m, 1H, $H_{f'}$); ^{13}C NMR (125.7 MHz, CD_3OD, 50 μL of CF_3COOD): δ = 171.9, 171.6, 139.8, 138.8, 138.2, 137.8, 133.8–134.5 (overlapped m, Ph-C), 129.6–130.4 (overlapped m, Ph-C), 58.1, 53.3, 52.5, 36.8, 36.3, 34.1, 31.7, 26.5; ^{31}P NMR (202.4 MHz, CD_3OD, 50 μL of CF_3COOD): δ = −6.4, −7.7, −22.1 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): *m*/*z* = 583.2261, calcd for $C_{34}H_{37}N_2O_3P_2$ $[M+H]^+$: 583.2279.



4.16. Preparation and characterization of 4

Compound **4** was synthesized by a DIC-promoted condensation of PPM with 1-carboxymethyl-3-methylimidazolium tetrafluoroborate. A mixture of PPM (0.56 g, 0.0012 mmol), 1-carboxymethyl-3-methyl-imidazolium tetrafluoroborate (0.28 g, 0.0012 mmol) and DIC (0.16 g, 0.0012 mmol) in 10 mL of degassed CH_2Cl_2 was stirred at room temperature for 10 h under an argon atmosphere. The completion of the reaction was monitored by TLC analysis. Then, the solvent was partially removed under reduced pressure, and the residue was purified by column chromatography (degassed SiO_2, EtOAc/MeOH/ H_2O = 15/6/2) under argon to afford the pure product **4** as a white solid; yield: 0.48 g (58.5%). mp: 149–150 °C; $[\alpha]_D^{20} = -34.8$ (*c* 0.25, MeOH); ^{1}H NMR (500.0 MHz, CD_3CN): δ = 8.30 (s, 1H, H^b), 7.32–7.54 (m, 21H, Ph-H and H^c or H^d), 7.21 (t, J = 1.6 Hz, 1H, H^d or H^c), 4.89 (d, $J_{ee'}$ = 16.8 Hz, 1H, H_e), 4.61 (d, $J_{e'e}$ = 16.8 Hz, 1H, $H_{e'}$), 4.11 (m, $J_{jg'}$ = 3.3 Hz, $J_{jg} = J_{jh} = J_{jh'} = J^j_{PCCH_{f'}}$ = 8.0 Hz, 1H, H_j), 3.85 (s, 3H, H_a), 3.67 (t, $J_{ff} = J_{fi}$ = 10.0 Hz, $J^f_{PCCH} = 0$ Hz 1H, H_f), 3.39 (q, $J_{ff'} = J_{fi} = J^f_{PCCH}$ = 10.0 Hz, 1H, H_f), 3.08 (m, J^i_{PCH} = 17 Hz, 1H, H_i), 2.97 (td, $J_{g'g}$ = 13.4 Hz, $J_{g'j} = J^{g'}_{PCH}$ = 3.3 Hz, 1H, $H_{g'}$), 2.22–2.26 (overlapped m, 2H, H_g and H_h), 1.88 (m, 1H, $H_{h'}$); ^{13}C NMR (125.7 MHz, CD_3CN): δ = 163.4, 139.9, 138.6, 138.1, 138.0, 137.5, 134.3, 133.7, 133.6, 130.3, 129.7, 129.5, 124.8, 123.9, 58.0, 51.8, 51.0, 37.0, 36.3, 35.8, 33.5; ^{31}P NMR (202.4 MHz, CD_3OD): δ = −6.7, −7.9, −21.5, −22.3 (two peaks P_α and P_β due to the two conformations of the RCO group at room temperature); HRMS (Q-Tof MS, ES+): m/z = 576.2329, calcd for $C_{35}H_{36}N_3OP_2$ $[M]^+$: 576.2334.



Acknowledgments

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References

1. (a) Fan, Q.; Deng, G.; Yi, B.; Chan, A. S. C. In *Asymmetric Organic Reactions*; Li, Y., Fan, Q., Chan, A. S. C., Eds.; Chemical Industry Press (CIP): Beijing, 2005; p 399; (b) Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem.* **2004**, *116*, 2555–2558.
2. (a) Lin, G. Q.; Li, Y. M.; Chan, A. S. C. *Principles and Applications of Asymmetric Synthesis*; Wiley: New York, 2011; b Qiu, L. Q.; Wu, J.; Chan, A. S. C. In *Asymmetric Organic Reactions*; Li, Y., Fan, Q., Chan, A. S. C., Eds.; Chemical Industry Press (CIP): Beijing, 2005; p 92; (c) Knowles, W. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998–2007; (d) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022.
3. (a) Frohning, C. D.; Kohlpainter, C. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 1996; p 29; (b) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2494; (c) Fan, Q. H.; Li, Y. M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385–3466.
4. (a) Berthod, B.; Mignani, G.; Woodward, G.; Lemaire, M. C. *Chem. Rev.* **2005**, *105*, 1801–1836; (b) Heitbaum, M.; Glorius, F.; Escher, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4732–4762; (c) Nielsen, M.; Thomsen, A. H.; Jensen, T. R.; Jakobsen, H. J.; Skibsted, J.; Gothelf, K. V. *Eur. J. Org. Chem.* **2005**, 342–347; (d) Saluzzo, C.; Halle, R.; Touchard, F.; Fache, F.; Schulz, E.; Lemaire, M. *J. Organomet. Chem.* **2000**, *603*, 30–39; (e) Baiker, A. *J. Mol. Catal. A: Chem.* **1997**, *115*, 473–493.
5. (a) Sinou, D. *Adv. Synth. Catal.* **2002**, *344*, 221–237; (b) Dwars, T.; Oehme, G. *Adv. Synth. Catal.* **2002**, *344*, 239–260.
6. (a) Studer, A.; Hadida, S.; Ferritto, R.; Kim, S. Y.; Jeger, P.; Wipf, P.; Curran, D. P. *Science* **1997**, *275*, 823–826; (b) Horvth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641–650.
7. Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475–493.
8. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
9. (a) Dupont, J.; de Souza, R. F. *Chem. Rev.* **2002**, *102*, 3667–3691; (b) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3093; (c) Paczal, A.; Kotschy, A. *Monatsh. Chem.* **2007**, *138*, 1115–1123; (d) Durand, J.; Teuma, E.; Gómez, M. C. R. *Chimie* **2007**, *10*, 152–177.
10. (a) Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2698–2700; (b) Guernik, S.; Wolfson, A.; Herskowitz, M.; Greenspoon, N.; Geresh, S. *Chem. Commun.* **2001**, 2314–2315; (c) Berger, A.; de Souza, R. F.; Delgado, M. R.; Dupont, J. *Tetrahedron: Asymmetry* **2001**, *12*, 1825–1828; (d) Frater, T.; Gubicza, L.; Szollosy, A.; Bakos, J. *Inorg. Chim. Acta.* **2006**, *359*, 2756–2759; (e) Boyle, K. L.; Lipsky, E. B.; Kalberg, C. S. *Tetrahedron Lett.* **2006**, *47*, 1311–1313.
11. (a) Ngo, H. L.; Hu, A.; Lin, W. *Chem. Commun.* **2003**, 1912–1913; (b) Berthod, M.; Joerger, J. M.; Mignani, G.; Vaultier, M.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, *15*, 2219–2221; (c) Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 2501–2504; (d) Lam, K. H.; Xu, L.; Feng, L.; Ruan, J.; Fan, Q.; Chan, A. S. C. *Can. J. Chem.* **2005**, *83*, 903–908.
12. (a) Yinghuai, Z.; Carpenter, K.; Bun, C. C.; Bahnmueller, S.; Ke, C. P.; Srid, V. S.; Kee, L. W.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 3792–3795; (b) Xiong, W.; Lin, Q.; Ma, H.; Zheng, H.; Chen, H.; Li, X. *Tetrahedron: Asymmetry* **2005**, *16*, 1959–1962.
13. (a) Gordon, C. M. *Appl. Catal., A* **2001**, *222*, 101–117; (b) Sheldon, R. A. *Chem. Commun.* **2001**, *23*, 2399–2407; (c) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.
14. (a) Ni, B.; Headley, A. D. *Chem. Eur. J.* **2010**, *16*, 4426–4436; (b) Lombardo, M.; Trombini, C. *ChemCatChem* **2010**, *2*, 135–145; (c) Šebesta, R.; Kmentová, I.; Toma, Š. *Green Chem.* **2008**, *10*, 484–496.
15. (a) Lee, S.-G.; Zhang, Y. J.; Piao, J. Y.; Yoon, H.; Song, C. E.; Choi, J. H.; Hong, J. *Chem. Commun.* **2003**, 2624–2625; (b) Geldbach, T. J.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 8114–8115; (c) Kawasaki, I.; Tsunoda, K.; Tsuji, T.; Yamaguchi, T.; Shibuta, H.; Uchida, N.; Yamashita, M.; Ohta, S. *Chem. Commun.* **2005**, 2134–2136; (d) Feng, X.; Pugin, B.; Küsters, E.; Sedelmeier, G.; Blaser, H.-U. *Adv. Synth. Catal.* **2007**, *349*, 1803–1807; (e) Gadenne, B.; Hesemann, P.; Moreau, J. J. E. *Tetrahedron Lett.* **2004**, *45*, 8157–8160; (f) Gadenne, B.; Hesemann, P.; Moreau, J. J. E. *Tetrahedron: Asymmetry* **2005**, *16*, 2001–2006; (g) Baleizão, C.; Gigante, B.; García, H.; Corma, A. *Tetrahedron* **2004**, *60*, 10461–10468; (h) Doherty, S.; Goodrich, P.; Hardacre, C.; Knight, J. G.; Nguyen, M. T.; Pârvulescu, V.; Paun, C. *Adv. Synth. Catal.* **2007**, *349*, 951–963; (i) Doherty, S.; Goodrich, P.; Hardacre, C.; Pârvulescu, V.; Paun, C. *Adv. Synth. Catal.* **2008**, *350*, 295–302; (j) Gavrilov, K. N.; Lyubimov, S. E.; Bondarev, O. G.; Maksimova, M. G.; Zheglov, S. V.; Petrovskii, P. V.; Davankov, V. A.; Reetz, M. T. *Adv. Synth. Catal.* **2007**, *349*, 609–616; (k) Yang, S.-D.; Shi, Y.; Sun, Z.-H.; Zhao, Y.-B.; Liang, Y.-M. *Tetrahedron: Asymmetry* **2006**, *17*, 1895–1900; (l) Šebesta, R.; Bilčík, F. *Tetrahedron: Asymmetry* **2009**, *20*, 1892–1896; (m) Šebesta, R.; Mečiarová, M.; Poláčková, V.; Veverková, E.; Kmentová, I.; Gajdošiková, E.; Cvengroš, J.; Buffa, R.; Gajda, V. *Coll. Czech. Chem. Commun.* **2007**, *72*, 1057–1068; (n) Pugin, B.; Groehn, V.; Moser, R.; Blaser, H. U. *Tetrahedron: Asymmetry* **2006**, *17*, 544–549.
16. (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley: New York, 1994; (b) Wolfson, A.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Organomet. Chem.* **2005**, *690*, 3558–3566; (c) Pugin, B.; Studer, M.; Kuesters, E.; Sedelmeier, G.; Feng, X. *Adv. Synth. Catal.* **2004**, *346*, 1481–1486; (d) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, Ch. A.; Liotta, Ch. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254–1255.
17. (a) Jessop, P. G.; Stanley, R. R.; Brown, R. A.; Eckert, C. A.; Liotta, C. L.; Ngo, T. T.; Pollet, P. *Green Chem.* **2003**, *5*, 123–128; (b) Ngo, H. L.; Hu, A.; Lin, W. *Tetrahedron Lett.* **2005**, *46*, 595–597; (c) öchsner, E.; Schneiders, K.; Junge, K.; Beller, M.; Wasserscheid, P. *Appl. Catal., A* **2009**, *364*, 8–14; (d) Floris, T.; Kluson, P.; Bartek, L.; Pelantova, H. *Appl. Catal., A* **2009**, *366*, 160–165.
18. (a) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265–8266; (b) Ojima, I.; Kogure, T.; Yoda, N. *J. Org. Chem.* **1980**, *45*, 4728–4739.
19. (a) Ojima, I. *Pure Appl. Chem.* **1984**, *56*, 99–110; (b) Ojima, I.; Kogure, T.; Yoda, N.; Suzuki, T.; Yatabe, M.; Tanaka, T. *J. Org. Chem.* **1982**, *47*, 1329–1334.
20. Ojima, I.; Kogure, T.; Yoda, Y. *Org. Synth.* **1985**, *63*, 18–22.
21. Dwars, T.; Schmidt, U.; Fischer, C.; Grassert, I.; Kempe, R.; Fröhlich, R.; Drauz, K.; Oehme, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2851–2853.
22. Stille, J. K.; Su, H.; Brechot, P.; Parrinello, G.; Hegedus, L. S. *Organometallics* **1991**, *10*, 1183–1189.
23. Wolfson, A.; Vankelecom, I. F. J.; Geresh, S.; Jacobs, P. A. *J. Mol. Catal. A: Chem.* **2003**, *198*, 39–45.

24. Nagel, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 435–436.
25. (a) Malmström, T.; Andersson, C. *Chem. Commun.* **1996**, 1135–1136; (b) Malmström, T.; Andersson, C. *J. Mol. Catal. A: Chem.* **1999**, *139*, 259–270.
26. (a) Dyson, P. J.; Laurenczy, G.; Ohlin, C. A.; Vallance, J.; Welton, T. *Chem. Commun.* **2003**, 2418–2419; (b) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. J. *J. Phys. Chem. B* **2002**, *106*, 7315–7320.
27. Daguenet, C.; Dyson, P. *J. Organomet.* **2004**, *23*, 6080–6083.
28. (a) Suarez, P. A. Z.; Dullins, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217; (b) Dyson, P. J.; Ellis, D. J.; Henderson, W.; Laurenczy, G. *Adv. Synth. Catal.* **2003**, *345*, 216–221.
29. Mehnert, C. P.; Dispenziere, N. C.; Cook, R. A. *Chem. Commun.* **2002**, 1610–1611.