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A comparison of the asymmetric hydrogenation catalyzed by rhodium complexes containing chiral ligands with a binaphthyl unit and those with a 5,5′,6,6′,7,7′,8,8′-octahydro-binaphthyl unit

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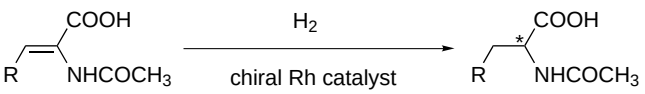
Abstract—The chiral ligands H_8–BINAPO and H_8–BDPAB were synthesized by reacting chlorodiphenylphosphine with H_8–BINOL and H_8–BINAM, respectively. Applications of these ligands in the Rh-catalyzed enantioselective hydrogenation of a variety of (*Z*)-acetamido-3-arylacrylic acid methyl esters provided chiral amino acid derivatives with good to excellent enantioselectivities (H_8–BINAPO: up to 84.0% e.e.; H_8–BDPAB: up to 97.1% e.e.). In the hydrogenation of acetamidoacrylic acid, 99% e.e. was obtained when a $[Rh(H_8\text{–BDPAB})]^+$ catalyst was used. The catalytic activities and enantioselectivities of $[Rh(H_8\text{–BINAPO})]^+$ and $[Rh(H_8\text{–BDPAB})]^+$ are substantially better than those obtained with the corresponding rhodium catalysts containing BINAPO (up to 64% e.e.) and BDPAB (up to 92.6% e.e.). © 2001 Published by Elsevier Science Ltd.

1. Introduction

Asymmetric catalytic hydrogenation is one of the most efficient and convenient methods for preparing a wide range of enantiomerically pure compounds. Historically, the desire for practical routes to α-amino acids ultimately led to the development of effective chiral diphosphine ligands, such as DIPAMP,[1] DIOP,[2] Chiraphos,[3] Norphos,[4] BPPM,[5] BDPP,[6] BINAP,[7] Duphos,[8] BICP,[9] and others,[10] for the enantioselective hydrogenation of α-amidoacrylates (α-enamides) (Eq. (1)).



(1)

The design of such diphosphine ligands remains an active area of research, and the homogeneous asymmetric catalytic hydrogenation of prochiral C=X (X=C, N, O, and so forth) double bonds is one of the most important applications of these enantioselective catalytic reactions. It has been found that many ligands with C_2 symmetry were effective in asymmetric hydrogenation reactions. For example, the aromatic BINAP ligand, which possesses C_2 axial chirality, has shown great asymmetric induction potential. It has been suggested that the highly skewed position of the naphthyl rings in BINAP is the determining factor in its effectiveness in asymmetric catalytic reactions.[11]

Takaya first prepared the atropisomeric ligand, H_8–BINAP,[12] which possesses a unique structural feature compared to the binaphthyl unit in BINAP. Recent research showed that the chiral catalysts derived from 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthyl ligands (e.g. H_8–BINAP,[13–15] H_8–BINOL,[16–18] H_8–BINAM,[18] H_8–BDPAB,[19] H_8–binaphthoxy,[20] H_8–MAPs[21]) exhibit higher efficiency and enantioselectivity for asymmetric reactions than those prepared from their parent ligands, due to the steric and electronic modulation in the H_8–binaphthyl backbone. To expand the scope of the previous studies and to provide more support of the rationale, it is of interest to examine the effectiveness of chiral ligands H_8–BINAPO **1** and H_8–BDPAB **3** in comparison with BINAPO **2** and BDPAB **4** in the asymmetric hydrogenation of dehydroamino acid derivatives and other substrates. Herein, we report the results of this comparative study and provide more evidence for the superior properties of the partially hydrogenated binaphthyl species (Fig. 1).

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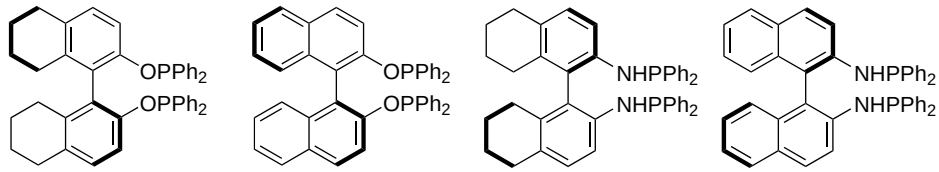


(*S*)-H_8-BINAPO, (*S*)-**1** (*S*)-BINAPO, (*S*)-**2** (*R*)-H_8-BDPAB, (*R*)-**3** (*R*)-BDPAB, (*R*)-**4**

Figure 1.

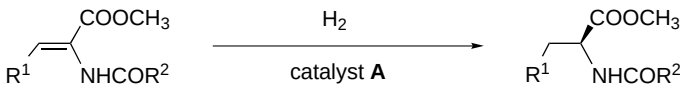
2. Results and discussion

It has been reported that H_8–BINOL[22] and H_8–BINAM[19,22b] can be obtained by partial hydrogenation of the corresponding BINOL and BINAM, respectively, without loss of enantiomeric excess. Ligands H_8–BINAPO **1** and H_8–BDPAB[19] **3** were conveniently prepared by the reaction of chlorodiphenylphosphine in the presence of an organic base with the corresponding H_8–BINOL and H_8–BINAM in 94 and 84% yield, respectively. For the purpose of comparison, BINAPO and BDPAB[23] ligands were also synthesized from BINOL and BINAM in a similar method, respectively. The cationic rhodium catalysts (**A**: [Rh(*S*)-**1**(COD)]BF_4, **B**: [Rh(*S*)-**2**(COD)]BF_4, **C**: [Rh(*R*)-**3**(COD)]BF_4, **D**: [Rh(*R*)-**4**(COD)]BF_4) were prepared in situ by stirring $[Rh(COD)Cl]_2$ and silver tetrafluoroborate with (*S*)-H_8–BINAPO, (*S*)-BINAPO, (*R*)-H_8–BDPAB and (*R*)-BDPAB, respectively, in THF at ambient temperature.

When catalyst **A** was used in the asymmetric hydrogenation of methyl (*Z*)-2-acetamidocinnamate under 100 psi H_2 in CH_2Cl_2 solvent at ambient temperature, it gave the desired product with 84% e.e. The e.e. obtained in the reaction with catalyst **A** was found to be insensitive to variations in hydrogen pressure, reaction temperature and the ratio of substrate to catalyst. A variety of methyl esters of (*Z*)-acetamido-3-arylacrylic acids were hydrogenated with catalyst **A** and the results were summarized in Table 1. It was found that moderate to good enantioselectivities were observed for the desired products and the substituents on the phenyl group of the methyl (*Z*)-2-acetamidocinnamate had a small effect on the enantioselectivity (entries 1–4). The electronic influence of the substituents on the enantioselectivity was not significant (entries 1, 4, 7). A comparison of the hydrogenation of (*Z*)-acetamido-3-arylacrylic acids or their esters with catalyst **A** and **B** was carried out and the results are summarized in Table 2. The experimental data clearly shows that the rate and enantioselectivity of the hydrogenation of either (*Z*)-acetamido-3-arylacrylic acids or their methyl esters catalyzed by catalyst **A** (containing (*S*)-H_8–BINAPO ligand) were higher than those from the same reaction catalyzed by catalyst **B** (containing (*S*)-BINAPO ligand). From Table 2, it can also be seen that the rate and enantioselectivities of the hydrogenation of (*Z*)-acetamido-3-arylacrylic acids were lower than those of the hydrogenation of their corresponding methyl esters when using catalyst **A** in the asymmetric hydrogenation reactions.

The asymmetric hydrogenation of methyl (*Z*)-2-acetamidocinnamate using catalyst **C** (containing (*R*)-H_8–BDPAB ligands) gave the desired product with higher e.e. (92.0% e.e.) than that obtained when using catalyst **A** (containing (*R*)-H_8–BINAPO ligand, 84.0% e.e.) in CH_2Cl_2. After optimizing the reaction conditions, the asymmetric hydrogenation of methyl (*Z*)-2-acetamidocinnamate using catalyst **C** gave the desired product with 96.1% e.e. under 1 atm. pressure of H_2 at ambient temperature in THF solvent. The rate of the reaction was very fast and the completion time for the

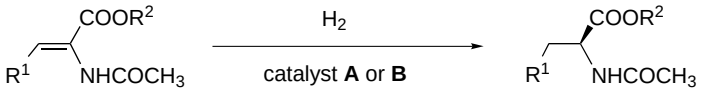
Table 1. The asymmetric hydrogenation of (*Z*)-acetamido-3-arylacrylic acid methyl esters using catalyst **A**[a]



Entry	R^1	R^2	Time (min)	Conv. (%)	E.e.[b] (%)
1	Phenyl	CH_3	10	100	84.0
2	*o*-Chloro-phenyl	CH_3	10	100	85.0
3	*m*-Chloro-phenyl	CH_3	10	100	78.3
4	*p*-Chloro-phenyl	CH_3	10	100	80.8
5	2-Furyl	Phenyl	10	100	63.9
6	H	CH_3	10	49.0	81.0
7	*p*-Methyl-phenyl	CH_3	10	100	83.5
8	*p*-Methyl-phenyl	Phenyl	10	95.7	80.0

[a] Sub./cat. = 500; pressure of H_2 = 100 psi; ambient temperature; solvent: dichloromethane. The conversion and e.e. values were determined by GLC using a Chrompack Chirasil-L-Val column.
[b] *S* configuration was obtained for all products.

Table 2. A comparison of the hydrogenation of substituted dehydroalanines with catalysts **A** and **B**[a]

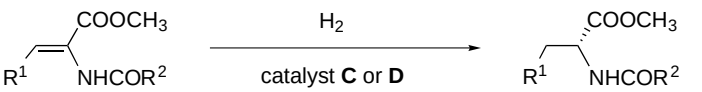


Entry	R^1	R^2	Catalyst	Time (min)	Conv. (%)	E.e.[b] (%)
1	Phenyl	CH_3	**A**	10	100	84.0
2	Phenyl	CH_3	**B**	10	85.5	64.0
3	Phenyl	H	**A**	30	81.9	74.2
4	Phenyl	H	**B**	30	71.2	18.0
5	*m*-Chloro-phenyl	CH_3	**A**	10	100	78.3
6	*m*-Chloro-phenyl	CH_3	**B**	10	70.3	54.7
7	*m*-Chloro-phenyl	H	**A**	30	87.9	37.0
8	*m*-Chloro-phenyl	H	**B**	30	56.3	10.5

[a] Sub./cat. = 500; pressure of H_2 = 100 psi; ambient temperature. The hydrogenation of methyl esters of (*Z*)-acetamido-3-arylacrylic acids were carried out in dichloromethane. The hydrogenation of (*Z*)-acetamido-3-arylacrylic acids were carried out in methanol. The conversion and e.e. values were determined by GLC using a Chrompack Chirasil-L-Val column.
[b] *S* configuration was obtained for all products.

reaction was only 10 min. In contrast to other rhodium/phosphine catalyst systems,[24] the addition of an organic base, such as triethylamine, decreased the enantioselectivity of the hydrogenation of methyl (*Z*)-2-acetamido-cinnamate. The enantioselectivities of catalyst **C** in the hydrogenation of a variety of (*Z*)-acetamido-3-aryl-acrylic acid methyl esters were found to be high (>90% e.e.) in all cases (Table 3). These results clearly show the high potential for the application of catalyst **C** in the asymmetric synthesis of chiral amino acids. Table 3 also shows the comparative catalytic activity of catalyst **C** and **D** in the asymmetric hydrogenation of methyl esters of (*Z*)-acetamido-3-arylacrylic acids. It is obvious that the enantioselectivity of catalyst **C** was higher than that of catalyst **D** in the same reaction (entries 1–5, 12, 15). Catalysts **C** and **D** were also tested in the hydrogenation of a variety of (*Z*)-acetamido-3-arylacrylic acids e.e.s of over 90% were observed with catalyst **C** in all cases (Table 4). It was found that polar or protic reaction media gave higher enantioselectivity and the enantioselectivity decreased with increasing hydrogen pressure. Similar to the hydrogenation of their methyl esters, the e.e. values of the hydrogenation products decreased significantly when an organic base was added

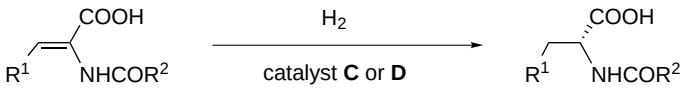
Table 3. The asymmetric hydrogenation of (*Z*)-acetamido-3-arylacrylic acid methyl esters using catalyst **C** or **D**[a]



Entry	R^1	R^2	Cat. **C**, e.e.[b] (%)	Cat. **D**, e.e.[b] (%)
1	Phenyl	CH_3	95.8	90.3
2	H	CH_3	97.1	92.6
3	*o*-Chloro-phenyl	CH_3	97.0	90.0
4	*m*-Chloro-phenyl	CH_3	94.0	90.2
5	*p*-Chloro-phenyl	CH_3	94.0	88.0
6	4-Bromo-phenyl	CH_3	95.5	–
7	4-Bromo-phenyl	Phenyl	96.4	–
8	4-Fluoro-phenyl	CH_3	92.9	–
9	4-Fluoro-phenyl	Phenyl	94.2	–
10	4-Methoxy-phenyl	CH_3	93.1	–
11	4-Methoxy-phenyl	Phenyl	95.2	–
12	*p*-Methyl-phenyl	CH_3	94.4	89.5
13	*p*-Methyl-phenyl	Phenyl	94.6	–
14	4-Nitro-phenyl	CH_3	90.7	–
15	3,4-Methylene-dioxyphenyl	CH_3	92.6	80.3
16	*trans*-Cinnamyl	CH_3	90.2	–
17	2-Furyl	CH_3	90.5	–
18	2-Furyl	Phenyl	93.2	–
19	*N*-Aceto-3-indole	Phenyl	92.5	–

[a] Sub./cat. = 100; pressure of H_2 = 30 psi; ambient temperature; time = 10 min.; solvent: THF; quantitative conversion for all cases. The conversion and e.e. values were determined by GLC using a Chrompack Chirasil-L-Val column.
[b] *R* configuration was obtained for all products.

Table 4. The asymmetric hydrogenation of a variety of dehydroamino acids using catalyst **C** or **D**[a]



Entry	R^1	R^2	Cat. **C**, e.e.[b] (%)	Cat. **D**, e.e.[b] (%)
1	Phenyl	CH_3	94.2	90.3
2	H	CH_3	99.0	93.5
3	*o*-Chloro-phenyl	CH_3	94.1	89.6
4	*m*-Chloro-phenyl	CH_3	92.8	88.2
5	*p*-Chloro-phenyl	CH_3	93.1	86.0
6	2-Methoxy-phenyl	CH_3	92.5	–
7	4-Nitro-phenyl	CH_3	90.0	–
8	3,4-Methylene-dioxyphenyl	CH_3	91.1	76.8
9	2-Furyl	Phenyl	93.9	–

[a] Sub./cat. = 100; pressure of H_2 = 30 psi; ambient temperature; time = 10 min; solvent: ethanol; quantitative conversion for all cases. The conversion and e.e. values were determined by GLC using a Chrompack Chirasil-L-Val column.
[b] *R* configuration was obtained for all products.

to the reaction. It can also be seen from Table 4 that the enantioselectivities in the hydrogenation of (*Z*)-acetamido-3-arylacrylic acids catalyzed by catalyst **C** were higher than those from the same reactions with catalyst **D** (entries 1–5, 8). These results further exhibited the generality of using the more sterically demanding H_8–binaphthyl unit in the C_2-symmetric chiral ligands. It was reported that the dihedral angle (80.3°) of the two tetralin rings in [Rh((*S*)-H_8–BINAP)(COD)]ClO_4[12b] is wider than those of the two naphthalene rings in the BINAP–Rh complexes reported (71.0–75.5°).[25] This difference is a reflection of the greater steric hindrance of hydrogen atoms attached to sp^3 carbon atoms in tetralin rings than that of hydrogen atoms on sp^2 carbon atoms in naphthalene rings. Unfortunately, no X-ray structures of the H_8–BINAPO–Rh and H_8–BDPAB–Rh complexes are available.

3. Conclusion

We have studied the effects of chiral bisphosphinite (H_8–BINAPO) and chiral bisaminophosphine (H_8–BDPAB) ligands prepared from H_8–BINOL and H_8–BINAM, respectively. Both ligands were found to be effective in the Rh-catalyzed hydrogenation of (*Z*)-acetamido-3-arylacrylic acids and their esters. The enantioselectivities of the catalyst containing chiral bisaminophosphine ligand in the hydrogenation of (*Z*)-acetamido-3-arylacrylic acids and their esters were found to be higher than those from the same reaction using a catalyst containing the chiral bisphosphinite ligand. Furthermore, both the H_8–binaphthyl chiral ligands exhibited higher catalytic activities and enantioselectivities than those prepared from their parents ligands. These findings show the excellent opportunities for the improvement of many existing catalyst systems.

4. Experimental

4.1. General considerations

All experiments were carried out under nitrogen atmosphere. Unless otherwise stated, commercial reagents were used as received without further purification. All solvents used were dried using standard, published methods and were distilled before use. The preparation of samples and the setup of reactions were either performed in a nitrogen-filled MBRAUN Lab Master 130 glovebox or using standard Schlenk-type techniques. The hydrogenation reactions were performed in a 50 mL stainless-steel autoclave from Parr company. NMR spectra were obtained on a BRUKER Model ADVANCE DPX 400 spectrometer (^1H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz). ^{13}C and ^{31}P spectra were referenced from Me_4Si and external 85% H_3PO_4, respectively. Melting points were determined using an Electrothermal 9100 apparatus in capillaries sealed under nitrogen. Mass analyses were performed on a V.G. MICROMASS, Fisons VG platform and a Finnigan Model Mat 95 ST spectrometer. Optical rotations were measured on a Perkin–Elmer Model 341 polarimeter. GLC and HPLC analyses were performed using a Hewlett–Packard Model HP 5890 Series II GC and a Hewlett–Packard Series 1050 HPLC, respectively.

4.2. Synthesis of (*S*)-2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [(*S*)-H_8-BINAPO], (*S*)-1

A solution of (*S*)-H_8–BINOL[22] (200 mg, 0.7 mmol) in diethyl ether (20 mL) containing dried pyridine (0.13 mL, 1.6 mmol) was charged to a 50 mL Schlenk flask under a nitrogen atmosphere. This flask was cooled to 0°C and a solution of chlorodiphenylphosphine (0.32 mL, 1.8 mmol) in THF (5 mL) was added dropwise.

The system was allowed to stir for 5 h at 0°C and the temperature was raised to room temperature. The solution was filtered to remove the solid. The solvent was evaporated in vacuo to give crude product (450 mg), which was dissolved in CH_2Cl_2 (2 mL) and then diethyl ether (10 mL) was added to the solution. The final solution was kept at −30°C for 24 h to allow the growth of pure crystals of (*S*)-H_8–BINAPO. After filtration and drying in vacuo, white, needle-like crystals were obtained (436 mg, 94% yield). Mp 130–132°C; $[\alpha]_D$ −82.0 ($c=1.0$, THF); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 20H), 6.99 (m, 4H), 2.72 (m, 4H), 2.23 (m, 4H), 1.52 (m, 4H), 1.30 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 152.8, 142.6, 142.5, 142.4, 137.3, 132.0, 129.9, 129.8, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.4, 115.8, 115.6, 29.8, 28.0, 23.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 103.89. HRMS: calcd for $C_{44}H_{40}O_2P_2$: 663.2582; found: 663.4310 $[M+H]^+$.

4.3. Synthesis of (*R*)-2,2′-bis(diphenylphosphinoamino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [(*R*)-H_8–BDPAB], (*R*)-3

Chlorodiphenylphosphine (0.76 mL, 4.28 mmol) and NEt_3 (1.0 mL, 7.04 mmol) were added in the solution of (*R*)-H_8–BINAM[19] (0.5 g, 1.71 mmol) in anhydrous CH_2Cl_2 (15 mL), and the mixture was stirred for 24 h under reflux. The solution was cooled, concentrated under reduced pressure and anhydrous diethyl ether (10 mL) was added. The precipitate was filtered and washed with anhydrous diethyl ether (10 mL). The solvent was removed in vacuo and the crude residue was purified by recrystallization from anhydrous diethyl ether (2 times) at −20°C for 24 h (85% yield). Mp 137–139°C; $[\alpha]_D$: −47.0 ($c=1.0$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (m, 22H), 6.98 (d, $J_{H\text{-}H}=$ 8.34 Hz, 2H), 4.27 (d, $J_{P\text{-}H}=7.0$ Hz, 2H), 2.67 (m, 4H), 2.10 (m, 4H), 1.58 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.9, 141.7, 141.2, 141.0, 140.6, 140.5, 136.1, 130.8, 130.4, 130.2, 129.6, 128.9, 128.7, 128.4, 128.3, 128.2, 123.2, 112.7, 112.5, 29.3, 27.3, 23.1, 23.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.25. HRMS: calcd for $C_{44}H_{42}N_2P_2$: 661.2901; found: 661.4382 $[M+H]^+$. Anal. calcd for $C_{44}H_{42}N_2P_2$: C, 79.97; H, 6.41; N, 4.24. Found: C, 79.78; H, 6.40; N, 4.24%.

4.4. Synthesis of [Rh(*S*)-1(COD)]BF_4 (catalyst A)

$[Rh(COD)Cl]_2$ (5.0 mg, 0.01 mmol) and $AgBF_4$ (4.0 mg, 0.02 mmol) in THF (2 mL) were stirred at room temperature for 30 min under a nitrogen atmosphere. The solution was filtered to remove the solid AgCl. After the addition of (*S*)-H_8–BINAPO (13 mg, 0.02 mmol) in THF (3 mL) to the solution, [Rh(*S*)-**1**(COD)]BF_4 (Catalyst **A**) in THF was obtained in situ (4×10^{-6} mol/mL). ^{31}P NMR (162 MHz, THF): δ 28.4 (d, $J_{Rh\text{-}P}=168.0$ Hz).

4.5. Synthesis of [Rh(*S*)-2(COD)]BF_4 (Catalyst B)

The procedure is the same as the synthesis of [Rh(*S*)-**1**(COD)]BF_4. ^{31}P NMR (162 MHz, THF): δ 125.5 (d, $J_{Rh\text{-}P}=170.0$ Hz).

4.6. Synthesis of [Rh(*R*)-3(COD)]BF_4 (Catalyst C)

The procedure is the same as the synthesis of [Rh(*S*)-**1**(COD)]BF_4. ^{31}P NMR (162 MHz, THF): δ 63.45 (d, $J_{Rh\text{-}P}=155.1$ Hz).

4.7. Synthesis of [Rh(*R*)-4(COD)]BF_4 (Catalyst D)

The procedure is the same as the synthesis of [Rh(*S*)-**1**(COD)]BF_4. ^{31}P NMR (162 MHz, THF): δ 69.06 (d, $J_{Rh\text{-}P}=158.0$ Hz).

4.8. A typical procedure for the catalytic asymmetric hydrogenation of methyl (Z)-2-acetamidocinnamate

A THF solution of Catalyst **C** (600 μL, 0.0024 mmol) and methyl (*Z*)-2-acetamidocinnamate (0.053 g, 0.24 mmol) in THF (10 mL) were charged to a 50 mL autoclave. The hydrogenation was carried out under 200 kPa of hydrogen pressure at room temperature for 10 min. A portion of the reaction mixture was analyzed by GLC to determine the product composition. Quantitative conversion of the starting material to the hydrogenation product, methyl (*R*)-2-acetamido-3-phenylpropanoate, with 95.8% e.e. was observed. (The e.e. was determined by chiral capillary GC using a Chrompack Chirasil-L-Val Column.)

4.9. A typical procedure for the catalytic asymmetric hydrogenation of *N*-acetamidoacrylic acid

A THF solution of Catalyst **C** (600 μL, 0.0024 mmol) and *N*-acetamidoacrylic acid (0.031 g, 0.24 mmol) in ethanol (10 mL) were charged to a 50 mL autoclave. The hydrogenation was carried out under 200 kPa of hydrogen pressure at room temperature for 10 min. A portion of the reaction mixture was analyzed by GLC to determine the product composition. Quantitative conversion of the starting material to the hydrogenation product, (*R*)-acetamidopropanoic acid, with 99.0% e.e. was observed. (The enantiomeric excess was determined by chiral capillary GC using a Chrompack Chirasil-L-Val Column after converting the product to methyl ester.)

Acknowledgements

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References

1. (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2567; (b) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946; (c) Schmidt, U.; Riedl, B.; Griesser, H.; Fitz, C. *Synthesis* **1991**, 655.

2. (a) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429; (b) Murrer, B. A.; Brown, J. M.; Chalonner, P. A.; Nicholson, P. N.; Parker, D. *Synthesis* **1979**, 350.
3. Fryzuk, M. D.; Bonisch, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.
4. Brunner, H.; Pieronczyk, W.; Schönhammer, B.; Streng, K.; Bernal, I.; Korp, J. *Chem. Ber.* **1981**, *114*, 1137.
5. Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265.
6. McNeil, P. A.; Roberts, N. K.; Bonisch, B. *J. Am. Chem. Soc.* **1981**, *193*, 2280.
7. Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.
8. (a) Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8158; (b) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125; (c) Burk, M. J.; Gross, M. F.; Martinez, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 9375.
9. Zhu, G.; Cao, P.; Jiang, Q.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 1799.
10. (a) Riley, D. P.; Shumate, R. E. *J. Org. Chem.* **1980**, *45*, 5187; (b) Bergstein, W.; Kleemann, A.; Martens, J. *Synthesis* **1981**, 76.
11. Ohta, T.; Takaya, H.; Noyori, R. *Inorg. Chem.* **1988**, *27*, 566.
12. (a) Zhang, X.; Mashima, K.; Koyano, K.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *Tetrahedron Lett.* **1991**, *32*, 7283; (b) Zhang, X.; Mashima, K.; Koyano, K.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Takaya, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2309.
13. Zhang, X.; Taketomi, T.; Yoshizumi, T.; Kumobayashi, H.; Akutagawa, S.; Mashima, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 3318.
14. Zhang, X.; Uemura, T.; Matsumura, K.; Kumobayashi, H.; Sayo, N.; Takaya, H. *Synlett* **1994**, *1*, 501.
15. Uemura, T.; Zhang, X.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Ohta, T.; Nozaki, K.; Takaya, H. *J. Org. Chem.* **1996**, *61*, 5510.
16. Zhang, F.-Y.; Chan, A. S. C. *Tetrahedron: Asymmetry.* **1997**, *8*, 3651.
17. Chan, A. S. C.; Zhang, F.-Y.; Yip, C.-W. *J. Am. Chem. Soc.* **1997**, *119*, 4080.
18. Liu, G.-B.; Tsukinoki, T.; Kanda, T.; Mitoma, Y.; Tashiro, M. *Tetrahedron Lett.* **1998**, *39*, 5991.
19. Zhang, F.-Y.; Pai, C.-C.; Chan, A. S. C. *J. Am. Chem. Soc.* **1998**, *120*, 5808.
20. Zhang, F.-Y.; Chan, A. S. C. *Tetrahedron: Asymmetry* **1998**, *9*, 1179.
21. Wang, Y.; Guo, H.; Ding, K. *Tetrahedron: Asymmetry* **2000**, *11*, 4153.
22. (a) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930; (b) Guo, H.; Ding, K. *Tetrahedron Lett.* **2000**, *41*, 10061.
23. Miyano, S.; Nawa, M.; Mori, A.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, 2171.
24. Zhu, G.; Cao, P.; Jiang, Q.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 1799.
25. (a) Toriumi, K.; Ito, T.; Takaya, H.; Souchi, T.; Noyori, R. *Acta Crystallogr., Sect. B* **1982**, *38*, 807; (b) Tani, K.; Yamagata, T.; Tatsuno, Y.; Yamagata, Y.; Tomita, K.; Akutagawa, S.; Kumobayashi, J.; Otsuka, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 217; (c) Yamagata, T.; Tani, K.; Tatsuno, Y.; Saito, T. *J. Chem. Soc., Chem. Commun.* **1988**, 466; **1989**, 67.