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Synthesis of new chiral monodentate aminophosphinites and their use in catalytic asymmetric hydrogenations

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Abstract

A general synthesis of chiral 4-amino-4,5-dihydro-3H-dinaphthophosphepines **5a**–**f** is described. The resulting monodentate chiral aminophosphinites have been tested in the rhodium-catalyzed asymmetric hydrogenation of methyl α-acetamidocinnamate and methyl α-acetamidoacrylate. Enantioselectivities up to 96% ee were obtained in the presence of **5a** and sodium dodecylsulfonate in toluene.

Keywords: Chiral aminophosphinites; Enantioselectivities; Toluene

1. Introduction

In homogeneous catalysis the performance of the respective metal catalyst is largely dependent on the surrounding ligands. Despite the recent development of new ligand classes, such as carbenes [1], still P-based compounds constitute the most important class of ligands for late transition metals. In asymmetric catalysis especially bidentate phosphine ligands have been found to give excellent control in a number of catalytic asymmetric reactions [2]. Among the different transition metal-catalyzed enantioselective reactions, hydrogenations of olefins, imines and ketones are the most important in industry. Until very recently, optically active diphosphines were essential as chiral ligands in order to achieve high selectivities in these reactions. Based on the important discovery by Reetz (phosphites **1**) [3], de Vries and co-workers (phosphoramidites **2**) [4], Pringle and Claver (phosphonites **3**) [5] and others [6] nowadays monodentate ligands (Scheme 1) have become increasingly important for catalytic asymmetric hydrogenations [7]. In general, monodentate phosphites and phosphoramidites are attracting most interest. However, the monodentate phosphines and phosphinites are also interesting due to their often easier synthesis compared to the corresponding bidentate ligands.

Parallel to the work of Zhang [8] and Gladiali [9], we have introduced last year new monodentate phosphines based on a 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine structure **4** [10]. Similar to phosphites and phosphoramidites these ligands give high enantioselectivities (up to 95% ee) in the hydrogenation of dehydroamino acid methyl esters and methyl itaconate, which are typical benchmark tests for asymmetric hydrogenations.

Having a reliable synthesis route for phosphepine ligands **4** in hand, we wondered whether related aminophosphinites based on the structure of **4** would be easily accessible and induce high enantioselectivities in benchmark hydrogenation reactions. With the exception of the description of the diethylamino derivative **5b** [10], such aminophosphinites have not been disclosed in the literature so far. Here, we report a straightforward synthesis of six aminophosphinites **5a**–**f** and preliminary data on the rhodium-catalyzed hydrogenation of methyl α-acetamidocinnamate in the presence of **5a**–**f**.

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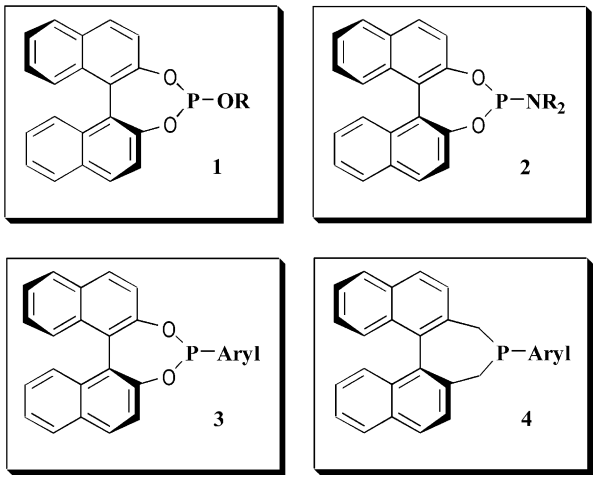


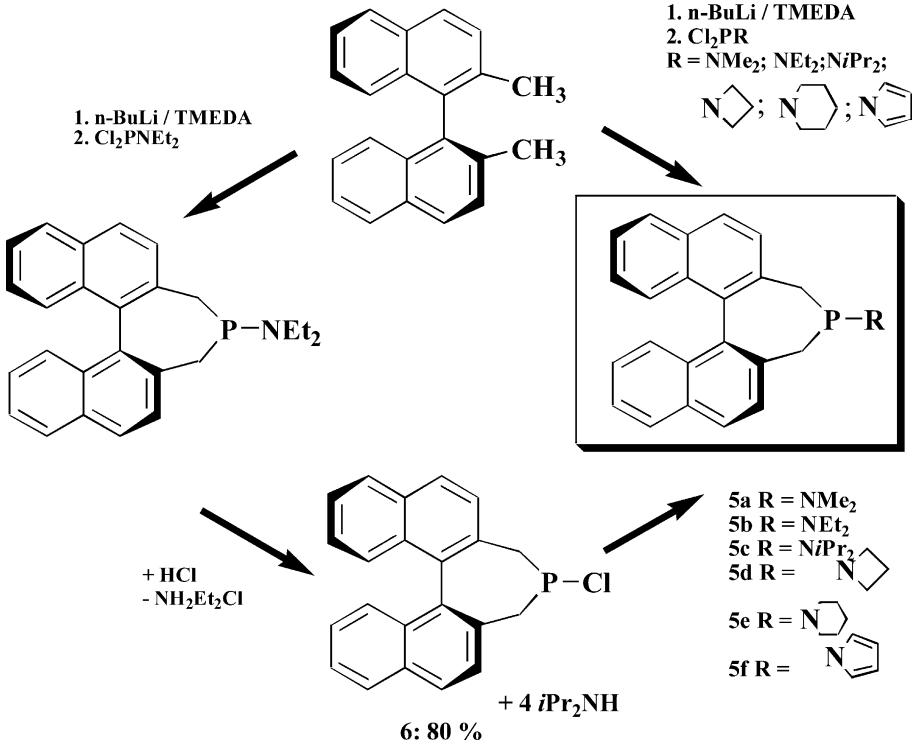
Scheme 1. Selection of recent developments of monodentate P-ligands.

2. Results

At the start of our investigations we envisioned the preparation of different 4-amino-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine ligands **5** based on our previously established route for ligands **4**. So far, only the 4-diethylamino derivative **5b** was prepared, but has not been investigated in catalytic reactions. As shown in Scheme 2 six different 4-amino-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine ligands were synthesized either directly or in a three-step sequence from homochiral 2,2′-dimethylbinaphthyl [11].

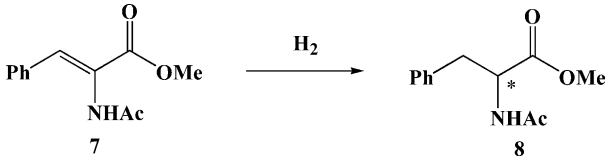
Double metallation of 2,2′-dimethylbinaphthyl with *n*-butyl lithium in the presence of TMEDA (tetramethylethylene diamine) [12] and quenching with commercially available dichloro(*N*,*N*-dimethylamino)phosphine or dichloro(*N*,*N*-diethylamino)phosphine gave **5a**–**b** in 72–80% yield [13]. In order to access other aminophoshinites, **5b** was subsequently reacted with HCl to give the corresponding chlorophosphepine **6** in 80% yield. It is worth mentioning that the chlorophosphepine **6** is also a useful building block for the synthesis of a variety of substituted 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines **4** by simple Grignard reaction. Ligands **5c**–**f** were prepared by the reaction of **6** and an excess of the corresponding amine (*N*,*N*-diisopropylamine, azetidine, piperidine, pyrrole). However, in most reactions varying amounts of by-products were produced, which could not be removed by standard purification procedures. Hence, the corresponding aminodichlorophosphines were prepared by the reaction of azetidine, piperidine, pyrrole and PCl_3 as described by Harris and co-workers [13]. Next, double lithiation of 2,2′-dimethylbinaphthyl and quenching with aminodichlorophosphines led to **5d**–**f** in 62–75% yield.

Having the desired ligands in hand we were interested in their catalytic behaviour. As a model reaction the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate **7** was studied at ambient pressure (Table 1). This reaction is generally accepted as a benchmark



Scheme 2. General synthesis of 4-amino-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine ligands **5**.

Table 1
Asymmetric hydrogenation of methyl α-acetamidocinnamate **7**



7 **8**

Entry	Ligand[a]	Solvent	*t*/2 [min][b]	Conv. [%]	ee [%] (R)
1	**5a**	Toluene	11	100	95
2	**5a**	Ethyl acetate	2	100	92
3	**5a**	THF	1	100	90
4	**5a**[c]	Toluene/SDS	10	100	96
5	**5a**[d]	Toluene/SDS	21	100	93
6	**5b**	Toluene	5	100	84
7	**5b**	Ethyl acetate	5	100	78
8	**5b**	Toluene/SDS	43	100	90
9	**5c**[c]	Toluene	–	15	26
10	**5c**	Ethyl acetate	–	43	9
11	**5d**	Toluene	–	59	42
12	**5d**	Ethyl acetate	5	100	42
13	**5e**	Toluene	15	100	84
14	**5e**	Ethyl acetate	28	98	73
15	**5e**[c]	Toluene/SDS	29	75	83
16	**5f**[c]	Toluene	7	100	60
17	**5f**[c]	Ethyl acetate	4	100	52

[a] Conditions: 1 mmol substrate; 0.01 mmol $[Rh(COD)_2]BF_4$; cat.:ligand = 1:2; 15 ml solvent; 25 °C.
[b] Halftime of hydrogenation.
[c] Conditions like[a] + 0.2 mmol SDS.
[d] Subst.: Rh: **5**a = 1 mmol: 0.005 mmol: 0.011 mmol + 0.2 mmol SDS.
[e] Prepared catalyst $[Rh(COD)L_2]BF_4$; L = **5f**.

hydrogenation test for new chiral ligands. Most catalytic tests were run with 1.0 mmol of substrate in 15 ml solvent in the presence of 1.0 mol% of rhodium catalyst at 25 °C and 1 bar of hydrogen. In general a P/Rh ratio of 2:1 was employed. In most cases the hydrogenations were finished within 1 h, showing the reasonable activities of the catalyst systems.

Although there is a close structural relationship between **5a**–**f** and our recently synthesized ligand class **4** [10], ligands with similar steric dimension behave quite different, e.g. **5a** gave 95% ee (Table 1, entry 1), while the corresponding (and sterically related) 4-isopropyl-4,5-dihydro-3*H*-dinaphtho[2,1-c;1′,2′-e]phosphepine gave only 46% ee under similar conditions. As can be seen from Table 1 only aminophosphonites with small alkyl groups attached to the nitrogen atom gave good to very good enantioselectivities in the model reaction. In contrast ligands **4** with alkyl groups attached to the phosphorus atom gave low enantioselectivities. Somewhat surprisingly the azetidinyl-substituted aminophosphinite **5d** gave a low enantioselectivity, which we cannot explain at present. In general, the new ligands **5** resemble in their catalytic behavior much more the synthesized phosphoramidates **2** of de Vries and Feringa. Hence, the presence of P–N bond has a significant influence on the enantioselectivity of the reaction.

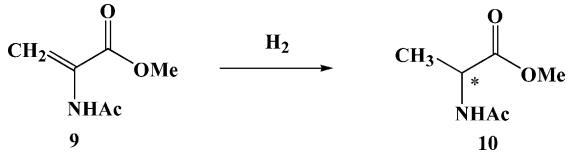
From the different solvents tested in the asymmetric hydrogenation of methyl α-acetamidocinnamate in the presence of **5a** (Table 1, entries 1–5) toluene gave the best enantioselectivities. However, faster reactions were observed in ethyl acetate and THF. The addition of a tenside (sodium dodecylsulfate = SDS) to the toluene solution improved the enantioselectivity further on [14].

Next, the combination of $[Rh(COD)_2]BF_4$/**5a**–**f** was used as catalyst precursor in asymmetric hydrogenations of methyl α-acetamidoacrylate **9** (Table 2). Except for **5c** all ligands led to excellent conversion. Best enantioselectivities (up to 71% ee) were obtained in the presence of **5a** in THF as solvent. In contrast to the hydrogenation of methyl α-acetamidocinnamate **7** (Table 1) only low ee's were obtained for methyl α-acetamidoacrylate **9** using toluene as solvent. Hence, most experiments were carried out in THF and ethyl acetate.

3. Conclusion

There is a continuing interest in the synthesis and application of new monodentate P-ligands, which can be modularly designed. Here, we describe for the first time a general synthesis of chiral 4-amino-4,5-dihydro-3*H*-dinaphthophosphepines **5** from 2,2′-dimethylbinaphthyl

Table 2
Asymmetric hydrogenation of methyl α-acetamidoacrylate **9**



9 **10**

Entry	Ligand[a]	Solvent	*t*/2 [min][b]	Conv. [%]	ee [%]
1	**5a**	THF	4	100	71 (R)
2	**5a**	Ethyl acetate	2	100	62 (R)
3	**5b**	THF	8	100	62 (R)
4	**5b**	Ethyl acetate	10	100	57 (R)
5	**5c**	THF	–	21	1 (S)
6	**5c**	Ethyl acetate	–	29	14 (R)
7	**5d**	THF	540	91	40 (R)
8	**5d**	Ethyl acetate	600	90	32 (R)
9	**5e**	THF	20	100	53 (R)
10	**5e**	Ethyl acetate	25	100	52 (R)
11	**5f**[c]	THF	3	100	58 (R)
12	**5f**[c]	Ethyl acetate	2	100	58 (R)

[a] Conditions: 1 mmol substrate; 0.01 mmol $[Rh(COD)_2]BF_4$; cat.:ligand = 1:2; 15 ml solvent; 25 °C.
[b] Halftime of hydrogenation.
[c] Catalyst $[Rh(COD)L_2]BF_4$; L = **5f**.

via double metallation and subsequent quenching with aminodichlorophosphines. Applying this straightforward sequence ligands **5a**–**f** are accessible in good yields in g-quantities. Preliminary catalytic testing of the new ligands in two well-known asymmetric hydrogenation reactions reveal the usefulness of these ligands. For example ligand **5a** induces one of the highest enantioselectivities ever reported with monodentate ligands for this benchmark reactions. In addition, having ligands **5** available, a missing link between ligand classes **2** and **4** has been closed. Hence, it should be possible in future to understand and develop more rationally new ligands based on the actual dinaphtho[2,1-c;1′,2′-e]phosphepine structure.

4. Experimental

4.1. General procedure for the synthesis of ligands *5a–f*

Metallation of chiral 2,2′-dimethylbinaphthyl with *n*-BuLi/TMEDA affords the crystalline dilithio species in 60–70% yield. Starting from 12.0 mmol dilithium salt of chiral 2,2′-dimethylbinaphthyl in 35 ml hexane 13.6 mmol of the corresponding amino dichlorophosphine in 15 ml hexane was added at 0 °C. After 2 h of reflux, hexane was replaced by 40 ml toluene to separate the formed LiCl. The obtained filtrate was evaporated. The residue was diluted with 10 ml dry acetone and 40 ml hexane were added to produce a small precipitate. After filtration and evaporation of the solvent ligands **5** were obtained in general in pure form. If necessary further purification can be achieved by recrystallization from toluene.

4.1.1. 4-Dimethylamino-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (*5a*)

Pale yellow solid, 80% yield. ^{1}H-NMR (25 °C, CD_2Cl_2): $\delta = 2.50$ (d, CH_3, 6H), 2.80 (t, CH_2, 2H), 2.93 (d, CH_2, 1H); 3.01 (d, CH_2, 1H); 7.08 (d, 1H), 7.17–7.21 (m, 4H), 7.36–7.42 (m, 1H), 7.55–7.61 (m, 2H), 7.87–7.93 (m, 4H). ^{13}C-NMR (25 °C, CD_2Cl_2): $\delta = 32.3$ (d, CH_2, $J = 17.2$ Hz), 35.7 (d, CH_2, $J = 31.5$ Hz), 41.8 (d, CH_3N, $J = 14.35$ Hz), 125.1 (d), 126.1 (d), 126.9 (d), 128.1 (d), 128.3, 128.5 (d), 129.3 (d), 132.5 (d), 133.2 (d), 136.0 (d). ^{31}P-NMR (25 °C, CD_2Cl_2): $\delta = 76.8$. MS (ES, 70 eV): $m/z = 355$ [M^+], 312, 265, 184, 132, 76, 60.

4.1.2. 4-Diethylamino-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (*5b*)

White solid, 72% yield. ^{1}H-NMR (25 °C, CD_2Cl_2): $\delta = 1.01$ (t, CH_3, 6H), 2.63–2.71 (q, CH_2, 1H, $J = 14.5$ Hz), 2.82–2.88 (m, CH_2, 5H); 3.03–3.06 (d, CH_2, 1H, $J = 11.5$ Hz); 7.12–7.24 (m, 4H), 7.37–7.44 (m, 2H), 7.56 (d, 1H), 7.89–7.95 (m, 4H). ^{13}C-NMR (25 °C, CD_2Cl_2): $\delta = 15.3$ (CH_3), 33.5 (d, CH_2–P, $J = 18.1$ Hz), 38.2 (d, CH_2–P, $J = 30.5$ Hz), 44.1 (d, CH_2–N, $J = 13.3$ Hz), 125.0 (d), 126.1 (d), 126.9, 128.2 (d), 128.5 (d), 128.7 (d), 132.5 (d), 133.4 (d), 134.3 (d) 136.1 (d). ^{31}P-NMR (25 °C, CD_2Cl_2): $\delta = 73.2$. MS (ES, 70 eV): $m/z =$ 383 [M^+], 340, 312, 297, 276, 265, 183, 138, 102, 74, 58, 46, 28.

4.1.3. 4-Diisopropylamino-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (**5c**)

Yellow oil, 68% yield. ^{1}H-NMR (25 °C, $CDCl_3$): δ = 1.21 (d, CH_3, 12H), 2.40 (d, CH_2, 2H), 2.64–2.87 (m, CH_2, 2H), 3.03–3.12 (sept, CH, 2H), 7.13–7.31 (m, 4H), 7.37–7.43 (m, 2H), 7.55 (d, 1H), 7.63 (d, 1H), 7.88–7.95 (m, 4H). ^{13}C-NMR (25 °C, $CDCl_3$): δ = 23.9 (CH_3, J = 4.5 Hz), 32.8 (d, CH_2, J = 17.2 Hz), 36.8 (d, CH_2, J = 28.6 Hz), 46.7 (d, CH, J = 5.7 Hz), 124.8, 125.9 (d), 126.0, 127.1 (d), 127.9, 128.2 (d), 128.4 (d), 132.4 (d), 132.6 (d) 134.2 (d). ^{31}P-NMR (25 °C, $CDCl_3$): δ = 46.0. MS (ES, 70 eV): m/z = 411 [M^+], 354, 312, 282, 265, 185, 126, 86, 44.

4.1.4. 4-Azetidinyl-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (**5d**)

Yellow solid, 65% yield. ^{1}H-NMR (25 °C, $CDCl_3$): δ = 2.18 (m, CH_2, 2H), 2.51–2.89 (m, CH_2, 4H), 3.45–3.61 (m, CH_2, 4H); 7.04 (d, 1H), 7.12–7.25 (m, 3H), 7.35–7.42 (m, 2H), 7.51 (d, 1H), 7.57 (d, 2H), 7.84–7.91 (m, 3H). ^{13}C-NMR (25 °C, $CDCl_3$): δ = 19.8 (d, CH_2, J = 14.3 Hz), 30.1 (d, CH_2–P, J = 17.2 Hz), 35.8 (d, CH_2–P, J = 26.7 Hz), 51.0 (d, CH_2, J = 6.7 Hz), 124.7 (d), 125.8 (d), 126.7 (d), 127.6 (d), 128.2 (d), 128.7, 132.1 (d), 132.7 (d) 133.9 (d), 135.4 (d). ^{31}P-NMR (25 °C, $CDCl_3$): δ = 68.0. MS (ES, 70 eV): m/z = 367 [M^+], 311, 297, 282, 265, 239, 183, 132, 101, 88, 70, 58, 42.

4.1.5. 4-Piperidinyl-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (**5e**)

White solid, 62% yield. ^{1}H-NMR (25 °C, CD_2Cl_2): δ = 1.14–1.56 (m, CH_2, 6H), 2.51–2.63 (q, CH_2, 1H), 2.79–2.91 (m, CH_2, 4H), 3.02 (d, CH_2, 1H), 7.07 (d, 1H), 7.12–7.22 (m, 3H), 7.39–7.41 (m, 2H), 7.54–7.60 (q, 2H), 7.86–7.92 (m, 4H). ^{13}C-NMR (25 °C, CD_2Cl_2): δ = 24.2 (CH_2), 25.1 (CH_2), 32.4 (d, CH_2–P, J = 18.1 Hz), 36.7 (d, CH_2–P, J = 30.5 Hz), 57.4 (CH_2), 125.0 (d), 126.1 (d), 126.9 (d), 128.1 (d), 128.5 (d), 128.9, 132.6 (d), 132.9 (d) 134.1 (d), 136.1 (d). ^{31}P-NMR (25 °C, CD_2Cl_2): δ = 74.4. MS (ES, 70 eV): m/z = 395 [M^+], 340, 312, 297, 276, 265, 184, 160, 132, 98, 84, 60.

4.1.6. 4-Pyrrolyl-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (**5f**)

White solid, 75% yield. ^{1}H-NMR (25 °C, $CDCl_3$): δ = 2.71–2.86 (m, CH_2, 2H), 3.05–3.19 (m, CH_2, 2H), 6.09–6.14 (m, CH_2, 2H), 6.46–6.50 (m, CH_2, 2H), 6.96 (d, 1H), 7.07–7.20 (m, 4H), 7.28–7.40 (m, 2H), 7.51 (d, 1H), 7.74–7.89 (m, 4H). ^{13}C-NMR (25 °C, $CDCl_3$): δ = 33.8 (d, CH_2–P, J = 15.3 Hz), 35.8 (d, CH_2–P, J = 24.8 Hz), 111.0 (CH_2=), 124.8 (d), 125.6 (d), 126.4, 127.0 (d), 127.6, 128.5 (CH_2=), 128.9 (d), 129.3, 132.0 (d), 133.0 (d) 134.3. ^{31}P-NMR (25 °C, $CDCl_3$): δ = 61.5. MS (ES, 70 eV): m/z = 377 [M^+], 356, 328, 311, 296, 282, 229, 163, 132, 114, 91, 65, 58, 39.

4.1.7. 4-Chloro-4,5-dihydro-3H-dinaphtho[2,1-c;1′,2′-e]phosphepine (**6**)

White solid, 80% yield. ^{1}H-NMR (25 °C, $CDCl_3$): δ = 2.65–2.71 (m, CH_2, 2H), 2.92–3.25 (m, CH_2, 2H), 7.11–7.18 (m, 4H), 7.32–7.43 (m, 4H), 7.80–7.84 (m, 4H). ^{13}C-NMR (25 °C, $CDCl_3$): δ = 40.3 (d, CH_2, J = 72.4 Hz), 41.4 (d, CH_2, J = 71.5 Hz), 124.8, 125.6, 126.0, 127.4, 127.9, 128.3, 128.7, 131.9, 132.2, 132.7. ^{31}P-NMR (25 °C, $CDCl_3$): δ = 115,1. MS (CI, Isobutan): m/z = 347 [M^+ + 1], 329, 311, 283, 275, 154, 93, 67.

4.2. Preparation of the Rh(II) complex of **5f**

A solution of ligand **5f** (2.4 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 etheric HBF_4 (1.2 mmol) is added and the solution is stirred for an additional hour. The solvent was removed and the residue was extracted in methanol to give red–brown solid (54% yield). ^{31}P NMR (25 °C, Acetone-d_6): δ = 97.5 J(P,Rh) = 169.2 Hz. MS (FAB pos.): m/z = 965 [M^+ -BF_4], 875 [M^+ -BF_4 -108].

4.3. Catalytic experiments

Hydrogenation was performed under normal pressure at 25 °C. A mixture of 0.005 mmol $[Rh(COD)_2]BF_4$, 0.055 mmol ligand **5a**–**f** and 0.5 mmol methyl α-acetamidocinnamate **7** or methyl α-acetamidoacrylate **9** was stirred for 15 min in 12.5 ml solvent. The hydrogenation flask was flushed several times with hydrogen. The reaction was followed by a volumetric measurement at 25 ± 0.5 °C. The enantiomeric excess was determined by GC (XE 60) or HPLC (Chiracel OD-H).

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