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Enantioselective rhodium-catalyzed hydrogenation of enol carbamates in the presence of monodentate phosphines

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Abstract—The rhodium-catalyzed asymmetric hydrogenation of different acyclic and cyclic enol carbamates to give optically active carbamates has been examined in the presence of chiral monodentate ligands based on a 4,5-dihydro-3*H*-dinaphthophosphepine motif **4**. The enantioselectivity is largely dependent upon the reaction conditions, the nature of substituents on the phosphorus ligand and structure of the enol carbamate. By applying the optimized reaction conditions, enantioselectivities of up to 96% ee have been achieved.
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1. Introduction

The importance of enantiomerically pure compounds is demonstrated by their widespread application as either building blocks or intermediates for the synthesis of pharmaceuticals, agrochemicals, polymers, natural compounds, auxiliaries, ligands and synthons in organic syntheses.[1] To serve the growing demand for enantiomerically pure compounds, various synthetic approaches have been developed. Within the different molecular transformations to chiral compounds, catalytic reactions offer an efficient and versatile strategy and present a key technology for the advancement of 'green chemistry', specifically for waste prevention, reducing energy consumption, achieving high atom efficiency and generating advantageous economics.[2] In this regard, the use of molecular hydrogen in reductions of C=C, C=O and C=N bonds is one of the most extensively studied fields. For activation of the hydrogen and transfer of chirality, the use of transition metal catalysts containing chiral ligands are essential. Over a period of nearly 30 years, the synthesis of new ligands focused mainly on bidentate phosphorus systems, because of the promising results in the first few years of homogeneous asymmetric hydrogenation. However, at the end of the 20th century, the situation changed and monodentate ligands received more attention.[3,4] The advantages of monodentate phosphorus ligands compared to bidentate ligands are their easier synthesis, high tunability and even a higher efficiency in the transfer of chiral information as observed in several cases. Important contributions in this field with excellent enantioselectivities for various classes of substrates were reported by Feringa and de Vries et al.[5] (phosphoramidites), Reetz et al.[6] (phosphites), Pringle and Claver et al.[7] (phosphonites) and Zhou et al. (spiro phosphoramidites).[8]

Following the effort of one of us (S.G.)[9] and parallel to the work of Zhang,[10] we constructed a ligand library of approximately 25 different monodentate phosphines based on a 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine framework **4** (Scheme 1), which is reminiscent of the 1,1′-binaphthol core, which is present in the ligands mentioned above (Scheme 1).[11] The potential of this ligand class **4** in asymmetric hydrogenation with molecular hydrogen, such as the reduction of α-amino acid precursors, dimethyl itaconate, enamides and β-ketoesters achieving enantioselectivities up to 95% ee was previously reported by us.[11] Moreover, other groups demonstrated the usefulness of these ligands in several catalytic asymmetric reactions.[12] The promising results obtained in the asymmetric hydrogenation of *N*-(1-phenylvinyl)acetamides with enantioselectivities of up to 95% ee and catalyst activities up to 2000 h^{-1} (TOF) motivated us to explore our ligand library **4** in the hydrogenation of structurally similar enol carbamates, which offer an alternative approach to chiral

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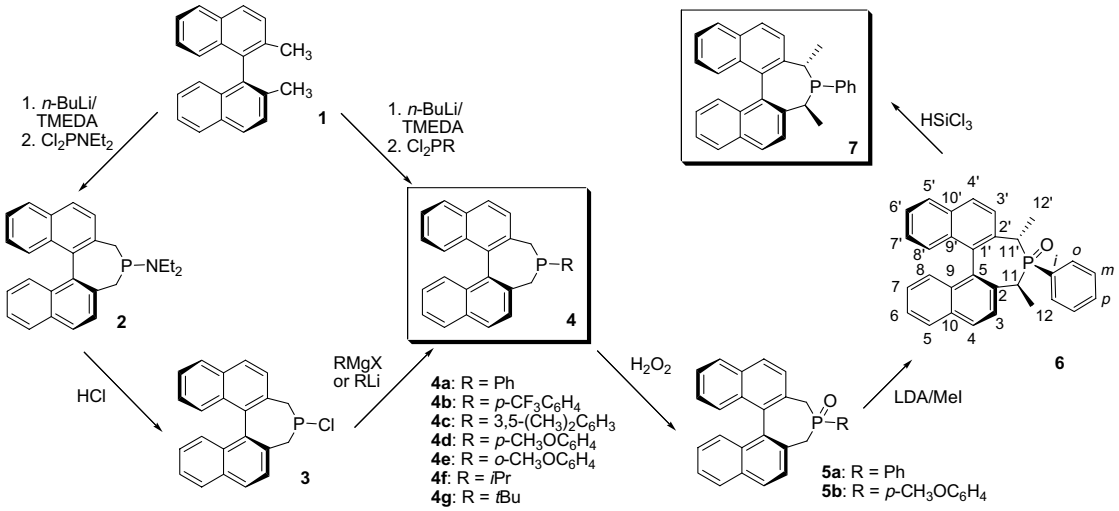


Scheme 1. General synthesis of ligands with 2,2′-binaphthyl framework.

alcohols. Pioneering work in the field of enantioselective hydrogenation of enol carbamates has been reported by Feringa, de Vries and Minnaard et al. who have scored enantioselectivities of up to 98% ee with rhodium-catalysts containing monodentate phosphoramidites (MonoPhos-family).

2. Results and discussion

2.1. Ligand synthesis

In general, the ligands were prepared by double metallation of 2,2′-dimethylbinaphthyl **1** with 2 equiv of *n*-butyl lithium, followed by quenching with diethylaminodichlorophosphine or with aryl and alkyl dichlorophosphines. Deprotection of the diethylamino phosphine **2** with gaseous HCl produced 4-chloro-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine **3** in 80% yield. This enantiomerically pure chlorophosphine is easily coupled with various Grignard reagents or organo-lithium compounds to give a broad selection of ligands **4**. In order to expand the application of this class of ligands, we prepared derivatives of **1**, bearing substituents on the aliphatic carbon at the α-position to the phosphorus. The desired bis-methylated product **7** has been obtained via a deprotonation–alkylation protocol. After the preliminary step of oxidation of 4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine **4a** with H_2O_2, lithiation and alkylation were performed by the addition of LDA (3 equiv) and CH_3I (2 equiv) at room temperature. The reaction is completely stereoselective, and only one of the possible dialkylated products is obtained (Scheme 1).

Recently, Widhalm et al. reported a similar approach to the synthesis of compound **7**, via the phosphepine sulfide instead of the oxide.[13] To compare the two procedures, the stereochemistry of the new stereogenic centres in the phosphepine oxide **6** was studied in detail.

The stereochemistry of compound **6** was confirmed by NMR spectroscopy. The initial ^{31}P NMR measurements displayed the occurrence of exclusively one enantiomer for **6** and **7** in each case, since only one single signal was found and racemization of the binaphthyl backbone over the course of reactions was excluded. In a two-dimensional

Table 1. Selected bond lengths [Å] and angles [°] of the phosphepine oxides **5a**, **5b** and **6**

5a		**6**		**5b**[a]	
P1–C1	1.812(5)	P1–C25	1.799(3)	P1–C1	1.824(4)
				[P2–C30]	[1.825(4)]
P1–C7	1.813(4)	P1–C22	1.832(2)	P1–C29	1.833(4)
				[P2–C58]	[1.846(4)]
P1–C28	1.814(5)	P1–C1	1.834(2)	P1–C8	1.837(4)
				[P2–C37]	[1.819(4)]
P1–O1	1.481(3)	P1–O1	1.483(2)	P1–O1	1.444(3)
				[P2–O3]	[1.407(5)]
C7–P1–C1	109.6(2)	C25–P1–C22	108.6(1)	C1–P1–C29	107.9 (2)
				[C30–P2–C37]	[107.2 (2)]
C28–P1–C1	104.0(2)	C25–P1–C1	104.2(1)	C1–P1–C8	105.4(2)
				[C30–P2–C58]	[103.0(2)]
C7–P1–C28	103.1(2)	C22–P1–C1	108.8 (1)	C29–P1–C8	102.3(2)
				[C58–P2–C37]	[100.8(2)]

[a] Values of the second molecule in the asymmetric unit are in brackets.

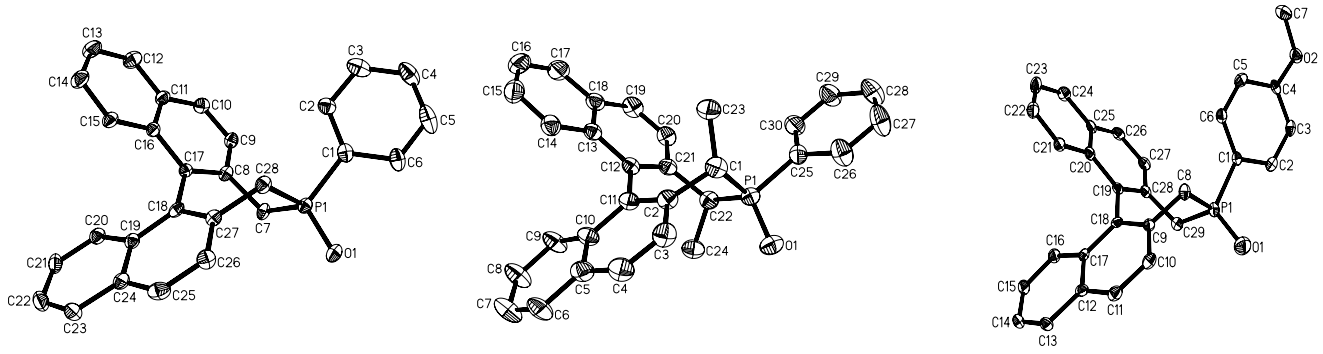


Figure 1. ORTEP plot of compounds **5a**, **6** and **5b**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability. With respect to compound **5b**, only one of the two symmetry-independent molecules of the asymmetric unit is depicted.

NOESY spectrum, correlations between the following protons were observed: *o*-Ph with H-3′, H-11′ and Me(12); H-3 with H-11 and H-3′ with H-11′, respectively, indicating the bis-axial orientation of both methyl groups. The spatial proximity of the methyl group Me(12) and of the phenyl group is also reflected by the difference in ^{1}H chemical shift values of both methyl groups (δMe(12) = 0.61 and Me(12′) = 0.95). The high-field shift of the signal for the methyl group Me(12) can be explained by the anisotropic effect of the phenyl substituent on the phosphorus.

In addition, useful structural data were gained by X-ray crystallography of oxide **6**. For comparison, X-ray structure analyses of the corresponding unsubstituted systems **5a** and **5b** were determined. Selected bond lengths and angles are shown in Table 1. The molecular structures of the three oxides are given in Figure 1. In the case of **5b**, two molecules have been found in the asymmetric unit with similar structural features. As expected in all compounds the substituents show an approximately tetrahedral arrangement at the phosphorus atom. The α,α-disubstituted phosphepine oxide **6** features shorter exocyclic (P1–C25 1.799(3) Å) than the endocyclic P–C bonds (P1–C22 1.832(2) Å and P1–C1 1.834(2) Å) in comparison with the unsubstituted system **5a** where all P–C bonds are equally long (Table 1). Furthermore, the α,α-substitution promotes a pronounced expansion of the endocyclic C–P–C angle up to 108.8(1)° (**6**) from 103.1(2)° (**5a**).

In accordance with the NMR studies and the X-ray structure analysis, the configuration of compound **6** was assigned to be (S,S,S_a). The stereochemistry of ligand **7** was allotted in analogy to the one of the corresponding oxide.

2.2. Catalytic experiments

The synthesis of enol carbamates **8**–**14** was carried out in analogy to literature protocols, by reacting the corresponding ketone with NaH and subsequent addition of the corresponding carbamoyl chloride.[5m,14]

Initial studies on the influence of reaction conditions were performed with 1-phenylvinyl *N*,*N*-diethylcarbamate **8** as substrate and 4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine **4a** as our standard ligand. Typically, we used an in situ pre-catalytic mixture of 1.0 mol % [Rh(cod)$_2$]BF$_4$ and 2.1 mol % of the ligand. All hydrogenation reactions were carried out in an eightfold parallel reactor array with a 3.0 ml reactor volume.[15]

First we investigated the influence of different solvents, such as methylene chloride, methanol, ethanol and 2-propanol in combination with a variation of the initial hydrogen pressure (1.0, 5.0, 10.0, 25.0 and 50.0 bar). Selected results are presented in Figure 2.

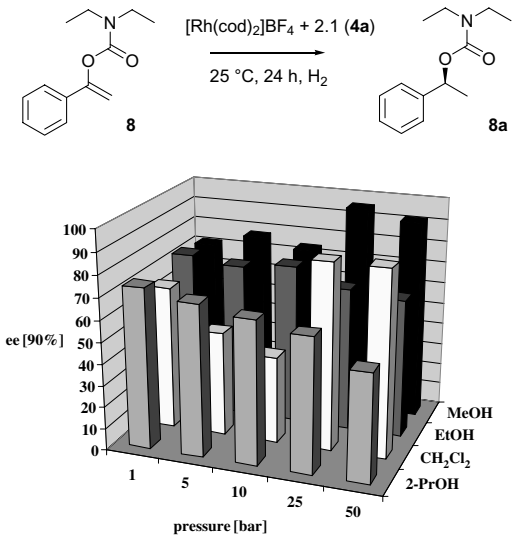


Figure 2. Solvent and pressure variation. Reactions were carried out at 25 °C for 24 h with 0.0024 mmol [Rh(cod)$_2$]BF$_4$, 0.005 mmol ligand **4a** and 0.24 mmol **8** in 2.0 ml solvent.

Surprisingly, by applying toluene as solvent in the hydrogenation of enol carbamate **8** no reaction occurred, while in previous studies toluene was found to be the solvent of choice for the hydrogenation of enamides and α-amino acids.[11c,e] The best enantioselectivities of up to 96% ee were obtained with methanol as solvent with a hydrogen pressure of 25 bar.

Two different pressure-enantioselectivity-dependencies have been noticed. In ethanol and 2-propanol, the enantioselectivity decreased when increasing the hydrogen pressure (1 bar: ethanol: 74% ee, 2-propanol: 74% ee, 50 bar: ethanol:

64% ee, 2-propanol: 50% ee) whereas in methylene chloride and methanol, the reverse behaviour was observed (1 bar: methanol: 72% ee, methylene chloride: 66% ee, 50 bar: methanol: 92% ee, methylene chloride: 86% ee). With the exception of 2-propanol (>99%), moderate to good conversions (60–90%) were observed at lower pressures within a reasonable time (24 h), while at higher pressure a complete conversion was achieved. The results indicated methanol as the solvent of choice (conversion: >99%; enantioselectivity: 96% ee). In addition, in order to estimate the effect of the protic solvent on the product structure the reaction was performed in methanol-d_4. Analysis of the ^{1}H NMR spectra showed that no incorporation of deuterium in the product had occurred. Therefore, one can rule out any interference of the solvent in the catalytic cycle due to transfer hydrogenation and/or protonolysis of Rh-C-species.[16]

In order to assess the optimum reaction conditions, a detailed pressure investigation was performed (Fig. 3). The results illustrated a constant range of enantioselectivity (~74% ee) between initial pressures of 1–18 bar, followed by an increase of up to a maximum of 96% ee at 25 bar. A further increase in the hydrogen pressure did not result in any improvement while enantioselectivities ranged between 92% and 94% ee in the region of 30–50 bar.

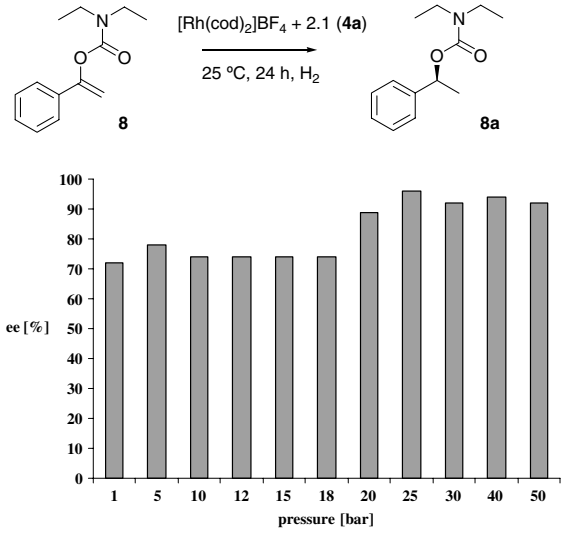


Figure 3. Study of pressure-enantioselectivity-dependency. Reactions were carried out at 25 °C for 24 h with 0.0024 mmol $[Rh(cod)_2]BF_4$, 0.005 mmol ligand **4a** and 0.24 mmol **8** in 2.0 ml methanol.

The optimal reaction conditions devised in the solvent-pressure investigation (methanol as solvent and 25 bar as initial hydrogen pressure) were applied in a temperature study (Fig. 4). With the model ligand **4a** in the hydrogenation of compound **8**, we observed a high stability of the enantioselectivity (94–96% ee) in the range of 10–90 °C albeit with a reduction of conversion at 90 °C. A further increase to 110 °C produced a racemic mixture of **8a**, probably as a result of ligand degradation.[17]

In order to evaluate the substituent effect at the phosphorus atom of the ligand, we studied the model reaction of 1-phenylvinyl *N*,*N*-diethylcarbamate **8** in the presence of eight different 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines **4a**–**4g** and **7** using the optimized reaction conditions (2.5 bar hydrogen pressure, methanol, 30 °C, 6 h). The results are presented in Table 2. In the hydrogenation of **8**, the best enantioselectivities of up to 90% and 72% ee, respectively, were achieved with ligand **4a** and **4d** (Table 2, entries 1 and 4). The presence of electron-donating groups, as well as electron-withdrawing groups onto the P-aryl substituent, led to a significant decrease of the stereoselectivity (Table 1, entries 2–5).

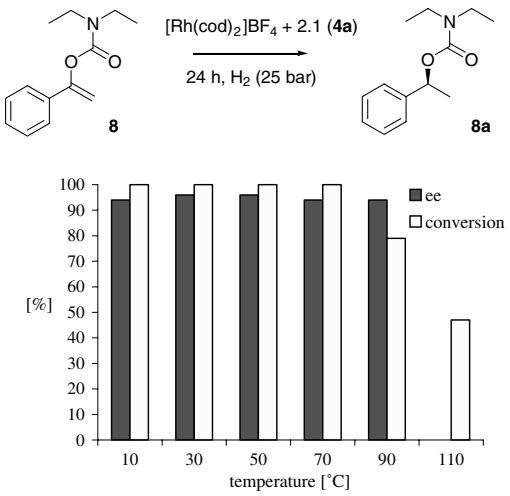
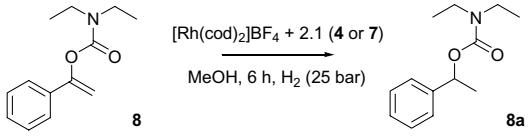


Figure 4. Dependency of enantioselectivity versus temperature. Reactions were carried out at corresponding temperature for 1–24 h with 0.0024 mmol $[Rh(cod)_2]BF_4$, 0.005 mmol ligand **4a** and 0.24 mmol **8** in 2.0 ml methanol.

Table 2. Hydrogenation of compound **8** with different 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines **4a**–**4g** and ligand **7**[a]



Entry	Ligand	Conv. (%)	Yield (%)	ee (%)
1	**4a**	>99	>99	**96 (*S*)**
2	**4b**	40	40	28 (*S*)
3	**4c**	>99	>99	66 (*S*)
4	**4d**	>99	>99	72 (*S*)
5	**4e**	>99	>99	51 (*S*)
6	**4f**	40	40	12 (*S*)
7	**4g**	41	41	50 (*R*)
8[b]	**7**	>99	>99	42 (*R*)

[a] All reactions were carried out at 25 °C under 25 bar pressure of hydrogen for 6 h with 0.0024 mmol $[Rh(cod)_2]BF_4$, 0.005 mmol ligand and 0.24 mmol **8** in methanol (2.0 ml).

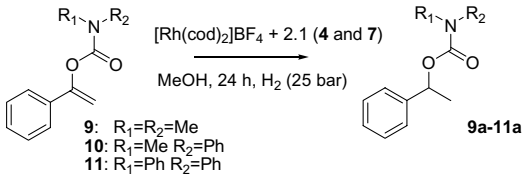
[b] 24 h.

Catalysts containing alkyl-substituted phosphepines **4f** or **4g** gave a significant lower activity and enantioselectivity compared to aryl-substituted phosphepines. Interestingly, in the case of ligand **4g** and **7**, the opposite enantiomer is formed during the reaction. A similar behaviour of the

tert-butyl ligand **4g** was previously reported for other asymmetric hydrogenations.[11c,f]

To explore the scope and limitation of our ligand toolbox, the asymmetric hydrogenation of a range of enol carbamates was performed under optimized conditions (Tables 3 and 4). First the influence of the substitution at the carbamoyl-nitrogen was investigated (Table 3).

Table 3. Variation of the protecting group in the substrate moiety[a]



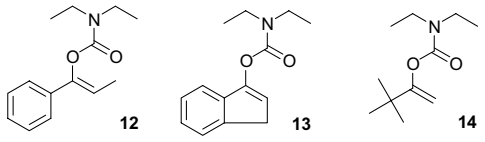
Entry	Ligand	R_1	R_2	Conv. (%)	Yield (%)	ee (%)
1	**4a**	Me	Me	>99	>99	68 (*S*)
2	**4b**	Me	Me	33	33	26 (*S*)
3	**4c**	Me	Me	87	87	65 (*S*)
4	**4d**	Me	Me	>99	>99	**75 (*S*)**
5	**4e**	Me	Me	99	99	40 (*S*)
6	**4f**	Me	Me	26	26	17 (*S*)
7	**4g**	Me	Me	44	44	33 (*R*)
8	**7**	Me	Me	80	80	27 (*R*)
9	**4a**	Me	Ph	>99	>99	58 (*S*)
10	**4b**	Me	Ph	98	98	37 (*S*)
11	**4c**	Me	Ph	>99	>99	61 (*S*)
12	**4d**	Me	Ph	>99	>99	**65 (*S*)**
13	**4e**	Me	Ph	>99	>99	42 (*S*)
14	**4f**	Me	Ph	53	53	4 (*S*)
15	**4g**	Me	Ph	>99	>99	45 (*R*)
16	**7**	Me	Ph	>99	>99	53 (*R*)
17	**4a**	Ph	Ph	>99	88	10 (*S*)
18	**4b**	Ph	Ph	98	77	Rac
19[b]	**4c**	Ph	Ph	89	75	41 (*S*)
20	**4d**	Ph	Ph	>99	87	11 (*S*)
21	**4e**	Ph	Ph	>99	87	55 (*S*)
22	**4f**	Ph	Ph	98	62	4 (*S*)
23	**4g**	Ph	Ph	>99	98	70 (*R*)
24	**7**	Ph	Ph	>99	98	**76 (*R*)**

[a] All reactions were carried out at 25 °C under 25 bar pressure of hydrogen for 24 h with 0.0024 mmol $[Rh(cod)_2]BF_4$, 0.005 mmol ligand and 0.24 mmol substrate in methanol (2.0 ml).
[b] Reaction was carried out for 6 h.

All substrates were hydrogenated under the optimized conditions with eight different ligands **4a**–**4g** and **7**. The enol carbamates **9**–**11** undergo the reaction with good conversion in most cases (Table 3). The negative influence on the activity was again observed by the electron-withdrawing substituent on the phenyl (entries 2, 10 and 18) and by the alkyl group on the phosphorus, mainly *i*-Pr (Table 3, entries 6, 7, 14 and 22). On the other hand in some cases a positive effect on the selectivity by substitution with electron donating groups was observed (Table 3, entries 4 and 12). Again the stereoselectivity was reversed in the case of ligand **7** and **4g**, with **7** being the higher inducer of chirality for system **11**. The overall results for the three substrates **9**–**11** are comparable, showing little influence of the different substituents on the carbamoyl nitrogen on the reaction path.

Finally, the sensitivity on the variations in the double bond was investigated. Table 4 summarizes the results for three substrates with different substitutions: substitution of the phenyl-group by an alkyl-group **14**, substitution in the 2-position of the 1,1-olefin **12** and a cyclic substrate **13**. Substrate *Z*-**12** was hydrogenated with excellent conversion and good enantioselectivity by ligand **4d**, while **13**, which is structurally related to the *E*-isomer of substrate **12**, fails to be hydrogenated with all the ligands but exceptionally ligand **7** (Table 4, entry 8). The alkyl enol carbamate **14** is best hydrogenated by ligands **4a** and **7**, again leading to an inversion of enantioselectivity with ligand **7**. In general the behaviour of substrates **12** and **14** is comparable to that of the previous enol carbamates.

Table 4. Variations of the substituent in the olefin[a]



Entry	Lig.	**12a**		**13a**		**14a**	
		Conv. (%)	ee[b] (%)	Conv. (%)	ee (%)	Conv. (%)	ee (%)
1	**4a**	94	50 (*S*)	<1	n.d.	>99	48
2	**4b**	10	12 (*R*)	<1	n.d.	24	1
3	**4c**	7	8 (*S*)	<1	n.d.	90	39
4	**4d**	93	**72** (*S*)	<1	n.d.	89	48
5	**4e**	29	14 (*S*)	<1	n.d.	81	Rac
6	**4f**	1	n.d.	<1	n.d.	39	11
7	**4g**	2	n.d.	<1	n.d.	44	42
8	**7**	37	6 (*R*)	30	n.d.	98	**−67**

[a] All reactions were carried out at 25 °C under 25 bar pressure of hydrogen for 24 h with 0.0024 mmol $[Rh(cod)_2]BF_4$, 0.005 mmol ligand and 0.24 mmol substrate in methanol (2.0 ml).
[b] The absolute configuration was assigned by analogy.

3. Conclusions

Monodentate phosphine ligands based on a 4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepines structure **4** and **7** have been successfully exploited in the rhodium-catalyzed asymmetric hydrogenation of various enol carbamates. The influences of different reaction parameters have been investigated. For the first time in this reaction a high enantioselectivity (up to 96% ee) was obtained in the presence of monodentate phosphines.

4. Experimental

4.1. General

^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Spectrometer AVANCE 500, 400 and 300 (^1H: 500.13 MHz, 400.13 MHz and 300.13 MHz; ^{13}C: 125.8 MHz, 100.6 MHz and 75.5 MHz; ^{31}P: 162.0 MHz). The calibration

of ^{1}H and ^{13}C spectra was carried out on solvent signals ($\delta(CDCl_3) = 7.25$ and 77.0). The ^{31}P chemical shifts are referenced to 85% H_3PO_4. Mass spectra were recorded on an AMD 402 spectrometer. Optical rotations were measured on a Gyromat-HP polarimeter. IR spectra were recorded as KBr pellets or Nujol mulls on a Nicolet Magna 550. All manipulations with air sensitive compounds were performed under argon atmosphere using standard Schlenk techniques. Toluene was distilled from sodium benzophenone ketyl under argon. Methanol was distilled from Mg under argon. Ethanol and 2-propanol were distilled from Na under argon. Methylene chloride was distilled from CaH_2 under argon. Dimethyl sulfoxide (on molecular sieves) and $[Rh(cod)_2]BF_4$ were purchased from Fluka and used without further purifications. Ligands **4** were synthesized according to our previously published protocols.[11]

4.2. Synthesis of ligands

4.2.1. (*S*)-4-Phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]-phosphepine oxide 5a. Ligand **4a** (1.5 g, 3.86 mmol) were dissolved in acetone (10 ml) and 7.7 ml of 10% sol. H_2O_2 (23 mmol) were added carefully, cooling with ice-bath. After few minutes stirring at room temperature, the solution was refluxed at 100 °C for 1 h. The solvent was evaporated and the resulting yellow oil taken up with CH_2Cl_2 and dried over $MgSO_4$. Purification by column chromatography (eluent: ethyl acetate/petroleum ether 4:1) yielded 1.17 g (75%) of white solid. Mp: 167–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 8.02$ (d, 1H, $^{3}J_{3,4} = 8.5$ Hz, H-4); 7.96, 7.95 (2d, 2H, $^{3}J_{5,6} = 8.2$ Hz, $^{3}J_{5',6'} = 8.2$ Hz, H-5, H-5′); 7.90 (d, 1H, $^{3}J_{3',4'} = 8.5$ Hz, H-4′); 7.70 (d, 1H, $^{3}J_{3,4} = 8.5$ Hz, H-3); 7.53–7.35 (m, 7H, H-6, H-6′, Ph); 7.29–7.21 (m, 3H), 7.16 (d, 1H, $^{3}J = 8.5$ Hz, H-7, H-7′, H-8, H-8′); 7.21 (d, 1H, $^{3}J_{3',4'} = 8.5$ Hz, H-3′); 3.36 (dd, 1H, $^{2}J_{H,H} = 14.2$ Hz, $^{2}J_{P,H} = 8.2$ Hz, H-11a); 3.32 (dd, 1H, $^{2}J_{P,H} = 22.5$ Hz, $^{2}J_{H,H} = 14.2$ Hz, H-11′a); 3.22 (dd, 1H, $^{2}J_{H,H} = 14.2$ Hz, $^{2}J_{P,H} = 13.0$ Hz, H-11b); 3.21 (dd, 1H, $^{2}J_{P,H} = 16.0$ Hz, $^{2}J_{H,H} = 14.2$ Hz, H-11′b). ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 134.0$ (d, $J = 4.0$ Hz), 133.4 (d, $J = 4.0$ Hz), 133.0 (d, $J = 1.8$ Hz), 132.9 (d, $J = 1.8$ Hz), 132.4 (d, $J = 2.5$ Hz), 132.2 (d, $J = 1.8$ Hz), 130.4 (d, $J = 8.2$ Hz), 129.6 (d, $J = 10.0$ Hz, C-1, C-1′, C-2, C-2′, C-9, C-9′, C-10, C-10′); 132.1 (d, $J = 2.5$ Hz, *p*-Ph); 132.0 (d, $J = 88.0$ Hz, *i*-Ph); 130.9 (d, $J = 8.5$ Hz, *o*-Ph); 129.4 (d, $J = 1.8$ Hz, C-4); 128.6 (d, $J = 1.8$ Hz, C-4′); 128.5 (d, $J = 11.0$ Hz, *m*-Ph); 128.5 (d, $J = 3.5$ Hz, C-3); 128.4, 128.2 (C-5, C-5′); 128.3 (d, $J = 4.5$ Hz, C-3′); 127.1, 126.7, 126.5, 126.3 (C-7, C-7′, C-8, C-8′); 125.9 (C-6); 125.6 (C-6′); 37.4 (d, $J = 65.0$ Hz, C-11′); 36.0 (d, $J = 64.0$ Hz, C-11). ^{31}P NMR (121.5 MHz, $CDCl_3$) $\delta = 54.0$. IR (KBr, cm^{-1}): 3052 m; 3008 w; 2951 w; 1618 w; 1592 w; 1508 m; 1435 m; 1405 m; 1359 w; 1328 w; 1251 m; 1221 s; 1199 m; 1159 m; 1114 m; 1102 m; 1061 w; 1026 w; 998 w; 973 w; 960 w; 931 w; 884 w; 866 w; 836 s; 833 m; 820 s; 802 w; 770 m; 752m; 742 s; 726 w; 713 w; 703 m; 694 m; 672 w; 661 m; 622 m; 586 w; 568 w; 544 m; 523 m; 496 w; 470 m; 436 w; 424 w. MS (ESI): *m*/*z* (%) = 404 ([M^+], 100); 365 (6); 266 (34); 202 (4); 139 (4); 73 (7). HRMS calcd for $C_{28}H_{21}O_1P$: 404.13245, found: 404.132628. $[\alpha]_D^{22} = +79.0$ (*c* 0.46, $CHCl_3$). Retention time: 64.6 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.2.2. (*S*)-4-(4-Methoxy)phenyl-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*:1′,2′-*e*]phosphepine oxide 5b. (*S*)-4-(4-Methoxy)-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine **4d** (4.2 mmol) was dissolved in acetone (15 ml) and a mixture of water (1.1 ml) and 35% sol. H_2O_2 (5.0 mmol) was added carefully. After stirring for 4 h at room temperature, the solvent was evaporated and the residue dissolved in dichloromethane. The organic phase was washed with water, brine and dried over $MgSO_4$. The solvent was removed to obtain an off-white foam. Yield: 99%. Mp: 112–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.03$–7.89 (m, 4H); 7.69 (dd, 1H, $J = 8.5$ Hz, $J = 1.2$ Hz); 7.51–7.41 (m, 2H); 7.40–7.31 (m, 2H, C_6H_4); 7.29–7.15 (m, 5H); 6.89 (m, 2H, C_6H_4); 3.83 (s, 3H, OMe); 3.37–3.12 (m, 4H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 162.5$ (d, $J = 3.0$ Hz, C_6H_4); 133.9 (d, $J = 3.8$ Hz); 133.5 (d, $J = 3.8$ Hz); 132.9 (d, $J = 2.0$ Hz); 132.7 (d, $J = 2.0$ Hz); 132.7 (d, $J = 10.2$ Hz, C_6H_4); 132.4 (d, $J = 2.5$ Hz); 132.1 (d, $J = 2.0$ Hz); 130.6 (d, $J = 8.2$ Hz); 129.8 (d, $J = 9.5$ Hz); 129.3 (d, $J = 1.8$ Hz); 128.6 (d, $J = 1.8$ Hz); 128.4 (d, $J = 3.8$ Hz); 128.4; 128.3 (d, $J = 4.5$ Hz); 128.2; 127.1; 126.7; 126.5; 126.3; 125.8; 125.6; 123.0 (d, $J = 93.5$ Hz, C_6H_4); 114.0 (d, $J = 12.0$ Hz, C_6H_4); 55.3 (OMe); 37.7 (d, $J = 66.0$ Hz, CH_2); 36.3 (d, $J = 64.2$ Hz, CH_2). ^{31}P NMR (121.5 MHz, $CDCl_3$) $\delta = 54.1$. IR (KBr, cm^{-1}): 3053 m; 2957 w; 2836 w; 1596 s; 1569 w; 1503 s; 1460 m; 1441 m; 1407 m; 1294 m; 1255 s; 1217 m; 1178 s; 1117 s; 1027 m; 931 w; 871 w; 816 s; 744 m; 684 w; 660 w; 623 w; 567 w; 544 m; 527 m; 496 w; 457 w; 419 w. MS (EI): *m*/*z* (%) = 434 ([M^+], 100); 282 (20); 279 (37); 266 (32); 121 (27). HRMS calcd for $C_{29}H_{23}O_2P$: 434.14302, found: 434.142805. $[\alpha]_D^{22} = -293$ (*c* 0.25, $CHCl_3$).

4.2.3. (*S*,*S*,*S*$_a$)-3,5-Dimethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine oxide 6. Phosphepine oxide **5** (1.37 g, 3.4 mmol) is dissolved in 14 ml of THF, followed by the addition of 0.42 ml (6.8 mmol) of methyl iodide. To the well stirred solution, 22 ml of LDA (11 mmol, 0.5 M) are added slowly at room temperature. The dark red solution was stirred for 1 h and afterwards quenched with few drops of water. The solvents were evaporated under reduced pressure. The product was taken up with 50 ml of CH_2Cl_2, washed with 50 ml of H_2O and the water phase extracted with CH_2Cl_2 (2 × 50 ml). The organic phases are dried over $MgSO_4$ and the solvents evaporated, yielding 1.45 g of light yellow foam. Purification by column chromatography on SiO_2, eluting with acetone/petroleum ether 1:1 yielded 0.56 g (38%) of a white solid. Mp: 292–305 °C. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 8.02$ (d, 1H, $^{3}J_{3',4'} = 8.5$ Hz, H-4′); 7.97 (d, 1H, $^{3}J_{3,4} = 8.5$ Hz, H-4); 7.95 (d, 1H, $^{3}J_{5,6} = 8.2$ Hz, H-5); 7.92 (d, 1H, $^{3}J_{5',6'} = 8.2$ Hz, H-5′); 7.72–7.68 (m, 2H, *o*-Ph); 7.65 (d, 1H, $^{3}J_{3,4} = 8.5$ Hz, H-3); 7.55 (d, 1H, $^{3}J_{3',4'} = 8.5$ Hz, H-3′); 7.50–7.39 (m, 5H, H-6, H-6′, *m*-, *p*-Ph); 7.24–7.18 (m, 3H), 7.05 (d, 1H, $^{3}J = 8.5$ Hz, H-7, H-7′, H-8, H-8′); 3.62 (m, 1H, $^{2}J_{P,H} = 15.0$ Hz, $^{3}J_{11',12'} = 7.7$ Hz, H-11′); 3.43 (dq, 1H, $^{2}J_{P,H} = 22.0$ Hz, $^{3}J_{11,12} = 7.7$ Hz, H-11); 0.95 (dd, 1H, $^{3}J_{P,H} = 14.0$ Hz, $^{3}J_{11',12'} = 7.7$ Hz, H-12′); 0.61

(dd, 1H, $^3J_{P,H} = 16.1$ Hz, $^3J_{11,12} = 7.7$ Hz, H-12). ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 135.2$ (d, $J = 3.2$ Hz, C-1′); 134.5 (d, $J = 5.0$ Hz, C-2′); 134.0 (d, $J = 7.0$ Hz, C-2); 133.9 (d, $J = 3.0$ Hz), 133.8 (d, $J = 1.8$ Hz), 133.4 (d, $J = 1.8$ Hz), 133.0 (d, $J = 1.5$ Hz), 132.8 (d, $J = 1.5$ Hz, C-1, C-9, C-9′, C-10, C-10′); 133.2 (d, $J = 83.0$ Hz, *i*-Ph); 131.7 (d, $J = 2.5$ Hz, *p*-Ph); 131.1 (d, $J = 8.2$ Hz, *o*-Ph); 130.1 (d, $J = 5.0$ Hz, C-3); 129.3 (d, $J = 6.8$ Hz, C-3′); 129.2 (C-4); 129.1 (C-4′); 128.2, 128.0 (C-5, C-5′); 128.2 (d, $J = 10.0$ Hz, *m*-Ph); 127.0, 126.6, 126.5, 126.3 (C-7, C-7′, C-8, C-8′); 126.1 (C-6); 125.7 (C-6′); 46.4 (d, $J = 59.5$ Hz, C-11); 43.2 (d, $J = 63.0$ Hz, C-11′); 17.0 (C-12); 14.6 (d, $J = 4.5$ Hz, C-12′). ^{31}P NMR (121.5 MHz, $CDCl_3$) $\delta = 51.3$. IR (KBr, cm^{-1}): 3039 m; 2990 m; 2931 m; 2874 w; 1618 w; 1594 m; 1568 w; 1504 m; 1455 w; 1436 m; 1375 w; 1341 w; 1325 w; 1292 w; 1253 m; 1225 w; 1184 m; 1166 s; 1112 m; 1092 m; 1057 m; 1028 w; 999 w; 957 w; 915 w; 896 m; 871 w; 838 m; 820 s; 796 w; 768 w; 756 m; 739 s; 711 m; 704 m; 689 m; 667 s; 632 w; 583 w; 564 s; 534 m; 520 w; 509 w; 482 m; 459 m; 418 w; 403 w. MS (ESI): *m*/*z* (%) = 432 ([M$^+$], 44); 417 (2); 388 (2); 360 (1); 328 (2); 293 (15); 278 (100); 265 (15); 231 (4); 208 (12); 179 (2); 145 (16); 132 (33); 77 (7); 47 (4). HRMS calcd for $C_{30}H_{25}OP$: 432.16375, found: 432.163562. $[\alpha]_D^{22} = +93.5$ (*c* 0.25, $CHCl_3$). Retention time: 58.6 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.2.4. (*S*,*S*,*S*$_a$)-3,5-Dimethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]phosphepine 7. Phosphepine oxide **6** (0.08 g, 0.2 mmol) was dissolved in dry toluene (6 ml) and triethylamine (0.2 ml, 1.4 mmol) was added to the solution. The mixture was cooled to 0 °C with an ice-bath and $HSiCl_3$ (0.1 ml, 1 mmol) was added. After the addition was complete, the solution was refluxed for 4 h. The reaction was quenched by 5 ml basic aqueous solution, and the aqueous phase washed with toluene (2×5 ml). The organic phase was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. Yield 70 mg (91%). Mp: 212 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.04$–7.90 (m, 4H); 7.73–7.63 (m, 3H); 7.55 (d, 1H, $J = 8.5$ Hz); 7.51–7.38 (m, 5H); 7.26–7.16 (m, 3H); 7.06 (d, 1H, $J = 8.5$ Hz); 3.62 (m, 1H, $^2J_{P,H} = 15.5$ Hz, $^3J_{H,Me} = 7.5$ Hz, C*H*Me); 3.43 (dq, 1H, $^2J_{P,H} = 22.0$ Hz, $^3J_{H,Me} = 7.5$ Hz, C*H*Me); 0.95 (dd, 3H, $^3J_{P,H} = 13.9$ Hz, $^3J_{H,Me} = 7.5$ Hz, Me); 0.61 (dd, 3H, $^3J_{P,H} = 16.0$ Hz, $^3J_{H,Me} = .5$ Hz, Me). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 141.2$ (d, $J = 2.5$ Hz); 138.5 (d, $J = 1.0$ Hz); 138.5 (d, $J = 25.8$ Hz); 134.7 (d, $J = 5.8$ Hz); 134.3; 133.9; 133.86 (d, $J = 2.8$ Hz); 132.8 (d, $J = 19.5$ Hz); 132.7; 132.2; 128.9 (d, $J = 3.0$ Hz); 128.8; 128.6 (d, $J = 1.0$ Hz); 128.4; 128.3 (d, $J = 3.2$ Hz); 128.2; 128.1; 127.9; 126.6; 126.5; 126.0; 126.0; 125.2; 125.1; 39.3 (d, $J = 20.0$ Hz, *C*HMe); 36.6 (d, $J = 20.0$ Hz, *C*HMe); 22.3 (d, $J = 35.5$ Hz, Me); 14.0 (d, $J = 3.5$ Hz, Me). ^{31}P NMR $\delta = 31.46$ (s). MS (ESI): *m*/*z* (%): 416 ([M$^+$], 100), 360 (10), 265 (38), 149 (9). HRMS: calcd for $C_{30}H_{25}P$ 416.16884, found: 416.167881. $[\alpha]_D^{25} = +87.5$ (*c* 0.2, $CHCl_3$).

4.3. General synthesis of enol carbamate derivates 8–14[14,5m]

A solution of sodium hydride (0.11 mol) in dry dimethyl sulfoxide (200 ml) was stirred for 2 h at 50 °C under an atmosphere of argon. The grey suspension was added dropwise to the corresponding ketone (0.1 mol) in 25 ml of dimethyl sulfoxide at room temperature. The orange solution was stirred for 15 min at room temperature and then cooled to 10 °C. The addition of the corresponding carbamoyl chloride (0.11 mol) in dimethyl sulfoxide (0.11 mol) was carried out in 30 min while maintaining the temperature at 10 °C. After stirring overnight at room temperature, the solution was carefully quenched with water (250 ml), extracted with *n*-hexane or heptane (3×250 ml), washed with brine (250 ml) and dried over $MgSO_4$ or Na_2SO_4. The solvents were removed in vacuo and the obtained yellow oil purified by column chromatography or crystallization.

4.3.1. 1-Phenylvinyl *N*,*N*-diethylcarbamate 8. Purification by column chromatography (eluent: ethylacetate/*n*-hexane 1:10) yielded a yellow oil. Yield: 18%. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.44$–7.39 (m, 2H, Ph); 7.30–7.19 (m, 3H, Ph); 5.35 (d, 1H, $J = 2.0$ Hz, =CH_2); 4.96 (d, 1H, $J = 2.0$ Hz, =CH_2); 3.35 (q, 2H, $J = 7.0$ Hz, CH_2); 3.25 (q, 2H, $J = 7.0$ Hz, CH_2); 1.20 (t, 3H, $J = 7.0$ Hz, CH_3); 1.10 (t, 3H, $J = 7.0$ Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 153.8$; 153.4; 135.2; 128.6; 128.4; 124.8; 101.3; 42.0; 41.7; 14.3; 13.3. IR (KBr, cm^{-1}): 3059 w; 3027 w; 2975 m; 2934 m; 2876 w; 1719 s; 1641 m; 1600 w; 1577 w; 1495 m; 1474 m; 1457 m; 1420 s; 1380 m; 1351 w; 1314 w; 1255 s; 1225 m; 1158 s; 1097 m; 1076 m; 1050 m; 1027 w; 981 w; 902 w; 869 m; 787 m; 771 m; 759 m; 703 m; w; 638 w; 578 w. MS (ESI): *m*/*z* (%) = 219 ([M$^+$], 9); 103 (12); 100 (100); 77 (16); 72 (72); 44 (16). HRMS calcd for $C_{13}H_{17}O_2N$: 219.1254, found: 219.1253. Retention time: 17.8 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.3.2. 1-Phenylvinyl *N*,*N*-dimethylcarbamate 9. Purification by column chromatography on silica gel eluting with hexane/ethyl acetate 4:1 yielded 6.4 g of an orange oil. Yield: 34%. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.48$–7.28 (m, 5H, Ph); 5.41 (1H, d, $J = 2.0$ Hz, =CH_2); 5.02 (d, 1H, $J = 2.0$ Hz, =CH_2); 3.10 (s, 3H, CH_3); 2.96 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 154.5$; 153.4; 135.1; 128.7; 128.5; 124.9; 101.6; 36.7; 36.4. IR (KBr, cm^{-1}): 3084 w, 3058 w, 3023 w, 2934 m, 1958 w, 1724 s, 1643 m, 1601 w, 1577 m, 1494 s, 1445 s, 1391 s, 1313 m, 1295 m, 1262 s, 1168 s, 1098 m, 1076 m, 1030 m, 928 m, 875 m, 858 m, 772 s, 759 m, 708 m, 692 m, 641 w, 581 w. MS (ESI): *m*/*z* (%) = 191 ([M$^+$], 12); 103 (4); 91 (4); 77 (7); 72 (100); 51 (5). HRMS calcd for $C_{11}H_{13}O_2N$: 191.09408, found: 191.09370. Retention time: 16.8 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.3.3. 1-Phenylvinyl *N*-methyl *N*-phenylcarbamate 10. Purification by column chromatography on silica gel eluting with *n*-hexane/ethyl acetate 1:1 followed by crystallization with acetone/diethylether/*n*-hexane 1:2:4. Yield: 25%. Mp: 56–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.42$–7.26 (m, 10H, Ph); 5.39 (1H, d, $J = 1.7$ Hz, =CH_2); 5.06 (d, 1H, $J = 1.7$ Hz, =CH_2); 3.38 (br s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 153.6$; 153.4; 143.0; 134.9; 129.2; 128.8; 128.4; 126.7 (br); 126.0 (br); 125.0; 101.6;

38.3. IR (KBr, cm^{-1}): 3762 w; 3407 w; 3119 w; 3085w; 3067 w; 3037 w; 2975 w; 2937 w; 2557 w; 1966w; 1891 w; 1813 w; 1717 s; 1643 m; 1592 m; 1578 w; 1493 s; 1446 m; 1420 m; 1370 s; 1294 m; 1257 s; 1180 w; 1146 s; 1088 m; 1072 m; 1050 w; 1025 m; 1004 w; 981 m; 916 w; 875 m; 840 w; 827 w; 771 m; 754 m; 705 s; 687 m; 602 w; 588 m; 563 w; 529 w; 429 w; 408 m. MS (ESI): m/z (%) = 253 ([M^+], 4); 134 (100); 119 (4); 106 (37); 91 (6); 77 (38); 65 (4); 51 (10); 39 (3). HRMS calcd for $C_{16}H_{15}O_2N$: 253.10973, found: 253.10977. Retention time: 23.1 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.3.4. 1-Phenylvinyl *N,N*-diphenylcarbamate 11. Crystallization from acetone/diethylether/*n*-hexane 1:2:5 yielded white-greenish crystals. Yield: 38%. Mp: 72–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.26–7.21 (m, 15H, Ph); 5.40 (1H, d, J = 2.2 Hz, =CH_2); 5.14 (1H, d, J = 2.2 Hz, =CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 153.2; 152.5; 142.2; 134.7; 129.1; 128.8; 128.4; 126.8; 126.5; 125.0; 101.6. IR (KBr, cm^{-1}): 3088 w; 3057 m; 1952 w; 1879 w; 1801 w; 1721 s; 1646 m; 1590 m; 1492 s; 1451 m; 1384 w; 1347 s; 1328 m; 1307 m; 1293 m; 1256 s; 1201 s; 1184 m; 1172 m; 1097 m; 1078 m; 1044 m; 1032 m; 1024 m; 913 w; 870 m; 836 w; 770 s; 761 s; 694 s; 638 m; 620 w; 597 m; 566 w; 530 m; 512 m; 443 w; 412 w. MS (ESI): m/z (%) = 315 ([M^+], 13); 196 (100); 168 (46); 103 (17); 91 (4); 77 (22); 51 (7). HRMS calcd for $C_{21}H_{17}O_2N$: 315.12538, found: 315.12538. Retention time: 28.2 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.3.5. (*Z*)-1-Phenylprop-1-enyl *N,N*-diethylcarbamate 12.[18] Colourless oil was obtained after column chromatography (eluent: ethyl acetate/*n*-hexane 1:10). Yield: 38%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40 (m, 2H, *o*-Ph); 7.30 (m, 2H, *m*-Ph); 7.23 (m, 2H, *p*-Ph); 5.85 (q, 1H, $^3J_{1,2}$ = 7.0 Hz, H-2); 3.49, 3.36 (2q, 4H, H-5, H-5′); 1.74 (d, 3H, $^3J_{1,2}$=7.0 Hz, H-1); 1.29, 1.17 (2t, 6H, $^3J_{5,6}$ = 7.0 Hz, $^3J_{5',6'}$ = 7.0 Hz, H-6, H-6′). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 153.4 (C=O); 147.3 (C–O); 136.0 (*i*-Ph); 128.3 (*m*-Ph); 127.6 (*p*-Ph); 124.3 (*o*-Ph); 112.4 (C-2); 42.1, 41.7 (C-5, C-5′); 14.4, 13.4 (C-6, C-6′); 11.4 (C-1). IR (KBr, cm^{-1}): 3058 w; 2975 m; 2934 m; 2875 w; 1717 s; 1673 m; 1600 w; 1577 w; 1495 m; 1474 m; 1458 m; 1420 s; 1380 m; 1351 w; 1313 m; 1258 s; 1225 m; 1158 s; 1116 m; 1097 m; 1061 m; 1033 w; 1006 m; 972 w; 951 w; 926 w; 851 w; 793 w; 753 s; 692 m; 652 w; 637 w; 574 w. MS (ESI): m/z (%) = 233 ([M^+], 6); 115 (9); 105 (8); 100 (100); 77 (12); 72 (52); 44 (12). HRMS calcd for $C_{14}H_{19}O_2N$: 233.14103, found: 233.14101. Retention time: 19.3 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5). Retention time (HPLC): 8.72 min (eluent: *n*-hexane/ethanol 98:2; flow: 1.0 ml/min).

4.3.6. 1*H*-Inden-3-yl *N,N*-diethyl carbamate 13. An orange oil was obtained after column chromatography (eluent: ethyl acetate/*n*-hexane 1:10). Yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34–7.10 (m, 4H); 6.19 (t, 1H, J = 2.3 Hz, CH); 3.41–3.27 (m, 4H, CH_2CH_3); 3.29 (d, 2H, J = 2.3 Hz, CH_2CH); 1.22–1.08 (m, 6H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 153.0; 149.4; 141.9; 139.7; 126.1; 125.4; 124.0; 117.8; 113.6; 42.3; 42.1; 34.8; 14.3; 13.4. IR (KBr, cm^{-1}): 3074 w; 3024 w; 2975 m; 2934 m; 2890 m; 1726 s; 1653 w; 1616 m; 1605 m; 1577 m; 1474 m; 1459 m; 1420 s; 1380 m; 1361 m; 1316 m; 1267 s; 1235 m; 1223 m; 1204 m; 1172 s; 1156 s; 1118 m; 1098 m; 1076 m; 1017 w; 973 m; 953 m; 932 m; 915 w; 844 w; 761 s; 717 m; 635 w; 593 w; 553 w; 511 w; 467 w; 412 w. MS (ESI): m/z (%) = 231 ([M^+], 6); 131 (10); 115 (6); 103 (11); 100 (100); 77 (14); 72 (62); 44 (17). HRMS calcd for $C_{14}H_{17}O_2N$: 231.12538; Found: 231.124840. Retention time: 21.3 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.3.7. 3,3-Dimethylbut-1-en-2-yl *N,N*-diethyl carbamate 14. A colourless oil was obtained after column chromatography (eluent: ethyl acetate/*n*-hexane 1:3). Yield: 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.76 (d, 1H, J = 1.9 Hz, =CH_2); 4.64 (d, 1H, J = 1.9 Hz, =CH_2); 3.31 (q, 4H, J = 7.0 Hz, CH_2CH_3); 1.16–1.12 (br, 6H, CH_2CH_3); 1.10 (s, 9H, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 163.0; 154.1; 96.2; 42.0; 41.6; 36.2; 27.9; 14.2; 13.4. IR (KBr, cm^{-1}): 3125 w; 2973 s; 2936 m; 2876 m; 1720 s; 1653 m; 1555 w; 1506 w; 1474 m; 1461 m; 1419 s; 1380 m; 1362 m; 1317 m; 1264 s; 1225 m; 1148 s; 1097 m; 1054 m; 979 m; 938 w; 859 m; 786 m; 756 m; 703 w; 655 w; 593 w; 488 w. MS (ESI): m/z (%) = 199 ([M^+], 1); 118 (1); 100 (100); 85 (2); 72 (50); 67 (3); 55 (5); 44 (15). HRMS calcd for $C_{11}H_{21}O_2N$: 199.15668, found: 199.155983. Retention time: 11.5 min (30 m HP Agilent Technologies 50-8-260/5-8-280/5-8-300/5).

4.4. General procedure for the catalytic hydrogenation of enol carbamates

The catalyst was generated in situ by stirring [Rh(cod)$_2$]-BF_4 (0.0024 mmol) and the corresponding 4,5-dihydro-3*H*-dinaphthophosphepines ligand (0.005 mmol) in 1.0 ml of solvent for a period of 10 min and afterwards transferring via syringe into the autoclave. A solution of the enol carbamate (0.24 mmol) and 1.0 ml solvent was transferred via syringe into the autoclave. Then, the autoclave was charged with hydrogen and stirred at the required temperature. After a predetermined time the hydrogen was released and the reaction mixture passed through a short plug of silica gel. The conversion and enantioselectivity were measured by GC and HPLC without further modifications.

4.4.1. 1-Phenylethyl *N,N*-diethylcarbamate 8a. Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.31–7.11 (m, 5H, Ph); 5.73 (d, 1H, J = 6.5 Hz, CH); 3.20 (q, 4H, J = 7.0 Hz, CH_2); 1.44 (d, 3H, J = 6.5 Hz, CH_3); 1.02 (t, 6H, J = 7.0 Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 155.1; 142.6; 128.2; 127.3; 125.7; 72.6; 41.5; 41.1; 22.7; 14.0; 13.4. IR (KBr, cm^{-1}): 3087 w; 3064 w; 3033 w; 2977 s; 2933 m; 2875 w; 1700 s; 1630 m; 1586 w; 1539 w; 1495 m; 1476 s; 1457 s; 1425 s; 1379 m; 1316 m; 2174 s; 1227 m; 1210 m; 1172 s; 1069 s; 1030 m; 1010 m; 998 m; 973 m; 940 w; 911 w; 877 w; 787 m; 766 m; 700 s; 630 w; 576 w; 535 m. MS (ESI): m/z (%) = 221 ([M^+], 2); 105 (100); 100 (5); 77 (16); 72 (5); 58 (7); 51 (6); 44 (8). HRMS calcd for $C_{13}H_{19}O_2N$: 221.14103, found: 221.140593. $[\alpha]_D^{23}$ = −146.1 (*c* 0.5, CH_2Cl_2/MeOH, 96% ee (*S*)). Conversions were determined by GC (Agilent Technologies, 30 m,

50–300 °C, (50-8-260/5-8-280/5-8-300/5)) and ees by HPLC (Whelk (*R*,*R*), (*S*)-**8a** 8.29 min and (*R*)-**8a** 28.7 min (eluent: *n*-hexane/ethanol 99:1; flow: 1.0 ml/min)).

4.4.2. (*S*)-1-Phenylethyl *N*,*N*-diethylcarbamate 8a. To a solution of (*S*)-1-phenylethanol (3.3 mmol) in THF (10 ml) was added NaH (3.4 mmol). The solution was stirred for 30 min at room temperature under an argon atmosphere. The solution was cooled to 0 °C and *N*,*N*-diethyl carbamoyl chloride (3.4 mmol) in THF (5 ml) was added. After stirring for 2 h at room temperature the reaction was quenched with water. The mixture was extracted with ethylacetate/*n*-hexane (1:1), washed with brine and dried over Na_2SO_4. The solvents were removed in vacuum and the crude oil was purified by flash column chromatography (ethylacetate/*n*-hexane 1:1) to yield a colourless oil (yield: 56%). The analytical data are in agreement with **8a** obtained by the hydrogenation protocol.

4.4.3. 1-Phenylethyl *N*,*N*-dimethylcarbamate 9a. Oil. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.34$–7.22 (m, 5H, Ph); 5.78 (q, 1H, $J = 6.6$ Hz, CH); 2.93 (br s, 3H, CH_3); 2.88 (br s, 3H, CH_3); 1.51 (d, 3H, $J = 6.6$ Hz, CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$) $\delta = 156.0$; 142.7; 128.5; 127.6; 125.9; 73.1; 36.4; 35.9; 22.9. IR (KBr, cm^{-1}): 3033 w; 2980 w; 2932 w; 1704 s; 1495 m; 1450 m; 1393 m; 1273 w; 1191 s; 1069 m; 1030 w; 1007 w; 995 w; 894 w; 844 w; 766 m; 700 m; 638 w; 569 w; 532 w. MS (ESI): *m*/*z* (%) = 193 ([M$^+$], 6); 134 (13); 121 (1); 105 (100); 90 (1); 77 (13); 63 (1); 51 (4). HRMS calcd for $C_{11}H_{15}O_2N$: 193.10973, found: 193.109345. $[\alpha]_D^{22} = -2.9$ (*c* 0.3, $CHCl_3$, 75% ee (*S*)). Conversions were determined by NMR and ees by HPLC (Chiralpak AD-H, (*R*)-**9a** 23.6 min and (*S*)-**9a** 31.3 min, eluent: *n*-hexane/ethanol 99:1; flow: 1.0 ml/min). The absolute configuration was assigned by analogy.

4.4.4. 1-Phenylethyl *N*-methyl *N*-phenylcarbamate 10a. Oil. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.35$–7.16 (m, 10H, Ph); 5.83 (q, 1H, $J = 6.5$ Hz, CH); 3.28 (s, 3H, CH_3); 1.47 (d, 3H, $J = 6.5$ Hz, $CHCH_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 155.0$; 143.4; 142.3; 128.8; 128.4; 127.6; 125.9 (br); 125.8; 125.7 (br); 73.8; 37.7; 23.0. IR (KBr, cm^{-1}): 3064 w; 3033 w; 3980 m; 2932 w; 1706 s; 1598 m; 1496 s; 1453 m; 1437 m; 1422 m; 1374 s; 1327 m; 1299 s; 1277 s; 1210 m; 1159 s; 1113 m; 1063 s; 1029 m; 1010 m; 997 m; 974 m; 912 w; 885 w; 819 w; 762 s; 698 s; 665 w; 625 w; 599 w; 544 m. MS (ESI): *m*/*z* (%) = 255 ([M$^+$], 1); 211 (2); 196 (7); 151 (1); 134 (2); 105 (100); 91 (1); 77 (20); 65 (2); 51 (7). HRMS calcd for $C_{16}H_{17}NO_2$: 255.12538, found: 255.125229. $[\alpha]_D^{22} = +19.9$ (*c* 0.26, $CHCl_3$, 65% ee (*S*)). Conversions were determined by NMR and ees by HPLC (Chiralcel OD-H, (*R*)-**10a** 25.4 min and (*S*)-**10a** 47.2 min, eluent: *n*-hexane/ethanol 99:1; flow: 1.0 ml/min). The absolute configuration was assigned by analogy.

4.4.5. 1-Phenylethyl *N*,*N*-diphenylcarbamate 11a. Crystals. Mp: 76–78 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 7.32$–7.14 (m, 15H, Ph), 5.88 (q, 1H, $J = 6.5$ Hz, CH), 1.47 (d, 3H, $J = 6.5$ Hz, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 154.1$; 142.6; 141.9; 128.9; 128.4; 127.7; 127.0; 126.1; 125.9; 74.3; 22.9. IR (KBr, cm^{-1}): 3064 w; 3033 m; 2984 m; 2934 w; 1702 s; 1591 s; 1491 s; 1450 m; 1369 s; 1343 s; 1325 s; 1299 s; 1281 s; 1220 s; 1208 s; 1178 m; 1159 w; 1128 w; 1058 s; 1048 s; 1023 s; 1008 m; 993 m; 951 w; 913 w; 901 w; 860 m; 837 w; 814 w; 781 m; 764 s; 758 s; 693 s; 672 m; 642 w; 622 w; 603 w; 548 s; 516 m; 492 w. MS (ESI): *m*/*z* (%) = 317 ([M$^+$], 2); 273 (2); 258 (2); 196 (1); 169 (41); 139 (1); 105 (100); 77 (12); 51 (5). HRMS calcd for $C_{21}H_{19}O_2N$: 317.14103, found: 317.141098. $[\alpha]_D^{21} = -16.8$ (*c* 0.33, $CHCl_3$, 76% ee (*R*)). Conversions were determined by NMR and ees by HPLC (Chiralcel OD-H, (*R*)-**11a** 6.8 min and (*S*)-**11a** 9.6 min, eluent: *n*-hexane/ethanol 99.5:0.5; flow: 1.0 ml/min). The absolute configuration was assigned by analogy.

4.4.6. 1-Phenylpropyl *N*,*N*-diethylcarbamate 12a. Colourless oil. Yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.28$–7.16 (m, 5H, Ph); 5.54 (1H, dd, $J = 6.4$ Hz, $J = 7.2$ Hz, $CHCH_2$); 3.23 (br, 4H, NCH_2); 1.83 (m, 2H, $CHCH_2CH_3$); 1.06 (br, 6H, NCH_2CH_3); 0.83 (t, 3H, $J = 7.4$ Hz, $CHCH_2CH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$) $\delta = 155.5$; 141.6; 128.3; 127.5; 126.4; 77.8; 41.8; 41.3; 29.9; 14.3; 13.6; 9.9. IR (KBr, cm^{-1}): 2972 m; 2934 m; 2877 w; 1700 s; 1475 m; 1457 m; 1424 m; 1380 w; 1273 s; 1226 w; 1171 s; 1063 m; 987 m; 903 w; 763 w; 700 m; 528 w. MS (ESI): *m*/*z* (%) = 235 ([M$^+$], 9); 162 (15); 119 (54); 100 (12); 91 (100); 77 (7). HRMS calcd for $C_{14}H_{19}O_2N$: 235.15668, found: 235.157242. $[\alpha]_D^{23} = -143.7$ (*c* 0.5, CH_2Cl_2/MeOH, 50% ee). Conversions and ees were determined by GC (Retention time: 17.9 min, 30 m HP Agilent Technologies 50–300 °C: 50-8-260/5-8-280/5-8-300/5) and HPLC (Whelk (*R*,*R*), *n*-hexane/ethanol 98:2, flow 1.0 ml/min, (*S*)-**12a** 4.84 min and (*R*)-**12a** 10.10 min).

4.4.7. 3,3-Dimethylbutan-2-yl *N*,*N*-diethylcarbamate 14a. Oil. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 4.56$ (q, 1H, $J = 6.4$ Hz, CH); 3.25 (br d, 4H, CH_2); 1.12 (d, 3H, $J = 6.4$ Hz, CH_3); 1.10 (t, 6H, CH_2CH_3); 0.90 (s, 9H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 155.9$; 78.1; 41.6; 34.4; 25.9; 15.3; 14.2. IR (KBr, cm^{-1}): 2971 s; 2935 m; 2874 w; 1696 s; 1653 w; 1559 w; 1540 w; 1506 w; 1475 m; 1457 m; 1423 s; 1395 w; 1378 m; 1365 w; 1316 w; 1275 m; 1227 w; 1210 w; 1174 m; 1076 m; 1007 w; 972 w; 893 w; 824 w; 783 w; 768 w; 744 w; 697 w; 617 w; 537 w. MS (ESI): *m*/*z* (%) = 201 ([M$^+$], 7); 186 (3); 144 (2); 116 (16); 100 (100); 85 (44); 72 (25); 58 (21); 43 (46). HRMS calcd for $C_{11}H_{23}O_2N$: 201.17233, found: 201.172292. $[\alpha]_D^{22} = +135$ (*c* 0.04, $CHCl_3$/MeOH, 67% ee). Conversions and ees were determined by GC (50m Chiraldex β-PH, 50.0 m × 250 μm × 0.25 μm, 100/25-4-180/5, (−)-**14a** 25.6 min and (+)-**14a** 26.0 min).

4.5. X-ray crystallographic studies of 5a, 5b and 6

Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods[19] and refined by full-matrix least-squares techniques against F^2.[20] XP (BRUKER AXS) was used for graphical representations. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 641493–641495. Copies of the data can be obtained free of charge on application to http://www.ccdc.cam.ac.uk/data_request/cif.

4.5.1. Compound 5a. Space group $P3_121$, trigonal, $a = 11.174(2)$, $c = 32.520(7)$ Å, $V = 3516(1)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.230$ g cm^{-3}, 18,941 reflections measured, 3621 were independent of symmetry, of which 2550 were observed ($I > 2\sigma(I)$), $R1 = 0.055$, wR^2 (all data) $= 0.145$, 281 parameters, Flack parameter $x = 0.05(18)$.

4.5.2. Compound 5b. Space group $P2_1$, monoclinic, $a = 7.985(2)$, $b = 11.407(2)$, $c = 12.625(3)$ Å, $\beta = 98.27(3)°$, $V = 1138.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.262$ g cm^{-3}, 15,617 reflections measured, 4452 were independent of symmetry, of which 2645 were observed ($I > 2\sigma(I)$), $R1 = 0.034$, wR^2 (all data) $= 0.059$, 289 parameters, Flack parameter $x = 0.02(8)$.

4.5.3. Compound 6. Space group $P2_1$, monoclinic, $a = 9.445(2)$, $b = 16.801(3)$, $c = 14.081(3)$ Å, $\beta = 91.75(3)°$, $V = 2233.4(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.292$ g cm^{-3}, 13,676 reflections measured, 7244 were independent of symmetry, of which 5881 were observed ($I > 2\sigma(I)$), $R1 = 0.047$, wR^2 (all data) $= 0.118$, 577 parameters, Flack parameter $x = -0.07(10)$.

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